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Supporting Information

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Supporting Information

ArX (X=I, Br, and Cl) Tolerated Electrophilic Amination of Arylboronic Acids by *N*-Chloroamides Catalyzed by CuCl at Room Temperature

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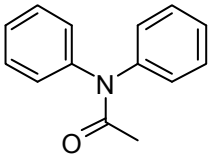
Experiment Details

Tetrahydrofuran (THF) was dried and distilled from sodium/benzophenone immediately prior to use under nitrogen atmosphere. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios.

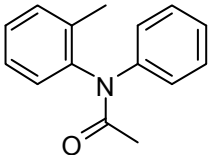
^{1}H and ^{13}C NMR data were recorded with a Varian Mercury (300 MHz) spectrometer with tetramethylsilane as an internal standard. All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument or a Waters Q-Tof Premier instrument, accurate masses were reported for the molecular ion ($[M]^{+}$, $[M+1]^{+}$). Analytical gas chromatography (GC) was performed using a Varian 3900 Gas Chromatography fitted with a flame ionization detector. For the ReactIR kinetic experiments, the reaction spectra were recorded using a ReactIR 4000 from Mettler-Toledo AutoChem fitted with a silicon-tipped (SiComp) probe. Data manipulation was carried out using the iC IR software, version 1. 05.

General procedure for the arylation of *N*-chloroamides by arylboronic acids: 1.0 mmol *N*-chloroamide, 0.5 mmol $ArB(OH)_2$, 0.05mmol CuCl and 1.5 mmol Na_2CO_3 were added to an oven dried schlenk tube. Then the tube was evacuated and refilled with nitrogen, and 1.5 mL THF was injected into it. The resulted suspension was stirred for 36 h at room temperature, quenched with 1 mL saturated sodium hyposulfite aqueous solution, extracted with ethyl acetate (3 * 20 mL). The organic phases were combined and dried over sodium sulphate. Pure product was obtained by silica gel chromatography.

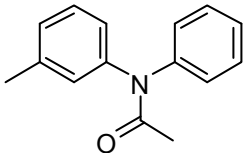
The spectroscopic data of all the products are presented below. All the known compounds gave satisfactory spectroscopic values and are analogue to spectroscopic data reported in the literature.



***N*,*N*-diphenylacetamide (3a)[1]** The isolated yield was 99%. ^{1}H NMR (300MHz, $CDCl_3$) 7.36-7.26 (m, 10H), 2.07 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.7, 143.7, 143.1, 129.9, 129.3, 128.8, 128.7, 128.1, 128.0, 126.7, 24.1; MS (EI) *m/e*: 210.4, 168.7, 117.8, 76.9, 43.0.

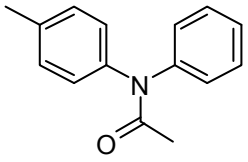


***N*-phenyl-*N*-*o*-tolylacetamide (3b)[2]** The isolated yield was 96%. ^{1}H NMR (300MHz, $CDCl_3$) 7.29-7.15 (m, 9H), 2.22 (s, 3H); 1.96 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.7, 141.9, 136.4, 132.1, 130.0, 128.9, 127.6, 125.6, 125.4, 24.2, 18.2; MS (EI) *m/e*: 224.5, 182.7, 166.8, 117.8, 76.9, 43.0.

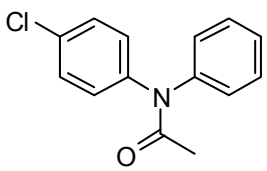


***N*-phenyl-*N*-*m*-tolylacetamide (3c)** The isolated yield was 98%. ^{1}H NMR (300MHz, $CDCl_3$) 7.36-7.06 (m, 9H), 2.34 (s, 3H), 2.06(s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 168.3, 127.2, 127.1,

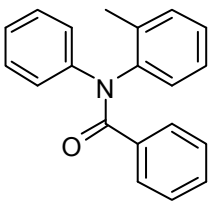
127.0, 126.9, 126.8, 126.7, 21.4, 19.0; MS (EI) *m/e*: 225.3, 183.4, 167.5, 118.4, 77.2, 43.2; HRMS(APCI) calcd for $C_{15}H_{15}NO(M^+)$: 225.1154; found: 225.1161.



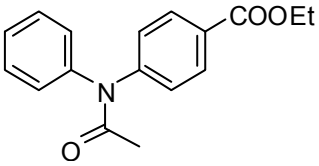
***N*-phenyl-*N*-*p*-tolylacetamide (3d)**[2] The isolated yield was 98%. ^{1}H NMR (300MHz, $CDCl_3$) 7.33-7.15 (m, 9H), 2.33 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 166.0, 138.6, 136.1, 125.8, 125.2, 124.6, 123.7, 123.0, 121.9, 19.3, 16.5; MS (EI) *m/e*: 225.3, 183.5, 167.5, 118.3, 77.2, 43.2.



***N*-(4-chlorophenyl)-*N*-phenylacetamide (3e)**[3] The isolated yield was 81%. ^{1}H NMR (300MHz, $CDCl_3$) 7.39-7.19 (m, 9H), 2.05 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.6, 143.1, 141.6, 129.9, 129.7, 129.6, 129.4, 128.6, 128.4, 128.0, 127.9, 127.8, 24.1; MS (EI) *m/e*: 245.3, 203.4, 167.5, 118.5, 75.2, 43.2.

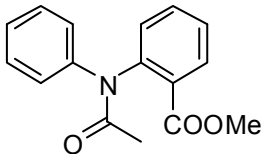


***N*-phenyl-*N*-*o*-tolylbenzamide (3f)**[4] The isolated yield was 90%. ^{1}H NMR (300MHz, $CDCl_3$) 7.47-7.08 (m, 14H), 2.27 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.5, 142.5, 136.3, 135.7, 131.6, 130.5, 129.2, 129.1, 128.1, 127.9, 127.3, 126.5, 126.0, 18.6; MS (EI) *m/e*: 285.4, 179.1, 104.5, 76.6, 50.8.

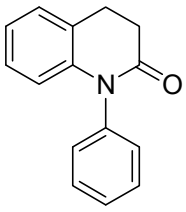


Ethyl 4-(*N*-phenylacetamido)benzoate (3g) The isolated yield was 92%. ^{1}H NMR (300MHz, $CDCl_3$) 8.02 (d, *J* =

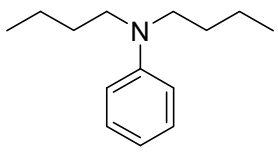
8.1, 2H), 7.44-7.25 (m, 7H), 4.36 (q, *J* = 7.2, 2H), 2.07 (s, 3H), 1.37 (t, *J* = 7.2, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 175.1, 170.6, 151.5, 147.3, 135.2, 134.5, 132.6, 130.9, 65.8, 28.9, 19.1; HRMS(APCI) calcd for $C_{17}H_{17}NO_3(M^+)$: 283.1220; found: 283.1208.



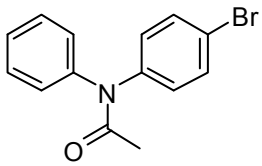
Methyl 2-(*N*-phenylacetamido)benzoate (3h)[5] The isolated yield was 94%. ^{1}H NMR (300MHz, $CDCl_3$) 8.02-7.08 (m, 9H), 3.91-3.85 (m, 3H), 2.05-2.00 (m, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 171.8, 167.4, 144.2, 142.6, 134.2, 133.4, 132.6, 131.8, 131.2, 130.3, 129.3, 129.1, 128.9, 128.5, 127.3, 126.5, 53.0, 23.9; HRMS(APCI) calcd for $C_{16}H_{15}NO_3(M^+)$: 269.1057; found: 269.1052.



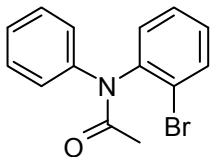
1-phenyl-3,4-dihydroquinolin-2(1H)-one (3i)[6] The isolated yield was 83%; ^{1}H NMR (300MHz, $CDCl_3$) 8.02-7.38 (m, 9H), 4.32-4.30 (d, *J* = 3.3, 2H), 4.08-4.07 (d, *J* = 1.5, 2H); ^{13}C NMR (75MHz, $CDCl_3$) 190.8, 133.1, 131.7, 126.8, 126.6, 126.5, 126.0, 123.5, 58.7, 57.1.



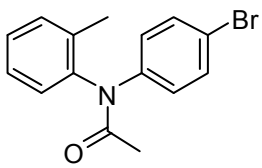
N,N-dibutylbenzenamine (3j)[7] The isolated yield was 11%; ^{1}H NMR (300MHz, $CDCl_3$) 7.17-7.09 (m, 2H), 6.59-6.52 (m, 3H), 3.21-3.15 (t, *J* = 7.6, 4H), 1.55-1.44 (m, 4H) , 1.34-1.21 (m, 4H) , 0.91-0.85 (t, *J* = 7.4, 6H); ^{13}C NMR (75MHz, $CDCl_3$) 148.4, 129.4, 115.3, 111.9, 51.0, 29.0, 20.6, 14.3.



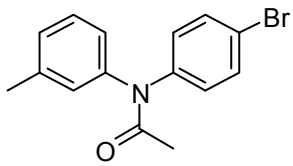
***N*-(4-bromophenyl)-*N*-phenylacetamide (3k)[8]** ^{1}H NMR (300MHz, $CDCl_3$) 7.45-7.13 (m, 9H), 2.05 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.6, 143.0, 142.1, 132.4, 130.0, 128.6, 128.4, 128.2, 24.1; MS (EI) *m/e*: 291.4, 249.5, 167.6, 118.5, 77.2, 43.2.



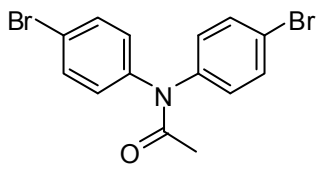
***N*-(2-bromophenyl)-*N*-phenylacetamide (3l)** The isolated yield was 92%. ^{1}H NMR (300MHz, $CDCl_3$) 7.63-7.16 (m, 9H), 2.00 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.0, 141.9, 134.0, 131.0, 129.8, 129.4, 128.9, 128.6, 127.4, 125.6, 23.6; HRMS (ESI) calcd for $C_{14}H_{12}BrNO$ $[M + H]^+$: 290.0181; found 290.0143.



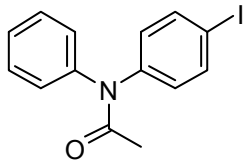
***N*-(4-bromophenyl)-*N*-o-tolylacetamide (3m)** The isolated yield was 97%. ^{1}H NMR (300MHz, $CDCl_3$) 7.30-7.05 (m, 8H), 2.09 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.6, 141.3, 137.9, 136.3, 132.2, 129.8, 129.1, 127.8, 126.9, 24.3, 18.2; HRMS (ESI) calcd for $C_{15}H_{14}BrNO$ $[M + H]^+$: 304.0337; found: 304.0404.



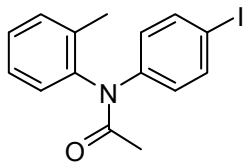
***N*-(4-bromophenyl)-*N*-*m*-tolylacetamide (3n)** The isolated yield was 99%. ^{1}H NMR (300MHz, $CDCl_3$) 7.45-7.05 (m, 8H), 2.34 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 168.0, 140.3, 129.7, 127.1, 126.5, 126.4, 125.6, 123.1, 21.5, 19.0; HRMS (ESI) calcd for $C_{15}H_{14}BrNO$ $[M + H]^+$: 304.0337; found: 304.0323.



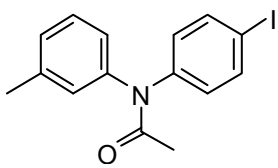
***N*,*N*-bis(4-bromophenyl)acetamide (3o)[9]** The isolated yield was 84%. ^{1}H NMR (300MHz, $CDCl_3$) 7.48-7.47 (m, 4H), 7.14-7.11 (m, 4H), 2.04 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) 170.3, 141.9, 133.0, 132.9, 130.2, 130.1, 129.6, 128.5, 128.4, 24.1.



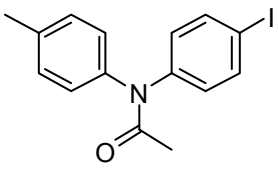
***N*-(4-iodophenyl)-*N*-phenylacetamide (3p)[10]** The isolated yield was 91%; ^{1}H NMR (300MHz, $CDCl_3$) 7.64-7.00 (m, 9H), 2.04 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$) 167.9, 140.3, 135.8, 127.4, 125.9, 21.6; HRMS (ESI) calcd for $C_{14}H_{12}INO$ $[M + H]^+$: 338.0042; found: 338.0018.



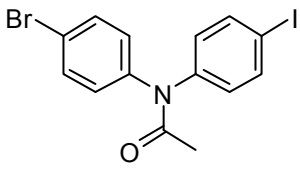
***N*-(4-iodophenyl)-*N*-*o*-tolylacetamide (3q)** The isolated yield was 99%; ^{1}H NMR (300MHz, $CDCl_3$) 7.59-7.03 (m, 8H), 2.18 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.6, 141.3, 137.9, 136.3, 132.2, 129.8, 129.1, 127.8, 126.9, 24.3, 18.2; HRMS (ESI) calcd for $C_{15}H_{14}INO$ $[M + H]^+$: 352.0198; found: 352.0171.



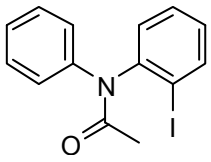
***N*-(4-iodophenyl)-*N*-*m*-tolylacetamide (3r)** The isolated yield was 99%; ^{1}H NMR (300MHz, $CDCl_3$) 7.63-7.00 (m, 8H), 2.32 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 168.0, 140.3, 136.1, 135.8, 131.2, 127.2, 126.5, 126.0, 123.0, 21.6, 19.0; HRMS (ESI) calcd for $C_{15}H_{14}INO$ $[M + H]^+$: 352.0198; found: 352.0251.



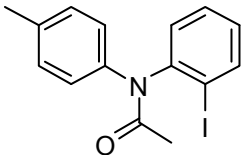
***N*-(4-iodophenyl)-*N*-p-tolylacetamide (3s)** The isolated yield was 95%; ^{1}H NMR (300MHz, $CDCl_3$) 7.63-7.00 (m, 8H), 2.34 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 167.9, 140.1, 137.6, 135.4, 127.8, 125.6, 125.5, 21.4, 18.6; HRMS (ESI) calcd for $C_{15}H_{14}INO$ $[M + H]^+$: 352.0198; found: 352.0248.



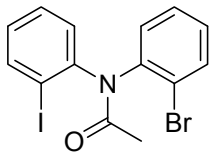
***N*-(4-bromophenyl)-*N*-(4-iodophenyl)acetamide (3t)** The isolated yield was 87%; ^{1}H NMR (300MHz, $CDCl_3$) 7.69-7.68 (m, 2H), 7.50-7.48 (m, 2H), 7.12 (d, J = 7.8, 2H), 6.99 (d, J = 7.8, 2H), 2.04 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 167.6, 140.0, 139.3, 136.3, 130.3, 127.2, 126.3, 21.6; HRMS (ESI) calcd for $C_{14}H_{11}BrINO$ $[M + H]^+$: 415.9147; found: 415.9139.



***N*-(2-iodophenyl)-*N*-phenylacetamide (3u)[11]** The isolated yield was 99%. ^{1}H NMR (300MHz, $CDCl_3$) 7.94-6.85 (m, 9H), 2.24-1.98 (m, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.2, 145.9, 141.0, 139.1, 131.0, 130.1, 128.8, 127.8, 125.9, 24.5.



***N*-(2-iodophenyl)-*N*-p-tolylacetamide (3v)** The isolated yield was 99%; ^{1}H NMR (300MHz, $CDCl_3$) 7.94-6.94 (m, 8H), 2.33-2.28 (m, 3H), 2.12-1.98 (m, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 165.5, 140.9, 136.2, 135.6, 131.2, 126.1, 125.7, 125.4, 124.9, 124.7, 124.4, 122.8, 121.2, 19.8, 16.5; HRMS (ESI) calcd for $C_{15}H_{14}INO$ $[M + H]^+$: 352.0198; found: 352.0235.



N-(2-bromophenyl)-N-(2-iodophenyl)acetamide (3w) The isolated yield was 81%; ^{1}H NMR (300MHz, $CDCl_3$) 7.98-6.97 (m, 8H), 2.12 (s, 3H); ^{13}C NMR (75MHz, $CDCl_3$) 170.6, 141.1, 140.6, 134.6, 134.3, 130.7, 130.3, 130.1, 129.6, 129.4, 129.1, 128.9, 123.9, 24.2; HRMS (ESI) calcd for $C_{14}H_{11}BrINO$ $[M + H]^+$: 415.9147; found: 415.9131.

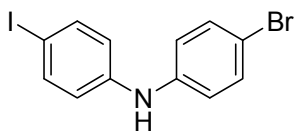
Procedure for the scale-up experiment [eq. (1)]:

Preparation of N-(4-bromophenyl)-N-(4-iodophenyl)acetamide 3t:

0.1 Mol *N*- (2-bromophenyl) -*N*-chloroacetamide, 0.12 mol $PhB(OH)_2$, 0.01 mol CuCl and 0.3 mol Na_2CO_3 were added to an oven dried schlenk flask, then the flask was transformed into glove box. 150 mL THF was injected into the system to start the reaction, and the process was monitored by GC. Final isolated yield of product **3t** was 87%.

Preparation of 4-bromo-*N*-(4-iodophenyl)benzenamine:

0.1 Mmol *N*-(4-bromophenyl)-N-(4-iodophenyl)acetamide, 0.3 mmol KOH, 1 mL EtOH and 0.2 mL water were added to a tube, and the resulted solution was stirred for 3 h at 60 ℃ in oil bath. Then the solution was dried by sodium sulphate. Purified product was obtained through silica gel chromatography and the isolated yield was 99%.



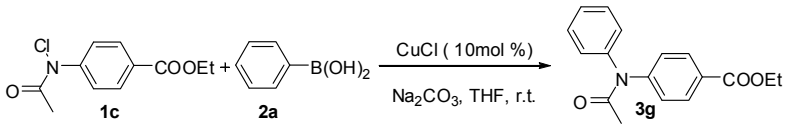
4-bromo-*N*-(4-iodophenyl)benzenamine[12] The isolated yield was 99%; ^{1}H NMR (300MHz, $CDCl_3$) 7.54-7.51 (d, J = 8.7, 2H), 7.37-7.34 (d, J = 8.7, 2H), 6.93-6.90 (d, J = 8.7, 2H), 6.81-6.78 (d, J = 8.4, 2H), 5.66 (br, 1H); ^{13}C NMR (75MHz, $CDCl_3$) 142.6, 141.6, 138.5, 132.6, 119.9, 113.8, 83.2.

[1] C. Heyde, I. Zug, H. Hartmann, *Eur. J. Org. Chem.* 2000, 3273-3278.
[2] W. Deng, C. Zhang, M. Liu, Y. Zou, L. Liu, Q.-X. Guo, *Chin. J. Chem.* 2005, *23*, 1241-1246.
[3] S. Y. Kim, G.-I. An, H. Rhee, *Synlett* 2003, 112-114.
[4] K. B. Wiberg, B. I. Rowland, *J. Am. Chem. Soc.* 1955, *77*, 2205-2209.
[5] N. P. Peet, S. Sunder, *J. Heterocycl. Chem.* 1976, *13*967 -971.
[6] G. Capozzi, A. Chimirri, S. Grasso, G. Romeo, *Heterocycles* 1984, *22*1759 -1762.
[7] X. Xie, T. Y. Zhang, Z. Zhang, *J. Org. Chem.* 2006, *71*, 6522-6529.
[8] P. Welzel, *Chem. Ber.* 1970, *103*, 1318-1333.
[9] J. Forrest, D. A. Liddell, S. H. Tucker, *Journal of the Chemical Society* 1946, 454-456.
[10] N. Itoh, T. Sakamoto, E. Miyazawa, Y. Kikugawa, *J. Org. Chem.* 2002, *67*, 7424-7428.
[11] F. M. Beringer, L. Kravetz, G. B. Topliss, *J. Org. Chem.* 1965, *30*, 1141-1148.
[12] P. Das, B. Basu, *Synth. Commun.* 2004, *34*, 2177-2184.

The effects of the ratio between N-halo-amidesand arylboronic acids [Footnote 54]

The excess of N-haloamides to arylboronic acids was to improve the conversion of arylbornic acids. The side products detected were mainly dechlorinated amides. The reaction of **1c** and **2a** was used to display the reaction results of different ratios of **1c** to **2a** (S Table 1).

S Table 1. The effect of the ratio between N-halo-amides and arylboronic acids.[a]



1c **2a** **3g**

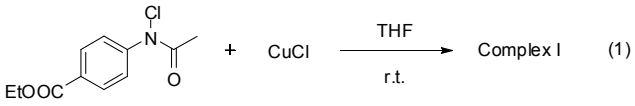
Entry	**2a** (mmol)	**1c** (mmol)	Yield[%][b]
1	0.65	0.50	74
2	0.65	1.00	83
3[c]	0.5	1.00	92[d]

[a] Reaction conditions: **1 c**, **2a**, Na_2CO_3 (1.5 mmol), CuCl (0.05 mmol) in THF (3 mL)at 25 ^oC for 36 h; [b] Yields determined by GC with naphthalene as the internal standard; [c] From Table 2, entry 6; [d]Isolated yield.

General ReactIR Experimental Details

All kinetic experiments were run at 25 ± 1 ^oC. For the ReactIR kinetic experiments, the reaction spectra were recorded using a ReactIR 4000 from Mettler-Toledo AutoChem fitted with a silicon-tipped (SiComp) probe. The spectra were acquired in 2 scans at a gain of one and a resolution of two using system ReactIR 3.0 software. Data manipulation was carried out using the iC IR software, version 1. 05.

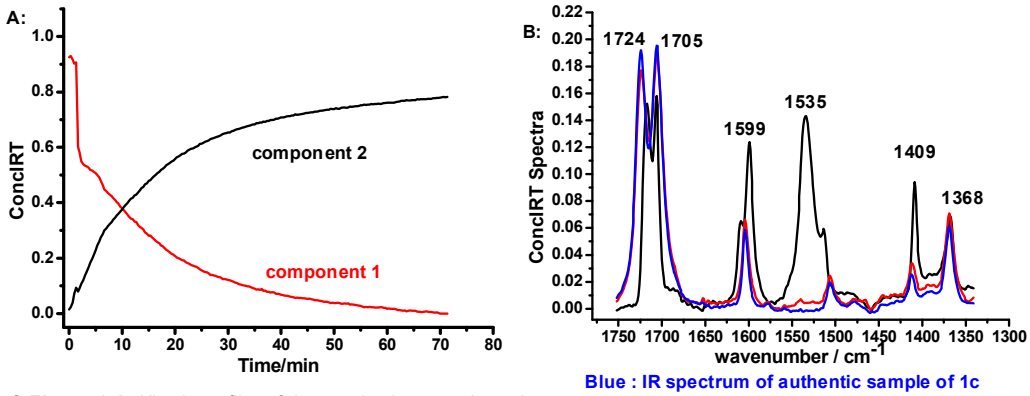
Stoichiometric reaction between N-chloroamide 1c and CuCl:



The experimental details:

The reaction was carried out as follows: an oven-dried three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept at room temperature. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with 2.5 mL THF solution of ethyl 4-(N-chloroacetamido)benzoate **1c** (0.5 mmol) and the data collection was started. Then copper(I) chloride (0.5 mmol) was added to initiate the reaction, and IR spectra were recorded over the course of the reaction.

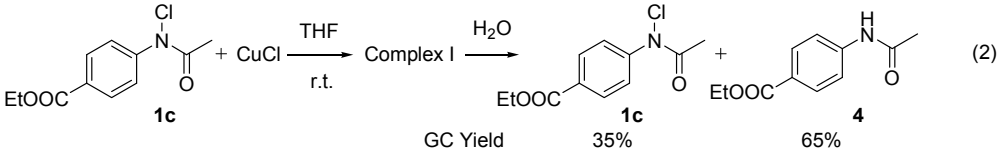
Data analysis:



S Figure 1. **A:** Kinetic profiles of the reaction between **1c** and CuCl Monitored by *in-situ* IR. **B:** ConcIRT spectra of component 1, component 2, and **1c**.

Based on the IR data gained in the above stoichiometric reaction of **1c** and CuCl, we found the generation of a new component **2** upon consumption of component **1** (S Figure 1A). Component **1** was assigned to **1c** based upon comparison of its ConcIRT Spectrum to that of **1c** (S Figure 1B), and component **2** was tentatively ascribed to be an adduct of **1c** and CuCl because its ConcIRT Spectrum contained peaks at 1724 cm-1, 1705 cm-1 (C=O), 1599cm-1 and 1535cm-1 (phenyl ring), similar to that of **1c** with some wave number shifts and peak strength changes.

Hydrolysis of the adduct from CuCl and N-chloroamide 1c



(2)

1 ML H_2O was added to the reaction mixture of **1c** (0.5 mmol) and CuCl (0.5 mmol), then recovered **1c** (35%) and the dechlorinated N-H compound **4** (65%) were detected by GC and the yields were determined with naphthalene as the internal standard.

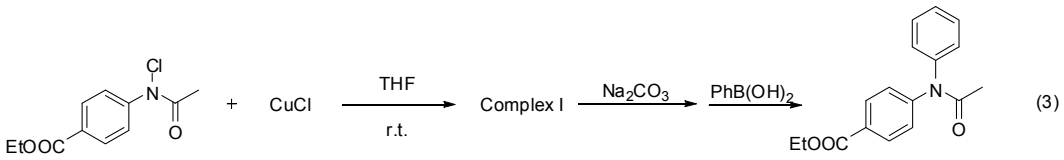
Test of the speculation in Scheme 1 by stoichiometric reactions:

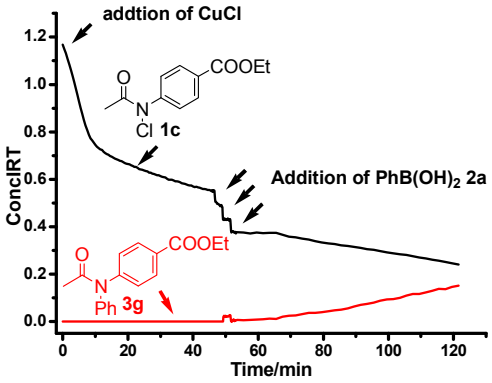
The experimental details (Supporting information [eq. (2)]):

The reaction was carried out as follows: an oven-dried three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept at room temperature. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with THF (2.5 mL) containing ethyl 4-(N-chloroacetamido)benzoate **1c** (0.5 mmol) and the data collection was started. Then copper(I) chloride (0.5 mmol) was added to initiate the reaction, followed by sequential addition of Na_2CO_3 (1.5 mmol) and $PhB(OH)_2$ (0.5 mmol). IR spectra were recorded over the course of the reaction.

Data analysis (S Figure 2):

Based on the IR data gained in the above stepwise reactions of **1c** and CuCl, Na_2CO_3 and $PhB(OH)_2$, we found the kinetic profiles clearly revealed that **1c** began to react on the addition of CuCl, and N-arylation product was formed as soon as $PhB(OH)_2$ was added. The addition was completed within 5 min, and 30% product **3g** was formed after 360 min.

