

Supplementary Experimental Information

Efficient Carbonylation Reactions in Phosphonium Salt Ionic Liquids: Anionic Effects

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General Details and Protocols:

Reactions were carried out under an Argon atmosphere in oven-dried glassware. All Ionic Liquids used were obtained from Cytec Canada Inc., Niagara Falls, Ontario. Ionic liquids were de-gassed under high vacuum for at least one hour immediately prior to use. All other fine chemicals were obtained from Aldrich. CIMS were run on a Micromass Quattro Ultima spectrometer fitted with a direct

injection probe (DIP) with ionization energy set at 70 eV and HRMS (CI) were performed with a Micromass Q-ToF Ultima spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV200 in CDCl_3 or CD_3OD , chemical shifts (δ) are reported in ppm and coupling constants (J) are expressed in Hz.

General Procedure followed throughout Table 1 and Table 2:

Synthesis of butyl 4-methylbenzoate. 4-Iodotoluene (100.0 mg, 0.459 mmol), palladium (II) acetate (4.1 mg, 0.0183 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (20.0 mg, 0.0366 mmol) were added consecutively to a cylindrical glass reaction vial into which was measured 0.5 g of trihexyl(tetradecyl) phosphonium bromide ionic liquid (pretreated by heating under vacuum for 1 hr at 100 °C). The tube was stoppered with a rubber septum, tightly sealed with parafilm and air evacuated from the mixture. After this, triethylamine (0.128 ml, 0.918 mmol) was introduced followed by *n*-butanol (0.084 ml, 0.918 mmol) and CO gas then pumped through an elongated syringe needle directly into the stirred solution at 60 °C and positive pressure maintained continuously during the course of the reaction via an outlet syringe bleeder. After TLC (10% EtOAc/Hex) indicated the reaction to be complete (within 8 hrs), the solution was poured into a methanol/water (3:2) solution (5 ml) and extracted with *n*-hexane (3 x 5 ml). The combined hexane fractions were dried over anhydrous Na_2SO_4 , filtered and concentrated under vacuum to give an amorphous residue which was chromatographed (10% EtOAc/Hex) on silica to give butyl 4-methylbenzoate in 93 % yield.

IL-Pd Catalyst Recycling Protocol:

Synthesis of butyl 4-methylbenzoate. 4-Iodotoluene (1.000 g, 4.59 mmol), palladium (II) acetate (41.0 mg, 0.183 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (200.0 mg, 0.366 mmol) were added consecutively to a round bottom flask into which was measured 5.0 g of trihexyl(tetradecyl) phosphonium bromide ionic liquid (pretreated by heating under vacuum for 1 hr at 100 °C). The flask was stoppered with a rubber septum, tightly sealed with parafilm and air evacuated from the mixture. Subsequently, triethylamine (1.28 ml, 9.18 mmol) was introduced followed by *n*-butanol (0.84 ml, 9.18 mmol) and the mixture purged with CO through an elongated syringe needle directly into the stirred solution at 60 °C. The reaction was maintained at 1 atm. pressure continuously during the course of the reaction via an outlet syringe bleeder. After TLC (10% EtOAc in Hexane) indicated the reaction to be complete (within 8 hrs), the flask was fitted for short path distillation (avoiding contact with air) and butyl 4-methyl benzoate (90% yield) distilled directly under vacuum from the mixture at 100 °C. The residual IL-Pd mixture was then handled further in a glove box where it was washed with argon-degassed methanol/water (3:2) solution (15 ml) and extracted with 5 x 15 ml *n*-hexane (also argon-degassed) which pulled the IL-Pd mixture into the upper organic layer. After removal of hexane, the residual IL-Pd mixture was vigorously stirred under vacuum for 1 hr at 100 °C then cooled to rt and recharged with 4-iodotoluene (1.000 g, 4.59 mmol), triethylamine (1.28 ml, 9.18 mmol) and *n*-butanol (0.84 ml, 9.18 mmol) (carefully avoiding contact with air at all stages of the operation). A second run, with no further addition of Pd(dppf) catalyst, was then conducted in the recycled IL at 60 °C under positive CO pressure. Conversion of 4-iodotoluene was complete and butyl 4-methylbenzoate was isolated in 85% yield from the second run.

Procedure for detection of 4-methylbenzoyl bromide

4-Bromotoluene (100.0 mg, 0.585 mmol), palladium (II) acetate (5.2 mg, 0.0233 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (25.8 mg, 0.0467 mmol) were added consecutively to a cylindrical glass reaction vial into which was measured 0.5 g of trihexyl(tetradecyl) phosphonium bromide ionic liquid (pretreated by heating under vacuum for 1 hr at 100 °C). The tube was stoppered with a rubber septum, tightly sealed with parafilm and air evacuated from the mixture. CO gas was then pumped through an elongated syringe needle directly into the stirred solution (without addition of nucleophile or base) at 60 °C and positive pressure maintained continuously during the course of the reaction via an outlet syringe bleeder. After 8 hrs, the cooled mixture was diluted with 1.5 ml dry CH₂Cl₂ (distilled over CaH₂) and subjected to GC analysis (see Figure 17a).

Procedure for detection of benzoyl bromide

Bromobenzene (100.0 mg, 0.637 mmol), palladium (II) acetate (5.7 mg, 0.0254 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (28.2 mg, 0.0509 mmol) were added consecutively to a cylindrical glass reaction vial into which was measured 0.5 g of trihexyl(tetradecyl) phosphonium bromide ionic liquid (pretreated by heating under vacuum for 1 hr at 100 °C). The tube was stoppered with a rubber septum, tightly sealed with parafilm and air evacuated from the mixture. CO gas was then pumped through an elongated syringe needle directly into the stirred solution (without addition of nucleophile or base) at 60 °C and positive pressure maintained continuously during the course of the reaction via an outlet syringe bleeder. After 8 hrs, the cooled mixture was diluted with 1.5 ml dry CH₂Cl₂ (distilled over CaH₂) and subjected to GC/MS analysis (see Figures 17b-c).

¹H NMR, ¹³C NMR and CIMS data for products described in Table 2

1. Butyl 4-methylbenzoate (Table 2, entry 1)

¹H NMR (CDCl₃, 200 MHz); δ (ppm): 7.93 (2H, d, *J*=8.0 Hz), 7.22 (2H, d, *J*=8.0 Hz), 4.30 (2H, t, *J*=6.0, 6.0 Hz), 2.40 (3H, s), 1.74 (2H, m), 1.47 (2H, m), 0.97 (3H, t, *J*=7.3, 7.3 Hz). ¹³C NMR (CDCl₃, 50 MHz); δ (ppm): 166.8 (s), 143.4 (s), 129.6 (2xd), 129.0 (2xd), 127.8 (s), 64.6 (t), 30.8 (t), 21.6 (q), 19.3 (t), 13.8 (q). CIMS 70 eV, *m/z* (rel. int.): 193 [M+1]⁺ (20), 136 (46), 119 (100), 91 (30).

2. Butyl 4-nitrobenzoate (Table 2, entry 5)

¹H NMR (CDCl₃, 200 MHz); δ (ppm): 8.29 (2H, d, *J*=8.0 Hz), 8.20 (2H, d, *J*=8.0 Hz), 4.38 (2H, t, *J*=6.6, 6.6 Hz), 1.78 (2H, m), 1.50 (2H, m), 0.99 (3H, t, *J*=7.3, 7.3 Hz). ¹³C NMR (CDCl₃, 50 MHz); δ (ppm): 172.0 (s), 157.2 (s), 142.6 (s), 137.5 (2xd), 130.3 (2xd), 72.6 (t), 37.4 (t), 26.0 (t), 20.5 (q). CIMS 70 eV, *m/z* (rel. int.): 224 [M+1]⁺ (12), 207 (46), 194 (47), 168 (98), 151 (100), 120 (87), 92 (74).

3. Butyl 2-nitrobenzoate (Table 2, entry 7)

¹H NMR (CDCl₃, 200 MHz); δ (ppm): 7.87 (1H, d, *J*=8.6 Hz), 7.69 (3H, m), 4.31 (2H, t, *J*=6.6, 6.6 Hz), 1.69 (2H, m), 1.42 (2H, m), 0.97 (3H, t, *J*=7.3, 7.3 Hz). ¹³C NMR (CDCl₃, 50 MHz); δ (ppm): 165.5 (s), 148.3 (s), 132.8 (d), 131.7 (d), 129.9 (d), 128.0 (s), 123.8 (d), 66.4 (t), 30.3 (t), 19.1 (t), 13.6 (q). CIMS 70 eV, *m/z* (rel. int.): 224 [M+1]⁺ (10), 190 (100), 150 (43), 119 (94), 91 (17).

4. Butyl cinnamate (Table 2, entry 8)

¹H NMR (CDCl₃, 200 MHz); δ (ppm): 7.69 (1H, d, *J*=16.0 Hz), 7.52 (2H, m), 7.38 (3H, m), 6.44 (1H, d, *J*=16.0 Hz), 4.21 (2H, t, *J*=6.6, 6.6 Hz), 1.69 (2H, m), 1.44 (2H, m), 0.99 (3H, t, *J*=7.2, 7.2 Hz). ¹³C NMR (CDCl₃, 50 MHz); δ (ppm): 167.1 (s), 144.6 (d),

134.5 (s), 130.2 (d), 128.9 (2xd), 128.1 (2xd), 118.3 (d), 64.4 (t), 30.8 (t), 19.2 (t), 13.8 (q). CIMS 70 eV, m/z (rel. int.): 205 $[M+1]^+$ (20), 148 (73), 131 (100), 103 (25), 83 (42).

5. *i*-Propyl 4-nitrobenzoate (Table 2, entry 9)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 8.28 (2H, d, $J=9.1$ Hz), 8.19 (2H, d, $J=9.1$ Hz), 5.29 (1H, m), 1.39 (6H, d, $J=6.3$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 171.0 (s), 157.3 (s), 142.7 (s), 137.5 (2xd), 130.3 (2xd), 76.5 (d), 28.7 (2xq). CIMS 70 eV, m/z (rel. int.): 210 $[M+1]^+$ (10), 180 (15), 168 (17), 150 (100), 138 (10), 120 (23), 104 (17), 92 (12).

6. *i*-Propyl 2-nitrobenzoate (Table 2, entry 10)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 7.90 (1H, d, $J=7.2$ Hz), 7.68 (3H, m), 5.27 (1H, m), 1.34 (6H, d, $J=6.2$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 164.9 (s), 148.2 (s), 132.8 (d), 131.5 (d), 129.8 (d), 128.3 (s), 123.8 (d), 70.5 (d), 21.4 (2xq). CIMS 70 eV, m/z (rel. int.): 210 $[M+1]^+$ (23), 190 (15), 168 (94), 150 (100), 121 (15), 104 (18), 93 (20).

7. *i*-Propyl cinnamate (Table 2, entry 11)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 7.67 (1H, d, $J=16.0$ Hz), 7.52 (2H, m), 7.37 (3H, m), 6.42 (1H, d, $J=16.0$ Hz), 5.15 (1H, m), 1.31 (6H, d, $J=6.2$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 166.5 (s), 144.3 (d), 134.6 (s), 130.1 (d), 128.9 (2xd), 128.0 (2xd), 118.8 (d), 67.8 (d), 21.9 (2xq). CIMS 70 eV, m/z (rel. int.): 191 $[M+1]^+$ (100), 148 (24), 131 (57), 119 (24), 103 (21), 91 (10).

8. *t*-Butyl 4-nitrobenzoate (Table 2, entry 12)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 8.26 (2H, d, $J=9.0$ Hz), 8.14 (2H, d, $J=9.0$ Hz), 1.61 (9H, s). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 171.0 (s), 157.5 (s), 144.8 (s), 137.3 (2xd), 130.2 (2xd), 89.8 (s), 34.9 (3xq). CIMS 70 eV, m/z (rel. int.): 224 $[M+1]^+$ (10), 206 (37), 150 (85), 137 (21), 120 (18), 104 (20), 92 (10).

9. *t*-Butyl 2-nitrobenzoate (Table 2, entry 13)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 7.83 (1H, d, $J=7.3$ Hz), 7.70 (1H, m), 7.60 (2H, m), 1.53 (9H, s). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 164.3 (s), 148.4 (s), 132.6 (d), 131.3 (d), 129.9 (d), 129.0 (s), 123.6 (d), 83.7 (s), 27.7 (3xq). CIMS 70 eV, m/z (rel. int.): 224 $[\text{M}+1]^+$ (10), 190 (83), 168 (10), 150 (35), 131 (57), 119 (68), 91 (30).

10. *t*-Butyl cinnamate (Table 2, entry 14)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 7.58 (1H, d, $J=16.0$ Hz), 7.50 (2H, m), 7.35 (3H, m), 6.36 (1H, d, $J=16.0$ Hz), 1.53 (9H, s). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 166.4 (s), 143.5 (d), 134.7 (s), 130.0 (d), 128.8 (2xd), 127.9 (2xd), 120.2 (d), 80.1 (s), 28.2 (3xq). CIMS 70 eV, m/z (rel. int.): 205 $[\text{M}+1]^+$ (10), 192 (100), 162 (15), 148 (95), 131 (67), 120 (95), 104 (12), 91 (23).

11. 4-Methylbenzoic acid (Table 2, entry 15)

^1H NMR (CD_3OD , 200 MHz); δ (ppm): 7.87 (2H, d, $J=7.6$ Hz), 7.25 (2H, d, $J=7.6$ Hz), 2.37 (3H, s). ^{13}C NMR (CD_3OD , 50 MHz); δ (ppm): 170.0 (s), 145.0 (s), 130.8 (2xd), 130.1 (2xd), 129.0 (s), 21.6 (q). CIMS 70 eV, m/z (rel. int.): 137 $[\text{M}+1]^+$ (40), 119 (85), 107 (12), 92 (100), 77 (10).

12. 4-Nitrobenzoic acid (Table 2, entry 16)

^1H NMR (CD_3OD , 200 MHz); δ (ppm): 8.29 (2H, d, $J=8.8$ Hz), 8.20 (2H, d, $J=8.8$ Hz). ^{13}C NMR (CD_3OD , 50 MHz); δ (ppm): 167.6 (s), 151.9 (s), 137.6 (s), 131.9 (2xd), 124.5 (2xd). CIMS 70 eV, m/z (rel. int.): 168 $[\text{M}+1]^+$ (25), 148 (74), 138 (47), 121 (32), 109 (17), 91 (20).

13. 2-Nitrobenzoic acid (Table 2, entry 17)

^1H NMR (CD_3OD , 200 MHz); δ (ppm): 7.85 (2H, m), 7.69 (2H, m). ^{13}C NMR (CD_3OD , 50 MHz); δ (ppm): 168.0 (s), 150.4 (s), 133.8 (d), 133.2 (d), 131.1 (d), 129.1 (s), 124.8 (d). CIMS 70 eV, m/z (rel. int.): 168 $[\text{M}+1]^+$ (30), 148 (64), 138 (40), 119 (72), 91 (64).

14. Cinnamic acid (Table 2, entry 18)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 11.2 (1H, bs), 7.82 (1H, d, $J=16.0$ Hz), 7.55 (2H, m), 7.42 (3H, m), 6.47 (1H, d, $J=16.0$ Hz). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 172.7 (s), 147.2 (d), 134.0 (s), 130.8 (d), 129.0 (2xd), 128.4 (2xd), 117.3 (d). CIMS 70 eV, m/z (rel. int.): 149 $[\text{M}+1]^+$ (20), 131 (27), 120 (10), 103 (20), 91 (18), 77 (17).

15. Diethyl 4-methylbenzamide (Table 2, entry 19)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 7.27 (2H, d, $J=8.0$ Hz), 7.18 (2H, d, $J=8.0$ Hz), 3.39 (4H, bd), 2.36 (3H, s), 1.16 (6H, bs). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 171.5 (s), 139.1 (s), 134.4 (s), 129.0 (2xd), 126.3 (2xd), 43.2 (t), 39.2 (t), 21.3 (q), 14.1 (q), 13.0 (q). CIMS 70 eV, m/z (rel. int.): 192 $[\text{M}+1]^+$ (10), 176 (12), 162 (15), 147 (10), 119 (100), 105 (10), 91 (20).

16. Diethyl 4-nitrobenzamide (Table 2, entry 20)

^1H NMR (CDCl_3 , 200 MHz); δ (ppm): 8.26 (2H, d, $J=8.6$ Hz), 7.53 (2H, d, $J=8.6$ Hz), 3.55 (2H, bd), 3.20 (2H, bd), 1.18 (6H, bd). ^{13}C NMR (CDCl_3 , 50 MHz); δ (ppm): 168.9 (s), 148.1 (s), 143.4 (s), 127.4 (2xd), 123.9 (2xd), 43.3 (t), 39.5 (t), 14.2 (q), 12.8 (q). CIMS 70 eV, m/z (rel. int.): 223 $[\text{M}+1]^+$ (100), 205 (45), 193 (17), 175 (19), 151 (44), 134 (10), 120 (25), 104 (43), 92 (17).

