

Supporting Information

Cu-Catalyzed Sequential Dehydrogenation-Conjugate Addition for β-Functionalization of Saturated Ketones: Scope and Mechanism

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I. General Considerations

A. General Information

All reactions were conducted under a nitrogen atmosphere. Unless otherwise noted, materials were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Propiophenone was simply distilled under reduced pressure and stored under nitrogen with 4 Å molecular sieves. 1,2-Dichlorobenzene was distilled over CaH₂ and stored under nitrogen. DME were distilled from Na and stored under nitrogen. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), ¹⁹F NMR (377 MHz) spectra were recorded in CDCl₃ solutions using a Bruker AVANCE 400 spectrometer. Calibration was done using tetramethylsilane (0 ppm) or residual undeuterated solvent CHCl₃ (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR). HRMS were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument: Thermo Fisher Scientific LTQ FT Ultra, Operation Mode: DART Positive).

B. General Procedures

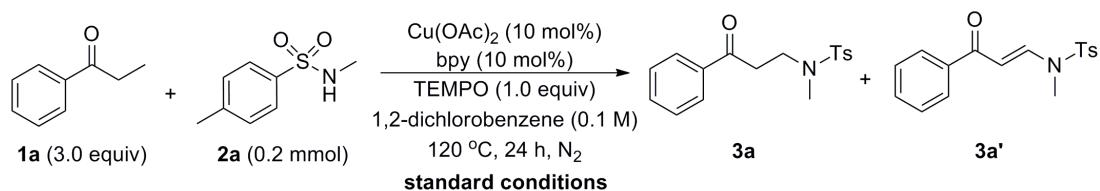
General Procedure for Catalytic Cu(OAc)₂/bpy System in 1,2-Dichlorobenzene: In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged with amine (0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol, 10 mol%), 2,2'-bipyridine (3.1 mg, 0.02 mmol, 10 mol%) and TEMPO (31.3 mg, 0.2 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then 1,2-dichlorobenzene (2.0 mL) and ketone (0.6 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 °C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product.

General Procedure for Stoichiometric Cu(OAc)₂ System in DME: In a nitrogen-filled glovebox, a 25 mL Schlenk tube equipped with a stir bar was charged with Cu(OAc)₂ (36.3 mg, 0.2 mmol), Cs₂CO₃ (65.2 mg, 0.2 mmol) and TEMPO (78.1 mg, 0.5 mmol). The tube was fitted with a rubber septum and moved out of the glove box. Then DME (2.0 mL), ketone (0.2 mmol) and 1,3-dicarbonyl compound (0.6 mmol) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 °C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and then purified by flash chromatography on silica gel to provide the corresponding product.

II. Experimental Data

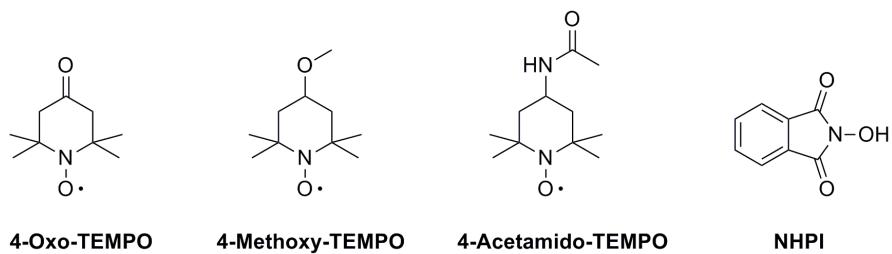
A. Copper-Catalyzed direct β -Amidation of Saturated Ketones

Table S1. Optimization of Reaction Conditions^a

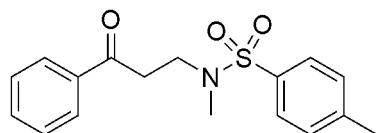


| entry | variations from standard conditions | yield (%) ^b | |
|-----------------|---|------------------------|-----|
| | | 3a | 3a' |
| 1 ^c | none | 95 | <5 |
| 2 | 1.5 equiv of 1a instead of 3.0 equiv | 72 | <5 |
| 3 | w/o Cu(OAc) ₂ | 0 | 0 |
| 4 | w/o TEMPO | 0 | 0 |
| 5 | w/o bpy | 62 | <5 |
| 6 | 1,10-phenanthroline instead of bpy | 94 | <5 |
| 7 | 0.2 equiv of pyridine instead of bpy | 76 | <5 |
| 8 | 0.5 equiv of pyridine instead of bpy | 87 | <5 |
| 9 | 0.2 equiv of TEMPO instead of 1.0 equiv | 54 | 0 |
| 10 | 0.5 equiv of TEMPO instead of 1.0 equiv | 82 | 0 |
| 11 | 2.0 equiv of TEMPO instead of 1.0 equiv | 79 | 16 |
| 12 | 2.0 equiv of 1a , 2.0 equiv of TEMPO | 52 | 40 |
| 13 | 0.2 equiv 4-Oxo-TEMPO instead of TEMPO | 0 | 0 |
| 14 | 0.2 equiv 4-Methoxy-TEMPO instead of TEMPO | 43 | 0 |
| 15 | 0.2 equiv 4-Acetamido-TEMPO instead of TEMPO | 39 | 0 |
| 16 | 0.2 equiv of TEMPO instead of 1.0 equiv | 0 | 0 |
| | 1 atm O ₂ instead of 1 atm N ₂ | | |
| 17 | 1 atm air instead of 1 atm N ₂ | 50 | <5 |
| 18 | 1.0 equiv of NHPI instead of TEMPO | 0 | 0 |
| 19 ^d | 2.0 equiv of <i>t</i> BuOOH instead of TEMPO | 0 | 0 |
| 20 | 2.0 equiv of <i>t</i> BuOO <i>t</i> Bu instead of TEMPO | 0 | 0 |
| 21 | CuSO ₄ instead of Cu(OAc) ₂ | 0 | 0 |
| 22 | Cu(OTf) ₂ instead of Cu(OAc) ₂ | 15 | 0 |
| 23 | CuCl ₂ instead of Cu(OAc) ₂ | 0 | 0 |
| 24 | PhCl instead of 1,2-dichlorobenzene | 90 | 0 |
| 25 | DME instead of 1,2-dichlorobenzene | 49 | 0 |
| 26 | DMF instead of 1,2-dichlorobenzene | 45 | 0 |
| 27 | DMSO instead of 1,2-dichlorobenzene | <5 | 0 |
| 28 | 1,4-dioxane instead of 1,2-dichlorobenzene | 49 | 0 |
| 29 | toluene instead of 1,2-dichlorobenzene | 73 | <5 |

^a Standard conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), Cu(OAc)₂ (0.02 mmol), bpy (0.02 mmol), TEMPO (0.2 mmol), 1,2-dichlorobenzene (2 mL), 120 °C, N₂ atmosphere, 24 h. ^b Isolated yields. ^c 52% of starting **1a** remained intact. Determined by GC using dodecane as an internal standard. ^d *t*BuOOH (5.0-6.0 M in decane) was used.

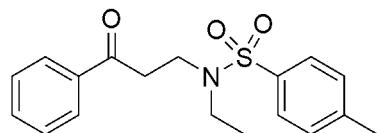


B. Products Data



N,4-Dimethyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (3a): Carried out with catalytic $\text{Cu}(\text{OAc})_2/\text{bpy}$ System: propiophenone (80.5 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

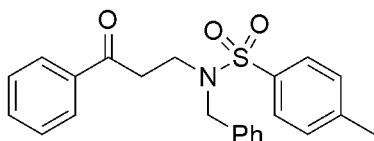
White solid (95% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl_3): δ 7.94 (d, J = 7.9 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.325 (d, J = 8.0 Hz, 2H), 3.45 (t, J = 7.0 Hz, 2H), 3.34 (t, J = 7.0 Hz, 2H), 2.82 (s, 3H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl_3): δ 198.1, 143.4, 136.4, 134.3, 133.4, 129.7, 128.7, 128.0, 127.4, 45.9, 38.1, 36.2, 21.5; **HRMS (ESI)** Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{NS} [\text{M} + \text{H}]^+$ 318.1158, found 318.1155.



N-Ethyl-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (3b): Carried out with catalytic $\text{Cu}(\text{OAc})_2/\text{bpy}$ System: propiophenone (80.5 mg, 0.6 mmol), *N*-ethyl-*p*-toluenesulfonamide (39.9 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

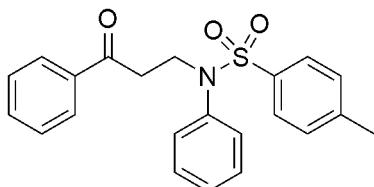
Colorless oil (68% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl_3): δ 7.95 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.54 (t, J = 7.3 Hz, 2H), 3.38 (t, J = 7.3 Hz, 2H), 3.27 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl_3): δ 198.4, 143.2, 136.6, 136.5, 133.4, 129.7, 128.7,

128.0, 127.1, 44.1, 43.2, 39.3, 21.5, 14.0; **HRMS** (ESI) Calcd for C₁₈H₂₂O₃NS [M + H]⁺ 332.1315, found 332.1309.



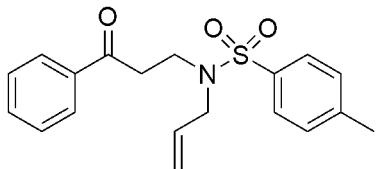
N-Benzyl-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (3c): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), N-benzyl-p-toluenesulfonamide (52.3 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (74% yield, eluent = petroleum ether/acetone (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 7.74 (d, *J* = 7.7 Hz, 4H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 7H), 4.35 (s, 2H), 3.50 (t, *J* = 7.5 Hz, 2H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.1, 143.5, 136.35, 136.29, 136.27, 133.22, 129.8, 128.7, 128.5, 128.4, 127.94, 127.88, 127.2, 53.45, 44.1, 38.6, 21.5; **HRMS** (ESI) Calcd for C₂₃H₂₄O₃NS [M + H]⁺ 394.1471, found 394.1464.



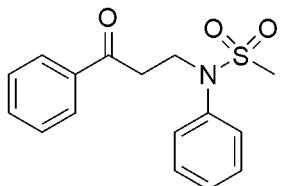
4-Methyl-N-(3-oxo-3-phenylpropyl)-N-phenylbenzenesulfonamide (3d): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), p-toluenesulfonanilide (49.5 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (88% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl₃): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33-7.30 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.09-7.07 (m, 2H), 3.98 (t, *J* = 7.5 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.9, 143.5, 139.5, 136.4, 134.9, 133.3, 129.4, 129.1, 128.7, 128.6, 128.0, 127.9, 127.75, 46.8, 38.3, 21.5; **HRMS** (ESI) Calcd for C₂₂H₂₂O₃NS [M + H]⁺ 380.1315, found 380.1310.



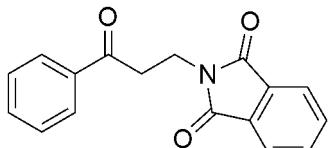
N-allyl-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (3e): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), N-allyl-p-toluenesulfonamide (42.3 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Colorless oil (83% yield, eluent = petroleum ether/acetone (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.74-5.64 (m, 1H), 5.22-5.13 (m, 2H), 3.85 (d, *J* = 6.4 Hz, 2H), 3.52 (t, *J* = 7.3 Hz, 2H), 3.35 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.3, 143.4, 136.448, 136.435, 133.3, 133.1, 129.7, 128.6, 128.0, 127.2, 119.2, 52.1, 43.2, 38.9, 21.4; **HRMS** (ESI) Calcd for C₁₉H₂₂O₃NS [M + H]⁺ 344.1315, found 344.1310.



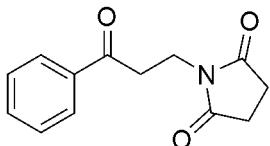
N-(3-Oxo-3-phenylpropyl)-N-phenylmethanesulfonamide (3f): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), N-phenylmethanesulfonamide (34.2 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (90% yield, eluent = hexane/EtOAc (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.89-7.86 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45-7.32 (m, 7H), 4.14 (t, *J* = 7.4 Hz, 2H), 3.28 (t, *J* = 7.4 Hz, 2H), 2.95 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.8, 139.2, 136.3, 133.4, 129.6, 128.6, 128.5, 128.3, 127.9, 46.9, 38.3, 37.0; **HRMS** (ESI) Calcd for C₁₆H₁₈O₃NS [M + H]⁺ 304.1002, found 304.0999.



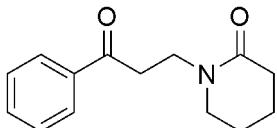
2-(3-Oxo-3-phenylpropyl)isoindoline-1,3-dione (3g): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), phthalimide (29.4 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (73% yield, eluent = petroleum ether/acetone (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.87-7.83 (m, 2H), 7.74-7.70 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.15 (t, *J* = 7.4 Hz, 2H), 3.43 (t, *J* = 7.4 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.3, 168.1, 136.4, 133.95, 133.3, 132.1, 128.6, 128.0, 123.2, 36.8, 33.5; **HRMS** (ESI) Calcd for C₁₇H₁₄O₃N [M + H]⁺ 280.0968, found 280.0964.



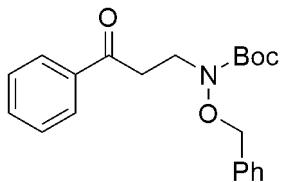
1-(3-Oxo-3-phenylpropyl)pyrrolidine-2,5-dione (3h): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), succinimide (19.8 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (68% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.96 (t, *J* = 7.3 Hz, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 2.71 (s, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.2, 176.96, 136.4, 133.4, 128.7, 128.0, 35.8, 34.4, 28.2; **HRMS** (ESI) Calcd for C₁₃H₁₄O₃N [M + H]⁺ 232.0968, found 232.0966.



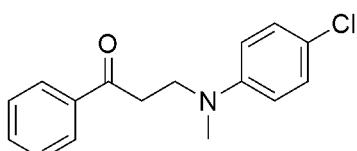
1-(3-Oxo-3-phenylpropyl)piperidin-2-one (3i): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 2-piperidone (19.8 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (63% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.39-3.38 (m, 2H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.37-2.36 (m, 2H), 1.775-1.745 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.1, 170.1, 136.7, 133.3, 128.6, 128.1, 49.3, 44.0, 36.7, 32.4, 23.3, 21.2; **HRMS** (ESI) Calcd for C₁₄H₁₈O₂N [M + H]⁺ 232.1332, found 232.1330.



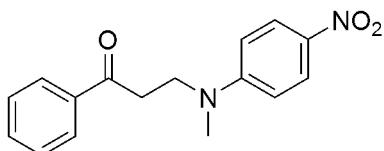
tert-Butyl benzylcarbamoyl(3-oxo-3-phenylpropyl)carbamate (3j): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), tert-butyl N-(benzyloxy)carbamate (44.7 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (57% yield, eluent = hexane/Et₂O (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45–7.32 (m, 7H), 4.85 (s, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H), 1.50 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.4, 156.4, 136.7, 135.5, 133.1, 129.5, 128.53, 128.51, 128.4, 128.0, 81.6, 76.9, 45.3, 35.9, 28.2; **HRMS** (ESI) Calcd for C₂₁H₂₆O₄N [M + H]⁺ 356.1856, found 356.1854.



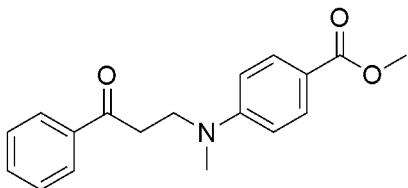
3-((4-Chlorophenyl)(methyl)amino)-1-phenylpropan-1-one (3k): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 4-chloro-N-methylaniline (28.3 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (60% yield, eluent = petroleum ether/Et₂O (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.785 (t, *J* = 7.0 Hz, 2H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.93 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.9, 147.0, 136.6, 133.1, 128.8, 128.4, 127.8, 121.2, 113.3, 47.9, 38.4, 34.8; **HRMS** (ESI) Calcd for C₁₆H₁₇ONCl [M + H]⁺ 274.0993, found 274.0990.



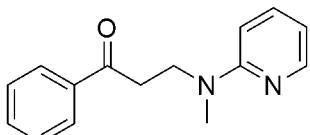
3-(Methyl(4-nitrophenyl)amino)-1-phenylpropan-1-one (3l): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), N-methyl-4-nitroaniline (30.4 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (62% yield, eluent = petroleum ether/dichloromethane (60:40)); **¹H NMR** (400 MHz, CDCl₃): δ 8.13-8.09 (m, 2H), 7.95-7.92 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.45 (m, 2H), 6.66-6.62 (m, 2H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.31 (t, *J* = 6.9 Hz, 2H), 3.13 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.1, 152.9, 137.1, 136.35, 133.5, 128.7, 127.9, 126.2, 110.2, 47.6, 39.0, 35.4; **HRMS** (ESI) Calcd for C₁₆H₁₇O₃N₂ [M + H]⁺ 285.1234, found 285.1234.



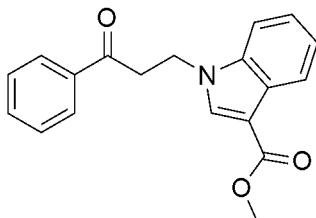
Methyl 4-(methyl(3-oxo-3-phenylpropyl)amino)benzoate (3m): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), methyl 4-(methylamino)benzoate (33.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (81% yield, eluent = petroleum ether/Et₂O (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.926-7.896 (m, 4H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.445 (t, *J* = 7.6 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.885 (t, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.26 (t, *J* = 7.0 Hz, 2H), 3.05 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.8, 167.3, 151.7, 136.6, 133.4, 131.4, 128.7, 128.0, 117.3, 110.7, 51.4, 47.5, 38.6, 35.4; **HRMS** (ESI) Calcd for C₁₈H₂₀O₃N [M + H]⁺ 298.1438, found 298.1433.



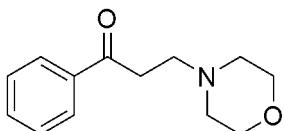
3-(Methyl(pyridin-2-yl)amino)-1-phenylpropan-1-one (3n): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 2-(methylamino)pyridine (21.6 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (75% yield, eluent = petroleum ether/Et₂O (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 8.18-8.17 (m, 1H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46-7.42 (m, 3H), 6.56-6.53 (m, 1H), 6.49 (d, *J* = 8.6 Hz, 1H), 3.99 (t, *J* = 7.0 Hz, 2H), 3.31 (t, *J* = 7.0 Hz, 2H), 3.07 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.7, 158.2, 148.0, 137.2, 136.9, 133.1, 128.5, 128.1, 111.6, 105.7, 46.2, 37.0, 36.5; **HRMS** (ESI) Calcd for C₁₅H₁₇ON₂ [M + H]⁺ 241.1335, found 241.1333.



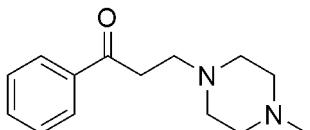
Methyl 1-(3-oxo-3-phenylpropyl)-1*H*-indole-3-carboxylate (3o): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), methyl indole-3-carboxylate (35.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (60% yield, eluent = petroleum ether/Et₂O (60:40)); ¹H NMR (400 MHz, CDCl₃): δ 8.19-8.17 (m, 1H), 7.94 (s, 1H), 7.885 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45-7.40 (m, 3H), 7.31-7.25 (m, 2H), 4.63 (t, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 3.51 (t, *J* = 6.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 196.8, 165.3, 136.2, 136.1, 134.7, 133.65, 128.7, 127.9, 126.8, 122.85, 121.94, 121.89, 109.6, 107.3, 50.9, 41.5, 38.3; HRMS (ESI) Calcd for C₁₉H₁₈O₃N [M + H]⁺ 308.1281, found 308.1277.



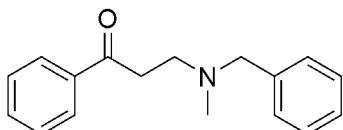
3-Morpholino-1-phenylpropan-1-one (3p): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), morpholine (17.4 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (73% yield, eluent = petroleum ether/acetone (80:20)); ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 3.71 (t, *J* = 4.6 Hz, 4H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 4.5 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 198.9, 136.85, 133.1, 128.6, 127.9, 66.9, 53.6, 53.5, 35.9; HRMS (ESI) Calcd for C₁₃H₁₈O₂N [M + H]⁺ 220.1332, found 220.1330.



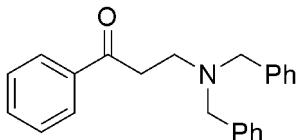
3-(4-Methylpiperazin-1-yl)-1-phenylpropan-1-one (3q): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 1-methylpiperazine (20.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (56% yield, eluent = hexane/acetone (60:40) + 5% Et₃N); **¹H NMR** (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.19 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.57-2.48 (m, 8H), 2.29 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.0, 136.9, 133.0, 128.6, 128.0, 55.0, 53.0, 45.9, 36.1; **HRMS** (ESI) Calcd for C₁₄H₂₁ON₂ [M + H]⁺ 233.1648, found 233.1645.



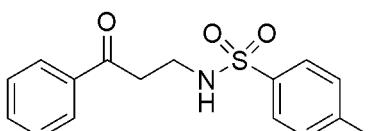
3-(Benzyl(methyl)amino)-1-phenylpropan-1-one (3r): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), *N*-methylbenzylamine (24.2 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (75% yield, eluent = hexane/Et₂O (60:40)); **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.29-7.21 (m, 5H), 3.56 (s, 2H), 3.18 (t, *J* = 7.3 Hz, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.4, 138.6, 136.9, 132.9, 129.0, 128.5, 128.2, 128.0, 127.0, 62.3, 52.4, 42.1, 36.8; **HRMS** (ESI) Calcd for C₁₇H₂₀ON [M + H]⁺ 254.1539, found 254.1537.



3-(Dibenzylamino)-1-phenylpropan-1-one (3s): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), dibenzylamine (39.5 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

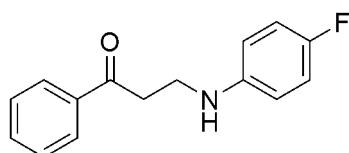
Colorless oil (62% yield, eluent = hexane/Et₂O (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 4H), 7.27 (t, *J* = 7.4 Hz, 4H), 7.20 (t, *J* = 6.9 Hz, 2H), 3.62 (s, 4H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.4, 139.2, 136.7, 132.7, 128.5, 128.3, 128.0, 127.9, 126.7, 58.4, 49.1, 36.8; **HRMS** (ESI) Calcd for C₂₃H₂₄ON [M + H]⁺ 330.1852, found 330.1848.



4-Methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (3t): Carried out with

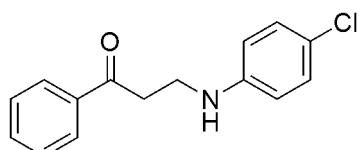
catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), *p*-toluenesulfonamide (34.2 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (67% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.865 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.30 (t, *J* = 6.4 Hz, 1H), 3.34 (q, *J* = 6.0 Hz, 2H), 3.21 (t, *J* = 5.6 Hz, 2H), 2.40 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.9, 143.4, 137.2, 136.1, 133.6, 129.7, 128.7, 127.9, 127.0, 38.3, 38.2, 21.4; **HRMS** (ESI) Calcd for C₁₆H₁₈O₃NS [M + H]⁺ 304.1002, found 304.0999.



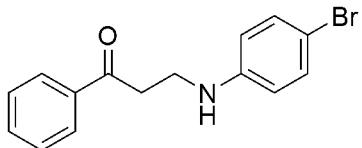
3-(4-Fluorophenylamino)-1-phenylpropan-1-one (3u): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 4-fluoroaniline (22.2 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (71% yield, eluent = petroleum ether/EtOAc (95:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.96-7.93 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.91-6.85 (m, 2H), 6.59-6.56 (m, 2H), 4.01 (brs, 1H), 3.56 (t, *J* = 6.1 Hz, 2H), 3.26 (t, *J* = 6.1 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.2, 156.0 (d, ¹J_{C-F} = 235.3 Hz), 144.1, 136.7, 133.4, 128.7, 128.0, 115.7 (d, ²J_{C-F} = 22.5 Hz), 114.0 (d, ³J_{C-F} = 7.5 Hz), 39.5, 37.5; **¹⁹F NMR** (377 MHz, CDCl₃): δ -127.8; **HRMS** (ESI) Calcd for C₁₅H₁₅ONF [M + H]⁺ 244.1132, found 244.1129.



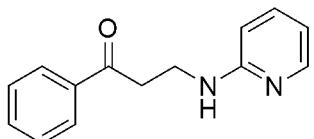
3-(4-Chlorophenylamino)-1-phenylpropan-1-one (3v): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 4-chloroaniline (25.5 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (76% yield, eluent = petroleum ether/EtOAc (95:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 4.17 (brs, 1H), 3.57 (t, *J* = 6.0 Hz, 2H), 3.25 (t, *J* = 6.0 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.1, 146.3, 136.6, 133.4, 129.1, 128.7, 128.0, 122.1, 114.1, 38.9, 37.4; **HRMS** (ESI) Calcd for C₁₅H₁₅ONCl [M + H]⁺ 260.0837, found 260.0834.



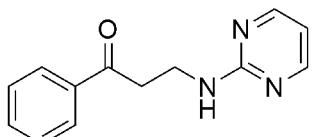
3-(4-Bromophenylamino)-1-phenylpropan-1-one (3w): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 4-bromoaniline (34.4 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (70% yield, eluent = petroleum ether/EtOAc (95:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.575 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 4.11 (brs, 1H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.26 (t, *J* = 6.0 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.1, 146.7, 136.6, 133.4, 132.0, 128.7, 128.0, 114.6, 109.1, 38.7, 37.4; **HRMS** (ESI) Calcd for C₁₅H₁₅ONBr [M + H]⁺ 304.0332, found 304.0329.



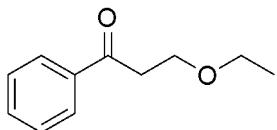
1-Phenyl-3-(pyridin-2-ylamino)propan-1-one (3x): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 2-aminopyridine (18.8 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (61% yield, eluent = petroleum ether/acetone (85:15)); **¹H NMR** (400 MHz, CDCl₃): δ 8.09 (d, *J* = 4.6 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38-7.34 (m, 1H), 6.55-6.52 (m, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 4.95 (brs, 1H), 3.81 (q, *J* = 6.0 Hz, 2H), 3.31 (t, *J* = 5.9 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.6, 158.3, 148.0, 137.1, 136.8, 133.2, 128.6, 128.0, 112.7, 108.0, 38.2, 36.6; **HRMS** (ESI) Calcd for C₁₄H₁₅ON₂ [M + H]⁺ 227.1179, found 227.1177.



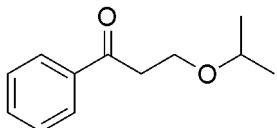
1-Phenyl-3-(pyrimidin-2-ylamino)propan-1-one (3y): Carried out with catalytic Cu(OAc)₂/bpy System: propiophenone (80.5 mg, 0.6 mmol), 2-aminopyrimidine (19.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (60% yield, eluent = petroleum ether/acetone (85:15)); **¹H NMR** (400 MHz, CDCl₃): δ 8.28 (d, *J* = 4.4 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.51 (t, *J* = 4.7 Hz, 1H), 5.73 (brs, 1H), 3.88 (q, *J* = 6.1 Hz, 2H), 3.32 (t, *J* = 5.9 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.1, 162.2, 158.0, 136.8, 133.2, 128.6, 128.0, 110.6, 38.3, 36.3; **HRMS** (ESI) Calcd for C₁₃H₁₄ON₃ [M + H]⁺ 228.1131, found 228.1129.



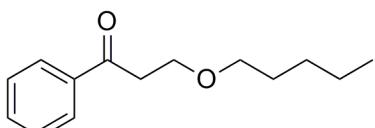
3-Ethoxy-1-phenylpropan-1-one (3z): Carried out with propiophenone (67.1 mg, 0.5 mmol), ethanol (230.3 mg, 5 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (78.7 mg, 0.5 mmol) and Li₂CO₃ (36.9 mg, 0.5 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (37% yield, eluent = petroleum ether/EtOAc (92:8)); **¹H NMR** (400 MHz, CDCl₃): δ 7.976-7.955 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 3.86 (t, *J* = 6.7 Hz, 2H), 3.536 (q, *J* = 7.0 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 1.195 (t, *J* = 7.0 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.4, 136.99, 133.06, 128.5, 128.1, 66.5, 65.7, 38.9, 15.1; This compound is known.¹ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



3-Isopropoxy-1-phenylpropan-1-one (3aa): Carried out with propiophenone (67.1 mg, 0.5 mmol), isopropyl alcohol (300.5 mg, 5 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (78.7 mg, 0.5 mmol) and Li₂CO₃ (36.9 mg, 0.5 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

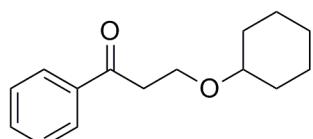
Pale yellow oil (36% yield, eluent = petroleum ether/EtOAc (92:8)); **¹H NMR** (400 MHz, CDCl₃): δ 7.976-7.954 (m, 2H), 7.573-7.536 (m, 1H), 7.47-7.44 (m, 2H), 3.85 (t, *J* = 6.7 Hz, 2H), 3.66-3.60 (m, 1H), 3.24 (t, *J* = 6.7 Hz, 2H), 1.16 (d, *J* = 6.2 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.45, 136.9, 132.9, 128.4, 127.9, 71.7, 63.2, 39.1, 21.9; This compound is known.² The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



3-(Pentyloxy)-1-phenylpropan-1-one (3ab): Carried out with propiophenone (67.1

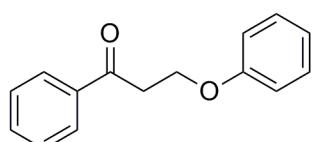
mg, 0.5 mmol), 1-pentanol (440.8 mg, 5 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (78.7 mg, 0.5 mmol) and Li₂CO₃ (36.9 mg, 0.5 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h. Phenyl vinyl ketone (5% based on the amount of ketone), pentanal (8% based on the amount of pentanol), 50% of propiophenone and 84% of pentanol were observed after the reaction was finished (determined by GC using dodecane as an internal standard).

Pale yellow oil (41% yield, eluent = petroleum ether/Et₂O (97:3)); ¹H NMR (400 MHz, CDCl₃): δ 7.98-7.96 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 3.86 (t, *J* = 6.7 Hz, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 1.60-1.53 (m, 2H), 1.34-1.26 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 198.51, 137.01, 133.06, 128.53, 128.10, 71.38, 65.99, 38.90, 29.31, 28.24, 22.48, 14.00; HRMS (ESI) Calcd for C₁₄H₂₁O₂ [M + H]⁺ 221.1537, found 221.1534.



3-(Cyclohexyloxy)-1-phenylpropan-1-one (3ac): Carried out with propiophenone (67.1 mg, 0.5 mmol), 1-cyclohexanol (500.8 mg, 5 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (78.7 mg, 0.5 mmol) and Li₂CO₃ (36.9 mg, 0.5 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h. Phenyl vinyl ketone (15% based the amount of ketone), cyclohexanone (1% based on the amount of pentanol), pentanol (94%) were observed after the reaction was finished (determined by GC using dodecane as an internal standard).

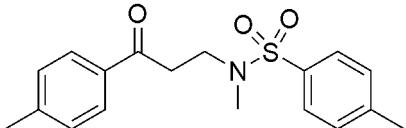
Pale yellow oil (32% yield, eluent = petroleum ether/Et₂O (97:3)); ¹H NMR (400 MHz, CDCl₃): δ 7.98-7.96 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 3.89 (t, *J* = 6.8 Hz, 2H), 3.32-3.24 (m, 3H), 1.94-1.89 (m, 2H), 1.72-1.71 (m, 2H), 1.54-1.51 (m, 1H), 1.30-1.15 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 198.74, 137.09, 133.02, 128.51, 128.10, 77.87, 63.14, 39.36, 32.17, 25.78, 24.07; HRMS (ESI) Calcd for C₁₅H₂₁O₂ [M + H]⁺ 233.1536, found 233.1538.



3-Phenoxy-1-phenylpropan-1-one (3ad): Carried out with propiophenone (26.8 mg, 0.2 mmol), phenol (94.1 mg, 1 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

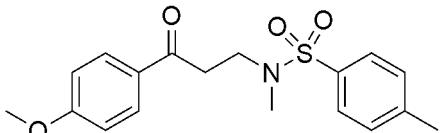
Pale yellow solid (44% yield, eluent = petroleum ether/Et₂O (97:3)); ¹H NMR (400 MHz, CDCl₃): δ 8.02-7.99 (m, 2H), 7.61-7.56 (m, 1H), 7.50-7.46 (m, 2H), 7.31-7.26

(m, 2H), 6.97-6.91 (m, 3H), 4.43 (t, $J = 6.6$ Hz, 2H), 3.47 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl₃): δ 197.64, 158.60, 136.77, 133.33, 129.45, 128.645, 128.12, 120.88, 114.53, 63.14, 38.15; This compound is known.² The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.



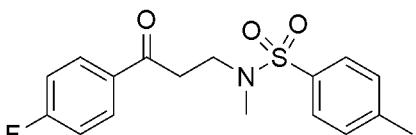
N,N-Dimethyl-N-(3-oxo-3-p-tolylpropyl)benzenesulfonamide (4a): Carried out with catalytic Cu(OAc)₂/bpy System: 4'-methylpropiophenone (88.9 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (89% yield, eluent = petroleum ether/dichloromethane (50:50)); ^1H NMR (400 MHz, CDCl₃): δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 3.44 (t, $J = 7.1$ Hz, 2H), 3.31 (t, $J = 6.9$ Hz, 2H), 2.81 (s, 3H), 2.435 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ 197.8, 144.3, 143.4, 134.4, 134.0, 129.7, 129.4, 128.2, 127.4, 46.0, 38.1, 36.2, 21.7, 21.5; HRMS (ESI) Calcd for C₁₈H₂₂O₃NS [M + H]⁺ 332.1315, found 332.1310.



N-(3-(4-Methoxyphenyl)-3-oxopropyl)-N,N-dimethylbenzenesulfonamide (4b): Carried out with catalytic Cu(OAc)₂/bpy System: 4'-methoxypropiophenone (98.52 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

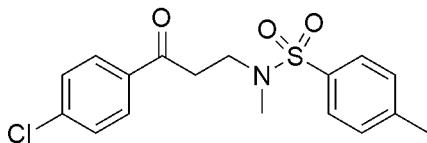
White solid (90% yield, eluent = petroleum ether/EtOAc (70:30)); ^1H NMR (400 MHz, CDCl₃): δ 7.93 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 3.44 (t, $J = 7.1$ Hz, 2H), 3.28 (t, $J = 7.1$ Hz, 2H), 2.81 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ 196.7, 163.7, 143.4, 134.4, 130.4, 129.7, 129.6, 127.4, 113.8, 55.5, 46.1, 37.8, 36.2, 21.5; HRMS (ESI) Calcd for C₁₈H₂₂O₄NS [M + H]⁺ 348.1264, found 348.1259.



N-(3-(4-Fluorophenyl)-3-oxopropyl)-N,N-dimethylbenzenesulfonamide (4c):

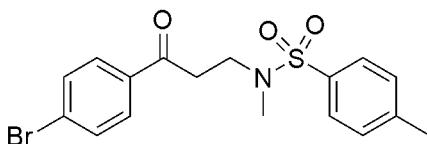
Carried out with catalytic Cu(OAc)₂/bpy System: 4'-fluoropropiophenone (91.3 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (94% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl₃): δ 8.00–7.96 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 3.44 (t, *J* = 7.0 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.82 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 196.6, 165.9 (d, ¹*J*_{C-F} = 255 Hz), 143.5, 134.3, 132.9 (d, ⁴*J*_{C-F} = 3.0 Hz), 130.7 (d, ³*J*_{C-F} = 9.3 Hz), 129.7, 127.4, 115.8 (d, ²*J*_{C-F} = 21.8 Hz), 45.9, 38.2, 36.3, 21.5; **¹⁹F NMR** (377 MHz, CDCl₃): δ -104.5; **HRMS** (ESI) Calcd for C₁₇H₁₉O₃NFS [M + H]⁺ 336.1064, found 336.1058.



***N*-(3-(4-Chlorophenyl)-3-oxopropyl)-N,4-dimethylbenzenesulfonamide (4d):**
Carried out with catalytic Cu(OAc)₂/bpy System: 4'-chloropropiophenone (101.2 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

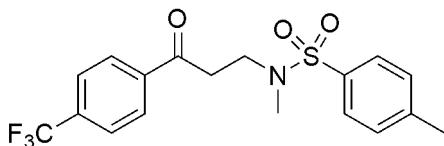
White solid (93% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 3.31 (t, *J* = 6.9 Hz, 2H), 2.82 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 196.9, 143.5, 139.9, 134.8, 134.2, 129.7, 129.4, 129.0, 127.4, 45.9, 38.3, 36.3, 21.5; **HRMS** (ESI) Calcd for C₁₇H₁₉O₃NCIS [M + H]⁺ 352.0769, found 352.0763.



***N*-(3-(4-Bromophenyl)-3-oxopropyl)-N,4-dimethylbenzenesulfonamide (4e):**
Carried out with catalytic Cu(OAc)₂/bpy System: 4'-bromopropiophenone (127.8 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

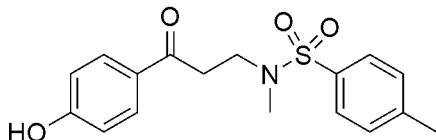
White solid (94% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl₃): δ 7.805 (d, *J* = 8.4 Hz, 2H), 7.686 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.325 (d, *J* = 8.1 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 3.30 (t, *J* = 6.9 Hz, 2H), 2.81 (s, 3H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.1, 143.5, 135.1,

134.2, 131.95, 129.7, 129.5, 128.6, 127.4, 45.8, 38.2, 36.3, 21.4; **HRMS** (ESI) Calcd for C₁₇H₁₉O₃NBrS [M + H]⁺ 396.0264, found 396.0258.



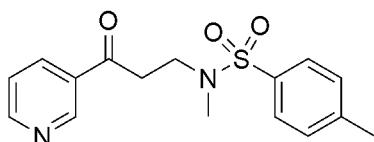
N,N-Dimethyl-N-(3-oxo-3-(4-(trifluoromethyl)phenyl)propyl)benzenesulfonamide (4f): Carried out with 4'--(trifluoromethyl) propiophenone (121.3 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 100 °C for 24 h.

White solid (79% yield, eluent = petroleum ether/dichloromethane (50:50)); **¹H NMR** (400 MHz, CDCl₃): δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.745 (d, *J* = 8.2 Hz, 2H), 7.696 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 2H), 3.38 (t, *J* = 6.5 Hz, 2H); 2.83 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.25, 143.6, 139.1, 134.7 (q, ²J_{C-F} = 32.9 Hz), 134.2, 129.8, 128.4, 127.4, 125.8 (q, ³J_{C-F} = 3.6 Hz), 123.5 (q, ¹J_{C-F} = 272.5 Hz), 45.8, 38.7, 36.5, 21.5; **¹⁹F NMR** (377 MHz, CDCl₃): δ -63.15; **HRMS** (ESI) Calcd for C₁₈H₁₉O₃NF₃S [M + H]⁺ 386.1032, found 386.1028.



N-(3-(4-Hydroxyphenyl)-3-oxopropyl)-N,N-dimethylbenzenesulfonamide (4g): Carried out with catalytic Cu(OAc)₂/bpy System: 4'-hydroxypropiophenone (90.1 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

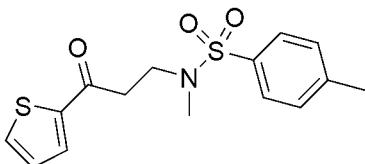
White solid (85% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, acetone-*d*₆): δ 9.16 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.40 (t, *J* = 7.3 Hz, 2H), 3.25 (t, *J* = 7.3 Hz, 2H), 2.81 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, acetone-*d*₆): δ 195.8, 162.0, 143.4, 135.0, 130.5, 129.7, 129.1, 127.4, 115.2, 45.9, 36.8, 35.2, 20.5; **HRMS** (ESI) Calcd for C₁₇H₂₀O₄NS [M + H]⁺ 334.1108, found 334.1104.



N,N-Dimethyl-N-(3-oxo-3-(pyridin-3-yl)propyl)benzenesulfonamide (4h): Carried out with 3-propionylpyridine (81.1 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide

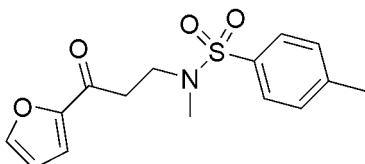
(37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (81% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 9.15 (s, 1H), 8.80 (d, *J* = 4.6 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.45-7.42 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.36 (t, *J* = 6.7 Hz, 2H), 2.83 (s, 3H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 197.1, 153.8, 149.5, 143.6, 135.3, 134.2, 131.7, 129.7, 127.4, 123.6, 45.5, 38.5, 36.4, 21.4; **HRMS** (ESI) Calcd for C₁₆H₁₉O₃N₂S [M + H]⁺ 319.1111, found 319.1106.



N,N-Dimethyl-N-(3-oxo-3-(thiophen-2-yl)propyl)benzenesulfonamide (4i): Carried out with catalytic Cu(OAc)₂/bpy System: 2-propionylthiophene (84.1 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

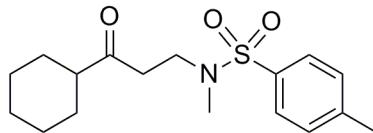
White solid (82% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (d, *J* = 3.7 Hz, 1H), 7.70-7.66 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 4.3 Hz, 1H), 3.44 (t, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 7.0 Hz, 2H), 2.81 (s, 3H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 190.9, 143.8, 143.5, 134.3, 134.1, 132.5, 129.7, 128.3, 127.4, 45.9, 38.9, 36.3, 21.5; **HRMS** (ESI) Calcd for C₁₅H₁₈O₃NS₂ [M + H]⁺ 324.0723, found 324.0717.



N-(3-(Furan-2-yl)-3-oxopropyl)-N,N-dimethylbenzenesulfonamide (4j): Carried out with catalytic Cu(OAc)₂/bpy System: 2-propionylfuran (74.5 mg, 0.6 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

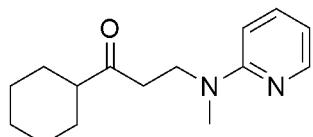
White solid (91% yield, eluent = petroleum ether/acetone (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.60 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 3.5 Hz, 1H), 6.56-6.55 (m, 1H), 3.43 (t, *J* = 7.0 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.80 (s, 3H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 186.9, 152.3, 146.7, 143.5, 134.4, 129.7, 127.4, 117.7, 112.4, 45.5, 38.0, 36.1, 21.5; **HRMS** (ESI) Calcd

for C₁₅H₁₈O₄NS [M + H]⁺ 308.0951, found 308.0947.



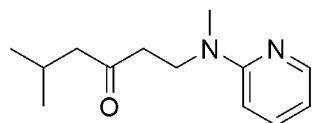
N-(3-Cyclohexyl-3-oxopropyl)-N,4-dimethylbenzenesulfonamide (4k): Carried out with cyclohexyl ethyl ketone (84.1 mg, 0.6 mmol), N-methyl-p-toluenesulfonamide (37.0 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Colorless oil (57% yield, eluent = petroleum ether/EtOAc (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H), 2.74 (s, 3H), 2.43 (s, 3H), 2.36-2.30 (m, 1H), 1.85-1.66 (m, 5H), 1.36-1.16 (m, 5H); **¹³C NMR** (100 MHz, CDCl₃): δ 212.09, 143.41, 134.18, 129.67, 127.39, 50.97, 45.41, 39.815, 36.12, 28.23, 25.73, 25.51, 21.455; **HRMS** (ESI) Calcd for C₁₇H₂₆O₃NS [M + H]⁺ 324.1628, found 324.1627.



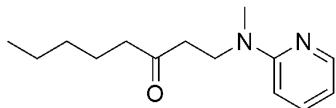
1-Cyclohexyl-3-(methyl(pyridin-2-yl)amino)propan-1-one (4l): Carried out with cyclohexyl ethyl ketone (84.1 mg, 0.6 mmol), 2-(methylamino)pyridine (21.6 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (69% yield, eluent = hexane/Et₂O (80:20)); **¹H NMR** (400 MHz, CDCl₃): δ 8.15-8.14 (m, 1H), 7.45-7.41 (m, 1H), 6.54-6.51 (m, 1H), 6.46 (d, *J* = 8.6 Hz, 1H), 3.80 (t, *J* = 6.8 Hz, 2H), 3.02 (s, 3H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.36-2.30 (m, 1H), 1.83-1.64 (m, 5H), 1.35-1.16 (m, 5H); **¹³C NMR** (100 MHz, CDCl₃): δ 213.4, 158.2, 147.9, 137.1, 111.5, 105.7, 51.2, 45.4, 38.2, 36.8, 28.3, 25.8, 25.6; **HRMS** (ESI) Calcd for C₁₅H₂₃ON₂ [M + H]⁺ 247.1805, found 247.1802.



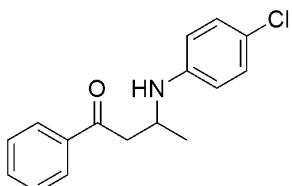
5-Methyl-1-(methyl(pyridin-2-yl)amino)hexan-3-one (4m): Carried out with ethyl isobutyl ketone (68.5 mg, 0.6 mmol), 2-(methylamino)pyridine (21.6 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (68% yield, eluent = hexane/Et₂O (80:20)); ¹**H NMR** (400 MHz, CDCl₃): δ 8.15-8.14 (m, 1H), 7.45-7.41 (m, 1H), 6.55-6.52 (m, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 3.81 (t, *J* = 6.8 Hz, 2H), 3.03 (s, 3H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.30 (d, *J* = 6.9 Hz, 2H), 2.17-2.09 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 6H); ¹³**C NMR** (100 MHz, CDCl₃): δ 210.2, 158.2, 147.9, 137.1, 111.6, 105.7, 52.4, 45.3, 40.9, 36.8, 24.5, 22.5; **HRMS** (ESI) Calcd for C₁₃H₂₁ON₂ [M + H]⁺ 221.1648, found 221.1645.



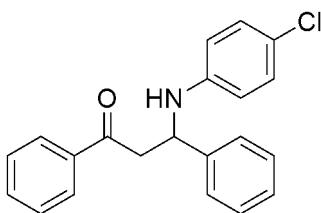
1-(Methyl(pyridin-2-yl)amino)octan-3-one (4n): Carried out with 3-octanone (76.9 mg, 0.6 mmol), 2-(methylamino)pyridine (21.6 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Colorless oil (60% yield, eluent = petroleum ether/Et₂O (60:40)); ¹**H NMR** (400 MHz, CDCl₃): δ 8.14 (d, *J* = 4.9 Hz, 1H), 7.45-7.41 (m, 1H), 6.53 (t, *J* = 6.0 Hz, 1H), 6.47 (d, *J* = 8.6 Hz, 1H), 3.81 (t, *J* = 6.8 Hz, 2H), 3.02 (s, 3H), 2.73 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.59-1.52 (m, 2H), 1.32-1.22 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃): δ 210.6, 158.2, 147.9, 137.1, 111.6, 105.7, 45.4, 43.3, 40.4, 36.8, 31.3, 23.4, 22.4, 13.8; **HRMS** (ESI) Calcd for C₁₄H₂₃ON₂ [M + H]⁺ 235.1805, found 235.1803.



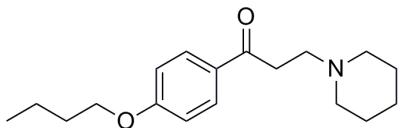
3-(4-Chlorophenylamino)-1-phenylbutan-1-one (4o): Carried out with butyrophenone (29.6 mg, 0.2 mmol), 4-chloroaniline (76.5 mg, 0.6 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol), TEMPO (31.3 mg, 0.2 mmol) and Na₂CO₃ (10.6 mg, 0.1 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Yellow oil (30% yield, eluent = petroleum ether/EtOAc (90:10)); ¹**H NMR** (400 MHz, CDCl₃): δ 7.93-7.91 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.12-7.08 (m, 2H), 6.56-6.52 (m, 2H), 4.13-4.05 (m, 1H), 3.87 (brs, 1H), 3.256 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.066 (dd, *J* = 8.3, 7.3 Hz, 1H), 1.30 (d, *J* = 6.4 Hz, 3H); ¹³**C NMR** (100 MHz, CDCl₃): δ 199.0, 145.4, 136.98, 133.3, 129.1, 128.6, 127.97, 121.98, 114.5, 45.8, 44.1, 20.8; **HRMS** (ESI) Calcd for C₁₆H₁₇ONCl [M + H]⁺ 274.0993, found 274.0992.



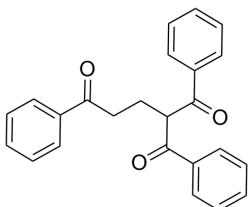
3-(4-Chlorophenylamino)-1,3-diphenylpropan-1-one (4p): Carried out with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), 4-chloroaniline (76.5 mg, 0.6 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (22% yield, eluent = petroleum ether/EtOAc (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 7.895 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46-7.40 (m, 4H), 7.34-7.30 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.466 (d, *J* = 8.8 Hz, 2H), 4.958-4.927 (m, 1H), 4.62 (s, 1H), 3.51-3.37 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 198.1, 145.5, 142.5, 136.5, 133.5, 128.9, 128.7, 128.2, 127.5, 126.26, 122.4, 114.9, 54.85, 46.2; **HRMS** (ESI) Calcd for C₂₁H₁₉ONCl [M + H]⁺ 336.1150, found 336.1150.



1-(4-Butoxyphenyl)-3-(piperidin-1-yl)propan-1-one (4q): The corresponding ketone 1-(4-butoxyphenyl)propan-1-one was prepared according to literature procedures.³ The reaction was carried out in 5 mmol scale with 1-(4-butoxyphenyl)propan-1-one (3.09 g, 15 mmol), piperidine (425.8 mg, 5 mmol), Cu(OAc)₂ (90.8 mg, 0.5 mmol), 2,2'-bipyridine (78.1 mg, 0.5 mmol) and TEMPO (781.2 mg, 5 mmol) in 1,2-dichlorobenzene (50 mL) at 120 °C for 24 h.

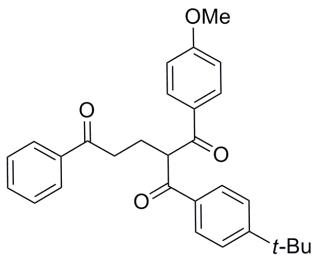
Pale yellow oil (65% yield, eluent = petroleum ether/acetone (90:10)+5% Et₃N); **¹H NMR** (400 MHz, CDCl₃): δ 7.936 (d, *J* = 8.8 Hz, 2H), 6.915 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.785 (t, *J* = 7.6 Hz, 2H), 2.455 (s, 4H), 1.82-1.75 (m, 2H), 1.615-1.575 (m, 4H), 1.545-1.446 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 3H). This compound is known.³ The ¹H NMR spectral data are in good agreement with the literature data.



2-Benzoyl-1,5-diphenylpentane-1,5-dione (6a): Carried out with propiophenone

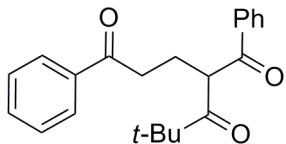
(80.5 mg, 0.6 mmol), 1,3-diphenyl-1,3-propanedione (44.8 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (91% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 8.09-8.07 (m, 4H), 7.97-7.95 (m, 2H), 7.58-7.53 (m, 3H), 7.48-7.42 (m, 6H), 5.61 (t, *J* = 6.8 Hz, 1H), 3.25 (t, *J* = 6.4 Hz, 2H), 2.56-2.51 (m, 2H); **¹³C NMR** (CDCl₃, 100MHz): δ 199.87, 196.37, 136.62, 135.83, 133.57, 133.24, 128.89, 128.67, 128.59, 127.97, 54.97, 35.98, 23.63; **HRMS** (ESI) *m/z* calculated for C₂₄H₂₁O₃ [M+H]⁺: 357.1485, found: 357.1482.



2-(4-(tert-Butyl)benzoyl)-1-(4-methoxyphenyl)-5-phenylpentane-1,5-dione (6b): Carried out with propiophenone (80.5 mg, 0.6 mmol), 1-(4-tert-Butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione (62.1 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

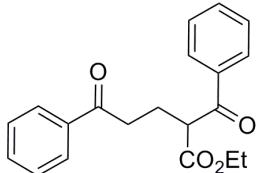
Pale yellow oil (97% yield, eluent = petroleum ether/ethyl acetate (100:8)); **¹H NMR** (400 MHz, CDCl₃): δ 8.11-7.89 (m, 6H), 7.56-7.42 (m, 5H), 6.96-6.90 (m, 2H), 5.59-5.49 (m, 1H), 3.85 (s, 3H), 3.25-3.18 (m, 2H), 2.53-2.50 (m, 2H), 1.31 (s, 9H); **¹³C NMR** (CDCl₃, 100MHz): δ 200.05, 196.05, 195.09, 163.88, 157.30, 136.69, 133.20, 131.14, 130.30, 128.71, 128.63, 128.58, 128.01, 125.84, 114.10, 55.48, 54.87, 36.13, 35.12, 30.99, 23.74; **HRMS** (ESI) *m/z* calculated for C₂₉H₃₁O₄ [M+H]⁺: 443.2217, found: 443.2210.



4-Benzoyl-6,6-dimethyl-1-phenylheptane-1,5-dione (6c): Carried out with propiophenone (80.5 mg, 0.6 mmol), 4,4-dimethyl-1-phenylpentane-1,3-dione (40.8 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

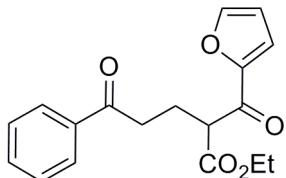
Pale yellow oil (92% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 8.20 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.59-7.51 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 5.30-5.276 (m, 1H),

3.12-3.01 (m, 2H), 2.39-2.29 (m, 2H), 1.05 (s, 9H); **¹³C NMR** (CDCl₃, 100MHz): δ 210.39, 199.90, 196.45, 136.63, 135.61, 133.62, 133.31, 128.95, 128.88, 128.67, 127.91, 53.58, 44.72, 35.89, 26.18, 24.45; **HRMS** (ESI) *m/z* calculated for C₂₂H₂₅O₃ [M+H]⁺: 337.1798, found: 337.1795.



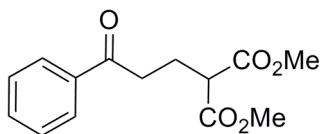
Ethyl 2-benzoyl-5-oxo-5-phenylpentanoate (6d): Carried out with propiophenone (80.5 mg, 0.6 mmol), ethyl benzoylacetate (38.4 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (70% yield, eluent = petroleum ether/ethyl acetate (100:6)); **¹H NMR** (400 MHz, CDCl₃): δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.60-7.53 (m, 2H), 7.50-7.43 (m, 4H), 4.58-4.55 (m, 1H), 4.18-4.12 (m, 2H), 3.23-3.05 (m, 2H), 2.49-2.37 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (CDCl₃, 100MHz): δ 199.22, 195.35, 169.86, 136.67, 135.98, 133.58, 133.18, 128.74, 128.60, 128.00, 61.40, 52.88, 35.67, 23.28, 13.94. This compound is known.⁴ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



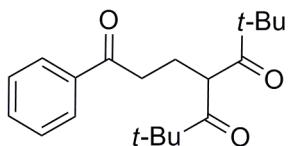
Ethyl 2-(furan-2-carbonyl)-5-oxo-5-phenylpentanoate (6e): Carried out with propiophenone (80.5 mg, 0.6 mmol), ethyl 3-(2-furyl)-3-oxopropanoate (36.4 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (60% yield, eluent = petroleum ether/ethyl acetate (100:6)); **¹H NMR** (400 MHz, CDCl₃): δ 7.940 (d, *J* = 7.9 Hz, 2H), 7.60-7.53 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 3.6 Hz, 1H), 6.56-6.55 (m, 1H), 4.29 (t, *J* = 7.1 Hz, 1H), 4.19-4.14 (m, 2H), 3.17-3.06 (m, 2H), 2.41 (q, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (CDCl₃, 100MHz): δ 199.11, 183.79, 169.39, 151.79, 147.11, 136.62, 133.16, 128.58, 127.99, 118.89, 112.58, 61.45, 53.10, 35.57, 22.85, 13.97; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₉O₅ [M+H]⁺: 315.1227, found: 315.1225.



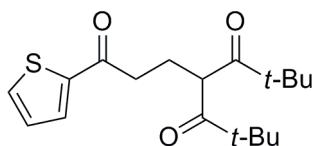
Dimethyl 2-(3-oxo-3-phenylpropyl)malonate (6f): Carried out with propiophenone (80.5 mg, 0.6 mmol), dimethyl malonate (26.4 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

White solid (51% yield, eluent = petroleum ether/ethyl acetate (100:8)); **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.57-7.54 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.74 (s, 6H), 3.57 (t, *J* = 7.2 Hz, 1H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.37-2.32 (m, 2H); **¹³C NMR** (CDCl₃, 100MHz): δ 198.60, 169.58, 136.61, 133.16, 128.59, 127.98, 52.53, 50.48, 35.50, 23.03; **HRMS** (ESI) *m/z* calculated for C₁₄H₁₇O₅ [M+H]⁺: 265.1071, found: 265.1070.



6,6-Dimethyl-1-phenyl-4-pivaloylheptane-1,5-dione (6g): Carried out with propiophenone (80.5 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

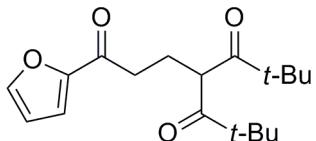
Yellow solid (96% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45-7.41 (m, 2H), 4.70 (t, *J* = 6.8 Hz, 1H), 2.91 (t, *J* = 6.5 Hz, 2H), 2.24-2.19 (m, 2H), 1.16 (s, 18H); **¹³C NMR** (CDCl₃, 100MHz): δ 211.03, 199.34, 136.49, 133.20, 128.60, 127.85, 54.07, 44.57, 36.18, 27.18, 23.96; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₉O₃ [M+H]⁺: 317.2111, found: 317.2111.



6,6-Dimethyl-4-pivaloyl-1-(thiophen-2-yl)heptane-1,5-dione (6h): Carried out with 2-propionylthiophene (84.1 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

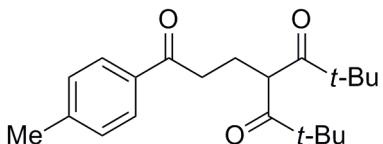
Yellow solid (93% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.69 (d, *J* = 3.7 Hz, 1H), 7.62 (d, *J* = 5.0 Hz, 1H), 7.12-7.10 (m, 1H), 4.70 (t, *J* = 6.8 Hz, 1H), 2.86 (t, *J* = 6.6 Hz, 2H), 2.24-2.19 (m, 2H), 1.17 (s,

18H); **¹³C NMR** (CDCl_3 , 100MHz): δ 211.10, 192.34, 143.78, 133.79, 132.15, 128.23, 54.13, 44.65, 36.90, 27.26, 24.17; **HRMS** (ESI) m/z calculated for $\text{C}_{18}\text{H}_{27}\text{O}_3\text{S} [\text{M}+\text{H}]^+$: 323.1675, found: 323.1675.



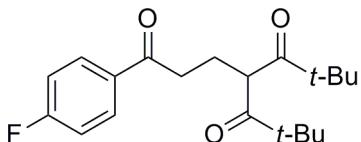
1-(Furan-2-yl)-6,6-dimethyl-4-pivaloylheptane-1,5-dione (6i): Carried out with 2-propionylfuran (74.5 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Yellow solid (90% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl_3): δ 7.55 (d, J = 1.3 Hz, 1H), 7.17 (d, J = 3.5 Hz, 1H), 6.51-6.50 (m, 1H), 4.65 (t, J = 6.8 Hz, 1H), 2.76 (t, J = 6.6 Hz, 2H), 2.21-2.16 (m, 2H), 1.15 (s, 18H); **¹³C NMR** (CDCl_3 , 100MHz): δ 210.96, 188.36, 152.30, 146.54, 117.34, 112.22, 54.10, 44.60, 36.00, 27.23, 23.68; **HRMS** (ESI) m/z calculated for $\text{C}_{18}\text{H}_{27}\text{O}_4 [\text{M}+\text{H}]^+$: 307.1904, found: 307.1904.



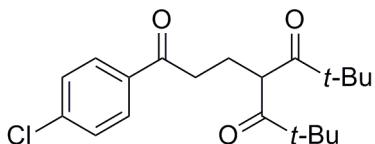
6,6-Dimethyl-4-pivaloyl-1-(p-tolyl)heptane-1,5-dione (6j): Carried out with 4'-methylpropiophenone (88.9 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (94% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl_3): δ 7.81 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 4.71 (t, J = 6.6 Hz, 1H), 2.89 (t, J = 6.3 Hz, 2H), 2.39 (s, 3H), 2.23-2.19 (m, 2H), 1.16 (s, 18H); **¹³C NMR** (CDCl_3 , 100MHz): δ 211.15, 199.05, 144.07, 134.09, 129.31, 128.03, 54.16, 44.62, 36.09, 27.22, 24.07, 21.58; **HRMS** (ESI) m/z calculated for $\text{C}_{21}\text{H}_{30}\text{O}_3 [\text{M}+\text{H}]^+$: 331.2268, found: 331.2267.



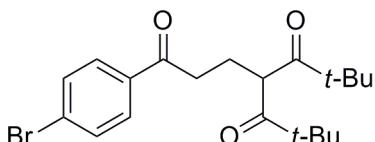
1-(4-Fluorophenyl)-6,6-dimethyl-4-pivaloylheptane-1,5-dione (6k): Carried out with 4'-fluoropropiophenone (91.3 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (99% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.97-7.94 (m, 2H), 7.12 (t, *J* = 8.3 Hz, 2H), 4.70 (t, *J* = 6.7 Hz, 1H), 2.89 (t, *J* = 6.5 Hz, 2H), 2.24-2.19 (m, 2H), 1.17 (s, 18H); **¹⁹F NMR** (377MHz, CDCl₃): δ -104.83; **¹³C NMR** (CDCl₃, 100MHz): δ 211.13, 197.82, 165.85 (d, *J* = 255.1 Hz), 132.98 (d, *J* = 3.0 Hz), 130.62 (d, *J* = 9.4 Hz), 115.79 (d, *J* = 21.9 Hz), 54.13, 44.66, 36.21, 27.26, 24.05; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₈O₃F [M+H]⁺: 335.2017, found: 335.2015.



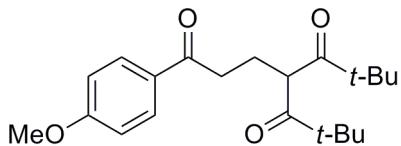
1-(4-Chlorophenyl)-6,6-dimethyl-4-pivaloylheptane-1,5-dione (6l): Carried out with 4'-chloropropiophenone (101.2 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (99% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 4.70 (t, *J* = 6.7 Hz, 1H), 2.89 (t, *J* = 6.3 Hz, 2H), 2.24-2.19 (m, 2H), 1.17 (s, 18H); **¹³C NMR** (CDCl₃, 100MHz): δ 211.11, 198.21, 139.79, 134.84, 129.38, 129.02, 54.07, 44.67, 36.25, 27.26, 23.96; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₈O₃Cl [M+H]⁺: 351.1721, found: 351.1719.



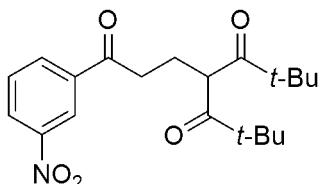
1-(4-Bromophenyl)-6,6-dimethyl-4-pivaloylheptane-1,5-dione (6m): Carried out with 4'-bromopropiophenone (127.8 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (94% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.68 (t, *J* = 6.8 Hz, 1H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.22-2.17 (m, 2H), 1.16 (s, 18H); **¹³C NMR** (CDCl₃, 100MHz): δ 211.05, 198.35, 135.21, 131.98, 129.45, 128.48, 54.02, 44.63, 36.19, 27.23, 23.91; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₈O₃Br [M+H]⁺: 395.1216, found: 395.1211.



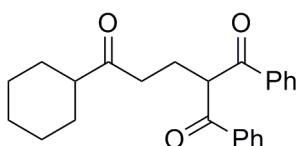
1-(4-Methoxyphenyl)-6,6-dimethyl-4-pivaloylheptane-1,5-dione (6n): Carried out with 4'-methoxypropiophenone (98.52 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow solid (73% yield, eluent = petroleum ether/ethyl acetate (100:7)); **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.71 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 2.86 (t, *J* = 6.5 Hz, 2H), 2.23-2.18 (m, 2H), 1.17 (s, 18H); **¹³C NMR** (CDCl₃, 100MHz): δ 211.20, 197.95, 163.61, 130.24, 129.67, 113.80, 55.44, 54.26, 44.64, 35.92, 27.24, 24.24; **HRMS** (ESI) *m/z* calculated for C₂₁H₃₁O₄ [M+H]⁺: 347.2217, found: 347.2214.



6,6-Dimethyl-1-(3-nitrophenyl)-4-pivaloylheptane-1,5-dione (6o): Carried out with 3'-nitropropiophenone (107.5 mg, 0.6 mmol), dipivaloylmethane (36.9 mg, 0.2 mmol), Cu(OAc)₂ (7.2 mg, 0.04 mmol), 2,2'-bipyridine (6.2 mg, 0.04 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

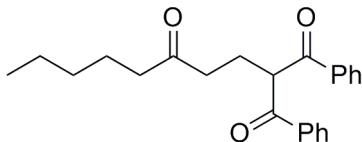
Pale yellow oil (71% yield, eluent = petroleum ether/EtOAc (90:10)); **¹H NMR** (400 MHz, CDCl₃): δ 8.75-8.74 (m, 1H), 8.44-8.41 (m, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.96 Hz, 1H), 4.72 (t, *J* = 6.7 Hz, 1H), 3.00 (t, *J* = 6.6 Hz, 2H), 2.26 (q, *J* = 6.6 Hz, 2H), 1.20 (s, 18H); **¹³C NMR** (100 MHz, CDCl₃): δ 210.99, 197.1, 148.5, 137.7, 133.5, 130.0, 127.5, 122.7, 53.9, 44.65, 36.5, 27.25, 23.7; **HRMS** (ESI) Calcd for C₂₀H₂₈NO₅ [M + H]⁺ 362.1962, found 362.1961.



2-Benzoyl-5-cyclohexyl-1-phenylpentane-1,5-dione (6p): Carried out with cyclohexyl ethyl ketone (84.1 mg, 0.6 mmol), 1,3-diphenyl-1,3-propanedione (44.8 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

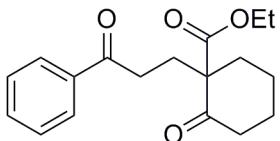
Pale yellow solid (51% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 8.03 (d, *J* = 7.5 HZ, 4H), 7.58-7.54 (m, 2H), 7.46 (t, *J* =

7.4 Hz, 4H), 5.48 (t, J = 6.6 Hz, 1H), 2.69 (t, J = 6.1 Hz, 2H), 2.35-2.30 (m, 3H), 1.78-1.65 (m, 5H), 1.30-1.16 (m, 5H); ^{13}C NMR (CDCl₃, 100MHz): δ 214.25, 196.38, 135.91, 133.55, 128.90, 128.65, 54.81, 50.88, 37.71, 28.47, 25.75, 25.57, 23.32; HRMS (ESI) m/z calculated for C₂₄H₂₇O₃ [M+H]⁺: 363.1955, found: 363.1954.



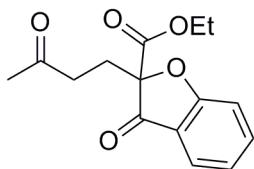
2-Benzoyl-1-phenyldecane-1,5-dione (6q): Carried out with 3-octanone (76.9 mg, 0.6 mmol), 1,3-diphenyl-1,3-propanedione (44.8 mg, 0.2 mmol), Cu(OAc)₂ (10.8 mg, 0.06 mmol), 2,2'-bipyridine (9.3 mg, 0.06 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (48% yield, eluent = petroleum ether/ethyl acetate (100:5)); ^1H NMR (400 MHz, CDCl₃) δ : 8.036 (d, J = 7.9 Hz, 4H), 7.57 (t, J = 7.1 Hz, 2H), 7.46 (t, J = 7.5 Hz, 4H), 5.50 (t, J = 6.8 Hz, 1H), 2.66 (t, J = 6.3 Hz, 2H), 2.37-2.30 (m, 4H), 1.58-1.51 (m, 2H), 1.29-1.19 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (CDCl₃, 100MHz): δ 211.33, 196.33, 135.85, 133.59, 128.91, 128.66, 54.76, 42.92, 39.75, 31.33, 23.58, 23.25, 22.38, 13.83; HRMS (ESI) m/z calculated for C₂₃H₂₇O₃ [M+H]⁺: 351.1955, found: .351.1950.



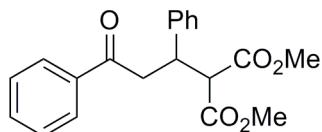
Ethyl 2-oxo-1-(3-oxo-3-phenylpropyl)cyclohexanecarboxylate (6r): Carried out with propiophenone (80.5 mg, 0.6 mmol), ethyl 2-oxocyclohexanecarboxylate (34.0 mg, 0.2 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (62.5 mg, 0.4 mmol) and Li₂CO₃ (14.8 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (43% yield, eluent = petroleum ether/ethyl acetate (100:8)); ^1H NMR (400 MHz, CDCl₃): δ 7.96 (d, J = 7.3 Hz, 2H), 7.56-7.52 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 4.24-4.16 (m, 2H), 3.18-3.10 (m, 1H), 2.92-2.83 (m, 1H), 2.55-2.43 (m, 3H), 2.29-2.21 (m, 1H), 2.08-2.00 (m, 2H), 1.80-1.77 (m, 1H), 1.69-1.63 (m, 2H), 1.57-1.50 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl₃, 100MHz): δ 208.16, 199.39, 172.03, 136.71, 132.99, 128.53, 128.07, 61.39, 60.22, 41.03, 36.82, 34.00, 29.15, 27.54, 22.54, 14.11; HRMS (ESI) m/z calculated for C₁₈H₂₃O₄ [M+H]⁺: 303.1591, found: 303.1588.



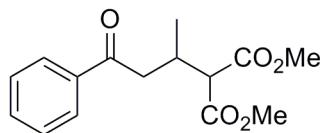
Ethyl 3-oxo-2-(3-oxobutyl)-2,3-dihydrobenzofuran-2-carboxylate (6s): Carried out with 2-butanone (43.3 mg, 0.6 mmol), 2-ethoxycarbonyl-3-coumaranone (41.2 mg, 0.2 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (62.5 mg, 0.4 mmol) and Cs₂CO₃ (65.2 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (41% yield, eluent = petroleum ether/ethyl acetate (100:5)); **¹H NMR** (400 MHz, CDCl₃): δ 7.68-7.645 (m, 2H), 7.195 (d, *J* = 8.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.60-2.50 (m, 3H), 2.39-2.34 (m, 1H), 2.11 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (CDCl₃, 100MHz): δ 206.22, 195.70, 172.14, 165.55, 138.64, 125.02, 122.78, 119.50, 113.51, 90.29, 62.71, 37.10, 29.81, 27.76, 13.96; **HRMS** (ESI) *m/z* calculated for C₁₅H₁₇O₅ [M+H]⁺: 277.1071, found: .277.1069.



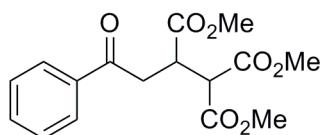
2-Benzoyl-1,3,5-triphenyl-pentane-1,5-dione (6t): Carried out with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), dimethyl malonate (79.2 mg, 0.6 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (78.1 mg, 0.5 mmol) and Cs₂CO₃ (65.2 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

White solid (50 % yield, eluent = petroleum ether/ethyl acetate (100:8)). This compound is known.⁵ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



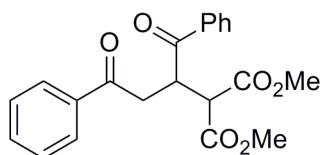
2-Benzoyl-3-methyl-1,5-diphenylpentane-1,5-dione (6u): Carried out with butyrophenone (29.6 mg, 0.2 mmol), dimethyl malonate (79.2 mg, 0.6 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (78.1 mg, 0.5 mmol) and Cs₂CO₃ (65.2 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (52% yield, eluent = petroleum ether/ethyl acetate (100:8)). This compound is known.⁶ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



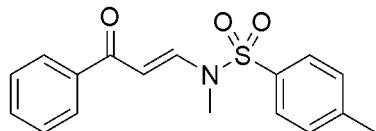
Trimethyl 4-oxo-4-phenylbutane-1,1,2-tricarboxylate (6v): Carried out with methyl 3-benzoylpropionate (115.2 mg, 0.6 mmol), dimethyl malonate (26.4 mg, 0.2 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (62.5 mg, 0.4 mmol) and Li₂CO₃ (14.8 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

Pale yellow oil (70% yield, eluent = petroleum ether/ethyl acetate (100:10); ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 4.03 (d, *J* = 6.5 Hz, 1H), 3.88-3.83 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 3.65-3.59 (m, 1H), 3.38-3.32 (m, 1H); ¹³C NMR (CDCl₃, 100MHz): δ 197.01, 172.55, 168.39, 168.33, 136.32, 133.32, 128.59, 128.05, 52.76, 52.70, 52.43, 51.93, 39.51, 37.40; HRMS (ESI) *m/z* calculated for C₁₆H₁₈O₇ [M+H]⁺: 323.1152, found: 323.1153.

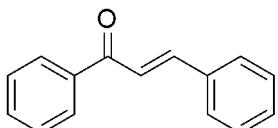


Dimethyl 2-(1,4-dioxo-1,4-diphenylbutan-2-yl)malonate (6w): Carried out with 1,2-dibenzoylethane (47.7 mg, 0.2 mmol), dimethyl malonate (79.2 mg, 0.6 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), TEMPO (78.1 mg, 0.5 mmol) and Cs₂CO₃ (65.2 mg, 0.2 mmol) in DME (2.0 mL) at 120 °C for 24 h.

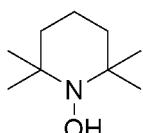
Yellow oil (54% yield, petroleum ether/ethyl acetate (100:10)). This compound is known.⁷ The spectral data are in good agreement with the literature data.



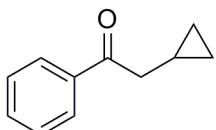
(E)-N,4-dimethyl-N-(3-oxo-3-phenylprop-1-enyl)benzenesulfonamide (3a'): White solid (eluent = petroleum ether/dichloromethane (50:50)); ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 13.5 Hz, 1H), 7.898-7.874 (m, 2H), 7.75-7.69 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 189.3, 144.9, 143.7, 138.5, 134.4, 132.4, 130.2, 128.5, 128.0, 127.2, 103.1, 32.4, 21.6; HRMS (ESI) Calcd for C₁₇H₁₈O₃NS [M + H]⁺ 316.1002, found 316.1001.



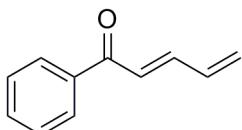
(E)-Chalcone (8): Pale yellow solid. **¹H NMR** (400 MHz, CDCl₃): δ 8.04-8.01 (m, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.66-7.64 (m, 2H), 7.61-7.49 (m, 4H), 7.43-7.41 (m, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 190.5, 144.8, 138.2, 134.8, 132.8, 130.5, 128.9, 128.6, 128.5, 128.4, 122.0. This compound is known.⁸ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



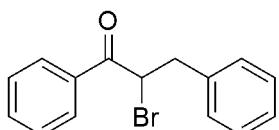
2,2,6,6-Tetramethylpiperidin-1-ol: This compound was synthesized according to literature procedures.⁹ White solid. **¹H NMR** (400 MHz, C₆D₆): δ 3.86 (s, 1H), 1.40-1.38 (m, 4H), 1.30-1.29 (m, 2H), 1.15 (s, 12H); **¹³C NMR** (100 MHz, C₆D₆): δ 58.3, 39.5, 17.2. This compound is known.⁹ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



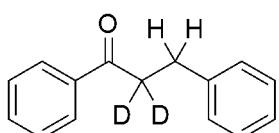
2-Cyclopropyl-1-phenylethanone (9): This compound was synthesized according to literature procedures.¹⁰ Colorless oil. **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 7.96 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45-7.41 (m, 2H), 2.86 (d, *J* = 6.8 Hz, 2H), 1.20-1.12 (m, 1H), 0.60-0.56 (m, 2H), 0.20-0.16 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 199.8, 136.7, 132.76, 128.4, 127.9, 43.6, 6.5, 4.4. This compound is known.¹¹ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



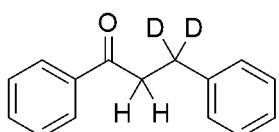
(E)-1-Phenylpenta-2,4-dien-1-one (10): Pale yellow oil (73% yield, eluent = petroleum ether/ethyl acetate (100:3)); **¹H NMR** (400 MHz, CDCl₃): δ 7.96-7.94 (m, 2H), 7.59-7.55 (m, 1H), 7.50-7.46 (m, 2H), 7.43-7.37 (m, 1H), 6.99 (d, *J* = 15.2 Hz, 1H), 6.65-6.55 (m, 1H), 5.72 (d, *J* = 16.9 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 190.7, 144.7, 137.9, 135.4, 132.76, 128.6, 128.4, 126.8, 126.2. This compound is known.¹² The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



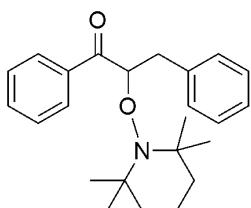
2-Bromo-1,3-diphenylpropan-1-one (11): White solid (71% yield, eluent = petroleum ether/Et₂O (95:5); ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46-7.42 (m, 2H), 7.30-7.20 (m, 5H), 5.32 (t, *J* = 7.3 Hz, 1H), 3.67 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.36 (dd, *J* = 14.2, 7.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 192.8, 137.5, 134.4, 133.7, 129.4, 128.8, 128.7, 128.6, 127.0, 46.6, 39.5. This compound is known.¹³ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



α-d₂-7: This compound was synthesized according to literature procedures.¹⁴ White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.98-7.95 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.32-7.19 (m, 5H), 3.06 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 141.2, 136.8, 133.1, 128.6, 128.5, 128.4, 128.0, 126.1, 30.0, 29.9. This compound is known.¹⁴ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.



β-d₂-7: This compound was synthesized according to literature procedures.¹⁵ White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.31-7.18 (m, 5H), 3.27 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 199.2, 141.2, 136.8, 132.99, 128.55, 128.47, 128.37, 127.99, 126.1, 40.2; 29.4. This compound is known.¹⁵ The ¹H and ¹³C NMR spectral data are in good agreement with the literature data.

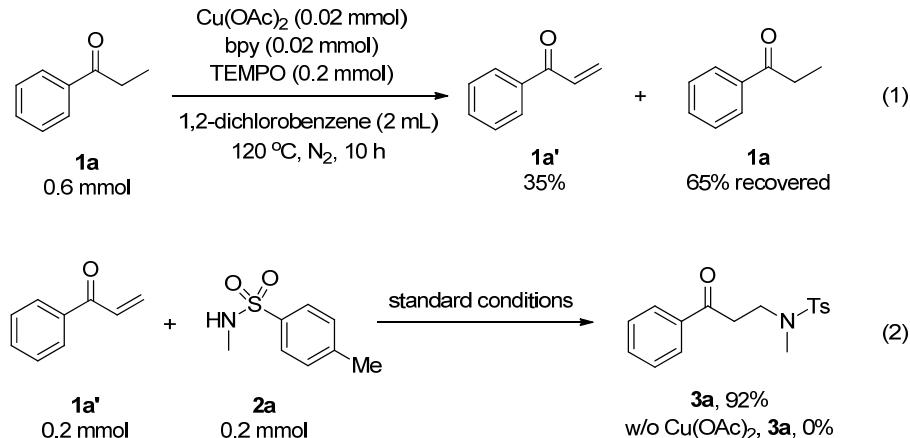


1,3-Diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propan-1-one (12): This compound was synthesized according to literature procedures.¹⁶ White solid (eluent = petroleum ether/EtOAc (98:2)). ¹H NMR (400 MHz, CDCl₃): δ 7.89-7.87 (m, 2H),

7.48-7.44 (m, 1H), 7.37-7.33 (m, 2H), 7.14-7.01 (m, 5H), 5.18 (dd, J = 10.1, 5.0 Hz, 1H), 3.44 (dd, J = 13.2, 5.0 Hz, 1H), 3.15 (dd, J = 13.2, 10.2Hz, 1H), 1.52-0.85 (m, 18H); **^{13}C NMR** (100 MHz, CDCl_3): δ 201.3, 136.9, 136.3, 132.6, 129.6, 129.0, 128.23, 128.18, 126.4, 88.7, 60.3, 59.7, 40.4, 39.4, 33.98, 20.3, 17.1; **HRMS** (ESI) Calcd for $\text{C}_{24}\text{H}_{32}\text{O}_2\text{N}$ [M + H]⁺ 366.2428, found 366.2428.

III. Experimental Procedures for Mechanistic Studies

A. Identification of the Dehydrogenation/Conjugate Addition Sequence

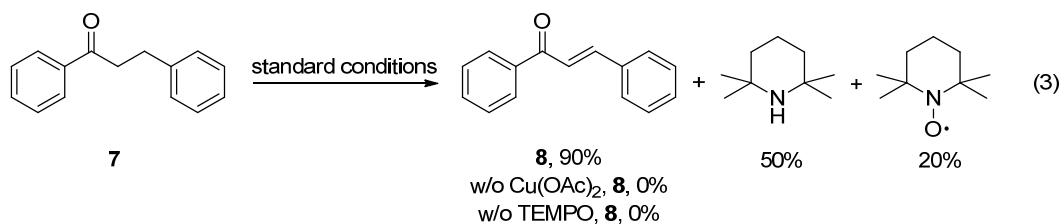


In eq 1, the reaction was conducted with propiophenone (80.5 mg, 0.6 mmol), $\text{Cu}(\text{OAc})_2$ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 10 h. Then the reaction was analyzed by GC using dodecane as internal standard. GC yield was reported.

Phenyl vinyl ketone was prepared according to literatures.¹⁷ In eq 2, the reaction was conducted with phenyl vinyl ketone (26.4 mg, 0.2 mmol), *N*-methyl-*p*-toluenesulfonamide (37.0 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h. After cooling to room temperature, the product **3a** was isolated by column chromatography in 92% yield (58.4 mg). The reaction performed in the absence of $\text{Cu}(\text{OAc})_2$ lead to no **3a** formation.

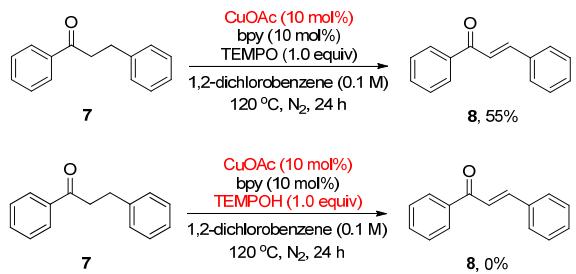
B.

1. The Behavior of 3-Phenylpropiophenone under Standard Conditions

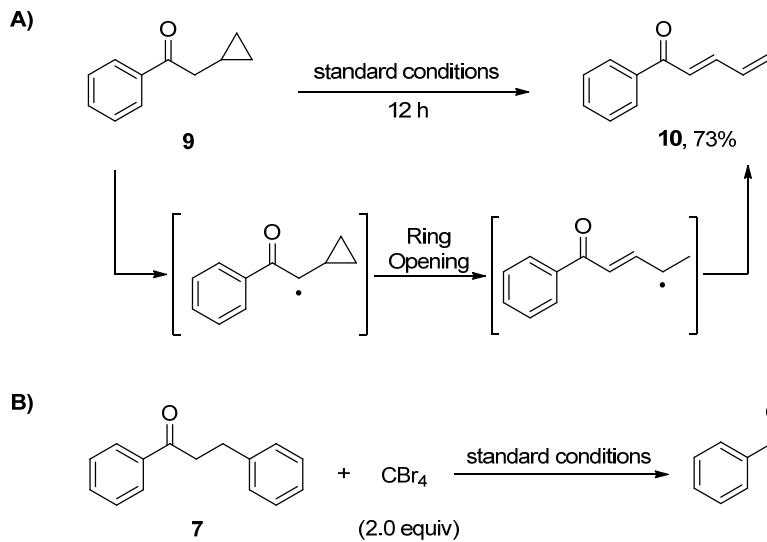


In eq 3, the reaction was performed with 3-phenylpropiophenone **7** (42.1 mg, 0.2 mmol), $\text{Cu}(\text{OAc})_2$ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h. The yields of 2,2,6,6-tetramethylpiperidine and TEMPO were reported as GC yield using dodecane as internal standard. Chalcone **8** was isolated by column chromatography and its yield was reported as isolated yield.

