

# **CHEMISTRY**

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### Supporting Information

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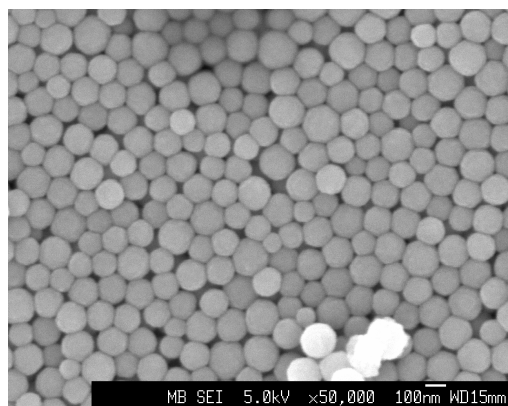
# **Organic-Inorganic Hybrid Polymer-Encapsulated Magnetic Nanobead Catalysts**

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

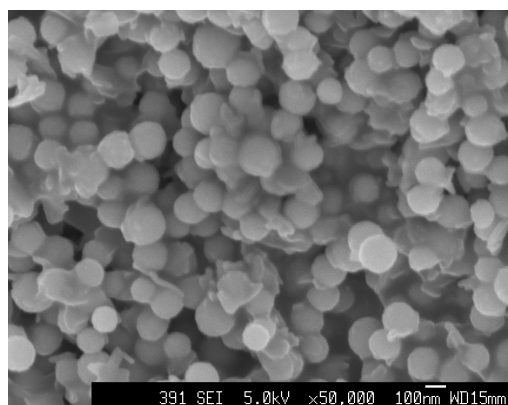
## Experimental

### 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(2*H*)-one (2).** To the solution of Cu-bpy HP-MB (0.78  $\mu\text{mol}$  as  $-\text{NH}_2$ ) in EtOH (1.5 mL) was added silyl enolate **1** (9.1 mg, 39  $\mu\text{mol}$ ). The mixture was agitated at room temperature for 48 h under oxygen atmosphere (1 atm). After treating with  $\text{P}(\text{OEt})_3$  (7  $\mu\text{L}$ , 39  $\mu\text{mol}$ ), 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** (1<sup>st</sup> use: 92 %, 2<sup>nd</sup> use: 92 %, 3<sup>rd</sup> use: 89 %, 4<sup>th</sup> use:

85 %, 5<sup>th</sup> 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  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.40(s, 3H,  $\text{CH}_3$ ), 2.19-2.29(m, 2H,  $\text{CH}_2$ ), 3.00-3.14(m, 2H,  $\text{CH}_2$ ), 3.86(br-s, 1H, OH), 7.26(d, 1H,  $J=7.6$  Hz, aromatic), 7.35(t, 1H,  $J=7.6$  Hz, aromatic), 7.52(dt,  $J=1.4, 7.6$  Hz, 1H, aromatic), 8.17(dd,  $J=1.4, 7.6$  Hz, 1H, aromatic);  $^{13}\text{C-NMR}$ (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{11}\text{H}_{13}\text{O}_2$  ( $\text{M}^+ + \text{H}$ ) 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  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36(s, 3H,  $\text{CH}_3$ ), 2.12-2.33(m, 2H,  $\text{CH}_2$ ), 2.27(s, 3H,  $\text{CH}_3$ ), 2.34(s, 3H,  $\text{CH}_3$ ), 2.72-2.98(m, 2H,  $\text{CH}_2$ ), 3.93(br-s, 1H, OH), 7.23(s, 1H, aromatic), 7.71(s, 1H, aromatic);  $^{13}\text{C-NMR}$ (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{13}\text{H}_{17}\text{O}_2$  ( $\text{M}^+ + \text{H}$ ) 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  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38(s, 3H,  $\text{CH}_3$ ), 2.10-2.17(m, 1H,  $\text{CH}_2$ ), 2.26-2.31(m, 1H,  $\text{CH}_2$ ), 2.67-2.79(m, 1H,  $\text{CH}_2$ ), 3.11-3.18(m, 1H,  $\text{CH}_2$ ), 3.88(s, 3H,  $\text{OCH}_3$ ), 3.90(br-s, 1H, OH), 7.05(d,  $J=8.0$  Hz, 1H, aromatic), 7.32(t,  $J=8.0$  Hz, 1H, aromatic), 7.62(d,  $J=8.0$  Hz, 1H, aromatic);  $^{13}\text{C-NMR}$ (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{12}\text{H}_{15}\text{O}_3$  ( $\text{M}^+ + \text{H}$ ) 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  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38(s, 3H,  $\text{CH}_3$ ), 2.16-2.26(m, 2H,  $\text{CH}_2$ ), 2.94-3.12(m, 1H,  $\text{CH}_2$ ), 3.87(s, 3H,  $\text{OCH}_3$ ), 3.87(br-s, 1H, OH), 6.70(s, 1H, aromatic), 7.32(d,  $J=8.7$  Hz, 1H, aromatic), 8.00(d,  $J=8.7$

Hz, 1H, aromatic);  $^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{12}\text{H}_{15}\text{O}_3(\text{M}^++\text{H})$  207.1021: found 207.1029.

