Supporting Information

## Tandem oxidation/oxidative C–H/C–H cross-coupling: synthesis of arylquinones from hydroquinones

Shuai Zhang, Feijie Song,\* Dongbing Zhao and Jingsong You\*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China Fax: 86-28-85412203; E-mail: jsyou@scu.edu.cn

#### Table of contents

| I. General remarks   | S3  |
|--|-----|
| II. Optimization of the tandem reaction of hydroquinones with arenes                               | S3  |
| III. General procedure for the synthesis of arylquinones   | S4  |
| IV. General procedure for the synthesis of heteroarylquinones                                      | S4  |
| V. Experimental data for the described substances  | S5  |
| VI. Mechanistic study  | S18 |
| VII. Confirmation of the structure of product <b>4c</b> by its derivation                          | S21 |
| VIII. References   | S22 |
| IX. Copies of <sup>1</sup> H, <sup>13</sup> C NMR and <sup>1</sup> H- <sup>1</sup> H NOESY spectra | S24 |

#### I. General remarks

NMR spectra were obtained on a Bruker AMX-400. The <sup>1</sup>H NMR (400 MHz) chemical shifts were measured relative to CDCl<sub>3</sub> (CDCl<sub>3</sub>:  $\delta$  = 7.26 ppm). The <sup>13</sup>C NMR (100 MHz) chemical shifts were given using CDCl<sub>3</sub> as the internal standard (CDCl<sub>3</sub>:  $\delta$  = 77.00 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all the reactions were carried out under air. All reagents were obtained from commercial suppliers and used without further purification.

#### II. Optimization of the tandem reaction of hydroquinones with arenes

A flame-dried sealable tube with a magnetic stir bar was charged with 1,4-naphthalenediol (67 mg, 0.4 mmol), palladium species, PivOH, oxidant, and DMSO (100  $\mu$ L, 1.4 mmol), and benzene (3.0 mL) under an N<sub>2</sub> atmosphere. The tube was sealed and the reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) to provide the desired product **3a**.

**Table S1.** Screening of the Pd-catalyzed cross-coupling of 1,4-naphthalenediol 1a with benzene $2a^a$ 

|       | OH<br>+ 1a OH 2a | Catalyst, Oxidant<br>PivOH, DMSO<br>140 °C, 24 h | Ph (          |                    |
|-------|------------------|--|---------------|--------------------|
| Entry | Catalyst (mol%)  | Oxidant (equiv)                                  | PivOH (equiv) | Yield of <b>3a</b> |
| 1     | none             | Ag <sub>2</sub> CO <sub>3</sub> (3.0)            | PivOH (2.0)   | $0^b$              |
| 2     | $Pd(OAc)_2(5)$   | Ag <sub>2</sub> CO <sub>3</sub> (3.0)            | PivOH (1.0)   | 18%                |
| 3     | $PdCl_{2}(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (3.0)            | PivOH (1.0)   | 74%                |

| 4                      | $Pd(acac)_2(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (3.0)                | PivOH (1.0) | 90%   |
|------------------------|--------------------|--|-------------|-------|
| 5                      | $Pd(acac)_2(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (3.0)                | PivOH (2.0) | 97%   |
| 6                      | $Pd(acac)_2$ (2.5) | Ag <sub>2</sub> CO <sub>3</sub> (3.0)                | PivOH (2.0) | 79%   |
| 7                      | $Pd(acac)_2(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (3.0)                | none        | trace |
| 8 <sup>c</sup>         | $Pd(acac)_2(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (3.0)                | PivOH (2.0) | 85%   |
| 9                      | $Pd(acac)_2(5)$    | Ag <sub>2</sub> CO <sub>3</sub> (1.2)/O <sub>2</sub> | PivOH (2.0) | 20%   |
| 10                     | $Pd(acac)_2(5)$    | Ag <sub>2</sub> O (3.0)                              | PivOH (2.0) | 33%   |
| 11                     | $Pd(acac)_2(5)$    | AgOAc (6.0)  | PivOH (2.0) | 88%   |
| 12                     | $Pd(acac)_2(5)$    | $Cu(OAc)_2$ (3.0)                                    | PivOH (2.0) | $0^b$ |
| 13                     | $Pd(acac)_2(5)$    | O <sub>2</sub>                                       | PivOH (2.0) | $0^b$ |
| 14                     | $Pd(acac)_2(5)$    | $PhI(OAc)_2$ (3.0)                                   | PivOH (2.0) | 29%   |
| 15                     | $Pd(acac)_2(5)$    | $Ag_2CO_3 (1.5)/$<br>Cu(OAc) <sub>2</sub> (1.5)      | PivOH (2.0) | 48%   |
| 16 <sup><i>d</i></sup> | $Pd(acac)_2(5)$    | $Ag_2CO_3$ (1.5)                                     | PivOH (2.0) | 90%   |