2. Control experiments Using Cu(I) as Catalyst Precursor



C. Experiments To Probe the Proposed Radical Intermediate



In eq A, the reaction was performed with cyclopropylmethyl phenyl ketone **9** (32 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 12 h. After cooling to room temperature, the ring-opening product diene **10** was isolated by column chromatography in 73% yield (23.2 mg).

In eq B, the reaction was performed with 3-phenylpropiophenone **7** (42.1 mg, 0.2 mmol), CBr₄ (132.6 mg, 0.4 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 24 h. After cooling to room temperature, the product **11** was isolated by column chromatography in 71% yield (41.3 mg).

D. Determination of the Kinetic Dependence of Reaction Components by Initial Rate Methods Using 3-Phenylpropiophenone as Model Substrate

General Methods: The reactions were conducted for specific times and then immediately quenched by immersing vessels into ice-cold water. Then dodecane as an internal standard was added to the reaction mixture and the mixture was analyzed by GC. The initial rate was determined from the data points of approximately first 20% conversion of the limiting reagents.

Kinetic Dependence on 3-Phenylpropiophenone: Reactions were performed with

3-phenylpropiophenone (12.6-126.2 mg, 0.06-0.6 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL). The mixture was kept stirring (at 330 rpm) at 120 °C using an aluminium-heating block. After 6-24 minutes, the mixture was added with dodecane (10 µL) as an internal standard using a microliter syringe and then analyzed by GC.



| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.03 | 6 | - | 0.0000167277 |
| | 12 | - | |
| | 18 | 0.00151038 | |
| | 24 | 0.00160053 | |
| | 30 | 0.00170947 | |
| | 36 | 0.00180862 | |

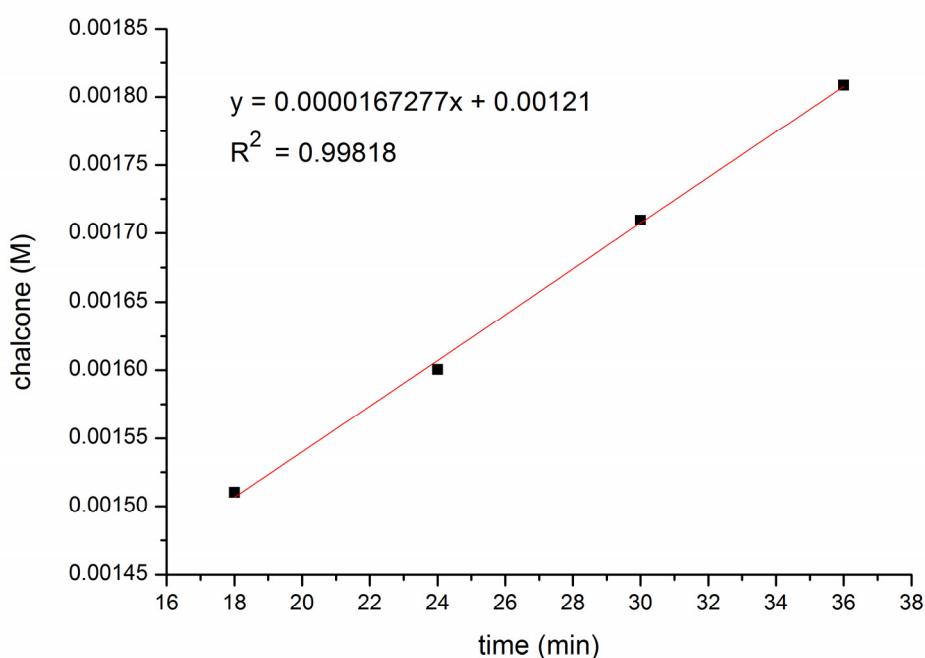


Figure S1. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.03M).

| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.05 | 6 | - | 0.0000821967 |
| | 12 | 0.00180955 | |
| | 18 | 0.00241601 | |
| | 24 | 0.00280089 | |
| | 30 | 0.00332519 | |

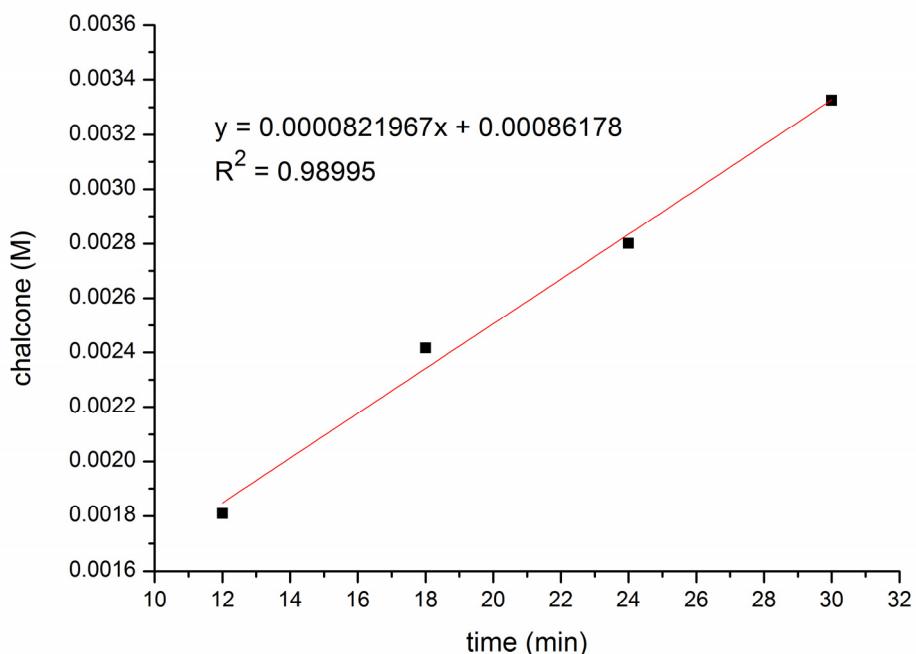


Figure S2. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.05M).

| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.075 | 6 | 0.00119068 | 0.000171526 |
| | 12 | 0.00183289 | |
| | 18 | 0.00312853 | |
| | 24 | 0.00418933 | |

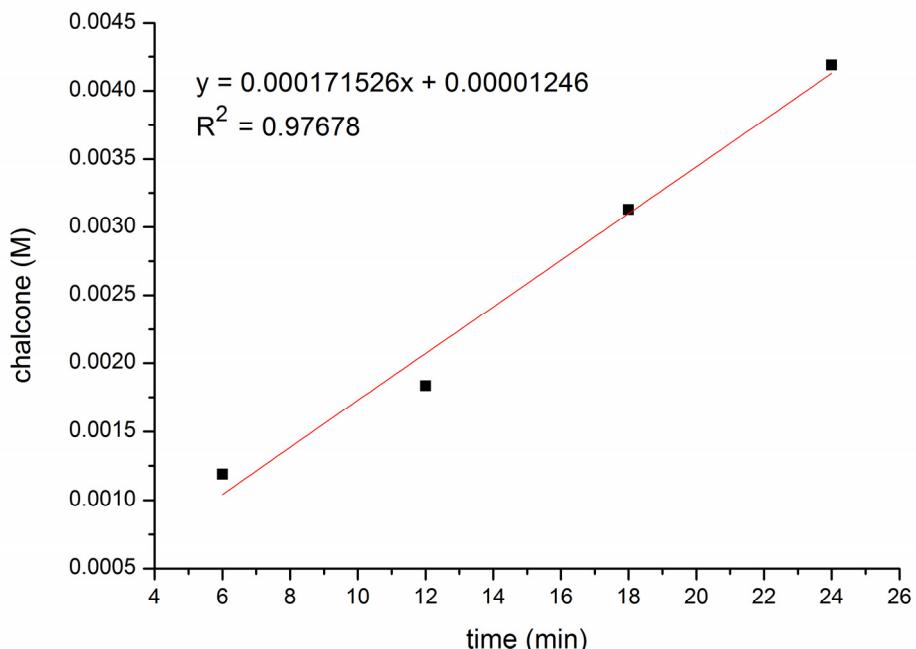


Figure S3. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.075M).

| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.1 | 6 | 0.00162934 | 0.000269279 |
| | 12 | 0.00271883 | |
| | 18 | 0.00490256 | |
| | 24 | 0.00629911 | |
| | 30 | 0.00799020 | |
| | 36 | 0.00931783 | |
| | 42 | 0.01128044 | |

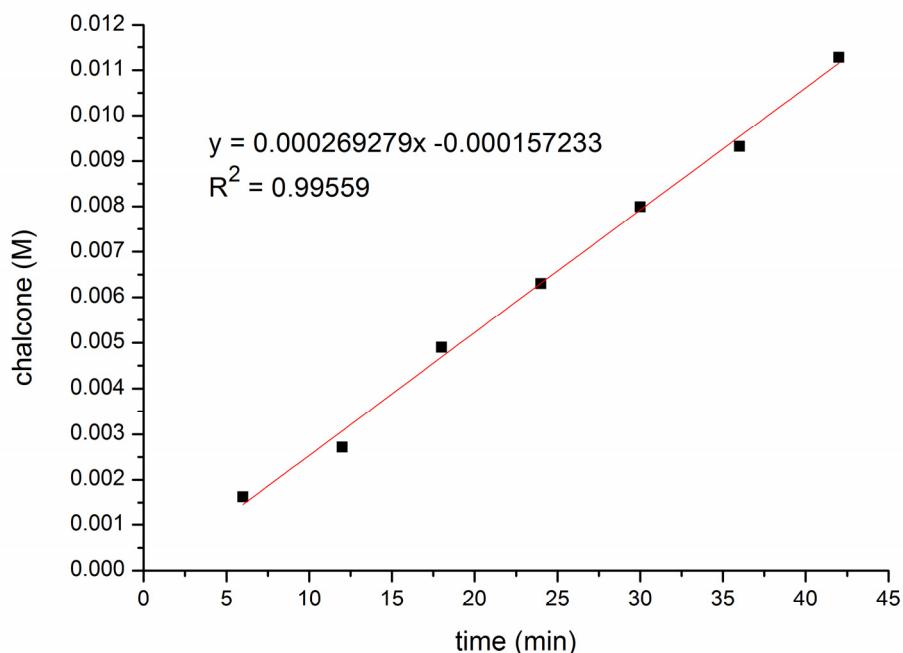


Figure S4. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.1M).

| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.15 | 6 | 0.00177448 | 0.000412319 |
| | 12 | 0.00316486 | |
| | 18 | 0.00606749 | |
| | 24 | 0.00905332 | |

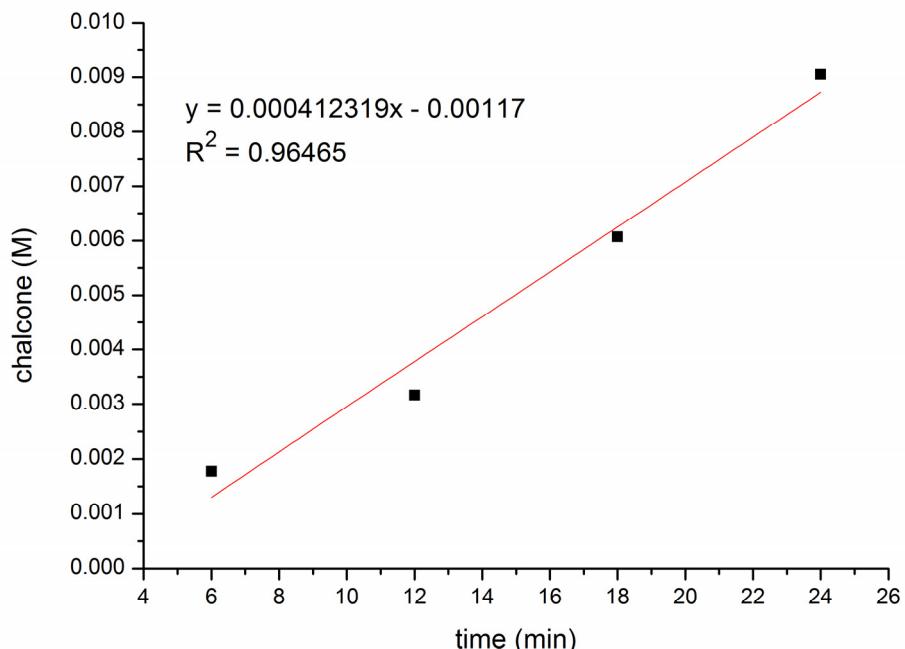


Figure S5. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.15M).

| [3-phenylpropiophenone] (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------------------------|-----------|----------------|----------------------|
| 0.2 | 6 | 0.00207151 | 0.000579242 |
| | 12 | 0.00694505 | |
| | 18 | 0.00987117 | |
| | 24 | 0.01268098 | |

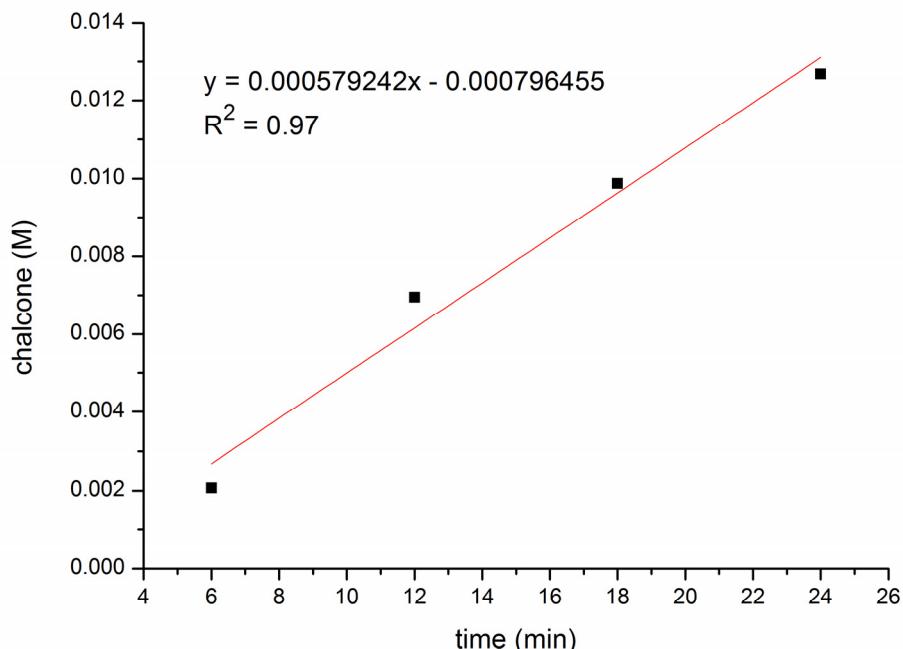


Figure S6. Initial rate data for the dehydrogenation of propiophenone to chalcone at propiophenone (0.2M).

| [3-phenylpropiophenone] (M) | initial rate (M/min) |
|-----------------------------|----------------------|
| 0.03 | 0.0000167277 |
| 0.05 | 0.0000821967 |
| 0.075 | 0.000171526 |
| 0.1 | 0.000269279 |
| 0.15 | 0.000412319 |
| 0.2 | 0.000579242 |

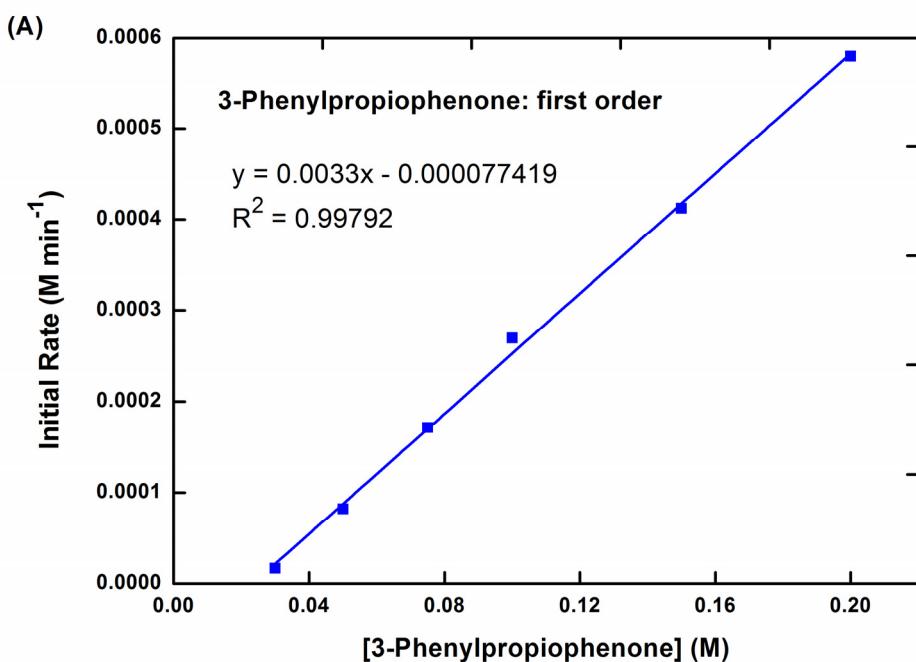
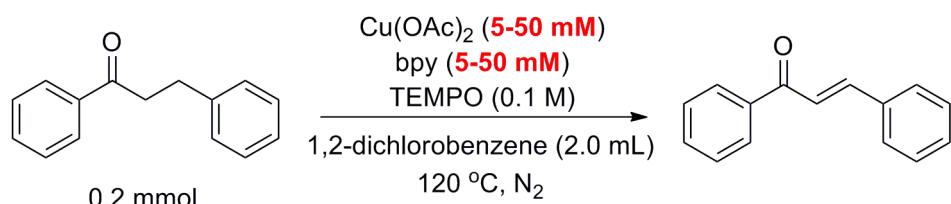


Figure S7. Plot of initial rate of ketone dehydrogenation at varying concentrations of 3-phenylpropiophenone.

Kinetic Dependence on Cu(OAc)₂/bpy: Reactions were performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), Cu(OAc)₂ (1.8-18.2 mg, 0.01-0.1 mmol), 2,2'-bipyridine (1.6-15.6 mg, 0.005-0.05 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL). The mixture was kept stirring (at 330 rpm) at 120 °C using an aluminium-heating block. After 6-24 minutes, the mixture was added with dodecane (10 µL) as an internal standard using a microliter syringe and then analyzed by GC.



| Cu(OAc) ₂ /bpy (mM) | time(min) | [chalcone] (M) | initial rate (M/min) |
|--------------------------------|-----------|----------------|----------------------|
| 5 | 6 | - | 0.00011552 |
| | 12 | 0.00187973 | |
| | 18 | 0.00253298 | |
| | 24 | 0.00345095 | |
| | 30 | 0.00388415 | |

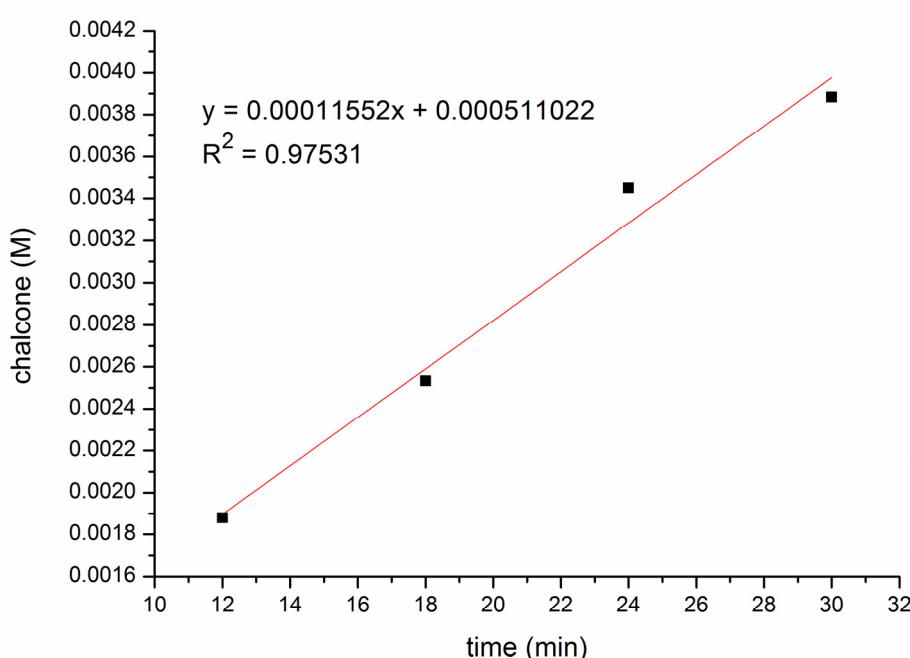


Figure S8. Initial rate data for the dehydrogenation of propiophenone to chalcone at Cu(OAc)₂/bpy (5 mM).

| $\text{Cu(OAc)}_2/\text{bpy}$ (mM) | time(min) | [chalcone] (M) | initial rate (M/min) |
|------------------------------------|-----------|----------------|----------------------|
| 20 | 6 | 0.00190491 | 0.000399594 |
| | 12 | 0.00359358 | |
| | 18 | 0.00560218 | |
| | 24 | 0.00922725 | |

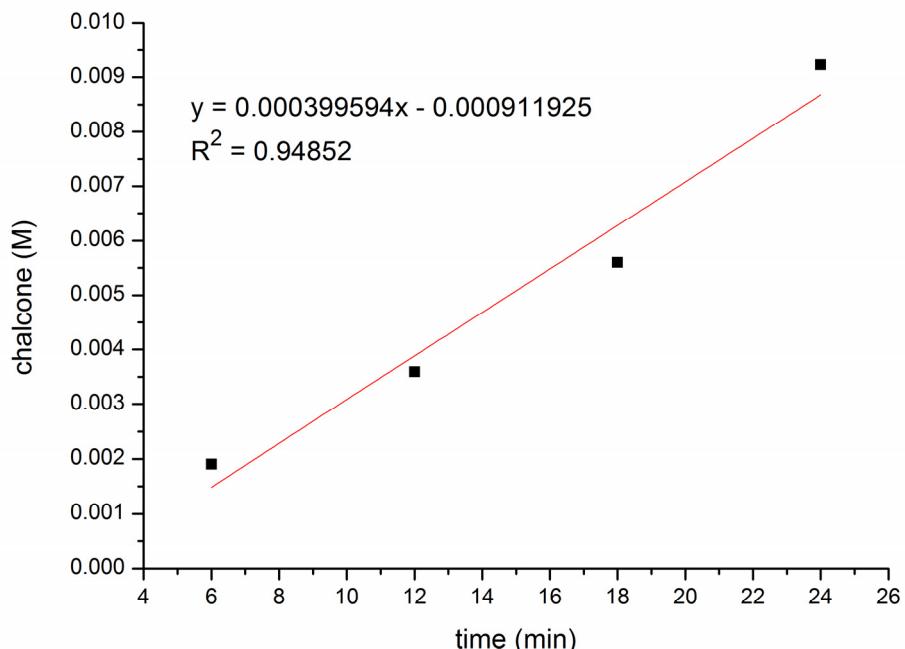


Figure S9. Initial rate data for the dehydrogenation of propiophenone to chalcone at $\text{Cu(OAc)}_2/\text{bpy}$ (20 mM).

| $\text{Cu(OAc)}_2/\text{bpy}$ (mM) | time(min) | [chalcone] (M) | initial rate (M/min) |
|------------------------------------|-----------|----------------|----------------------|
| 30 | 6 | 0.00227423 | 0.000614232 |
| | 12 | 0.00482986 | |
| | 18 | 0.00831339 | |
| | 24 | 0.01339769 | |

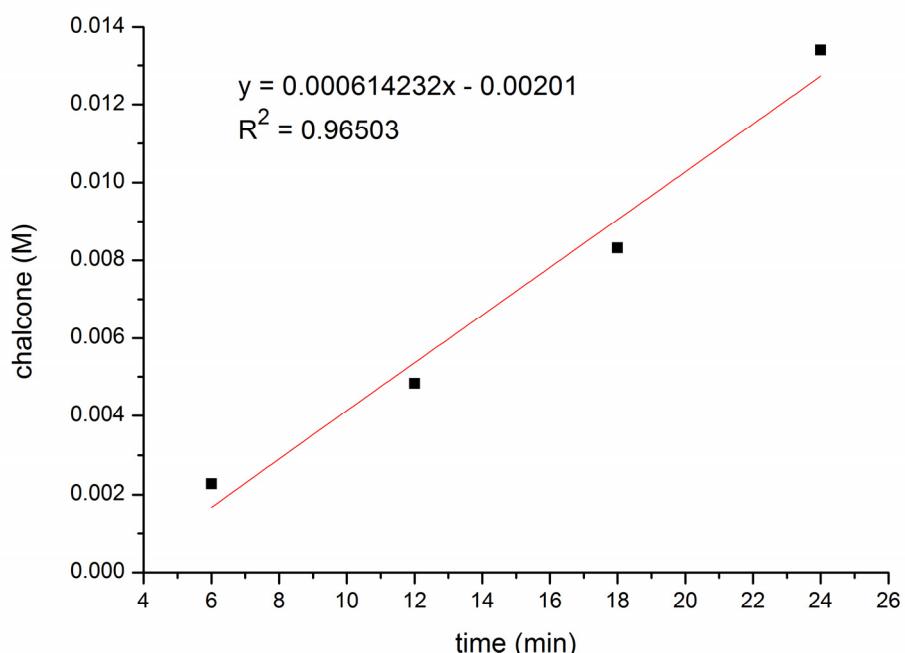


Figure S10. Initial rate data for the dehydrogenation of propiophenone to chalcone at $\text{Cu(OAc)}_2/\text{bpy}$ (30 mM).

| $\text{Cu(OAc)}_2/\text{bpy}$ (mM) | time(min) | [chalcone] (M) | initial rate (M/min) |
|------------------------------------|-----------|----------------|----------------------|
| 50 | 6 | 0.00293728 | 0.000835368 |
| | 12 | 0.00811677 | |
| | 18 | 0.01373677 | |
| | 24 | 0.01777131 | |

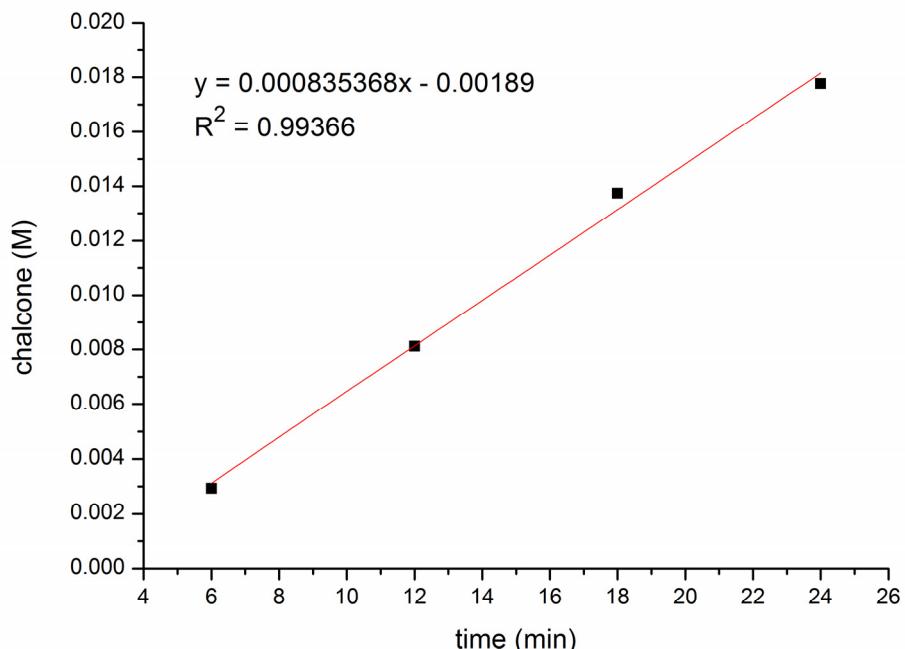


Figure S11. Initial rate data for the dehydrogenation of propiophenone to chalcone at $\text{Cu(OAc)}_2/\text{bpy}$ (50 mM).

| [Cu(OAc) ₂ /bpy] (mM) | initial rate (M/min) |
|----------------------------------|----------------------|
| 5 | 0.00011552 |
| 10 | 0.000269279 |
| 20 | 0.000399594 |
| 30 | 0.000614232 |
| 50 | 0.000835368 |

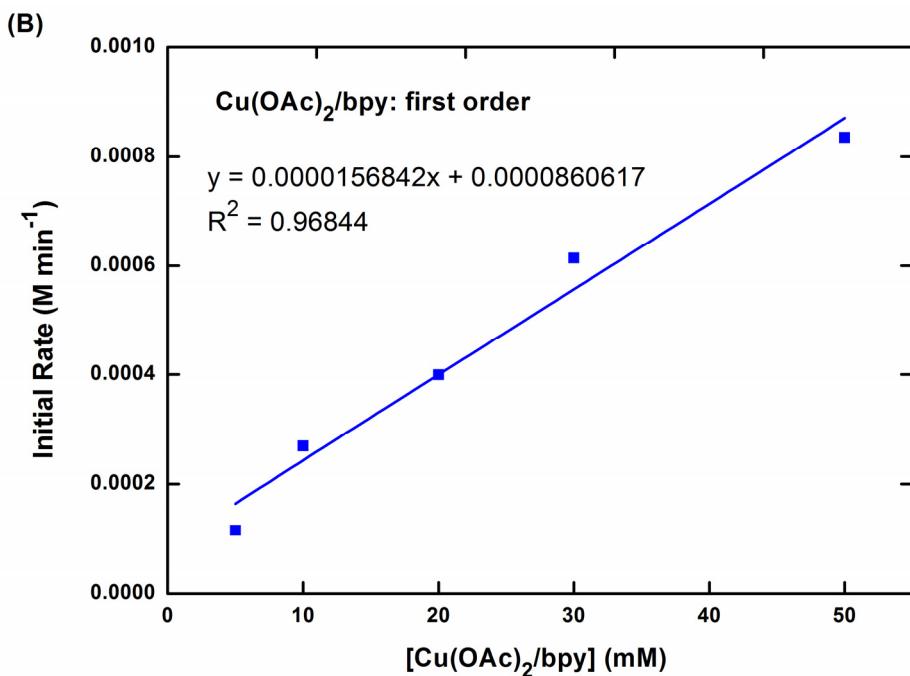
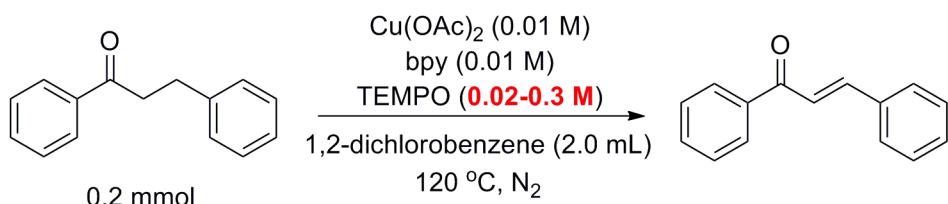


Figure S12. Plot of initial rate of ketone dehydrogenation at varying concentrations of Cu(OAc)₂/bpy.

Kinetic Dependence on Cu(OAc)₂/bpy: Reactions were performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (6.3-93.9 mg, 0.04-0.6 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C. The mixture was kept stirring (at 330 rpm) at 120 °C using an aluminium-heating block. After 6-24 minutes, the mixture was added with dodecane (10 µL) as an internal standard using a microliter syringe and then analyzed by GC.



| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.02 | 6 | - | 0.000307655 |
| | 12 | 0.00157258 | |
| | 18 | 0.00341407 | |
| | 24 | 0.00532340 | |
| | 30 | 0.00708923 | |

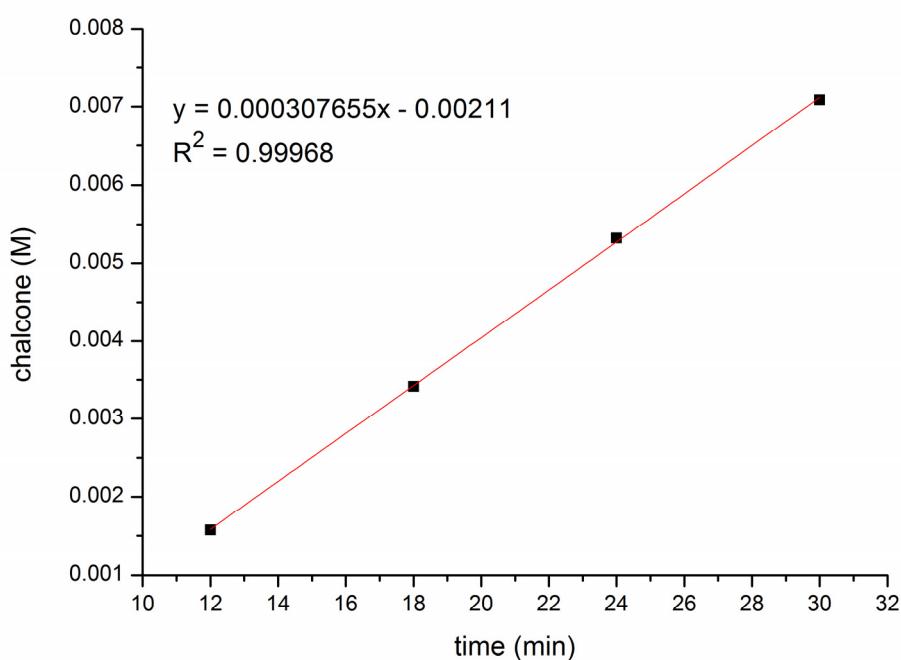


Figure S13. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.02 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.04 | 6 | 0.00170873 | 0.000223425 |
| | 12 | 0.00287503 | |
| | 18 | 0.00431398 | |
| | 24 | 0.00569758 | |

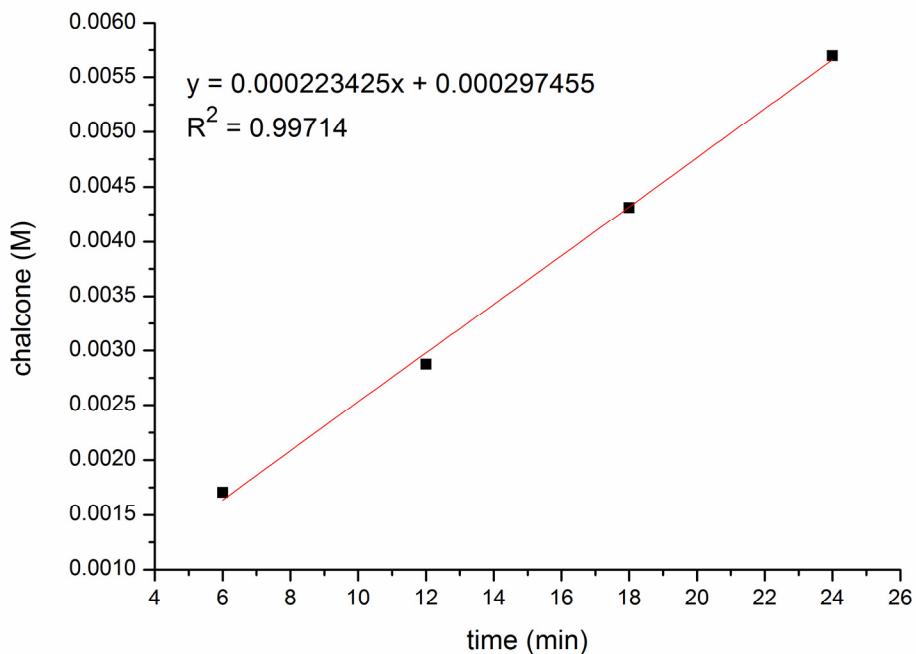


Figure S14. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.04 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.06 | 6 | 0.00131072 | 0.000289149 |
| | 12 | 0.00251578 | |
| | 18 | 0.00420889 | |
| | 24 | 0.00652934 | |

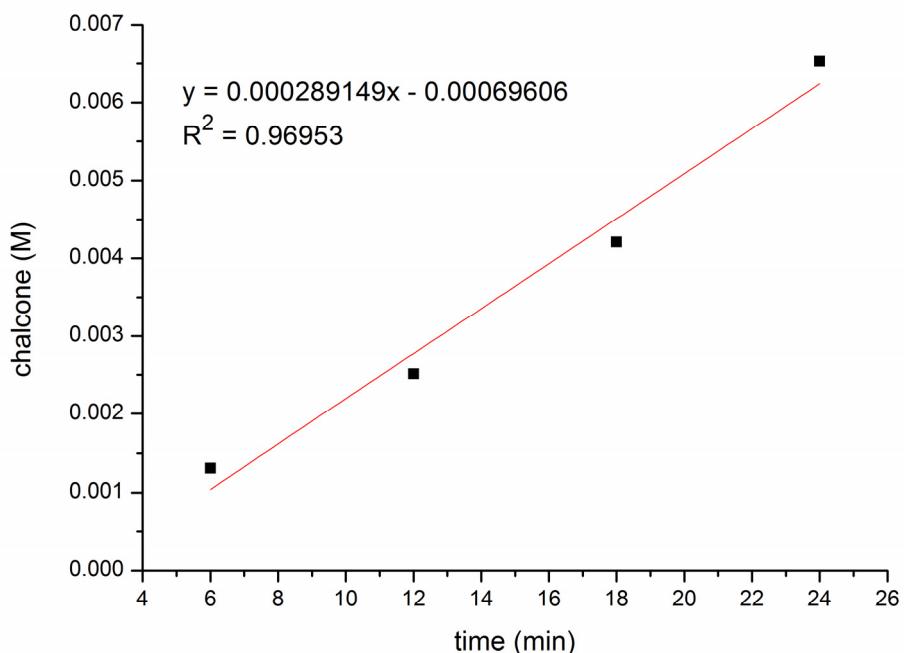


Figure S15. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.06 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.08 | 6 | 0.00215526 | 0.000261579 |
| | 12 | 0.00324616 | |
| | 18 | 0.00503420 | |
| | 24 | 0.00679083 | |

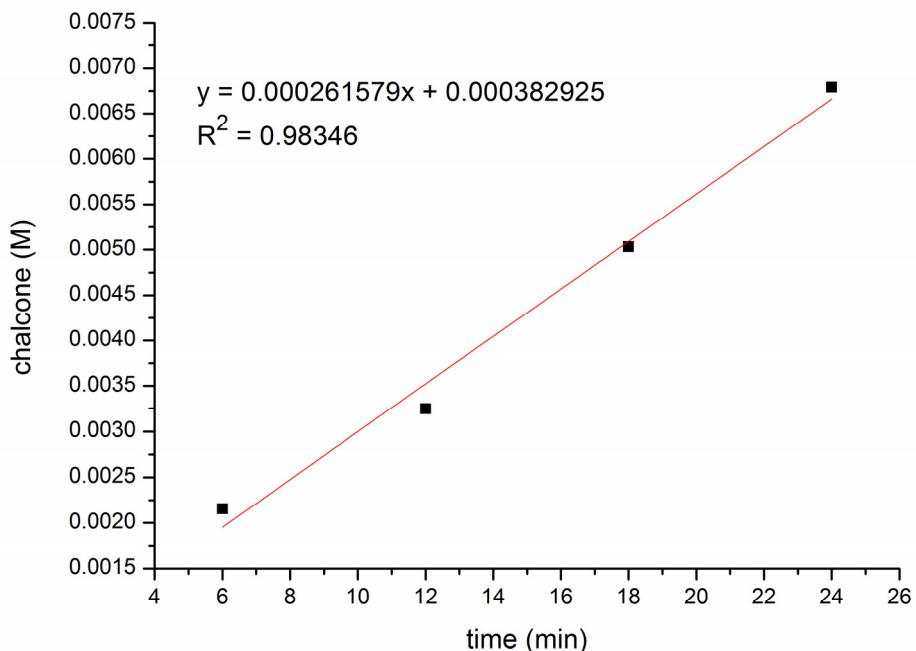


Figure S16. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.08 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.15 | 6 | 0.00167506 | 0.000260552 |
| | 12 | 0.00304404 | |
| | 18 | 0.00472974 | |
| | 24 | 0.00632419 | |

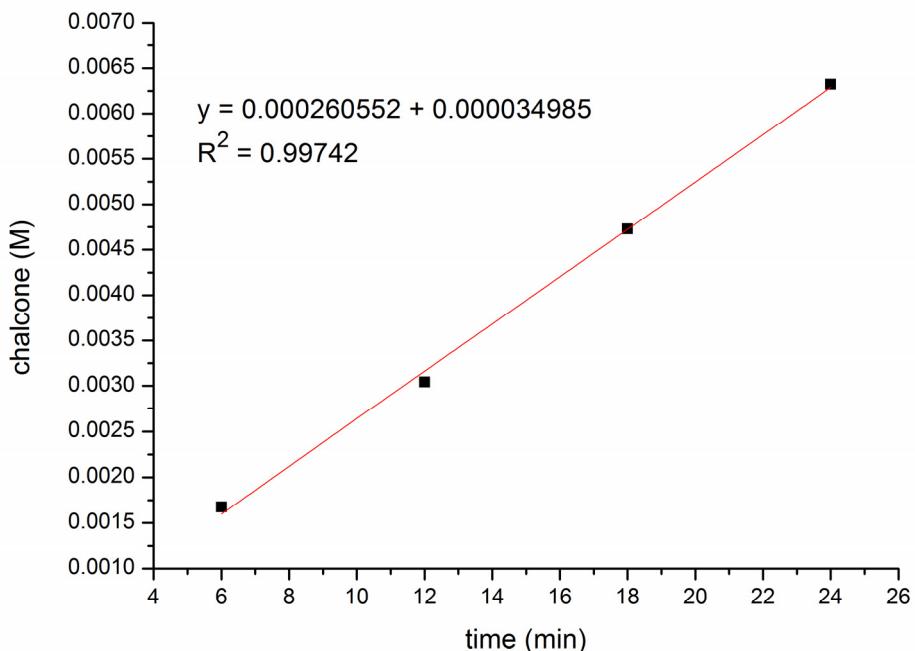


Figure S17. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.15 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.2 | 6 | 0.00155940 | 0.00025692 |
| | 12 | 0.00317995 | |
| | 18 | 0.00507539 | |
| | 24 | 0.00606599 | |

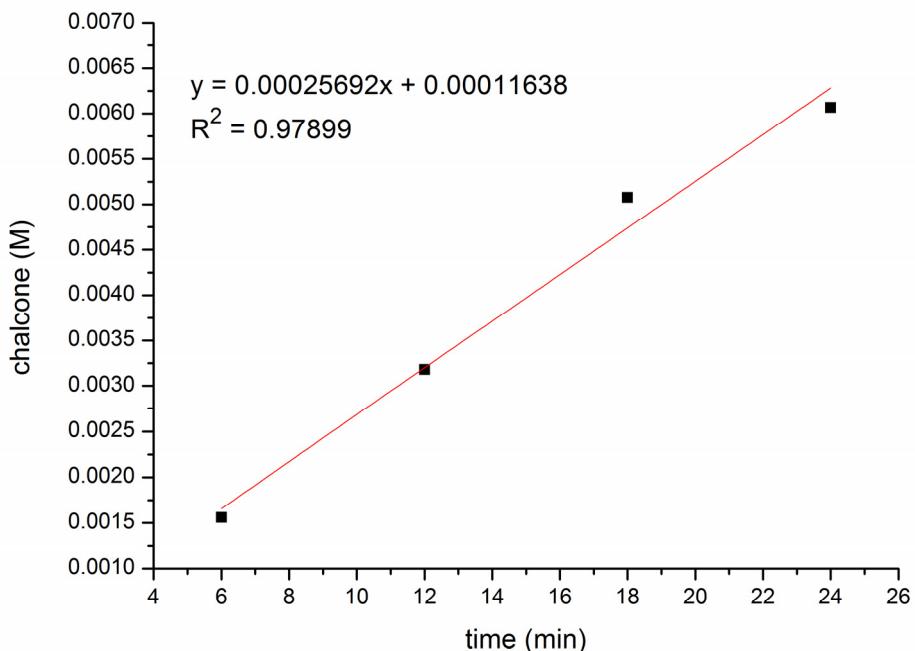


Figure S18. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.2 M).

| TEMPO (M) | time(min) | [chalcone] (M) | initial rate (M/min) |
|-----------|-----------|----------------|----------------------|
| 0.3 | 6 | 0.00176952 | 0.000251986 |
| | 12 | 0.00289252 | |
| | 18 | 0.00454498 | |
| | 24 | 0.00625842 | |

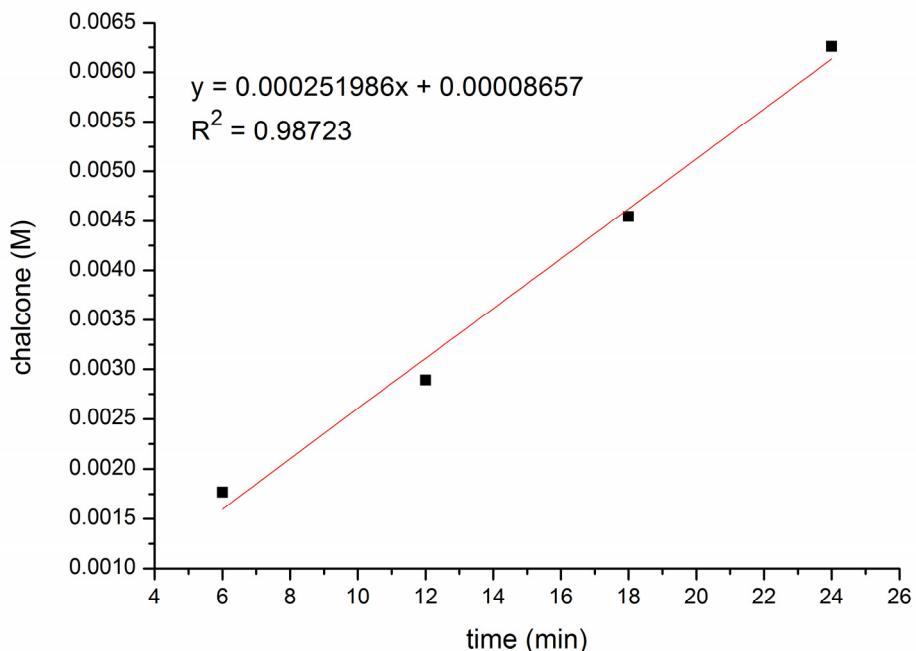


Figure S19. Initial rate data for the dehydrogenation of propiophenone to chalcone at TEMPO (0.3 M).

| [TEMPO] (M) | initial rate (M/min) |
|-------------|----------------------|
| 0.02 | 0.000307655 |
| 0.04 | 0.000223425 |
| 0.06 | 0.000289149 |
| 0.08 | 0.000261579 |
| 0.1 | 0.000269279 |
| 0.15 | 0.000260552 |
| 0.2 | 0.00025692 |
| 0.3 | 0.000251986 |

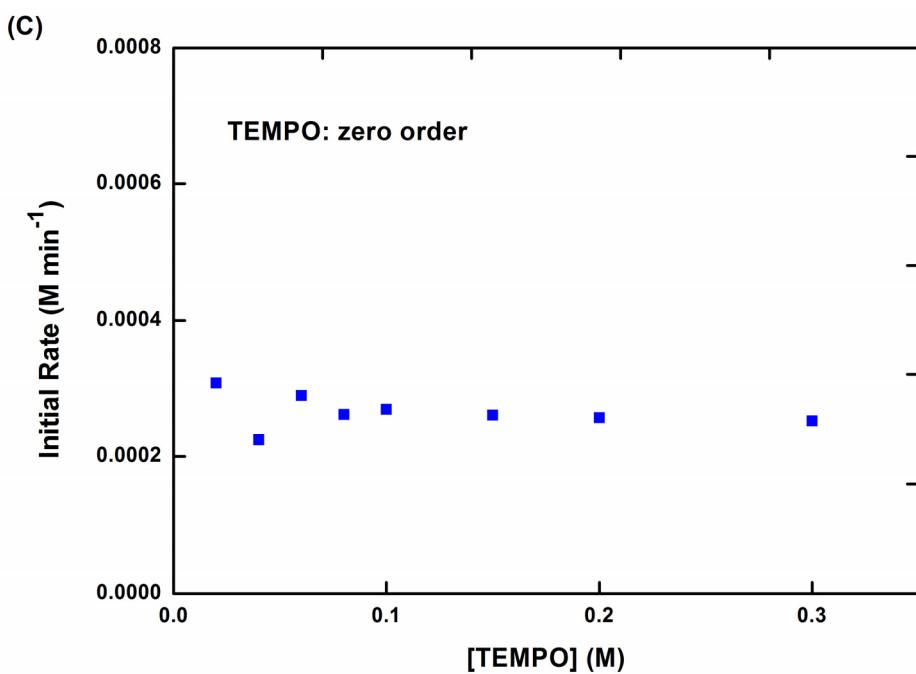
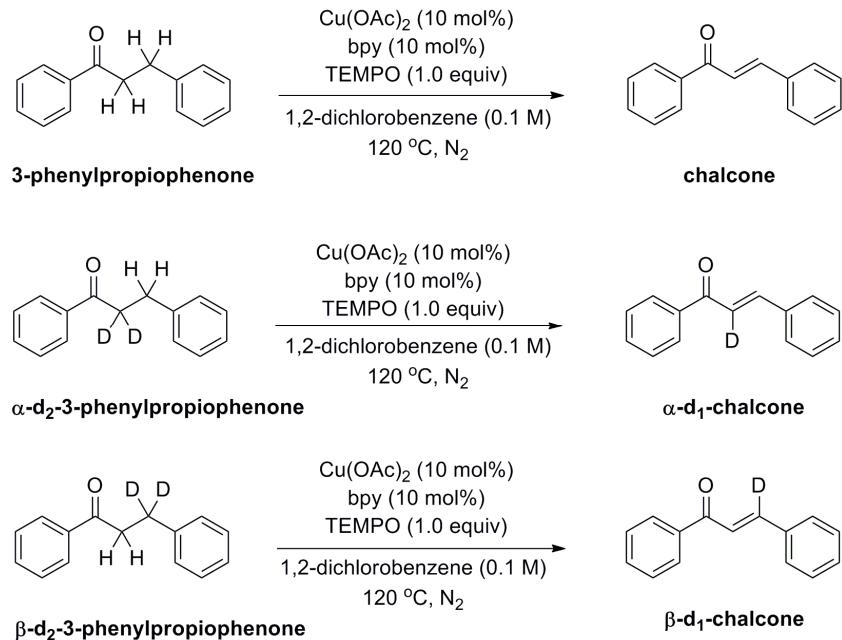


Figure S20. Plot of initial rate of ketone dehydrogenation at varying concentrations of TEMPO.

E. Kinetic Isotope Effect Studies

Intermolecular parallel KIE experiments with 3-phenylpropiophenone, α -d₂-3-phenylpropiophenone and β -d₂-3-phenylpropiophenone



Reactions were performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol) or α -d₂-3-phenylpropiophenone (42.5 mg, 0.2 mmol) or β -d₂-3-phenylpropiophenone (42.5 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C in separated vessels.. The mixture was kept stirring (at 330 rpm) at 120 °C using an aluminium-heating block. After 6-42 minutes, the vessels were immediately immersed into ice-cold water to quench the reaction. Then the mixture was added with dodecane (10 μ L) as an internal standard using a microliter syringe and then analyzed by GC.

| starting ketone | time (min) | chalcone (M) | initial rate (M/min) |
|--|------------|--------------|-------------------------|
| 3-phenylpropiophenone (7) | 6 | 0.00162934 | 0.000269279 |
| | 12 | 0.00271883 | |
| | 18 | 0.00490256 | |
| | 24 | 0.00629911 | |
| | 30 | 0.00799020 | |
| | 36 | 0.00931783 | |
| | 42 | 0.01128044 | |
| α -d ₂ -3-phenylpropiophenone (α -d ₂ - 7) | 6 | - | 0.0000505883 |
| | 12 | - | |
| | 18 | 0.00149046 | |
| | 24 | 0.00177055 | |
| | 30 | 0.00203581 | |
| | 36 | 0.00238349 | |
| | 42 | 0.00270164 | |
| β -d ₂ -3-phenylpropiophenone (β -d ₂ - 7) | 6 | 0.00159865 | 0.00026325 |
| | 12 | 0.00258997 | |
| | 18 | 0.00485421 | |
| | 24 | 0.00609758 | |
| | 30 | 0.00781638 | |
| | 36 | 0.00912075 | |
| | 42 | 0.01099938 | |

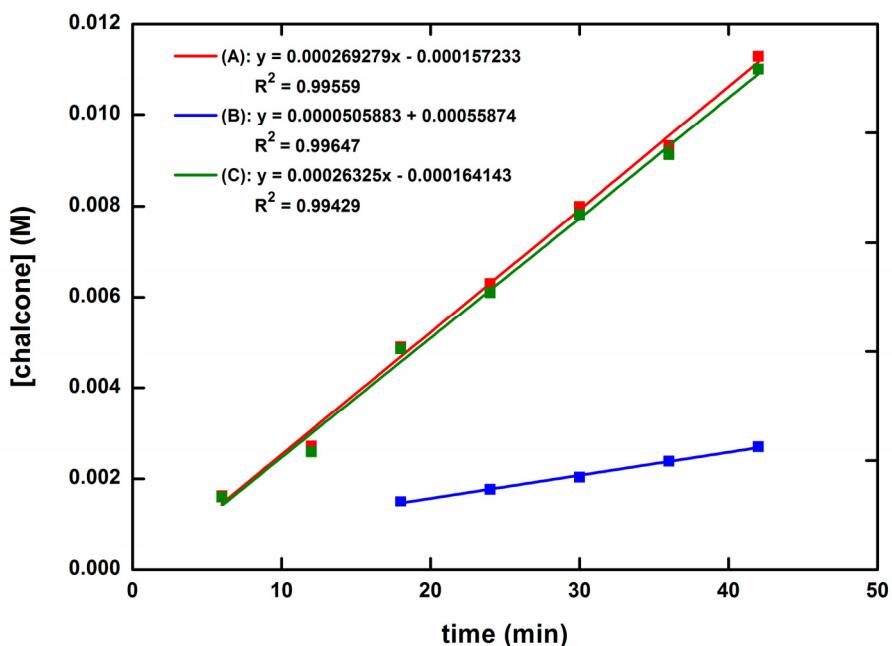
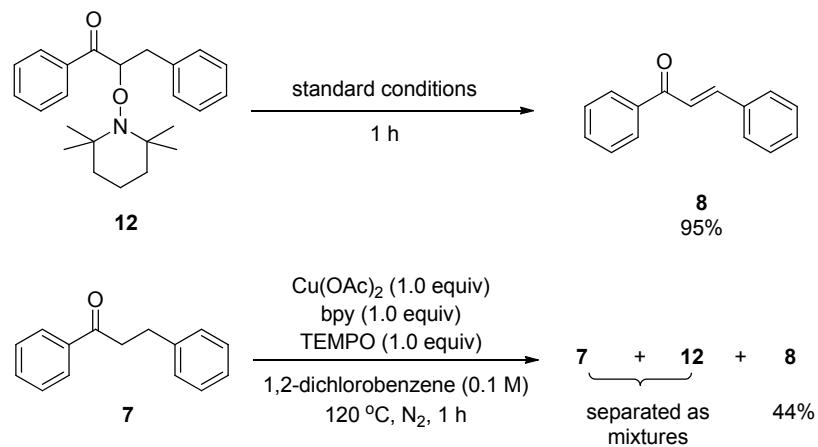


Figure S21. (A) Plot of initial rate data for dehydrogenation of 3-phenylpropiophenone (**7**) (B) Plot of initial rate data for dehydrogenation of α -d₂-3-phenylpropiophenone (α -d₂-**7**) (C) Plot of initial rate data for dehydrogenation of β -d₂-3-phenylpropiophenone (β -d₂-**7**).

The KIE between **7** and α -d₂-**7**: $0.000269279/0.0000505883 = 5.32$;
The KIE between **7** and β -d₂-**7**: $0.000269279/0.00026325 = 1.02$.

F. Behavior of **12** under Standard Conditions and Observation of **12** by NMR



Independently prepared **12**¹⁶ was conducted with Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol) and TEMPO (31.3 mg, 0.2 mmol) in

1,2-dichlorobenzene (2.0 mL) at 120 °C for 1 h. After cooling to room temperature, **8** was separated by column chromatography in 95% isolated yield.

To directly observe the formation of **12**, the reaction was performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), Cu(OAc)₂ (36.3 mg, 0.2 mmol), 2,2'-bipyridine (31.2 mg, 0.2 mmol) and TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 1 h. After cooling to room temperature, the reaction mixture was loaded to silica gel chromatography. Since **7** and **12** have the same polarity on silica gel column and hard to be separated, the mixtures of **7** and **12** were isolated (23 mg). The mixtures of **7** and **12** were analyzed by ¹H NMR and the spectrum was illustrated as spectrum (C). The ¹H NMR spectra of pure **7** and **12** was also provided as spectrum (A) and spectrum (B) for convenient comparison.

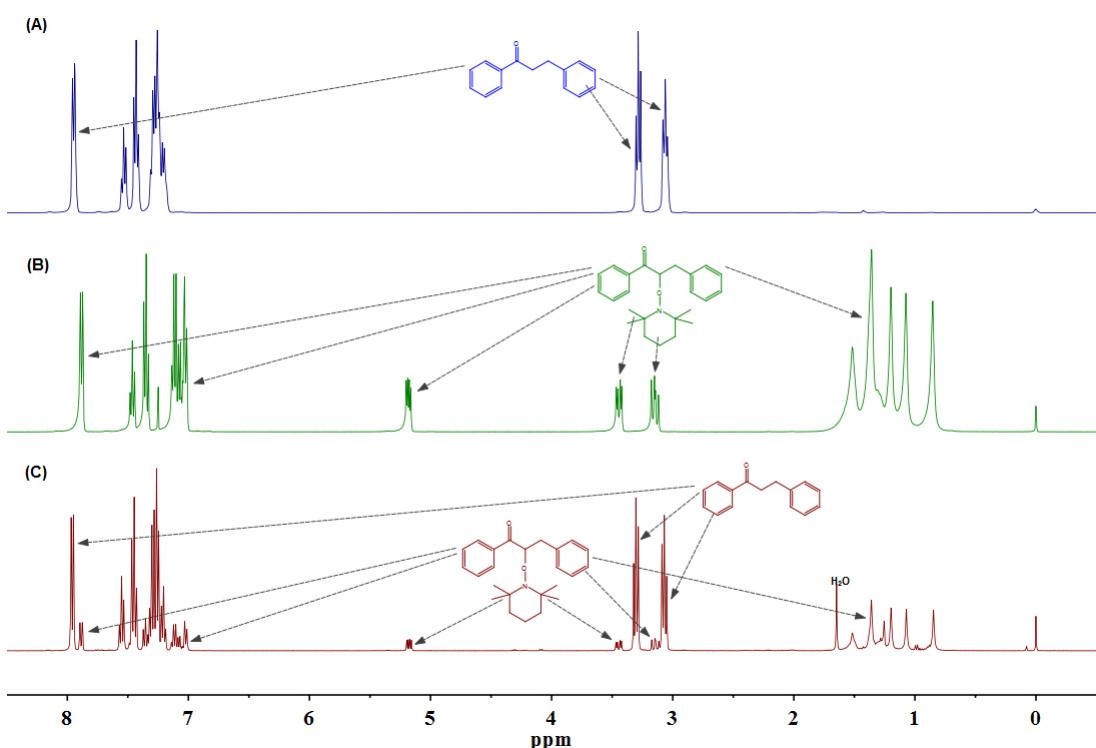
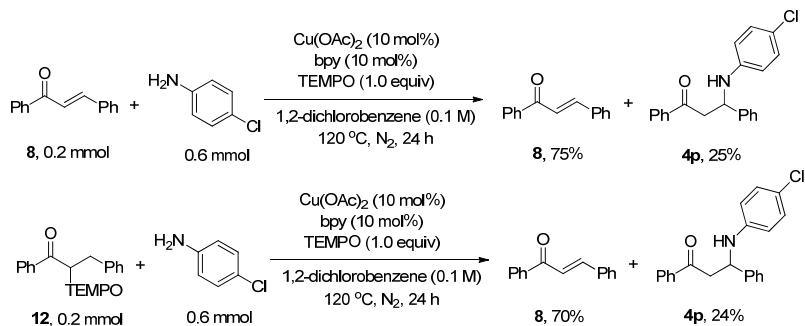


Figure S22. (A) The ¹H NMR spectrum of pure **7** (B) The ¹H NMR spectrum of pure **12** (C) The ¹H NMR spectrum of isolated **7** and **12** mixtures.

G. Control Experiments using **8** or **12** as starting materials to react with anilines



H. Investigation of Copper Species by EPR and UV-Visible Spectroscopic Studies

EPR Analysis:

The reactions were performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol), TEMPO (15.6 mg, 0.1 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 0.5 h, 1 h and 2 h intervals. At indicated time, the vessels were immediately immersed into ice-cold water to quench the reaction. Then the quenched reaction solutions (0.2 mL) were added to quartz tubes in glove box and subject to EPR analysis at 100K under N₂ protection (Instrument : Bruker-BioSpin: E500).

UV-Visible Analysis:

The reactions were performed with 3-phenylpropiophenone (42.1 mg, 0.2 mmol), Cu(OAc)₂ (3.6 mg, 0.02 mmol), 2,2'-bipyridine (3.1 mg, 0.02 mmol), TEMPO (31.3 mg, 0.2 mmol) in 1,2-dichlorobenzene (2.0 mL) at 120 °C for 0.5 h, 1 h and 2 h intervals. At indicated time, the vessels were immediately immersed into ice-cold water to quench the reaction. Then the quenched reaction solutions was diluted by 1,2-dichlorobenzene to 10 mL under N₂ atmosphere. Then the solutions were added to quartz cuvette (3.0 mL) and subject to UV-Vis analysis at room temperature under N₂ protection (Instrument: PerkinElmer, Lambda 35). The solutions of pure Cu^{II}(OAc)₂/bpy (3.6 mg, 0.02 mmol+3.1 mg, 0.02 mmol) and pure Cu^IOAc/bpy (2.4 mg, 0.02 mmol+3.1 mg, 0.02 mmol) in 1,2-dichlorobenzene (10.0 mL) were also recorded for comparison.

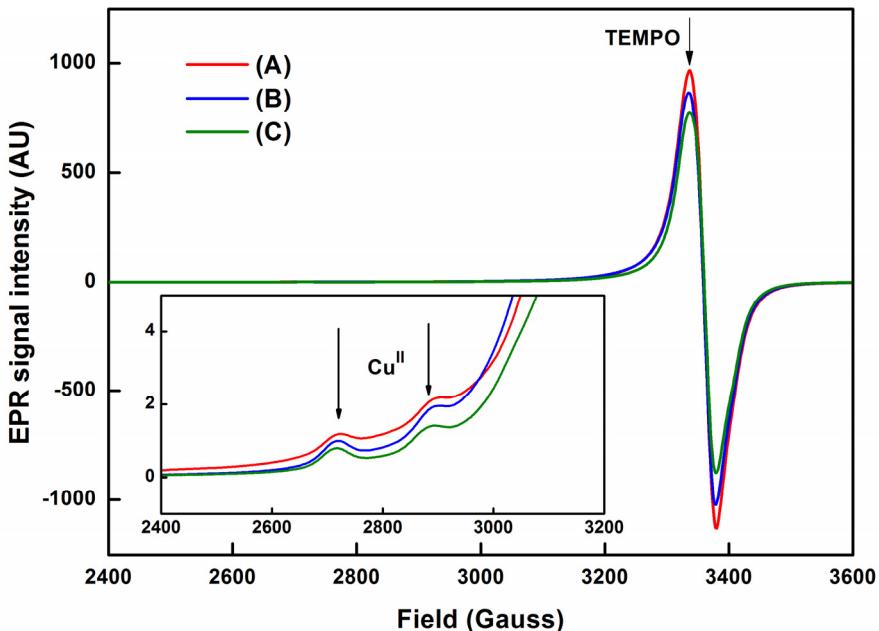


Figure S23. EPR spectra of Cu species at 100K for reactions performed for (A) 0.5 h (B) 1.0 h (C) 2.0 h.

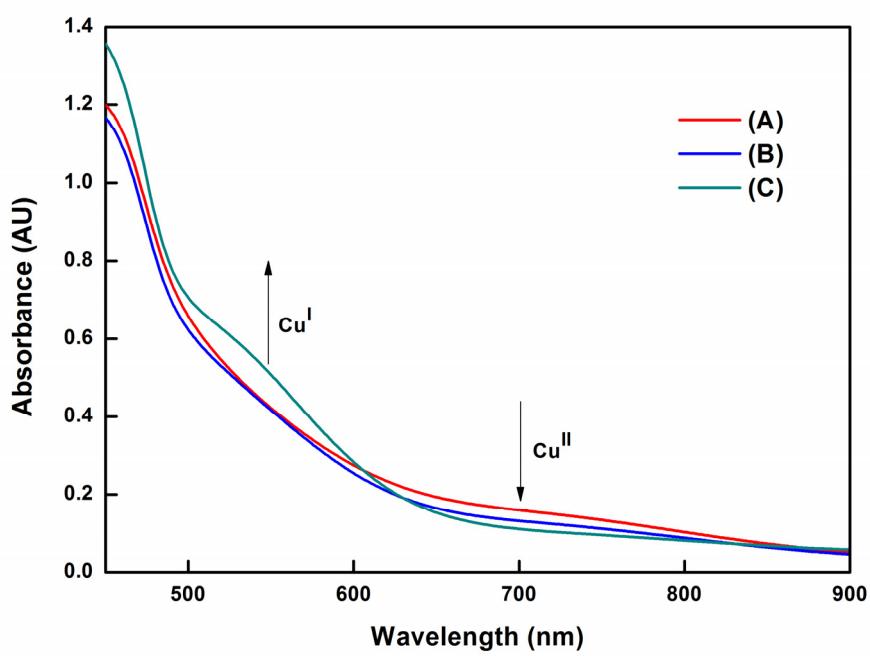


Figure S24. UV-Visible Spectra of Cu Species at room temperature for reactions performed for (A) 0.5 h (B) 1.0 h (C) 2.0 h.

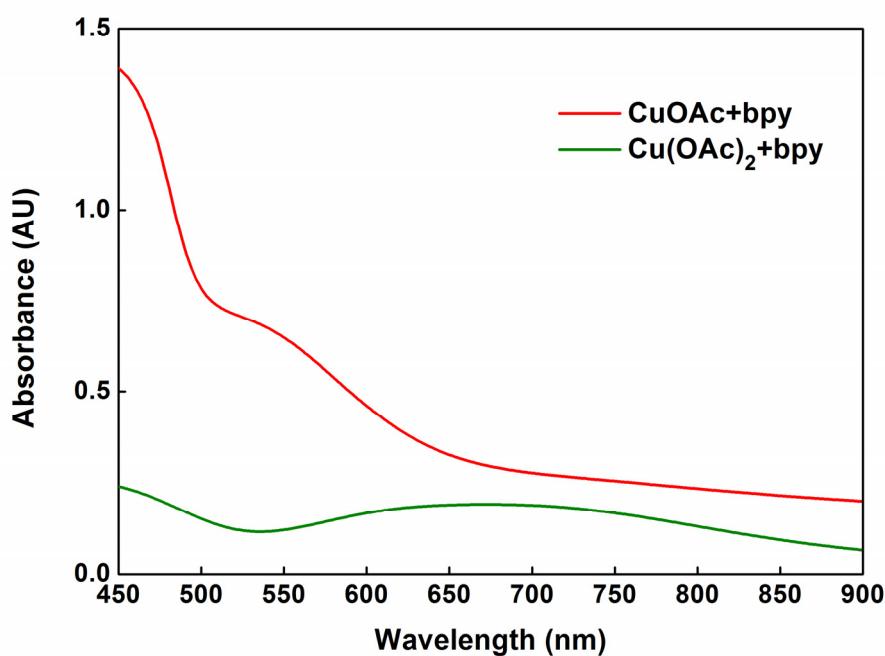


Figure S25. UV-Visible Spectra of pure $\text{Cu}^{\text{II}}(\text{OAc})_2/\text{bpy}$ and pure $\text{Cu}^{\text{I}}\text{OAc}/\text{bpy}$.

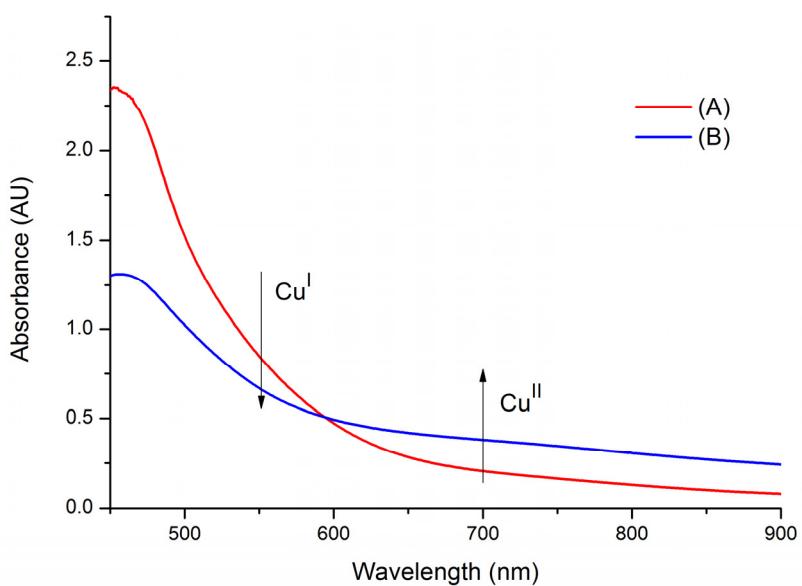


Figure S26. UV-Visible Spectra for the reaction of CuOAc/bpy and TEMPO. (A) Conditions: 2 mM CuOAc, 2 mM bpy, 20 mM TEMPO in 2.0 mL 1,2-dichlorobenzene (freshly prepared). (B) Conditions: 2 mM CuOAc, 2 mM bpy, 20 mM TEMPO in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 1 h).

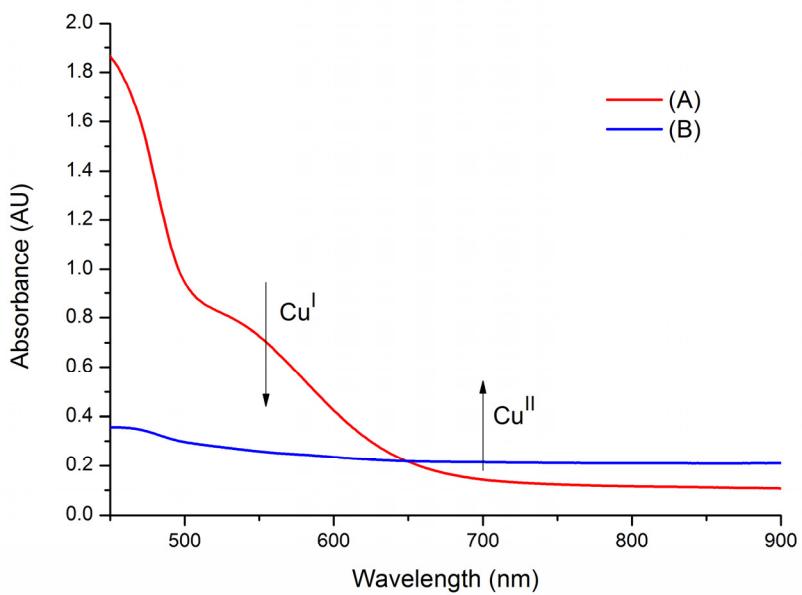


Figure S27. UV-Visible Spectra for the reaction of CuOAc/bpy and TEMPOH. (A) Conditions: 2 mM CuOAc, 2 mM bpy, 20 mM TEMPOH in 2.0 mL 1,2-dichlorobenzene (freshly prepared). (B) Conditions: 2 mM CuOAc, 2 mM bpy, 20 mM TEMPOH in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 1 h).

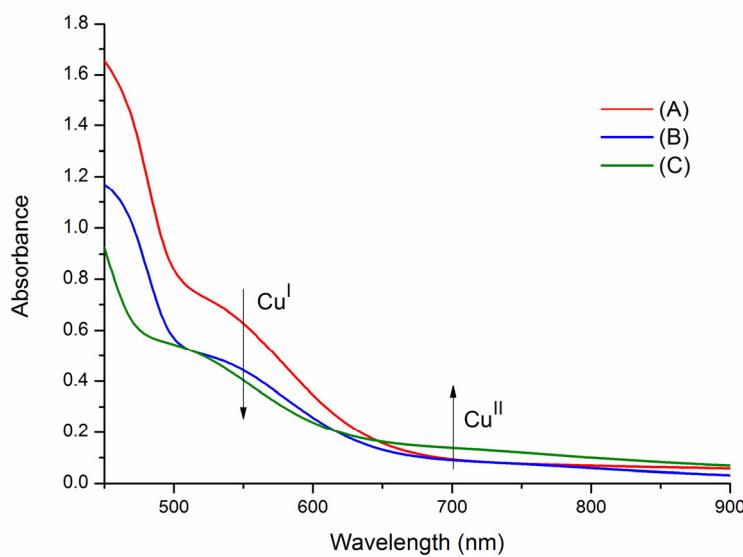


Figure S28. UV-Visible Spectra for the reaction of CuOAc/bpy and TEMPO. (A) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPO in 2.0 mL 1,2-dichlorobenzene (freshly prepared). (B) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPO in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 2 h). (C) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPO in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 10 h).

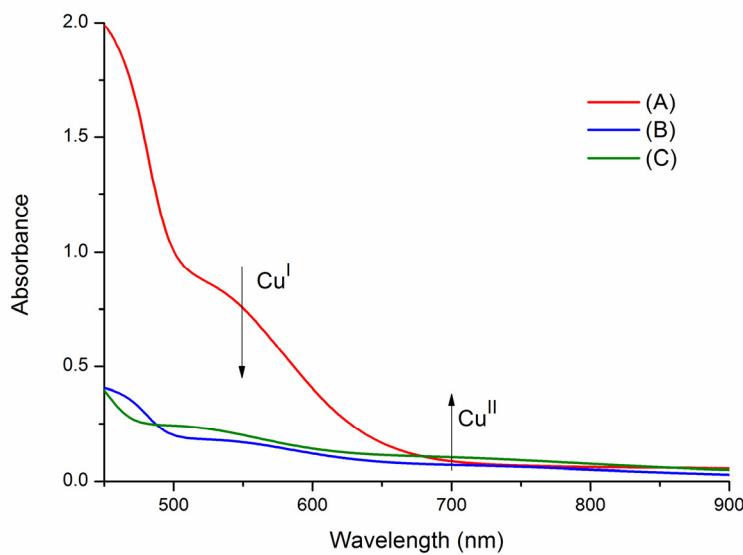


Figure S29. UV-Visible Spectra for the reaction of CuOAc/bpy and TEMPO. (A) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPOH in 2.0 mL 1,2-dichlorobenzene (freshly prepared). (B) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPOH in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 2 h). (C) Conditions: 2 mM CuOAc, 2 mM bpy, 2 mM TEMPOH in 2.0 mL 1,2-dichlorobenzene (after heated at 120 °C for 10 h).

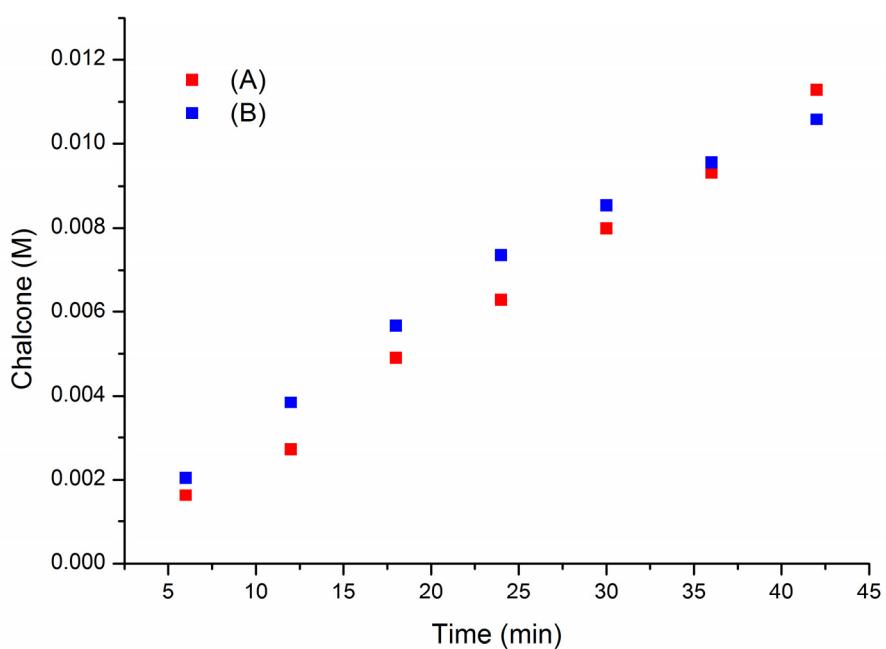
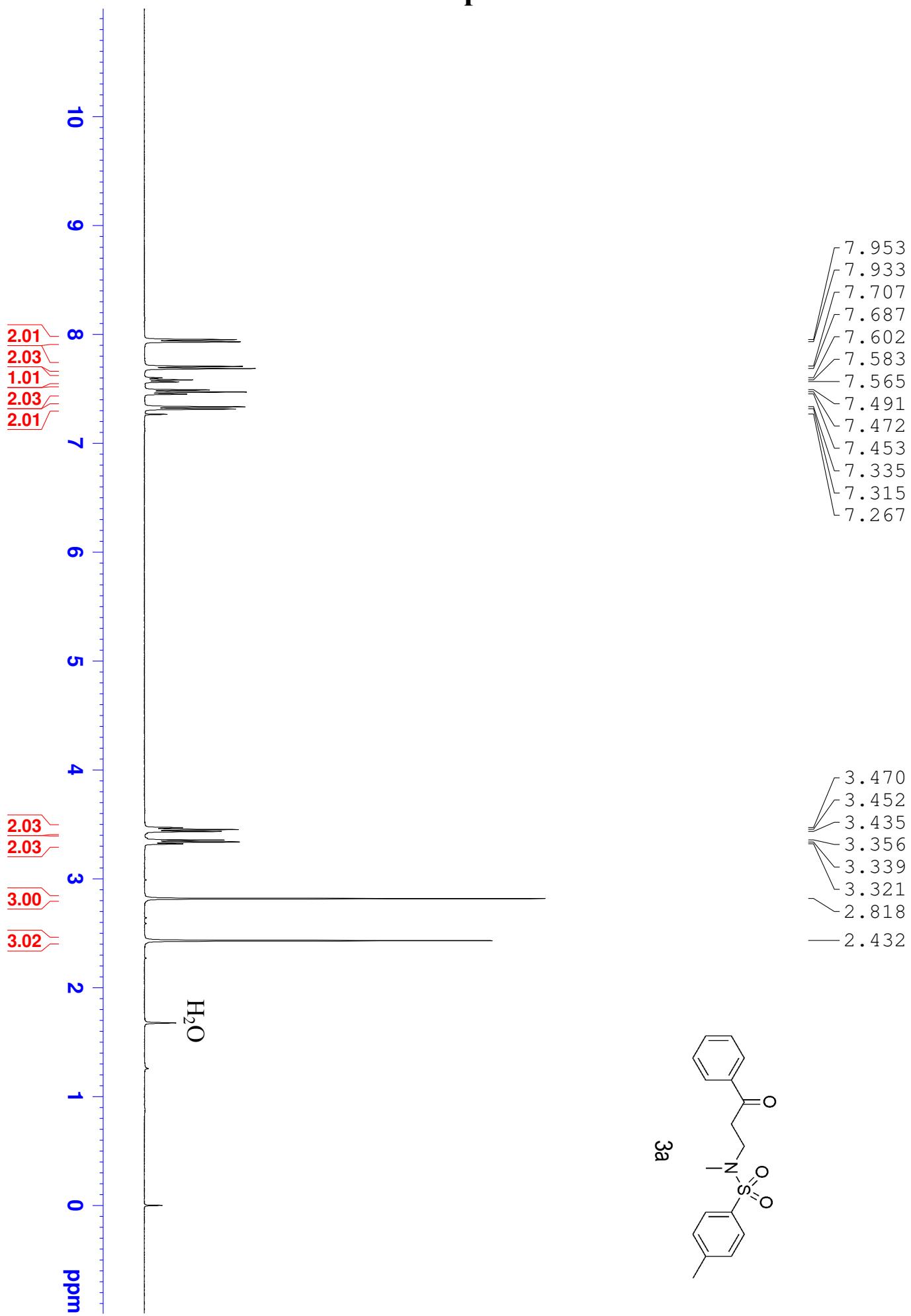


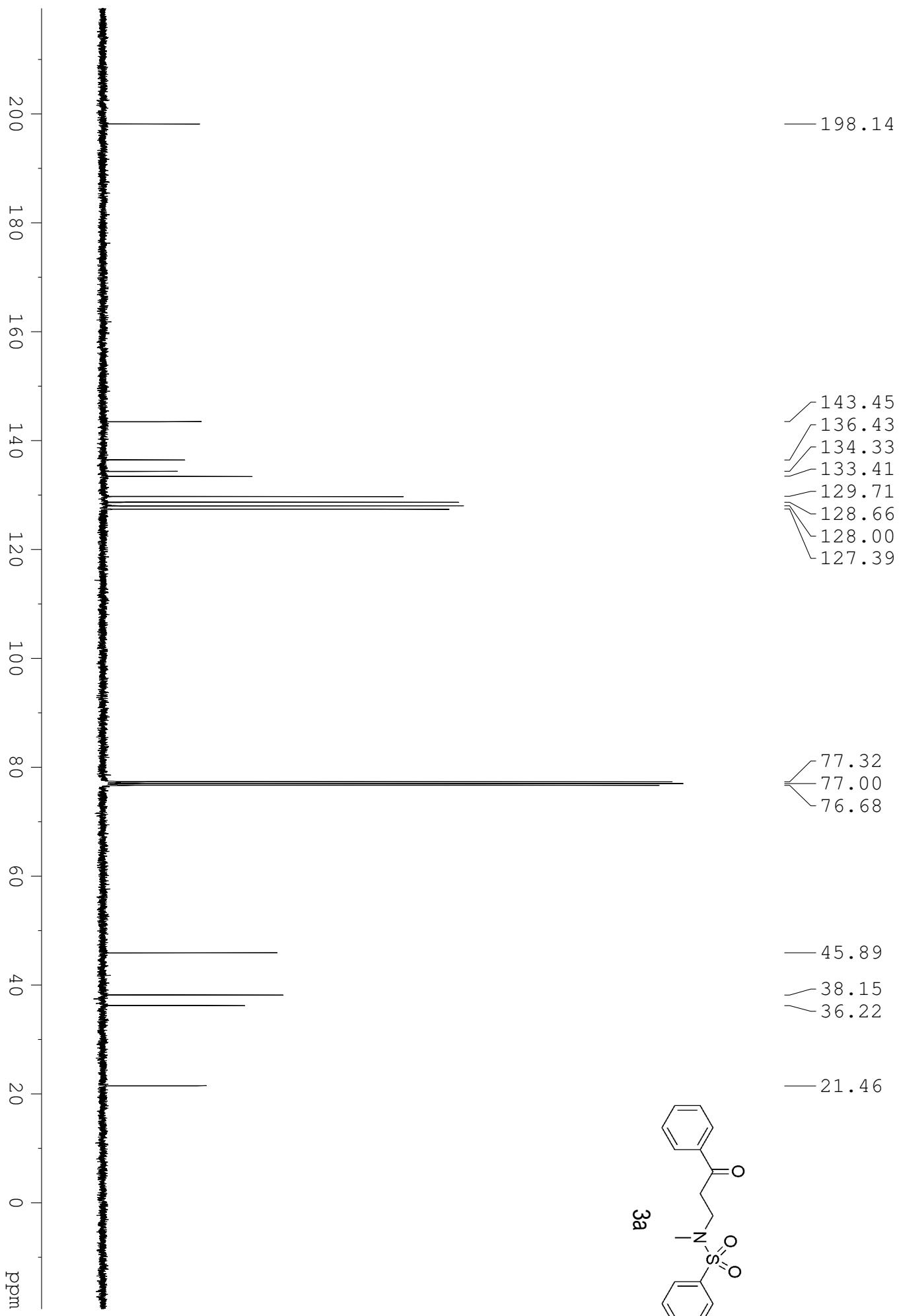
Figure S30. Plot of initial rate of 3-propiophenone dehydrogenation under conditions: (A) 0.1 M 3-phenylpropiophenone, **10 mM Cu(OAc)₂**, 10 mM bpy, 0.1 M TEMPO, 2.0 mL 1,2-dichlorobenzene, N₂, 120 °C. (B) 0.1 M 3-phenylpropiophenone, **10 mM CuOAc**, 10 mM bpy, 0.1 M TEMPO, 2.0 mL 1,2-dichlorobenzene, N₂, 120 °C. Yields were determined by GC using dodecane as an internal standard.

