C−H Arylation of Benzoquinone in Water through Aniline Activation: Synergistic Effect of Graphite-Supported Copper Oxide Nanoparticles

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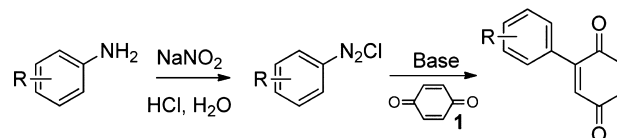**S** Supporting Information

ABSTRACT: A homemade CuONPs/Gr catalyst was found to be efficient for the C−H arylation of benzoquinone. This methodology represents the first example of a Meerwein arylation catalyzed by a heterogeneous catalyst.
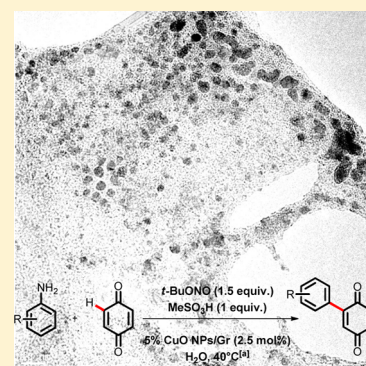
The arylation of α,β-unsaturated compounds is usually executed through a palladium-catalyzed Heck reaction.[1] This reaction is now a part of the arsenal in the tool box of every synthetic chemist and has found industrial developments.[2] Although almost every kind of olefin is compatible with the Heck process, benzoquinone-type partners are still reluctant to react under Heck protocols. This failure has been ascribed to the unusual electronic properties of benzoquinone and their ability to coordinate with palladium. In order to overcome this issue, a prehalogenation of benzoquinone is required to allow the arylation via a Suzuki or Stille reaction.[3] On the other hand, the direct C−H arylation of benzoquinones has been recently successfully reported by the group of Baran through the homolytic cleavage of boronic acids.[4] Actually, the addition of aryl radicals to benzoquinone is a well-known process, mostly performed by homolytic decomposition of aryl diazonium chlorides.[5] This transformation is usually carried out in a two-steps one-pot procedure starting with the preparation of diazonium chlorides in HCl solution followed by the addition of the latter into an aqueous solution of benzoquinone **1** in the presence of a base (2−10 equiv) as buffer (Scheme 1).

Although rather effective, this approach suffers from several drawbacks: (1) the preparation of the aryl diazonium chloride requires a large excess of HCl, (2) as a consequence, an excess of a base is required for the neutralization of the strongly acidic solution containing the diazonium, and (3) most aryl diazonium chlorides are very unstable and sometimes explosive
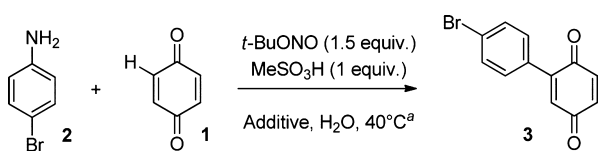
above 0 °C. In order to address these issues, we recently reported the direct C−H arylation of benzoquinone with anilines under neutral conditions without any acid or base.[6] Although the procedure was particularly well suited for nitro-based sensitive substrates, an excess of benzoquinone (2 equiv) was required in order to reach synthetically acceptable yields. The separation of unreacted benzoquinone from the coupling product was sometimes rather difficult, and a more efficient procedure was still required for further developments. In this paper, we report our studies in this field that addressed the issues discussed above. Of particular importance, we discovered the beneficial synergistic effect of graphite-supported copper nanoparticles on the reaction efficiency.

We started a careful optimization study with the arylation of benzoquinone **1** with 4-bromoaniline **2** (Table 1). In order to

Scheme 1. C−H Arylation of Benzoquinone with Aryldiazonium Chlorides

Table 1. Optimization Studies with a Homogeneous Metal Source

| entry	additive	loading (mol %)	yield[b] (%)
1			30[c]
2			52
3	hydroquinone	10	79
4	$FeSO_4 \cdot 7H_2O$	100	54
5	$TiCl_3$	100	25
6	CuCl	100	55
7	Cu_2O	100	67
8	$CuSO_4 \cdot 5H_2O$	100	70
9	$CuCl_2$	100	80
10	CuO	100	83
11	$Cu(OAc)_2 \cdot H_2O$	100	85
12	$Cu(OAc)_2 \cdot H_2O$	1	82

