

(Supplementary Information)

Improved Protocol for Mono-nitration of Phenols with Bismuth(III) and Iron(III) Nitrates

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1. Experimental section

1.1. General Remarks

Melting points were determined on a digital melting-point apparatus, using standard open capillary method. NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a FT NMR spectrometer (300.1 for ¹H and 75.4 for ¹³C or 600.6 for ¹H and 151.0 for ¹³C) at 22 °C. The chemical shifts values δ are given in parts per million (ppm) downfield relative to TMS, and coupling constants J are in Hertz (Hz). Multiplicity (s=singlet, d=doublet, t=triplet, dd=doublet of doublets, m=multiplet, br=broad). Residual solvent central peaks were measured; CDCl₃ δ ¹H 7.26, ¹³C 77.00; DMSO-*d*₆ δ ¹H 2.50, ¹³C 39.43. Infrared spectra were recorded on a FT-IR instrument in KBr pellets or as thin films, and wave number were expressed in cm⁻¹. The progress of the reaction was monitored by thin layer chromatography on silica gel coated plates (Merck 60F₂₅₄), and visualization was accomplished with UV light and/or on iodine vapour. Chromatographic purification was performed using silica gel column chromatography (Merck 60, particle size 70–230 mesh). Yields refer to isolated compounds, estimated to be >98% pure as determined by ¹H NMR.

Bi(NO₃)₃·5H₂O, Fe(NO₃)₃·9H₂O, (NH₄)₂Ce(NO₃)₆, substituted phenols, silica gel 60 (70–230 mesh), acetone and other solvents were purchased from commercial suppliers.

Acetone and solvent for column chromatography were distilled before using. The purity of the products were confirmed by comparison of their melting point, ^1H NMR, ^{13}C NMR and IR spectra with data given in literature.

1.2. General procedure for the nitration of phenolic compounds

To a solid mixture of phenol (1–3 equiv) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 equiv) or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 equiv) was added acetone (10 ml/mmol). The resulting mixture was stirred at room temperature under air or at reflux for 2–24 hours, Tables 1 and 2. When the reaction was completed the insoluble materials were filtered off using a pad of Celite and the residue was washed by acetone (ca. 5 ml/mmol). The filtrate was treated by NaHCO_3 (0.1 g/mmol) until evolution of CO_2 stopped. Insoluble material was filtered off again, and the solvent was removed under vacuum in a water bath 25–35°C. The nitrated products were separated or purified using silica gel chromatography, to give pure phenolic compounds. All products were characterized by ^1H NMR, ^{13}C NMR and IR and were identified by comparison of the spectral data and melting points with those reported in literature and characterized.

2-Nitro-4-phenylphenol (2a)

4-Phenylphenol (**1a**) (3.40 g, 20 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) and acetone (100 mL) were used. Yellow prisms (4.0 g, 93% yield), mp: 70.0–70.5 °C (lit.¹ 68–69 °C). Column chromatography (petroleum ether/EtOAc=10/1) $R_f=0.52$. The NMR spectra are in agreement with those reported in the literature.² ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 11.12 (s, 1H, OH), 8.12 (d, $J=2.4$ Hz, 1H, H-3), 7.87 (dd, $J=8.7, 2.4$ Hz, 1H, H-5), 7.66 (d, $J=8.0$ Hz, 2H, H-2', H-6'), 7.45 (dd, $J=8.0, 7.3$ Hz, 2H, H-3', H-5'), 7.36 (t, $J=7.3$ Hz, 1H, H-4'), 7.22 (d, $J=8.7$ Hz, 1H, H-6); ^{13}C NMR ($\text{DMSO}-d_6$): δ 151.4 (C), 137.8 (C), 137.2 (C), 133.1 (CH), 131.3 (C), 129.0 (2·CH), 127.5 (CH), 126.2 (2·CH), 122.6 (CH), 119.6 (CH); IR (KBr): 3283

cm⁻¹ (OH), 3074, 3033 cm⁻¹ (ArH), 1635 cm⁻¹ (C=C), 1542, 1315 cm⁻¹ (NO₂), 1255 cm⁻¹ (C–O).

