

# J | A | C | S

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Rev

## Supporting Information

### Palladium Catalyzed Hydrocarboxylation of Allenes

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Compound **3a**; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.32 (m, 5H), 6.66 (d, J = 16.0 Hz, 1H), 6.29 (dt, J = 16.0, 7.0 Hz, 1H), 4.72 (d, J = 6.5 Hz, 2H), 2.10 (s, 3H); HRMS: Calc'd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>(M<sup>+</sup>): 176.0836. Found: 176.0840. Anal. Calc'd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>: C, 74.977; H, 6.863. Found: C, 74.372; H, 7.067.

Compound **3b**; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.32 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.15 (dt, J = 16.0, 7.0 Hz, 1H), 4.70 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H), 2.09 (s, 3H); Anal. calc'd for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: C, 69.885; H, 6.841. Found: C, 69.817; H, 6.953.

Compound **3c**; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.56 (d, J = 7.0 Hz, 2H), 7.48 (d, J = 7.0 Hz, 2H), 6.68 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 18.0, 7.0 Hz, 1H), 4.75 (d, J = 6.5 Hz, 2H), 2.13 (s, 3H); Anal. Calc'd for C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>O<sub>2</sub>: C, 59.018; H, 4.539. Found: C, 59.212; H, 4.633.

Compound **3d**; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.32 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.15 (dt, J = 16.0, 7.0 Hz, 1H), 4.71 (d, J = 7.0 Hz, 2H), 3.80 (s, 3H), 2.34 (q, J = 7.0 Hz, 2H), 1.16 (t, J = 7.0 Hz, 3H); Anal. Calc'd for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.888; H, 7.321. Found: C, 71.149; H, 7.255.

Compound **3e**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.35 (d,  $J = 8.0$  Hz, 2H), 7.42 (m, 5H), 6.84 (d,  $J = 8.0$  Hz), 6.73 (d,  $J = 16.0$  Hz, 1H), 6.40 (dt,  $J = 16.0, 7.0$  Hz, 1H), 4.98 (d,  $J = 7.0$  Hz, 2H); HRMS: Calc'd for  $\text{C}_{16}\text{H}_{14}\text{O}_2(\text{M}^+)$ : 238.0993. Found: 238.0998.

Compound **3f**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.09 (d,  $J = 7.0$  Hz, 2H), 7.42 (m, 5H), 6.84 (d,  $J = 7.0$  Hz, 2H), 6.68 (d,  $J = 16.0$  Hz), 6.25 (dt,  $J = 16.0, 6.5$  Hz, 1H), 4.95 (d,  $J = 6.5$  Hz, 2H), 3.78 (s, 3H); Anal. Calc'd for  $\text{C}_{17}\text{H}_{16}\text{O}_3$ : C, 76.100; H, 6.010. Found: C, 75.960; H, 6.109.

Compound **3g**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.22 (d,  $J = 7.0$  Hz, 2H), 7.61 - 7.48 (m, 5H), 7.28 (d,  $J = 7.0$  Hz, 2H), 6.67 (d,  $J = 16.0$  Hz, 1H), 6.39 (dt,  $J = 16.0, 6.0$  Hz, 1H), 4.96 (d,  $J = 6.0$  Hz, 2H), HRMS: Calc'd for  $\text{C}_{16}\text{H}_{13}^{79}\text{BrO}_2(\text{M}^+)$ : 316.0098. Found: 316.0105.

Compound **3h**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J = 16.0$  Hz, 1H), 7.35 (m, 10H), 6.77 (d,  $J = 16.0$  Hz, 1H), 6.48 (d,  $J = 16.0$  Hz, 1H), 6.35 (dt,  $J = 16.0, 6.0$  Hz, 1H), 4.87 (d,  $J = 6.0$  Hz, 2H), HRMS: Calc'd for  $\text{C}_{18}\text{H}_{16}\text{O}_2(\text{M}^+)$ : 264.1149. Found: 264.1138.

Compound **3i**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 16.0$  Hz, 1H), 7.54 - 7.38 (m, 5H), 7.34 (d,  $J = 8.0$  Hz, 2H), 6.86 (d,  $J = 8.0$  Hz), 6.65 (d,  $J = 16.0$  Hz, 1H), 6.46 (d,  $J = 16.0$  Hz, 1H), 6.22 (dt,  $J = 16.0, 6.0$  Hz, 1H), 4.84 (d,  $J = 6.0$  Hz, 2H), 3.80 (s, 3H); Anal. Calc'd for  $\text{C}_{19}\text{H}_{18}\text{O}_3$ : C, 77.530; H, 6.163. Found: C, 77.054; H, 5.948.

Compound **3j**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J = 16.0$  Hz, 1H), 7.40 (m, 9H), 6.66 (d,  $J = 16.0$  Hz, 1H), 6.48 (d,  $J = 16.0$  Hz, 1H), 6.31 (dt,  $J = 16.0, 6.0$  Hz, 1H), 4.85 (d,  $J = 6.0$  Hz, 2H); HRMS: Calc'd for  $\text{C}_{18}\text{H}_{15}^{35}\text{ClO}_2(\text{M}^+)$ : 298.0759. Found: 298.0769.

Compound **3k**;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.32 (d,  $J = 8.0$  Hz, 2H), 6.88 (d,  $J = 8.0$  Hz, 2H), 6.61 (d,  $J = 16.0$  Hz, 1H), 6.12 (dt,  $J = 16.0, 6.0$  Hz, 1H), 5.08 (m, 1H), 4.77 (d,  $J = 6.0$  Hz, 2H), 4.34 (m, 1H), 3.81 (s, 3H), 1.45 (s, 9H), 1.40 (d,  $J = 7.0$  Hz, 3H); HRMS:

Calc'd for  $C_{18}H_{25}NO_5(M^+)$ : 335.1731. Found: 335.1733. Anal. Calc'd for  $C_{18}H_{25}NO_5$ : C, 64.459; H, 7.512; N, 4.176. Found: C, 60.156; H, 7.069; N, 3.916.

Compound **3l**;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.41-6.91 (m, 9H), 6.17 (t,  $J = 6.5$  Hz, 1H), 6.12 (t,  $J = 6.5$  Hz, 1H, Z-isomer), 4.62 (d,  $J = 6.5$  Hz, 2H), 2.07 (s, 3H); Anal. Calc'd for  $C_{17}H_{15}O_2F$ : C, 75.539; H, 5.593. Found: C, 75.174; H, 6.094.

Compound **3m**;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.34-6.98 (m, 5H), 5.68 (t,  $J = 6.0$  Hz, 1H), 4.19 (d,  $J = 6.0$  Hz, 2H), 2.06 (s, 3H), 1.16 (s, 9H); Anal. Calc'd for  $C_{15}H_{20}O_2$ : C, 77.549; H, 8.676. Found: C, 76.435; H, 9.173.

