

## *Supporting Information*

### **Highly efficient metal-free approach to *meta*- and multiple-substituted phenols via a simple oxidation of cyclohexenones**

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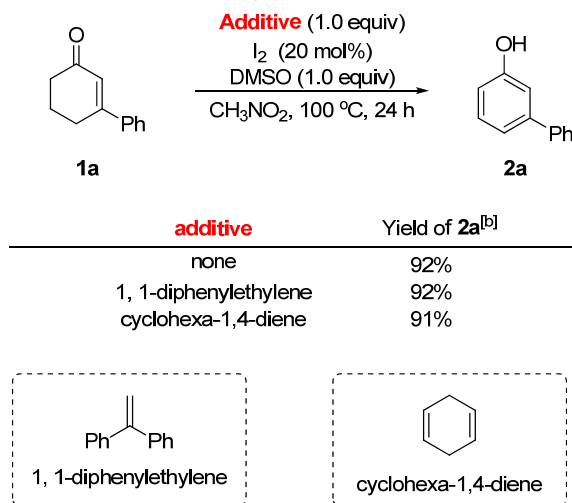
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## General Remarks

I<sub>2</sub> was purchased from Sigma-Aldrich Chemical Company. DMSO, CH<sub>3</sub>NO<sub>2</sub> and other solvents were purchased from Beijing Chemical Works and used as received without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. <sup>1</sup>H-NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with CDCl<sub>3</sub> (tetramethylsilane,  $\delta$  = 0 ppm) or CD<sub>3</sub>SOCD<sub>3</sub> (dimethyl sulfoxide,  $\delta$  = 2.50 ppm). <sup>13</sup>C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl<sub>3</sub> ( $\delta$  = 77.00 ppm) or CD<sub>3</sub>SOCD<sub>3</sub> (dimethyl sulfoxide,  $\delta$  = 39.50 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionisation (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer.

## The Effect of Radical Inhibitors<sup>[a]</sup>

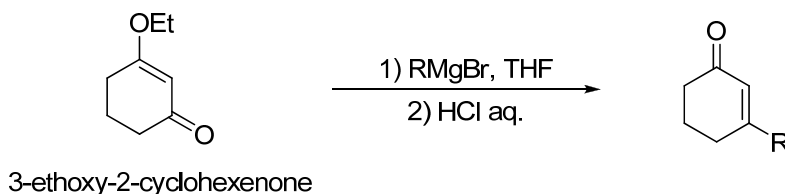


[a] Reaction conditions: **1a** (0.5 mmol), Additive (1.0 equiv), I<sub>2</sub> (20 mol%), DMSO (1.0 equiv), CH<sub>3</sub>NO<sub>2</sub> (1 mL) was stirred at 100 °C for 24 h. [b] Isolated yields.

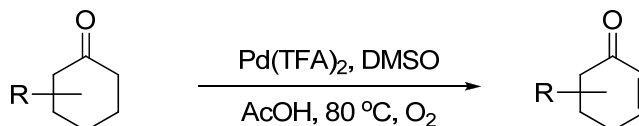
The reactions performed well in the presence of 1,1-diphenylethylene or cyclohexa-1,4-diene producing the desired product **2a** in 92% and 91% yields, respectively, which indicate that a radical process might not be involved in the present reaction system.

## Experimental Section

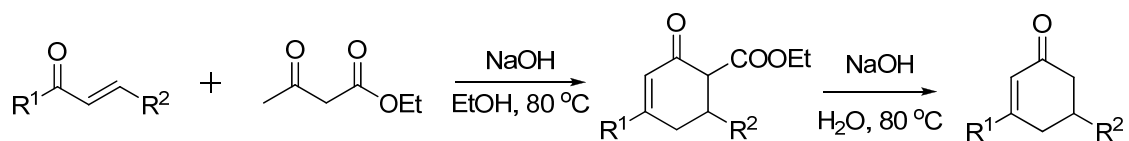
### 1) Materials Preparation



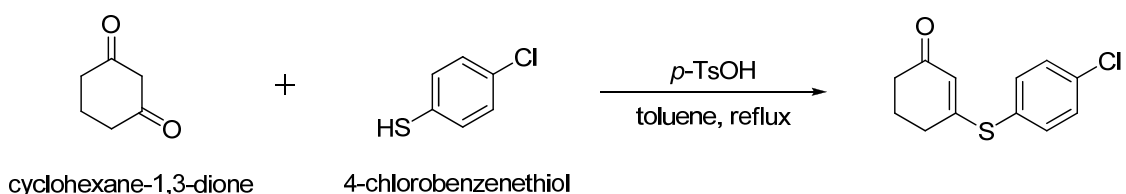
Substrates 3-substituted 2-cyclohexenones **1a-1i**, **1w-1x** were prepared according to the literature<sup>1</sup>: 3-ethoxy-2-cyclohexenone (10 mmol, 1.0 equiv) in THF (10 mL) was added dropwise to a solution of a *Grignard* reagent RMgBr (1 M in Et<sub>2</sub>O or THF, 1.5-2.0 equiv) at 0 °C under argon. Once the addition was complete, the resulting solution was allowed to warm to room temperature and stirred until TLC indicated complete disappearance of the starting material (2-18 h). The reaction was slowly quenched with diluted aqueous acid (1 M HCl) at 0 °C. The layers were separated, and the aqueous layer extracted with ethyl acetate (3×10 mL). The combined organic layers were washed successively with saturated aqueous NaHCO<sub>3</sub> solution, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, eluent: petroleum ether-ethyl acetate) to yield 3-substituted 2-cyclohexenones.



