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Ortho-Vinylation Reaction of Phenols with Ethyne

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Supplementary materials

¹H-NMR and ¹³C-NMR spectra were obtained on a Varian Gemini 200 (200 MHz), a Varian Gemini 2000 (300 MHz), a Varian Mercury (400 MHz), a JEOL α -500 (500 MHz), or a Brucker AM-600 (600 MHz). Chemical shift values are given in ppm relative to internal Me₄Si. IR spectra were recorded on a JASCO FT/IR-7000, a JASCO A-200, or a JASCO FT/IR-410. MS spectra were taken with a HITACHI M-2500, a HITACHI M-52G, or a JEOL JMS-01SG-2. Chlorobenzene and 1,2-dichloroethane were distilled from CaH₂, and stored over MS4A.

Acetates of 2-ethenylphenol.

2-Ethenyl-4-methylphenyl acetate. ¹H-NMR (400MHz, CDCl₃) δ 2.31 (3H, s), 2.34 (3H, s), 5.30 (1H, d, *J* = 12.0 Hz), 5.74 (1H, d, *J* = 17.6 Hz), 6.70 (1H, dd, *J* = 10.8, 17.6 Hz), 6.91 (1H, d, *J* = 8.0 Hz); 7.08 (1H, dd, *J* = 3.6, 8.0 Hz), 7.36 (1H, d, *J* = 1.6 Hz). ¹³C-NMR (100MHz, CDCl₃) δ 21.0, 21.1, 116.0, 122.1, 126.8, 129.3, 129.6, 130.3, 135.6, 145.7, 169.2. IR (neat) 1765 cm⁻¹. MS *m/z* 176 (M^+ , 13), 134 (M^+-CH_2CO , 100). HRMS Calcd for C₁₁H₁₂O₂: 176.0837. Found: 176.0831.

2-Ethenyl-4-(*t*-butyl)phenyl acetate. $^1\text{H-NMR}$ (200MHz, CDCl_3) δ 1.33 (9H, s), 2.32 (3H, s), 5.31 (1H, dd, $J = 1.2, 11.1$ Hz), 5.75 (1H, dd, $J = 1.2, 17.6$ Hz), 6.74 (1H, dd, $J = 11.1, 17.7$ Hz), 6.96 (1H, d, $J = 8.6$ Hz), 7.31 (1H, dd, $J = 2.4, 8.5$ Hz), 7.55 (1H, d, $J = 2.4$ Hz). $^{13}\text{C-NMR}$ (50MHz, CDCl_3) δ 20.9, 31.3, 34.5, 115.9, 121.9, 123.3, 125.9, 129.1, 130.9, 145.7, 148.8, 169.4. IR (neat) 1769, 1632 cm^{-1} . MS m/z 218 (M^+ , 25), 176 ($\text{M}^+-\text{CH}_2\text{CO}$, 58), 161 ($\text{M}^+-\text{Me}-\text{CH}_2\text{CO}$, 100). HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1303.

2-Ethenyl-4-phenylphenyl acetate. $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 2.38 (3H, s), 5.41 (1H, d, $J = 10.8$ Hz), 5.86 (1H, d, $J = 17.6$ Hz), 6.83 (1H, dd, $J = 11.2, 17.6$ Hz), 7.15 (1H, d, $J = 8.0$ Hz), 7.38 (1H, t, $J = 7.6$ Hz), 7.47 (2H, t, $J = 8.4$ Hz), 7.52 (1H, dd, $J = 2.8, 8.0$ Hz), 7.60 (2H, d, $J = 8.0$ Hz), 7.79 (1H, d, $J = 2.4$ Hz). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 21.0, 116.6, 122.7, 125.2, 127.0, 127.2, 127.3, 128.6, 130.2, 130.2, 147.2, 169.0. IR (neat) 1766, 1630 cm^{-1} . MS m/z 238 (M^+ , 11), 196 ($\text{M}^+-\text{CH}_3\text{CO}$, 100). HRMS Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: 238.0983. Found: 238.0993.

2-Ethenyl-6-methylphenyl acetate. $^1\text{H-NMR}$ (600MHz, CDCl_3) δ 2.15 (3H, s), 2.34 (3H, s), 5.30 (1H, dd, $J = 1.2, 11.1$ Hz), 5.72 (1H, dd, $J = 1.2, 17.6$ Hz), 6.69 (1H, dd, $J = 11.0, 17.6$ Hz), 7.12 (1H, t, $J = 7.5$ Hz), 7.14 (1H, dd, $J = 2.1, 7.5$ Hz), 7.39 (1H, dd, $J = 2.1, 7.2$ Hz). $^{13}\text{C-NMR}$ (150MHz, CDCl_3) δ 16.2, 20.4, 116.3, 124.0, 126.0, 130.3, 130.4, 130.6, 146.8, 168.7 (One peak is overlapped). IR (neat) 3412, 1765 cm^{-1} . MS m/z 176 (M^+ , 30), 134 ($\text{M}^+-\text{CH}_2\text{CO}$, 100). HRMS Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: 176.0837. Found: 176.0835. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 74.97; H, 6.86%. Found: C, 75.05; H, 6.96%.

2-Ethenyl-5-methylphenyl acetate and 2-ethenyl-3-methyl-1-phenyl acetate. $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 2.26 (1.5H, s), 2.32 (1.5H, s), 2.33 (1.5H, s), 2.34 (1.5H, s), 5.27 (0.5H, dd, $J = 1.6, 11.2$ Hz), 5.46 (0.5H, dd, $J = 2.0, 18.0$ Hz), 5.50 (0.5H, dd, $J = 2.0, 11.8$ Hz), 5.70 (0.5H, d, $J = 17.6$ Hz), 6.57 (0.5H, dd, $J = 11.2, 17.6$ Hz), 6.69 (0.5H, dd, $J = 10.8, 17.2$ Hz), 6.85 (0.5H, s), 6.87 (0.5H, d, $J = 8.4$ Hz), 7.02 (0.5H, d, $J = 8.8$ Hz), 7.07 (0.5H, d, $J = 7.2$ Hz), 7.16 (0.5H, t, $J = 8.4$ Hz), 7.45 (0.5H, d, $J = 8.0$ Hz). The mixture was deacetylated, and the isomers were separated by silica gel chromatography. **2-Ethenyl-3-methylphenol.** $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 2.26 (3H, s), 5.55 (1H, s), 5.57 (1H, dd, $J = 1.6, 19.6$ Hz), 5.68 (1H, dd, $J = 1.6, 10.4$ Hz), 6.69 (1H, dd, $J = 11.2, 18.6$ Hz), 6.774 (1H, d, $J = 7.2$ Hz), 6.77 (1H, d, $J = 8.0$ Hz), 7.06 (1H, t, $J = 8.0$ Hz). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 20.3, 112.9, 120.3, 121.8, 123.8, 128.1, 132.2, 137.1, 152.5. IR

(neat) 3450 cm^{-1} . MS m/z 134 (M^+ , 100), 91 ($\text{M}^+ \text{-CH}_3\text{CO}$, 34). HRMS Calcd for $\text{C}_9\text{H}_{10}\text{O}$: 134.0732. Found: 134.0733. **2-Ethenyl-5-methylphenol.** $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 2.29 (3H, s), 4.97 (1H, s), 5.29 (1H, dd, $J = 1.2, 10.8\text{ Hz}$), 5.68 (1H, dd, $J = 1.6, 17.6\text{ Hz}$), 6.61 (1H, s), 6.72 (1H, d, $J = 8.0\text{ Hz}$), 6.89 (1H, dd, $J = 10.8, 17.6\text{ Hz}$), 7.26 (1H, d, $J = 7.2\text{ Hz}$). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 21.3, 114.7, 116.4, 121.7, 121.8, 127.1, 131.3, 139.0, 152.5. IR (neat) 3450 cm^{-1} . MS m/z 134 (M^+ , 100), 91 ($\text{M}^+ \text{-CH}_3\text{CO}$, 33). HRMS Calcd for $\text{C}_9\text{H}_{10}\text{O}$: 134.0732. Found: 134.0717.

2-Ethenyl-3-(*t*-butyl)phenyl acetate. $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 1.39 (9H, s), 2.21 (3H, s), 5.24 (1H, dd, $J = 2.4, 17.6\text{ Hz}$), 5.47 (1H, dd, $J = 2.4, 12.0\text{ Hz}$), 6.81 (1H, dd, $J = 10.7, 18.0\text{ Hz}$), 6.89 (1H, d, $J = 8.0\text{ Hz}$), 7.23 (1H, t, $J = 8.0\text{ Hz}$), 7.30 (1H, dd, $J = 1.6, 8.0\text{ Hz}$). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 21.3, 31.3, 36.6, 119.4, 120.0, 123.6, 127.4, 131.7, 133.5, 148.7, 149.6, 169.4. IR (neat) 1763 cm^{-1} . MS m/z 218 (M^+ , 11), 176 ($\text{M}^+ \text{-CH}_2\text{CO}$, 64), 161 ($\text{M}^+ \text{-C}_4\text{H}_9$, 100). HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1302.

2-Ethenyl-5-(*t*-butyl)phenyl acetate. $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 1.31 (9H, s), 2.33 (3H, s), 5.28 (1H, d, $J = 11.2\text{ Hz}$), 5.71 (1H, dd, $J = 1.6, 17.6\text{ Hz}$), 6.68 (1H, dd, $J = 10.8, 17.2\text{ Hz}$), 7.01 (1H, d, $J = 2.4\text{ Hz}$), 7.24 (1H, dd, $J = 2.0, 8.0\text{ Hz}$), 7.49 (1H, d, $J = 8.8\text{ Hz}$). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 21.1, 31.3, 34.8, 115.4, 119.3, 123.2, 125.9, 127.1, 130.1, 147.6, 152.3, 169.1. IR (neat) 1768 cm^{-1} . MS m/z 218 (M^+ , 17), 176 ($\text{M}^+ \text{-CH}_2\text{CO}$, 72), 161 ($\text{M}^+ \text{-C}_4\text{H}_9$, 100). HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1306.

1-Ethenyl-2-naphthol acetate. $^1\text{H-NMR}$ (400MHz, CDCl_3) δ 2.32 (3H, s), 5.62 (1H, dd, $J = 2.4, 17.6\text{ Hz}$), 5.72 (1H, dd, $J = 2.4, 10.7\text{ Hz}$), 6.95 (1H, dd, $J = 10.7, 17.6\text{ Hz}$), 7.19 (1H, d, $J = 8.8\text{ Hz}$), 7.44-7.54 (2H, m), 7.78 (1H, d, $J = 8.8\text{ Hz}$), 7.83 (1H, d, $J = 8.0\text{ Hz}$), 8.09 (1H, d, $J = 8.0\text{ Hz}$). $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ 21.1, 121.5, 121.8, 125.1, 125.6, 126.6, 127.1, 128.3, 128.7, 129.8, 131.9, 132.2, 145.3, 169.5. IR (neat) 1758 cm^{-1} . MS m/z 212 (M^+ , 21), 170 ($\text{M}^+ \text{-CH}_2\text{CO}$, 100). HRMS Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: 212.0837. Found: 212.0835.

2-Ethenyl-4-(*t*-butyldimethylsilyloxy)phenyl acetate. Mp 74.3-75.1 °C (hexane). $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 0.21 (6H, s), 0.99 (9H, s), 2.30 (3H, s), 5.31 (1H, dd, $J = 11.0, 1.1\text{ Hz}$), 5.69 (1H, dd, $J = 17.6, 1.1\text{ Hz}$), 6.67 (1H, dd, $J = 17.6, 11.2\text{ Hz}$), 6.74 (1H, dd, $J = 8.7, 2.8\text{ Hz}$), 6.89 (1H, d, $J = 8.7\text{ Hz}$), 7.00 (1H, d, $J = 2.8\text{ Hz}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ -4.5, 18.1, 20.8, 25.6, 116.2,

117.1, 120.1, 123.1, 130.3, 130.9, 142.1, 153.4, 169.5. FT-IR (KBr) 1761, 1752, 872 cm⁻¹. MS (EI, 70 eV) *m/z* 292 (M^+ , 43), 250 (M^+-CH_2CO , 100), 193 ($M^+-CH_2CO-C_4H_9$, 99). HRMS (EI, 70eV) Calcd for C₁₆H₂₄O₃Si: 292.1492. Found: 292.1506.

2-Ethenyl-4-(triethylsilyloxy)phenyl acetate. ¹H-NMR (400 MHz, CDCl₃) δ 0.74 (6H, q, *J* = 8.1 Hz), 1.01 (9H, t, *J* = 8.2 Hz), 2.30 (3H, s), 5.30 (1H, d, *J* = 11.0 Hz), 5.68 (1H, d, *J* = 17.6 Hz), 6.67 (1H, dd, *J* = 11.0, 17.6 Hz), 6.74 (1H, dd, *J* = 3.0, 8.6 Hz), 6.88 (1H, d, *J* = 8.6 Hz), 7.01 (1H, d, *J* = 2.9 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.9, 6.6, 20.9, 116.2, 116.9, 120.0, 123.1, 130.3, 130.8, 142.1, 153.4, 170.0. FT-IR (neat) 1767 cm⁻¹. MS (EI, 70 eV) *m/z* 292 (M^+ , 43), 250 (M^+-CH_2CO , 100). HRMS (EI, 70eV) Calcd for C₁₆H₂₄O₃Si: .292.1408. Found: 292.1515.

2-Ethenyl-1,4-benzendiol diacetate. ¹H-NMR (400 MHz, CDCl₃) δ 2.30 (3H, s), 2.33 (3H, s), 5.36 (1H, brd, *J* = 11.0 Hz), 5.73 (1H, brd, *J* = 17.6 Hz), 6.70 (1H, dd, *J* = 17.6, 11.0 Hz), 7.01 (1H, dd, *J* = 8.8, 2.7Hz), 7.05 (1H, d, *J* = 9.0 Hz), 7.28 (1H, d, *J* = 2.2 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.7, 20.9, 117.1, 119.0, 121.6, 123.3, 129.6, 131.2, 145.2, 148.2, 169.0, 169.1. FT-IR (neat) 1767, 916, 835 cm⁻¹. MS (EI, 70 eV) *m/z* 220 (M^+ , 19), 178 (M^+-CH_2CO , 22), 136 ($M^+-CH_2CO-CH_2CO$, 100). HRMS (EI, 70eV) Calcd for C₁₂H₁₂O₄: 220.0736. Found: 220.0732.

3-Ethenyl-4-acetoxyphenyl pivalate. ¹H-NMR (400 MHz, CDCl₃) δ 1.36 (9H, s), 2.32 (3H, s), 5.37 (1H, dd, *J* = 11.0, 0.7 Hz), 5.74 (1H, dd, *J* = 17.6, 1.0 Hz), 6.71 (1H, dd, *J* = 17.6, 11.0 Hz), 6.98 (1H, dd, *J* = 8.8, 2.7 Hz), 7.04 (1H, s), 7.25 (1H, d, *J* = 2.7 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.8, 27.1, 39.1, 117.2, 119.1, 121.6, 123.3, 129.7, 131.2, 145.2, 148.8, 169.1, 175.9. FT-IR (neat) 1767, 1758, 911 cm⁻¹. MS (EI, 70 eV) *m/z* 262 (M^+ , 14), 220 (M^+-CH_2CO , 49), 136 ($M^+-CH_2CO-C_5H_8CO$, 100). HRMS (EI, 70eV) Calcd for C₁₅H₁₈O₄: 262.1203. Found: 262.1192. Anal. Calcd for C₁₅H₁₈O₄: C; 69.06, H; 6.30%. Found: C; 68.68, H; 6.92%.

2-Ethenyl-4-(benzyloxycarbonyloxy)phenyl acetate. ¹H-NMR (400 MHz, CDCl₃) δ 2.32 (3H, s), 5.27 (2H, s), 5.37 (1H, brd, *J* = 11.1 Hz), 5.73 (1H, dd, *J* = 17.6, 0.6 Hz), 6.70 (1H, dd, *J* = 17.6, 11.0 Hz), 7.05 (1H, d, *J* = 8.8 Hz), 7.11 (1H, dd, *J* = 8.8, 2.7 Hz), 7.37-7.51 (6H, m). ¹³C-NMR (100 MHz, CDCl₃) δ 20.8, 70.4, 117.4, 118.7, 121.1, 123.5, 128.5, 128.7, 128.8, 129.5, 131.4, 134.6, 145.4, 148.8, 153.4, 169.0. IR (neat) 1767, 1630, 932, 903 cm⁻¹. MS (EI, 70 eV) *m/z* 312 (M^+ , 38), 226 ($M^+-C_3H_2CO_3$, 100). HRMS (EI, 70eV) Calcd for C₁₈H₁₆O₅: 312.0997. Found: 312.1000.

