Experimental section

All reactions were carried out under inert atmosphere (Ar). THF and ether were dried and freshly distilled from sodium/benzophenone. DMF was dried by distillation over calcium hydride. Flash chromatography was carried out with Merck silica gel (silica gel, 230-400 Mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200MHz) or a Bruker AMX 400 (400MHz) nuclear magnetic resonance spectrometer using $CDCl_3$ as the solvant. Chemical shifts are given in ppm (referring to Me_4Si). The mass spectra were obtained on a Hewlett Packard (engine 5989A) in direct introduction mode (70eV). IR spectra were recorded on a Nicolet 250FT-IR spectrophotometer. Melting points are uncorrected. (*Z*)-3-iodoprop-2-enoic acid and (*Z*)-3-iodobut-3-enoic acid were prepared were preprared by previously reported procedure (ref 12c). 4-methoxybut-2-ynoic acid was prepared by carbonatation of 3-methoxybut-1-ynlmagnesium bromide. Tributylstannylacetylene, propynoic acid, tetrolic acid, 3-trimethylsilylprop-2-ynoic acid and 3-phenylpropynoic acid are commercially availaible.

(*Z*)-3-iodo-4-methoxybut-2-enoic acid

In a 100 mL flask, at -40 °C, to 11.4 g (0.1 mol) of 4-methoxybut-2-ynoic acid were added 17 mL (0.13 mol) of hydroiodic acid (57% from Lancaster corp.). After stirring for 6h at 0°C, a saturated solution of sodium bicarbonate were added until pH 7 is reached then the reaction mixture was washed with 50 mL of 2M HCl and extracted with diethylether (3x50 mL). The organic phases were dried over magnesium sulfate and concentrated affording 19.4 g (80% yield) of a 96/4 mixture of stereoisomers *Z* and *E* of 3-iodo-4-methoxybut-2-enoic acid. The pure Z-acid is obtained by cristallisation (petroleum ether/ether = 85/15). IR: 1700, 1626, 1308, 1266, 1112. ^{1}H NMR (200 MHz) ($CDCl_3$) δ(ppm): 3.46 (3H, s), 4.23 (2H, d, $^4J_{1H}$ = 1.8Hz), 6.85 (1H, t, $^4J_{2H}$ = 1.8Hz), 10.5(1H, bs). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 58.5, 81.7, 119.0, 122.9, 169.2. MS (70eV) : m/z = 242 (M, 100), 127 (17), 115 (99), 87 (34), 85 (18), 84 (17), 83 (40), 69 (32), 57 (19), 55 (24), 45 (45), 39 (30).

(*Z*)-3-iodo-3-phenylpropenoic acid

In a 100 mL flask, at 20 °C, to 14.6 g (0.1 mol) of 3-phenylpropynoic acid were added 17 mL (0.13 mol) of hydroiodic acid (57% from Lancaster corp.). After stirring for 16h at 75°C, a saturated solution of sodium bicarbonate were added until pH 7 is reached then the reaction mixture was washed with 50 mL of 2M HCl and extracted with diethylether (3x50 mL). The organic phases were dried over magnesium sulfate and concentrated affording 19.2 g (70% yield) of (*Z*)-3-iodo-3-phenylpropenoic acid. Mp = 140°C. IR (KBr) : 3456, 3063, 2808, 1690, 1599, 1240, 1210, 750, 703. ^{1}H NMR (200 MHz) ($CDCl_3$) δ(ppm): 6.84 (1H, s), 7.4-7.85 (5H, m), 10.05 (1H, s). ^{13}C NMR δ (ppm) : 115.9, 128.3, 129.3, 129.5, 130.8, 144.1, 165.7. MS (70eV) : m/z = 147 (73), 103 (25), 102 (48), 77 (54), 76 (24), 75 (15), 74 (14), 69 (86), 63 (12), 52 (10).

(*Z*)-3-iodo-3-trimethylsilylpropenoic acid

In a 100 mL flask, at -40 °C, to 14.2 g (0.1 mol) of 3-trimethylsilylpro-2-ynoic acid were added 17 mL (0.13 mol) of hydroiodic acid (57% from Lancaster corp.). After stirring for 3h at 100°C, a saturated solution of sodium bicarbonate were added until pH 7 is reached then the reaction mixture was washed with 50 mL of 2M HCl and extracted with diethylether (3x50 mL). The organic phases were dried over magnesium sulfate and concentrated affording 16.7 g (62% yield) of a 92/8 mixture of stereoisomers *Z* and *E* of 3-iodo-3-trimethylsilylpropenoic acid. The pure Z-acid is obtained by cristallisation (petroleum ether/ether = 85/15). IR : 3077, 2783, 2573, 1698, 1587, 1207, 867. ^{1}H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.30 (9H, s), 7.04 (1H, s), 10.50 (1H, bs). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): -1.67, 129.9, 133.8, 169.1.

MS (70eV) : m/z = 270 (M, 29), 255 (28), 185 (23), 127 (16), 83 (50), 75 (100), 73 (63), 67 (14), 55 (20), 53 (49), 45 (46), 44 (12), 43 (77).

General procedure for the preparation of 4-substituted (*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one:

To a DMF (35 mL) solution containing 4.87 g (10 mmol) of tributylstannyl (Z)-3-iodoprop-2-enoate and 0.115 g (0.1 mmol) of tetrakis(triphenylphosphine)palladium(0) is added dropwise 5.67 g (18 mmol) of tributyl(ethynyl)stannane dissolved in 5 mL of DMF. The mixture is stirred at 25° C for 16h, then extracted with diethylether (4x25 mL). The organic layer was washed with a saturated solution of ammonium chloride (3x25 mL), dried over magnesium sulphate and concentrated in vaccuo. The (*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one **1a** (2.5 g) is purified by column chromatography on silica gel (eluent: hexane/Et_2O/Et_3N: 90/8/2).

(*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one **1a**

IR : 2957, 2923, 2855, 1776, 1746, 1612, 1558. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.9 (9H, t, $^3J_{2H}$ = 7.2Hz), 1.02-1.68 (18H, m), 6.14 (1H, dd, $^5J_{1H}$ = 1.8Hz, $^4J_{1H}$ = 0.5Hz, $^2J_{Sn-H}$ = 23-26Hz), 6.31 (1H, dd, $^3J_{1H}$ = 5.5Hz, $^5J_{1H}$ = 1.8Hz), 7.24 (1H, dd, $^3J_{1H}$ = 5.5Hz, $^4J_{1H}$ = 0.5Hz).^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 11.4 (3C, $^1J_{Sn-C}$ = 341-357Hz), 14.1 (3C), 27.7 (3C, $^3J_{Sn-C}$ = 58Hz), 29.4 (3C, $^2J_{Sn-C}$ = 22Hz), 116.3 ($^1J_{Sn-C}$ = 268-280Hz), 123, 144 ($^3J_{Sn-C}$ = 17Hz), 158 ($^2J_{Sn-C}$ = 34Hz), 170.3.^{119}Sn NMR ($CDCl_3$) δ(ppm): - 42.7. MS : m/z = 329 (M-57, 44), 273 (17), 217 (16), 96 (13), 81 (18), 57 (30), 56 (20), 55 (15), 54 (11), 44 (11), 43 (14), 42 (21), 41 (100), 40 (13), 39 (37).

(*E*)-5-tributylstannylmethylidene-4-methyl-5*H*-furan-2-one **1b**

IR : 2950, 2920, 2860, 2840, 1770, 1750, 1605. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.91 (9H, t, $^3J_{2H}$ = 7Hz), 1.03-1.62 (18H, m), 2.18 (3H, d, $^4J_{1H}$ = 1.7Hz), 5.98 (1H, d, $^5J_{1H}$ = 0.7Hz, $^2J_{Sn-H}$ = 10-12Hz), 6.03-6.07 (1H, qd, $^4J_{3H}$ = 1.7Hz, $^5J_{1H}$ = 0.7Hz). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 11.5 (3C, $^1J_{Sn-C}$ = 343-359Hz), 13.2, 13.5 (3C), 27 (3C, $^3J_{Sn-C}$ = 60-62Hz), 28.8 (3C, $^2J_{Sn-C}$ = 24Hz), 112.1 ($^1J_{Sn-C}$ = 272-284Hz), 120.1, 154.2 , 159.1 ($^2J_{Sn-C}$ = 29Hz), 169.3. ^{119}Sn NMR ($CDCl_3$) δ(ppm): - 45.5. MS : m/z = 343 (M-57, 100), 231 (27), 95 (40), 93 (20), 65 (12), 57 (20), 56 (11), 43 (12), 41 (79), 40 (10), 39 (39). (*E*)-stereochemistry was determined by NOESY NMR experiment.

(*E*)-5-tributylstannylmethylidene-4-methoxymethyl-5*H*-furan-2-one **1c**

IR: 2956, 2924, 2854, 1774, 1761, 1605, 1464. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.93 (9H, t, $^3J_{2H}$ = 7Hz), 1.04-1.62 (18H, m), 3.47 (3H, s), 4.35 (2H, dd, $^4J_{1H}$ = 1.5Hz, $^5J_{1H}$ = 0.7Hz), 6.02 (1H, td, $^5J_{1H}$ = 0.8Hz, $^5J_{2H}$ = 0.7Hz, $^2J_{Sn-H}$ = 11Hz), 6.3 (1H, td, $^4J_{2H}$ = 1.5Hz, $^5J_{1H}$ = 0.8 Hz). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 11.3 (3C, $^1J_{Sn-C}$ = 344-360Hz), 13.4 (3C), 27.1 (3C, $^3J_{Sn-C}$ = 61Hz), 28.8 (3C, $^2J_{Sn-C}$ = 21Hz), 58.8, 67.0, 113.0 ($^1J_{Sn-C}$ = 267-280Hz), 119.2, 154.8 ($^3J_{Sn-C}$ = 8Hz), 155.9 ($^2J_{Sn-C}$ = 28Hz), 168.5. ^{119}Sn NMR ($CDCl_3$) δ(ppm): - 42.1. MS : m/z = 373 (M-57, 15), 120 (5), 110 (27), 67 (16), 57 (42), 56 (17), 55 (18), 53 (13), 45 (16), 43 (15), 42 (24), 41 (100), 40 (10), 39 (47).

(*E*)-5-tributylstannylmethylidene-4-phenyl-5*H*-furan-2-one **1d**

IR: 3080, 2956, 2924, 2854, 1777, 1748, 1602. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.87 (9H, t, $^3J_{2H}$ = 6.8Hz), 1.15-1.5 (18H, m), 6.2 (1H, d, $^5J_{1H}$ = 1.8Hz, $^2J_{Sn-H}$ = 9Hz), 6.25 (1H, d, $^5J_{1H}$ = 1.8Hz), 7.36-7.6 (5H, m). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 11.8 (3C, $^1J_{Sn-C}$ = 345-361Hz), 14.2 (3C), 27.6 (3C, $^3J_{Sn-C}$ = 62Hz), 29.4 (3C, $^2J_{Sn-C}$= 21Hz), 117.2 ($^1J_{Sn-C}$ =266-279Hz), 120.5, 129.1 (2C), 129.7 (2C), 130.8, 132.3, 157.9 ($^2J_{Sn-C}$ = 19Hz), 158.0, 168.7. ^{119}Sn

NMR ($CDCl_3$) δ(ppm): - 41.2. MS: m/z = 405 (M-57, 100), 349 (9), 291 (17), 233 (25), 177 (22), 175 (17), 173 (17), 157 (37), 155 (17), 145 (23), 143(17), 141 (15), 137 (27), 135 (21), 133 (13), 129 (10), 127 (20), 121 (16), 57 (10), 41 (50), 39 (13).

(*E*)-5-tributylstannylmethylidene-4-trimethylsilyl-5*H*-furan-2-one **1e**

IR : 2958, 2923, 2854, 1775, 1750, 1600, 1463, 1192. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 0.34 (9H, s), 0.92 (9H, t, $^3J_{2H}$ = 7.2Hz), 1.06-1.62 (18H, m), 5.83 (1H, d, $^5J_{1H}$ = 0.8Hz, $^2J_{Sn\text{-}H}$ = 30Hz), 6.31 (1H, d, $^5J_{1H}$ = 0.8Hz). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): -0.6 (3C), 11.3 (3C, $^1J_{Sn\text{-}C}$ = 341-357Hz), 14.2 (3C), 27.7 (3C, $^3J_{Sn\text{-}C}$ = 57Hz), 29.6 (3C8, $^2J_{Sn\text{-}C}$ = 22Hz), 118.3 ($^1J_{Sn\text{-}C}$ = 268-280Hz), 129.3, 159.4, 164.9 ($^3J_{Sn\text{-}C}$ = 17Hz), 171.3. ^{119}Sn NMR ($CDCl_3$) δ(ppm): - 43.2. MS : m/z = 401 (M,-57, 100), 289 (16), 153 (35), 145 (19), 143 (14), 141 (10), 137 (12), 135 (14), 83 (10), 73 (67), 57 (13), 45 (14), 41 (43), 39 (10).

