Palladium-Catalyzed Oxidative Tandem Reaction of Allylamines with Aryl Halides Leading to α,β-Unsaturated Aldehydes

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Supporting Information

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(A) Typical Experimental Procedure

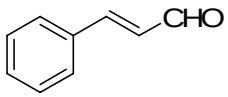
(a) Remark

Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and ^{13}C NMR spectra were measured on a 300 MHz spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. All reactions under nitrogen atmosphere were conducted using standard Schlenk techniques. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

(b) Typical Experimental Procedure for Pd-Catalyzed Tandem Reactions of N-Allylbenzenamine and Aryl halides:

A mixture of *N*-allyl-*N*-methylaniline **1** (0.25 mmol), aryl halide **2** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), PPh_3 (0.02 mmol), NaOAc (0.4 mmol), TBAB (0.2 mmol), and DMF (2 mL) was strred under air atmosphere at 100-120 °C for the indicated time (Tables 1 and 2) until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was poured into ethyl acetate, washed with brine (3 × 10 mL), and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate = 30:1) to afford the desired product.

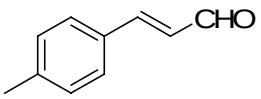
(B) Analytical Data for 3-15



Cinnamaldehyde (3)[1-3]

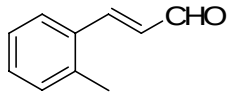
R_f = 0.43 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.70 (d, J = 7.7 Hz, 1H，-CHO), 7.58-7.55 (m, 1H, H-Ar), 7.50 (d, J = 16.0 Hz, 1H, =CH), 7.45-7.43 (m, 4H, H-Ar), 6.72 (dd, J = 7.7 Hz, J = 16.0 Hz, 1H, =CH); ^{13}C NMR (75

MHz, $CDCl_3$) δ: 193.6, 152.6, 133.9, 131.1, 129.0, 128.5, 128.4; MS (EI, 70 eV) *m/z* (%): 132 (M^+, 59), 131 (100), 103 (57), 77 (51).



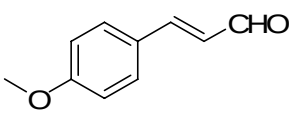
4-Methyl-cinnamaldehyde (4)[3]

R_f = 0.44 (petroleum ether/EtOAc = 10:1); ^1H NMR (300 MHz, $CDCl_3$) δ: 9.68 (d, *J* = 7.7 Hz, 1H, -CHO), 7.49-7.43 (m, 3H, H-Ar, =CH), 7.26-7.23 (m, 2H, H-Ar), 6.69 (dd, *J* = 7.7 Hz, *J* = 15.9 Hz, 1H, =CH), 2.40 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.7, 152.9, 131.3, 129.8, 129.1, 128.5, 127.7, 21.5; MS (EI, 70 eV) *m/z* (%): 146 (M^+, 17), 145 (18), 131 (100), 115 (37).



2-Methyl-cinnamaldehyde (5)[1,3]

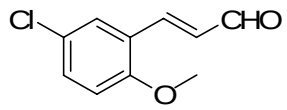
R_f = 0.44 (petroleum ether/EtOAc = 10:1); ^1H NMR (300 MHz, $CDCl_3$) δ: 9.73 (d, *J* = 7.7 Hz, 1H, -CHO), 7.78 (d, *J* = 15.8 Hz, 1H, =CH), 7.61-7.58 (m, 1H, H-Ar), 7.36-7.23 (m, 3H, H-Ar), 6.67 (dd, *J* = 7.7 Hz, *J* = 15.8 Hz, 1H, =CH), 2.48 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.7, 150.1, 137.8, 132.7, 131.1, 130.9, 129.5, 126.7, 126.5, 19.6; MS (EI, 70 eV) *m/z* (%): 146 (M^+, 21), 145 (15), 131 (100), 115 (47).



4-Methoxy-cinnamaldehyde (6)[1-4]

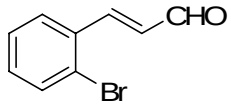
R_f = 0.23 (petroleum ether/EtOAc = 10:1); ^1H NMR (300 MHz, $CDCl_3$) δ: 9.66 (d, *J* = 7.7 Hz, 1H, -CHO), 7.53 (d, *J* = 8.7 Hz, 2H, H-Ar), 7.43 (d, *J* = 15.9 Hz, 1H,

=CH), 6.95 (d, *J* = 8.7 Hz, 2H, H-Ar), 6.61 (dd, *J* = 7.7 Hz, *J* = 15.9 Hz, 1H, =CH), 3.86 (s, 3H, -OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.6, 162.1, 152.6, 130.2, 126.6, 126.4, 114.4, 55.3; MS (EI, 70 eV) *m/z* (%): 162 (M^+, 100), 161 (60), 131 (53).



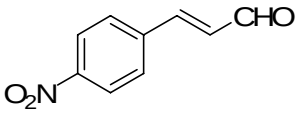
5-Chloro-2-methoxy-cinnamaldehyde (7)[7]

R_f = 0.32 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.69 (d, *J* = 7.8 Hz, 1H, -CHO), 7.74 (d, *J* = 16.1 Hz, 1H, =CH), 7.50 (s, 1H, H-Ar), 7.35 (d, *J* = 8.9 Hz, 1H, H-Ar), 6.88(d, *J* = 8.9 Hz, 1H, H-Ar), 6.75 (dd, *J* = 7.8 Hz, *J* = 16.1 Hz, 1H, =CH), 3.89 (s, 3H, -OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.1, 156.7, 146.3, 131.9, 129.9, 128.2, 125.9, 124.3, 112.6, 55.9; MS (EI, 70 eV) *m/z* (%): 196 (M^+, 28), 165 (100), 125 (58), 89 (64).



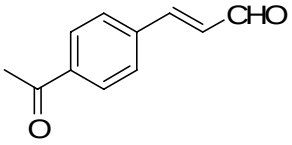
2-Bromo-cinnamaldehyde (8)[5]

R_f = 0.49 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.77 (d, *J* = 7.7 Hz,1H, -CHO), 7.90 (d, *J* = 15.9 Hz, 1H, =CH), 7.67-7.64 (m, 2H, H-Ar), 7.37-7.30 (m, 1H, H-Ar), 7.28-7.26 (m, 1H, H-Ar), 6.67 (dd, *J* = 7.7 Hz, *J* = 15.9 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.4, 150.5, 133.8, 133.6, 132.1, 130.7, 128.0, 127.9, 125.7; MS (EI, 70 eV) *m/z* (%): 212 (M^+ + 2, 4), 210 (M^+, 4), 131 (100), 103 (34).



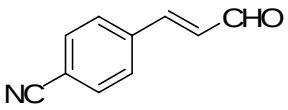
4-Nitro-cinnamaldehyde (9)[1-3]

R_f = 0.23 (petroleum ether/EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ:9.78 (d, *J* = 7.4 Hz, 1H, -CHO), 8.30 (d, *J* = 8.7 Hz, 2H, H-Ar), 7.75 (d, *J* = 8.7 Hz, 2H, H-Ar), 7.55 (d, *J* = 16.1 Hz, 1H, =CH), 6.82 (dd, *J* = 7.4Hz, *J* = 16.1 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.7, 148.7, 139.8, 131.6, 128.9, 128.2, 124.2; MS (EI, 70 eV) *m/z* (%): 177 (M^+, 25), 159 (100), 130 (92), 77 (94).



4-Acetyl-cinnamaldehyde (10)[1,3]

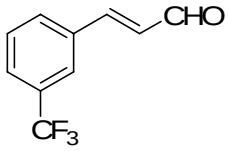
R_f = 0.20 (petroleum ether/EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.75 (d, *J* = 7.6 Hz, 1H, -CHO), 8.02 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.67 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.53 (d, *J* = 16.0 Hz, 1H, =CH), 6.79 (dd, *J* = 7.6 Hz, *J* = 16.0 Hz, 1H, =CH). 2.65 (s, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.1, 193.2, 150.5, 138.5, 138.0, 130.3, 128.8, 128.4, 26.6; MS (EI, 70 eV) *m/z* (%): 174 (M^+, 90), 159 (74), 131 (100), 103 (70).



4-Cyano-cinnamaldehyde (11)[1,3,4]

R_f = 0.22 (petroleum ether/EtOAc = 5:1);. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.75 (d, *J* = 7.5 Hz, 1H, -CHO), 7.72 (d, *J* = 8.5Hz, 2H, H-Ar), 7.66 (d, *J* = 8.5Hz, 2H, H-Ar), 7.48 (d, *J* = 16.1Hz, 1H, =CH), 6.76 (dd, *J* = 7.5Hz, *J* = 16.1 Hz, 1H, =CH); ^{13}C NMR

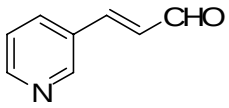
(75 MHz, $CDCl_3$) δ:192.9, 149.4, 138.1, 132.8, 131.1, 128.7, 118.1, 114.2; MS (EI, 70 eV) *m/z* (%): 157 (M^+, 71), 156 (100), 129 (63), 128 (65);



3-Trifluoromethy-cinnamaldehyde (12) [3]

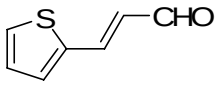
R_f = 0.37 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.75 (d, *J* = 7.5 Hz, 1H, -CHO), 7.81 (s, 1H, H-Ar), 7.76 (d, *J* = 7.8 Hz, 1H, H-Ar), 7.70 (d, *J* = 7.8 Hz, 1H, H-Ar), 7.58-7.55 (m, 1H, H-Ar), 7.50 (d, *J* = 16.0 Hz,, 1H, =CH), 6.78 (dd, *J* = 7.5 Hz, *J* = 16.0 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.9, 150.2, 134.8, 131.1, 130.0, 129.7, 127.5, 127.4, 127.2 (q, $J_{C\text{-}F}$ = 270.7 Hz), 125.1;

MS (EI, 70 eV) *m/z* (%): 200 (M^+, 7), 199 (19), 151 (51), 131 (100).



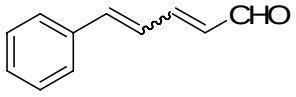
(*E*)-3-(Pyridin-3-yl)acrylaldehyde (13) [2, 4]

Rf = 0.20 (2:1 petroleum ether/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ:9.72 (d, *J* = 7.5 Hz, 1H, -CHO), 8.77 (s, 1H, H-Ar), 8.64 (s, 1H, H-Ar), 7.88 (d, *J* = 7.8 Hz, 1H, H-Ar), 7.48 (d, *J* = 16.1 Hz, 1H, =CH), 7.39-7.35 (m, 1H, H-Ar), 6.82 (dd, *J* = 7.5Hz, *J* = 16.1 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.9, 151.8, 149.9, 148.3, 134.4, 130.2, 129.8, 123.9; MS (EI, 70 eV) *m/z* (%): 133 (M^+, 60), 132 (87), 79 (78), 51 (100).



(*E*)-3-(Thiophen-2-yl)acrylaldehyde (14)[6]

R_f = 0.29 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.63 (d, *J* = 7.7 Hz, 1H, -CHO), 7.58 (d, *J* = 15.6 Hz, 1H, =CH), 7.50 (d, *J* = 5.1 Hz, 1H, H-Ar), 7.36 (d, *J* = 3.6 Hz, 1H, H-Ar), 7.11 (dd, *J* = 3.6 Hz, *J* = 5.1 Hz, 1H, H-Ar), 6.51 (dd, *J* = 7.7 Hz, *J* = 15.6 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.8, 144.2, 139.2, 131.9, 130.3, 128.5, 127.4; MS (EI, 70 eV) *m/z* (%): 138 (M^+, 100), 137 (26), 110 (52), 109 (55).



5-Phenylpenta-2,4-dienal (15)[2]

R_f = 0.36 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.62 (d, *J* = 7.9 Hz, 1H, -CHO), 7.52-7.49 (m, 2H, H-Ar), 7.41-7.37 (m, 3H, H-Ar), 7.28-7.26 (m, 1H, =CH), 7.03-7.00 (m, 2H, =CH), 6.28 (dd, *J* = 7.9 Hz, *J* = 15.2 Hz, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.5, 151.9, 142.4, 135.6, 131.6, 129.6, 128.9, 127.5, 126.2; MS (EI, 70 eV) *m/z* (%): 158 (M^+, 51), 157 (17), 129 (100), 128 (69).

