General procedure for the $CrCl_2/NiCl_2$ Mediated Reaction of 1a with Hydrocinnamaldehyde. A solution of 2-bromo-1-propenyl acetate (170 mg, .93 mmol) and hydrocinnamaldehyde (50 mg, .37 mmol) in DMF (2.5 mL) was added to a mixture of $CrCl_2$ (160 mg, 1.3 mmol) and $NiCl_2$ (0.10 mol %). The reaction was stirred at room temperature for eight hours. The reaction mixture was then quenched with 0.20 mL of an aqueous solution of ethylenediamine (12.6 M) and stirred for 15 minutes during which time the solution turned from green to purple. The mixture was poured over water (3 mL) and extracted with ether (3 x 7 mL). The combined organic layers were washed with 2N HCl (1 x 3 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography (20% EtOAc/hexanes) to yield the allylic alcohol as a colorless oil (80 mg, 93%). IR (neat, cm^{-1}) 3444, 1740; ^1H NMR (300 MHz, $CDCl_3$) δ7.35–7.18 (m, 5H), 5.26 (s, 1H), 5.19 (s, 1H), 4.69 (d, J = 13.4 Hz, 1H), 4.62 (d, J = 13.4 Hz, 1H), 4.21 (t, J = 6.5 Hz, 1H), 2.83-2.63 (m, 2H), 2.08 (s, 3H), 1.97-1.88 (m, 2H), 1.81 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.8, 146.0, 141.6, 128.4 (2C), 125.9, 113.9, 72.5, 64.0, 37.0, 31.8, 20.9; MS *m/z* ($M^+ + 1$) calcd 235.1334, obsd 235.1320.

Coupling of 1a to Cyclohexanecarboxaldehyde. colorless oil; IR (neat, cm^{-1}) 3461, 1744; ^1H NMR (300 MHz, $CDCl_3$) δ 5.19 (s, 1H), 5.16 (s, 1H), 4.62 (d, J = 13.5 Hz, 1H), 4.59 (d, J = 13.5 Hz, 1H), 3.88 (d, J = 7.3 Hz, 1H), 2.09 (s, 3H), 1.74-1.53 (m, 6H), 1.43-0.94 (m, 5H), (OH not apparent); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.7, 144.9, 114.7, 78.8, 63.8, 41.3, 29.7, 28.3, 26.3, 26.1, 25.9, 20.9; MS *m/z* ($M^+ + 1$) calcd 213.1491, obsd 213.1469.

Coupling of 1a to Benzaldehyde. colorless oil; IR (neat, cm^{-1}) 3448, 1741; ^1H NMR (300 MHz, $CDCl_3$) δ7.42–7.28 (m, 5H), 5.41 (s, 1H), 5.29 (s, 1H), 4.57 (d, J = 13.6 Hz, 1H), 4.44 (d, J = 13.6 Hz, 1H), 4.21 (t, J = 6.5 Hz, 1H), 2.38 (br s, 1H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.8, 145.4, 141.2, 128.5, 127.9, 126.4, 114.4, 75.2, 64.1, 20.8; MS *m/z* ($M^+ + 1 - H_2O$) calcd 189.0916, obsd 189.0938.

Coupling of 1a to *p*-Anisaldehyde. colorless oil; IR (neat, cm^{-1}) 3458, 1738; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 5.40 (s, 1H), 5.27 (s, 1H), 5.22 (s, 1H), 4.55 (d, J = 13.4 Hz, 1H), 4.42 (d, J = 13.4 Hz, 1H), 3.79 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.7, 159.3, 145.6, 133.3, 127.8, 113.9, 113.8, 74.6, 64.2, 55.3, 20.8; MS *m/z* (M^+ + 1) calcd 236.1049, obsd 236.1039.

Coupling of 1a to Heptaldehyde. colorless oil; IR (neat, cm^{-1}) 3436, 1744; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.21 (s, 1H), 5.15 (s, 1H), 4.66 (d, J = 13.4 Hz, 1H), 4.59 (d, J = 13.4 Hz, 1H), 4.17 (dd, J = 6.6 Hz, J = 6.4 Hz, 1H), 2.08 (s, 3H), 1.83 (br s, 1H), 1.57 (m, 2H), 1.28 (m, 8H), .89 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.8, 146.2, 113.6, 73.5, 64.0, 35.5, 31.7, 29.1, 25.5, 22.6, 20.9, 14.0; MS *m/z* (M^+ + 1) calcd 215.1647, obsd 215.1650.

Coupling of 1b to Cyclohexanecarboxaldehyde. colorless oil; IR (neat, cm^{-1}) 3468, 1721; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.1 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 5.29 (s, 1H), 5.22 (s, 1H), 4.88 (d, J = 13.7 Hz, 1H), 4.86 (d, J = 13.7 Hz, 1H), 3.95 (d, J = 7.3 Hz, 1H), 1.99-1.51 (m, 6H), 1.25-0.97 (m, 5H), (OH not apparent); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 166.3, 144.9, 133.0, 130.0, 129.6, 128.4, 114.9, 78.9, 64.1, 41.3, 29.7, 28.3, 26.3, 26.1, 25.9; MS *m/z* (M^+ + 1) calcd 275.1647, obsd 275.1626.

2-bromo-1-propenyl acetate (1a). Cesium acetate (3.63 g, 18.9 mmol) was added to a solution of freshly distilled 2,3-dibromopropene (3.44 g, 17.2 mmol) in DMF (15 mL). The reaction mixture was reacted overnight at 40°C and then poured over a saturated $NaHCO_3$ solution (10 mL) and extracted with ether (3 x 20 mL). The combined organic layers were washed with water (3 x 5 mL), dried over $MgSO_4$, filtered and concentrated. The crude material was distilled under reduced pressure (46-48°C, 12 mm Hg) to yield **1a** as a colorless liquid (2.2 g, 72%).

2-bromo-1-propenyl benzoate (1b). Benzoic acid (1.22 g, 10.0 mmol) and N,N-diisopropylethylamine (1.29 g, 10.0 mmol) were added to a solution of freshly distilled 2,3-dibromopropene (1.0 g, 5.0 mmol) in DMF (10 mL). The reaction mixture was stirred for 3 hours at 60°C and then poured over a saturated NH_4Cl solution (5 mL) and extracted with ether (3 x 15 mL). The combined organic layers were washed with $NaHCO_3$ solution (2 x 5 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified via flash chromatography (10% EtOAc/hexanes) to yield **1b** as a colorless liquid (1.18 g, 98%).

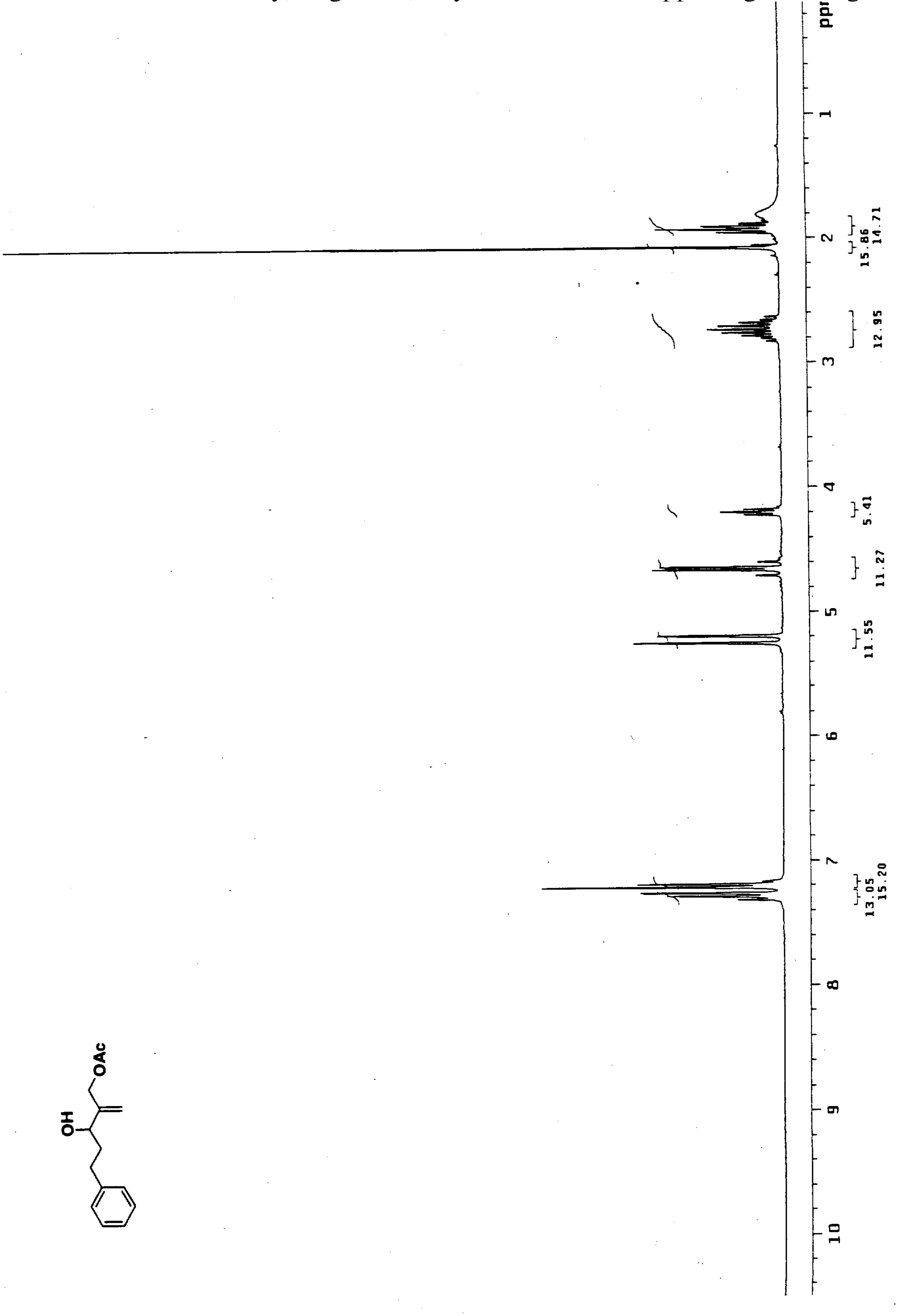
2-iodo-penten-3-ol (3c). Ethyl magnesium bromide (2.75 mL, 3 M in THF) was slowly added to a solution of 2-iodo-propenal (prepared by the method of Segall, *Mutat. Res.* **1985**, *158*, 61-68) (0.75 g, 4.1 mmol) in ether (10 mL) at 0°C. The reaction mixture was stirred for 1 hour and then poured over NH_4Cl (5 mL) and extracted with ether (3 x 10 mL). The combined organic layers were washed successively with $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude material was purified via flash chromatography to yield **3c** as a colorless oil (0.57 g, 65%).