2-Ethenyl-4-(*p*-toluenesulfonyloxy)phenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.31 (3H, s), 3.45 (3H, s), 5.33 (1H, brd, J = 11.0 Hz), 5.58 (1H, brd, J = 17.6 Hz), 6.63 (1H, dd, J = 17.6, 11.0 Hz), 6.86 (1H, dd, J = 8.8, 2.7 Hz), 6.96 (1H, d, J = 8.8 Hz), 7.15 (1H, d, J = 2.9 Hz), 7.33 (2H, d, J = 8.4 Hz), 7.73 (2H, d, J = 8.3 Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.7, 21.6, 117.7, 120.5, 122.2, 123.6, 128.5, 129.2, 129.7, 131.6, 132.0, 145.5, 146.2, 147.1, 168.8. FT-IR (neat) 1767, 907 cm^{-1} . MS (EI, 70 eV) m/z 332 (M^+ , 27), 306 ($\text{M}^+-\text{C}_2\text{H}_2$, 16), 290 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 267 ($\text{M}^+-\text{CH}_2\text{CO}-\text{C}_2\text{H}_2$, 79). HRMS (EI, 70eV) Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_5\text{S}$: .332.0718 Found: 332.0711.

2-Ethenyl-4-(trifluoromethanesulfonyloxy)phenyl acetate. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 2.32 (3H, s), 5.44 (1H, dd, J = 11.1, 0.6 Hz), 5.78 (1H, dd, J = 17.6, 0.7 Hz), 6.72 (1H, dd, J = 17.6, 11.1 Hz), 7.13 (1H, dd, J = 8.9, 0.8 Hz), 7.18 (1H, dd, J = 8.9, 2.5 Hz), 7.45 (1H, d, J = 2.4 Hz). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 20.5, 118.5, 118.6 (q, J = 318.7 Hz), 119.0, 121.0, 124.4, 128.8, 132.5, 147.0, 147.1, 168.6. FT-IR (neat) 1771, 938, 909, 854 cm^{-1} . MS (EI, 70 eV) m/z 310 (M^+ , 36), 268 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 135 ($\text{M}^+-\text{CH}_2\text{CO}-\text{CF}_3\text{SO}_2$, 88). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_9\text{O}_5\text{SF}_3$: 310.0123. Found: 310.0123.

6-Ethenyl-2-methoxyphenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.35 (3H, s), 3.82 (3H, s), 5.34 (1H, dd, J = 11.0, 1.2 Hz), 5.76 (1H, dd, J = 17.6, 1.2 Hz), 6.75 (1H, dd, J = 17.6, 11.0 Hz), 6.88 (1H, dd, J = 6.4, 3.4 Hz), 7.16 (1H, d, J = 3.2 Hz), 7.17 (1H, d, J = 6.1 Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.4, 56.0, 111.3, 116.7, 117.8, 126.3, 130.1, 131.4, 137.4, 151.3, 168.7. FT-IR (neat) 3004, 2838, 1767, 1578, 1476, 1275, 1213, 1173, 916, 787 cm^{-1} . MS (EI, 70 eV) m/z 192 (M^+ , 30), 150 ($\text{M}^+-\text{CH}_2\text{CO}$, 100). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: 192.0786. Found: 192.0792.

6-Ethenyl-2-(*t*-butyldimethylsilyloxy)phenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 0.20 (6H, s), 0.98 (9H, s), 2.31 (3H, s), 5.31 (1H, dd, J = 11.2, 1.2 Hz), 5.74 (1H, dd, J = 17.6, 1.1 Hz), 6.72 (1H, dd, J = 17.6, 11.0 Hz), 6.82 (1H, dd, J = 7.7, 1.5 Hz), 7.07 (1H, t, J = 7.9 Hz), 7.15 (1H, dd, J = 7.8, 1.5 Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ -4.6, 18.1, 20.6, 25.6, 116.4, 118.5, 119.3, 126.1, 130.5, 131.8, 139.6, 147.6, 168.3. FT-IR (neat) 1771, 911, 839, 792, 783 cm^{-1} . MS (EI, 70 eV) m/z 292 (M^+ , 1), 235 ($\text{M}^+-\text{C}_4\text{H}_9$, 37), 193 ($\text{M}^+-\text{C}_4\text{H}_9-\text{CH}_2\text{CO}$, 100). HRMS (EI, 70eV) Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Si}$: 292.1495. Found: 292.1492.

6-Ethenyl-3-methoxyphenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.33 (3H, s), 3.80 (3H, s), 5.21 (1H, dd, $J = 11.0, 1.0$ Hz), 5.63 (1H, dd, $J = 17.6, 1.2$ Hz), 6.59 (1H, d, $J = 2.7$ Hz), 6.65 (1H, dd, $J = 17.6, 11.0$ Hz), 6.79 (1H, dd, $J = 8.7, 2.6$ Hz), 7.49 (1H, d, $J = 8.8$ Hz) $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.9, 55.5, 107.8, 116.4, 112.6, 114.1, 127.1, 129.9, 148.7, 159.9, 169.2. FT-IR (neat) 1765, 1628, 893, 817 cm^{-1} . MS (EI, 70 eV) m/z 192 (M^+ , 31), 150 ($\text{M}^+-\text{CH}_2\text{CO}$, 100). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: 192.0788. Found: 192.0795.

2-Ethenyl-3-methoxyphenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.29 (3H, s), 3.86 (3H, s), 5.54 (1H, dd, $J = 12.0, 2.2$ Hz), 5.85 (1H, dd, $J = 17.8, 2.2$ Hz), 6.75 (1H, dd, $J = 18.1, 11.0$ Hz), 6.75 (1H, dd, $J = 8.1, 1.0$ Hz), 6.79 (1H, d, $J = 8.3$ Hz), 7.21 (1H, t, $J = 8.3$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.1, 55.8, 108.5, 115.0, 119.6, 127.3, 128.2, 130.5, 149.1, 158.5, 169.3. FT-IR (neat) 1769, 1626, 749 cm^{-1} . MS (EI, 70 eV) m/z 192 (M^+ , 67), 150 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 135 ($\text{M}^+-\text{C}_3\text{H}_5\text{O}$, 65). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: 192.0786. Found: 192.0784.

6-Ethenyl-3-(*t*-butyldiphenylsilyloxy)phenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.09 (9H, s), 2.24 (3H, s), 5.15 (1H, dd, $J = 11.0, 1.0$ Hz), 5.54 (1H, dd, $J = 17.6, 1.0$ Hz), 6.52-6.57 (2H, m), 6.58 (1H, dd, $J = 17.6, 11.0$ Hz), 7.24 (1H, d, $J = 8.7$ Hz), 7.35-7.46 (6H, m), 7.68-7.73 (4H, m). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 19.4, 20.8, 26.4, 114.0, 114.1, 117.7, 123.2, 126.6, 127.8, 129.9, 123.0, 132.4, 135.4, 148.5, 155.9, 168.9. FT-IR (neat) 1769, 1611, 910, 821 cm^{-1} . MS (EI, 70 eV) m/z 416 (M^+ , 22), 359 ($\text{M}^+-\text{C}_4\text{H}_9$, 82), 317 ($\text{M}^+-\text{C}_4\text{H}_9-\text{CH}_2\text{CO}$, 100). HRMS (EI, 70eV) Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3\text{Si}$: 416.1808. Found 416.1803.

2-Ethenyl-3-(*t*-butyldiphenylsilyloxy)phenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.08 (9H, s), 2.29 (3H, s), 5.54 (1H, dd, $J = 12.0, 2.2$ Hz), 5.83 (1H, dd, $J = 17.8, 2.2$ Hz), 6.31 (1H, dd, $J = 8.3, 1.0$ Hz), 6.57 (1H, dd, $J = 8.1, 1.0$ Hz), 6.75 (1H, dd, $J = 8.1, 1.0$ Hz), 6.92 (1H, dd, $J = 18.2, 12.0$ Hz), 7.35-7.46 (6H, m), 7.68-7.73 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 19.5, 21.2, 26.4, 115.3, 117.0, 119.3, 122.2, 127.4, 127.9, 128.4, 130.0, 132.3, 135.4, 149.2, 154.1, 169.2. FT-IR (neat) 1767, 1603, 745, 702 cm^{-1} .

6-Ethenyl-1,3-benzendiol diacetate. Isolated by alumina column chromatography. Silica gel chromatography caused decomposition. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.29 (3H, s), 2.32 (3H, s), 5.33 (1H, dd, $J = 11.0, 1.0$ Hz), 5.72 (1H, dd, $J = 17.6, 1.0$ Hz), 6.71 (1H, dd, $J = 17.6, 11.0$ Hz), 6.90 (1H, d, $J = 2.4$ Hz), 6.99 (1H, dd, $J = 8.6, 2.2$ Hz), 7.55 (1H, d, $J = 8.5$ Hz). $^{13}\text{C-NMR}$ (100

MHz, CDCl₃) δ 20.8, 21.0, 116.1, 116.4, 119.4, 126.9, 127.9, 129.6, 148.0, 150.3, 168.8, 168.9. FT-IR (neat) 1768, 1630, 916, 827 cm⁻¹. MS (EI, 70 eV) *m/z* 220 (M⁺, 23), 178 (M⁺-CH₂CO, 30), 136 (M⁺-CH₂COx2, 100). HRMS (EI, 70eV) Calcd for C₁₂H₁₂O₄: 220.0735. Found: 220.0729.

2-Ethenyl-1,3-benzendiol diacetate. Isolated by alumina column chromatography. Silica gel chromatography caused decomposition. ¹H-NMR (400 MHz, CDCl₃) δ 2.29 (6H, s), 5.50 (1H, dd, *J* = 11.7, 1.7 Hz), 5.71 (1H, dd, *J* = 18.1, 1.9 Hz), 6.49 (1H, dd, *J* = 18.1, 11.7 Hz), 6.97 (2H, d, *J* = 8.3 Hz), 7.28 (1H, t, *J* = 8.3 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.9, 120.3, 120.9, 124.5, 126.8, 127.9, 149.0, 168.8. FT-IR (neat) 1770, 1630, 756 cm⁻¹. MS (EI, 70 eV) *m/z* 220 (M⁺, 25), 178 (M⁺-CH₂CO, 31), 136 (M⁺-CH₂COx2, 100). HRMS (EI, 70eV) Calcd for C₁₁H₁₂O₃: 220.0735. Found: 220.0742.

4-Ethenyl-3-acetoxyphenyl pivalate. Mp 84.1-86.2 °C (hexane). ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (9H, s), 2.32 (3H, s), 5.33 (1H, dd, *J* = 11.1, 1.1 Hz), 5.72 (1H, dd, *J* = 17.6, 1.2 Hz), 6.71 (1H, dd, *J* = 17.6, 11.0 Hz), 6.87 (1H, d, *J* = 2.4 Hz), 6.97 (1H, dd, *J* = 8.5, 2.3 Hz), 7.55 (1H, d, *J* = 8.5 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.8, 27.1, 39.1, 116.0, 116.3, 119.4, 126.8, 127.7, 129.7, 148.1, 150.8, 168.9, 176.5. FT-IR (KBr) 1771, 1753, 1628, 910 cm⁻¹. MS (EI, 70 eV) *m/z* 262 (32, M⁺), 220 (34, M⁺-CH₂CO), 136 (100, M⁺-C₇H₁₀O₂). HRMS (EI, 70eV) Calcd for C₁₅H₁₈O₄: 262.1205. Found: 262.1200.

2-Ethenyl-3-acetoxyphenyl pivalate. ¹H-NMR (200 MHz, CDCl₃) δ 1.35 (9H, s), 2.28 (3H, s), 5.49 (1H, dd, *J* = 11.7, 1.9 Hz), 5.65 (1H, dd, *J* = 18.0, 1.9 Hz), 6.48 (1H, dd, *J* = 17.9, 11.6 Hz), 6.92 (1H, dd, *J* = 8.0, 1.1 Hz), 6.96 (1H, dd, *J* = 6.6, 1.1 Hz), 7.26 (1H, dd, *J* = 7.7, 7.1 Hz). ¹³C-NMR (50 MHz, CDCl₃) δ 20.9, 27.0, 39.0, 120.0, 120.1, 120.9, 124.8, 126.6, 127.8, 148.9, 149.2, 168.7, 176.2. FT-IR (neat) 1771, 1752, 974, 933, 754 cm⁻¹. MS (EI, 70 eV) *m/z* 262 (M⁺, 37), 220 (M⁺-CH₂CO, 30), 178 (M⁺-C₄H₈CO, 12), 136 (M⁺-C₄H₈CO-CH₂CO, 100). HRMS (EI, 70eV) Calcd for C₁₅H₁₈O₄: 262.1205. Found: 262.1219.

6-Ethenyl-3-trifluoromethanesulfonyloxyphenyl acetate. ¹H-NMR (400 MHz, CDCl₃) δ 2.35 (3H, s), 5.43 (1H, dd, *J* = 11.2, 0.8 Hz), 5.78 (1H, dd, *J* = 17.7, 0.7 Hz), 6.72 (1H, dd, *J* = 17.6, 11.0 Hz), 7.07 (1H, d, *J* = 2.5 Hz), 7.17 (1H, dd, *J* = 8.6, 2.4 Hz), 7.63 (1H, d, *J* = 8.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.7, 116.3, 118.2, 118.5 (q, *J* = 328 Hz), 119.5, 127.6, 128.9, 130.8, 148.2, 148.3, 168.4. FT-IR (neat) 1774, 1633, 963, 904, 835 cm⁻¹. MS (EI, 70 eV) *m/z* 310 (M⁺, 10), 284

($M^+ - C_2H_2$, 36), 242 ($M^+ - CH_2CO - C_2H_2$, 100). HRMS (EI, 70 eV) Calcd for $C_{11}H_9O_5SF_3$: 310.0123. Found: 310.0118.

2-Ethenyl-3-trifluoromethanesulfonyloxyphenyl acetate. 1H -NMR (200 MHz, $CDCl_3$) δ 2.30 (3H, s), 5.68 (1H, dd, J = 11.7, 1.5 Hz), 5.81 (1H, dd, J = 18.0, 1.5 Hz), 6.57 (1H, dd, J = 18.1, 11.7 Hz), 7.12, (1H, dd, J = 8.1, 1.1 Hz), 7.21 (1H, dd, J = 8.3, 1.0 Hz), 7.26 (1H, t, J = 8.3 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 20.9, 118.5 (q, J = 320.4 Hz), 119.3, 123.0, 123.7, 125.4, 125.8, 128.4, 147.5, 149.4, 168.6. FT-IR (neat) 1777, 1633, 970, 750 cm^{-1} . MS (EI, 70 eV) m/z 310 (M^+ , 11), 284 ($M^+ - C_2H_2$, 35), 242 ($M^+ - CH_2CO - C_2H_2$, 100). HRMS (EI, 70 eV) Calcd for $C_{11}H_9O_5SF_3$: 310.0123. Found: 310.0121.

6-Ethenyl-5-acetoxy-1,3-benzendiol dipivalate. Mp 84.1-86.2 °C (hexane). 1H -NMR (400 MHz, $CDCl_3$) δ 1.32 (9H, s), 1.33 (9H, s), 2.27 (3H, s), 5.47 (1H, dd, J = 11.8, 2.0 Hz), 5.63 (1H, dd, J = 18.0, 1.9 Hz), 6.42 (1H, dd, J = 17.9, 11.7 Hz), 6.78 (1H, d, J = 2.0 Hz), 6.81 (1H, d, J = 2.0 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 20.9, 27.0, 27.1, 39.1, 113.8, 113.9, 121.0, 122.3, 126.2, 149.0, 149.3, 149.9, 168.5, 176.1. FT-IR (KBr) 1771, 1755, 907 cm^{-1} . MS (EI, 70 eV) m/z 362 (M^+ , 78), 320 ($M^+ - C_2H_2$, 66), 278 ($M^+ - C_4H_8CO$, 61), 236 ($M^+ - C_4H_8CO - C_2H_2$, 100). HRMS (EI, 70 eV) Calcd for $C_{20}H_{26}O$: 362.1728. Found 362.1736.

2-Ethenyl-3,5-bis(*t*-butyldimethylsilyloxy)phenyl acetate. 1H -NMR (400 MHz, $CDCl_3$) δ 0.20 (6H, s), 0.22 (6H, s), 0.96 (9H, s), 0.99 (9H, s), 2.26 (3H, s), 5.31 (1H, dd, J = 2.2, 11.8 Hz), 5.64 (1H, dd, J = 2.5, 18.1 Hz), 6.19 (1H, d, J = 2.2 Hz), 6.21 (1H, d, J = 2.2 Hz), 6.60 (1H, dd, J = 11.8, 18.1 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ -4.4, -4.1, 18.2, 18.3, 21.2, 25.6, 25.7, 108.2, 109.1, 116.2, 117.2, 128.1, 149.8, 154.9, 155.1, 168.9. FT-IR (neat) 1772 cm^{-1} . MS (EI, 70 eV) m/z 422 (M^+ , 91), 366 ($M^+ - C_4H_8$, 14), 323 ($M^+ - C_4H_8 - CH_3CO$, 100). HRMS (EI, 70 eV) Calcd for $C_{22}H_{38}O_4Si_2$: 422.2308. Found: 422.2306.