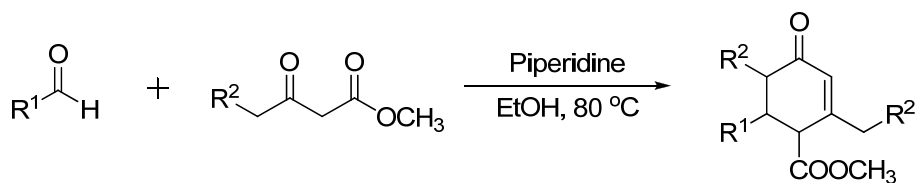
Substrates mono-substituted 2-cyclohexenones **1k-1l**, **1n-1o** were prepared according to the literature<sup>2</sup>: to a 100 ml round-bottom flask equipped with a stir bar was added Pd(TFA)<sub>2</sub> (0.05 equiv) and mono-substituted cyclohexanone (5 mmol). A reflux condenser was placed on the flask and sealed with a septum. A balloon was attached via a needle. The flask and balloon were purged and filled with O<sub>2</sub>, followed by addition of DMSO (0.1 equiv) and acetic acid (20 ml). The flask was stirred at 80 °C for 12 h. After 12 h, O<sub>2</sub> was vented from the flask. Acetic acid was removed under vacuum using a rotovap. The crude product was purified by flash column chromatography (silica gel, eluent: petroleum ether-ethyl acetate) to yield mono-substituted 2-cyclohexenones.



Substrates 3,5-diarylcyclohexenones **1q-1r**, and **8** were prepared according to the literature<sup>3</sup>: to a 100 mL three-necked, round-bottomed flask was added chalcone (10 mmol), ethyl acetoacetate (12 mmol, 1.2 equiv), NaOH (0.29 g), and anhydrous ethanol (10 ml). The reaction was heated in an oil bath to reflux with vigorous stirring for an appropriate time until TLC indicated complete disappearance of the starting material (2-5 h). Then 80 ml water was added. And Then NaOH (1.44 g) was following added and continued to reflux (2-5 h). After cooling a period of time, the solution was washed with saturated aqueous NaHCO<sub>3</sub> solution to neutral, dried. The crude product was purified by flash column chromatography (silica gel, eluent: petroleum ether-ethyl acetate) to yield 3,5-diarylcyclohexenones.



Substrate 3-thioether substituted cyclohexenone **1v** was prepared according to the literature<sup>4</sup>: a mixture of cyclohexane-1,3-dione (1.12 g, 10 mmol), 4-chlorobenzenethiol (1.58 g, 11 mmol, 1.1 equiv) and *p*-TsOH (5 mol%) in toluene (10 ml) was refluxed at a Dean-Stark trap until the separation of H<sub>2</sub>O had finished (ca. 3 h). The solvent was removed in vacuo and crude product was purified by flash column chromatography (silica gel, eluent: petroleum ether-ethyl acetate) to yield 3-(4-chlorophenylthio) cyclohex-2-enone.



Substrates multiple-substituted 2-cyclohexenones **1s-1u** were prepared according to the literature<sup>5</sup>: piperidine (2 mmol, 40 mol%) was added to a solution of aldehyde (5 mmol) and methyl acetoacetate (10 mmol) in EtOH (8 mL). The resulting mixture was stirred at 80 °C for 6 h. The reaction mixture was then quenched with aqueous NH<sub>4</sub>Cl solution, extracted with diethyl ether, and washed with brine. The organic layer was dried with

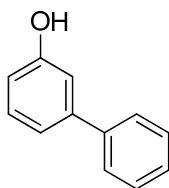
anhydrous MgSO<sub>4</sub>. The solution was concentrated by rotary evaporation, and the residue was purified by flash column chromatography (silica gel, eluent: petroleum ether-ethyl acetate) to yield multiple-substituted 2-cyclohexenones.

## 2) General Procedure

**1a** (86 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ L, 1.0 equiv), CH<sub>3</sub>NO<sub>2</sub> (1.0 mL) were added to a 25 mL tube with a magnetic bar. Then the tube was sealed with a cap, and the mixture was stirred at 100 °C for 24 h. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) aqueous solution, extracted with ethyl acetate (3 $\times$ 5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to get the desired phenol product **2a**.

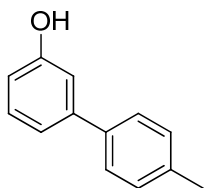
**3a** (56 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL) were added to a 25 mL tube with a magnetic bar. The mixture was stirred under air at 80 °C for 24 h. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) aqueous solution, extracted with ethyl acetate (3 $\times$ 5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to get the desired phenol product **4a**.