Figures 1a-16b. ^1H NMR and ^{13}C NMR spectra of products described in Table 2 (see below)

Figure 17a. GC/MS spectrum indicating detection of 4-methylbenzoyl bromide in reaction run without base or nucleophile (see below)

Figure 17b-c. GC/MS spectra indicating detection of benzoyl bromide and by-products in reaction run without base or nucleophile (see below)

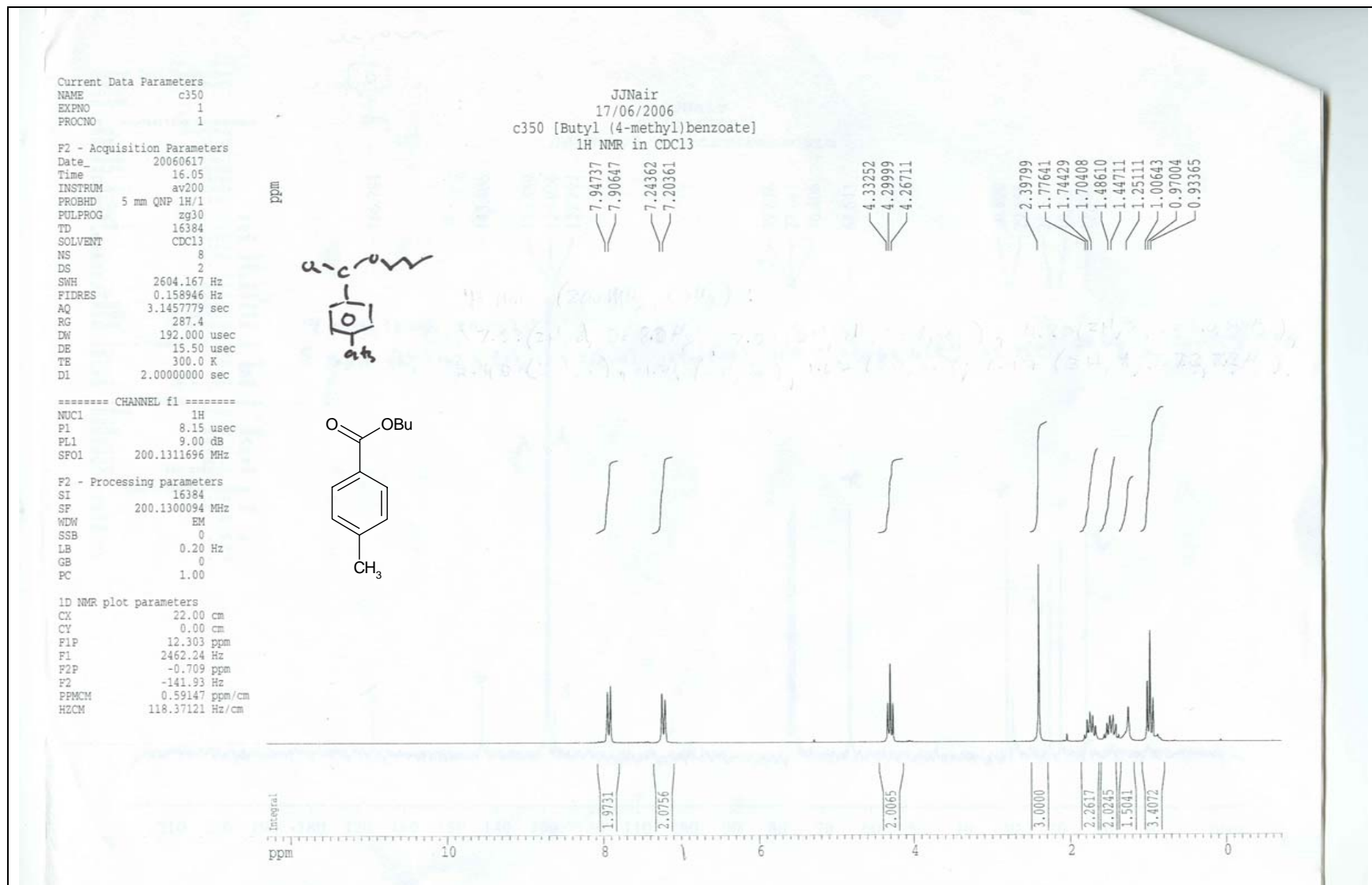


Figure 1a: ¹H NMR spectrum of butyl 4-methylbenzoate (Table 2, entry 1)

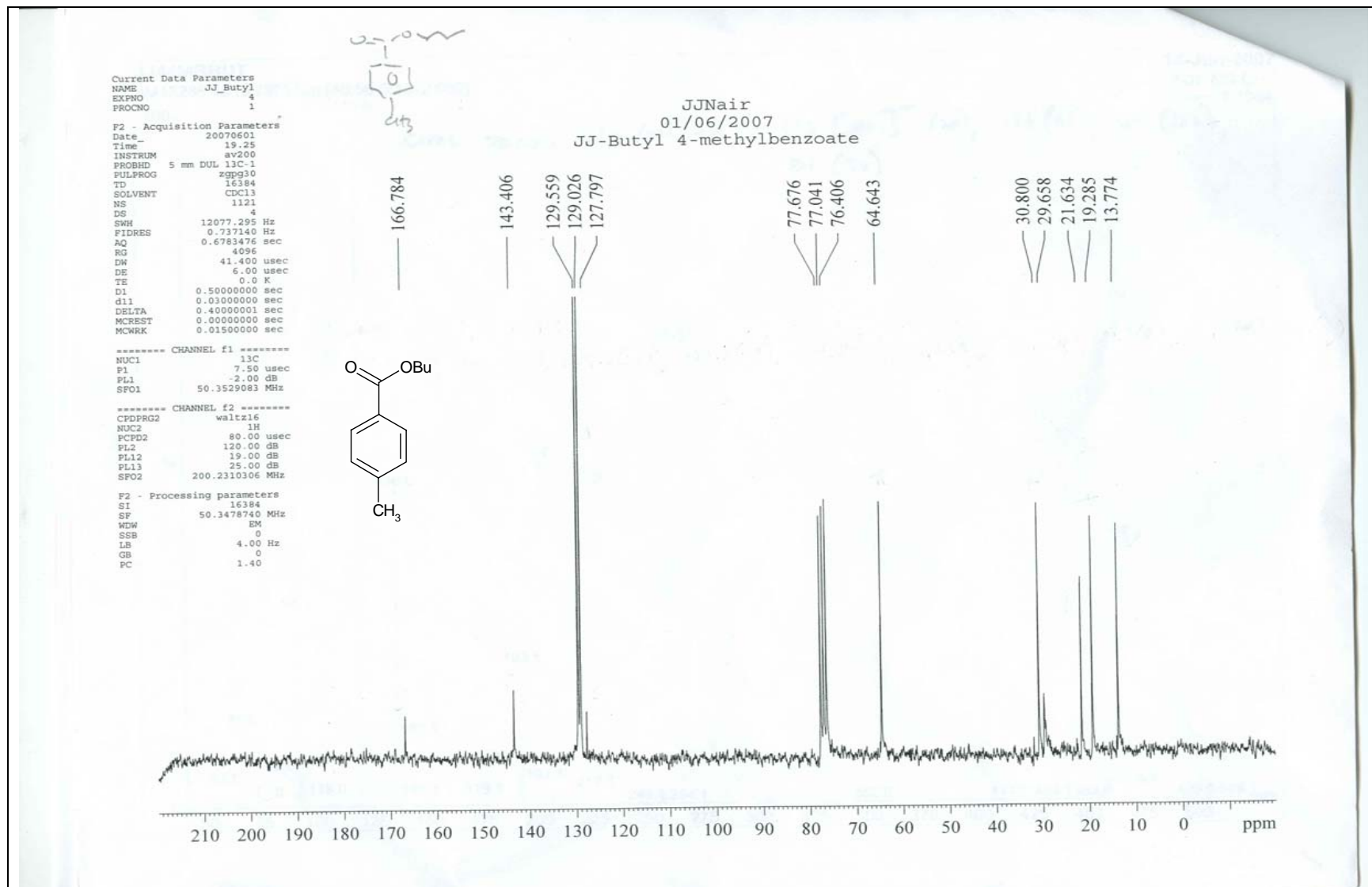


Figure 1b: ¹³C NMR spectrum of butyl 4-methylbenzoate (Table 2, entry 1)

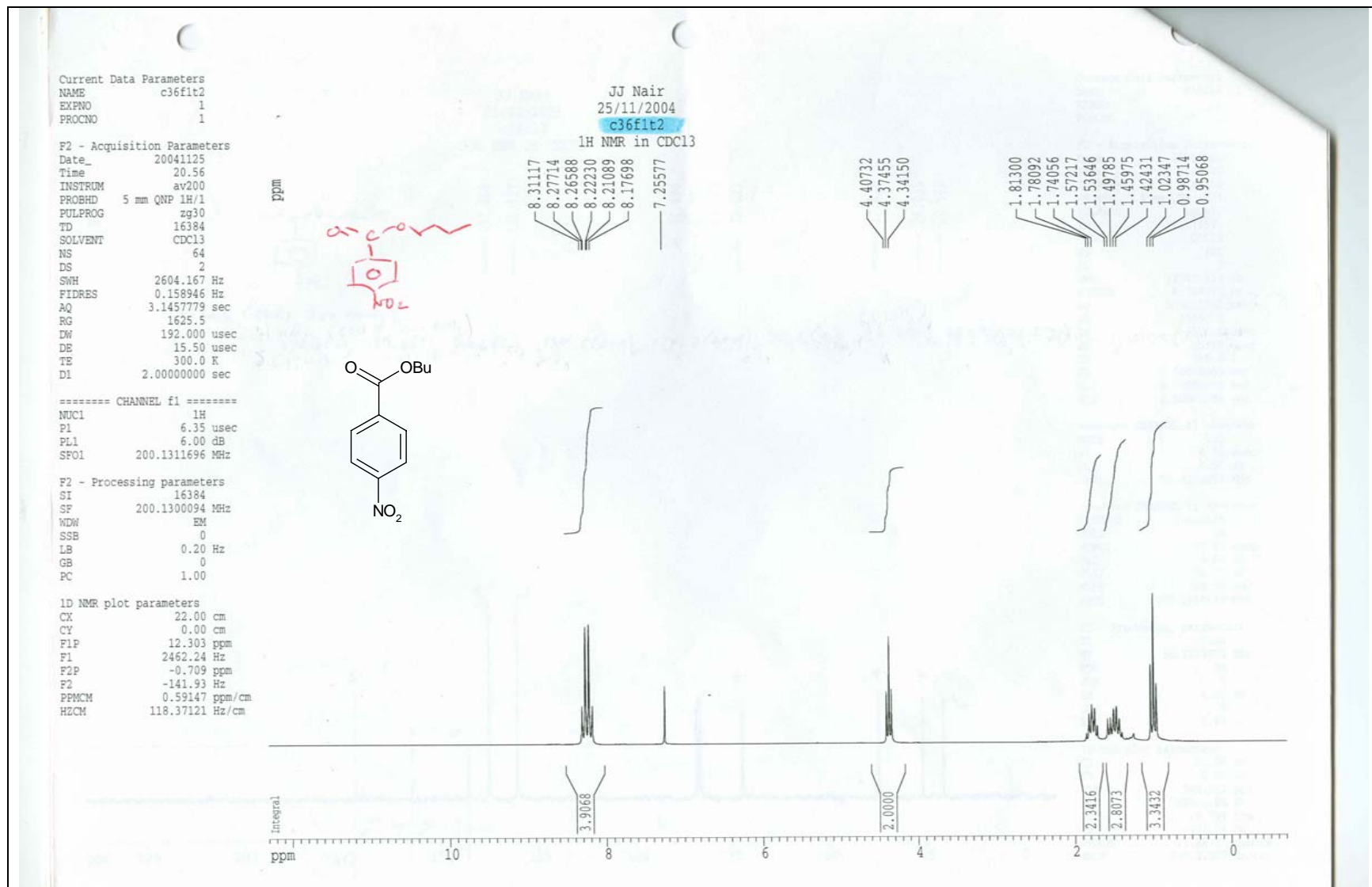


Figure 2a: ^1H NMR spectrum of butyl 4-nitrobenzoate (Table 2, entry 5)

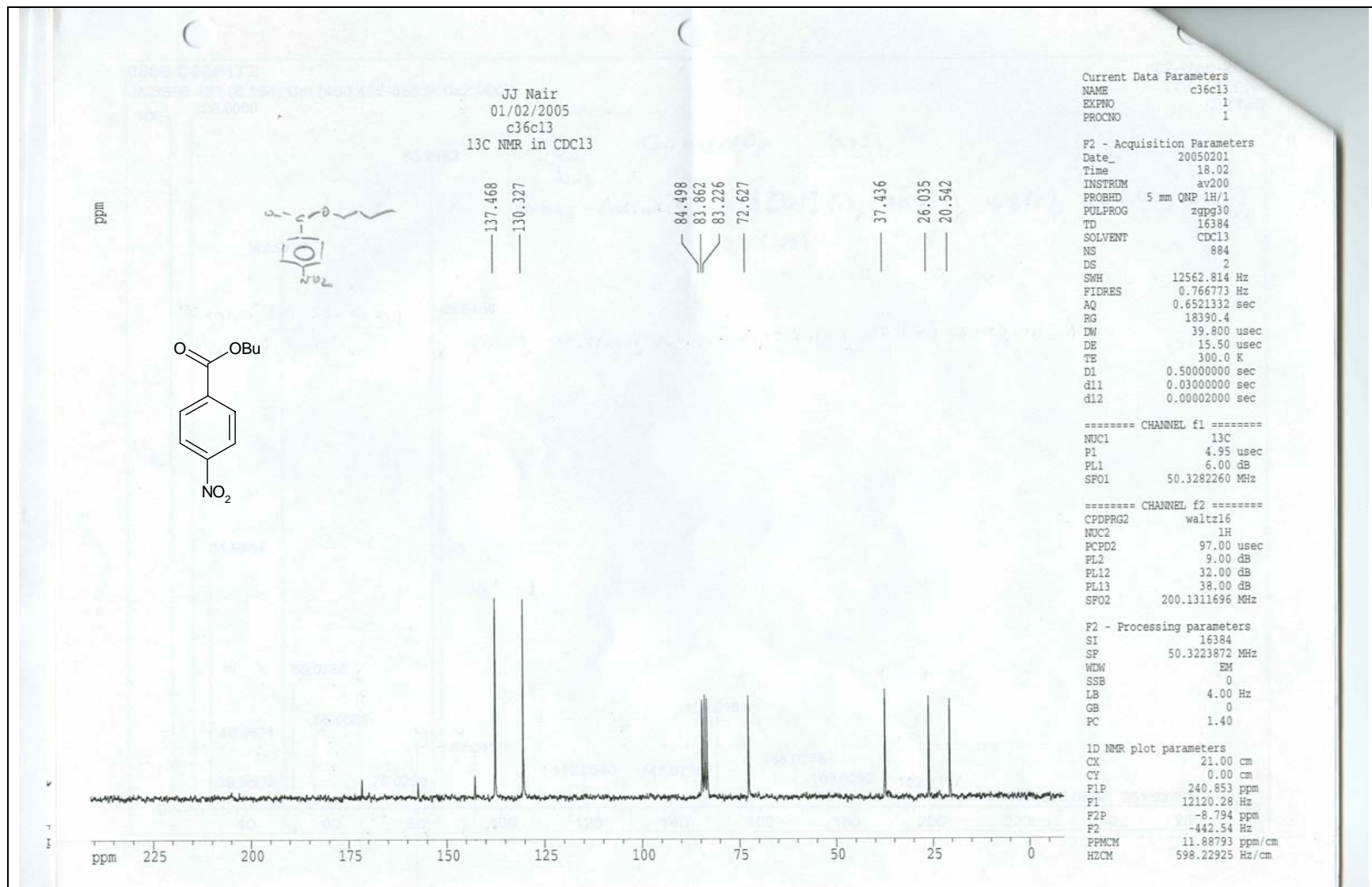


Figure 2b: ¹³C NMR spectrum of butyl 4-nitrobenzoate (Table 2, entry 5)

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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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Time 18.06
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PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 2
SWH 2705.628 Hz
FIDRES 0.165138 Hz
AQ 3.0278132 sec
RG 287.4
DW 184.800 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 7.40 usec
PL1 -2.00 dB
SFO1 200.2310306 MHz

F2 - Processing parameters

SI 16384
SF 200.2300060 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

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7.885
7.859
7.851
7.756
7.746
7.722
7.712
7.688
7.655
7.646
7.642
7.626
7.603
7.595
7.566
7.250

4.347
4.314
4.281

1.761
1.727
1.693
1.654
1.617
1.492
1.456
1.418
1.380
1.343
1.308
0.971

JJNair
22/06/2007
JJ_2NBA-Butyl_1H

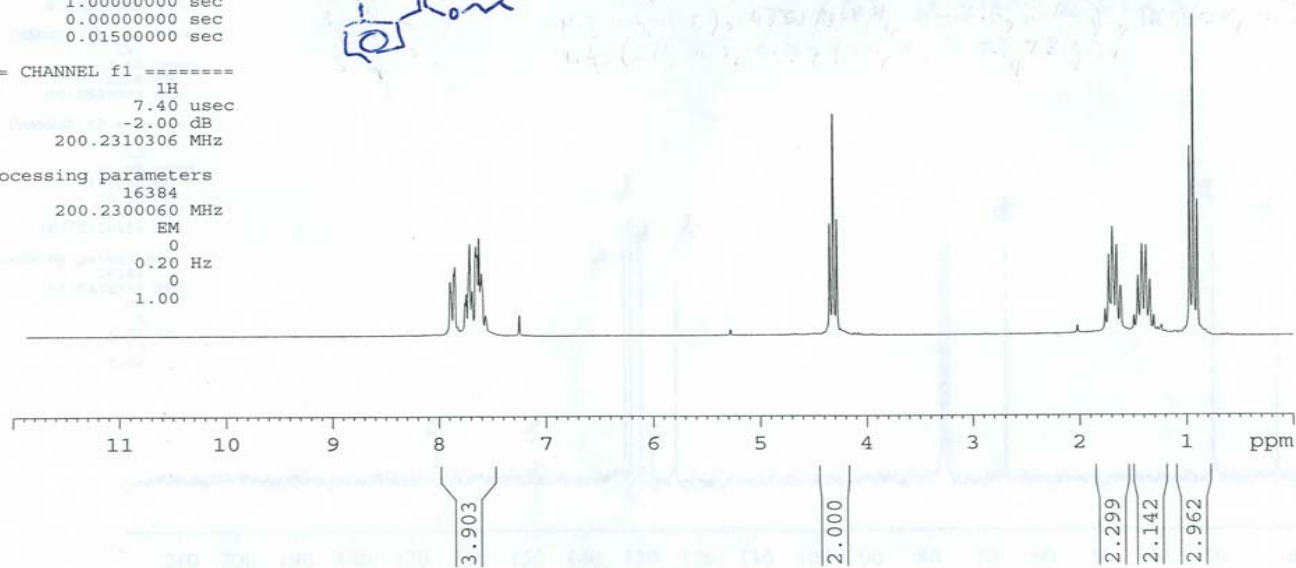
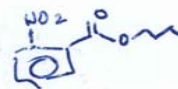
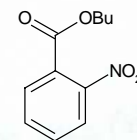


Figure 3a: ¹H NMR spectrum of butyl 2-nitrobenzoate (Table 2, entry 7)

