Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information for

# Copper-Catalyzed Intermolecular $C_{sp2}$-H Amidation of Unactivated Arenes by *N*-Tosyloxycarbamates

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## Experimental Section

**General Procedures.** Manipulations were carried out using either Schlenk tube techniques under an inert atmosphere or in an Ace Glass glass pressure reactors. Copper salts, ligands and other additives were obtained commercially. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded either on a Varian 300 MHz or 500 MHz NMR spectrometer. $^{1}H$ NMR peaks are labeled as singlet (s), doublet (d), triplet (t) and multiplet (m). Mass spectra were acquired in the ESI (+) mode. The *N*-reagents namely, *N*-Tosyloxytroccarbamate,[1] *N*-Mesitylsulfonyloxytroccarbamate,[1] *N*-(4-nitrophenyl)sulfonyloxytroccarbamate[1] and *N*-Tosyl-*tert*-butyloxycarbamate[2] were synthesized using literature procedures. Similarly, the aryl carbmate isomers namely, 2,2,2-Trichloroethyl-*N*-phenylcarbamate (**1**),[3] 2,2,2-Trichloroethyl-*N*-*p*-tolylcarbamate (***p*-2**),[4] 2,2,2-Trichloroethyl-*N*-*m*-ethylphenylcarbamate (***m*-3**),[5] 2,2,2-Trichloroethyl-*N*-*o*-methoxyphenylcarbamate (***o*-5**),[6] 2,2,2-Trichloroethyl-*N*-*p*-methoxyphenylcarbamate (***p*-5**),[6] 2,2,2-Trichloroethyl-*N*-*m*-chlorophenylcarbamate (***m*-6**),[6] 2,2,2-Trichloroethyl-*N*-*p*-chlorophenylcarbamate (***p*-6**),[5] 2,2,2-Trichloroethyl-*N*-*m*-trifluoromethylphenylcarbamate (***m*-7**),[7] were identified in the mixture based on literature NMR data.

**General procedure for screening reactions**

To a stirred mixture of catalyst (0.026 mmol), ligand (0.024 mmol) in benzene (*ca.* 0.5 mL) was added *N*-tosyloxycarbamate (0.050 g, 0.138 mmol) and the entire mixture was allowed to stir at 140 $^{o}$C for the stipulated amount of time. The reaction mixture was cooled to room temperature, filtered through a pad of silica and the filtrate concentrated under vacuum. The residue was re-dissolved in $CDCl_3$ and analyzed by $^{1}$H NMR using a known amount of 1,3,5-trimethoxybenzene as an internal standard.

**Table S1**. Screening of other transition-metal catalysts for amination of benzene.[a]

| entry | catalyst | conversion (%) | yield (%) |
|---|---|---|---|
| 1 | $Co(BF_4)_2 \bullet 6H_2O$ (20) | 12 | 0 |
| 2 | $Fe(acac)_2$ (20) | 100 | 23 |
| 3 | $FeCl_2$/Neocuproine (20) | - | 8 |
| 4 | $Fe(OAc)_2$ (20) | - | 3 |
| 5 | $Fe(OTf)_2 \bullet 2CH_3CN$ | 87 | trace |
| 6 | $Fe(OTf)_2 \bullet 2CH_3CN$/Neocuproine | 95 | 23 |

[a]Reaction conditions: oxycarbamate (0.054 g, 0.138 mmol), catalyst and ligand in benzene (*ca.* 0.5 mL) at 140 $^{o}$C in sealed tube for 16 h.

**Table S2**. Ligand variation.[a]

| entry | ligand/loading | conversion (%) | yield (%) |
|---|---|---|---|
| 1 | $PPh_3$ (40 %) | 88 | 22 |
| 2 | dppm (20 %) | 100 | 25 |
| 3 | dppf (20 %) | 100 | 57 |
| 4 | dppp (20 %) | 87 | 33 |
| 5 | $[(Neo)Cu(PPh_3)_2]PF_6$ (20 %) | 100 | 35 |
| 6 | PMDETA (20 %) | 100 | 20 |
| 7 | PhCN (0.1 mL) | 74 | 31 |
| 8 | DMSO (0.05 mL) | 89 | trace |
| 9 | NMP (1 equiv.) | - | 24 |
| 10 | pivalic acid (40 %) | 57 | 32 |
| 11 | picolinic acid (20 %) | 27 | trace |
| 12 | pyridine-2,6-dicarboxylic acid (20 %) | 54 | 24 |
| 13. | $^{3,5Me2}$TPz (20 %) | nd | 25 |
| 14 | bisoxazolyl (20 %) | nd | 38 |
| 15[b] | pyridine (40 %) | nd | 12 |
| 16 | bipyridine (20 %) | 78 | 32 |
| 17 | 4,4'-dimethylbipyridine (20 %) | 20 | 6 |
| 18[b] | phenanthroline (20 %) | 64 | 25 |
| 19 | 4,7-dimethylphenanthroline (20 %) | 87 | 24 |
| 20 | Neocuproine (20 %) | 100 | 48 |
| **21**[c] | **Neocuproine (20 %)** | **100** | **75** |

[a]Reaction conditions: Tosyloxycarbamate (0.050 g, 0.138 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.010 g, 0.027 mmol) and ligand in benzene (*ca.* 0.5 mL) at 140 °C in sealed tube for 16 h. [b]After 48 h. [c]Reaction carried out in 1 mL benzene. Conversion and yield with respect to 1,3,5-trimethoxybenzene as an internal standard. dppm = diphenylphosphinomethane, dppf = diphenylphosphinoferrocene, dppp = diphenylphosphinopropane, PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine, TPz = tris(pyrazolyl)hydroborate, nd = not determined.

**Table S3**. Amination of benzene using *N*-Mesitylsulfonyloxycarbamate.

| entry | additive/loading | conversion (%) | yield (%) |
|---|---|---|---|
| 1 | - | 95 | 10 |
| 2 | Neocuproine (20) | - | 39 |
| 3 | Neocuproine (40) | - | 20 |

[a]Reaction conditions: Mesitylsulfonyloxycarbamate (0.054 g, 0.138 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.010 g, 0.027 mmol) and ligand in benzene (*ca.* 0.5 mL) at 140 $^oC$ in sealed tube for 16 h.

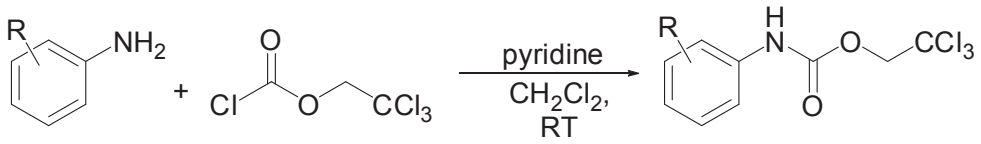
**Table S4.** Catalyst variation using Neocuproine.

| entry | copper precursor | conversion | yield[b] |
|---|---|---|---|
| 1 | $Cu_2O$ (20 %) | 100 | 57 (40) |
| 2 | $\{Cu(OTf)\}_2$•toluene | 100 | 40 (20) |
| 3 | CuI | 100 | 20 |
| 4 | Cu(I)TC | 100 | 48 (16) |

[a]Reaction conditions: Tosyloxycarbamate (0.050 g, 0.138 mmol) and [Cu] (0.027 mmol) and Neocuproine (0.0056 g, 0.027 mmol) in benzene (*ca.* 1 mL) at 140 $^oC$ in sealed tube for 16 h. Conversion and yield with respect to 1,3,5-trimethoxybenzene NMR internal standard. [b]Yields in paranthesis for reactions in absence of ligand.

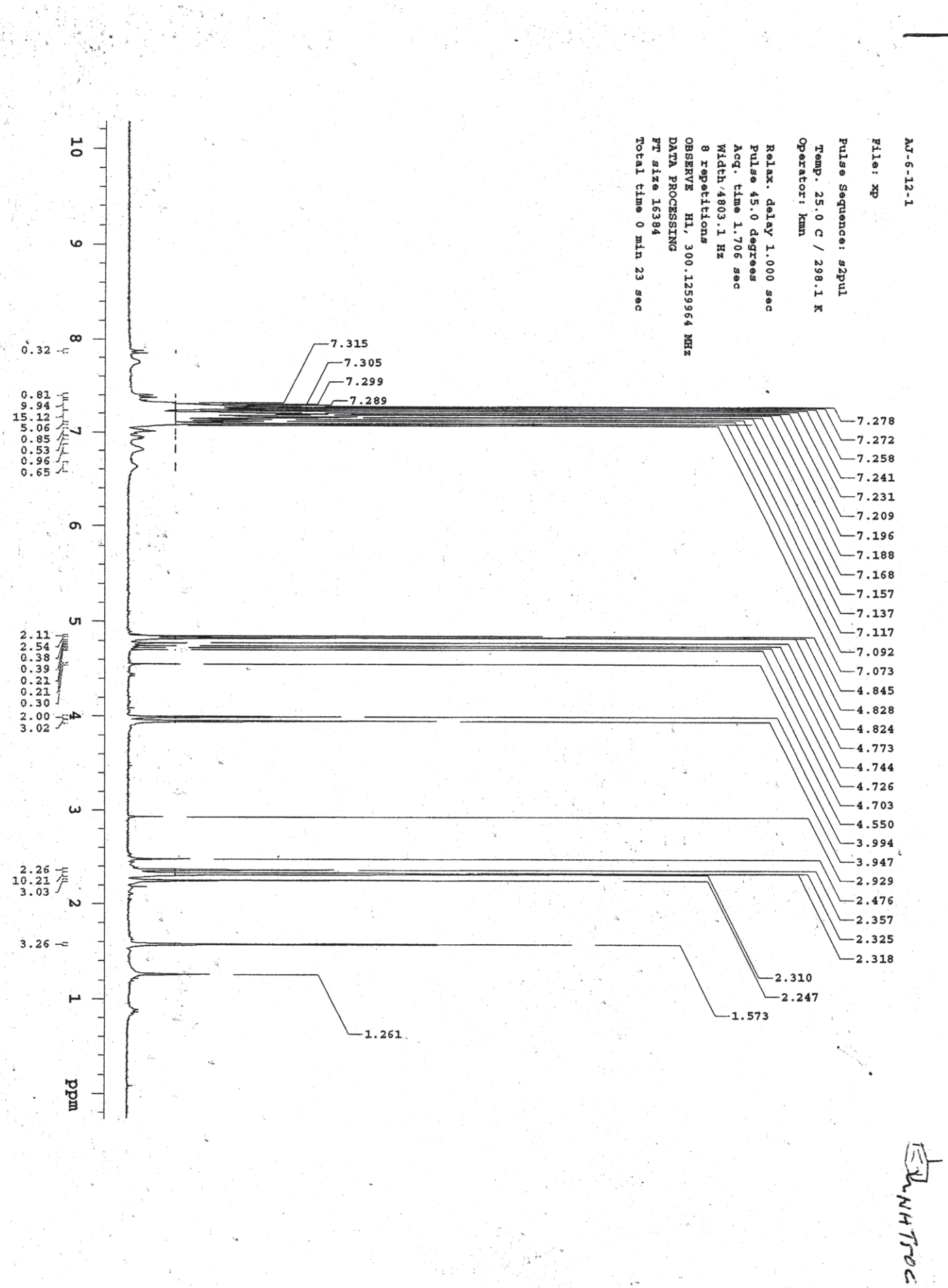
**General procedure for amination of arenes**. To a stirred mixture of $[Cu(CH_3CN)_4]PF_6$ (0.010 g, 0.026 mmol) and neocuproine (0.005 g, 0.024 mmol) in the respective arene (*ca.* 1 mL) was added *N*-tosyloxy-2,2,2-trichloroethylcarbamate (0.050 g, 0.138 mmol) and the mixture was allowed to stir at 140 $^oC$ for 8 hours. The reaction mixture was subsequently cooled to room temperature, filtered through a pad of silica to remove copper containing species, and the filtrate concentrated under vacuum. The residue was purified by silica chromatography using 5-15 % $Et_2O$ in hexanes to obtain the regioisomeric mixture of aminated arene. The regioisomers were identified either based on literature NMR data or by carrying out chemical syntheses of the authentic Troccarbamates starting from the commercially available anilines. The isomeric ratio was determined by NMR integrations on the methylene (-OC$\underline{H_2}$CCl$_3$) protons of the Troc group using 1,3,5-trimethoxybenzene as an internal standard.

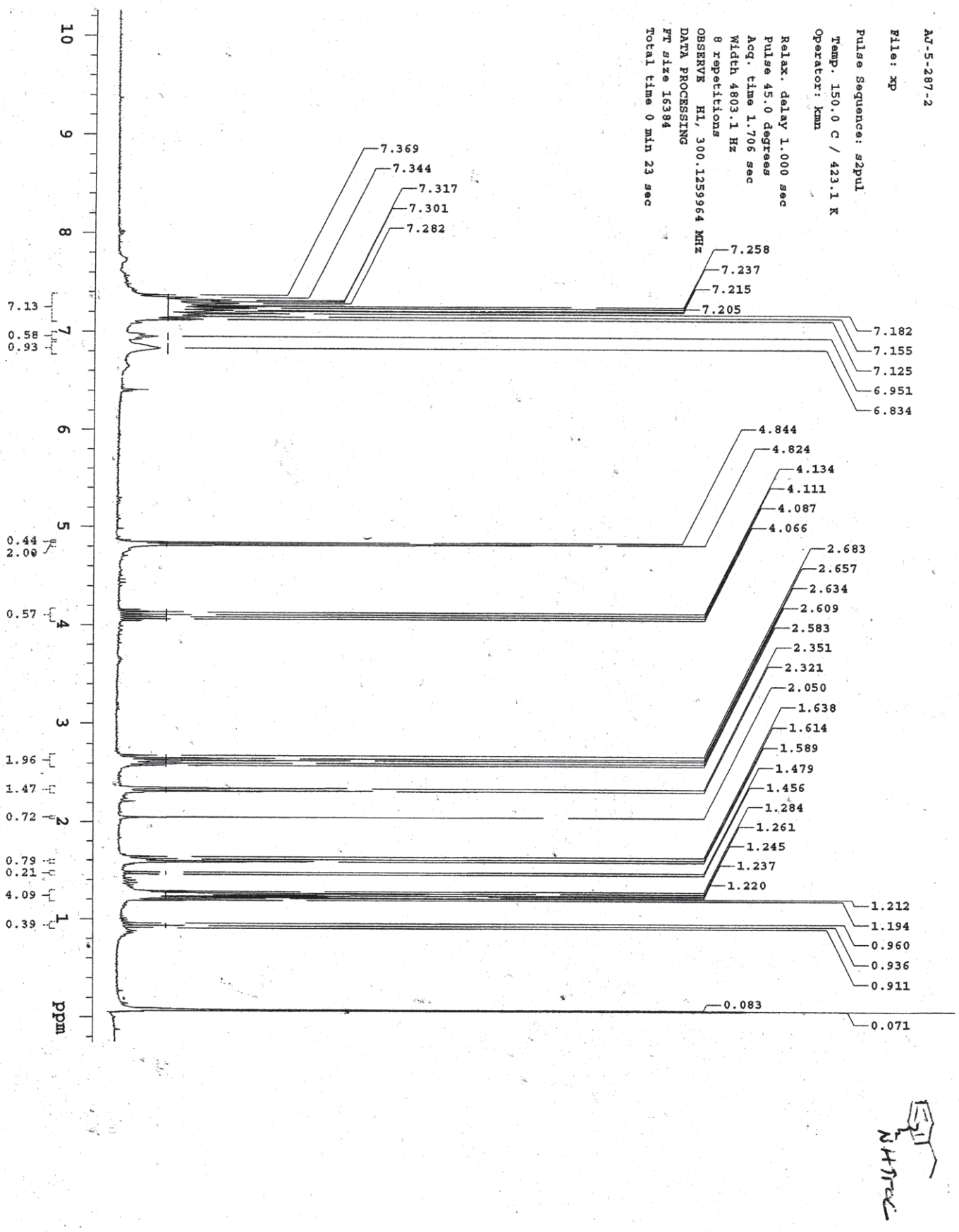
**General procedure for the syntheses of Troc carbamates**. To a stirred mixture of the aniline (2.31 mmol) and pyridine (0.2 mL, 2.49 mmol), $CH_2Cl_2$ (*ca.* 10 mL) at room temperature was added drop wise Troccarbonyl chloride (0.34 mL, 2.47 mmol) and the reaction mixture was allowed to stir overnight. It was then diluted with $CH_2Cl_2$ (*ca.* 10 mL) and washed successively with $H_2O$, 5 % NaOH solution and 5 % HCl. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and then concentrated under vacuum to yield the product carbamate.