## Analytical Data for Products



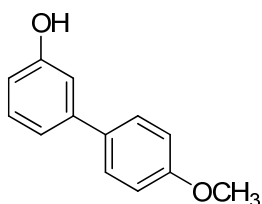
1):

**3-Phenylphenol (2a).**<sup>6</sup> The reaction of 3-phenylcyclohexenone **1a** (86 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ L, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 78 mg (92%) of **2a** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2a**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (d,  $J$  = 7.2 Hz, 2 H), 7.41 (t,  $J$  = 7.2 Hz, 2 H), 7.35-7.27 (m, 2 H), 7.16 (d,  $J$  = 8.0 Hz, 1 H), 7.05 (t,  $J$  = 2.0 Hz, 1 H), 6.82-6.79 (s, 1 H), 5.16 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.7, 142.9, 140.6, 129.9, 128.7, 127.4, 127.0, 119.7, 114.1, 114.0 ppm; HRMS  $m/z$  (ESI) calcd for C<sub>12</sub>H<sub>11</sub>O ( $M + H$ )<sup>+</sup> 171.0804, found 171.0804.



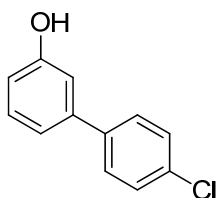
2):

**4'-Methylbiphenyl-3-ol (2b).**<sup>7</sup> The reaction of 3-*p*-tolylcyclohex-2-enone **1b** (93 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 86 mg (94%) of **2b** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2b**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (d, *J* = 8.0 Hz, 2 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.02 (s, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.14 (brs, 1 H), 2.36 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.6, 142.8, 137.7, 137.2, 129.9, 129.4, 126.8, 119.5, 113.9, 113.8, 21.0 ppm; MS (70 ev): *m/z* (%): 115.1 (15), 65.1 (30), 184.1 (M<sup>+</sup>, 100).



3):

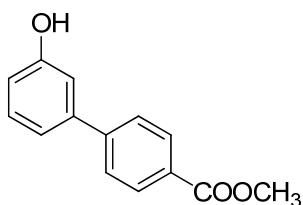
**4'-Methoxybiphenyl-3-ol (2c).**<sup>7</sup> The reaction of 3-(4-methoxyphenyl)cyclohex-2-enone **1c** (101 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 95 mg (95%) of **2c** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2c**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 8.4 Hz, 2 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 7.6 Hz, 1 H), 6.99 (s, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 6.78-6.75 (m, 1 H), 5.18 (brs, 1 H), 3.82 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.1, 155.7, 142.5, 133.2, 129.9, 128.1, 119.3, 114.2, 113.7, 113.6, 55.3 ppm; MS (70 ev): *m/z* (%): 128.1 (30), 157.1 (40), 185.0 (50), 200.1 (M<sup>+</sup>, 100).



4):

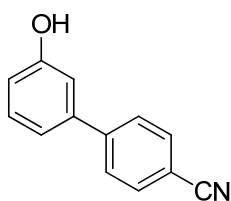
**4'-Chlorobiphenyl-3-ol (2d).**<sup>7</sup> The reaction of 3-(4-chlorophenyl)cyclohex-2-enone **1d** (103 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 96 mg (94%) of **2d** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2d**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (d, *J* = 8.8 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H),

7.27 (t,  $J = 7.6$  Hz, 1 H), 7.10 (d,  $J = 7.6$  Hz, 1 H), 6.99 (s, 1 H), 6.83-6.80 (m, 1 H), 5.38 (brs, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.6, 141.7, 138.9, 133.5, 130.1, 128.8, 128.2, 119.6, 114.5, 113.9 ppm; MS (70 ev):  $m/z$  (%): 115.0 (10), 141.1 (15), 204.0 ( $\text{M}^+$ , 100).



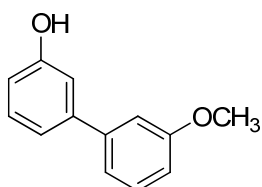
5):

**Methyl 3'-hydroxybiphenyl-4-carboxylate (2e).**<sup>7</sup> The reaction of methyl 4-(3-oxocyclohex-1-enyl)benzoate **1e** (115 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (35  $\mu\text{L}$ , 1.0 equiv), in  $\text{CH}_3\text{NO}_2$  (1.0 mL), at 100  $^\circ\text{C}$  for 24 h, afforded 99 mg (87%) of **2e** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2e**: white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (d,  $J = 8.4$  Hz, 2 H), 7.61 (d,  $J = 8.4$  Hz, 2 H), 7.32 (t,  $J = 8.0$  Hz, 1 H), 7.17 (d,  $J = 7.6$  Hz, 1 H), 7.11 (s, 1 H), 6.91-6.88 (m, 1 H), 5.81 (brs, 1 H), 3.94 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.3, 156.2, 145.3, 141.5, 130.1, 130.0, 128.8, 127.0, 119.6, 115.2, 114.2, 52.2 ppm; MS (70 ev):  $m/z$  (%): 115.0 (15), 139.1 (20), 197.0 (100), 228.1 ( $\text{M}^+$ , 70).



