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Supporting Information

One-pot Synthesis of Fused Tricyclic Heterocycles with Quaternary Carbon Stereocentre via Novel Sequential Pauson-Khand Reaction and Formal [3+3] Cycloaddition

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Typical procedure for the synthesis of 1, 6, 8-endiynes.

1. 1-(5-(Allyloxy)penta-1,3-diynyl)benzene (2a):

A solution of 3-(prop-2-ynyloxy)prop-1-ene (0.961 g, 10.0 mmol), (bromoethynyl) benzene (3.621g, 20.0 mmol), i-Pr_2NH (2.024 g, 20.0 mmol), $Pd(PPh_3)_4$(115.6 mg, 0.10 mmol) and CuI (19 mg, 0.10 mmol) in 20 mL THF was stirred at r.t. till the reaction was complete which was determined by TLC analysis. 50 ml of water was added and the mixture was extracted by ether three times. The combined organic layers were washed by saturated brine solution and dried over $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography on silica gel (hexanes: ethyl ether = 30:1) to afford **2a** (1.457 g, 74%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2 H), 7.28-7.20 (m, 3 H), 5.85-5.80 (m, 1 H), 5.27-5.12 (m, 2 H), 4.20 (s, 2 H), 4.01(d, *J* = 6.0 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 133.50, 132.34, 129.07, 128.17, 121.17, 117.85, 78.54, 77.81, 73.13, 70.71, 70.53, 57.53; MS (EI) *m/z* (%): [M^+] (1.32), 139 (100); HRMS calcd for $C_{14}H_{12}O$: 196.0888, found:196.0876.

2. Dimethyl 2-allyl-2-(5-phenylpenta-2,4-diynyl)malonate (2b):

yield: 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2 H), 7.40-7.32 (m, 3 H), 5.70-5.65 (m, 1 H), 5.28-5.18 (m, 2 H), 3.80 (s, 6 H), 3.02 (s, 2 H), 2.87 (d, *J* = 7.0 Hz, 2 H); ^{13}C NMR (125.8MHz, $CDCl_3$) δ 169.88, 132.51,131.44,129.03,128.31,121.63, 120.14, 78.34, 75.58, 73.88, 67.95, 56.97,52.85, 36.80, 23.90; MS (EI) *m/z* (%): 310 [M^+] (2.52), 250 (100); HRMS calcd for $C_{19}H_{18}O_4$: 310.1205, found: 310.1205.

3. Dimethyl 2-allyl-2-(5-(4-methoxyphenyl)penta-2,4-diynyl)malonate (2c):

yield: 77%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42(d, *J* = 9.0 Hz, 2 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 5.64-5.61 (m, 1 H), 5.24-5.14 (m, 2 H), 3.81 (s, 3 H), 3.76 (s, 6 H), 2.98 (s, 2 H), 2.83(d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.94, 160.26, 134.14, 131.55, 120.08, 114.09, 113.61, 77.70, 75.80, 72.75, 68.22, 57.06, 55.28, 52.83, 36.84, 23.97; MS (EI) *m/z* (%): 340 [M^+] (29.05), 280 (100); HRMS calcd for $C_{20}H_{20}O_5$: 340.1311; found: 340.1311.

4. Dimethyl 2-allyl-2-(5-(naphthalen-1-yl)penta-2,4-diynyl)malonate (2d):

yield: 62%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1 H), 7.77(d, *J* = 8.5 Hz, 2 H), 7.66 (d, *J* = 7.0 Hz, 1 H), 7.53-7.43 (m, 2 H), 7.36-7.32 (m, 1 H), 5.65-5.55 (m, 1 H), 5.20-5.08(m, 2 H), 3.72 (s, 6 H), 2.98 (s, 2 H), 2.81 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.78, 133.80, 132.93, 131.95, 131.38, 129.45, 128.34, 126.99, 126.57, 125.84, 124.98, 120.06, 119.15, 79.39, 78.41, 73.86, 68.04, 56.91, 52.75, 36.79, 23.94; MS (EI) *m/z* (%): 360 [M^+] (34.77), 300 (100); HRMS calcd for $C_{23}H_{20}O_4$: 360.1362, found: 360.1362.

5. Dimethyl 2-allyl-2-(nona-2,4-diynyl)malonate (2e):

yield: 67%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67-5.62 (m, 1 H), 5.24-5.14 (m, 2 H), 3.77 (s, 6 H), 2.91 (s, 2 H), 2.83 (d, *J* =7.0 Hz, 2 H), 2.27 (t, *J* = 7.0 Hz, 2 H), 1.59-1.50 (m, 2 H), 1.47-1.41 (m, 2 H), 0.93 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.98, 131.57, 120.00, 78.59, 71.03, 68.33, 64.88, 57.01, 52.80, 36.73, 30.20, 23.57, 21.90, 18.84, 13.47; MS (EI) *m/z* (%): 290[M^+] (0.31), 230 (100); HRMS calcd for $C_{17}H_{22}O_4$: 290.1518, found: 290.1519.

6. Dimethyl 2-allyl-2-(6-(benzyloxy)hexa-2,4-diynyl)malonate (2f):

yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, 5 H), 5.65-5.62 (m, 1 H), 5.23 (d, *J* = 17.0 Hz, 1 H), 5.18 (d, *J* = 10.0 Hz, 1 H), 4.62 (s, 2 H), 4.25 (s, 2 H), 3.79 (s, 6 H), 2.95 (s, 2 H), 2.84 (d, *J* = 7.0 Hz, 2 H), ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.84, 137.10, 131.41, 128.44, 128.09, 127.95, 120.17, 75.04, 72.78, 71.78, 71.02, 67.41, 57.57, 56.91, 52.87, 36.79, 23.63; MS (EI) *m/z* (%): 263 [M^+-$PhCH_2$] (10.65), 91 (100); HRMS calcd for $C_{21}H_{22}O_5$: 354.1467, found: 354.1468.

7. *N*-allyl-4-methyl-N-(5-phenylpenta-2,4-diynyl)benzenesulfonamide (2g):

yield: 68%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77(d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.0 Hz, 2 H), 7.40-7.31 (m, 5 H), 5.76-5.73 (m, 1 H), 5.35-5.25 (m, 2 H), 4.23 (s, 2 H), 3.85 (d, *J* = 7.0 Hz, 2 H), 2.41(s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 143.82, 135.54, 132.47, 131.77, 129.59, 129.38, 128.43, 127.73, 121.21, 120.22, 76.75, 75.51, 73.01, 70.19, 49.43, 36.76, 21.54; MS (EI) *m/z* (%): 374 [M^+] (1.38), 194 (100); HRMS calcd for $C_{21}H_{19}NO_2S$: 349.1136, found: 349.1140.

8. *N*-allyl-4-methyl-N-(nona-2,4-diynyl)benzenesulfonamide (2h):

yield: 70%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72(d, *J* = 9.0 Hz, 2 H), 7.31 (d, *J* = 9.0 Hz, 2 H), 5.74-5.69 (m, 1 H), 5.30-5.20 (m, 2 H), 4.12(s, 2 H), 3.78 (d, *J* = 7.0 Hz, 2H), 2.42 (s, 3 H), 2.22 (t, *J* = 6.5 Hz, 2 H), 1.51-1.35 (m, 4 H), 0.94-0.89 (m, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 143.57, 135.83, 131.89, 129.51, 127.73, 119.93, 80.39, 70.66, 68.50, 64.26, 49.29, 36.61, 30.17, 21.83, 21.47, 18.79, 13.42; MS (EI) *m/z* (%): 329 [M^+] (0.86), 91 (100); HRMS calcd for $C_{19}H_{23}NO_2S$: 329.1449, found: 329.1448.

9. **4-Methyl-N-(2-methylallyl)-N-(5-phenylpenta-2,4-diynyl)-benzenesulfonami-de (2i):**

yield: 69%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.30-7.23 (m, 5 H), 4.93 (s, 2 H), 4.10 (s, 2 H), 3.67 (s, 2 H), 2.33 (s, 3 H), 1.71(s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 143.79, 139.06, 135.50, 132.48, 129.56, 129.37, 128.44, 127.78, 121.27, 115.81, 76.74, 75.48, 73.04, 70.20, 52.90, 36.47, 21.56, 19.66; MS (EI) *m/z* (%): 363 [M^+] (1.39), 139 (100); HRMS calcd for $C_{22}H_{21}NO_2S$: 363.1293, found: 363.1293.

10. *N*-(But-3-enyl)-4-methyl-N-(5-phenylpenta-2,4-diynyl)-benzenesulfonamide (2j):

yield: 73%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73(d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.38-7.28 (m, 5 H), 5.81-5.73 (m, 1 H), 5.14-5.04 (m, 2 H), 4.25 (s, 2 H), 3.26 (t, *J* = 7.0 Hz, 2 H), 2.37 (s, 3 H), 2.37-2.31 (m, 2 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 143.70, 135.53, 134.37, 132.45, 129.53, 129.39, 128.41, 127.63, 121.13, 117.30, 76.78, 75.61, 72.96, 70.14, 46.07, 37.40, 32.21, 21.48; MS (EI) *m/z* (%): 322 [M^+-C_3H_5] (47.48), 139 (100); HRMS calcd for $C_{22}H_{21}NO_2S$: 363.1293, found: 363.1293.

Typical procedure for Rhodium-catalyzed cyclopent-2-enone derivatives synthesis

11. **6-(phenylethynyl)-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (3a):**

A solution of (5-(allyloxy)penta-1,3-diynyl)benzene **2a** (58.9 mg, 0.30 mmol), (5.8 mg, 0.015 mmol, 5 mmol%) in 10 mL THF was refluxed under CO for 48 hours. The reaction was complete which was determined by TLC analysis. After cooling down to rt, 10 mL of water was added and the mixture was extracted by ether three times. The combined organic layers were washed by saturated brine solution and dried over $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography on silica gel (hexanes: ethyl ether = 3:1) to afford 43.2 mg of **3a** (yield: 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2 H), 7.35-7.26(m, 3 H), 4.77 (d, *J* =17.0 Hz, 1 H), 4.67 (d, *J* = 17.0 Hz, 1 H), 4.36 (dd, *J* = 8.0, 7.0 Hz, 1 H), 3.37-3.32(m, 1 H), 3.28 (dd, *J* = 11.0, 8.0 Hz, 1 H), 2.78 (dd, *J* = 18.0, 6.0 Hz, 1 H), 2.25 (dd, *J* = 18.0, 4.0 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 204.49, 183.62, 131.83, 128.98, 128.29, 122.10, 120.80, 98.47, 78.53, 71.71, 65.96, 44.06, 39.03; MS (EI) *m/z* (%): 224 [M^+] (34.54), 105 (100); HRMS calcd for $C_{15}H_{12}O_2$: 224.0837 found: 224.0837.

12. **Dimethyl 5-oxo-6-(phenylethynyl)-3, 3a, 4, 5-tetrahydropentalene-2, 2 (1H)– dicarb-oxylate (3b):**

yield: 83%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.48 (m, 2 H), 7.31-7.25(m, 3 H), 3.78 (s, 3 H), 3.75(s, 3 H), 3.49 (d, *J* = 20.0 Hz, 1 H), 3.41 (d, *J* = 20.0 Hz, 1 H), 3.16-3.15(m, 1 H), 2.83 (dd, *J* = 13.0, 8.0 Hz, 1 H), 2.75 (dd, *J* = 18.0, 6.0 Hz, 1 H), 2.20 (dd, *J* = 18.0, 4.0 Hz, 1 H), 1.77 (dd, *J* = 13.0, 12.0 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 204.72, 185.46, 171.63, 170.85, 131.80, 128.74, 128.22, 122.37, 121.73, 97.67, 78.91, 60.49, 53.28, 53.12, 43.43, 41.64, 39.03, 35.51; MS(EI) *m/z* (%): 224 [M^+] 338(74.37), 278(100); HRMS calcd for $C_{20}H_{18}O_5$: 338.1154, found: 338.1153.

13. **Dimethyl 6-((4-methoxyphenyl)ethynyl)-5-oxo-3, 3a, 4, 5-tetrahydro- pentalene -2, 2(1H)-**

dicarboxylate (3c):

yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H) 3.83 (s, 3 H), 3.81(s, 3 H), 3.78(s, 3 H), 3.51 (d, *J* = 20.0 Hz, 1 H), 3.43 (d, *J* = 20.0 Hz, 1 H), 2.87-2.76(m, 1 H), 2.85 (dd, *J* = 12.5, 7.5 Hz, 1 H), 2.78 (dd, *J* = 18.0, 6.5 Hz, 1 H), 2.23 (dd, *J* = 18.0, 3.5 Hz, 1 H), 1.79 (t, *J* = 12.5 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 204.93, 184.57, 171.74, 170.95, 160.04, 133.41, 122.06, 114.55, 113.95, 97.91, 76.74, 60.59, 55.28, 53.31, 53.15, 43.39, 41.70, 39.16, 35.57; MS (EI) *m/z* (%): 368 [M^+] (100); HRMS calcd for $C_{21}H_{20}O_6$: 368.1260 found: 368.1260.

14. Dimethyl 6-(naphthalen-1-ylethynyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2 (1H)-dicarboxylate (3d):

yield: 82%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41(d, *J*= 9.0 Hz, 1H), 7.86 (d, *J*= 8.0 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.61(dd, *J*= 8.0, 7.0 Hz, 1 H), 7.53(t, *J* = 7.0 Hz, 1 H), 7.44 (t, *J* = 8.0 Hz, 1 H), 3.83 (s, 3 H), 3.82 (s, 3 H), 3.60 (d, *J* = 19.5 Hz, 1 H), 3.52 (d, *J* = 19.5 Hz, 1 H), 3.26-3.22 (m, 1 H), 2.89 (dd, *J* = 13.0, 7.5 Hz, 1 H), 2.83 (dd, *J* = 18.0, 6.5 Hz, 1 H), 2.28 (dd, *J* = 18.0, 3.0 Hz, 1 H), 1.85 (t, *J* = 13.0 Hz, 1 H); ^{13}C NMR (125.8MHz, $CDCl_3$) δ 204.68, 184.98, 171.71, 170.92, 133.08, 130.86, 129.37, 128.22, 127.07, 126.48, 126.19, 125.10, 122.01, 120.09, 95.97, 83.89, 60.62, 53.35, 53.19, 43.58, 41.76, 39.14, 35.66; MS (EI) *m/z* (%): 388 [M^+] (100); HRMS calcd for $C_{24}H_{20}O_5$: 388.1311, found: 388.1314.

15. Dimethyl 6-(hex-1-ynyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicar- boxylate (3e):

yield: 72%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 3 H), 3.76 (s, 3 H), 3.41 (d, *J* = 20.0 Hz, 1 H), 3.33 (d, *J* = 20.0 Hz, 1 H), 3.05-3.13 (m, 1 H), 2.81 (dd, *J* = 13.0, 8.0 Hz, 1 H), 2.71 (dd, *J* = 18.0, 7.0 Hz, 1 H), 2.40 (t, *J* = 7.5 Hz, 2 H), 2.19 (dd, *J* = 18.0, 3.0 Hz, 1 H), 1.73(dd, *J* = 13.0, 12.0 Hz, 1 H), 1.57-1.54 (m, 2 H), 1.45-1.41 (m, 2 H), 0.916(t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 205.55, 184.22, 171.75, 170.98, 122.27, 99.67, 70.19, 60.54, 53.26, 53.11, 43.12, 41.52, 39.09, 35.34, 30.57, 21.93, 19.36, 13.54; MS (EI) *m/z* (%): 303 [M^+-CH_3] (3.17), 274 (100); HRMS calcd for $C_{18}H_{22}O_5$: 318.1467, found: 318.1467.

16. **Dimethyl6-(3-(benzyloxy)prop-1-ynyl)-5-oxo-3, 3a, 4, 5-tetrahydropentalene- 2, 2 (1H)-dicarboxylate (3f)**:

yield: 58%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 4 H), 7.24-7.23(m, 1 H), 4.57 (s, 2 H), 4.31(s, 2 H), 3.73 (s, 3H), 3.70 (s, 3 H), 3.39 (d, *J* = 20.0 Hz, 1 H), 3.31 (d, *J* = 20.0 Hz, 1 H), 3.23-3.05 (m, 1 H), 2.76 (dd, *J* = 13.0, 8.0 Hz, 1 H), 2.68 (dd, *J* = 18.0, 6.5 Hz, 1 H), 2.13 (dd, *J* = 18.0, 3.0 Hz, 1 H), 1.71 (dd, *J* =13.0, 12.0 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 204.68, 186.10, 171.60, 170.78, 137.29, 128.37, 128.10, 127.81, 121.23, 93.87, 76.24, 71.62, 60.46, 57.79, 53.27, 53.11, 43.39, 41.53, 38.96, 35.43.

17. **6-(2-Phenylethynyl)-2-tosyl-2,3,3a,4-tetrahydrocyclopenta[c]pyrrol-5(1*H*)-one (3g):** yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.37-7.27(m, 5 H), 4.46 (d, *J* =17.0 Hz, 1 H), 4.19(d, *J* = 17.0 Hz, 1 H), 4.07 (dd, *J* = 9.0, 8.0 Hz, 1 H), 3.23-3.21 (m, 1 H), 2.74 (dd, *J* = 18.0, 7.0 Hz, 1 H), 2.66 (dd, *J* = 9.0, 1.0 Hz, 1 H), 2.44(s, 3 H), 2.16 (dd, *J* = 18.0 , 3.0 Hz, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 203.05, 178.11, 144.25, 133.50, 131.92, 130.08, 129.25, 128.39, 127.47, 122.44, 121.85, 99.40, 77.91, 52.52, 48.02, 42.41, 39.60, 21.55; MS (EI) *m/z* (%): 388 [M^+](65.45), 195 (100); HRMS calcd for $C_{22}H_{19}NO_3S$: 377.1086, found: 377.1086.

18. **6-(Hex-1-ynyl)-2-tosyl-2,3,3a,4-tetrahydrocyclopenta[c]pyrrol-5(1H)-one(2h).** yield: 53%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 4.28 (d, *J* = 17.0 Hz, 1 H), 4.02(d, *J* =17.0 Hz, 1 H), 3.94 (dd, *J* = 9.0, 8.5 Hz, 1 H), 3.10-3.00 (m, 1 H), 2.58 (dd, *J* = 18.0, 6.5 Hz, 1 H), 2.53 (dd, *J* = 11.0, 9.0 Hz, 1 H), 2.37(s, 3H), 2.32(t, *J* = 7.0 Hz, 2 H), 2.02 (dd, *J* = 18.0 , 3.5 Hz, 1 H), 1.50-1.40 (m, 2 H), 1.38-1.30 (m, 2 H), 0.85 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125.8 Hz, $CDCl_3$) δ 203.78, 177.14, 144.10, 133.45, 129.94, 127.35, 122.82, 101.50, 69.39, 52.45, 47.78, 41.95, 39.36, 30.31, 21.83, 21.45, 19.26, 13.45; MS (EI) *m/z* (%): 357 [M^+](30.56), 91 (100); HRMS calcd for Exact Mass: $C_{20}H_{23}NO_3S$: 357.1399, found: 357.1400.

19. **3a-Methyl-6-(phenylethynyl)-2-tosyl-2,3,3a,4-tetrahydrocyclopenta[c]pyrrol-5(1H)-one (3i):** yield: 66%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.29-7.27(m, 5 H), 4.37 (d, *J* = 17.5 Hz, 1 H), 4.14(d, *J* = 17.5 Hz, 1 H), 3.66 (d, *J* = 9.5 Hz, 1 H), 2.79 (d, *J* = 9.5 Hz, 1 H), 2.43 (d, *J* = 17.5 Hz, 1 H), 2.37 (s, 3 H), 2.30 (d, *J* = 17.5 Hz, 1 H), 1.17(s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.68, 181.26, 144.09, 133.71, 131.85, 129.94, 129.18, 128.32, 127.32, 121.79, 121.00, 99.13, 77.83, 58.01, 47.94, 47.49, 46.70, 25.14, 21.47 ; MS (EI) *m/z* (%): 391 [M^+] (100); HRMS calcd for $C_{23}H_{21}NO_3S$: 391.1242, found: 391.1242.

20. **7-(phenylethynyl)-2-tosyl-3, 4, 4a, 5-tetrahydro-1H-cyclopenta[c]pyridin-6 (2H)-one (3j)**: yield: 77%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66(d, *J* = 8.0 Hz, 2 H), 7. 48 (d, *J* = 8.0 Hz, 2 H), 7.33-7.22 (m, 5 H), 4.98 (d, *J* = 17.0 Hz, 1 H), 3.94 (d, *J* = 17.0 Hz, 1 H), 3.31 (d, *J* = 15.0 Hz, 1 H), 2.65-2.58 (m, 3 H), 2.35 (s, 3 H), 2.03-1.95 (m, 2 H), 1.22-1.35 (m, 1 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 203.17, 171.53, 144.09, 132.00, 129.86, 129.08, 128.34, 127.73, 124.82, 122.09, 99.45, 77.89, 46.63, 45.56, 40.73, 38.10, 31.85, 21.51; MS (EI) *m/z* (%): 391 [M^+] (75.71), 208 (100); HRMS calcd for $C_{23}H_{21}NO_3S$: 391.1242, found: 391.1242.

21. 4ba:

yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.35 （m , 5 H）, 4.15 (d, *J* =14.1 Hz,1 H),4.00 (d, *J* =14.1Hz,1 H), 3.70 (s, 3 H), 3.65 (s, 3 H), 2.91 (dd, *J* =13.5,8.1 Hz, 1 H), 2.78-2.56 (m, 2 H), 2.51 (s, 2 H), 2.43 (d, *J* = 13.5 Hz, 1 H), 2.35 (s, 3 H), 2.25-2.18 (m, 1 H), 2.10 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.58, 199.87, 172.47, 171.62, 157.72, 155.53, 136.60, 129.00, 128.51, 126.73, 121.84, 118.61, 60.95, 52.93, 52.87, 50.73, 50.06, 45.60, 42.21, 40.51, 34.91, 32.59, 18.98; MS (EI) m/z (%): 438 [M+] (7.00), 293 (100); HRMS calcd for $C_{25}H_{26}O_7$: 438.1677, found: 438.1679.

22. 4ga:

yield: 68%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.32-7.20 (m, 5 H), 4.15 (d, *J* = 14.0 Hz, 1 H), 4.00(d, *J* = 14.0 Hz, 1 H), 3.38-3.33 (m, 1 H), 3.22 (d, *J* = 10.0 Hz, 1 H), 3.10 (d, *J* = 10.0 Hz, 1 H), 3.04 (d, *J* = 10.0 Hz, 1 H), 2.80-2.74 (m, 1 H), 2.69 (dd, *J* = 19.0, 11.0 Hz, 1 H), 2.44 (s, 3 H), 2.29 (s, 3 H), 2.23 (dd, *J* = 19.0,7.0 Hz, 1 H), 2.02 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.04, 200.79, 159.00, 153.24, 143.85, 136.04, 132.10, 129.68, 129.06, 128.59, 127.85, 126.92, 119.21, 115.23, 61.85, 55.35, 49.43, 44.91, 40.78, 34.85, 32.58, 21.56, 18.35; MS (EI) m/z (%): 477 [M+] (1.14), 322 (100); HRMS calcd for $C_{27}H_{27}NO_5S$: 477.1610, found: 477.1610.

23. 4gb:

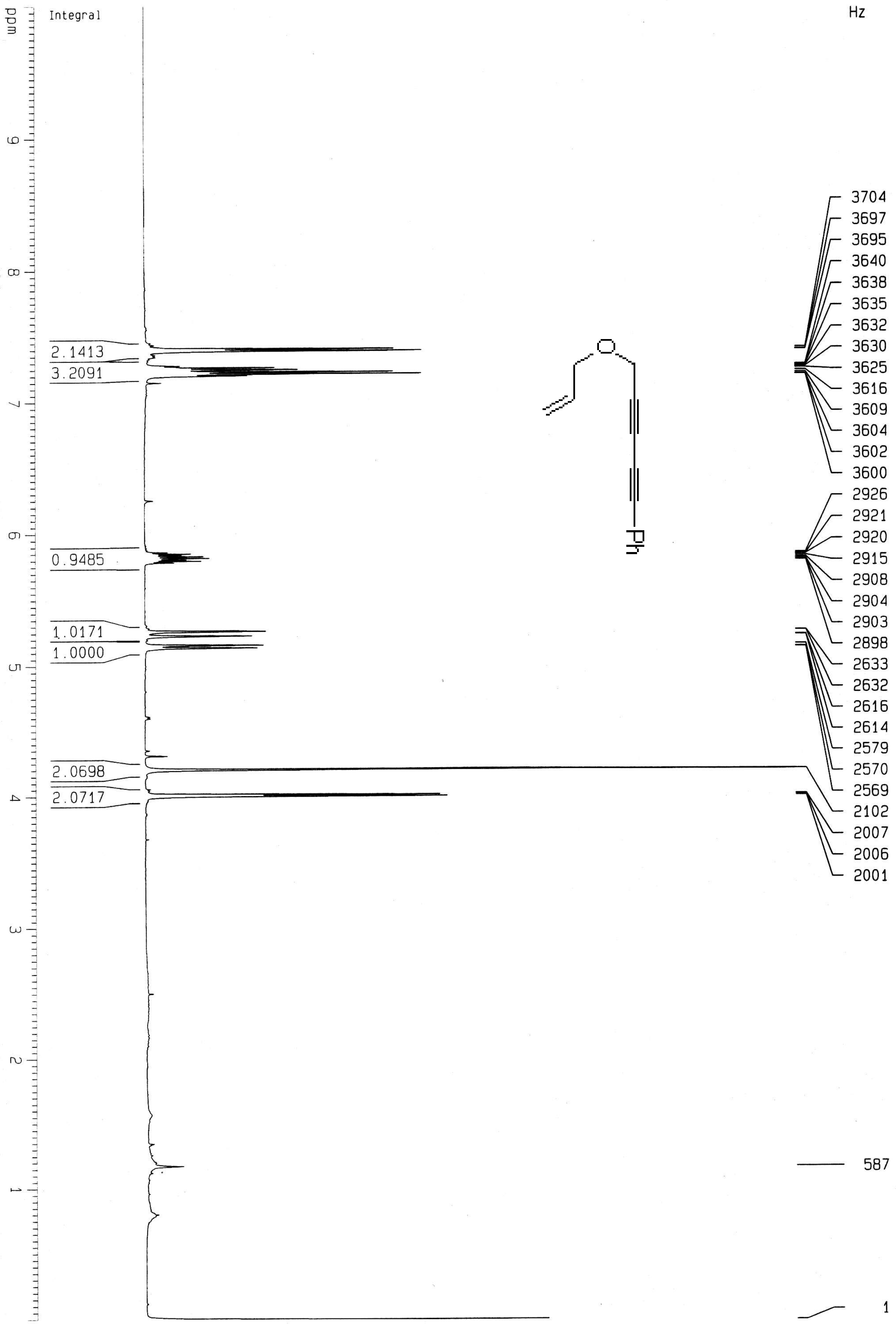
yield: 40%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* =7.8 Hz, 2 H), 7.33 (d, *J* = 7.8 Hz, 2 H), 7.27-7.20 (m, 5 H), 4.2 (d, *J* =14.4 Hz, 1 H), 4.06-3.90 (m, 3 H), 3.35 (d, *J* = 9.0 Hz, 1 H), 3.29-3.23 (m, 2 H), 2.88-2.70 (m, 3 H), 2.43 (s, 3 H), 2.32 (d, *J* =14.7 Hz,1 H), 2.09 (s, 3 H), 1.07 (t, *J* =7.2 Hz ,3 H); ^{13}C NMR（75 MHz, $CDCl_3$）δ 201.99, 165.83, 158.73, 158.30, 143.70, 135.99, 132.01, 129.55, 129.01, 128.54, 128.02, 126.85, 116.06, 109.67, 62.04, 60.71, 56.28, 48.20, 45.18, 40.92, 34.74, 21.47, 18.47, 13.86; MS (EI) m/z (%): 505 [M^+-2H] (2.23), 322 (100); HRMS calcd for $C_{28}H_{29}NO_6S$: 507.1716, found: 507.1726.