<sup>*a*</sup> Reaction conditions: 1,4-naphthalenediol **1a** (0.4 mmol), benzene **2a** (3.0 mL), palladium species, PivOH, oxidant, and DMSO (1.4 mmol) at 140 °C for 24 h. Isolated yield on **1a**. <sup>*b*</sup> 1,4-Naphthoquinone **5a** was obtained as the single product. <sup>*c*</sup> No DMSO was added. <sup>*d*</sup> 1,4-Naphthoquinone **5a** instead of 1,4-naphthalenediol **1a** was used as the starting material.

#### III. General procedure for the synthesis of arylquinones

A flame-dried sealable tube with a magnetic stir bar was charged with hydroquinone (0.4 mmol), Pd(acac)<sub>2</sub> (6.1 mg, 0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (331 mg, 1.2 mmol), PivOH (82 mg, 0.8 mmol), DMSO (100 µL, 1.4 mmol) and arene (3.0 mL) under air. The tube was sealed and the reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel to provide the desired product.

#### IV. General procedure for the synthesis of heteroarylquinones

A flame-dried sealable tube with a magnetic stir bar was charged with 1,4-naphthalenediol (67 mg, 0.4 mmol),  $Pd(acac)_2$  (6.1 mg, 0.02 mmol),  $Ag_2CO_3$  (331

mg, 1.2 mmol), PivOH (82 mg, 0.8 mmol), DMSO (100  $\mu$ L, 1.4 mmol), heteroarenes (0.8 mmol) and DCE (3.0 mL) under air. The tube was sealed and the reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel to provide the desired product.

#### V. Experimental data for the described substances



#### 2-Phenyl-1,4-naphthoquinone (3a)<sup>1</sup>

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3a** as a yellow solid (91 mg, 97% yield). M.p.: 108-110 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.09 (s, 1H), 7.48-7.49 (m, 3H), 7.56-7.58 (m, 2H), 7.79 (t, *J* = 4.4 Hz, 2H), 8.11-8.14 (m, 1H), 8.18-8.20 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 125.9, 127.0, 128.4, 129.4, 130.0, 132.0, 132.4, 133.4, 133.8, 133.9, 135.2, 148.1, 184.3, 185.1 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>10</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 257.0578, found 257.0582.



# 2-*m*-Tolyl-1,4-naphthoquinone (3b)<sup>2</sup> and 2-*p*-tolyl-1,4-naphthoquinone (3b')<sup>2</sup> Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded the mixture of **3b** and **3b'** as a yellow solid (93 mg, 94% yield). The ratio of **3b/3b'** was 1.9/1 as determined by <sup>1</sup>H NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, a mixture of two isomers): $\delta$ = 2.43 (s, CH<sub>3</sub>, major + minor isomer), 7.07 (s, CH, major + minor isomer), 7.28-7.30 (m, CH, major + minor isomer), 7.36-7.38 (m, CH, major

isomer), 7.49 (d, J = 8.0 Hz, C<u>H</u>, minor isomer), 7.77-7.78 (m, C<u>H</u>, major + minor isomer), 8.11-8.13 (m, C<u>H</u>, major + minor isomer), 8.18-8.20 (m, C<u>H</u>, major + minor isomer) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, a mixture of two isomers):  $\delta = 21.38$ , 21.42, 125.88, 125.92, 126.5, 127.0, 128.4, 129.2, 129.4, 130.0, 130.5, 130.8, 132.0, 132.1, 132.4, 132.5, 133.3, 133.7, 133.76, 133.77, 133.83, 134.5, 135.1, 138.1, 140.4, 148.0, 148.3, 184.4, 184.5, 185.16, 185.18 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>17</sub>H<sub>12</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 271.0735, found 271.0736.

The structures of **3b** and **3b'** were confirmed by their characteristic peaks shown as follows. The ratio of **3b/3b'** = (1.79/3)/(0.62/2) = 1.9/1.



