

# Biaryl Coupling and Oxidation Reactions of Aromatic Alcohols Catalyzed by VO(acac)<sub>2</sub>

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## Abstract

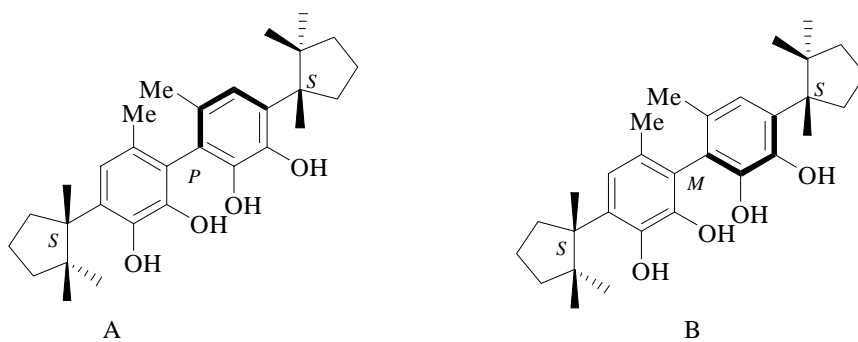
The biaryl coupling of substituted aromatic alcohols and the oxidation of *p*-hydroquinones with molecular oxygen catalyzed by VO(acac)<sub>2</sub> were achieved in good to excellent yields.

**Key Words:** Biaryl coupling, VO(acac)<sub>2</sub>, Oxidation, Aromatic Alcohols

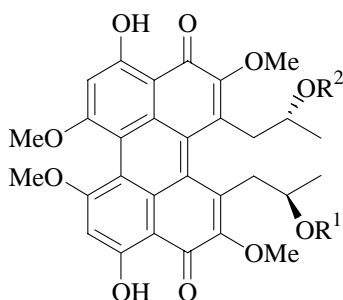
## 1. Introduction

Biaryl moiety is the core structural component of many important natural products such as mastigophorenes (1) [1], calphostins (2) [2], vancomycin (3) [3], colchicine (4) [4], korupen-

samines (5) [5], etc. Optically active biaryl compounds such as 1,1'-bi-2-naphthol and its derivatives have been widely used in the enantioselective synthesis as a source of chirality [6].

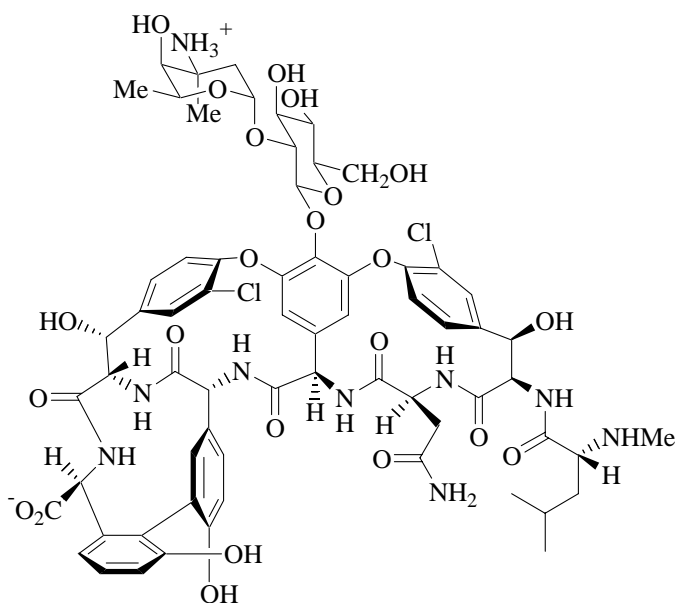


Mastigophorenes (1)

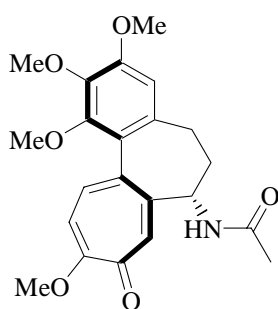


Calphostins (2)