24. 4gc:

yield: 48%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* =8.1 Hz, 2 H), 7.40-7.20 (m, 10 H), 7.08-7.03 (m, 2 H), 4.46 (d, *J* =14.7 Hz, 1 H), 3.97 (d, *J* =14.7 Hz, 1 H), 3.88-3.76 (m, 2 H), 3.48-3.40 (m, 2 H), 3.38-3.28 (m, 1 H), 3.20 (d, *J* = 9.6 Hz, 1 H), 2.90-2.72 (m, 2 H), 2.50-2.30 (m, 5 H), 0.78 (t, *J* =7.2 Hz, 3 H); ^{13}C NMR（75MHz,$CDCl_3$）δ 202.06, 166.40, 159.16, 155.84, 143.74, 135.89, 132.59, 132.37, 130.12, 129.64, 129.31, 128.59, 128.27, 128.03, 127.91, 126.99, 115.68, 110.30, 61.96, 60.83, 55.77, 48.74, 44.87, 41.17, 34.93, 21.55, 13.23; MS (EI) m/z (%): 569 [M^+] (1.32), 414 (100); HRMS calcd for $C_{33}H_{31}NO_6S$:569.1872, found: 569.1881.

25. 4gd:

yield: 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 2 H), 7.35-720 (m, 7 H), 4.12-4.08 (m, 2 H), 3.73-3.65 (m, 1 H), 3.44 (d, *J* = 8.7 Hz, 1 H), 3.26 (d, *J* =9.6 Hz, 1 H), 3.10-3.00 (m, 1 H), 2.72 (dd, *J* = 19.5, 10.8 Hz, 1 H), 2.53 (d, *J* = 9.6 Hz, 1 H), 2.50-2.30 (m, 6 H), 2.25 (t, *J* = 6.9 Hz, 2 H), 2.00-1.80 (m, 2 H); ^{13}C NMR（75 MHz,$CDCl_3$）δ 202.73, 196.95, 167.00, 157.07, 143.71, 135.94, 132.26, 129.59, 129.06, 128.66, 127.89, 126.99, 117.50, 115.79, 62.46, 56.62, 46.58, 44.93, 39.98, 37.97, 34.63, 27.40, 21.59, 20.06; MS (EI) m/z (%): 489 [M^+] (1.35), 334 (100); HRMS calcd for $C_{28}H_{27}NO_5S$: 489.1603, found: 489.1610.



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3604
3602
3600
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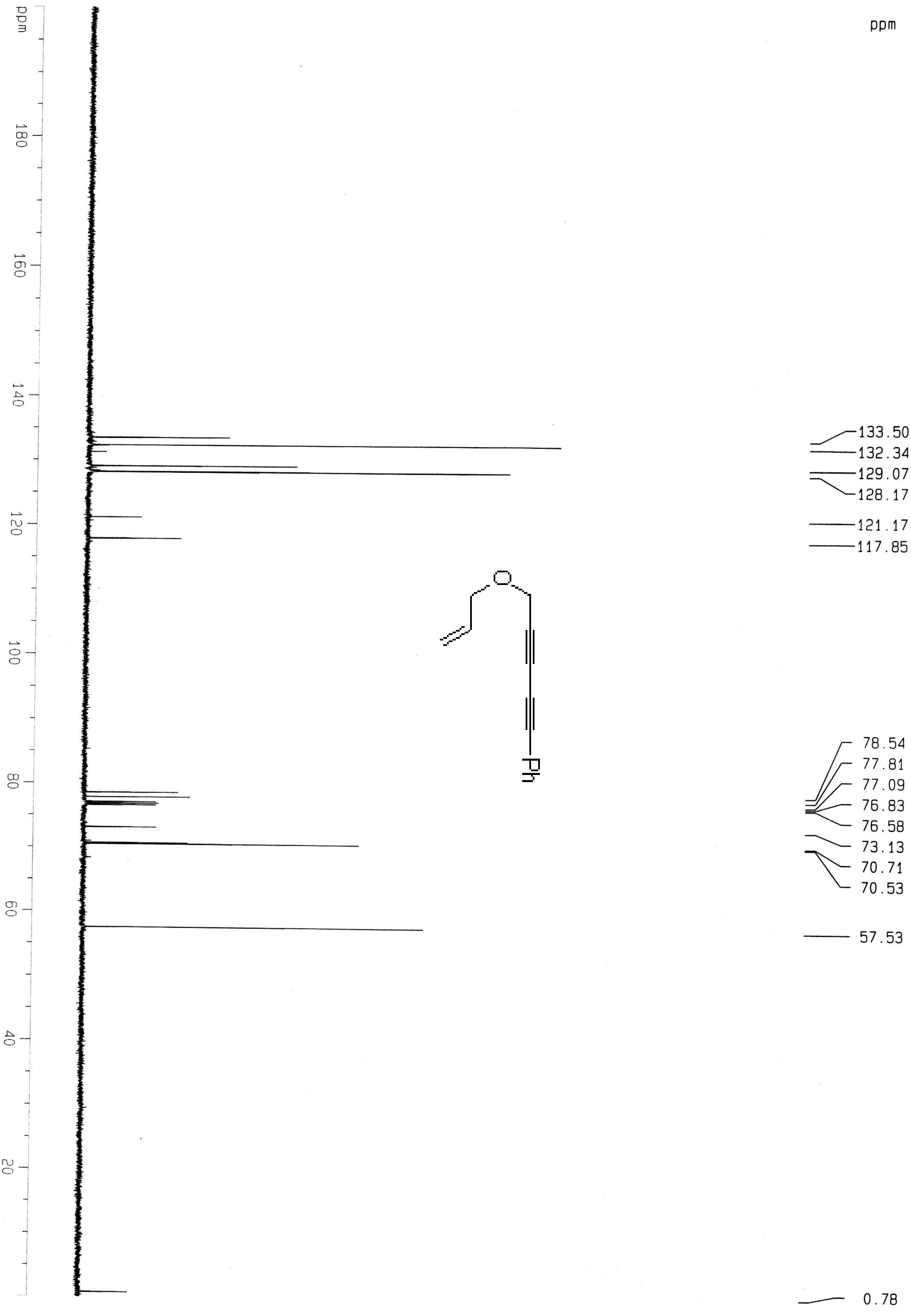
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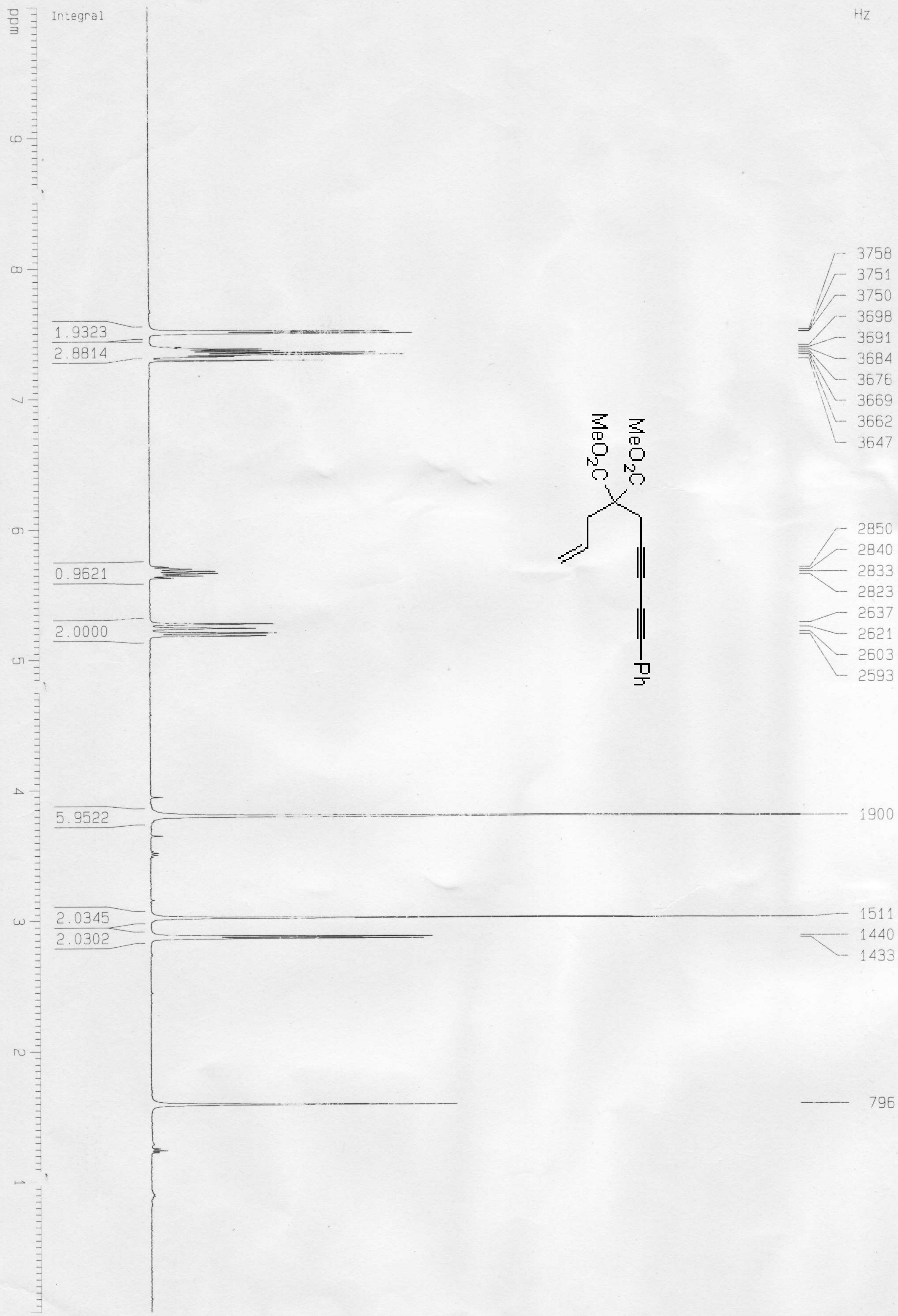

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MeO_2C
Ph


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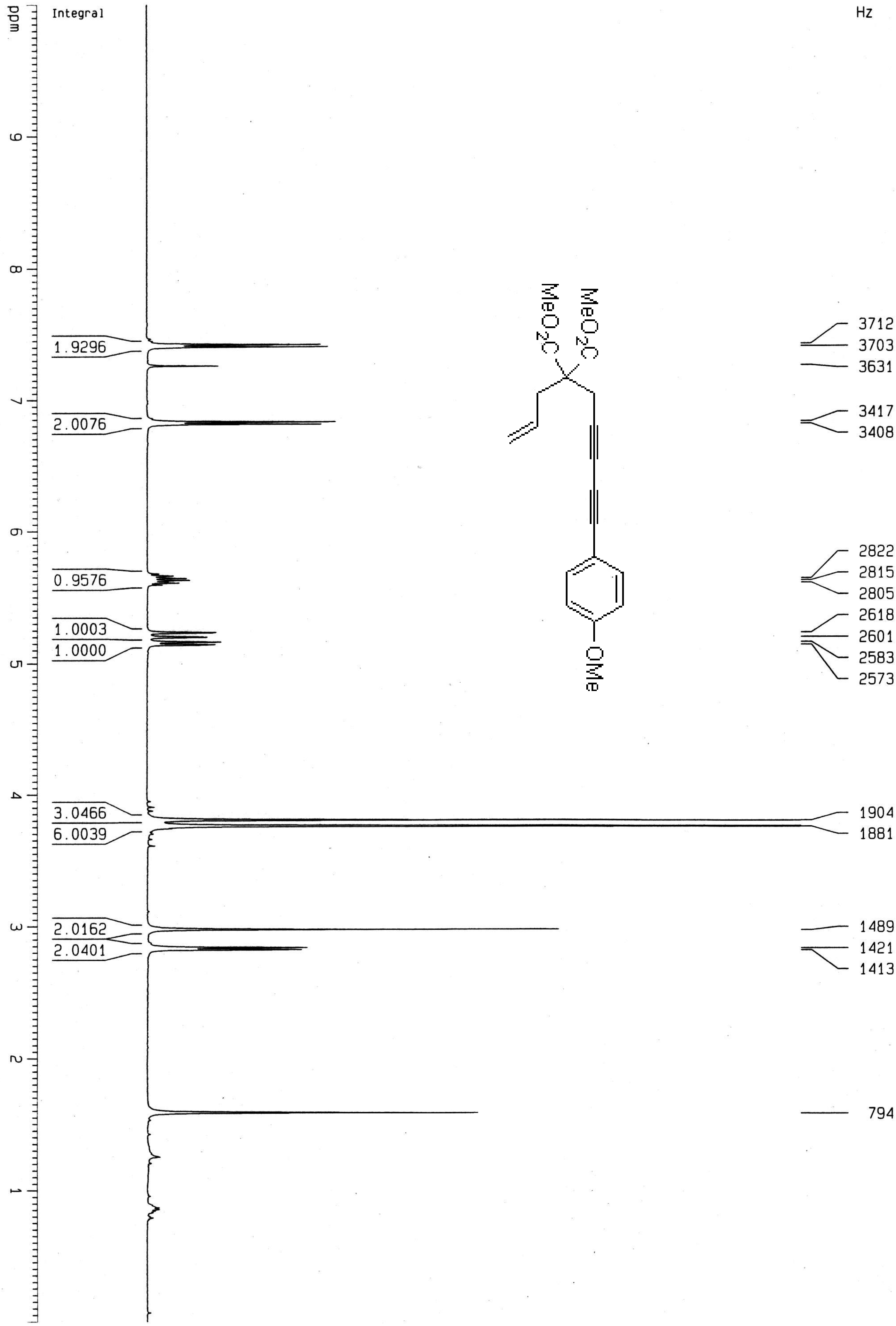

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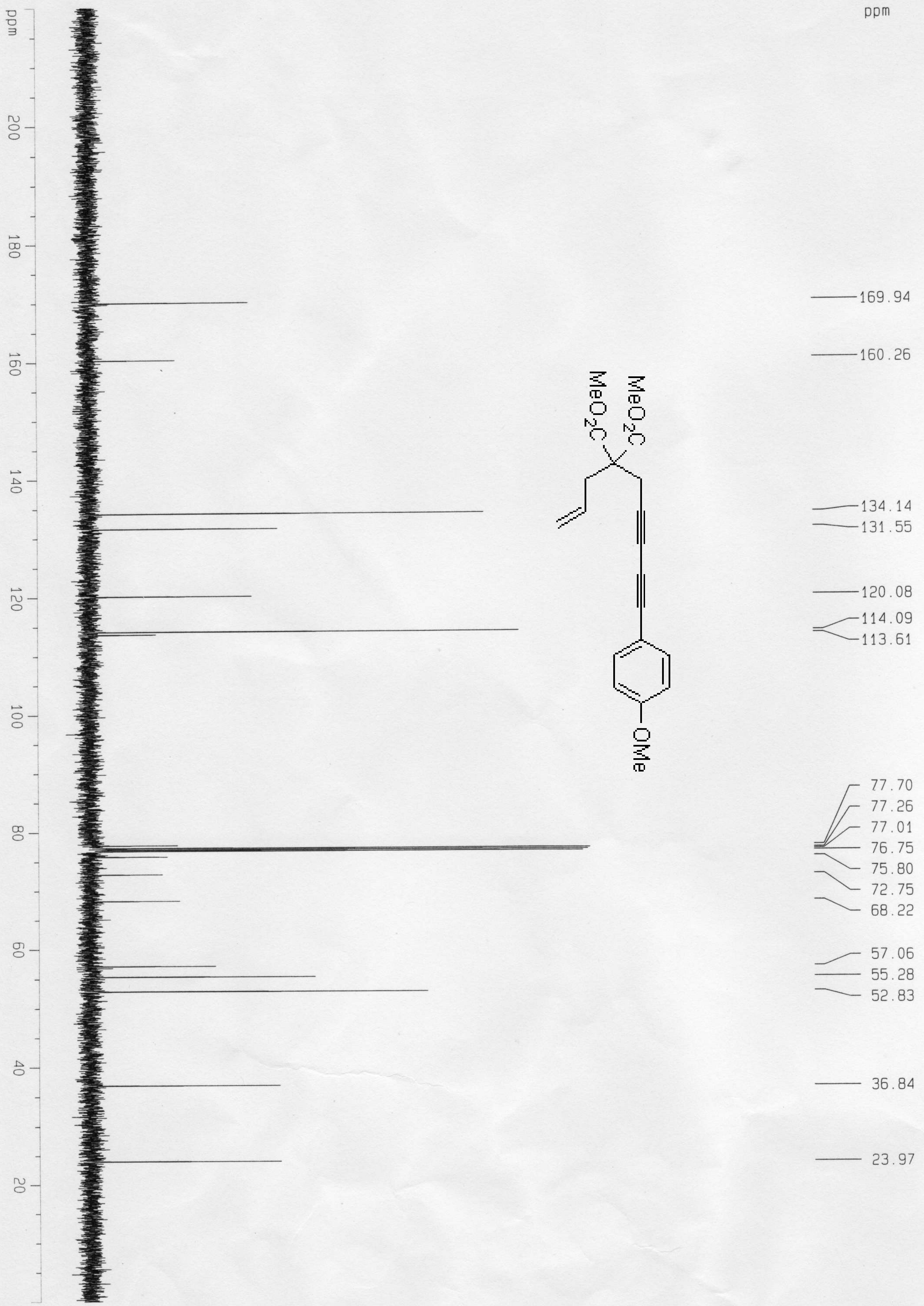

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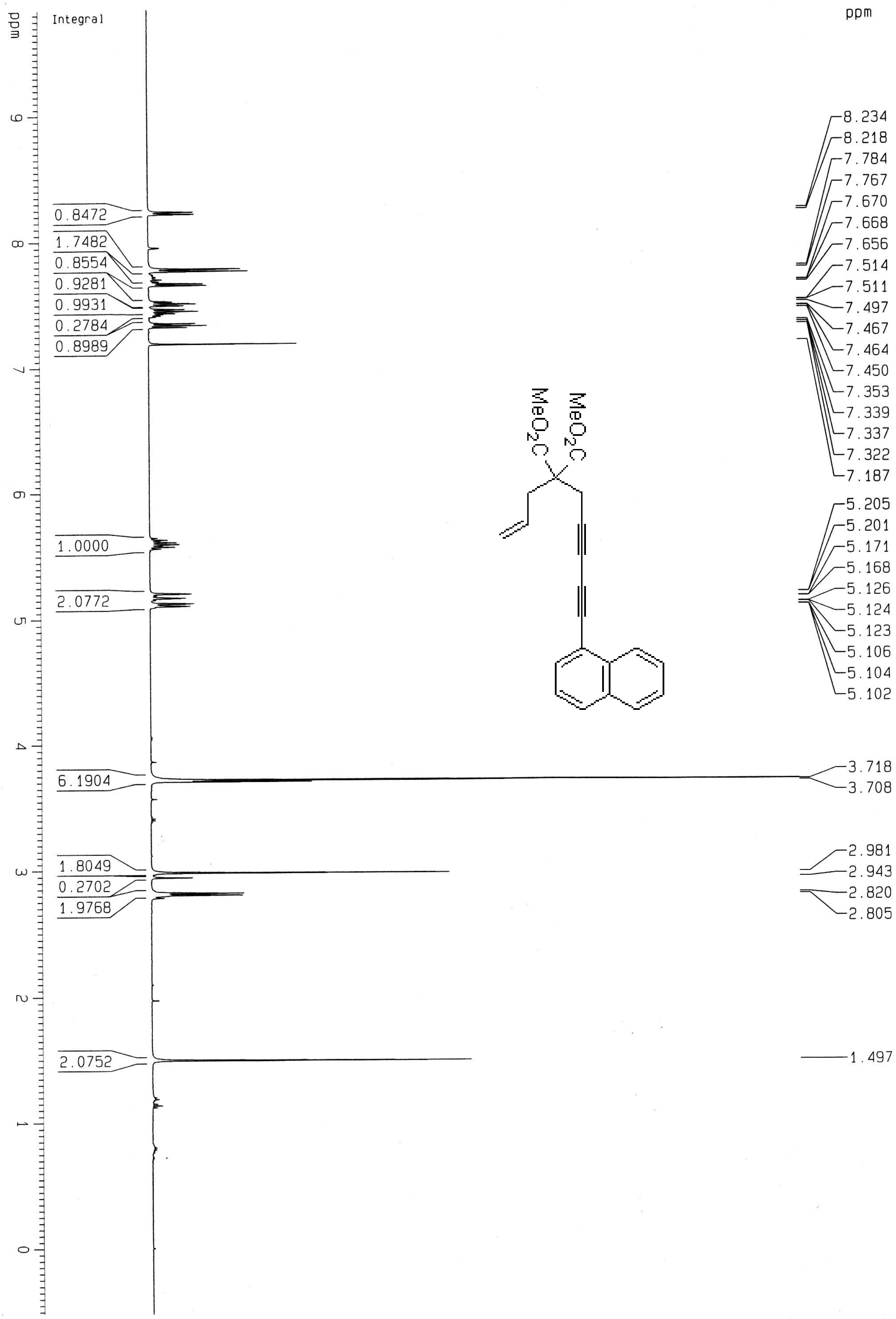
OMe



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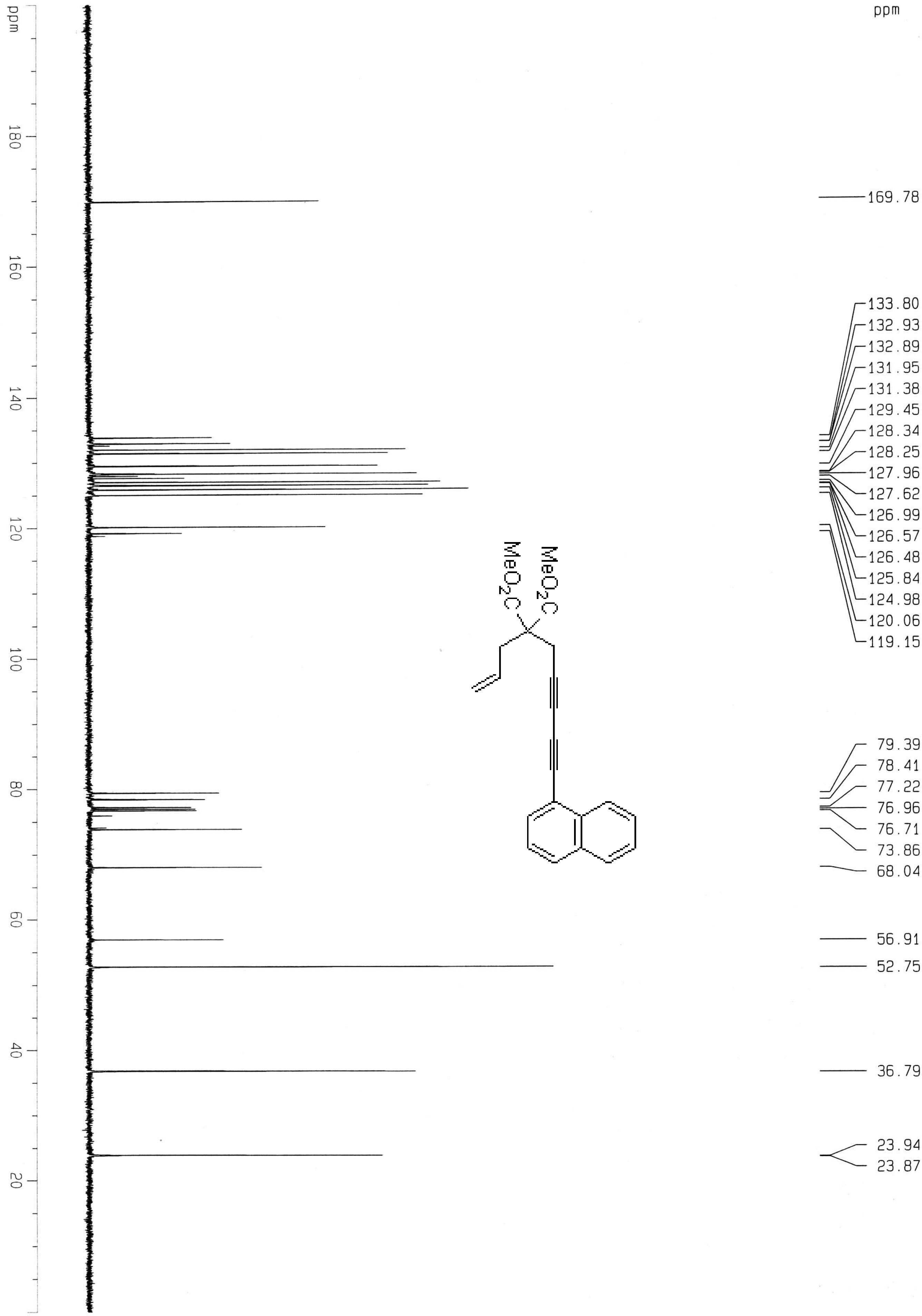
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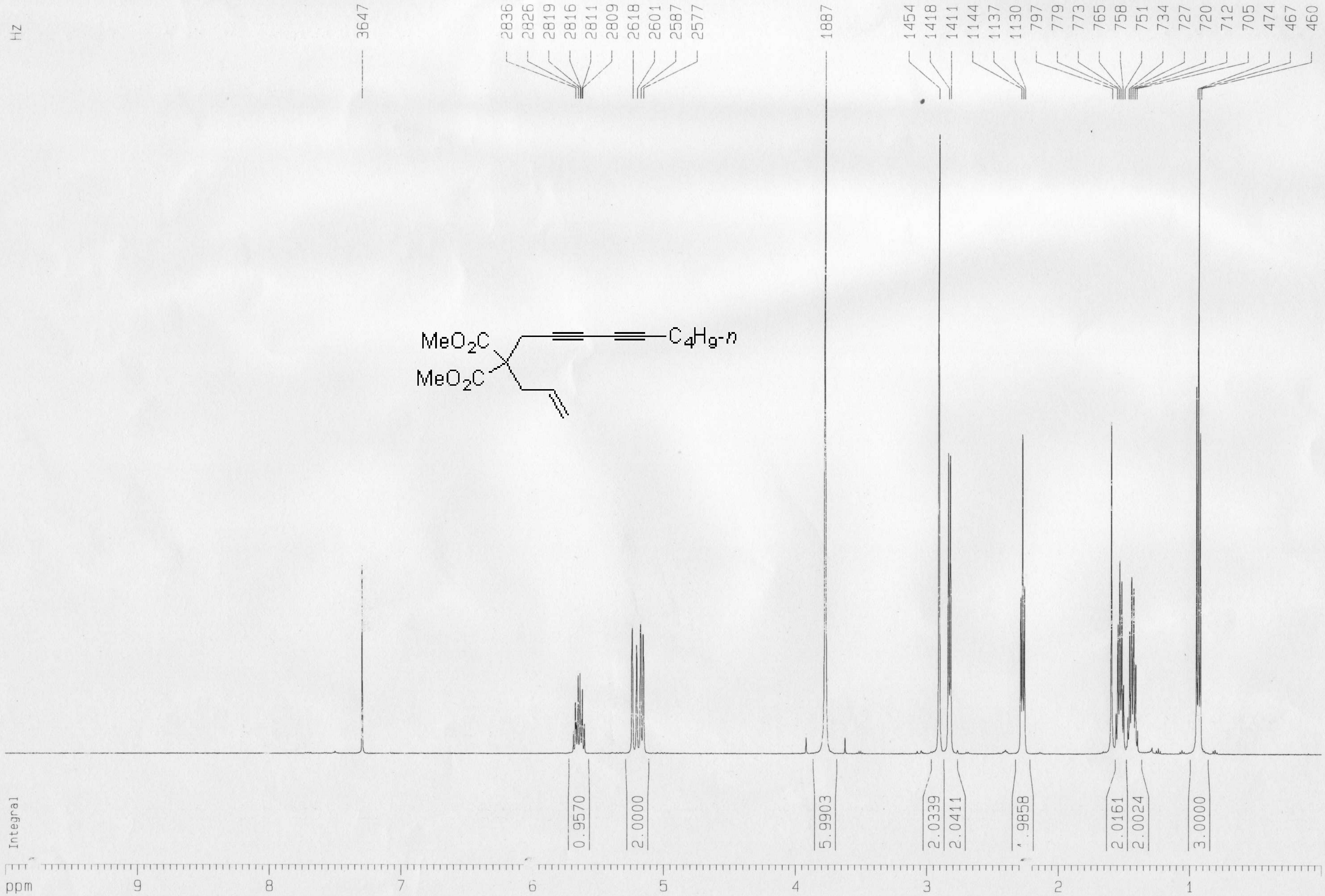