#### 2-(3,4-Dimethylphenyl)-1,4-naphthoquinone (3c)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3c** as a yellow solid (90 mg, 86% yield). M.p.: 151-153 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.33 (s, 6H), 7.06 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.36 (s, 1H), 7.77 (t, *J* = 4.0 Hz, 2H), 8.10-8.13 (m, 1H), 8.17-8.19 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 19.7, 19.8, 125.8, 126.9, 127.0, 129.8, 130.5, 130.9, 132.1, 132.5, 133.7, 133.7, 134.4, 136.7, 139.1, 148.1, 184.6, 185.2 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>14</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 285.0891, found 285.0889.



#### 2-(2,5-Dimethylphenyl)-1,4-naphthoquinone (3d)

Purification by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2 = 1/1$ ,

v/v) afforded **3d** as a yellow solid (64 mg, 61% yield). M.p.: 80-81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.18 (s, 3H), 2.35 (s, 3H), 6.92 (s, 1H), 7.00 (s, 1H), 7.17 (s, 2H), 7.77-7.79 (m 2H), 8.13-8.17 (m, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 19.8, 20.8, 126.0, 126.9, 129.7, 130.1, 130.2, 132.0, 132.2, 133.0, 133.6, 133.8, 135.2, 136.7, 150.7, 184.0, 185.1 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>15</sub>O<sub>2</sub> [M+H]<sup>+</sup> 263.1072, found 263.1073.



#### 2-(2-Methoxy-5-methylphenyl)-1,4-naphthoquinone (3e)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 2/1 to 4/3, v/v) afforded **3e** as a yellow solid (67 mg, 60% yield). M.p.: 98-100 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.33 (s, 3H), 3.76 (s, 3H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.73-7.77 (m, 2H), 8.09-8.17 (m, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 20.4, 55.8, 111.2, 123.0, 125.9, 126.9, 129.8, 130.9, 131.4, 132.1, 132.5, 133.5, 133.6, 136.6, 148.2, 155.1, 183.6, 185.2 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>14</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 301.0841, found 301.0838.

The structure of compound **3e** was further confirmed by <sup>1</sup>H-<sup>1</sup>H NOESY analysis.





#### 2-(Benzo[d][1,3]dioxol-5-yl)-1,4-naphthoquinone (3f)<sup>3</sup>

Purification by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2 = 2/1$ , v/v) afforded **3f** as a yellow solid (40 mg, 36% yield). M.p.: 179-181 °C. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.04$  (s, 2H), 6.90 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 7.10 (d, J = 1.2 Hz, 1H), 7.12 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.74-7.79 (m, 2H), 8.09-8.11 (m, 1H), 8.16-8.18 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 101.6$ , 108.5, 109.8, 124.1, 125.9, 127.0, 127.2, 132.0, 132.5, 133.8, 134.1, 147.4, 147.8, 149.4, 184.5, 185.1 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 301.0477, found 301.0474.



#### 2-(Benzo[d][1,3]dioxol-4-yl)-1,4-naphthoquinone (3f')

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 2/1, v/v) afforded **3f'** as a yellow solid (38 mg, 34% yield). M.p.: 186-188 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.02 (s, 2H), 6.917 (d, *J* = 3.2 Hz, 1H), 6.920 (d, *J* = 6.0 Hz, 1H), 7.04 (dd, *J* = 6.0 Hz, 3.2 Hz, 1H), 7.25 (s, 1H), 7.75-7.79 (m, 2H), 8.10-8.12 (m, 1H), 8.16-8.18 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 101.1, 110.0, 115.4, 121.6, 123.2, 126.0, 127.0, 131.9, 132.4, 133.8, 133.9, 136.6, 143.7, 146.1, 147.8, 183.4, 185.1 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 301.0477, found 301.0478.



#### 2-(4-(Dimethylamino)phenyl)-1,4-naphthoquinone (3g)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3g** as a black solid (45 mg, 40% yield). M.p.: 128-130 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.04 (s, 6H), 6.75 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.71-7.76 (m, 2H), 8.08-8.10 (m, 1H), 8.15-8.17 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 40.1, 111.7, 120.5, 125.7, 126.9, 131.0, 131.1, 132.3, 132.9, 133.3, 133.5, 147.4, 151.7, 185.2, 185.5 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>15</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 300.1000, found 300.0999.



