Organic-Inorganic Hybrid Polymer-Encapsulated Magnetic Nanobead Catalysts

Takayoshi Arai,* Toru Sato, Hirofumi Kanoh, Katsumi Kaneko, Koichi Oguma and Akira Yanagisawa
Experimental

SEM images of low magnification

(a) original amino functionalized magnetic beads

(b) Cu-bpy organic-inorganic hybrid polymer-encapsulated magnetic beads.

General procedure for the Cu-bpy HP-MB catalyzed synthesis of α-hydroxyketone (Entry 2, Table 1), and reuse of Cu-bpy HP-MB:

**Synthesis of 3,4-dihydro-2-hydroxy-2-methylnaphthalen-1(2H)-one (2).** To the solution of Cu-bpy HP-MB (0.78 µmol as -NH₂) in EtOH (1.5 mL) was added silyl enolate 1 (9.1 mg, 39 µmol). The mixture was agitated at room temperature for 48 h under oxygen atmosphere (1 atm). After treating with P(OEt)₃ (7 µL, 39 µmol), the Cu-bpy HP-MB was recovered by making cohere under an external magnetic field. From the organic phase, the solvents were evaporated *in vacuo*, and the residues were purified by column chromatography on silica gel to give α-hydroxyketone 2 (1ˢᵗ use: 92 %, 2ᵈ use: 92 %, 3ʳᵈ use: 89 %, 4ᵗʰ use:
85 %, 5\textsuperscript{th} use: 84 %) as colorless oil. TLC $R_f$ 0.32 (1:3 ethyl acetate/hexane); IR (neat) 3479, 2971, 2932, 1683, 1602, 1456, 1370, 1289, 1222, 1154, 1096, 970, 740 cm\textsuperscript{-1}; $^1$H-NMR(400 MHz, CDCl\textsubscript{3}) $\delta$ 1.40(s, 3 H, CH\textsubscript{3}), 2.19-2.29(m, 2 H, CH\textsubscript{2}), 3.00-3.14(m, 2 H, CH\textsubscript{2}), 3.86(br-s, 1 H, OH), 7.26(d, 1 H, $J$=7.6 Hz, aromatic), 7.35(t, 1 H, $J$=7.6 Hz, aromatic), 7.52(dt, $J$=1.4, 7.6 Hz, 1 H, aromatic), 8.17(dd, $J$=1.4, 7.6 Hz, 1 H, aromatic); $^{13}$C-NMR(100 MHz, CDCl\textsubscript{3}) $\delta$ 23.9, 26.8, 35.8, 73.6, 126.9, 128.0, 129.0, 130.0, 134.0, 143.4, 201.8. HRMS (FAB+) calcd for C\textsubscript{11}H\textsubscript{13}O\textsubscript{2} (M$^+$+H) 177.0916: found 177.0909.

3,4-dihydro-2-hydroxy-2,5,7-trimethylnaphthalen-1(2H)-one (entry 1 in Table 2). TLC $R_f$ 0.51 (1:3 ethyl acetate/hexane); IR (neat) 3485, 2971, 2930, 2863, 1680, 1610, 1475, 1369, 1306, 1132, 1097, 1050, 984, 871 cm\textsuperscript{-1}; $^1$H-NMR(400 MHz, CDCl\textsubscript{3}) $\delta$ 1.36(s, 3 H, CH\textsubscript{3}), 2.12-2.33(m, 2 H, CH\textsubscript{2}), 2.27(s, 3 H, CH\textsubscript{3}), 2.34(s, 3 H, CH\textsubscript{3}), 2.72-2.98(m, 2 H, CH\textsubscript{2}), 3.93(br-s, 1 H, OH), 7.23(s, 1 H, aromatic), 7.71(s, 1 H, aromatic); $^{13}$C-NMR(100 MHz, CDCl\textsubscript{3}) $\delta$ 202.5, 138.8, 136.6, 136.4, 129.9, 125.9, 73.2, 35.4, 24.2, 23.9, 20.9, 19.2, 1.0. HRMS (FAB+) calcd for C\textsubscript{13}H\textsubscript{17}O\textsubscript{2}(M$^+$+H) 205.1229: found 205.1243.

