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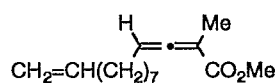
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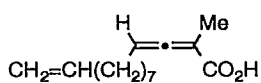
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**(±) Methyl 2-Methyl-2,3,12-tridecatrienoate (8b).**

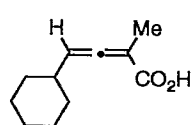
Undecylenic acid (3.81 mL, 3.48 g, 18.87 mmol) was added to a stirred solution of  $(\text{COCl})_2$  (11.98 g, 9.00 mL, 94.27 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) and the mixture was allowed to stir for two hours. The reaction mixture was concentrated under reduced pressure to give the corresponding carboxylic acid chloride which was subjected to the procedure described for allenic ester **1a** to afford 3.35 g (91%) of allenic ester **8b** as an oil: IR (film) 1961, 1717  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.78 (ddt, 1H,  $J = 17.1, 10.3, 6.7$  Hz), 5.43 (m, 1H), 4.96 (dd, 1H,  $J = 17.1, 2.0$  Hz), 4.90 (dd, 1H,  $J = 10.3, 2.1$  Hz), 3.70 (s, 3H), 2.06 (q, 2H,  $J = 7.1$  Hz), 2.00 (m, 2H), 1.84 (d, 3H,  $J = 3.0$  Hz), 1.44 - 1.25 (m, 10H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  210.5, 168.8, 139.5, 136.0, 114.5, 95.7, 94.2, 52.4, 34.1, 29.6, 29.5, 29.3, 29.1, 28.3, 15.7. Anal Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_2$ : C, 76.22; H, 10.24. Found: C, 76.05; H, 10.23.

**(±) Methyl 4-Cyclohexyl-2-methyl-2,3-butadienoate (8c).** The procedure described for allenic ester **8a** was employed with 2-cyclohexylacetic acid (2.07 g, 14.59 mmol) to afford 1.75 g (62%) of allenic ester **8c** as an oil: IR (film) 1956, 1711  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.42 (m, 1H), 3.70 (s, 3H), 2.11 (m, 1H), 1.84 (d, 3H,  $J = 2.9$  Hz), 1.68 (m, 5H), 1.40 - 1.15 (m, 5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.3, 168.3, 99.5, 96.0, 51.8, 36.9, 32.8, 32.6, 25.9, 25.74, 25.71, 15.2. Anal Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}_2$ : C, 74.19; H, 9.34. Found: C, 73.91; H, 9.39.

**(±) 2-Methyl-2,3,12-tridecatrienoic Acid (9b).**

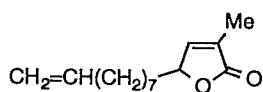
The procedure described for allenic acid **9a** was employed with 0.125 g (0.530 mmol) allenic ester **8b** to afford 0.099 g (84%) of allenic acid **9b** as a waxy solid: IR (film) 3076, 1957, 1681  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.79 (ddt, 1H,  $J = 17.0, 10.2, 6.7$  Hz), 5.51 (m, 1H), 4.97 (dd, 1H,  $J = 17.0, 2.1$  Hz), 4.91 (dd, 1H,  $J = 10.2, 2.1$  Hz), 2.10 (q, 2H,  $J = 7.0$  Hz), 2.00 (q, 2H,  $J = 7.0$  Hz), 1.84 (d, 3H,  $J = 2.9$  Hz), 1.44 - 1.25 (m, 10H);  $^{13}\text{C}$  NMR (101

MHz, CDCl<sub>3</sub>)  $\delta$  211.3, 173.8, 139.1, 114.1, 95.2, 94.3, 33.8, 29.2, 29.0, 28.88, 28.86, 28.7, 27.7, 14.8.



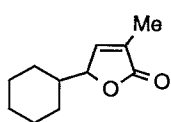
( $\pm$ ) **4-Cyclohexyl-2-methyl-2,3-butadienoic Acid (9c)**. The procedure described for allenic acid **9a** was employed with allenic ester **8c** (0.245 g, 1.263 mmol) to afford 0.153 g (67%) of allenic acid **9c** as a waxy solid: IR (film)

3090, 1950, 1681 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.50 (m, 1H), 2.15 (m, 1H), 1.84 (d, 3H,  $J$  = 2.9 Hz), 1.70 (m, 5H), 1.40 - 1.15 (m, 5H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  210.6, 173.9, 100.0, 96.0, 37.0, 32.74, 32.66, 25.9, 25.82, 25.80, 14.88.



( $\pm$ ) **4-Hydroxy-2-methyl-2,12-tridecadienoic Acid Lactone (10b)**. The procedure described for butenolide **10a** was employed with

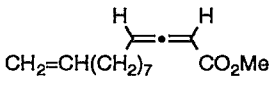
allenic acid **9b** (0.086 g, 0.387 mmol) to afford 0.069 g (80%) of butenolide **10b** as an oil: IR (film) 1754, 1641 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (s, 1H), 5.78 (ddt, 1H,  $J$  = 17.0, 10.2, 6.7 Hz), 4.97 (dd, 1H,  $J$  = 17.0, 2.1 Hz), 4.91 (dd, 1H,  $J$  = 10.2, 2.1 Hz), 4.85 (m, 1H), 2.01 (q, 2H,  $J$  = 7.1 Hz), 1.89 (t, 3H,  $J$  = 1.8 Hz), 1.65 (m, 1H), 1.60 (m, 1H), 1.44 - 1.25 (m, 10H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  174.7, 149.1, 139.4, 130.2, 114.6, 81.5, 34.1, 33.9, 29.63, 29.58, 29.3, 29.2, 25.4, 11.0. Anal Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C, 75.63; H, 9.97. Found: C, 75.74; H, 10.01.

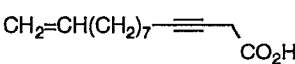


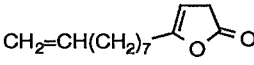
( $\pm$ ) **4-Cyclohexyl-4-hydroxy-2-methyl-2-butenic Acid Lactone (10c)**. The procedure described for butenolide **10a** was employed with allenic

acid **9c** (0.176 g, 0.978 mmol) with one variation: The reaction mixture was heated at reflux for 16 h. Butenolide **10c** (0.120 g, 68%) was isolated as an oil: IR (film) 1748, 1653 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.03 (t, 1H,  $J$  = 1.5 Hz), 4.65 (m, 1H), 1.89 (t, 3H,  $J$  = 1.7 Hz), 1.70 (m, 6H), 1.30 - 1.00 (m, 5H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 147.4,

130.1, 85.2, 41.4, 28.5, 28.2, 26.1, 25.8, 25.7, 10.6. Anal Calcd for  $C_{11}H_{16}O_2$ : C, 73.30; H, 8.95. Found: C, 73.19; H, 9.04.

 (±) **Methyl-2,3,12-Tridecatrienoate (11b)**. The procedure described for allenic ester **8a** was employed with 2.50 mL (2.28 g, 12.37 mmol) undecylenic acid and 4.55 g (13.61 mmol) of methyltriphenylphosphorylidene acetate to afford 2.08 g (76%) of allenic ester **11b** as an oil: IR (film) 1959, 1719, 1639  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  5.79 (ddt, 1H,  $J = 17.1, 10.3, 6.7$  Hz), 5.57 (m, 2H), 4.99 (dd, 1H,  $J = 17.1, 2.0$  Hz), 4.93 (dd, 1H,  $J = 10.3, 2.1$  Hz), 3.72 (s, 3H), 2.12 (m, 2H), 2.02 (q, 2H,  $J = 7.2$  Hz), 1.40 - 1.20 (m, 10H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  212.4, 166.7, 139.1, 114.2, 95.4, 87.9, 51.9, 33.7, 29.1, 29.02, 28.96, 28.85, 28.6, 27.4. Anal Calcd for  $C_{14}H_{22}O_2$ : C, 75.63; H, 9.79. Found: C, 75.77; H, 10.02.

 **3-Tridecyn-12-enoic Acid (12b)**. The procedure described for acid **12a** was employed with allenic ester **11b** (0.331 g, 1.491 mmol) to afford 0.296 g (95%) of acid **12b** as a waxy solid: IR (film) 3272, 1952, 1709, 1633  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  5.78 (ddt, 1H,  $J = 17.1, 10.3, 6.7$  Hz), 4.97 (dd, 1H,  $J = 17.1, 2.0$  Hz), 4.92 (dd, 1H,  $J = 10.3, 2.1$  Hz), 3.31 (t, 2H,  $J = 2.4$  Hz), 2.18 (m, 2H), 2.02 (q, 2H,  $J = 7.5$  Hz), 1.40 - 1.20 (m, 10H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.1, 139.1, 114.1, 84.4, 70.6, 33.7, 28.94, 28.93, 28.8, 28.7, 28.6, 25.9, 18.7. Anal Calcd for  $C_{13}H_{20}O_2$ : C, 74.96; H, 9.68. Found: C, 74.86; H, 9.64.

 **5-(8-Nonenyl)-2(3H)-furanone (13b)**. The procedure described for butenolide **10a** was employed with acid **12b** (0.244 g, 1.173 mmol) to afford 0.233 g (95%) of enol lactone **13b** as an oil: IR (film) 1799, 1755, 1675  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  5.82 (ddt, 1H,  $J = 17.1, 10.3, 6.7$  Hz), 5.04 (dd, 1H,  $J = 17.1, 1.6$  Hz), 4.92 (m, 2H), 3.15 (q, 2H,  $J = 2.4$  Hz), 2.26 (dt, 2H,  $J = 7.2, 1.4$  Hz), 2.01 (q, 2H,  $J = 7.3$

Hz), 1.54 (m, 2H), 1.40 - 1.20 (m, 8H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 157.3, 139.0, 114.2, 98.1, 83.4, 33.9, 33.7, 29.1, 28.9, 28.8, 28.2, 25.7.

**(±)-12-[(Methoxymethoxy)-8-dodecyn-7-ol (15).** To a mixture of 4-pentyn-1-ol (4.52 g, 5.00 mL, 53.73 mmol) and Hunig's base (27.78 g, 37.44 mL, 214.9 mmol) in 100 mL of  $\text{CH}_2\text{Cl}_2$  at 0 °C was added 8.16 mL (8.65 g, 107.5 mmol) of MOMCl. The reaction mixture was warmed to rt, stirred for 16 h, and then quenched with saturated  $\text{NaHCO}_3$  and extracted with  $\text{Et}_2\text{O}$ . The combined  $\text{Et}_2\text{O}$  extracts were dried over  $\text{MgSO}_4$  and concentrated under reduced pressure to give 6.07 g (88%) of 5-[(methoxymethoxy)-1-pentyne as an oil that was carried on without purification :  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.61 (s, 2H), 3.61 (t, 2H,  $J = 6.2$  Hz), 3.35 (s, 3H), 2.30 (dt, 2H,  $J = 7.1, 2.7$  Hz), 1.93 (t, 1H,  $J = 2.6$  Hz), 1.79 (app p, 2H,  $J = 6.7$  Hz).