### 2-(4-Chloro-3,5-dimethylphenyl)-1,4-naphthoquinone(3h)and2-(3-chloro-2,4-dimethylphenyl)-1,4-naphthoquinone(3h')

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded the mixture of **3h** and **3h'** as a yellow solid (82 mg, 69% yield). The ratio of **3h/3h'** was 1.3:1 as determined by <sup>1</sup>H NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, a mixture of two isomers):  $\delta$  = 2.24 (s, CH<sub>3</sub>, minor isomer), 2.436 (s, CH<sub>3</sub>, minor isomer), 2.444 (s, CH<sub>3</sub>, major isomer), 6.91 (s, CH, minor isomer), 6.99 (d, CH, *J* = 7.6 Hz, minor isomer), 7.05 (s, CH, major isomer), 7.16 (d, *J* = 7.6 Hz, CH, minor isomer), 7.30 (s, CH, major isomer), 7.77-7.80 (m, CH, major + minor isomer), 8.10-8.19 (m, CH, major + minor isomer) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, a mixture of two isomers):  $\delta$  = 19.0, 20.8, 21.0, 125.9, 126.1, 126.9, 126.98, 127.05, 128.0, 129.2, 131.1, 131.99, 132.04, 132.4, 132.9, 133.8, 133.86, 133.92, 134.0, 134.6, 135.0, 135.6, 136.5, 136.8, 136.9, 137.7, 147.3, 150.1, 183.9, 184.3, 184.95, 185.03 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>ClNaO<sub>2</sub>[M+Na]<sup>+</sup> 319.0502, found 319.0504.

The structures of **3h** and **3h'** were confirmed by their characteristic peaks shown as follows. The ratio of **3h/3h'** = (1.10/2)/0.42 = 1.3/1.





2-(4-Chlorophenyl)-1,4-naphthoquinone

and

 $(3i)^{2}$ 

#### 2-(3-chlorophenyl)-1,4-naphthoquinone (3i')<sup>2</sup>

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded the mixture of **3i** and **3i'** as a yellow solid (80 mg, 74% yield). The ratio of **3i/3i'** was 1.1/1 as determined by <sup>1</sup>H NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, a mixture of two isomers):  $\delta$  = 7.059 (s, C<u>H</u>, minor isomer), 7.063 (s, C<u>H</u>, major isomer), 7.38-7.45 (m, C<u>H</u>, major + minor isomer), 7.52 (d, *J* = 8.4 Hz, C<u>H</u>, major isomer), 7.57 (s, C<u>H</u>, minor isomer), 7.78-7.79 (m, C<u>H</u>, major + minor isomer), 8.10-8.12 (m, C<u>H</u>, major + minor isomer), 8.16-8.18 (m, C<u>H</u>, major + minor isomer) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, a mixture of two isomers):  $\delta$  = 126.00, 126.03, 127.0, 127.1, 127.5, 128.7, 129.4, 129.7, 130.0, 130.7, 131.7, 131.9, 132.0, 132.19, 132.24, 133.9, 133.96, 133.97, 134.02, 134.4, 135.0, 135.2, 135.6, 136.4, 146.7, 146.8, 183.9, 184.1, 184.8, 184.9 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>9</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> 291.0189, found 291.0195.

The structures of **3i** and **3i'** were confirmed by their characteristic peaks shown as follows. The ratio of 3i/3i' = (1.10/2)/0.48 = 1.1/1.



#### 2-(3,4-Dichlorophenyl)-1,4-naphthoquinone (3j)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3j** as a yellow solid (80 mg, 66% yield). M.p.: 203-204 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.07 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.80 (t, *J* = 4.4 Hz, 2H), 8.11-8.14 (m, 1H), 8.17-8.19 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 126.1, 127.1, 128.6, 130.5, 131.3, 132.0, 132.1, 132.9, 133.1, 134.1, 134.5, 135.6, 145.7, 183.8, 184.7 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>9</sub>Cl<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 302.9980, found 302.9980.



#### 2-(2,5-Difluorophenyl)-1,4-naphthoquinone (3k)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3k** as a yellow solid (44 mg, 41% yield). M.p.: 129-131 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.08 (s, 1H), 7.12-7.15 (m, 3H), 7.78-7.80 (m, 2H), 8.11-8.13 (m, 1H), 8.15-8.18 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 117.0, 117.1, 117.2, 117.3, 117.6, 117.67, 117.74, 117.8, 117.86, 117.91, 118.0, 118.1, 122.4, 122.5, 122.6, 122.7, 126.2, 127.1, 131.9, 132.0, 134.0, 134.1, 137.80, 137.82, 143.2, 154.75, 154.79, 157.0, 157.1, 157.22, 157.25, 159.46, 159.50, 182.7, 184.5 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>9</sub>F<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 271.0571, found 271.0572.



