

Supporting Information

Directed C-C Bond Cleavage of Cyclopropane Intermediate Generated from *N*-Tosylhydrazones and Stable Enaminones: Expedient Synthesis of Functionalized 1, 4-Ketoaldehydes

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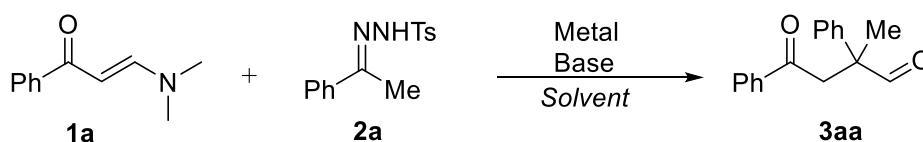
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General methods:

All reactions were carried out in flame or oven-dried glassware under argon atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 300 or 400 MHz Bruker spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ^1H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in CDCl_3). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-ToF premier TM mass spectrometer.

Screening reaction condition^a:

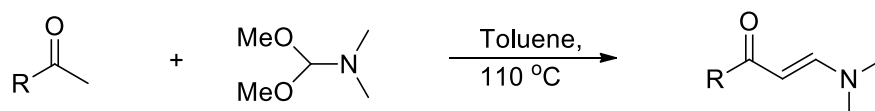


entry	metal	base	solvent	yield (%) ^b
1	CuI	LiO ^t Bu	ACN	14
2	CuI	LiO ^t Bu	DCE	11
3	CuI	LiO ^t Bu	Dioxane	18
4	CuI	LiO ^t Bu	PhCH ₃	38
5	CuI	Cs ₂ CO ₃	PhCH ₃	15
6	CuI	LiOH	PhCH ₃	8
7	CuI	NaOH	PhCH ₃	3
8	CuI	KOH	PhCH ₃	trace
9	CuI	Na ₂ CO ₃	PhCH ₃	7
10	CuI	K ₂ CO ₃	PhCH ₃	47
11	CuCl	K ₂ CO ₃	PhCH ₃	39
12	CuBr	K ₂ CO ₃	PhCH ₃	63
13	Cu(OTf)	K ₂ CO ₃	PhCH ₃	58
14	CuF ₂	K ₂ CO ₃	PhCH ₃	27

15	CuBr ₂	K ₂ CO ₃	PhCH ₃	40
16	Cu(acac) ₂	K ₂ CO ₃	PhCH ₃	26
17	CuSCN	K ₂ CO ₃	PhCH ₃	23
18	CuBF ₄ (CH ₃ CN) ₄	K ₂ CO ₃	PhCH ₃	43
19	CuPF ₆ (CH ₃ CN) ₄	K ₂ CO ₃	PhCH ₃	41

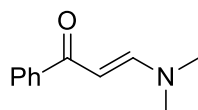
^aConditions: A mixture of **1a** (0.1 mmol, 1 equiv), **2a** (0.2 mmol, 2 equiv), base (0.20 mmol, 2.0 equiv), catalyst (20 mol %) and solvent (1 mL) were sealed in Schlenk tube under Ar atmosphere at 80 °C and the mixture was stirred for 24h or until the **1a** was consumed completely. ^bYields were determined by ¹H NMR vs an internal standard.

General procedure for the synthesis of enaminones¹:



To a stirred solution of ketone (5.0 mmol, 1.0 eq.) in toluene (5.0 mL), 1,1-dimethoxy-N,N-dimethylmethanamine (7.0 mmol, 1.4 eq.) was added and stirred at 110 °C. After completion of the reaction (monitored by TLC), it was quenched with water, extracted with ethyl acetate and dried with anhydrous Na₂SO₄. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 1 : 1) to give the desired product **1**.

(*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a**):

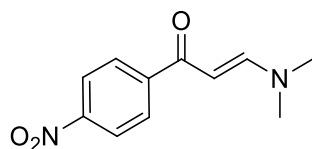


The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 91 - 92 °C. Yield 67%; ¹H NMR (400 MHz, CDCl₃) δ 7.91 - 7.89 (m, 2H), 7.81 - 7.78 (d, *J* = 12.3 Hz, 1H), 7.47 - 7.38 (m, 3H), 5.73 - 5.70 (d, *J* = 12.3 Hz, 1H), 3.12 (s, 1H), 2.91 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 188.6, 154.1, 140.4, 130.8,

¹Y. Jiang, V. Y. K. Zhong, L. Emmanuvel and C.-M. Park, *Chem. Commun.*, 2012. **48**, 3133-3135.

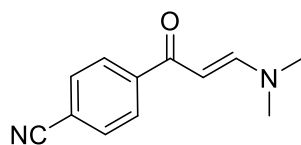
128.0, 127.4, 92.1, 45.0, 37.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{14}NO$: 177.2429. Found: 177.2425.

(E)-3-(Dimethylamino)-1-(4-nitrophenyl)prop-2-en-1-one (1b):



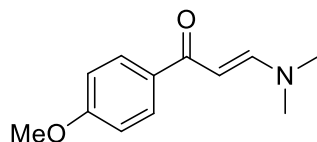
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 148 - 149 °C. Yield 67%; 1H NMR (400 MHz, $CDCl_3$) δ 8.25 - 8.23 (m, 2H), 8.01 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 12.4 Hz, 1H), 5.68 (d, J = 12.0 Hz, 1H), 3.21 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 155.2, 149.0, 146.0, 128.3, 123.3, 91.9, 45.3, 37.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}N_2O_3$: 221.0926. Found: 221.0932.

(E)-4-(3-(Dimethylamino)acryloyl)benzonitrile (1c):



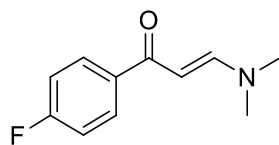
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp. 117 - 118 °C. Yield 75%; 1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 12.2 Hz, 1H), 7.70 (d, J = 8.7 Hz, 2H), 5.66 (d, J = 12.2 Hz, 1H), 3.19 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 156.0, 145.2, 132.9, 128.9, 119.6, 114.9, 92.6, 46.2, 38.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_2O$: 202.2524. Found: 202.2521.

(E)-3-(Dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (1d):



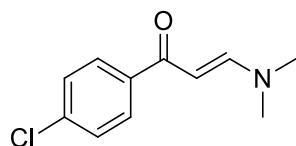
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 90 - 91 °C. Yield 82%; ^1H NMR (400 MHz, CDCl_3) δ 7.90 - 7.87 (m, 2H), 7.77 (d, J = 12.4 Hz, 1H), 6.90 - 6.87 (m, 1H), 5.69 (d, J = 12.4 Hz, 1H), 3.82 (s, 3H), 3.06 - 2.92 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.3, 161.9, 153.7, 133.0, 129.4, 113.2, 91.6, 55.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_2$: 206.1181. Found: 206.1182.

(E)-3-(Dimethylamino)-1-(4-fluorophenyl)prop-2-en-1-one (1e):



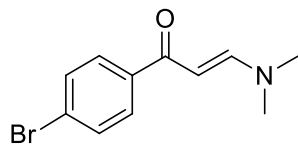
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 83 - 84 °C. Yield 88%; ^1H NMR (400 MHz, CDCl_3) δ 7.93 - 7.90 (m, 2H), 7.81 (d, J = 12.4 Hz, 1H), 7.10 - 7.05 (m, 2H), 5.67 (d, J = 12.4 Hz, 1H), 3.15 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.0, 165.7, 163.2, 154.3, 136.6 (J = 3.0 Hz), 129.7 (J = 9.0 Hz), 114.9 (J = 21 Hz), 91.6, 45.0, 37.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{13}\text{FNO}$: 194.0981. Found: 194.0984.

(E)-1-(4-Chlorophenyl)-3-(dimethylamino)prop-2-en-1-one (1f):



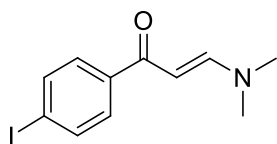
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 88 - 89 °C. Yield 83%; ^1H NMR (400 MHz, CDCl_3) δ 7.86 - 7.83 (m, 2H), 7.80 (d, J = 12.4 Hz, 1H), 7.39 - 7.35 (m, 2H), 5.66 (d, J = 12.4 Hz, 1H), 3.15 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 154.5, 138.8, 136.9, 128.9, 128.2, 91.6, 45.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{13}\text{ClNO}$: 210.0686. Found: 210.0690.

(E)-1-(4-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (1g):



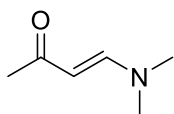
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 82 - 83 °C. Yield 84%; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 12.4$ Hz, 1H), 7.78 - 7.76 (m, 2H), 7.54 - 7.52 (m, 2H), 5.65 (d, $J = 12.0$ Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 154.5, 139.2, 131.2, 129.1, 125.4, 91.6, 45.0, 37.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{13}\text{BrNO}$: 254.0181. Found: 254.0184.

(E)-3-(Dimethylamino)-1-(4-iodophenyl)prop-2-en-1-one (1h):



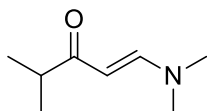
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 121 - 122 °C. Yield 65%; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 12.4$ Hz, 1H), 7.75 - 7.73 (m, 2H), 7.63 - 7.61 (m, 2H), 5.64 (d, $J = 12.4$ Hz, 1H), 3.12 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 154.4, 139.7, 129.0, 97.7, 91.4, 45.0, 37.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{11}\text{H}_{13}\text{INO}$: 302.0042. Found: 302.0039.

(E)-4-(Dimethylamino)but-3-en-2-one (1j):



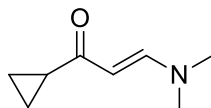
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 57 %; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, $J = 12.8$ Hz, 1H), 5.05 (d, $J = 12.8$ Hz, 1H), 2.96 - 2.90 (m, 6H), 2.10 (s, 3H); HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_6\text{H}_{12}\text{NO}$: 114.0919, Found: 114.0924.

(E)-1-(Dimethylamino)-4-methylpent-1-en-3-one (1k):



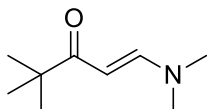
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 62 %; ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 12.6$ Hz, 1H), 5.05 (d, $J = 12.6$ Hz, 1H), 2.96 - 2.80 (m, 6H), 2.60 - 2.51 (m, 1H), 1.10 (d, $J = 3.3$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.3, 152.6, 93.6, 39.5, 19.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_8\text{H}_{16}\text{NO}$: 142.1232, Found: 142.1224

(E)-1-Cyclopropyl-3-(dimethylamino)prop-2-en-1-one (1l):



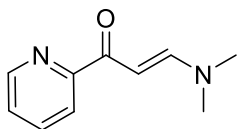
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 58 %; ^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, $J = 12.6$ Hz, 1H), 5.20 (d, $J = 12.6$ Hz, 1H), 2.95 (d, 6H), 1.83 - 1.75 (m, 1H), 1.03 - 0.98 (m, 2H), 0.77 - 0.71 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 151.7, 95.8, 44.7, 37.1, 19.8, 9.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_8\text{H}_{14}\text{NO}$: 141.2108. Found: 141.2112.

(E)-1-(Dimethylamino)-4,4-dimethylpent-1-en-3-one (1m):



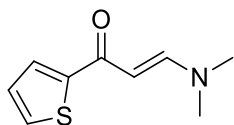
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 47 %; ^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, $J = 12.4$ Hz, 1H), 5.24 (d, $J = 12.4$ Hz, 1H), 2.94 (s, 6H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.6, 153.2, 90.5, 41.9, 27.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{18}\text{NO}$: 156.1388, found: 156.1389.

(E)-3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (1n):



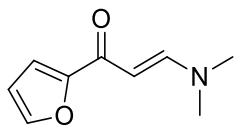
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp. 124 - 125 °C. Yield 71%; ^1H NMR (300 MHz, CDCl_3) δ 8.64 - 8.62 (m, 1H), 8.15 (d, 1H), 7.92 (d, $J = 12.7$ Hz, 1H), 7.83 - 7.77 (m, 1H), 7.38 - 7.34 (m, 1H), 6.45 (d, $J = 12.7$ Hz, 1H), 3.18 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.7, 156.0, 154.6, 148.1, 136.6, 125.3, 121.9, 90.9, 45.0, 37.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}$: 178.2310. Found: 178.2314.

(E)-3-(Dimethylamino)-1-(thiophen-2-yl)prop-2-en-1-one (1o):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 117 - 118 °C. Yield 79%; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 12.4$ Hz, 1H), 7.62 - 7.61 (m, 1H), 7.47 - 7.45 (m, 1H), 7.08 - 7.06 (m, 1H), 5.62 (d, $J = 12.0$ Hz, 1H), 3.10 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.6, 153.4, 147.3, 130.0, 128.2, 127.4, 91.5, 44.8, 37.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{12}\text{NOS}$: 182.0640. Found: 182.0640.

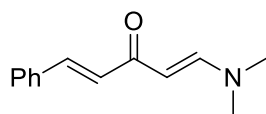
(E)-3-(Dimethylamino)-1-(furan-2-yl)prop-2-en-1-one (1p):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 80 - 81 °C. Yield 81%; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d,

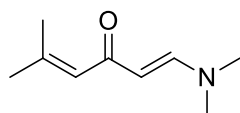
$J = 12.4$ Hz, 1H), 7.49 (s, 1H), 7.06 (d, $J = 2.8$ Hz, 1H), 6.48 (s, 1H), 5.68 (d, $J = 12.8$ Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.4, 154.7, 153.5, 144.1, 113.3, 111.7, 91.4, 44.9, 37.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{12}\text{NO}_2$: 166.0868. Found: 166.0869.

(1E, 4E)-1-(Dimethylamino)-5-phenylpenta-1, 4-dien-3-one (1q):



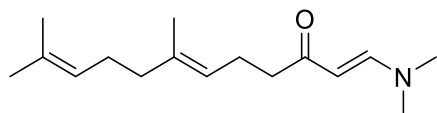
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 99 - 100 °C. Yield 78%; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 12.4$ Hz, 1H), 7.59 - 7.54 (m, 3H), 7.38 - 7.32 (m, 3H), 6.79 (d, $J = 12.8$ Hz, 1H), 5.28 (d, $J = 12.8$ Hz, 1H), 3.12 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.2, 153.3, 138.3, 135.7, 129.1, 128.6, 128.2, 127.8, 96.3, 44.9, 37.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$: 202.1232. Found: 202.1229.

(E)-1-(Dimethylamino)-5-methylhexa-1, 4-dien-3-one (1r):



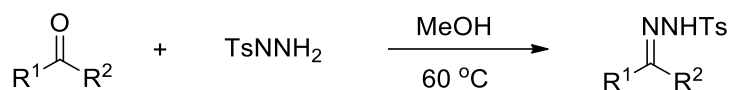
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 43 %; ^1H NMR (300 MHz, CDCl_3) δ 7.54 (d, $J = 12.6$ Hz, 1H), 5.97 - 5.96 (t, $J = 0.9$ Hz, 1H), 5.06 (d, $J = 12.6$ Hz, 1H), 2.96 - 2.94 (m, 6H), 2.14 (d, $J = 0.9$ Hz, 3H), 1.85 (d, $J = 0.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.1, 152.7, 149.0, 125.9, 98.2, 58.3, 27.4, 20.3, 18.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_9\text{H}_{16}\text{NO}$: 155.2374. Found: 155.2370.

(1E, 6E)-1-(Dimethylamino)-6, 11-dimethyldodeca-1, 6, 10-trien-3-one (1s):



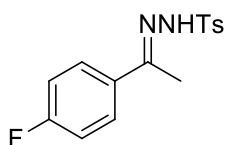
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 72%; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 12.8 Hz, 1H), 5.17 - 5.03 (m, 2H), 5.03 (d, J = 12.4 Hz, 1H), 3.00 - 2.84 (m, 6H), 2.36 - 2.29 (m, 4H), 2.06 - 2.03 (m, 3H), 1.99 - 1.97 (m, 1H), 1.62 - 1.59 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 197.5, 152.1, 135.5, 135.3, 131.3, 131.1, 124.4, 124.2, 123.6, 95.7, 41.5, 39.6, 31.8, 26.6, 26.5, 25.6, 24.2, 24.1, 23.3, 17.5, 17.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{28}\text{NO}$: 250.2171. Found: 250.2177.

General procedure for the synthesis of hydrazone:



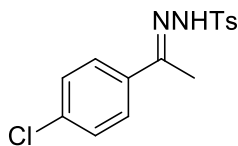
A solution of pure TsNNH_2 (5 mmol) in methanol (5 mL) was stirred at 60 $^\circ\text{C}$ until the TsNNH_2 was completely dissolved. The mixture was cooled to room temperature. Then carbonyl compounds were dropped to the mixture slowly. After approximately 5 minutes the crude products could be obtained as solid precipitations. The precipitations were washed by petroleum ether then kept in vacuo to give the pure products.

N'-(1-(4-Fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2b):



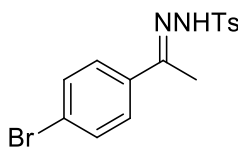
The title compound was prepared according to the general procedure. The product was obtained as white solid in a *cis* : *trans* of 7 : 93. Mp. 150 - 151 $^\circ\text{C}$. Yield: 90%. ^1H NMR (400 MHz, CDCl_3) δ 8.01 - 7.97 & 7.92 - 7.90 (m, 2H), 7.81 - 7.79 & 7.65 - 7.62 (m, 2H), 7.61 - 7.59 (m, 1H), 7.38 - 7.32 (m, 2H), 7.17 - 7.11 & 7.05 - 7.00 (m, 2H), 2.60 & 2.42 (s, 3H), 2.46 & 2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 162.3, 151.8, 144.2, 135.2, 133.4, 129.6, 128.2 (d, J = 8.4 Hz), 128.0, 115.2 (d, J = 21.56Hz), 21.5, 13.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{16}\text{FN}_2\text{O}_2\text{S}$: 308.3711. Found: 308.3715.

N'-(1-(4-Chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2c):



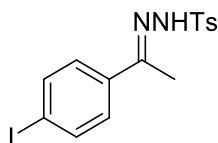
The title compound was prepared according to the general procedure. The product was obtained as white solid in a *cis* : *trans* of 7 : 93. Mp. 166 - 167 °C. Yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.91 - 7.89 & 7.81 - 7.79 (m, 2H), 7.75 & 7.60 - 7.59 (m, 1H), 7.58 - 7.57 & 7.45 - 7.42 (m, 2H), 7.38 - 7.36 & 7.34 - 7.30 (m, 4H), 2.60 & 2.42 (s, 3H), 2.46 & 2.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 144.3, 135.7, 135.5, 135.2, 129.6, 128.4, 128.0, 127.5, 21.6, 13.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₁₆ClN₂O₂S: 324.8257. Found: 324.8253.

N'-(1-(4-Bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2d):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid in a *cis* : *trans* of 13 : 87. Mp. 185 - 186 °C. Yield: 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.91 - 7.89 & 7.83 - 7.79 (m, 2H), 7.62 - 7.60 & 7.57 (m, 1H), 7.53 - 7.51 (m, 2H), 7.48 - 7.46 (m, 2H), 7.38 - 7.36 & 7.34 - 7.32 (m, 2H), 2.59 & 2.42 (s, 3H), 2.46 & 2.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 144.3, 136.1, 135.2, 131.4, 129.6, 128.1, 127.8, 123.9, 21.6, 13.3; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₁₆BrN₂O₂S: 369.2767. Found: 369.2769.

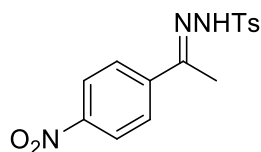
N'-(1-(4-Iodophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2e):



The title compound was prepared according to the general procedure. The product was obtained as white solid in a *cis* : *trans* of 4 : 96. Mp. 199 - 200 °C. Yield: 84%. ¹H NMR (400

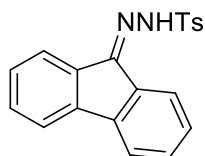
MHz, CDCl₃) δ 7.90 - 7.88 & 7.81 - 7.80 (m, 2H), 7.79 - 7.78 & 7.69 - 7.67 (m, 2H), 7.53 - 7.51 (m, 2H), 7.49 (s, 1H), 7.39 - 7.36 (m, 2H), 7.33 - 7.31 (m, 2H), 2.46 & 2.42 (s, 3H), 2.17 & 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 144.3, 137.5, 136.7, 135.2, 129.6, 128.1, 127.9, 96.0, 21.6, 13.1; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₁₆N₂O₂S: 416.2772. Found: 416.2774.

4-Methyl-N'-(1-(4-nitrophenyl)ethylidene)benzenesulfonohydrazide (2j):



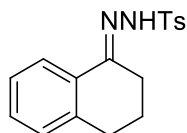
The title compound was prepared according to the general procedure. The product was obtained as white solid in a *cis* : *trans* of 5 : 95. Mp. 196 - 197 °C. Yield: 91%. ¹H NMR (400 MHz, CDCl₃) δ 8.32 - 8.31 & 8.22 - 8.19 (m, 2H), 8.12 - 8.10 & 7.92 - 7.90 (m, 2H), 7.82 - 7.80 (m, 3H), 7.36 - 7.34 (m, 2H), 2.69 & 2.43 (s, 3H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 148.2, 144.7, 143.0, 135.0, 129.8, 128.1, 127.0, 123.6, 21.6, 13.3; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₁₆N₃O₄S: 335.3782. Found: 335.3781.

N'-(9H-fluoren-9-ylidene)-4-methylbenzenesulfonohydrazide (2o):



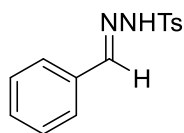
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp. 181 - 182 °C. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.99 - 7.97 (m, 2H), 7.87 - 7.85 (m, 1H), 7.70 - 7.68 (m, 1H), 7.63 - 7.61 (m, 1H), 7.52 - 7.51 (m, 1H), 7.45 - 7.41 (m, 1H), 7.36 - 7.29 (m, 4H), 7.26 - 7.23 (m, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 144.6, 142.5, 139.7, 136.3, 134.6, 131.7, 130.4, 129.6, 129.5, 128.4, 128.2, 128.1, 126.3, 122.2, 120.8, 119.7, 21.6; HRMS (ESI) m/z [M+H]⁺: Calcd for C₂₀H₁₇N₂O₂S: 350.4341. Found: 350.4244.

N'-(3,4-Dihydronaphthalen-1(2H)-ylidene)-4-methylbenzenesulfonohydrazide (2p):



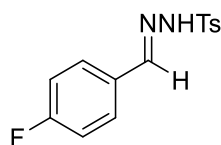
The title compound was prepared according to the general procedure. The product was obtained as white solid. Mp. 183 - 184 °C. Yield: 82%. ^1H NMR (400 MHz, CDCl_3) δ 7.99 - 7.97 (m, 1H), 7.94 - 7.92 (m, 2H), 7.70 (s, 1H), 7.33 - 7.31 (m, 2H), 7.24 - 7.17 (m, 2H), 7.09 - 7.08 (m, 1H), 2.72 - 2.69 (m, 2H), 2.48 - 2.44 (m, 2H), 2.41 (s, 3H), 1.91 - 1.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 144.1, 139.8, 135.4, 131.5, 129.6, 128.3, 128.1, 126.4, 125.0, 29.2, 25.4, 21.6, 21.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$: 316.4179. Found: 316.4177.

(E)-N'-(benzylidene-4-methylbenzenesulfonyl)hydrazide (2q):



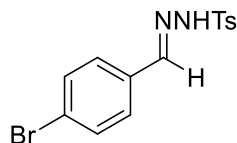
The title compound was prepared according to the general procedure. The product was obtained as white solid. Mp. 127 - 128 °C. Yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1H), 7.90 - 7.87 (d, 2H), 7.80 (s, 1H), 7.60 - 7.50 (t, 2H), 7.40 - 7.20 (m, 5H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 144.3, 135.2, 133.3, 130.4, 129.8, 128.6, 128.0, 127.4, 21.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$: 276.3540. Found: 276.3543.

(E)-N'-(4-fluorobenzylidene)-4-methylbenzenesulfonylhydrazide (2r):



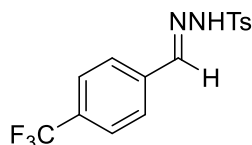
The title compound was prepared according to the general procedure. The product was obtained as white solid. Mp. 123 - 124 °C. Yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.89 - 7.86 (m, 2H), 7.75 - 7.73 (m, 1H), 7.59 - 7.54 (m, 2H), 7.34 - 7.31 (m, 2H), 7.07 - 7.01 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 162.7, 147.0, 144.4, 135.1, 129.8, 129.5 (d, J = 12.1 Hz), 129.2 (d, J = 34.2 Hz), 127.9, 115.8 (d, J = 87.8 Hz), 21.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}_2\text{S}$: 294.3445. Found: 294.3447.

(E)-N'-(4-Bromobenzylidene)-4-methylbenzenesulfonohydrazide (2s):



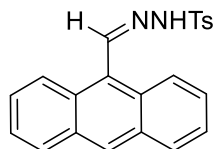
The title compound was prepared according to the general procedure. The product was obtained as white solid. Mp. 178 - 179 °C. Yield: 80%. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.88 - 7.85 (m, 2H), 7.70 (s, 1H), 7.50 - 7.42 (m, 4H), 7.33 - 7.30 (m, 2H), 2.41 (s, 3H) ; ¹³C NMR (100 MHz, CDCl₃) δ 146.3, 144.5, 135.1, 132.1, 131.9, 129.8, 128.7, 127.9, 124.8, 21.6; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₄H₁₄BrN₂O₂S: 355.2501. Found: 355.2505.

(E)-4-Methyl-N'-(4-(trifluoromethyl)benzylidene)benzenesulfonohydrazide (2t):



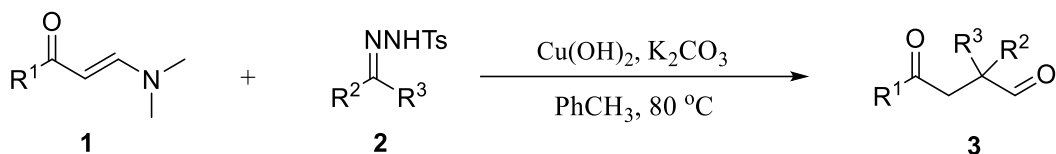
The title compound was prepared according to the general procedure. The product was obtained as white solid. Mp. 164 - 165 °C. Yield: 87%. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.89 - 7.86 (d, 2H), 7.77 (s, 1H), 7.71 - 7.60 (m, 4H), 7.35 - 7.32 (m, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.7, 144.6, 136.5, 135.0, 131.9 (d, *J* = 128.6 Hz), 129.8, 127.9, 127.5, 125.6 (d, *J* = 14.5 Hz), 125.1, 122.4; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₅H₁₄F₃N₂O₂S: 344.3520. Found: 344.3521.

N'-(Anthracen-9-ylmethylene)-4-methylbenzenesulfonohydrazide (2u):



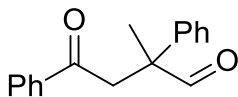
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp. 163 - 164 °C. Yield: 87%. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.47 (s, 1H), 8.23 - 8.19 (m, 3H), 8.00 - 7.97 (m, 4H), 7.50 - 7.40 (m, 4H), 7.39 - 7.36 (m, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 146.8, 144.5, 135.4, 131.1, 130.1, 130.0, 129.9, 128.9, 128.4, 127.0, 125.3, 124.6, 124.2, 21.7; HRMS (ESI) m/z [M+H]⁺: Calcd for C₂₂H₁₉N₂O₂S: 376.4714. Found: 376.4711.

General procedure for synthesis of 1, 4-ketoaldehydes:



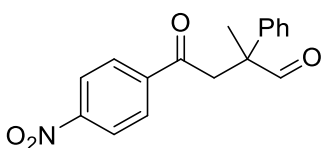
A mixture of **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 2.0 equiv.), K₂CO₃ (0.4 mmol, 2.0 equiv.), Cu(OH)₂ (0.02 mmol, 10 mol %) and solvent (4 mL) was sealed in a Schlenk tube under Ar protection at 80 °C and the mixture was stirred for 24h or until the **1a** was consumed completely. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 1 : 5) to give the desired product.

2-Methyl-4-oxo-2, 4-diphenylbutanal (3aa):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 96%. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.43 (m, 2H), 7.39 - 7.28 (m, 5H), 3.78 - 3.68 (m, 2H), 1.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 197.2, 139.8, 136.8, 133.4, 128.9, 128.6, 128.1, 127.4, 126.9, 51.8, 46.1, 20.7; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₇O₂: 253.1229, Found: 253.1228.

2-Methyl-4-(4-nitrophenyl)-4-oxo-2-phenylbutanal (3ba):



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 125 - 126 °C. Yield 81%; ^1H NMR (300 MHz, CDCl_3) δ 9.66 (s, 1H), 8.27 (d, J = 8.7 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.41 - 7.36 (m, 2H), 7.32 - 7.28 (m, 3H), 3.68 (s, 2H), 1.74, (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 195.9, 150.4, 141.2, 138.9, 129.1, 127.7, 126.9, 123.8, 52.1, 46.2, 20.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_4$: 298.1079, Found: 298.1078.

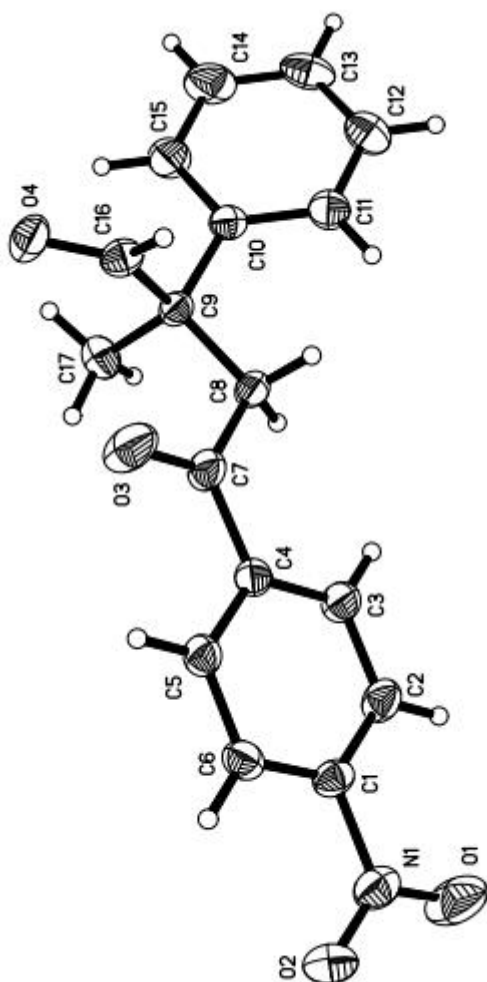
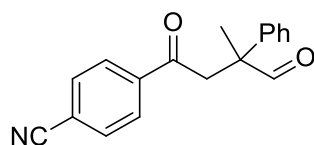


Table 1. Sample and crystal data for 3ba

Identification code	3ba
Chemical formula	$\text{C}_{17}\text{H}_{15}\text{NO}_4$

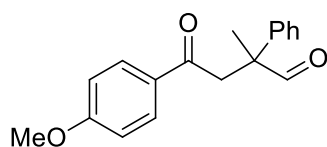
Formula weight	297.30 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.150 x 0.170 x 0.370 mm
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 6.3645(5) Å $\alpha = 90^\circ$ b = 14.4689(12) Å $\beta = 99.228(3)^\circ$ c = 15.7267(12) Å $\gamma = 90^\circ$
Volume	1429.5(2) Å ³
Z	4
Density (calculated)	1.381 g/cm ³
Absorption coefficient	0.099 mm ⁻¹
F(000)	624

4-(3-Methyl-4-oxo-3-phenylbutanoyl)benzonitrile (3ca):



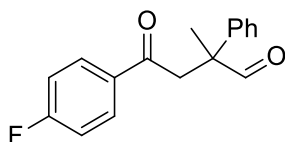
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 127 - 128 °C. Yield: 78%. ¹H NMR (400 MHz, CDCl₃) δ 9.65 (s, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.3, Hz, 2H), 7.40 - 7.36 (m, 2H), 7.31 - 7.27 (m, 3H), 3.69 - 3.64 (m, 2H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.9, 196.1, 139.8, 139.0, 132.8, 129.1, 128.5, 127.7, 126.9, 117.8, 116.5, 52.1, 46.0, 20.0; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₈H₁₆NO₂: 278.1181, Found: 278.1180.

4-(4-Methoxyphenyl)-2-methyl-4-oxo-2-phenylbutanal (3da):



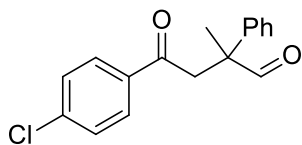
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 104 - 105 °C. Yield: 97%. ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.93 - 7.91 (d, *J* = 8.8 Hz, 2H), 7.39 - 7.35 (m, 2H), 7.34 - 7.32 (m, 2H), 7.30 - 7.28 (m, 1H), 6.93 - 6.90 (m, 2H), 3.86 (s, 3H), 3.73 - 3.64 (m, 2H), 1.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.6, 195.7, 163.7, 139.9, 130.4, 129.8, 128.9, 127.3, 126.9, 113.7, 55.5, 51.8, 45.7, 20.9; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₈H₁₉O₃: 283.1334, Found: 278.1331.

4-(4-Fluorophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ea):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 90%. ¹H NMR (400 MHz, CDCl₃) δ 9.71 (s, 1H), 7.97 - 7.94 (m, 2H), 7.40 - 7.36 (m, 2H), 7.33 - 7.27 (m, 3H), 7.14 - 7.08 (m, 2H), 3.73 - 3.63 (m, 2H), 1.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.4, 195.7, 165.9 (d, *J* = 253.8 Hz), 139.6, 133.3 (d, *J* = 3.3 Hz), 130.8 (d, *J* = 9.3 Hz), 129.0, 127.5, 126.9, 115.7 (d, *J* = 21.8 Hz), 51.9, 45.9, 20.6; HRMS (ESI) *m/z* [M+H]⁺: Calcd for C₁₇H₁₆O₂F: 271.1134, Found: 271.1140.

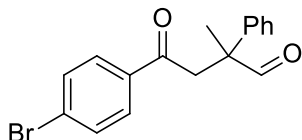
4-(4-Chlorophenyl)-2-methyl-4-oxo-2-phenylbutanal (3fa):



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 70 - 71 °C. Yield: 91%. ¹H NMR (400 MHz, CDCl₃) δ 9.70 (s, 1H), 7.87 - 7.84 (m, 2H), 7.43 - 7.39 (m, 2H), 7.37 - 7.36 (m, 2H), 7.32 - 7.27 (m, 3H), 3.71 - 3.62 (m, 2H), 1.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.3, 196.0, 139.8, 139.5, 135.2,

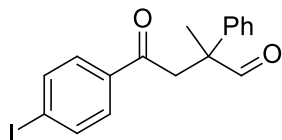
129.5, 129.0, 128.9, 127.5, 126.9, 51.9, 45.9, 20.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}O_2Cl$: 287.0839. Found: 287.0837.

4-(4-Bromophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ga):



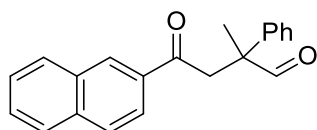
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 70 - 71 °C. Yield: 97%. 1H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.79 - 7.76 (m, 2H), 7.59 - 7.56 (m, 2H), 7.39 - 7.36 (m, 2H), 7.32 - 7.26 (m, 3H), 3.70 - 3.61 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 196.2, 139.8, 139.4, 135.6, 131.9, 129.6, 129.0, 128.5, 127.5, 126.8, 51.9, 45.8, 20.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}O_2Br$: 331.0334. Found: 331.0329.

4-(4-Iodophenyl)-2-methyl-4-oxo-2-phenylbutanal (3ha):



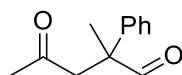
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 69 - 70 °C, Yield: 82%. 1H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.8 (d, J = 8 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.39 - 7.35 (m, 2H), 7.31 - 7.28 (m, 3H), 3.69 - 3.60 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 196.5, 139.4, 137.9, 136.1, 129.4, 129.0, 127.5, 126.8, 101.3, 51.9, 45.8, 20.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}NO_2$: 379.0195. Found: 379.0199.

2-Methyl-4-(naphthalen-2-yl)-4-oxo-2-phenylbutanal (3ia):



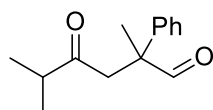
The title compound was prepared according to the general procedure. The product was obtained as canary yellow solid, Mp. 102 - 103 °C, Yield: 94 %. ^1H NMR (400 MHz, CDCl_3) δ 9.80 (s, 1H), 8.46 (s, 1H), 8.00 - 7.93 (m, 2H), 7.87 (d, J = 8 Hz, 2H), 7.63 - 7.54 (m, 2H), 7.39 - 7.38 (m, 4H), 7.32 - 7.28 (m, 1H), 3.87 (s, 2H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.6, 197.2, 139.8, 135.7, 134.2, 132.4, 130.0, 129.6, 129.0, 128.7, 128.5, 127.8, 127.5, 127.0, 126.9, 123.7, 52.0, 46.1, 20.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2$: 303.1385, Found: 303.1383.

2-Methyl-4-oxo-2-phenylpentanal (3ja):



The title compound was prepared according to the general procedure. The product was obtained as pale oil, Yield 70%; ^1H NMR (300 MHz, CDCl_3) ^1H NMR (400 MHz, CDCl_3) δ 9.56 (s, 1H), 7.30 - 7.35 (m, 2H), 7.35 - 7.31 (m, 1H), 7.28 - 7.26 (m, 3H), 3.20 - 3.0 (m, 2H), 2.08 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.0, 201.0, 139.2, 129.0, 127.5, 126.8, 51.9, 50.4, 31.0, 19.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for: $\text{C}_{12}\text{H}_{15}\text{O}_2$: 191.1072 Found: 191.1078.

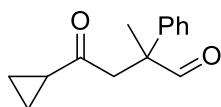
2, 5-Dimethyl-4-oxo-2-phenylhexanal (3ka):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield 54%; ^1H NMR (300 MHz, CDCl_3) δ 9.62 (s, 1H), 7.41 - 7.36 (m,

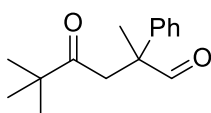
2H), 7.31 - 7.27 (m, 3H), 3.25 - 3.11 (m, 2H), 2.60 - 2.51 (m, 1H), 1.61 (s, 3H), 1.09 (d, $J = 6.9$ Hz, 3H), 1.04 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.9, 201.2, 139.6, 128.9, 127.4, 126.8, 51.7, 47.7, 41.3, 20.2, 18.0, 17.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$: 219.1385, Found: 219.1378.

4-Cyclopropyl-2-methyl-4-oxo-2-phenylbutanal (3la):



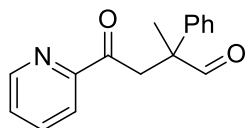
The title compound was prepared according to the general procedure. The product was obtained as colorless oil, Yield 58%; ^1H NMR (300 MHz, CDCl_3) δ 9.60 (s, 1H), 7.39 - 7.35 (m, 2H), 7.30 - 7.25 (m, 3H), 3.32 - 3.23 (m, 2H), 1.88 - 1.79 (m, 1H), 1.58 (s, 3H), 1.03 - 0.89 (m, 2H), 0.87- 0.74 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 201.0, 139.5, 128.9, 127.4, 126.9, 51.8, 50.5, 21.3, 20.2, 11.1, 11.08; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2$: 217.1229, Found: 217.1232.

2, 5, 5-Trimethyl-4-oxo-2-phenylhexanal (3ma):



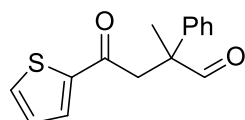
The title compound was prepared according to the general procedure. The product was obtained as colorless oil, Yield 29%; ^1H NMR (300 MHz, CDCl_3) δ 9.64 (s, 1H), 7.39 - 7.34 (m, 2H), 7.29 - 7.24 (m, 3H), 3.27 - 3.20 (m, 2H), 1.56 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 213.2, 201.4, 139.9, 128.8, 127.3, 126.8, 51.5, 44.7, 44.2, 26.2, 20.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$: 233.1542, Found: 233.1546.

2-Methyl-4-oxo-2-phenyl-4-(pyridin-2-yl)butanal (3na):



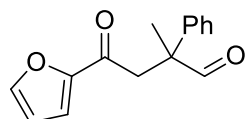
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield 61%; ^1H NMR (300 MHz, CDCl_3) δ 9.78 (s, 1H), 8.68 - 8.66 (m, 1H), 7.99 - 7.96 (m, 1H), 7.84 - 7.79 (m, 1H), 7.49 - 7.45 (m, 1H), 7.37 (d, $J = 4.2$ Hz, 4H), 7.29 - 7.25 (m, 2H), 4.07 - 3.98 (m, 2H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 199.2, 153.2, 148.9, 140.0, 137.0, 128.8, 127.4, 127.3, 127.0, 121.8, 52.0, 44.6, 21.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_2$: 254.1181, Found: 254.1185.

2-Methyl-4-oxo-2-phenyl-4-(thiophen-2-yl)butanal (30a):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield 88%; ^1H NMR (300 MHz, CDCl_3) δ 9.68 (s, 1H), 7.68 - 7.67 (m, 1H), 7.63 - 7.61 (m, 1H), 7.42 - 7.25 (m, 5H), 7.11 - 7.08 (m, 1H), 3.65 - 3.59 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 190.2, 144.2, 139.3, 134.1, 132.3, 129.0, 128.2, 127.5, 126.9, 52.1, 46.3, 20.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{S}$: 259.0793, Found: 259.0794.

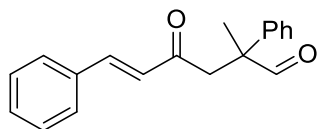
4-(Furan-2-yl)-2-methyl-4-oxo-2-phenylbutanal (3pa):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield 93%; ^1H NMR (300 MHz, CDCl_3) δ 9.67 (s, 1H), 7.54 - 7.53 (m, 1H), 7.39 - 7.27 (m, 5H), 7.14 - 7.13 (m, 1H), 6.51 - 6.49 (m, 1H), 3.54 - 3.53 (m, 2H), 1.66

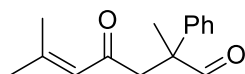
(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 186.5, 152.7, 146.5, 139.3, 128.9, 127.5, 126.9, 117.4, 112.4, 52.1, 45.1, 20.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_3$: 243.1021, Found: 243.1018.

(E)-2-Methyl-4-oxo-2, 6-diphenylhex-5-enal (3qa):



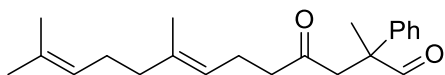
The title compound was prepared according to the general procedure. The product was obtained as colorless oil, Yield: 64 %. ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.50 (d, J = 16.2 Hz, 1H), 7.49 - 7.47 (m, 2H), 7.40 - 7.37 (m, 5H), 7.33 - 7.27 (m, 3H), 6.63 (d, J = 16.2 Hz, 1H), 3.39 - 3.35 (m, 2H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.1, 197.3, 143.2, 139.5, 134.3, 130.7, 128.9, 128.4, 127.5, 127.0, 126.1, 52.1, 48.2, 20.2. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2$: 279.1385, Found: 279.1381.