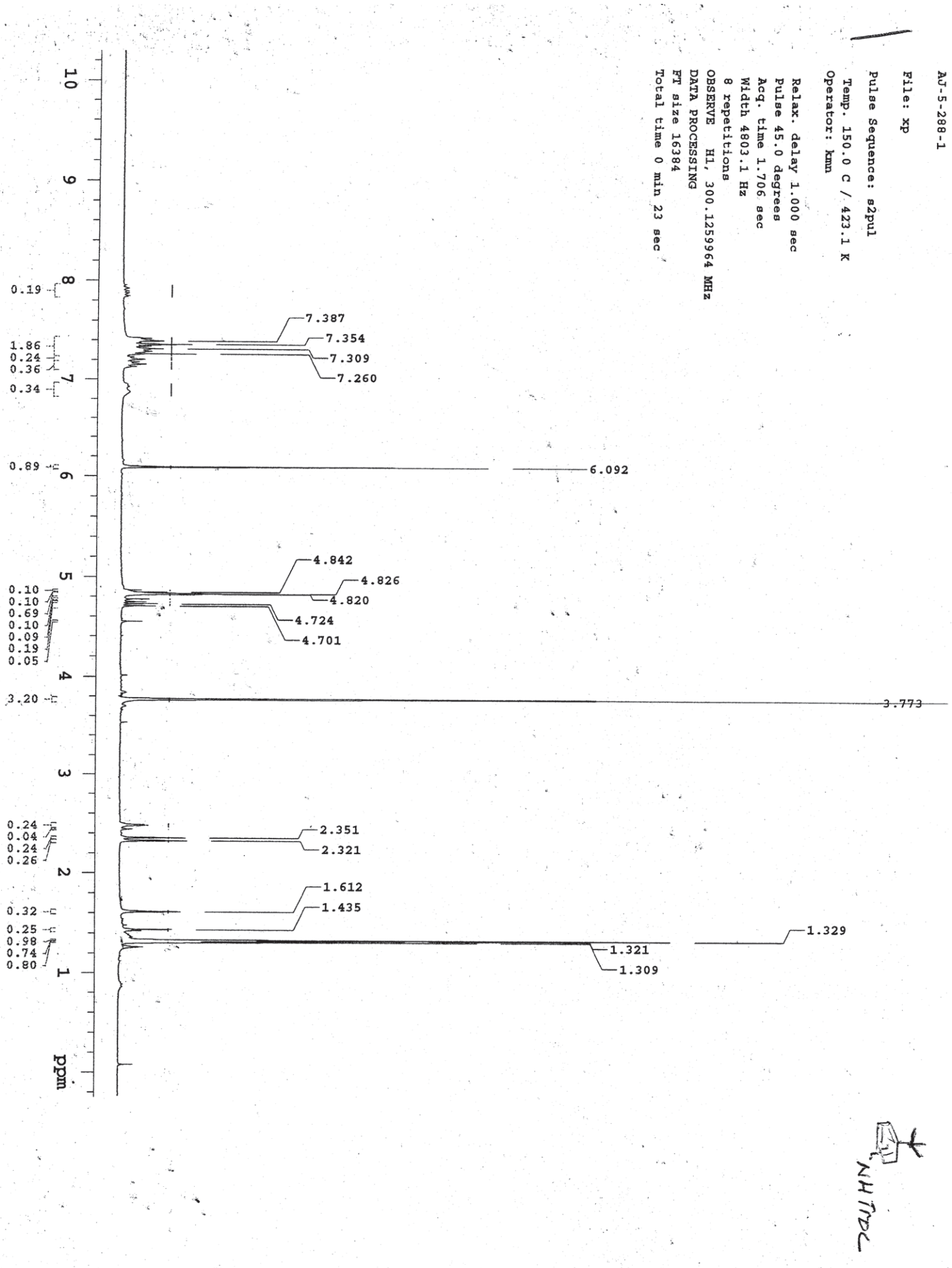


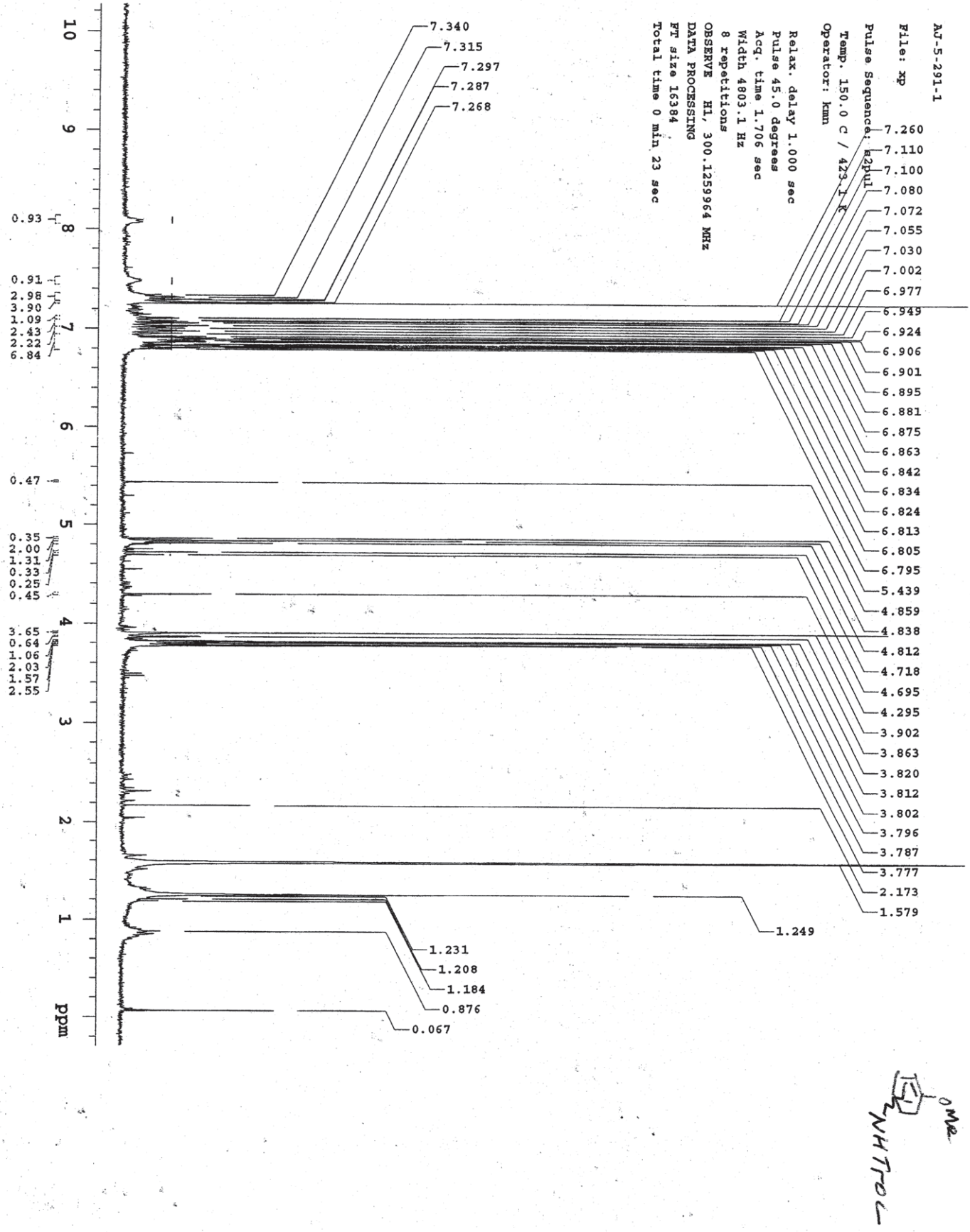

**Equation S1.**

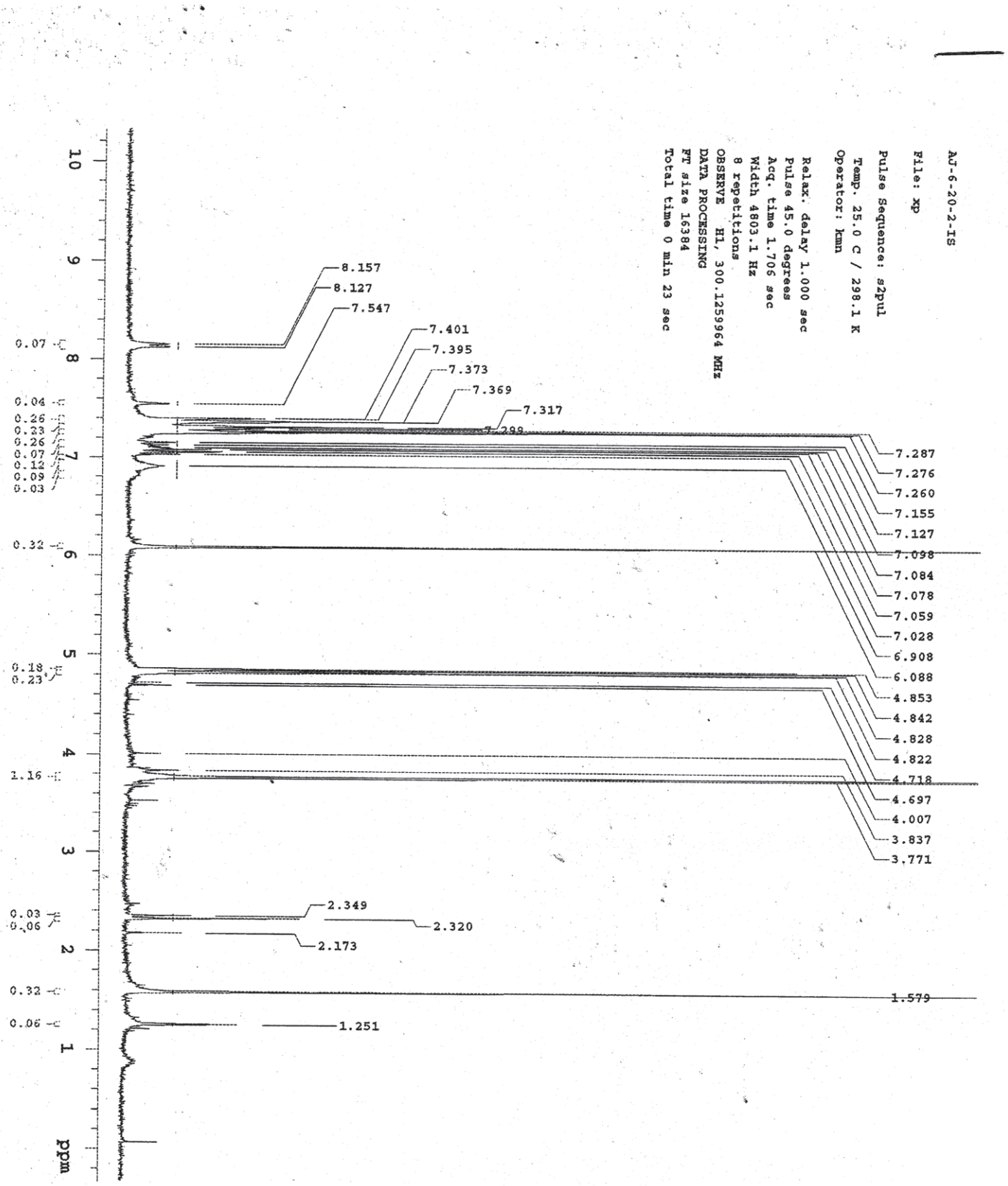
A *scaled up* reaction using TrocNHOTs (0.50 g, 1.4 mmol), $[Cu(CH_3CN)_4]PF_6$ (0.10 g, 0.28 mmol), and neocuproine (0.057 g, 0.27 mmol) in 10 mL of benzene was heated at 140 $^oC$ for 8 hr. Workup of the reaction mixture as described above (SI p. 7) gave a 55% yield of 2,2,2-trichloroethyl-*N*-phenylcarbamate (**1**).

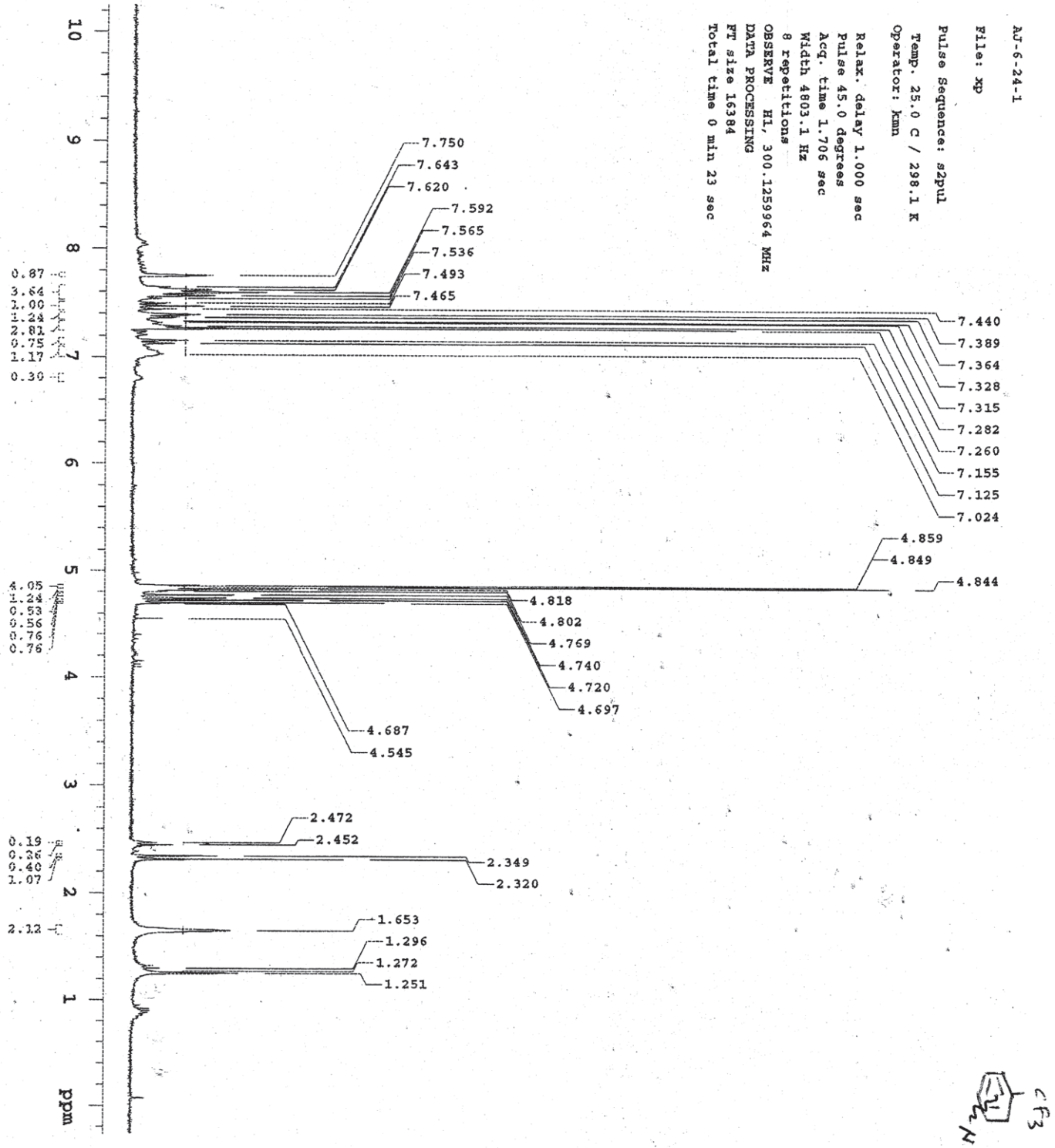












**Characterization data for 2,2,2-Trichloroethyl-*N*-arylcarbamates.**

**2,2,2-Trichloroethyl-*N*-phenylcarbamate** (**1**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.42 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.34 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.12 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 6.91 (br, 1H), 4.83 (s, 2H).

**2,2,2-Trichloroethyl-*N*-*o*-tolylcarbamate** (***o*-2**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 7.74 (br, 1H), 7.23-7.19 (m, 2H), 7.09 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 6.62 (br, 1H), 4.84 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 150.1, 135.1, 130.8, 127.1, 125.2, 121.9, 95.5, 74.8, 17.9. HRMS (ESI) Calcd for $C_{10}H_{10}Cl_3NO_2$ $(M+H)^+$ requires *m/z* = 281.9855, found *m/z* = 281.9850.

**2,2,2-Trichloroethyl-*N*-*m*-tolylcarbamate** (***m*-2**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.26 (d, $^{3}J_{HH}$ = 6.0 Hz, 1H), 7.23-7.20 (m, 2H), 6.93 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H), 6.91 (br, 1H), 4.83 (s, 2H), 2.35 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 151.6, 139.2, 136.9, 129.0, 125.0, 119.5, 116.0, 95.3, 74.5, 21.5. HRMS (ESI) Calcd for $C_{10}H_{10}Cl_3NO_2$ $(M+H)^+$ requires *m/z* = 281.9855, found *m/z* = 281.9850.

**2,2,2-Trichloroethyl-*N*-*o*-ethylphenylcarbamate** (***o*-3**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.72 (br, 1H), 7.27-7.21 (m, 2H), 7.15 (t, $^{3}J_{HH}$ = 6.9 Hz, 1H), 6.64 (br, 1H), 4.84 (s, 2H), 2.64 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.26 (t, $^{3}J_{HH}$ = 7.8 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 152.4, 134.8, 134.2, 128.7, 126.8, 125.5, 122.6, 95.4, 74.6, 24.2, 13.9. HRMS (ESI) Calcd for $C_{11}H_{13}Cl_3NO_2$ $(M+H)^+$ requires *m/z* = 296.0012, found *m/z* = 296.0006.

**2,2,2-Trichloroethyl-*N*-*p*-ethylphenylcarbamate** (***p*-3**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.33 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.17 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.82 (br, 1H), 4.82 (s, 2H), 2.62 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.22 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 151.8, 140.4, 134.7, 128.6, 119.3, 95.5, 74.6, 28.3, 15.8. HRMS (ESI) Calcd for $C_{11}H_{13}Cl_3NO_2$ $(M+Na)^+$ requires *m/z* = 317.9831, found *m/z* = 317.9822.

**2,2,2-Trichloroethyl-*N*-*m*-*tert*-butylphenylcarbamate** (***m*-4**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.39 (br, 1H), 7.29-7.24 (m, 2H), 7.17-7.13 (m, 1H), 6.87 (br, 1H), 4.83 (s, 2H), 1.32 (s, 9H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 152.5, 151.6, 136.7, 128.9, 121.3, 116.1, 95.3, 74.4, 34.8, 31.3. HRMS (ESI) Calcd for $C_{13}H_{16}Cl_3NO_2(M+H)^+$ requires *m/z* = 324.0325, found *m/z* = 324.0316.

**2,2,2-Trichloroethyl-*N*-*p*-*tert*-butylphenylcarbamate** (***p*-4**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.35 (br s, 4H), 6.84 (br, 1H), 4.83 (s, 2H), 1.31 (s, 9H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 151.7, 147.2, 134.4, 126.0, 118.8, 95.4, 74.5, 34.3, 31.4. HRMS (ESI) Calcd for $C_{13}H_{16}Cl_3NO_2(M+H)^+$ requires *m/z* = 324.0325, found *m/z* = 324.0316.

**2,2,2-Trichloroethyl-*N*-*m*-methoxyphenylcarbamate** (***m*-5**): $^{1}$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.23 (t, $^{3}J_{HH}$ = 9.0 Hz, 1H), 7.13 (br s, 1H), 6.94-6.90 (m, 2H), 6.67 (dd, $^{3}J_{HH}$ = 9.0 Hz and $^{4}J_{HH}$ = 3.0 Hz, 1H), 4.82 (s, 2H), 3.81 (s, 3H). $^{13}$C NMR ($CDCl_3$, 75

MHz, 25 °C) δ 160.3, 151.4, 138.3, 129.9, 111.1, 109.8, 104.6, 95.2, 74.5, 55.3. HRMS (ESI) Calcd for $C_{10}H_{10}Cl_3NO_3(M+Na)^+$ requires *m/z* = 319.9624, found *m/z* = 319.9624.

**2,2,2-Trichloroethyl-*N*-*p*-methoxyphenylcarbamate** (***p*-5**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 7.33 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.88 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 6.74 (br, 1H), 4.81 (s, 2H), 3.79 (s, 3H).

**2,2,2-Trichloroethyl-*N*-*o*-chlorophenylcarbamate** (***o*-6**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 8.14 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.38 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.35 (br, 1H), 7.30 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.06 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 4.85 (s, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) δ 151.3, 133.9, 129.2, 127.9, 124.5, 120.2, 95.0, 74.6. HRMS (ESI) Calcd for $C_9H_7Cl_4NO_2$ $(M+Na)^+$ requires *m/z* = 323.9129, found *m/z* = 323.9189.