2-Ethenyl-3,5-bis(triethylsilyloxy)phenyl acetate. The reaction was quenched by stirring with K_2CO_3 in methanol-water (5:1) for 4 h at room temperature. 1H -NMR (400 MHz, $CDCl_3$) δ 0.72 (12H, q, J = 8.0 Hz), 0.76 (18H, q, J = 8.0 Hz), 2.26 (3H, s), 5.31 (1H, dd, J = 2.2, 11.8 Hz), 5.71 (1H, dd, J = 2.4, 18.1 Hz), 6.21 (1H, d, J = 2.4 Hz), 6.23 (1H, d, J = 2.2 Hz), 6.59 (1H, dd, J = 12.0, 18.1 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 4.9, 5.1, 6.5, 6.6, 21.2, 108.0, 108.8, 115.8, 117.1,

127.8, 149.8, 155.1, 155.1, 168.9. FT-IR (neat) 1772 cm⁻¹. MS (EI, 70 eV) *m/z* 422 (M^+ , 100), 380 ($M^+-C_2H_2$, 88). HRMS (EI, 70eV) Calcd for C₂₂H₃₈O₄Si₂: 422.2308. Found: 422.2317.

2-Ethenyl-4-nitrophenol. Isolated without acetylation. ¹H-NMR (400 MHz, CDCl₃) δ 5.51 (1H, dd, *J* = 1.0, 11.3 Hz), 5.88 (1H, dd, *J* = 0.7, 17.6 Hz), 6.63 (1H, br), 6.90 (1H, d, *J* = 8.8 Hz), 6.93 (1H, dd, *J* = 11.3, 17.9 Hz), 8.05 (1H, dd, *J* = 2.9, 9.0 Hz), 8.32 (1H, d, *J* = 2.7 Hz). ¹³C-NMR (100 MHz, CD₃OD) δ 116.4, 116.5, 123.3, 125.4, 126.6, 131.5, 141.8, 161.9. FT-IR (neat) 3450 cm⁻¹. MS (EI, 70 eV) *m/z* 165 (M^+ , 100), 139 (67). HRMS (EI, 70eV) Calcd for C₈H₇NO₂: 165.0425. Found: 165.0441.

2-Ethenyl-4-fluorophenyl acetate. ¹H-NMR (400 MHz, CDCl₃) δ 2.32 (3H, s), 5.39 (1H, d, *J* = 11.0 Hz), 5.75 (1H, d, *J* = 17.6 Hz), 6.68 (1H, ddd, *J* = 1.7, 11.2, 17.6 Hz), 6.96 (1H, ddd, *J* = 2.6, 7.5, 11.0 Hz), 7.00 (1H, dd, *J* = 5.4, 8.8 Hz), 7.24 (1H, dd, *J* = 3.0, 9.5 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.7, 112.5 (*J* = 43 Hz), 115.3 (*J* = 24 Hz), 117.4, 123.9 (*J* = 9 Hz), 129.5 (*J* = 12 Hz), 131.8 (*J* = 8 Hz), 143.7 (*J* = 3 Hz), 160.4 (*J* = 243 Hz), 169.2. FT-IR (neat) 1765, 1209, 1172 cm⁻¹. MS (EI, 70 eV) *m/z* 180 (M^+ , 13), 138 (M^+-CH_2CO , 100), 109 (M^+-CH_2CO-F , 23). HRMS (EI, 70eV) Calcd for C₁₀H₉O₂F: 180.0586. Found: 180.0585.

2-Ethenyl-4-trifluoromethylphenyl acetate. The reaction was quenched with K₂CO₃ in methanol at room temperature overnight to avoid hydrolysis of trifluoromethyl group. ¹H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 5.44 (1H, dd, *J* = 0.7, 11.0 Hz), 5.84 (1H, dd, *J* = 0.7, 17.6 Hz), 6.76 (1H, dd, *J* = 11.0, 17.6 Hz), 7.18 (1H, d, *J* = 8.6 Hz), 7.54 (1H, dd, *J* = 2.2, 8.5 Hz), 7.81 (1H, d, *J* = 2.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 21.0, 122.0, 123.5 (q, *J* = 273 Hz), 123.5 (q, *J* = 6 Hz), 126.4, 127.9, 128.4, 129.9 (q, *J* = 29 Hz), 130.9 (q, *J* = 1 Hz), 148.9, 169.0. FT-IR (neat) 1770 cm⁻¹. MS (EI, 70 eV) *m/z* 230 (M^+ , 12), 188 (M^+-Me , 100). HRMS (EI, 70eV) Calcd for C₁₁H₉O₂F₃: 230.0555. Found: 230.0561.

2-Ethenyl-4-cyanophenyl acetate. Mp 77.6-78.6 °C (ether-hexane). ¹H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 5.47 (1H, d, *J* = 11.0 Hz), 5.82 (1H, d, *J* = 17.6 Hz), 6.72 (1H, dd, *J* = 11.0, 17.6 Hz), 7.19 (1H, d, *J* = 8.3 Hz), 7.56 (1H, dd, *J* = 2.0, 8.3 Hz), 7.85 (1H, d, *J* = 2.2 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.7, 110.2, 118.1, 118.9, 123.9, 128.6, 130.7, 131.7, 131.9, 150.9, 168.3. FT-IR (KBr) 2231, 1753 cm⁻¹. MS (EI, 70 eV) *m/z* 187 (M^+ , 16), 145 (M^+-CH_2CO , 100). HRMS (EI, 70eV) Calcd for C₁₁H₉NO₂: 187.0633 Found: 187.0634.

6-Ethenyl-2-cyanophenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.43 (3H, s), 5.47 (1H, dd, $J = 0.5, 11.0$ Hz), 5.82 (1H, dd, $J = 0.5, 17.6$ Hz), 6.70 (1H, dd, $J = 11.2, 17.6$ Hz), 7.33 (1H, t, $J = 7.8$ Hz), 7.58 (1H, dd, $J = 1.5, 7.6$ Hz), 7.79 (1H, dd, $J = 1.5, 7.8$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.4, 108.2, 115.1, 118.7, 126.5, 128.7, 131.0, 132.1, 133.7, 149.5, 168.0. FT-IR (neat) 2235, 1772 cm^{-1} . MS (EI, 70 eV) m/z 187 (M^+ , 17), 145 ($\text{M}^+-\text{CH}_2\text{CO}$, 100). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_9\text{NO}_2$: 187.0633 Found: 187.0629.

6-Ethenyl-2-fluorophenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.36 (3H, s), 5.39 (1H, d, $J = 11.0$ Hz), 5.78 (1H, dd, $J = 1.0, 17.6$ Hz), 6.73 (1H, dd, $J = 11.1, 17.6$ Hz), 7.06 (1H, ddd, $J = 1.5, 8.1, 9.6$ Hz), 7.17 (1H, dt, $J = 5.4, 8.1$ Hz), 7.32 (1H, brd, $J = 7.8$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.2, 115.3 ($J = 19$ Hz), 117.6, 121.3 ($J = 4$ Hz), 126.5 ($J = 7$ Hz), 129.4 ($J = 3$ Hz), 132.6, 135.7 ($J = 14$ Hz), 154.4 ($J = 246$ Hz), 168.0. FT-IR (neat) 1770, 1209, 1180 cm^{-1} . MS (EI, 70 eV) m/z 180 (M^+ , 14), 138 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 109 ($\text{M}^+-\text{CH}_2\text{CO}-\text{F}$, 23). HRMS (EI, 70eV) Calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{F}$: 180.0586. Found: 180.0587.

6-Ethenyl-2-trifluoromethylphenyl acetate. The reaction was quenched with K_2CO_3 in methanol at room temperature overnight to avoid hydrolysis of trifluoromethyl group. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.36 (3H, s), 5.43 (1H, d, $J = 10.7$ Hz), 5.80 (1H, d, $J = 17.6$ Hz), 6.66 (1H, dd, $J = 10.7, 17.6$ Hz), 7.33 (1H, t, $J = 8.4$ Hz), 7.57 (1H, d, $J = 8.4$ Hz), 7.75 (1H, d, $J = 8.4$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.4, 118.2, 123.0 (q, $J = 271$ Hz), 123.5 (q, $J = 31$ Hz), 126.1 (q, $J = 5$ Hz), 126.1, 129.3, 130.2, 132.9, 145.5 (q, $J = 2$ Hz), 168.4. FT-IR (neat) 1774 cm^{-1} . MS (EI, 70 eV) m/z 230 (M^+ , 12), 188 (M^+-Me , 100). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_9\text{O}_2\text{F}_3$: 230.0555. Found: 230.0553.

6-Ethenyl-3-fluorophenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.33 (3H, s), 5.31 (1H, d, $J = 10.5$ Hz), 5.68 (1H, d, $J = 17.6$ Hz), 6.68 (1H, dd, $J = 11.3, 17.6$ Hz), 6.82 (1H, dd, $J = 2.0, 9.0$ Hz), 6.95 (1H, dt, $J = 2.2, 9.4$ Hz), 7.53 (1H, dd, $J = 6.3, 8.8$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.8, 110.3 ($J = 14.4$ Hz), 113.4 ($J = 21.3$ Hz), 116.6 ($J = 2.3$ Hz), 126.5 ($J = 3.8$ Hz), 127.5 ($J = 9.2$ Hz), 129.5, 148.4 ($J = 10.6$ Hz), 162.0 ($J = 249.8$ Hz), 168.7. FT-IR (neat) 1770 cm^{-1} . MS (EI, 70 eV) m/z 180 (M^+ , 18), 138 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 109 ($\text{M}^+-\text{CH}_2\text{CO}-\text{F}$, 27). HRMS (EI, 70eV) Calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{F}$: 180.0586. Found: 180.0598.

2-Ethenyl-3-fluorophenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.32 (3H, s), 5.55 (1H, dt, $J = 11.8, 1.5$ Hz), 5.92 (1H, ddd, $J = 1.0, 1.5, 18.1$ Hz), 6.57 (1H, dd, $J = 12.0, 18.1$ Hz), 6.87 (1H, dt, $J = 18.1, 1.0$ Hz), 6.98 (1H, ddd, $J = 1.0, 8.3, 10.3$ Hz), 7.21 (1H, dt, $J = 6.2, 8.4$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.8, 112.7 ($J = 24$ Hz), 115.6 ($J = 24$ Hz), 117.6, 124.1 ($J = 10$ Hz), 129.6 ($J = 2$ Hz), 132.0 ($J = 8$ Hz), 143.9 ($J = 3$ Hz), 160.5 ($J = 243$ Hz), 169.3. FT-IR (neat) 1772 cm^{-1} . MS (EI, 70 eV) m/z 180 (M^+ , 13), 138 ($\text{M}^+-\text{CH}_2\text{CO}$, 100), 109 ($\text{M}^+-\text{CH}_2\text{CO}-\text{F}$, 28). HRMS (EI, 70eV) Calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{F}$: 180.0586. Found: 180.0594.

2-Ethenyl-3-nitrophenol. Isolated without acetylation. Mp 71.0-71.6 °C (hexane-ether). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.621 (1H, dd, $J = 0.7, 18.1$ Hz), 5.81 (1H, dd, $J = 1.2, 11.5$ Hz), 6.10 (1H, s), 6.90 (1H, dd, $J = 1.5, 8.1$ Hz), 7.23 (1H, dd, $J = 1.2, 8.0$ Hz), 7.31 (1H, t, $J = 8.3$ Hz), 7.59 (1H, dd, $J = 0.7, 8.1$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 116.4, 119.8, 120.8, 121.9, 128.7, 129.6, 148.3, 153.6. FT-IR (KBr) 3462 cm^{-1} . MS (EI, 70 eV) m/z 165 (M^+ , 35), 148 (51), 136 (100). HRMS (EI, 70eV) Calcd for $\text{C}_8\text{H}_7\text{NO}_3$: 165.0425. Found: 165.0427.

6-Ethenyl-3-nitrophenol. Isolated without acetylation. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.57 (1H, d, $J = 11.3$ Hz), 5.59 (1H, s), 5.92 (1H, d, $J = 17.8$ Hz), 6.97 (1H, dd, $J = 11.3, 17.8$ Hz), 7.53 (1H, d, $J = 8.6$ Hz), 7.68 (1H, d, $J = 1.9$ Hz), 7.79 (1H, dd, $J = 2.2, 8.5$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 110.9, 116.0, 119.6, 127.6, 130.0, 131.6, 147.6, 153.1. FT-IR (KBr) 3412, 1630 cm^{-1} . MS (EI, 70 eV) m/z 165 (M^+ , 100), 91 (50). HRMS (EI, 70eV) Calcd for $\text{C}_8\text{H}_7\text{NO}_3$: 165.0425. Found: 165.0415.

6-Ethenyl-3-trifluoromethylphenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.35 (3H, s), 5.46 (1H, d, $J = 17.6$ Hz), 5.84 (1H, d, $J = 17.6$ Hz), 6.75 (1H, dd, $J = 11.2, 17.6$ Hz), 7.33 (1H, brs), 7.47 (1H, d, $J = 8.0$ Hz), 7.66 (1H, d, $J = 8.0$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 20.8, 118.8, 120.1 (q, $J = 3$ Hz), 122.9 (q, $J = 4$ Hz), 123.4 (q, $J = 273$ Hz), 127.1, 129.4, 130.6 (q, $J = 34$ Hz), 133.8 (q, $J = 2$ Hz), 147.8, 168.8. FT-IR (neat) 1772 cm^{-1} . MS (EI, 70 eV) m/z 230 (M^+ , 25), 188 (M^+-Me , 100). HRMS (EI, 70eV) Calcd for $\text{C}_{11}\text{H}_9\text{O}_2\text{F}_3$: 230.0555. Found: 230.0561.

2-Ethenyl-3-trifluoromethylphenyl acetate. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.26 (3H, s), 5.53 (1H, dd, $J = 1.7, 17.8$ Hz), 5.58 (1H, dd, $J = 1.7, 11.7$ Hz), 6.68 (1H, ddq, $J = 11.8, 17.8, 1.6$ Hz), 7.24 (1H, d, $J = 7.9$ Hz), 7.36 (1H, t, $J = 8.0$ Hz), 7.56 (1H, d, $J = 7.3$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.0, 122.0, 123.6 (q, $J = 273$ Hz), 123.6 (q, $J = 6$ Hz), 126.5, 127.9, 128.4, 129.8 (q, $J =$

30 Hz), 130.9, 148.9, 169.0. FT-IR (neat) 1770 cm⁻¹. MS (EI, 70 eV) *m/z* 230 (M^+ , 7), 188 (M^+-Me , 100). HRMS (EI, 70eV) Calcd for C₁₁H₉O₂F₃: 230.0555. Found: 230.0559.

Acetates of 2,6-diethenylphenols.

2,6-Diethenyl-4-(*t*-butyl)phenyl acetate. ¹H-NMR (200 MHz, CDCl₃) δ 1.35 (9H, s), 2.34 (3H, s), 5.32 (2H, dd, *J* = 11.1, 0.6 Hz), 5.75 (2H, dd, *J* = 17.6, 1.2 Hz), 6.77 (2H, dd, *J* = 17.6, 9.4 Hz), 7.48 (2H, s). ¹³C-NMR (50 MHz, CDCl₃) δ 20.4, 31.2, 34.4, 116.2, 122.9, 129.9, 130.8, 143.3, 148.5, 168.8. IR (neat) 1769, 1011, 920, 828, 669 cm⁻¹. MS (EI) *m/z* 244 (M^+ , 8), 161 (100). HRMS. Calcd for C₁₆H₂₀O₂: 244.1463. Found: 244.1448.

2,6-Diethenylphenyl acetate. ¹H-NMR (200 MHz, CDCl₃) δ 2.35 (3H, s), 5.34 (2H, dd, *J* = 11.1, 1.1 Hz), 5.75 (2H, dd, *J* = 17.6, 1.2 Hz), 6.71 (2H, dd, *J* = 17.6, 10.7 Hz), 7.20 (1H, t, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 8.0 Hz). ¹³C-NMR (50 MHz, CDCl₃) δ 20.3, 116.5, 125.7, 126.0, 130.2, 130.7, 145.3, 168.6. IR (neat) 1769, 1011, 917, 803 cm⁻¹. MS (EI) *m/z* 188 (M^+ , 9), 112 (100).

2,6-Diethenyl-4-methylphenyl acetate. ¹H-NMR (200 MHz, CDCl₃) δ 2.34 (3H, s), 2.35 (3H, s), 5.31 (2H, dd, *J* = 11.1, 1.1 Hz), 5.72 (2H, dd, *J* = 18.2, 1.2 Hz), 6.67 (2H, dd, *J* = 17.6, 11.1 Hz), 7.29 (2H, s). ¹³C-NMR (50 MHz, CDCl₃) δ 20.4, 20.9, 116.3, 126.3, 130.3 (two peaks), 135.5, 143.3, 168.9. IR (neat) 1771 cm⁻¹. MS (EI) *m/z* 202 (M^+ , 15), 160 (100), 145 (79).

2,6-Diethenyl-4-(*t*-butyldimethylsilyloxy)phenyl acetate. The reaction mixture was treated with excess K₂CO₃ and methanol for 1 h at room temperature. ¹H-NMR (200MHz, CDCl₃) δ 0.22 (6H, s), 1.00 (9H, s), 2.33 (3H, s), 5.31 (2H, dd, *J* = 11.0, 1.1 Hz), 5.68 (2H, dd, *J* = 17.5, 1.1 Hz), 6.63 (2H, dd, *J* = 17.5, 11.0 Hz), 6.92 (2H, s). ¹³C-NMR (50 MHz, CDCl₃) δ -4.5, 18.1, 20.4, 25.6, 116.5, 116.8, 130.4, 131.7, 139.9, 153.3, 169.0. IR (neat) 1771, 1593, 988, 911, 851, 783 cm⁻¹. MS (EI) *m/z* 318 (M^+ , 32), 276 (100).