**3,4-dihydro-2-hydroxy-2-propylnaphthalen-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  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88(t,  $J=7.3$  Hz, 3H,  $\text{CH}_3$ ), 1.23-1.39(m, 1H,  $\text{CH}_2$ ), 1.43-1.71(m, 3H,  $\text{CH}_2$ ), 2.15(dt,  $J=5.5, 13.0$  Hz, 1H,  $\text{CH}_2$ ), 2.34(ddd,  $J=2.2, 5.5, 13.0$  Hz, 1H,  $\text{CH}_2$ ), 2.95-3.14(m, 2H,  $\text{CH}_2$ ), 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);  $^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{13}\text{H}_{17}\text{O}_2(\text{M}^++\text{H})$  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  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.17(dt,  $J=5.6, 12.8$  Hz, 1H,  $\text{CH}_2$ ), 2.33-2.47(m, 3H,  $\text{CH}_2 \times 2$ ), 2.95-3.16(m, 2H,  $\text{CH}_2$ ), 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);  $^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  26.1, 33.5, 40.3, 75.3, 119.1, 126.9, 128.0, 129.0, 130.1, 132.1, 134.1, 143.4, 201.0. HRMS (FAB+) calcd for  $\text{C}_{13}\text{H}_{15}\text{O}_2(\text{M}^++\text{H})$  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  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.60-1.75(m, 2H,  $\text{CH}_2$ ), 1.83-1.90(m, 2H,  $\text{CH}_2$ ), 2.13-2.25(m, 2H,  $\text{CH}_2$ ), 2.50-2.58(m, 1H,  $\text{CH}_2$ ), 2.70(dt,  $J=6.3, 13.8$  Hz, 1H,  $\text{CH}_2$ ), 2.97(d,  $J=13.8$  Hz, 1H,  $\text{CH}_2$ ), 3.14(d,  $J=13.8$  Hz, 1H,  $\text{CH}_2$ ), 3.86(br-s, 1H, OH), 7.18-7.29(m, 5H, aromatic);

$^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{13}\text{H}_{17}\text{O}_2$  ( $\text{M}^+ + \text{H}$ ) 205.1229: found 205.1219.

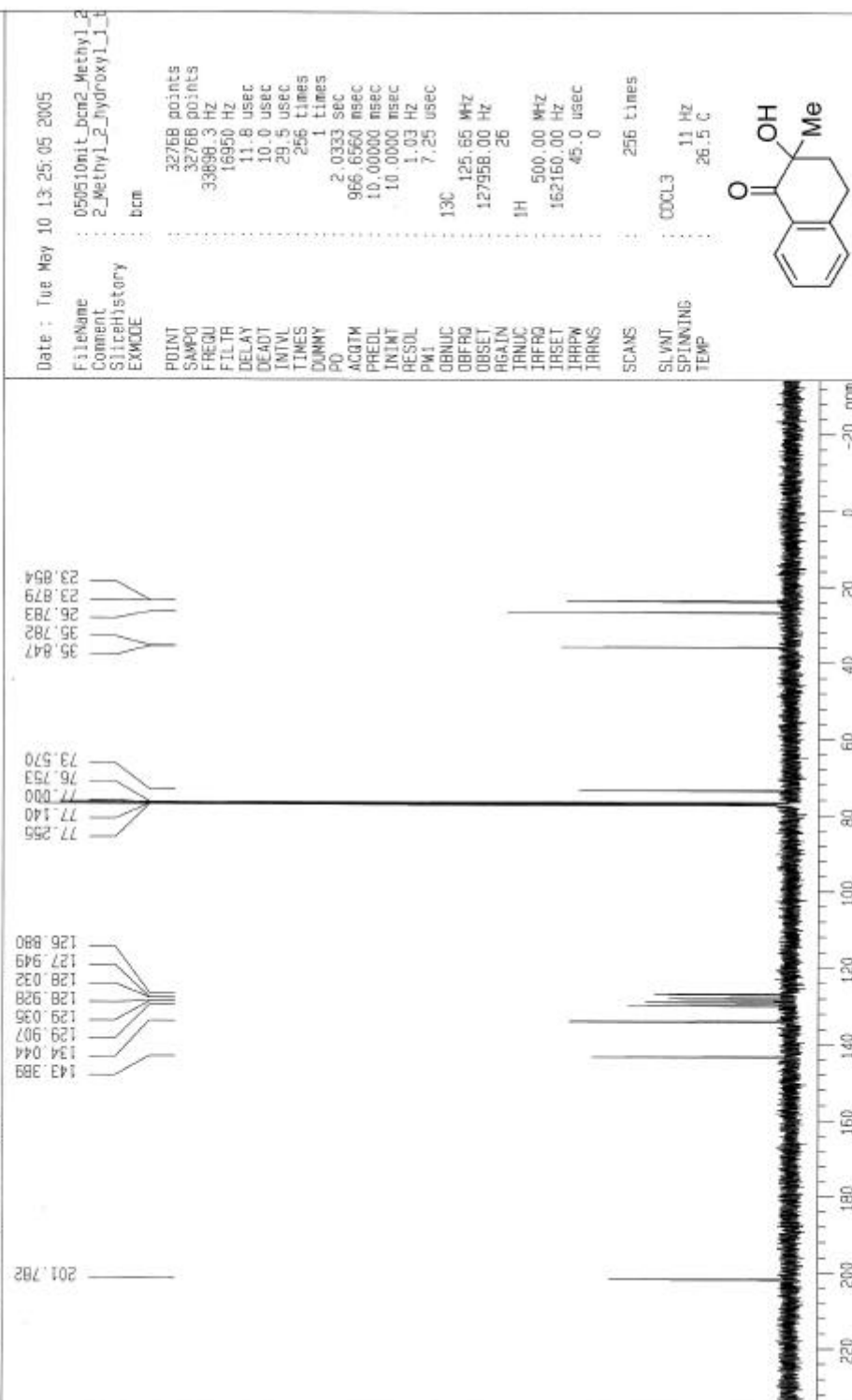
**2-hydroxy-2-methyl-1-phenylpropan-1-one (entry 7 in Table 2).** TLC  $R_f$  0.33 (1:3 ethyl acetate/hexane); IR (neat) 3452, 2979, 1669, 1597, 1446, 1365, 1259, 1168, 956, 714, 694  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.64(s, 6H, 2 x  $\text{CH}_3$ ), 4.10(br-s, 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);  $^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.88(s, 3H,  $\text{CH}_3$ ), 3.81(s, 3H,  $\text{OCH}_3$ ), 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);  $^{13}\text{C}$ -NMR(100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{C}_{16}\text{H}_{15}\text{O}_2$  ( $\text{M}^+ + \text{H} - \text{H}_2\text{O}$ ) 239.1072: found 239.1069.