To a stirred solution of 5-[(methoxymethoxy)-1-pentyne (6.07 g, 47.42 mmol) in THF (100 mL) at -78 °C was added 28.45 mL of a 2.5 M solution of *n*-BuLi in hexanes. After 1 h, heptaldehyde (13.24 mL, 10.83 g, 94.84 mmol) was added and the reaction mixture was stirred at -78 °C for an additional 0.5 h and then warmed to rt. After 2 h, the reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  and diluted with  $\text{Et}_2\text{O}$ . The layers were separated and the organic layer was washed with saturated  $\text{NH}_4\text{Cl}$  and brine, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 20% ethyl acetate in hexanes gave 7.53 g (66%) of alcohol **15** as an oil: IR (film) 3419, 2227  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.60 (s, 2H), 4.32 (tt, 1H,  $J = 6.6, 2.0$  Hz), 3.60 (t, 2H,  $J = 6.2$  Hz), 3.35 (s, 3H), 2.32 (tt, 2H,  $J = 7.1, 2.0$  Hz), 1.77 (app p, 2H,  $J = 6.5$  Hz), 1.71 - 1.17 (m, 11H), 0.87 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  96.2, 83.9, 82.0, 66.0, 62.4, 55.0, 38.1, 31.7, 28.9, 28.7, 25.1, 22.5, 15.4, 14.0.

**(±)-1-[(Methoxymethoxy)-4-(tributylstannyl)-4,5-dodecadiene (17).** The procedure of Marshall and Wang<sup>3b</sup> was employed to prepare 3.37 g (78%) of allenyl stannane **17** from alcohol **15** (2.04 g, 8.45 mmol) as an oil: IR (film) 1930  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$

4.62 (m, 1H), 4.60 (s, 2H), 3.53 (t, 2H,  $J = 6.6$  Hz), 3.34 (s, 3H), 2.09 (dt, 2H,  $J = 4.9, 3.0$  Hz), 1.90 (q, 2H,  $J = 7.1$  Hz), 1.72 (app p, 2H,  $J = 7.3$  Hz), 1.51 - 0.85 (m, 38H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  202.2, 96.4, 92.5, 82.8, 67.3, 55.0, 31.8, 30.0, 29.7, 29.4, 29.2, 29.03, 29.03, 27.3, 22.7, 14.1, 13.7, 10.0.

**(S)-1-*n*-Pentyl-2-propynyl Methanesulfonate (22b).** The procedure used to prepare mesylate **22a** was followed with 0.073 mL (0.50 mmol) of (*S*)-1-octyn-3-ol, 0.06 mL (0.75 mmol) of methanesulfonyl chloride, and 0.14 mL of  $\text{Et}_3\text{N}$  in 3.3 mL of  $\text{CH}_2\text{Cl}_2$ .  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.16 (dt, 1H,  $J = 6.6, 1.8$  Hz), 2.70 (d, 1H,  $J = 2.2$  Hz), 1.90 (m, 2H), 1.54-1.30 (m, 6H), 0.90 (t, 3H, 6.97 Hz).

**2-Heptynyl Methanesulfonate (22c).** The procedure used to prepare mesylate **22a** was followed with 0.34 g (3.0 mmol) of 2-heptyn-1-ol, 0.35 mL (4.5 mmol) of methanesulfonyl chloride, and 0.83 mL (6.0 mmol) of  $\text{Et}_3\text{N}$  in 20 mL of  $\text{CH}_2\text{Cl}_2$ .  $^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.85 (t, 2H,  $J = 2.2$  Hz), 3.11 (s, 3H), 2.26 (tt, 2H,  $J = 6.9, 2.2$  Hz), 1.54-1.37 (m, 4H), 0.92 (t, 3H,  $J = 6.9$  Hz).

**(R)-Benzyl 2-*n*-Heptyl-2,3-pentadienoate (23a).** The procedure used to prepare allenic ester **23b** was followed with 0.148 g (0.60 mmol) of mesylate **22a**, 0.014 g (0.015 mmol) of  $\text{Pd}_2\text{dba}_3$ , 0.031 g (0.12 mmol) of  $\text{Ph}_3\text{P}$ , 0.091 g (0.66 mmol) of  $\text{K}_2\text{CO}_3$ , and 0.93 mL (9.0 mmol) of benzyl alcohol in 6.0 mL of THF to give 0.145 g (84%) of allenic ester **23a** as a colorless oil. IR (film) 3034, 2925, 1953, 1712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.30 (m, 5H), 5.50 (m, 1H), 5.19 (s, 2H), 2.23 (ddd, 2H,  $J = 6.6, 2.9$  Hz), 1.76 (d, 3H,  $J = 7.3$  Hz), 1.46-1.23 (m, 10H), 0.89 (dd, 3H,  $J = 13.9, 1.8$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) 210.5, 167.4, 136.4, 128.3, 127.7, 127.5, 99.9, 89.7, 66.1, 31.9, 29.2, 29.0, 28.5, 28.1, 22.7, 14.2, 13.4; Anal Calcd for  $\text{C}_{19}\text{H}_{26}\text{O}_2$ : C, 79.68; H, 9.15; Found: C, 79.60; H, 9.10.  $[\alpha]_D -26.3$  ( $\text{CHCl}_3$ , *c.*

0.32).  $[\alpha]_D -26.3$  ( $\text{CHCl}_3$ ,  $c$ . 0.32). The ee of this sample was estimated to be 80% based on its subsequent conversion to iodobutenolide **24a**.

**(R)-2-(Trimethylsilyl)ethyl 2,3-Nonadienoate (23d)**. The procedure used to prepare allenic ester **23c** was employed with 0.32 g (1.59 mmol) of mesylate **22b**, 5.8 mg (0.0064 mmol) of  $\text{Pd}_2\text{dba}_3$ , 0.013 g (0.051 mmol) of  $\text{Ph}_3\text{P}$ , and 1.14 mL (7.94 mmol) of 2-TMS ethanol in 15.9 mL of THF to give 0.323 g (80%) of allenic ester **23d** as a yellow oil. IR (film) 1953, 1714,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.58 (m, 2H), 4.23 (dddd, 2H,  $J = 4.76, 1.47$  Hz), 2.12 (dddd, 2H,  $J = 6.96, 3.30$  Hz), 1.49-1.28 (m, 6H), 1.41 (m, 2H), 1.29 (t, 3H,  $J = 6.97$  Hz). Anal Calcd for  $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}$ : C, 66.09; H, 10.30; Found: C, 66.01; H, 10.34.  $[\alpha]_D -112.7$  ( $\text{CHCl}_3$ ,  $c$ . 0.54); HPLC analysis on a Regis (*R, R*) Whelk-O column showed this sample to be of 95% ee.

**(R)-Benzyl 2,3-Nonadienoate (23e)** The procedure used to prepare allenic ester **23c** was followed with 0.278 g (1.37 mmol) of mesylate **22b**, 4.6 mg (0.005 mmol) of  $\text{Pd}_2\text{dba}_3$ , 10.5 mg (0.04 mmol) of  $\text{Ph}_3\text{P}$ , and 0.52 mL of benzyl alcohol in 10 mL of THF to give 0.265 g (80%) of allenic ester **23e** as a yellow oil. IR (film) 3073, 2872, 1964, 1719, 1448  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (bs, 5H), 5.63 (m, 2H), 5.19 (bs, 2H), 2.13 (m, 2H), 1.40-1.30 (m, 6H), 0.88 (t, 3H,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  227.8, 212.4, 165.9, 135.9, 128.4, 127.9, 95.5, 87.9, 66.4, 31.2, 28.4, 27.5, 22.4, 14.1. Anal Calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_2$ : C, 78.65; H, 8.25. Found: C, 78.74; H, 8.24;  $[\alpha]_D -114.8$  ( $\text{CHCl}_3$ ,  $c$ . 0.82); HPLC analysis on a Regis (*R, R*) Whelk-O column showed this sample to be of 93% ee.

**Benzyl 2-Butyl-2,3-butadienoate (23f)**. The procedure used to prepare allenic ester **23c** was followed with 0.18 g (0.98 mmol) of mesylate **22c**, 4.5 mg (0.0049 mmol) of  $\text{Pd}_2\text{dba}_3$ , 0.010 g (0.039 mmol) of  $\text{Ph}_3\text{P}$ , and 0.51 mL of benzyl alcohol in 9.8 mL of THF to give 0.172 g (76%) of allenic ester **23f** as a yellow oil. IR (film) 3066, 2953, 1968, 1942, 1713, 1456  $\text{cm}^{-1}$ ;

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.30 (m, 5H), 5.20 (bs, 2H), 5.13 (t, 2H,  $J = 3.3$  Hz), 2.25 (m, 4H), 0.91 (t, 3H,  $J = 7.3$  Hz).

**(*R*)-5-*n*-Pentyl-4-iodo-2(5H)-furanone (24b).** The procedure used to prepare iodobutenolide **24a** was followed with 0.10 g (0.39 mmol) of allenic ester **23d**, and 0.79 mL of 1.0 M iodine monobromide in  $\text{CH}_2\text{Cl}_2$  to give 0.095 g (89%) of iodobutenolide **24b** as a yellow solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.50 (d, 1H,  $J = 1.8$  Hz), 4.49 (m, 1H), 2.03 (m, 2H), 1.60 (m, 2H), 1.42-1.29 (m, 4H), 0.89 (t, 3H,  $J = 6.6$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CHCl}_3$ )  $\delta$  170.9, 129.9, 125.2, 88.0, 32.5, 31.3, 23.4, 22.4, 14.0; Anal Calcd for  $\text{C}_9\text{H}_{13}\text{O}_2\text{I}$ : C, 38.59; H, 4.68; Found: C, 38.68; H, 4.63;  $[\alpha]_{\text{D}}^{25} 27.8$  ( $\text{CHCl}_3$ ,  $c$  0.39); HPLC analysis on a Regis (*R*, *R*) Whelk-O column showed this sample to be of 95% ee.

**3-*n*-Butyl-4-iodo-2(5H)-furanone (24c).** The procedure used to prepare iodobutenolide **24a** was followed with 0.10 g (0.43 mmol) of allenic ester **23g**, and 0.86 mL of 1.0 M iodine monobromide in  $\text{CH}_2\text{Cl}_2$  to give 0.095 g (83%) of iodobutenolide **24c** as a white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CHCl}_3$ )  $\delta$  4.72 (s, 2H), 2.35, (t, 2H,  $J = 7.3$  Hz), 1.52 (m, 2H), 1.37 (m, 2H) 0.94 (t, 3H,  $J = 7.0$  Hz).

**(*R*)-5-*n*-Pentyl-2(5H)-furanone (25b) A. From Iodobutenolide 25b..** The procedure used to prepare butenolide **25a** was followed with 0.076 g (0.28 mmol) of iodobutenolide **24b**, 1.3 mg (0.0014 mmol) of  $\text{Pd}_2\text{dba}_3$ , 1.5 mg (0.0056 mmol) of  $\text{Ph}_3\text{P}$ , and 0.08 mL (0.29 mmol) of  $\text{Bu}_3\text{SnH}$  in 2.8 mL of THF to give 0.030 g (70%) of butenolide **25b** as a colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd, 1H,  $J = 5.7, 1.5$  Hz), 6.10 (dd, 1H,  $J = 5.7, 2.0$  Hz), 5.03 (m, 1H), 1.71 (m, 2H), 1.48-1.28 (m, 6H), 0.89 (t, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 156.3, 121.2, 83.4, 33.1, 31.4, 24.6, 22.4, 13.9;  $[\alpha]_{\text{D}}^{25} -62.6$  ( $\text{CHCl}_3$ ,  $c$  0.73); HPLC analysis on a Regis (*R*, *R*) Whelk-O column showed this sample to be of 95% ee.