$CrCl_2$/$NiCl_2$ Mediated Reaction of 3c with Hydrocinnamaldehyde A solution of 2-iodo-penten-3-ol (134 mg, .63 mmol) and hydrocinnamaldehyde (28 mg, .21 mmol) in DMF (1.5 mL) was added to a mixture of $CrCl_2$ (103 mg, .84 mmol) and $NiCl_2$ (0.10 mol %). The reaction was stirred at room temperature for eight hours. The reaction mixture was then quenched with 0.15 mL of an aqueous solution of ethylenediamine (12.6 M) and stirred for 15 minutes during which time the solution turned from green to purple. The mixture was poured over water (2 mL) and extracted with ether (3 x 5 mL). The combined organic layers were washed successively with 2N HCl (1 x 2 mL), dried over $MgSO_4$, filtered and concentrated. **4c** was purified via flash chromatography (50% EtOAc/hexanes) to yield an inseparable mixture of syn and anti isomers as a colorless oil (23 mg, 50%). IR (neat, cm^{-1}) 3401; ^1H NMR (300 MHz, $CDCl_3$) δ7.32–7.17 (overlapping m, 10 H), 5.17 (s, 1H), 5.15 (s, 1H), 5.14 (s, 1H), 5.13 (s, 1H), 4.24 (overlapping dd, J = 6.5 Hz, 2H), 4.15 (overlapping t, 2H), 2.85-2.61 (overlapping m, 4H), 2.06-1.92 (overlappting m, 4H), 1.75-1.60 (overlapping m, 4H), 0.95 (overlapping t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 153.3, 152.1, 142.0 (2C), 128.7 (4C), 126.1 (2C), 112.2, 111.8, 75.2, 75.1, 73.2, 72.8, 38.3, 37.7, 32.5, 32.4, 29.5, 28.9, 10.5, 10.4; MS *m/z* (M^+ - H_2O) calcd 202.1358, obsd 202.1369

Silylation Procedure. The product from the coupling of **1b** with cyclohexanecarboxaldehyde (128 mg, .467 mmol), TBSCl (350 mg, 2.54 mmol) and imidazole (260 mg, 3.82 mmol) were stirred in DMF (8 mL) for 3 hours at 50°C. The reaction mixture was poured over a saturated solution of NH_4Cl (3 mL) and extracted with ether (3 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude material was purified via flash chromatography (10% EtOAc/hexanes) to yield **5** as a colorless oil (134 mg, 64%). IR (neat, cm^{-1}) 1726; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.1 Hz, 2H), 5.23 (s, 1H), 5.11 (s, 1H), 4.84 (d, J = 14.0 Hz, 1H), 4.80 (d, J = 14.0 Hz, 1H), 3.87 (d, J = 7.3 Hz, 1H), 1.96-1.44 (m, 6H), 1.25-0.88 (m, 5H), 0.90 (s, 9H), 0.05 (s, 3H), .01 (s, 3H), (OH not apparent); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 166.5, 145.2, 133.2, 130.5 129.8, 128.6, 114.2, 80.3, 64.1, 42.2, 30.1, 29.0, 26.8, 26.5, 26.4, 26.1, 18.5, -4.3, -4.8; MS *m/z* (M^+ + 1) calcd 389.2512, obsd 389.2536.

Coupling of 5 to Benzaldehyde. To a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (5 mole % generated *in situ*) in THF (2.5 mL) is added **5** (30 mg, .077 mmol), diethyl zinc (0.37 mL, 1.0 M in hexanes) and benzaldehyde (16 mg, .15 mmol). The flask was fitted with a reflux condenser and the mixture was reacted at 50°C for 12 hours. The mixture was quenched with NH_4Cl (.50 mL) and extracted with ether (3 x 5 mL). The combined organic layers were washed successively with $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude material was purified via flash chromatography to yield an inseparable mixture of syn and anti (3:1) isomers as a colorless oil (24 mg, 83%). Spectral data for this product is identical to those reported in the literature.[7]

Coupling of 5 to Cyclohexanecarboxaldehyde. This compound was prepared according to the above procedure and isolated as an inseparable mixture of syn and anti isomers (3:1, colorless oil, 61%). Spectral data for this product is identical to those reported in the literature.[7]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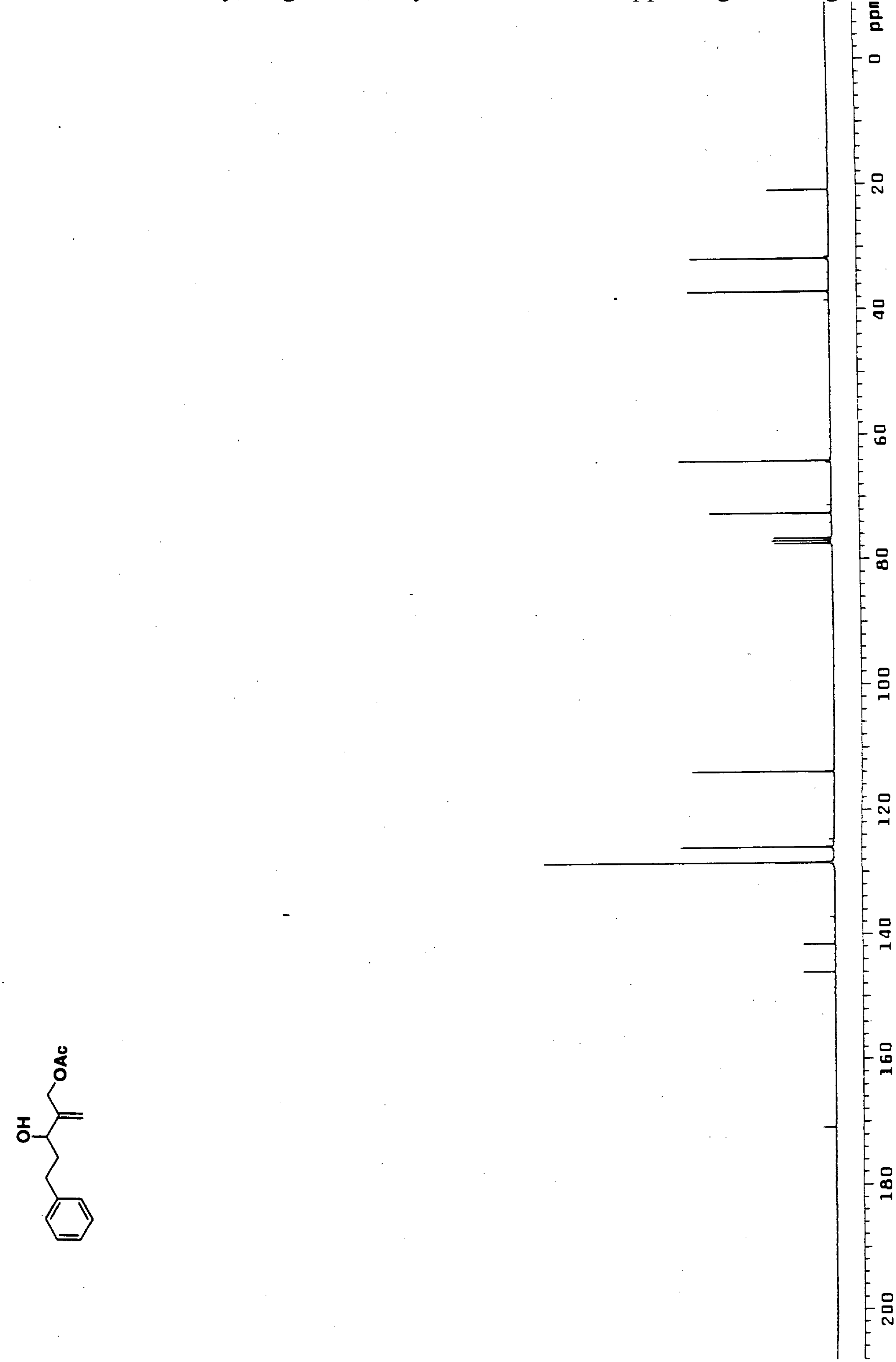

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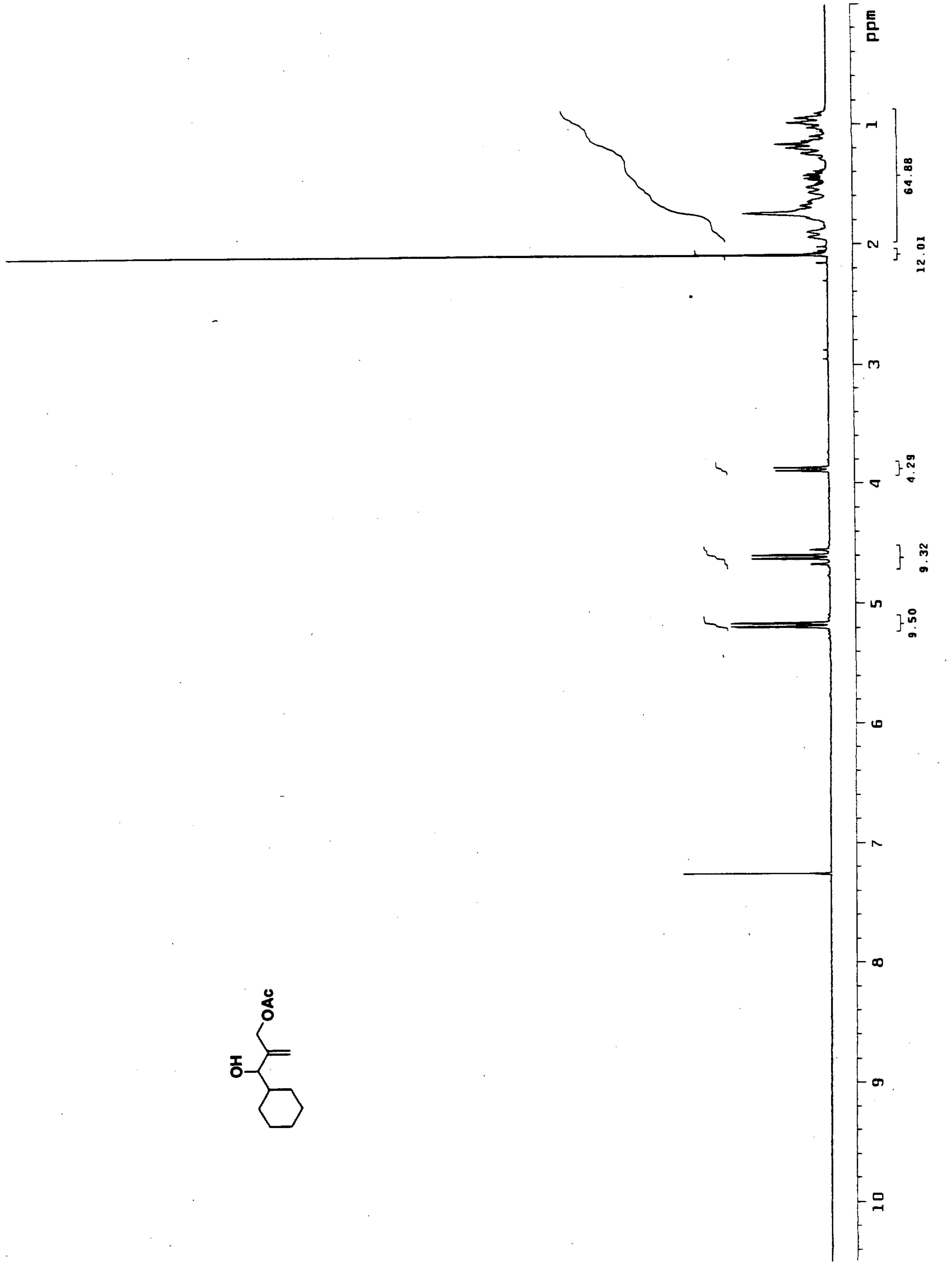