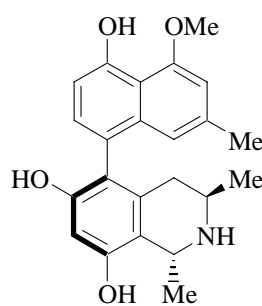
- A  $R^1 = \text{Bz}$ ,  $R^2 = \text{Bz}$
- B  $R^1 = \text{Bz}$ ,  $R^2 = \text{H}$
- C  $R^1 = \text{Bz}$ ,  $R^2 = \text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{OH}$
- D  $R^1 = \text{H}$ ,  $R^2 = \text{H}$



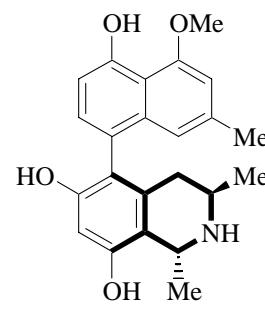
Vancomycin (3)



Colchicine (4)



A



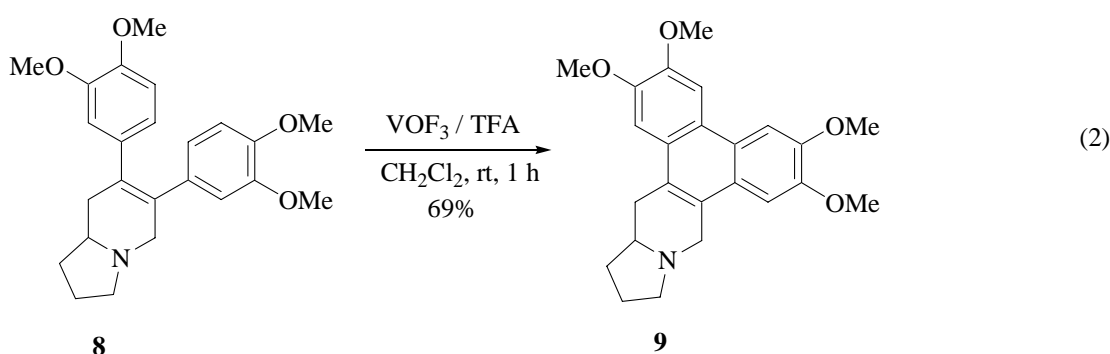
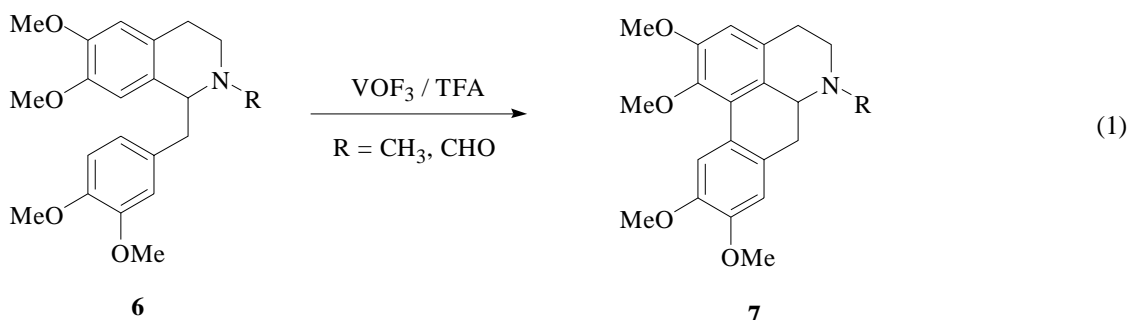
B

Korupensamines (5)

Oxidative biaryl coupling of phenols has received considerable attention owing both to its utility as a synthetic reaction and its proposed involvement in the biosynthesis of many natural products containing biaryl segment. [7] Documented methods for the oxidative coupling of 2-naphthols made use of various transitional metal species as oxidants both in stoichiometric and catalytic amounts. For example, Fe (III) [8], Mn (III) [9] and Cu (II)-amine [10] were used in stoichiometric amount to mediate the coupling. Whereas CuCl<sub>2</sub>-amine/AgCl, [10c] CuCl(OH)-TMEDA/O<sub>2</sub> [11], CuSO<sub>4</sub>(Al<sub>2</sub>O<sub>3</sub>)/O<sub>2</sub> [12] and FeCl<sub>3</sub> in the presence of ultra-sound irradiation [8a] were employed as catalytic systems to assist the oxidative coupling.