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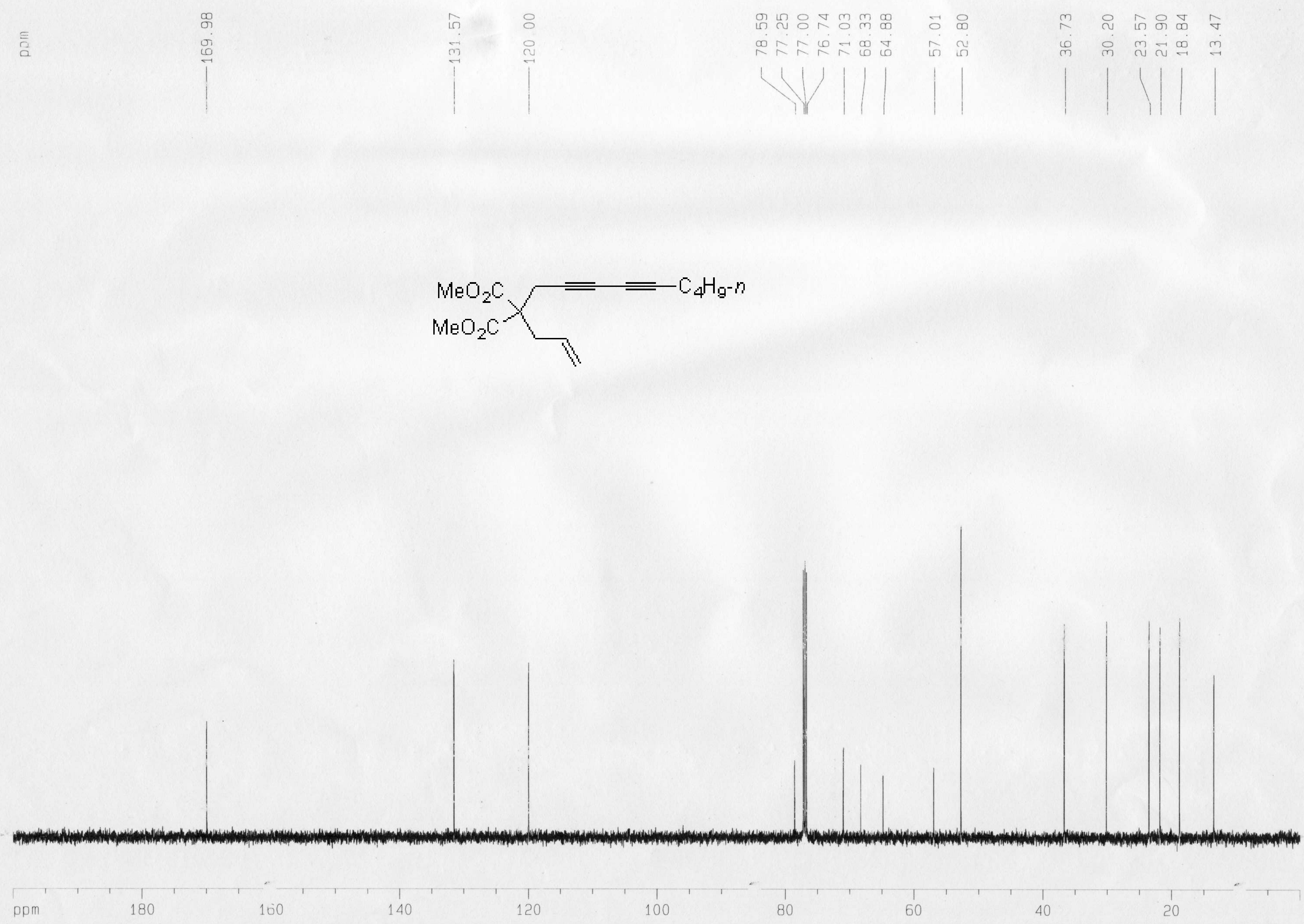
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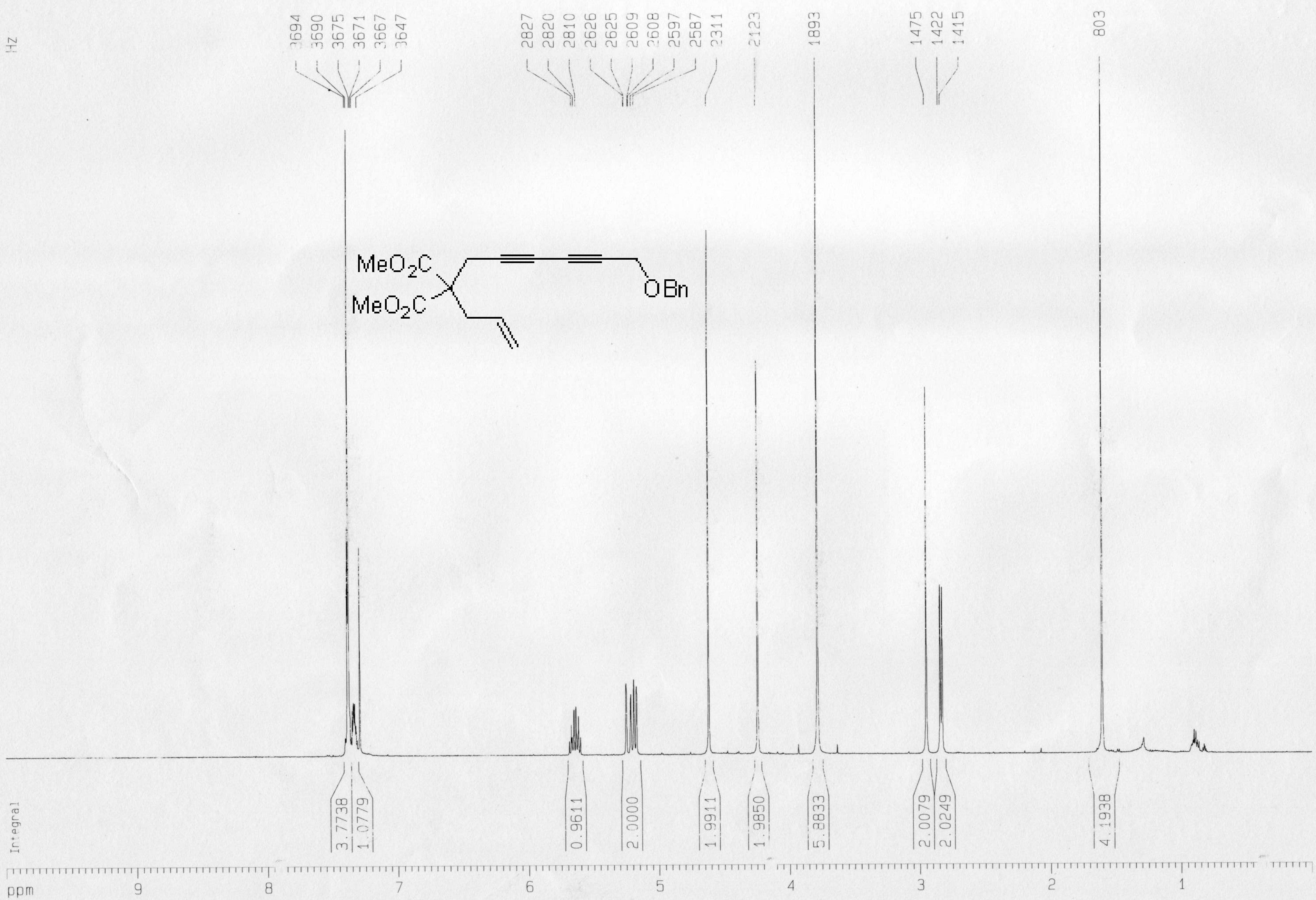

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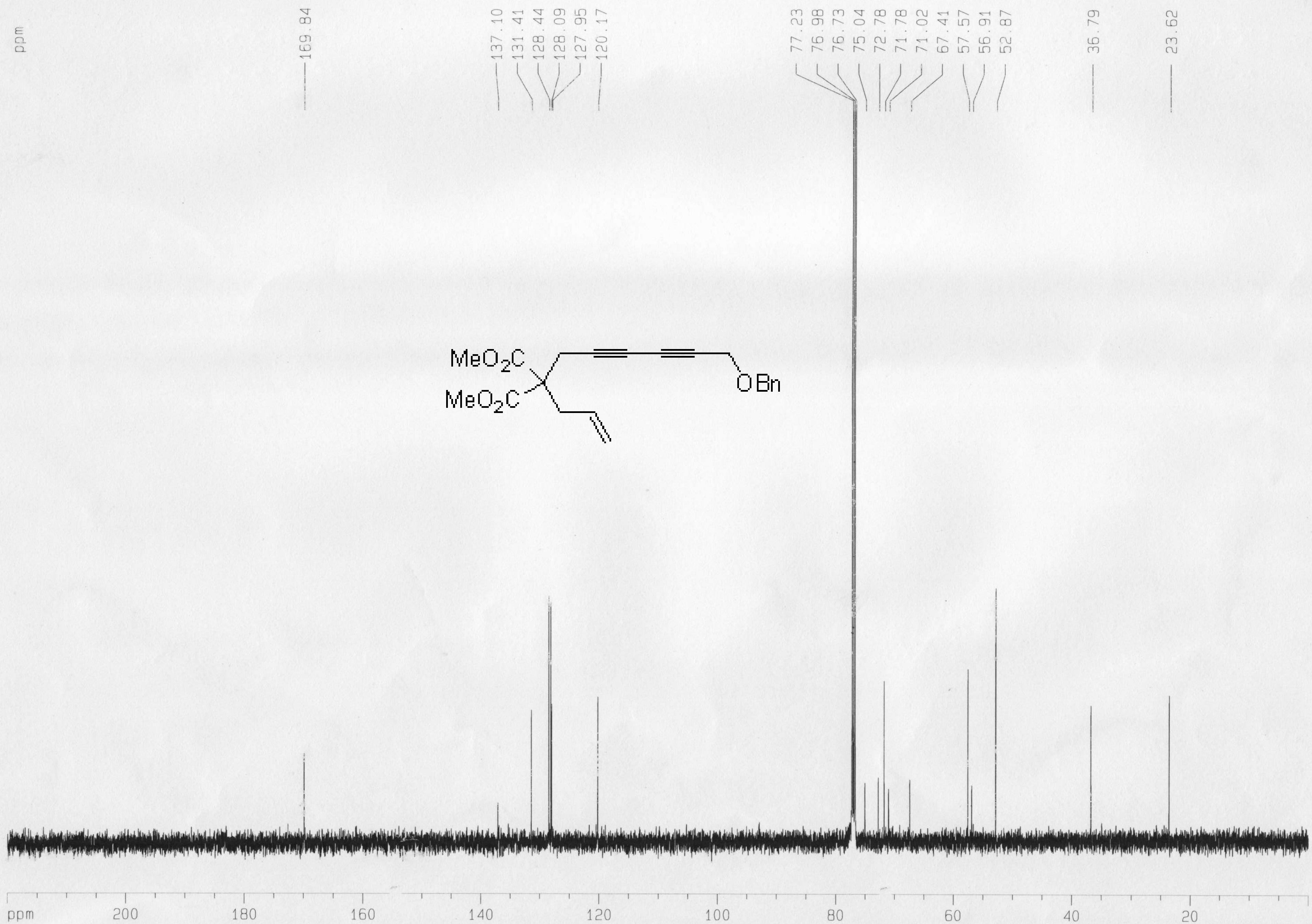

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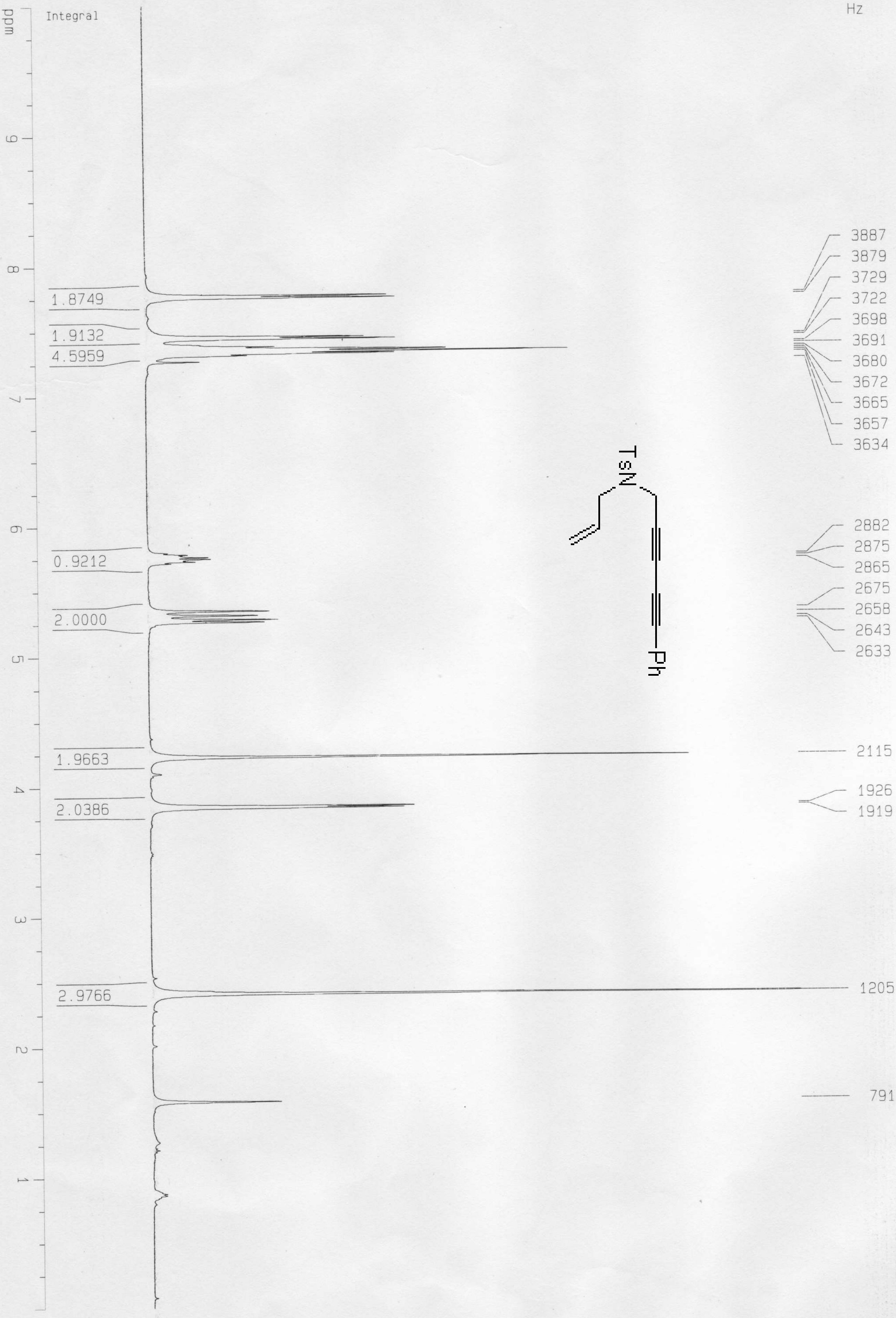

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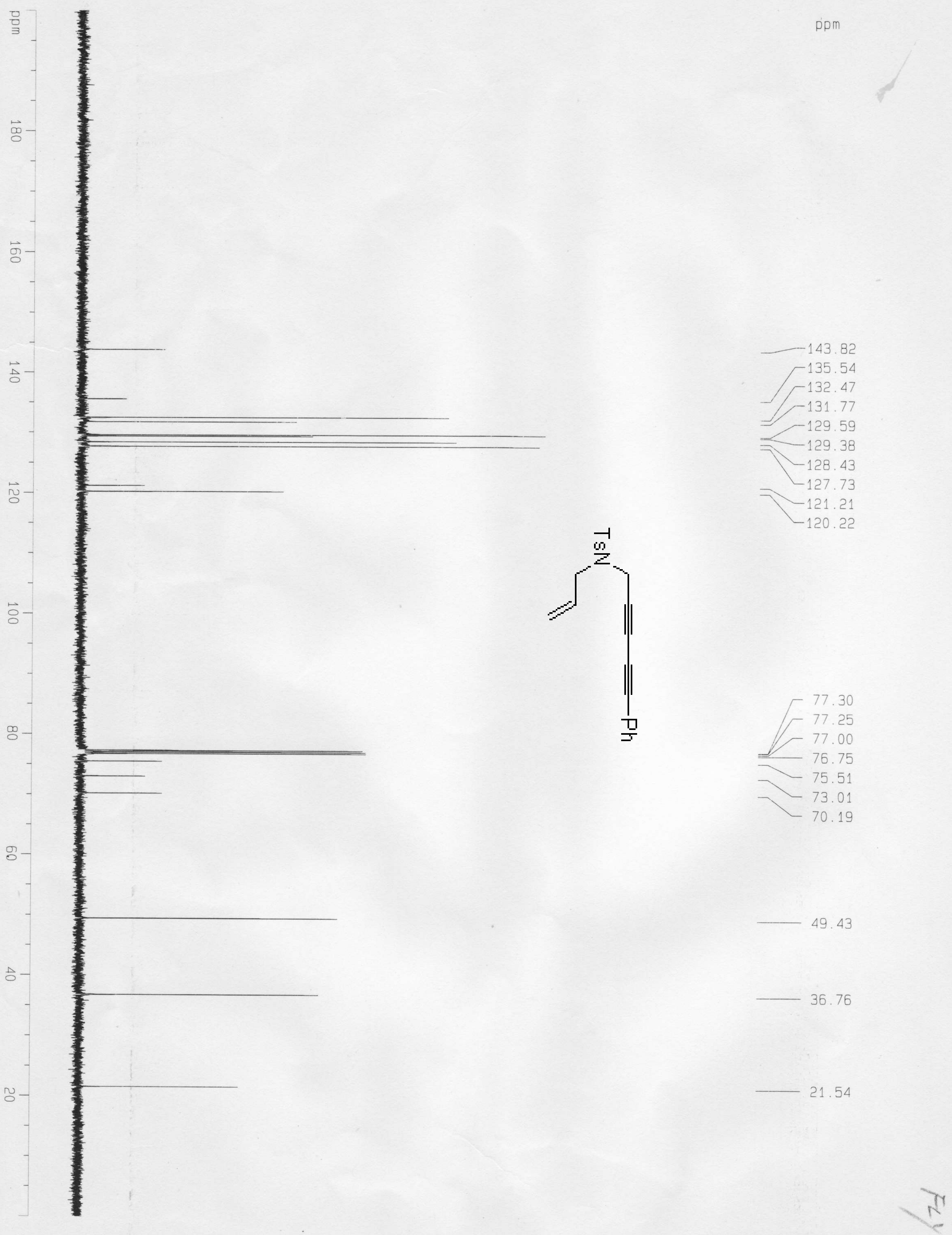
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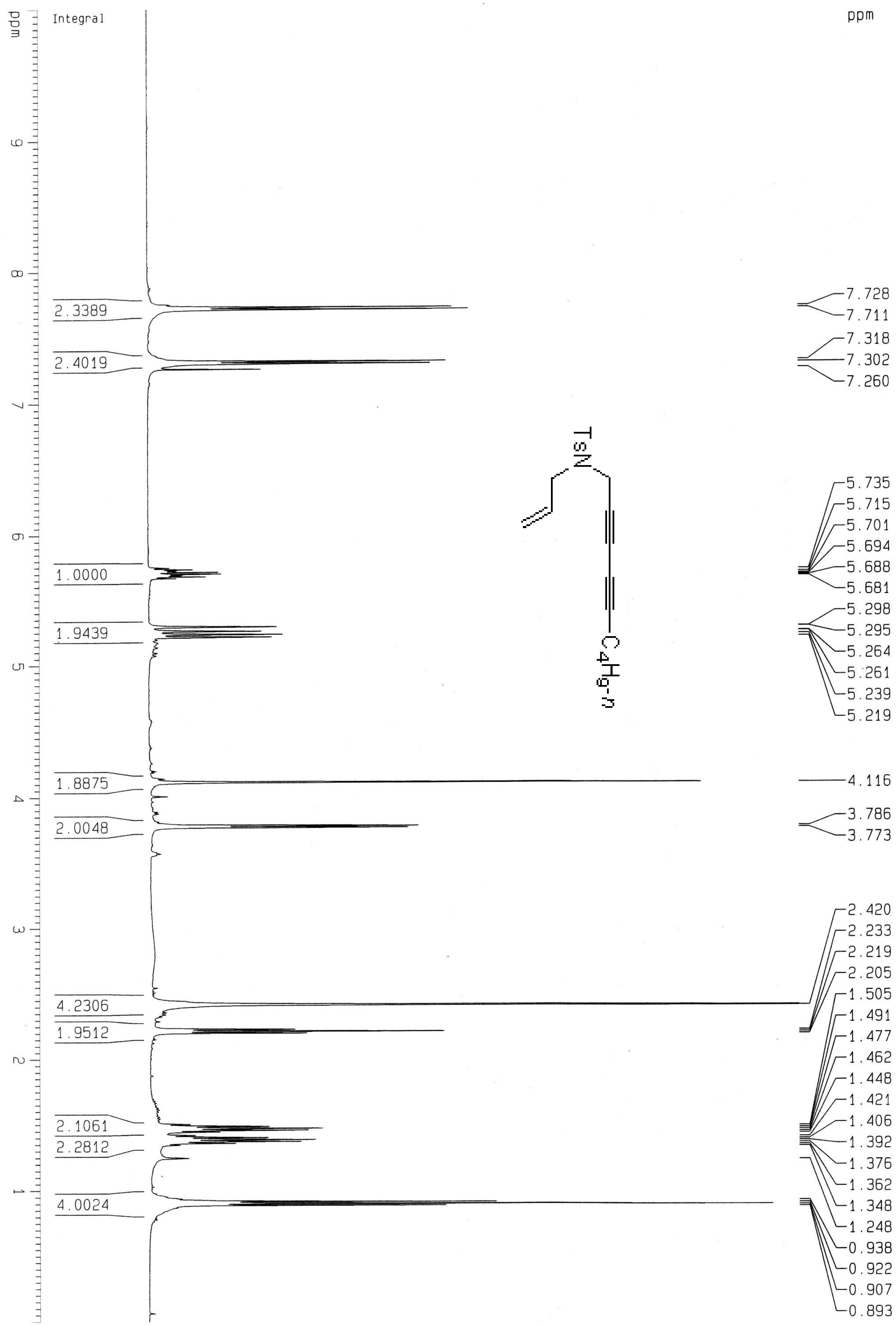
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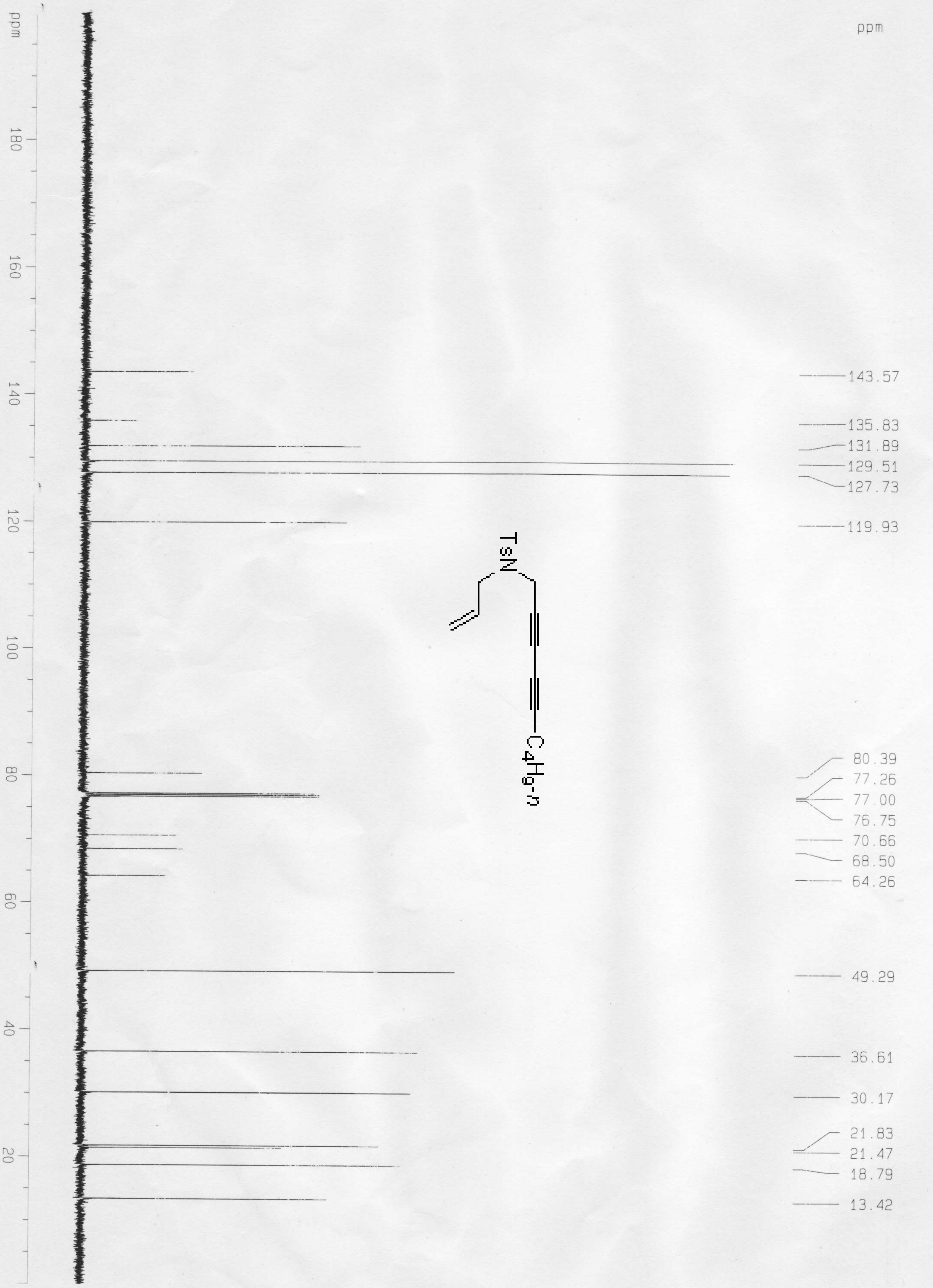

