Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Trinuclear Mn^{2+}/Zn^{2+} based microporous coordination polymers as efficient catalysts for *ipso*-hydroxylation of boronic acids

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Table S1. Selected bond distances (Å) and angles (º) for compounds **1** and **2**.

Bond Parameters	$[Mn_3(bpdc)_3(bipy)].2NO_3$ (**1**)	$[Zn_3(bpdc)_3(bipy)].2NO_3.4H_2O$ (**2**)
Distances/Å		
M(1)-O(1)	1.9599(1)	1.9526(3)
M(1)-O(2)	1.9441(1)	1.9371(3)
M(1)-O(3)	1.9407(1)	1.9341(3)
M(1)-N(1)	2.0685(1)	2.0629(3)
M(2)-O(4A)	2.0483(1)	2.0535(5)
M(2)-O(4B)	2.1449(1)	2.1087(5)
M(2)-O(5A)	2.1137(1)	2.0348(4)
M(2)-O(5B)	2.0520(1)	2.0643(5)
M(2)-O(6A)	2.0478(1)	2.0536(5)
M(2)-O(6B)	2.0607(1)	2.1354(5)
Angles/°		
M(1)-O(1)-C(1)	109.914(7)	109.868(2)
M(1)-O(2)-C(2)	126.656(5)	124.459(2)
M(1)-O(3)-C(3)	124.965(5)	126.110(3)
M(2)-O(6A)-C(3)	132.159(5)	143.229(3)
M(2)-O(6B)-C(3)	131.172(5)	137.348(3)
M(2)-O(5A)-C(2)	123.470(5)	133.414(3)
M(2)-O(5B)-C(2)	128.044(5)	130.807(4)
M(2)-O(4A)-C(1)	146.422(7)	126.626(4)
M(2)-O(4B)-C(1)	136.577(7)	123.685(3)
O(1)-M(1)-N(1)	106.033(6)	105.810(2)
O(2)-M(1)-N(1)	97.479(5)	97.421(2)
O(3)-M(1)-N(1)	96.139(5)	95.939(2)
O(1)-M(1)-O(2)	113.875(4)	113.013(1)
O(1)-M(1)-O(3)	120.777(4)	121.524(2)
O(2)-M(1)-O(3)	116.629(3)	117.032(2)