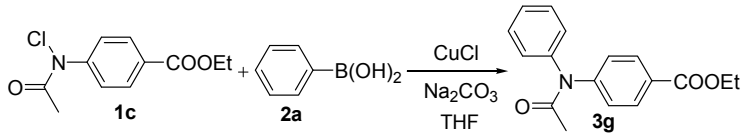




S Figure 2. Kinetic profiles of the reaction between **1c** and **3g** Monitored by in-situ IR during the period of 0-120 min.

The effect of temperature (S table 2):

S Table 2. The effect of temperature.[a]



Entry	Temperature	Time	GC Yield[%]
1	25°C	8.0 h	85
2	40°C	3.0 h	93
3	60°C	2.0 h	95

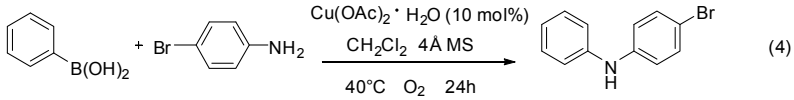
[a] Reaction conditions: **1 c** (1.0 mmol), **2a** (0.5mmol), Na_2CO_3 (1.5 mmol), CuCl (0.05 mmol) in THF (3 mL);

The reaction was carried out as follows: an oven-dried three necked reaction vessel was fitted with a magnetic stirring bar. The IR probe was inserted through an adapter into the middle neck; the other two necks were capped by septa for injections and a nitrogen line. The reaction vessel was kept in a thermostatic waterbath. Following evacuation under vacuum and flushing with nitrogen for three times, the three necked vessel was charged with THF (3.0 mL) containing ethyl 4-(N-chloroacetamido)benzoate (1.0 mmol) **1c**, $PhB(OH)_2$ (0.5 mmol), copper(I) chloride (0.05 mmol) and Na_2CO_3 (1.5 mmol), then the data collection was started. IR

spectra were recorded over the course of the reaction, and the reaction yield was determined by GC.

Comparing experiments between our method and Cu(II)-mediated oxidative coupling (Chan-Lam-Evans procedure and one of modified procedure) [Footnote 55]

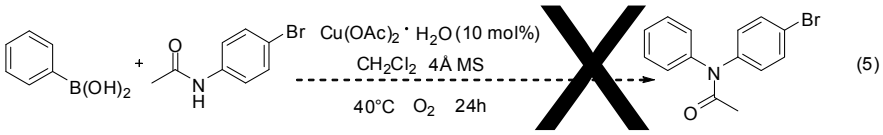
The Procedure for the Cross-Coupling of $PhB(OH)_2$ with 4-bromoaniline[13]



(4)

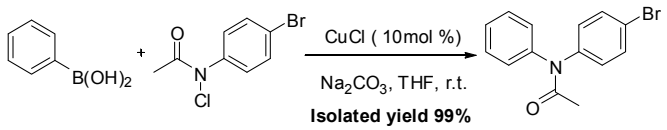
53% yield was reported in original paper (OL 2003, 4397)
50% was obtained when we repeated the reaction

A suspension of $PhB(OH)_2$ (243.8 mg, 2.00 mmol), $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.100 mmol), and powdered 4Å molecular sieves (0.750 g) in CH_2Cl_2 (8.00 mL) was stirred for 5 min at room temperature. To this stirring suspension was added 4-bromoaniline (172.0 mg, 1.00 mmol). The reaction mixture was then sealed with a rubber septum, and stirred under an atmosphere of O_2 at 40 ℃. After 24 h, the crude reaction mixture was filtered through a plug of celite to remove the molecular sieves and any insoluble by products and then concentrated in vacuum to afford the crude mixture. The product was isolated by silica gel column chromatography (yield 50%) (Supporting information [eq. (4)]). MS (EI) *m/e*: 249.2, 168.2, 141.0, 77.0, 51.0.



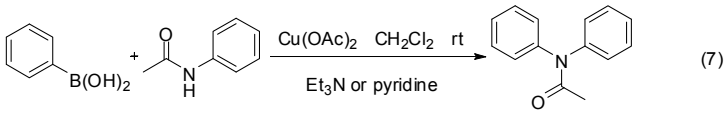
(5)

When N-(4-bromophenyl)acetamide was used as the substrate in place of 4-bromoaniline and the reaction was carried out under identical conditions, no desired coupling product [N-(4-bromophenyl)-N-phenylacetamide] was detected (Supporting information [eq. (5)]).

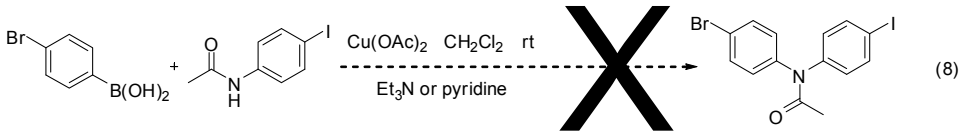


When N-chloroamide was employed as the starting material, and subjected our conditions, excellent yield for the desired cross-coupling product was obtained (99% in Table 3, entry 3 of manuscript).

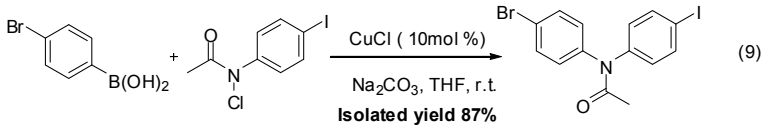
The Procedure for the Cross-Coupling of $PhB(OH)_2$ with N-phenylacetamide[14]



A slurry of N-phenylacetamide, arylboronic acid (2 equiv), anhydrous $Cu(OAc)_2$ (1 equiv), a tertiary amine such as triethylamine or pyridine (2 equiv) in methylene chloride (2 mL) was stirred at room temperature for 48 h. The yield of the reaction was determined by GC (35%) (Supporting information [eq. (7)]). MS (EI) *m/e*: 210.4, 168.7, 117.8, 76.9, 43.0.



When N-(4-iodophenyl)acetamide was used in place of N-phenylacetamide, and 4-bromophenylboronic acid was used in place of $PhB(OH)_2$, no N-(4-bromophenyl)-N-(4-iodophenyl)acetamide was detected (Supporting information [eq. (8)]).

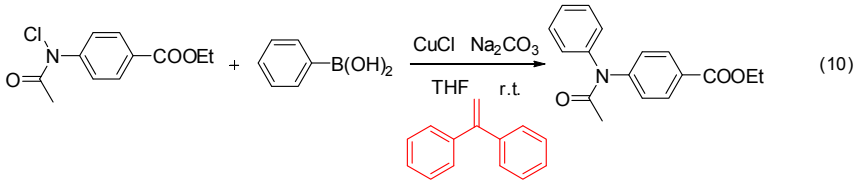


The reaction of corresponding N-chloroamide with $ArB(OH)_2$ took place smoothly at room temperature (87% yield, Table 3, entry 11 in the manuscript).

[13] T. D. Quach, R. A. Batey, *Org. Lett.* 2003, *5*, 4397-4400.
[14] D. M. T. Chan, K. L. Monaco, R.-P. Wang, M. P. Winters, *Tetrahedron Lett.* 1998, *39*, 2933-2936.

The effects of the radical scavenger (1,1-diphenylethylene)

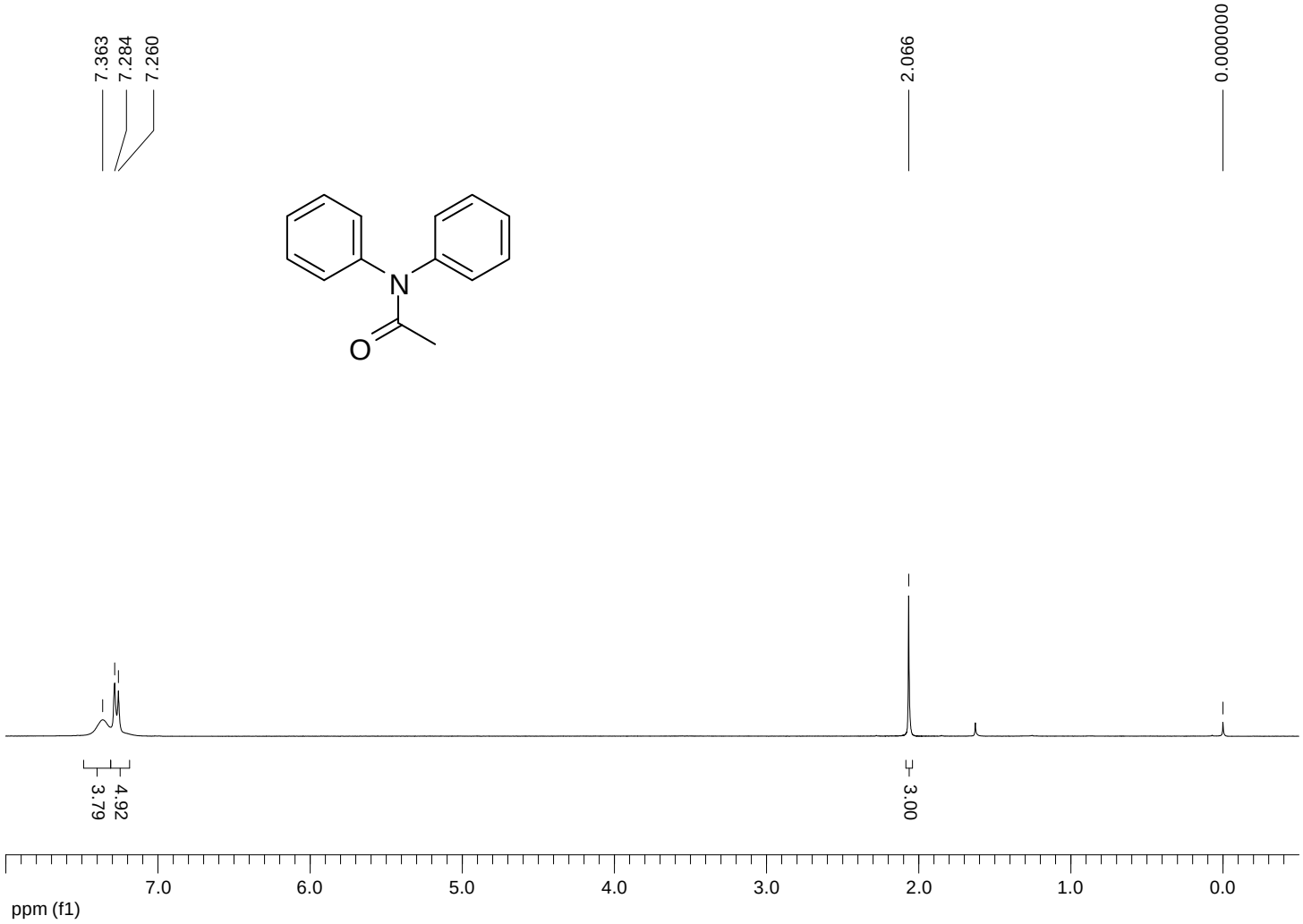
To understand whether the mechanism of the C-N coupling catalyzed by CuCl is SET or radical based mechanistic pathways, we added radical scavenger (**1,1-diphenylethylene**) into the reaction system monitored by *in-situ* IR.



(10)

0.5 Mmol N-chloroamide **1c**, 0.5 mmol $ArB(OH)_2$, 0.05mmol CuCl and 1.5 mmol Na_2CO_3 were mixed together in THF， followed by addition of 0.5 mmol 1,1-diphenylethylene. The kinetic profiles clearly revealed that the reaction was not inhibited, and N-chloroamide **1c** reacted smoothly with concomitant formation of N-arylation product (S Figure 3). The reaction reached 75 % yield (determined by GC) after 300 min. In the control experiment without 1,1-diphenylethylene, the yield was 74% after 300 min.

Table1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7.260
2.066
0.000000
N
O
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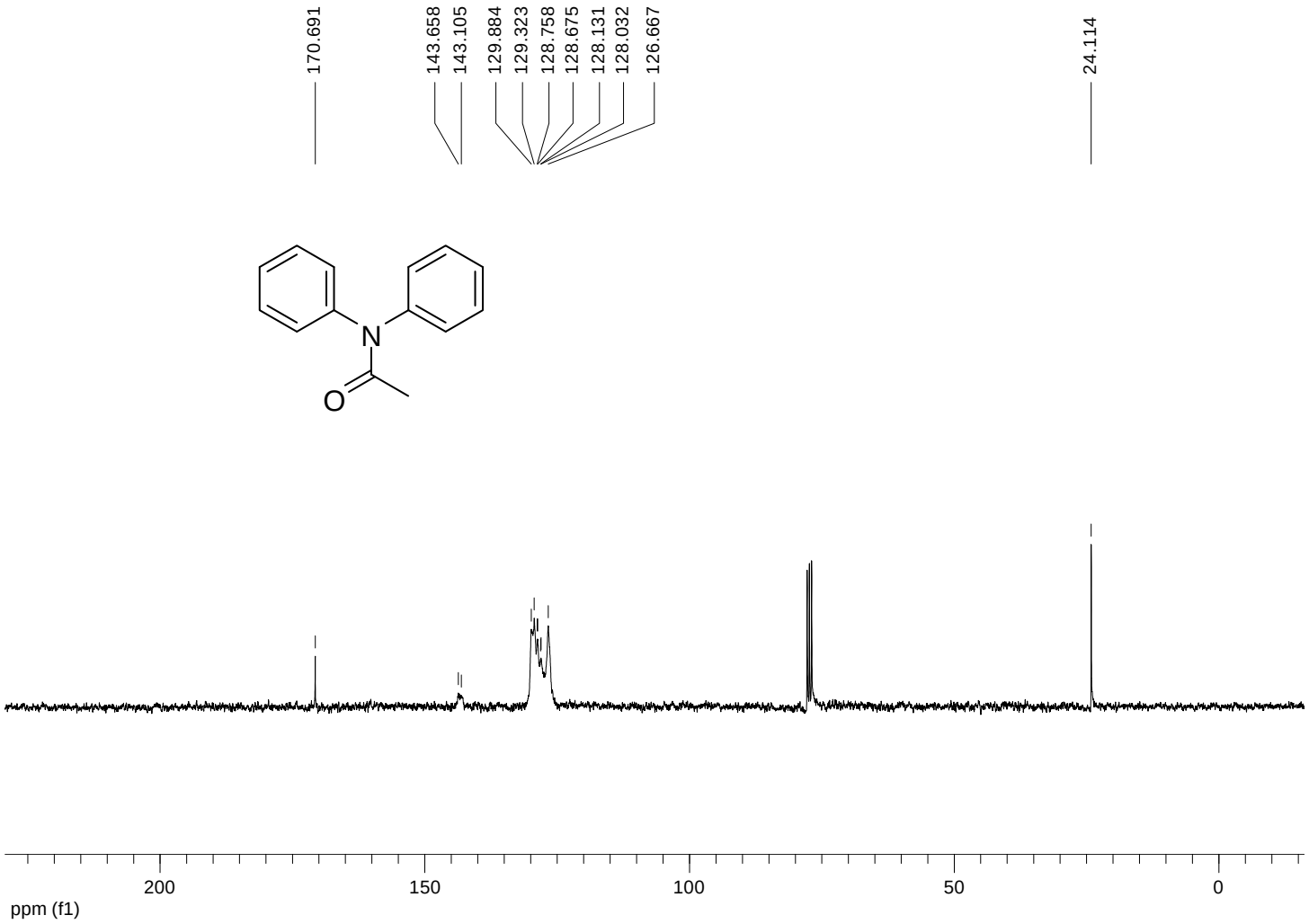
4.92
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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143.658
143.105
129.884
129.323
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128.675
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128.032
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24.114
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O
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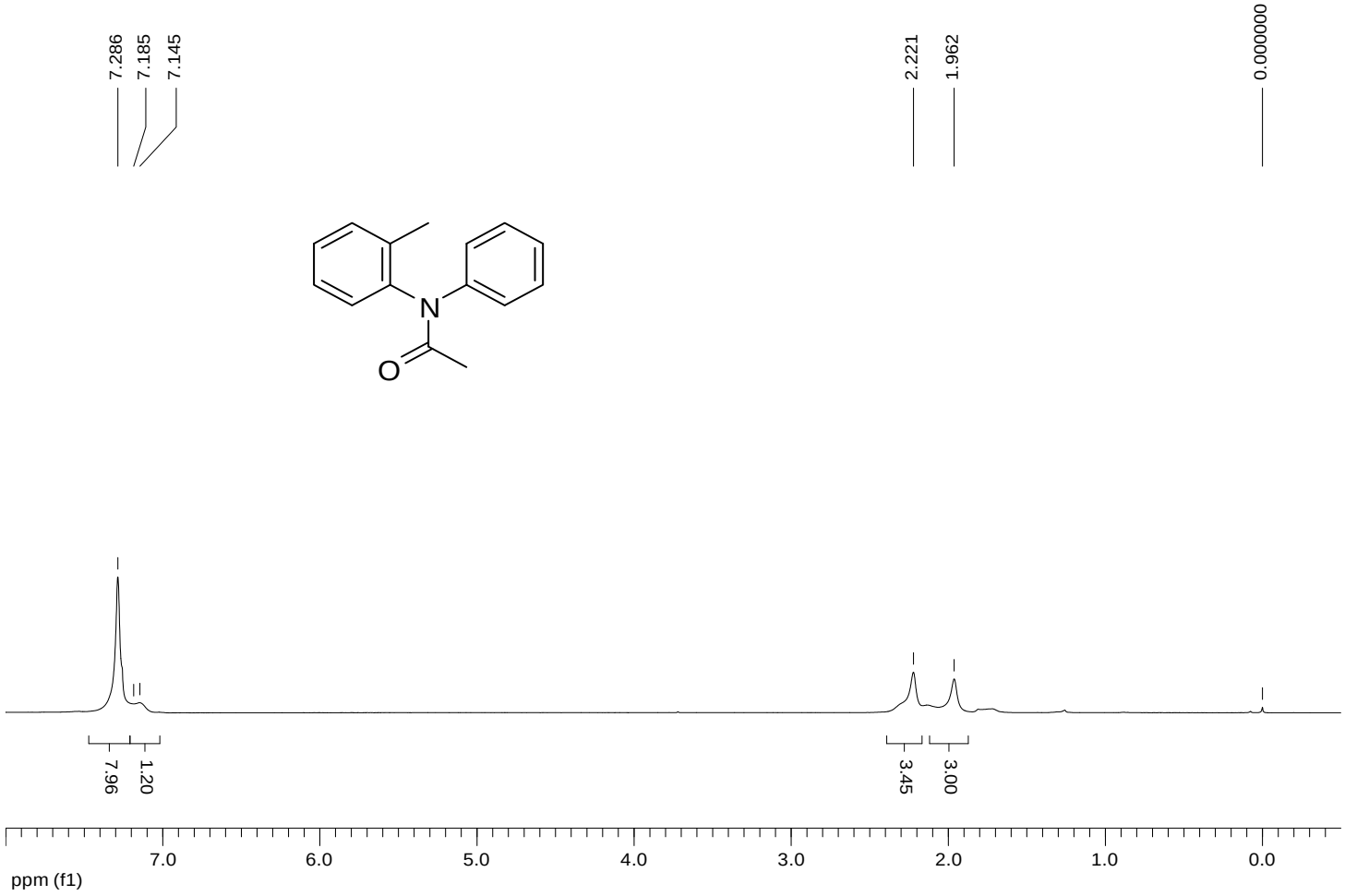
150
100
50
0
ppm (f1)

Table2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N
O
7.96
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3.00
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5.0
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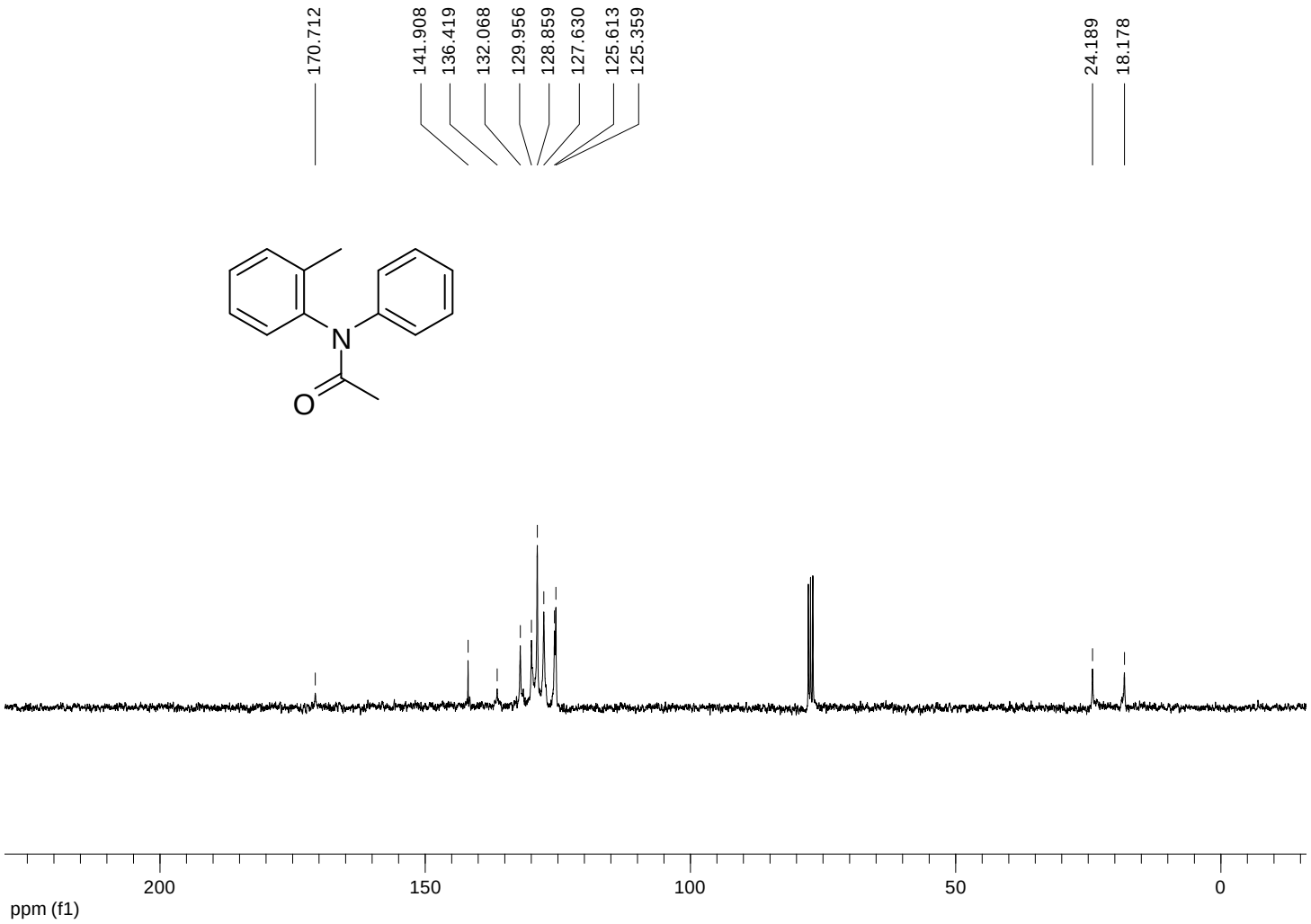
3.0
2.0
1.0
0.0
ppm (f1)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125.359
24.189
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O
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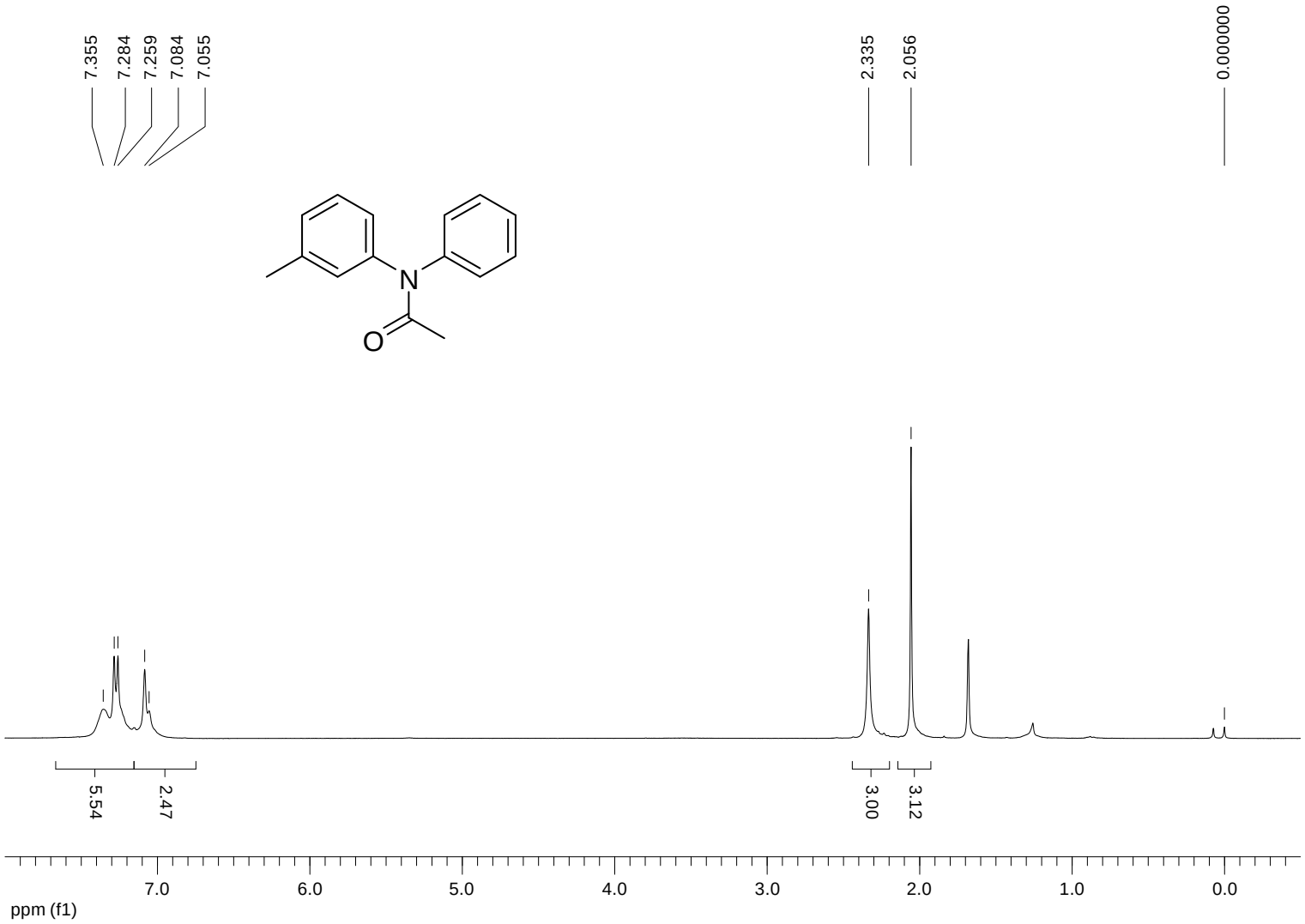
150
100
50
0
ppm (f1)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7.055
2.335
2.056
0.000000
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O
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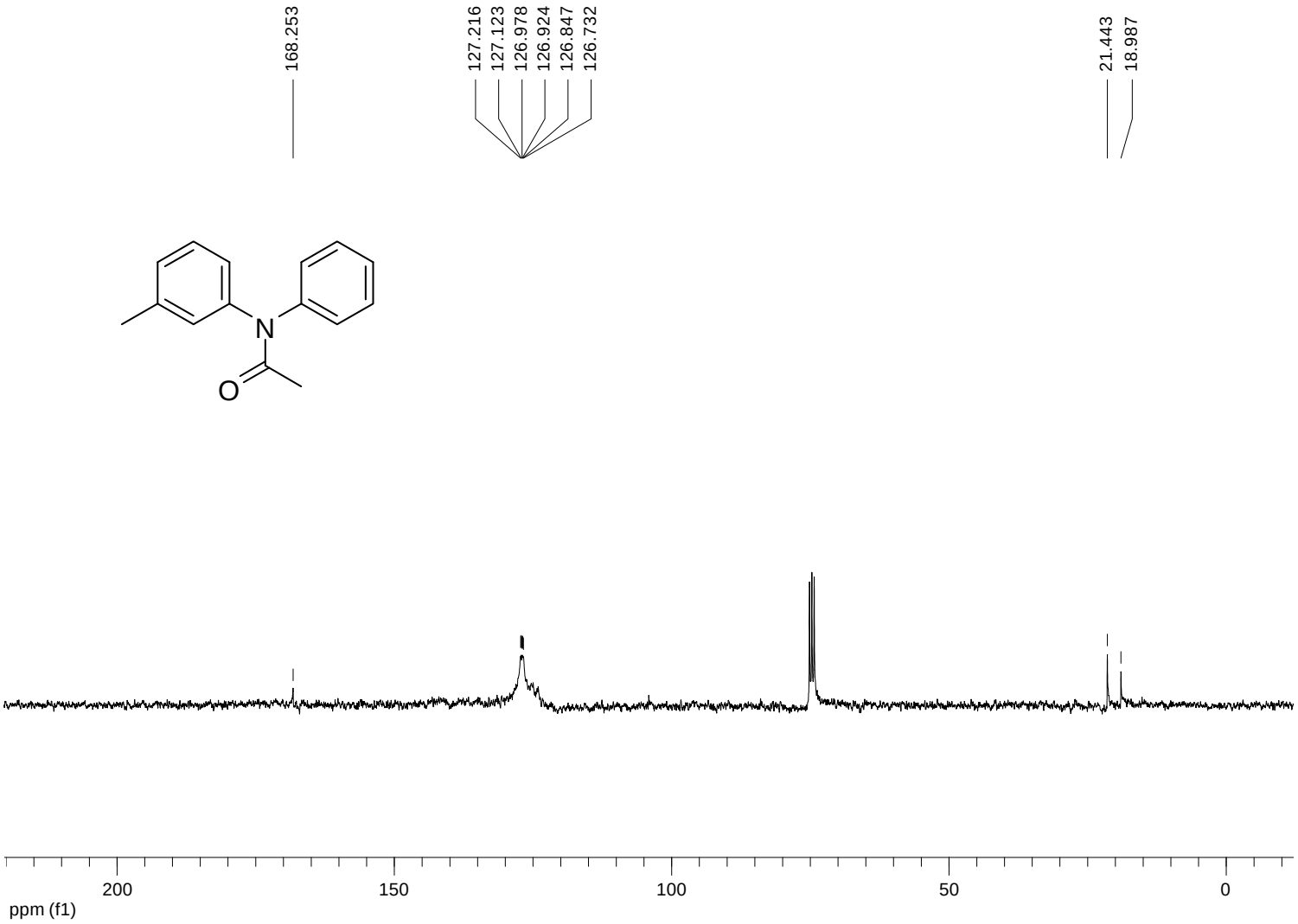
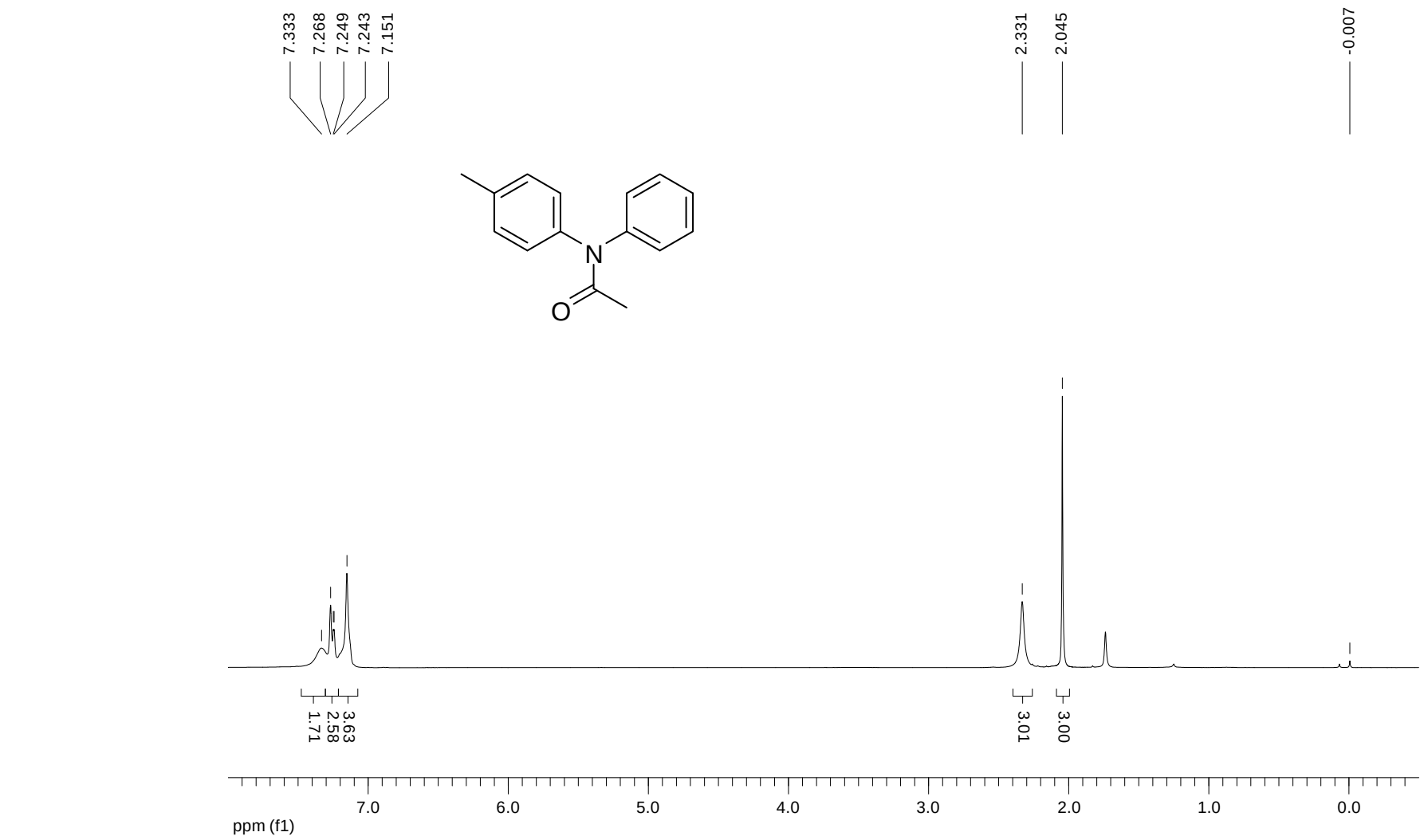
3.12
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