#### 2-(3,5-Bis(trifluoromethyl)phenyl)-1,4-naphthoquinone (3l)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **31** as a yellow solid (41 mg, 28% yield). M.p.: 122-124 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.16 (s, 1H), 7.80-7.85 (m, 2H), 7.99 (s, 1H), 8.04 (s, 2H), 8.13-8.15 (m, 1H), 8.19-8.21 (m, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 119.0, 121.7, 123.4-123.6 (m), 124.4, 126.3, 127.2, 129.6, 131.5, 131.8, 131.9, 132.0, 132.1,

132.5, 134.36, 134.39, 135.3, 136.6, 145.2, 183.4, 184.3 ppm. HRMS (ESI<sup>+</sup>): calcd for  $C_{18}H_8F_6NaO_2[M+Na]^+$  393.0326, found 393.0325.



2-(2,4-Dimethyl-3-nitrophenyl)-1,4-naphthoquinone(3m)and2-(3,5-dimethyl-4-nitrophenyl)-1,4-naphthoquinone (3m')

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded the mixture of **3m** and **3m'** as a yellow solid (88 mg, 72% yield). The ratio of **3m/3m'** was 3.6:1 as determined by <sup>1</sup>H NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, a mixture of two isomers):  $\delta$  = 2.13 (s, CH<sub>3</sub>, major isomer), 2.35 (s, CH<sub>3</sub>, major isomer), 2.37 (s, CH<sub>3</sub>, minor isomer), 6.93 (s, CH, major isomer), 7.05 (s, CH, minor isomer), 7.20 (d, *J* = 8.0 Hz, CH, major isomer), 7.23 (d, *J* = 8.0 Hz, CH, major isomer), 7.32 (s, CH, minor isomer), 7.77-7.82 (m, CH, major + minor isomer), 8.10-8.18 (m, CH, major + minor isomer) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, a mixture of two isomers):  $\delta$  = 15.6, 17.3, 17.5, 126.1, 126.3, 127.06, 127.09, 127.9, 128.7, 129.79, 129.85, 130.5, 130.6, 131.87, 131.92, 132.0, 132.1, 133.3, 134.11, 134.14, 135.0, 136.0, 137.5, 146.5, 148.6, 152.6, 183.5, 183.8, 184.63, 184.65 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>14</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 308.0923, found 308.0919.

The structures of **3m** and **3m'** were confirmed by their characteristic peaks shown as follows. The ratio of 3m/3m' = 1.04/(0.57/2) = 3.6/1.





#### 5-(3,4-Dimethylphenyl)-2,3-dimethyl-1,4-benzoquinone (3n)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3n** as an orange solid (68 mg, 71% yield). M.p.: 107-108 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.11 (s, 3H), 2.14 (s, 3H), 2.34 (s, 6H), 6.82 (s, 1H), 7.21-7.24 (m, 2H), 7.28 (s, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 12.0, 12.6, 19.6, 19.7, 126.7, 129.6, 130.2, 130.7, 131.6, 136.5, 138.7, 140.5, 141.1, 145.6, 186.8, 187.5 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1229, found 241.1236.



#### 5-(2,5-Dimethylphenyl)-2,3-dimethyl-1,4-benzoquinone (30)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **30** as a yellow solid (55 mg, 57% yield). M.p.: 68-69 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.09 (s, 6H), 2.12 (s, 3H), 2.32 (s, 3H), 6.64 (s, 1H), 6.90 (s, 1H), 7.13 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 12.1, 12.6, 19.8, 20.8, 129.7, 129.8, 130.1, 132.9, 133.4, 134.0, 135.1, 140.7, 141.1, 148.1, 186.3, 187.6 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1229, found 241.1228.



#### 5-(3,4-Dichlorophenyl)-2,3-dimethyl-1,4-benzoquinone (3p)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3p** as a yellow solid (59 mg, 53% yield). M.p.: 131-134 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.08 (s, 3H), 2.10 (s, 3H), 6.80 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 12.2, 12.7, 128.4, 130.4, 131.1, 132.7, 132.8, 133.0, 134.2, 141.1, 141.3, 143.3, 186.0,

187.0 ppm. HRMS (ESI<sup>+</sup>): calcd for  $C_{14}H_{11}Cl_2O_2 [M+H]^+$  281.0136, found 281.0135.