Vanadium complexes exhibit a rich redox chemistry providing potential tools in the organic

synthesis [13]. Utility of oxovanadium compounds in C-C bond formation is amply demonstrated in a myriad of organic transformations. Oxovanadium compounds such as VOCl<sub>3</sub> and VOF<sub>3</sub> are capable of mediating the oxidative coupling of a various phenols and aromatic ethers. This coupling is well utilized in the synthesis of many natural products. For example, the oxidative coupling of laudausine (6) in the presence of VOF<sub>3</sub>/trifluoroacetic acid furnished glaucine (7) [14] (Eq. 1). The conversion of septicine (8) into phenanthroindolizidine alkaloid tylophorine (9) [15] by VOF<sub>3</sub> (Eq. 2) and the synthesis of glycopeptides antibiotics, vancomycin [3] through VOF<sub>3</sub> induced biaryl coupling are some other examples illustrating the applicability of oxovanadium species in the synthesis of some prominent bioactive natural products.

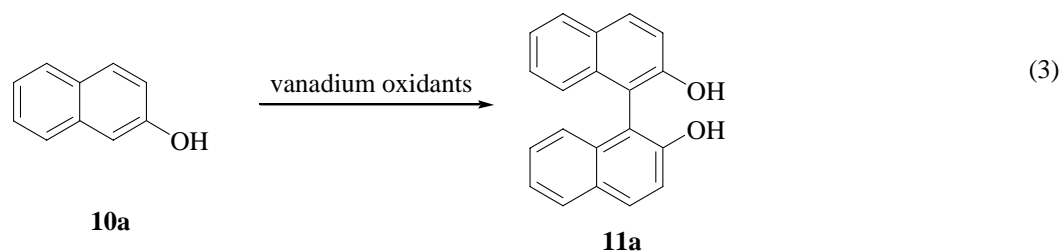


However, most of these methods have their own limitations either involving tedious procedures as in the case of preparation of aforementioned copper complexes or requiring harsh reaction conditions when oxidant such as FeCl<sub>3</sub> was used in combination with ultra-sound irradiation. In the light of these observations, it is important to find a more convenient method for the coupling of aromatic alcohols. Here, we report the reaction of 2-naphthols and substituted phenols with molecular oxygen catalyzed by VO(acac)<sub>2</sub>.

## 2. Results and Discussion

At the outset, we have studied the ability of various oxovanadium compounds such as VOCl<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, VO(salen)ClO<sub>4</sub>·(H<sub>2</sub>O) and VO(acac)<sub>2</sub> in the oxidative coupling of 2-naphthol (**10a**) in the absence of any external oxidant (Eq. 3). The results are shown in Table 1. Oxidation of 2-naphthol using stoichiometric amount of VOCl<sub>3</sub> in dichloromethane at 0 °C for 0.5 h afforded the BINOL (**11a**) in 74% yield. However, similar results were observed when the amount of VOCl<sub>3</sub> was reduced to 0.5 equivalents. Coupling was very sluggish when V<sub>2</sub>O<sub>5</sub> was used, yielding the BINOL in only 53% yield even after 72 h, presumably due

to its poor solubility in dichloromethane. Increasing the amount of V<sub>2</sub>O<sub>5</sub> to 3 equivalents and raising the temperature led to significant enhancement in the yield of product. Vanadium pentoxide failed to react in protic solvents such as H<sub>2</sub>O or methanol although it is more soluble in these solvents. This phenomenon presumably due to the competition of coordination sites by the solvent molecules and the coupling reaction was retarded. Sterically hindered oxovanadium salen complex, VO(salen)ClO<sub>4</sub>·(H<sub>2</sub>O) was prepared by a two step procedure [16] starting from salen and was used in 0.5 equivalents to promote the coupling. The reaction did not proceed in dichloromethane, whereas in 1,2-dichloroethane at 80 °C, BINOL was obtained in 64% yield. Another vanadium species, VO(acac)<sub>2</sub> was not useful in inducing the coupling. Obviously, V(IV) species could not mediate the oxidative coupling in these reactions. The fact that, similar yields were obtained irrespective of the number of equivalents of VOCl<sub>3</sub> may be attributed to the conversion of V<sup>V</sup> to V<sup>III</sup> during the course of the reaction. Thus, while the yields were moderate with VOCl<sub>3</sub>, other vanadium species either did not react or required harsh reaction conditions to accomplish the oxidative coupling.