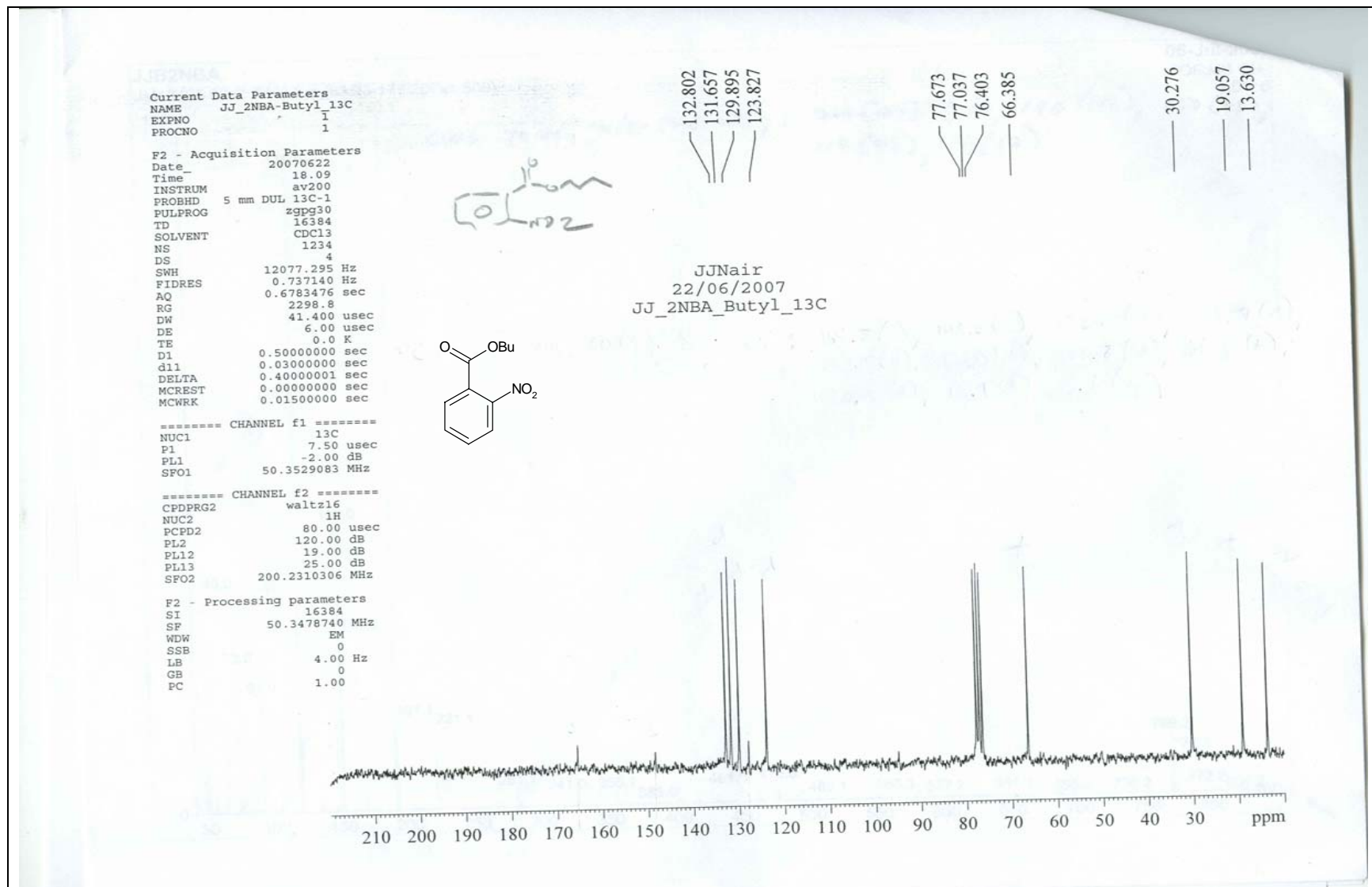


Figure 3b: ¹³C NMR spectrum of butyl 2-nitrobenzoate (Table 2, entry 7)

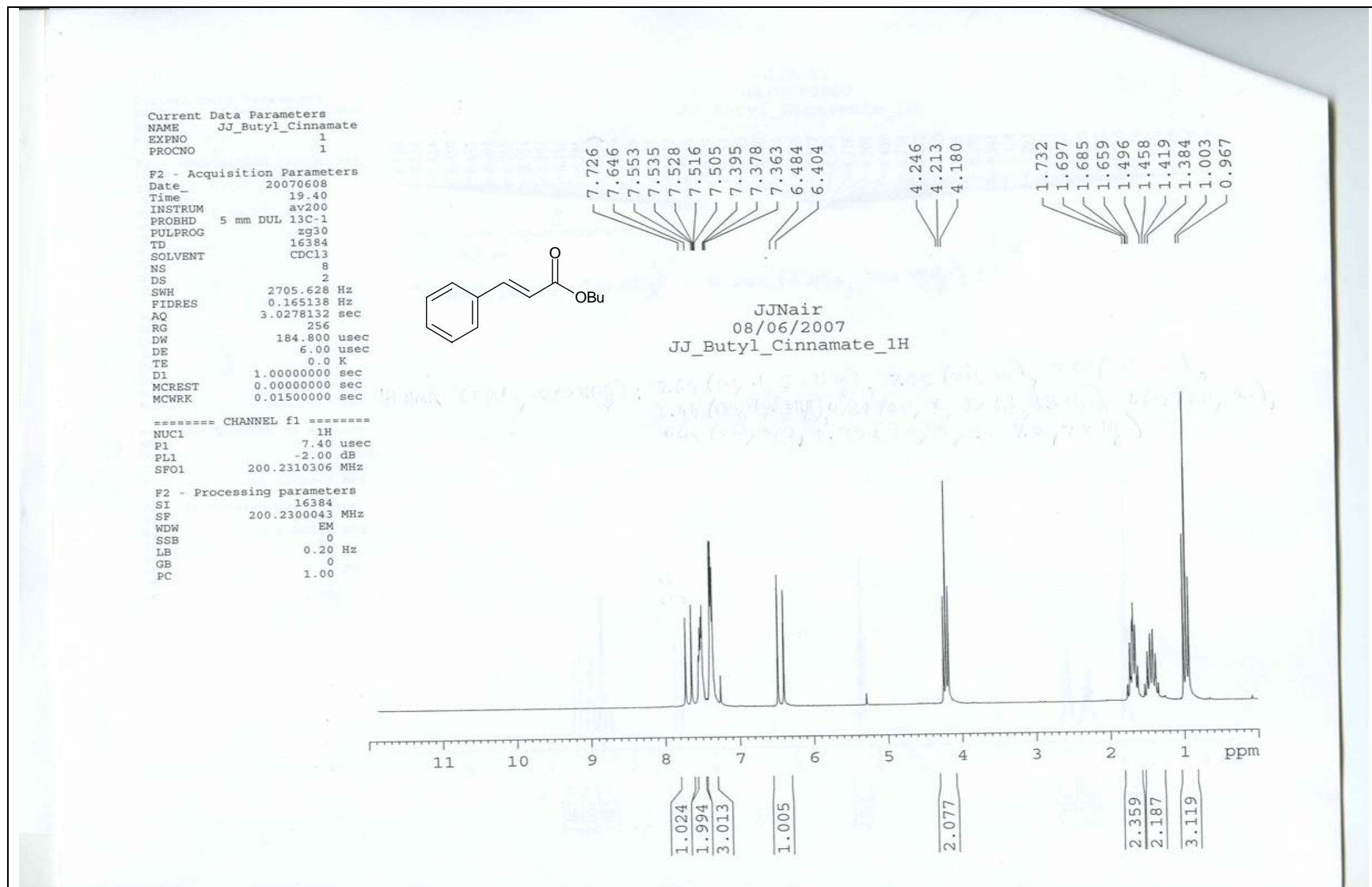
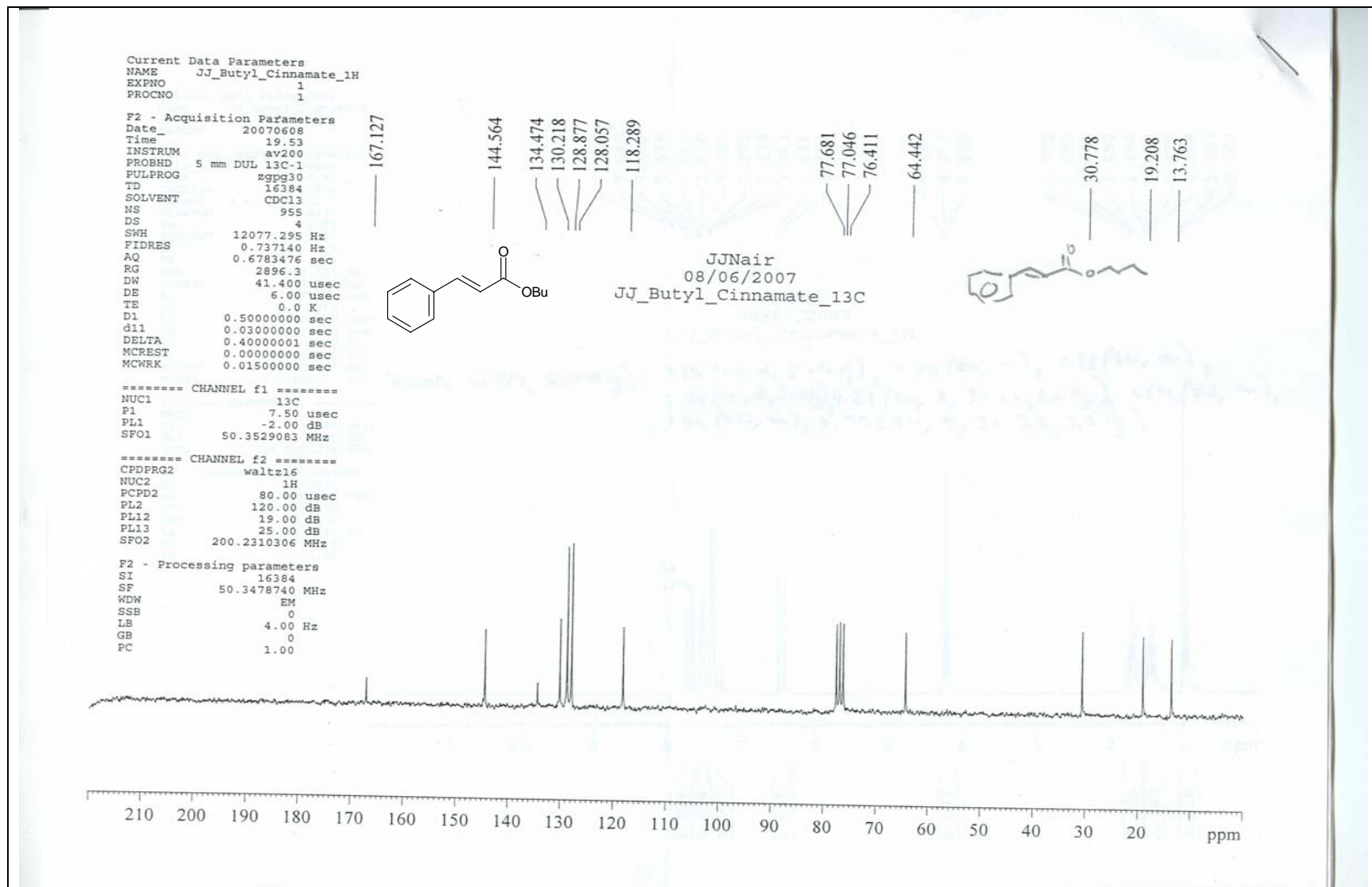


Figure 4a: ¹H NMR spectrum of butyl cinnamate (Table 2, entry 8)



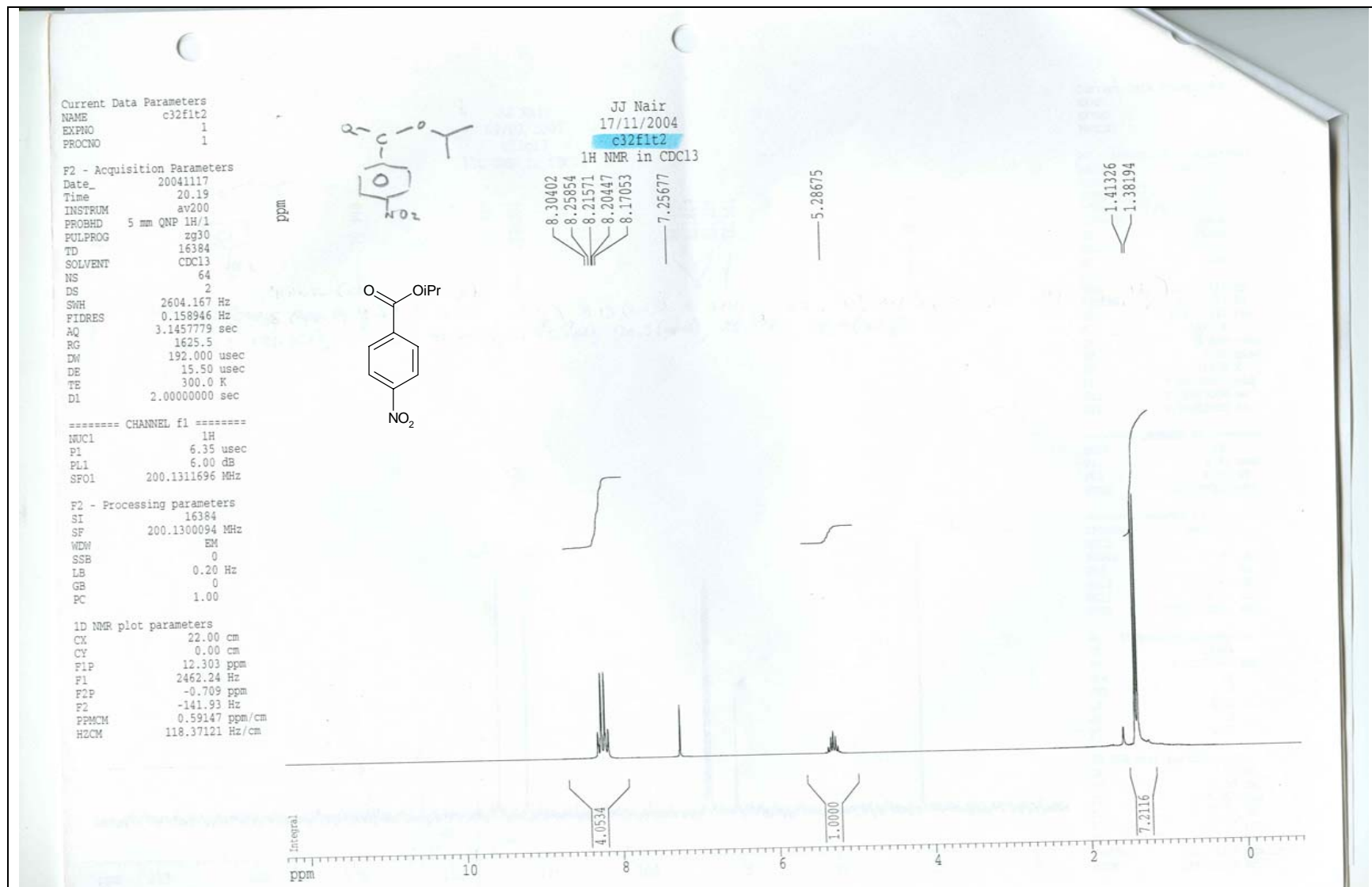


Figure 5a: ¹H NMR spectrum of *i*-propyl 4-nitrobenzoate (Table 2, entry 9)

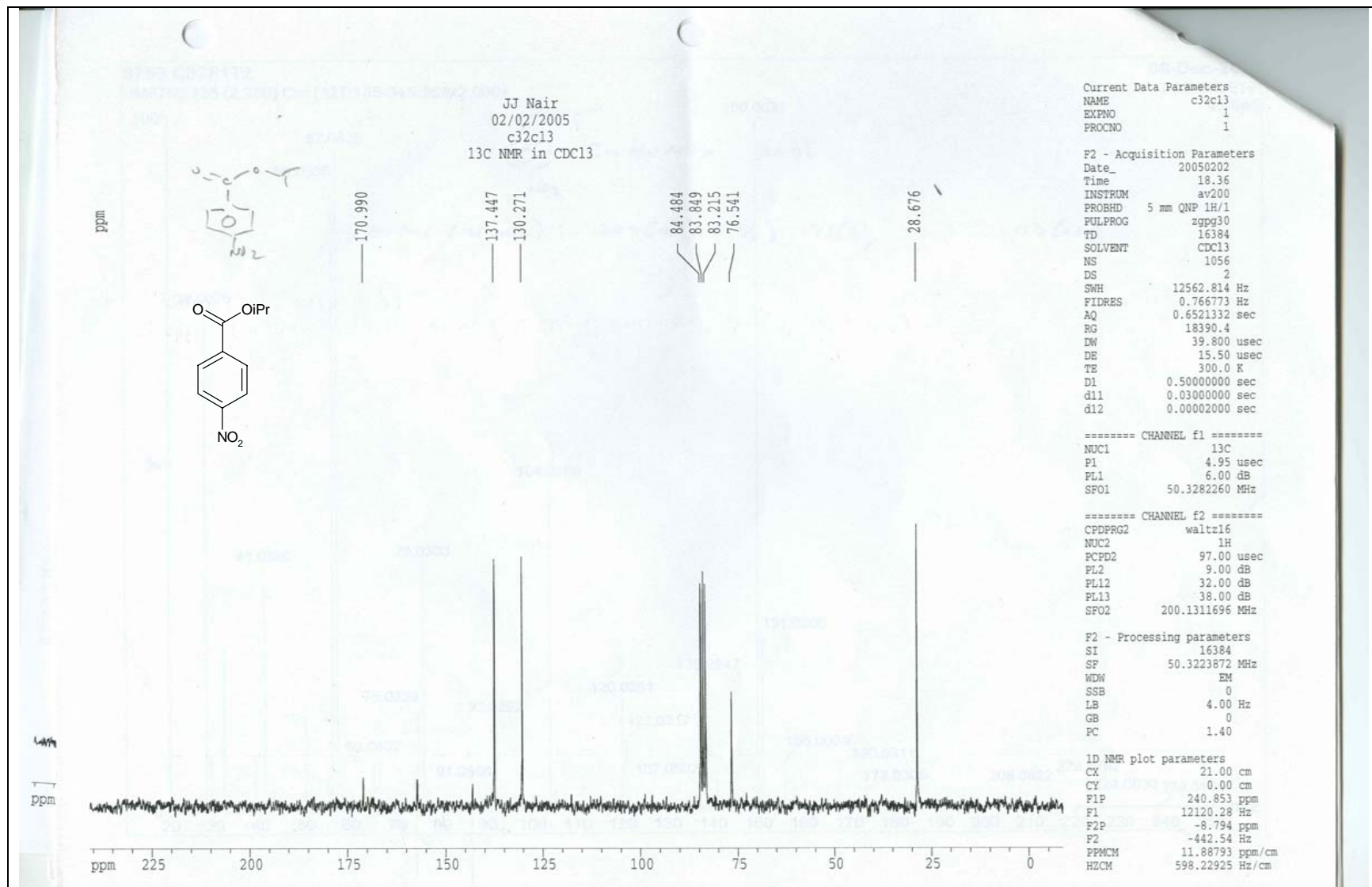


Figure 5b: ¹³C NMR spectrum of *i*-propyl 4-nitrobenzoate (Table 2, entry 9)

