**INTRODUCTION**

Indole and its derivatives, as a common subunit in various pharmaceutically attractive and naturally occurring products, have been widely applied in the fields of synthetic chemistry, materials science, and medicinal chemistry. Particularly, the indole nucleus is a structural component of a large number of biologically active natural and unnatural compounds. Incorporation of the indole nucleus into quinone frameworks serves as a platform for the synthesis of a potentially valuable class of indole derivatives where indolylquinones are versatile building blocks for the construction of biologically active natural products. In this regard, indoles represent a system of particular interest and importance. Thus, the C-2 and C-3 selective methods would be valuable. Previous methods reported the incorporation of quinones into the C-3 position of indoles (Scheme 1). The Pirrung group and others have reported that the Lewis acids [such as Bi(OTf)$_3$, Pd(OAc)$_2$, CuBr$_2$, InBr$_3$, etc.] can catalyze the conjugate addition reaction of indoles with quinones to give 3-indolylquinones. Such a reaction can be catalyzed by some Bronsted acids. Iron hydroxide nanoparticles can catalyze the coupling reaction between $p$-benzoquinone and 2-methylindole, and 3-indolylquinone was also achieved via oxidative C–C coupling of hydroquinones with indoles over Ag$_2$O and Fe$_3$O$_4$/povidone-phosphotungstic acid catalysts using H$_2$O$_2$ in tetrahydrofuran. All of these methods have certain limitations, such as the need for metals to act as catalysts, the use of a toxic organic solvent, and the limited substrate scope or low yields. It is noteworthy that coupling of indoles with 1,4-benzoquinones provides the desired product “in water”. The method needs long reaction time and involves one indolyl-1,4-naphthoquinone. Therefore, it is highly desirable to develop a simple and environmentally benign protocol to construct indolyl-1,4-naphthoquinones.

In organic chemistry, chemists have an increasing interest in developing “green” processes and sustainability, which are important issues in every area of human activity. The use of solvents is a key aspect among the 12 principles of green chemistry. Water has emerged as a potentially useful and safe solvent and is abundant, nontoxic, noncorrosive, and nonflammable. There are some challenges in organic reactions in aqueous media. First, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water. Second, most organic substances are insoluble in water. On the other hand, water possesses many unique physical and chemical properties: a large temperature window in which it remains in the liquid state; extensive hydrogen bonding; high heat capacity; large dielectric constant; and...
optimum oxygen solubility to maintain aquatic life forms, which dramatically enhance the rates and affect the selectivity of a wide variety of organic reactions. \(^{17}\)

Tris(pentafluorophenyl)borane \([\text{B(C}_6\text{F}_5)_3]\), which has received significant attention as a nonconventional, nontoxic, air-stable, water-tolerant, thermal abiding, and frustrated Lewis acid, \(^{18}\) has been widely employed in a number of transformations in organic chemistry including hydrogenation reactions, \(^{19}\) hydroisolation \(^{20}\) of unsaturated organic functions, dehydrogenative coupling of alcohols and amines, \(^{21}\) dehydrogenative oxidation, \(^{22}\) and other transformations. \(^{23}\) Owing to its highly electrophilic but sterically protected nature, \([\text{B(C}_6\text{F}_5)_3]\) has been commonly employed as the Lewis acid component in frustrated Lewis pair (FLP) chemistry to activate small molecules and in metal-free catalysis. \(^{24}\)

Generally, the coordination of water with a Lewis acidic metal complex leads to the weakening of the O–H bond. \(^{25}\) In this respect, the interaction of \([\text{B(C}_6\text{F}_5)_3]\) with water has been thoroughly investigated by different groups. \(^{26}\) Recently, the group of Tang reported that \([\text{B(C}_6\text{F}_5)_3]\) catalyzes \(\alpha\)-diazoester insertion into the O–H bond in water, affording various \(\alpha\)-hydroxyesters. \(^{27}\) Our concept was to utilize the Bronsted acid \([\text{B(C}_6\text{F}_5)_3]\)-catalyzed conversion of \(\text{C}==\text{O}\) and the subsequent nucleophilic addition. Herein, we report a \([\text{B(C}_6\text{F}_5)_3]\)-catalyzed C(sp\(^2\))–H and C(sp\(^3\))–H bond coupling of 1,4-naphthoquinones with the C-3 position of indole derivatives through conjugate addition of indole compounds to 1,4-naphthoquinones, followed by in situ dehydrogenation in water, wherein water and part of the catalyst were recycled under mild conditions.