Table 1. Oxidation of 2-naphthol (**10a**) into BINOL (**11a**) by vanadium oxidants

Entry	Oxidant (equiv)	Solvent	Temp (°C)	Time (h)	Yield (%)
1	VOCl <sub>3</sub> (1)	CH <sub>2</sub> Cl <sub>2</sub>	0	0.5	74
2	VOCl <sub>3</sub> (0.5)	CH <sub>2</sub> Cl <sub>2</sub>	0	0.5	68
3	V <sub>2</sub> O <sub>5</sub> (1)	CH <sub>2</sub> Cl <sub>2</sub>	25	72	53
4	V <sub>2</sub> O <sub>5</sub> (3)	CH <sub>2</sub> Cl <sub>2</sub>	reflux	3	80
5	V <sub>2</sub> O <sub>5</sub> (1)	MeOH	reflux	24	0
6	V <sub>2</sub> O <sub>5</sub> (1)	H <sub>2</sub> O	reflux	24	0
7	VO(salen)ClO <sub>4</sub> (H <sub>2</sub> O) (0.5)	ClCH <sub>2</sub> CH <sub>2</sub> Cl	80	24	64
8	VO(acac) <sub>2</sub> (1)	CH <sub>2</sub> Cl <sub>2</sub>	reflux	24	trace

To achieve a catalytic cycle in the vanadium catalyzed coupling of phenols, it requires a suitable oxidant, which will selectively oxidize the low valent vanadium species to the pentavalent vanadium species without interfering with the coupling process. Accordingly, we have used VO(acac)<sub>2</sub> as a precatalyst in combination with molecular oxygen to mediate the oxidative coupling in naphthols and phenols [17]. Oxidants such as H<sub>2</sub>O<sub>2</sub>, <sup>t</sup>BuOOH and oxone were found to be not very rewarding in conjunction with 10 mol% VO(acac)<sub>2</sub>. When *N*-methylmorpholine *N*-oxide was used as the terminal oxidant there was no coupling product.

Instead, a Modified Mannich type product was obtained [18]. Gratifyingly, molecular oxygen served as a gainful oxidant in this catalytic coupling of 2-naphthols (**10a-d**) conducted in dichloromethane at room temperature, and the corresponding 1,1'-bi-2-naphthols (**11a-d**) were furnished in moderate to good yields (Table 2). Although phenol could not be coupled under these reaction conditions, substituted phenols such as 2,4-dimethylphenol (**12a**) and 2,3,5-trimethylphenol (**12b**) afforded the corresponding *ortho-ortho* coupled products (**13**) in moderate yields (Eq. 4).