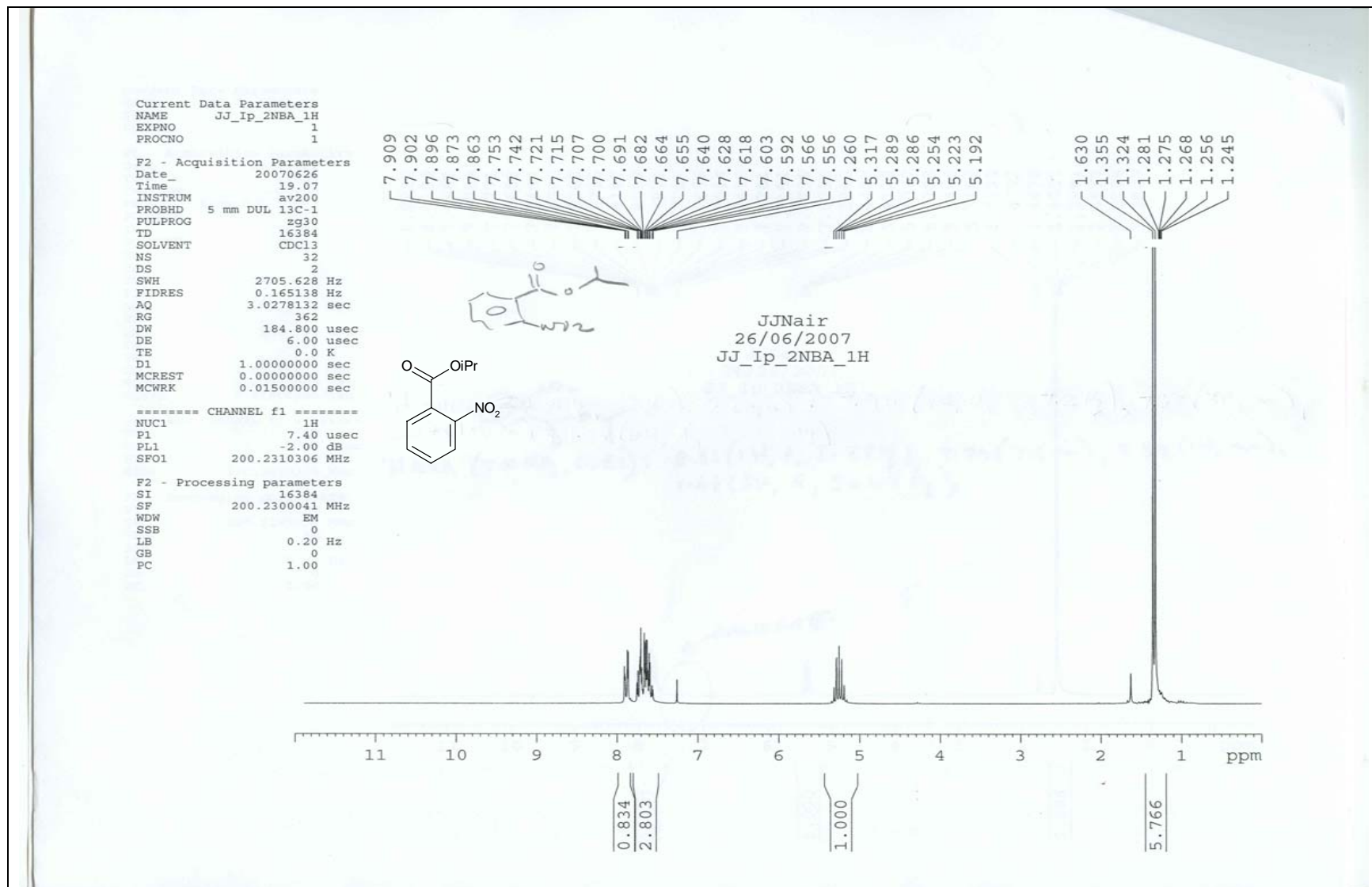


Figure 6a: ^1H NMR spectrum of *i*-propyl 2-nitrobenzoate (Table 2, entry 10)

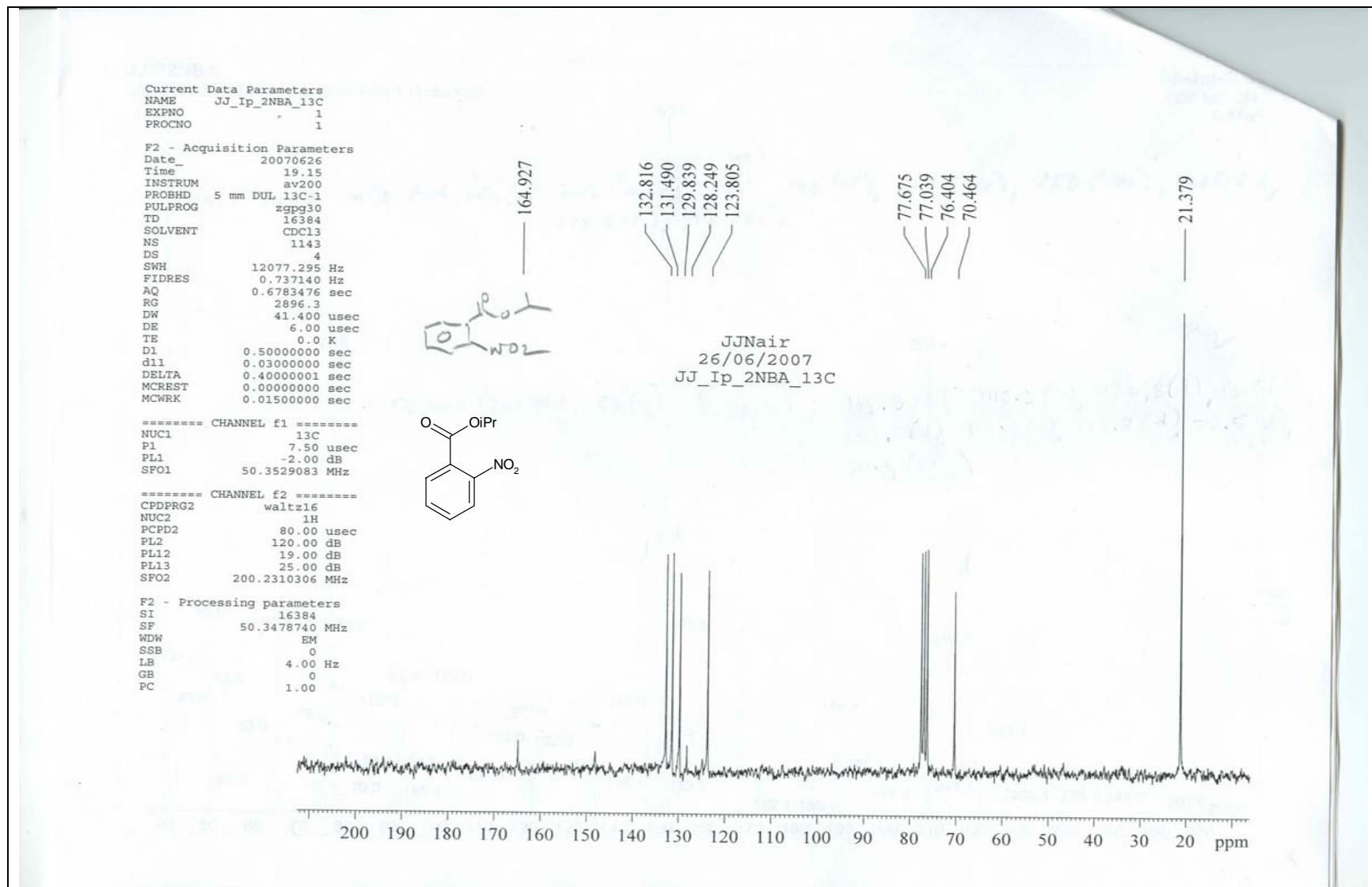


Figure 6b: ^{13}C NMR spectrum of *i*-propyl 2-nitrobenzoate (Table 2, entry 10)

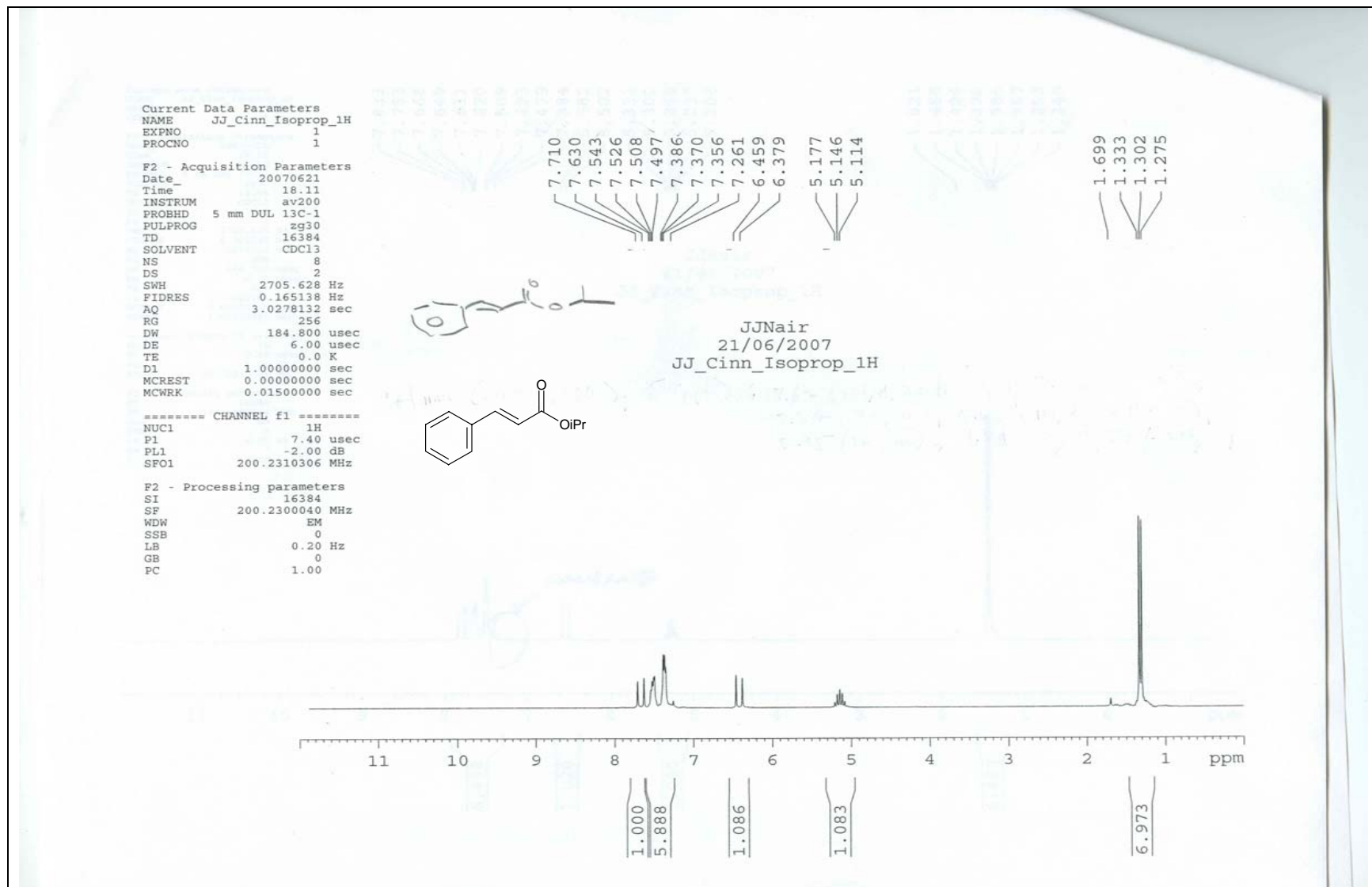


Figure 7a: ^1H NMR spectrum of *i*-propyl cinnamate (Table 2, entry 11)

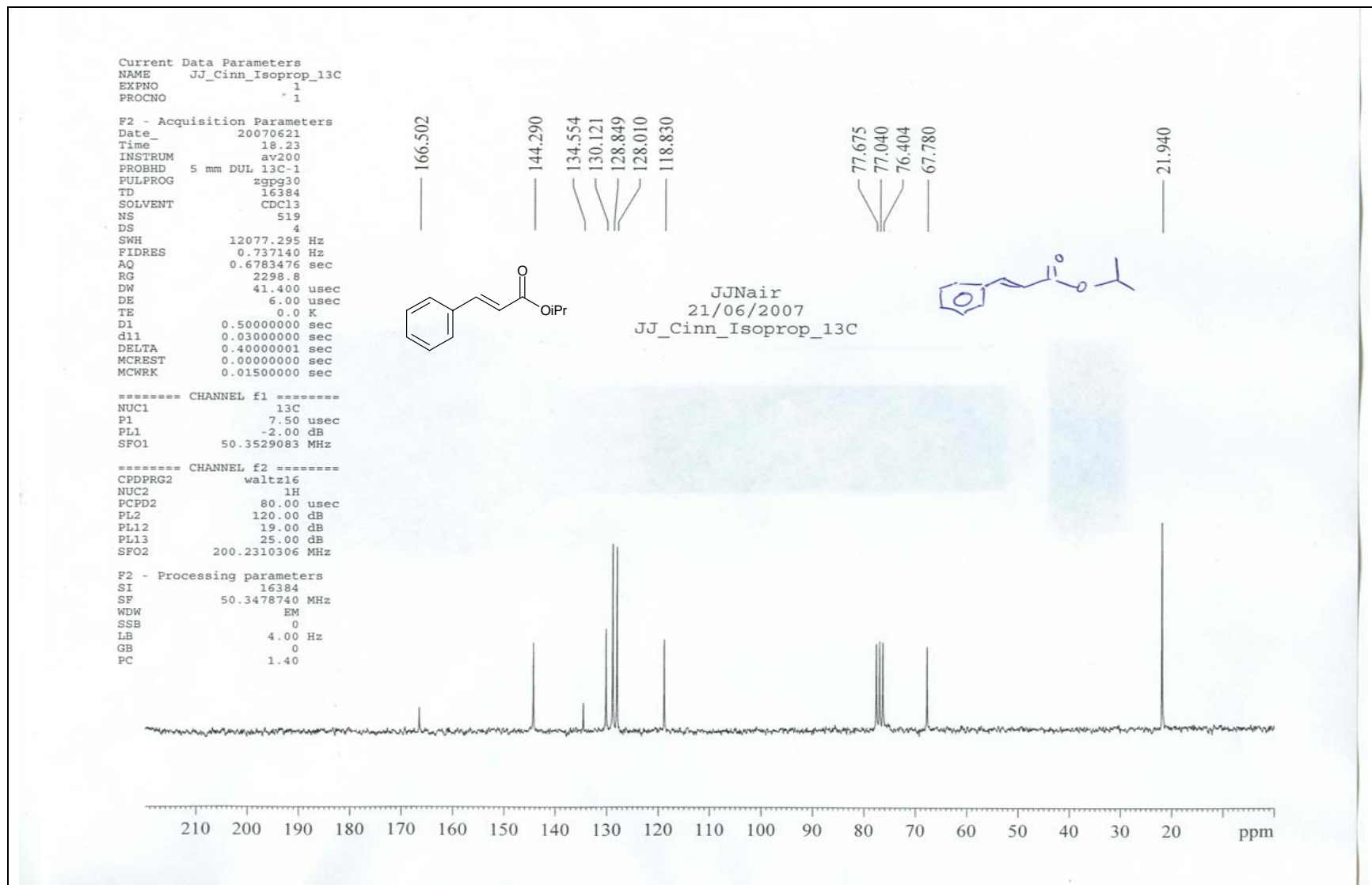


Figure 7b: ¹³C NMR spectrum of *i*-propyl cinnamate (Table 2, entry 11)

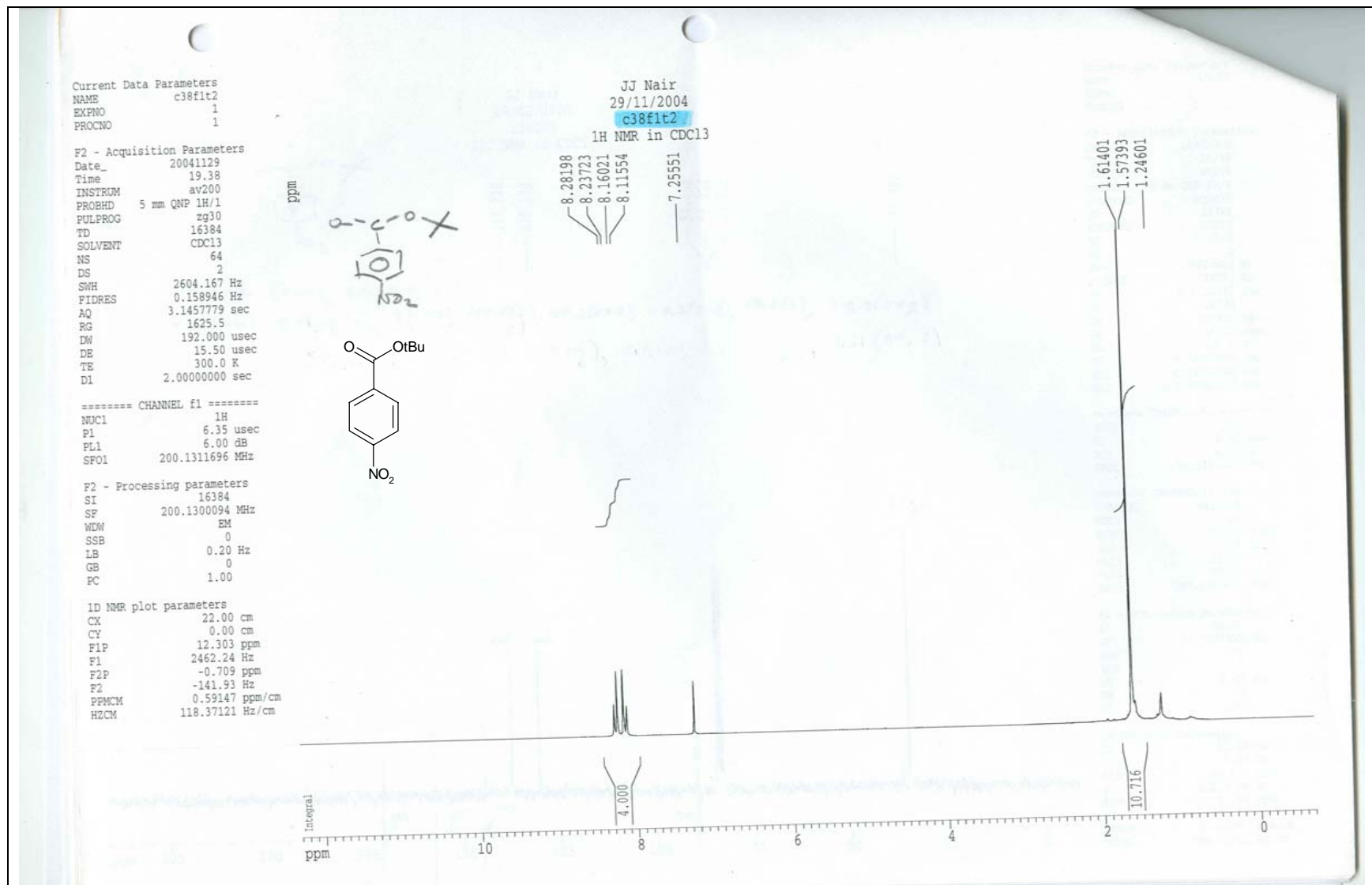


Figure 8a: ^1H NMR spectrum of *t*-butyl 4-nitrobenzoate (Table 2, entry 12)