**RESULTS AND DISCUSSION**

Initially, we commenced our study by monitoring a test reaction of 1,4-naphthoquinone \(1\text{a}\) with 1-methyl-1\(\text{H}\)-indole \(2\text{a}\) (1.0 equiv) \("\text{in water}\" for 24 h at room temperature (Table 1, entry 1). It is noteworthy that our work is different from that of Li’s group about substrates, \(^{10}\) in which good yields were not obtained in the absence of other catalysts. Thus, the reaction was carried out in the presence of \(1\text{a}\) (0.4 mmol), \(2\text{a}\) (0.4 mmol), the Lewis acid catalyst agent (mmol %), and water (2 mL) for 2 h under an air atmosphere. \(^{10}\)

![Scheme 1. Approaches to 3-Indolylquinone Compounds](image)

**Table 1. Optimization of the Reaction Conditions**

| entry | \(1\text{a}/2\text{a}\) | catalyst (mol %) | temp (°C) | yield (%) |
|-------|-----------------|-----------------|------------|-----------|
| 1     | 1:1             | B(\text{C}_6\text{F}_5)_3 (3) | 25         | 70        |
| 2     | 1:1             | Bi(OTf)_3 (3)   | 25         | 19        |
| 3     | 1:1             | Cu(OTf)_2 (3)   | 25         | 10        |
| 4     | 1:1             | La(OTf)_3 (3)   | 25         | 10        |
| 5     | 1:1             | Sm(OTf)_3 (3)   | 25         | 12        |
| 6     | 1:1             | Fe(OTf)_2 (3)   | 25         | 26        |
| 7     | 1:1             | FeCl_3 (3)      | 25         | 24        |
| 8     | 1:1             | ZnCl_2 (3)      | 25         | trace     |
| 9     | 1:1             | BiCl_3 (3)      | 25         | 57        |
| 10    | 1:1             | HCl (3)         | 25         | 43        |
| 11    | 1:1             | HOAC (3)        | 25         | NR        |
| 12    | 1:1             | B(C_6F_5)_3 (1) | 25         | 55        |
| 13    | 1:1             | B(C_6F_5)_3 (5) | 25         | 81        |
| 14    | 1:2             | B(C_6F_5)_3 (5) | 25         | 68        |
| 15    | 1:2             | B(C_6F_5)_3 (5) | 25         | 64        |
| 16    | 2:1             | B(C_6F_5)_3 (5) | 60         | 91        |
| 17    | 1:1             | B(2,4,6-F_3C_6H_2) (5) | 60 | 68        |
| 18    | 1:1             | B(3,4,5-F_3C_6H_2) (5) | 60 | 71        |
| 19    | 1:1             | B(2,4,6-F_3C_6H_2) (5) | 60 | 36        |

\(^{a}\)Unless otherwise specified, the reactions were carried out in the presence of \(1\text{a}\) (0.4 mmol), \(2\text{a}\) (0.4 mmol), the Lewis acid catalyst (mmol %), and water (2 mL) for 2 h under an air atmosphere. \(^{10}\)

\(^{b}\)Isolated yields. \(^{c}\)Without catalysts for 24 h. \(^{d}\)No reactions.

Further work is in progress.
various reaction parameters, the best yield of catalysts under 60 °C for 2 h (entry 20). After the evaluation of various reaction parameters, the best yield of 3aa (91%) was obtained by employing 1a (0.4 mmol), 2a (1 equiv), and B(C6F5)3 (5 mol %) in water as the sole solvent in open air under 60 °C for 2 h (entry 17). A notable B(C6F5)3 acceleration was observed in these reactions for 2 h. Using the ratio of indole/quinone = 1:1 was also atom-economical.