#### 2-(1-Methyl-1*H*-indol-3-yl)-1,4-naphthoquinone (3q)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1, v/v) afforded **3q** as a black solid (25 mg, 22% yield). M.p.: 176-178 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.84 (s, 3H), 7.28-7.33 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.68-7.72 (m, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 8.08-8.13 (m, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 33.4, 107.3, 110.1, 120.6, 121.7, 122.9, 125.6, 126.2, 126.7, 128.5, 132.2, 132.8, 133.1, 133.6, 135.7, 137.3, 141.8, 185.1, 185.7 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>19</sub>H<sub>14</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 288.1025, found 288.1025.

The position of quinonyl substitutent on indole ring was confirmed by <sup>1</sup>H-<sup>1</sup>H NOESY spectrum.





2-(5-Butylfuran-2-yl)-1,4-naphthoquinone (3r)

Purification by column chromatography on silica gel (petroleum ether/ethyl ether = 25/1, v/v) afforded **3r** as a dark red solid (35 mg, 31% yield). M.p.: 68-70 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.96$  (t, J = 7.2 Hz, 3H), 1.36-1.46 (m, 2H), 1.65-1.72 (m, 2H), 2.71 (t, J = 7.6 Hz, 2H), 6.24 (d, J = 3.6 Hz, 1H), 7.24 (s, 1H), 7.55 (d, J = 3.2 Hz, 1H), 7.72-7.74 (m, 2H), 8.07-8.13 (m, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 13.8$ , 22.3, 28.0, 29.9, 109.6, 120.7, 125.9, 126.58, 126.63, 132.2, 132.4, 133.4, 133.8, 135.3, 145.2, 161.0, 183.5, 184.9 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>17</sub>O<sub>3</sub>

[M+H]<sup>+</sup> 281.1178, found 281.1175.

#### 2-Phenyl-1,4-benzoquinone (4a)<sup>4</sup>

Hydroquinone was used as the starting material. Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4a** as a yellow solid (21 mg, 28% yield). M.p.: 104-106 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.82-6.89 (m, 3H), 7.46-7.48 (m, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 128.5, 129.2, 130.0, 132.6, 136.1, 137.0, 145.8, 186.5, 187.5 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>8</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 207.0422, found 207.0420.



#### 2,6-Diphenyl-1,4-benzoquinone (4b)

Hydroquinone was used as the starting material. Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4b** as a orange red solid (37 mg, 36% yield). M.p.: 132-134 °C (lit:<sup>5</sup> 138 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.93 (s, 2H), 7.46-7.47 (m, 6H), 7.51-7.53 (m, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 128.6, 129.3, 130.1, 132.5, 133.2, 145.6, 187.0 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup> 261.0916, found 261.0910.



#### 2,5-Diphenyl-1,4-benzoquinone (4b')

Hydroquinone was used as the starting material. Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4b'** as a yellow solid (25 mg, 24% yield). M.p.: 208-210 °C (lit:<sup>6</sup> 214 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 6.98$  (s, 2H), 7.47-7.48 (m, 6H), 7.54-7.56 (m, 4H) ppm. <sup>13</sup>C NMR

(CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 128.5, 129.3, 130.1, 132.5, 133.1, 145.6, 187.0 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup> 261.0916, found 261.0918.



#### 2-tert-Butyl-6-phenyl-1,4-benzoquinone (4c)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4c** as orange oil (62 mg, 64% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.33 (s, 9H), 6.67 (s, 1H), 6.77 (s, 1H), 7.44 (s, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 29.3, 35.6, 128.3, 129.3, 129.7, 131.4, 131.5, 133.5, 147.8, 156.3, 186.7, 188.2 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1229, found 241.1228.

The structure of **4c** was further confirmed by its transformation to and identification of **4c-2** (*vide infra*).



#### 2-tert-Butyl-5-phenyl-1,4-benzoquinone (4c')

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4c'** as an orange solid (30 mg, 31% yield). M.p.: 89-91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.33 (s, 9H), 6.69 (s, 1H), 6.78 (s, 1H), 7.44-7.49 (m, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 29.2, 35.1, 128.5, 129.2, 129.9, 132.1, 132.4, 134.7, 144.3, 155.8, 187.7, 187.8 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1229, found 241.1225.