2, 6-Dimethyl-4-oxo-2-phenylhept-5-enal (3ra):



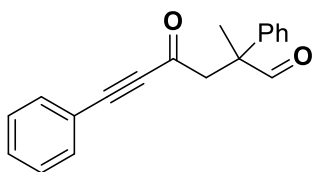
The title compound was prepared according to the general procedure. The product was obtained as pale oil, Yield 52%; ^1H NMR (300 MHz, CDCl_3) δ 9.66 (s, 1H), 7.39 - 7.34 (m, 2H), 7.29 - 7.24 (m, 3H), 6.02 - 6.01 (m, 1H), 3.23 - 3.08 (m, 2H), 2.09 (d, J = 0.6 Hz, 3H), 1.85 (d, J = 0.9 Hz, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.4, 197.7, 156.8, 139.8, 128.8, 127.3, 126.9, 123.7, 52.0, 51.2, 27.7, 20.8, 20.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 231.1385, Found: 231.1392.

(E)-2, 7, 12-Trimethyl-4-oxo-2-phenyltrideca-7, 11-dienal (3sa):



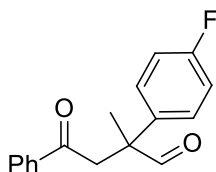
The title compound was prepared according to the general procedure. The product was obtained as colorless oil, Yield: 75%. ^1H NMR (400 MHz, CDCl_3) δ 9.57 (s, 1H), 7.39 - 7.45 (t, 2H), 7.30 - 7.24 (m, 3H), 5.08 - 5.05 (m, 1H), 5.02 - 4.98 (t, 1H), 3.15 - 3.03 (m, 2H), 2.45 - 2.37 (m, 1H), 2.34 - 2.27 (m, 1H), 2.22 - 2.17 (m, 2H), 2.06 - 2.01 (m, 2H), 1.96 - 1.93 (m, 2H), 1.67 (s, 3H), 1.60 - 1.59 (d, 6H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 201.1, 139.4, 136.5, 131.4, 128.9, 127.5, 126.8, 124.2, 122.3, 51.9, 49.7, 43.7, 39.6, 26.6, 25.7, 22.3, 20.0, 17.7, 16.0. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{22}\text{H}_{31}\text{O}_2$: 327.2324, Found; 327.2322.

2-Methyl-4-oxo-2,6-diphenylhex-5-ynal (3ta):



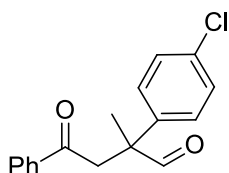
The title compound was prepared according to the general procedure. The product was obtained as pale brown oil, Yield: 41%. ^1H NMR (400 MHz, CDCl_3) δ 9.58 (s, 1H), 7.49 - 7.47 (d, 2H), 7.45 - 7.43 (m, 1H), 7.41 - 7.38 (m, 2H), 7.38 - 7.34 (m, 2H), 7.33 (s, 1H), 7.31 - 7.28 (m, 2H), 3.40 - 3.46 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.20, 184.5, 139.4, 138.5, 133.1, 129.0, 128.6, 127.7, 127.1, 119.7, 91.5, 88.2, 52.3, 52.0, 19.6. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$: 277.1229, Found: 277.1225.

2-(4-Fluorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ab):



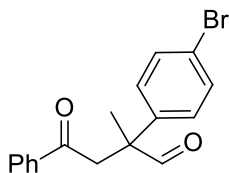
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 9.70 (s, 1H), 7.94 - 7.92(m, 2H), 7.59 - 7.56 (m, 1H), 7.47 - 7.43 (m, 2H), 7.32 - 7.29 (m, 2H), 7.08 - 7.04 (m, 2H), 3.70(s, 2H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.1, 197.0, 161.9 (d, $J = 245.6$ Hz), 136.6, 135.3 (d, $J = 3.1$ Hz), 133.4, 128.6 (d, $J = 7.8$ Hz), 128.6, 128.0, 115.7 (d, $J = 21.3$ Hz), 51.3, 46.1, 20.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$ F: 271.1134. Found: 271.1139.

2-(4-Chlorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ac):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 92%. ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.94 - 7.92 (m, 2H), 7.59 - 7.55 (m, 1H), 7.47 - 7.44 (m, 2H), 7.35 - 7.32 (m, 2H), 7.28 - 7.27 (m, 1H), 7.26 - 7.25 (m, 1H), 3.70 (s, 2H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 196.9, 138.3, 136.6, 133.5, 133.4, 129.0, 128.7, 128.3, 128.1, 51.4, 46.1, 20.9; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Cl}$: 287.0839. Found: 287.0838.

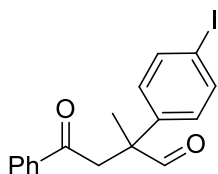
2-(4-Bromophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ad):



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 54 - 55 °C. Yield: 89%. ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.94 - 7.92(m, 2H), 7.60 - 7.56 (m, 1H), 7.50 - 7.44 (m, 4H), 7.22 - 7.20 (m, 2H), 3.71(s,

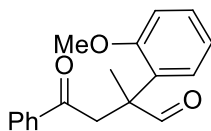
2H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 196.8, 138.9, 136.6, 133.5, 132.0, 128.7, 128.1, 121.6, 51.5, 46.0, 20.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}$: 331.0334. Found: 331.0336.

2-(4-Iodophenyl)-2-methyl-4-oxo-4-phenylbutanal (3ae):



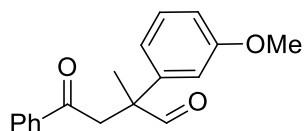
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 78 - 79 °C. Yield: 70%. ^1H NMR (400 MHz, CDCl_3) δ 9.70 (s, 1H), 7.93 - 7.91(m, 2H), 7.70 - 7.68 (m, 2H), 7.60 - 7.56 (m, 1H), 7.47 - 7.44 (m, 2H), 7.10 - 7.07 (m, 2H), 3.70(s, 2H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 196.8, 139.6, 136.6, 133.5, 128.9, 128.7, 128.1, 93.2, 51.5, 46.0, 20.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{I}$: 379.0195. Found: 379.0200.

2-(2-Methoxyphenyl)-2-methyl-4-oxo-4-phenylbutanal (3af):



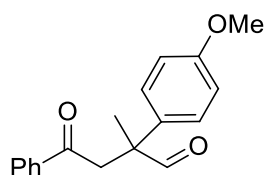
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 98 - 99 °C. Yield: 95%. ^1H NMR (400 MHz, CDCl_3) δ 9.74 (s, 1H), 7.88 - 7.86(m, 2H), 7.53 - 7.50 (m, 1H), 7.41 - 7.38 (m, 2H), 7.47 - 7.44 (m, 2H), 7.30 - 7.23 (m, 2H), 3.79 (s, 3H), 3.74 - 3.69 (m, 2H); 1.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.5, 198.4, 156.2, 137.2, 133.0, 128.9, 128.4, 128.1, 128.0, 121.1, 111.1, 55.3, 50.2, 43.9, 20.4; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3$: 283.1334. Found: 283.1336.

2-(3-Methoxyphenyl)-2-methyl-4-oxo-4-phenylbutanal (3ag):



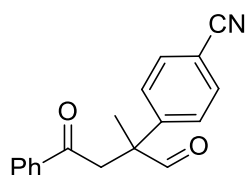
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 84%. ^1H NMR (400 MHz, CDCl_3) δ 9.72 (s, 1H), 7.95 - 7.92(m, 2H), 7.59 - 7.54 (m, 1H), 7.47 - 7.43 (m, 2H), 7.31 - 7.27 (m, 1H), 6.92 - 6.90 (m, 1H), 6.88 - 6.86 (m, 2H), 6.82 - 6.80 (m, 1H) 3.78 (s, 3H), 3.72 - 3.71 (m, 2H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.3, 197.2, 159.9, 141.4, 136.7, 133.3, 129.9, 128.6, 128.1, 119.1, 113.3, 112.1, 55.2, 51.8, 46.0, 20.7; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3$: 283.1334. Found: 283.1335.

2-(4-Methoxyphenyl)-2-methyl-4-oxo-4-phenylbutanal (3ah):



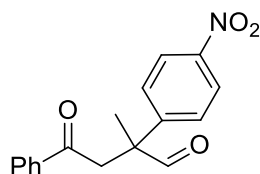
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 66 - 67 °C. Yield: 76%. ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.95 - 7.92(m, 2H), 7.59 - 7.55 (m, 1H), 7.47 - 7.43 (m, 2H), 7.25 - 7.23 (m, 2H), 6.92 - 6.88 (m, 2H), 3.80 (s, 3H), 3.69 (s, 2H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.3, 197.4, 158.8, 136.8, 133.3, 131.3, 128.6, 128.1, 114.3, 55.3, 51.1, 45.9, 20.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_3$: 283.1334. Found: 283.1336.

4-(2-Methyl-1,4-dioxo-4-phenylbutan-2-yl)benzonitrile (3ai):



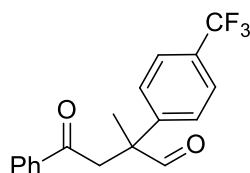
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 90 - 91 °C. Yield: 43%. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 1H), 7.94 - 7.92 (m, 2H), 7.68 - 7.66 (m, 2H), 7.49 - 7.46 (m, 4H), 3.77 (s, 2H), 1.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.6, 196.4, 145.5, 136.2, 133.7, 132.5, 128.8, 128.1, 127.8, 118.4, 111.3, 52.0, 46.2, 21.2; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₈H₁₆NO₂: 278.1181. Found: 278.1182.

2-Methyl-2-(4-nitrophenyl)-4-oxo-4-phenylbutanal (3aj):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 136 - 137 °C. Yield: 68%. ¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 8.24 - 8.21 (m, 2H), 7.94 - 7.92 (m, 2H), 7.62 - 7.58 (m, 2H), 7.54 - 7.51 (m, 2H), 7.49 - 7.45 (m, 2H), 3.80 (s, 2H), 1.72 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.4, 196.3, 147.5, 147.0, 136.2, 133.8, 128.8, 128.1, 128.0, 123.9, 52.0, 46.4, 21.5; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₇H₁₆NO₄: 298.1079. Found: 298.1089.

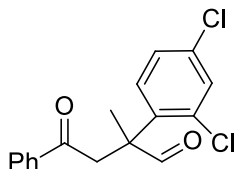
2-Methyl-4-oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanal (3ak):



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 60 - 61 °C. Yield: 73%. ¹H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 7.95 - 7.92 (m, 2H), 7.64 - 7.61 (m, 2H), 7.59 - 7.57 (m, 1H), 7.48 - 7.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 201.0, 196.7, 144.1, 136.4, 133.6, 129.6 (q, *J* = 32.4), 128.1,

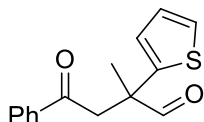
127.4, 125.8 (q, $J = 7.4$ Hz), 125.3, 122.6, 51.8, 46.3, 21.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{16}O_2F_3$: 321.1102. Found: 321.1108.

2-(2, 4-Dichlorophenyl)-2-methyl-4-oxo-4-phenylbutanal (3al):



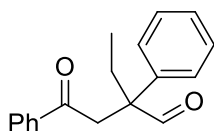
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 92%. 1H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.91 – 7.89(m, 2H), 7.59 – 7.55 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.28 – 7.27 (m, 1H), 7.26 – 7.25 (m, 1H) 3.93 – 3.84 (m, 2H), 1.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 197.4, 137.2, 136.6, 134.3, 133.5, 130.7, 130.6, 129.5, 128.7, 128.0, 127.5, 52.1, 44.5, 21.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{15}O_2Cl_2$: 321.0449. Found: 321.0447.

2-Methyl-4-oxo-4-phenyl-2-(thiophen-2-yl)butanal (3am):



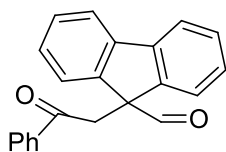
The title compound was prepared according to the general procedure. The product was obtained as brown oil, Yield: 22%. 1H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.97 – 7.95(m, 2H), 7.61 – 7.57 (m, 1H), 7.49 – 7.45 (m, 2H), 7.29 – 7.29 (m, 1H), 7.03 – 7.01 (m, 1H), 6.98 – 6.97 (m, 1H) 3.85 – 3.72 (m, 2H), 1.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 196.7, 144.3, 136.5, 133.5, 128.7, 128.2, 127.4, 125.3, 125.0, 50.0, 47.6, 21.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{15}O_2S$: 259.0793. Found: 259.0789.

2-Ethyl-4-oxo-2, 4-diphenylbutanal (3an):



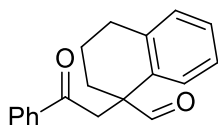
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 88%. ^1H NMR (400 MHz, CDCl_3) δ 9.84 (s, 1H), 7.96 - 7.94 (m, 2H), 7.59 - 7.55 (m, 1H), 7.48 - 7.44 (m, 2H), 7.38 - 7.34 (m, 2H), 7.31 - 7.28 (m, 2H), 3.83 - 3.74 (m, 2H), 2.36 - 2.26 (m, 1H), 2.11 - 2.02 (m, 2H), 0.78 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 197.4, 138.7, 136.7, 133.4, 128.8, 128.7, 128.1, 127.4, 127.2, 55.8, 42.3, 27.3, 8.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2$: 267.1385. Found: 267.1386.

9-(2-Oxo-2-phenylethyl)-9H-fluorene-9-carbaldehyde (3ao):



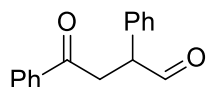
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.160 - 161 °C. Yield: 57%. ^1H NMR (400 MHz, CDCl_3) δ 9.34 (s, 1H), 7.92 - 7.90 (m, 2H), 7.83 - 7.82 (m, 2H), 7.66 - 7.64 (m, 2H), 7.56 - 7.52 (m, 1H), 7.49 - 7.46 (m, 2H), 7.44 - 7.40 (m, 2H); 7.38 - 7.34 (m, 2H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 196.3, 142.7, 141.9, 136.4, 133.4, 128.9, 128.6, 128.1, 128.0, 125.7, 120.3, 63.6, 45.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{22}\text{H}_{17}\text{O}_2$: 313.1229. Found: 313.1233.

1-(2-Oxo-2-phenylethyl)-1, 2, 3, 4-tetrahydronaphthalene-1-carbaldehyde (3ap):



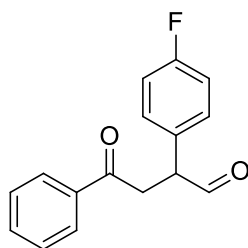
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.126 - 127 °C. Yield: 40%. ¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 1H), 7.93 - 7.92(m, 2H), 7.58 - 7.54 (m, 1H), 7.46 - 7.42 (m, 2H), 7.25 - 7.24 (m, 1H), 7.21 - 7.15 (m, 3H), 3.80 - 3.57 (m, 2H), 2.90 - 2.80 (m, 2H), 2.44 - 2.38 (m, 1H), 2.22 - 2.16 (m, 1H), 1.99 - 1.82 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 197.1, 138.7, 136.9, 133.6, 133.2, 130.0, 128.6, 128.2, 128.1, 127.2, 126.5, 51.2, 47.1, 29.9, 28.8, 19.3; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₉H₁₉O₂: 279.1385. Found: 279.1378.

4-Oxo-2, 4-diphenylbutanal (3aq):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 79%. ¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 7.99 - 7.96(t, 2H), 7.59 - 7.55 (m, 1H), 7.48 - 7.37 (m, 4H), 7.34 - 7.25 (m, 3H), 4.48 - 4.45 (m, 1H), 3.96 (dd, *J*₁ = 8.4 Hz, *J*₂ = 18 Hz, 1H), 3.23 (dd, *J*₁ = 4.9 Hz, *J*₂ = 18 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 197.3, 136.5, 135.5, 133.3, 129.3, 129.1, 128.6, 128.1, 127.9, 53.7, 39.5; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₆H₁₅O₂: 239.1072. Found: 239.1061.

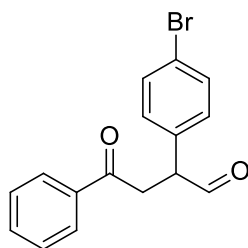
2-(4-Fluorophenyl)-4-oxo-4-phenylbutanal (3ar):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.49 - 50 °C. Yield: 73%. ¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.98 - 7.95 (m, 2H), 7.58 - 7.55 (m, 2H), 7.49 - 7.44 (m, 2H), 7.25 - 7.05 (m, 4H), 4.46 -

4.42 (m, 1H), 3.93 (dd, $J_1 = 8.1$ Hz, $J_2 = 18$ Hz, 1H), 3.22 (dd, $J_1 = 5.2$ Hz, $J_2 = 18$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 197.1, 136.4, 133.5, 131.2, 130.8, 128.7, 128.1, 116.4, 116.2, 52.8, 39.6; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{F}$: 257.0978. Found: 257.0987.

2-(4-Bromophenyl)-4-oxo-4-phenylbutanal (3as):



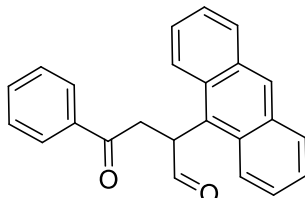
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 79%. ^1H NMR (400 MHz, CDCl_3) δ 9.78 (s, 1H), 7.97 - 7.94(m, 2H), 7.60 - 7.54 (m, 1H), 7.53 - 7.43 (m, 4H), 7.17 - 7.13 (m, 2H), 4.43 - 4.39 (m, 1H), 3.92 (dd, $J_1 = 8.1$ Hz, $J_2 = 18$ Hz, 1H), 3.22 (dd, $J_1 = 5.2$ Hz, $J_2 = 18$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 196.9, 162.4 (d, 245.7), 136.3, 133.4, 131.1 (d, $J = 3.3$ Hz), 130.7 (d, $J = 8.2$ Hz), 128.6, 128.1, 116.2 (d, $J = 21.5$ Hz), 52.8, 39.5; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Br}$: 317.0177, Found: 317.0181.

4-Oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanal (3at):

The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.102 - 103 °C. Yield: 74%. ^1H NMR (400 MHz, CDCl_3) δ 9.83 (s, 1H), 7.99 - 7.96(m, 2H), 7.67 - 7.64 (m, 2H), 7.61 - 7.57 (m, 1H), 7.50 - 7.40 (m, 4H), 4.56 - 4.51 (m, 1H), 3.98 (dd, $J_1 = 8.0$ Hz, $J_2 = 18$ Hz, 1H), 3.28 (dd, $J_1 = 5.2$ Hz, $J_2 = 18$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 196.7, 139.6, 136.1, 133.5, 129.5, 130.2 (q, $J =$

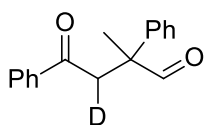
64.1 Hz), 129.5, 128.7, 128.1, 126.1 (q, $J = 7.4$ Hz), 125.2, 122.5, 53.3, 39.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{14}O_2F_3$: 307.0946. Found: 307.0933.

2-(Anthracen-9-yl)-4-oxo-4-phenylbutanal (3au):



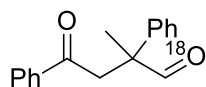
The title compound was prepared according to the general procedure. The product was obtained as red solid, Mp. 102 - 103 °C. Yield: 42%. 1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.60 - 8.49(m, 2H), 8.07 - 7.97 (m, 4H), 7.90 - 7.48 (m, 6H), 7.44 - 7.39 (m, 2H), 5.98 - 5.95 (m, 1H), 4.58 (dd, $J_1 = 6.7$ Hz, $J_2 = 18$ Hz, 1H), 3.31 (dd, $J_1 = 3.8$ Hz, $J_2 = 18$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 197.4, 136.4, 133.4, 131.8, 129.7, 128.9, 128.7, 128.6, 128.3, 127.0, 126.7, 125.2, 124.0, 48.1, 38.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{24}H_{19}O_2$: 339.1385, Found: 339.1396.

2-Methyl-4-oxo-2, 4-diphenylbutanal-3-*d* (3ax)



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 58%. 1H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.95 - 7.93 (m, 2H), 7.59 - 7.55 (m, 1H), 7.47 - 7.43 (m, 2H), 7.40 - 7.27 (m, 5H), 3.78 - 3.69 (m, 1.5 H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 197.3, 197.2, 139.7, 136.8, 133.3, 128.9, 128.6, 128.1, 127.4, 126.9, 51.8, 46.0, 20.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{16}O_2D$: 254.1291, Found: 254.1291.

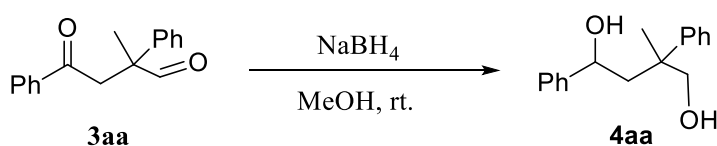
2-Methyl-4-oxo-2,4-diphenylbutanal-¹⁸O (3ay)



The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 50%. ¹H NMR (400 MHz, CDCl₃) δ 9.74 (s, 1H), 7.95 - 7.93 (m, 2H), 7.59 - 7.55 (m, 1H), 7.47 - 7.43 (m, 2H), 7.40 - 7.33 (m, 4H), 7.30 - 7.27 (m, 1H), 3.78 - 3.69 (m, 2H), 1.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.5, 197.2, 139.7, 136.7, 133.4, 128.9, 128.6, 128.1, 127.4, 126.9, 51.8, 46.0, 20.7; HRMS (ESI) m/z [M+H]⁺: Calcd for C₁₇H₁₇¹⁶O¹⁸O: 255.1271, Found: 255.1271.

Application of 1, 4-ketoaldehydes

3-Methyl-1,3-diphenylbutane-1,4-diol (4aa)²:

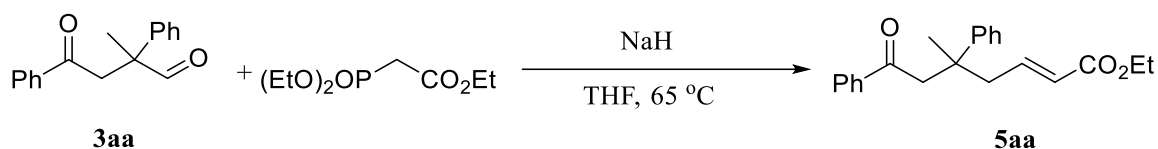


To a solution of 2-methyl-4-oxo-2,4-diphenylbutanal **3aa** (0.20 mmol, 50.2 mg) in MeOH (2.00 mL) was added NaBH₄ (0.4 mmol, 83.2 mg) at room temperature and the reaction mixture was stirred at the same temperature for 30 min under nitrogen atmosphere. The mixture was poured into H₂O (5 mL) and extracted with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and dried with Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography to give **4aa** (97% yield) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 - 7.36 (m, 4H), 7.33 - 7.30 (m, 2H), 7.27 - 7.23 (m, 4H), 4.59 (d, *J* = 8.68 Hz, 1H), 4.09 (d, *J* = 11.4 Hz, 1H), 3.77 (d, *J* = 11.4 Hz, 1H), 3.44 (s, 1H), 2.76 (s, 1H), 2.24 - 2.11 (m, 2H), 1.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.5, 145.2,

² H. Suzuki, S. Yoshioka, A. Igesaka, H. Nishioka and Y. Takeuchi, *Tetrahedron.*, 2013, **69**, 6399 - 6403.

128.6, 128.6, 127.5, 126.6, 126.2, 125.4, 71.7, 69.7, 48.8, 43.2, 27.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{21}O_2$: 257.1542, Found: 257.1539.

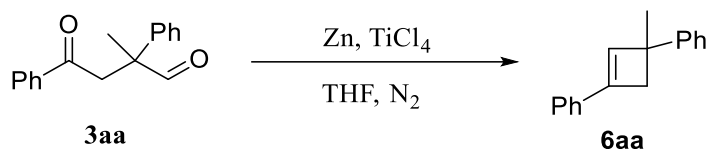
(E)-Ethyl 5-methyl-7-oxo-5, 7-diphenylhept-2-enoate (5aa)³:



A flame-dried round-bottomed flask (RBF) was charged with sodium hydride (0.3 mmol, 12 mg, 60% suspension in mineral oil) and THF (1 ml), then cooled to 0 °C. Triethylphosphonoacetate (0.26 mmol, 51.5 μ l) was added dropwise. The reaction was stirred at 0 °C for 10 min., then 2-methyl-4-oxo-2,4-diphenylbutanal **3aa** (0.2 mmol, 50.4 mg) was added dropwise and the mixture was heated to reflux for 16 h. The reaction was cooled to room temperature and H_2O : $EtOAc$ = 1:1 (10 ml) was added. The layers were separated and the aqueous layer was extracted with $EtOAc$ (2×5 ml). The combined organic layers were washed with 1 M $NaOH$ (5 ml), H_2O (20 ml) and brine (10 ml), then dried (Na_2SO_4). After removal of the solvent, the residue was subjected to column chromatography to give **5aa** (89% yield) as yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.84 (m, 1H), 7.55 - 7.50 (m, 1H), 7.43 - 7.36 (m, 2H), 7.34 (d, J = 16.0 Hz, 1H), 7.31 - 7.28 (m, 4H), 7.22 - 7.18 (m, 1H), 5.82 (d, J = 16.0 Hz, 1H), 4.21 - 4.16 (m, 2H), 3.61 - 3.50 (m, 2H), 1.67 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.8, 155.3, 144.8, 137.5, 133.0, 128.5, 127.9, 126.6, 126.2, 119.2, 60.4, 48.0, 43.3, 25.3, 14.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{22}H_{25}O_3$: 337.1804, Found: 337.1814.

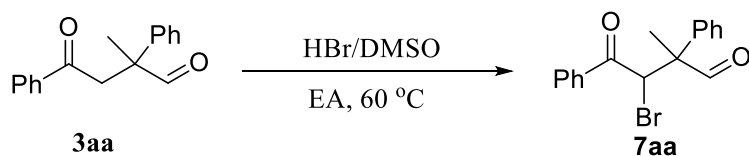
(3-Methylcyclobut-1-ene-1, 3-diyl)dibenzene (6aa)⁴:

³ E. C. A. De Silva, P. J. Silk, P. Mayo, N. K. Hillier and G. C. Cutler, *J. Chem. Eool.*, 2013, **39**, 1169 - 1181.



In a flame-dried flask, dry THF (2 mL) was added to zinc dust (1.6 mmol, 0.1046 g). The flask was cooled in an ice bath, and titanium tetrachloride (0.8 mmol, 88 μ L) was added dropwise. A yellow cloud formed and the solution became dark blue. The resulting (dark blue) solution was refluxed for 1.0 h then cooled to 0 $^{\circ}$ C and a solution of **3aa** (0.2 mmol, 50.4 mg) in THF (2 mL) was added to the reaction mixture. The reaction mixture was then heated to reflux for 3 h. After cooling the reaction to ambient temperature, 10 mL water was added and gas evolution was seen. After the bubbling subsided, the mixture was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over Na₂SO₄, filtered and the solvent was removed *in vacuo*. The resulting colorless liquid was purified by column chromatography (SiO₂, 9:1 petroleum ether:ethyl acetate) to give **6aa** (69 % yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.40 - 7.38 (m, 4H), 7.35 - 7.27 (m, 5H), 7.21 - 7.17 (m, 1H), 2.99 - 2.89 (m, 2H), 1.63 (s, 3H).

3-Bromo-2-methyl-4-oxo-2,4-diphenylbutanal (**7aa**)⁵:



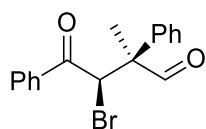
Aldehyde **3aa** (0.2 mmol, 50.4 mg) and DMSO (0.24 mmol, 17 μ L) were dissolved in EA (2 mL). Aqueous hydrobromic acid (1.2 mmol, 48%, 19.4 mg) was added to the solution at 60 $^{\circ}$ C and the mixture were stirred for 0.5 h under air at that temperature. After cooling down to

⁴ (a) M. D. Connors and N. S. Goroff, *Org. Lett.*, 2016, **18**, 4262-4265. (b) V. L. Carrillo, A. M. Echavarren, *J. Am. Chem. Soc.*, 2010, **132**, 9292-9294.

⁵ S. Song, X. W. Li, X. Sun, Y. Z. Yuan and N. Jiao, *Green Chem.*, 2015, **17**, 3285-3289.

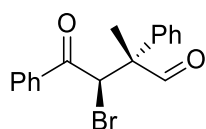
room temperature and concentrating in vacuum, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the brominated product.

3-Bromo-2-methyl-4-oxo-2, 4-diphenylbutanal (7aa, isomer-1):



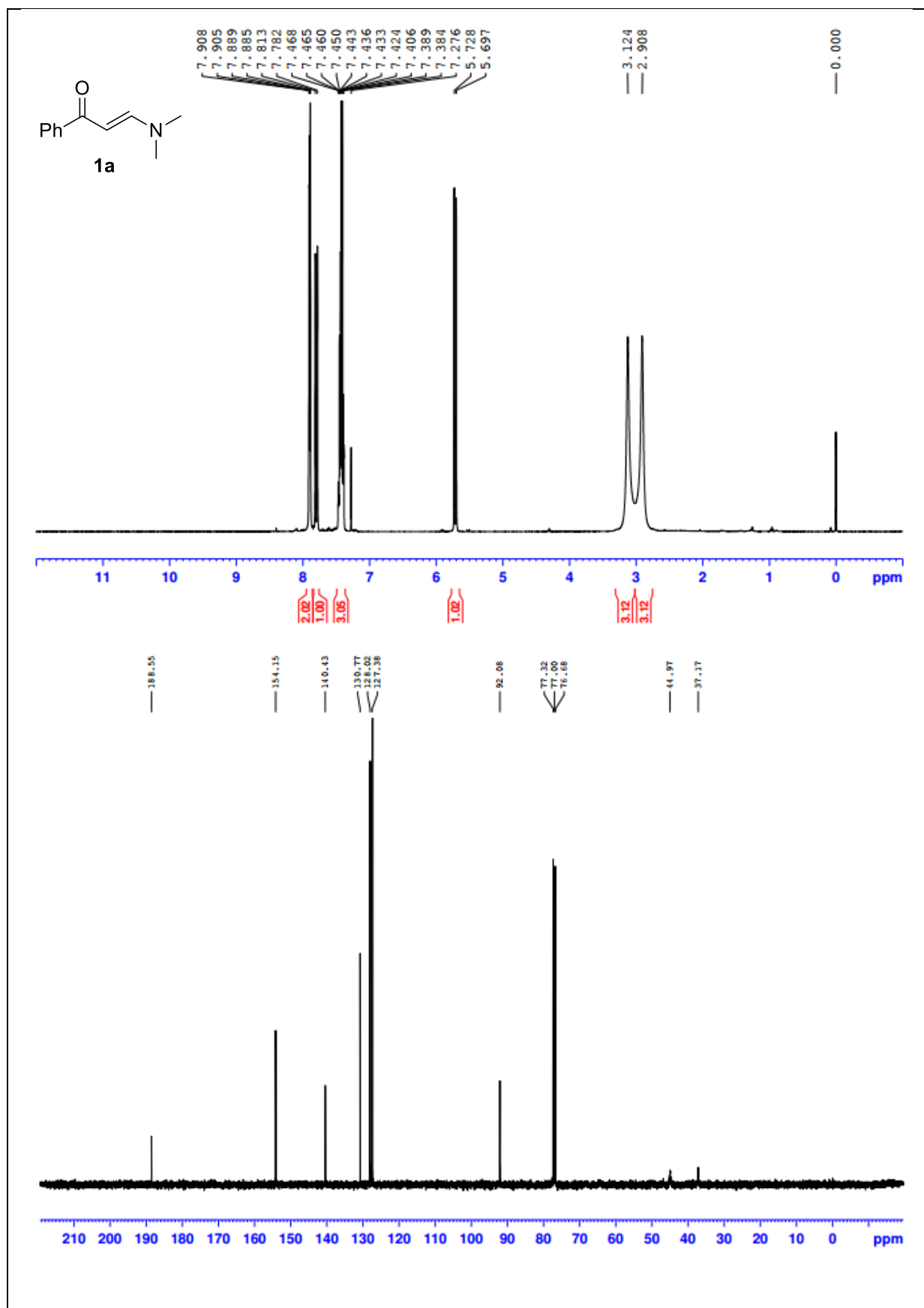
The title compound was prepared according to the general procedure. The product was obtained as yellow oil, Yield: 24%. ^1H NMR (400 MHz, CDCl_3) δ 9.67 (s, 1H), 7.98 - 7.96 (m, 2H), 7.61 - 7.57 (m, 1H), 7.50 - 7.46 (m, 2H), 7.44 - 7.33 (m, 5H), 5.62 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 193.4, 137.1, 135.0, 133.6, 129.0, 128.7, 128.7, 128.7, 128.3, 127.6, 57.5, 53.0, 17.1; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}$: 331.0334, Found: 331.0330.

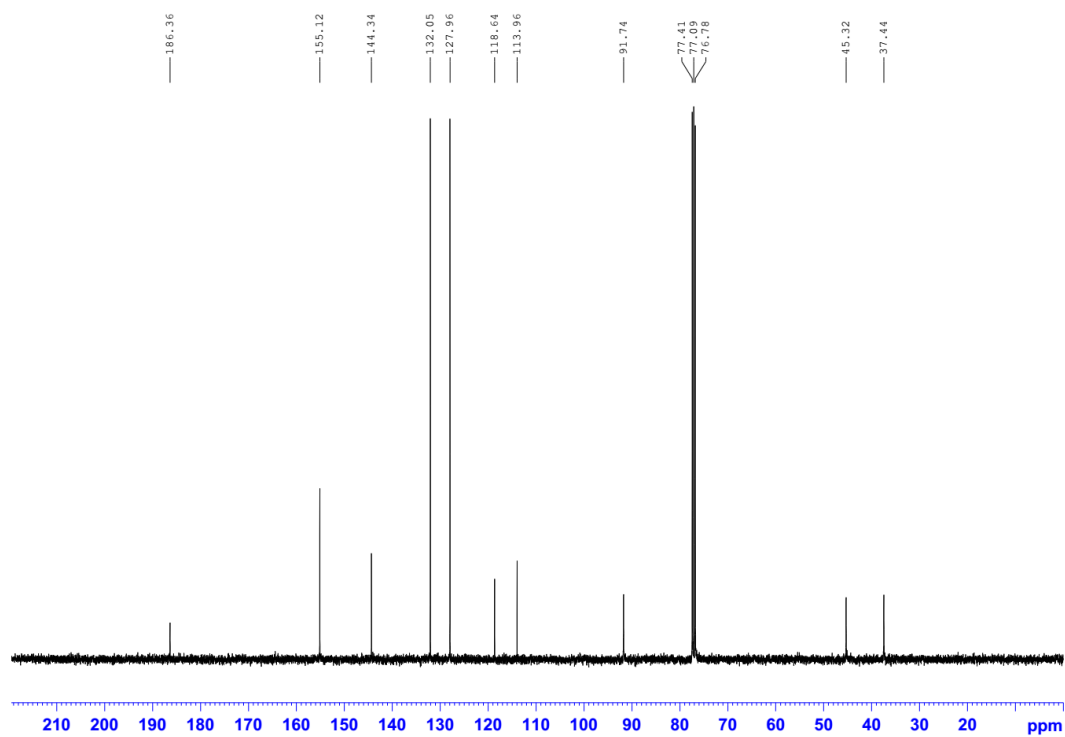
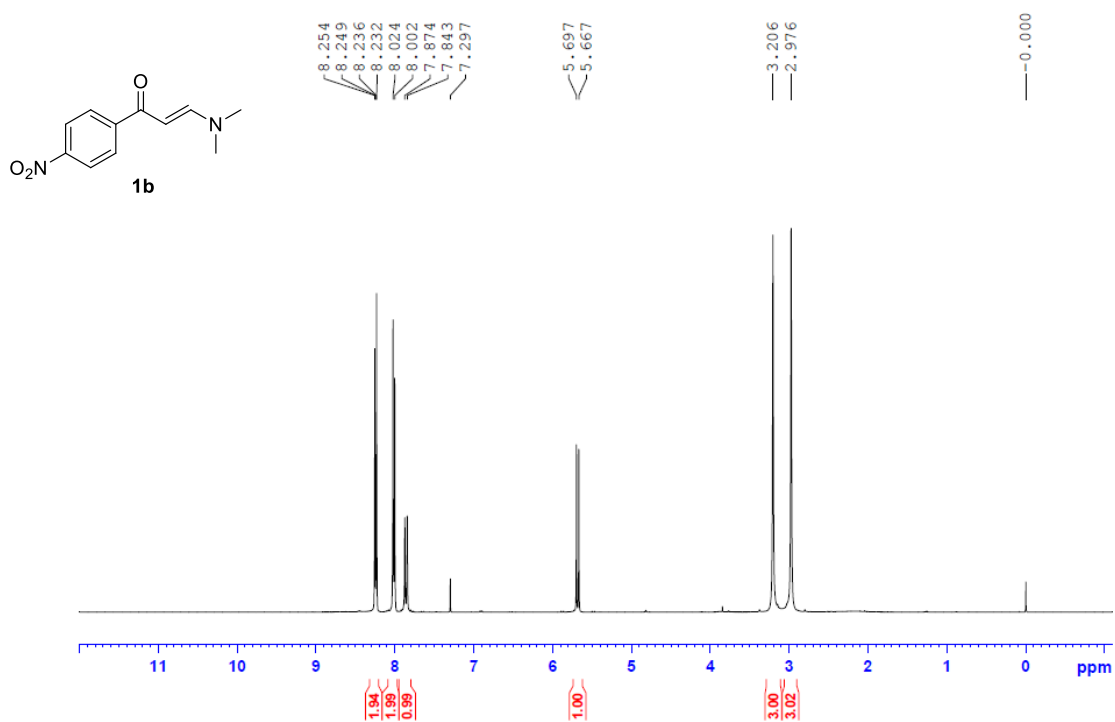
3-Bromo-2-methyl-4-oxo-2, 4-diphenylbutanal (7aa, isomer-2):

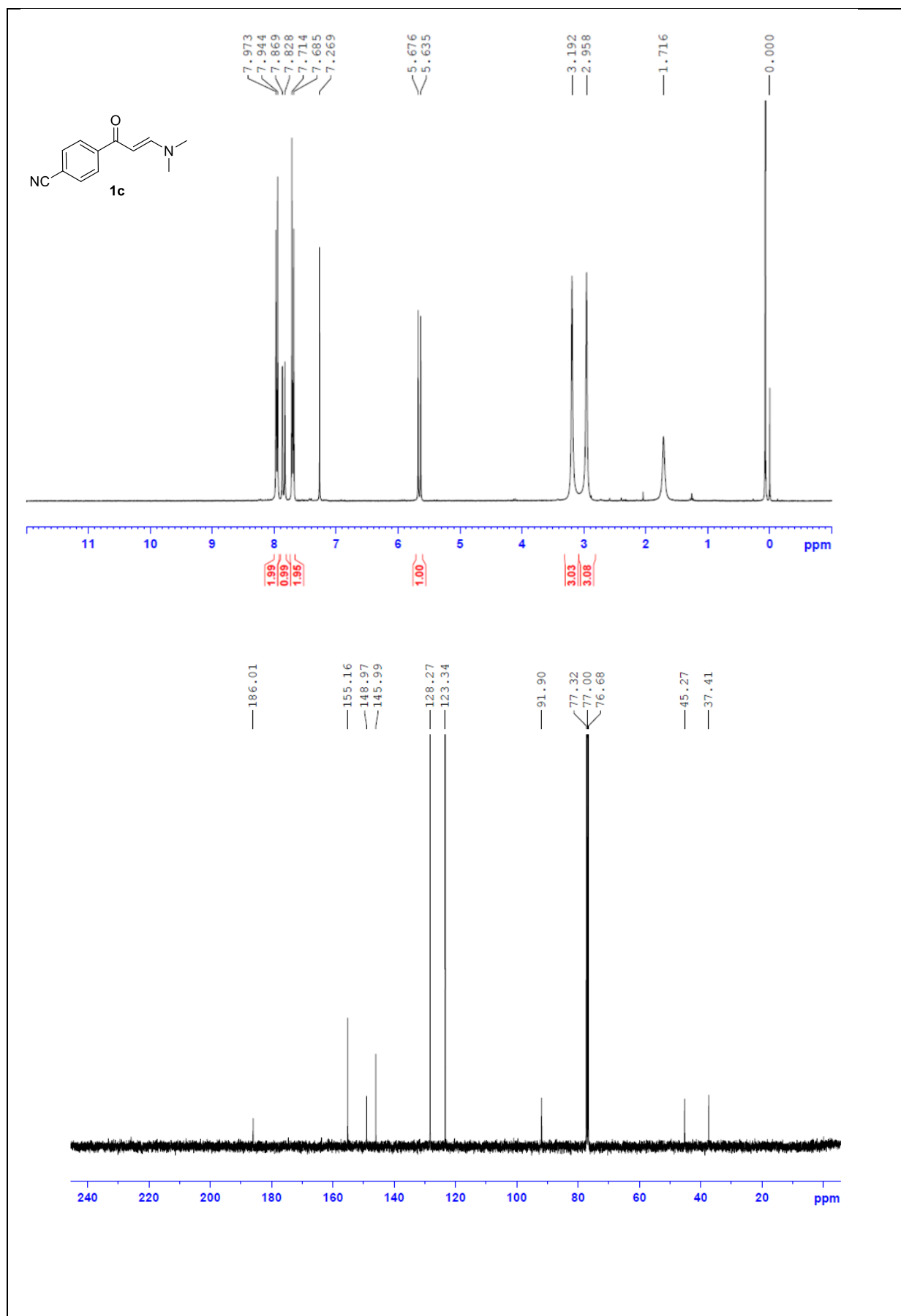


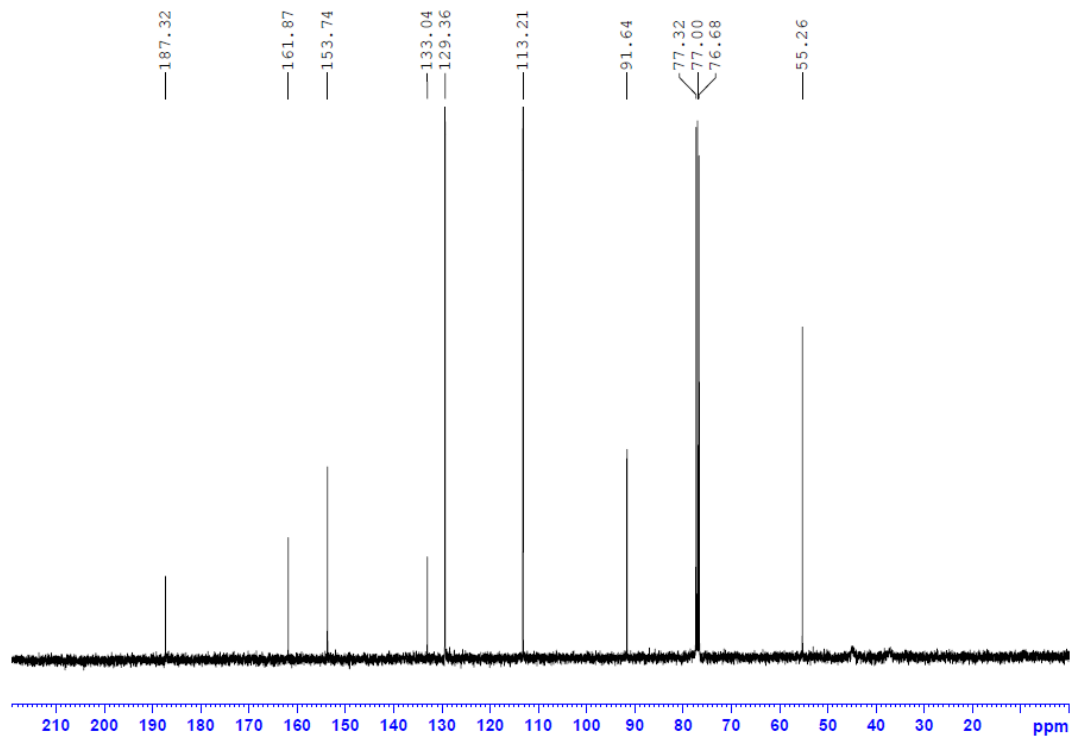
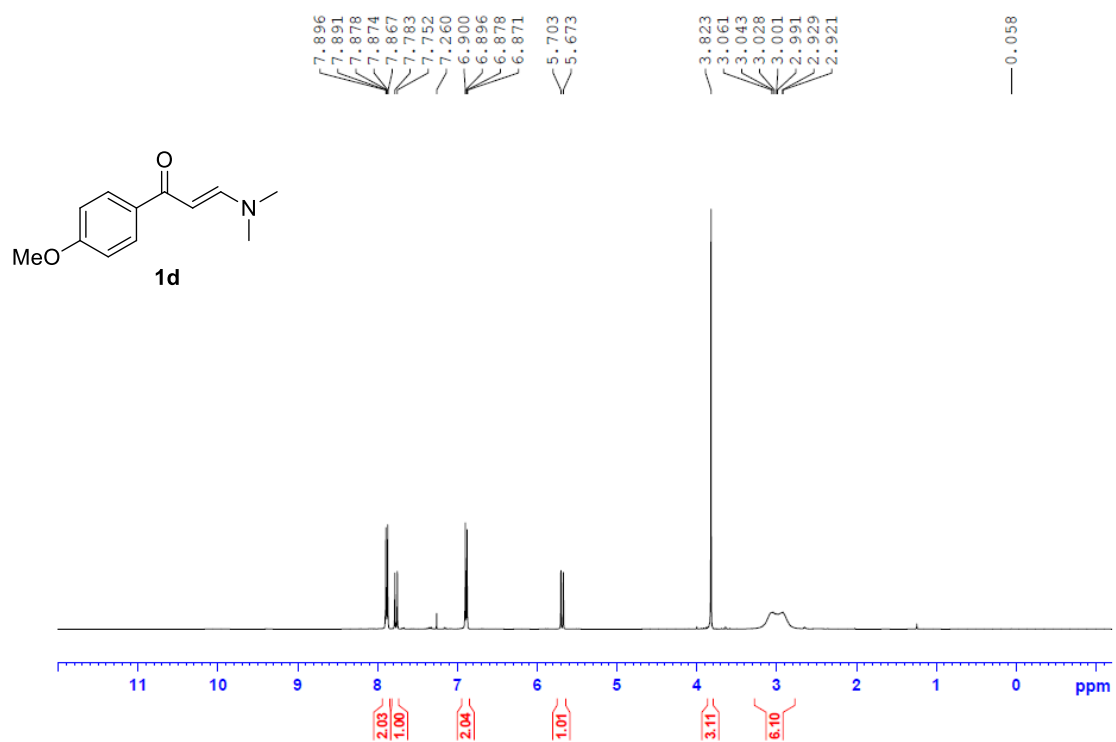
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 85 - 86 °C. Yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 9.64 (s, 1H), 7.87 - 7.85 (m, 2H), 7.57 - 7.53 (m, 1H), 7.32 - 7.29 (m, 4H), 7.25 - 7.23 (m, 1H), 6.02 (s, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 192.5, 135.9, 134.8, 133.8, 129.0, 128.7, 128.5, 128.2, 127.5, 55.4, 48.6, 18.0; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}$: 331.0334, Found: 331.0330.