168.253
127.216
127.123
126.978
126.924
126.847
126.732
21.443
18.987
N
O
200
150
100
50
0
ppm (f1)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7.243
7.151
2.331
2.045
-0.007
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O
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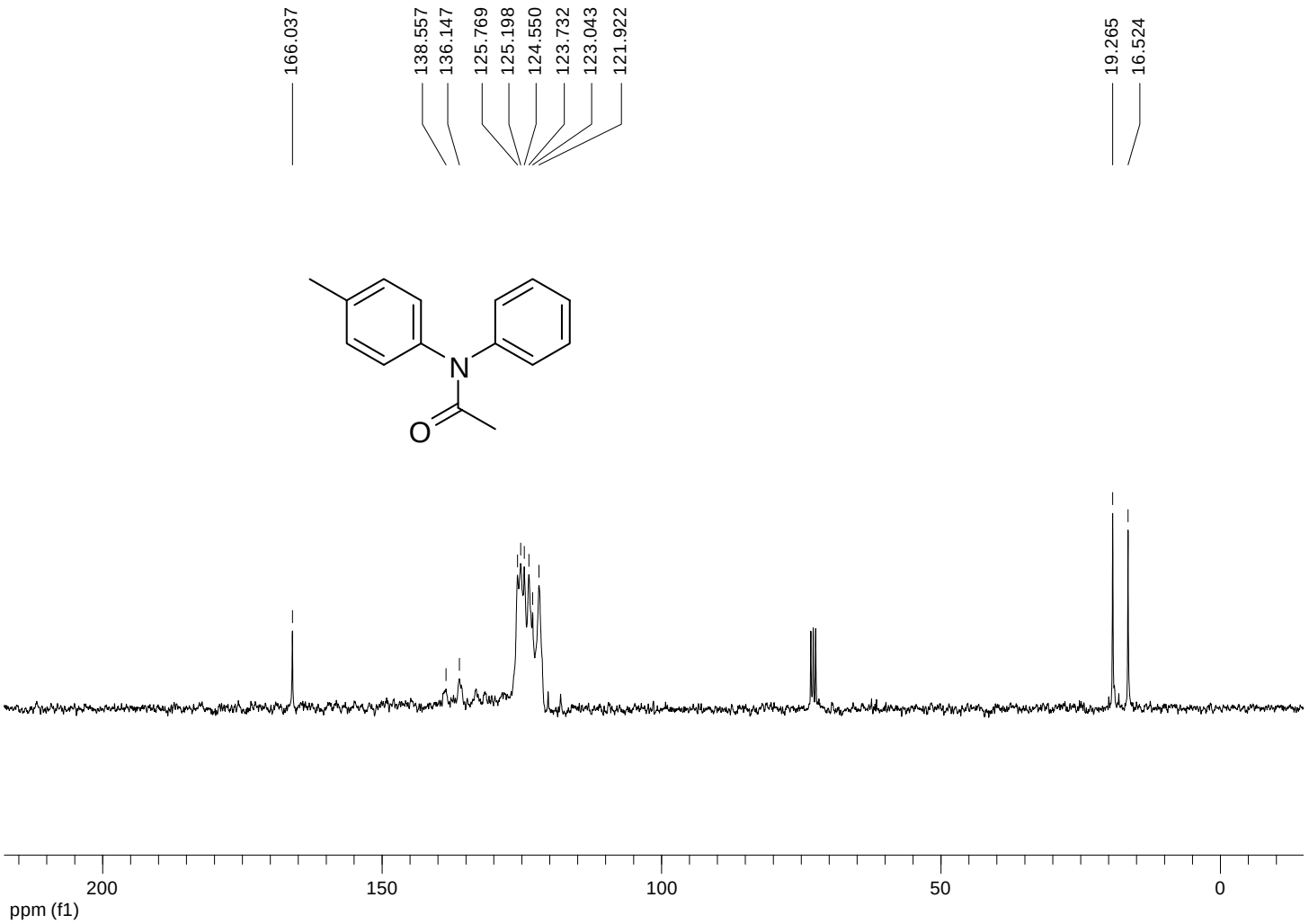
3.01
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


166.037
138.557
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125.769
125.198
124.550
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123.043
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16.524
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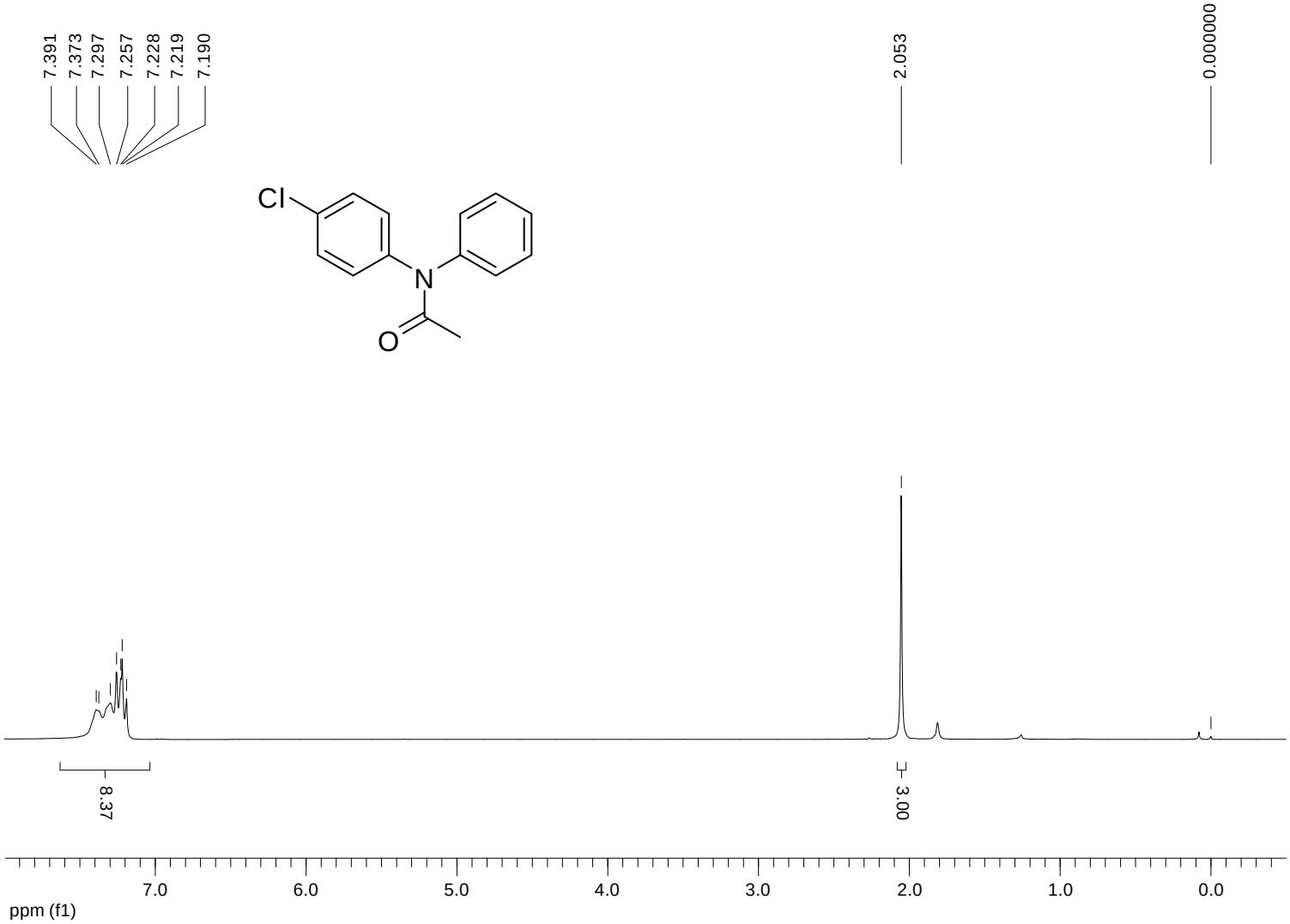
O
200
150
100
50
0
ppm (f1)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0.000000
Cl
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O
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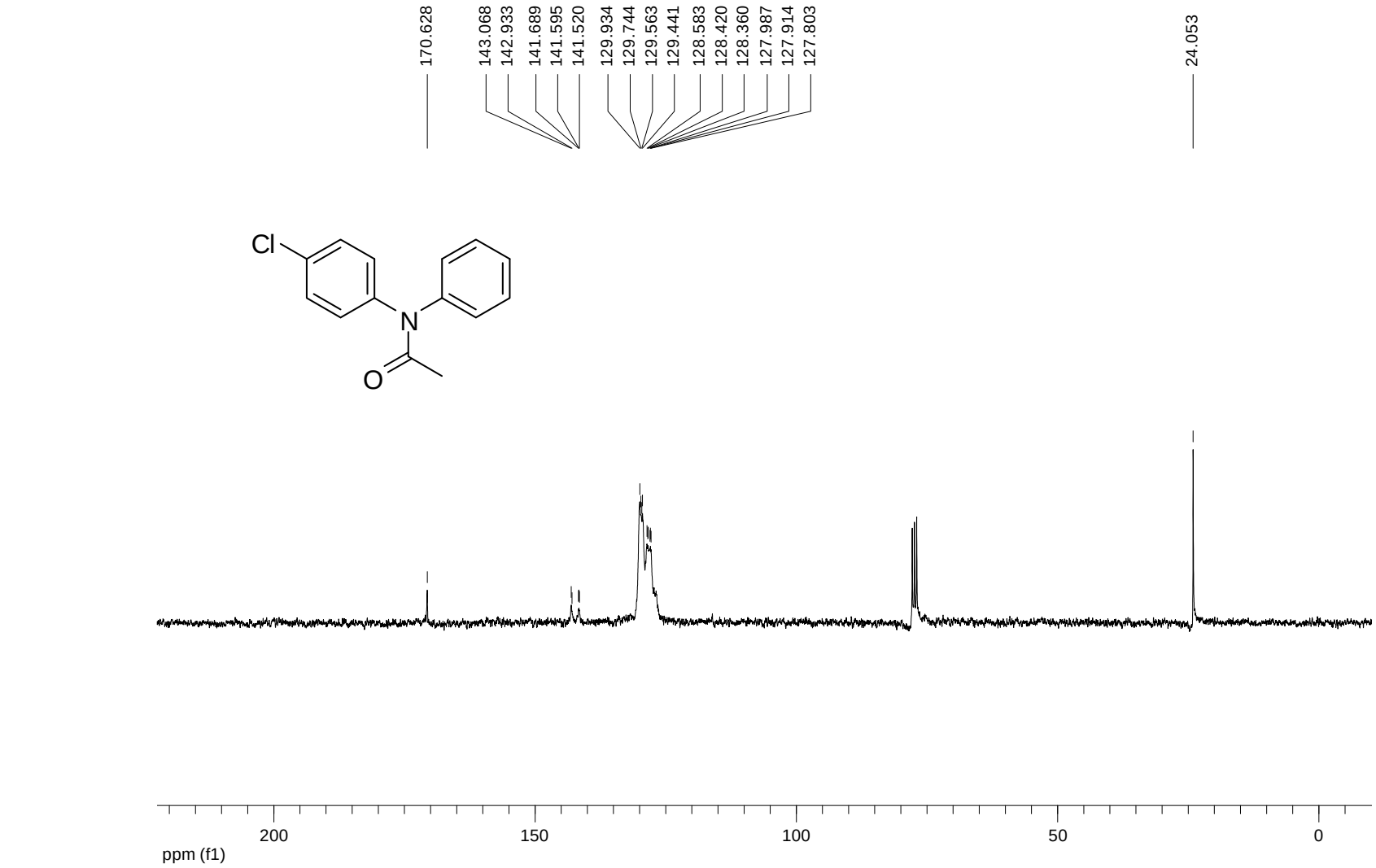
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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141.595
141.520
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129.744
129.563
129.441
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128.420
128.360
127.987
127.914
127.803
24.053
Cl
N
O
200
150
100
50
0
ppm (f1)