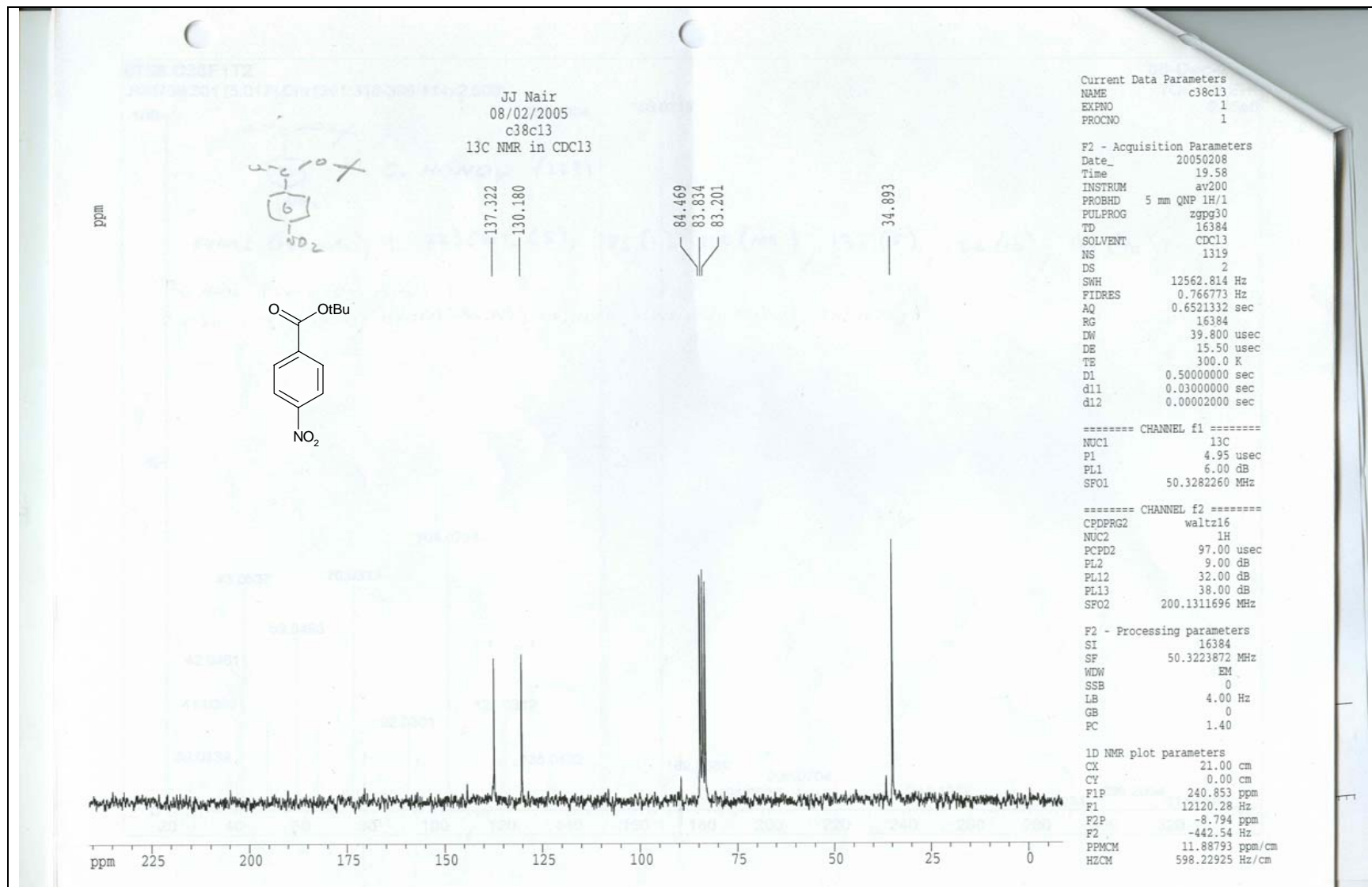


Figure 8b: ¹³C NMR spectrum of *t*-butyl 4-nitrobenzoate (Table 2, entry 12)

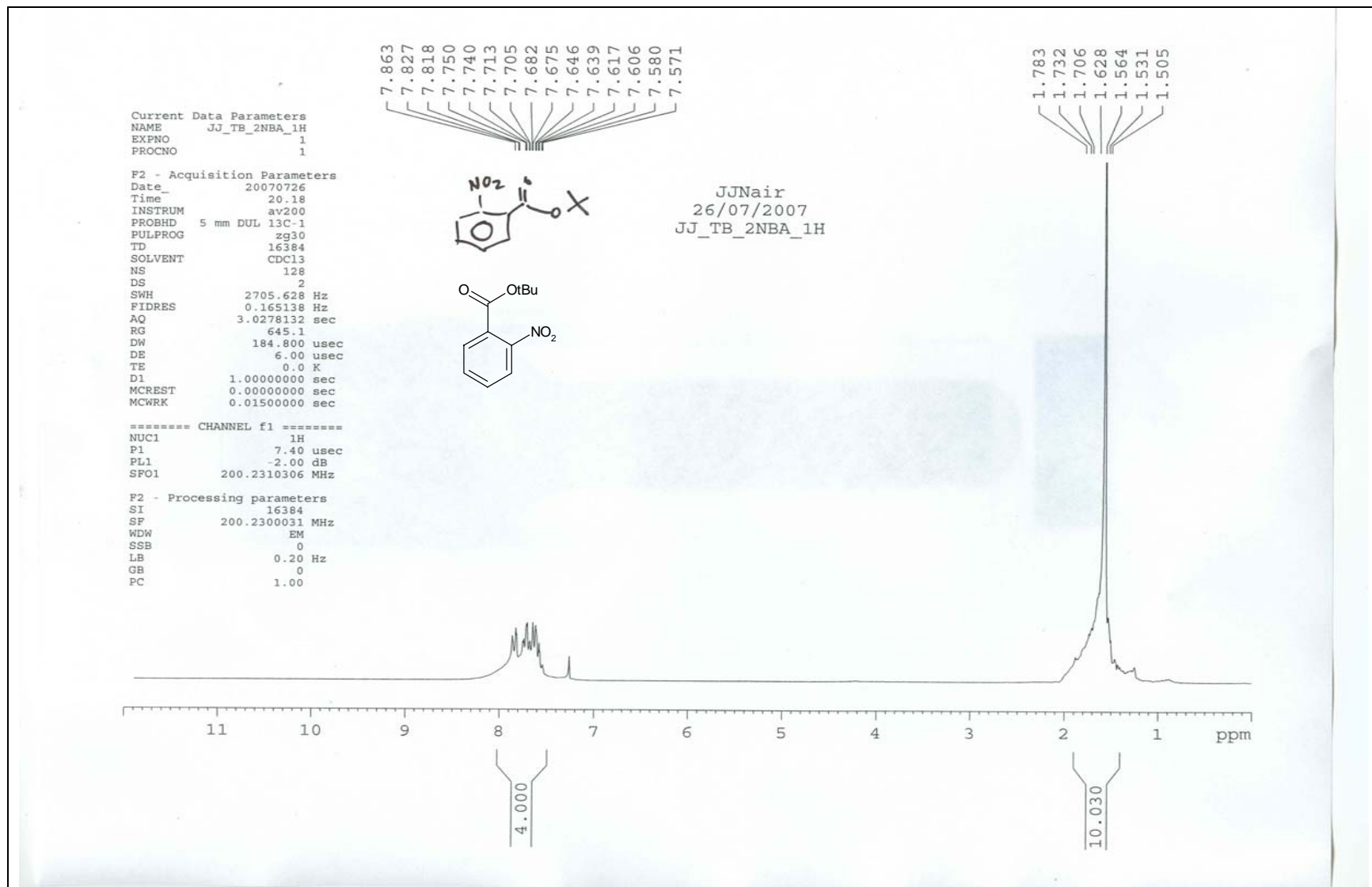


Figure 9a: ^1H NMR spectrum of *t*-butyl 2-nitrobenzoate (Table 2, entry 13)

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PROCNO 1

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PULPROG zgpg30
TD 16384
SOLVENT CDCl3
NS 2226
DS 4
SWH 12077.295 Hz
FIDRES 0.737140 Hz
AQ 0.6783476 sec
RG 2896.3
DW 41.400 usec
DE 6.00 usec
TE 0.0 K
D1 0.50000000 sec
d11 0.03000000 sec
DELTA 0.40000001 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 -2.00 dB
SFO1 50.3529083 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 200.2310306 MHz

F2 - Processing parameters
SI 16384
SF 50.3478740 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

164.284

148.409

132.638

131.256

129.880

128.953

123.590

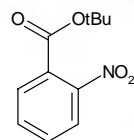
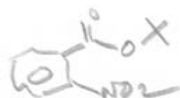
83.707

77.672

77.037

76.403

27.705



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JJ_TB_2NBA_13C

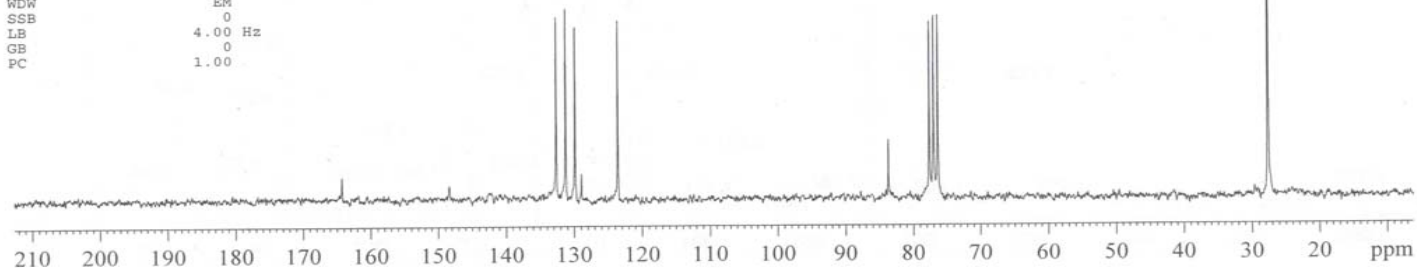


Figure 9b: ¹³C NMR spectrum of *t*-butyl 2-nitrobenzoate (Table 2, entry 13)

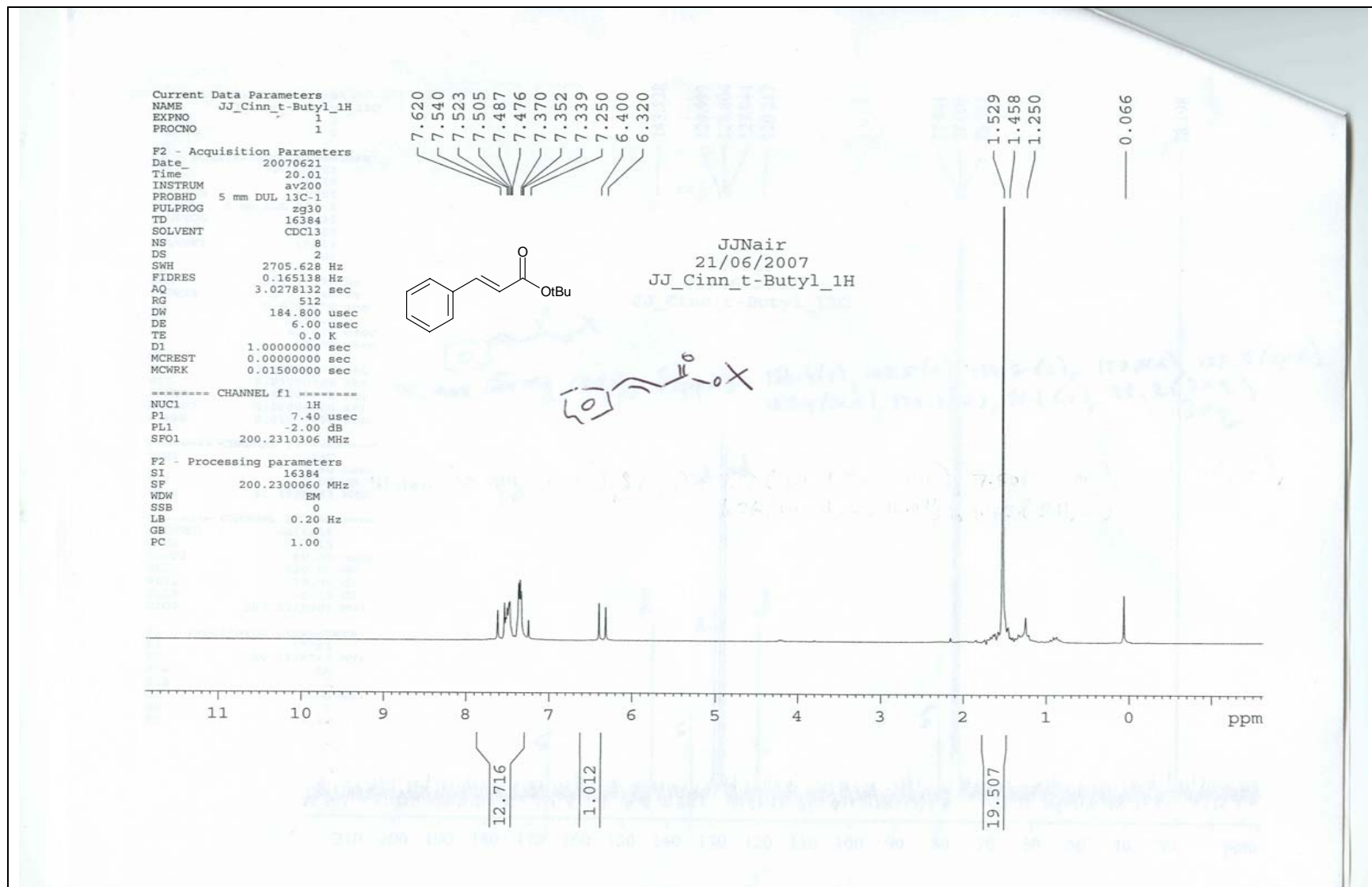


Figure 10a: ^1H NMR spectrum of *t*-butyl cinnamate (Table 2, entry 14)

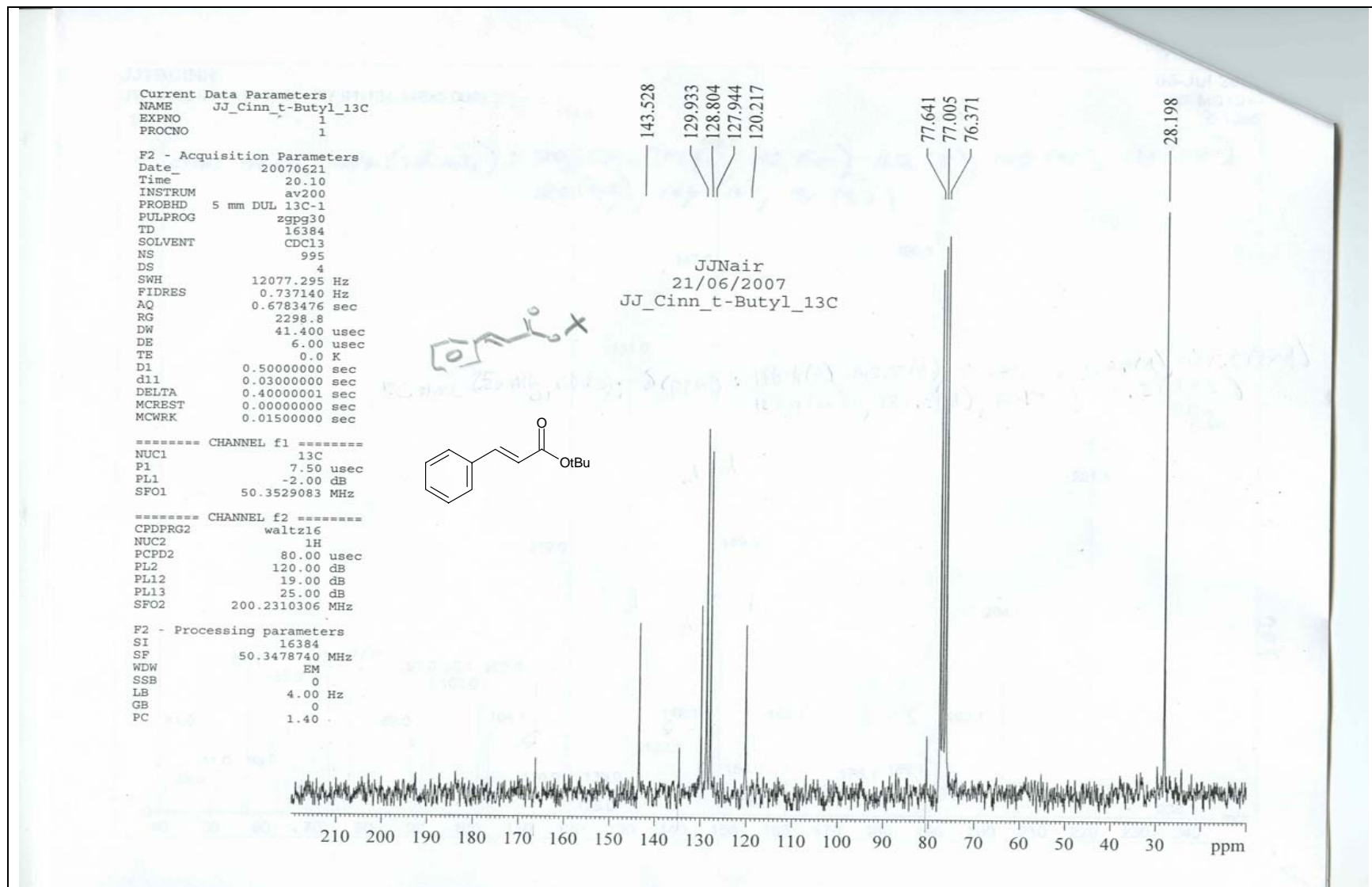


Figure 10b: ^{13}C NMR spectrum of *t*-butyl cinnamate (Table 2, entry 14)