**B. From Mesylate 22b.** In a flame dried, argon flushed flask, a solution of 2.3 mg (0.0025 mmol) of Pd<sub>2</sub>dba<sub>3</sub> and 2.6 mg (0.010 mmol) of Ph<sub>3</sub>P in 2.5 mL of THF was stirred under a stream of CO gas for ~ 2min. This Pd (0) solution was transferred by syringe to a Parr pressure reactor containing 0.102 g (0.50 mmol) of mesylate **22b** in 2.5 mL of THF, then 0.36 mL of water was added. The Parr reactor was charged with 200 psi of CO gas. After 1 h at rt, the gas was vented and the mixture was extracted with EtOAc, washed with brine (2x), and dried over MgSO<sub>4</sub>. After filtration the solution containing the crude acid **27b** was used directly.

The above solution of acid was placed in a flask covered with aluminum foil to exclude light. To this was added 0.017 g (0.10 mmol) of AgNO<sub>3</sub>. After stirring for 18 h, the reaction mixture was filtered through Celite. The filtrate was washed with sat. NaHCO<sub>3</sub>, brine, and dried over MgSO<sub>4</sub>. Following filtration and concentration under reduced pressure, the crude product was purified by flash chromatography to afford 0.07 g (91%) of butenolide **26b** as a yellow oil. HPLC analysis on a Regis (*R,R*) Whelk-O column showed this sample to be of 60% ee.

**3-*n*-Butyl-2(5H)-furanone (25c).** The procedure used to prepare butenolide **25a** was followed with 0.084 g (0.31 mmol) of iodobutenolide **24c**, 5.7 mg (0.0062 mmol) of Pd<sub>2</sub>dba<sub>3</sub>, 0.13 g (0.049 mmol) of Ph<sub>3</sub>P, and 0.091 mL (0.34 mmol) of Bu<sub>3</sub>SnH in 3.1 mL of THF to give 0.34 g (79%) of butenolide **25c** as a yellow oil. IR (film) 3092, 2968, 1753, 1453 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CHCl<sub>3</sub>) δ 7.09 (bs, 1H), 4.75 (m, 2H), 2.27 (m, 2H), 1.60-1.27 (m, 4H) 0.91 (t, 3H, J = 7.3 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.3, 143.9, 134.3, 70.1, 29.5, 25.0, 22.3, 13.8.

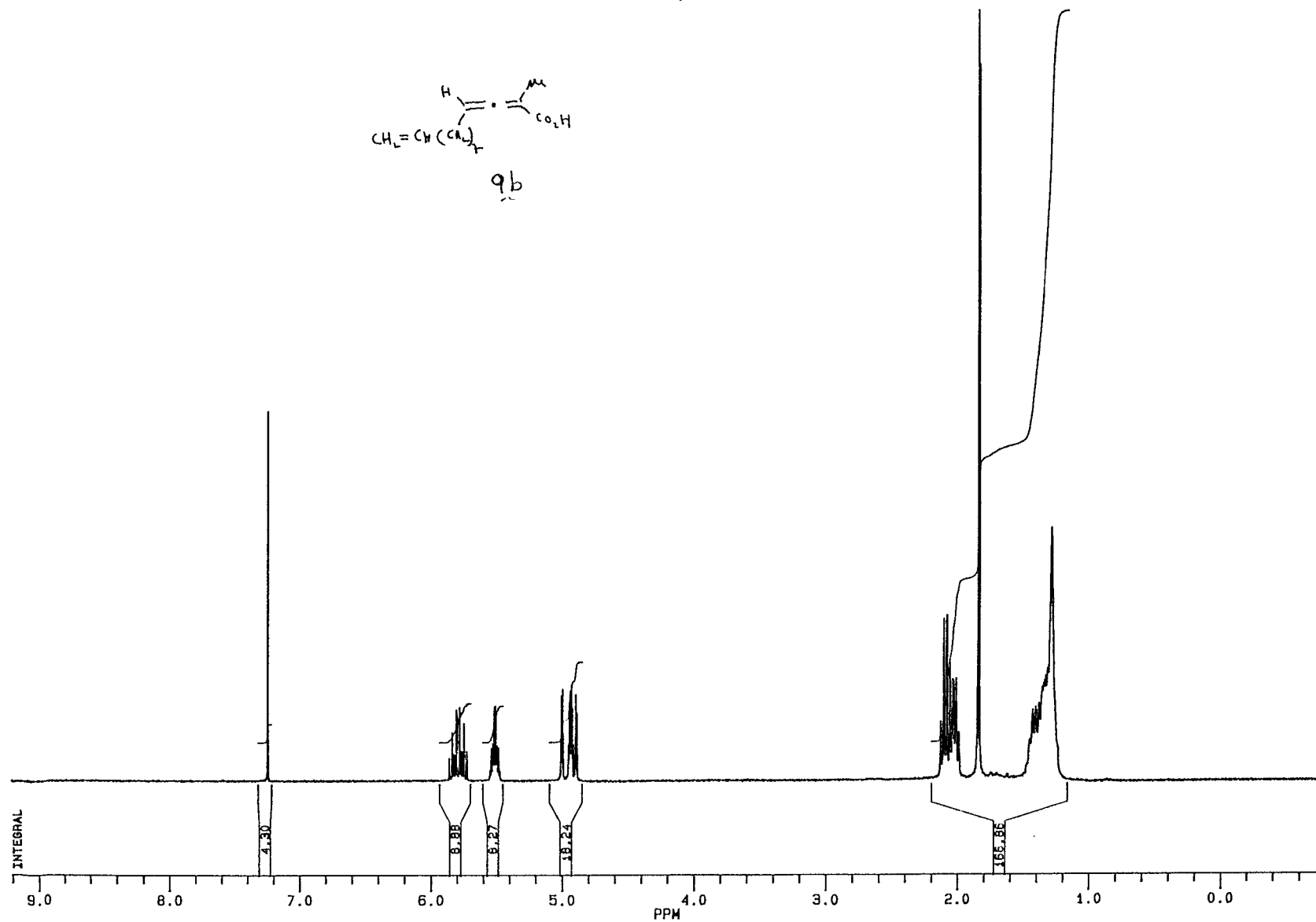
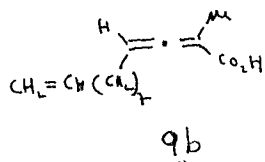
**(*S*)-5-*n*-hexyl-4-iodo-[3-((Methoxymeth)oxy)propyl]-2(5H)-furanone (28).** The procedure used to prepare iodobutenolide **24a** was followed with 0.071 g (0.25 mmol) of allenic ester (*S*)-**19**, and 0.38 mL of 1.0 M iodine monobromide in CH<sub>2</sub>Cl<sub>2</sub> to give 0.067 g (70%) of iodobutenolide **28** as a yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.85 (dd, 1H, J = 7.5, 3.3 Hz), 4.61 (s, 2H), 3.63 (t, 2H, J = 6.4 Hz), 3.36 (s, 3H), 2.43 (t, 2H, J = 7.3 Hz), 2.02 (m,

2H), 1.84 (m, 2H), 1.55 (m, 2H), 1.42-1.26 (m, 6H), 0.87 (t, 3H,  $J = 6.8$  Hz);  $[\alpha]_D -10.6$  ( $\text{CHCl}_3$ ,  $c$  0.64); HPLC analysis on a Regis (*R, R*) Whelk-O column showed this sample to be of 70% ee.

**(*S*)-5-*n*-hexyl-[3-((Methoxymeth)oxy)propyl]-2(5H)-furanone (29).** **A. From Iodobutenolide 28.** The procedure used to prepare butenolide **26a** was followed with 0.065 g (0.17 mmol) of iodobutenolide **28**, 3.1 mg (0.0034 mmol) of  $\text{Pd}_2\text{dba}_3$ , 7.1 mg (0.027 mmol) of  $\text{Ph}_3\text{P}$ , and 0.05 mL (0.18 mmol) of  $\text{Bu}_3\text{SnH}$  in 1.7 mL of THF to give 0.046 g (99%) of butenolide **29** as a yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (m, 1H), 4.88 (m, 1H), 4.59 (s, 2H), 3.54 (t, 2H,  $J = 6.2$  Hz), 3.34 (s, 3H), 2.37 (m, 2H), 1.84 (m, 2H), 1.64 (m, 2H), 1.46-1.20 (m, 6H), 0.86 (t, 3H,  $J = 7.0$  Hz);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 148.1, 133.6, 96.3, 81.2, 66.7, 55.1, 33.5, 31.6, 29.0, 27.8, 24.9, 22.5, 22.2, 14.0;  $[\alpha]_D$  21.1 ( $\text{CHCl}_3$ ,  $c$  0.31); HPLC analysis on a Chiracel OB-H column showed this sample to be of 70% ee.

**B. From Mesylate (*R*)-16.** In a flame dried, argon flushed flask, a solution of 2.3 mg (0.0025 mmol) of  $\text{Pd}_2\text{dba}_3$  and 2.6 mg (0.010 mmol) of  $\text{Ph}_3\text{P}$  in 2.5 mL of THF was stirred under a stream of CO gas for ~2min. This Pd (0) solution was transferred by syringe to a Parr pressure reactor containing 0.16 g (0.50 mmol) of mesylate (*R*)-**16** in 2.5 mL of THF, then 0.36 mL of water was added. The Parr reactor was charged with 200 psi of CO gas. After 1 h at rt, the gas was vented and the mixture was extracted with EtOAc, washed with brine (2x), and dried over  $\text{MgSO}_4$ . After filtration the solution containing the crude acid was used directly.

The above solution of acid was placed in a flask covered with aluminum foil to exclude light. To this was added 0.017 g (0.10 mmol) of  $\text{AgNO}_3$ . After stirring for 18 h., the reaction mixture was filtered through Celite. The filtrate was washed with sat.  $\text{NaHCO}_3$ , brine, and dried over  $\text{MgSO}_4$ . Following filtration and concentration under reduced pressure, the crude product was purified by flash chromatography to afford 0.087 g (61%) of butenolide **29** as a yellow oil. HPLC analysis on a Chiracel OB-H column showed this sample to be of 60% ee.