3,4-dihydro-2-hydroxy-5-methoxy-2-methylnaphthalen-1(2H)-one (entry 2 in Table 2). TLC $R_f$ 0.36 (1:3 ethyl acetate/hexane); IR (neat) 3734, 3477, 2935, 1685, 1581, 1472, 1261, 1187, 983, 751 cm\textsuperscript{-1}; $^1$H-NMR(400 MHz, CDCl\textsubscript{3}) $\delta$ 1.38(s, 3 H, CH\textsubscript{3}), 2.10-2.17(m, 1 H, CH\textsubscript{2}), 2.26-2.31(m, 1 H, CH\textsubscript{2}), 2.67-2.79(m, 1 H, CH\textsubscript{2}), 3.11-3.18(m, 1 H, CH\textsubscript{2}), 3.88(s, 3 H, OCH\textsubscript{3}), 3.90(br-s, 1 H, OH), 7.05(d, $J$=8.0 Hz, 1 H, aromatic), 7.32(t, $J$=8.0 Hz, 1 H, aromatic), 7.62(d, $J$=8.0 Hz, 1 H, aromatic); $^{13}$C-NMR(100 MHz, CDCl\textsubscript{3}) $\delta$ 202.2, 156.9, 132.4, 130.9, 127.5, 119.4, 114.7, 73.4, 55.6, 35.1, 23.8, 21.0. HRMS (FAB+) calcd for C\textsubscript{12}H\textsubscript{15}O\textsubscript{3}(M$^+$+H) 207.1021: found 207.1028.

3,4-dihydro-2-hydroxy-6-methoxy-2-methylnaphthalen-1(2H)-one (entry 3 in Table 2). TLC $R_f$ 0.31 (1:3 ethyl acetate/hexane); IR (neat) 3466, 2928, 1660, 1590, 1494, 1456, 1340, 1299, 1260, 1224, 1137, 1089, 1024, 969, 840 cm\textsuperscript{-1}; $^1$H-NMR(400 MHz, CDCl\textsubscript{3}) $\delta$ 1.38(s, 3 H, CH\textsubscript{3}), 2.16-2.26(m, 2 H, CH\textsubscript{2}), 2.94-3.12(m, 1 H, CH\textsubscript{2}), 3.87(s, 3 H, OCH\textsubscript{3}), 3.87(br-s, 1 H, OH), 6.70(s, 1 H, aromatic), 7.32(d, $J$=8.7 Hz, 1 H, aromatic), 8.00(d, $J$=8.7
Hz, 1H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 200.4, 164.2, 146.0, 130.5, 123.2, 113.7, 112.6, 73.3, 55.5, 35.8, 27.2, 24.1. HRMS (FAB+) calcd for C$_{12}$H$_{15}$O$_3$(M$^+$+H) 207.1021: found 207.1029.

3,4-dihydro-2-hydroxy-2-propynaphthalen-1(2H)-one (entry 4 in Table 2). TLC $R_f$ 0.47 (1:8 ethyl acetate/hexane); IR (neat) 3492, 2957, 2931, 2871, 1681, 1603, 1455, 1286, 1233, 1154, 1098, 991, 740 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 0.88( t, $J$= 7.3 Hz, 3H, CH$_3$), 1.23-1.39(m, 1H, CH$_2$), 1.43-1.71(m, 3H, CH$_2$), 2.15(dt, $J$=5.5, 13.0 Hz, 1H, CH$_2$), 2.34(ddd, $J$=2.2, 5.5, 13.0 Hz, 1H, CH$_2$), 2.95-3.14(m, 2H, CH$_2$), 3.87(br-s, 1H, OH), 7.25(d, $J$=7.7 Hz, 1H, aromatic), 7.34(t, $J$=7.7 Hz, 1H, aromatic), 7.52(dt, $J$=1.5, 7.5 Hz, 1H, aromatic), 8.01(dd, $J$=1.5, 7.5 Hz, 1H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 14.2, 16.3, 26.5, 33.9, 37.7, 75.8, 126.8, 127.9, 129.0, 130.3, 133.9, 143.4, 202.0. HRMS (FAB+) calcd for C$_{13}$H$_{17}$O$_2$(M$^+$+H) 205.1229: found 205.1212.

2-allyl-3,4-dihydro-2-hydroxynaphthalen-1(2H)-one (entry 5 in Table 2). TLC $R_f$ 0.24 (1:10 ethyl acetate/hexane); IR (neat) 3481, 3074, 2930, 1681, 1603, 1287, 1231, 1155, 995, 741 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 2.17(dt, $J$=5.6, 12.8 Hz, 1H, CH$_2$), 2.33-2.47(m, 3H, CH$_2$ x 2), 2.95-3.16(m, 2H, CH$_2$), 3.84(br-s, 1H, OH), 5.13(dd, $J$=9.4, 18.3 Hz, 2H, olefinic), 5.88(ddt, $J$=7.5, 9.4, 18.3 Hz, 1H, olefinic), 7.27(dt, $J$=7.7 Hz, 1H, aromatic), 7.35(t, $J$=7.5 Hz, 1H, aromatic), 7.53(dt, $J$=1.2, 7.5 Hz, 1H, aromatic), 8.02(dd, $J$=1.2, 7.7 Hz, 1H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 26.1, 33.5, 40.3, 75.3, 119.1, 126.9, 128.0, 129.0, 130.1, 132.1, 143.4, 201.0. HRMS (FAB+) calcd for C$_{13}$H$_{15}$O$_2$(M$^+$+H) 203.1072: found 203.1079.