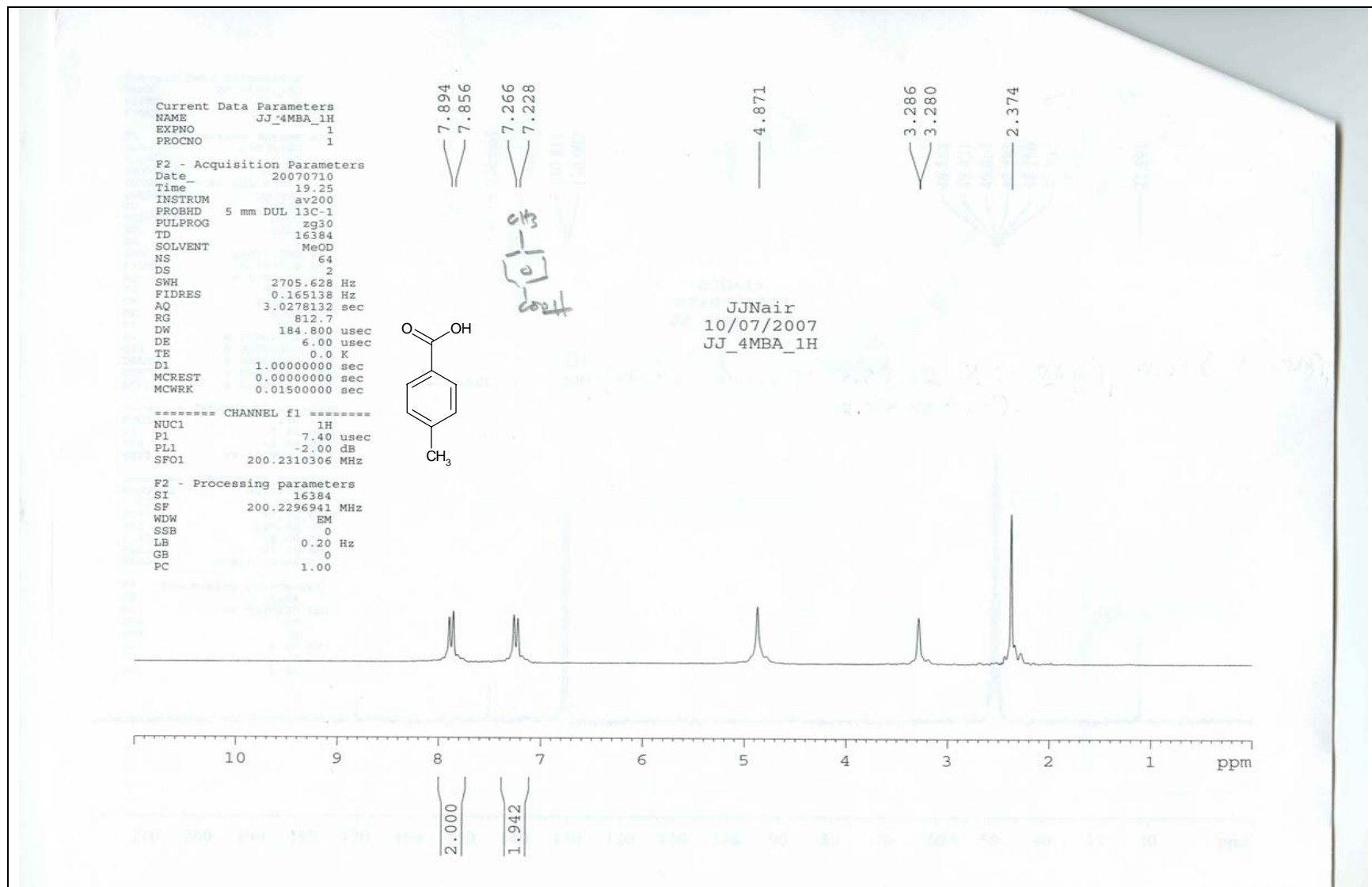


Figure 11a: ^1H NMR spectrum of 4-methylbenzoic acid (Table 2, entry 15)

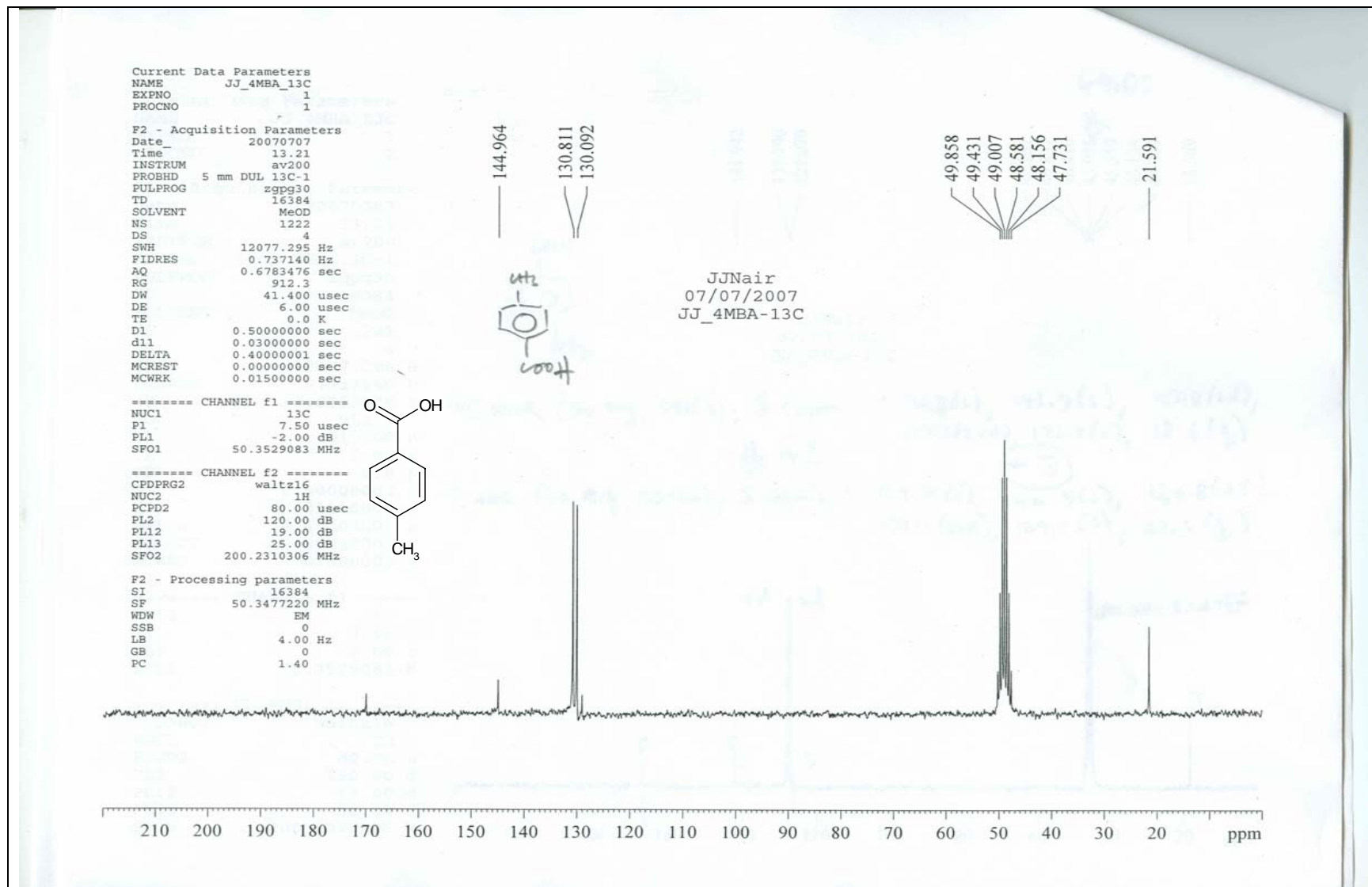


Figure 11b: ^{13}C NMR spectrum of 4-methylbenzoic acid (Table 2, entry 15)

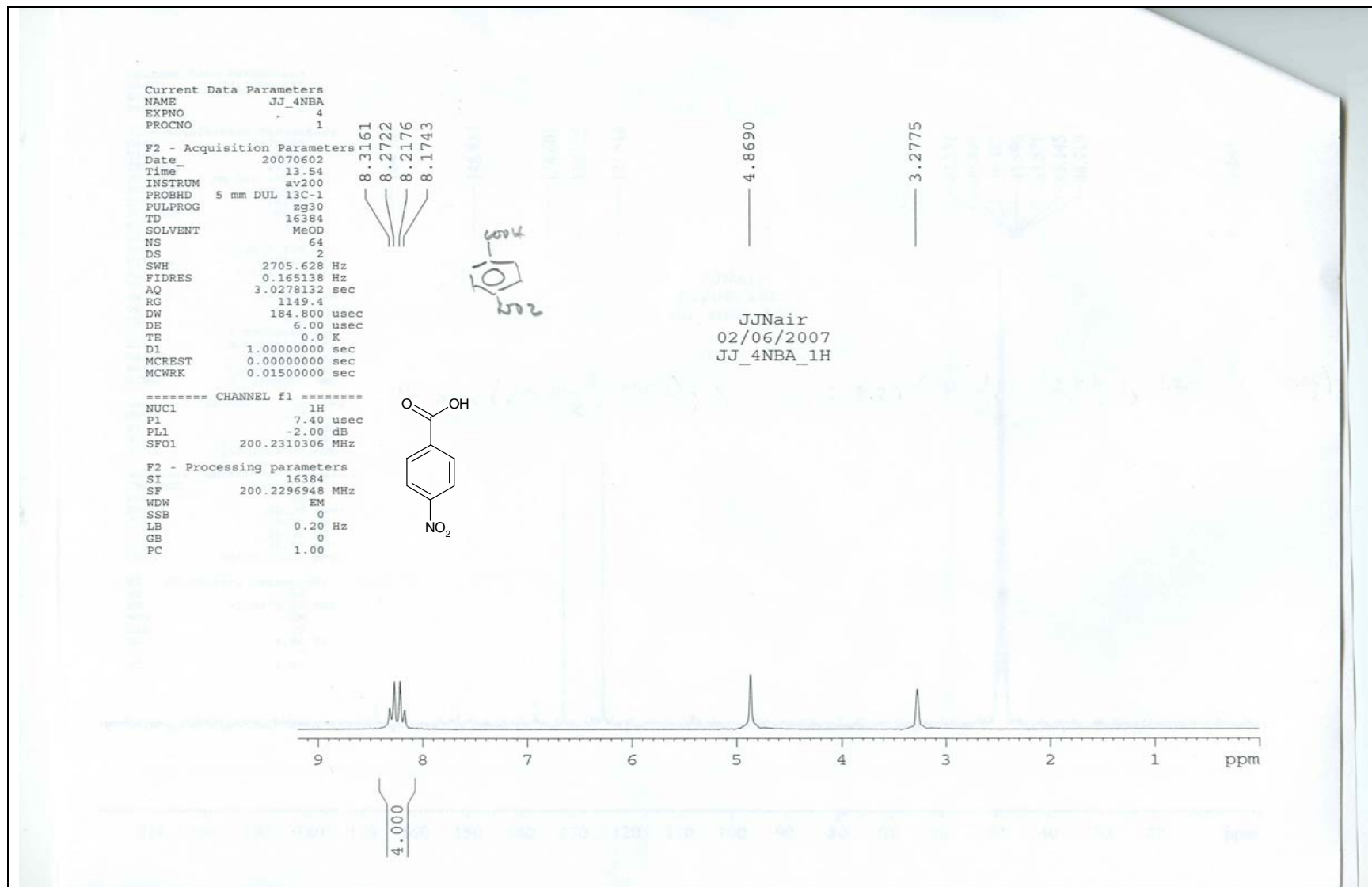


Figure 12a: ^1H NMR spectrum of 4-nitrobenzoic acid (Table 2, entry 16)

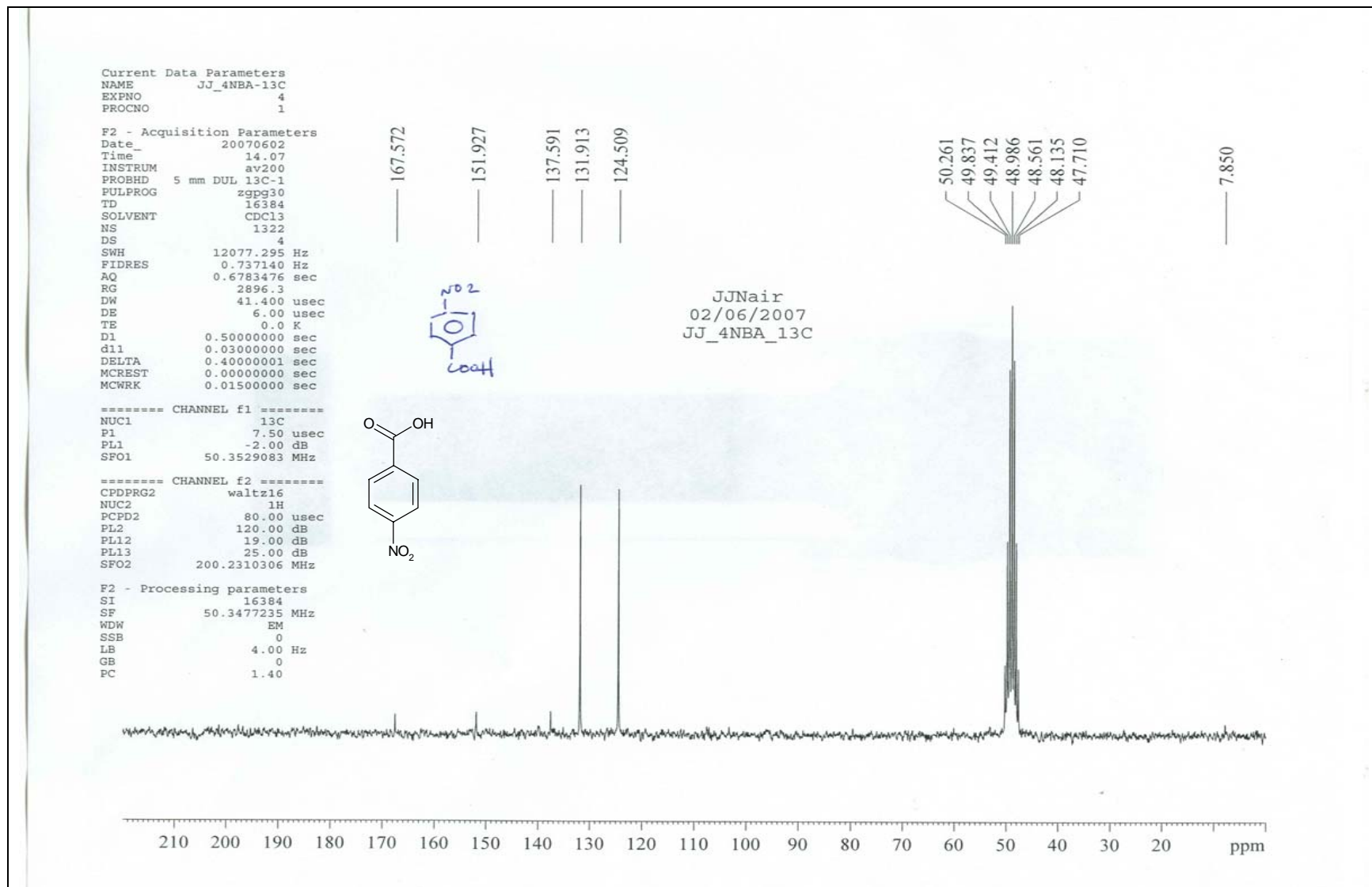


Figure 12b: ¹³C NMR spectrum of 4-nitrobenzoic acid (Table 2, entry 16)