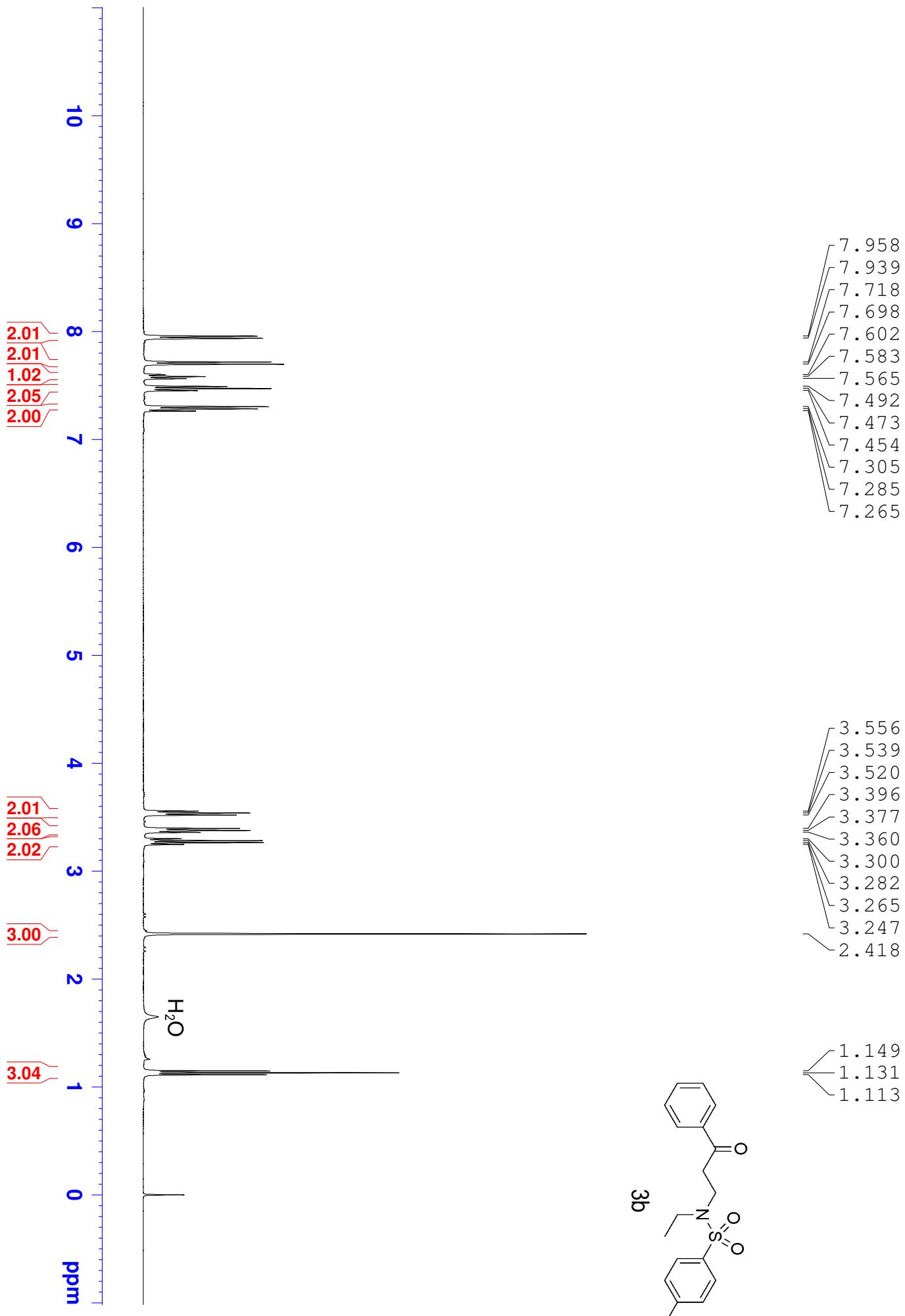
IV. References

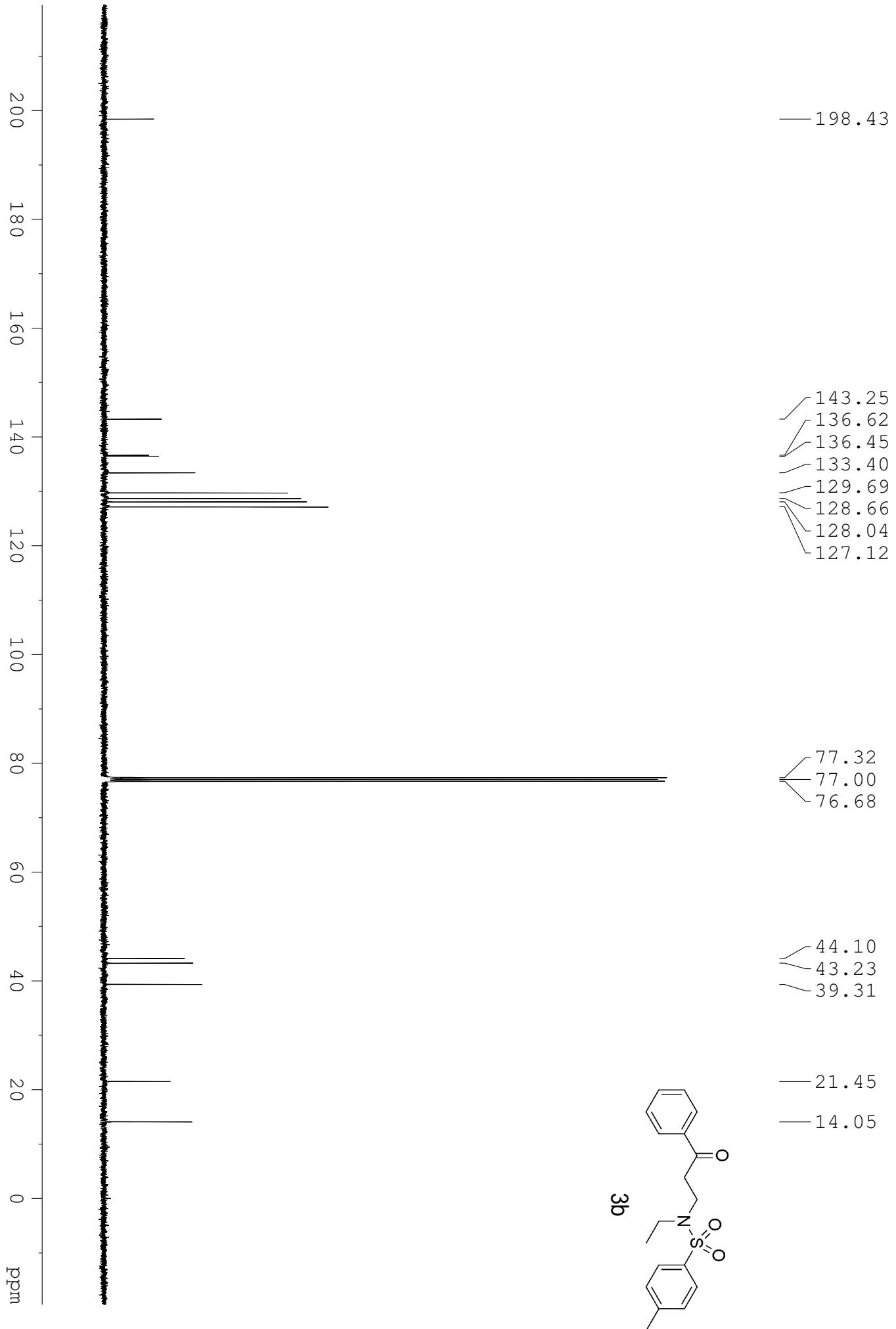
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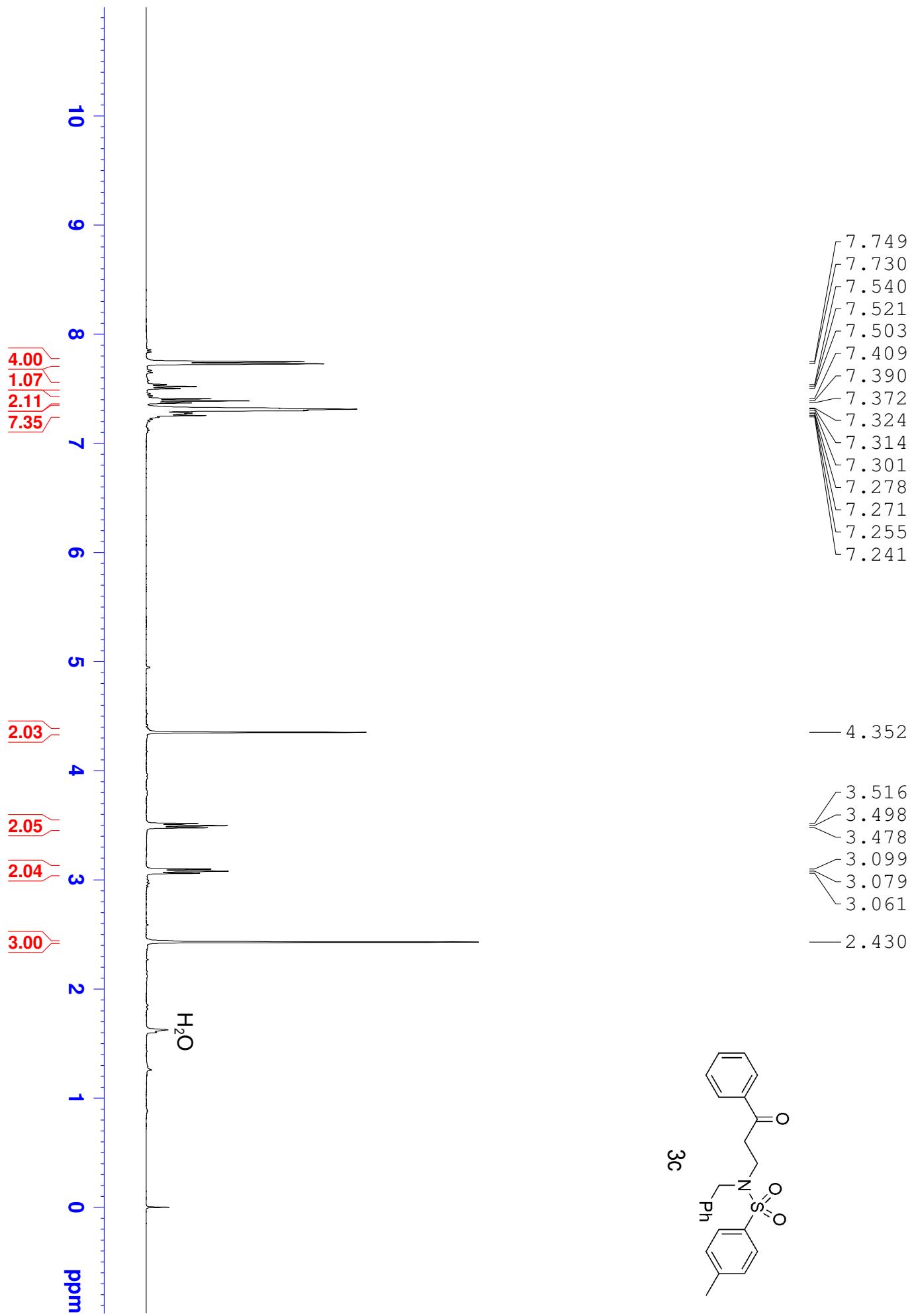
V. ^1H , ^{13}C and ^{19}F NMR Spectra of Compounds

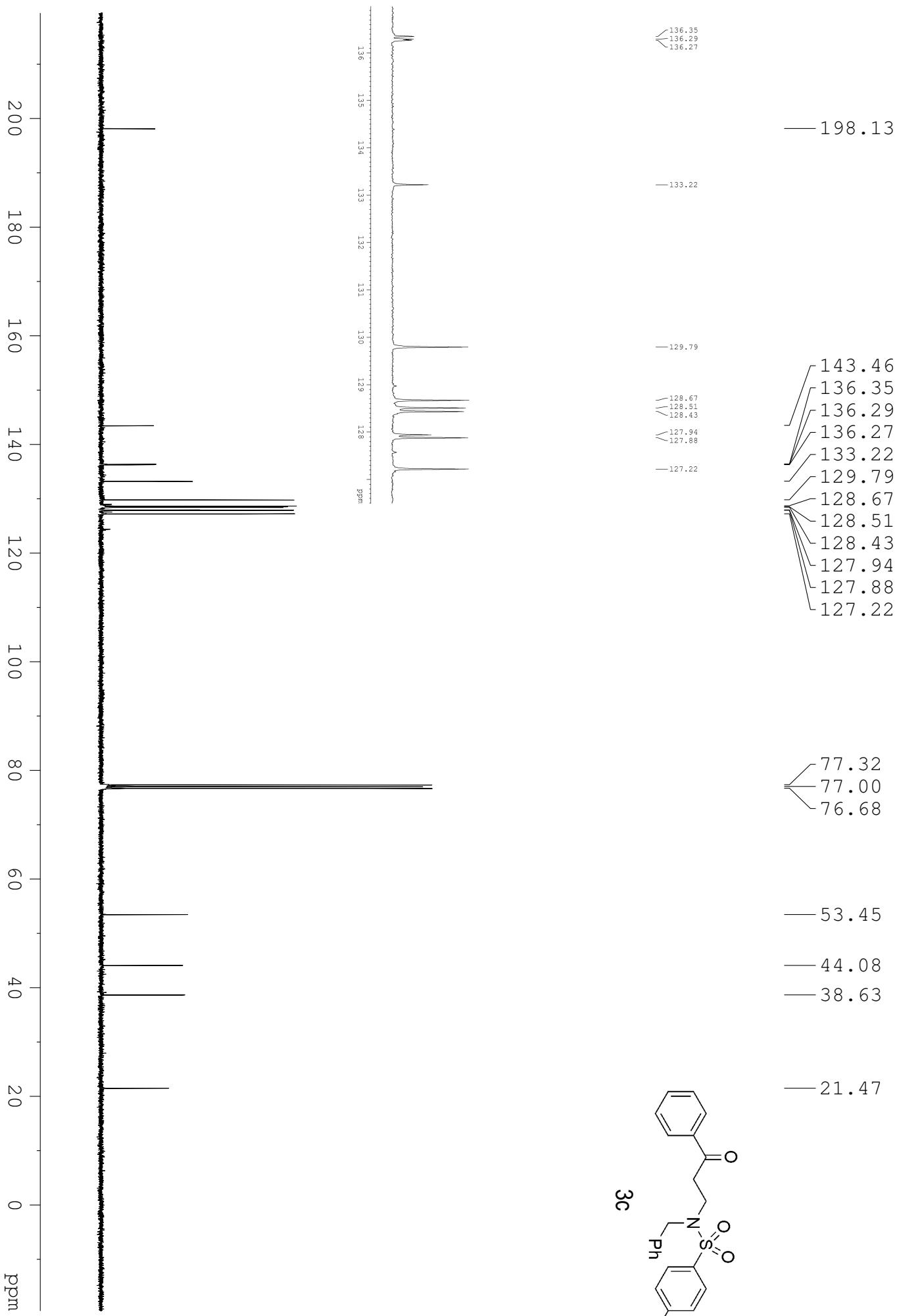


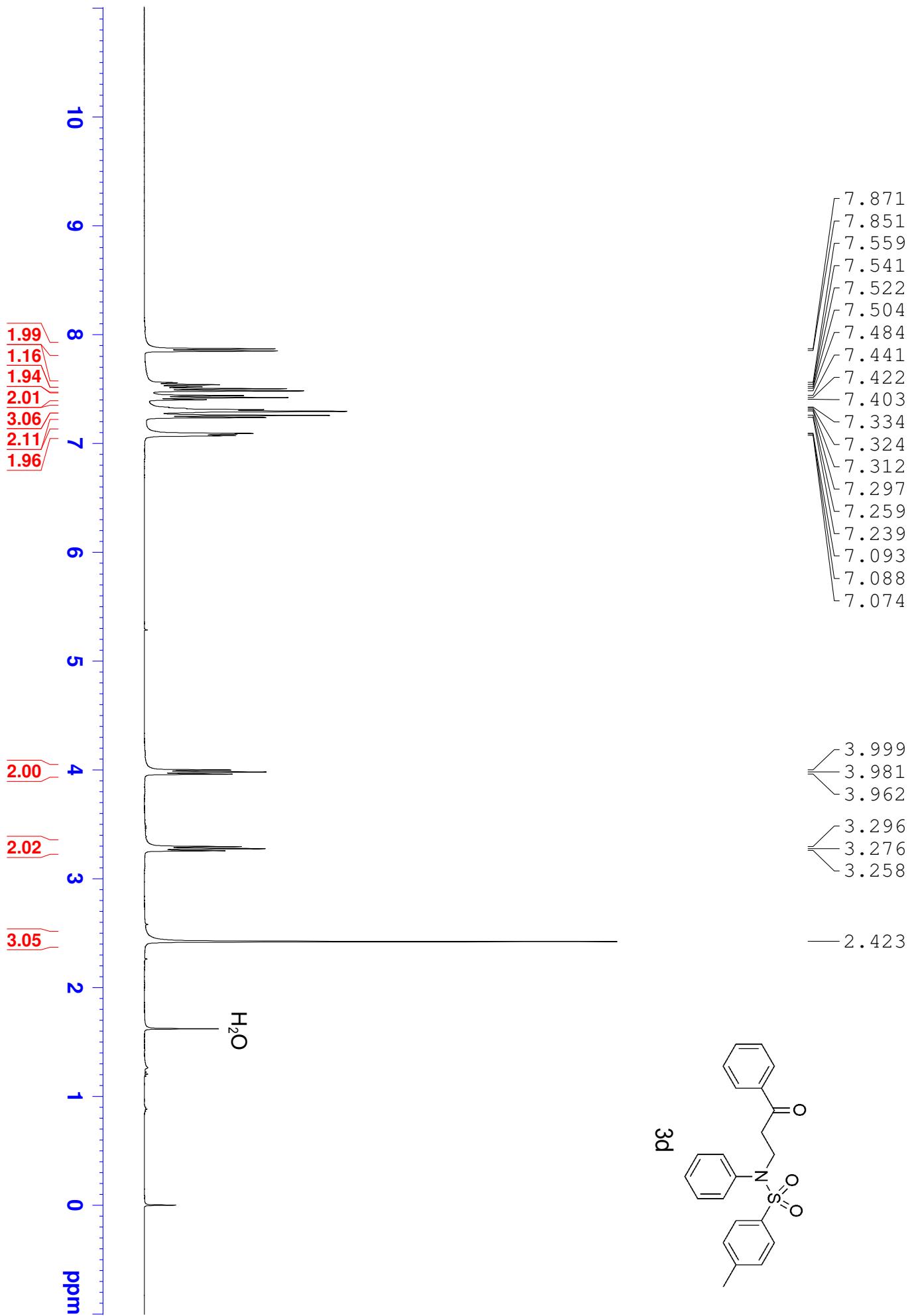


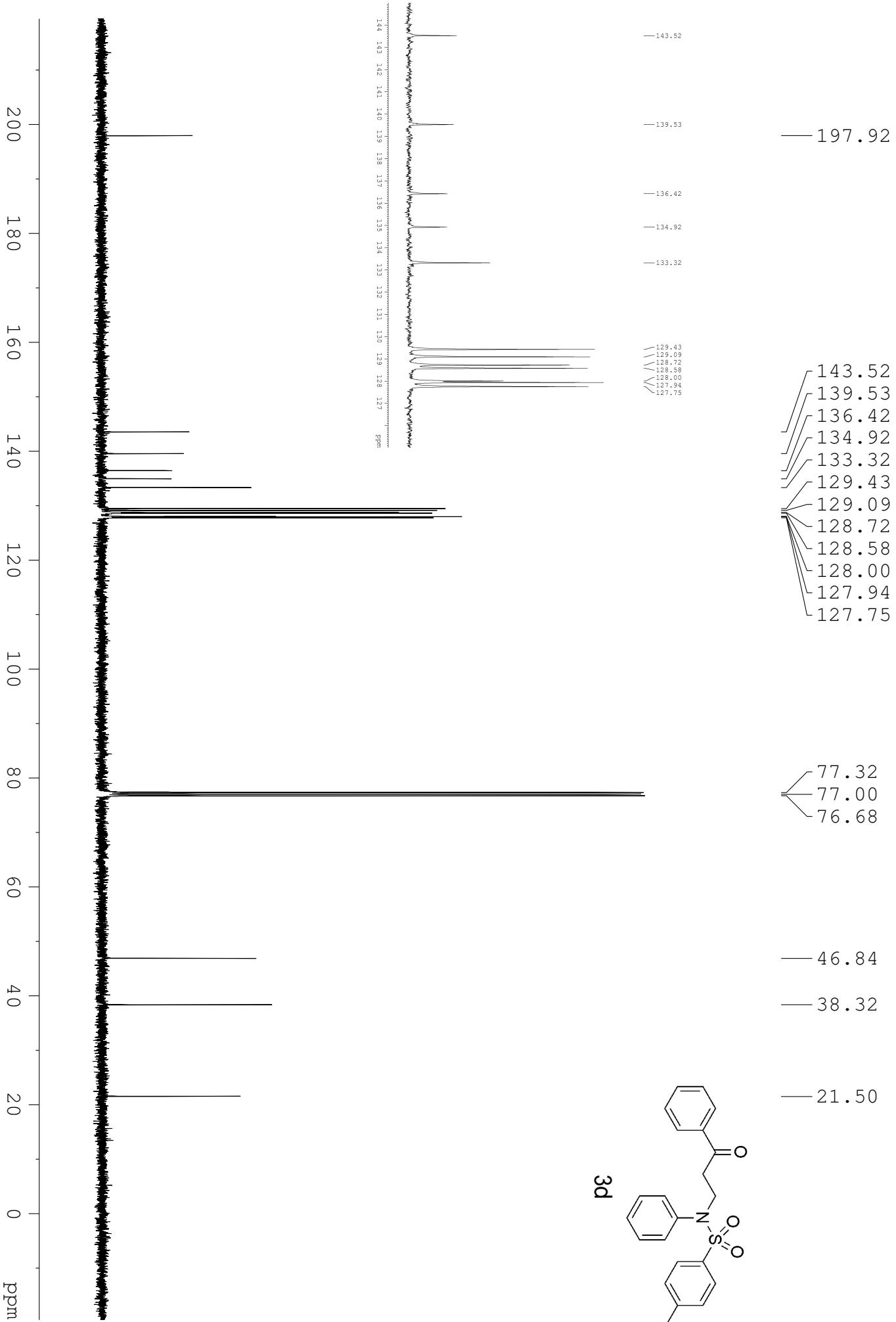


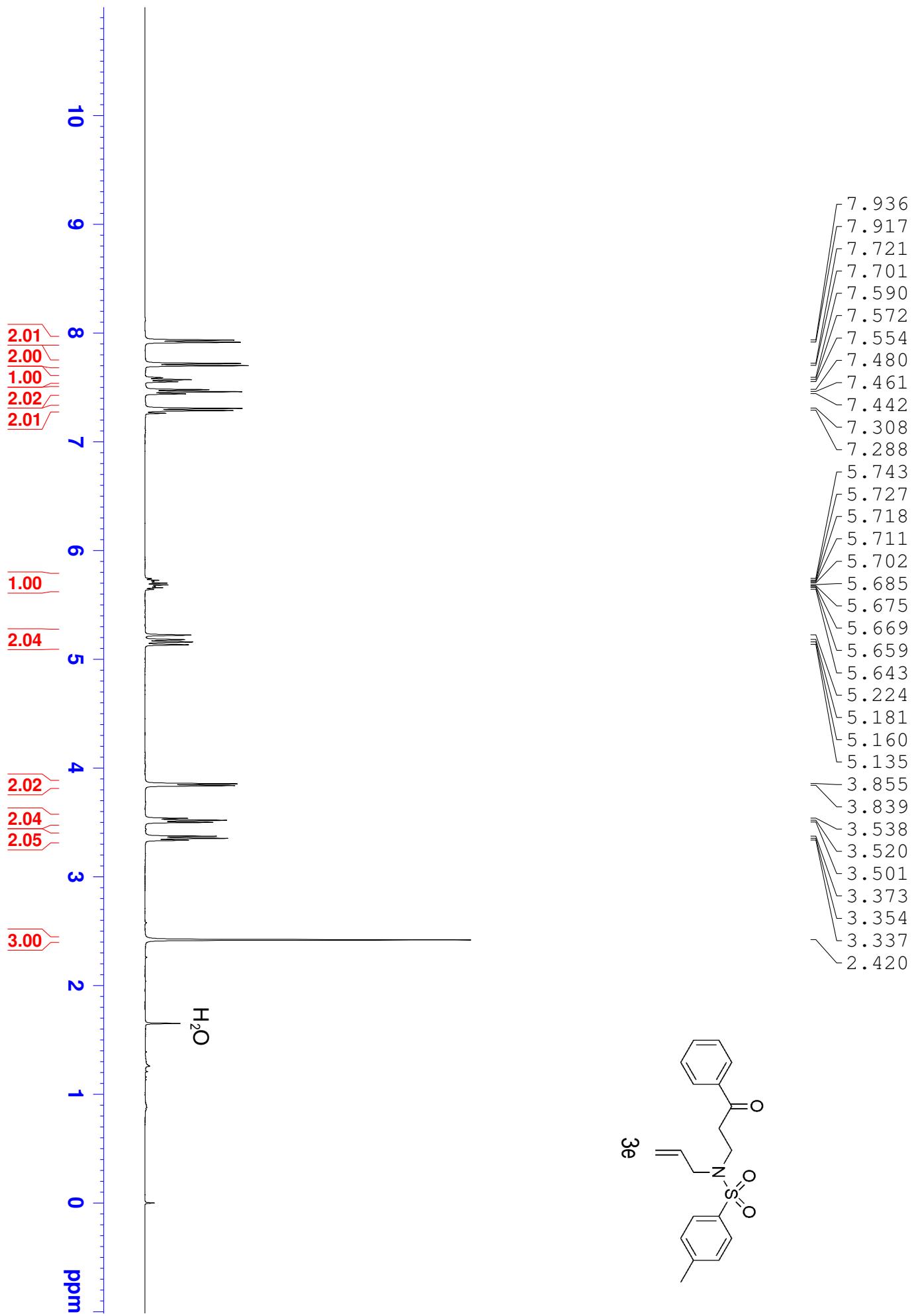


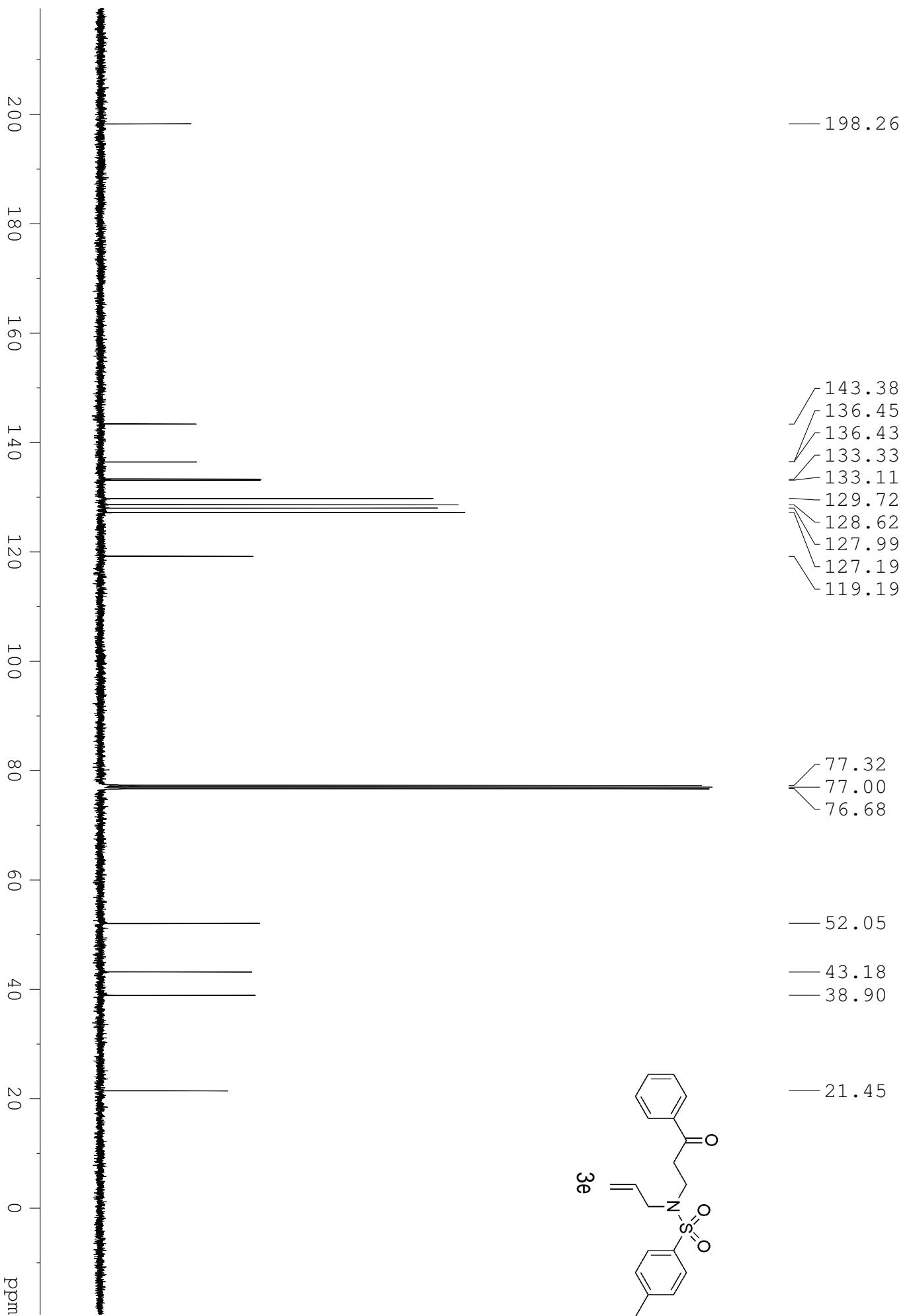


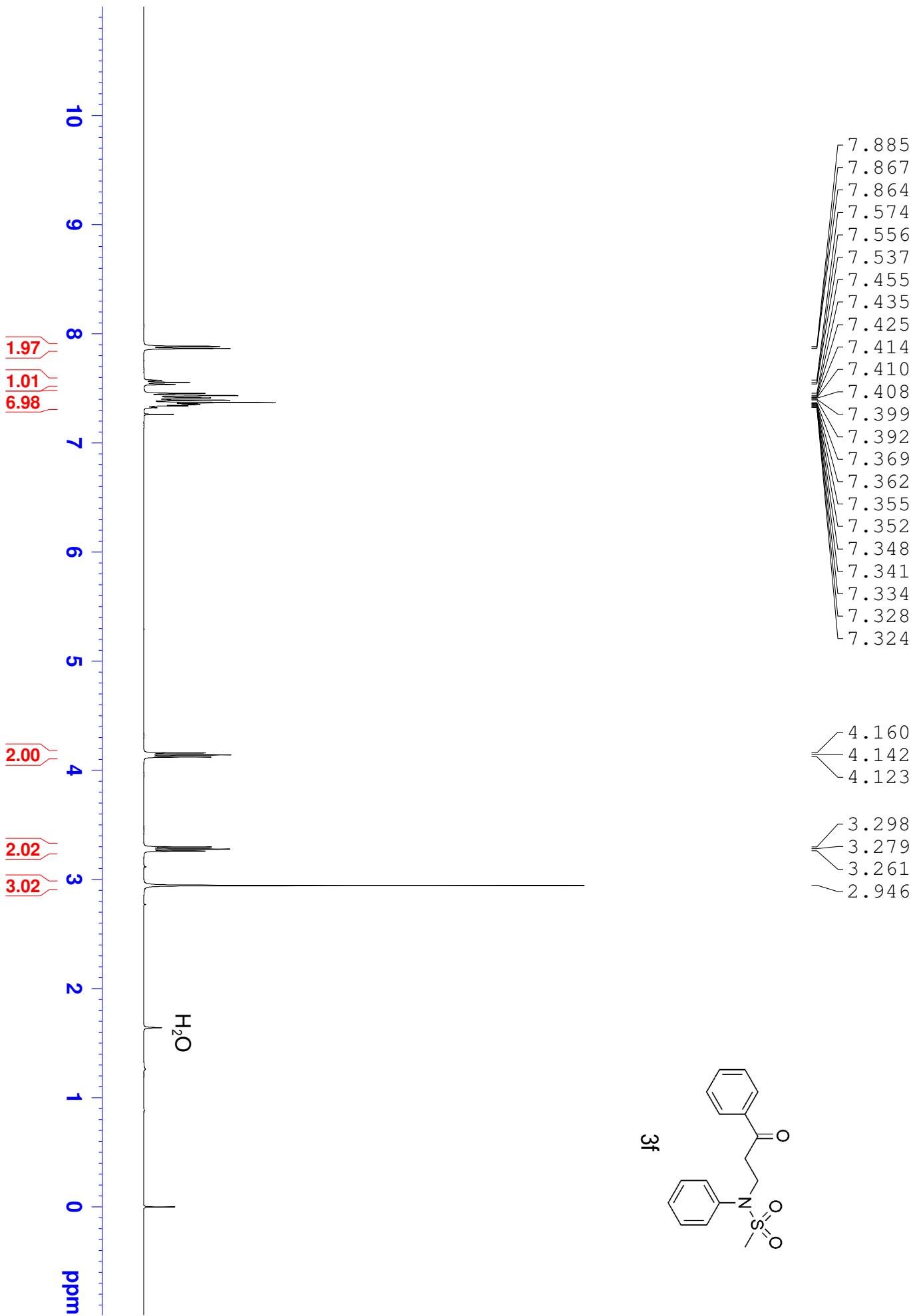


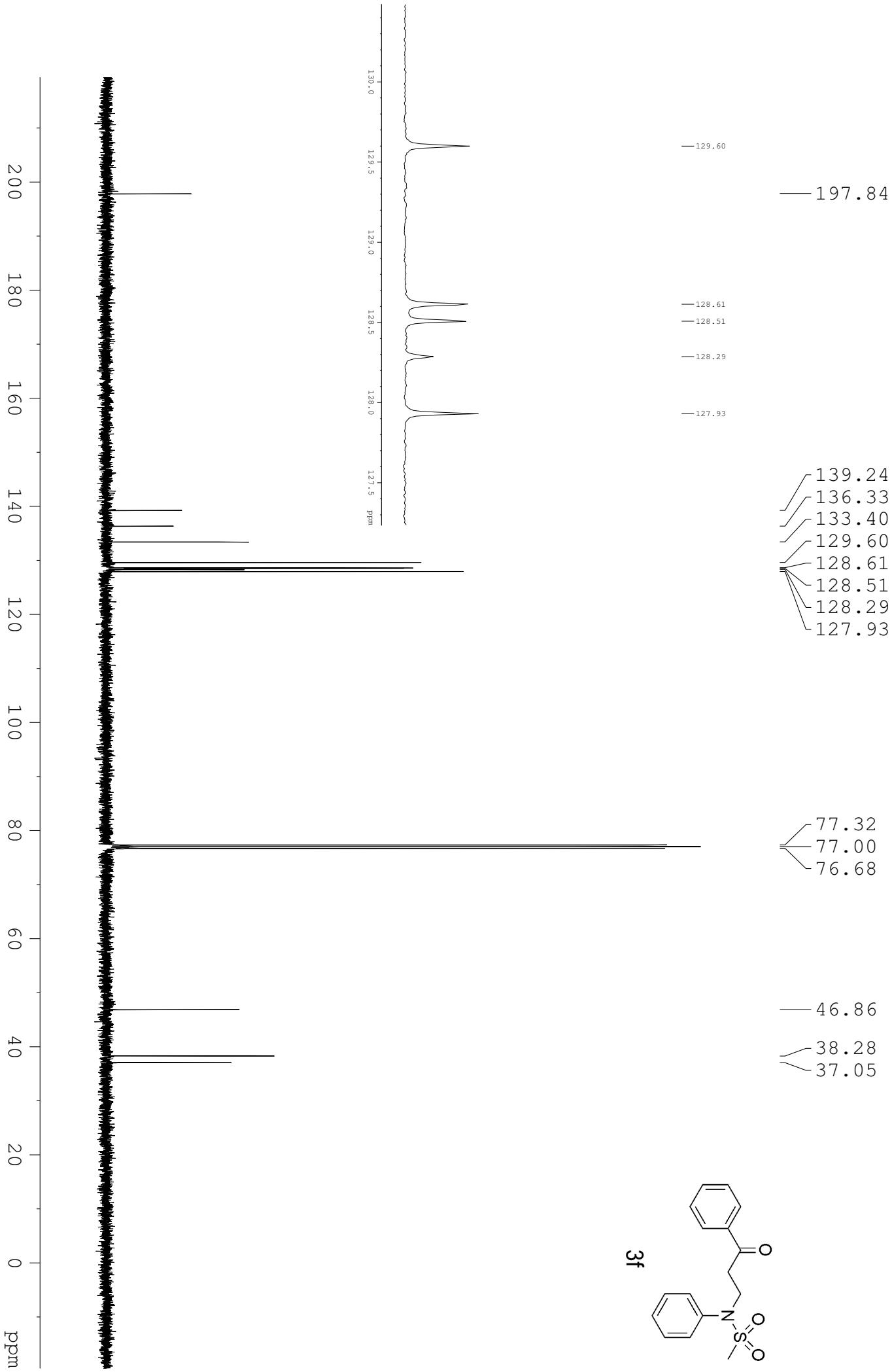


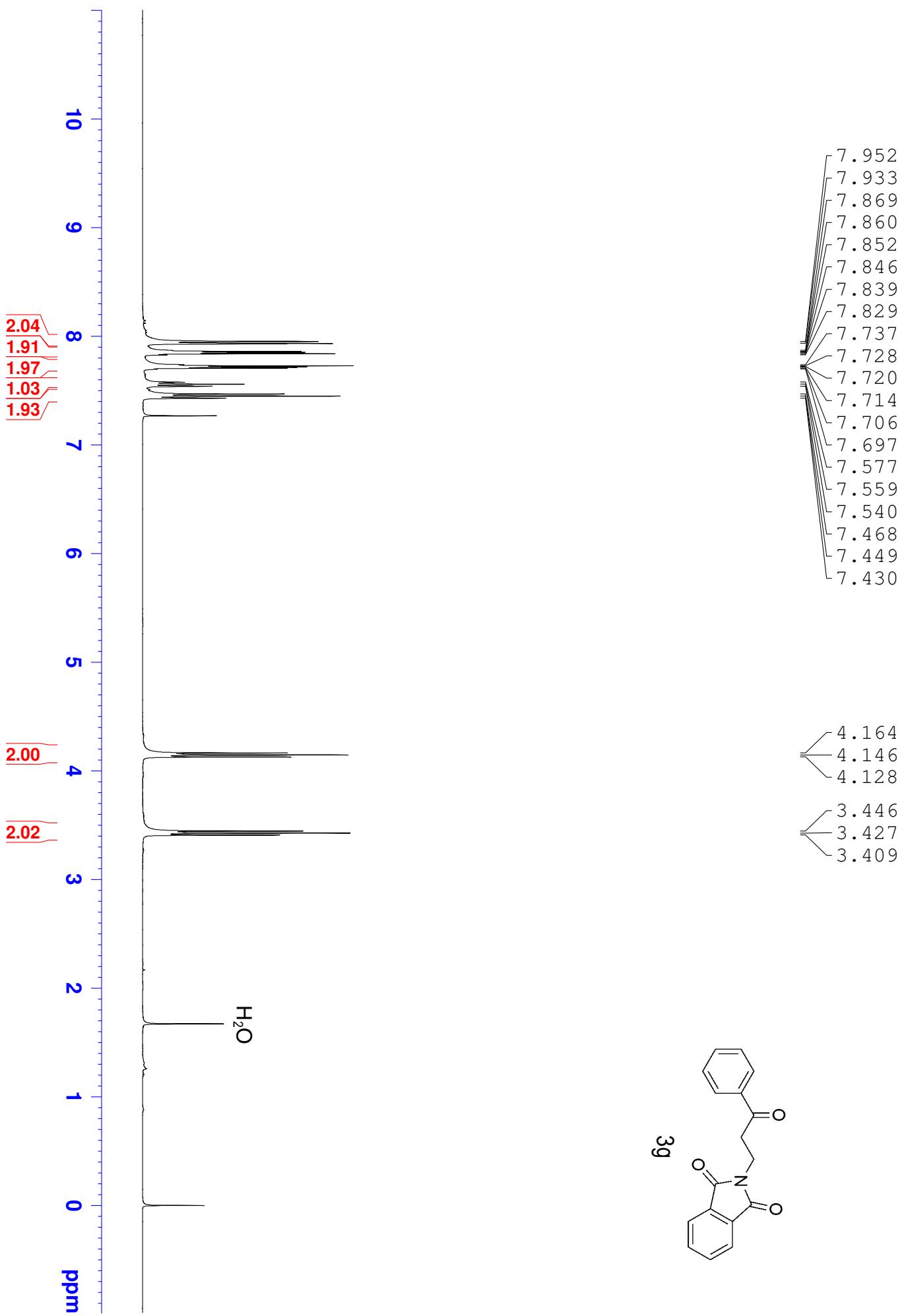


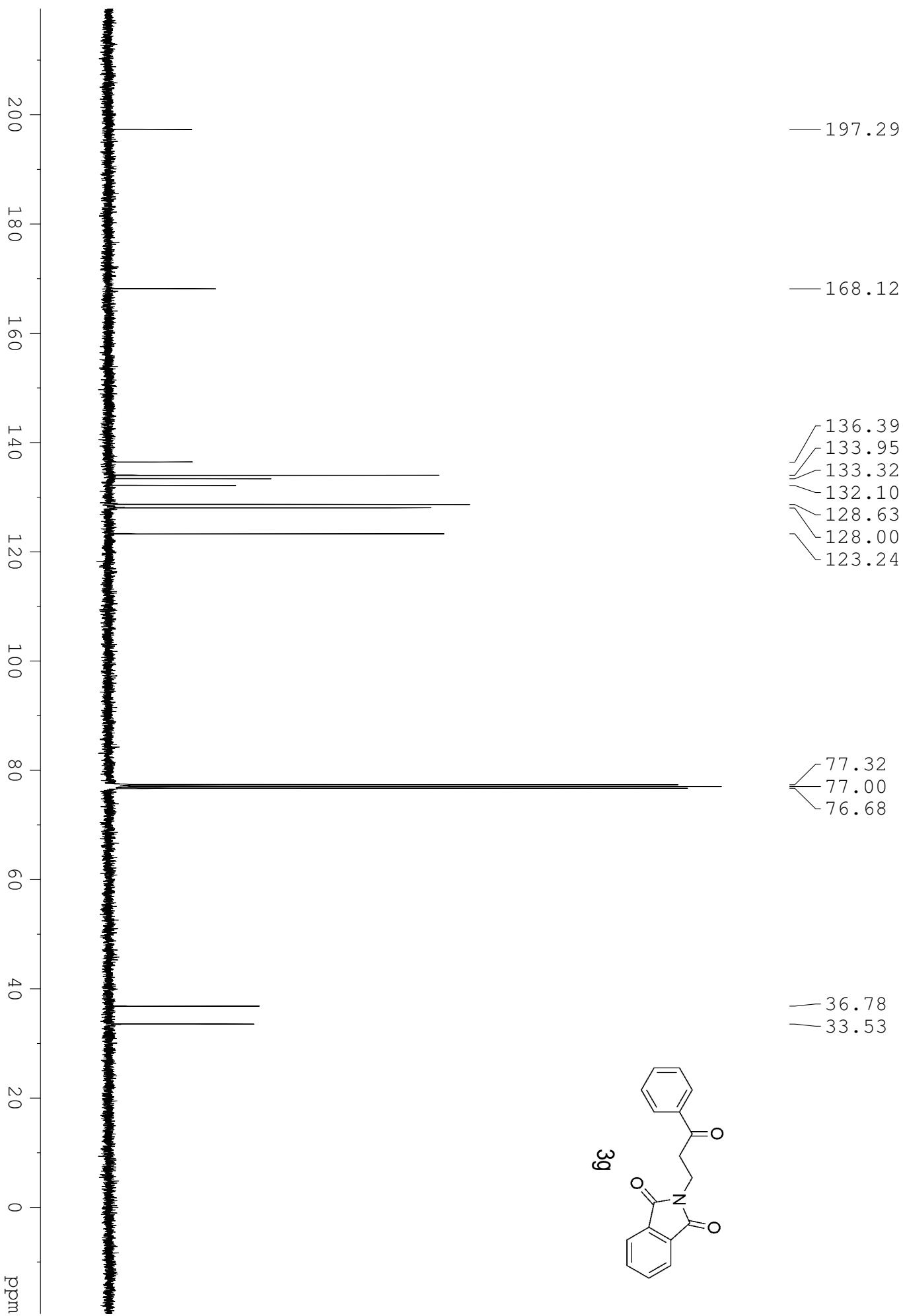


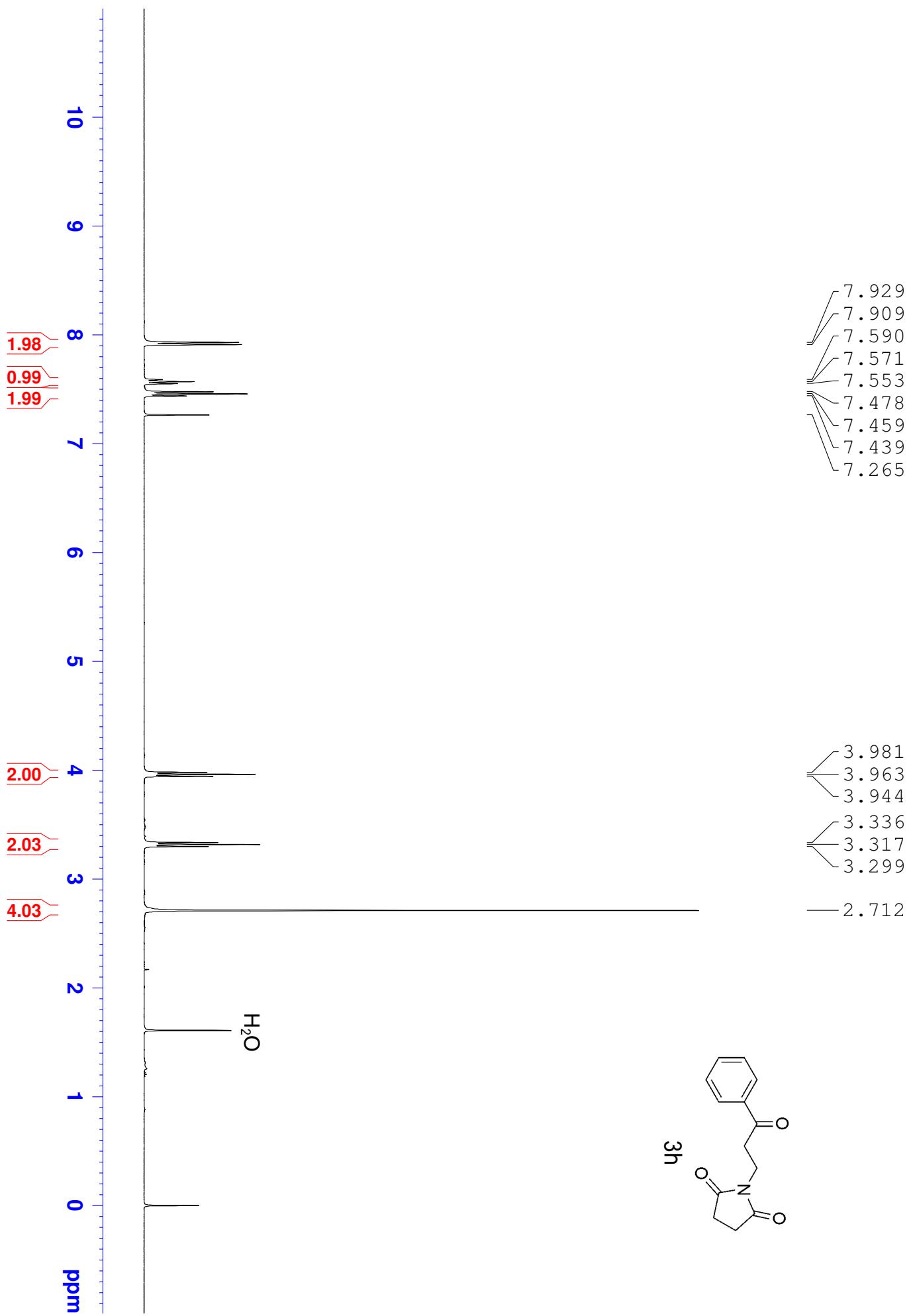


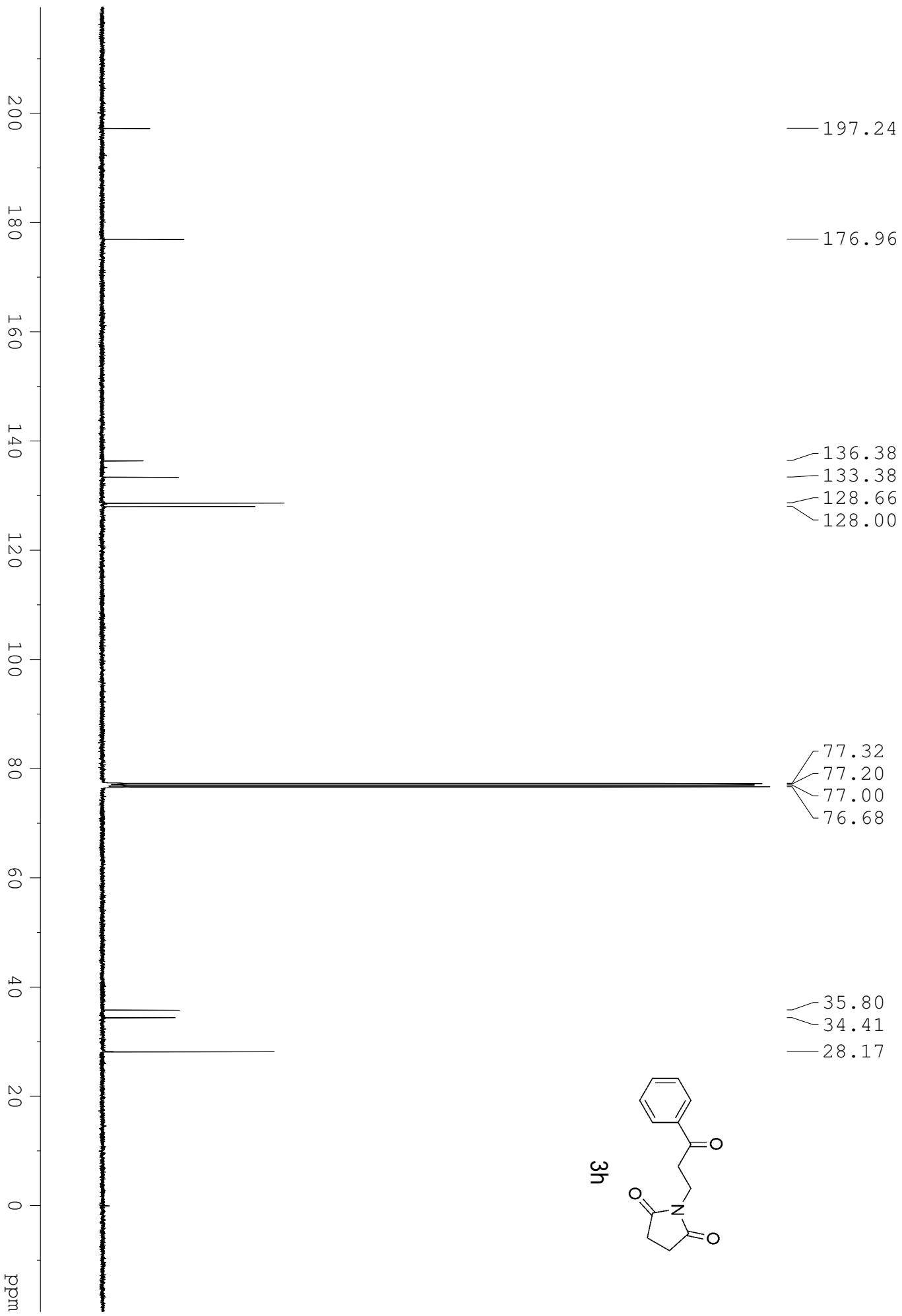


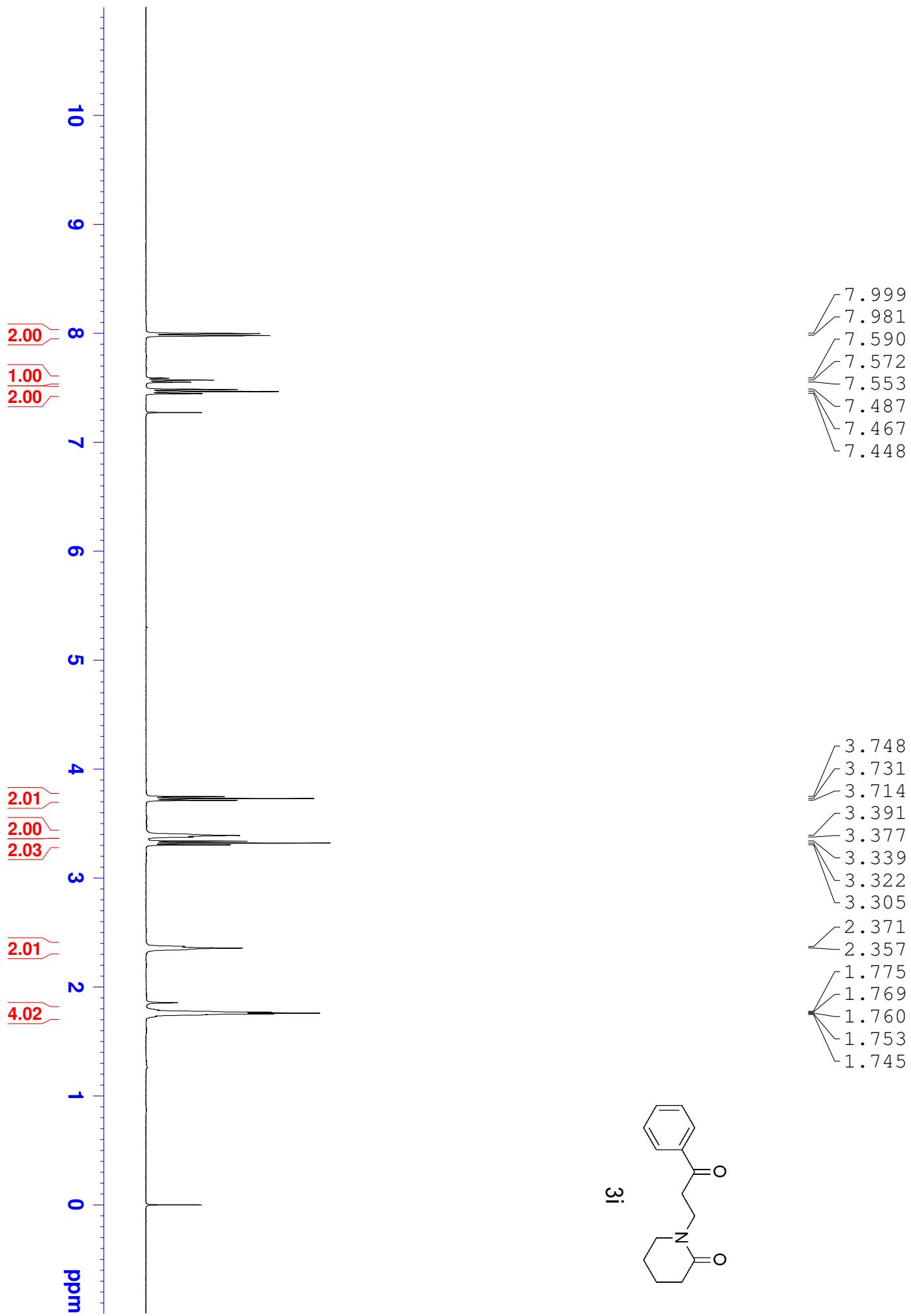


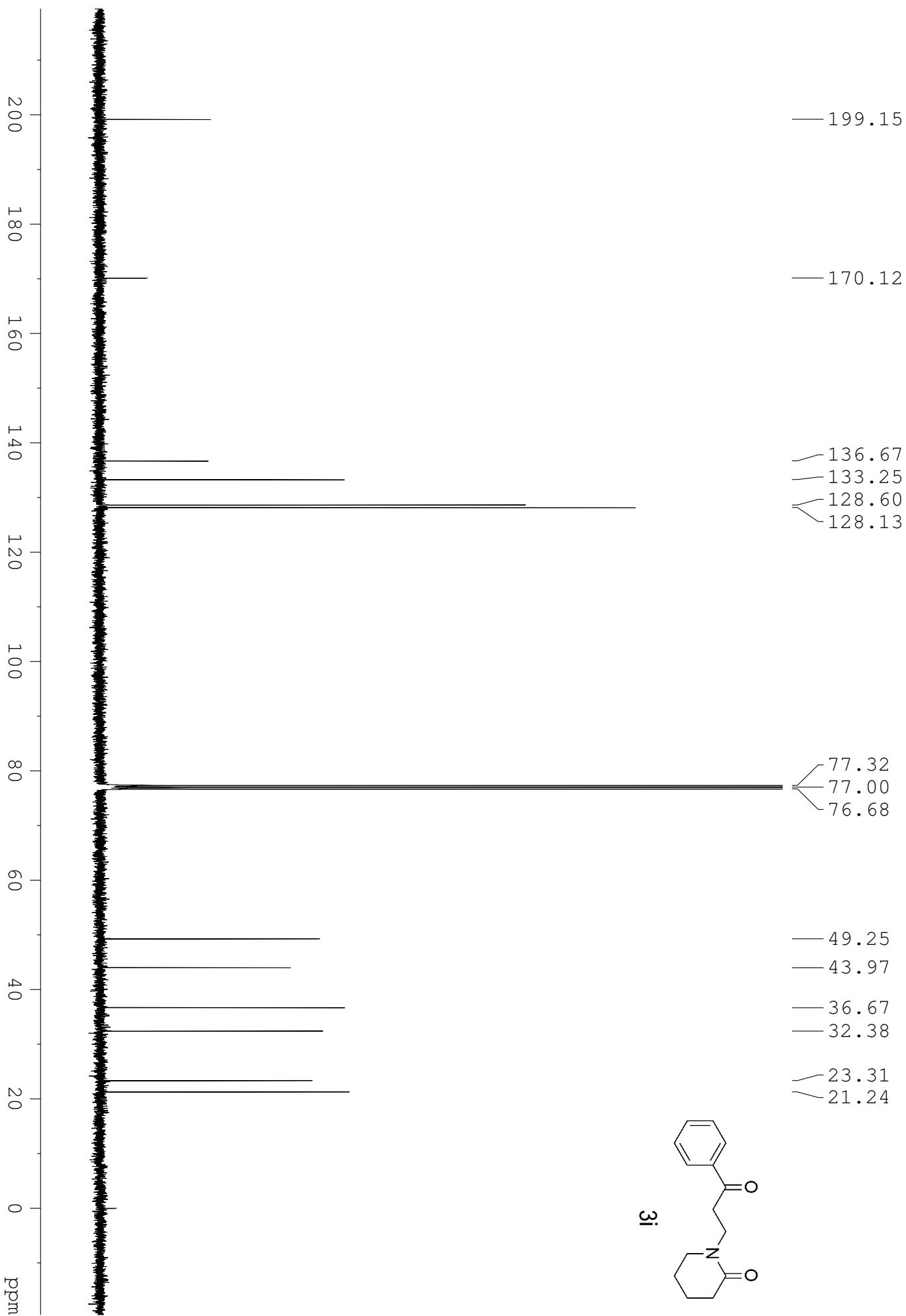


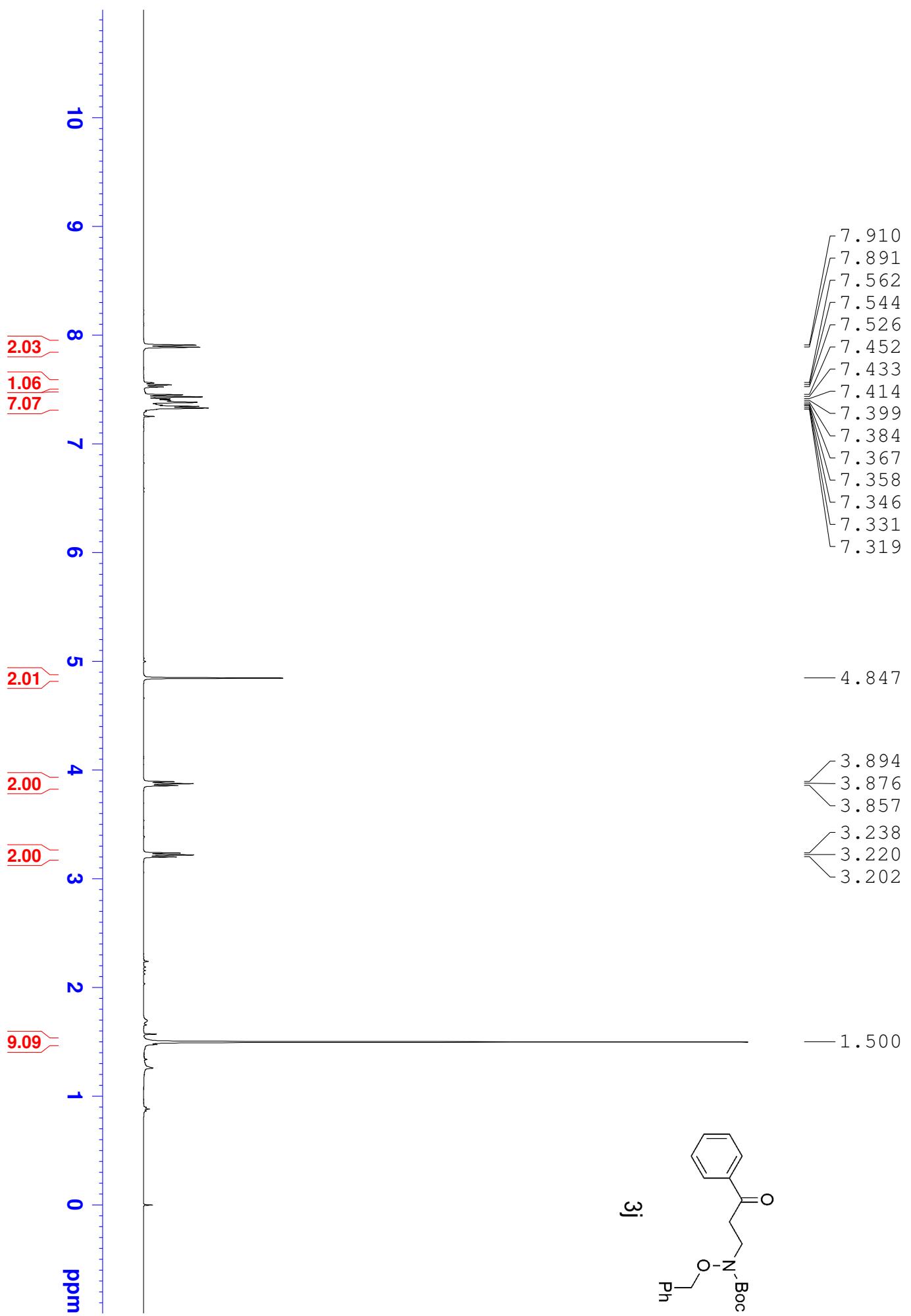


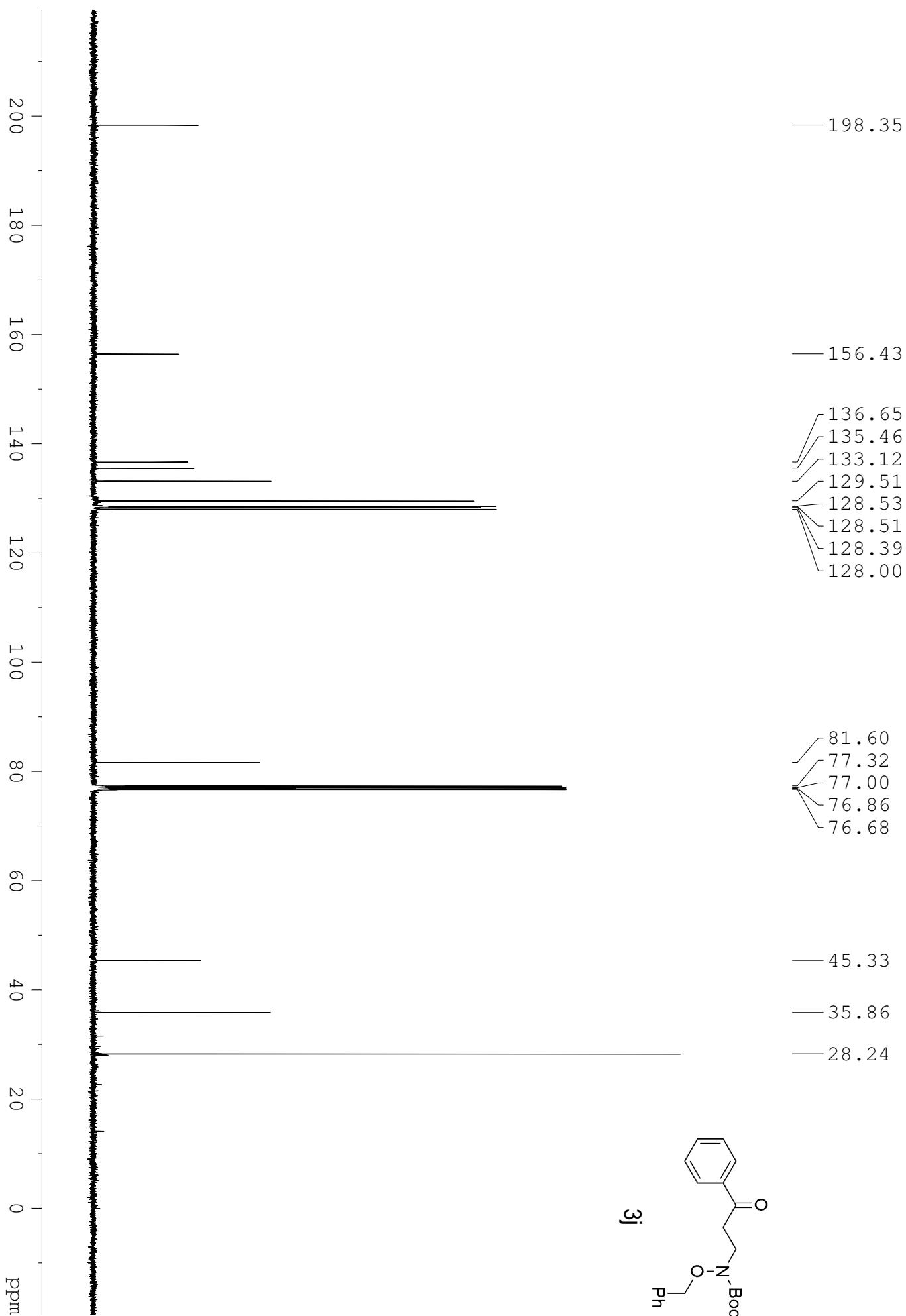


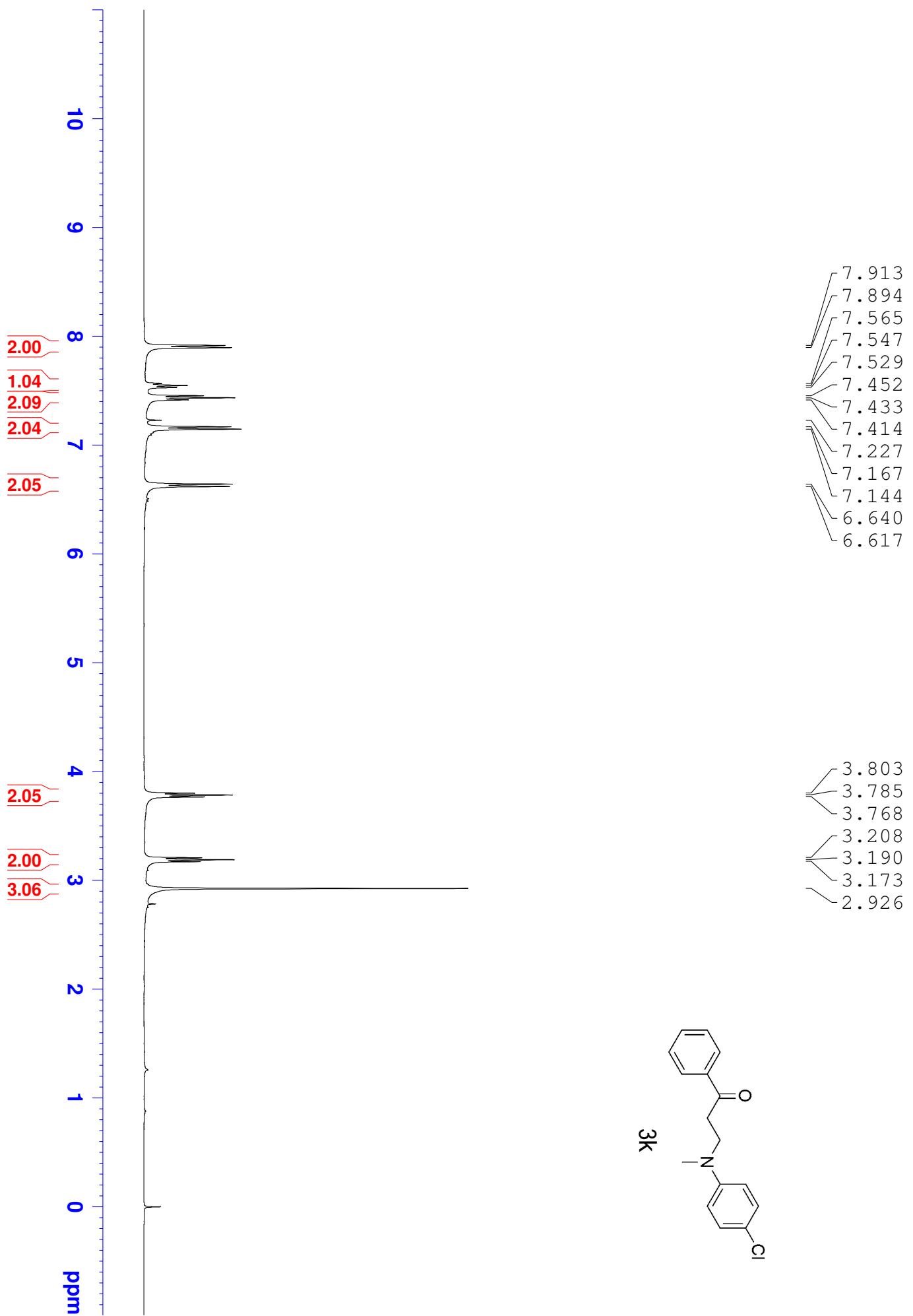


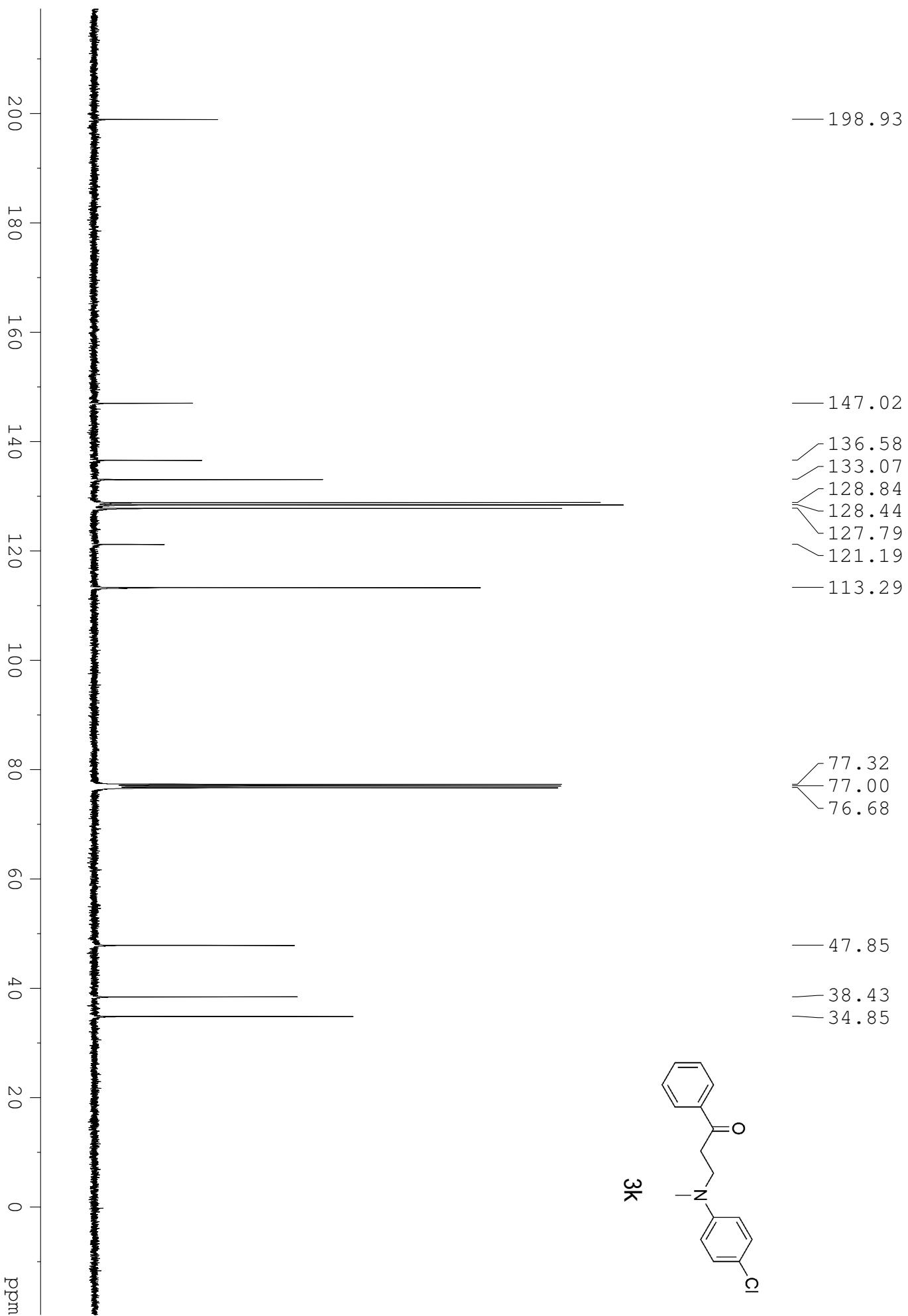




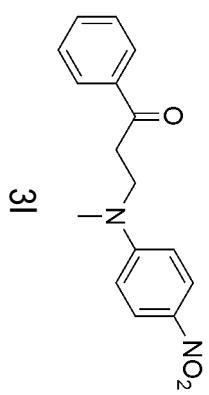
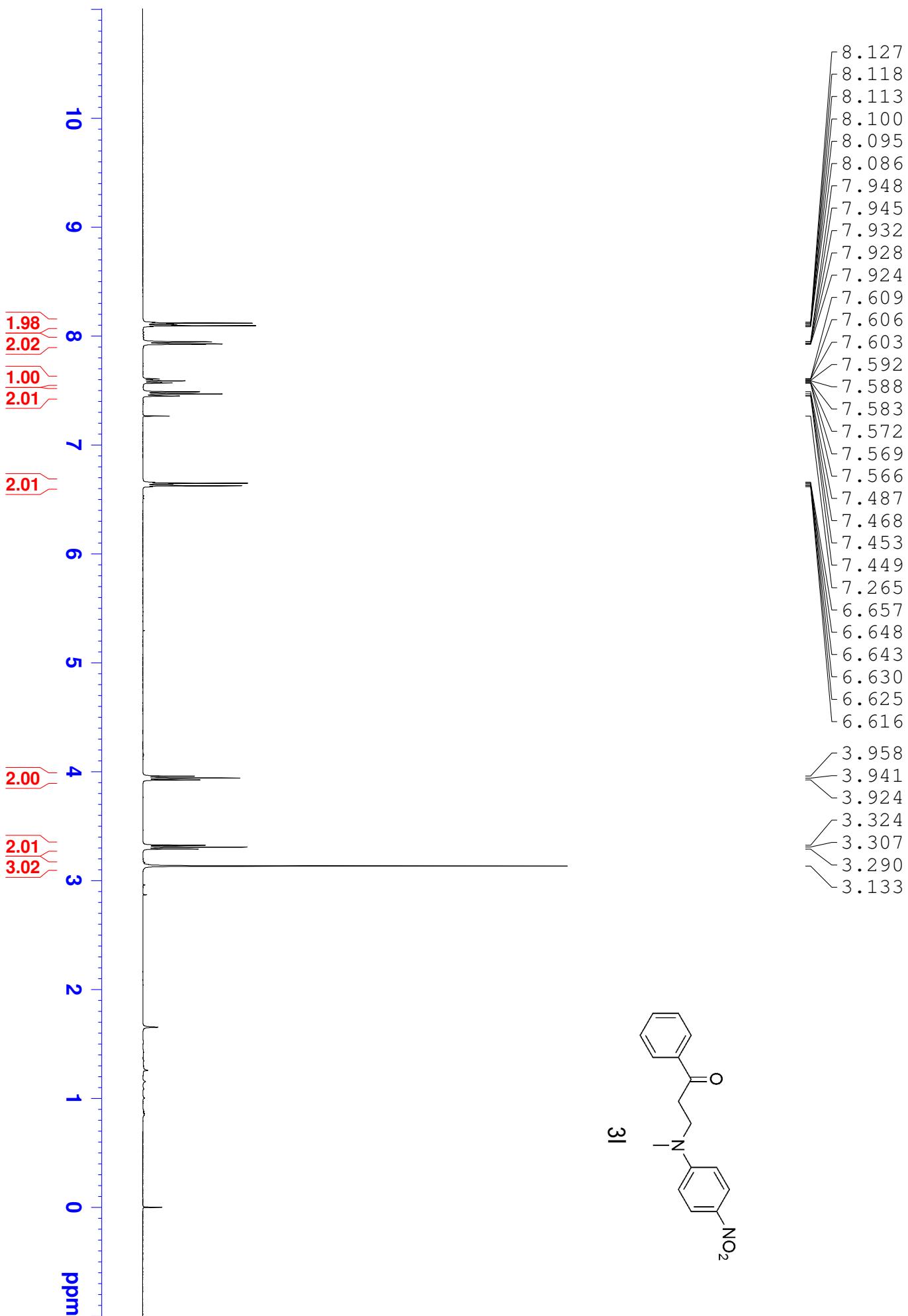


