**A Convenient Synthesis of Phenols**

Renate Kristianslund, Anders Vik and Trond Vidar Hansen

*School of Pharmacy, Department of Pharmaceutical Chemistry, University of Oslo, PO Box 1068 Blindern, N-0316, Oslo, Norway.*

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**General Information**

All commercially available reagents and solvents were used in the form they were supplied without any further purification. The stated yields are based on isolated material. Thin layer chromatography was performed on silica gel 60 F254aluminum-backed plates fabricated by Merck. Flash column chromatography was performed on silica gel 60 (40-63 μm) fabricated by Merck. NMR spectra were recorded on a Bruker AVII 400 or a Bruker AVIII HD 400spectrometer at 400 MHz or a Bruker AVII600 spectrometer at 600 MHz for 1H NMR, and at 100 MHz or 150 MHz for 13C NMR. Coupling constants (*J*) are reported in hertz and chemical shifts are reported in parts per million (δ) relative to the central residual protium solvent resonance in 1H NMR (CDCl3= δ7.27, and CD3OD= δ 3.31) and the central carbon solvent resonance in 13C NMR (CDCl3= δ 77.00 ppm, and CD3OD = δ 49.00). Mass spectra were recorded at 70 eV on Micromass Prospec Q or Micromass QTOF 2W spectrometer using ESI as the method of ionization. High resolution mass spectra were recorded at 70 eV on Micromass Prospec Q or MicromassQTOF 2W spectrometer using ESI as the method of ionization.

**General experimental procedure:**



Water (4 mL) and HBF4 (~48-50% aq. sol., 4 mL) were added to the aniline (0.50 mmol, 1.0 equiv.) and stirred for a couple of minutes at room temperature. NaNO2 (0.038 g, 1.1 equiv.) in water (2.8 mL) was added dropwise at 0°C and stirred for 30 minutes. To the cold solution of the resulting diazonium salt was added sat. aq. copper(II)sulfate (50 mL), followed by copper(I)oxide (1.0 equiv., 0.072 g), and stirred at room temperature for 30 minutes. The reaction mixture was extracted with CH2Cl2, dried (MgSO4) and evaporated *in vacuo*. The crude products were purified by flash chromatography on silica.

**4-Methylphenol (4)**



Prepared according to the general procedure. Yield: 22 mg (40 %). Spectral data were in accordance with literature values [1]. 1H NMR (400 MHz, CDCl3) δ 7.04 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 2.3 Hz, 1H), 4.73 (s, 3H), 2.28 (s, 3H).

**3-Methylphenol (5)**



Prepared according to the general procedure. Yield: 29 mg (53 %). Spectral data were in accordance with literature values [2]. 1H NMR (400 MHz, CDCl3) δ 7.13 (t, *J* = 7.7 Hz, 1H), 6.67 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.72 – 6.58 (m, 2H), 5.03 (s, 1H), 2.32 (s, 3H).

**2,5-Dimethylphenol (6)**



Prepared according to the general procedure. Yield: 37 mg (61 %). Spectral data were in accordance with literature values [3]. 1H NMR (400 MHz, CDCl3) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.56 (s, 1H), 2.28 (s, 3H), 2.21 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 153.5, 137.1, 130.7, 121.4, 120.4, 115.6, 20.94, 15.24.

**5-Methoxy-2-methylphenol (7)**



Prepared according to the general procedure. Yield: 46 mg (67 %). Spectral data were in accordance with literature values [4].1H NMR (400 MHz, CDCl3) δ 7.01 (d, *J* = 8.2 Hz, 1H), 6.43 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.40 (d, *J* = 2.5 Hz, 1H), 5.00 (s, 1H), 3.76 (s, 3H), 2.18 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 158.9, 154.5, 131.2, 115.8, 105.9, 101.4, 55.3, 14.7.

**3-Hydroxy-4-methylbenzoic acid methyl ester (8)**



Prepared according to the general procedure. Yield: 71 mg (86 %). Spectral data were in accordance with literature values [5]. 1H NMR (400 MHz, CDCl3) δ 7.61 (d, *J* = 1.6 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 6.15 (s, 1H), 3.91 (s, 3H), 2.30 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 167.6, 154.1, 130.9, 130.4, 128.7, 121.7, 115.8, 52.2, 16.1.

