Supporting Information For:

Diaryl Ethers Using Fischer Chromium Carbene Mediated Benzannulation.

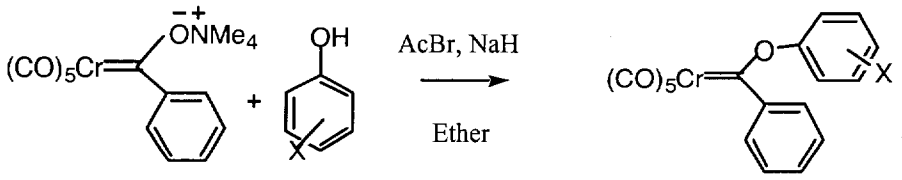
Shon R. Pulley,* Subhabrata Sen, Andrei Vorogushin, and Erika Swanson
Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211-7600

Experimental Section:

General Information: All air or moisture sensitive reactions were carried out in oven dried (120^0 C) or flame dried glassware under an argon atmosphere. Reactive liquids were transferred by syringe or cannula and were charged to the reaction flask through a rubber septa. Diethyl ether and tetrahydrofuran were freshly distilled prior to use from sodium and benzophenone ketyl under nitrogen and methylene chloride was freshly distilled from calcium hydride under nitrogen. Analytical thin layer chromatography was performed with Aldrich silica gel plates (0.25mm thickness) with F_{254} indicator. Compounds were visualized under UV lamp or by staining with potassium permanganate solution and heating to approximately 250^{0}C. Flash column chromatography was carried out using 230-400 mesh silica gel with technical grade solvents which were distilled prior to use. Radial chromatography was performed on plates prepared from Silica gel 60 with PF_{254} indicator.

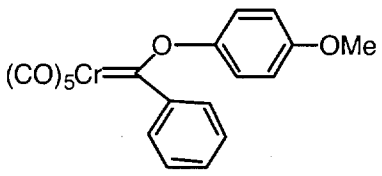
^{1}H-NMR spectra were recorded on a Bruker AMX-250, AMX-300 or AMX-500 at 250, 300 or 500 MHz, respectively. ^{13}C spectra were obtained on the same instruments at 62.9, 75.5 or 125.8 MHz in $CDCl_3$ solutions with tetramethylsilane (^{1}H spectra) or $CDCl_3$ (^{13}C spectra) as an internal reference, unless otherwise stated. Infrared spectra were obtained on a Nicolet 550 Magna FTIR spectrometer as neat oils or thin films. Measurements of optical rotation were performed on Jasco DIP-370 Digital Polarimeter in CH_2Cl_2. Ultrasonic irradiation was carried

out with a high energy sonochemical apparatus from Ace Glass. Elemental Analysis were performed by M-H-W Laboratories (Phoenix AZ). High resolution mass spectra were obtained in house or from University of Nebraska-Lincoln Mass Spectrometry Laboratory.



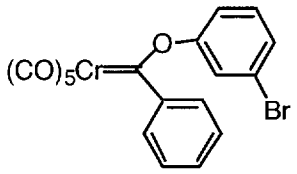
X = 4-t-Bu, 4-OMe, 3-Br

General procedure for Pentacarbonyl [(aryloxy)(phenyl)carbene] chromium(0) 5a-d. To a solution of tetramethyl ammonium salt **3** (R = Phenyl) in CH_2Cl_2, at 0C, was added the AcBr (1.1eq.). The deep red mixture was immediately treated, via cannula, with the appropriate sodium or lithium phenolate (prepared by adding NaH to an Et_2O solution of phenol). The reaction mixture was stirred for 30min. followed by treating the mixture with silica gel and removing the solvent at reduced pressure. The crude product was purified by flash column chromatography on silica gel with 5% EtOAc/Hexane to yield the desired carbenes **5a-d** as a red solid or red oil.

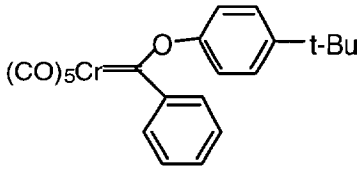


Pentacarbonyl[(4-methoxyphenyl))(phenyl)carbene]chromium(0) 5b. Tetramethyl ammonium salt **3** (0.13g, 0.35mmol), CH_2Cl_2 (6ml), AcBr (0.085g, 0.7mmol), 4-methoxyphenol (0.124g, 1mmol), NaH (0.024g, 1mmol), carbene **5b** (0.05g, 45%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 3.85 (s, 3H), 7.05 (m, 4H), 7.44 (m, 3H), 7.49 (m, 2H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 55.8,

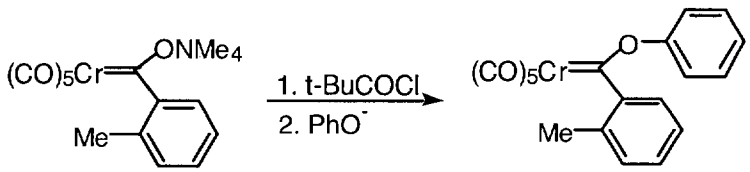
115.3, 122.4, 124.7, 127.9, 131.0, 153.6, 154.5, 158.9, 215.3, 224.9, 352.1; IR (CH_2Cl_2) 3064, 2994, 1957, 1511, 1180, 919cm^{-1}. Carbene characterized and its benzannulation product.



Pentacarbonyl[(3-bromophenoxy)(phenyl)carbene]chromium(0) 5c. Tetramethyl ammonium salt **3** (0.1g, 0.28mmol), CH_2Cl_2 (6ml), AcBr (0.04g, 0.35mmol), 3-bromophenol (0.087g, 0.5mmol), NaH (0.012g, 0.5mmol), carbene **5b** (0.08g, 64%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.13 (d, J = 7.8 Hz, 1H), 7.44 (m, 8H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 120.5, 123.3, 124.9, 125.2, 128.0, 130.5, 131.4, 154.2, 159.6, 215.1, 224.6, 351.6; IR (CH_2Cl_2) 3062, 2992, 1953, 1666, 1290, 938 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_9O_6BrCr$: 451.8988 (^{79}Br); found 451.8961.

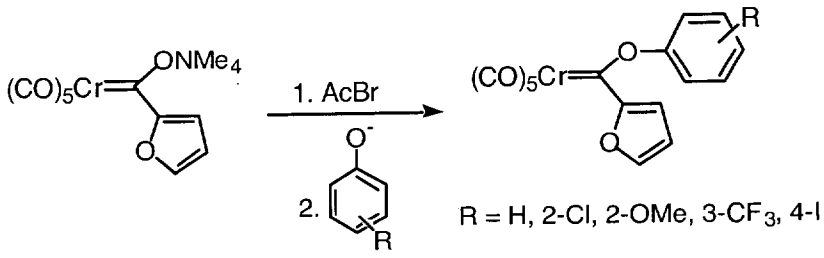


Pentacarbonyl[(4-t-butylphenoxy)(phenyl)carbene]chromium(0) 5d. Tetramethyl ammonium salt **3** (0.13g, 0.35mmol), CH_2Cl_2 (6ml), AcBr (0.049g, 0.4mmol), 4-t-butylphenol (0.075g, 0.5mmol), NaH (0.012g,).5mmol), carbene **5c** (0.06g, 41%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.35 (s, 9H), 7.10 (d, J = 8.5 Hz, 2H), 7.49 (m, 7H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 31.4, 34.7, 120.8, 124.8, 127.3, 127.9, 131.1, 151.1, 154.7, 157.7, 215.2, 225.1, 351.6; IR (CH_2Cl_2) 3061, 2972, 2344, 2065, 1958, 1660, 1507, 1190cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{22}H_{18}O_6Cr$: 430.0509,



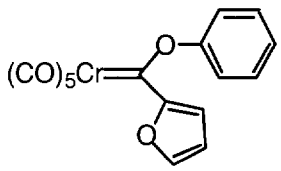
found 430.0472.

Pentacarbonyl[(phenoxy)(toluel)carbene]chromium(0) 6. To the solution of the tetramethyl ammonium salt **3** (0.10g, 0.26mmol) in CH_2Cl_2 (6ml) was added freshly distilled pivaloyl chloride (0.036g, 0.3mmol) followed immediately by the addition of sodium phenolate via cannula{ formed by addition of NaH (0.010g, 0.4mmol) to an ethereal solution (5ml) of PhOH (0.038g, 0.4mmol). Then the solvent was removed *in vacuo* The crude product was purified by flash column chromatography on silica gel with 10% EtOAc/Hexane to yield the desired carbene **6** (0.045g, 45%) as red solid : ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.18 (m, 6H), 7.33 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 19.40, 121.1, 123.6, 125.2, 126.8, 127.4, 128.4, 130.2, 130.5, 154.7, 159.3, 214.9, 224.8, 360.9; IR (CH_2Cl_2) 3949, 3059, 2989, 2695, 2304, 1716, 916 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{19}H_{12}O_6Cr$: 388.0039, found 387.9942.

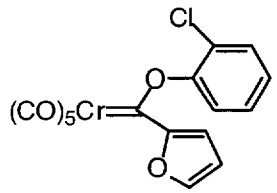


General Procedure to synthesise Pentacarbonyl [(aryloxy)(furyl)carbene] chromium(0) 7a-e. To a solution of tetramethyl ammonium salt **3** (R = Furyl) in CH_2Cl_2, at rt., was added AcBr. The deep purple reaction mixture was immediately treated with the appropriate solution of sodium phenolate (prepared by adding NaH to an ethereal solution of phenol). When the reaction mixture turned completely red the solvent was removed *in vacuo* and the crude product was purified by flash column chromatography on silica gel with 5% EtOAc/Hexane to yield the

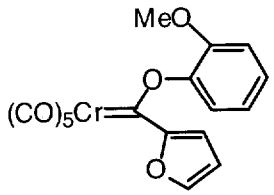
desired carbene as red solid. The carbenes **7a-e** were characterized as their benzannulation products.



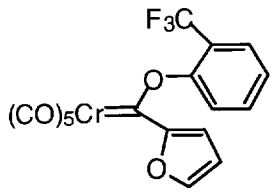
Pentacarbonyl[(phenoxy)(furyl)carbene]chromium(0) 7a. Tetramethyl ammonium salt **3** (0.094g, 0.26mmol), CH_2Cl_2 (4ml), AcBr (0.037g, 0.3 mmol), NaH (0.012g, 0.5mmol), PhOH (0.047g, 0.5mmol), Ether (6ml), carbene **7a** (0.0965g, 94%): R_f = 0.51 (25% EtOAc/Hexanes); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.95 (s,1H), 7.53-7.47 (m,2H), 7.42-7.39 (d, *J* =7.22 Hz, 1H), 7.23-7.20 (d, *J* = 8.21Hz, 2H), 7.13-7.11 (d, *J* =3.58 Hz, 1H), 6.67 (m, 1H).); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 313.0, 224.6, 216.3, 165.2, 158.6, 151.1, 129.9, 127.0, 122.6, 113.4, 112.8; IR ($CDCl_3$) 1992, 1931, 1536, 1226, 1124, 1195, 1087, 1026, 969cm^{-1}.



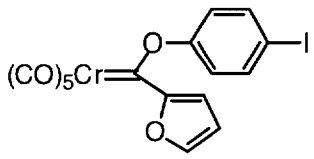
Pentacarbonyl[(2-chlorophenoxy)(furyl)carbene]chromium(0) 7b. Tetramethyl ammonium salt **3** (0.094g, 0.26mmol), CH_2Cl_2 (4ml) AcBr(0.037g, 0.3mmol), NaH(0.018g, 0.74mmol), 2-chlorophenol (0.095g, 0.74mmol), Et_2O (5ml), carbene **7b** (0.088g, 85%) : R_f = 0.6 (10% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.98 (s , 1H), 7.51-7.49 (d, *J* = 7.9 Hz, 2H), 7.45-7.38 (m, 2H), 7.35 -7.30 (m, 1H), 7.18-7.17 (d, *J* =3.6 Hz, 1H), 6.69-6.68 (dd, *J* = 2.5 Hz, 2.5 Hz 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 314.1, 224.5, 215.9, 165.1, 154.5, 151.8, 130.9, 128.0, 124.5, 113.5, 112.7; IR ($CDCl_3$) 1996, 1942, 1543, 1436, 1236, 1113, 1083, 883 cm^{-1}.



Pentacarbonyl[(2-methoxyphenoxy)(furyl)carbene]chromium(0) 7c. Tetramethyl ammonium salt **3** (0.126gms, 0.35mmols), CH_2Cl_2 (4ml), AcBr (0.049g, 0.39mmol), NaH (0.024g, 1mmol), 2-methoxyphenol (0.78g, 0.63mmol) Et_2O (5ml), carbene **7c** (0.094g, 62%): R_f = 0.37 (5% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.93-7.92 (m, 1H), 7.36-7.30 (m, 1H), 7.25-7.24 (m, 1H), 7.17-7.15 (m, 1H), 7.09-7.06 (d, J = 10.65 Hz, 1H), 7.03-6.98 (m, 1H), 6.66-6.63 (m, 1H), 3.79 (s, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 315.0, 224.6, 216.3, 164.9, 151.1, 150.9, 147.2, 127.9, 123.7, 120.6, 113.3, 113.2, 112.4, 55.32; IR (CH_2Cl_2) 3410, 1643, 1392, 1130, 845, 776 cm^{-1}.

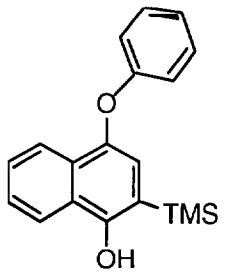


Pentacarbonyl[(3-trifloromethylphenoxy)(furyl)carbene]chromium(0) 7d. Tetramethyl ammonium salt **3** (0.200g, 0.6mmol), CH_2Cl_2 (4ml), AcBr (0.86g, 0.7mmol), CH_2Cl_2 (6ml), NaH (0.024g, 1mmol), 3-α,α,α-triflorocresolate (0.162g, 1mmol), Et_2O (6ml), carbene **7d** (0.250g, 97%): R_f = 0.71 (25% EtOAc/Hexanes); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.66-7.60 (m, 2H), 7.49 (s, 1H), 7.45-7.42 (m, 1H), 7.14-7.13 (m, 1H), 6.69-6.68 (m, 1H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 312.4, 224.2, 216.0, 165.4, 151.8, 132.7, 130.5, 126.34, 123.7, 122.0 (q, J_{C-F} = 212.83, CF_3), 113.6, 112.8; IR (CH_2Cl_2) 3440, 1935, 1640, 1329, 1202, 827cm^{-1}.