4-Chloro-5-methyl-2-nitrophenol (2b)

4-Chloro-5-methylphenol (**1b**) (2.83 g, 20 mmol), Bi(NO₃)₃·5H₂O (4.85 g, 10 mmol) and acetone (100 mL) were used. Bright yellow flakes (1.63 g, 43% yield), mp: 134.5–136.0 °C (CH₂Cl₂) (lit.³ 136–138 °C). Column chromatography (CH₂Cl₂), R_f=0.77. The NMR spectra are in agreement with those reported in the literature.⁴ ¹H NMR (300 MHz, CDCl₃): δ 10.43 (s, 1H, OH), 8.08 (s, 1H, H-3), 7.05 (s, 1H, H-6), 2.42 (s, 3H, CH₃); ¹³C NMR (75 MHz CDCl₃): δ 153.3 (C), 147.6 (C), 131.8 (C), 125.8 (C), 124.5 (CH), 121.4 (CH), 20.8 (CH₃); IR (KBr): 3282 cm⁻¹ (OH), 3102, 3050 cm⁻¹ (ArH), 2996, 2928 cm⁻¹ (CH₃), 1624 cm⁻¹ (C=C), 1513, 1309 cm⁻¹ (NO₂), 1261 cm⁻¹ (C–O), 852 cm⁻¹ (C–Cl).

2-Benzyl-6-nitrophenol (2d)⁵

2-Benzylphenol (**1d**) (3.68 g, 20 mmol), Bi(NO₃)₃·5H₂O (4.85 g, 10 mmol) in acetone (100 mL) were used. Yellow prisms (1.65 g, 36% yield), mp: 65.0–66.5 °C. Column chromatography (petroleum ether/EtOAc=40/1) R_f=0.35. ¹H NMR (600 MHz, CDCl₃): δ 11.03 (s, 1H, OH), 8.03 (dd, *J*=8.5, 1.5 Hz, 1H, H-5), 7.43 (dd, *J*=7.4, 1.5 Hz, 1H, H-3), 7.35 (dd, *J*=7.8, 7.3 Hz, 2H, H-3', H-5'), 7.28 (d, *J*=7.3 Hz, 2H, H-2', H-6'), 7.27 (t, *J*=7.8 Hz, 1H, H-4'), 6.94 (dd, *J*=8.5, 7.4 Hz, 1H, H-4), 4.11 (s, 2H, CH₂); ¹³C NMR (75 MHz, CDCl₃): δ 153.3 (C), 139.1 (C), 137.8 (CH), 133.6 (C), 132.5 (C), 128.9 (2·CH), 128.5 (2·CH), 126.4 (CH), 123.1 (CH), 119.4 (CH), 35.4 (CH₂); IR (KBr): 3212cm⁻¹ (OH), 3087, 3063, 3029 cm⁻¹ (ArH), 2926, 2843 cm⁻¹ (CH₂), 1610 cm⁻¹ (C=C), 1541, 1334 cm⁻¹ (NO₂), 1248 cm⁻¹ (C–O). This compound has been mentioned in the Japanese patent.⁵

5-Methoxy-2-nitrophenol (2e)

3-Methoxyphenol (**1e**) (1.86 g, 15 mmol), Bi(NO₃)₃·5H₂O (2.43 g, 5.0 mmol) in acetone (75 mL) were used. Yellow prisms (740 mg, 29% yield), mp: 93.5–94.0 °C (lit.⁶ 92–95 °C).

Column chromatography (chloroform) $R_f=0.77$. The NMR spectra are in agreement with those reported in the literature.⁶ ^1H NMR (300 MHz, CDCl_3): δ 11.04 (s, 1H, OH), 8.03 (d, $J=8.1$ Hz, 1H, H-3), 6.54 (d, $J=2.7$ Hz, 1H, H-6), 6.52 (dd, $J=8.1, 2.7$ Hz, 1H, H-4), 3.88 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, CDCl_3): δ 167.0 (C), 157.9 (C), 127.7 (C) 126.9 (CH), 109.4 (CH), 101.3 (CH), 56.1 (OCH_3); IR (KBr): 3465 cm^{-1} (OH), 3094 cm^{-1} (ArH), 2989, 2950, 2920 cm^{-1} (CH_3), 1622 cm^{-1} (C=C), 1509, 1334 cm^{-1} (NO_2), 1253, 1176, 1094 cm^{-1} (C–O).

