

Nickel-Mediated Oxidative α -C(sp³)-H Functionalization of Amides with Allylic Alcohols Terminated by Radical 1,2-Aryl Migration

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Supporting Information

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(A) Typical experimental procedure

(a) General Considerations:

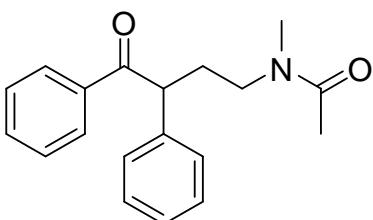
The ^1H , ^{13}C and ^{19}F NMR spectra were recorded in CDCl_3 solvent on a 400 MHz NMR spectrometer. Melting points are uncorrected. IR spectra were recorded with a FTIR spectrophotometer by using KBr optics. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV with EI ion source and signals were given in m/z with relative intensity (%) in brackets. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry.

(b) Typical Procedures for the Synthesis of Substrates 1: All of compounds 1 were synthesized according to the literature.^[1]

(c) Typical Experimental Procedure for the Nickel-Catalyzed Oxidative C(sp³)-H Functionalization of Amides with α,α -Diaryl Allylic Alcohols via Radical 1,2-Aryl Migration:

Allylic alcohol **1** (0.2 mmol), *N,N*-substituted amides **2** (1 mL), DTBP (di-*tert*-butyl peroxide) (0.6 mmol) was stirred at 150 °C (oil bath temperature) under air for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was diluted in Et_2O , and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the product.

(B) Analytical data for **3** and **4**

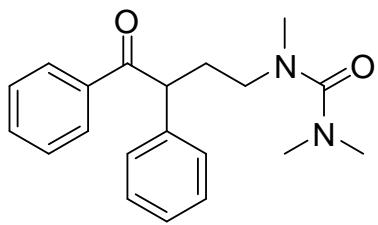


N-Methyl-*N*-(4-oxo-3,4-diphenylbutyl)acetamide (**3aa**):

Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ : 7.96-7.93 (m, 2H), 7.50-7.44 (m, 1H), 7.40-7.35 (m, 2H), 7.32-7.20 (m, 4H), 7.17 (t, $J = 7.2$ Hz, 1H), 4.68-4.50 (m, 1H), 3.56-3.22 (m, 2H), 2.89 (d,

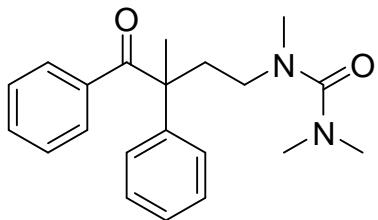
(%): 281 (M^+ , 5), 236 (28), 105 (100); HRMS m/z (ESI) calcd for $C_{18}H_{19}NNaO_2$ ($[M+Na]^+$)

304.1303, found 304.1301.



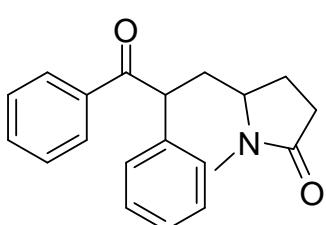
1,1,3-T trimethyl-3-(4-oxo-3,4-diphenylbutyl)urea (3ac):

Colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ : 7.94 (d, $J = 8.8$ Hz, 2H), 7.49-7.45 (m, 1H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.30-7.25 (m, 4H), 7.21-7.17 (m, 1H), 4.57 (t, $J = 7.2$ Hz, 1H), 3.27-3.10 (m, 2H), 2.78 (s, 3H), 2.62 (s, 6H), 2.53-2.45 (m, 1H), 2.08-2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 199.2, 165.3, 139.3, 136.6, 132.9, 129.0, 128.7, 128.5, 128.1, 127.1, 51.1, 48.7, 38.5, 36.4, 31.8; IR (KBr, cm^{-1}): 1680, 1636, 1495, 1385; LRMS (EI, 70 eV) m/z (%): 324 (M^+ , 1), 280 (2), 252 (2), 196 (26), 129 (100); HRMS m/z (ESI) calcd for $C_{20}H_{25}N_2O_2$ ($[M+H]^+$) 325.1911, found 325.1902.

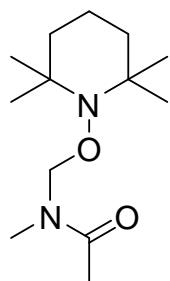


1,1,3-T trimethyl-3-(3-methyl-4-oxo-3,4-diphenylbutyl)urea (3gc):

Colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ : 7.49 (d, $J = 8.4$ Hz, 2H), 7.43-7.41 (m, 6H), 7.26 (t, $J = 7.6$ Hz, 2H), 3.12-2.96 (m, 2H), 2.70 (s, 9H), 2.39-2.30 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 203.1, 165.3, 143.4, 136.4, 131.7, 129.5, 129.0, 128.0, 127.0, 126.1, 53.5, 46.6, 38.5, 37.3, 36.3, 23.7; IR (KBr, cm^{-1}): 1674, 1644, 1599, 1507; LRMS (EI, 70 eV) m/z (%): 338 (M^+ , 1), 294 (1), 210 (20), 129 (89), 115 (100); HRMS m/z (ESI) calcd for $C_{21}H_{27}N_2O_2$ ($[M+H]^+$) 339.2067, found 339.2060.



170.5, 136.7, 136.4, 136.2, 136.1, 133.6, 133.2, 132.9, 132.5, 132.4, 129.2, 128.8, 128.7, 128.6, 128.5, 127.7 (2C), 127.6, 127.5, 127.0, 126.5, 126.2, 126.0, 125.8, 125.6, 51.3, 50.8, 48.9, 45.9, 35.8, 33.1, 32.3, 31.5, 21.6, 21.0; IR (KBr, cm^{-1}): 1678, 1637, 1597, 1406; LRMS (EI, 70 eV) m/z (%): 345 (M^+ , 20), 272 (70), 224 (20), 105 (100); HRMS m/z (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2$ ($[\text{M}+\text{H}]^+$) 346.1802, found 346.1797.



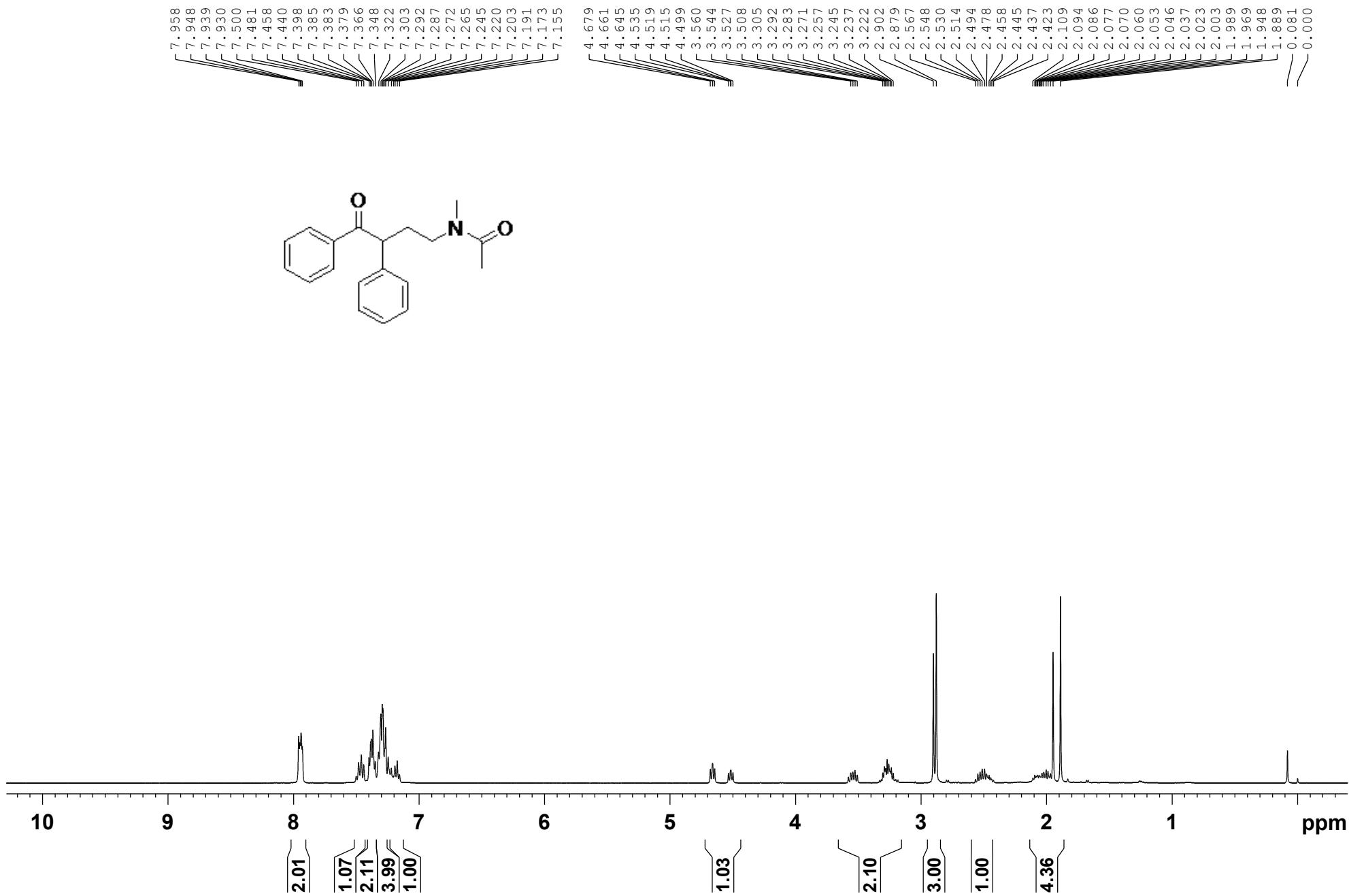
N-Methyl-N-((2,2,6,6-tetramethylpiperidin-1-yloxy)methyl)acetamide (4):

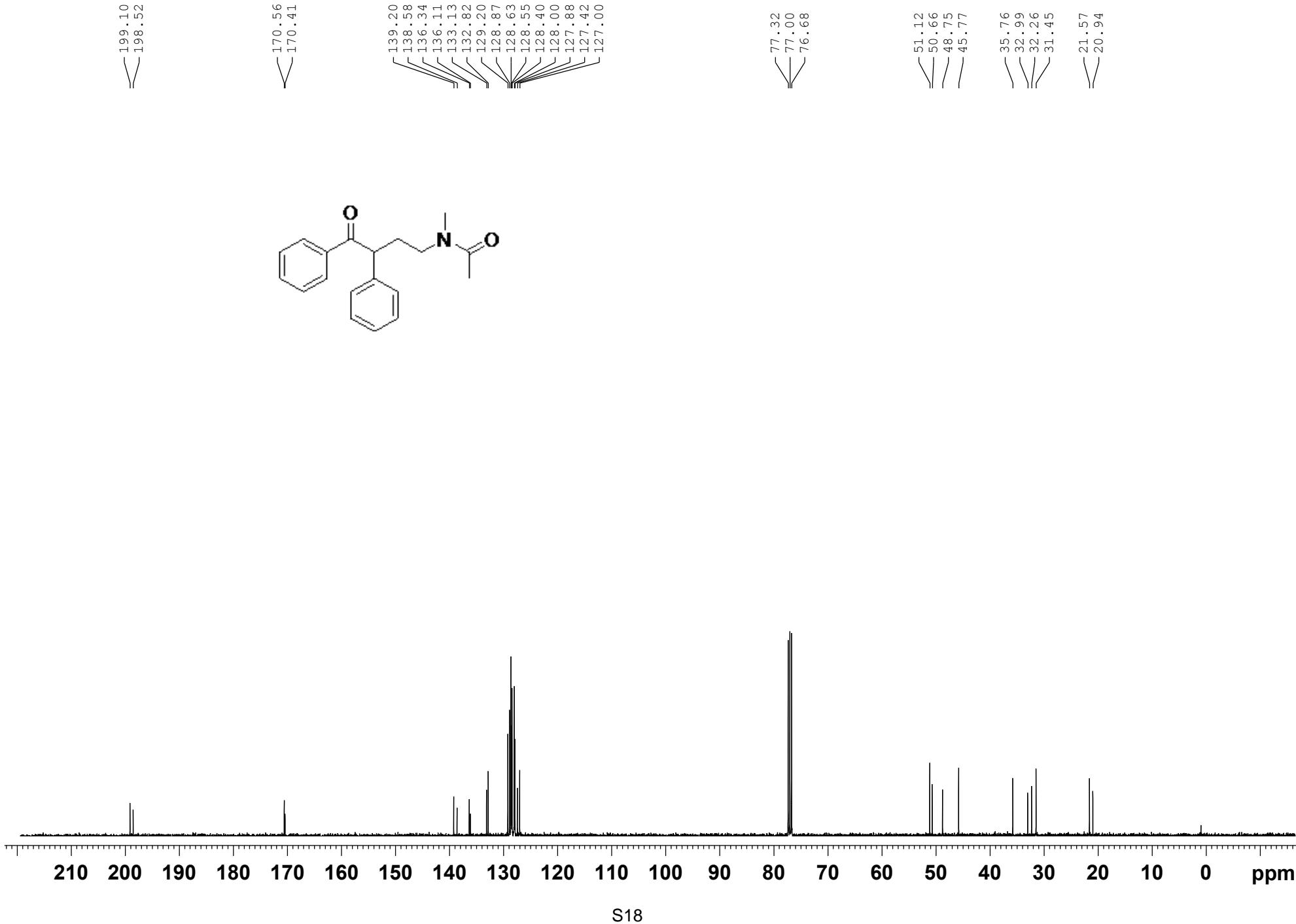
Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ : 4.96 (s, 0.4H), 4.91 (s, 1.6H), 3.11 (s, 0.6H), 3.04 (s, 2.4H), 2.22 (s, 2.4H), 2.10 (s, 0.6H), 1.59-1.52 (m, 1H), 1.48-1.44 (m, 4H), 1.36-1.32 (m, 1H), 1.17, 1.11 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 171.6, 171.1, 85.4, 81.4, 77.3, 77.0, 76.7, 59.9, 59.7, 39.8, 39.7, 35.9, 34.0, 33.1, 32.9, 22.0, 21.5, 20.0, 17.0 (2C); IR (KBr, cm^{-1}): 1651, 1466, 1441, 1374; LRMS (EI, 70 eV) m/z (%): 242 (M^+ , 1), 184 (2), 157 (6), 142 (166), 86 (100); HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$) 243.2067, found 243.2066.

(D) Reference

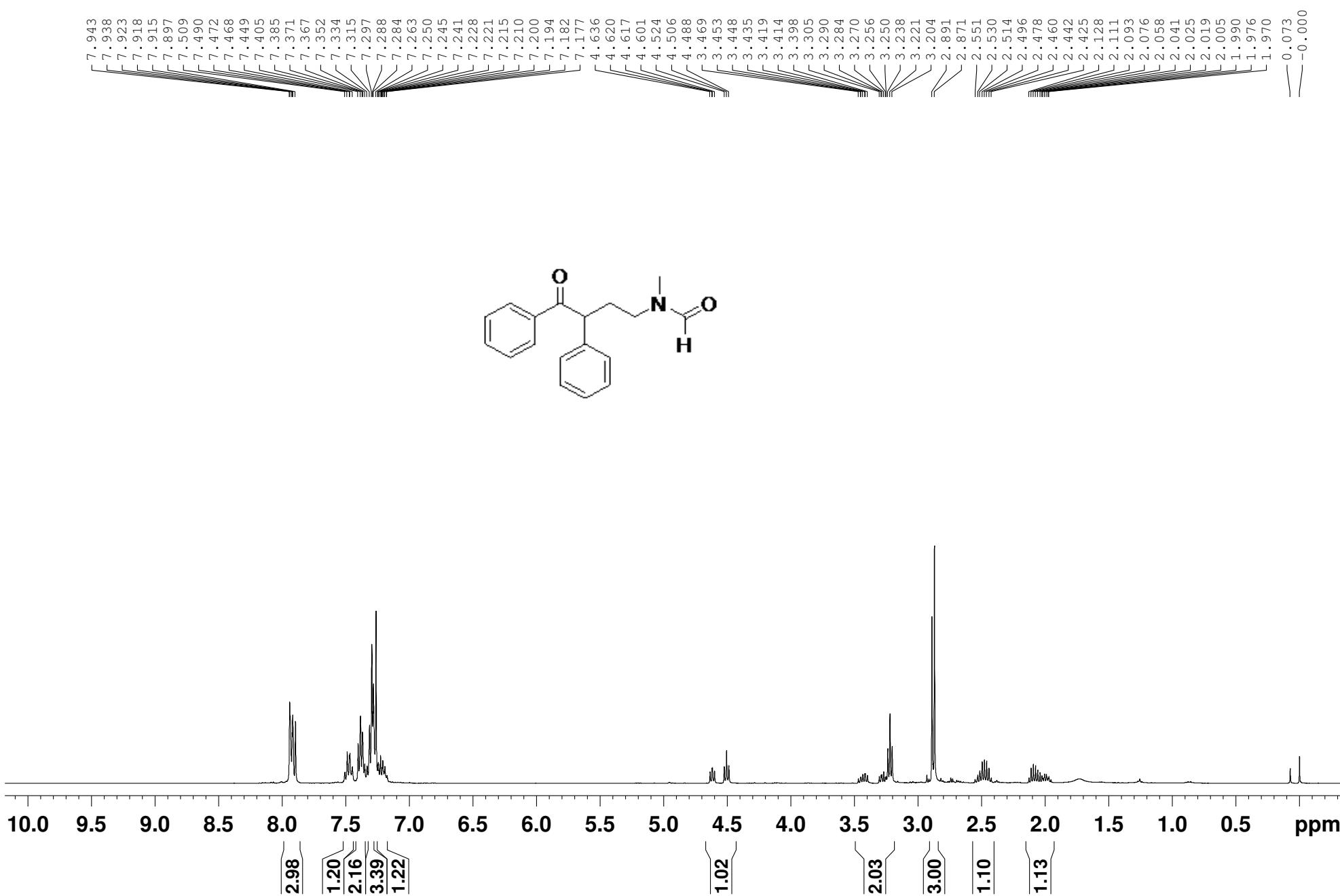
- [1] H. Li, F.-M. Zhang, Y.-Q. Tu, Q.-W. Zhang, Z.-M. Chen, Z.-H. Chen, J. Li, *Chem. Sci.*, **2011**, 2, 1839.

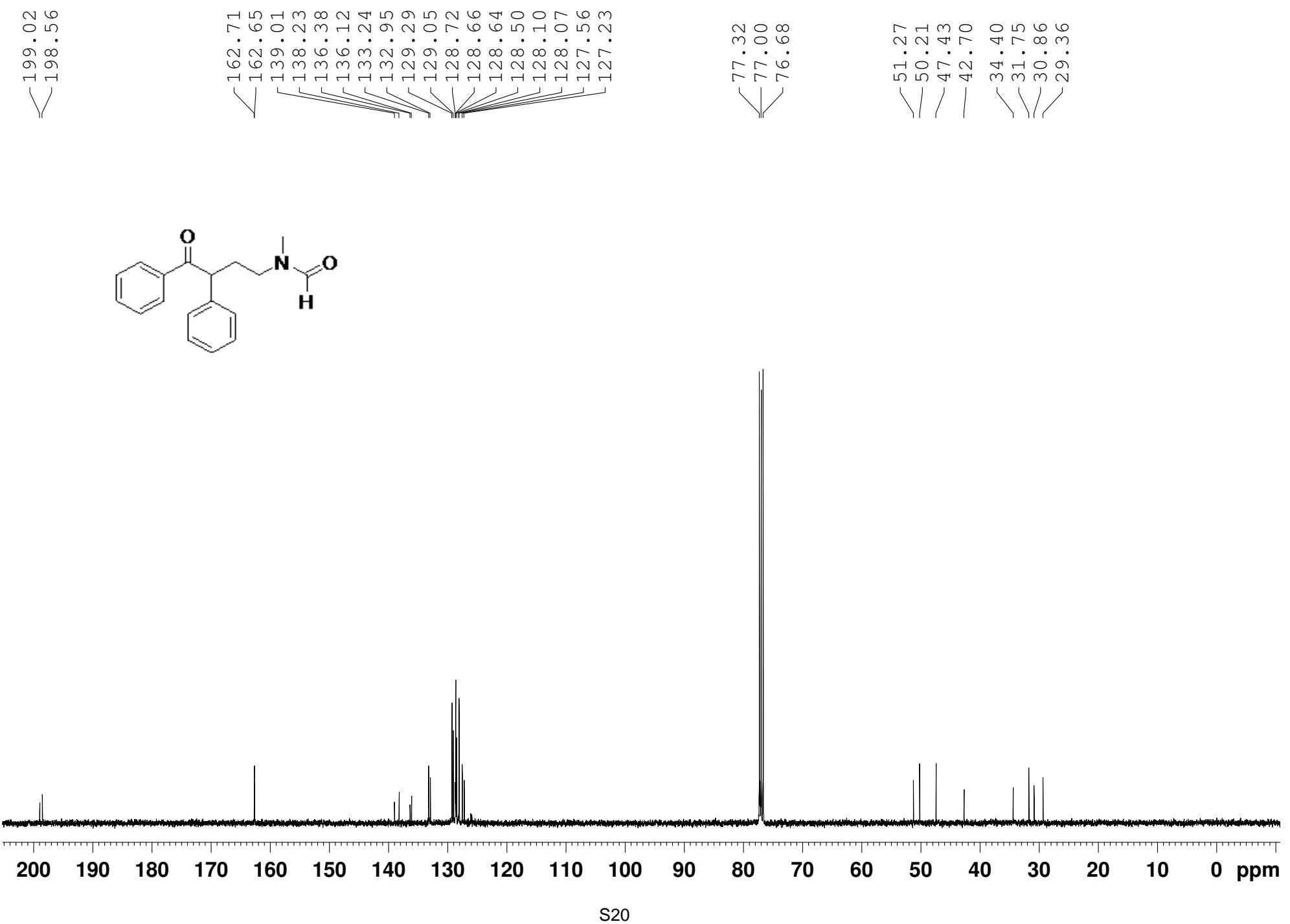
N-Methyl-N-(4-oxo-3,4-diphenylbutyl)acetamide (3aa)



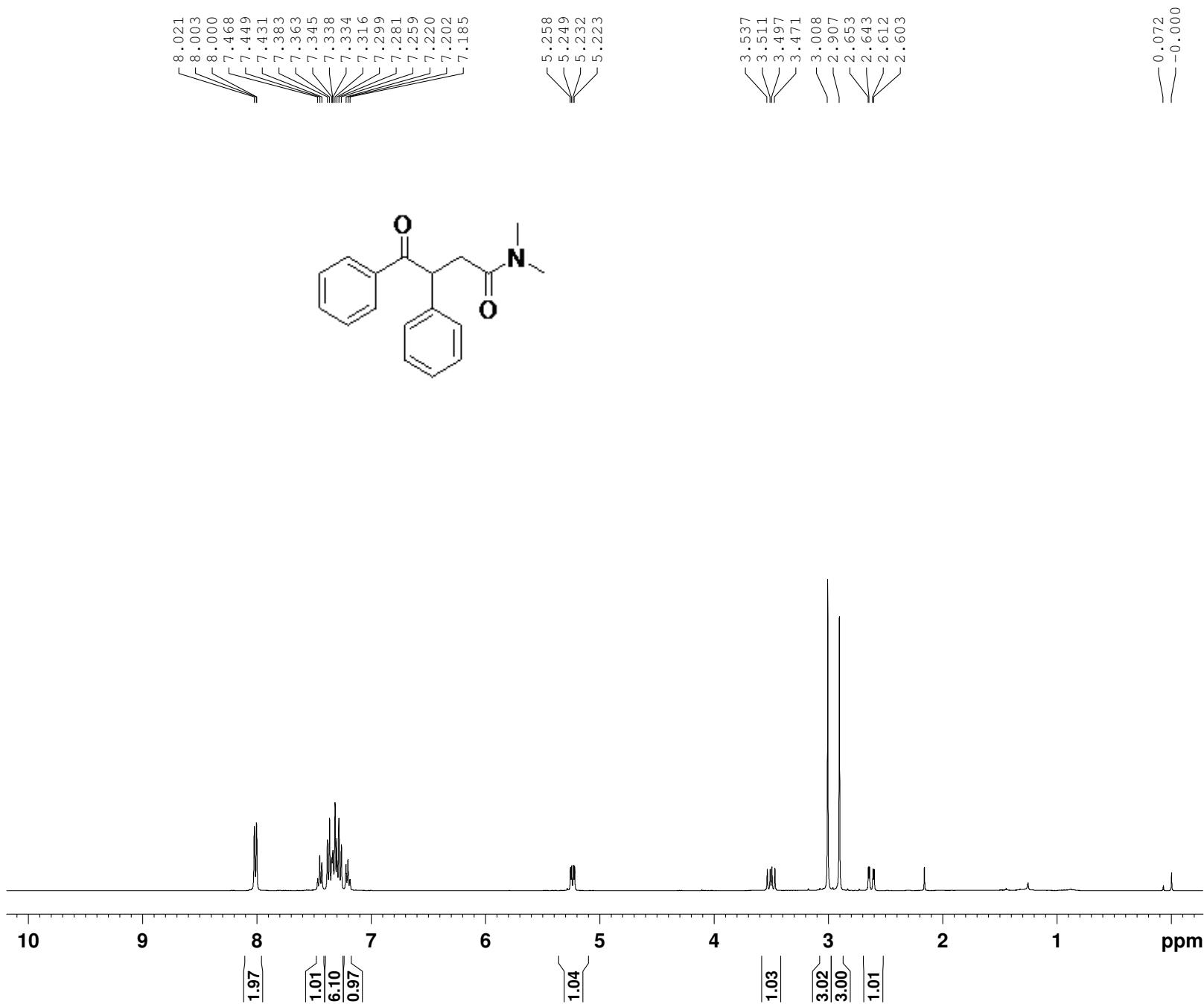


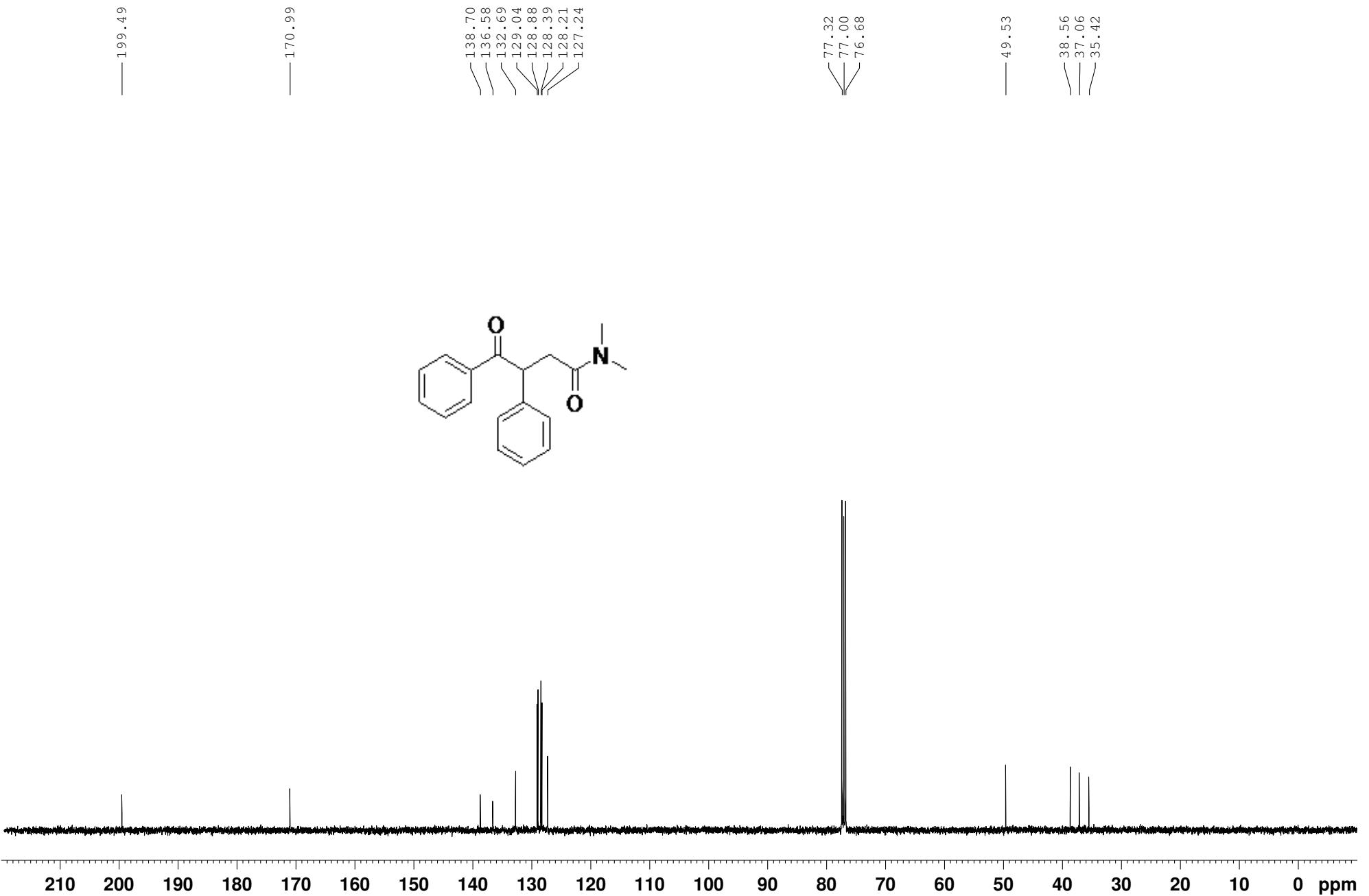
N-Methyl-N-(4-oxo-3,4-diphenylbutyl)formamide (3ab)