[a]Reaction conditions: aniline (1 mmol), $MeSO_3H$ (1 mmol), t-BuONO (1.5 mmol), benzoquinone (0.9 mmol), and additive (see table entries) were stirred at 40 °C for 24 h. [b]Isolated yields after flash chromatography on silica gel. [c]$MeSO_3H$ was omitted.

improve the purification process complicated by the presence of unreacted benzoquinone **1** in the crude mixture, we worked with a slight excess of aniline **2**. The use of $MeSO_3H$ (1 equiv) that promotes the formation of the corresponding diazonium salt increases the yield (52% vs 30% for entry 2 vs 1) but still at an unacceptable level. In our previous work,[6] we proposed that in the absence of metal and external reducing agent, the homolytic decomposition of the diazonium function was initiated by trace of hydroquinone contained in the commercial samples of benzoquinone. Although we initially failed to prove the presence of hydroquinone by ^{1}H NMR, we pursued this hypothesis to elucidate the mechanism operating. A careful HPLC analysis showed that commercial samples as well as freshly recrystallized batches of benzoquinone roughly contain 0.5−1% of hydroquinone. In order to prove the role of hydroquinone in mediating the diazonium reduction, we carried out the reaction with 10 mol % of hydroquinone. Although the yield was spectacularly improved (79%), the isolation of the expected compound **3** was complicated by the presence of inseparable tarry material. To avoid the presence of oligomers, we reasoned that a reducing metal could significantly help the homolytic decomposition of the diazonium function to generate an aryl radical, and thereby could work in a synergistic fashion with traces of hydroquinone contained in commercial samples of benzoquinone.

In this way, we evaluated Fe-, Ti-, and Cu-based aryl radical promoters. Surprisingly, $FeSO_4 \cdot 7H_2O$ did not impact the reaction outcome, and $TiCl_3$ was even detrimental for the arylation, although they have been both successfully employed for the Meerwein arylation.[7] By contrast, copper complexes were all active for the studied transformation. As a general comment, copper(I) complexes were usually less active than copper(II)-based promoters. Among the various sources of copper(II) complexes, $Cu(OAc)_2 \cdot H_2O$ displayed the highest yields (entries 8−12). More interestingly, the activity of $Cu(OAc)_2 \cdot H_2O$ remains high when used as catalyst with a loading as low as 1 mol % without any trace of tarry material

(entries 11 and 12). Lowering of the copper loading to 0.5 mol % resulted in a rapid decrease of the reaction yield (<65%). With these interesting preliminary results in hand, we explored the opportunity to develop a heterogeneous version of this process by impregnating carbon material with copper nanoparticles. To the best of our knowledge, the use of a metal-based heterogeneous catalyst has never been described for the Meerwein arylation.

We recently reported that palladium nanoparticles (NPs) could be efficiently prepared from a methanolic solution of palladium acetate under an atmosphere of H_2 (1 atm) at room temperature and heterogenized in the presence of carbon material.[8] Following this efficient strategy, we exposed a methanolic solution of $Cu(OAc)_2 \cdot H_2O$ to an atmosphere of H_2, in the presence of graphite as support, furnishing CuNPs/Gr catalyst with ~5 wt % of metal loading on the support as determined by ICP analysis. Interestingly, the use of other sources of Cu(II) such as CuO and $CuCl_2$ led to a much lower loading on the support, likely due to their poor solubility in MeOH. High-resolution transmission electron microscopy (HRTEM) analysis of 5% CuNPs/Gr showed a homogeneous distribution of copper nanoparticles onto the support (Figure 1). This is a remarkable result considering the simplicity of the
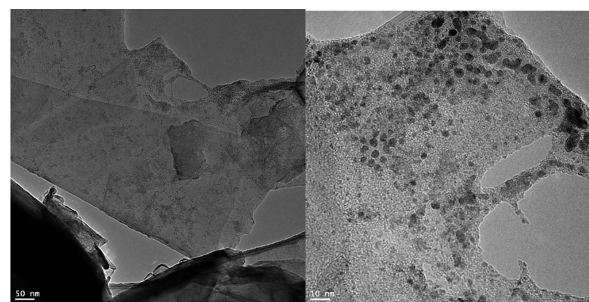
Figure 1. HRTEM picture of 5% CuNPs/Gr catalyst at different magnifications.

preparation procedure. The TEM picture at low magnification (Figure 1a) shows that CuNPs are uniformly dispersed on the sheets of graphite and without formation of aggregate. A selected enlargement (Figure 1b) shows spherical CuNPs with a crystallite size <5 nm, although a high local concentration of NPs. A closest analysis of the crystallite size distribution calculated on 128 NPs revealed an average diameter of 3.1 nm, with 83% of NPs being in the range 2−4 nm (see Figure S1, Supporting Information).