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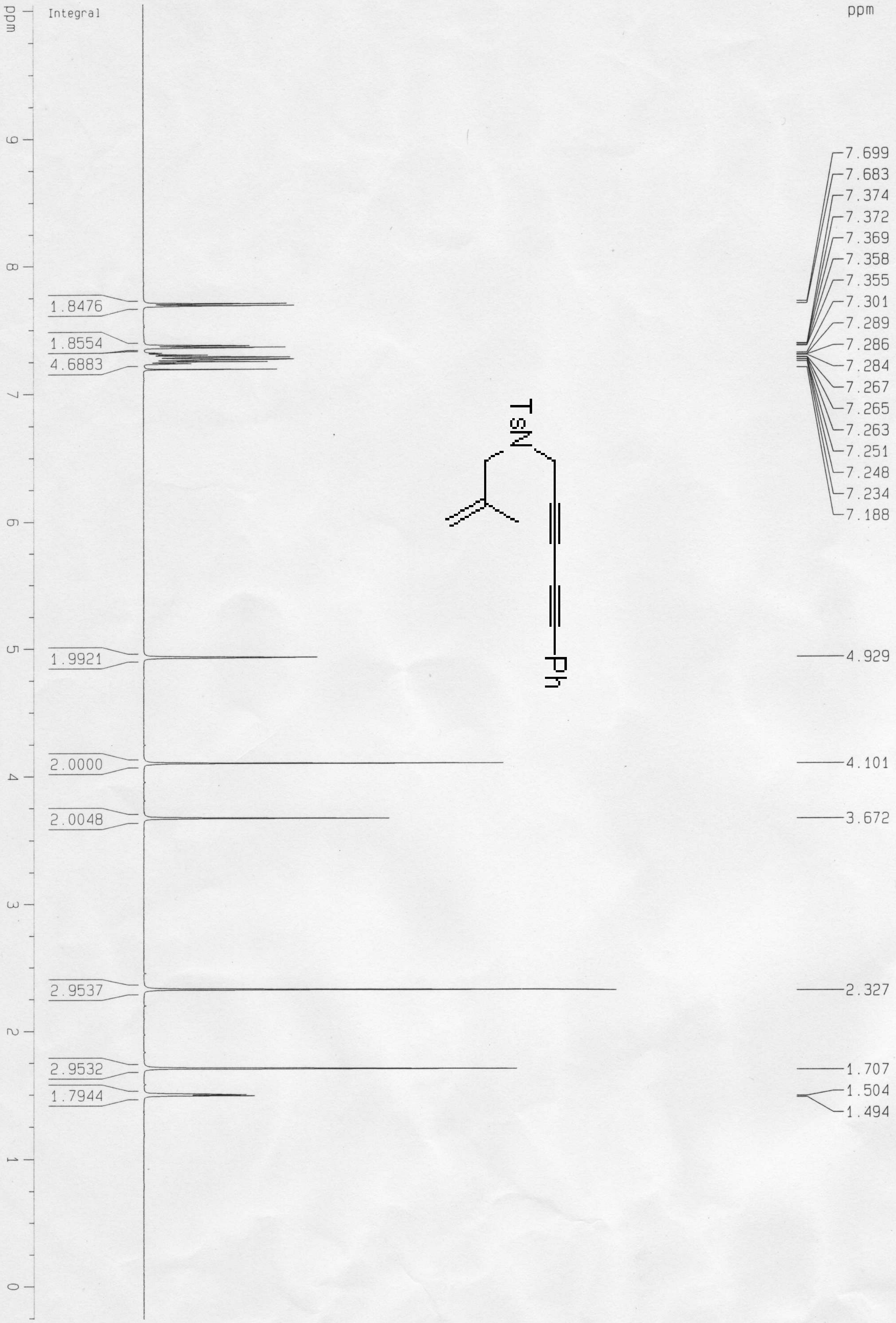

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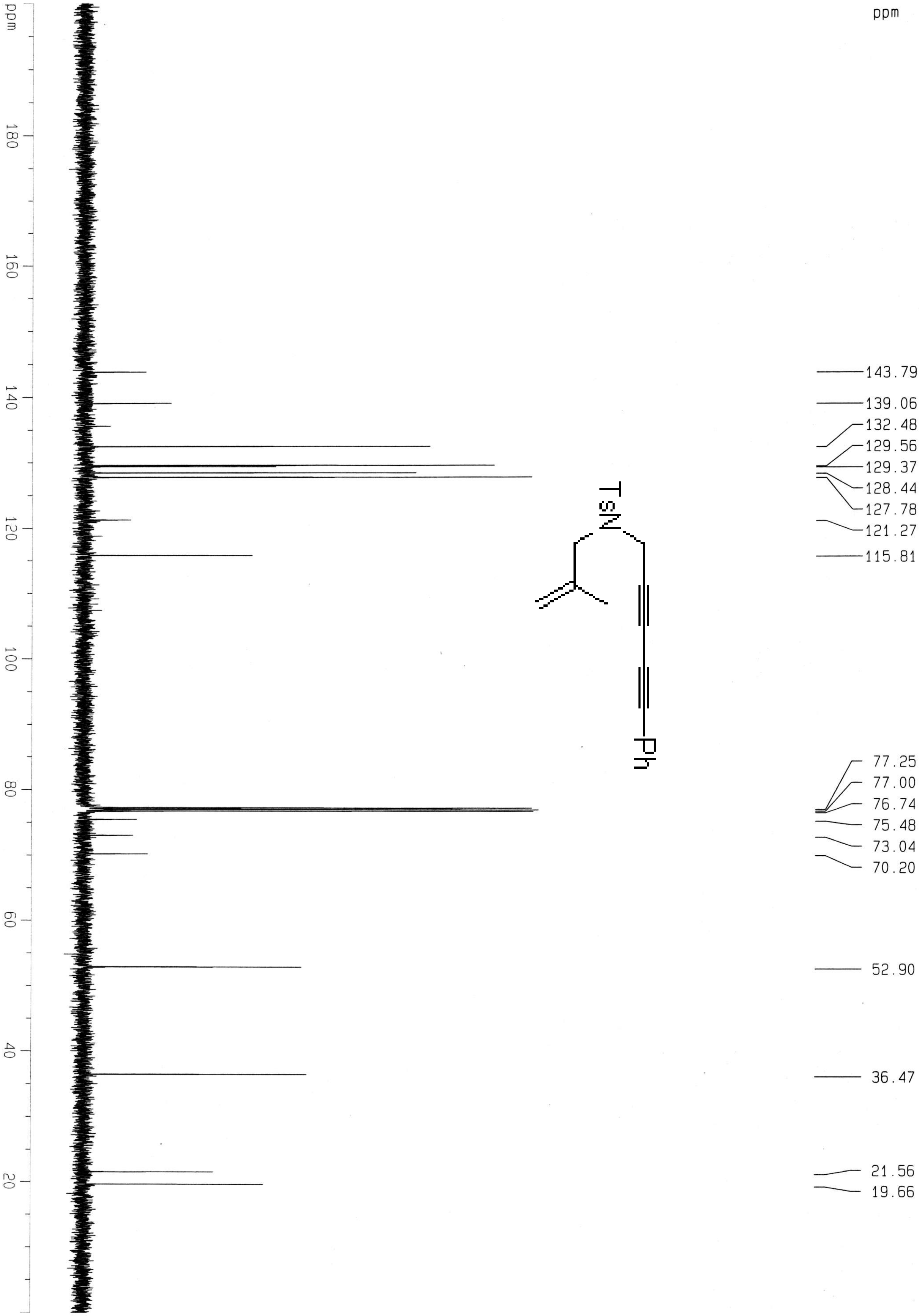
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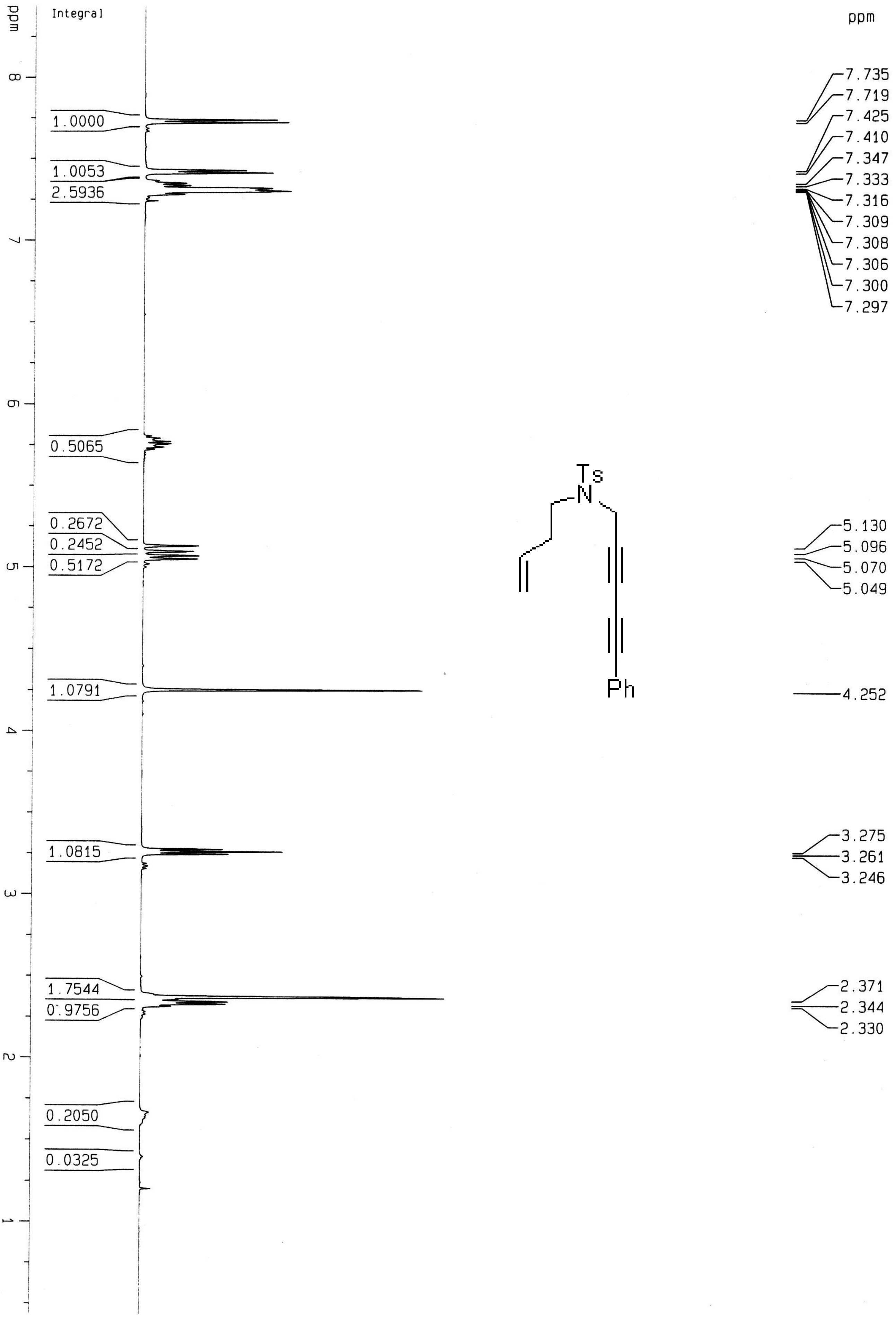
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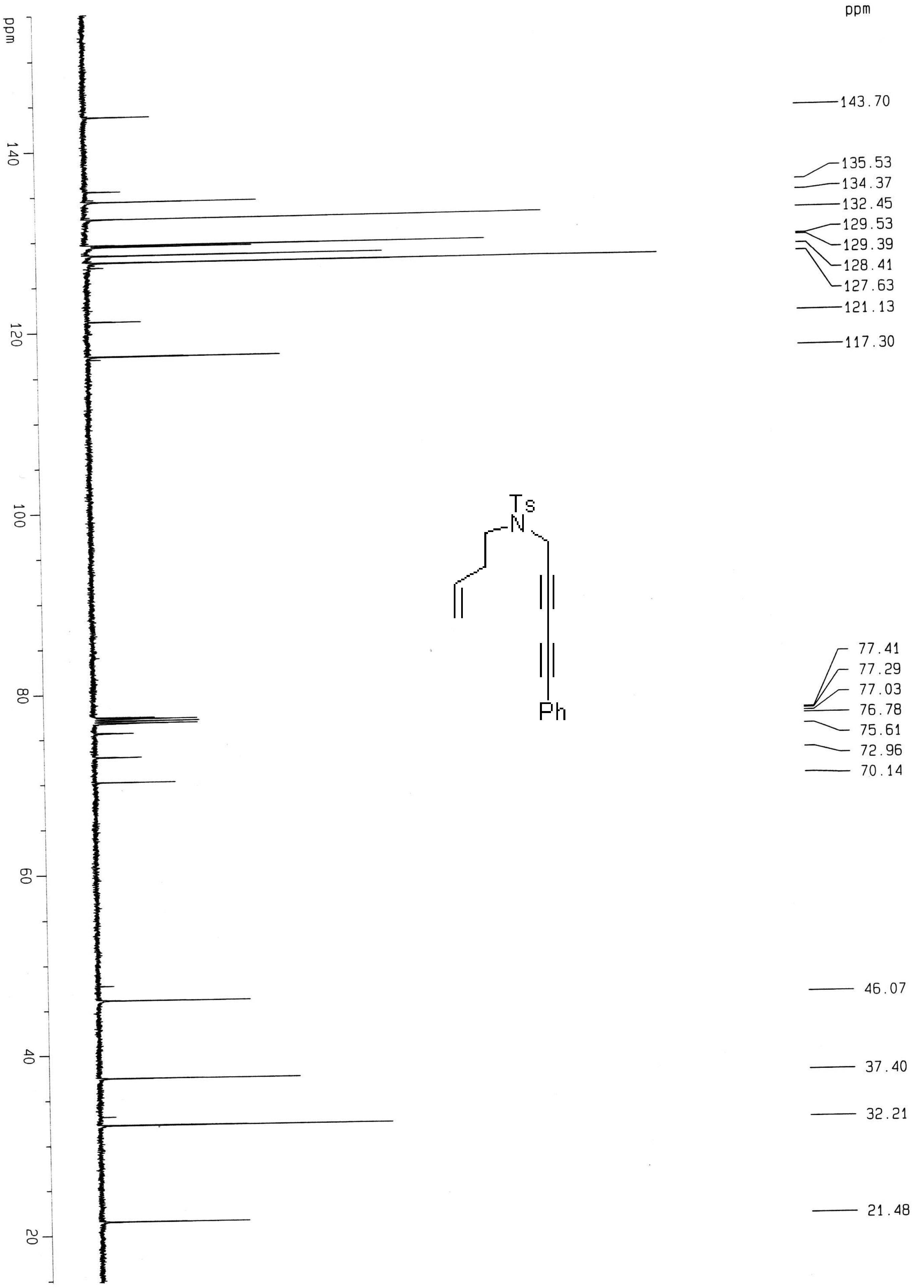
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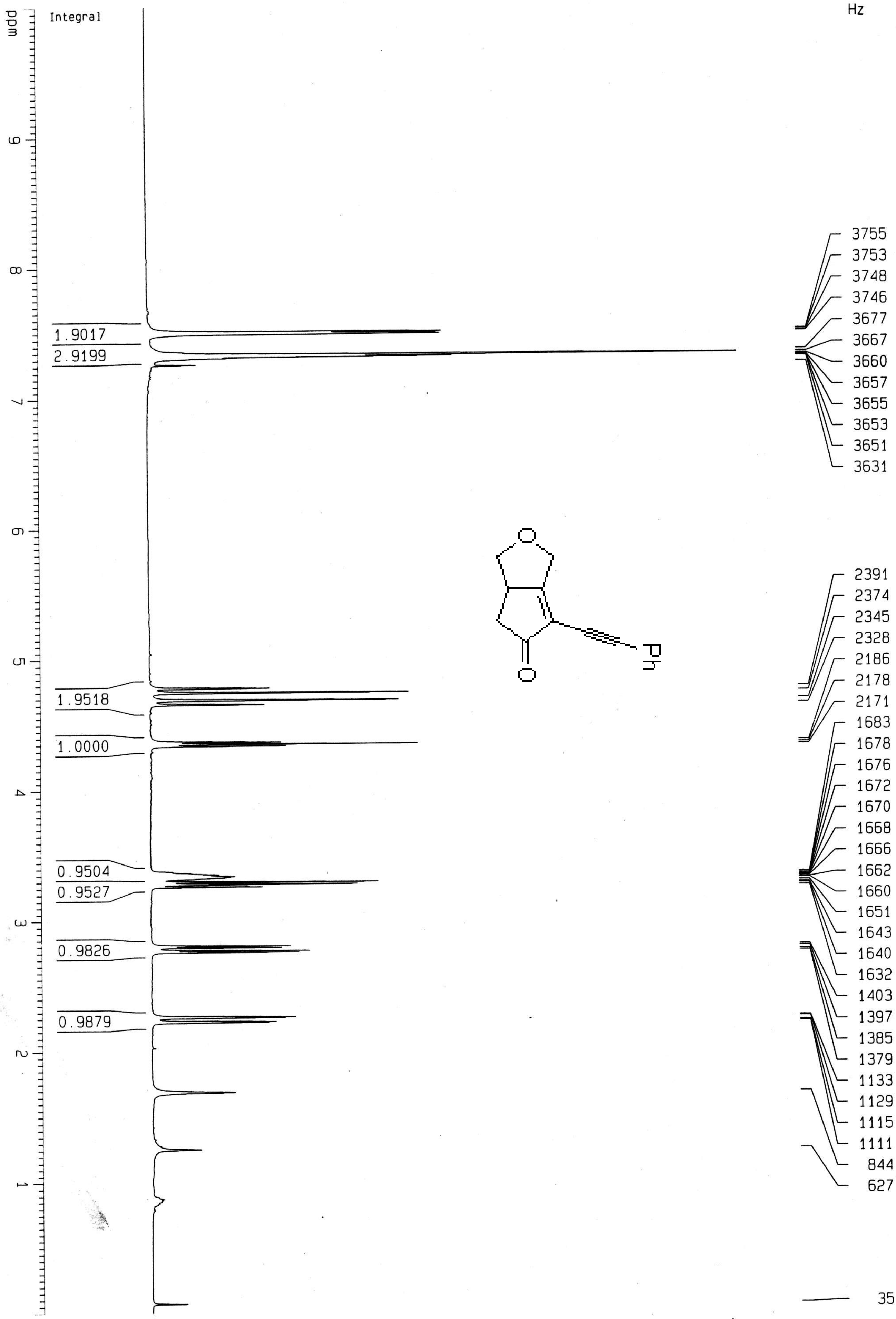
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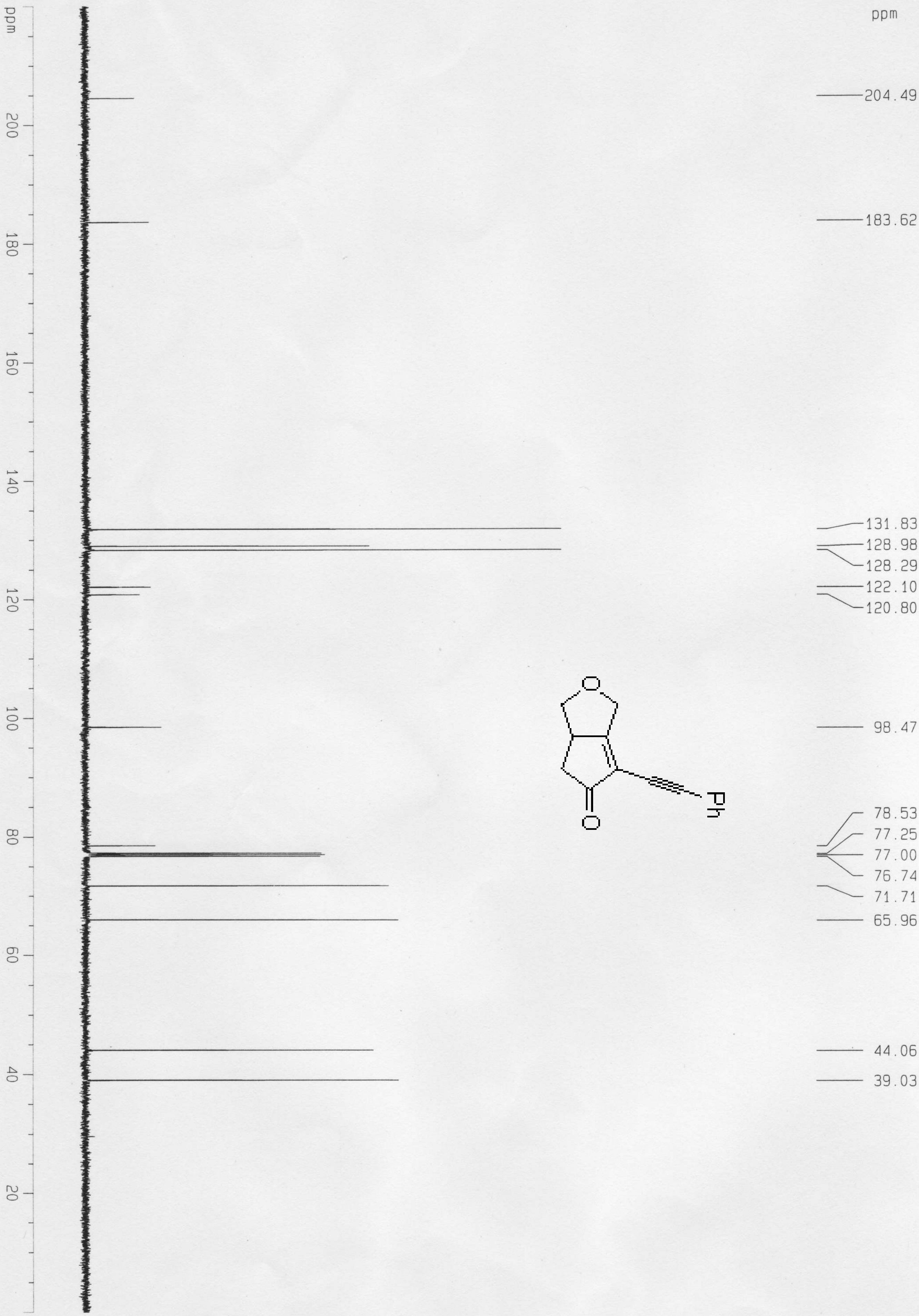
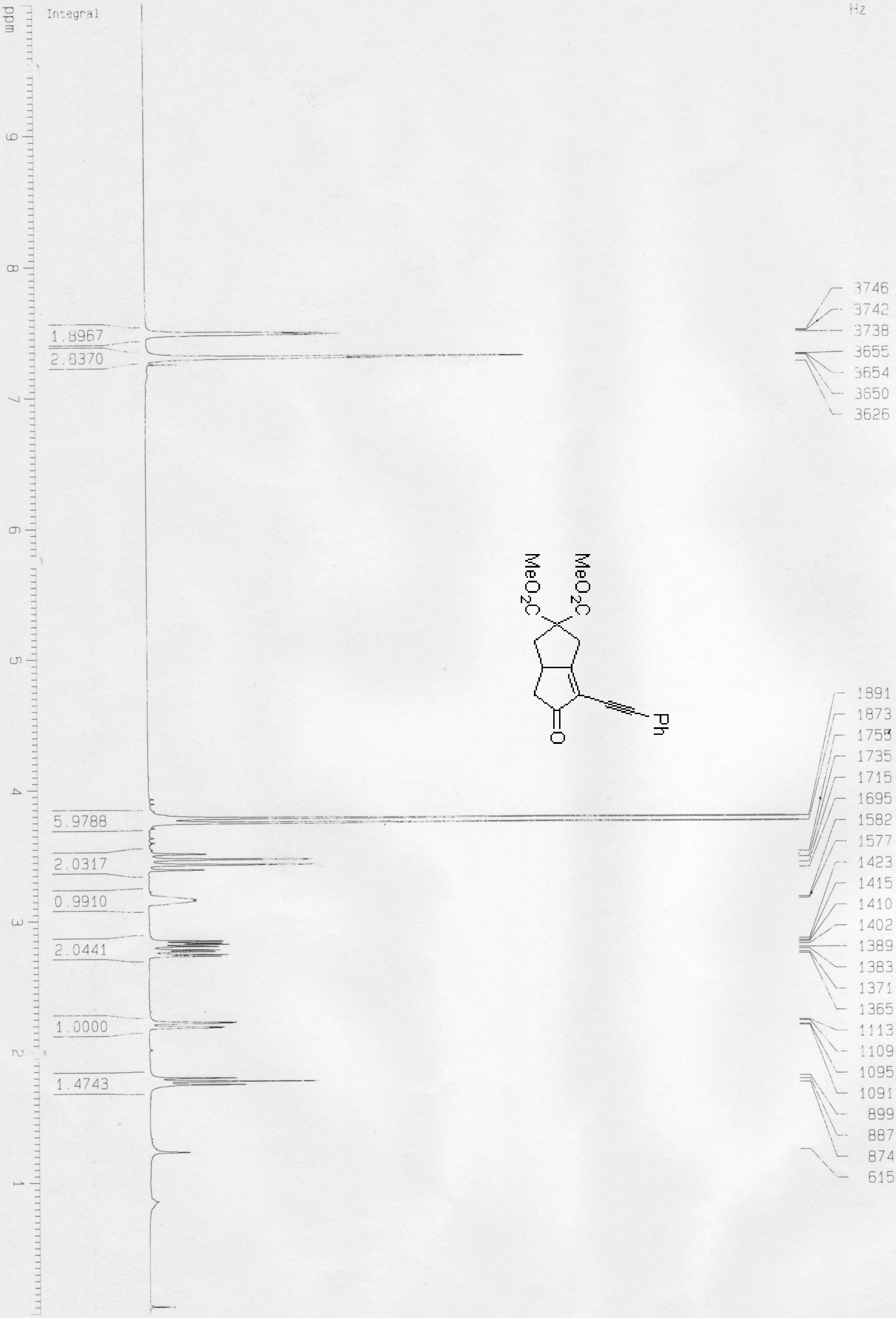
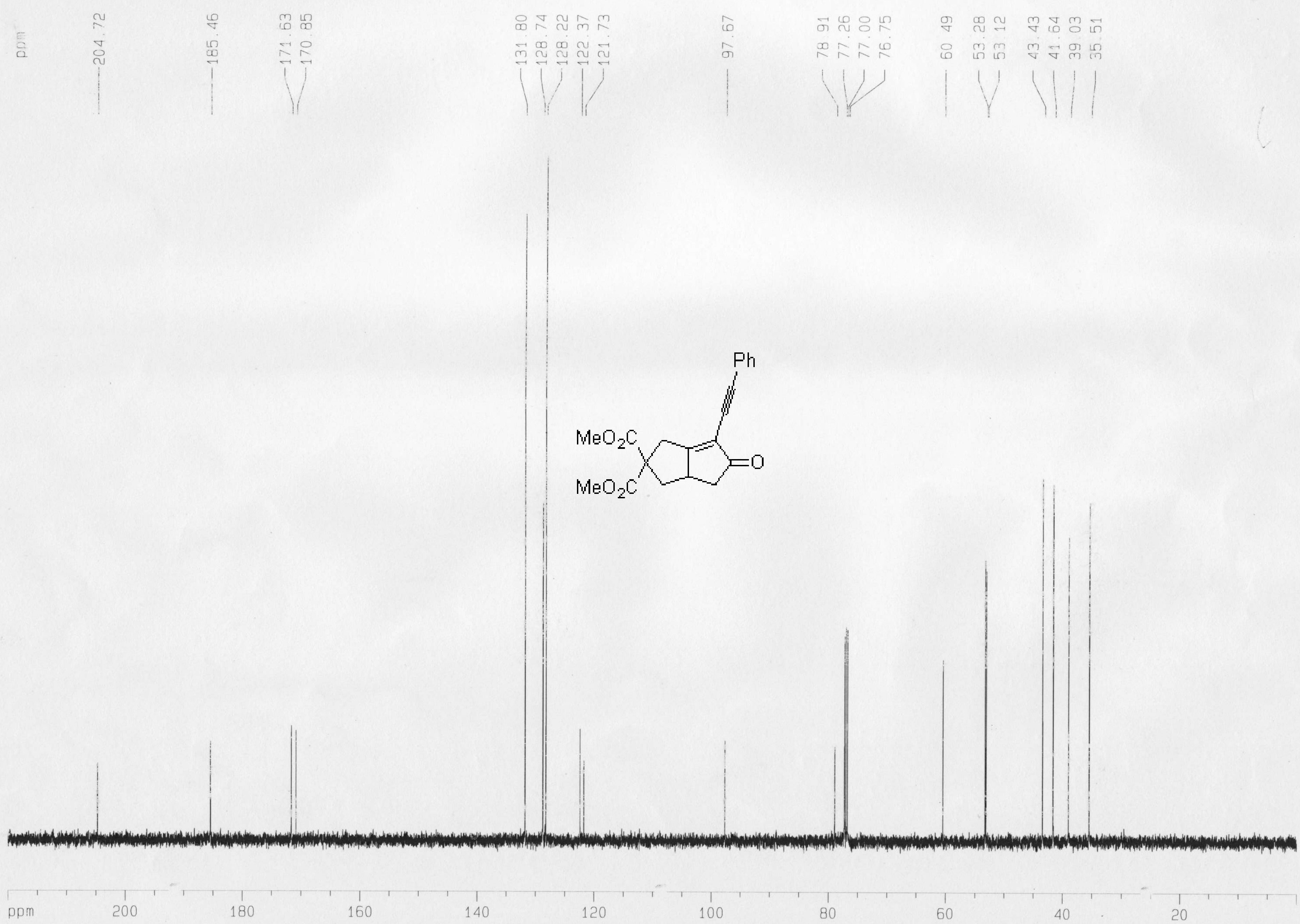
1133
1129
1115
1111
844
627
35
O
Ph
O