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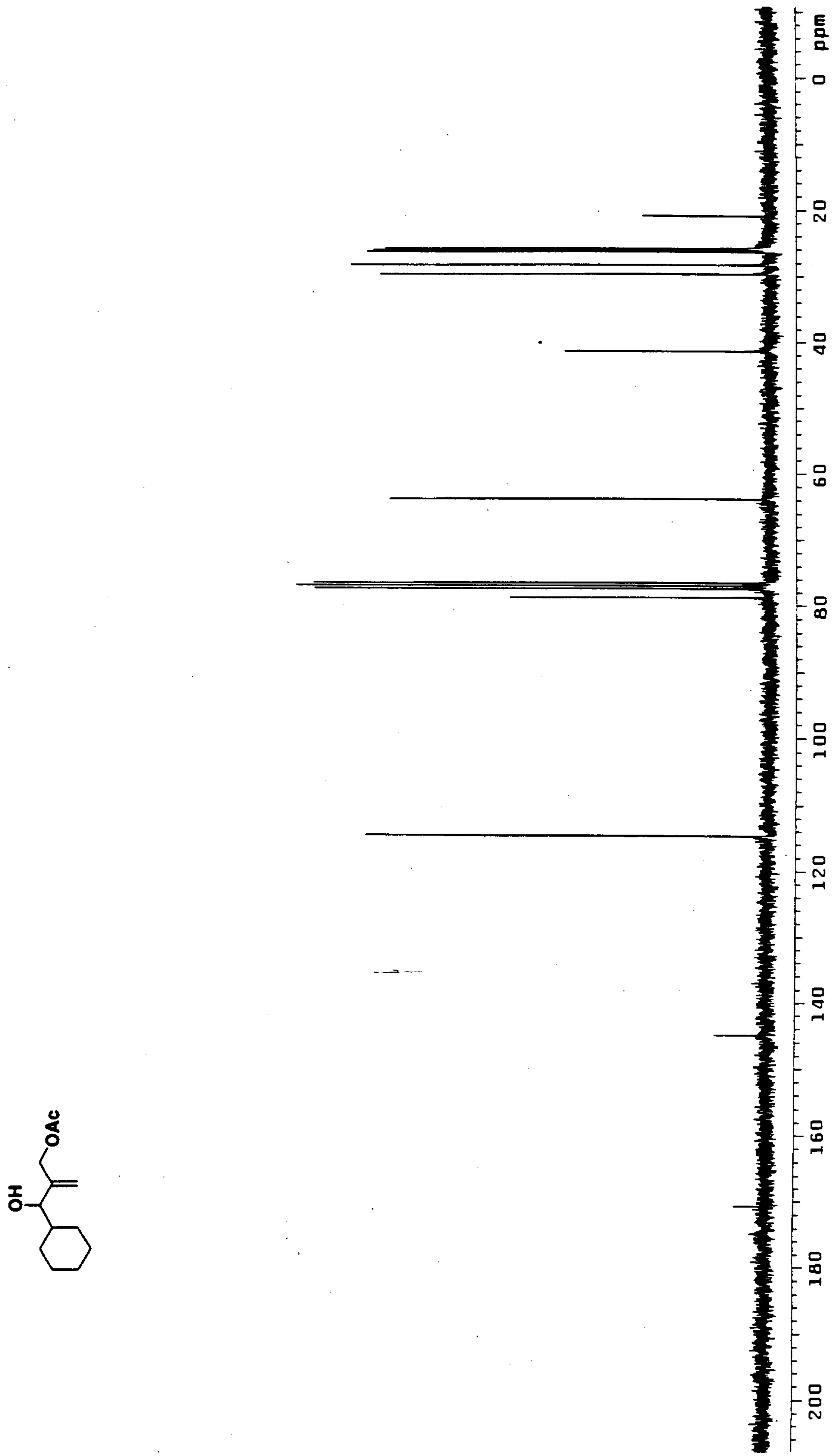

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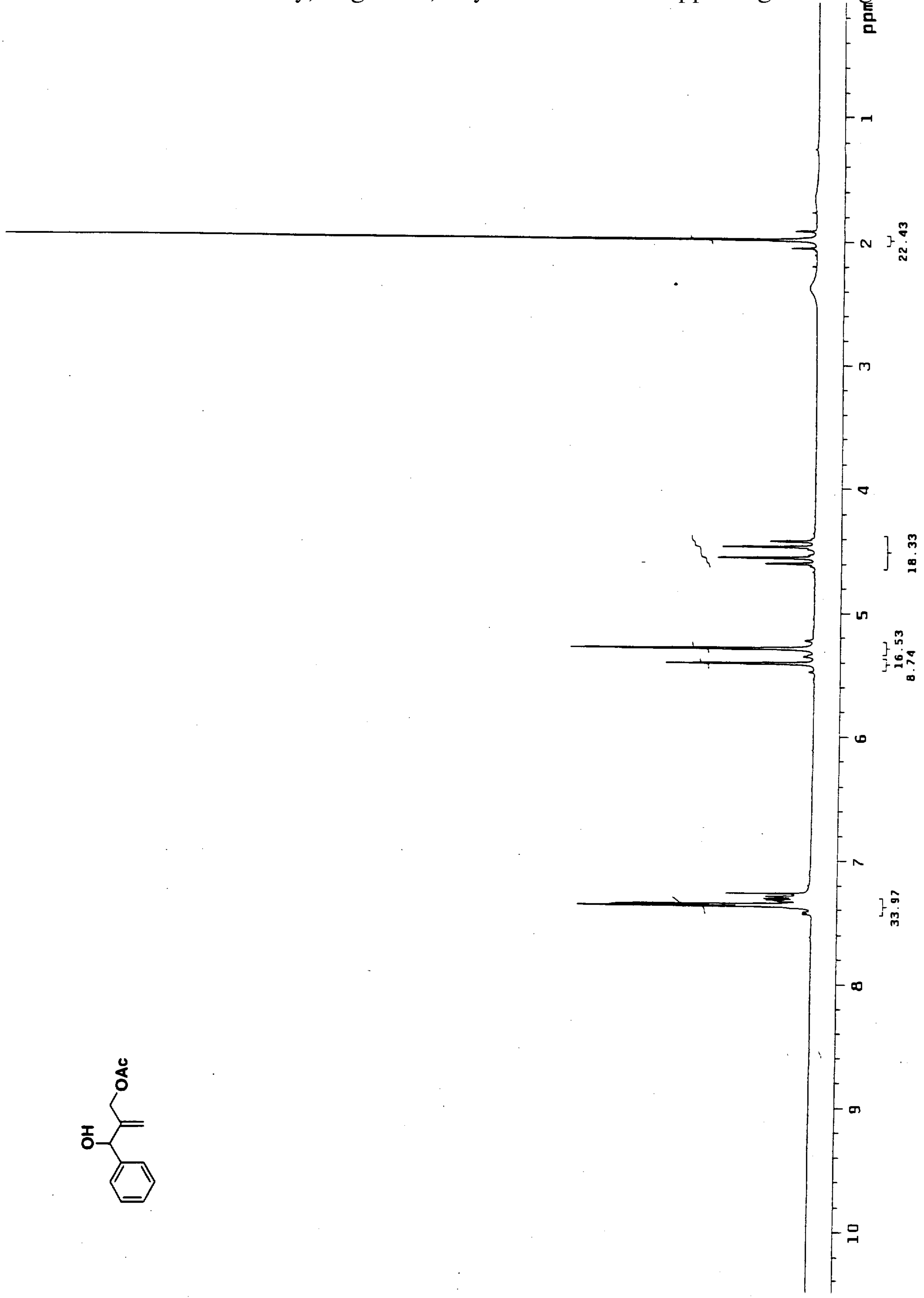
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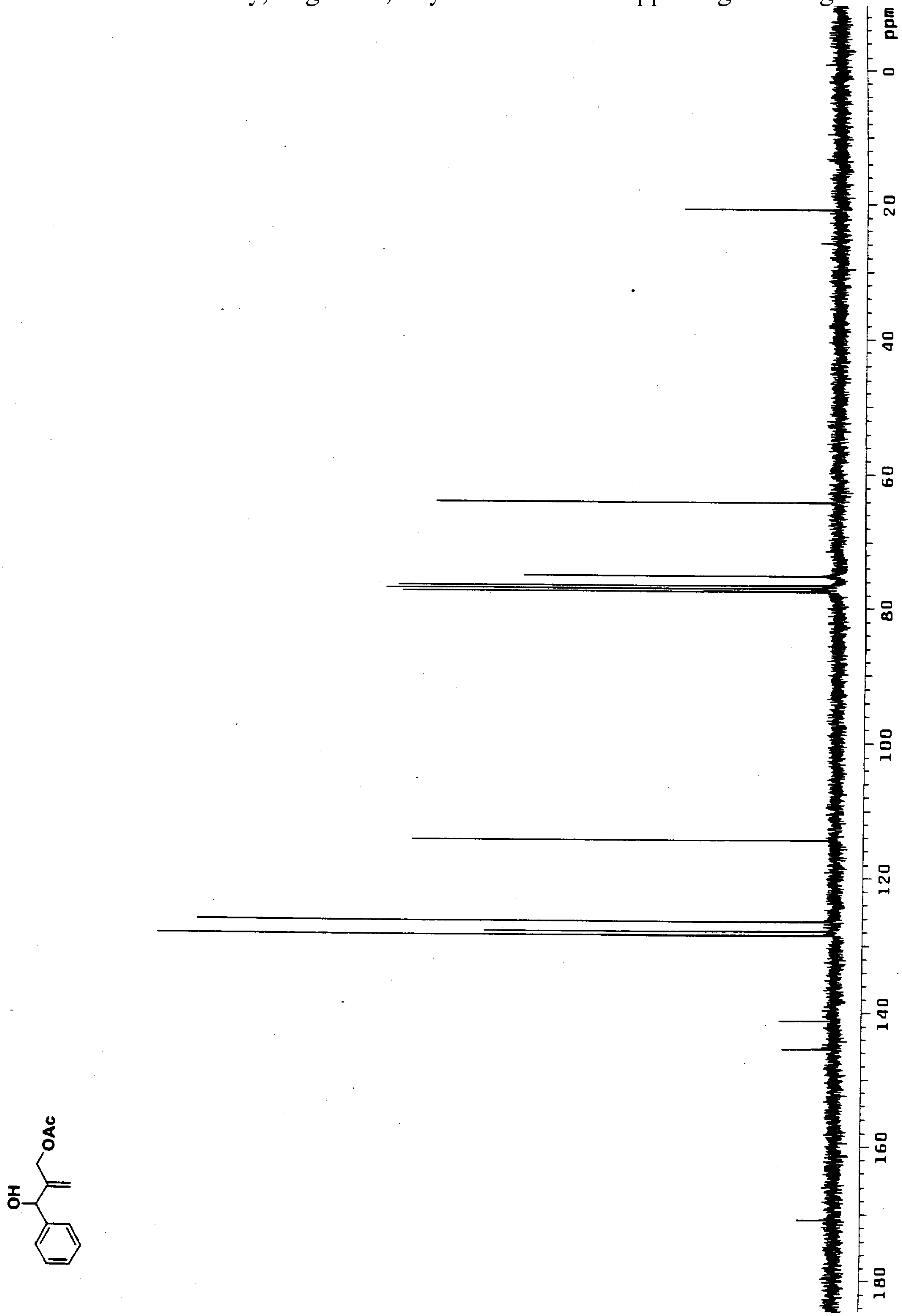