References

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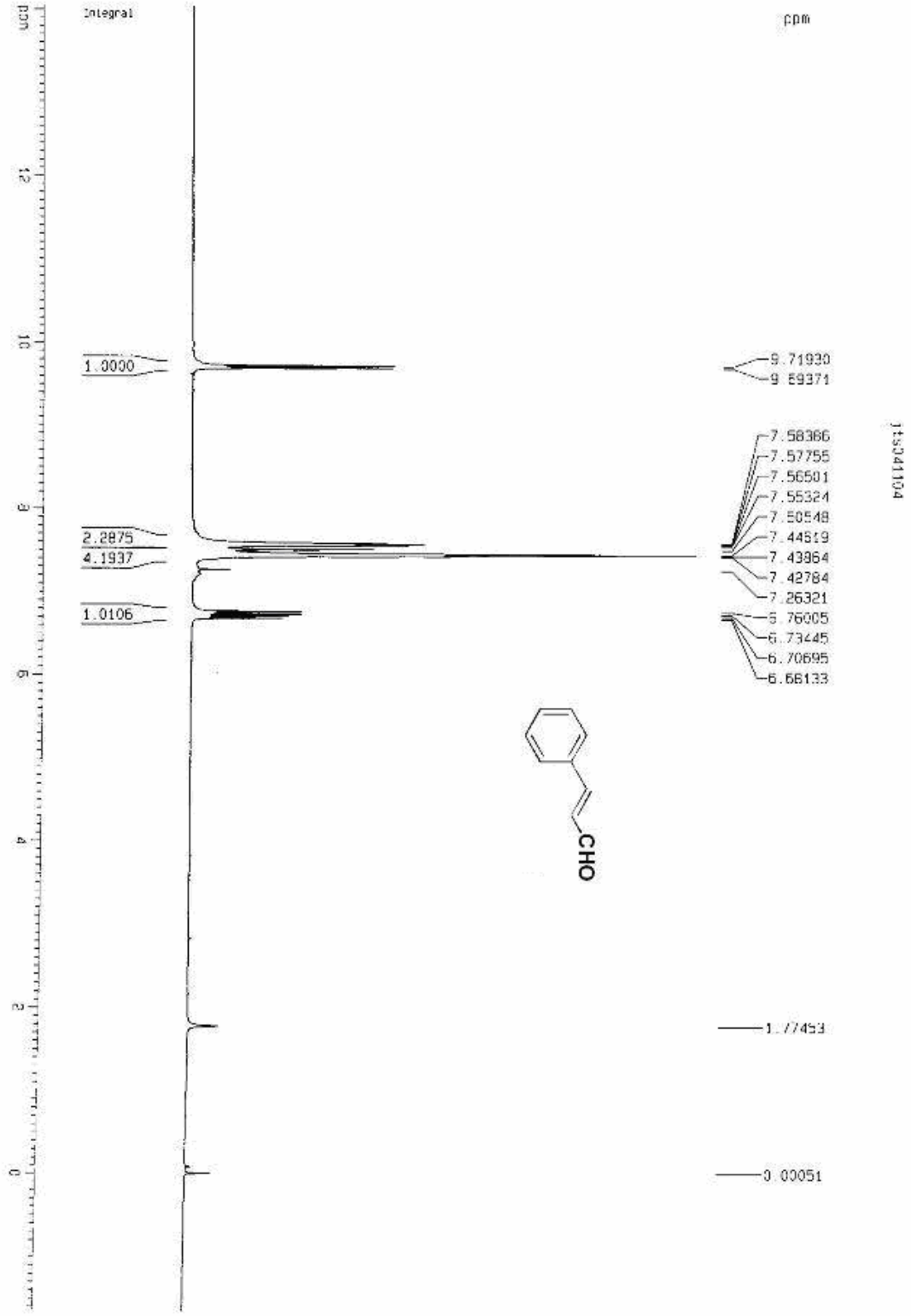
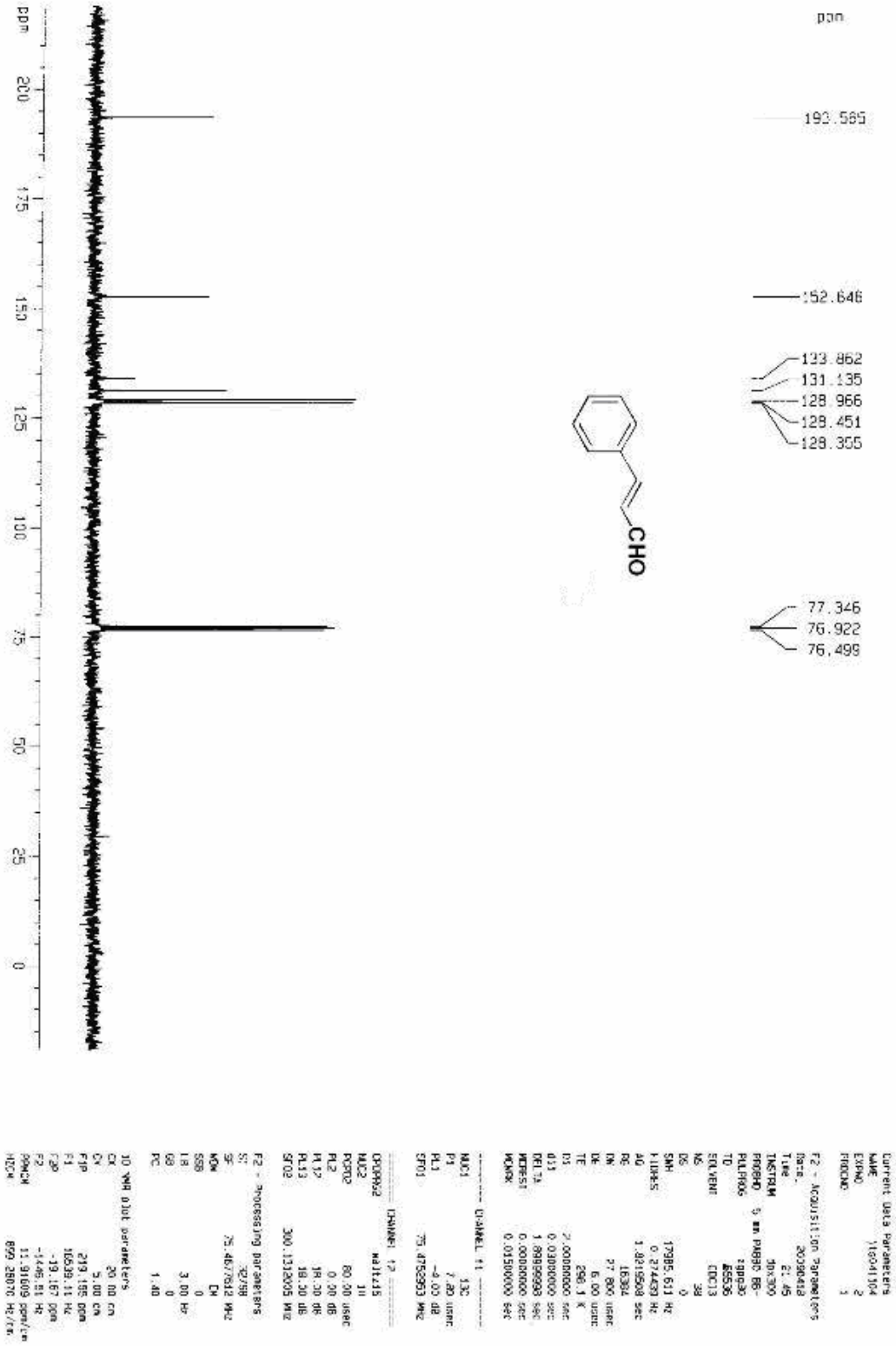
(D) Spectra

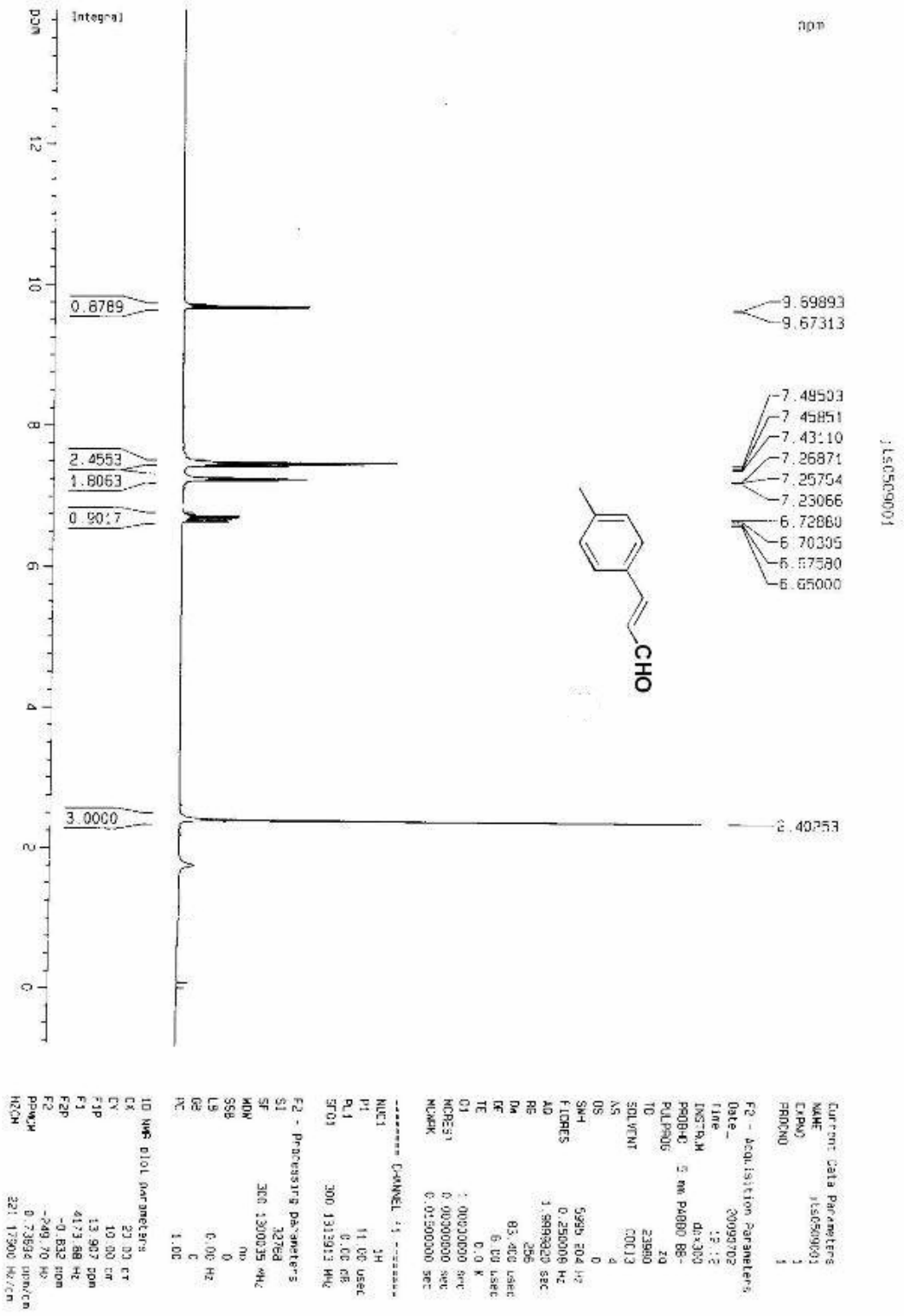
Cinnamaldehyde (3)



Cinnamaldehyde (3)



4-Methyl-cinnamaldehyde (4)