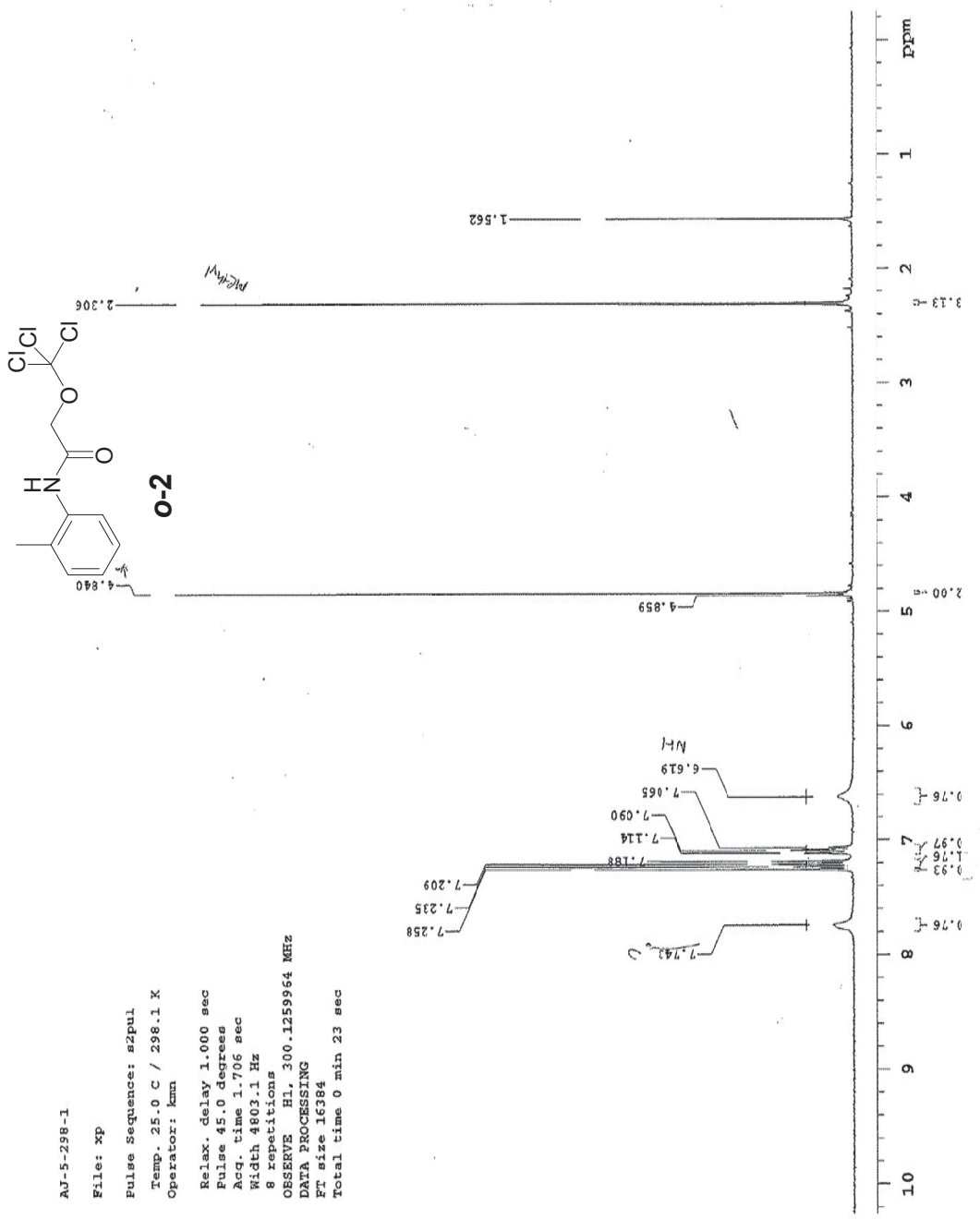
**2,2,2-Trichloroethyl-*N*-*m*-chlorophenylcarbamate** (***m*-6**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 7.55 (br, 1H), 7.27-7.25 (m, 2H), 7.11-7.08 (m, 1H), 6.87 (br, 1H), 4.83 (s, 2H).

**2,2,2-Trichloroethyl-*N*-*p*-chlorophenylcarbamate** (***p*-6**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 7.38 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.30 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 6.86 (br, 1H), 4.82 (s, 2H).

**2,2,2-Trichloroethyl-*N*-*o*-trifluoromethylphenylcarbamate** (***o*-7**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 8.05 (d, $^3J_{HH}$ = 9.0 Hz, 8.1 Hz), 7.64-7.56 (m, 2H), 7.26 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.10 (br, 1H), 4.84 (s, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 °C) δ 151.8, 134.6,

133.0, 126.2 (q, $J_{C-F}$ = 24 Hz), 124.6, 123.9 (q, $J_{C-F}$ = 1080 Hz), 123.5, 95.0, 74.7. $^{19}$F NMR ($CDCl_3$, 282 MHz, 25 $^{o}$C): δ -115.4. HRMS (ESI) Calcd for $C_{10}H_7Cl_3F_3NO_2$ $(M+Na)^+$ requires *m/z* = 357.9392, found *m/z* = 357.9392.