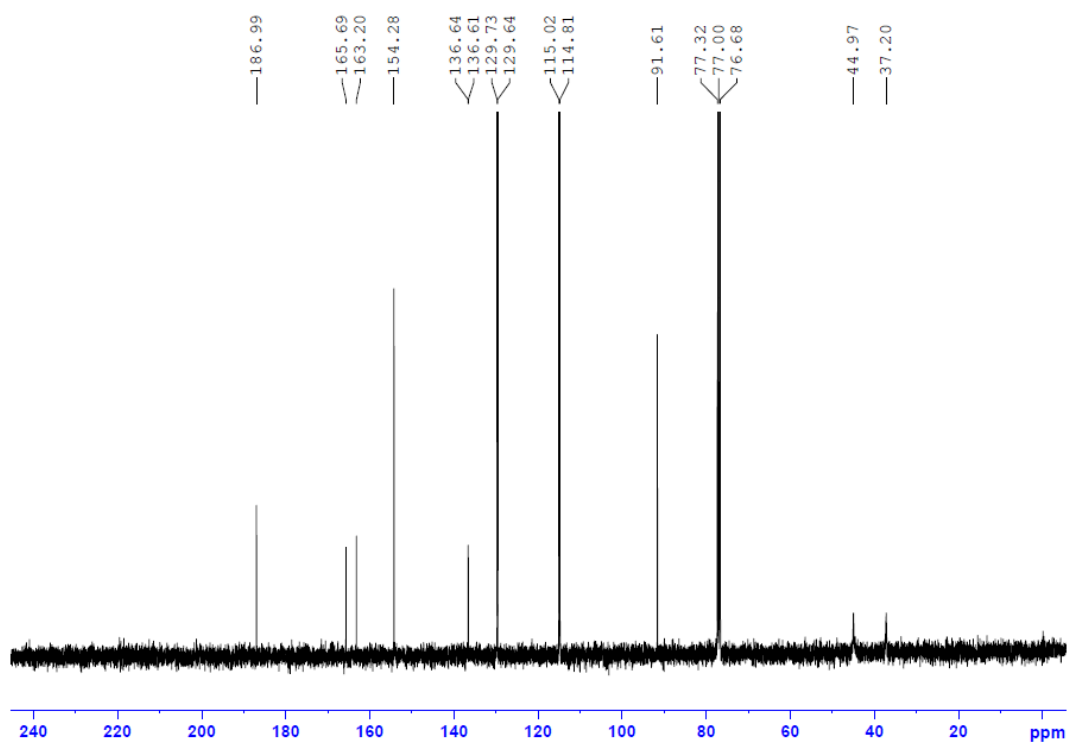
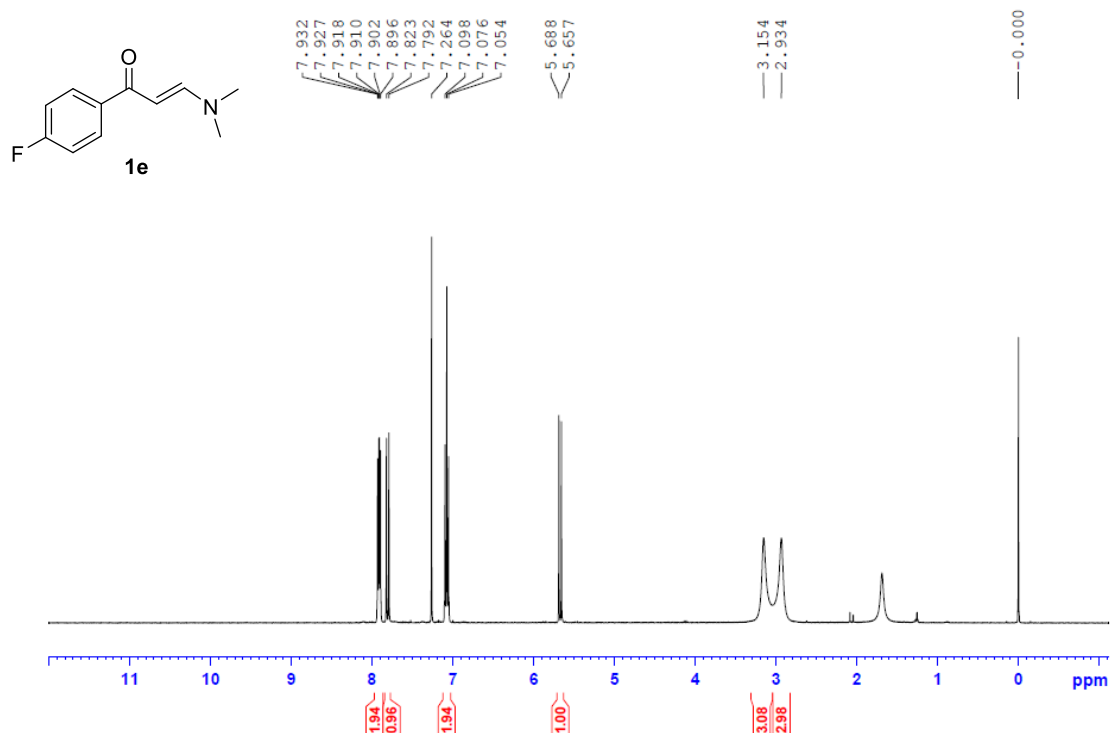
NMR Spectra for enaminones:

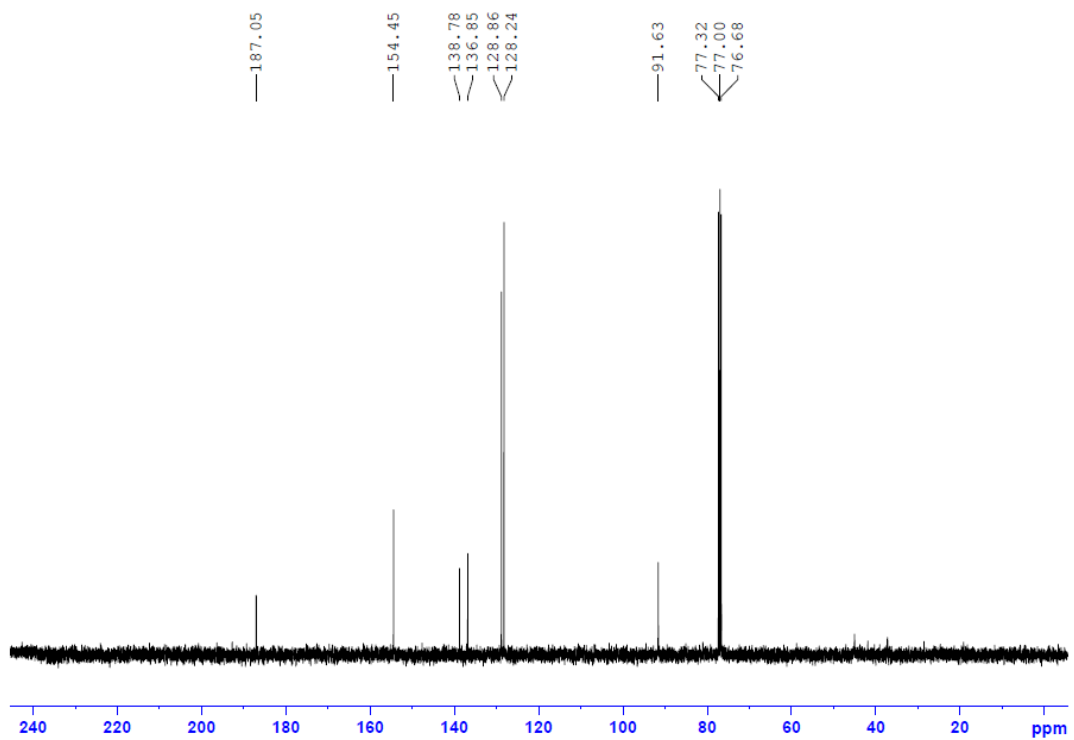
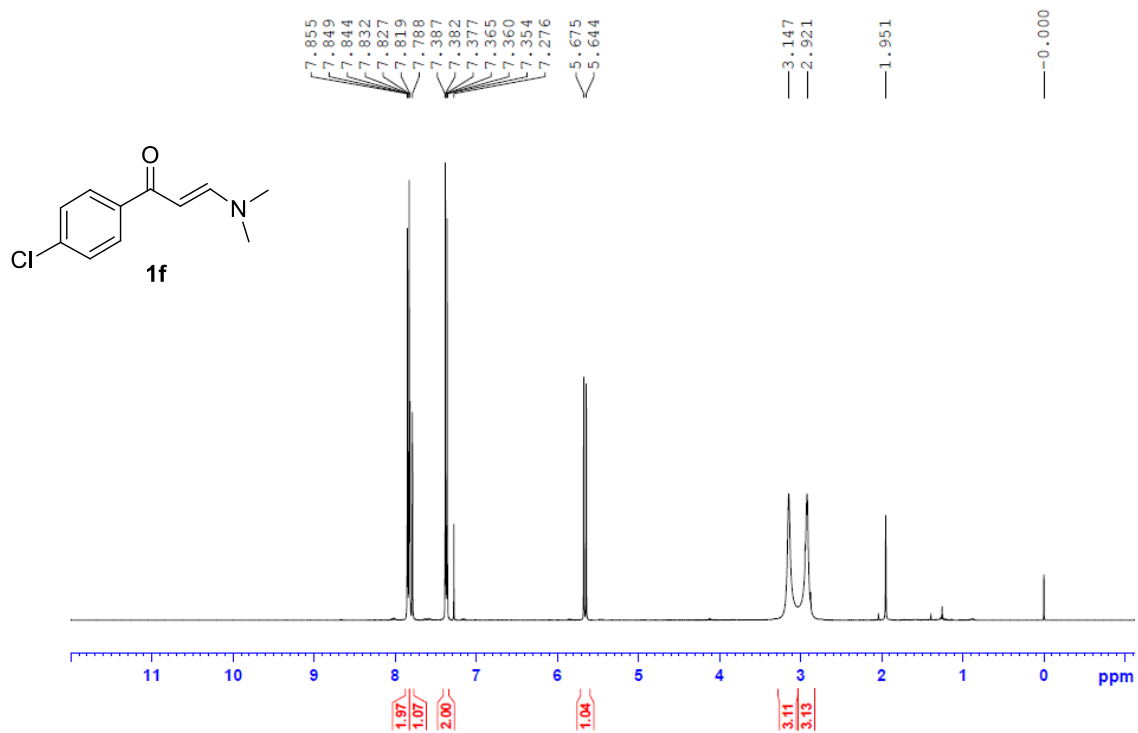


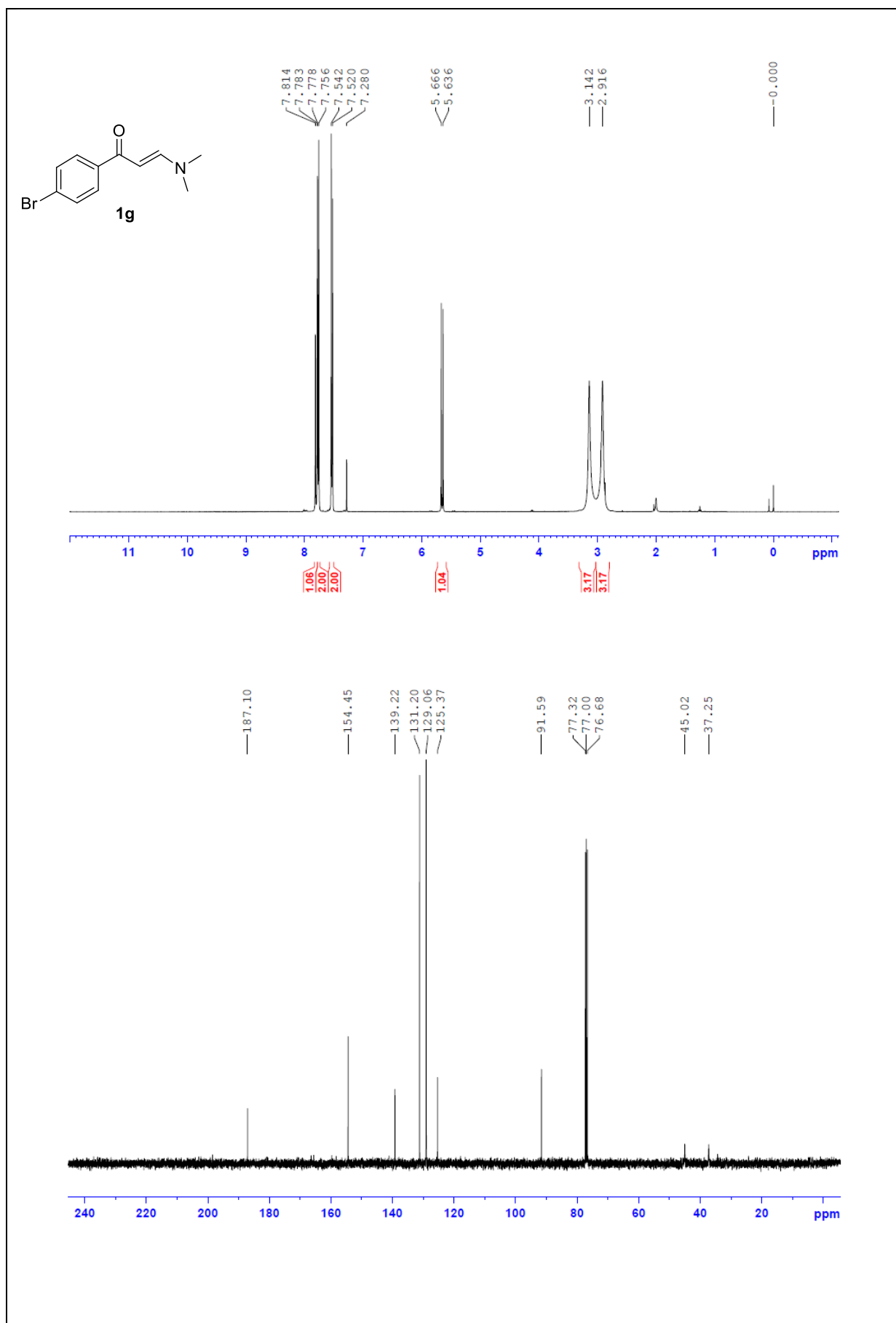


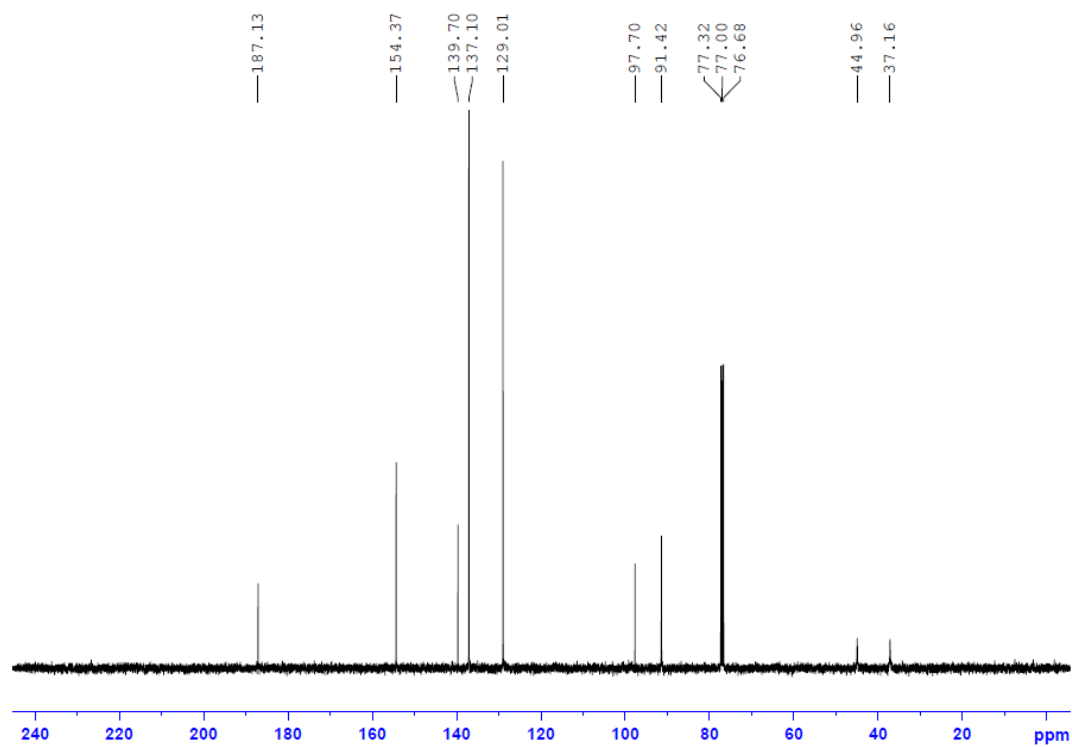
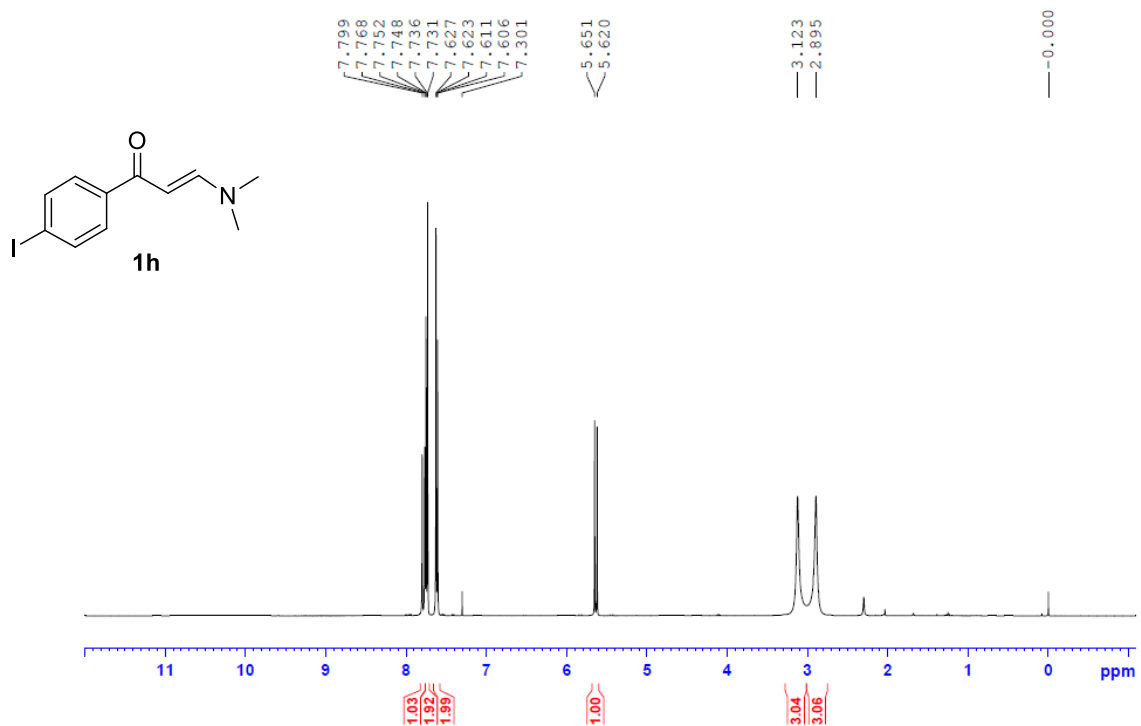


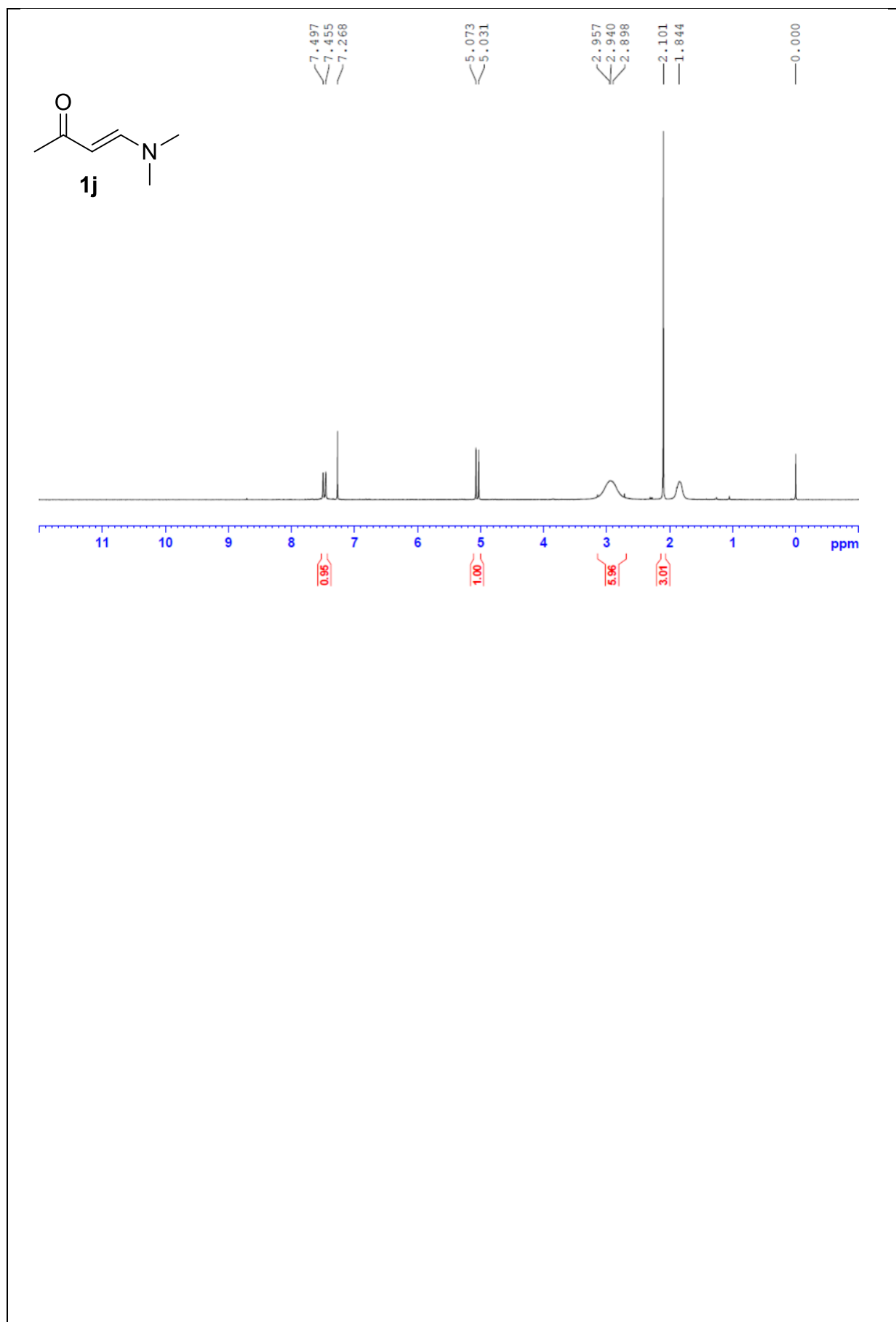


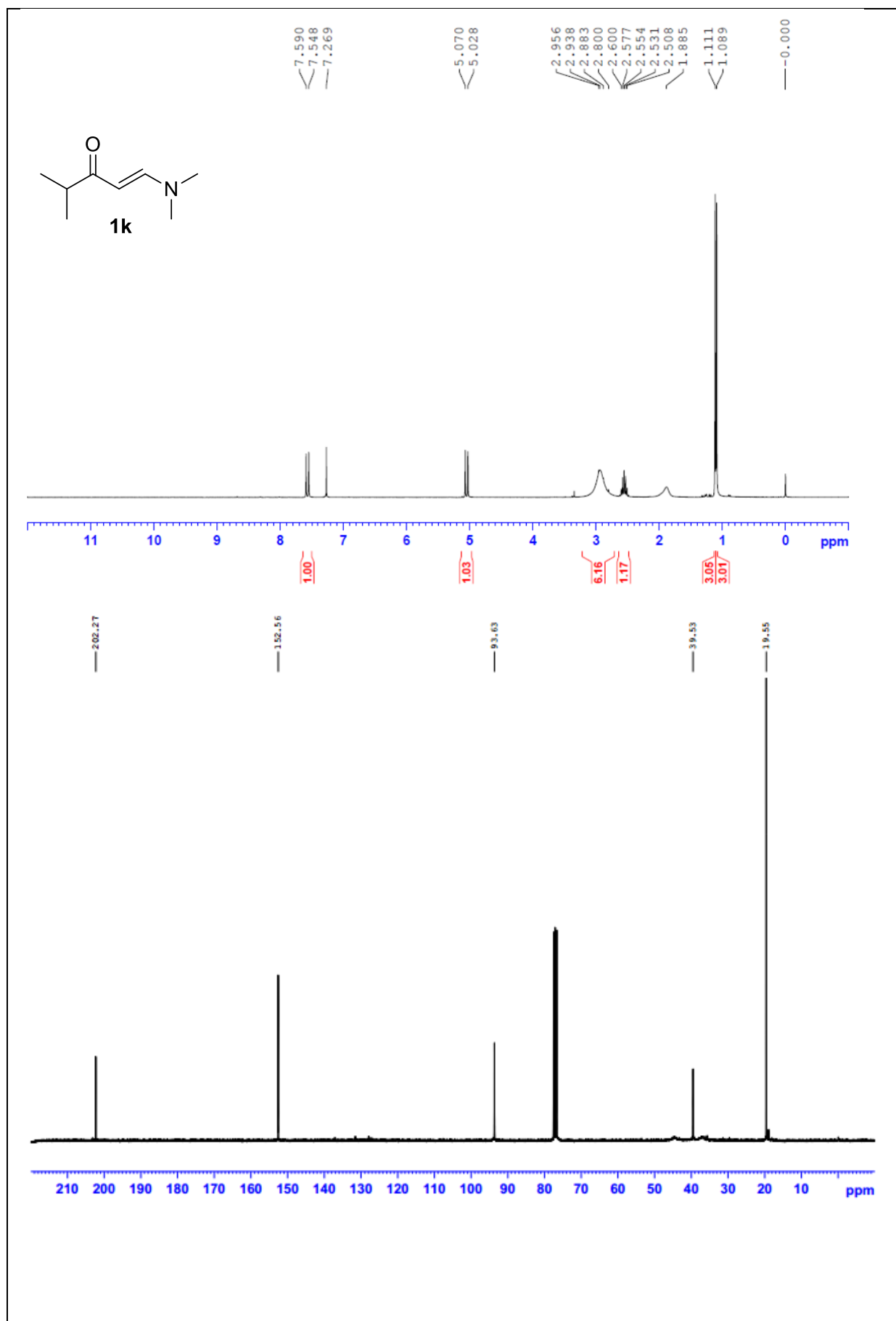


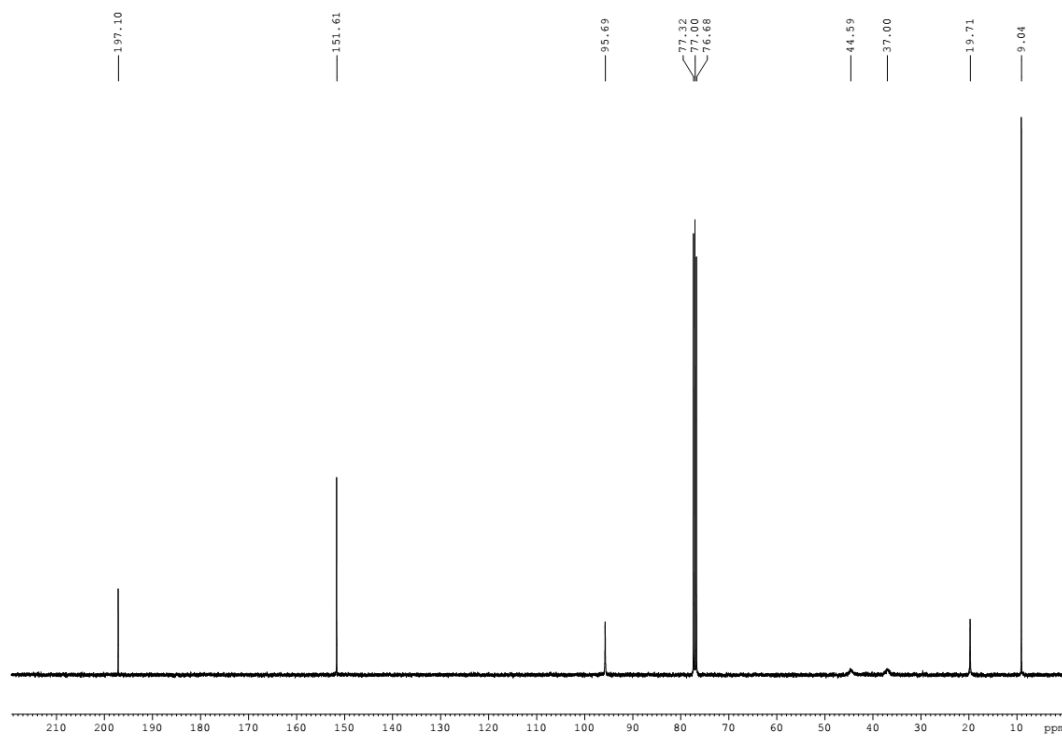
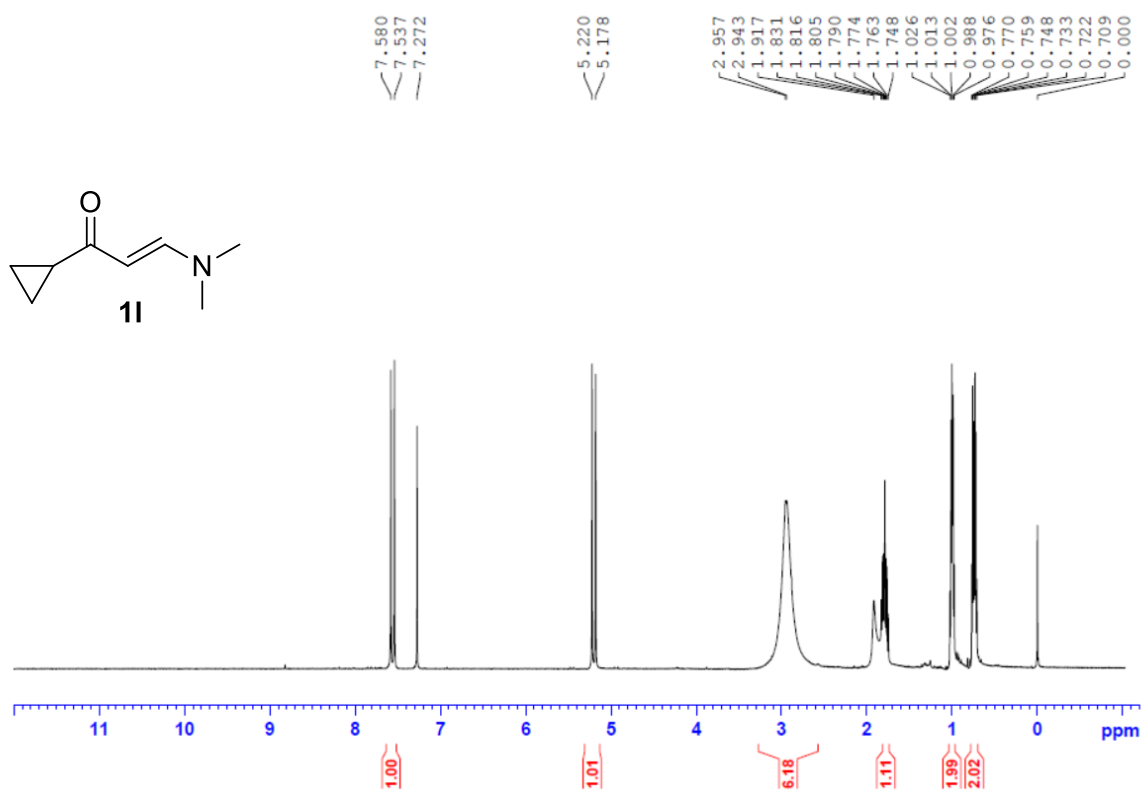