4-Ethyl-2-nitrophenol (2f)

4-Ethylphenol (**1f**) (7.33 g, 60 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (14.6 g, 30 mmol) and acetone (300 mL) were used. Yellow transparent oil (8.02g, 80% yield) (lit.⁷ oil). Column chromatography (petroleum ether/ $\text{EtOAc}=10/1$) $R_f=0.61$. The NMR spectra are in agreement with those reported in the literature.⁷ ^1H NMR (300 MHz, CDCl_3): δ 10.44 (s, 1H, OH), 7.88 (d, $J=2.1$ Hz, 1H, H-3), 7.41 (dd, $J=8.6, 2.1$ Hz, 1H, H-5), 7.06 (d, $J=8.6$ Hz, 1H, H-6), 2.63 (q, $J=7.6$ Hz, 2H, CH_2), 1.23 (t, $J=7.6$ Hz, 3H, CH_3); ^{13}C NMR (75 MHz, CDCl_3): δ 153.2 (C), 137.6 (C and CH), 136.4 (C), 123.1 (CH), 119.6 (CH), 27.5 (CH_2), 15.1 (CH_3); IR (KBr): 3255 cm^{-1} (OH), 3076 cm^{-1} (ArH), 2969, 2935, 2875 cm^{-1} (CH_2CH_3), 1631 cm^{-1} (C=C), 1540, 1318 cm^{-1} (NO_2), 1239 cm^{-1} (C–O).

4-Bromo-2-nitrophenol (2g)

4-Bromophenol (**1g**) (3.46 g, 20 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) and acetone (100 mL) were used. Yellow prisms (3.8 g, 87% yield), mp: $89.0\text{--}90.5\text{ }^\circ\text{C}$ (lit.⁸ $89\text{--}92\text{ }^\circ\text{C}$). Column chromatography (petroleum ether/ $\text{EtOAc}=30/1$) $R_f=0.55$. The NMR spectra are in agreement with those reported in the literature.⁸ ^1H NMR (300 MHz, CDCl_3): δ 10.43 (s, 1H, OH), 8.23 (d, $J=2.4$ Hz, 1H, H-3), 7.66 (dd, $J=9.0, 2.4$ Hz, 1H, H-5), 7.07 (d, $J=9.0$ Hz, 1H, H-6); ^{13}C NMR (75 MHz, CDCl_3): δ 154.1 (C), 140.3 (CH), 134.0 (C), 127.3 (CH), 121.7

(CH), 111.7 (C); IR (KBr): 3437, 3273 cm^{-1} (OH), 3100, 3089, 3069 cm^{-1} (CH), 1615 cm^{-1} (C=C), 1533, 1316 cm^{-1} (NO_2), 1237 cm^{-1} (C–O), 662 cm^{-1} (C–Br).

6-Nitro-2-phenylphenol (2h)

2-Phenylphenol (**1h**) (3.40 g, 20 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) in acetone (100 mL) were used. Yellow prisms (1.92 g, 45% yield), mp: 62.5–63.5 °C (lit.⁹ 59.5–60 °C). Column chromatography (petroleum ether/EtOAc=10/1) $R_f=0.54$. The NMR spectra are in agreement with those reported in the literature.¹⁰ ^1H NMR (300 MHz, CDCl_3): δ 11.15 (s, 1H, OH), 8.14 (dd, $J=8.5, 1.6$ Hz, 1H, H-5), 7.65 (dd, $J=7.5, 1.6$ Hz, 1H, H-3), 7.38–7.62 (m, 5H, Ph), 7.06 (dd, $J=8.5, 7.5$ Hz, 1H, H-4); ^{13}C NMR (75 MHz, CDCl_3): δ 152.7 (C), 138.3 (CH), 135.7 (C), 134.0 (C), 132.9 (C), 129.2 (2·CH), 128.3 (2·CH), 128.0 (CH), 124.2 (CH), 119.7 (CH); IR (KBr): 3436, 3257 cm^{-1} (OH), 3099, 3077, 3056, 3029 cm^{-1} (ArH), 1604 cm^{-1} (C=C), 1542, 1331 cm^{-1} (NO_2), 1251 cm^{-1} (C–O).