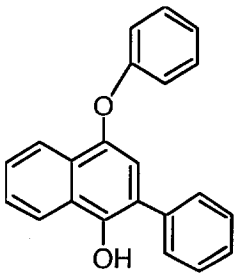


Pentacarbonyl[(4-iodophenoxy)(furyl)carbene]chromium(0) 7e. Tetramethyl ammonium salt **3** (0.085g, 0.24mmol), CH_2Cl_2 (4ml) AcBr (30υl, 0.3mmol), NaH(0.024g, 1mmol), 4-iodophenol (0.176g, 0.8mmol), Et_2O (5ml), carbene **7e** (0.056g, 50%): R_f = 0.62 (10% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.94 (s,1H), 7.82-7.79 (d, J = 8.3 Hz, 2H), 7.11-7.10 (d, J = 3.1 Hz, 1H), 6.99-6.96 (d, J = 8.3 Hz, 2H), 6.66 (s, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ312.5, 224.3, 216.1, 165.2, 158.3, 151.5, 138.9, 124.8, 113.4, 112.9; IR (CH_2Cl_2) 3424, 1943, 1649, 1214, 1038, 1010 cm^{-1}.

General procedure for Benzannulation. A schlenk reaction vessel was charged with carbene complexes **5-7**, the appropriate alkyne, then diluted with THF to a concentration of 0.05M (based on carbene). The solution was freeze-thaw-degassed (-196°C to 25°C, three times) and the reaction vessel maintained under positive argon pressure. The reaction mixture was heated to 55°C with stirring. When the starting carbene was consumed (TLC, 16-36h), the reaction flask was cooled to room temperature and stirred open air for 0.5h. The crude reaction mixture was filtered through celite and solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the biaryl ethers.

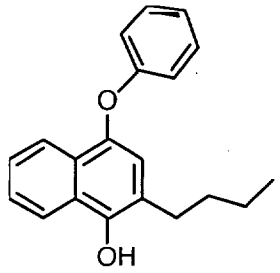


4-Phenoxy-2-trimethylsilanyl-naphthalen-1-ol (8a). Following general procedure for Benzannulation, carbene **5a** (0.07g, 0.19mmol), trimethylsilylacetylene (0.074g, 0.75mmol), THF (5ml), 45°C for 24h, air oxidation and flash column chromatography (25% EtOAc/Hexane) yielded **8a** (0.035g, 61%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.48 (m, 2H), 7.25 (m, 2H), 7.08-6.90 (m, 4H), 5.41 (s, 1H), 0.38 (s, 9H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 159.5, 153.0, 144.9, 129.6, 128.4, 126.8, 126.0, 125.2, 122.6, 121.9, 120.8, 118.5, 116.4, -0.55; IR (CH_2Cl_2) 3596, 3062, 2974, 1592, 1378, 1272, 1077, 735cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{19}H_{20}O_2Si$: 308.1233 , found 308.1218.

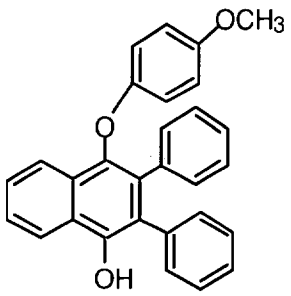


4-Phenoxy-2-phenyl-naphthalen-1-ol (8b). Following general procedure for benzannulation, carbene **5a** (0.07g, 0.187mmol), phenyl acetylene (0.038g, 0.374mmol), THF (5ml), 45°C for 24h, air oxidation and flash column chromatography (33% EtOAc/Hexane) yielded **8b** (0.052g, 88%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.31 (d, *J* =7.7 Hz, 1H), 8.06 (d, *J* =7.5 Hz, 1H), 7.45 (m, 7H), 7.27 (m, 2H), 7.01 (m, 4H), 5.75 (s, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 159.1, 145.5, 144.5, 136.4, 129.7, 129.6, 129.3, 128.04, 127.7, 126.7, 126.3, 125.4, 122.7, 122.3, 122.03,

120.8, 117.2, 117.0; IR (CH_2Cl_2) 3550, 3063, 2995, 1679, 1598, 1392, 1311, 1273, 899 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{22}H_{16}O_2$: 312.1150, found 312.1205.

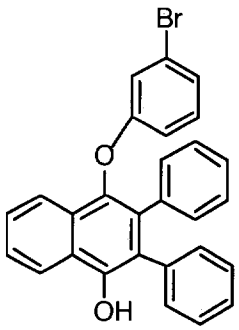


2-Butyl-4-Phenoxy-naphthalen-1-ol (8c). Following general procedure for benzannulation, carbene **5a** (0.13g, 0.35mmol), 1-hexyne (0.056g, 0.695mmol), THF (7ml), 45^{0}C for 24h, after air oxidation and flash column chromatography yielded **8c** (0.015g, 60%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.7 Hz, 1H), 7.40 (t, *J* = 8 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.96 (s, 1H), 6.92 (d, *J* = 3.8 Hz, 2H), 5.09 (s, 1H), 2.73 (t, *J* = 2.6 Hz, 2H), 1.63 (m, 2H), 1.40 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 159.3, 145.2, 144.9, 129.7, 129.6, 126.7, 126.0, 125.6, 122.1, 122.1, 121.6, 121.3, 117.9, 116.8, 32.1, 29.7, 22.5, 13.9; IR (CH_2Cl_2) 3601, 3057, 2994, 2318, 1598, 1497, 1263, 897, 752cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{20}H_{20}O_2$: 292.1463, found 292.1484.

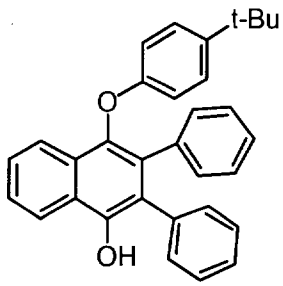


4-(4-Methoxy-phenoxy)-2,3-diphenyl-naphthalen-1-ol (9). Following general procedure for benzannulation, carbene **5b** (0.05g, 0.125mmol), diphenyl acetylene (0.045g, 0.25mmol), THF (5ml), 45^{0}C for 36h, air oxidation and flash column chromatography (25% EtOAc/Hexane) yielded **9** (0.045g, 86%): ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.33 (dd, *J* =7.3 Hz, 1.5 Hz, 1H), 7.94

(dd, J = 7.3 Hz, 1.5 Hz, 1H), 7.50 (m, 2H), 7.23 (m, 5H), 7.00 (s, 5H), 6.59 (m, 4H), 5.56 (s, 1H), 3.66 (s, 3H)); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 153.8, 153.7, 145.0, 141.3, 136.2, 134.8, 132.0, 131.1, 130.4, 128.9, 128.3, 127.8, 127.1, 127.1, 126.4, 125.9, 124.4, 122.8, 122.7, 121.9, 116.0, 114.2, 1112.0, 55.5; IR (CH_2Cl_2) 3544, 3058, 2983, 2844, 1596, 1388, 1072, 895, 726cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{29}H_{22}O_3$: 418.1569, found 418.1571.

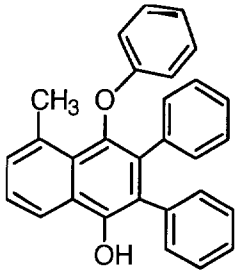


4-(3-Bromo-phenoxy)-2,3-diphenyl-naphthalen-1-ol (10). Following general procedure for benzannulation, carbene 5c (0.065g, 0.143mmol), diphenyl acetylene (0.052g, 0.287mmol), THF (5ml), 45C for 36h, air oxidation and flash column chromatography (33% EtOAc/Hexane) yielded 10 (0.062g, 93%): 1H-NMR (250 MHz, CDCl3) 8.34 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.53 (m, 2H), 7.23 (m, 5H), 6.98 (m, 7H), 6.82 (m, 1H), 6.58 (dt, J = 7.6 Hz, 1.8 Hz, 1H), 5.59 (s, 1H); ^{13}C-NMR (62.9 MHz, CDCl3) 160.0, 146.1, 140.3, 135.8, 134.6, 131.9, 131.1, 130.4, 130.2, 129.0, 127.9, 127.4, 127.2, 126.6, 126.1, 124.5, 124.3, 122.9, 122.5, 122.3, 121.8, 118.8, 114.3; IR (CH_2Cl_2) 3531, 3063, 2315, 1593, 1274, 897, 749cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{28}H_{19}BrO_2$: 466.0569 (^{79}Br), found 466.0605.

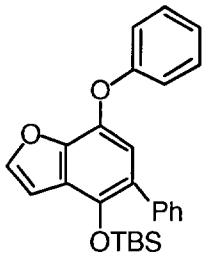


4-(4-tert-Butyl-phenoxy)-2,3-diphenyl-naphthalen-1-ol (11). Following general procedure for benzannulation, carbene 5d (0.035g, 0.0814mmol), diphenyl acetylene (0.043g, 0.24mmol), THF (5ml), 450C for 36h, air oxidation and flash column chromatography (33% EtOAc/Hexane) yielded 11 (0.025g, 70%): 1H-NMR (250 MHz, CDCl3) 8.33 (d, J = 7.8 Hz, 1H), 7.94 (d, J =

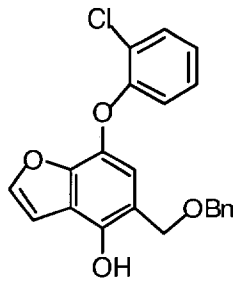
7.6 Hz, 1H), 7.51 (m, 2H), 7.22 (m, 6H), 7.07 (d, J = 8.9 Hz, 2H), 6.98 (s, 4 H), 6.56 (d, J = 8.9 Hz, 2H), 5.53 (s, 1H), 1.21 (s, 9H); ^{13}C-NMR (62.9 MHz, $CDCl_3$) d 157.4, 145.6, 143.6, 141.2, 136.2 134.9, 132.0, 131.1, 130.5, 129.0, 128.6, 128.3, 127.8, 127.1, 126.3, 125.9, 125.8, 124.4, 122.9, 122.7, 121.9, 114.9, 33.96, 31.40; IR (CH_2Cl_2) 3543, 3061, 2972, 1438, 1279, 899cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{32}H_{28}O_2$: 444.2089, found 444.2105.



5-Methyl-4-phenoxy-2,3-diphenyl-naphthalen-1-ol (12). Following general procedure for benzannulation, carbene **6** (0.06g, 0.16mmol), diphenylacetylene (0.08g, 0.46mmol), THF (7ml), 45^{0}C for 36h, air oxidation and flash column chromatography (25% EtOAc/Hexane) yielded **12** (0.047g, 76%) : ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.26 (d, J = 8.2 Hz, 1H), 7.42 (m, 1H), 7.22 (m, 6H), 6.98 (t, J = 7.6 Hz, 2H), 6.91 (s, 5H), 6.74 (t, J = 8.3 Hz, 1H), 6.45 (m, 2H), 2.70 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.4 (145.9, 142.3, 136.4, 134.7, 133.9, 132.8, 131.02, 130.7, 130.4, 128.9, 128.3, 127.7, 126.8, 126.1, 125.8, 125.4, 122.1, 120.9, 120.7, 115.6, 23.9); IR (CH_2Cl_2) 3542 3066 2932 2329 1662 1280 1223 1128 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{29}H_{22}O_2$: 402.1619, found 402.1589.

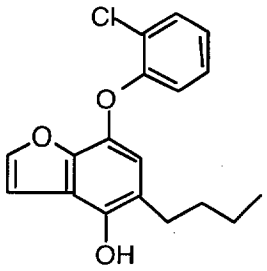


tert-Butyl-dimethyl-(7-phenoxy-5-phenyl-benzofuran-4-yloxy)-silane (13). Following general procedure for benzannulation, carbene **7a** (0.0965g, 0.26mmol), phenylacetylene (0.120g, 0.66mmol), THF (8ml), 50°C for 24h, followed by air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **13** (0.056g, 73%). The pure product in THF (1ml) was treated with pyridine (25ul, 0.19 mmol), and TBSCl (26mg, 0.19mmol). The solvent was removed *in vacuo* and the crude product purified by flash column chromatography (20%EtOAc/Hexane) to yield the OTBMS ether of **13** (45 mg, 0.11mmol) as white oil.: R_f = 0.55 (20% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.53-7.49 (m, 3H), 7.38-7.27 (m, 5H), 7.08-6.97 (m, 4H), 6.84-6.83 (d, J = 1.25 Hz, 1H), 0.93 (s, 9H), -0.27 (s, 6H)); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 144.52, 130.16, 129.58, 128.04, 126.74, 122.72, 118.13, 117.11, 105.69, 25.72, 18.20, -4.59; IR (CH_2Cl_2) 3069, 2998, 2377, 2326, 1486, 1273cm^{-1}; Anal. Calc'd for $C_{26}H_{29}O_3Si$: C, 74.96; H, 6.77. Found C, 75.16; H, 6.83.