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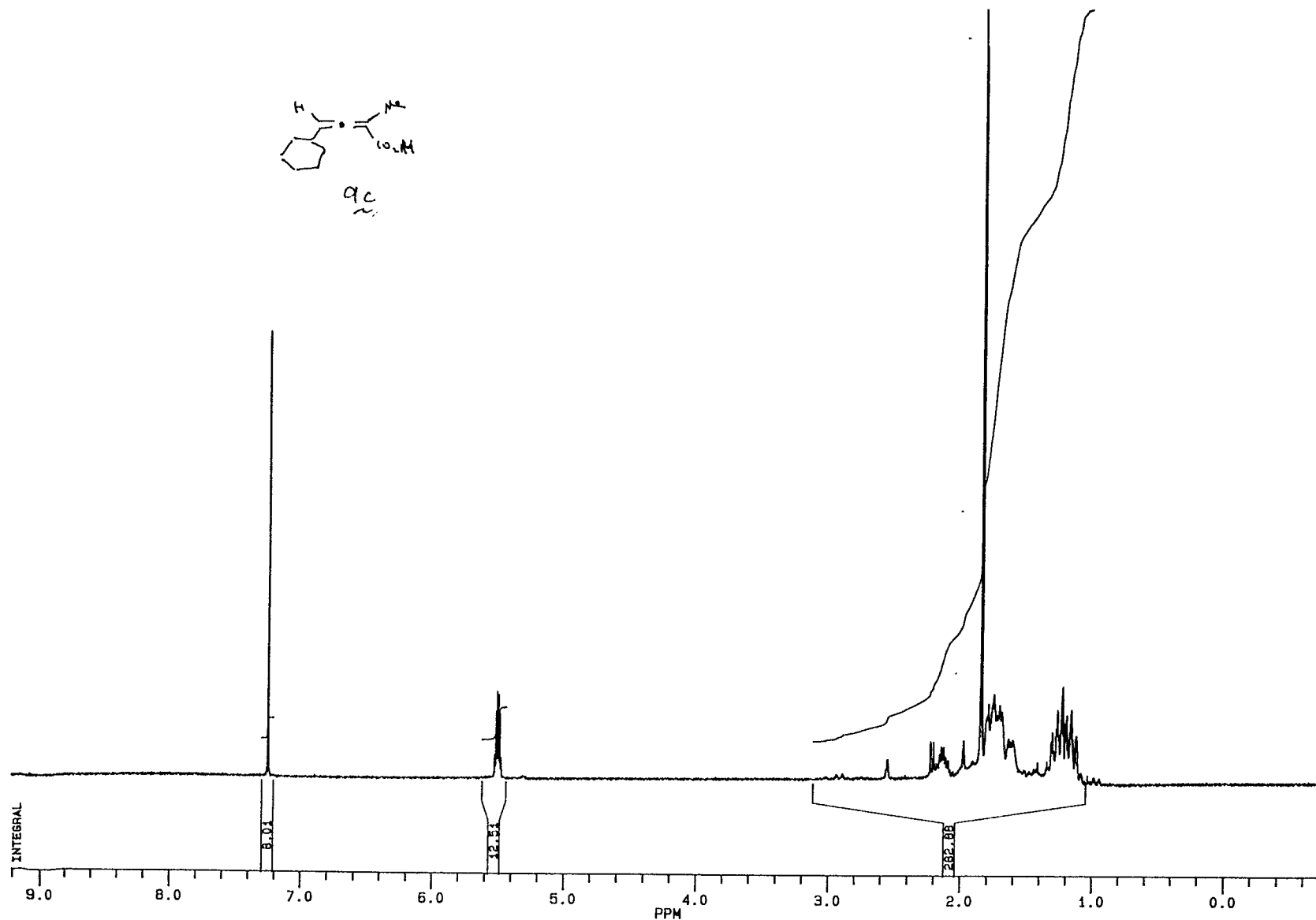
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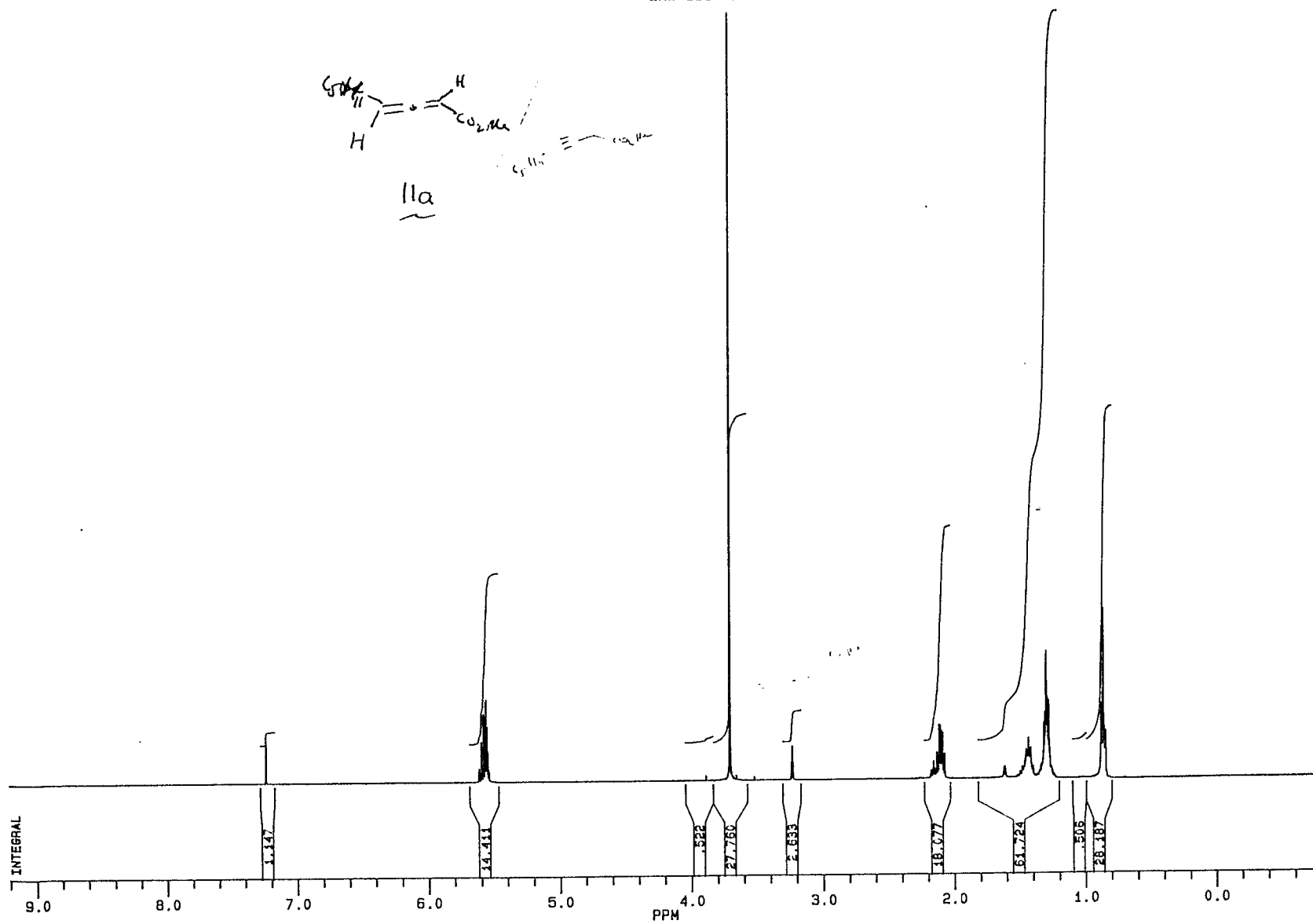
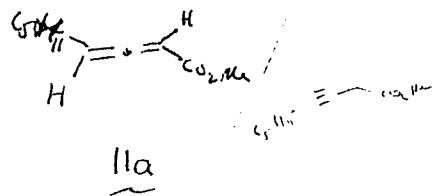
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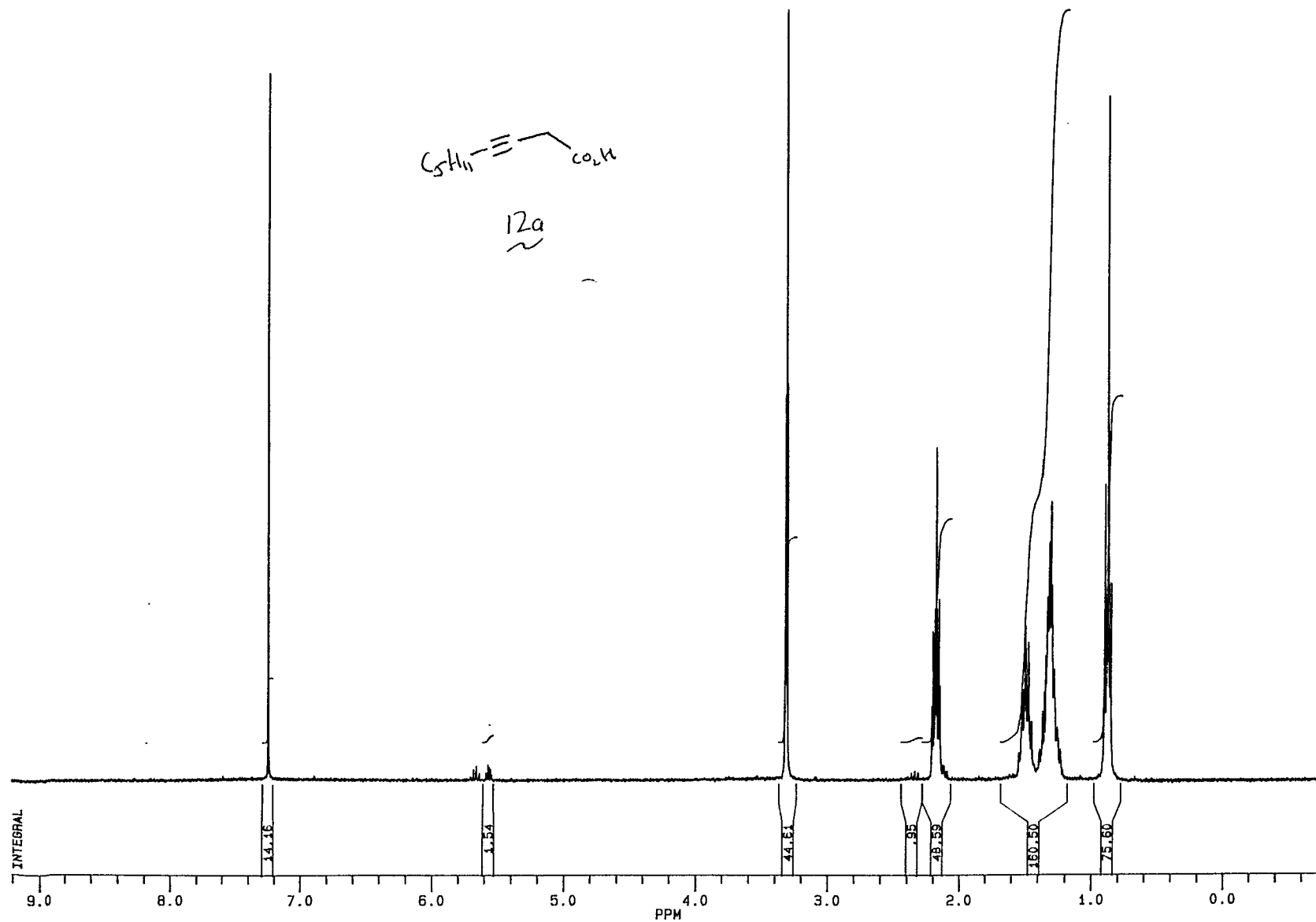
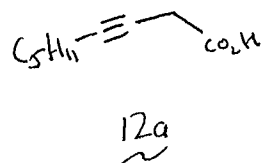
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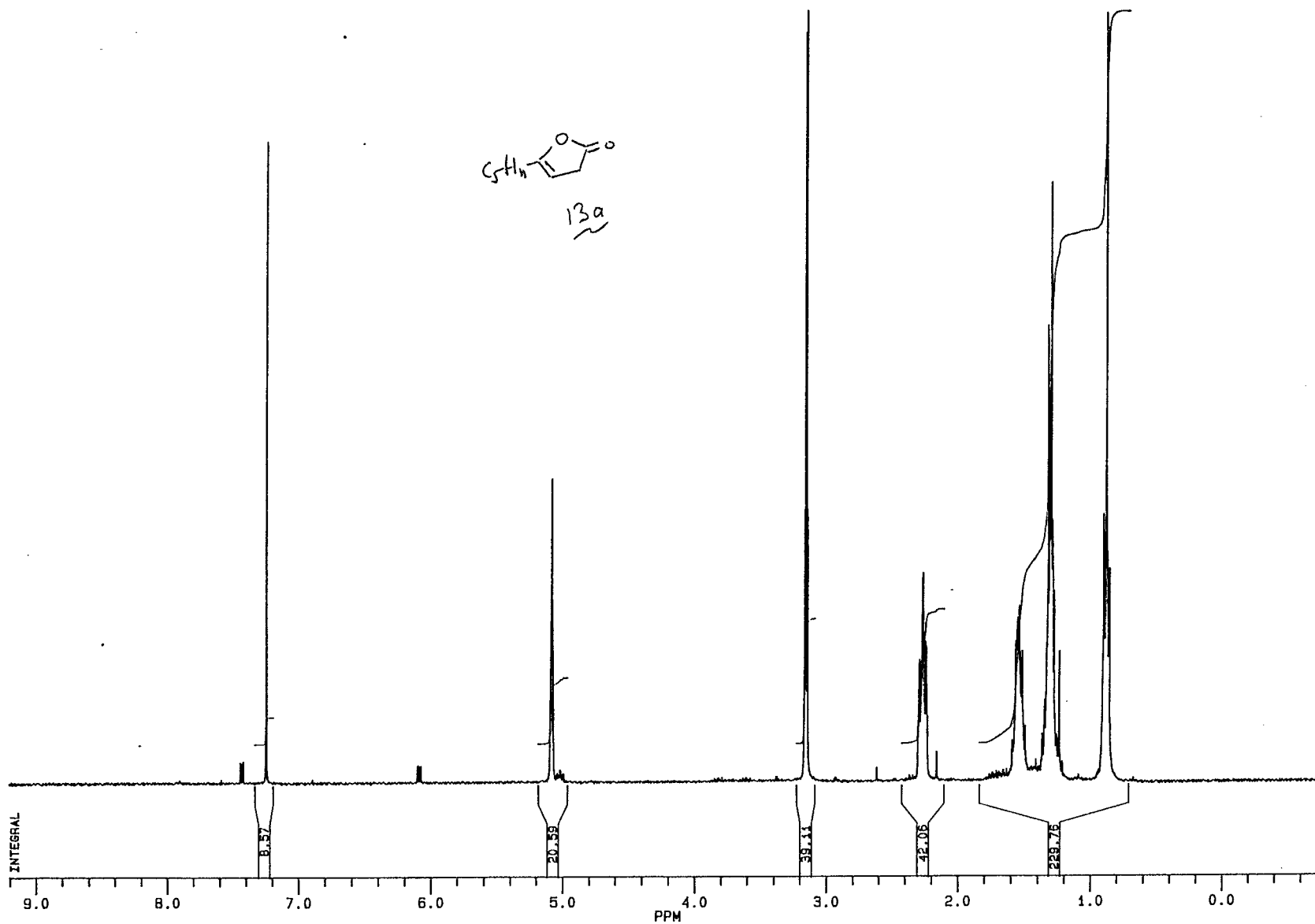
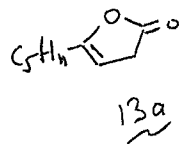