With the optimized conditions established, we evaluated the scope and the influence of the substituents on the indole moiety. The results are presented in Table 2. When free NH-indole (2b) was used as the substrate under identical conditions, 3ab was obtained in 83% yield. It is noteworthy that other N-alkylindoles (2a and 2c) also proved to be suitable coupling partners to provide the corresponding products in good yields (91 and 86%). Unfortunately, due to the highly electron-deficient acetyl present at the N position, no product was detected when N-acetylindole (2d) was used. Notably, N-allylindole (2e) also worked well under this protocol and afforded the desired product 3ae in 75% yield. Unfortunately, the reaction did not work when 2f was used as a substrate (3af). The electron-rich indoles with a substituent at the 2-position are good reactants. 2-Methylindole and 2-allylindole reacted well to give the corresponding products 3ag and 3ah in 90 and 81% yields, respectively.

Table 2. Substrate Scope with Respect to the Indoles

| R       | 1a       | 2a       | 3aa       |
|---------|----------|----------|-----------|
| Cl      | 86%      | 3a       | 70%       |
| H       | 86%      | 3a       | 70%       |
| Br      | 86%      | 3a       | 70%       |

†Reaction conditions: 1a (0.4 mmol), 2 (0.4 mmol), B(C6F5)3 (5 mol %), H2O (2 mL), 60 °C, 2 h, under an air atmosphere. The isolated yield was based on 1a.
Based on previous reports and summary, the reaction mechanism is hypothesized in Scheme 3. At first, the Lewis acid \( B(C_6F_5)_3 \) with \( \text{H}_2\text{O} \) gives a coordinated adduct, which may exist in equilibrium.\(^{28}\) The reaction is probably the Bronsted acid activation of 1,4-naphthoquinone (1a) by \( B(C_6F_5)_3\text{-H}_2\text{O} \).\(^{29}\) The in situ generated electrophilic species A reacts with N-methylindole (2b) in the 3-position to form 1,4-hydroquinone intermediate B and generate an anionic hydroxyboron \([B(C_6F_5)_3\text{-OH}]^-\). Then 1,4-naphthoquinone oxidized the 1,4-hydroquinone intermediate B into the N-methylindole-substituted 1,4-naphthoquinone (3aa). At the same time, 1a was regenerated by the oxidation of the 1,4-hydroquinone C under an air atmosphere in water.\(^{10}\)

**CONCLUSIONS**

In summary, we have developed the \( B(C_6F_5)_3 \)-catalyzed \( \text{C(sp}^2)\text{-H} \) and \( \text{C(sp}^2)\text{-H} \) bond coupling of 1,4-naphthoquinones with the C-3 position of indole derivatives. \( B(C_6F_5)_3 \) was able to catalyze a wide range of reactions involving indoles and 1,4-naphthoquinones to yield products in moderate to good yields under open-air conditions. Based on previous reports and summary, the proposed reaction mechanism is hypothesized. This new protocol has proved to be economical, practical, and eco-friendly without employing any base and organic solvent. Besides, the recycling and recovery of \( B(C_6F_5)_3 \) and \( \text{H}_2\text{O} \) as the solvent were reported in the reaction at first. Thus, the easy and rapid recycling protocol met the goal of green and sustainable chemistry. The procedure should be a facile and convenient method with the prospect of industrial applications.

**EXPERIMENTAL SECTION**

**General Information.** Chemicals and analytical-grade solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. All reagents were weighed and handled in air at room temperature. Analytical thin-layer chromatography (TLC) was performed on glass plates of silica gel GF-254 with detection by UV light (254 and 365 nm). Column chromatography was carried out on silica gel (200−300 mesh).\(^{1}\) H NMR spectra were recorded at 400 MHz and \(^{13}\)C NMR spectra were recorded at 101 MHz using an Agilent 400 MHz NMR spectrometer. Chemical shifts were calibrated using a residual undeuterated solvent as an internal reference \([\text{^1H NMR: CDCl}_3 \ 7.26 \text{ppm, dimethyl}\]
sulfoxide (DMSO)-d$_6$ 2.50 ppm; $^{13}$C NMR: CDCl$_3$ 77.16 ppm, DMSO-d$_6$ 39.52 ppm]. Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet); coupling constants (J) are reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was performed on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were measured with a micro melting point apparatus.