#### 2-Methoxy-5-phenyl-1,4-benzoquinone (4d)<sup>7</sup>

Purification by column chromatography on silica gel (petroleum ether/ $CH_2Cl_2 = 1/1$ , v/v) afforded **4d** as an orange yellow solid (65 mg, 76% yield). M.p.: 192-194 °C. <sup>1</sup>H

NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.87 (s, 3H), 6.05 (s, 1H), 6.81 (s, 1H), 7.43-7.48 (m, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 56.3, 108.0, 128.4, 129.5, 130.1, 130.8, 132.7, 146.5, 158.6, 182.2, 186.6 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>11</sub>O<sub>3</sub> [M+H]<sup>+</sup> 215.0708, found 215.0708.

#### 2,3-Dimethyl-5-phenyl-1,4-benzoquinone (4e)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4e** as a yellow solid (75 mg, 88% yield). M.p.: 42-44 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 2.08 (s, 3H), 2.11 (s, 3H), 6.81 (s, 1H), 7.41-7.47 (m, 5H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 12.1, 12.7, 128.4, 129.2, 129.7, 132.4, 133.3, 140.8, 141.2, 145.7, 186.7, 187.6 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup> 213.0916, found 213.0920.



#### (5-Methyl-3,6-dioxo-2-phenylcyclohexa-1,4-dienyl)methyl pivalate (4f)

Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **4f** as yellow oil (54 mg, 43% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.16 (s, 9H), 2.14 (s, 3H), 4.76 (s, 2H), 6.74 (s, 1H), 7.18-7.20 (m, 2H), 7.41-7.42 (m, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 15.9, 27.1, 38.7, 58.6, 128.1, 129.4, 129.5, 131.2, 133.4, 137.6, 146.0, 146.9, 177.6, 186.5, 186.7 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>19</sub>H<sub>20</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 335.1259, found 335.1264.

The structure of compound 4f was further confirmed by <sup>1</sup>H-<sup>1</sup>H NOESY analysis.





(4,5-Dimethyl-3,6-dioxo-2-phenylcyclohexa-1,4-dienyl)methyl pivalate (4g) Purification by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded 4g as yellow oil (52 mg, 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.15 (s, 9H), 2.09 (s, 3H), 2.12 (s, 3H), 4.76 (s, 2H), 7.17-7.20 (m, 2H), 7.39-7.41 (m, 3H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 12.5, 12.6, 27.1, 38.7, 58.7, 128.0, 129.2, 129.4, 131.8, 137.1, 141.0, 141.2, 146.7, 177.6, 186.2, 186.6 ppm. HRMS (ESI<sup>+</sup>): calcd for C<sub>20</sub>H<sub>22</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 349.1416, found 349.1420.

The structure of compound 4g was further confirmed by <sup>1</sup>H-<sup>1</sup>H NOESY analysis.



#### **VI.** Mechanistic study

(i). Arylation of 1,4-naphthoquinone 5a with benzene in the presence of TEMPO



A flame-dried sealable tube with a magnetic stir bar was charged with 1,4-naphthoquinone (64 mg, 0.4 mmol), Pd(acac)<sub>2</sub> (6.1 mg, 0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (331 mg, 1.2 mmol), PivOH (82 mg, 0.8 mmol), DMSO (100  $\mu$ L, 1.4 mmol), TEMPO (12.5 mg, 0.08 mmol) and benzene (3.0 mL) under air. The tube was sealed and the

reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) to provide **3a** in 78% yield (73 mg).

#### (ii). The competition reaction between *o*-xylene and 1,2-dichlorobenzene



A flame-dried sealable tube with a magnetic stir bar was charged with 1,4-naphthoquinone (64 mg, 0.4 mmol), Pd(acac)<sub>2</sub> (6.1 mg, 0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (166 mg, 0.6 mmol), PivOH (82 mg, 0.8 mmol), DMSO (100  $\mu$ L, 1.4 mmol), *o*-xylene (1.5 mL) and 1,2-dichlorobenzene (1.5 mL) under air. The tube was sealed and the reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl ether = 6/1, v/v) afforded **3c** (70 mg, 67% yield) and **3j** (9 mg, 7% yield) respectively.