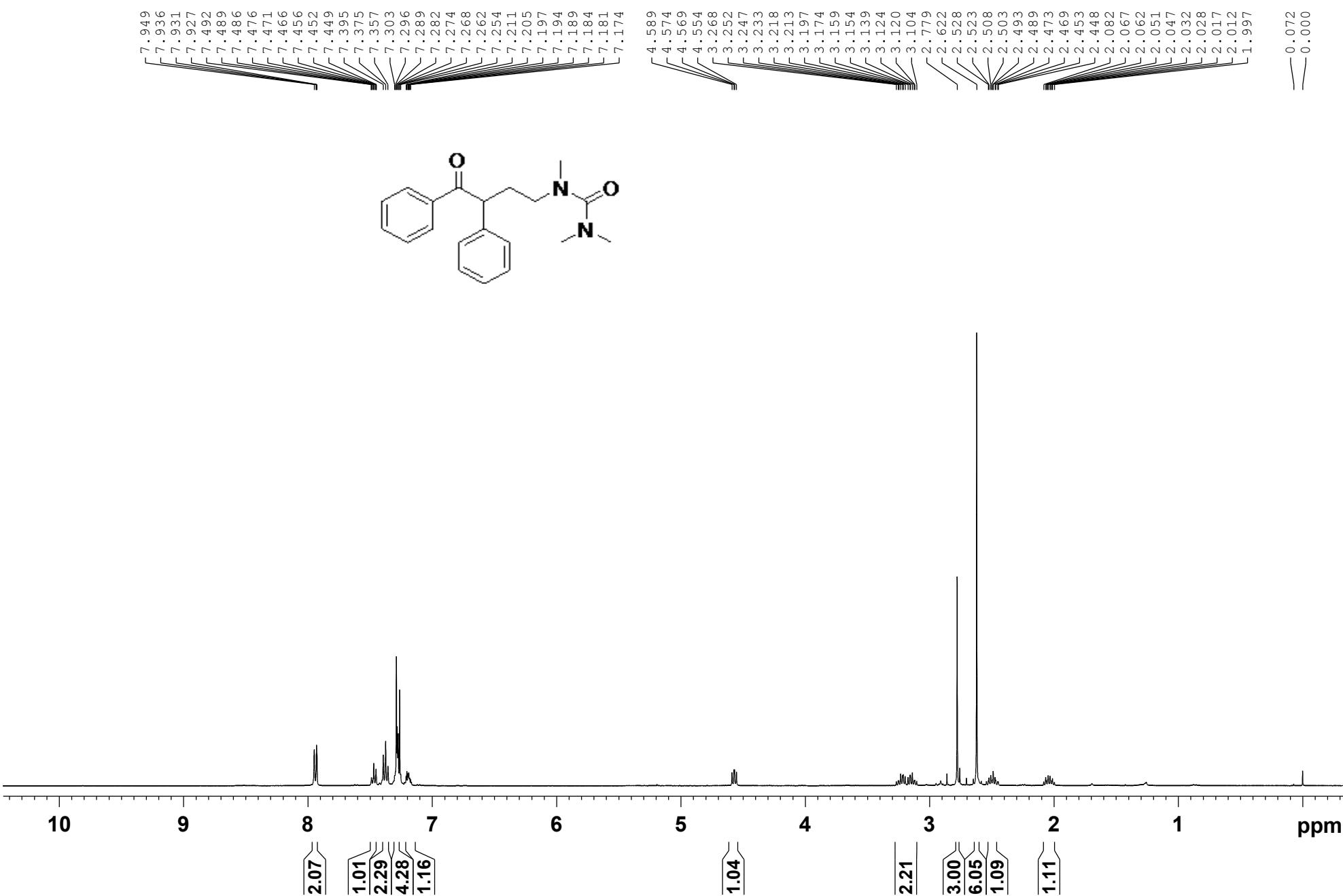


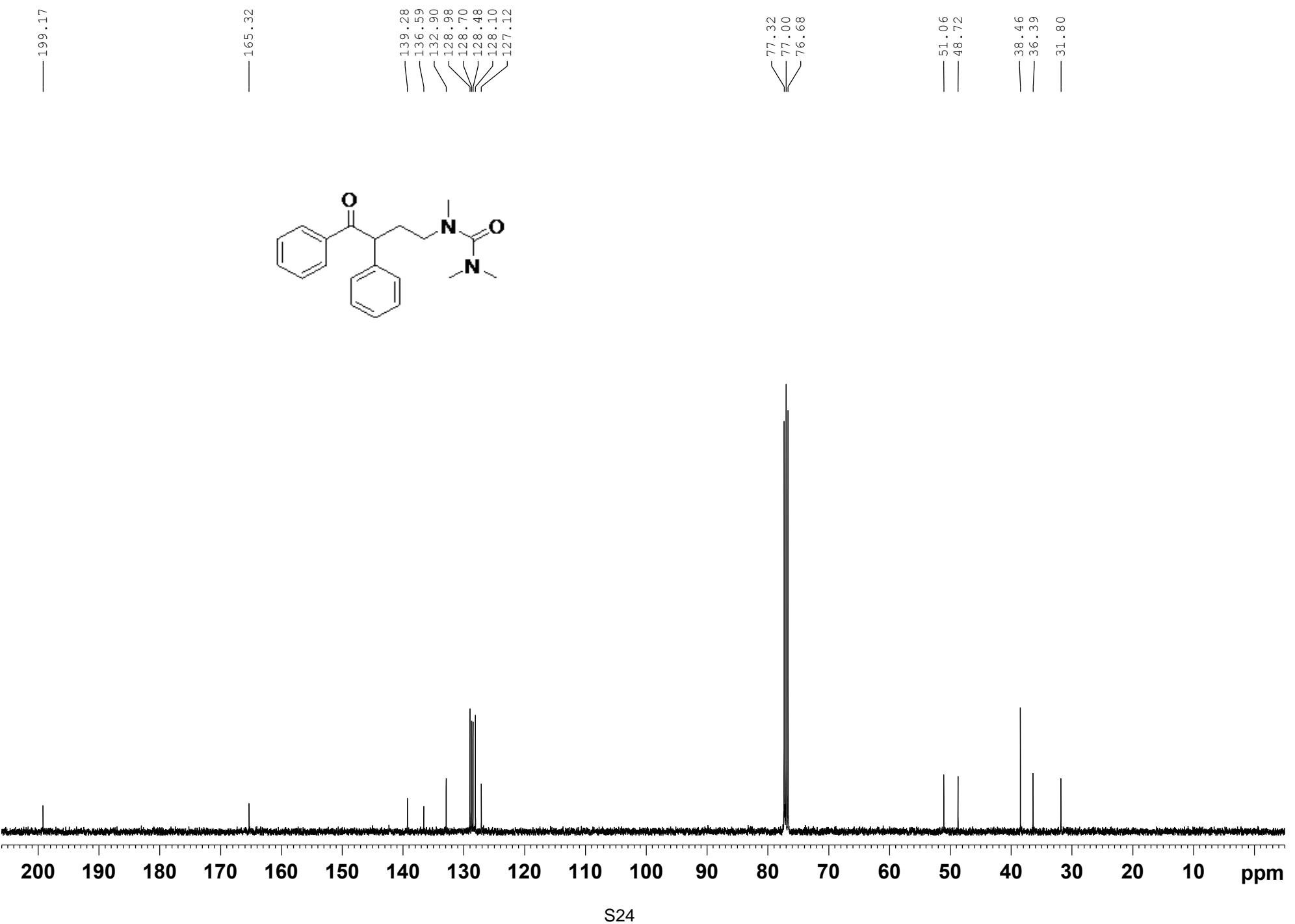
N,N-Dimethyl-4-oxo-3,4-diphenylbutanamide (3ab')



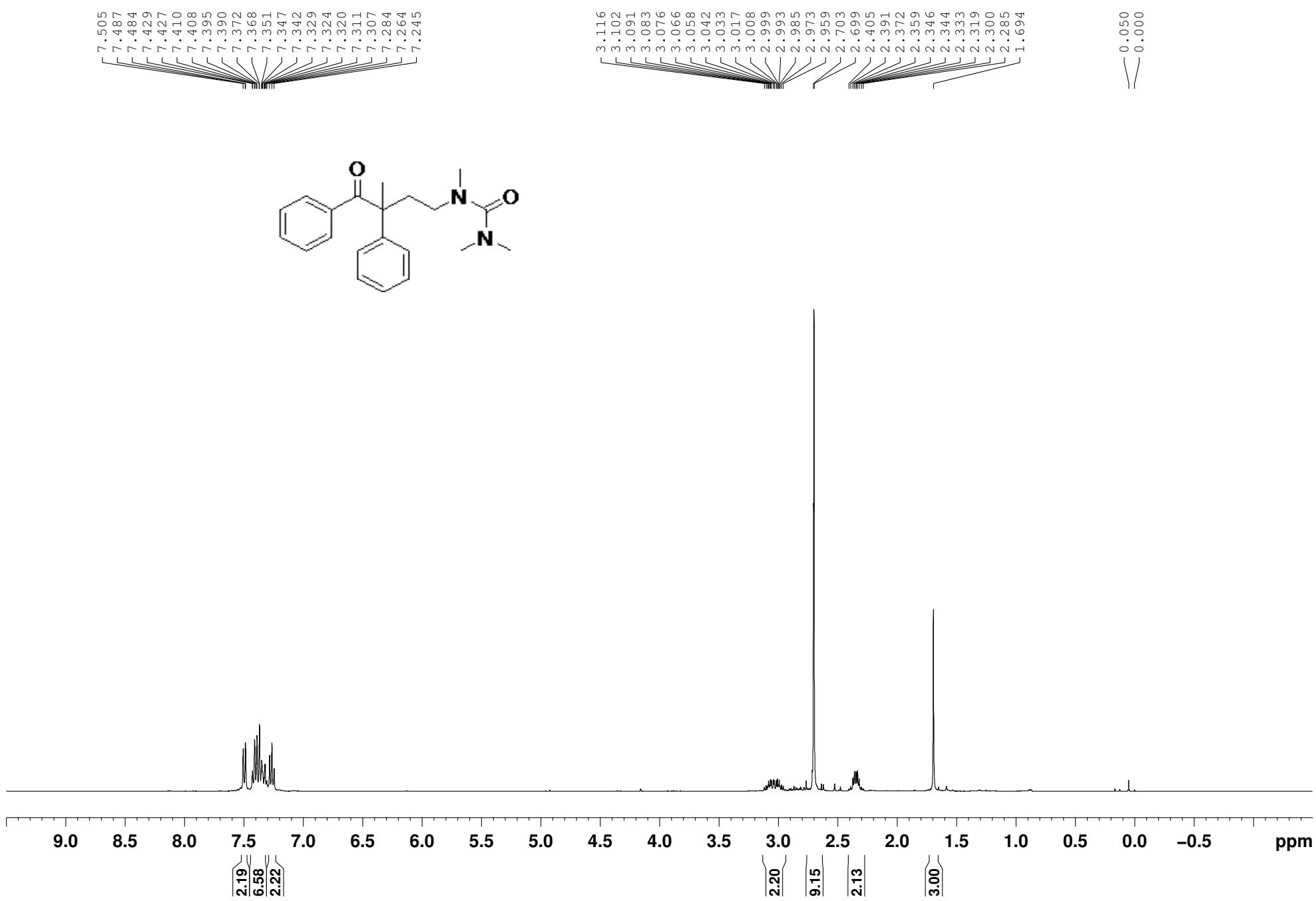


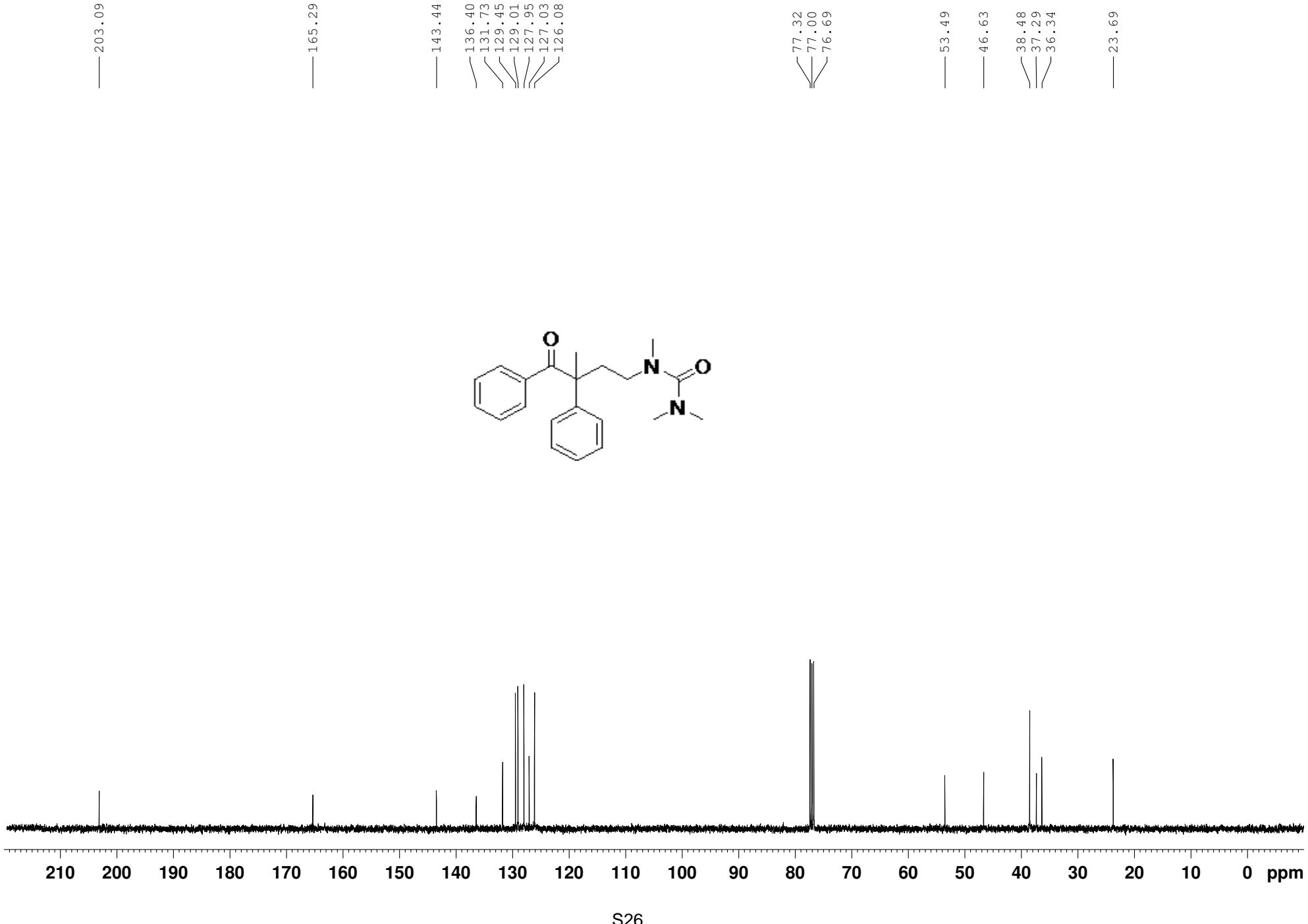
1,1,3-Trimethyl-3-(4-oxo-3,4-diphenylbutyl)urea (3ac)



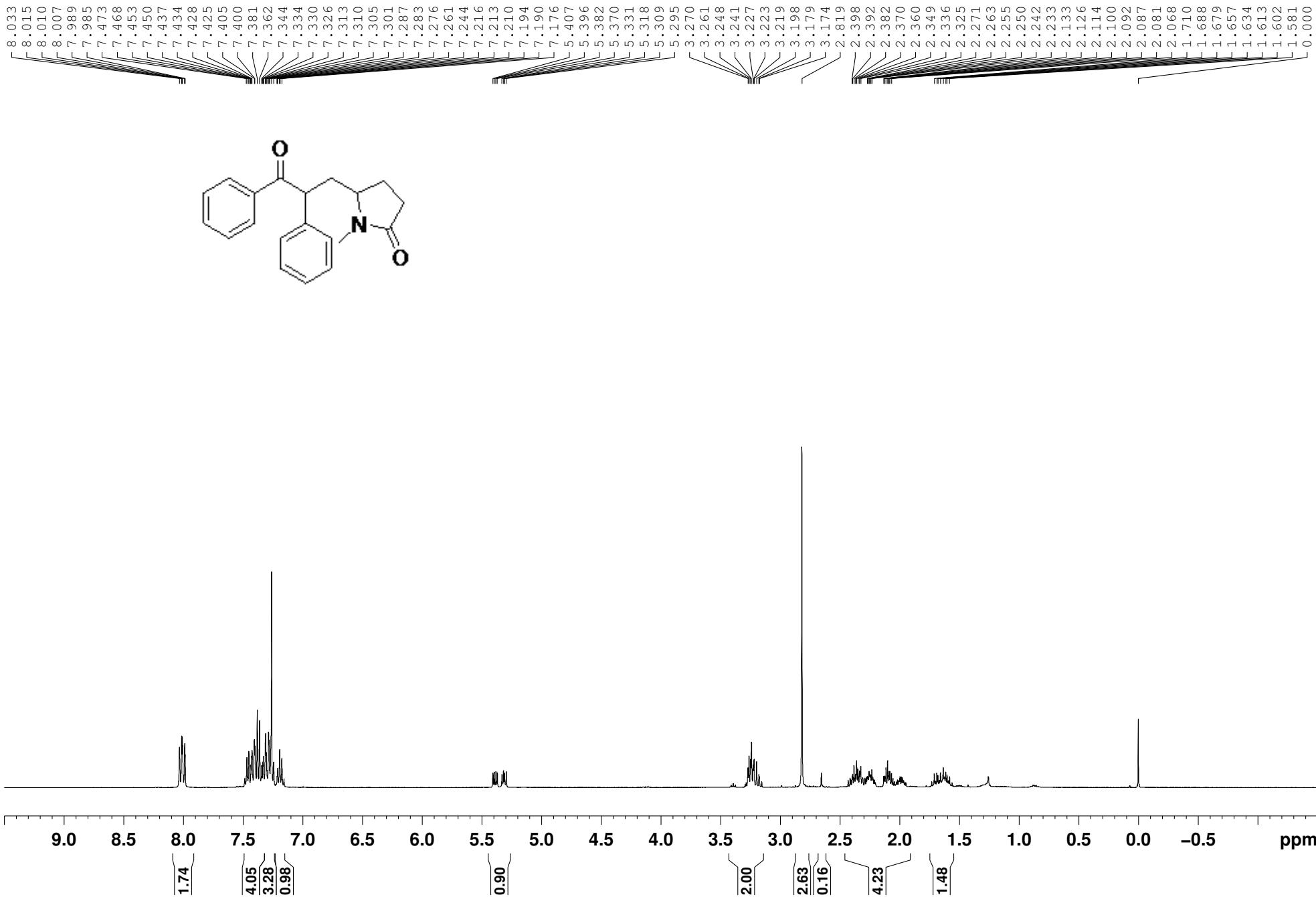


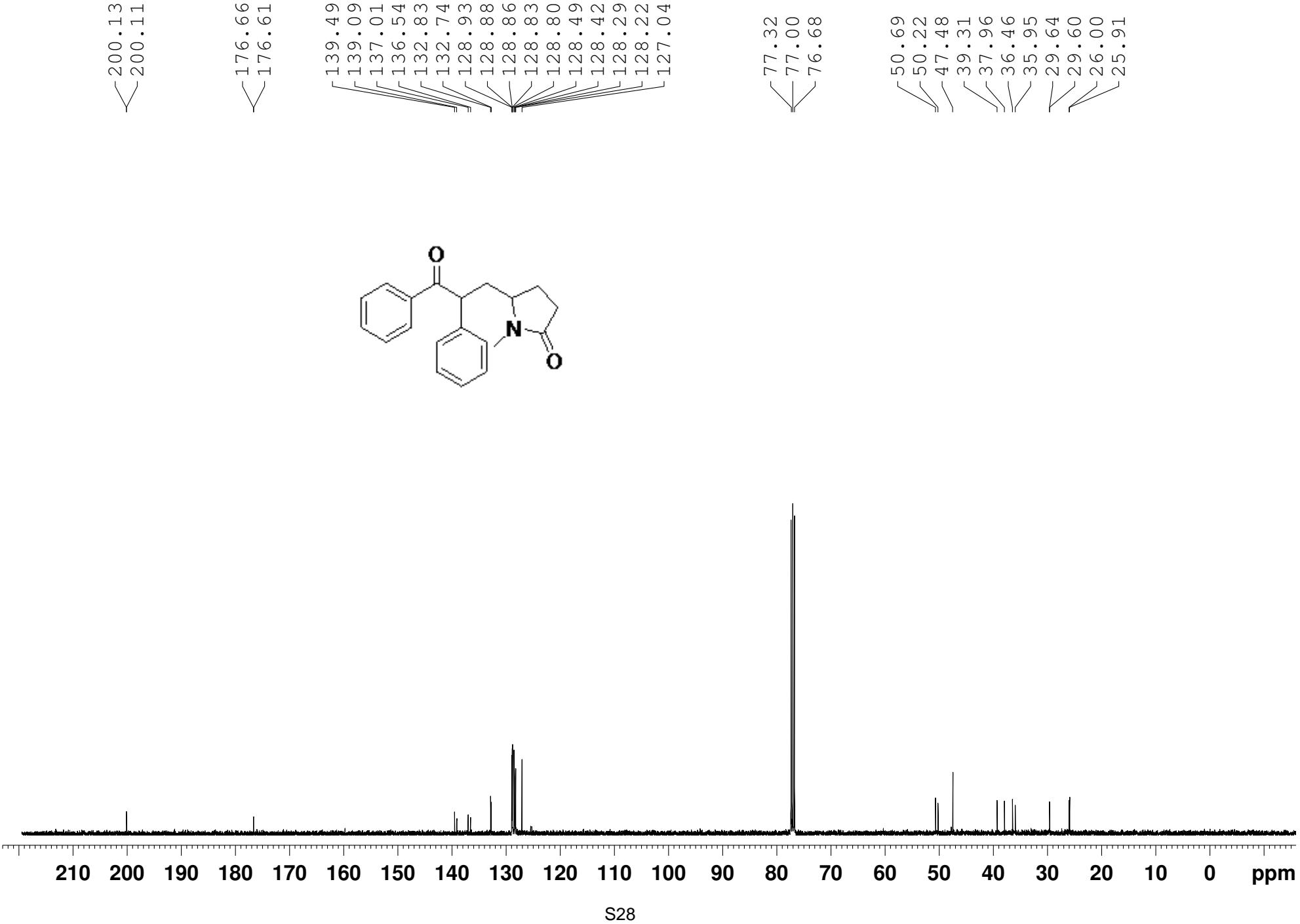
1,1,3-Trimethyl-3-(3-methyl-4-oxo-3,4-diphenylbutyl)urea (3gc)



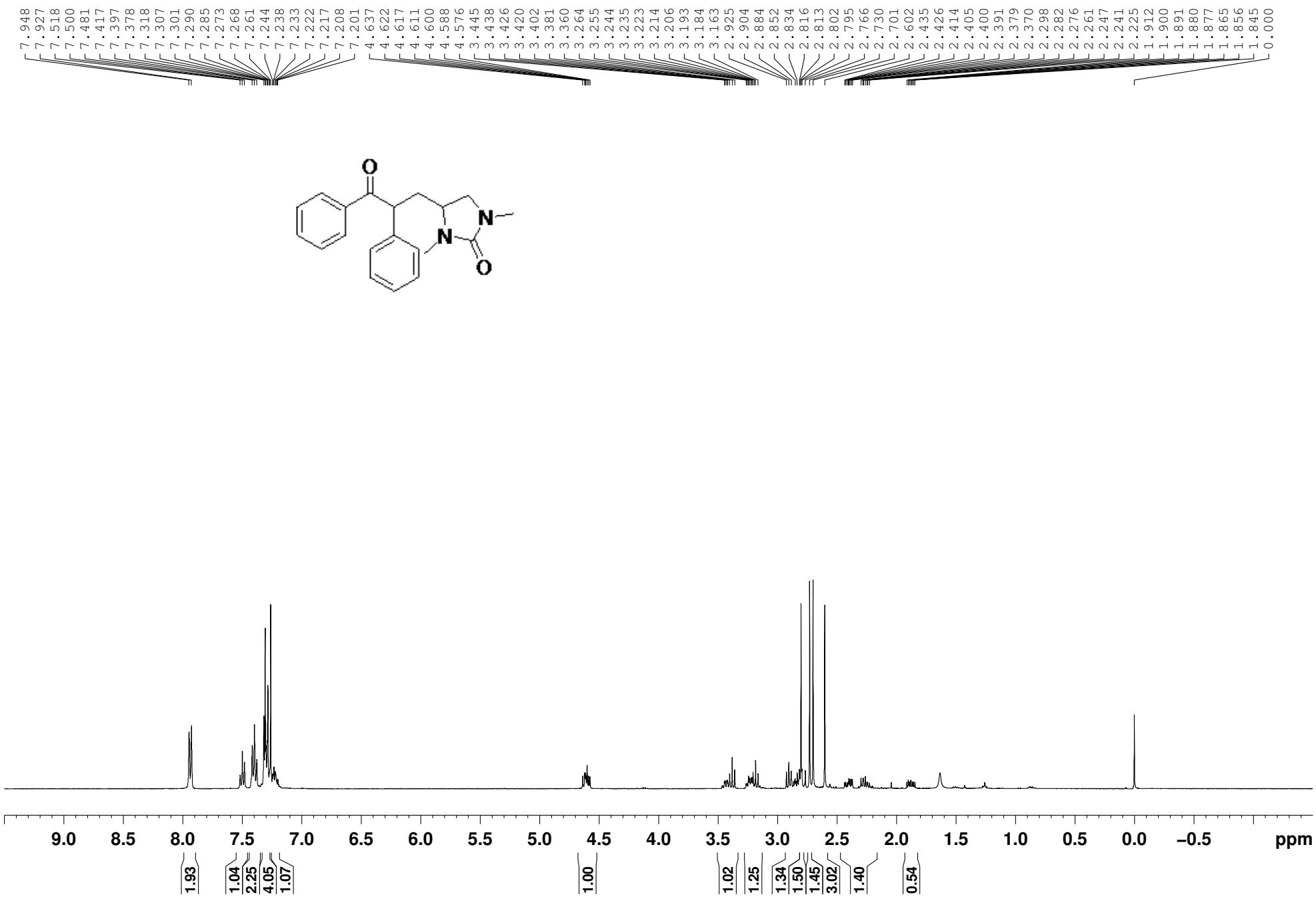


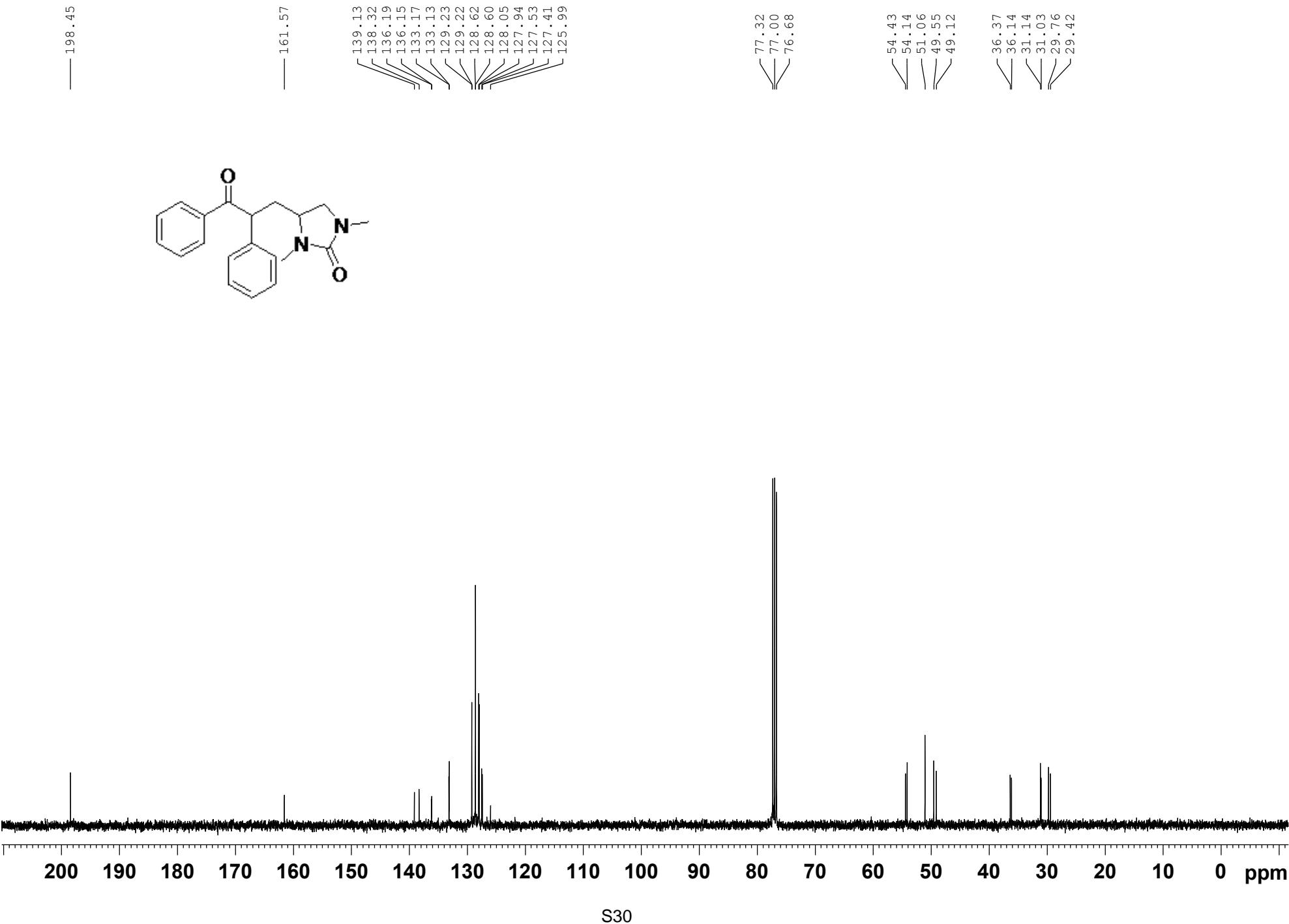
1-Methyl-5-(3-oxo-2,3-diphenylpropyl)pyrrolidin-2-one (3ad)