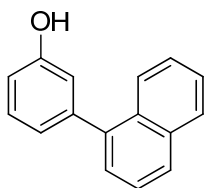
6):

**3'-Hydroxybiphenyl-4-carbonitrile (2f).**<sup>7</sup> The reaction of 4-(3-oxocyclohex-1-enyl)benzonitrile **1f** (99 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (35  $\mu\text{L}$ , 1.0 equiv), in  $\text{CH}_3\text{NO}_2$  (1.0 mL), at 100  $^\circ\text{C}$  for 24 h, afforded 87 mg (90%) of **2f** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2f**: white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 8.4$  Hz, 2 H), 7.66 (d,  $J = 8.4$  Hz, 2 H), 7.34 (t,  $J = 8.0$  Hz, 1 H), 7.15 (d,  $J = 7.6$  Hz, 1 H), 7.06 (s, 1 H), 6.90-6.88 (m, 1 H), 5.05 (brs, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.2, 145.2, 140.8, 132.5, 130.3, 127.7, 119.7, 118.8, 115.6, 114.1, 111.1 ppm; MS (70 ev):  $m/z$  (%): 140.0 (15), 166.0 (20), 195.1 ( $\text{M}^+$ , 100).



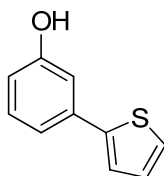
7):

**3'-Methoxybiphenyl-3-ol (2g).**<sup>7</sup> The reaction of 3-(3-methoxyphenyl)cyclohex-2-enone **1g** (101 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 86 mg (86%) of **2g** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2g**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33-7.25 (m, 2 H), 7.13 (t, *J* = 6.0 Hz, 2 H), 7.08 (t, *J* = 2.4 Hz, 1 H), 7.03 (t, *J* = 2.4 Hz, 1 H), 6.90-6.87 (m, 1 H), 6.82-6.79 (m, 1 H), 5.36 (brs, 1 H), 3.83 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.7, 155.7, 142.7, 142.2, 129.9, 129.7, 119.7, 119.6, 114.3, 114.1, 112.9, 112.7, 55.3 ppm; MS (70 ev): *m/z* (%): 128.1 (20), 157.1 (20), 170.1 (15), 200.1 (M<sup>+</sup>, 100).



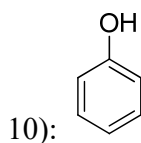
8):

**3-(Naphthalen-1-yl)phenol (2h).** The reaction of 3-(naphthalen-1-yl)cyclohex-2-enone **1h** (111 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 101 mg (92%) of **2h** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2h**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92-7.82 (m, 3 H), 7.50-7.45 (m, 2 H), 7.39 (t, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 7.2 Hz, 1 H), 6.93 (s, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 5.20 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.3, 142.3, 139.7, 133.7, 131.4, 129.4, 128.2, 127.7, 126.7, 126.0, 125.9, 125.7, 125.3, 122.6, 117.0, 114.1 ppm; MS (70 ev): *m/z* (%): 189.1 (30), 201.0 (20), 220.1 (M<sup>+</sup>, 100).

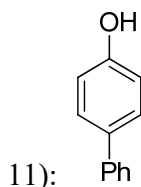


9):

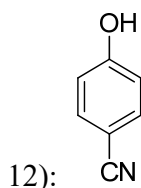
**3-(Thiophen-2-yl)phenol (2i).**<sup>8</sup> The reaction of 3-(thiophen-2-yl)cyclohex-2-enone **1i** (89 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 72 mg (82%) of **2i** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2i**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.27-7.17 (m, 4 H), 7.08 (s, 1 H), 7.05 (t, *J* = 4.4 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.13 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.7, 143.8, 135.9, 130.1, 127.9, 124.9, 123.3, 118.6, 114.4, 112.7 ppm; MS (70 ev): *m/z* (%): 115.0 (15), 147.0 (20), 176.0 (M<sup>+</sup>, 100).



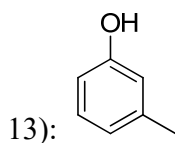
**Phenol (2j).**<sup>6</sup> The reaction of cyclohex-2-enone **1j** (48 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 41 mg (88%) of **2j** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2j**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (t,  $J$  = 8.0 Hz, 2 H), 6.93 (t,  $J$  = 7.2 Hz, 1 H), 6.82 (t,  $J$  = 8.0 Hz, 2 H), 5.08 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.3, 129.6, 120.8, 115.2 ppm; MS (70 ev):  $m/z$  (%): 55.1 (10), 66.1 (40), 94.1 (M<sup>+</sup>, 100).



