

SUPPORTING INFORMATION

Radical–Polar Crossover Reactions: Oxidative Coupling of 1,3-dioxolanes with Electron-Deficient Alkenes and Vinylarenes Based on a Radical Addition and Kornblum–DeLaMare Rearrangement

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I. General Information

All manipulations were carried out under air atmosphere. Co(salen) and TBHP (70% aqueous solution) were purchased from Sigma-Aldrich. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on Bruker 400 M spectrometers using CDCl_3 as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^1H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference; ^{13}C NMR spectra was recorded with CDCl_3 ($\delta = 77.0$ ppm) as internal reference.

II. General procedures for reactions

General procedures for products 4, 5, 7, 8, 13

Electro-deficient alkenes (0.2 mmol), Vinylarenes (0.4 mmol), masked aldehyde/THF (1.6 mmol), Co(salen) (0.004 mmol), DBU (0.2 mmol), TBHP (7 equiv, 70% aqueous solution) and 0.5 mL acetonitrile were added to a tube under air. The reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, extracted repeatedly with ethyl acetate, dried over MgSO_4 . It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded product with Petroleum/Ethyl acetate mixtures.

General procedures for product 10

1.0 mmol of **4a** in methanol (5.0 mL) in the presence of 10% TsOH under reflux for 3 h, and the reaction mixture was treated with 0.1 M HCl at 40 °C for 7 h. After removal of the organic solvent in vacuum, the residue was purified by flash silica gel column chromatographic purification afforded product with Petroleum/Ethyl acetate mixtures.

General procedures for products 11, 14

1.0 mmol of **8a/13** in acetone (5.0 mL) by the use of 5% TsOH at 40 °C for 3 h and then removed of organic solvent in vacuum. The crud product was purified by flash silica gel column chromatographic afforded product with Petroleum/Ethyl acetate mixtures.

General procedures for product 12

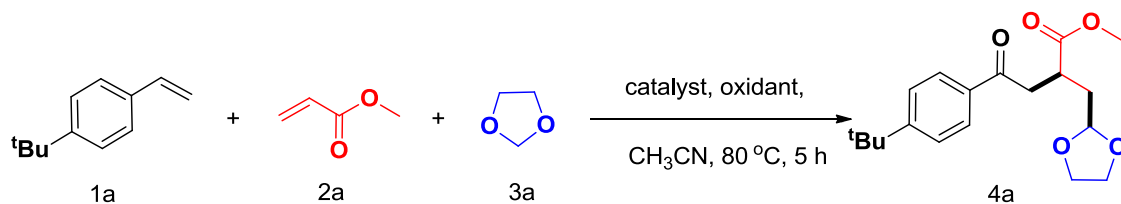
1.0 mmol of **4a**, 1.0 mmol of NaBH_4 and 5 mL methanol were added to a flask. After

the reaction was stirred at room temperature for 1 h, 0.1 mmol of 36% HCl was added and stirred for another 2 h. It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded product with Petroleum/Ethyl acetate mixtures.

General procedures for product 15

A tube was charged with 0.5 mmol of **14**, 2.0 mL methanol and 2.0 ml of NH₃ (7 M in methanol). The solution was stirred at room temperature for 24 h and then removal of the organic solvent in vacuum, followed by flash silica gel column chromatographic purification afforded product with Petroleum/Ethyl acetate mixtures.

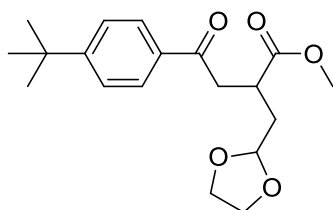
Table S1. Optimization of reaction conditions.^[a]



Entry	Catalyst	Oxidant	Additive	Yield
1	Co(salen)	TBHP	DBU	83 %
2	Co(salen)	-	DBU	N.D. ^[b]
3	-	TBHP	DBU	<5 %
4	Co(salen)	TBHP	-	51 %
5	CoCl ₂	TBHP	DBU	35 %
6	Co(acac) ₂	TBHP	DBU	66 %
7	I ₂	TBHP	DBU	9 %
8	TBAI	TBHP	DBU	<5 %
9	Fe(acac) ₃	TBHP	DBU	16 %
10	Cu(OAc) ₂	TBHP	DBU	64 %
11	AgNO ₃	TBHP	DBU	26 %
12	NiCl ₂	TBHP	DBU	19 %
13	RuCl ₃	TBHP	DBU	30 %
14	PdCl ₂	TBHP	DBU	15 %
15	Mn(acac) ₂	TBHP	DBU	16 %
16	Co(salen)	Oxone	DBU	<5 %
17	Co(salen)	H ₂ O ₂ (30 %)	DBU	N.D. ^[b]
18	Co(salen)	TBPP	DBU	<5 %
19	Co(salen)	CHP	DBU	63 %
20	Co(salen)	DTBP	DBU	N.D. ^[b]
21	Co(salen)	O ₂	DBU	N.D. ^[b]
22	Co(salen)	TBHP	Cs ₂ CO ₃	32 %
23	Co(salen)	TBHP	Et ₃ N	39 %
24	Co(salen)	TBHP	NaOAc	45 %
25	Co(salen)	TBHP	DABCO	69 %
26	Co(salen)	TBHP	DMAP	42 %

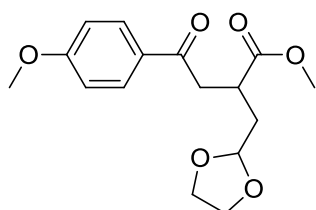
[a] 0.2 mmol of **2a**, 2.0 equiv of **1a**, 8.0 equiv of **3a**, 2 mmol % of catalyst, 1.0 equiv additive, and 7.0 equiv oxidant, 0.5 mL CH₃CN at 80 °C for 5 h. [b] Not detected.

Compound characterizations



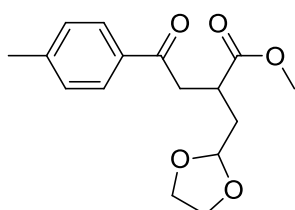
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (4a).

Colorless oil, 83% yield (56 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 3.97 – 3.94 (m, 2H), 3.85 – 3.82 (m, 2H), 3.70 (s, 3H), 3.52 – 3.45 (m, 1H), 3.30 – 3.21 (m, 2H), 2.20 – 2.14 (m, 1H), 1.94 – 1.89 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 175.4, 156.8, 133.9, 127.9, 125.4, 102.7, 64.9, 64.8, 51.9, 40.3, 35.9, 35.4, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{19}\text{H}_{27}\text{O}_5$: 335.1858, Found: 335.1865 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1732, 1685, 1585, 1569, 1484, 1437, 1214, 1168, 816.

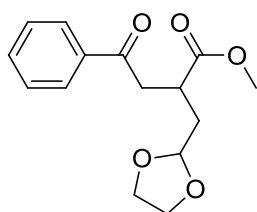


Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-methoxyphenyl)-4-oxobutanoate (4b).

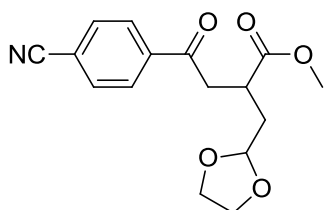
Colorless oil, 75% yield (46 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 3.98 – 3.82 (m, 7H), 3.70 (s, 3H), 3.52 – 3.42 (m, 1H), 3.29 – 3.17 (m, 2H), 2.19 – 2.13 (m, 1H), 1.97 – 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 175.6, 163.5, 130.3, 129.6, 113.6, 102.7, 64.9, 64.8, 55.4, 51.90, 40.1, 36.0, 35.5; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{16}\text{H}_{21}\text{O}_6$: 309.1338, Found: 309.1356 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1732, 1674, 1599, 1576, 1510, 158, 1258, 1220, 1165, 830.



Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-oxo-4-(p-tolyl)butanoate (4c). Colorless oil, 82% yield (48 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 4.03 – 3.96 (m, 2H), 3.88 – 3.82 (m, 2H), 3.70 (s, 3H), 3.50 – 3.44 (m, 1H), 3.28 – 3.20 (m, 2H), 2.41 (s, 3H), 2.18 – 2.14 (m, 1H), 1.98 – 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 175.5, 143.9, 134.0, 129.2, 128.1, 102.7, 64.9, 64.8, 51.9, 40.3, 36.0, 35.4, 21.6; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{16}\text{H}_{21}\text{O}_5$: 293.1389, Found: 293.1395 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1732, 1681, 1607, 1573, 1437, 1223, 1167, 810.

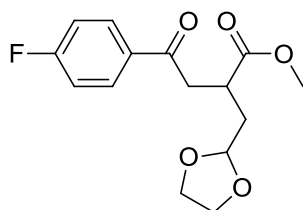


Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-oxo-4-phenylbutanoate (4d). Colorless oil, 61% yield (34 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 4.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 3.96 – 3.92 (m, 2H), 3.88 – 3.82 (m, 2H), 3.71 (s, 3H), 3.54 – 3.47 (m, 1H), 3.30 – 3.23 (m, 2H), 2.21 – 2.15 (m, 1H), 1.99 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 175.4, 136.5, 133.1, 128.5, 127.8, 102.7, 64.84, 64.79, 51.9, 40.3, 35.9, 35.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{15}\text{H}_{18}\text{O}_5\text{Na}$: 301.1052, Found: 301.1062 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1684, 1597, 1580, 1448, 1216, 1168, 754, 690.



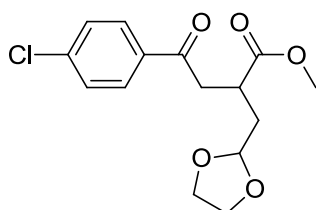
Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-cyanophenyl)-4-oxobutanoate (4e). Colorless oil, 33% yield (20 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 4.97 (t, J = 4.0 Hz, 1H), 3.98 – 3.91 (m, 2H), 3.87 – 3.82 (m, 2H), 3.71 (s, 3H), 3.563 – 3.49 (m, 1H), 3.32 – 3.22 (m, 2H), 2.22 – 2.16 (m, 1H), 2.01 – 1.94 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 175.0, 139.5, 132.4, 128.4, 117.8, 116.3, 102.6, 64.83, 64.77, 52.0, 40.4, 35.8, 35.0; HRMS (ESI-TOF): Anal.

Calcd. For $C_{16}H_{17}NO_5Na$: 326.1004, Found:326.0999 ($M+Na^+$); IR (neat, cm^{-1}): ν 2231, 1731, 1691, 1607, 1597, 1437, 1215, 1168, 827.



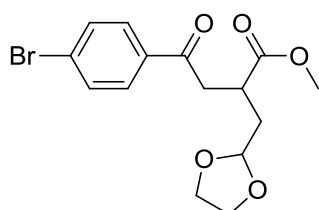
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-fluorophenyl)-4-oxobutanoate (4f).

Colorless oil, 76% yield (45 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2H), 7.13 (t, J = 8.0 Hz, 2H), 4.97 (t, J = 4.0 Hz, 1H), 3.98 – 3.91 (m, 2H), 3.88 – 3.82 (m, 2H), 3.70 (s, 3H), 3.51 – 3.45 (m, 1H), 3.29 – 3.19 (m, 1H), 2.20 – 2.14 (m, 1H), 1.98 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 175.2, 166.9, 164.3, 132.9, 132.9, 130.6, 130.5, 115.6, 115.4, 102.6, 64.8, 64.7, 51.8, 40.1, 35.8, 35.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{17}FO_5Na$: 319.0958, Found:319.0962 ($M+Na^+$); IR (neat, cm^{-1}): ν 1732, 1685, 1596, 1507, 1437, 1221, 1156, 832.



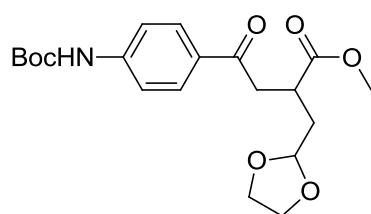
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-chlorophenyl)-4-oxobutanoate (4g).

Colorless oil, 65% yield (41 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 4.97 (t, J = 4.0 Hz, 1H), 3.97 – 3.91 (m, 2H), 3.85 – 3.82 (m, 2H), 3.70 (s, 3H), 3.52 – 3.44 (m, 1H), 3.29 – 3.19 (m, 2H), 2.20 – 2.14 (m, 1H), 1.98 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 175.2, 139.3, 134.6, 129.3, 128.7, 102.6, 64.80, 64.75, 51.9, 40.2, 35.8, 35.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{17}^{35}ClO_5Na$: 335.0662, $C_{15}H_{17}^{35}Cl^{37}ClO_5Na$: 337.0633, Found:335.0664, 337.0633 ($M+Na^+$); IR (neat, cm^{-1}): ν 1733, 1683, 1605, 1590, 1488, 1437, 1218, 1168, 824.



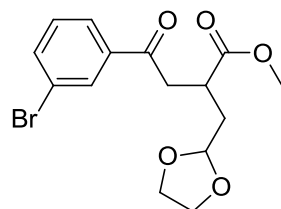
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-bromophenyl)-4-oxobutanoate (4h).

Colorless oil, 71% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 4.97 (t, J = 4.0 Hz, 1H), 3.97 – 3.91 (m, 2H), 3.88 – 3.82 (m, 2H), 3.70 (s, 3H), 3.50 – 3.43 (m, 1H), 3.29– 3.18 (m, 2H), 2.19 – 2.14 (m, 1H), 1.98 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 175.3, 135.2, 131.8, 129.5, 128.3, 102.6, 64.9, 64.8, 52.0, 40.2, 36.0, 35.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{15}\text{H}_{17}^{79}\text{BrO}_5\text{Na}$: 379.0157, $\text{C}_{15}\text{H}_{17}^{79}\text{Br}^{81}\text{BrO}_5\text{Na}$:381.0137, Found: 379.0147, 381.0140 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1685, 1585, 1569, 1484, 1214, 1194, 816.



Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-((tert-butoxycarbonyl)amino)phenyl)-4-oxobutanoate (4i).

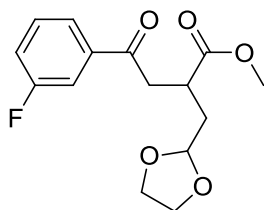
Colorless oil, 49% yield (39 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 12.0 Hz, 2H), 7.36 (s, 1H), 4.98 (t, J = 4.0 Hz, 1H), 3.98 – 3.97 (m, 2H), 3.86 – 3.83 (m, 2H), 3.69 (s, 3H), 3.53 – 3.46 (m, 1H), 3.31 – 3.21 (m, 2H), 2.21 – 2.15 (m, 1H), 1.99 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 175.5, 152.2, 143.2, 130.8, 129.3, 117.3, 102.6, 80.9, 64.73, 64.68, 51.8, 40.0, 35.9, 35.3, 28.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{28}\text{NO}_7$: 394.1866, Found:394.1862 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 3335, 1728, 1675, 1602, 1589, 1525, 1226, 1150,1438, 834.



Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(3-bromophenyl)-4-oxobutanoate (4j).

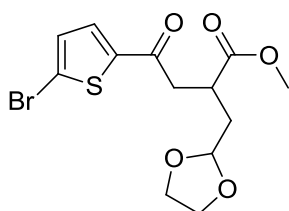
Colorless oil, 65% yield (47 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 4.97 (t, J = 4.0 Hz, 1H), 3.98 – 3.94 (m, 2H), 3.85 – 3.82 (m, 2H), 3.70 (s, 3H), 3.50 – 3.44 (m, 1H), 3.29 – 3.19 (m, 2H), 2.21 – 2.14 (m, 1H), 1.99 – 1.92 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ

196.6, 175.2, 138.2, 135.9, 131.0, 130.1, 126.5, 122.8, 102.7, 64.9, 64.8, 52.0, 40.3, 35.8, 35.2; HRMS(ESI-TOF):Anal.Calcd.For $^{15}\text{H}_{18}^{79}\text{BrO}_5$: 357.0338, $\text{C}_{15}\text{H}_{18}^{79}\text{Br}^{81}\text{BrO}_5$:359.0317, Found: 357.0349, 359.0328 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1734, 1682, 1605, 1568, 1437, 1221, 1167, 1109, 826, 739.



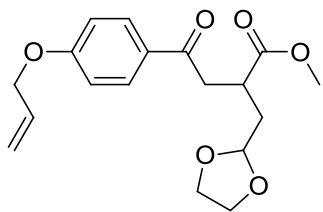
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(3-fluorophenyl)-4-oxobutanoate (4k).

Colorless oil, 67% yield (40 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 12.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.27 (t, J = 8.0 Hz, 1H), 4.98 (t, J = 6.0 Hz, 1H), 3.98 – 3.97 (m, 2H), 3.86 – 3.83 (m, 2H), 3.71 (s, 3H), 3.53 – 3.46 (m, 1H), 3.31 – 3.21 (m, 2H), 2.21 – 2.15 (m, 1H), 1.99 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 175.0, 163.8, 161.5, 138.6, 138.6, 130.2, 130.2, 123.7, 120.2, 120.0, 114.8, 114.6, 102.7, 64.90, 64.85, 52.0, 40.5, 35.9, 35.2; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{15}\text{H}_{17}\text{FO}_5\text{Na}$: 319.0958, Found:319.0977 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1688, 1614, 1588, 1486, 1438, 1240, 1166, 788, 683.



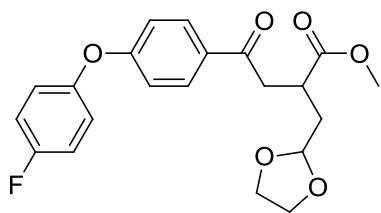
Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(5-bromothiophen-2-yl)-4-oxobutanoate (4l).

Colorless oil, 44% yield (32 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 4.0 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 4.96 (t, J = 4.0 Hz, 1H), 3.97 – 3.91 (m, 2H), 3.88 – 3.82 (m, 2H), 3.69 (s, 3H), 3.38 – 3.32 (m, 1H), 3.27 – 3.22 (m, 1H), 3.14 – 3.08 (m, 1H), 2.20 – 2.13 (m, 1H), 1.97-1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 189.8, 175.0, 145.2, 132.1, 131.2, 122.7, 102.7, 64.91, 64.85, 52.0, 40.2, 36.0, 35.2; HRMS (ESI-TOF):Anal.Calcd. For $\text{C}_{13}\text{H}_{15}^{79}\text{BrSO}_5\text{Na}$:384.9721, $\text{C}_{15}\text{H}_{17}^{79}\text{Br}^{81}\text{BrO}_5\text{Na}$:386.9701, Found: 384.9722, 386.9704 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1786, 1740, 1585, 1549, 1441, 1087, 1046, 880.



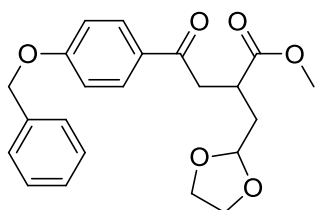
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-(allyloxy)phenyl)-4-oxobutanoate (4m).

Colorless oil, 62% yield (42 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 12.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.10 - 6.00 (m, 1H), 5.45 - 5.40 (m, 1H), 5.33 - 5.31 (m, 1H), 4.98 (t, $J = 6.0$ Hz, 1H), 4.61 - 4.59 (m, 2H), 3.97 - 3.91 (m, 2H), 3.88 - 3.82 (m, 2H), 3.70 (s, 3H), 3.47 - 3.41 (m, 1H), 3.26 - 3.17 (m, 2H), 2.19 - 2.13 (m, 1H), 1.97 - 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.7, 175.4, 162.4, 132.3, 130.1, 129.7, 118.0, 114.3, 102.8, 68.69, 64.8, 64.7, 51.8, 40.0, 36.0, 35.4; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{18}\text{H}_{22}\text{O}_6\text{Na}$: 357.1314, Found: 357.1313 ($\text{M} + \text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1675, 1598, 1575, 1509, 1437, 1256, 1166, 829.



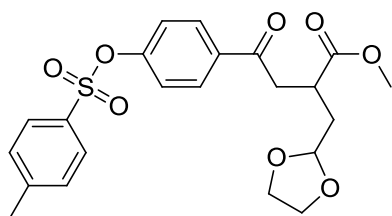
Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(4-fluorophenoxy)phenyl)-4-oxobutanoate (4n).

Colorless oil, 61% yield (47 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.11 - 7.02 (m, 4H), 6.96 (d, $J = 8.0$ Hz, 2H), 4.97 (t, $J = 4.0$ Hz, 1H), 4.02 - 3.88 (m, 2H), 3.84 - 3.77 (m, 2H), 3.70 (s, 3H), 3.52 - 3.42 (m, 1H), 3.30 - 3.17 (m, 2H), 2.19 - 2.13 (m, 1H), 1.97 - 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.3, 175.4, 162.1, 160.6, 158.2, 151.1, 151.1, 131.3, 130.3, 121.7, 121.6, 116.8, 116.7, 116.5, 102.7, 64.84, 64.79, 51.9, 40.1, 36.0, 35.4; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{21}\text{H}_{21}\text{FO}_6\text{Na}$: 411.1220, Found: 411.1216 ($\text{M} + \text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1680, 1604, 1593, 1580, 1496, 1437, 1250, 1213, 853.



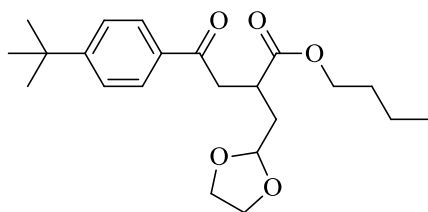
Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-(benzyloxy)phenyl)-4-oxobutanoate (4o).

Colorless oil, 60% yield (46 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 8.0 Hz, 2H), 7.49 – 7.32 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 5.13 (s, 2H), 4.97 (t, J = 4.0 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.84 – 3.81 (m, 2H), 3.70 (s, 3H), 3.47– 3.41 (m, 1H), 3.27 – 3.16 (m, 2H), 2.19– 2.13 (m, 1H), 1.97 – 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 175.5, 162.5, 136.0, 130.2, 129.8, 128.5, 128.1, 127.3, 114.4, 102.7, 69.95, 64.8, 64.7, 51.8, 40.0, 36.0, 35.4; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{22}\text{H}_{24}\text{O}_6\text{Na}$: 407.1471, Found:407.1474 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1674, 1598, 1575, 1509, 1437, 1219, 1166, 829.



Methyl 2-((1, 3-dioxolan-2-yl)methyl)-4-oxo-4-(4-(tosyloxy)phenyl)butanoate (4p).

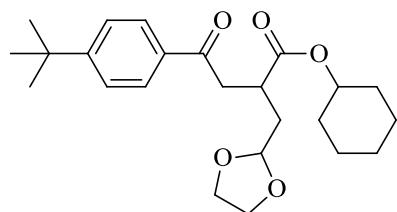
Colorless oil, 58% yield (52 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.96 (t, J = 4.0 Hz, 1H), 4.02 – 3.91 (m, 2H), 3.85 – 3.81 (m, 2H), 3.70 (s, 3H), 3.49 – 3.43 (m, 1H), 3.39 – 3.17 (m, 2H), 2.46 (s, 3H), 2.19 – 2.13 (m, 1H), 1.97 – 1.91 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.6, 175.3, 152.9, 145.7, 135.1, 131.9, 129.9, 129.7, 128.4, 122.4, 102.7, 64.9, 64.8, 51.9, 40.3, 35.8, 35.2, 21.6; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{22}\text{H}_{24}\text{SO}_8\text{Na}$: 471.1090, Found:471.1087 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1732, 1686, 1596, 1498, 1437, 1176, 1152, 842.



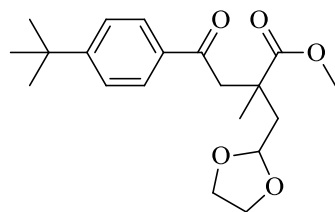
Butyl 2-((1, 3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (5a).

Colorless oil, 68% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 2H), 3.96 – 3.88 (m, 2H), 3.83 – 3.82 (m, 2H), 3.50 – 3.44 (m, 1H), 3.28 – 3.19 (m, 2H), 2.20 –

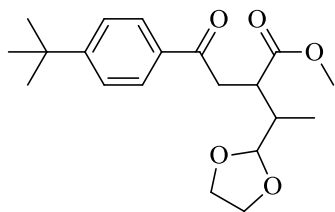
2.16 (m, 1H), 1.96 – 1.91 (m, 1H), 1.63 – 1.56 (m, 2H), 1.38 – 1.34 (m, 11H), 0.90 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 174.8, 156.6, 134.0, 127.9, 125.3, 102.9, 64.8, 64.7, 64.4, 40.1, 36.2, 35.3, 34.9, 30.9, 30.4, 19.0, 13.6; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{22}\text{H}_{32}\text{O}_5\text{Na}$: 399.2147, Found: 399.2156 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1731, 1683, 1605, 1568, 1435, 1169, 1108, 828.



Cyclohexyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (5b). Colorless oil, 63% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 4.98 (t, J = 4.0 Hz, 1H), 4.79 – 4.74 (m, 1H), 3.98 – 3.88 (m, 2H), 3.85 – 3.80 (m, 2H), 3.49 – 3.42 (m, 1H), 3.26 – 3.18 (m, 2H), 2.21 – 2.15 (m, 1H), 1.94 – 1.89 (m, 1H), 1.81 – 1.77 (m, 2H), 1.70 – 1.68 (m, 2H), 1.43 – 1.22 (m, 15H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 173.9, 156.5, 134.1, 127.8, 125.2, 102.8, 72.49, 64.7, 64.6, 40.0, 36.5, 35.3, 34.9, 31.2, 30.9, 25.2, 23.4; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{24}\text{H}_{34}\text{O}_5\text{Na}$: 425.2304, Found: 425.2316 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1726, 1683, 1606, 1568, 1450, 1172, 1109, 828.

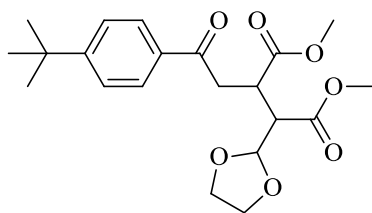


Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-2-methyl-4-oxobutanoate (5c). Colorless oil, 49% yield (34 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 4.96 (t, J = 6.0 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.79 – 3.76 (m, 2H), 3.68 (s, 3H), 3.53 (d, J = 12.0 Hz, 1H), 3.28 (d, J = 12.0 Hz, 1H), 2.11 (d, J = 4.0 Hz, 2H), 1.39 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 176.8, 156.5, 134.4, 127.7, 125.2, 102.0, 64.5, 64.4, 51.8, 46.4, 41.7, 41.5, 35.0, 31.0, 26.5, 23.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{29}\text{O}_5$: 349.2015, Found: 349.2004 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1733, 1684, 1605, 1560, 1434, 1194, 1108, 829.



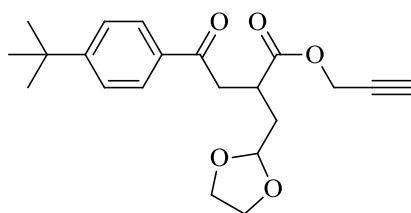
Methyl 2-(1-(1,3-dioxolan-2-yl)ethyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (5d).

Colorless oil, 53% yield (37 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 4.85 (t, J = 4.0 Hz, 1H), 3.97 – 3.91 (m, 2H), 3.90 – 3.82 (m, 2H), 3.68 (s, 3H), 3.58 – 3.49 (m, 1H), 3.41 – 3.30 (m, 1H), 3.20 – 3.19 (m, 1H), 2.36 – 2.17 (m, 1H), 1.34 (s, 9H), 1.04–1.02 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 198.0, 175.1, 174.6, 156.7, 156.6, 134.3, 134.2, 127.9, 125.4, 125.4, 106.1, 105.7, 65.1, 65.0, 64.84, 64.78, 51.8, 51.6, 41.6, 40.8, 38.8, 38.0, 37.9, 36.1, 35.0, 31.0, 12.1, 10.8; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{29}\text{O}_5$: 349.2015, Found: 349.2013 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1733, 1682, 1605, 1568, 1436, 1191, 1108, 826.



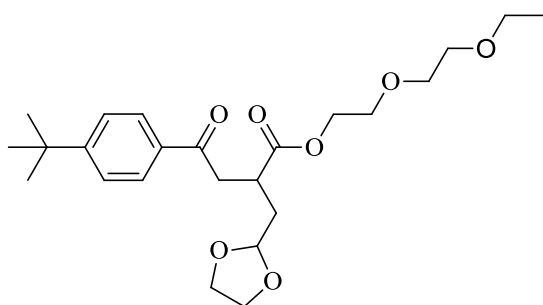
Dimethyl 2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-3-(1,3-dioxolan-2-yl)succinate (5e).