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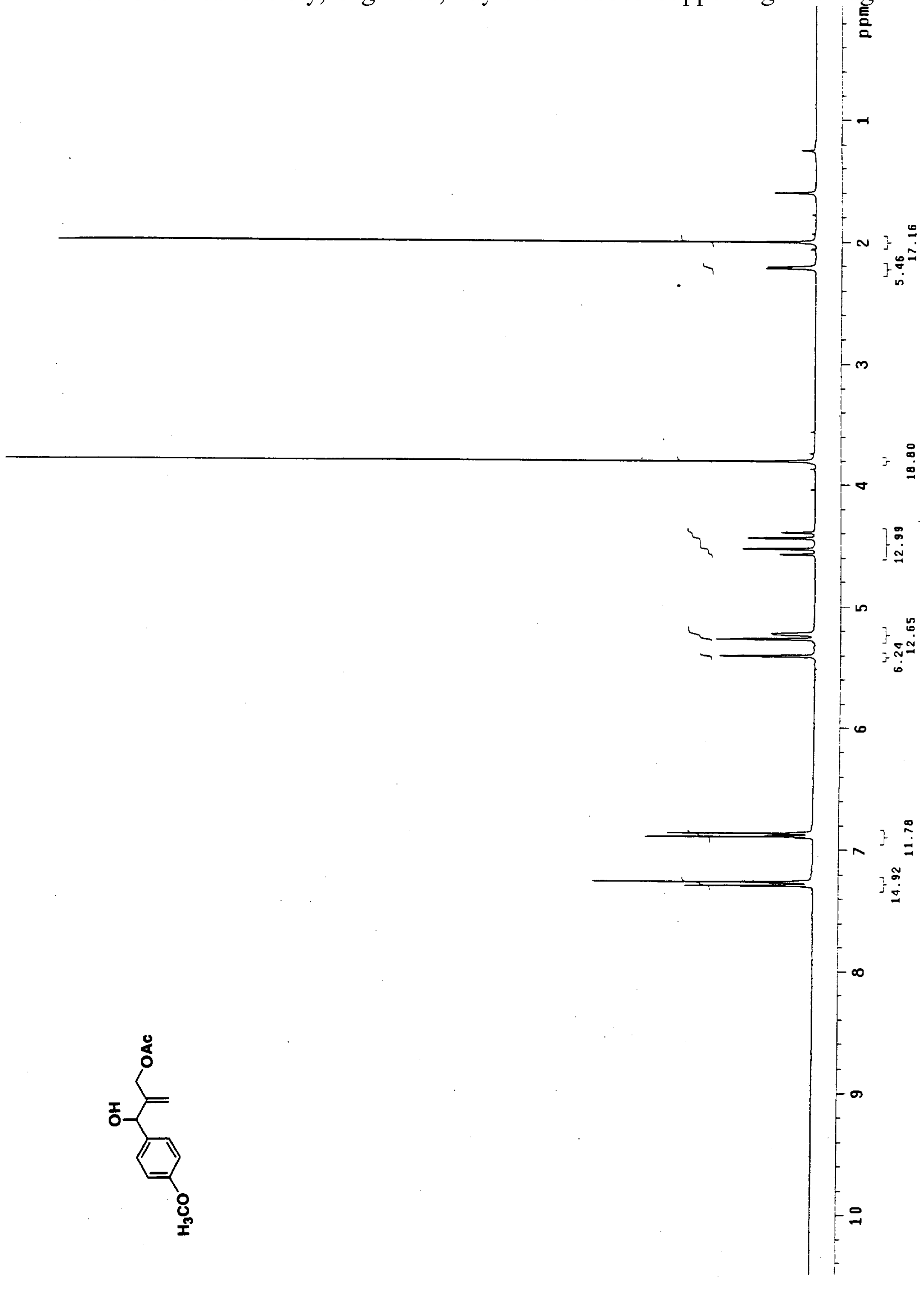
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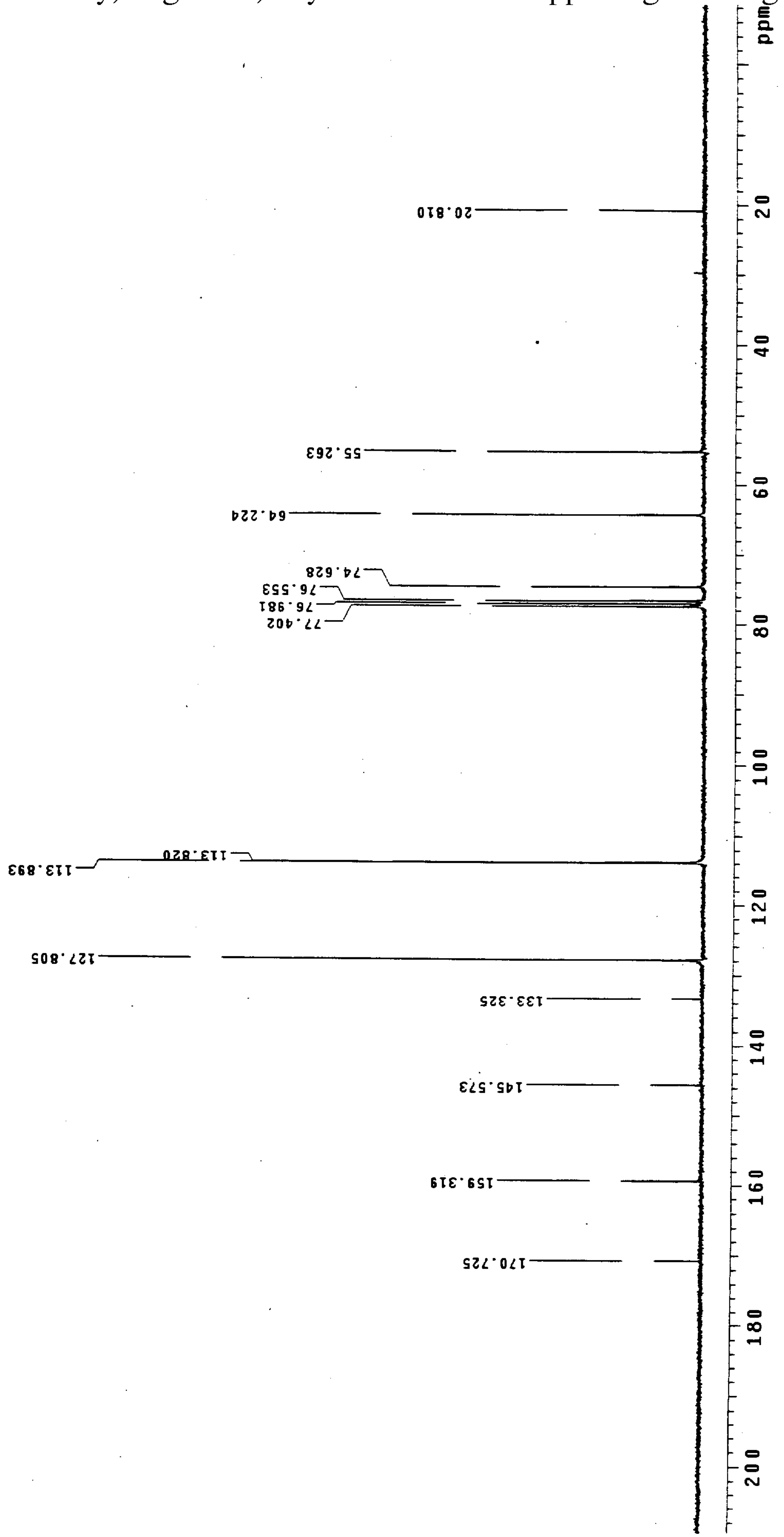
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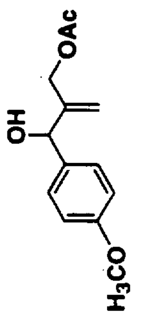
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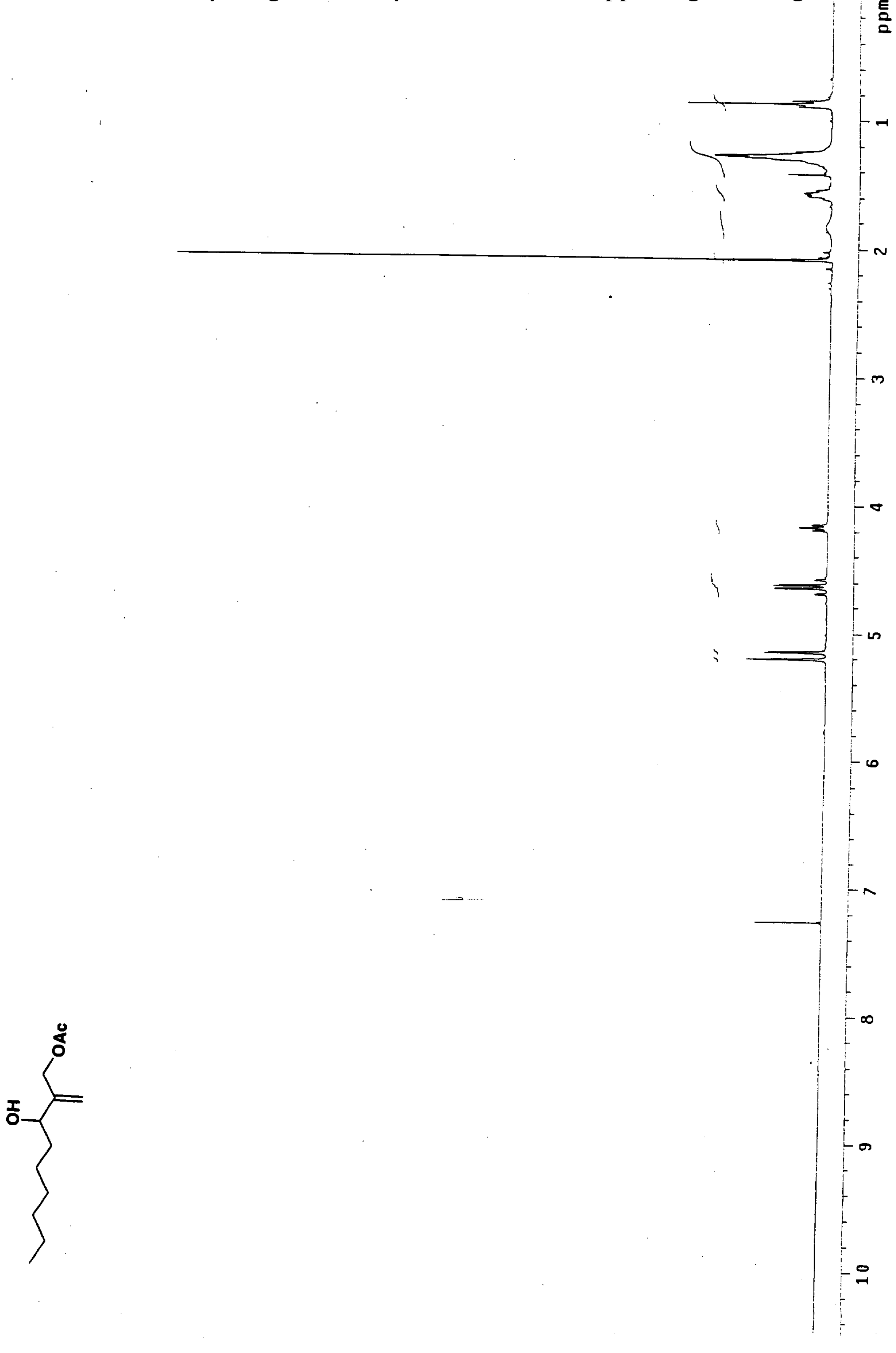
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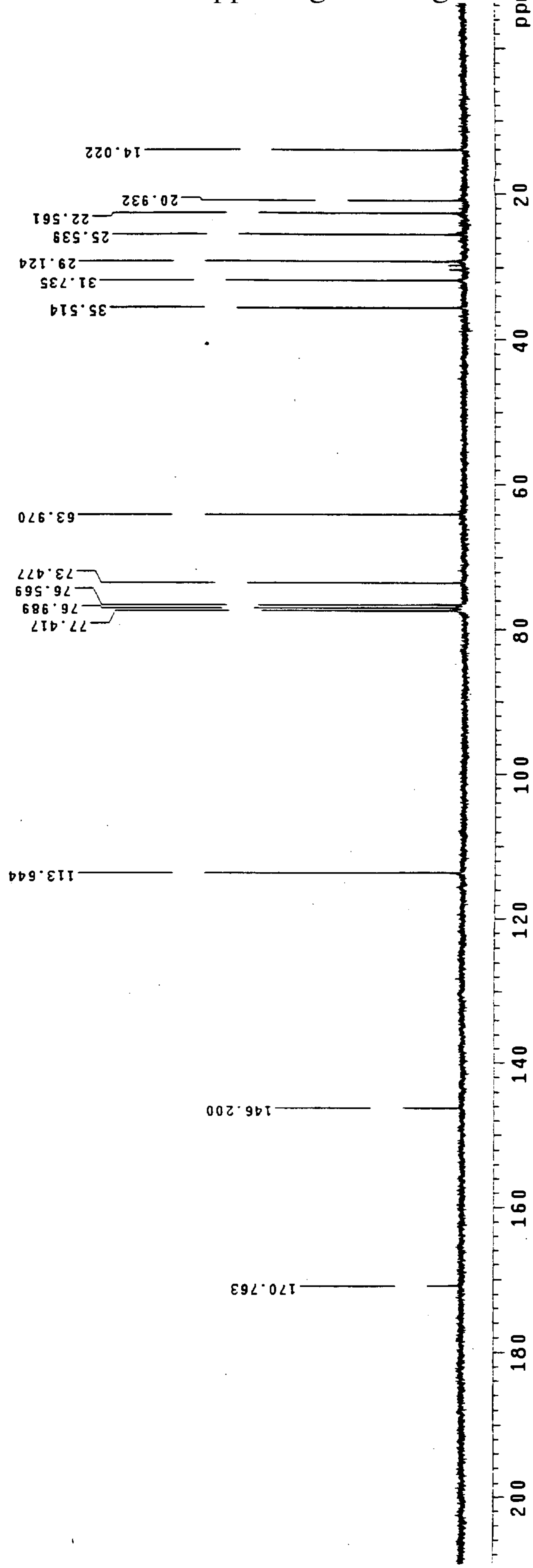
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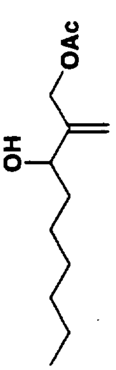
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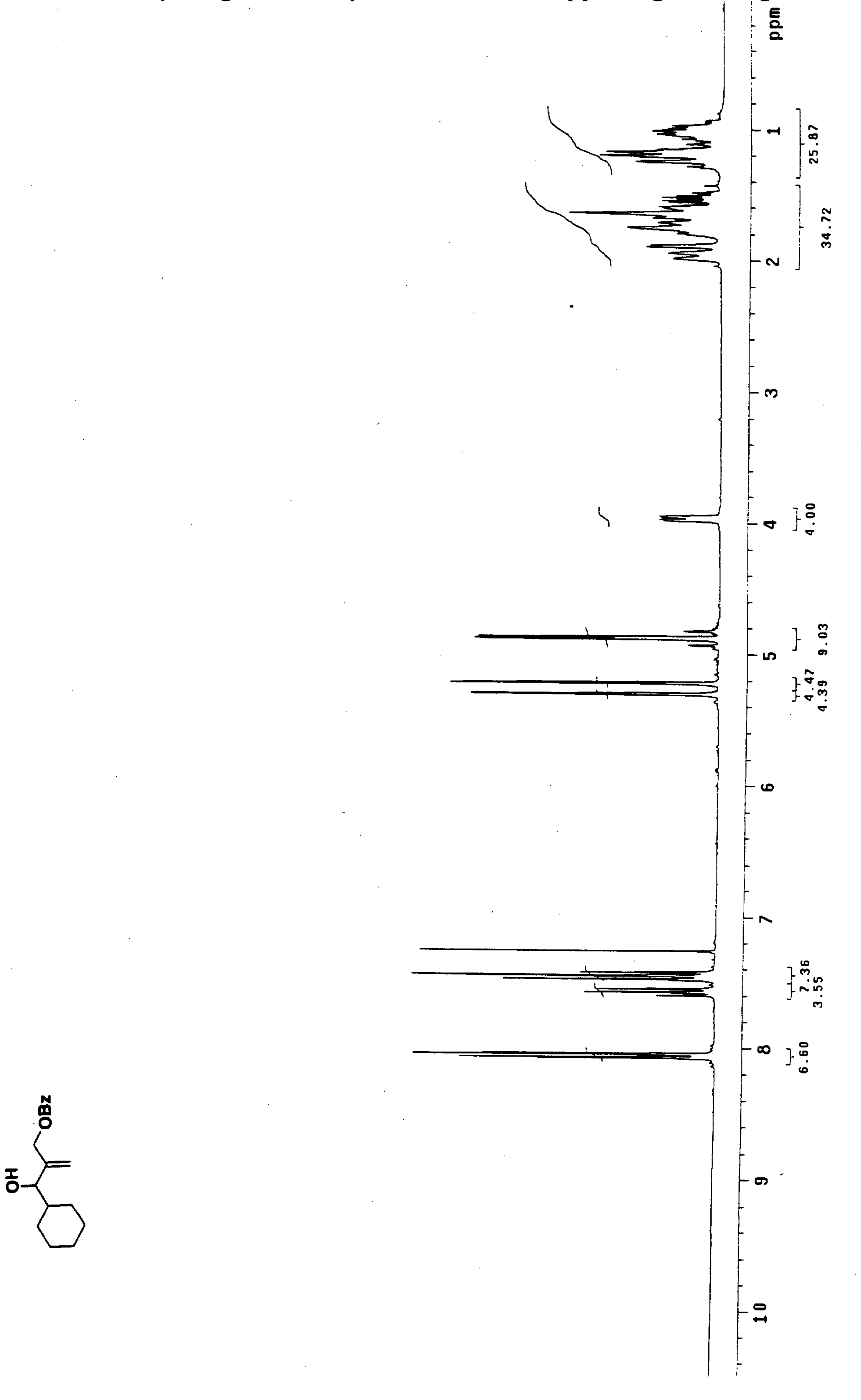