The composition of copper species at the surface of graphite was investigated by X-ray photoelectron spectroscopy (XPS) analysis.[9] The binding energy of the Cu $2p_{3/2}$ peak at 934.0 eV and the satellite shakeup detected near 938−946 eV are characteristic of Cu^{2+} species (see Figure S2, Supporting Information). The absence of Cu 2p peaks associated to metallic Cu and Cu^+ at lower binding energy (932.5 eV) indicates that copper species are only present as Cu^{2+}. This result indicates that the catalyst mainly consists of graphite-supported copper oxide NPs. It was assumed that Cu(II) was reduced by H_2/MeOH to Cu(0) which rapidly oxidized to CuO during the catalyst treatment. The absence of ester peaks by XPS excluded any residual $Cu(OAc)_2 \cdot H_2O$ impregnated onto the surface of graphite. We determined the CuO NPs size (t)[10] considering the inelastic meam free path of Cu2p λ_1, Cu3p λ_2 in the CuO layer as 1.2 and 2.4 nm respectively[11] and the

average surface powder angle relative to the analyzer as 45° (see formula S1, Supporting Information). The average diameter (t) of NPs was estimated to be 3.1 ± 0.8 nm and is consistent with the estimation realized from HRTEM pictures.

We next investigated the catalytic activity of these freshly prepared heterogeneous catalysts (Table 2).

Table 2. Optimization Studies with Heterogeneous Copper Catalysts

entry	catalyst	loading (mol %)	yield[b] (%)
1	5% Cu/Gr	5	82
2	5% Cu/Gr	2.5	82
3	5% Cu/Gr	1	69
4	3% Cu/C[c]	10	34
5	graphite		46

[a]Reaction conditions: aniline (1 mmol), MeSO₃H (1 mmol), t-BuONO (1.5 mmol), benzoquinone (0.9 mmol), and heterogeneous copper catalyst (see table entries) were stirred at 40 °C for 24 h. [b]Isolated yields after flash chromatography on silica gel. [c]Commercially available from Aldrich.

We discovered that graphite-supported CuO NPs also display the synergistic effect, comparable to that observed with a homogeneous molecular complex, with, however, a slightly higher loading. Indeed, with loading lower than 2.5 mol % Cu, a significant decreased yield was obtained (entry 2 vs. 3). Interestingly, our homemade catalyst was much more active than the commercial 3% Cu/C catalyst that displayed a detrimental effect on the reaction outcome (entry 5). The result from the background reaction, carried out in the presence of copper-free graphite, showed that the spectacular yield enhancement could not be attributed to the support (entry 5 vs entry 2, Table 1). This result represents the first example of a Meerwein arylation carried out in the presence of a heterogeneous catalyst. From a larger perspective, examples of organic reactions involving free-radical species and working with a heterogeneous catalyst are extremely rare and essentially limited to polymerization processes.[12] With an optimized procedure in hand, we next explored the scope of this synthetically useful transformation (Table 3). The reaction conditions are compatible with a variety of substituents including halogens (**3a–g**), cyanide (**3h**), ketone (**3i**), nitro (**3j,k**), ester (**3l–m**), and methoxy (**3n**). The conditions used in this transformation do not affect radical-reactive substituents such as halogens including iodine atom, and no trace of hydrolysis of the ester function has been observed. It is also noteworthy that the mild conditions developed for this process allow the handling of an acid-sensitive free alkyne (compound **3o**). These results suggest that further functionalization using palladium- (cross-coupling reactions) and copper-catalyzed reactions (click chemistry) as well as standard synthetic chemistry could be envisaged for inducing molecular complexity. The synergistic effect of copper is exemplified in several examples (compounds **3a**, **3b**, **3d**, and **3l**) and enhances the yields of the 3-arylbenzoquinones up to 40%. Meerwein arylation carried out with CuCl₂ is frequently contaminated with unwanted Sandmeyer-type byproducts by chlorine