(*E*) and (*Z*)-5-iodomethylidene-5*H*-furan-2-one **2**

1.78 g (7 mmol) of iodine in 50 mL of diethylether are added dropowise at 0°C to an etheral solution (30 mL) of 2.31 g (6 mmol) of **1a**. The mixture is stirred at 0° C for 1h. Then the organic layer was washed with a 5% solution of sodium thiosulfate (3x15 mL), dried over magnesium sulphate and concentrated in vaccuo. The pure (*E*)-5-iodomethylidene-5*H*-furan-2-one **2** (1.99 g, 90% yield) is obtained and, after 6 hours, quantitatively isomerises into (*Z*)-5-iodomethylidene-5*H*-furan-2-one **2.** (*E*)-**2**: ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 6.41 (1H, s), 6.60 ($1H_3$, d, $^3J_{1H}$ = 5.6Hz), 7.72 ($1H_4$, d, $^3J_{1H}$ = 5.6Hz). (*Z*)-**2**: IR : 3056, 1775, 1753, 1627, 1551, 1290, 1151, 931. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 6.26 (1H, s), 6.34 ($1H_3$, d, $^3J_{1H}$ = 5.4Hz), 7.37 ($1H_4$, d, $^3J_{1H}$ = 5.4Hz). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 63.7, 121.7, 141.2, 156.8, 168.5. MS : m/z = 222 (M, 65), 168 (13), 95 (23), 54 (21), 50 (19), 41 (11), 39 (100), 38 (24), 37 (13). Anal. Calcd for $C_5H_3O_2I$ C, 27.03; H, 1.36; I, 57.18 found C, 27.16; H, 1.35; I, 57.19

General procedure for cross-coupling reactions:

To a DMF (50 mL) solution of the aryliodide (8.4 mmol), 10.1 mmol (3.9 g) of (*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one **1a** diluted in DMF (10 mL) are added dropwise. At the end of the addition, dichlorobis(acetonitrile)palladium (II) (129 mg, 0.5 mmol) is added. The mixture is stirred for 3h at 25°C then hydrolysed with a saturated solution of ammonium chloride. The aqueous layer is extracted with diethylether (3x20 mL). After the usual treatment, the crude products are purified by column chromatography on silica gel (petroleum ether/Et_2O/Et_3N, 88/10/2, as eluent).

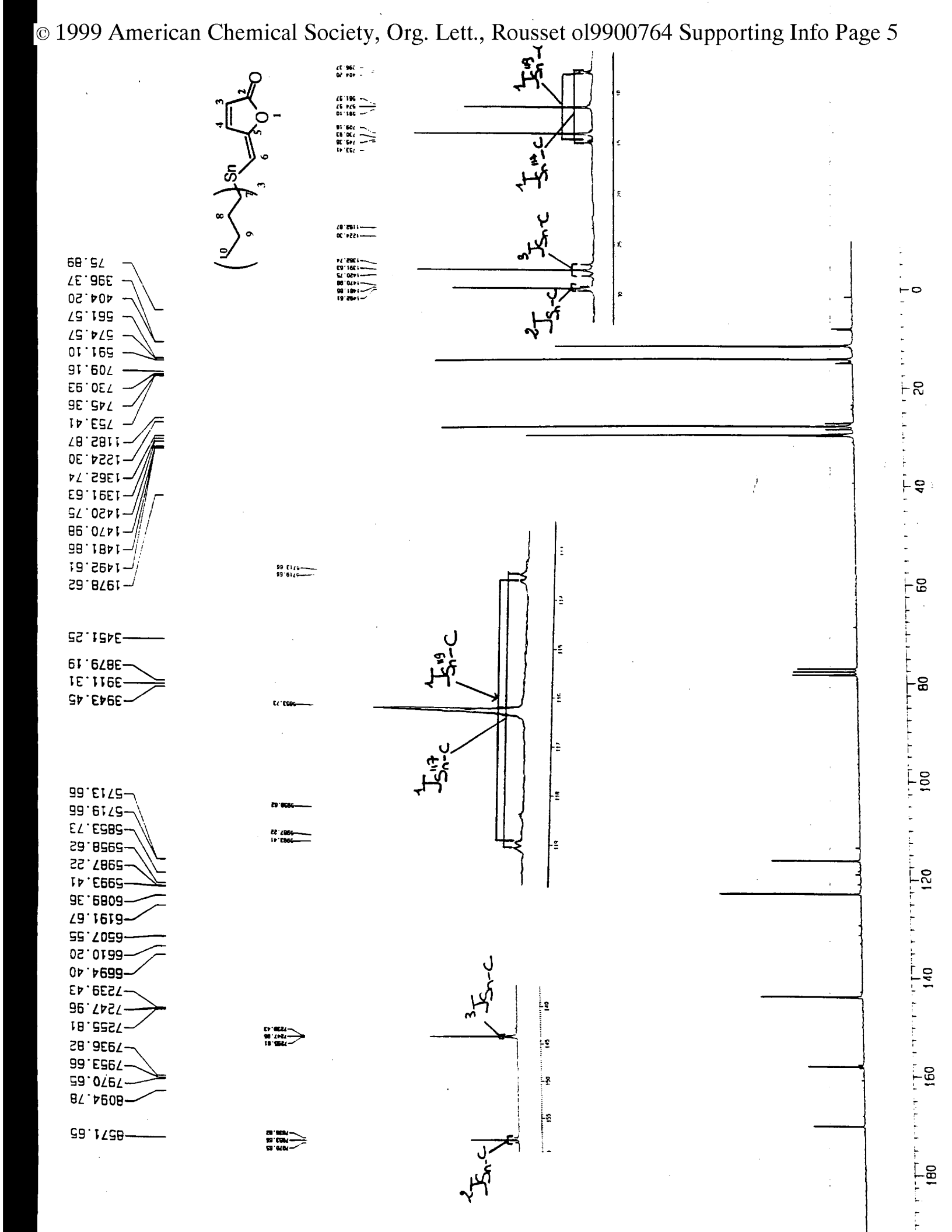
(*Z*)-5-benzylidene-5*H*-furan-2-one **3** (see ref 3b)

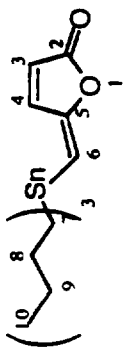
Mp = 82-84 °C. IR : 3117, 3102, 3035, 3028, 3012, 1791, 1762, 1745, 1550, 1438. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 6.08 (1H, s); 6.18 (1H, d, $^3J_{1H}$ = 5.3Hz); 7.30-7.48 (3H, m); 7.47 (1H, d, $^3J_{1H}$ = 5.3Hz); 7.74-7.78 (2H, m). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 114.8, 118.7, 129.4, 129.9, 131.3, 133.4, 145.8, 149, 170.8. MS : m/z = 172 (M, 100), 144 (33), 118 (14), 116 (52), 115 (68), 90 (42), 89 (46), 86 (14), 72 (10), 64 (11), 63 (33), 62 (13), 58 (24), 57 (19), 51 (17), 50 (12), 45 (14), 39 (25), 38 (10)

(*E*)-5-thienylmethylidene-5*H*-furan-2-one **4**

Mp = 104-106 °C. IR : 3115, 3104, 3097, 1792, 1762, 1545, 1435. ^1H NMR (200 MHz) ($CDCl_3$) δ(ppm): 6.31 (1H, d, $^3J_{1H}$ = 5.5Hz), 6.83 (1H, bs), 7.04 (1H, dd, $^3J_{1H}$ = 4.8Hz, $^3J_{1H}$ = 2.9Hz), 7.14 (1H, d, $^3J_{1H}$ = 2.9Hz), 7.38 (1H, d, $^3J_{1H}$

= 4.8Hz), 8.01 (1H, d, $^{3}J_{1H}$ = 5.5Hz). ^{13}C NMR (50.2 MHz) ($CDCl_3$) δ(ppm): 109.9, 121.7, 128.6, 129.0, 131.9, 135.0, 140.4, 149.4, 169.7. MS: m/z = 178(M, 100), 150 (19), 122 (55), 121 (32), 96 (57), 95 (12), 89 (10), 78 (16), 70 (28), 69 (16), 63 (13), 62 (31), 54 (18), 51 (12), 48 (20), 45 (28), 39 (17). Anal. Calcd for $C_9H_6O_2S$ C, 60.67; H, 3.39; found C, 60.87; H, 3.38

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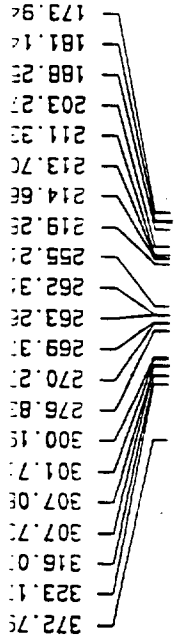