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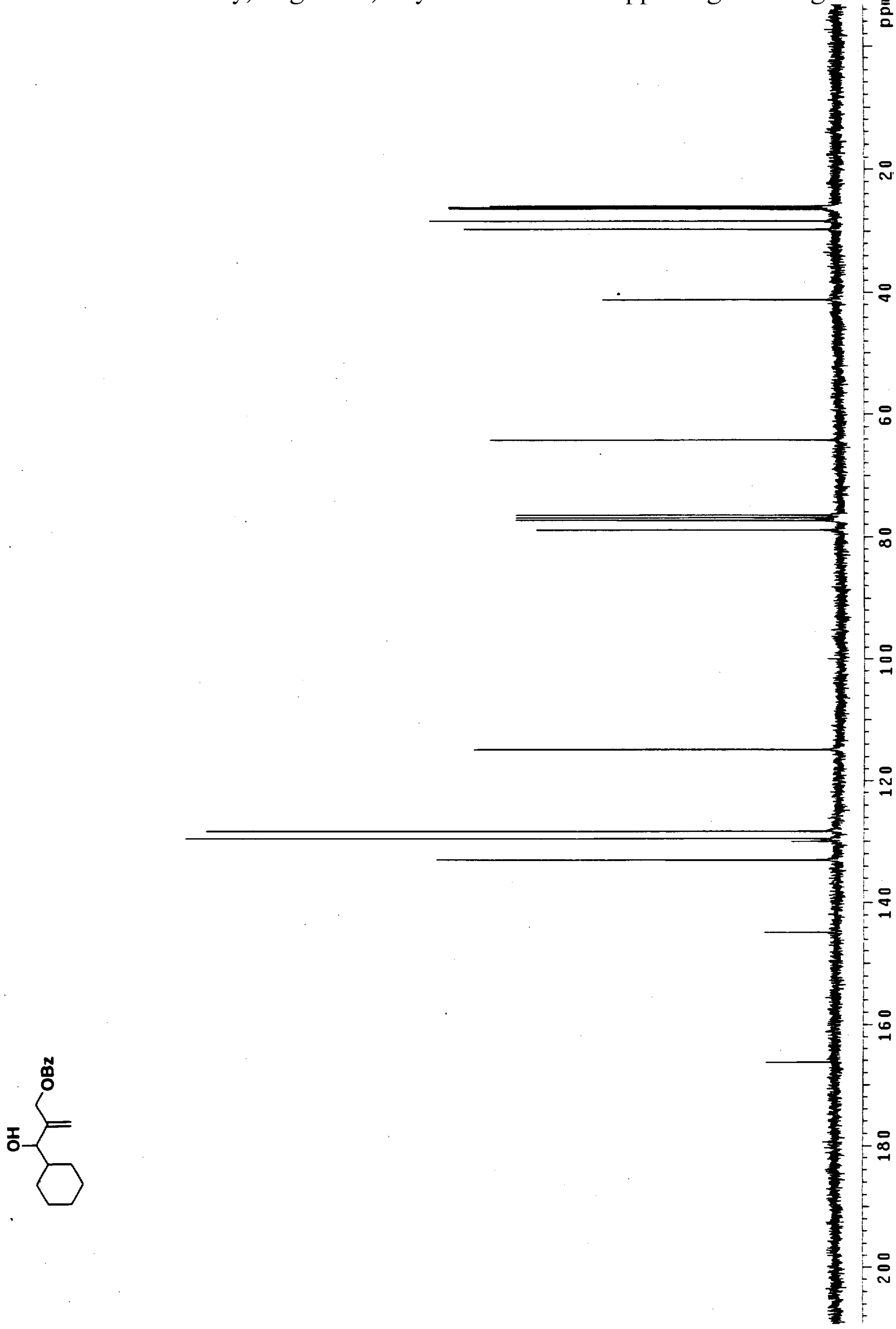