Colorless oil, 74% yield (58 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.93–7.90 (m, 2H), 7.49–7.46 (m, 2H), 5.31 (t, J = 6.0 Hz, 1H), 4.01 – 3.84 (m, 5H), 3.74 (s, 3H), 3.69 (d, J = 4.0 Hz, 3H), 3.64–3.57 (m, 1H), 3.36 – 3.15 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 197.1, 173.5, 173.0, 171.1, 170.6, 156.8, 156.8, 133.9, 133.8, 127.9, 127.9, 125.4, 102.6, 102.5, 65.1, 64.97, 64.95, 64.8, 52.1, 52.0, 50.4, 50.2, 39.1, 38.4, 37.3, 37.2, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{21}\text{H}_{29}\text{O}_7$: 393.1913, Found: 393.1919 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1735, 1682, 1606, 1436, 1225, 1193, 827.

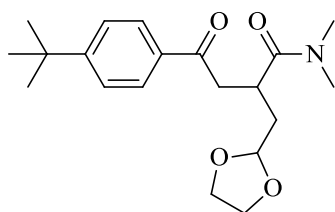


Prop-2-yn-1-yl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate

te (5f). Colorless oil, 47% yield (34 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 5.00 (t, J = 4.0 Hz, 1H), 4.77-4.64 (m, 2H), 4.00 – 3.93 (m, 2H), 3.84 – 3.81 (m, 2H), 3.52 – 3.42 (m, 1H), 3.33 – 3.24 (m, 2H), 2.45 (t, J = 4.0 Hz, 1H), 2.22-2.17 (m, 1H), 2.00 – 1.94 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 174.3, 157.0, 134.0, 128.0, 125.5, 76.68, 74.73, 65.0, 64.9, 52.2, 40.2, 35.9, 35.2, 35.1, 31.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{21}\text{H}_{26}\text{O}_5\text{Na}$: 381.1678, Found: 381.1690 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1743, 1677, 1606, 1270, 1222, 1109, 1046, 879.

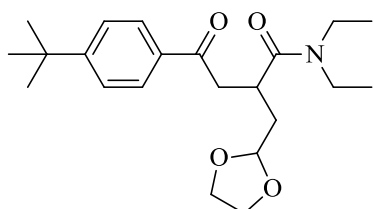


2-(2-ethoxyethoxy)ethyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (5g). Colorless oil, 68% yield (59 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 4.99 (t, J = 4.0 Hz, 1H), 4.26 (t, J = 6.0 Hz, 2H), 3.99 – 3.91 (m, 2H), 3.86 – 3.68 (m, 2H), 3.69 (t, J = 4.0 Hz, 2H), 3.62 – 3.60 (m, 2H), 3.55-3.45 (m, 5H), 3.32 – 3.22 (m, 2H), 2.22 – 2.16 (m, 1H), 1.98-1.92 (m, 1H), 1.34 (s, 9H), 1.19 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 174.9, 156.8, 134.1, 128.0, 125.5, 102.8, 70.5, 69.7, 69.0, 66.6, 64.9, 64.8, 63.7, 40.2, 36.1, 35.3, 35.1, 31.0, 15.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{24}\text{H}_{37}\text{O}_7$: 437.2539, Found: 437.2538 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1733, 1683, 1605, 1222, 1171, 1109, 830.

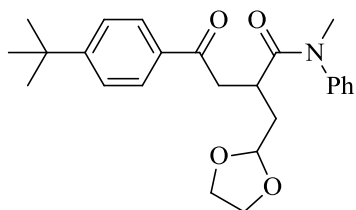


2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-N,N-dimethyl-4-oxobutanamide (5h). Colorless oil, 60% yield (42 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 4.90 (t, J = 4.0 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.84

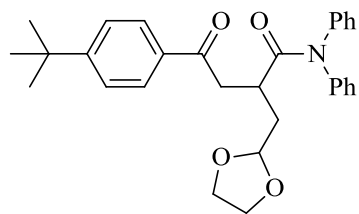
– 3.81 (m, 2H), 3.68-3.58 (m, 2H), 3.24 (s, 3H), 3.12 (d, $J = 16.0$ Hz, 1H), 2.95 (s, 3H), 2.09 – 2.03 (m, 1H), 1.88 – 1.83 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 175.0, 156.7, 134.0, 128.0, 125.4, 102.8, 64.9, 64.8, 42.0, 37.4, 36.3, 35.9, 35.1, 32.0, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{29}\text{NO}_4\text{Na}$: 370.1994, Found: 370.2001 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1680, 1638, 1605, 1567, 1140, 1108, 831.



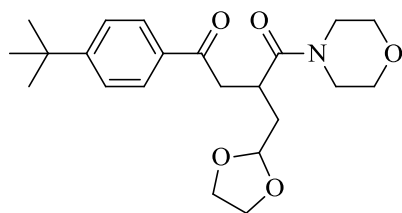
2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-N,N-diethyl-4-oxobutanamide (5i). Colorless oil, 62% yield (47 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 4.91 (t, $J = 4.0$ Hz, 1H), 4.00 – 3.93 (m, 2H), 3.87 – 3.83 (m, 2H), 3.60 – 3.42 (m, 5H), 3.30 – 3.15 (m, 2H), 2.06-2.00 (m, 1H), 1.92 – 1.81 (m, 1H), 1.33 – 1.29 (m, 12H), 1.07 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 173.8, 156.6, 134.3, 128.0, 125.3, 102.7, 64.8, 64.6, 41.9, 41.5, 40.3, 36.4, 34.9, 32.3, 31.0, 14.2, 12.7; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{22}\text{H}_{33}\text{NO}_4\text{Na}$: 398.2307, Found: 398.2312 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1726, 1681, 1605, 1566, 1460, 1220, 1138, 1074, 832.



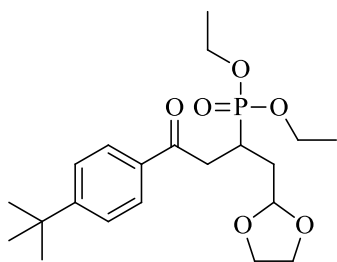
2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-N-methyl-4-oxo-N-phenylbutanamide (5j). Colorless oil, 30% yield (25 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.34 (m, 7H), 4.67 (t, $J = 4.0$ Hz, 1H), 3.82 – 3.72 (m, 4H), 3.62-3.55 (m, 1H), 3.27 (s, 3H), 3.15 – 3.09 (m, 2H), 1.95 – 1.89 (m, 1H), 1.79 – 1.73 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 174.4, 156.5, 143.6, 129.5, 128.0, 127.8, 127.6, 125.3, 102.9, 64.7, 64.5, 41.0, 37.7, 35.9, 35.0, 33.7, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{25}\text{H}_{31}\text{NO}_4\text{Na}$: 432.2151, Found: 432.2165 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1676, 1648, 1604, 1493, 1363, 1136, 1073, 830.



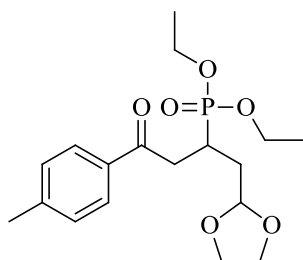
2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxo-N,N-diphenylbutanamide (5k). Colorless oil, 42% yield (40 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.59 – 7.58 (m, 2H), 7.44 – 7.40 (m, 4H), 7.27 – 7.23 (m, 5H), 7.12 (s, 1H), 4.77 (t, J = 4.0 Hz, 1H), 3.86 – 3.65 (m, 5H), 3.45 – 3.42 (m, 1H), 3.20 – 3.15 (m, 1H), 2.11 – 2.05 (m, 1H), 1.92 – 1.86 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.2, 174.5, 156.5, 143.0, 142.5, 134.1, 129.3, 129.1, 128.6, 127.9, 127.6, 126.6, 125.8, 125.2, 102.8, 64.6, 64.4, 41.0, 35.8, 34.9, 34.6, 30; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{30}\text{H}_{33}\text{NO}_4\text{Na}$: 494.2307, Found: 494.2321 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1676, 1660, 1597, 1492, 1454, 1396, 1163, 827.



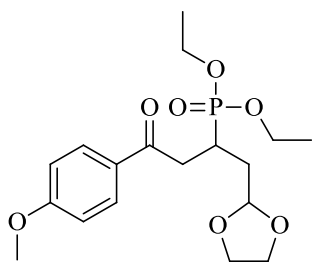
2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-1-morpholinobutane-1,4-dione (5l). Colorless oil, 62% yield (48 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 4.89 (t, J = 4.0 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.88 – 3.79 (m, 4H), 3.74 – 3.58 (m, 8H), 3.1 – 3.08 (m, 1H), 2.11 – 2.05 (m, 1H), 1.89 – 1.82 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 173.6, 156.8, 133.9, 127.9, 125.4, 102.5, 66.8, 66.7, 64.8, 64.8, 46.3, 42.3, 41.9, 36.3, 35.0, 31.3, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{22}\text{H}_{31}\text{NO}_5\text{Na}$: 412.2100, Found: 412.2112 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1734, 1681, 1605, 1567, 1508, 1437, 1222, 1168, 1109, 827.



Diethyl(4-(4-(tert-butyl)phenyl)-1-(1,3-dioxolan-2-yl)-4-oxobutan-2-yl)phosphonate (7a). Colorless oil, 80% yield (66 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 5.03 (t, J = 8.0 Hz, 1H), 4.15 – 4.07 (m, 4H), 3.93 – 3.73 (m, 4H), 3.40 – 3.25 (m, 2H), 3.09 – 2.98 (m, 1H), 2.25 – 2.15 (m, 1H), 1.88 – 1.79 (m, 1H), 1.34 (s, 9H), 1.31 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 196.8, 156.7, 134.3, 128.0, 125.4, 103.2, 103.0, 64.8, 64.5, 62.0, 61.9, 61.8, 61.7, 37.8, 37.8, 35.0, 33.1, 33.1, 31.0, 27.4, 26.0, 16.3, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{21}\text{H}_{33}\text{PO}_6\text{Na}$: 435.1912, Found: 435.1910 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1684, 1605, 1439, 1231, 1107, 1021, 824.

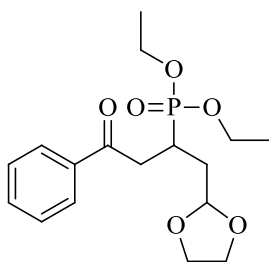


Diethyl (1-(1,3-dioxolan-2-yl)-4-oxo-4-(p-tolyl)butan-2-yl)phosphonate (7b). Colorless oil, 69% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.03 (t, J = 6.0 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.92 – 3.72 (m, 4H), 3.40 – 3.27 (m, 2H), 3.09 – 2.98 (m, 1H), 2.41 (s, 3H), 2.24 – 2.26 (m, 1H), 1.87 – 1.79 (m, 1H), 1.31 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 196.8, 143.7, 134.4, 129.2, 128.1, 103.2, 103.0, 64.7, 64.5, 61.97, 61.90, 61.8, 61.7, 37.7, 37.7, 33.1, 33.0, 27.5, 26.0, 21.6, 16.3, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{18}\text{H}_{27}\text{PO}_6\text{Na}$: 393.1443, Found: 393.1447 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1684, 1608, 1409, 1228, 1025, 808.



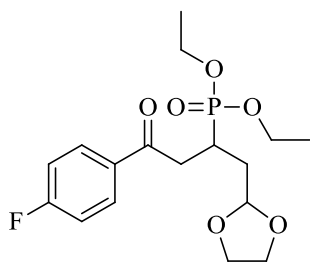
Diethyl(1-(1,3-dioxolan-2-yl)-4-(4-methoxyphenyl)-4-oxobutan-2-yl)phosphonate

(7c). Colorless oil, 63% yield (49 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 5.03 (t, J = 4.0 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.93 – 3.75 (m, 7H), 3.38 – 3.21 (m, 2H), 3.06 – 2.97 (m, 1H), 2.24 – 2.15 (m, 1H), 1.89 – 1.79 (m, 1H), 1.31 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 195.7, 163.4, 130.3, 130.0, 113.7, 103.2, 103.1, 64.8, 64.6, 62.0, 62.0, 61.9, 61.8, 55.5, 37.5, 37.5, 33.2, 33.1, 27.6, 26.2, 16.4, 16.4; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{18}\text{H}_{27}\text{PO}_6\text{Na}$: 409.1392, Found: 409.1410 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1679, 1601, 1578, 1513, 1240, 1173, 1025, 833.



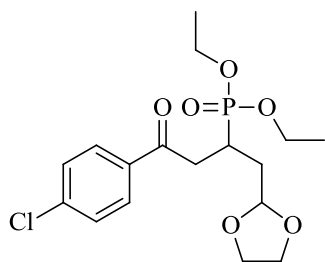
Diethyl (1-(1, 3-dioxolan-2-yl)-4-oxo-4-phenylbutan-2-yl)phosphonate (7d).

Colorless oil, 71% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.96 (m, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 6.0 Hz, 2H), 5.02 (t, J = 4.0 Hz, 1H), 4.15 – 4.08 (m, 4H), 3.92 – 3.74 (m, 4H), 3.38 – 3.32 (m, 2H), 3.10 – 2.99 (m, 1H), 2.27 – 2.17 (m, 1H), 1.90 – 1.80 (m, 1H), 1.31 – 1.27 (m, 6H) ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 197.2, 136.9, 132.9, 128.5, 128.0, 103.1, 103.0, 64.7, 64.5, 62.0, 61.9, 61.8, 61.7, 37.9, 37.9, 33.0, 33.0, 27.5, 26.0, 16.3, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{17}\text{H}_{25}\text{PO}_6\text{Na}$: 379.1286, Found: 379.1275 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1691, 1449, 1226, 1046, 1027, 880.



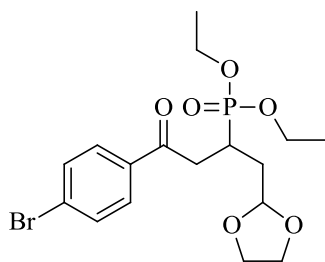
Diethyl(1-(1,3-dioxolan-2-yl)-4-(4-fluorophenyl)-4-oxobutan-2-yl)phosphonate (7e).

Colorless oil, 62% yield (46 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.98 (m, 2H), 7.14 (t, J = 10.0 Hz, 2H), 5.01 (t, J = 4.0 Hz, 1H), 4.12 – 4.07 (m, 4H), 3.91 – 3.74 (m, 4H), 3.35 – 3.29 (m, 2H), 3.07 – 2.96 (m, 1H), 2.26 – 2.17 (m, 1H), 1.89 – 1.79 (m, 1H), 1.32 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 195.7, 166.9, 164.4, 133.3, 133.3, 130.7, 130.6, 115.7, 115.5, 103.2, 103.0, 64.8, 64.5, 62.0, 62.0, 61.9, 61.8, 37.8, 37.8, 32.99, 32.95, 27.6, 26.2, 16.4, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{17}\text{H}_{24}\text{PO}_6\text{Na}$: 397.1192, Found: 397.1203 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1691, 1599, 1509, 1232, 1024, 836.

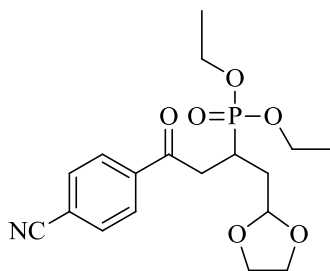


Diethyl (4-(4-chlorophenyl)-1-(1,3-dioxolan-2-yl)-4-oxobutan-2-yl)phosphonate (7f).

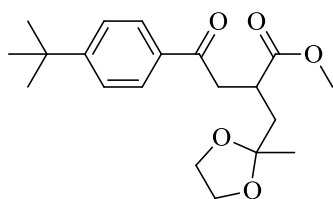
Colorless oil, 65% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.00 (t, J = 4.0 Hz, 1H), 4.15 – 4.07 (m, 4H), 3.88 – 3.73 (m, 4H), 3.34 – 3.29 (m, 2H), 3.07 – 2.95 (m, 1H), 2.26 – 2.17 (m, 1H), 1.88 – 1.79 (m, 1H), 1.32 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 196.1, 139.3, 135.2, 129.4, 128.8, 103.1, 103.0, 64.7, 64.4, 62.0, 62.0, 61.9, 61.8, 37.82, 37.80, 32.93, 32.89, 27.6, 26.1, 16.4, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{17}\text{H}_{24}^{35}\text{ClPO}_6\text{Na}$: 413.0897, $\text{C}_{17}\text{H}_{24}^{35}\text{Cl}^{37}\text{ClPO}_6\text{Na}$: 415.0867, Found: 413.0878, 415.0865 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1693, 1591, 1226, 1046, 1025, 881.



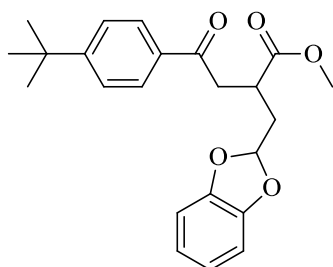
Diethyl (4-(4-bromophenyl)-1-(1,3-dioxolan-2-yl)-4-oxobutan-2-yl)phosphonate (7g). Colorless oil, 60% yield (52 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 4.99 (t, J = 4.0 Hz, 1H), 4.15 – 4.07 (m, 4H), 3.89 – 3.73 (m, 4H), 3.33 – 3.28 (m, 2H), 3.16 – 2.95 (m, 1H), 2.26 – 2.17 (m, 1H), 1.88 – 1.80 (m, 1H), 1.31 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 196.3, 135.7, 131.8, 129.6, 128.1, 103.2, 103.0, 64.8, 64.5, 62.1, 62.0, 61.91, 61.85, 37.9, 37.8, 33.0, 32.9, 27.6, 26.2, 16.4, 16.3; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{17}\text{H}_{24}^{79}\text{BrPO}_6\text{Na}$: 457.0392, $\text{C}_{17}\text{H}_{24}^{79}\text{Br}^{81}\text{BrPO}_6\text{Na}$: 459.0317, Found: 457.0399, 459.0377 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1693, 1587, 1439, 1225, 1070, 1025, 881.



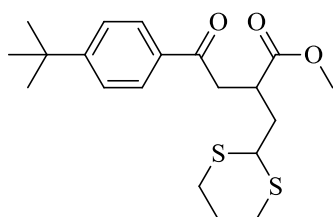
Diethyl (4-(4-cyanophenyl)-1-(1,3-dioxolan-2-yl)-4-oxobutan-2-yl)phosphonate (7h). Colorless oil, 58% yield (44 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 4.97 (t, J = 4.0 Hz, 1H), 4.16 – 4.08 (m, 4H), 3.88 – 3.73 (m, 4H), 3.37 – 3.31 (m, 2H), 3.08 – 2.93 (m, 1H), 2.27 – 2.20 (m, 1H), 1.88 – 1.81 (m, 1H), 1.32 – 1.28 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.3, 196.2, 140.0, 132.4, 128.5, 117.9, 116.2, 103.2, 103.0, 64.8, 64.5, 62.2, 62.1, 62.02, 61.95, 38.24, 38.21, 32.9, 32.8, 27.70, 26.3, 16.41, 16.35; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{17}\text{H}_{24}^{35}\text{ClPO}_6\text{Na}$: 413.0897, $\text{C}_{18}\text{H}_{24}\text{NPO}_6\text{Na}$: 404.1239, Found: 404.1249 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 2234, 1699, 1225, 1046, 1026, 880.



Methyl 4-(4-(tert-butyl)phenyl)-2-((2-methyl-1,3-dioxolan-2-yl)methyl)-4-oxobutanoate (8a). Colorless oil, 73% yield (51 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 3.93-3.92 (m, 4H), 3.69 (s, 3H), 3.43-3.36 (m, 1H), 3.26 – 3.20 (m, 2H), 2.25-2.19 (m, 1H), 1.94-1.89 (m, 1H), 1.36 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 176.1, 156.9, 133.9, 127.9, 125.5, 109.1, 64.5, 51.8, 41.0, 40.4, 36.2, 35.0, 31.0, 24.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{28}\text{O}_5\text{Na}$: 371.1834, Found: 371.1840 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1734, 1682, 1605, 1568, 1437, 1220, 1166, 827.

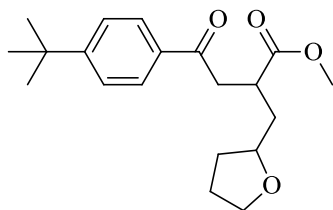


Methyl 2-(benzo[d][1,3]dioxol-2-ylmethyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (8b). Yellow oil, 81% yield (62 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 6.80 – 6.73 (m, 4H), 6.23 (t, J = 4.0 Hz, 1H), 3.70 (s, 3H), 3.5 – 3.48 (m, 1H), 3.41 – 3.35 (m, 1H), 3.29 – 3.24 (m, 1H), 2.50 – 2.43 (m, 1H), 2.27 – 2.21 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 174.8, 157.0, 147.2, 133.8, 128.0, 125.5, 121.5, 109.7, 108.5, 52.1, 40.1, 35.9, 35.5, 35.1, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{23}\text{H}_{26}\text{O}_5\text{Na}$: 405.1678, Found: 405.1677 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1735, 1682, 1605, 1483, 1437, 1231, 1193, 826.

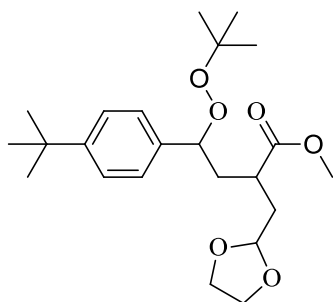


Methyl 2-((1,3-dithian-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-oxobutanoate (8c). Colorless oil, 35% yield (27 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz,

2H), 7.48 (d, $J = 8.0$ Hz, 2H), 4.08 (t, $J = 8.0$ Hz, 1H), 3.71 (s, 3H), 3.48 – 3.36 (m, 2H), 3.21–3.15 (m, 1H), 2.87 – 2.83 (m, 4H), 2.32–2.24 (m, 1H), 2.12 – 1.97 (m, 2H), 1.91 – 1.69 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 174.9, 157.0, 133.9, 128.0, 125.5, 52.0, 44.6, 40.1, 37.9, 37.0, 35.0, 31.0, 29.7, 29.6, 25.7; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{28}\text{S}_2\text{O}_3\text{Na}$: 403.1378, Found:403.1374 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1733, 1681, 1605, 1567, 1435, 1268, 1221, 1192, 1166, 826.

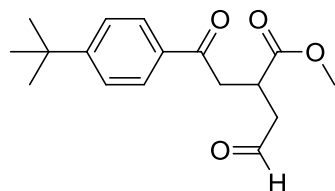


Methyl 4-(4-(tert-butyl)phenyl)-4-oxo-2-((tetrahydrofuran-2-yl)methyl)butanoate (8 d). Colorless oil, 58% yield (39 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 3.92 – 3.80 (m, 2H), 3.70 (s, 3H), 3.50 – 3.40 (m, 1H), 3.26 – 3.17 (m, 2H), 2.06 – 1.69 (m, 6H), 1.50 – 1.46 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 175.8, 156.2, 133.7, 127.8, 124.5, 76.5, 76.4, 67.3, 67.2, 51.3, 40.2, 39.7, 38.0, 37.7, 37.4, 37.0, 34.6, 31.3, 31.1, 30.6, 25.2, 25.1; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{20}\text{H}_{28}\text{O}_4\text{Na}$: 355.1885, Found:355.1882 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1734, 1682, 1605, 1568, 1436, 1221, 1191, 1166, 826.

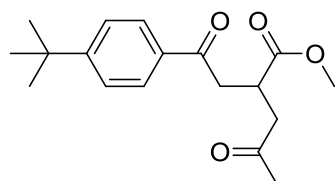


Methyl 2-((1,3-dioxolan-2-yl)methyl)-4-(4-(tert-butyl)phenyl)-4-(tert-butylperoxy)butanoate (9). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 8.0$ Hz, 2H), 7.27 – 7.22 (m, 2H), 4.91 – 4.82 (m, 2H), 3.93 – 3.77 (m, 4H), 3.62 (d, $J = 28.0$ Hz, 3H), 2.88 – 2.61 (m, 1H), 2.37 – 1.99 (m, 3H), 1.87 – 1.81 (m, 1H), 1.31 (s, 9H), 1.19 (d, $J = 8.0$ Hz, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.7, 175.7, 150.5, 150.4, 137.8, 137.5, 126.6, 126.5, 125.1, 125.0, 102.6, 83.6, 83.6, 80.23, 80.18, 64.90, 64.87, 51.6,

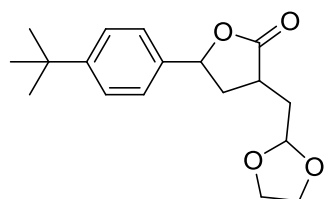
51.5, 37.8, 37.7, 36.8, 36.3, 34.5, 31.3, 26.4; HRMS (ESI-TOF): Anal. Calcd. For $C_{23}H_{36}O_6Na$: 431.2410, Found:431.2403 ($M+Na^+$); IR (neat, cm^{-1}): ν 1736, 1617, 1576, 1508, 1437, 1363, 1241, 1195, 1141, 829.



Methyl 4-(4-(tert-butyl)phenyl)-4-oxo-2-(2-oxoethyl)butanoate (10). Colorless oil, 95% yield (276 mg). 1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 3.71 (s, 3H), 3.55 – 3.46 (m, 2H), 3.28 – 3.22 (m, 1H), 3.03 – 2.97 (m, 1H), 2.83-2.77 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 196.9, 174.2, 157.2, 133.7, 127.9, 125.5, 52.2, 44.6, 39.2, 35.1, 34.4, 31.0; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{22}O_4Na$: 313.1416, Found:313.1412 ($M+Na^+$); IR (neat, cm^{-1}): ν 1730, 1681, 1605, 1568, 1508, 1438, 1223, 1108, 1047, 828.

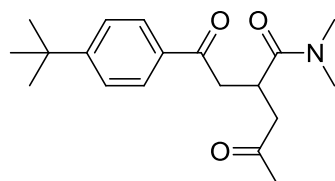


Methyl 2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-4-oxopentanoate (11). Colorless oil, 98% yield (298 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 3.69 (s, 3H), 3.47 – 3.41 (m, 2H), 3.30 – 3.23 (m, 1H), 3.04 – 2.98 (m, 1H), 2.80 – 2.75 (m, 1H), 2.17 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 197.2, 174.7, 157.1, 133.8, 128.0, 125.5, 52.1, 44.0, 39.2, 35.5, 35.1, 31.0, 30.0; HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{24}O_4Na$: 327.1572, Found:327.1582 ($M+Na^+$); IR (neat, cm^{-1}): ν 1735, 1717, 1681, 1605, 1568, 1508, 1436, 1363, 1222, 1192, 1160, 828.



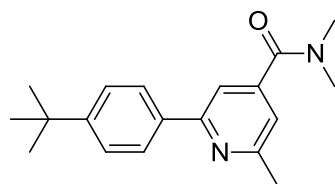
3-((1, 3-dioxolan-2-yl)methyl)-5-(4-(tert-butyl)phenyl)dihydrofuran-2(3H)-one (12). Colorless oil, 78% yield (237 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz,

2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.35 – 5.31 (m, 1H), 5.02 (t, $J = 6.0$ Hz, 1H), 3.99 – 3.93 (m, 2H), 3.88 – 3.82 (m, 2H), 3.00 – 2.92 (m, 1H), 2.87 – 2.80 (m, 1H), 2.44 – 2.39 (m, 1H), 2.03 – 1.94 (m, 1H), 1.84 – 1.77 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.2, 151.5, 135.7, 125.5, 125.3, 102.5, 79.7, 64.9, 64.7, 38.7, 37.4, 34.5, 34.0, 31.2; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{18}\text{H}_{24}\text{O}_4\text{Na}$: 327.1572, Found: 327.1576 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1753, 1512, 1432, 1167, 1088, 1104, 823.