Table 3. Scope of the Reaction
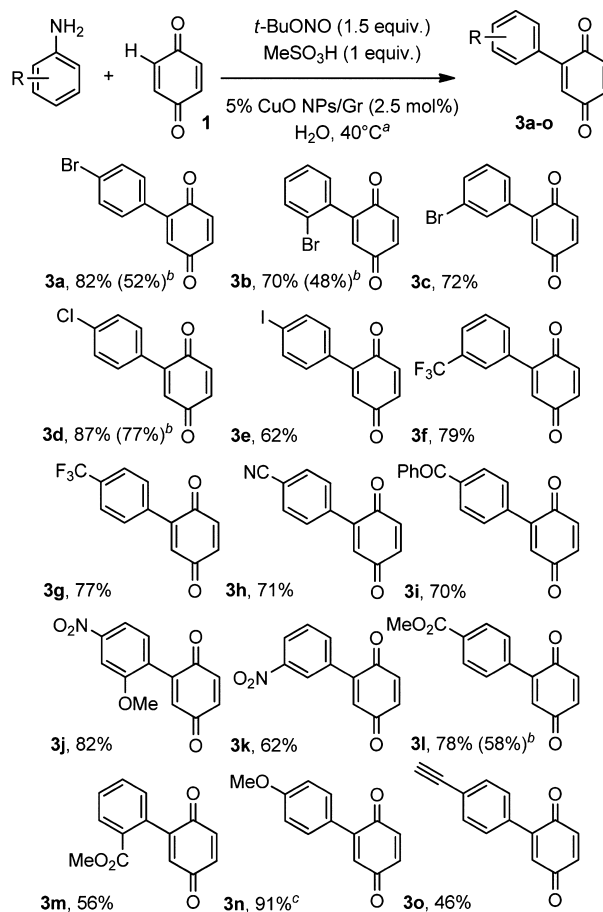
[a]Reaction conditions: aniline (1 mmol), MeSO₃H (1 mmol), t-BuONO (1.5 mmol), benzoquinone (0.9 mmol), and CuONPs/Gr (2.5 mol %) were stirred at 40 °C for 24 h. [b]Yields in parentheses: the CuONPs/Gr catalyst was omitted. [c]CaCO₃ was used as additive.

trapping, thereby decreasing the expected product yields. With our 5% CuONPs/Gr catalyst, these side products cannot be formed, and the crudes are usually very clean, mainly containing the expected product and the remaining starting material. From an environmental point of view, the process only requires reagents with low toxicity and generates t-BuOH, H₂O, and N₂ as byproducts.

The easy catalyst recovery by a single filtration is a salient advantage of heterogeneous catalysis, allowing the metal reprocessing and even sometimes the catalyst recycling. Accordingly, we evaluated the robustness of our CuONPs/Gr catalyst on a few catalytic cycles for the synthesis of **3a**. We determined that the catalytic activity was essentially conserved after the first reuse (80%), and even after the fifth cycle only a negligible decrease of the yield was observed (76%). The true nature of the catalysis (i.e., heterogeneous vs homogeneous) is still unknown at this time, and we are currently working at its elucidation. However, ICP-MS analysis of the crude reaction mixture after a simple filtration only showed marginal leaching. Indeed, only 3.3% and 0.02% of soluble copper species (based on the initial amount introduced) remained in solution after the first and second run, respectively. This methodology can be easily extended to the C–H arylation of naphthoquinones providing a few modifications (Scheme 2). For instance, because the naphthoquinone **4** is mostly insoluble in water, the

Scheme 2. C–H Arylation of Naphthoquionone 4
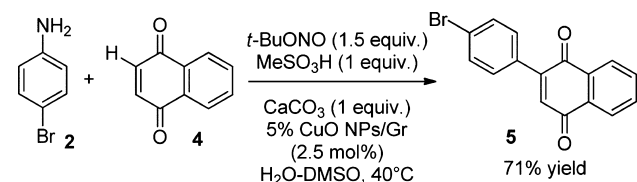
use of DMSO as cosolvent proved to be required. Moreover, the sensitivity of **4** toward acidic conditions prompted us to use CaCO$_3$ as buffer.