7.469
7.445
7.258
7.232
7.209
7.143
7.121
7.096
7.080
2.270
0.000000
N
O
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7.0
6.0
5.0
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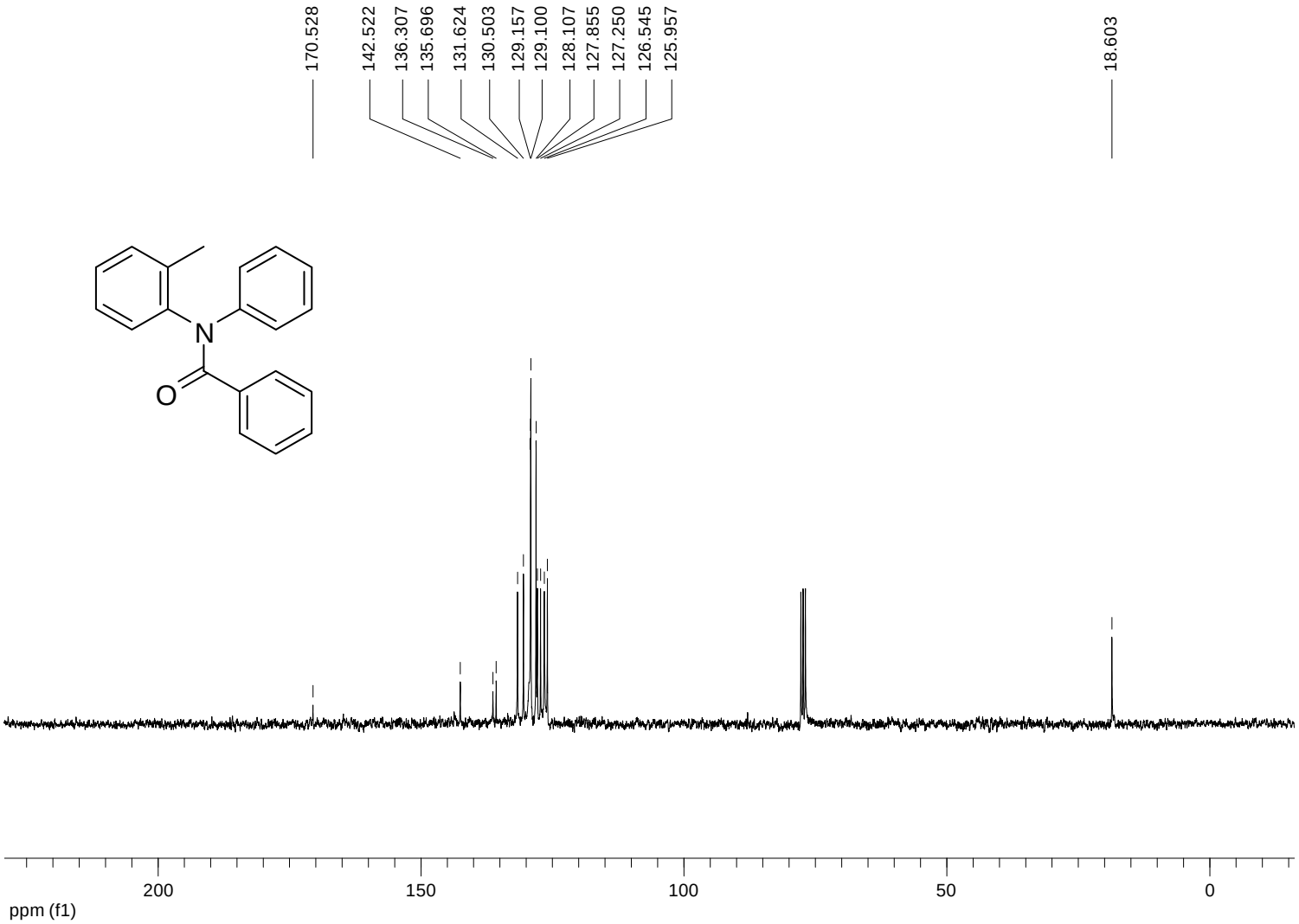
0.0
ppm (f1)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142.522
136.307
135.696
131.624
130.503
129.157
129.100
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O
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150
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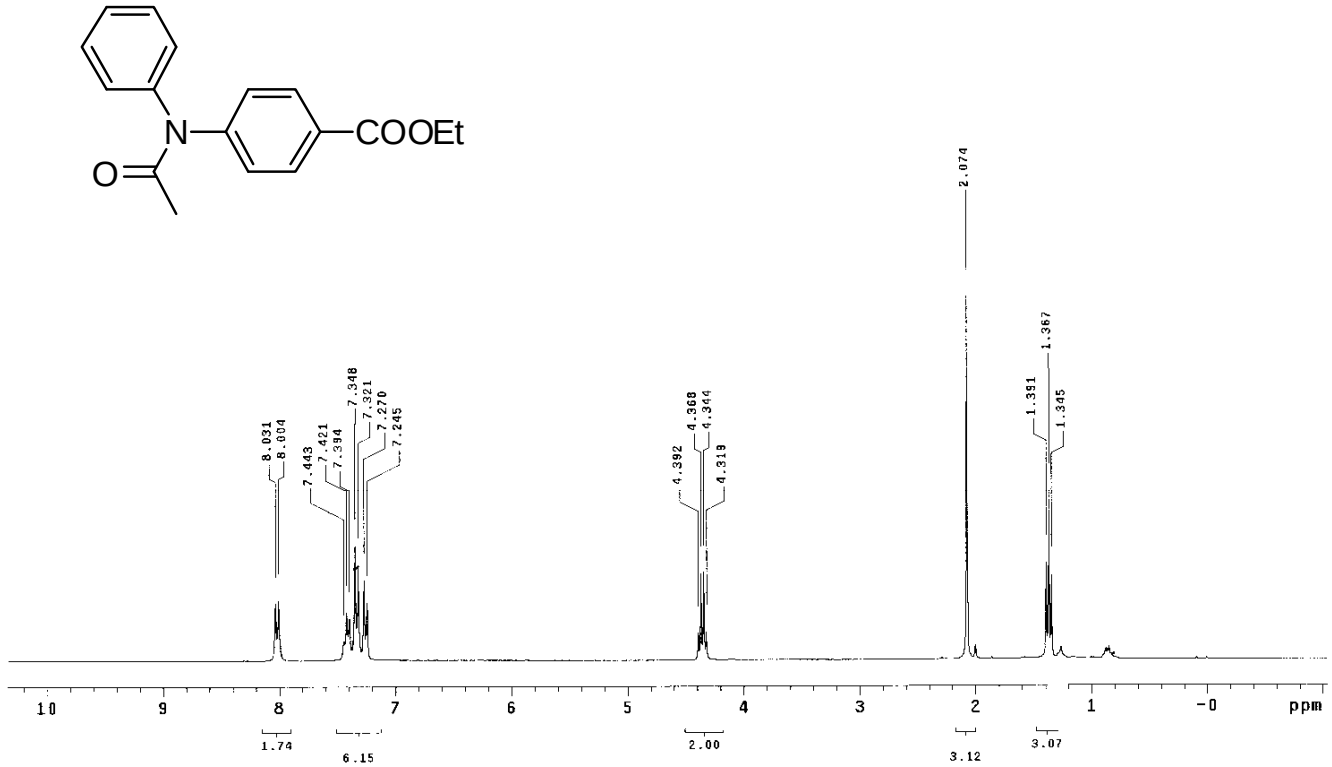
ppm (f1)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O
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7.443
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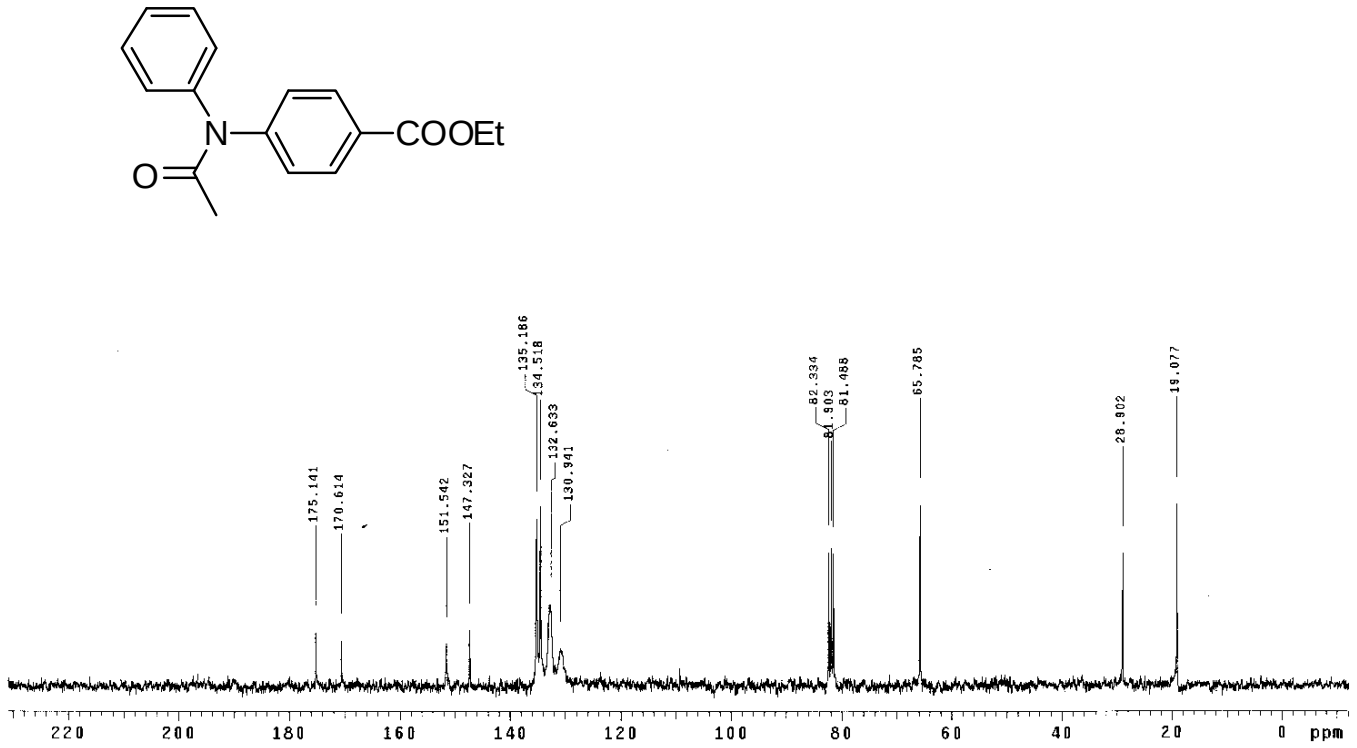
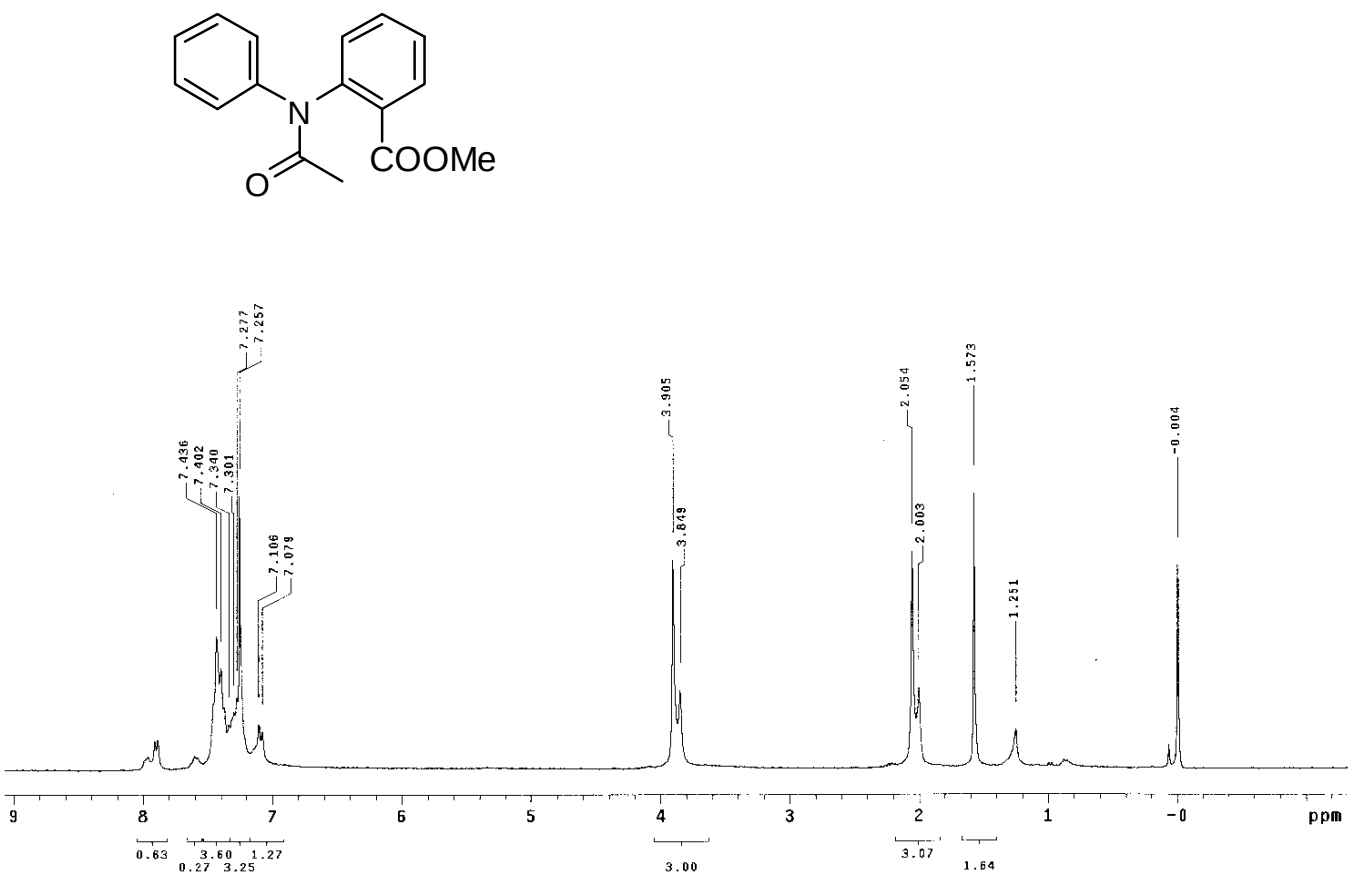
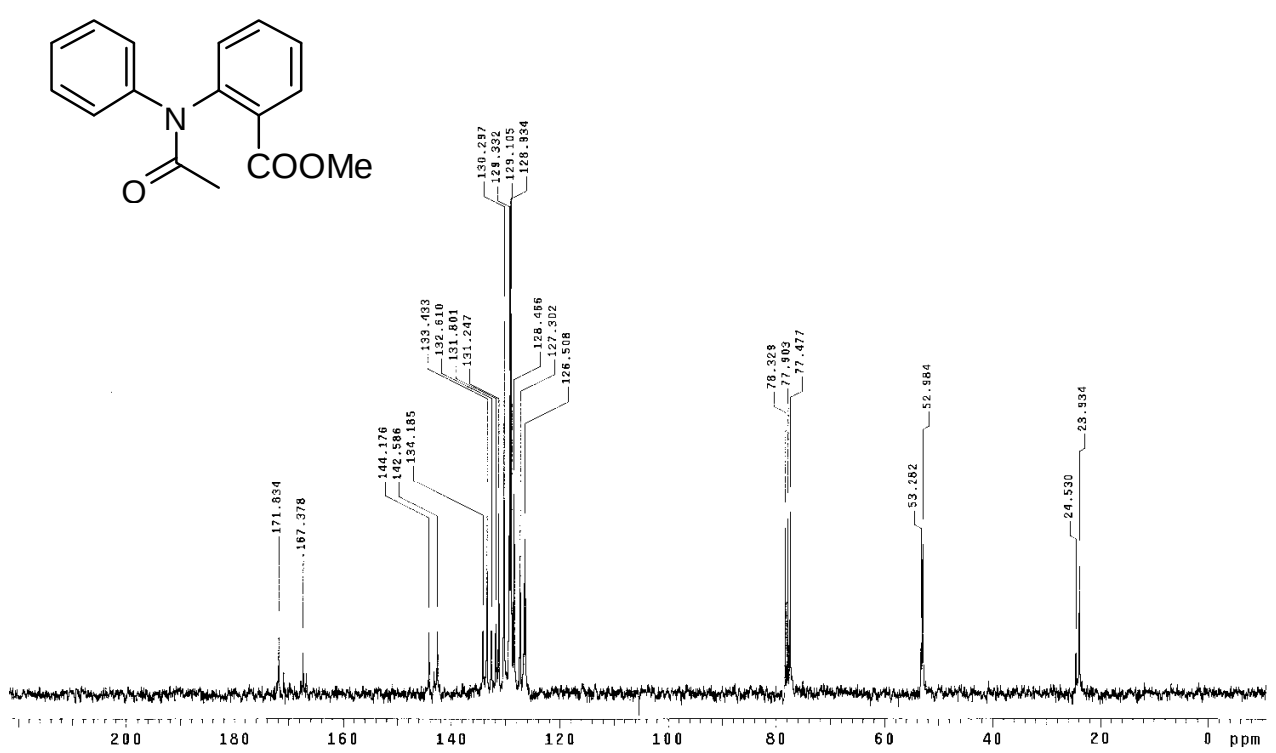
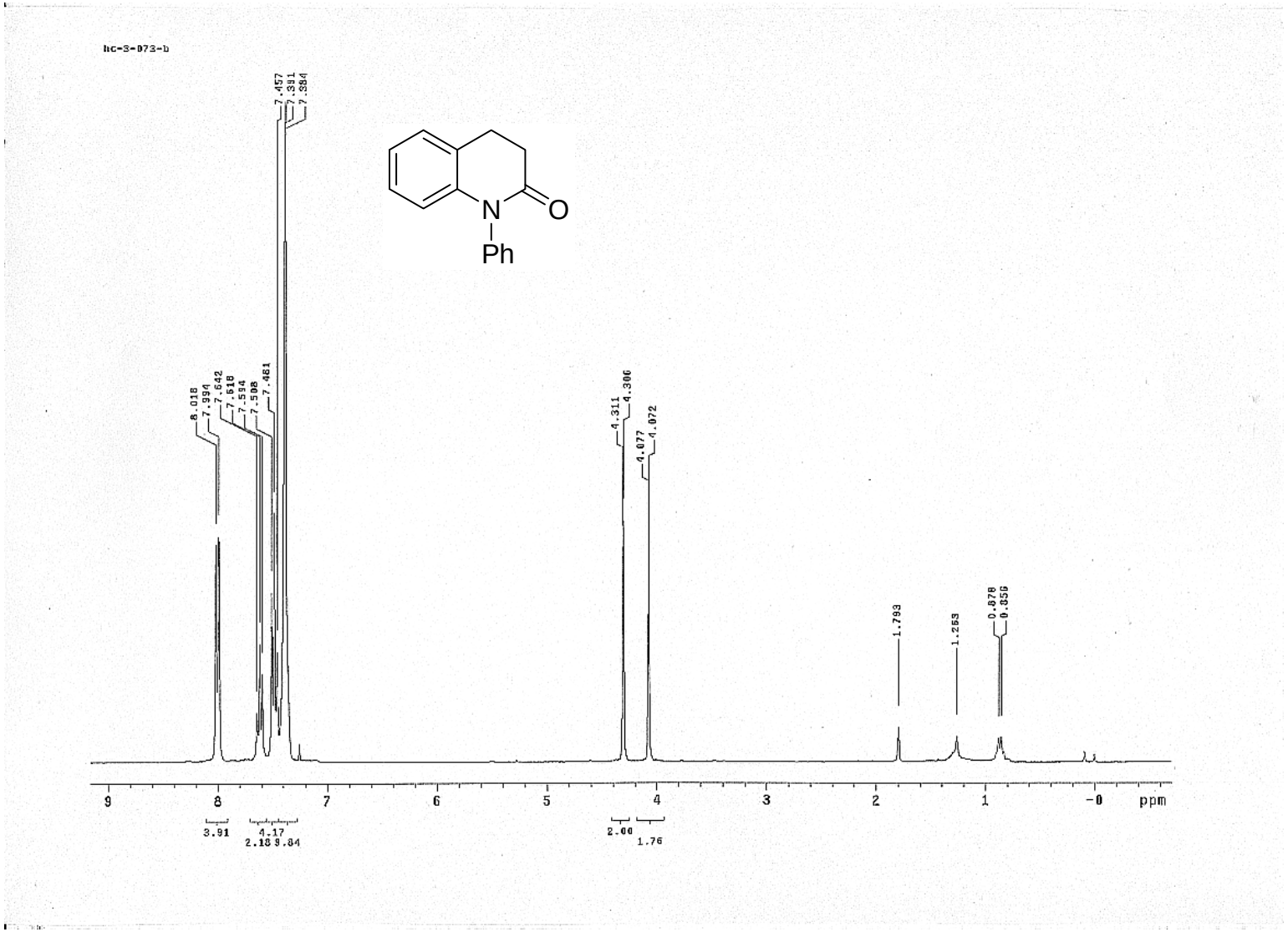
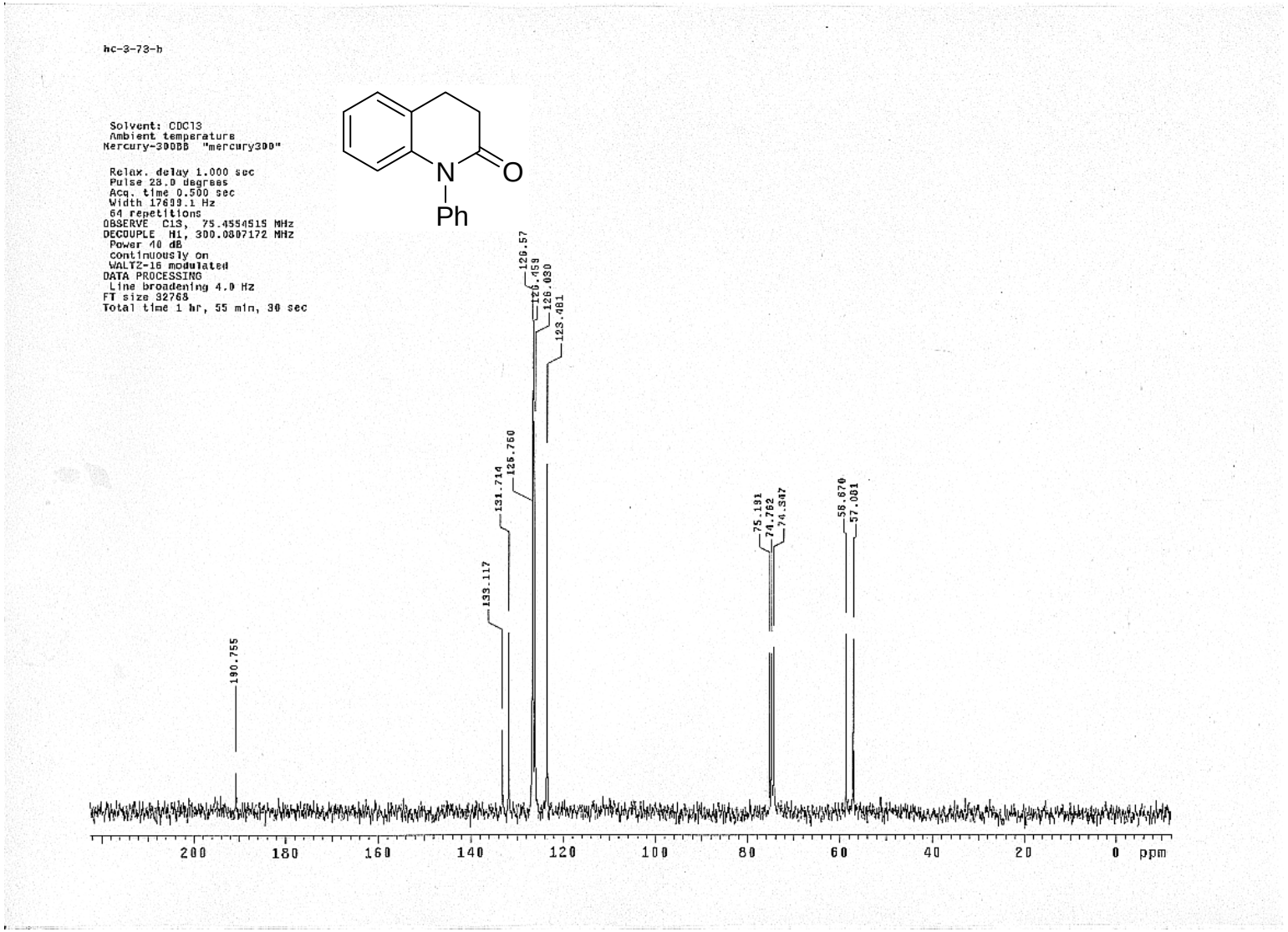
7.394
7.348
7.321
7.270
7.245
4.392
4.368
4.344
4.319
2.074
1.391
1.367
1.345
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.74
6.15
2.00
3.12
3.07

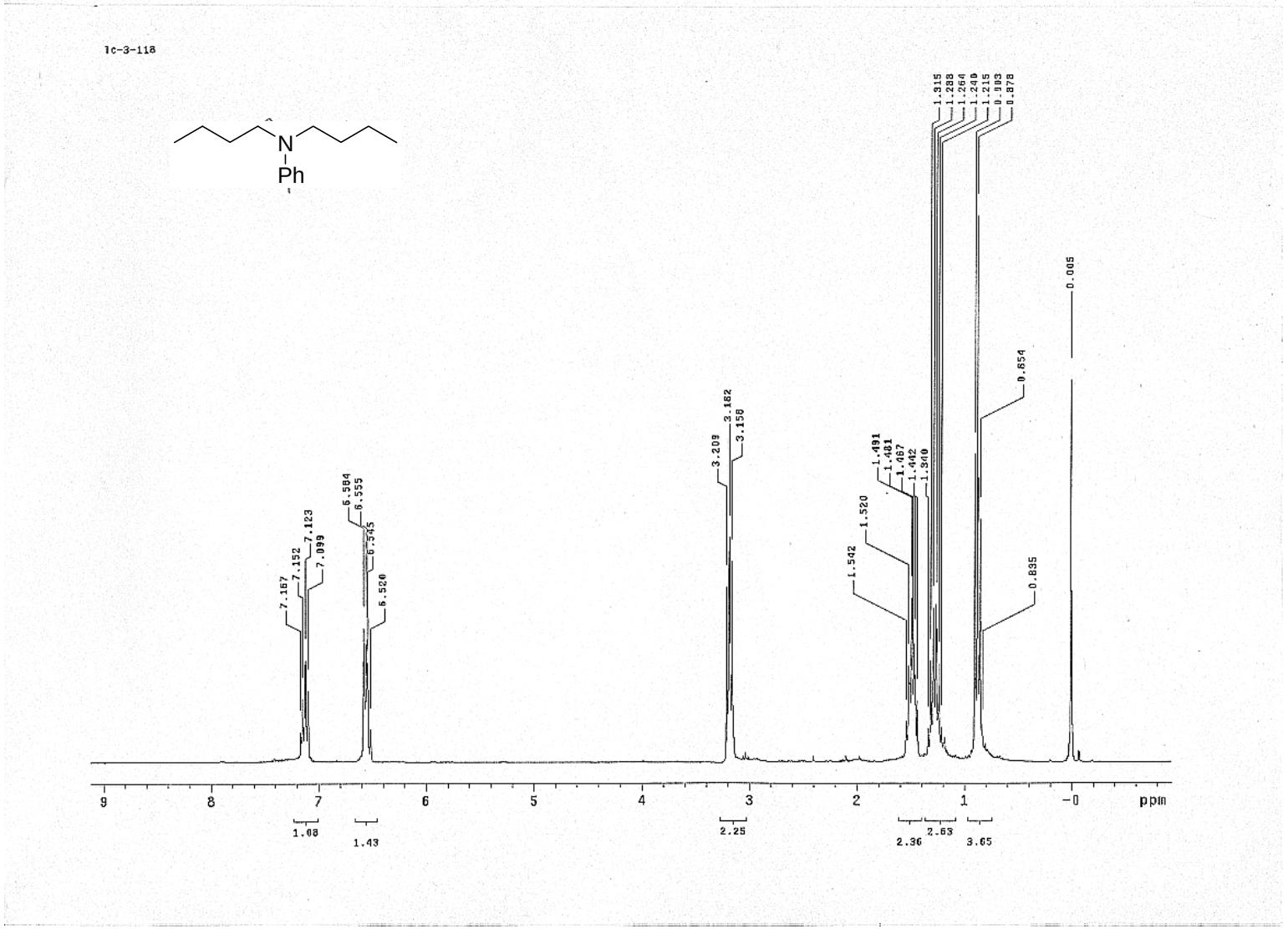

N
O
COOEt
175.141
170.614
151.542
147.327
135.186
134.518
132.633
130.941
82.334
81.903
81.488
65.785
28.902
19.077
220
200
180
160
140
120
100
80
60
40
20
0
ppm


N
O
COOMe
7.436
7.402
7.340
7.301
7.277
7.257
7.106
7.079
3.905
3.849
2.054
2.003
1.573
1.251
-0.004
9
8
7
6
5
4
3
2
1
-0
ppm
0.63
3.60
1.27
0.27
3.25
3.00
3.07
1.64


N
O
COOMe
171.834
167.378
144.176
142.586
134.185
133.433
132.610
131.801
131.247
130.287
129.332
129.105
128.834
128.456
127.302
126.508
78.328
77.903
77.477
52.984
53.282
23.934
24.530
200
180
160
140
120
100
80
60
40
20
0
ppm


hc-3-073-b
8.018
7.994
7.642
7.618
7.514
7.508
7.481
7.457
7.391
7.384
4.311
4.306
4.077
4.072
1.793
1.253
0.878
0.859
N
O
Ph
9
8
7
6
5
4
3
2
1
-0
ppm
3.91
4.17
2.18
3.84
2.00
1.76


hc-3-73-b
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.500 sec
Width 17699.1 Hz
64 repetitions
OBSERVE C13, 75.4554515 MHz
DECOUPLE H1, 300.0807172 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 32768
Total time 1 hr, 55 min, 30 sec
N
O
Ph
190.755
133.117
131.714
126.760
126.57
126.459
126.080
123.481
75.181
74.762
74.347
58.670
57.081
200
180
160
140
120
100
80
60
40
20
0
ppm


lc-3-118
N
Ph
7.167
7.152
7.123
7.099
6.584
6.555
6.545
6.520
3.209
3.182
3.156
1.542
1.520
1.491
1.481
1.467
1.442
1.340
1.315
1.288
1.264
1.240
1.215
0.903
0.878
0.854
0.835
0.005
9
8
7
6
5
4
3
2
1
-0
ppm
1.08
1.43
2.25
2.36
2.63
3.65