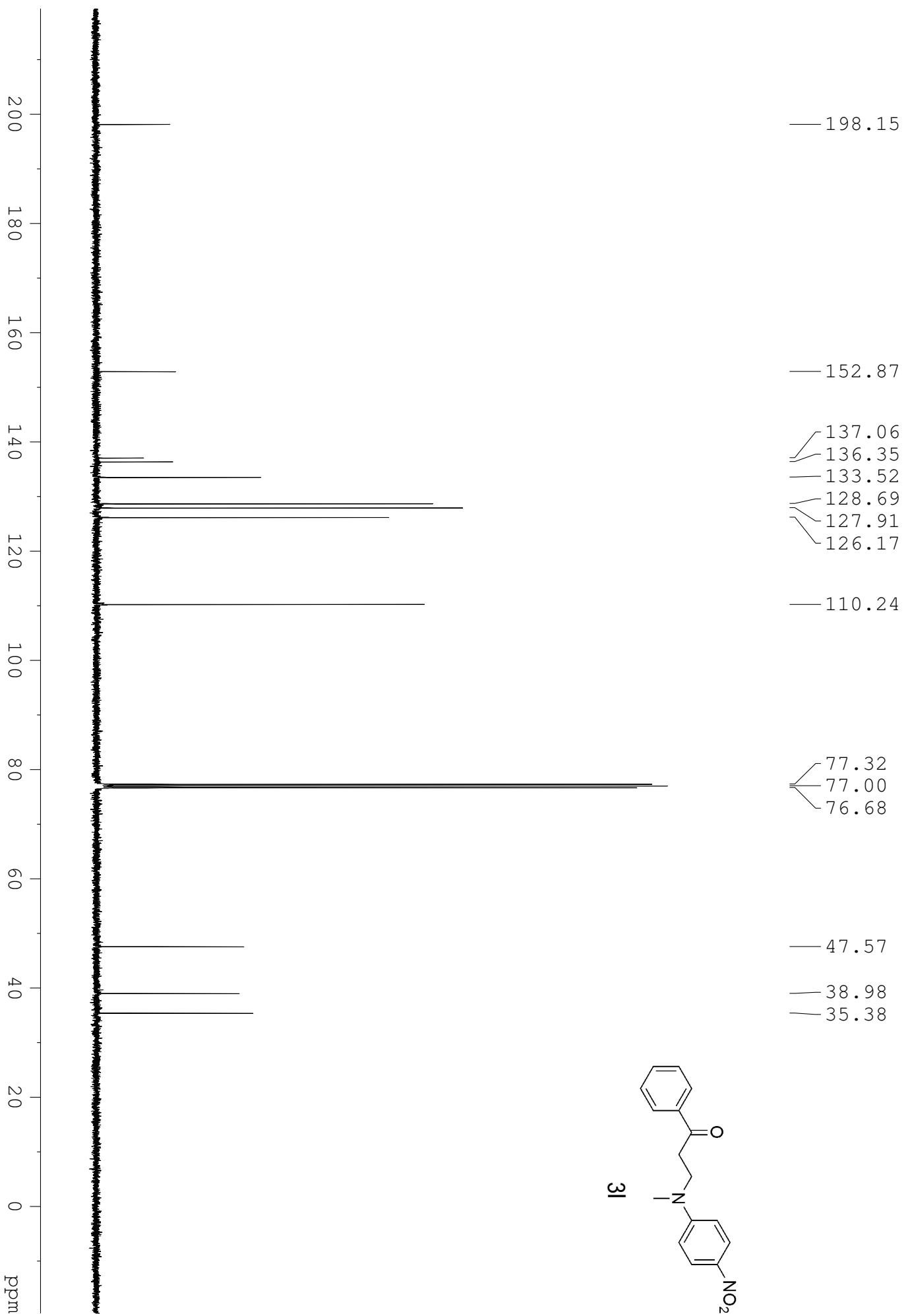




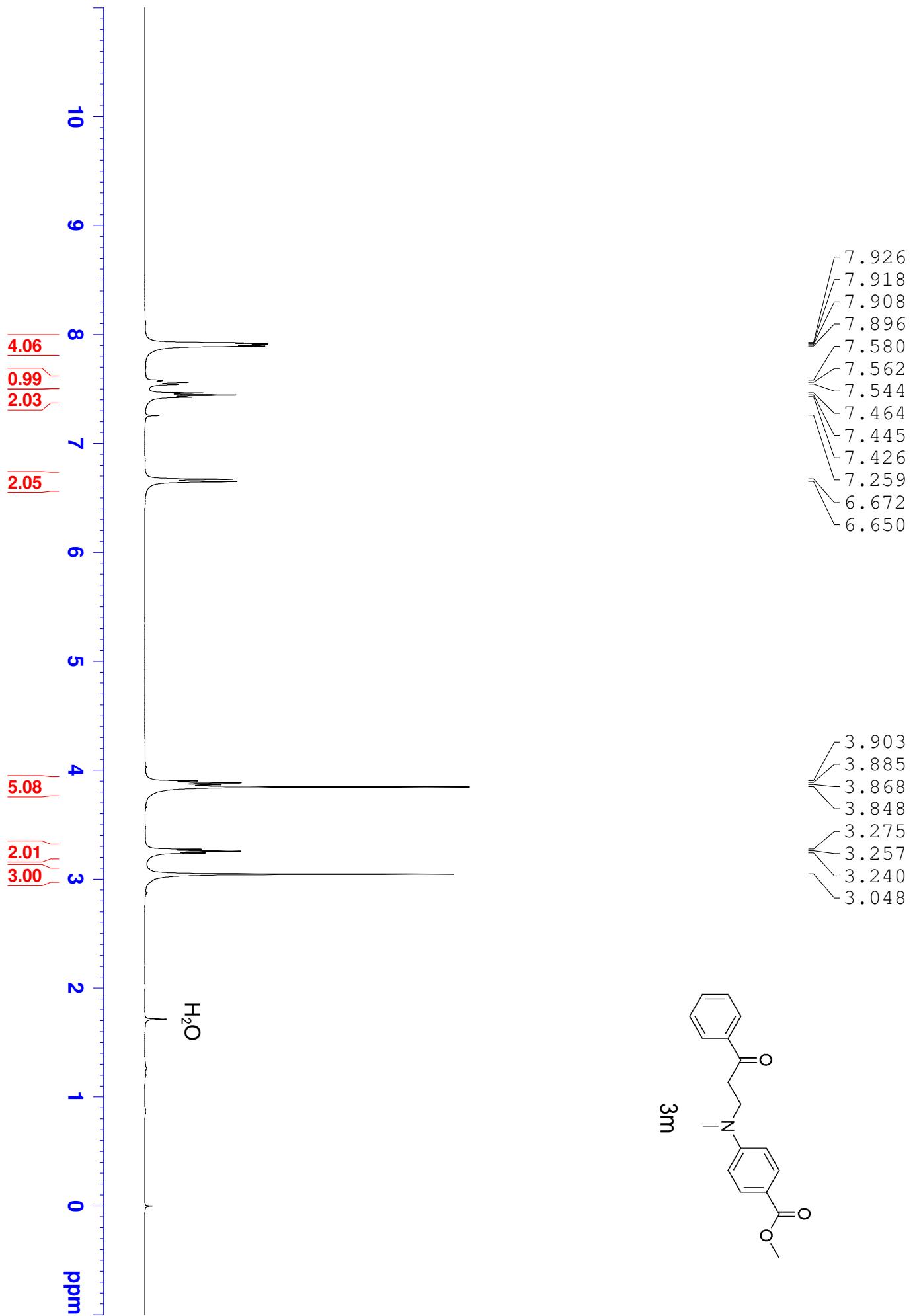


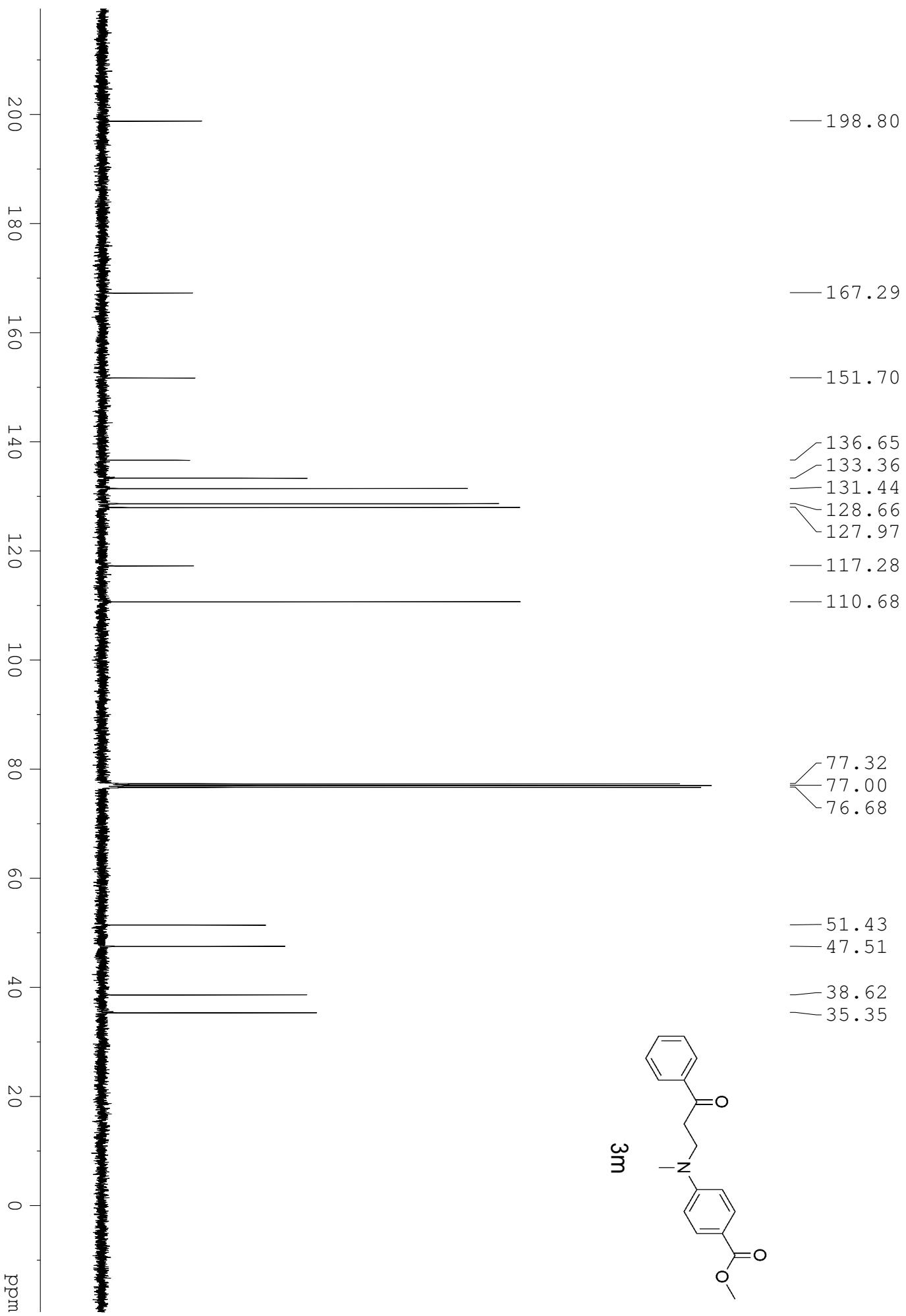
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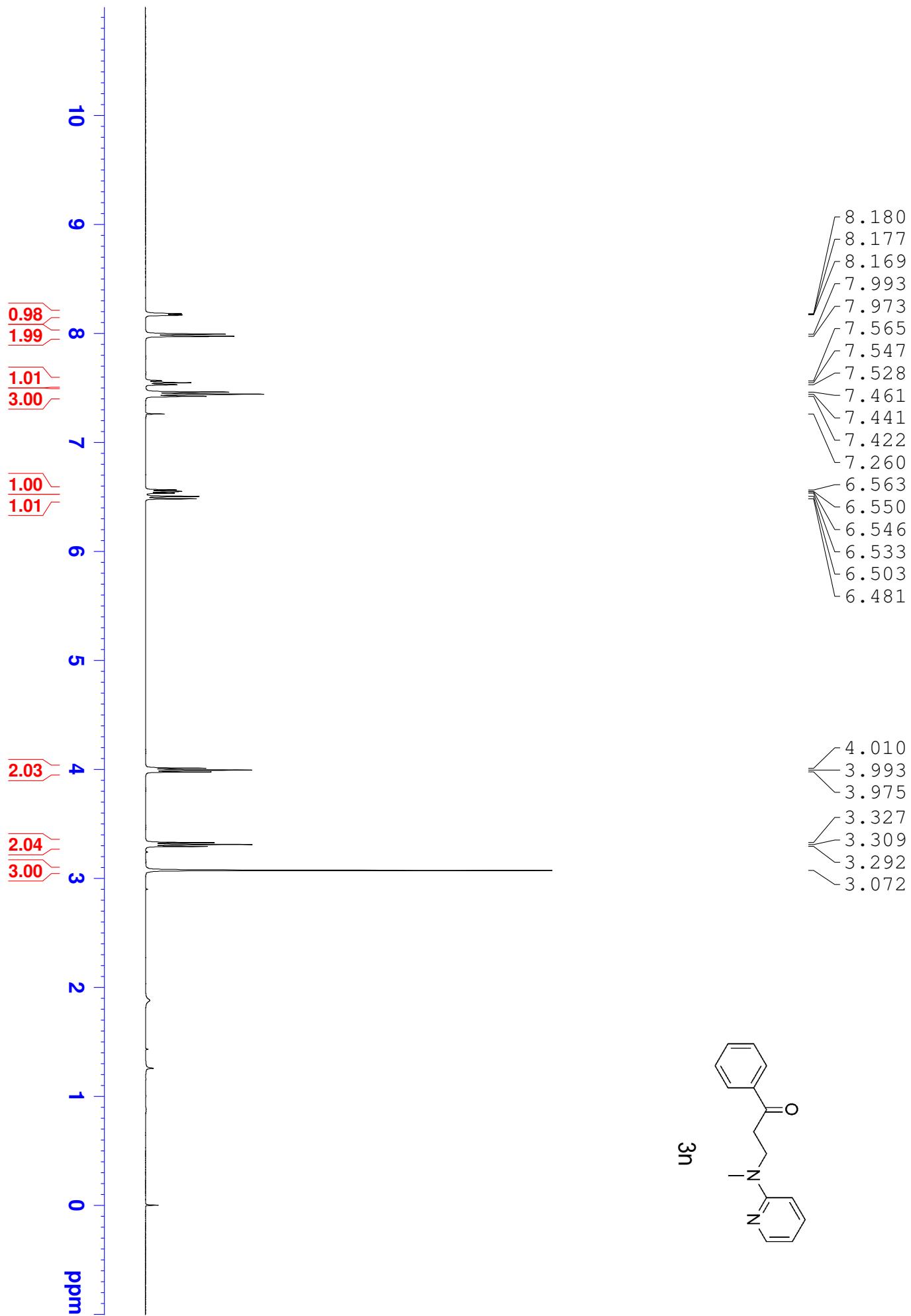


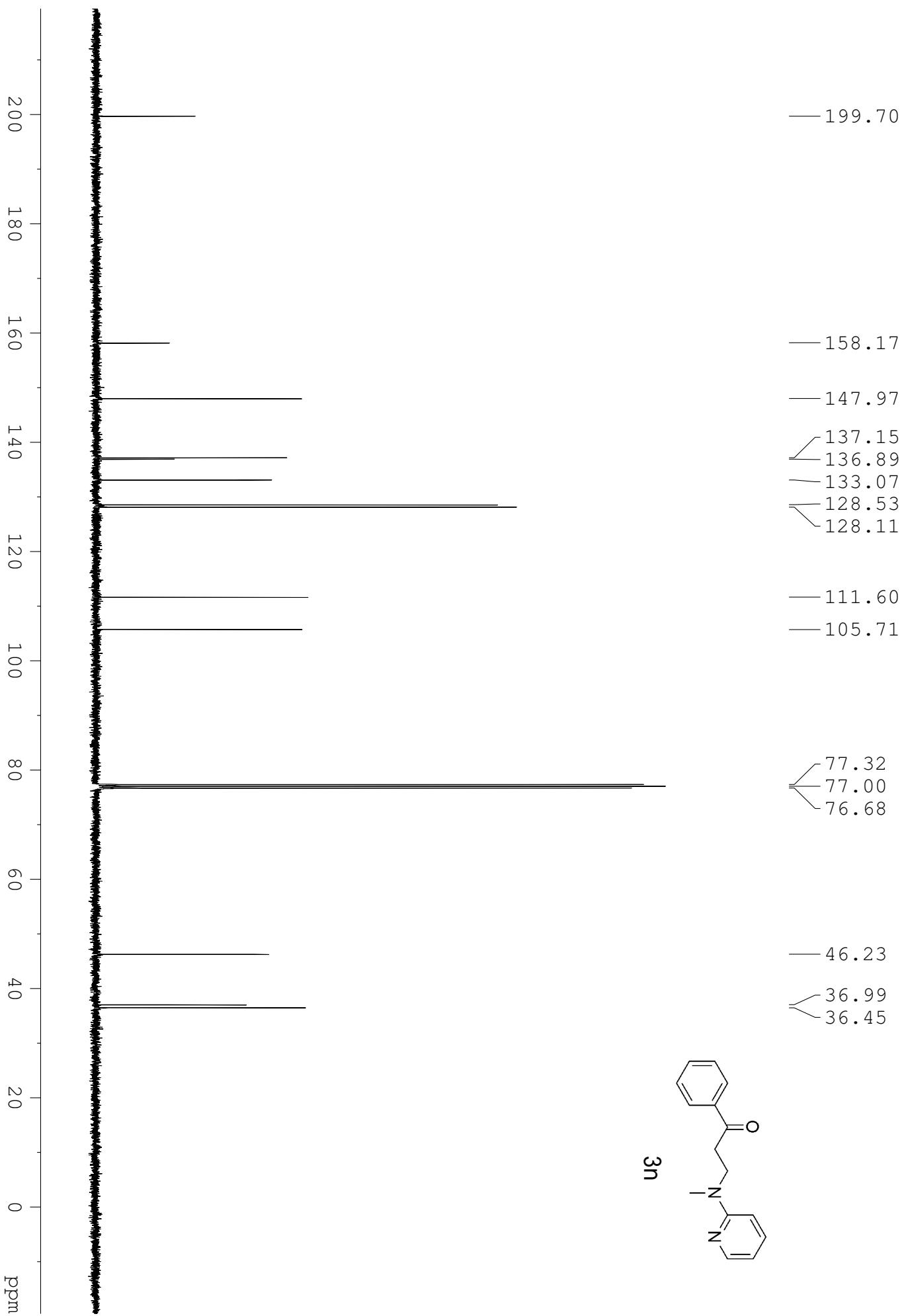


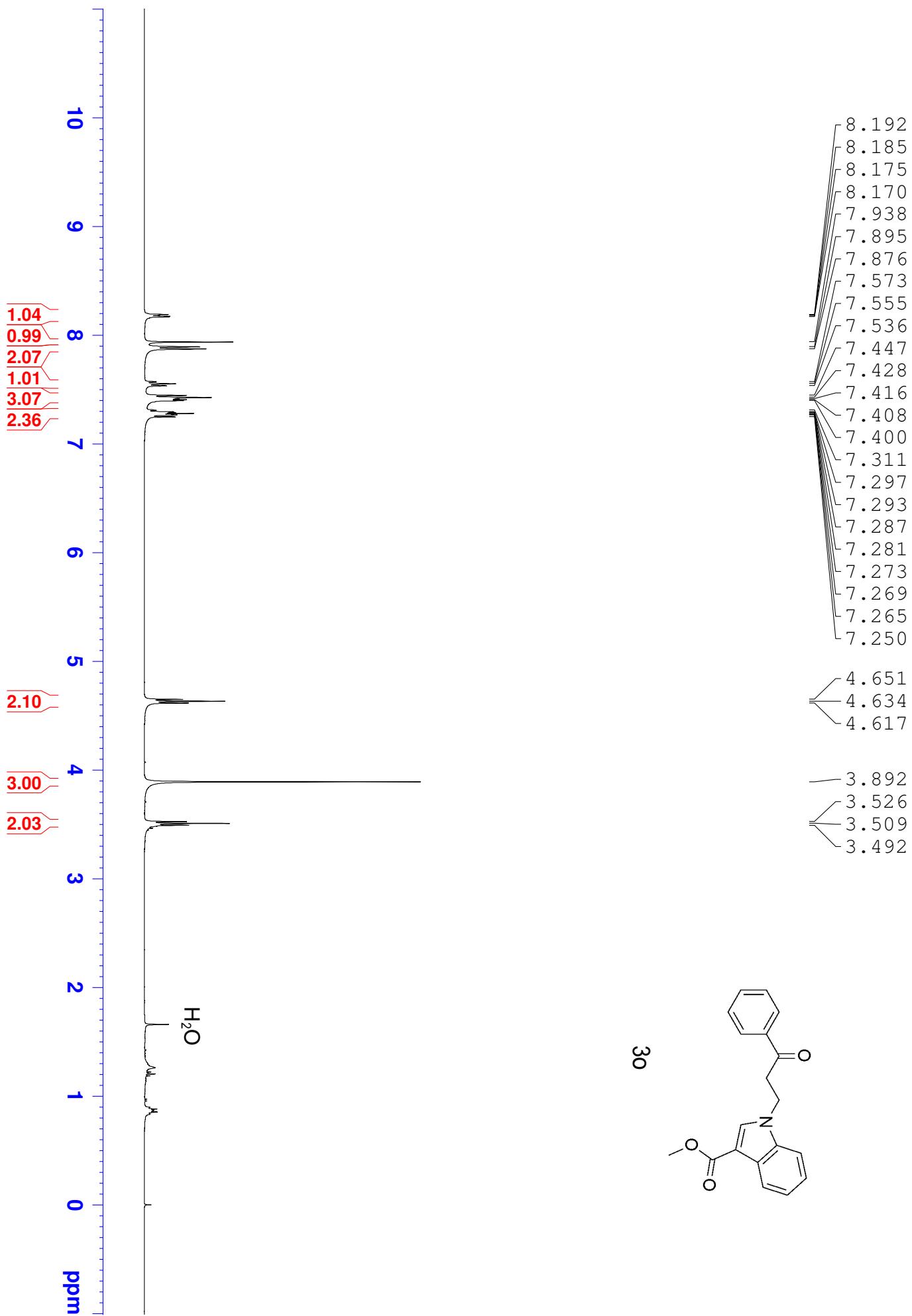
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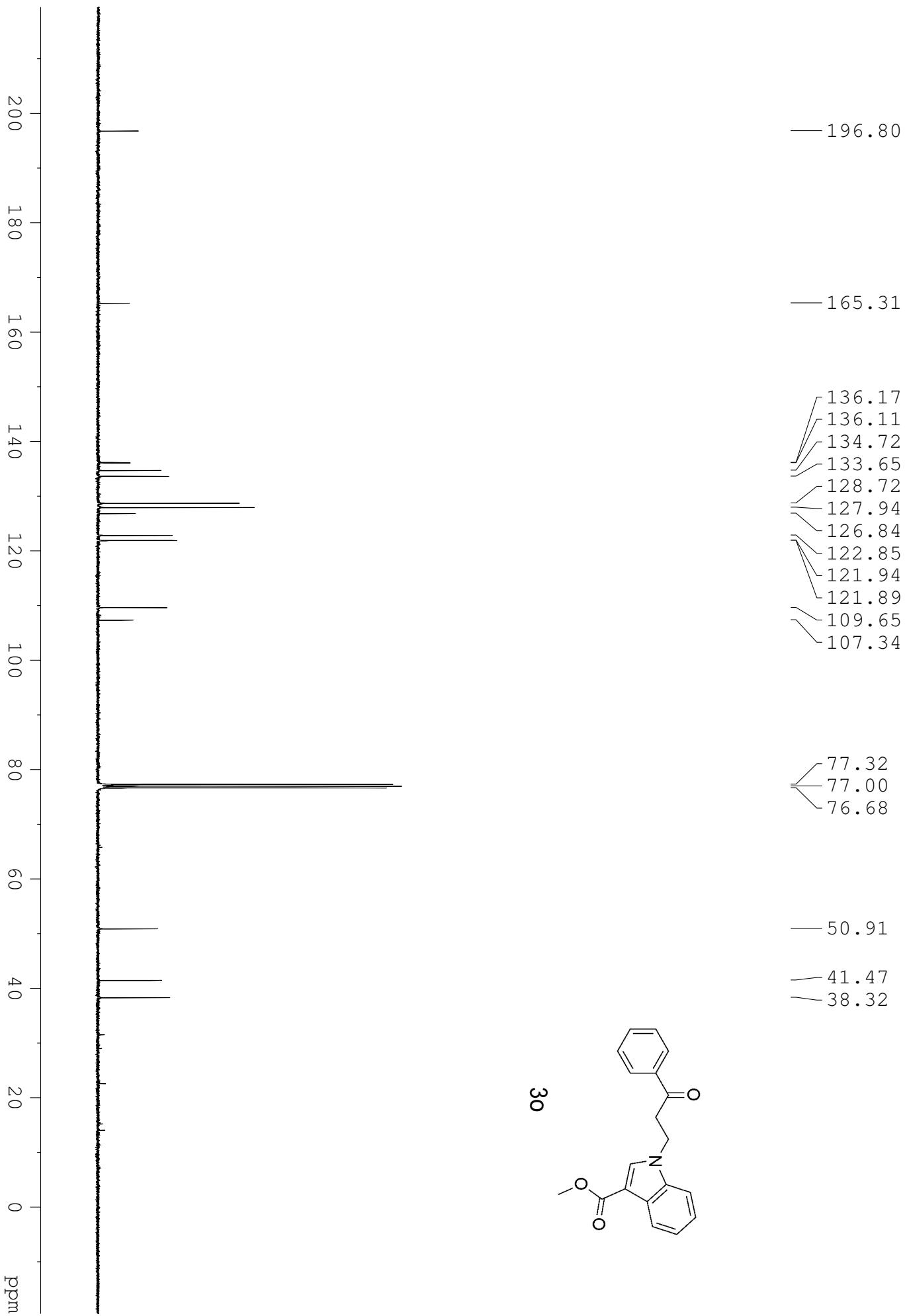


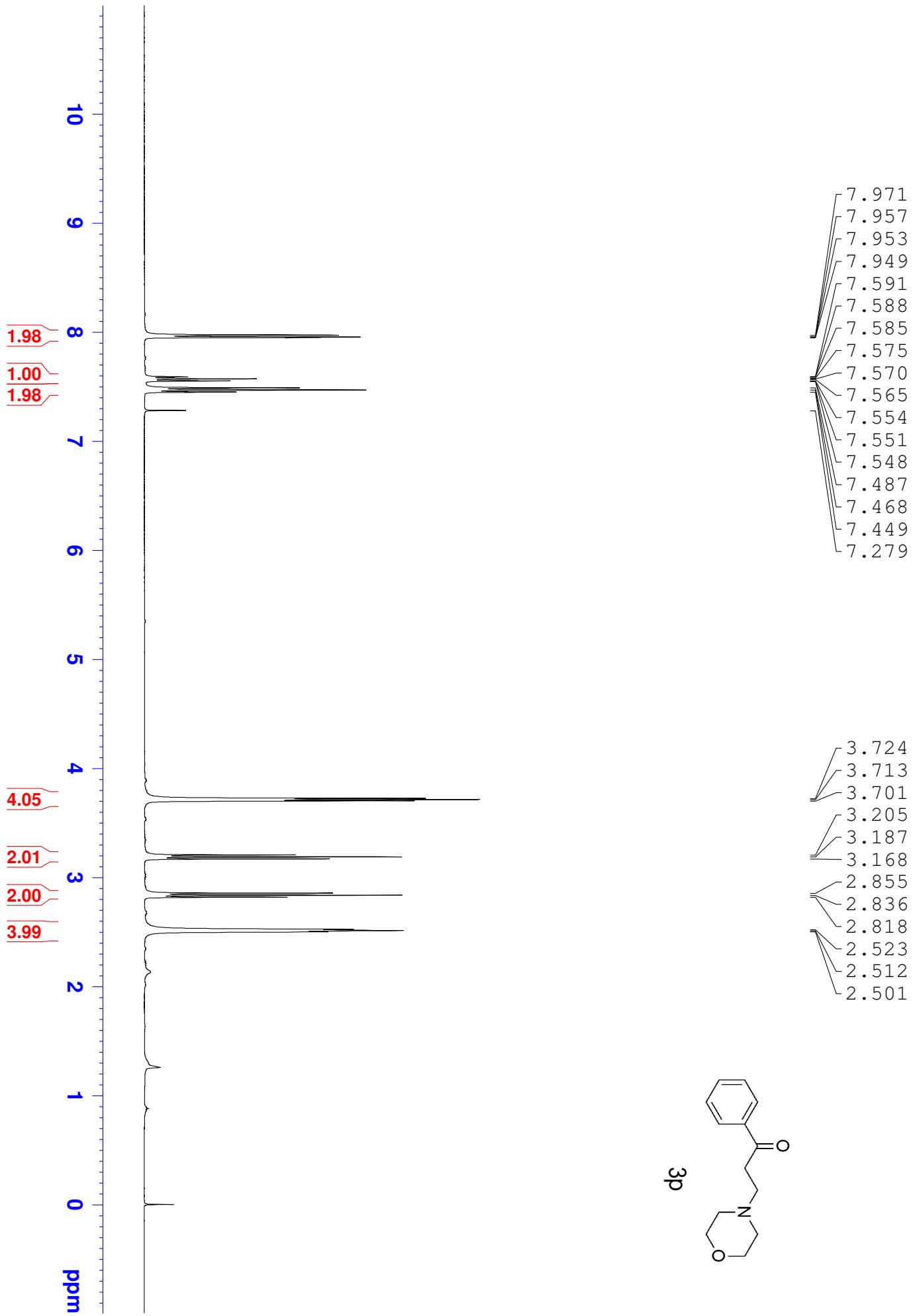


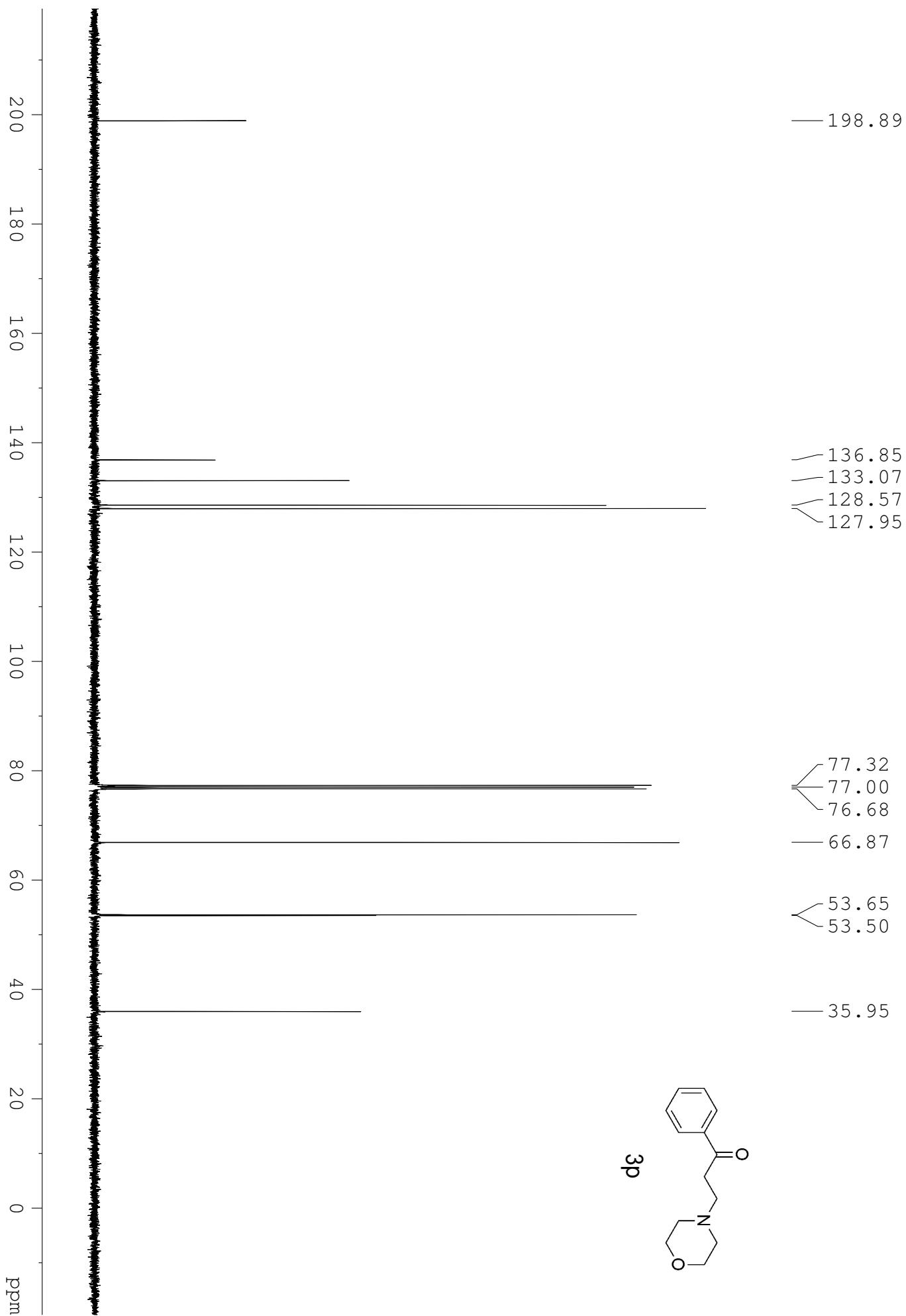




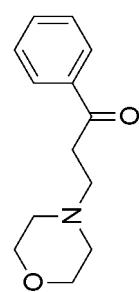


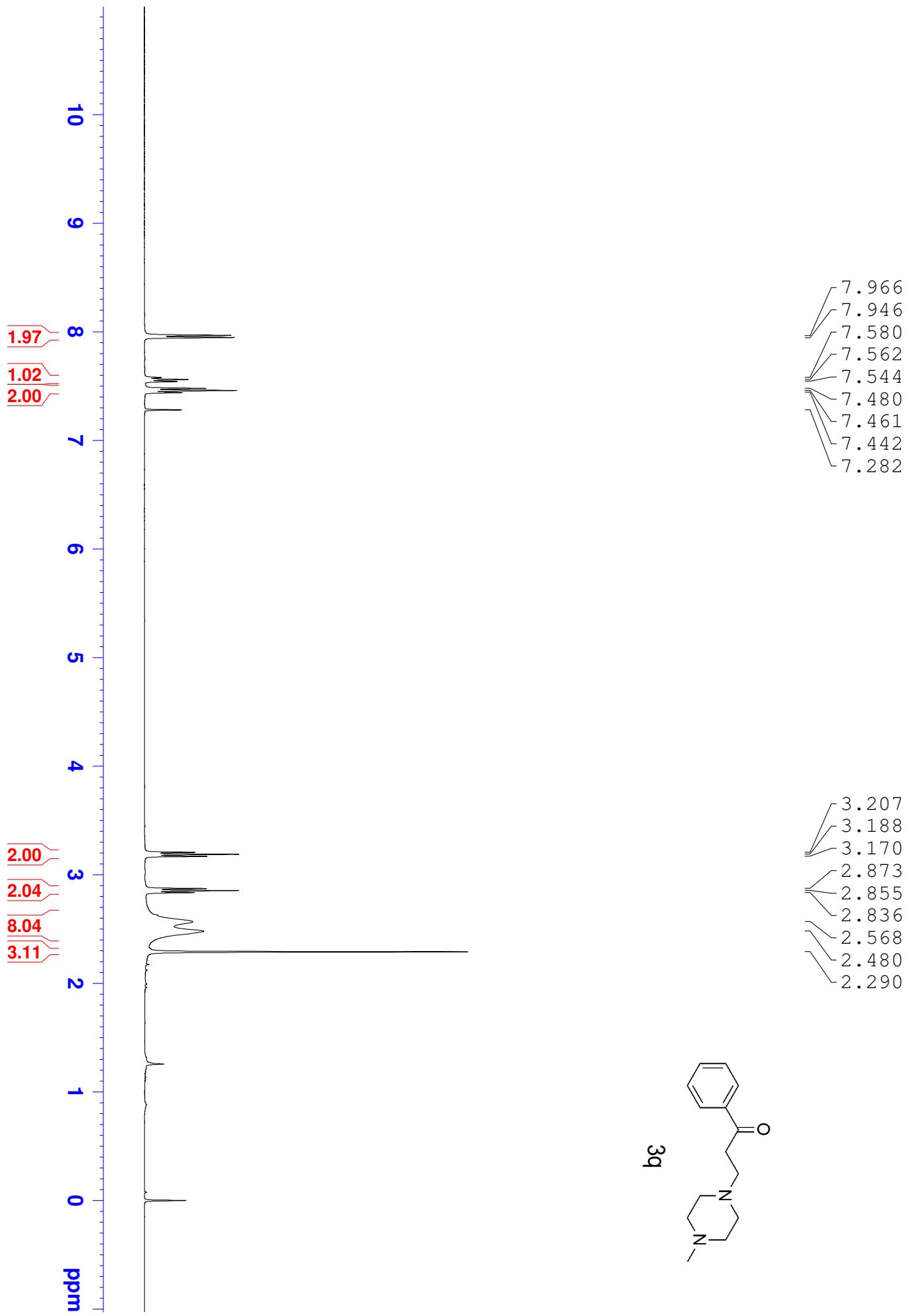


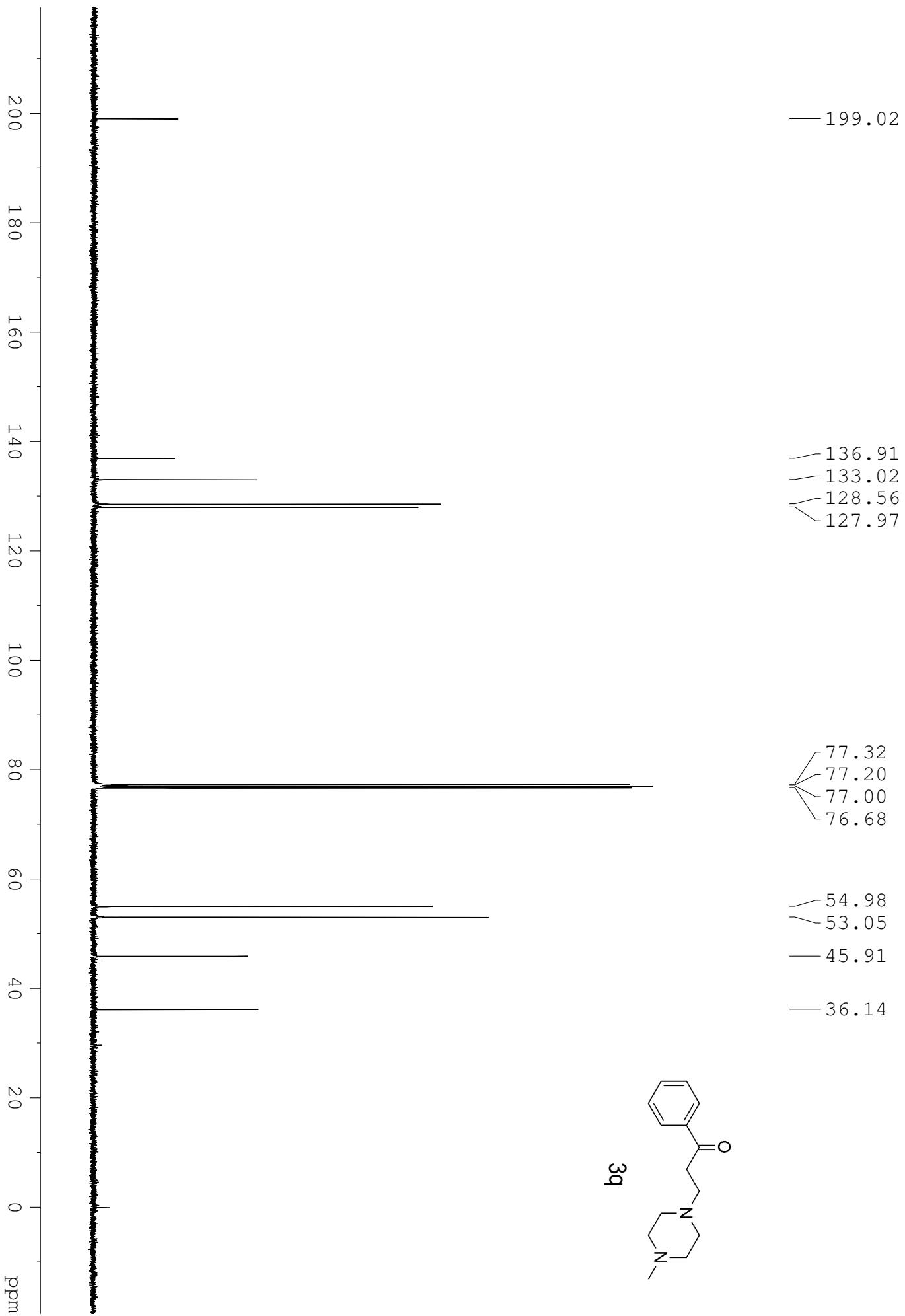




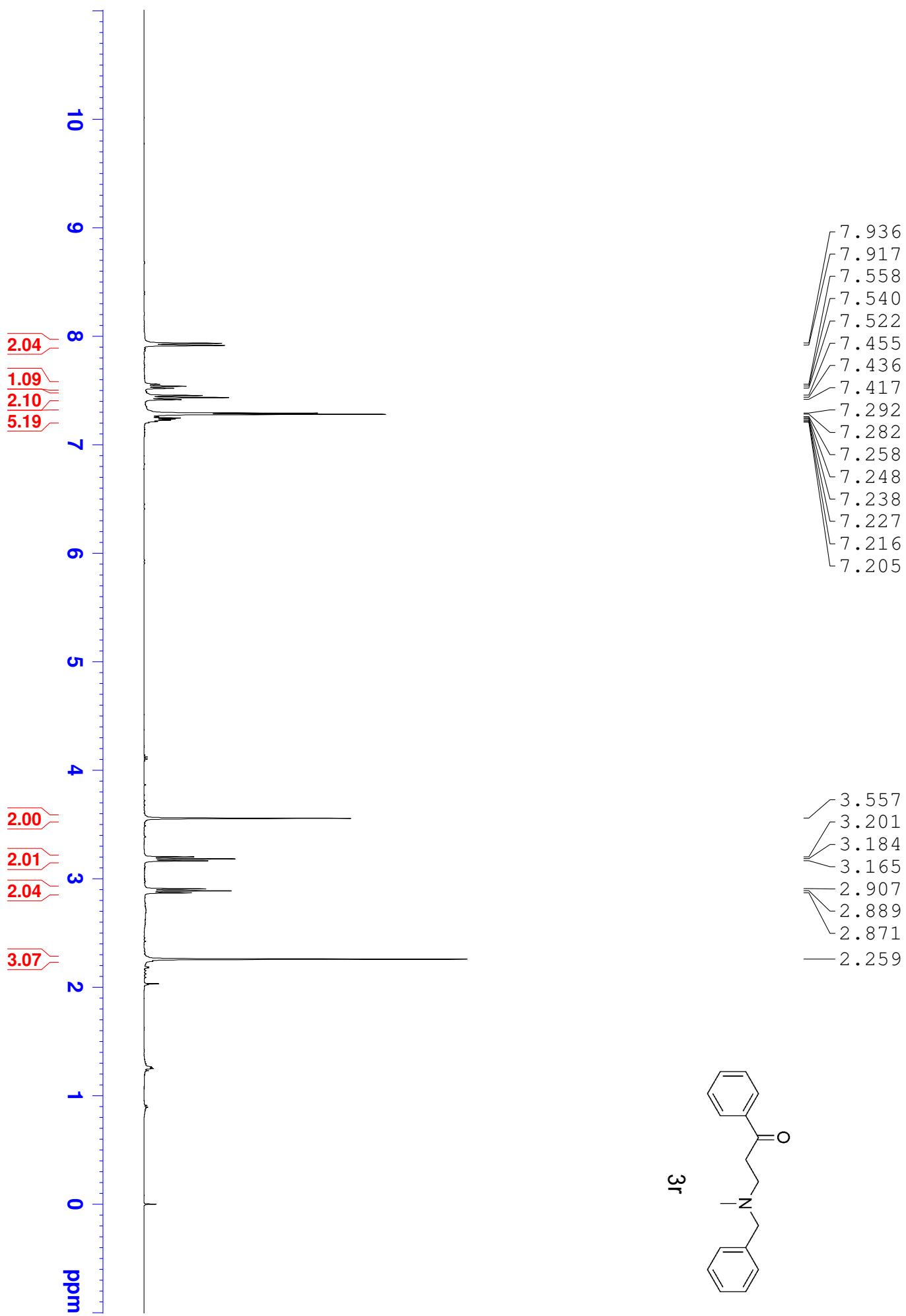
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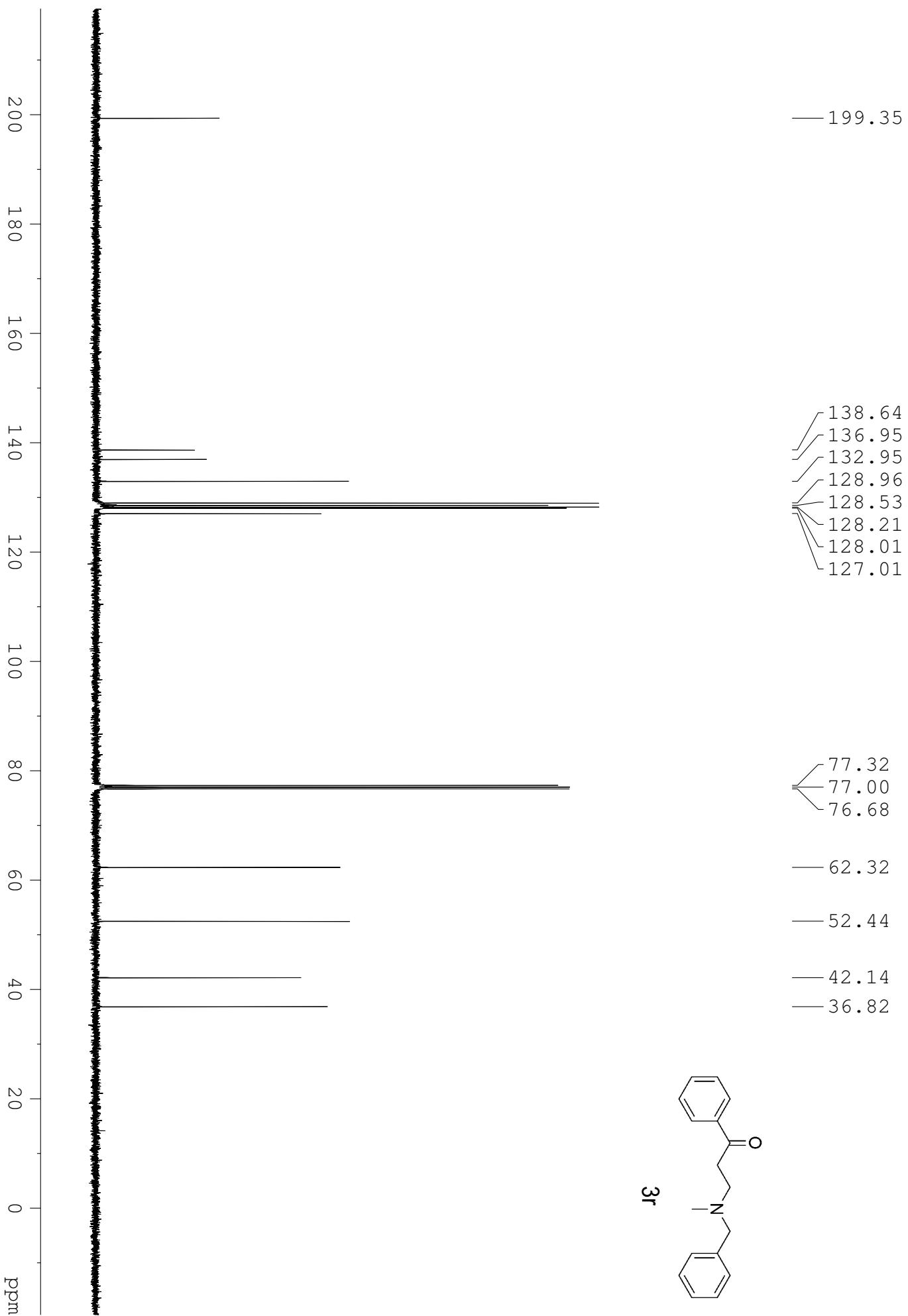




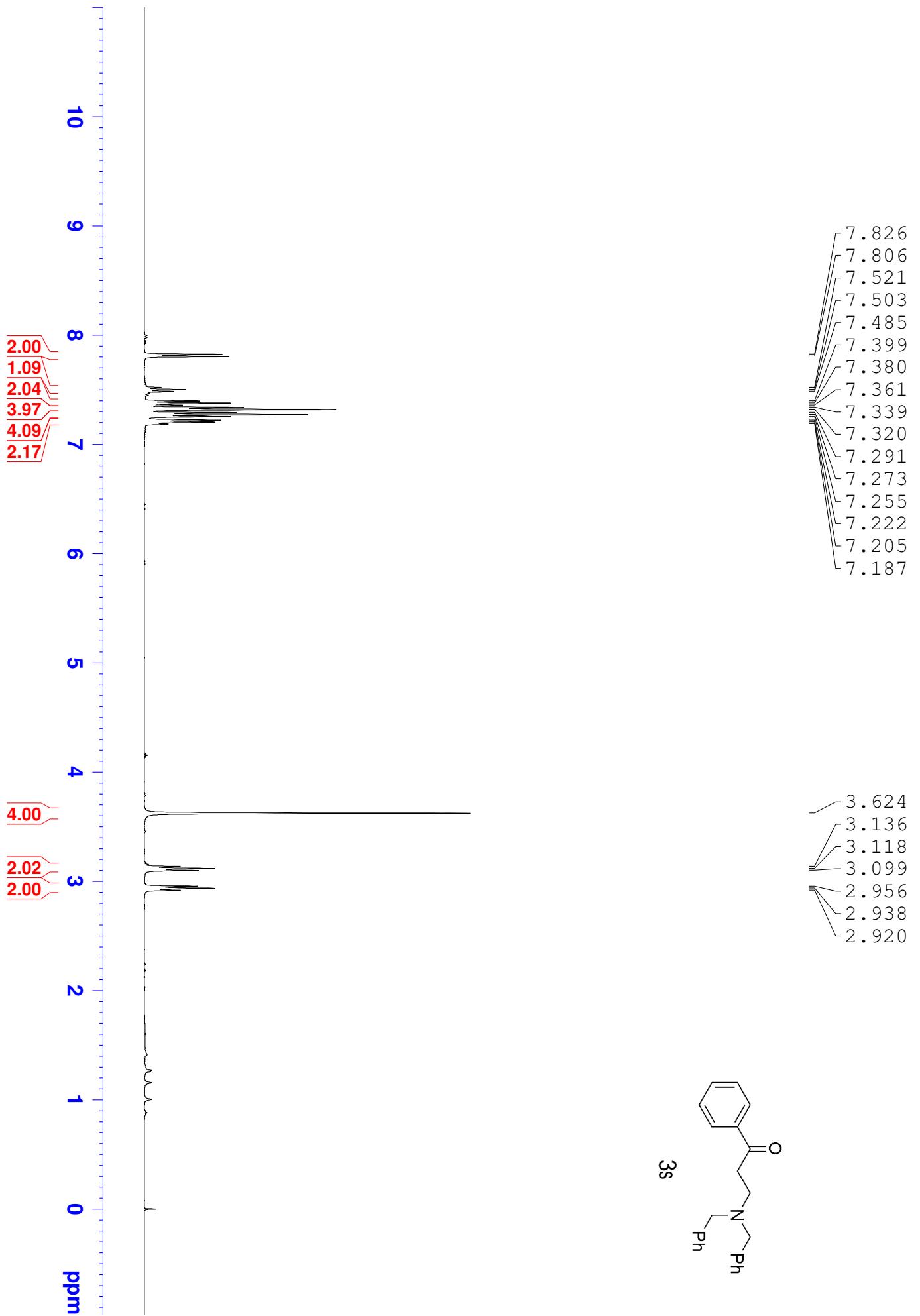


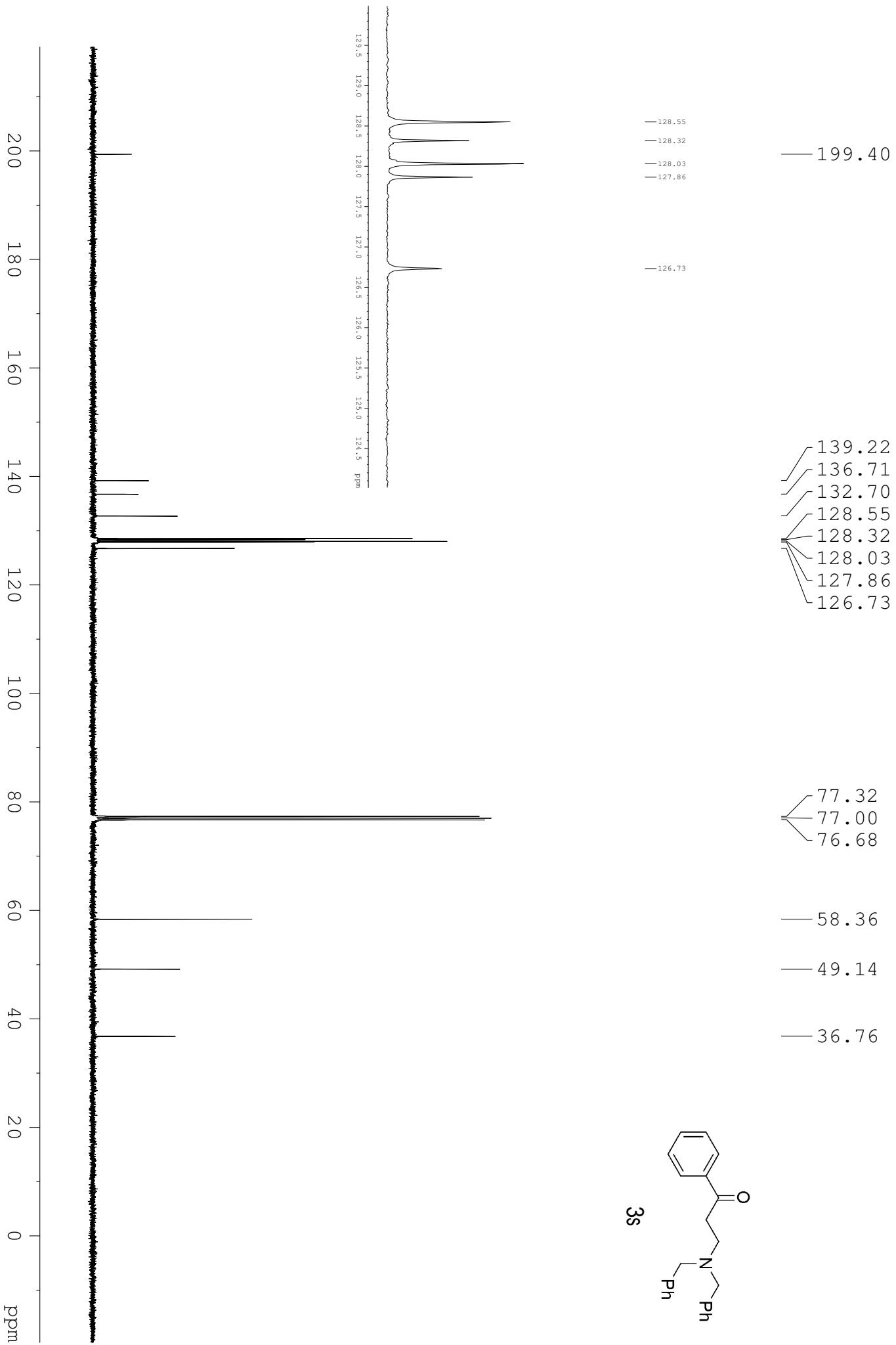
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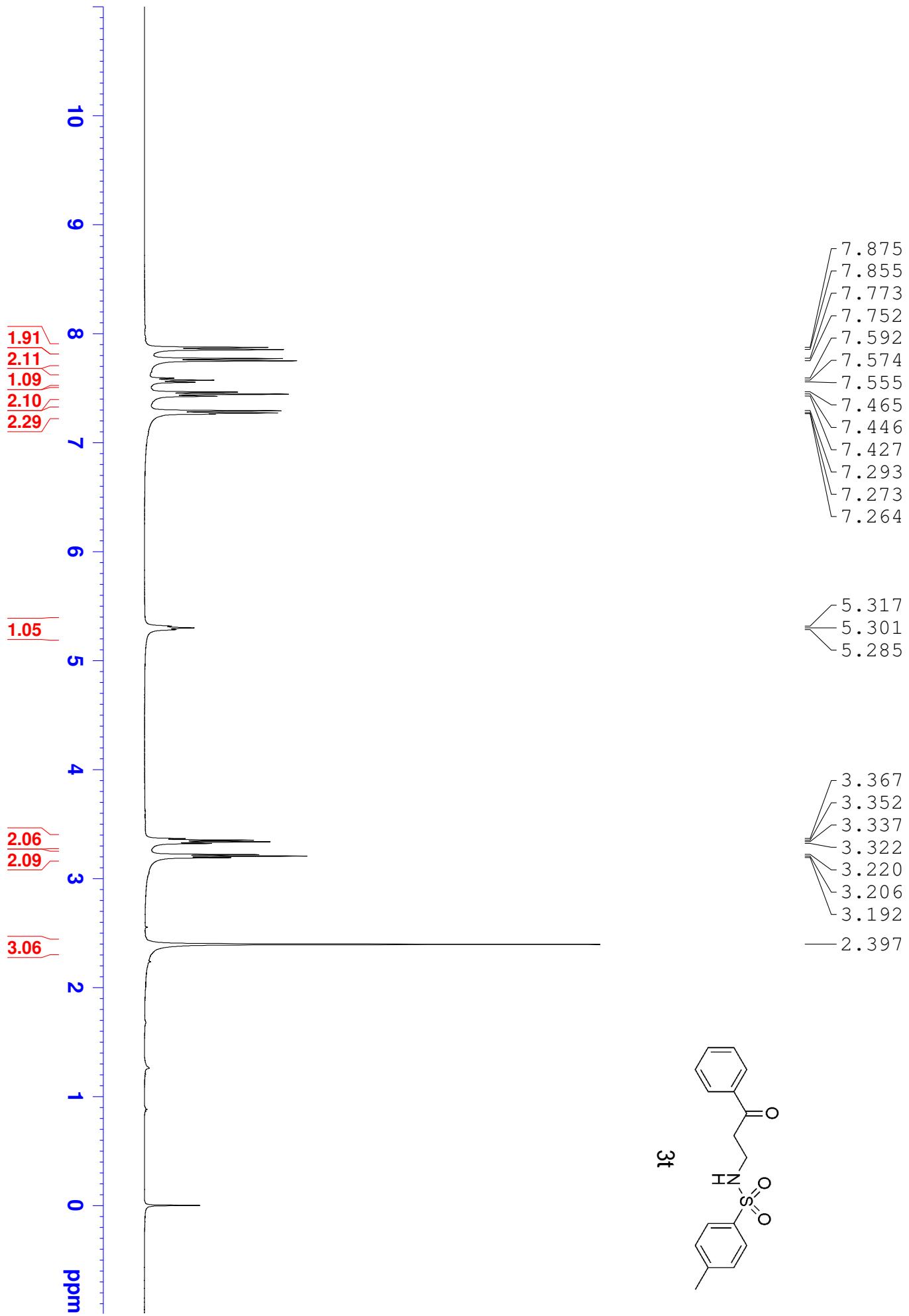


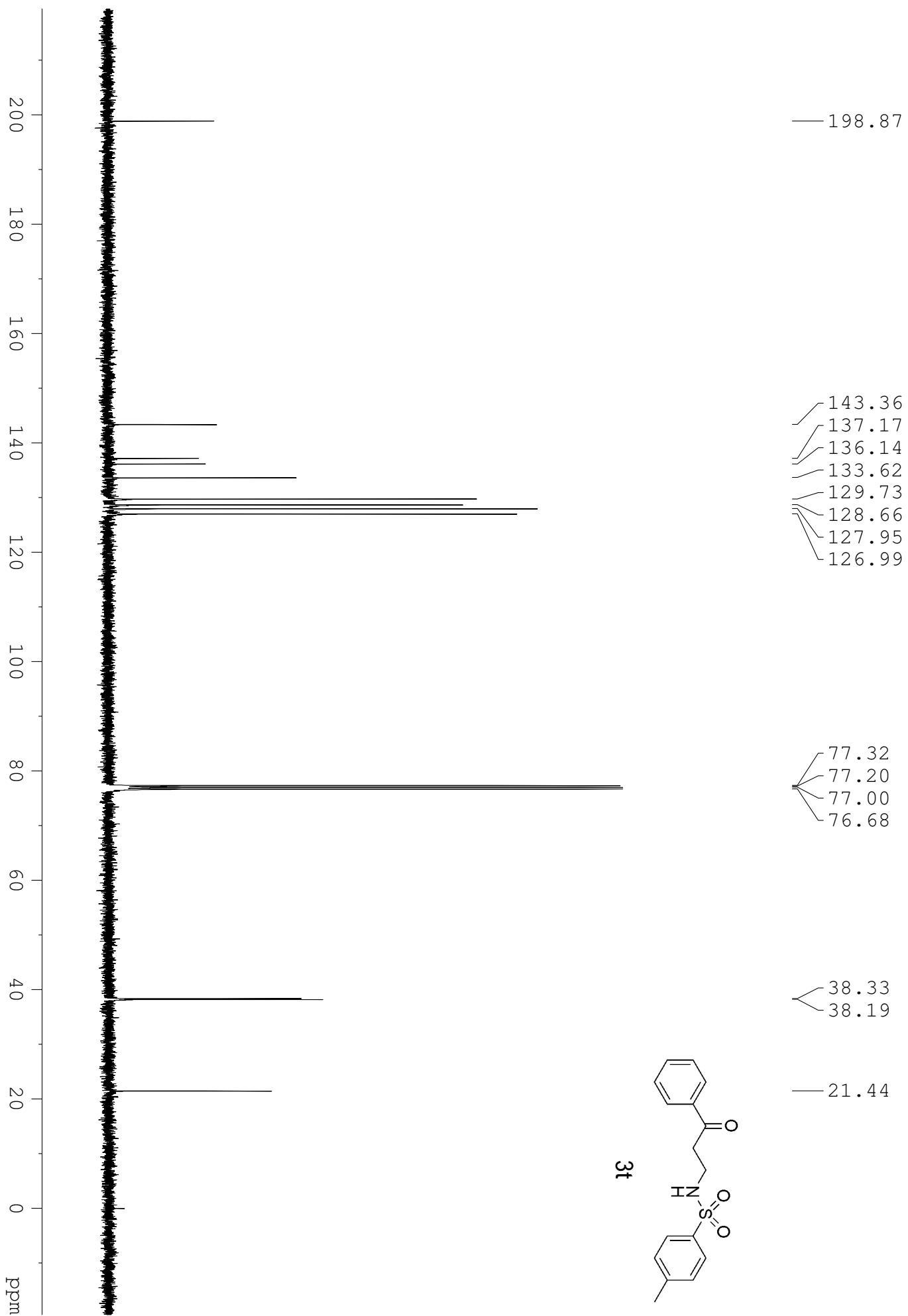


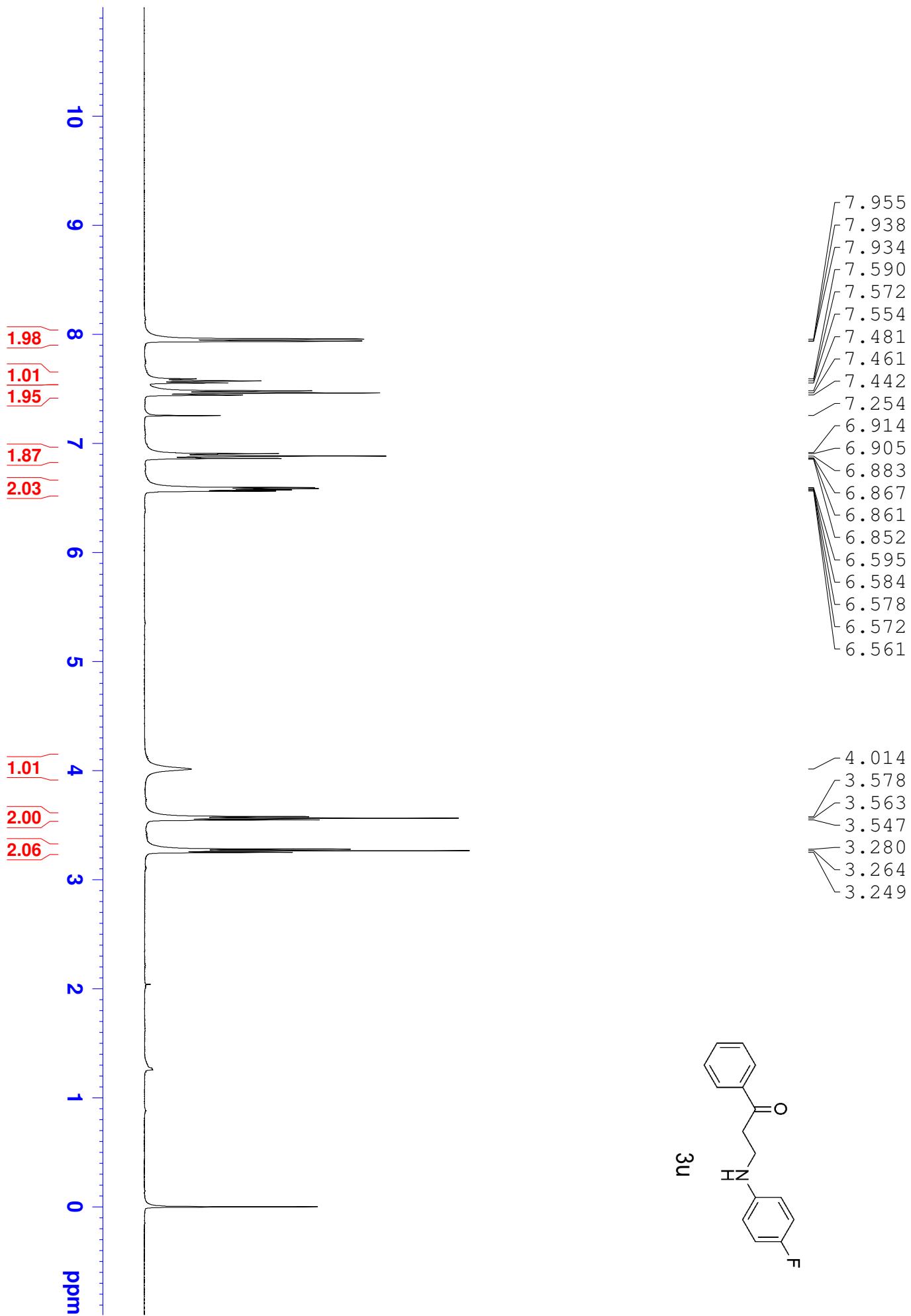
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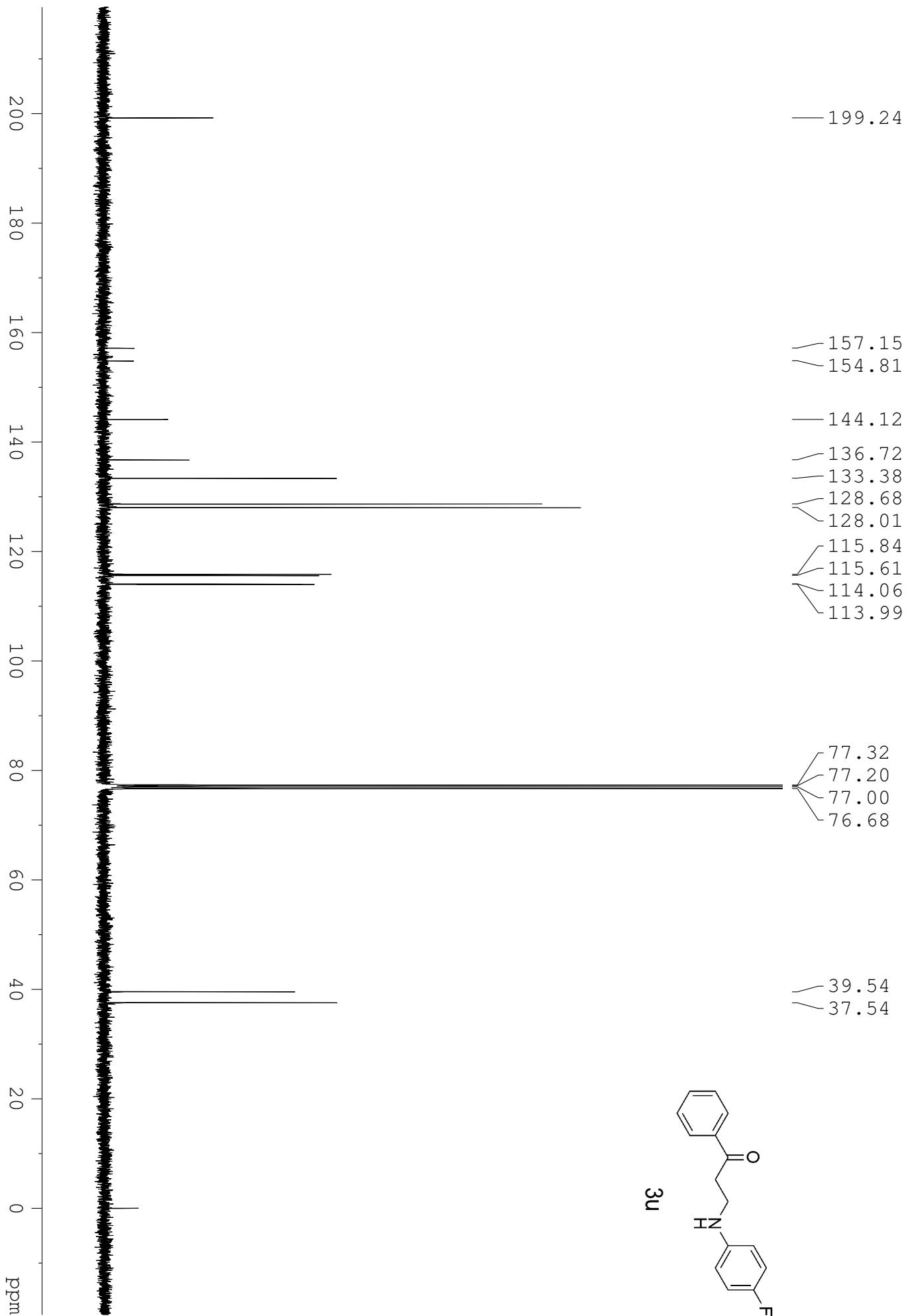




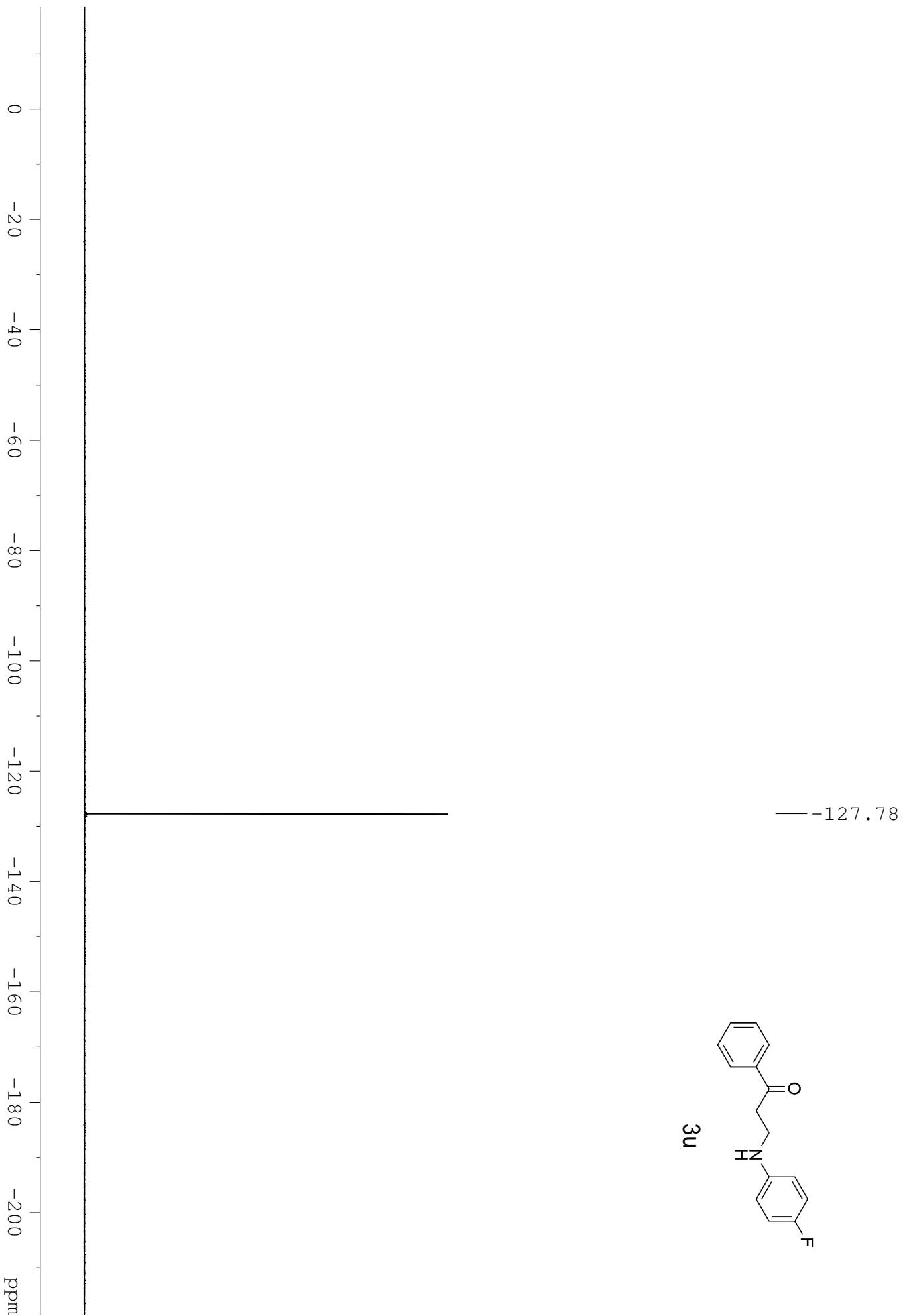


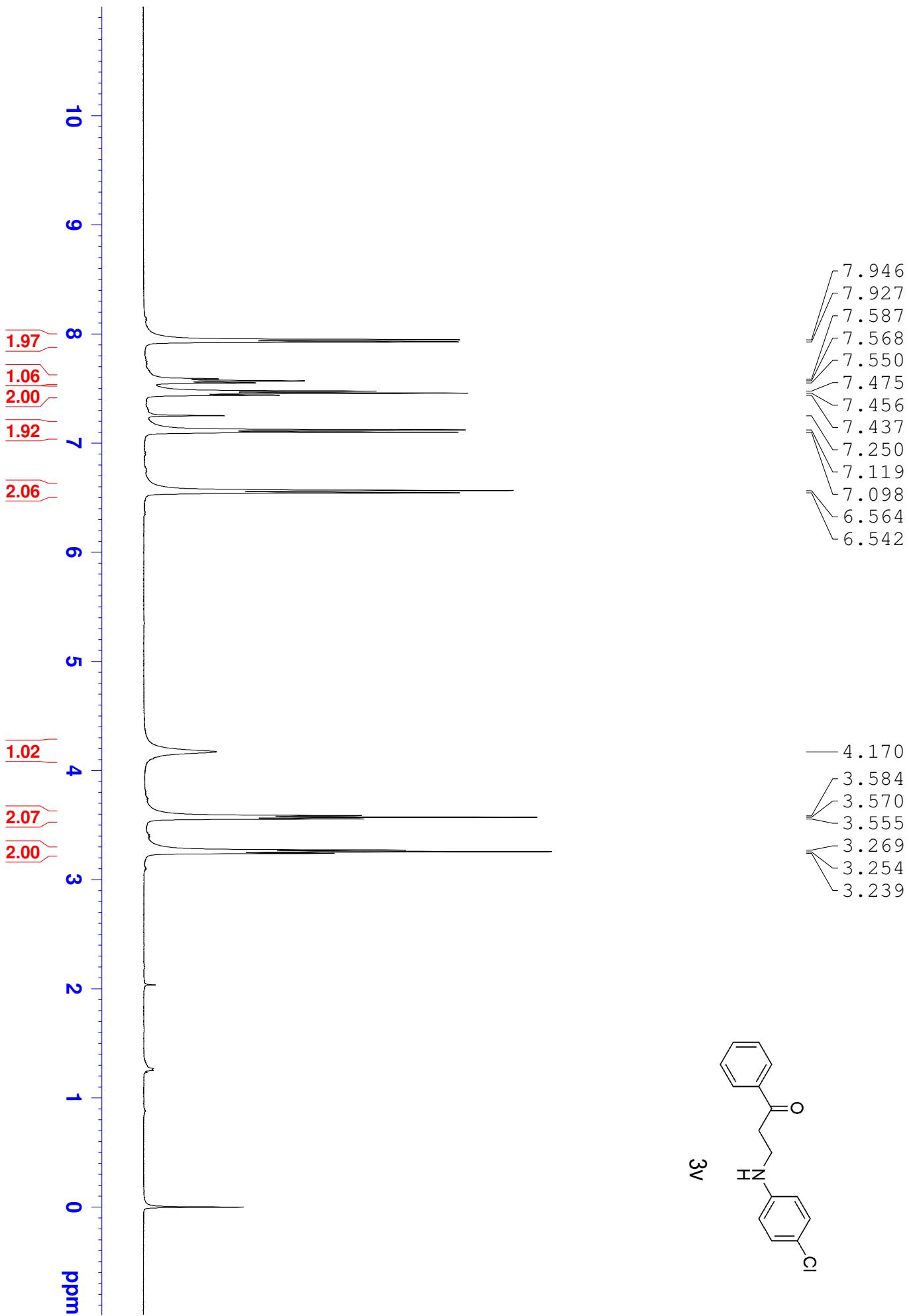


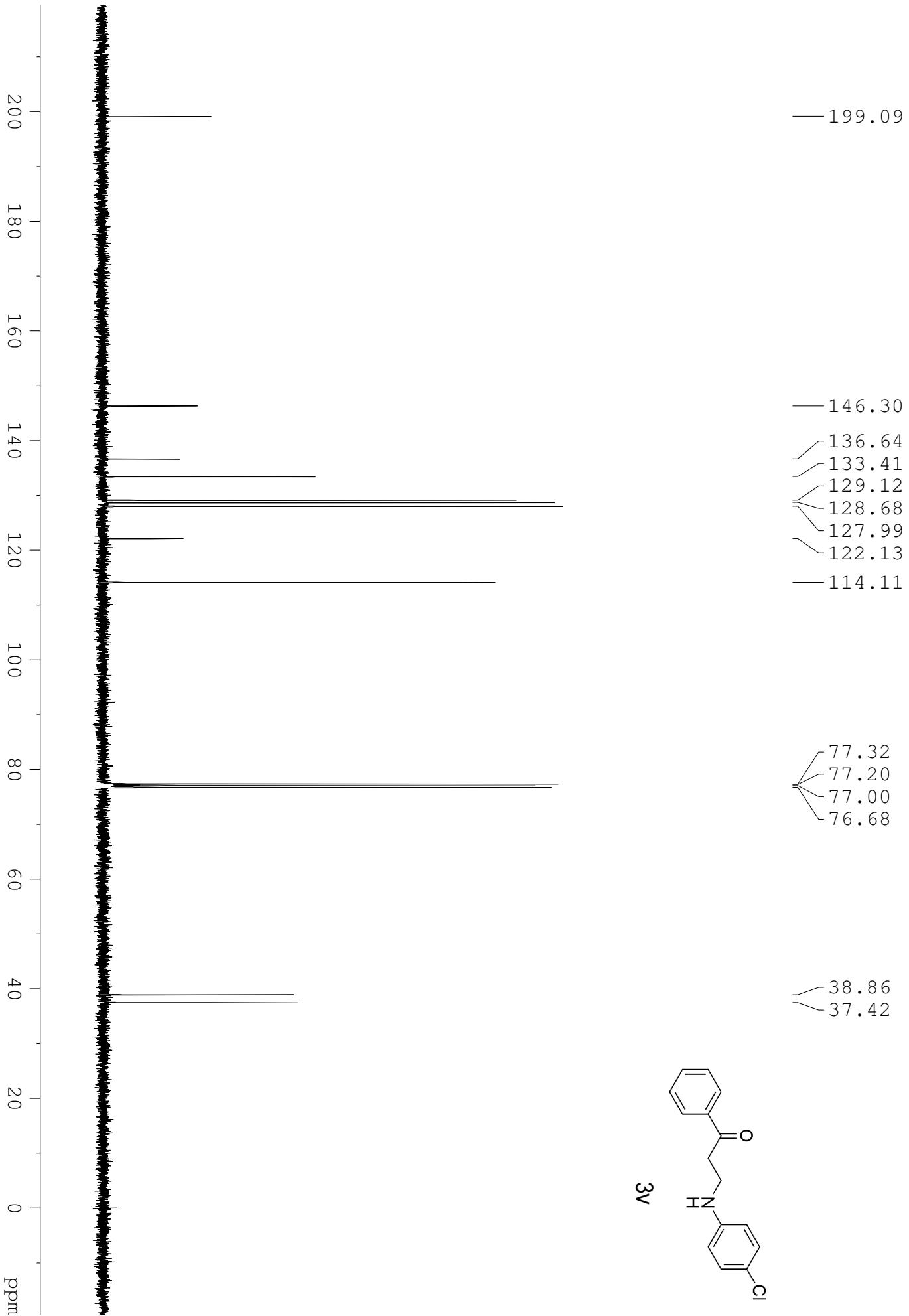


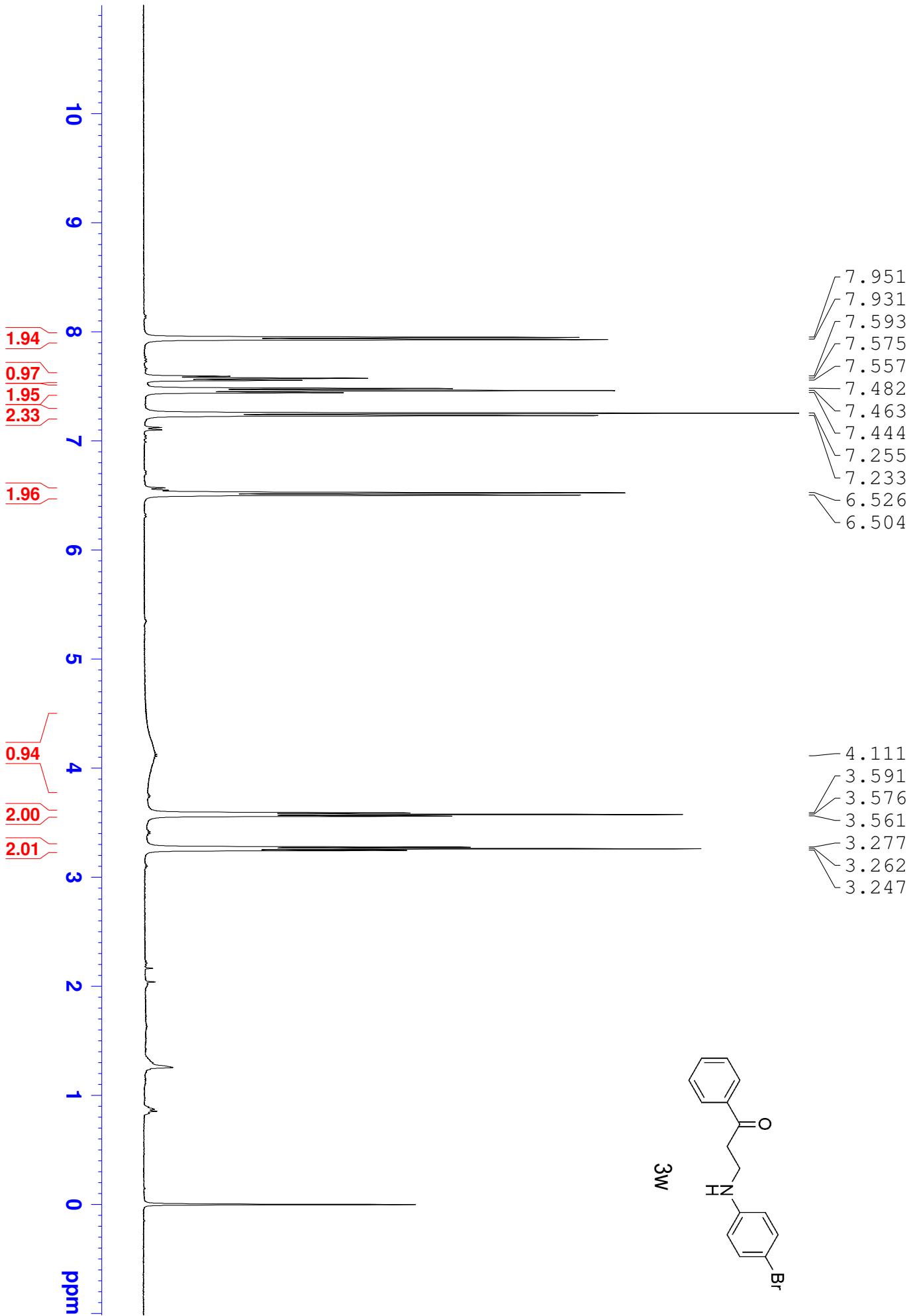


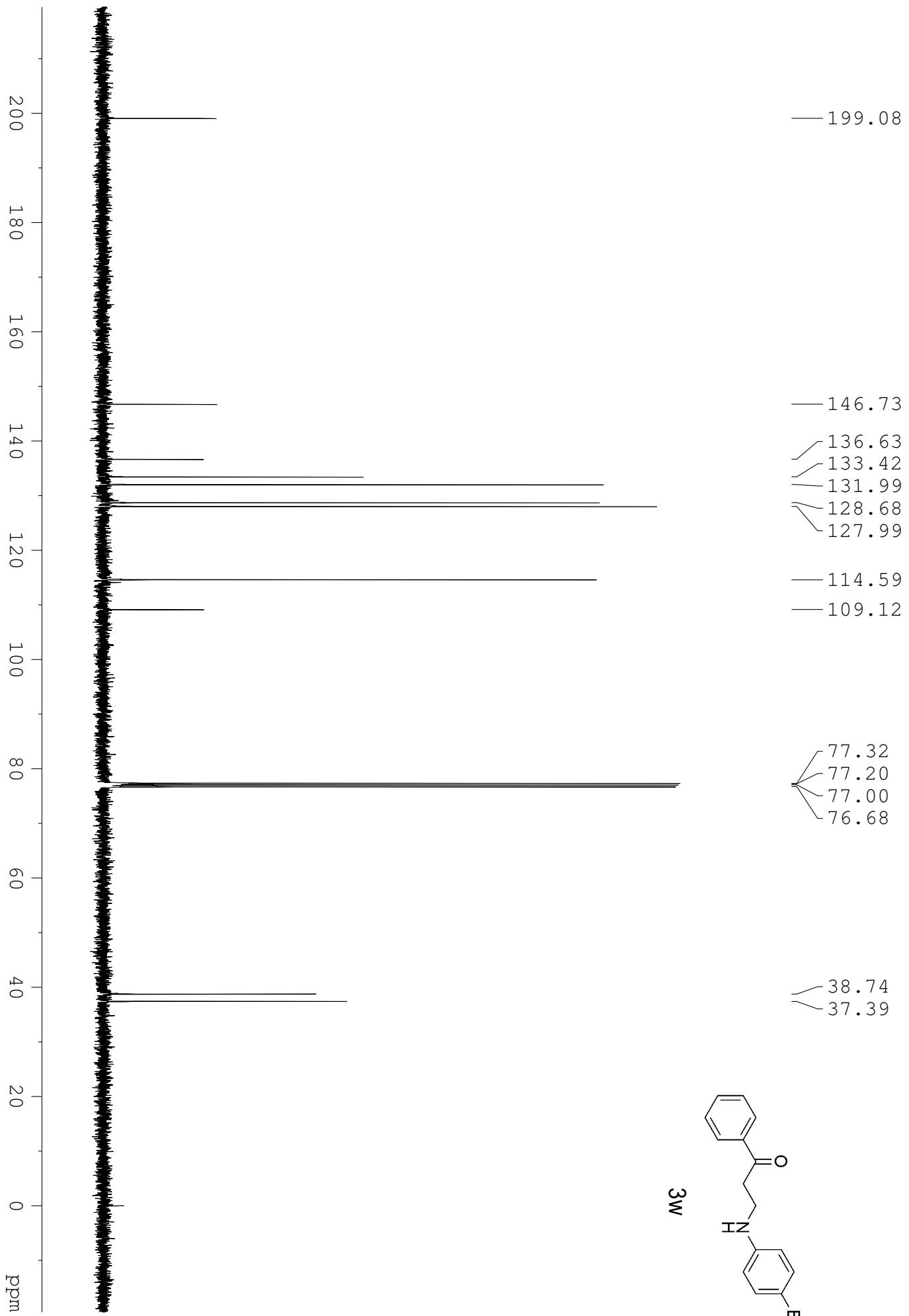
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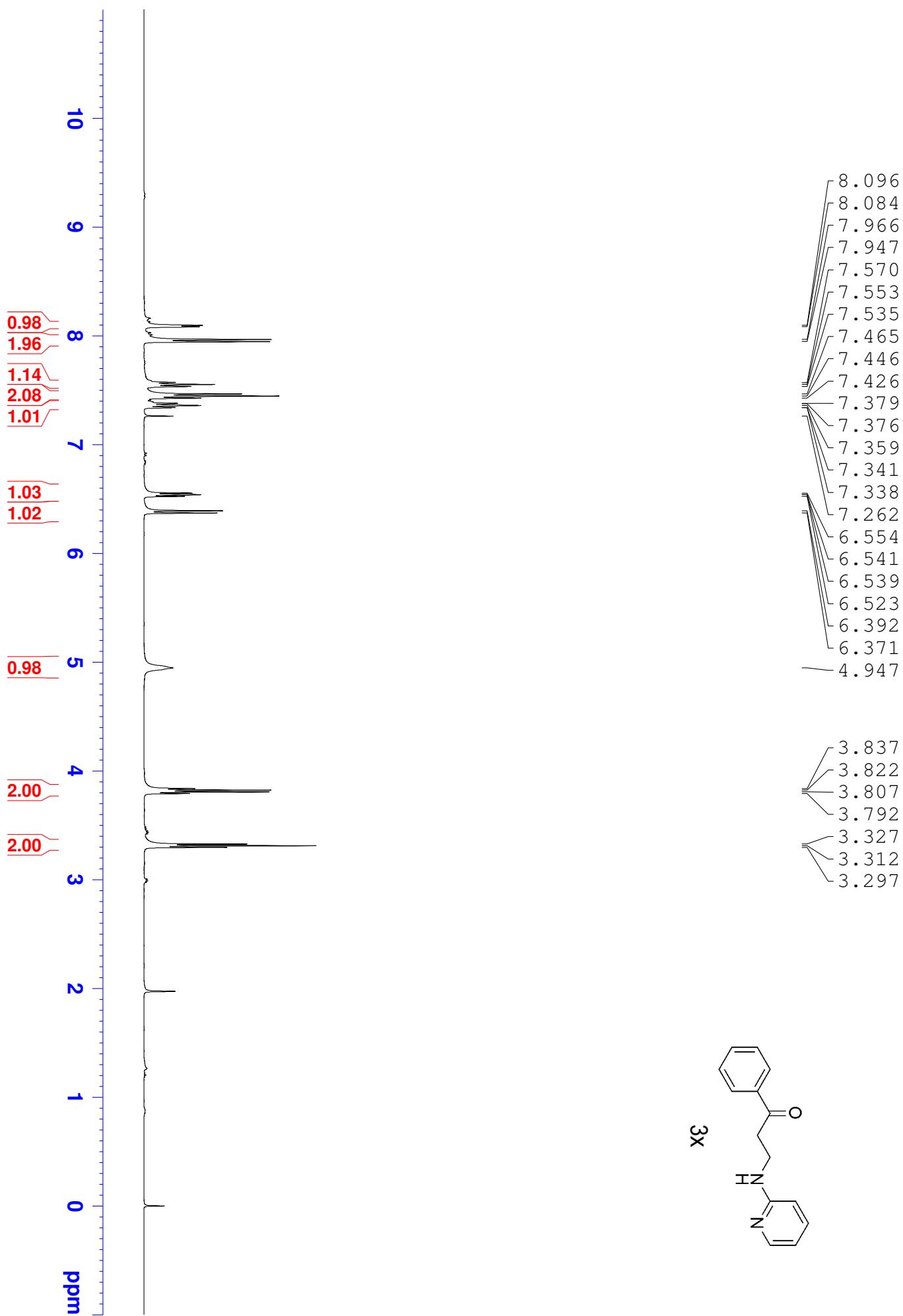