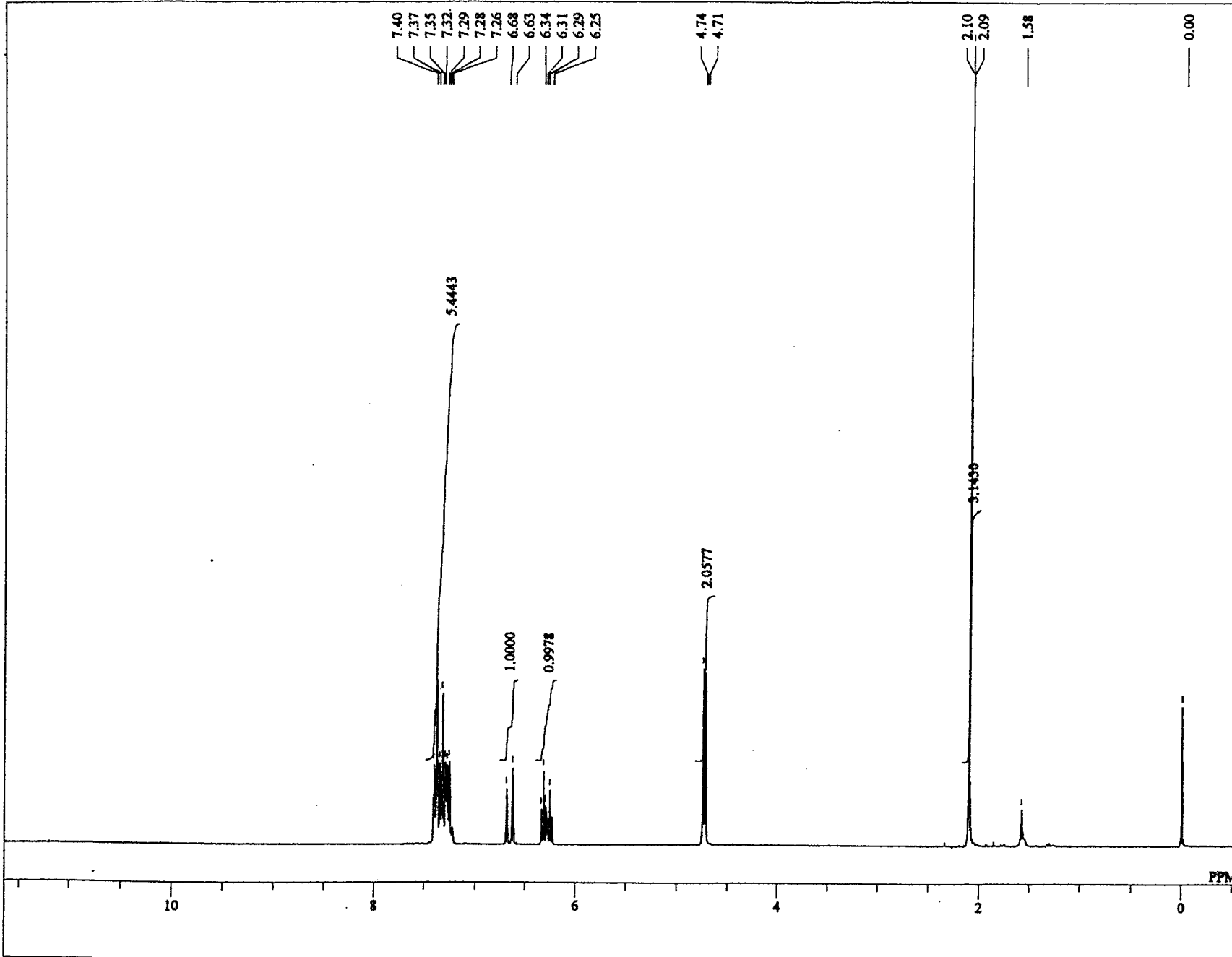
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Compound **3n**;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.41-7.21 (m, 5H), 6.53 (d,  $J = 15.0$  Hz, 1H), 5.82 (dt,  $J = 15.0, 6.5$  Hz, 1H), 4.58 (d,  $J = 6.5$  Hz, 2H), 2.01 (s, 3H); Anal. Calc'd for  $C_{11}H_{12}O_2S$ : C, 63.434; H, 5.807. Found: C, 63.624; H, 5.774.

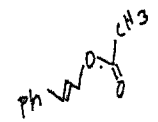
Z-isomer: 6.46 (d,  $J = 9.0$  Hz, 1H), 5.88 (dt,  $J = 9.0, 6.5$  Hz, 1H), 4.78 (d,  $J = 6.5$  Hz, 2H), 2.02 (s, 3H);