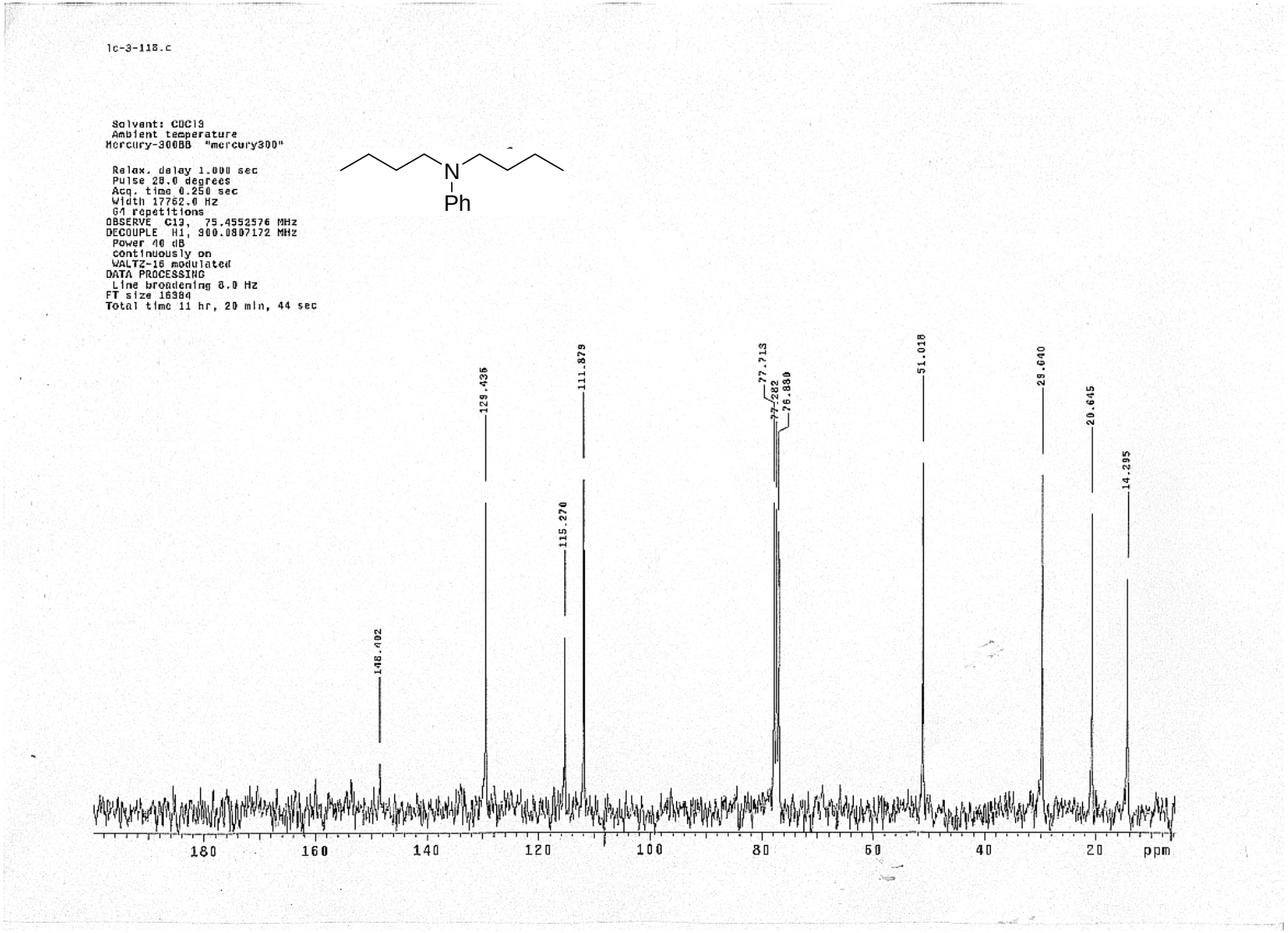
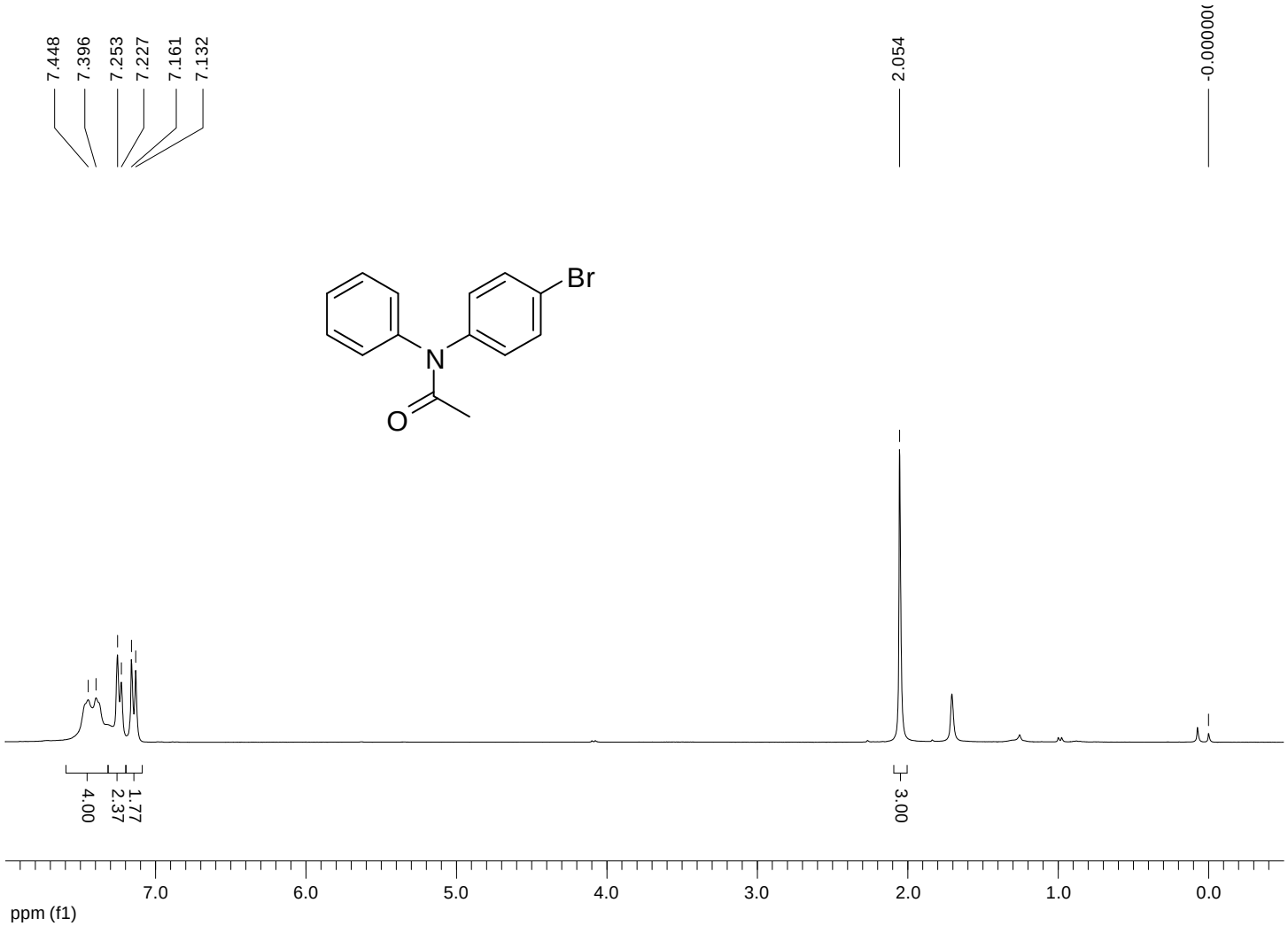
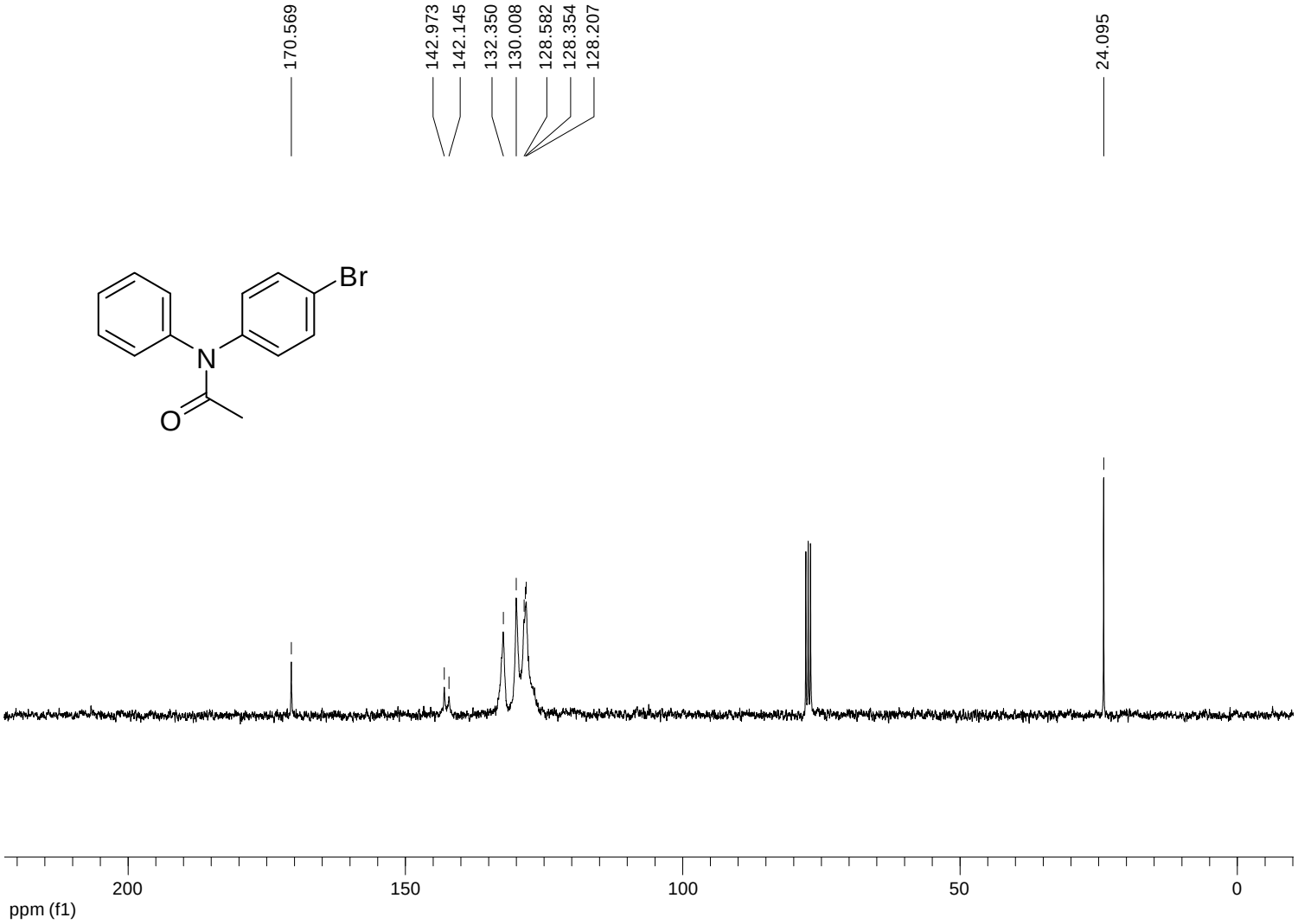
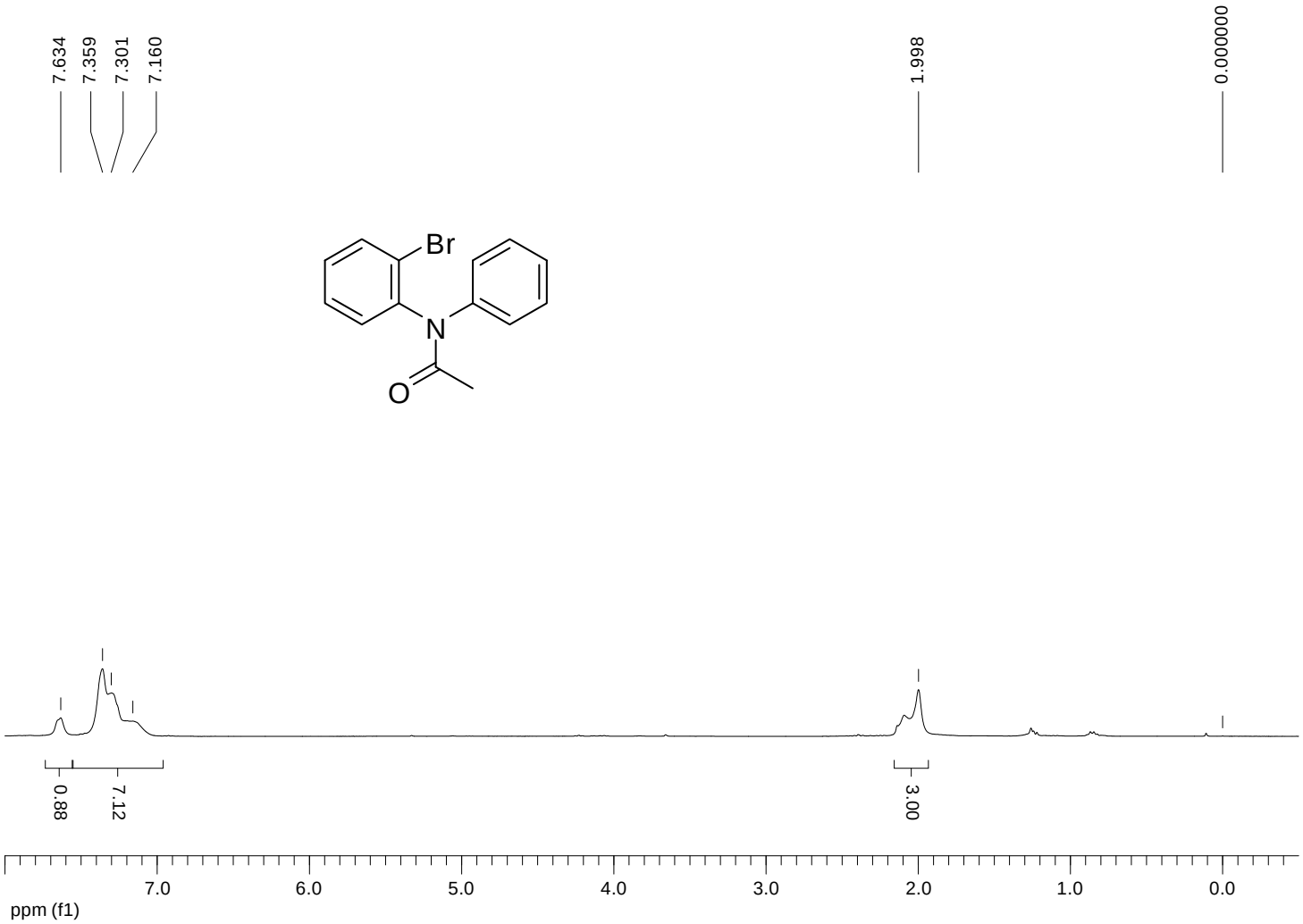
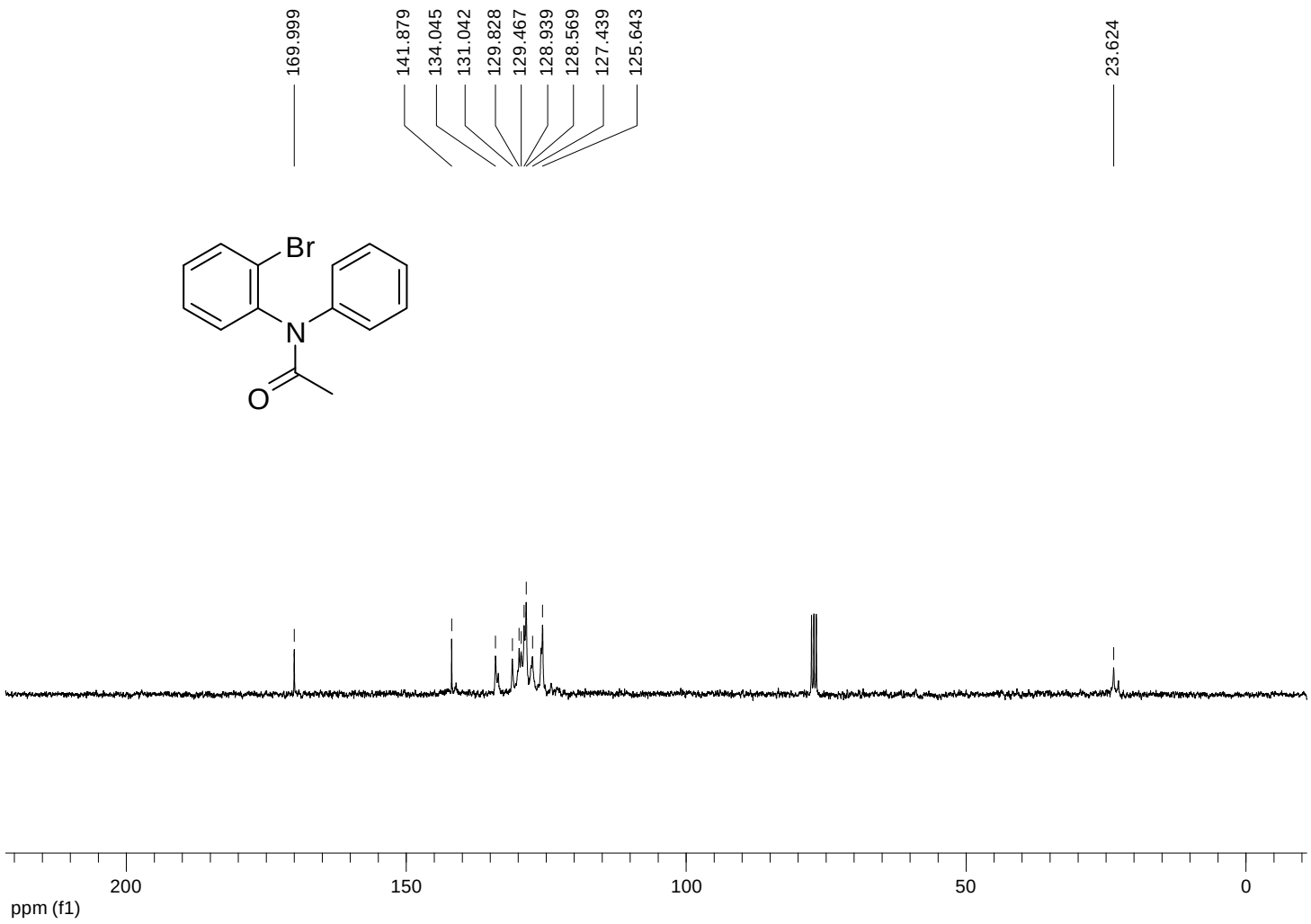

lc-3-118.c
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"
Relax. delay 1.000 sec
Pulse 28.0 degrees
Acq. time 0.250 sec
Width 17762.6 Hz
64 repetitions
OBSERVE C13, 75.4552576 MHz
DECOUPLE H1, 300.0807172 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.0 Hz
FT size 16384
Total time 11 hr, 20 min, 44 sec
N
Ph
148.102
129.436
115.270
111.879
77.713
77.282
76.850
51.018
29.640
20.645
14.295
180
160
140
120
100
80
60
40
20
ppm

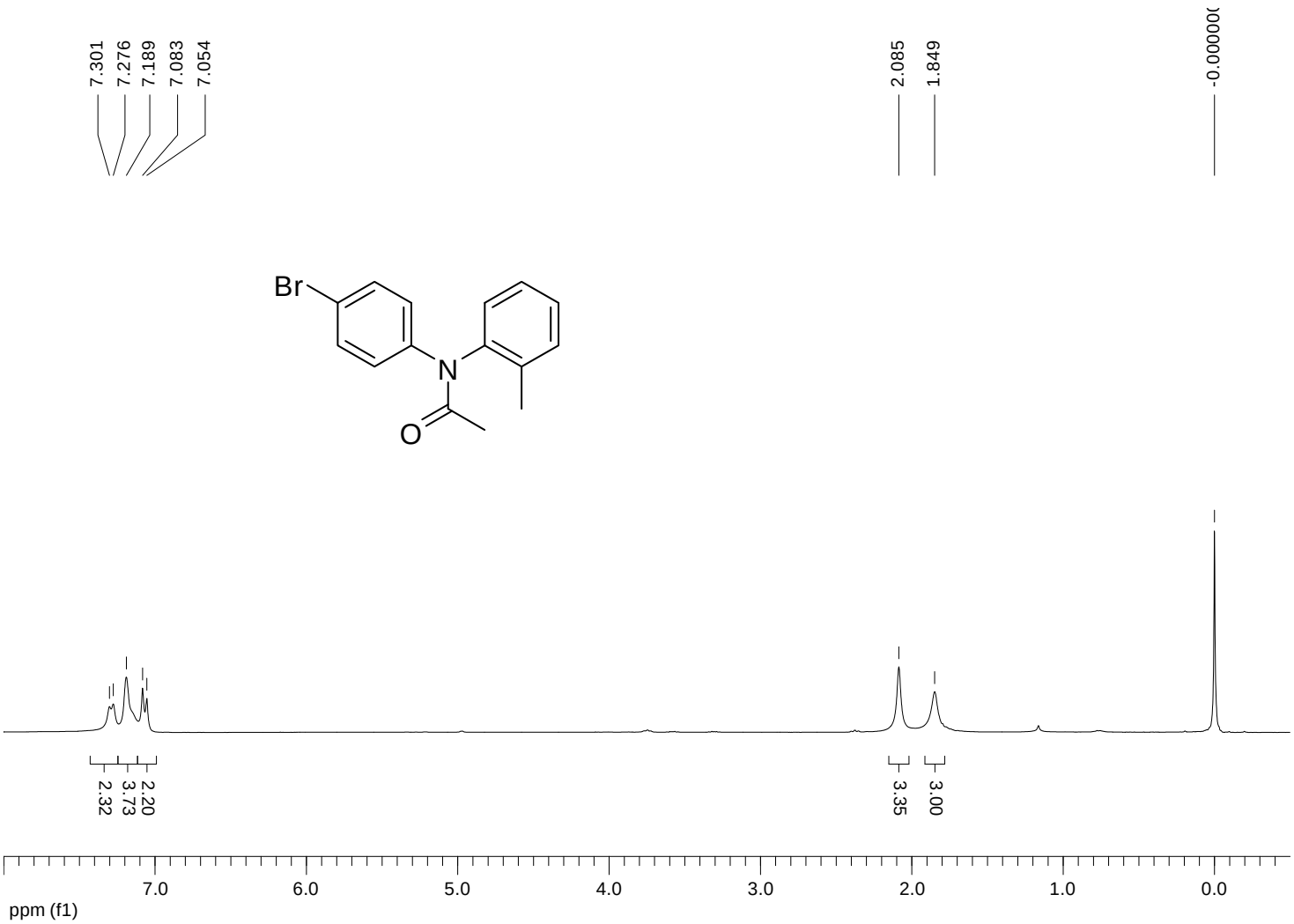
Table3

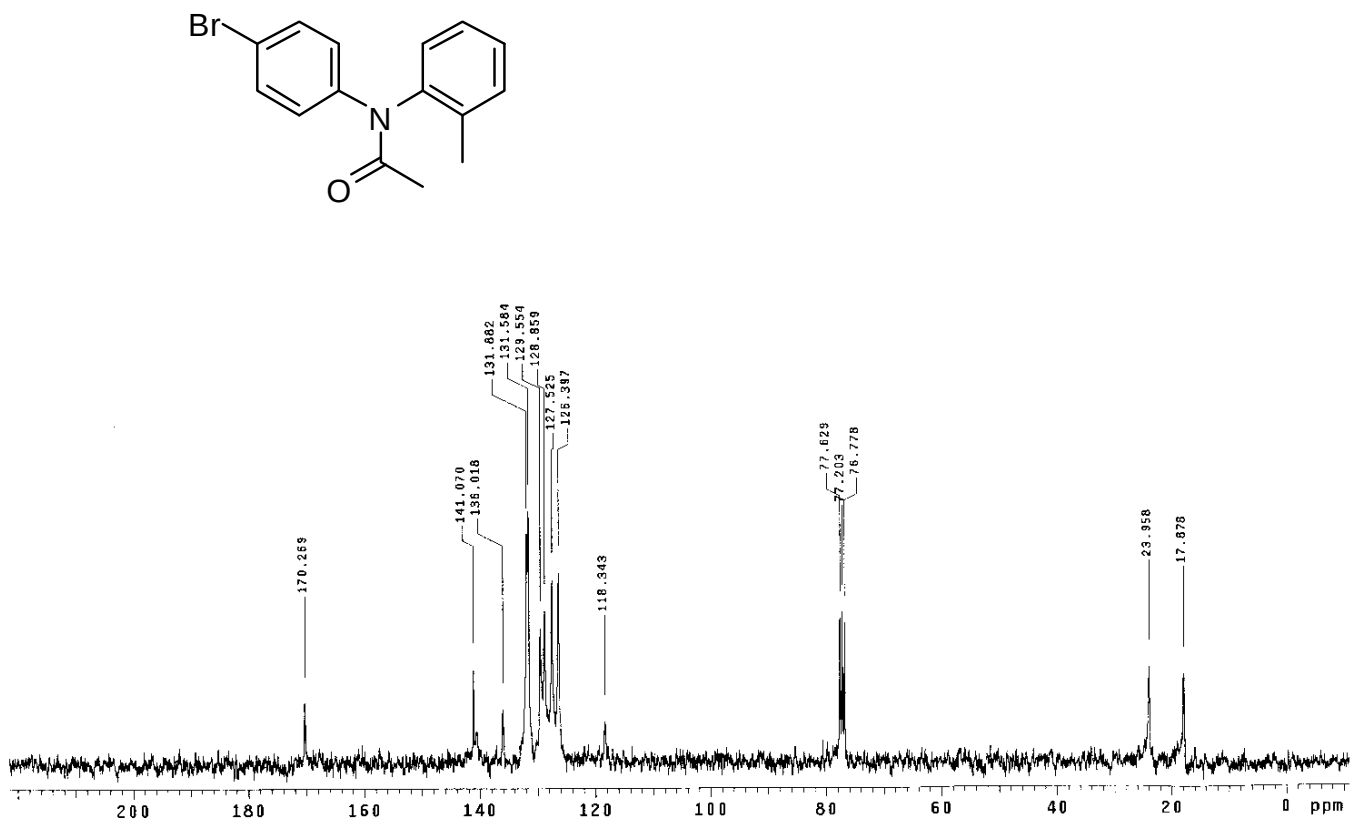

7.448
7.396
7.253
7.227
7.161
7.132
2.054
-0.000000
Br
N
O
4.00
2.37
1.77
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

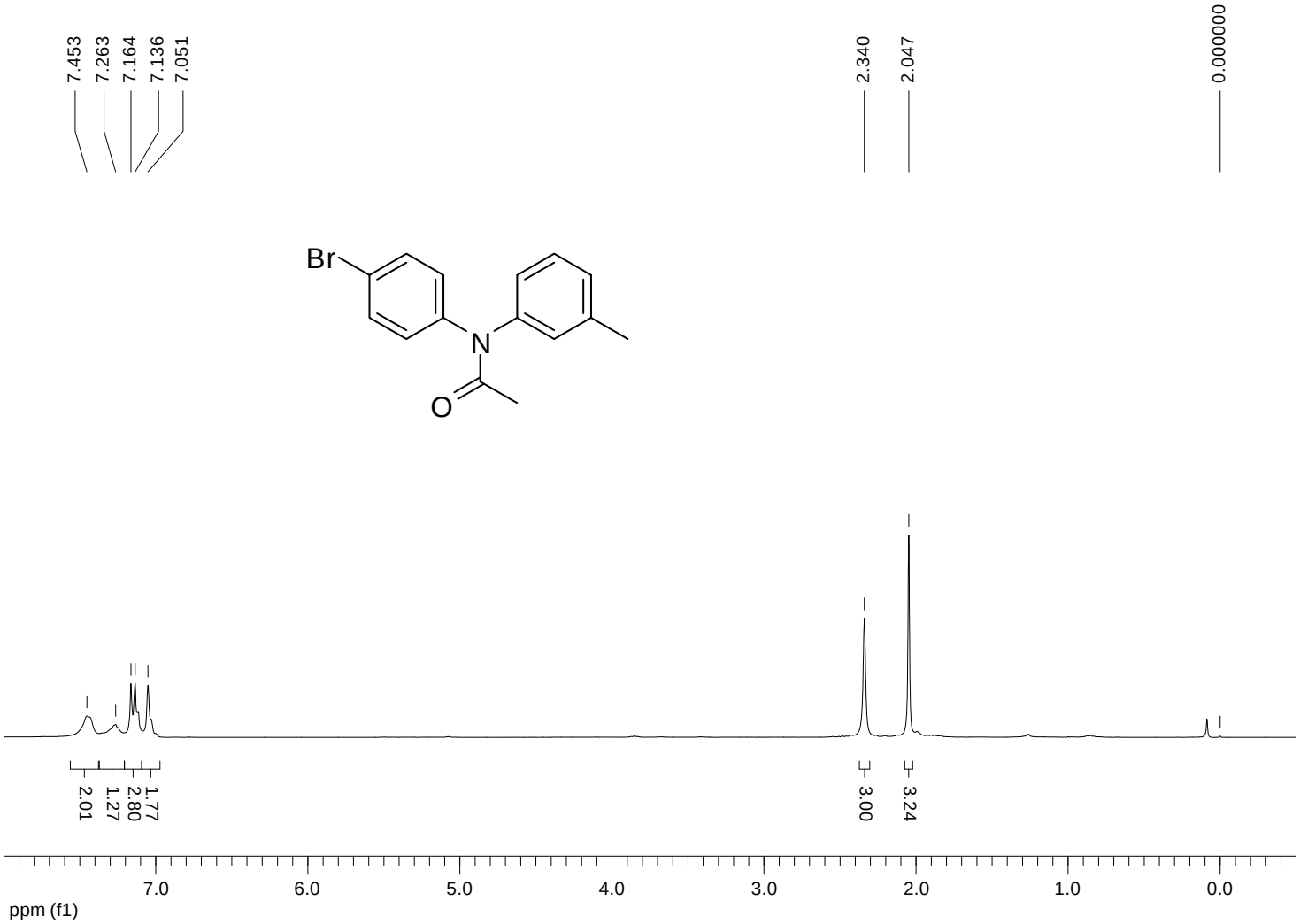

170.569
142.973
142.145
132.350
130.008
128.582
128.354
128.207
24.095
Br
N
O
200
150
100
50
0
ppm (f1)