#### (iii). Intermolecular kinetic isotope effect



A flame-dried sealable tube with a magnetic stir bar was charged with

1,4-naphthalenediol (67 mg, 0.4 mmol), Pd(acac)<sub>2</sub> (6.1 mg, 0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (331 mg, 1.2 mmol), PivOH (82 mg, 0.8 mmol), DMSO (100  $\mu$ L, 1.4 mmol), benzene (1.5 mL) and benzene-*d*<sub>6</sub> (1.5 mL) under air. The tube was sealed and the reaction mixture was stirred at 140 °C for 6 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3a** and **3a**-*d*<sub>5</sub> as an inseparable mixture (75 mg, 80% yield). The ratio of **3a/3a**-*d*<sub>5</sub> was 1.39/0.61 as determined by <sup>1</sup>H NMR (*k*<sub>H</sub>/*k*<sub>D</sub> = 2.3).



(iv). Arylation of 1,4-naphthoquinone in the presence of stoichiometric amounts of Pd(acac)<sub>2</sub>



A flame-dried sealable tube with a magnetic stir bar was charged with 1,4-naphthoquinone (32 mg, 0.2 mmol), Pd(acac)<sub>2</sub> (61 mg, 0.2 mmol), PivOH (41 mg,

0.4 mmol), DMSO (50  $\mu$ L, 0.7 mmol) and benzene (1.5 mL) under air. The tube was sealed and the reaction mixture was stirred at 140 °C for 24 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica gel, and washed with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was collected and concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 1/1, v/v) afforded **3a** in 92% yield (43 mg).

#### VII. Confirmation of the structure of product 4c by its derivation<sup>8</sup>



To a solution of 2-tert-butyl-6-phenyl-1,4-benquinone 4c (160 mg, 0.66 mmol) in ethyl acetate (5.0 mL) was added a 10% Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> aqueous solution (5.0 mL). The mixture was stirred vigorously at room temperature for 2 h under nitrogen. The mixture was extracted with ethyl acetate for three times and the combined organic phases were washed with brine, dried over anhydrous MgSO<sub>4</sub>, and evaporated to give the crude product 4c-1. 4c-1 was then dissolved in DMF (2.0 mL) and NaH (66 mg, 1.65 mmol) was added under nitrogen. MeI (103 µL, 1.65 mmol) was subsequently added slowly at 0 °C. The resulting solution was then warmed to and stirred at room temperature for overnight. The reaction solution was diluted with 10 mL of EtOAc, washed with brine for three times, dried over MgSO<sub>4</sub>, and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) to afford 4c-2 as light yellow oil (120 mg, 67% yield). The structure of 4c-2 was determined by <sup>1</sup>H, <sup>13</sup>C, and <sup>1</sup>H-<sup>1</sup>H NOESY NMR analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.43$  (s, 9H), 3.22 (s, 3H), 3.80 (s, 3H), 6.70 (s, 1H), 6.89 (s, 1H), 7.34 (t, J) = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H) ppm. <sup>13</sup>C NMR  $(CDCl_3, 100 \text{ MHz}): \delta = 30.7, 35.3, 55.4, 60.5, 113.0, 127.0, 128.4, 129.0, 135.8,$ 139.9, 144.3, 151.2, 154.6 ppm.

The structure of compound **4c-2** was further confirmed by <sup>1</sup>H-<sup>1</sup>H NOESY analysis.



#### **VIII. References**

- 1 M. T. Molina, C. Navarro, A. Moreno and A. G. Csákÿ, Org. Lett., 2009, 11, 4938.
- 2 M. L. N. Rao, and S. Giri, *RSC Adv.*, 2012, **2**, 12739.
- 3 K. M. Dawood, *Tetrahedron*, 2007, **63**, 9642.
- 4 H. Miyamura, M. Shiramizu, R. Matsubara and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2008, 47, 8093.
- 5 F. Minisci, A. Citterio, E. Vismara, F. Fontana and S. D. Bernardinis, *J. Org. Chem.*, 1989, **54**, 728.
- 6 P. R. Shildneck and R. Adams, J. Am. Chem. Soc., 1931, 53, 2373.
- 7 R. A. de Oliveira, E. V. Gusevskaya and F. Carazza, J. Braz. Chem. Soc., 2002, 13, 110.
- 8 L. A. Carpino, S. A. Triolo and R. A. Berglund. J. Org. Chem., 1989, 54, 3303.



#### IX. Copies of <sup>1</sup>H, <sup>13</sup>C NMR and <sup>1</sup>H-<sup>1</sup>H NOESY spectra











fl (ppm)





























S42























fl (ppm)





f1 (ppm)





fl (ppm)