3a

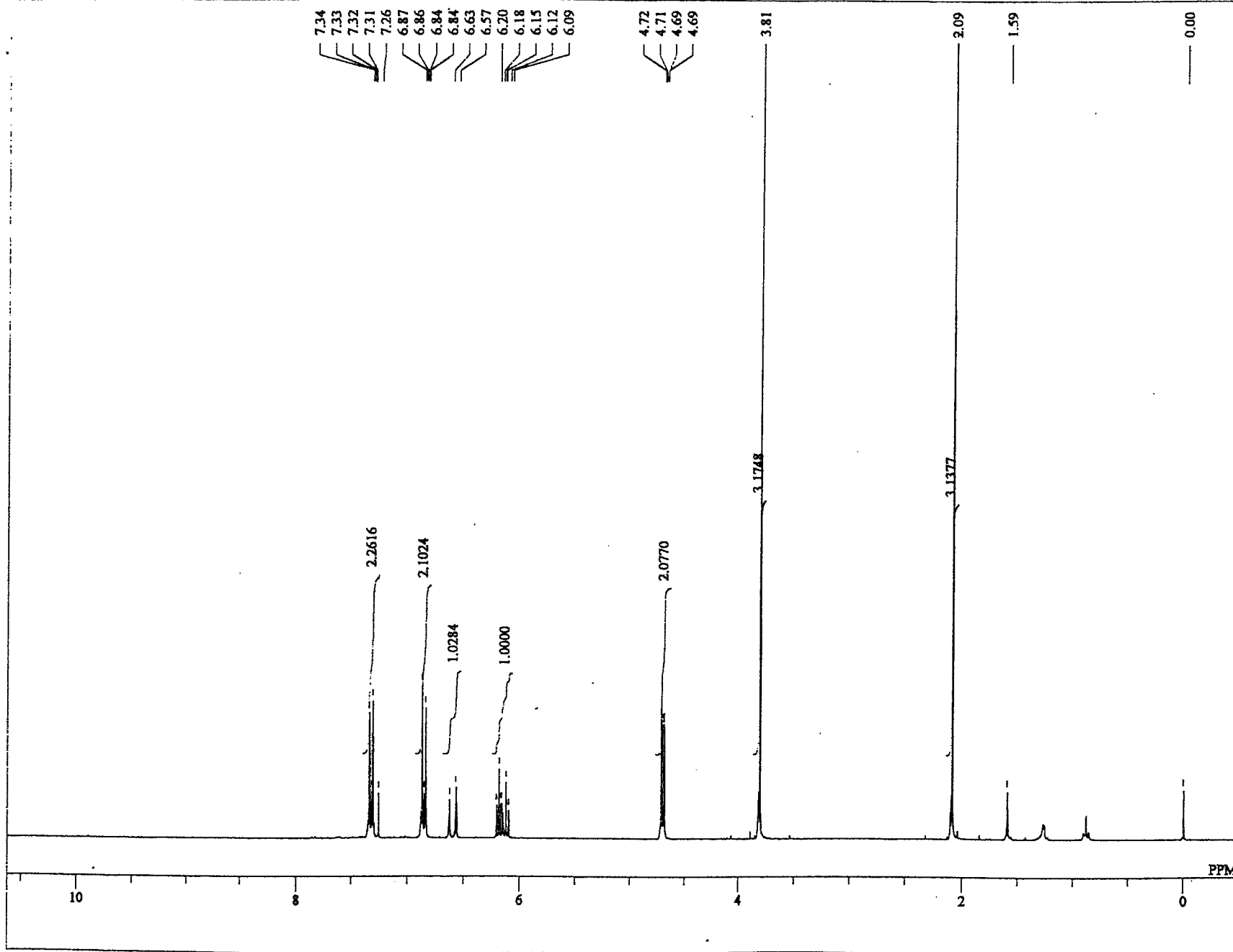
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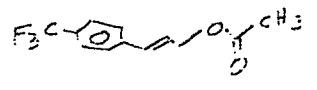
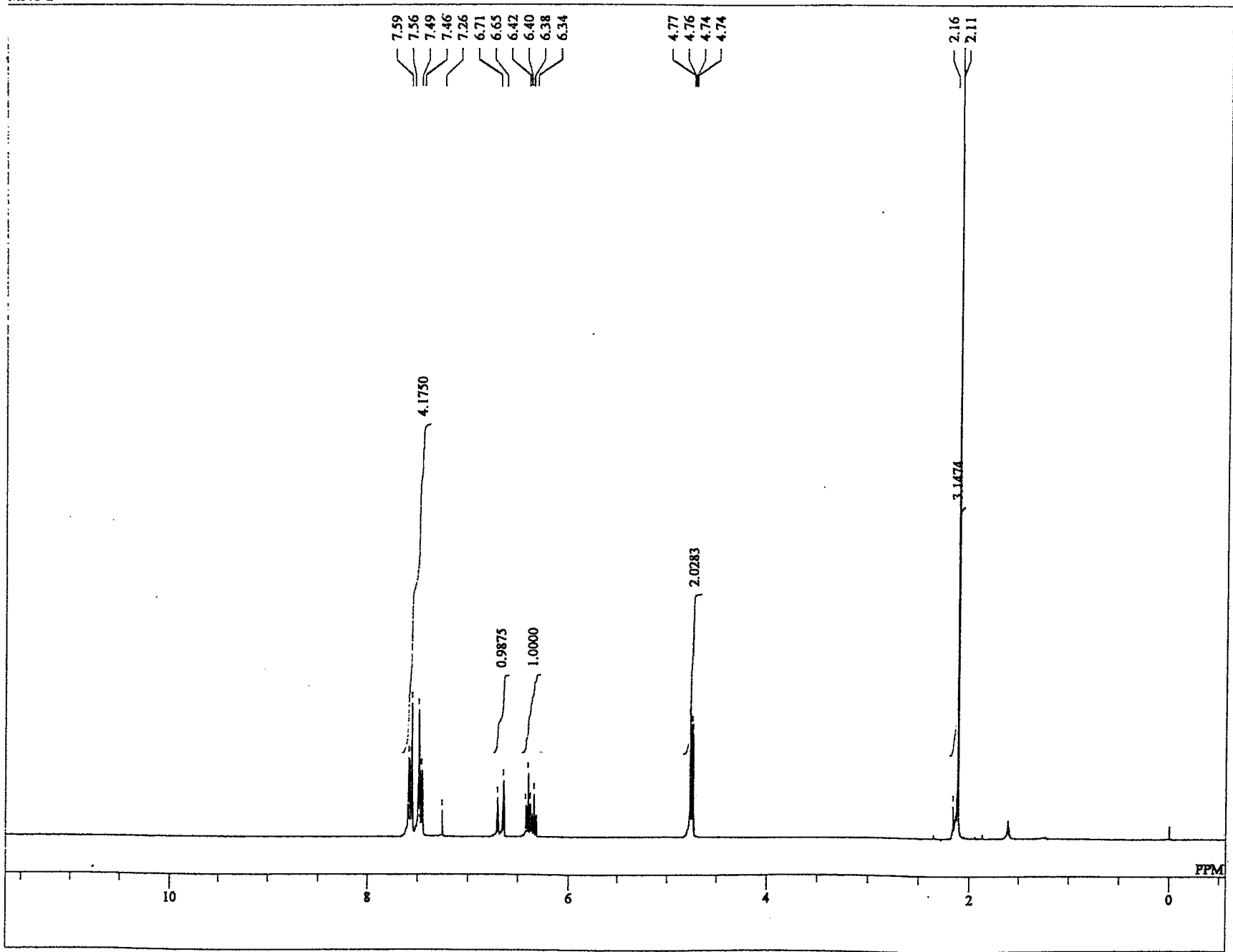
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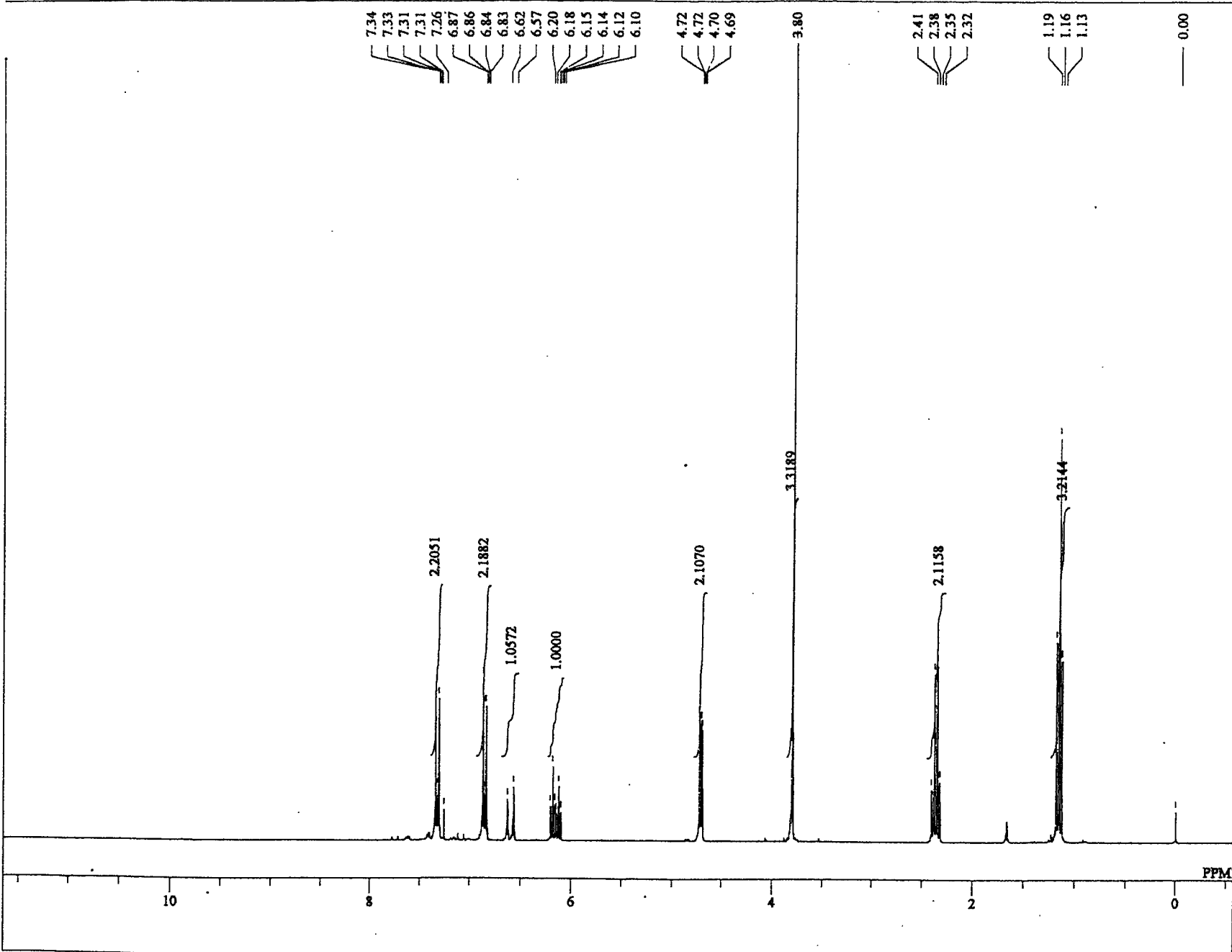
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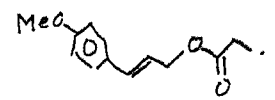