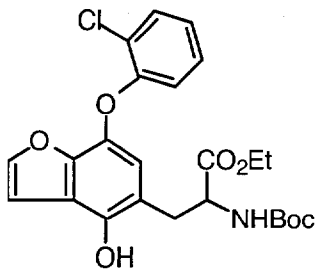


5-Benzyloxymethyl-7-(2-chloro-phenoxy)-benzofuran-4-ol (14). Following general procedure for benzannulation, carbene **7b** (0.052g, 0.16mmol), *O*-benzyl propargyl alcohol (0.07g, 0.48mmol), THF (5ml), 55°C for 33h, air oxidation and flash column chromatography (25% EtOAc/Hexane) yielded **14** (0.015g, 25%) as colorless oil. Alternatively when the reaction was sonicated with the same amount of starting material the reaction time was reduced to 5h and the yield increased to 59% (0.042g). R_f = 0.45 (25% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ

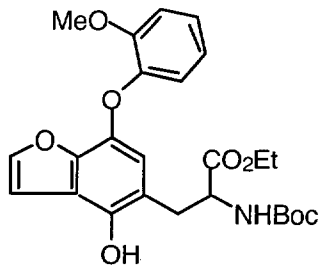
7.85 (s (1H), 7.52-7.51 (d, J =2.15Hz, 1H), 7.46-7.43 (dd, J =7.8, 4.5 Hz, 1H), 7.37 (s, 1H), 7.35 (s, 4H), 7.34-7.32 (m, 2H), 7.15-7.5 (m, 1H) 7.0 (m, 1H), 6.92-6.91 (d, J =2.15Hz, 1H), 6.8-6.79 (m, 1H), 6.60 (s, 1H), 4.78 (s, 2H), 4.75-4.70 (d, J =2.15Hz, 1H), 4.61 (s, 2H).); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 153.6, 146.7, 144.7, 136.6, 133.5, 130.6, 128.5, 127.6, 127.0, 123.6, 120.0, 117.5, 115.2, 114.7, 104.5, 72.54, 71.31; IR ($CDCL_3$) 3347, 3067, 2870, 1669, 1489, 1327, 1110cm^{-1}; Anal. calc'd for $C_{22}H_{17}ClO_4$: C, 69.39; H,4.50; Found C, 69.50; H, 4.64.



5-Butyl-7-(2-chloro-phenoxy)-benzofuran-4-ol (15). Following general procedure for benzannulation, carbene **7b** (0.062g, 0.19mmol), 1-Hexyne (0.064ml, 0.56mmol), THF (6ml), 53^{0}C for 40h, after air oxidation and flash column chromatography yielded **15** (0.030g, 42%). Alternatively when the reaction was sonicated with the same amount of starting material the reaction time was reduced to 2h and the yield increased to 59% (0.042gm).: R_f = 0.4 (25% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.56-7.44 (m, 2H),(s, 1H), 7.12-7.09 (m, 1H), 7.02-6.97 (m, 1H), 6.97-6.75 (m, 3H), 4.76 (s, 1H), 2.66-2.60 (t, J = 6.7 Hz, 2H), 1.63-1.54 (m, 2H), 1.43-1.37 (m, 2H), 0.96-0.90 (t, J =7.3 Hz, 3H)); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.8, 144.9, 142.9, 133.9, 127.7, 123.5, 121.5, 119.2, 117.3, 103.6, 32.40, 31.60, 29.10, 25.30, 22.50, 21.04, 14.10); IR (CH_2Cl_2) 2956, 2361, 1582, 1479, 1231cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_{17}O_3Cl$ (M + Na^+) 316.0866, found 316.0827.

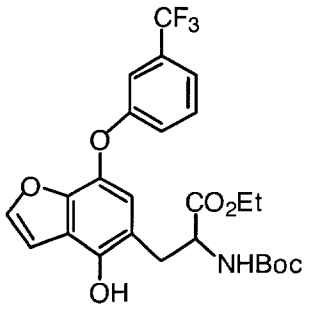


2-tert-Butoxycarboxylamino-3-[4-hydroxy-7-(2-chloro-phenoxy)-benzofuran-5-yl] propionic acid ethyl ester (17a). Following general procedure for benzannulation, carbene **7b** (0.068g, 0.26mmol), N-Boc-ethylpropargylglycinate **16** (0.135g, 0.514mmol), THF (5ml), 45°C for 29h, air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **17a** (0.0 22 g, 34%): R_f = 0.19 (20% EtOAc/Hexanes); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.45 (s (1H), 7.50-7.42 (m, 2H), 7.12-6.93 (m, 3H), 6.81 (m, 1H), 6.63 (s, 1H), 5.65 (d, *J* =5.51Hz, 1H), 4.31-4.10 (m, 3H), 3.23 (m, 1H), 2.97 (m, 1H), 1.46 (s, 9H), 1.17 (t, *J* =7.2 Hz, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 171.9, 156.5, 153.8, 146.0, 144.4, 133.4, 130.6, 127.6, 123.6, 120.1, 118.5, 117.5, 115.5, 104.7, 81.41, 61.89, 54.63, 34.62, 29.71, 27.96, 22.89, 14.06; IR ($CDCl_3$) 3342, 1673, 1494, 1226, 1155, 1047cm^{-1}. Anal. Calc'd for $C_{24}H_{26}ClNO_7$: C, 60.57; H, 5.51. Found C, 60.39; H, 5.25.

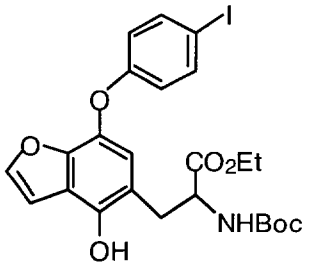


2-tert-Butoxycarboxylamino-3-[4-hydroxy-7-(2-methoxy-phenoxy)-benzofuran-5-yl] propionic acid ethyl ester (17b). Following general procedure for benzannulation, carbene **7c** (0.044g, 0.11mmol),N-Boc-ethylpropargylglycinate **16** (0.37g, 0.13mmol), THF (5ml), 45°C for 36h, air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **17b** (0.0 14

g, 26%): R_f = 0.19 (20% EtOAc/Hexanes); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.20 (s (1H), 7.49 (d, *J* = 1.07 Hz, 1H), 7.02 (m, 2H), 6.91 (d, *J* =2.12 Hz, 1H), 6.81 (m, 2H), 6.63 (s, 1H), 4.32 (m, 1H), 4.12 (q, J= 7.06 Hz, 2H), 3.85 (s, 3H), 3.23 (m, 1H), 1.60 (s, 3H), 1.43 (s, 9H), 1.16 (t, *J* =7.1 Hz, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 172.1, 156.4, 150.2, 147.0, 146.1, 144.2, 123.5, 120.8, 119.9, 117.7, 118.5, 117.5, 115.3, 112.7, 104.5, 81.20, 61.90, 56.13, 30.90, 28.30, 14.10, -0.03; IR ($CDCl_3$) 3420, 2074, 1660, 1503, 744cm^{-1}. HRMS (EI) *m/z* Calc'd for $C_{25}H_{29}NO_8$: 471.1893. Found 471.1875.

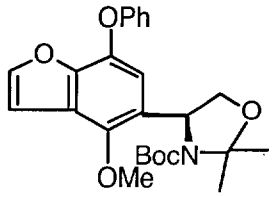


2-tert-Butoxycarboxylamino-3-[4-hydroxy-7-(3-trifloromethyl-phenoxy)-benzofuran-5-yl] propionic acid ethyl ester (17c). Following general procedure for benzannulation, carbene **7d** (0.2131g, 0.49mmol),N-Boc-ethylpropargylglycinate **16** (0.2788g, 0.985mmol), THF (11ml), 45^{0}C for 17h, air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **17c** (0.179g, 35%): Rf = 0.21 (20% EtOAc/Hexanes); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.8 (s,1H), 7.45 (d, J = 1.7 Hz, 1H), 7.35 (m, 1H), 7.24 (m, 1H), 7.21 (s, 1H), 6.96 (d, J = 2.1 Hz, 1H), 7.06 (m, 1H), 6.74 (s, 1H), 6.6 (s, 1H), 4.36 (m, 1H), 4.15 (m, 2H), 3.23 (m, 1H), 3.0 (m, 1H), 1.46 (s, 9H), 1.18 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ 172.1, 158.7, 156.5, 146.4, 146.0, 144.3, 132.4, 132.3, 131.7, 130.9, 130.0, 123.8(q, J_{C-F} =273 Hz, CF_3), 120.0, 119.4, 119.0, 118.9, 115.9 , 113.4, 104.8, 81.32, 61.80, 54.60, 34.20, 28.20, 14.03; IR (KBr) 3664, 3335, 2986, 1729, 1689, 1334, 1209, 1170cm^{-1}. Anal. Calc'd for $C_{25}H_{26}F_3NO_7$: C, 58.94; H, 5.14. Found C, 58.73; H, 5.38



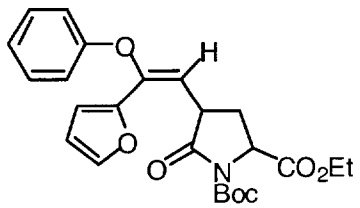
2-tert-Butoxycarboxylamino-3-[4-hydroxy-7-(4-iodo-phenoxy)-benzofuran-5-yl]

propionic acid ethyl ester (17d). Following general procedure for benzannulation, carbene **7e** (0.031g, 0.065mmol),N-Boc-ethylpropargylglycinate **16** (0.0368g, 0.13mmol), THF (5ml), 45^{0}C for 24h, air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **17d** (0.020g, 43%).: R_f = 0.21 (20% EtOAc/Hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.56 (d, *J* = 1.74 Hz, 2H), 7.51 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz 1H), 6.73 (d, *J* = 1.7 Hz, 2H), 6.65 (s, 1H), 5.65 (s, 1H), 4.31 (m, 1H), 4.17 (m, 2H), 3.27 (m, 1H), 2.95 (m, 1H), 1.49 (s, 9H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (125.8 MHz, $CDCl_3$) δ 171.9, 158.5, 156.6, 146.6, 144.4, 138.3, 132.7, 129.5, 123.8, 119.9, 118.8, 104.8, 84.80, 81.50, 62.10, 28.10, 22.70, 14.10; IR (CH_2Cl_2) 3380, 2983, 2936, 2344, 1718, 1885, 1584, 1355, 1483, 1046cm^{-1}. Anal. Calc'd for $C_{24}H_{26}INO_7$: C, 50.81; H, 4.62. Found C, 50.88; H, 4.70.



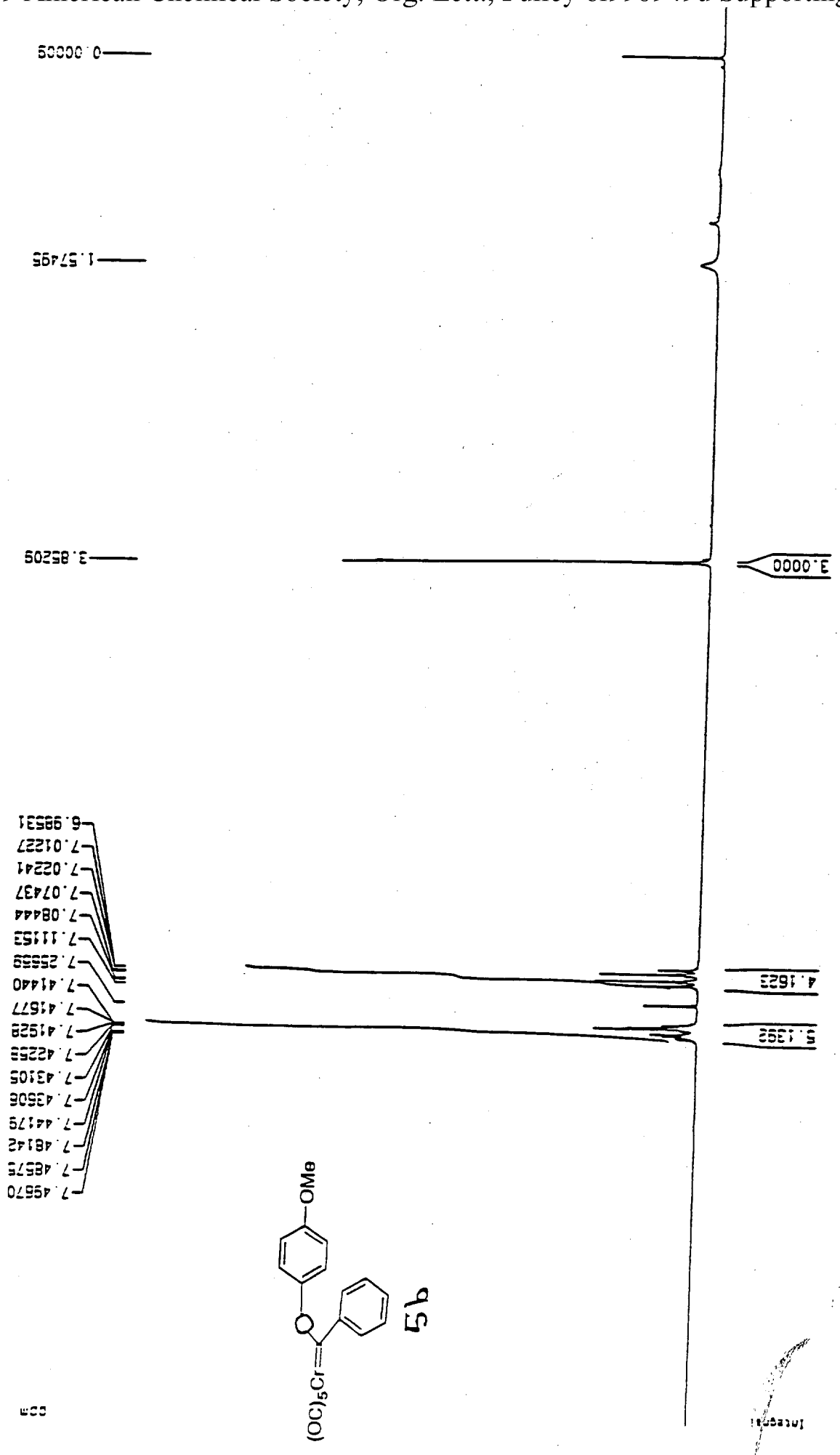
4-(4-Methoxy-7-phenoxy-benzofuran-5-yl)-2,2-dimethyl-oxazolidine-3-carboxylic acid tert-butyl ester (20). Following general procedure for benzannulation, carbene **7a** (0.146 g, 0.40 mmol), ethynyloxazolidine **19** (0.139 g, 0.60 mmol), THF (8 ml), 50^{0}C for 21h, followed by air oxidation and flash column chromatography (20% EtOAc/Hexane) yielded **20** (53%). Alternatively when the reaction was sonicated with the same amount of starting material the reaction time was reduced to 2h and the yield increased to 59%. The pure product (66.3 mg, 0.15 mmol) in THF (6.0 ml) was treated with potassium carbonate (29.7 mg, 0.30 mmol) and methyl iodide (9.2 μL, 0.19mmol) at 50^{0}C for 12h . The suspension was filtered and partitioned between saturated sodium bicarbonate and diethyl ether. The organic layer was collected, washed with brine, and dried with magnesium sulfate. The solvent was removed, and the crude