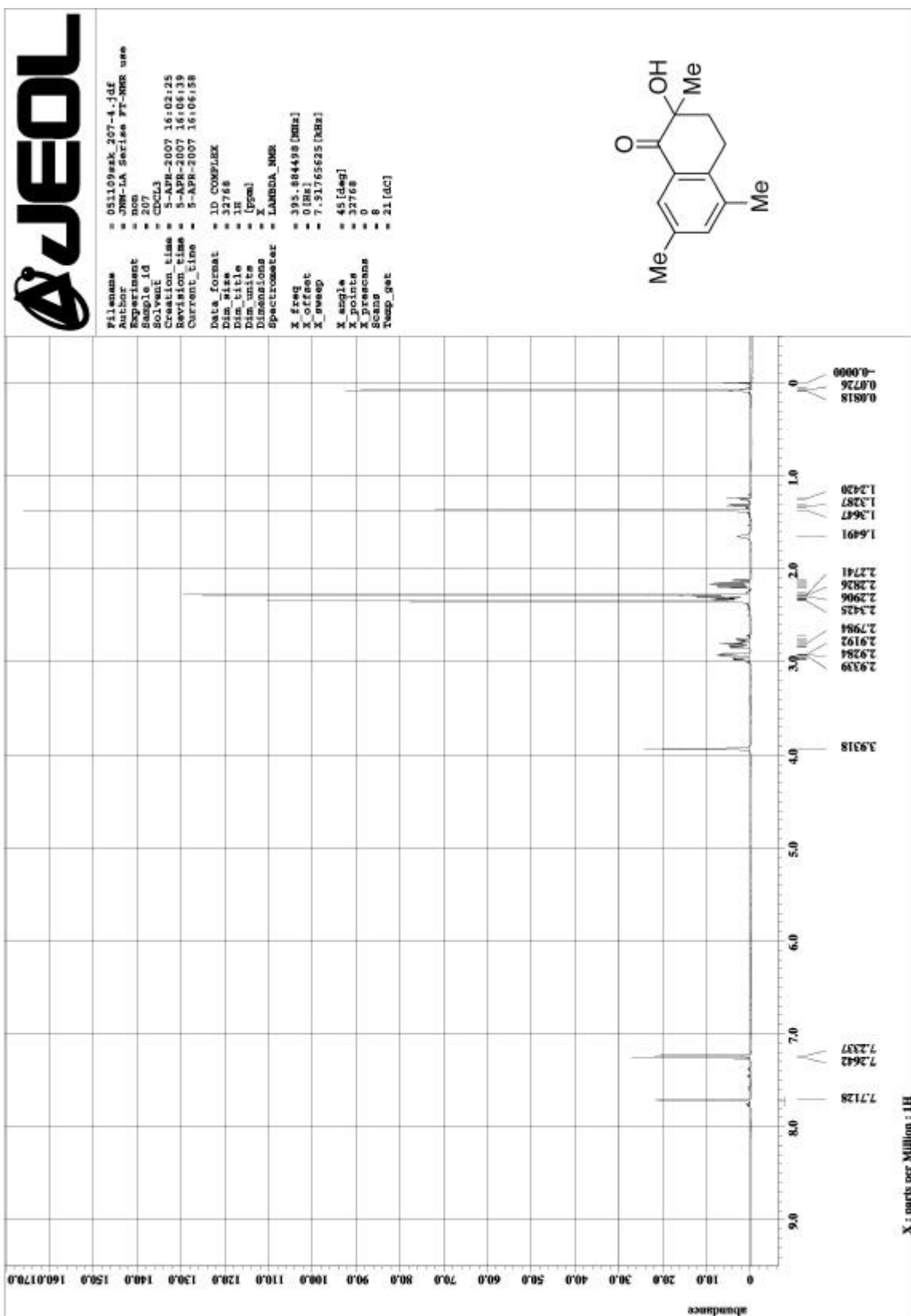
**2-hydroxy-4,4-dimethyl-2-phenylpentan-3-one (entry 9 in Table 2).** TLC  $R_f$  0.54 (1:3 ethyl acetate/hexane); IR (neat) 3494, 2969, 1689, 1481, 1446, 1363, 1220, 1147, 1118, 1068, 1041, 993, 912, 775, 734, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.07(s,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