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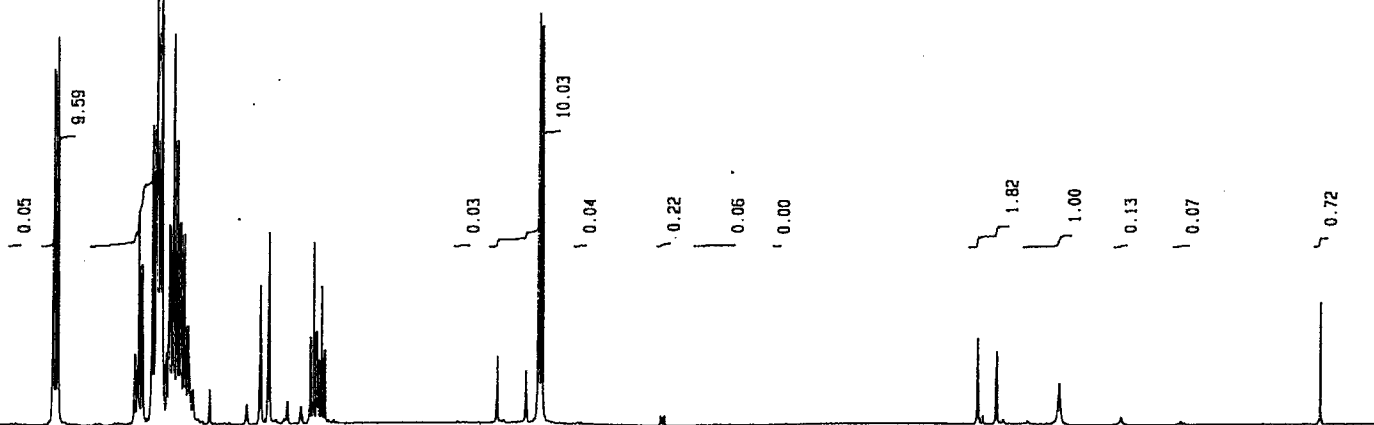
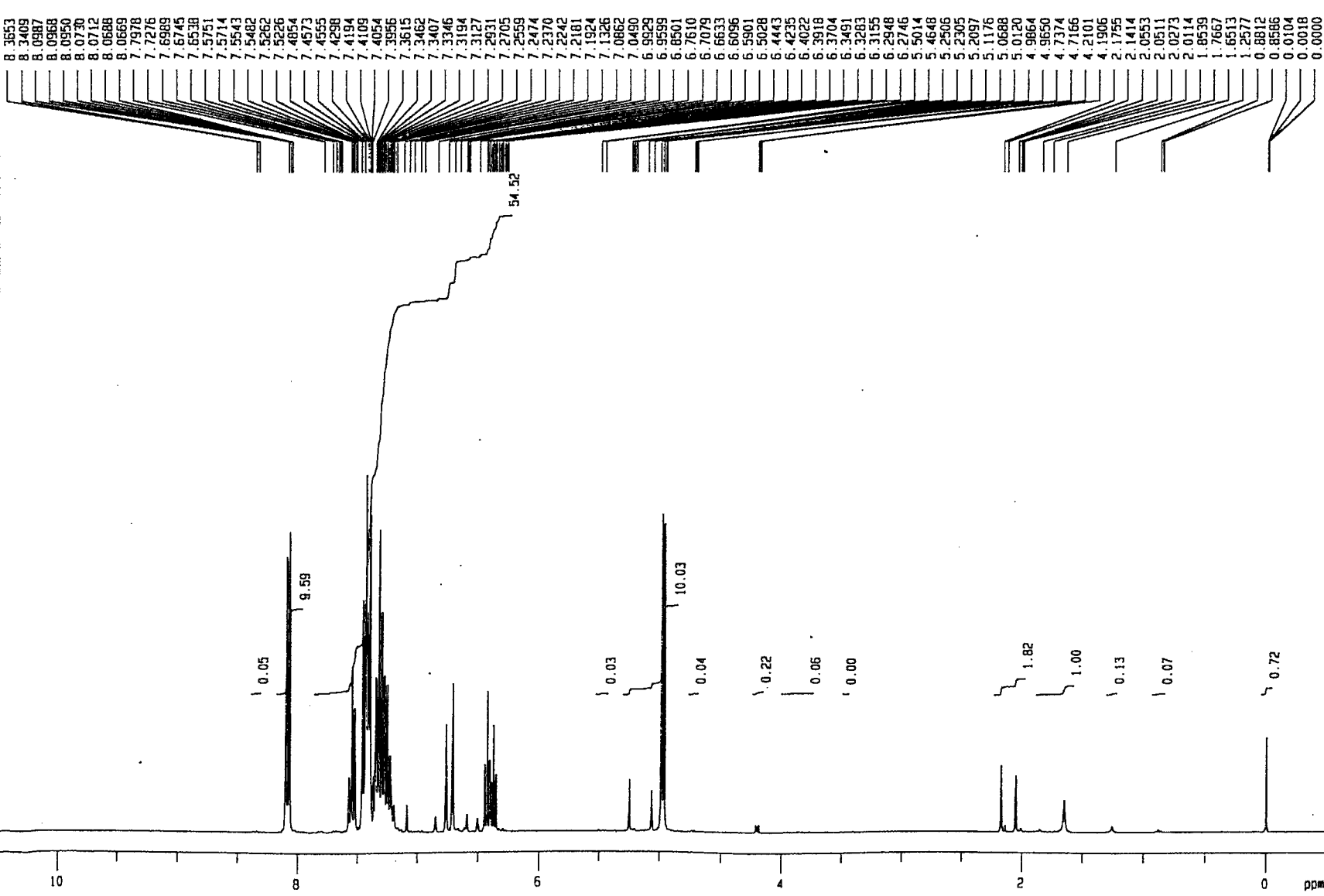
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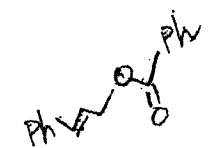
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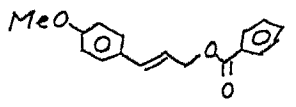
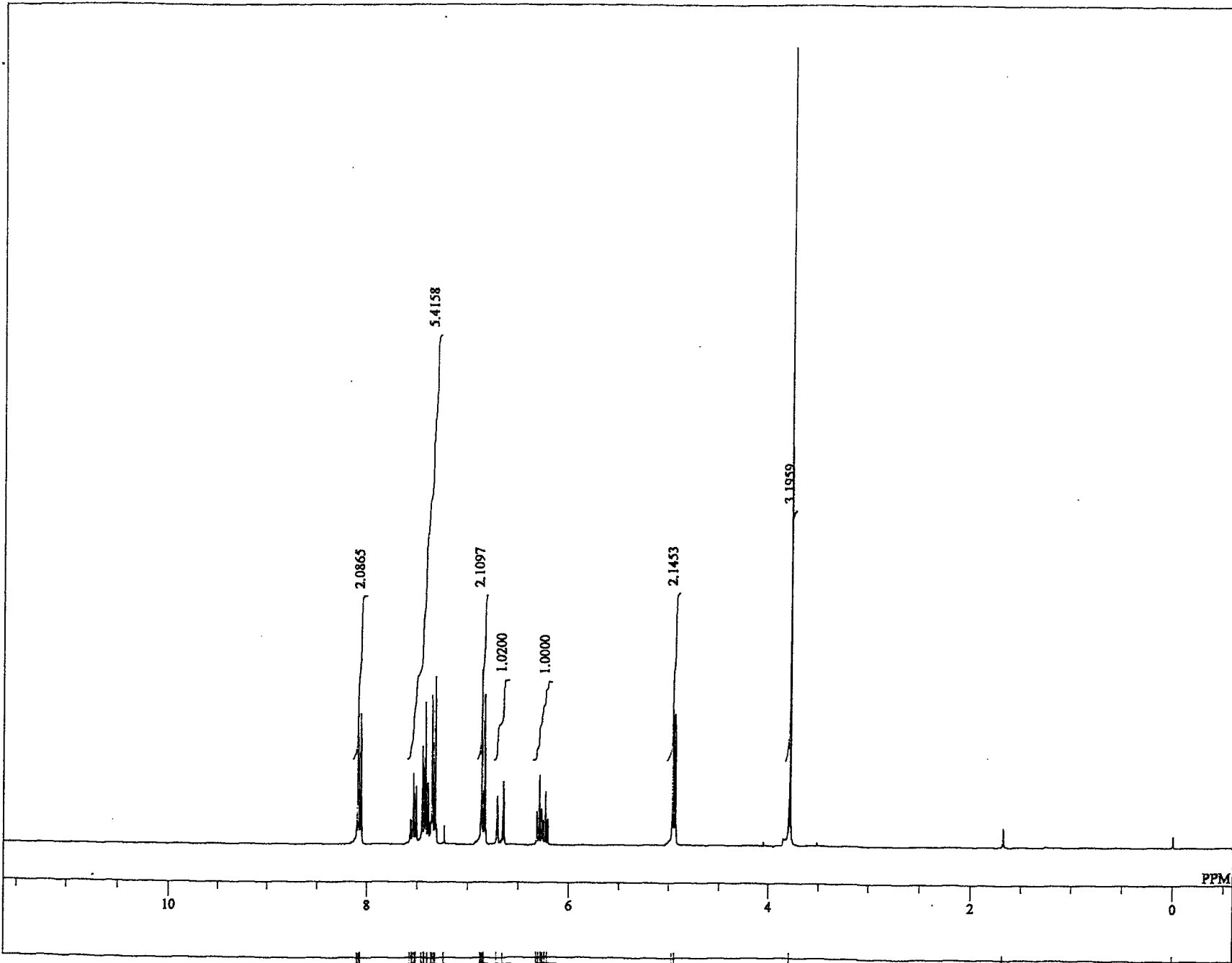
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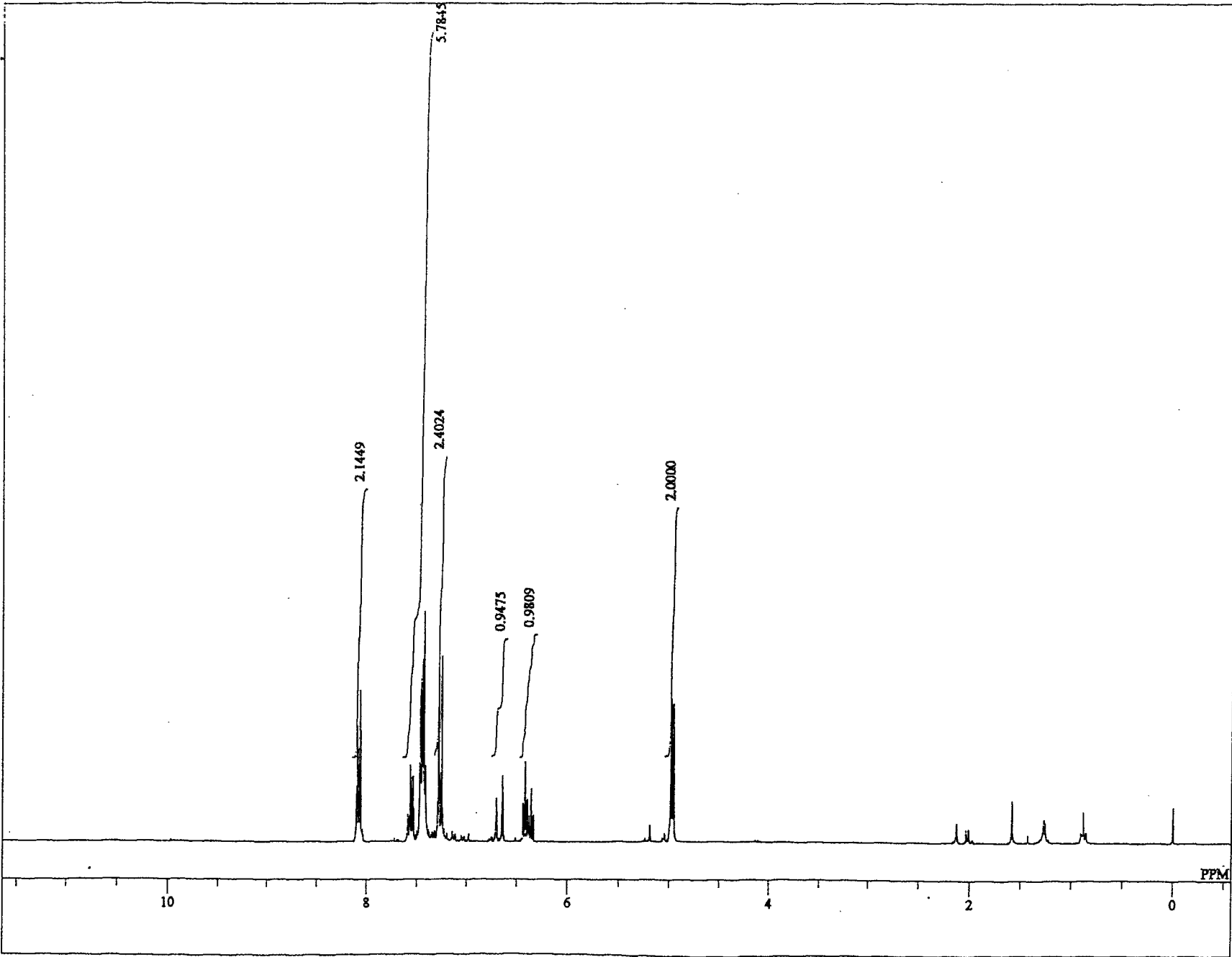