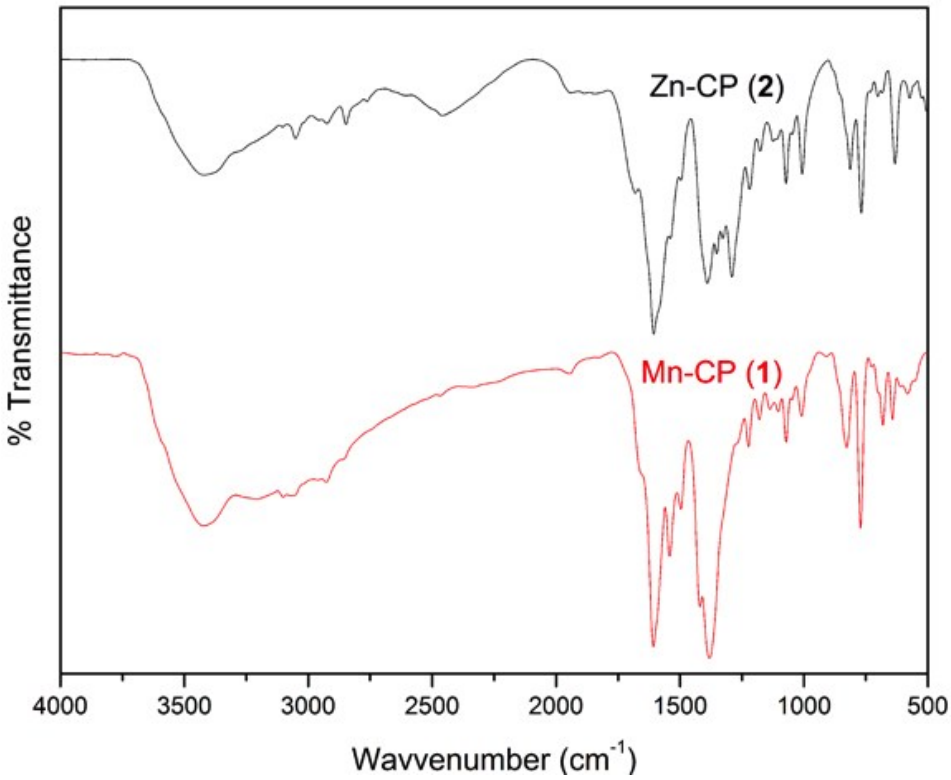


Figure S1. FT-IR (KBr phase) spectrum of $[Mn(bpdc)_3(bipy)].2DMF$ (**1**) and $[Zn(bpdc)_3(bipy)].2DMF.4H_2O$ (**2**)