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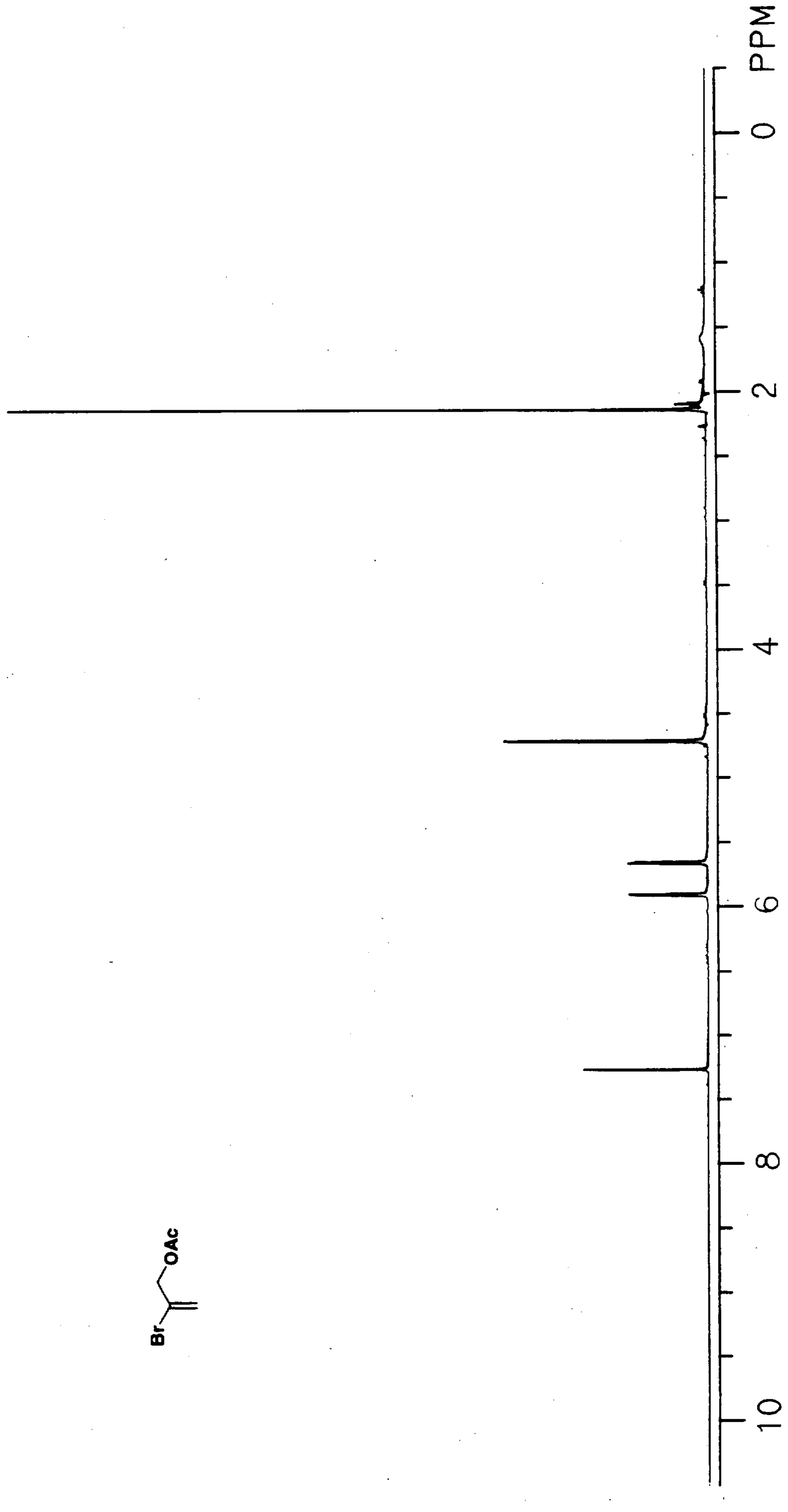

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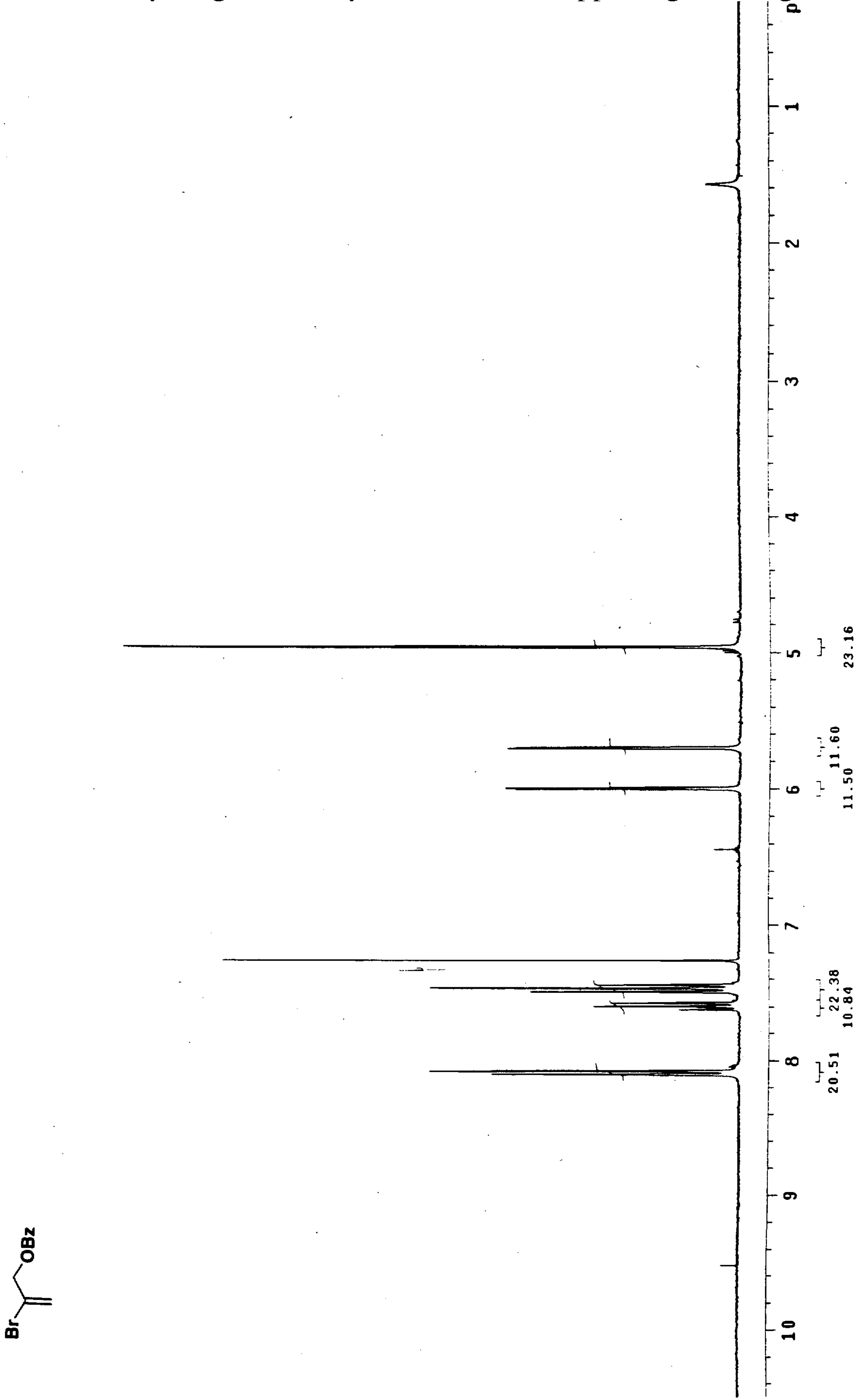

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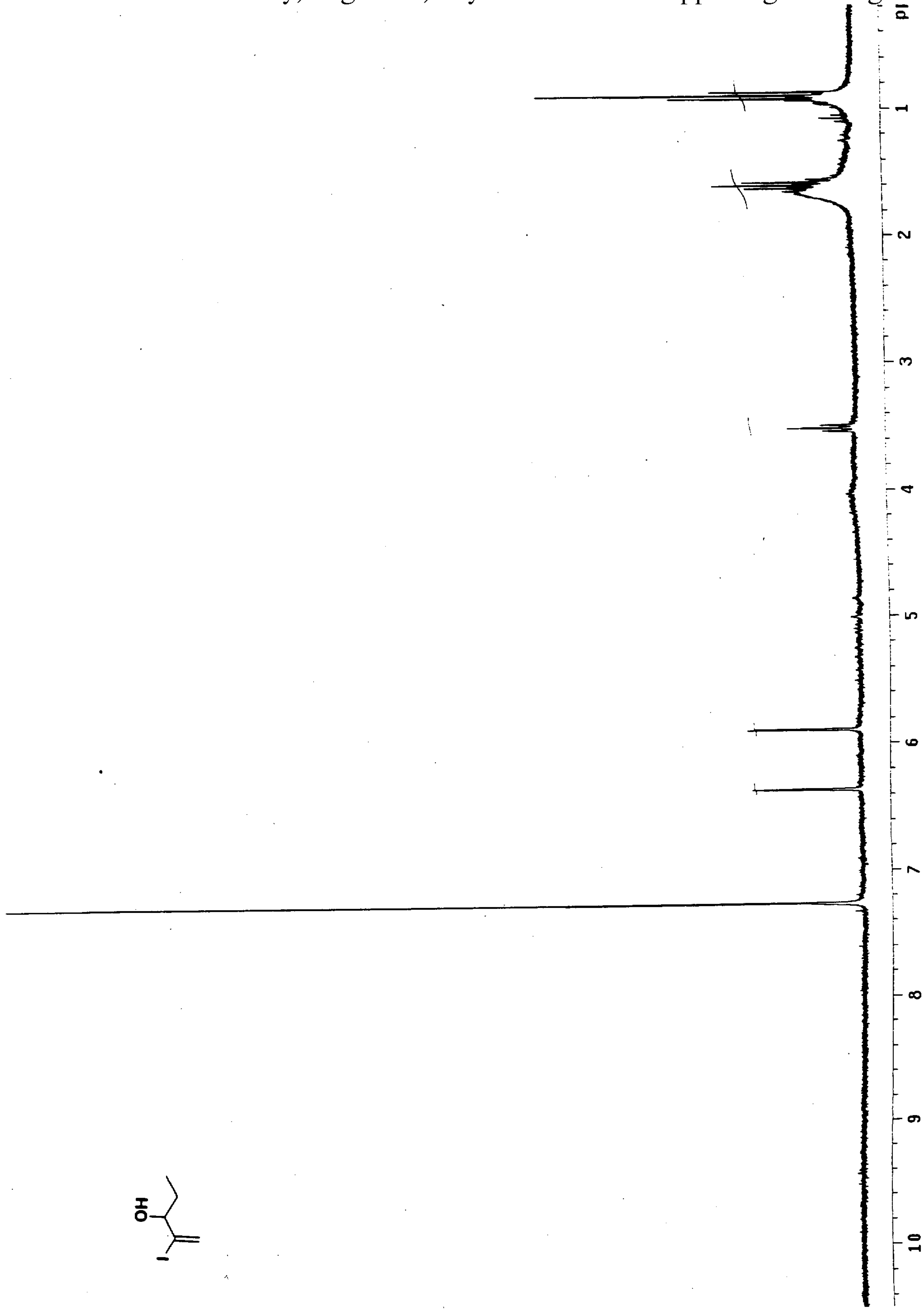