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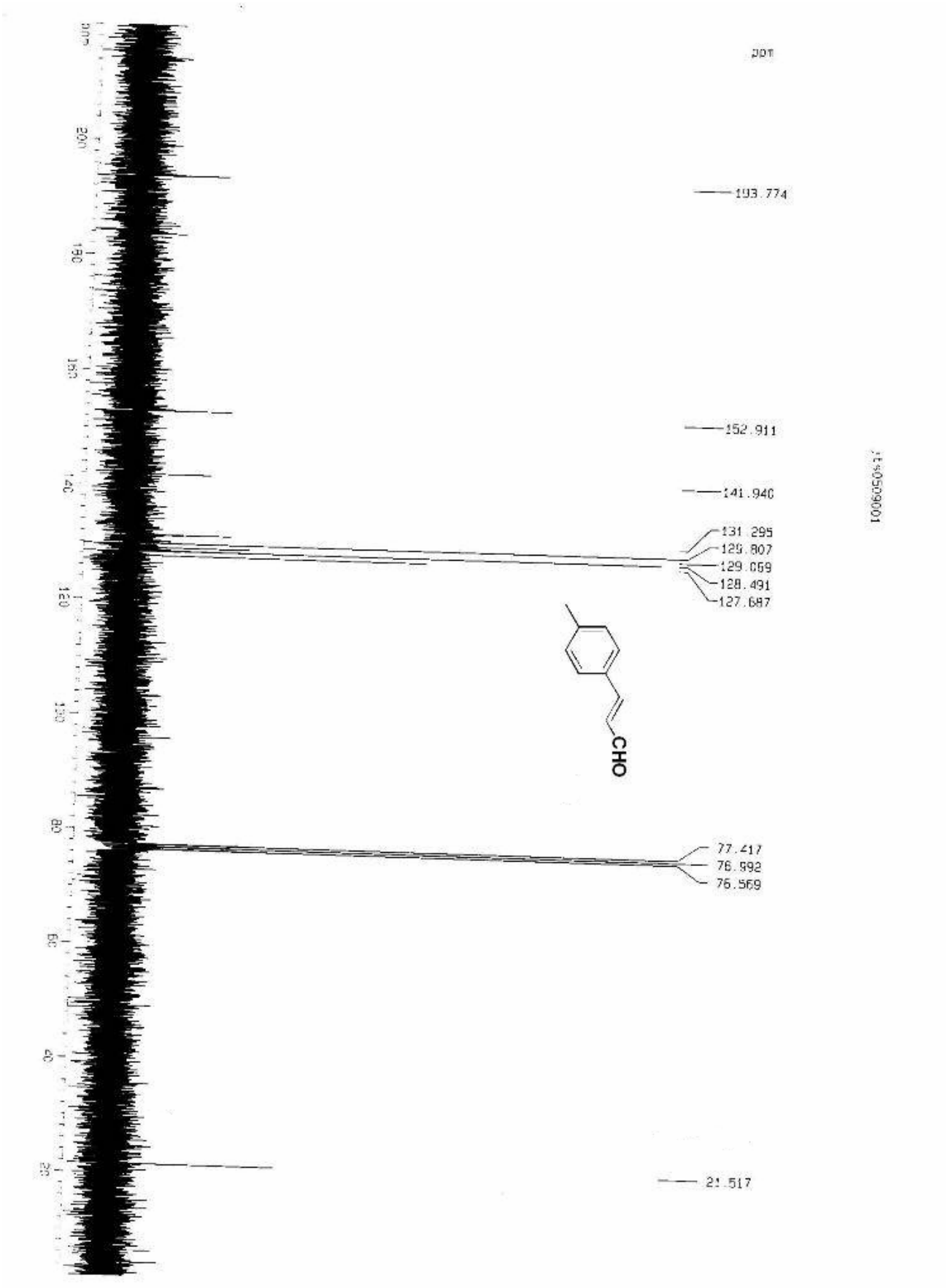
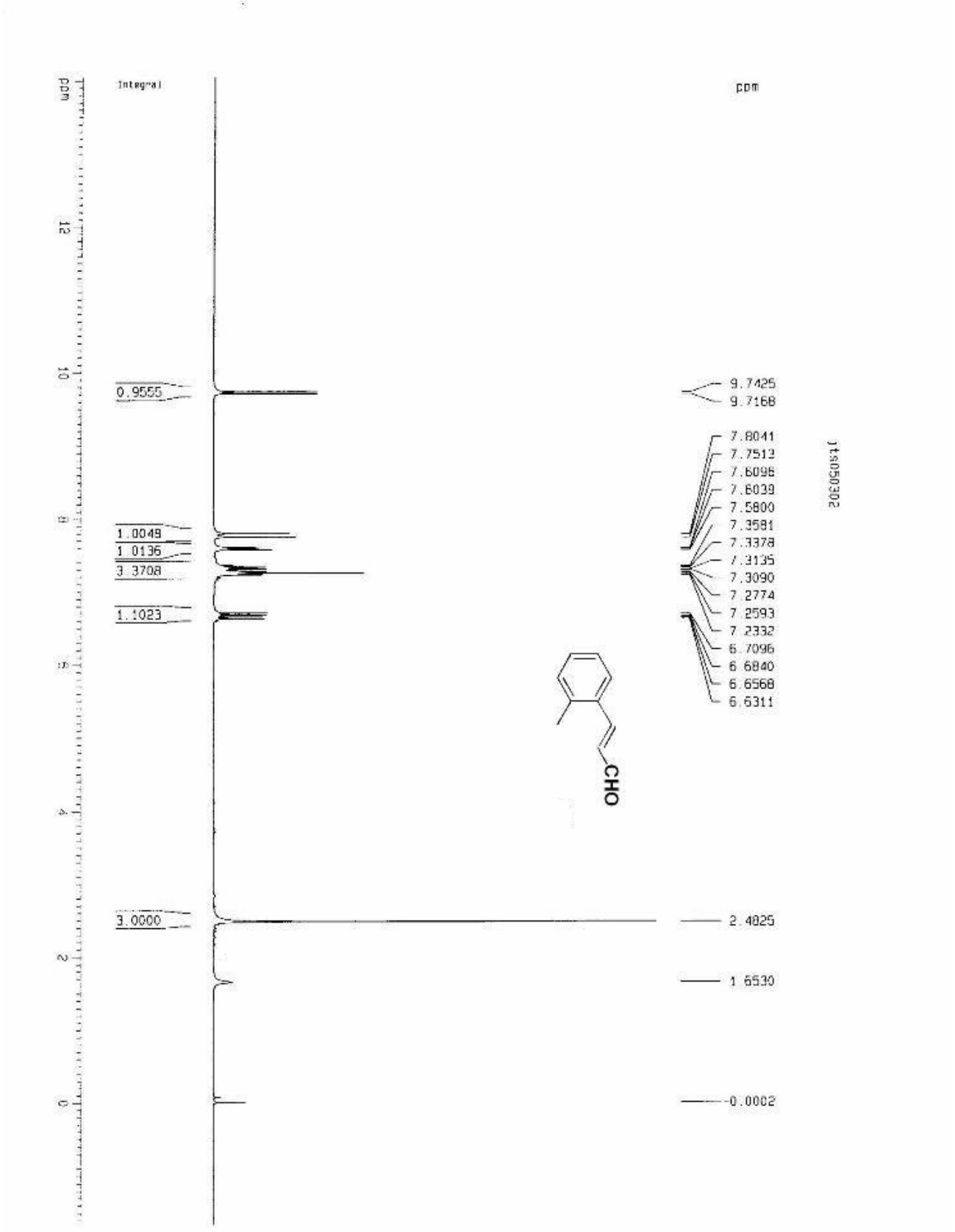
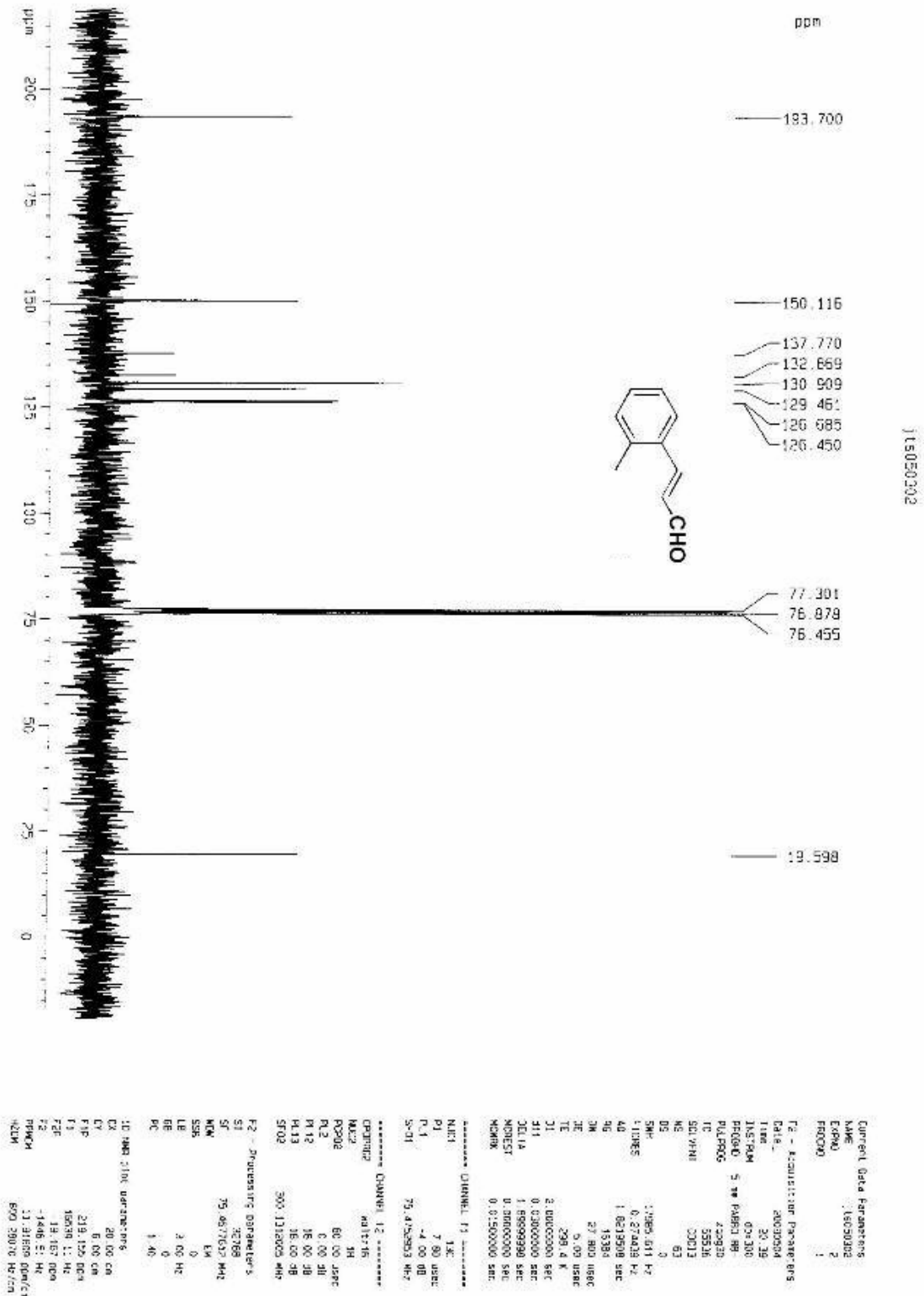


2-Methyl-cinnamaldehyde (5)



2-Methyl-cinnamaldehyde (5)