ppm
200
180
160
140
120
100
80
60
40
20
ppm
204.49
183.62
131.83
128.98
128.29
122.10
120.80
98.47
78.53
77.25
77.00
76.74
71.71
65.96
44.06
39.03
Ph


ppm
Integral
Hz
9
8
7
6
5
4
3
2
1
1.8967
2.8370
5.9788
2.0317
0.9910
2.0441
1.0000
1.4743
3746
3742
3738
3655
3654
3650
3626
1891
1873
1755
1735
1715
1695
1582
1577
1423
1415
1410
1402
1389
1383
1371
1365
1113
1109
1095
1091
899
887
874
615
MeO2C
MeO2C
Ph
O


ppm
204.72
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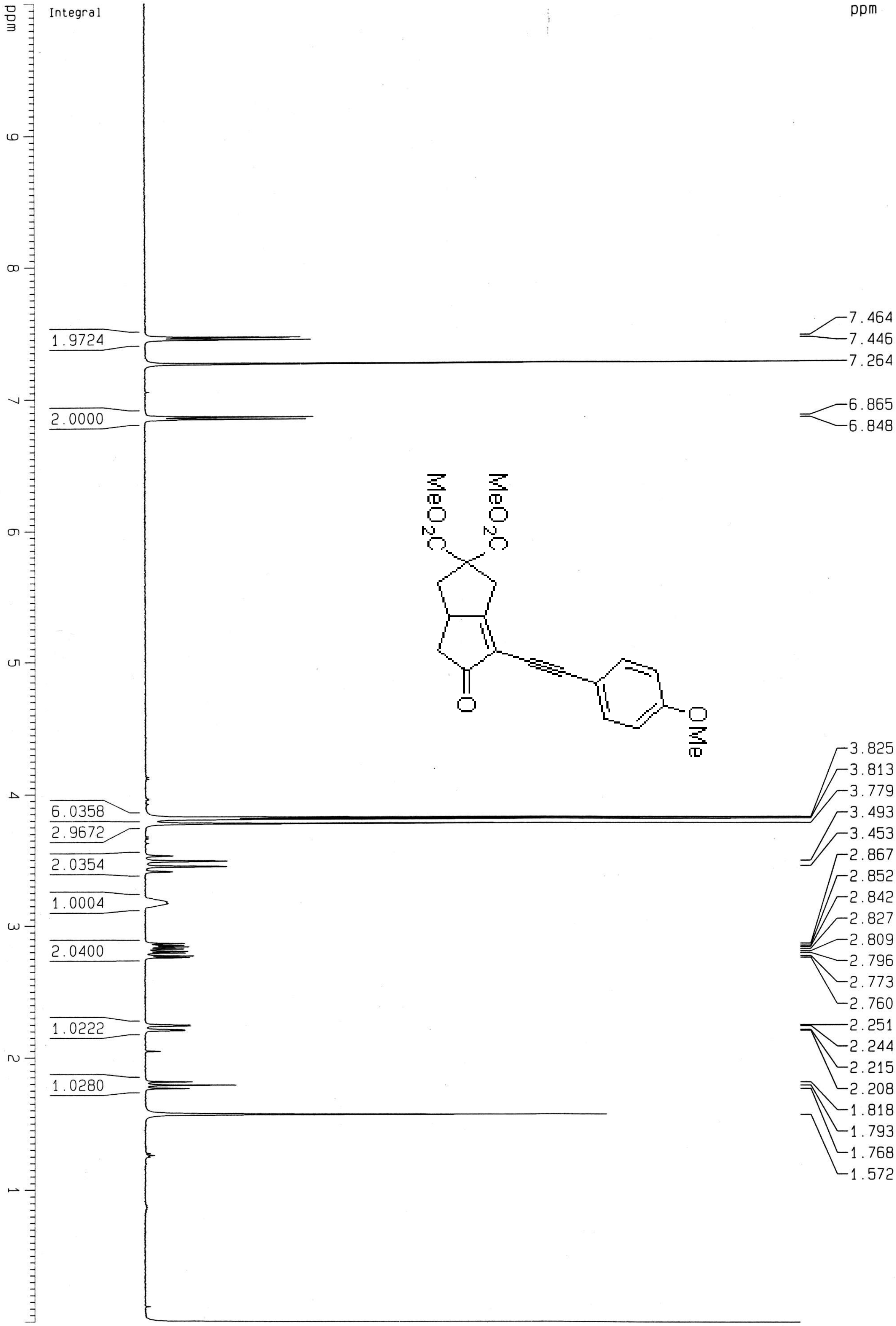
171.63
170.85
131.80
128.74
128.22
122.37
121.73
97.67
78.91
77.26
77.00
76.75
60.49
53.28
53.12
43.43
41.64
39.03
35.51
MeO2C
MeO2C
Ph
O
ppm
200
180
160
140
120
100
80
60
40
20


ppm
Integral
ppm
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2.9672
2.0354
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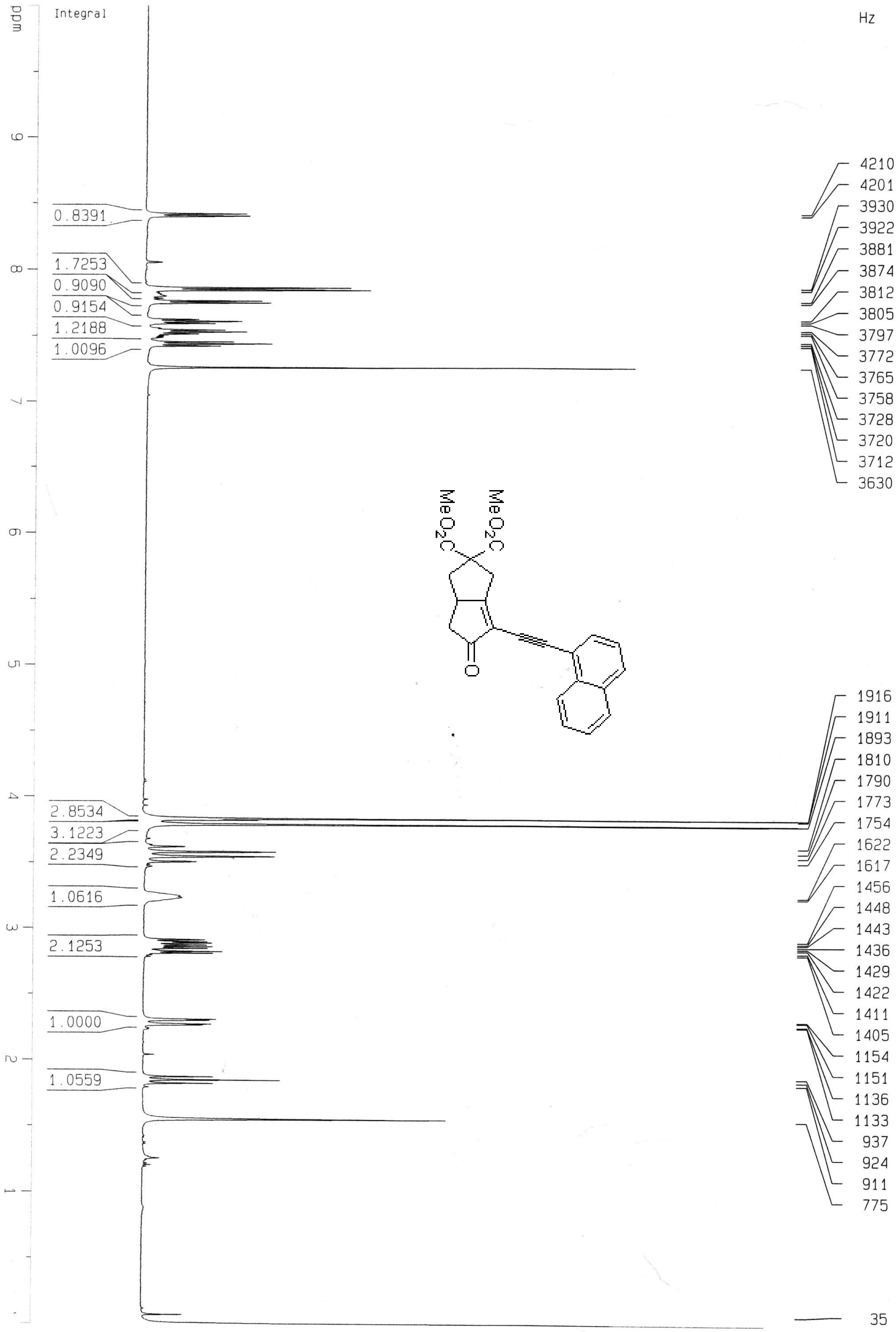
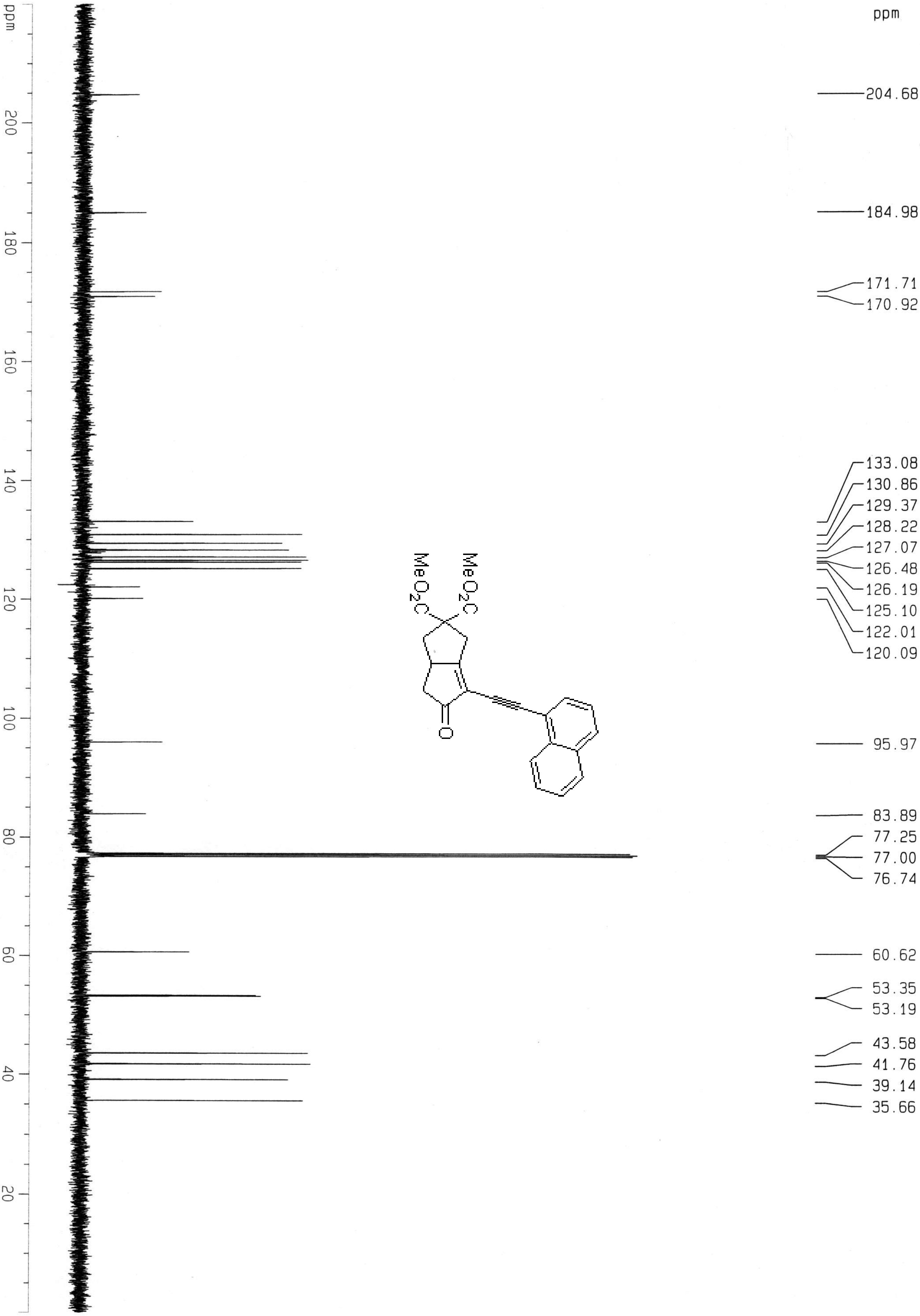
2.0400
1.0222
1.0280
7.464
7.446
7.264
6.865
6.848
3.825
3.813
3.779
3.493
3.453
2.867
2.852
2.842
2.827
2.809
2.796
2.773
2.760
2.251
2.244
2.215
2.208
1.818
1.793
1.768
1.572
MeO2C
MeO2C
O
OMe


ppm
204.93
184.57
171.74
170.95
160.04
133.41
122.06
114.55
113.95
97.91
77.74
77.25
77.00
76.74
60.59
55.28
53.31
53.15
43.39
41.70
39.16
35.57
MeO2C
MeO2C
O
OMe
ppm
200
180
160
140
120
100
80
60
40
20



ppm
Integral
Hz
9
8
7
6
5
4
3
2
1
0.8391
1.7253
0.9090
0.9154
1.2188
1.0096
2.8534
3.1223
2.2349
1.0616
2.1253
1.0000
1.0559
4210
4201
3930
3922
3881
3874
3812
3805
3797
3772
3765
3758
3728
3720
3712
3630
1916
1911
1893
1810
1790
1773
1754
1622
1617
1456
1448
1443
1436
1429
1422
1411
1405
1154
1151
1136
1133
937
924
911
775
35
MeO2C
MeO2C
O


ppm
204.68
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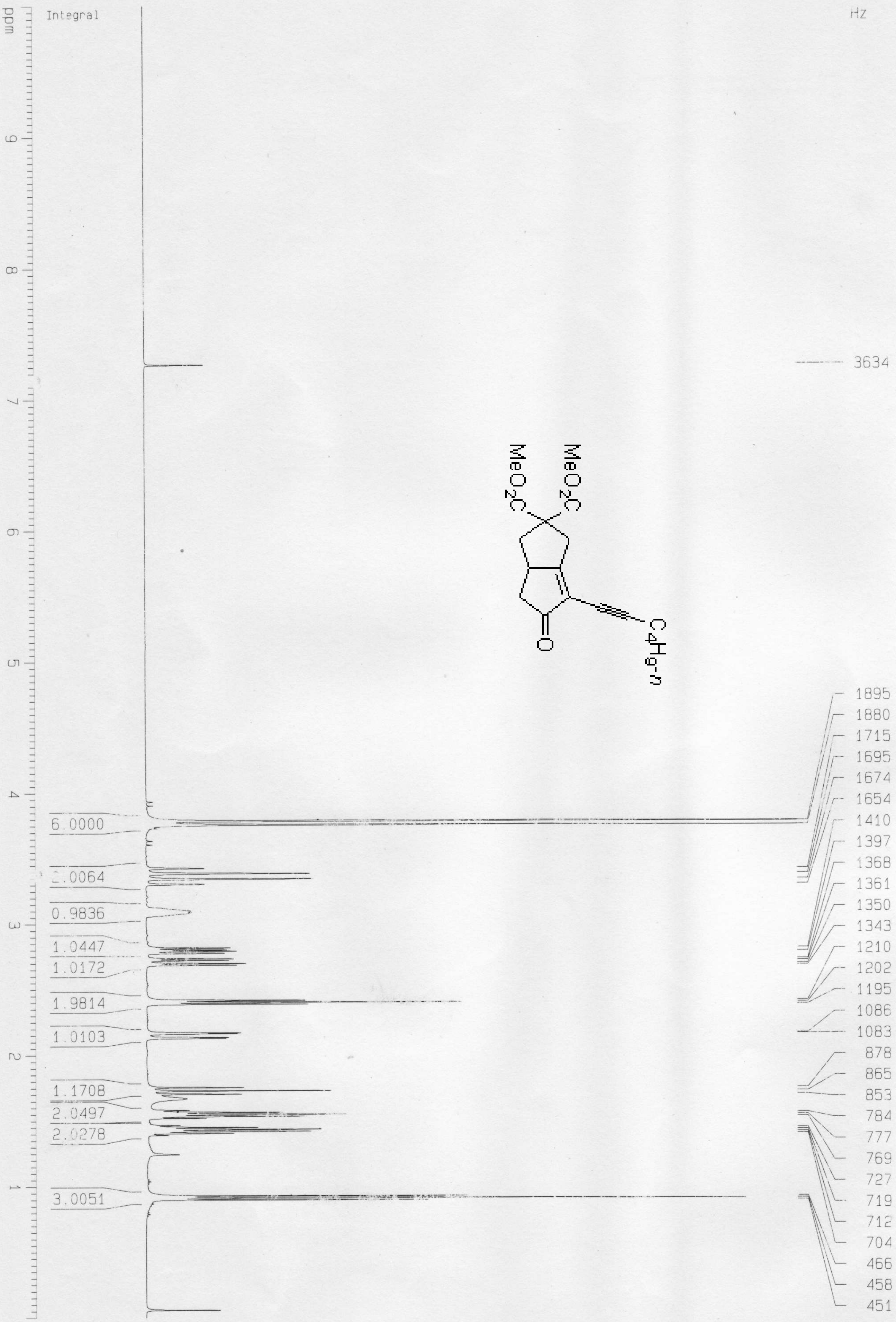
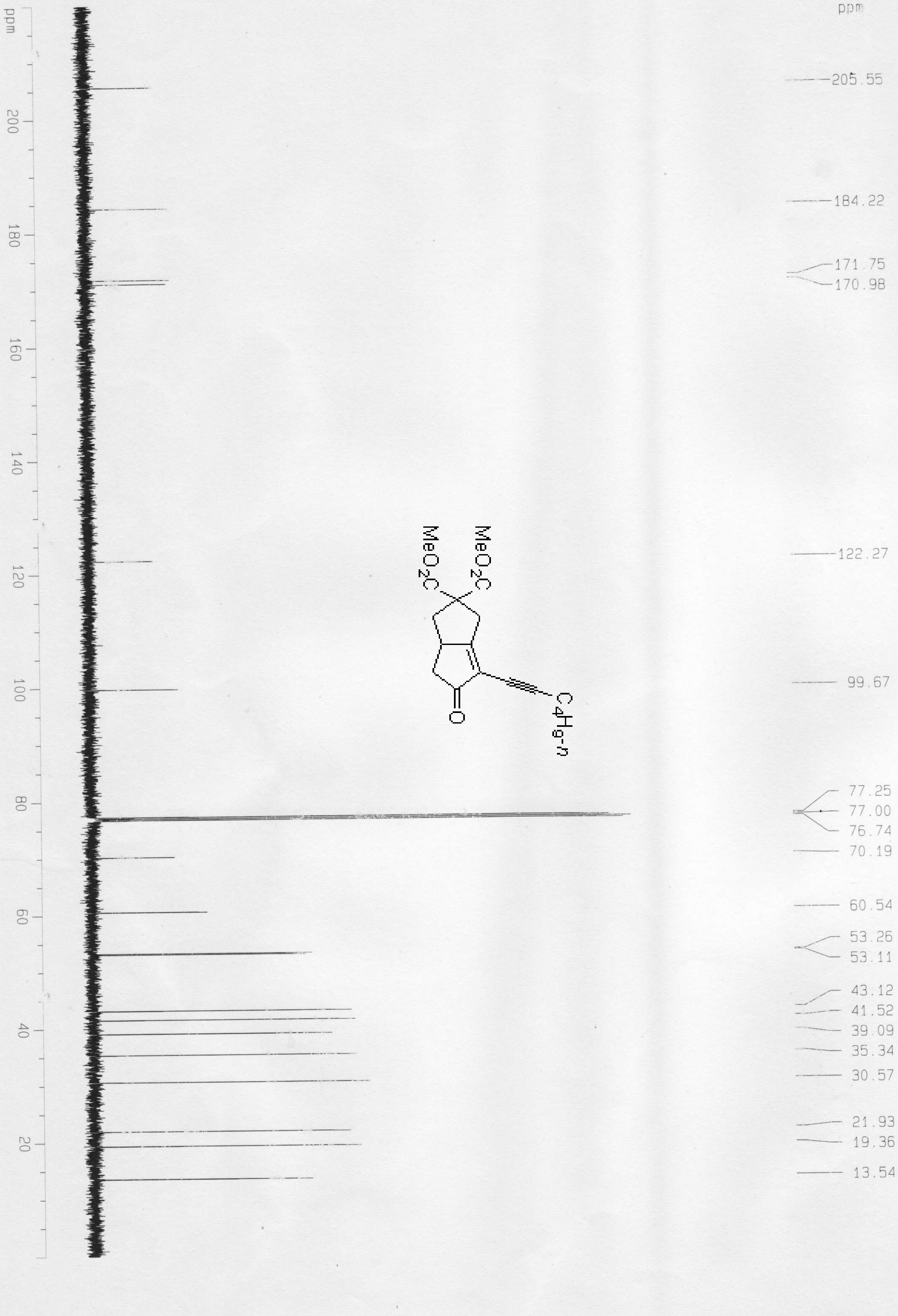
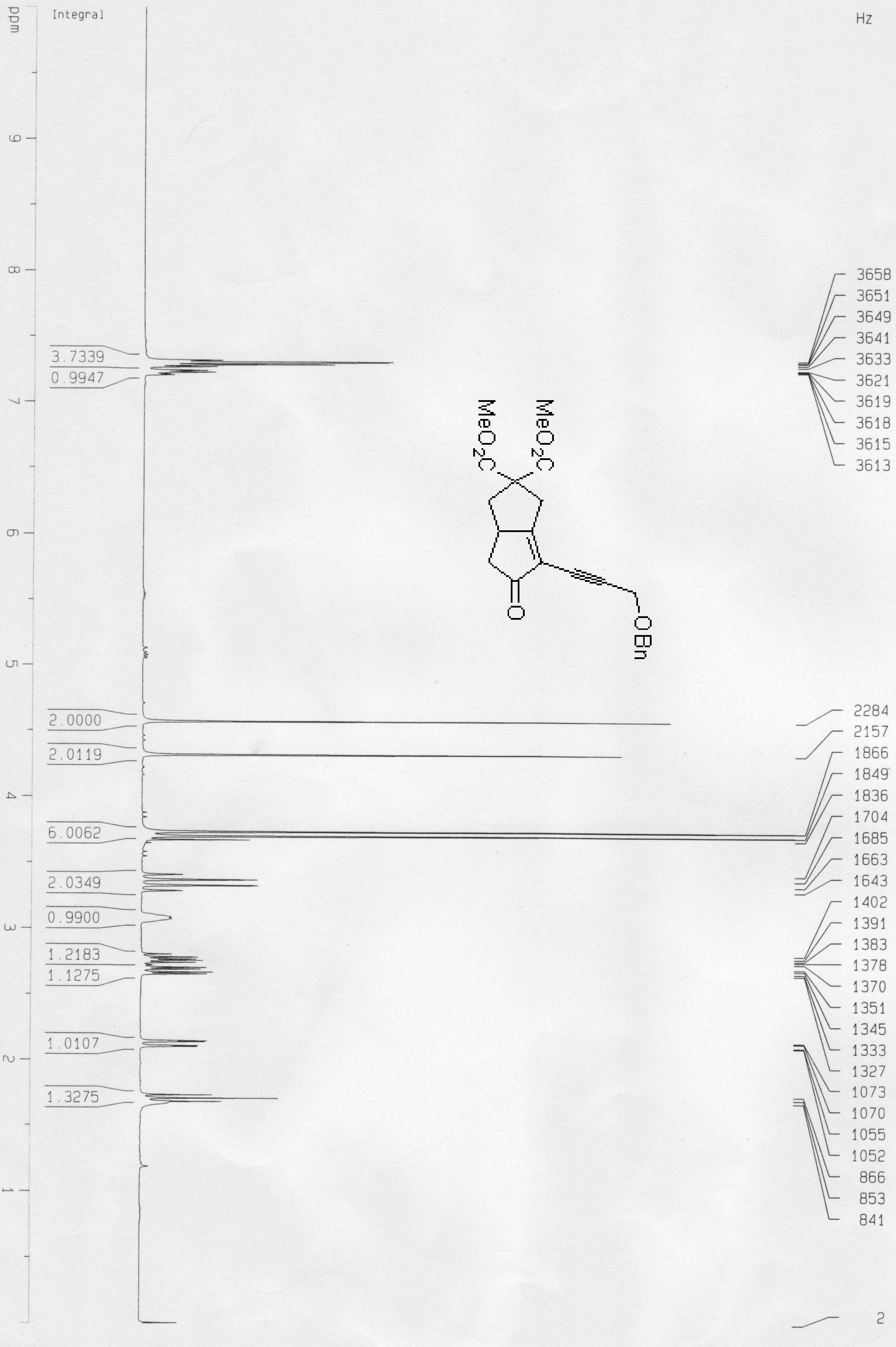
171.71
170.92
133.08
130.86
129.37
128.22
127.07
126.48
126.19
125.10
122.01
120.09
95.97
83.89
77.25
77.00
76.74
60.62
53.35
53.19
43.58
41.76
39.14
35.66
MeO2C
MeO2C
O