ortho-Nitro-5-indanols (2i, 3i)

5-Indanole (**1i**) (2.74 g, 20 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.85 g, 10 mmol) and acetone (100 mL) were used. Mixtures of regioisomers 6-nitro-5-indanol (**2i**) and 4-nitro-5-indanol (**3i**) molar ratio 2:1. Yellow prisms (2.86 g, 80% yield), mp: 39–42 °C. Column chromatography (petroleum ether/EtOAc=40/1) $R_f=0.4$. The NMR spectra are in agreement with those reported in the literature.¹¹ IR (KBr): 3211 cm^{-1} (OH), 2959, 2849 cm^{-1} (CH_2), 1638, 1611 cm^{-1} (C=C), 1530, 1315 cm^{-1} (NO_2), 1238 cm^{-1} (C–O). ^1H NMR (300 MHz, CDCl_3) isomer **2i**^{11a}: 10.73 (s, 1H, OH), 7.90 (s, 1H, H-7), 6.97 (s, 1H, H-4), 2.98–2.86 (m, 4H, CH_2 -1 and CH_2 -3) 2.20–2.05 (m, 2H, CH_2 -2). ^1H NMR (CDCl_3) isomer **3i**^{11b}: 10.66 (s, 1H, OH), 7.38 (d, $J=8.3$ Hz, 1H, H-7), 6.95 (d, $J=8.3$ Hz, 1H, H-6), 3.37 (t, $J=7.5$ Hz, 2H, CH_2 -3), 2.90 (tt, $J=7.5$ Hz, 2H, CH_2 -2), 2.12 (t, $J=7.5$ Hz, 2H, CH_2 -1).

4-Chloro-3,5-dimethyl-2-nitrophenol (2j)

4-Chloro-3,5-dimethylphenol (**1j**) (6.26 g, 40 mmol), Bi(NO₃)₃·5H₂O (9.70 g, 20 mmol) and acetone (200 mL) were used. Yellow powder (6.45 g, 80% yield), mp: 89–91 °C (lit.¹² 90 °C). Column chromatography (CH₂Cl₂) R_f=0.76. The NMR spectra are in agreement with those reported in the literature.¹³ ¹H NMR (300 MHz, DMSO-*d*₆): δ 10.98 (s, 1H, OH), 6.88 (s, 1H, H-6), 2.28 (s, 3H, CH₃), 2.19 (s, 3H, CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 147.1 (C), 139.6 (C), 139.1 (C), 127.9 (C), 123.4 (C), 116.6 (CH), 20.6 (CH₃), 15.2 (CH₃); IR (KBr): 3386, 3347 cm⁻¹ (OH), 2986, 2964, 2930 cm⁻¹ (CH₃), 1608, 1590 cm⁻¹ (C=C), 1523, 1361 cm⁻¹ (NO₂), 1245 cm⁻¹ (C–O), 854 cm⁻¹ (C–Cl).

2,4-Dimethyl-6-nitrophenol (2k)

2,4-Dimethylphenol (**1k**) (12.2 g, 100 mmol), Bi(NO₃)₃·5H₂O (24.2 g, 50 mmol) and acetone (500 mL) were used. Orange-yellow solid (14.5 g, 87% yield), mp: 71–72 °C (lit.¹⁴ 64–66 °C). Column chromatography (petroleum ether) R_f=0.15. The NMR spectra are in agreement with those reported in the literature.¹⁴ ¹H NMR (300 MHz, CDCl₃): δ 10.76 (s, 1H, OH), 7.74 (br s, 1H, H-5), 7.27 (br s, 1H, H-3), 2.30 (s, 6H, 2×CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 151.7 (C), 139.4 (CH), 132.9 (C), 128.9 (2-C), 121.8 (CH), 20.2 (CH₃), 15.6 (CH₃); IR(KBr): 3443, 3152 cm⁻¹ (OH), 3076 cm⁻¹ (ArH), 2961 cm⁻¹ (CH₃), 1625 cm⁻¹ (C=C), 1543, 1315 cm⁻¹ (NO₂), 1257 cm⁻¹ (C–O).