**Procedure for the Gam-Scale Reaction.** To a solution of H$_2$O (100 mL) were added 1,4-naphthoquinone 1a (3.16 g, 20 mmol), N-methylindole 2a (2.62 g, 20 mmol), and B(C$_6$F$_5$)$_3$ (0.51 g, 1 mmol). The mixture was stirred at 60 °C (the temperature of the oil bath) for 2 h under an air atmosphere. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (100 mL) and the aqueous phase was extracted with EtOAc (3 × 100 mL, then 3 × 30 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give 5.29 g of 2-(3-N-methylindolyl)-1,4-naphthoquinone in 92% yield.

**General Procedures for the Synthesis of 3-Indolylquinones.** To a solution of H$_2$O (2 mL) were added 1 (0.4 mmol), 2 (0.4 mmol), and B(C$_6$F$_5$)$_3$ (10.2 mg, 0.02 mmol). The mixture was stirred at 60 °C (the temperature of the oil bath) for about 2−5 h under an air atmosphere. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (2 mL) and then extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc) to afford the desired pure product 3.

**2-(1-Methyl-1H-indol-3-yl)naphthalene-1,4-dione (3aa).** The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), N-methylindole (2a, 52.5 mg, 0.4 mmol), and B(C$_6$F$_5$)$_3$ (10.2 mg, 0.02 mmol) in H$_2$O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3aa as a black solid (91% yield), mp 178−180 °C. $R_f$ = 0.50 (petroleum ether/EtOAc = 7/1). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99−7.88 (m, 3H), 7.81−7.76 (m, 1H), 7.57−7.50 (m, 2H), 7.21 (s, 1H), 7.16 (d, $J = 10.1$ Hz, 1H), 7.11 (dd, $J = 14.0$, 7.4 Hz, 2H), 3.67 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 185.70, 184.49, 184.28, 183.70, 135.77, 135.69, 135.63, 133.09, 132.86, 132.83, 128.57, 126.76, 126.26, 125.64, 122.97, 121.73, 120.61, 110.14, 107.57, 33.41.

**2-(1H-Indol-3-yl)naphthalene-1,4-dione (3ab).** The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), indole (2b, 46.8 mg, 0.4 mmol), and B(C$_6$F$_5$)$_3$ (10.2 mg, 0.02 mmol) in H$_2$O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ab as a red solid (83% yield), mp 199−201 °C. $R_f$ = 0.40 (petroleum ether/EtOAc = 7/1). $^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 12.00 (s, 1H), 8.20 (d, $J = 2.1$ Hz, 1H), 8.07−8.00 (m, 1H), 7.95 (d, $J = 4.8$ Hz, 1H), 7.82 (dd, $J = 10.7$, 6.6 Hz, 3H), 7.49 (d, $J = 7.4$ Hz, 1H), 7.25−7.13 (m, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 185.42, 184.56, 142.54, 137.14, 134.49, 134.03, 132.97, 132.91, 132.10, 128.11, 126.95, 125.59, 123.01, 121.71, 120.44, 113.04, 107.78.
Methyl 3-(1,4-Dioxo-1,4-dihydropyridine-2-yl)-1-methyl-1H-indole-2-carboxylate (3aj). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), methyl-1-methyl-1H-indole-2-carboxylic acid (2j, 75.7 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3aj as a red solid (72% yield), mp 206–208 °C. 

1H NMR (400 MHz, DMSO-d6) δ 8.23–8.13 (m, 2H), 7.83–7.73 (m, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.50–7.37 (m, 2H), 7.29–7.23 (m, 1H), 7.17 (s, 1H), 4.11 (s, 3H), 3.70 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 185.03, 184.61, 184.6, 153.61, 143.93, 138.56, 134.63, 133.71, 132.58, 132.32, 128.8, 126.68, 126.09, 125.50, 125.27, 121.91, 120.27, 113.52, 110.69, 51.84, 32.01. HRMS calc for C21H16NO4 (M + H)+ 346.1074, found 346.1072.