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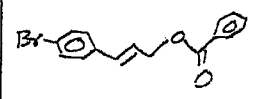
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10S

M999-2\*

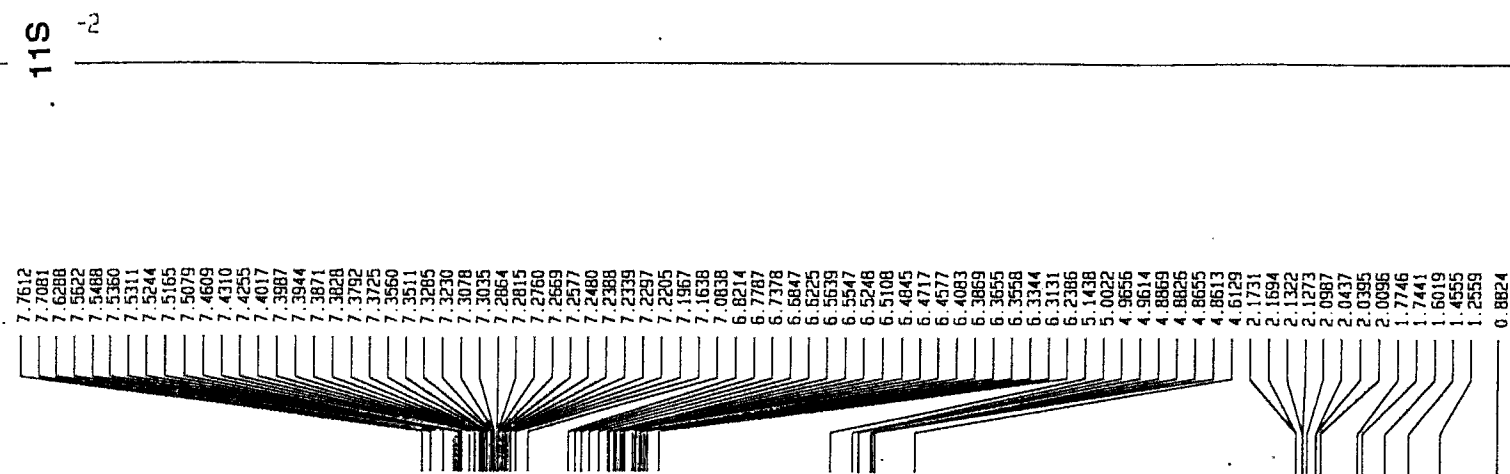
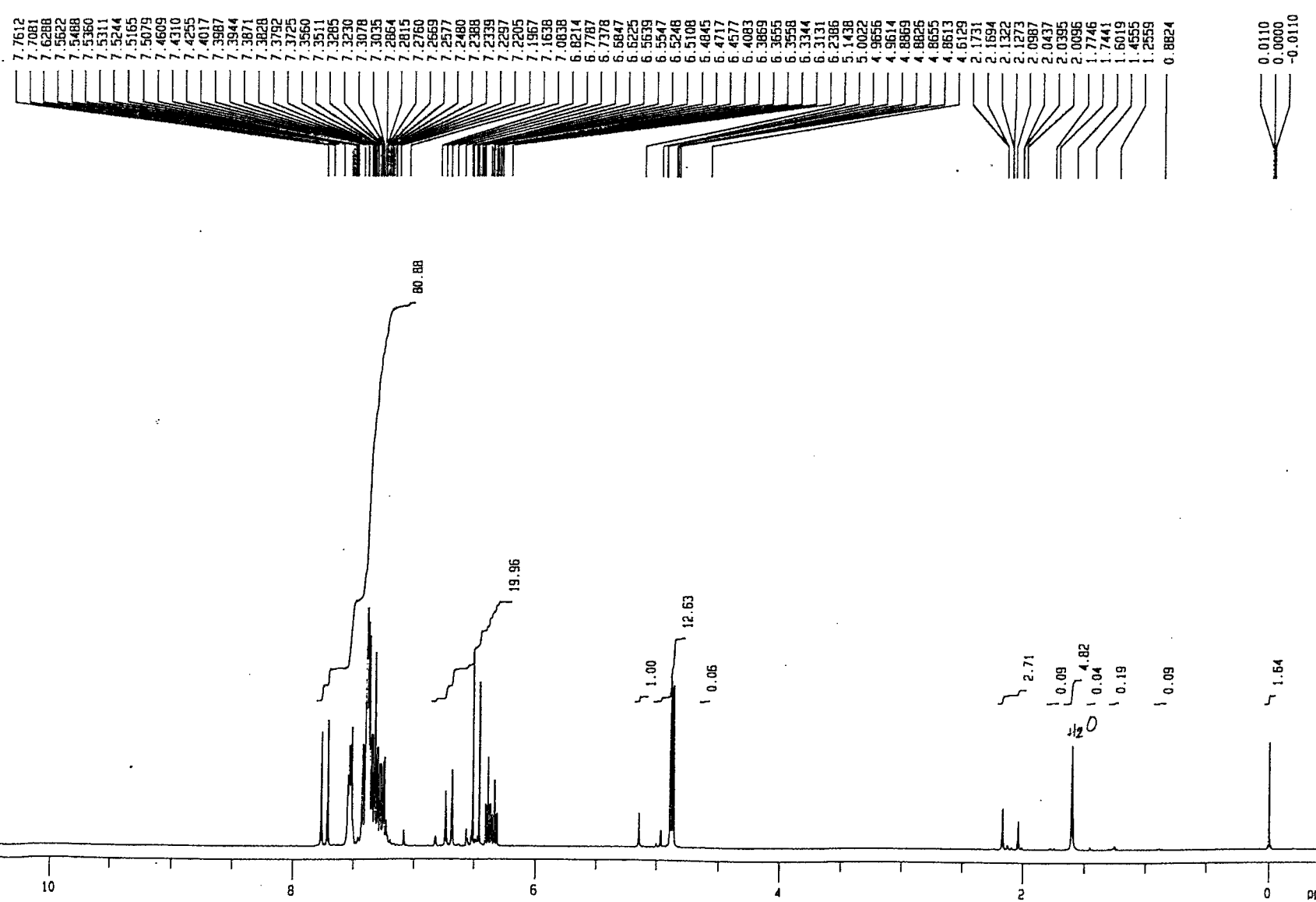