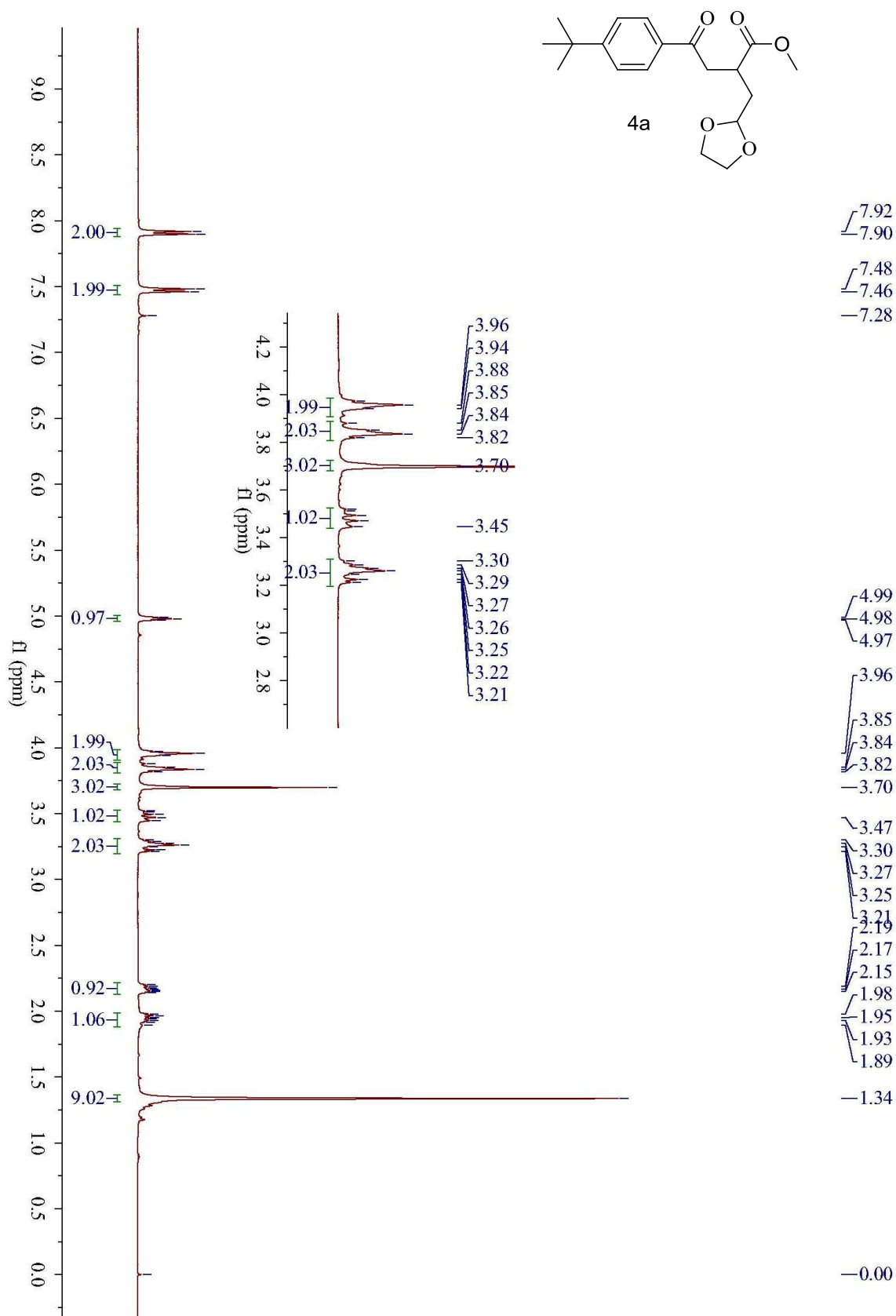
2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-N,N-dimethyl-4-oxopentanamide (14).

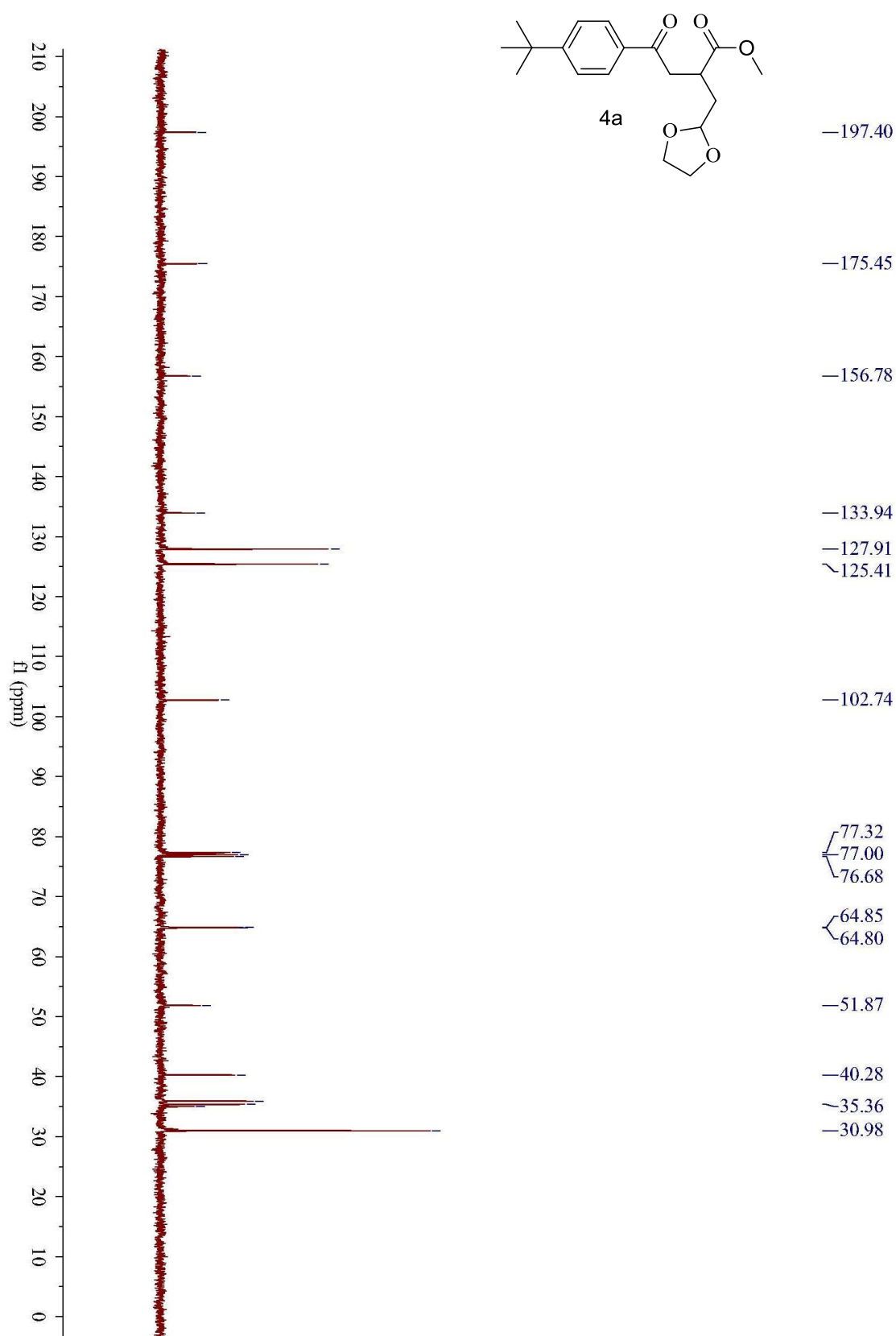
Colorless oil, 97% yield (308 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 3.86 – 3.79 (m, 1H), 3.35 – 3.29 (m, 1H), 3.25 (s, 3H), 3.10 – 2.97 (m, 2H), 2.94 (s, 3H), 2.68 – 2.62 (m, 1H), 2.14 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.0, 197.8, 174.8, 157.1, 133.9, 128.0, 125.9, 125.6, 46.1, 40.9, 37.7, 35.9, 35.1, 31.8, 31.0, 30.0; MS (ESI-quadrupole): Anal. Calcd. For $\text{C}_{19}\text{H}_{28}\text{NO}_3$: 318, Found: 318 ($\text{M}+\text{H}^+$); IR (neat, cm^{-1}): ν 1718, 1710, 1681, 1601, 1163, 1123, 1034, 1010, 819.

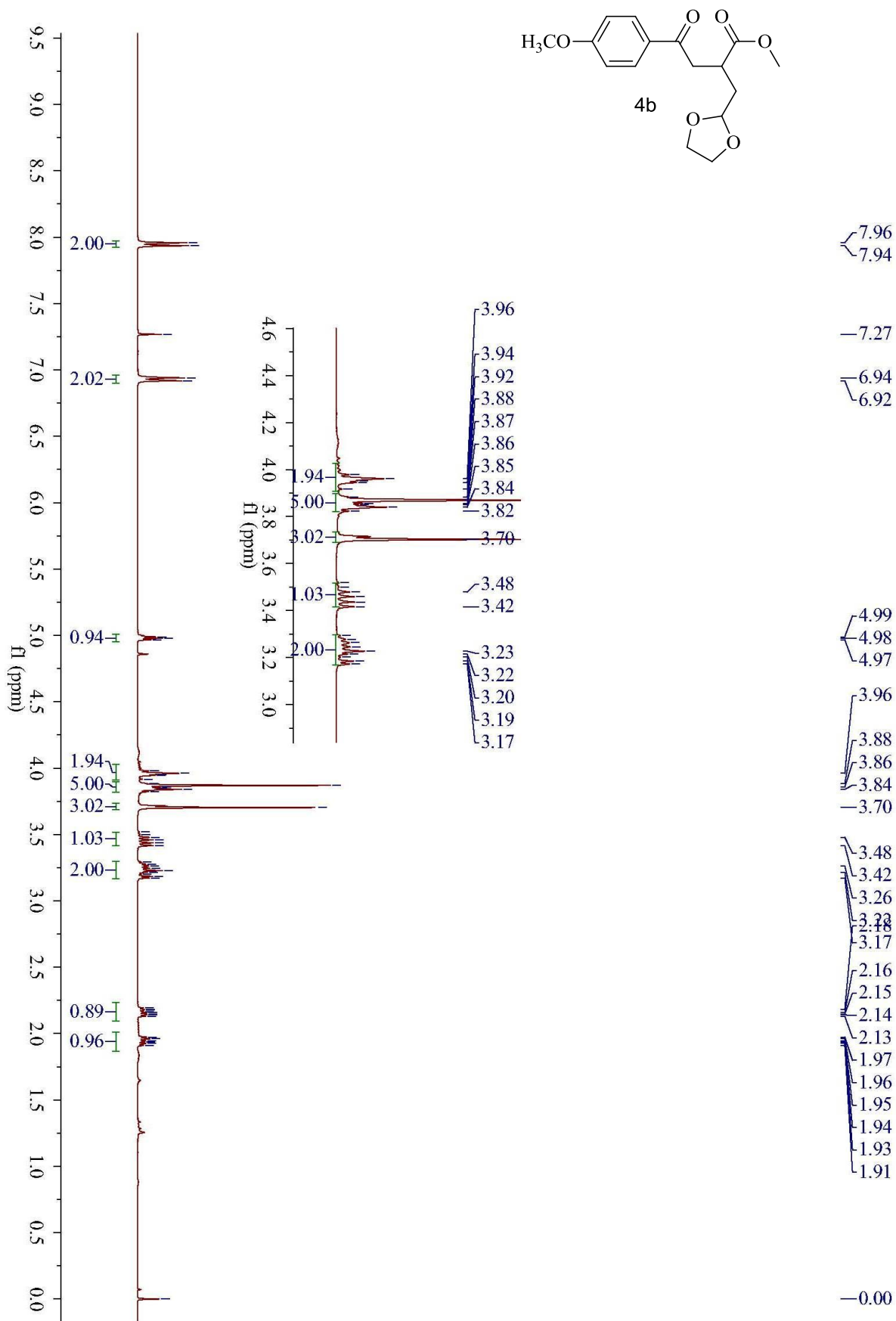


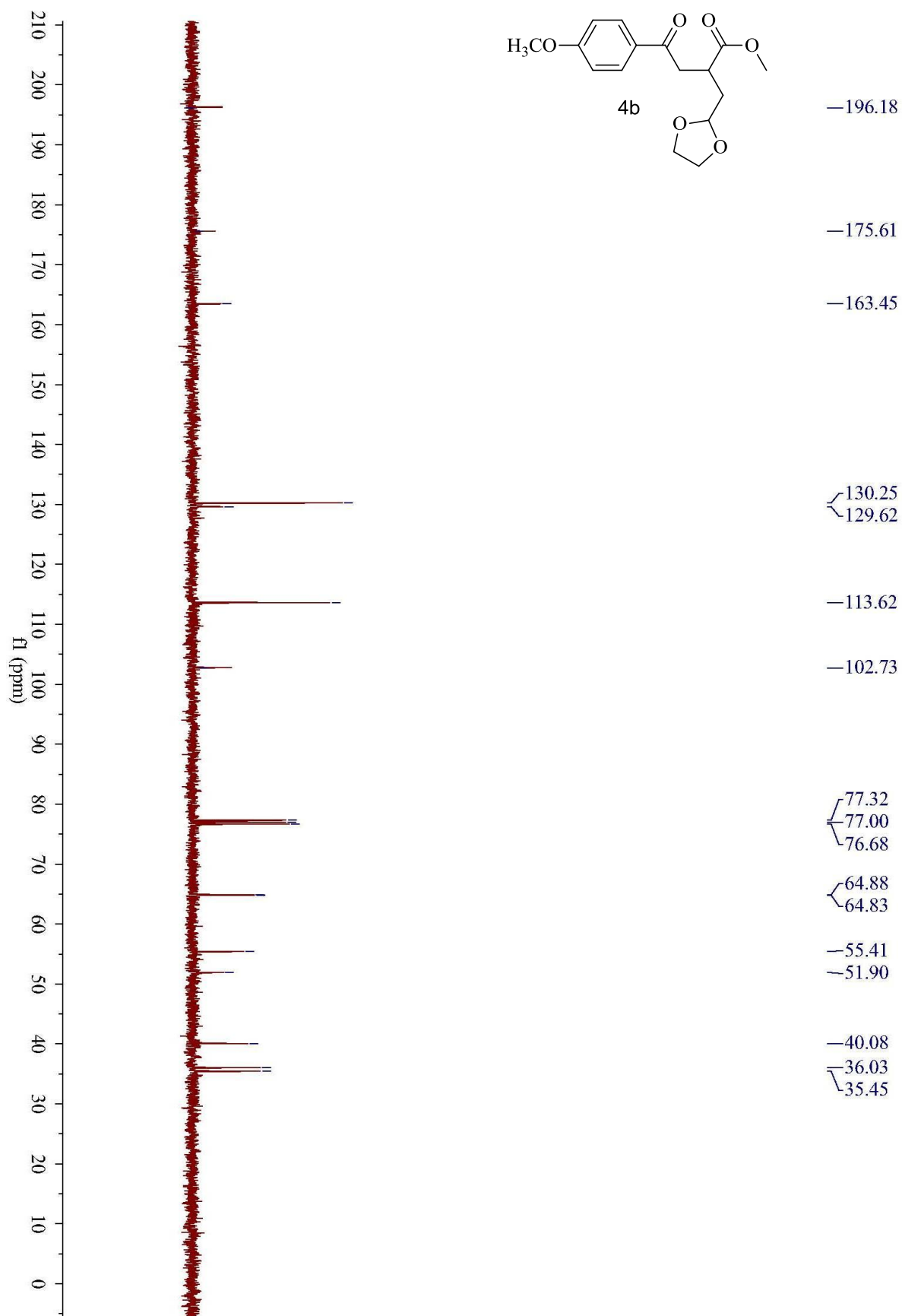
2-(4-(tert-butyl)phenyl)-N,N,6-trimethylisonicotinamide (15). Yellow oil, 78% yield (116 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 3H), 7.06 (s, 1H), 3.14 (s, 3H), 2.97 (s, 3H), 2.64 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 158.9, 152.2, 144.9, 136.2, 126.6, 125.6, 118.5, 114.7, 39.1, 35.0, 34.6, 31.2, 24.7; HRMS (ESI-TOF): Anal. Calcd. For $\text{C}_{19}\text{H}_{24}\text{N}_2\text{ONa}$: 319.1786, Found: 319.1782 ($\text{M}+\text{Na}^+$); IR (neat, cm^{-1}): ν 1629, 1554, 1449, 1401, 1264, 1263, 1187, 841.