**2,2,2-Trichloroethyl-*N*-*p*-trifluoromethylphenylcarbamate** (***p*-7**): $^1$H NMR ($CDCl_3$, 300 MHz, 25 $^{o}$C) δ 7.62-7.53 (m, 4H), 7.07 (br, 1H), 4.84 (s, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz, 25 $^{o}$C) δ 151.4, 140.2, 126.4 (q, $J_{C-F}$ = 13 Hz), 126.2, 124.0 (q, $J_{C-F}$ = 1080 Hz), 118.5, 94.9, 74.6. HRMS (ESI) Calcd for $C_{10}H_7Cl_3F_3NO_2$ $(M+Na)^+$ requires *m/z* = 357.9392, found *m/z* = 357.9389.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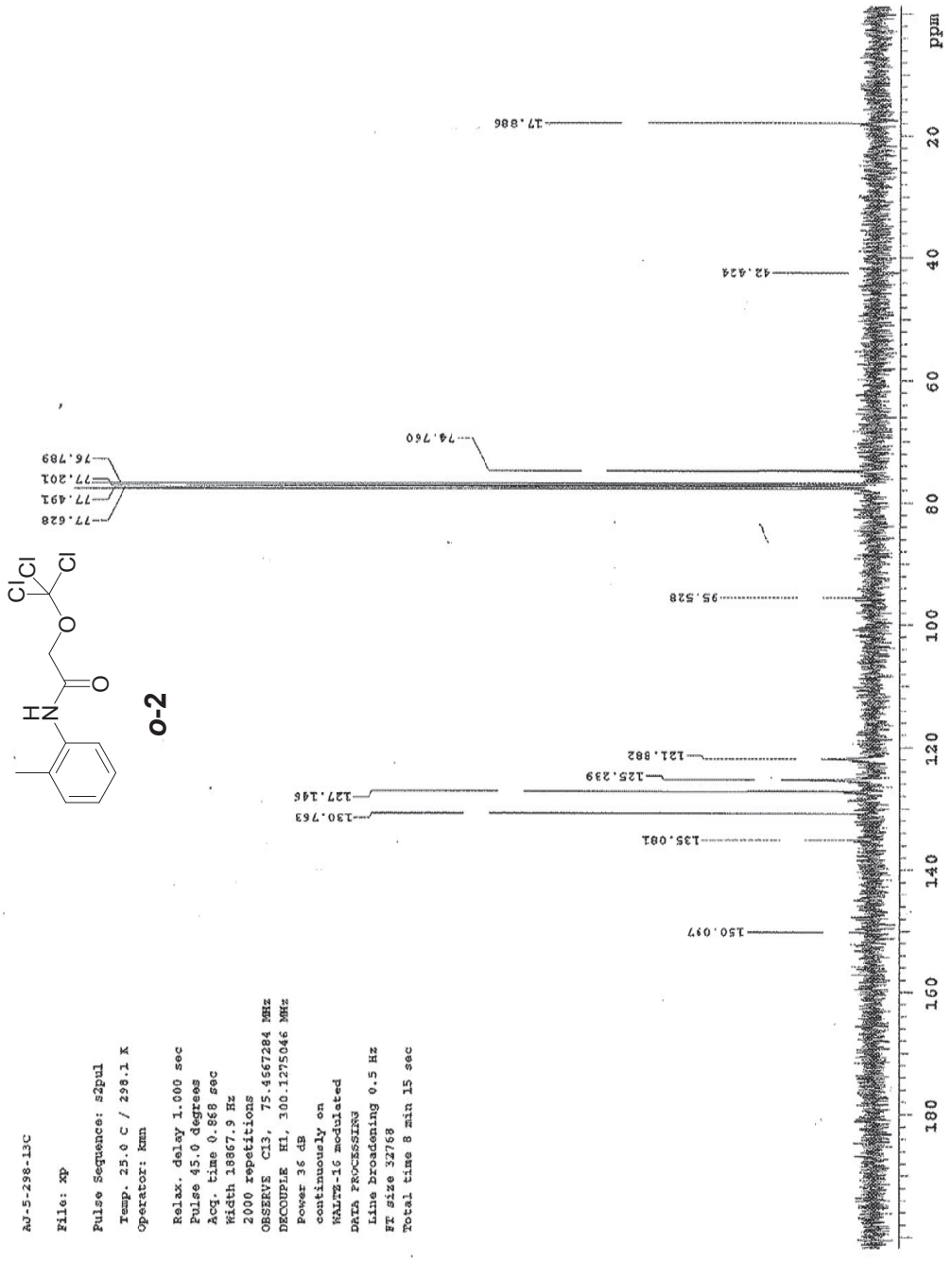
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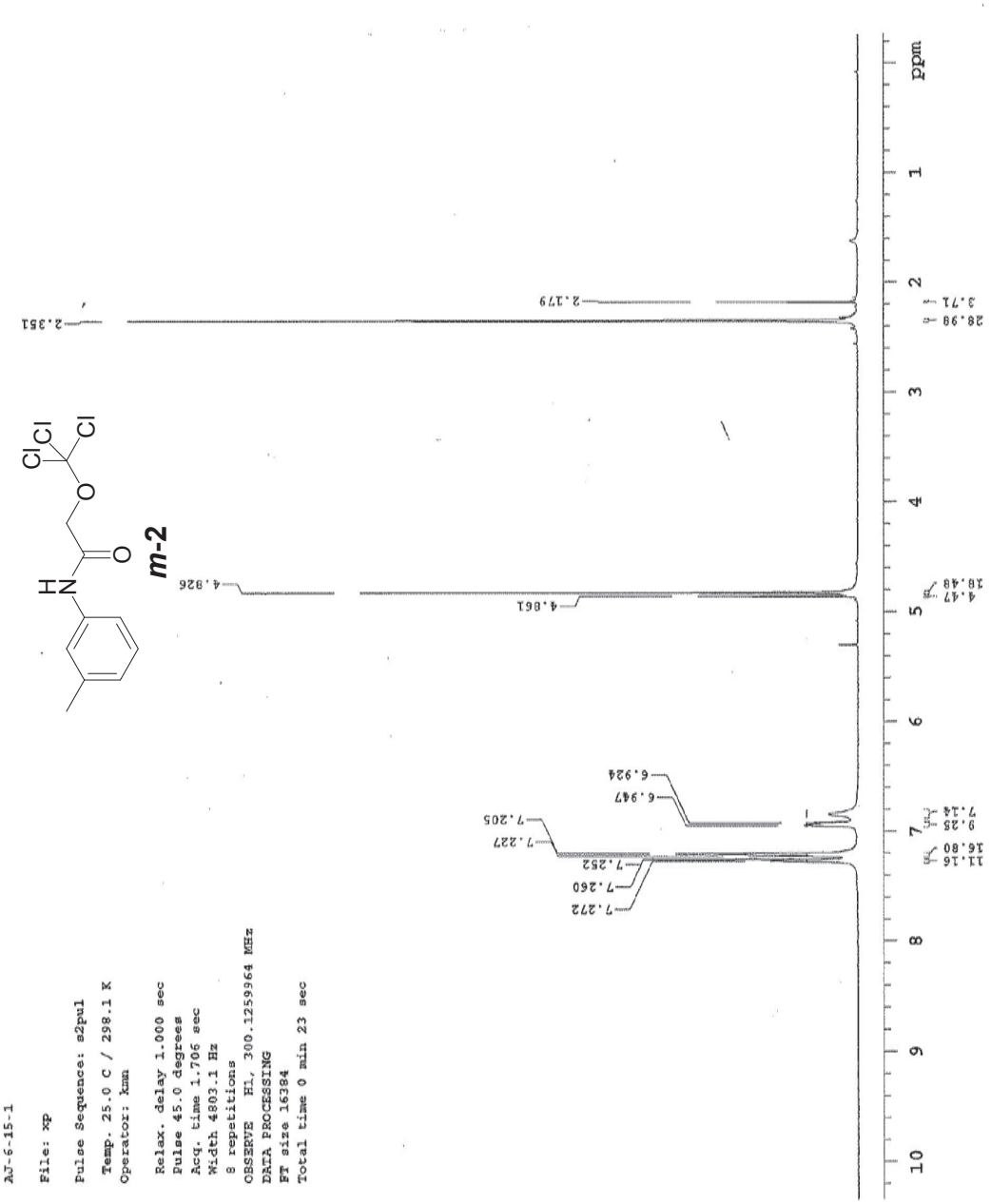
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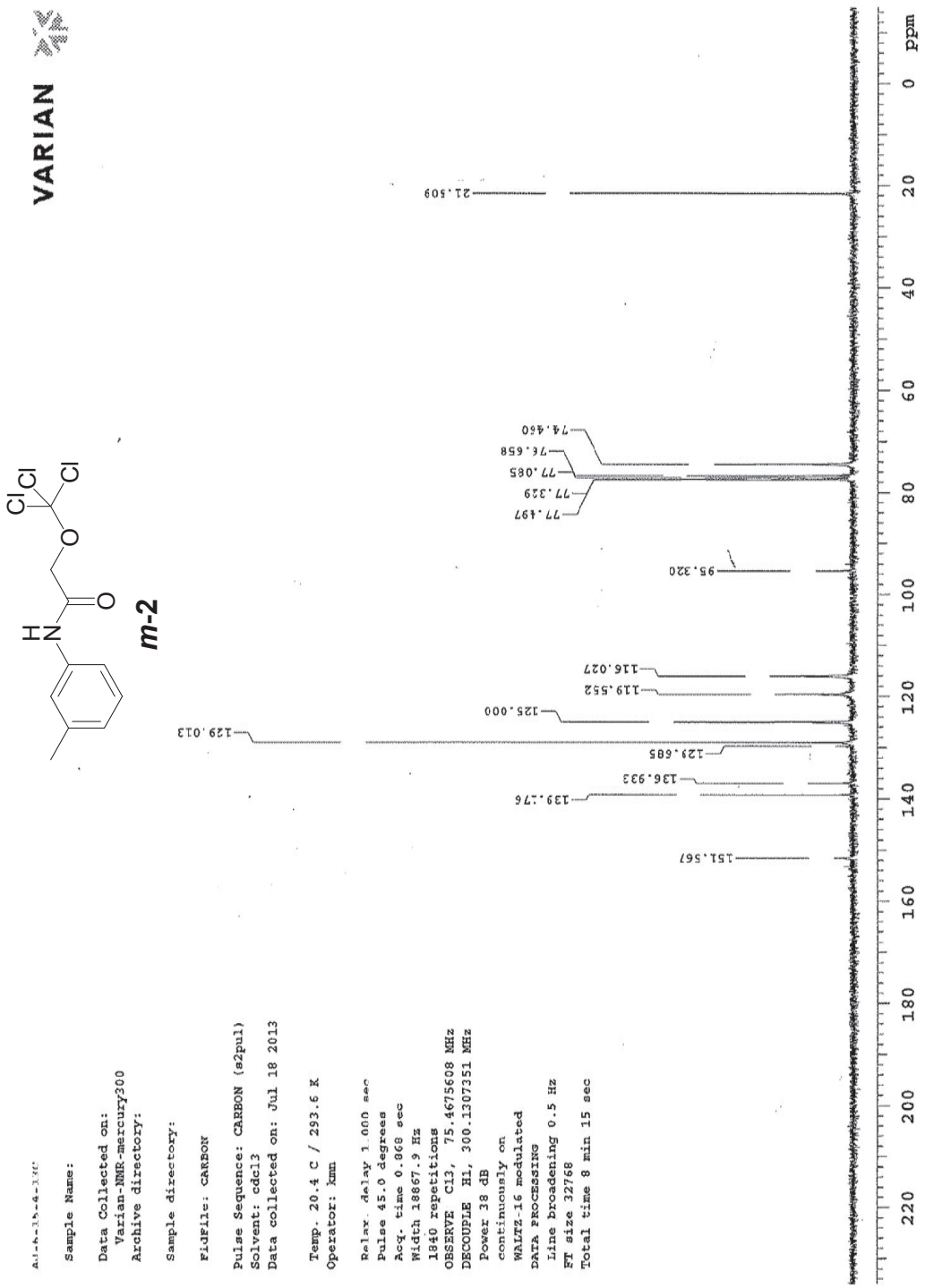
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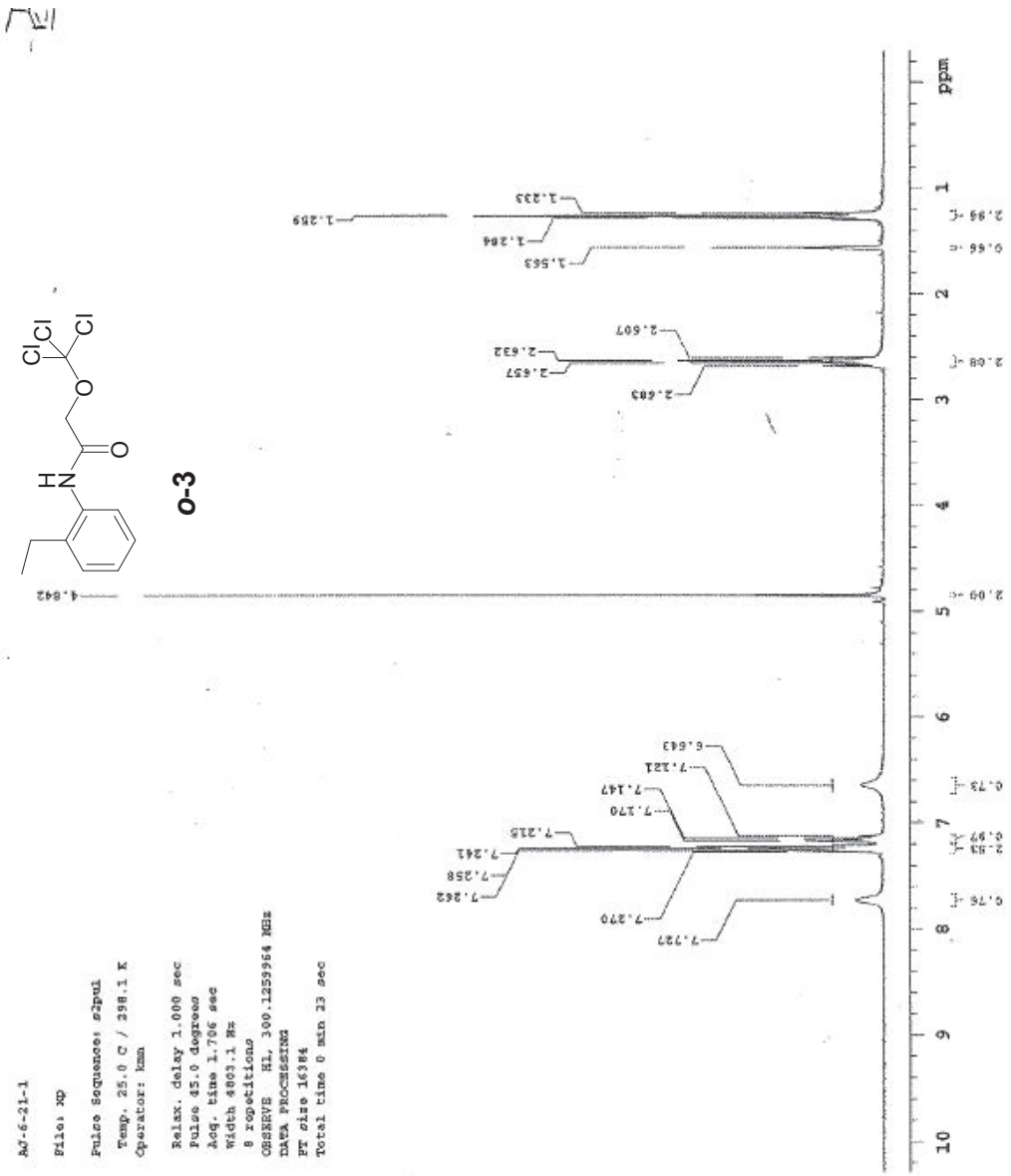
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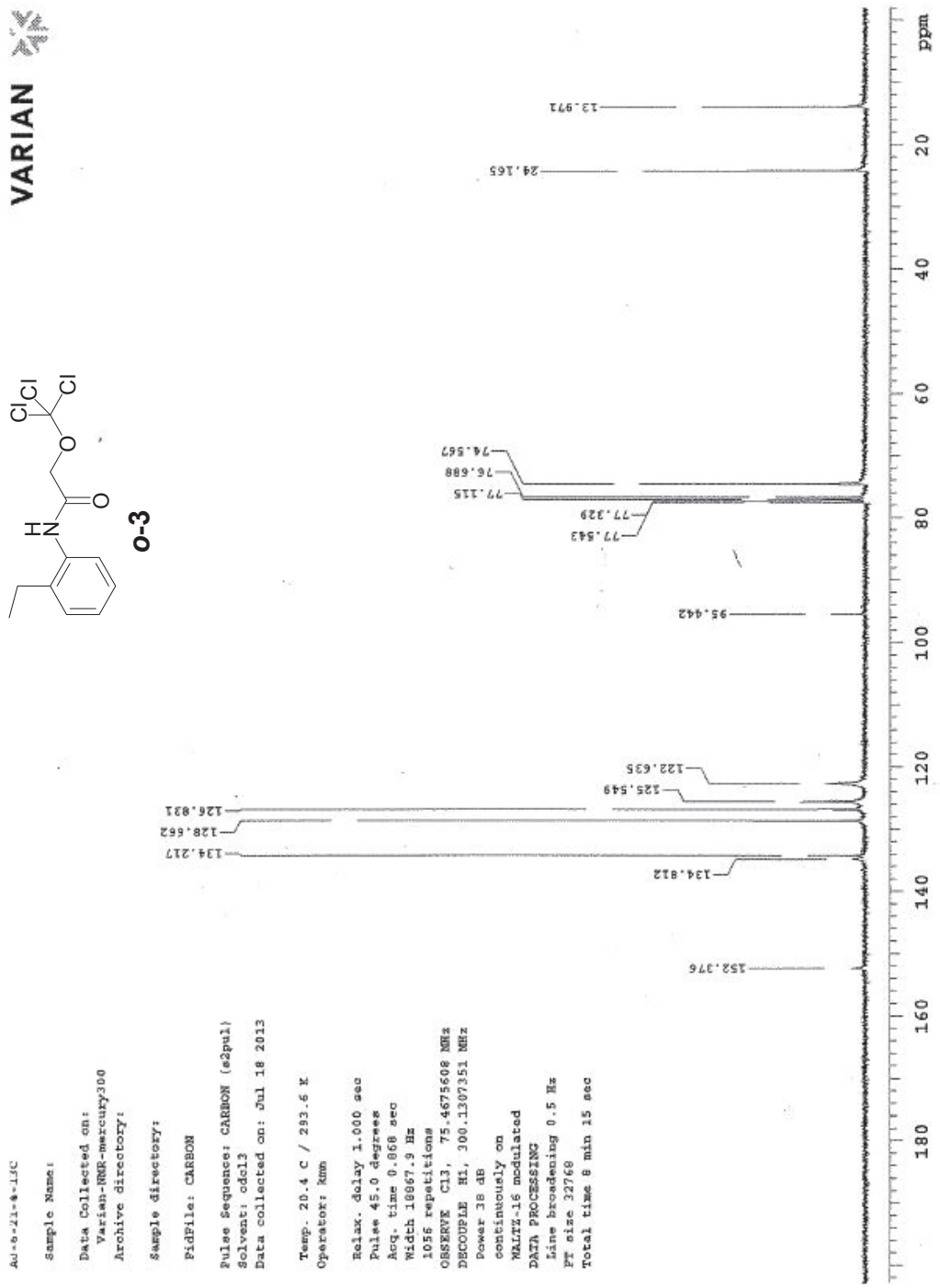
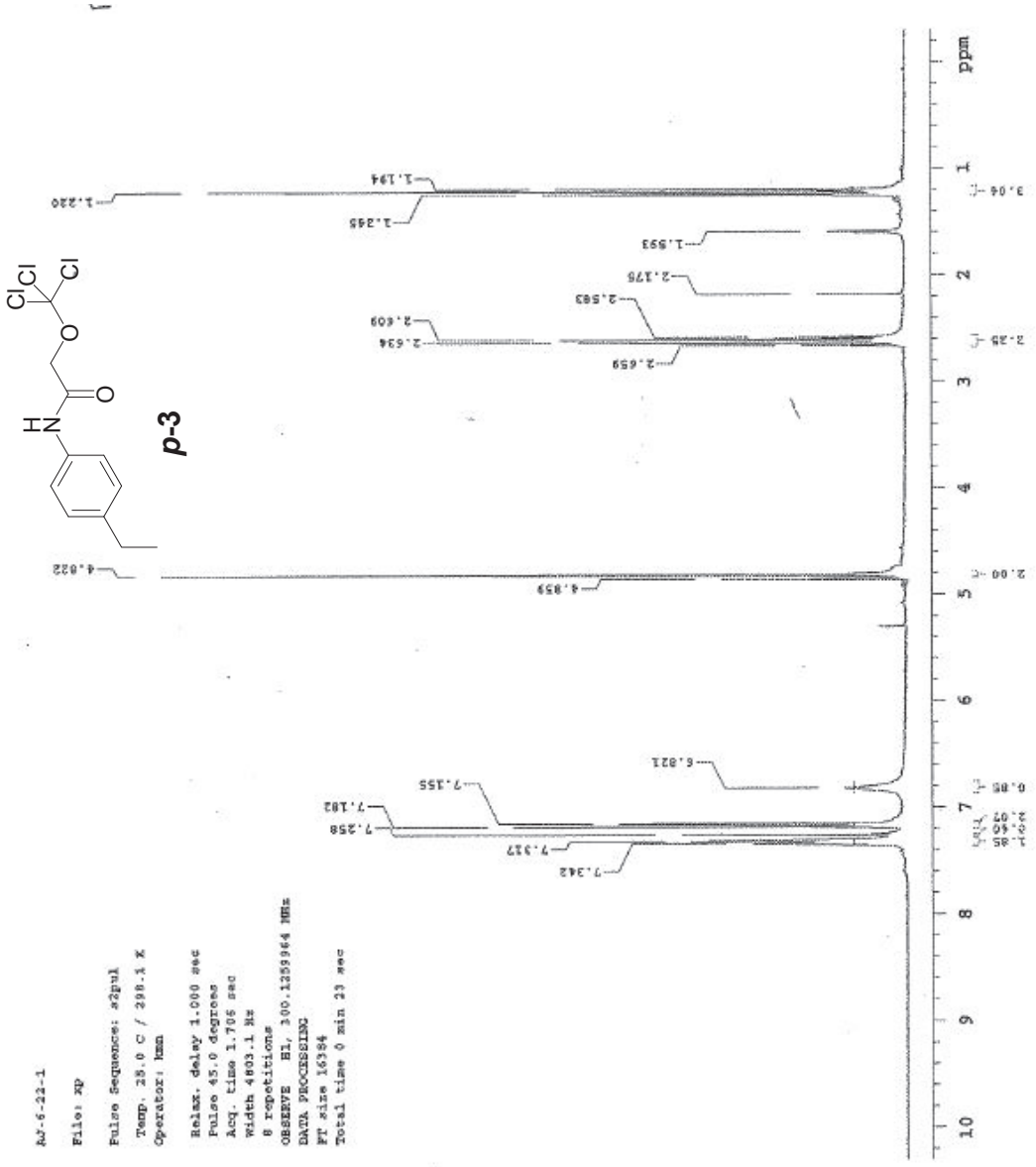
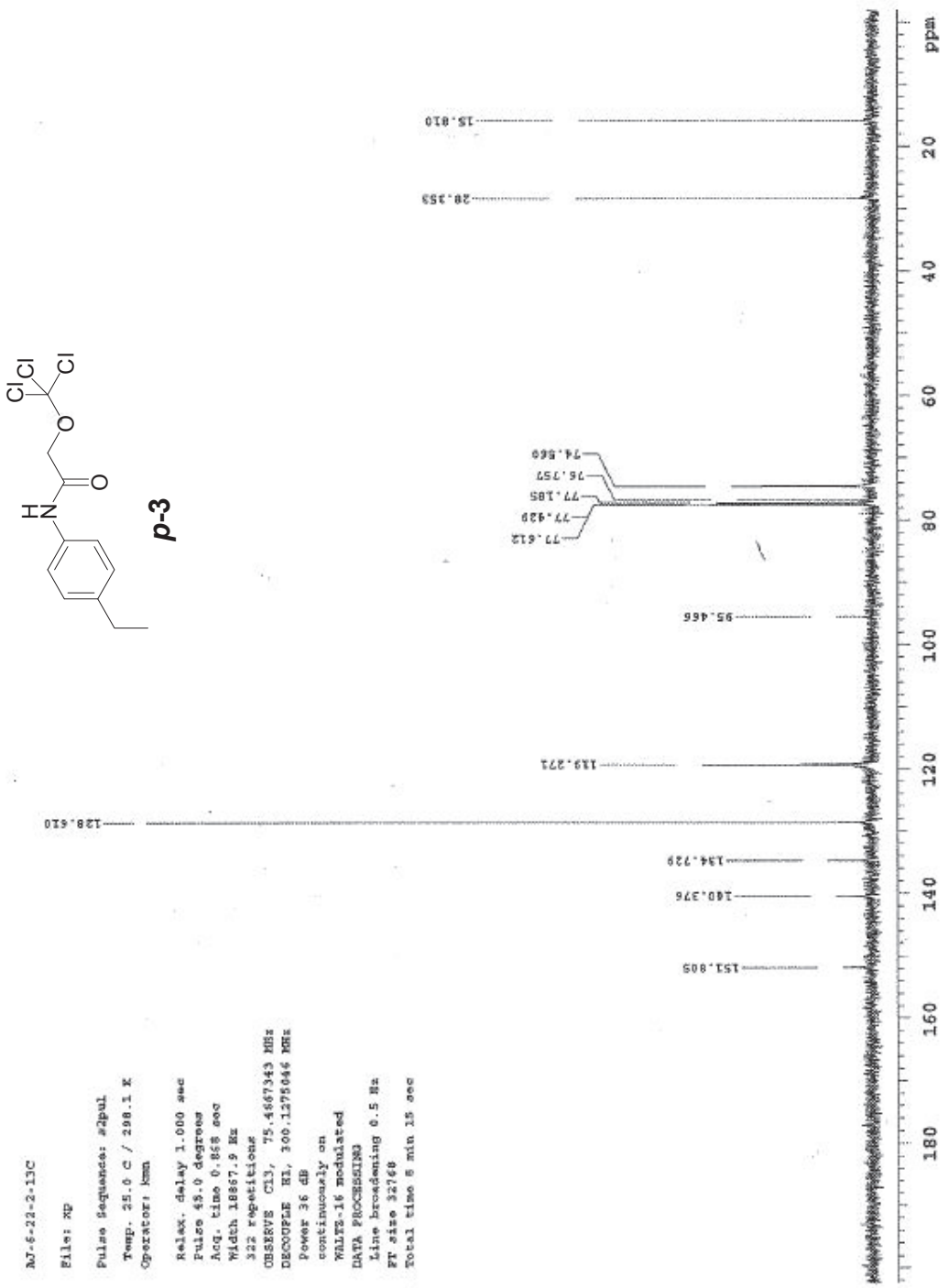
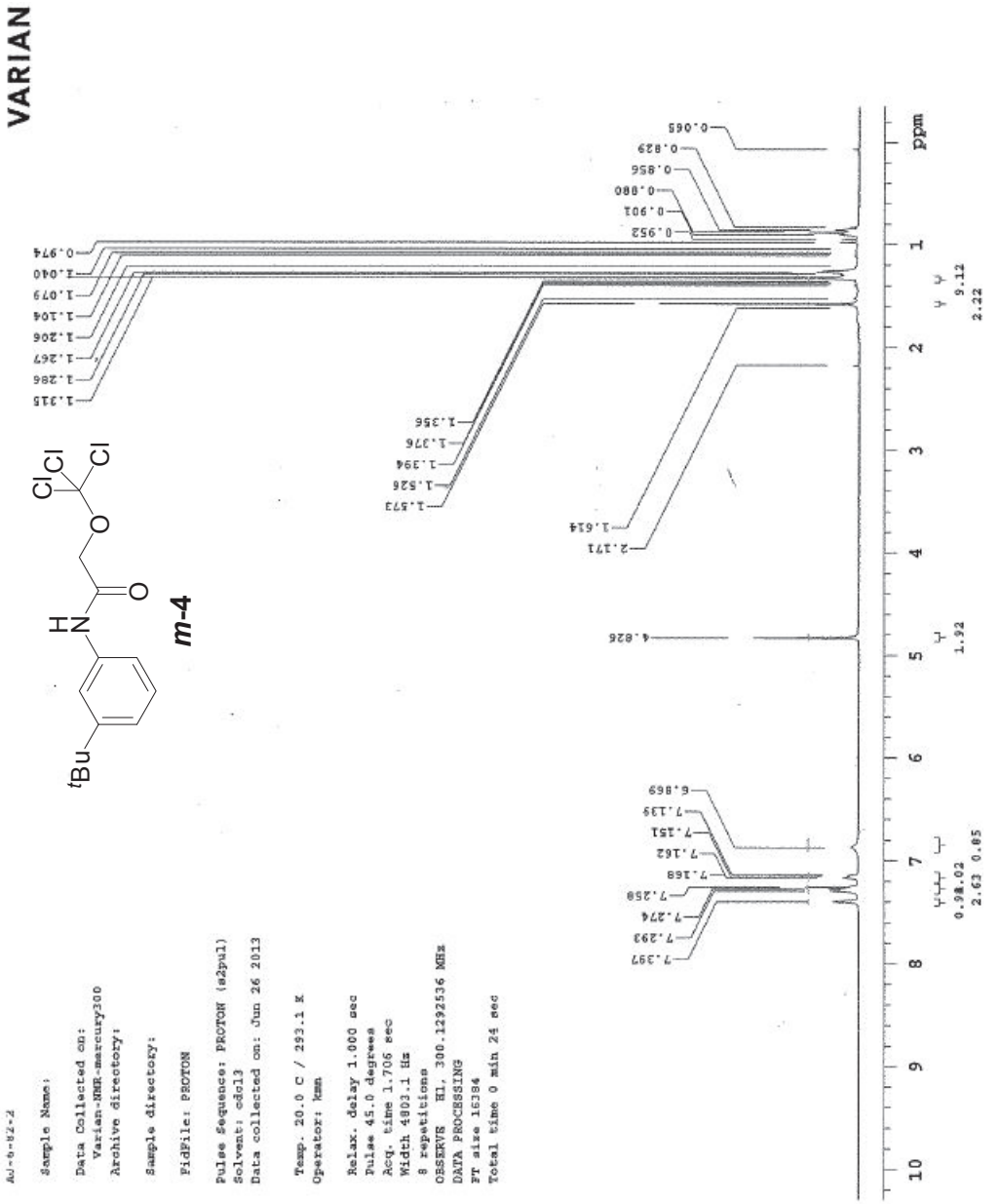
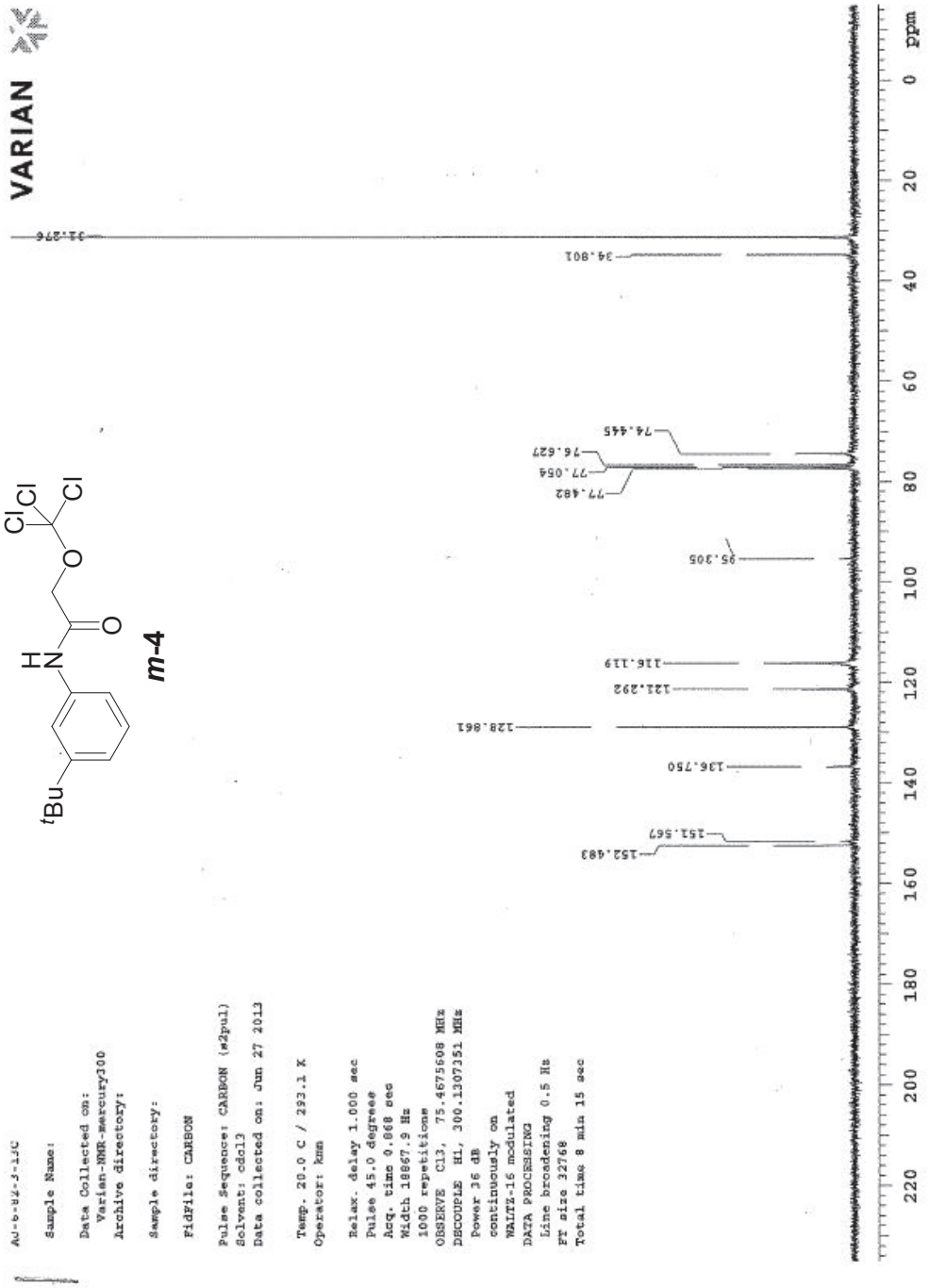
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1259964 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 33 sec