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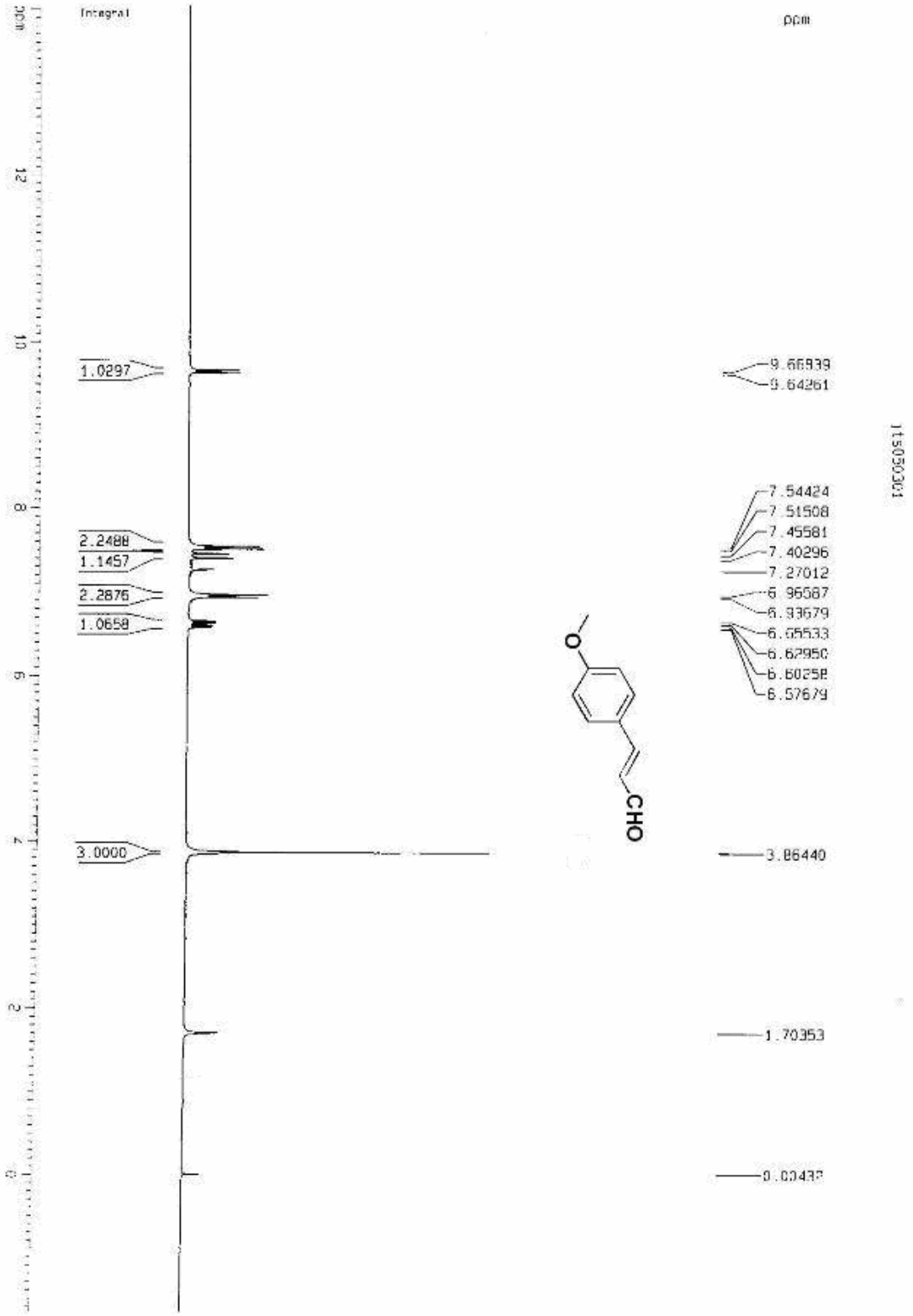
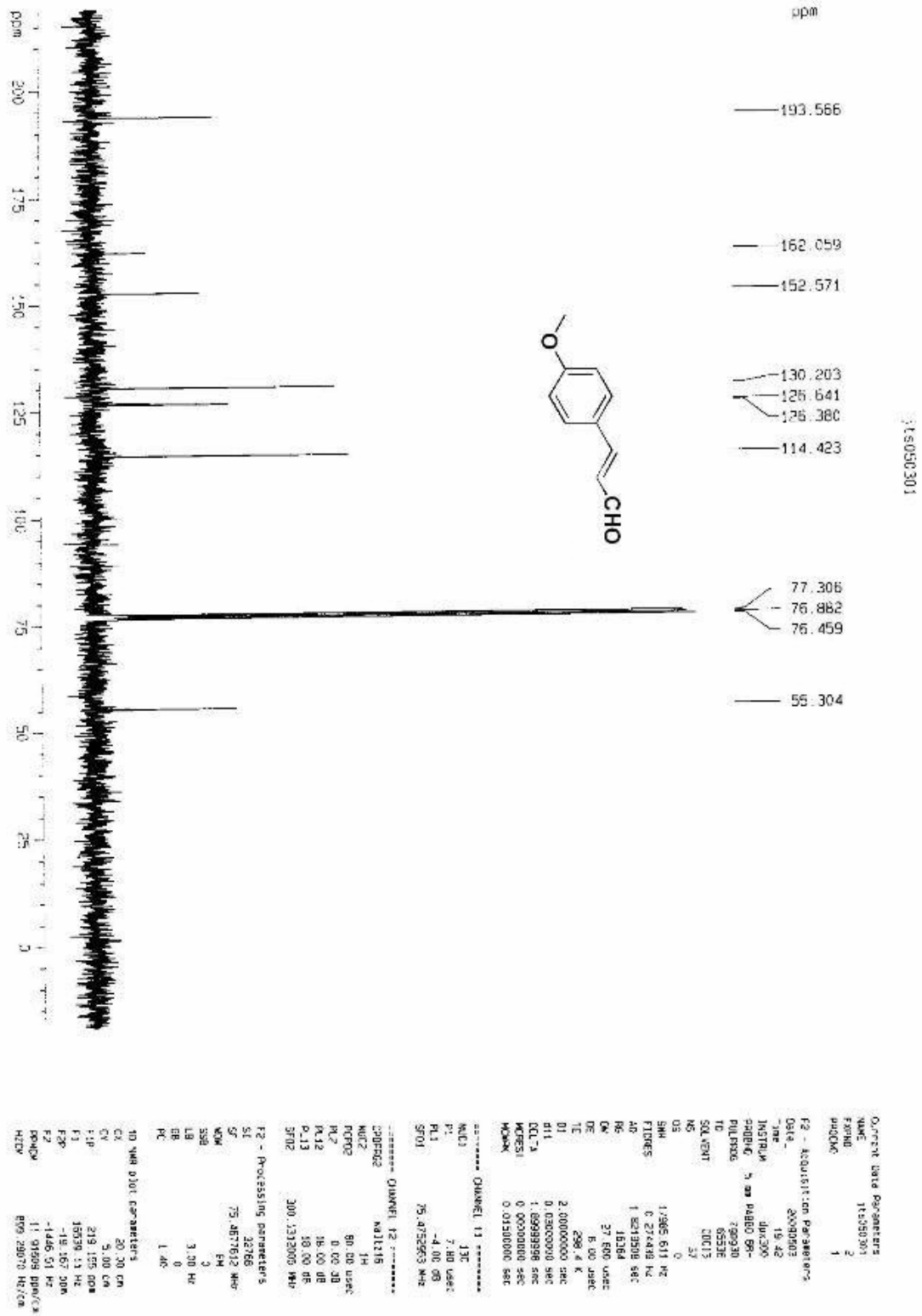
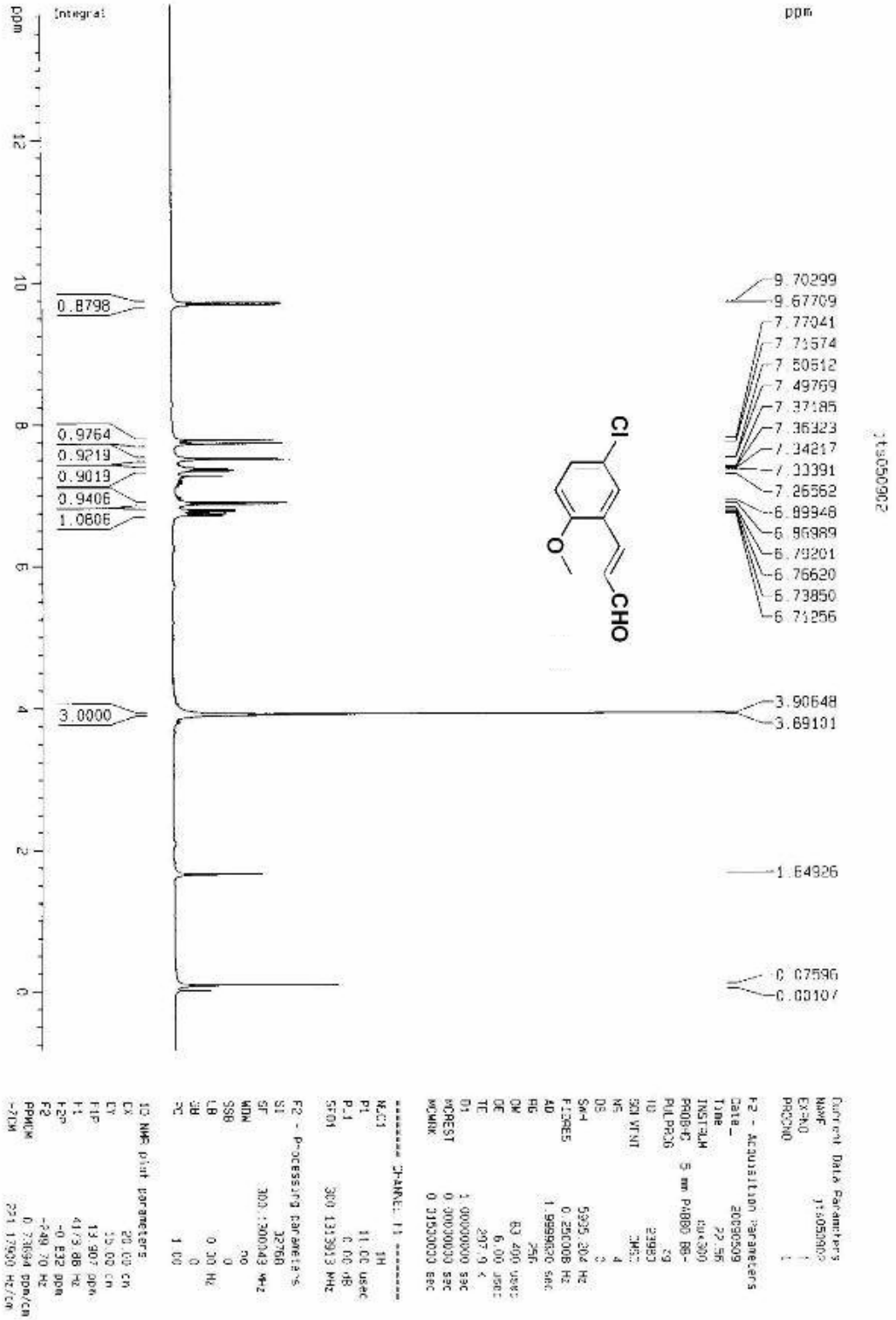


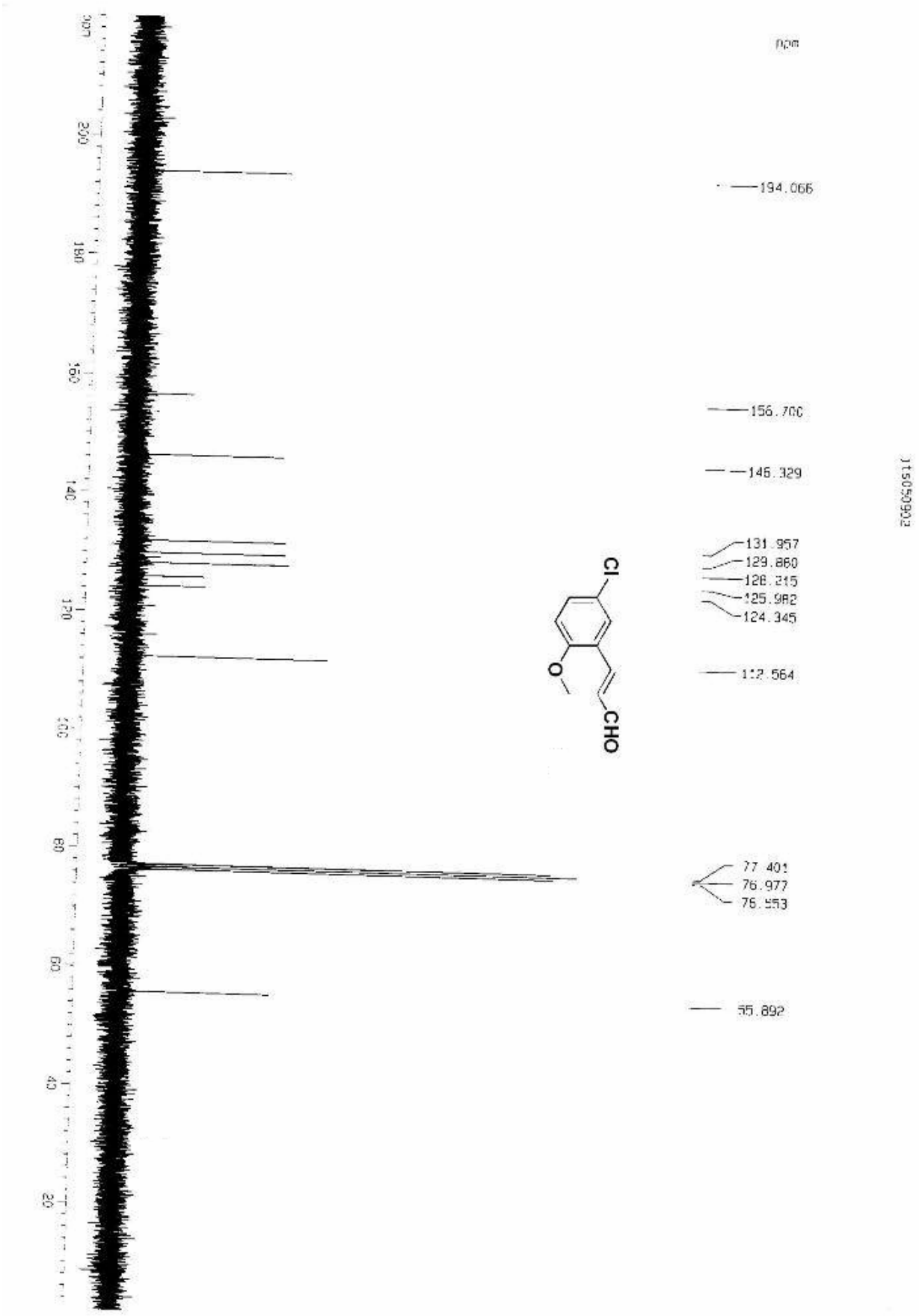
4-Methoxy-cinnamaldehyde (6)



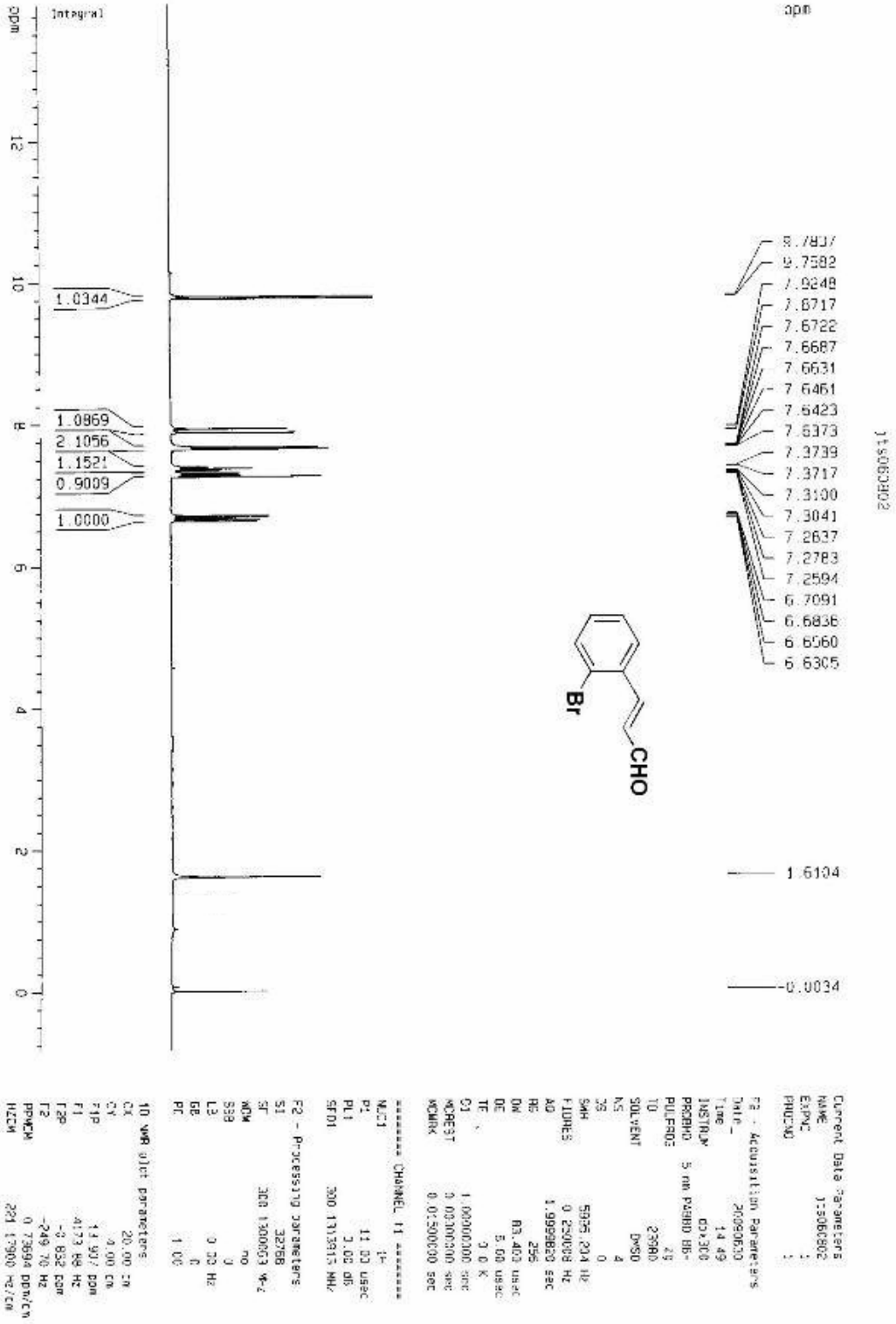
5-Chloro-2-methoxy-cinnamaldehyde (7)