**3-Hydroxy-4-methylbenzyl alcohol (9)**



Prepared according to the general procedure. Yield: 21 mg (30 %). Spectral data were in accordance with literature values [6]. 1H NMR (400 MHz, CDCl3) δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.79 (m, 2H), 5.07 (s, 1H), 4.62 (s, 2H), 2.24 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 154.0, 140.0, 131.1, 123.3, 119.2, 113.6, 65.1, 15.5.

**5-Ethynyl-2-methoxyphenol (10)**



Prepared according to the general procedure. Yield: 22 mg (30 %). Spectral data were in accordance with literature values [7]. 1H NMR (400 MHz, CDCl3) δ 7.07 – 7.01 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.62 (s, 1H), 3.88 (s, 3H), 2.97 (s, 1H); 13C NMR (101 MHz, CDCl3) δ 147.3, 145.3, 124.8, 118.0, 114.9, 110.4, 83.6, 75.6, 55.9.

**Catechol (11)**



Prepared according to the general procedure. Yield: 20 mg (36 %). Spectral data were in accordance with literature values [8]. 1H NMR (600 MHz, MeOD) δ 6.75 (dd, *J* = 5.9, 3.6 Hz, 1H), 6.65 (dd, *J* = 5.9, 3.5 Hz, 1H); 13C NMR (151 MHz, MeOD) δ 146.3, 120.9, 116.4.

**3,4-Dimethoxyphenol (12)**



Prepared according to the general procedure. Yield: 14 mg (18 %). Spectral data were in accordance with literature values [9]. 1H NMR (400 MHz, CD3OD) δ 6.76 (d, *J* = 8.7 Hz, 1H), 6.45 (d, *J* = 2.7 Hz, 1H), 6.30 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H); 13C NMR (101 MHz, CD3OD) δ 153.4, 151.6, 143.7, 115.2, 107.1, 101.9, 57.6, 56.3.

**3-Methoxyphenol (13)**



Prepared according to the general procedure. Yield: 41 mg (66 %). Spectral data were in accordance with literature values [1]. 1H NMR (600 MHz, CD3OD) δ 7.06 (t, *J* = 8.1 Hz, 1H), 6.41 – 6.35 (m, 3H), 3.74 (s, 3H); 13C NMR (151 MHz, CD3OD) δ 162.4, 159.6, 130.8, 108.8, 106.1, 102.3, 55.5.

**4-Hydroxy-*N*-(5-methyl-3-isoxazolyl)benzenesulfonamide (14)**



Prepared according to the general procedure. Yield: 88 mg (69 %). Spectral data were in accordance with literature values [10]. 1H NMR (600 MHz, CD3OD) δ 7.74 – 7.70 (m, 2H), 6.88 – 6.84 (m, 2H), 6.11 (d, *J* = 1.1 Hz, 1H), 2.31 (d, *J* = 0.9 Hz, 3H); 13C NMR (151 MHz, CD3OD) δ 171.9, 163.4, 159.4, 131.0, 130.6, 116.6, 96.4, 12.3.

**4-Nitrophenol (15)**



Prepared according to the general procedure. Yield: 60 mg (87 %). Spectral data were in accordance with literature values [11]. 1H NMR (400 MHz, CDCl3) δ 8.25 – 8.11 (m, 2H), 6.95 – 6.87 (m, 2H), 5.62 (s, 1H); 13C NMR (101 MHz, CDCl3) δ 161.0, 141.8, 126.3, 115.6.

**3,4,5-Trimethoxyphenol (16)**



Prepared according to the general procedure. Yield: 70 mg (76 %). Spectral data were in accordance with literature values [12]. 1H NMR (400 MHz, CDCl3) δ 6.09 (s, 2H), 4.81 (s, 1H), 3.81 (s, 6H), 3.78 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 153.8, 152.1, 132.0, 92.9, 61.0, 56.0.