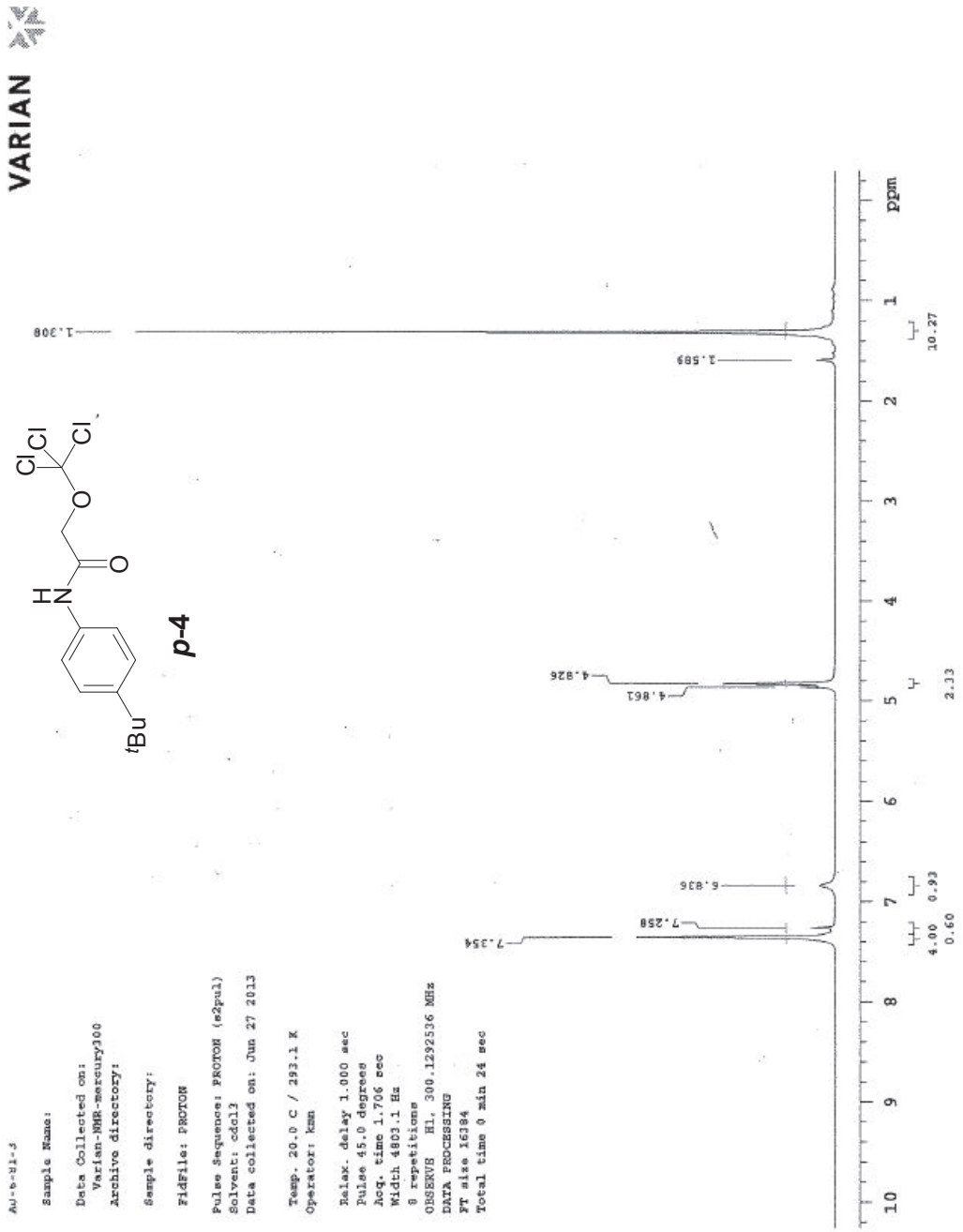

VARIAN
o-3
Cl
Cl
Cl
O
O
H
N
Ad-6-21-6-13C
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
PidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 18 2013
Temp. 20.4 C / 293.6 K
Operator: kmm
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1056 repetitions
OBSERVE C13, 75.4675608 MHz
DECOUPLE H1, 300.1307351 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
13.971
24.165
74.567
76.688
77.115
77.329
77.543
95.442
122.635
125.549
126.831
128.662
134.217
134.812
152.376
180
160
140
120
100
80
60
40
20
ppm

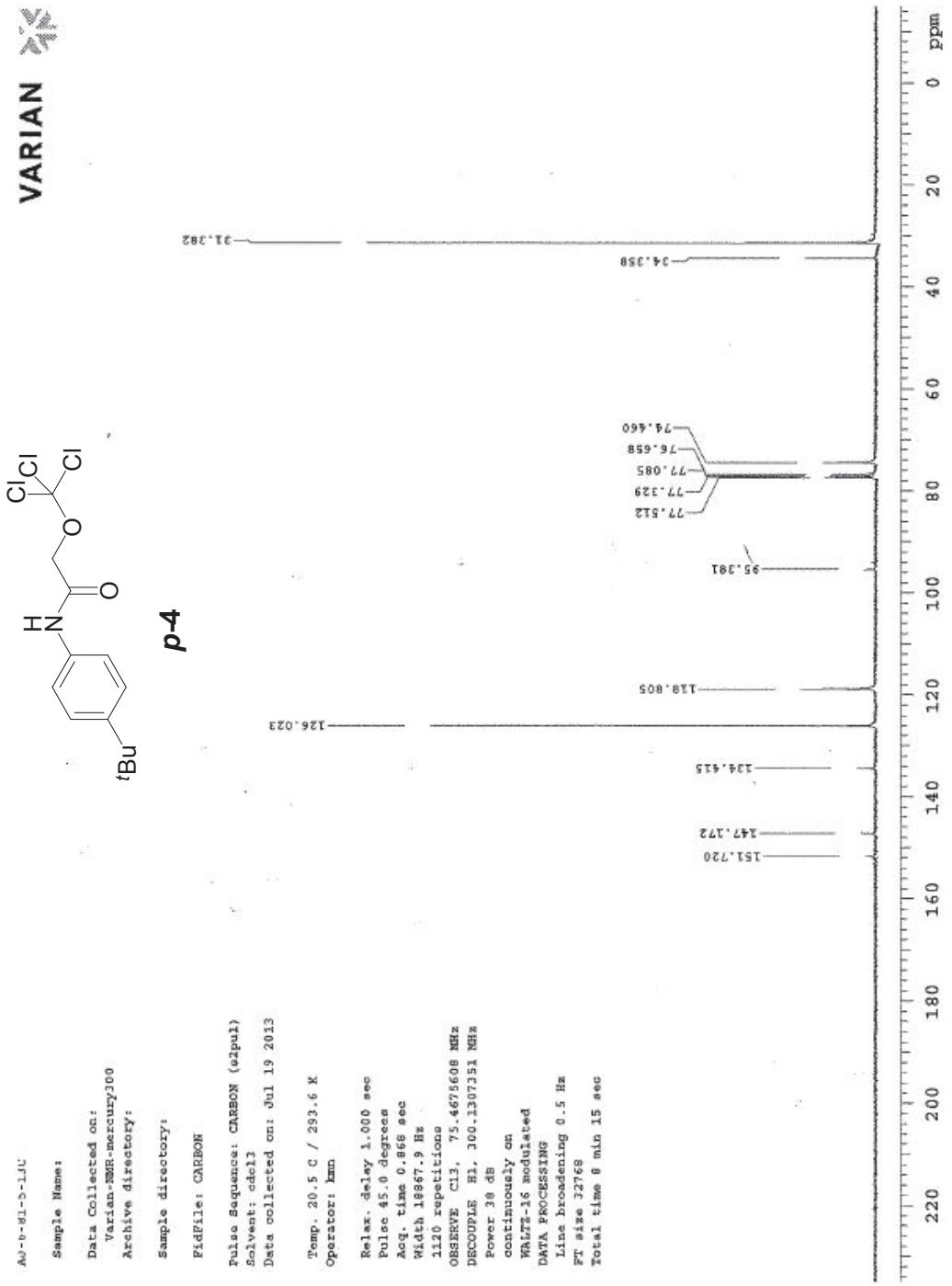

p-3
AJ-6-22-1
File: ap
Pulse Sequence: s2pul
Temp. 25.0 C / 298.1 K
Operator: hmm
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.705 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1259964 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
1.220
1.194
1.345
1.953
2.175
2.583
2.609
2.634
2.659
4.022
4.859
6.821
7.155
7.182
7.258
7.317
7.342
ppm

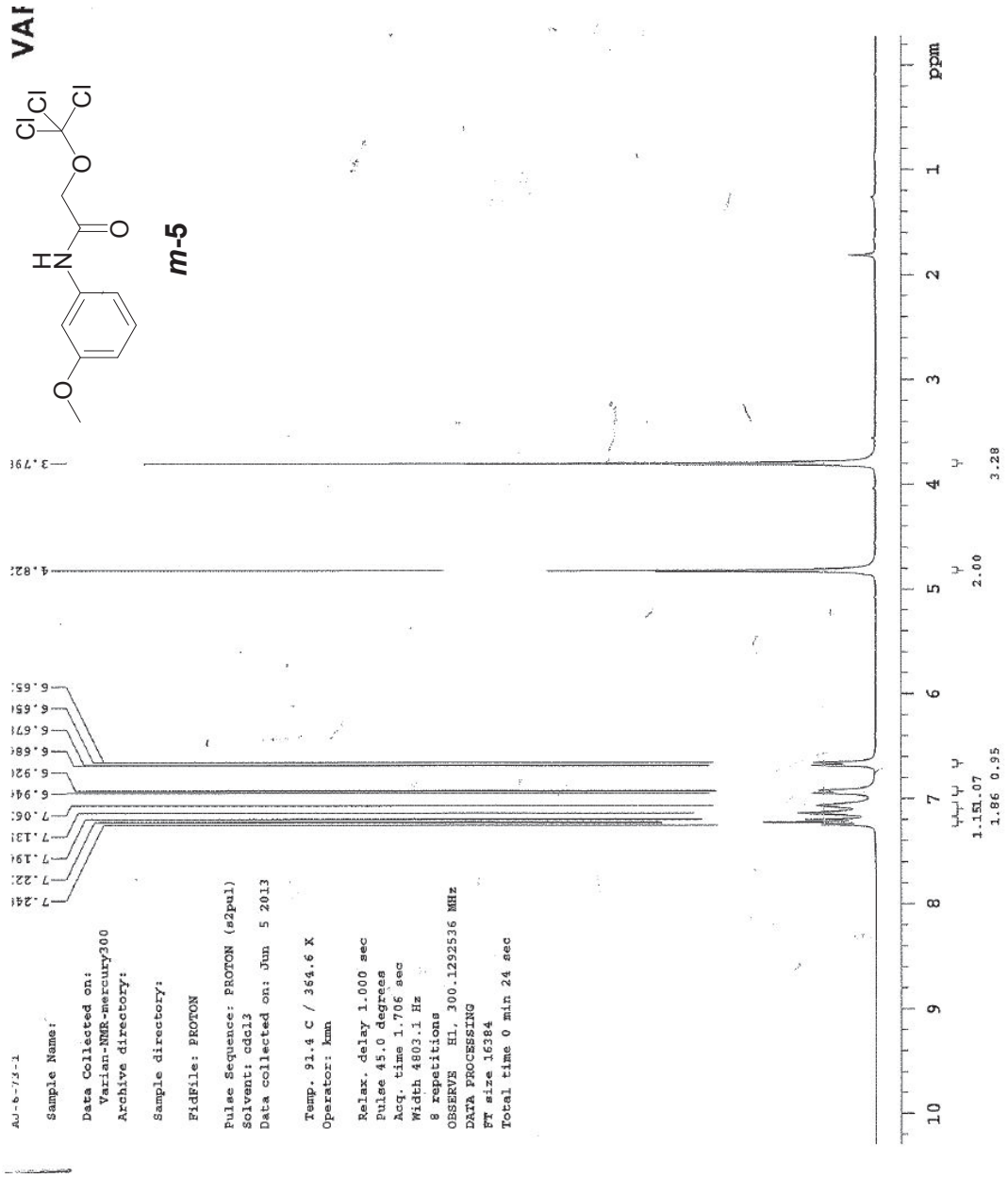

p-3
15.810
28.353
74.860
76.757
77.185
77.429
77.612
95.466
139.271
128.610
134.729
140.376
151.805
ppm
20
40
60
80
100
120
140
160
180
AJ-6-22-2-13C
File: xp
Pulse Sequence: s2pul
Temp. 25.0 C / 298.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 48.0 degrees
Acq. time 0.858 sec
Width 18867.9 Hz
322 repetitions
OBSERVE C13, 75.4667343 MHz
DECOUPLE H1, 300.1275046 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32760
Total time 8 min 15 sec

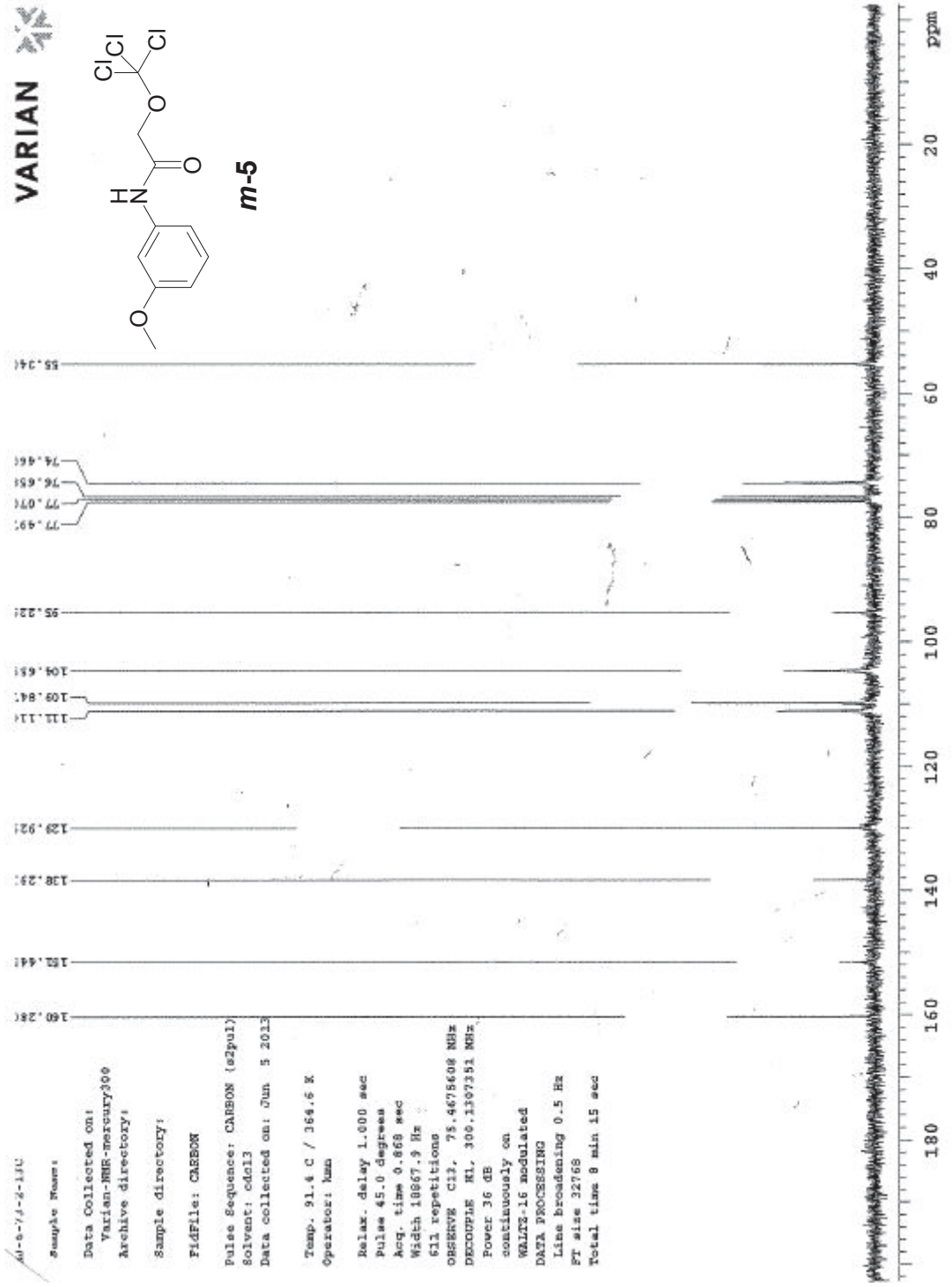

VARIAN
Au-b-82-2
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 26 2013
Temp. 20.0 C / 293.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1292536 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec
m-4
ppm
9.12
2.22
1.92
0.98.02
2.63 0.65

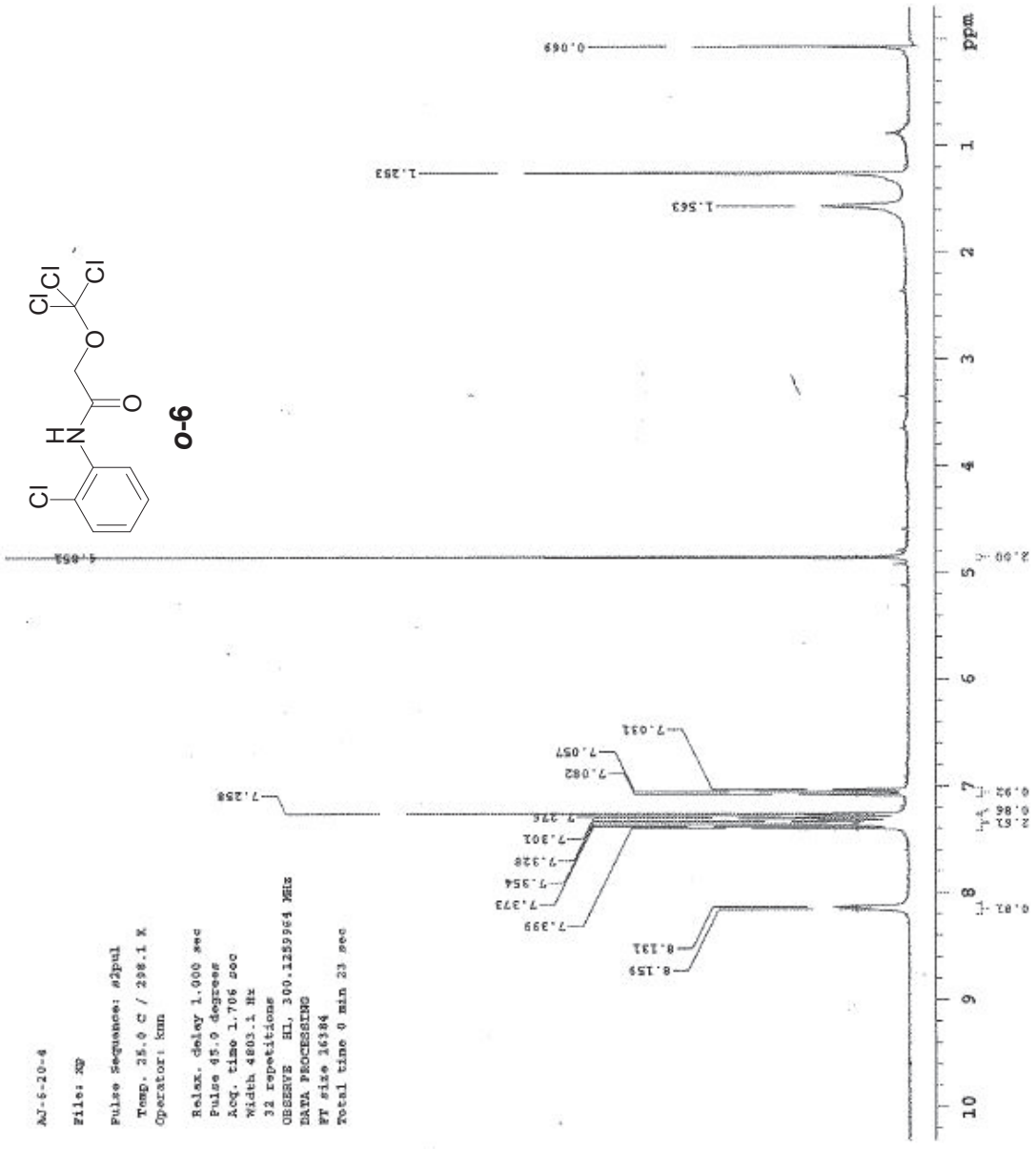

VARIAN
m-4
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 27 2013
Temp. 20.0 C / 293.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 0.868 sec
Width 18867.9 Hz
1000 repetitions
OBSERVE C13, 75.4675608 MHz
DECOUPLE H1, 300.1307351 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
34.276
34.801
74.445
76.627
77.054
77.482
95.305
116.119
121.292
128.861
136.750
151.567
152.483
220
200
180
160
140
120
100
80
60
40
20
0
ppm