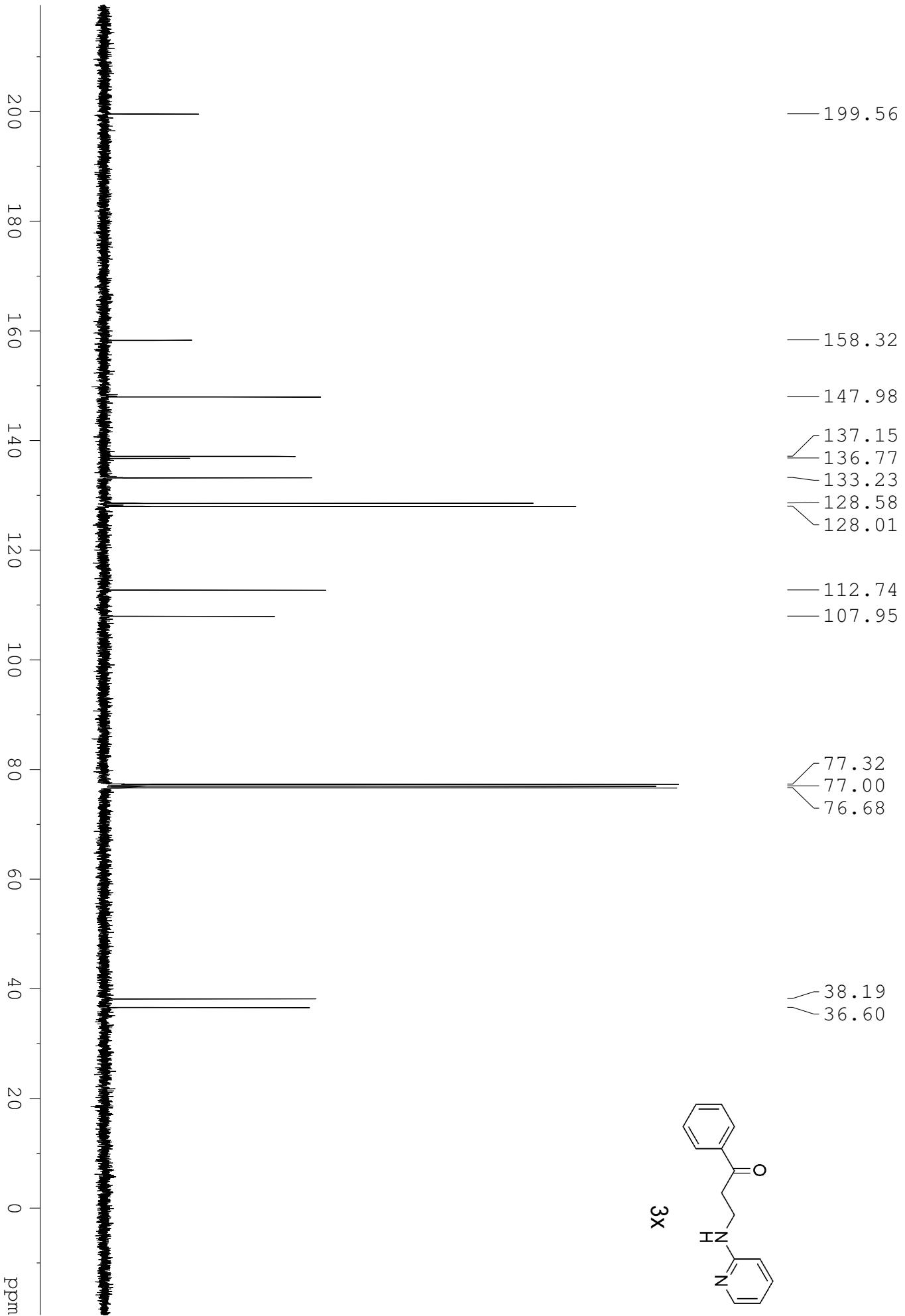


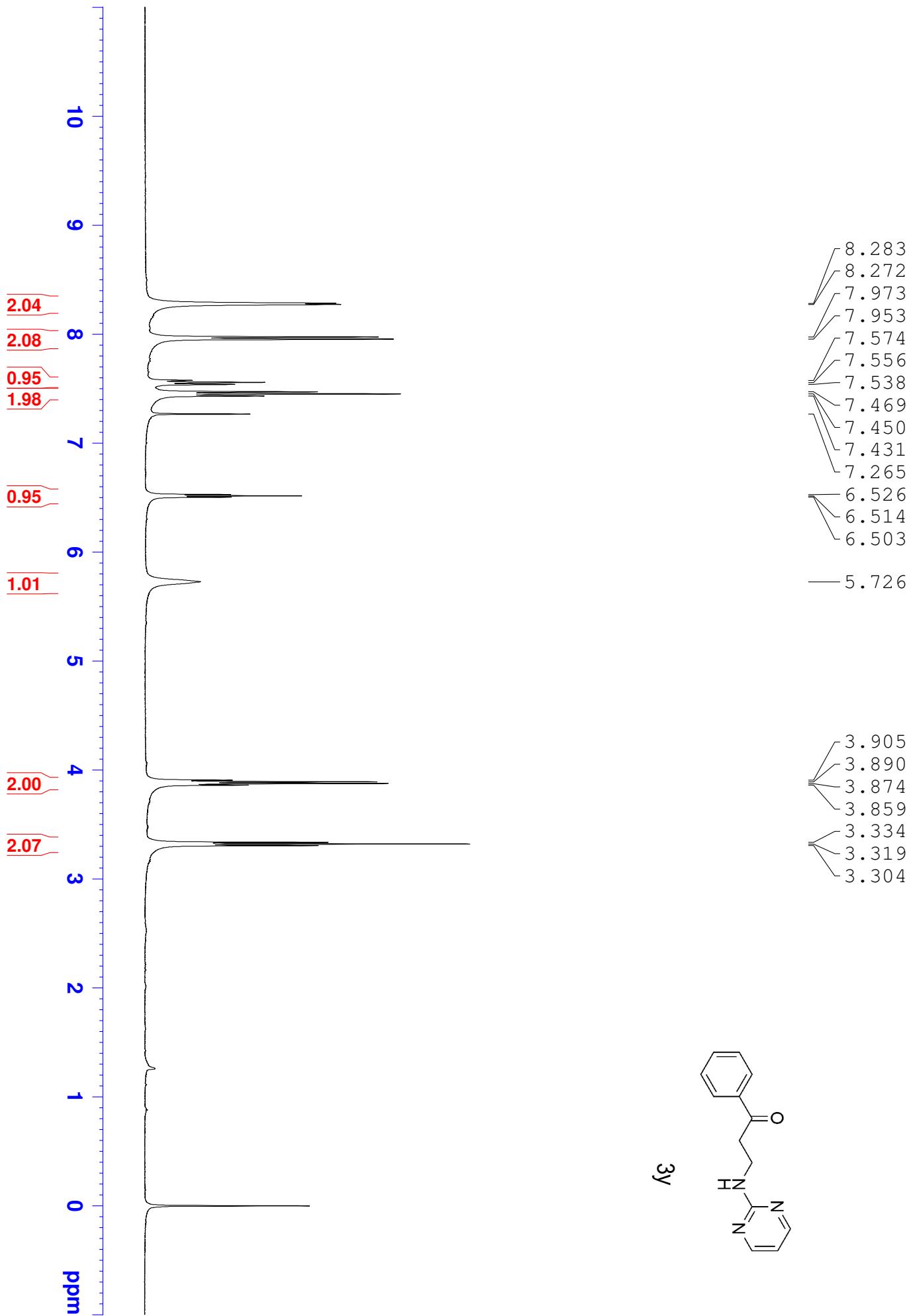


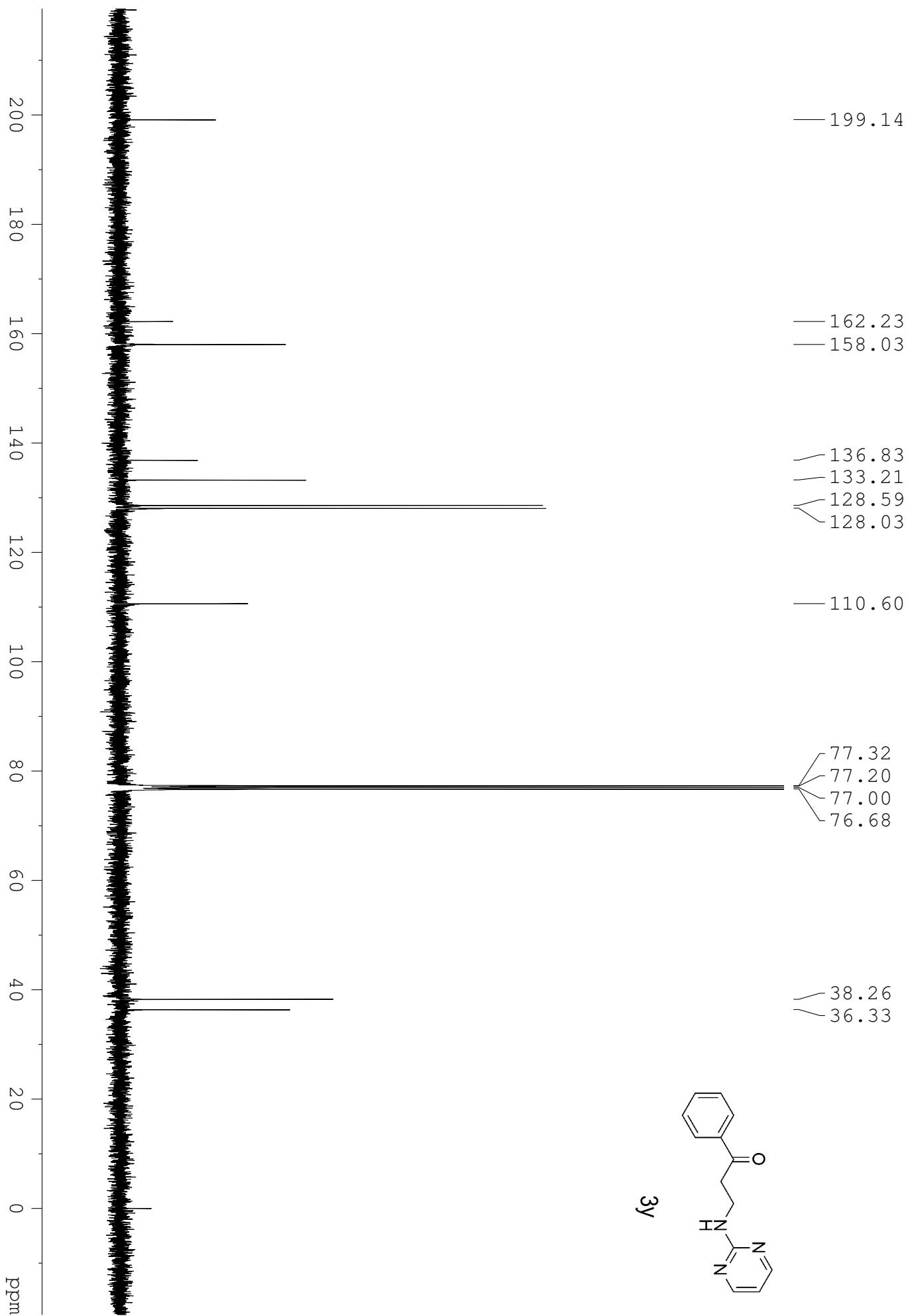


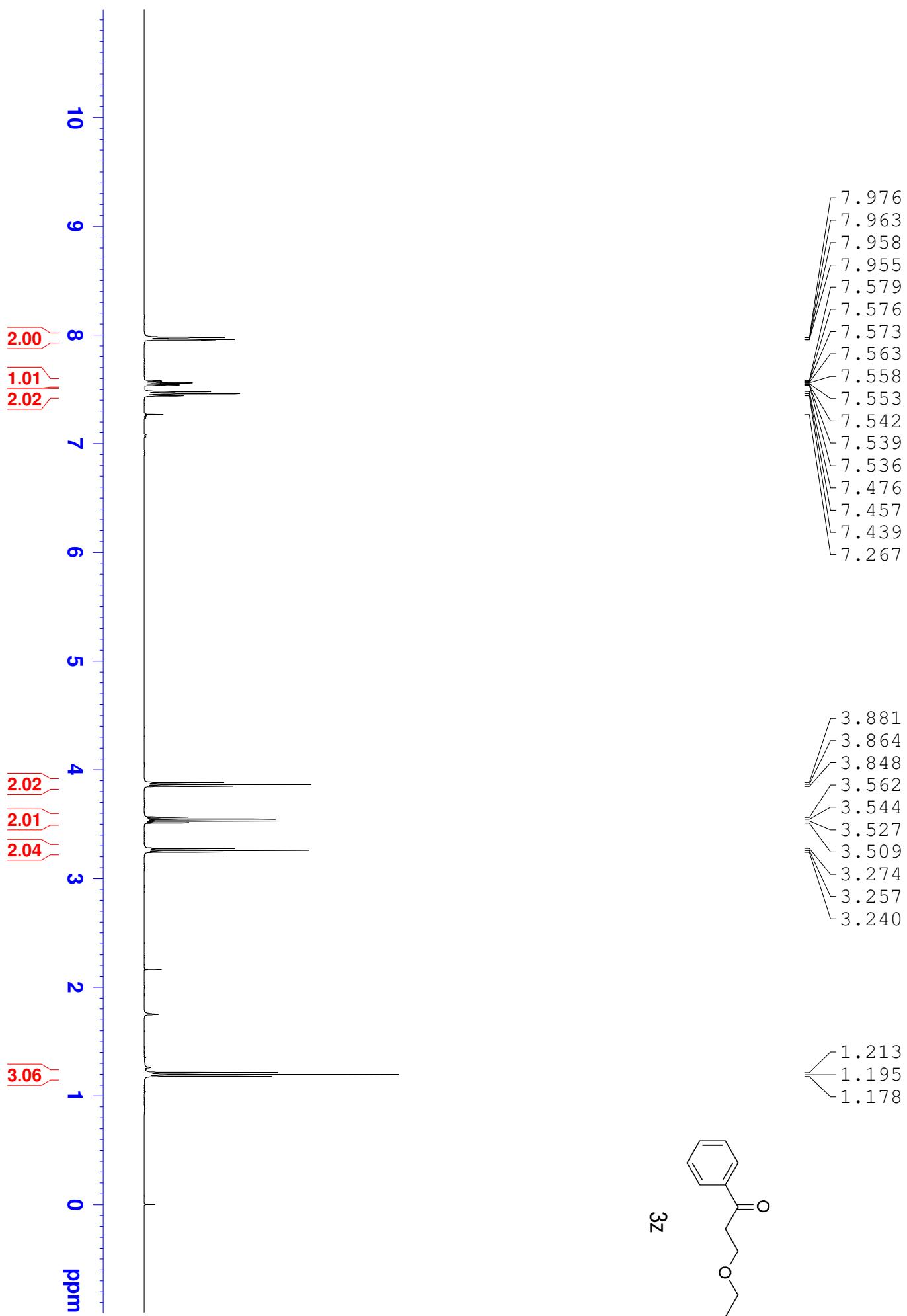


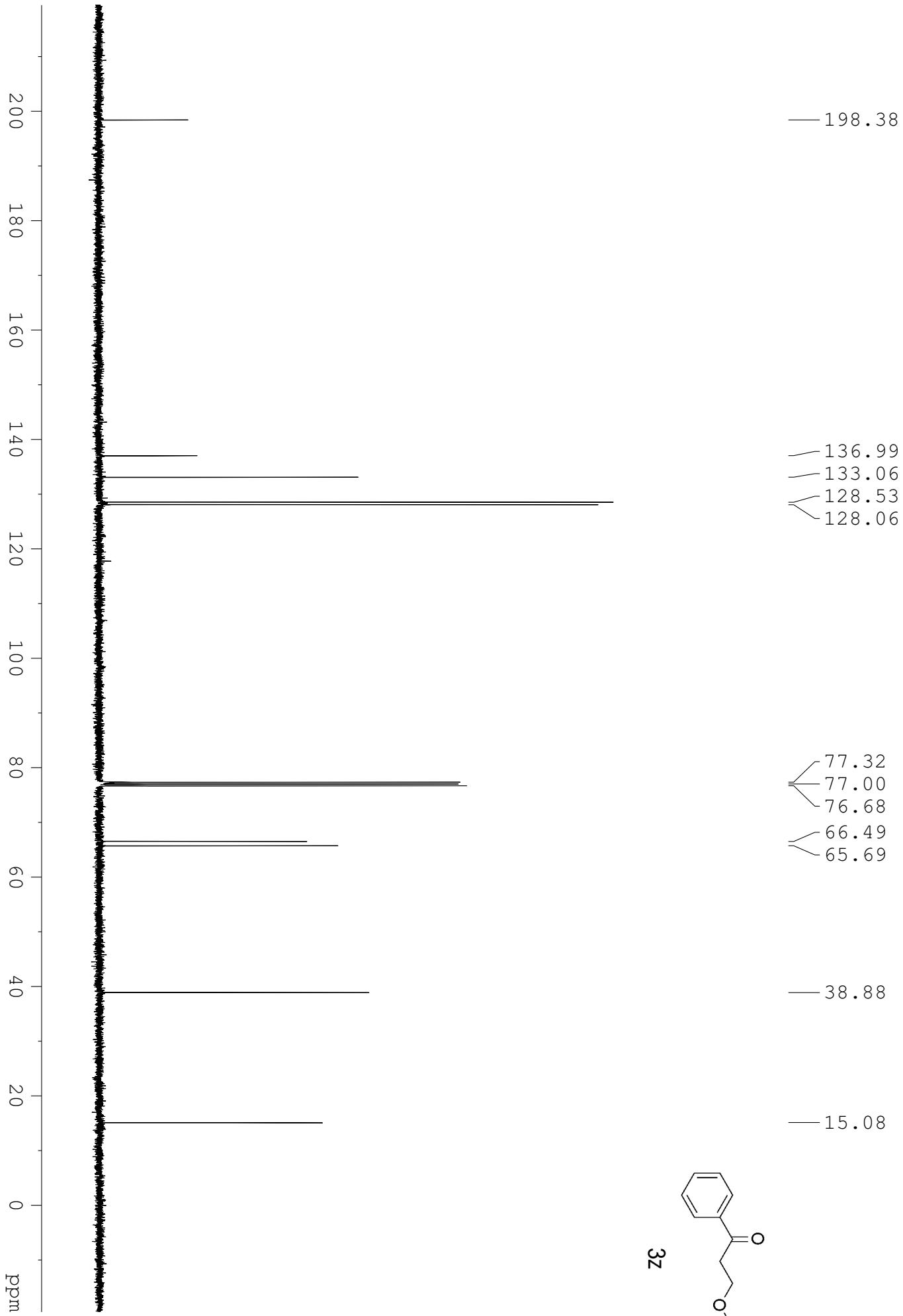


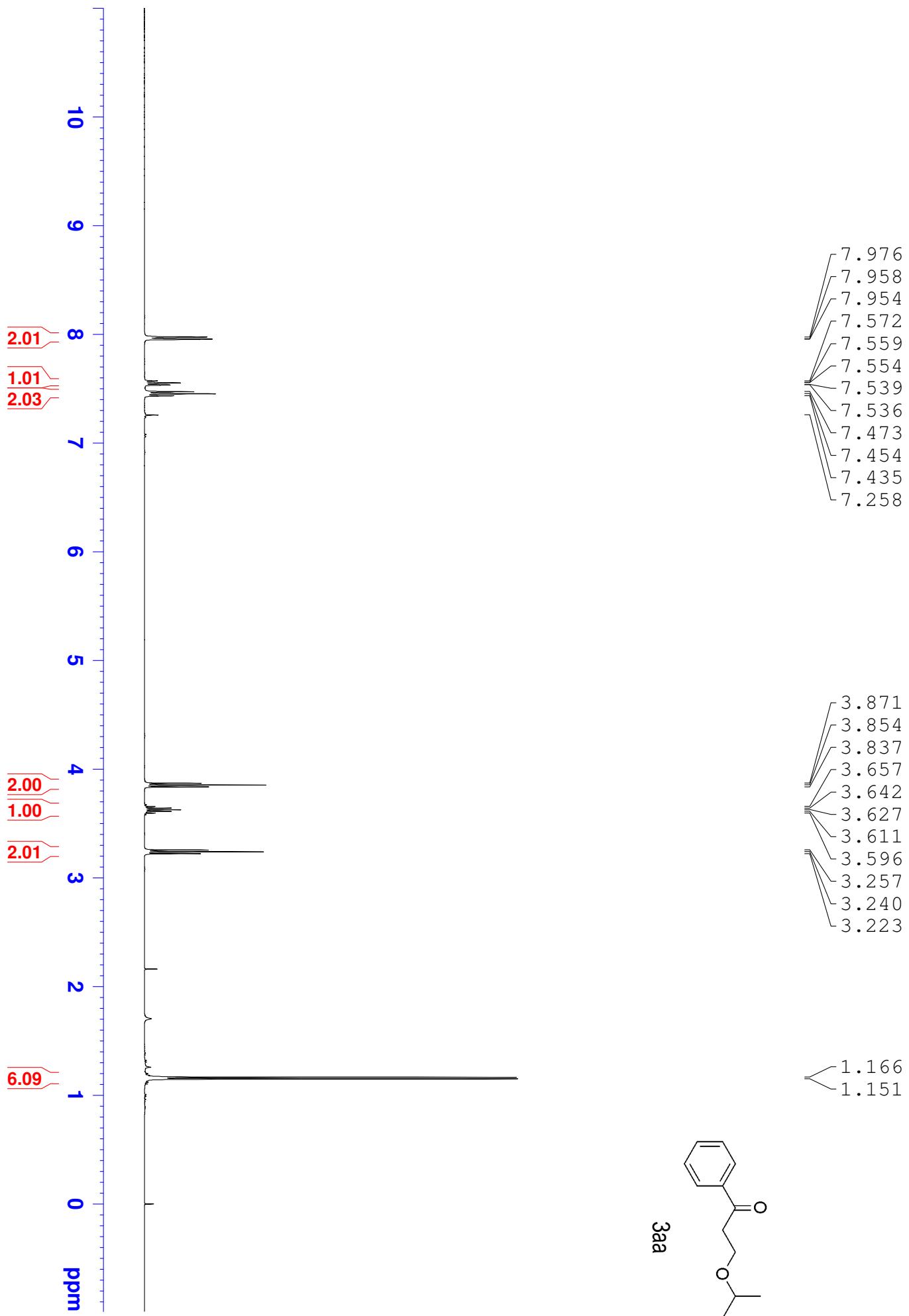


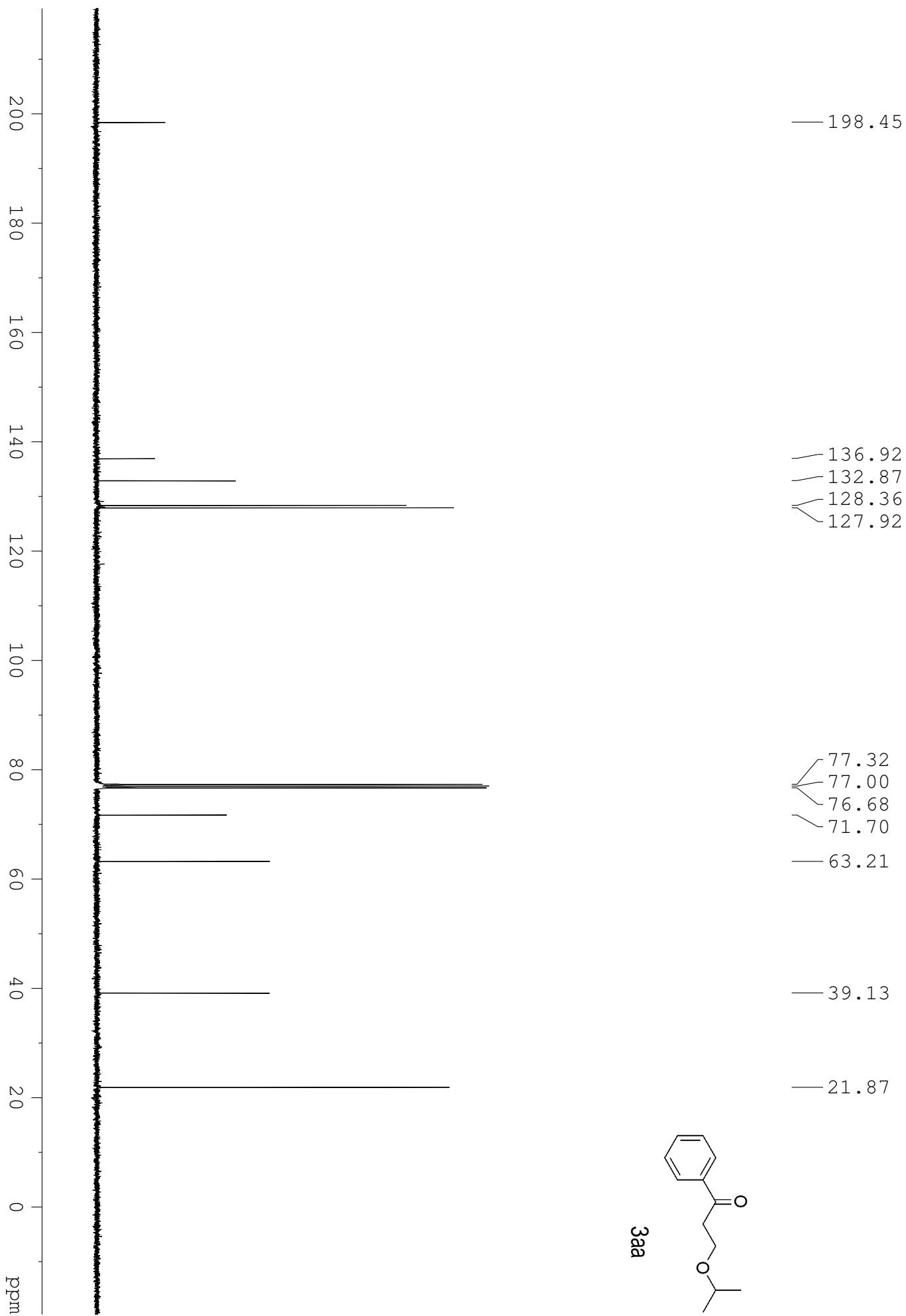


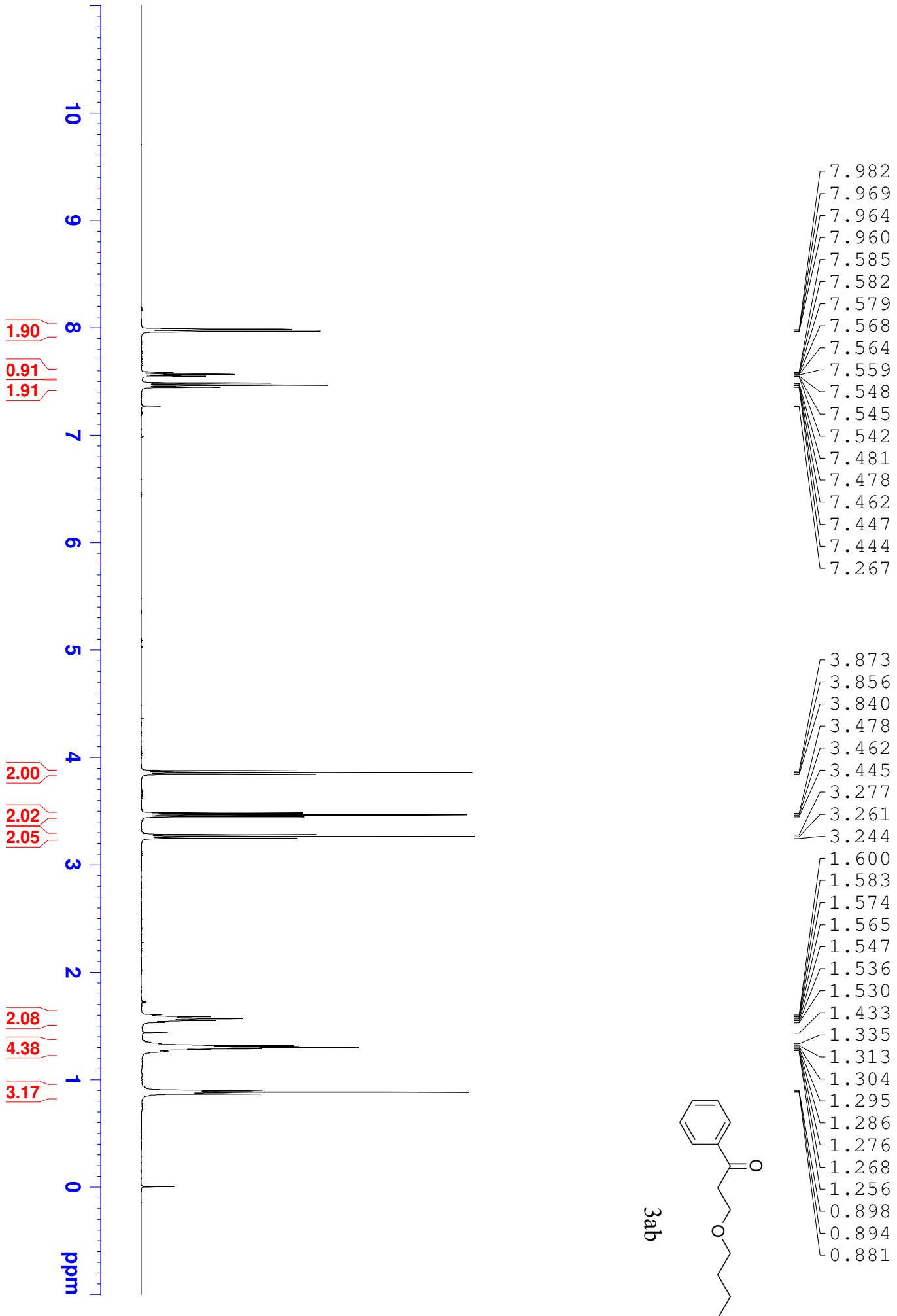


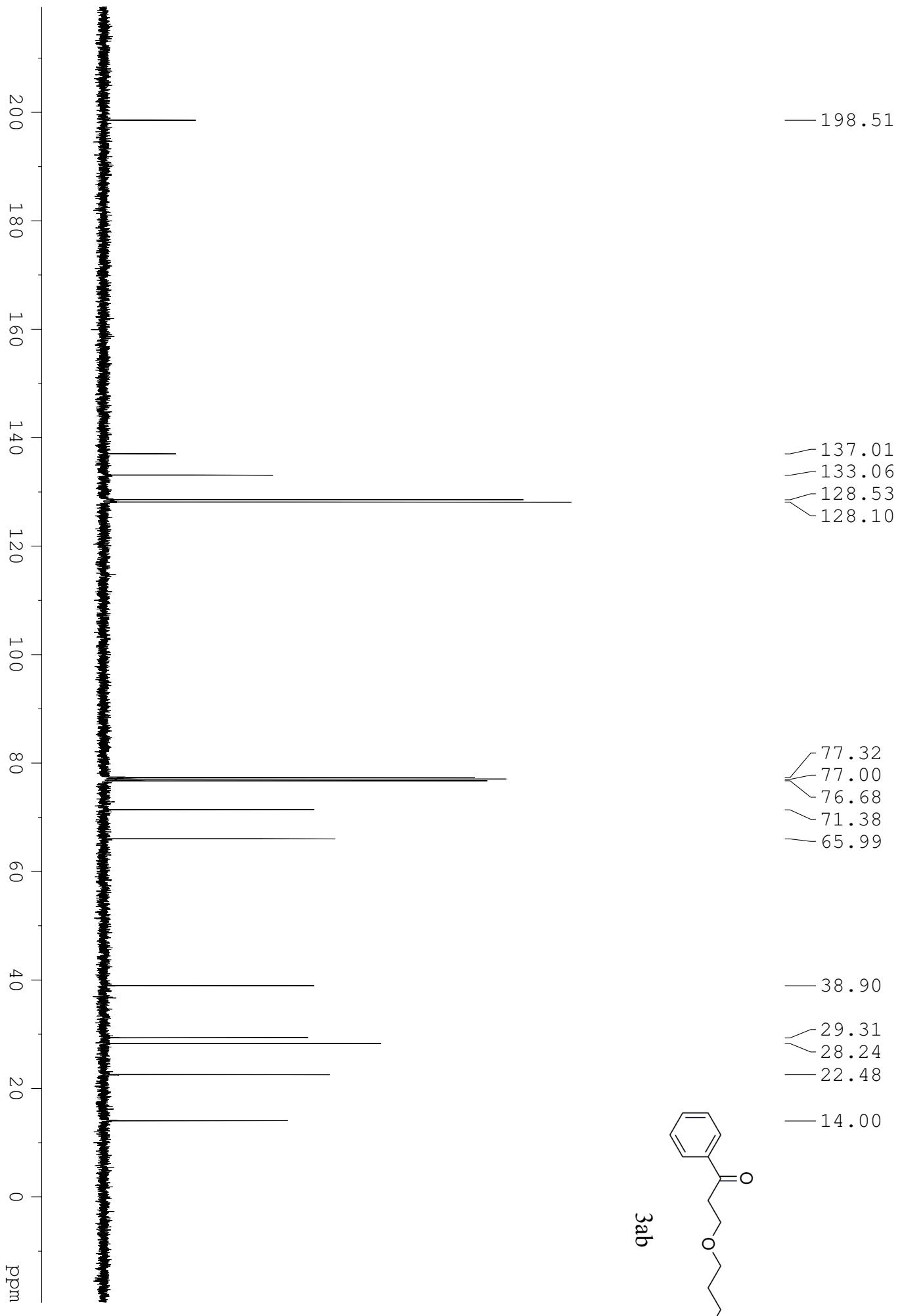


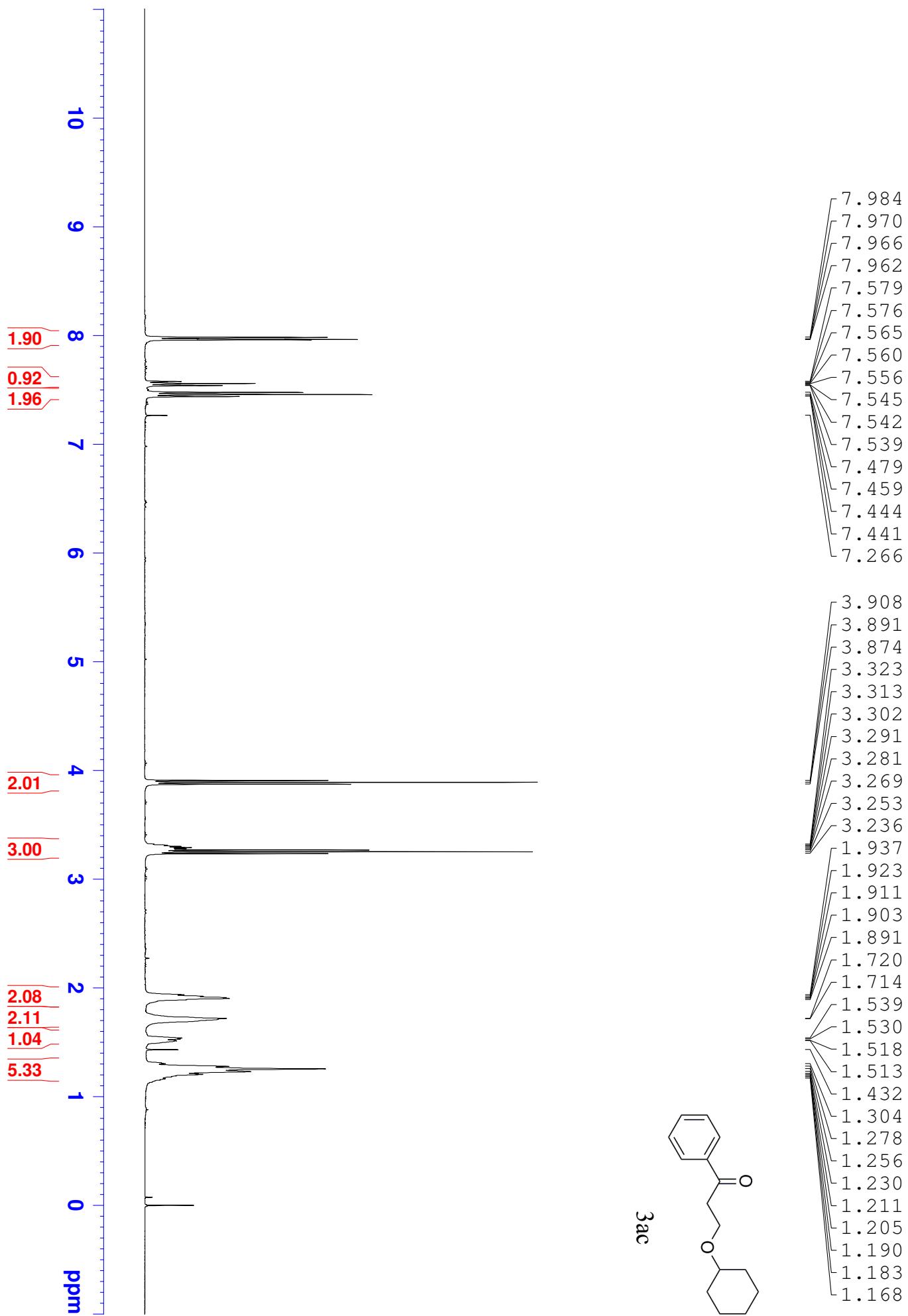


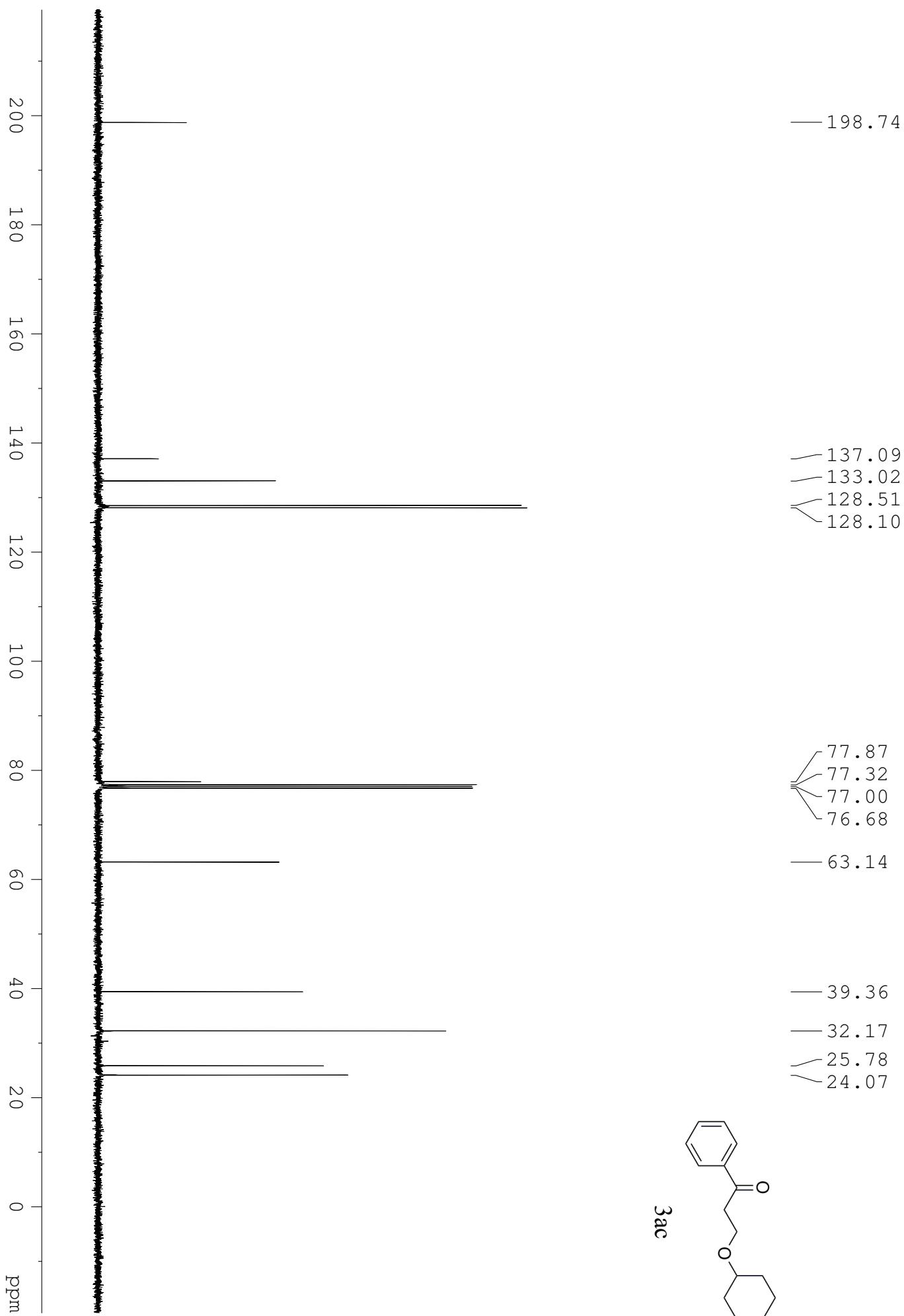




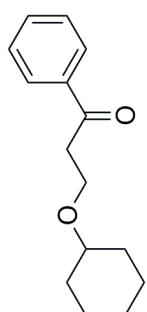


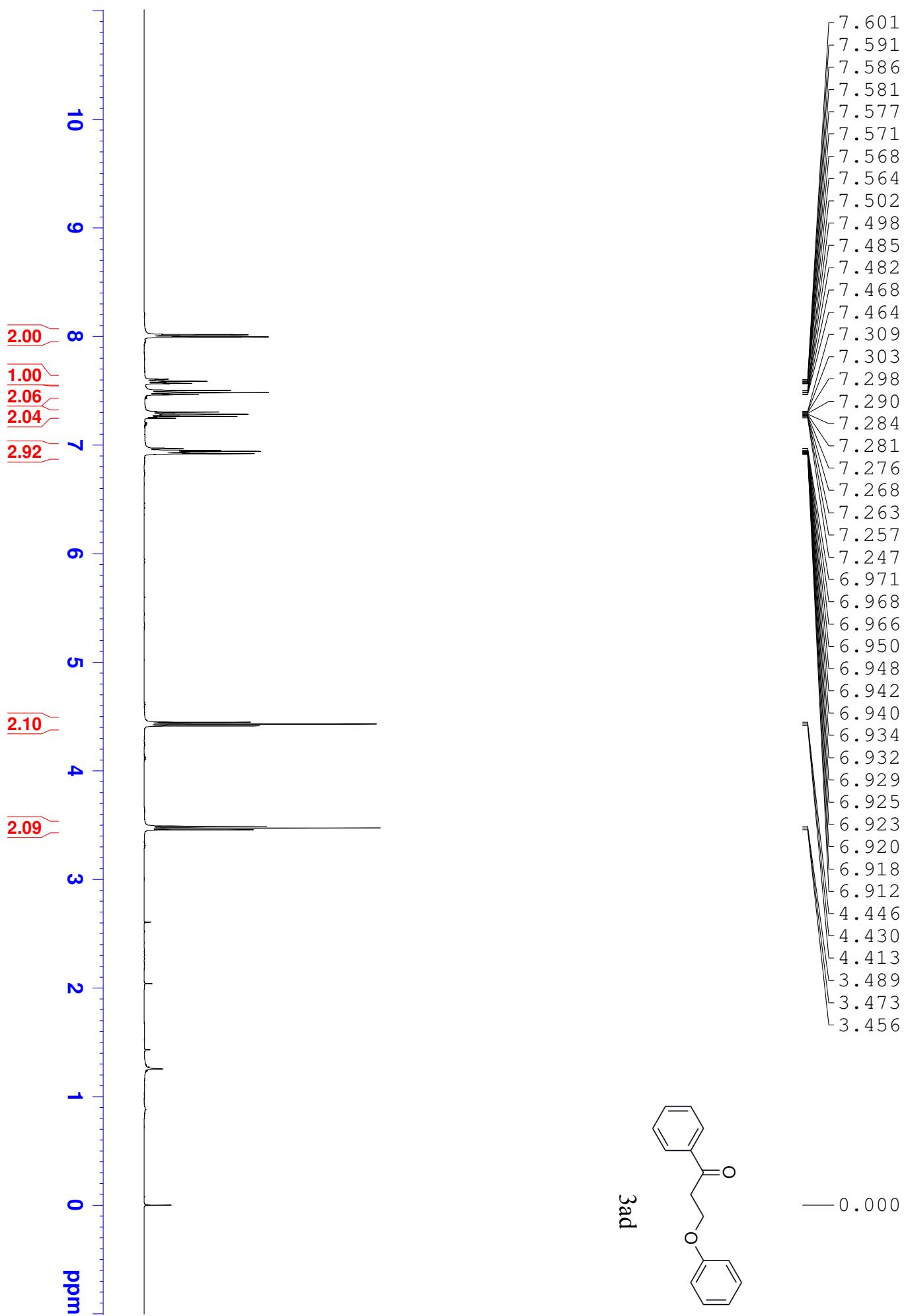


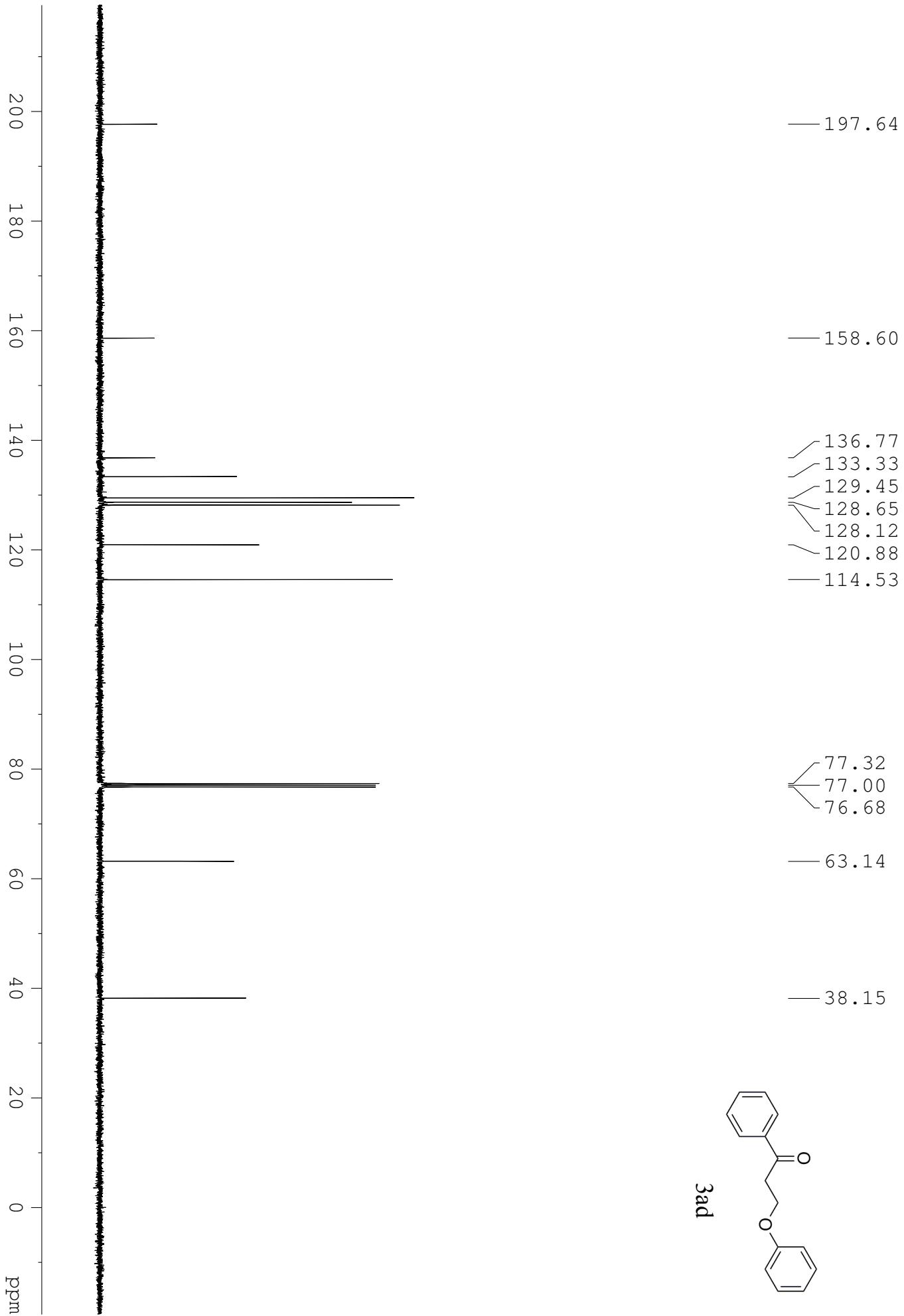




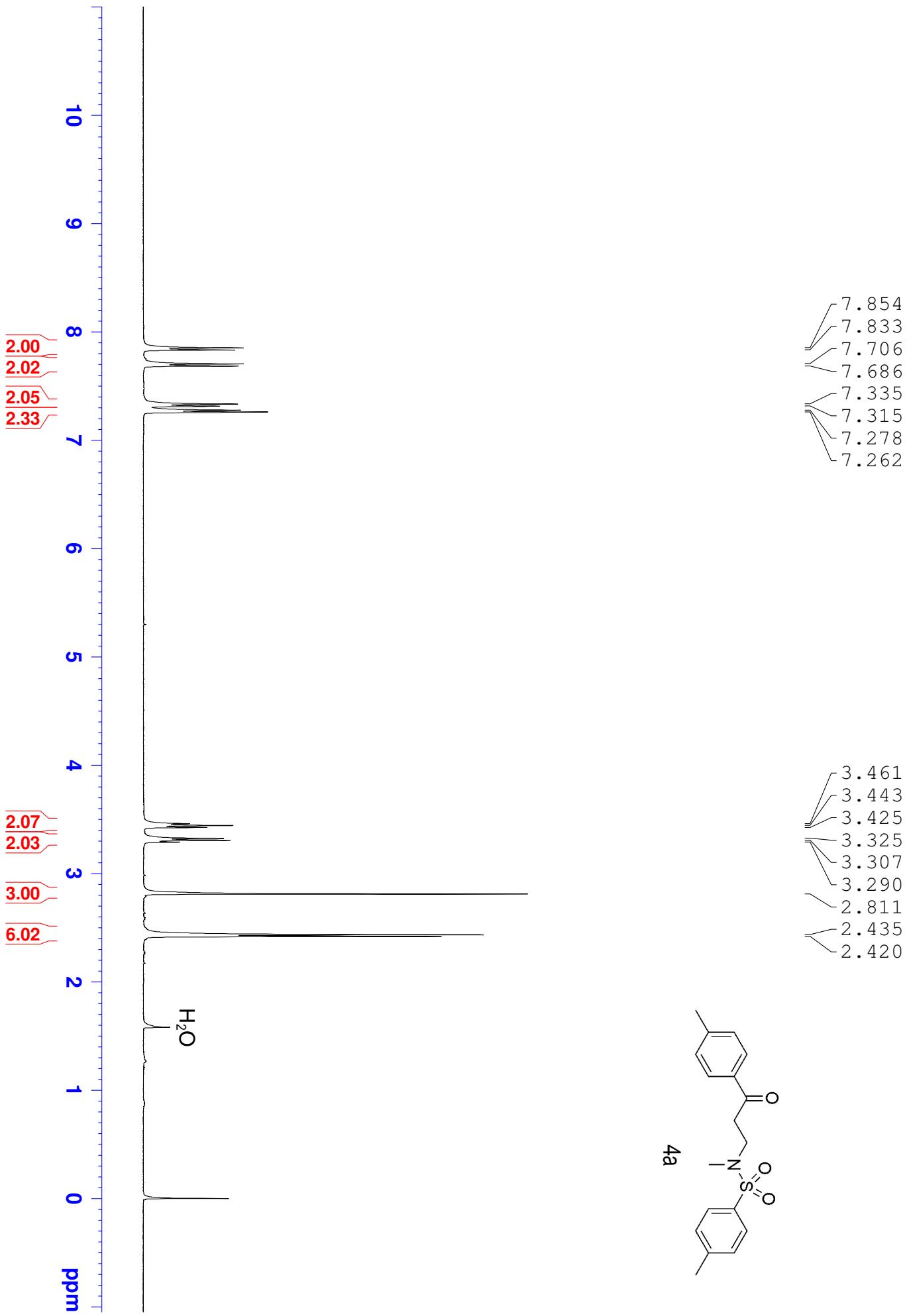
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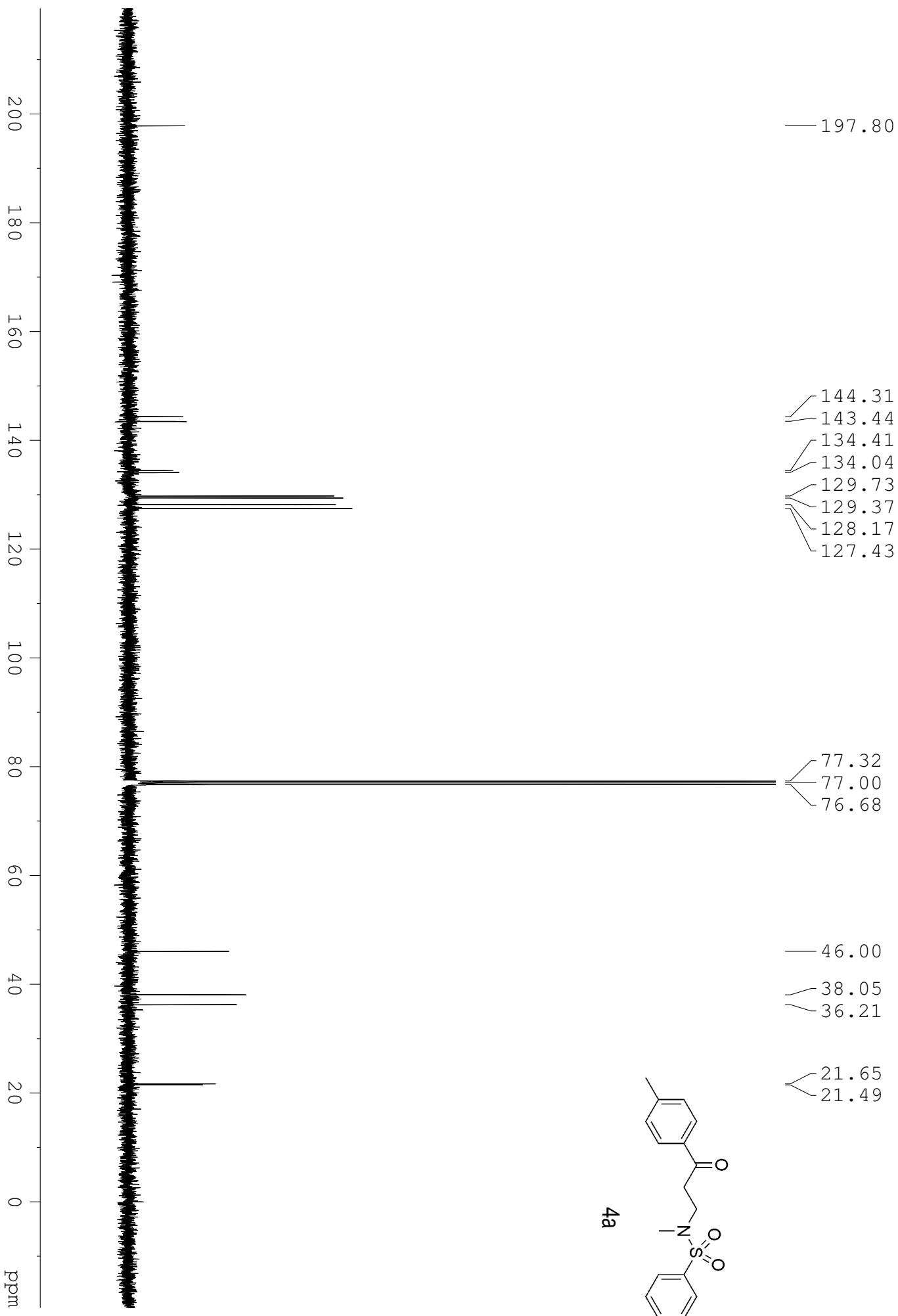




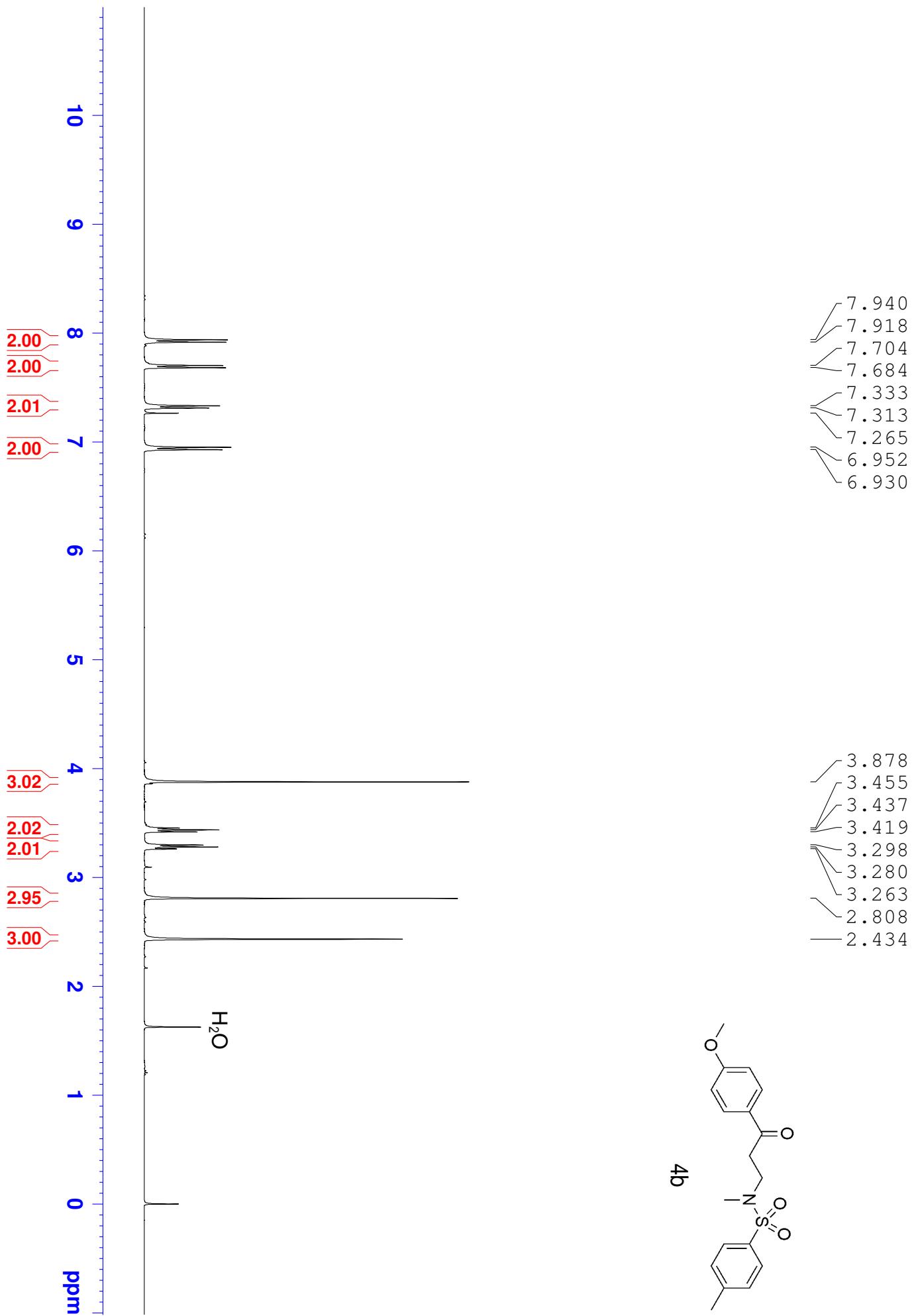


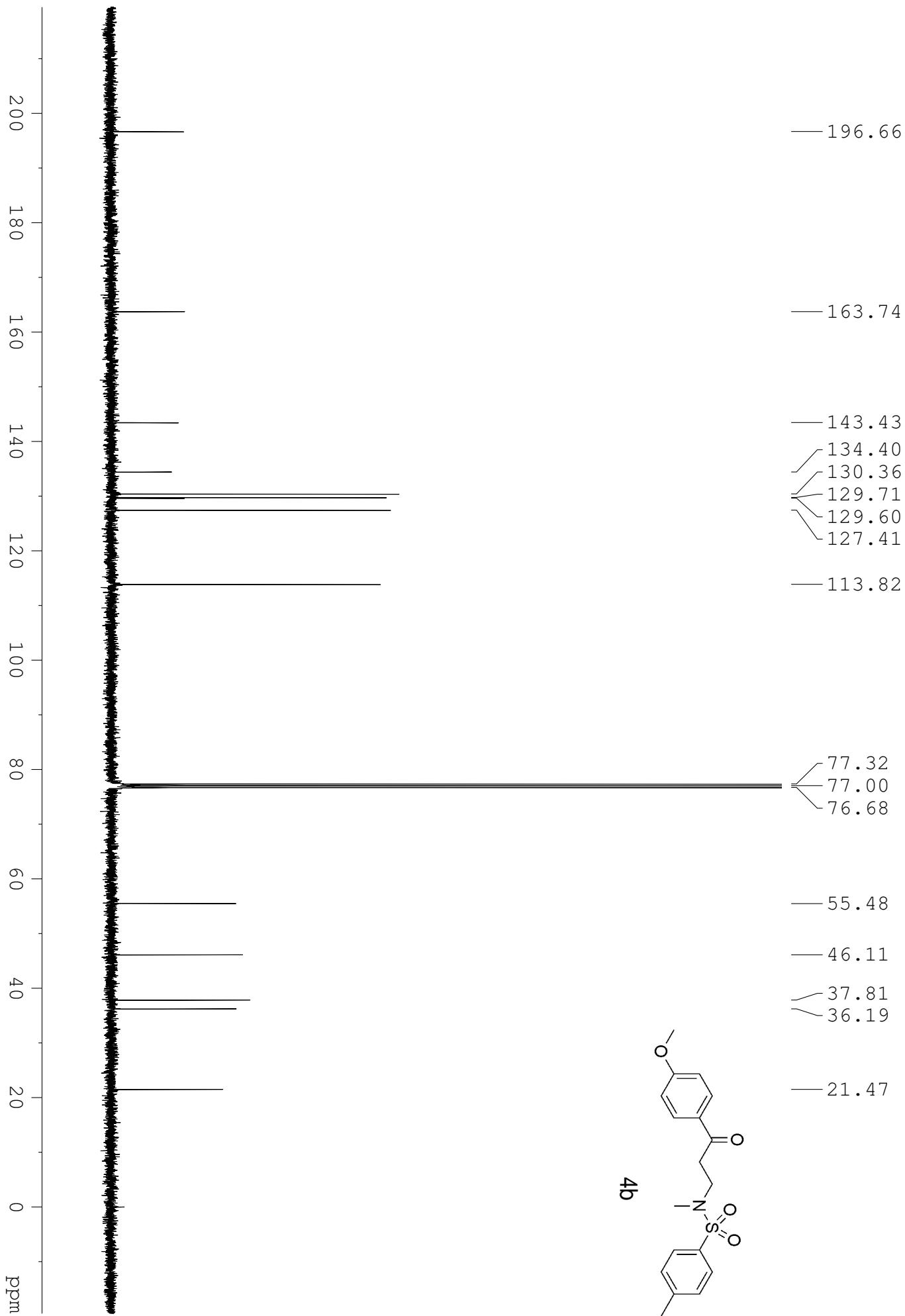
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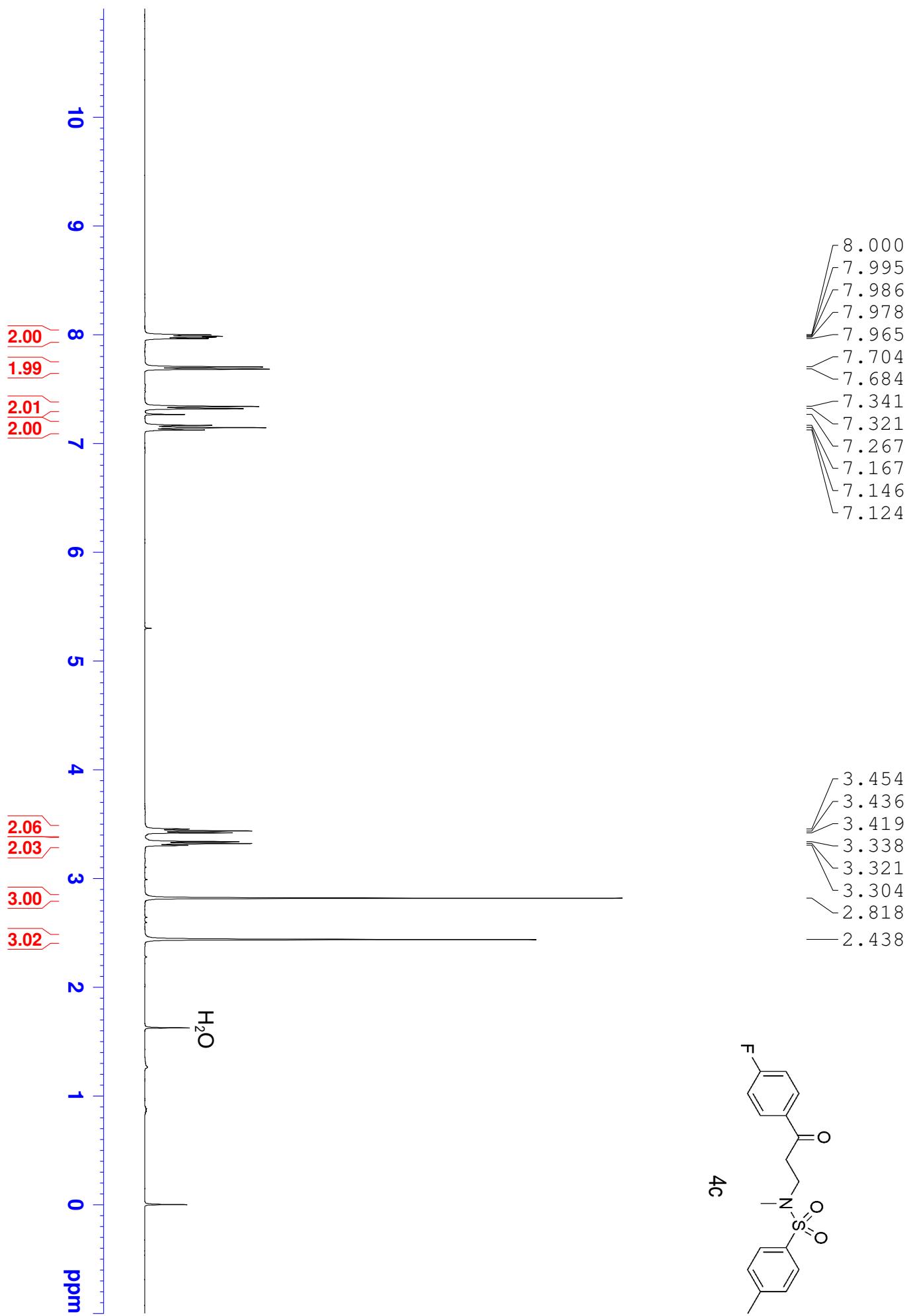




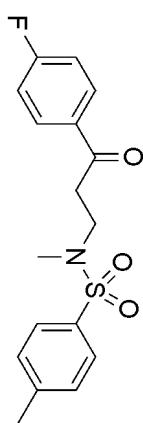
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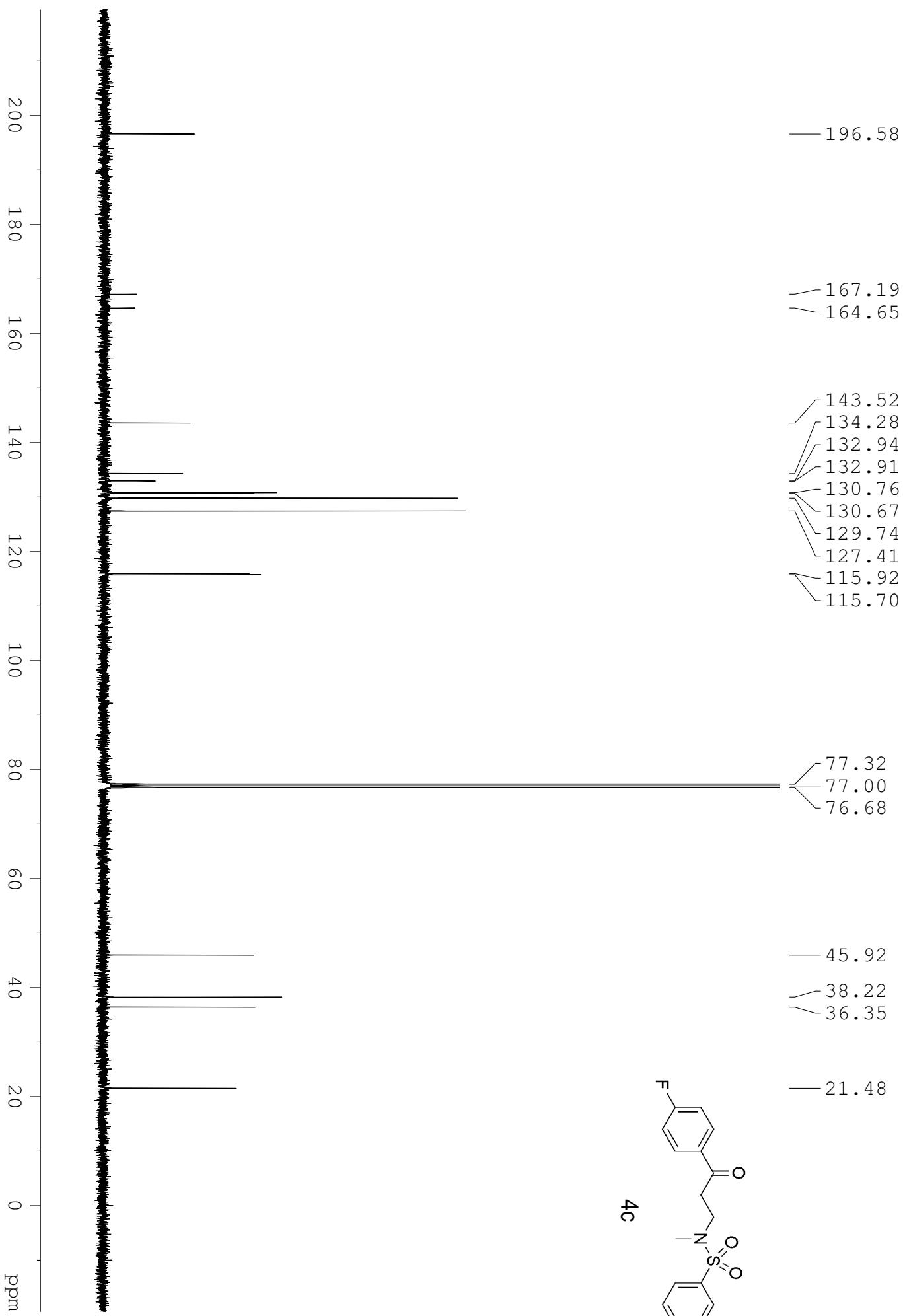


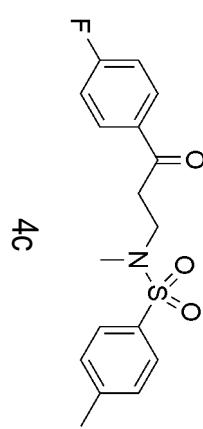
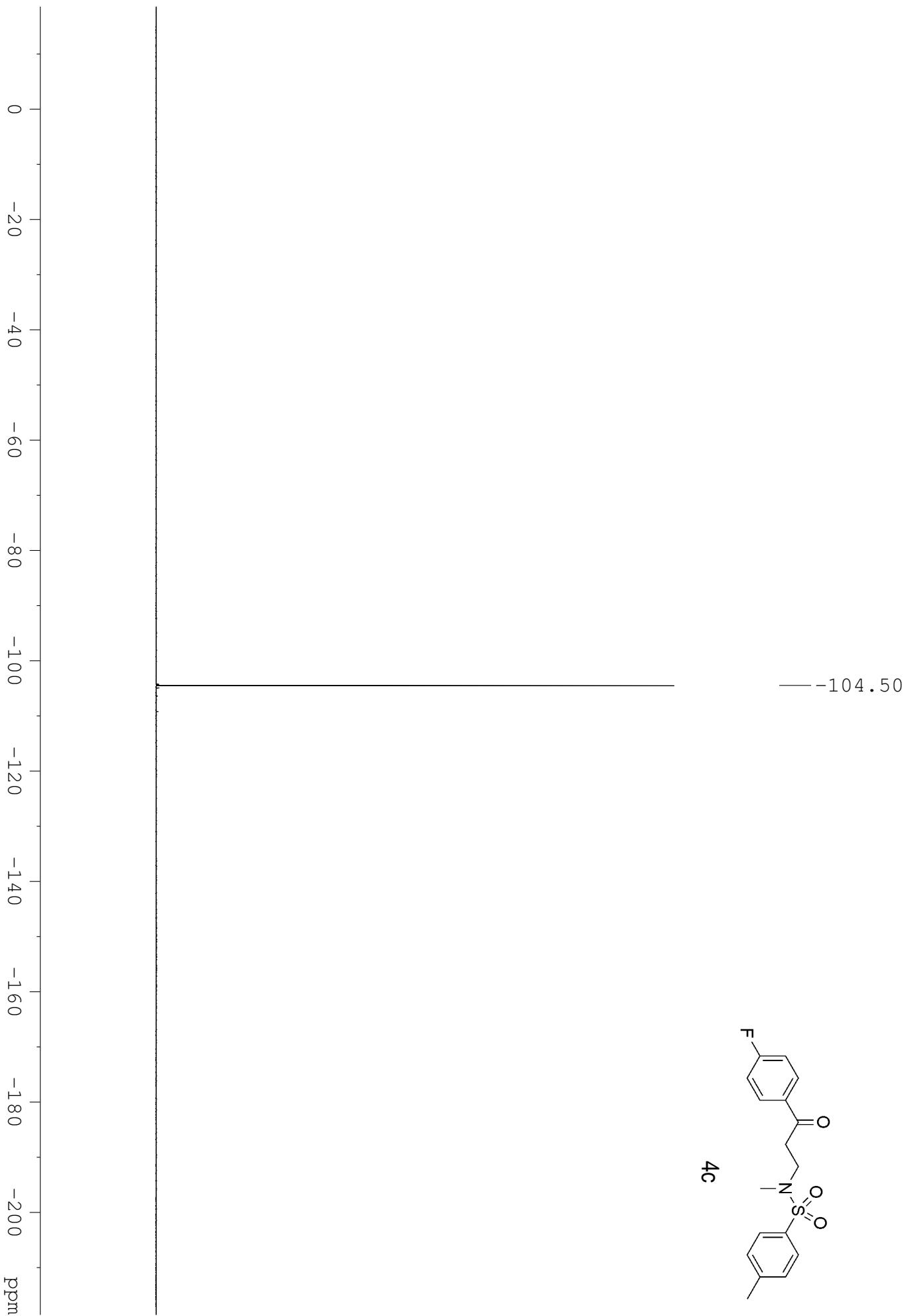