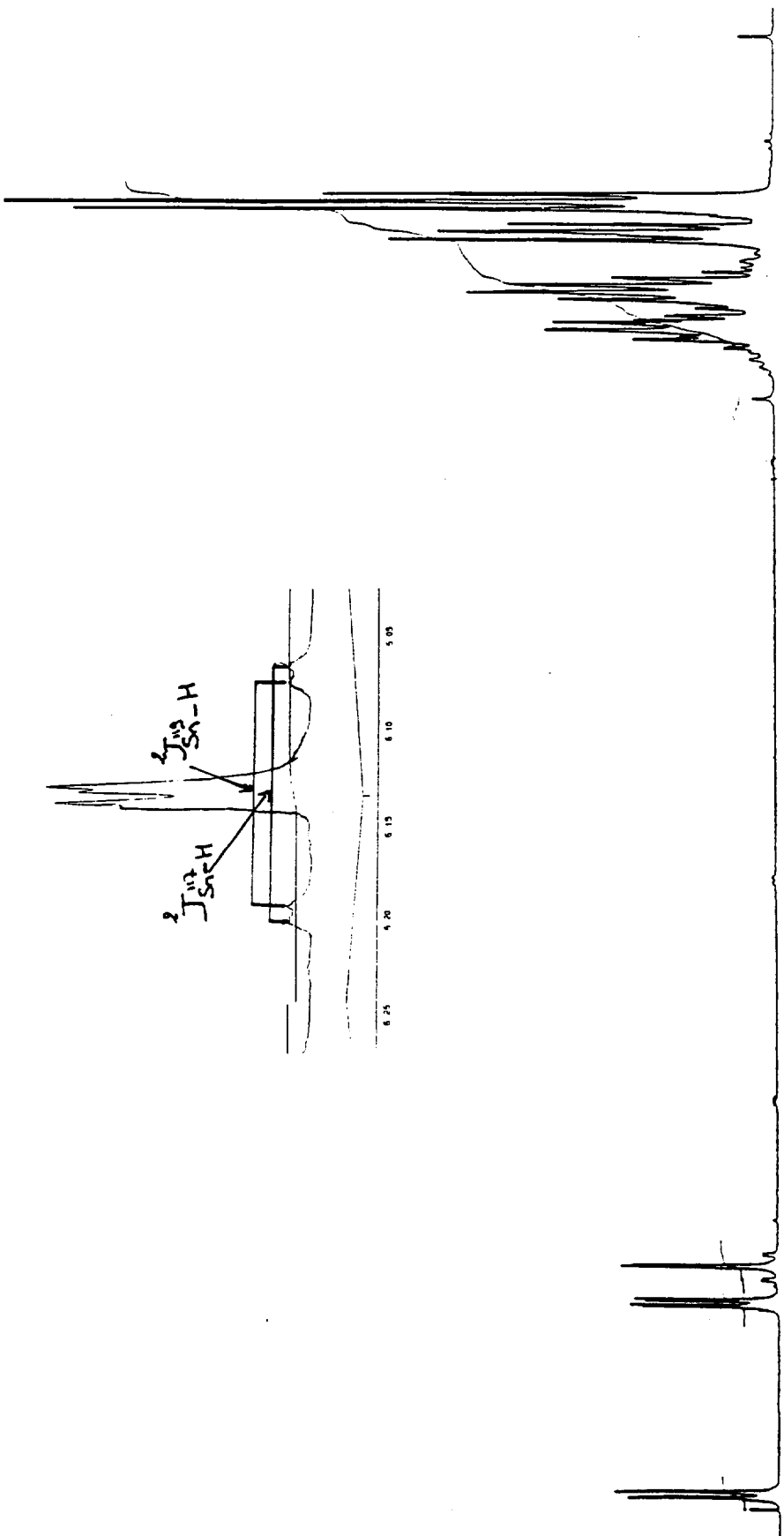

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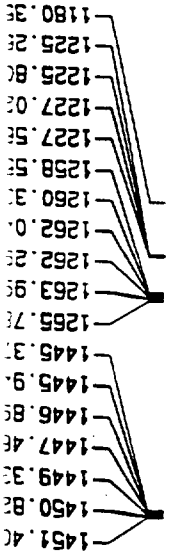
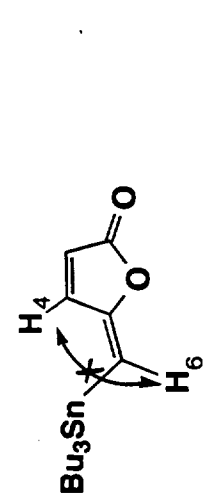
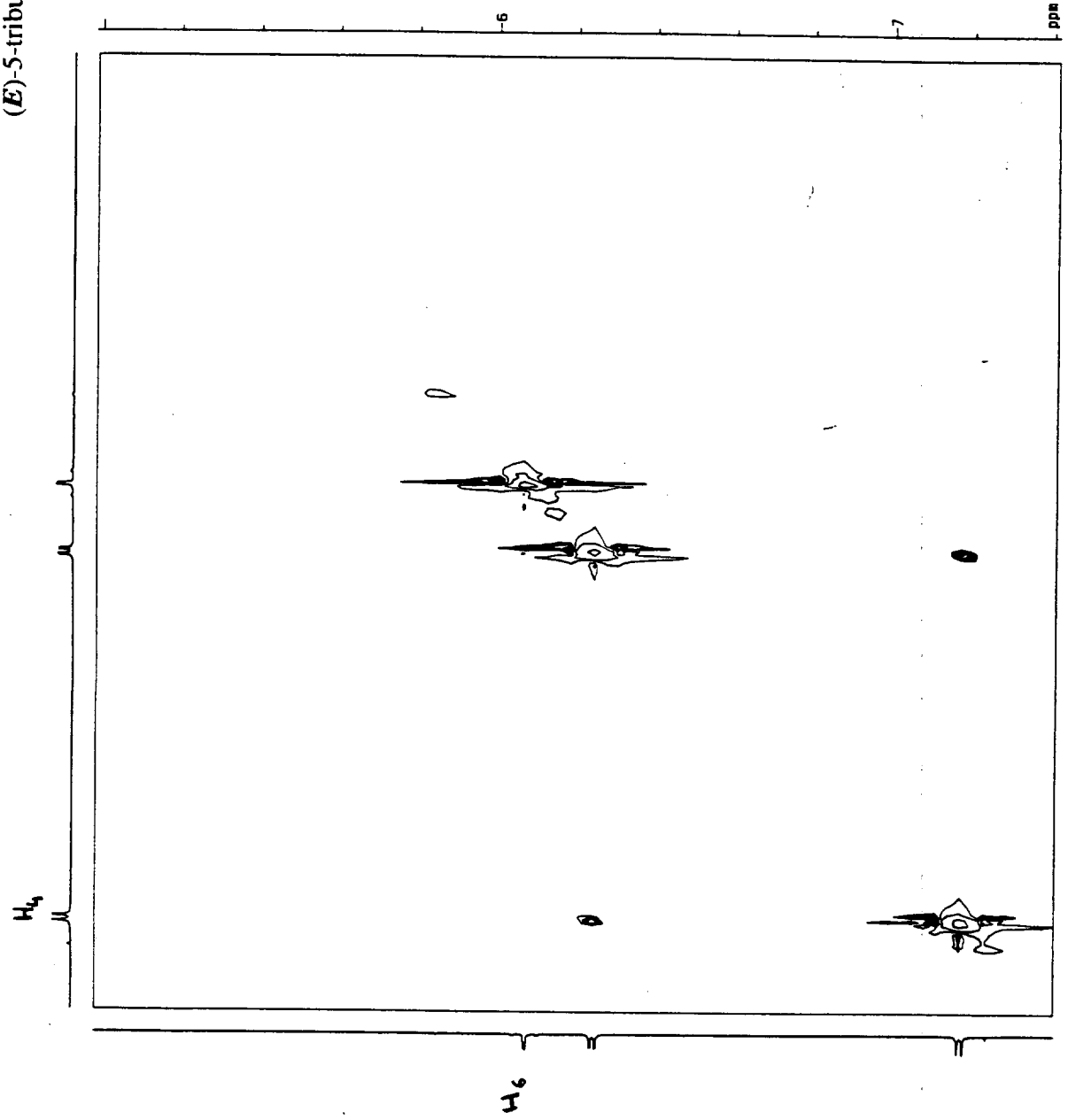
$^2J^{117}_{Sn-H}$





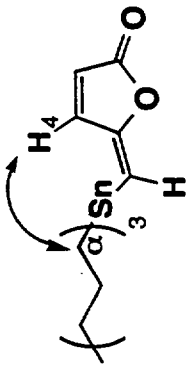
(*E*)-5-tributylstannylmethylidene-*5H*-furan-2-one

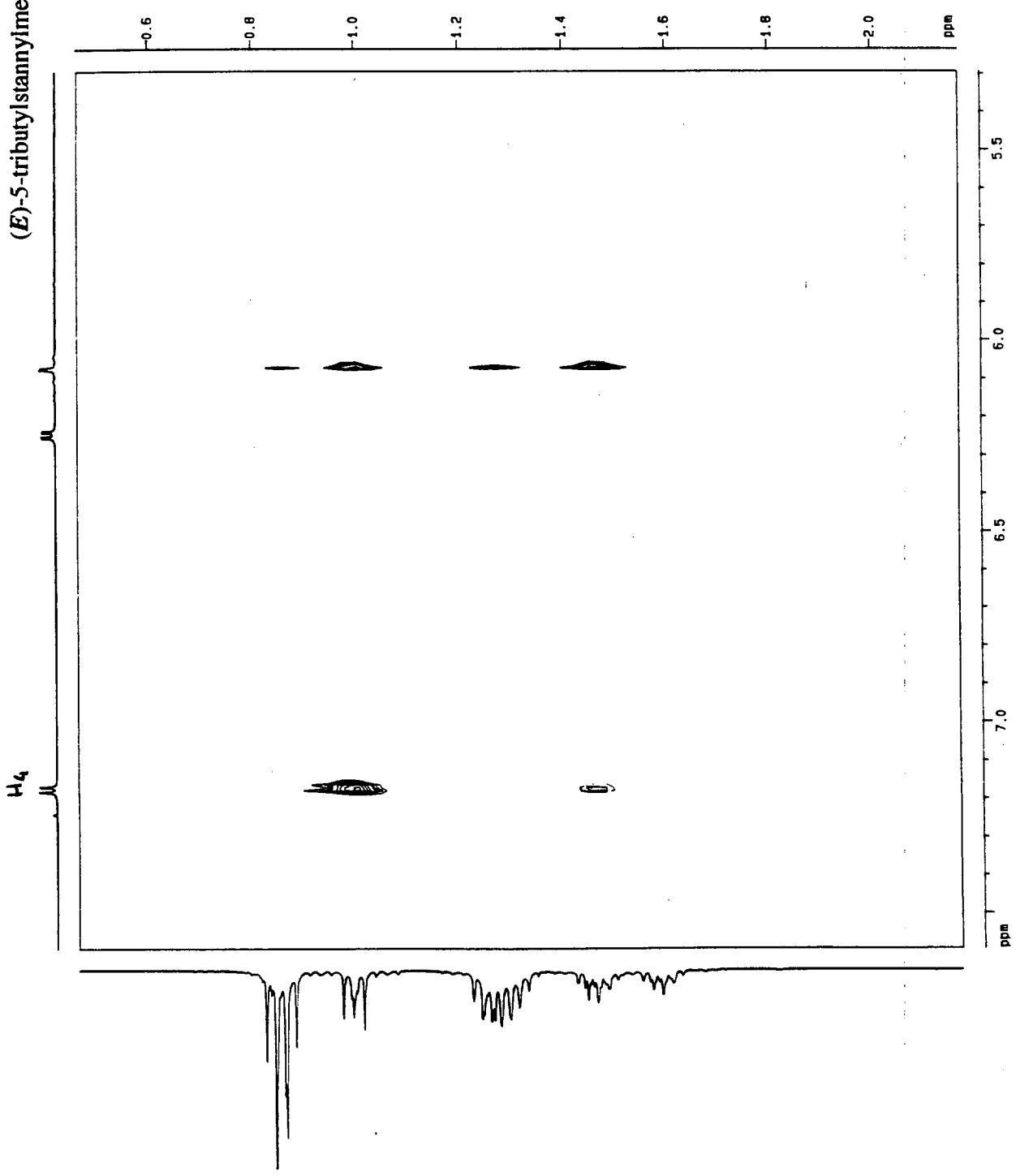
NOESY ($CDCl_3$)



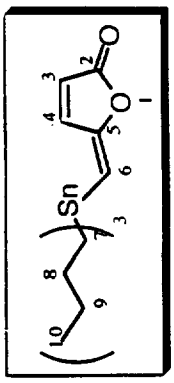
NOESY ($CDCl_3$)

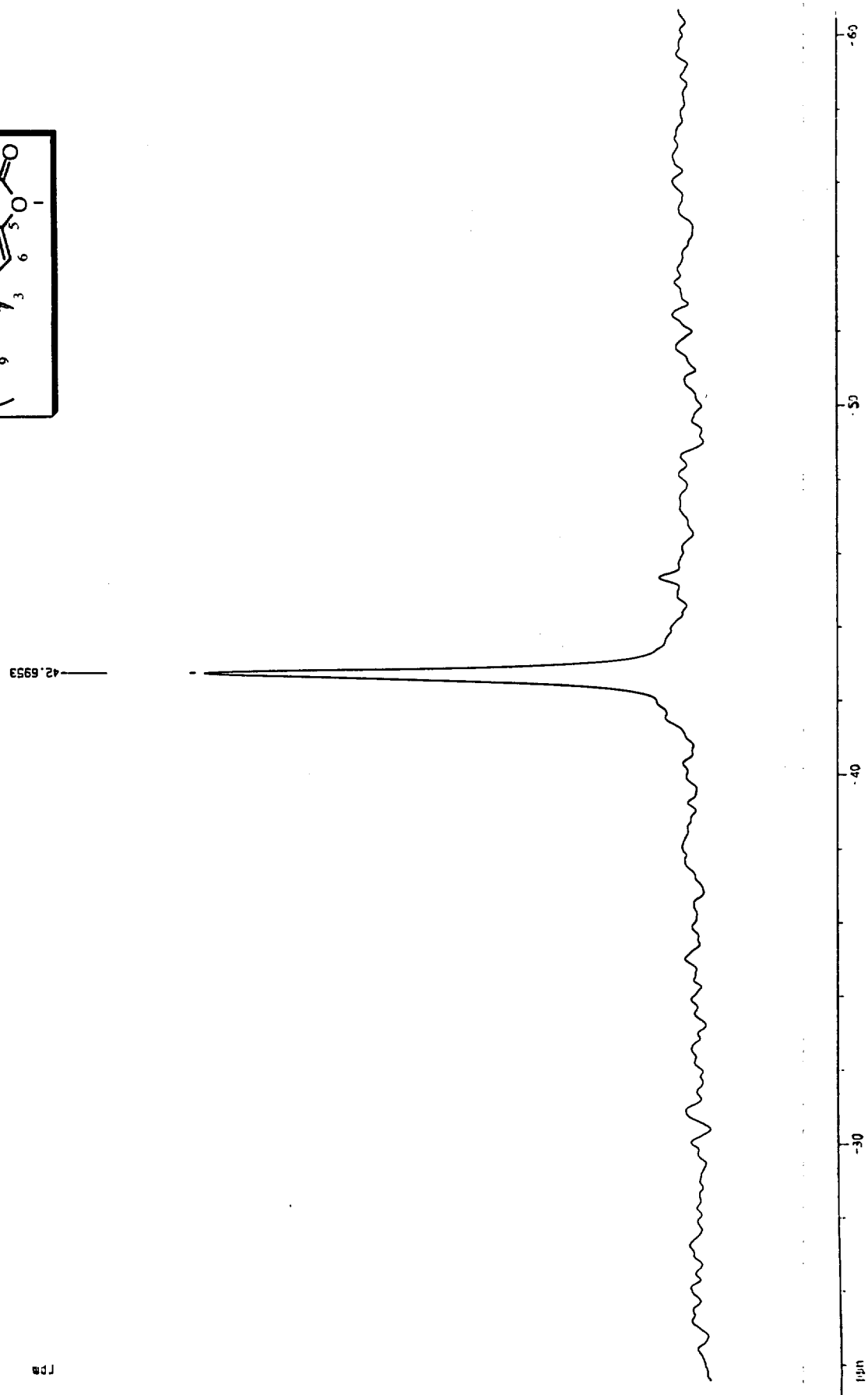
(*E*)-5-tributylstannylmethylidene-5*H*-furan-2-one