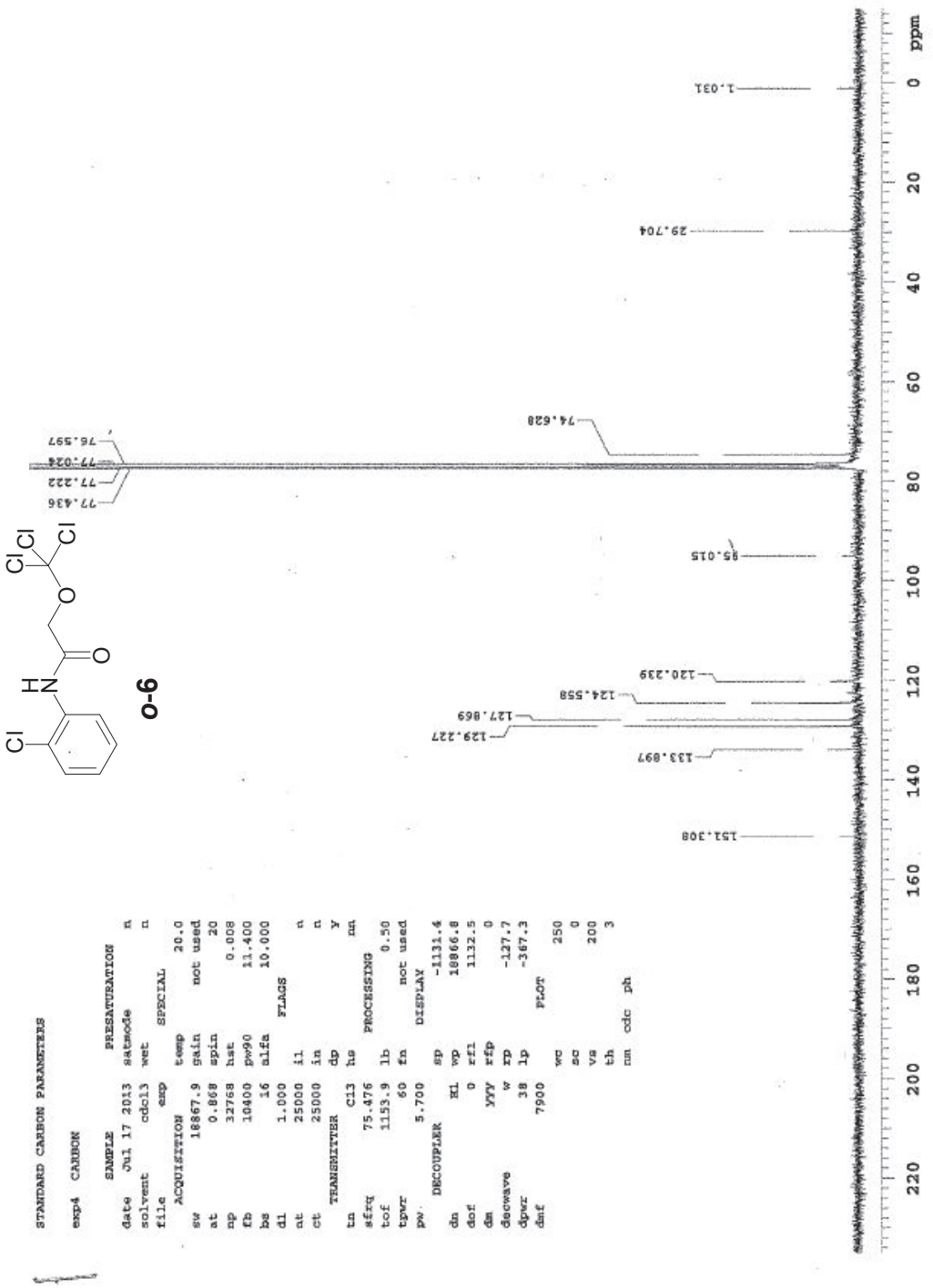

VARIAN
Au-b-Yi-5
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 27 2013
Temp. 20.0 C / 293.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1292536 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec
p-4
1.308
1.589
4.826
4.861
6.836
7.258
7.354
10.27
2.33
4.00
0.93
0.60
ppm

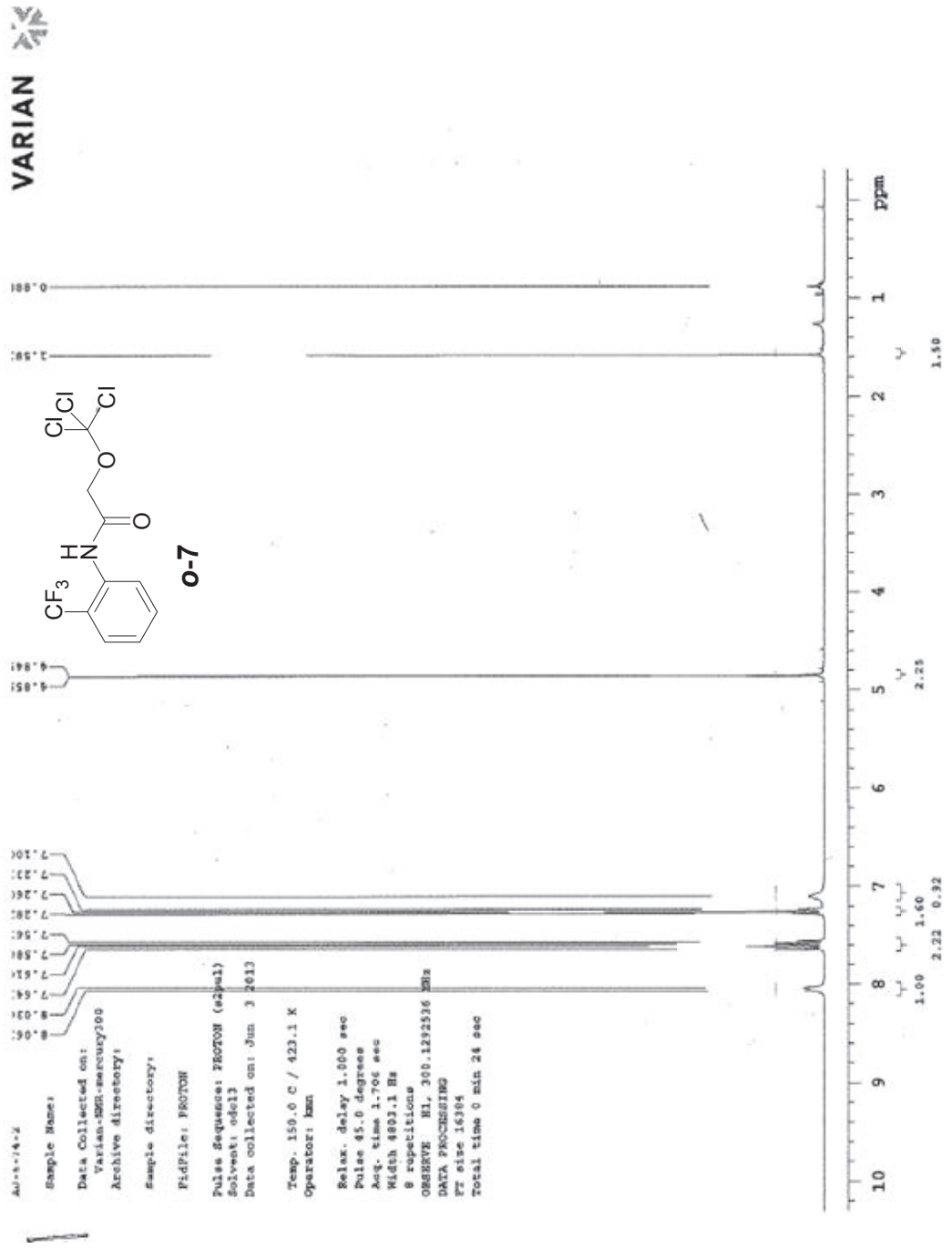

VARIAN
AJ-b-81-5-13C
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 19 2013
Temp. 20.5 C / 293.6 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1120 repetitions
OBSERVE C13, 75.4675608 MHz
DECOUPLE H1, 300.1307351 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 15 sec
p-4
31.382
34.358
74.460
76.658
77.085
77.329
77.512
95.381
118.805
126.023
134.415
147.172
151.720
220
200
180
160
140
120
100
80
60
40
20
0
ppm

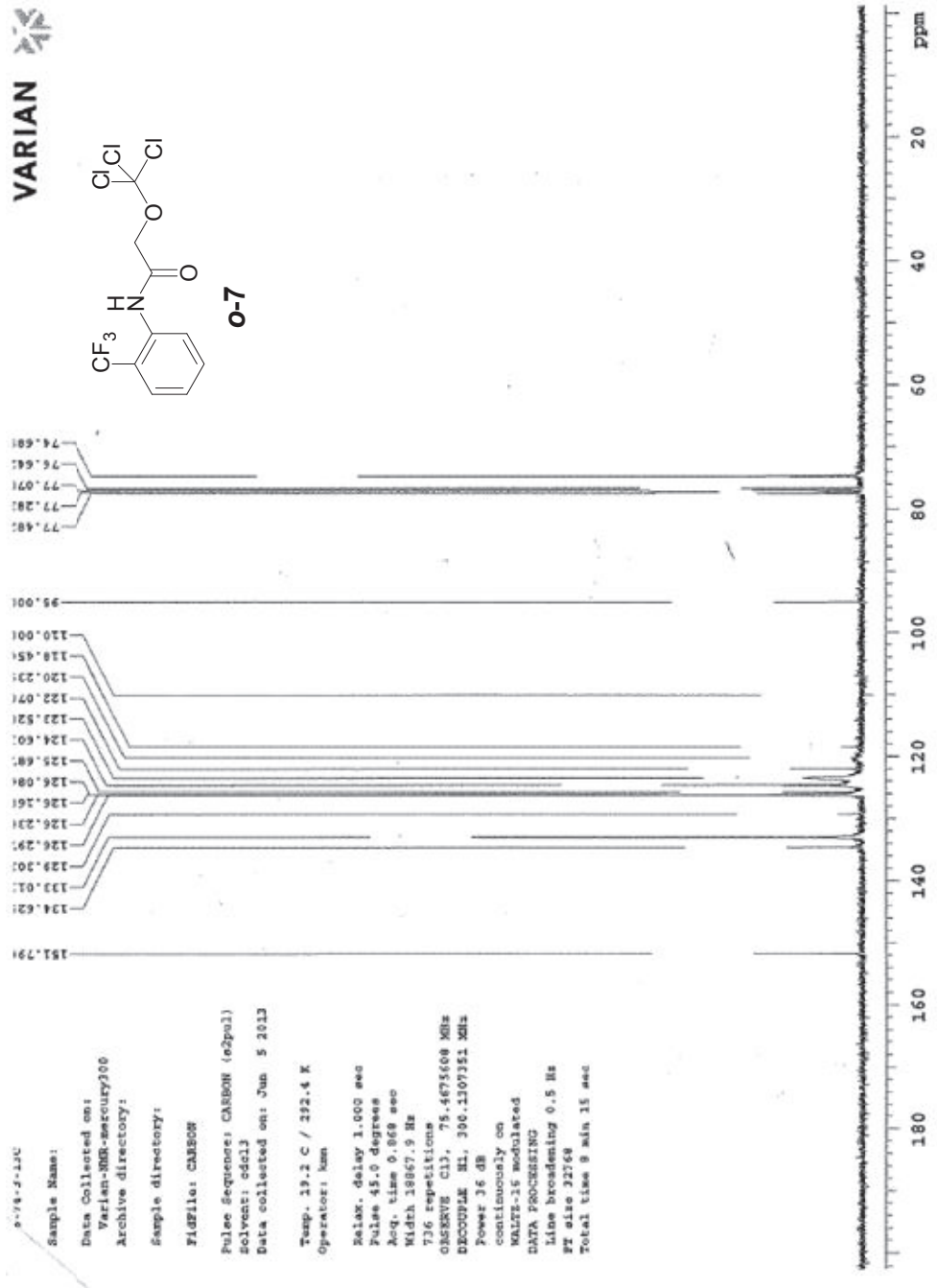

VAI
m-5
Cl
Cl
Cl
O
O
H
N
O
O
Aj-6-74-1
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 5 2013
Temp. 91.4 C / 364.6 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1292536 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec
7.24
7.22
7.19
7.13
7.06
6.94
6.92
6.68
6.67
6.65
6.65
4.82
3.79
ppm
1.15
1.07
1.86
0.95
2.00
3.28

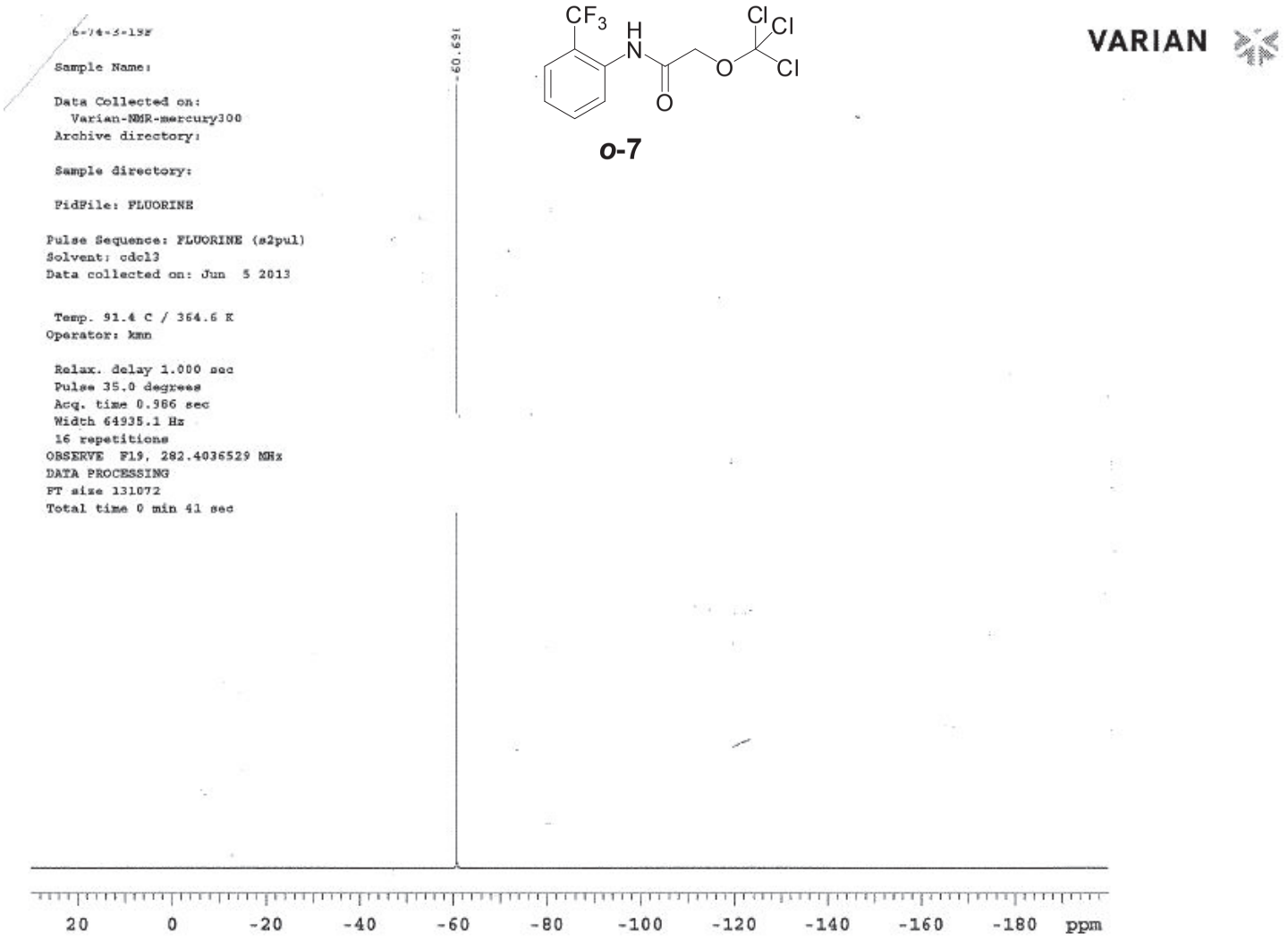

VARIAN
m-5
Cl
Cl
Cl
O
O
H
N
O
O
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 5 2013
Temp. 91.4 C / 364.6 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
611 repetitions
OBSERVE C13, 75.4675608 MHz
DECOUPLE H1, 300.1397351 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
160.281
152.441
138.291
129.921
111.111
109.841
109.651
95.221
77.491
77.071
76.651
74.461
55.341
180
160
140
120
100
80
60
40
20
ppm


o-6
AJ-6-20-4
File: zg
Pulse sequence: s2pul
Temp. 25.0 C / 298.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
32 repetitions
OBSERVE H1, 300.1259964 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
ppm

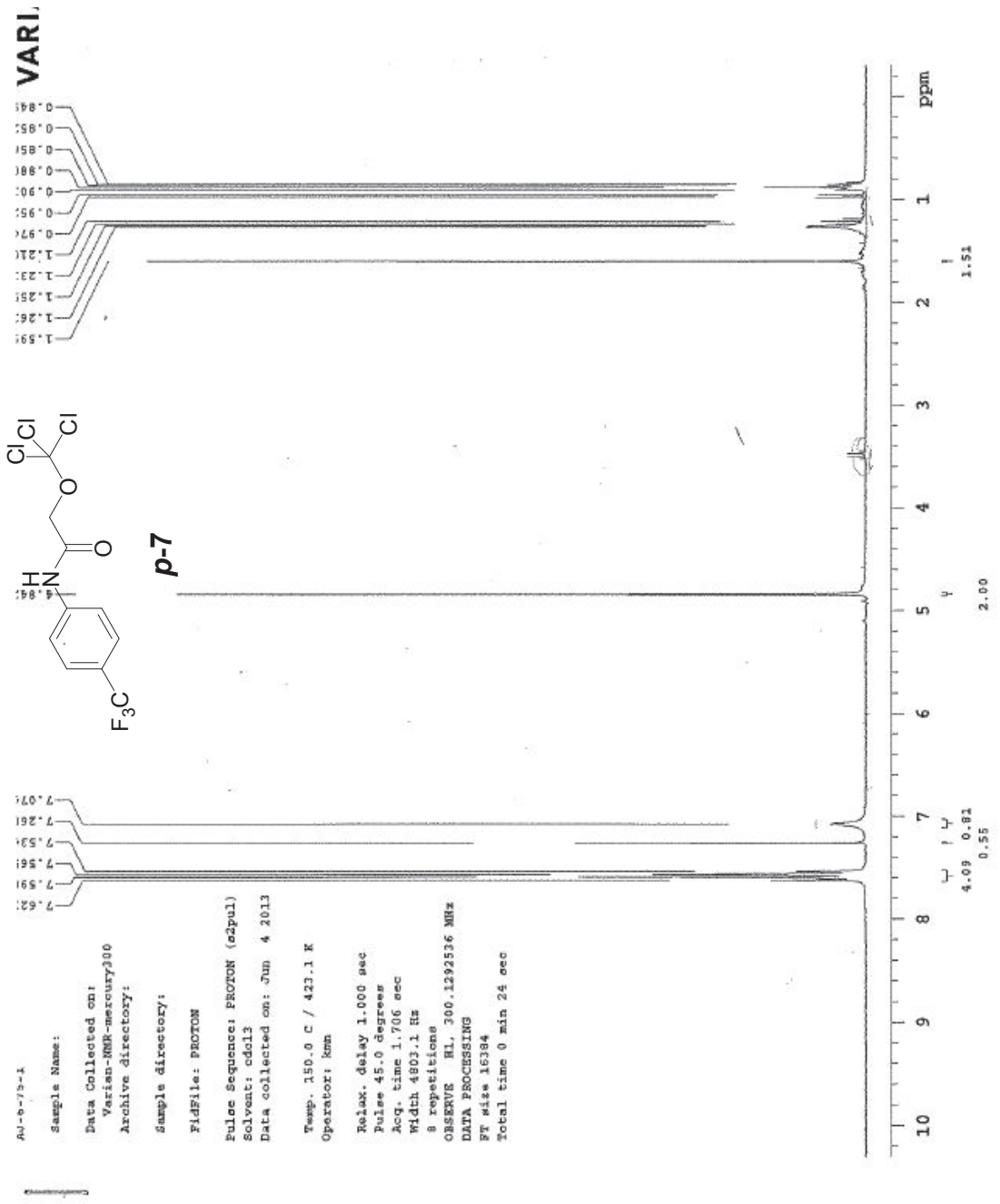

STANDARD CARBON PARAMETERS
exp4 CARBON
SAMPLE
date Jul 17 2013
solvent cdcl3
file exp
ACQUISITION
sw 18867.9
at 0.868
np 32768
fb 10400
bs 16
d1 1.000
at 25000
ct 25000
TRANSMITTER
tn C13
sfrq 75.476
tof 1153.9
tpwr 60
pw 5.700
DECOUPLER
dn H1
dof 0
dm yyy
dmmwave w
dpwr 38
dmf 7900
PRESATURATION
satmode n
wet n
SPECIAL
temp 20.0
gain not used
spin 20
hst 0.008
pw90 11.400
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.50
fn not used
DISPLAY
sp -1131.4
wp 10866.8
rfl 1132.5
rfp 0
rp -127.7
lp -367.3
FLAG
wc 250
sc 0
vs 200
th 3
nm cdc ph
O-6
77.436
77.222
77.034
76.597
74.628
29.704
1.031
85.015
120.339
124.558
127.869
129.227
133.897
151.308
220 200 180 160 140 120 100 80 60 40 20 0 ppm