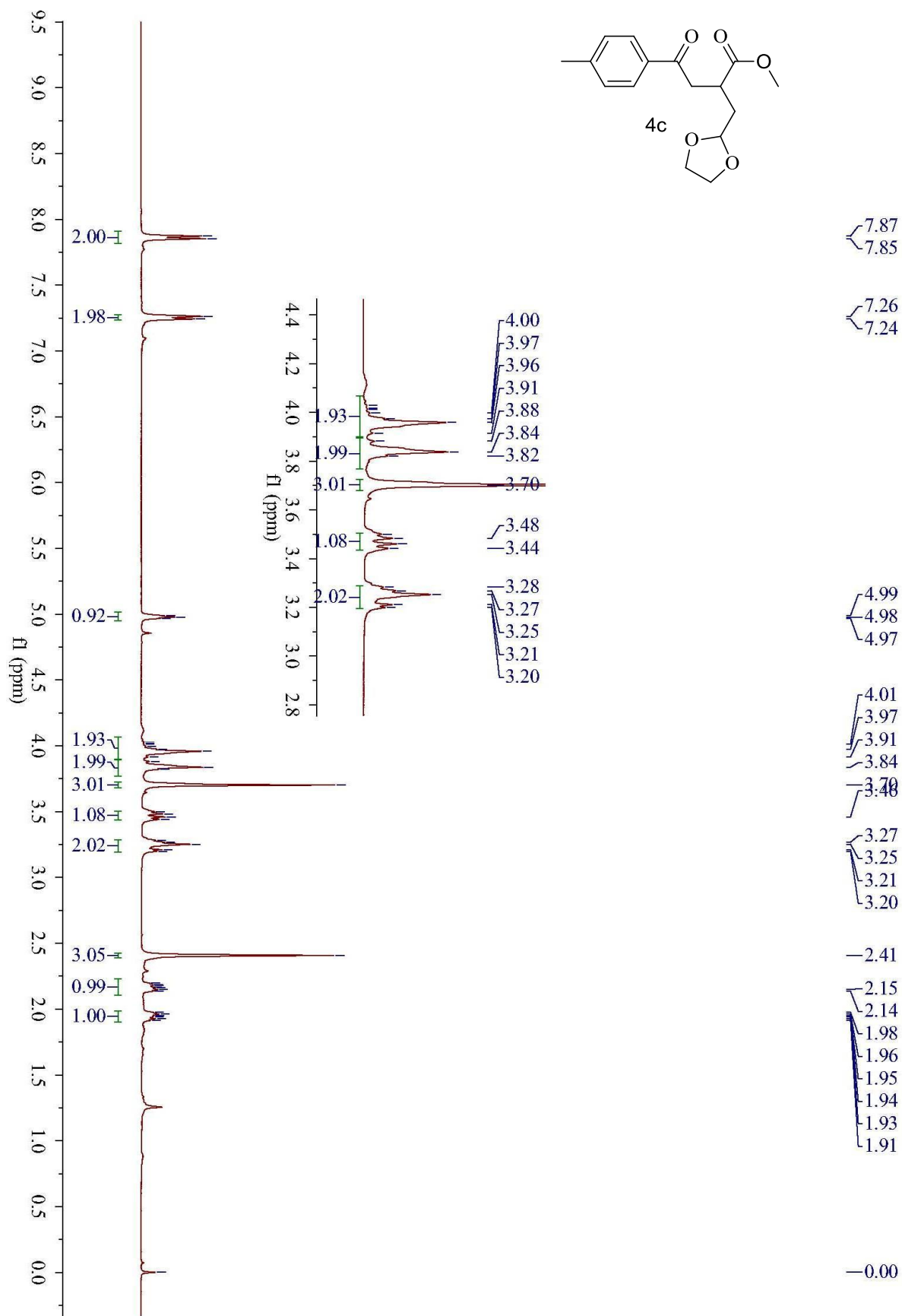
Spectroscopic Data for Products

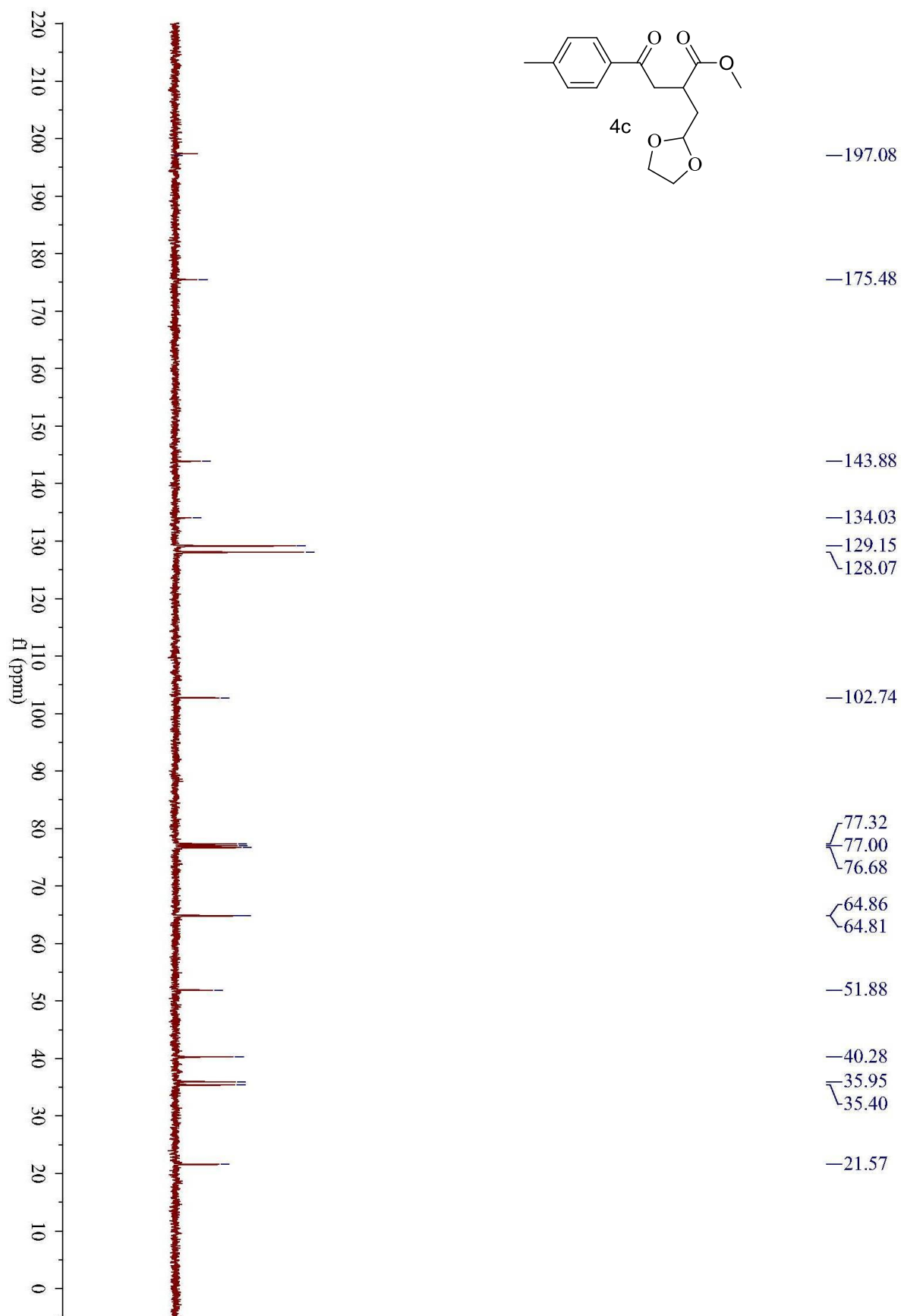


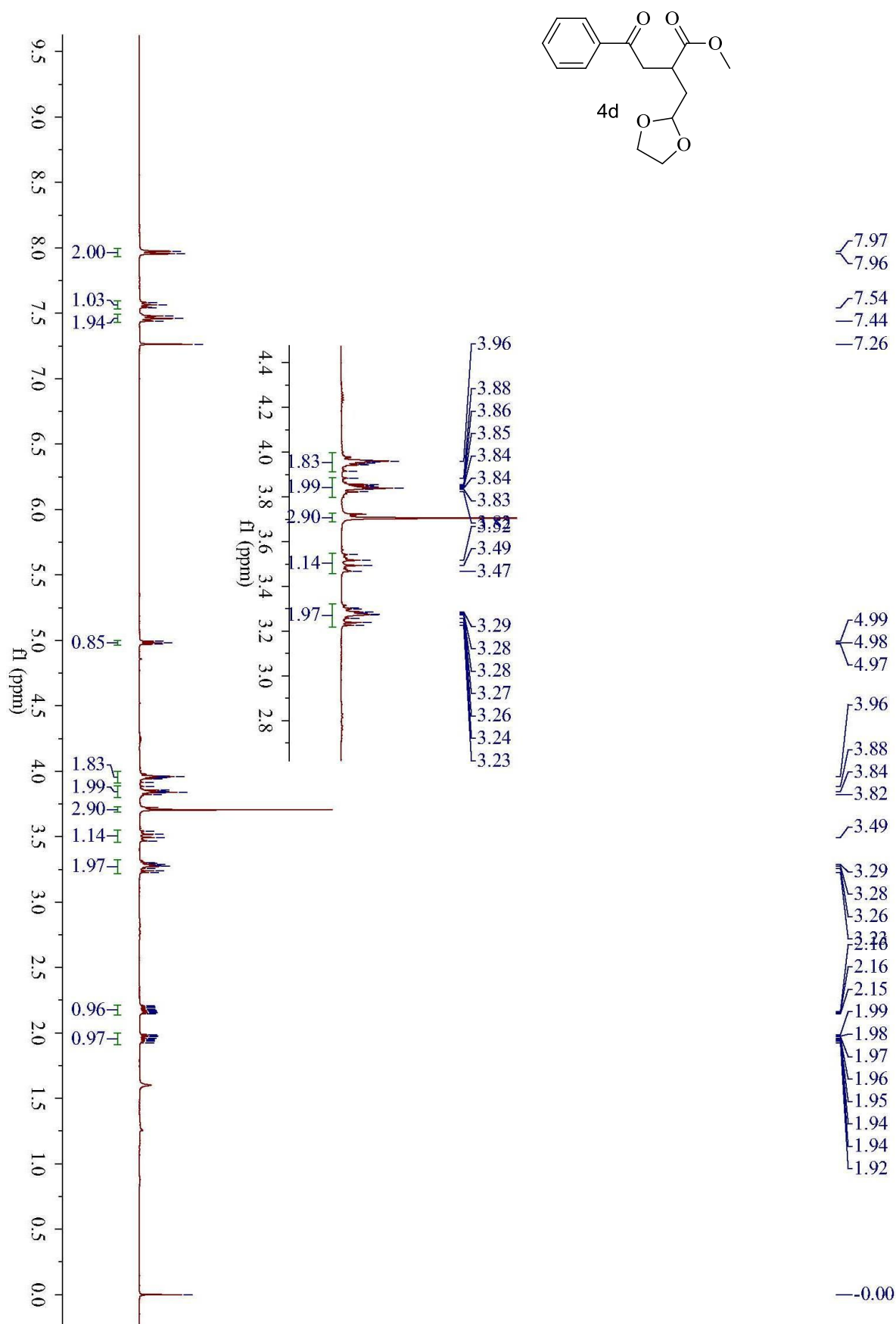


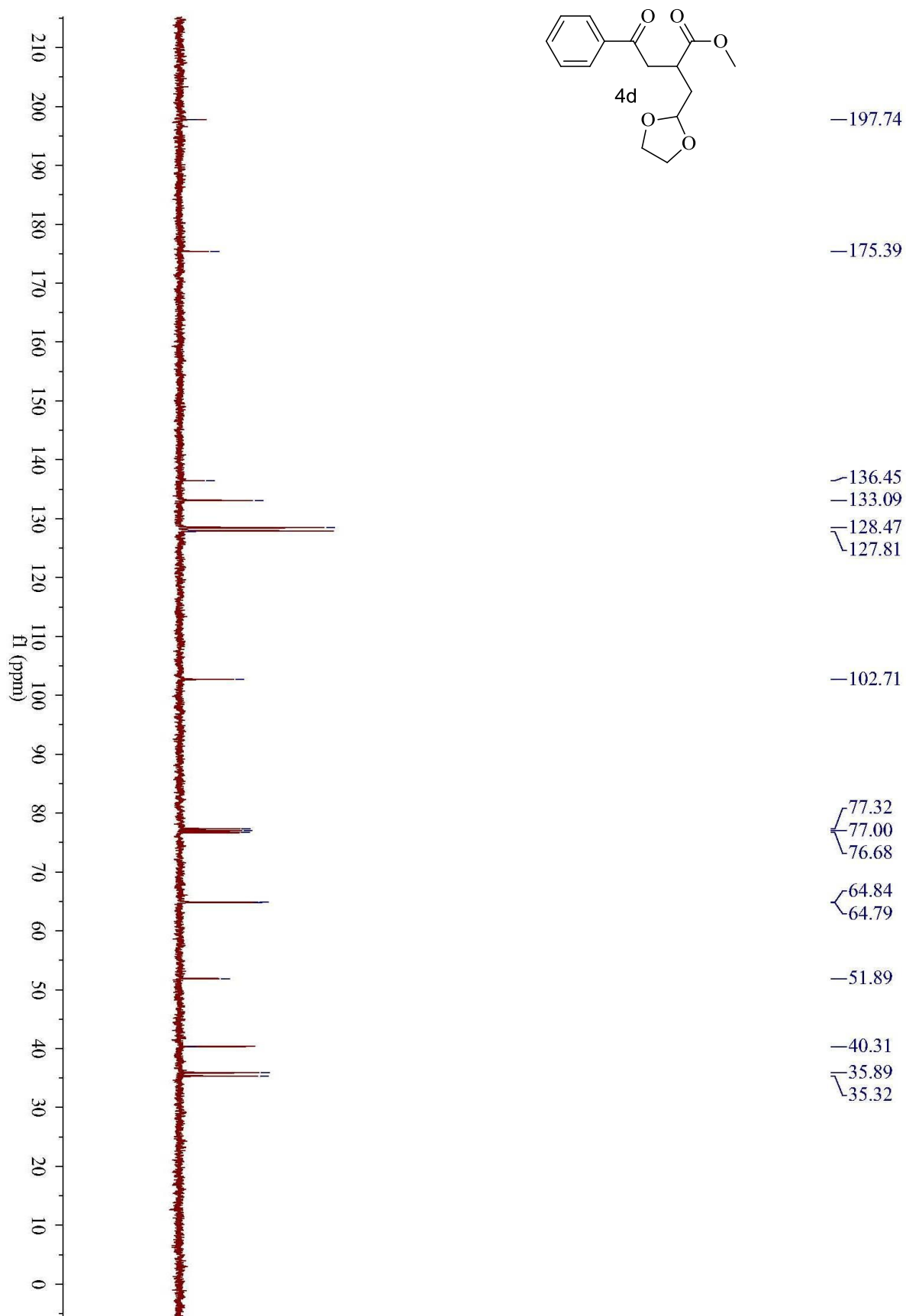


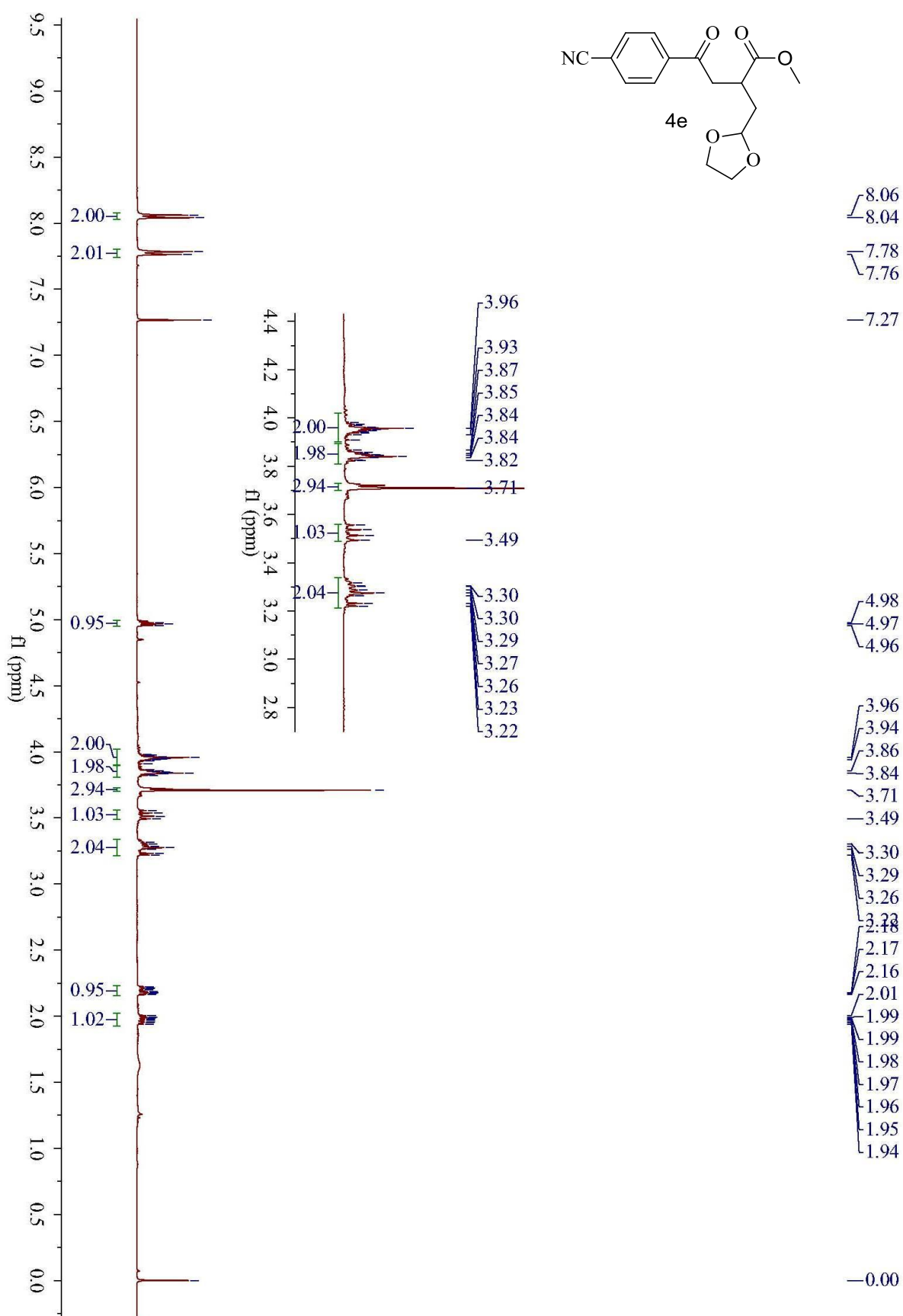


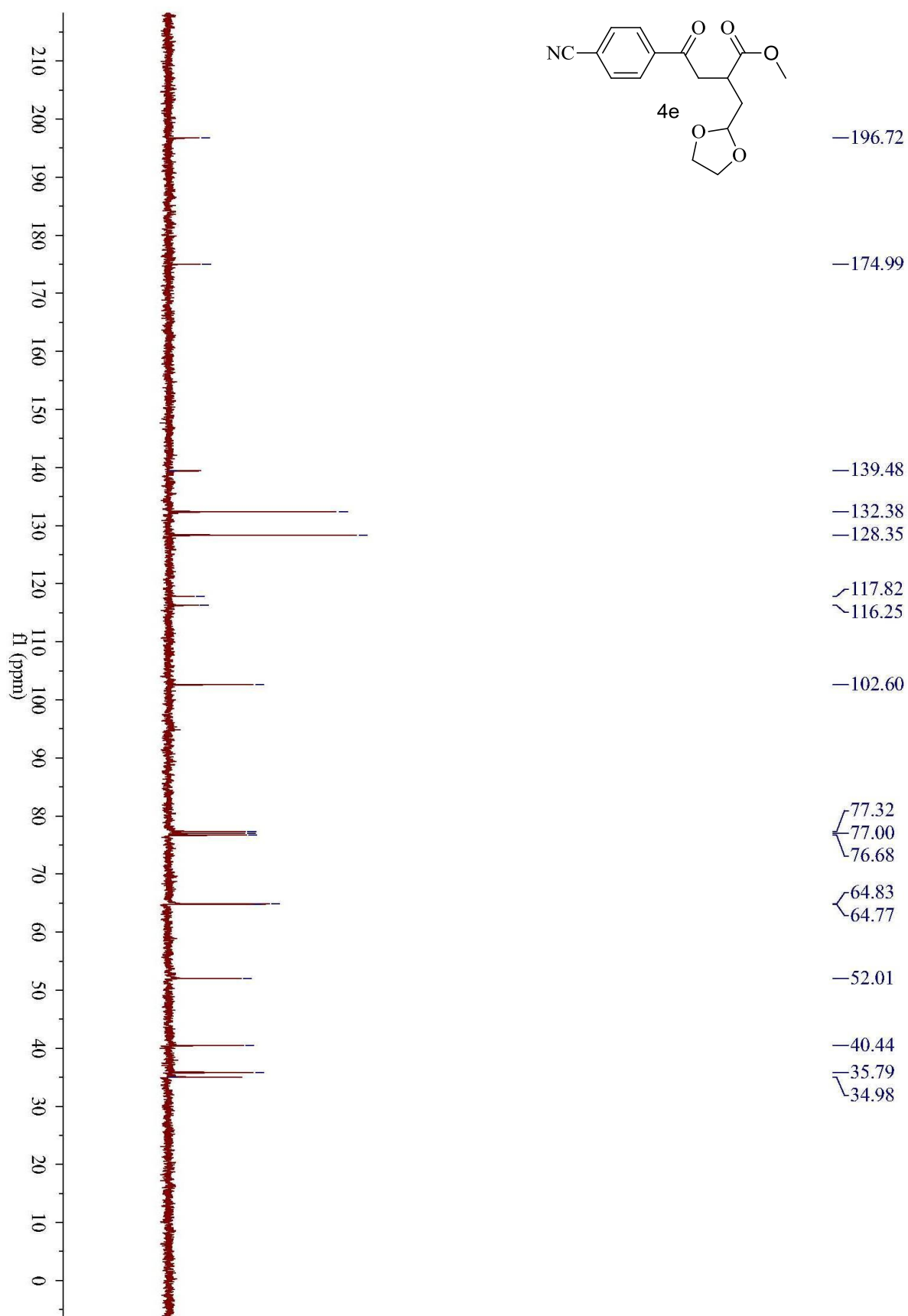


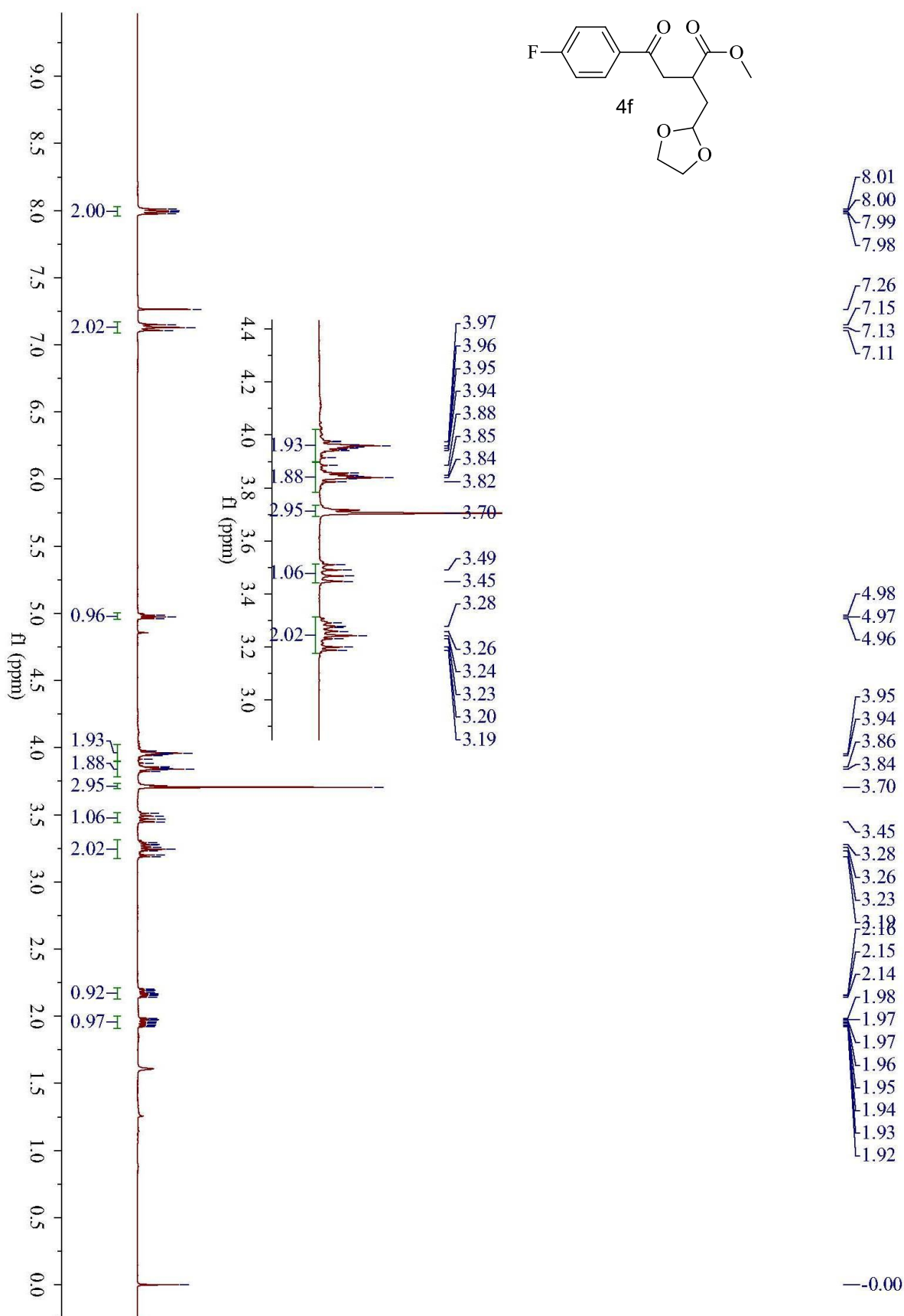


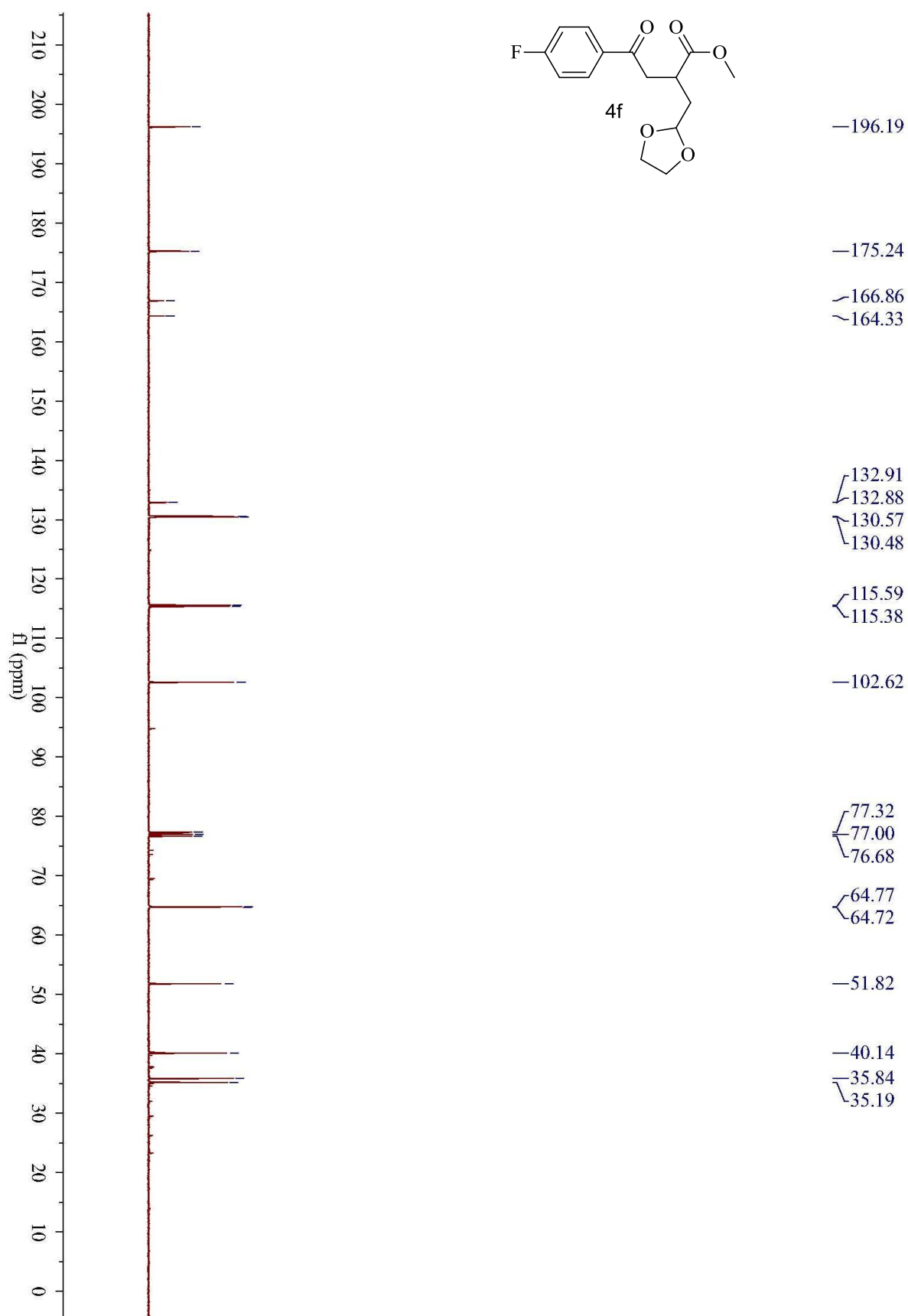