ppm
Integral
Hz
3634
6.0000
2.0064
0.9836
1.0447
1.0172
1.9814
1.0103
1.1708
2.0497
2.0278
3.0051
1895
1880
1715
1695
1674
1654
1410
1397
1368
1361
1350
1343
1210
1202
1195
1086
1083
878
865
853
784
777
769
727
719
712
704
466
458
451
MeO2C
MeO2C
C4H9-n
O

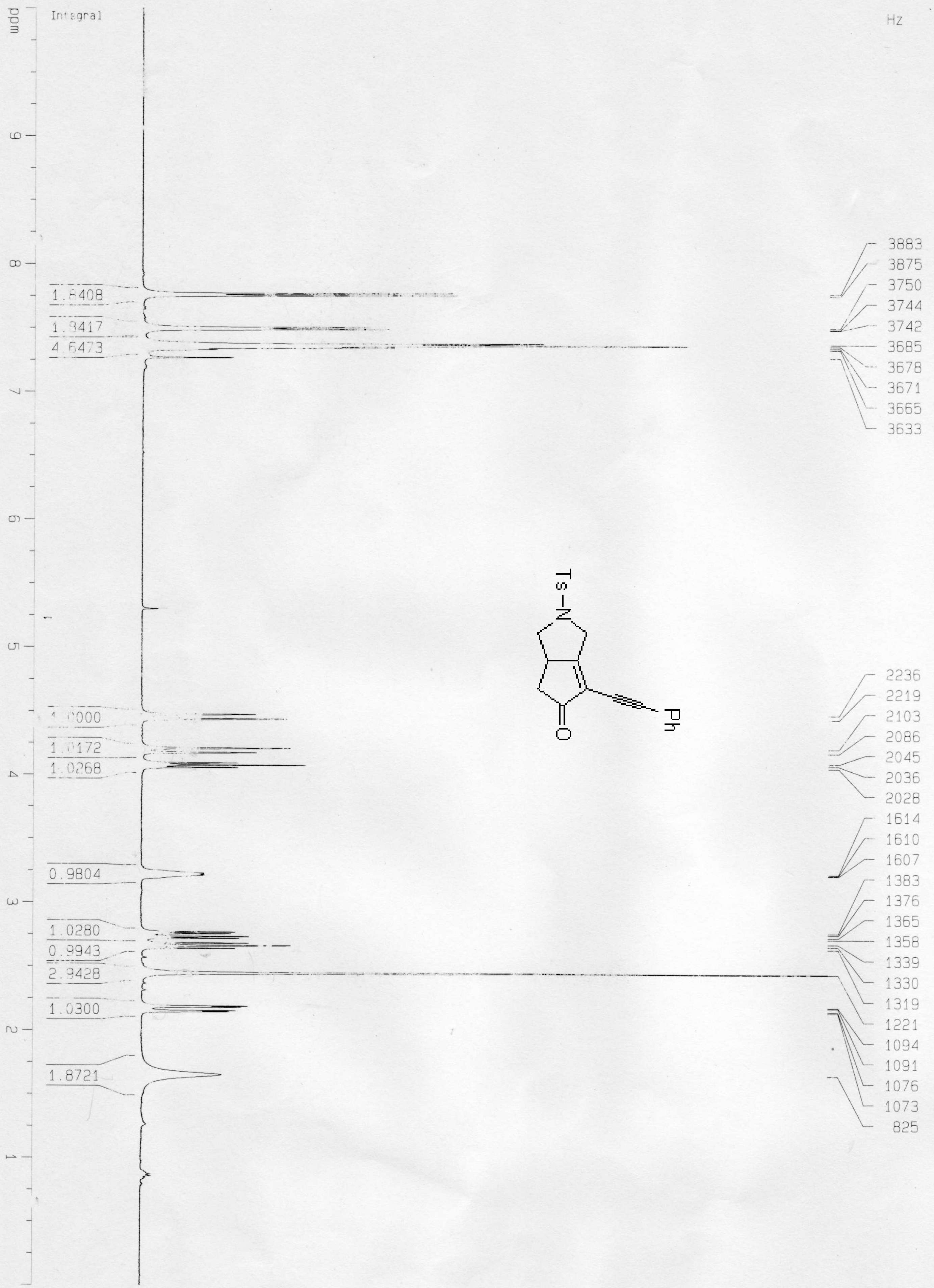


ppm
200
180
160
140
120
100
80
60
40
20
ppm
205.55
184.22
171.75
170.98
122.27
99.67
77.25
77.00
76.74
70.19
60.54
53.26
53.11
43.12
41.52
39.09
35.34
30.57
21.93
19.36
13.54
MeO2C
MeO2C
O
C4H9-n



ppm
Integral
Hz
9
8
7
6
5
4
3
2
1
3.7339
0.9947
2.0000
2.0119
6.0062
2.0349
0.9900
1.2183
1.1275
1.0107
1.3275
3658
3651
3649
3641
3633
3621
3619
3618
3615
3613
2284
2157
1866
1849
1836
1704
1685
1663
1643
1402
1391
1383
1378
1370
1351
1345
1333
1327
1073
1070
1055
1052
866
853
841
2
MeO2C
MeO2C
O
OBn


ppm
200
180
160
140
120
100
80
60
40
20
MeO2C
MeO2C
O
OBn
ppm
204.68
186.10
171.60
170.78
137.29
128.37
128.10
127.81
121.23
93.87
77.25
77.00
76.74
76.24
71.62
60.46
57.79
53.27
53.11
43.39
41.53
38.96
35.43



ppm
Integral
Hz
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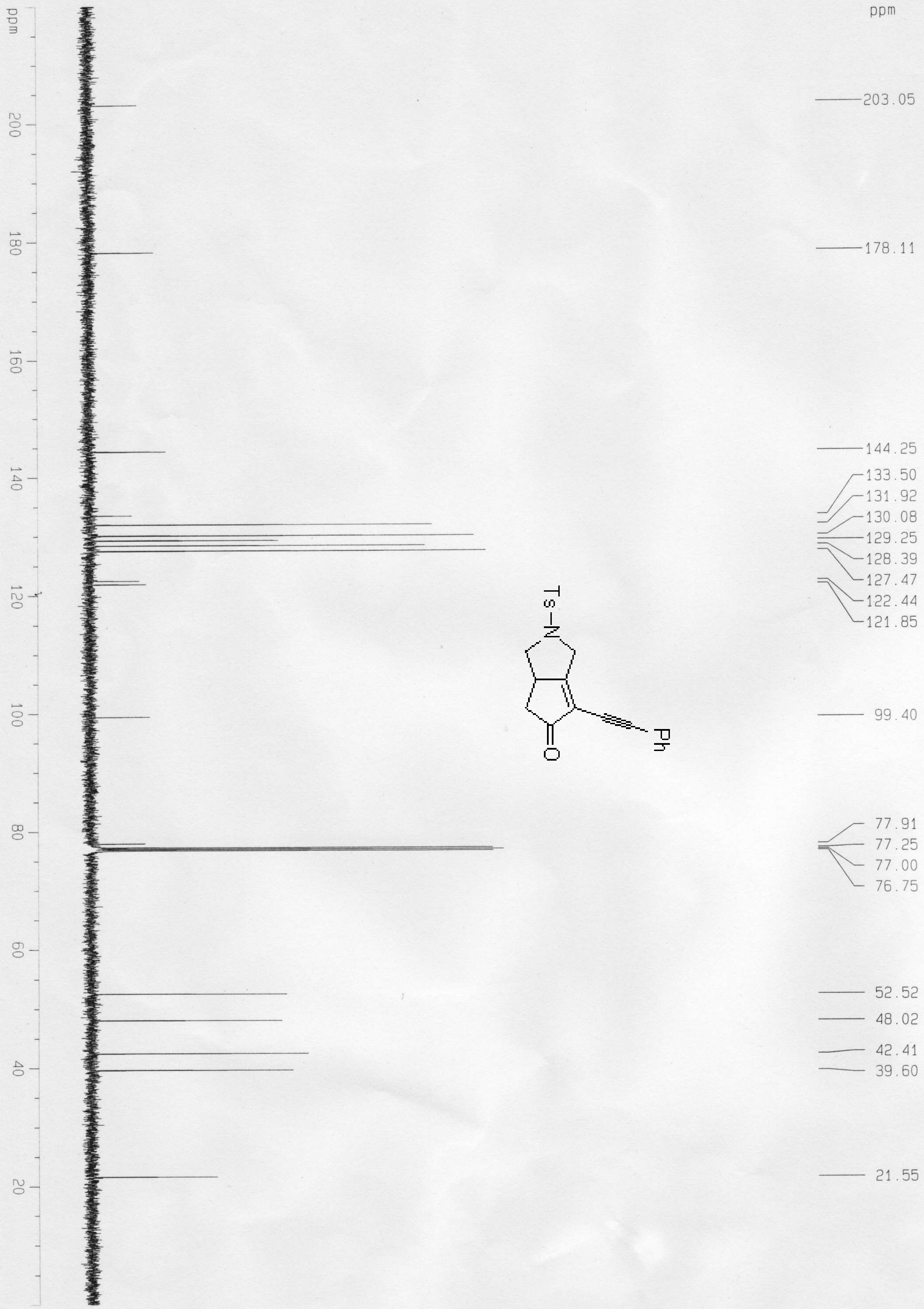
8
7
6
5
4
3
2
1
1.6408
1.3417
4.6473
1.0000
1.0172
1.0268
0.9804
1.0280
0.9943
2.9428
1.0300
1.8721
3883
3875
3750
3744
3742
3685
3678
3671
3665
3633
2236
2219
2103
2086
2045
2036
2028
1614
1610
1607
1383
1376
1365
1358
1339
1330
1319
1221
1094
1091
1076
1073
825
Ts–N
O
Ph


ppm
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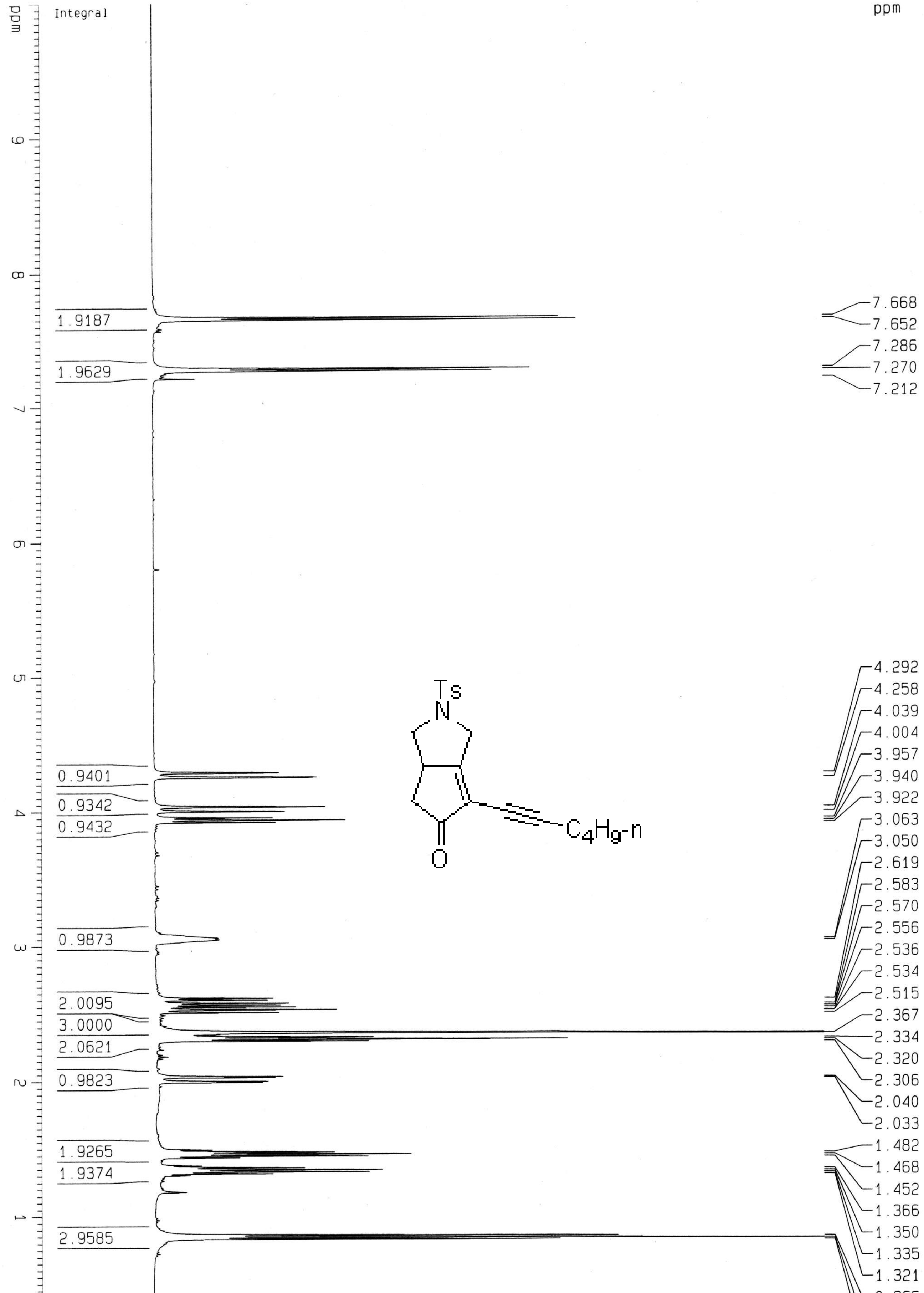
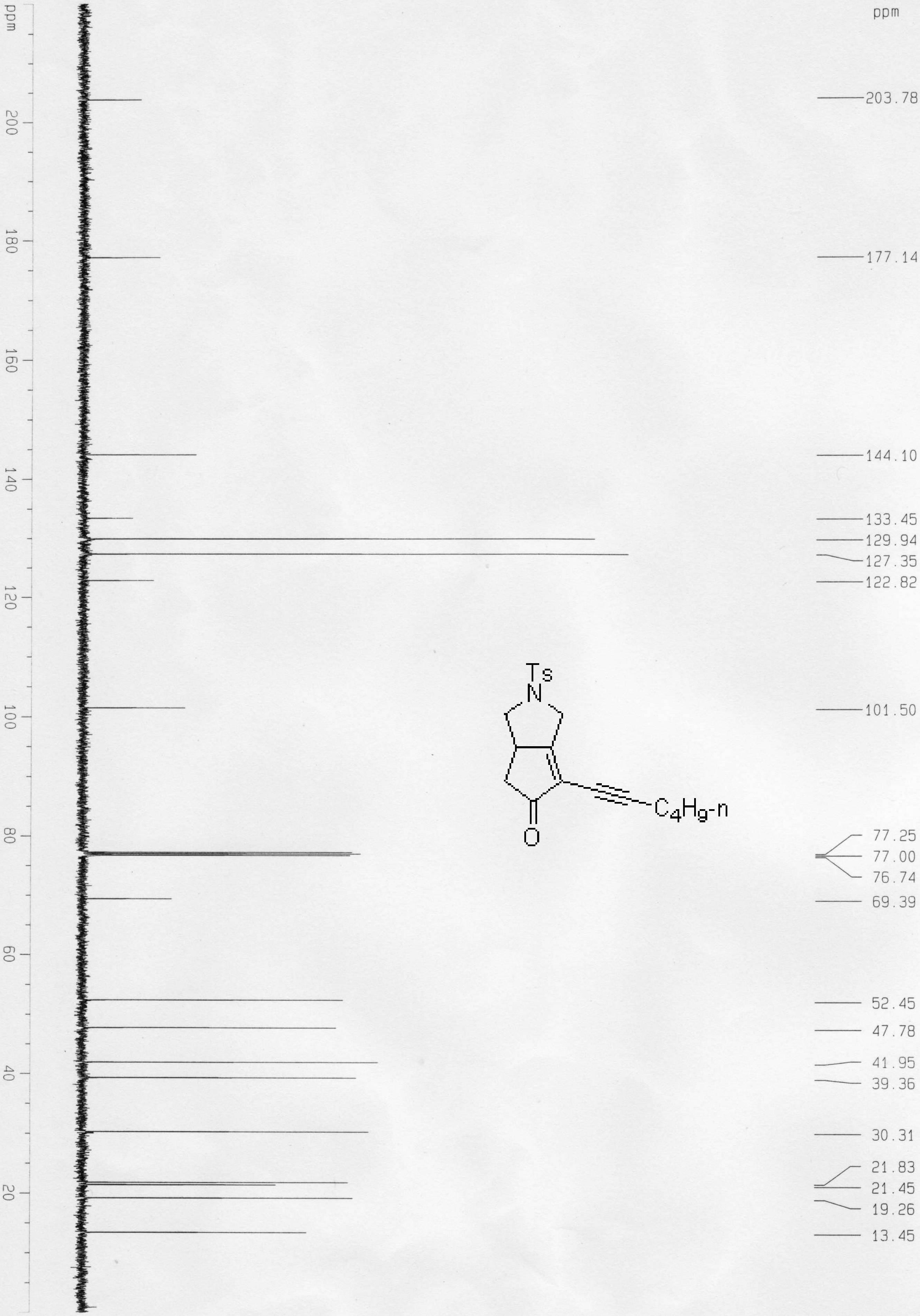
133.50
131.92
130.08
129.25
128.39
127.47
122.44
121.85
99.40
77.91
77.25
77.00
76.75
52.52
48.02
42.41
39.60
21.55
Ts–N
O
Ph



ppm
Integral
ppm
9
8
7
6
5
4
3
2
1
1.9187
1.9629
0.9401
0.9342
0.9432
0.9873
2.0095
3.0000
2.0621
0.9823
1.9265
1.9374
2.9585
7.668
7.652
7.286
7.270
7.212
4.292
4.258
4.039
4.004
3.957
3.940
3.922
3.063
3.050
2.619
2.583
2.570
2.556
2.536
2.534
2.515
2.367
2.334
2.320
2.306
2.040
2.033
1.482
1.468
1.452
1.366
1.350
1.335
1.321
0.865
0.851
0.836
Ts
N
O
C4H9-n


ppm
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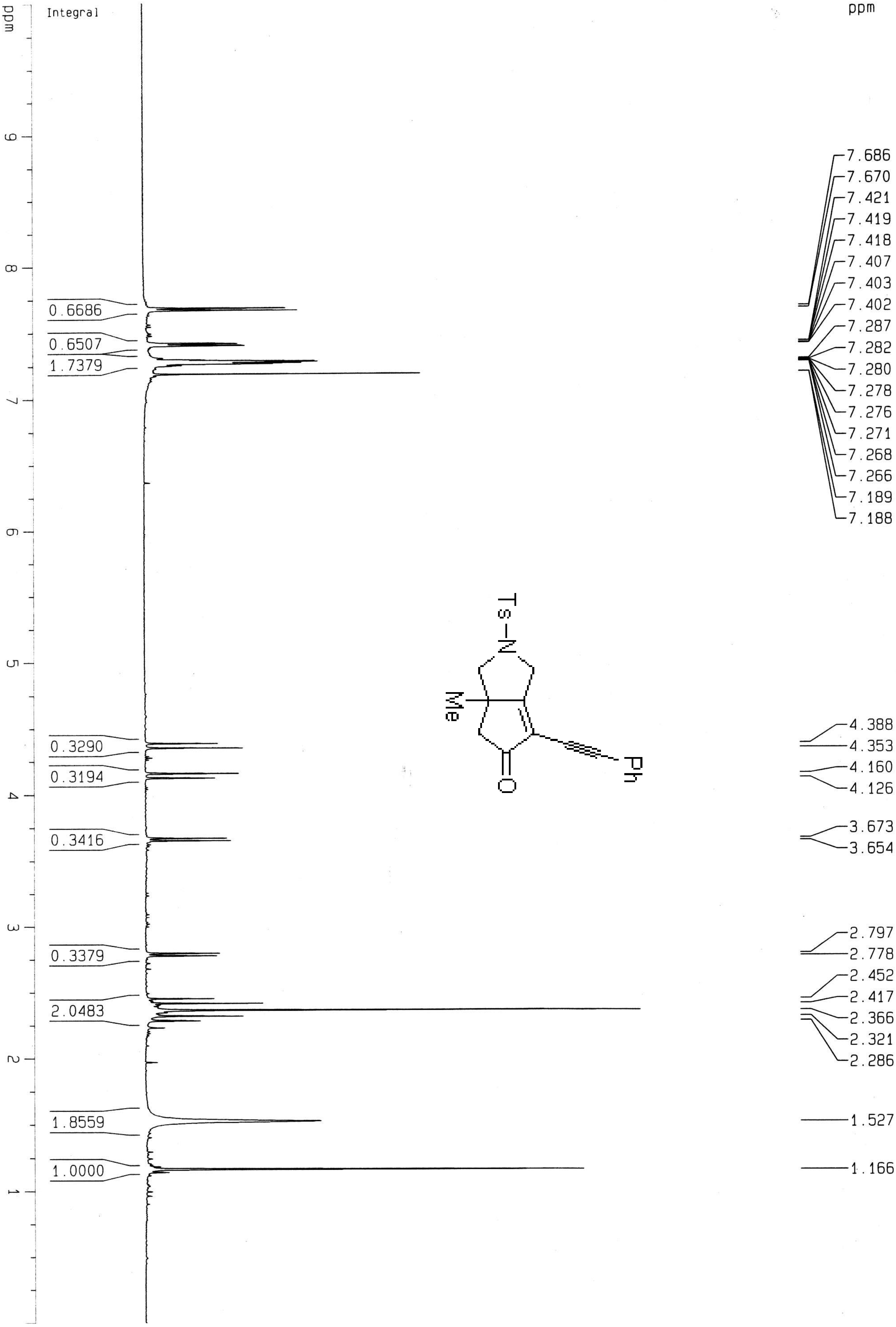
144.10
133.45
129.94
127.35
122.82
101.50
77.25
77.00
76.74
69.39
52.45
47.78
41.95
39.36
30.31
21.83
21.45
19.26
13.45
Ts
N
O
C4H9-n