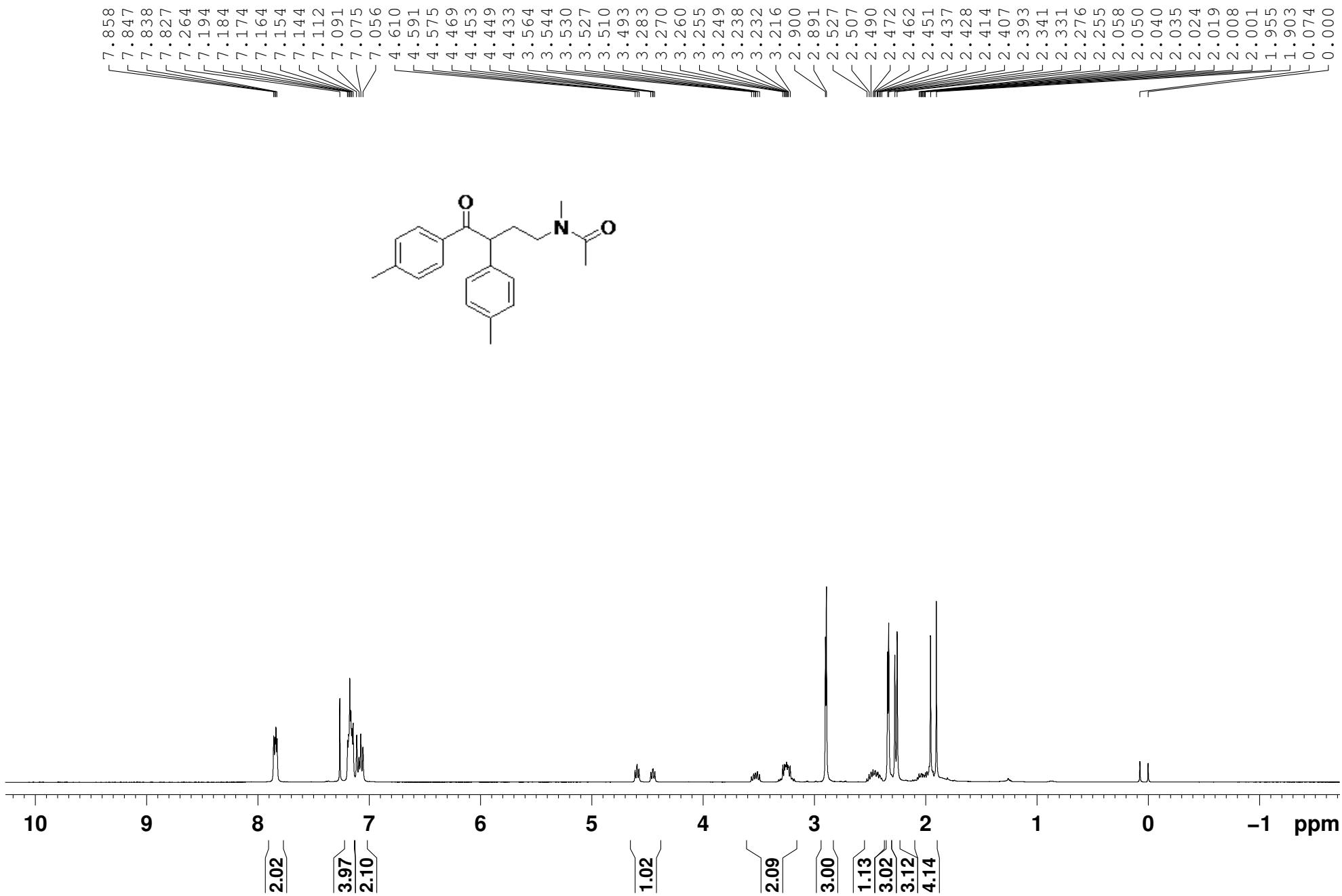


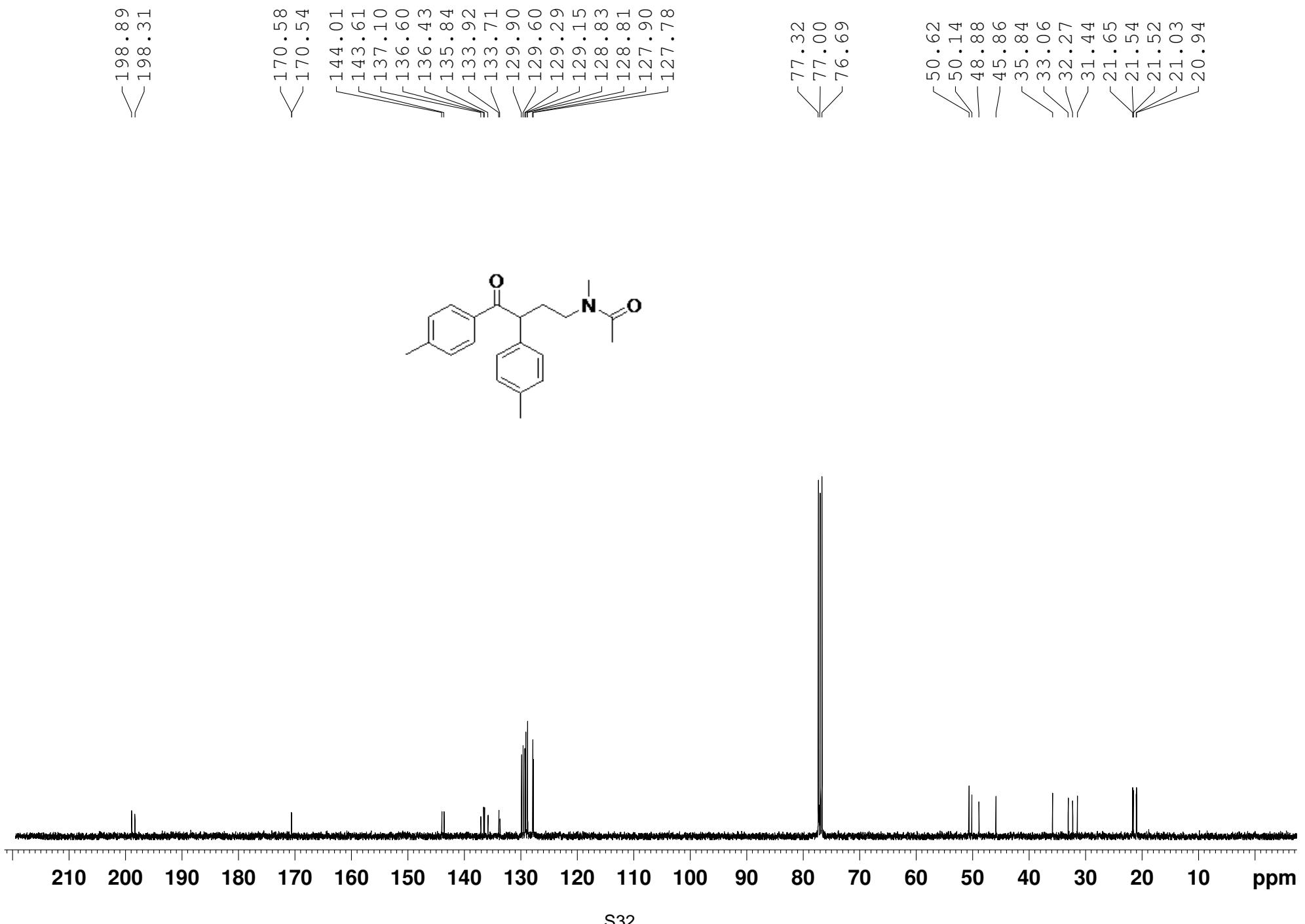
1,3-Dimethyl-4-(3-oxo-2,3-diphenylpropyl)imidazolidin-2-one (3ae)



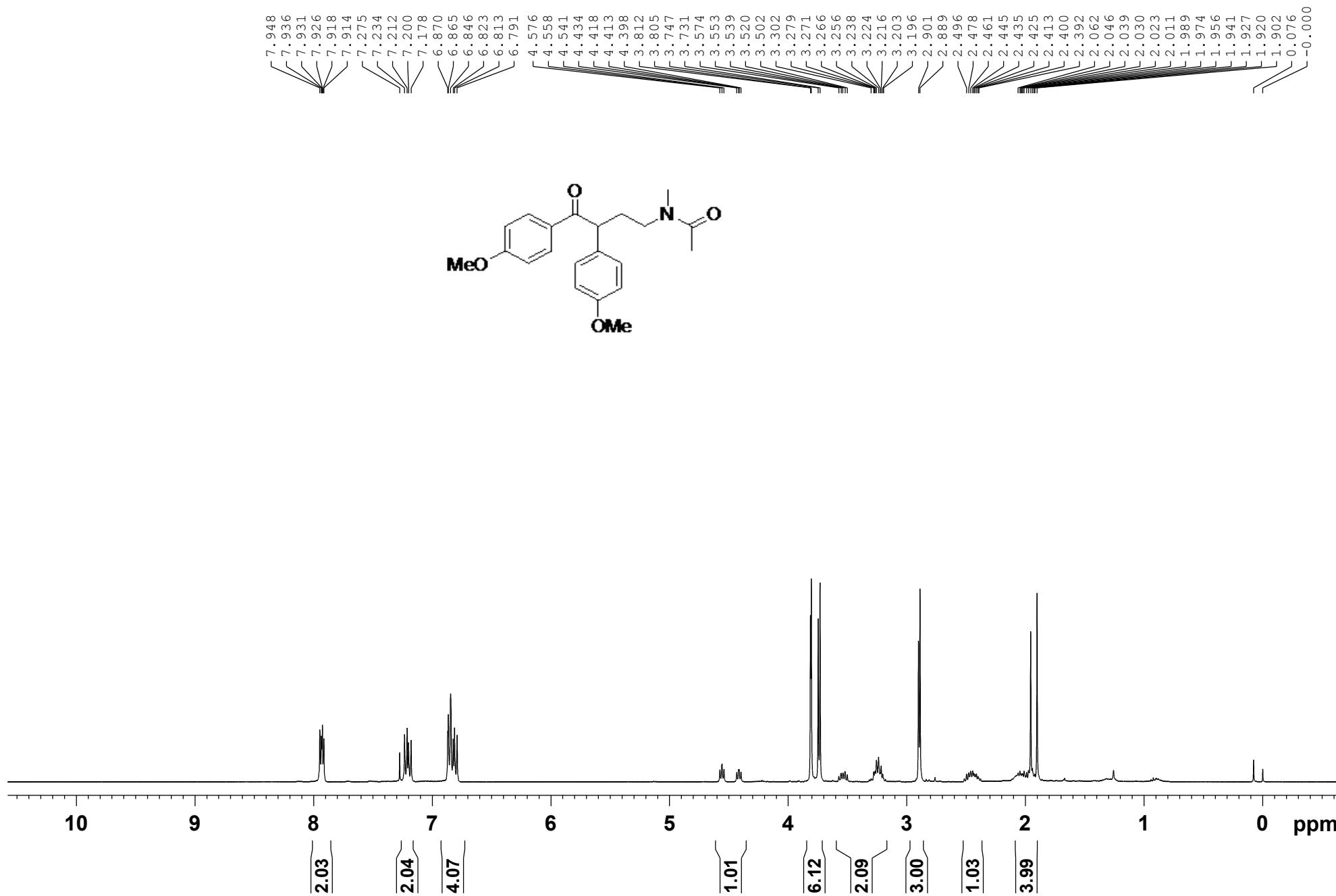


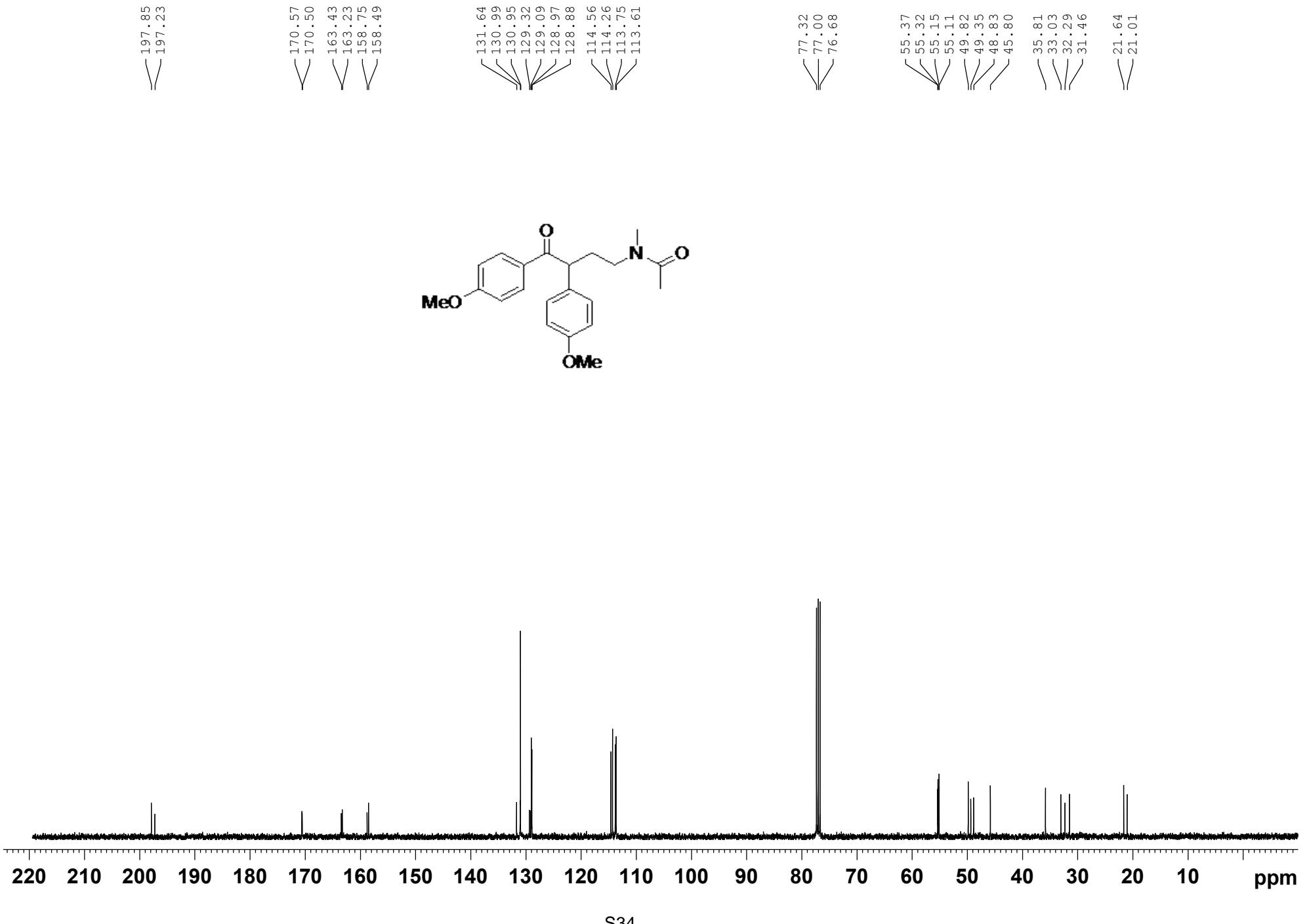
N-Methyl-N-(4-oxo-3,4-diphenylbutyl)acetamide (3ba)



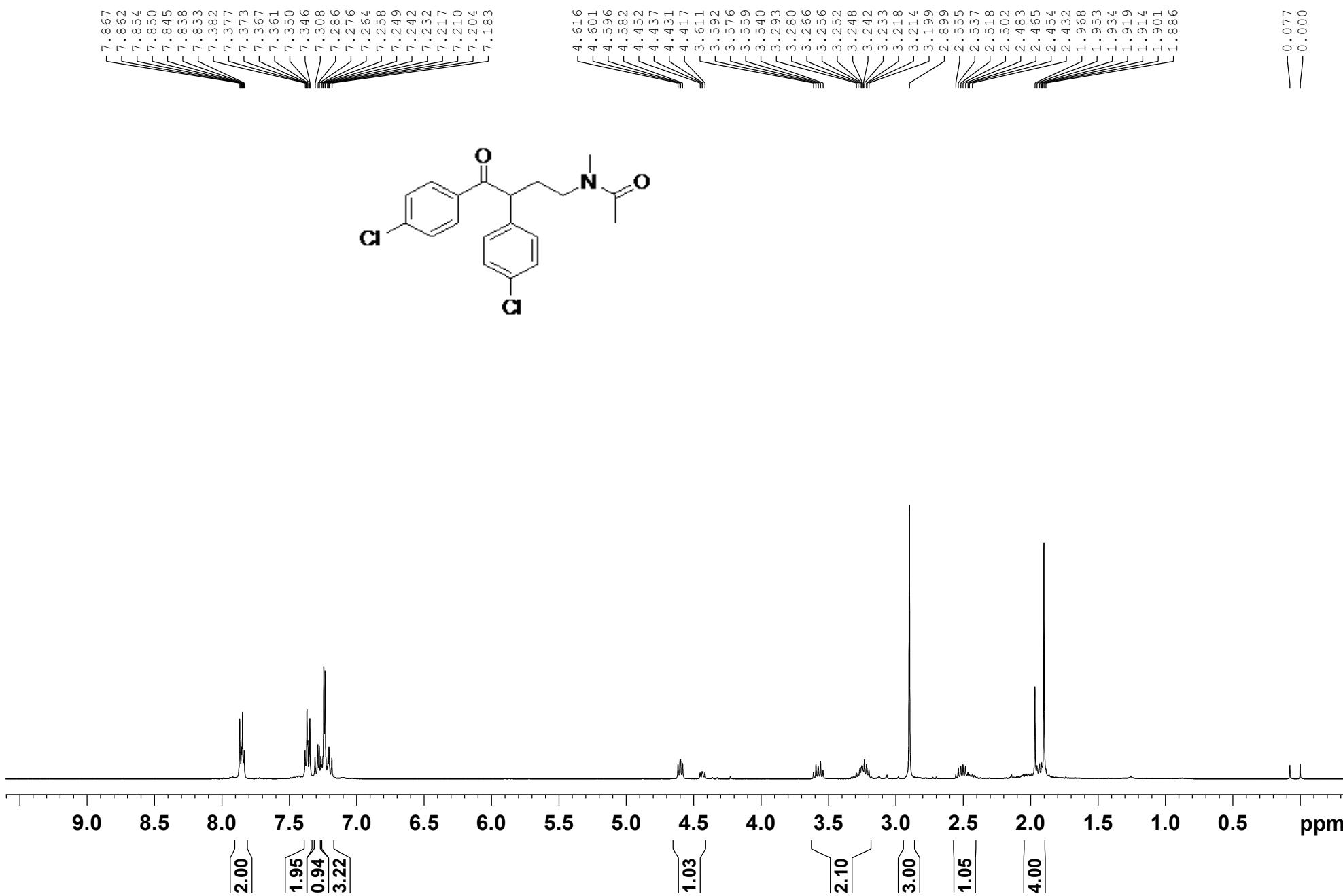


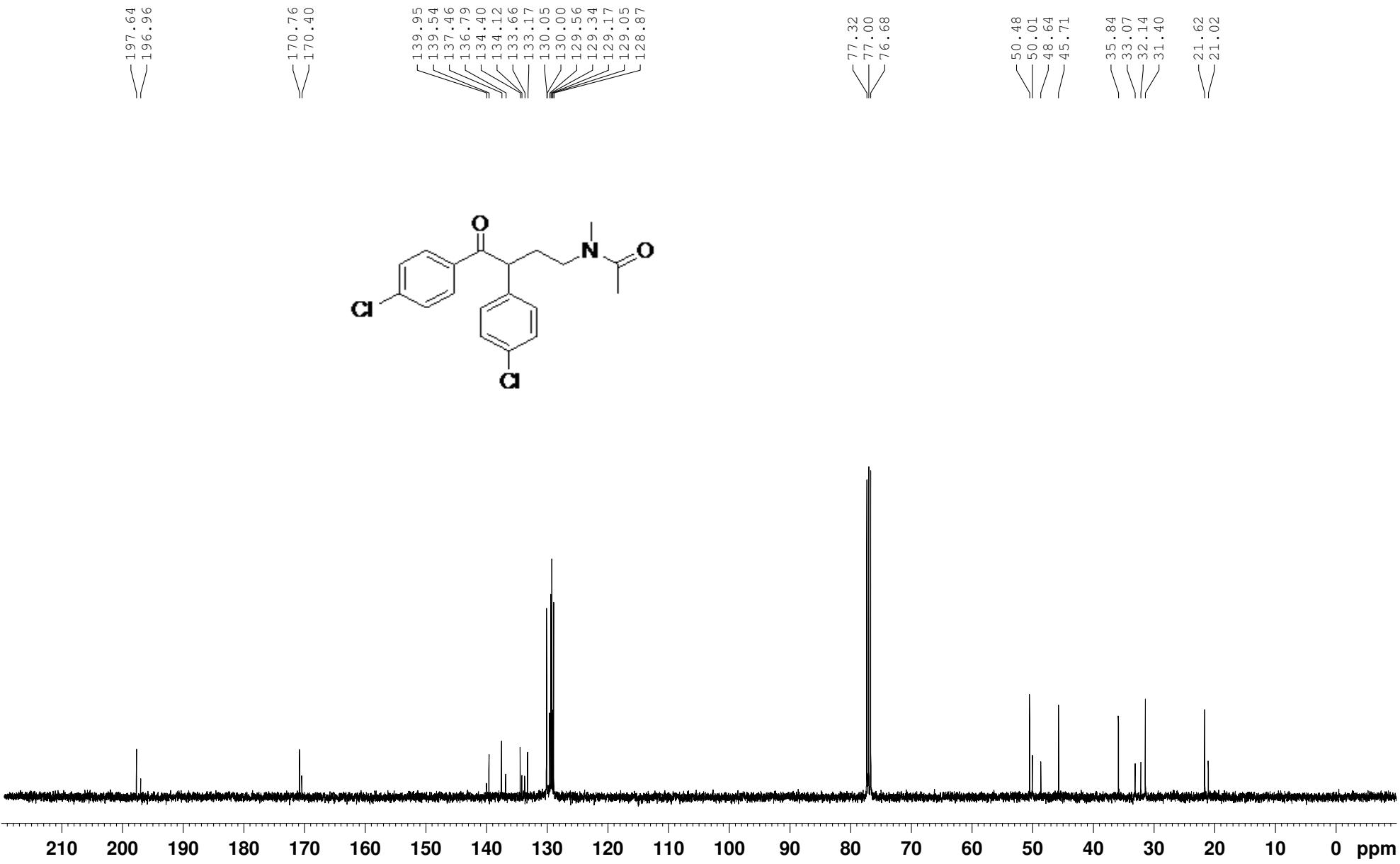
N-(3,4-Bis(4-methoxyphenyl)-4-oxobutyl)-N-methylacetamide (3ca)