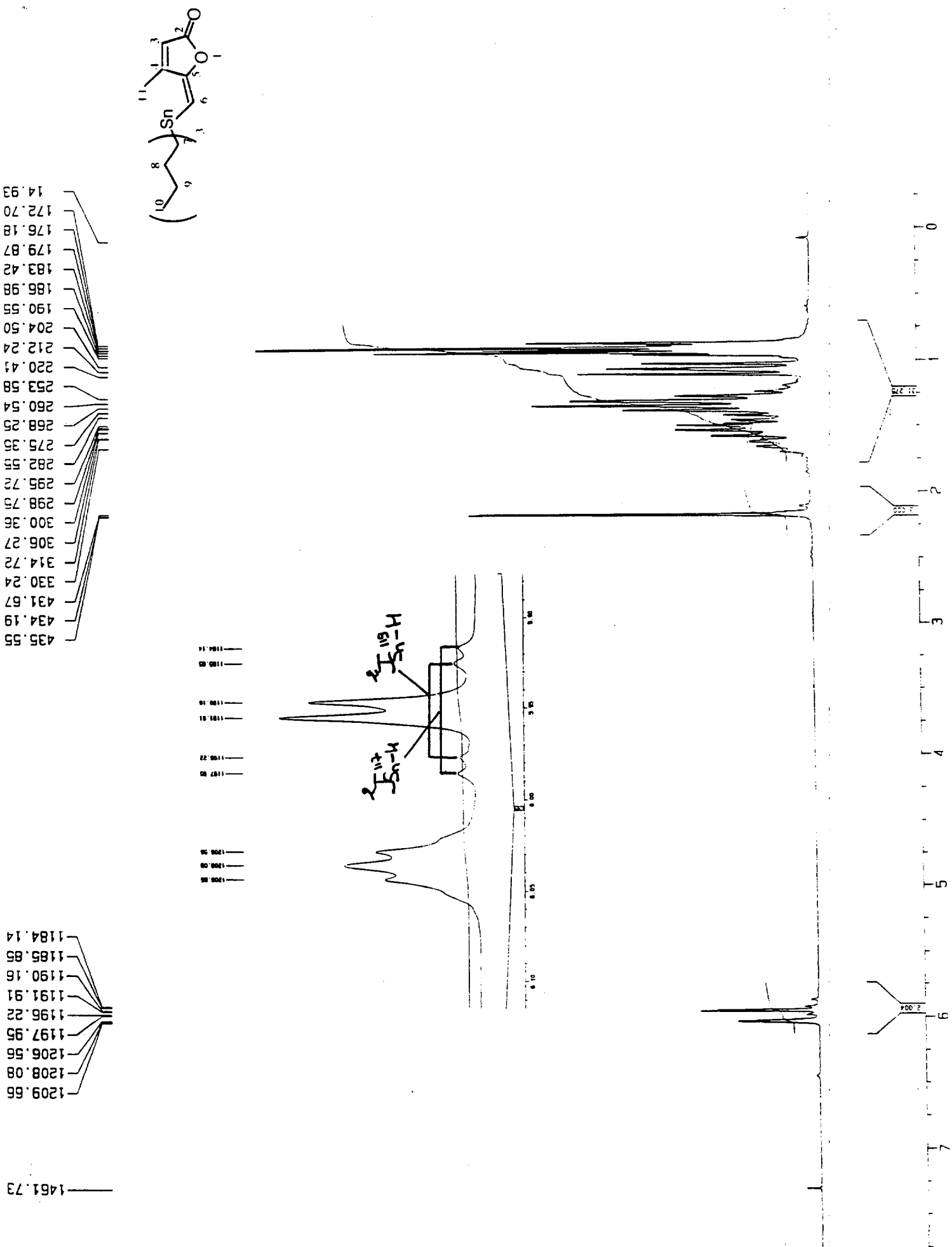


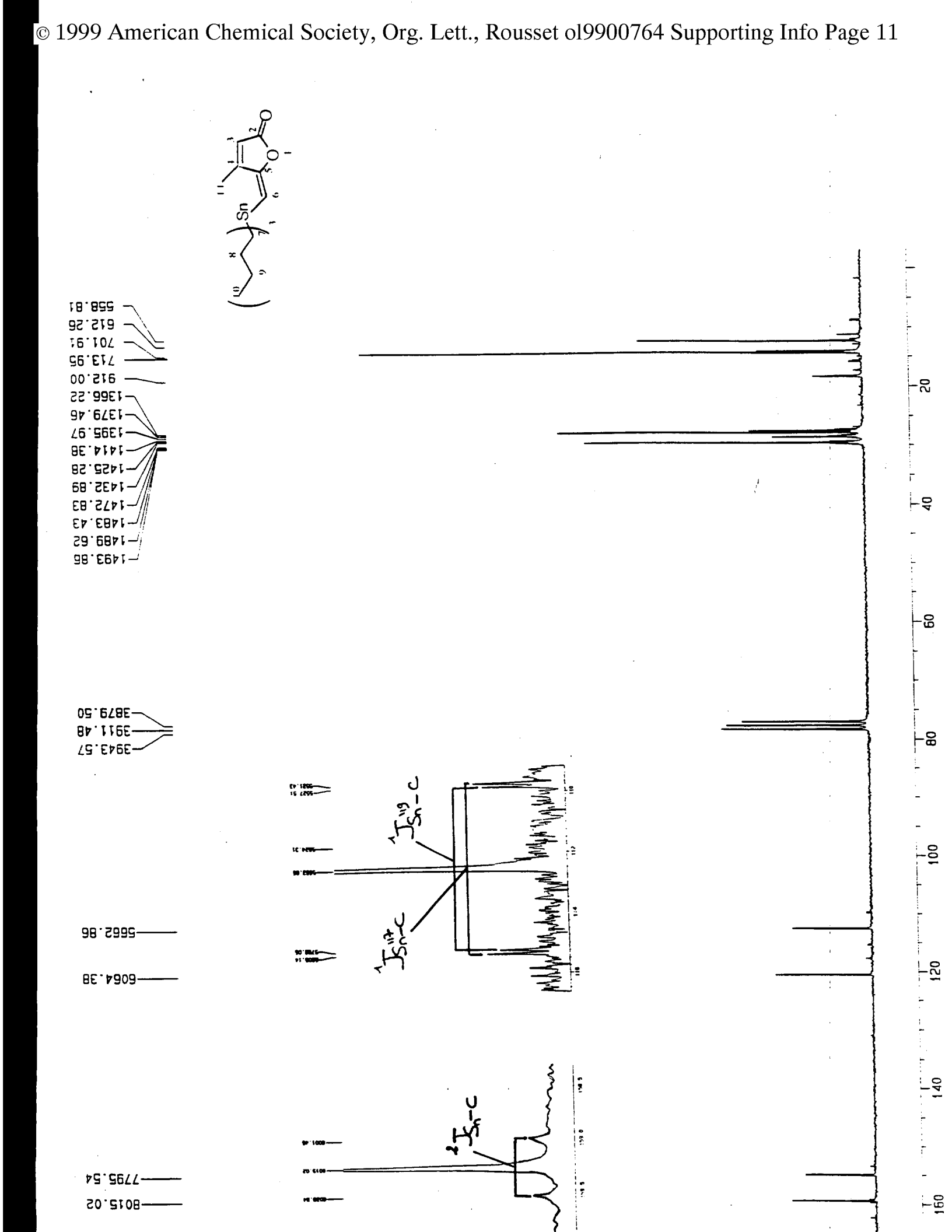


RMN ^{119}Sn ($CDCl_3$)

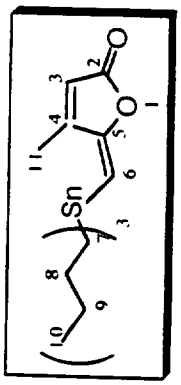


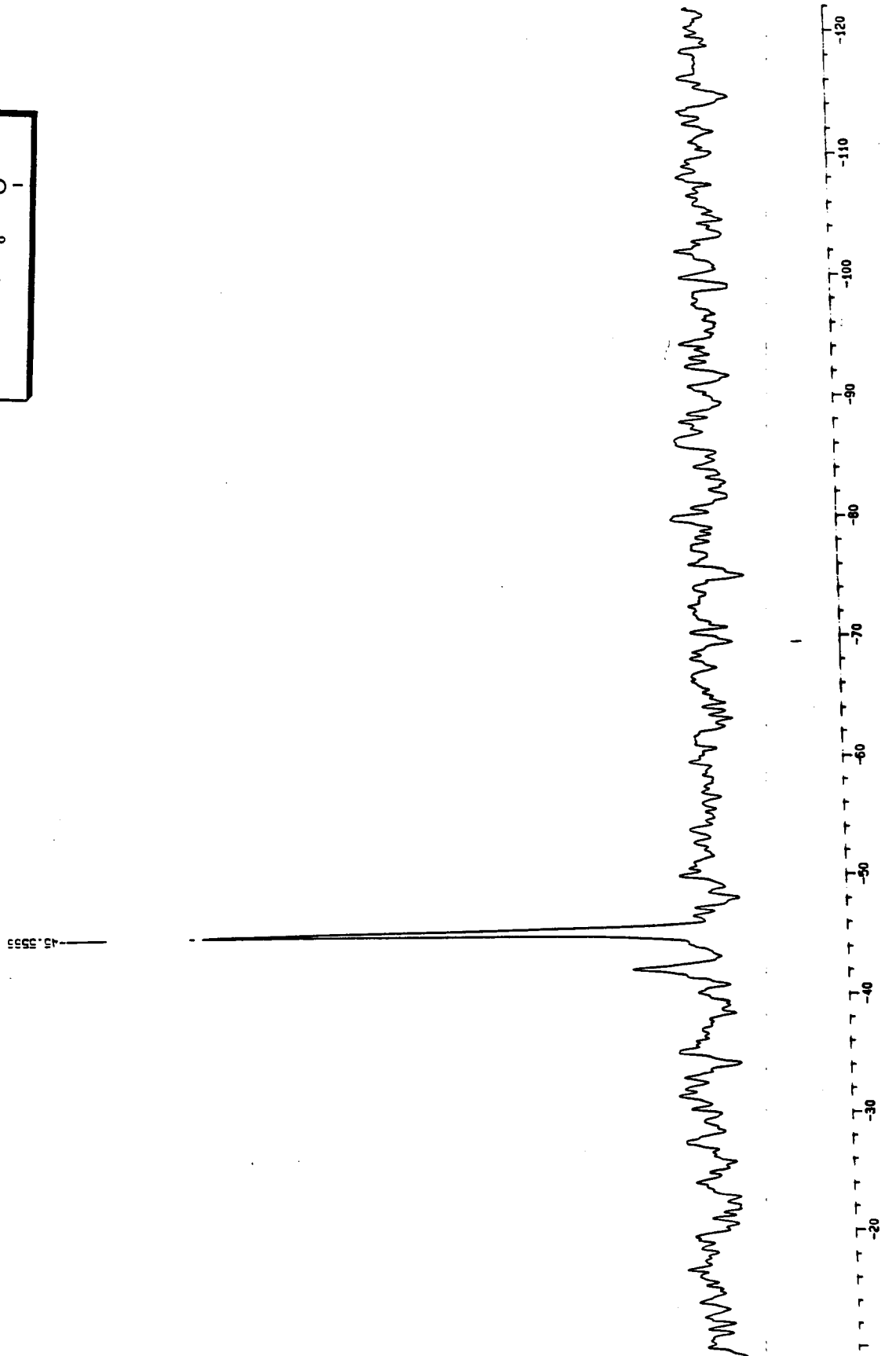


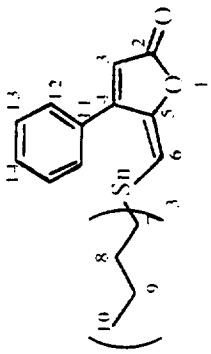


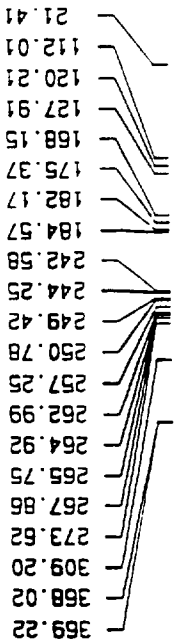


RMN ^{119}Sn ($CDCl_3$)