1-Nitro-2-naphthol (2l)

2-Naphthol (**1l**) (0.36 g, 2.5 mmol), Bi(NO₃)₃·5H₂O (0.60 g, 1.25 mmol) and acetone (12.5 mL) were used. Orange prisms (0.24 g, 52% yield), mp: 101.0–101.5 °C (EtOH/H₂O=5/1) (lit.¹⁵ 104.0–106.0 °C). Column chromatography (petroleum ether/EtOAc=3/1) R_f=0.55. The NMR spectra are in agreement with those reported in the literature.¹⁵ ¹H NMR (600 MHz, CDCl₃): δ 12.18 (s, 1H, OH), 8.93 (d, *J*=8.9 Hz, 1H, H-8), 8.01 (d, *J*=9.0 Hz, 1H, H-4), 7.81 (d, *J*=7.9 Hz, 1H, H-5), 7.73 (ddd, *J*=8.9, 7.1, 1.4 Hz, 1H, H-7), 7.51 (ddd, *J*=7.9, 7.1, 0.9 Hz, 1H, H-6), 7.25 (d, *J*=9.0 Hz, 1H, H-3); ¹³C NMR (75

MHz, CDCl₃): δ 158.7 (C), 139.1 (CH), 130.9 (CH), 129.2 (CH), 128.6 (C), 128.0 (C), 126.8 (C), 125.5 (CH), 123.1 (CH), 119.2 (CH); IR(KBr): 3452 cm⁻¹ (OH), 3065 cm⁻¹ (ArH), 1623 cm⁻¹ (C=C), 1544 cm⁻¹, 1378 cm⁻¹ (NO₂), 1243 cm⁻¹ (C=O).

4-Chloro-3-methyl-2-nitrophenol (3b)

4-Chloro-5-methylphenol (**1b**) (2.83 g, 20 mmol), Bi(NO₃)₃·5H₂O (4.85 g, 10 mmol) and acetone (100 mL) were used. Yellow crystals (1.50 g, 40% yield), mp: 69.5–73.5 °C (petroleum ether) (lit.⁸ 69.0–71.5 °C). Column chromatography (CH₂Cl₂) R_f=0.69. The NMR spectra are in agreement with those reported in the literature.⁸ ¹H NMR (300 MHz, CDCl₃): δ 9.38 (br s, 1H, OH), 7.49 (d, *J*=9.0 Hz, 1H, H-5), 6.97 (d, *J*=9.0 Hz, 1H, H-6), 2.59 (s, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 152.4 (C), 135.5 (CH), 133.1 (C), 127.0 (C), 125.7 (C), 117.6 (CH), 18.0 (CH₃); IR (KBr): 3420 cm⁻¹ (OH), 3080 (ArH), 2987 cm⁻¹ (CH₃), 1597 cm⁻¹ (C=C), 1528, 1343 cm⁻¹ (NO₂), 1217 cm⁻¹ (C–O), 834 cm⁻¹ (C–Cl).

3-Methoxy-2-nitrophenol (3e)

3-Methoxyphenol (**1e**) (1.86 g, 15 mmol), Bi(NO₃)₃·5H₂O (2.43 g, 5.0 mmol) in acetone (75 mL) were used. Yellow crystals (119 mg, 4.7% yield), mp: 49.5–51.0 °C (petroleum ether) (lit.¹⁶ 53 °C). Column chromatography (chloroform) R_f=0.54. The NMR spectra are in agreement with those reported in the literature.¹⁷ ¹H NMR (600 MHz, CDCl₃): δ 10.19 (s, 1H, OH), 7.40 (dd, *J*=8.5 Hz, 1H, H-5), 6.70 (d, *J*=8.5 Hz, 1H, H-4 or H-6), 6.54 (d, *J*=8.5 Hz, 1H, H-4 or H-6), 3.94 (s, 1H, OCH₃). ¹³C NMR (75 MHz, CDCl₃): δ 155.8 (C), 155.6 (C), 153.7 (CH), 127.1 (C), 110.6 (CH), 103.6 (CH), 56.7 (OCH₃); IR (KBr): 3425 cm⁻¹ (OH), 2990, 2945, 2846 cm⁻¹ (CH₃), 1603 cm⁻¹ (C=C), 1542, 1359 cm⁻¹ (NO₂), 1234, 1179, 1086 cm⁻¹ (C–O).