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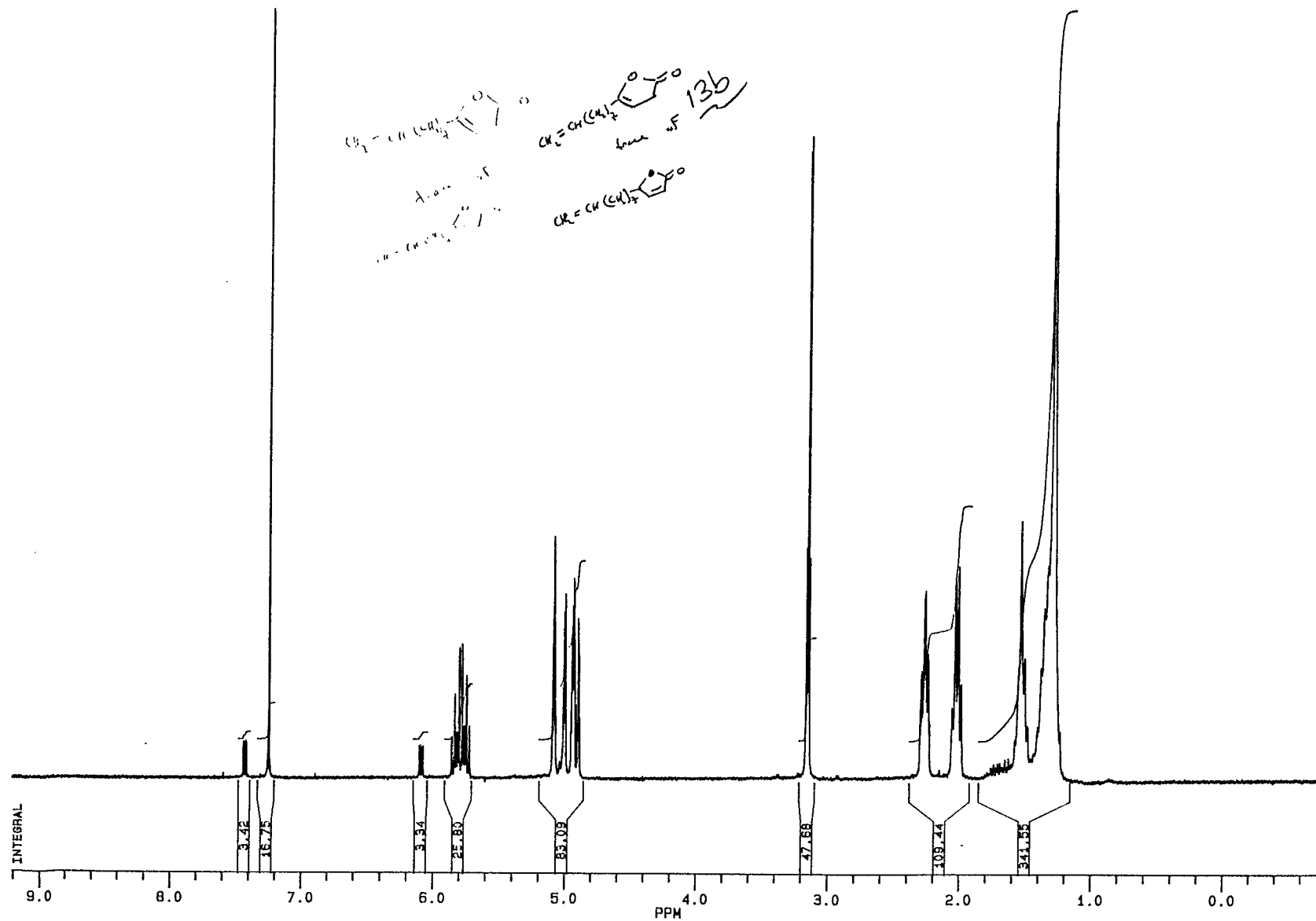
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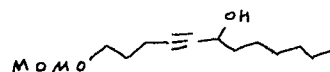
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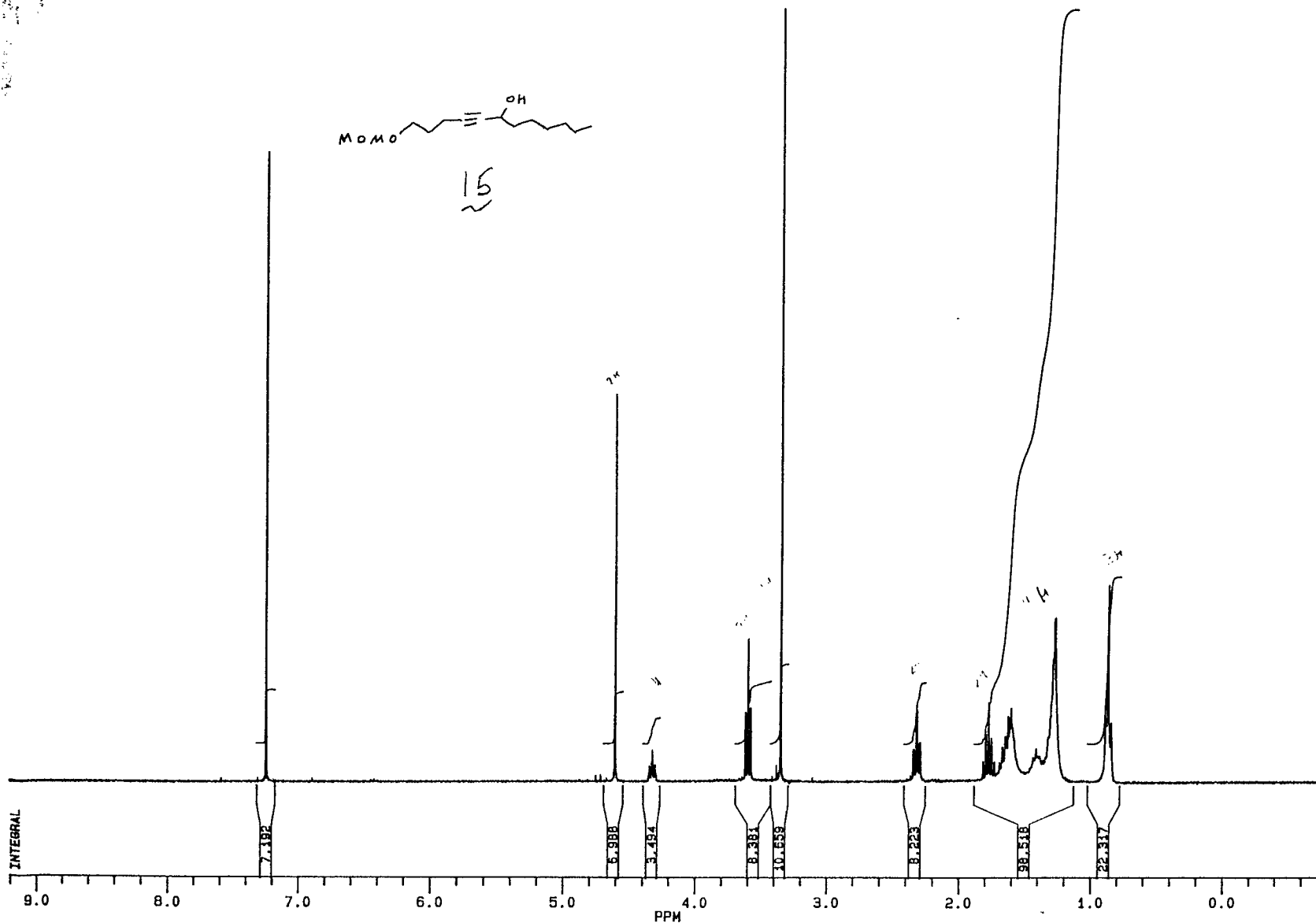
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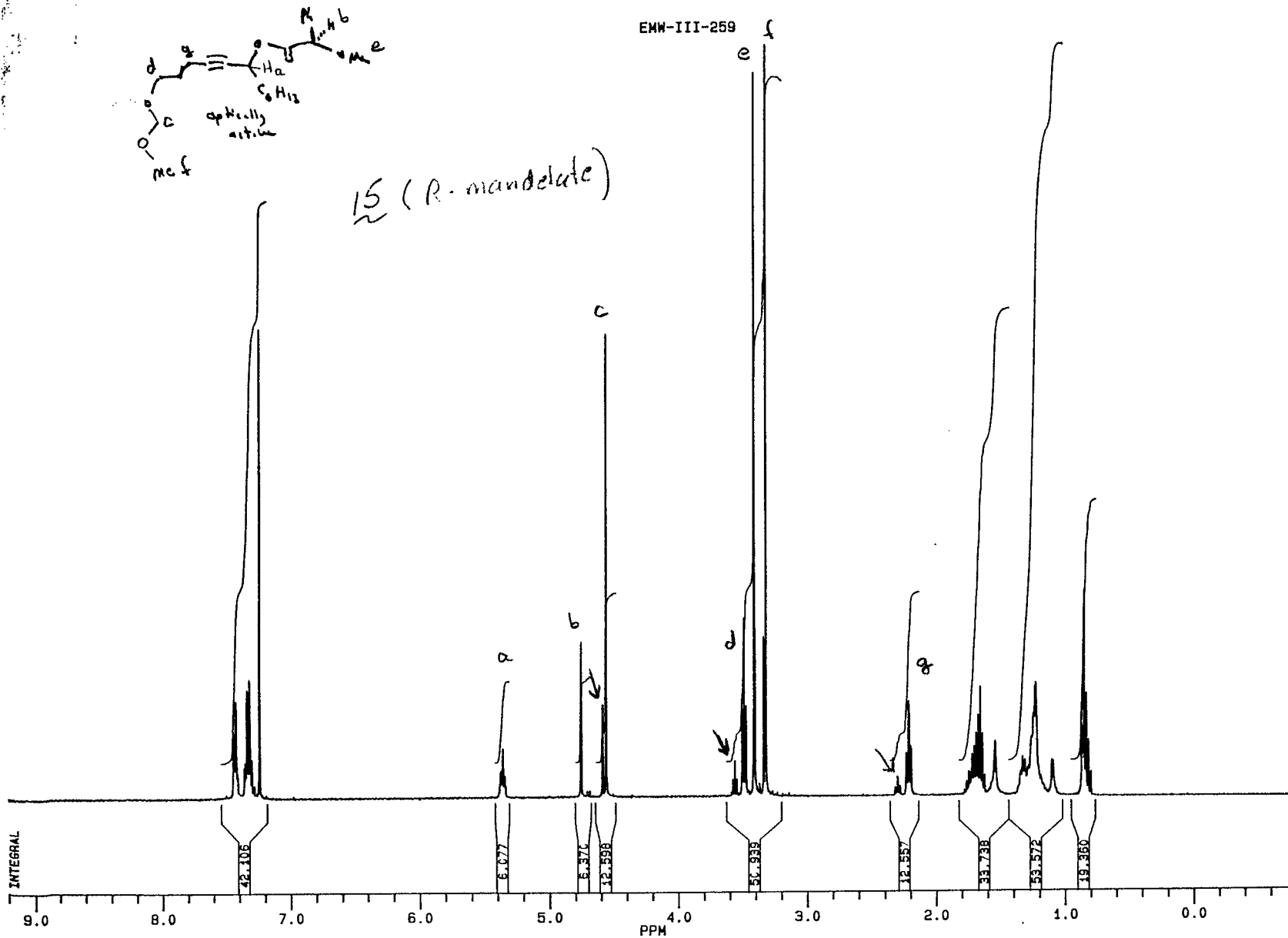
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15  
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BAUER