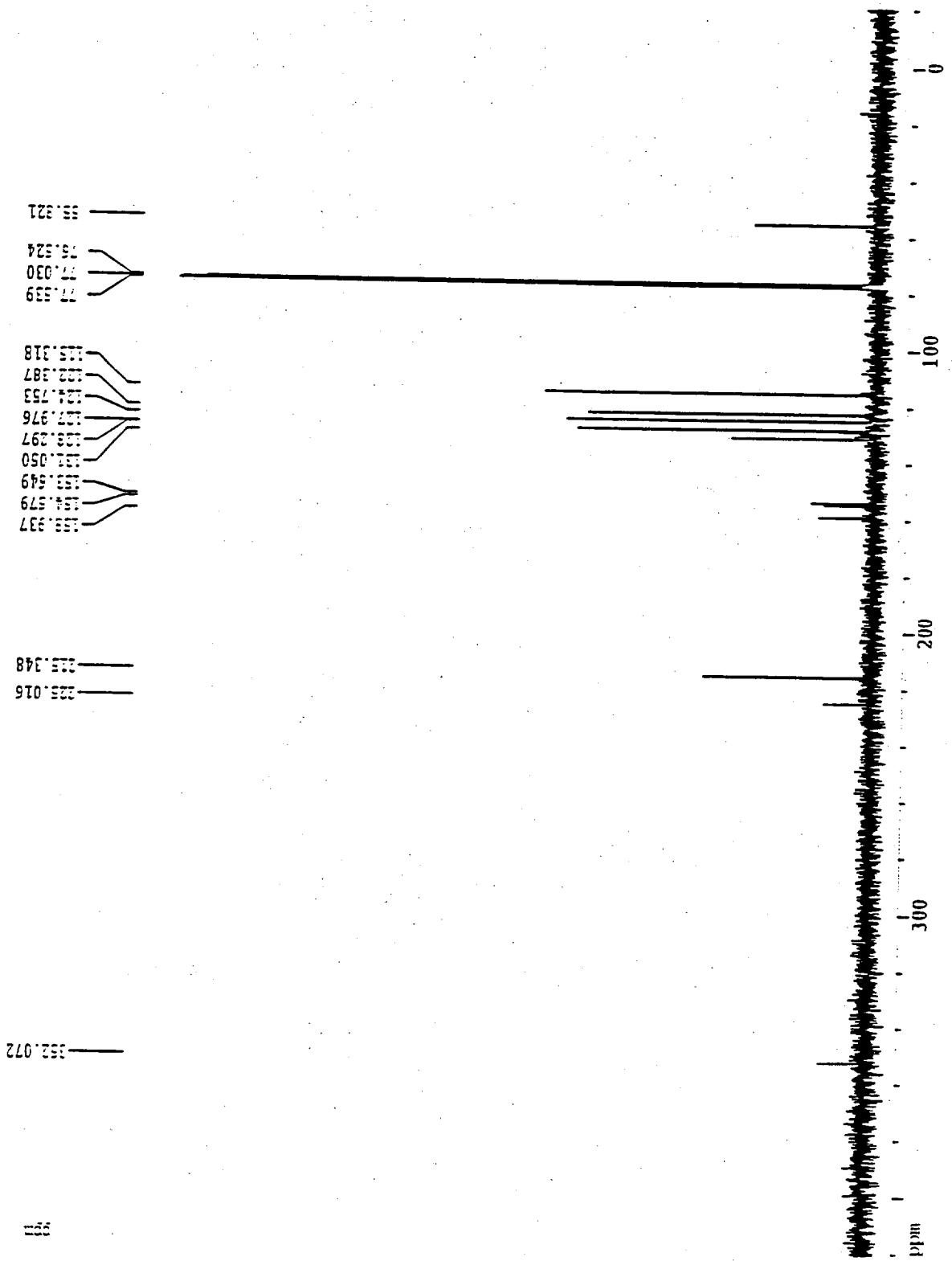
product purified by flash column chromatography (15%EtOAc-Hexane) to yield **20** as the O-methyl ether (83%) as a colorless oil: R_f = 0.26 (15% EtOAc/Hexane); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.33 (s, 1H), 7.30 (s, 1H), 6.91 (d, *J* =2.1 Hz, 1H), 6.81(m, 2H), 6.63 (s,

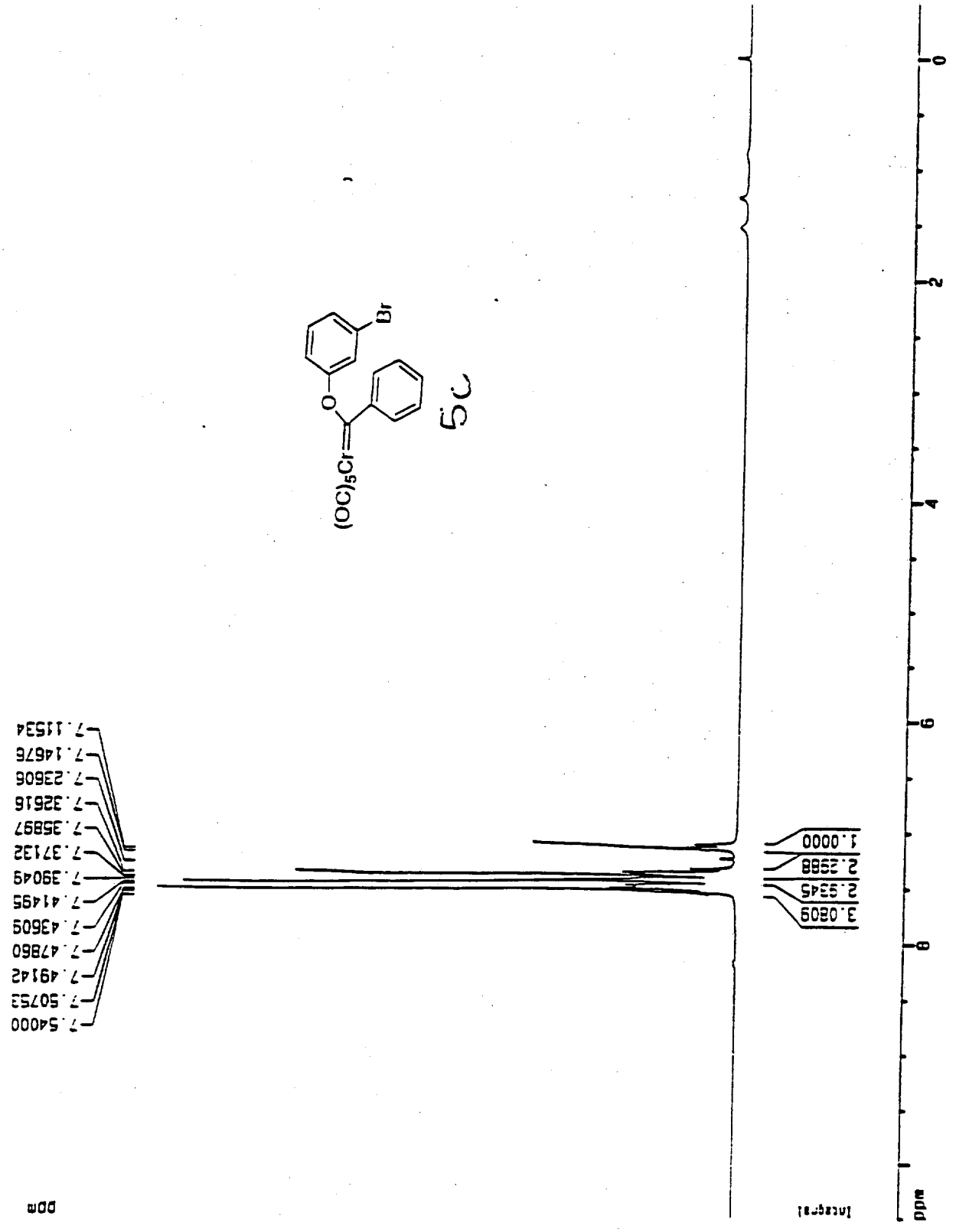


1H), 4.32(m, 1H), 4.12 (q, *J* = 7.06 Hz), 4.03 (s, 1H), 3.80 (d, *J* = 8.7 Hz, 1H), 1.56 (s, 3H), 1.54 (s, 3H), 1.30 (s, 9H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 158.2, 145.7, 144.7, 129.6, 133.8, 122.6, 120.1, 116.6, 115.1, 113.9, 110.5, 104.3, 78.50, 77.20, 70.40, 55.70, 28.30, 27.20, 24.30; IR (CH_2Cl_2) 34.02, 29.01, 17.06, 16.59, 14.95 cm^{-1}. $[\alpha]^D_{20}$ 7° (CH_2Cl_2). Anal. Calc'd for $C_{25}H_{29}NO_6$: C, 68.32 ; H,6.65 ; N, 3.19. Found C, 68.34; H, 6.54; N, 3.21.

4-[2-Furan-2-yl-2-(3-trifloromethyl-phenoxy)-vinyl]-5-oxo-pyrrolidine-1,2-dicarboxylic acid-1-tert-butyl-2-ethyl ester (18). ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.41-7.2 (m, 5H), 6.32-6.33 (dd, *J* = 1.59, 1.81 Hz, 1H), 6.17 (m, 1H), 5.93 (m, 1H), 5.29 (s, 0.5H), 4.60 (dd, *J* = 1.68, 1.78 Hz, 1H), 4.48 (t, *J* = 7.83, 0.3H), 4.29-4.15 (m, 2H), 3.68 (m, 1H), 3.48 (s, 1H), 2.26 (m, 1H), 1.49 (s, 9H), 1.33-1.18 (m, 3H); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 172.6, 170.8, 157.2, 149.2, 147.8, 144.2, 143.6, 132.2, 130.3, 119.13, 118.5, 112.9, 111.5, 111.3, 109.0, 108.9, 83.90, 83.60, 61.70, 57.30, 53.40, 40.10, 39.30, 29.80, 29.60, 28.90, 13.90. IR ($CDCl_3$) 3483, 2983, 1796, 1602, 1207, 747 cm^{-1}.



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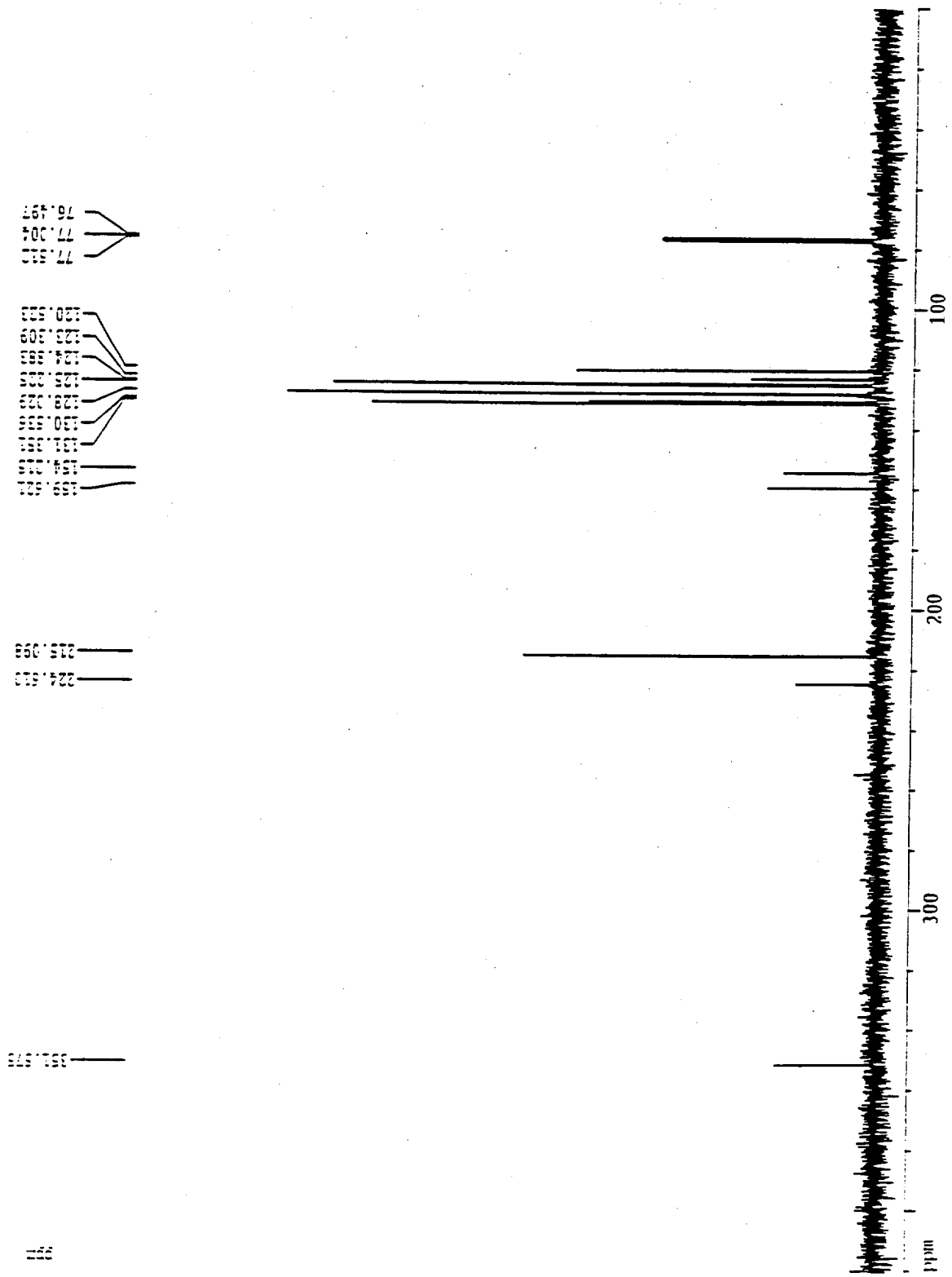