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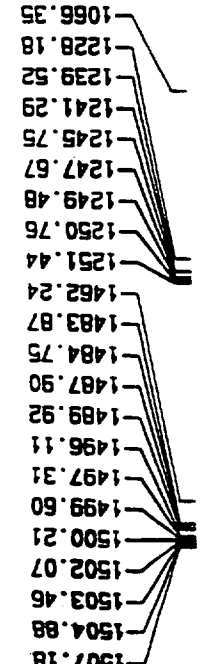
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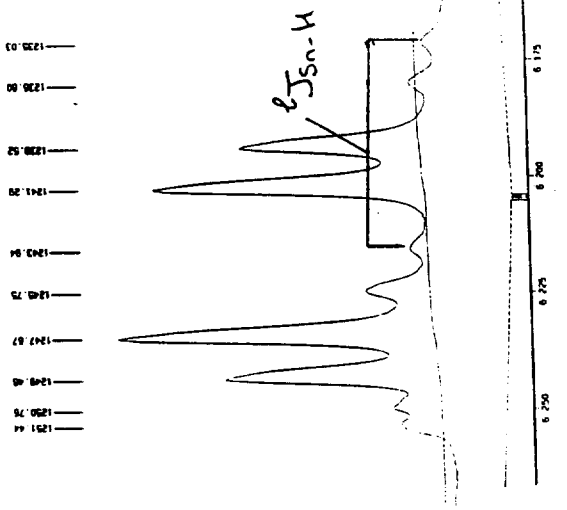
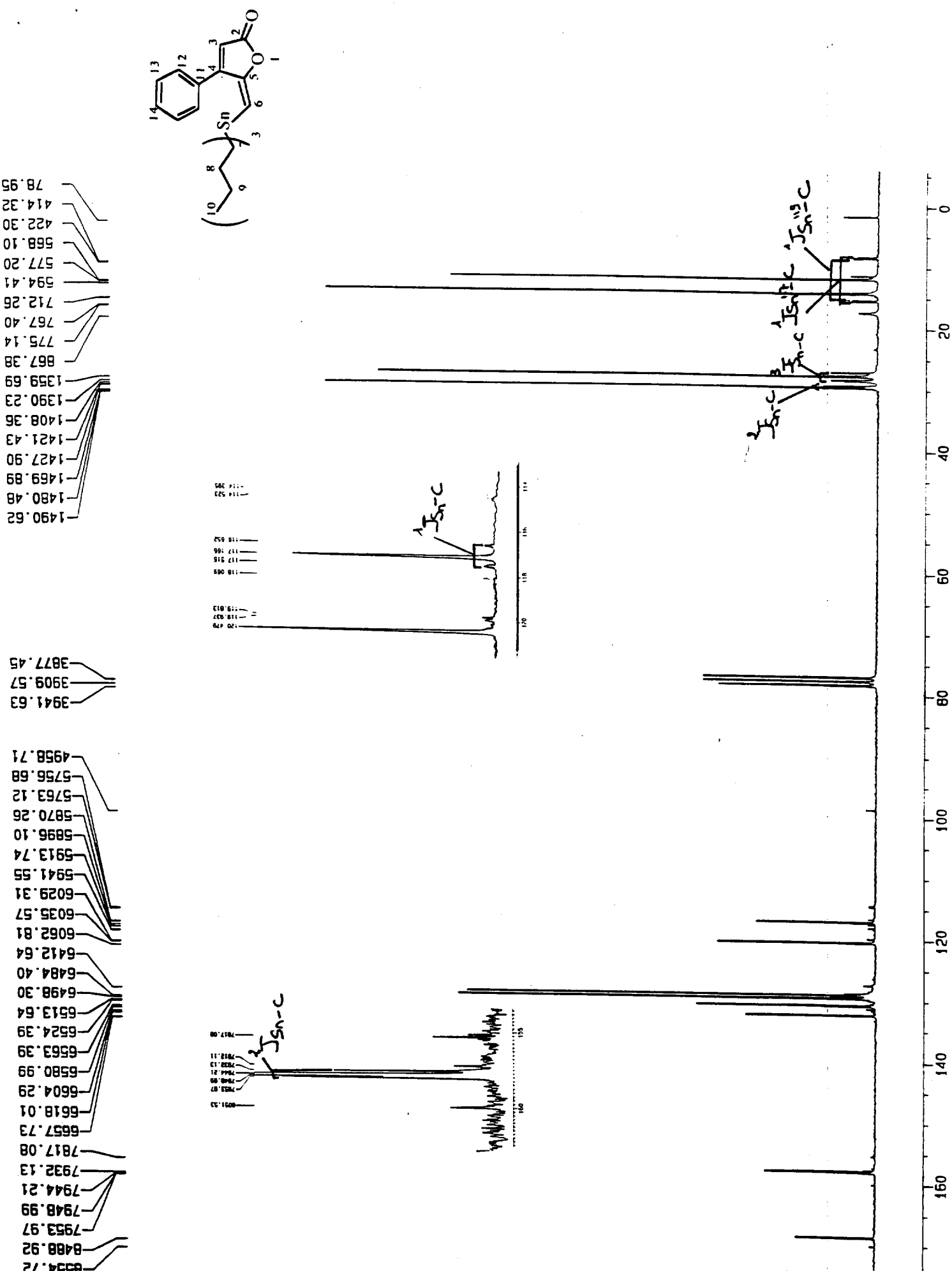
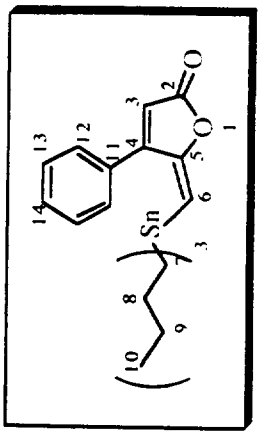
1504.88