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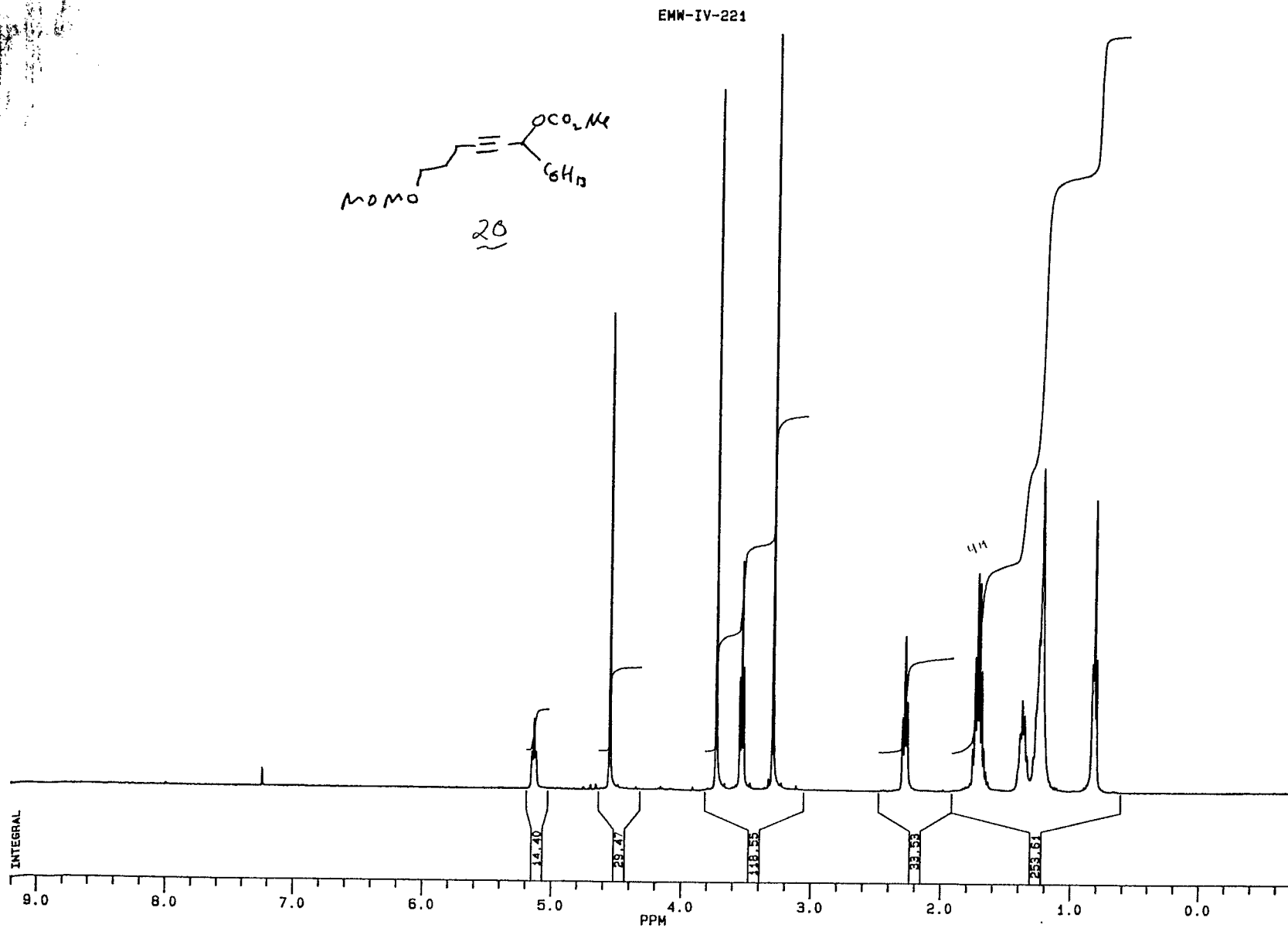
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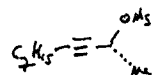
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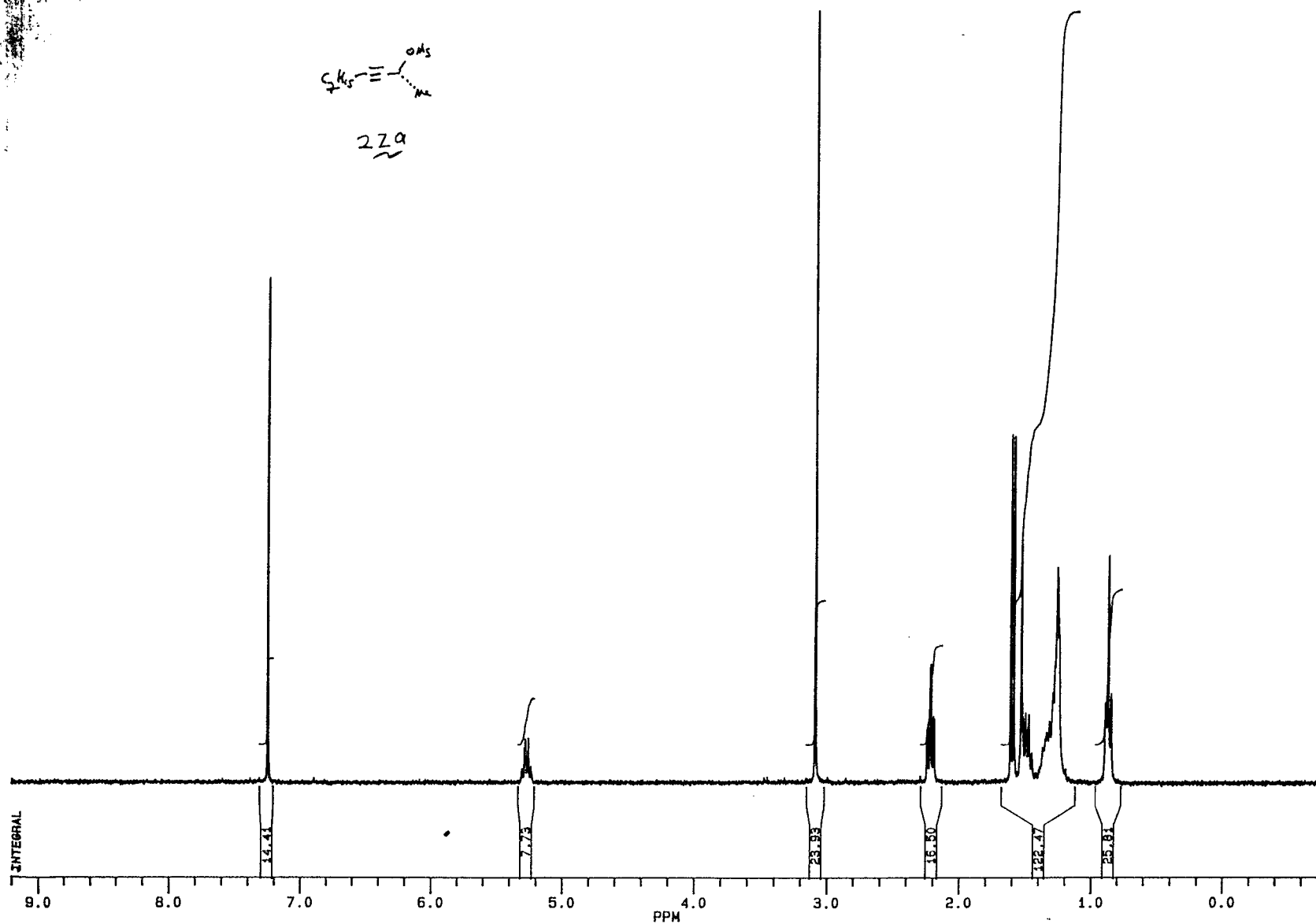
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229