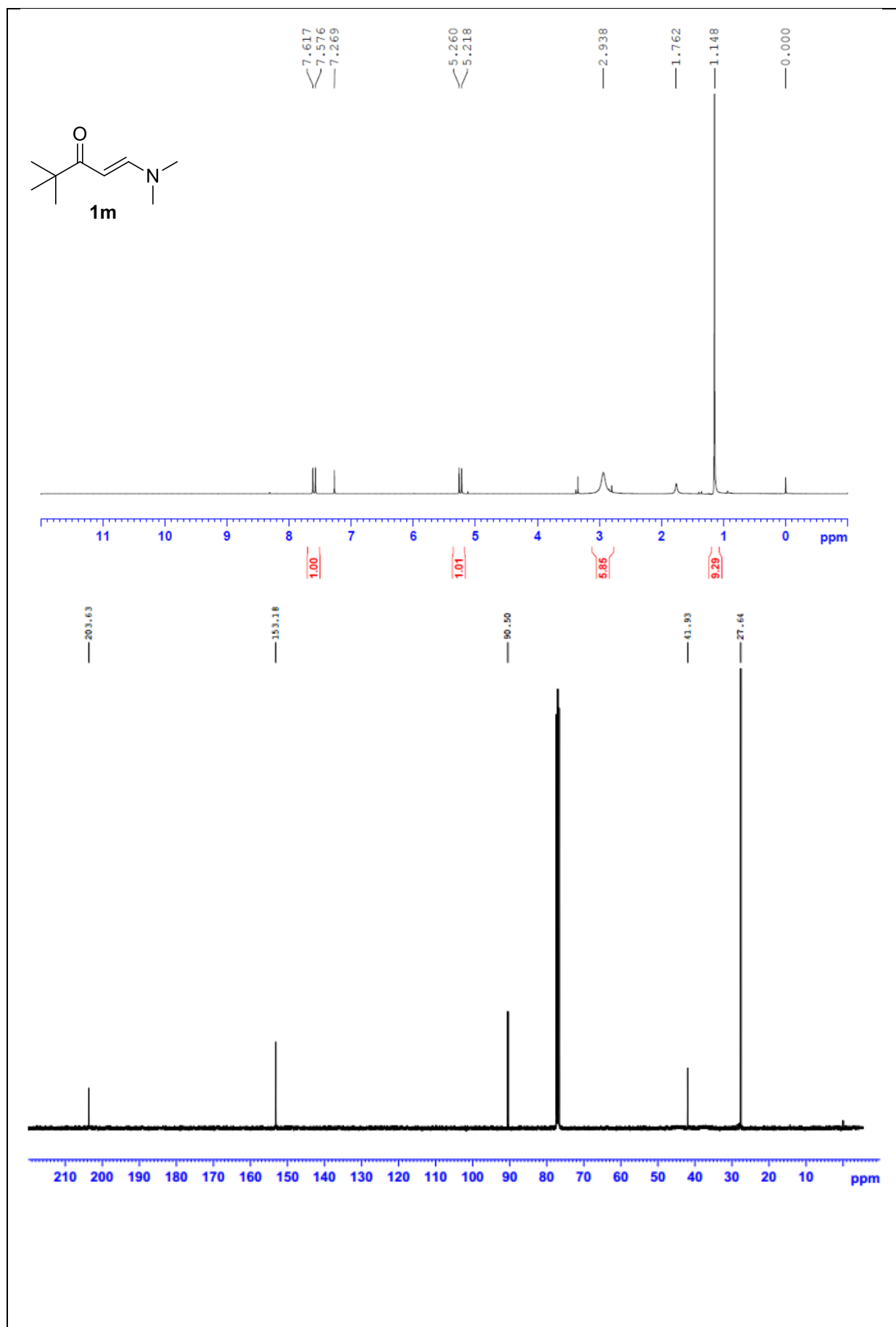


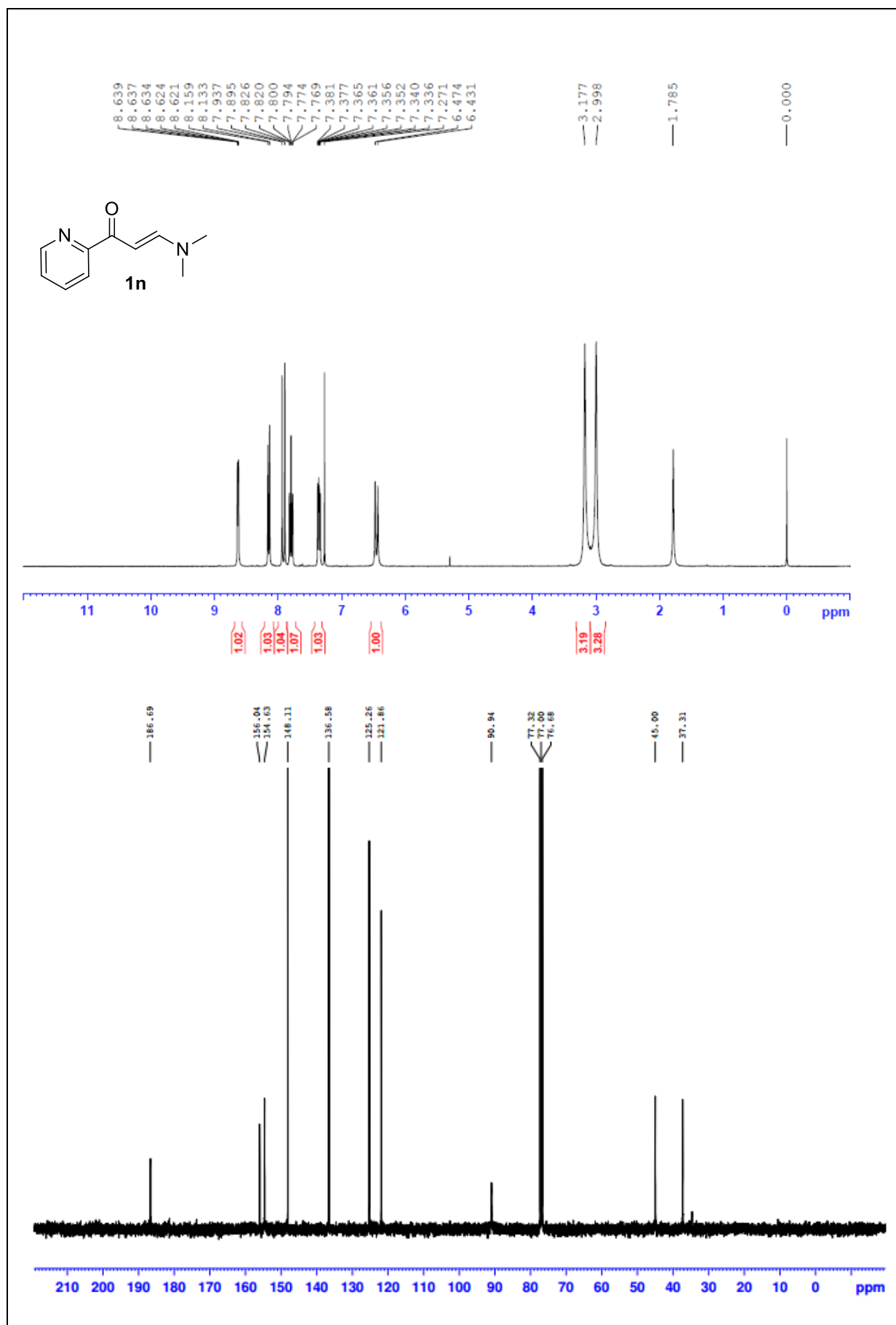


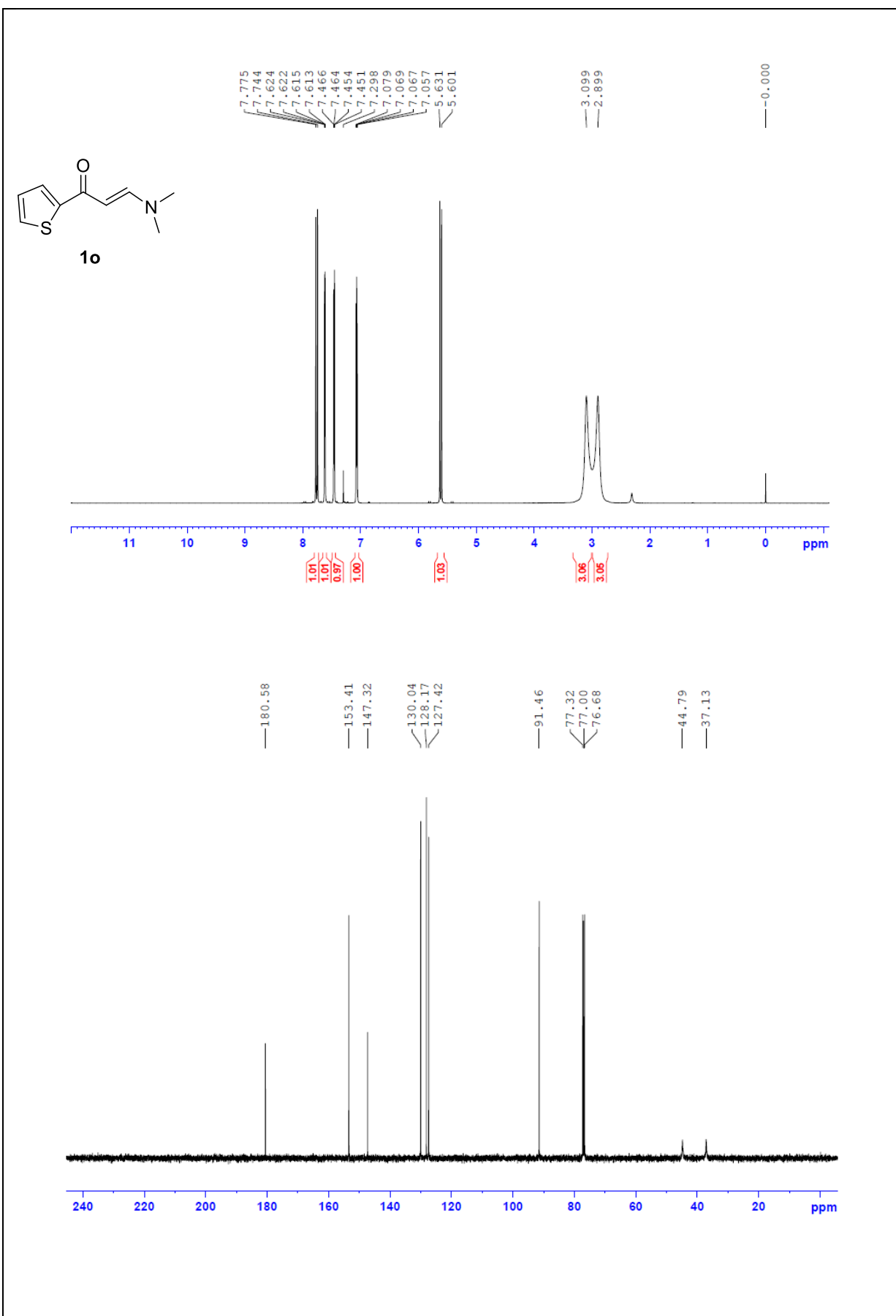


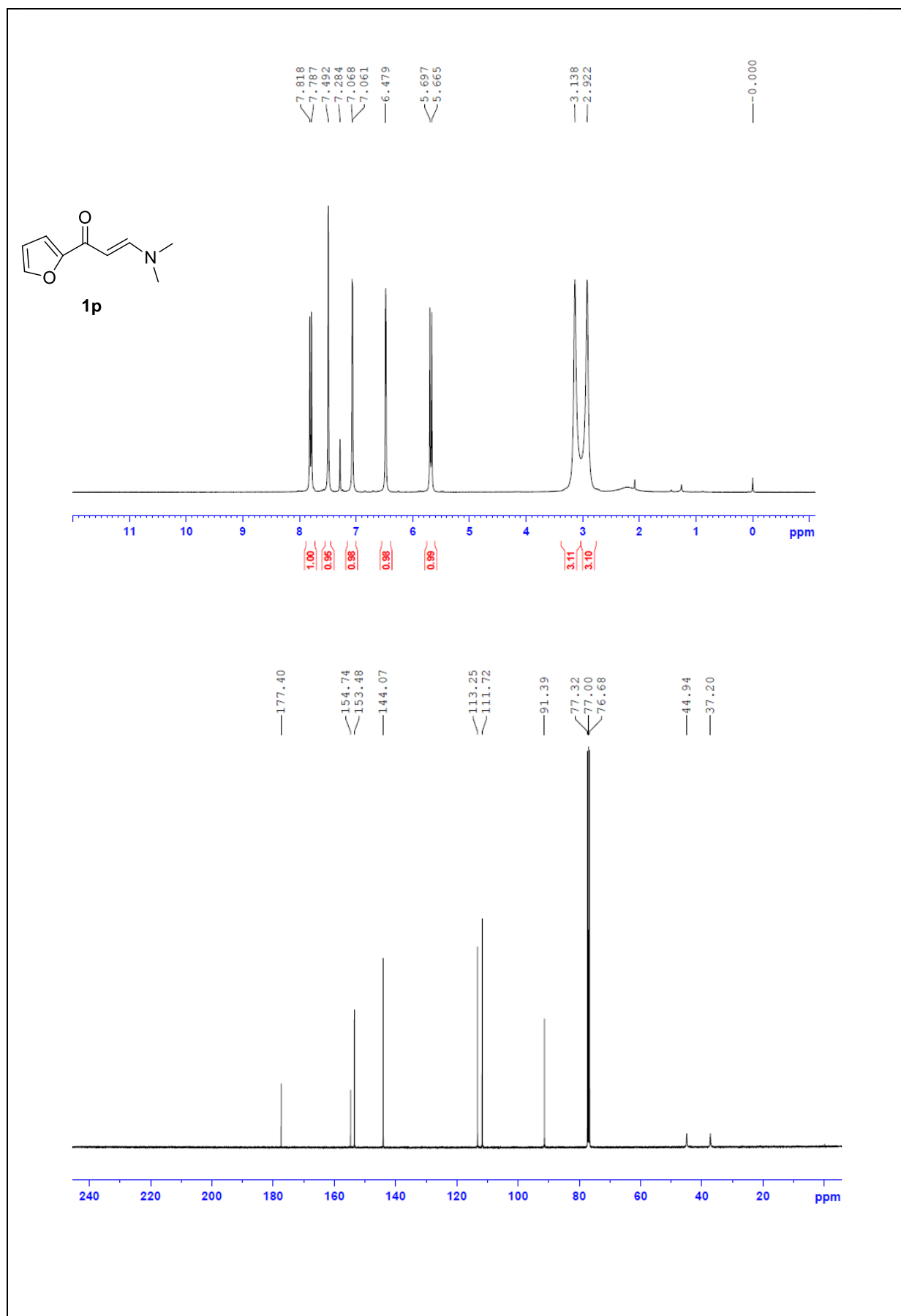


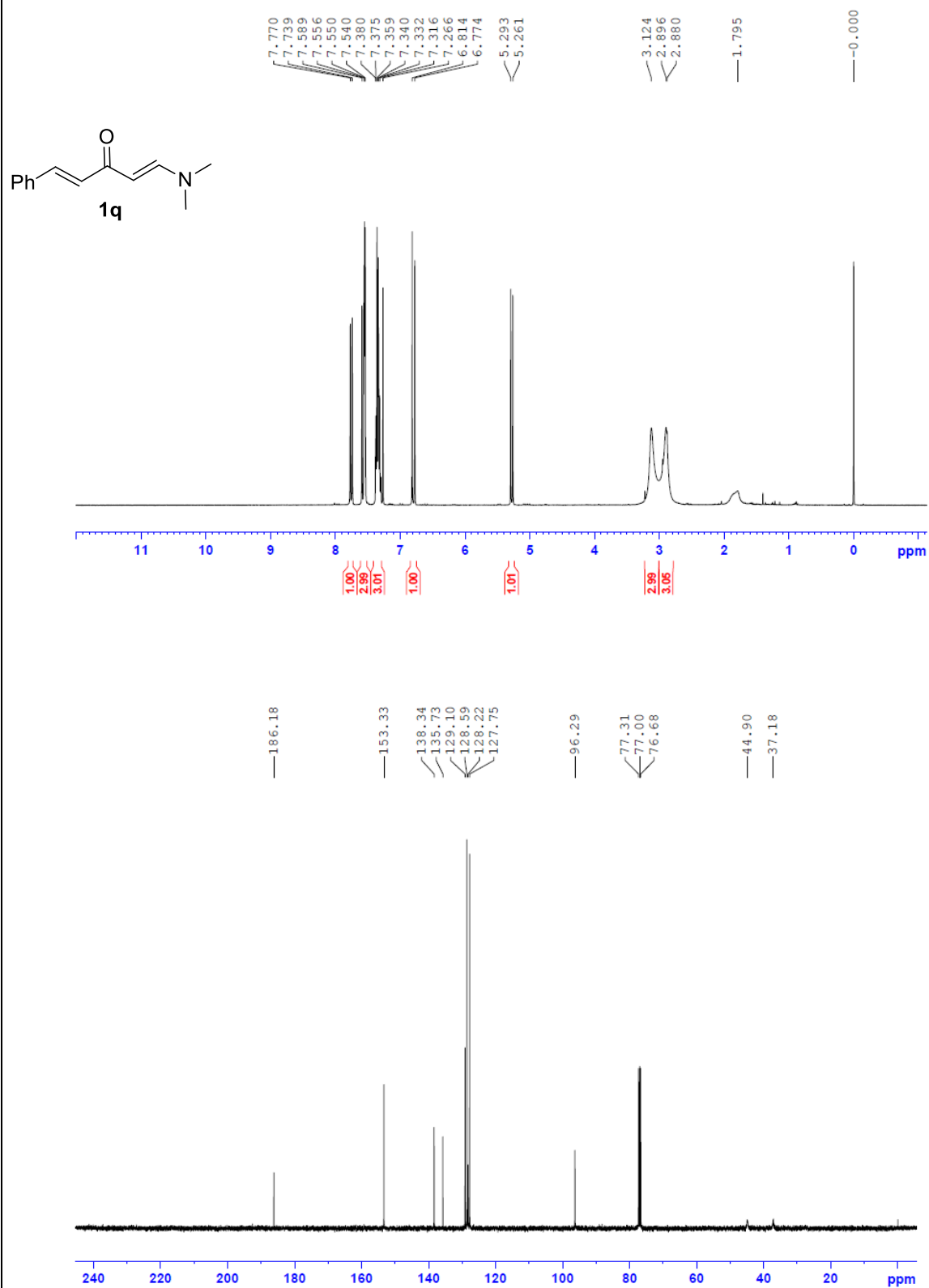


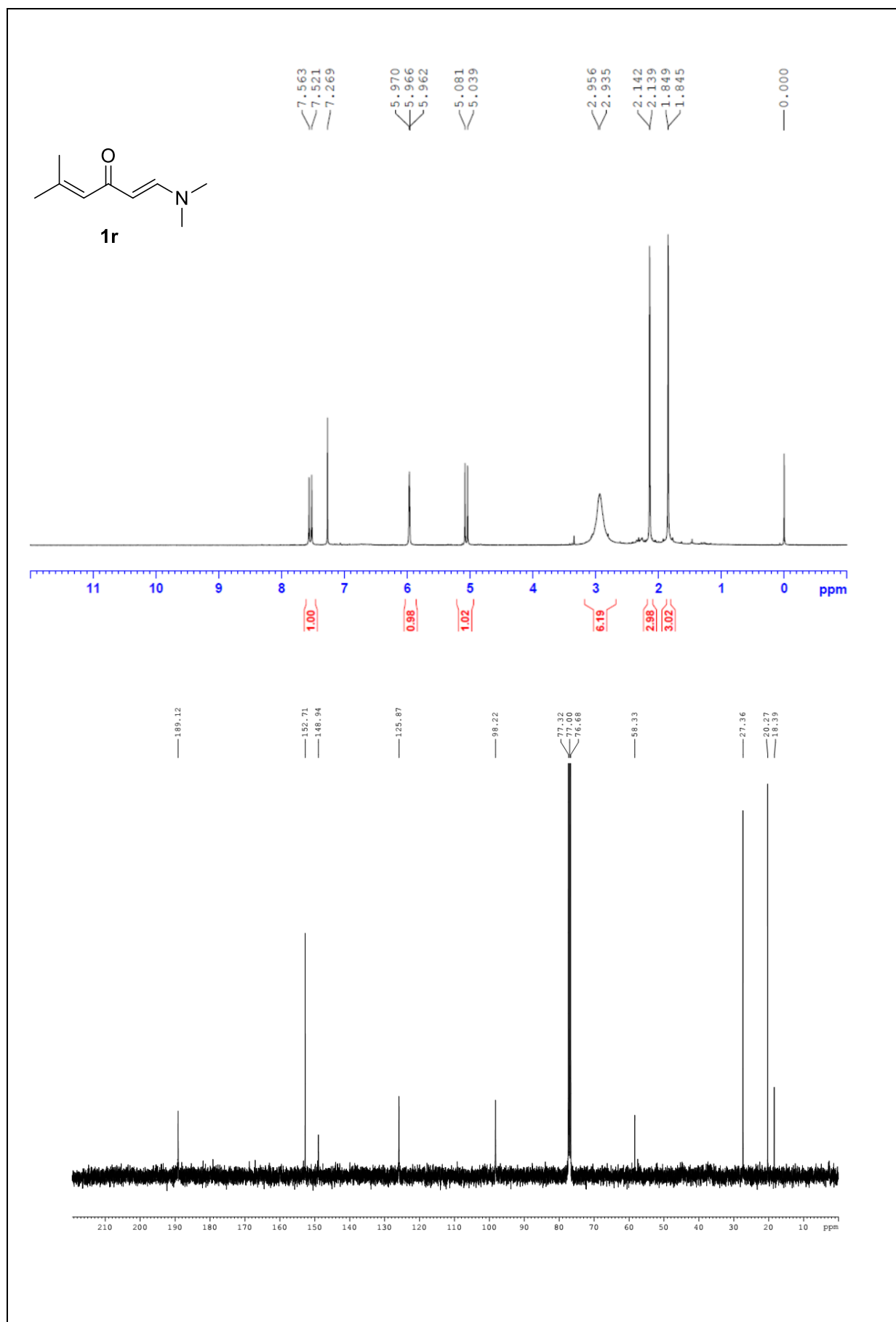


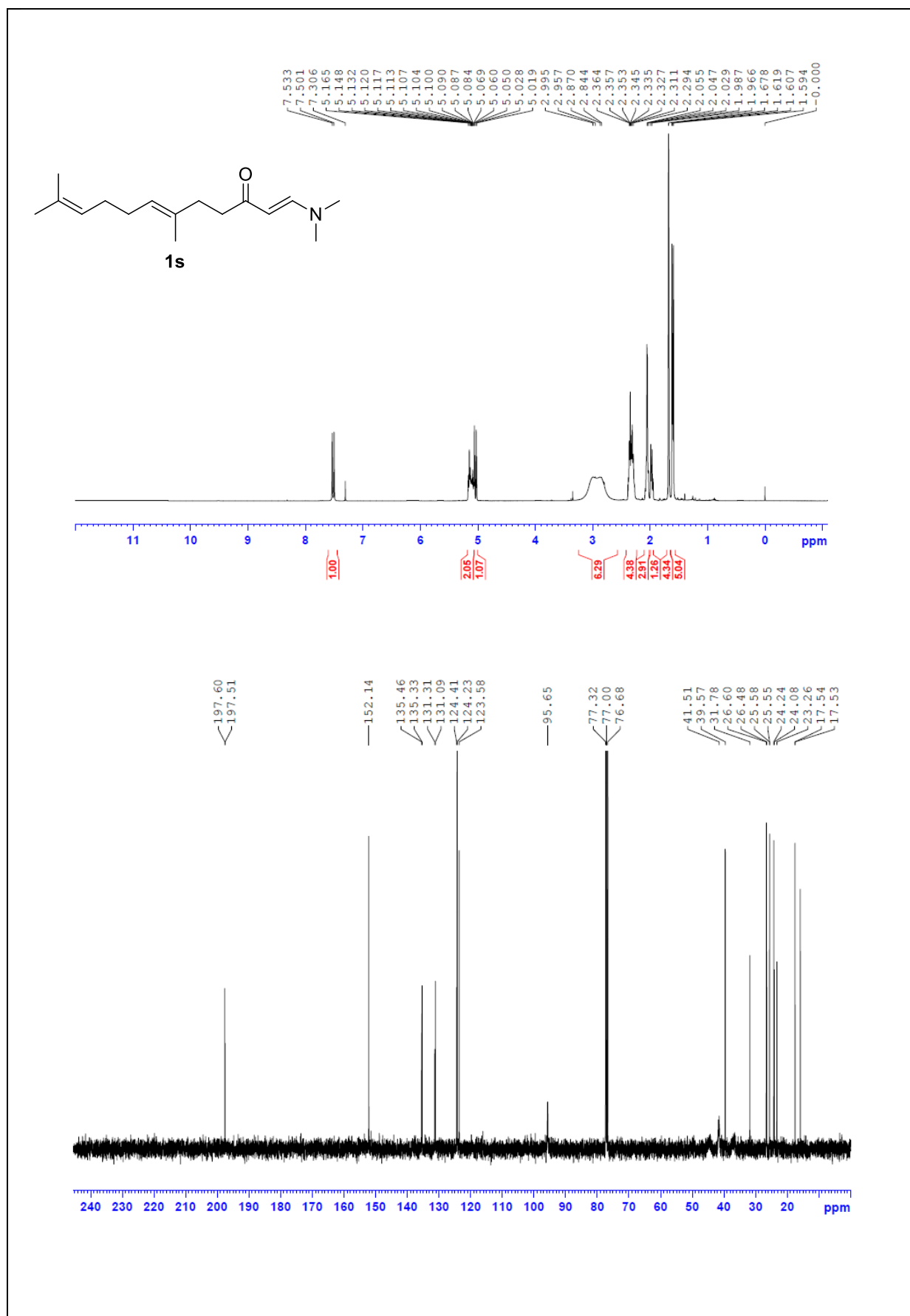




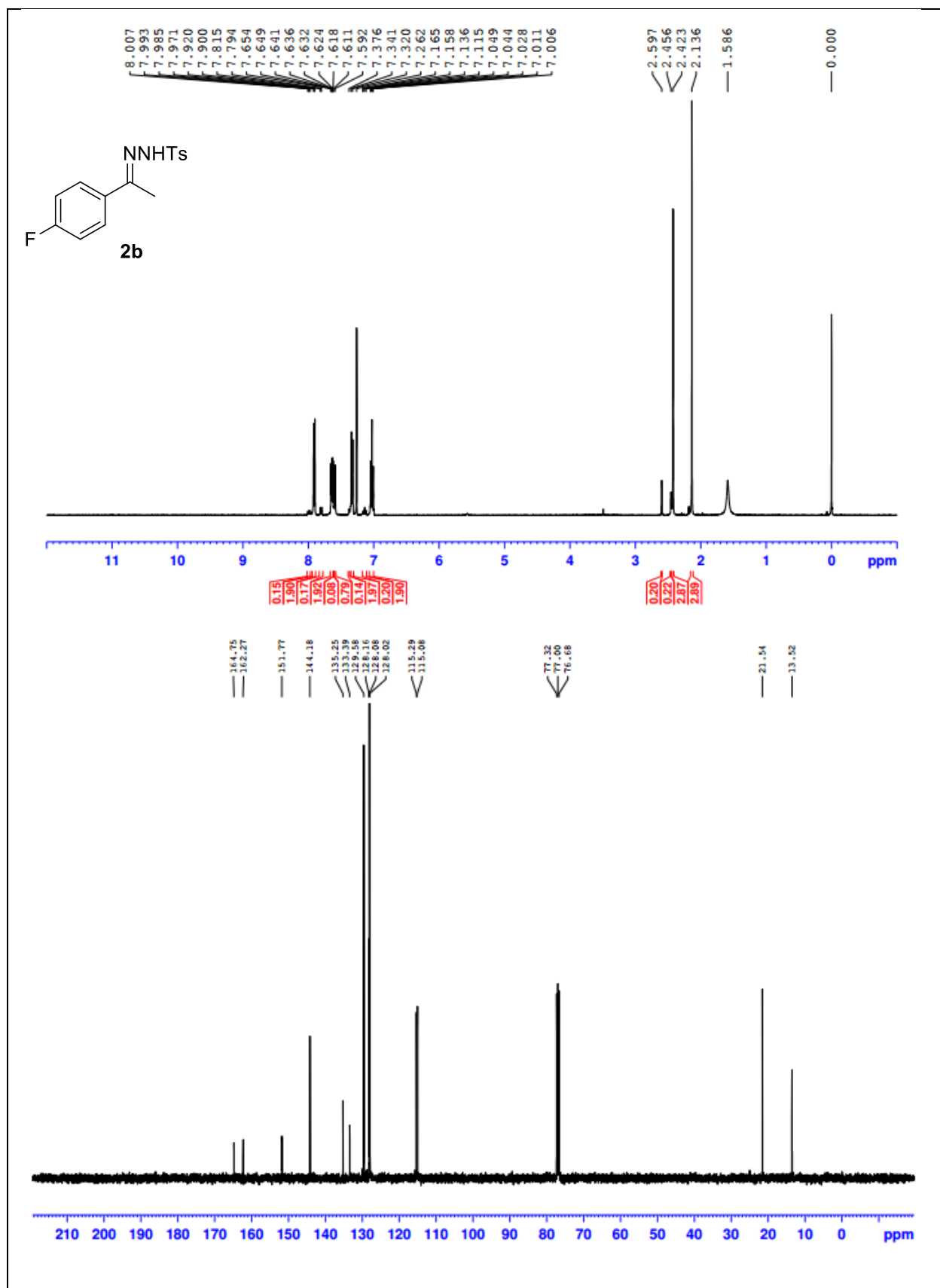


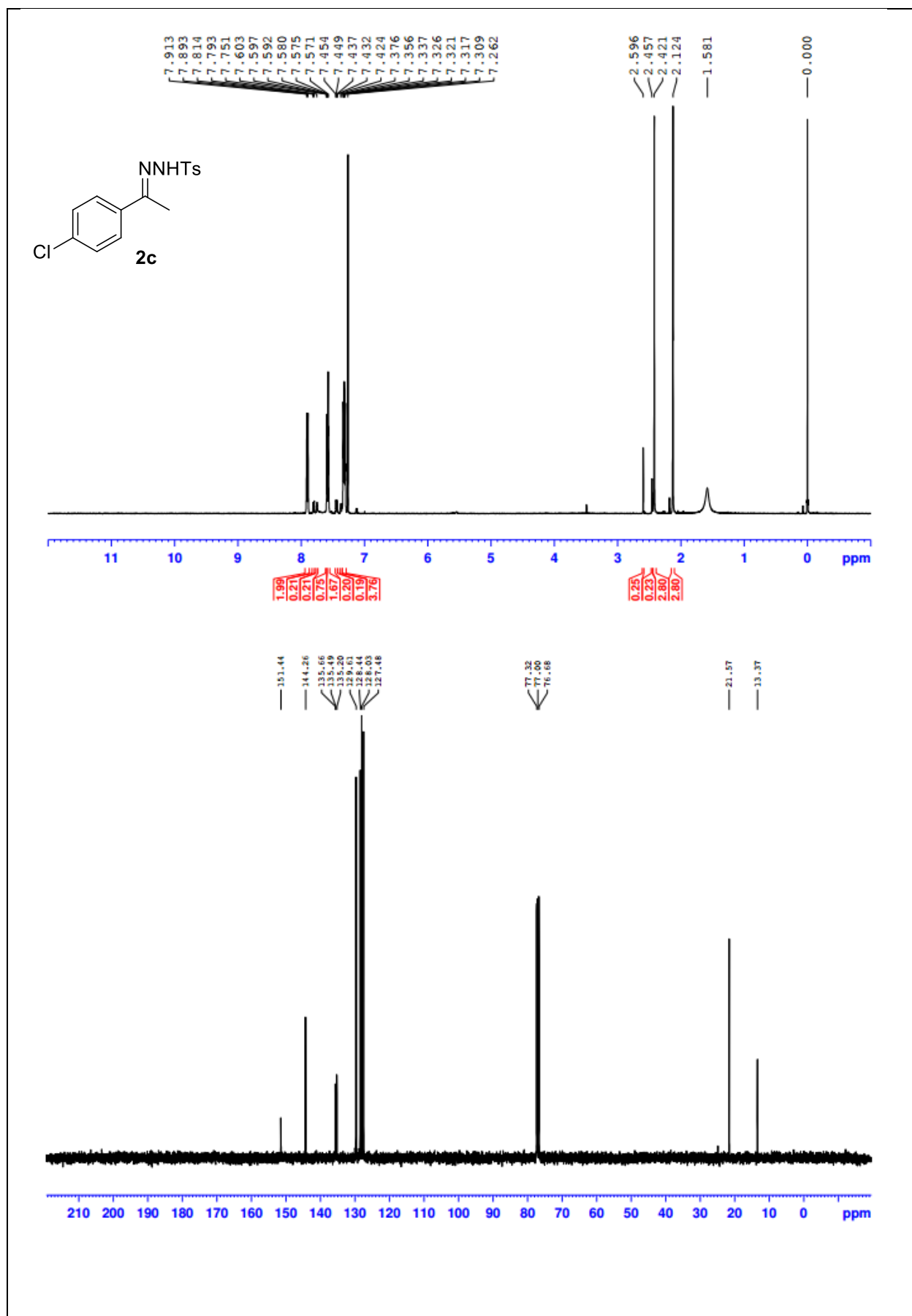


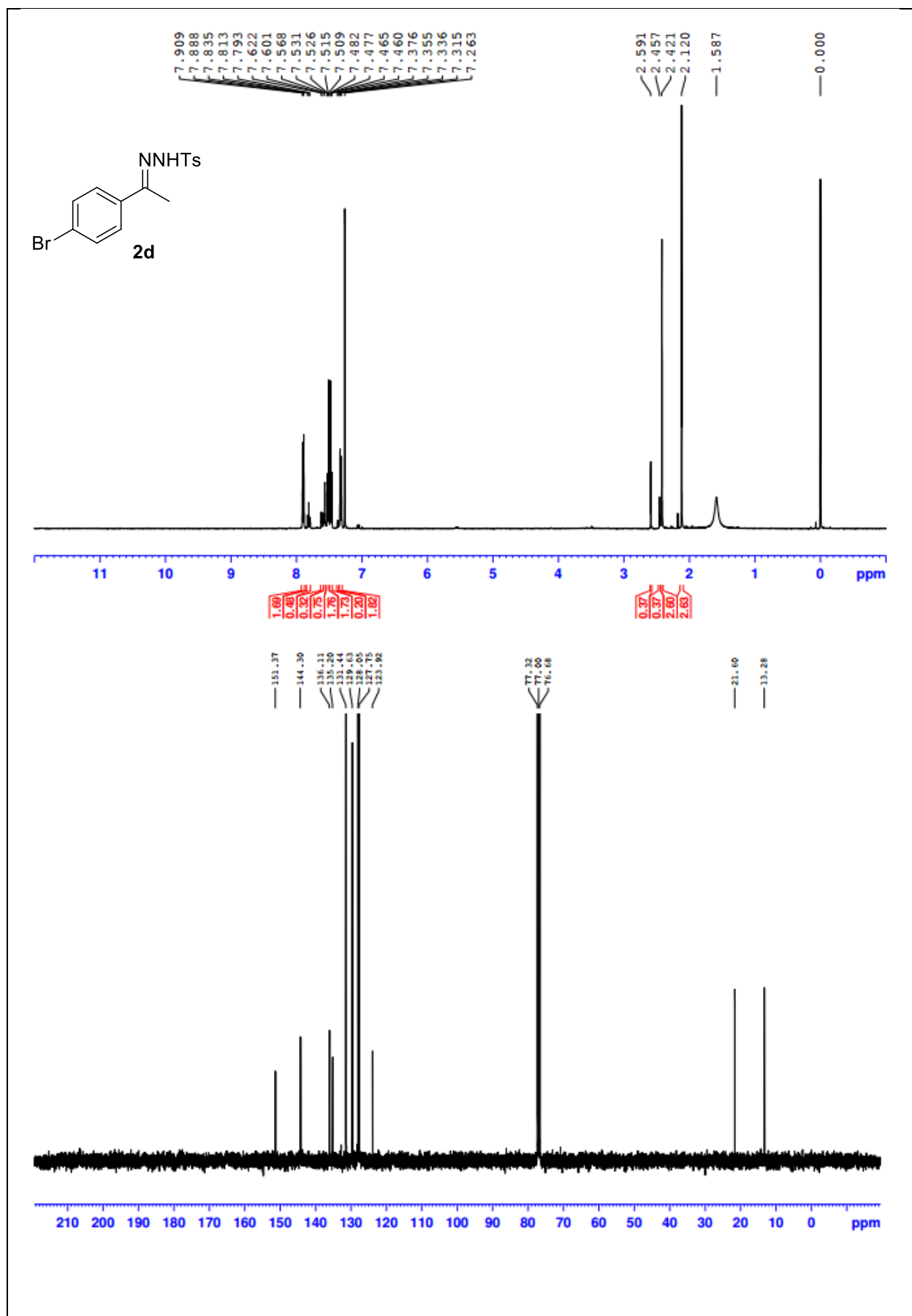


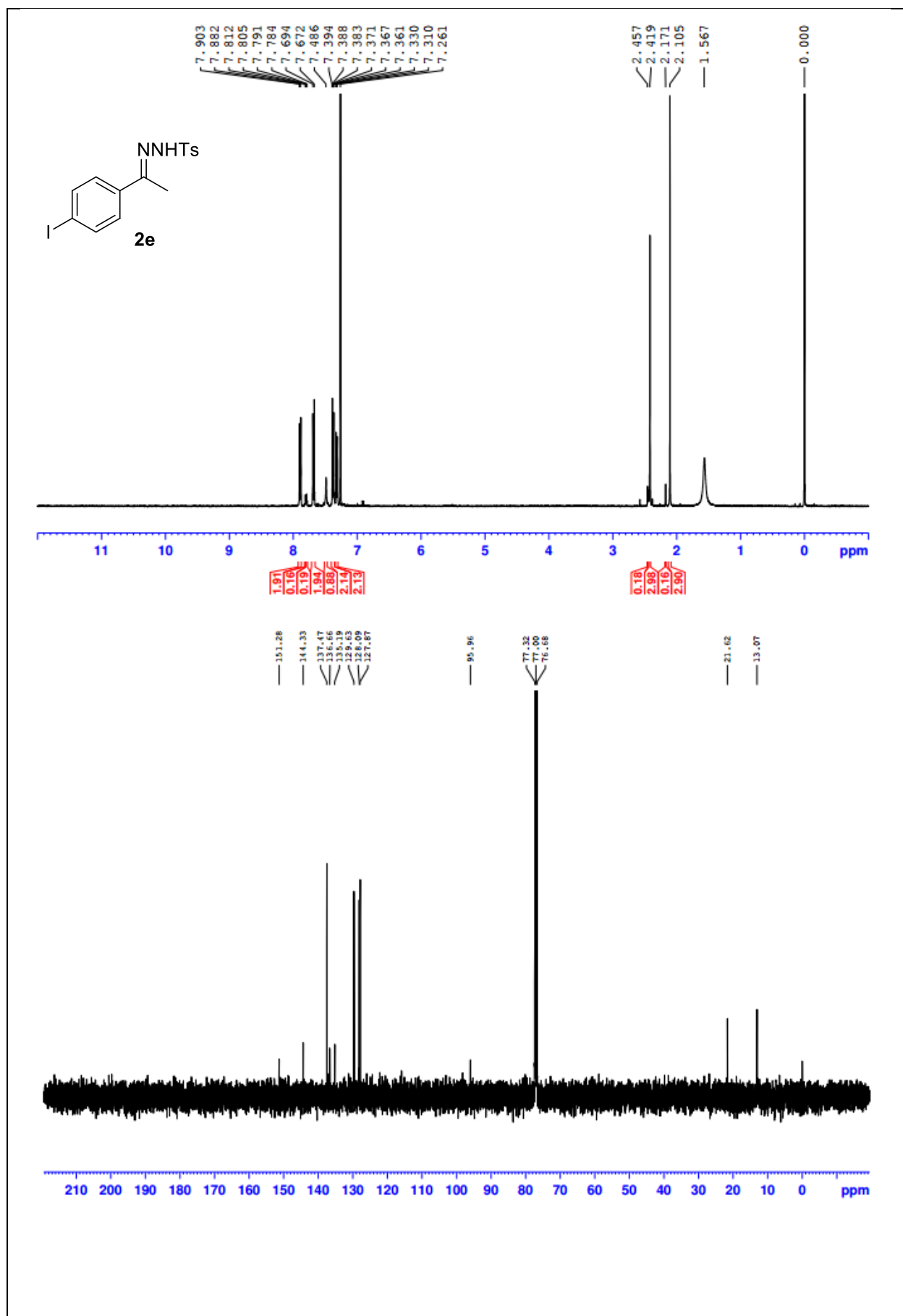


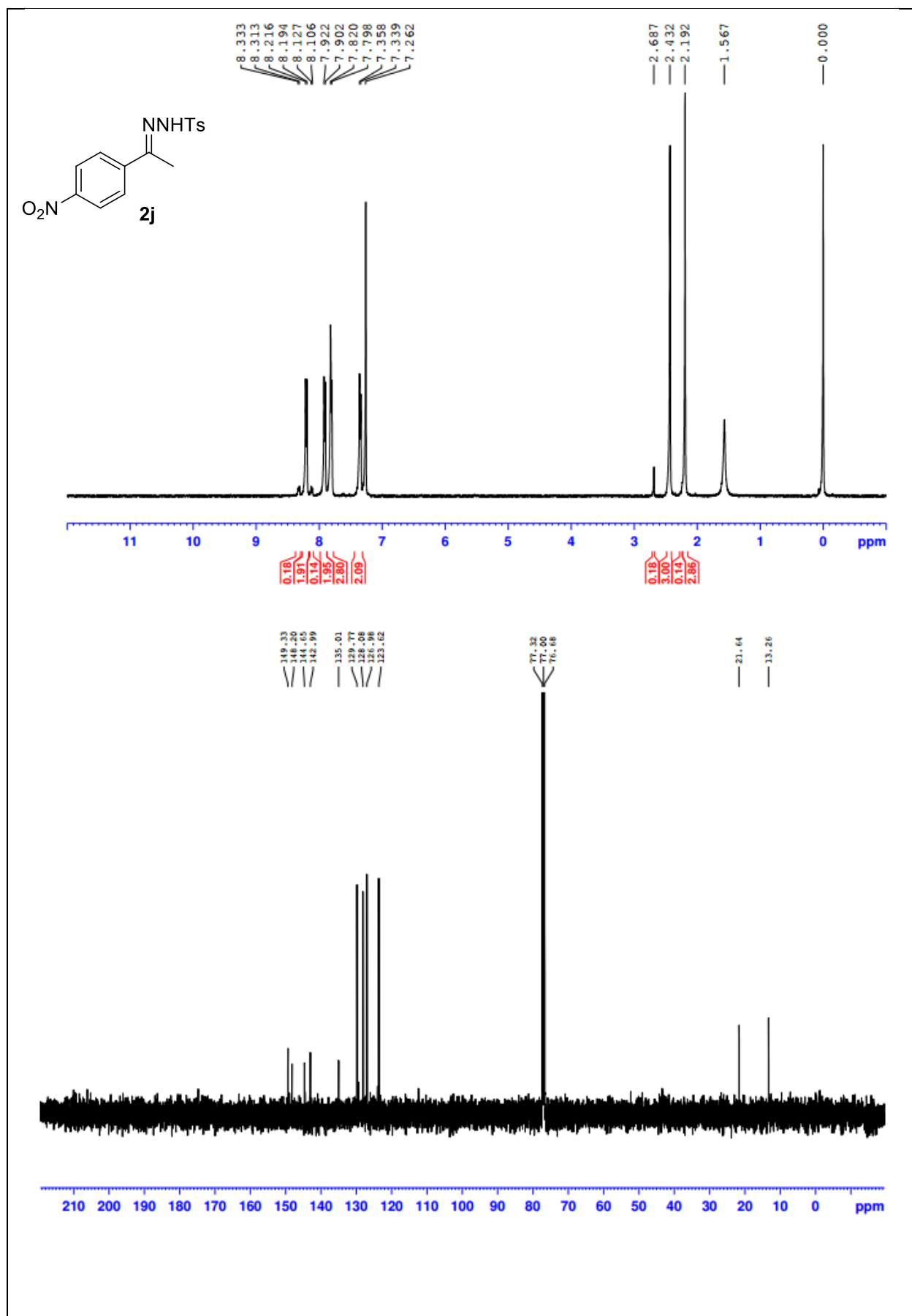
NMR Spectra for hydrazones:

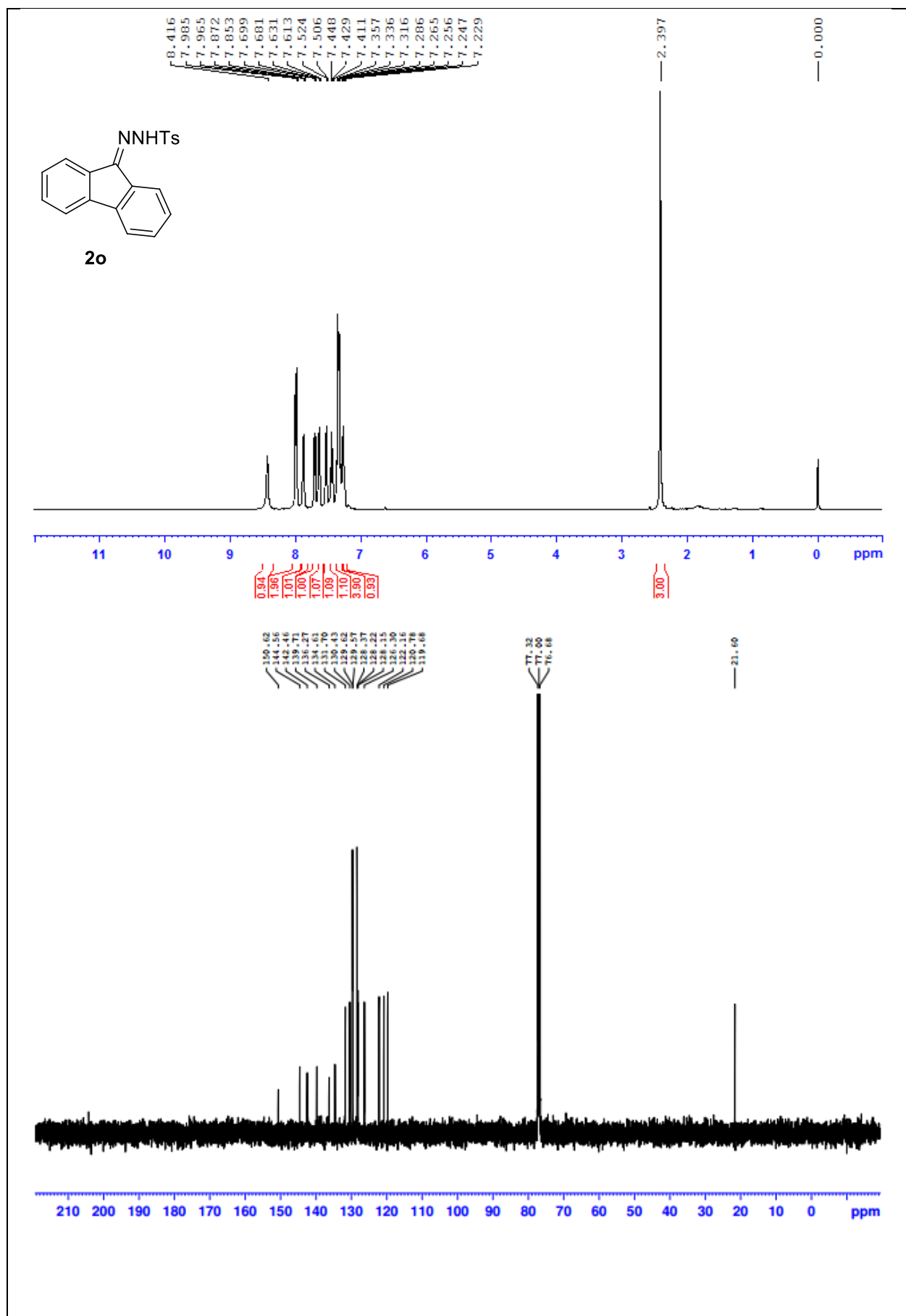


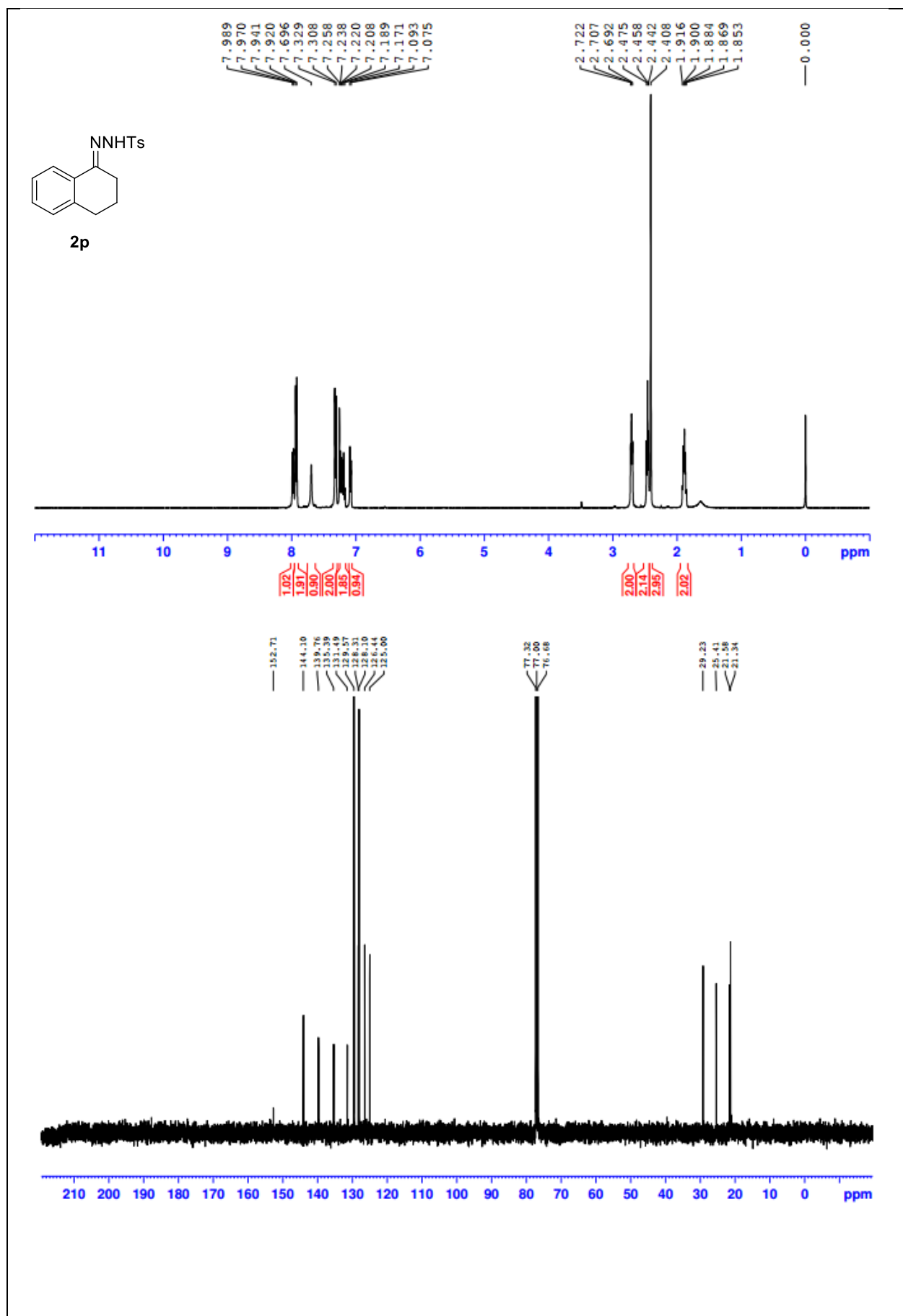


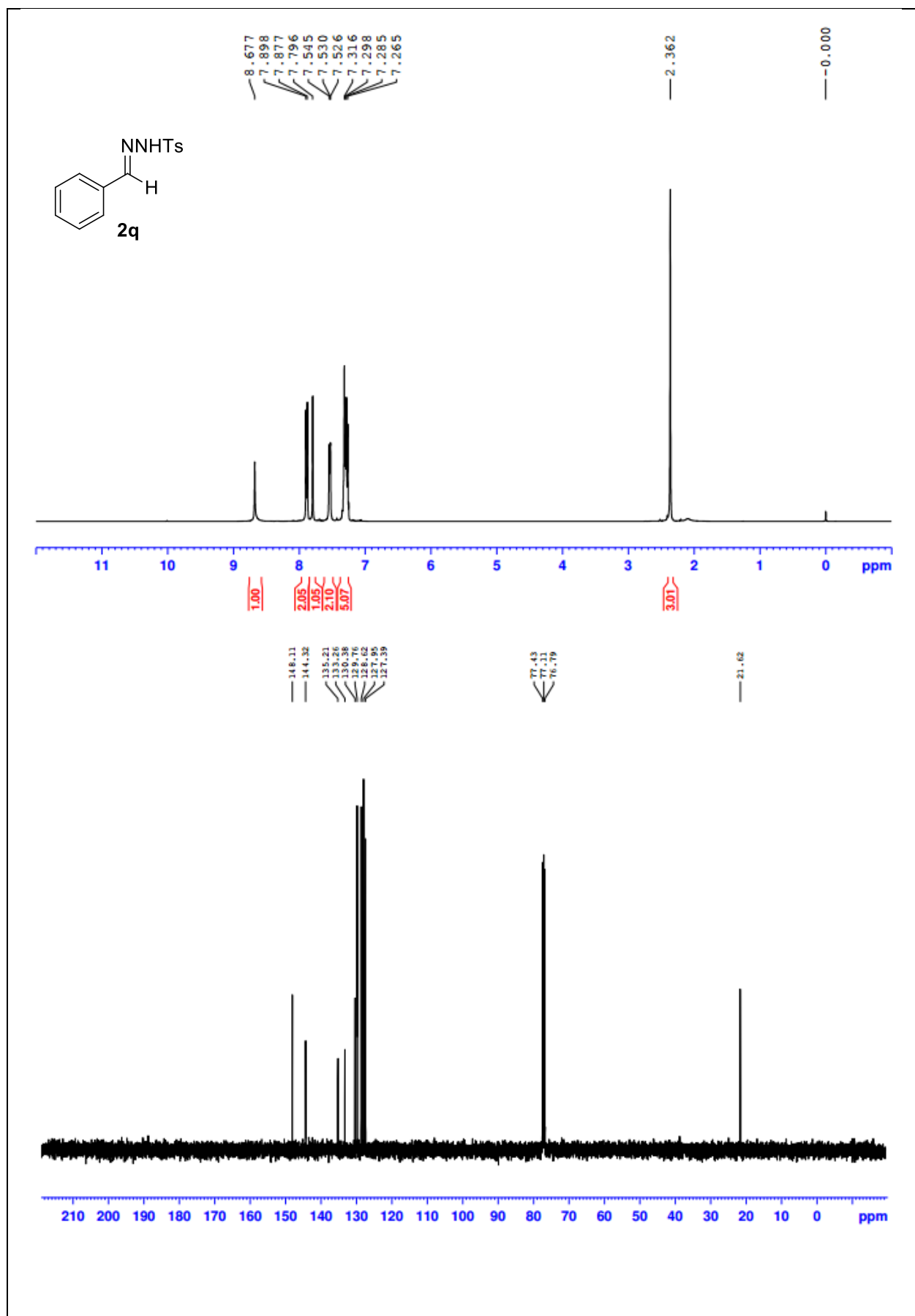


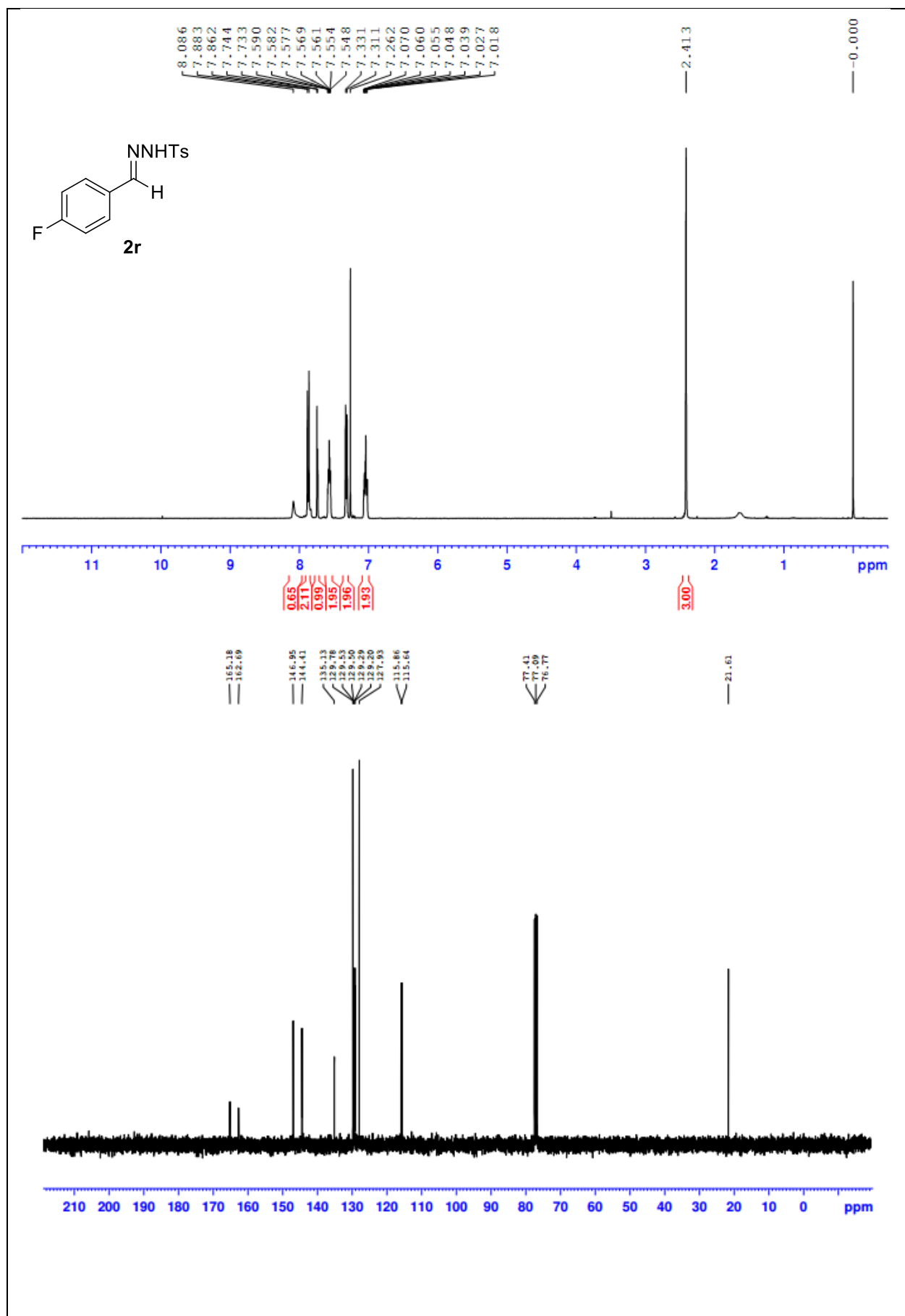


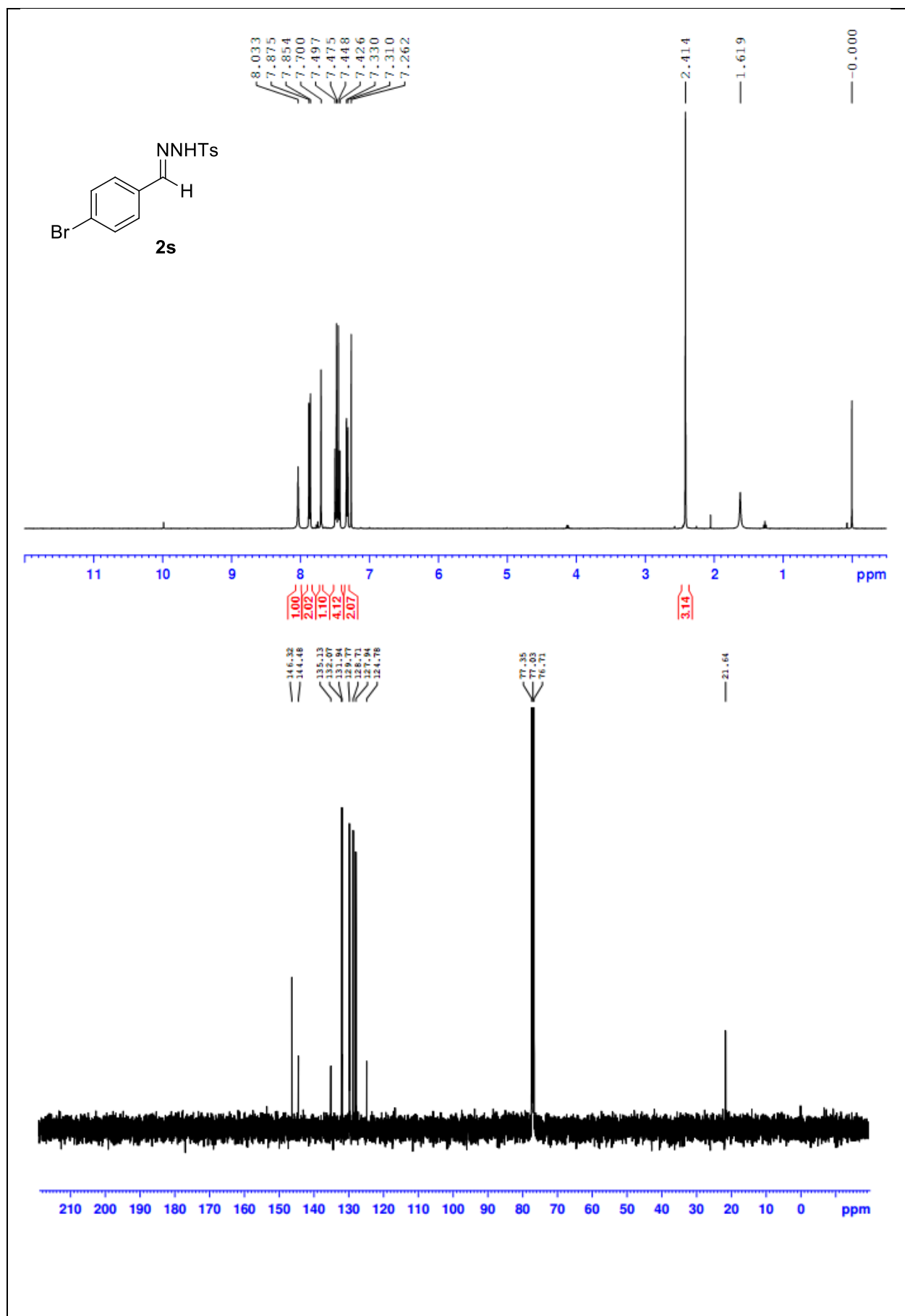


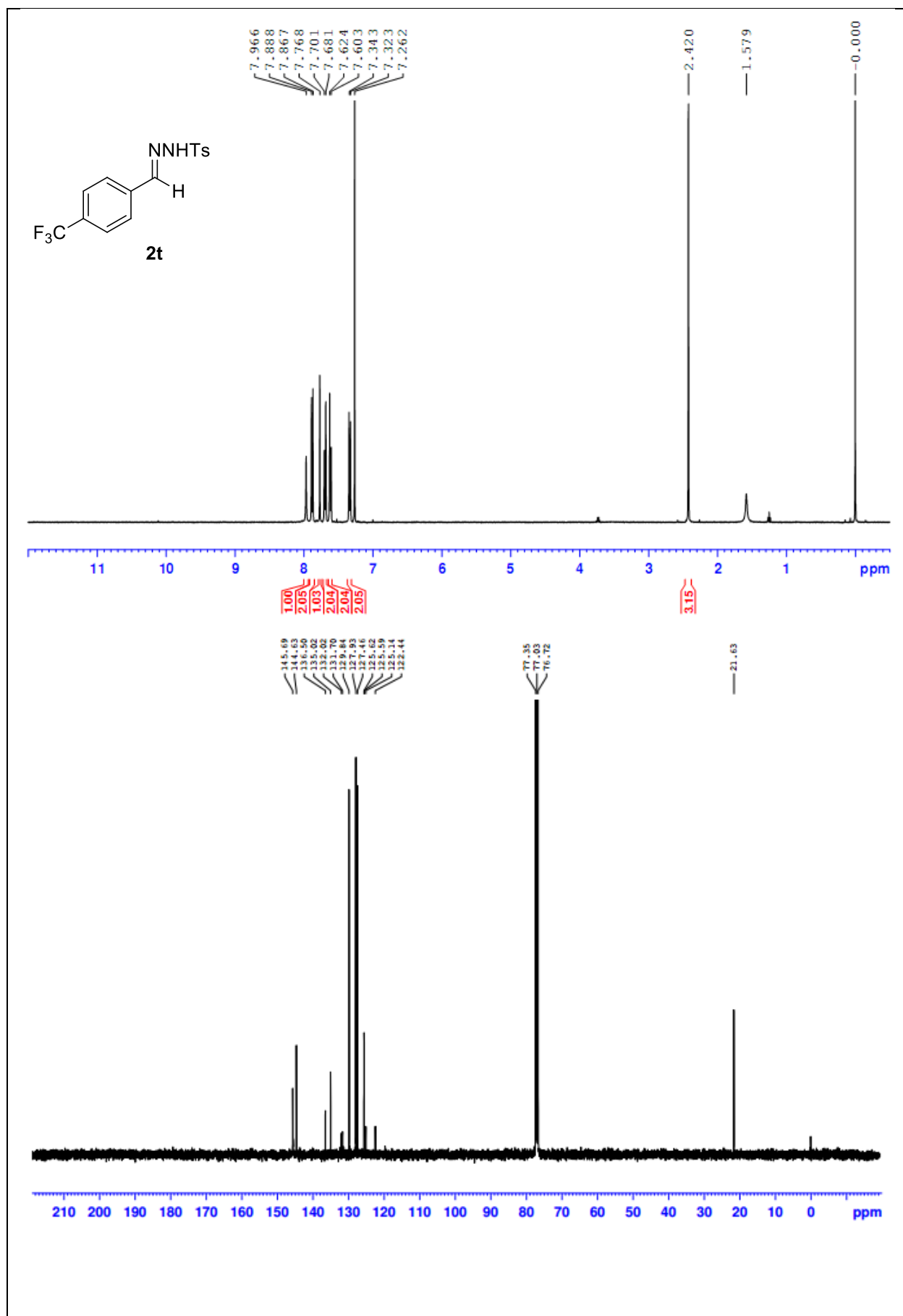


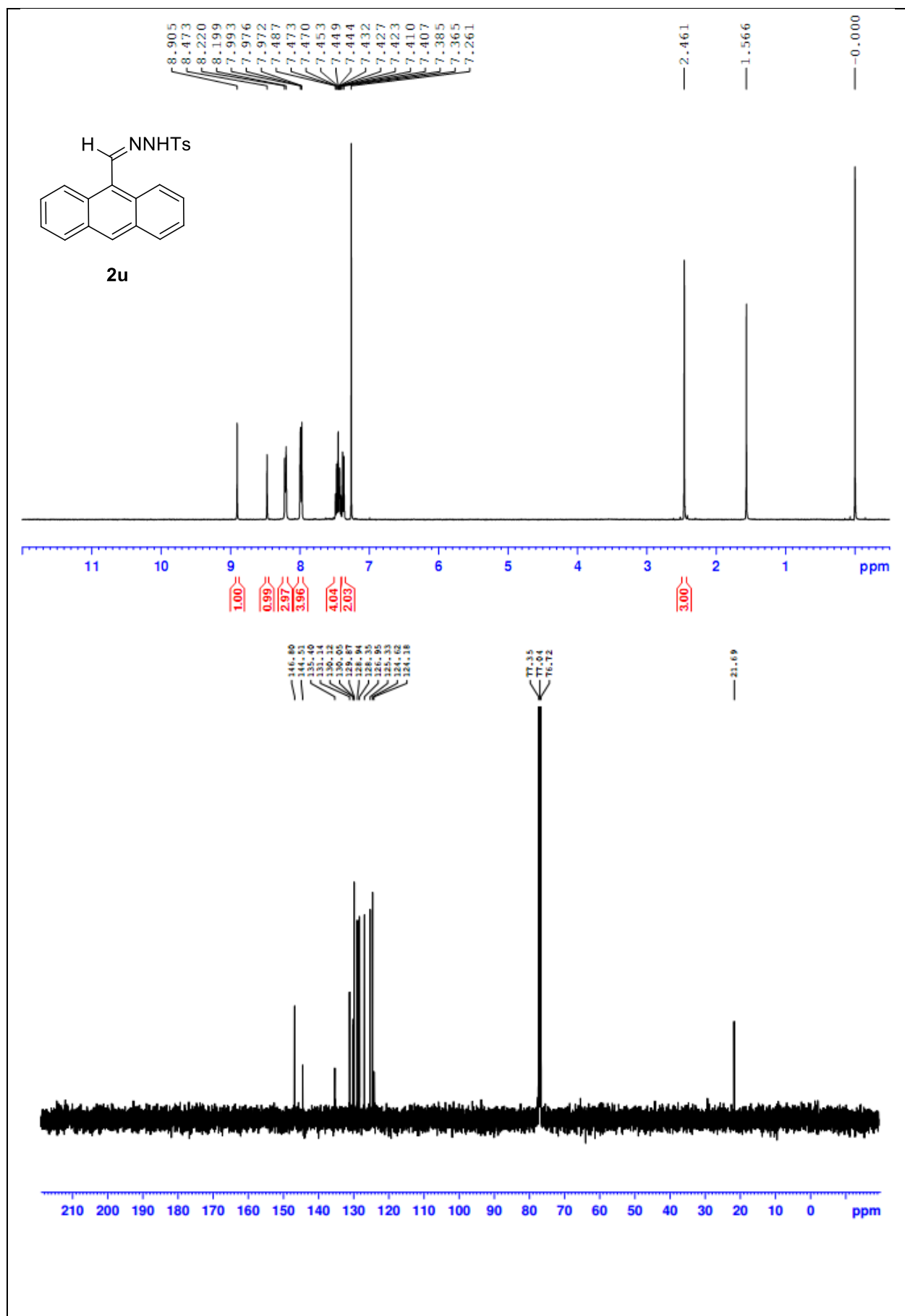




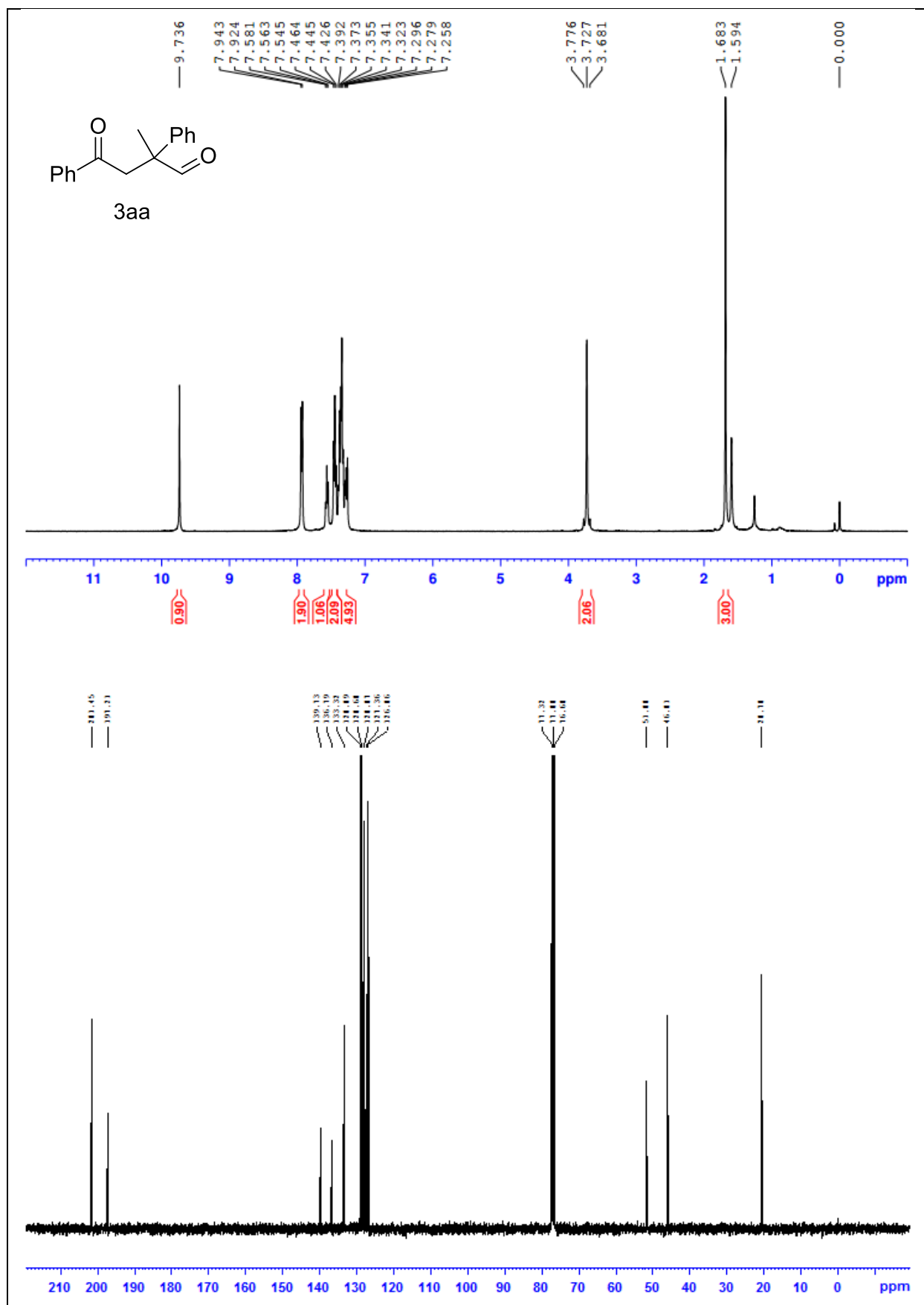


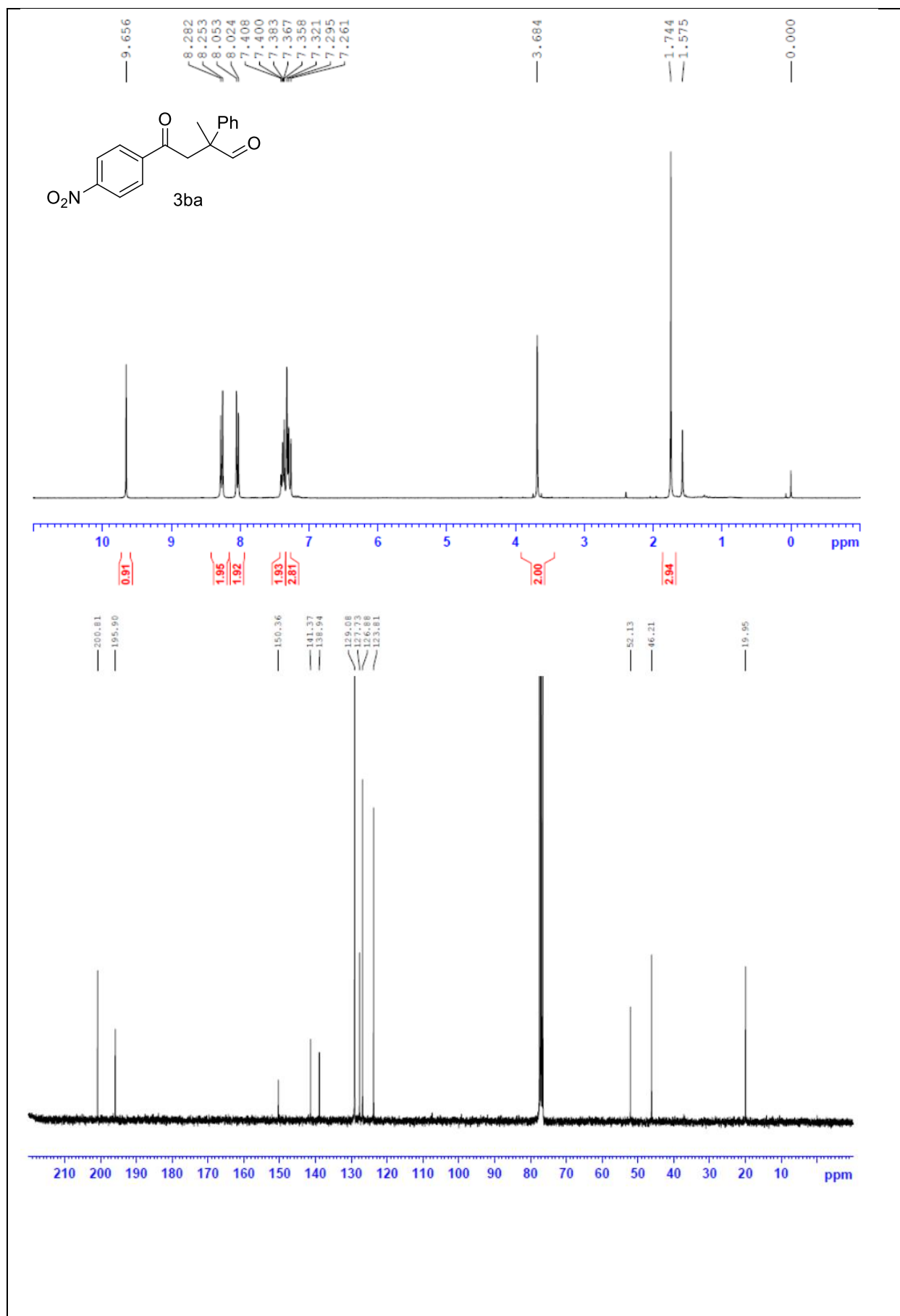


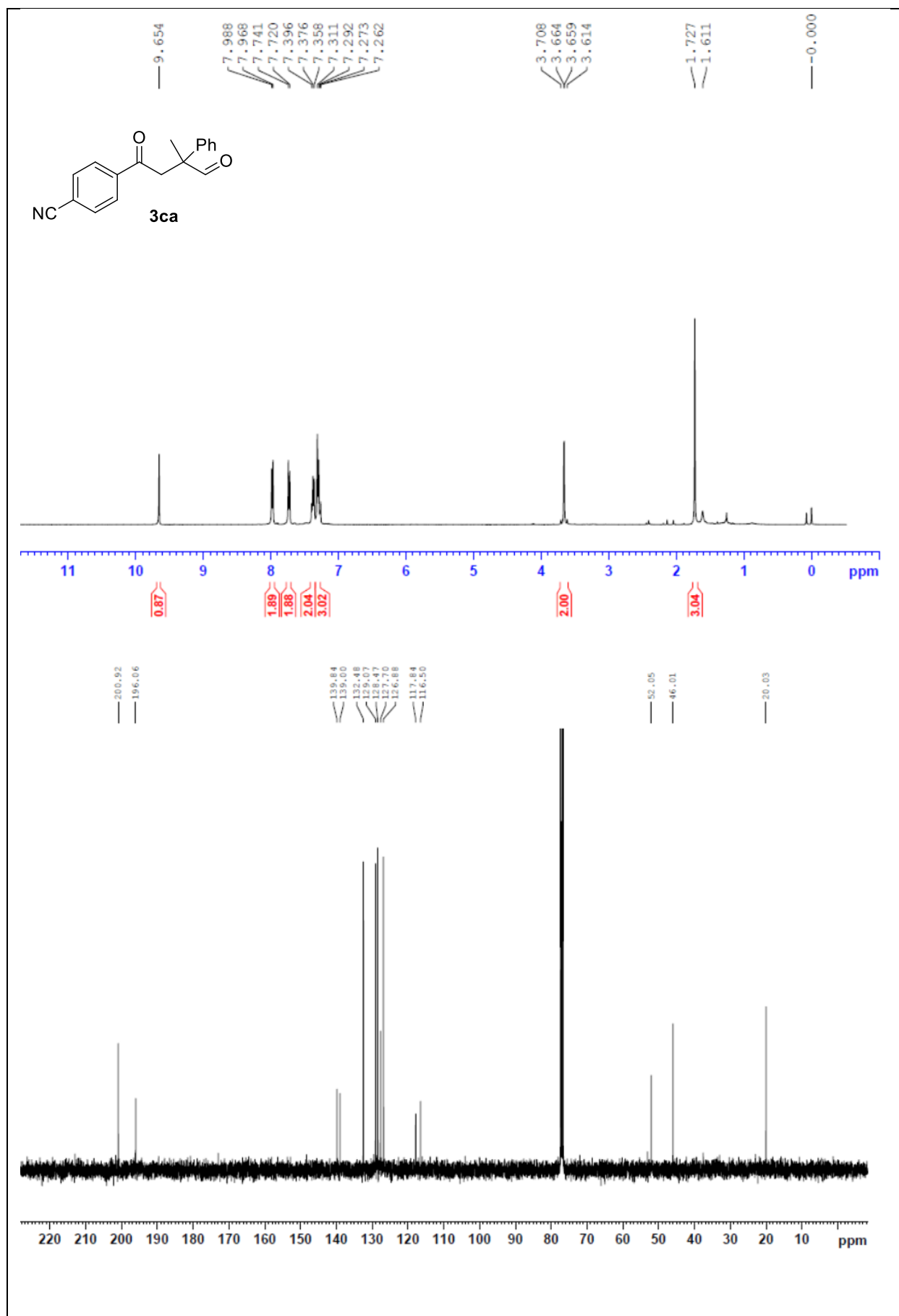


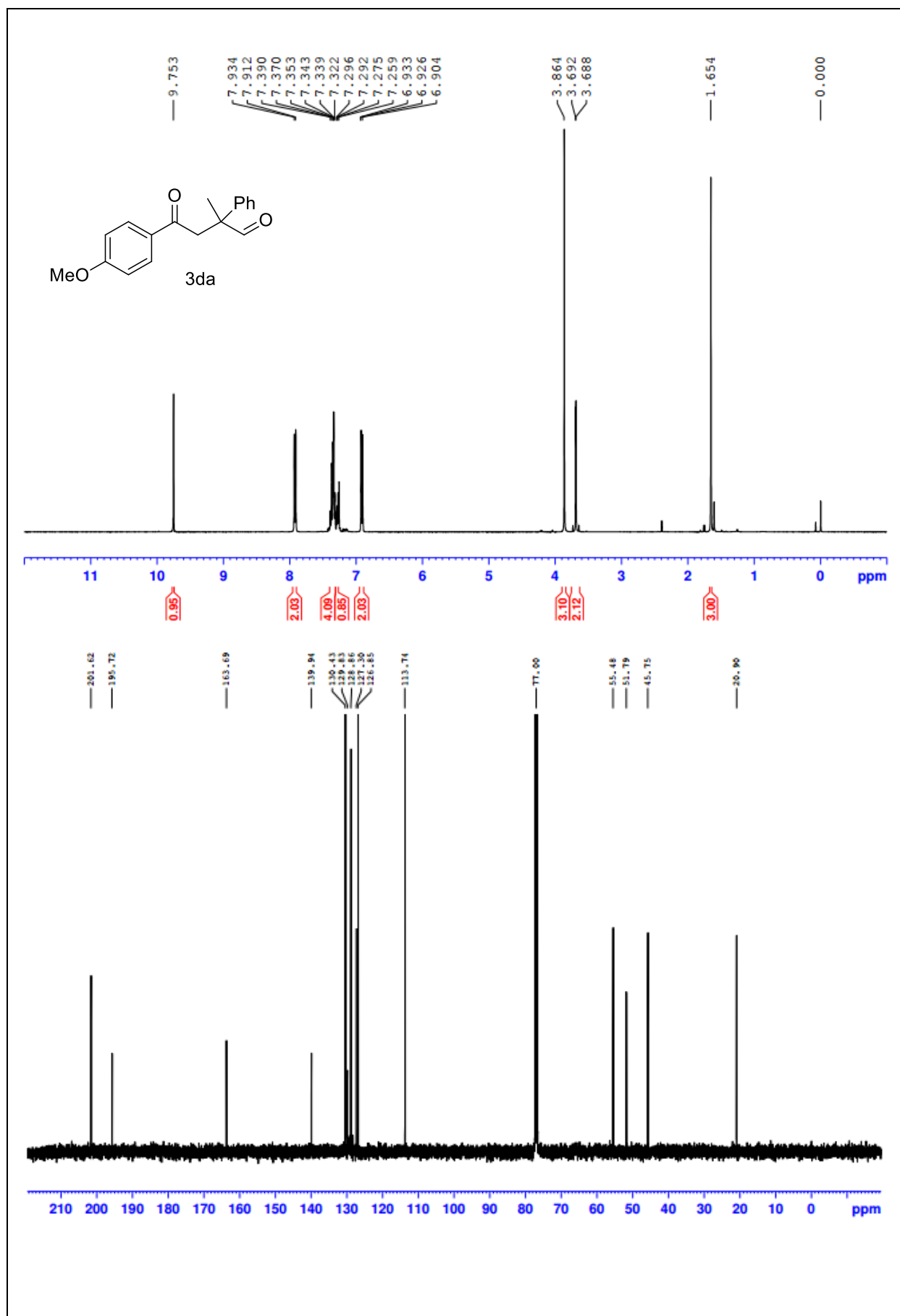


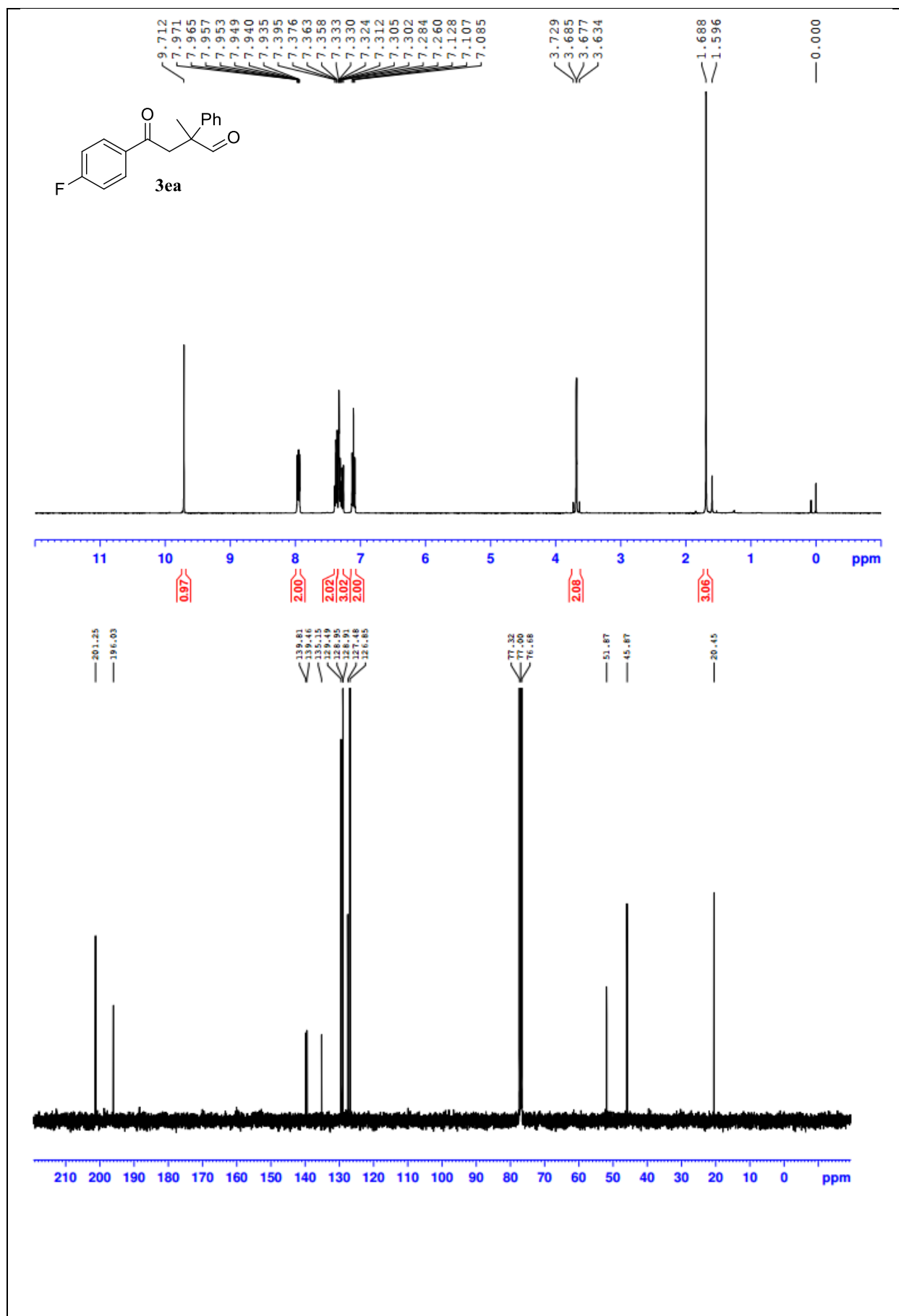
NMR Spectra for 1, 4-ketoaldehydes:

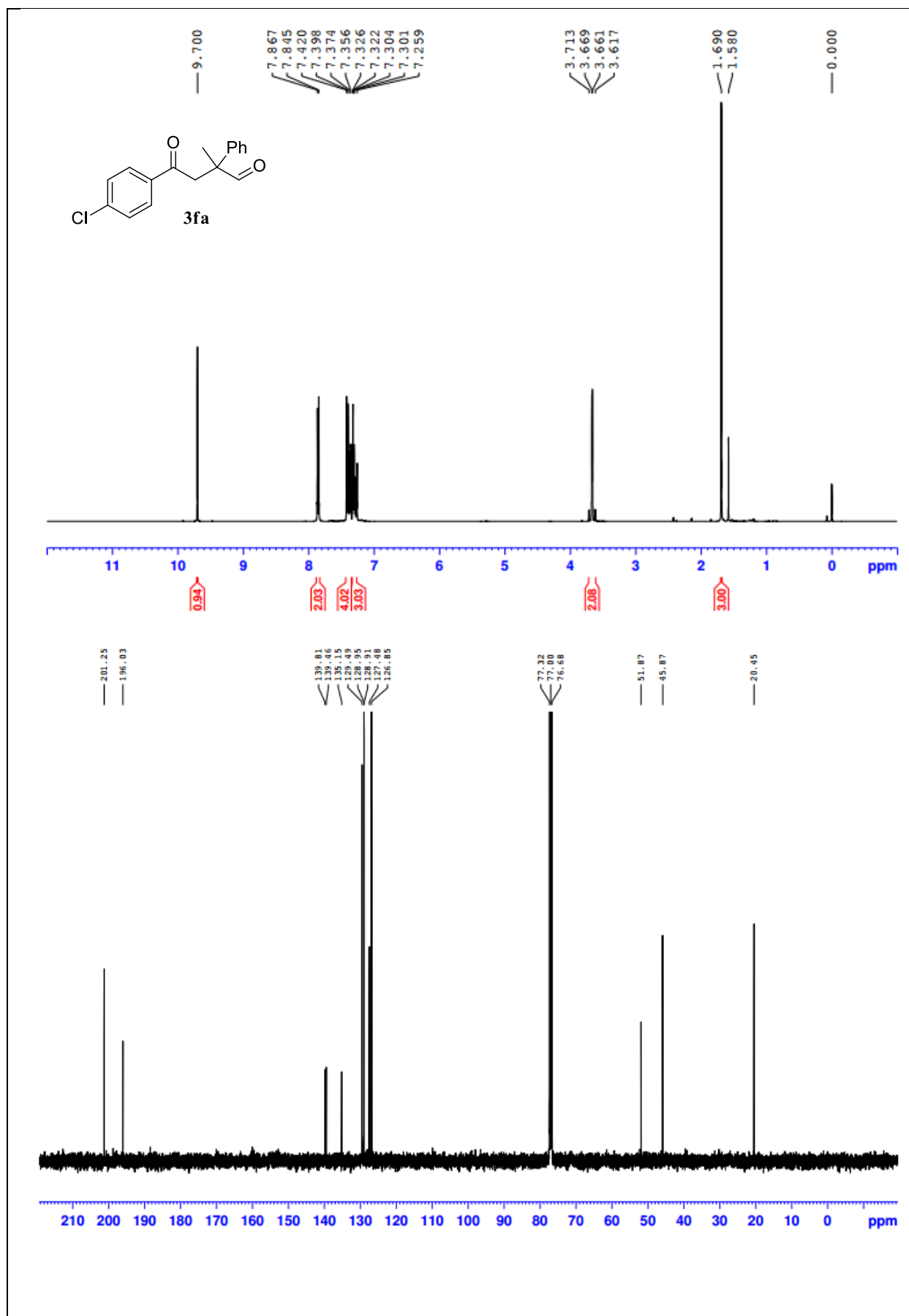


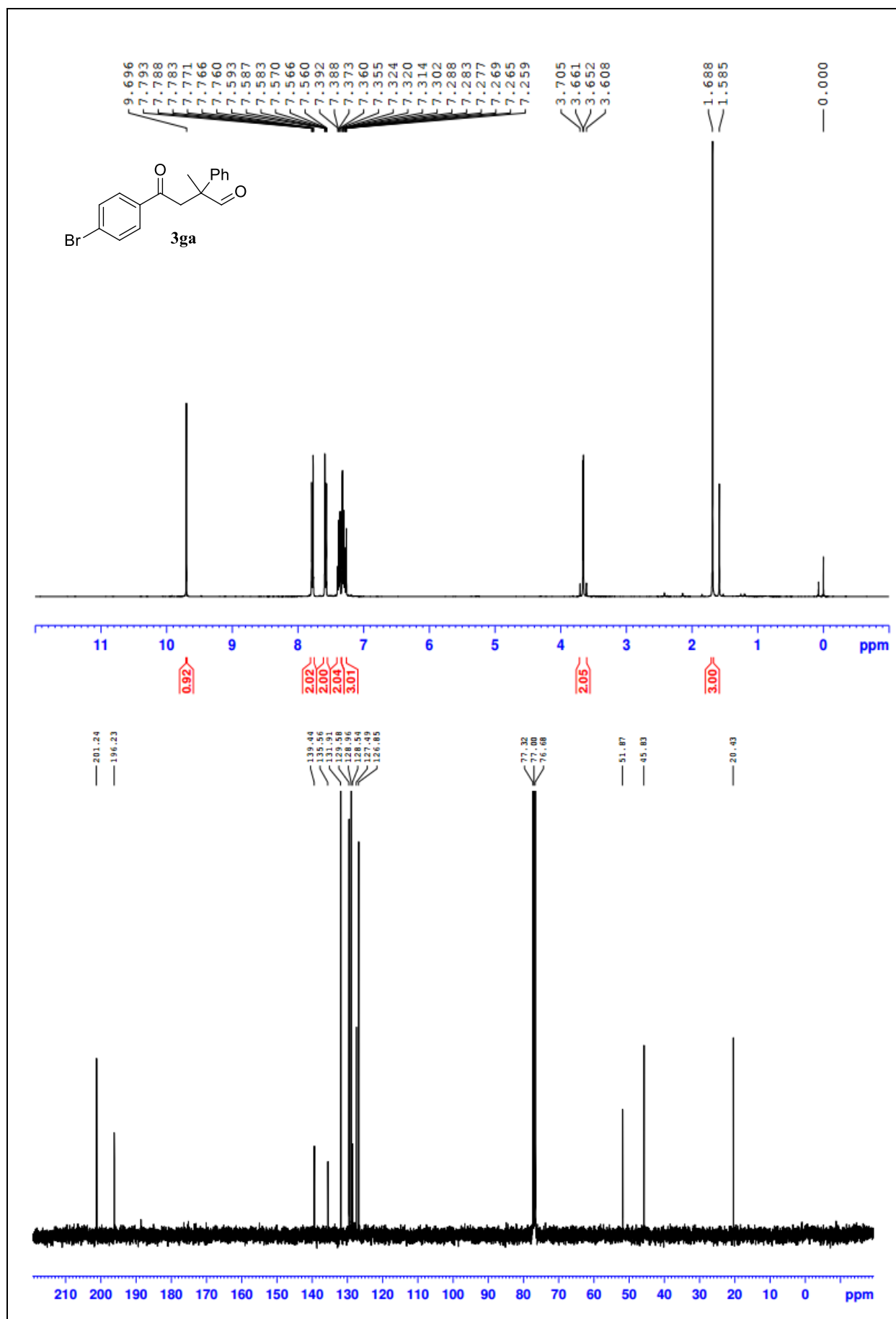


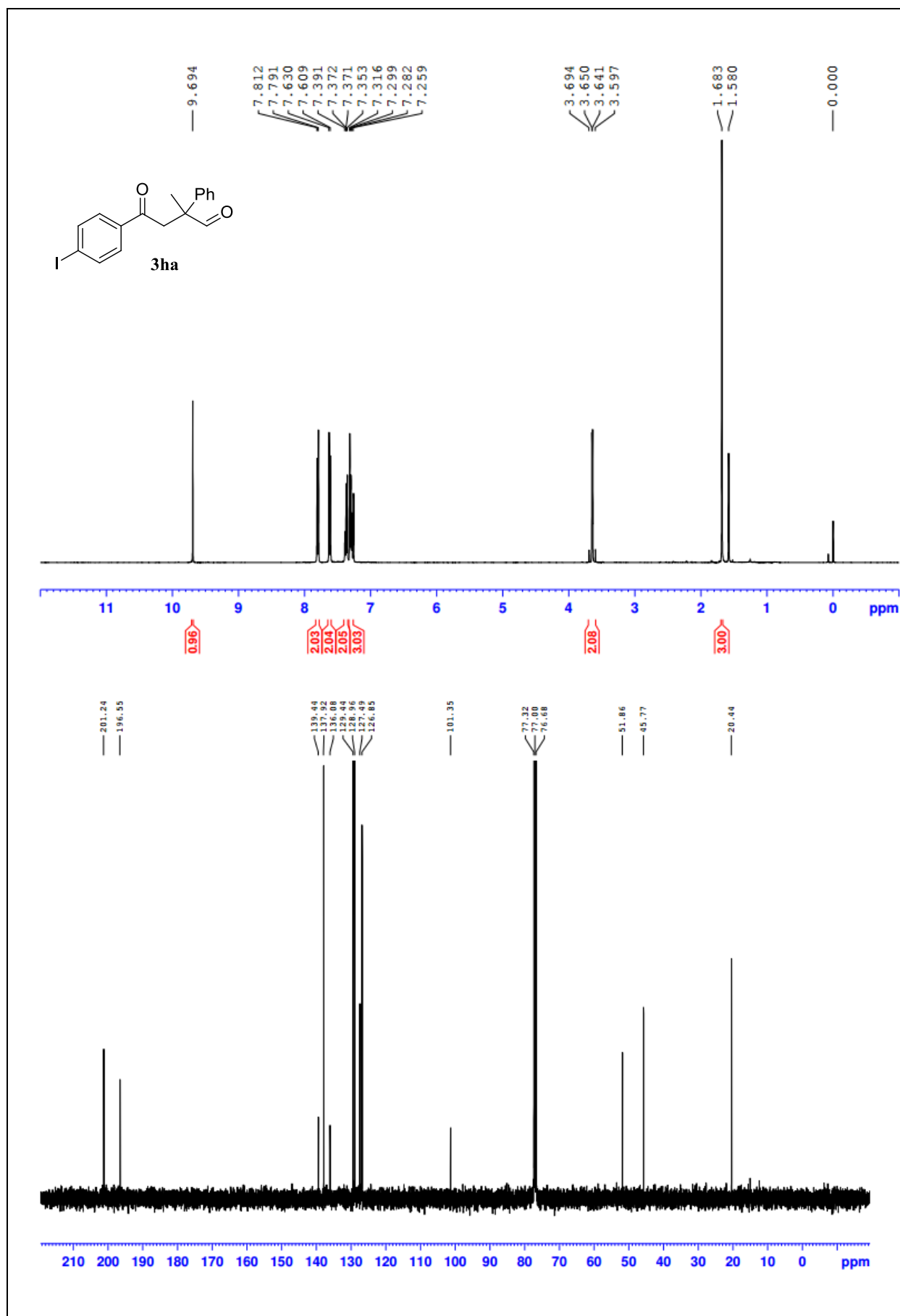


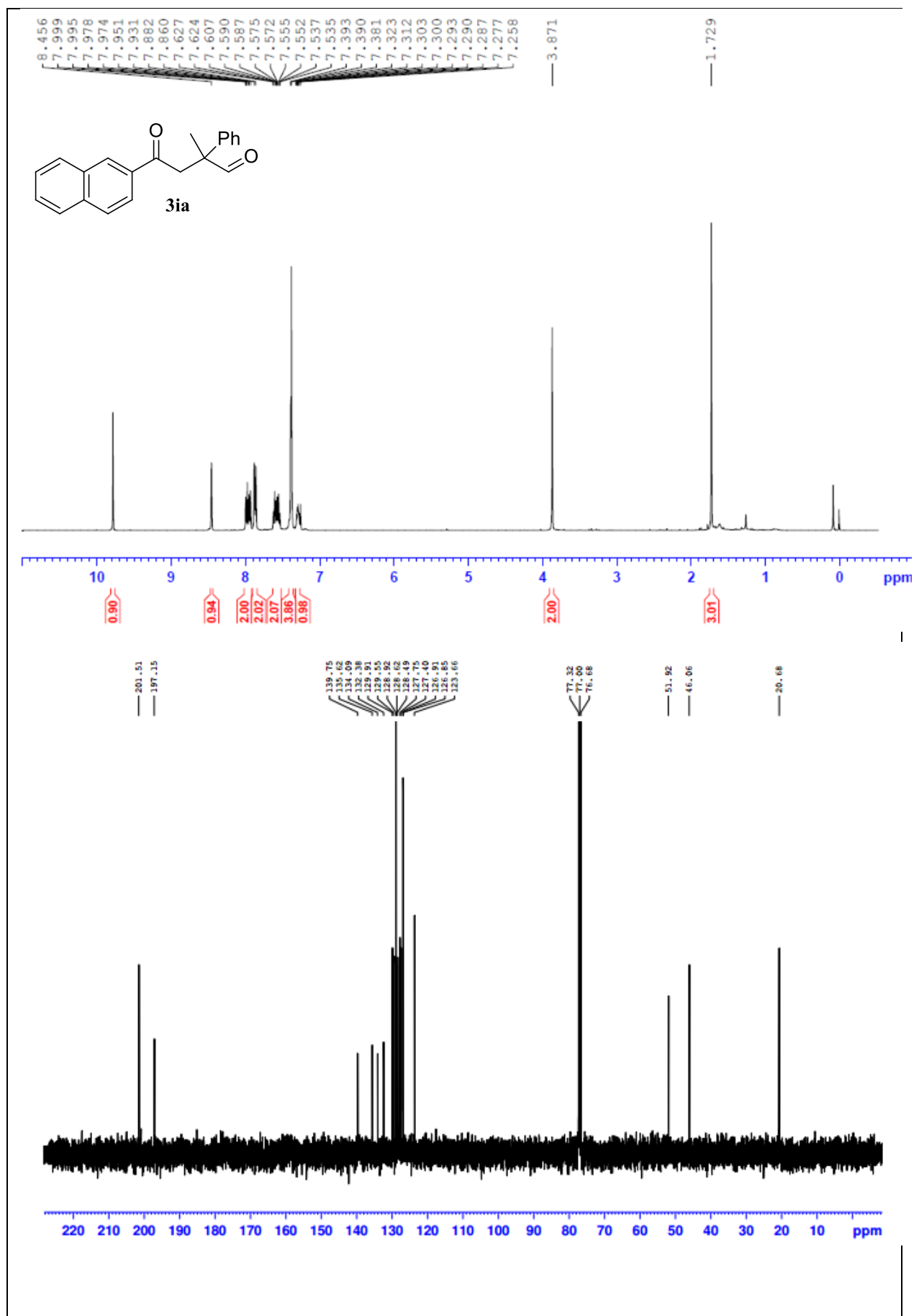


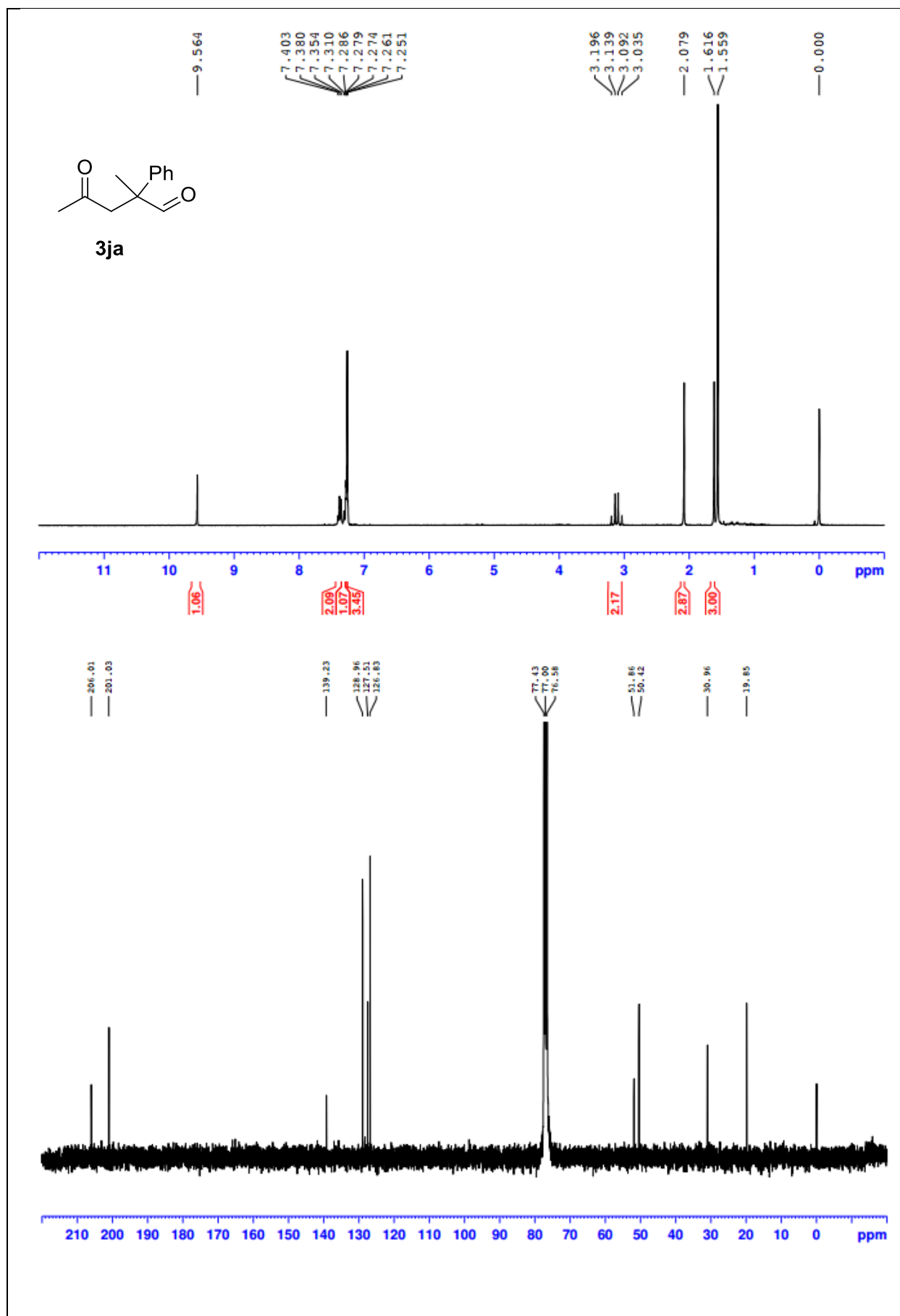


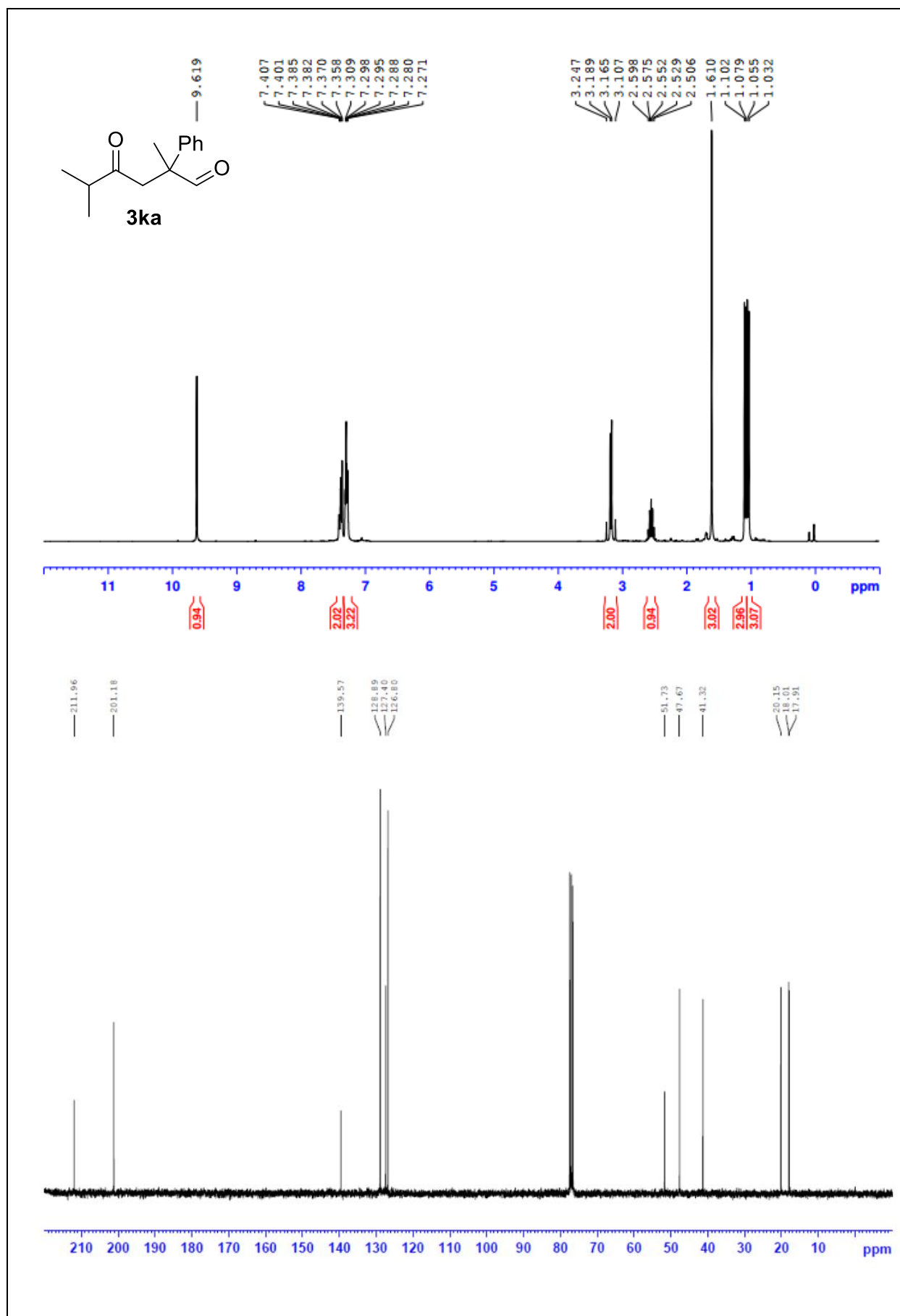


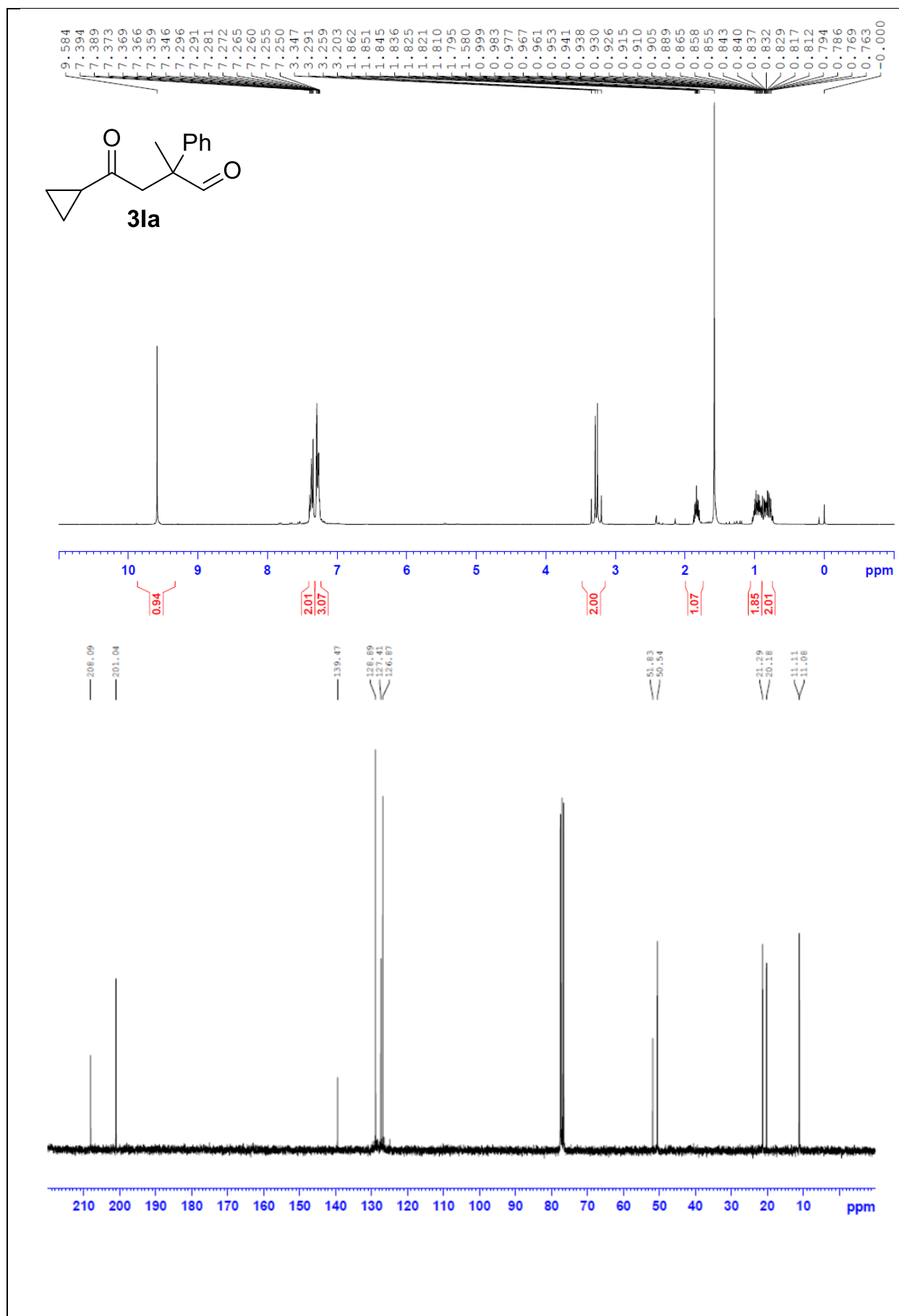


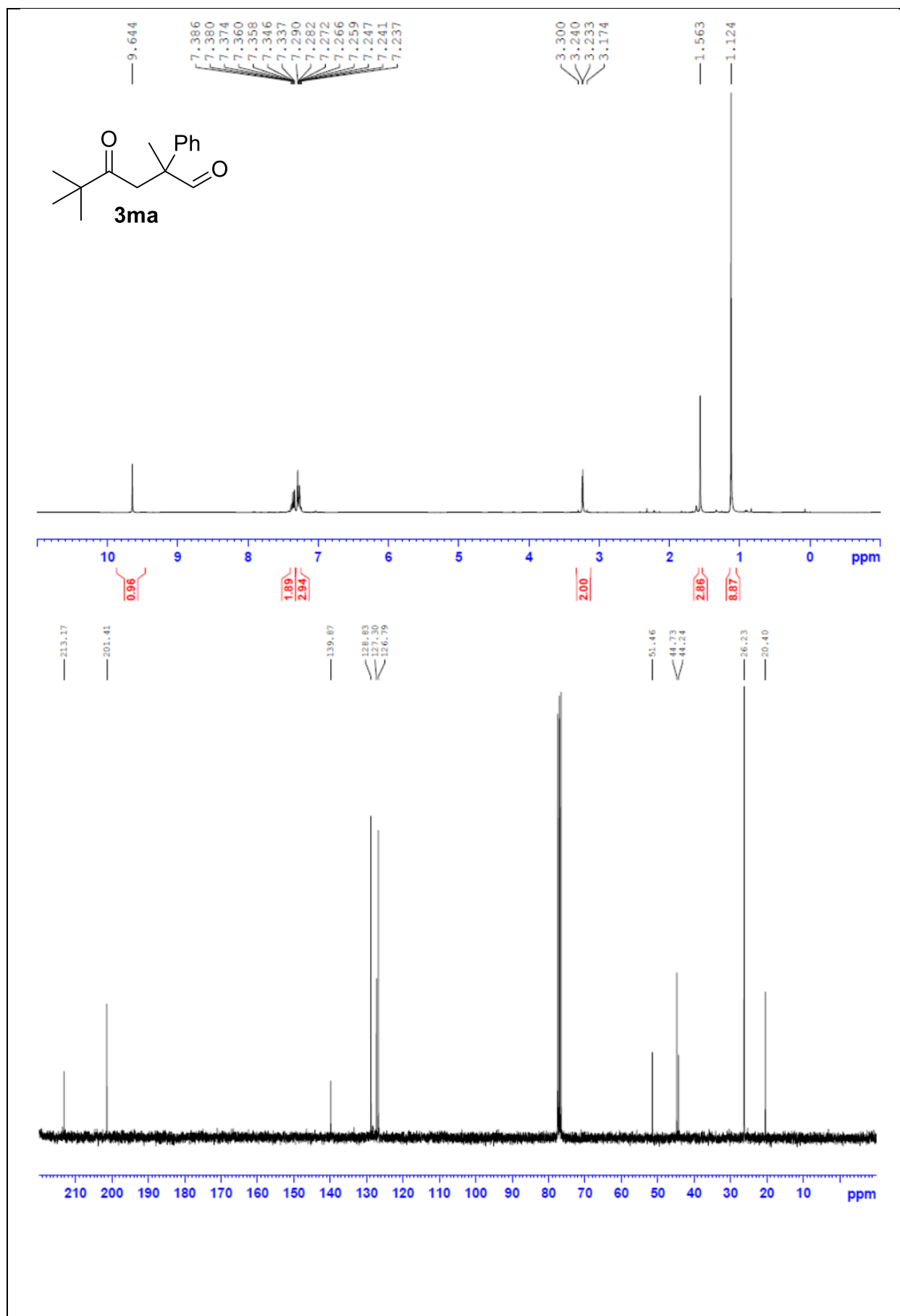


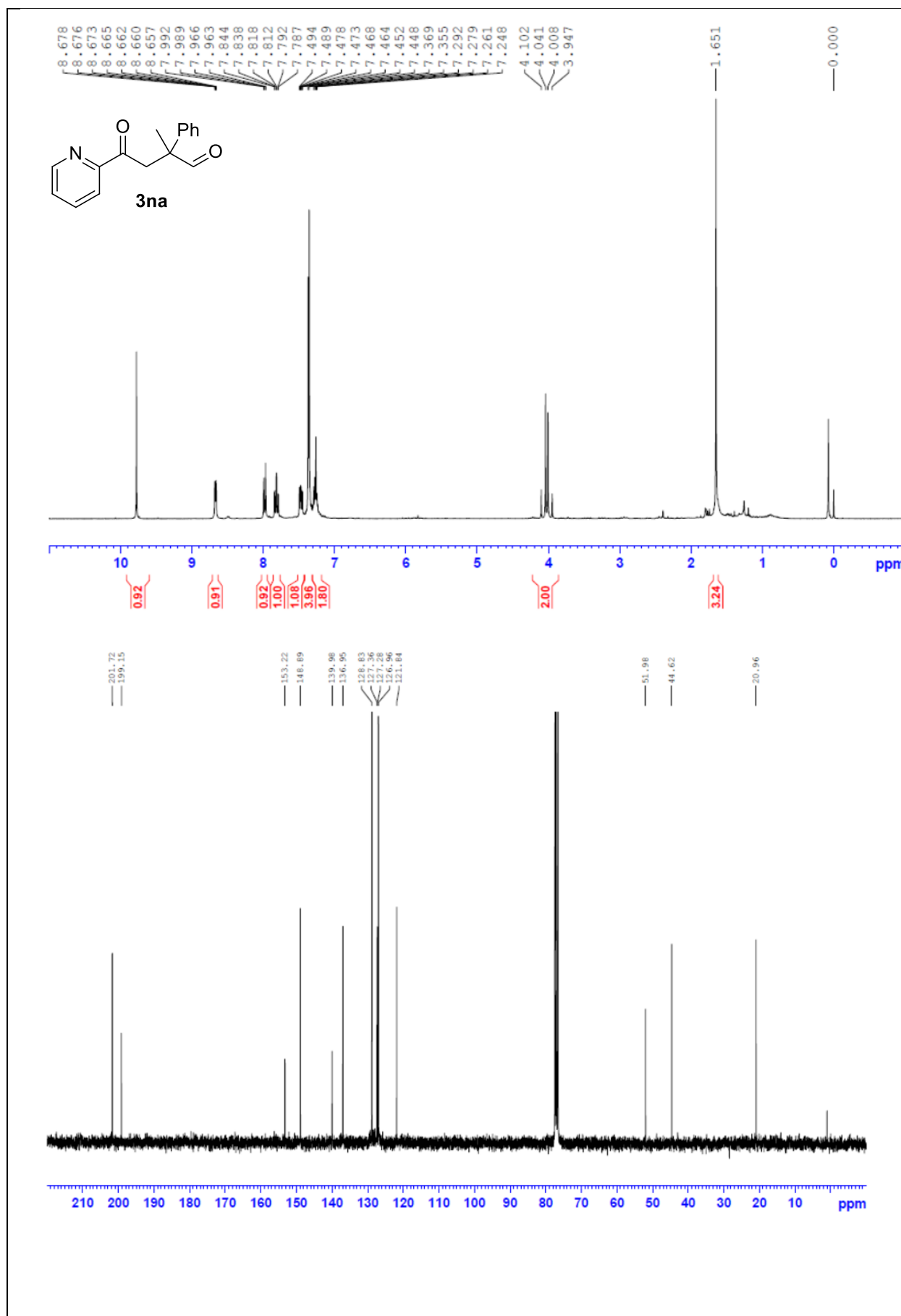


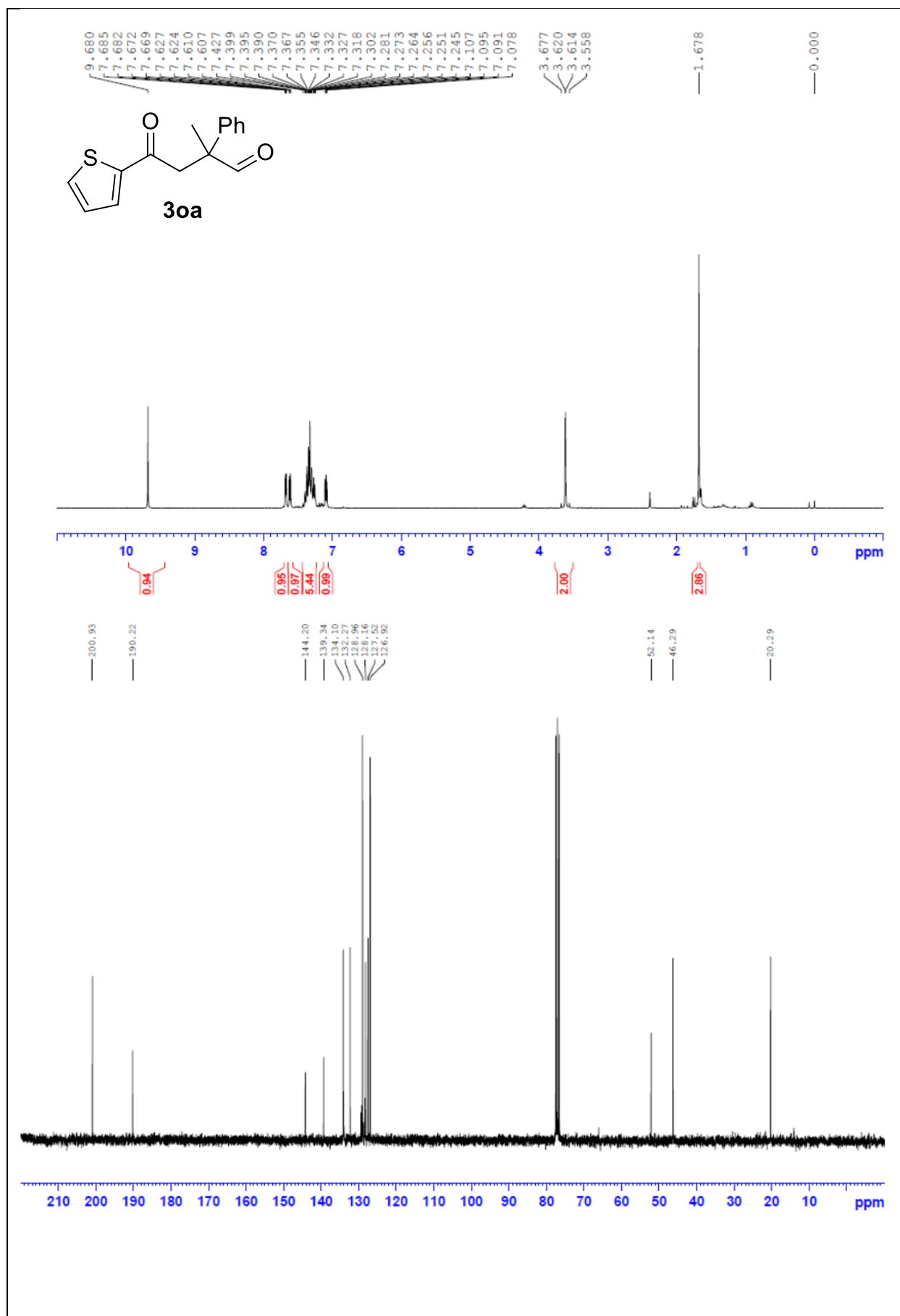


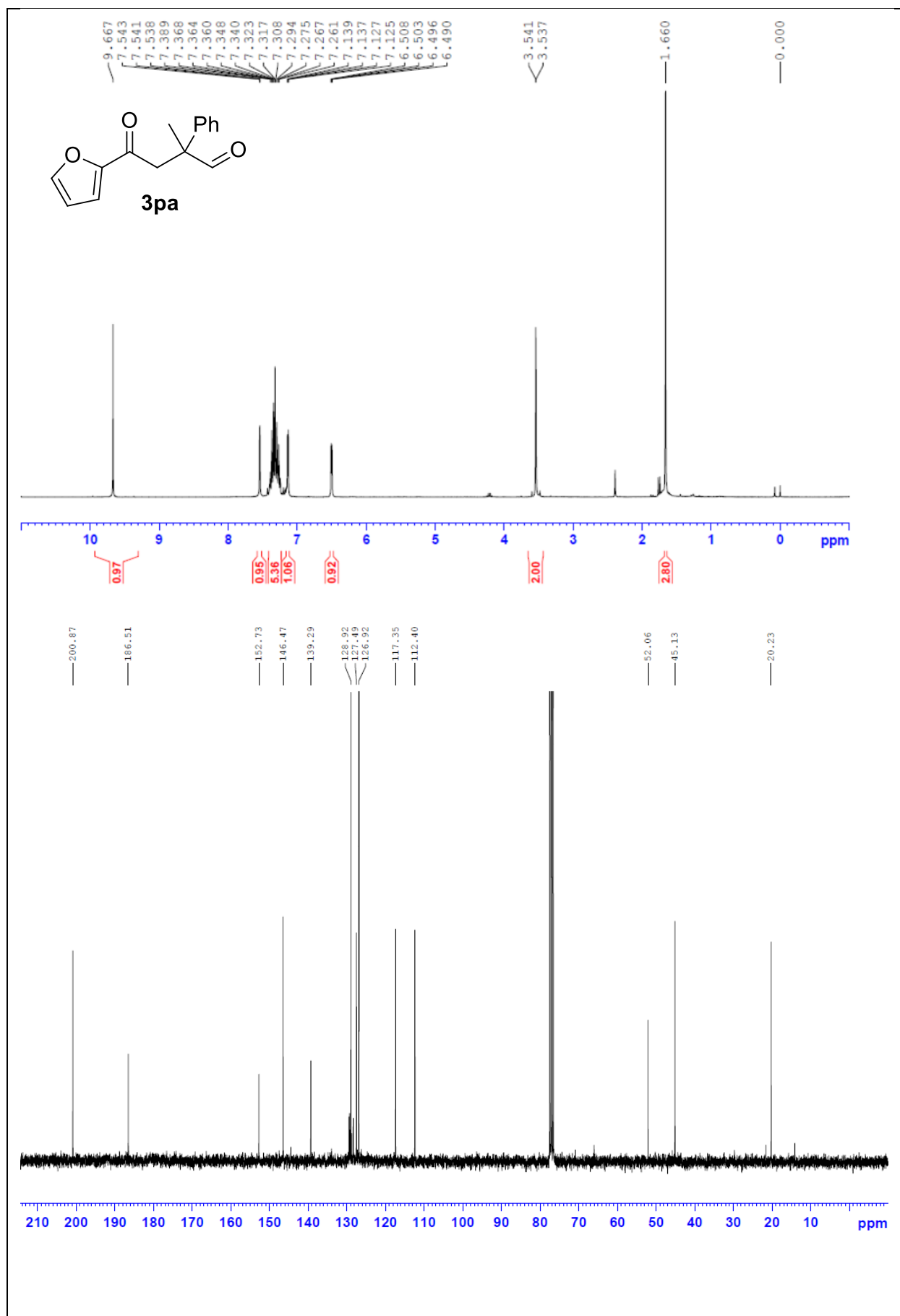


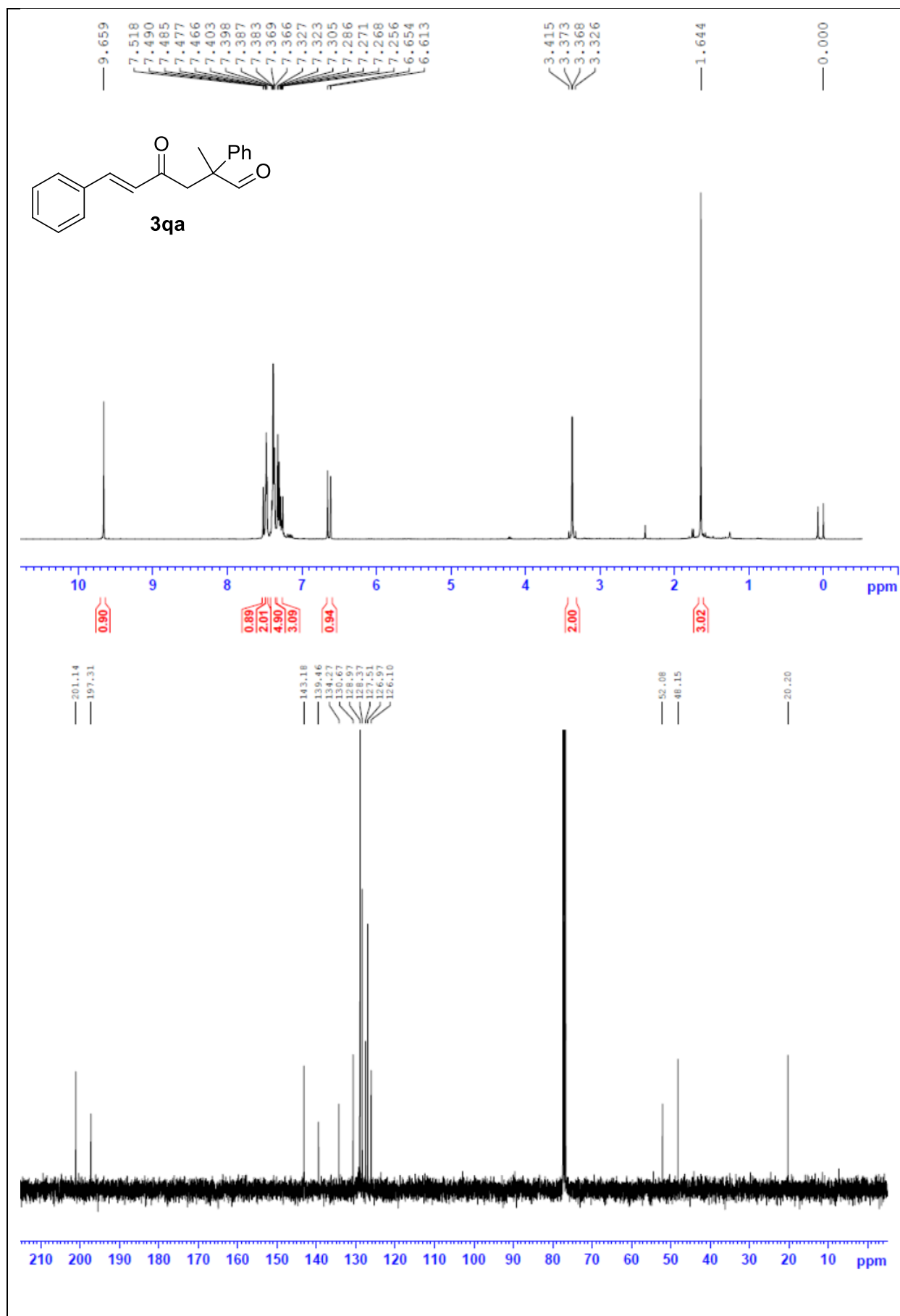