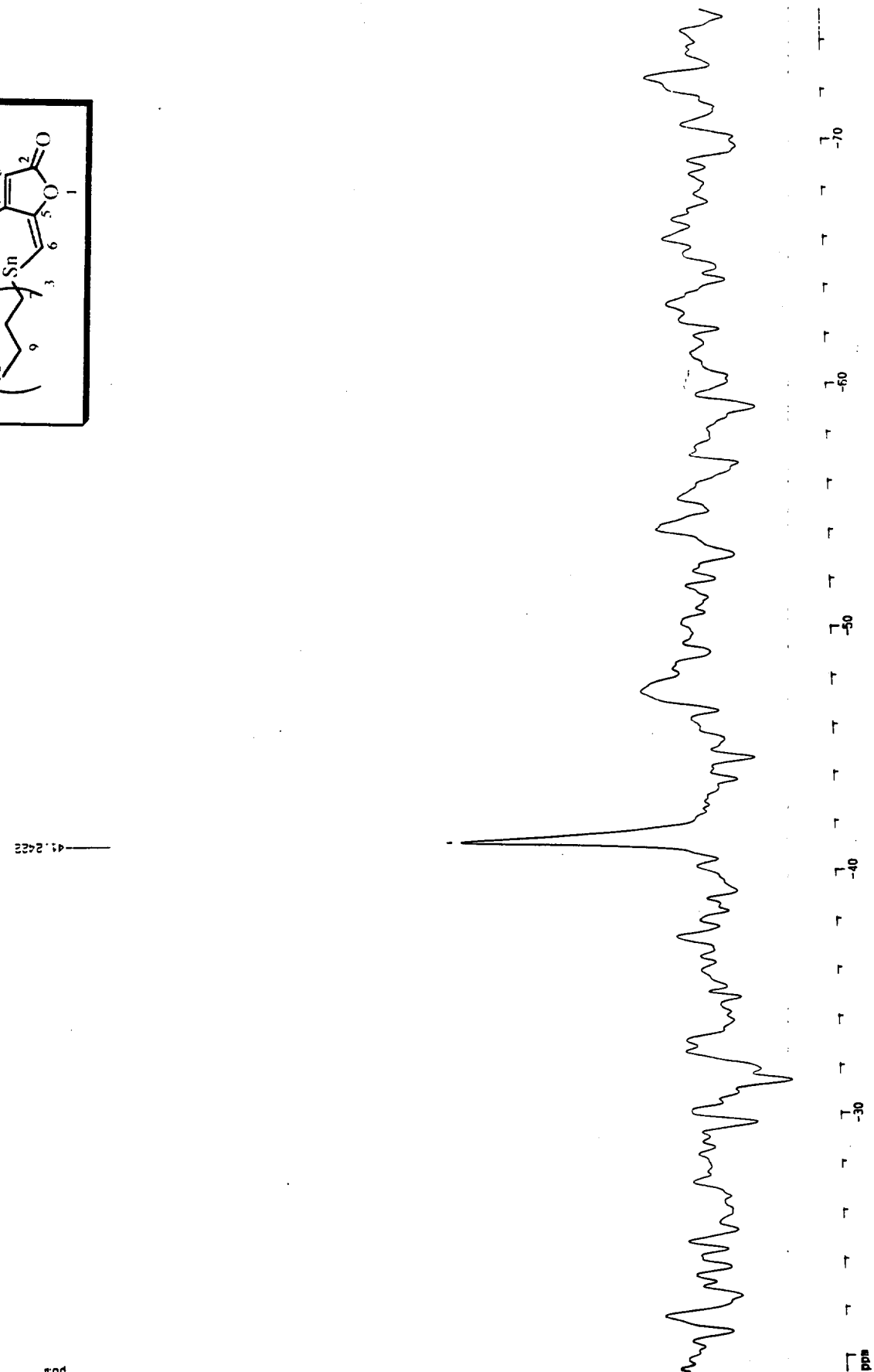

$^{2}J_{Sn-H}$

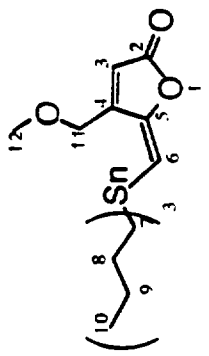
5.994
24.147
2.000
3.224

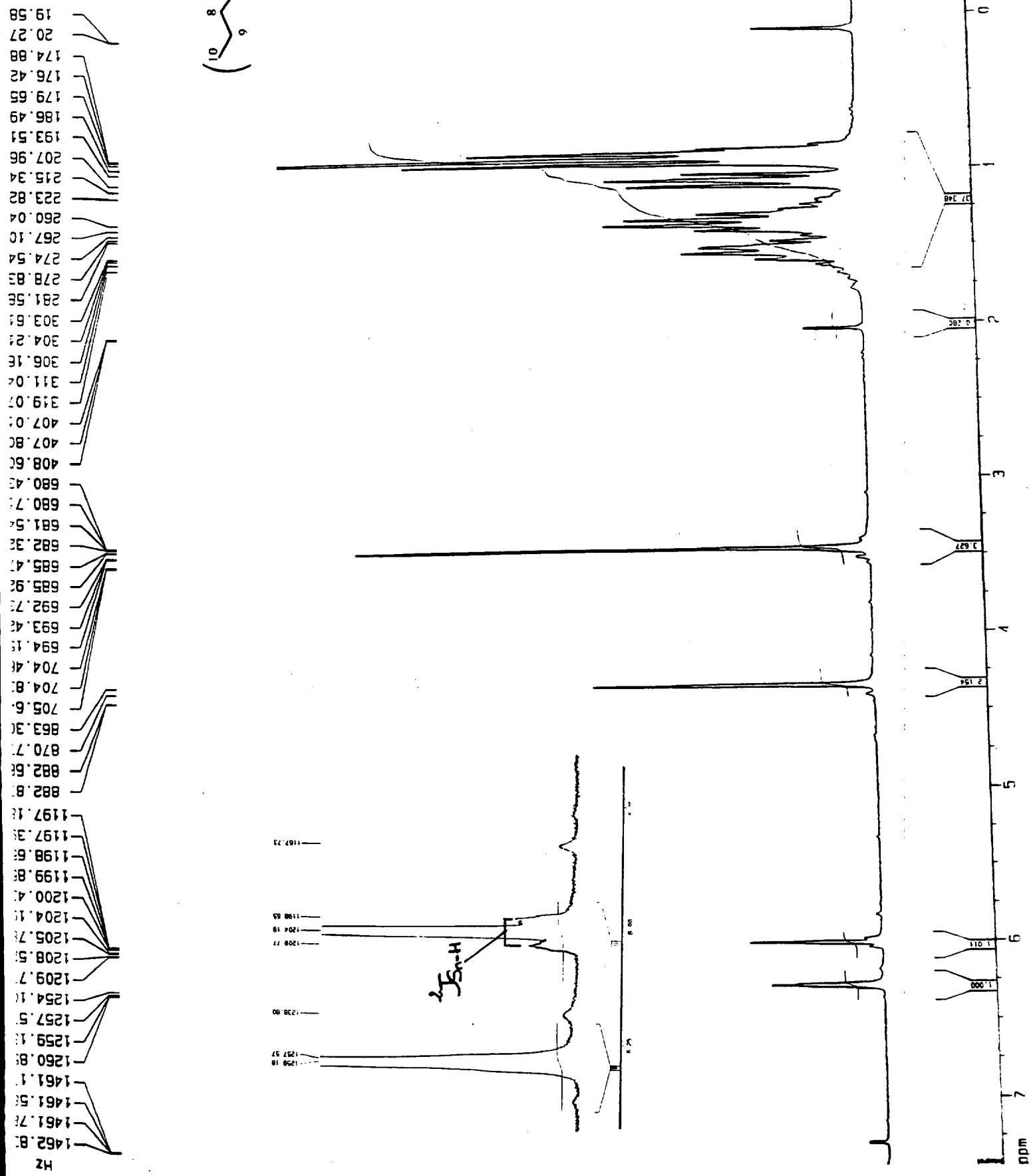


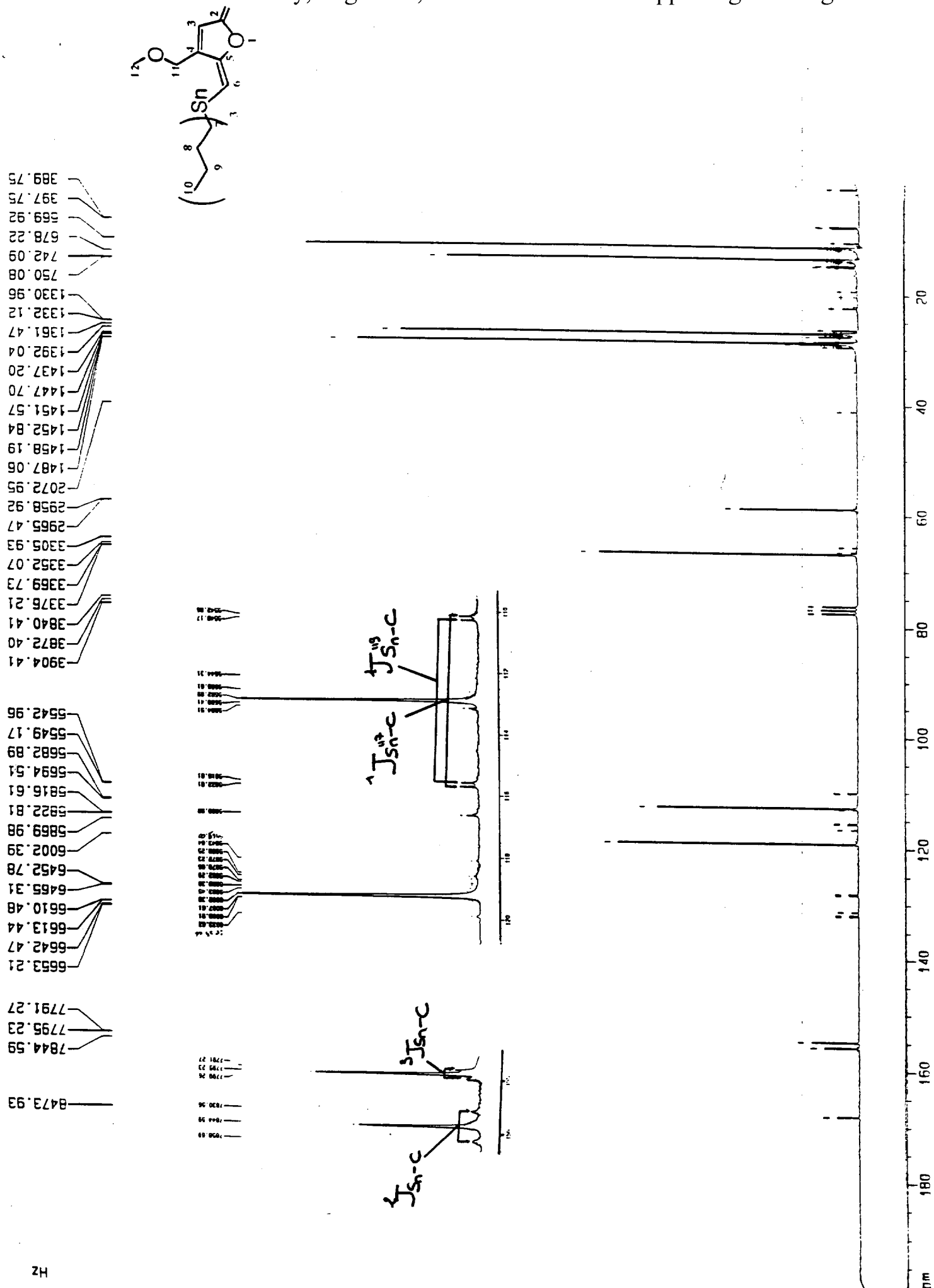
RMN ^{119}Sn ($CDCl_3$)