2,6-Dimethyl-4-nitrophenol (4c)

2,6-Dimethylphenol (**1c**) (1.22 g, 10 mmol), Bi(NO₃)₃·5H₂O (2.4 g, 5.0 mmol) and acetone (50 mL) were used. Yellow prisms (1.09 g, 65% yield), mp: 166.5–167.0 °C

(EtOH/H₂O=7/3) (lit.¹⁸ 162–165 °C). Column chromatography (CH₂Cl₂) R_f=0.63. The NMR spectra are in agreement with those reported in the literature.¹⁹ ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.87 (s, 1H, OH), 7.88 (s, 2H, H-3, H-5), 2.24 (s, 6H, 2×CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 160.0 (C), 139.0 (C), 125.0 (2×C), 123.9 (2×CH₃), 16.5 (2×CH₃); IR (KBr): 3466 cm⁻¹ (OH), 3081 cm⁻¹ (ArH), 2952, 2921, 2853 cm⁻¹ (CH₃), 1594 cm⁻¹ (C=C), 1508, 1335 cm⁻¹ (NO₂), 1186 cm⁻¹ (C–O).

2-Benzyl-4-nitrophenol (4d)

2-Benzylphenol (**1d**) (3.68 g, 20 mmol), Bi(NO₃)₃·5H₂O (4.85 g, 10 mmol) in acetone (100 mL) were used. Yellow-beige crystals (2.58 g, 56% yield), mp: 119–120 °C. Column chromatography (CH₂Cl₂) R_f=0.31. The NMR spectra are in agreement with those reported in the literature.²⁰ ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.18 (s, 1H, OH), 8.01 (dd, *J*=8.8, 2.8 Hz, 1H, H-5), 7.96 (d, *J*=2.8 Hz, 1H, H-3), 7.15–7.35 (m, 5H, Ph), 6.98 (d, *J*=8.8 Hz, 1H, H-6), 3.95 (s, 2H, CH₂); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 161.7 (C), 139.7 (C), 139.4 (C), 128.8 (C), 128.7 (2×CH), 128.4 (2×CH), 126.1 (CH), 125.9 (CH), 124.0 (CH), 115.1 (CH), 34.8 (CH₂); IR (KBr): 3268 cm⁻¹ (OH), 3072, 3030 cm⁻¹ (ArH), 1592 cm⁻¹ (C=C), 1494, 1328 cm⁻¹ (NO₂), 1273 cm⁻¹ (C–O).

3-Methoxy-4-nitrophenol (4e)

3-Methoxyphenol (**1e**) (1.86 g, 15 mmol), Bi(NO₃)₃·5H₂O (2.43 g, 5.0 mmol) in acetone (75 mL) were used. Pale brown solid (870 mg, 34% yield), mp: 145–146 °C (lit.²¹ 143–145 °C). Column chromatography (chloroform/OEtAc) R_f=0.36. The NMR spectra are in agreement with those reported in the literature.²² ¹H NMR (600 MHz, DMSO-*d*₆): δ 10.88 (s, 1H, OH), 7.88 (d, *J*=9.0 Hz, 1H, H-5), 6.60 (d, *J*=2.3 Hz, 1H, H-2), 6.46 (dd, *J*=9.0, 2.3 Hz, 1H, H-6), 3.86 (s, 3H, OCH₃). ¹³C NMR (DMSO-*d*₆): δ 163.9 (C), 155.6 (C), 130.8 (C), 128.2 (CH), 107.4 (CH), 100.3 (CH), 56.3 (OCH₃); IR (KBr): 3349 cm⁻¹ (OH), 3076 cm⁻¹

(ArH), 2953 cm^{-1} (CH_3), 1627 cm^{-1} ($\text{C}=\text{C}$), 1516, 1314 cm^{-1} (NO_2), 1244, 1209, 1097 cm^{-1} ($\text{C}-\text{O}$).