ppm
Integral
ppm
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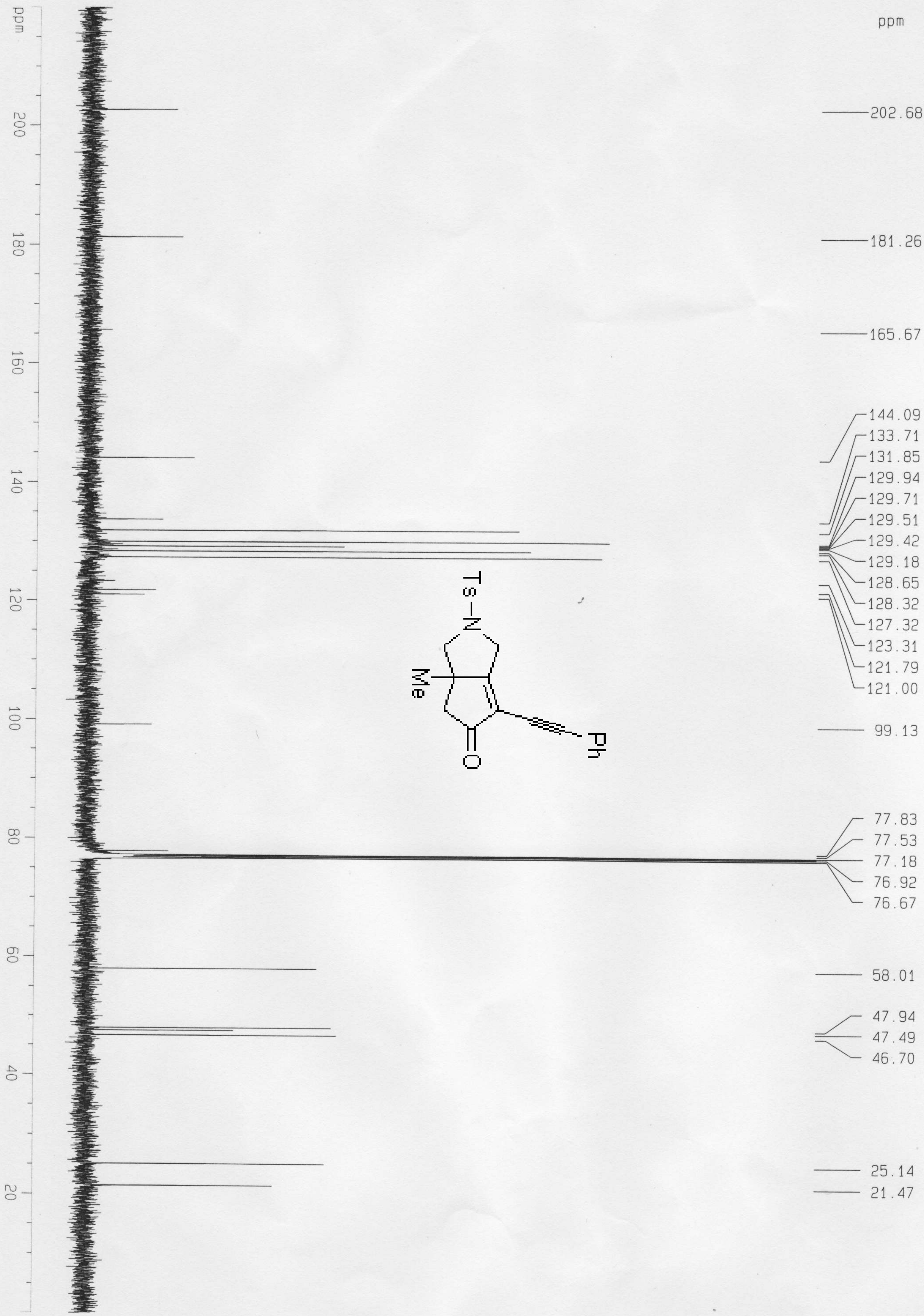
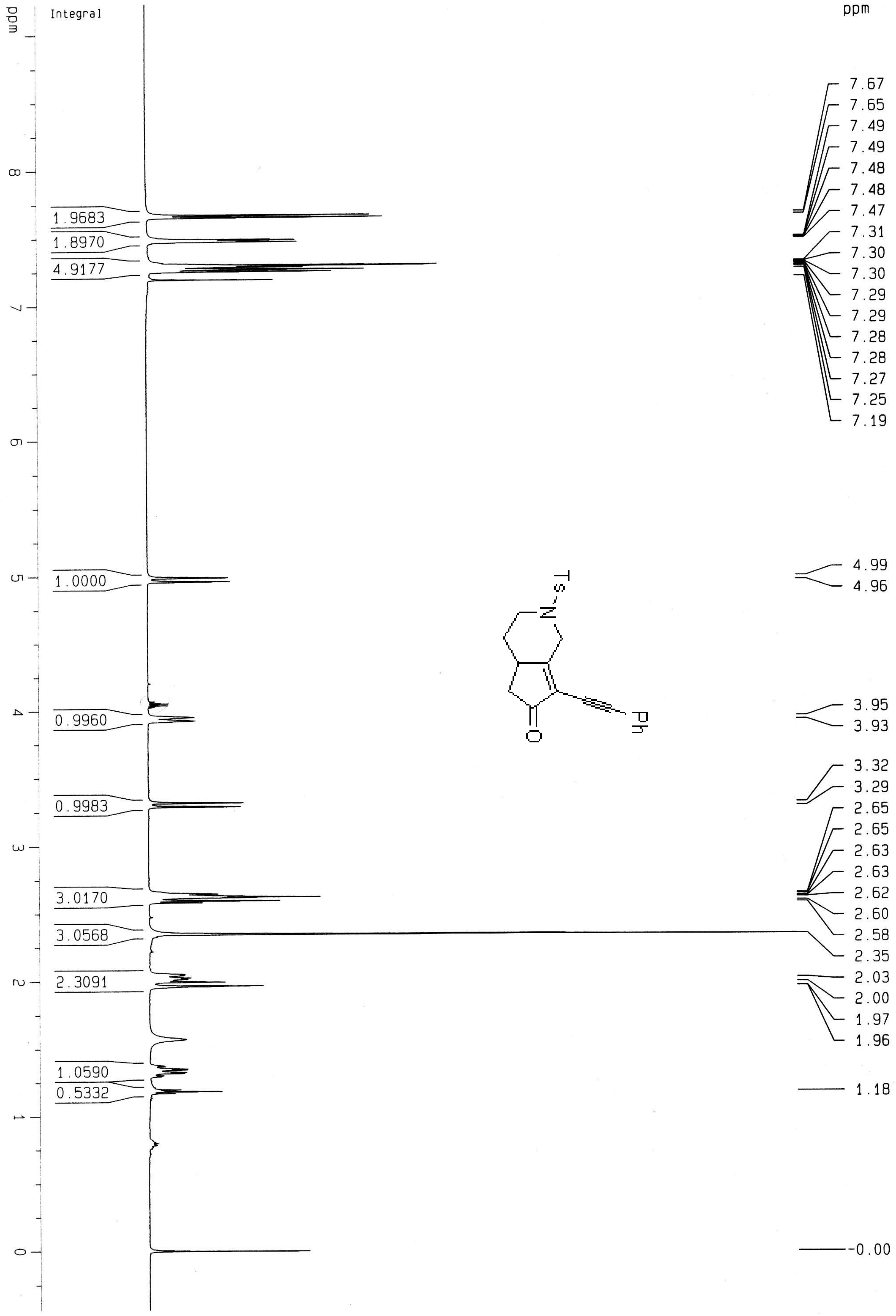
7.670
7.421
7.419
7.418
7.407
7.403
7.402
7.287
7.282
7.280
7.278
7.276
7.271
7.268
7.266
7.189
7.188
4.388
4.353
4.160
4.126
3.673
3.654
2.797
2.778
2.452
2.417
2.366
2.321
2.286
1.527
1.166
0.6686
0.6507
1.7379
0.3290
0.3194
0.3416
0.3379
2.0483
1.8559
1.0000
Ts–N
Me
Ph
O



ppm
202.68
181.26
165.67
144.09
133.71
131.85
129.94
129.71
129.51
129.42
129.18
128.65
128.32
127.32
123.31
121.79
121.00
99.13
77.83
77.53
77.18
76.92
76.67
58.01
47.94
47.49
46.70
25.14
21.47
ppm
200
180
160
140
120
100
80
60
40
20
Ts
N
Me
O
Ph



ppm
Integral
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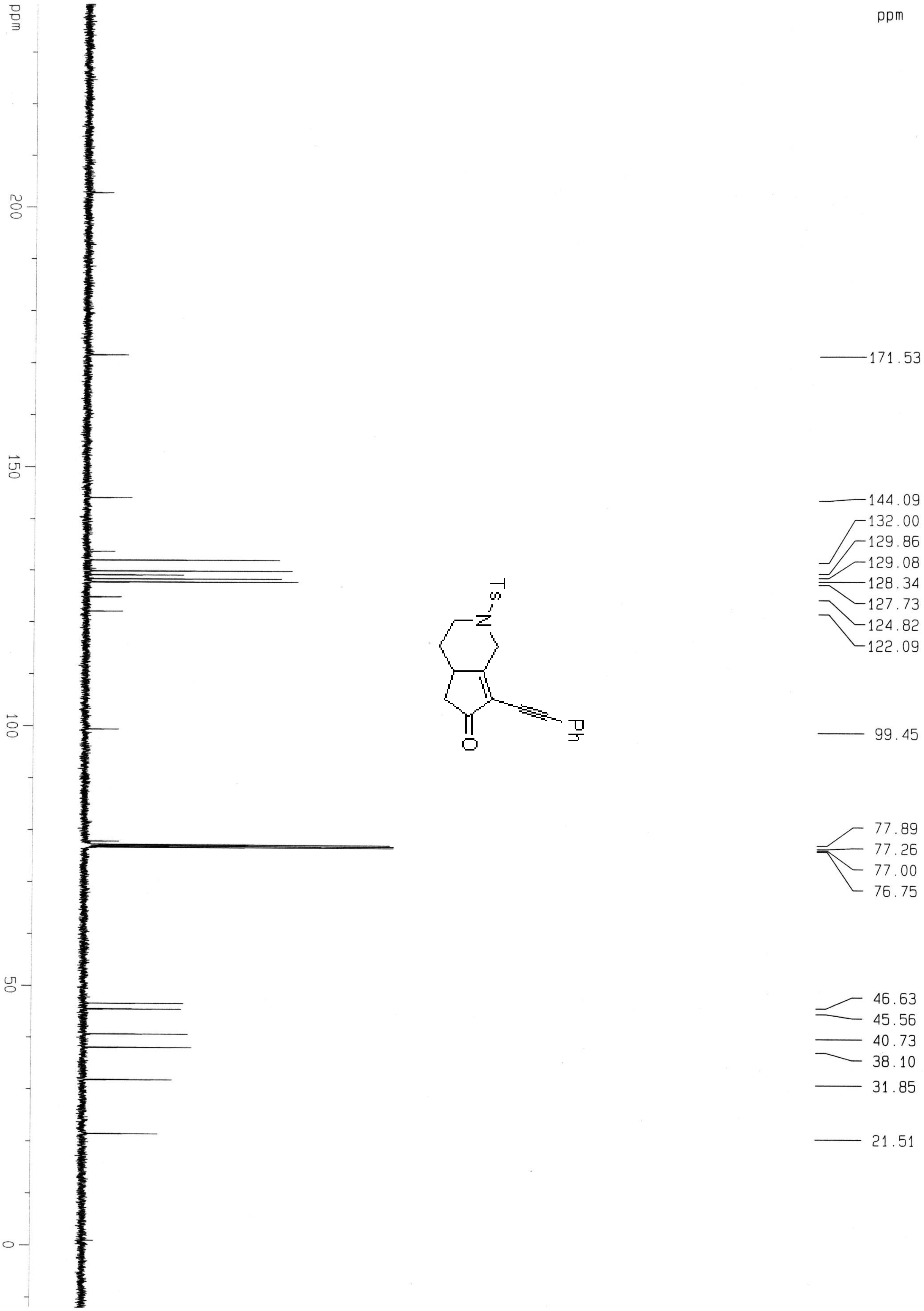
1.0000
0.9960
0.9983
3.0170
3.0568
2.3091
1.0590
0.5332
ppm
7.67
7.65
7.49
7.49
7.48
7.48
7.47
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.25
7.19
4.99
4.96
3.95
3.93
3.32
3.29
2.65
2.65
2.63
2.63
2.62
2.60
2.58
2.35
2.03
2.00
1.97
1.96
1.18
-0.00
Ts
N
Ph
O


ppm
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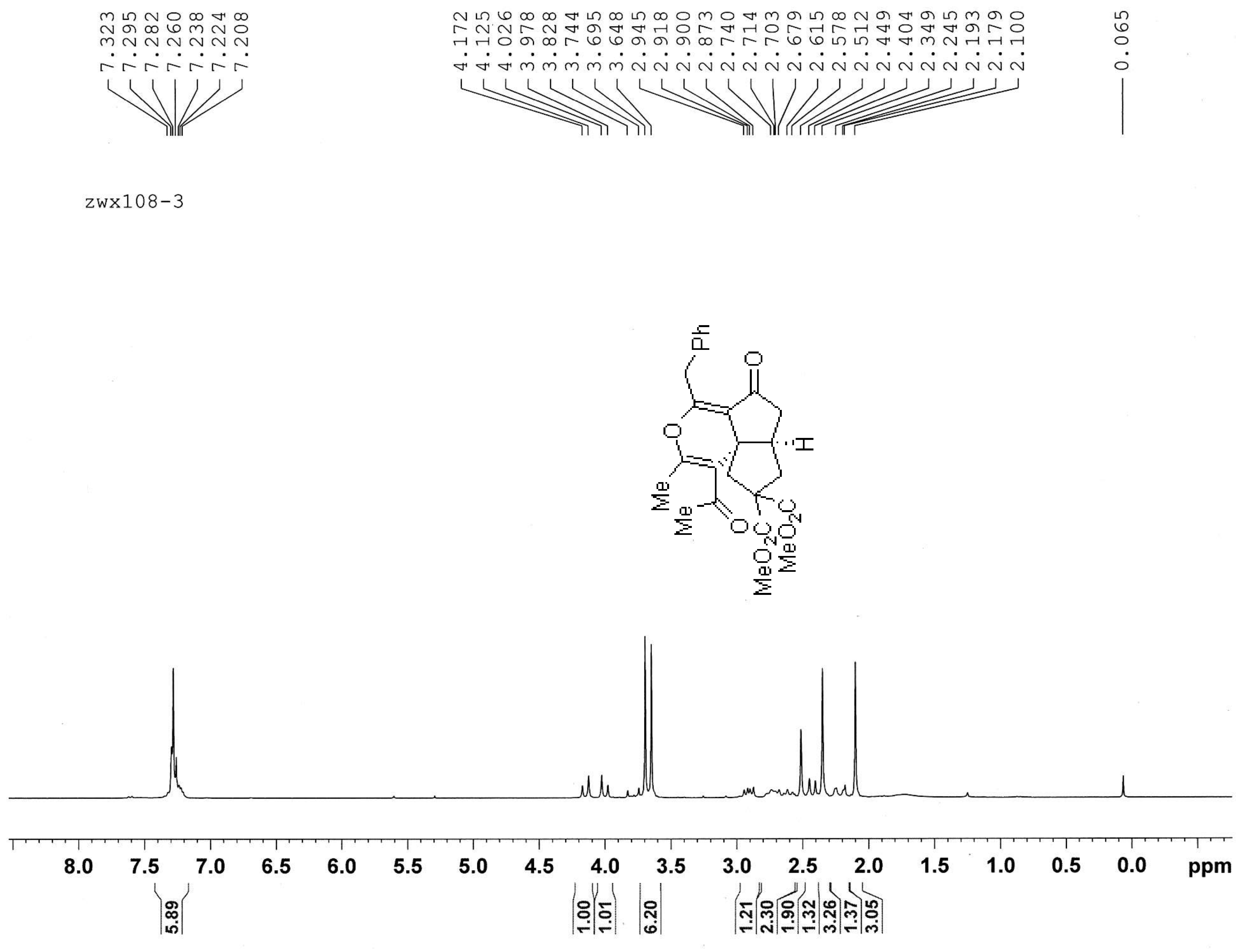
132.00
129.86
129.08
128.34
127.73
124.82
122.09
99.45
77.89
77.26
77.00
76.75
46.63
45.56
40.73
38.10
31.85
21.51
ppm
200
150
100
50
0
Ts
N
Ph
O



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7.282
7.260
7.238
7.224
7.208
4.172
4.125
4.026
3.978
3.828
3.744
3.695
3.648
2.945
2.918
2.900
2.873
2.740
2.714
2.703
2.679
2.615
2.578
2.512
2.449
2.404
2.349
2.245
2.193
2.179
2.100
0.065
zwx108-3
Ph
O
Me
Me
O
MeO2C
MeO2C
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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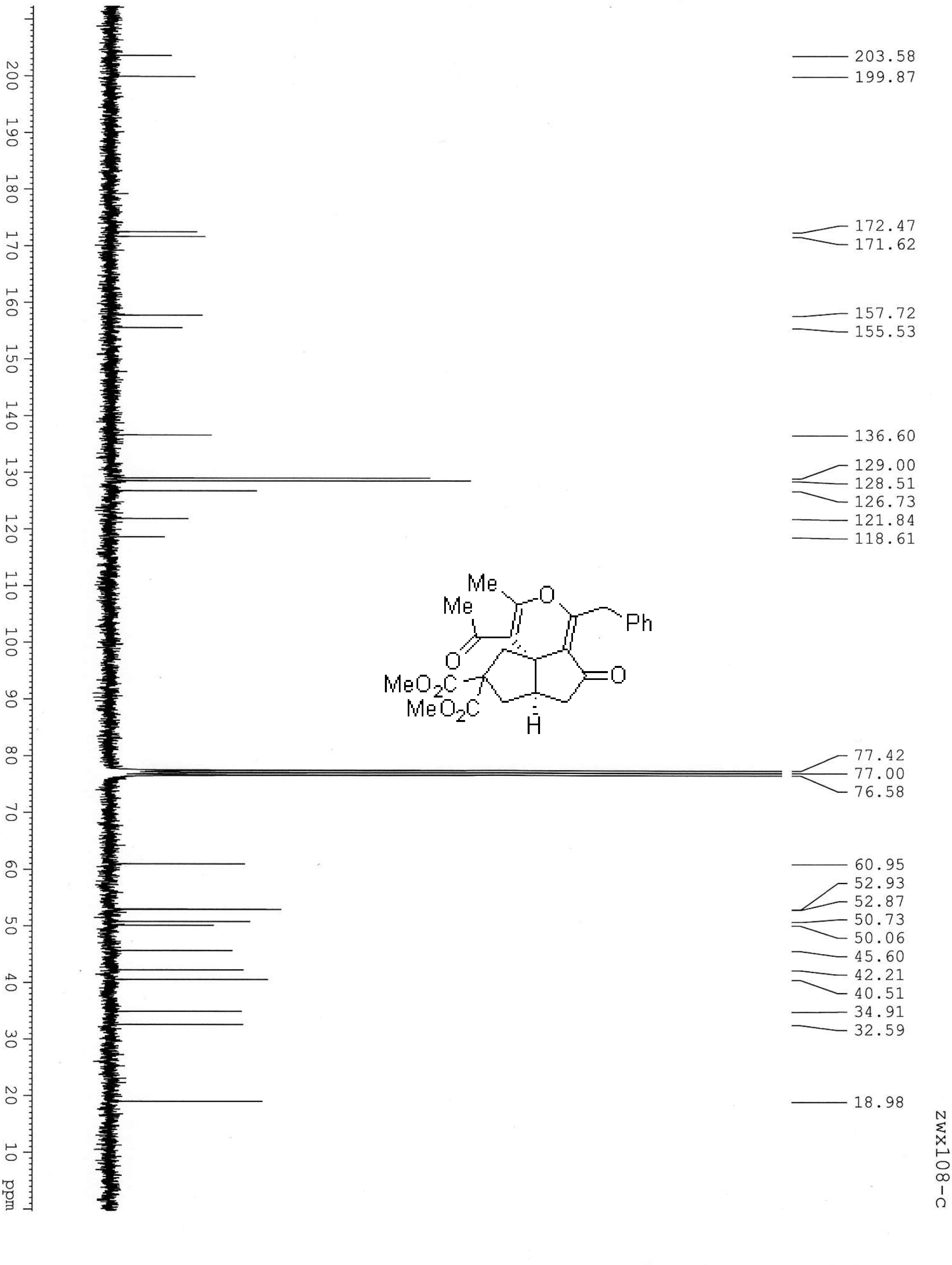
1.00
1.01
6.20
1.21
2.30
1.90
1.32
3.26
1.37
3.05



203.58
199.87
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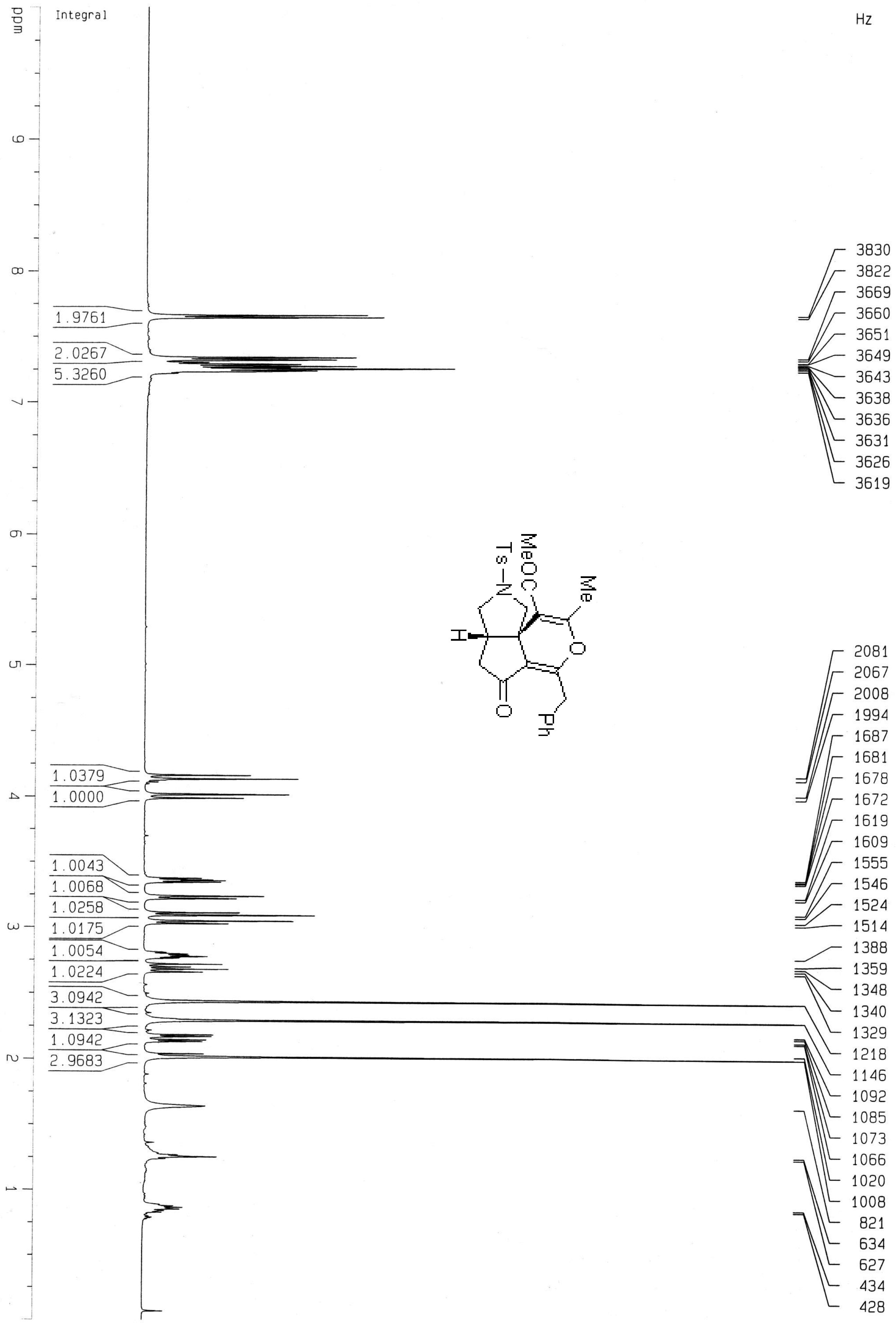
157.72
155.53
136.60
129.00
128.51
126.73
121.84
118.61
77.42
77.00
76.58
60.95
52.93
52.87
50.73
50.06
45.60
42.21
40.51
34.91
32.59
18.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Me
Me
O
Ph
O
O
MeO2C
MeO2C
H
zwx108-c



ppm
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1.0379
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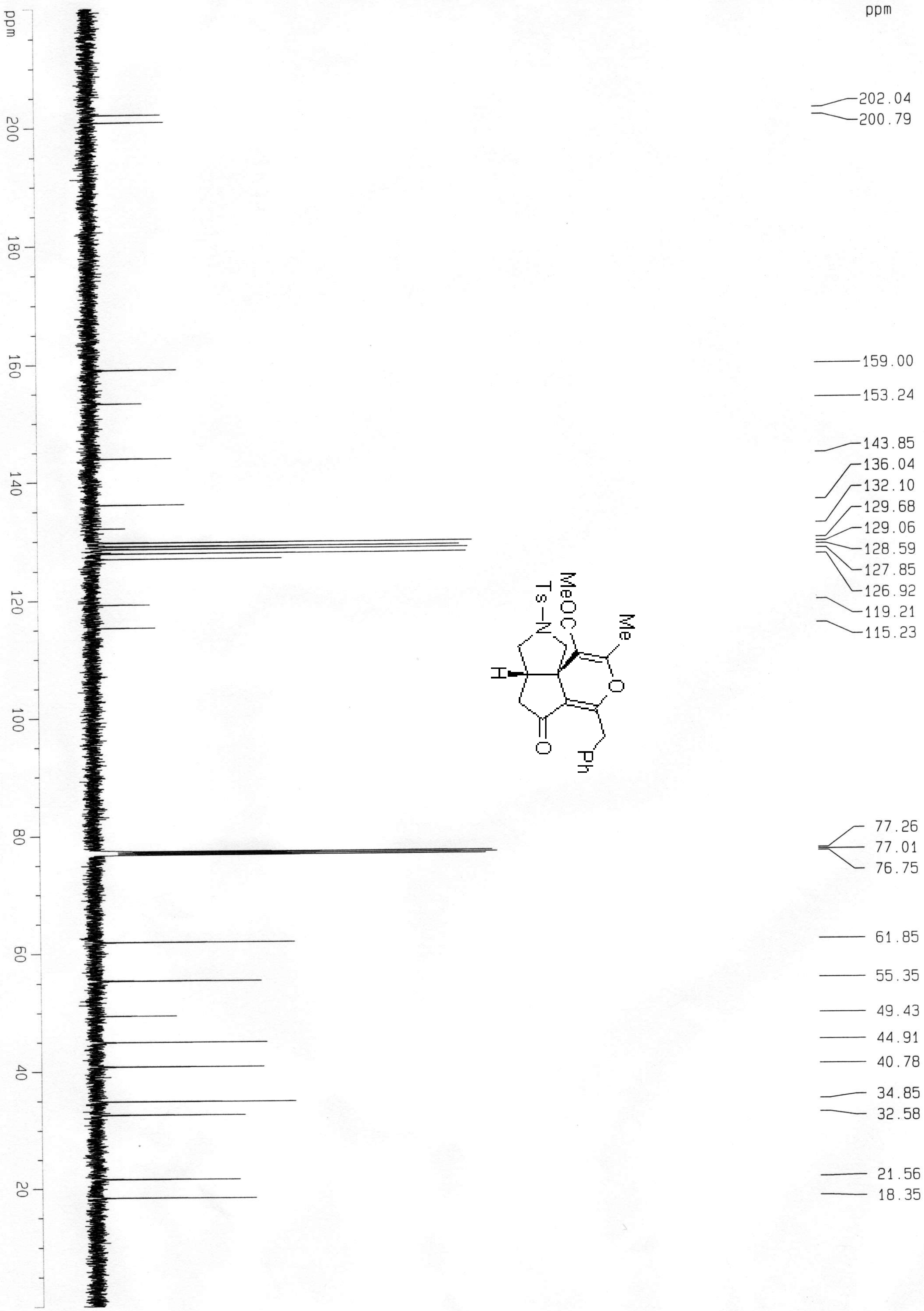
1.0068
1.0258
1.0175
1.0054
1.0224
3.0942
3.1323
1.0942
2.9683
3830
3822
3669
3660
3651
3649
3643
3638
3636
3631
3626
3619
2081
2067
2008
1994
1687
1681
1678
1672
1619
1609
1555
1546
1524
1514
1388
1359
1348
1340
1329
1218
1146
1092
1085
1073
1066
1020
1008
821
634
627
434
428
MeOC
Ts–N
Me
O
H
O
Ph