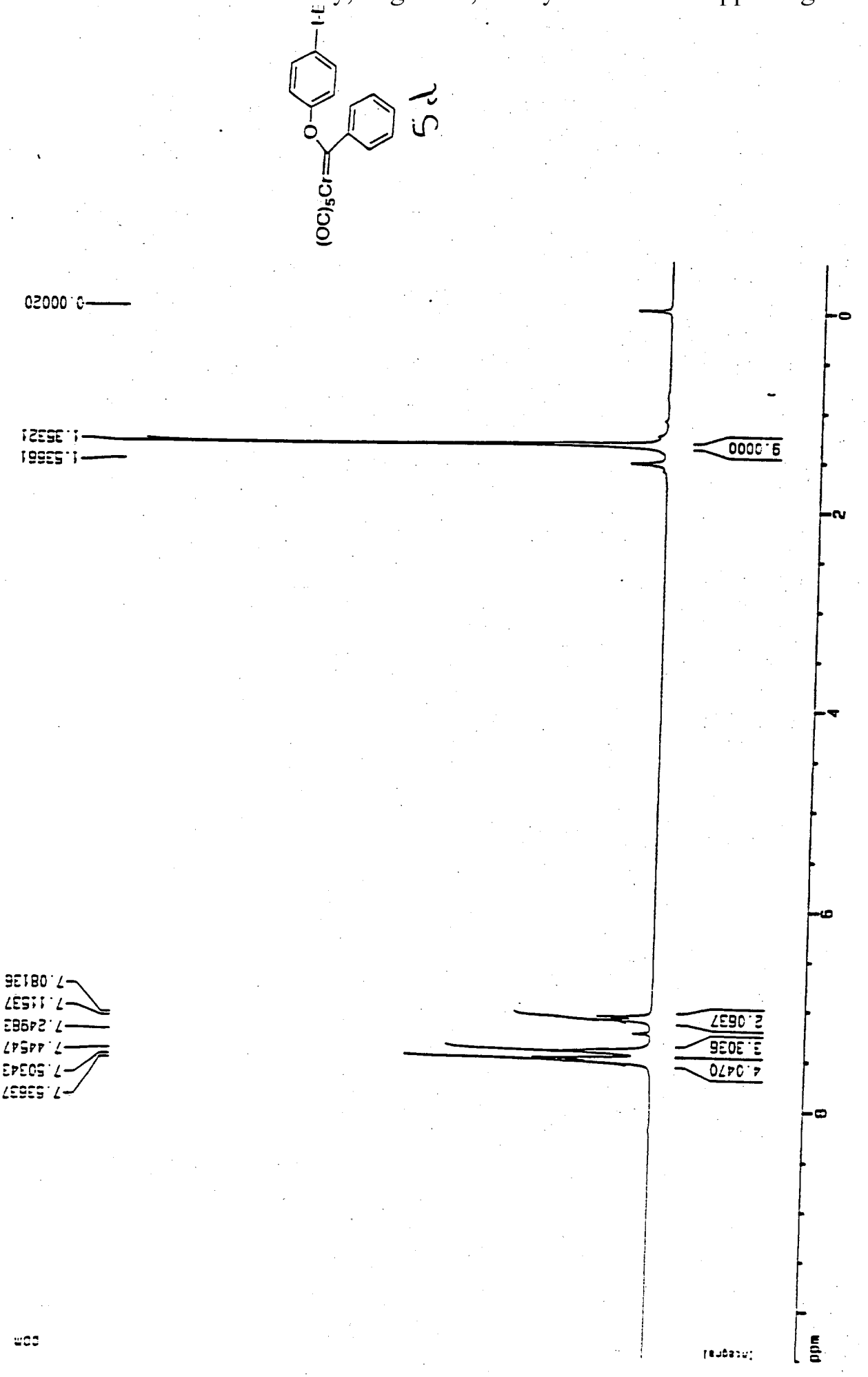

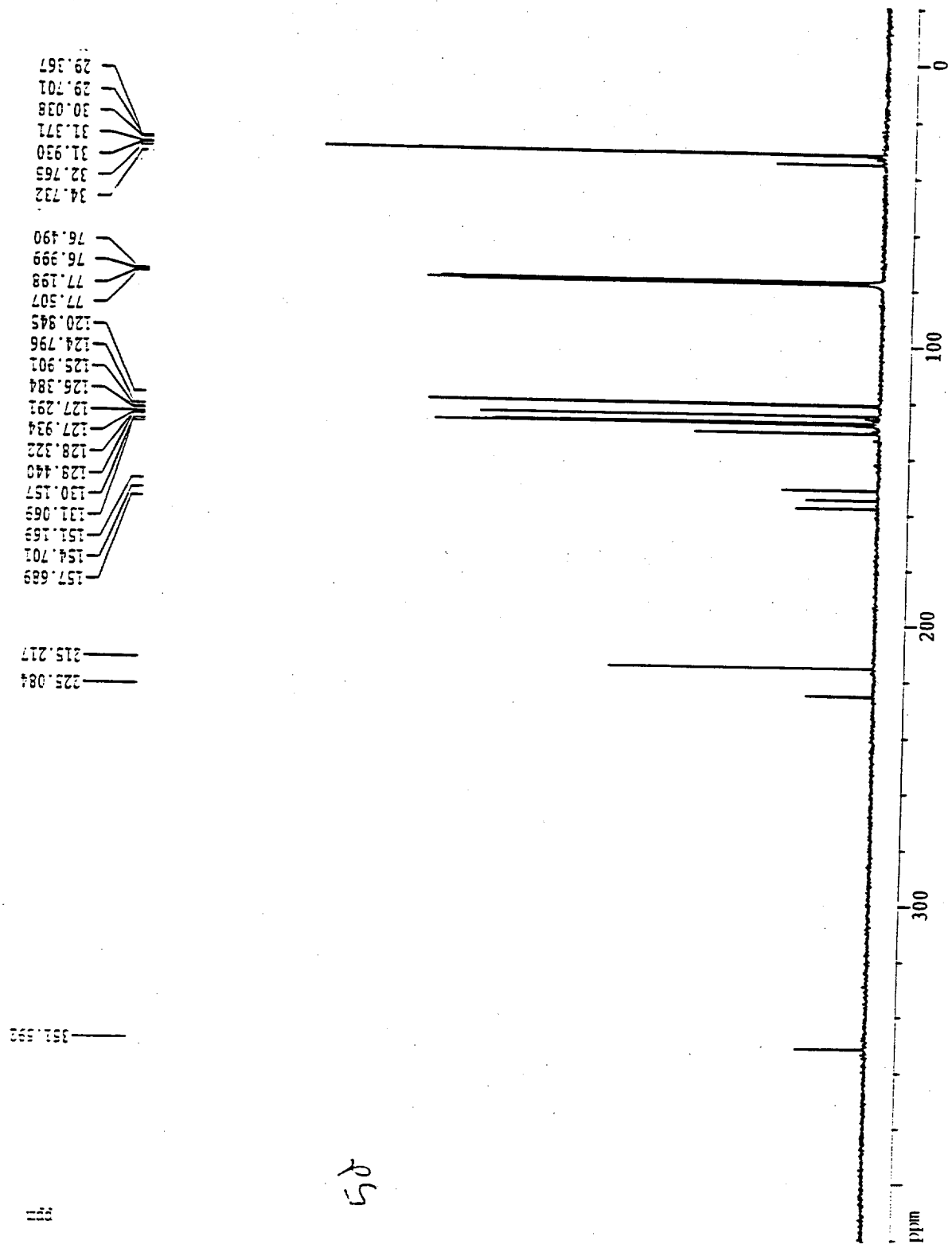

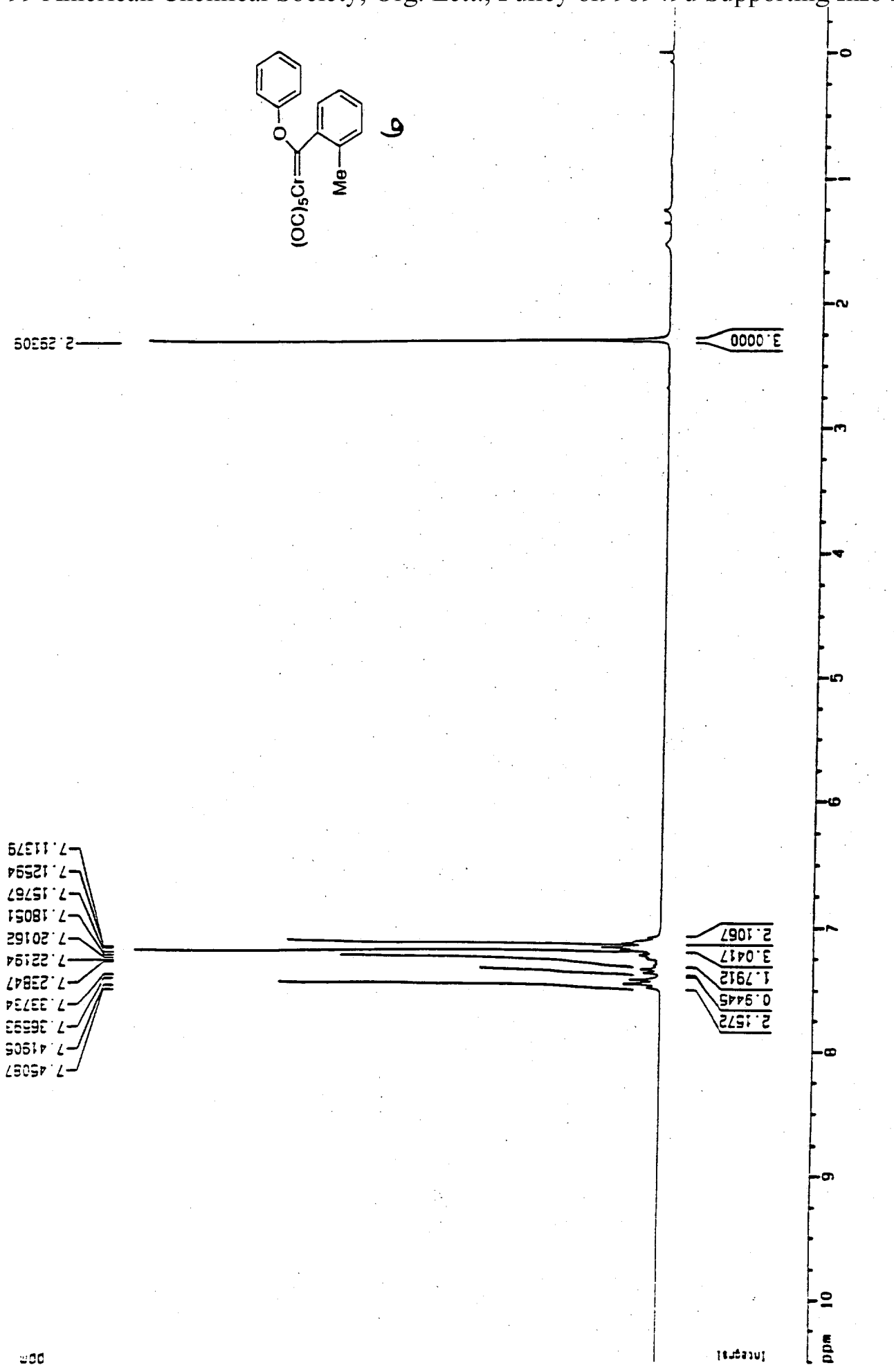


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19.246
19.401
30.927
76.485
76.995
77.194
77.500
121.145
125.252
125.473
125.574
125.899
126.021
126.085
126.210
127.437
128.189
128.471
128.837
129.463
129.591
130.178
130.223
130.560
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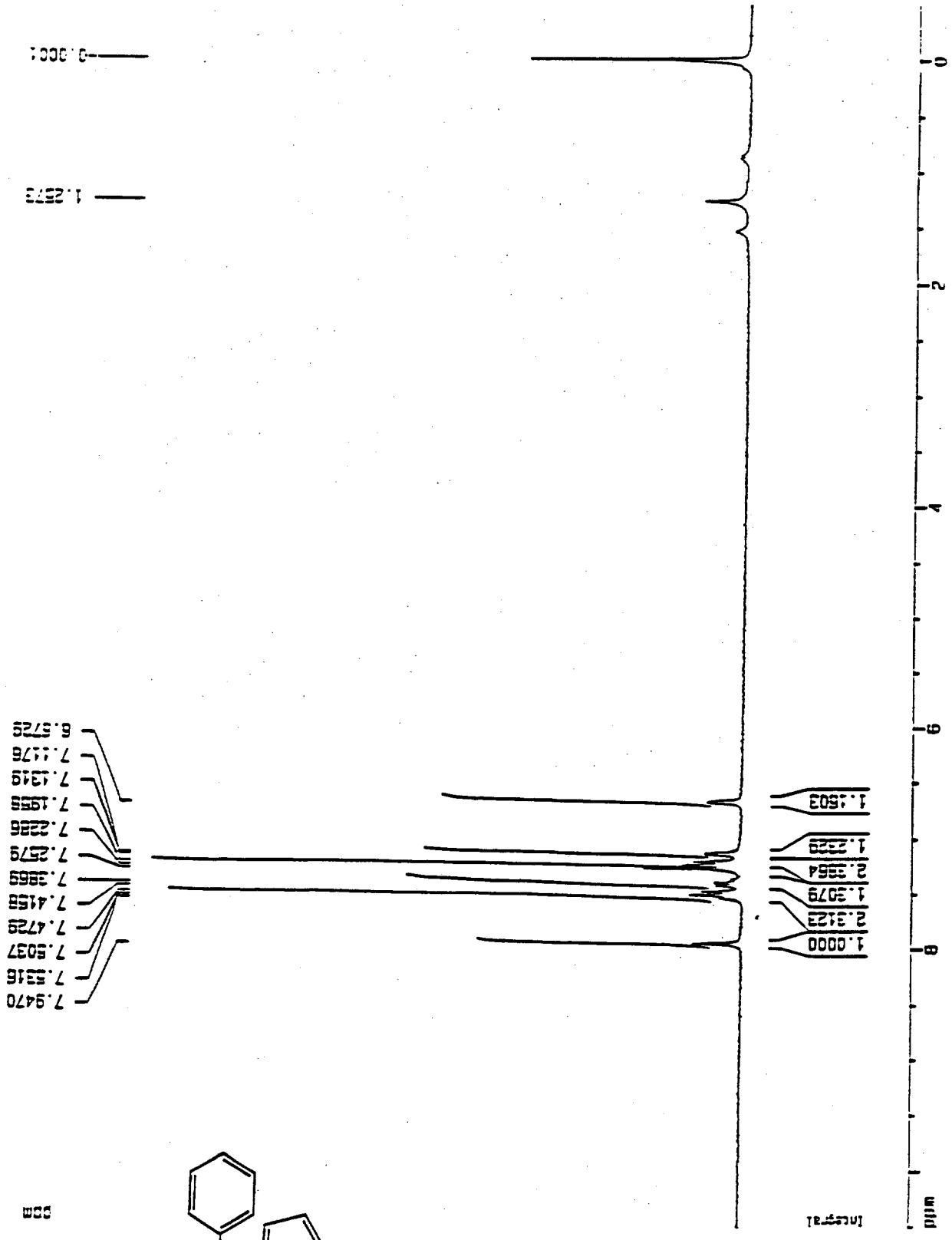
360.826
ppm
0
100
200
300