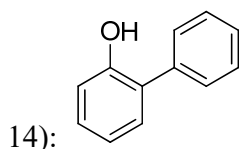
**Biphenyl-4-ol (2k).**<sup>6</sup> The reaction of 4-phenylcyclohex-2-enone **1k** (86 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 78 mg (92%) of **2k** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2k**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (t,  $J$  = 6.8 Hz, 2 H), 7.47 (d,  $J$  = 8.8 Hz, 2 H), 7.41 (t,  $J$  = 7.2 Hz, 2 H), 7.30 (t,  $J$  = 7.2 Hz, 1 H), 6.90 (t,  $J$  = 8.8 Hz, 2 H), 4.82 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.9, 140.7, 134.0, 128.7, 128.3, 126.7, 115.6 ppm; MS (70 ev):  $m/z$  (%): 115.1 (20), 141.1 (20), 170.1 (M<sup>+</sup>, 100).



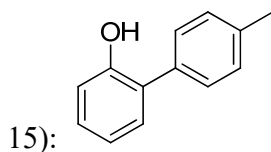
**4-Hydroxybenzonitrile (2l).**<sup>9</sup> The reaction of 4-oxocyclohex-2-enecarbonitrile **1l** (61 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 52 mg (88%) of **2l** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2l**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56 (d,  $J$  = 8.8 Hz, 2 H), 6.93 (d,  $J$  = 8.8 Hz, 2 H), 6.30 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.9, 134.3, 119.1, 116.4, 103.3 ppm; MS (70 ev):  $m/z$  (%): 64.0 (20), 91.0 (20), 119.0 (M<sup>+</sup>, 100).



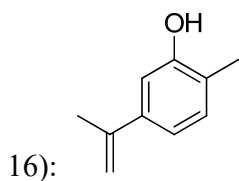
***m*-Cresol (2m).**<sup>6</sup> The reaction of 3-methylcyclohex-2-enone **1m** (55 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 33 mg (61%) of **2m** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2m**: colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.11 (t, *J* = 8.0 Hz, 1 H), 6.74 (d, *J* = 7.6 Hz, 1 H), 6.65-6.62 (m, 2 H), 5.07 (brs, 1 H), 2.29 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.3, 139.8, 129.4, 121.5, 116.0, 112.2, 21.2 ppm; MS (70 ev): *m/z* (%): 79.1 (50), 90.1 (10), 108.1 (M<sup>+</sup>, 100).



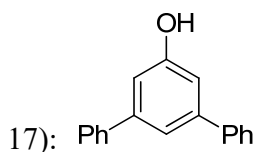
**Biphenyl-2-ol (2n).**<sup>7</sup> The reaction of 2-phenylcyclohex-2-enone **1n** (86 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (70  $\mu$ l, 2.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 64 mg (75%) of **2n** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2n**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51-7.48 (m, 4 H), 7.42-7.38 (m, 1 H), 7.29-7.23 (m, 2 H), 7.02-6.97 (m, 2 H), 5.20 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.3, 137.0, 130.2, 129.2, 129.1, 129.0, 128.1, 127.8, 120.8, 115.8 ppm; MS (70 ev): *m/z* (%): 115.1 (40), 141.1 (50), 170.1 (M<sup>+</sup>, 100).



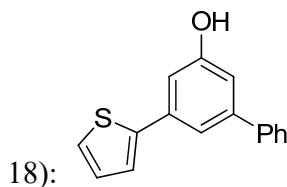
**4'-Methylbiphenyl-2-ol (2o).**<sup>10</sup> The reaction of 2-*p*-tolylcyclohex-2-enone **1o** (93 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (70  $\mu$ l, 2.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 69 mg (75%) of **2o** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2o**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (d, *J* = 7.6 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.24-7.20 (m, 2 H), 7.00-6.95 (m, 2 H), 5.23 (brs, 1 H), 2.39 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.4, 137.6, 134.0, 130.1, 129.9, 128.9, 128.7, 128.0, 120.7, 115.6, 21.1 ppm; HRMS *m/z* (ESI) calcd for C<sub>13</sub>H<sub>13</sub>O (M + H)<sup>+</sup> 185.0961, found 185.0961.



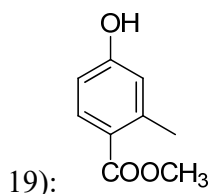
**2-Methyl-5-(prop-1-en-2-yl)phenol (2p).**<sup>5</sup> The reaction of carvone **1p** (75 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 8 h, afforded 57 mg (77%) of **2p** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2p**: colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.06 (d, *J* = 7.6 Hz, 1 H), 6.96 (dd, *J* = 1.6, 7.6 Hz, 1 H), 6.87 (d, *J* = 1.6 Hz, 1 H), 5.30 (brs, 1 H), 5.01-4.97 (m, 2 H), 2.22 (s, 3 H), 2.08 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.4, 142.6, 140.4, 130.7, 123.0, 117.9, 112.0, 111.8, 21.6, 15.4 ppm; MS (70 ev): *m/z* (%): 77.1 (40), 108.1 (50), 133.1 (60), 148.1 (M<sup>+</sup>, 100).