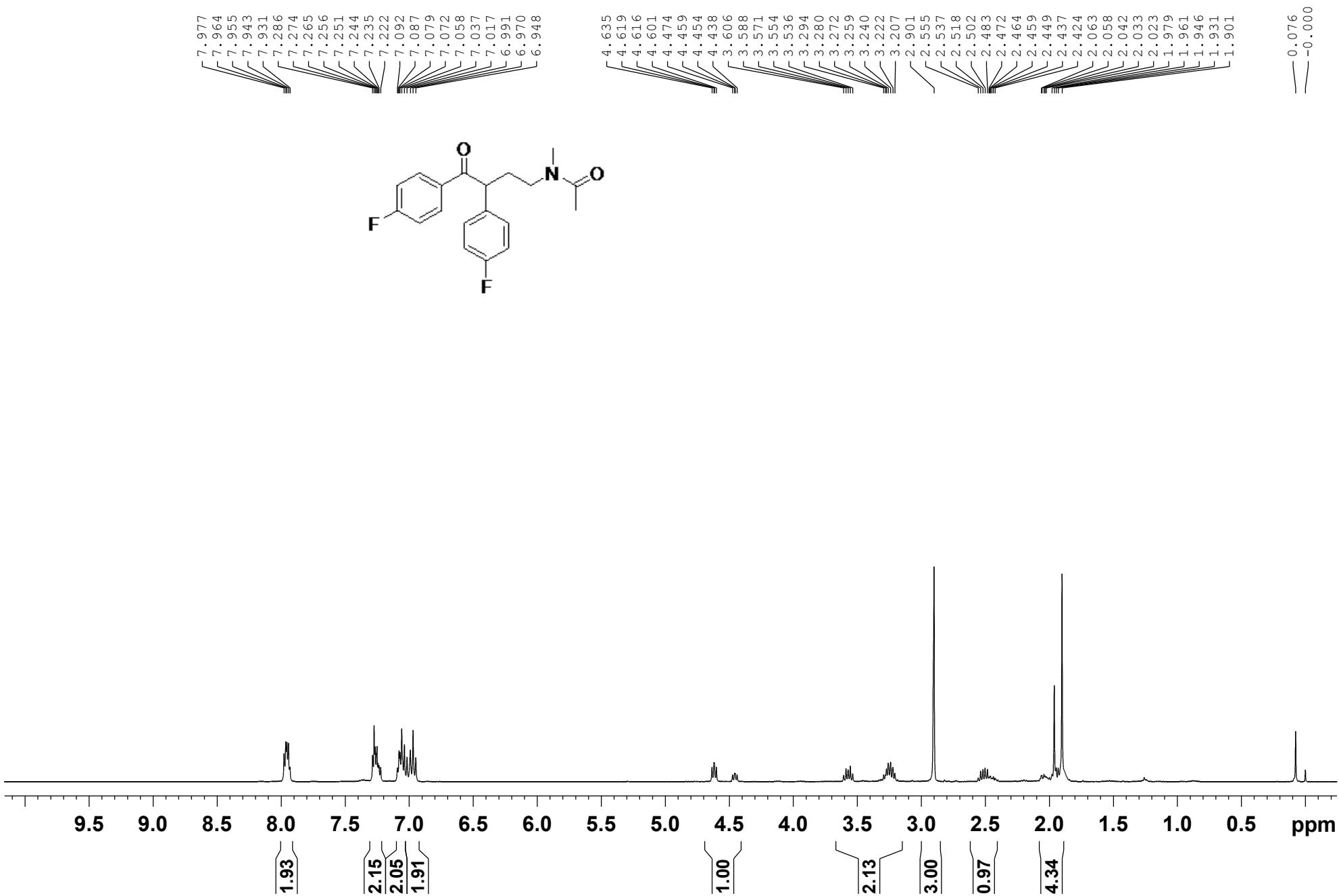


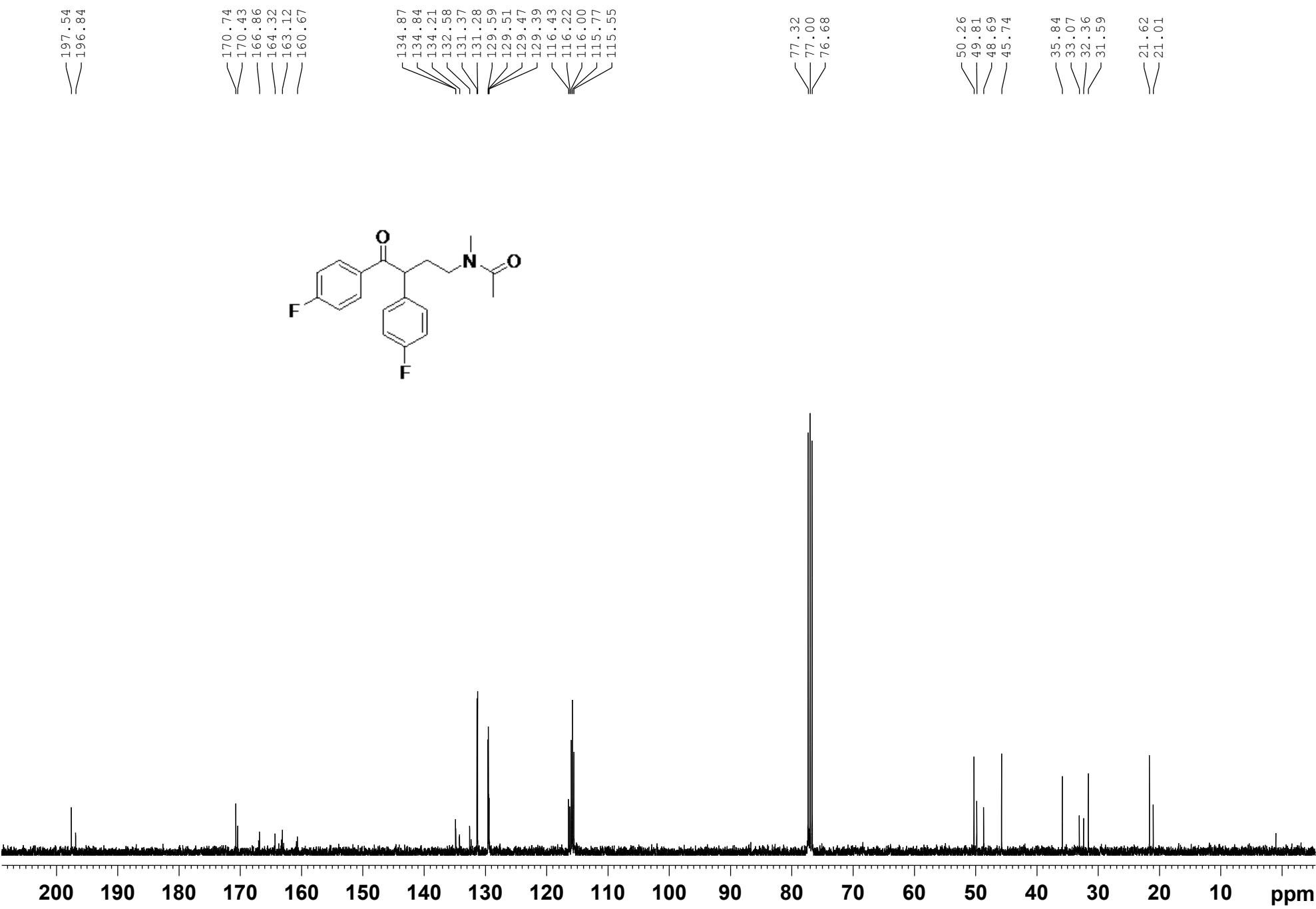
N-(3,4-Bis(4-chlorophenyl)-4-oxobutyl)-N-methylacetamide (3da)

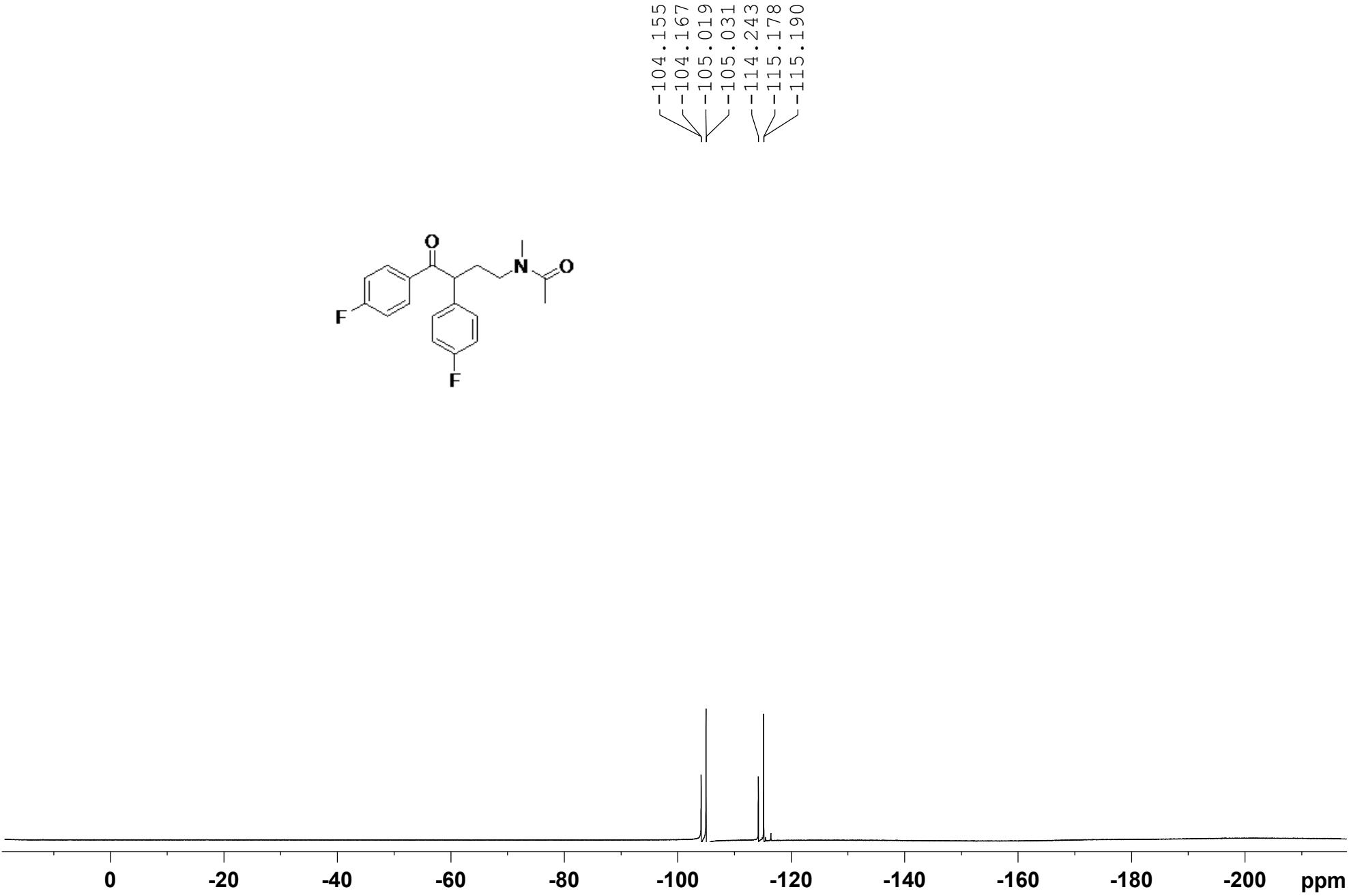




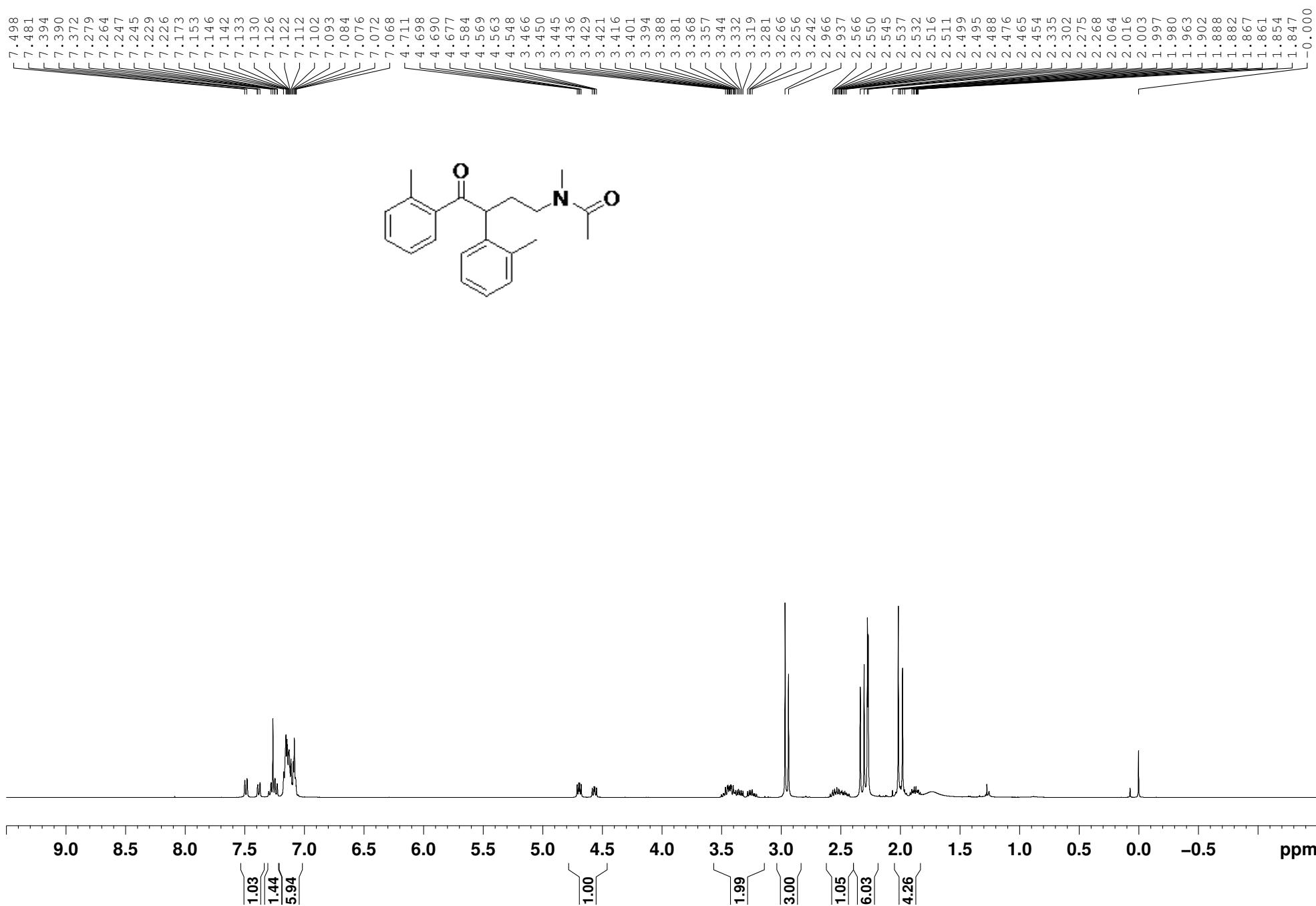
N-(3,4-Bis(4-fluorophenyl)-4-oxobutyl)-N-methylacetamide (3ea)

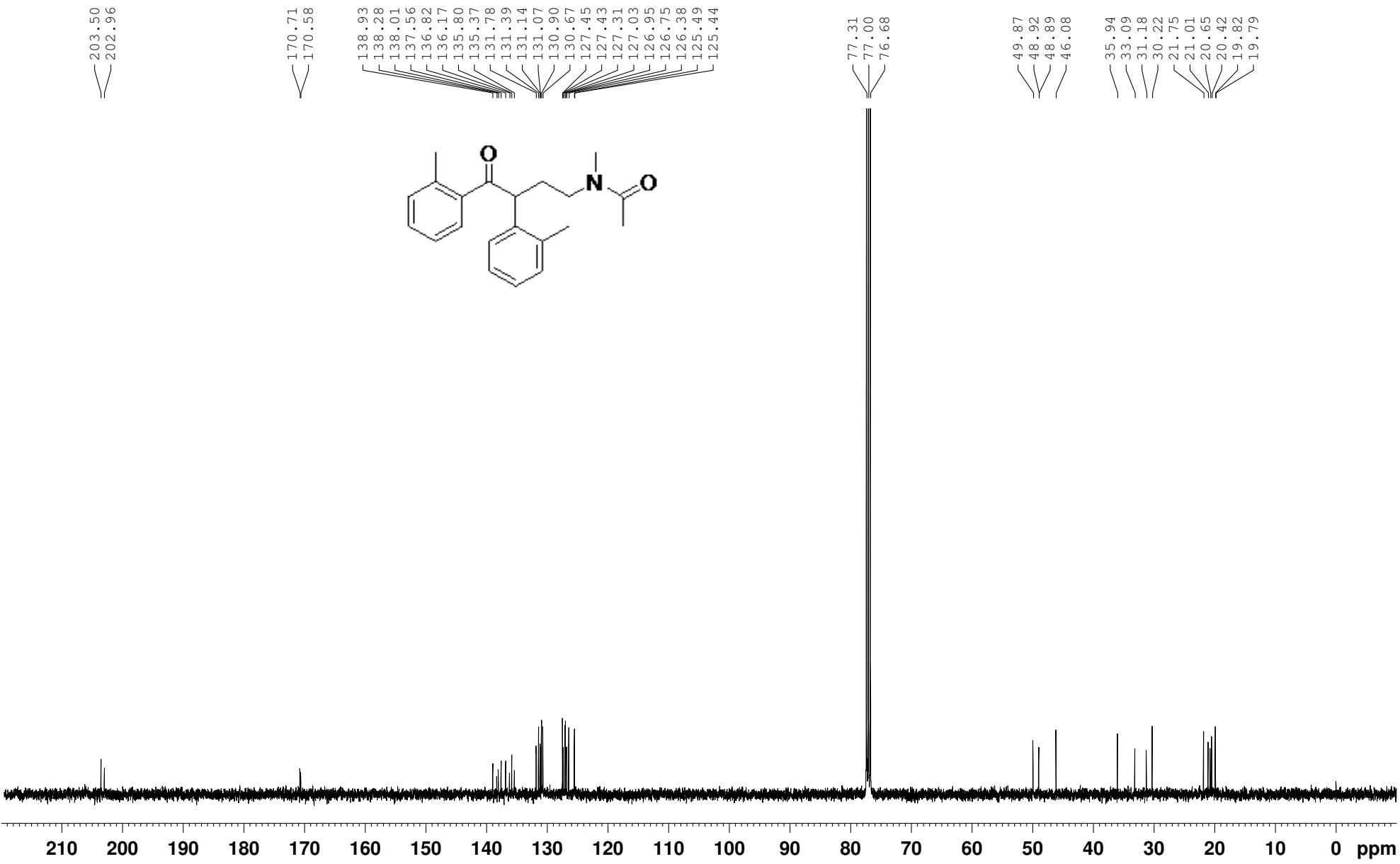


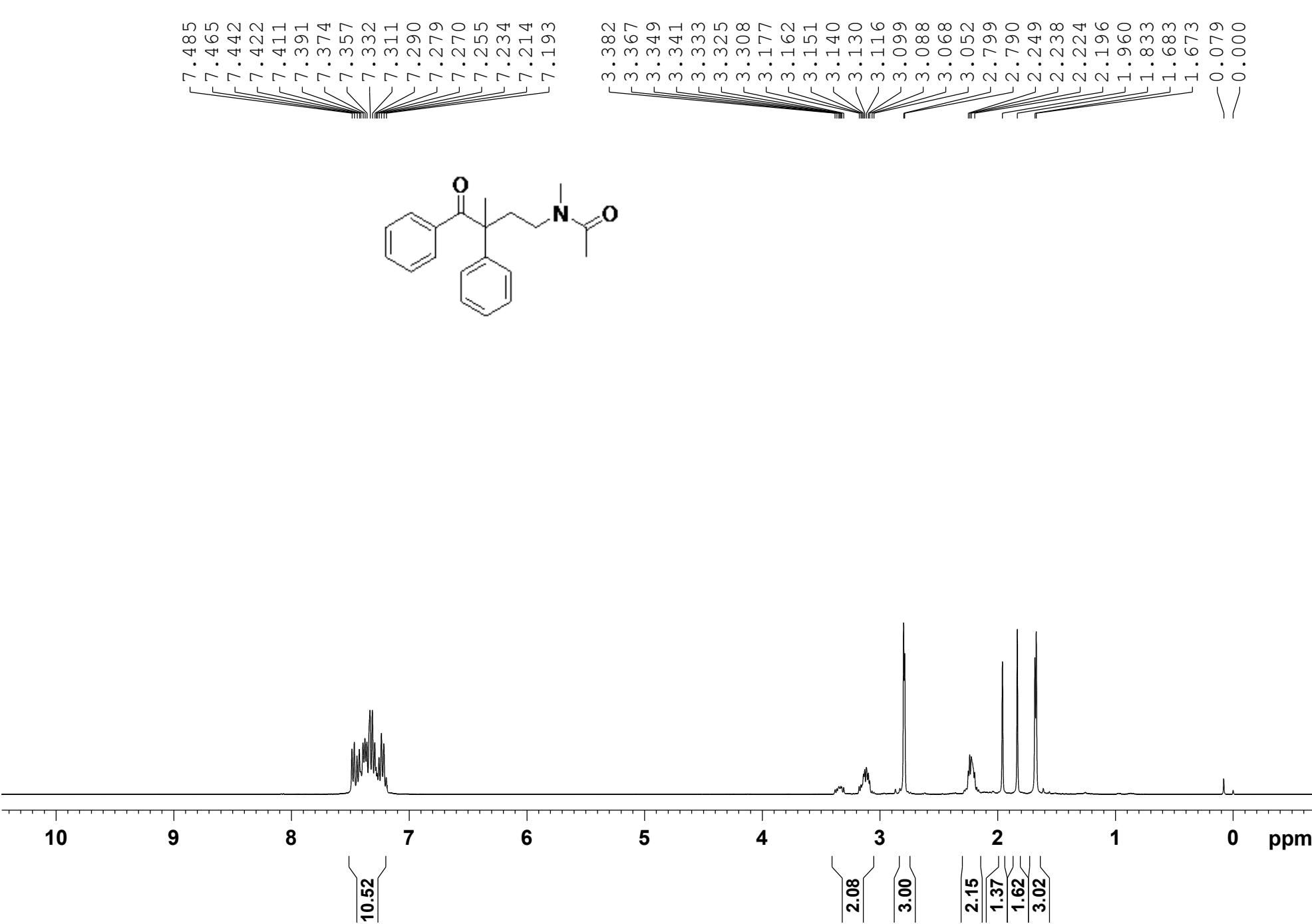


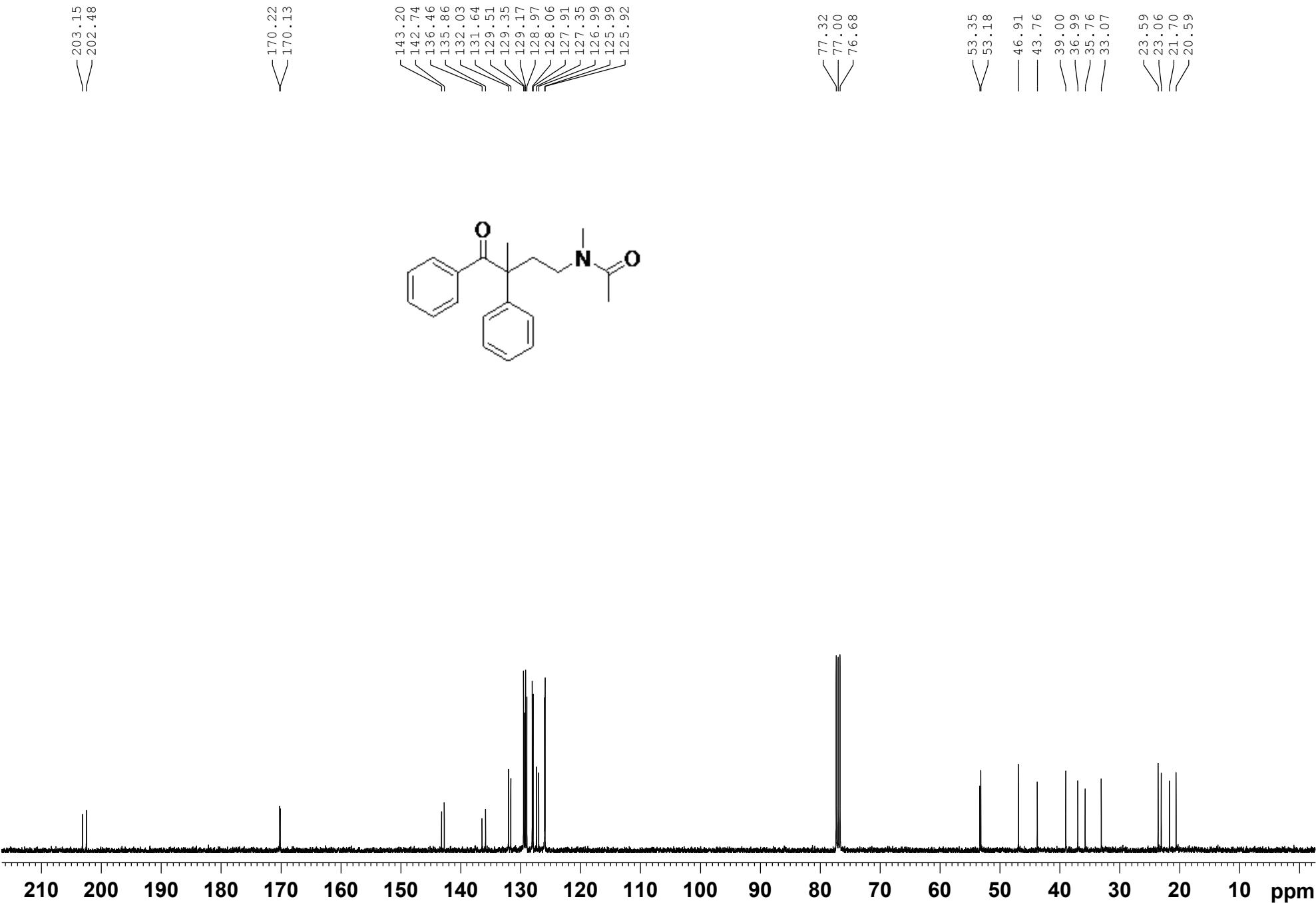


N-Methyl-N-(4-oxo-3,4-dio-tolylbutyl)acetamide (3fa)