ppm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7.3869
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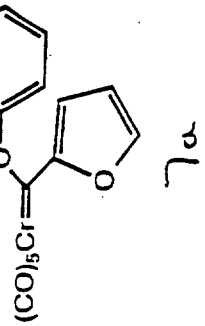
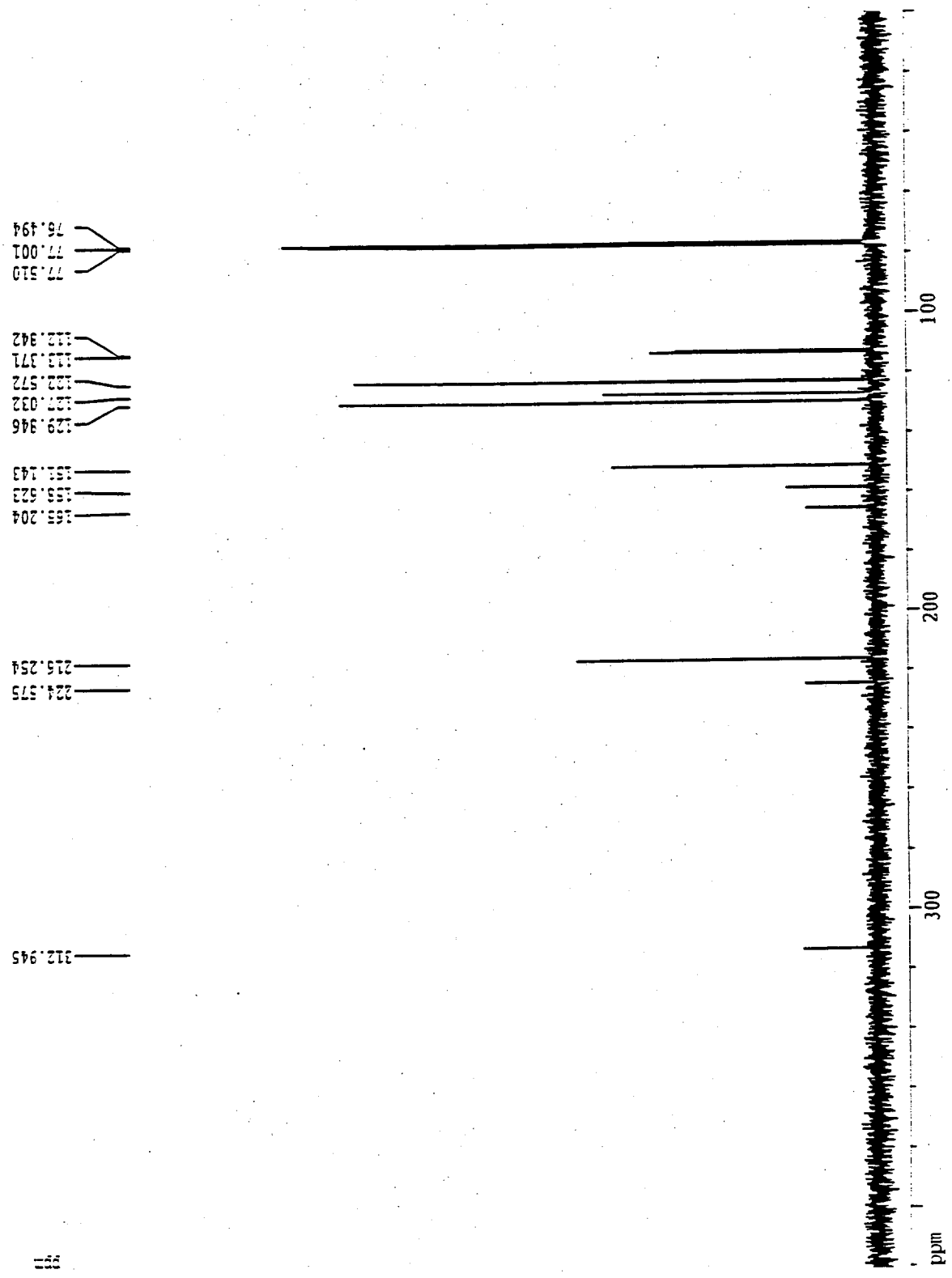
1.3079
2.3123
1.0000
ppm


O
O
(CO)5Cr

7d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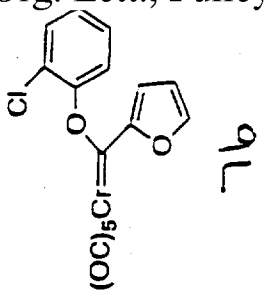
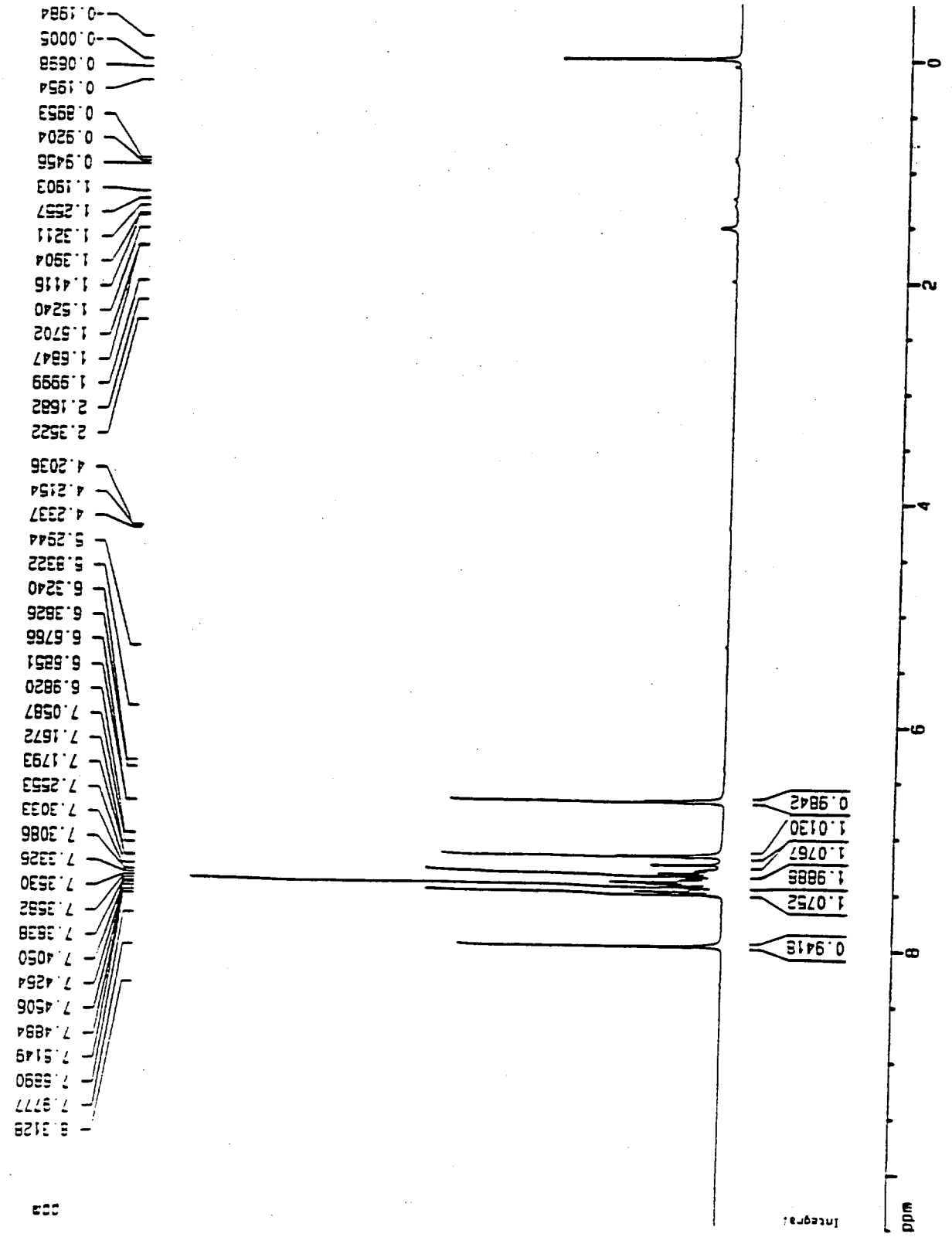
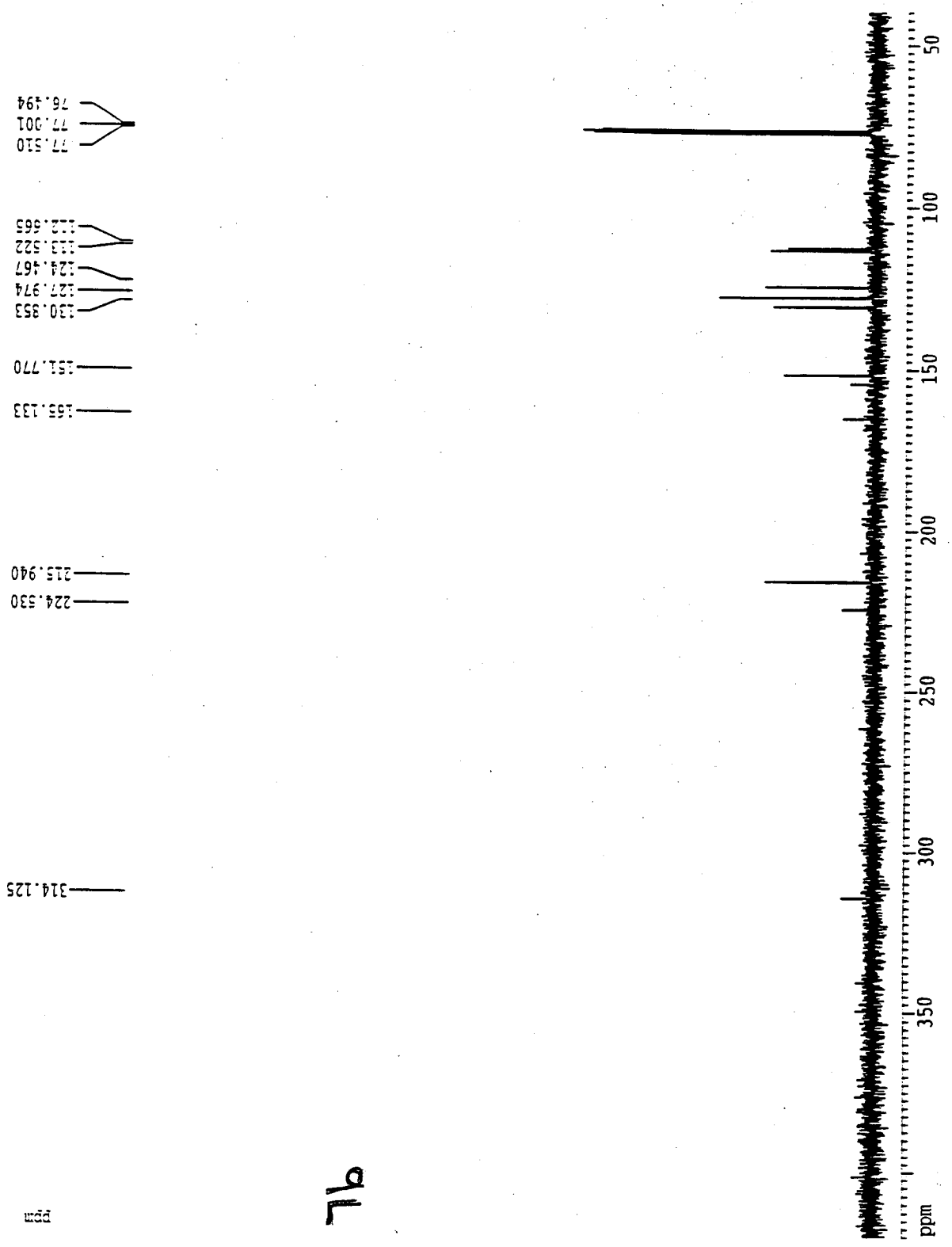
77.001
77.510
112.842
113.371
122.572
127.032
129.946
151.143
156.622
165.204
216.254
224.575
312.945
ppm
100
200
300