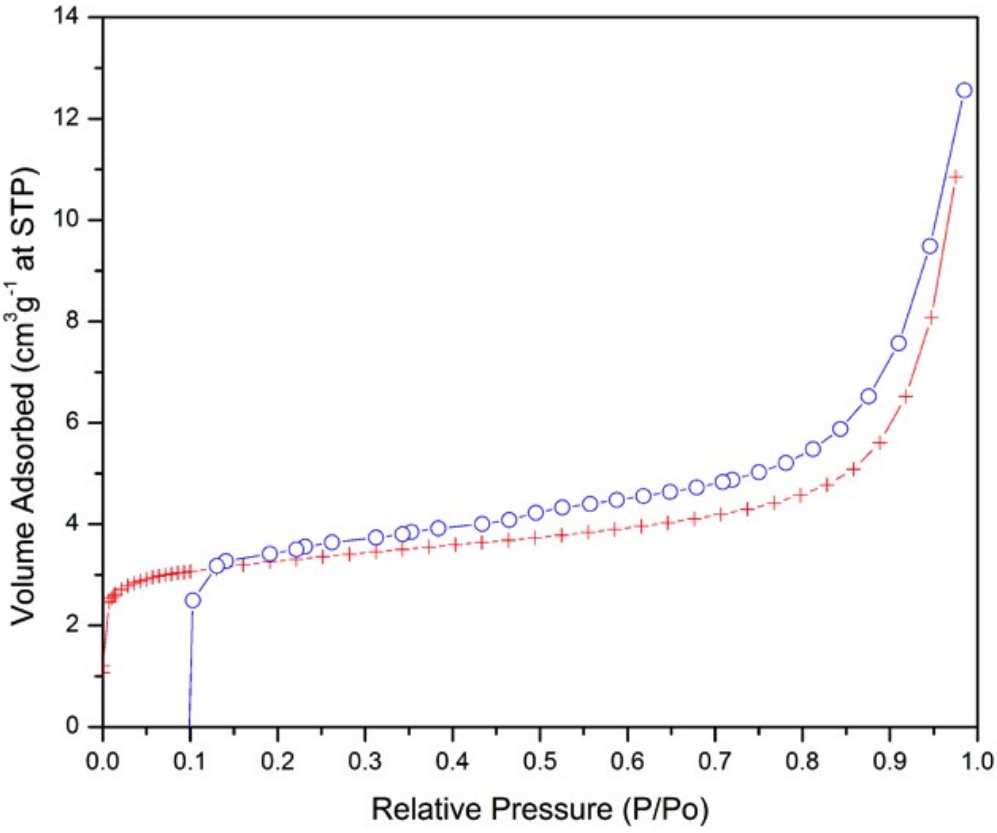
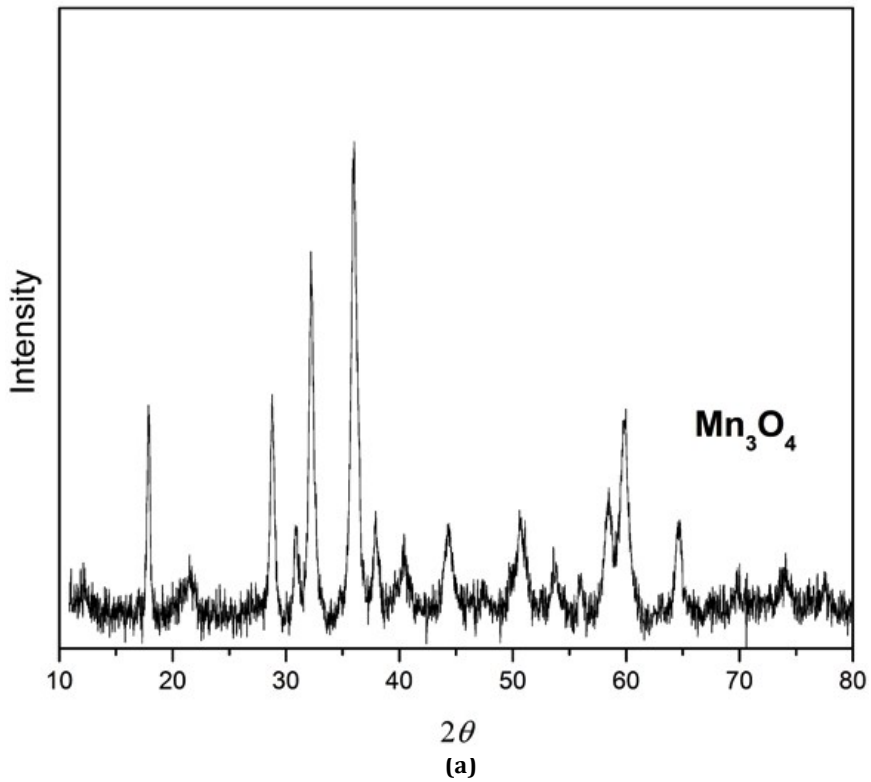
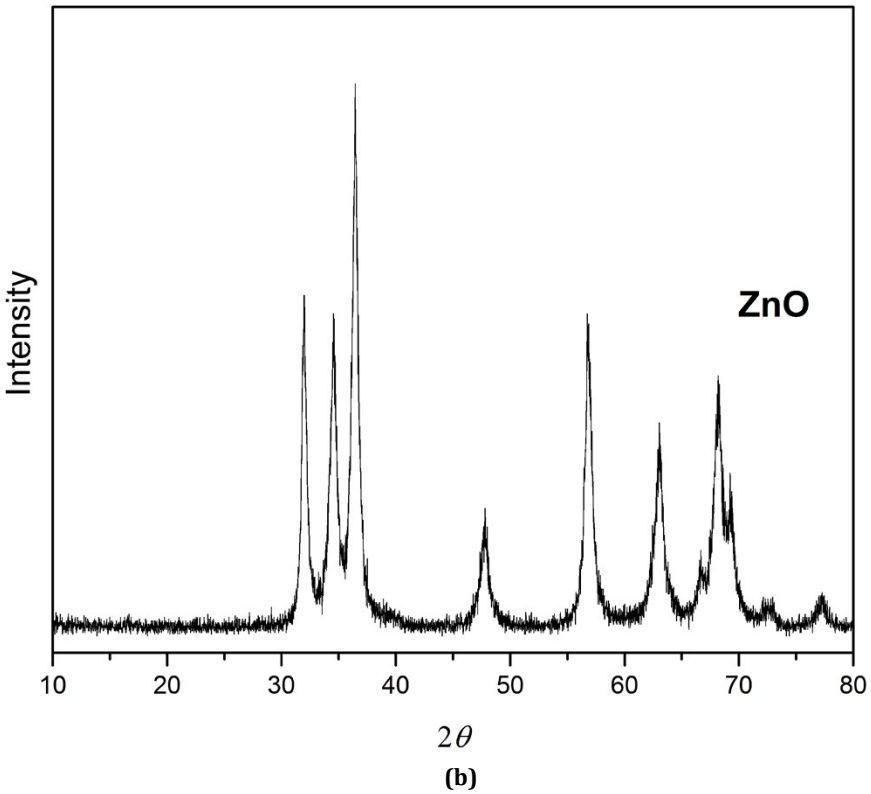


Figure S2. BET surface are curve of $[Zn(bpdc)_3(bipy)].2DMF.4H_2O$ (**2**)



(a)



(b)

Figure S3. Indexed PXRD patterns for calcined products of (**a**) [Mn(bpdc)$_3$(bipy)].2DMF (**1**) and (**b**) [Zn(bpdc)$_3$(bipy)].2DMF.4H$_2$O (**2**)