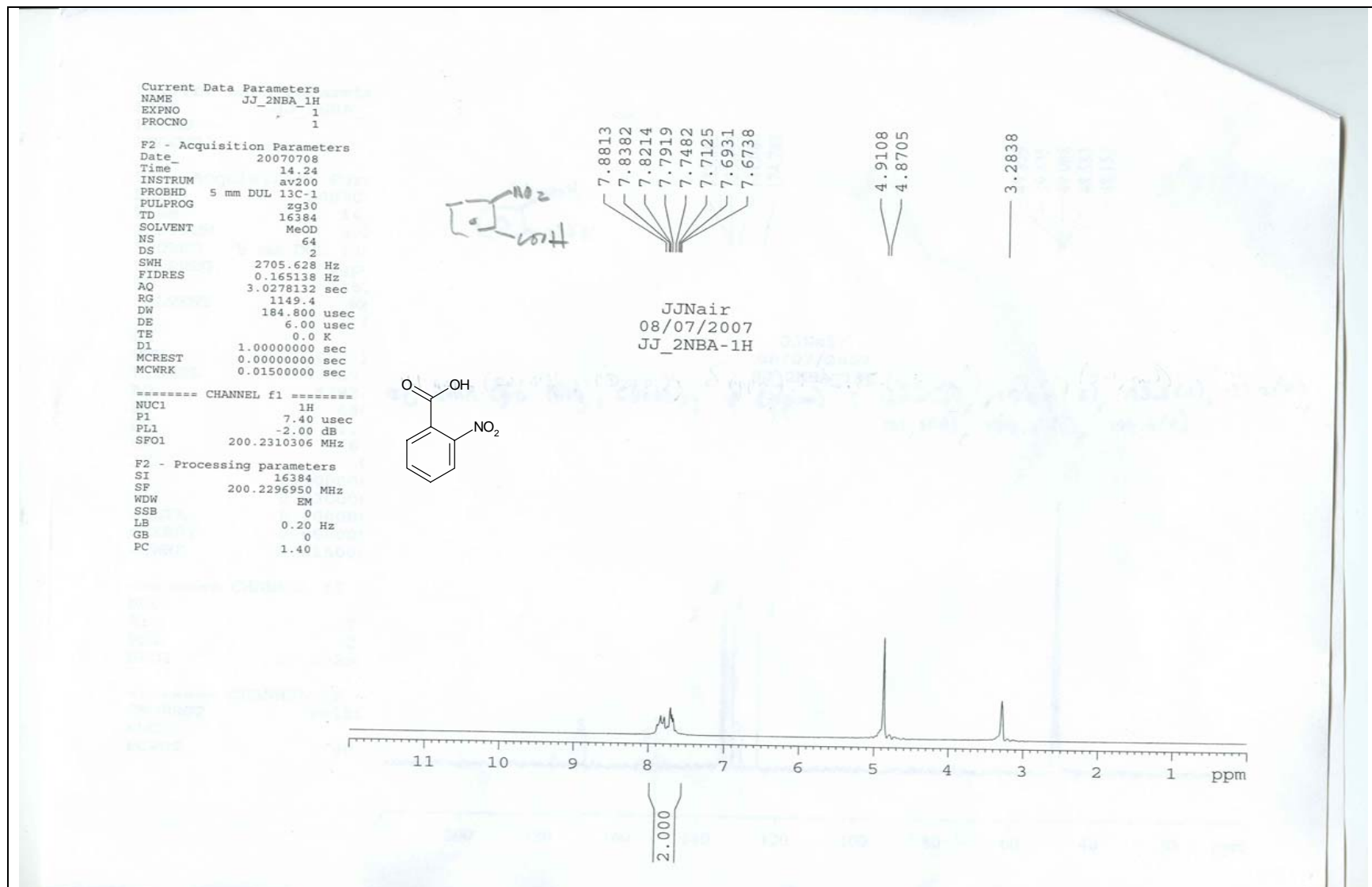


Figure 13a: ^1H NMR spectrum of 2-nitrobenzoic acid (Table 2, entry 17)

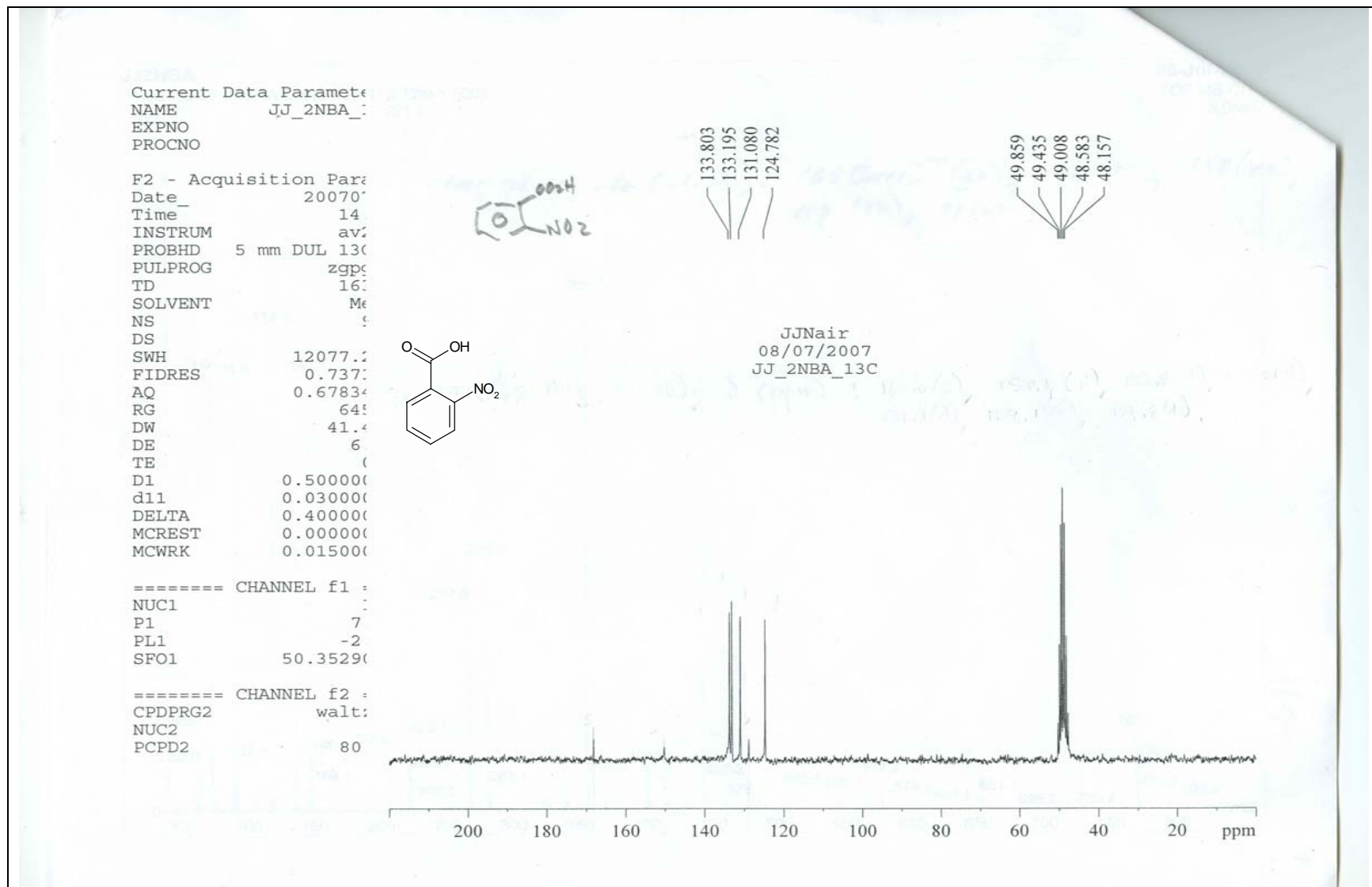


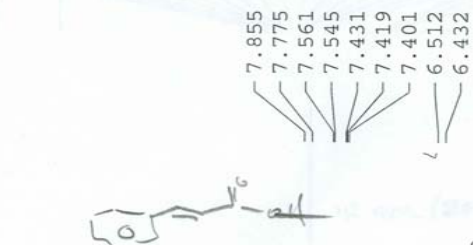
Figure 13b: ^{13}C NMR spectrum of 2-nitrobenzoic acid (Table 2, entry 17)

Current Data Parameters
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EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070606
Time 19.55
INSTRUM av200
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 8
DS 2
SWH 2705.628 Hz
FIDRES 0.165138 Hz
AQ 3.0278132 sec
RG 512
DW 184.800 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.40 usec
PL1 -2.00 dB
SFO1 200.2310306 MHz

F2 - Processing parameters
SI 16384
SF 200.2300041 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00



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06/06/2007
JJ_Cinn_1H

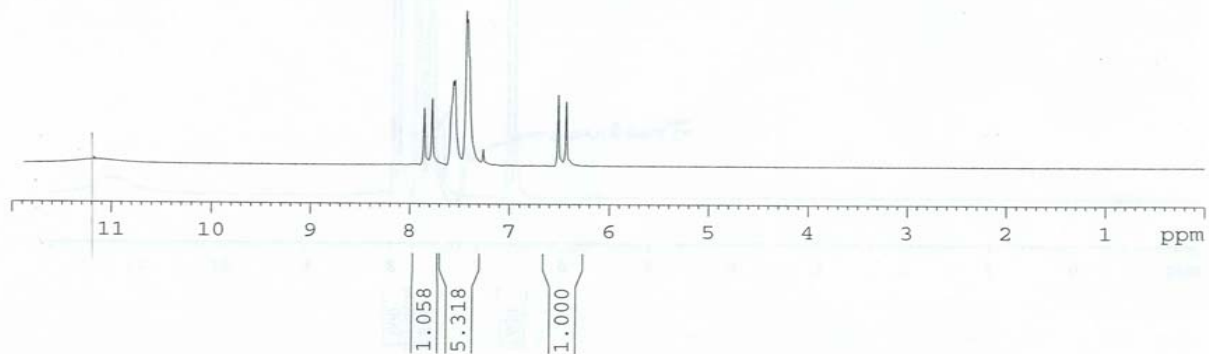
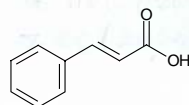


Figure 14a: ^1H NMR spectrum of cinnamic acid (Table 2, entry 18)

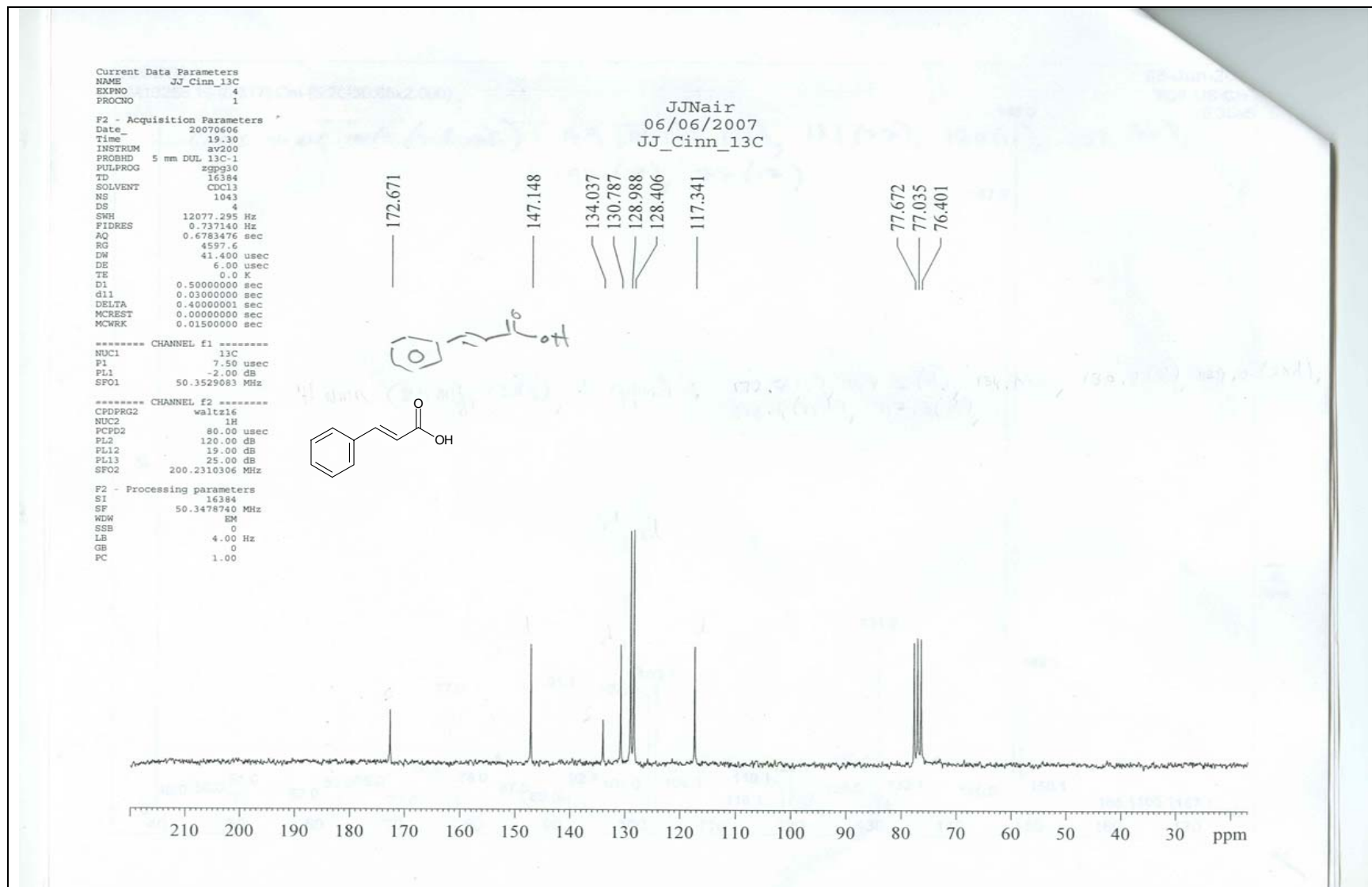


Figure 14b: ^{13}C NMR spectrum of cinnamic acid (Table 2, entry 18)

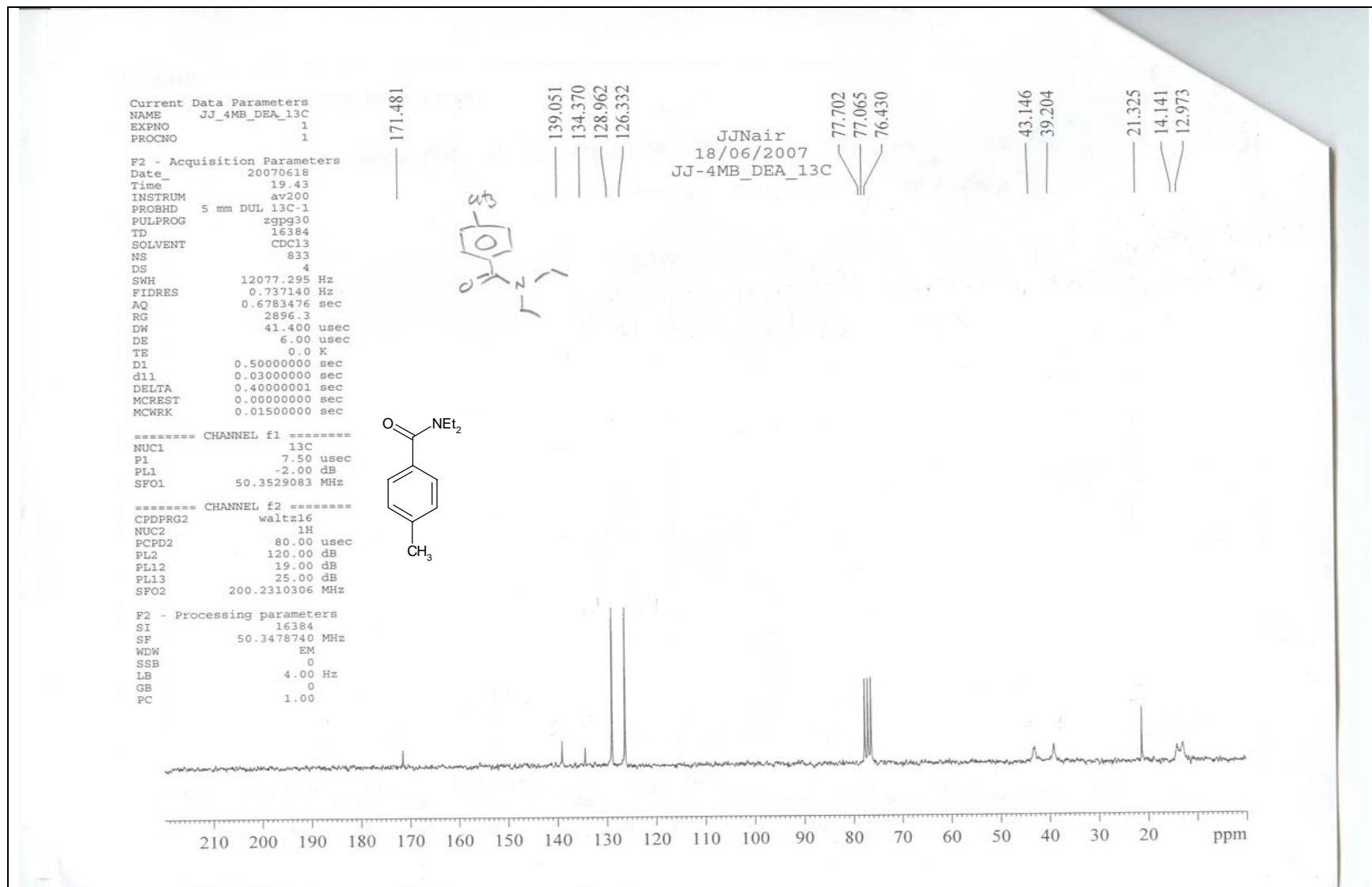


Figure 15b: ^{13}C NMR spectrum of diethyl 4-methylbenzamide (Table 2, entry 19)