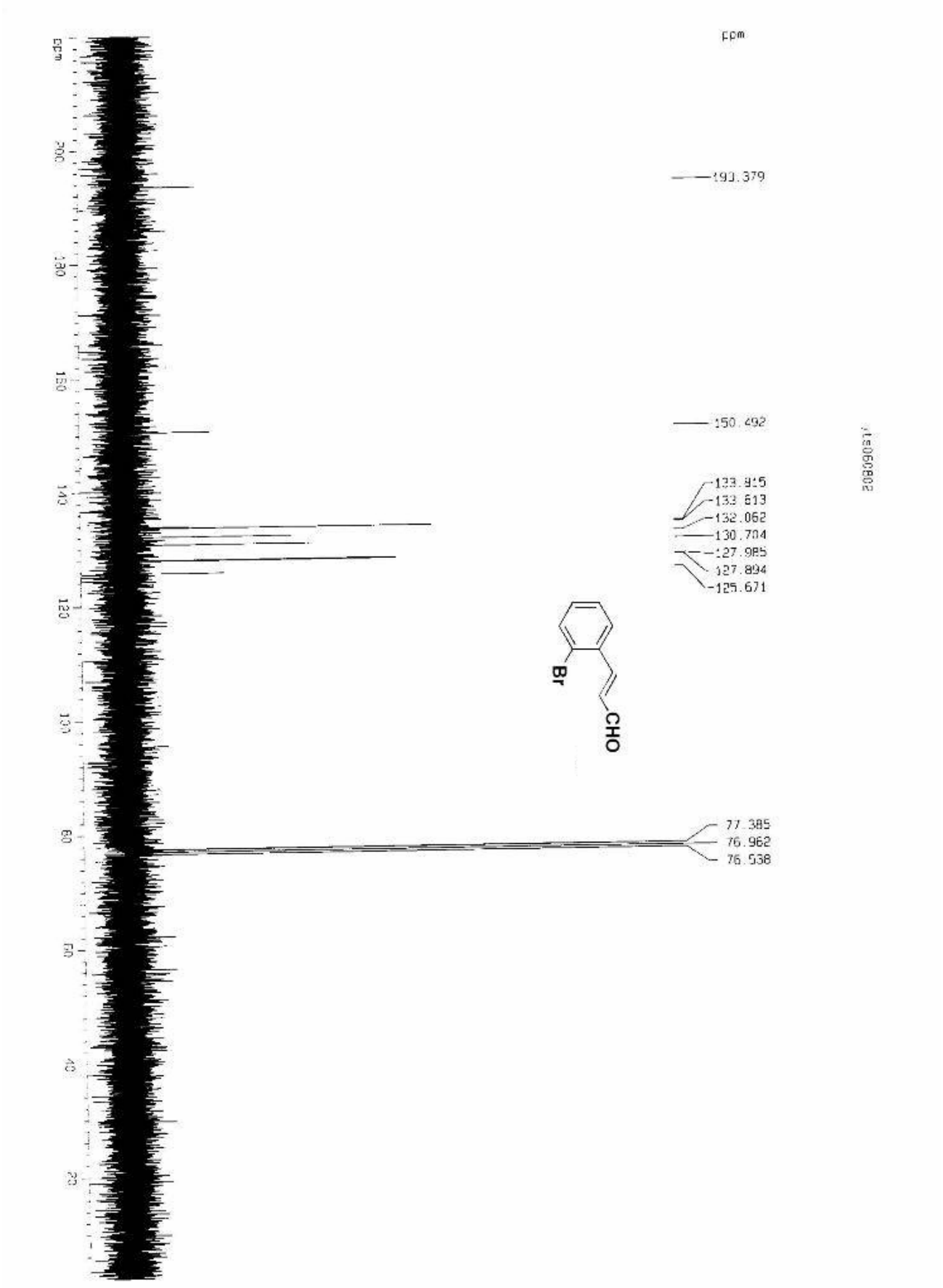
5-Chloro-2-methoxy-cinnamaldehyde (7)



2-Bromo-cinnamaldehyde (8)



2-Bromo-cinnamaldehyde (8)



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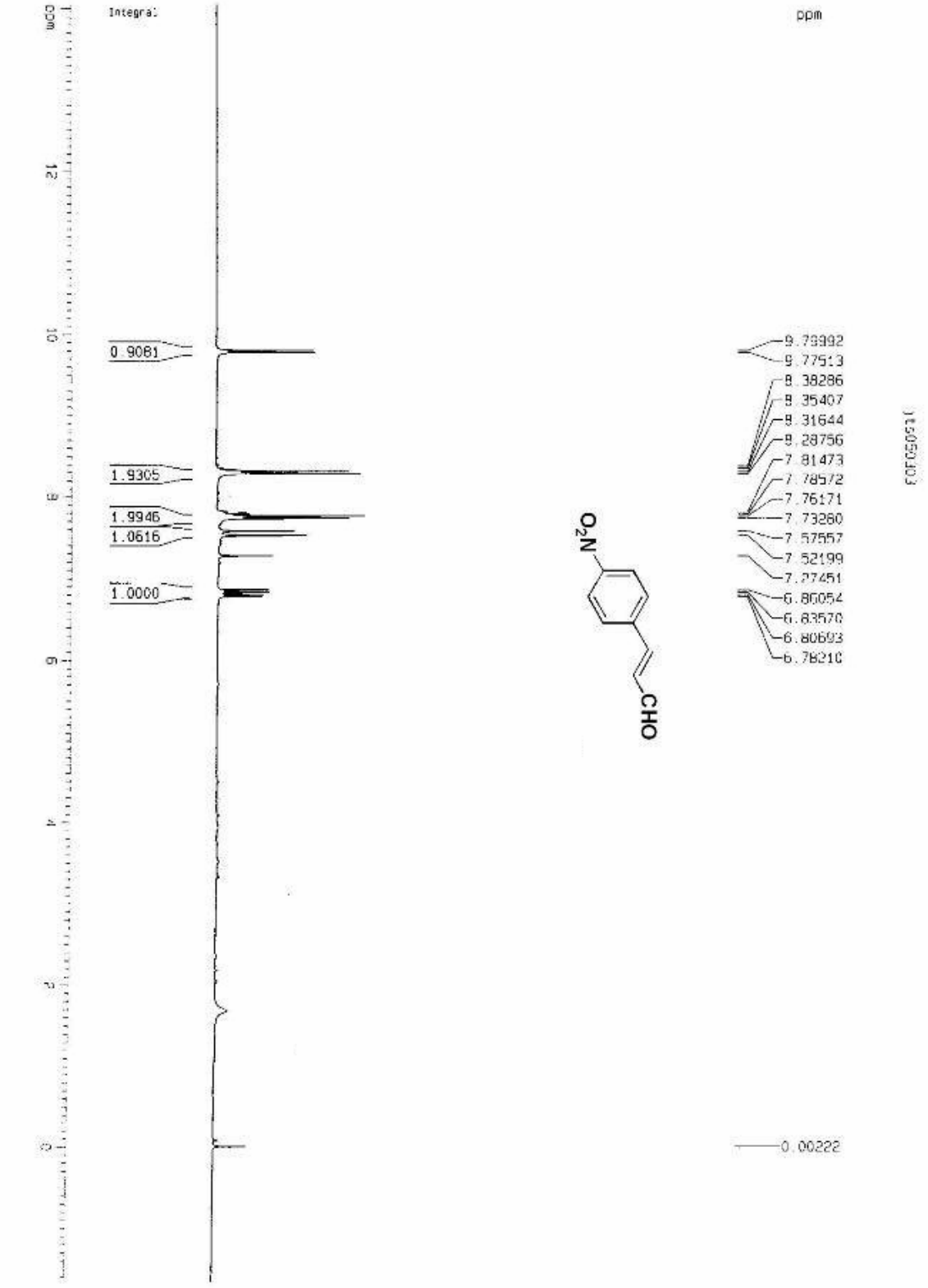

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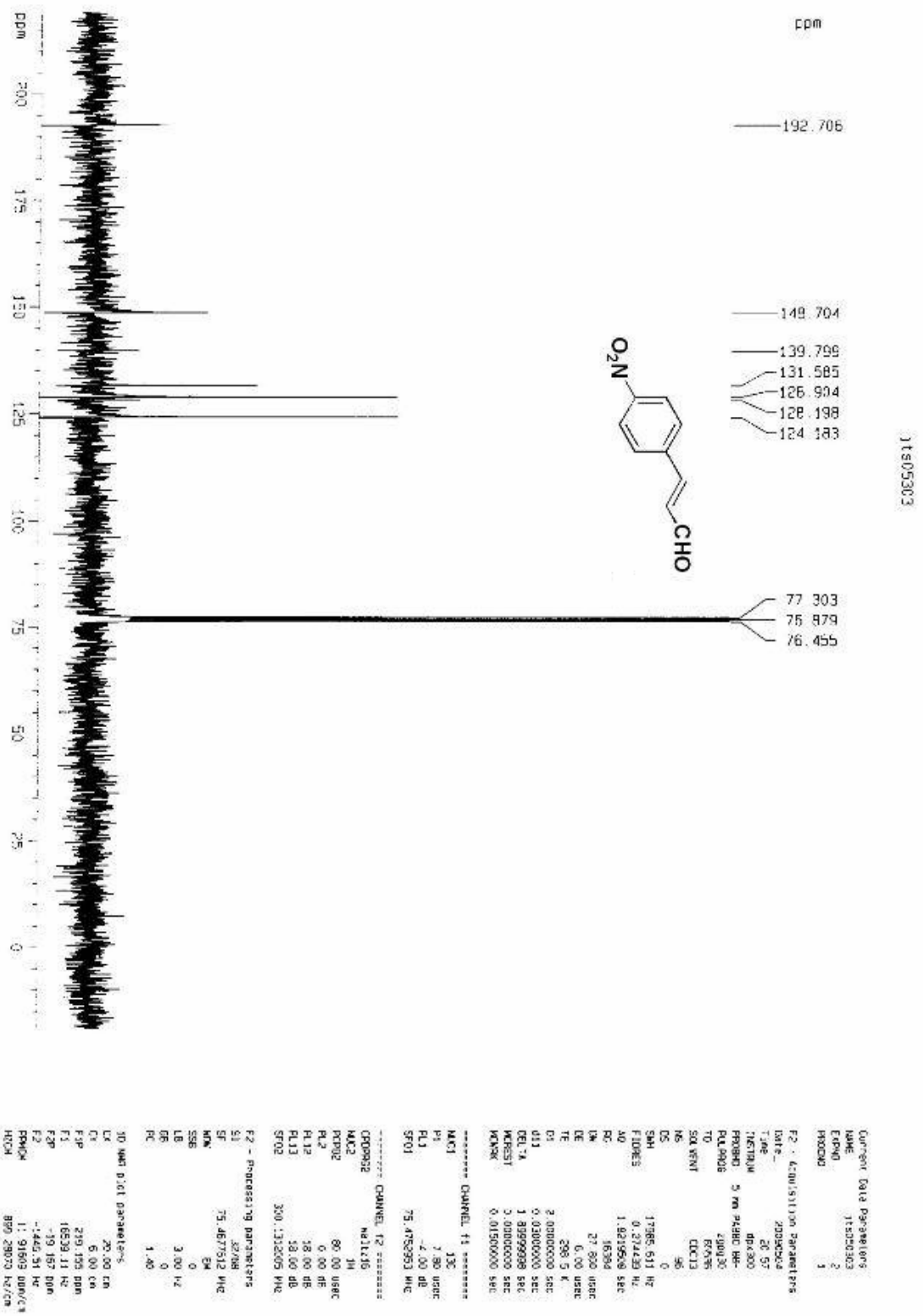