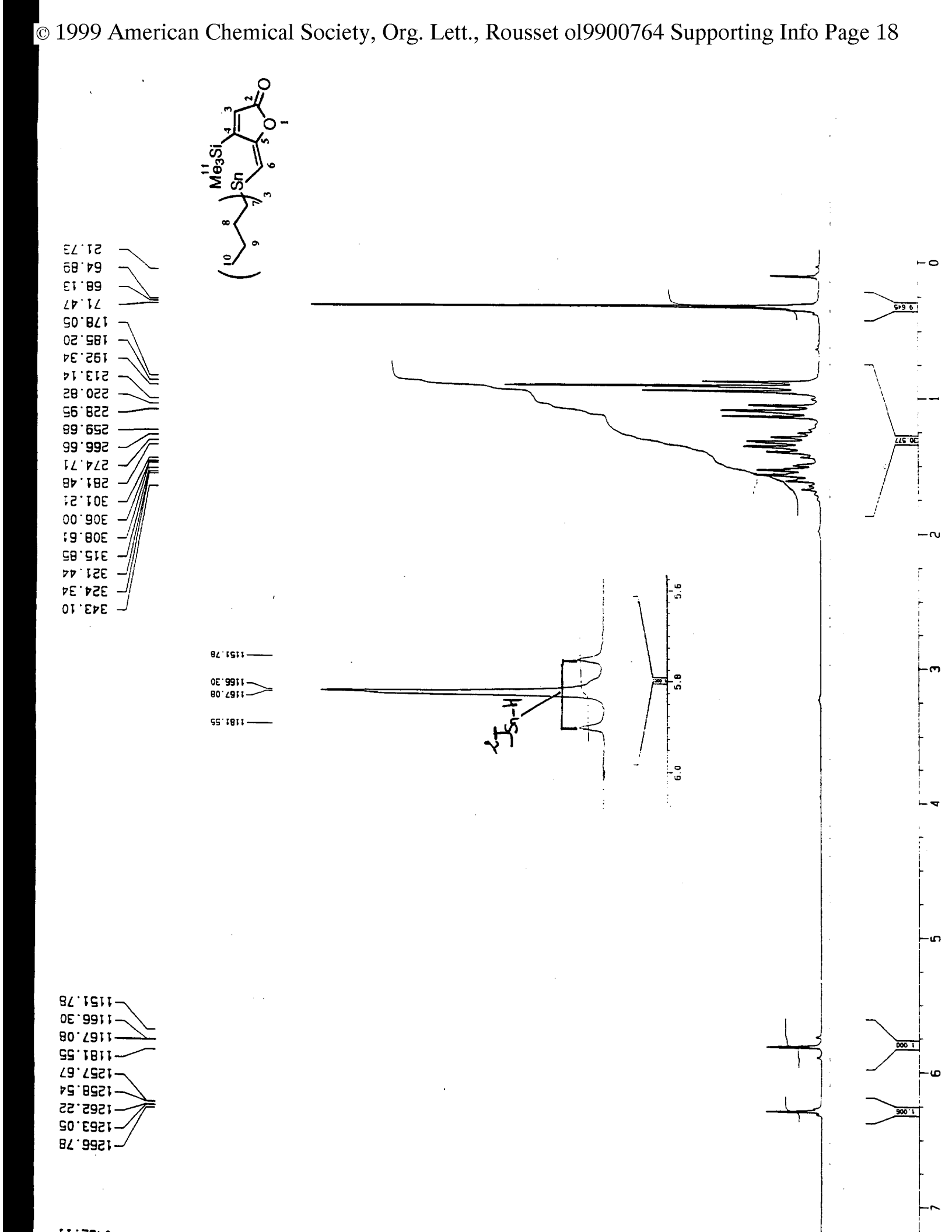


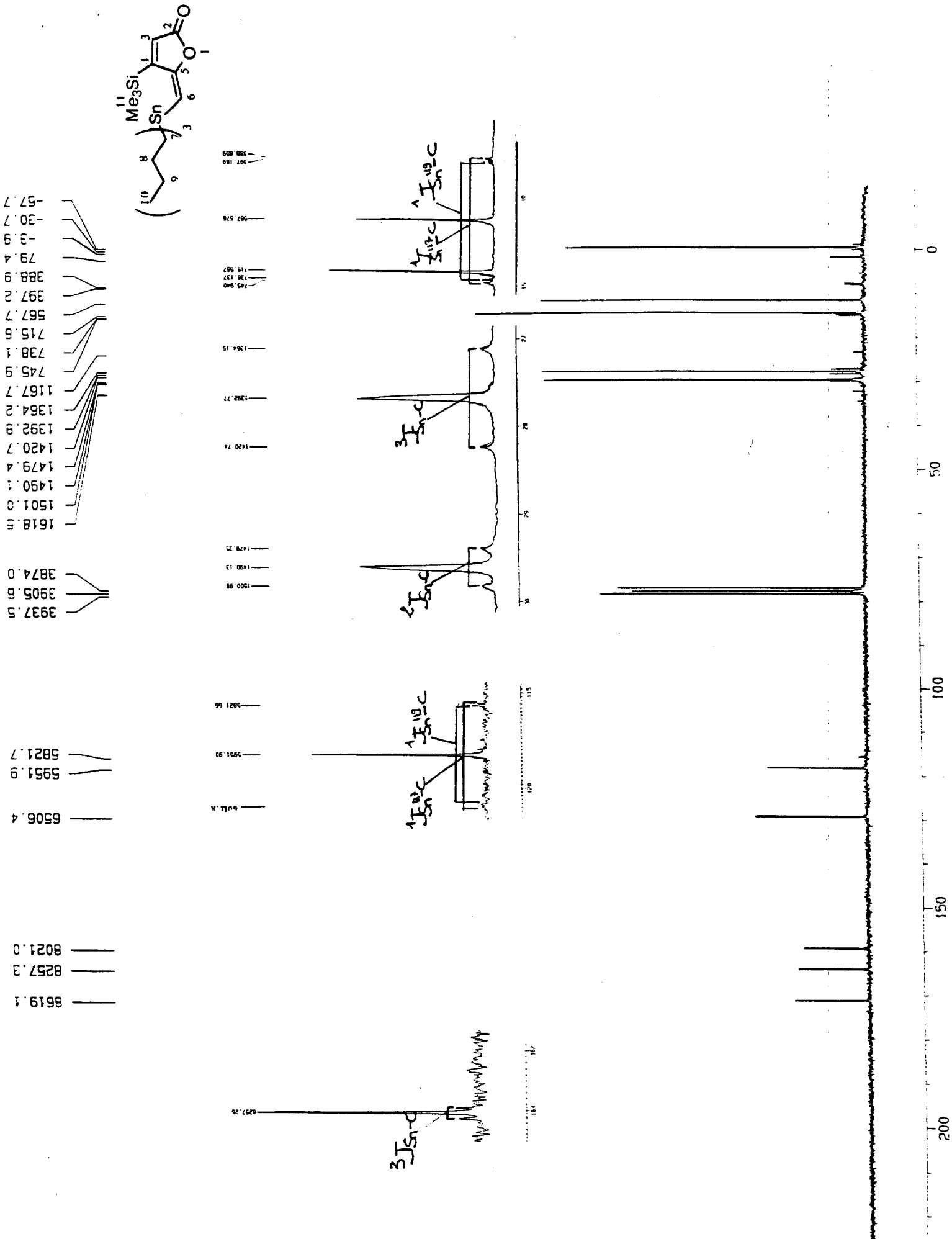




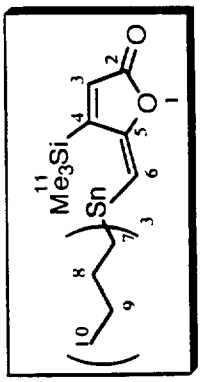


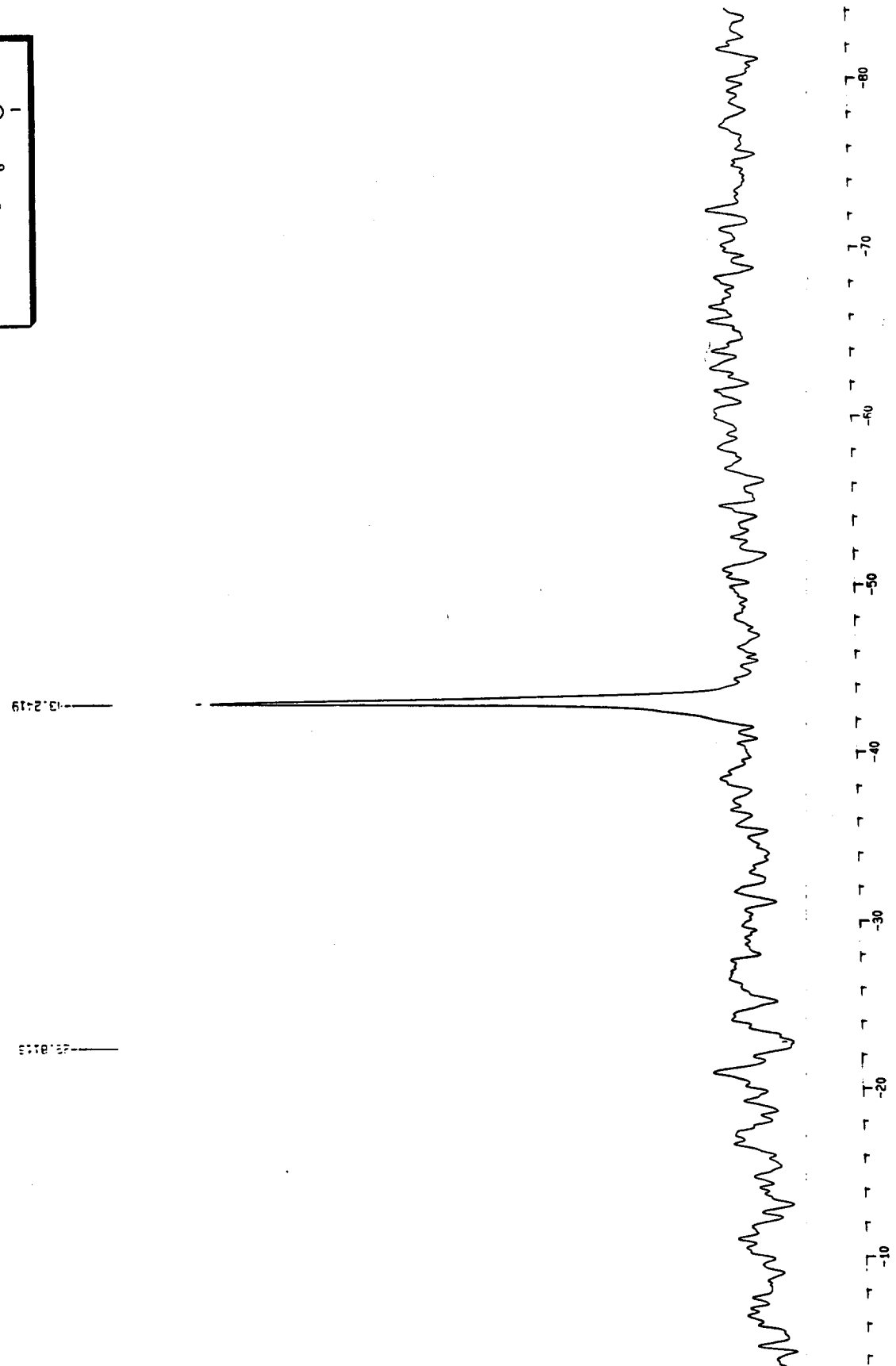


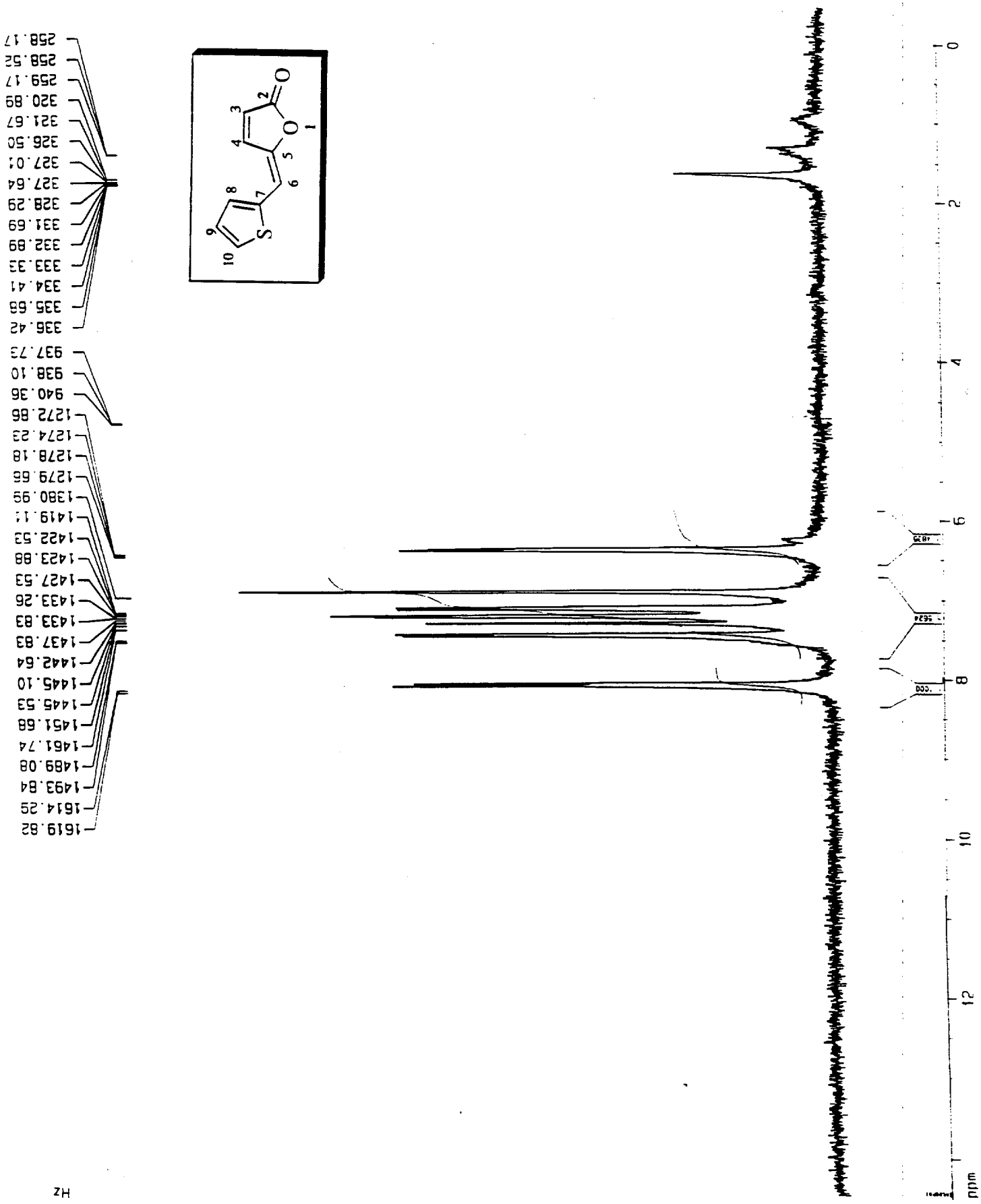


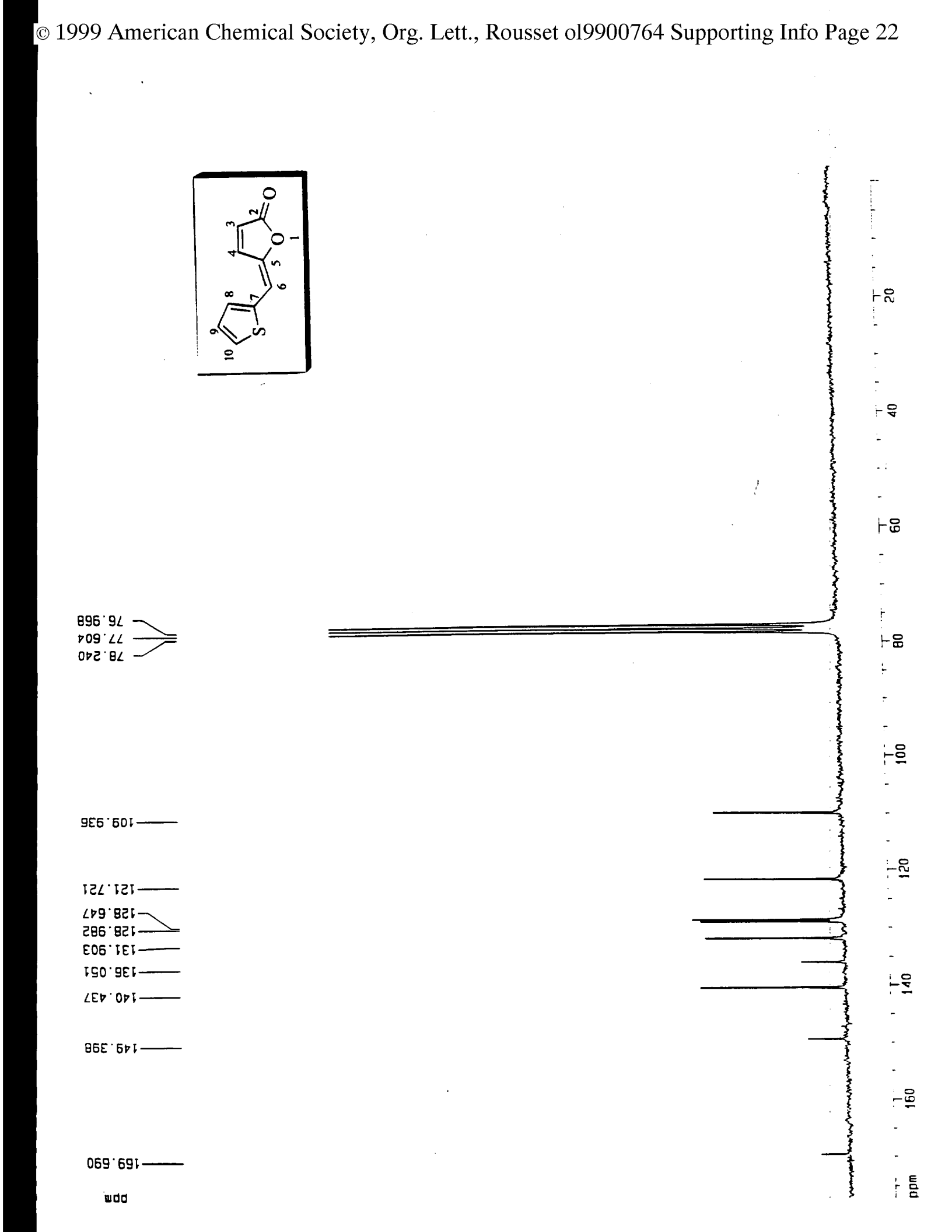


RMN ^{119}Sn ($CDCl_3$)