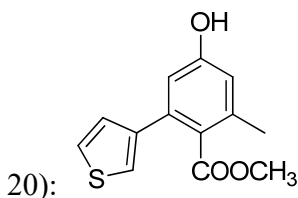
**3,5-Diphenylphenol (2q).**<sup>6</sup> The reaction of 3,5-diphenylcyclohex-2-enone **1q** (124 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35 μL, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 107 mg (87%) of **2q** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2q**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (d, *J* = 7.2 Hz, 4 H), 7.41-7.36 (m, 5 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 7.02 (d, *J* = 1.2 Hz, 2 H), 5.47 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.0, 143.3, 140.6, 128.7, 127.5, 127.1, 118.9, 113.0 ppm; HRMS *m/z* (ESI) calcd for C<sub>18</sub>H<sub>15</sub>O (M + H)<sup>+</sup> 247.1117, found 247.1119.



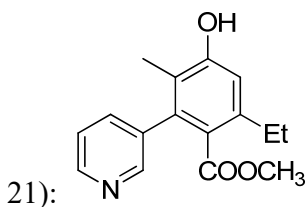
**5-(Thiophen-2-yl)biphenyl-3-ol (2r).**<sup>11</sup> The reaction of 3-phenyl-5-(thiophen-2-yl)cyclohex-2-enone **1r** (127 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35 μL, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 120 mg (95%) of **1r** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **1r**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55 (t, *J* = 7.2 Hz, 2 H), 7.43-7.39 (m, 3 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.29 (d, *J* = 3.6 Hz, 1 H), 7.26 (d, *J* = 5.2 Hz, 1 H), 7.05-7.03 (m, 2 H), 6.95 (s, 1 H), 5.31 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.0, 143.7, 143.5, 140.3, 136.2, 128.7, 127.9, 127.6, 127.1, 125.0, 123.5, 117.7, 113.3, 111.7 ppm; HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>13</sub>OS (M + H)<sup>+</sup> 253.0682, found 253.0683.



**Methyl 4-hydroxy-2-methylbenzoate (2s).**<sup>5</sup> The reaction of methyl 2-methyl-4-oxocyclohex-2-enecarboxylate **1s** (84 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 60 mg (72%) of **2s** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2s**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d, *J* = 9.2 Hz, 1 H), 6.78 (s, 1 H), 6.72-6.70 (m, 2 H), 3.87 (s, 3 H), 2.55 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.3, 159.3, 143.4, 133.3, 121.2, 118.4, 112.7, 51.8, 22.1 ppm; HRMS *m/z* (ESI) calcd for C<sub>9</sub>H<sub>11</sub>O<sub>3</sub> (M + H)<sup>+</sup> 167.0703, found 167.0703.

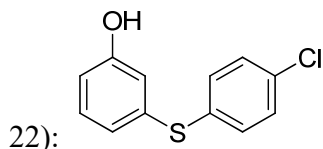


**Methyl 4-hydroxy-2-methyl-6-(thiophen-3-yl)benzoate (2t).** The reaction of methyl 2-methyl-4-oxo-6-(thiophen-3-yl)cyclohex-2-enecarboxylate **1t** (125 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 90 mg (73%) of **2t** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2t**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.28 (m, 1 H), 7.18 (dd, *J* = 1.6, 3.2 Hz, 1 H), 7.05 (dd, *J* = 1.2, 4.8 Hz, 1 H), 6.66 (d, *J* = 2.4 Hz, 1 H), 6.58 (d, *J* = 2.0 Hz, 1 H), 6.23 (brs, 1 H), 3.65 (s, 3 H), 2.28 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  171.2, 156.4, 140.8, 137.7, 136.6, 127.6, 125.6, 125.2, 122.2, 116.0, 113.7, 52.1, 19.7 ppm; HRMS *m/z* (ESI) calcd for C<sub>13</sub>H<sub>12</sub>NaO<sub>3</sub>S (M + Na)<sup>+</sup> 271.0399, found 271.0400.

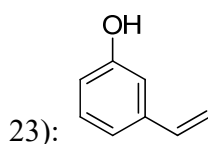


**Methyl 6-ethyl-4-hydroxy-3-methyl-2-(pyridin-3-yl)benzoate (2u).** The reaction of methyl 2-ethyl-5-methyl-4-oxo-6-(pyridin-3-yl)cyclohex-2-enecarboxylate **1u** (137 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 106 mg (78%) of **2u** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2u**: white solid; <sup>1</sup>H NMR (400 MHz,

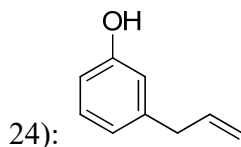
CDCl<sub>3</sub>):  $\delta$  11.03 (s, 1 H), 8.84 (d,  $J$  = 1.6 Hz, 1 H), 8.57 (dd,  $J$  = 1.6, 4.2 Hz, 1 H), 7.77 (d,  $J$  = 8.0 Hz, 1 H), 7.37-7.34 (m, 1 H), 6.84 (brs, 1 H), 3.57 (s, 3 H), 2.72 (q,  $J$  = 7.2 Hz, 2 H), 2.33 (s, 3 H), 1.21 (t,  $J$  = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.5, 157.1, 148.1, 147.1, 142.6, 138.2, 136.4, 133.9, 124.3, 124.0, 123.4, 113.8, 51.7, 24.5, 14.6, 11.2 ppm; HRMS  $m/z$  (ESI) calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub> (M + H)<sup>+</sup> 272.1281, found 272.1274.