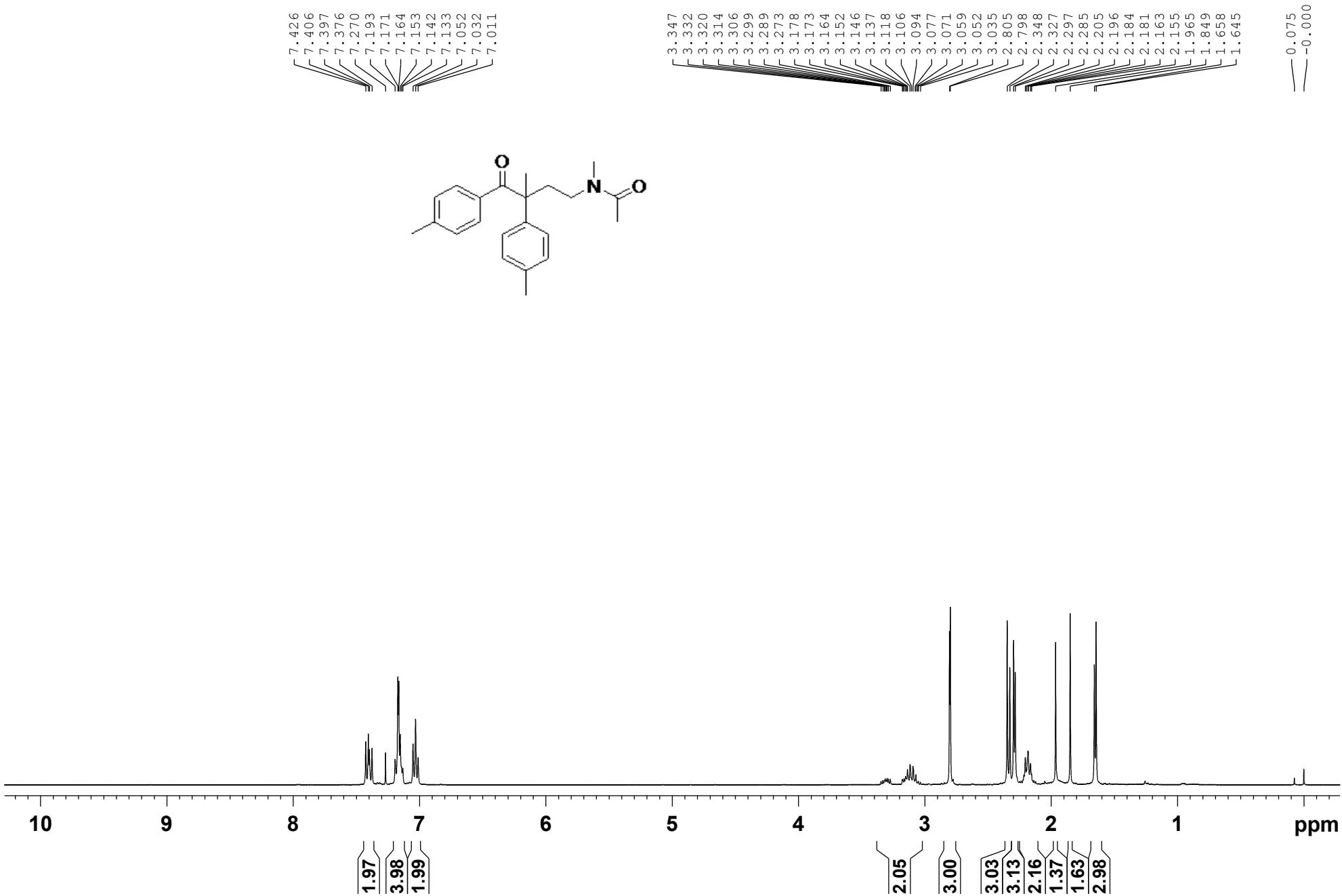


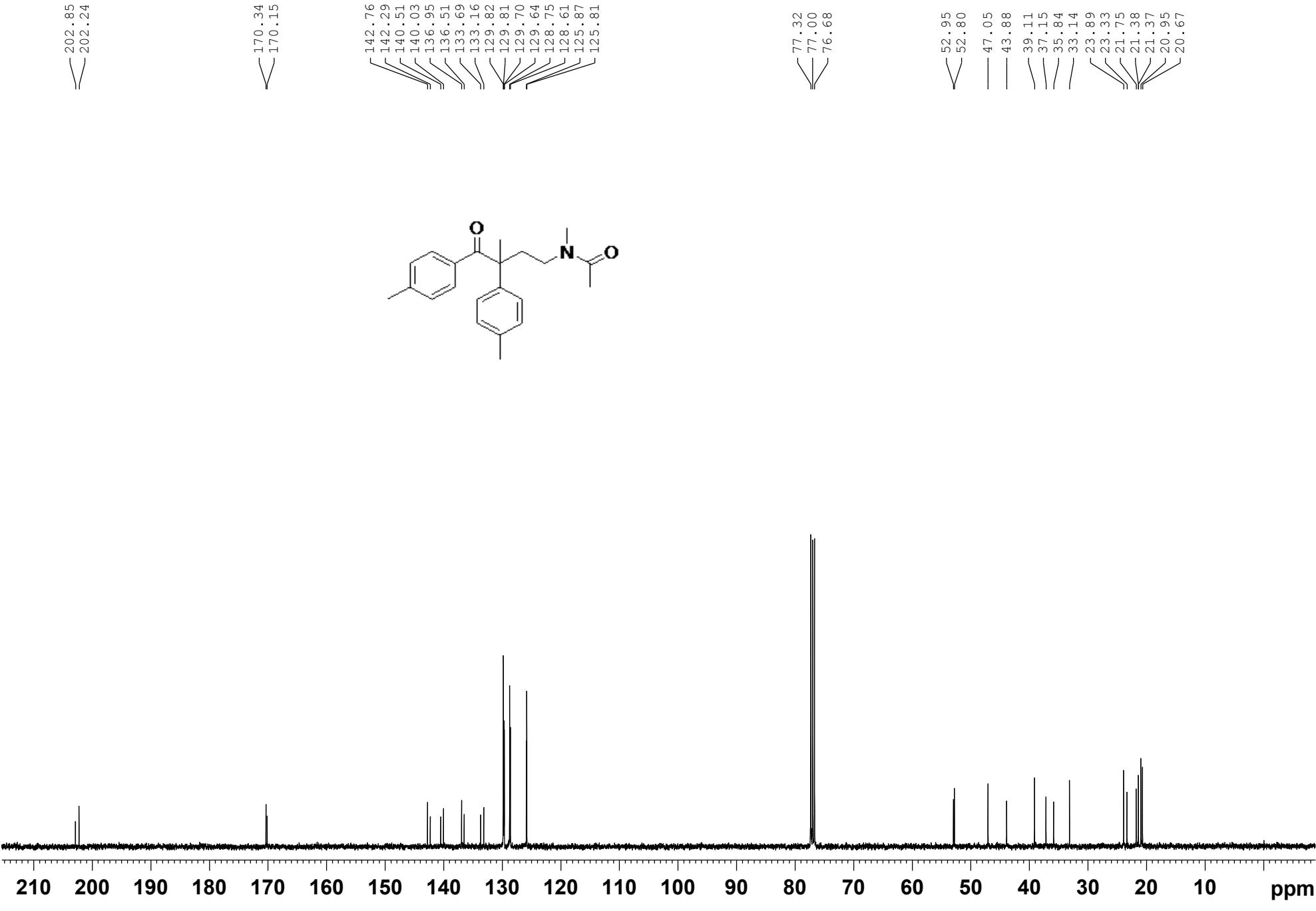




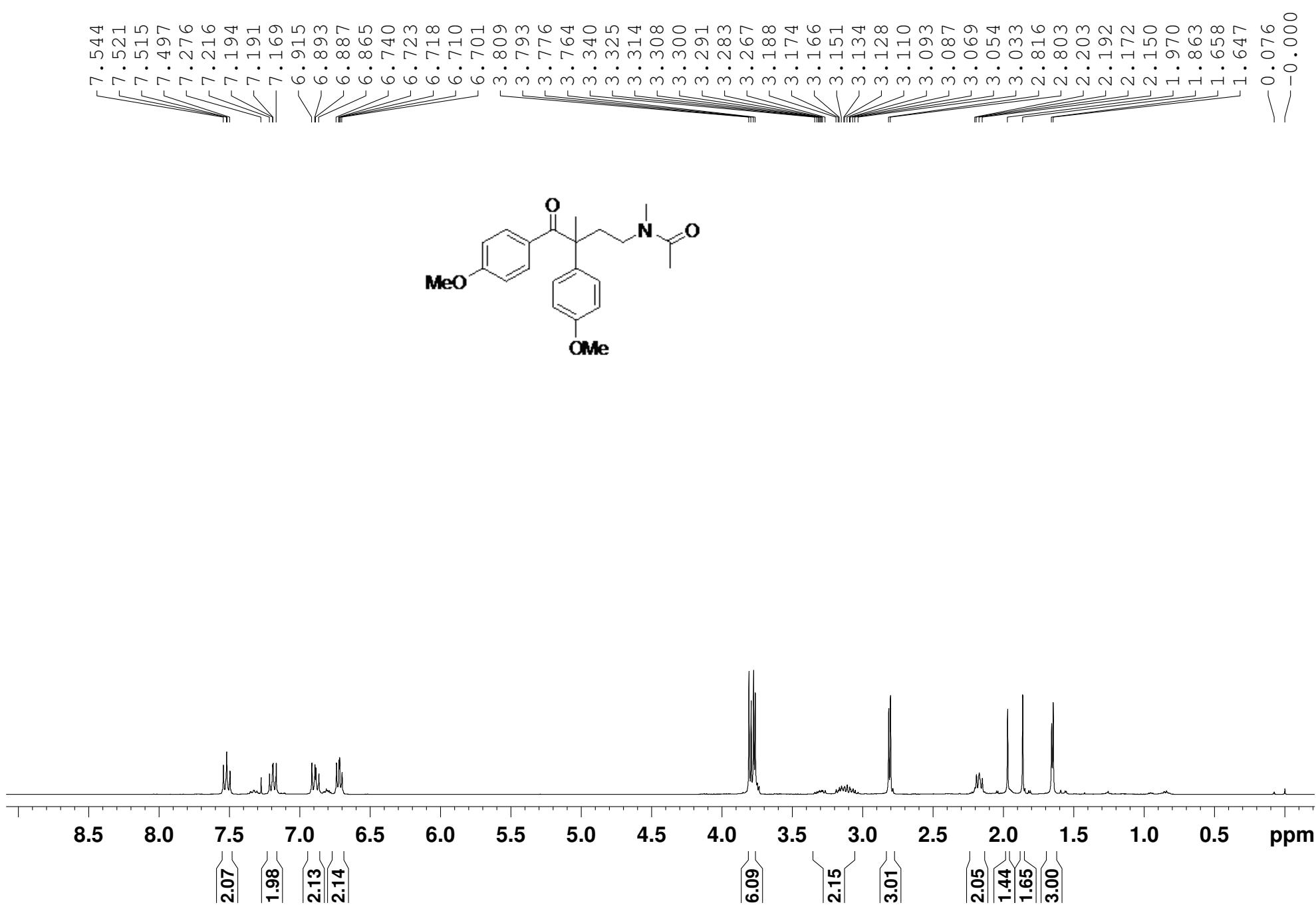


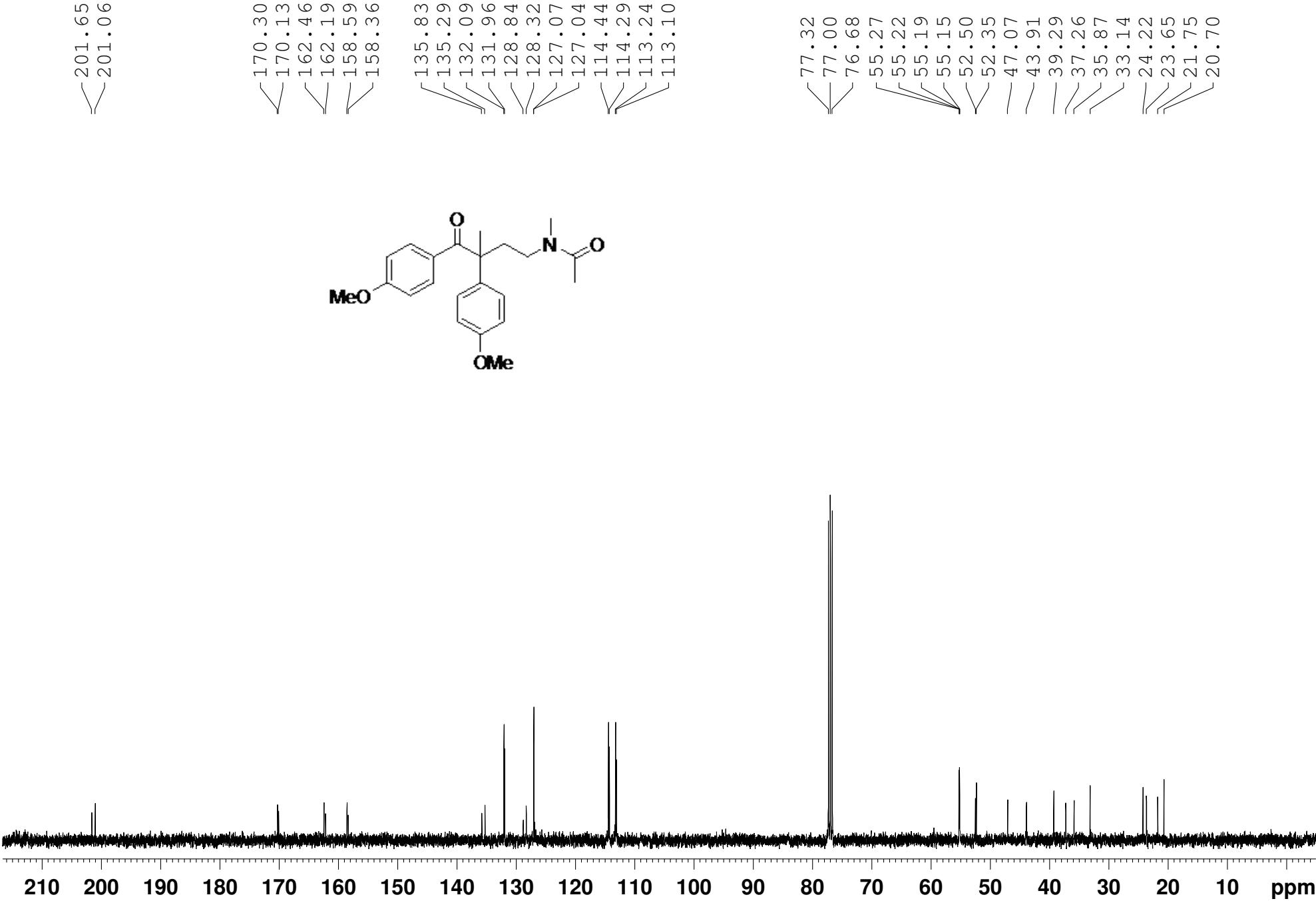
N-Methyl-N-(3-methyl-4-oxo-3,4-diphenylbutyl)acetamide (3ha)



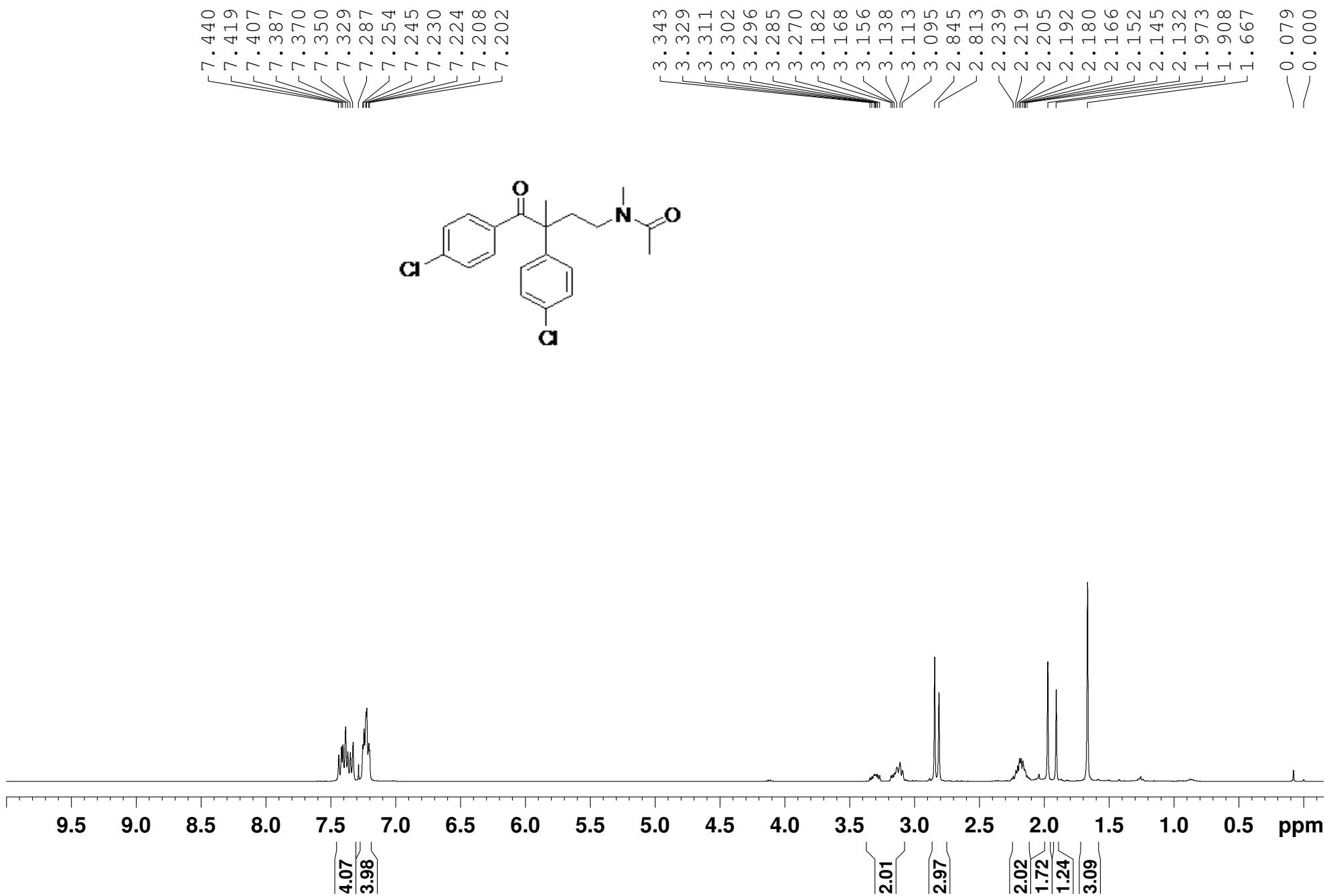


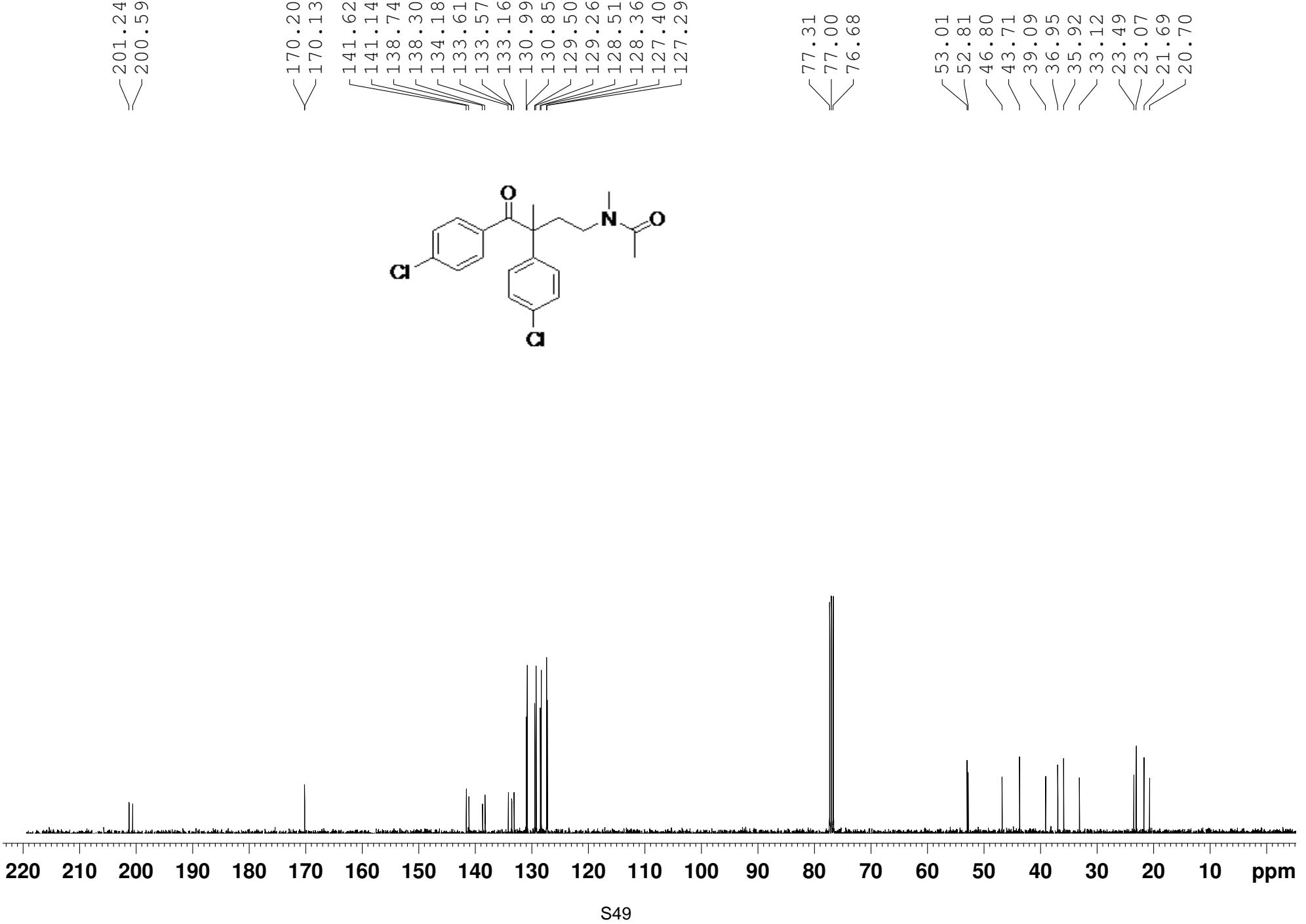
N-(3,4-Bis(4-methoxyphenyl)-3-methyl-4-oxobutyl)-N-methylacetamide (3ia)



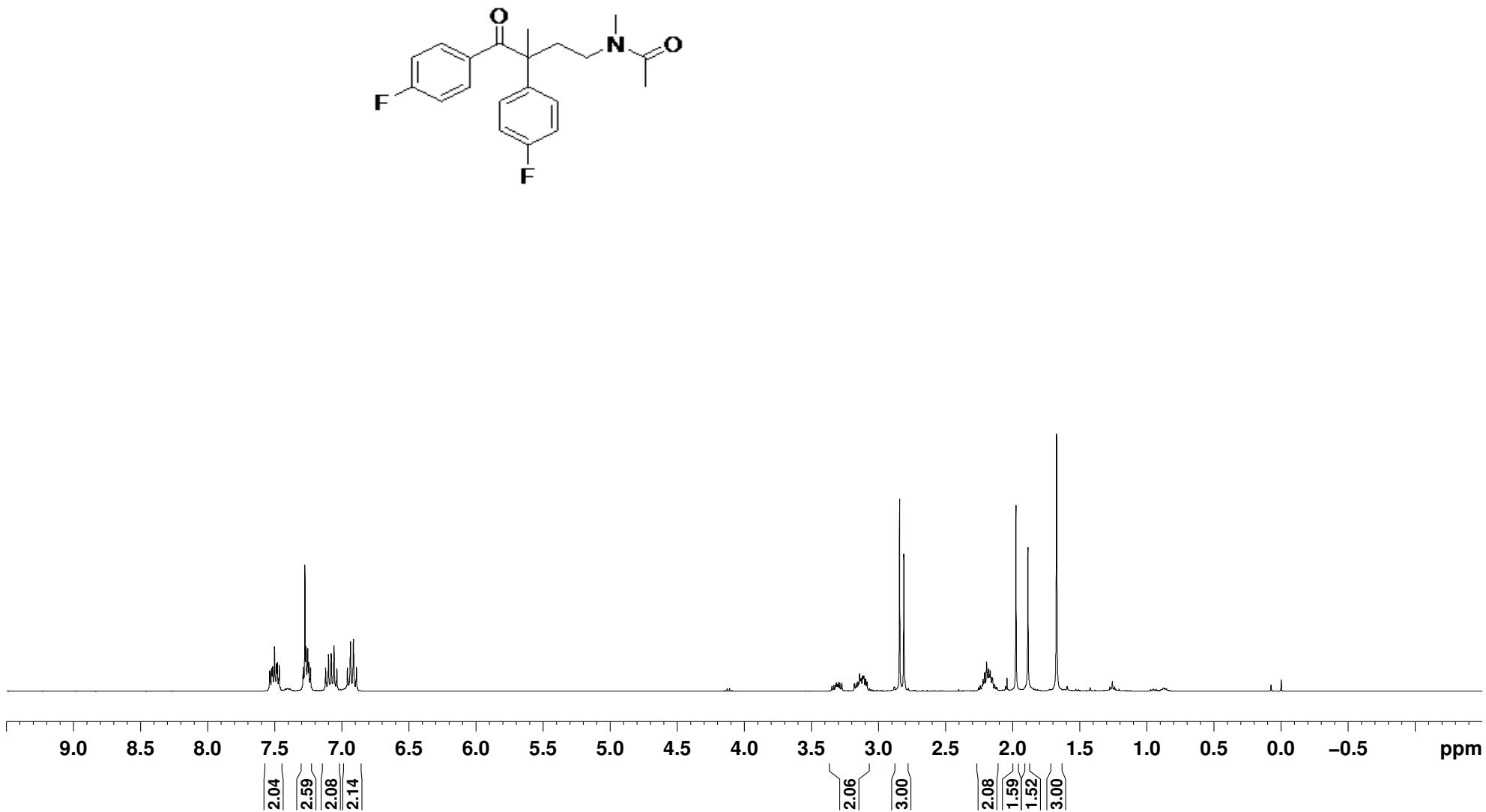
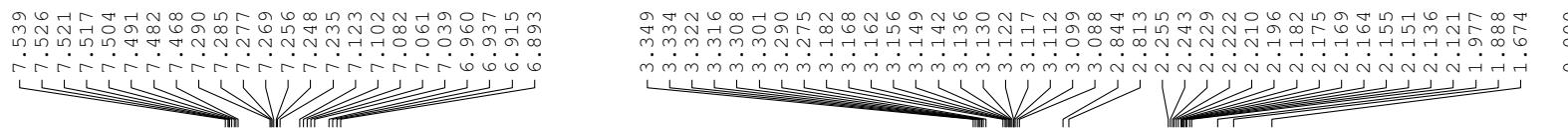


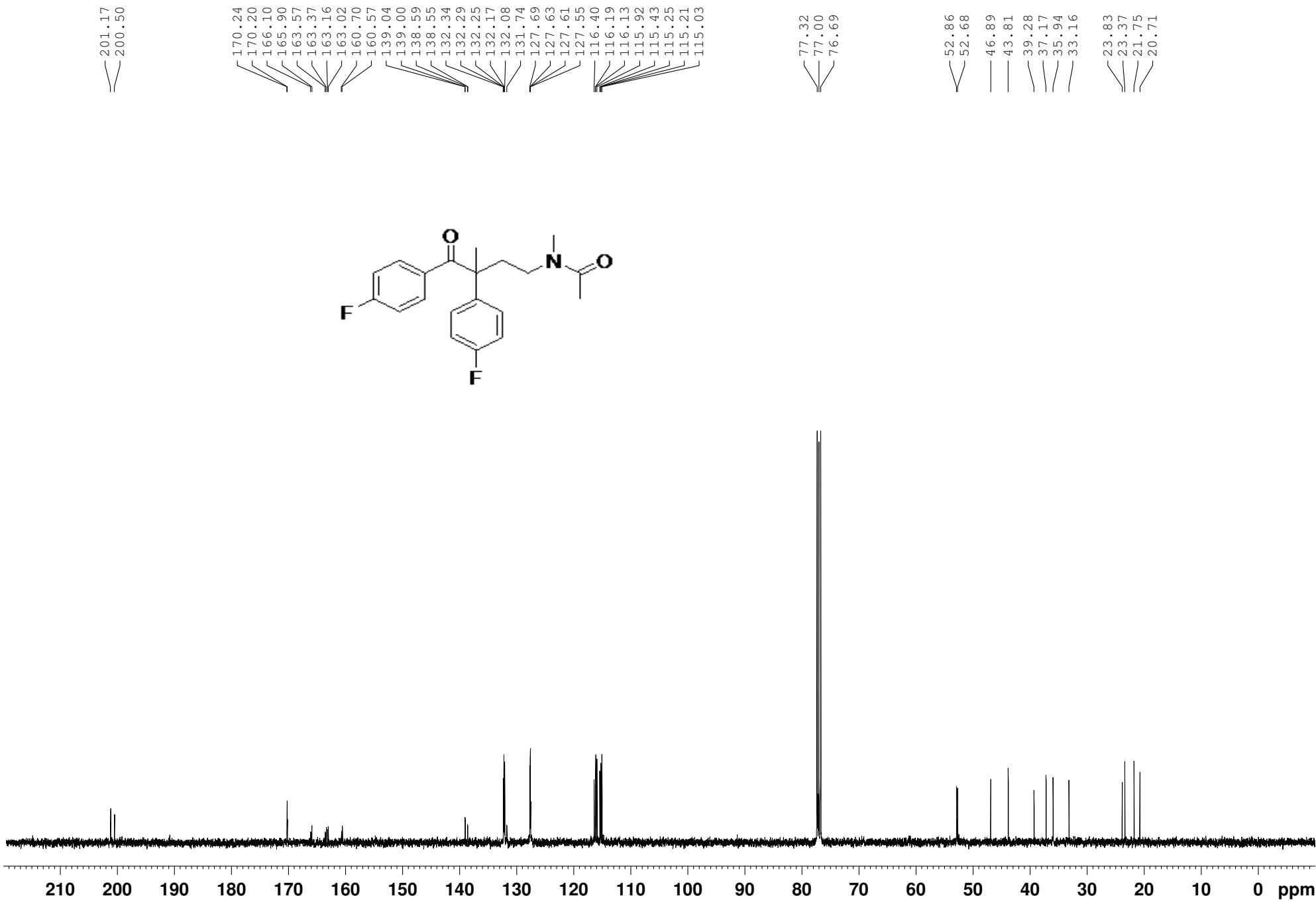
N-(3,4-Bis(4-chlorophenyl)-3-methyl-4-oxobutyl)-N-methylacetamide (3ja)