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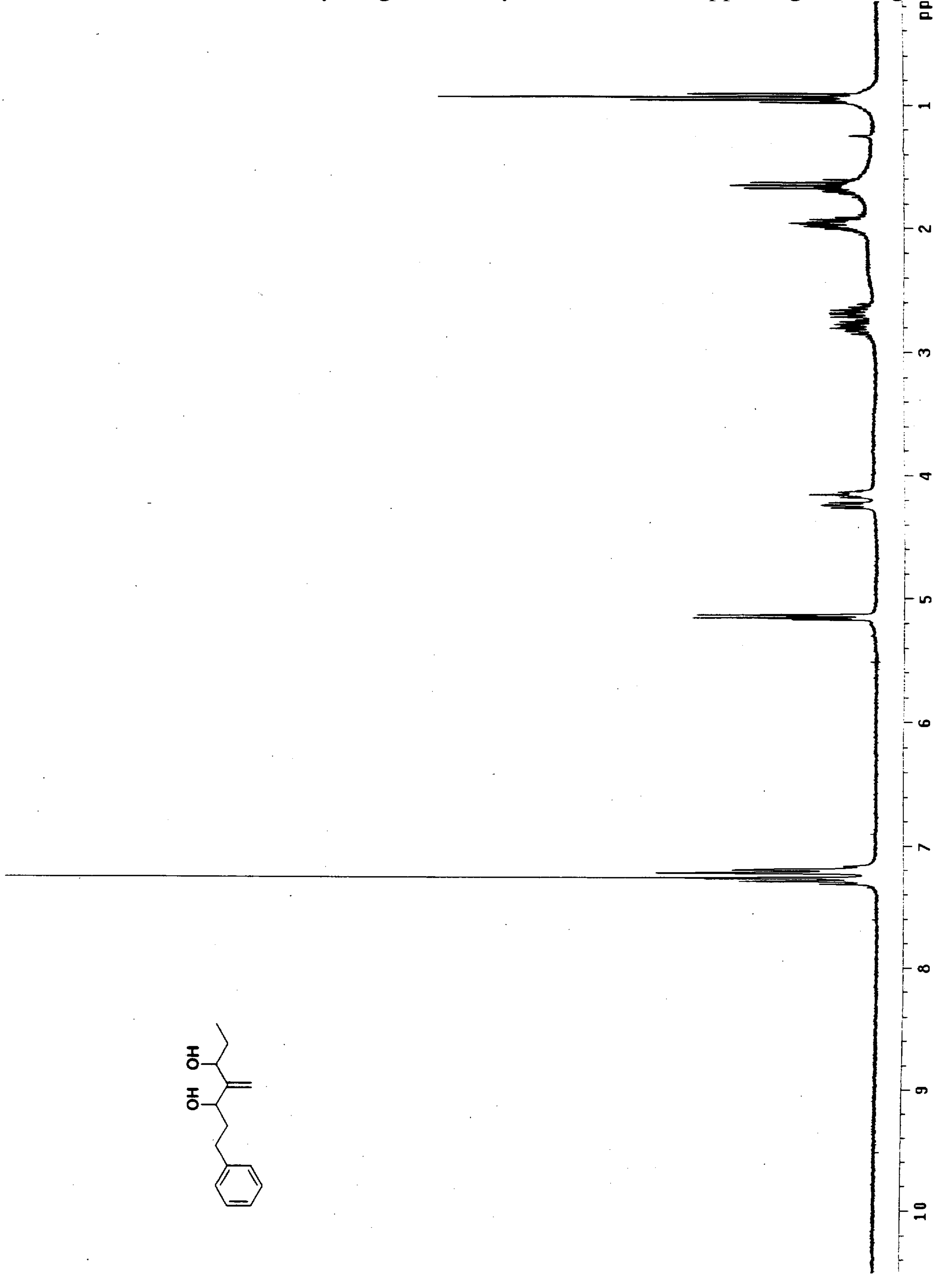

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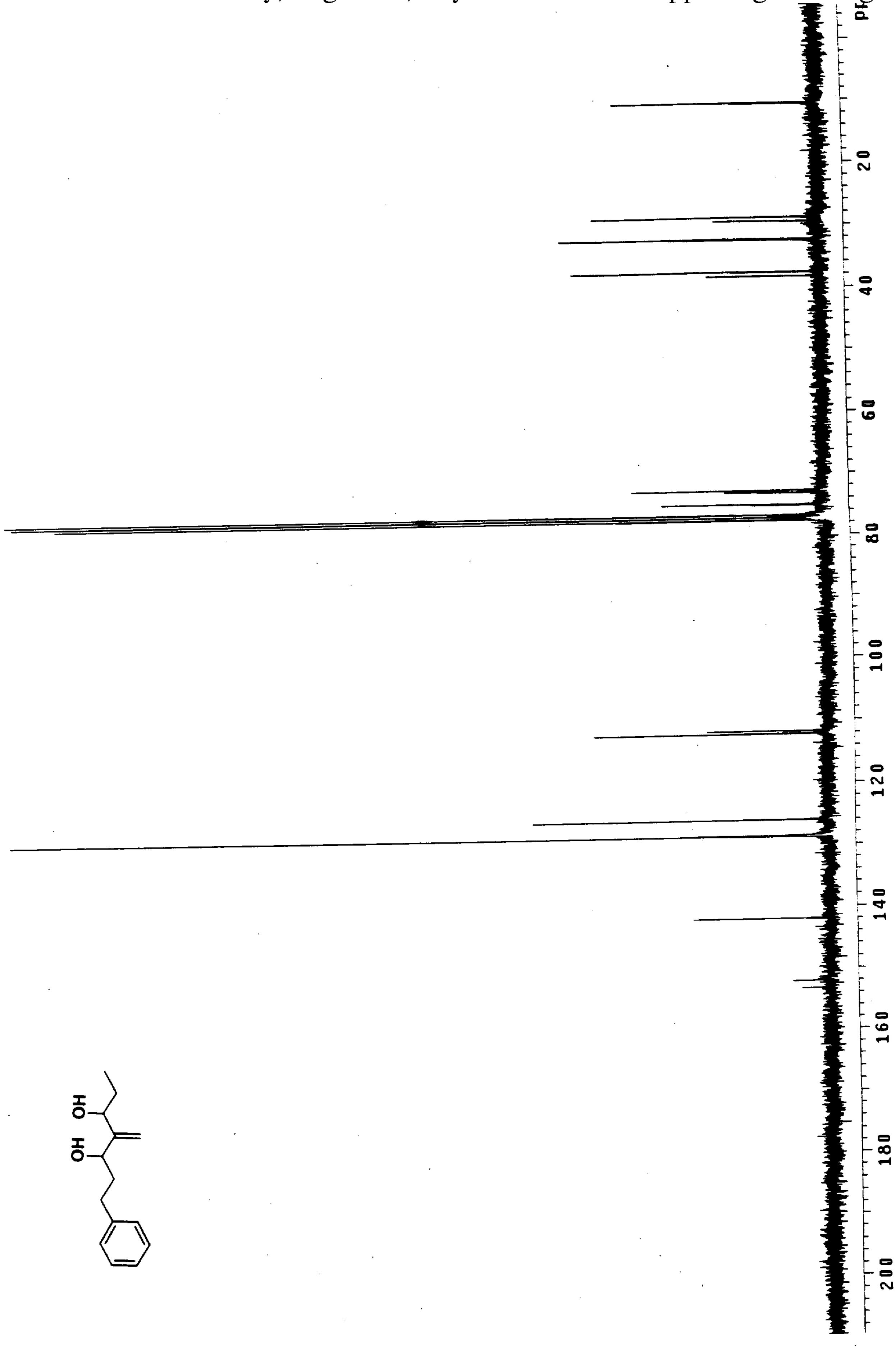

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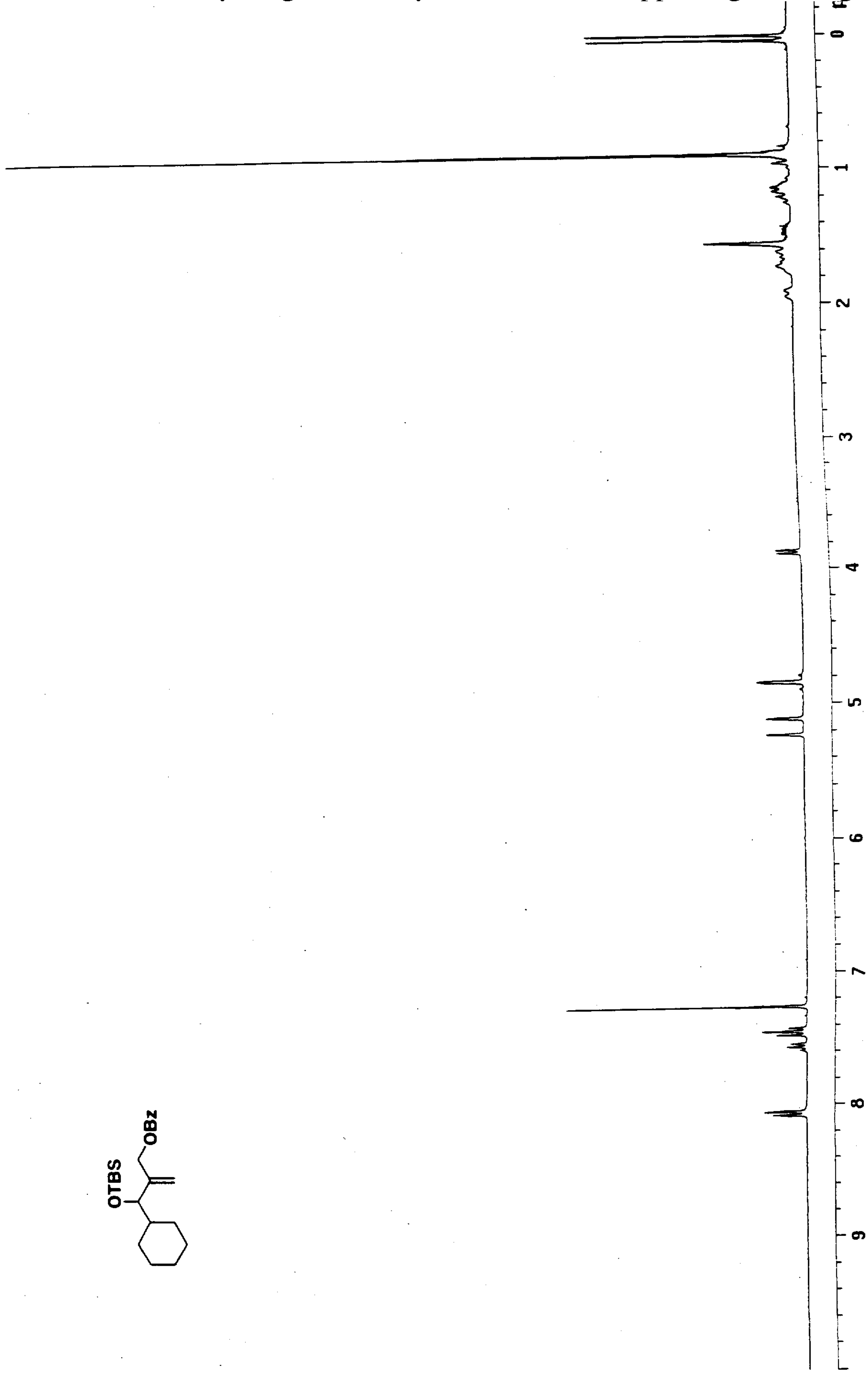