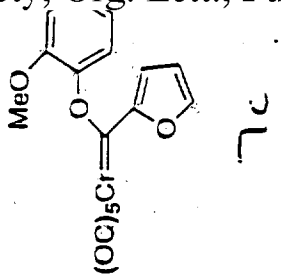


9L

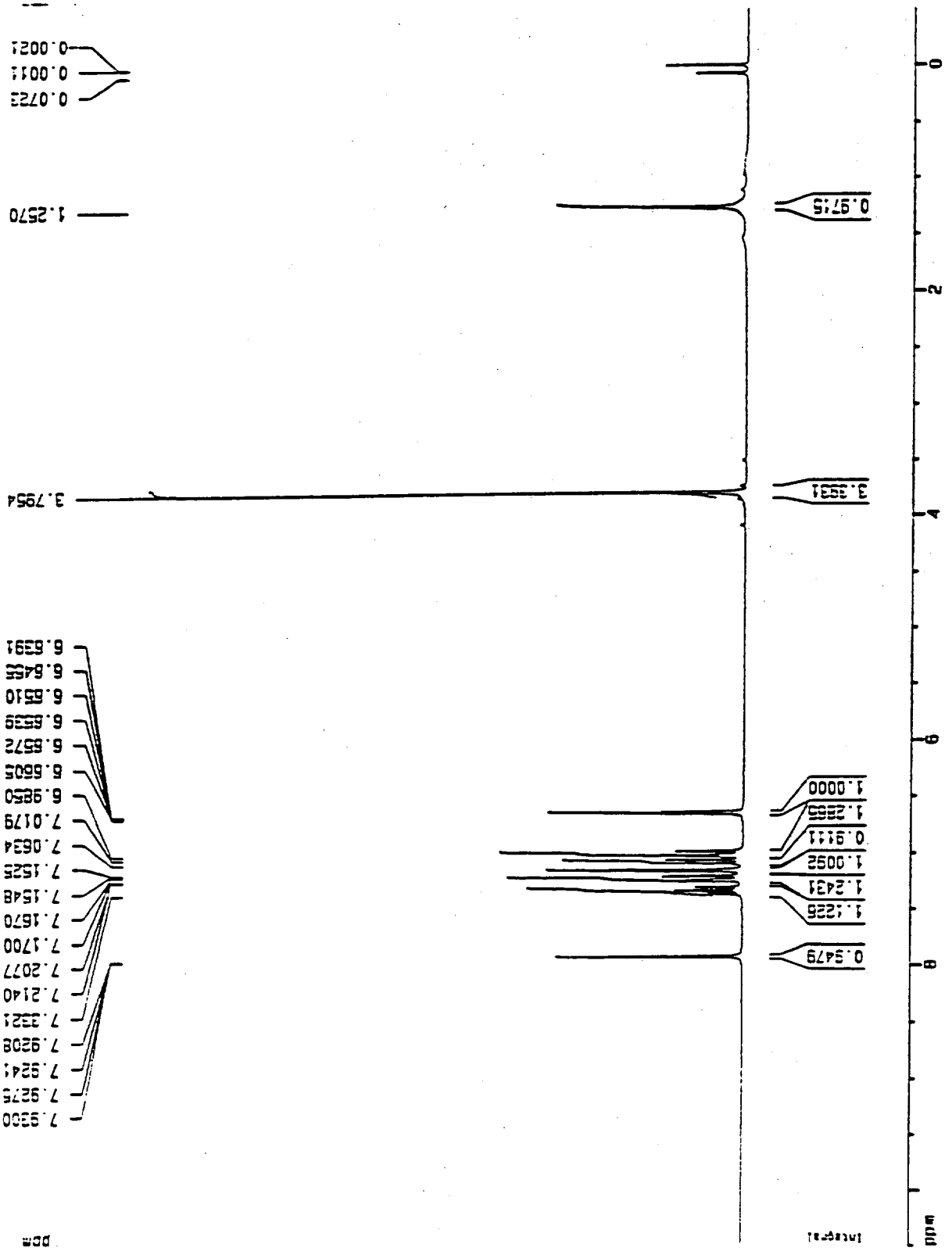


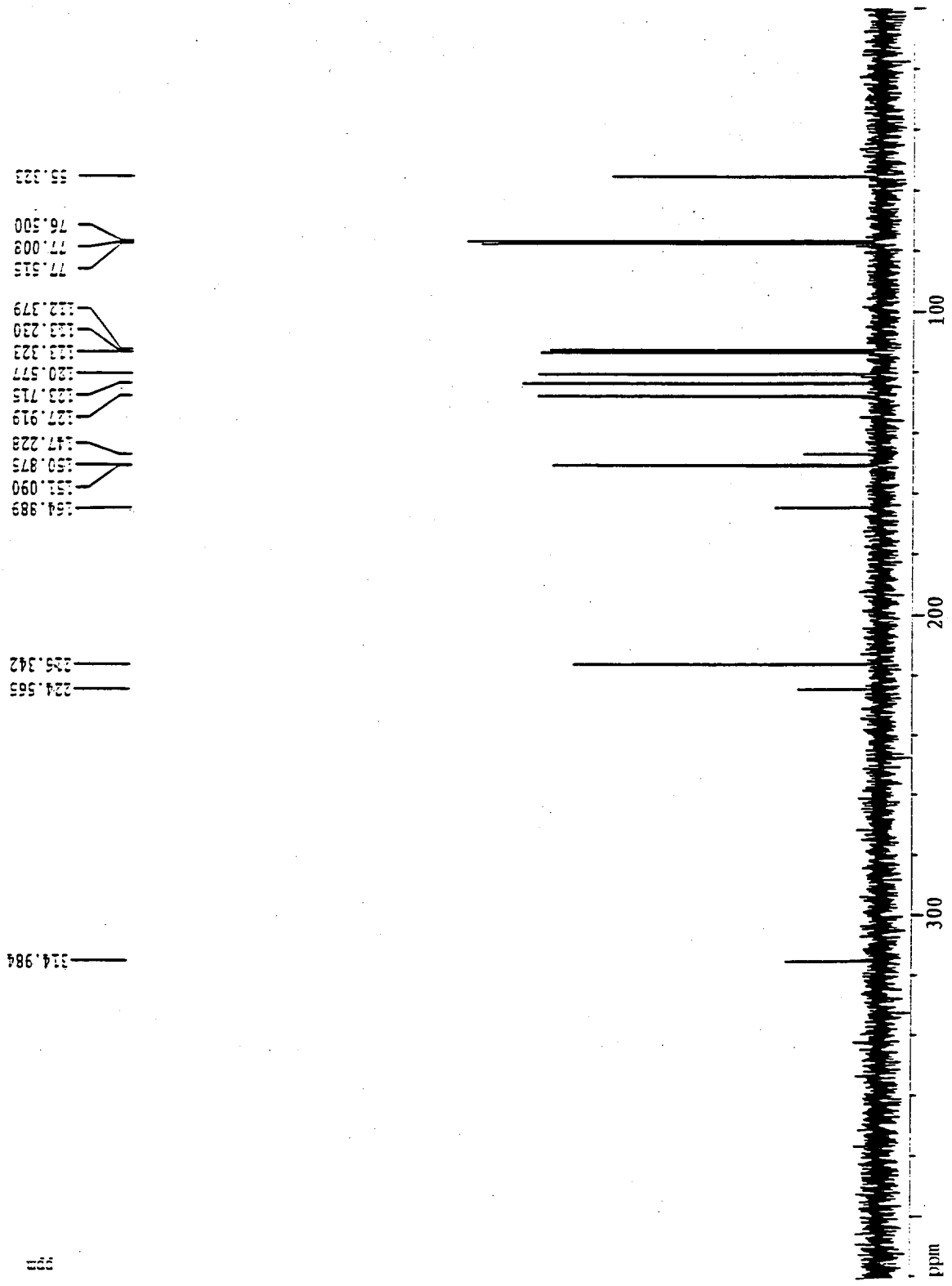


7b

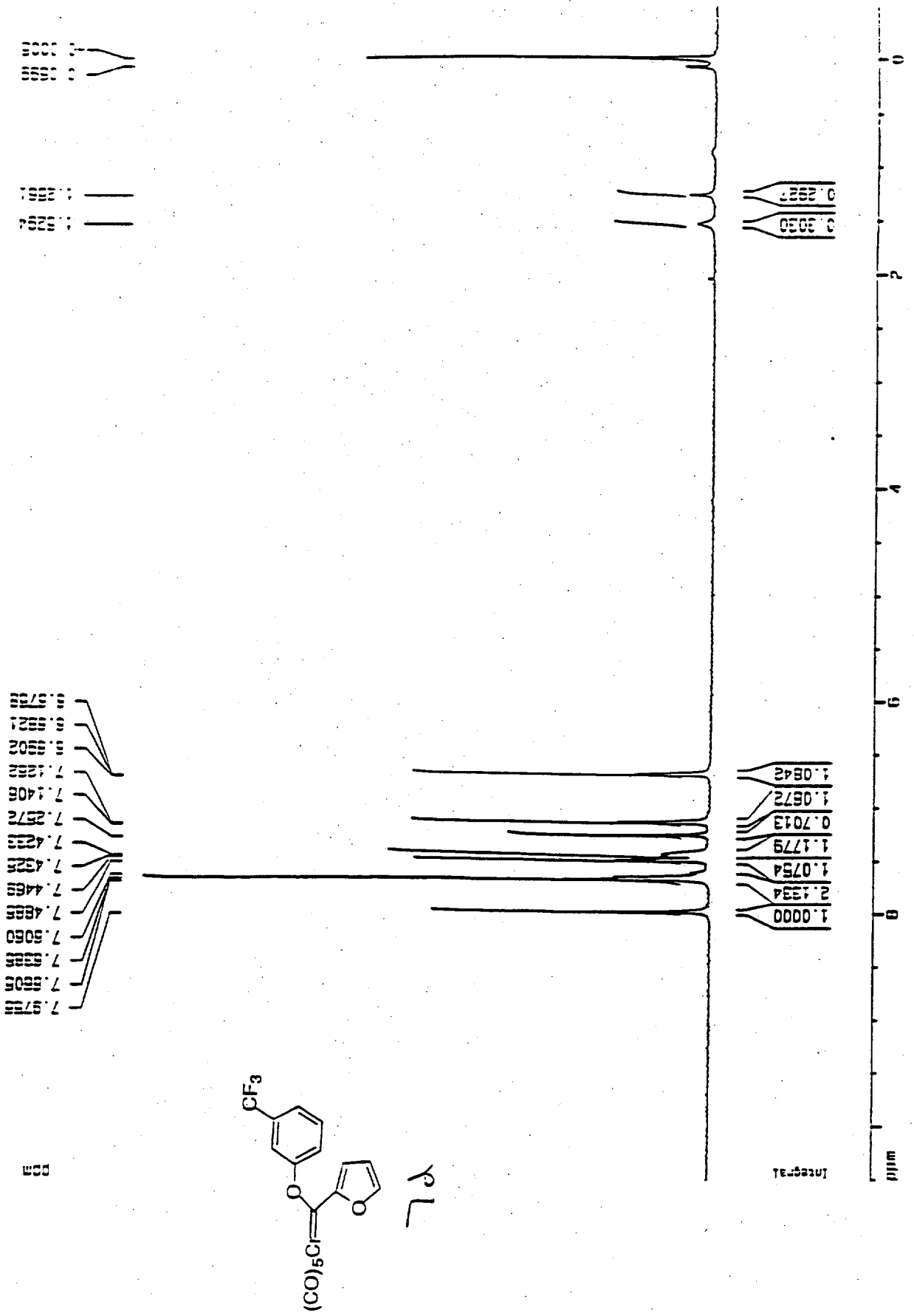


7c





AV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7.5060
7.4885
7.4669
7.4325
7.4233
7.2572
7.1406
7.1282
5.8502
5.8321
5.8128
1.0000
2.1334
1.0754
1.1779
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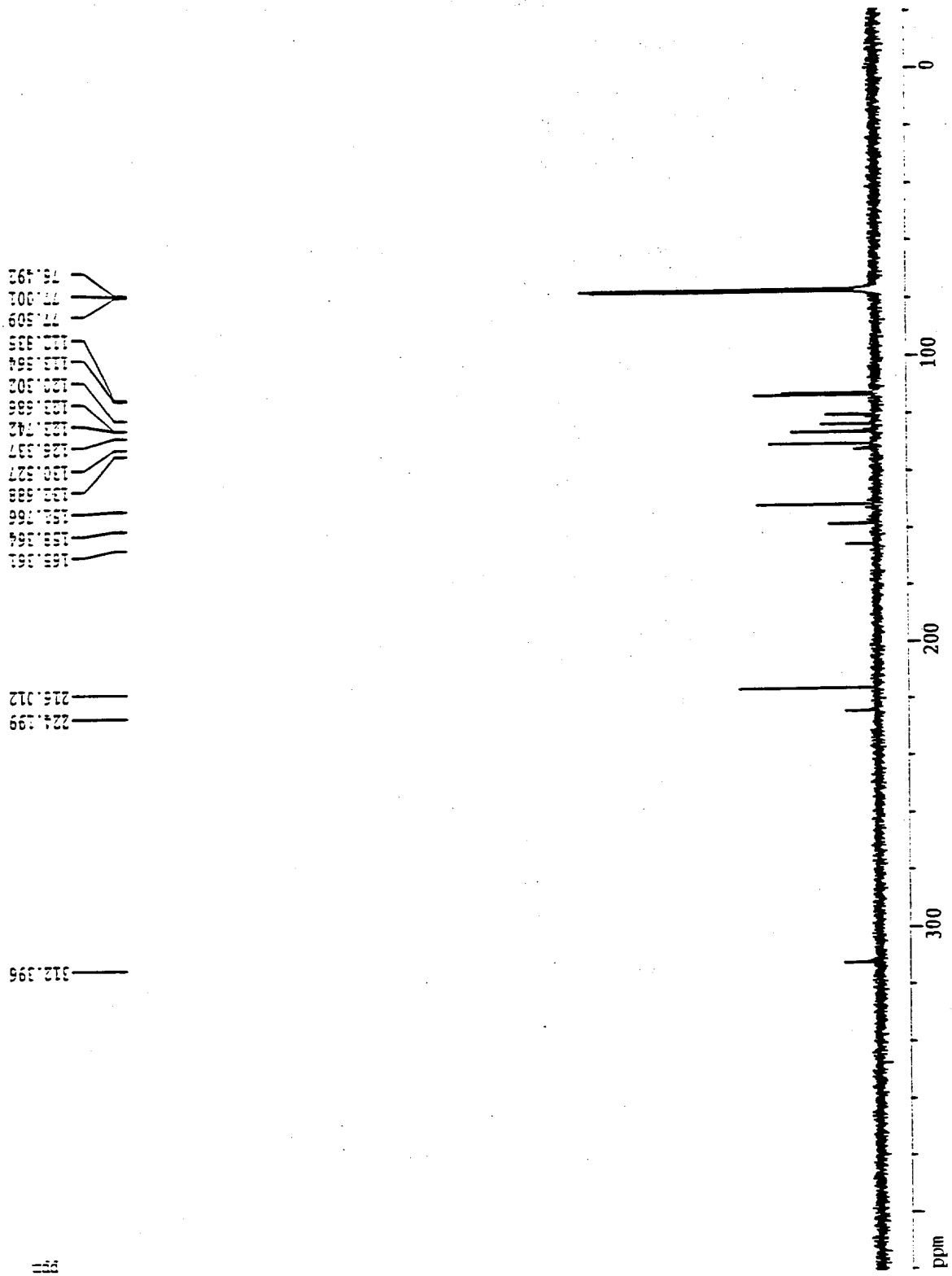