**3-(4-Chlorophenylthio)phenol (2v).** The reaction of 3-(4-chlorophenylthio)cyclohex-2-enone **1v** (119 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35  $\mu$ l, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 100 mg (85%) of **2v** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2v**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.28-7.25 (m, 4 H), 7.16 (t,  $J$  = 8.0 Hz, 1 H), 6.88-6.86 (m, 1 H), 6.74 (t,  $J$  = 6.4 Hz, 1 H), 6.71-6.88 (m, 1 H), 5.09 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.0, 137.0, 133.5, 133.4, 132.7, 130.3, 129.3, 122.9, 117.1, 114.3 ppm; HRMS  $m/z$  (ESI) calcd for C<sub>12</sub>H<sub>10</sub>ClOS (M + H)<sup>+</sup> 237.0135, found 237.0138.

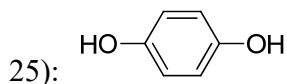


**3-Vinylphenol (2w).**<sup>12</sup> The reaction of 3-vinylcyclohex-2-enone **1w** (61 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (70  $\mu$ l, 2.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 8 h, afforded 27 mg (45%) of **2w** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2w**: colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.19 (t,  $J$  = 7.6 Hz, 1 H), 6.98 (d,  $J$  = 7.6 Hz, 1 H), 6.88 (s, 1 H), 6.74-6.62 (m, 2 H), 5.72 (d,  $J$  = 18.0 Hz, 1 H), 5.24 (d,  $J$  = 10.8 Hz, 1 H), 4.80 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.6, 139.3, 136.4, 129.7, 119.1, 114.8, 114.3, 112.7 ppm; MS (70 ev):  $m/z$  (%): 65.0 (20), 91.1 (80), 120.1 (M<sup>+</sup>, 100).

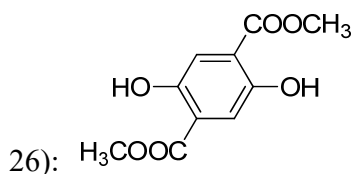


**3-Allylphenol (2x).**<sup>13</sup> The reaction of 3-allylcyclohex-2-enone **1x** (68 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (70  $\mu$ l, 2.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 8 h, afforded 33 mg (49%) of **2x** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **2x**: colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

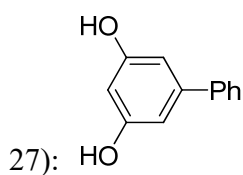
$\delta$  7.15 (t,  $J$  = 7.6 Hz, 1 H), 6.89 (d,  $J$  = 8.0 Hz, 1 H), 6.79 (s, 1 H), 6.66 (dd,  $J$  = 2.4, 8.0 Hz, 1 H), 6.34 (d,  $J$  = 15.6 Hz, 1 H), 6.27-6.16 (m, 1 H), 4.79 (brs, 1 H), 1.87-1.85 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.5, 139.7, 130.6, 129.6, 126.2, 118.7, 113.7, 112.4, 18.3 ppm; MS (70 ev):  $m/z$  (%): 77.0 (30), 105.1 (30), 134.1 ( $\text{M}^+$ , 100).



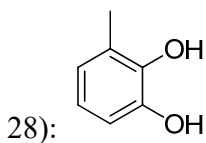
**1,4-Dihydroxybenzene (4a).**<sup>14</sup> The reaction of methyl cyclohexane-1,4-dione **3a** (56 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 45 mg (82%) of **4a** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **4a**: white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  8.60 (s, 2 H), 6.56 (s, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  149.7, 115.6 ppm; MS (70 ev):  $m/z$  (%): 53.0 (30), 81.0 (40), 110.0 ( $\text{M}^+$ , 100).



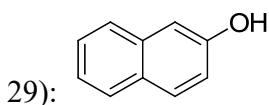
**Dimethyl 2,5-dihydroxyterephthalate (4b).**<sup>15</sup> The reaction of dimethyl 2,5-dioxocyclohexane-1,4-dicarboxylate **3b** (114 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 98 mg (87%) of **4b** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **4b**: yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.03 (s, 2 H), 7.43 (s, 2 H), 3.96 (s, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.4, 152.8, 118.2, 117.6, 52.7 ppm; MS (70 ev):  $m/z$  (%): 134.0 (30), 162.0 (80), 194.0 (100), 226.0 ( $\text{M}^+$ , 30).