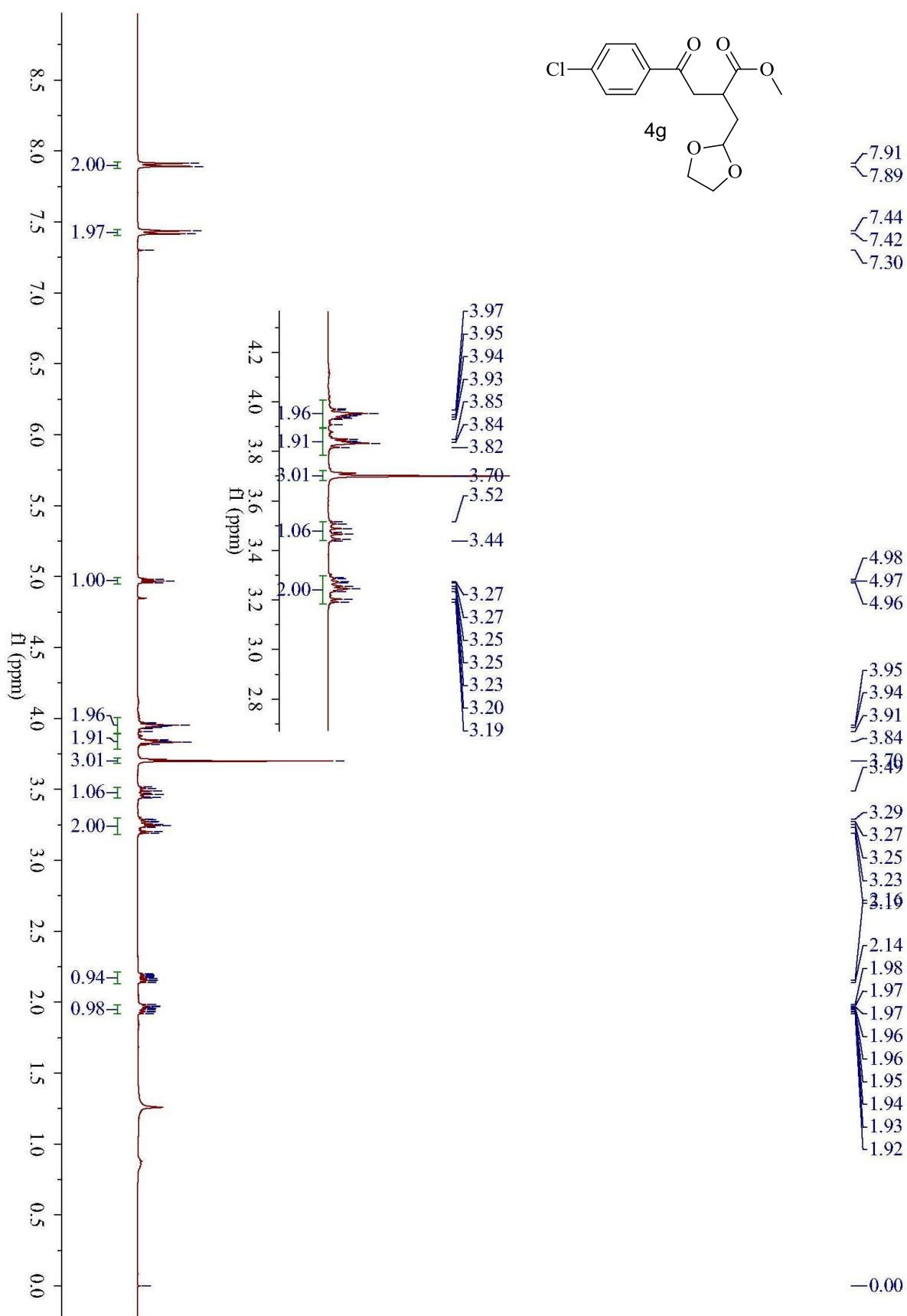


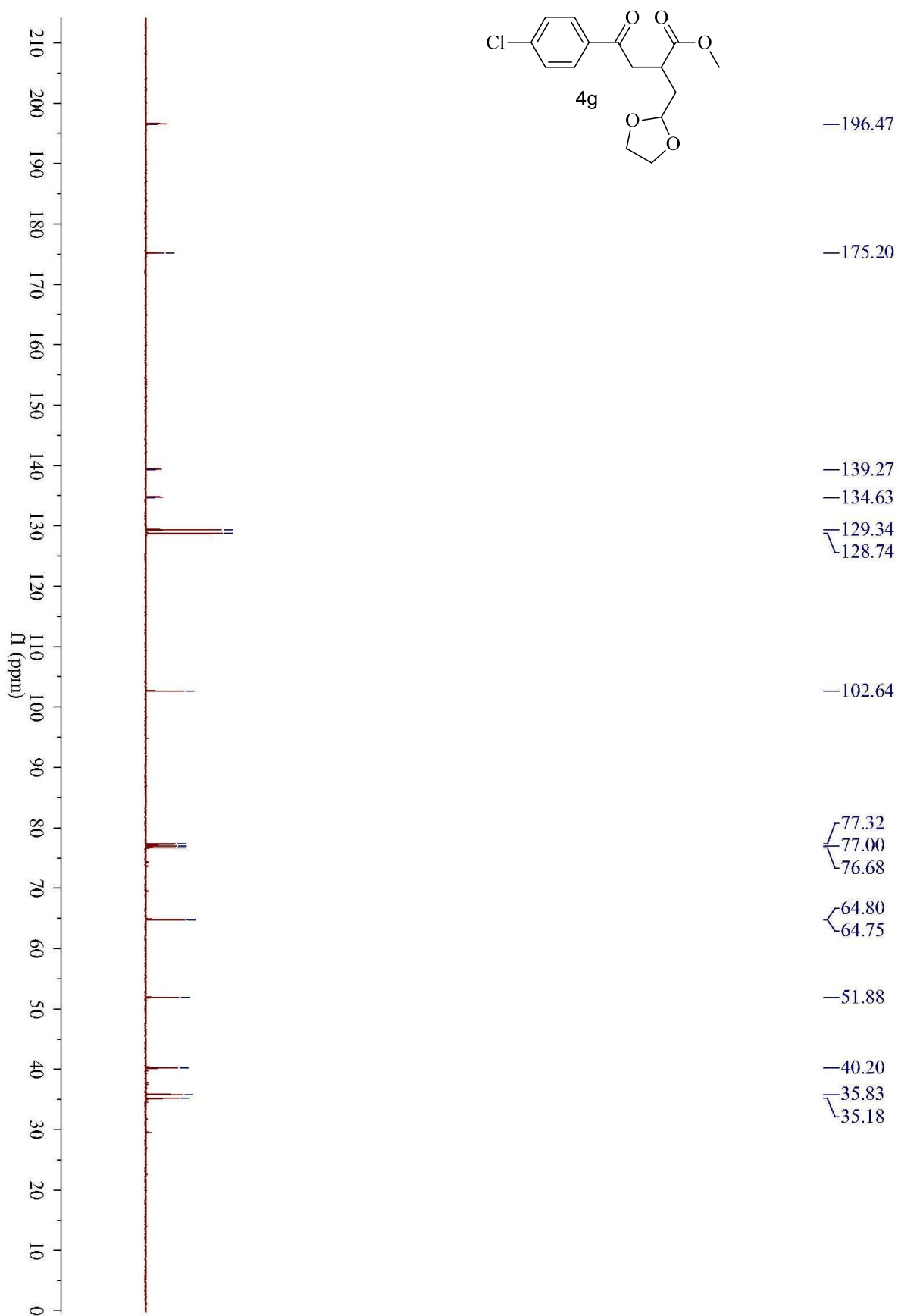


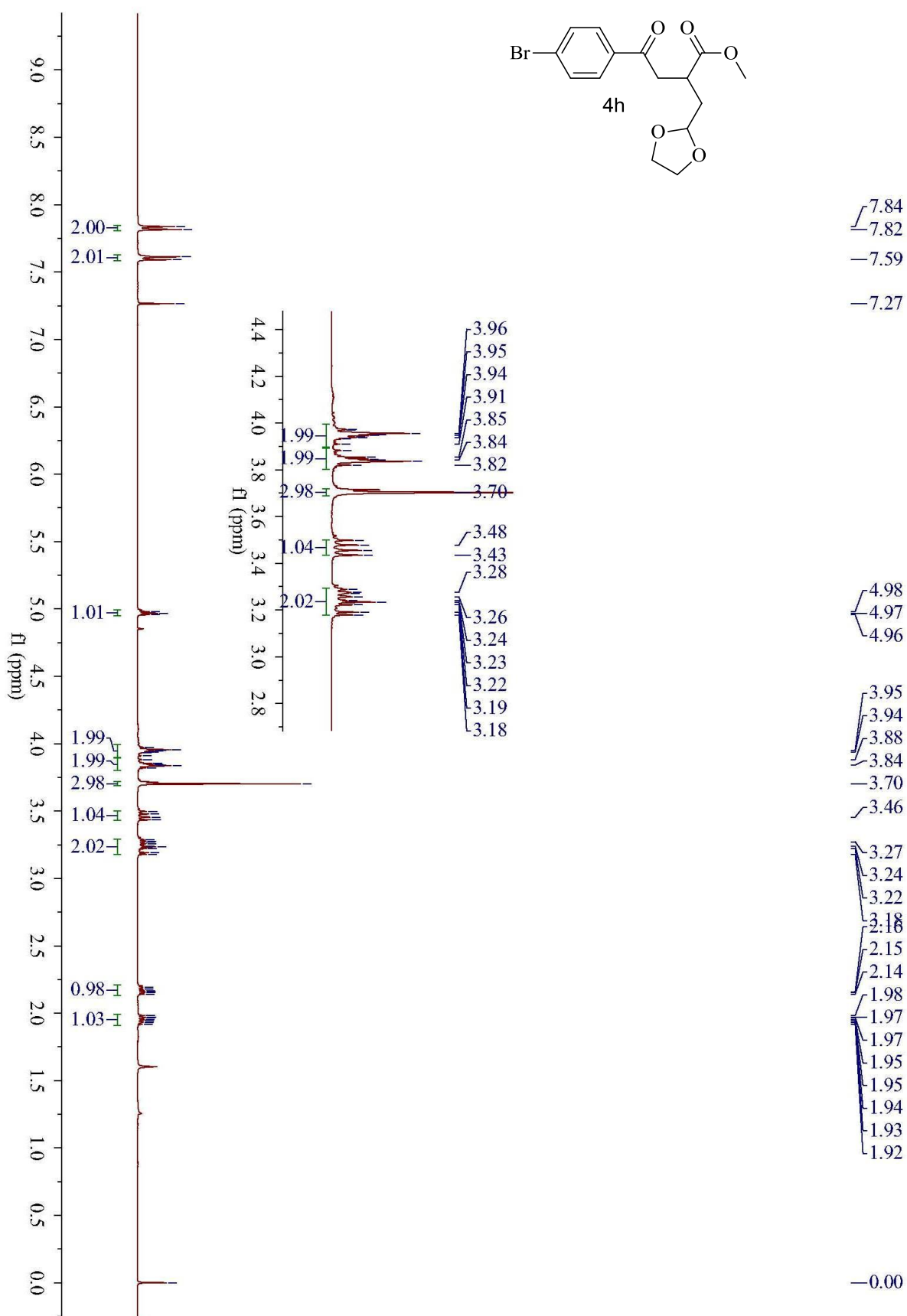


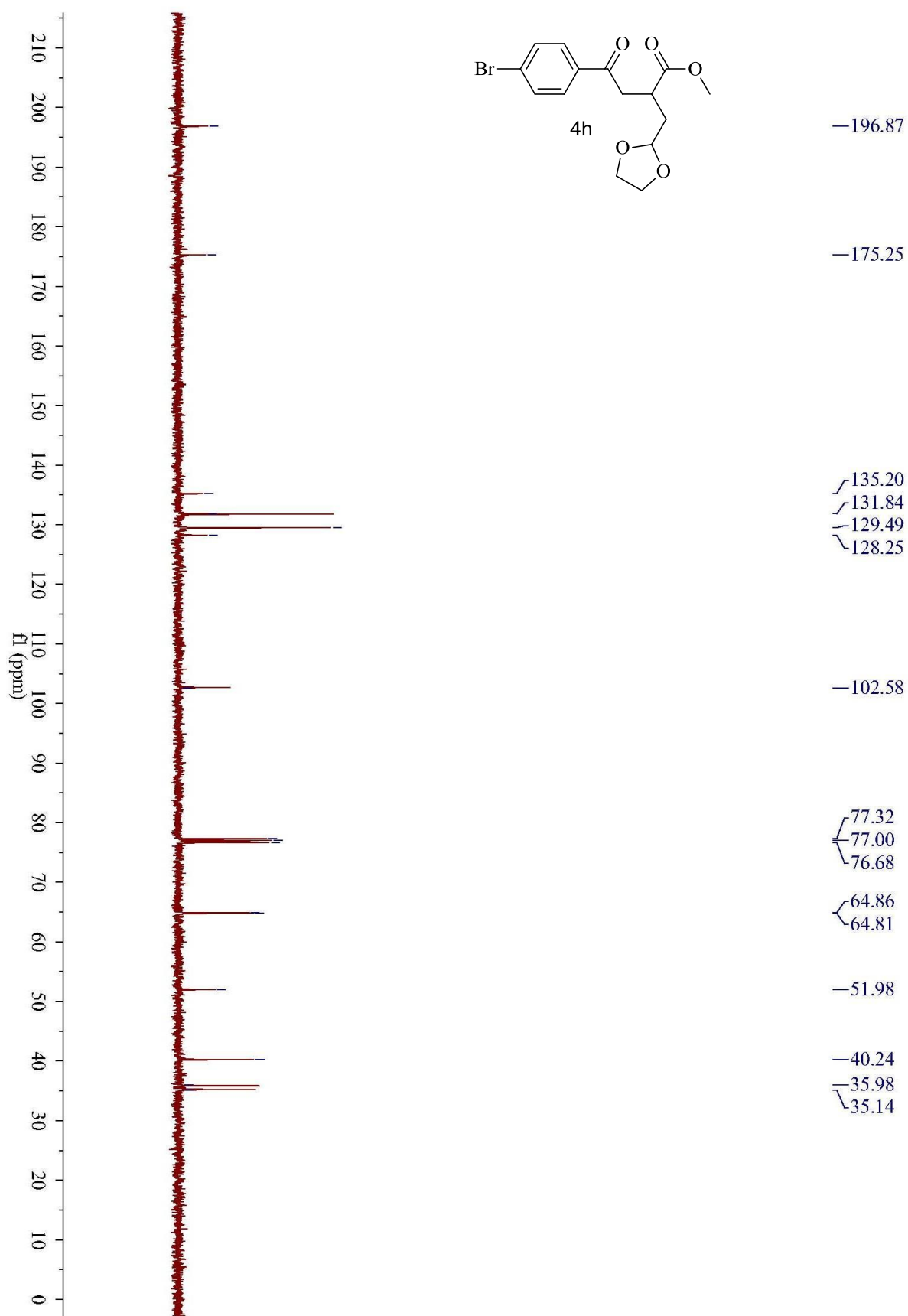


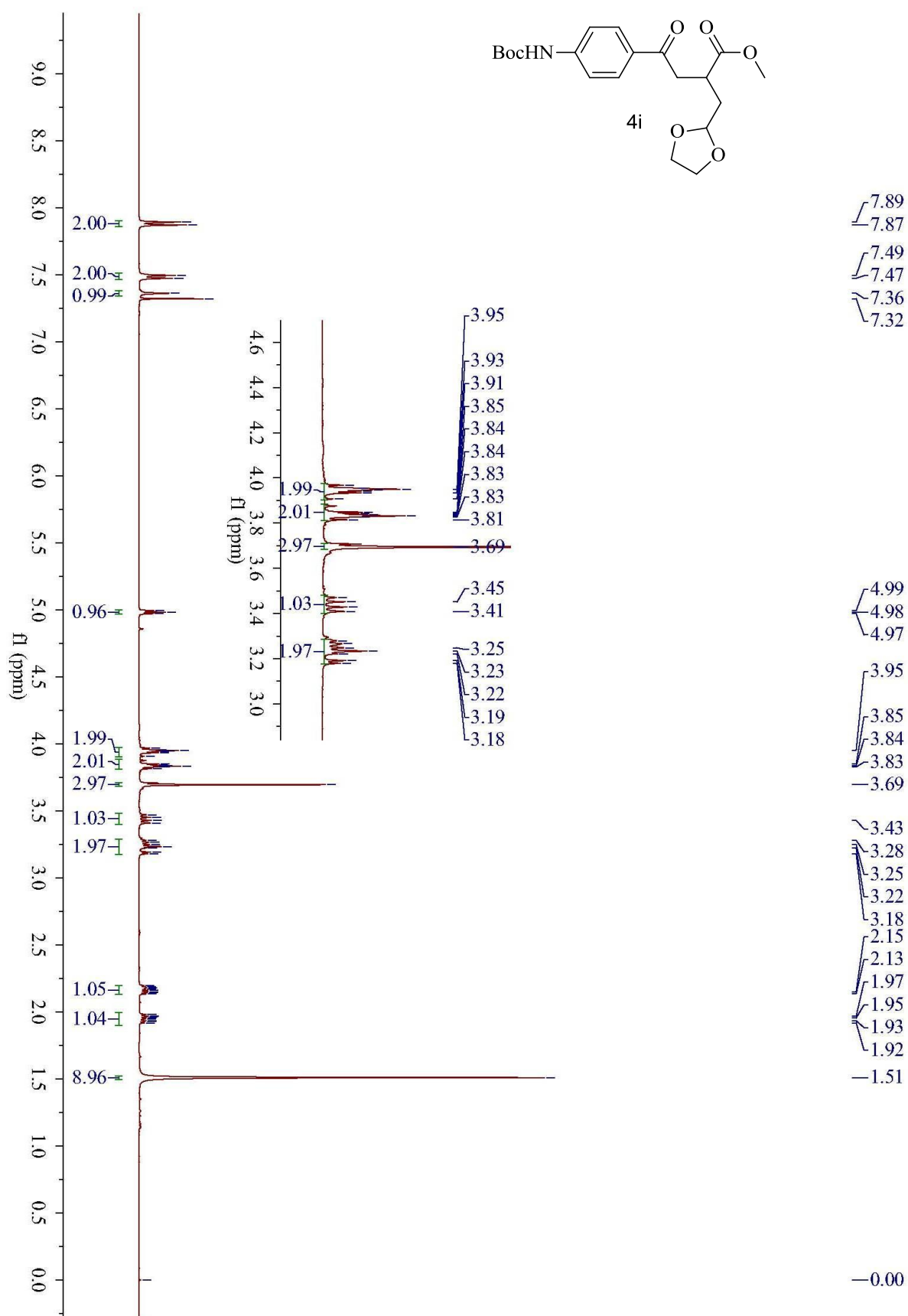


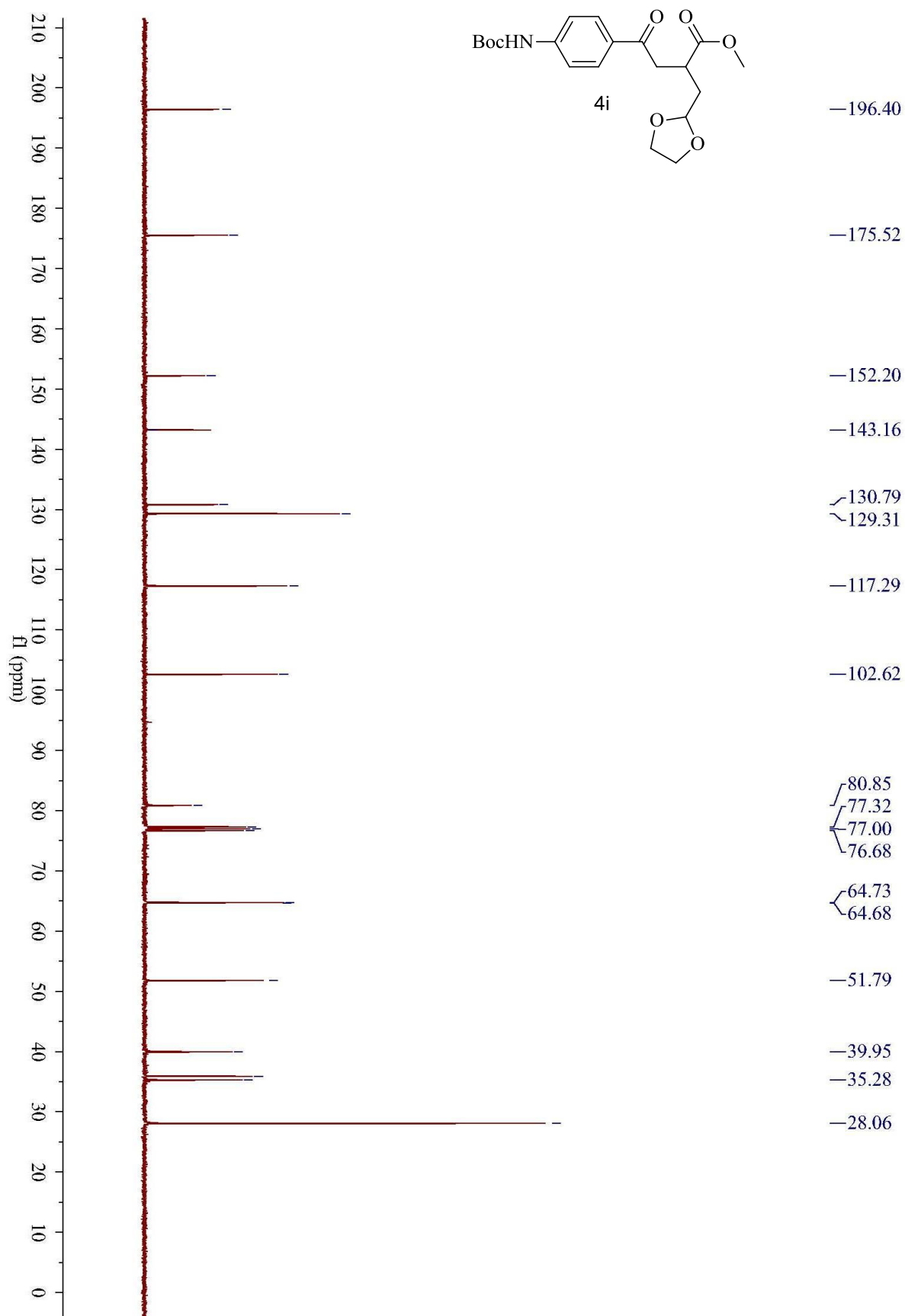


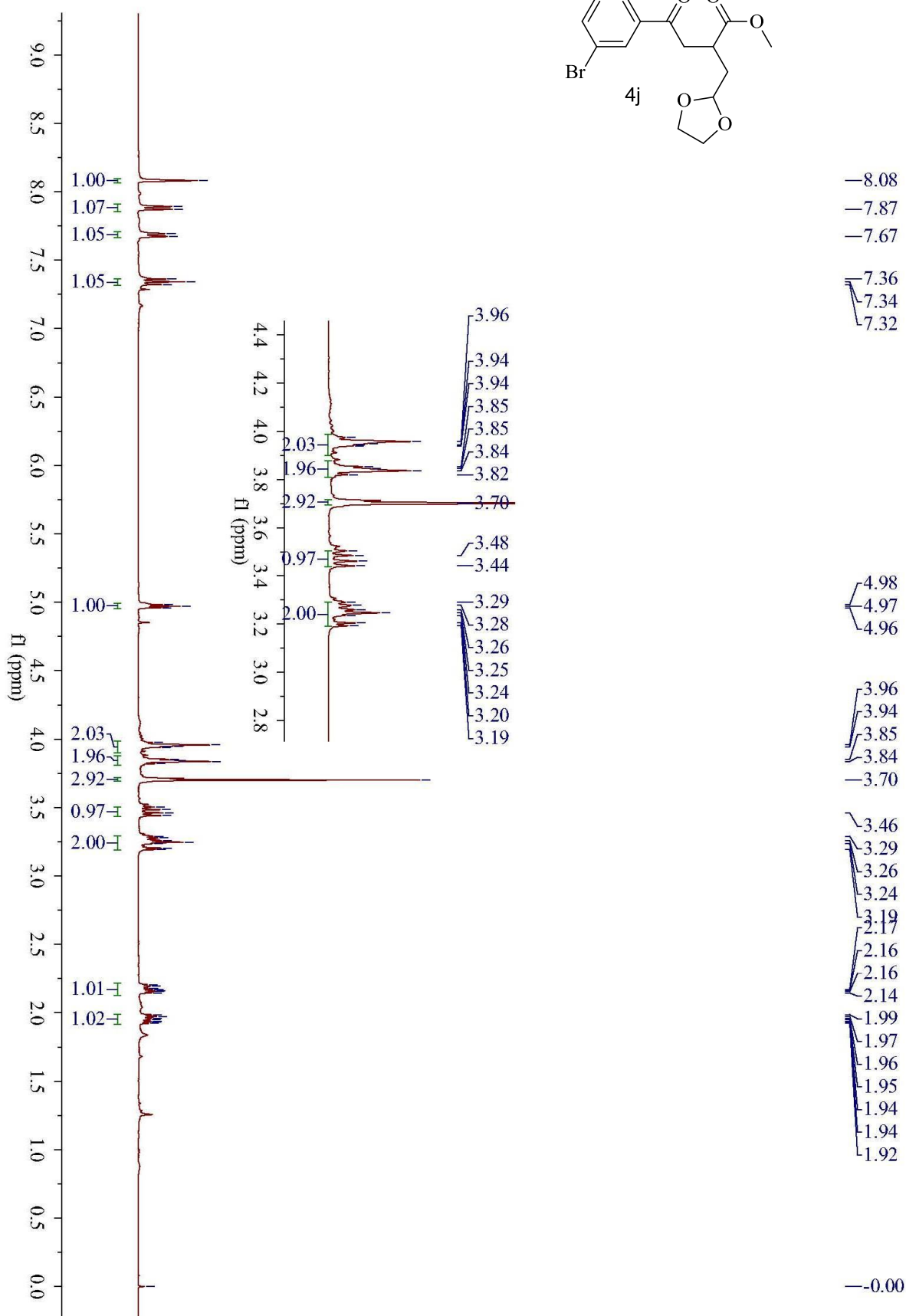
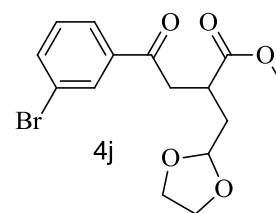