2-(4-Fluoro-1H-indol-3-yl)naphthalene-1,4-dione (3ak). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 4-fluoro-1H-indole (2k, 54.0 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3ak as a blackish-purple solid (76% yield), mp 246–248 °C. 

1H NMR (400 MHz, DMSO-d6) δ 12.34 (s, 1H), 8.25–8.20 (m, 1H), 8.19–8.08 (m, 2H), 8.04–7.98 (m, 2H), 7.50 (d, J = 8.1 Hz, 1H), 7.35 (td, J = 8.0, 5.2 Hz, 1H), 7.28 (d, J = 2.7 Hz, 1H), 7.06 (d, J = 12.2, 7.9 Hz, 1H).

13C NMR (101 MHz, DMSO-d6) δ 184.85, 184.61, 157.10, 154.66, 153.54, 143.25, 132.10, 132.05, 131.99, 126.95, 125.74, 112.41, 110.43, 109.99, 109.37, 107.04, 106.79, 106.57. 19F NMR (376 MHz, DMSO-d6) δ −113.74. HRMS calc for C24H16FNO4 (M + H)+ 392.0774, found 392.0774.

2-(4-Chloro-1H-indol-3-yl)naphthalene-1,4-dione (3al). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 4-chloro-1H-indole (2l, 60.6 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3al as a blackish-purple solid (75% yield), mp 225–227 °C. 

1H NMR (400 MHz, DMSO-d6) δ 12.08 (s, 1H), 8.15 (s, 1H), 7.99 (s, 1H), 7.92 (d, J = 4.3 Hz, 1H), 7.82–7.72 (m, 3H), 7.45 (d, J = 8.5 Hz, 1H), 7.18–7.07 (m, 2H).

13C NMR (101 MHz, DMSO-d6) δ 185.03, 184.58, 142.10, 135.63, 134.50, 134.09, 133.73, 132.79, 132.06, 129.12, 126.96, 126.20, 125.63, 122.90, 119.78, 114.44, 109.99, 107.76.

2-(5-Bromo-1H-indol-3-yl)naphthalene-1,4-dione (3ap). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 5-bromo-1H-indole (2p, 78 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3ap as a reddish-purple solid (71% yield), mp 239–241 °C. 

1H NMR (400 MHz, DMSO-d6) δ 12.01 (s, 1H), 8.05 (s, 1H), 7.92 (s, 1H), 7.82 (d, J = 15.5 Hz, 2H), 7.71 (d, J = 3.8 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.03 (d, J = 5.2 Hz, 1H).

13C NMR (101 MHz, DMSO-d6) δ 185.03, 184.61, 142.11, 135.86, 134.52, 134.11, 133.48, 132.78, 132.06, 129.25, 127.44, 126.96, 126.54, 125.45, 122.70, 118.46, 114.18, 107.67.

2-(5-Methoxy-1H-indol-3-yl)naphthalene-1,4-dione (3aq). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 5-methoxy-1H-indole (2q, 58.8 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3aq as a black solid (83% yield), mp 152–154 °C. 

1H NMR (400 MHz, DMSO-d6) δ 11.85 (s, 1H), 8.09 (d, J = 2.9 Hz, 1H), 8.00–7.95 (m, 1H), 7.92–7.88 (m, 1H), 7.77–7.73 (m, 2H), 7.35 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 7.11 (s, 1H), 6.81 (dd, J = 8.8, 2.1
Hz, 1H), 3.75 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 185.47, 184.49, 155.41, 142.61, 134.41, 133.90, 133.41, 132.87, 131.22, 127.56, 126.90, 126.20, 125.53, 113.71, 112.48, 107.63, 102.97, 55.91.

2-(5-(Allyloxy)-1H-indol-3-yl)naphthalene-1,4-dione (3ar). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 5-allyloxy-1H-indole (2r, 69.3 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ar as a blackish-purple solid (65% yield), mp 258−261 °C.

13C NMR (400 MHz, DMSO-d6) δ 185.11, 184.60, 140.09, 137.58, 134.53, 134.13, 133.52, 132.81, 132.03, 128.91, 127.46, 126.96, 125.63, 124.39, 121.91, 121.73, 112.55, 107.98.