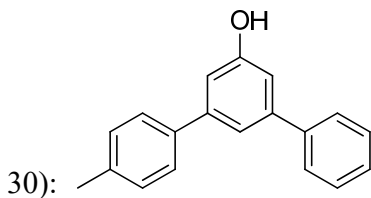
**Biphenyl-3,5-diol (4c).**<sup>16</sup> The reaction of methyl 5-phenylcyclohexane-1,3-dione **3c** (94 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 84 mg (90%) of **4c** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **4c**: white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  9.39 (s, 2 H), 7.54 (d,  $J$  = 7.6 Hz, 2 H), 7.41 (t,  $J$  = 7.2 Hz, 2 H), 7.31 (t,  $J$  = 7.6 Hz, 1 H), 6.51 (s, 2 H), 6.29 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  158.9, 142.3, 140.7, 128.8, 127.4, 126.5, 105.0, 101.8 ppm; MS (70 ev):  $m/z$  (%): 115.0 (10), 128.1 (10), 186.1 ( $\text{M}^+$ , 100).



**3-Methylbenzene-1,2-diol (4d).**<sup>17</sup> The reaction of 3-methylcyclohexane-1,2-dione **3d** (63 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 16 mg (26%) of **4d** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **4d**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl<sub>3</sub>): δ 6.70 (s, 2 H), 5.14 (s, 2 H), 2.25 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>Cl<sub>3</sub>): δ 142.9, 142.0, 124.4, 122.9, 120.1, 112.9, 15.4 ppm. The yield of product **4d** is really not good (26% yield). We have tried to employ the GC-MS as well as <sup>1</sup>H NMR method to find some byproduct. However, no obvious byproduct was detected. The starting material **3d** is fully converted, whereas affording product **4d** in low yield. When **4d** was tested as substrate under the standard conditions, 87% of **4d** could be isolated. And thus the low reaction yield is not attributed to the unstable of **4d** under the standard conditions. On the basis of above results, we think that probably because of the easy decomposition character of reaction intermediate, such as α-iodo cyclohexenone **B** (see the proposed mechanism in Text), leading the low yield of product **4d**.

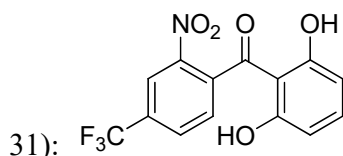


**Naphthalen-2-ol (4e).**<sup>18</sup> The reaction of methyl 2-tetralone **3e** (73 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 48 mg (66%) of **4e** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **4e**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl<sub>3</sub>): δ 7.77-7.37 (m, 2 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.14 (d, *J* = 2.4 Hz, 1 H), 7.09 (dd, *J* = 2.4, 8.8 Hz, 1 H), 4.95 (s, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>Cl<sub>3</sub>): δ 153.2, 134.5, 129.8, 128.9, 127.7, 126.5, 126.3, 123.6, 117.6, 109.4 ppm; MS (70 ev): *m/z* (%): 89.1 (10), 115.1 (70), 144.1 (M<sup>+</sup>, 100).



**(4'-Methylphenyl)-5-phenylphenol (7).**<sup>6</sup> The reaction of 3-(4'-methylphenyl)-5-phenylcyclohexenone **8** (132 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (35 μL, 1.0 equiv), in CH<sub>3</sub>NO<sub>2</sub> (1.0 mL), at 100 °C for 24 h, afforded 112 mg (86%) of **7** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **7**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.58 (d, *J* = 7.2 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz,

2 H), 7.41 (t,  $J = 7.6$  Hz, 2 H), 7.37-7.32 (m, 2 H), 7.22 (d,  $J = 7.6$  Hz, 2 H), 7.00 (s, 2 H), 5.21 (brs, 1 H), 2.38 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.0, 143.33, 143.30, 140.7, 137.7, 137.4, 129.4, 128.7, 127.5, 127.1, 126.9, 118.7, 112.8, 112.7, 21.0 ppm; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{19}\text{H}_{17}\text{O}$  ( $\text{M} + \text{H}$ ) $^+$  261.1274, found 261.1276.



**(2,6-Dihydroxyphenyl)(2-nitro-4-(trifluoromethyl)phenyl)methanone (10).** The reaction of 2-(2-nitro-4-(trifluoromethyl)benzoyl)cyclohexane-1,3-dione **9** (165 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 60 °C for 24 h, afforded 118 mg (72%) of **10** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **10**: yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{Cl}_3$ ):  $\delta$  8.88 (brs, 2 H), 8.45 (s, 1 H), 7.97 (d,  $J = 8.0$  Hz, 1 H), 7.49 (d,  $J = 8.0$  Hz, 1 H), 7.32-7.25 (m, 1 H), 6.35 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{Cl}_3$ ):  $\delta$  196.0, 160.7, 145.2, 141.8, 138.0, 132.0 (q,  $J = 34.4$  Hz), 130.9 (q,  $J = 2.7$  Hz), 127.9, 122.6 (q,  $J = 272.2$  Hz), 121.2 (q,  $J = 3.4$  Hz), 108.9, 108.5 ppm; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{14}\text{H}_9\text{F}_3\text{NO}_5$  ( $\text{M} + \text{H}$ ) $^+$  328.0427, found 328.0429.

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