2,6-Diethenyl-4-(*t*-butyldiphenylsilyloxy)phenyl acetate. The reaction mixture was treated with excess K₂CO₃ and methanol for 1 h at room temperature. ¹H-NMR (200MHz, CDCl₃) δ 1.13 (9H, s), 2.28 (3H, s), 5.15 (2H, dd, *J* = 11.6, 0.7 Hz), 5.32 (2H, dd, *J* = 17.5, 0.7 Hz), 6.51 (2H, dd, *J* = 17.4, 11.0 Hz), 6.82 (2H, s), 7.34-7.43 (6H, m), 7.70-7.75 (4H, m). ¹³C-NMR (50 MHz, CDCl₃) δ 19.5, 20.4, 26.6, 116.5, 127.8, 130.0, 130.1, 130.1, 131.4, 132.7, 135.5, 139.6, 153.3, 169.0. IR (KBr) 1771, 1591, 1013, 984, 909, 874, 795 cm⁻¹. MS (EI) *m/z* 442 (M^+ , 69), 385 (100).

2,6-Diethenyl-4-phenylphenyl acetate and 2-ethenyl-4-phenylphenyl acetate. $^1\text{H-NMR}$ (200 MHz, CDCl_3 , ^mmonovinyl derivative, ^ddivinyl derivative) δ 2.37 (3H, s), 2.39 (3H, s), 5.39 (2+1H, dd, J = 11.0, 1.0 Hz)^{m,d}, 5.82 (1H, dd, J = 17.6, 1.1 Hz)^m, 5.84 (2H, dd, J = 17.6, 1.1 Hz)^d, 6.76 (1H, dd, J = 17.7, 11.2 Hz)^m, 6.80 (2H, dd, J = 17.5, 11.1 Hz)^d, 7.13 (1H, d, J = 8.3 Hz)^m, 7.39-7.49 (7+1H, m), 7.52-7.61 (3H, m), 7.67 (2H, s)^d, 7.76 (1H, d, J = 1.4 Hz)^m. $^{13}\text{C-NMR}$ (50 MHz, CDCl_3 , mixture of mono- and divinyl derivatives) δ 20.3, 20.6, 116.4, 116.8, 122.7, 124.5, 125.0, 126.8, 126.9, 127.1, 127.2, 128.5, 130.0, 130.1, 130.2, 130.9, 139.0, 139.1, 140.0, 140.1, 144.8, 147.1, 168.6, 168.9. IR (neat) 1769, 1011, 919, 886, 764 cm^{-1} . MS (EI) m/z 264 (M^+ , 4)^d, 238 (M^+ , 10)^m, 196 (100).

2,6-Diethenyl-4-pivaloyloxyphenyl acetate. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 1.37 (9H, s), 2.35 (3H, s), 5.36 (2H, dd, J = 11.1, 0.9 Hz), 5.73 (2H, dd, J = 17.6, 1.0 Hz), 6.65 (2H, dd, J = 17.6, 10.5 Hz), 7.16 (2H, s). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 20.7, 27.0, 39.0, 117.5, 118.4, 129.8, 132.0, 142.7, 148.7, 169.0, 176.7. IR (neat) 1767, 1595, 1011, 911, 835, 760 cm^{-1} . MS (EI) m/z 288 (M^+ , 2), 57 (C_4H_9 , 100). HRMS. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_4$: 288.1362. Found: 288.1357.

2,6-Diethenyl-3-methylphenyl acetate. $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 2.27 (3H, s), 2.31 (3H, s), 5.27 (1H, dd, J = 17.6, 1.2 Hz), 5.44 (1H, dd, J = 15.2, 2.0 Hz), 5.51 (1H, dd, J = 9.1, 2.0 Hz), 5.70 (1H, dd, J = 17.6, 1.2 Hz), 6.54 (1H, dd, J = 17.8, 11.7 Hz), 6.68 (1H, dd, J = 17.2, 10.6 Hz), 7.06 (1H, d, J = 8.1 Hz), 7.37 (1H, d, J = 7.9 Hz). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 20.2, 20.8, 115.6, 120.0, 124.5, 127.0, 127.9, 128.2, 130.4, 131.0, 137.2, 145.6, 168.8. IR (neat) 1769, 1025, 915, 826 cm^{-1} . MS (EI) m/z 202 (M^+ , 21), 160 (100), 145 (96).

2,6-Diethenyl-3-methoxyphenyl acetate. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.31 (3H, s), 3.86 (3H, s), 5.22 (1H, dd, J = 11, 1 Hz), 5.48 (1H, dd, J = 12, 2 Hz), 5.63 (1H, dd, J = 17.5, 1 Hz), 5.83 (1H, dd, J = 18, 2.5 Hz), 6.62 (1H, dd, J = 11, 18 Hz), 6.64 (1H, dd, J = 11, 17.5 Hz), 6.80 (1H, d, J = 8.5 Hz), 7.43 (1H, d, J = 8.5 Hz). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 20.9, 55.9, 108.9, 114.7, 119.9, 120.1, 123.8, 125.6, 127.5, 130.3, 146.6, 157.9, 168.8. IR (neat) 1769, 1630, 1180, 1096, 913, 814 cm^{-1} . MS (EI) m/z 218 (M^+ , 43), 176 ($\text{M}^+-\text{CH}_2\text{CO}$, 100). HRMS. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$: 218.0942. Found: 218.0944.

2,6-Diethenyl-3-(*t*-butyldimethylsilyloxy)phenyl acetate. The reaction mixture was treated with excess K_2CO_3 in THF-water for 1 h at room temperature. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 0.22

(6H, s), 0.99 (9H, s), 2.29 (3H, s), 5.22 (1H, dd, $J = 11.0, 1.0$ Hz), 5.44 (1H, dd, $J = 11.5, 2.0$ Hz), 5.62 (1H, dd, $J = 18.0, 1.0$ Hz), 5.72 (1H, dd, $J = 18.0, 2.0$ Hz), 6.61 (1H, dd, $J = 18.0, 12.0$ Hz), 6.63 (1H, dd, $J = 18.0, 11.0$ Hz), 6.71 (1H, d, $J = 8.5$ Hz), 7.33 (1H, d, $J = 8.5$ Hz). ^{13}C -NMR (125 MHz, CDCl_3) δ -4.1, 18.3, 21.0, 25.7, 114.6, 117.3, 119.4, 122.9, 124.1, 125.1, 128.5, 130.3, 146.7, 154.0, 168.7. IR (neat) 1771, 1630, 1038, 909, 843, 781 cm^{-1} . MS (EI) m/z 318 (M^+ , 28%), 261 ($\text{M}^+-\text{C}_4\text{H}_9$, 27) 219 ($\text{M}^+-\text{C}_4\text{H}_9-\text{CH}_2\text{CO}$, 100). HRMS. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Si}$: 318.1651. Found: 318.1698.

2,6-Diethenyl-3-(*t*-butyldiphenylsilyloxy)phenyl acetate. The reaction mixture was treated with excess K_2CO_3 in THF-water for 1 h at room temperature. ^1H -NMR (200 MHz, CDCl_3) δ 1.07 (9H, s), 2.31 (3H, s), 5.14 (1H, dd, $J = 11.0, 1.1$ Hz), 5.49 (1H, dd, $J = 17.6, 1.2$ Hz), 5.55 (1H, dd, $J = 11.8, 2.2$ Hz), 5.82 (1H, dd, $J = 18.1, 2.2$ Hz), 6.31 (1H, d, $J = 8.8$ Hz), 6.58 (1H, dd, $J = 17.6, 11.0$ Hz), 6.86 (1H, dd, $J = 18.1, 11.9$ Hz), 7.00 (1H, d, $J = 8.8$ Hz), 7.37-7.44 (6H, m), 7.69-7.74 (4H, m). ^{13}C -NMR (50 MHz, CDCl_3) δ 19.4, 20.9, 26.4, 114.4, 117.2, 119.4, 122.4, 123.8, 124.7, 127.8, 128.5, 130.0, 130.0, 132.2, 135.3, 146.5, 153.6, 168.7. IR (neat) 1771, 1630, 1042, 911, 822, 783 cm^{-1} . MS (EI) m/z 442 (M^+ , 19), 343 ($\text{M}^+-\text{C}_4\text{H}_9-\text{CH}_2\text{CO}$, 100). HRMS. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_3\text{Si}$: 442.1964. Found: 442.1955.

2,6-Diethenyl-3,5-bis(*t*-butyldimethylsilyloxy)phenyl acetate. The reaction mixture was treated with excess K_2CO_3 in THF-water for 1 h at room temperature. ^1H -NMR (200 MHz, CDCl_3) δ 0.22 (12H, s), 0.99 (18H, s), 2.23 (3H, s), 5.33 (2H, dd, $J = 11.8, 2.3$ Hz), 5.65 (2H, dd, $J = 18.0, 2.3$ Hz), 6.23 (1H, s), 6.56 (2H, dd, $J = 18.0, 11.8$ Hz). ^{13}C -NMR (50 MHz, CDCl_3) δ -4.1, 18.3, 21.3, 25.7, 108.4, 116.8, 117.7, 128.3, 148.0, 153.4, 168.5. IR (neat) 1773, 1630, 1006, 901, 812, 781 cm^{-1} . MS (EI) m/z 448 (M^+ , 100), 349 ($\text{M}^+-\text{C}_4\text{H}_9-\text{CH}_2\text{CO}$, 98). HRMS. Calcd for $\text{C}_{24}\text{H}_{40}\text{O}_4\text{Si}_2$: 448.2465. Found: 448.2457.

2,6-Diethenylphenols.

2,6-Diethenylphenol. ^1H -NMR (200 MHz, CDCl_3) δ 5.37 (1H, s), 5.41 (2H, dd, $J = 11.2, 1.3$ Hz), 5.71 (2H, dd, $J = 17.7, 1.4$ Hz), 6.89 (1H, t, $J = 7.3$ Hz), 6.92 (2H, dd, $J = 17.7, 11.2$ Hz), 7.27 (2H, d, $J = 7.7$ Hz). ^{13}C -NMR (50 MHz, CDCl_3) δ 116.5, 120.5, 125.2, 126.7, 131.5, 150.0. IR (neat)

3538, 1630, 996, 915, 806, 748 cm⁻¹. MS (EI) *m/z* 146 (M^+ , 64), 43 (M^+-103 , 100). HRMS. Calcd for C₁₀H₁₀O: 146.0731. Found: 146.0735.

2,6-Diethenyl-4-methylphenol. ¹H-NMR (200 MHz, CDCl₃) δ 2.27 (3H, s), 5.20 (1H, s), 5.37 (2H, dd, *J* = 11.2, 1.4 Hz), 5.70 (2H, dd, *J* = 17.7, 1.4 Hz), 6.89 (2H, dd, *J* = 17.7, 11.2 Hz), 7.08 (2H, s). ¹³C-NMR (50 MHz, CDCl₃) δ 20.5, 116.3, 125.0, 127.3, 129.6, 131.7, 148.0. IR (neat) 3538, 1630, 996, 911, 864, 787 cm⁻¹. MS (EI) *m/z* 160 (M^+ , 81), 145 (M^+-Me , 100). HRMS. Calcd for C₁₁H₁₂O: 160.0888. Found: 160.0891.

2,6-Diethenyl-4-methoxyphenol. ¹H-NMR (200 MHz, CDCl₃) δ 3.80 (3H, s), 4.98 (1H, s), 5.40 (2H, dd, *J* = 11.2, 1.2 Hz), 5.72 (2H, dd, *J* = 17.7, 1.3 Hz), 6.86 (2H, s), 6.92 (2H, dd, *J* = 17.9, 11.2 Hz). ¹³C-NMR (50 MHz, CDCl₃) δ 55.7, 111.8, 116.5, 126.3, 131.5, 144.4, 153.3. IR (neat) 3424, 1601, 996, 915, 851 cm⁻¹. MS (EI) *m/z* 176 (M^+ , 100), 161 (M^+-Me , 54). HRMS. Calcd for C₁₁H₁₂O₂: 176.0836. Found: 176.0834.

2,6-Diethenyl-4-(*t*-butyldimethylsilyloxy)phenol. ¹H-NMR (200 MHz, CDCl₃) δ 0.18 (6H, s), 0.99 (9H, s), 4.98 (1H, s), 5.38 (2H, dd, *J* = 11.0, 1.3 Hz), 5.67 (2H, dd, *J* = 17.8, 1.3 Hz), 6.77 (2H, s), 6.88 (2H, dd, *J* = 17.8, 11.1 Hz). ¹³C-NMR (125 MHz, CDCl₃) δ -4.5, 18.2, 25.7, 116.5, 117.8, 126.1, 131.6, 144.7, 149.0. IR (neat) 3444, 1599, 988, 911, 853, 781 cm⁻¹. MS (EI) *m/z* 276 (M^+ , 100), 219 ($M^+-C_4H_9$, 93). HRMS. Calcd for C₁₆H₂₄O₂Si: 276.1546. Found: 276.1551.

2,6-Diethenyl-4-(*t*-butyldiphenylsilyloxy)phenol. ¹H-NMR (200 MHz, CDCl₃) δ 1.11 (9H, s), 4.85 (1H, s), 5.23 (2H, dd, *J* = 11.1, 1.3 Hz), 5.37 (2H, dd, *J* = 17.6, 1.3 Hz), 6.67 (2H, s), 6.75 (2H, dd, *J* = 18.5, 11.9 Hz), 7.33-7.43 (6H, m), 7.70-7.74 (4H, m). ¹³C-NMR (50 MHz, CDCl₃) δ 19.5, 26.6, 116.3, 117.3, 125.9, 127.7, 129.9, 131.2, 133.0, 135.6, 144.3, 149.1. IR (neat) 3552, 1597, 988, 915, 847, 741 cm⁻¹. MS (EI) *m/z* 400 (M^+ , 49), 343 ($M^+-C_4H_9$, 100). HRMS. Calcd for C₂₆H₂₈O₂Si: 400.1858. Found: 400.1855.

2,6-Diethenyl-3-methylphenol. ¹H-NMR (200 MHz, CDCl₃) δ 2.22 (3H, s), 5.25 (1H, dd, *J* = 11.2, 1.3 Hz), 5.56 (1H, dd, *J* = 18.1, 1.4 Hz), 5.71 (1H, dd, *J* = 11.4, 1.3 Hz), 5.72 (1H, dd, *J* = 17.7, 1.4 Hz), 5.83 (1H, s), 6.66 (1H, dd, *J* = 17.7, 1.4 Hz), 6.72 (1H, d, *J* = 7.9 Hz), 6.99 (1H, dd, *J* = 17.8, 11.2 Hz), 7.25 (1H, d, *J* = 7.9 Hz). ¹³C-NMR (50 MHz, CDCl₃) δ 20.0, 113.8, 120.9, 121.6, 122.3, 124.1, 125.5, 131.7, 132.5, 136.5, 149.8. IR (neat) 3522, 1628, 998, 907, 816 cm⁻¹.

MS (EI) m/z 160 (M^+ , 91), 145 (M^+-15 , 100). HRMS. Calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0898.

Alkenylphenols.

