

General procedure for the reaction of pyrazoline-5-ones and catechols/hydroquinones

Catechol or hydroquinone (1 mmol) and pyrazolinone (1.5 mmol) were taken in 15 mL of buffer solution. Then, purified laccase (400U) was added to the resultant solution and stirred well. The progress of the reaction was monitored by TLC examination at an interval of every 30 min. Upon completion of the reaction, the reaction mixture was extracted with ethylacetate (3x15). The organic layer was dried over anhydrous Na₂SO₄. The product was purified by column chromatography using aluminium oxide as a stationary phase and hexane:ethyl acetate (80:20) as a mobile phase. Products were unambiguously characterized by spectral data.

Characterization of the products:

Compound 3a: 3-Methyl-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR (KBr) 3448, 3441, 1656, 1590, 1515, 1491, 1479 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.09 (s, 3H, CH₃), 5.33 (s, br, OH), 7.33 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.45-7.62 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 13.01, 107.00, 114.14, 116.19, 120.11, 123.24, 125.12, 128.99, 135.19, 139.81, 144.11, 144.89, 145.56, 149.35

Compound 3b: 3,7-Dimethyl-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR (KBr) 3446, 3440, 1654, 1590, 1513, 1489, 1475 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.03 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 5.29 (s, br, OH), 7.31 (s, 1H, ArH), 7.40-7.58 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 10.21, 12.98, 106.82, 114.11, 116.49, 119.10, 123.42, 125.56, 129.01, 135.49, 139.85, 144.10, 144.84, 145.76, 149.75

Compound 3c: 3-Methyl-7-methoxy-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR(KBr) 3440, 3439, 1650, 1590, 1515, 1491, 1479, 1125 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.15 (s, 3H, CH₃), 3.92 (s, 3H, OCH₃), 5.46 (s, br, OH), 7.67 (s, 1H, ArH), 7.70-7.92 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 13.67, 65.21, 107.49, 115.14, 116.69, 120.71, 123.74, 126.02, 129.89, 135.79, 139.93, 144.71, 145.49, 145.96, 149.85

Compound 3f: 3-Methyl-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR (KBr) 3441, 3435, 1650, 1590, 1515, 1491, 1483 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.04 (s, 3H, CH₃), 5.30 (s, br, OH), 7.31 (s, 1H, ArH), 7.33 (s, 1H, ArH), 12.62 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 12.90, 105.78, 112.11, 133.79, 138.90, 143.11, 144.34, 145.12, 148.35

Compound 3g: 3,7-Dimethyl-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR (KBr) 3439, 3430, 1648, 1587, 1510, 1490, 1481 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.03 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 5.29 (s, br, OH), 7.03 (s, 1H, ArH), 12.60 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 9.89, 12.85, 105.70, 112.01, 133.12, 139.00, 143.65, 144.43, 145.62, 148.53

Compound 3h: 3-Methyl-7-methoxy-1*H*-benzofuro[2,3-*c*]pyrazole-5,6-diol: IR (KBr) 3437, 3429, 1650, 1590, 1515, 1489, 1483, 1109 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.10 (s, 3H, CH₃), 3.79 (s, 3H, OCH₃), 5.39 (s, br, OH), 7.38 (s, 1H, ArH), 12.69 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 12.98, 68.20, 105.68, 112.09, 134.10, 138.94, 143.10, 144.54, 145.67, 148.23

Compound 5a: 3-Methyl-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3450, 3448, 1659, 1593, 1513, 1495, 1481 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.06 (s, 3H, CH₃), 5.35 (s, br, OH), 6.83 (d, 1H, ArH), 6.92 (d, 1H, ArH), 7.50-7.62 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 13.8, 106.12, 114.23, 117.89, 119.21, 124.24, 126.12, 129.09, 135.89, 139.80, 144.01, 144.09, 145.01, 149.45

Compound 5b: 3,6-Dimethyl-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3448, 3445, 1660, 1589, 1510, 1491, 1480 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.06 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 5.30 (s, br, OH), 6.81 (s, 1H, ArH), 7.38-7.51 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 10.12, 13.12, 106.67, 113.90, 117.13, 120.01, 124.42, 126.56, 128.98, 135.12, 139.81, 144.00, 144.09, 145.07, 150.01

Compound 5c: 3-Methyl-6-methoxy-1-phenyl-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3453, 3450, 1661, 1593, 1515, 1498, 1488, 1119 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.06 (s, 3H, CH₃), 3.52 (s, 3H, OCH₃), 5.56 (s, br, OH), 6.90 (s, 1H, ArH), 7.47-7.59 (m, 5H, ArH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 14.45, 64.67, 107.34, 114.78, 118.19, 120.11, 124.89, 126.92, 129.91, 136.01, 139.80, 144.45, 144.73, 145.39, 150.12

Compound 5f: 3-Methyl-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3444, 3431, 1649, 1592, 1510, 1491, 1484 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.04 (s, 3H, CH₃), 5.30 (s, br, OH), 6.31 (d, 1H, ArH), 6.33 (d, 1H, ArH), 12.62 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 12.67, 105.70, 112.01, 133.54, 138.45, 143.10, 144.13, 145.00, 148.15

Compound 5g: 3,6-Dimethyl-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3441, 3436, 1649, 1592, 1519, 1490, 1481 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.01 (s, 3H, CH₃), 2.24 (s, 3H, CH₃), 5.20 (s, br, OH), 6.31 (s, 1H, ArH), 12.23 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 9.69, 12.35, 105.69, 112.00, 133.01, 138.56, 143.15, 144.13, 145.02, 148.35

Compound 5h: 3-Methyl-6-methoxy-1*H*-benzofuro[2,3-*c*]pyrazole-4,7-diol: IR (KBr) 3446, 3435, 1650, 1590, 1519, 1495, 1483, 1128 cm⁻¹; ¹H NMR, δ (400MHz, DMSO-*d*₆) 2.10 (s, 3H, CH₃), 3.59 (s, 3H, OCH₃), 5.39 (s, br, OH), 6.38 (s, 1H, ArH), 12.29 (s, br, NH); ¹³C NMR, δ (100MHz, DMSO-*d*₆) 12.90, 68.11, 105.15, 112.00, 133.90, 138.14, 143.01, 143.67, 145.14, 148.03