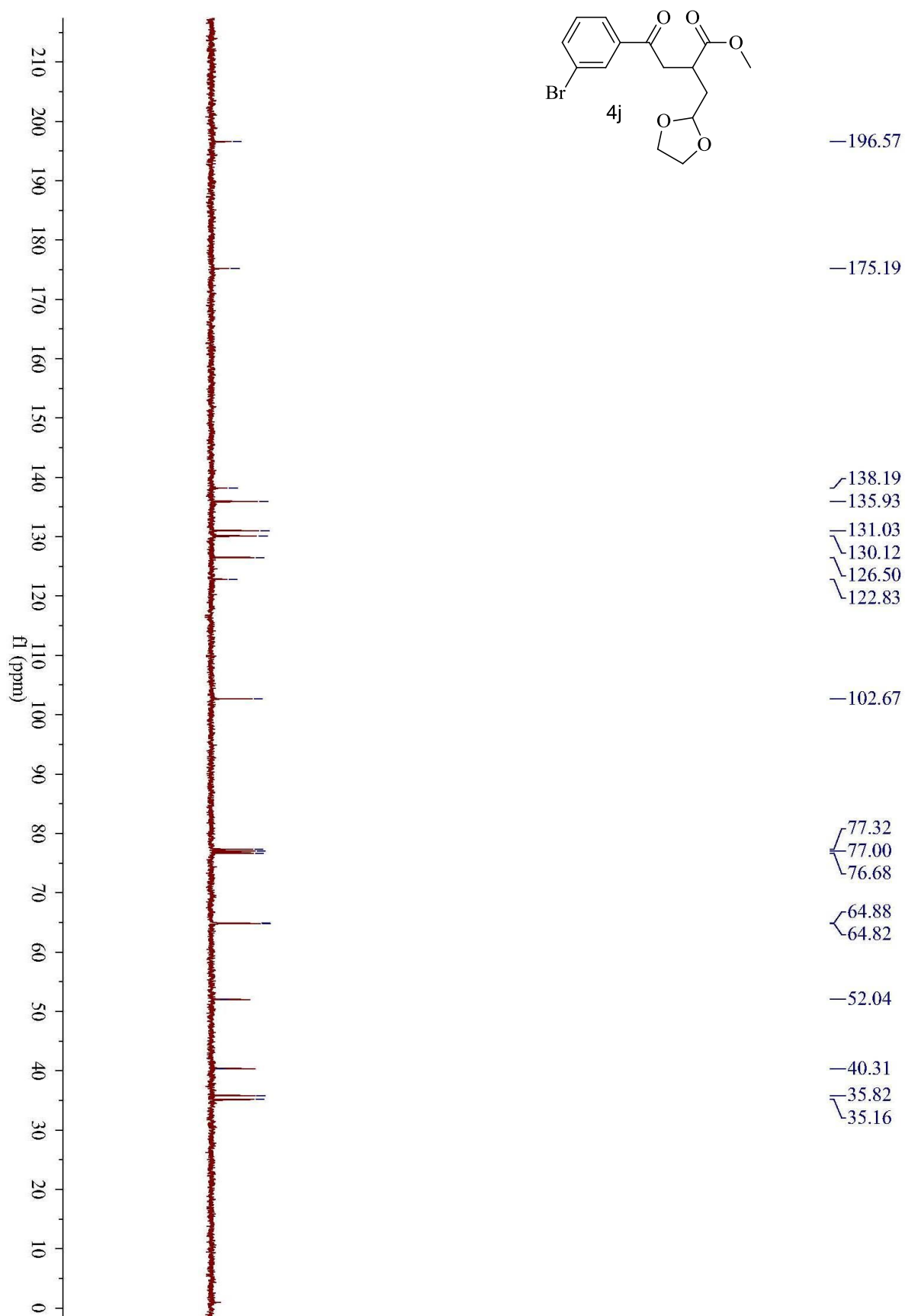


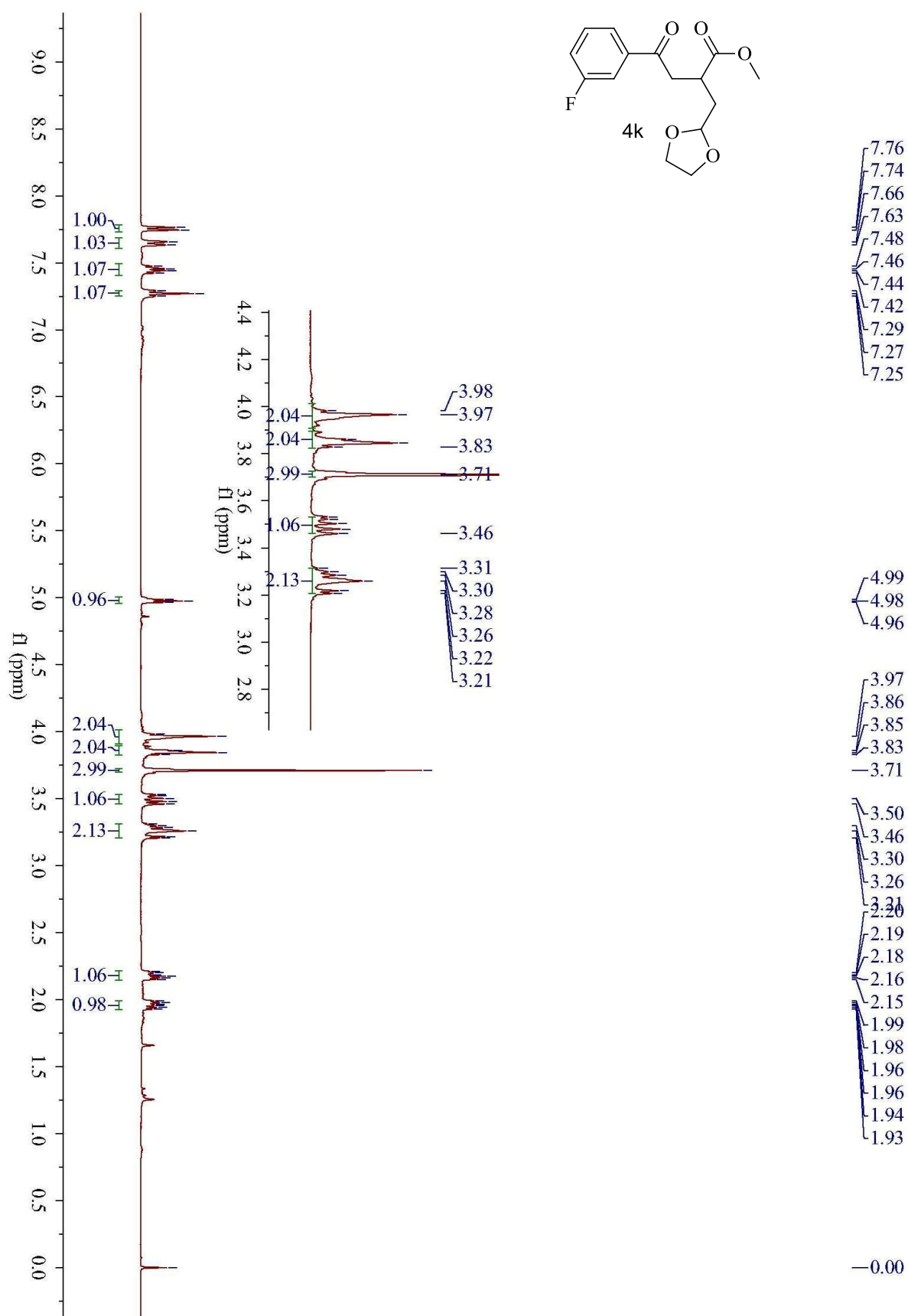


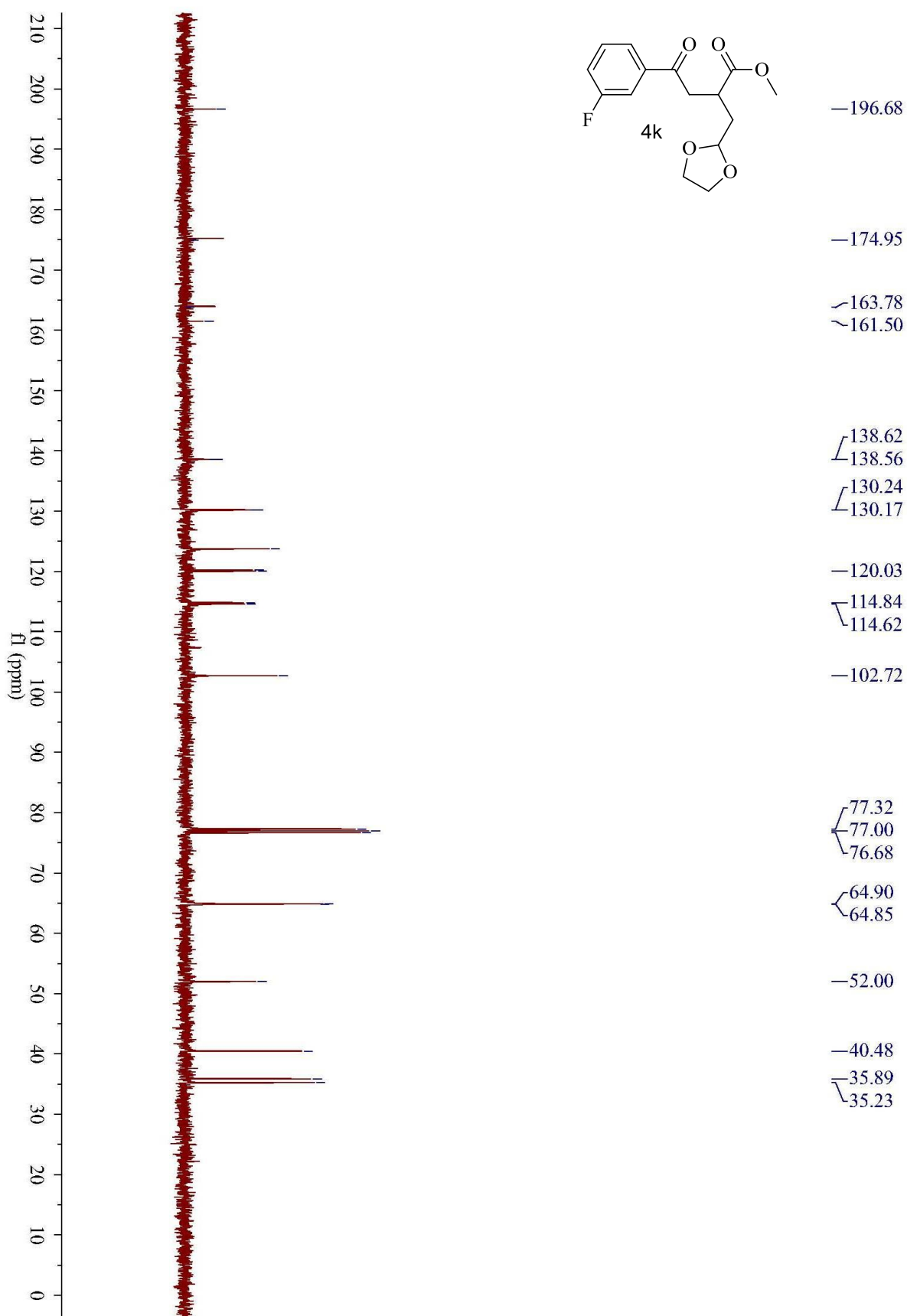


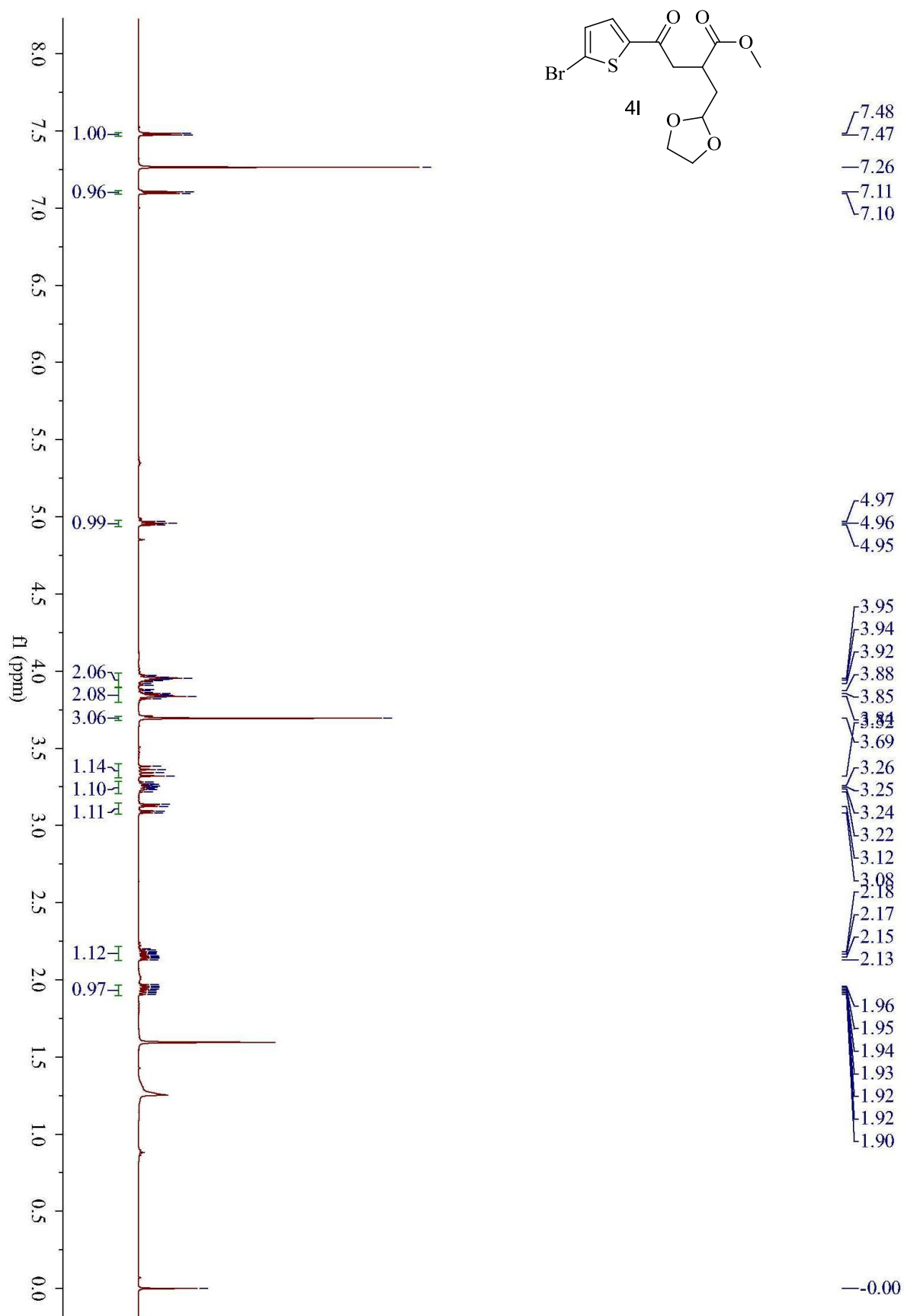


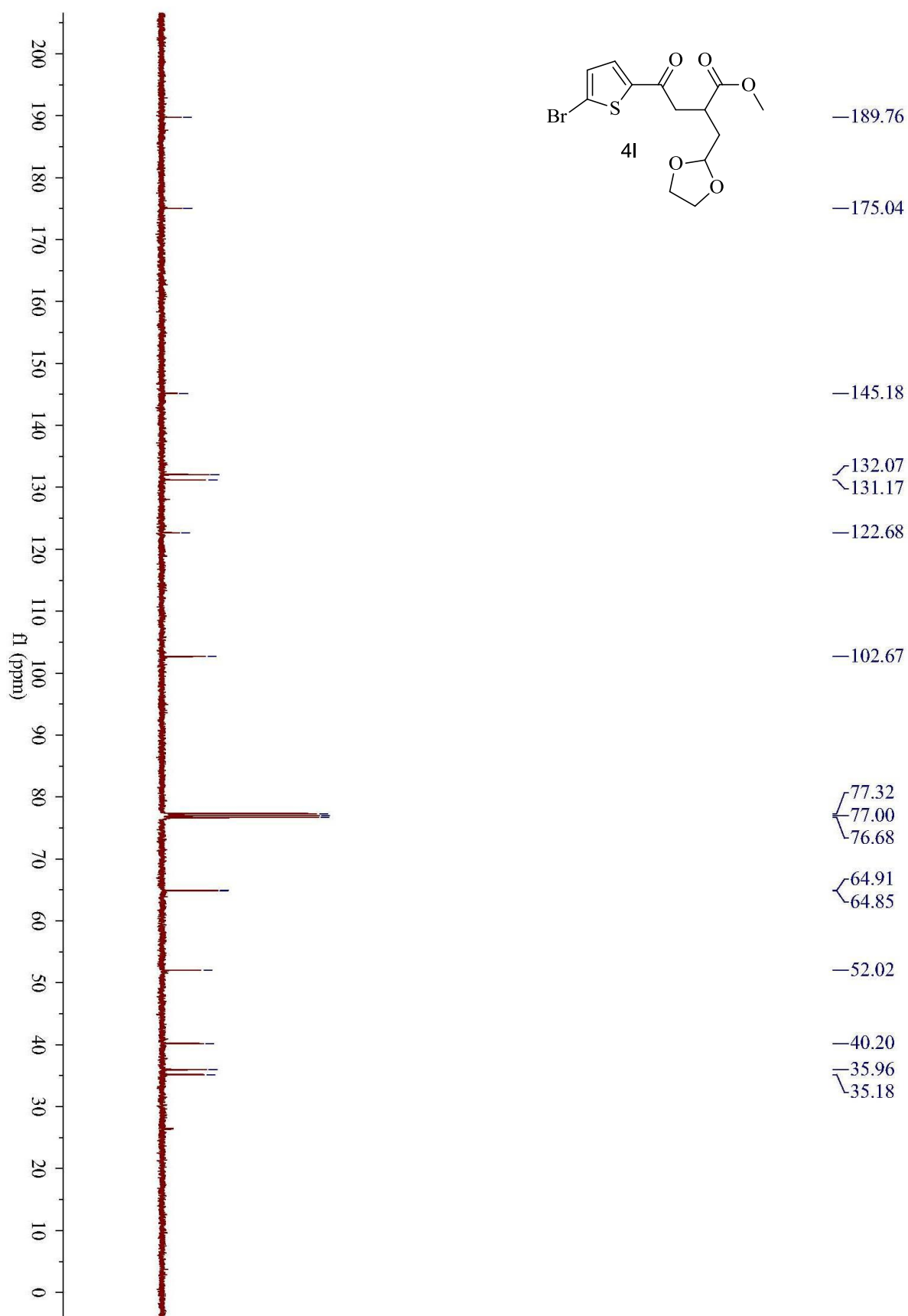


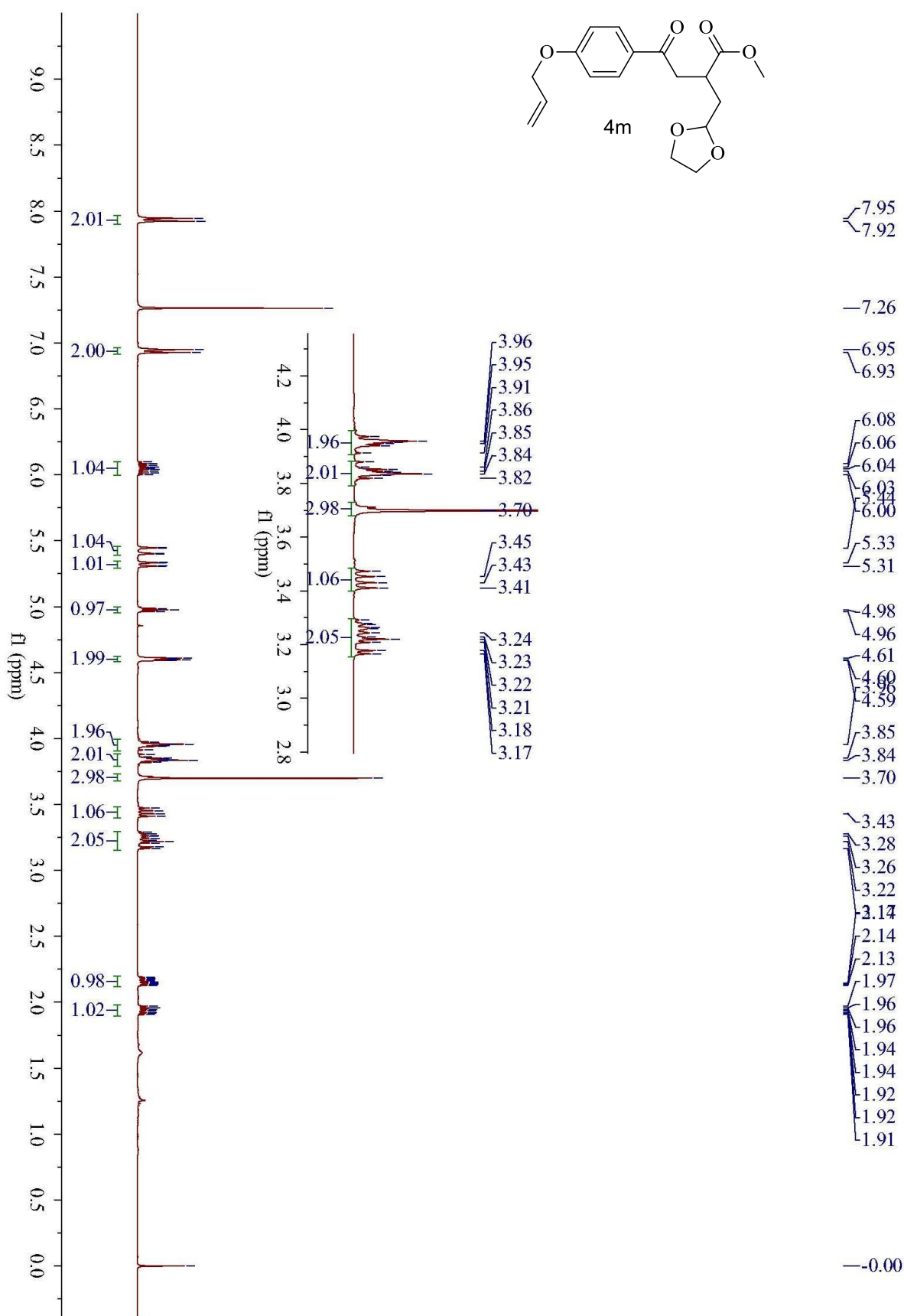


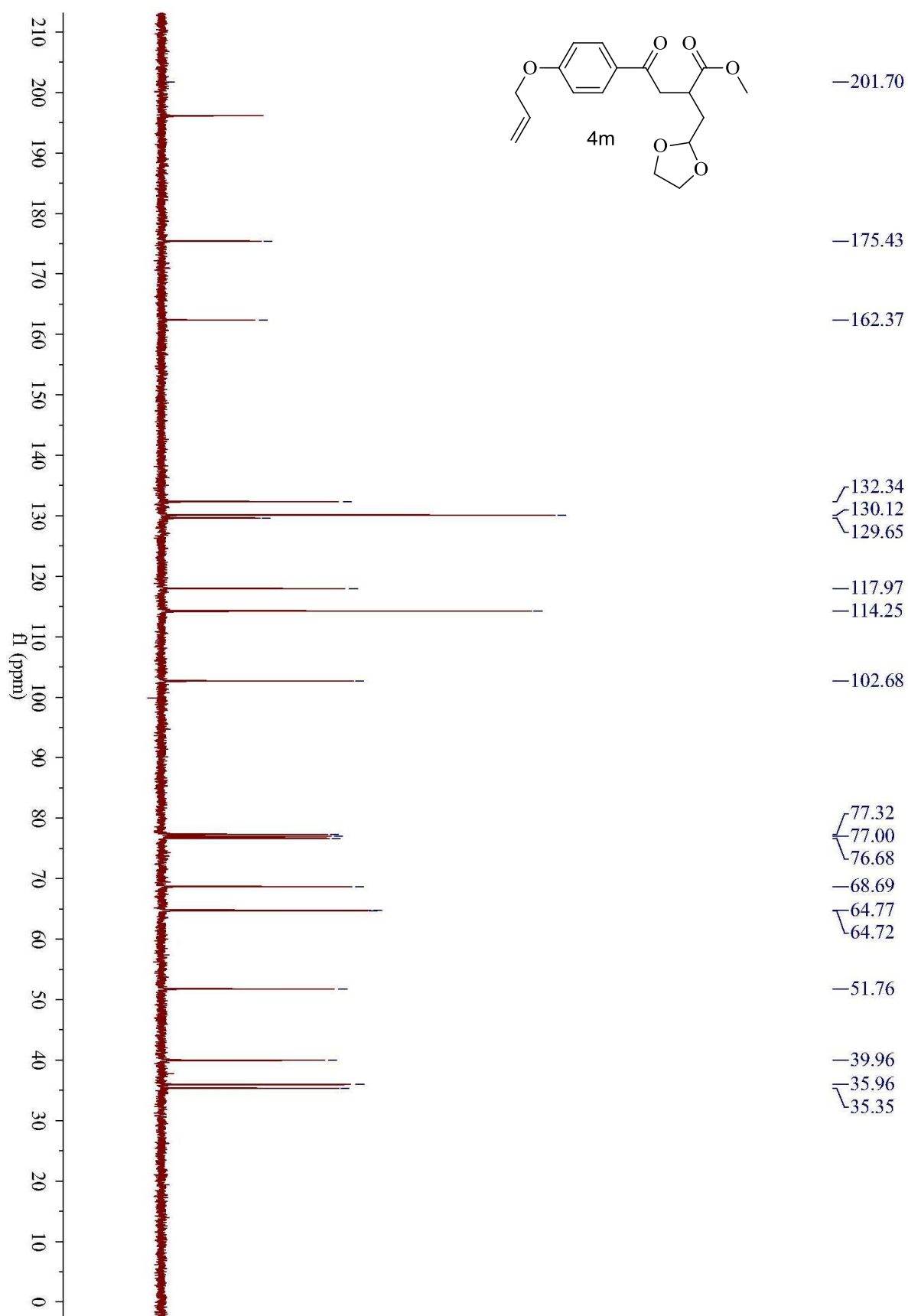


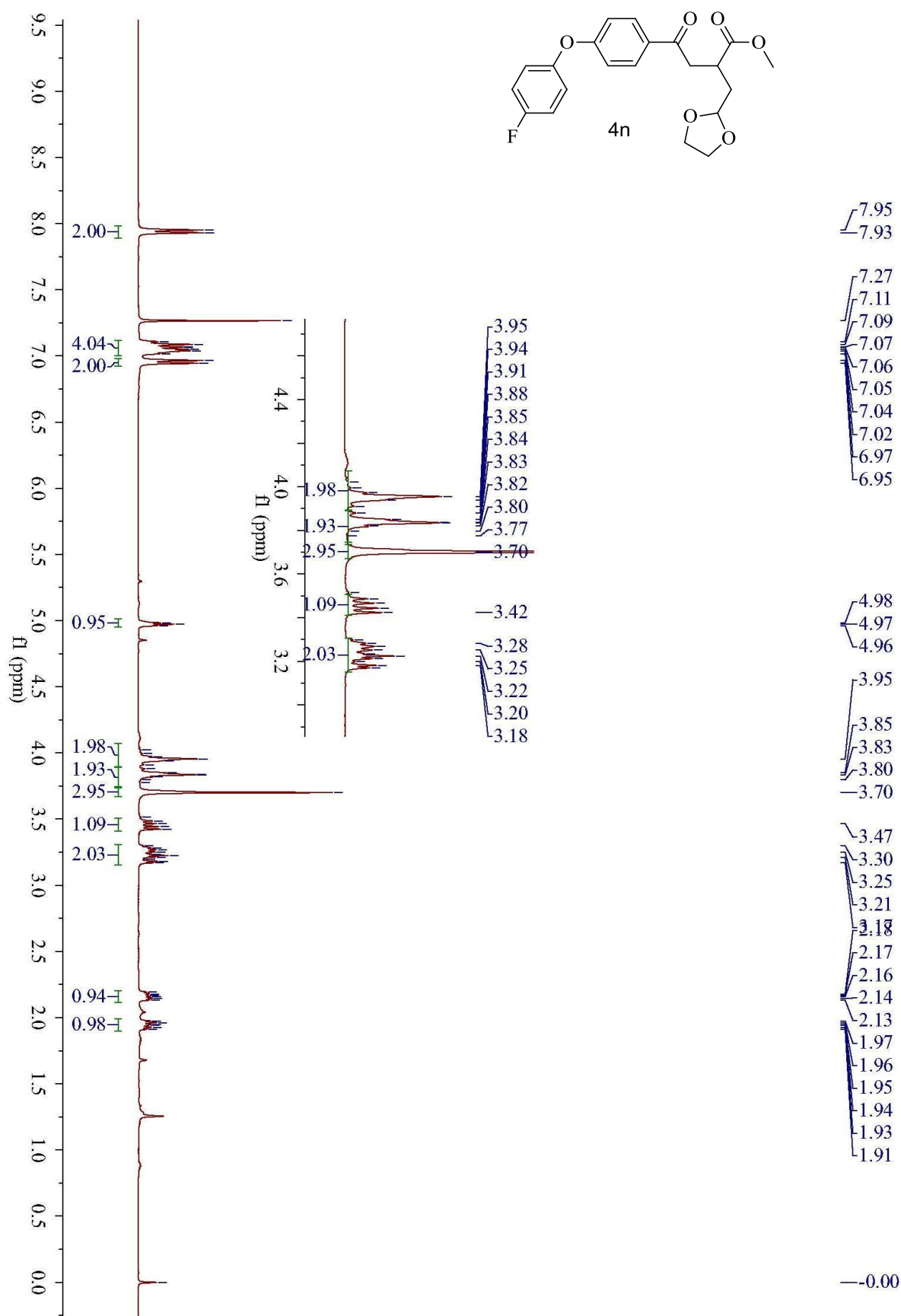


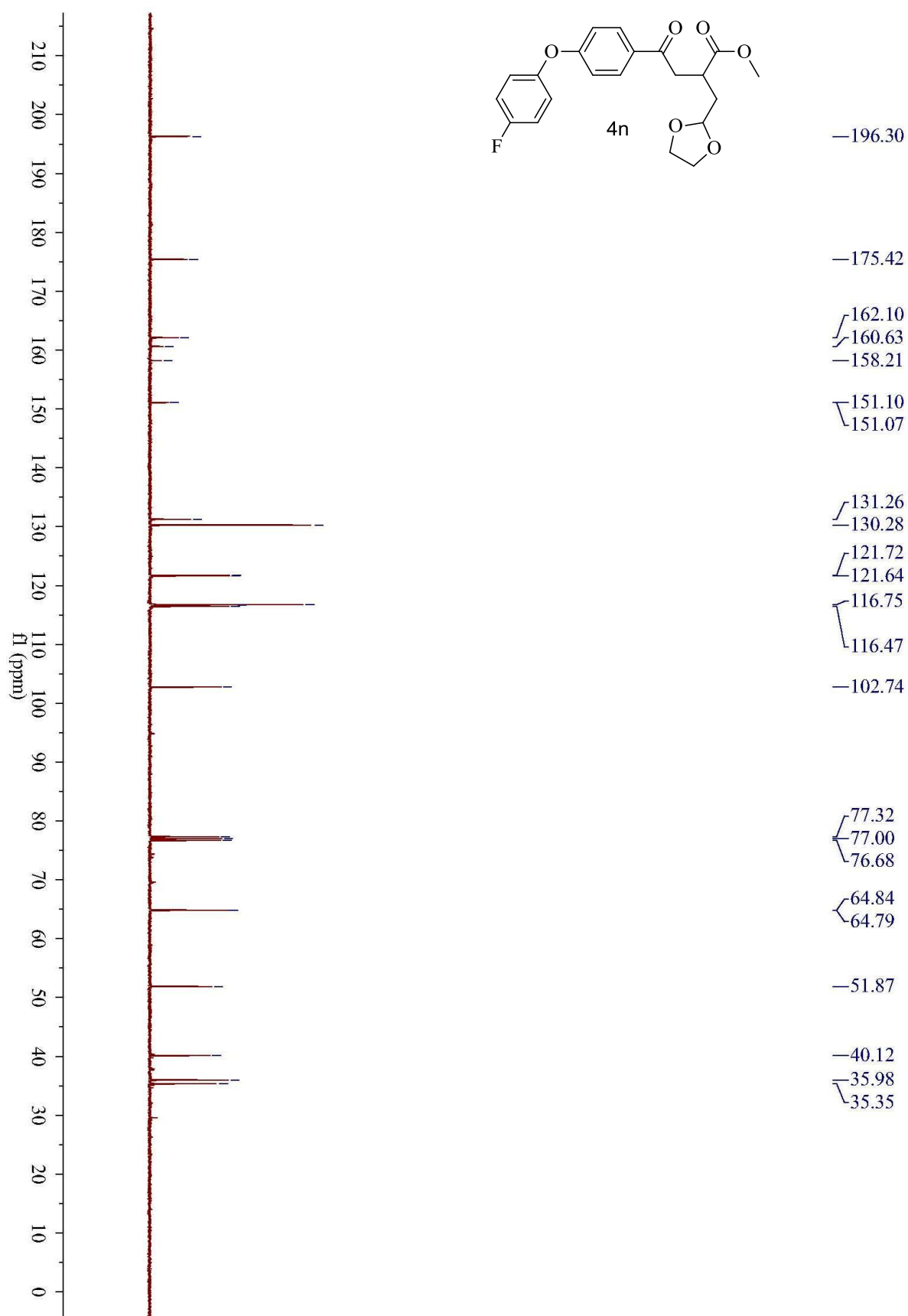