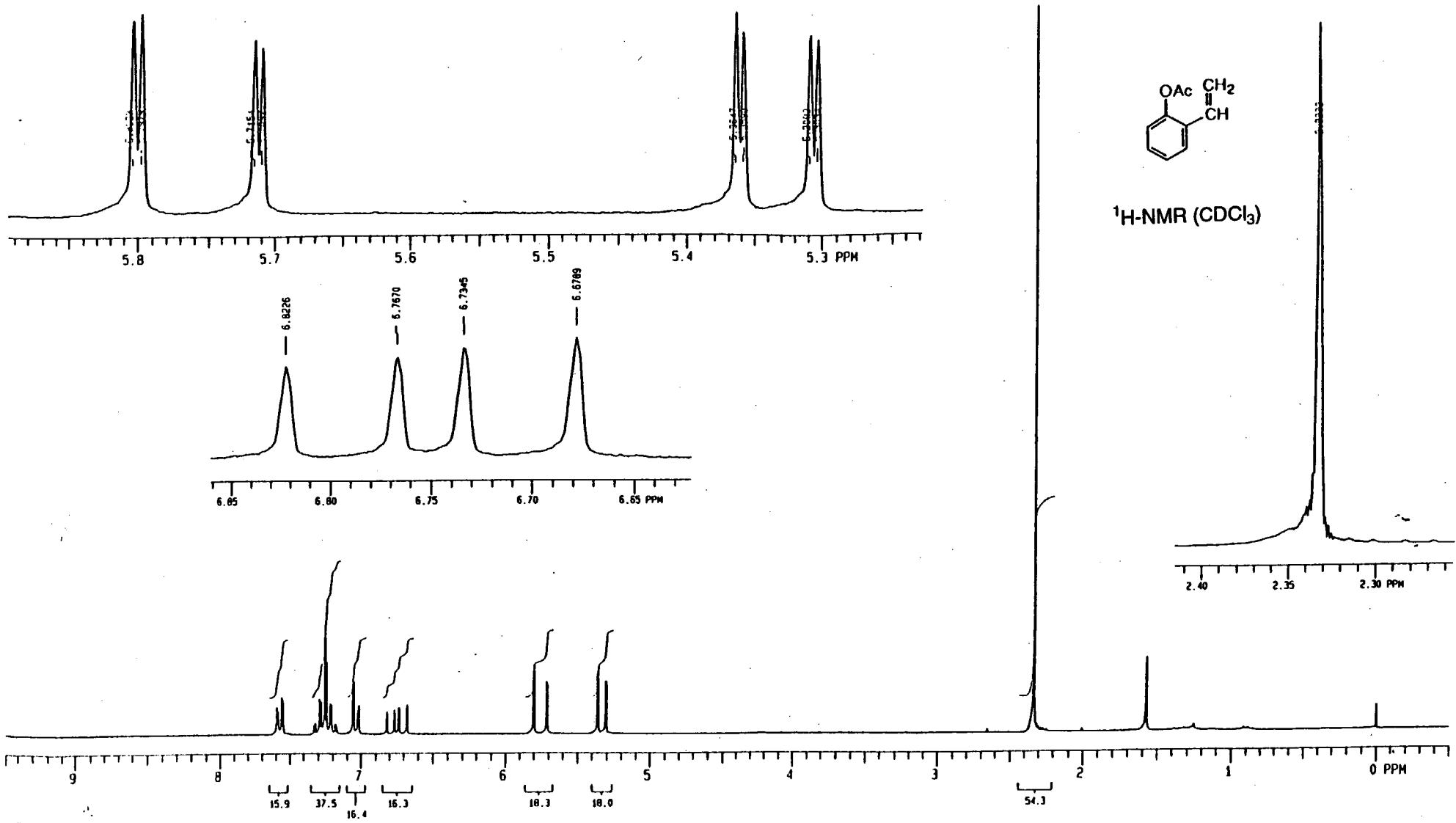
3-Methoxy-6-(1-phenylethenyl)phenol. 1H -NMR (400MHz, $CDCl_3$) δ 3.79 (3H, s), 5.28 (1H, s), 5.36 (1H, d, J = 1.2 Hz), 5.77 (1H, s), 6.49 (1H, dd, J = 8.8, 2.8 Hz), 6.50 (1H, d, J = 2.8 Hz), 7.01 (1H, d, J = 8.8 Hz), 7.32 (3H, m), 7.36 (2H, m). ^{13}C -NMR (100MHz, $CDCl_3$) δ 55.3, 101.0, 106.6, 115.9, 119.9, 127.1, 128.4, 128.5, 130.9, 139.7, 144.9, 154.0, 160.5. IR (neat) 3508, 1621 cm^{-1} . MS (EI) m/z 226 (M^+ , 57), 225 (M^+-H , 100), 211 (M^+-Me , 24). HRMS Calcd for $C_{15}H_{14}O_2$: 226.0994. Found: 226.0976.

3-Methoxy-2-(1-phenylethenyl)phenol. Mp 68.5-69.2 °C (EtOH, hexane). 1H -NMR (400MHz, $CDCl_3$) δ 3.61 (3H, s), 5.38 (1H, s), 5.48 (1H, s), 6.09 (1H, d, J = 1.6 Hz), 6.49 (1H, d, J = 8.0 Hz), 6.67 (1H, d, J = 8.0 Hz), 7.21 (1H, t, J = 8.0 Hz), 7.28 (3H, m), 7.34 (2H, m). ^{13}C -NMR (100MHz, $CDCl_3$) δ 55.9, 103.0, 108.1, 116.4, 117.4, 125.8, 128.0, 128.2, 129.1, 138.9, 141.1, 153.7, 157.5. IR (neat) 3504, 1576 cm^{-1} . MS (EI) m/z 226 (M^+ , 96), 225 (M^+-H , 100), 211 (M^+-Me , 67). HRMS Calcd for $C_{15}H_{14}O_2$: 226.0994. Found: 226.0998.

2-(1-Phenylethenyl)phenol. 1H -NMR (200MHz, $CDCl_3$) δ 5.16 (1H, s), 5.42 (1H, d, J = 1.2 Hz), 5.87 (1H, d, J = 1.2 Hz), 6.9-7.0 (2H, m), 7.13 (1H, ddd, J = 0.7, 1.8, 7.2 Hz), 7.2-7.3 (1H, m), 7.3-7.4 (5H, m). ^{13}C -NMR (50MHz, $CDCl_3$) δ 115.8, 116.7, 120.4, 127.0, 127.5, 128.5, 128.6, 129.4, 130.4, 139.4, 145.2, 153.0. IR (neat) 3524, 1605, 1576 cm^{-1} . MS (EI) m/z 196 (M^+ , 62), 195 (M^+-H , 100), 181 (M^+-Me , 32), 165 (M^+-MeO , 11). HRMS Calcd for $C_{14}H_{12}O$: 196.0888. Found: 196.0844.

4-Cyano-2-(1-phenylethenyl)phenol. 1H -NMR (400 MHz, $CDCl_3$) δ 5.44 (1H, s), 5.90 (1H, s), 5.93 (1H, s), 7.01 (1H, d, J = 8.4 Hz), 7.31 (2H, m), 7.36 (3H, m), 7.46 (1H, d, J = 2.0 Hz), 7.53 (1H, dd, J = 8.0, 2.4 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 103.9, 116.9, 118.1, 118.8, 126.7, 128.7, 128.8, 129.0, 133.4, 134.5, 138.0, 143.2, 156.8. IR (neat) 3306, 2227, 1600 cm^{-1} . MS (EI) m/z 221 (M^+ , 61), 110 (M^+-H , 100), 206 (M^+-Me , 45). HRMS Calcd for $C_{15}H_{11}ON$: 221.0840. Found: 221.0843.

3-Cyano-6-(1-phenylethenyl)phenol. Mp 137.5-139.0 °C (toluene). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.46 (1H, s), 5.54 (1H, s), 6.18 (1H, s), 7.19 (1H, dd, J = 8.0, 2.4 Hz), 7.34 (7H, m). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 113.4, 117.4, 120.0, 120.4, 125.3, 126.3, 128.8, 129.0, 129.6, 130.7, 137.2, 141.0, 153.3. IR (CHCl_3) 3320, 2237 cm^{-1} . MS (EI) m/z 221 (M^+ , 75), 110 (M^+-H , 100), 206 (M^+-Me , 68). HRMS Calcd for $\text{C}_{15}\text{H}_{11}\text{ON}$: 221.0840. Found: 221.0859.



rme,dac,mono

sp1 stdth

SAMPLE DEC. & VT

te Aug 20 97 dfrq 400.450

lvent CDCl₃ dn H1

ie exp dpwr 32

ACQUISITION dof 0

rq 400.451 dm non

H1 dmm c

1.002 dmf 200

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3400 prc ft

16 fn not used

56

2.6 werr

3.000 wexp procplot

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16 wnt

16

not used

FLAGS

n

n

y

DISPLAY

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456.9

0

34

100.000

cdc ph

9

8

7

6

5

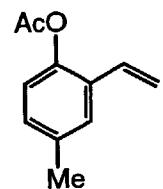
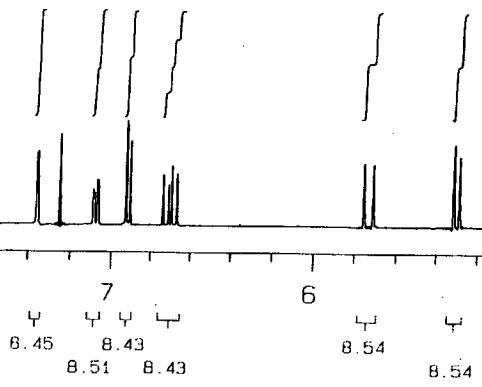
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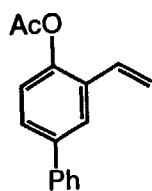
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2

1

0 ppm

¹H-NMR (CDCl₃)



¹H-NMR (CDCl₃)

-Ph, mono, OAc

xpi std1h

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solvent CDCl₃ dn H1
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16 fn not used
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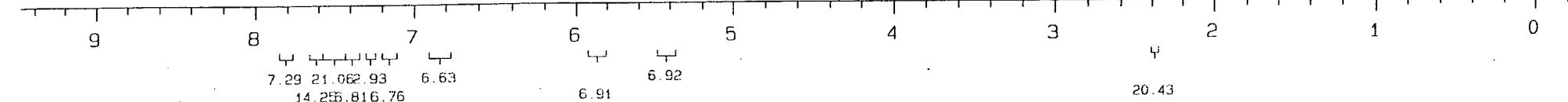
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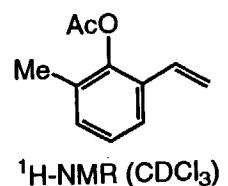
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ain not used

FLAGS

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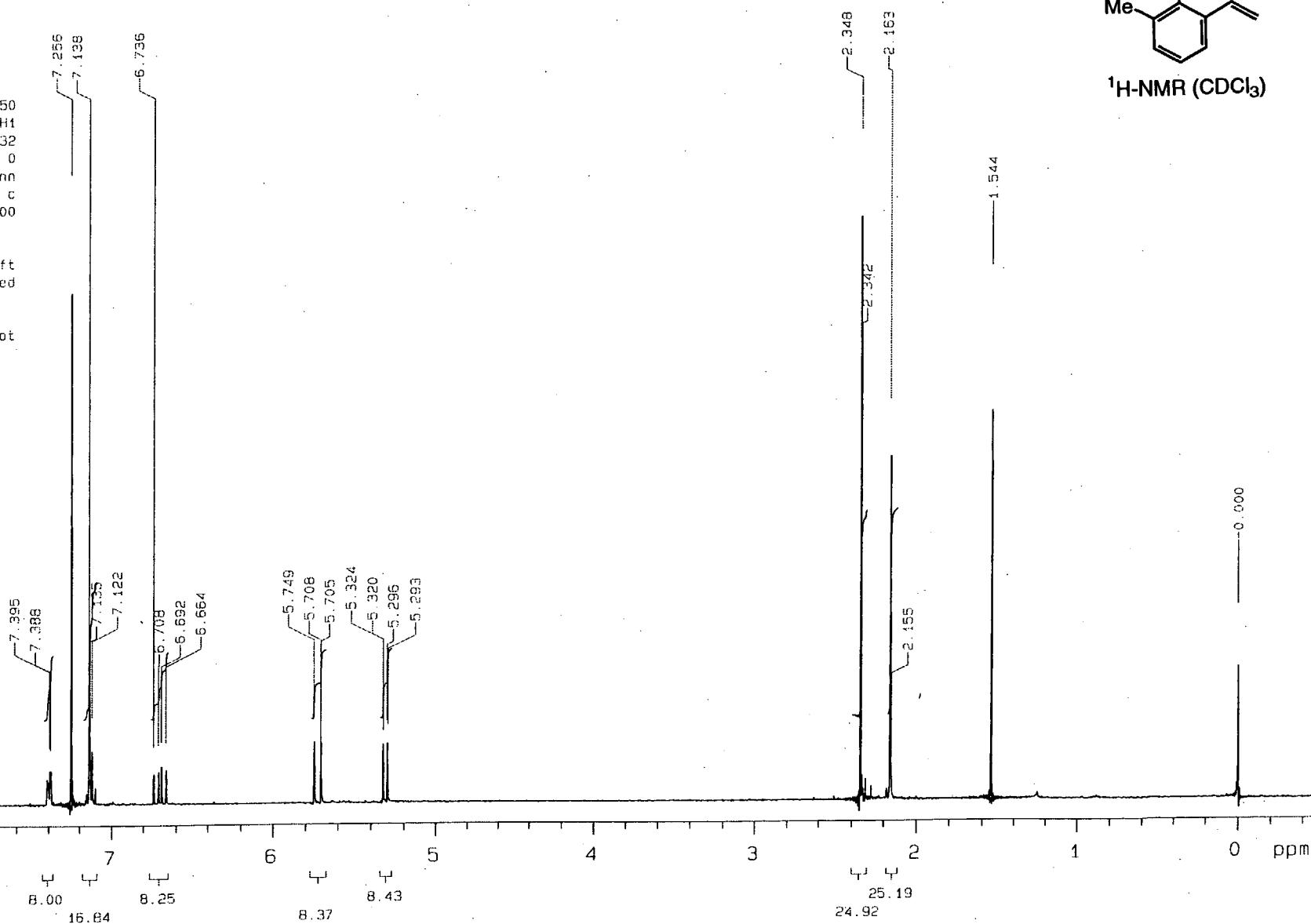
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2576.60
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2907.3
38
100.000
cdc ph





esol, mono, oac
std1h

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H1 dmm c
1.002 dmf 200
12032 PROCESSING
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3400 proc ft
16 fn not used
56
5.1 werr
3.000 wexp procplot
600.0 wbs
16 wnt
16
k n
not used
FLAGS
a n
d n
DISPLAY
-200.9
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0
385
10.40
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0
7
100.000
cdc ph



-tBu, mono, oac, x

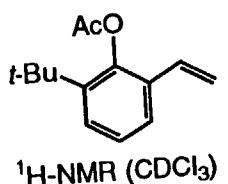
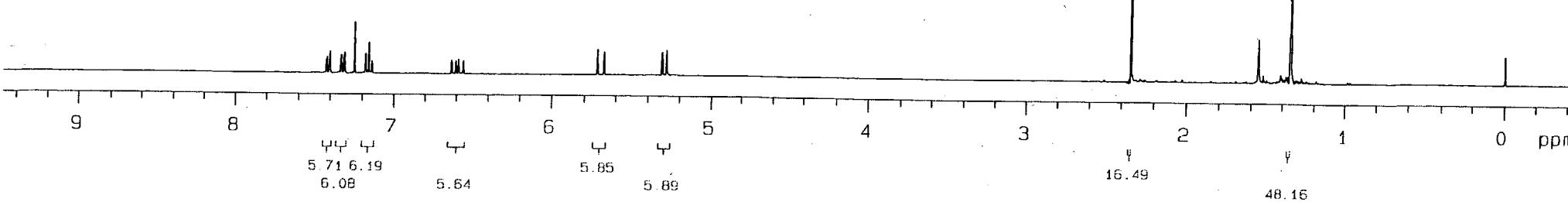
xpi std1h

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 H1 dmm c
 1.002 dmf 200
 12032 PROCESSING
 6006.9 wfile
 3400 presc ft
 16 fn not used
 56

WR 5.1 werr
 3.000 wexp procplot
 f 600.0 wbs
 16 wnt
 16

LOCK n
 IN not used
 FLAGS n
 n
 y

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 4004.1
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 45
 100.000
 cdc ph

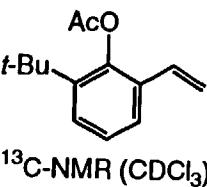


21.547

20.501

34.738

21.547



tBu, mono, DAC

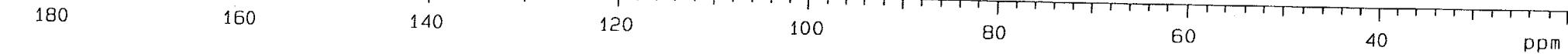
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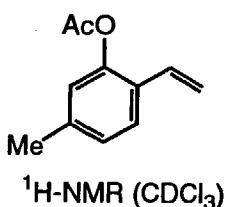
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 e exp dpwr 43
 ACQUISITION dof 0
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 C13 d1m w
 1.199 dmf 9900
 59968 PROCESSING
 25000.0 1b 1.00
 13800 wfile
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 6.5
 0 801 werr
 1600.0 wexp
 2048 wbs
 304 wnt
 ck n
 a not used
 FLAGS n
 a

DISPLAY

1987.5
 16859.2
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 ph qd





me, oac, mono, up

p1 std1h

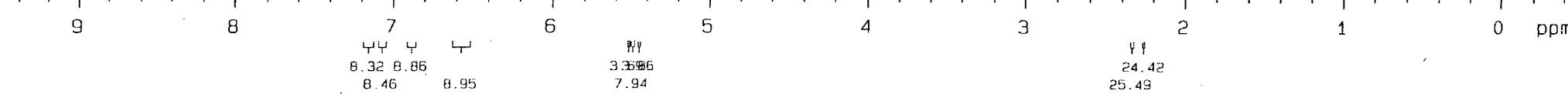
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 1.002 dmf 200
 12032 PROCESSING
 6006.9 wfile
 3400 proc ft
 16 fn not used
 56
 5.1 werr
 3.000 wexp procplot
 600.0 wbs
 16 wnt
 16
 n
 not used