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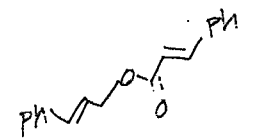


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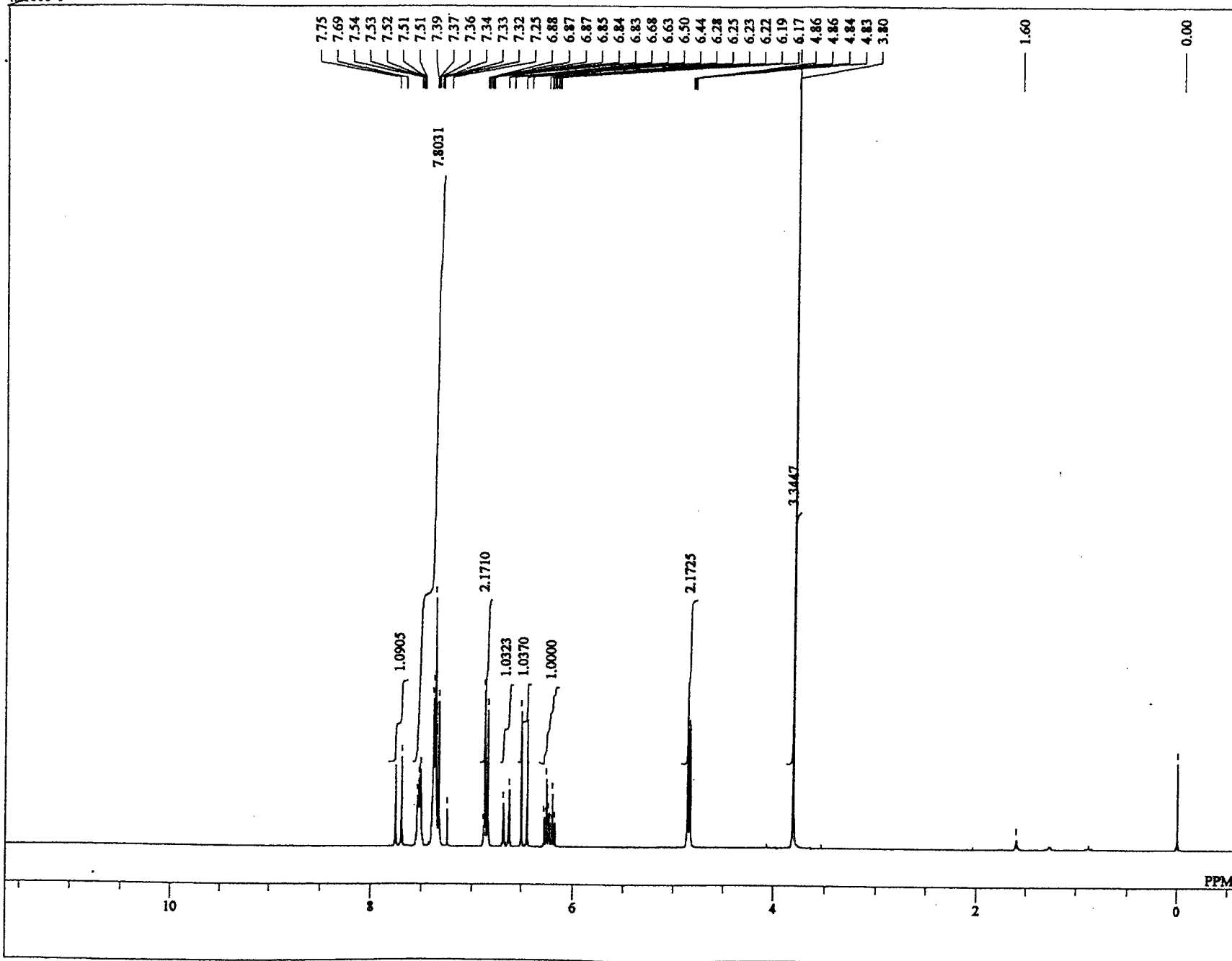


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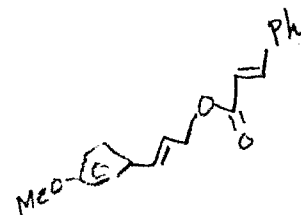