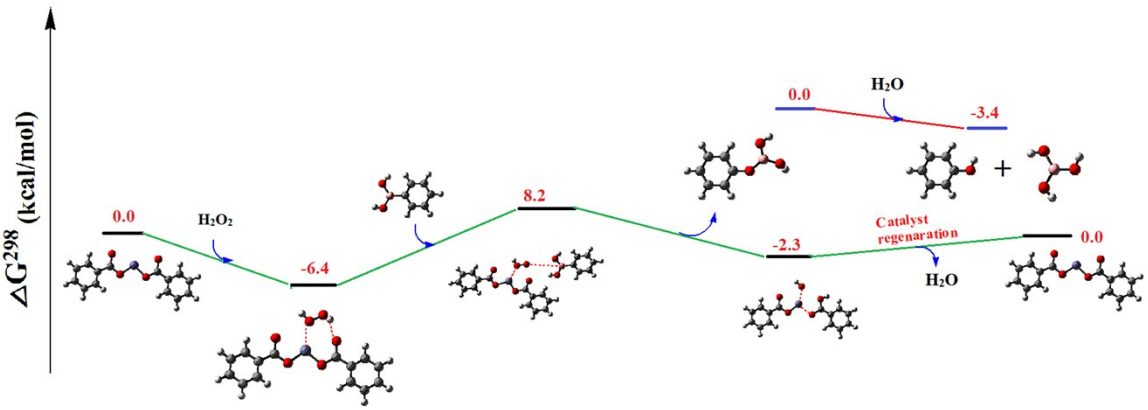


Figure S4. Energetics of the [Zn(bpdc)$_3$(bipy)].2DMF.4H$_2$O (**2**) catalyzed *ipso*-hydroxylation of phenyl boronic acid.

NMR data

^{1}H and ^{13}C NMR spectra were recorded with a JNM ECS 400 MHz NMR spectrophotometer (JEOL) using deuterated Chloroform ($CDCl_3$) and tetramethylsilane (TMS) as the internal standard. Chemical shift values are expressed in ppm. Coupling constants are expressed in Hertz (Hz).). The signals are reported as "s"= singlet, "b"= broad, "d"= doublet, "t"= triplet, "q"= quartet and "m"= multiplet.

a. Phenol: (Entry I, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24 (d, *J*= 8Hz, 2H), 6.81 (d, *J*= 8Hz, 3H), 4.23 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.4, 129.6, 120.8, 115.3

b. 4-nitrophenol: (Entry II, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (d, *J*= 8Hz, 2H), 6.91 (d, *J*= 8Hz, 2H), 5.94 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.8, 141.7, 126.4, 115.8

c. 4-aminophenol: (Entry III, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.34 (s, br, 1H), 6.46 (d, *J*= 8Hz, 2H), 6.43 (d, *J*= 8Hz, 2H), 4.46 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.7, 141.0, 116.0, 115.6

d. **4-methoxyphenol:** (Entry IV, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.75-6.78 (m, 4H), 4.42 (s, br, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.8, 149.5, 116.1, 114.9, 55.6

e. **2-methylphenol:** (Entry V, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.09-7.11 (m, 2H), 6.81-6.85 (m, 1H), 6.75 (d, *J*= 8Hz, 1H), 5.19 (s, br, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.5, 139.9, 129.5, 121.6, 116.1, 102.5, 29.8, 21.4 15.6

f. **2, 6-dimethylphenol:** (Entry VI, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.96-6.98 (m, 2H), 6.76 (d, *J*= 8Hz, 1H), 4.7 (s, br, 1H), 2.27-2.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.2, 128.6, 123.0, 120.2, 15.9

g. **3-methylphenol:** (Entry VII, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.09-7.11 (m, 1H), 6.73-6.75 (m, 1H), 6.65-6.66 (m, 2H), 4.31 (s, br, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.5, 139.9, 129.5, 121.6, 116.1, 112.4, 21.4

h. **3-cyanophenol:** (Entry VIII, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32-7.34 (m, 2H), 7.26-7.24 (m, 1H), 7.12 (m, 1H), 5.75 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.0, 130.7, 124.7, 120.6, 118.7, 113.1