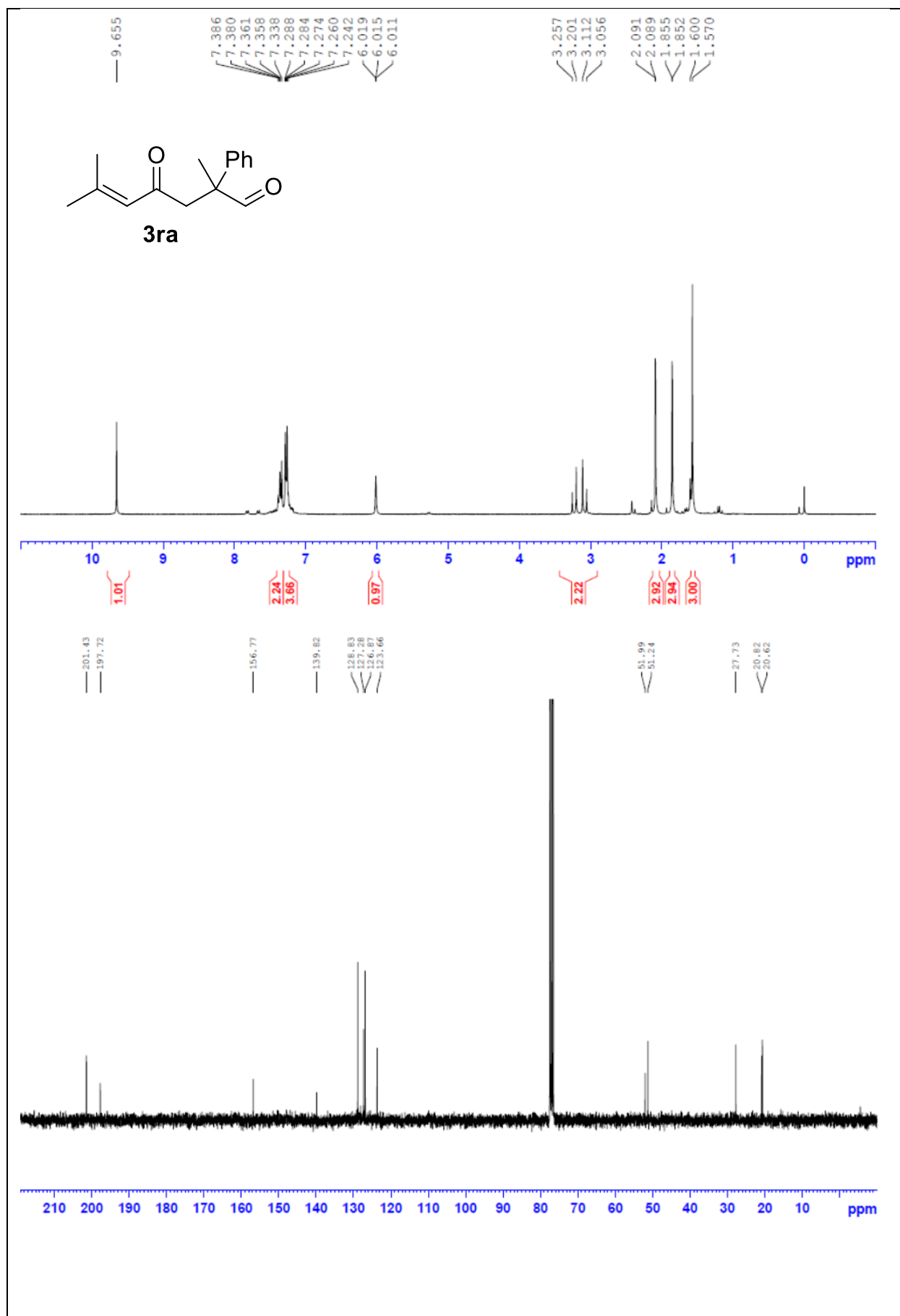


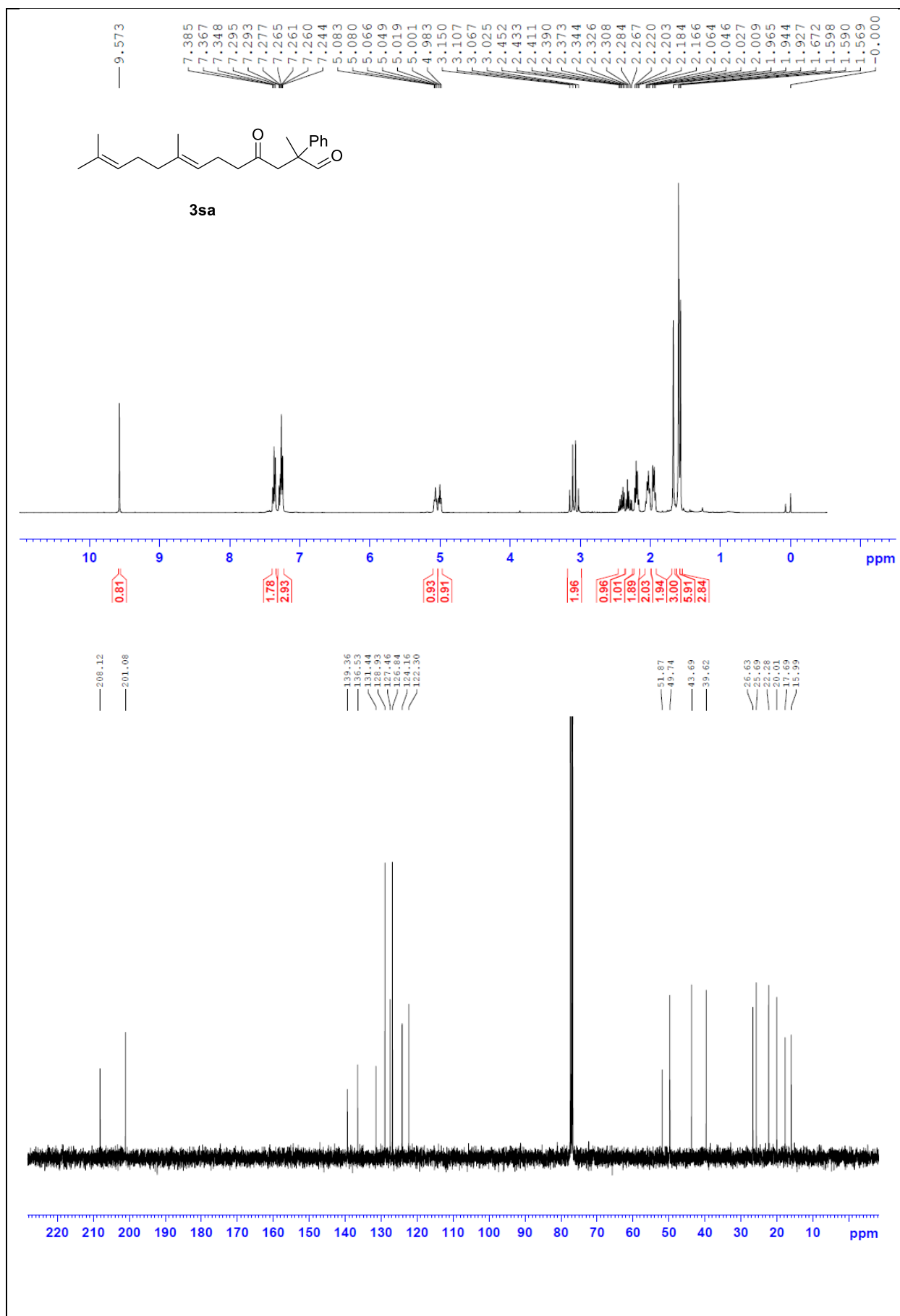


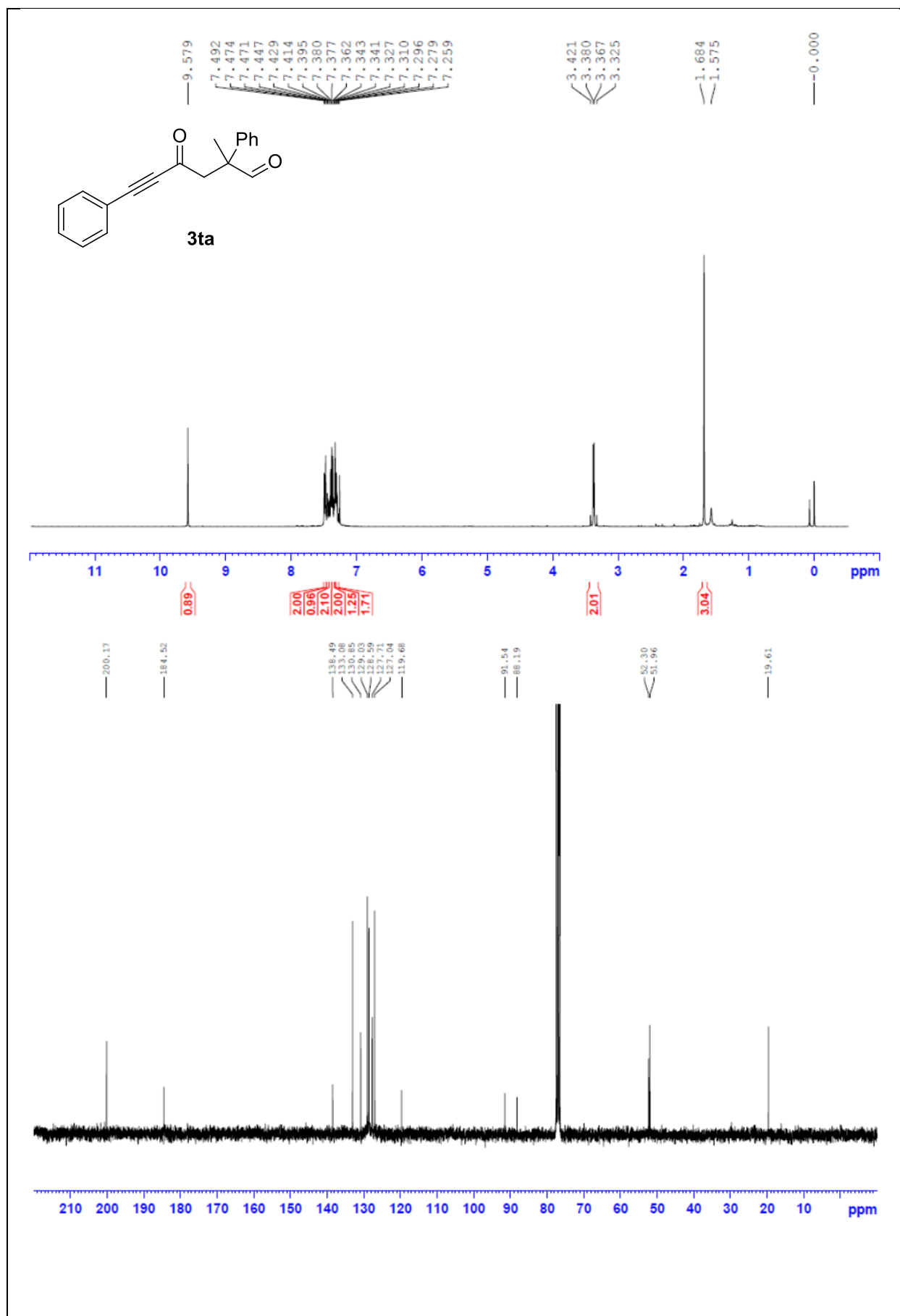


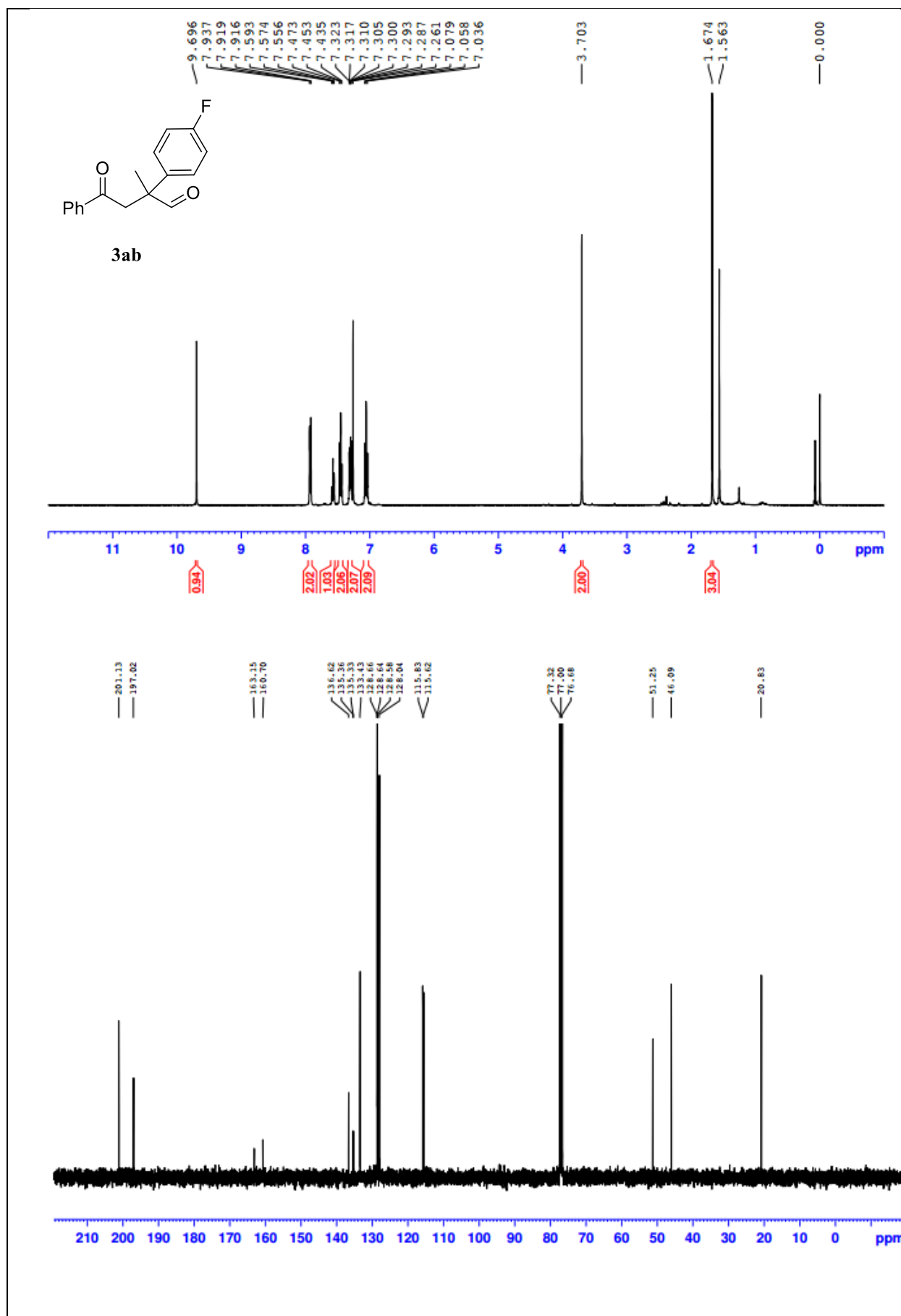


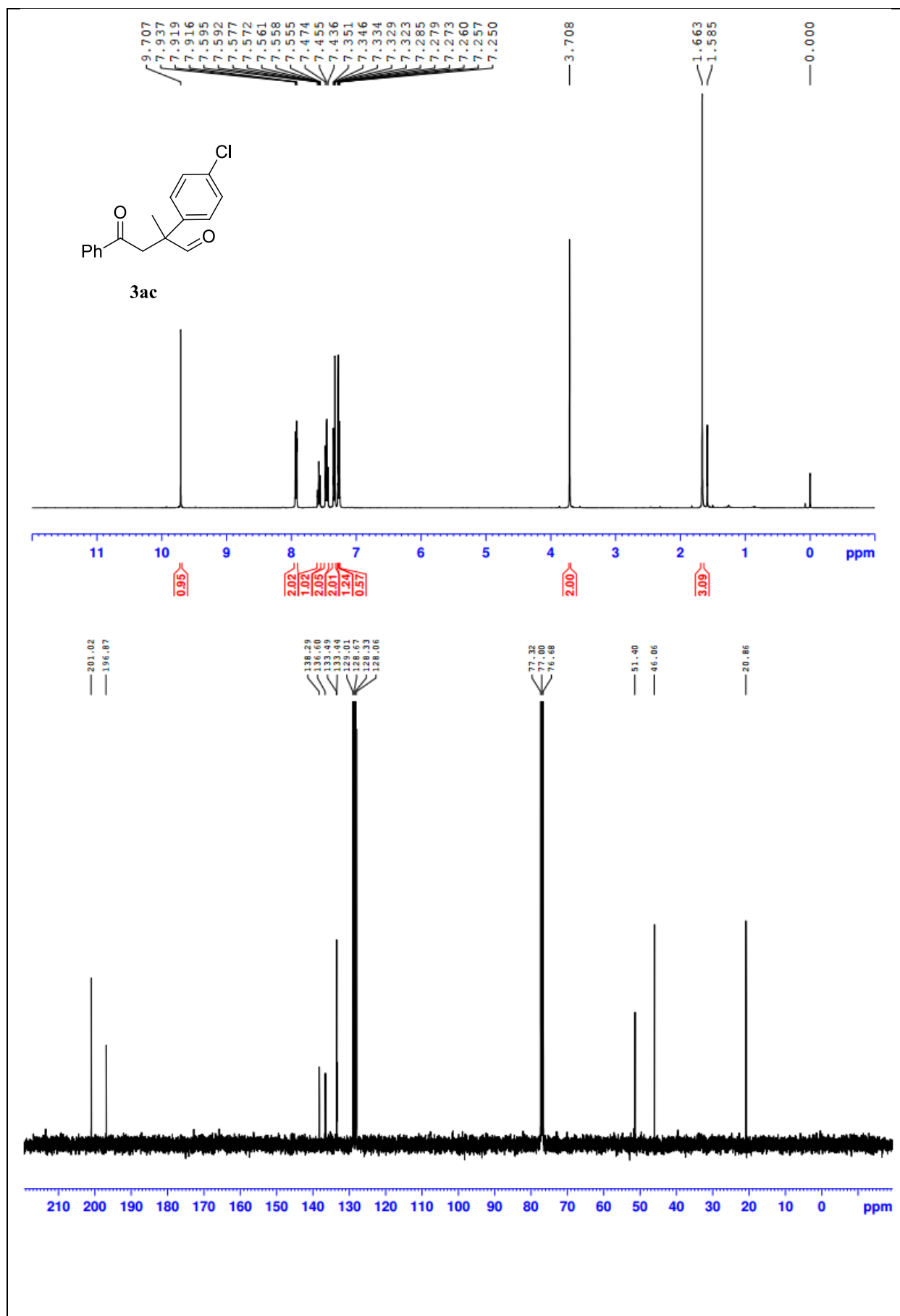


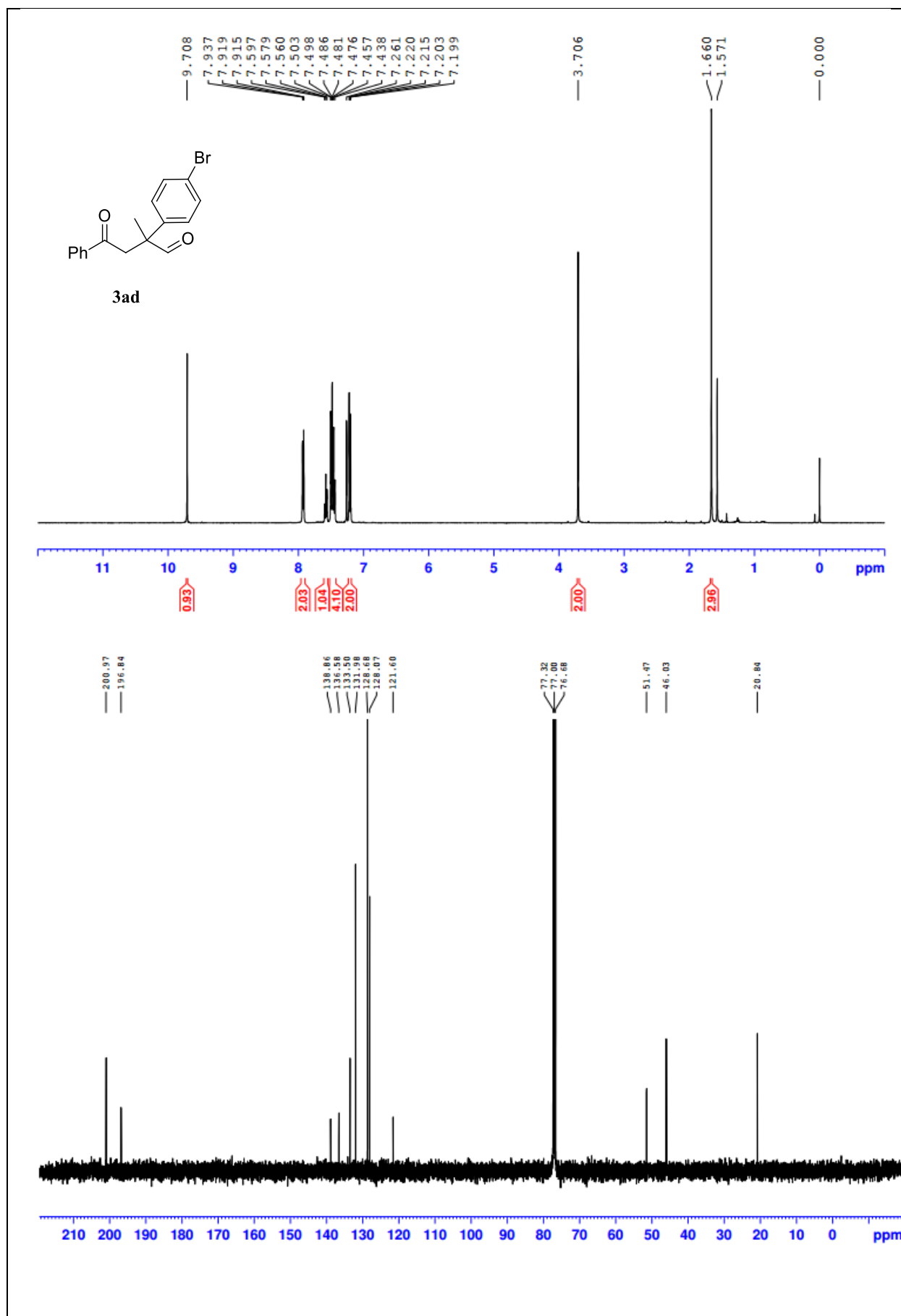


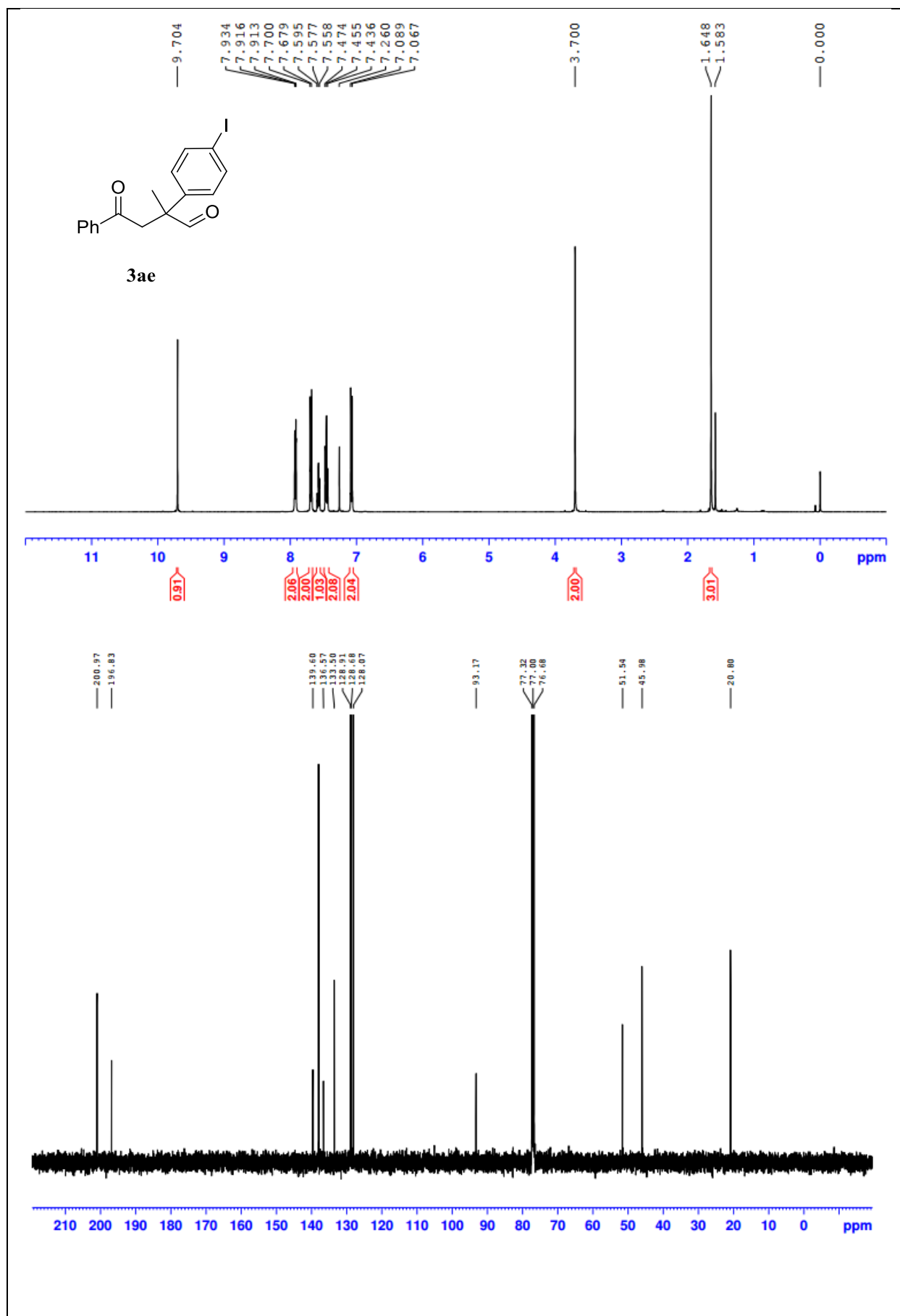


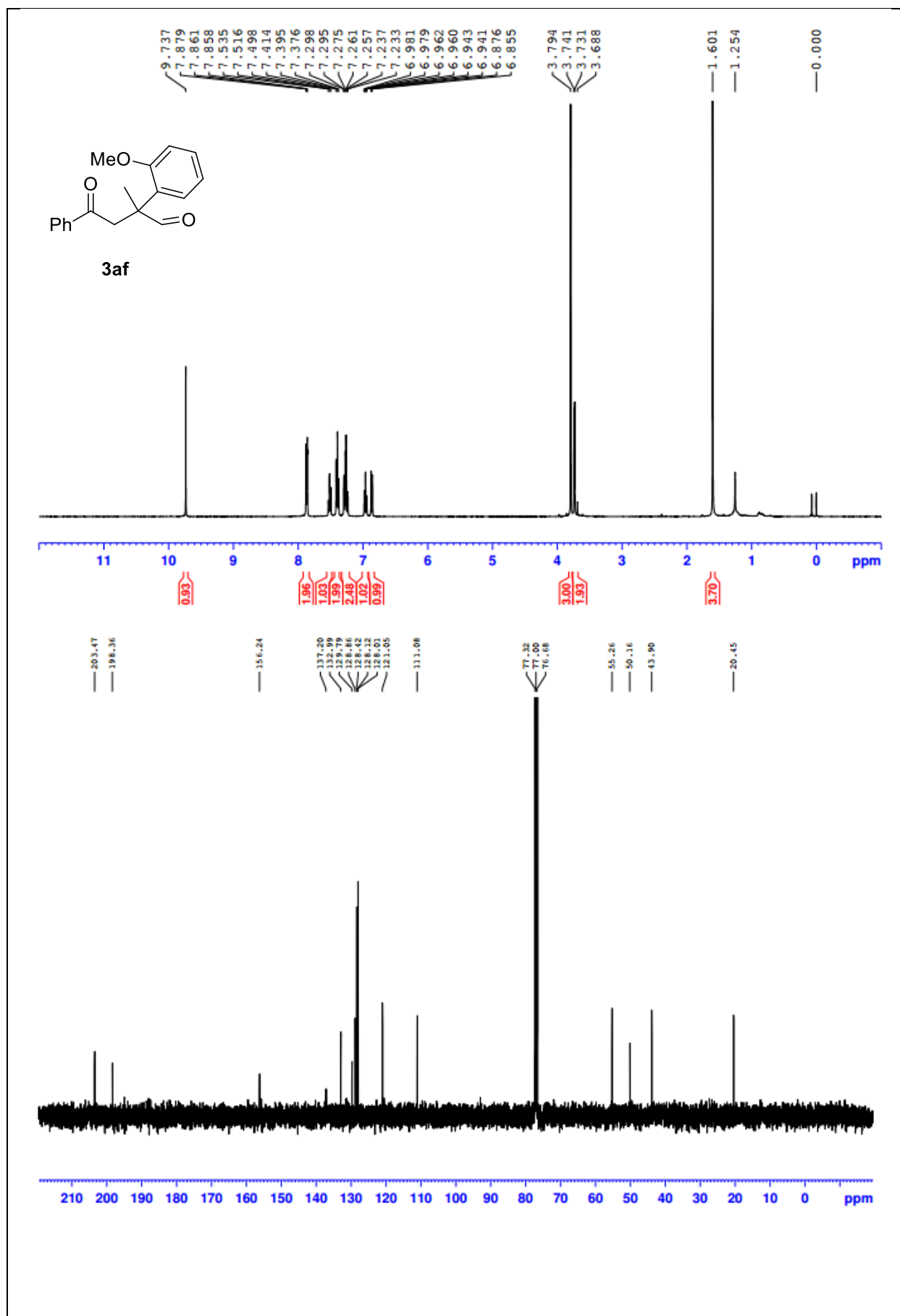


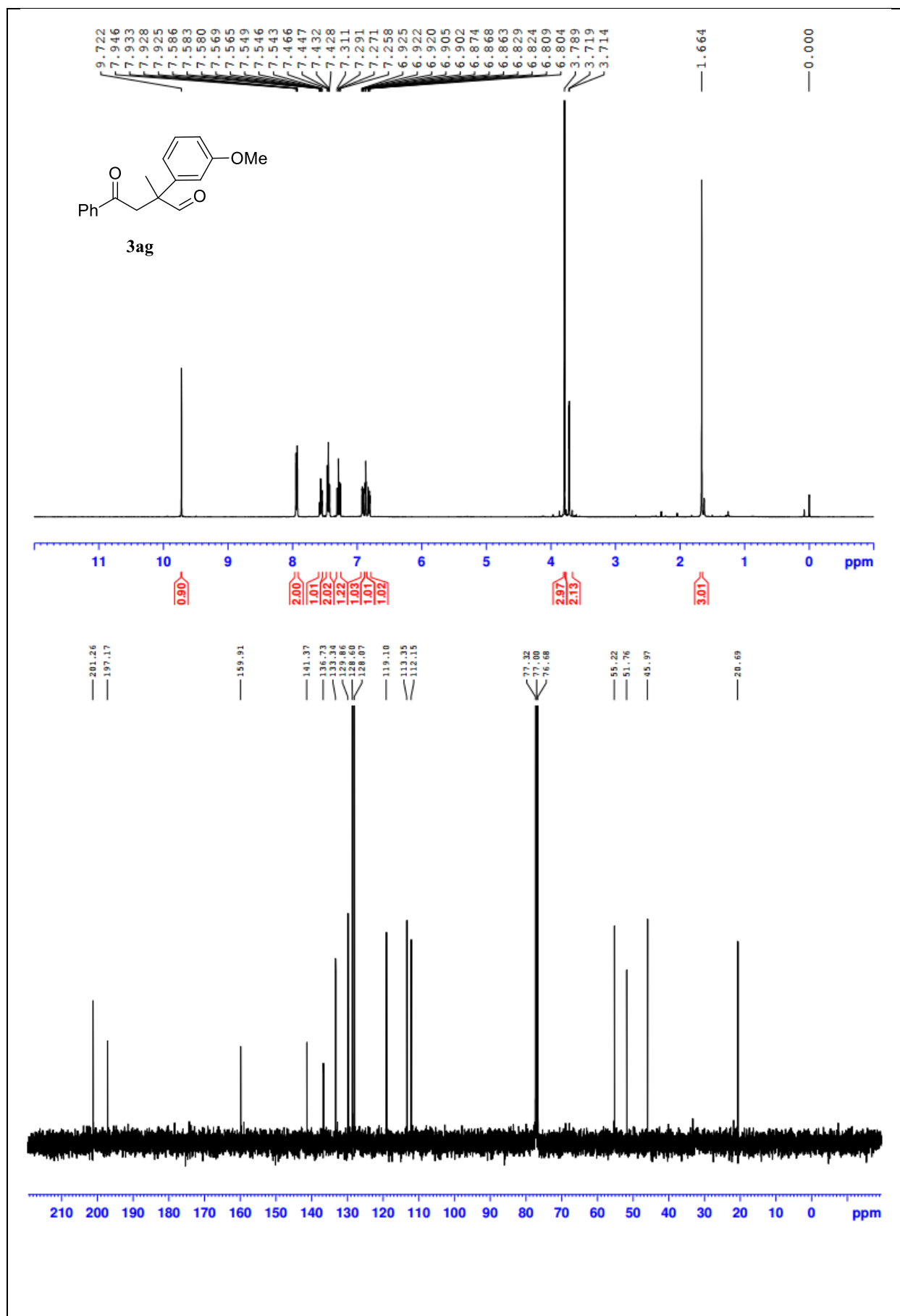


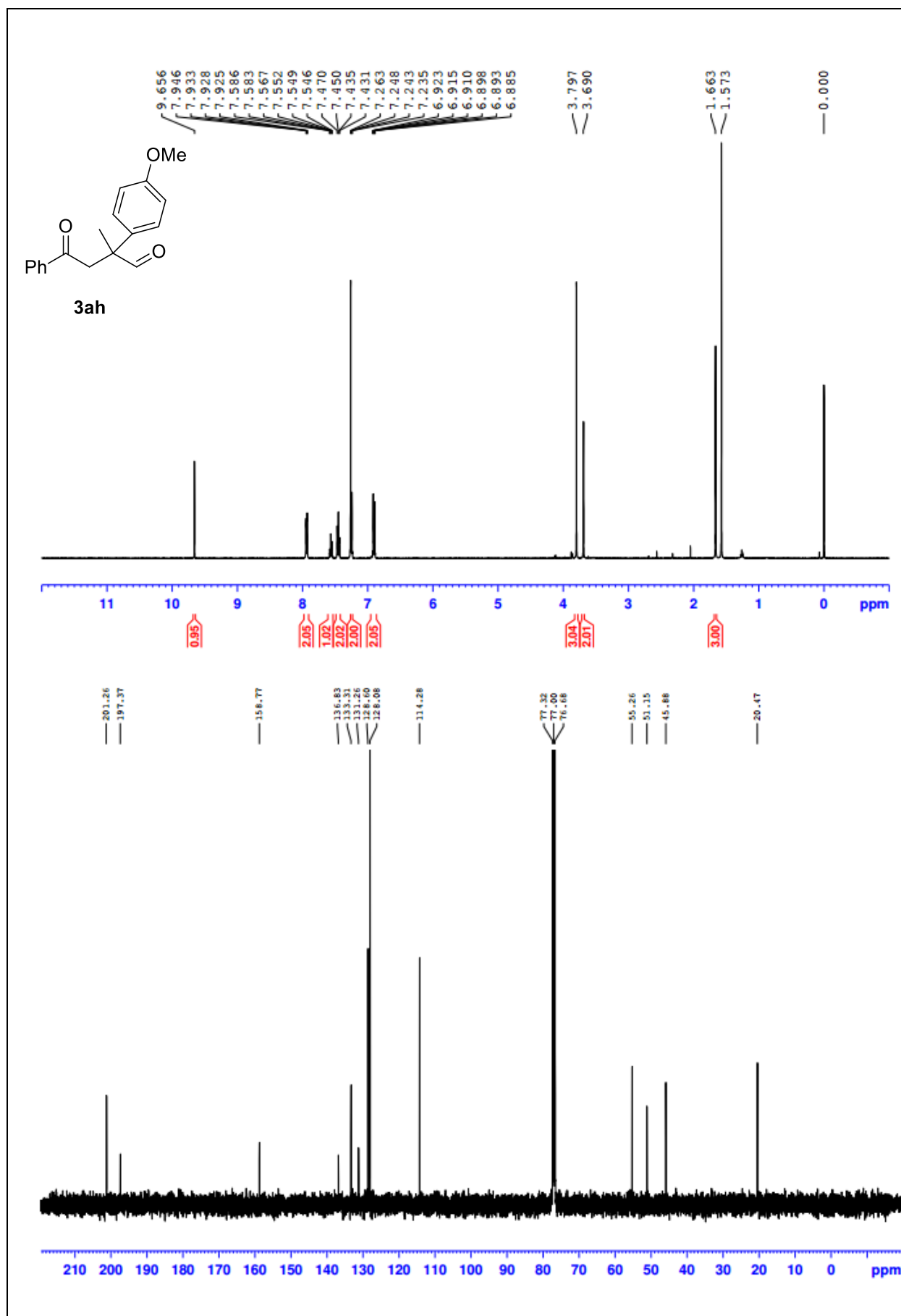


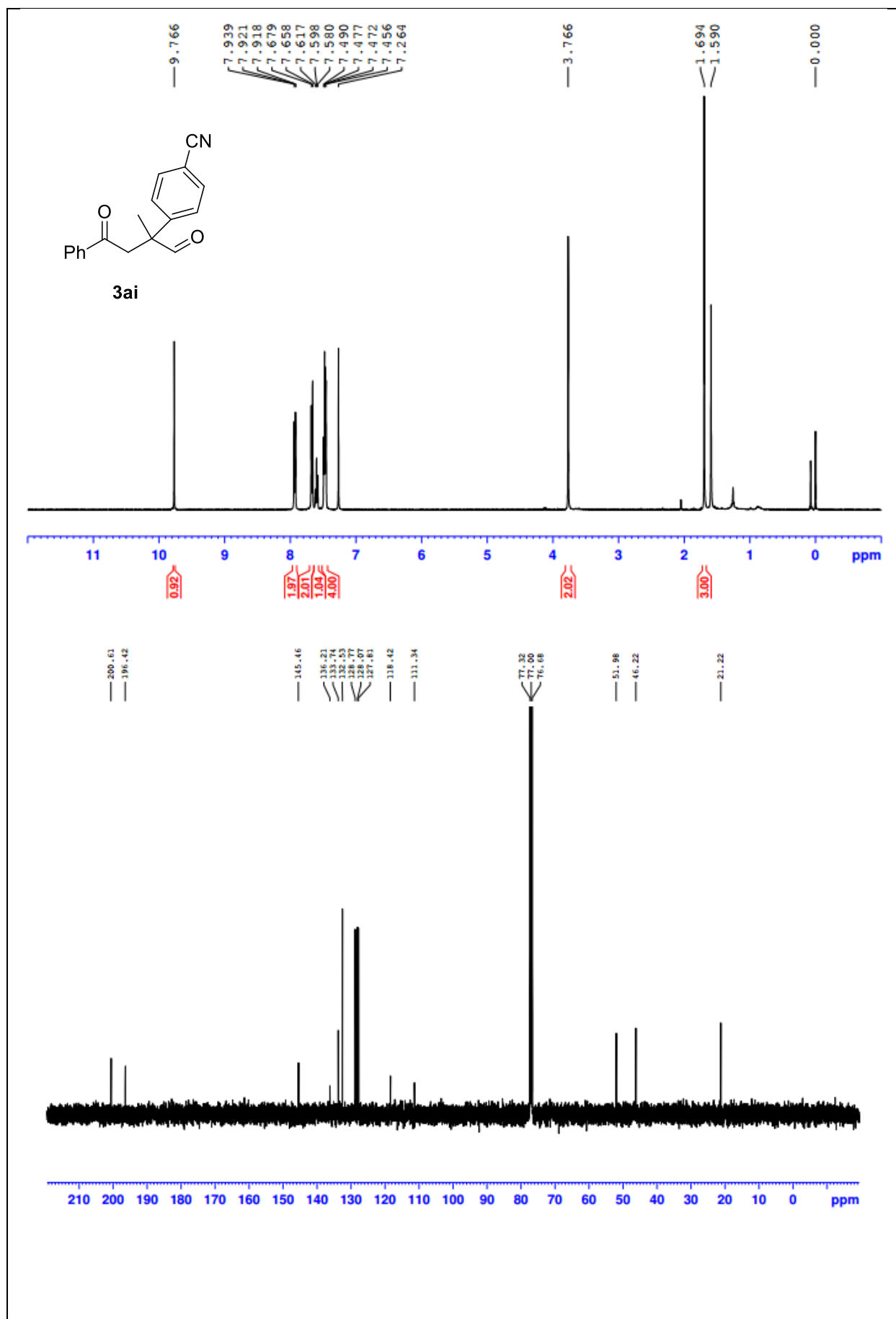


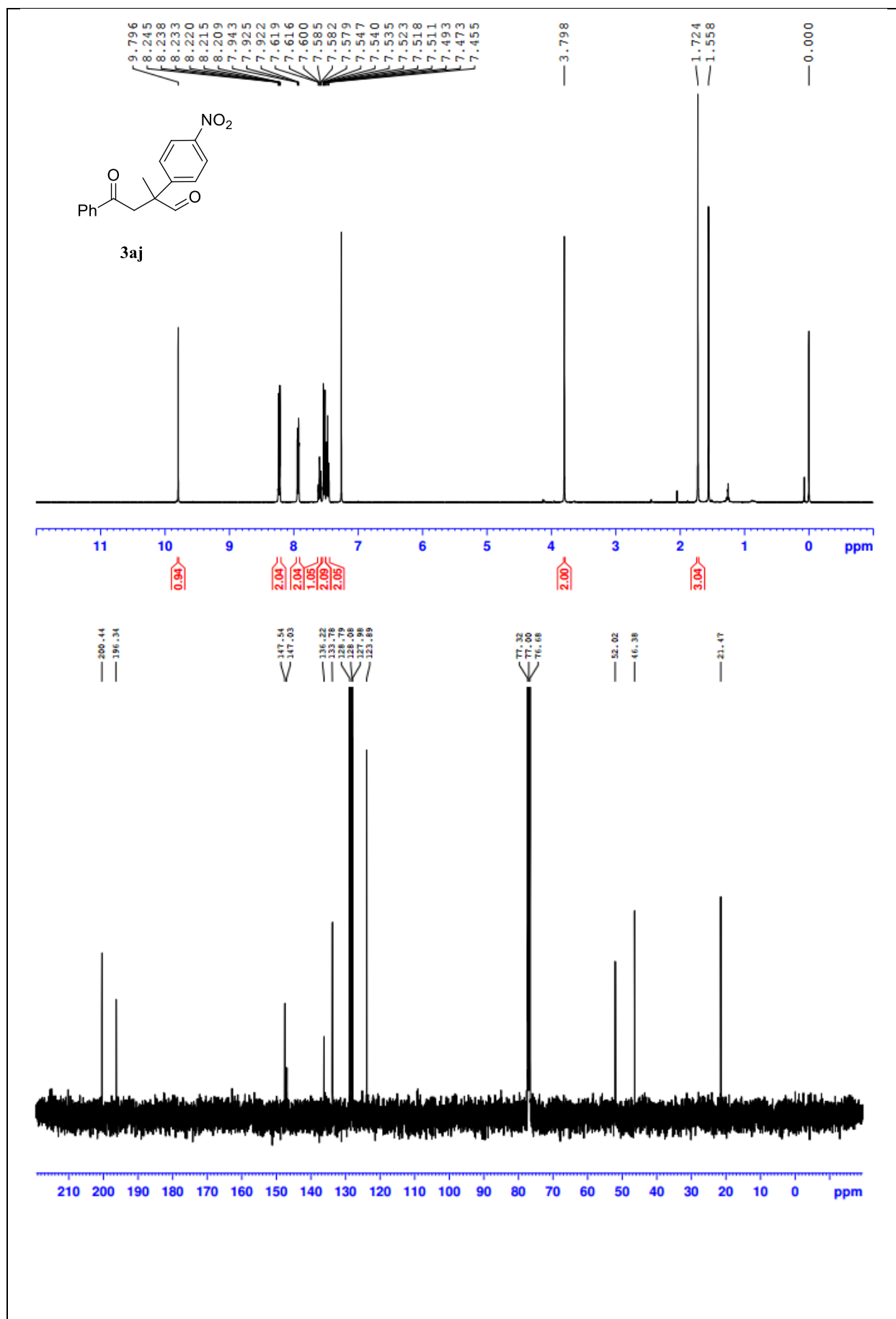