FLAGS

DISPLAY

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 4004.1
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 20
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 cdc ph



n-tBu, mono, 5, OAc

expi std1h

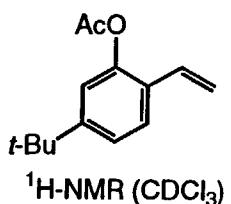
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 n H1 dmm c
 t 1.002 dm 200
 p 12032 PROCESSING
 w 6006.9 wfile
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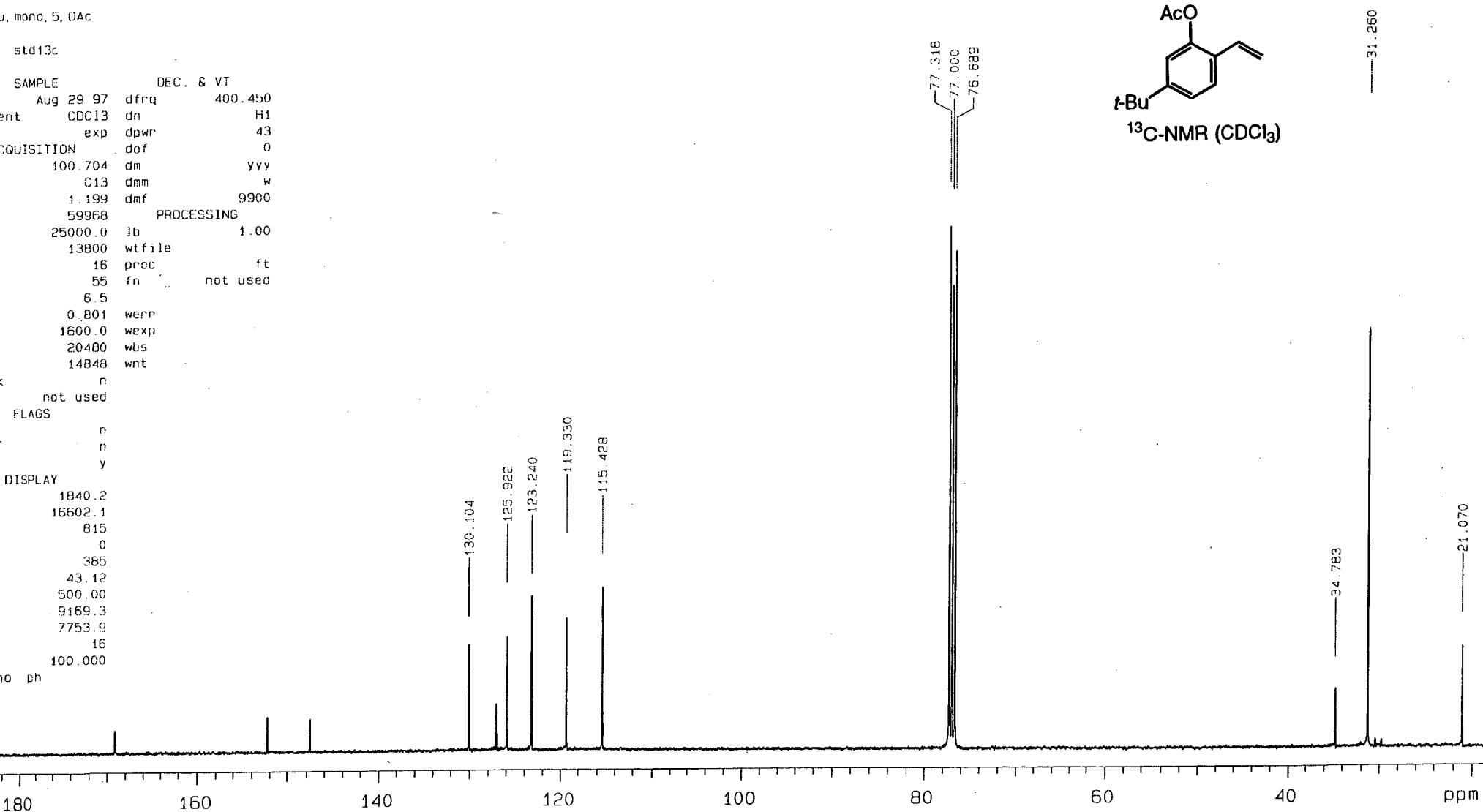
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tBu, mono, 3, OAc

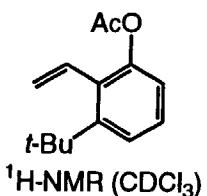
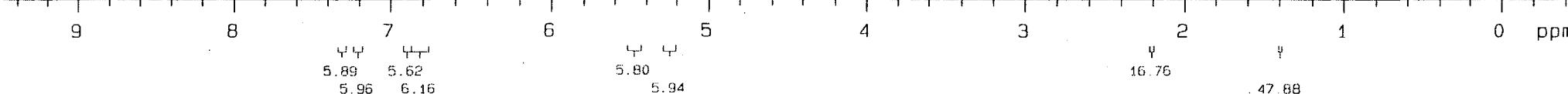
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 12032 PROCESSING
 6006.9 wfile
 3400 proc ft
 16 fn not used
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 5.1 werr
 3.000 wexp procplot
 600.0 wbs
 16 wnt
 16
 n
 n not used
 FLAGS n n y

DISPLAY

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 4004.1
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 cdc ph



t-Bu, mono, 3, OAc

pi stat3c

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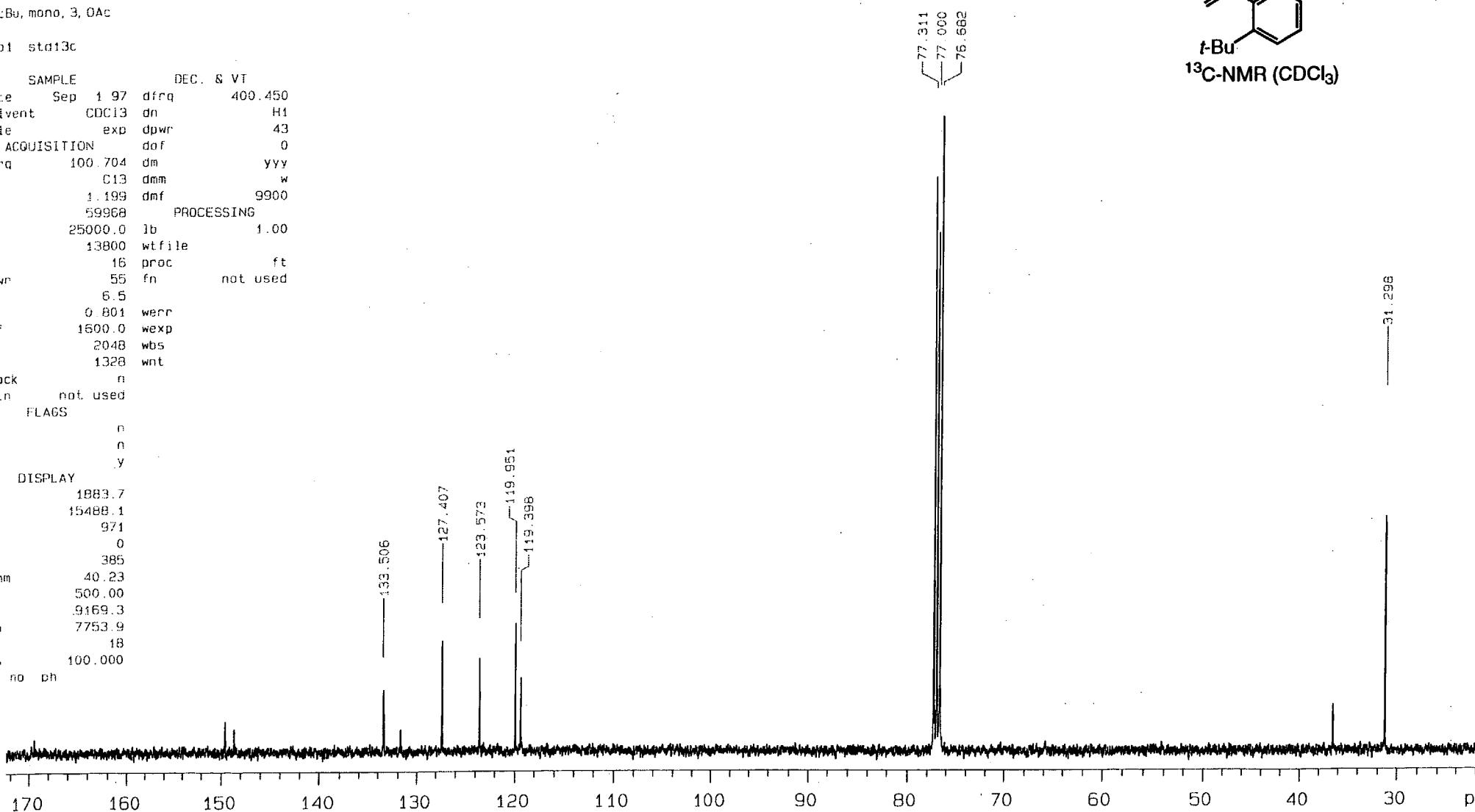
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 FLAGS

DISPLAY

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¹³C-NMR (CDCl₃)



epholt, mono, oac

std1h

SAMPLE DEC. & VI

Date Aug 22 97 dfreq 400.450

Solvent CDCl₃ dn H1

Exp. dpwr 32

Acquisition def 0

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H1 dmm c

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12032 PROCESSING

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3400 proc ft

16 fn not used

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3.000 wexp procplot

500.0 wbs

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n

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DISPLAY

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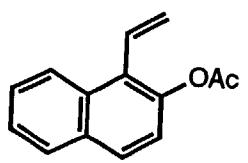
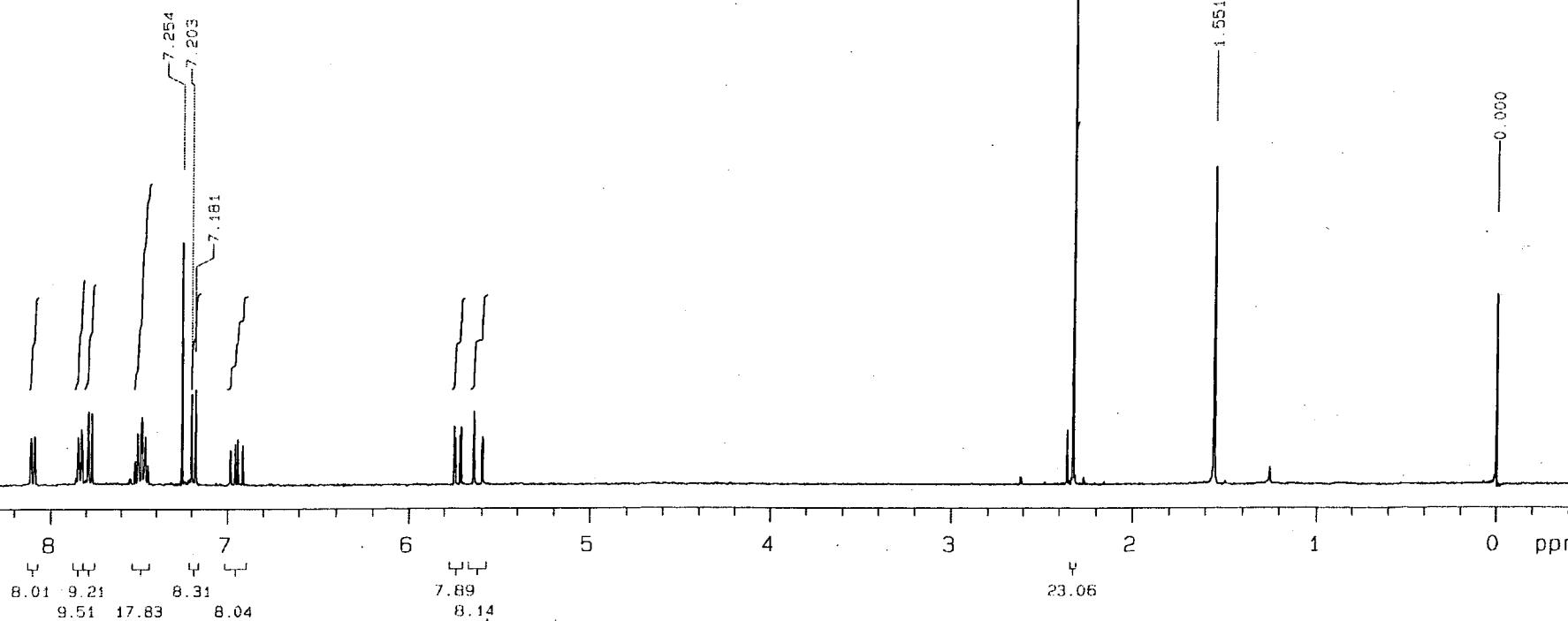
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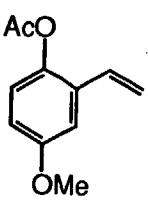
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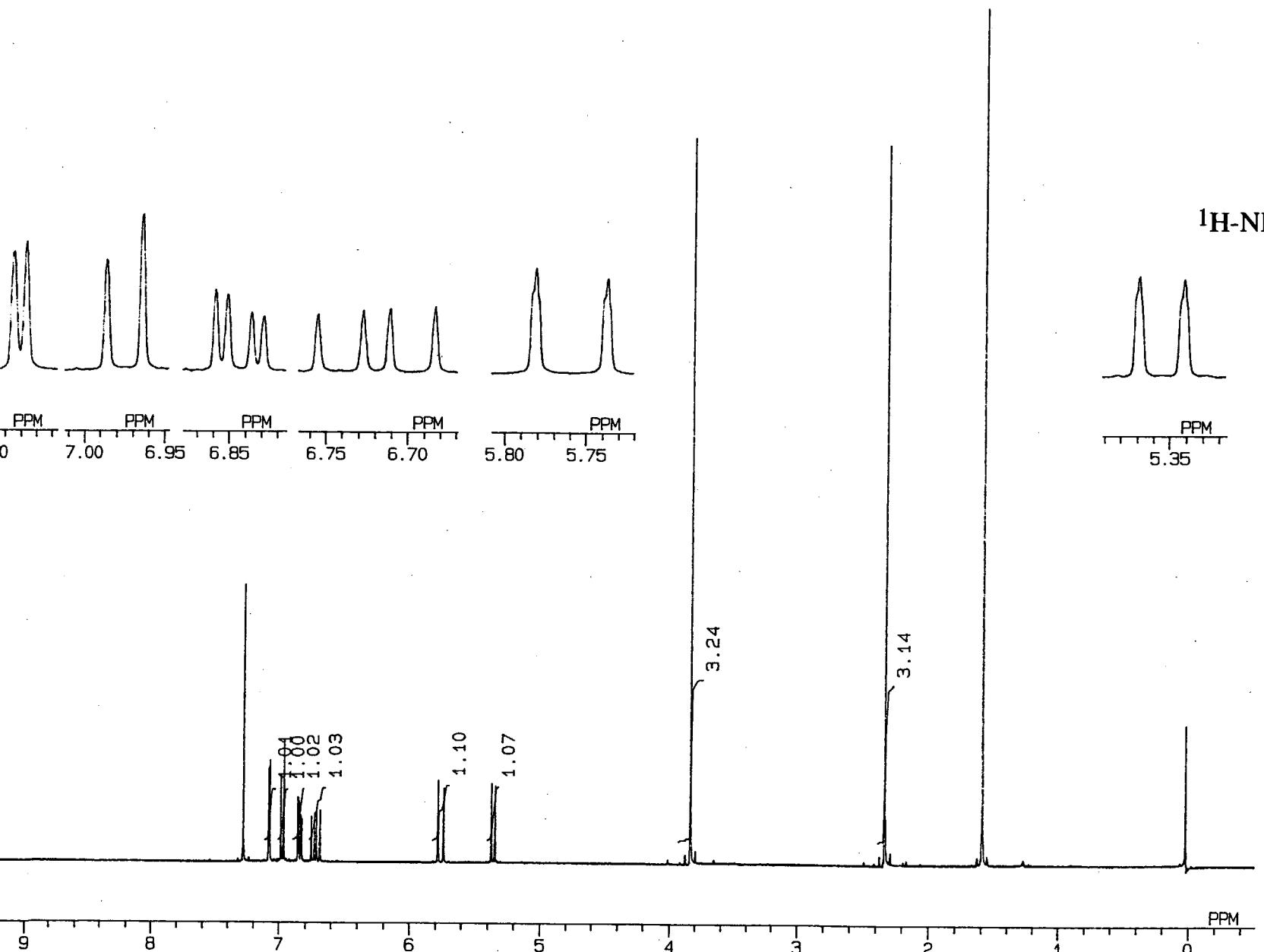
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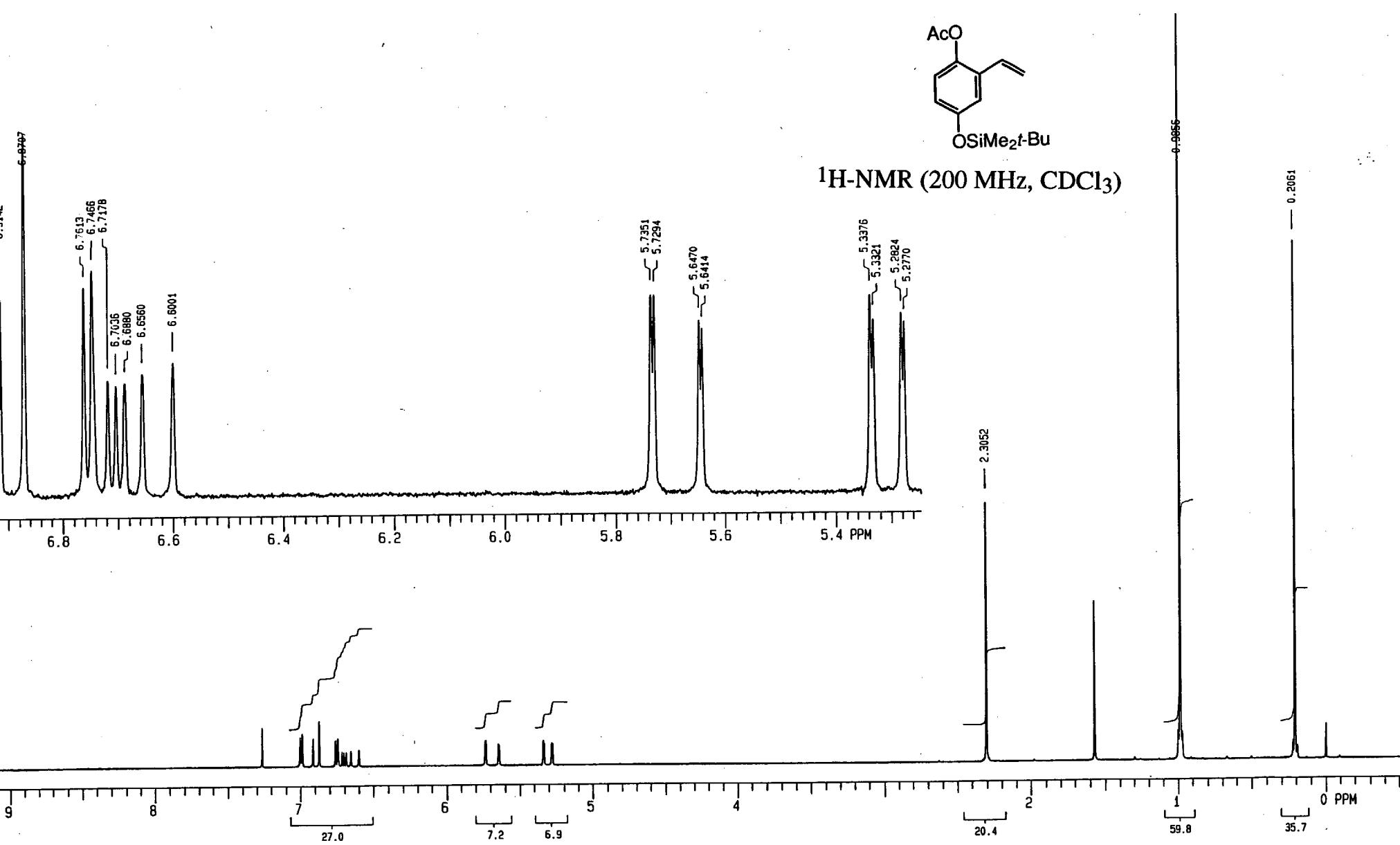
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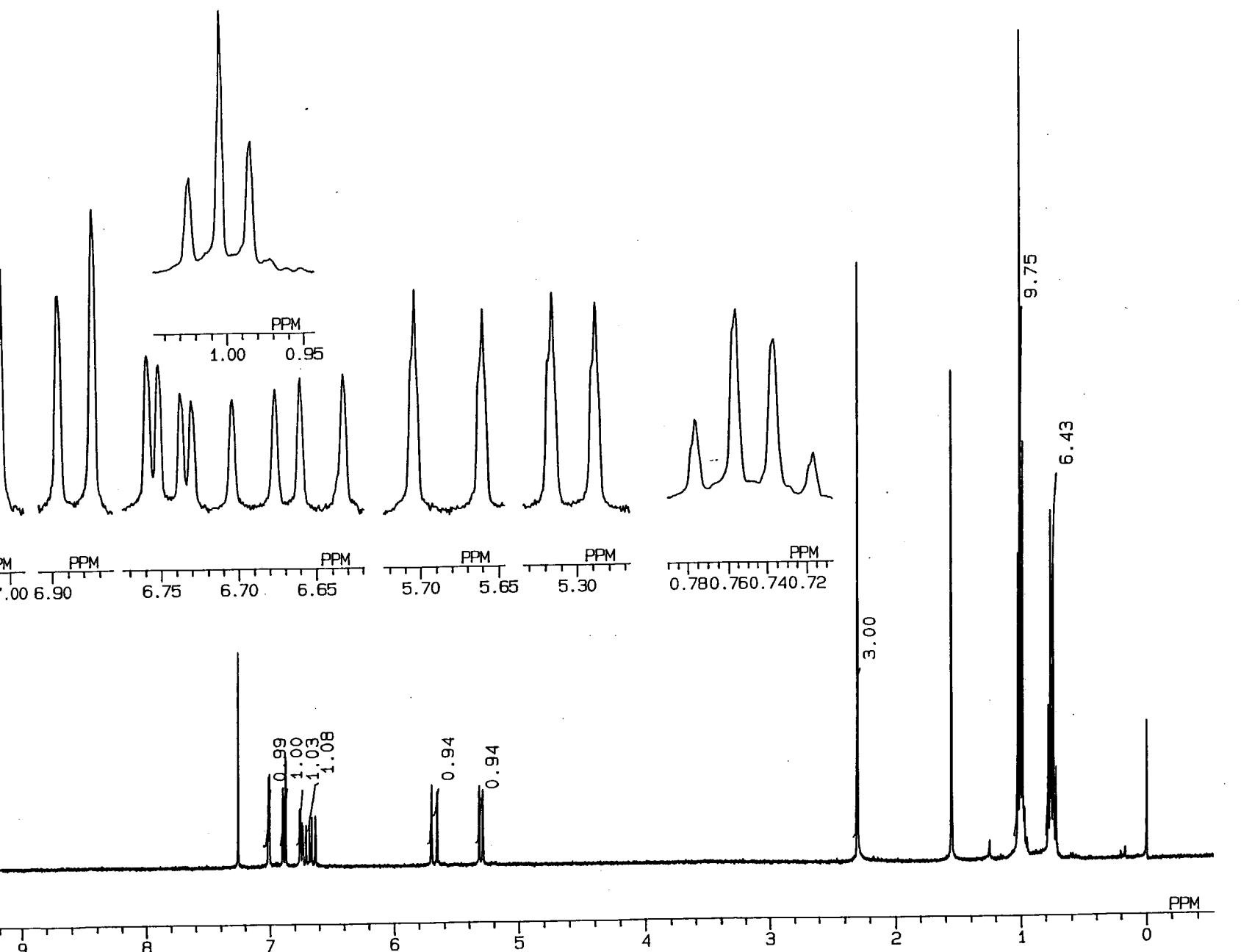
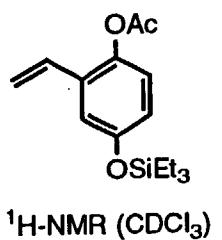
¹H-NMR (CDCl₃)