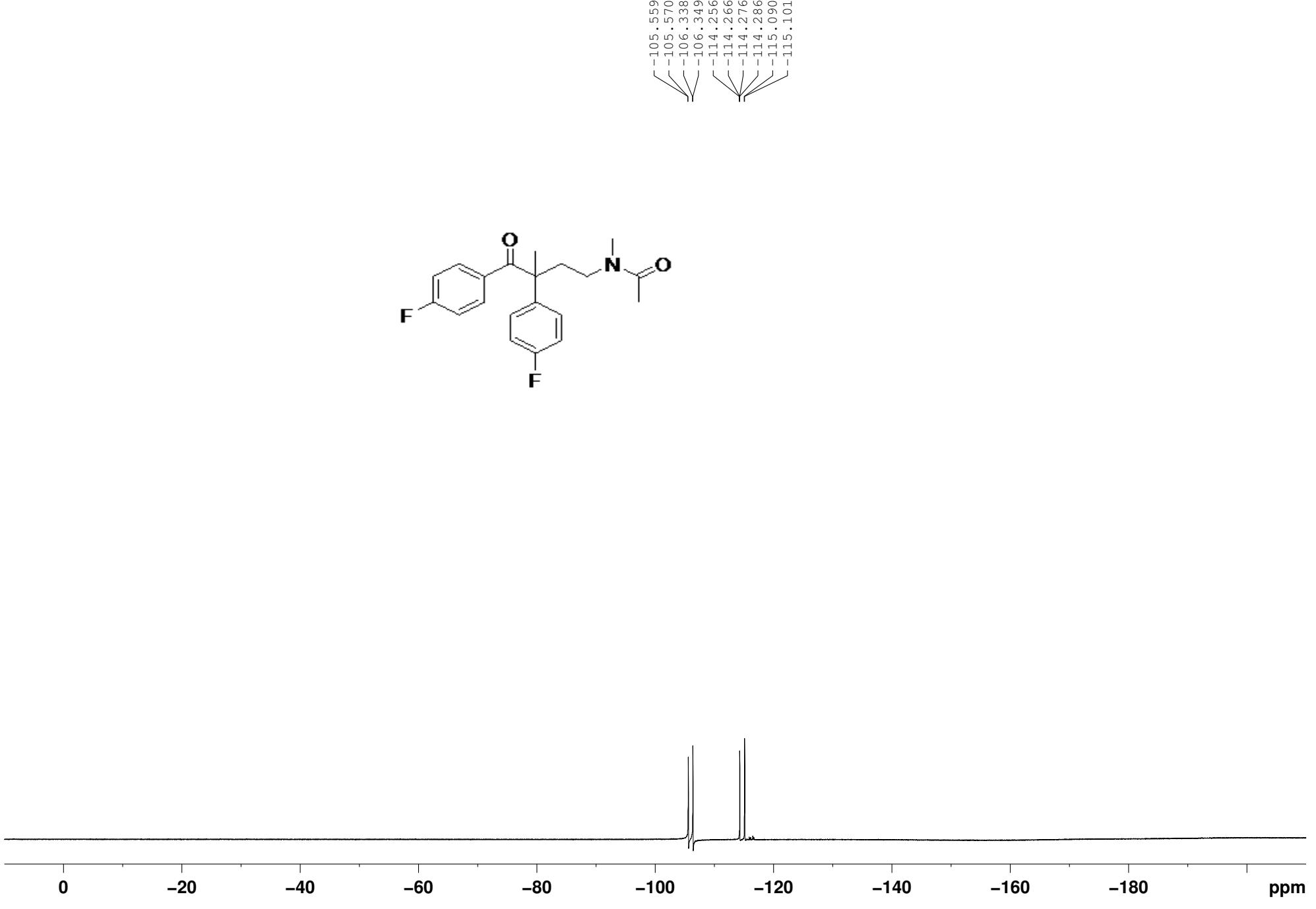




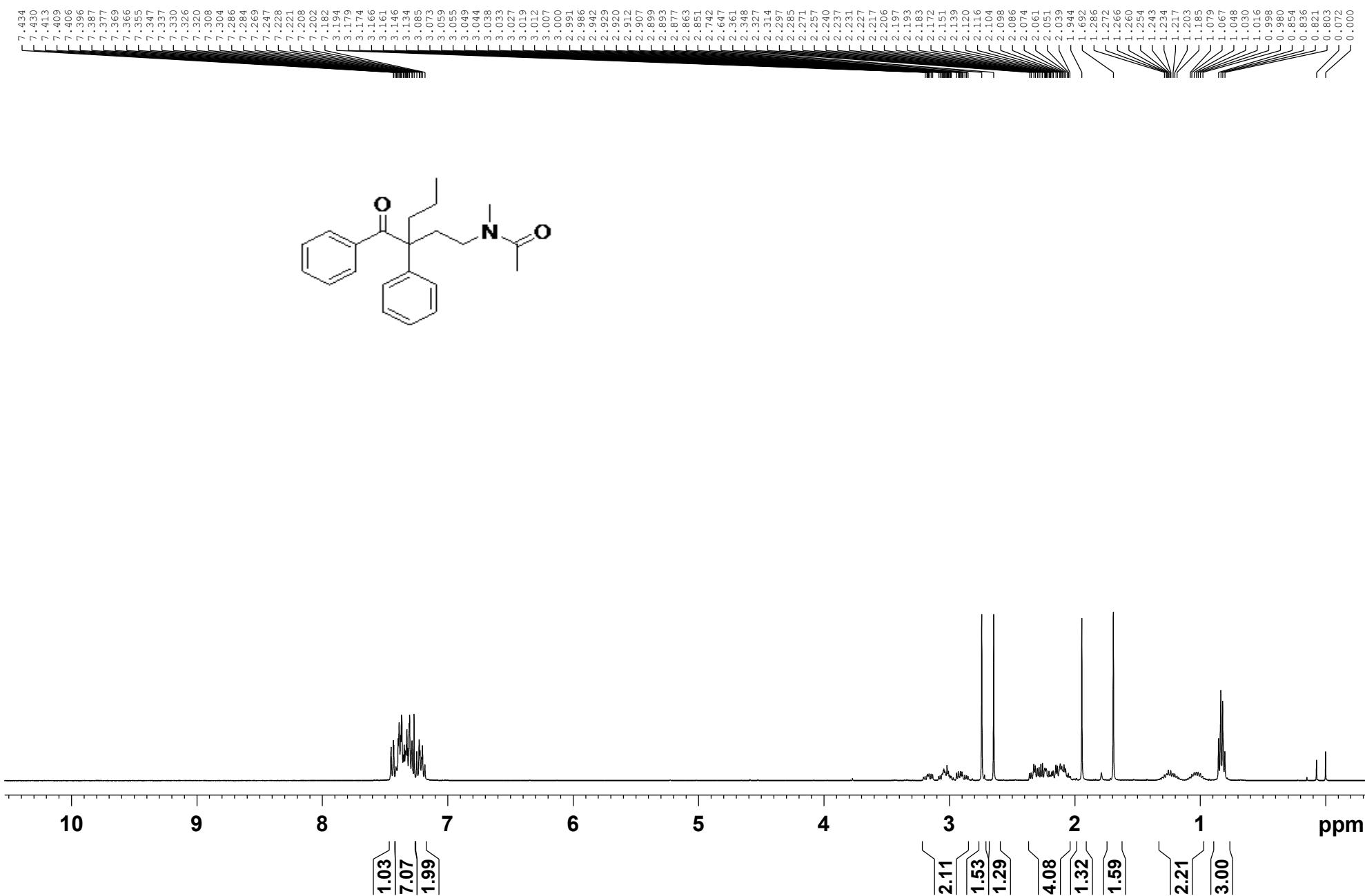
N-(3,4-Bis(4-fluorophenyl)-3-methyl-4-oxobutyl)-N-methylacetamide (3ka)

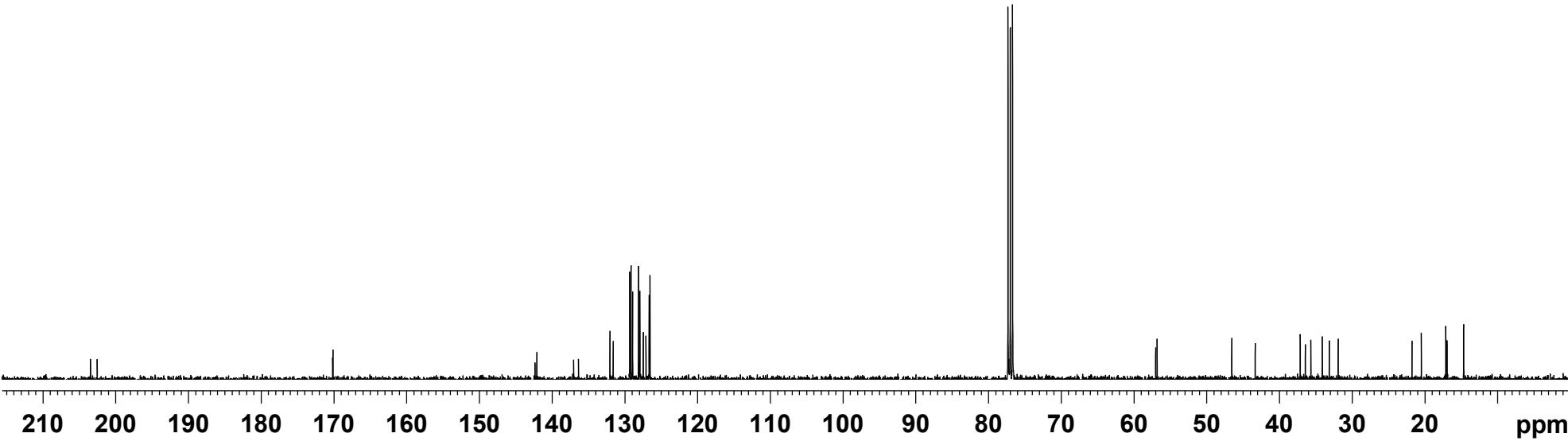






N-(3-Benzoyl-3-phenylhexyl)-N-methylacetamide (3la)





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< 202.523

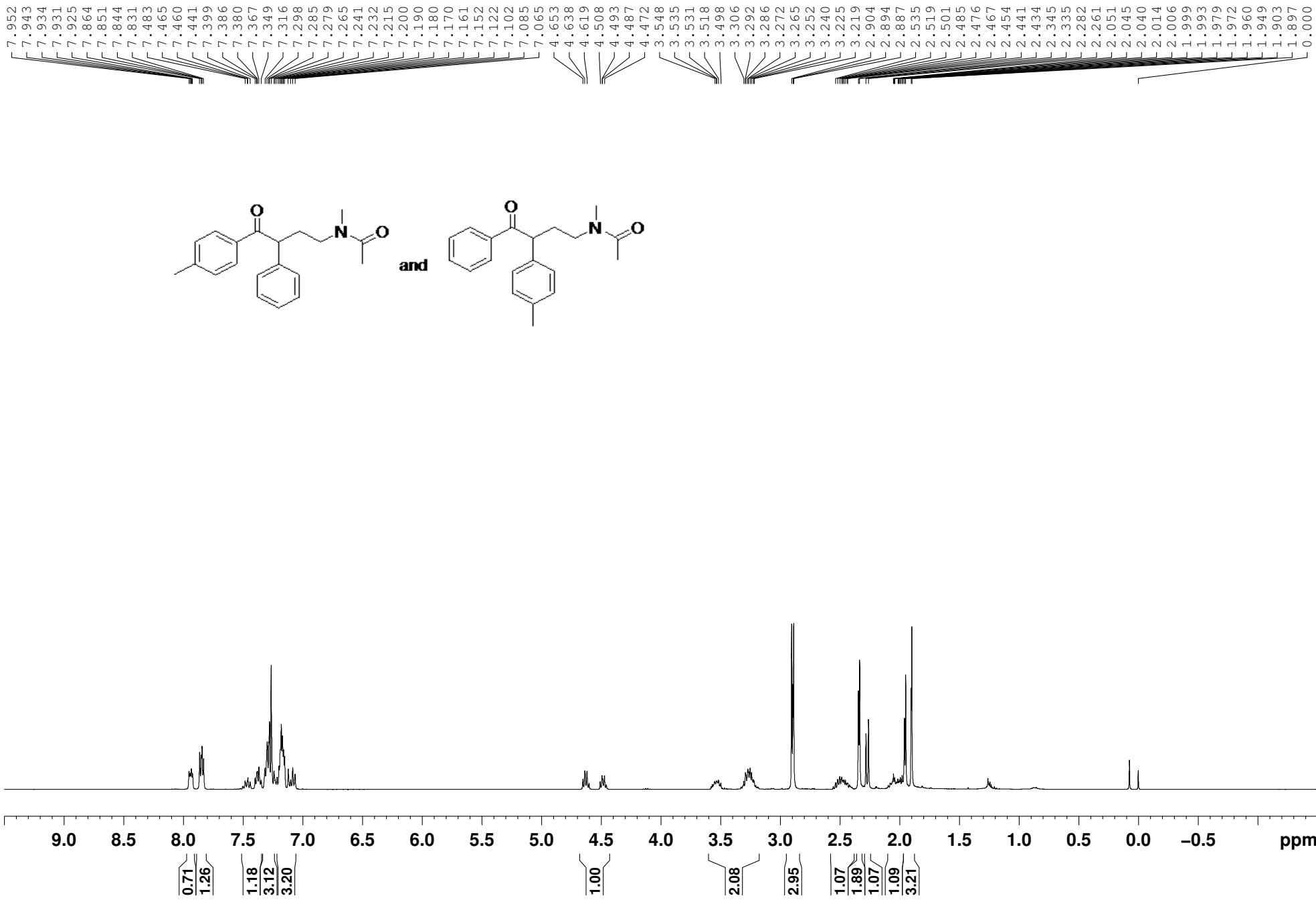
< 170.174
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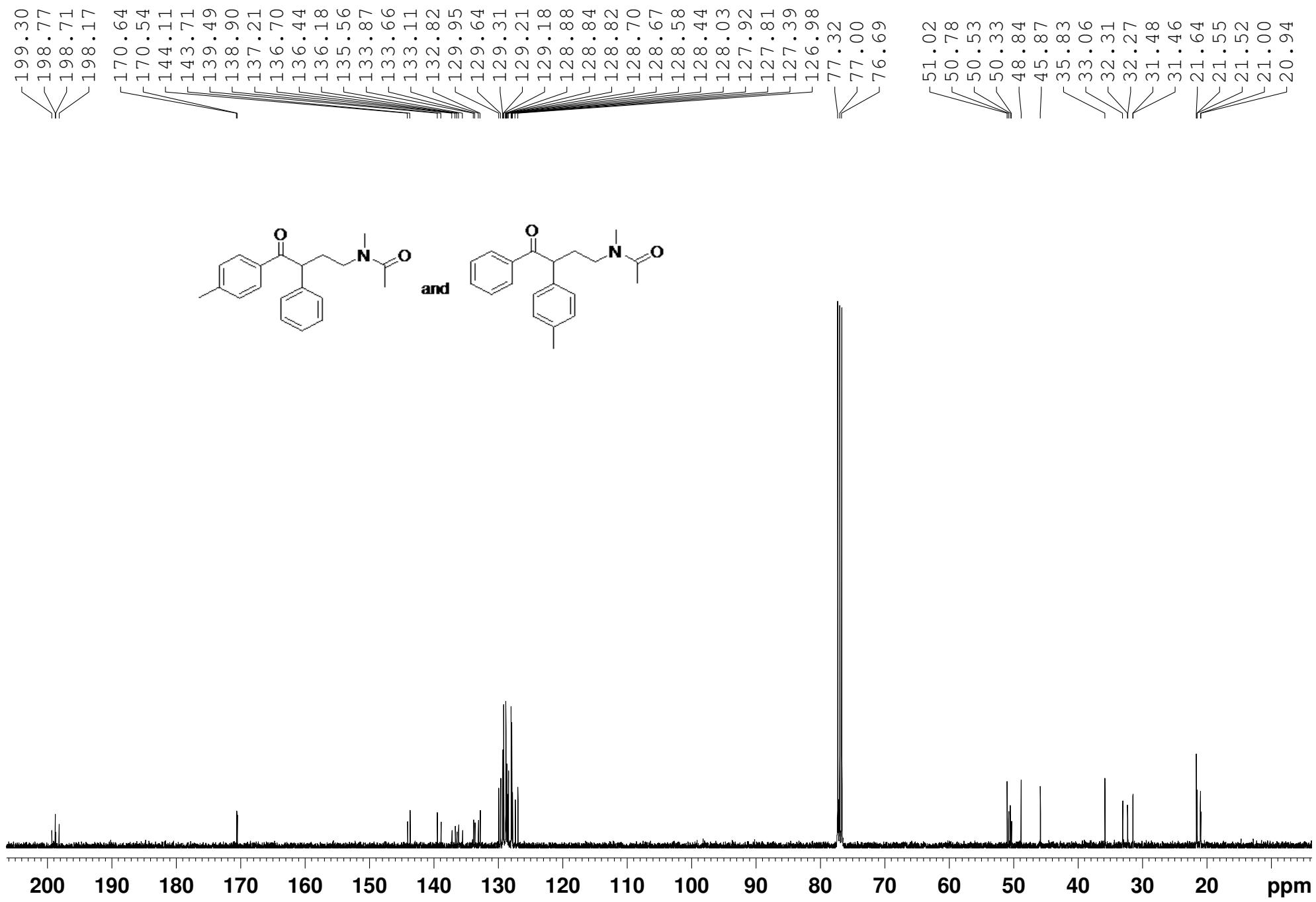
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126.655
126.544

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77.004
76.686

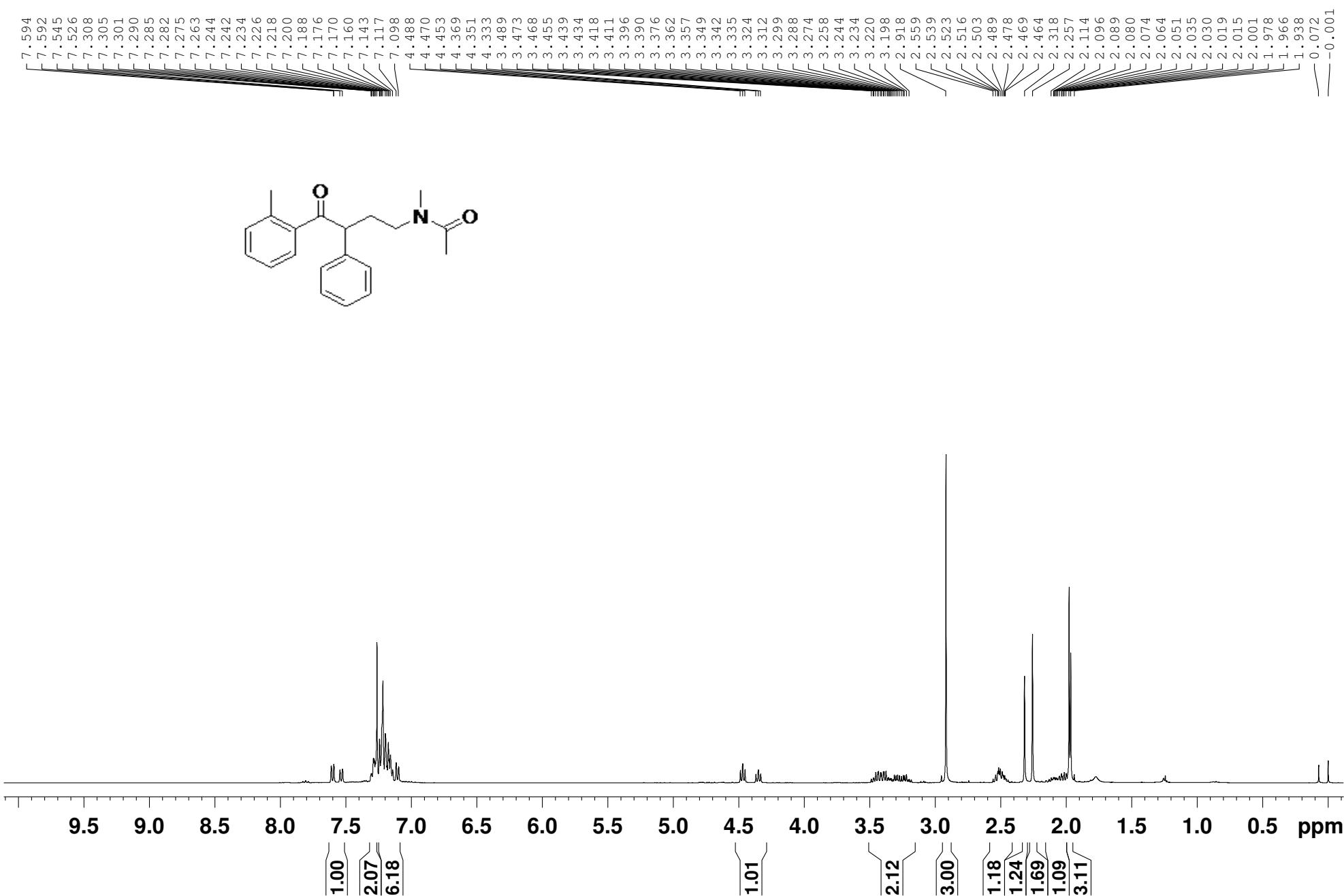
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14.647

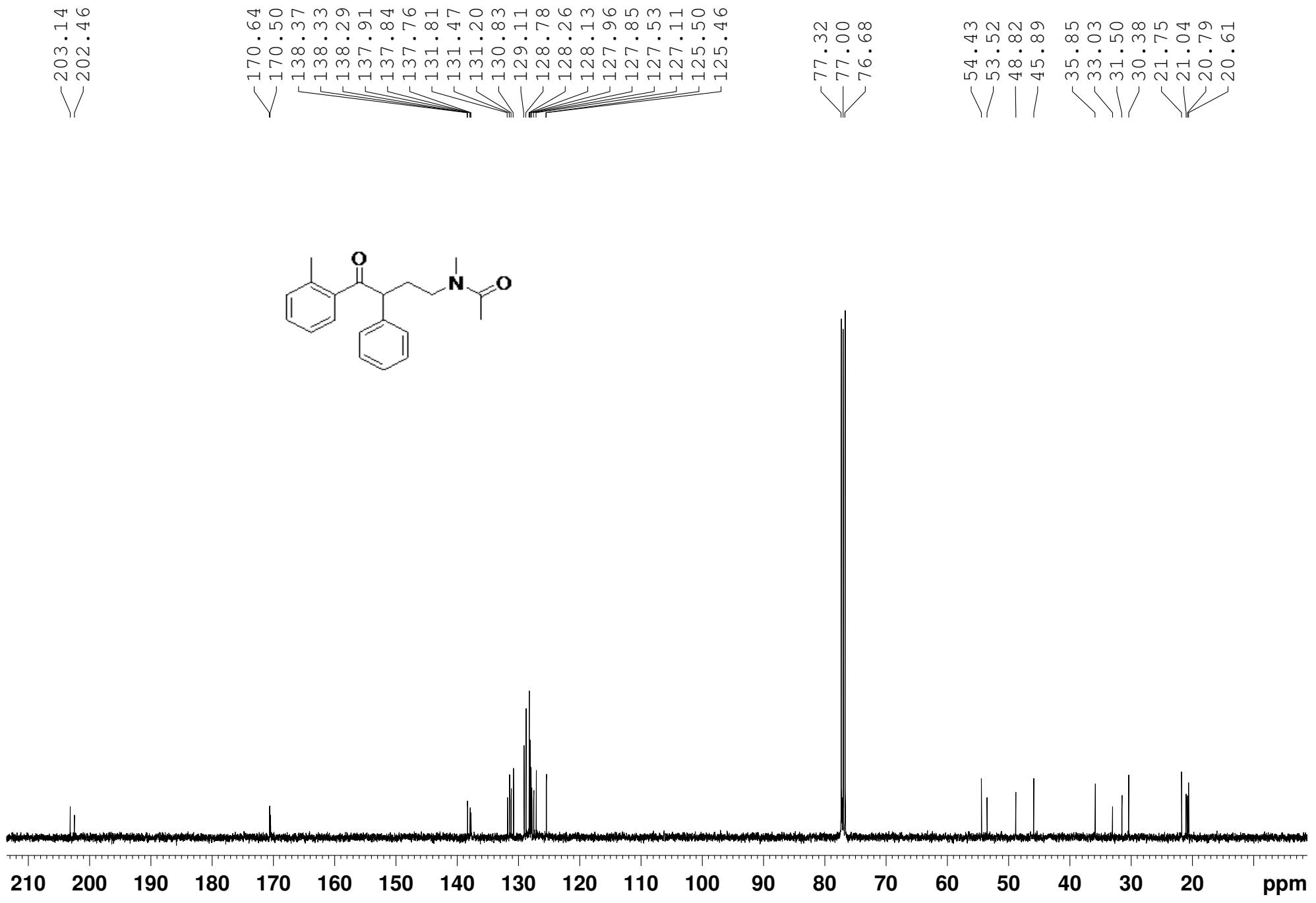
N-Methyl-N-(4-oxo-3-phenyl-4-p-tolylbutyl)acetamide (3ma) and N-Methyl-N-(4-oxo-4-phenyl-3-p-tolylbutyl)acetamide (3ma')



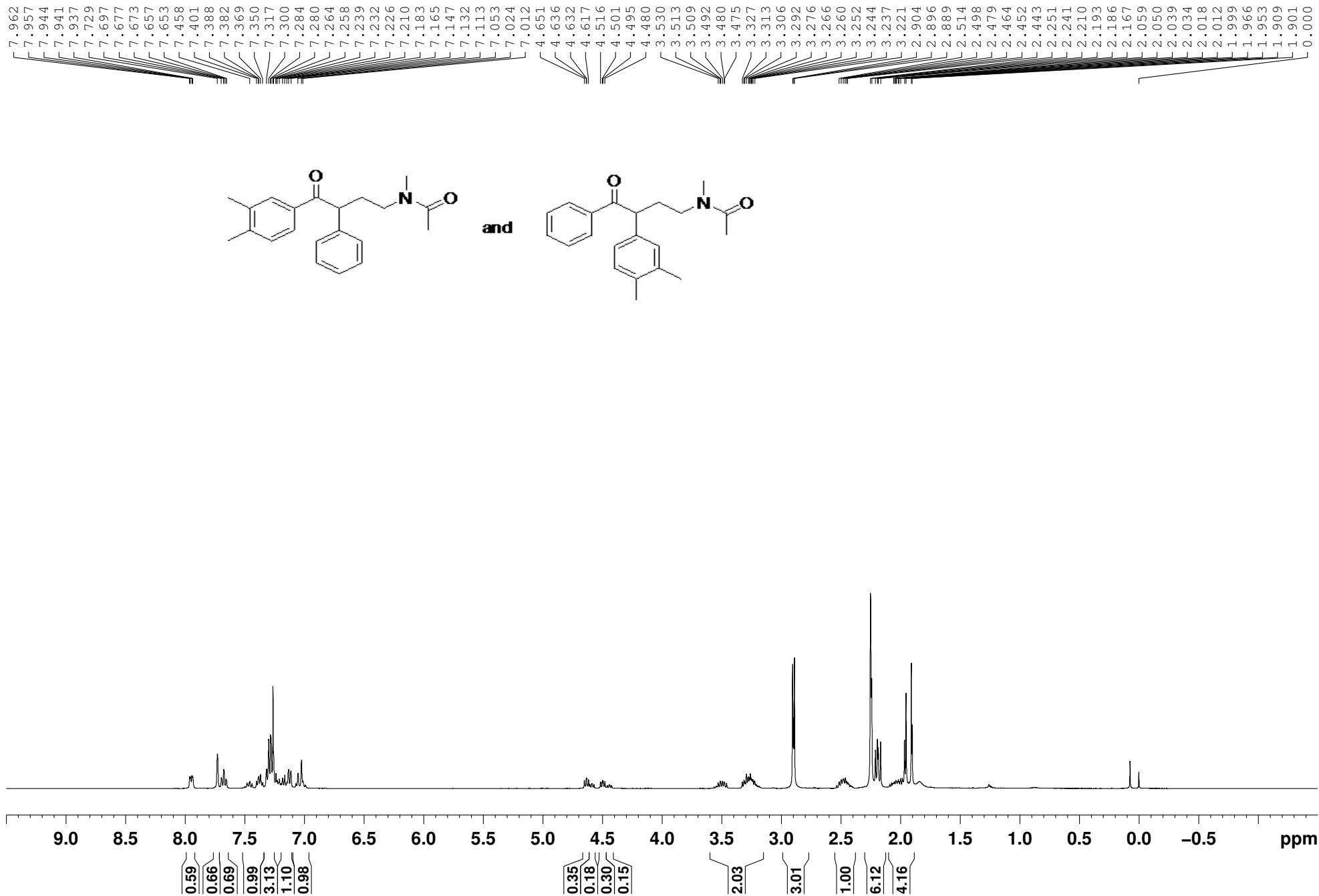


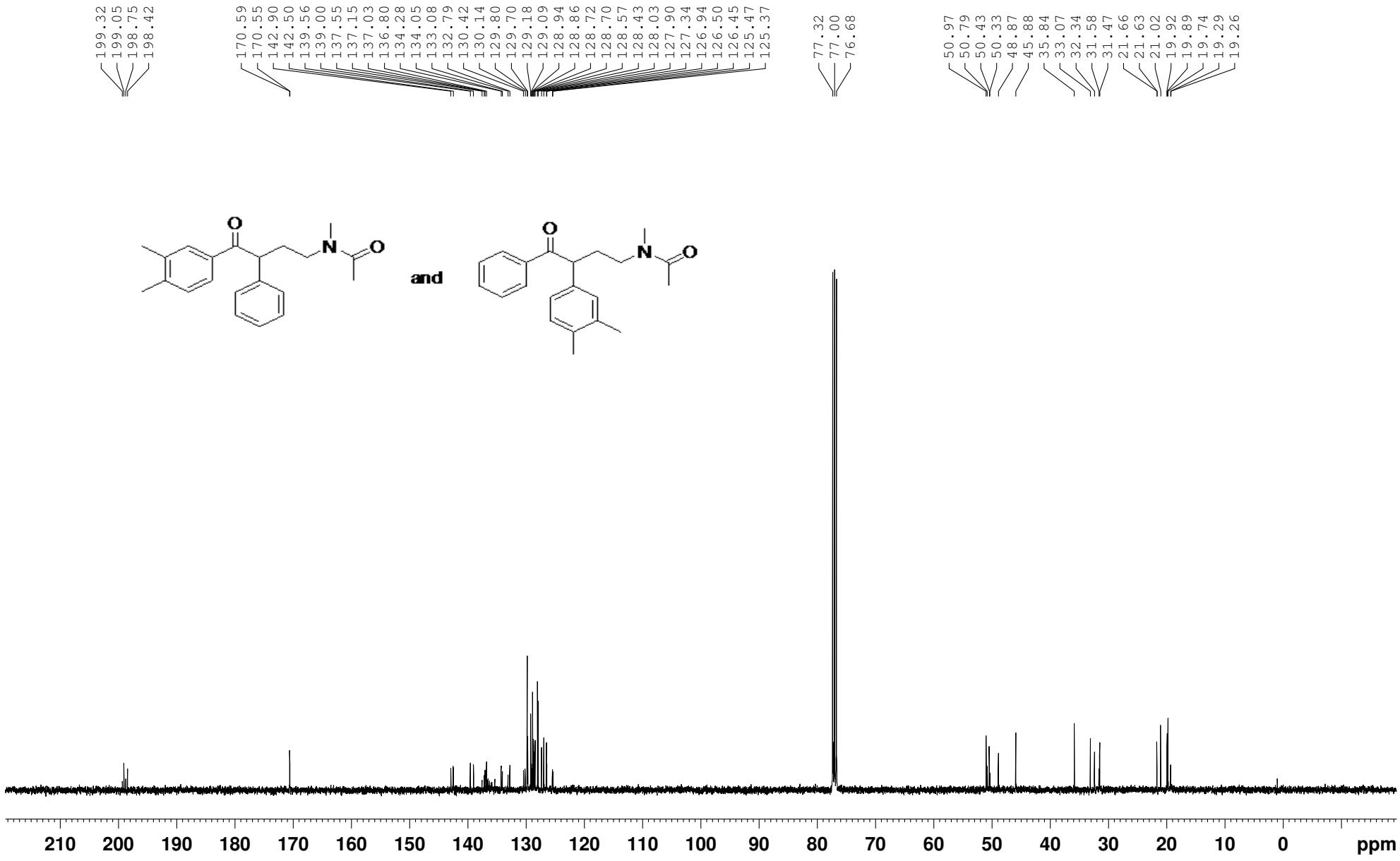
N-Methyl-N-(4-oxo-3-phenyl-4-o-tolylbutyl)acetamide (3na)