i. **4-chlorophenol:** (Entry IX, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.18 (d, *J*= 8Hz, 2H), 6.76 (d, *J*= 8Hz, 2H), 5.0 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.2, 129.5, 125.6, 116.7

j. **4-formylphenol:** (Entry X, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.86 (s, 1H), 7.81 (d, *J*= 8.4Hz, 2H), 6.98 (d, *J*= 8.4Hz, 2H), 6.59 (s, br, 1H) 2.20 (acetone); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.4, 161.7, 132.6, 129.8, 116.1

k. **4-ethylphenol:** (Entry XI, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.05 (d, *J*= 8Hz, 2H), 6.76 (d, *J*= 8Hz, 2H), 4.18 (s, br, 1H), 2.57 (q, *J*= 8Hz, 2H), 1.20 (t, *J*= 8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.5, 136.3, 128.9, 115.3, 28.0, 15.9

l. **4-*tert*-butylphenol:** (Entry XII, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26 (d, *J*= 7.2Hz, 2H), 6.75 (d, *J*= 7.2Hz, 2H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.1, 143.6, 126.2, 114.8, 34.1, 31.6

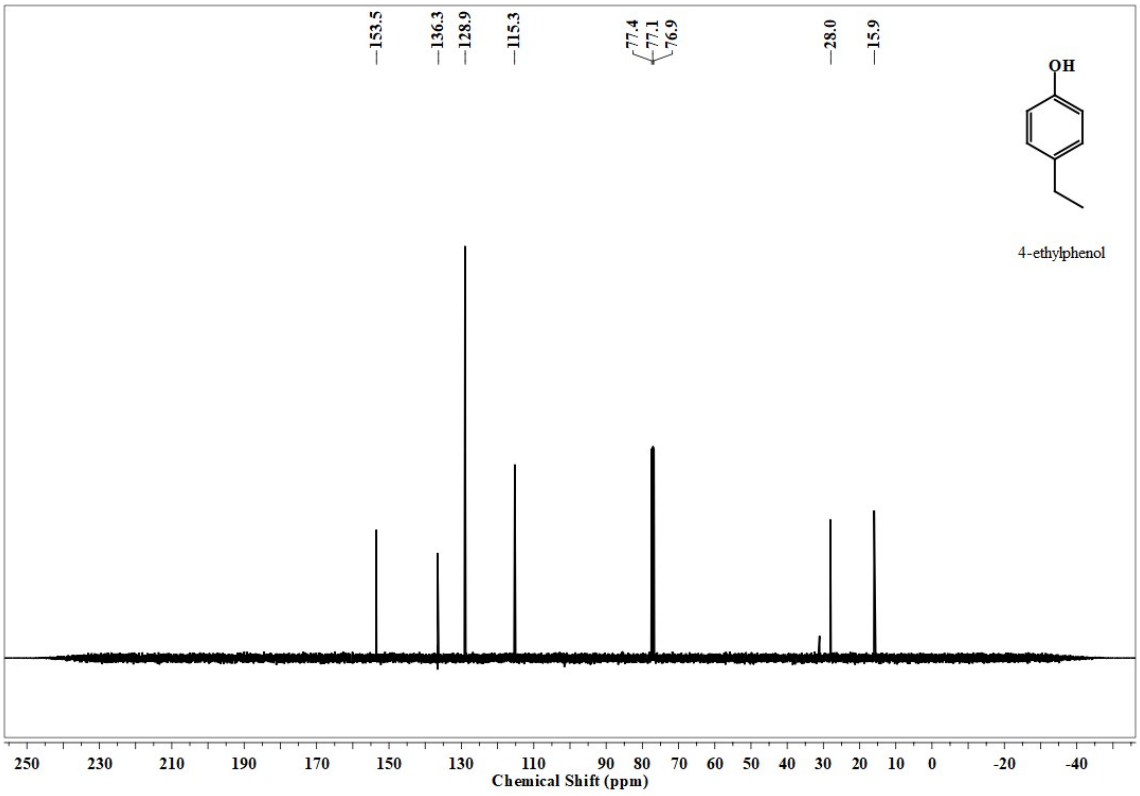
m. **2, 4-difluorophenol:** (Entry XIII, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.96-6.99 (m, 1H), 6.68-6.69 (m, 1H), 6.52-6.55 (m, 1H), 2.92 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.1, 143.7, 117.4, 110.8, 105, 104.8