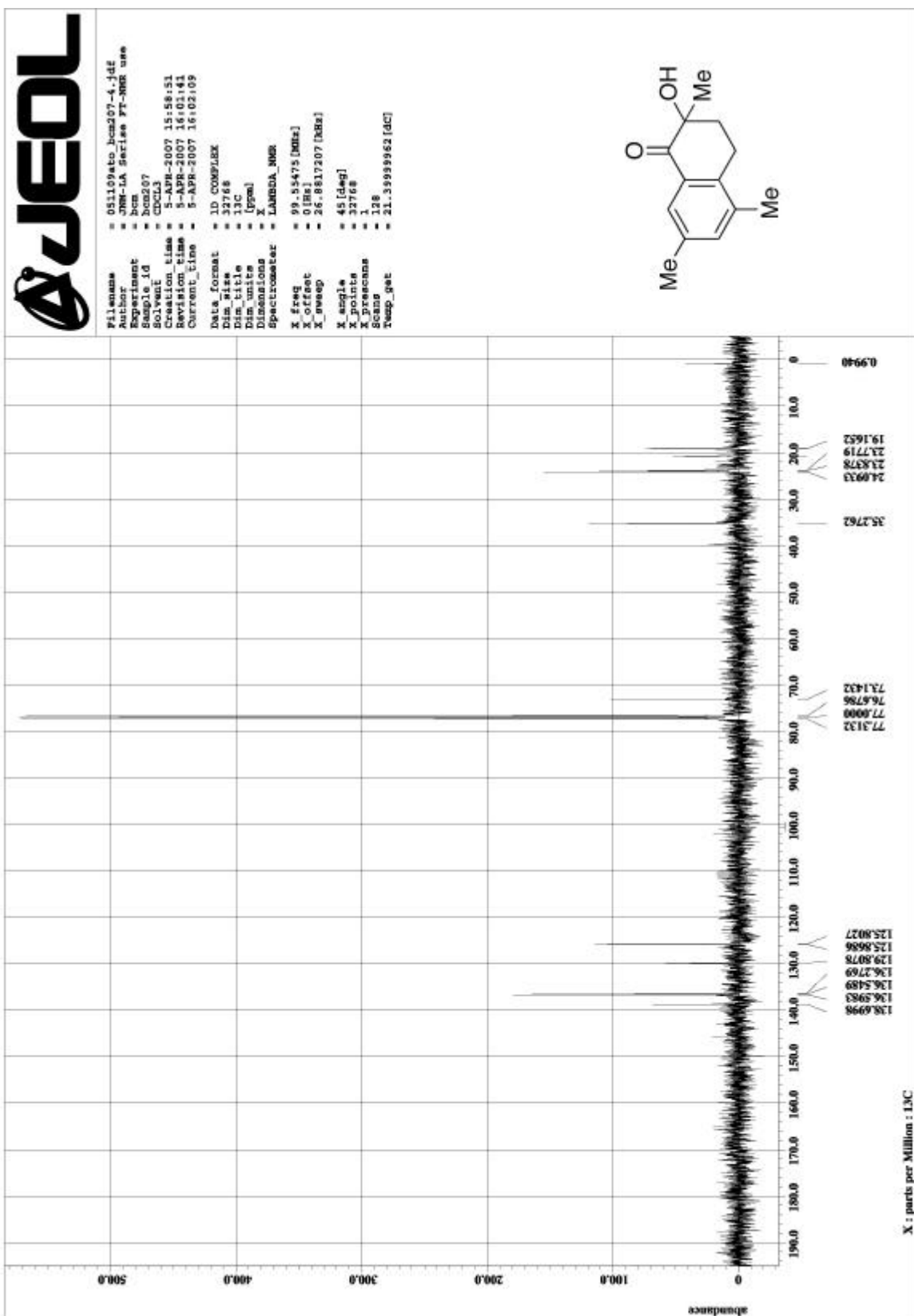


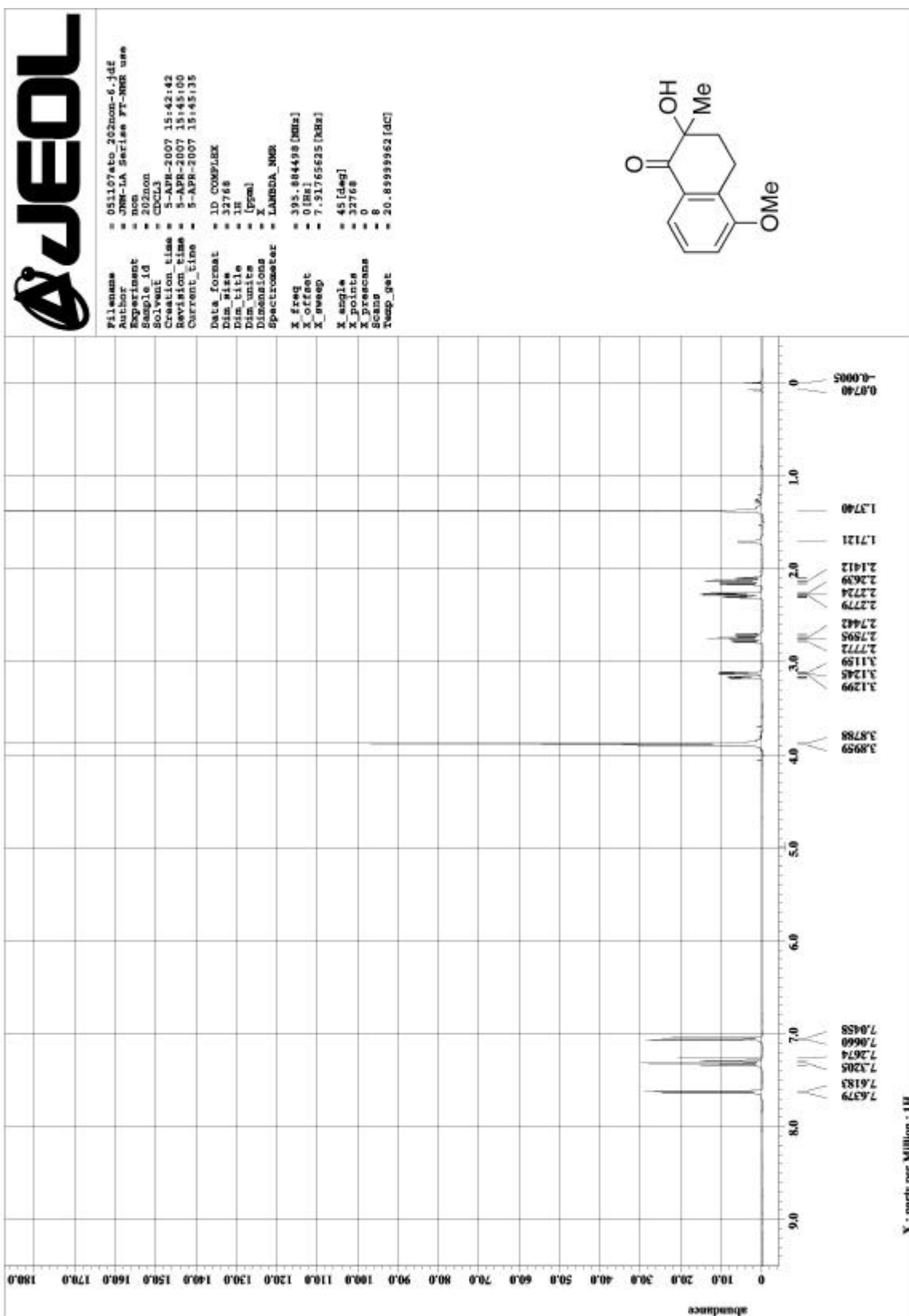
# <sup>13</sup>C-NMR (CDCl<sub>3</sub>)