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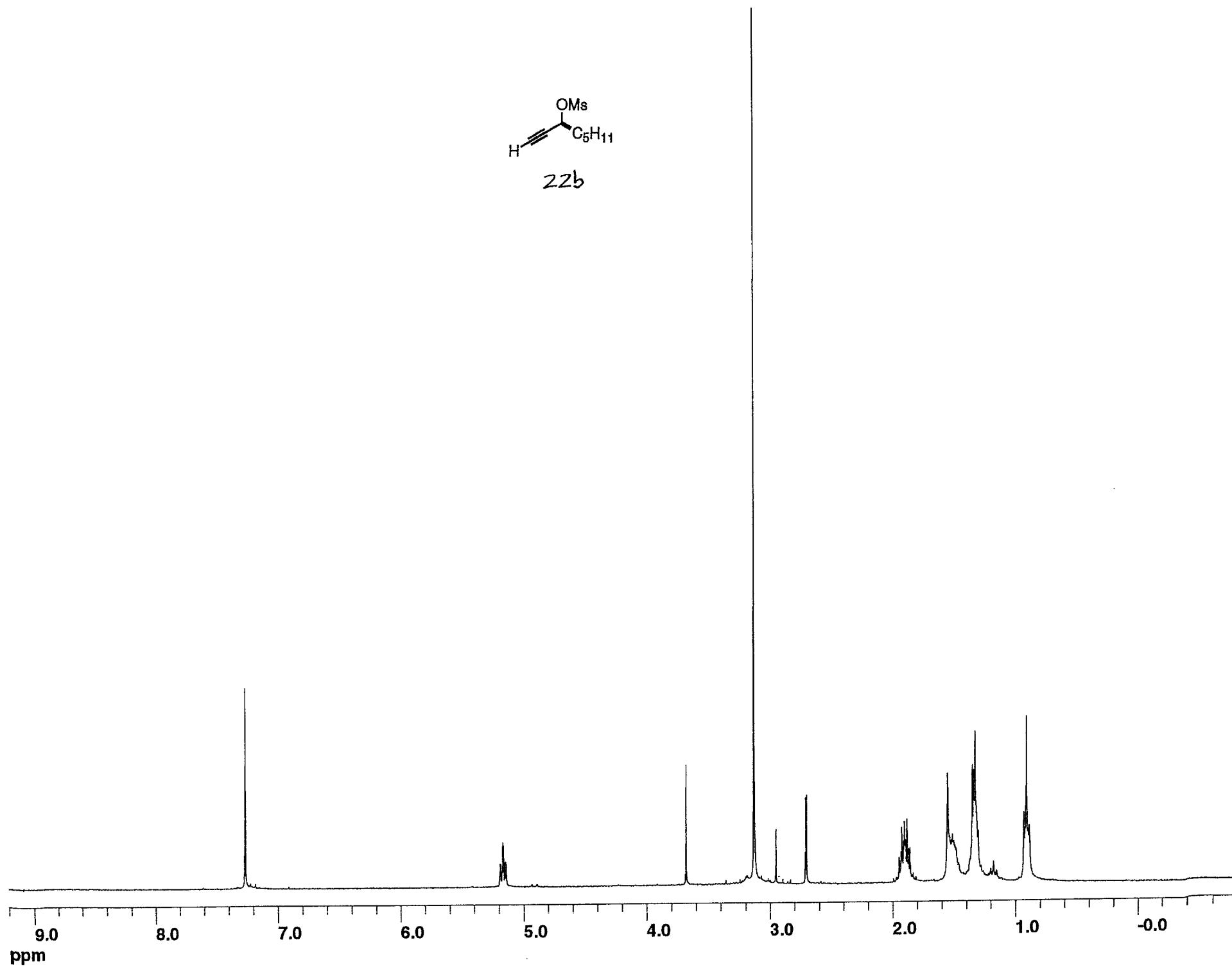
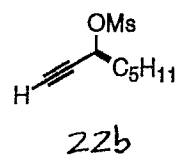
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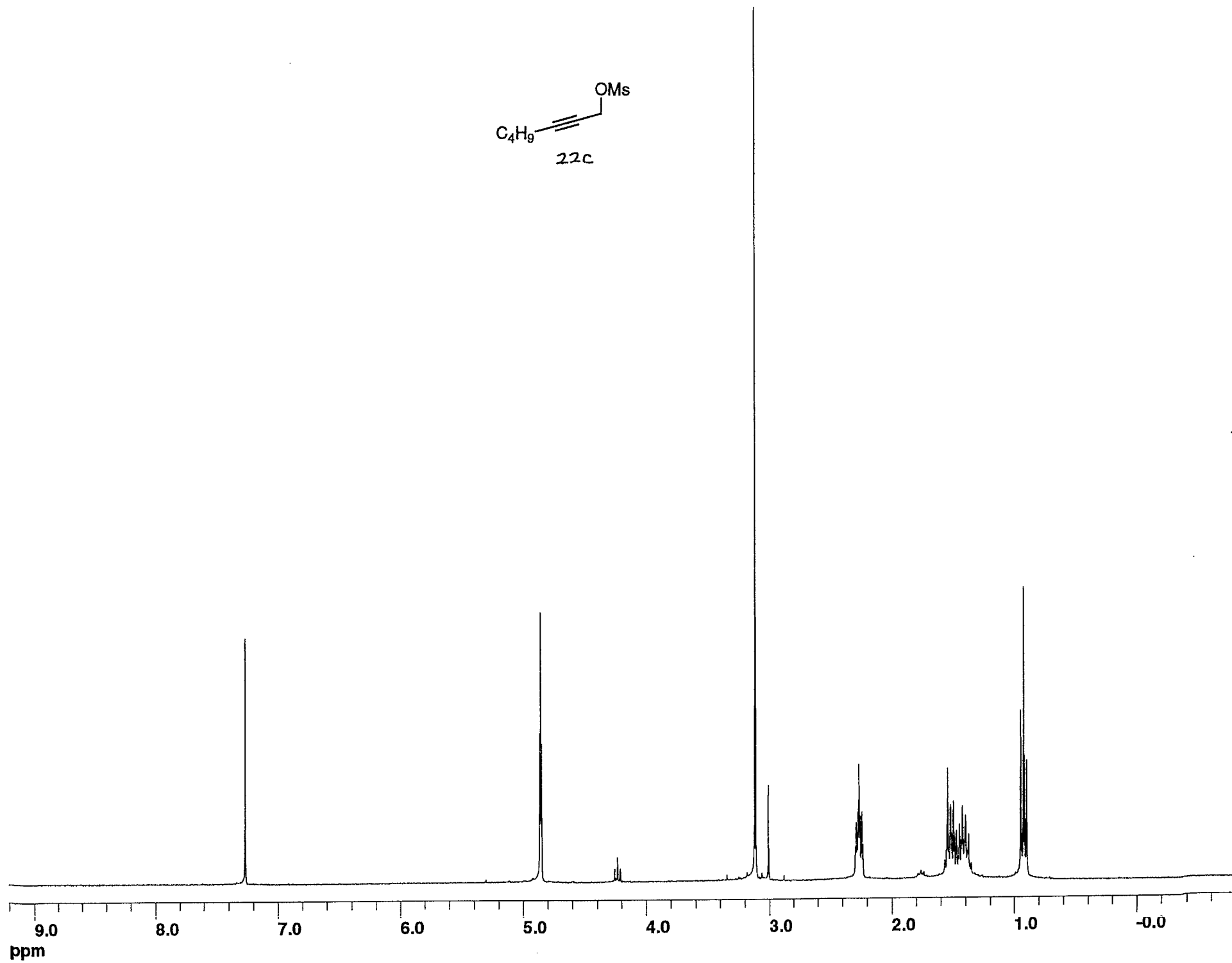
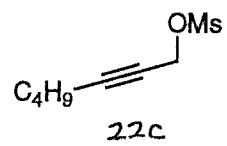
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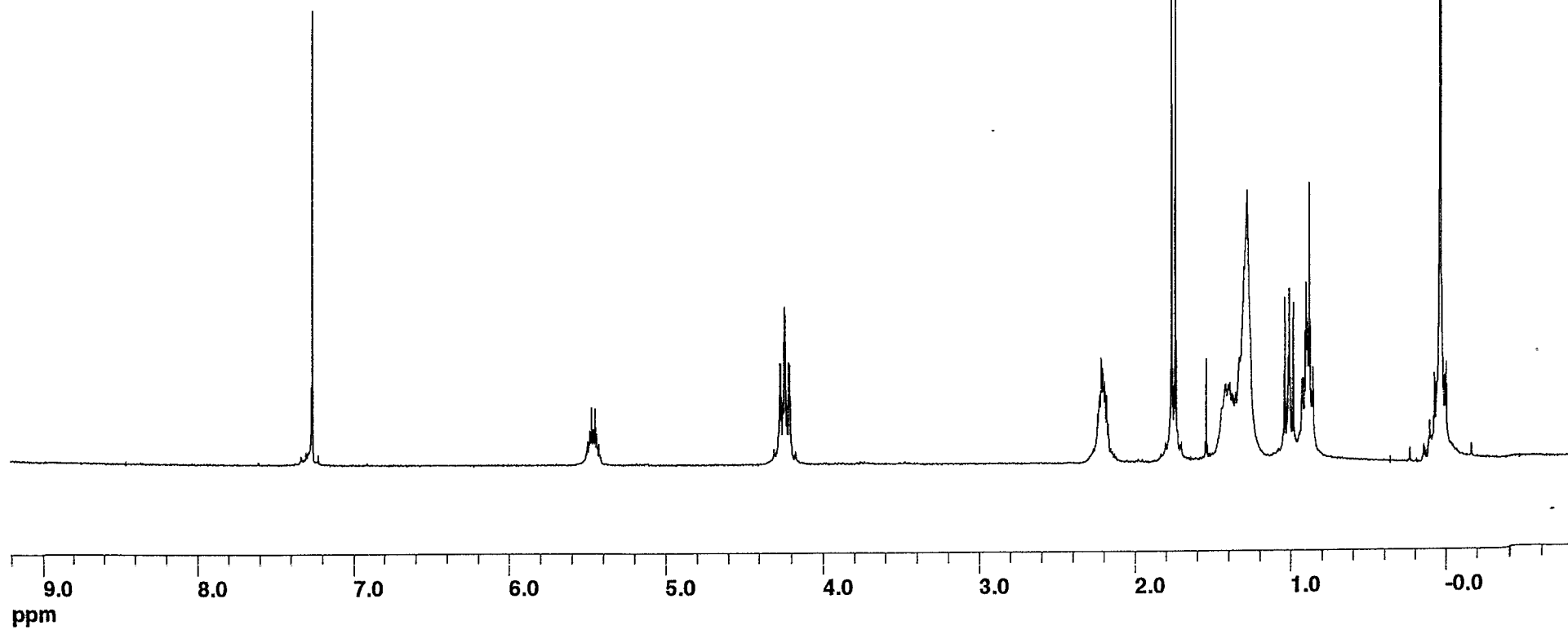
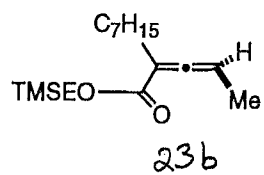
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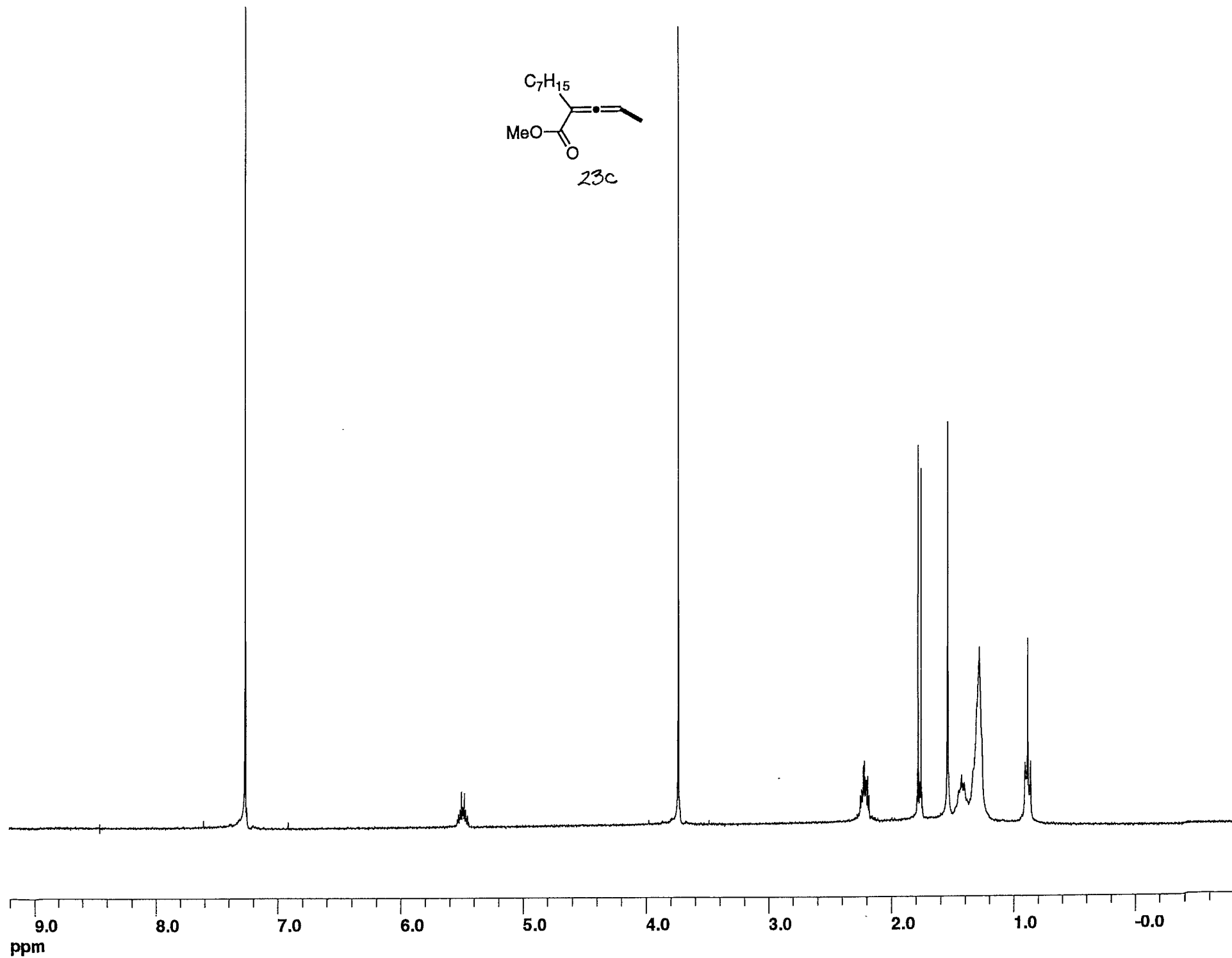
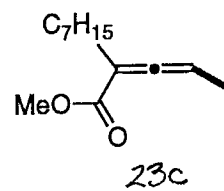
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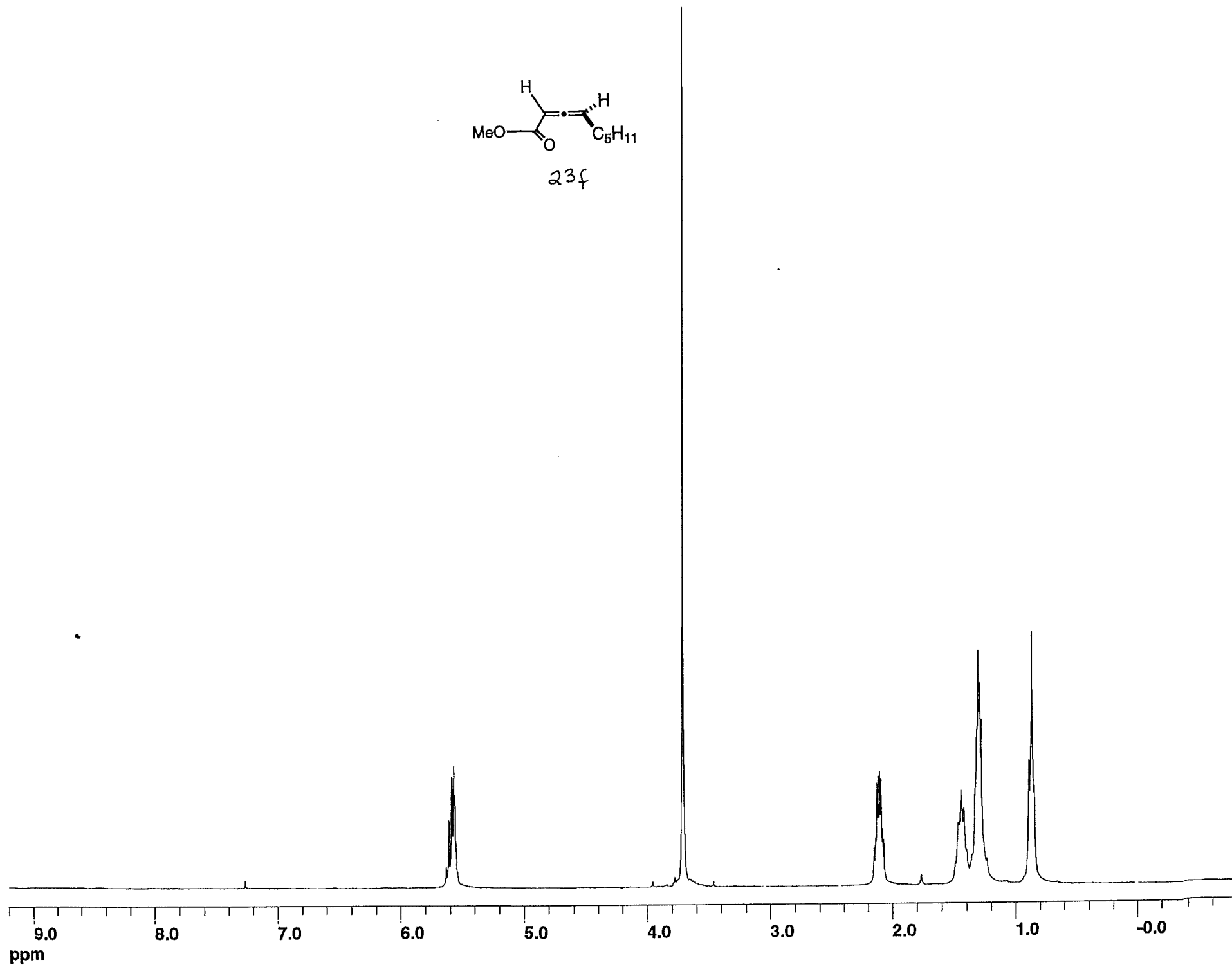
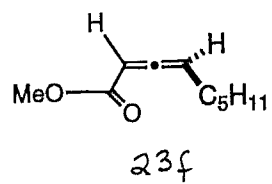