In summary, we have described the beneficial synergistic effect of graphite-supported copper(II) oxide nanoparticles with hydroquinone for the radical C–H arylation of benzoquinone with in situ activated anilines. This work represents the first Meerwein arylation under heterogeneous catalysis. The mild and experimentally simple conditions developed allow the coupling of benzoquinone with variously substituted anilines. The robustness of the CuONPs/Gr catalyst was demonstrated over five recycling experiments.

■ EXPERIMENTAL SECTION

Preparation of the CuONPs/Gr Catalyst. Distilled methanol (60 mL) at 25 °C was degassed with H$_2$ during 5 min. Copper(II) acetate monohydrate (0.4 g, 2 mmol) was added, and the resulting mixture was stirred until complete dissolution. Graphite (0.5 g) was then added, and the mixture was diluted with distilled methanol (5 mL) and degassed with H$_2$ during 5 min. The mixture was then refluxed overnight under H$_2$ atmosphere (1 atm). The solid phase was separated by filtration and washed with distilled methanol (3 × 5 mL), deionized water (3 × 5 mL), and acetone (3 × 5 mL). The filtrate was then dried under vacuum overnight to give a black solid. The ICPMS analysis showed a Cu/graphite catalyst at 4.5−5% w/w.

General Procedure for the C–H Arylation of Benzoquinone. To a mixture of aniline and MeSO$_3$H (65 μL, 1.0 mmol) in H$_2$O (5 mL) at 25 °C was added t-BuONO (180 μL, 1.5 mmol). The reaction mixture was stirred for 5 min and diluted with H$_2$O (5 mL). Benzoquinone (97.3 mg, 0.9 mmol) and the 5% CuONPs/Gr catalyst (2.5% mol) were added successively. The temperature was warmed to 40 °C, and the mixture was stirred for 24 h. The mixture was cooled to 5 °C, and the precipitate was collected by filtration. The solid was washed with ethyl acetate (50 mL). The recovered organic layer was dried on Na$_2$SO$_4$, filtered and evaporated to dryness. The crude was purified by flash chromatography on silica gel to give the pure product. The same procedure was considered using a homogeneous catalyst for the optimization studies reported in Table 1.

2-(4-Bromophenyl)-1,4-benzoquinone (3a). The crude product was purified by flash chromatography on silica gel to give the product as a pale orange solid (193.9 mg, 82%): R_f = 0.30 (petroleum ether/DCM 50/50); mp 113−115 °C (lit.[6] mp 114−115 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, 2H, J = 8.7 Hz), 7.35 (d, 2H, J = 8.7 Hz), 6.88−6.81 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.4, 186.3, 144.9, 137.1, 136.5, 132.8, 132.0 (2C), 131.6, 130.9 (2C), 125.0; IR ν 3050, 2925, 1649, 1592, 1488 cm^{-1}; HRMS (MALDI) calcd for C$_{12}$H$_9$BrO$_2$ [M + 2H]$^+$ 263.9780, found 263.9778.[13]

2-(2-Bromophenyl)-1,4-benzoquinone (3b). The crude product was purified by flash chromatography on silica gel to give the product as a brown-orange solid (165.5 mg, 70%): R_f = 0.25 (petroleum ether/DCM 50/50); mp 96−97 °C (lit.[5b] mp 98−100 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, 1H, J = 7.8, 1.2 Hz), 7.38 (app dt, 1H, J = 7.8, 7.5, 1.2 Hz), 7.30 (app dt, 1H, J = 7.8, 7.5, 1.8 Hz), 7.20 (dd, 1H, J = 7.5, 1.8 Hz), 6.91−6.84 (m, 2H), 6.76 (d, 1H, J = 2.3 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.4, 185.2, 147.8, 137.0, 136.6, 134.9, 134.7, 133.1, 131.0, 130.7, 127.5, 122.8; IR ν 3062, 1659, 1601 cm^{-1}; HRMS (MALDI) calcd for C$_{12}$H$_9$BrO$_2$ [M + 2H]$^+$ 263.9780, found 263.9778.[2]