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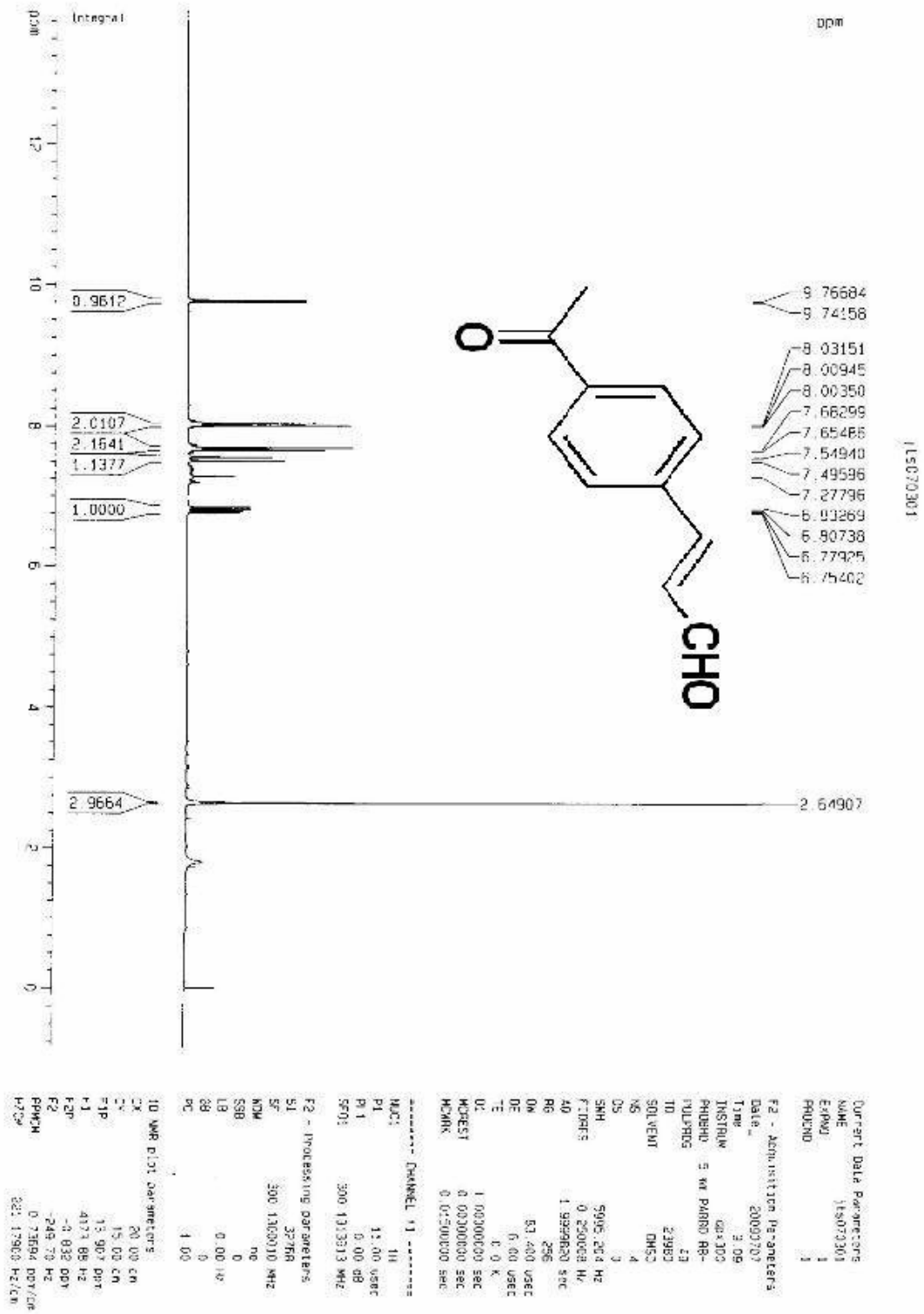
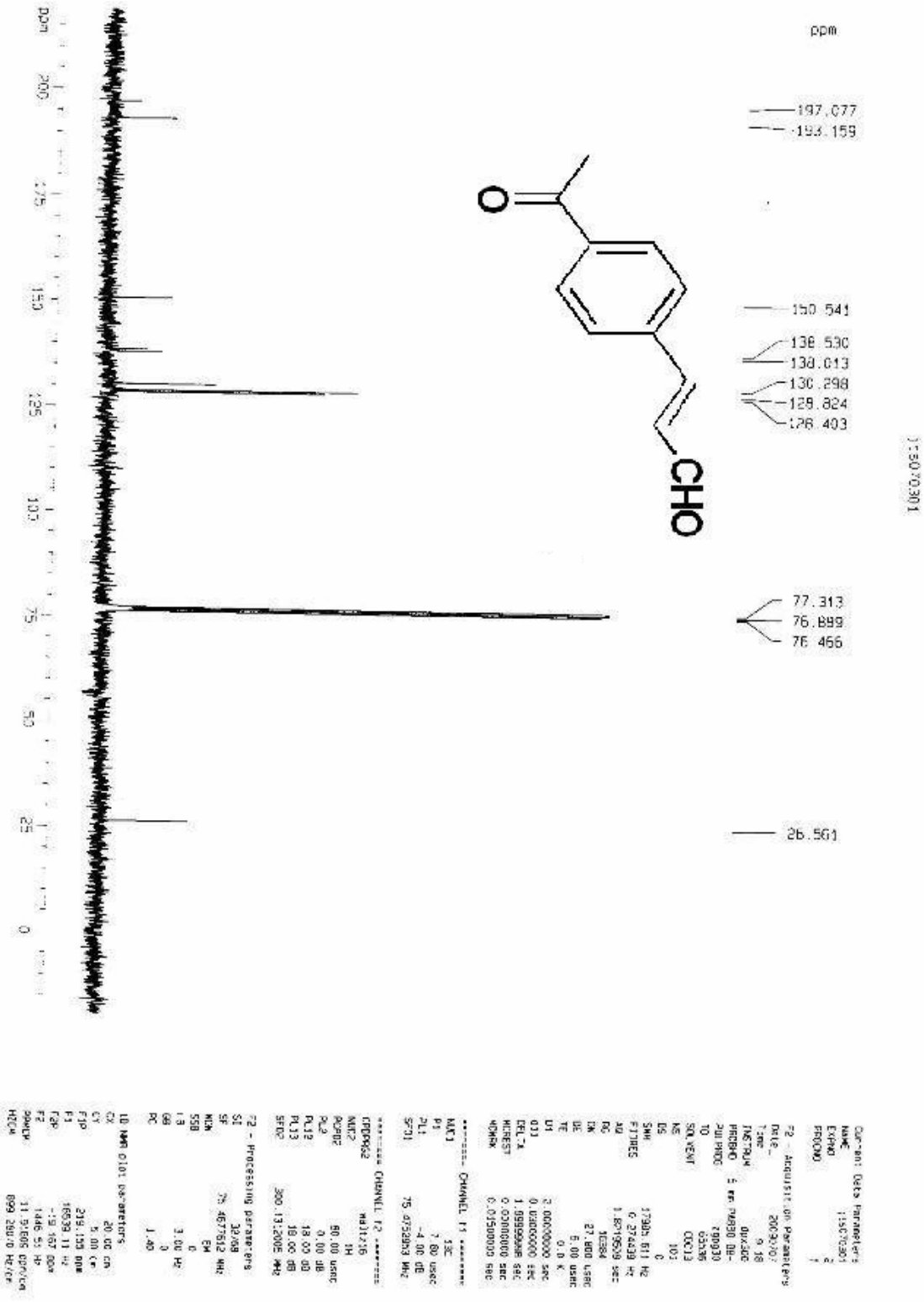
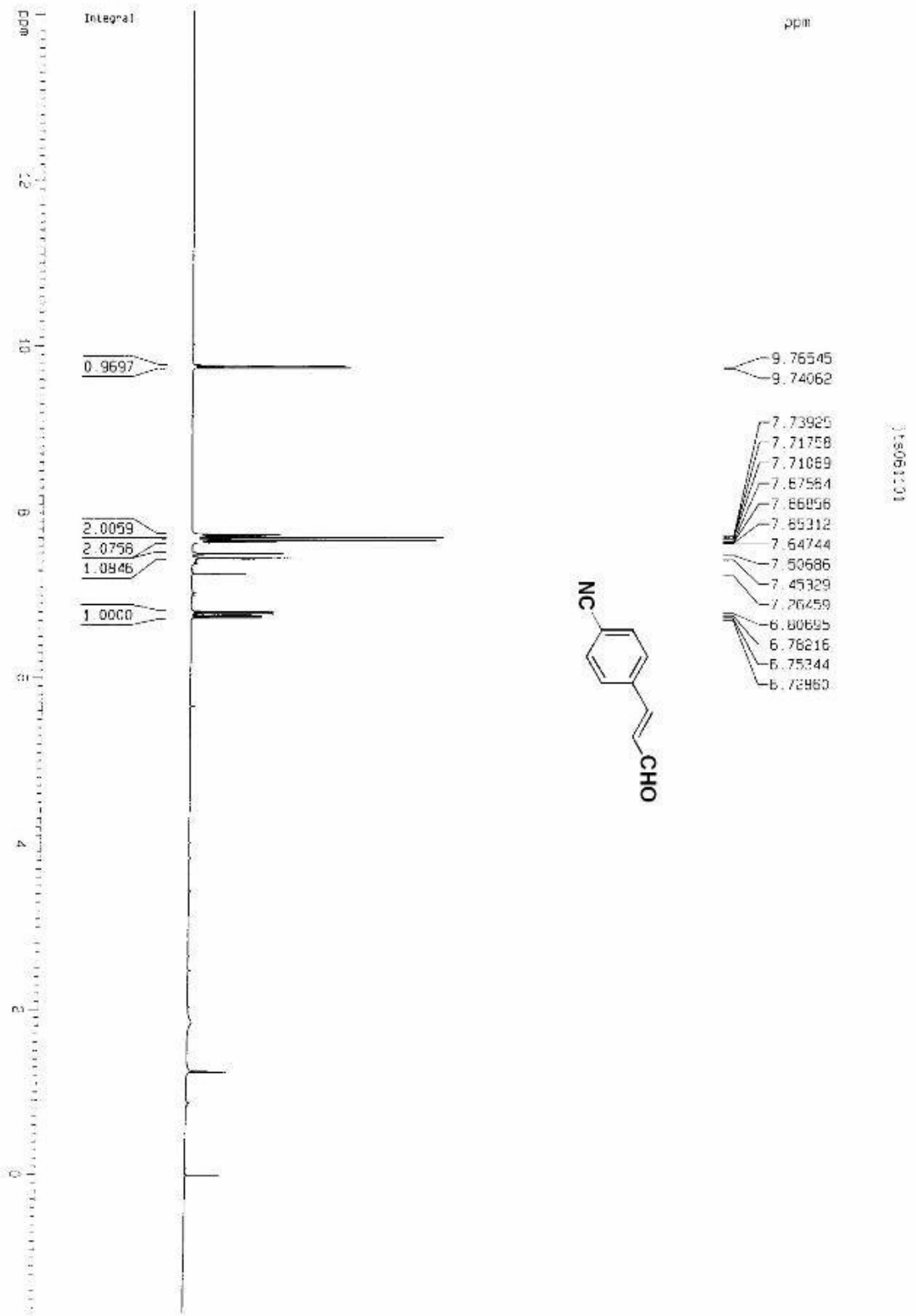


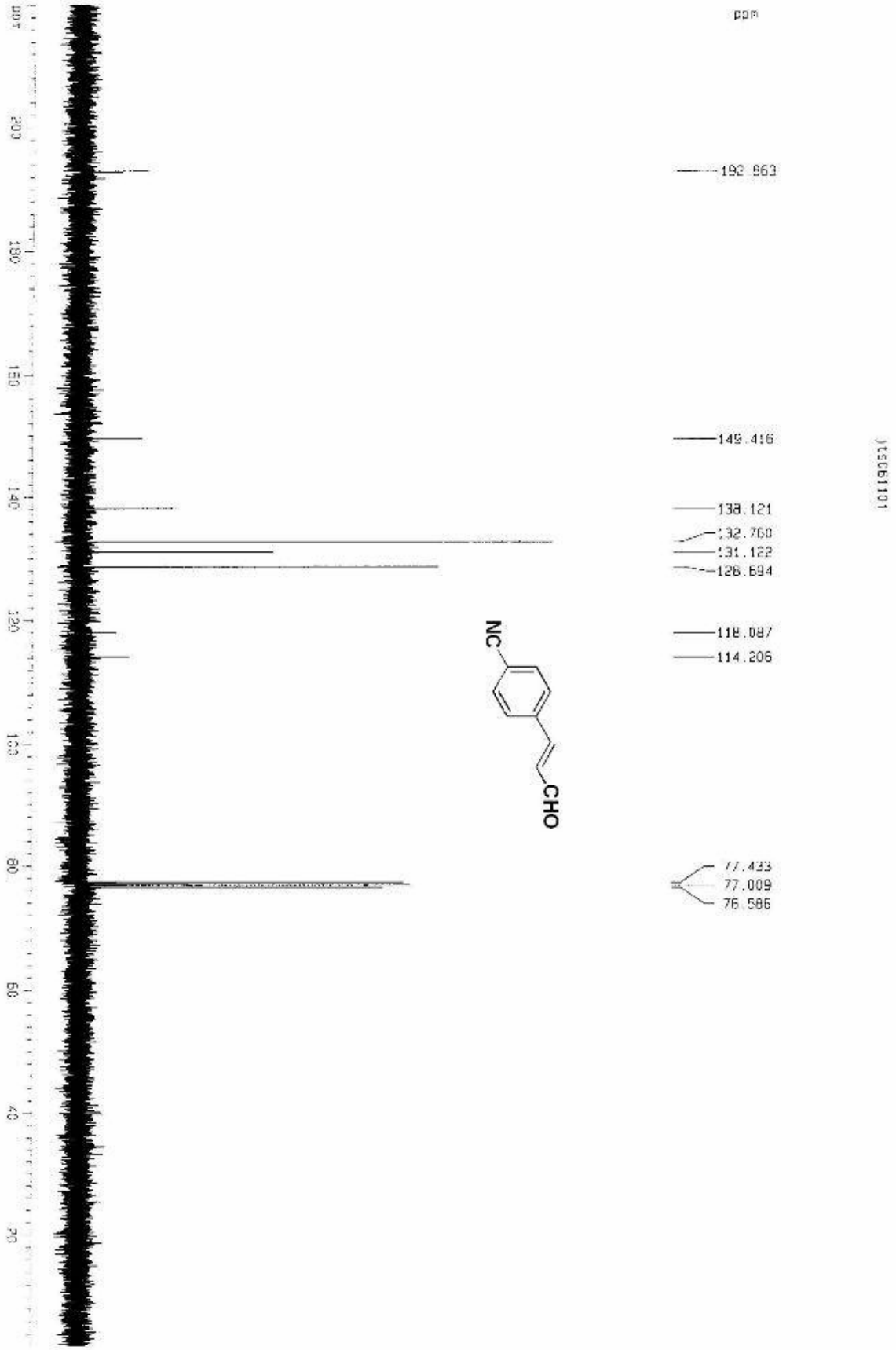
4-Acetyl-cinnamaldehyde (10)