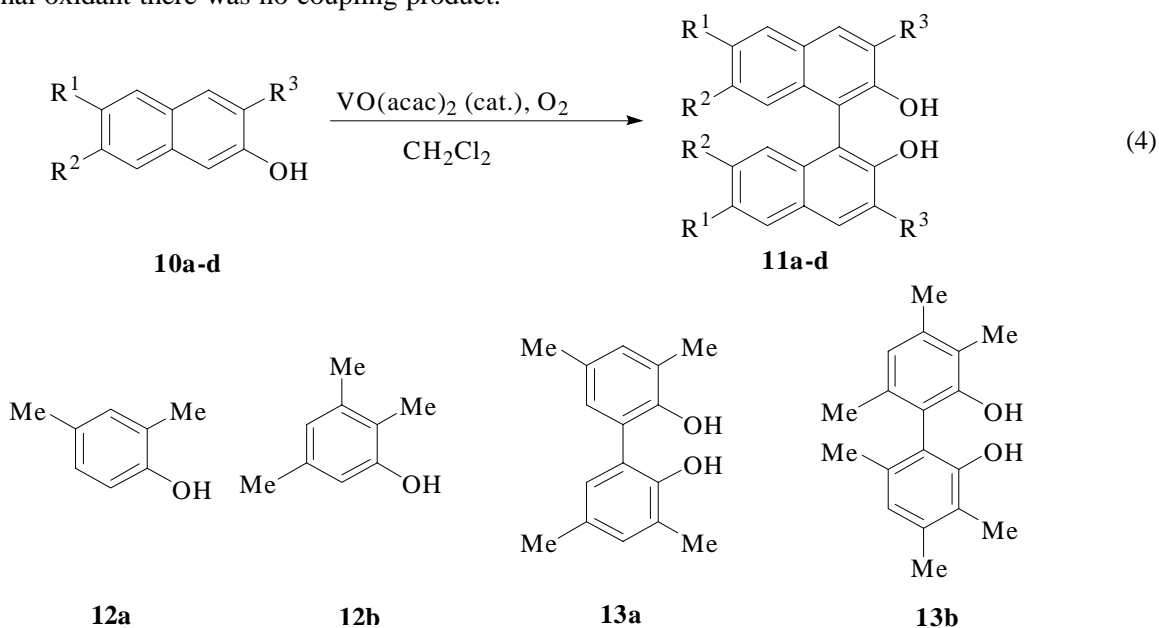
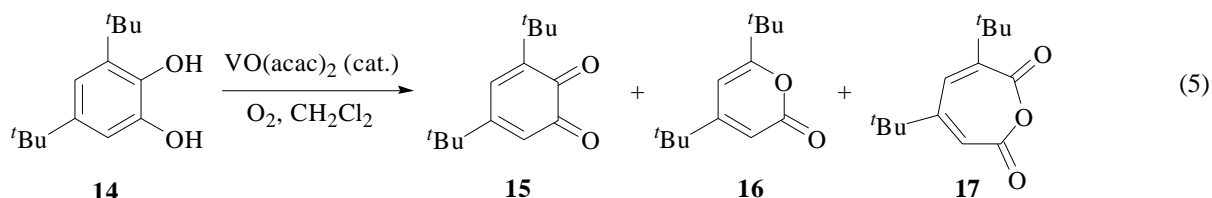


Table 2. Oxidative coupling of 2-naphthols (**10a-d**) and phenols (**12a,b**) catalyzed by VO(acac)<sub>2</sub>

ArOH	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time (h)	Product	Yield (%)
<b>10a</b>	H	H	H	24	<b>11a</b>	92
<b>10b</b>	Br	H	H	24	<b>11b</b>	90
<b>10c</b>	H	OMe	H	9	<b>11c</b>	76
<b>10d</b>	H	H	CO <sub>2</sub> Me	120	<b>11d</b>	35
<b>12a</b>				120	<b>13a</b>	66
<b>12b</b>				48	<b>13b</b>	62

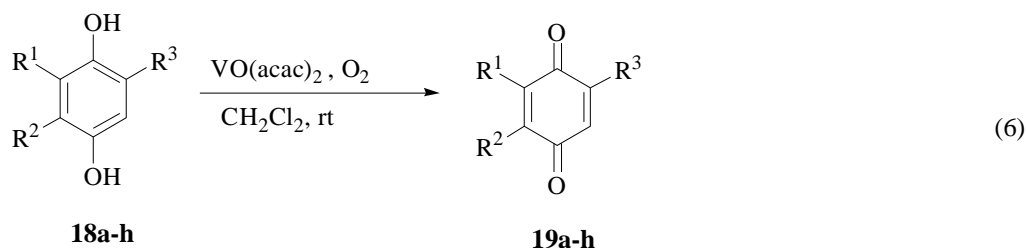
On the other hand, it was reported that aerobic oxidation of 3,5-di-*tert*-butylpyrocatechol (**14**) in the presence of VO(acac)<sub>2</sub> gave orthoquinone (**15**)

in only 15% yield along with two other compounds, lactone (**16**) and anhydride (**17**) (Eq. 5) [19].



In an extension of our study, vanadyl acetylacetonate catalyzed aerobic oxidation of phenols was also tested with *para*-hydroquinones to provide the corresponding quinones. Oxidation of various hydroquinone derivatives (**18**) using catalytic amount of tetravalent vanadium species,

VO(acac)<sub>2</sub>, in the presence of molecular oxygen furnished the corresponding quinones (**19**) as sole products in good to excellent yields (Table 3) thus providing a new facile entry to quinones (Eq. 6) [20].