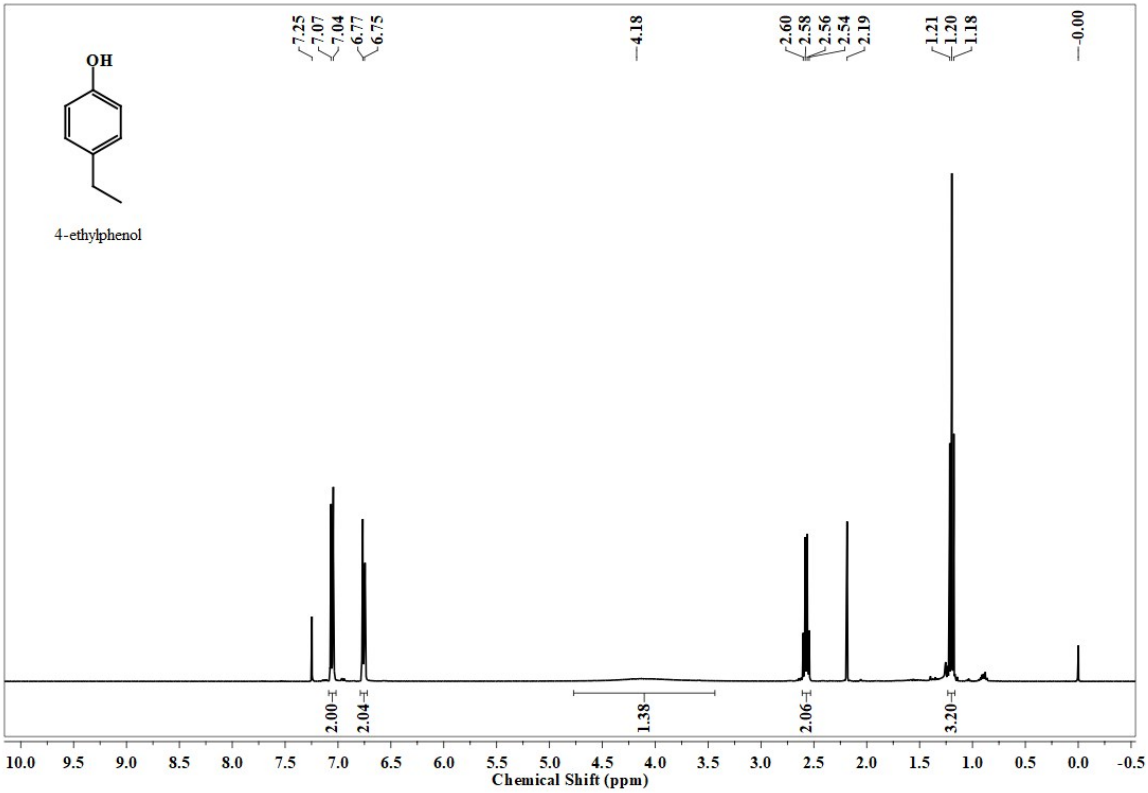
n. **2-hydroxythiophene:** (Entry XIV, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.96-6.99 (m, 1H), 6.68-6.69 (m, 1H), 6.52-6.55 (m, 1H), 2.92 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.1, 143.7, 117.4, 110.8, 105, 104.8

o. **6-methoxypyridine-3-ol:** (Entry XV, Table 3): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75-7.76 (m, 1H), 7.36 (s, br, 1H), 7.24-7.27 (m, 1H), 6.69-6.71 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.4, 148.3, 132.2, 128.8, 111.0, 54.2

Representative ^{1}H and ^{13}C NMR spectra

Product: 4-ethylphenol




OH
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7.07
7.04
6.77
6.75
4.18
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2.58
2.56
2.54
2.19
1.21
1.20
1.18
0.00
2.00
2.04
1.38
2.06
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Chemical Shift (ppm)