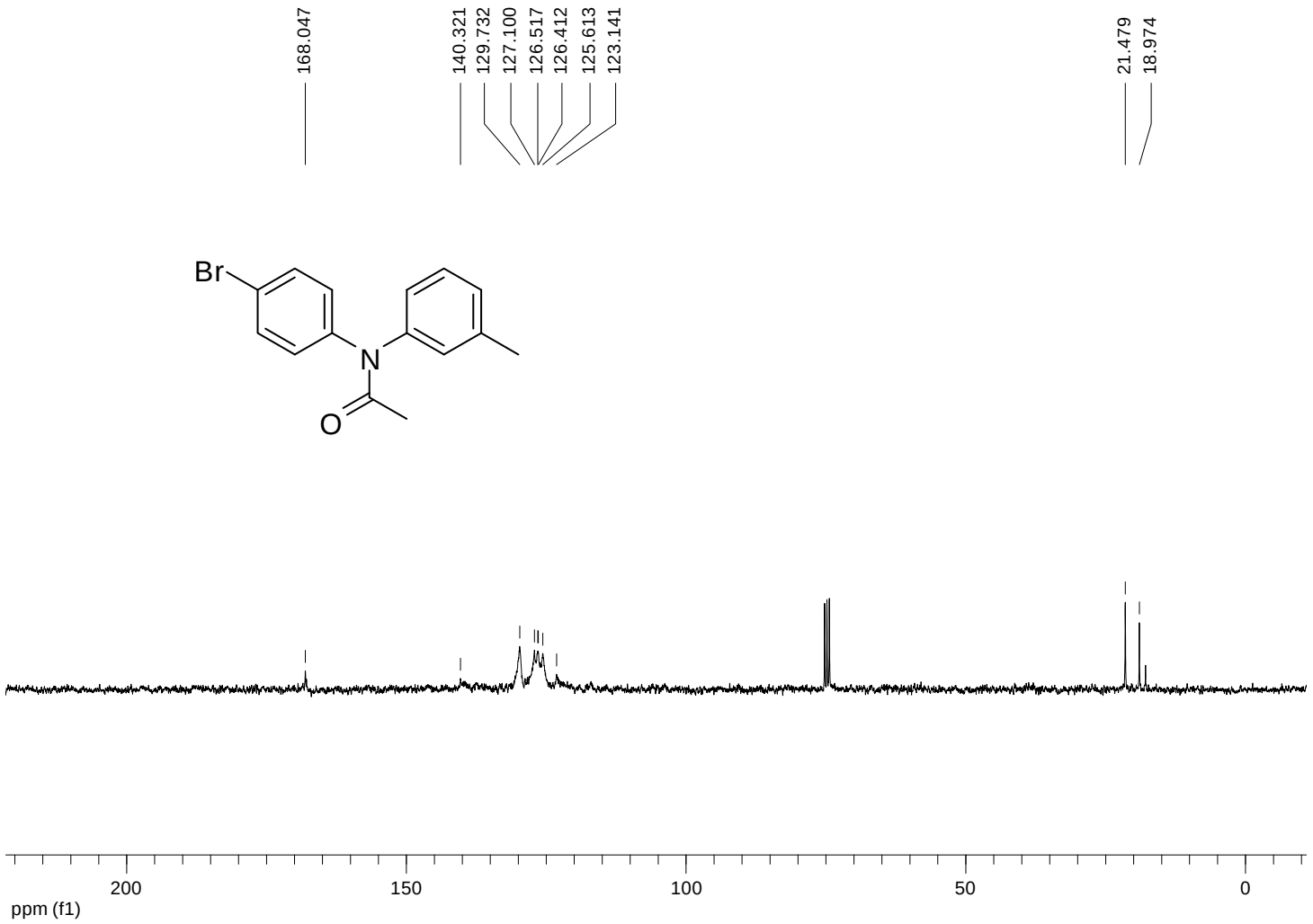

7.634
7.359
7.301
7.160
1.998
0.000000
Br
N
O
0.88
7.12
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

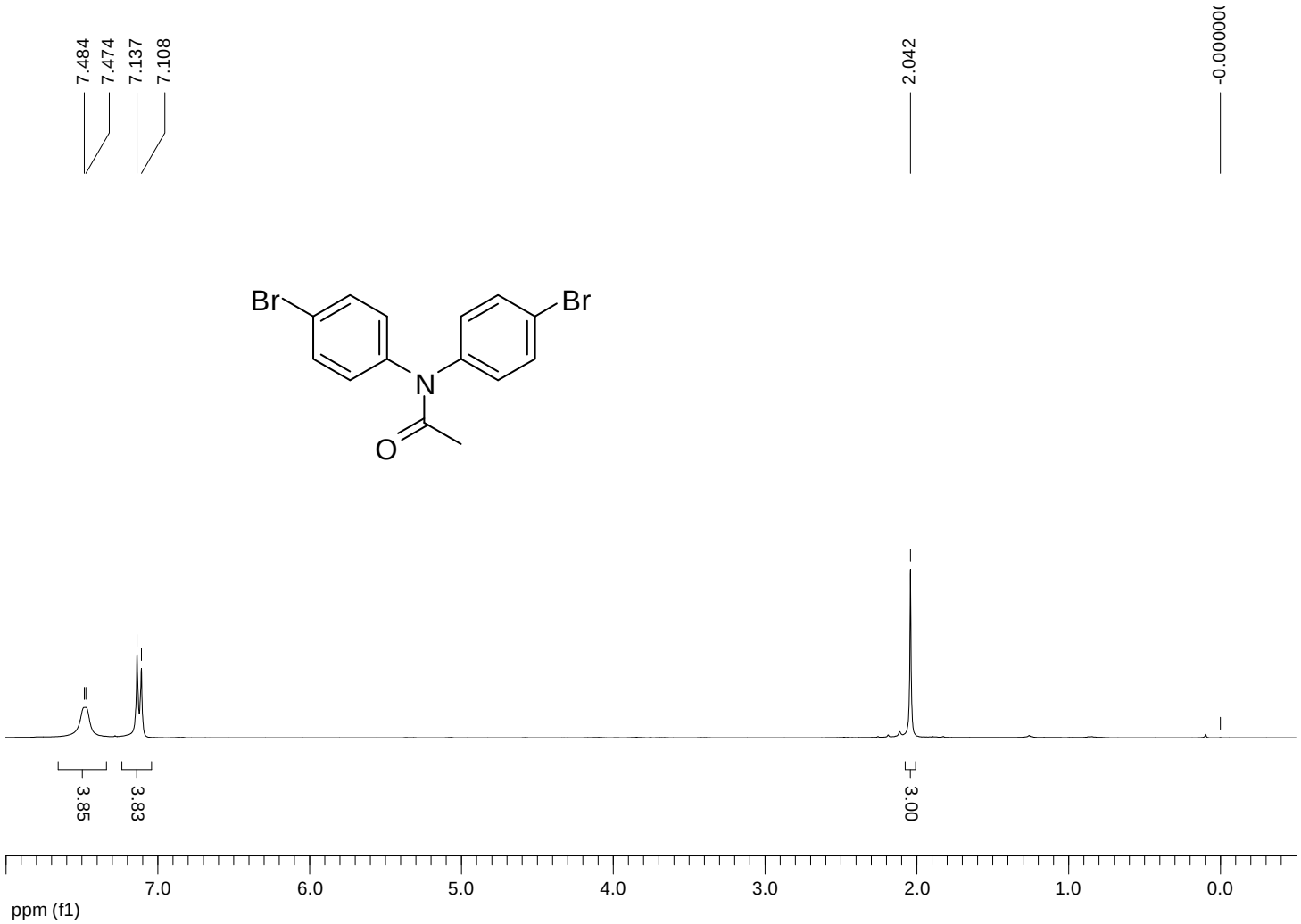

169.999
141.879
134.045
131.042
129.828
129.467
128.939
128.569
127.439
125.643
23.624
Br
N
O
200
150
100
50
0
ppm (f1)

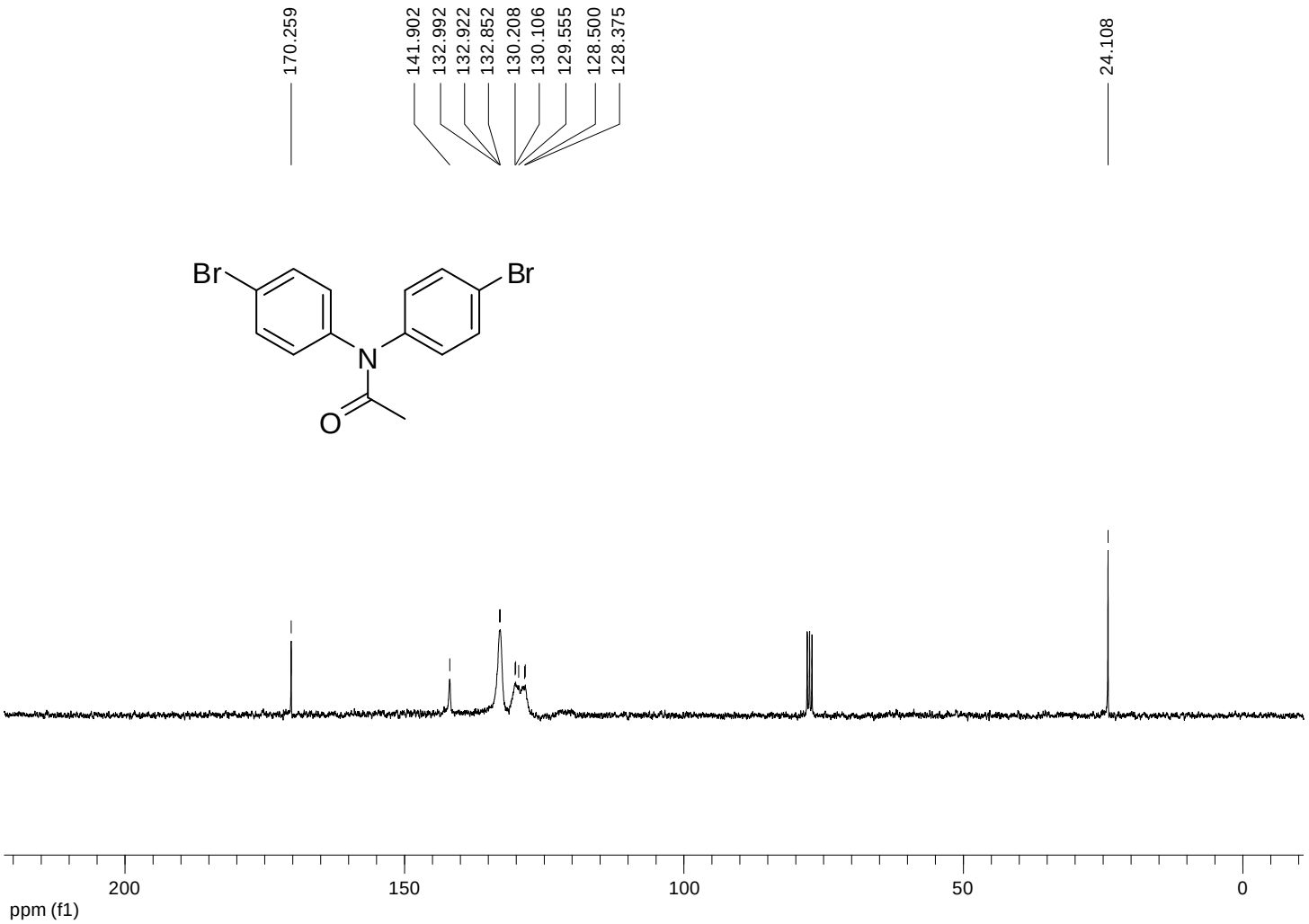

7.301
7.276
7.189
7.083
7.054
2.085
1.849
-0.000000
Br
N
O
2.32
3.73
2.20
3.35
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

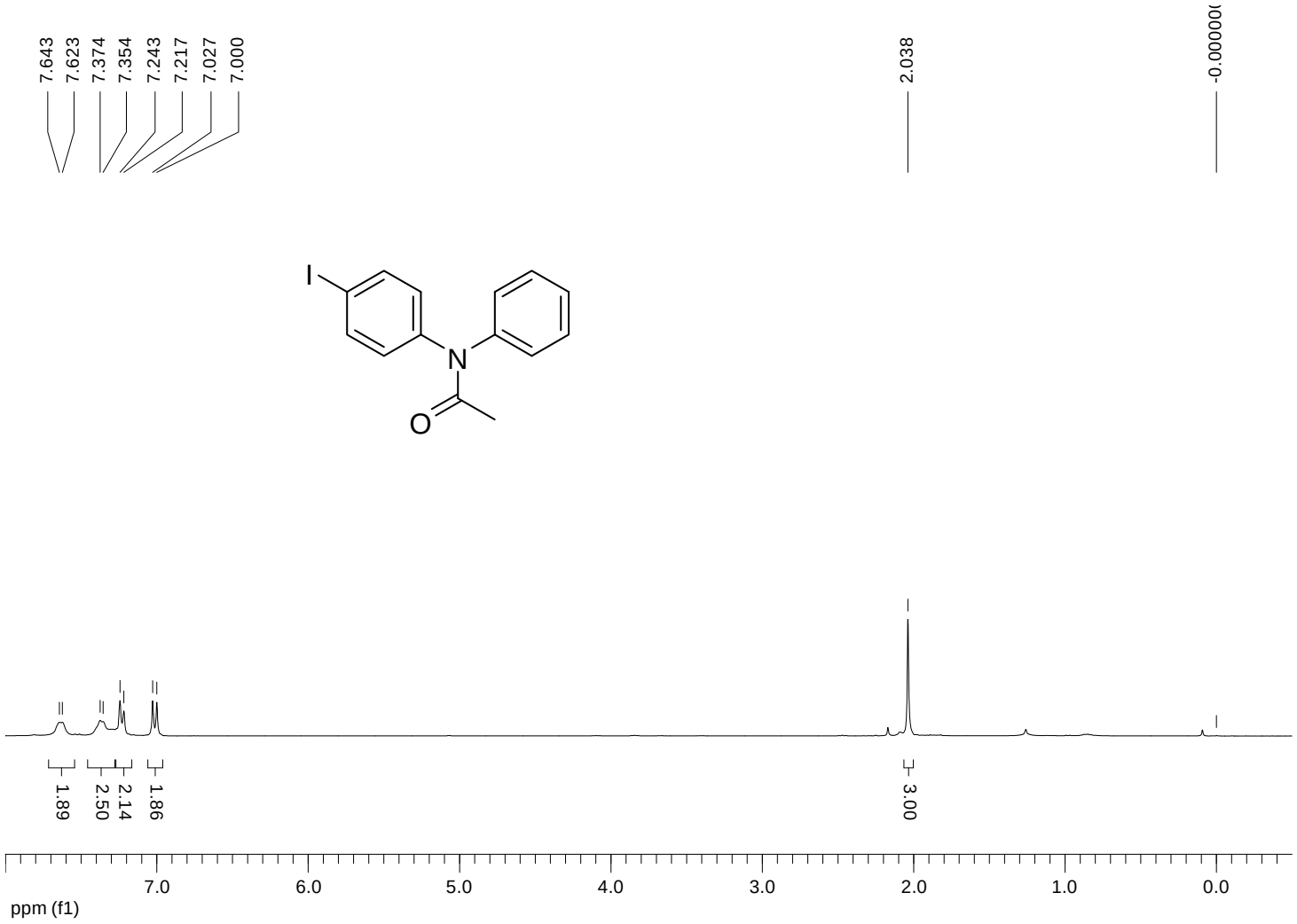

Br
N
O
170.269
141.070
136.018
131.882
131.584
129.554
128.959
127.525
126.397
118.343
77.629
77.203
76.778
23.958
17.878
200
180
160
140
120
100
80
60
40
20
0
ppm

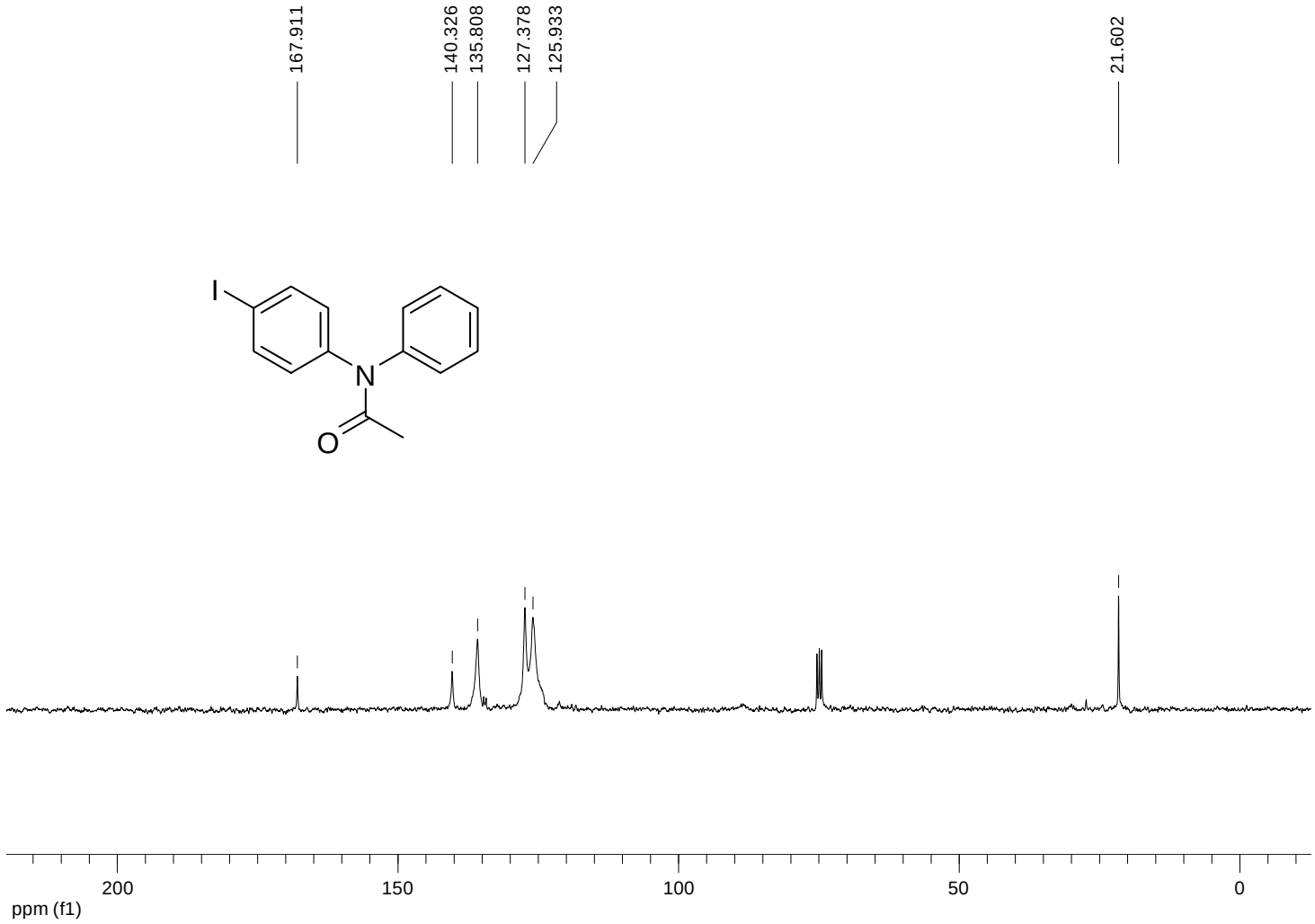

7.453
7.263
7.164
7.136
7.051
2.340
2.047
0.000000
Br
N
O
2.01
1.27
2.80
1.77
3.00
3.24
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

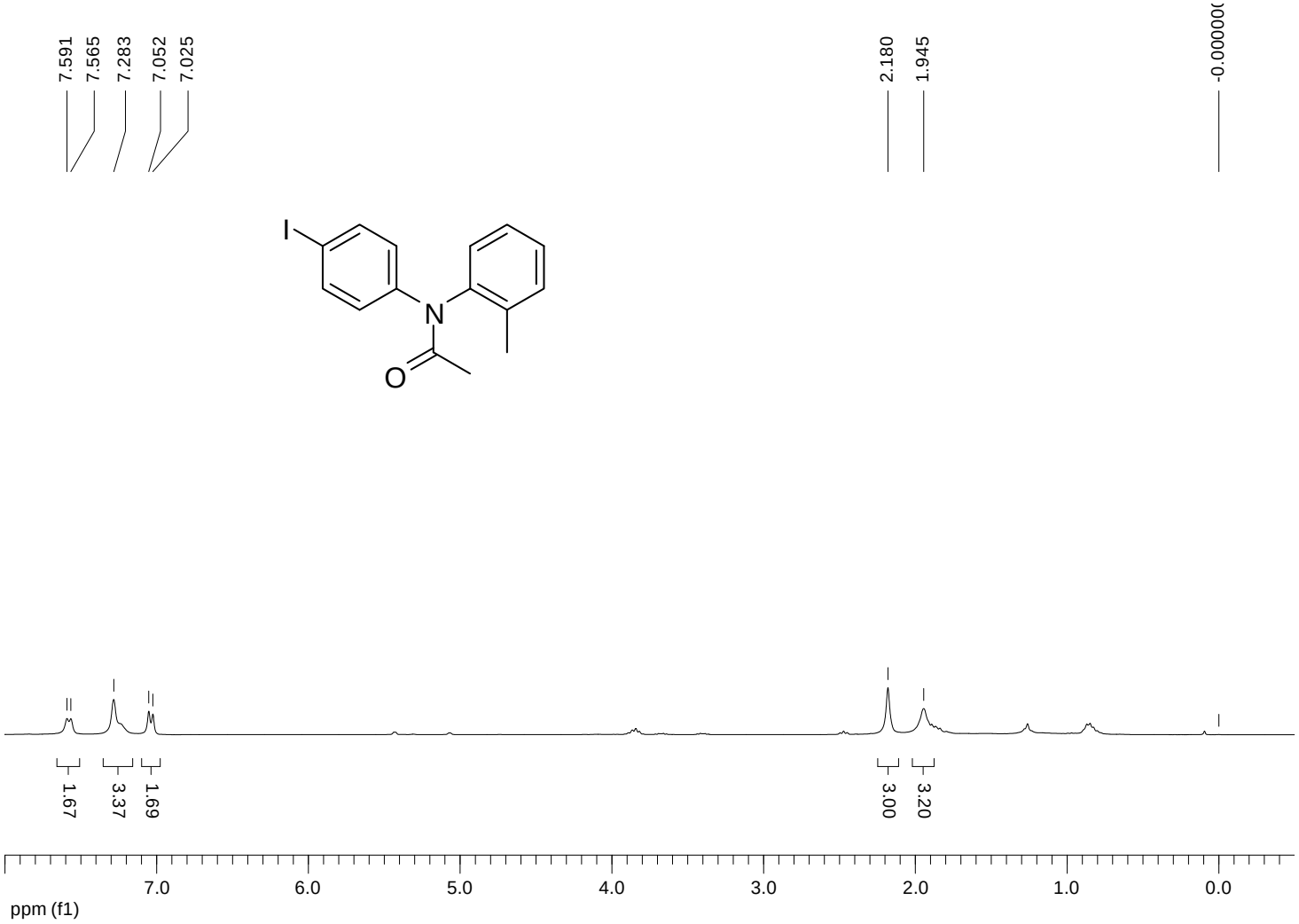

168.047
140.321
129.732
127.100
126.517
126.412
125.613
123.141
21.479
18.974
Br
N
O
200
150
100
50
0
ppm (f1)

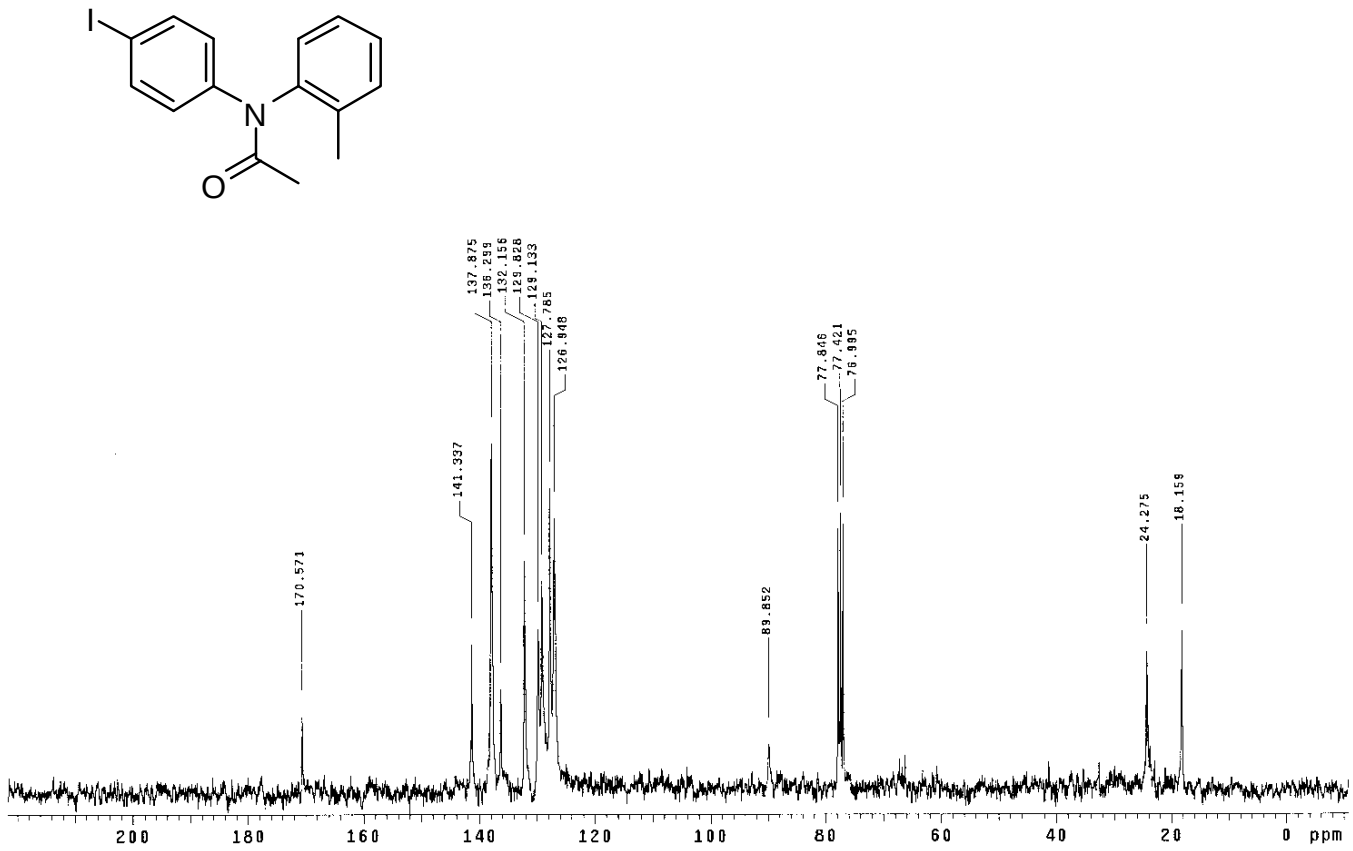

7.484
7.474
7.137
7.108
2.042
-0.000001
Br
Br
N
O
3.85
3.83
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