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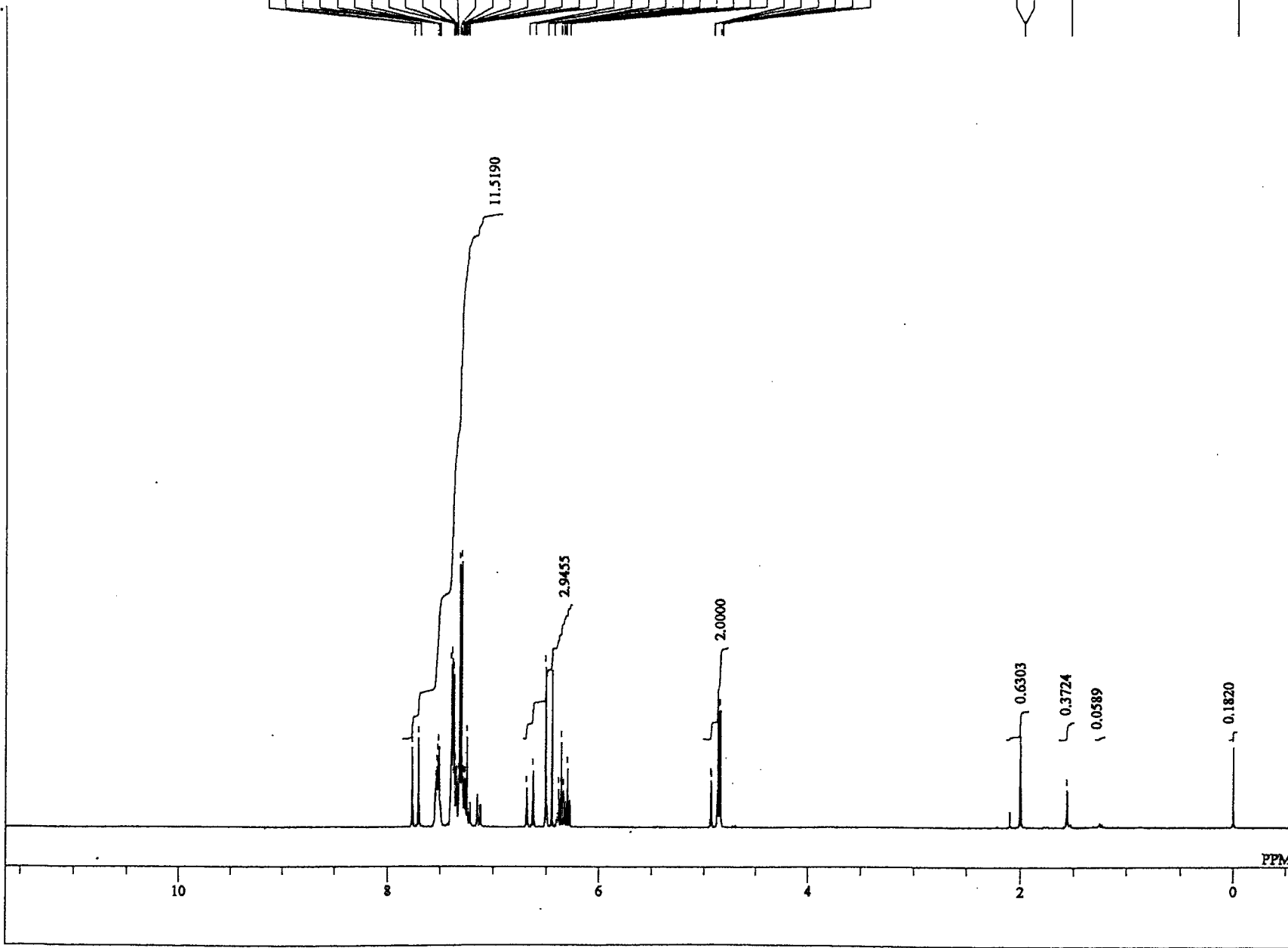
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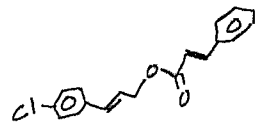
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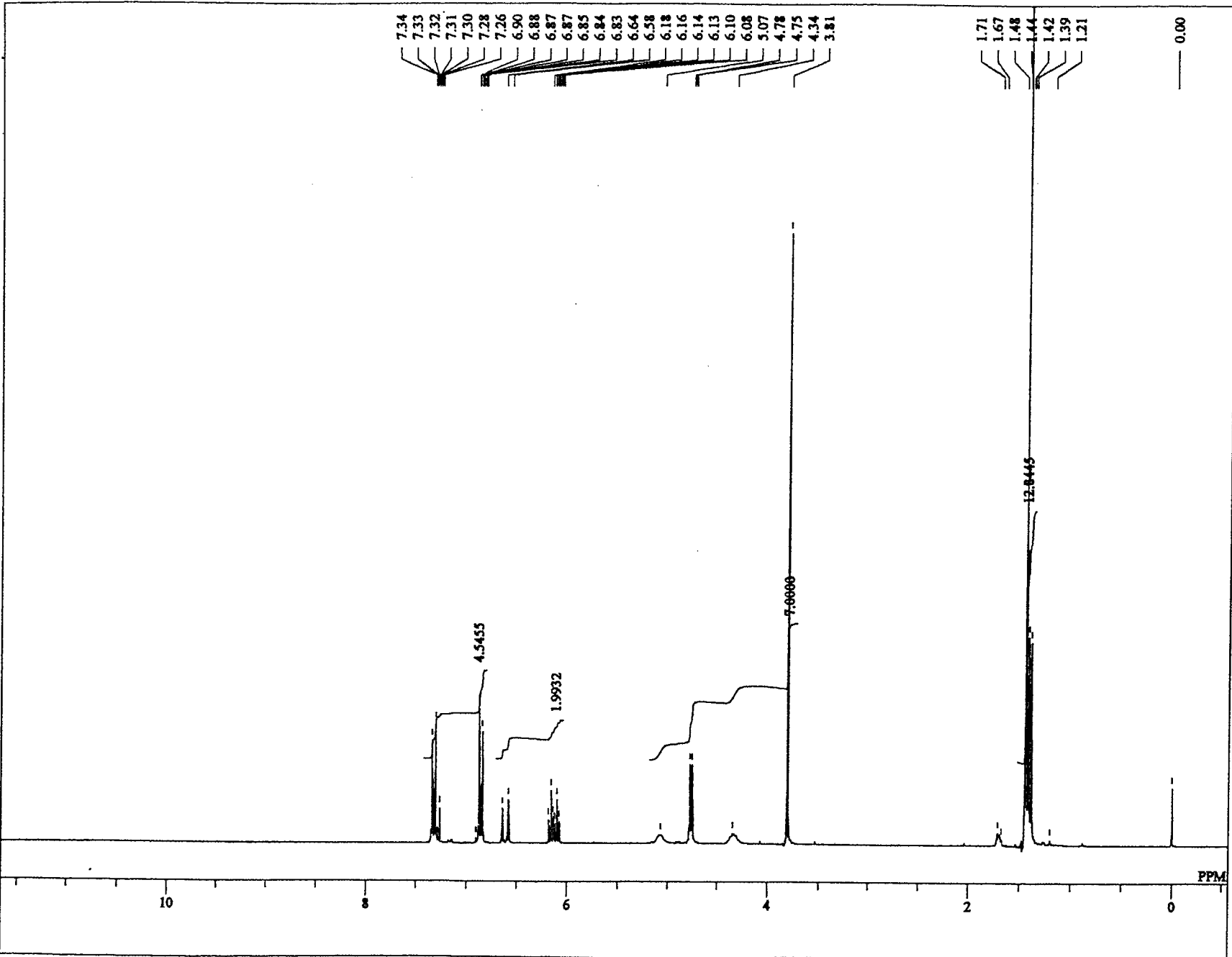
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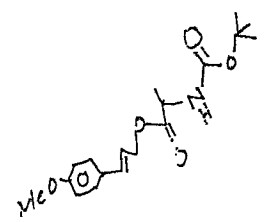
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M093-2