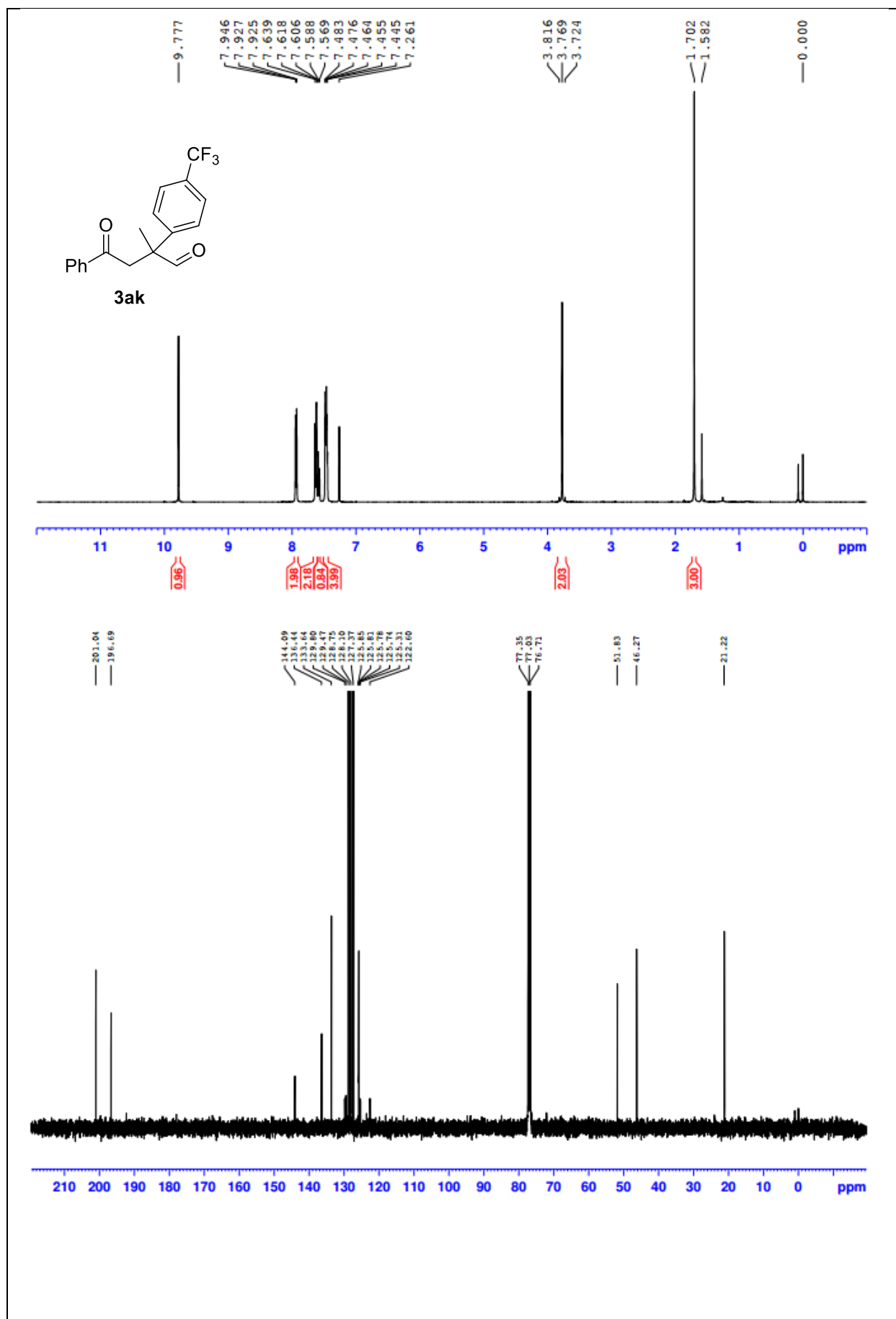


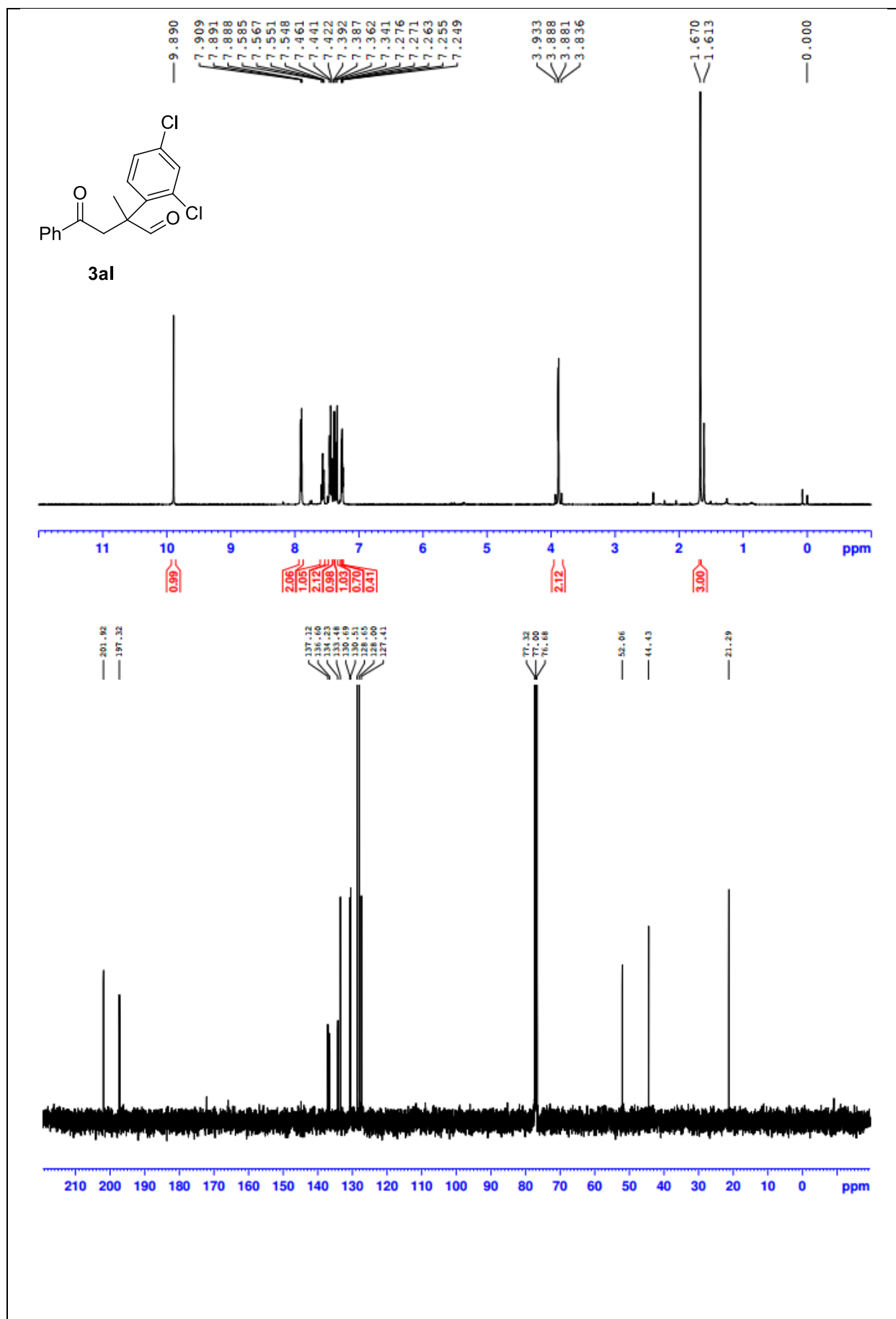


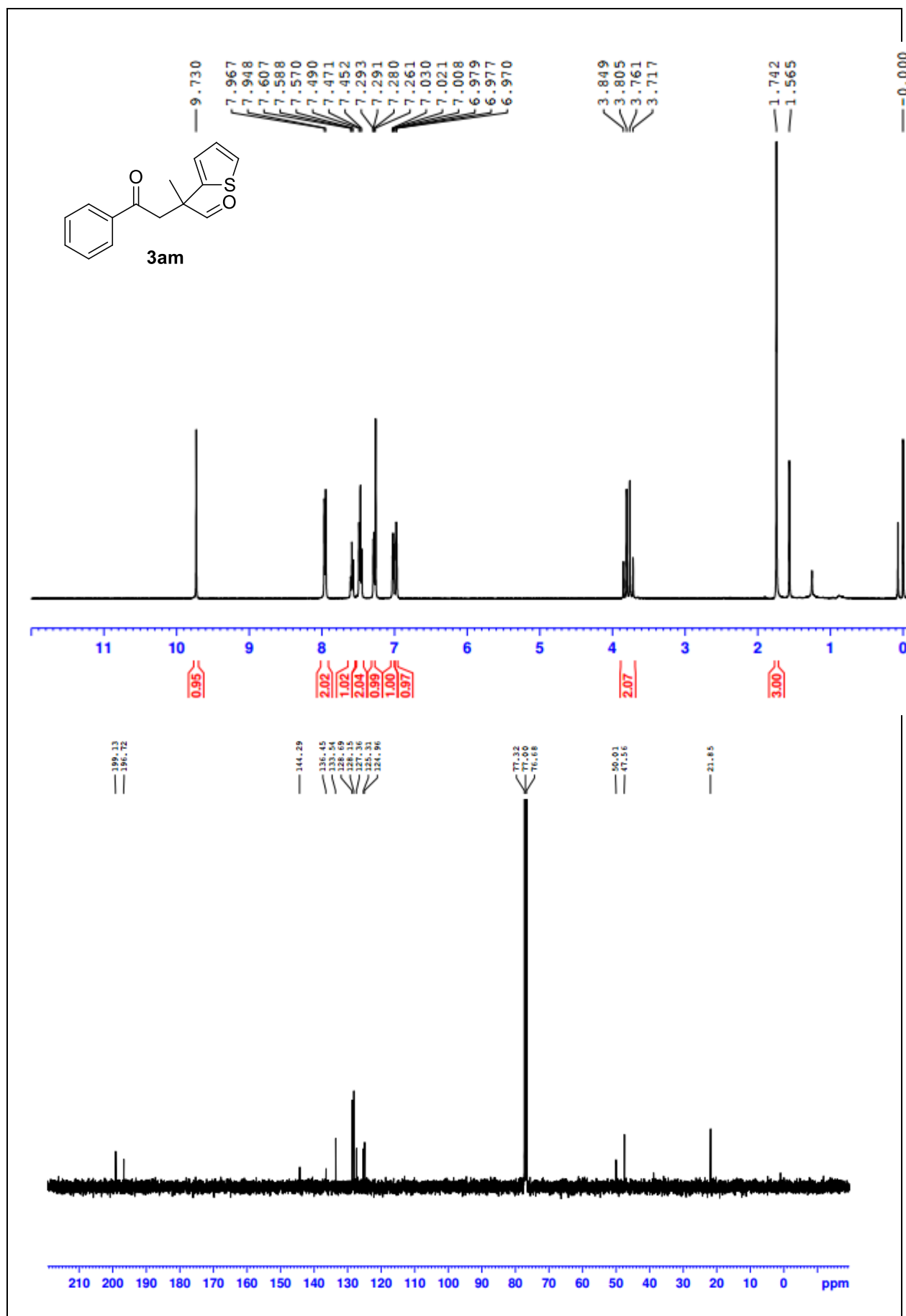


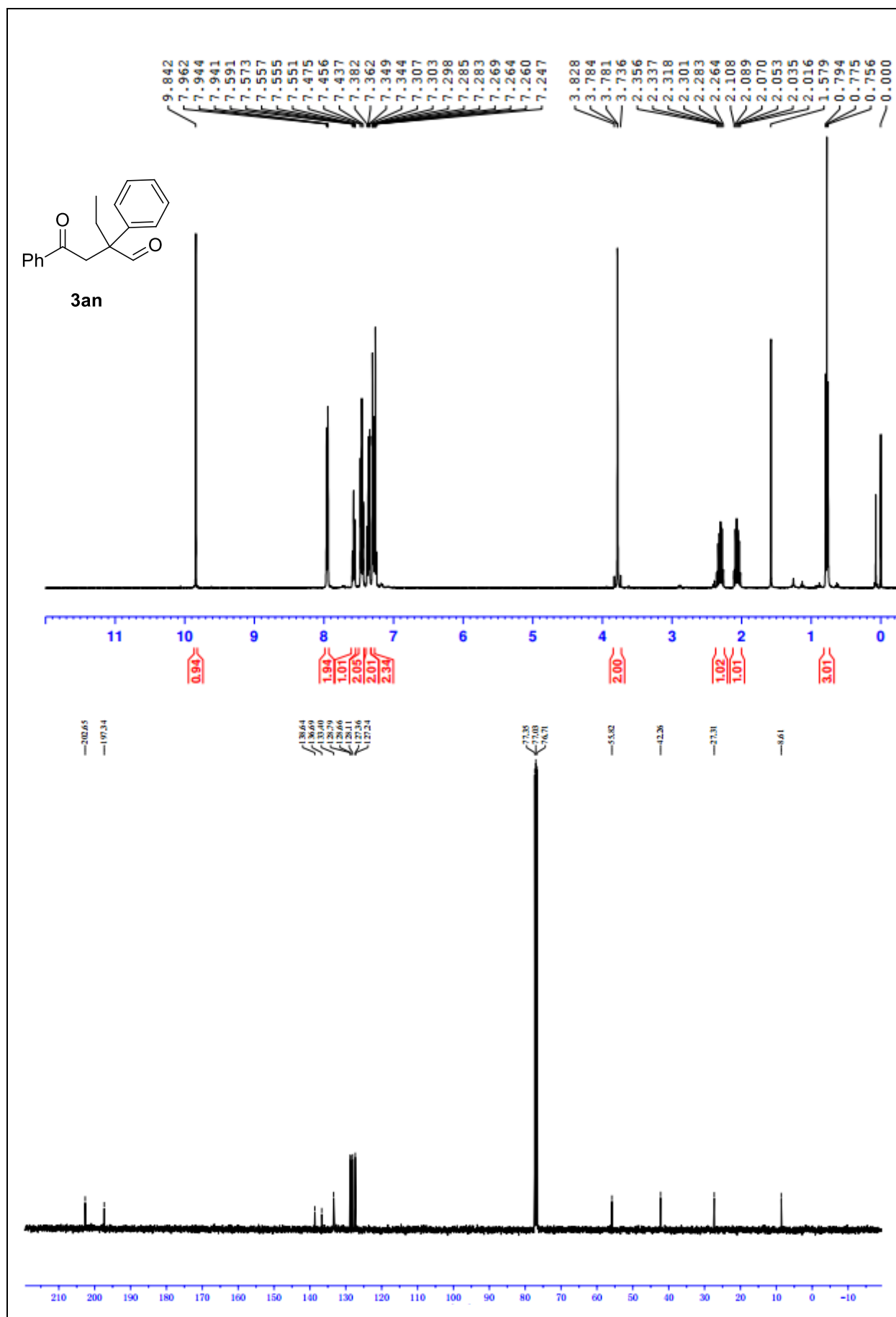


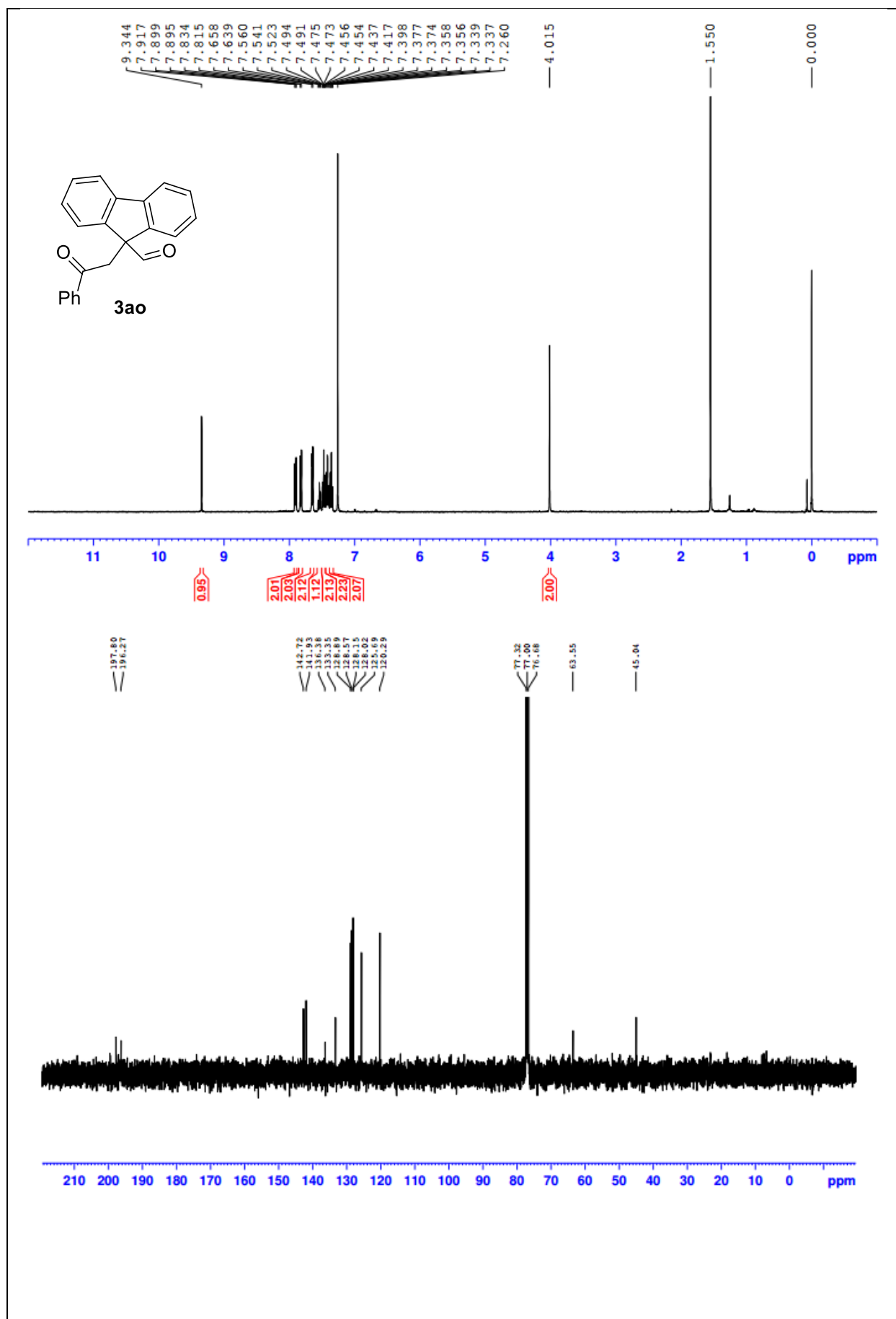


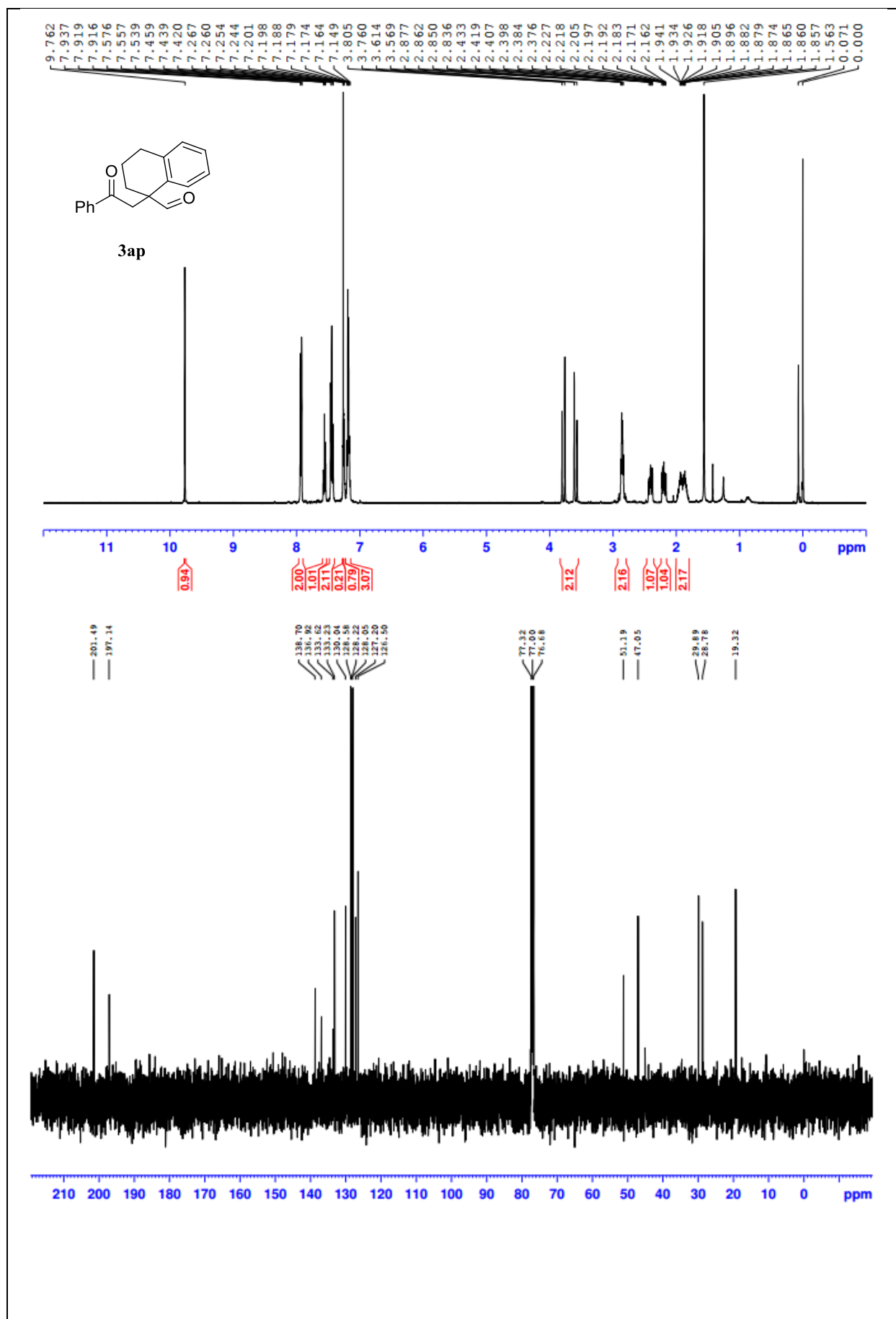


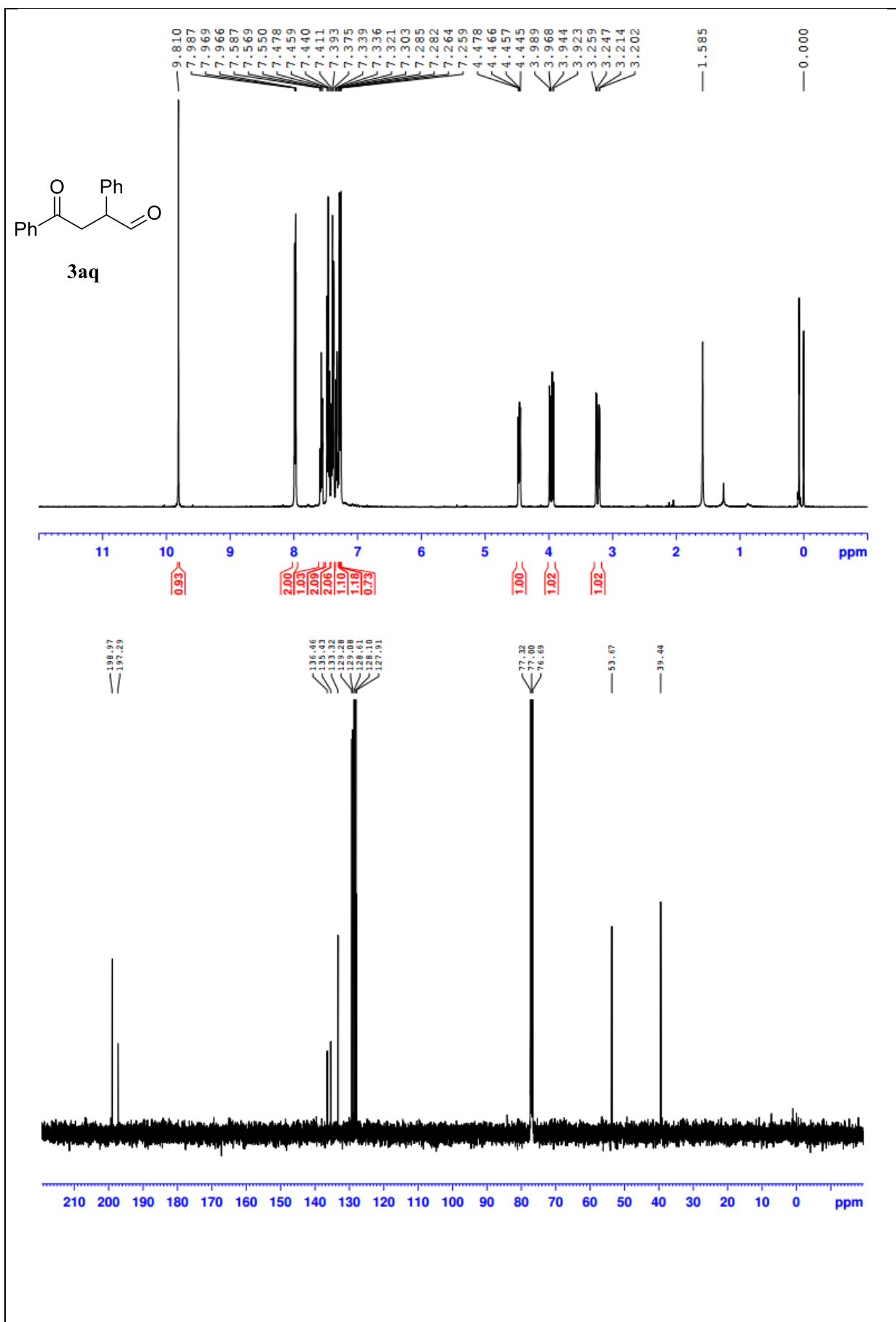


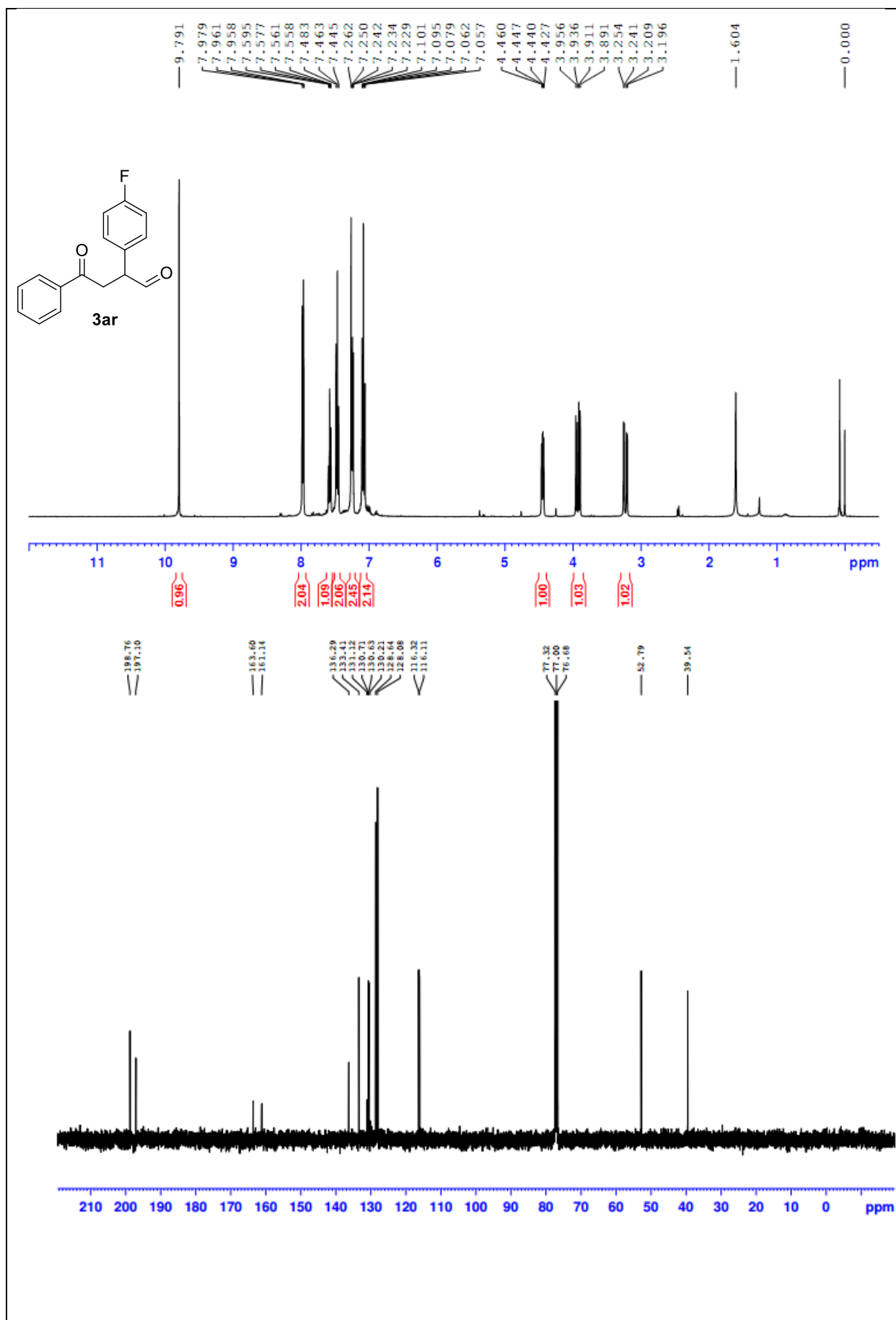


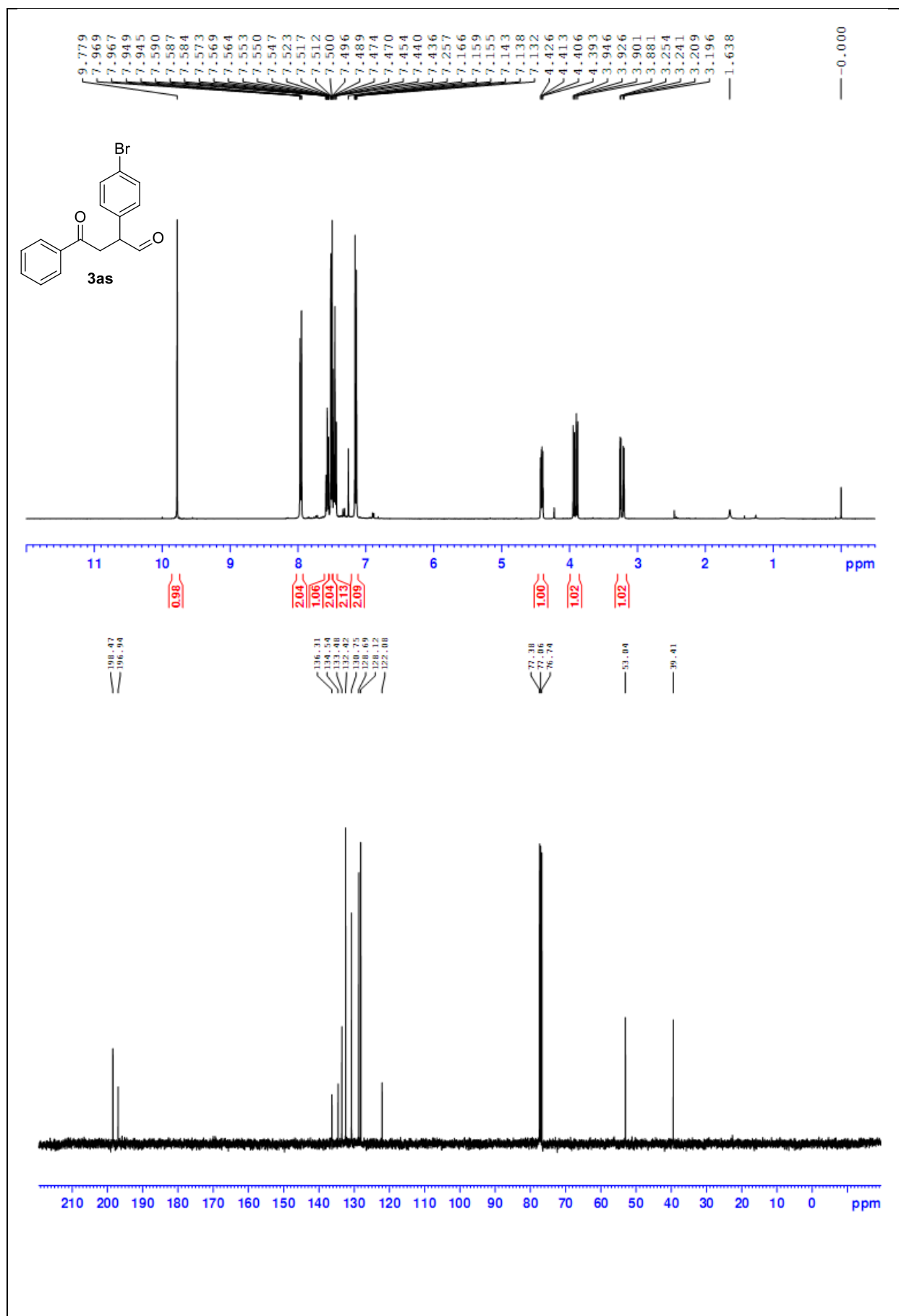


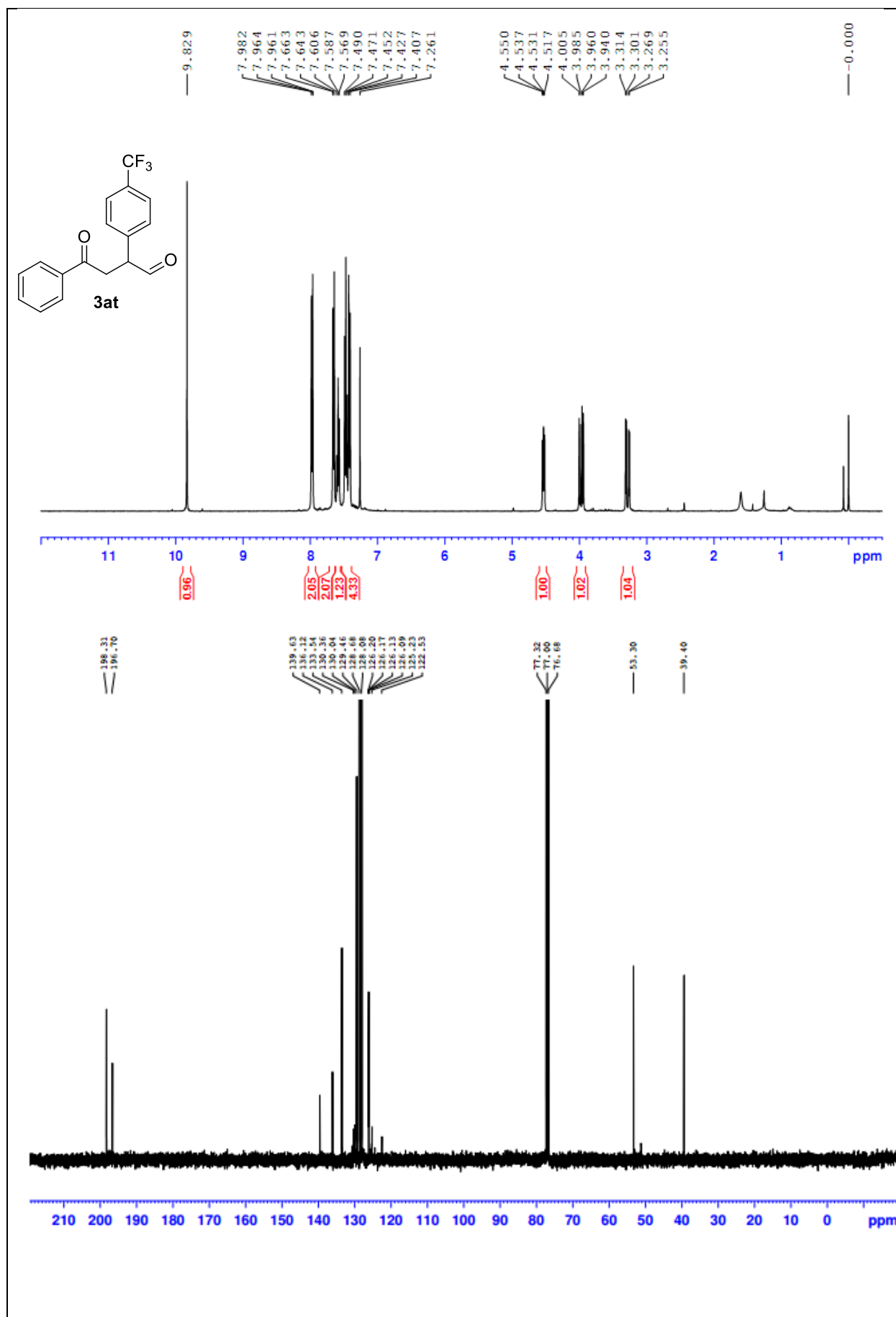


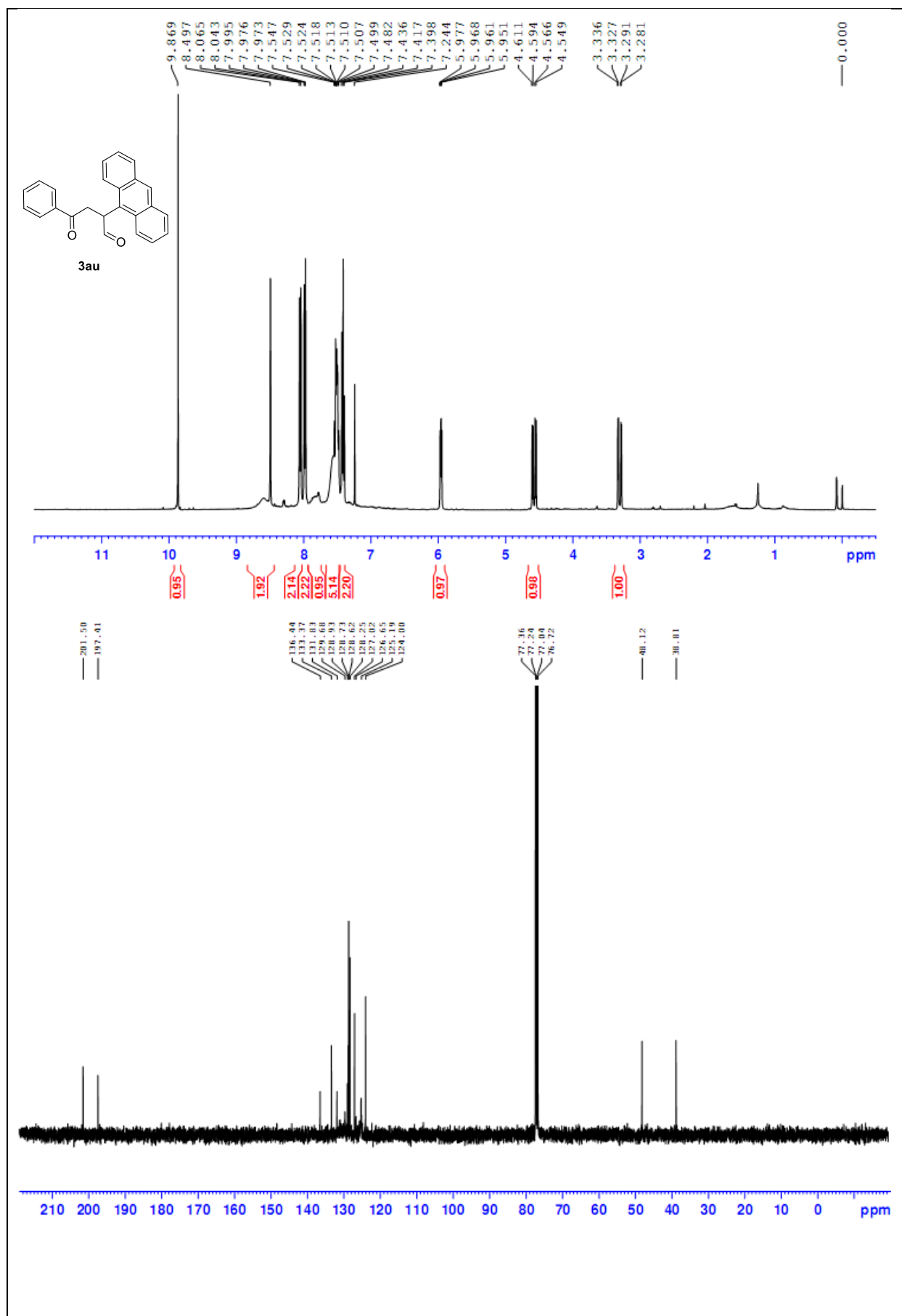












NMR Spectra for applications of 1, 4-ketoaldehydes