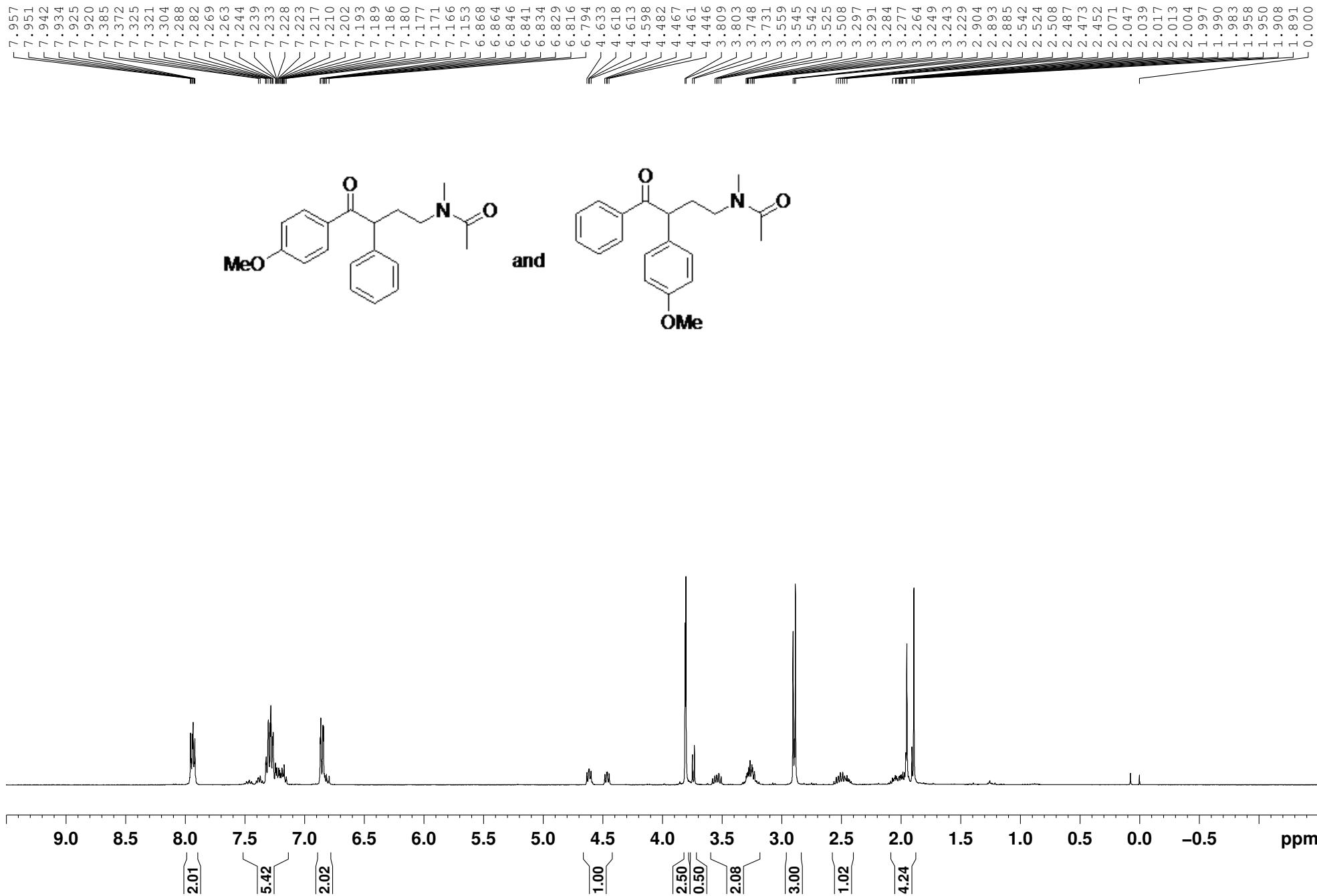


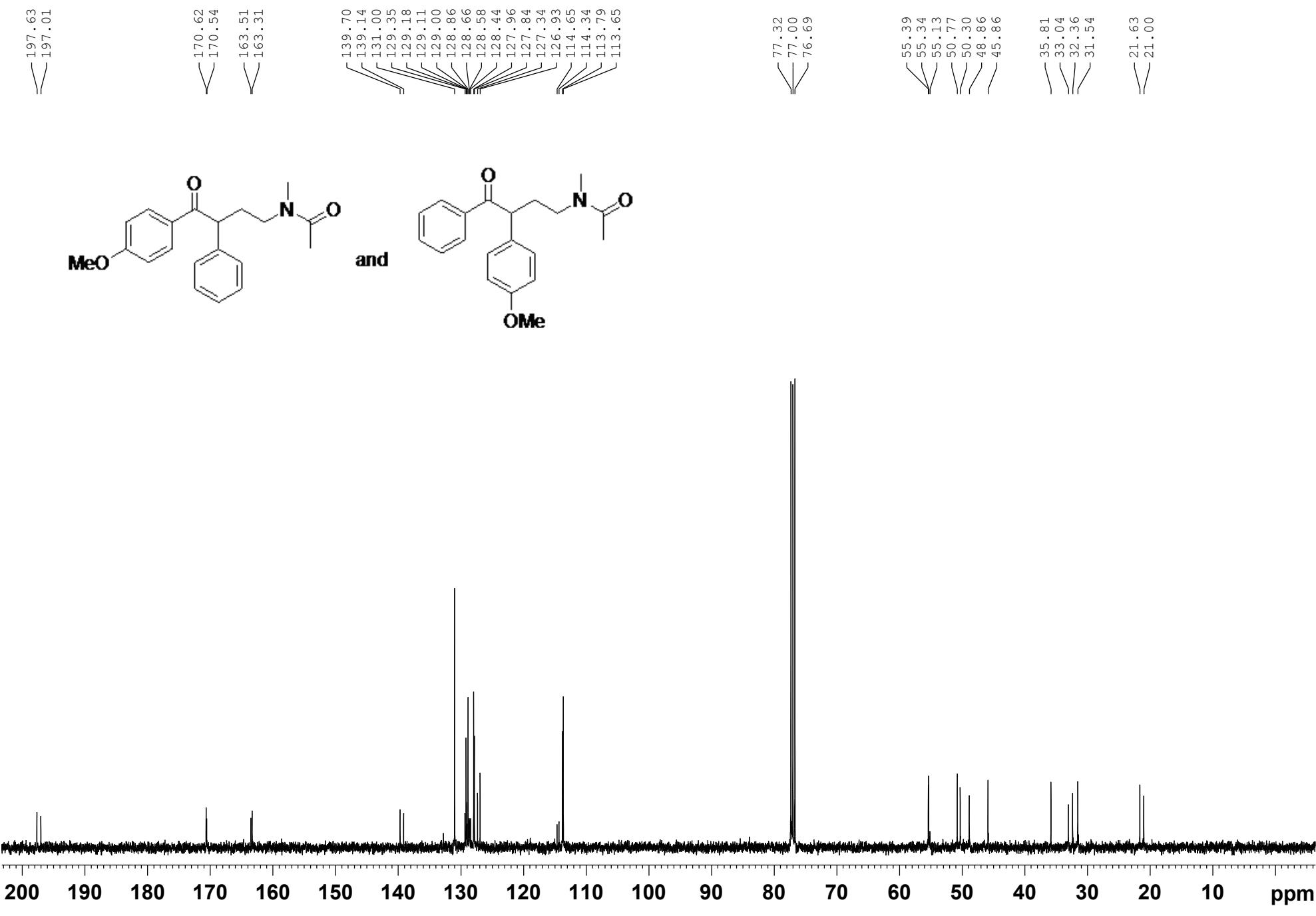
N-(4-(3,4-Dimethylphenyl)-4-oxo-3-phenylbutyl)-N-methylacetamide (3oa) and N-(3-(3,4-Dimethylphenyl)-4-oxo-4-phenylbutyl)-N-methylacetamide (3oa')

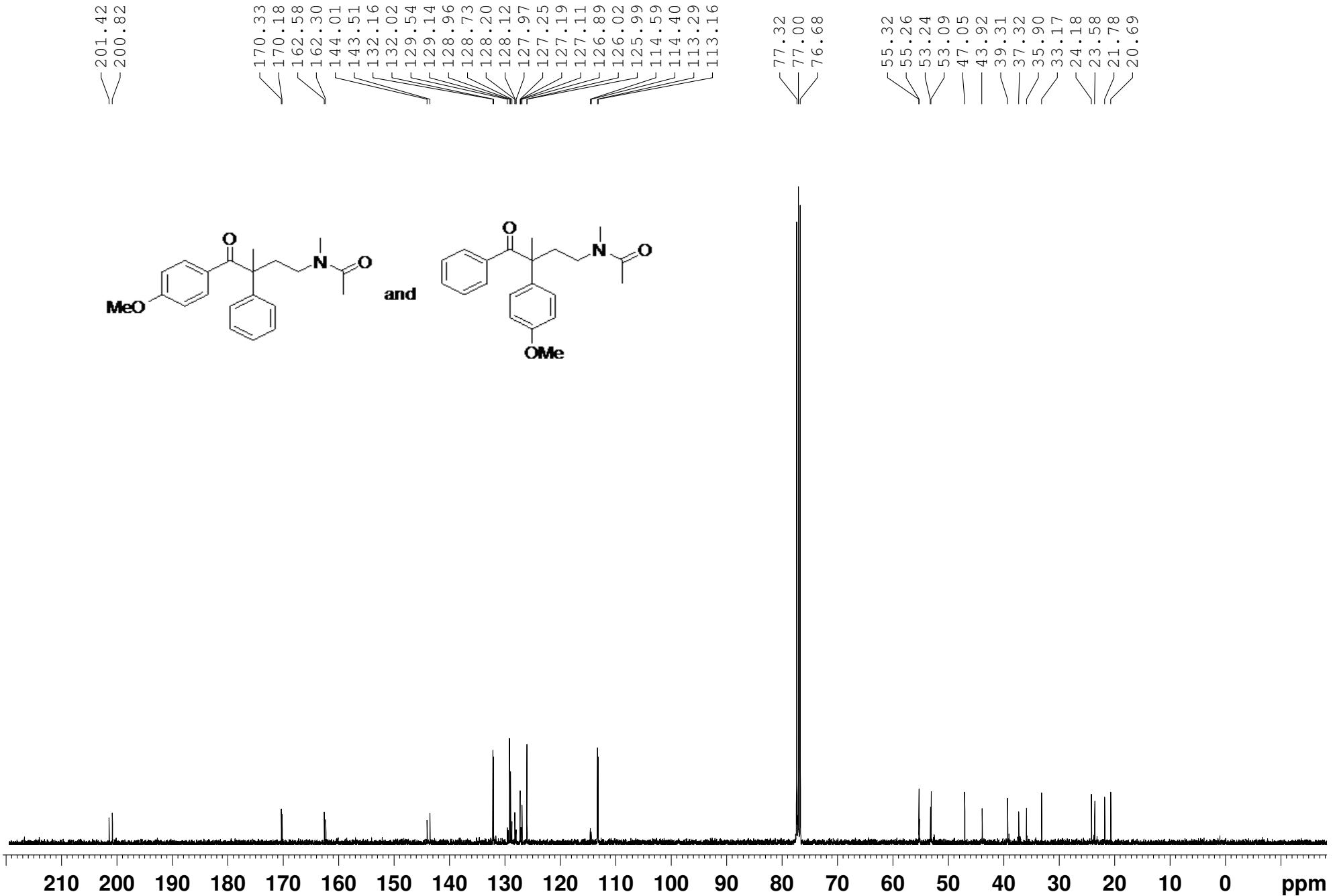




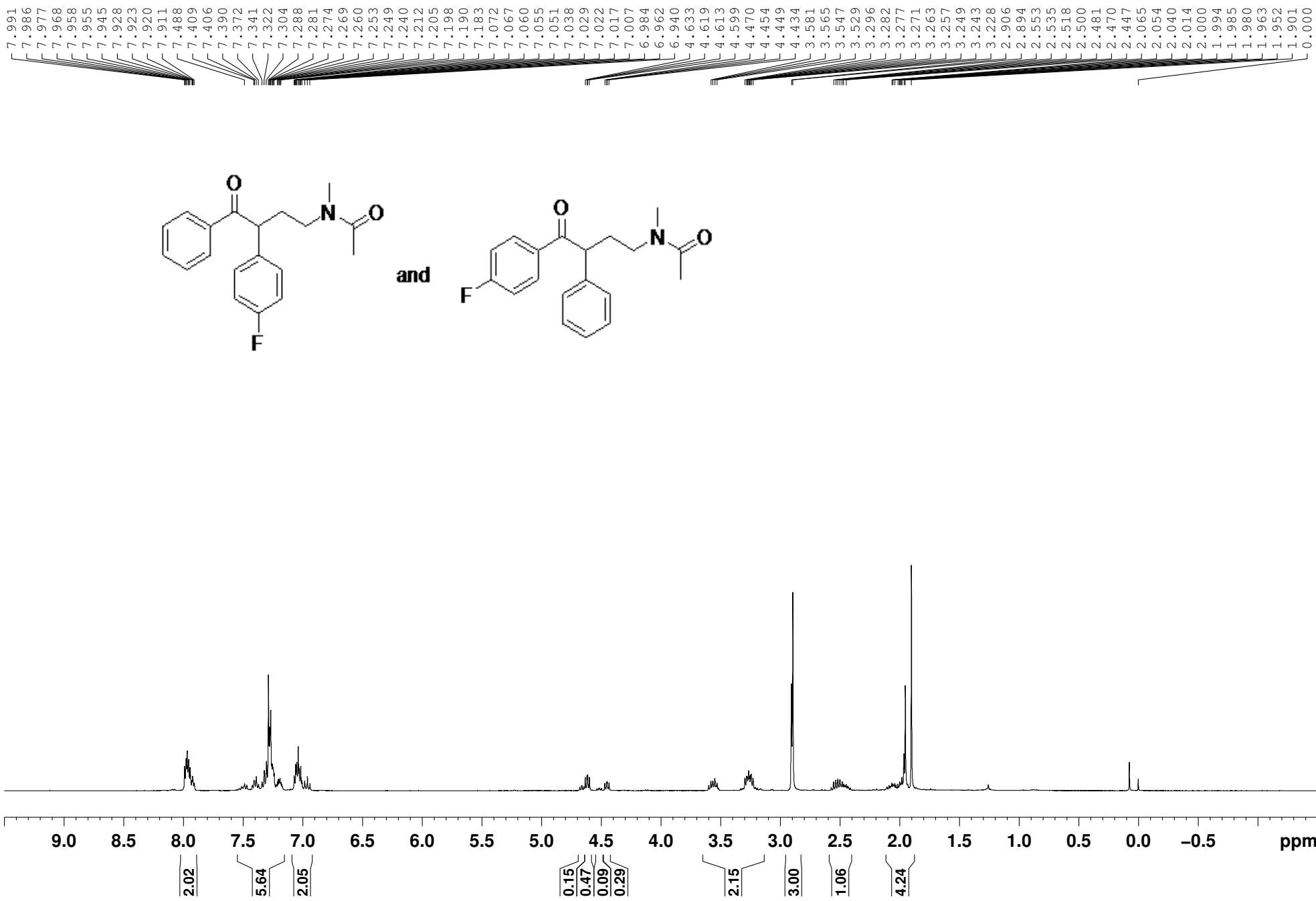
N-(4-(4-Methoxyphenyl)-4-oxo-3-phenylbutyl)-N-methylacetamide (3pa) and N-(3-(4-Methoxyphenyl)-4-oxo-4-phenylbutyl)-N-methylacetamide (3pa')

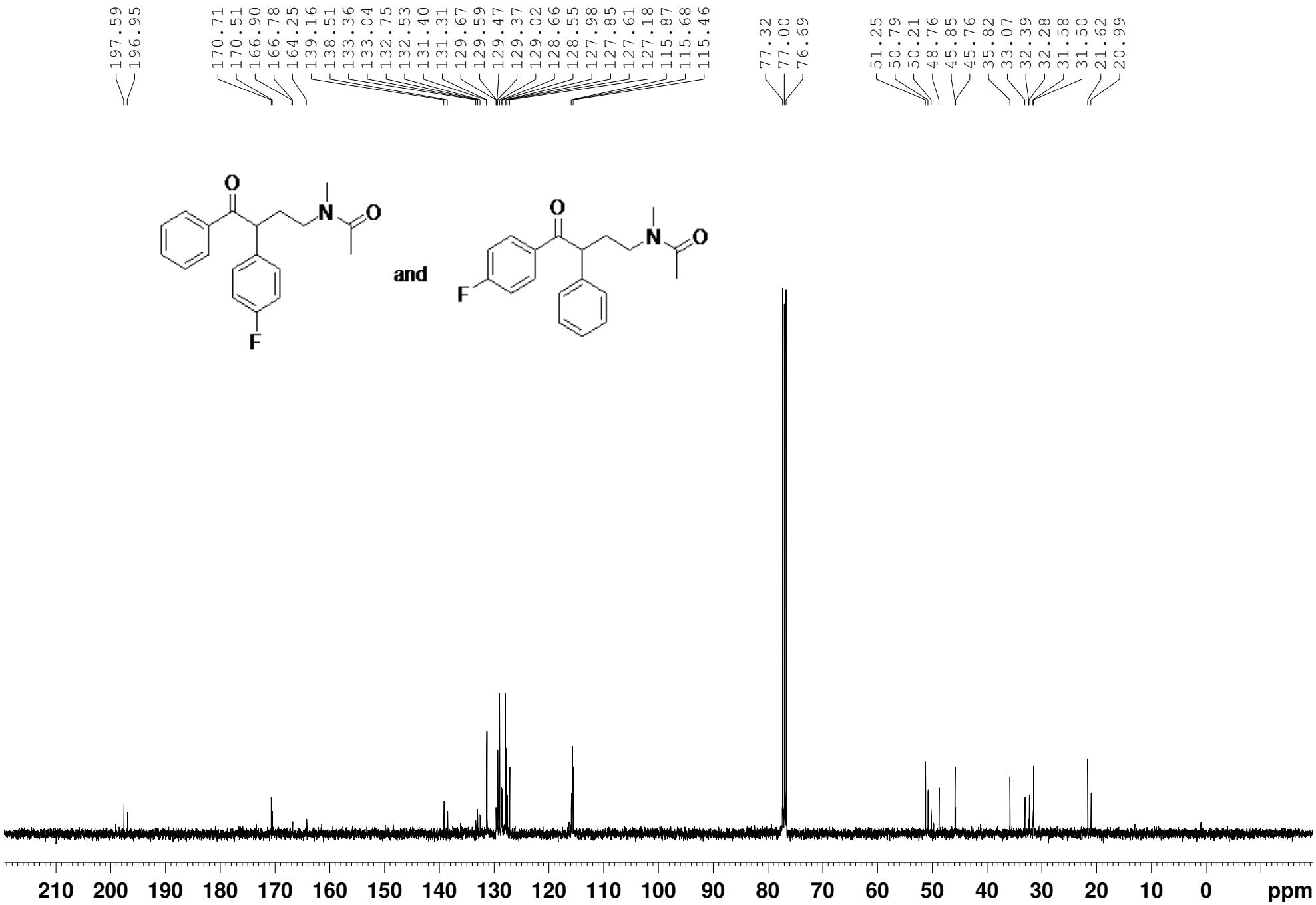


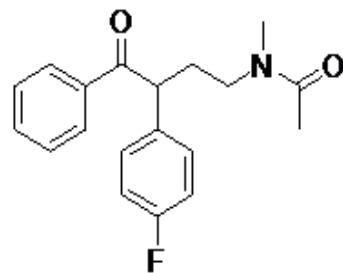




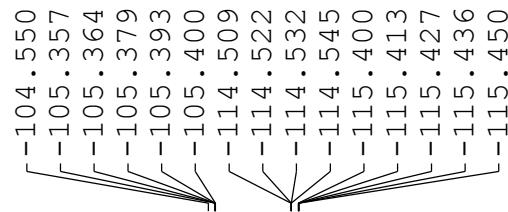
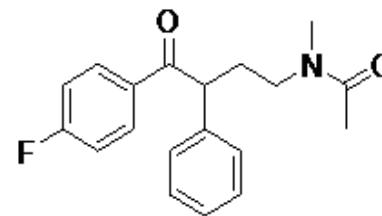
N-(3-(4-Fluorophenyl)-4-oxo-4-phenylbutyl)-N-methylacetamide (3ra) and N-(4-(4-Fluorophenyl)-4-oxo-3-phenylbutyl)-N-methylacetamide (3ra')



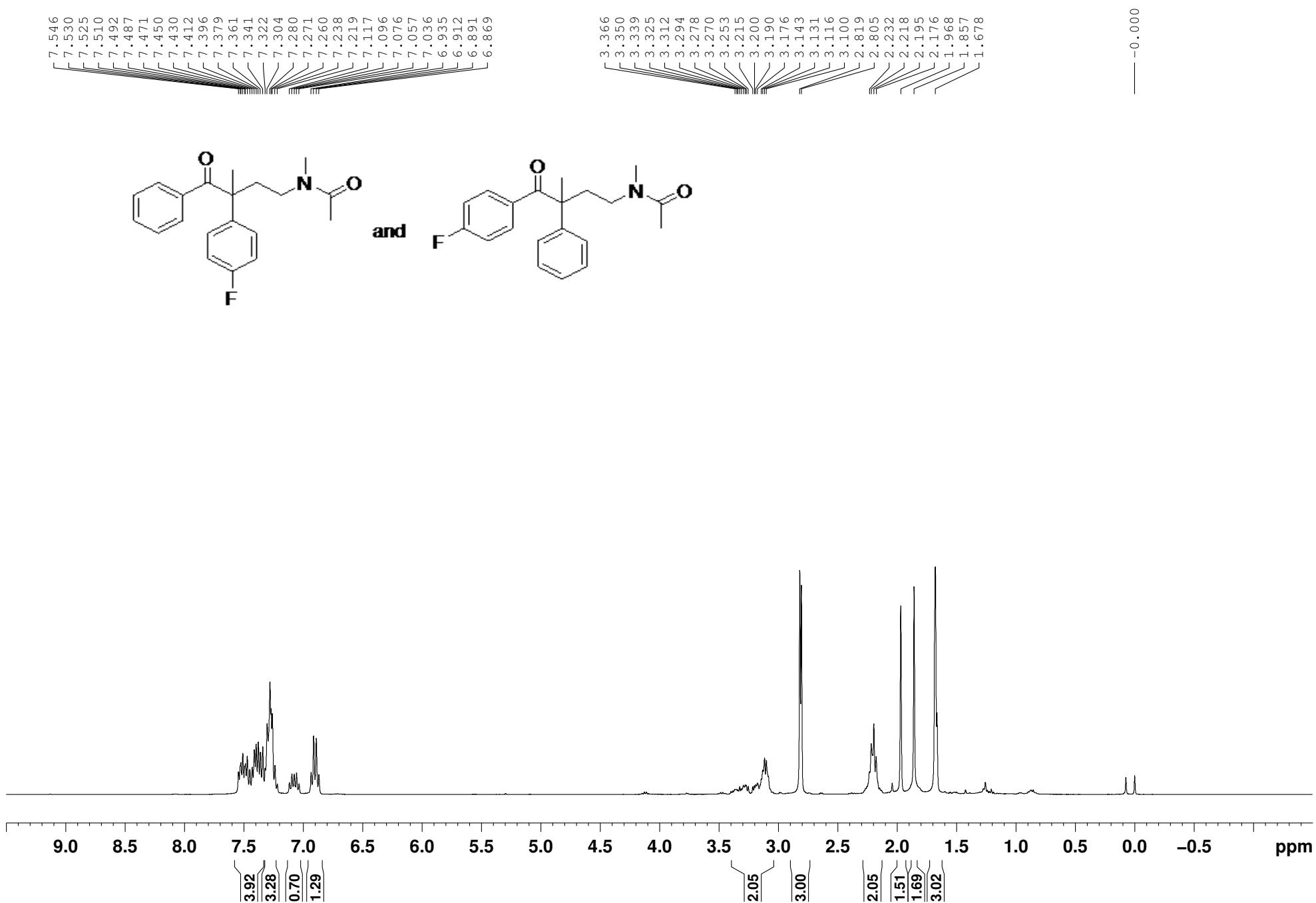


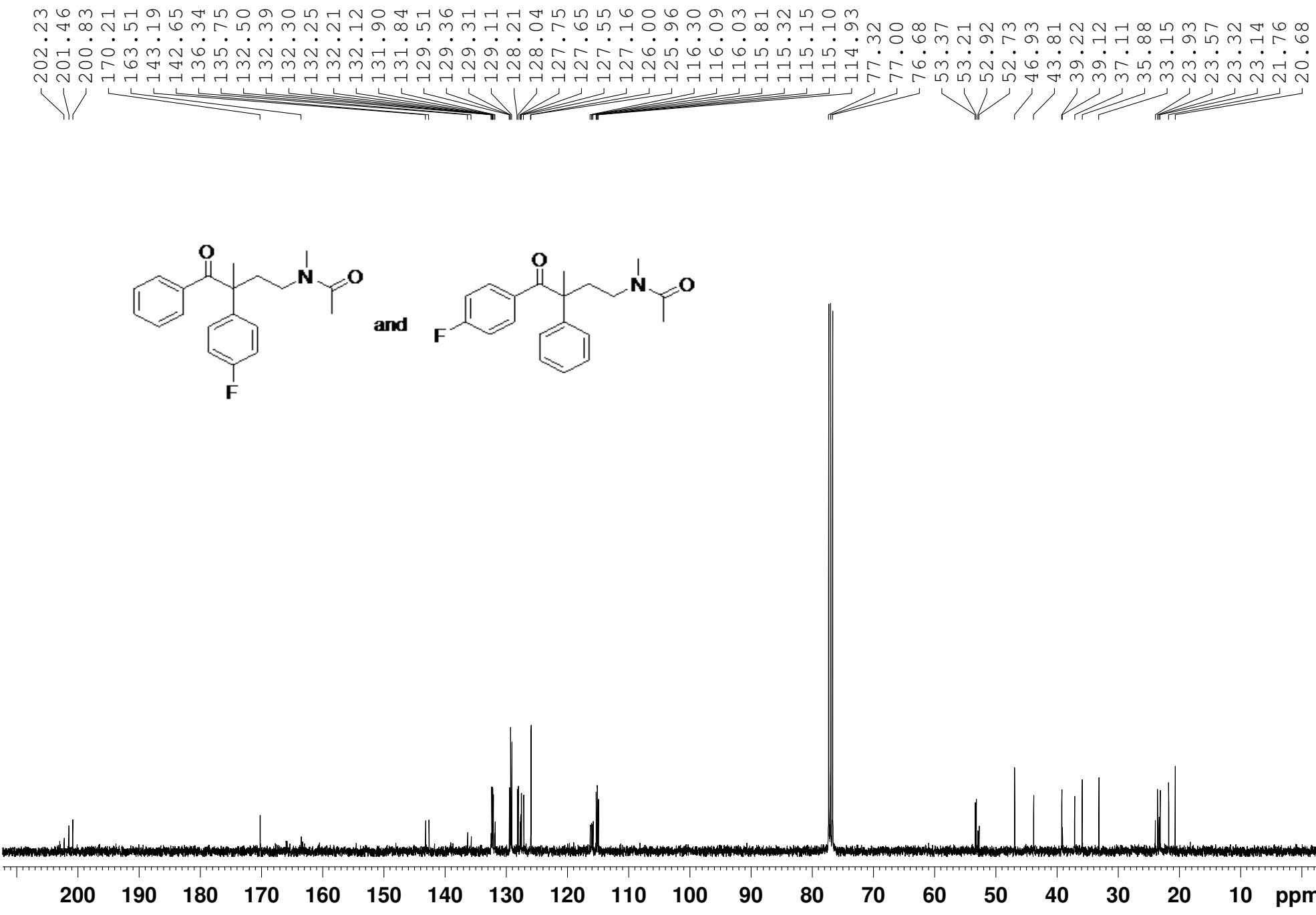


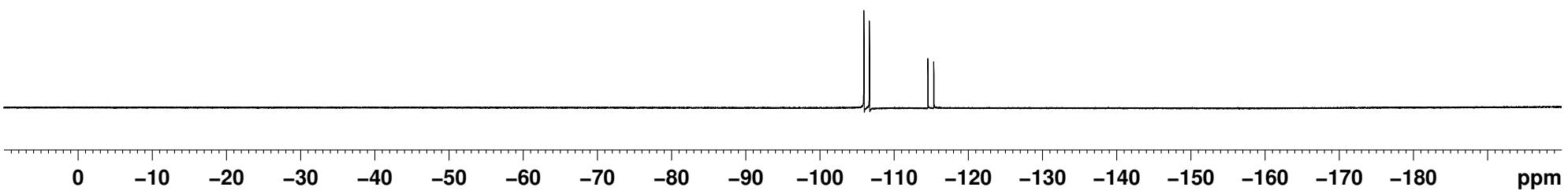
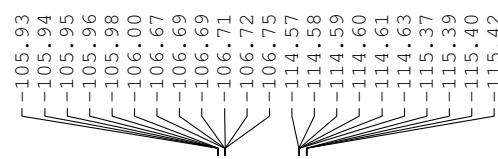
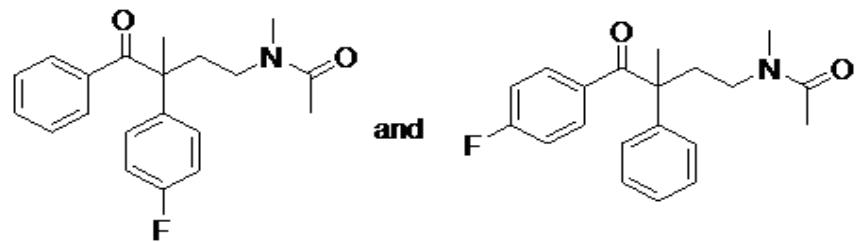
and