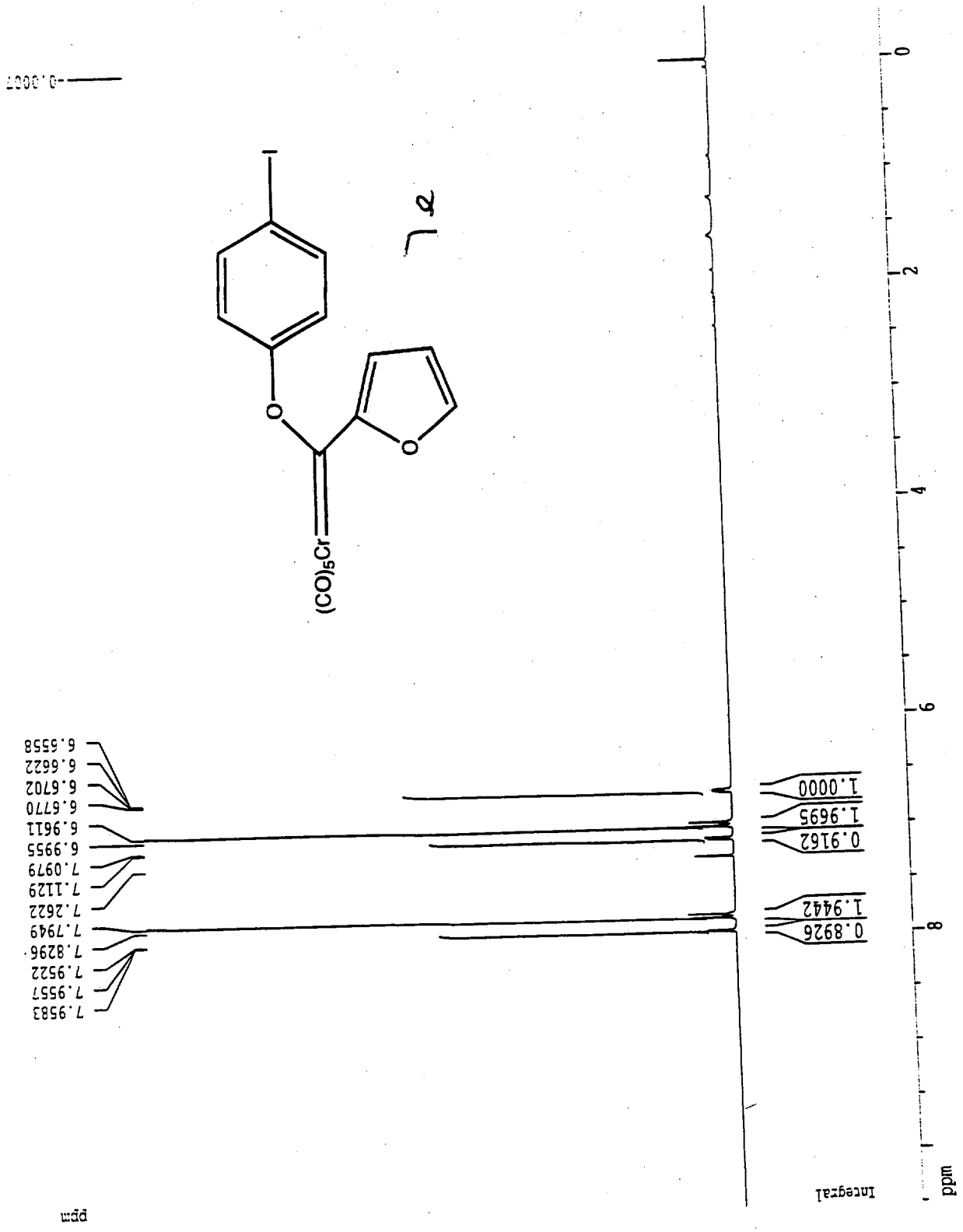
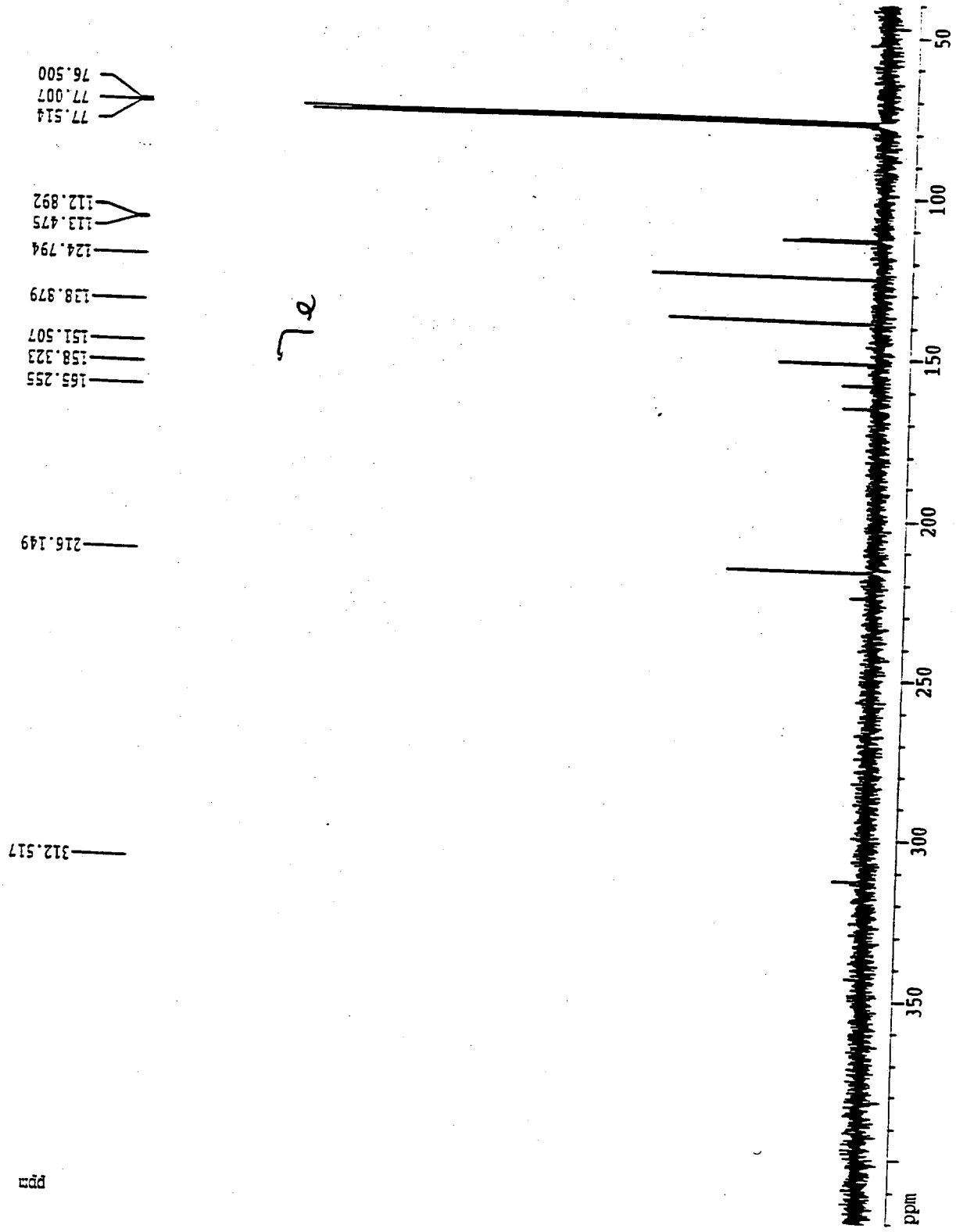
1.0842
0.3030
0.2827
PPM
Integral

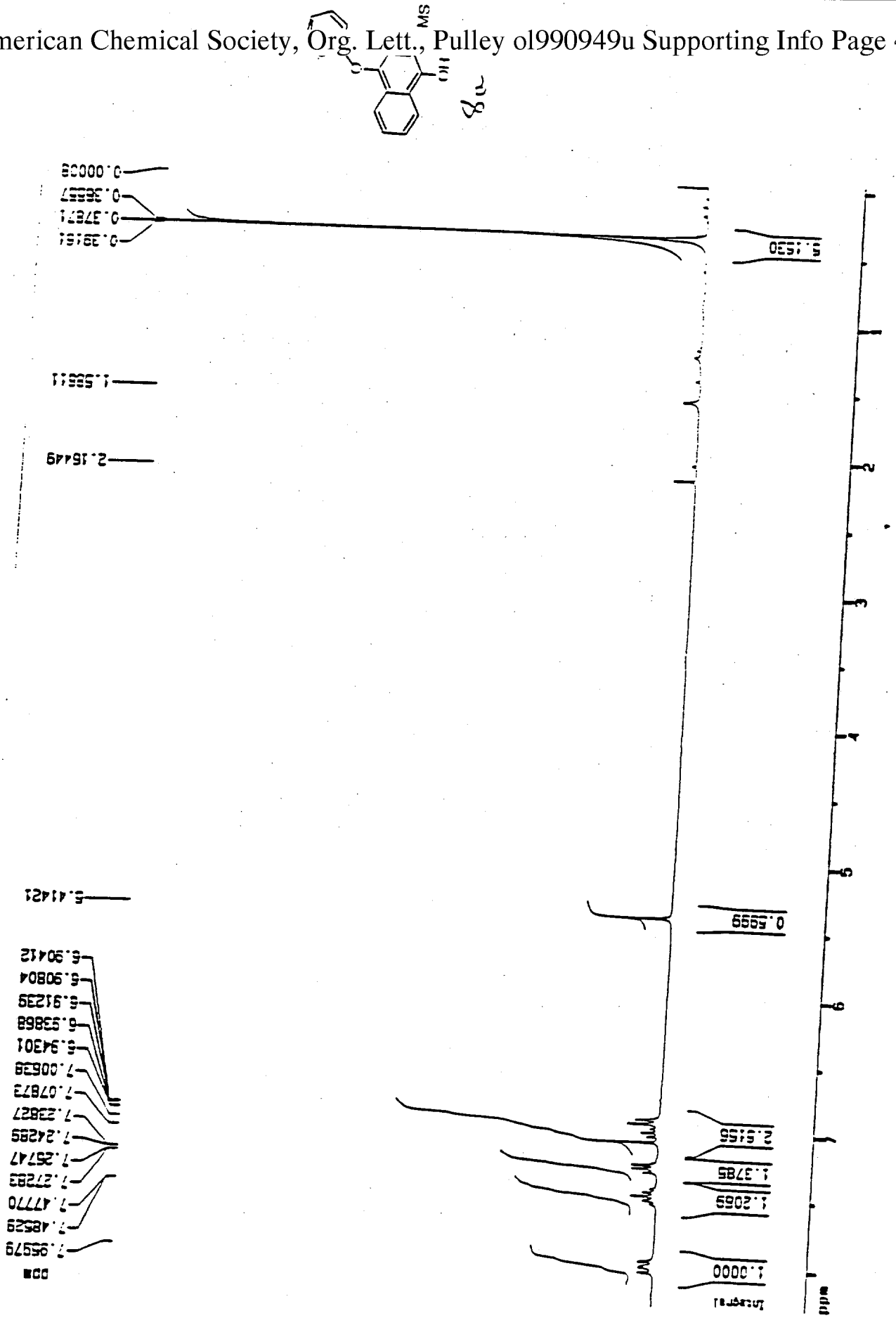
CF3
O
O
(CO)5Cr

5








MS
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5.41421
5.90412
5.90804
5.91239
5.93868
5.94301
7.00638
7.07873
7.23827
7.24289
7.25747
7.27283
7.47770
7.48529
7.95979
PPM
5.1530
0.5999
2.5155
1.3785
1.2069
1.0000
Integral
ppm