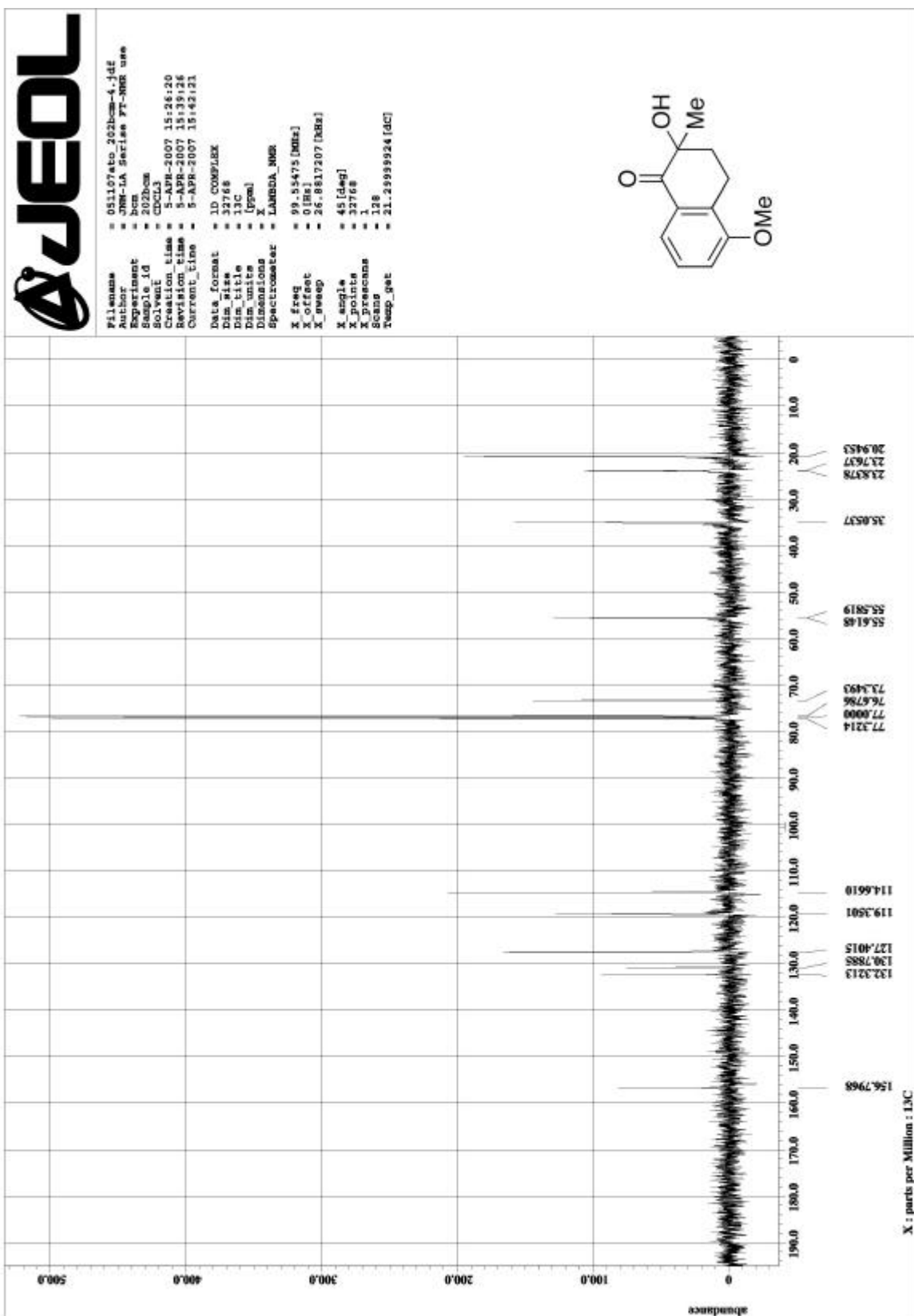


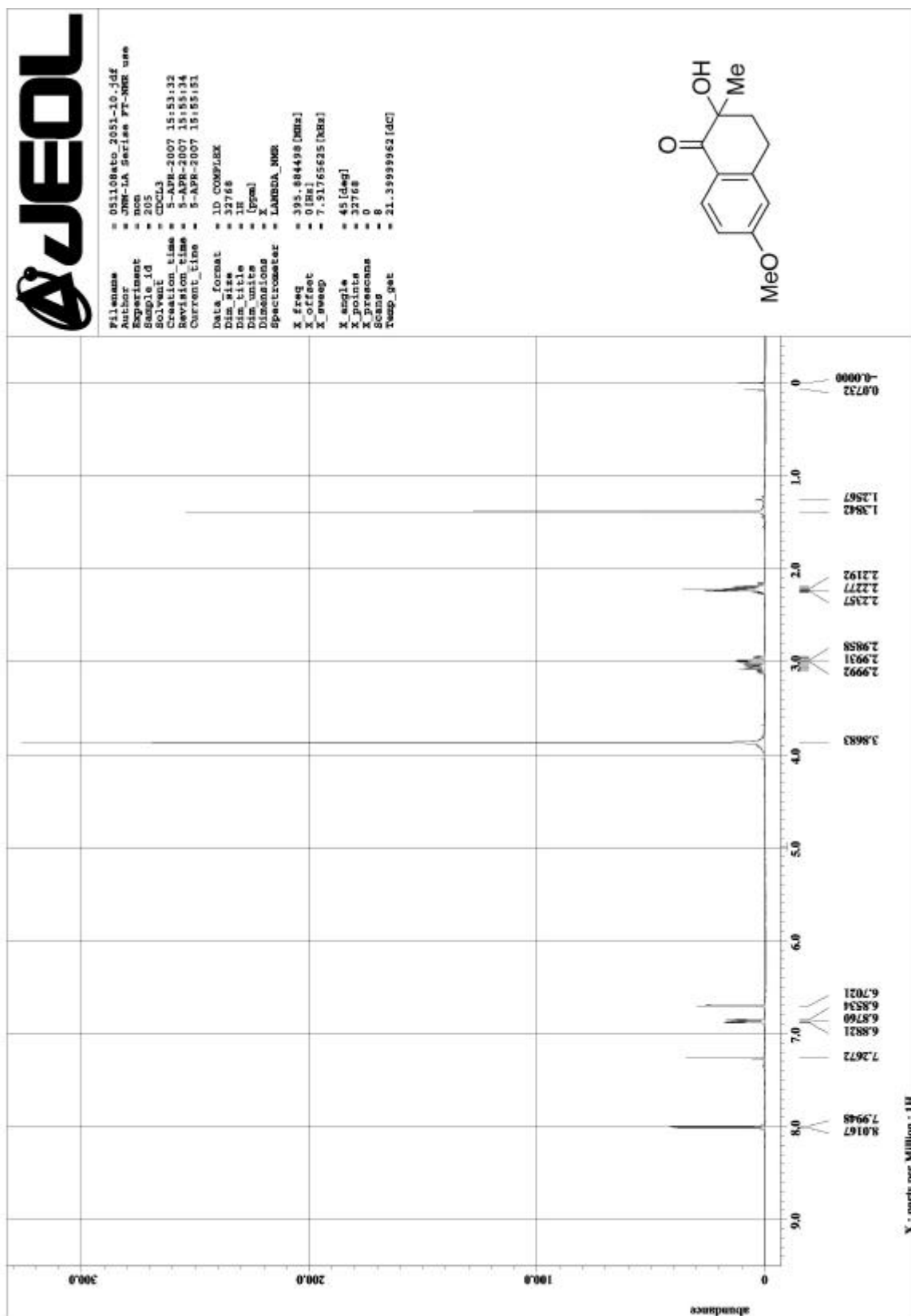