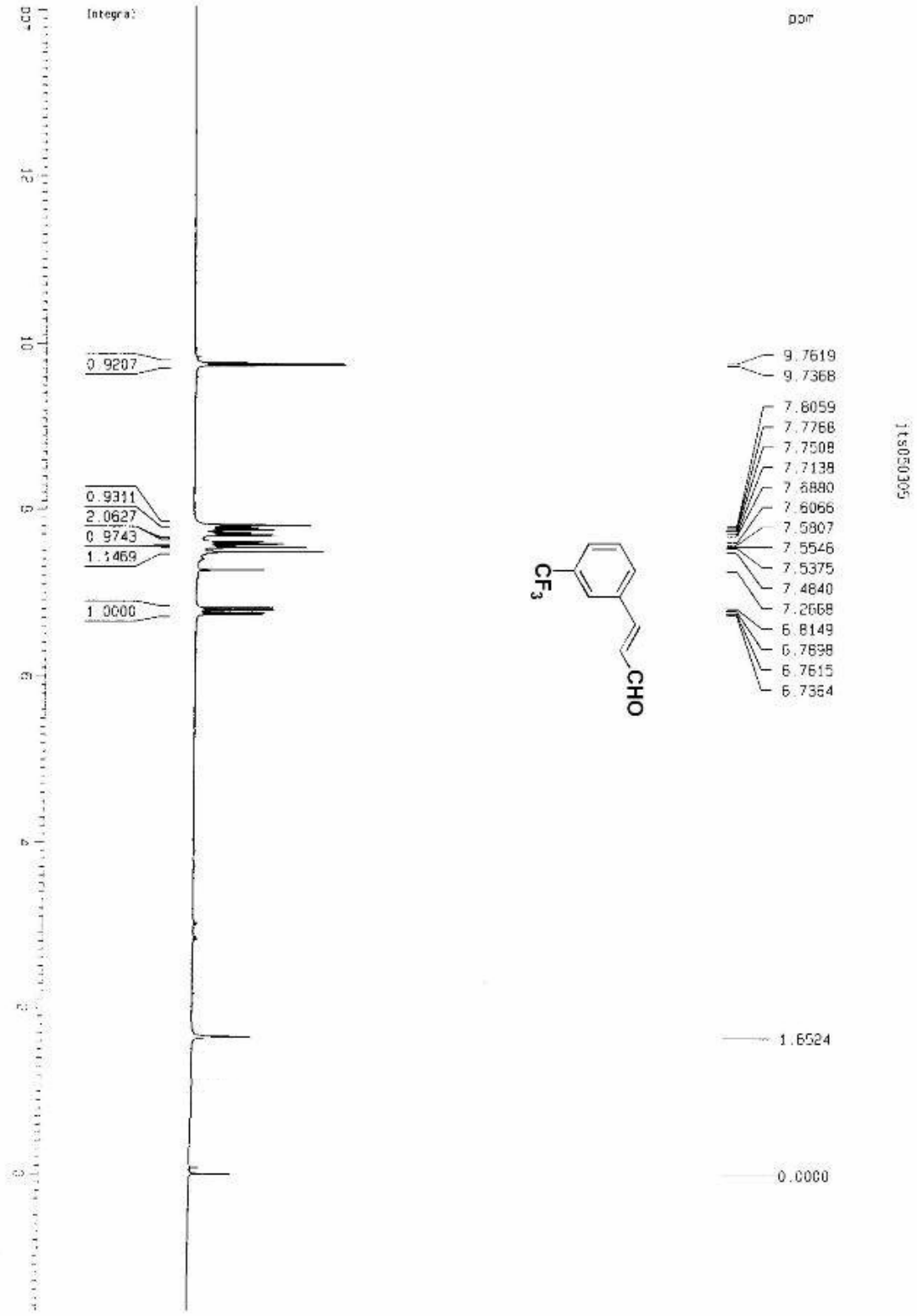
4-Cyano-cinnamaldehyde (11)



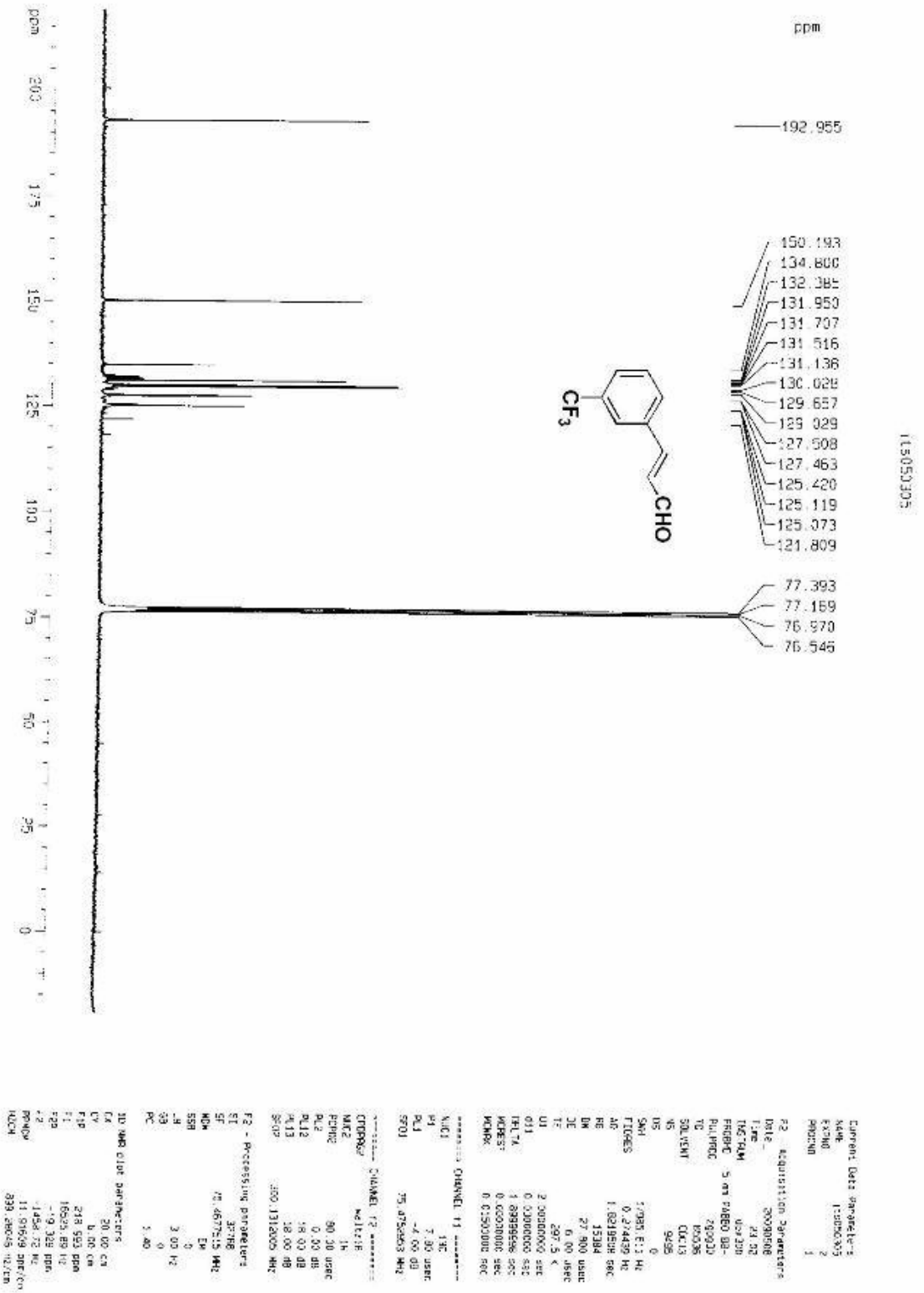
4-Cyano-cinnamaldehyde (11)



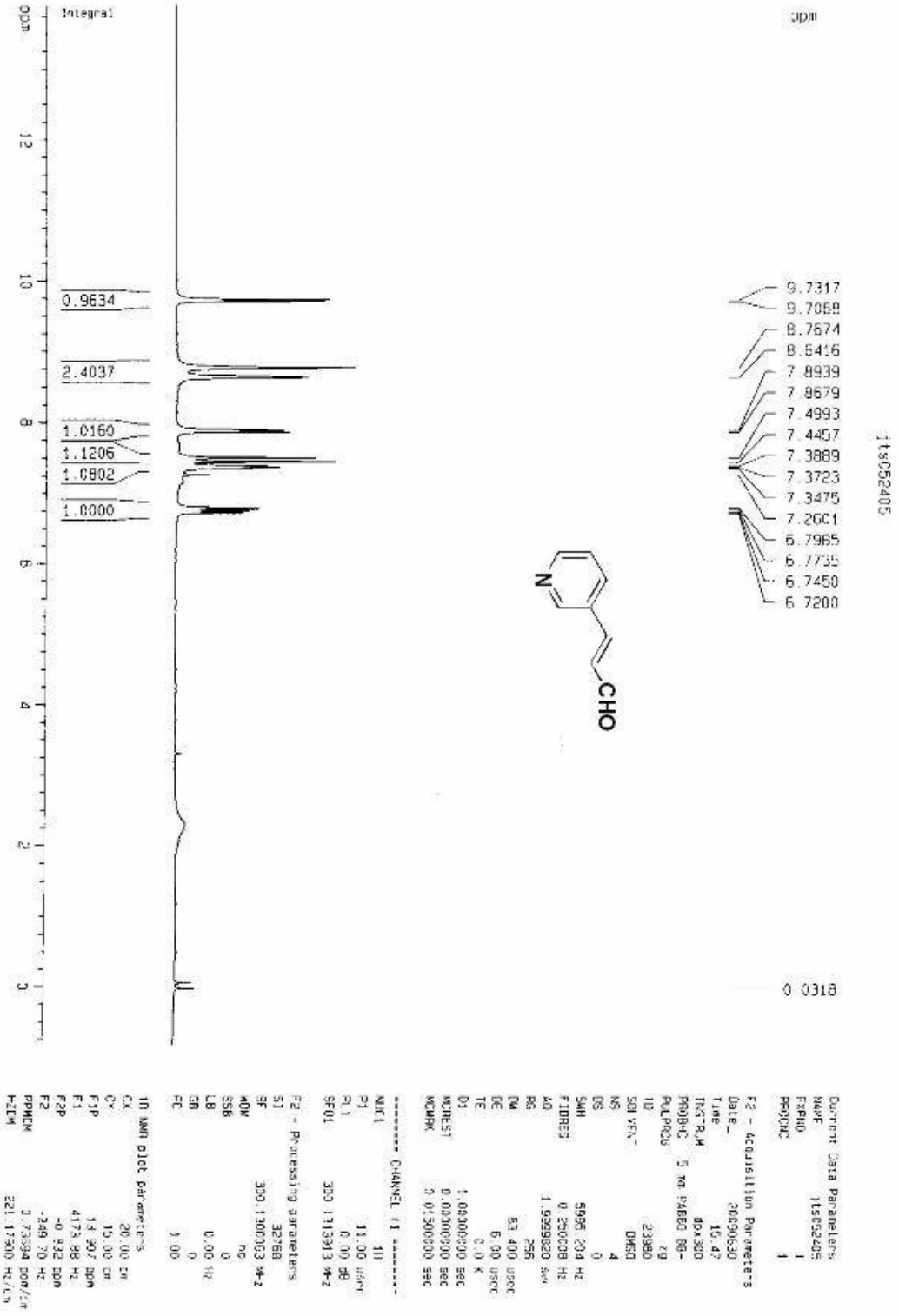
3-Trifluoromethy-cinnamaldehyde (12)



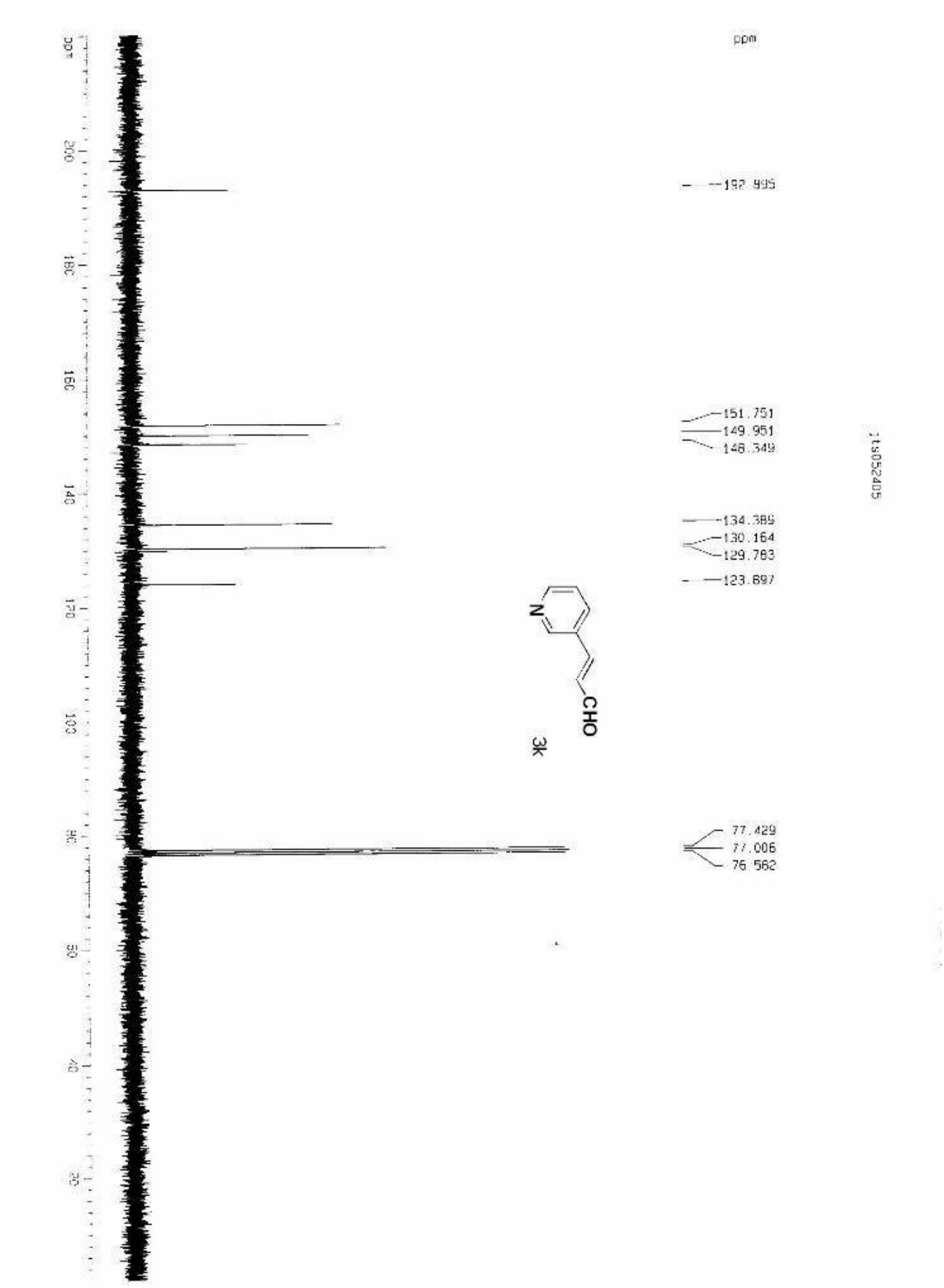
3-Trifluoromethy-cinnamaldehyde (12)