Table 3. Oxidation of hydroquinones **18a-h** catalyzed by VO(acac)<sub>2</sub>

Hydroquinone	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time (h)	Product	Yield (%)
<b>18a</b>	H	H	H	10	<b>19a</b>	75
<b>18b</b>	Me	H	H	14	<b>19b</b>	76
<b>18c</b>	Me	Me	H	15	<b>19c</b>	76
<b>18d</b>	Me	Me	Me	14	<b>19d</b>	97
<b>18e</b>	<sup>t</sup> Bu	H	H	10	<b>19e</b>	92
<b>18f</b>	Ph	H	H	20	<b>19f</b>	88
<b>18g</b>	Br	H	H	25	<b>19g</b>	72
<b>18h</b>	SPh	H	H	12	<b>19h</b>	85

A plausible mechanism for the vanadium catalyzed oxidation of hydroquinones is depicted in Figure 1. Disproportionation of oxovanadium(IV) complex to the vanadium(V) and vanadium(III) and subsequent molecular oxygen oxidation of vanadium(III) to vanadium(V) constitutes the catalytic cycle in this oxidation reaction [21].

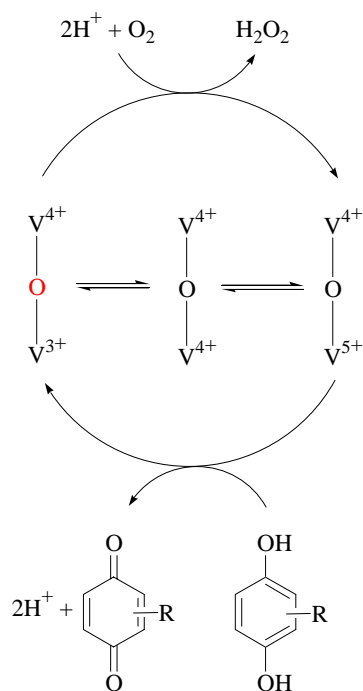


Figure 1. A plausible catalytic cycle for the oxidation of hydroquinone

In conclusion, an efficient and simple method for the oxidation of hydroquinones and biaryl coupling of aromatic alcohols has been demonstrated. This method employed oxovanadium acetylacetonate, a stable and cheap catalyst, and molecular oxygen to oxidize hydroquinones to quinones and induce the coupling of 2-naphthols and phenols to BINOL and biphenols respectively at room temperature in moderate to high yields.

### 3. Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker-400 spectrometer at 400 and 100 MHz, respectively.  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to the residual protonated solvent resonance:  $\text{CHCl}_3$ ,  $\delta$  7.26. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened. Coupling constants ( $J$ ) are reported in hertz.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to solvent resonance:  $\text{CDCl}_3$ ,  $\delta$  77.0. Mass spectral data include the molecular ion designated as M.

### 3.1 Typical Procedure

A stirred mixture of 2-naphthol, substituted phenol or hydroquinone (1 mmol), and  $\text{VO}(\text{acac})_2$  (26.5 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was exposed under an atmospheric pressure of molecular oxygen at room temperature. The mixture was filtered through a short column of silica gel and the silica gel was washed with  $\text{EtOAc}$  (40 mL). The filtrate was concentrated and purified by column chromatography to afford the corresponding coupling or oxidation product.

#### 2,2'-Binaphthol (**IIa**) [22a]

$^1\text{H}$  NMR:  $\delta$  7.96 (d,  $J$  = 9.0 Hz, 2H), 7.88 (d,  $J$  = 8.0 Hz, 2H), 7.25-7.41 (m, 6H), 7.13 (d,  $J$  = 8.3 Hz, 2H), 5.04 (br, 2H);  $^{13}\text{C}$  NMR:  $\delta$  152.8 (C), 133.5 (C), 131.4 (CH), 129.4 (C), 128.4 (CH), 127.51 (CH), 124.2 (CH), 104.6 (CH), 117.8 (CH), 110.9 (C); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3486, 3403, 3055, 2963, 1798, 1618, 1596; MS  $m/z$  286 ( $\text{M}^+$ ).