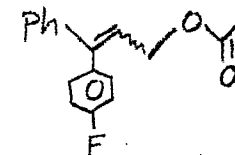
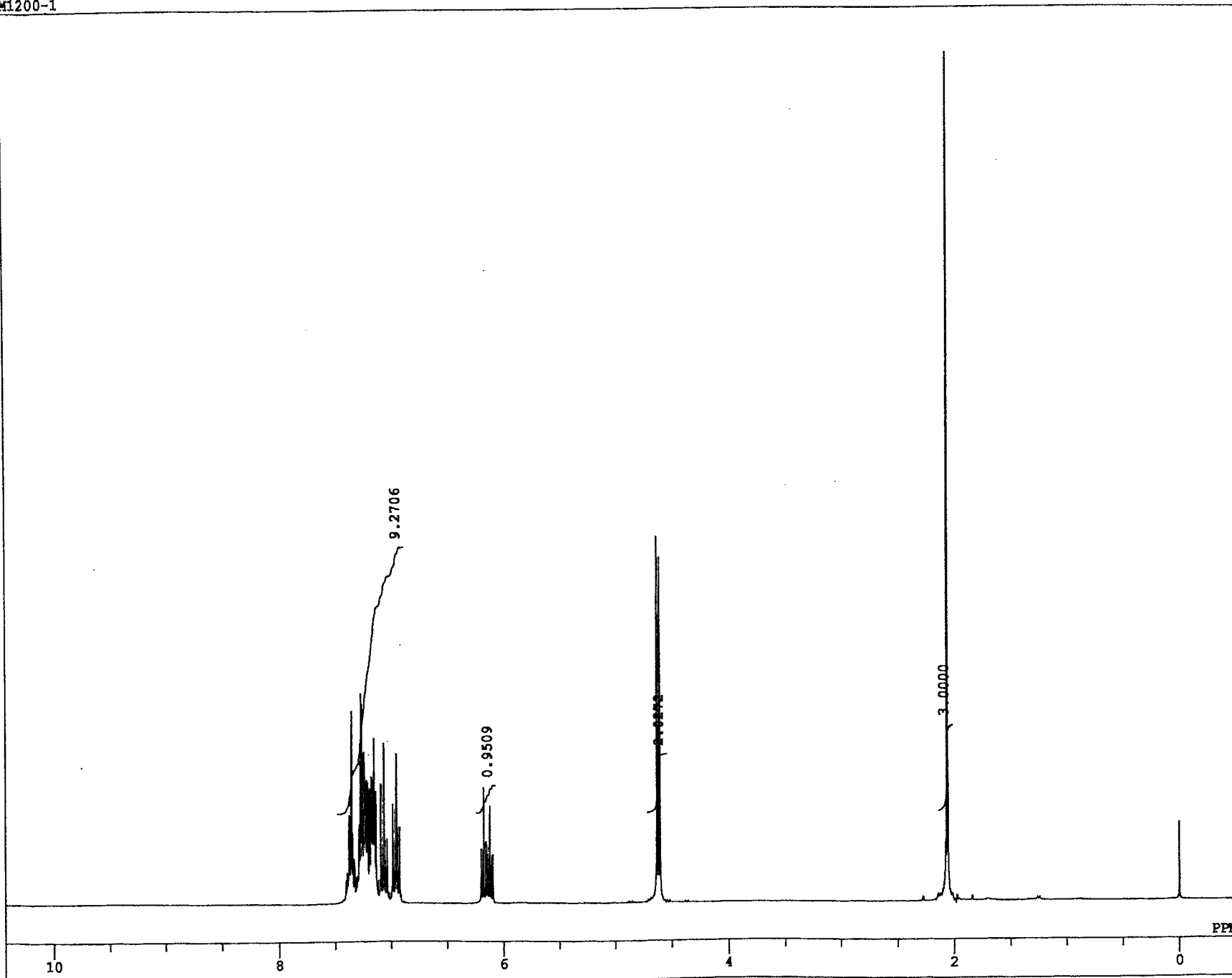
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PD 1.551 sec  
PW1 5.3 us  
IRNUC 1H  
CTEMP 24.8 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12



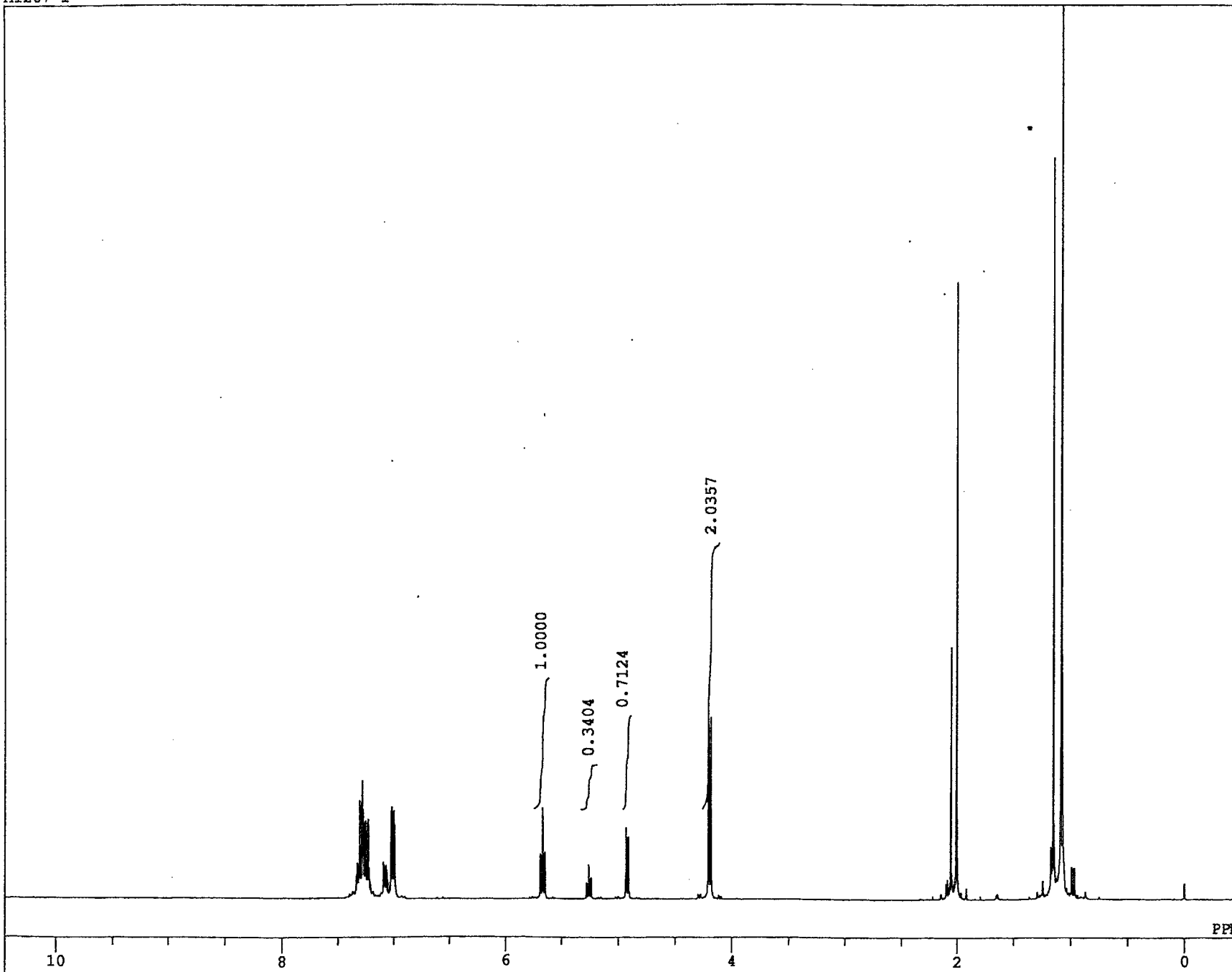


M1207-1

3M

DFILE C:\WINNMR95\COMM  
COMNT M1207-1  
DATIM Mon Feb 23 17:52:  
OBNUC 1H  
EXMOD NON  
OBFRQ 300.40 MHz  
OBSET 130.00 KHz  
OBFIN 1150.0 Hz  
POINT 16384  
FREQU 3300.3 Hz  
SCANS 8  
ACQTM 4.964 sec  
PD 1.551 sec  
PW1 5.3 us  
IRNUC 1H  
CTEMP 20.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

16S



DFILE C:\WINNMR95\COMMO  
COMNT M1213-1  
DATIM Thu Feb 26 18:43:  
OBNUC 1H  
EXMOD NON  
OBFRQ 300.40 MHz  
OBSET 130.00 KHz  
OBFIN 1150.0 Hz  
POINT 16384  
FREQU 3300.3 Hz  
SCANS 8  
ACQTM 4.964 sec  
PD 1.551 sec  
PW1 5.3 us  
IRNUC 1H  
CTEMP 20.2 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 17

17S