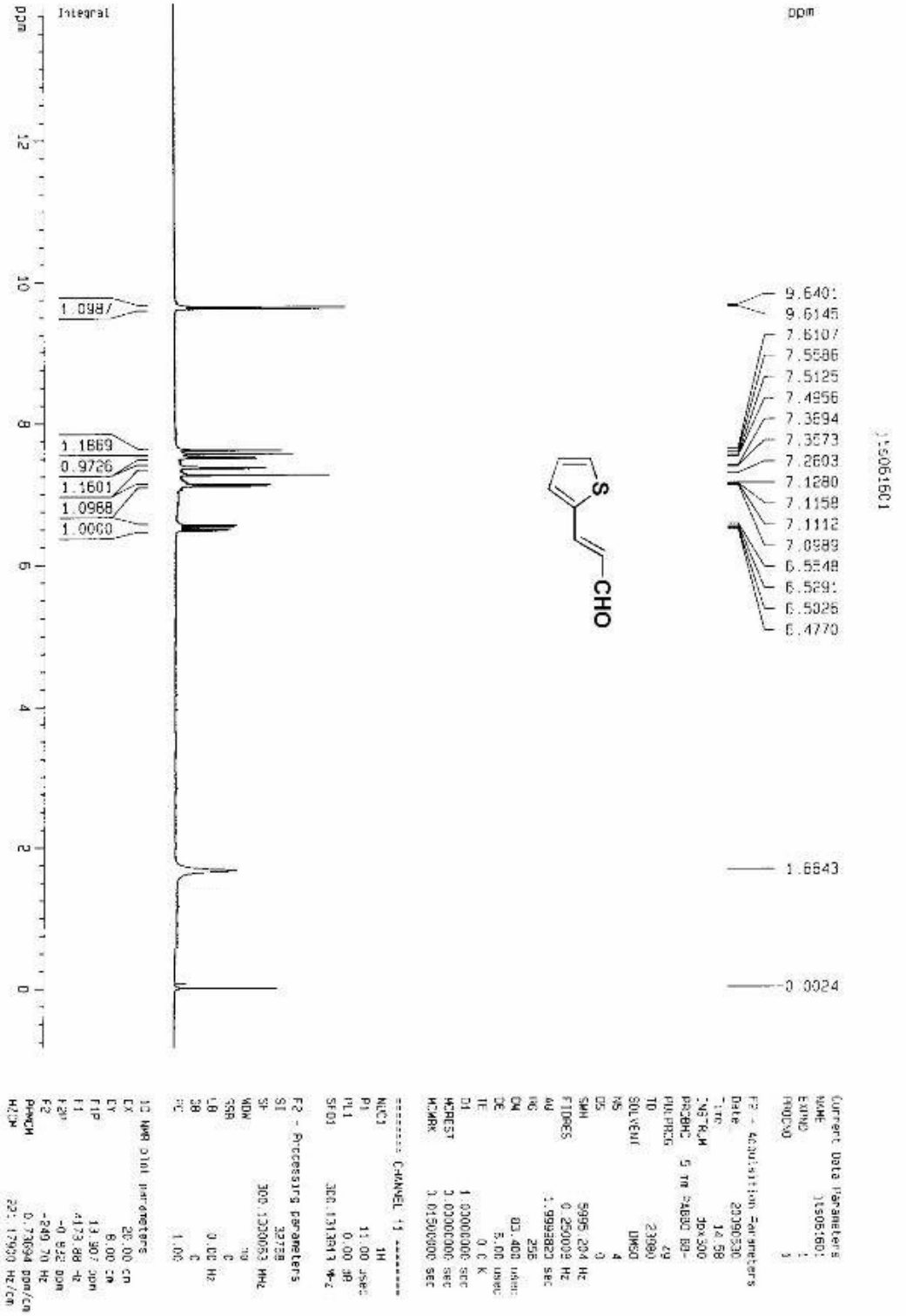
(*E*)-3-(Pyridin-3-yl)acrylaldehyde (13)



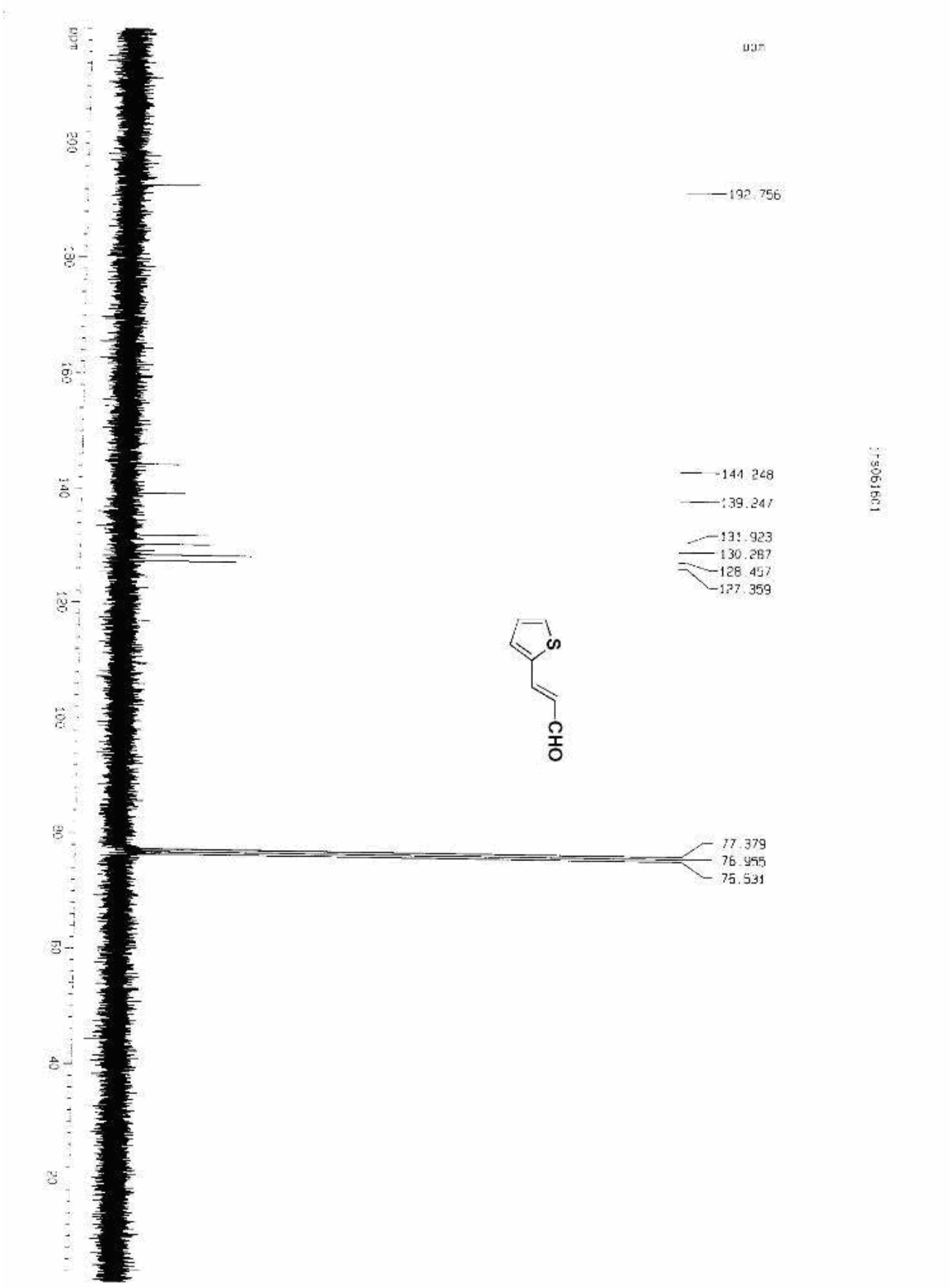
(*E*)-3-(Pyridin-3-yl)acrylaldehyde (13)



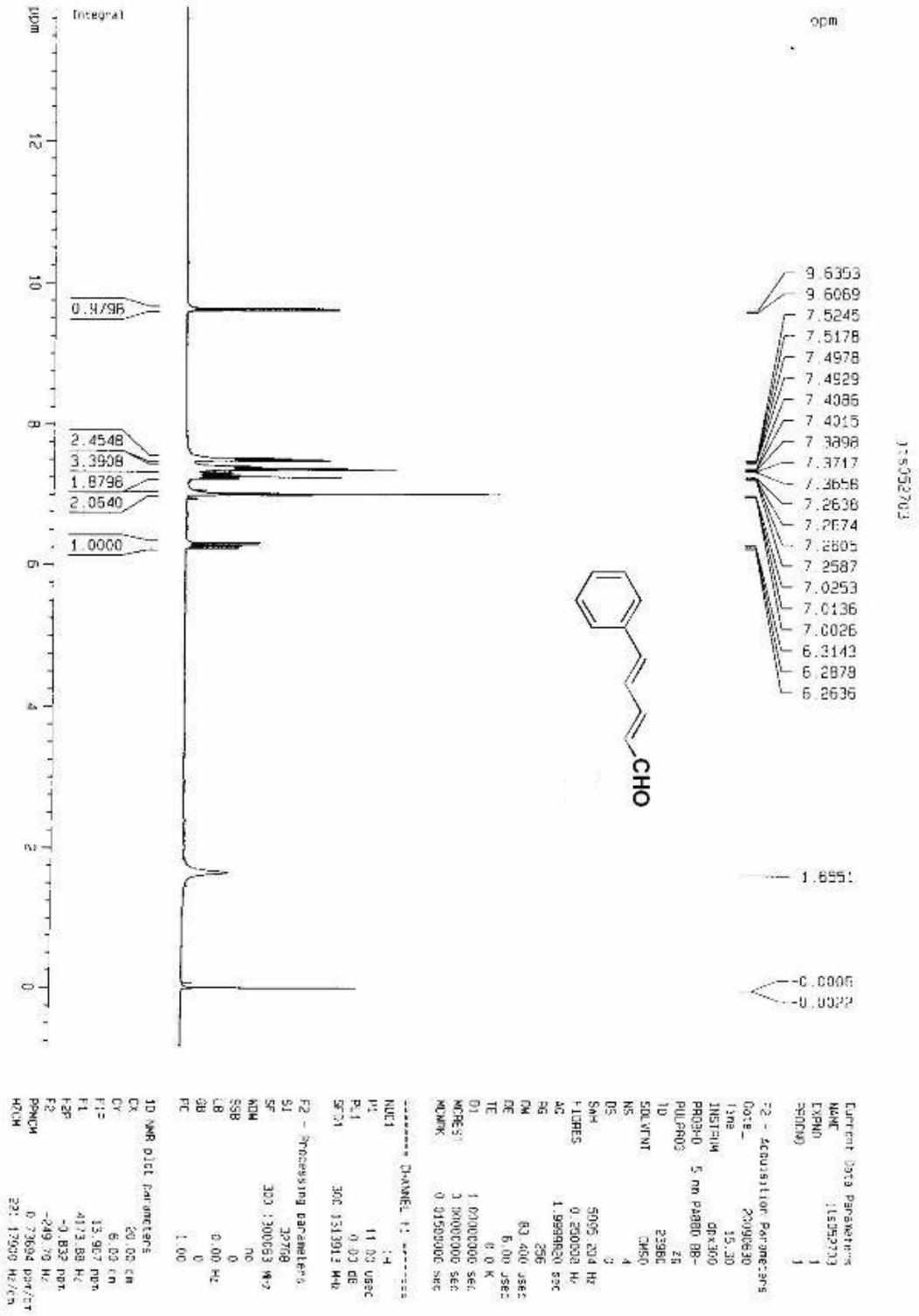
(*E*)-3-(Thiophen-2-yl)acrylaldehyde (14)



(*E*)-3-(Thiophen-2-yl)acrylaldehyde (14)



5-Phenylpenta-2,4-dienal (15)



5-Phenylpenta-2,4-dienal (15)