2-(3-Bromophenyl)-1,4-benzoquinone (3c). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (169.7 mg, 72%): R_f = 0.29 (petroleum ether/DCM 60/40); mp 134−139 °C (lit.[4] mp 138−144 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (app t, 1H, J = 1.5 Hz), 7.59 (app dt, 1H, J = 7.8, 1.5 Hz), 7.40 (app dt, 1H, J = 7.8, 1.5 Hz), 7.32 (app t, 1H, J = 7.8 Hz), 6.89−6.82 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.3, 186.2, 144.7, 137.1, 136.5, 134.7, 133.3, 133.2, 132.2, 130.2, 128.0, 122.7; IR ν 3073, 3060, 2958, 1683, 1652, 1593, 1555 cm^{-1}; HRMS (MALDI) calcd for C$_{12}$H$_9$BrO$_2$ [M + 2H]$^+$ 263.9780, found 263.9789.[2]

2-(4-Chlorophenyl)-1,4-benzoquinone (3d). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (171.9 mg, 87%): R_f = 0.18 (petroleum ether/DCM 60/40); mp 127−129 °C (lit.[4] mp 129.5 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (d, 2H, J = 8.9 Hz), 7.52 (d, 2H, J = 8.9 Hz), 6.99−6.90 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 186.2, 144.0, 137.3, 136.1, 134.7, 132.4, 131.6, 131.2 (2C), 128.3 (2C); IR ν 3068, 1648, 1595, 1490 cm^{-1}; HRMS (ESI) calcd for C$_{12}$H$_8$ClO$_2$ [M + H]$^+$ 219.0213, found 219.0219.

2-(4-Iodophenyl)-1,4-benzoquinone (3e). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (173.2 mg, 62%): R_f = 0.21 (petroleum ether/DCM 50/50); mp 137−141 °C (lit.[4] mp 130−135 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, 2H, J = 8.6 Hz), 7.21 (d, 2H, J = 8.6 Hz), 6.88−6.81 (m, 3H,); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.4, 186.3, 145.1, 137.9 (2C), 137.1, 136.5, 132.8, 132.2, 130.9 (2C), 97.1; IR ν 3246, 3060, 2922, 1642, 1595, 1579 cm^{-1}; HRMS (MALDI) calcd for C$_{12}$H$_9$IO$_2$ [M + 2H]$^+$ 311.9642, found 311.9646.[2]

2-(3-Trifluoromethylphenyl)-1,4-benzoquinone (3f). The crude product was purified by flash chromatography on silica gel to give the product as a brown solid (179.4 mg, 79%): R_f = 0.24 (petroleum ether/DCM 60/40); mp 60−63 °C (lit.[14] mp 60−61 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (s, 1H), 7.84−7.82 (m, 2H), 7.70 (app t, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 2.5 Hz), 7.02−6.93 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 186.1, 143.9, 137.3, 136.1, 133.8, 133.3, 133.1, 129.3, 129.0 (q, J = 31.0 Hz), 126.1, 126.0, 124.0 (q, J = 271.0 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.13; IR ν 3052, 1659, 1609, 1586 cm^{-1}; HRMS (ESI) calcd for C$_{13}$H$_8$F$_3$O$_2$ [M + H]$^+$ 253.0482, found 253.0482.

2-(4-Trifluoromethylphenyl)-1,4-benzoquinone (3g). The crude product was purified by flash chromatography on silica gel to give the product as a pale brown solid (174.2 mg, 77%): R_f = 0.30 (petroleum ether/DCM 50/50); mp 104−113 °C (lit.[4] mp 105−108 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, 2H, J = 8.1 Hz), 7.73 (d, 2H, J = 8.1 Hz), 7.04 (d, 1H, J = 2.5 Hz), 7.02−6.94 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.5, 186.0, 144.0, 137.3 (2C), 137.0, 136.2, 133.4, 130.2 (2C), 129.4 (q, J = 31.0 Hz), 124.9 (q, J = 3.7 Hz), 124.0 (q, J = 270.0 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ −61.33; IR ν 3074, 1649, 1597 cm^{-1}; HRMS (ESI) calcd for C$_{13}$H$_8$F$_3$O$_2$ [M + H]$^+$ 253.0482, found 253.0483.

2-(4-Cyanophenyl)-1,4-benzoquinone (3h). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (134.4 mg, 71%): R_f = 0.28 (petroleum ether/DCM 10/90); mp 210−211 °C (lit.[5e] mp 210−211 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, 2H, J = 8.6 Hz), 7.71 (d, 2H, J = 8.6 Hz), 7.05 (d, 1H J = 2.5 Hz), 7.02−6.92 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.5, 185.8, 143.8, 137.5, 137.3, 136.2, 133.5, 132.0 (2C), 130.3 (2C), 118.4, 112.1; IR ν 3092, 3063, 3047, 2238, 1661, 1590 cm^{-1}; HRMS (ESI) calcd for C$_{13}$H$_8$NO$_2$ [M + H]$^+$ 210.0560, found 210.0559.