#### 6,6'-Dibromo-2,2'-binaphthol (**IIb**) [22b]

$^1\text{H}$  NMR:  $\delta$  8.03 (d,  $J$  = 2.0 Hz, 2H), 7.88 (d,  $J$  = 9.0 Hz, 2H), 7.38 (dd,  $J$  = 9.0, 2.0 Hz, 2H), 7.35 (dd,  $J$  = 9.0, 2.0 Hz, 2H), 6.94 (d,  $J$  = 9.0 Hz, 2H), 5.06 (br, 2H);  $^{13}\text{C}$  NMR:  $\delta$  153.0 (C), 131.9 (C), 130.9 (CH), 130.7 (CH), 130.6 (CH), 130.5 (CH), 125.9 (CH), 119.0 (CH), 118.0 (C), 110.8 (C); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3459, 3017, 2949, 1614, 1586, 1495, 1408, 1382, 1337, 1268; MS  $m/z$  444 ( $\text{M}^+$ ).

#### 7,7'-Dimethoxy-2,2'-binaphthol (**IIc**) [22b]

$^1\text{H}$  NMR:  $\delta$  7.79 (d,  $J$  = 9.0 Hz, 2H), 7.72 (d,  $J$  = 9.0 Hz, 2H), 6.99 (dd,  $J$  = 9.0, 2.4 Hz, 2H), 6.45 (d,  $J$  = 2.4 Hz, 2H), 5.15 (br, 2H), 3.53 (s, 6H);  $^{13}\text{C}$  NMR:  $\delta$  158.9 (C), 153.2 (C), 134.7 (C), 130.9 (CH), 129.9 (CH), 124.7 (CH), 115.9 (CH), 115.0 (CH), 110.2 (C), 103.1 (CH), 55.0 ( $\text{CH}_3$ ); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3422, 3007, 2831, 2025, 1917, 1514, 1465, 1432, 1380, 1339; MS  $m/z$  346 ( $\text{M}^+$ ).

#### 3,3'-Dimethoxycarbonyl-2,2'-binaphthol (**IIId**) [22b]

$^1\text{H}$  NMR:  $\delta$  8.68 (s, 2H), 7.90-7.92 (m, 2H), 7.32-7.34 (m, 4H), 7.14-7.16 (m, 2H), 4.03 (s, 6H);  $^{13}\text{C}$  NMR:  $\delta$  170.7 (C), 154.1 (C), 137.3 (C), 132.9 (CH), 129.9 (CH), 129.5 (CH), 127.3 (C), 124.8 (CH), 124.0 (CH), 117.0 (C), 114.2 (CH), 52.7 ( $\text{CH}_3$ ); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  3474, 3175, 2953, 1682, 1625, 1601, 1575, 1503, 1442; MS  $m/z$  402 ( $\text{M}^+$ ).

#### 3,3',5,5'-Tetramethyl-2,2'-biphenol (**IIa**) [22c]

$^1\text{H}$  NMR:  $\delta$  7.00 (s, 2H), 6.87 (s, 2H), 5.15 (br, 2H), 2.28 (s, 12H);  $^{13}\text{C}$  NMR:  $\delta$  149.1 (C), 131.9 (CH), 129.9 (C), 128.5 (CH), 125.2 (C), 122.2 (C), 20.4 ( $\text{CH}_3$ ), 16.1 (CH); IR:  $\nu_{\text{max}}/\text{cm}^{-1}$

3484, 3002, 2914, 2851, 1736, 1625, 1482, 1441, 1338, 1332; MS m/z 242 (M<sup>+</sup>).

**3,3',4,4',6,6'-Hexamethyl-2,2'-biphenol (13b)** [22d]

<sup>1</sup>H NMR: δ 6.73 (s, 2H), 4.75 (s, 2H), 2.28 (s, 6H), 2.17 (s, 6H), 1.92 (s, 6H); <sup>13</sup>C NMR: δ 151.6 (C), 138.5 (C), 135.0 (C), 123.7 (CH), 120.3 (C), 116.9 (C), 19.9 (CH<sub>3</sub>), 19.2 (CH<sub>3</sub>), 11.7 (CH<sub>3</sub>); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3517, 3470, 2972, 2920, 2862, 1732, 1619, 1562, 1456, 1394, 1298, 1242; MS m/z 270 (M<sup>+</sup>).

