Supporting information for

Catalytic Oxidation of 3,5-Di-*tert*-butylcatechol by a Series of Mononuclear
Manganese Complexes: Synthesis, Structure, and Kinetic Investigation

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Hmimppa:

IR (KBr, cm⁻¹): 3438(s), 3047(w), 2921(w), 2860(w), 2851(w), 1721(w), 1597(vs), 1525(s), 1497(s),
1450(s), 1378(w), 1333(w), 1250(s), 1198(m), 1151(m), 1129(s), 1097(m), 1046(m), 1007(m), 927(w),
894(w), 840(w), 741(s), 667(w), 580(w), 554(w), 441(s).

¹H -NMR-Spektren (300 MHz, DMSO-d₆):

δ [ppm]: 3.35 (s, 3H, CH₃), 4.20 (s, 2H, imidazolyl-CH₂), 4.34 (s, 2H, pyridyl-CH₂), 5.73 (d, 1H, phenol-CH), 6.67 (dd, 1H, phenol-CH), 6.76 (d, 1H, imidazole-CH), 6.81 (dd, 1H, phenol-CH), 6.84 (d, 1H, imidazole-H), 6.87 (dd, 1H, phenol-CH), 7.11 (dd, 1H, pyridine-CH), 7.19 (dd, 1H, pyridine-CH), 7.64 (ddd, 1H, pyridine-CH), 8.48 (d, 1H, pyridine-CH)

¹³C -NMR-Spektra (75 MHz, DMSO-d₆):

δ [ppm]: 32.3 (CH₃), 49.5 (imidazolyl-CH₂), 59.1 (pyridyl-CH₂), 116.4 (phenol-C), 119.0 (phenol-C), 122.1 (phenol-C), 122.3 (imidazole-C), 122.4 (phenol-C), 122.8 (pyridine-C), 124.5 (pyridine-C), 125.4 (imidazole-C), 136.9 (phenol-C), 138.6 (pyridine-C), 144.5 (phenol-C), 148.3 (pyridine-C), 152.4 (imidazole-C), 158.6 (pyridine-C)

MS-Spectra (70eV):

m/z (%) 294 (54) [M]⁺, 202 (100) [M - CH₂C₃H₄N]⁺, 199 (24) [M - CH₂C₄H₅N₂]⁺, 96 (46) [CH₂C₄H₅N₂]⁺, 95 (26) [CH₃C₄H₅N₂]⁺, 93 (34) [C₆H₅OH]⁺

[Mn(bpia)(OAc)(OCH₃)](PF₆) (**1**)

IR (KBr, cm⁻¹): 3429(br), 3135(w), 2930(w), 2802(w), 1613(s), 1574(w), 1552(w), 1510(m), 1483(w), 1456(w), 1444(m), 1381(s), 1352(w), 1326(s), 1285(w), 1165(m), 1156(m), 1121(w), 1102(w), 1046(s), 1019(m), 999(w), 976(w), 953(w), 841(vs), 797(w), 776(w), 761(m), 741(w), 682(w), 655(w), 575(m), 558(s), 517(w).

MS-Spectra (ESI, methanol):

m/z: 438 ([Mn(bpia)(OAc)(OCH₃)]⁺)

[Mn(bipa)(OAc)(OCH₃)](PF₆) (**2**)

IR (KBr, cm^{-1}): 3164(w), 3140(w), 3110(w), 3070(w), 3037(w), 2929(w), 2803(w), 1614(s), 1575(w), 1513(m), 1483(w), 1446(m), 1383(s), 1328(s), 1289(m), 1164(m), 1102(w), 1050(s), 1021(m), 977(w), 899(m), 839(vs), 761(m), 659(m), 643(w), 616 (w), 582(m), 558(s), 523(w).

MS-Spectra (ESI, methanol):

m/z: 441 ($[\text{Mn}(\text{bipa})(\text{OAc})(\text{OCH}_3)]^+$)

$[\text{Mn}(\text{bipa})(\text{Cl})_2](\text{ClO}_4)$ (**4**)

IR (KBr, cm^{-1}): 3432(br), 3142(m), 3133(m), 2931(w), 1605(m), 1551(w), 1507(s), 1496(m), 1473(w), 1454(m), 1439(m), 1433(m), 1361(w), 1346(w), 1322(w), 1293(w), 1277(m), 1161(s), 1096(vs), 1029(m), 970(w), 957(w), 881(w), 789(w), 767(s), 757(s), 662(w), 623(s), 541(w), 517(w).

MS-Spectra (ESI):

m/z: 421 – 426 isotop cluster ($[\text{Mn}(\text{bipa})(\text{Cl})_2]^+ + \text{H}$), in acetonitrile

417 – 420 isotop cluster ($[\text{Mn}(\text{bipa})(\text{Cl})(\text{MeOH})]^+ + \text{H}$), in methanol

$[\text{Mn}(\text{Hmimppa})(\text{Cl})_2] \cdot \text{CH}_3\text{OH}$ (**5**)

IR (KBr, cm^{-1}): 3415(s), 3144(w), 3121(w), 3103(w), 3054(w), 2913(w), 1640(w), 1603(s), 1569(w), 1502(vs), 1453(vs), 1343(m), 1281(s), 1242(s), 1157(m), 1111(s), 1095(s), 1050(w), 1030(w), 1013(m), 974(m), 949(m), 845(w), 770(vs), 743(vs), 677(w), 662(w), 638(w), 593(w), 579(w).

EPR spectrum of **5** in ethanol.

[Mn(mimppa)(TCC)]·2CHCl₃ (**6**)

IR (KBr, cm⁻¹): 3120(w), 3063(w), 2924(w), 1604(m), 1591(m), 1509(m), 1481(s), 1434(vs), 1372(m), 1299(s), 1277(s), 1246(s), 1155(m), 1109(w), 1091(w), 1051(w), 1021(w), 976(s), 851(m), 810(s), 790(s), 763(s), 749(s), 654(s), 578(s), 530(w), 496(w), 452(w).