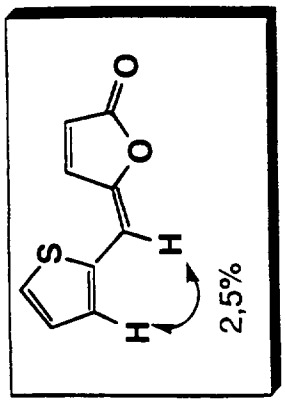


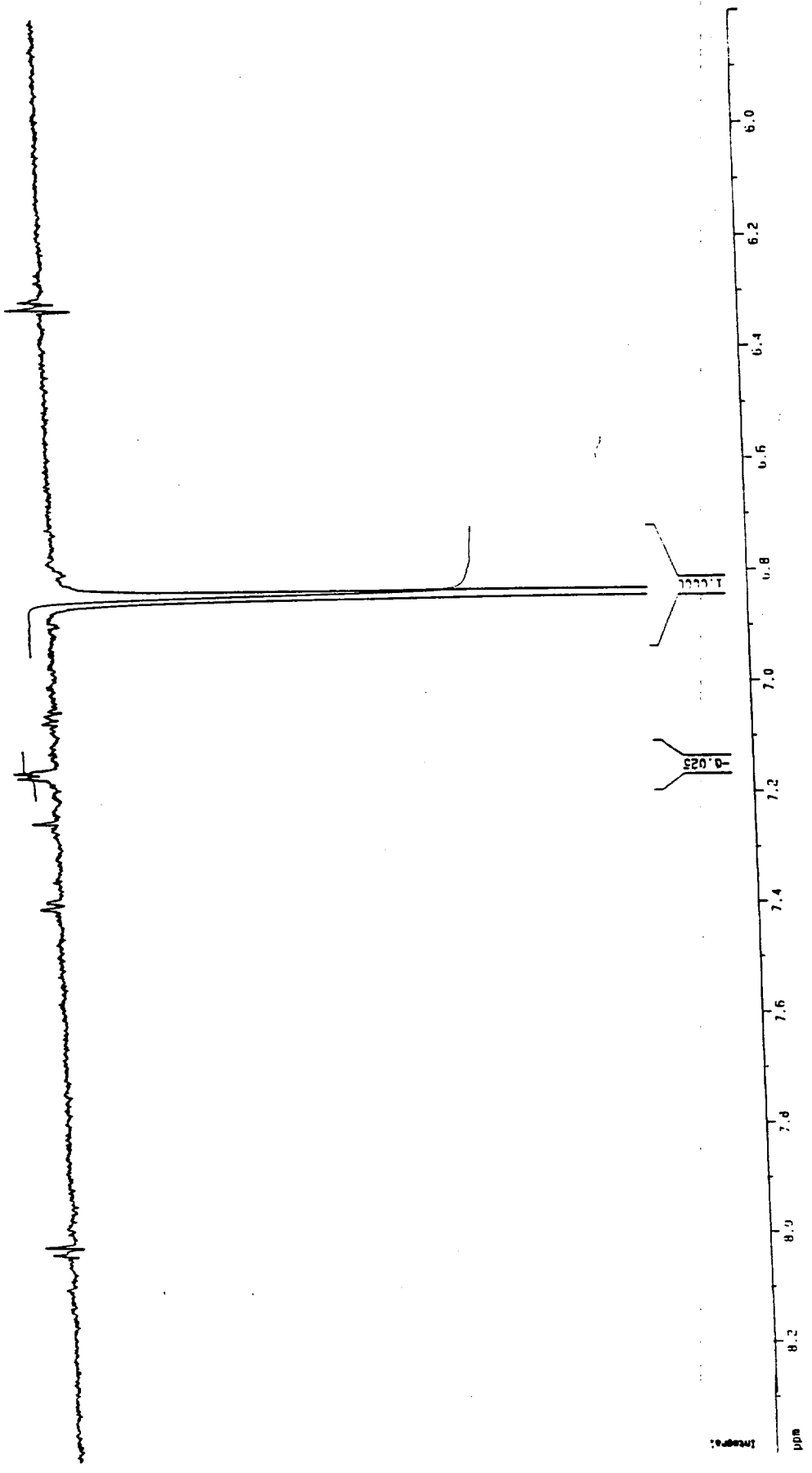


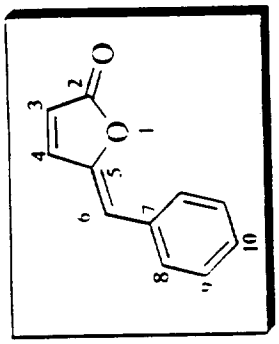


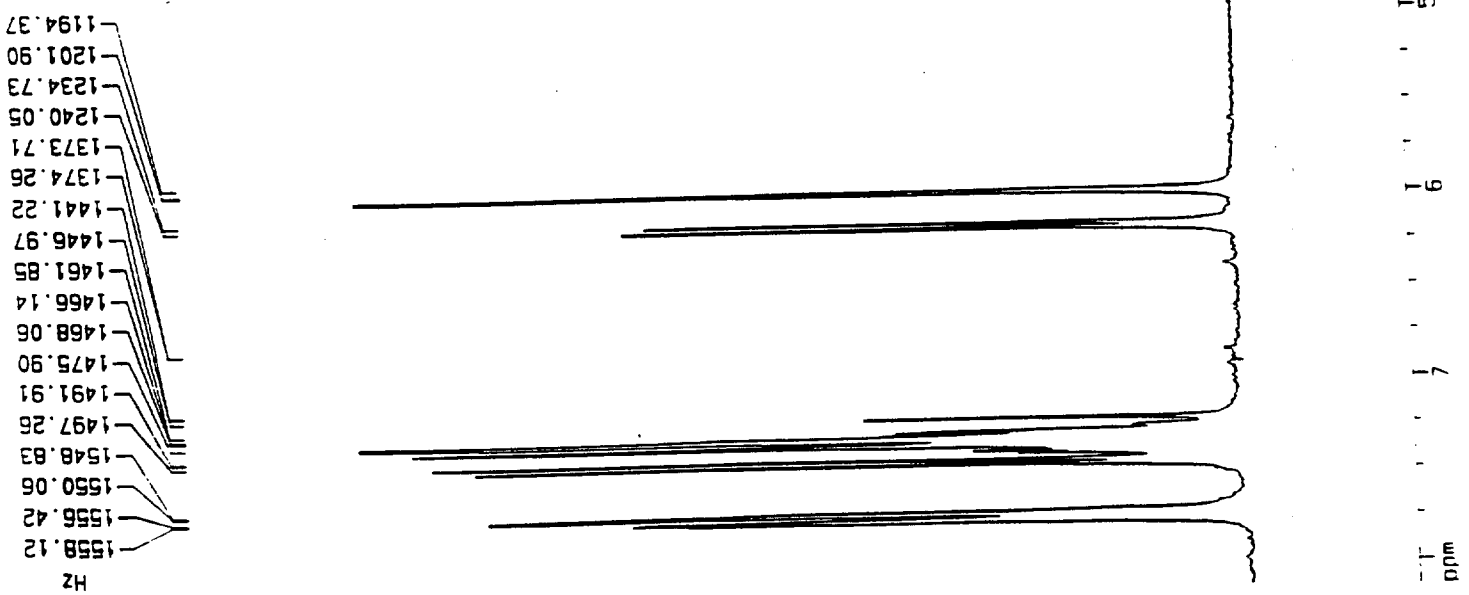


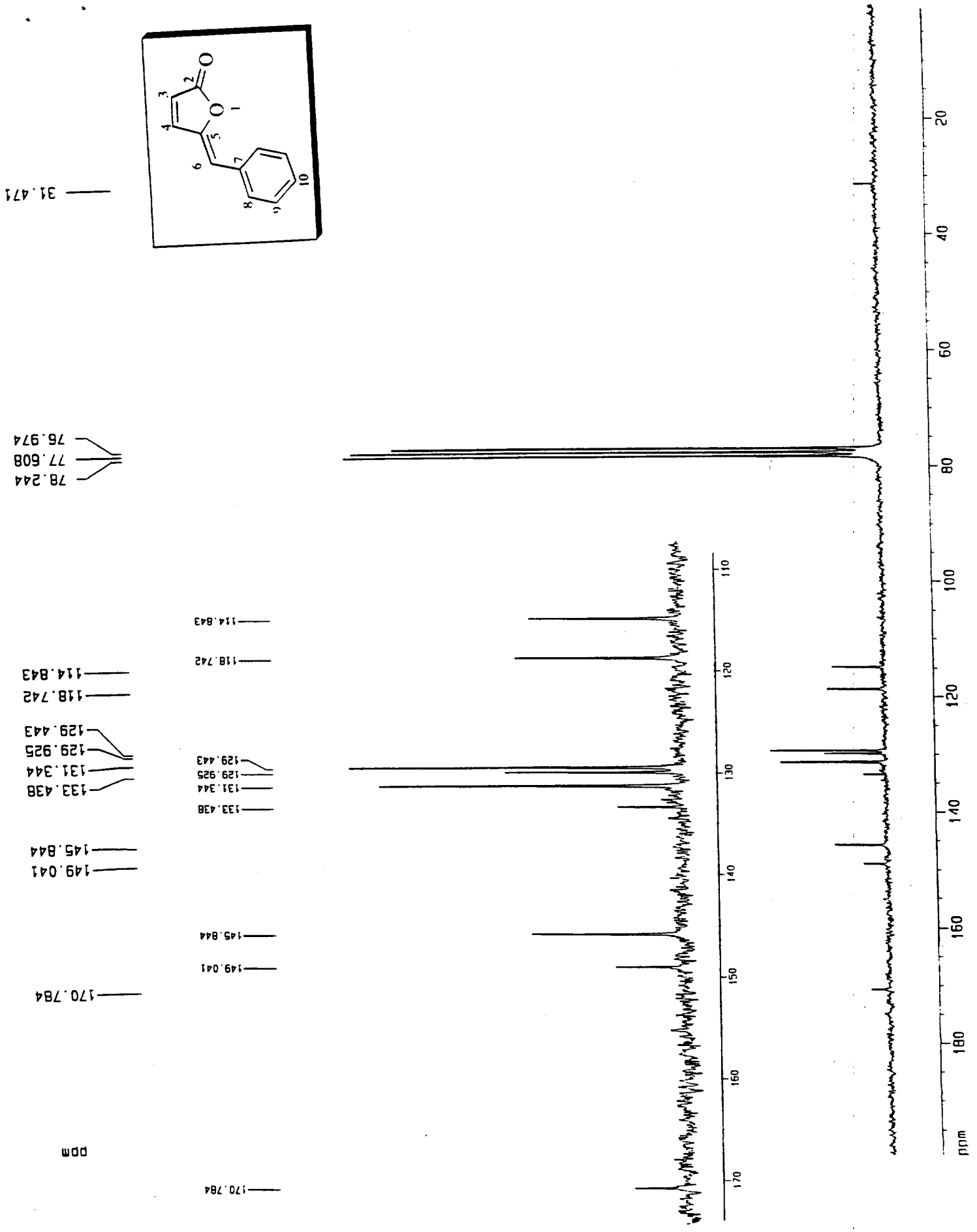
NOE DIFF ($CDCl_3$)

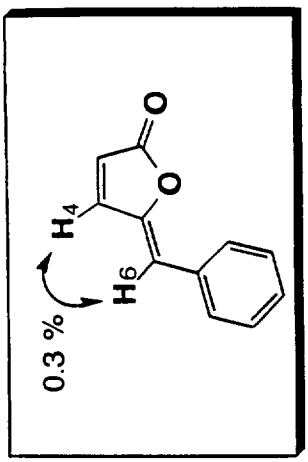












NOE DIFF ($CDCl_3$)