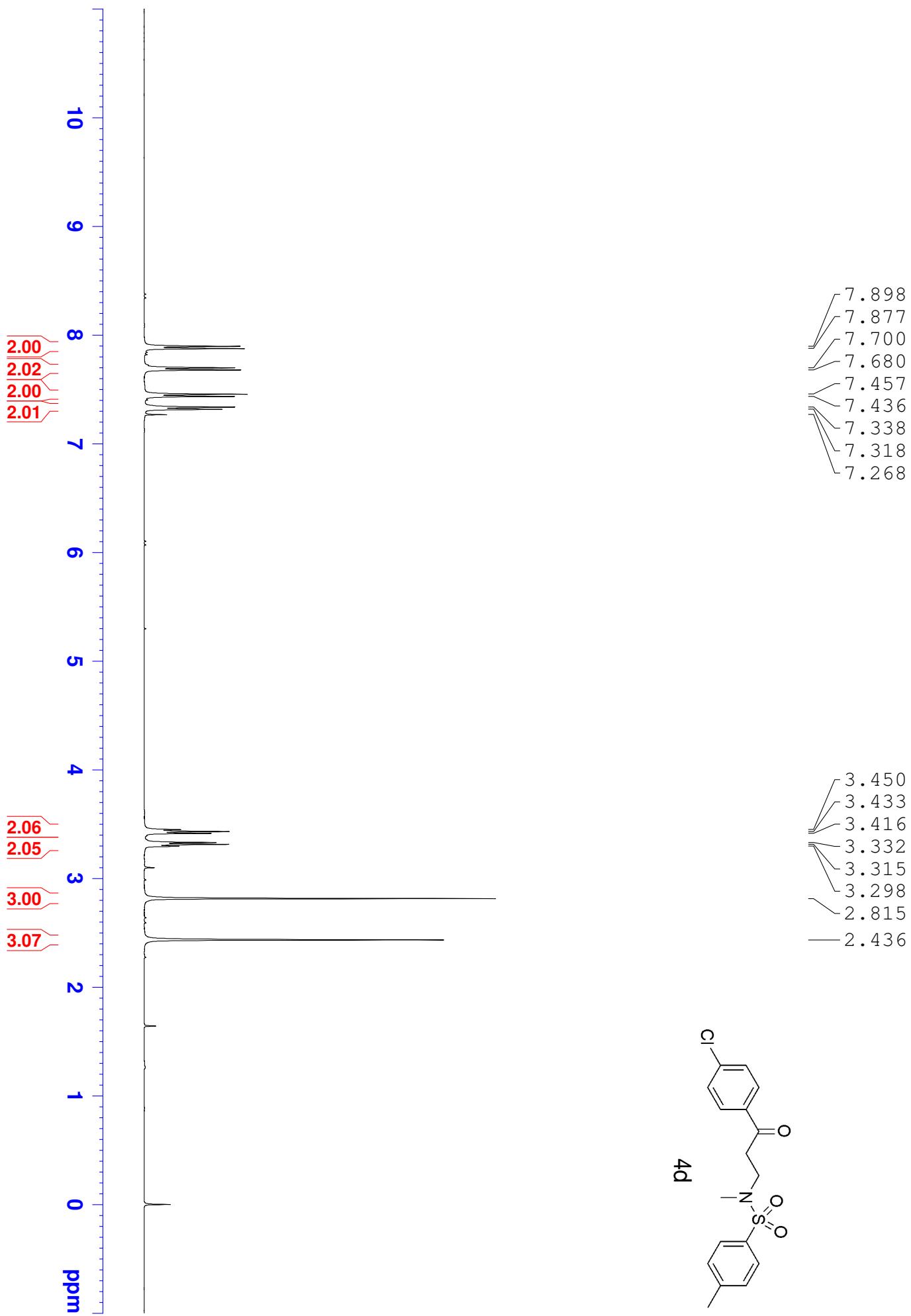


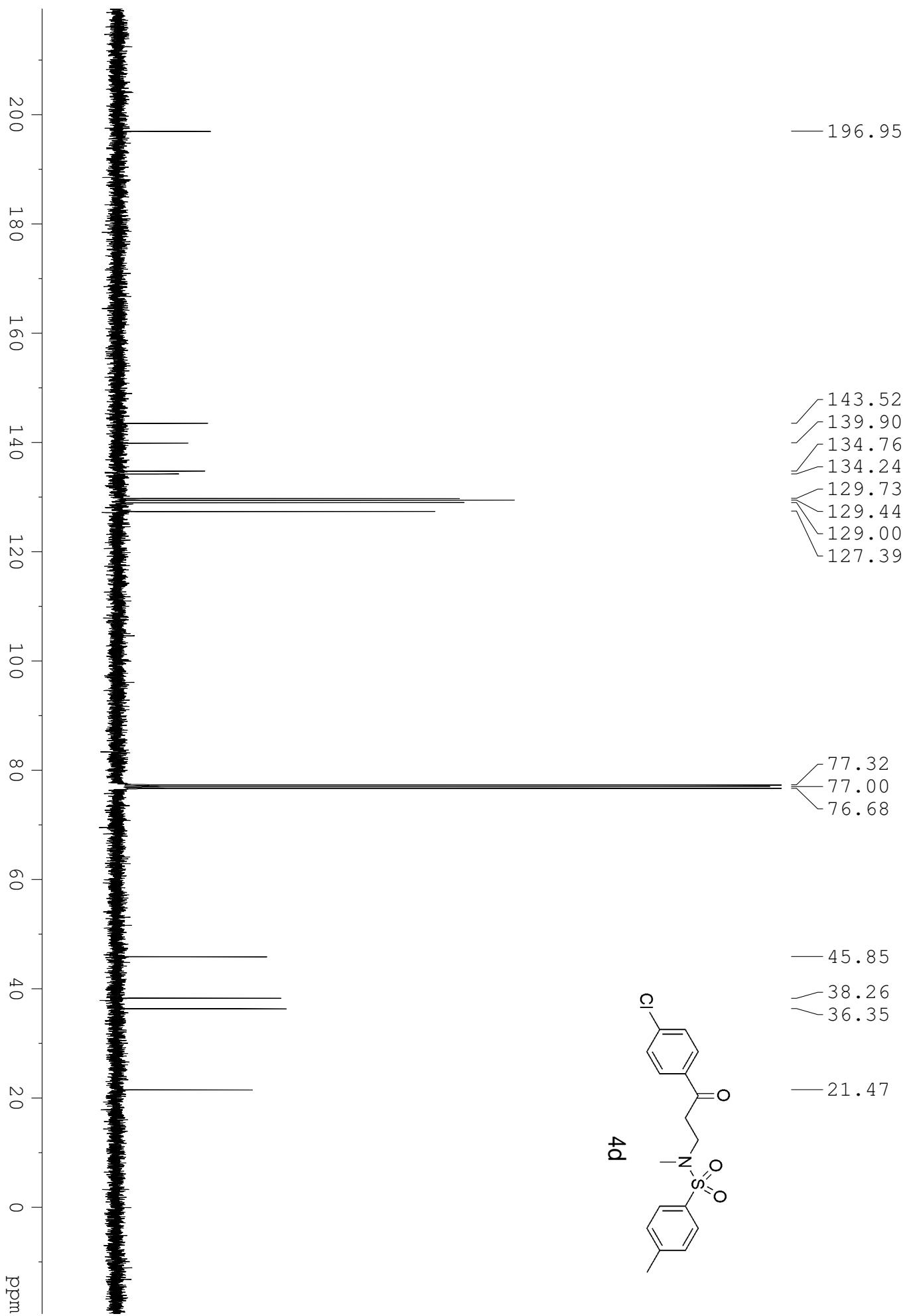
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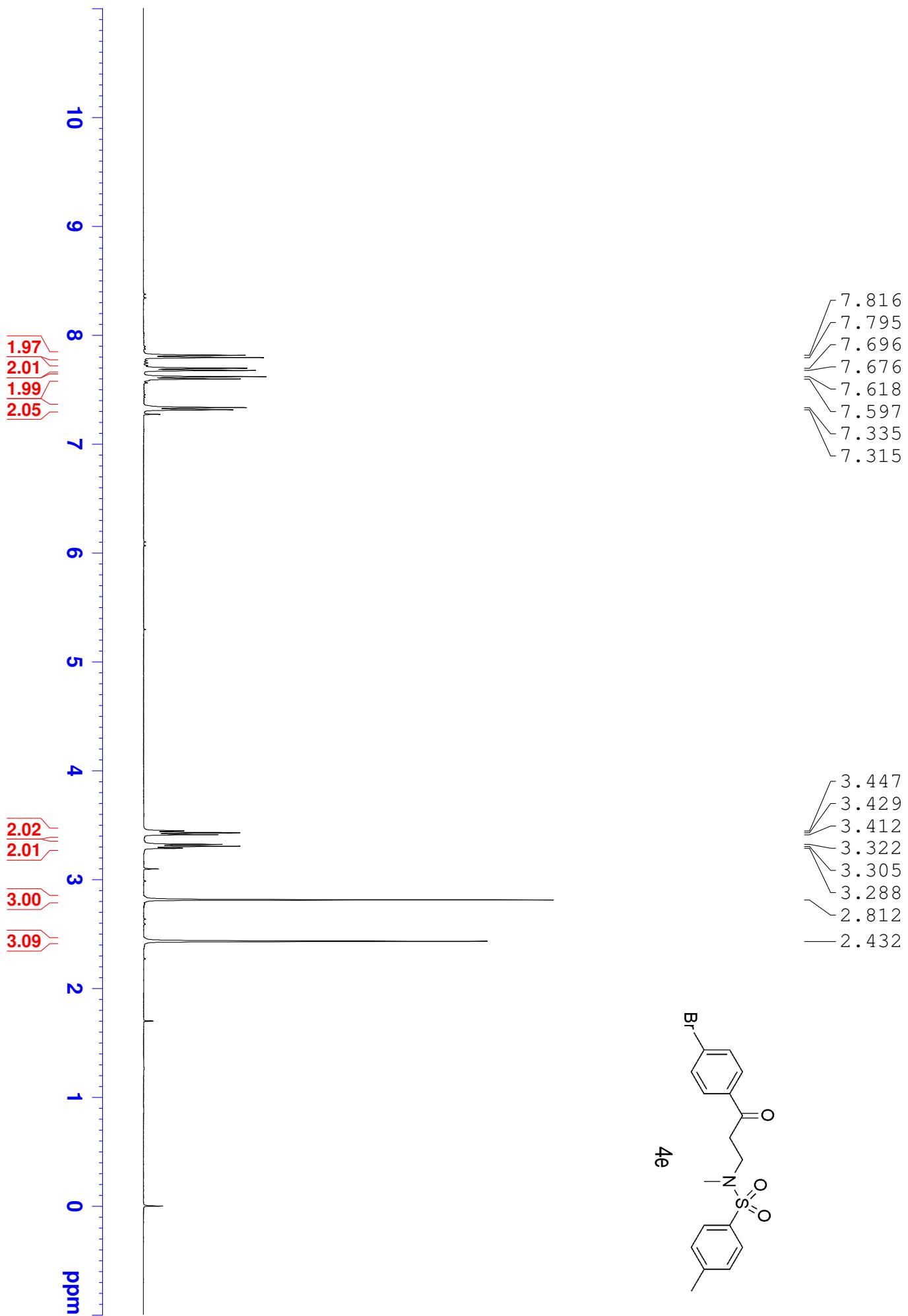


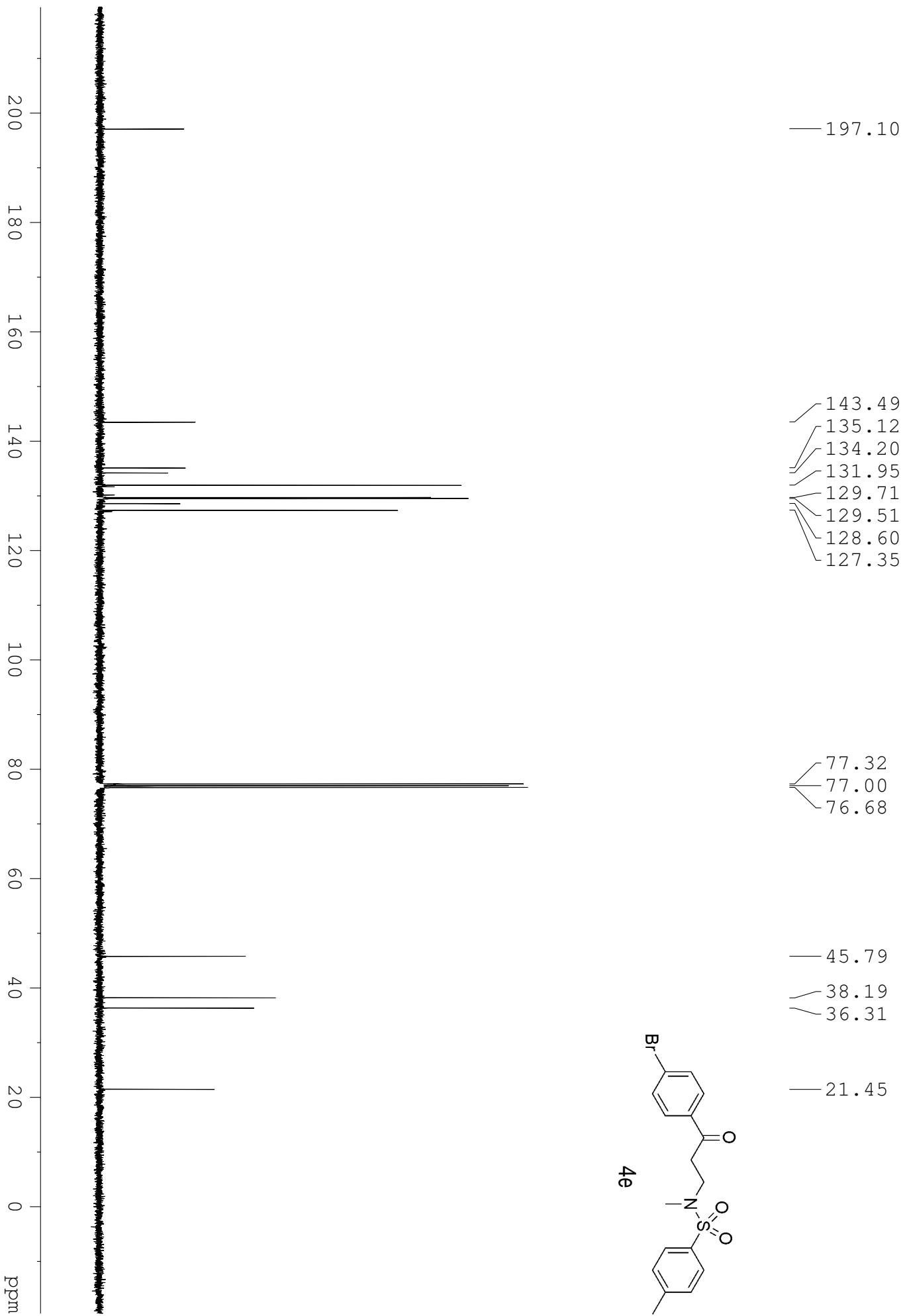


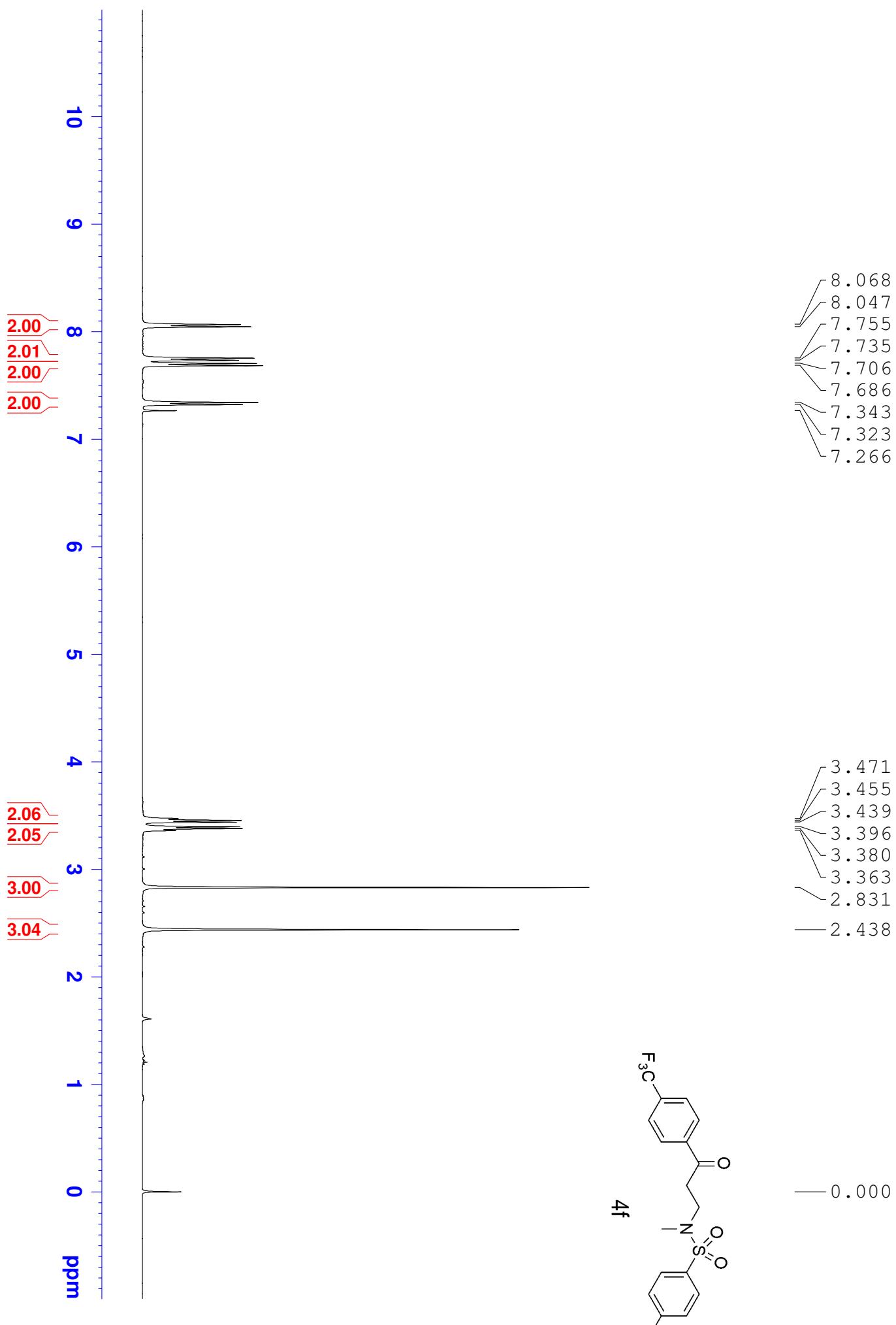


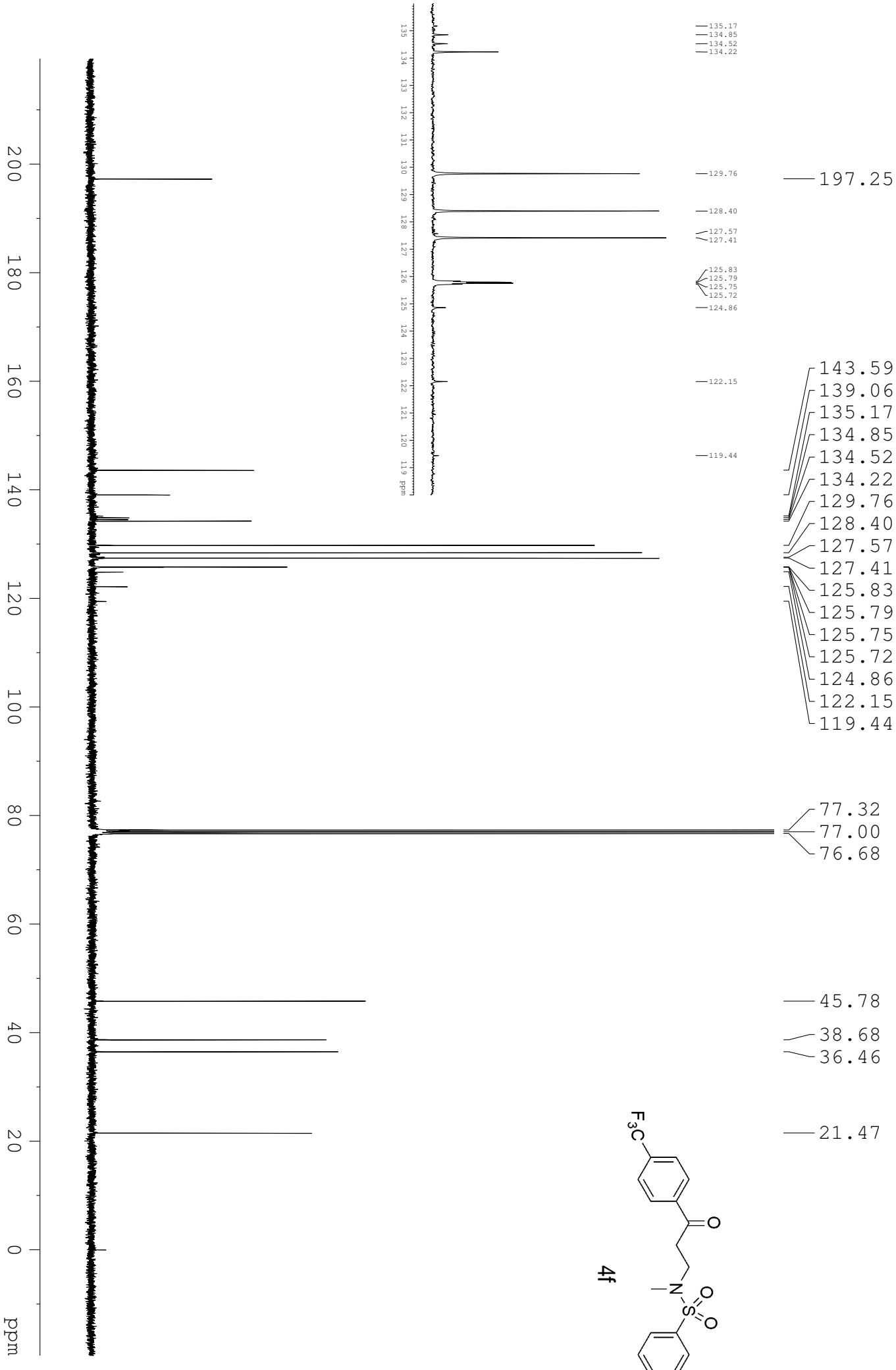


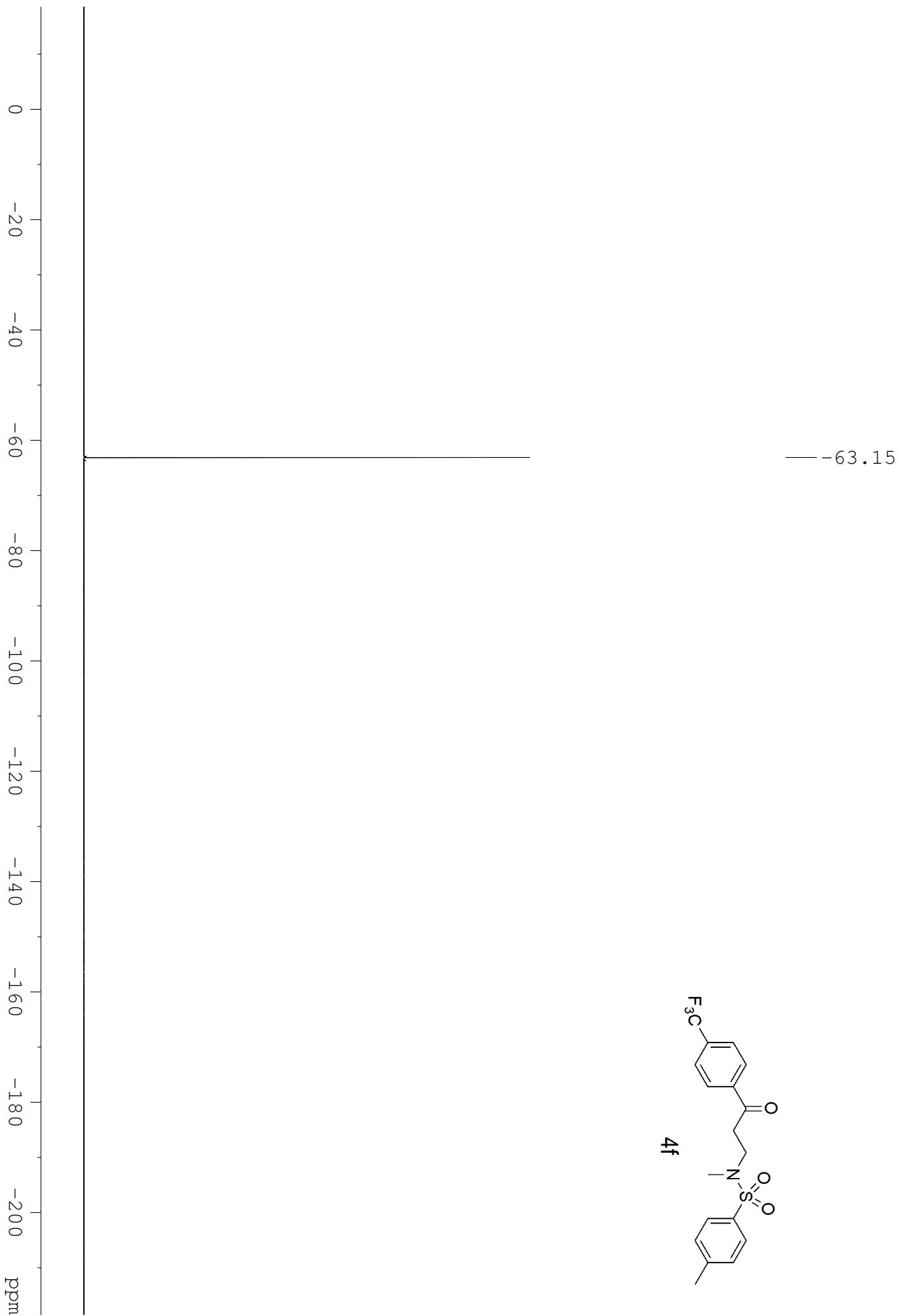


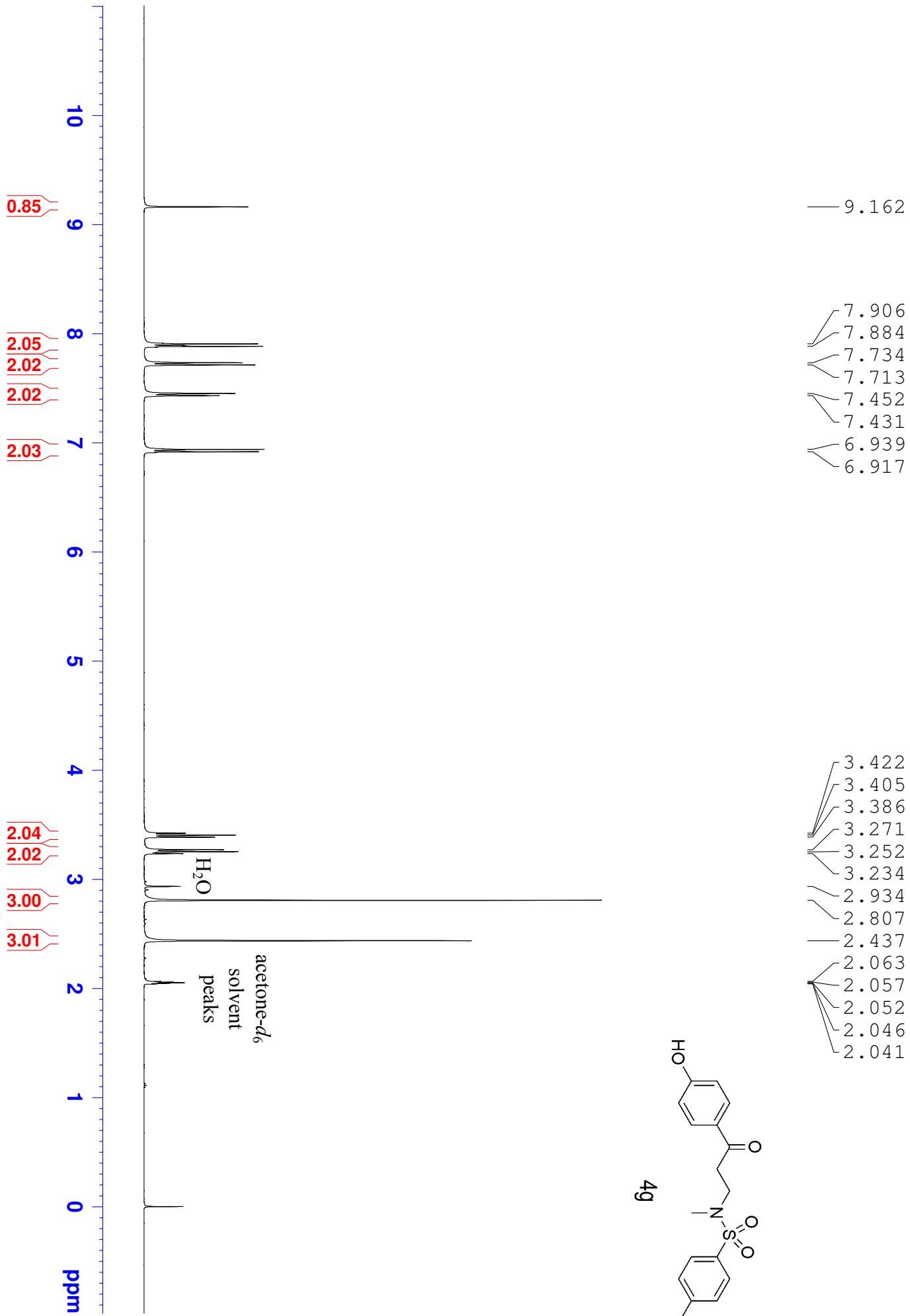


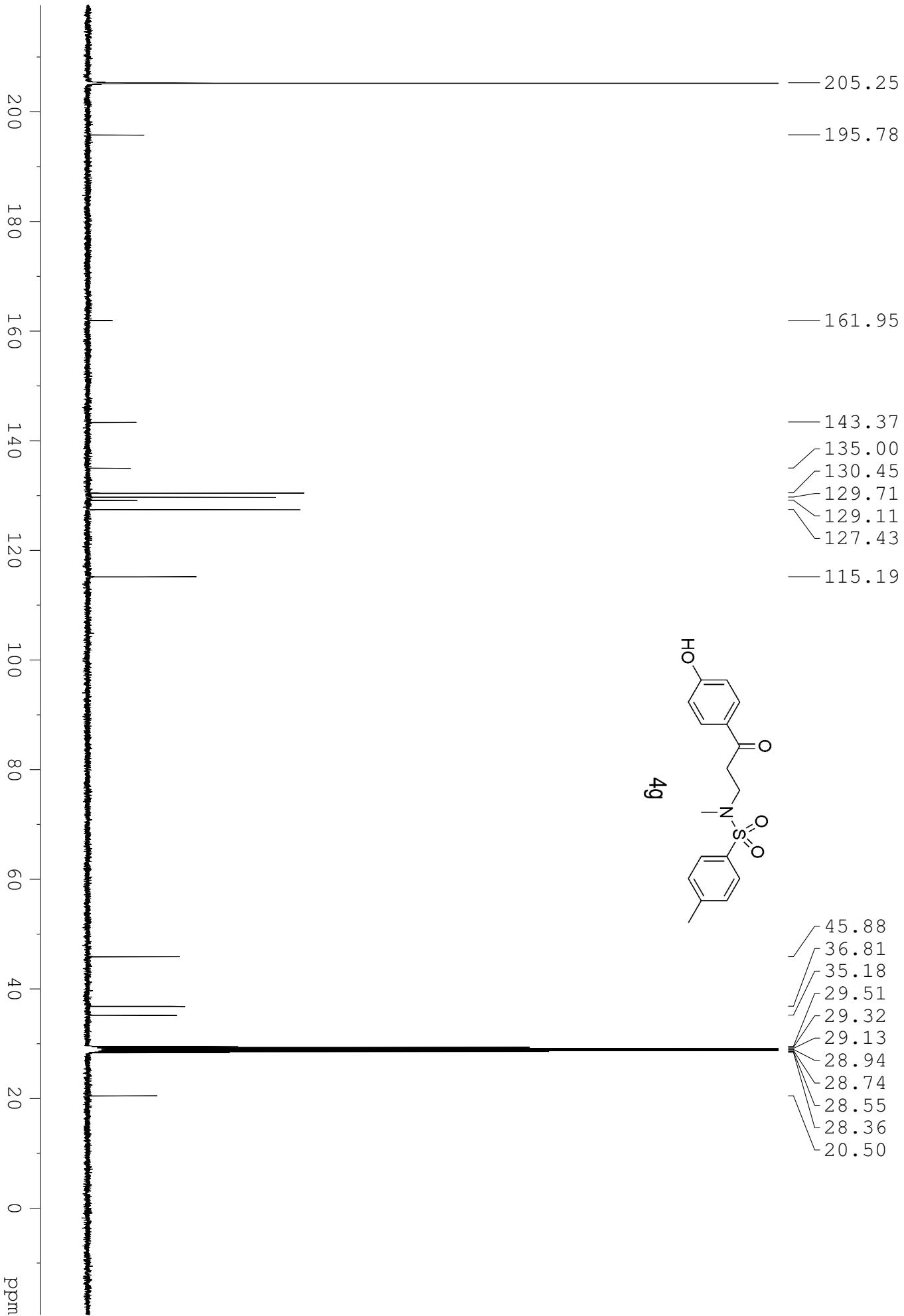


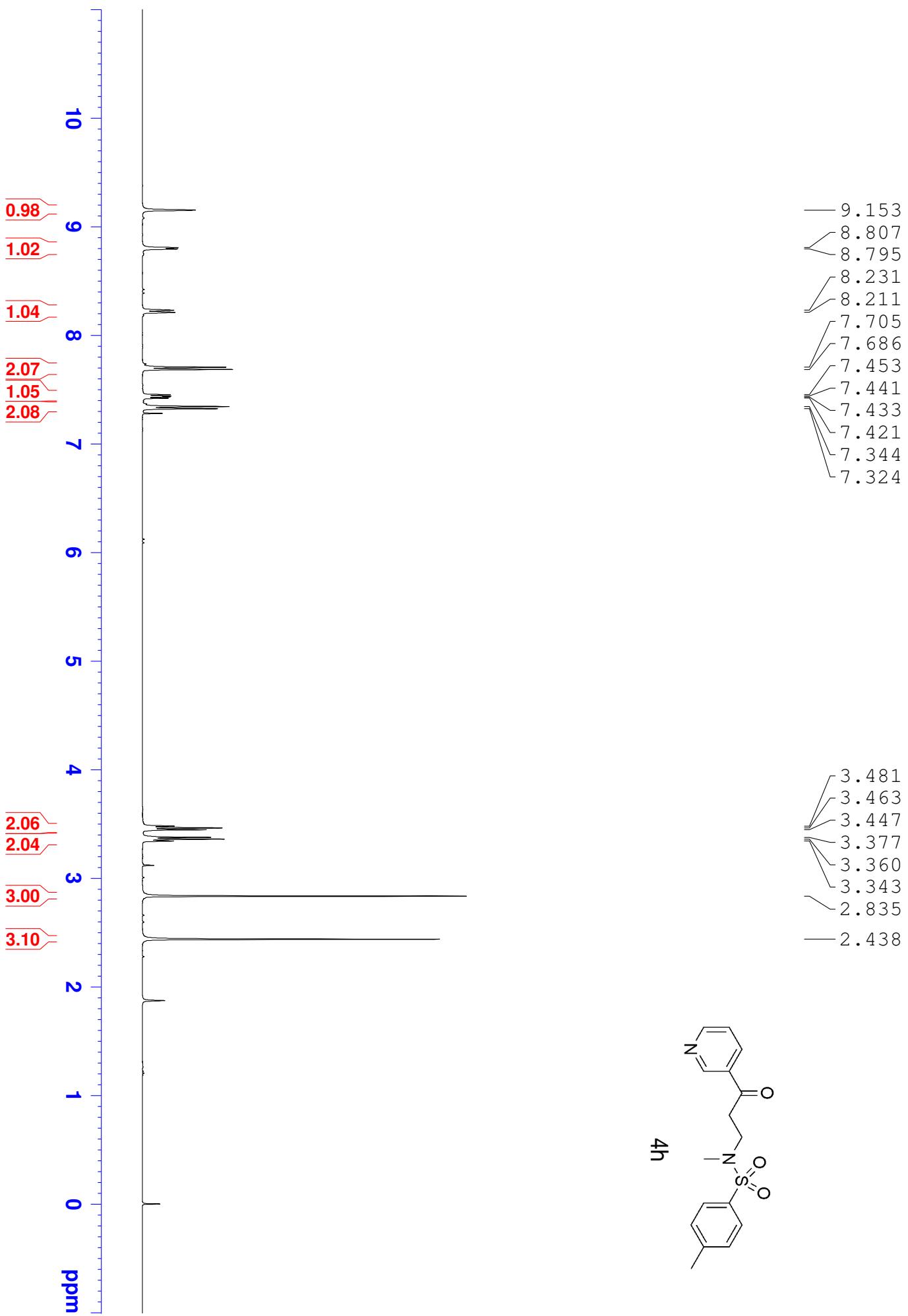


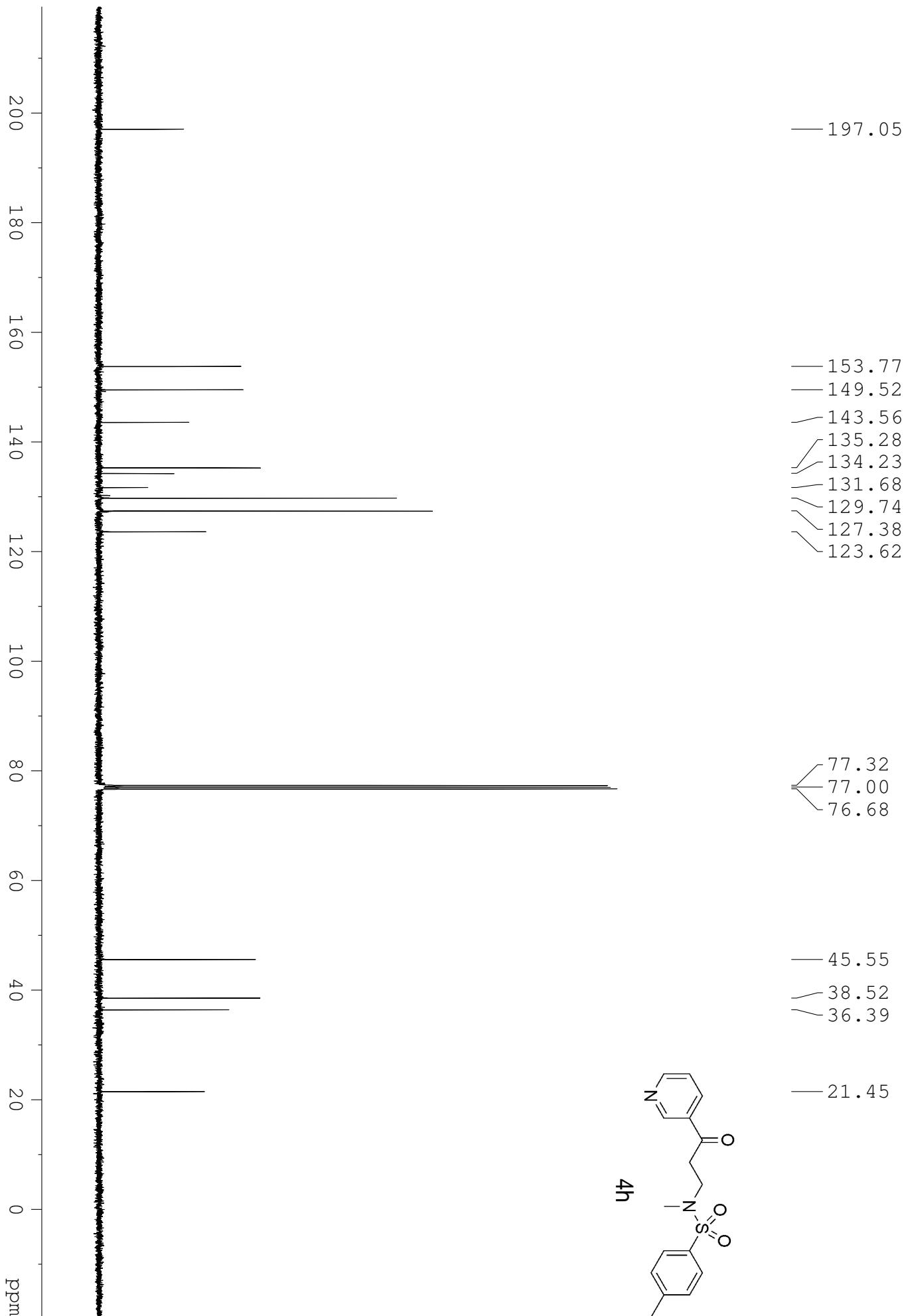


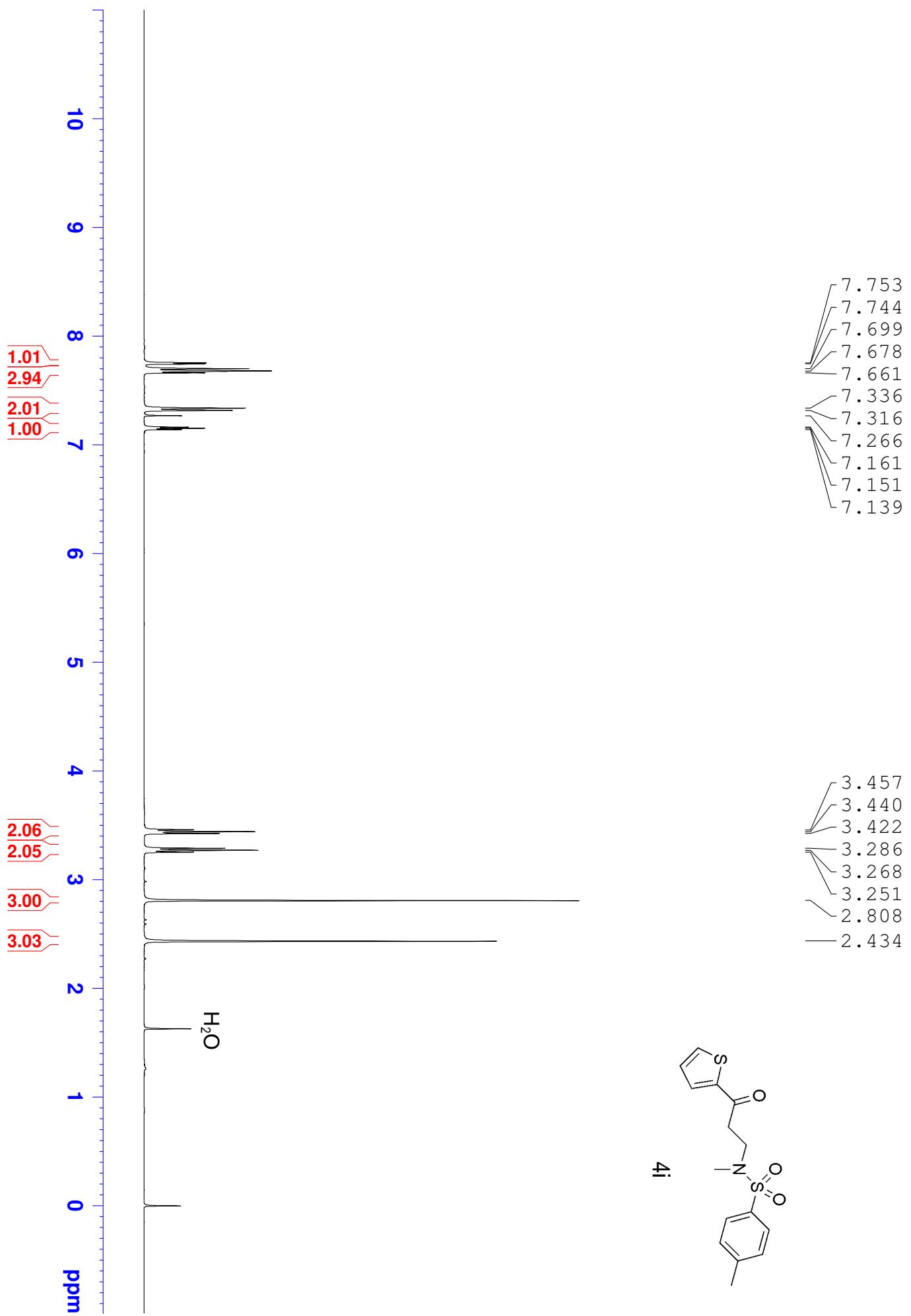


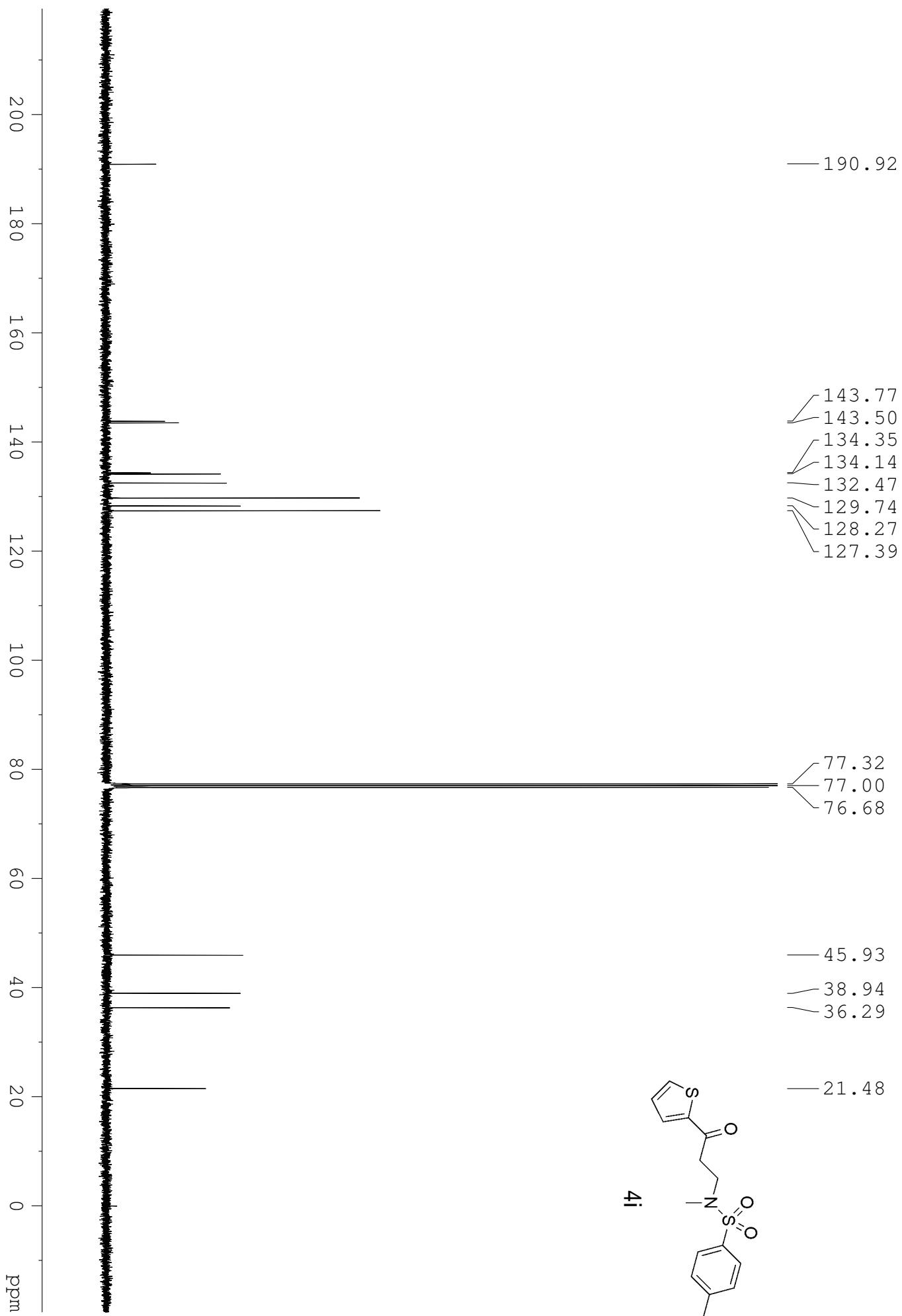




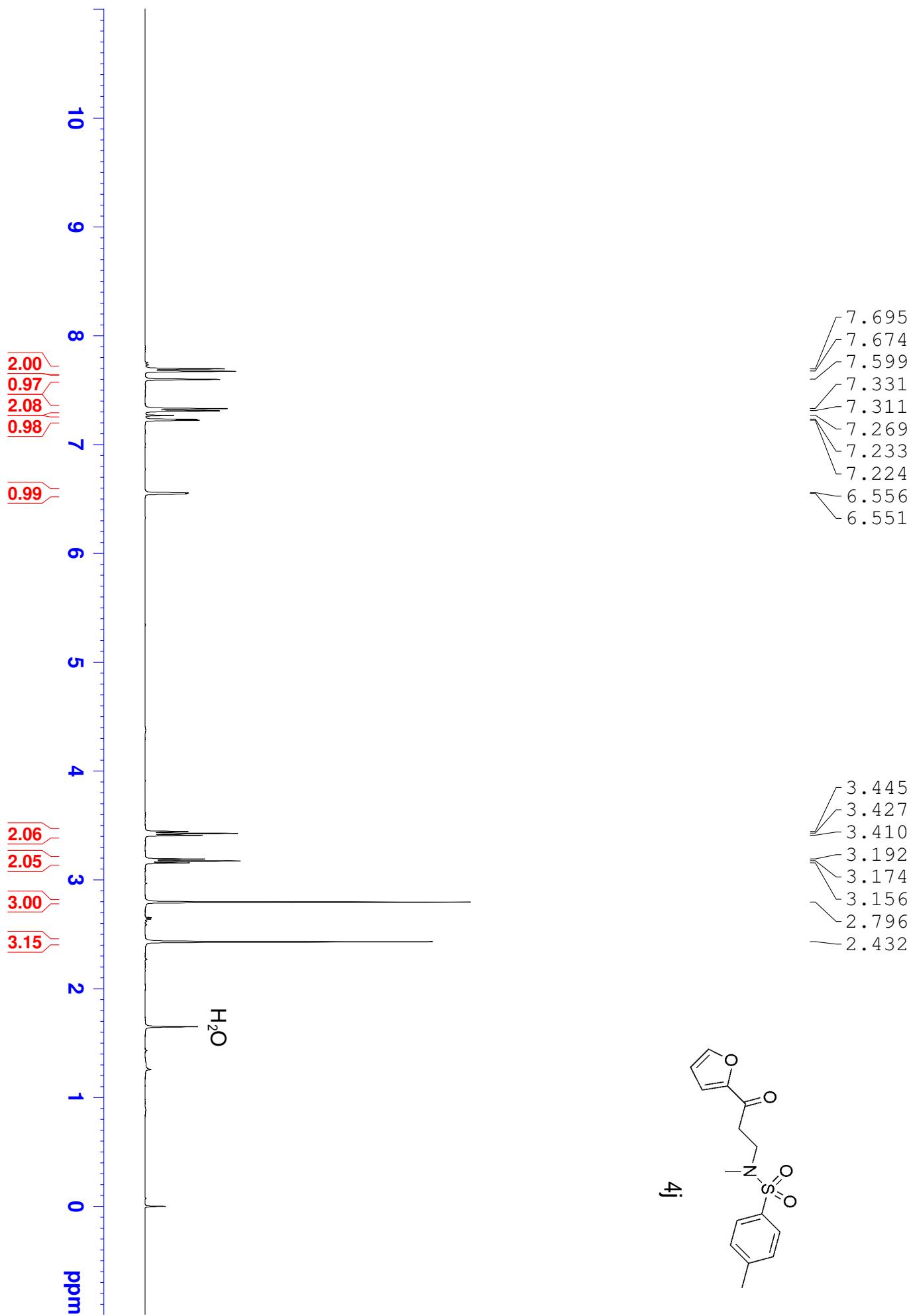


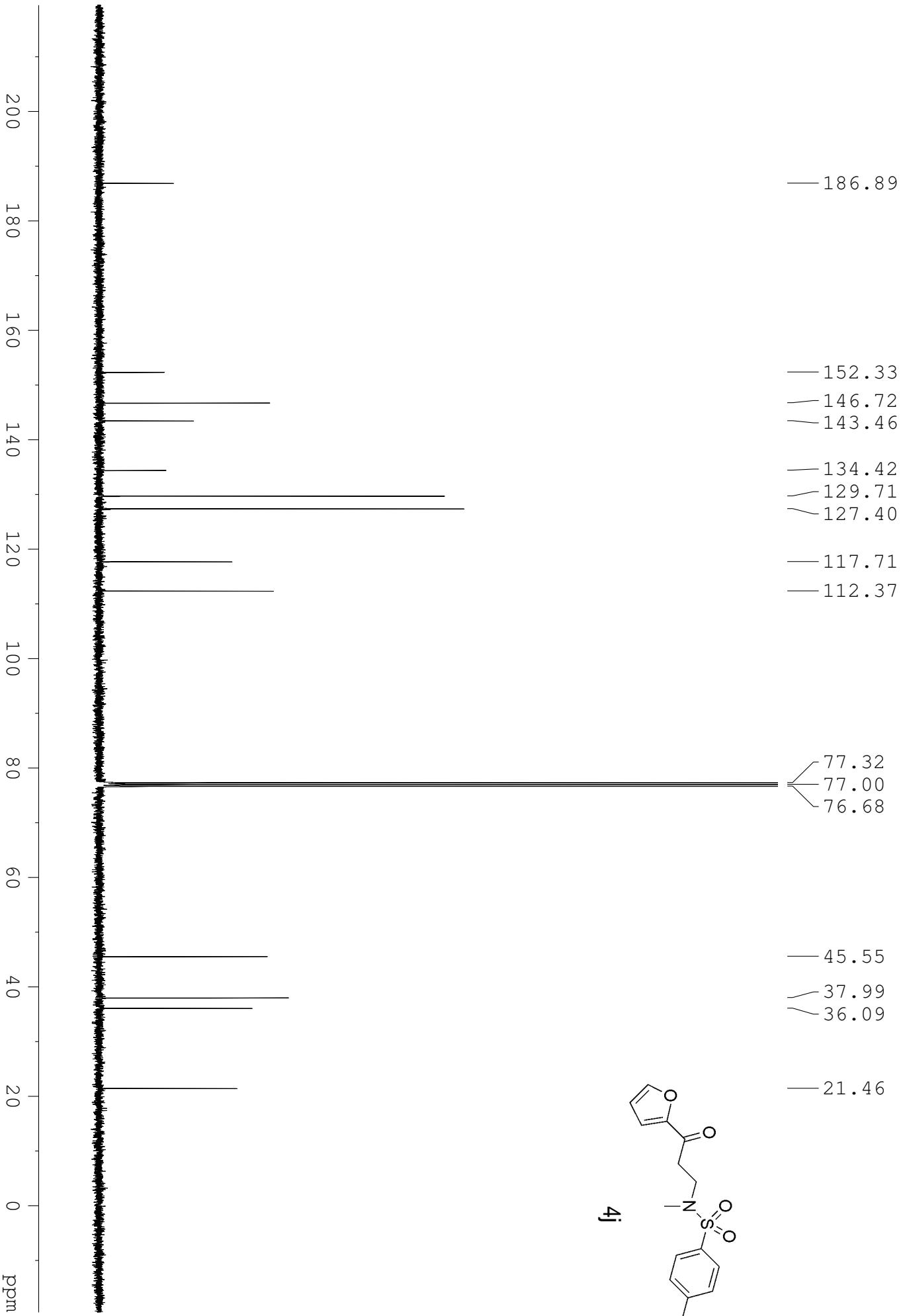




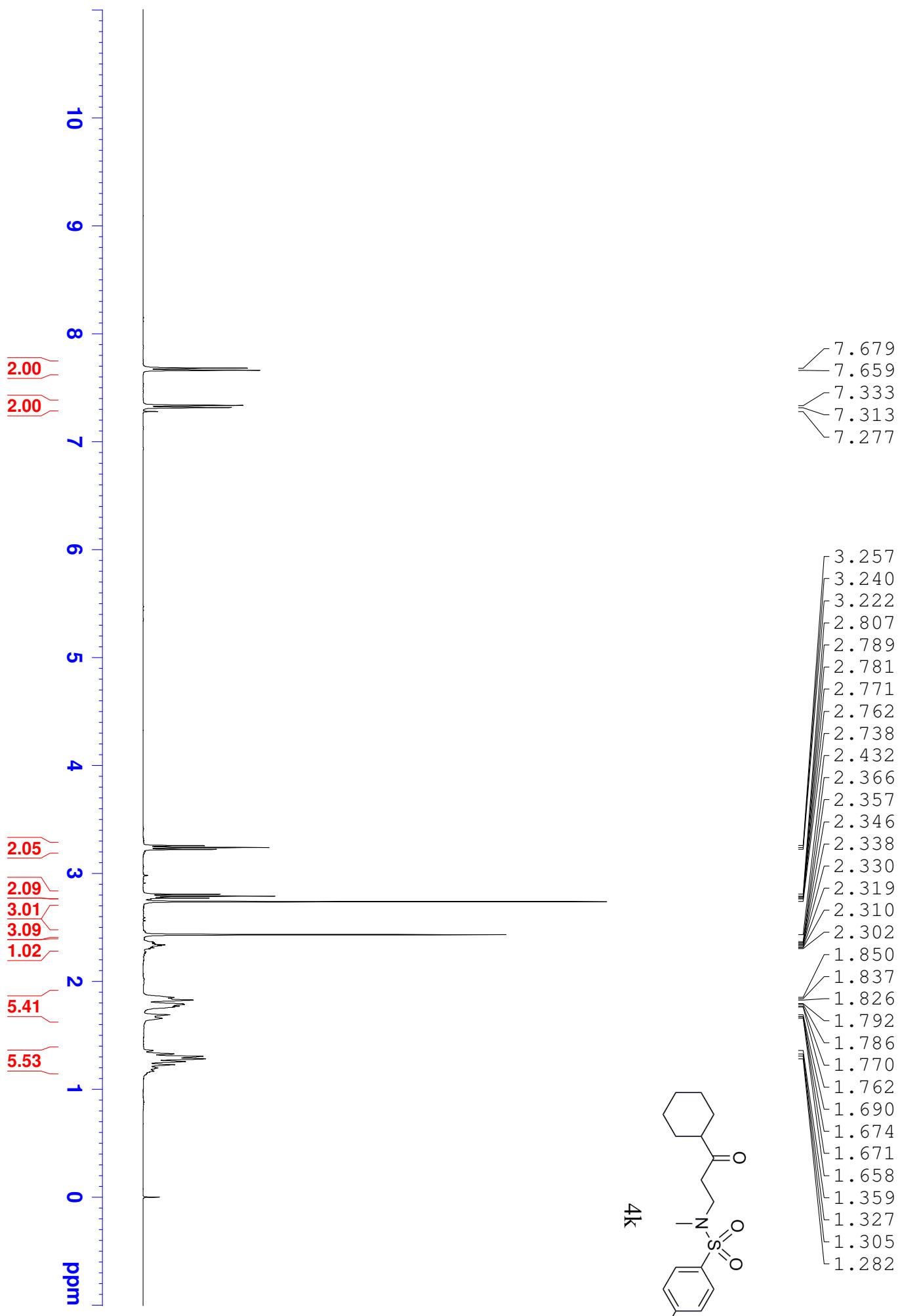


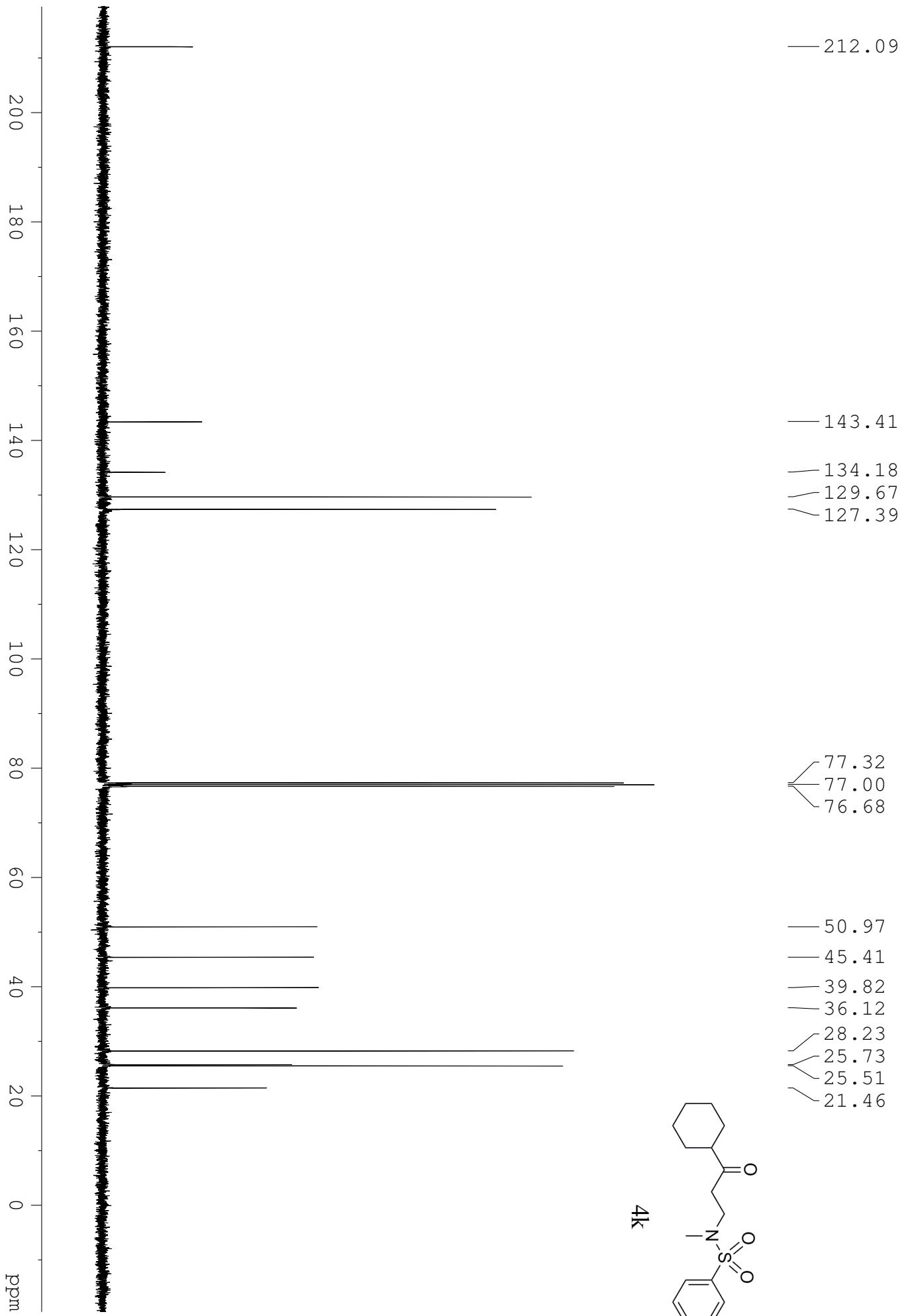
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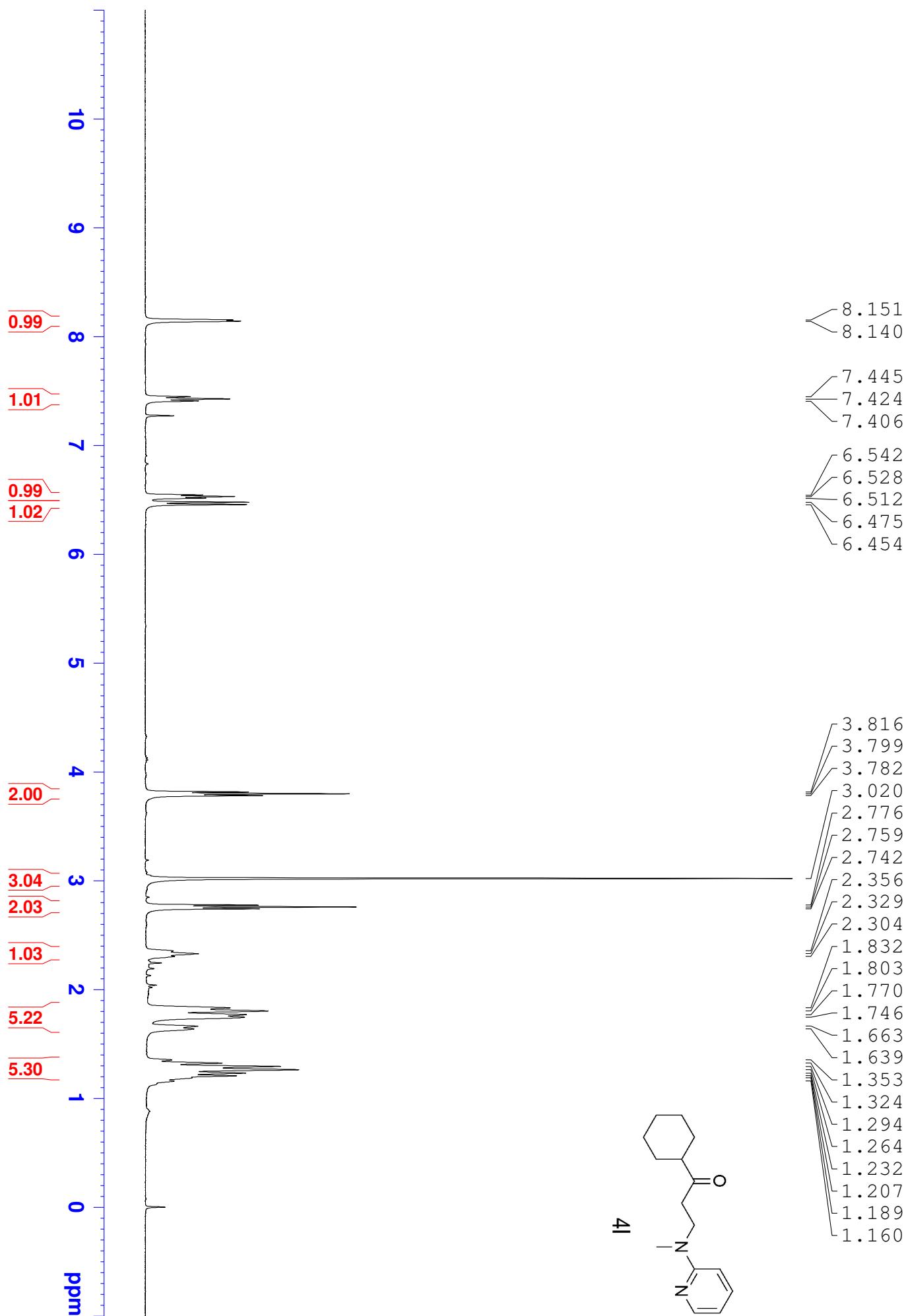


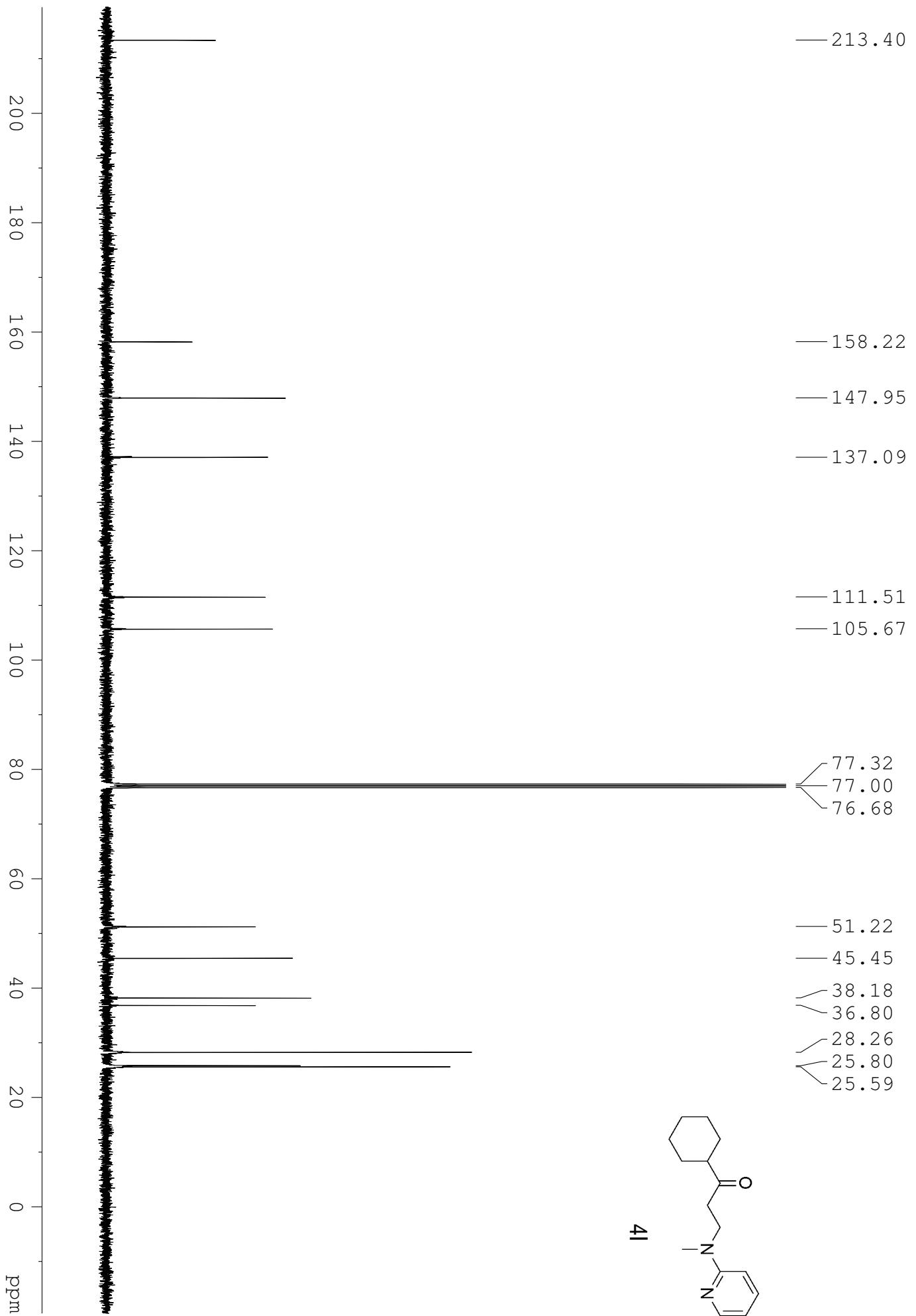


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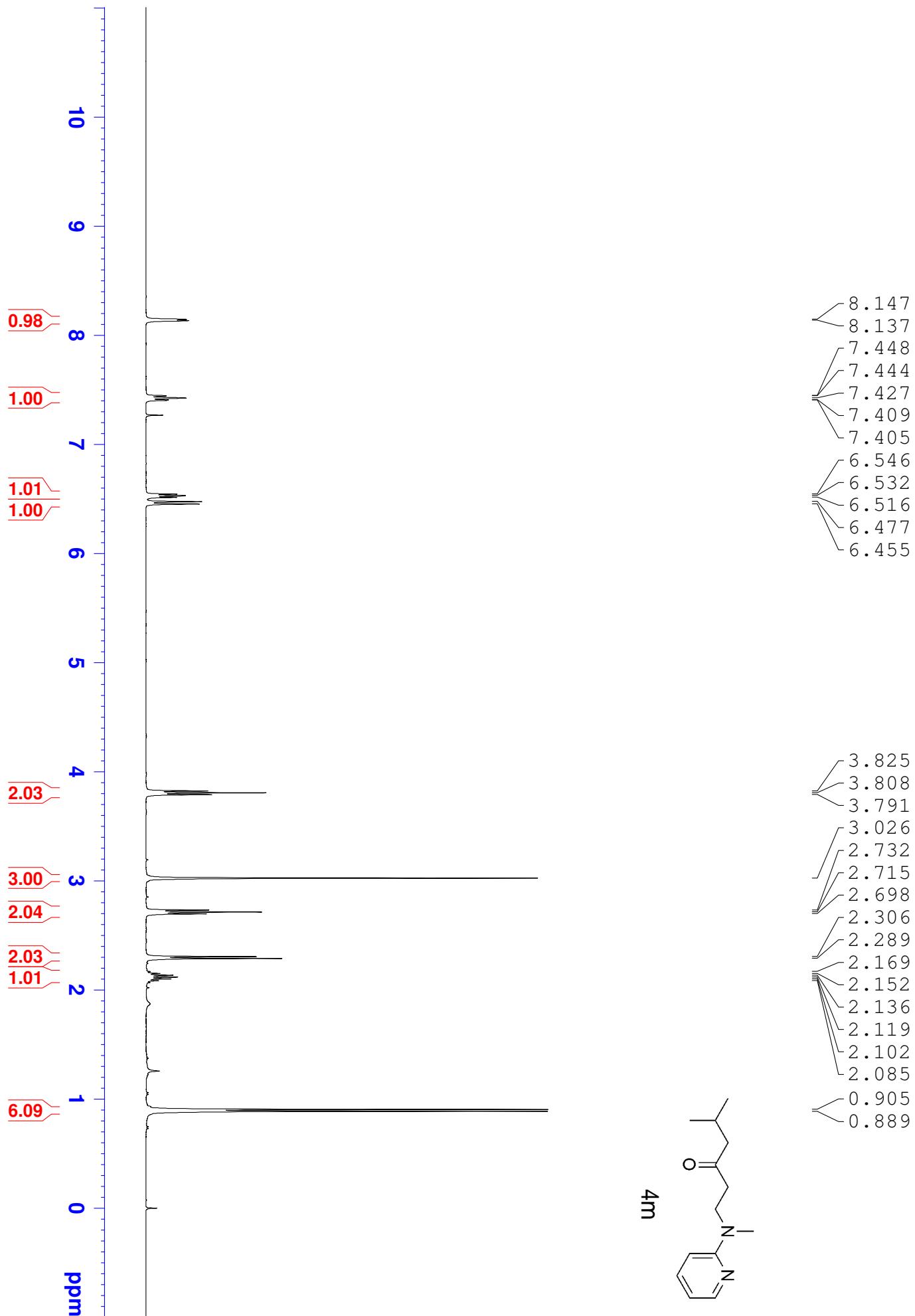


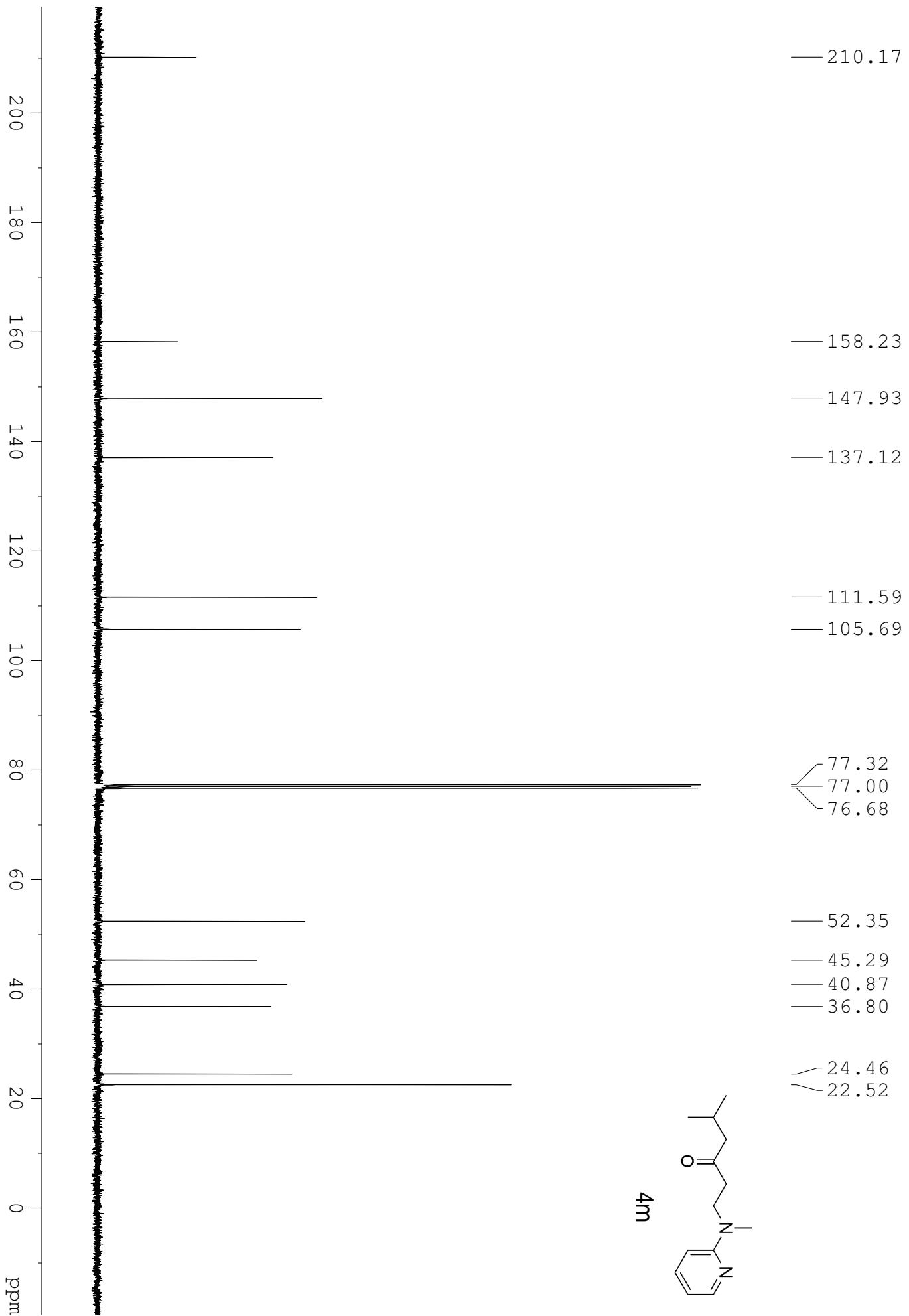




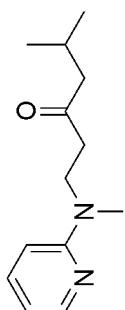


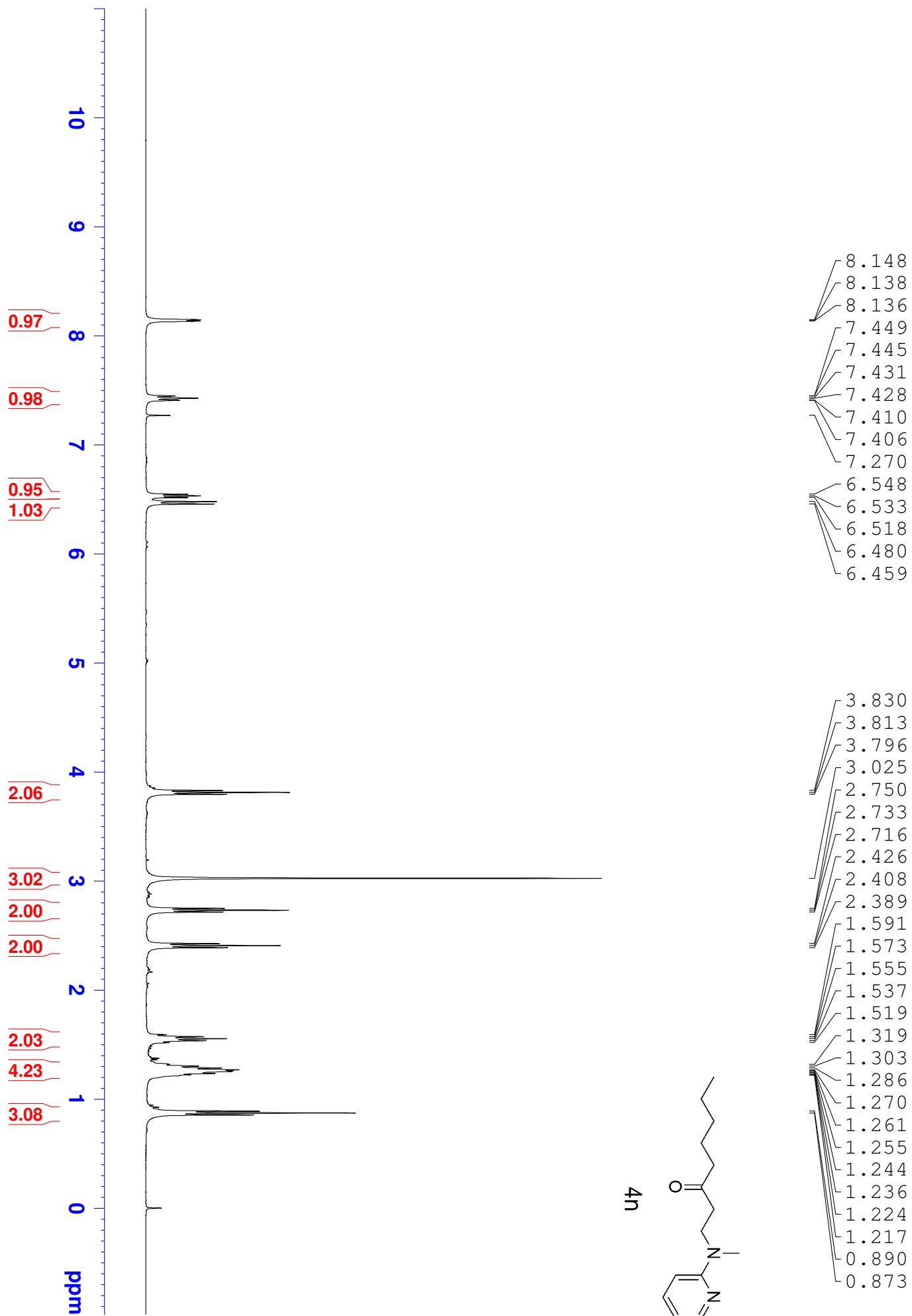
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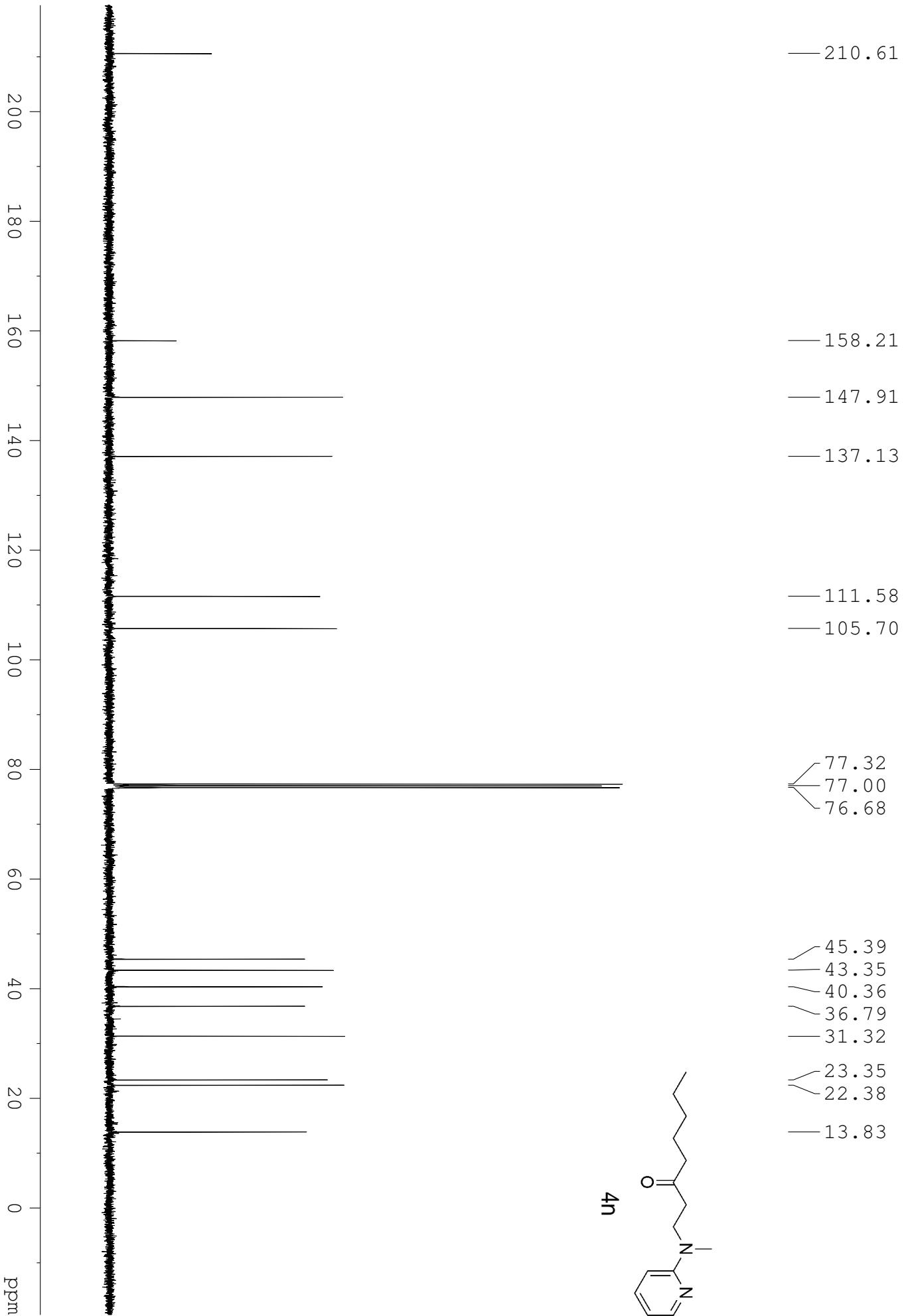