4-Nitro-2-phenylphenol (4h)

2-phenylphenol (**1h**) (3.40 g, 20 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (4.850 g, 10 mmol) in acetone (100 mL) were used. Orange-yellow crystals (1.8 g, 42% yield), mp: 127.5–128.5 °C (n-hexane/EtOAc=5/1), (lit.²³ 124–125 °C). Column chromatography (petroleum ether/EtOAc=5/1) $R_f=0.14$. The NMR spectra are in agreement with those reported in the literature.¹⁰ ^1H NMR (300 MHz, CDCl_3): δ 8.19 (d, $J=2.8$ Hz, 1H, H-3), 8.17 (dd, $J=8.3, 2.8$ Hz, 1H, H-5), 7.45–7.60 (m, 5H, Ph), 7.08 (d, $J=8.3$ Hz, 1H, H-6), 6.03 (br s, 1H, OH); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 160.9 (C), 139.8 (C), 136.2 (C), 129.0 (2 \times CH), 128.3 (C), 128.2 (2 \times CH), 127.6 (CH), 126.0 (CH), 124.7 (CH), 116.3 (CH); IR (KBr): 3326 cm^{-1} (OH), 3072, 3036 cm^{-1} (ArH), 1588 cm^{-1} ($\text{C}=\text{C}$), 1496, 1327 cm^{-1} (NO_2), 1288 cm^{-1} (br, C–O).

3,3',5,5'-Tetramethyl-4,4'-diphenoquinone (5c)

2,6-Dimethylphenol (**1c**) (1.22 g, 10 mmol), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.4 g, 5.0 mmol) and acetone (50 mL) were used. Brown-red powder (0.20 g, 17% yield), mp: 186 °C (decomposition) (lit.²⁴ 184–185 °C), Column chromatography (methylene chloride) $R_f=0.17$. The NMR spectra are in agreement with those reported in the literature.²⁵ ^1H NMR (300 MHz, CDCl_3): δ 7.72 (s, 4H, CH), 2.15 (s, 12H, CH_3); ^{13}C NMR (300 MHz, CDCl_3): δ 187.3 (2 \cdot C), 138.9 (4 \times C), 135.6 (2 \times C), 129.6 (br 4 \times CH) 17.7 (br 4 \times CH_3); IR (KBr): 3055 cm^{-1} ($\text{C}=\text{CH}$), 2943, 2916 cm^{-1} (CH_3), 1592 cm^{-1} ($\text{C}=\text{O}$).

2,4-Dimethylanisole (7k)

To a stirred solution of 2,4-dimethylphenol (**7m**) (6.11g, 50 mmol) and iodomethane (8.55g, 3.78ml, 60 mmol) in DMF (75 mL) was added K_2CO_3 (10.4g, 75 mmol). The resultant suspension was heated at 60°C for 60 h. The reaction mixture was filtered, the cake washed with EtOAc (150 ml) and the filtrate washed with brine (3 \times 150ml). The organic layer was

dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel 60 (70–230 mesh) (hexane/EtOAc=40/1, R_f=0.75) to give 2,4-dimethylanisole (5.1g, 37 mmol, 75%) as a transparent oil. Bp 190 °C (lit.²⁶ 192 °C). The NMR spectra are in agreement with those reported in the literature.²⁷ ¹³C NMR (75 MHz, CDCl₃): δ 155.6 (C), 131.4 (CH), 129.2 (C), 126.9 (CH), 126.2 (C), 109.8 (CH), 55.2 (OCH₃), 20.3 (CH₃), 16.0 (CH₃); IR (film): 2999, 2949, 2923, 2834 cm⁻¹ (CH₃), 1615 cm⁻¹ (C=C), 1254, 1038 cm⁻¹ (C–O).

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