2-(1H-Pyrrolo[2,3-b]pyridin-3-yl)naphthalene-1,4-dione (3av). The reaction was conducted with 1,4-naphthoquinone (1a, 63.3 mg, 0.4 mmol), 4H-pyrrolo[2,3-b]pyridine (2v, 47.2 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3av as a red-orange solid (71% yield), mp 160−162 °C.

1H NMR (400 MHz, CDCl3) δ 8.35 (d, J = 3.9 Hz, 1H), 8.20−8.08 (m, 2H), 8.06 (s, 1H), 7.97−7.88 (m, 1H), 7.84 (d, J = 3.9 Hz, 1H), 7.81−7.68 (m, 2H), 7.16 (d, J = 7.7, 4.8 Hz, 1H), 6.65 (d, J = 3.9 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 184.96, 181.61, 148.56, 143.51, 140.63, 134.37, 133.68, 131.70, 131.61, 129.42, 129.24, 127.62, 127.07, 126.03, 122.59, 103.95. HRMS calcd for C21H15N3O2·(M + H)+ 375.0815, found 375.0817.

2-Methyl-3-(1-methyl-1H-indol-3-yl)-3-phenylnaphthalene-1,4-dione (3ba). The reaction was conducted with 2-phenyl-1,4-naphthoquinone (1b, 68.9 mg, 0.4 mmol), 1-methyl-1H-indole (2a, 52.5 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 5 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ba as a red solid (75% yield), mp 182−184 °C.

1H NMR (400 MHz, CDCl3) δ 8.35−7.92 (m, 2H), 7.59−7.51 (m, 2H), 7.22 (d, J = 8.2 Hz, 1H), 7.16−7.07 (m, 3H), 7.01 (t, J = 7.1 Hz, 1H), 3.72 (s, 3H), 2.05 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 185.79, 184.65, 142.57, 140.06, 136.67, 133.41, 133.29, 134.45, 131.76, 127.07, 126.61, 126.08, 121.99, 120.63, 120.25, 109.79, 106.91, 33.21, 15.90. HRMS calcd for C25H21N3O2·(M + H)+ 392.1167, found 392.1183.

2-(1-Methyl-1H-indol-3-yl)-3-phenylnaphthalene-1,4-dione (3ca). The reaction was conducted with 2-phenyl-1,4-naphthoquinone (1c, 93.7 mg, 0.4 mmol), 1-methyl-1H-indole (2a, 52.5 mg, 0.4 mmol), and B(C6F5)3 (10.2 mg, 0.02 mmol) in H2O (2 mL) at 60 °C for 5 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ca as a black solid (65% yield), mp 258−260 °C.

1H NMR (400 MHz, CDCl3) δ 8.20−7.92 (m, 2H), 7.59−7.51 (m, 2H), 7.22 (d, J = 8.2 Hz, 1H), 7.16−7.07 (m, 3H), 7.01 (t, J = 7.1 Hz, 1H), 3.72 (s, 3H), 2.05 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 185.54, 184.43, 142.58, 142.07, 136.17, 136.60, 134.77, 133.68, 133.35, 132.54, 132.44, 130.57, 128.43, 128.03, 127.90, 127.58, 126.63, 126.50, 126.48, 121.80, 120.95, 120.00, 109.26, 105.72, 33.13. HRMS calcd for C25H21N3O2·(M + H)+ 364.1332, found 364.1334.
h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3da as a red solid (68% yield), mp 226–228 °C. Rf = 0.50 (petroleum ether/EtOAc = 7/1). 1H NMR (400 MHz, DMSO-d6) δ 8.08 (dd, J = 8.5, 4.2 Hz, 2H), 7.91–7.86 (m, 2H), 7.39 (s, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 8.3, 5.8 Hz, 2H), 6.99 (dt, J = 16.8, 8.0 Hz, 4H), 6.78 (t, J = 7.5 Hz, 1H), 3.77 (s, 3H). 13C NMR (101 MHz, DMSO-d6) δ 185.08, 183.79, 141.70, 140.08, 136.62, 134.70, 118.51, 117.03, 110.64, 109.36, 103.46, 99.76, 99.35, 93.98, 92.22, 88.50, 87.88, 85.01.