2-(4-Benzoylphenyl)-1,4-benzoquinone (3i). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (182.1 mg, 70%): R_f = 0.33 (DCM); mp 108−116 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81−7.75 (m, 3H), 7.72−7.68 (m, 3H), 7.63−7.55 (m, 3H), 7.05 (d, 1H, J = 2.5 Hz), 7.00−6.94 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.3, 187.6, 186.2, 144.3, 137.7, 137.3, 136.8, 136.7, 136.1, 133.1, 132.8, 129.6 (2C), 129.5 (2C), 129.3 (2C), 128.6 (2C); IR ν 3061, 1652, 1589

cm^{-1}; HRMS (ESI) calcd for C$_{19}$H$_{13}$O$_3$ [M + H]$^+$ 289.0859, found 289.0858.

2-(2-Methoxy-4-nitrophenyl)-1,4-benzoquinone (3j). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (191.8 mg, 82%): R$_f$ = 0.19 (petroleum ether/ethyl acetate 80/20); mp 151−153 °C (lit.[6] mp 156−157 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (dd, 1H, J = 8.3, 2.1 Hz), 7.79 (d, 1H, J = 2.1 Hz), 7.32 (d, 1H, J = 8.3 Hz), 6.90−6.82 (m, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.1, 184.8, 157.8, 149.9, 144.0, 137.1, 136.5, 135.2, 131.1, 129.0, 115.8, 106.6, 56.7; IR ν 3123, 3084, 2988, 2956, 2853, 1734, 1591, cm^{-1}; HRMS (ESI) calcd for C$_{13}$H$_{10}$NO$_5$ [M + H]$^+$ 260.0554, found 260.0563.

2-(3-Nitrophenyl)-1,4-benzoquinone (3k). The crude product was purified by flash chromatography on silica gel to give the product as a beige solid (127.1 mg, 62%): R$_f$ = 0.26 (petroleum ether/DCM 30/70); mp 102−104 °C (lit.[5a] mp 105−107 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 (app t, 1H, J = 2.0 Hz), 8.31 (ddd, 1H, J = 8.2, 2.4, 1.0 Hz), 7.97 (app dt, 1H, J = 8.0, 1.2 Hz), 7.76 (app t, 1H, J = 8.0 Hz), 7.12 (d, 1H, J = 2.5 Hz), 7.04−6.96 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.5, 185.9, 147.5, 143.2, 137.3, 136.2, 135.8, 134.3, 133.4, 129.8, 124.3, 124.1; IR ν 3083, 1661, 1530 cm^{-1}; HRMS (ESI) calcd for C$_{12}$H$_8$NO$_4$ [M + H]$^+$ 230.0459, found 230.0458.

2-(4-Methoxycarbonylphenyl)-1,4-benzoquinone (3l). The crude product was purified by flash chromatography on silica gel, to give the product as an unstable orange solid (170.5 mg, 78%): R$_f$ = 0.24 (petroleum ether/ethyl acetate 80/20); mp 144−150 °C (lit.[4] mp 145−152 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, 2H, J = 8.4 Hz), 7.53 (d, 2H, J = 8.4 Hz), 6.88−6.84 (m, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.3, 186.2, 166.5, 145.1, 137.1, 137.0, 136.5, 133.5, 131.5, 129.7 (2C), 129.4 (2C), 52.4; IR ν 3049, 2959, 1729, 1654, 1590 cm^{-1}; HRMS (ESI) calcd for C$_{14}$H$_{11}$O$_4$ [M + H]$^+$ 243.0663, found 243.0661.