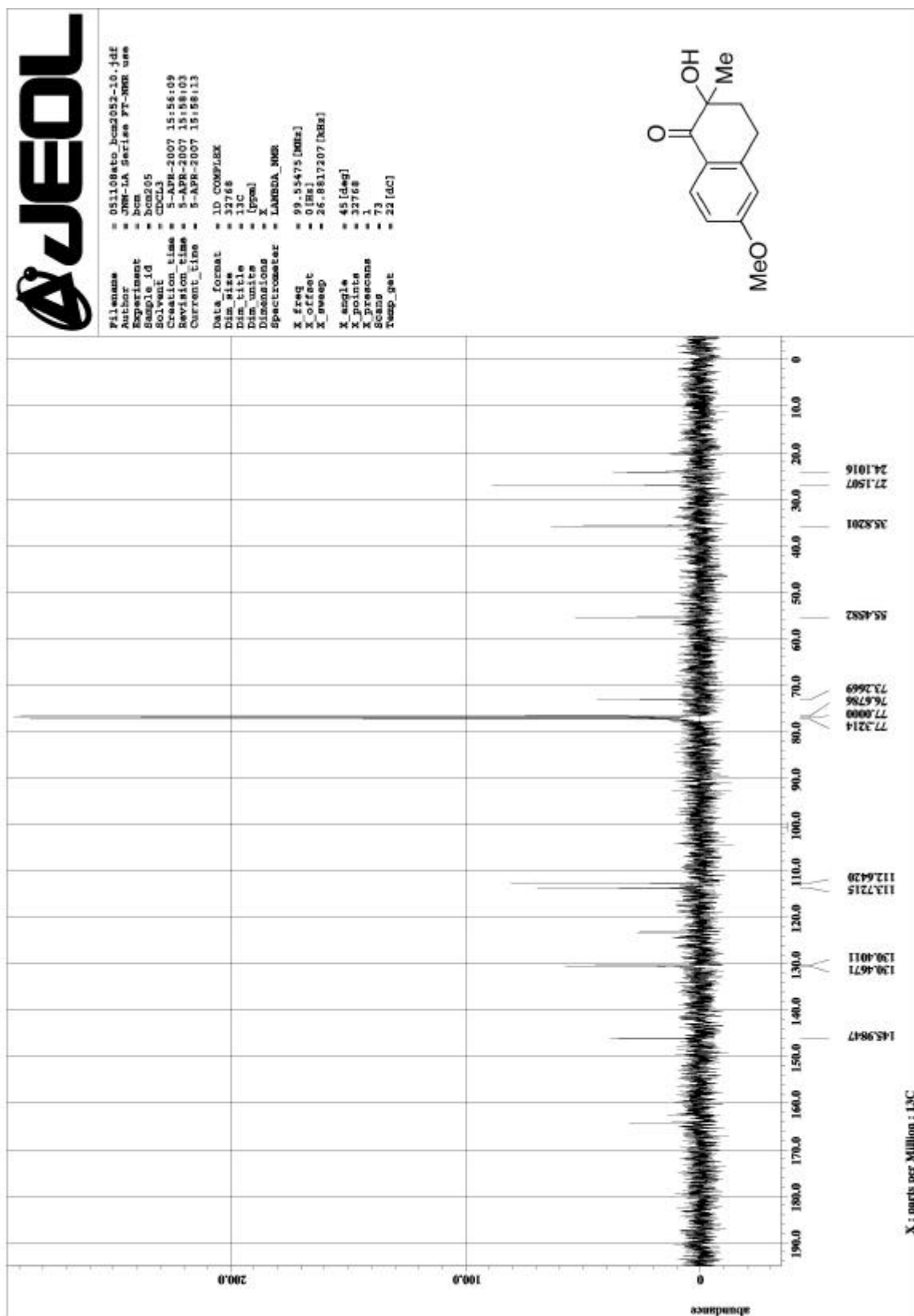


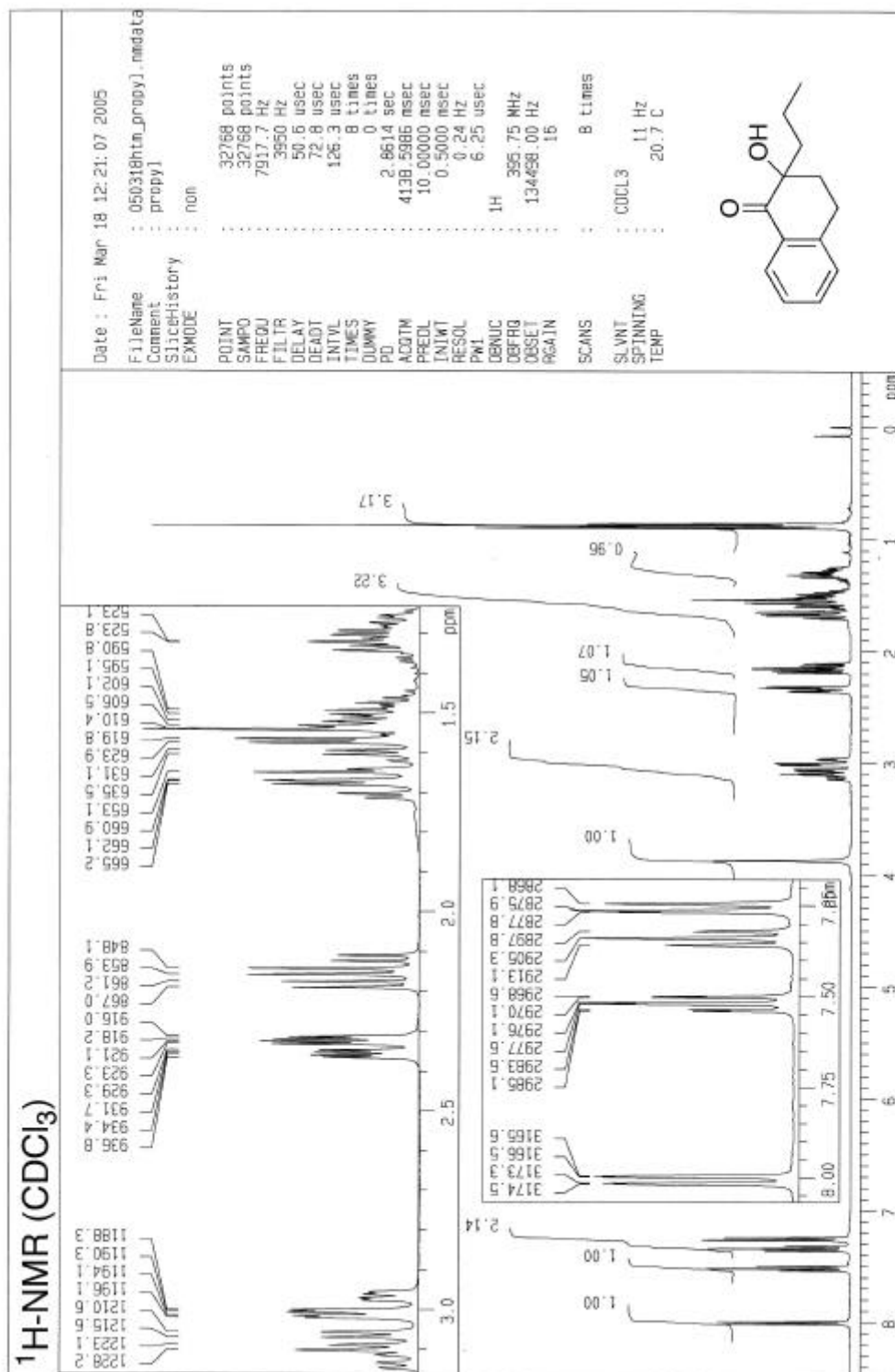