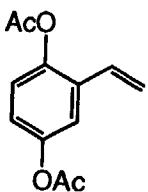


$^1\text{H-NMR}$ (400 MHz, CDCl_3)

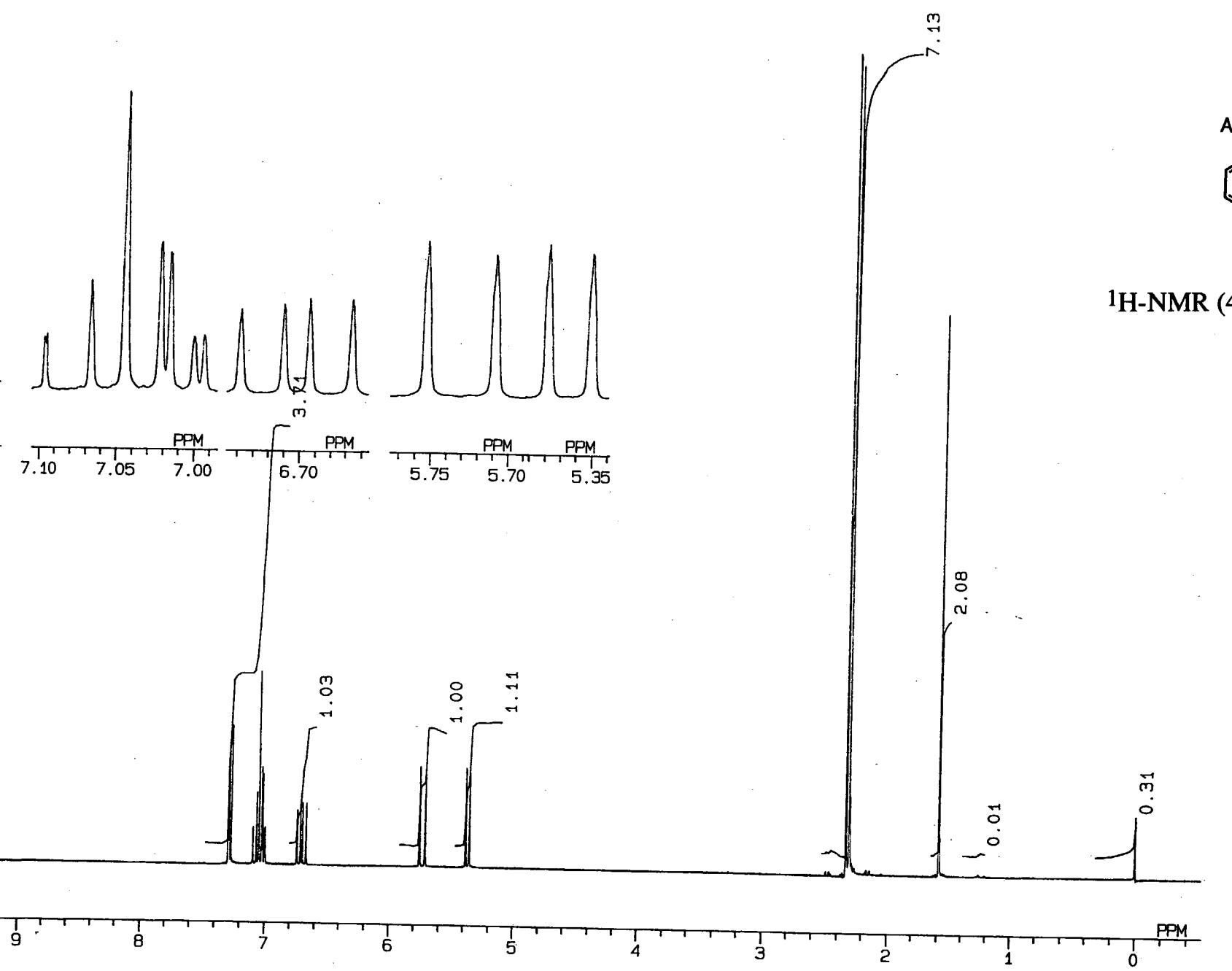


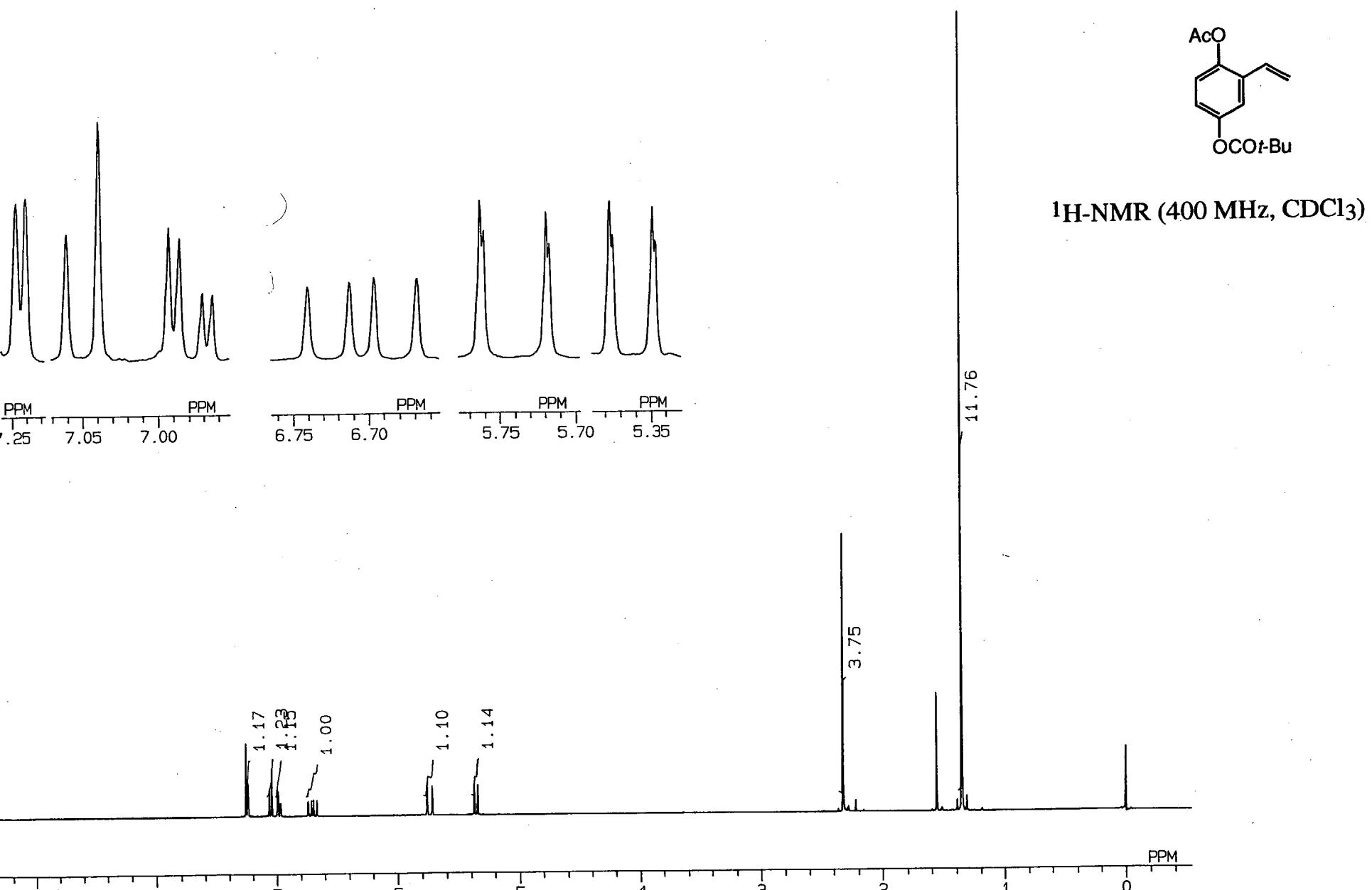




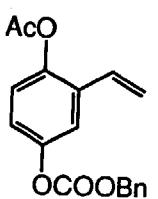


¹H-NMR (400 MHz, CDCl₃)