ppm
202.04
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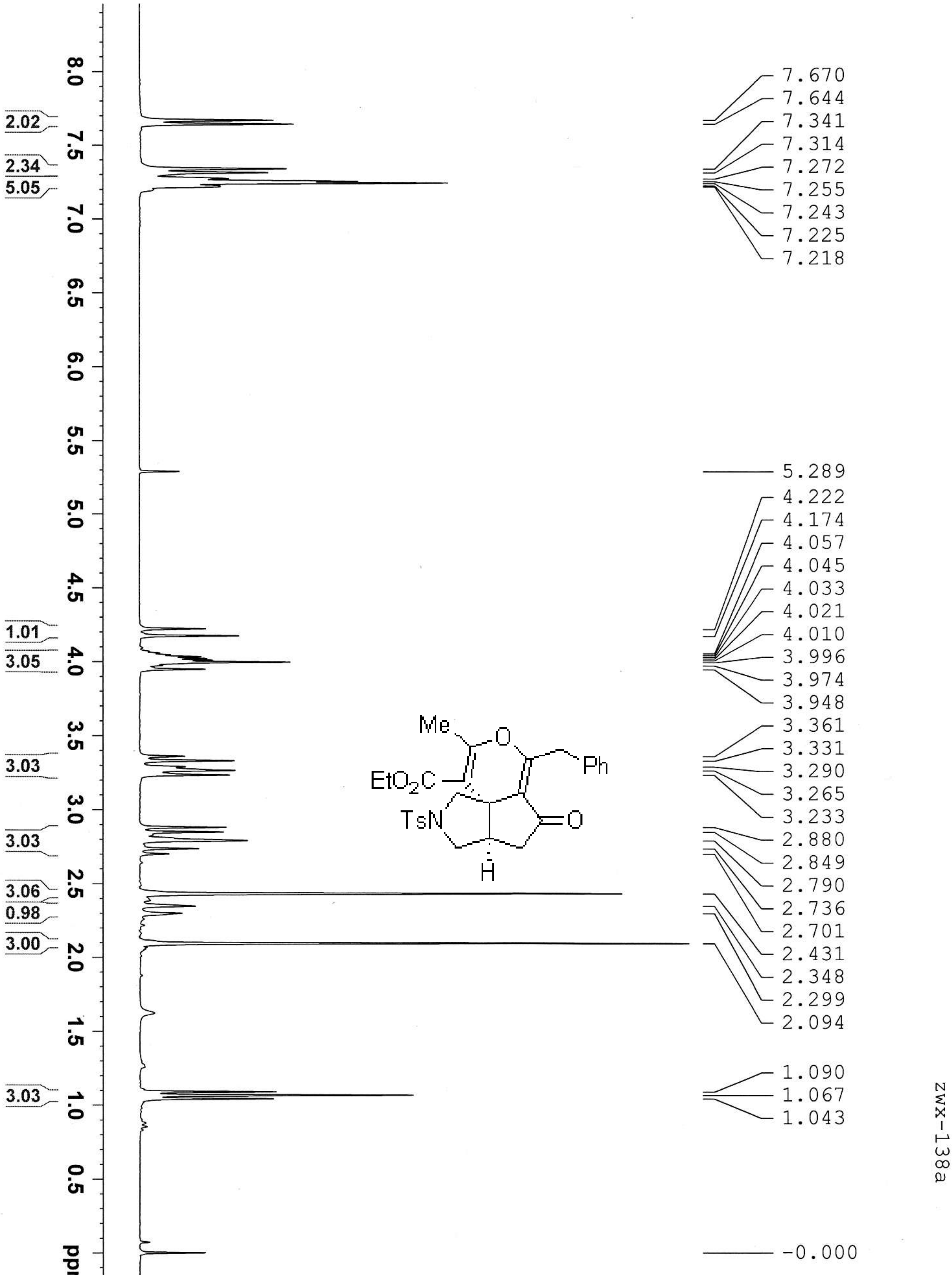
159.00
153.24
143.85
136.04
132.10
129.68
129.06
128.59
127.85
126.92
119.21
115.23
77.26
77.01
76.75
61.85
55.35
49.43
44.91
40.78
34.85
32.58
21.56
18.35
ppm
200
180
160
140
120
100
80
60
40
20
MeOC
Ts—N
Me
O
H
O
Ph



7.670
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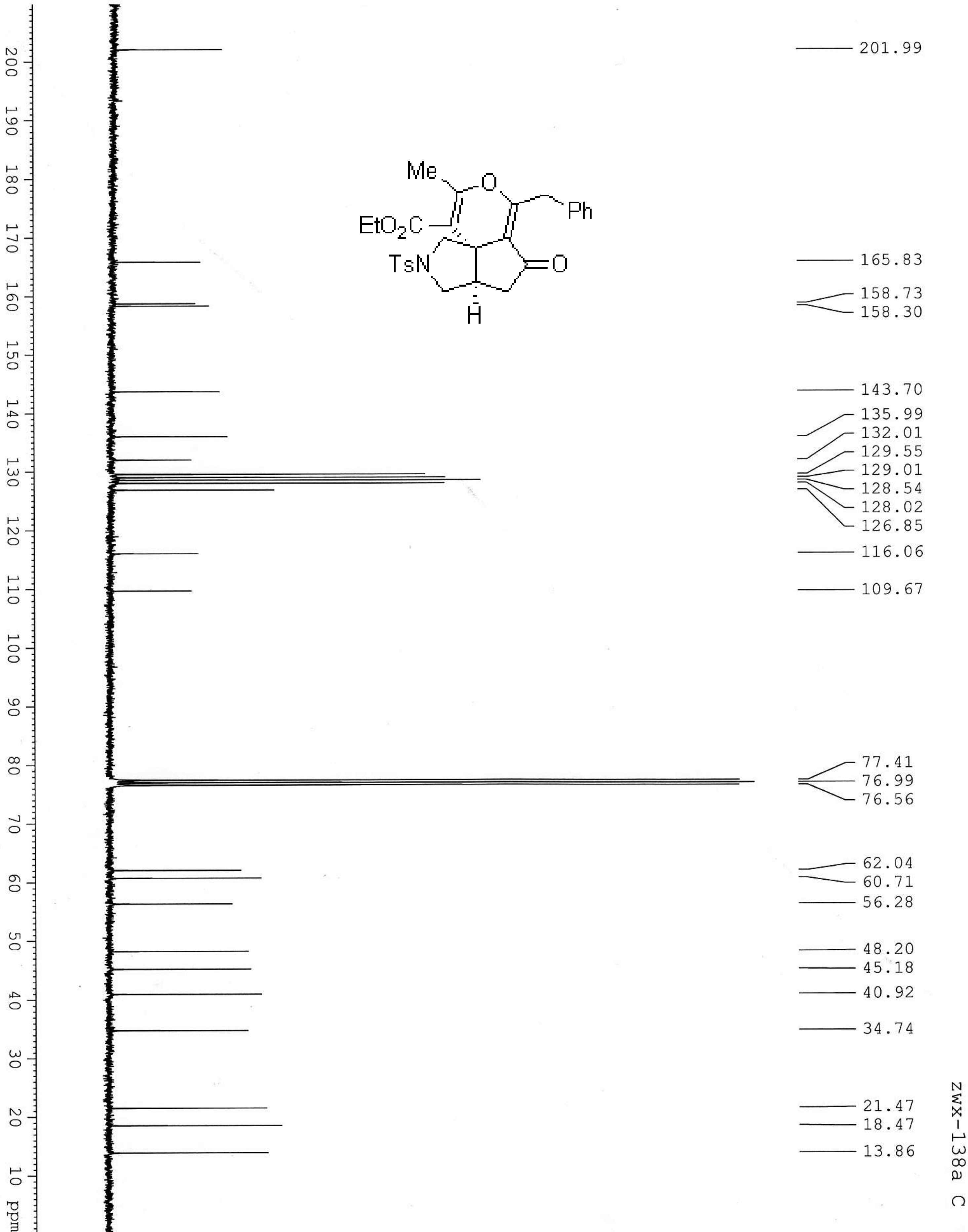
7.272
7.255
7.243
7.225
7.218
5.289
4.222
4.174
4.057
4.045
4.033
4.021
4.010
3.996
3.974
3.948
3.361
3.331
3.290
3.265
3.233
2.880
2.849
2.790
2.736
2.701
2.431
2.348
2.299
2.094
1.090
1.067
1.043
-0.000
2.02
2.34
5.05
1.01
3.05
3.03
3.03
3.06
0.98
3.00
3.03
Me
O
Ph
EtO2C
TsN
O
H
ppm
zwx-138a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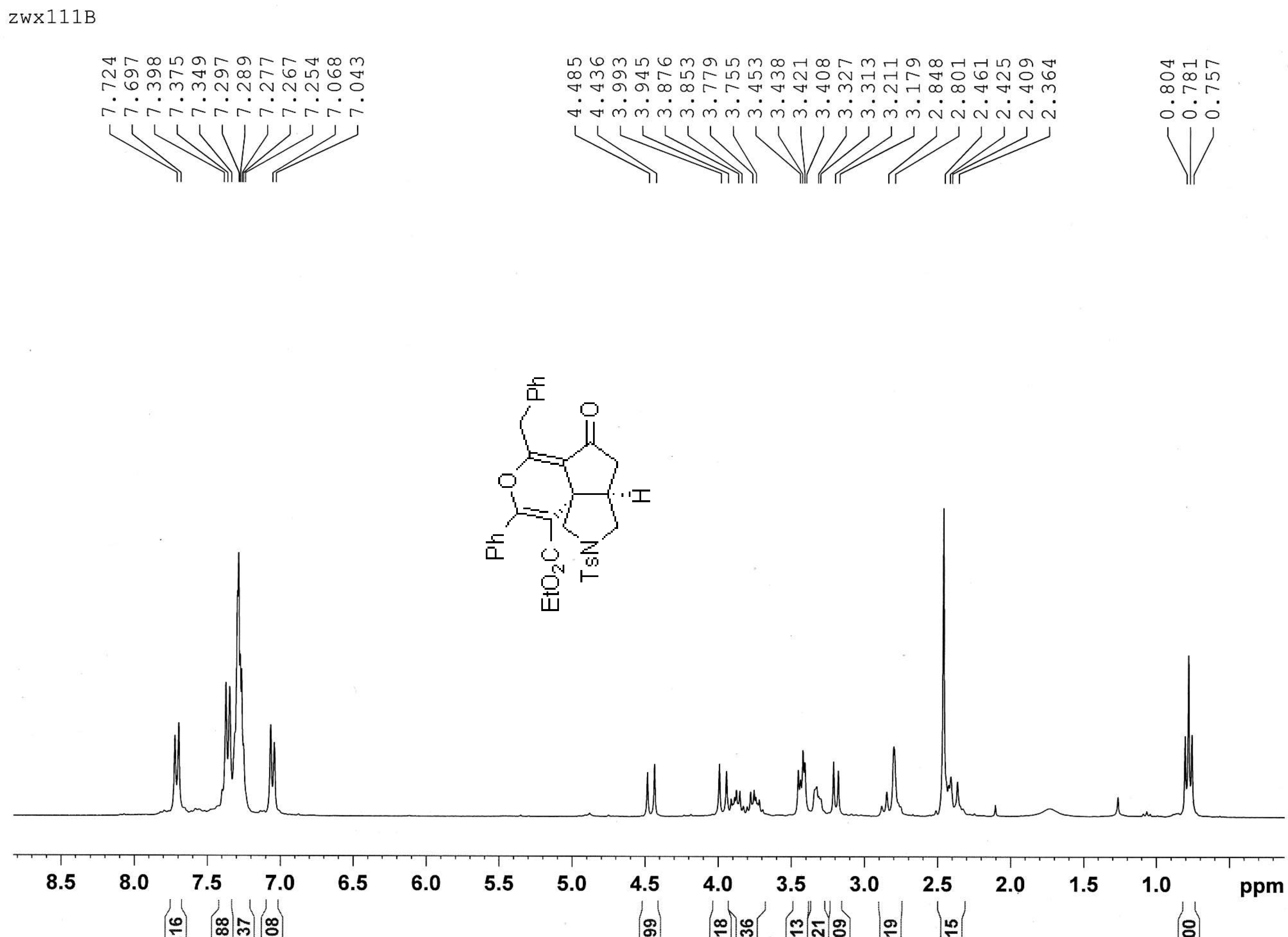
158.30
143.70
135.99
132.01
129.55
129.01
128.54
128.02
126.85
116.06
109.67
77.41
76.99
76.56
62.04
60.71
56.28
48.20
45.18
40.92
34.74
21.47
18.47
13.86
zwx-138a C
ppm
Me
O
Ph
EtO2C
TsN
O
H


zwx111B
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7.398
7.375
7.349
7.297
7.289
7.277
7.267
7.254
7.068
7.043
4.485
4.436
3.993
3.945
3.876
3.853
3.779
3.755
3.453
3.438
3.421
3.408
3.327
3.313
3.211
3.179
2.848
2.801
2.461
2.425
2.409
2.364
0.804
0.781
0.757
Ph
O
Ph
O
EtO2C
TsN
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.16
3.88
8.37
2.08
0.99
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2.36
2.13
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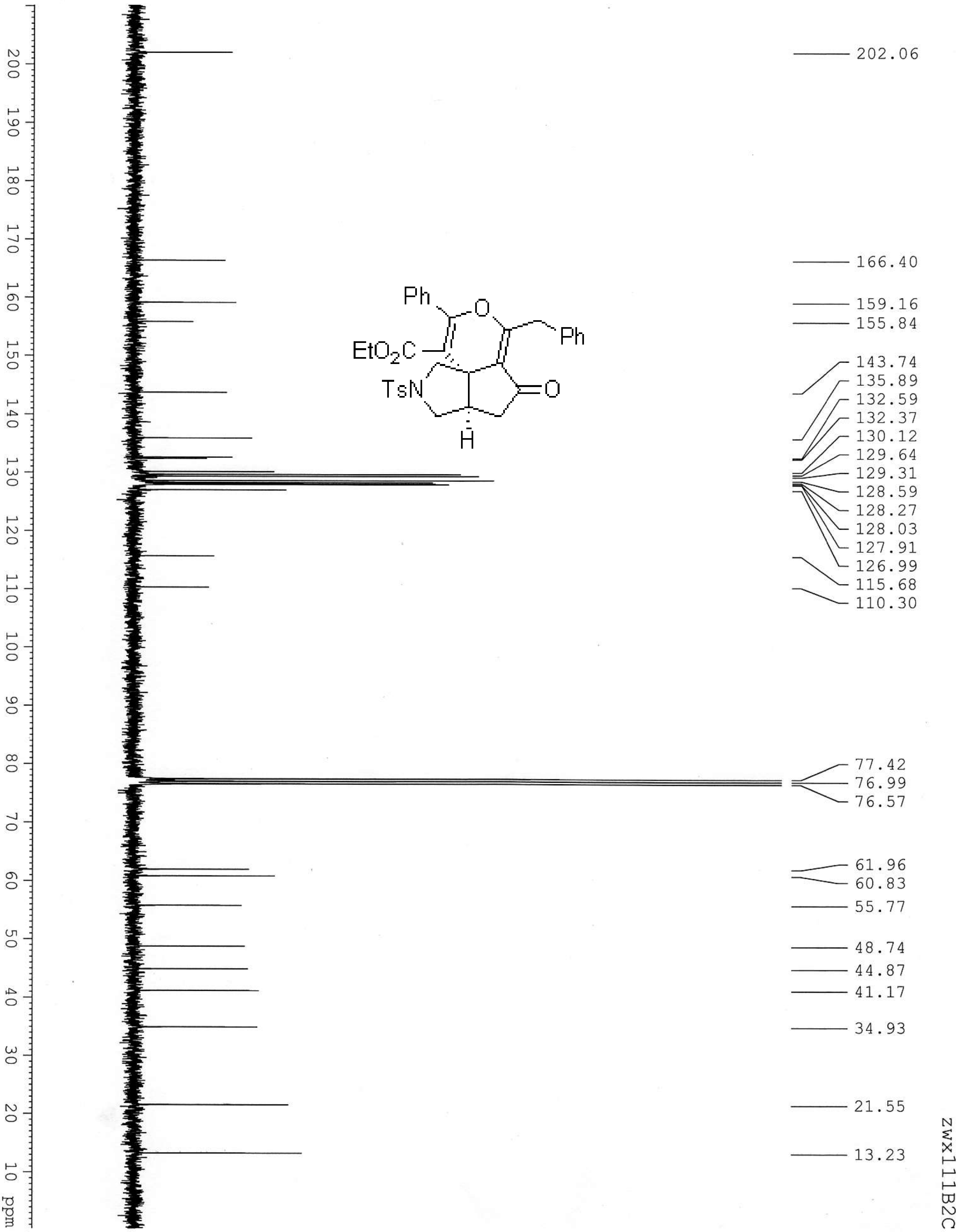
3.00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128.27
128.03
127.91
126.99
115.68
110.30
77.42
76.99
76.57
61.96
60.83
55.77
48.74
44.87
41.17
34.93
21.55
13.23
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Ph
EtO_2C
TsN
O
H
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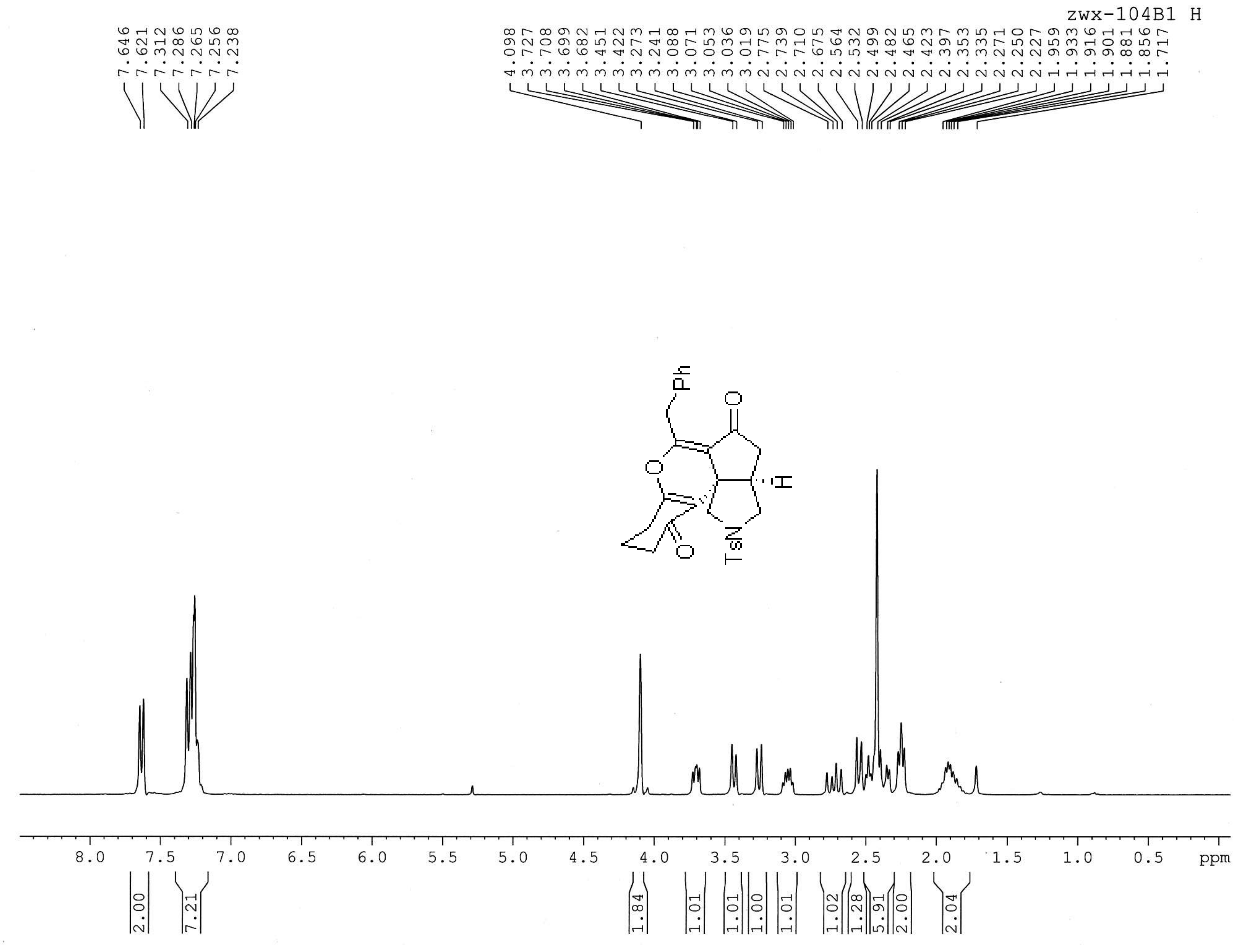
zwx111B2C



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7.256
7.238
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3.699
3.682
3.451
3.422
3.273
3.241
3.088
3.071
3.053
3.036
3.019
2.775
2.739
2.710
2.675
2.564
2.532
2.499
2.482
2.465
2.423
2.397
2.353
2.335
2.271
2.250
2.227
1.959
1.933
1.916
1.901
1.881
1.856
1.717
Ph
O
O
O
TsN
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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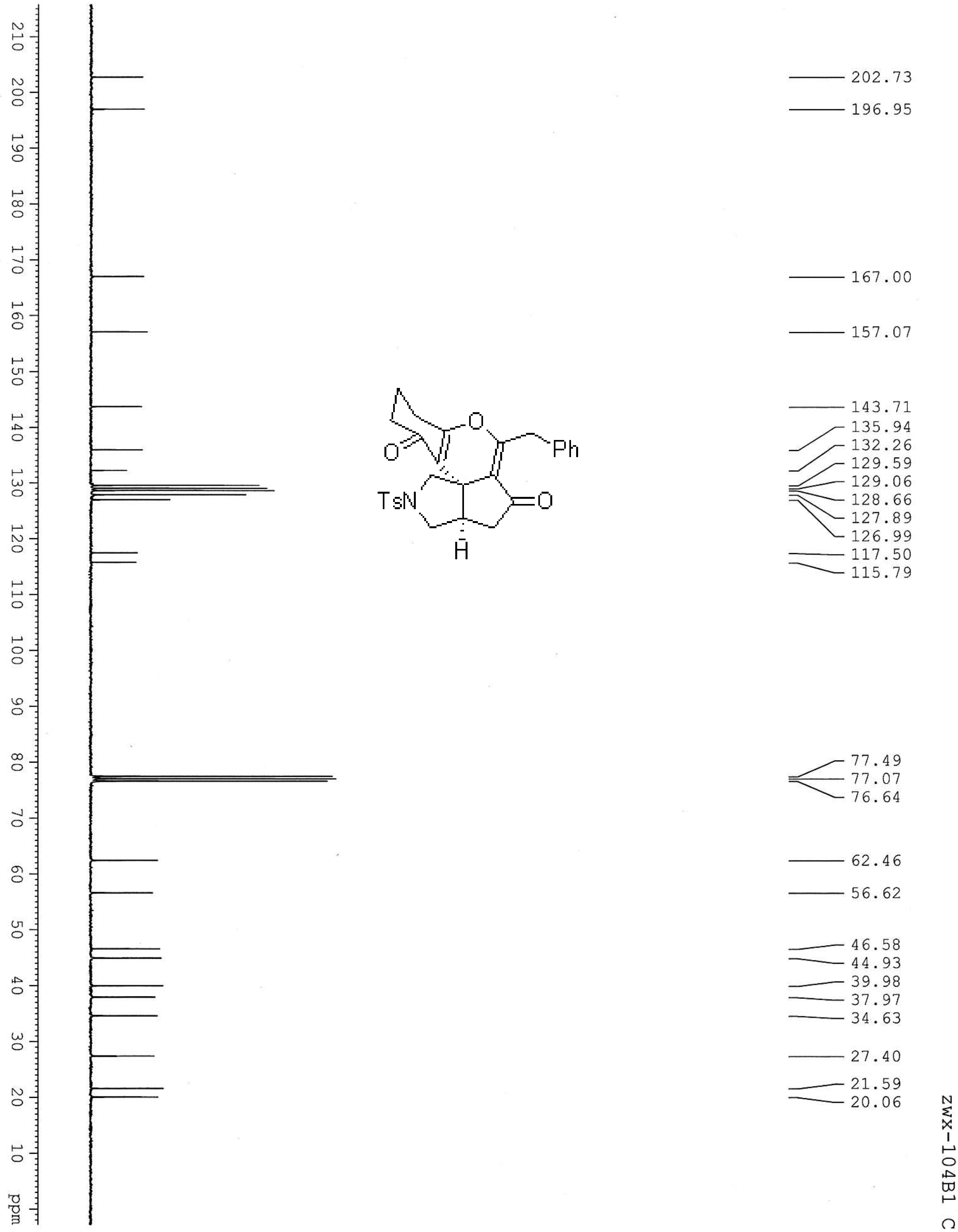
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115.79
77.49
77.07
76.64
62.46
56.62
46.58
44.93
39.98
37.97
34.63
27.40
21.59
20.06
TsN
Ph
O
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
zwx-104B1 C