1H NMR (400 MHz, CDCl3) δ 8.39 (dd, J = 5.9, 3.1 Hz, 1H), 8.26 (dd, J = 5.9, 3.0 Hz, 1H), 7.92–7.89 (m, 2H), 7.60–7.51 (m, 3H), 7.30 (t, J = 6.9 Hz, 1H), 4.26 (s, 3H), 3.80 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 181.18, 178.22, 161.70, 146.41, 138.78, 138.08, 134.21, 133.95, 131.95, 131.36, 127.39, 126.53, 125.56, 123.98, 121.73, 121.36, 116.03, 110.88, 51.97, 32.29. HRMS calcld for C24H22BrN3O3+ (M + H)+ 424.0179, found 424.0180.

3,5-Dimethyl-2-(1-methyl-1H-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ia). The reaction was conducted with 2,6-dimethylcyclohexa-2,5-diene-1,4-dione (1i, 44.7 mg, 0.4 mmol), 1-methyl-1H-indole (2a, 52.5 mg, 0.4 mmol), and HC(O)OH (10.2 mg, 0.2 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ia as a black solid (66% yield), mp 118–120 °C. Rf = 0.50 (petroleum ether/EtOAc = 7/1). 1H NMR (400 MHz, CDCl3) δ 7.42 (s, 1H), 7.18 (dd, J = 16.3, 8.0 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.75 (s, 1H), 3.83 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 181.34, 180.15, 145.76, 139.67, 137.51, 136.70, 133.29, 132.73, 127.15, 121.86, 120.67, 120.16, 110.64, 106.64, 33.17, 15.92, 15.29. HRMS calcld for C20H18BrNO3+ (M + H)+ 266.1176, found 266.1179.

2,3,5-Trimethyl-6-(1-methyl-1H-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ja). The reaction was conducted with 2,5,3-trimethylcyclohexa-2,5-diene-1,4-dione (1j, 70.8 mg, 0.4 mmol), 1-methyl-1H-indole (2a, 52.5 mg, 0.4 mmol), and HC(O)OH (10.2 mg, 0.2 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 3ja as a dark-red solid (69% yield), mp 131–133 °C. Rf = 0.50 (petroleum ether/EtOAc = 7/1). 1H NMR (400 MHz, CDCl3) δ 7.20 (dd, J = 13.7, 7.7 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 2.01 (d, J = 7.2 Hz, 6H), 1.94 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 187.75, 186.62, 140.51, 140.36, 139.25, 137.46, 136.66, 132.50, 127.22, 121.78, 120.65, 120.07, 110.57, 106.61, 33.13, 15.19, 12.87, 12.69. HRMS calcld for C22H21N2O3+ (M + H)+ 280.1332, found 280.1335.

2,5-Dichloro-3-(1-methyl-1H-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ka). The reaction was conducted with 2,5-dichlorocyclohexa-2,5-diene-1,4-dione (1k, 70.8 mg, 0.4 mmol), 1-methyl-1H-indole (2a, 52.5 mg, 0.4 mmol), and HC(O)OH (10.2 mg, 0.2 mmol) in H2O (2 mL) at 60 °C for 2 h under an air atmosphere. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3ka as a black solid (75% yield), mp 107.83, 33.46. HRMS calcld for C19H13BrNO3+ (M + H)+ 366.0124, found 366.0130.
The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/1) to yield the desired product 3la as a black solid (72% yield), mp 161–163 °C, Rf = 0.30 (petroleum ether/EtOAc = 7/1). 1H NMR (400 MHz, DMSO-d$_6$) δ 7.67 (s, 1H), 7.51 (d, J = 6.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 3.87 (s, 3H). 13C NMR (101 MHz, DMSO-d$_6$) δ 178.33, 177.65, 143.41, 139.15, 136.28, 135.91, 133.54, 131.20, 125.76, 122.20, 121.77, 120.25, 112.55, 106.28.

Crystallographic data file of 3ga (CIF)

X-ray crystal structure of 3ga and spectra of all compounds (PDF)

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**Notes**

The authors declare no competing financial interest.

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