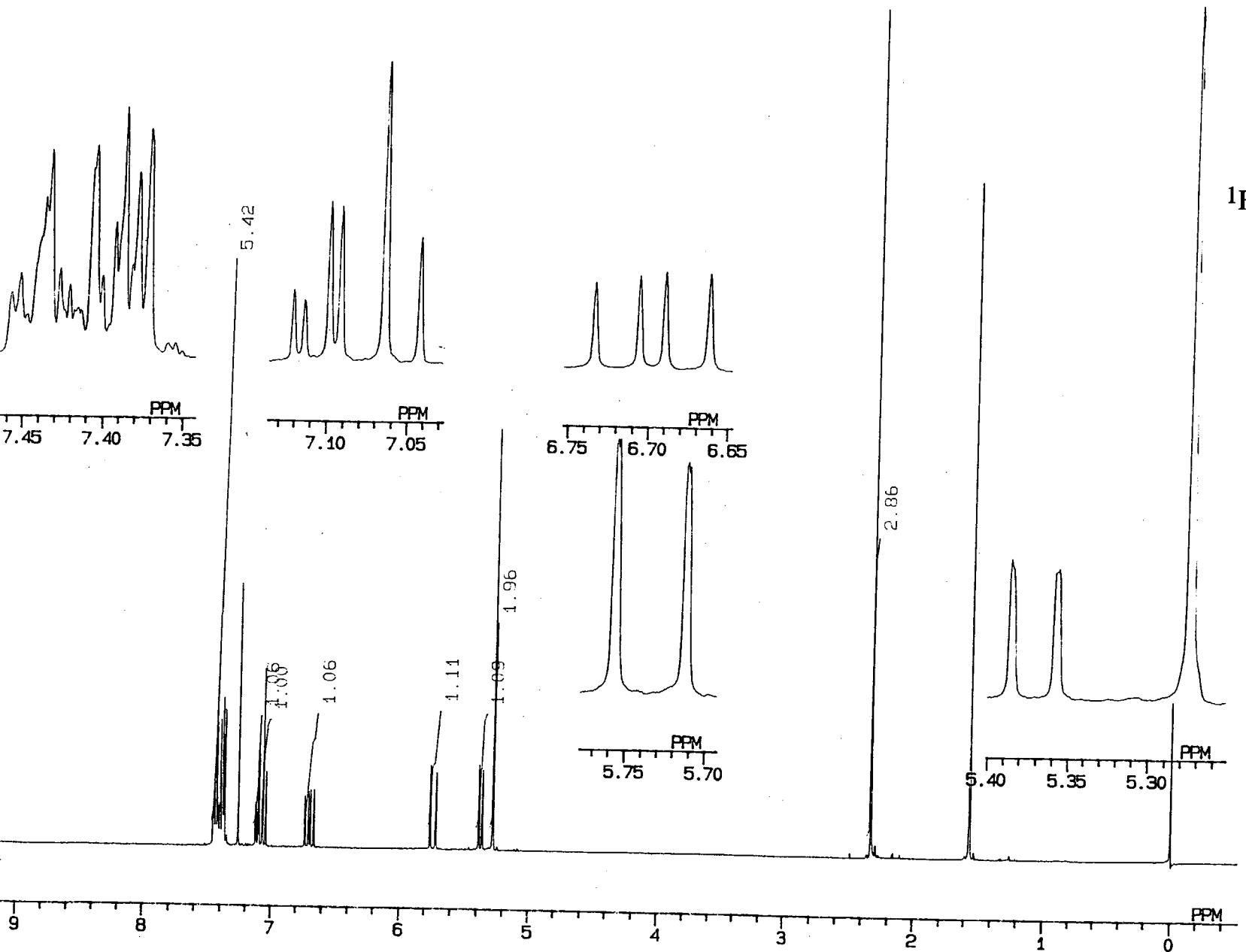




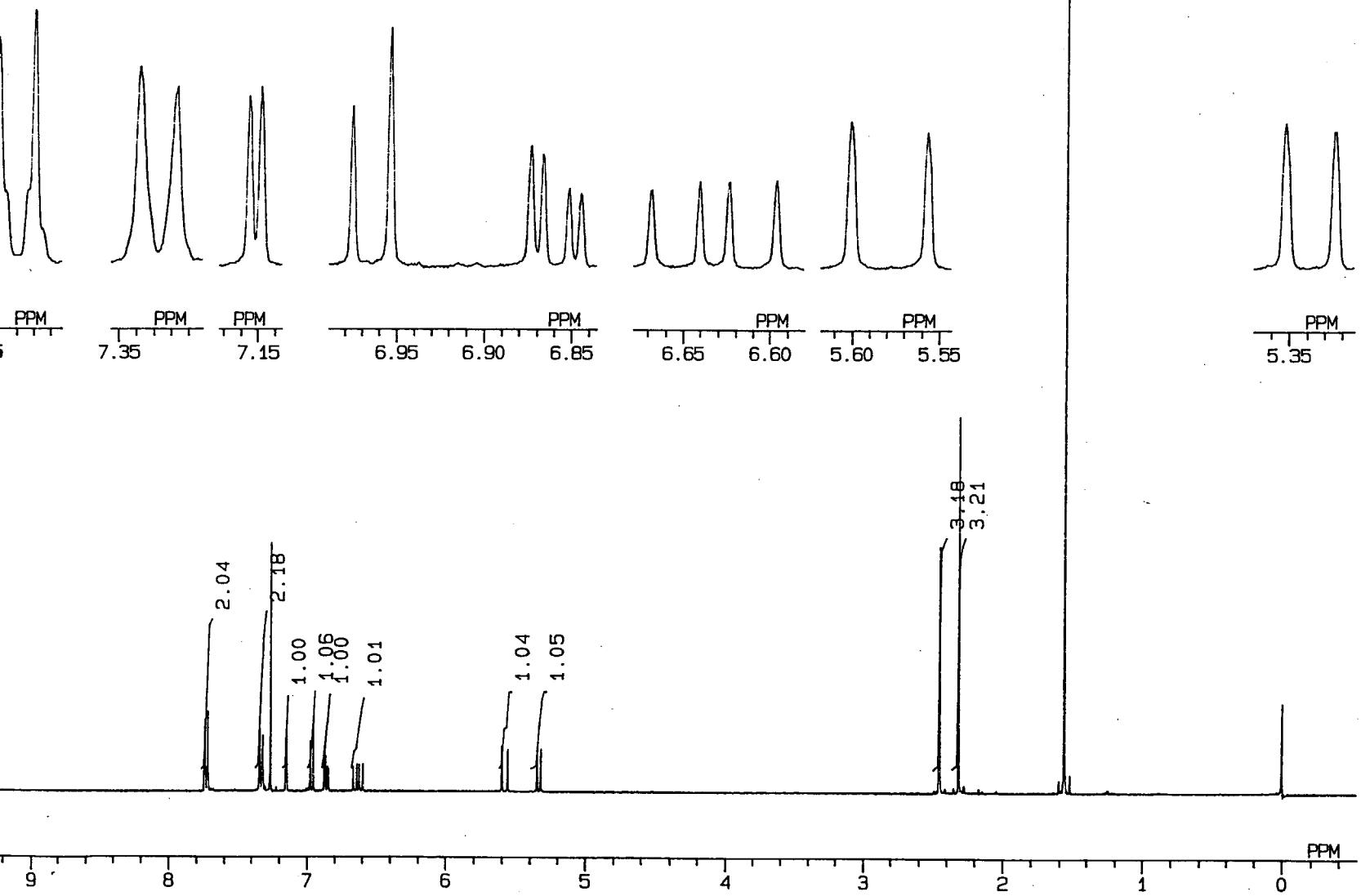
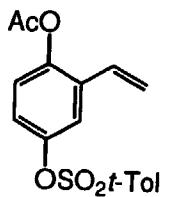
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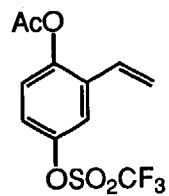


$^1\text{H-NMR}$ (400 MHz, CDCl_3)

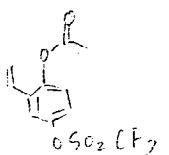
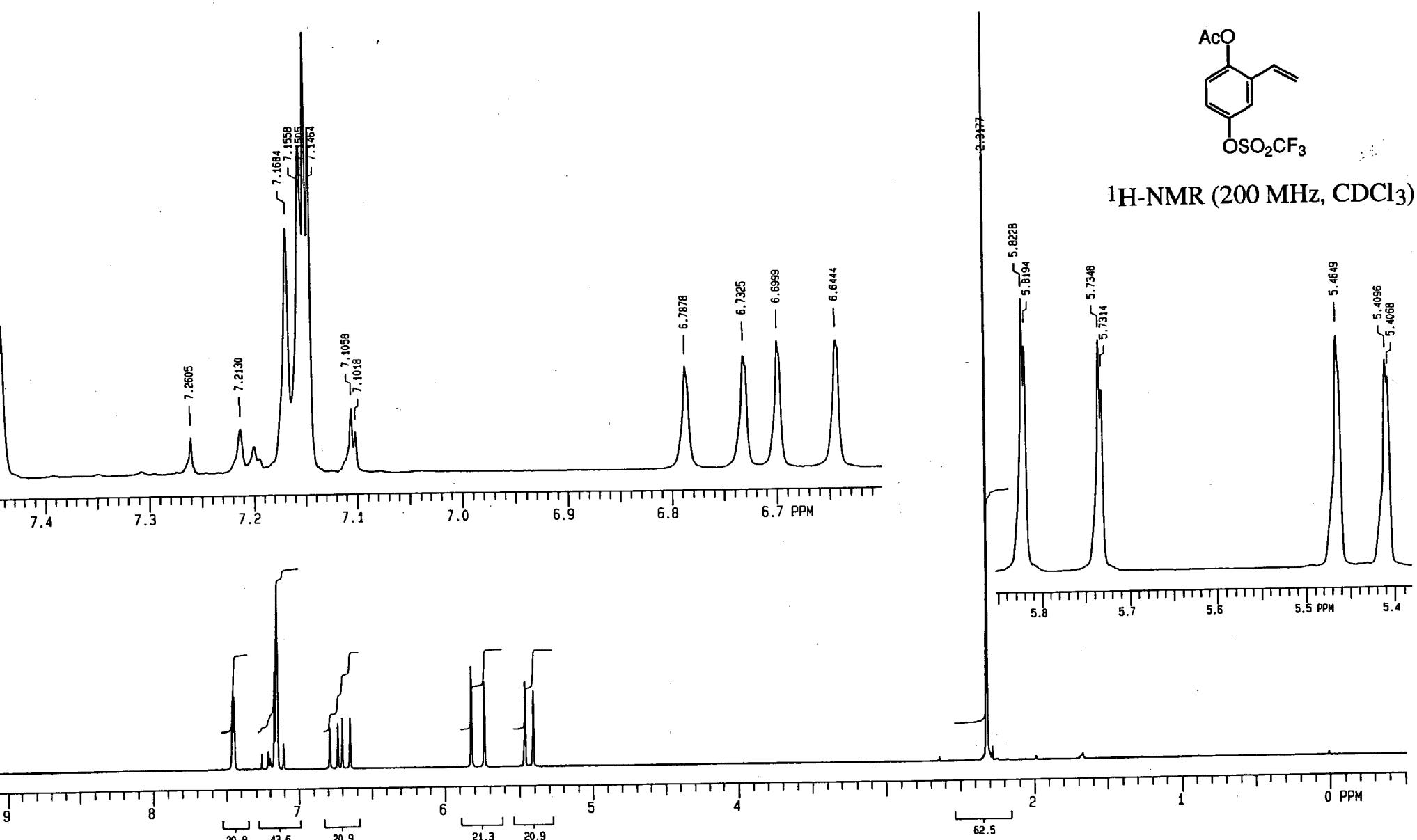


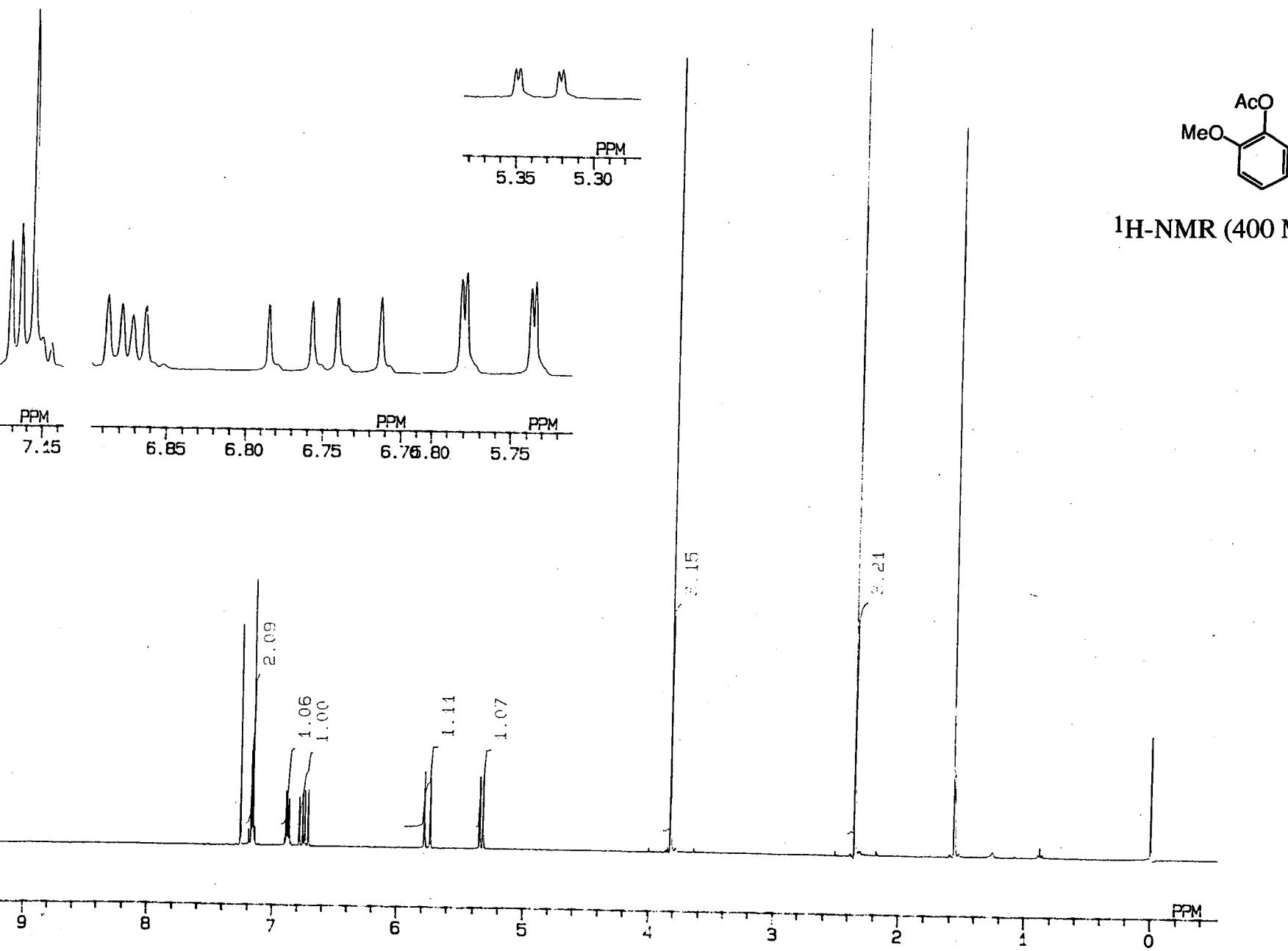
¹H-NMR (400 MHz, CDCl₃)



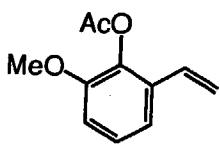


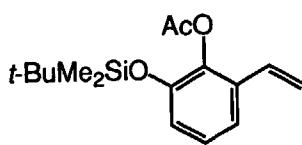
$^1\text{H-NMR}$ (200 MHz, CDCl_3)



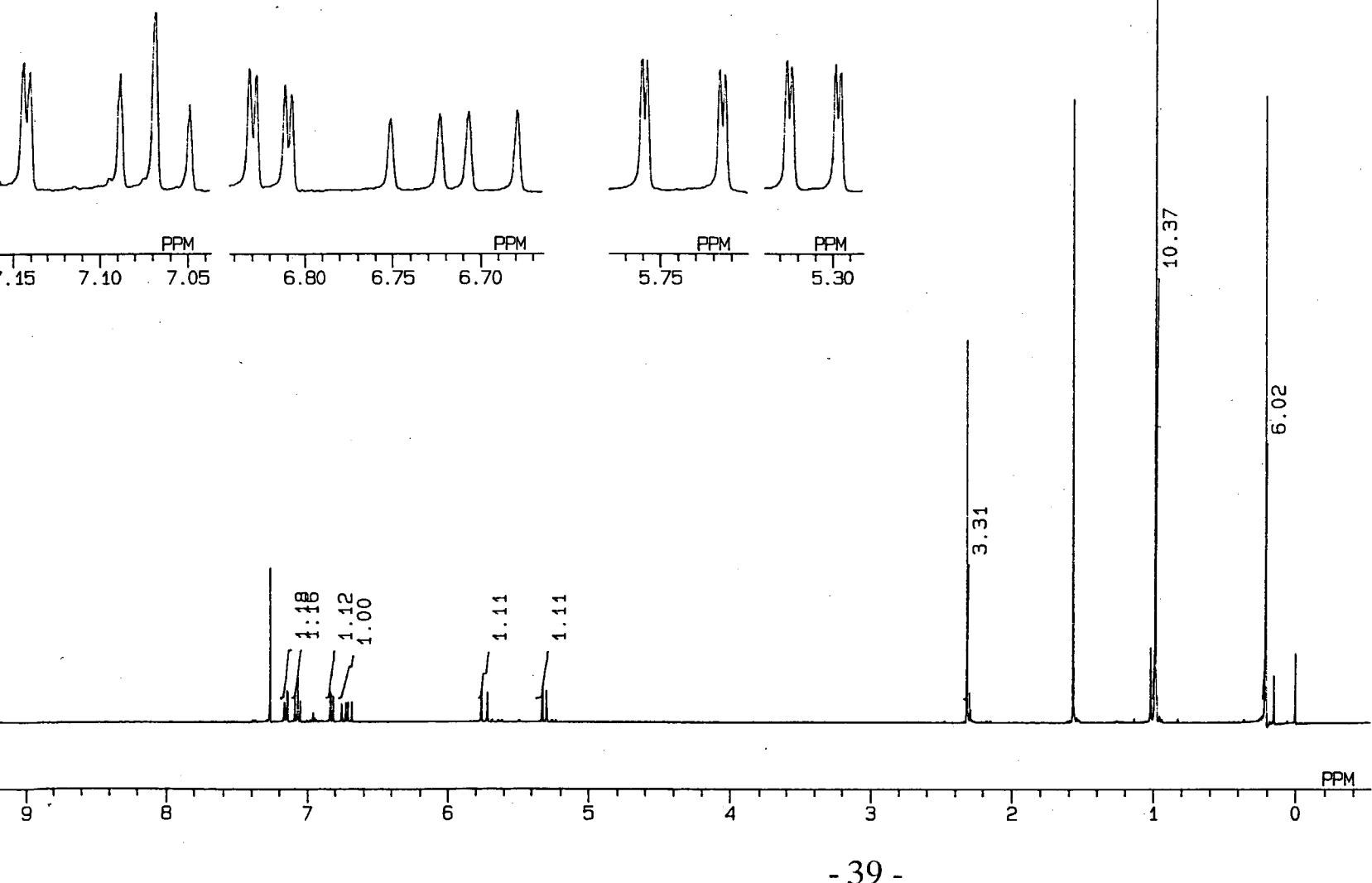


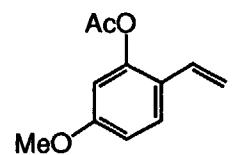
^1H -NMR (400 MHz, CDCl_3)





¹H-NMR (400 MHz, CDCl₃)





¹H-NMR (400 MHz, CDCl₃,