**2-Hydroxybenzamide (17)**



Prepared according to the general procedure. Yield: 30 mg (44 %). Spectral data were in accordance with literature values [13]. 1H NMR (400 MHz, (CD3)2SO) δ 13.03 (s, 1H), 8.39 (s, 1H), 7.89 (s, 1H), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.44 – 7.35 (m, 1H), 6.90 – 6.82 (m, 2H); 13C NMR (101 MHz, (CD3)2SO) δ 172.1, 161.1, 134.1, 128.1, 118.4, 117.4, 114.3.

**2-Hydroxybenzoic acid methyl ester (18)**



Prepared according to the general procedure. Yield: 38 mg (50 %). Spectral data were in accordance with literature values [13]. 1H NMR (400 MHz, CDCl3) δ 10.76 (s, 1H), 7.84 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 6.98 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.92 – 6.84 (m, 1H), 3.95 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 170.6, 161.6, 135.7, 129.9, 119.1, 117.6, 112.4, 52.26.

**3,5-Dinitrophenol (19)**



Prepared according to the general procedure. Yield: 60 mg (65 %). Spectral data were in accordance with literature values [14]. 1H NMR (400 MHz, (CD3)2SO) δ 11.46 (s, 1H), 8.31 – 8.24 (m, 1H), 7.92 (d, *J* = 1.9 Hz, 2H); 13C NMR (101 MHz, (CD3)2SO) δ 159.1, 148.8, 115.9, 108.7.

**3-Iodo catechol (20)**



Prepared according to the general procedure. Yield: 46 mg (39 %). Spectral data were in accordance with literature values [15]. 1H NMR (400 MHz, CDCl3) δ 7.19 (dd, J = 8.1 and 1.4 Hz, 1H), 6.88 (dd, J = 8.1 and 1.4 Hz, 1H), 6.62 (t, J = 8.1 Hz, 1H), 5.40 (s, 1H) and 5.31 (s, 1H).





**Figure 1.** 1H NMR spectrum of compound **4**.





**Figure 2.** 1H NMR spectrum of compound **5**.





**Figure 3.** 1H NMR spectrum of compound **6**.





**Figure 4.** 13C NMR spectrum of compound **6**.





**Figure 5.** 1H NMR spectrum of compound **7**.





**Figure 6.** 13C NMR spectrum of compound **7**.





**Figure 7.** 1H NMR spectrum of compound **8**.





**Figure 8.** 13C NMR spectrum of compound **8**.





**Figure 9.** 1H NMR spectrum of compound **9**.





**Figure 10.** 13C NMR spectrum of compound **8**.





**Figure 11.** 1H NMR spectrum of compound **10**.





**Figure 12.** 13C NMR spectrum of compound **10**.





**Figure 13.** 1H NMR spectrum of compound **11**.





**Figure 14.** 13C NMR spectrum of compound **11**.





**Figure 15.** 1H NMR spectrum of compound **12**.





**Figure 16.** 13C NMR spectrum of compound **12**.





**Figure 17.** 1H NMR spectrum of compound **13**.





**Figure 18.** 13C NMR spectrum of compound **13**.





**Figure 19.** 1H NMR spectrum of compound **14**.

 **Figure 20.** 13C NMR spectrum of compound **14**.







**Figure 21.** 1H NMR spectrum of compound **15**.





**Figure 22.** 13C NMR spectrum of compound **15**.





**Figure 23.** 1H NMR spectrum of compound **16**.





**Figure 24.** 13C NMR spectrum of compound **16**.





**Figure 25.** 1H NMR spectrum of compound **17**.





**Figure 26.** 13C NMR spectrum of compound **17**.





**Figure 27.** 1H NMR spectrum of compound **18**.





**Figure 28.** 13C NMR spectrum of compound **18**.





**Figure 29.** 1H NMR spectrum of compound **19**.





**Figure 30.** 13C NMR spectrum of compound **19**.





**Figure 31.** 1H NMR spectrum of compound **20**.





**Figure 32.** 13C NMR spectrum of compound **20**.

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