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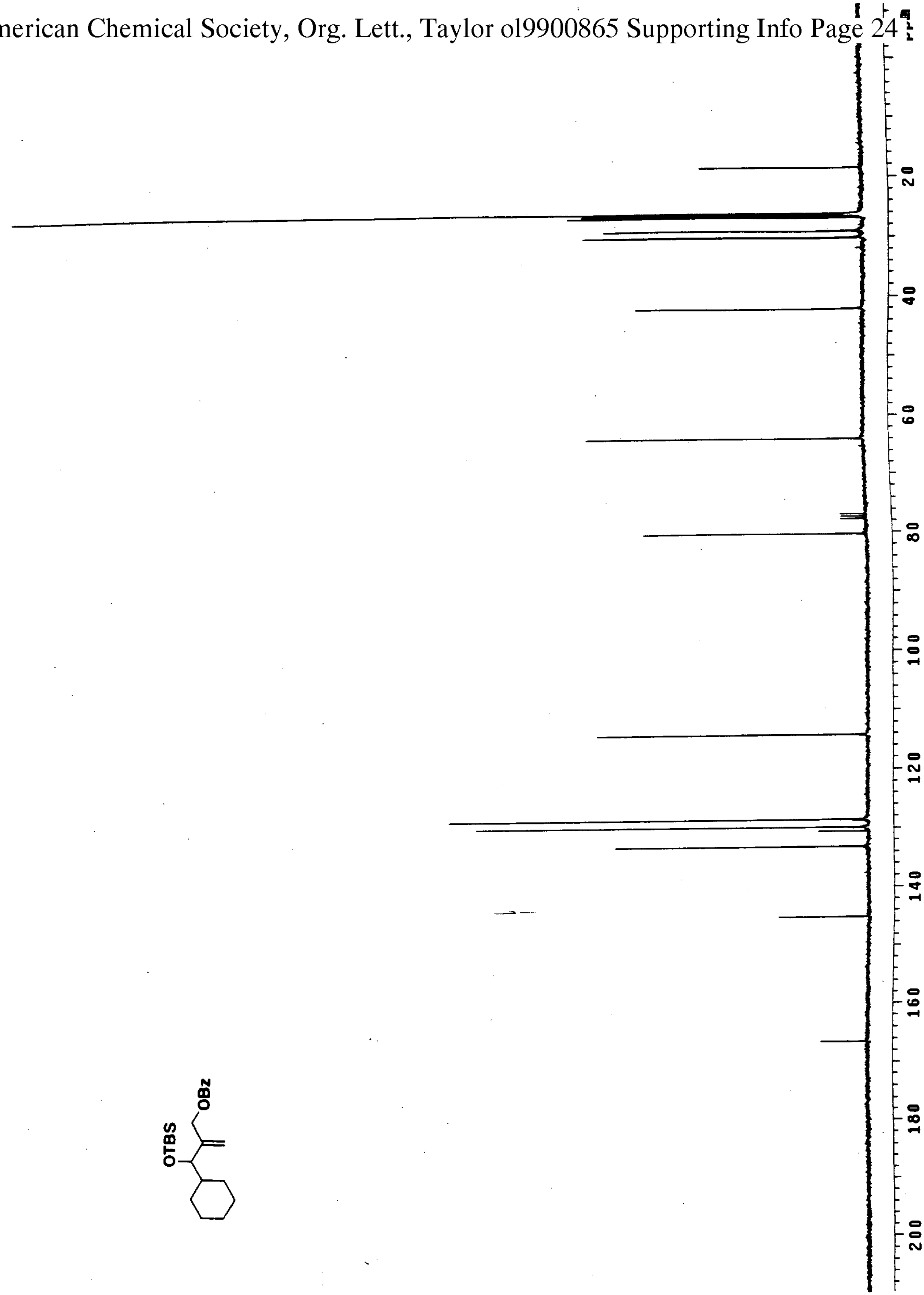

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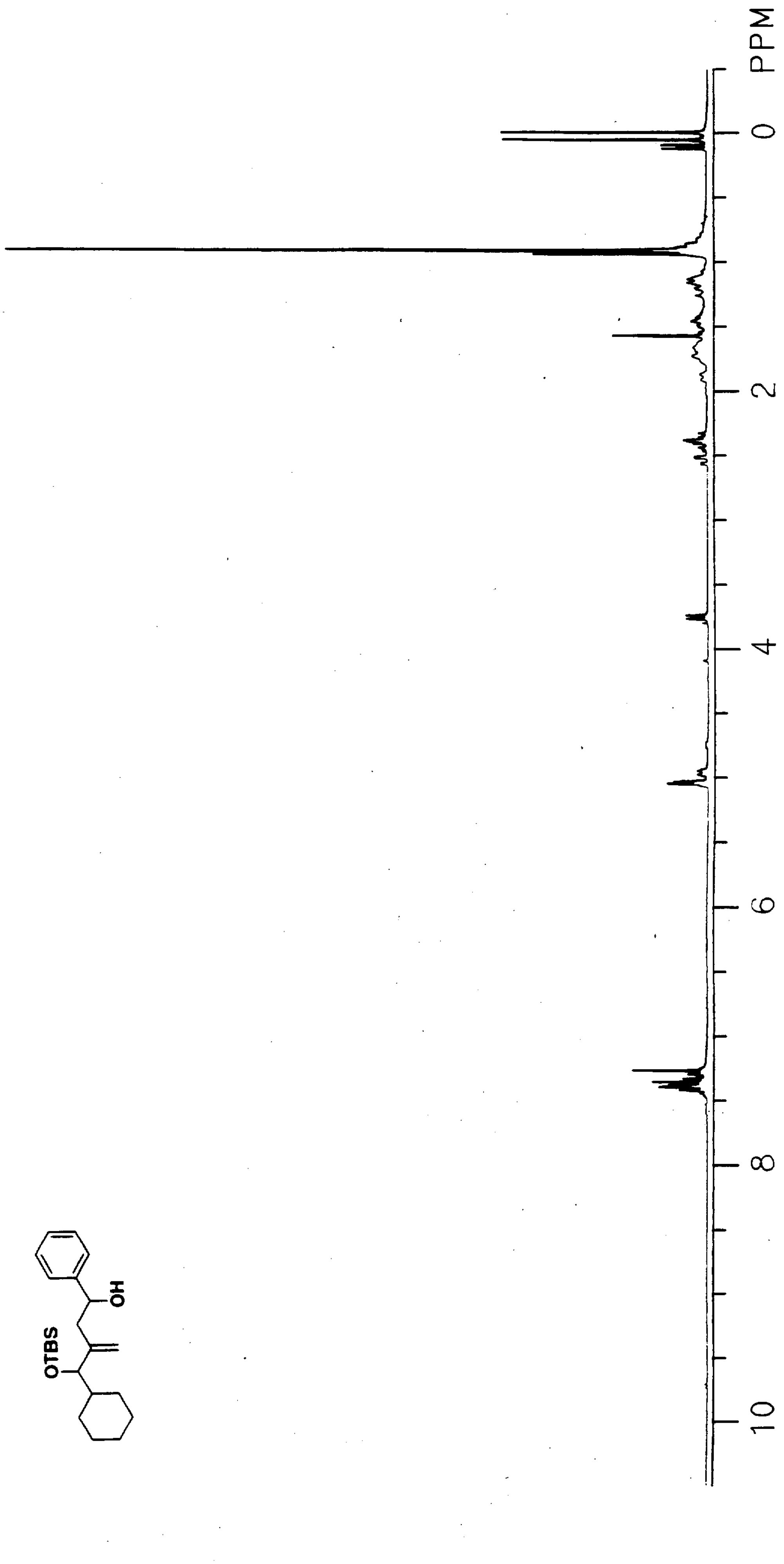

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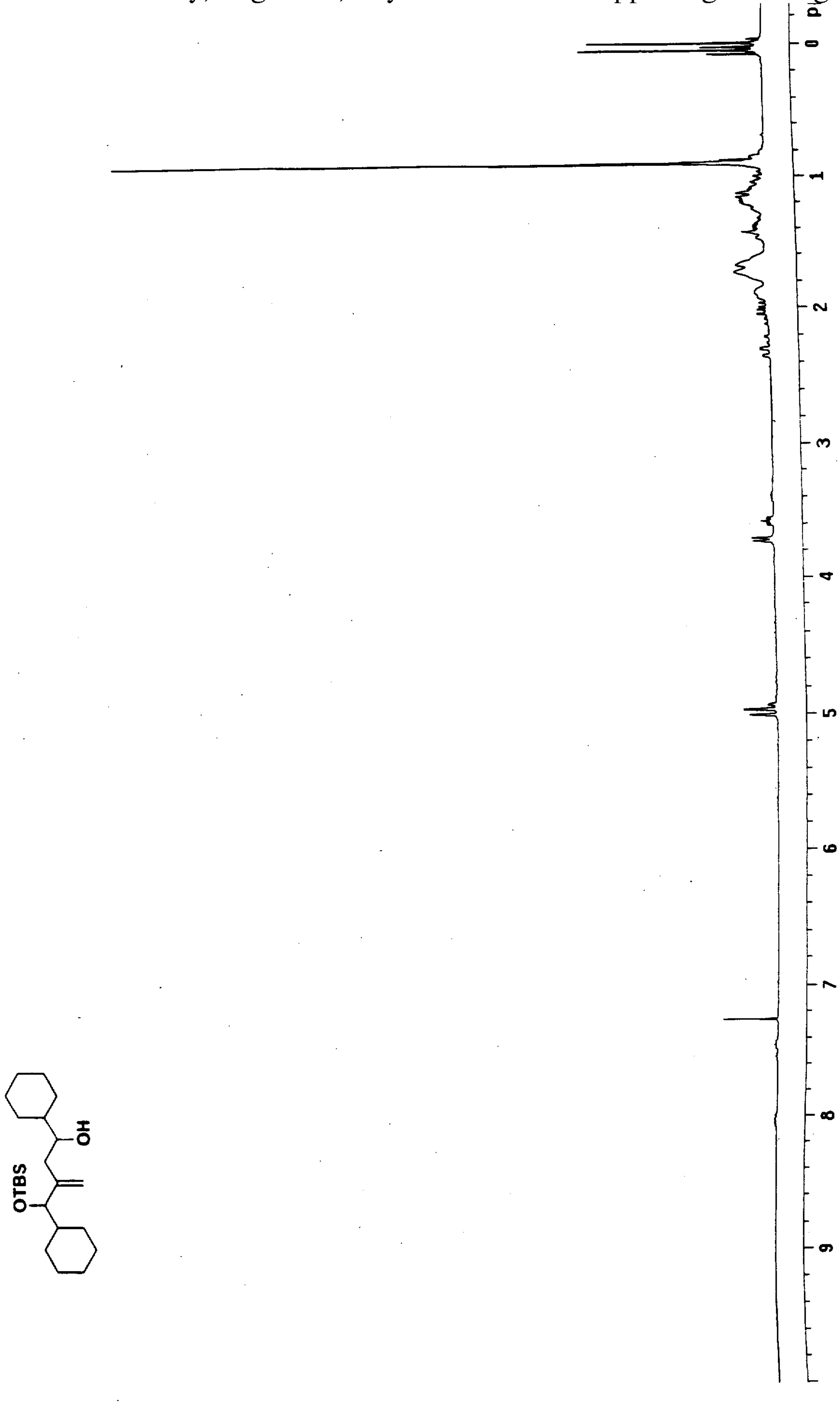

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