2-benzyl-2-hydroxycyclohexan-1-one (entry 6 in Table 2). TLC $R_f$ 0.32 (1:7 ethyl acetate/hexane); IR (neat) 3482, 2938, 2864, 1707, 1495, 1451, 1089, 702 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 1.60-1.75(m, 2H, CH$_2$), 1.83-1.90(m, 2H, CH$_2$), 2.13-2.25(m, 2H, CH$_2$), 2.50-2.58(m, 1H, CH$_2$), 2.70(dt, $J$=6.3, 13.8 Hz, 1H, CH$_2$), 2.97(d, $J$=13.8 Hz, 1H, CH$_2$), 3.14(d, $J$=13.8 Hz, 1H, CH$_2$), 3.86(br-s, 1H, OH), 7.18-7.29(m, 5H, aromatic);
$^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 22.8, 28.0, 38.6, 40.4, 43.3, 79.3, 127.0, 128.3, 130.1, 135.3, 213.3. HRMS (FAB+) calcd for C$_{13}$H$_{17}$O$_2$ (M$^+$+H) 205.1229: found 205.1219.

**2-hydroxy-2-methyl-1-phenylpropan-1-one (entry 7 in Table 2).** TLC $R_f$ 0.33 (1:3 ethyl acetate/hexane); IR (neat) 3452, 2979, 1669, 1597, 1446, 1365, 1259, 1168, 956, 714, 694 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 1.64(s, 6H, 2 x CH$_3$), 4.10(br-s, 1H, OH), 7.46(t, $J$=7.3 Hz, 2H, aromatic), 7.57(tt, $J$=1.5, 7.3 Hz, 1H, aromatic), 8.01(dd, $J$=1.5, 7.3 Hz, 2H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 28.4, 76.2, 128.4, 129.6, 132.9, 133.7, 204.7.

**2-hydroxy-2-(4-methoxyphenyl)-1-phenylpropan-1-one (entry 8 in Table 2).** TLC $R_f$ 0.24 (1:3 ethyl acetate/hexane); IR (neat) 3450, 2931, 1671, 1606, 1509, 1448, 1297, 1178, 1029, 833, 707 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 1.88(s, 3H, CH$_3$), 3.81(s, 3H, OCH$_3$), 4.80(br-s, 1H, OH), 6.90(d, $J$=9.0 Hz, 2H, aromatic), 7.30(t, $J$=7.2 Hz, 2H, aromatic), 7.36(d, $J$=9.0 Hz, 2H, aromatic), 7.45(t, $J$=7.2 Hz, 1H, aromatic), 7.67(d, $J$=7.2 Hz, 2H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 202.3, 159.4, 134.5, 133.5, 132.9, 130.2, 128.3, 127.9, 114.9, 78.5, 55.3, 25.9. HRMS (FAB+) calcd for C$_{16}$H$_{15}$O$_2$ (M$^+$+H-H$_2$O) 239.1072: found 239.1069.

**2-hydroxy-4,4-dimethyl-2-phenylpentan-3-one (entry 9 in Table 2).** TLC $R_f$ 0.54 (1:3 ethyl acetate/hexane); IR (neat) 3494, 2969, 1689, 1481, 1446, 1363, 1220, 1147, 1118, 1068, 1041, 993, 912, 775, 734, 700 cm$^{-1}$; $^1$H-NMR(400 MHz, CDCl$_3$) $\delta$ 1.07(s, 9H, C(CH$_3$)$_3$), 1.83(s, 3H, CH$_3$), 4.36(br-s, 1H, OH), 7.27-7.35(m, 5H, aromatic); $^{13}$C-NMR(100 MHz, CDCl$_3$) $\delta$ 141.9, 128.5, 127.8, 125.9, 80.6, 44.3, 28.5, 25.7.
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![Chemical Structure](image-url)
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![Chemical Structure Image](image)
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$^{13}$C-NMR (CDCl$_3$)