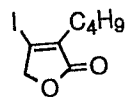




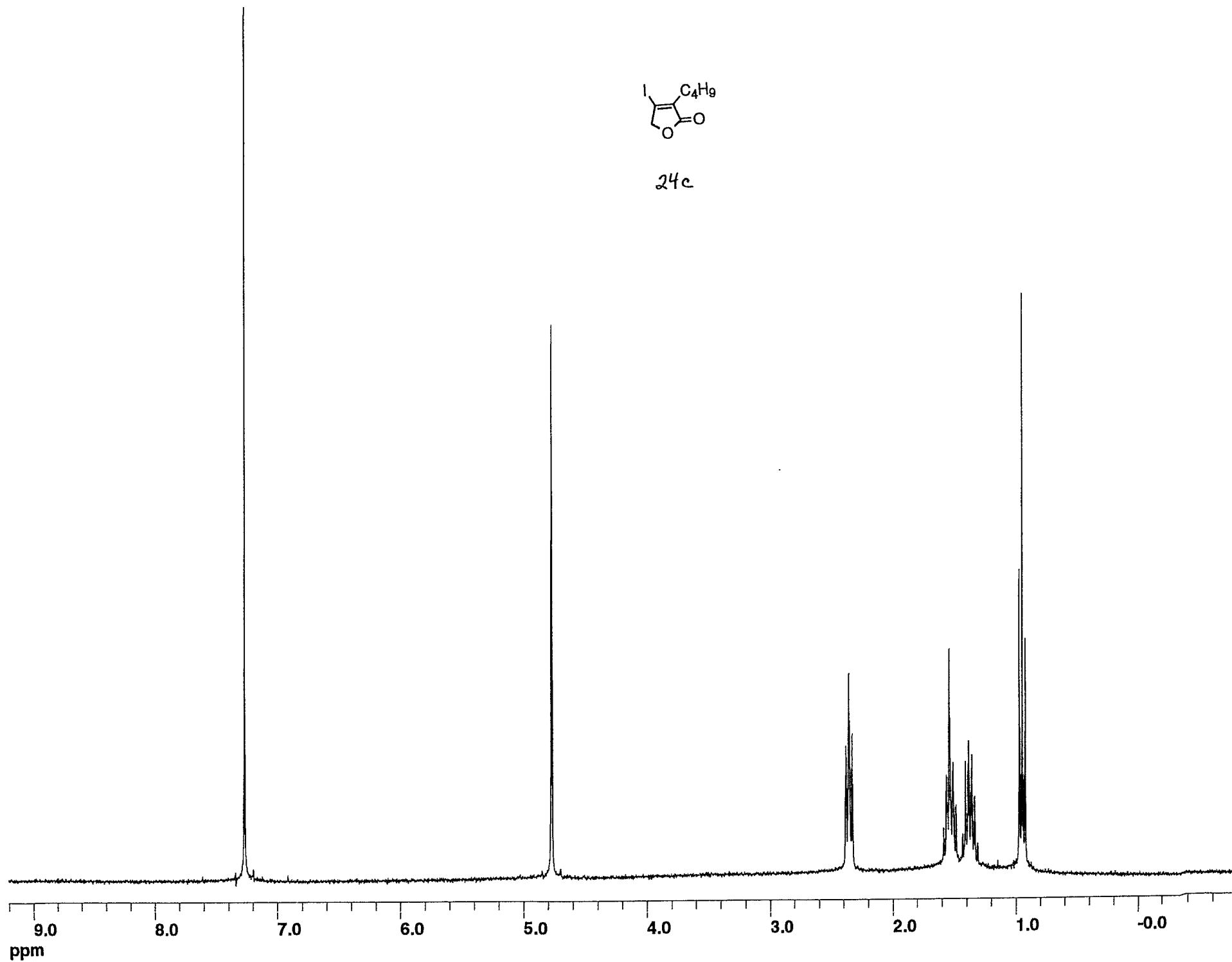


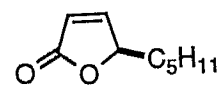






24c





25b