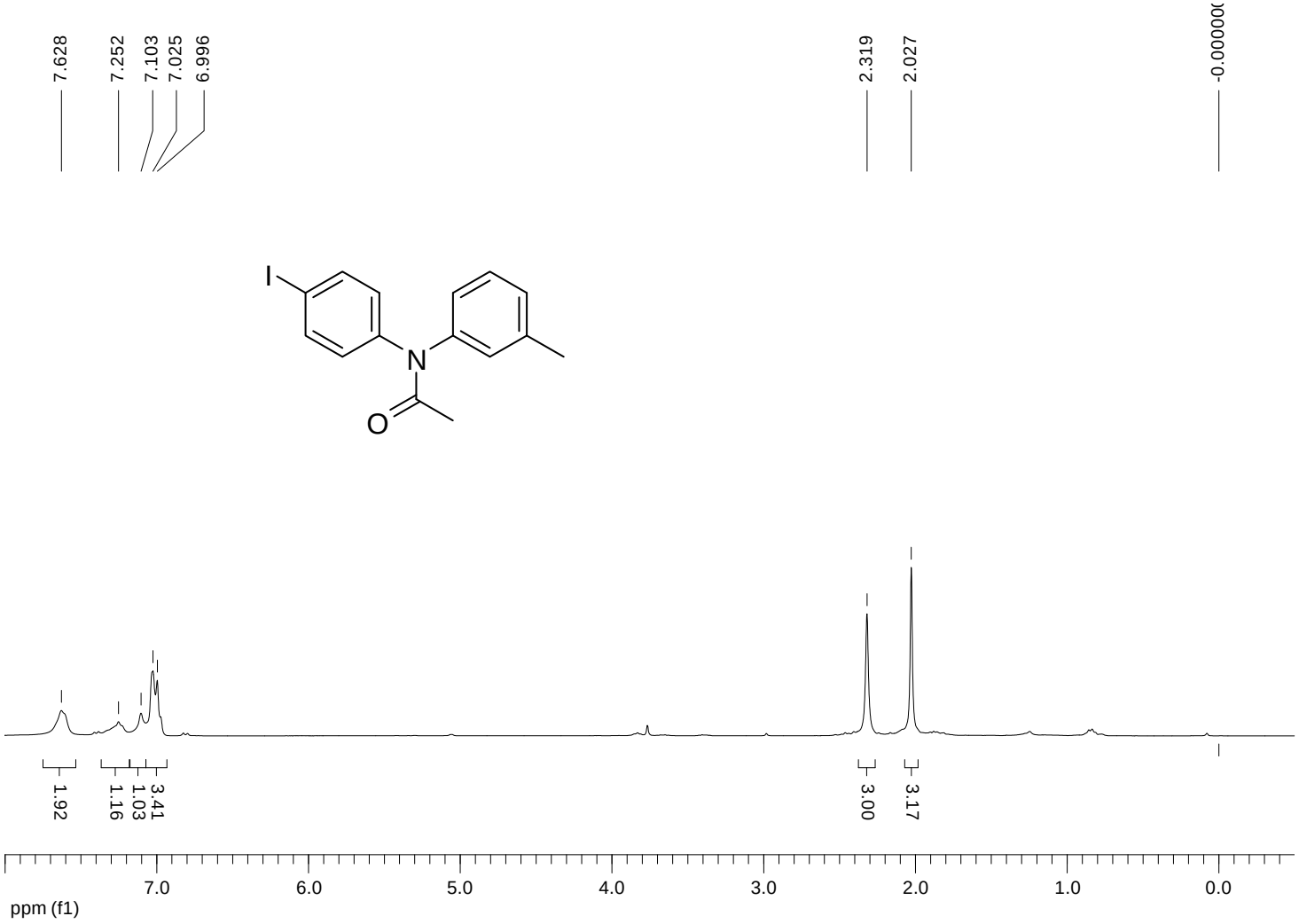

170.259
141.902
132.992
132.922
132.852
130.208
130.106
129.555
128.500
128.375
24.108
Br
Br
N
O
200
150
100
50
0
ppm (f1)

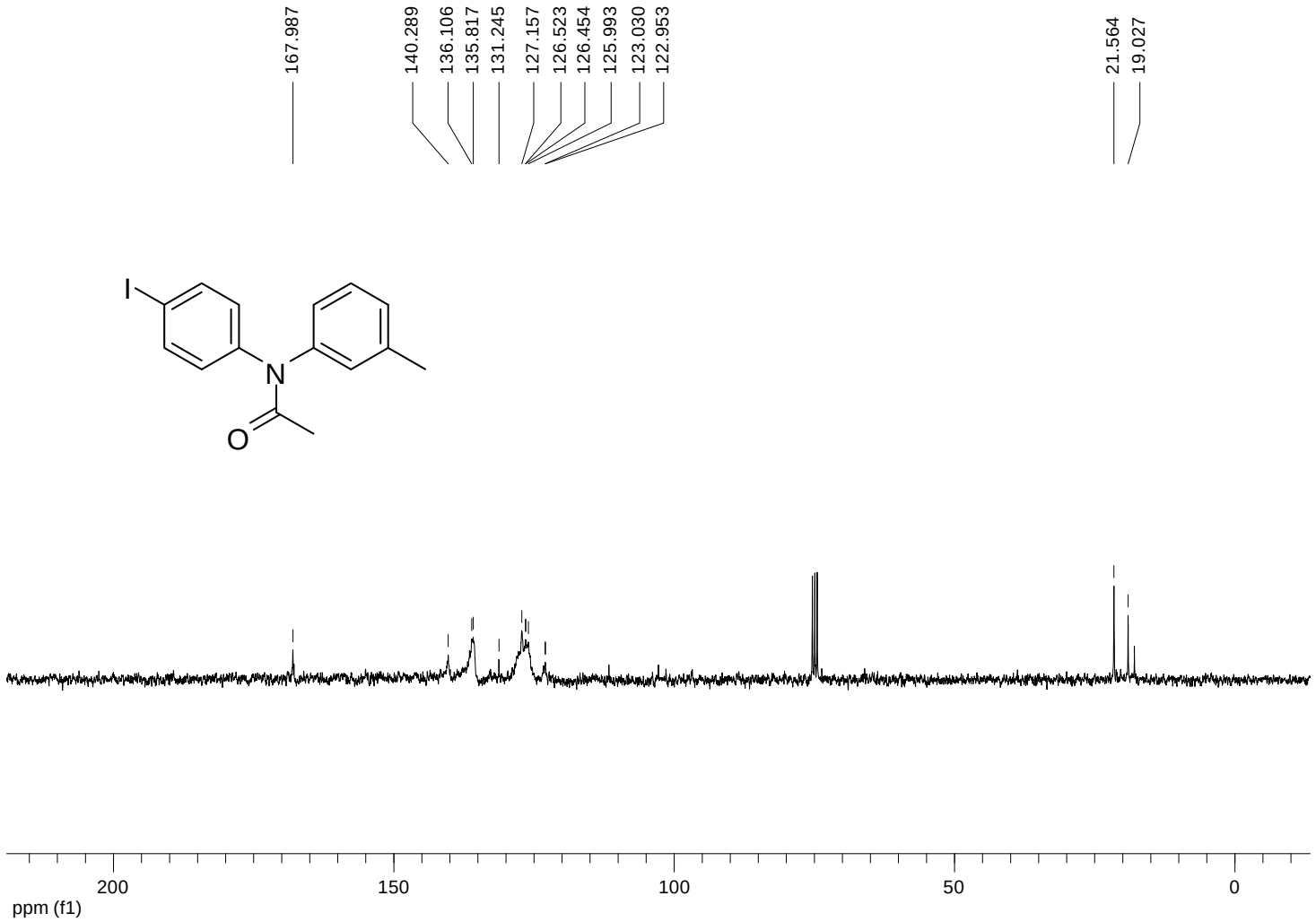

7.643
7.623
7.374
7.354
7.243
7.217
7.027
7.000
2.038
-0.000000
I
N
O
1.89
2.50
2.14
1.86
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

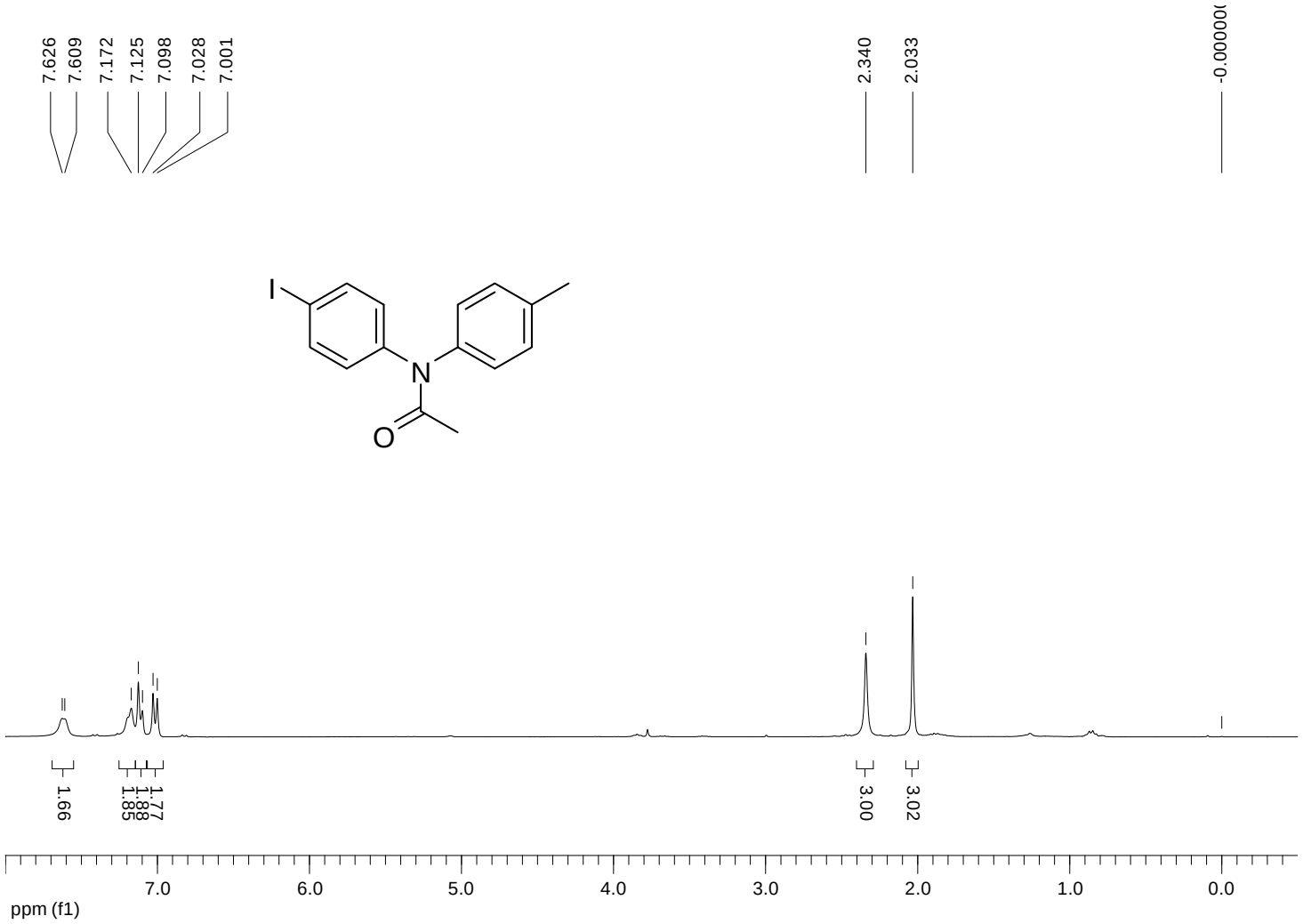

167.911
140.326
135.808
127.378
125.933
21.602
I
N
O
200
150
100
50
0
ppm (f1)

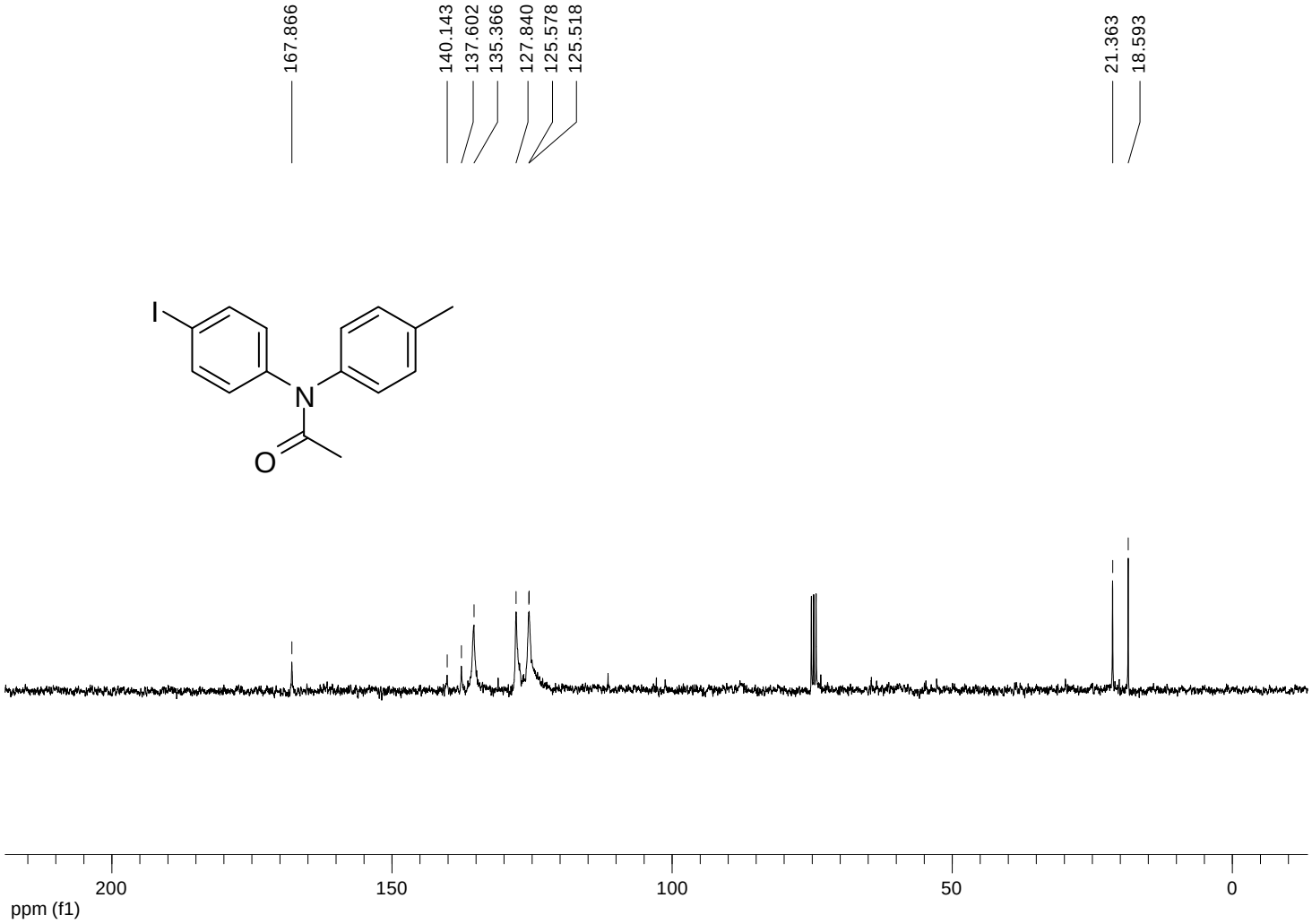

7.591
7.565
7.283
7.052
7.025
2.180
1.945
-0.000000
I
N
O
1.67
3.37
1.69
3.00
3.20
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

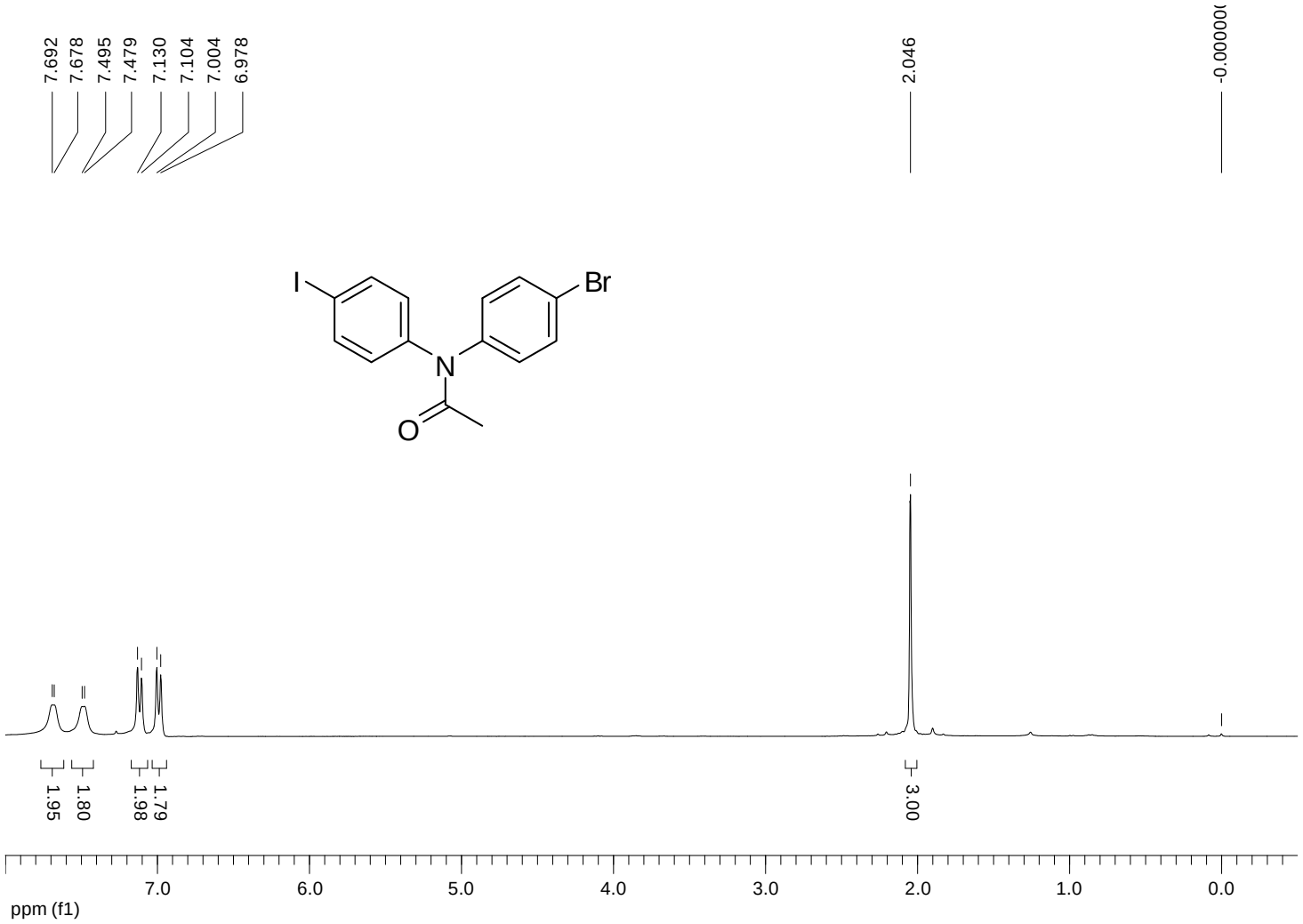

I
N
O
170.571
141.337
137.875
136.259
132.156
129.828
129.133
127.765
126.948
89.852
77.846
77.421
76.995
24.275
18.159
200
180
160
140
120
100
80
60
40
20
0 ppm

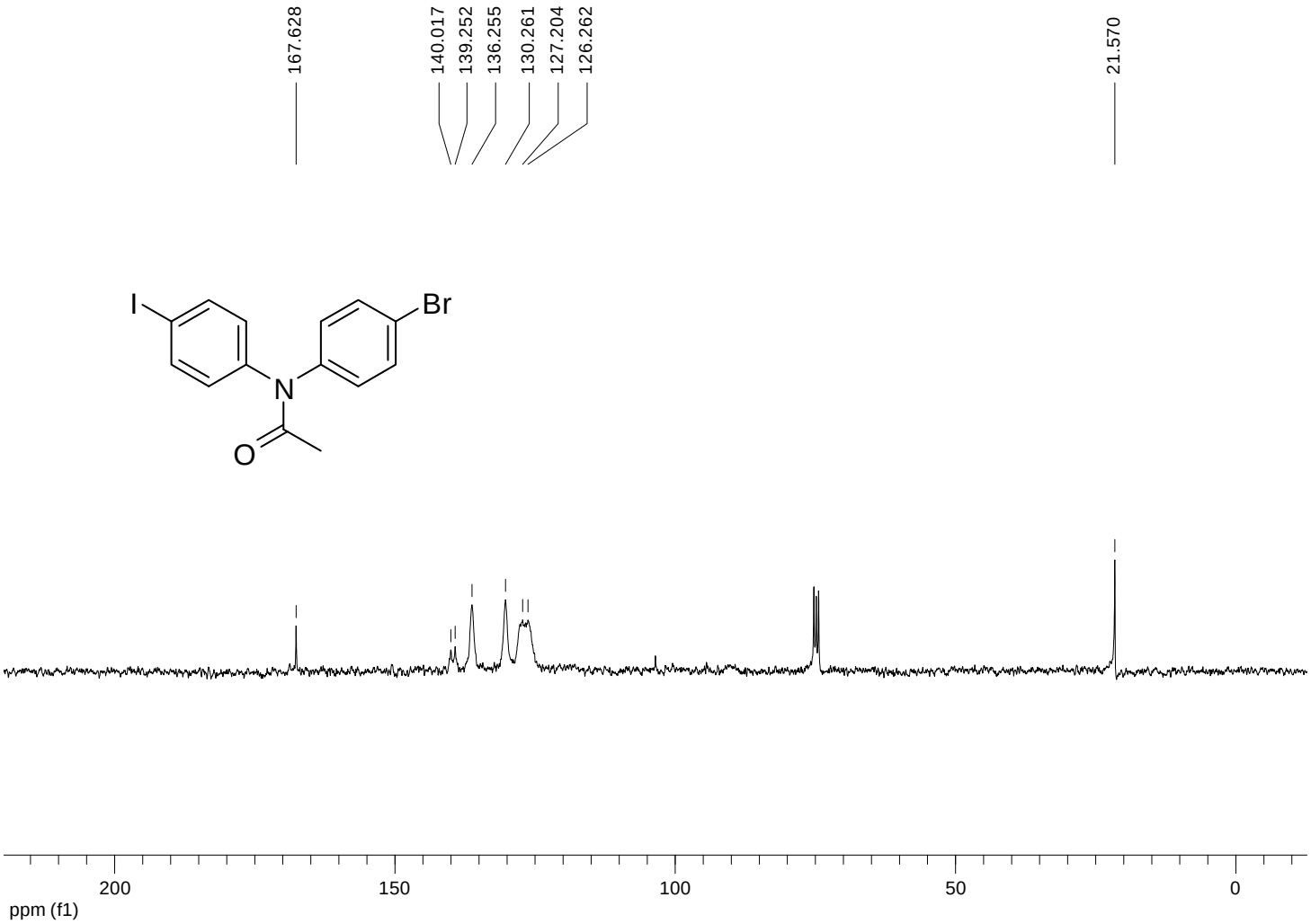

7.628
7.252
7.103
7.025
6.996
2.319
2.027
-0.000000
I
N
O
1.92
1.16
1.03
3.41
3.00
3.17
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

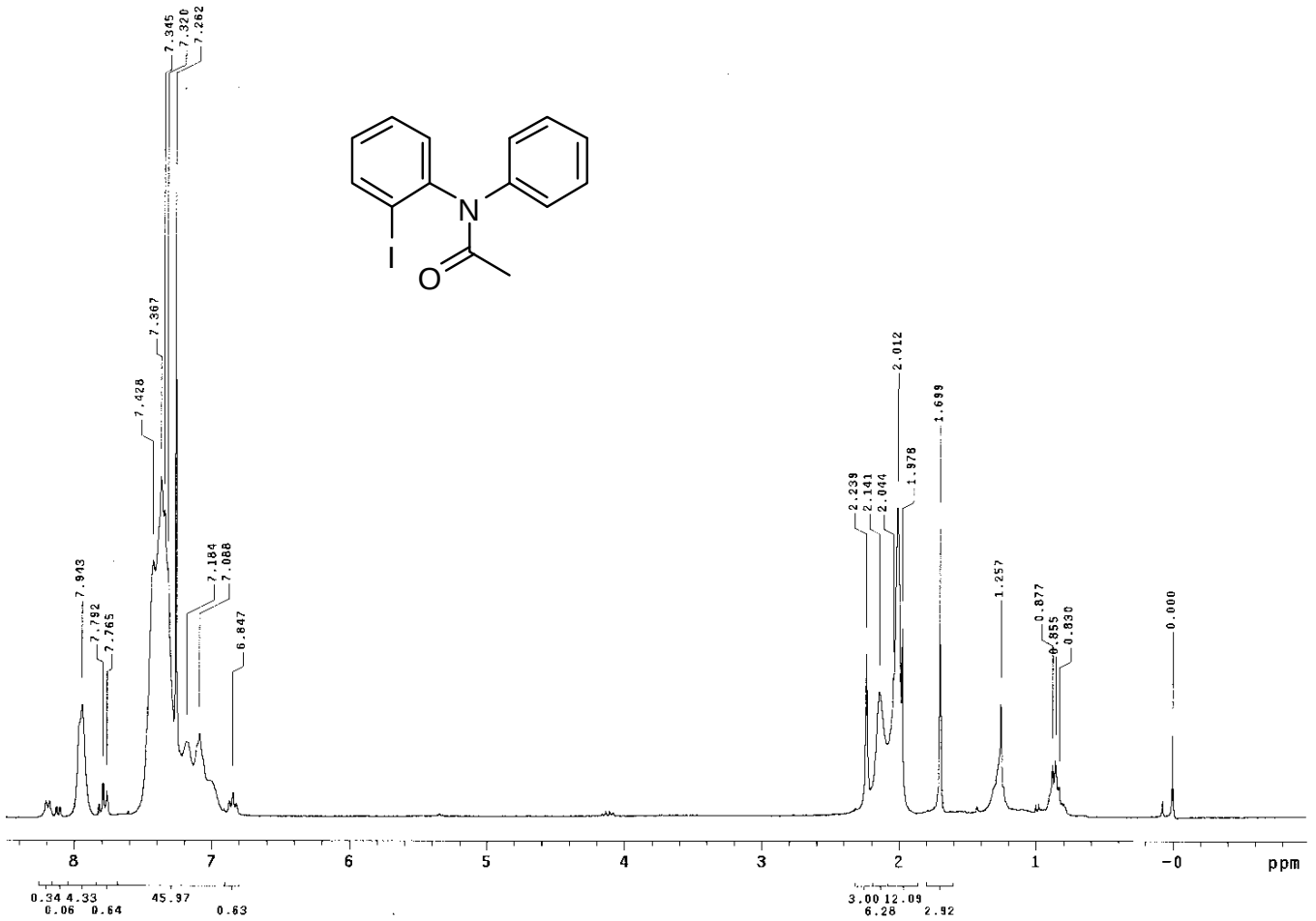

167.987
140.289
136.106
135.817
131.245
127.157
126.523
126.454
125.993
123.030
122.953
21.564
19.027
I
N
O
200
150
100
50
0
ppm (f1)