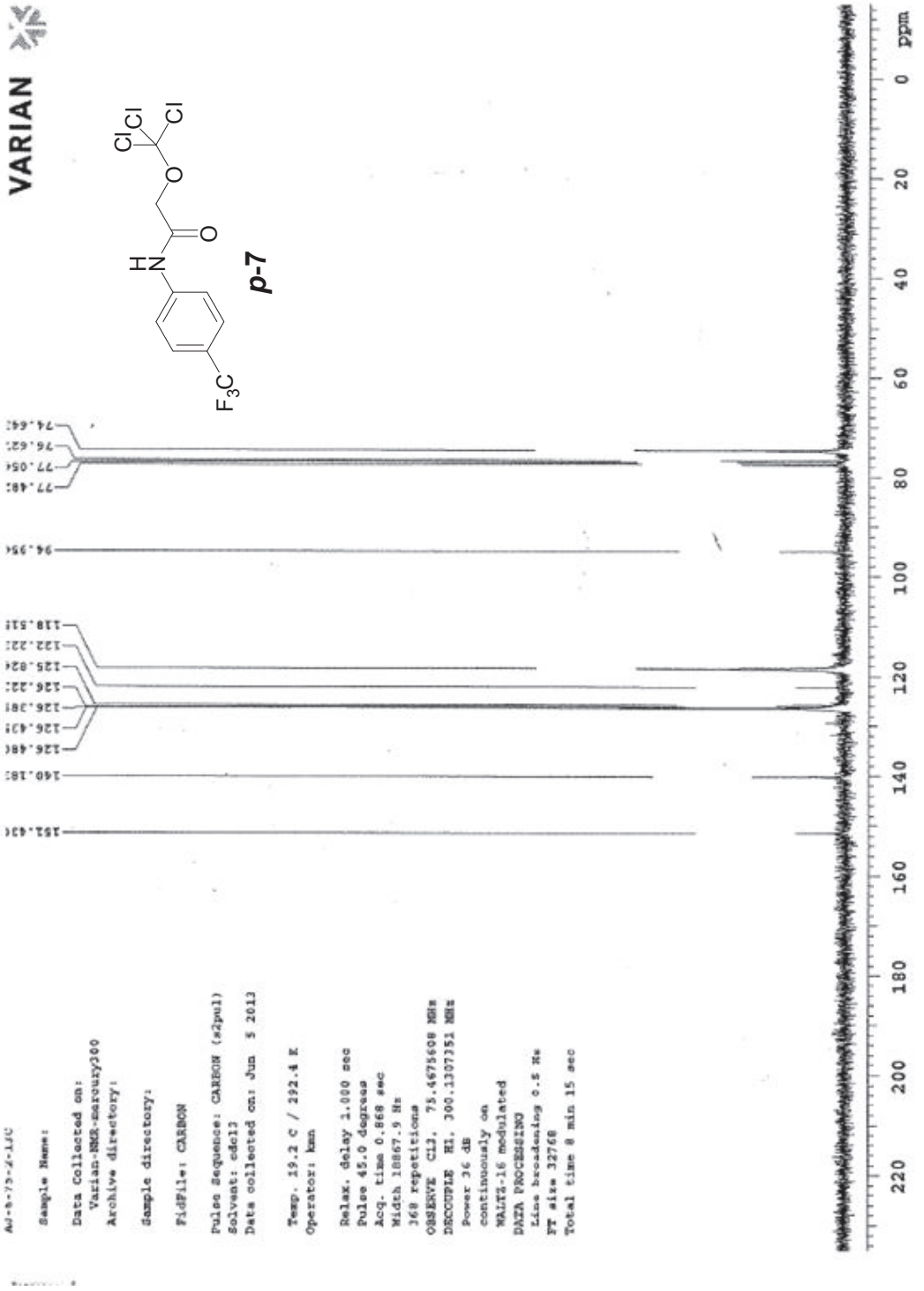

VARIAN
Sample Name:
Data Collected on:
Varian-NMR-mercury200
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 3 2013
Temp. 150.0 C / 423.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1292536 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec
ppm
o-7

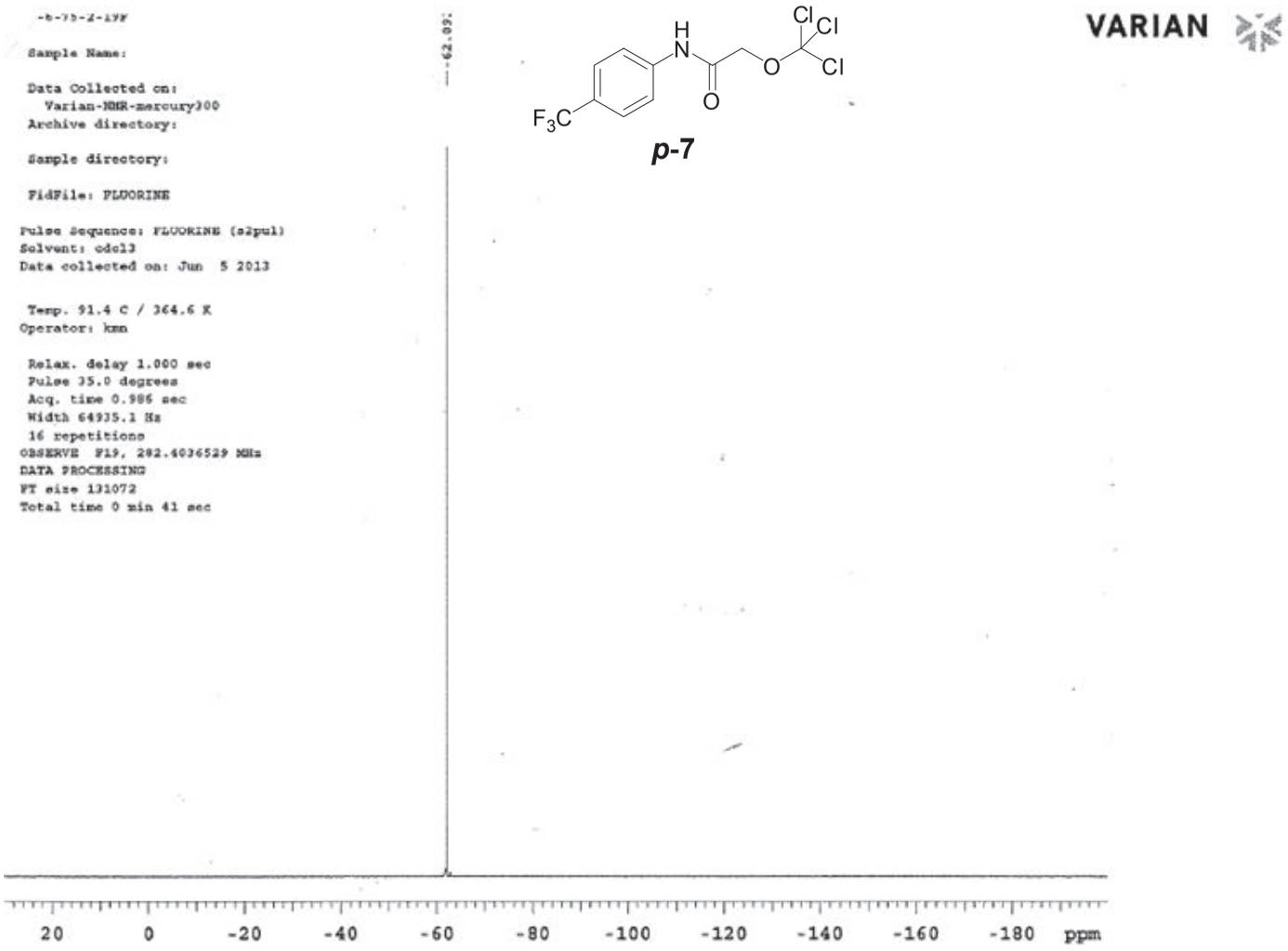

VARIAN
Cl
Cl
Cl
O
O
H
N
CF3
o-7
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 5 2013
Temp. 19.2 C / 292.4 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
736 repetitions
OBSERVE C13, 75.4675600 MHz
DECOUPLE H1, 300.1307351 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 9 min 15 sec
ppm




***o*-7**


VARI
p-7
Cl
Cl
Cl
O
O
H
N
F3C
ppm
1
2
3
4
5
6
7
8
9
10
1.51
2.00
4.09
0.81
0.55
Au-8-79-1
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 4 2013
Temp. 150.0 C / 423.1 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1292536 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 24 sec


VARIAN
p-7
Sample Name:
Data Collected on:
Varian-NMR-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 5 2013
Temp. 19.2 C / 292.4 K
Operator: kmn
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
368 repetitions
OBSERVE C13, 75.4675608 MHz
DECOUPLE H1, 300.1307351 MHz
Power 36 dB
continously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
ppm