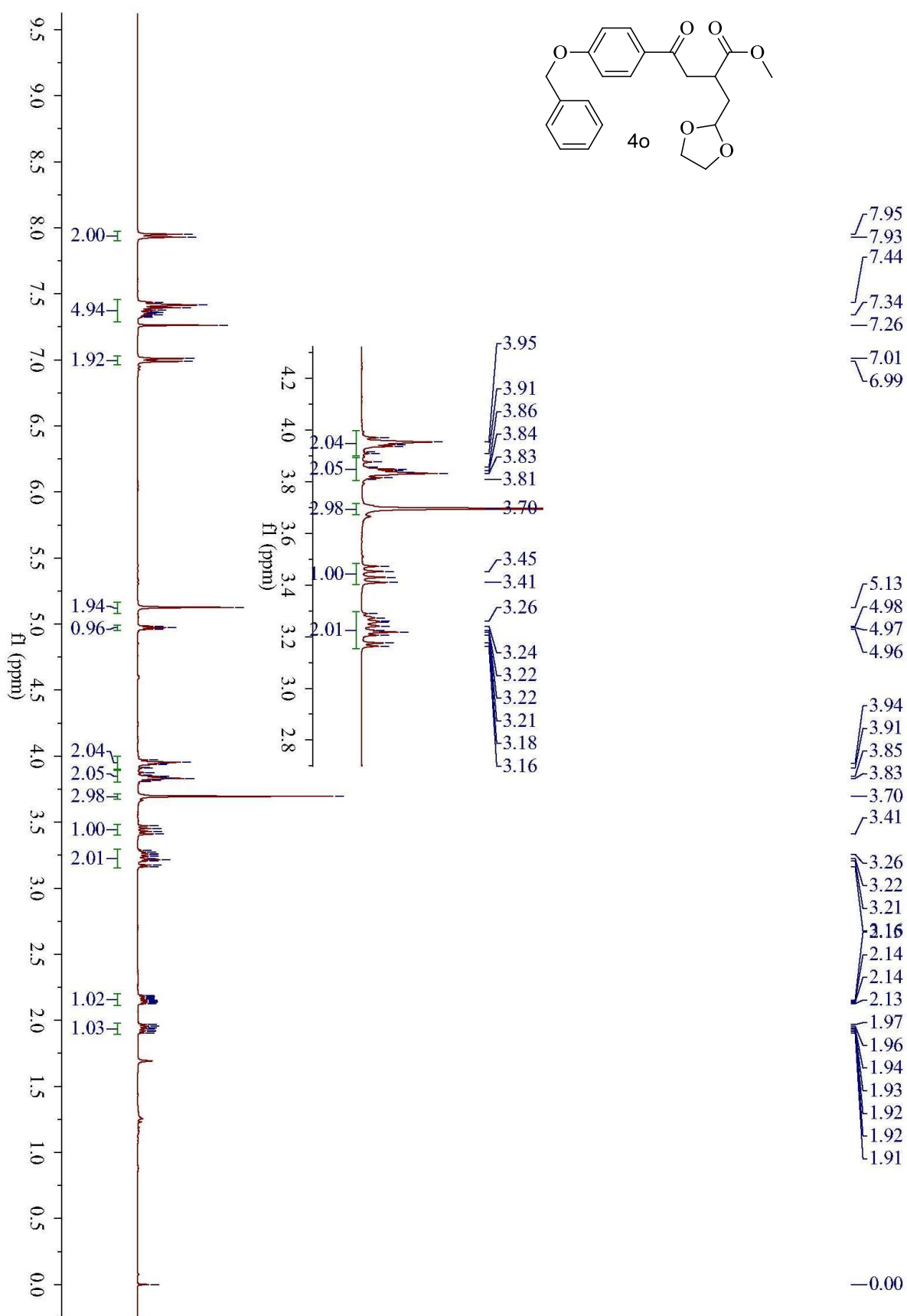


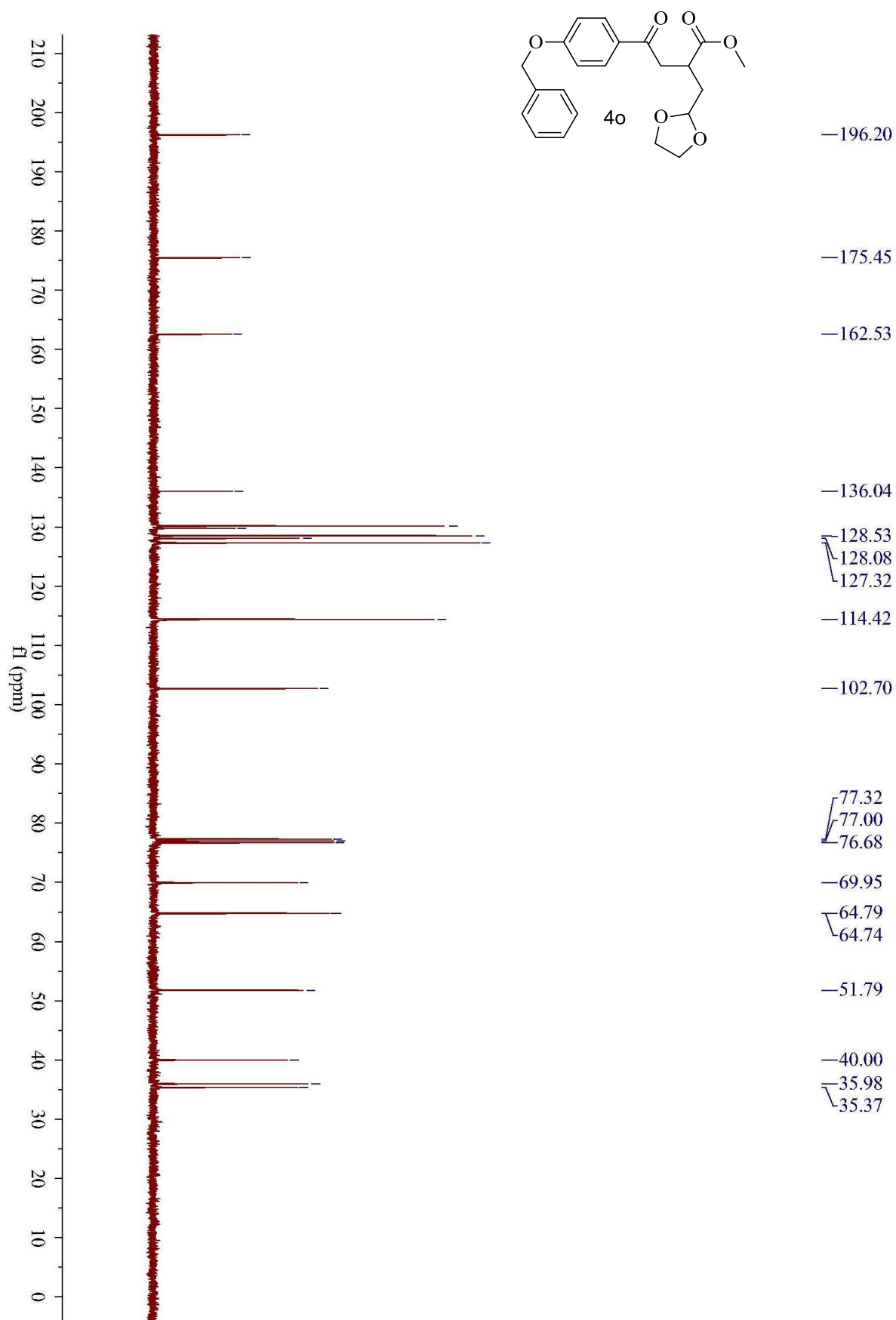


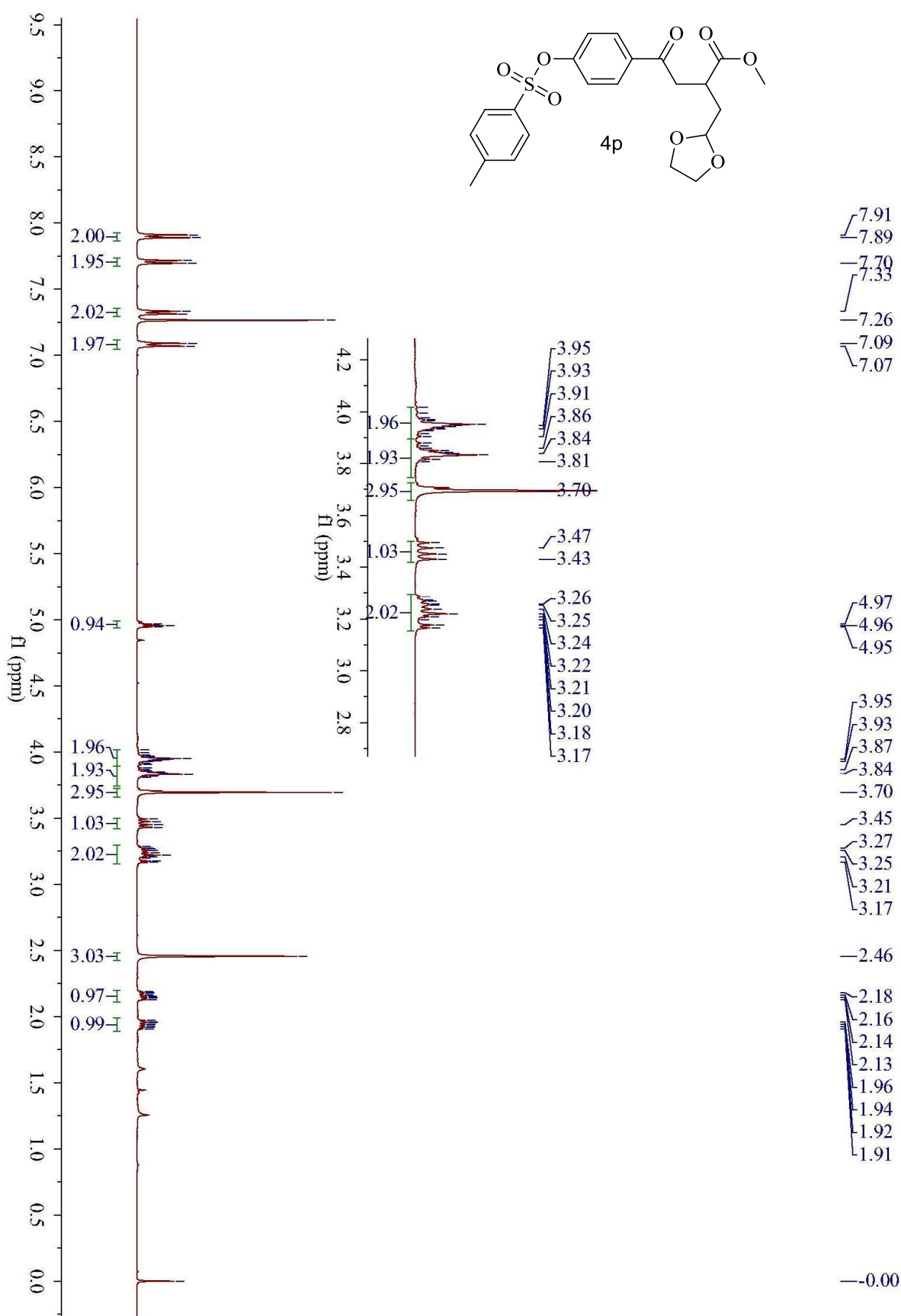


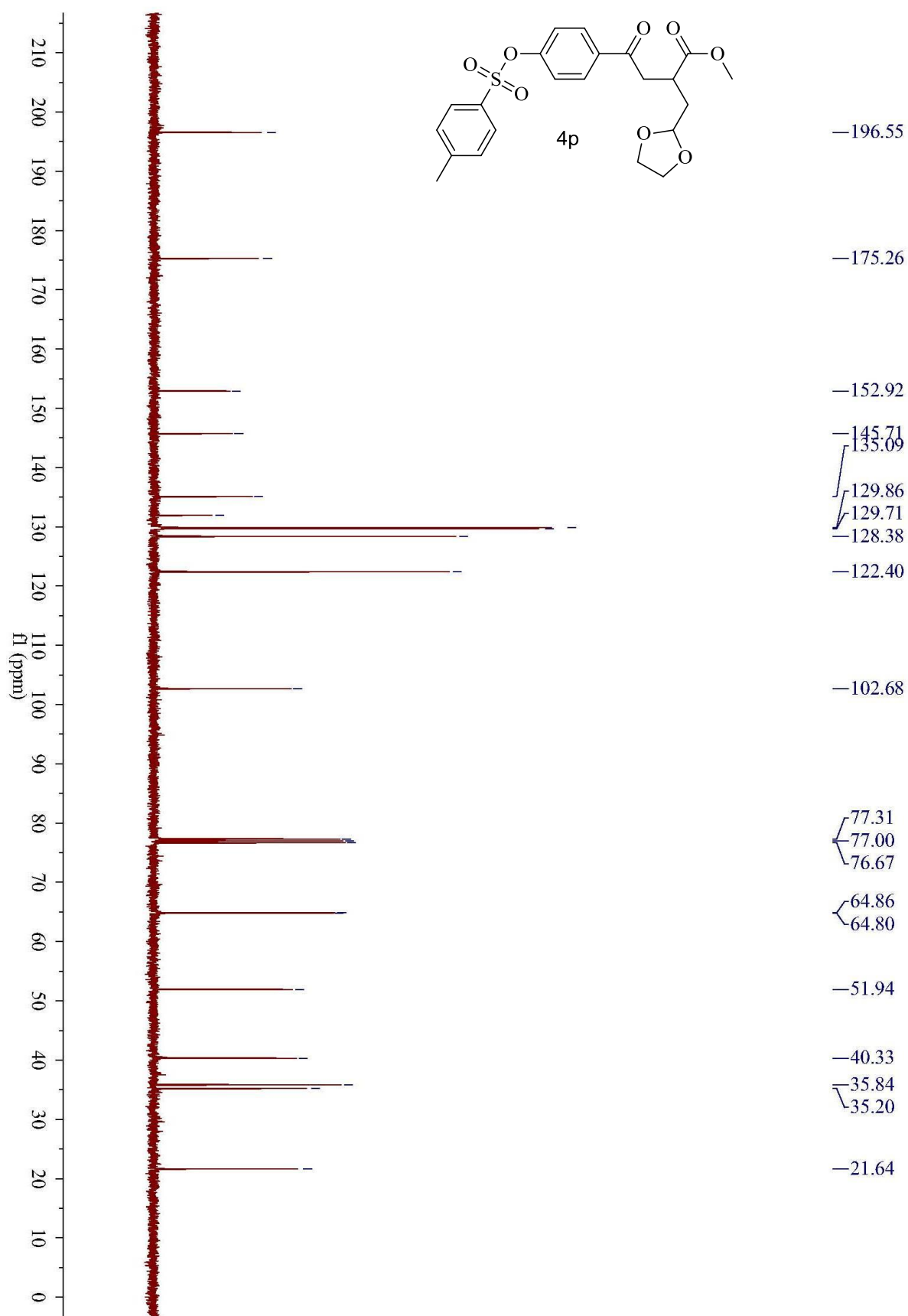


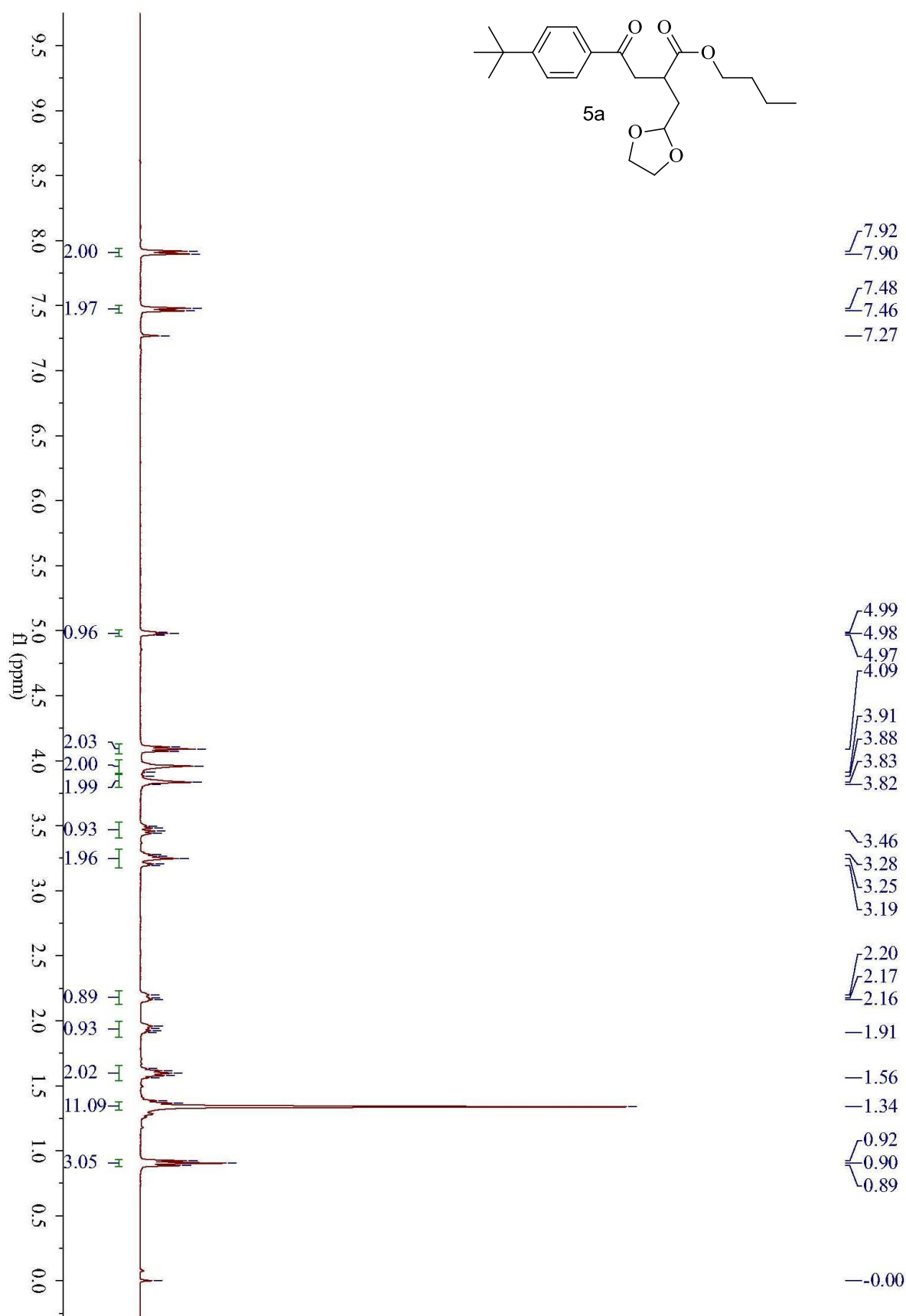


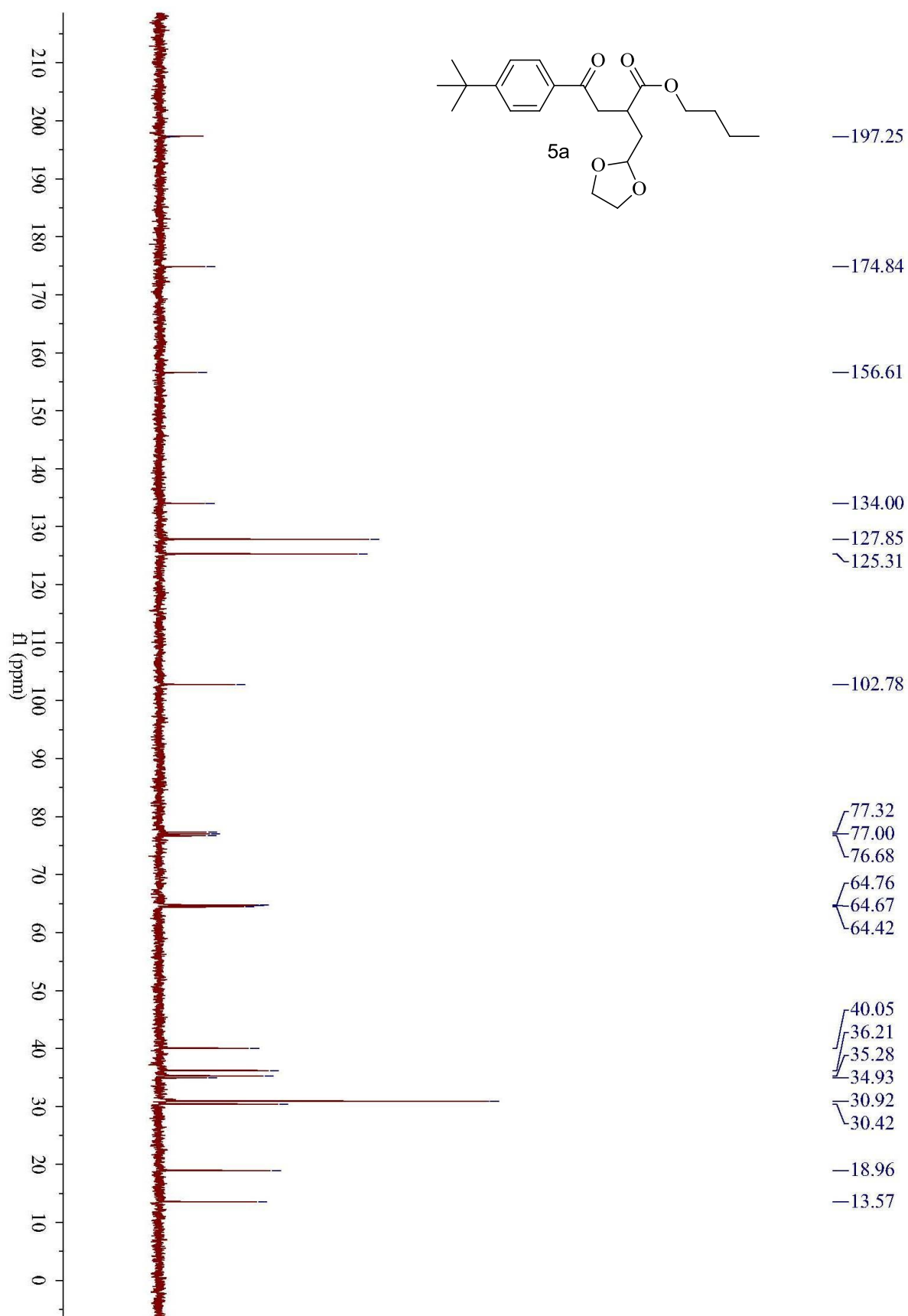


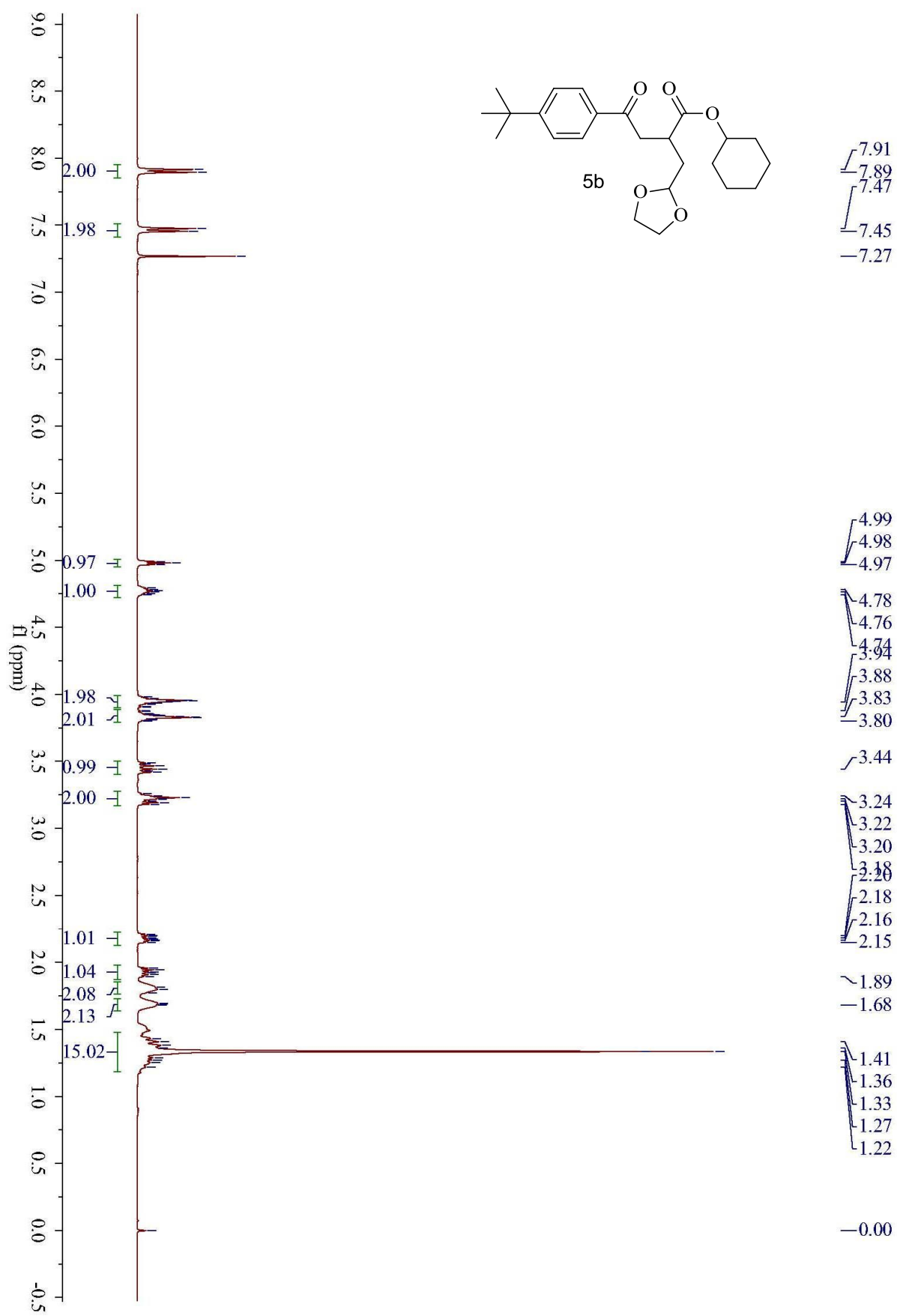


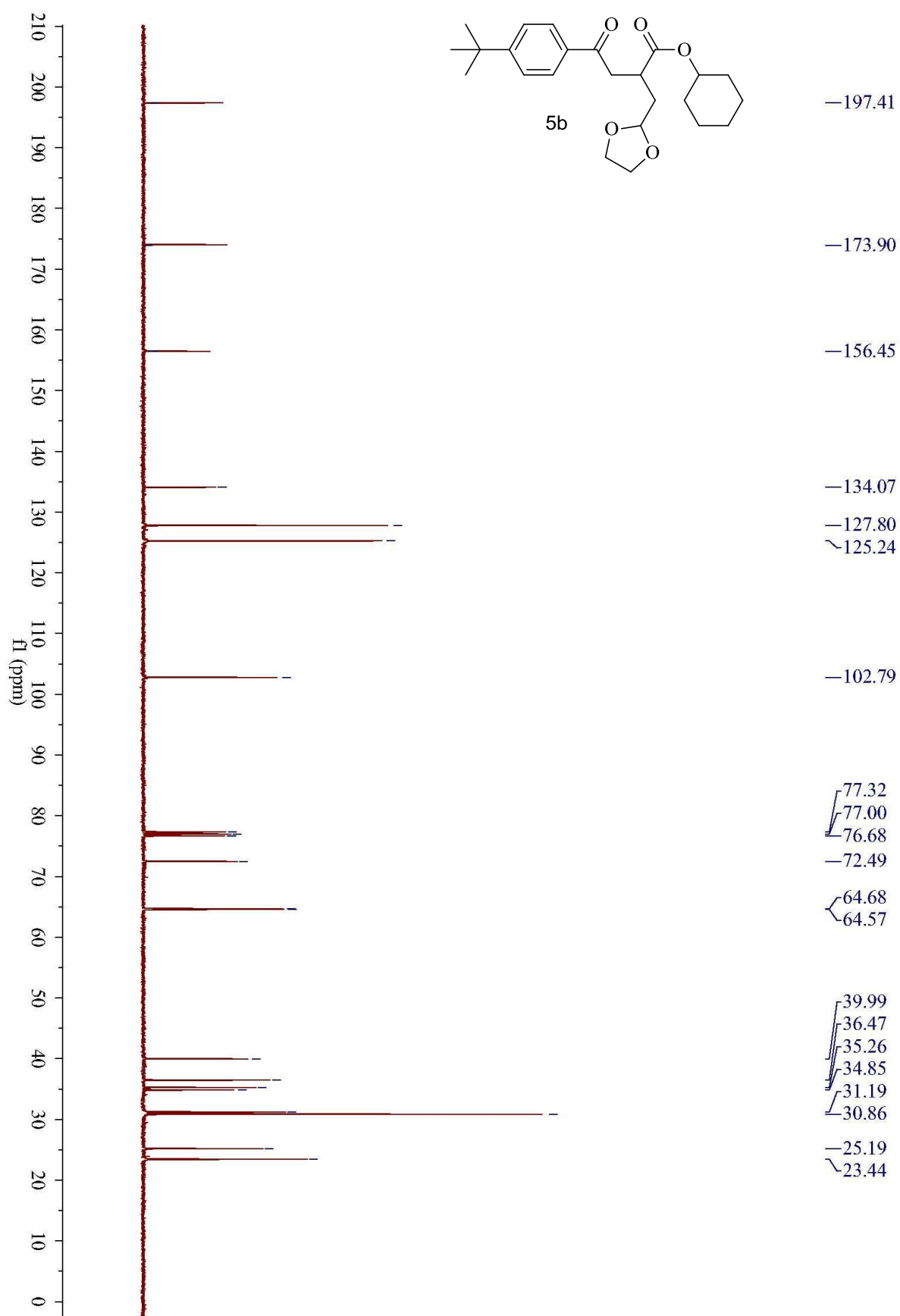