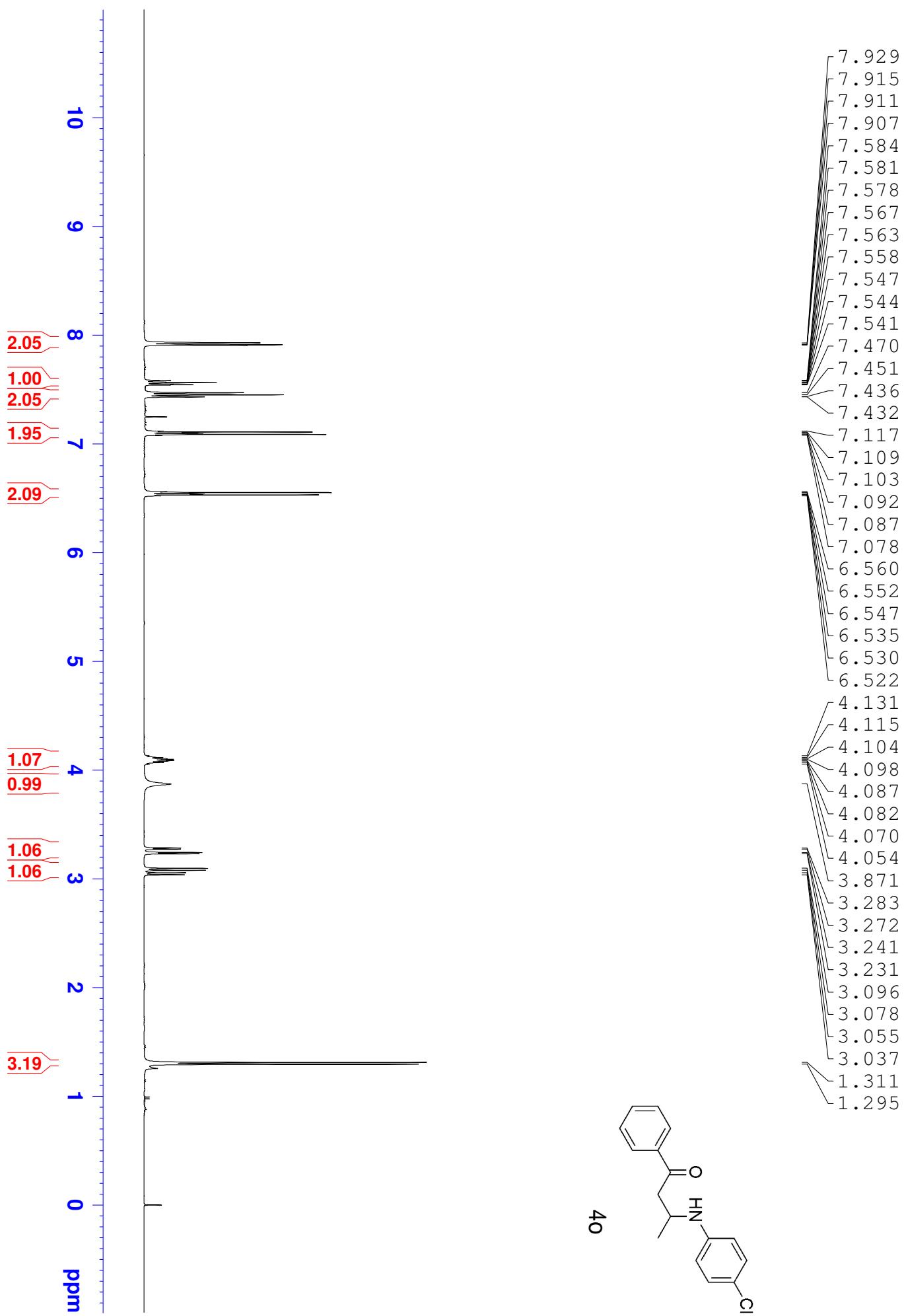


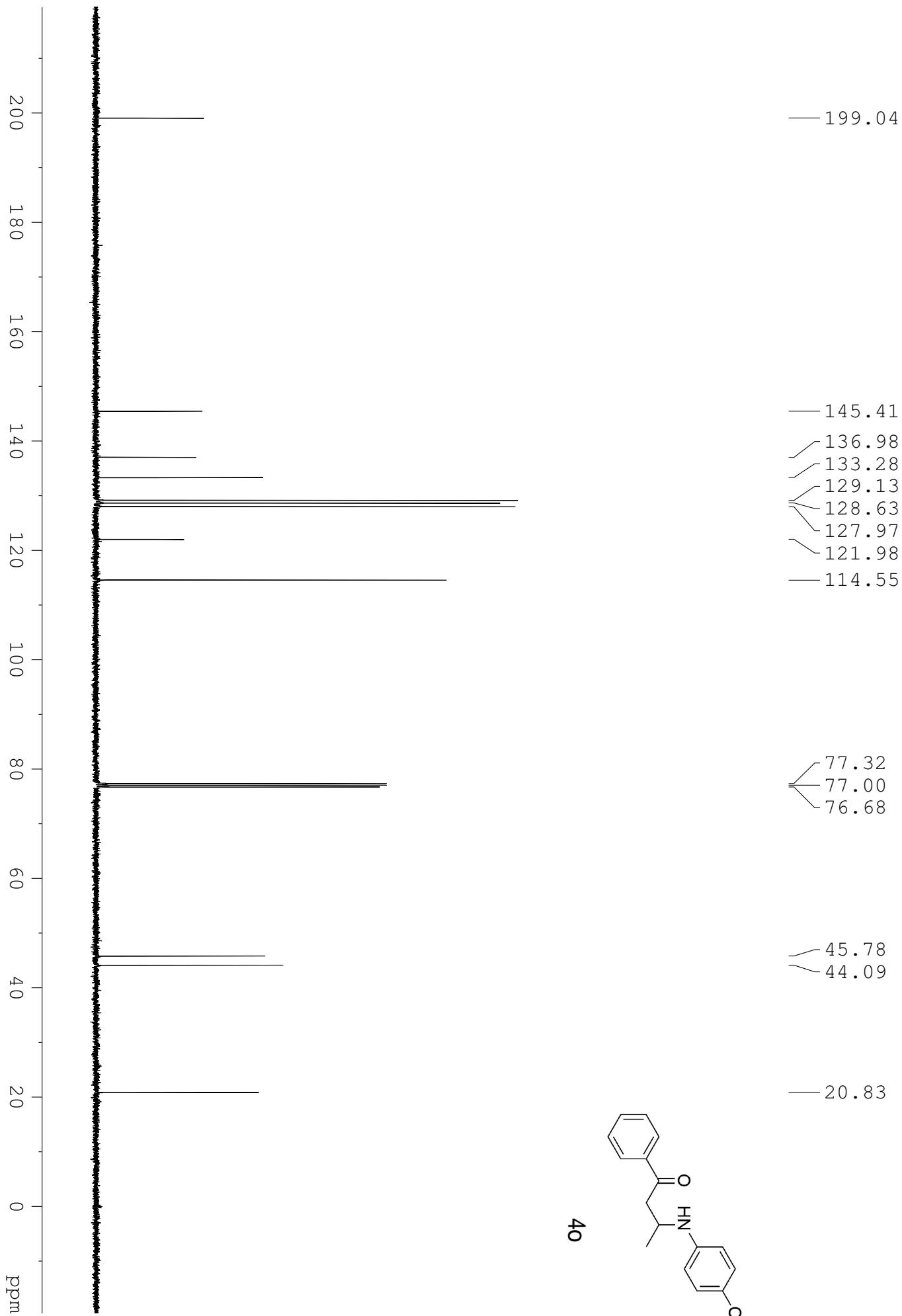
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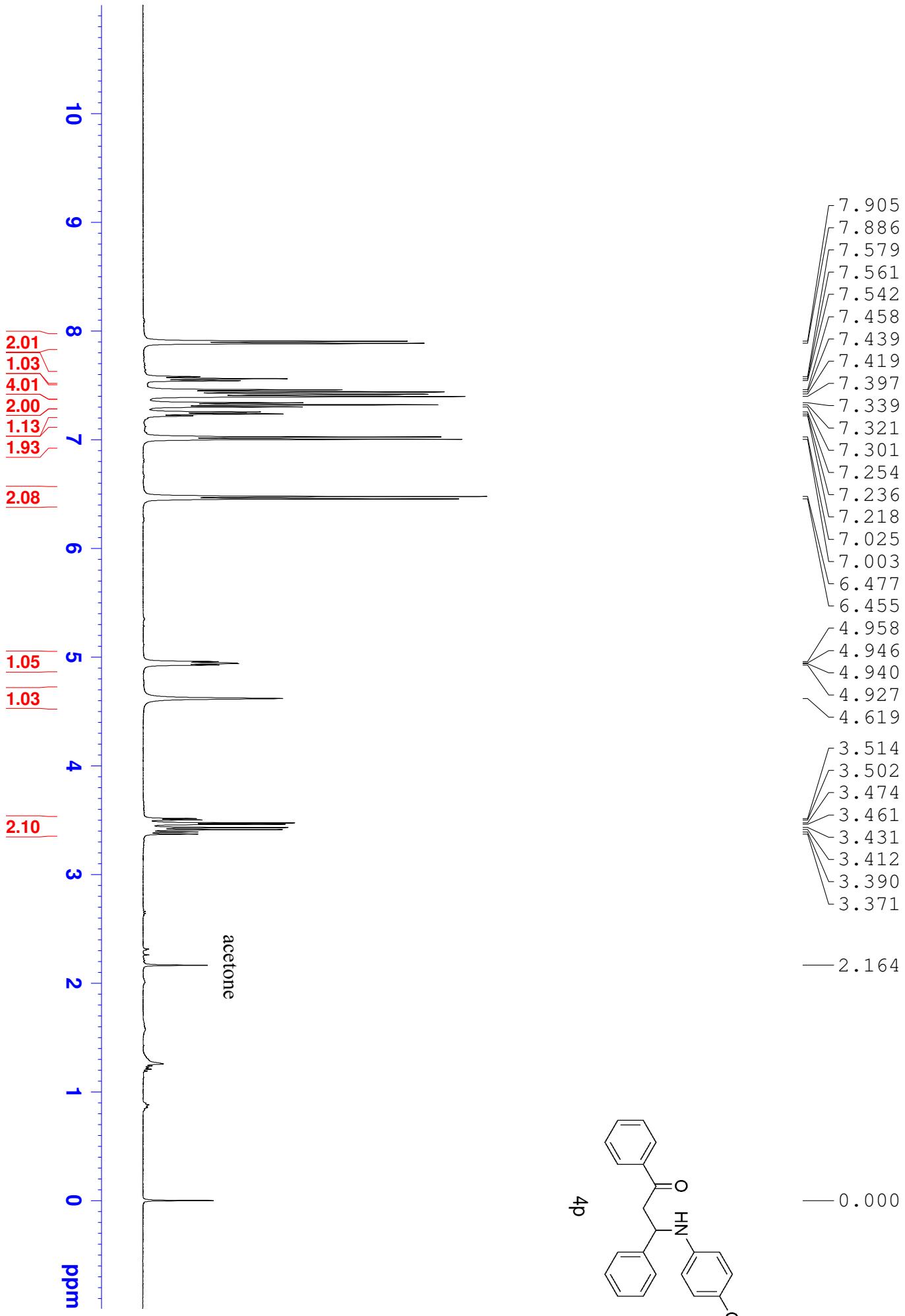


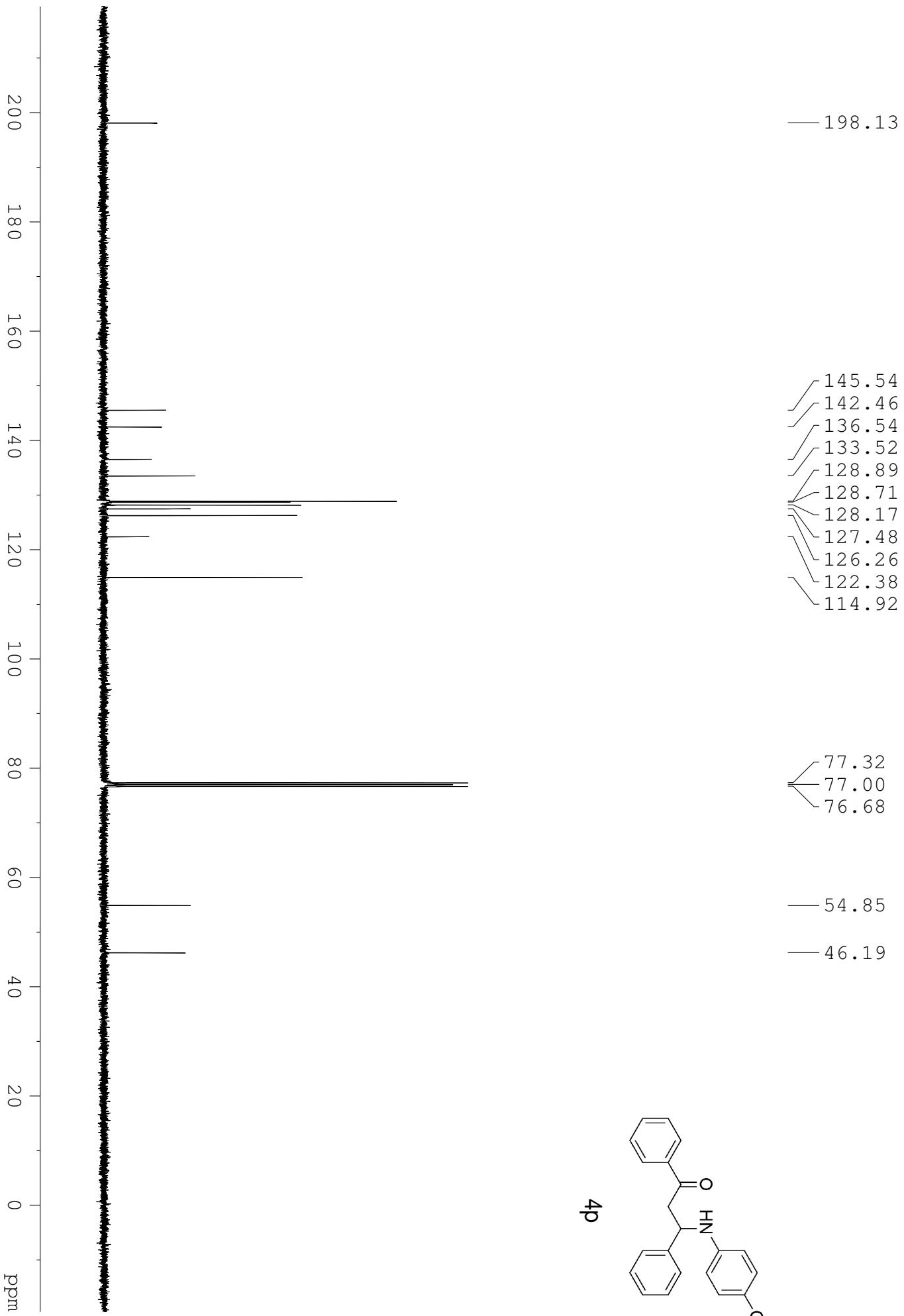


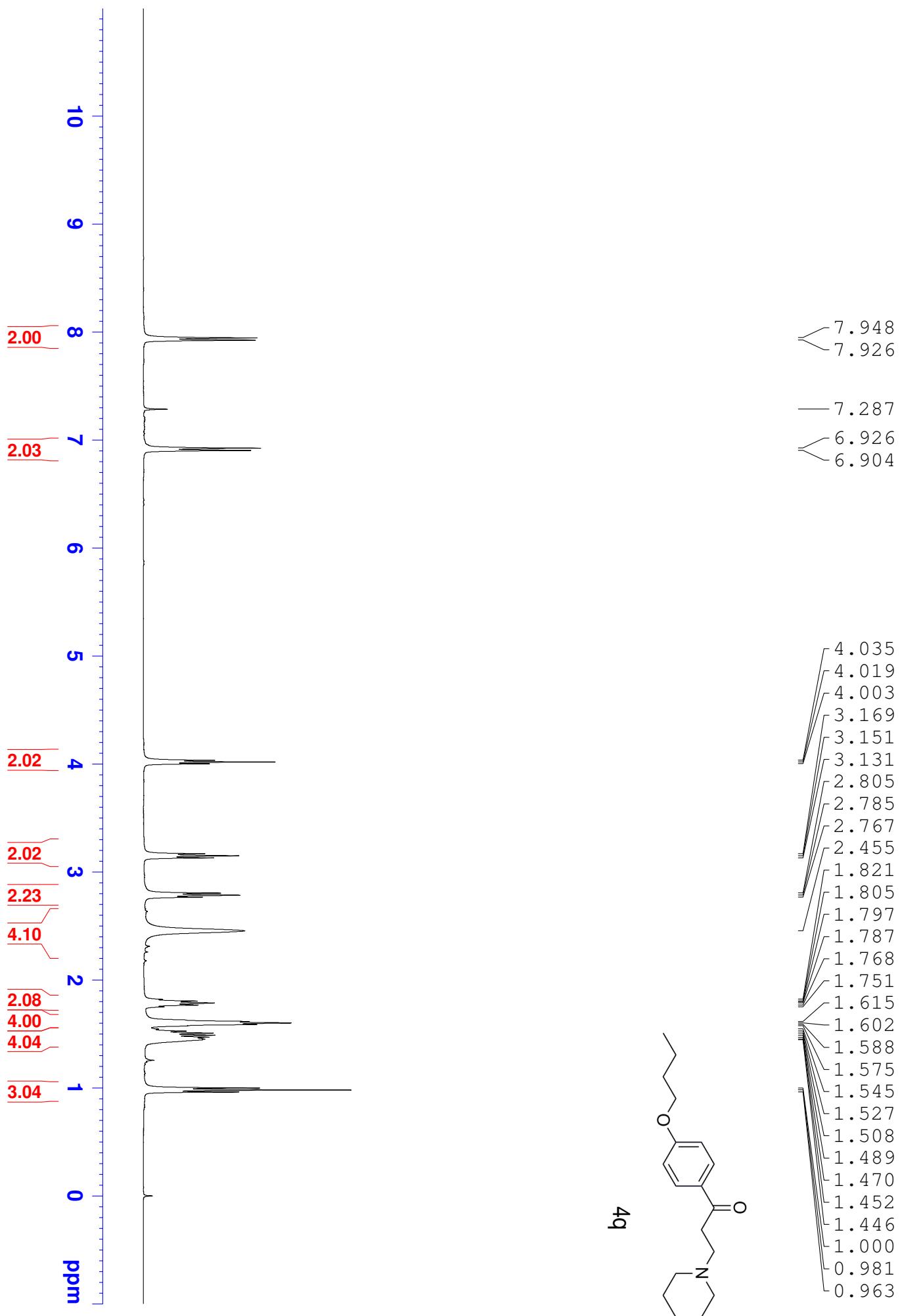


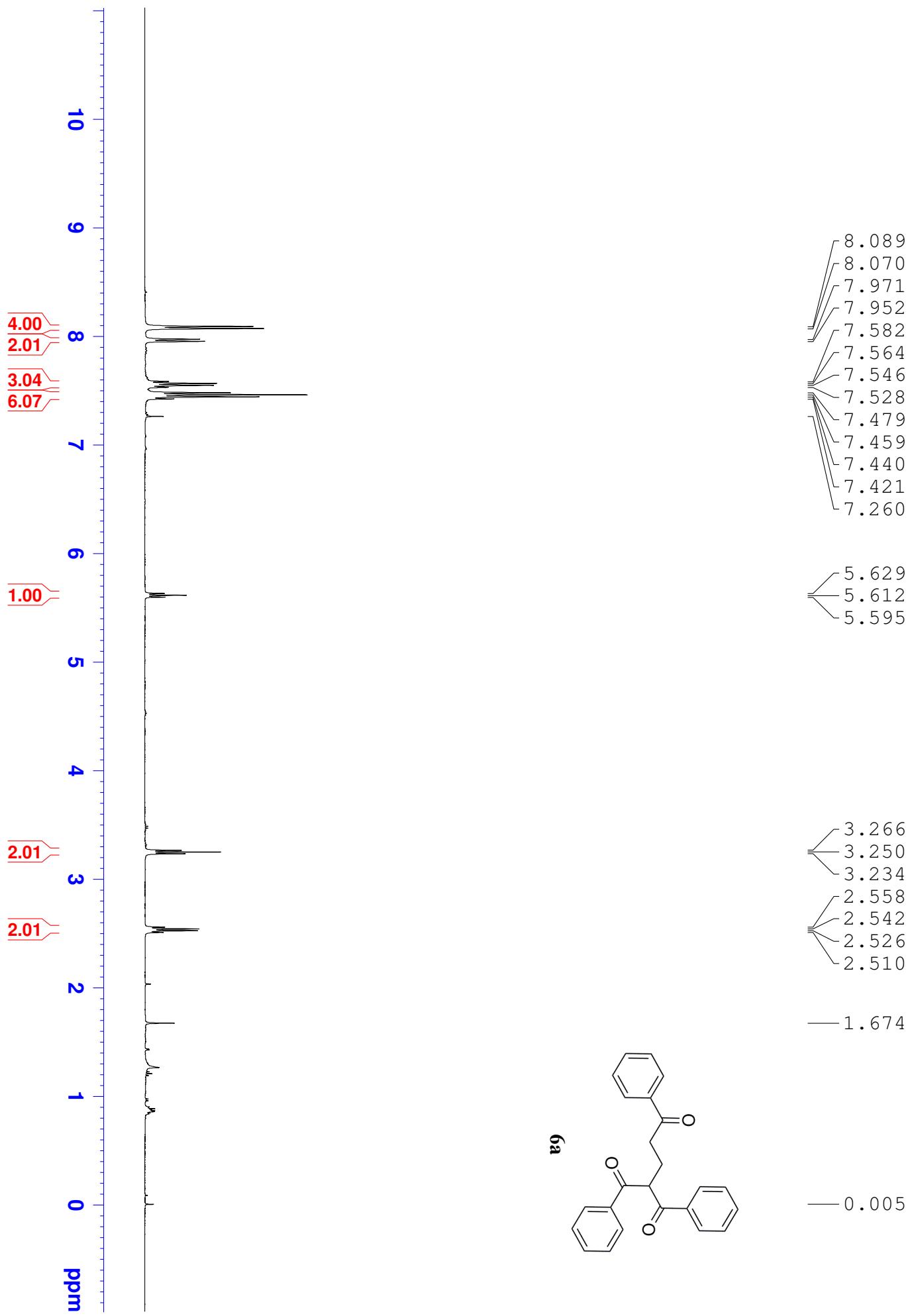


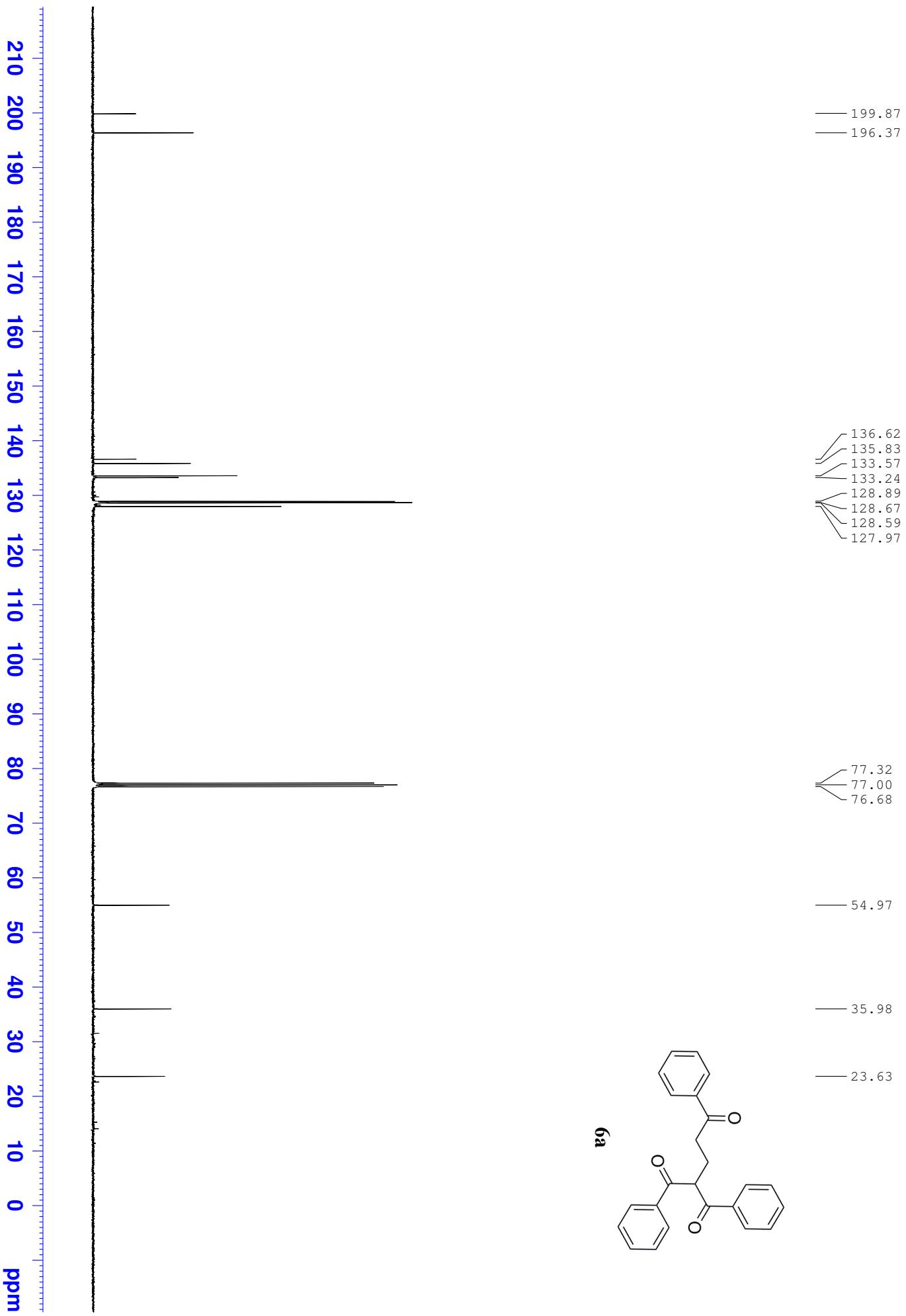


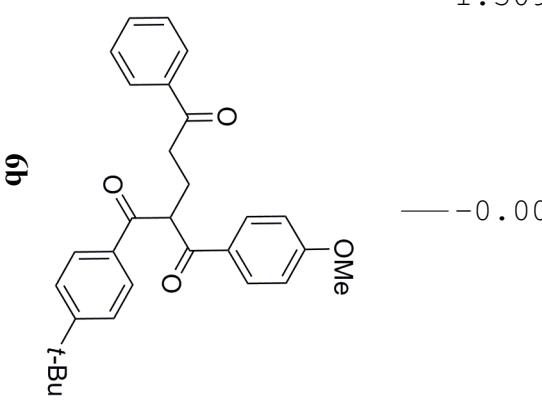
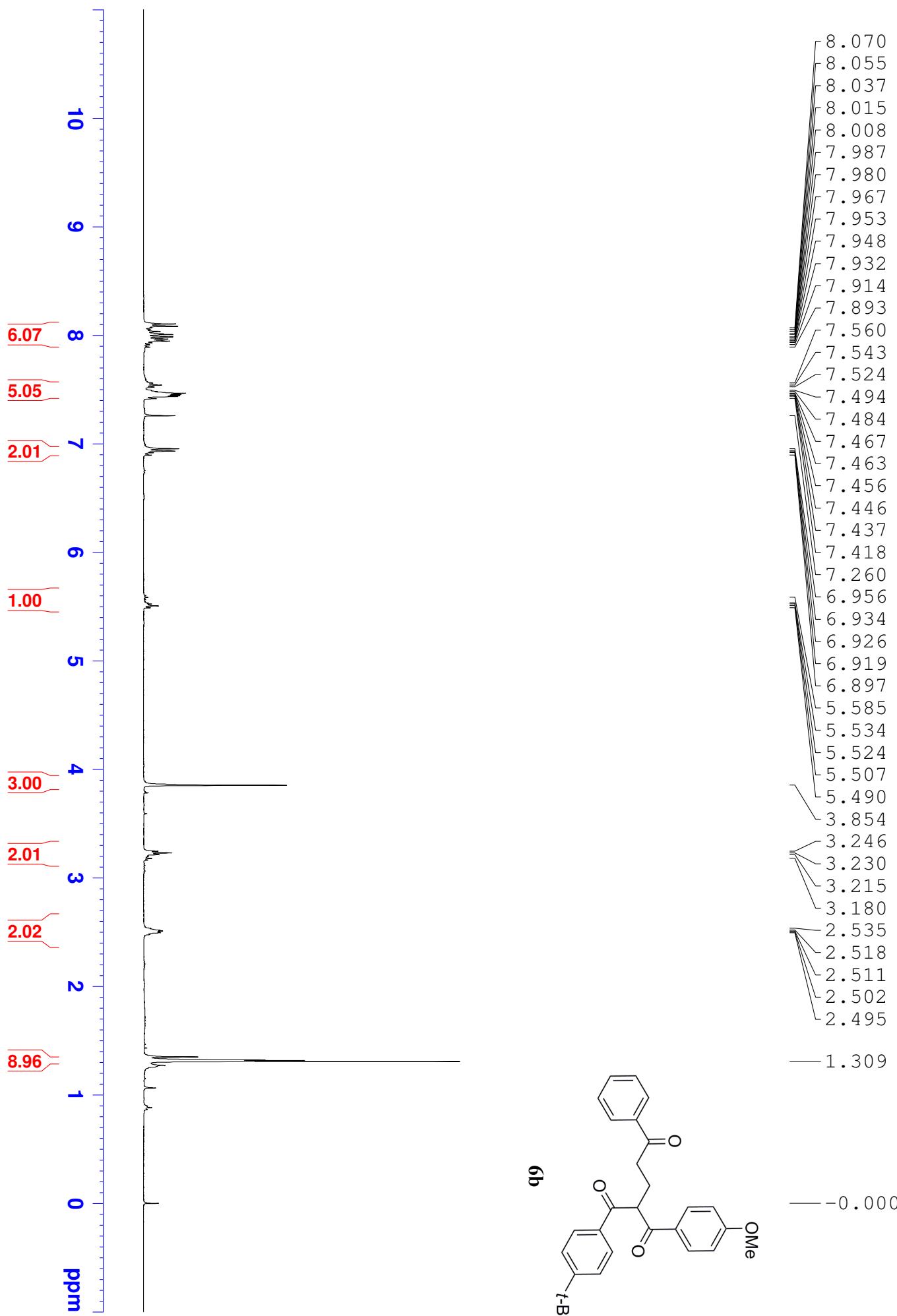


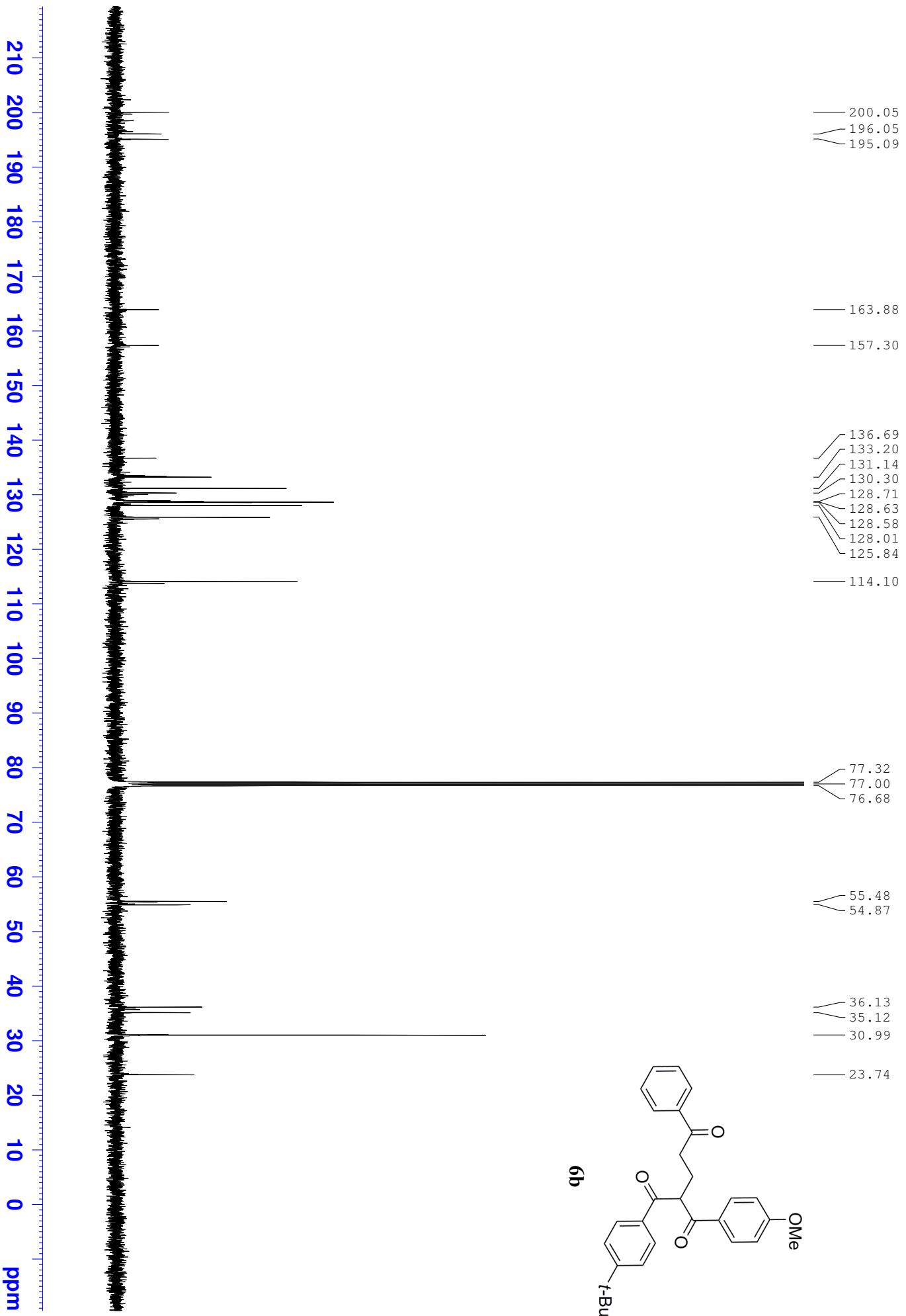




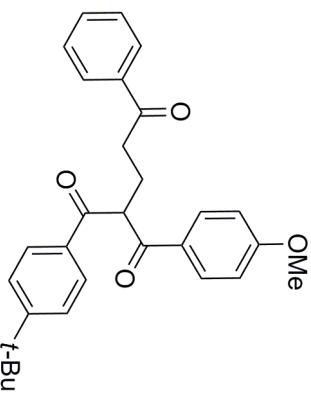


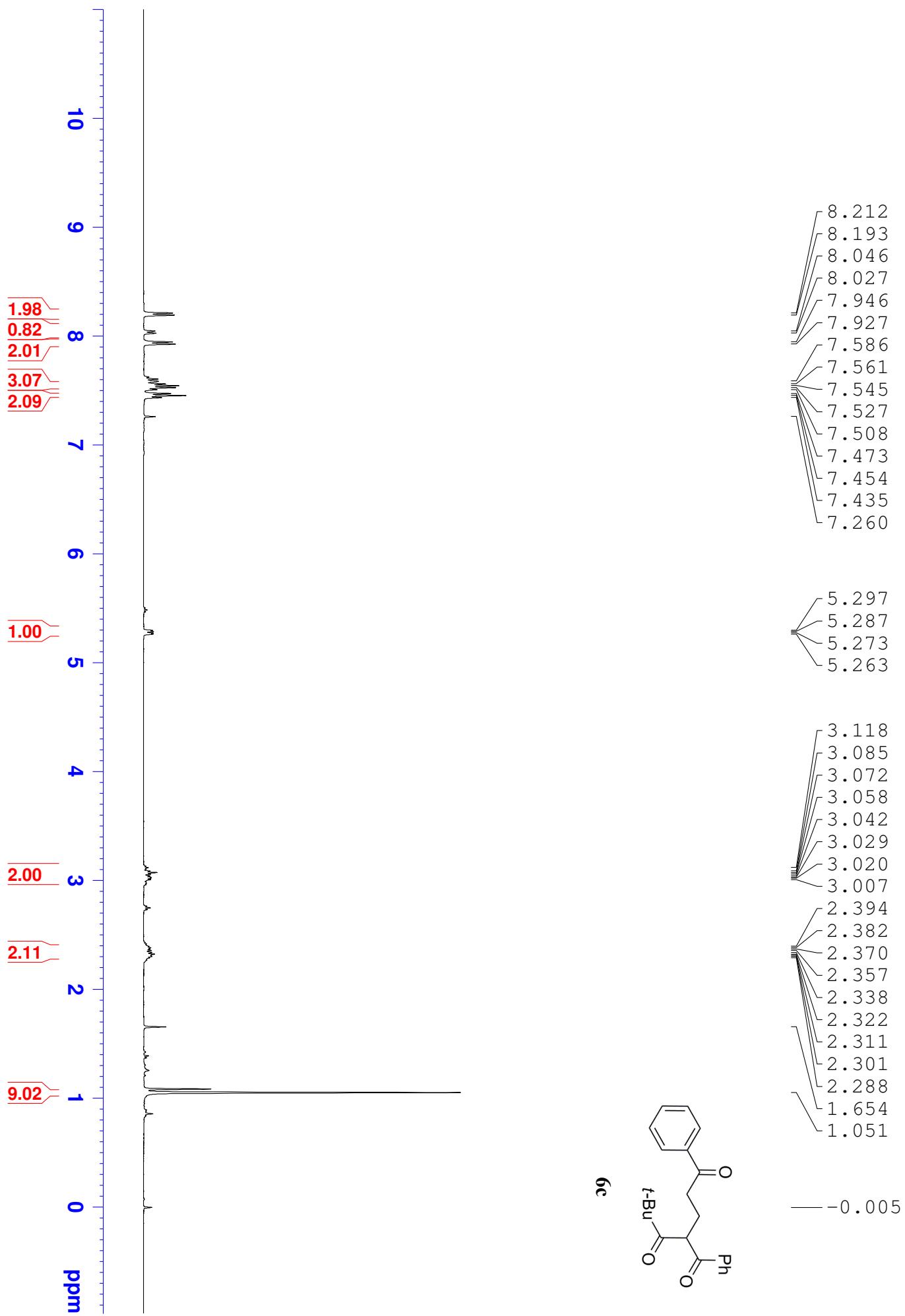


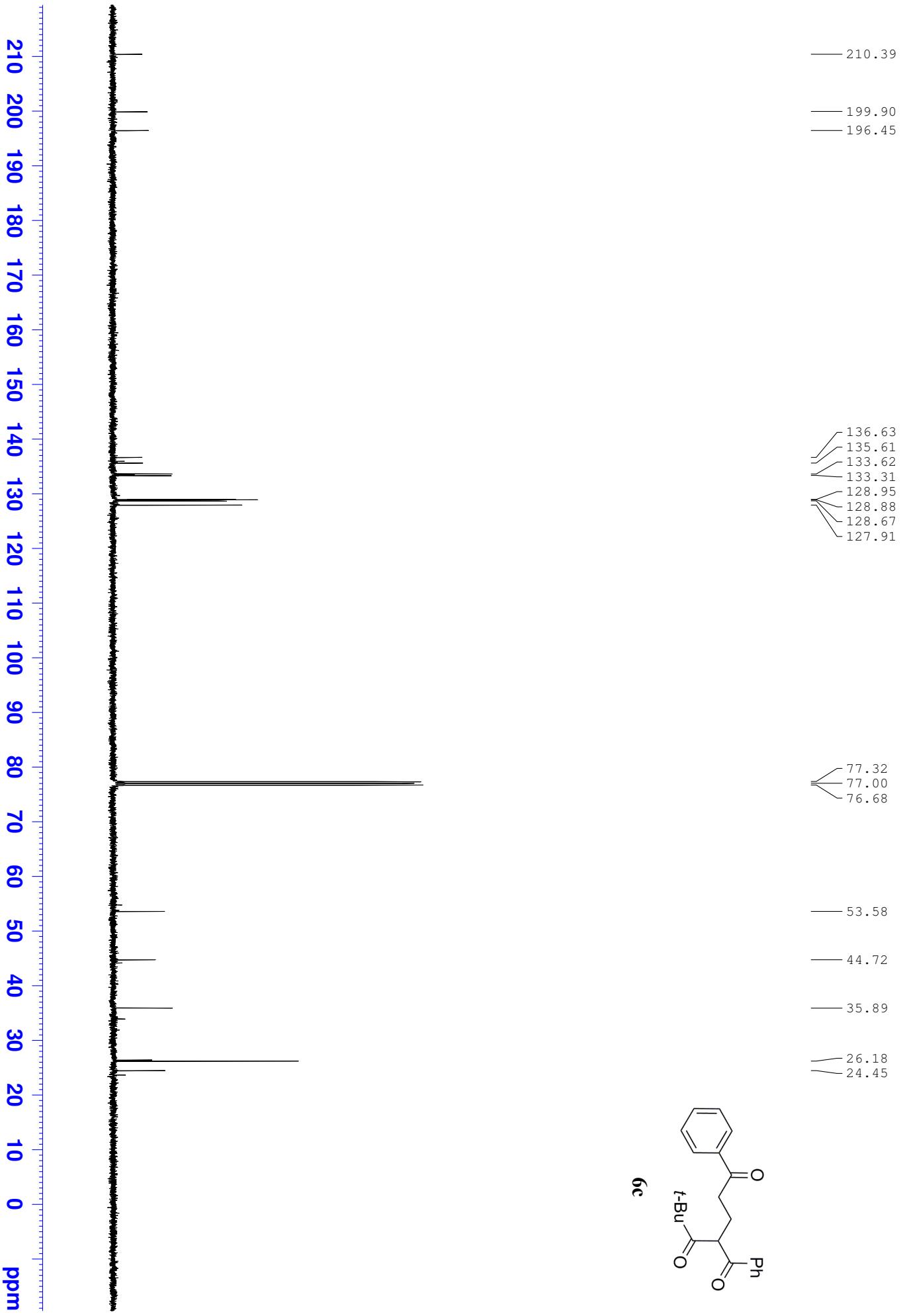


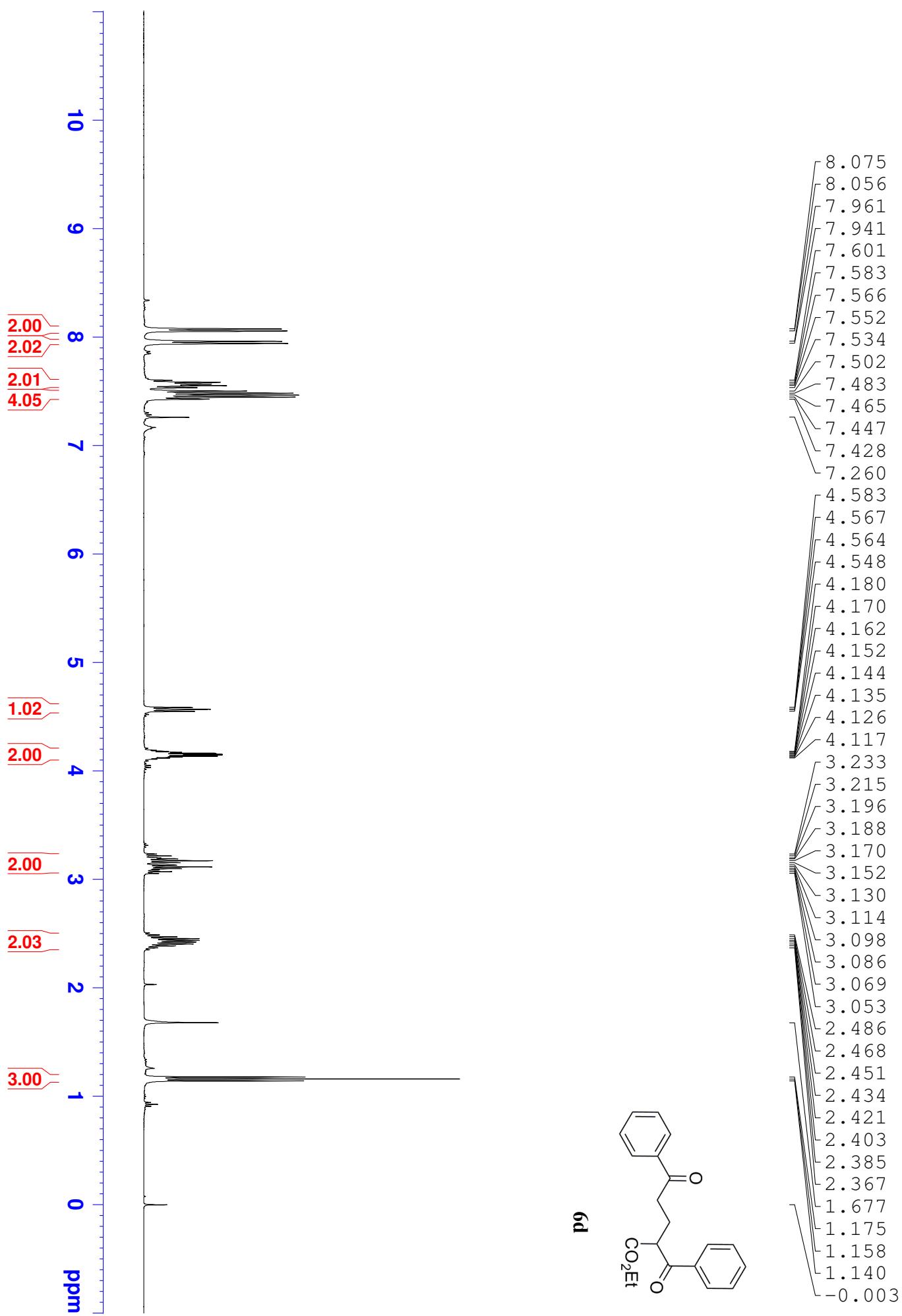


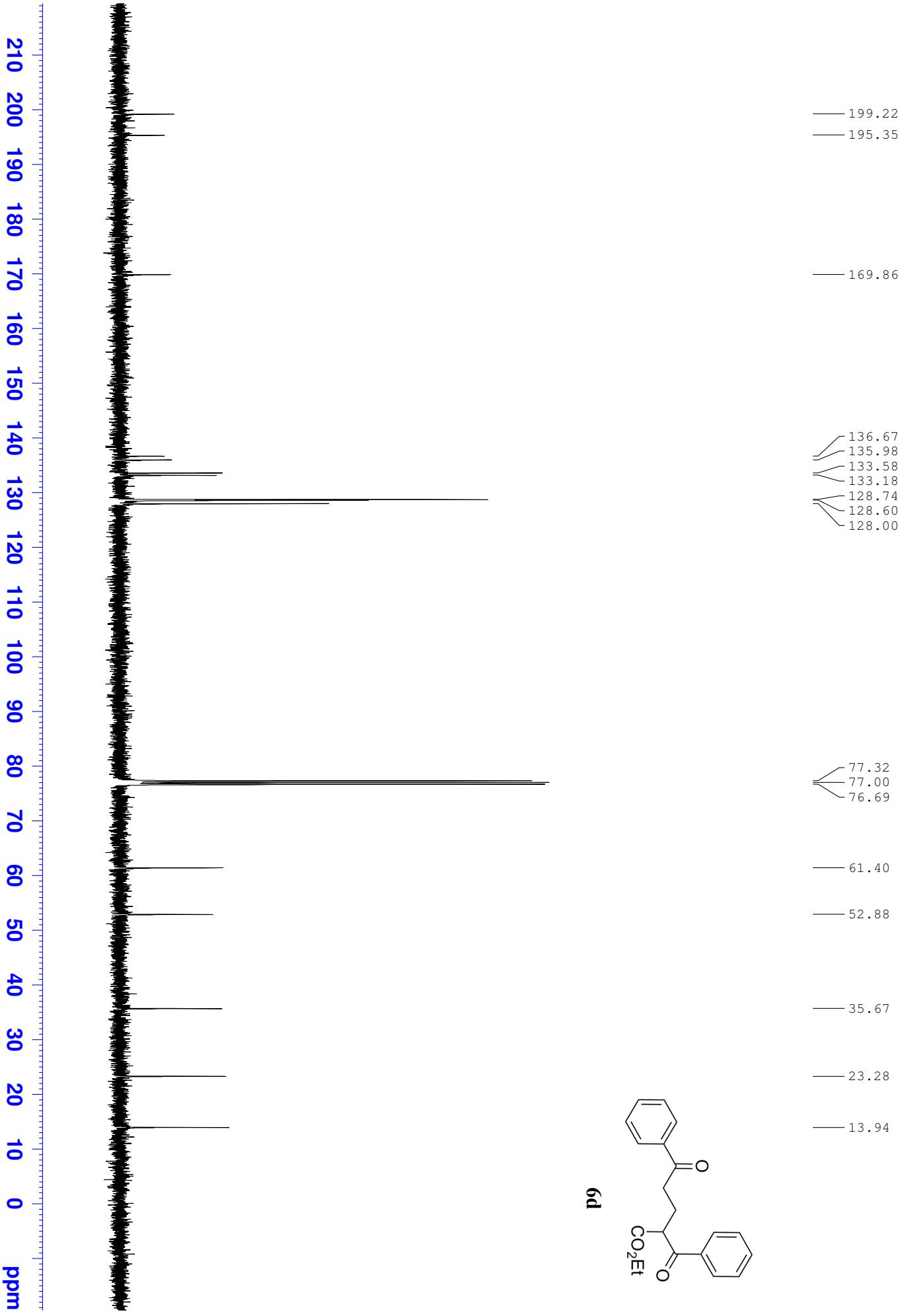
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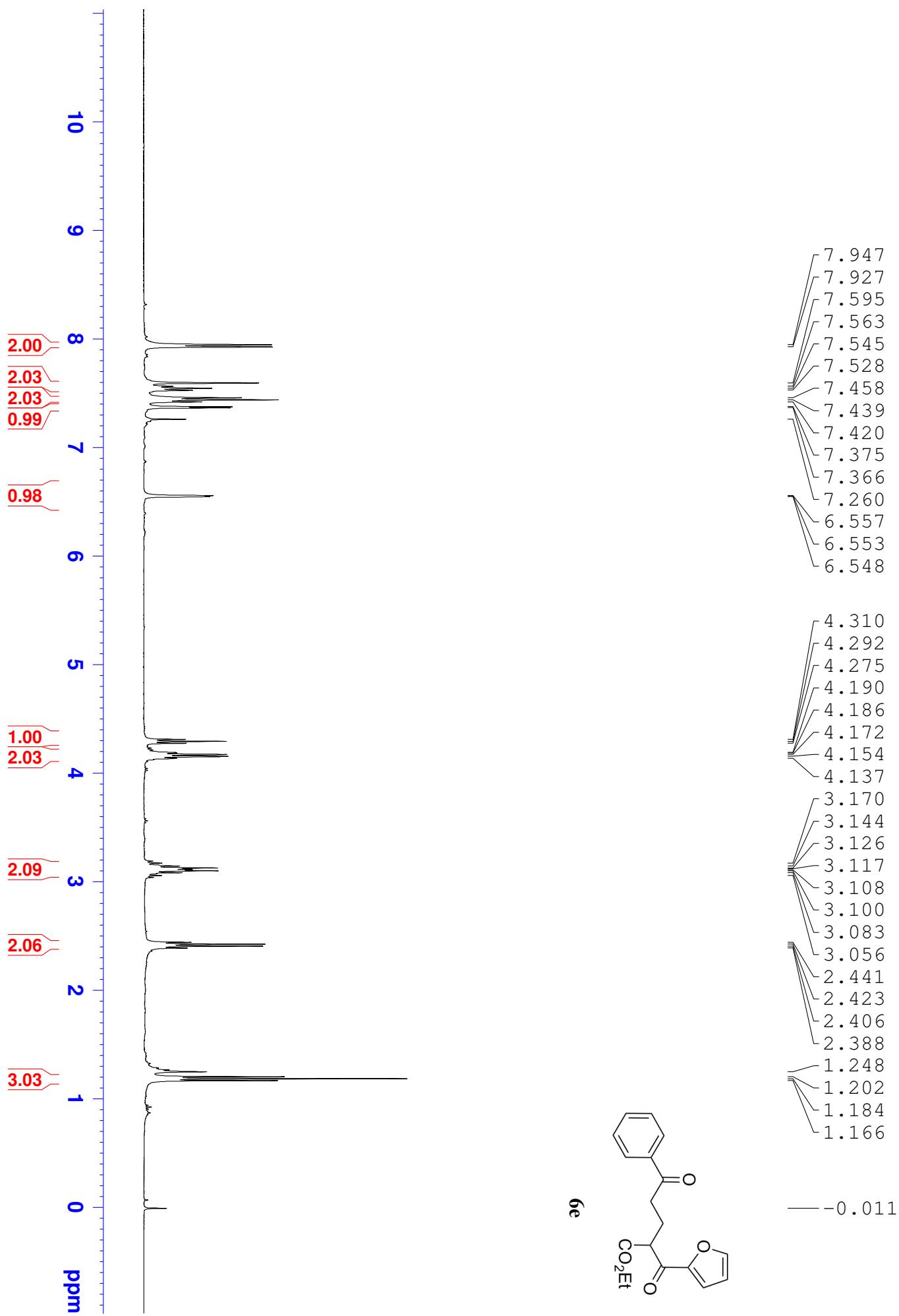


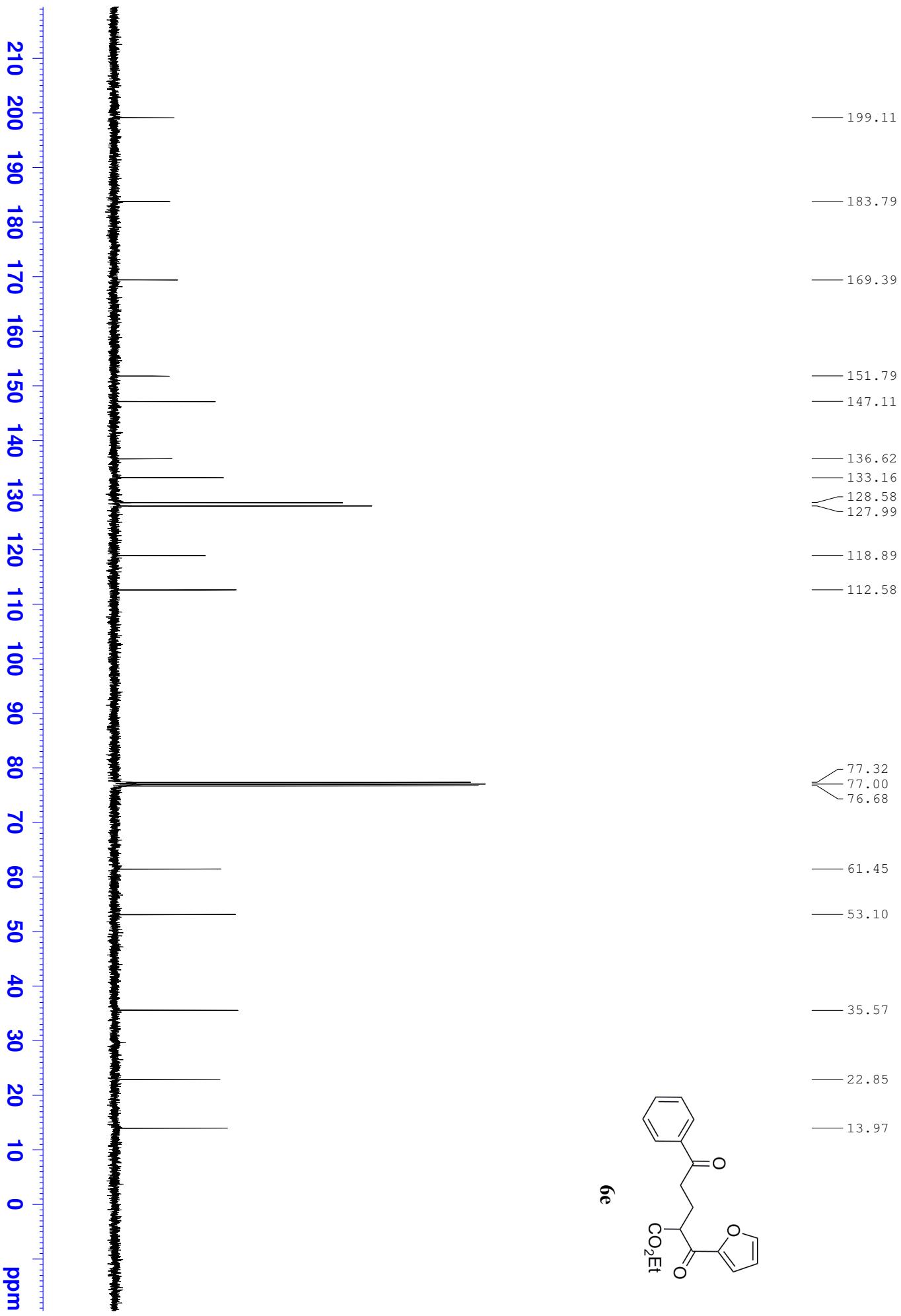




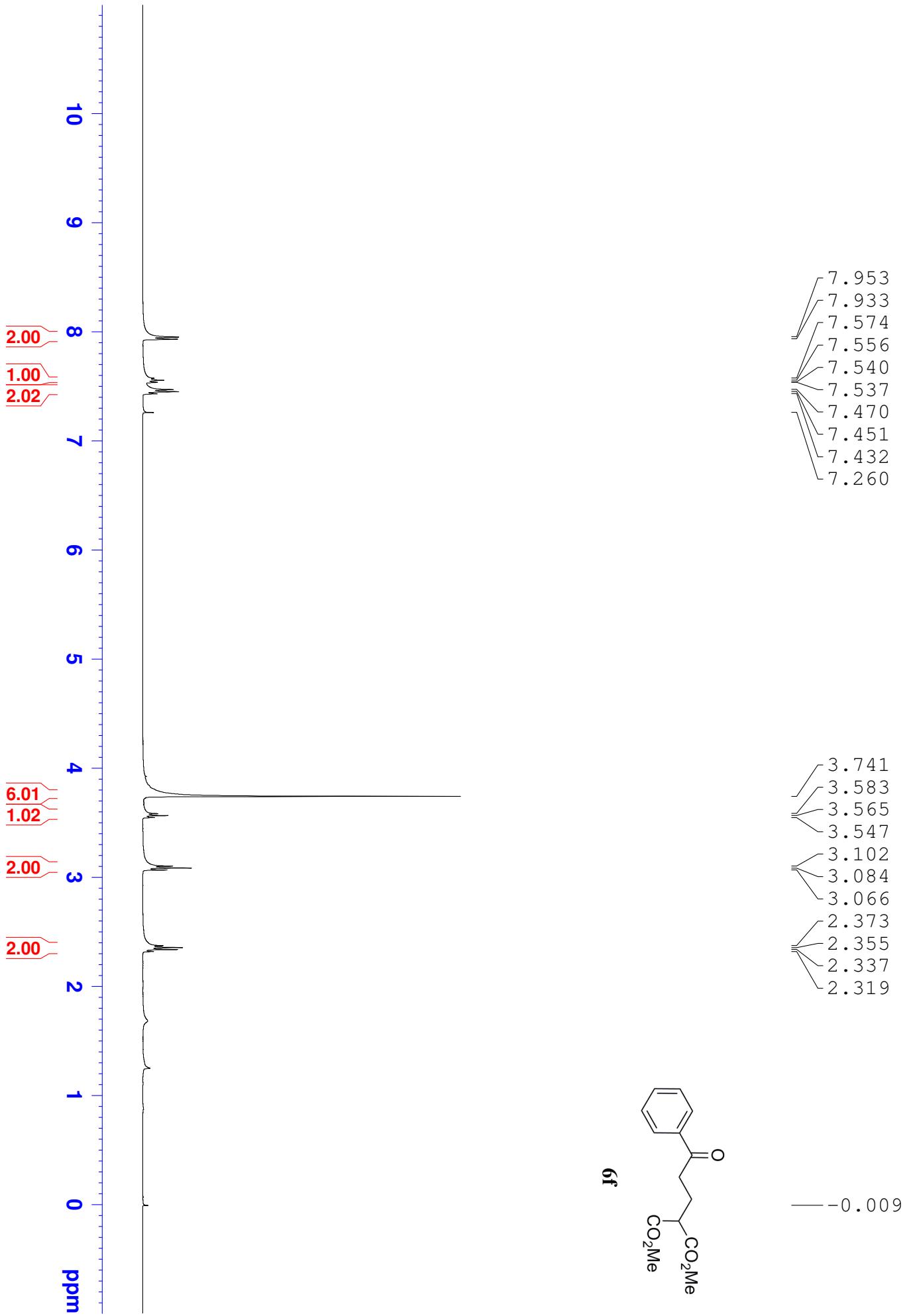


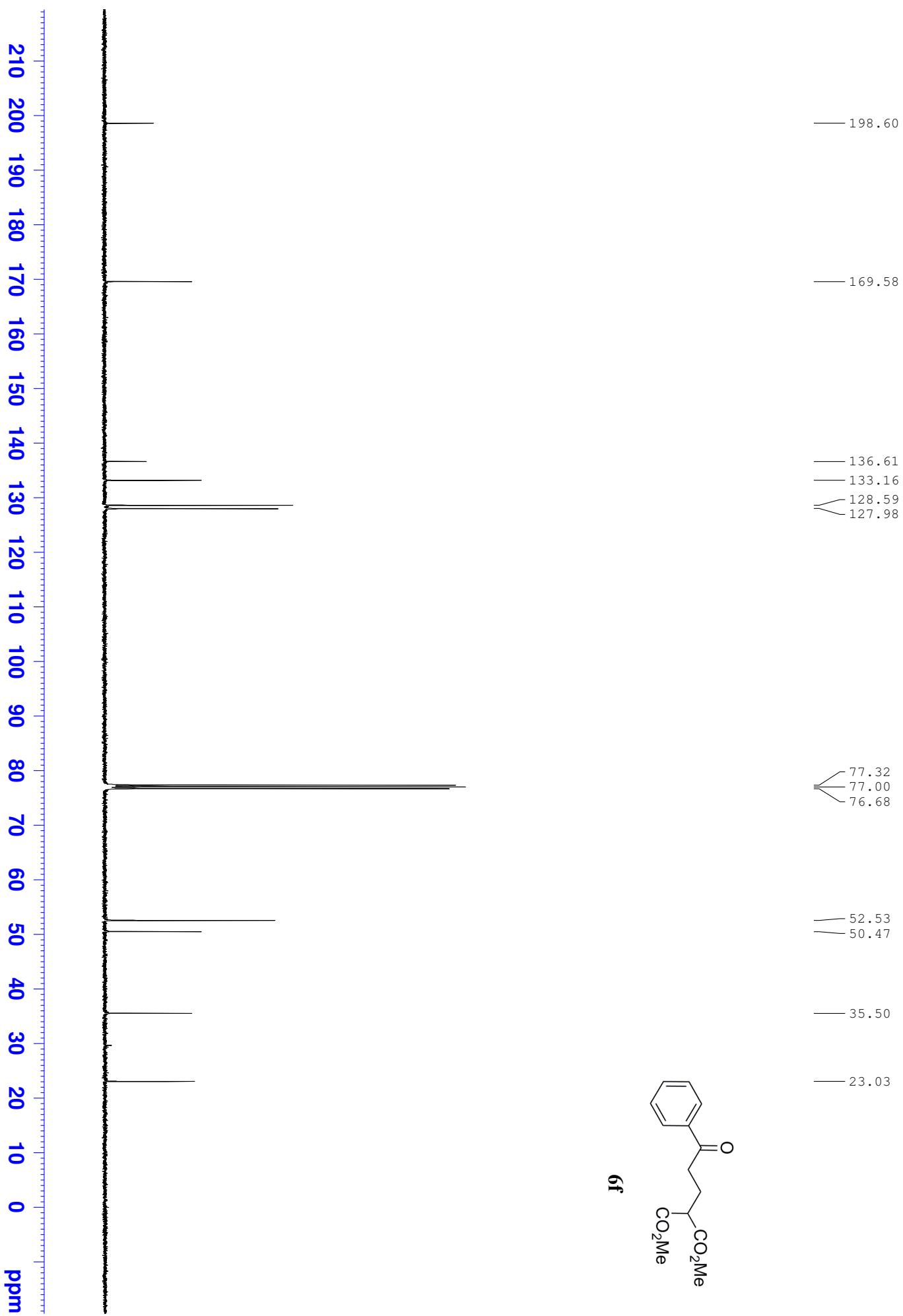




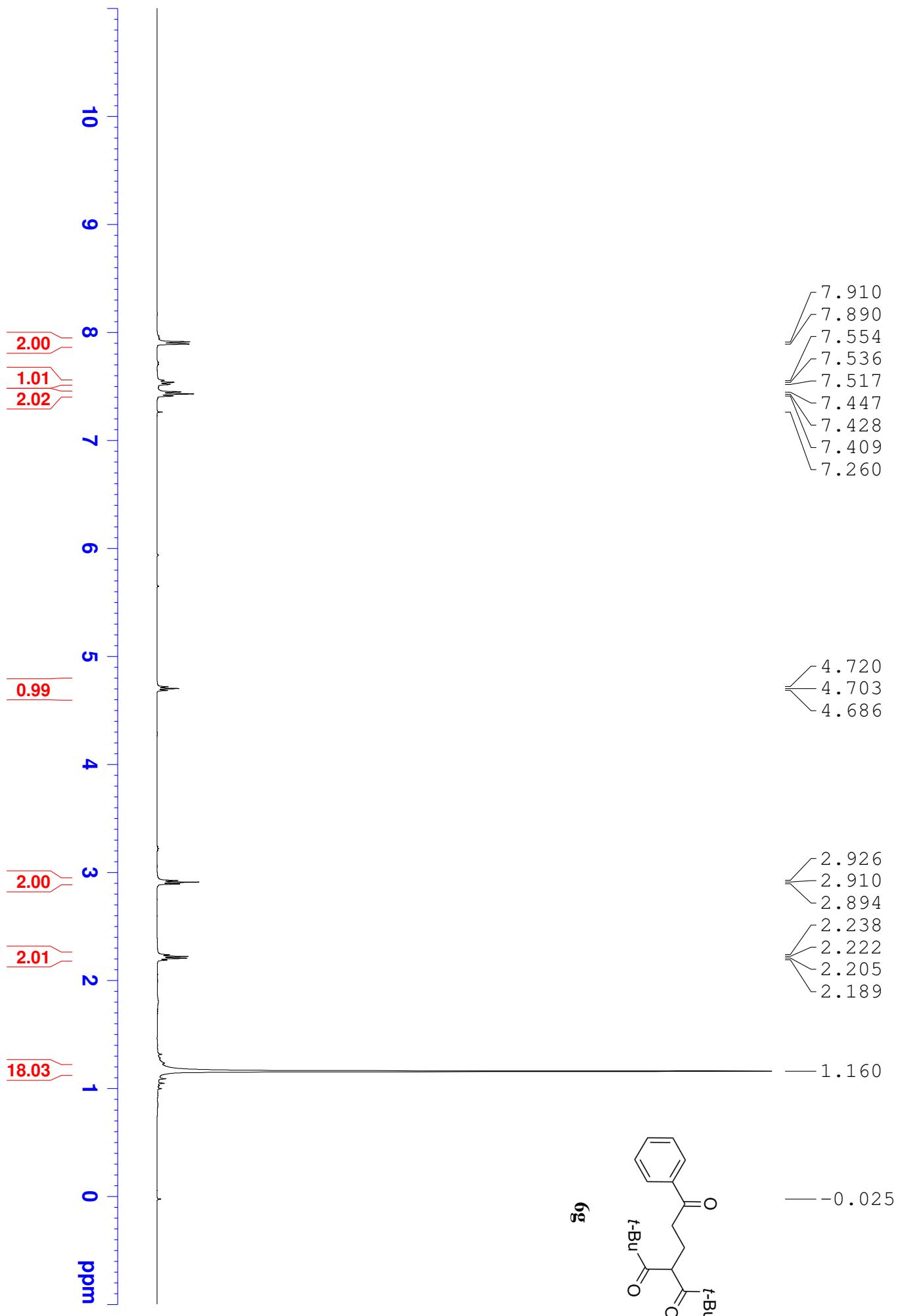


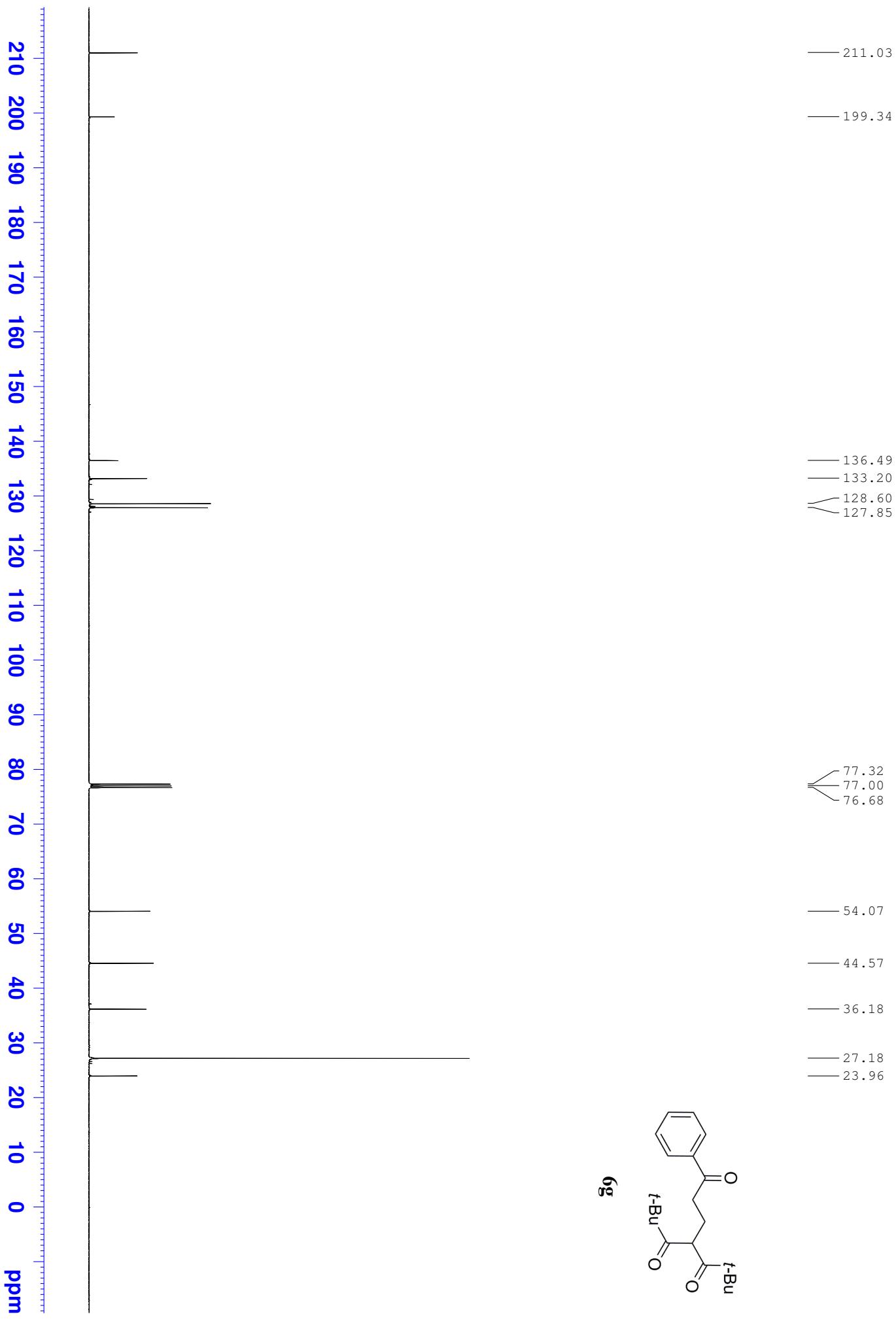
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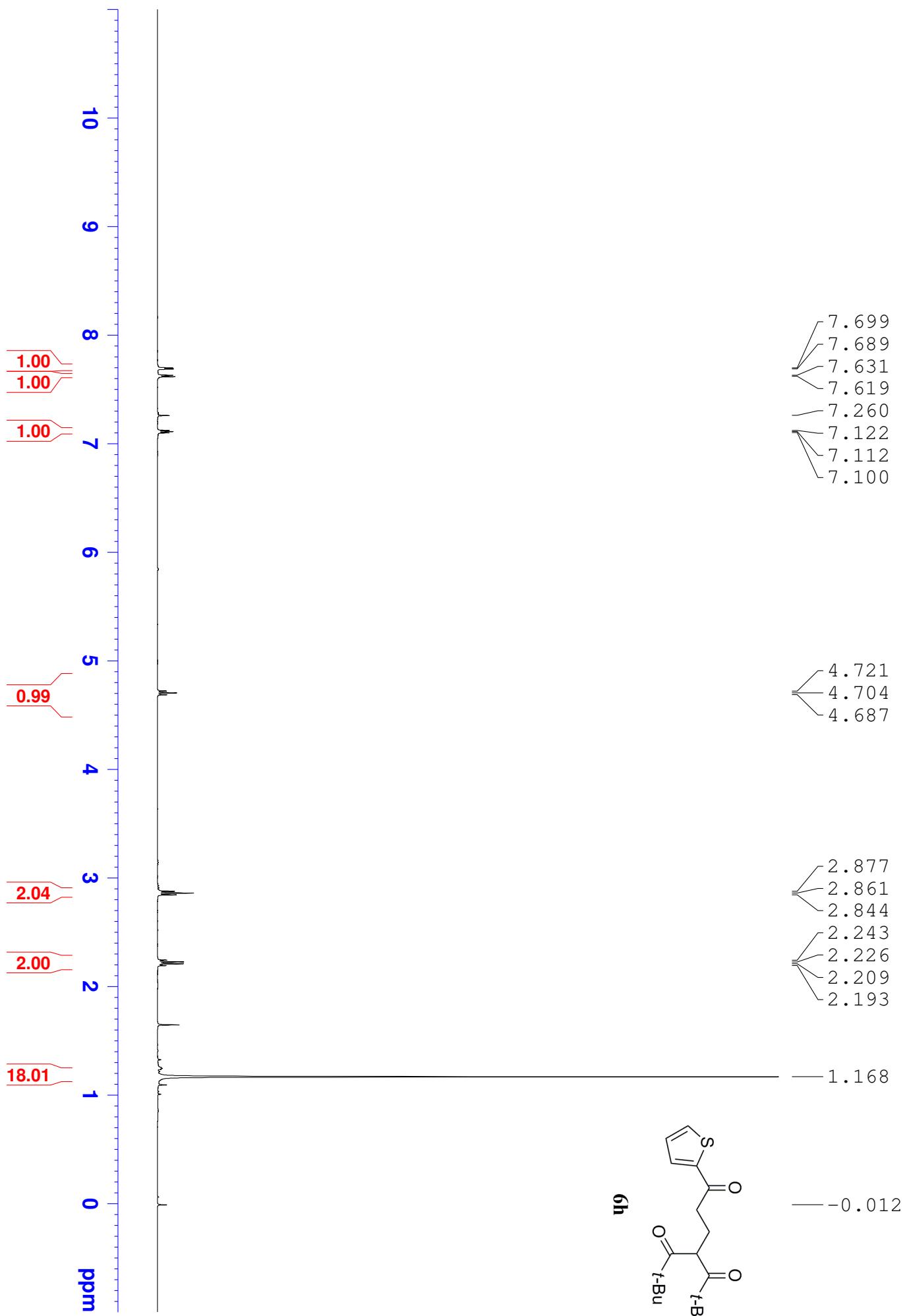


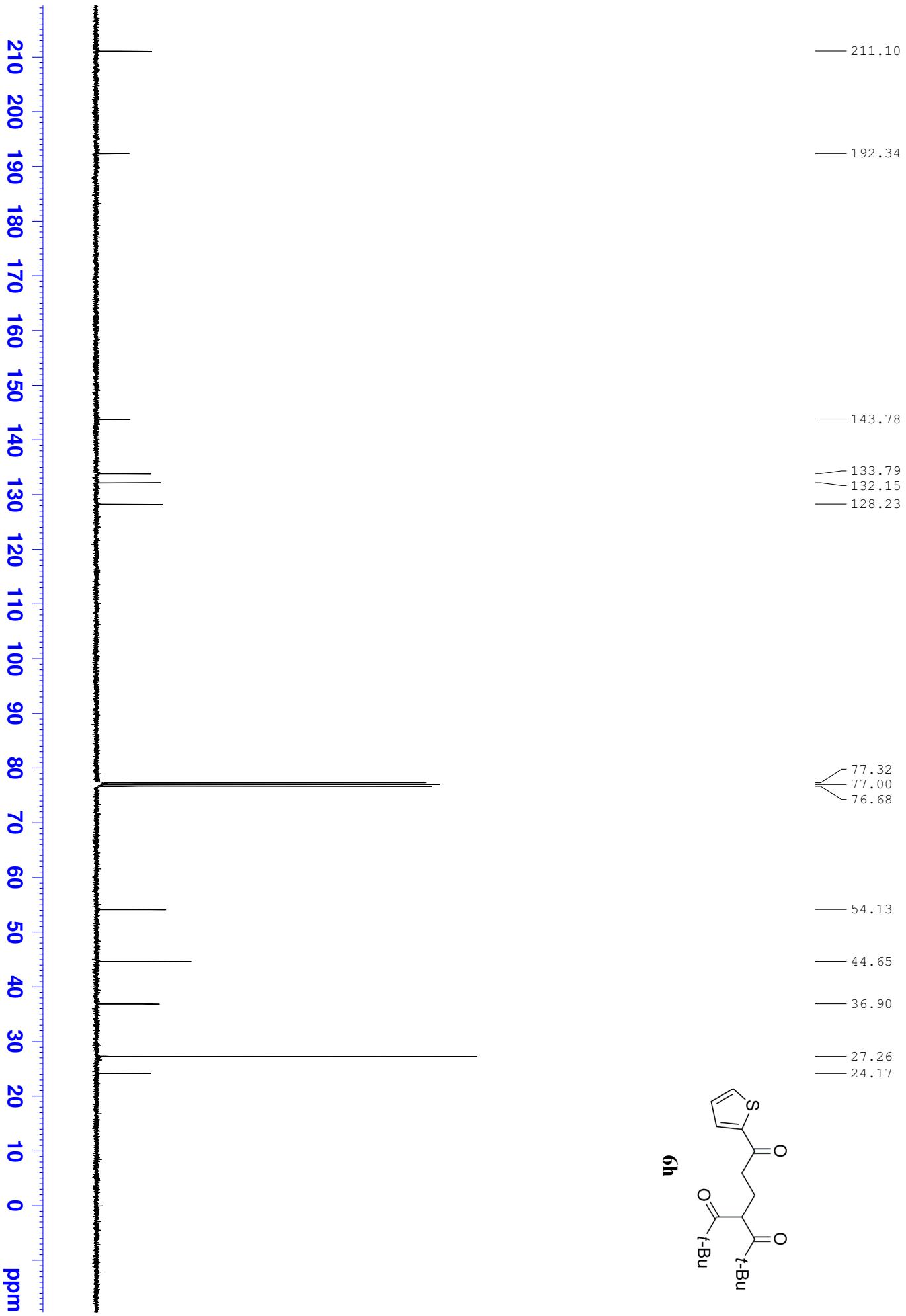


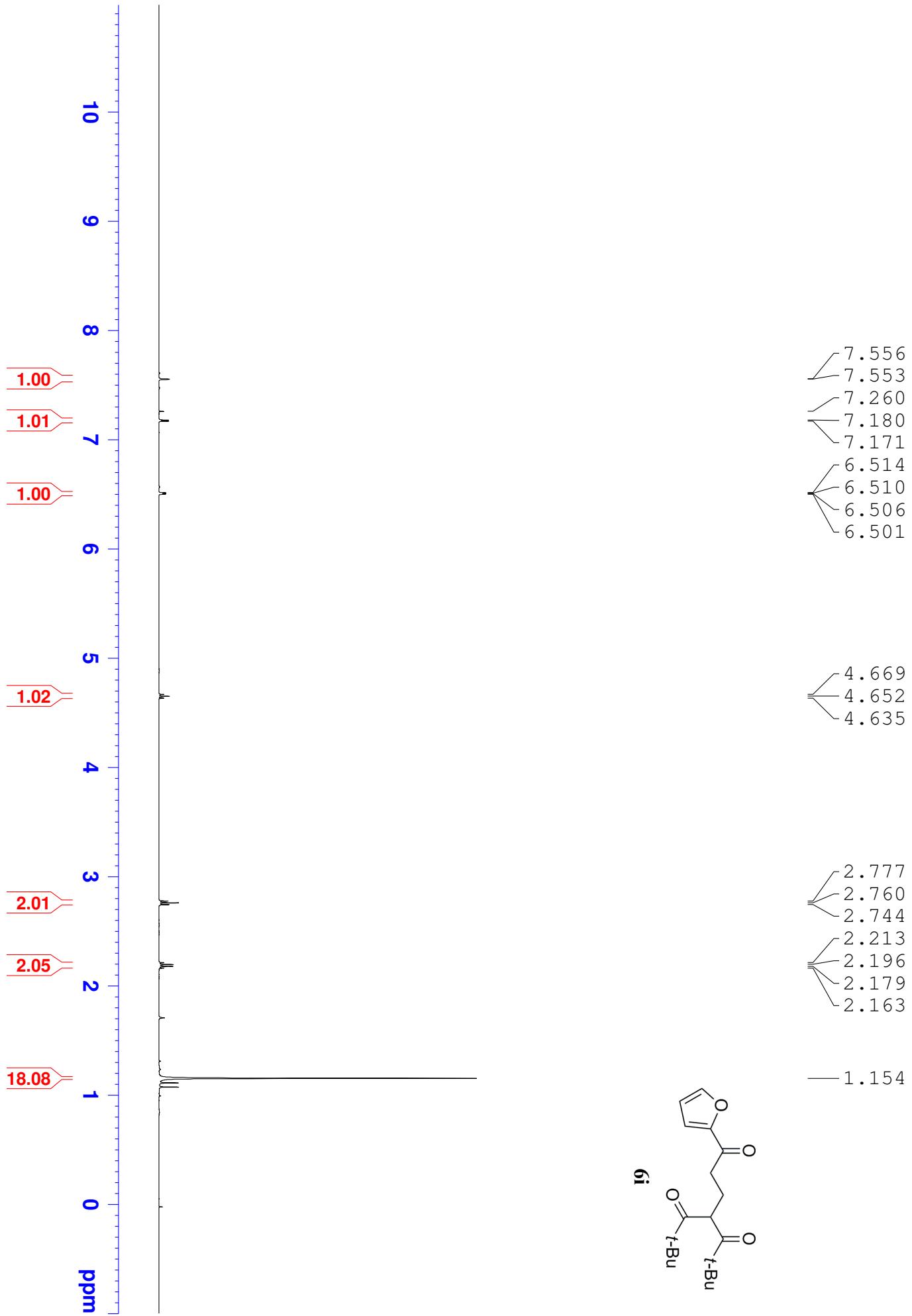
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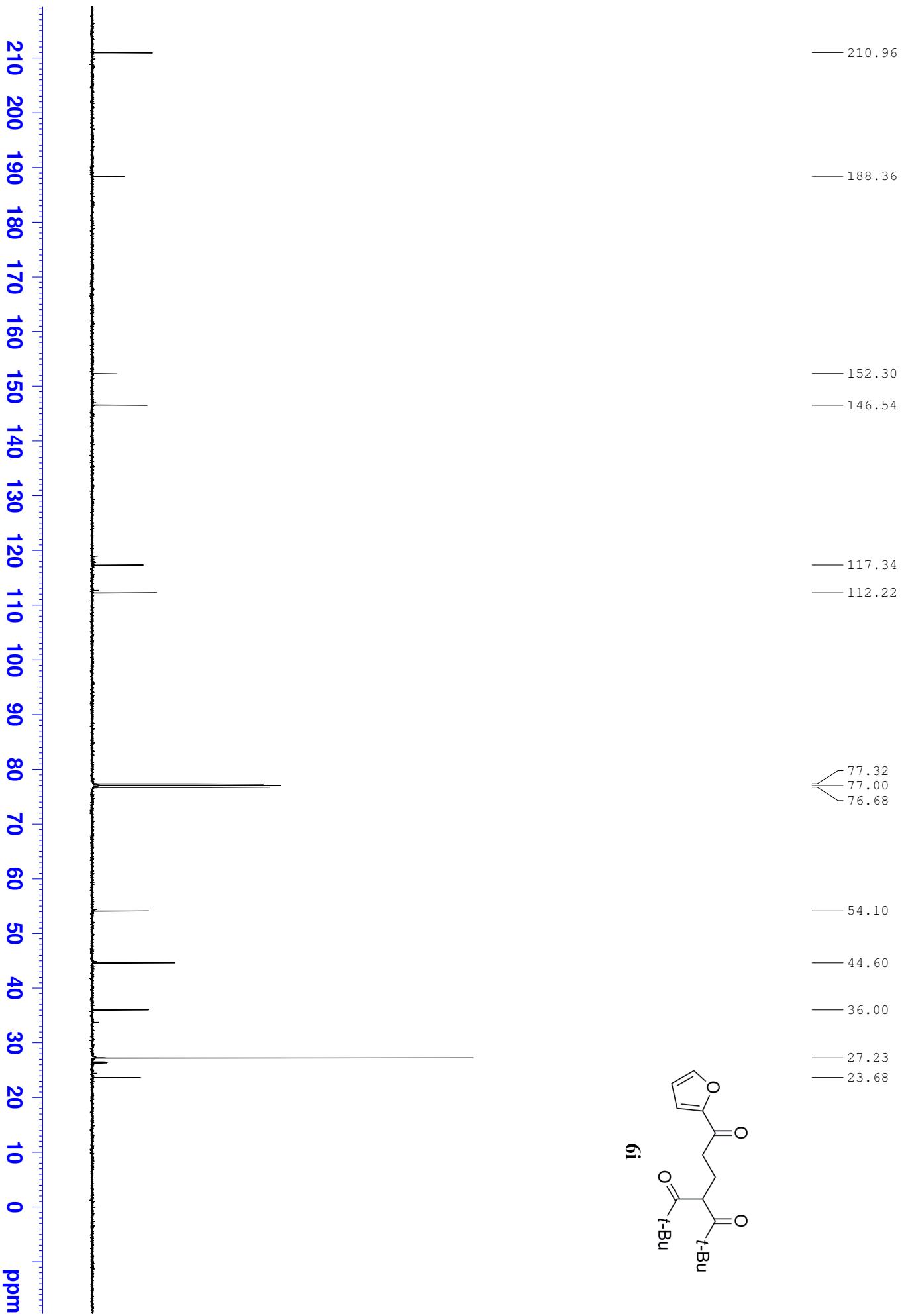