**Procedure for the KIE experiment**. A mixture of $[Cu(CH_3CN)_4]PF_6$ (0.010 g, 0.026 mmol), neocuproine (0.005 g, 0.024 mmol) and *N*-tosyloxy-2,2,2-trichloroethylcarbamate (0.050 g, 0.138 mmol) in an equimolar solution of benzene (0.5 mL) and benzene-$d_6$ (0.5 mL) was stirred at 140 $^oC$ for 8 hours. The reaction mixture was cooled to room temperature and filtered through a plug of silica. The filtrate was subsequently analyzed by NMR spectroscopy and GC-MS analysis.

```
File        : C:\HPCHEM\1\DATA\1074KMNB.D
Operator    : Foster
Acquired    :  7 Feb 2013  13:47      using AcqMethod SF83110A
Instrument  :   GC/MS Ins
Sample Name: AJ-5-290-1
Misc Info   : 25:1 split
Vial Number: 1
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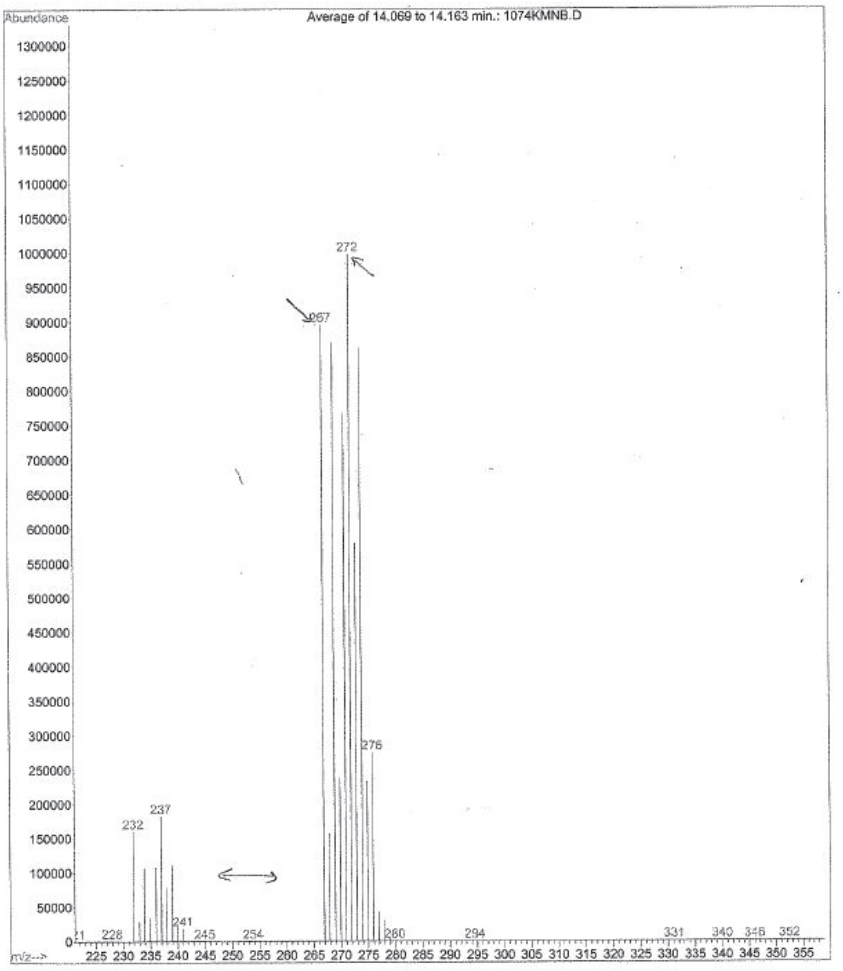
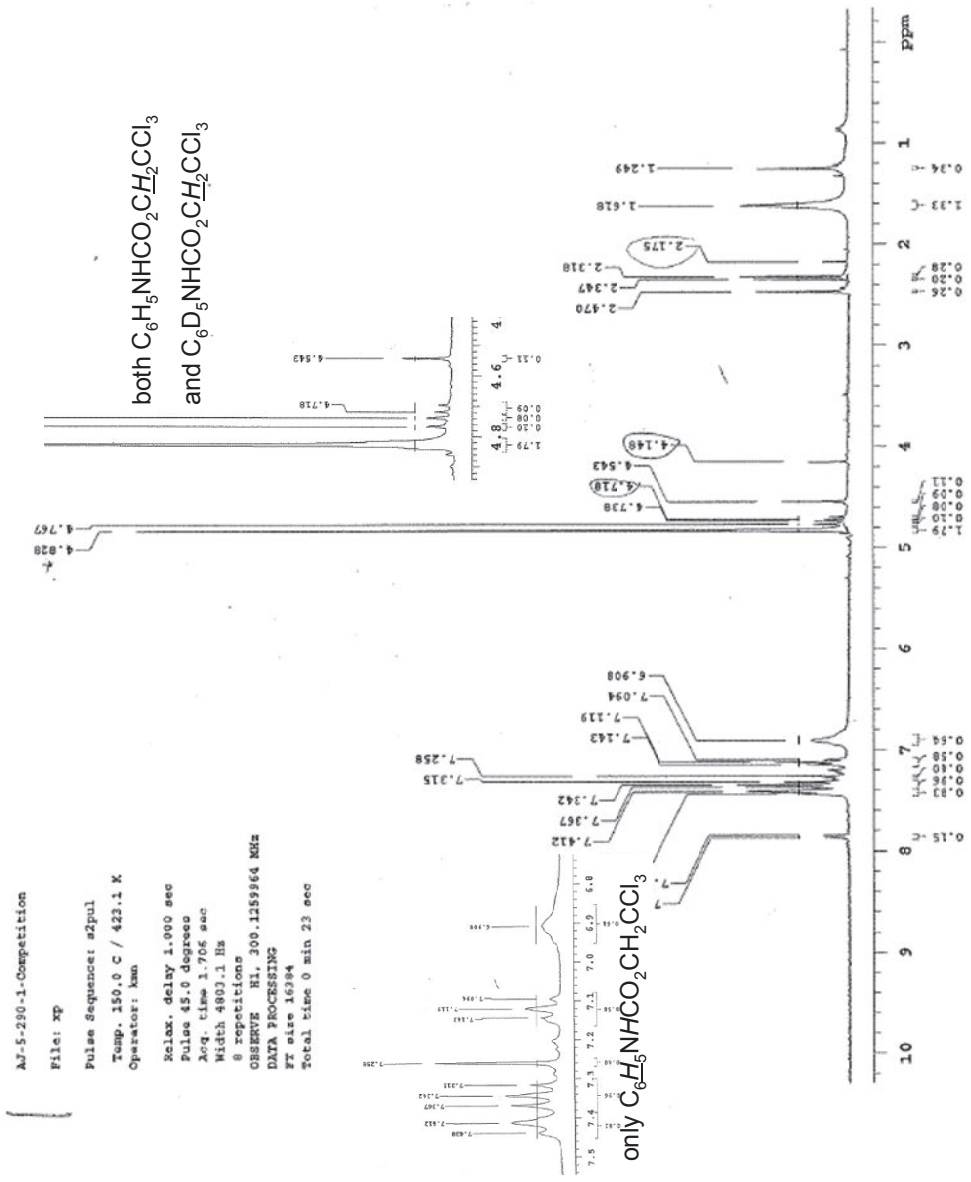





$^1$H NMR data from the KIE experiment showing contributions to the $-OC\underline{H}_2CCl_3$ resonance from dueterated product.

**Procedure for the Competition experiment**. A mixture of $[Cu(CH_3CN)_4]PF_6$ (0.010 g, 0.026 mmol), neocuproine (0.005 g, 0.024 mmol) and *N*-tosyloxy-2,2,2-trichloroethylcarbamate (0.050 g, 0.138 mmol) in an equimolar solution of benzene (0.5 mL) and Ar-Z (0.5 mL) was stirred at 140 °C for 8 hours. The reaction mixture was cooled to room temperature and filtered through a plug of silica. The filtrate was concentrated under vacuum to dryness and then subsequently analyzed by NMR on a Varian 500 MHz spectrometer. The product ratio was determined by NMR integrations on the methylene ($-OC\underline{H_2}CCl_3$) protons of the Troc group using 1,3,5-trimethoxybenzene as an internal standard.

**Table S5.** Competition experiment between various arenes and benzene.

| entry | Z-Ar | Z-Ar-NHTroc/PhNHTroc |
|---|---|---|
| 1. | toluene | 3.19 |
| 2. | *tert*-butylbenzene | 0.58 |
| 3. | anisole | 7.19 |
| 4. | chlorobenzene | 8.76 |

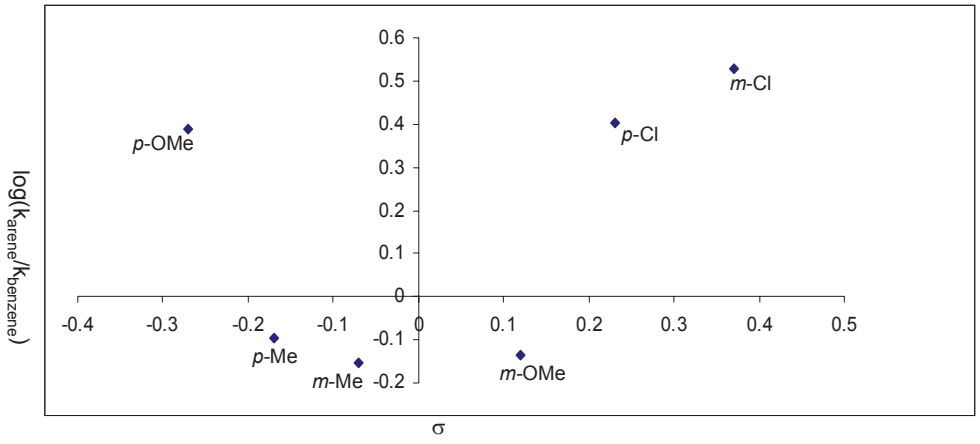
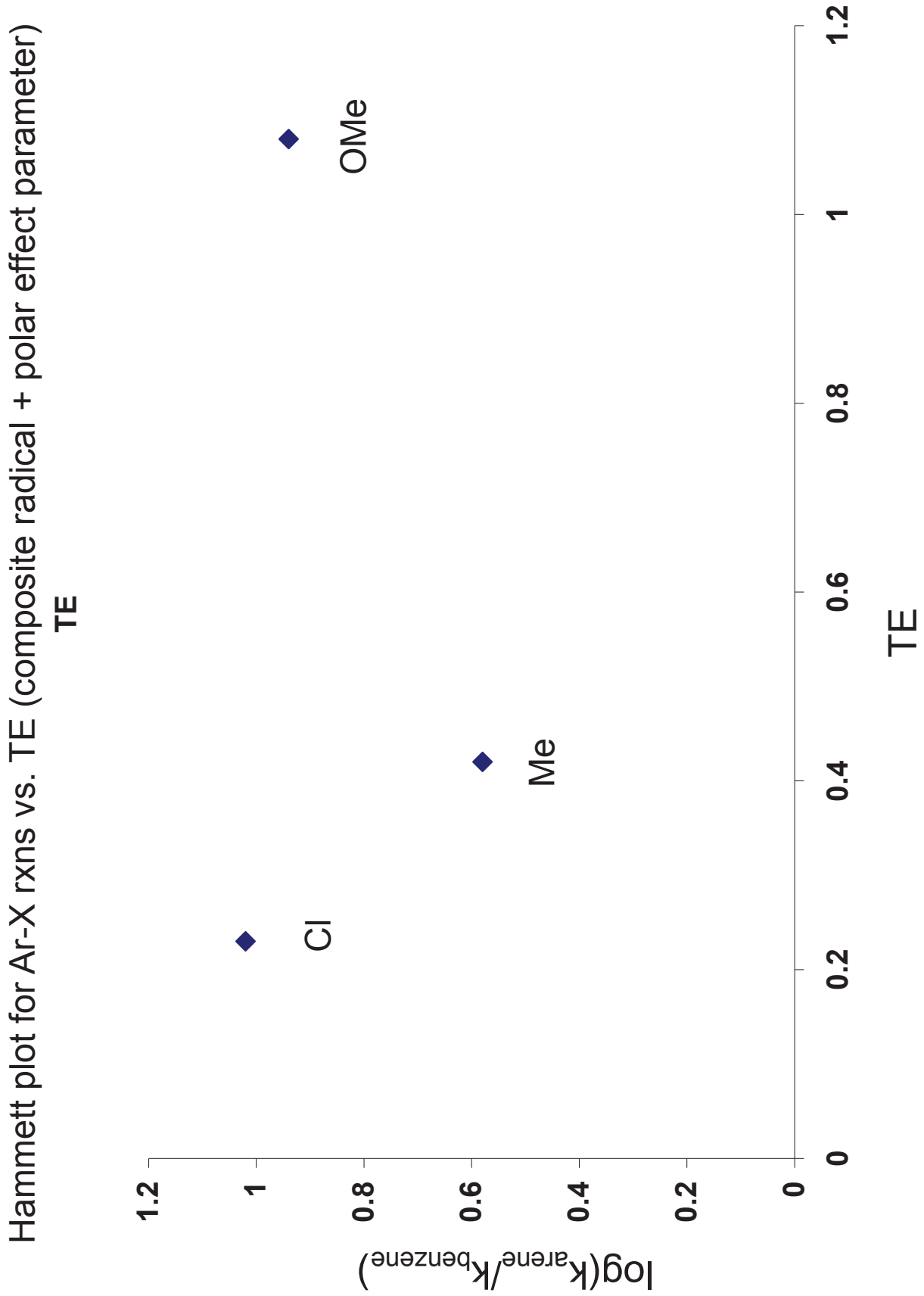
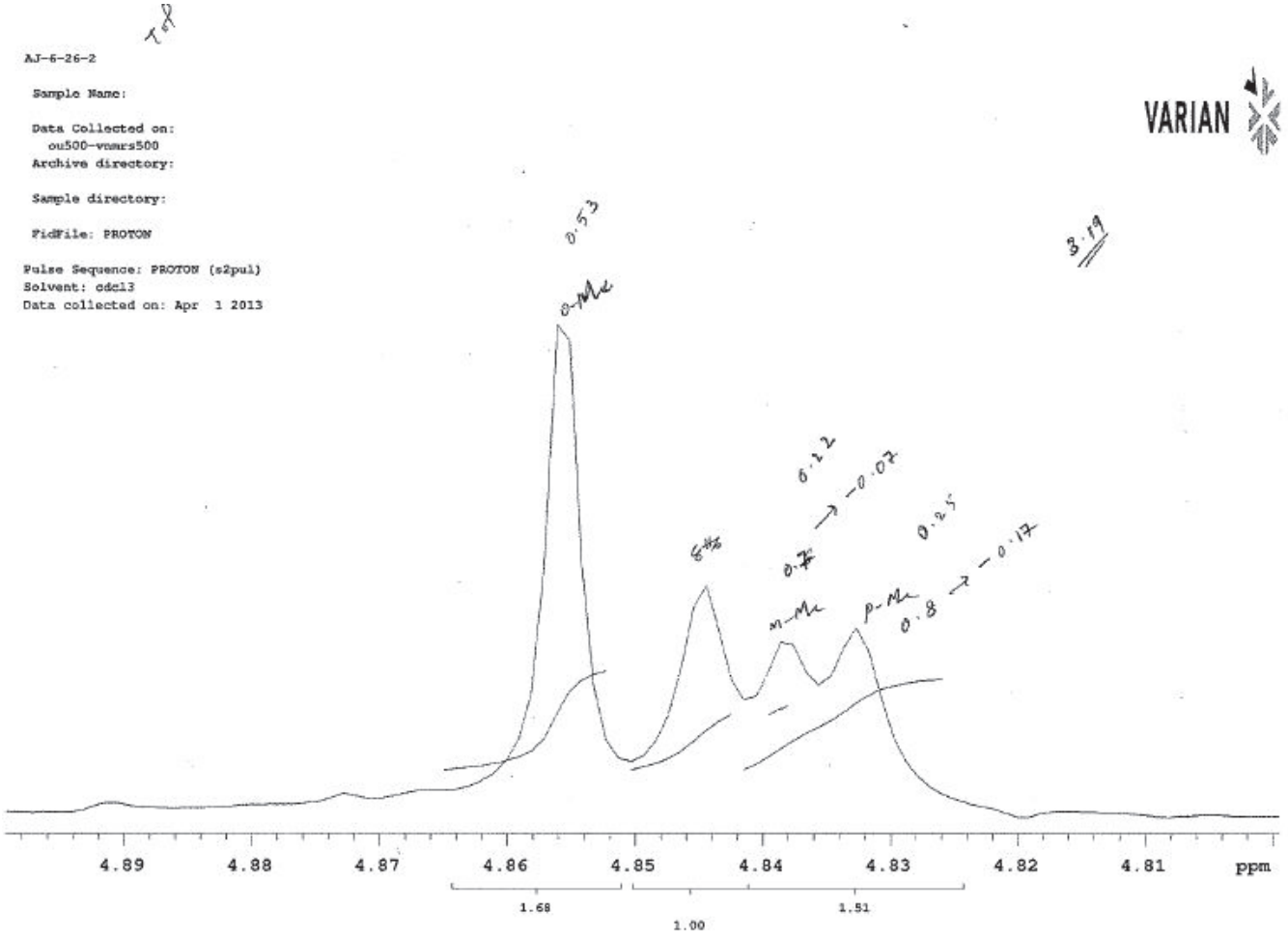
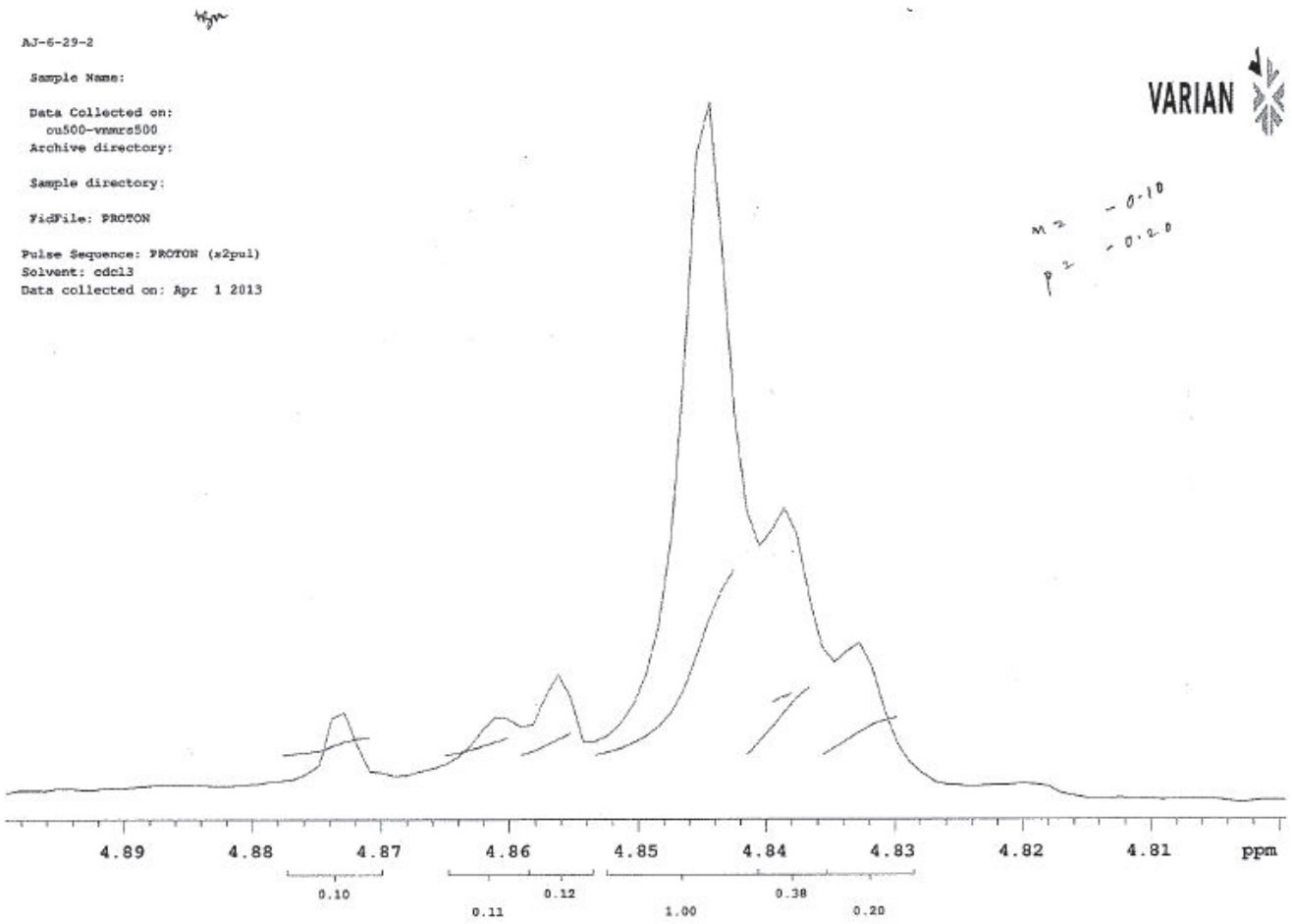



**Figure**. Hammett plot of relative reactivity of the *meta*- and *para*- isomers *vs* σ.

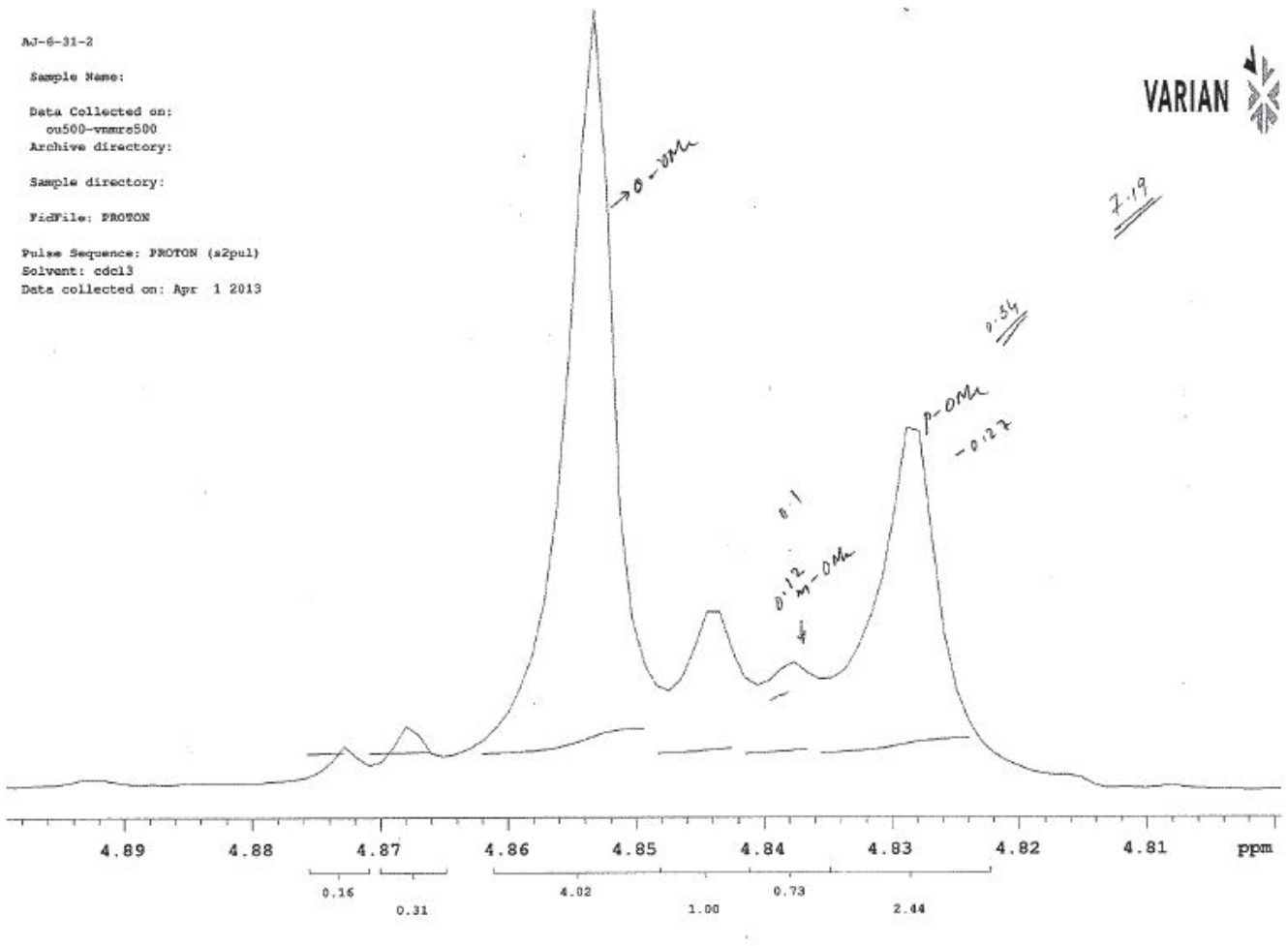




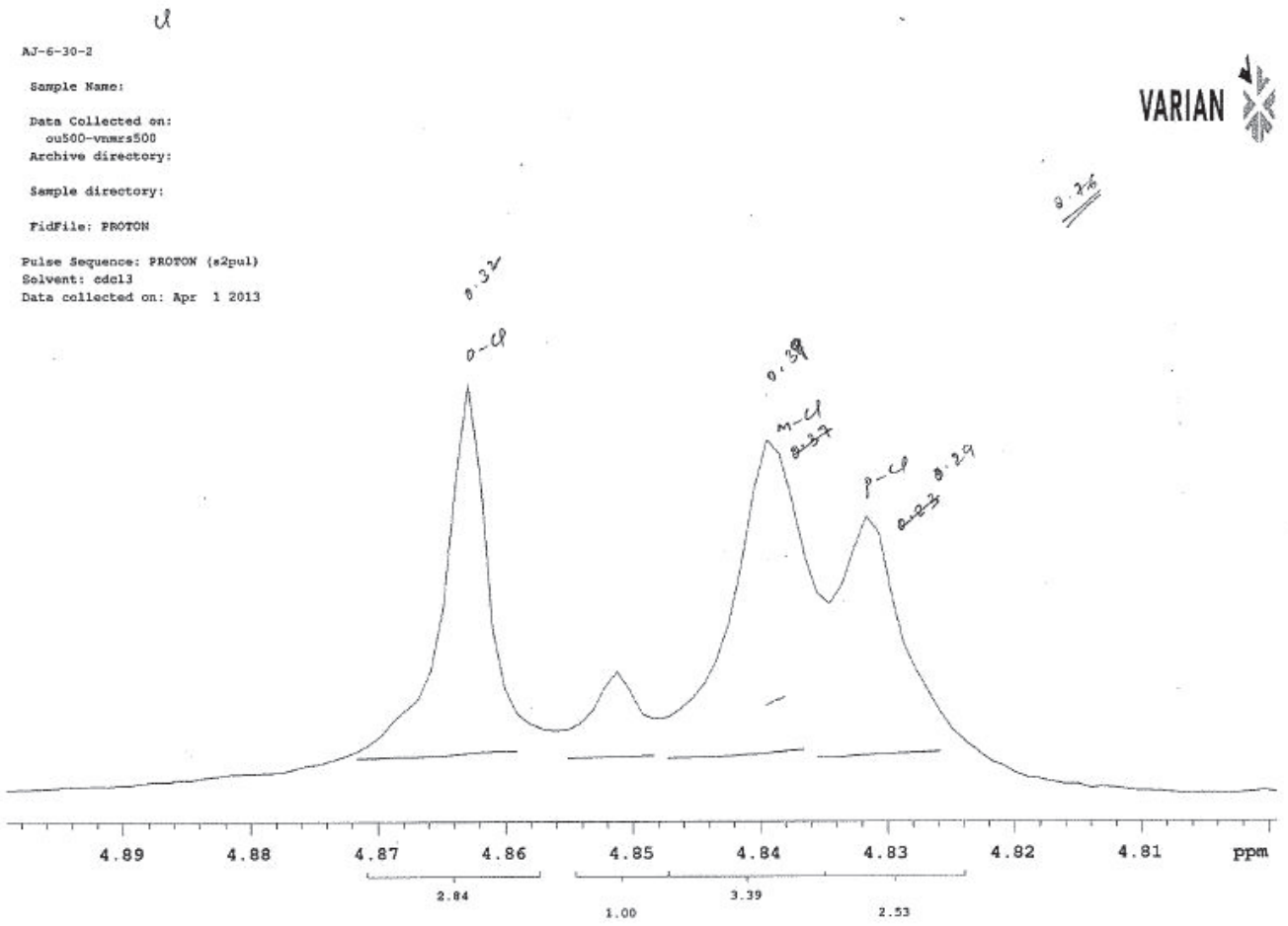

Competition experiment between toluene and benzene.




Competition experiment between *tert*-butylbenzene and benzene.




Competition experiment between anisole and benzene.




Competition experiment between chlorobenzene and benzene.

## References

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