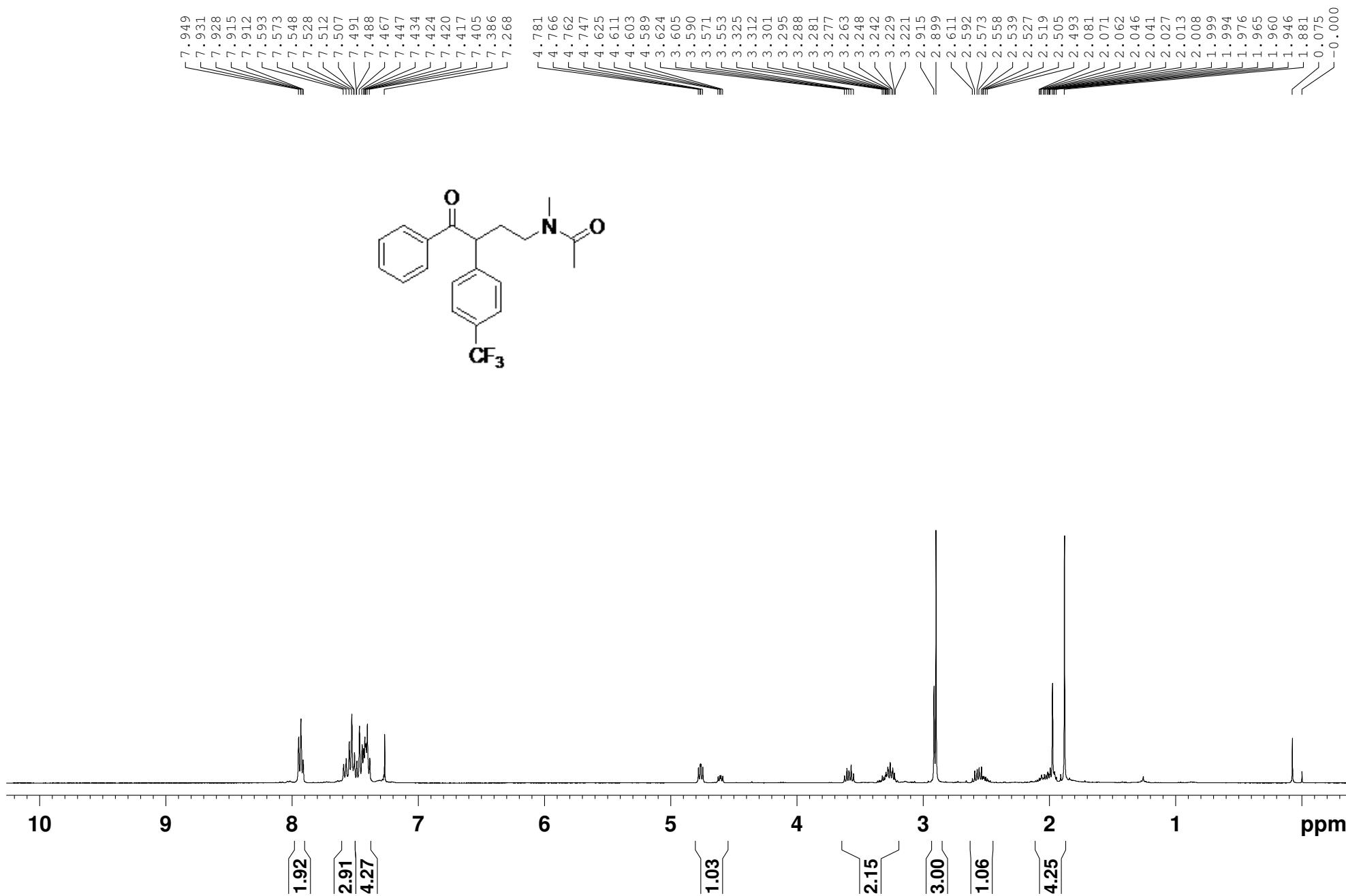
N-(3-(4-Fluorophenyl)-3-methyl-4-oxo-4-phenylbutyl)-N-methylacetamide (3sa) and N-(4-(4-Fluorophenyl)-3-methyl-4-oxo-3-phenylbutyl)-N-methylacetamide (3sa')

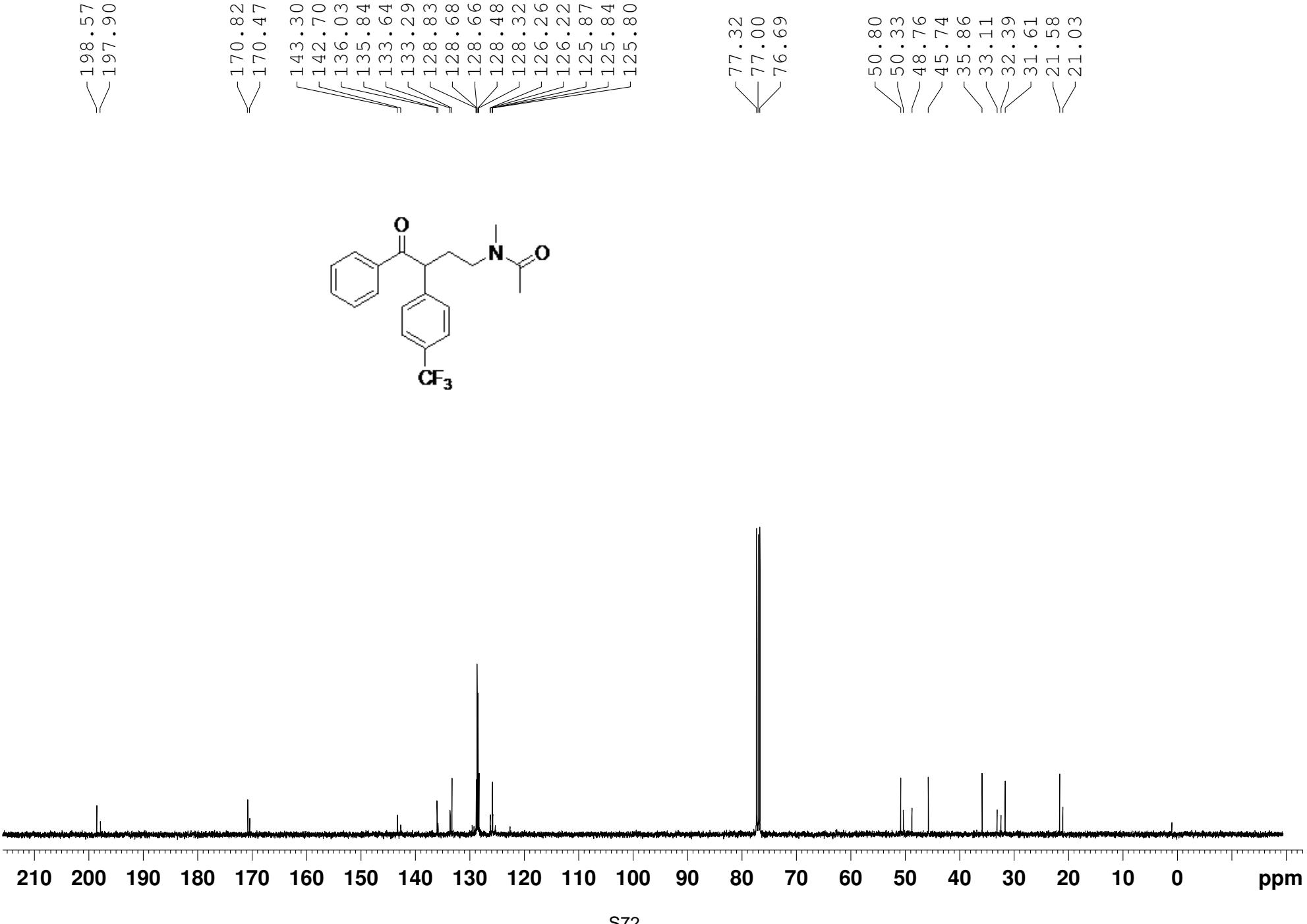




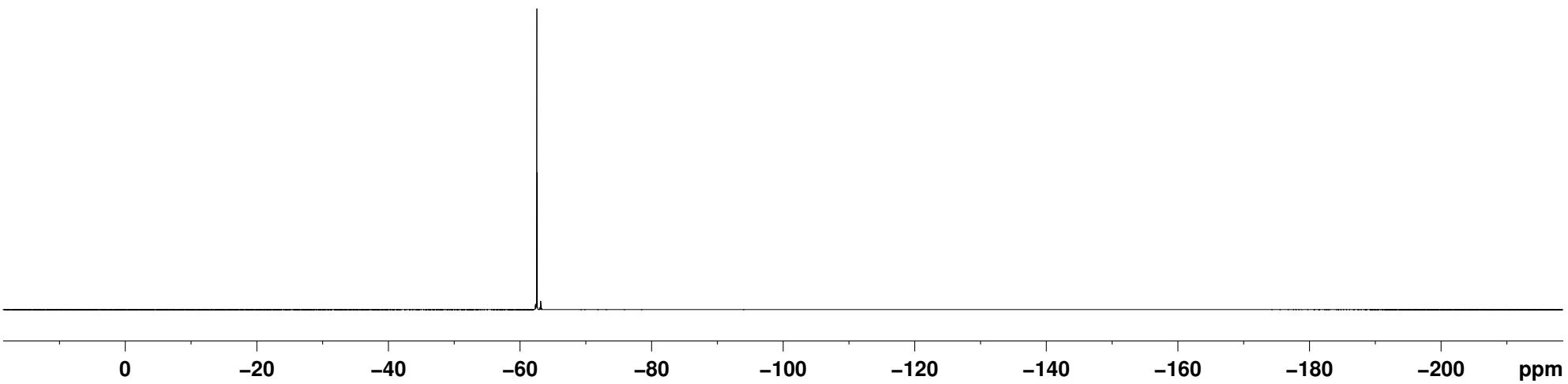
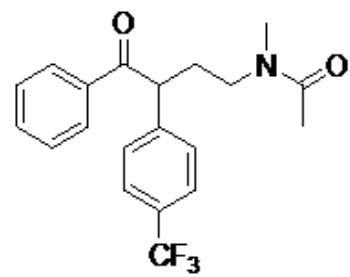


N-Methyl-N-(4-oxo-4-phenyl-3-(4-(trifluoromethyl)phenyl)butyl)acetamide (3ta)

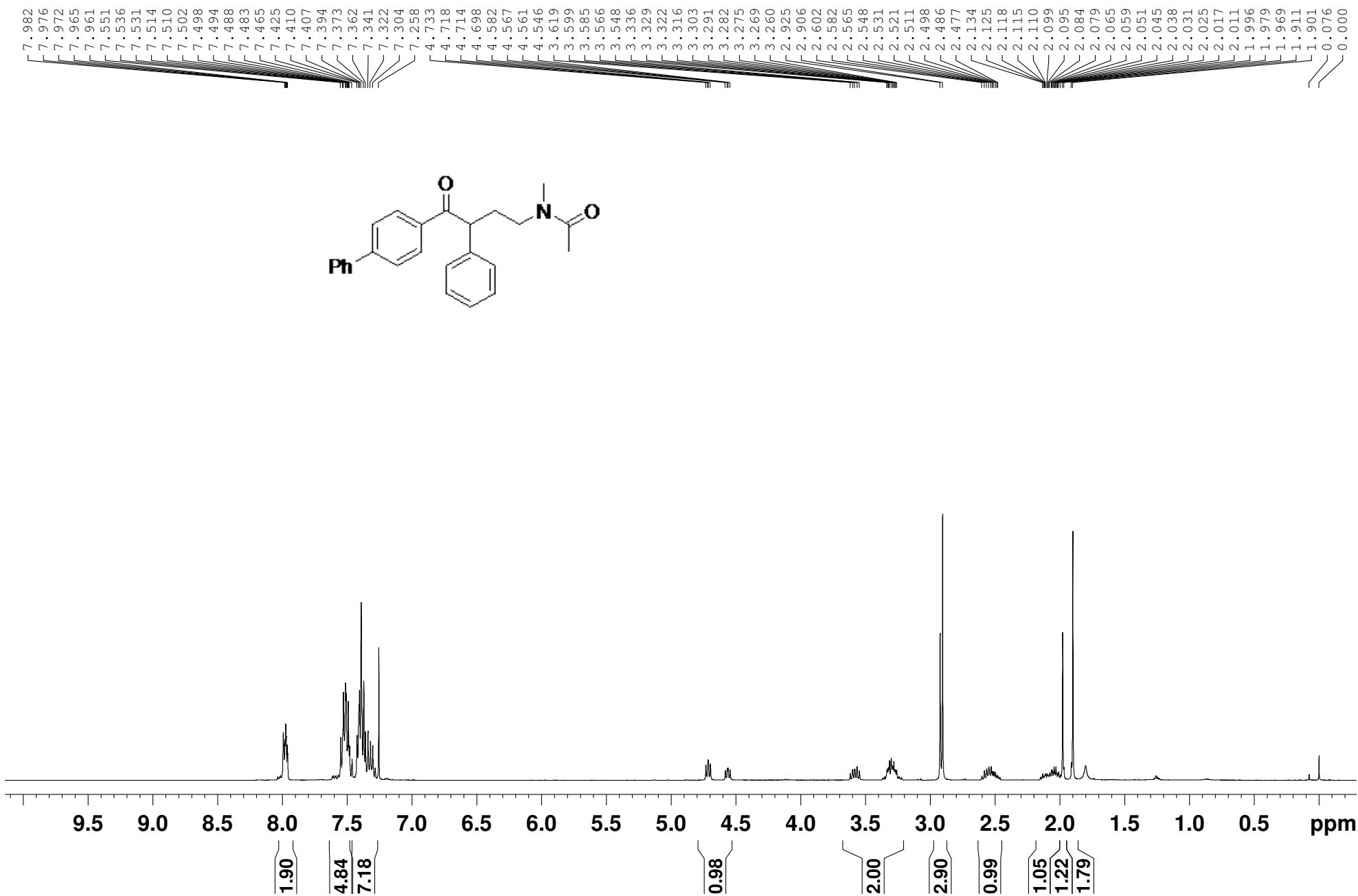


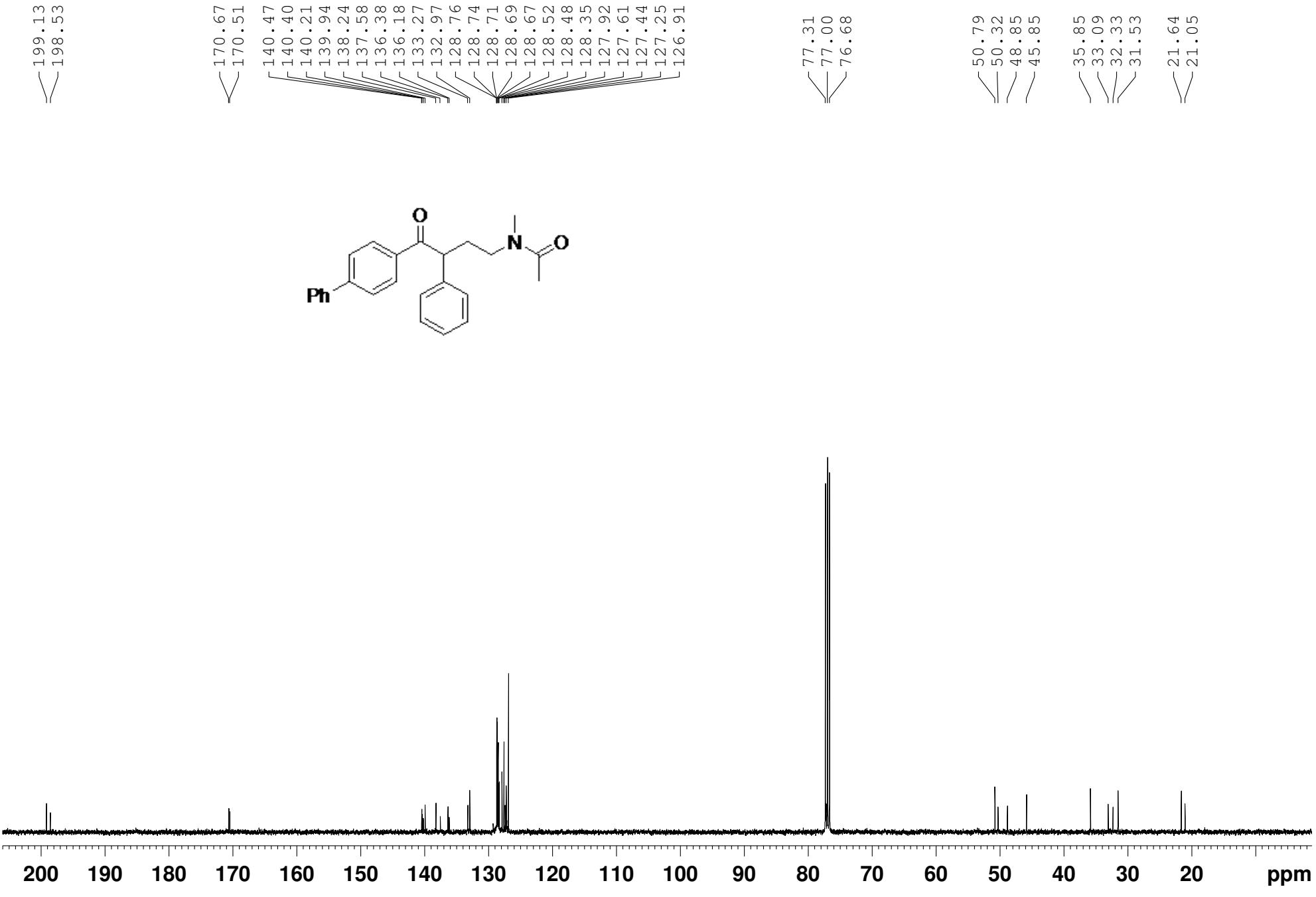


-62.59
-62.66

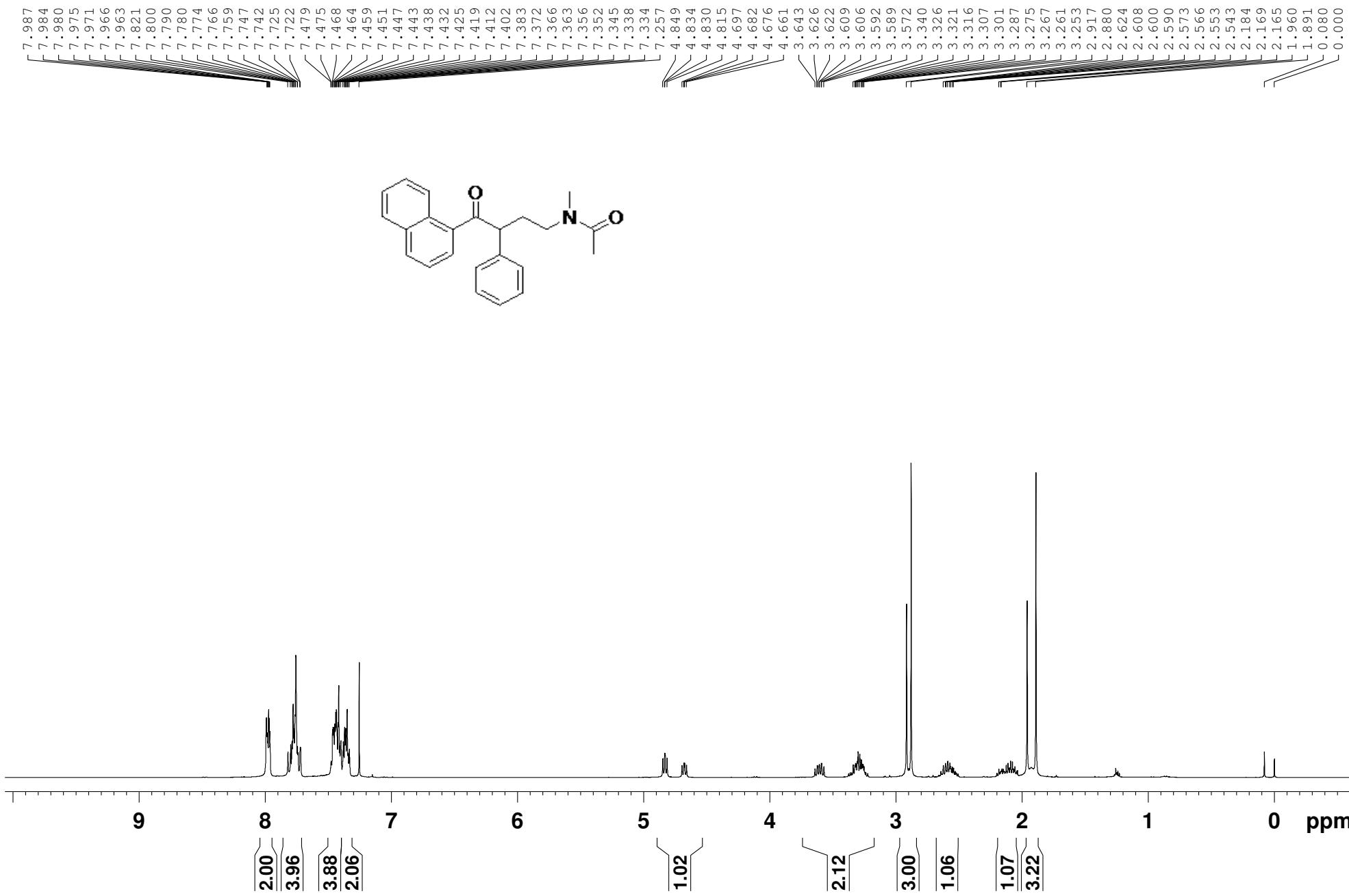


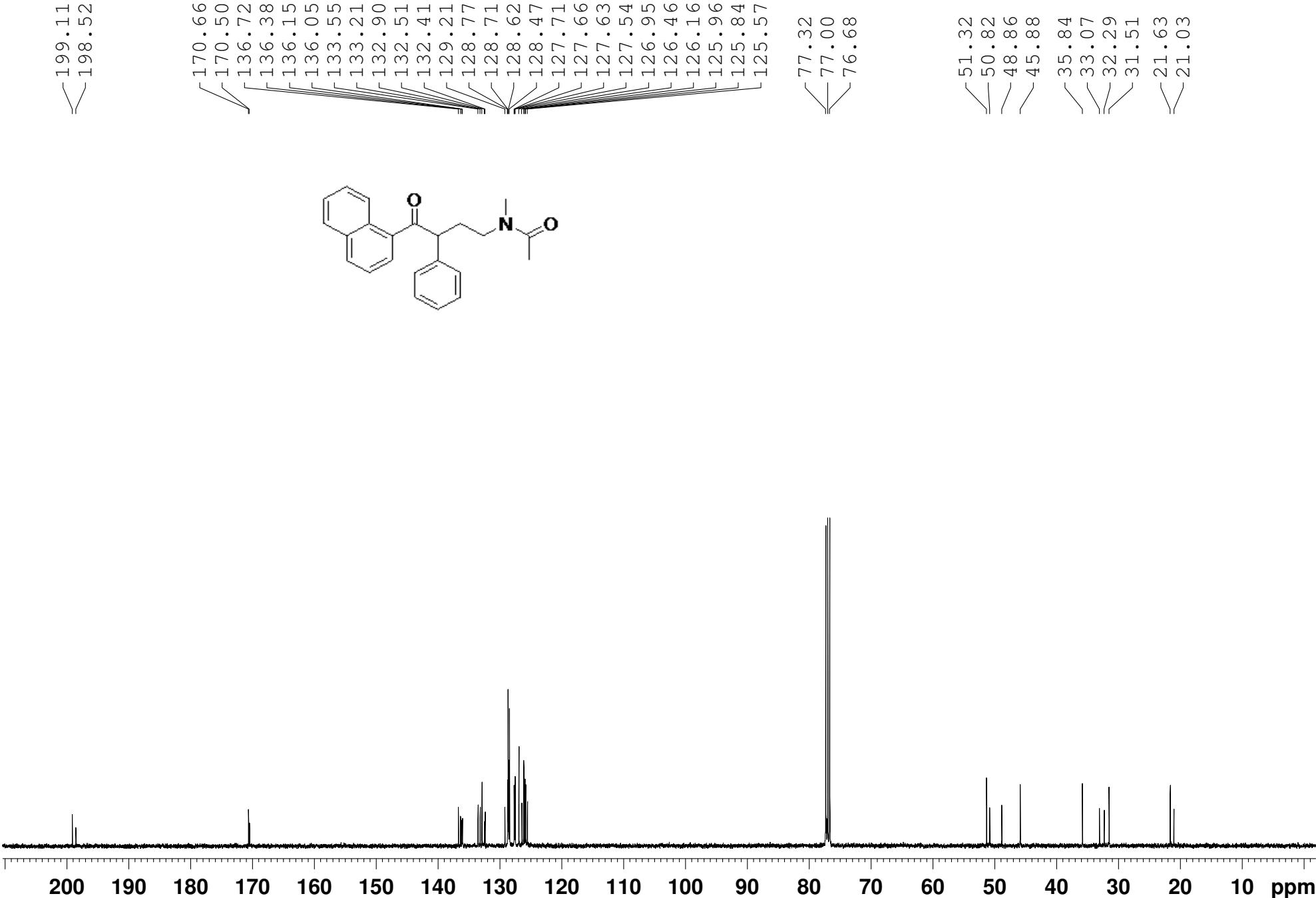
N-(4-(Biphenyl-4-yl)-4-oxo-3-phenylbutyl)-N-methylacetamide (3ua)





N-Methyl-N-(4-(naphthalen-1-yl)-4-oxo-3-phenylbutyl)acetamide (3va)





N-Methyl-N-((2,2,6,6-tetramethylpiperidin-1-yloxy)methyl)acetamide (4)