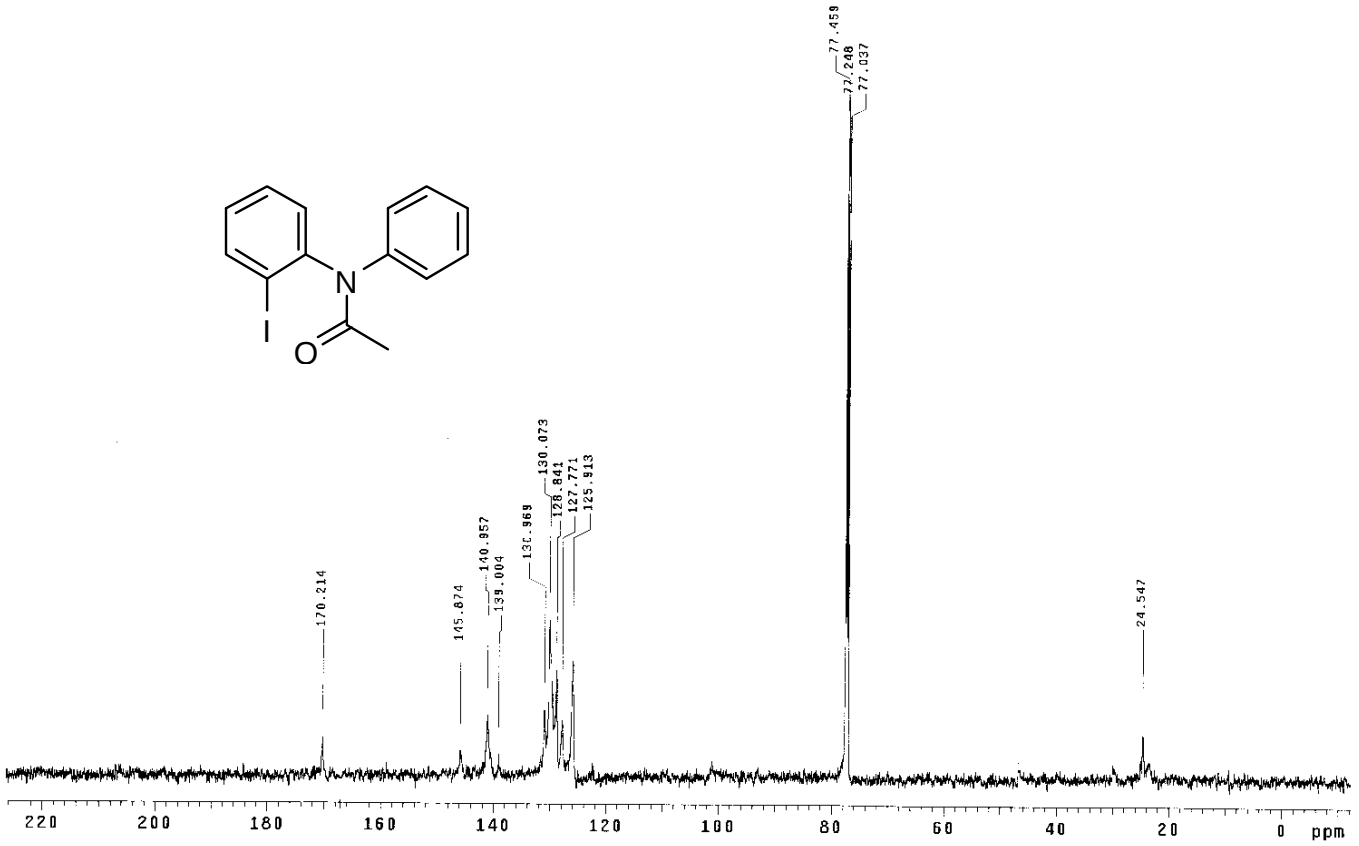

7.626
7.609
7.172
7.125
7.098
7.028
7.001
2.340
2.033
-0.000000
I
N
O
1.96
1.85
1.88
1.77
3.00
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

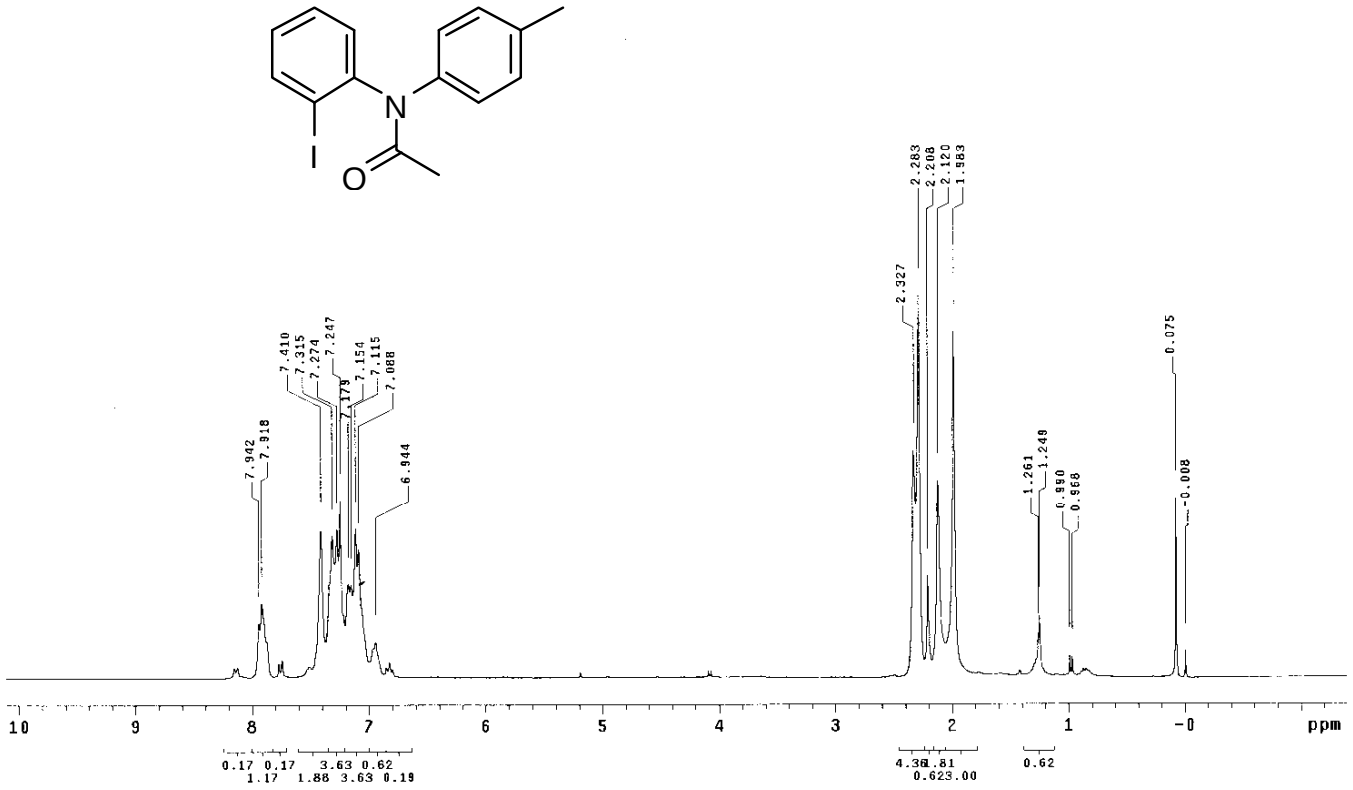

167.866
140.143
137.602
135.366
127.840
125.578
125.518
21.363
18.593
I
N
O
200
150
100
50
0
ppm (f1)

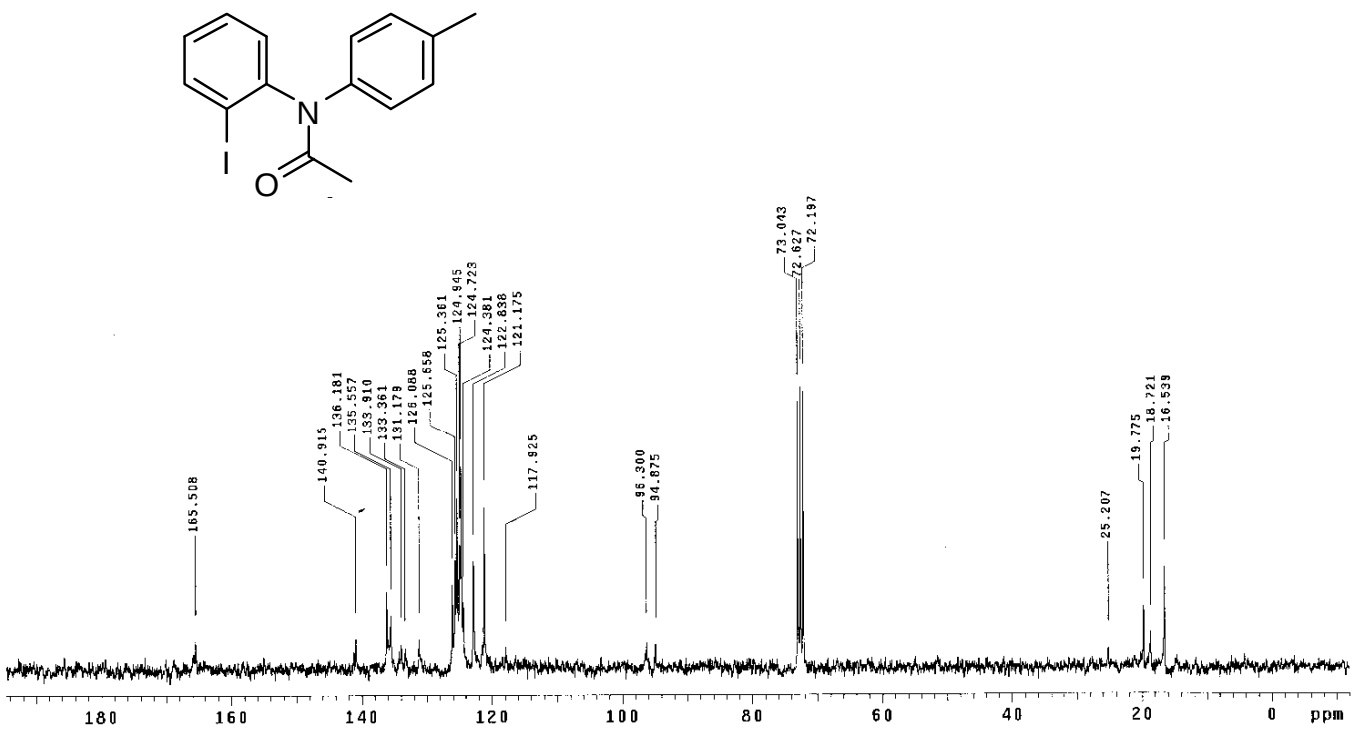

7.692
7.678
7.495
7.479
7.130
7.104
7.004
6.978
2.046
-0.000000
I
Br
N
O
1.95
1.80
1.98
1.79
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

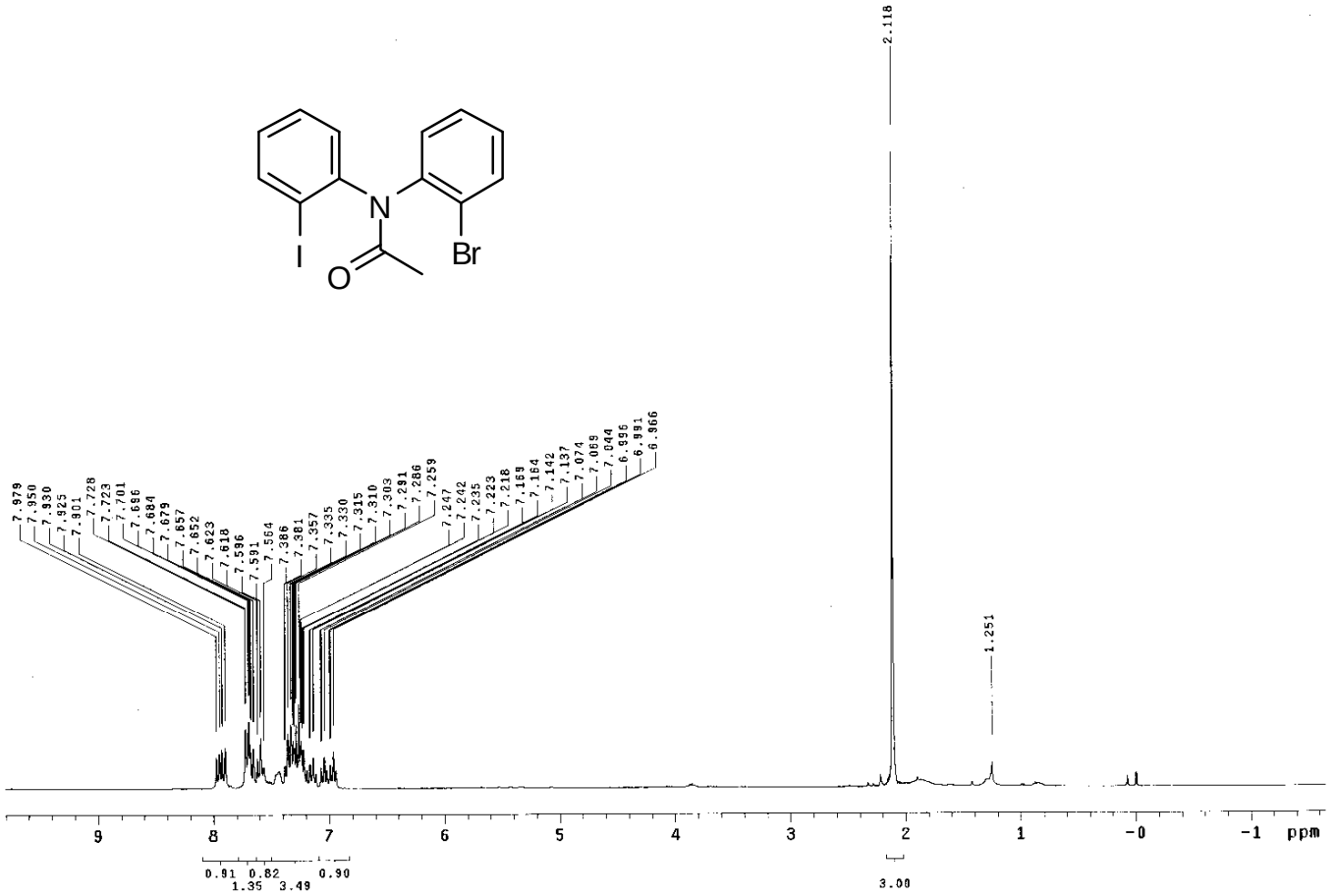

167.628
140.017
139.252
136.255
130.261
127.204
126.262
21.570
I
Br
N
O
200
150
100
50
0
ppm (f1)


7.945
7.920
7.262
7.428
7.367
7.913
7.792
7.765
7.184
7.068
6.847
2.239
2.141
2.044
1.978
2.012
1.699
1.257
0.877
0.855
0.830
0.000
N
I
O
8
7
6
5
4
3
2
1
-0
ppm
0.34 4.33
0.06 0.64
45.97
0.63
3.00 12.09
6.28 2.92


N
I
O
170.214
145.874
140.957
139.004
130.073
128.841
127.771
125.913
77.459
77.248
77.037
24.547
220
200
180
160
140
120
100
80
60
40
20
0
ppm


N
I
O
7.942
7.918
7.410
7.315
7.274
7.247
7.154
7.115
7.088
6.944
2.327
2.283
2.208
2.120
1.983
1.261
1.248
0.960
0.868
0.075
-0.008
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.17 0.17 3.63 0.62
1.17 1.88 3.63 0.19
4.38 1.81
0.623.00
0.62


N
I
O
165.508
140.915
136.181
135.557
133.910
133.361
131.179
126.068
125.658
125.361
124.945
124.723
124.381
122.838
121.175
117.925
96.300
94.875
73.043
72.627
72.197
25.207
19.775
18.721
16.539
180
160
140
120
100
80
60
40
20
0
ppm


N
I
O
Br
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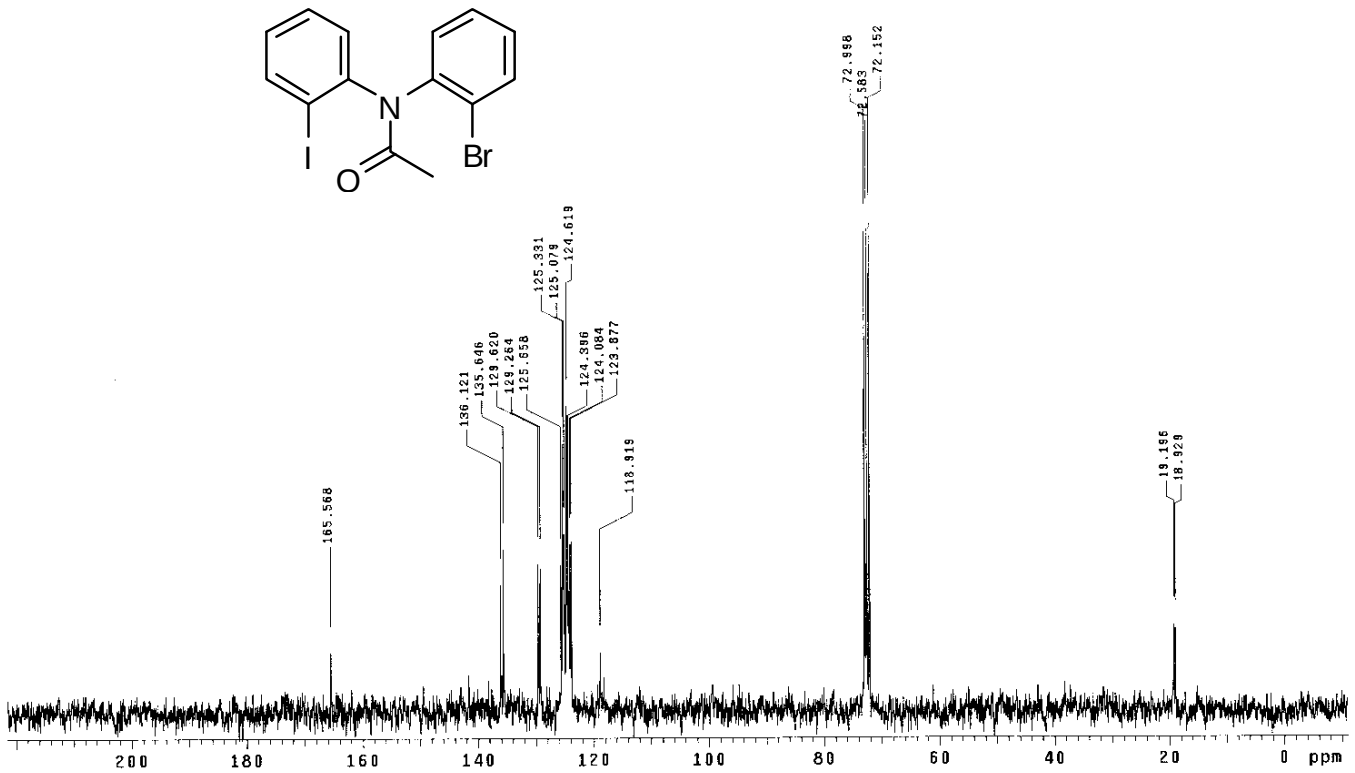
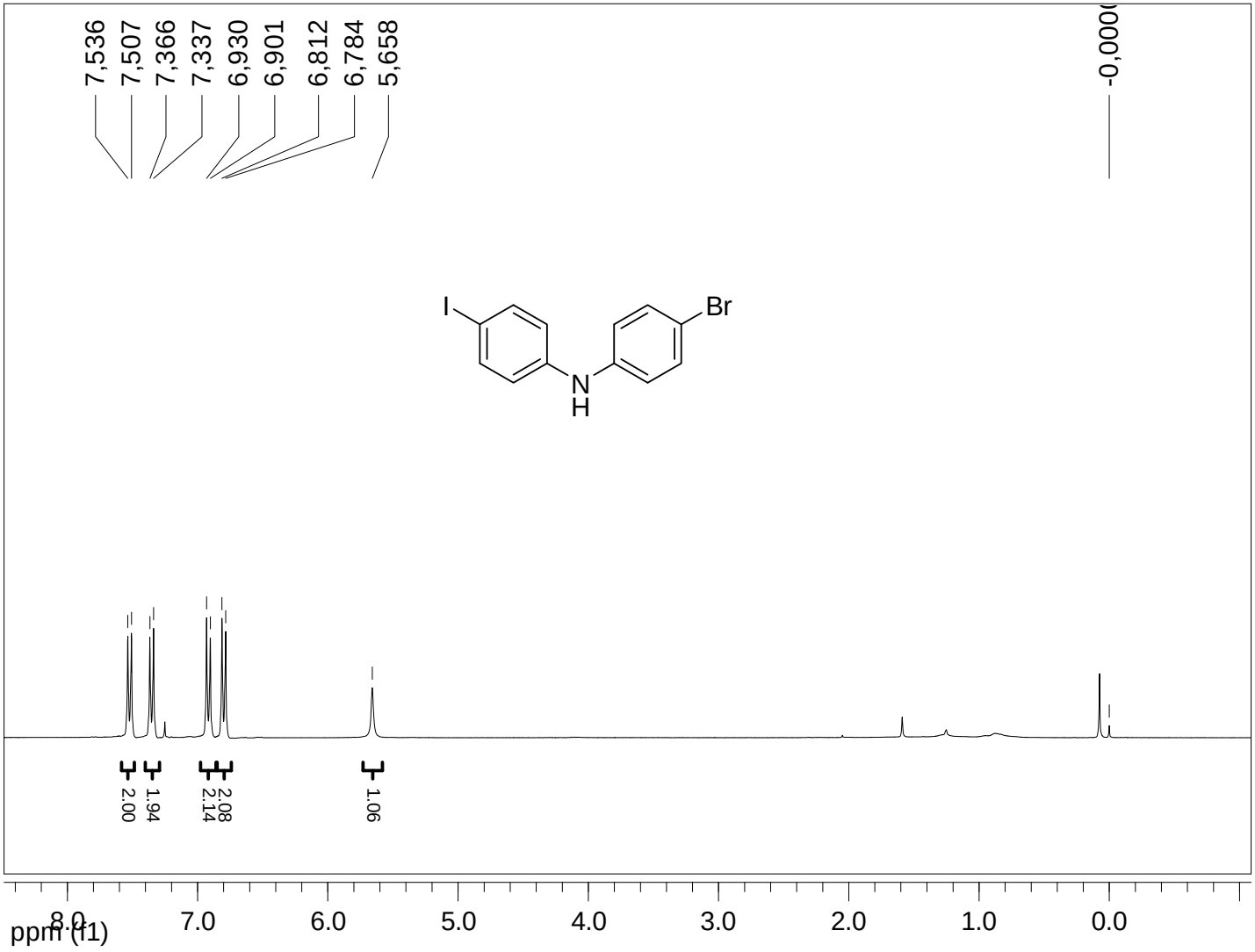
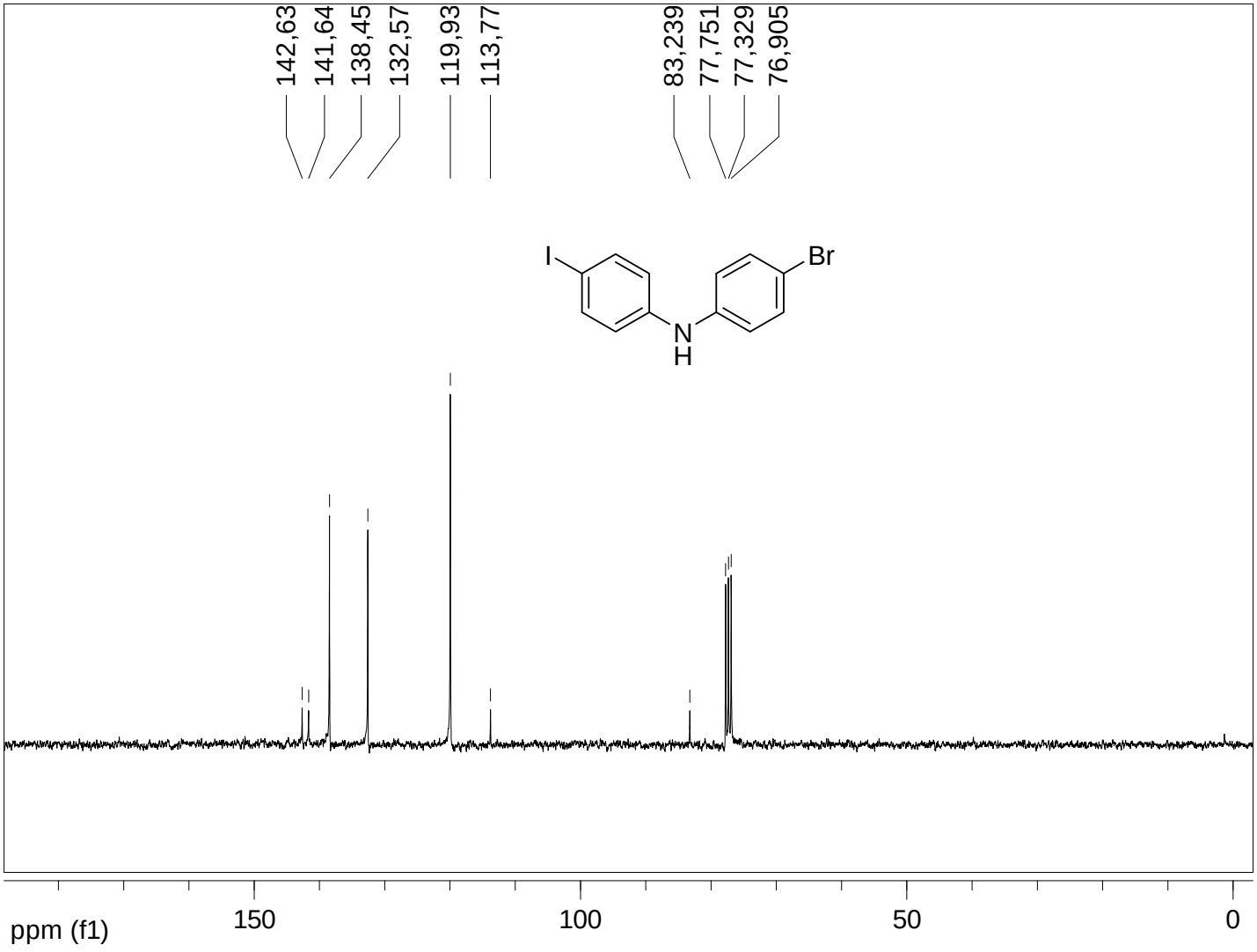
7.930
7.925
7.901
7.728
7.723
7.701
7.686
7.684
7.679
7.657
7.652
7.623
7.618
7.596
7.591
7.564
7.386
7.381
7.357
7.335
7.330
7.315
7.310
7.303
7.291
7.286
7.259
7.247
7.242
7.235
7.223
7.218
7.189
7.164
7.142
7.137
7.074
7.069
7.044
6.996
6.991
6.966
2.118
1.251
9
8
7
6
5
4
3
2
1
-0
-1
ppm
0.91 0.82 0.90
1.35 3.49
3.00


N
I
O
Br
165.568
136.121
135.646
129.620
129.264
125.858
125.331
125.079
124.619
124.396
124.084
123.877
118.919
72.998
72.583
72.152
19.155
18.929
200
180
160
140
120
100
80
60
40
20
0
ppm


7,536
7,507
7,366
7,337
6,930
6,901
6,812
6,784
5,658
-0,000
I
Br
N
H
2.00
1.94
2.08
2.14
1.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


142,63
141,64
138,45
132,57
119,93
113,77
83,239
77,751
77,329
76,905
I
Br
N
H
ppm (f1)
150
100
50
0