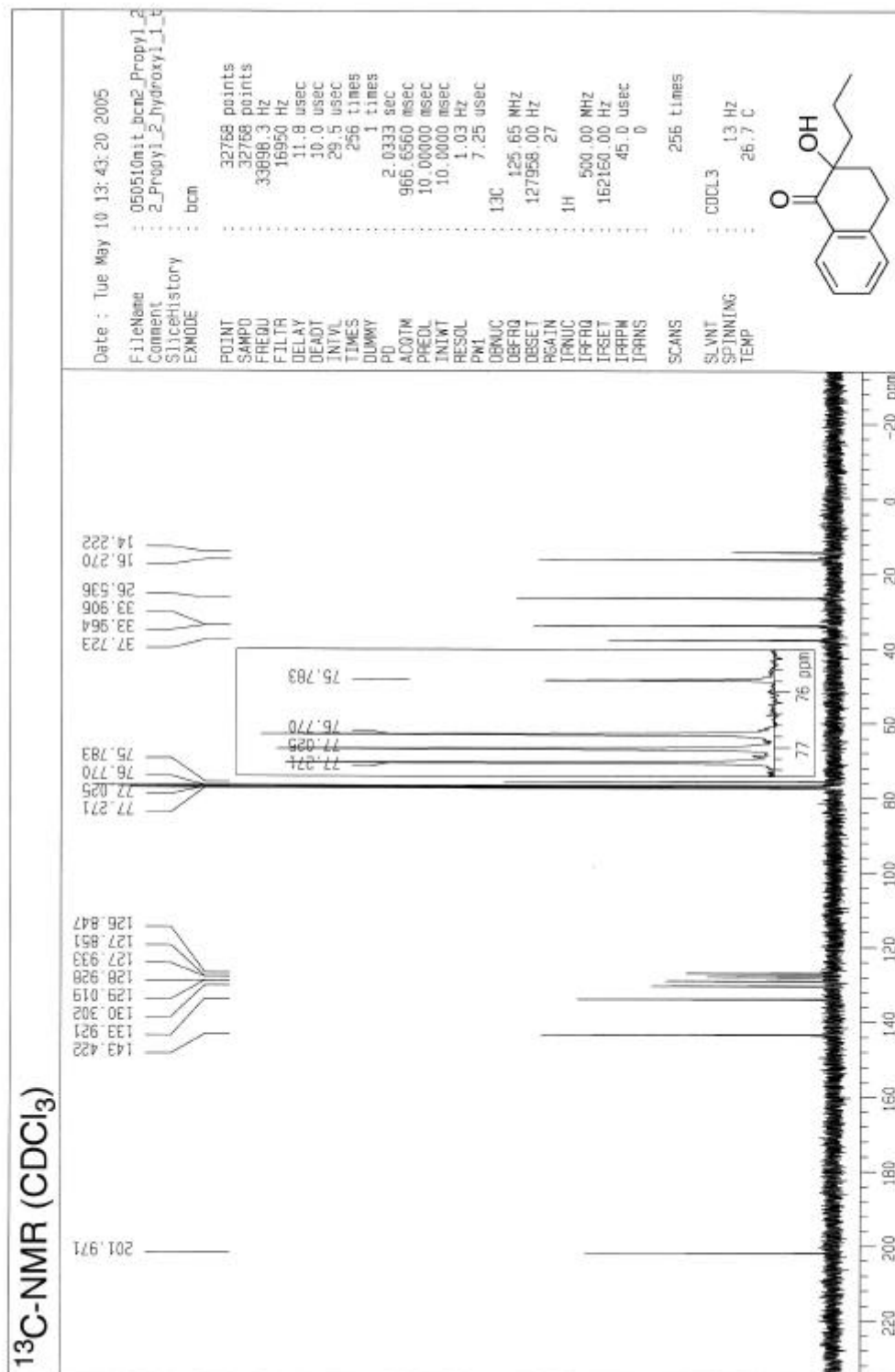






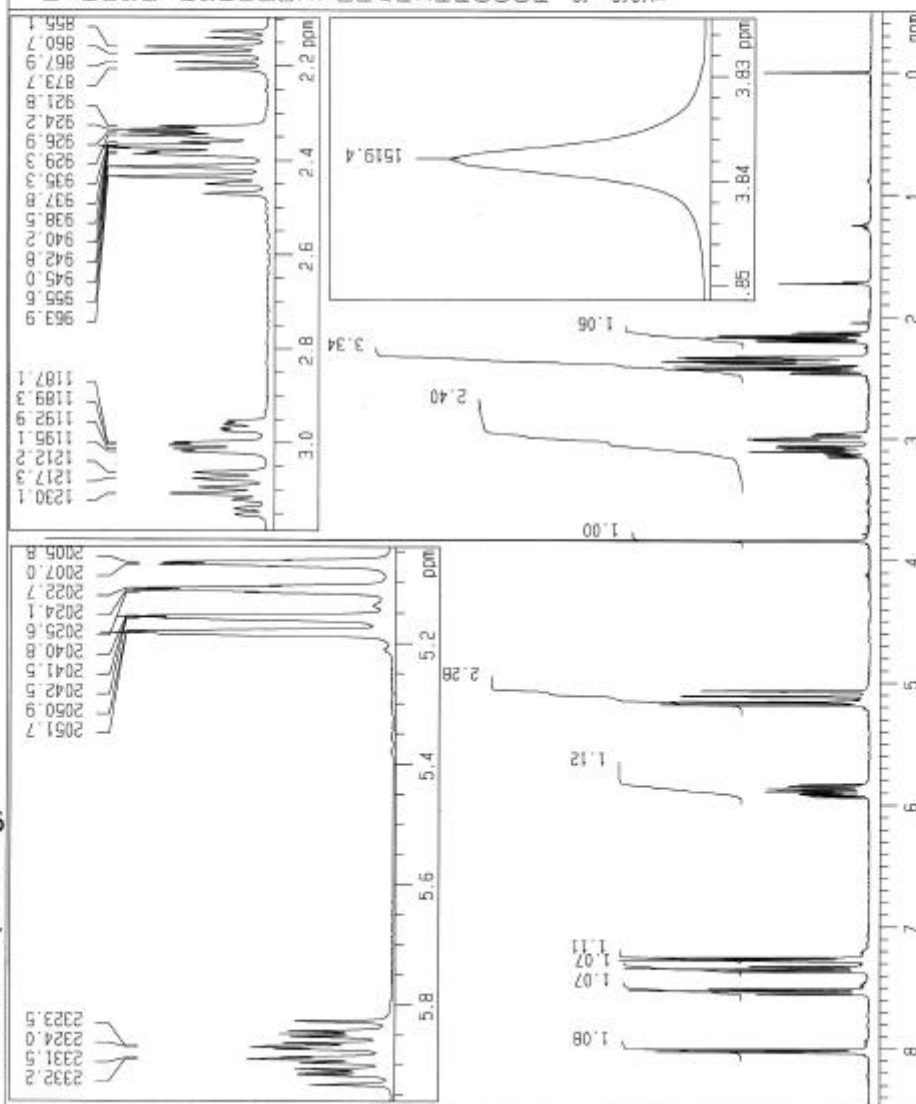








**<sup>1</sup>H-NMR (CDCl<sub>3</sub>)**



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