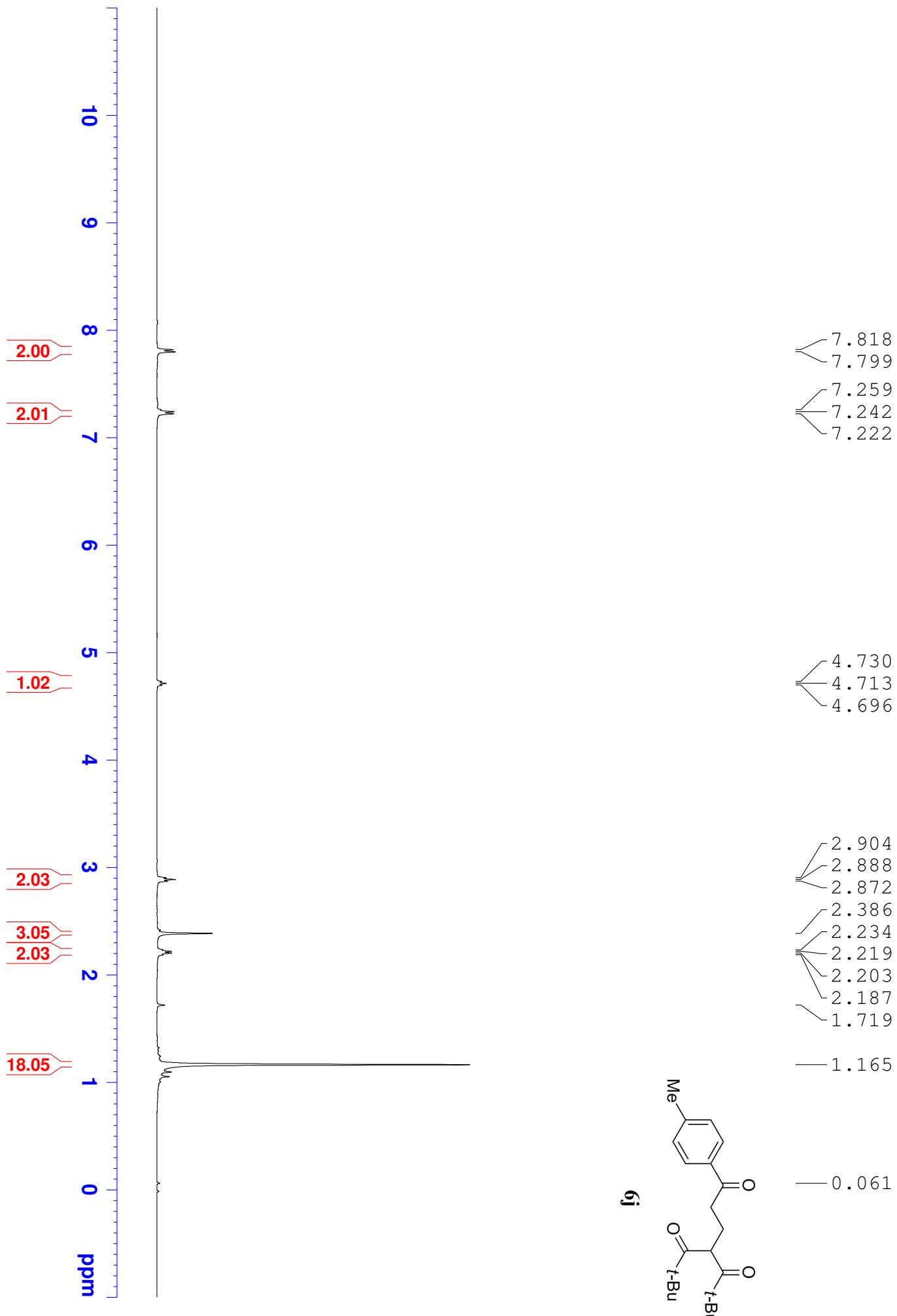


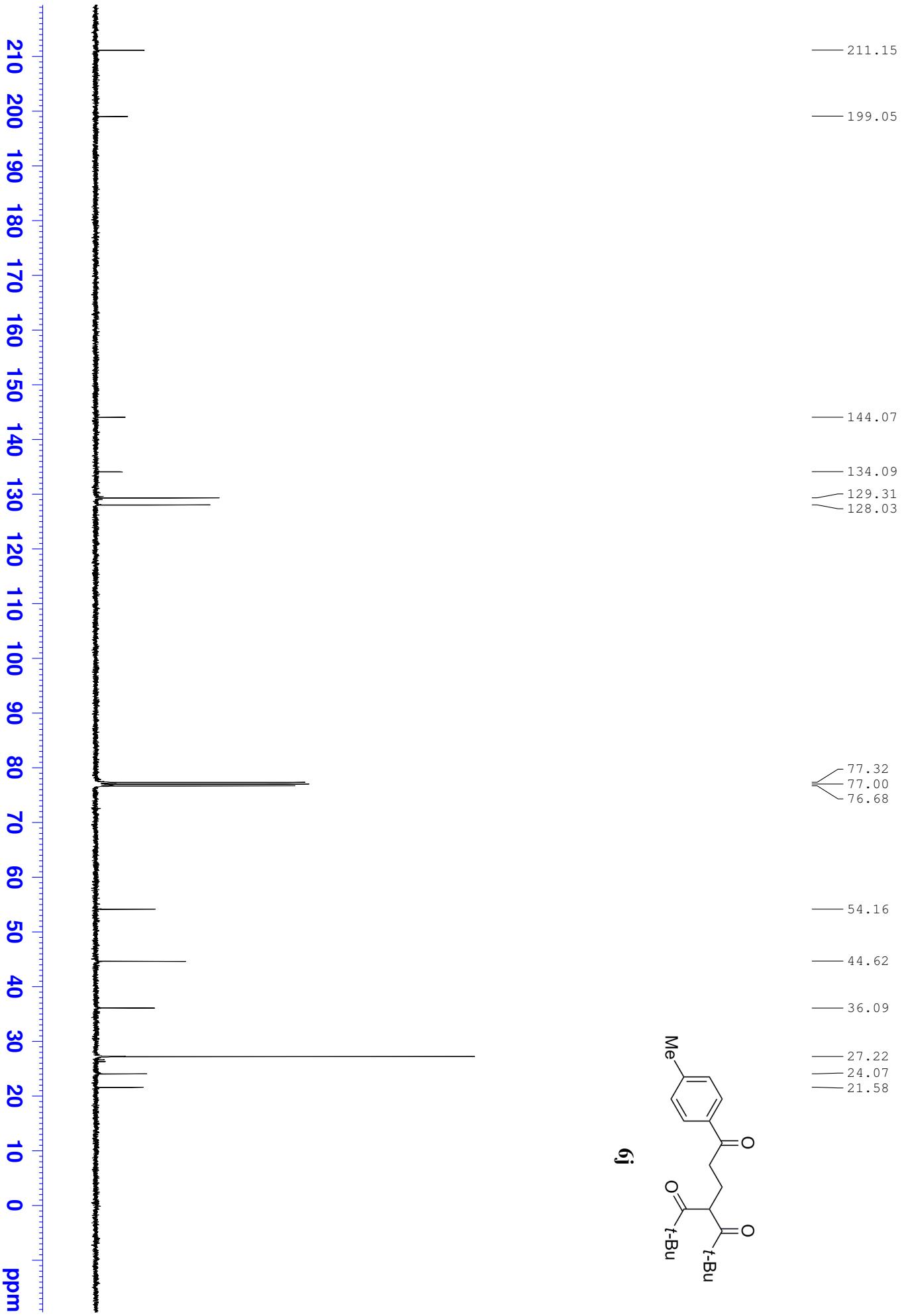


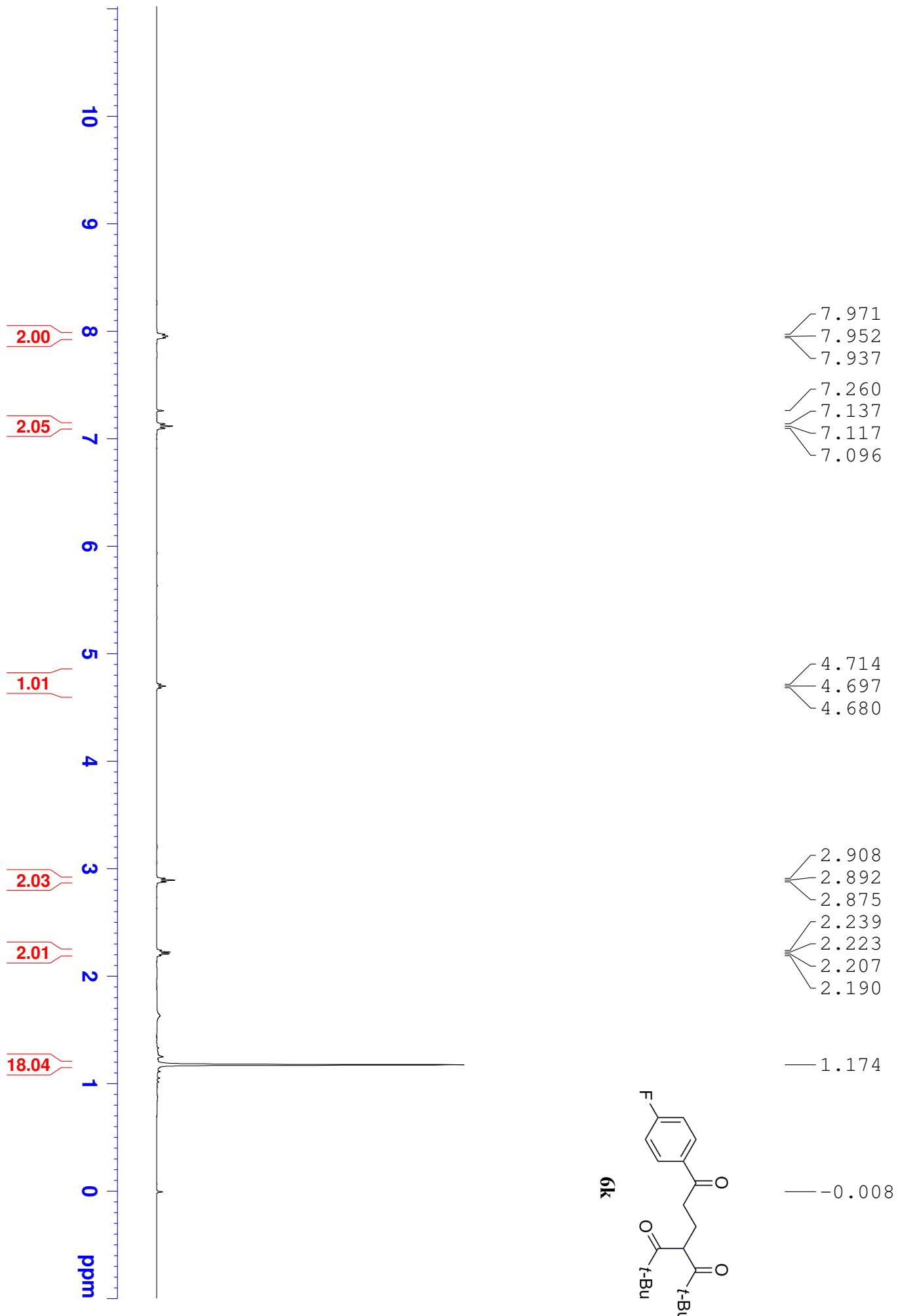


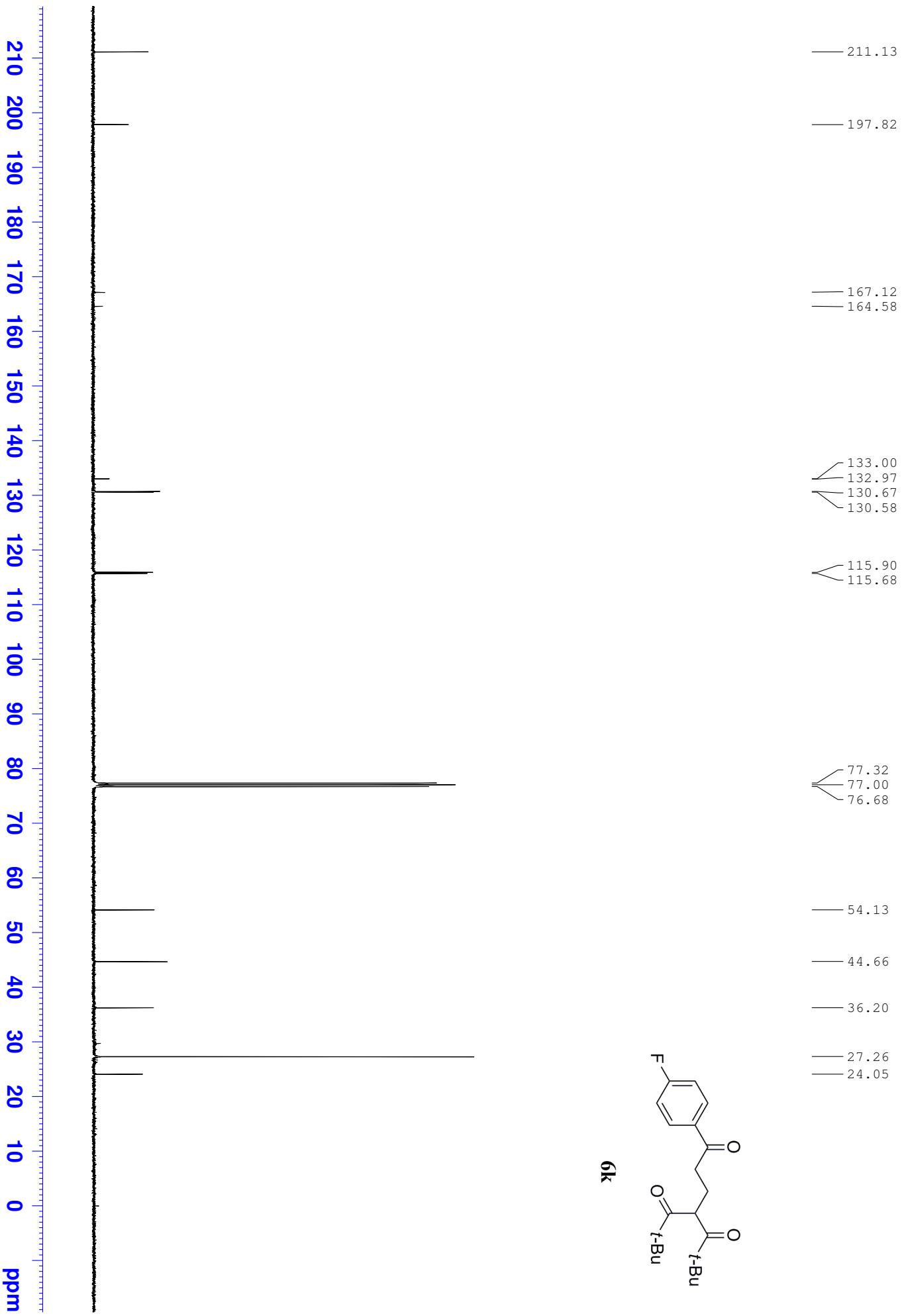




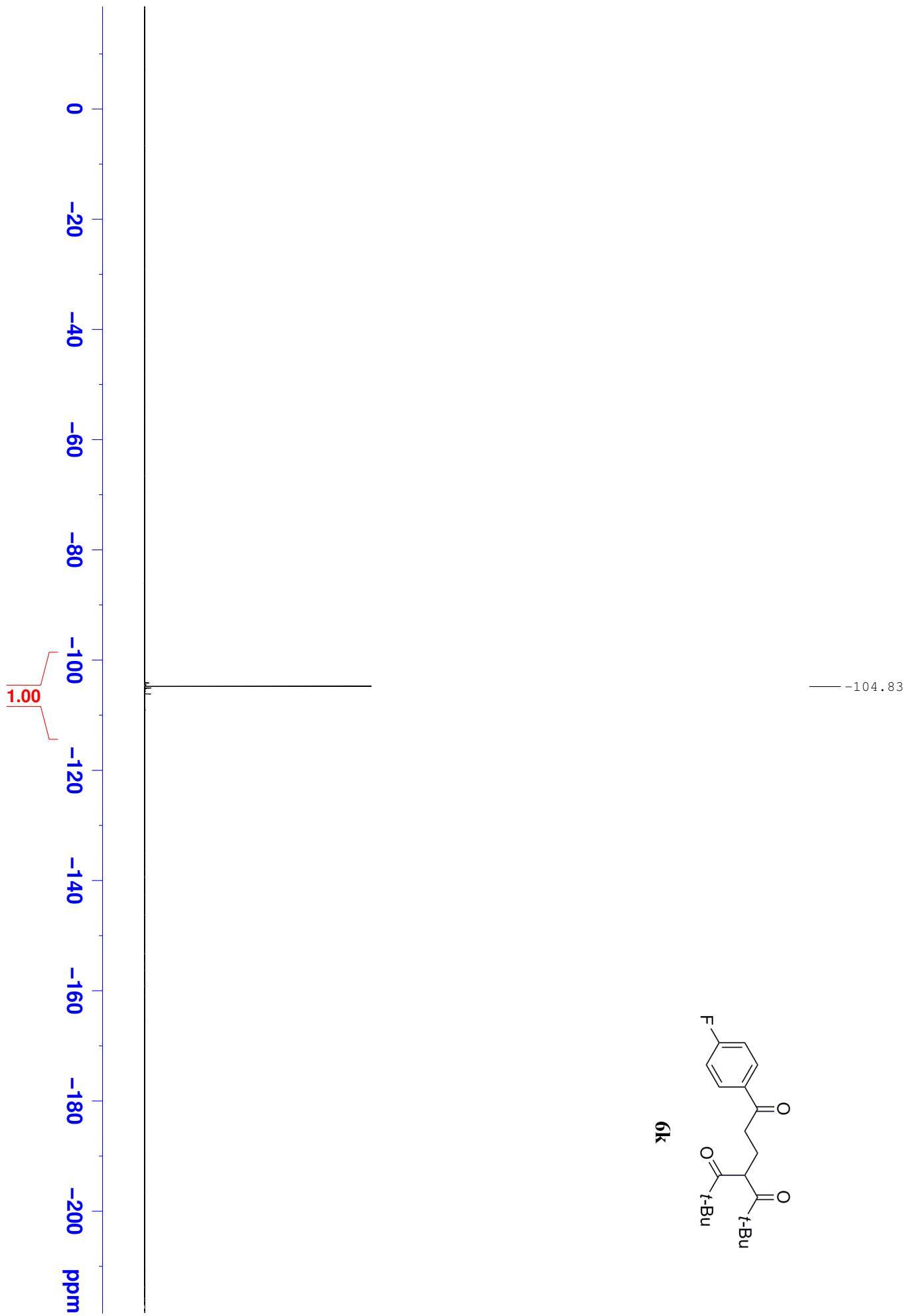


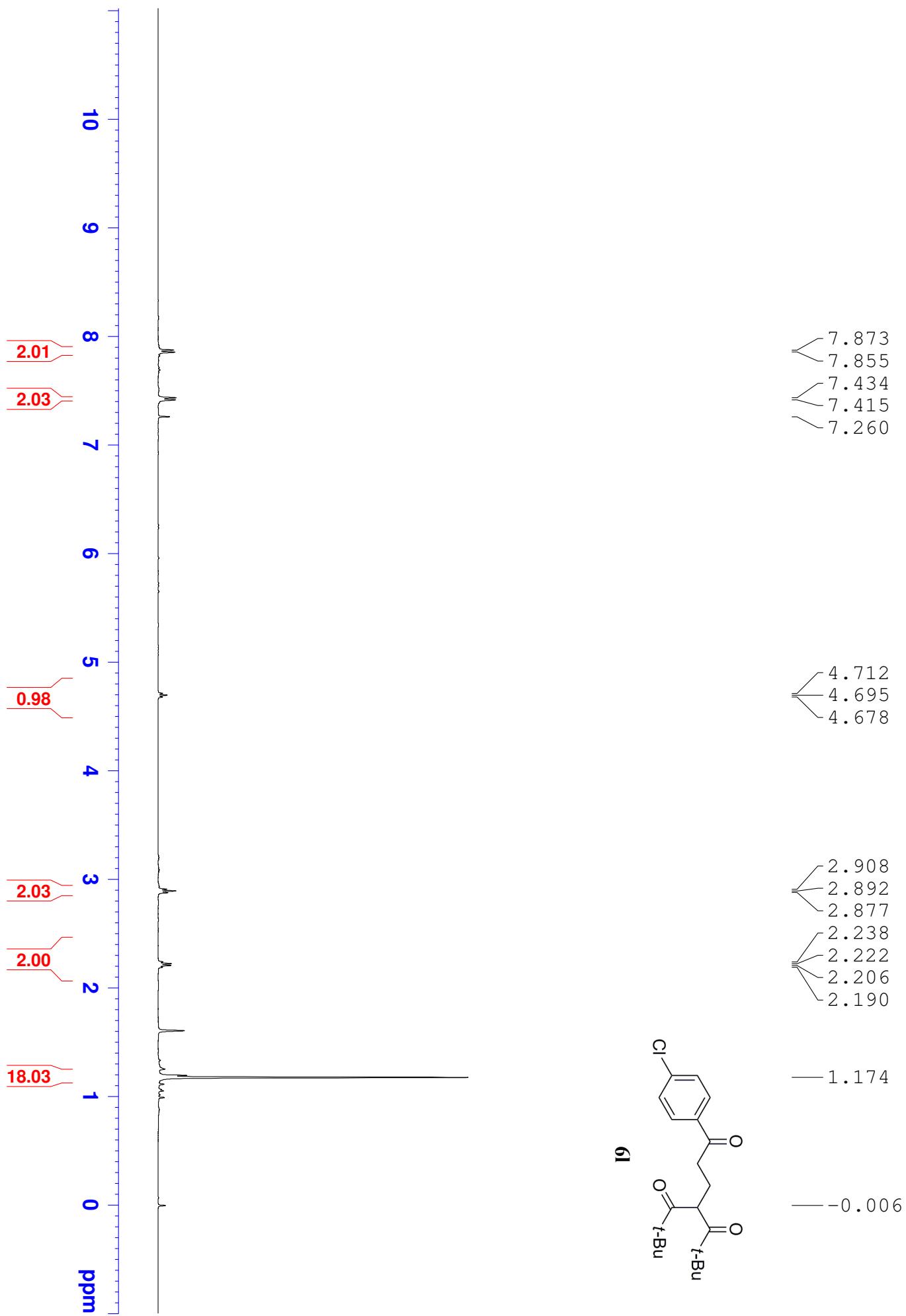


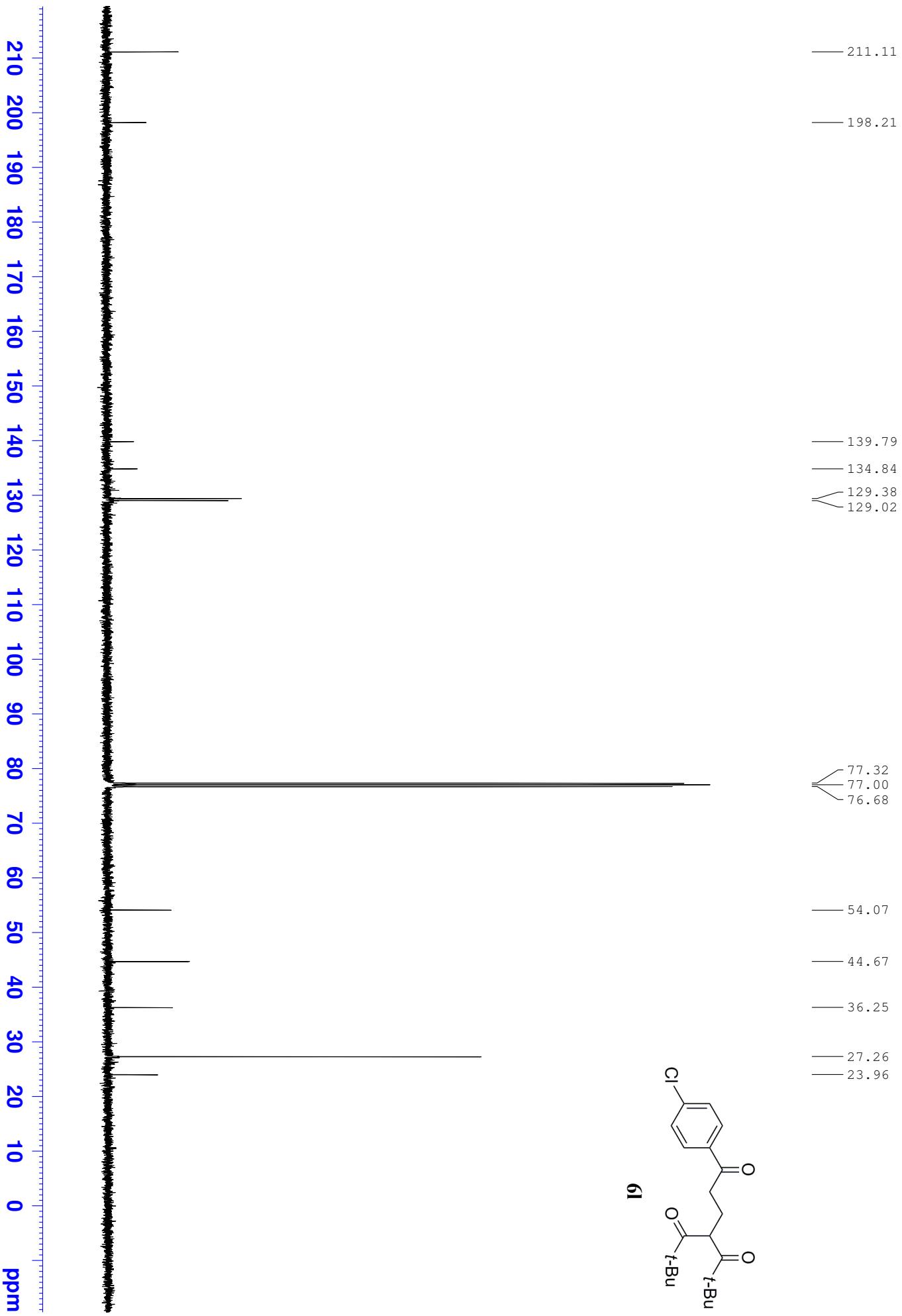


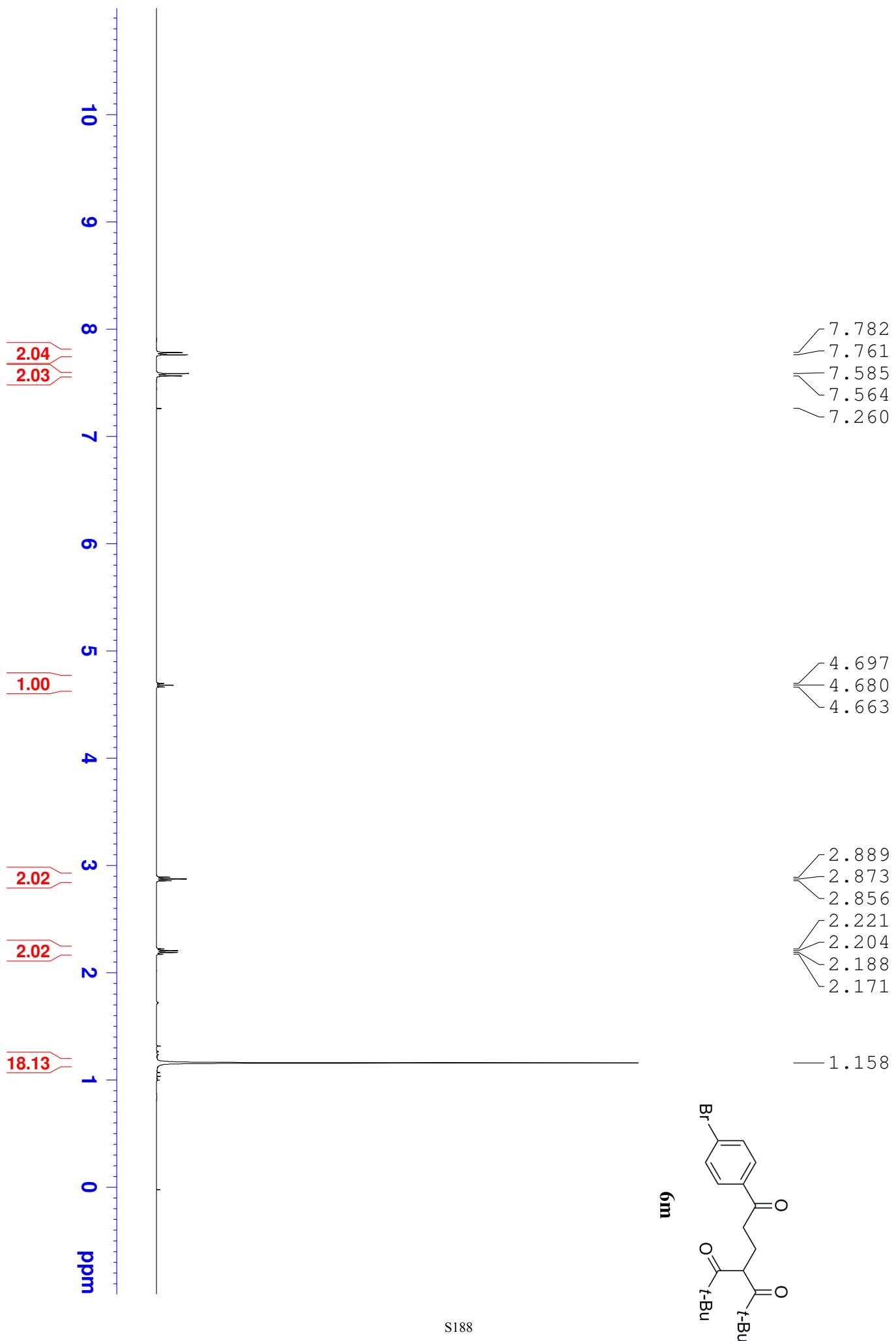


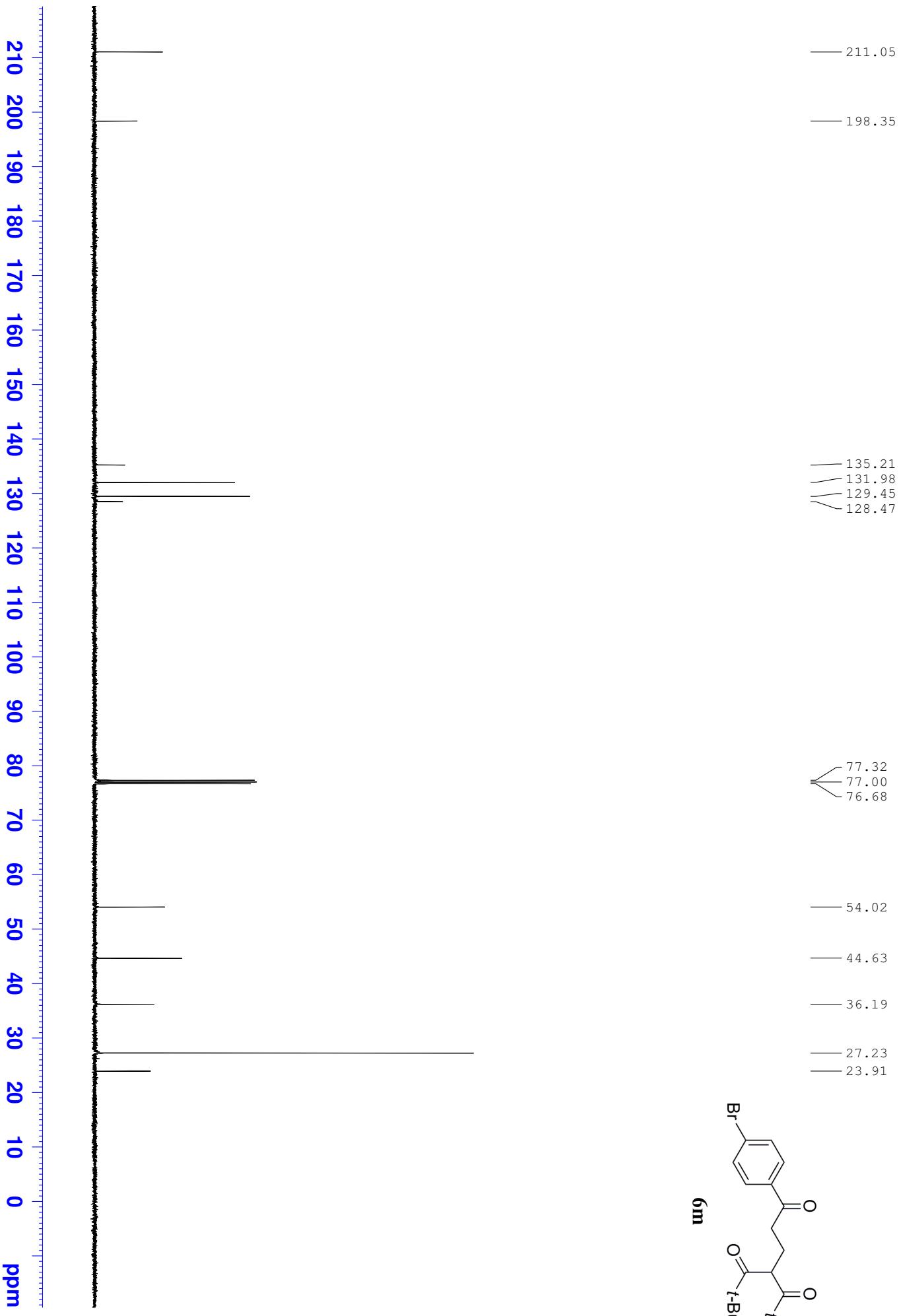
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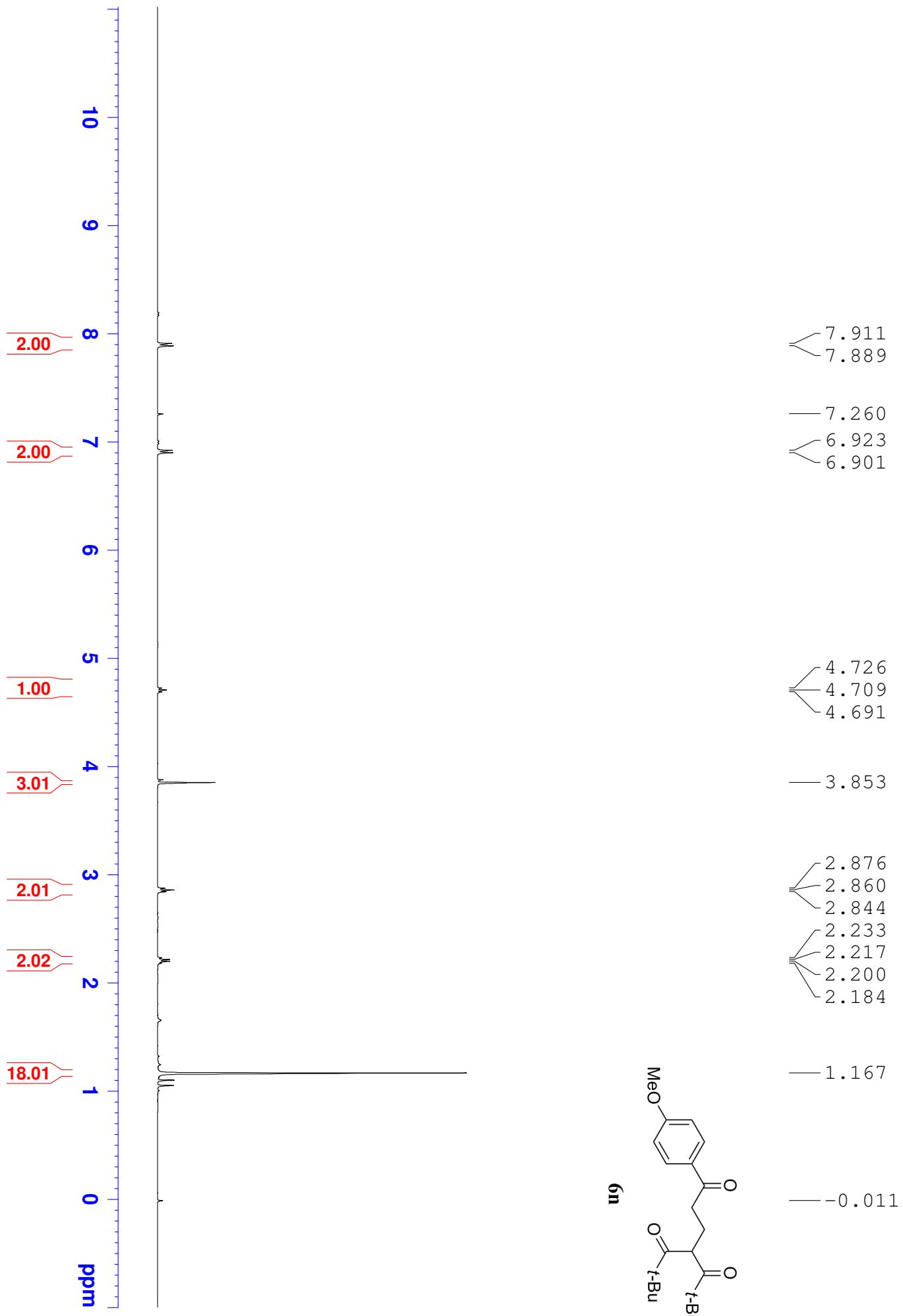


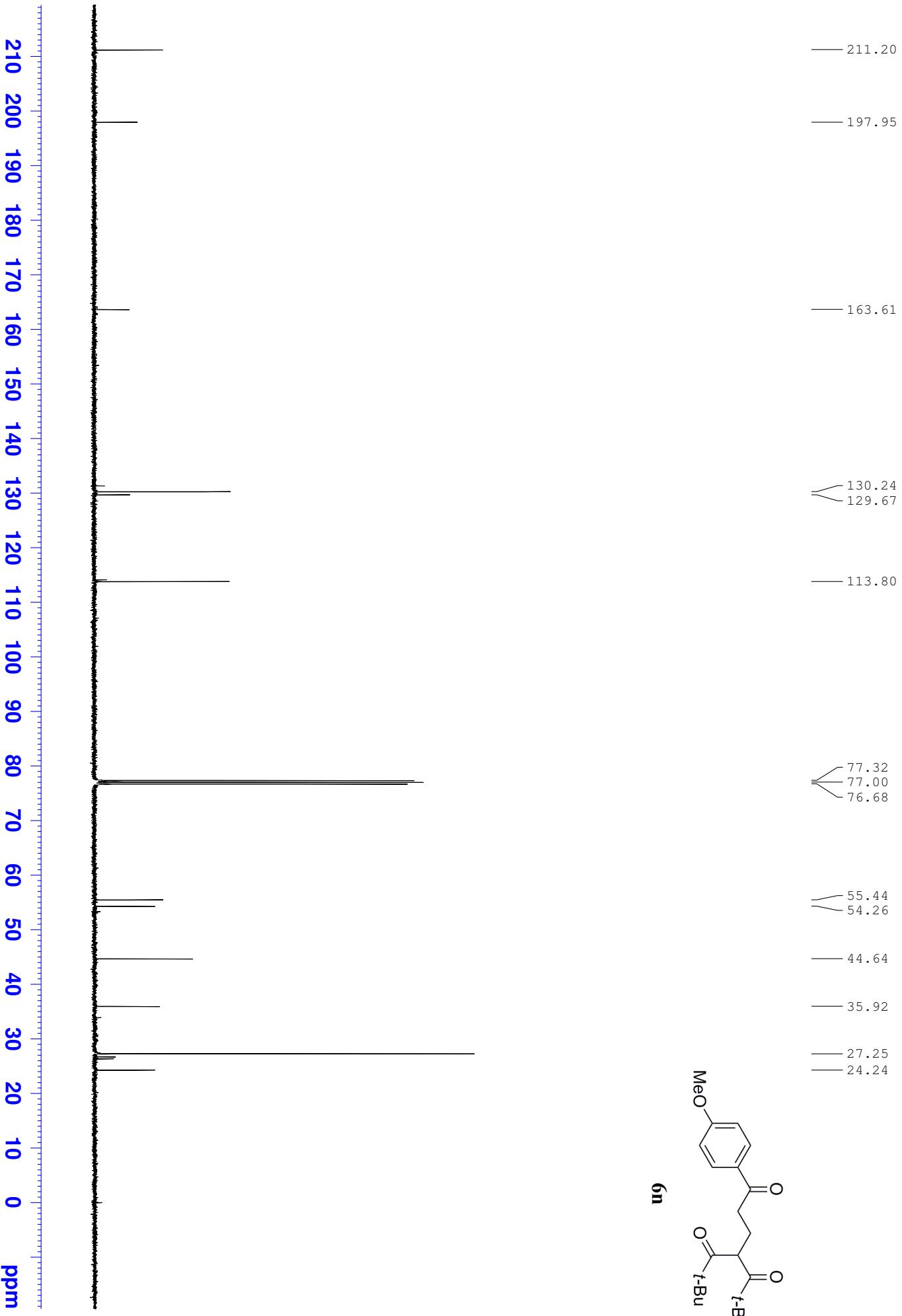


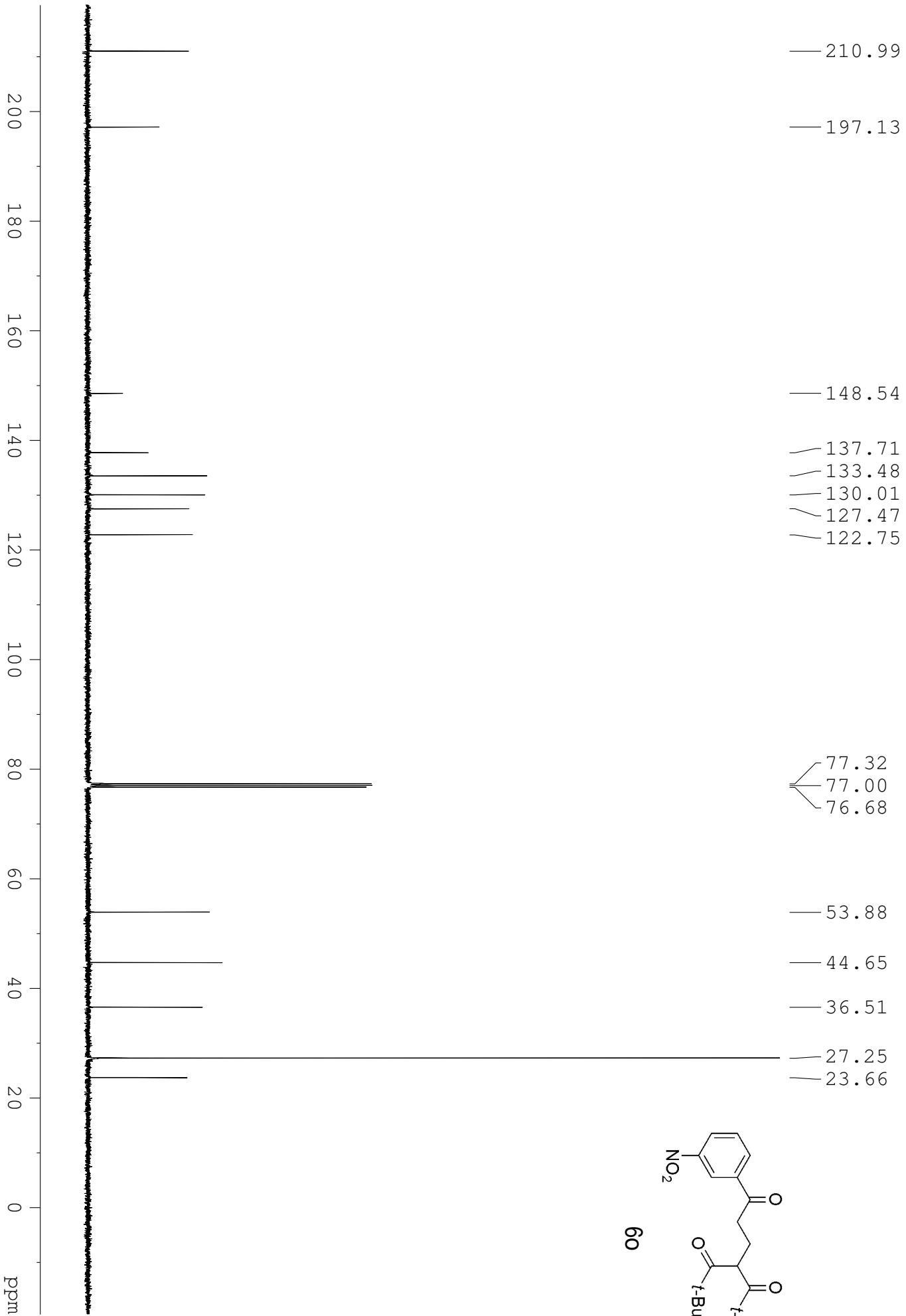


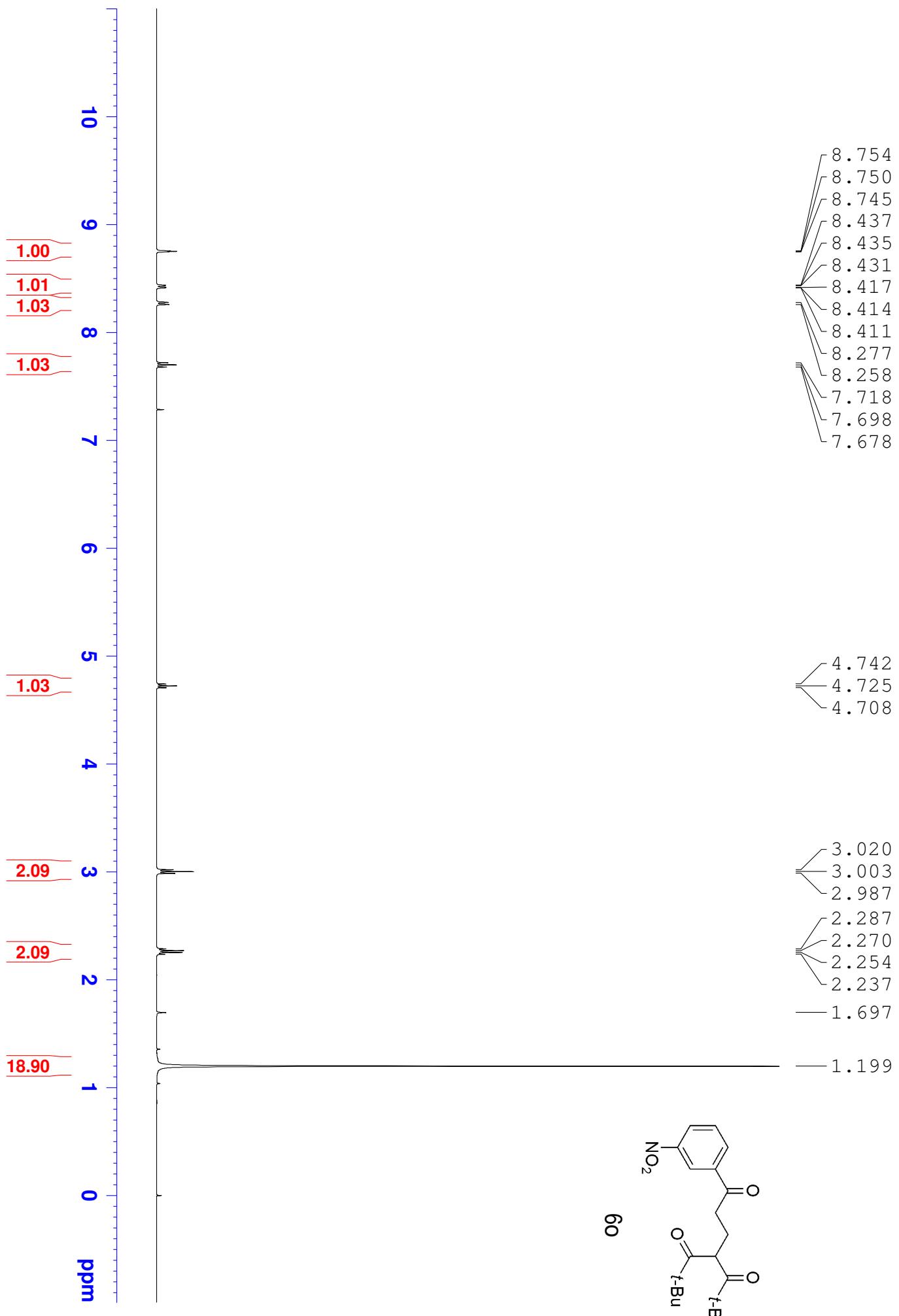


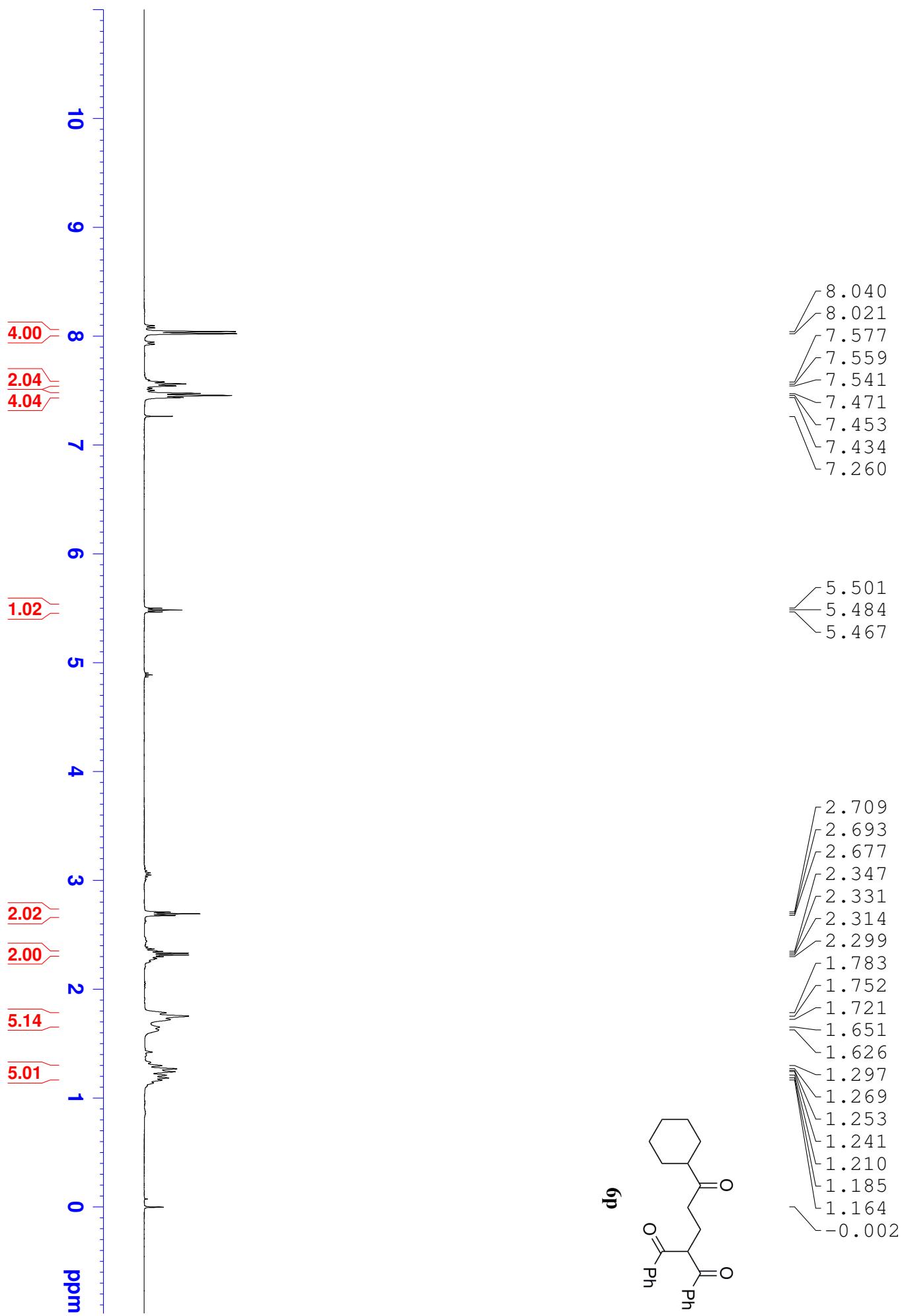


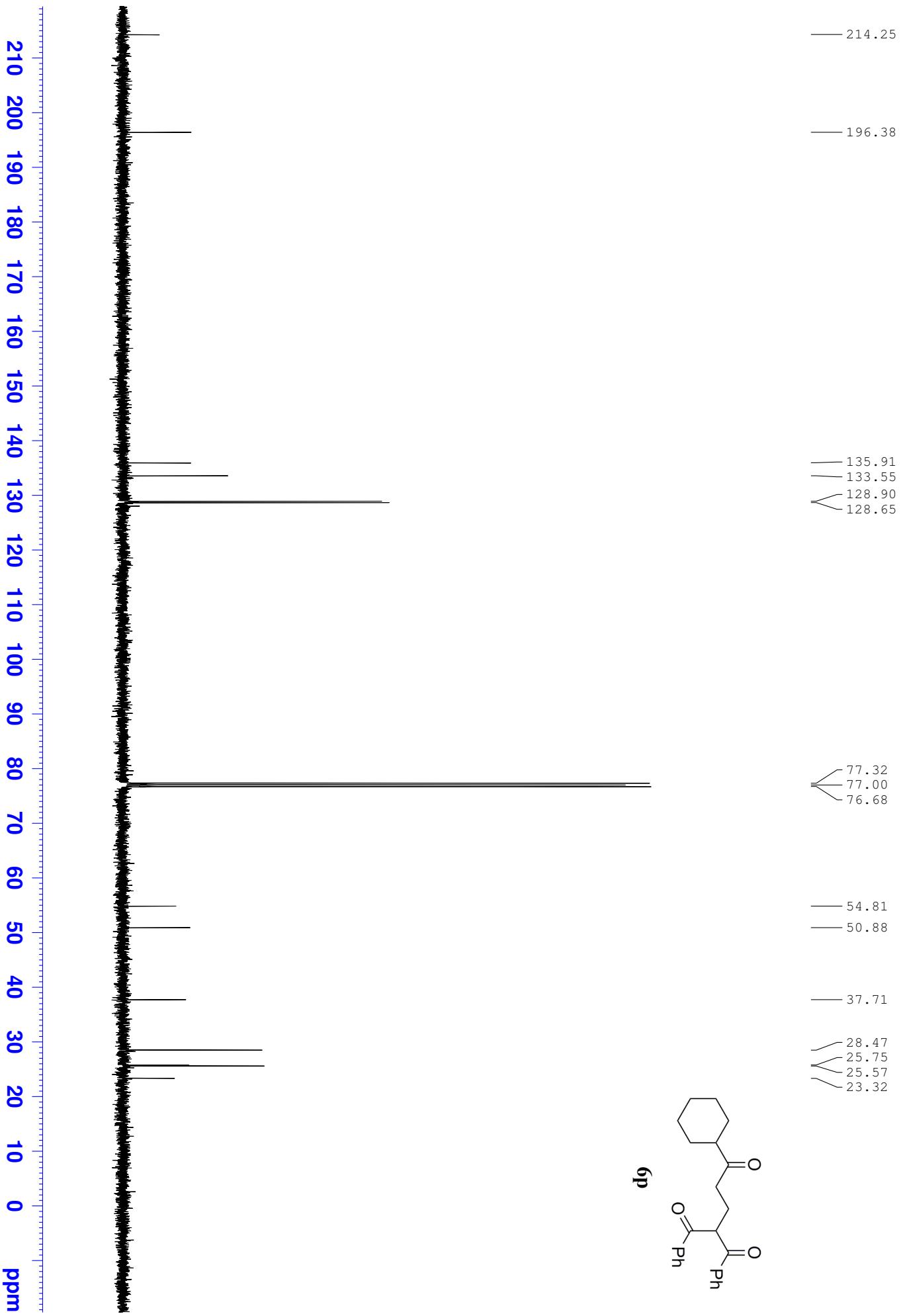


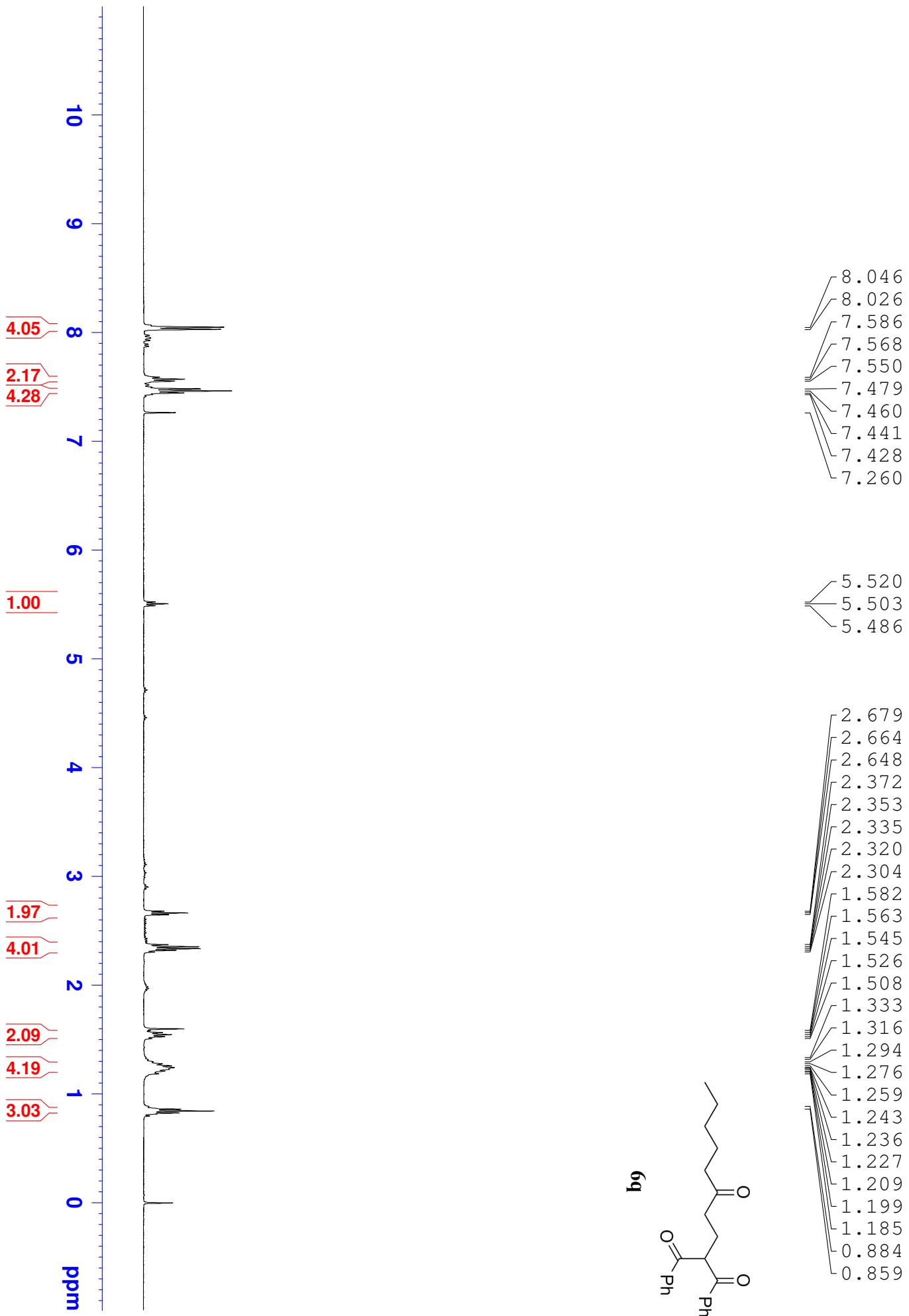


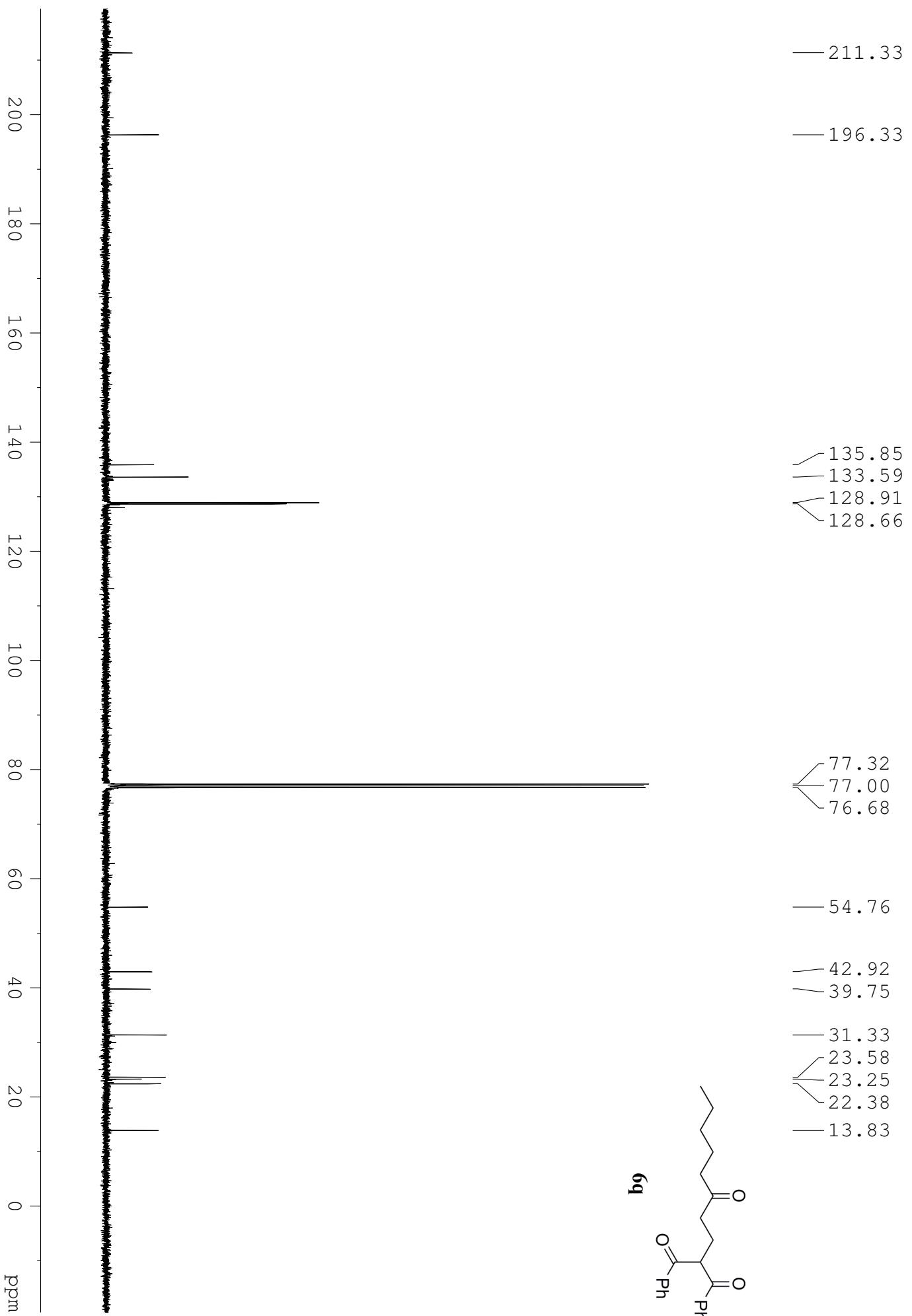


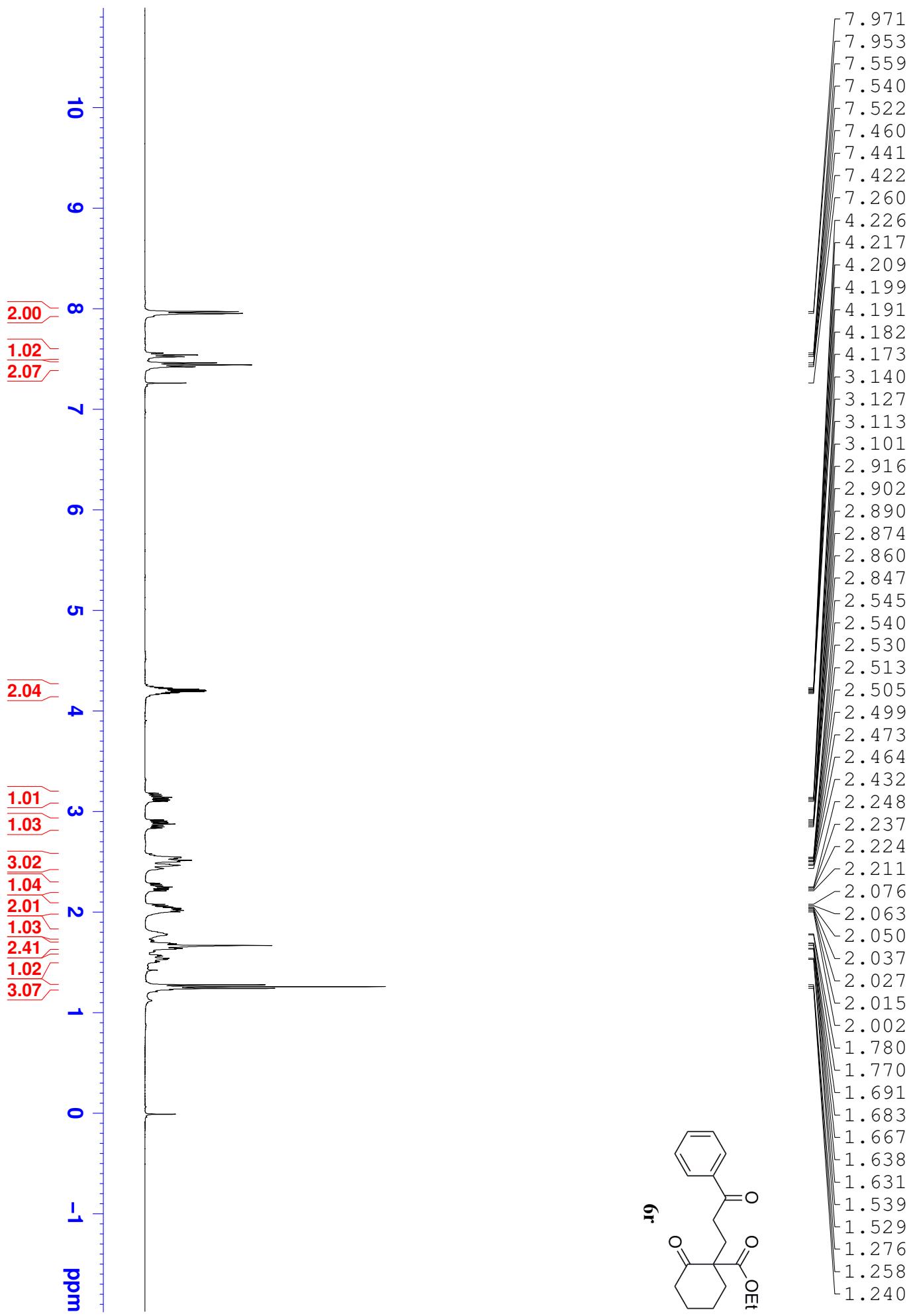


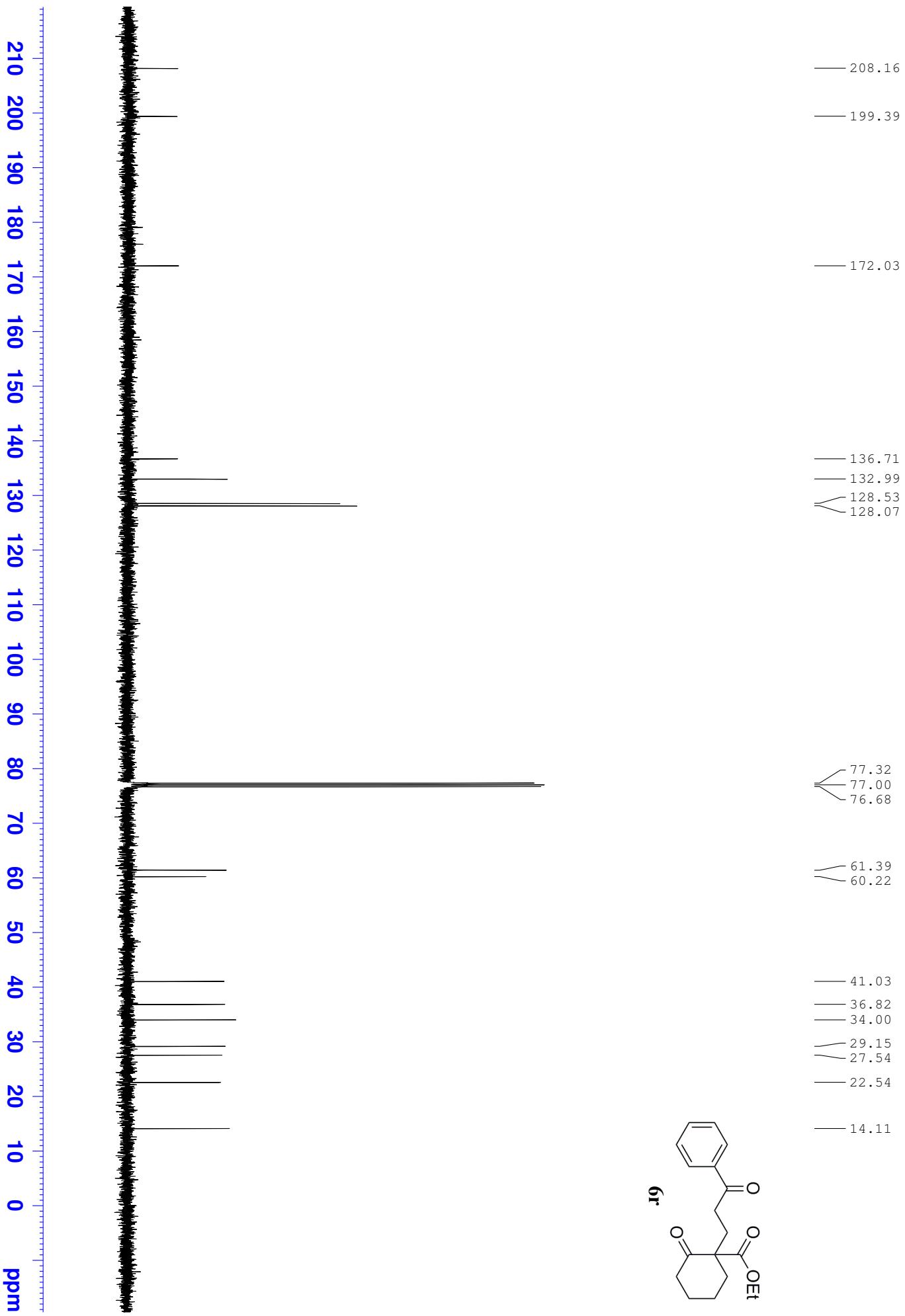


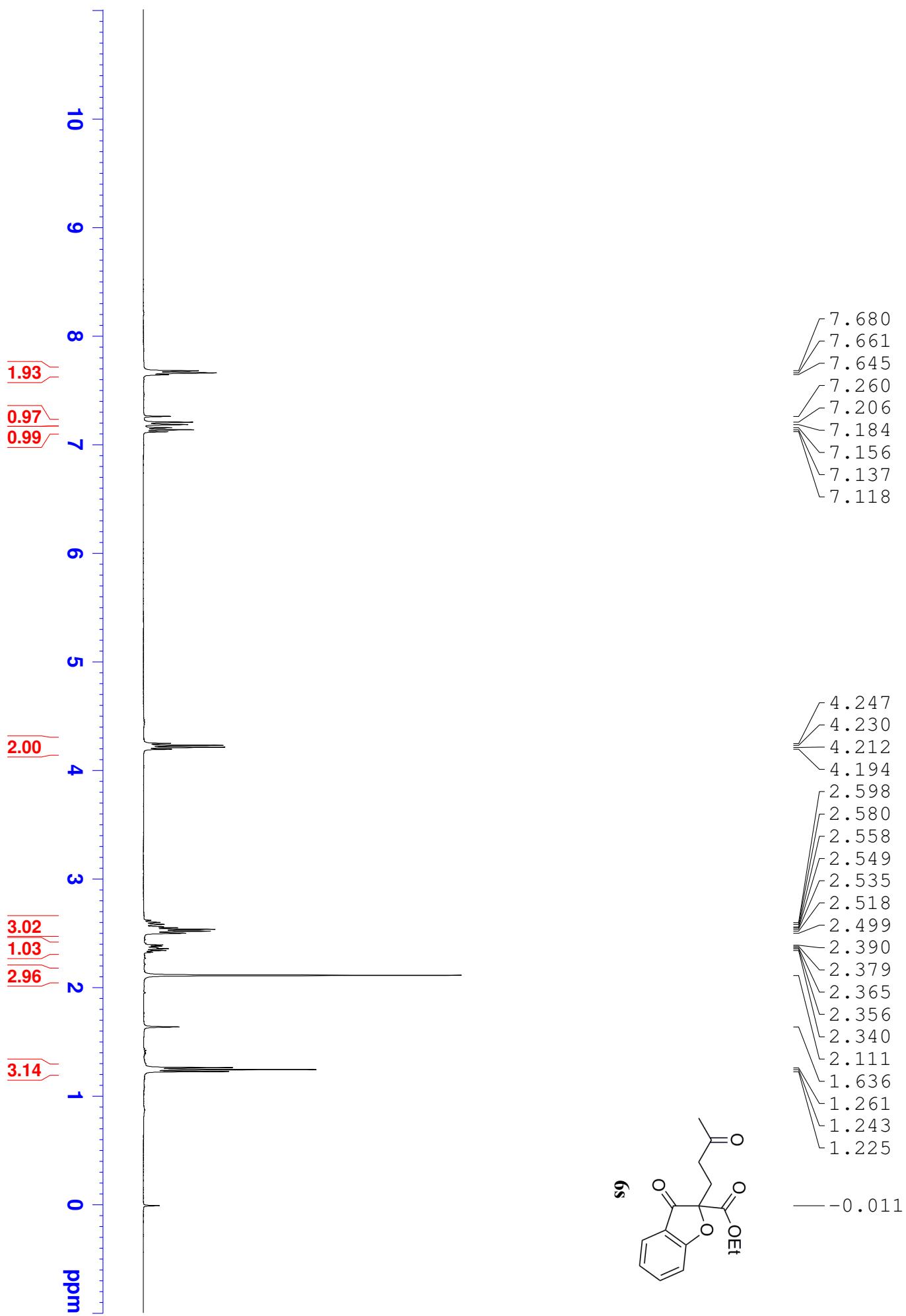


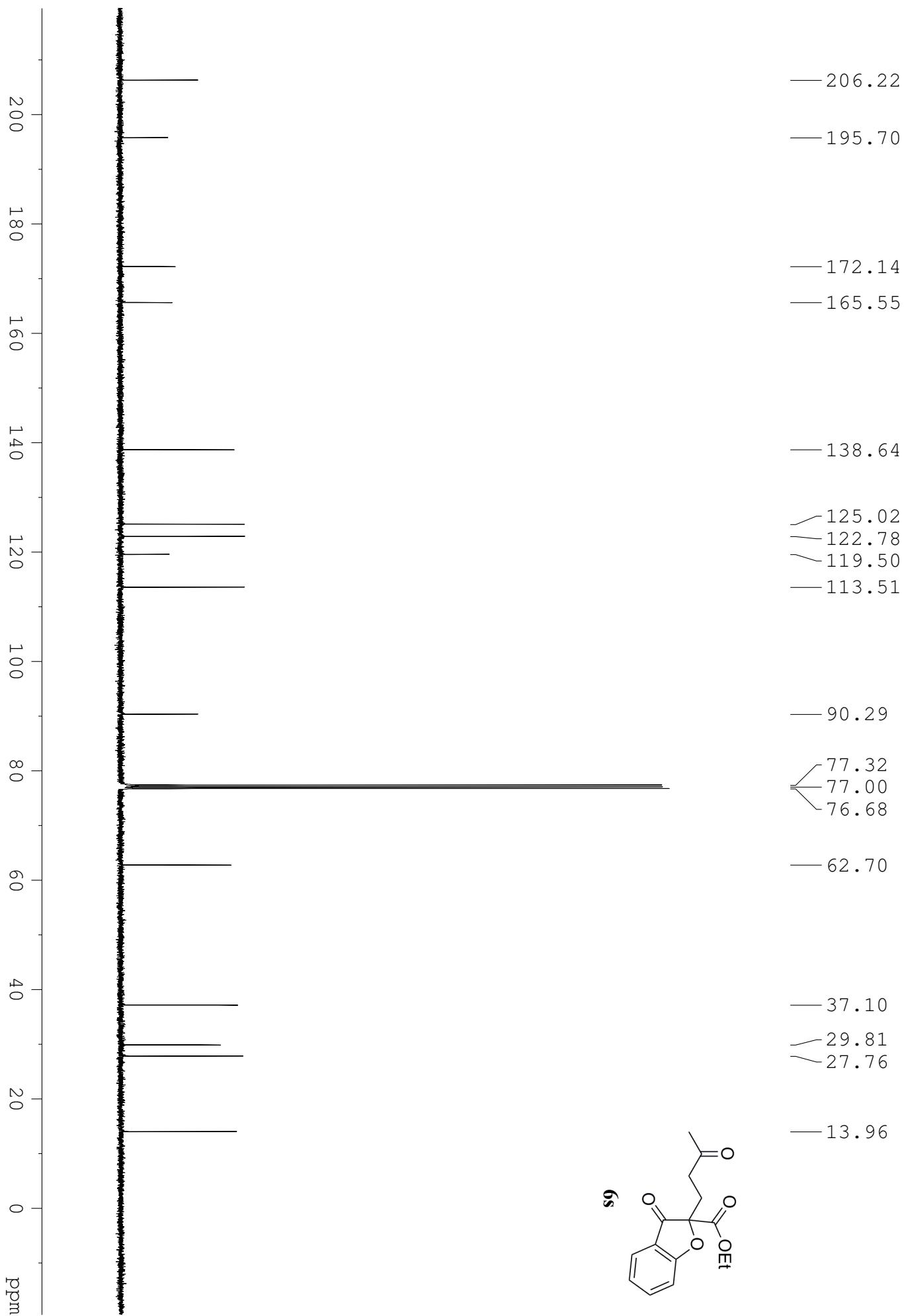


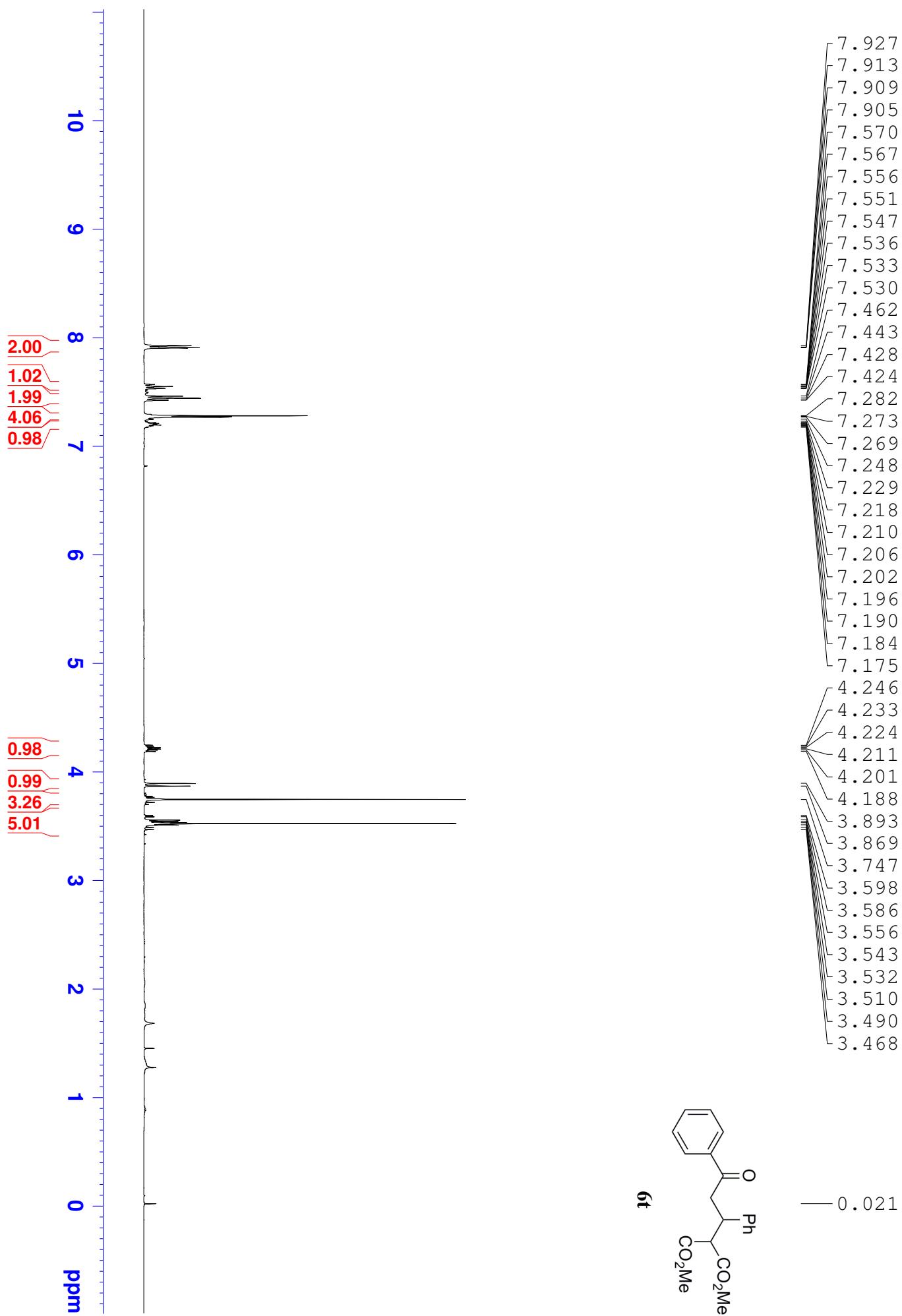


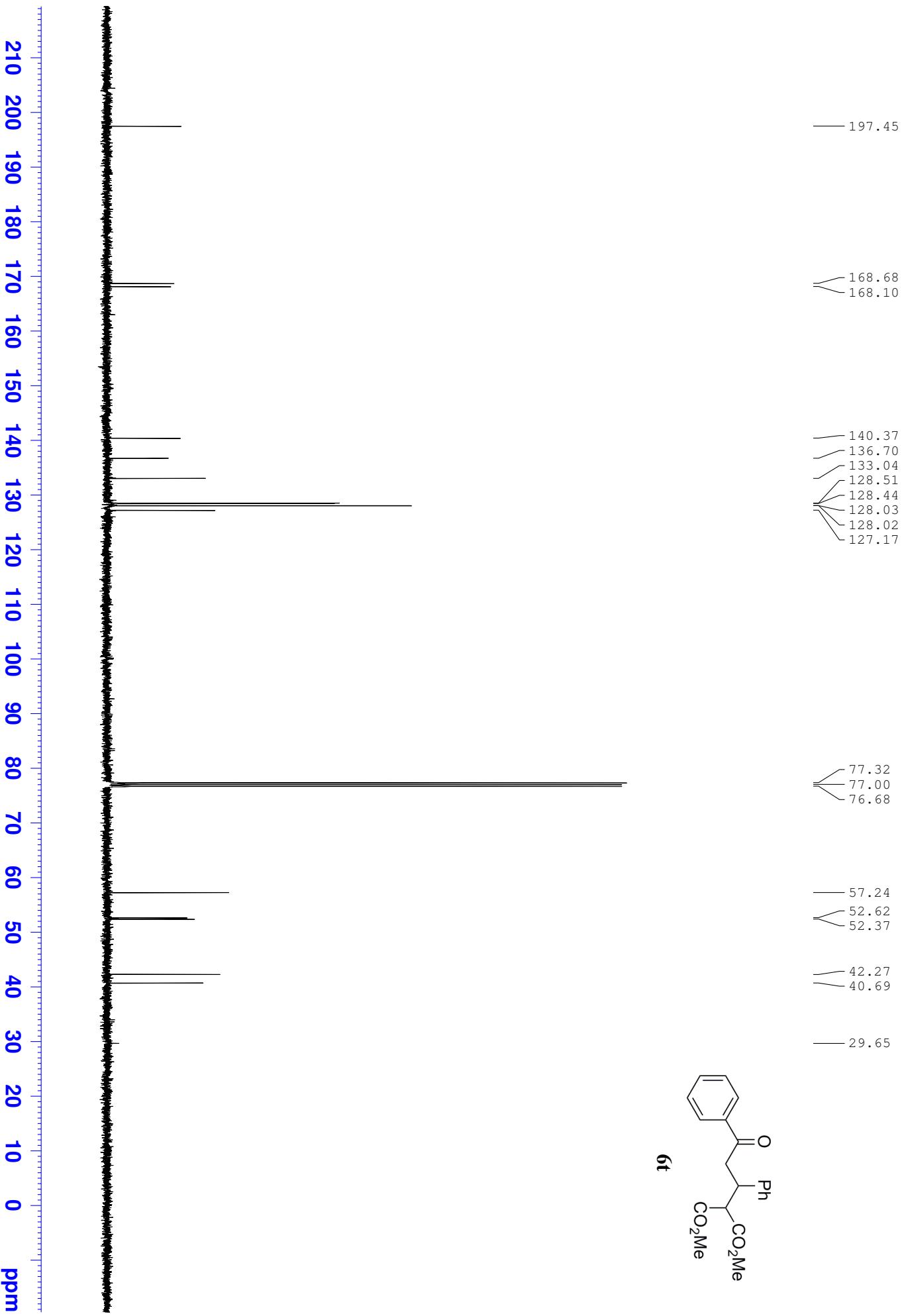












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