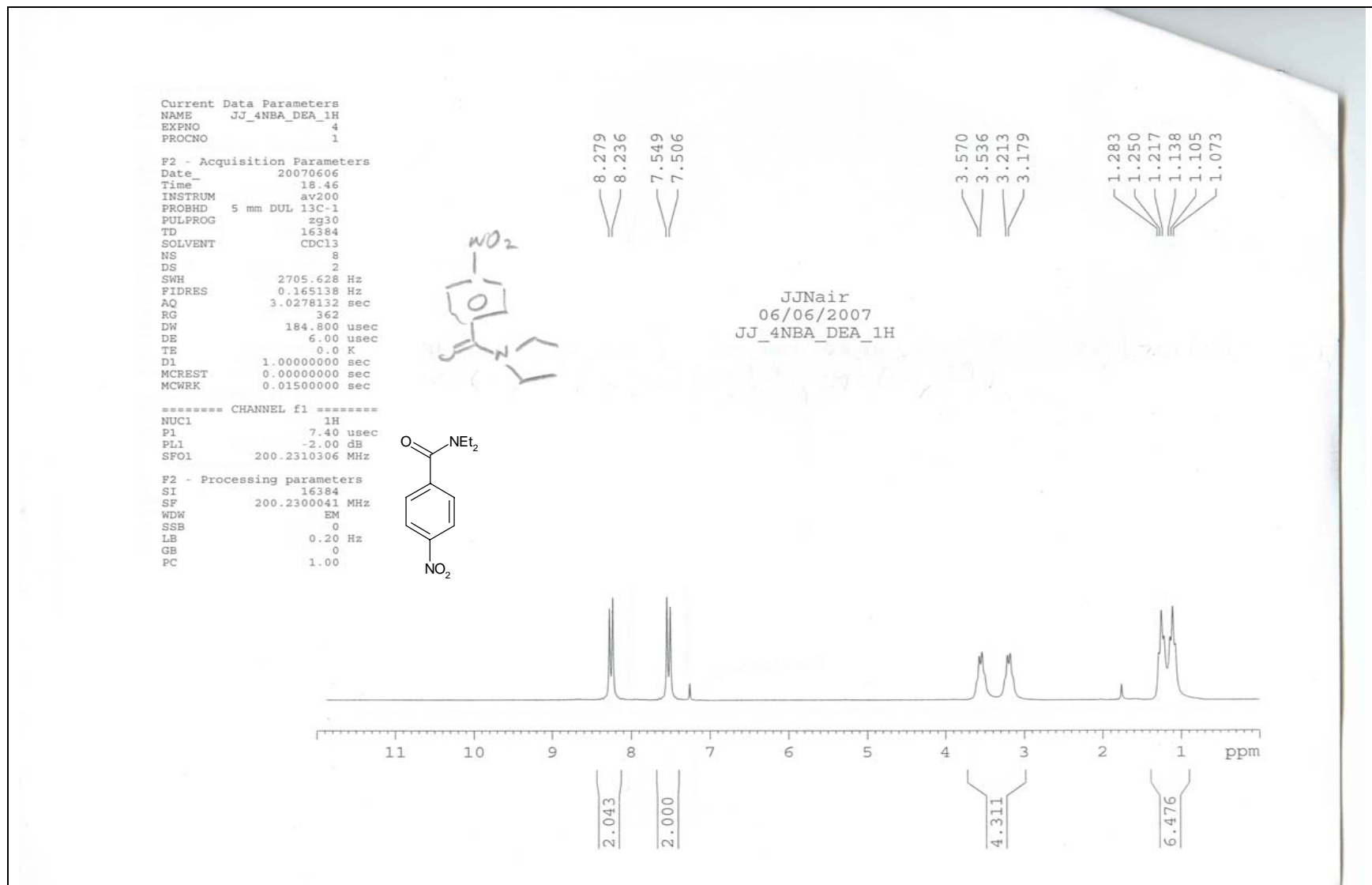


Figure 16a: ¹H NMR spectrum of diethyl 4-nitrobenzamide (Table 2, entry 20)

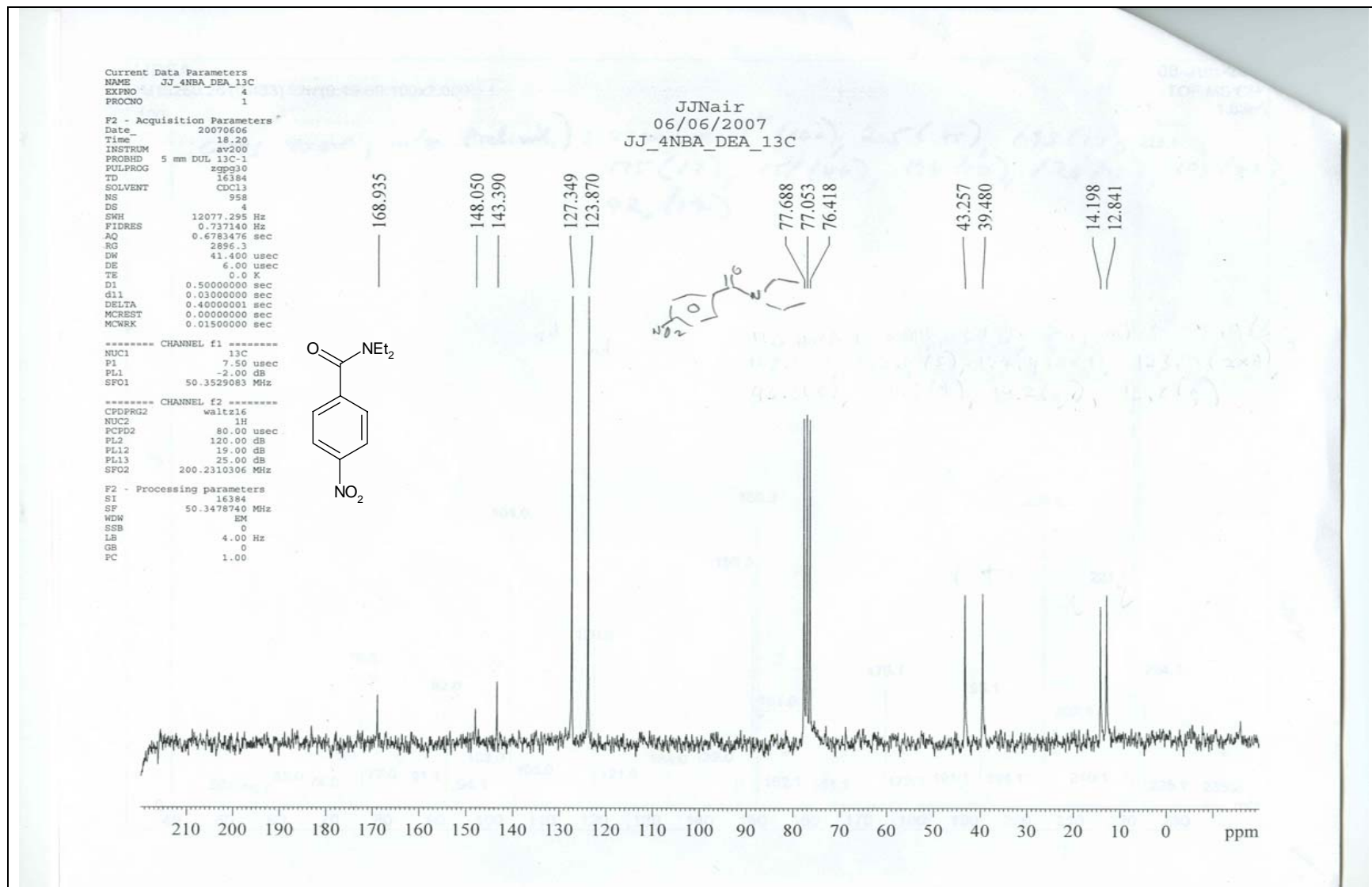


Figure 16b: ^{13}C NMR spectrum of diethyl 4-nitrobenzamide (Table 2, entry 20)

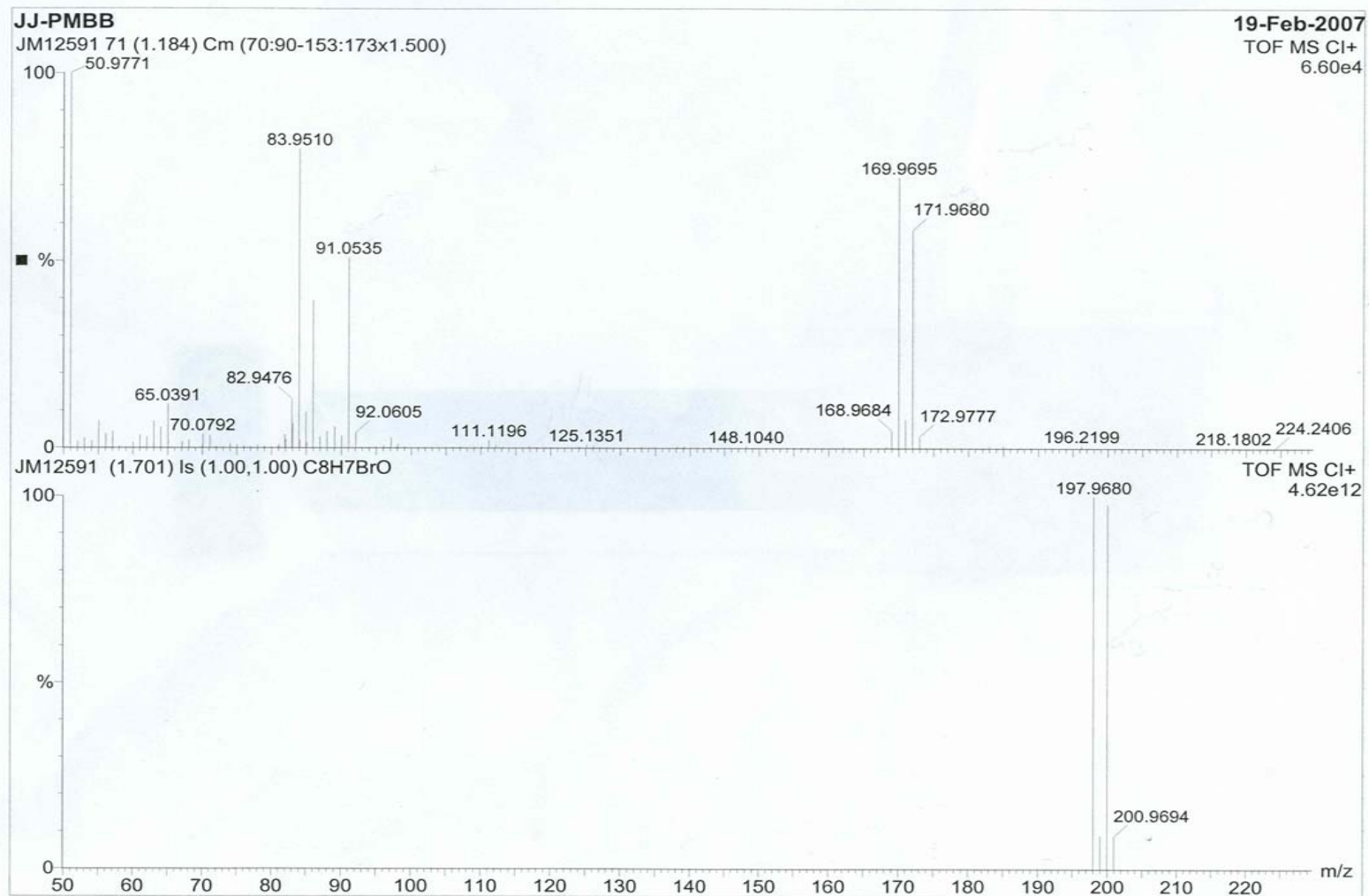


Figure 17a: CIMS spectrum of 4-methylbenzoyl bromide detected in reaction run without base or nucleophile

File : D:\DATA\1049\PDcox.D
Operator : SZ
Acquired : 5 Jul 2007 10:44 using AcqMethod DYCKMS
Instrument : 6890/5973
Sample Name: M: pd carbonylation run, for JMN
Misc Info : neat
Vial Number: 1

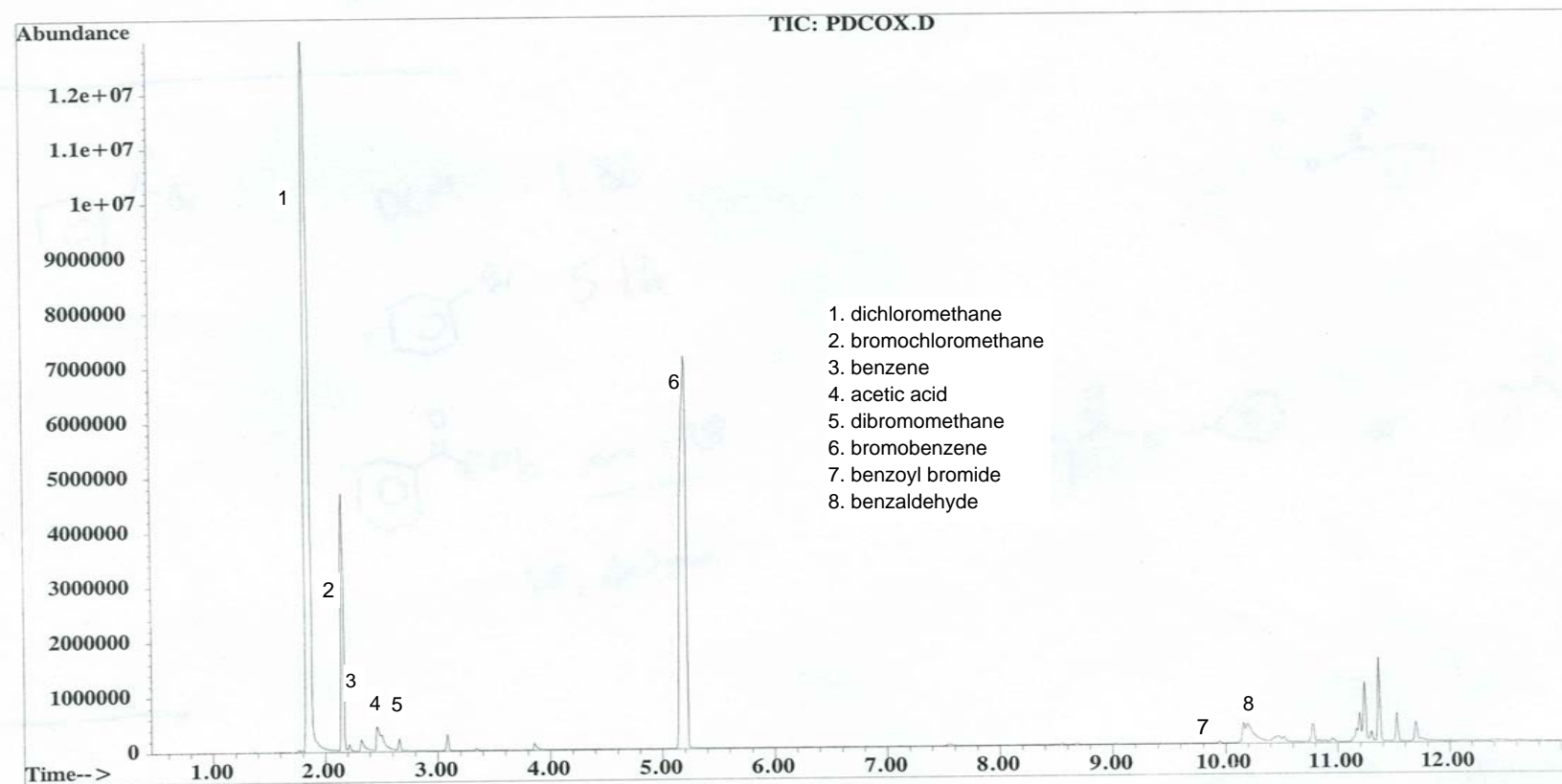


Figure 17b: GC spectrum showing benzoyl bromide (peak at 9.943 min) detected in reaction run without base or nucleophile

File : D:\DATA\1049\PDCCOX.D
Operator : SZ
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Instrument : 6890/5973
Sample Name : M: pd carbonylation run, for JMN
Misc Info : neat
Vial Number: 1

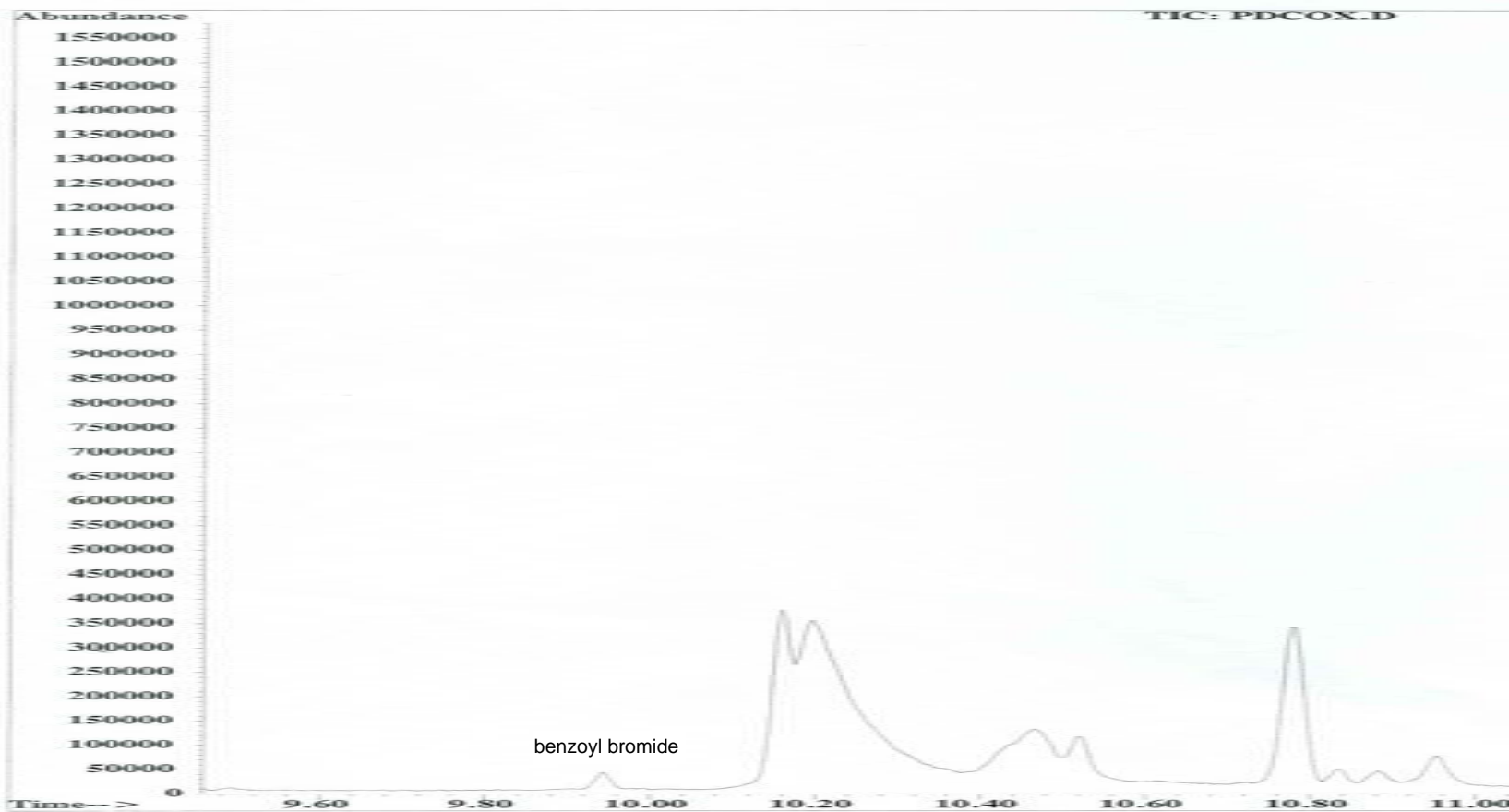


Figure 17c: Expansion of Figure 17b showing benzoyl bromide peak at 9.943 min