2-(2-Methoxycarbonylphenyl)-1,4-benzoquinone (3m). The crude product was purified by flash chromatography on silica gel to give the product as an orange solid (121.9 mg, 56%): R$_f$ = 0.19 (petroleum ether/DCM 10/90); mp 103−105 °C (lit.[5b] mp 107−109 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (ddd, 1H, J = 7.7, 1.4, 0.4 Hz), 7.61 (app td, 1H, J = 7.7 Hz, J = 7.7 Hz, J = 1.4 Hz), 7.52 (app td, 1H, J = 7.7 Hz, J = 7.7 Hz, J = 1.4 Hz), 7.27 (ddd, 1H, J = 7.7, 1.4 Hz, 0.4 Hz), 6.88−6.79 (m, 2H), 6.68 (d, 1H, J = 2.2 Hz), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.6, 185.9, 166.8, 150.2, 137.0, 136.8, 135.1, 132.9, 131.0, 130.5, 130.2, 130.1, 129.9, 52.5; IR ν 3064, 3039, 3004, 2953, 2838, 1709, 1655, 1597, 1487 cm^{-1}; HRMS (ESI) calcd for C$_{14}$H$_9$O$_4$ [M − H]$^-$ 241.0506, found 241.0510.

2-(4-Methoxyphenyl)-1,4-benzoquinone (3n). The crude product was purified by flash chromatography on silica gel, to give the product as an orange solid (175.4 mg, 91%): R$_f$ = 0.30 (petroleum ether/DCM 40/60); mp 113−115 °C (lit.[4] mp 105−108 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, 2H, J = 8.9 Hz), 6.95 (d, 2H, J = 8.9 Hz), 6.76−6.84 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 187.7, 187.2, 161.5, 145.3, 137.1, 136.3, 131.2, 131.0, 125.1, 114.3, 55.5; IR ν 3055, 3041, 2963, 2935, 1658, 1606 cm^{-1}; HRMS (ESI) calcd for C$_{13}$H$_{11}$O$_3$ [M + H]$^+$ 215.0703, found 215.0700.

2-(4-Ethynylphenyl)-1,4-benzoquinone (3o). The crude product was purified by flash chromatography on silica gel, to give the product as an orange solid (86.5 mg, 46%): R$_f$ = 0.27 (petroleum ether/DCM 50/50); mp 117−123 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (s, 4H), 6.99−6.91 (m, 3H), 4.32 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 186.2, 144.3, 137.3, 136.1, 133.2, 132.5, 131.4 (2C), 129.6 (2C), 123.0, 83.0, 82.4; IR ν 3251, 3054, 1652, 1587, 1546, 1506 cm^{-1}; HRMS (ESI) calcd for C$_{14}$H$_9$O$_2$ [M + H]$^+$ 209.0608, found 209.0603.

2-(4-Bromophenyl)-1,4-naphthoquinone (5). A mixture of aniline (172 mg, 1 mmol) and MeSO$_3$H (65 µL, 1.0 mmol) in H$_2$O (5 mL) at 25 °C was stirred for 5 min until no solid remains in solution. Then, t-BuONO (180 µL, 1.5 mmol) was added to the reaction mixture. After 5 min of stirring, CaCO$_3$ (100 mg, 1 mmol) and the mixture was stirred for an additional 30 min. Naphthoquinone (158 mg, 0.9 mmol), 5% CuONPs/Gr (2.5% mol), and DMSO (5 mL) were successively added. The temperature was warmed to 40 °C,

and the mixture was stirred 24 h. The mixture was filtered on Buchner. The liquid part was extracted three times with Et$_2$O and the solid part was washed with DCM. The recovered organic layer was dried on Na$_2$SO$_4$, filtered, and evaporated to dryness. The crude was purified by flash chromatography on silica gel (5% EtOAc−petroleum ether) to give the pure product as an orange solid (198 mg, 71%): R$_f$ = 0.31 (petroleum ether/DCM 50/50); mp 165−166 °C (lit.[15] mp 164−166 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14−8.19 (m, 1H), 8.09−8.13 (m, 1H), 7.75−7.80 (m, 2H), 7.60 (dt, 2H, J = 2.4, 8.7 Hz), 7.60 (dt, 2H, J = 2.4, 8.7 Hz), 7.06 (s, 1H), 6.99−6.91 (m, 3H), 4.32 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 185.2, 184.4, 147.3, 135.5, 134.3, 134.3, 132.7, 132.6, 132.4, 132.1, 131.3, 127.4, 126.4, 125.1; IR ν 3093, 3033, 1670, 1658, 1599, 1583 cm^{-1}; MS (CI) m/z 312 (^{79}Br), 314 (^{81}Br).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1 and S2, formula S1, XPS details, and ^{1}H, ^{19}F, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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