**2-Methyl-1,4-benzoquinone (19b)** [22e]

<sup>1</sup>H NMR: δ 6.52-6.68 (m, 3H), 1.95 (s, 3H); <sup>13</sup>C NMR: δ 167.4 (C), 167.3 (C), 145.6 (C), 136.2 (CH), 136.1 (CH), 133.0 (CH), 15.3 (CH<sub>3</sub>); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3447, 1655, 1601, 1431, 1374, 1348, 1301, 1097; MS m/z 122 (M<sup>+</sup>).

**2,3-Dimethyl-1,4-benzoquinone (19c)** [22f]

<sup>1</sup>H NMR: δ 6.65 (s, 2H), 1.96 (s, 6H); <sup>13</sup>C NMR: δ 187.3 (C), 140.9 (C), 136.1 (CH), 12.1 (CH<sub>3</sub>); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3056, 1656, 1602, 1439, 1381, 1366, 1310, 1266, 1137, 1105; MS m/z 136 (M<sup>+</sup>).

**2,3,5-Trimethyl-1,4-benzoquinone (19d)** [22g]

<sup>1</sup>H NMR: δ 6.28 (s, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.73 (s, 3H); <sup>13</sup>C NMR: δ 187.1 (C), 186.7 (C), 144.8 (C), 140.3 (C), 140.2 (C), 132.6 (CH), 15.3 (CH<sub>3</sub>), 11.8 (CH<sub>3</sub>), 11.5 (CH<sub>3</sub>); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3270, 2925, 1650, 1609, 1438, 1376, 1355, 1317, 1262, 1189; MS m/z 150 (M<sup>+</sup>).

**2-tert-Butyl-1,4-benzoquinone (19e)** [22h]

<sup>1</sup>H NMR: δ 6.62-6.64 (m, 2H), 6.54 (s, 1H), 1.22 (s, 9H); <sup>13</sup>C NMR: δ 188.3 (C), 187.3 (C), 155.9 (C), 138.5 (CH), 134.8 (CH), 131.3 (CH), 35.1 (C), 28.9 (CH<sub>3</sub>); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3303, 3250, 3065, 2963, 2875, 1655, 1591, 1483; MS m/z 164 (M<sup>+</sup>).

**2-Phenyl-1,4-benzoquinone (19f)** [22i]

<sup>1</sup>H NMR: δ 7.45-7.37 (m, 5H), 6.83-6.75 (m, 3H); <sup>13</sup>C NMR: δ 187.5 (C), 186.5 (C), 145.8 (C), 136.9 (CH), 136.1 (CH), 132.6 (CH), 130.0 (CH), 129.1 (CH), 128.4 (CH); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3600, 3500, 1645, 1625, 1545, 1500, 1490, 1410; MS m/z 184 (M<sup>+</sup>).

**2-Bromo-1,4-benzoquinone (19g)** [22j]

<sup>1</sup>H NMR: δ 7.26 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 10.1 Hz, 1H), 6.79 (dd, *J* = 10.1, 2.3 Hz, 1H); <sup>13</sup>C NMR: δ 184.6 (C), 179.2 (C), 138.1 (CH), 137.5 (C), 136.7 (CH), 135.8 (CH); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3070, 3021, 2922, 2850, 1674, 1667, 1582, 1460, 1308; MS m/z 188 (M<sup>+</sup>).

**2-(Phenylthio)-1,4-benzoquinone (19h)** [22k]

<sup>1</sup>H NMR: δ 7.49-7.45 (m, 5H), 6.82-6.64 (m, 2H), 5.86 (s, 1H); <sup>13</sup>C NMR: δ 184.4 (C), 183.8 (C), 154.4 (C), 137.4 (CH), 135.8 (CH), 135.5 (CH), 130.0 (CH), 130.5 (CH), 130.3 (CH), 126.8 (C), 125.8 (CH); IR: ν<sub>max</sub>/cm<sup>-1</sup> 3055, 1665, 1640, 1610, 1566, 1470, 1440; MS m/z 216 (M<sup>+</sup>).

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