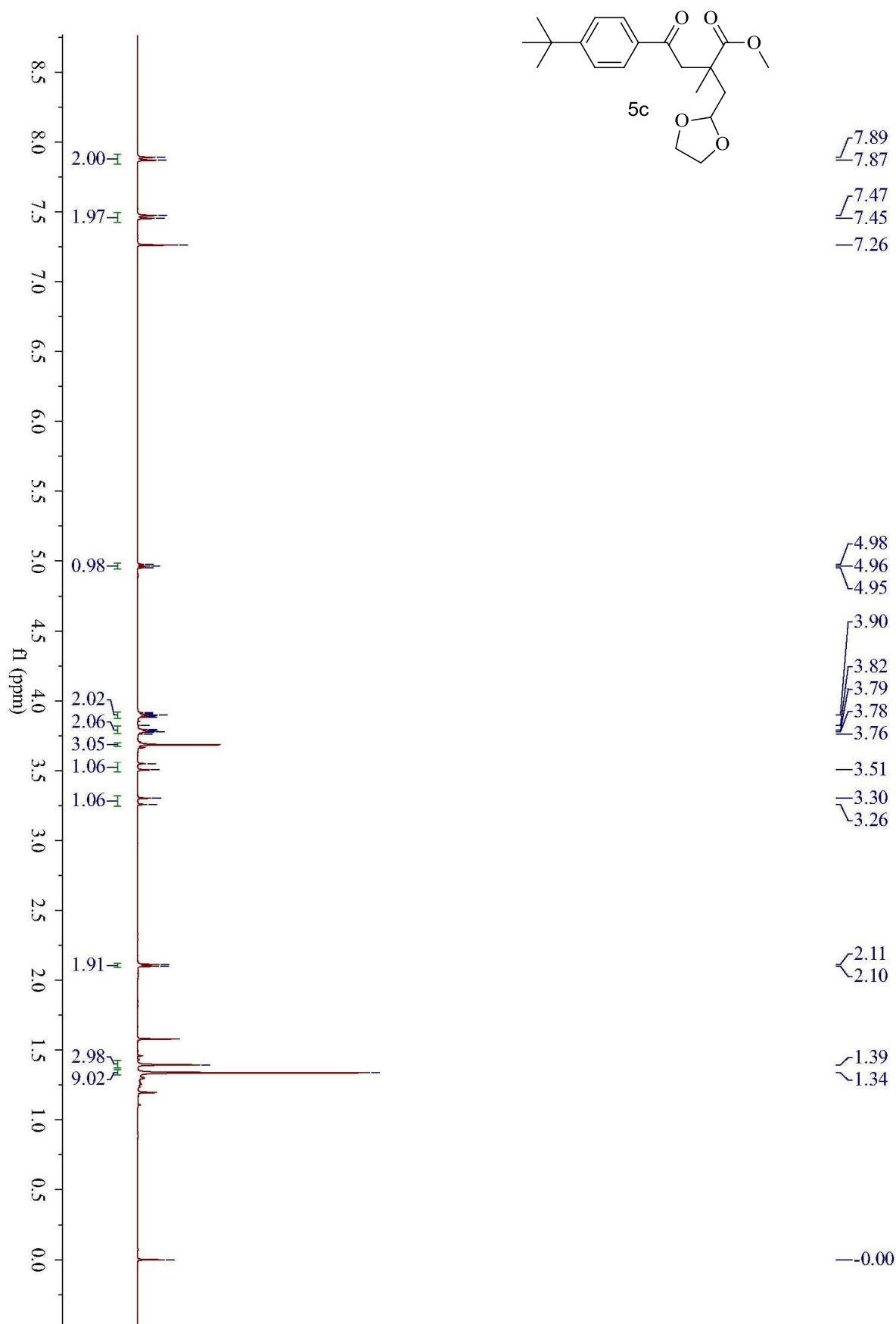


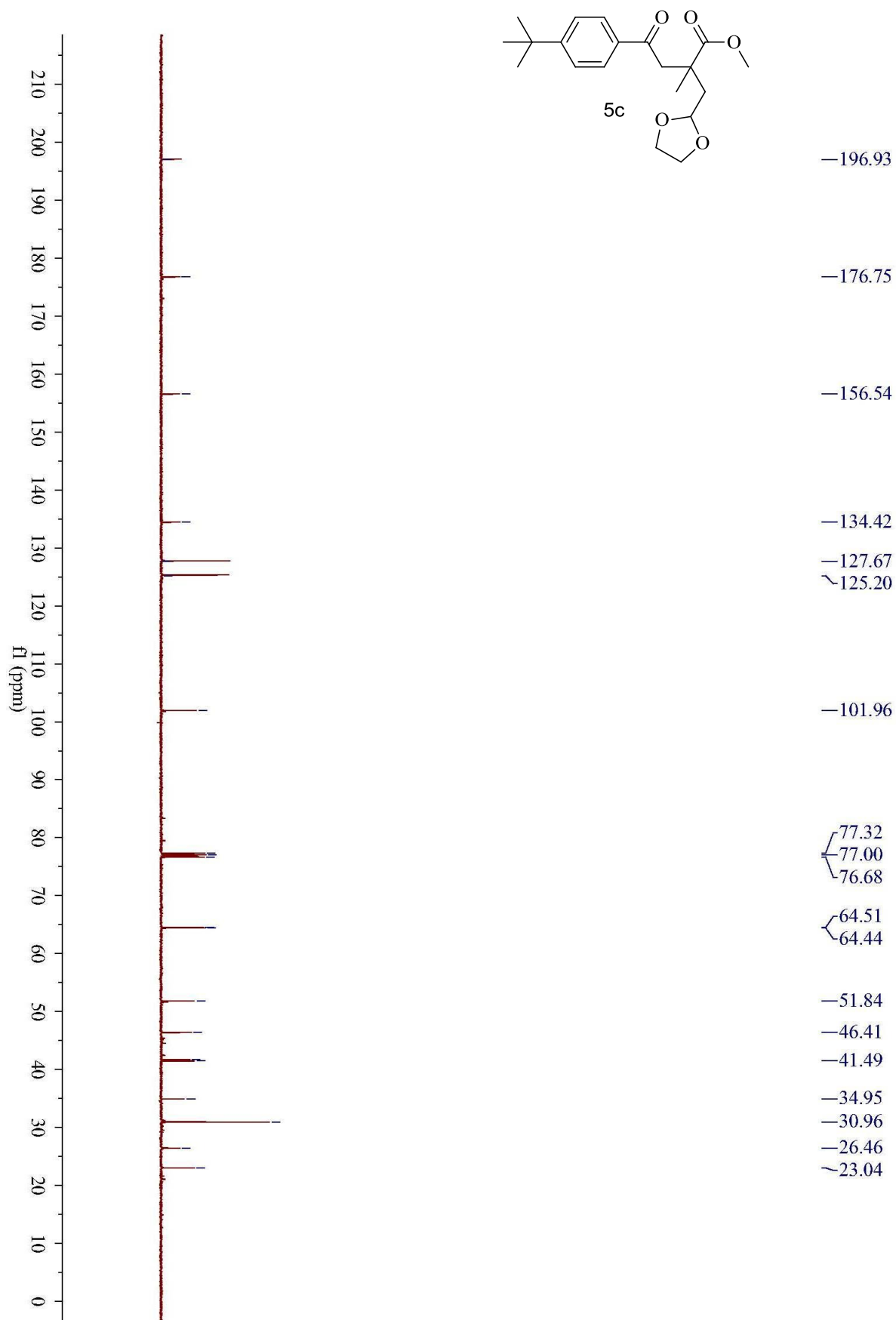


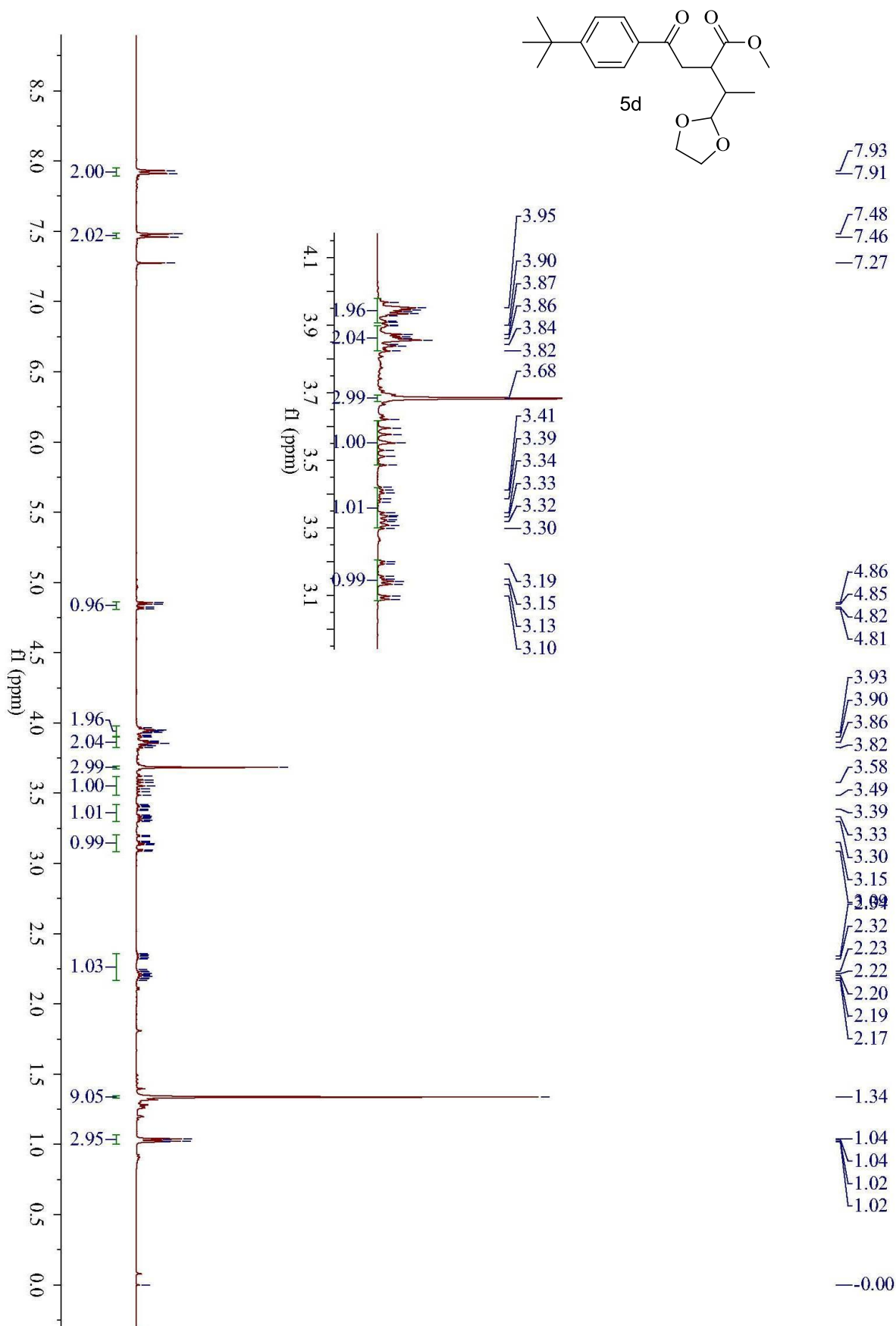


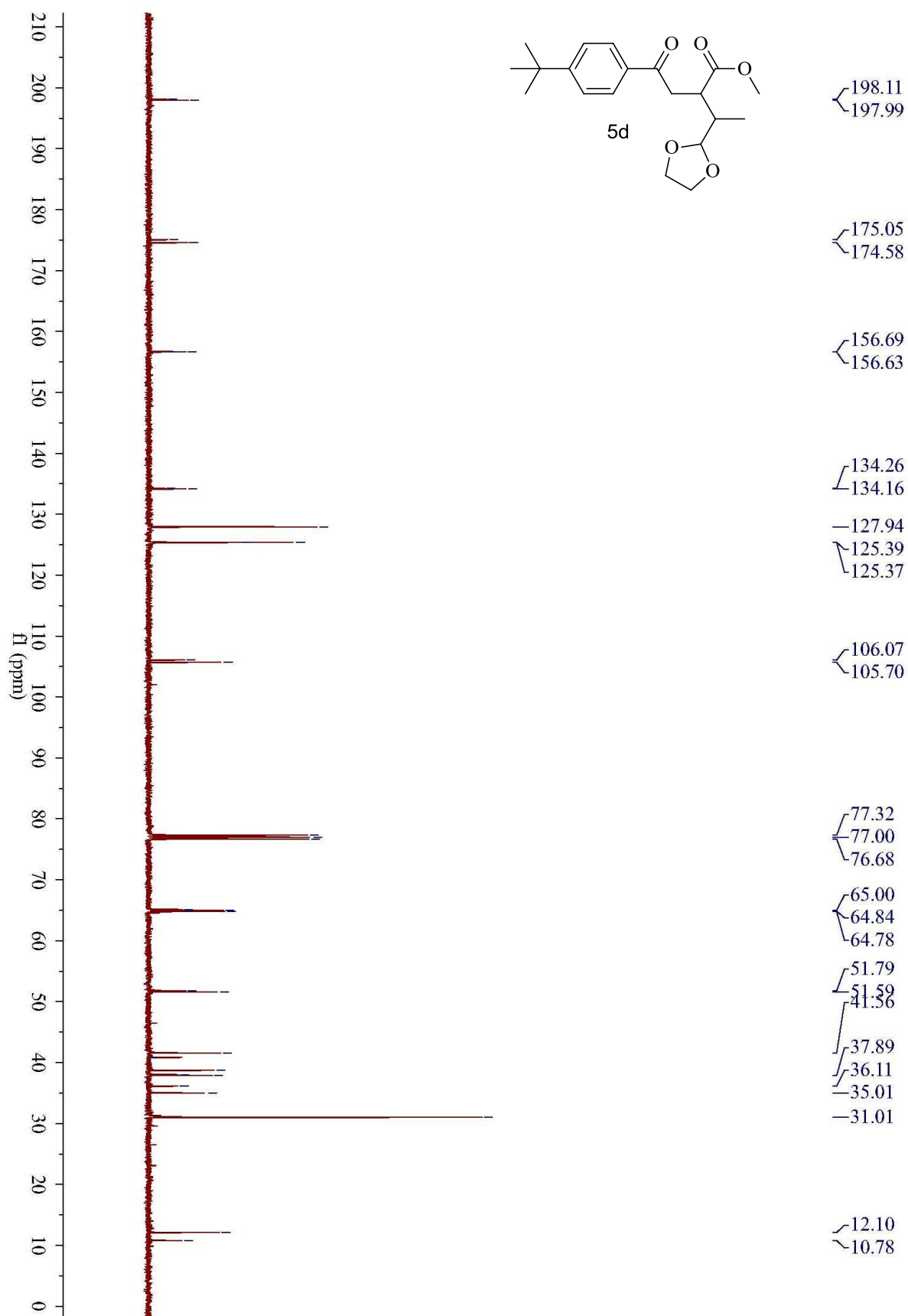


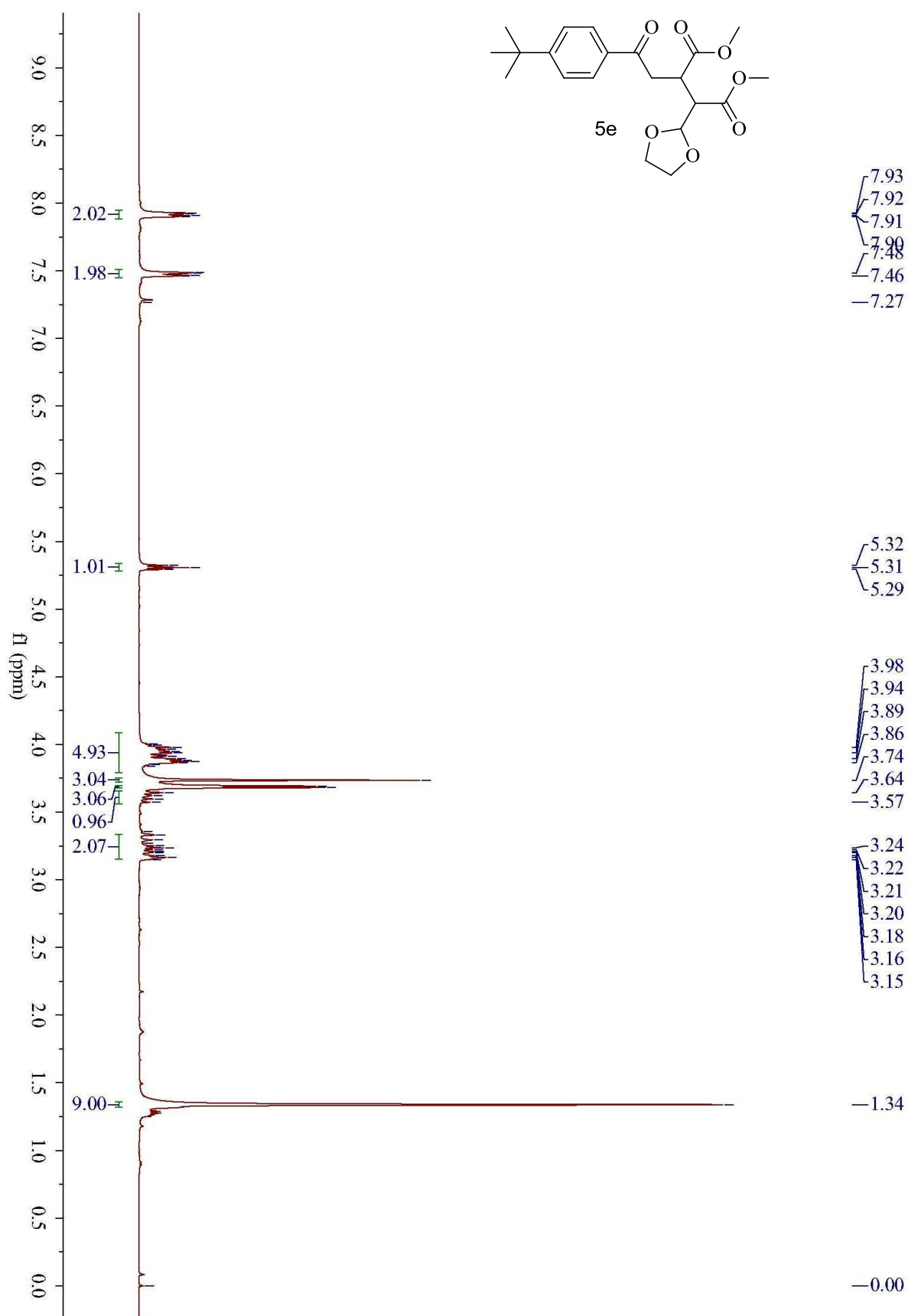


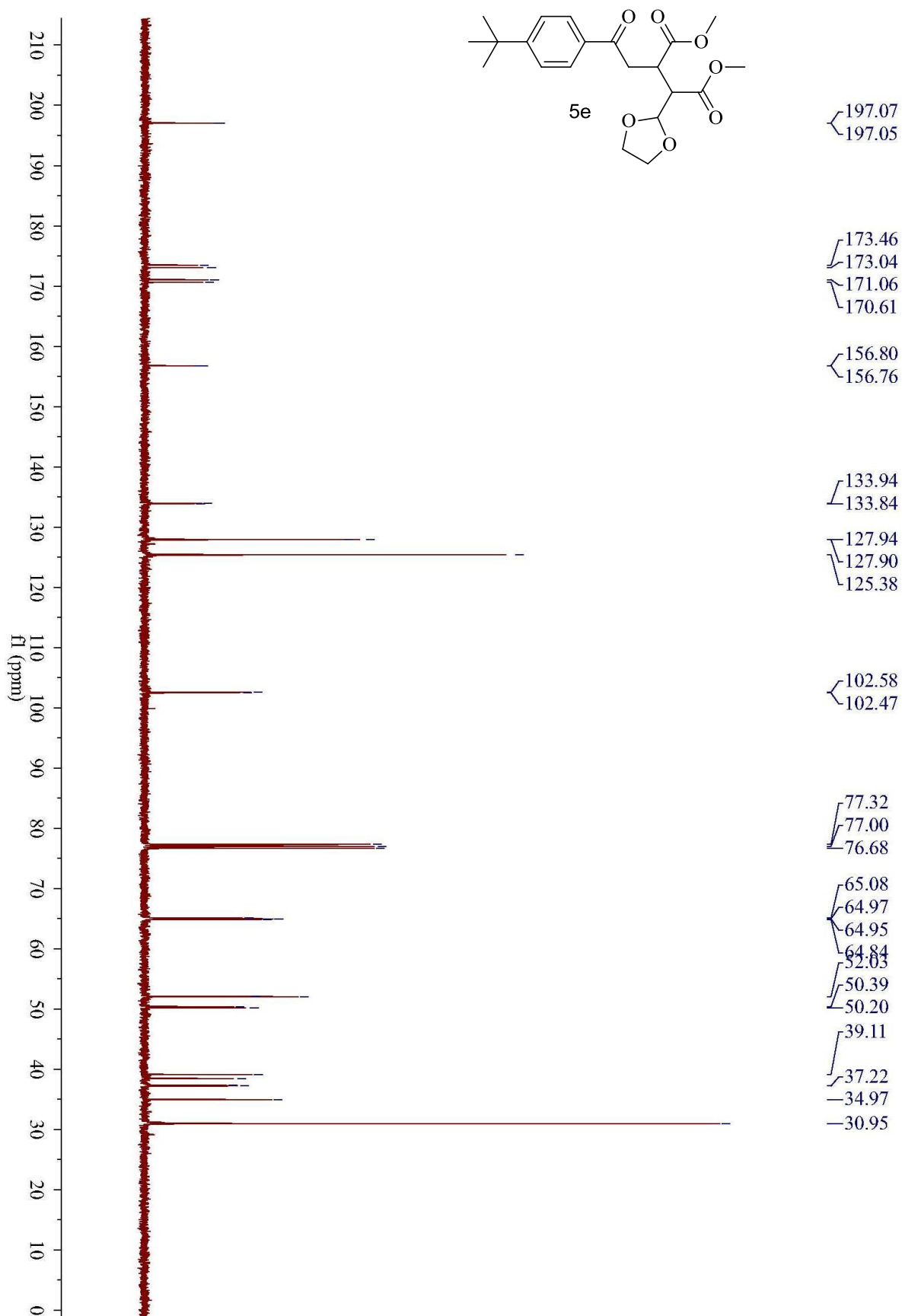


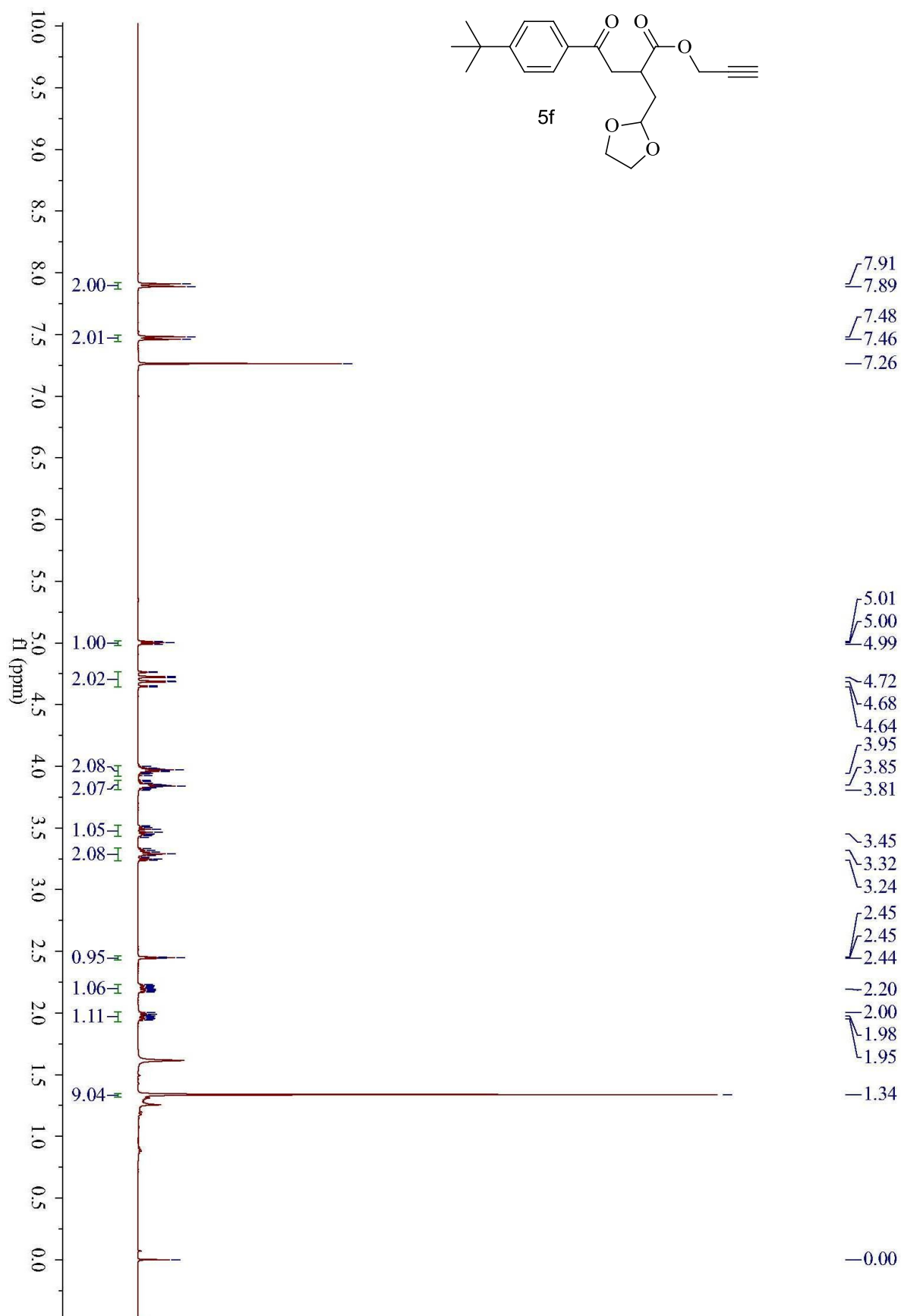


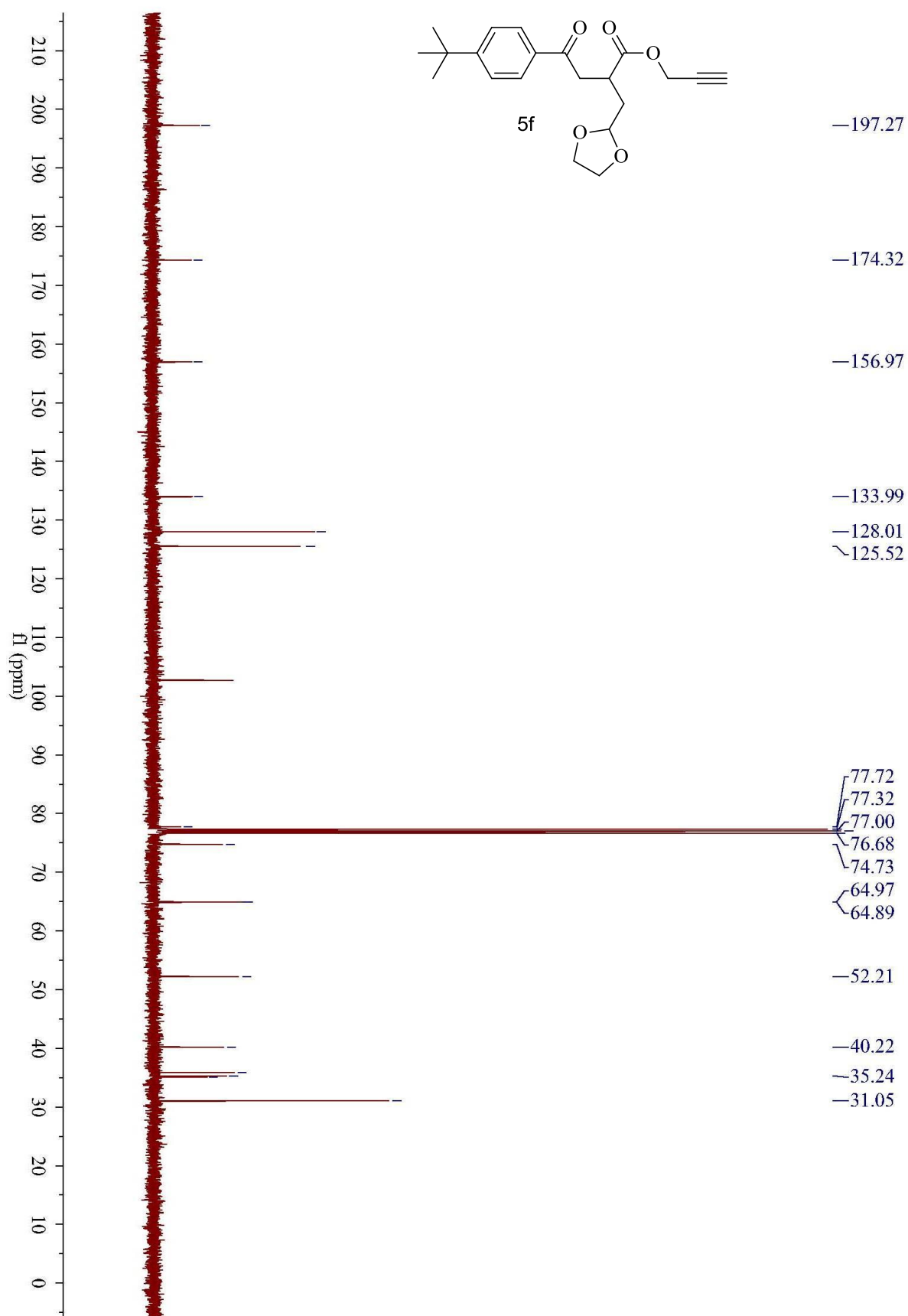


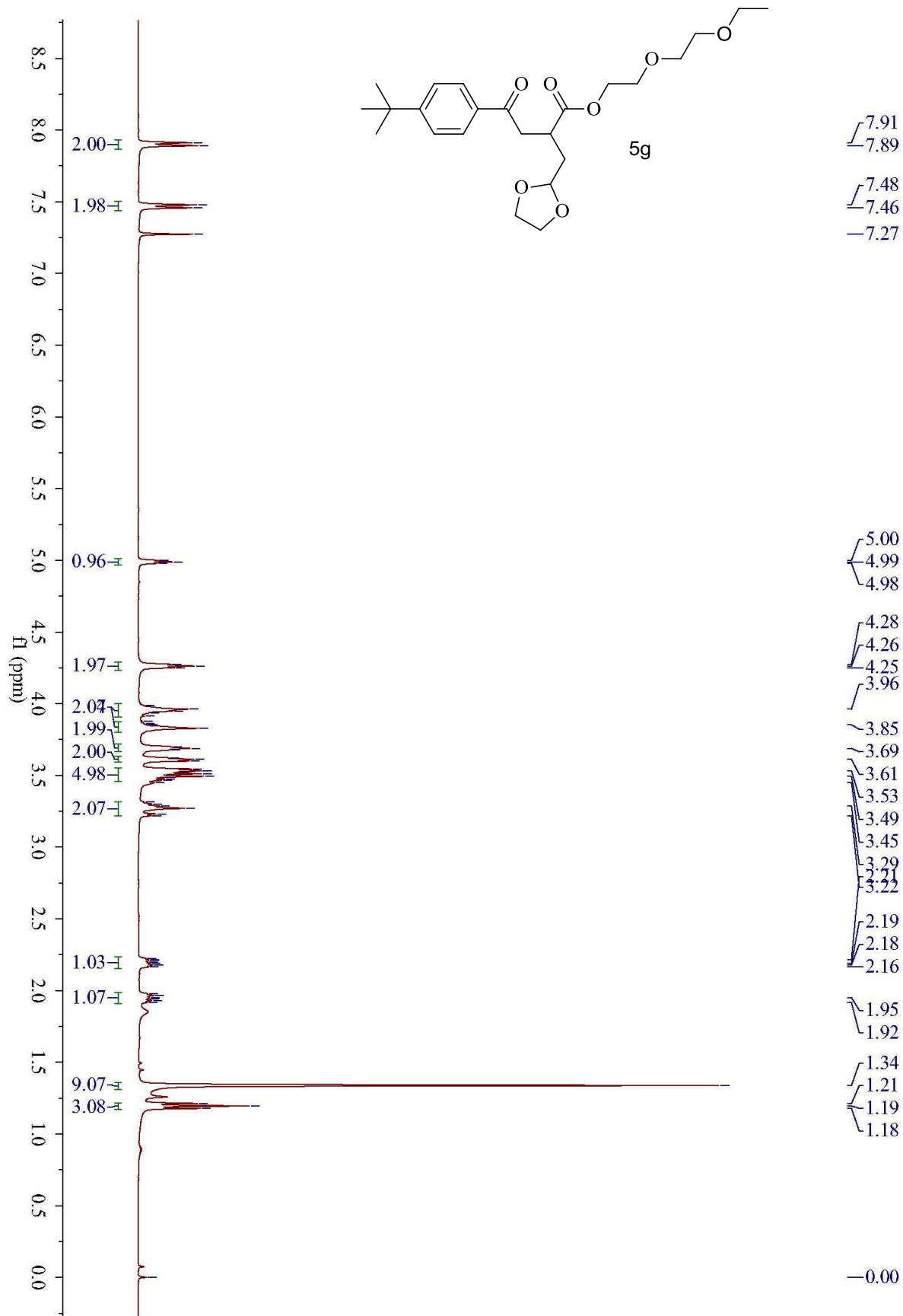


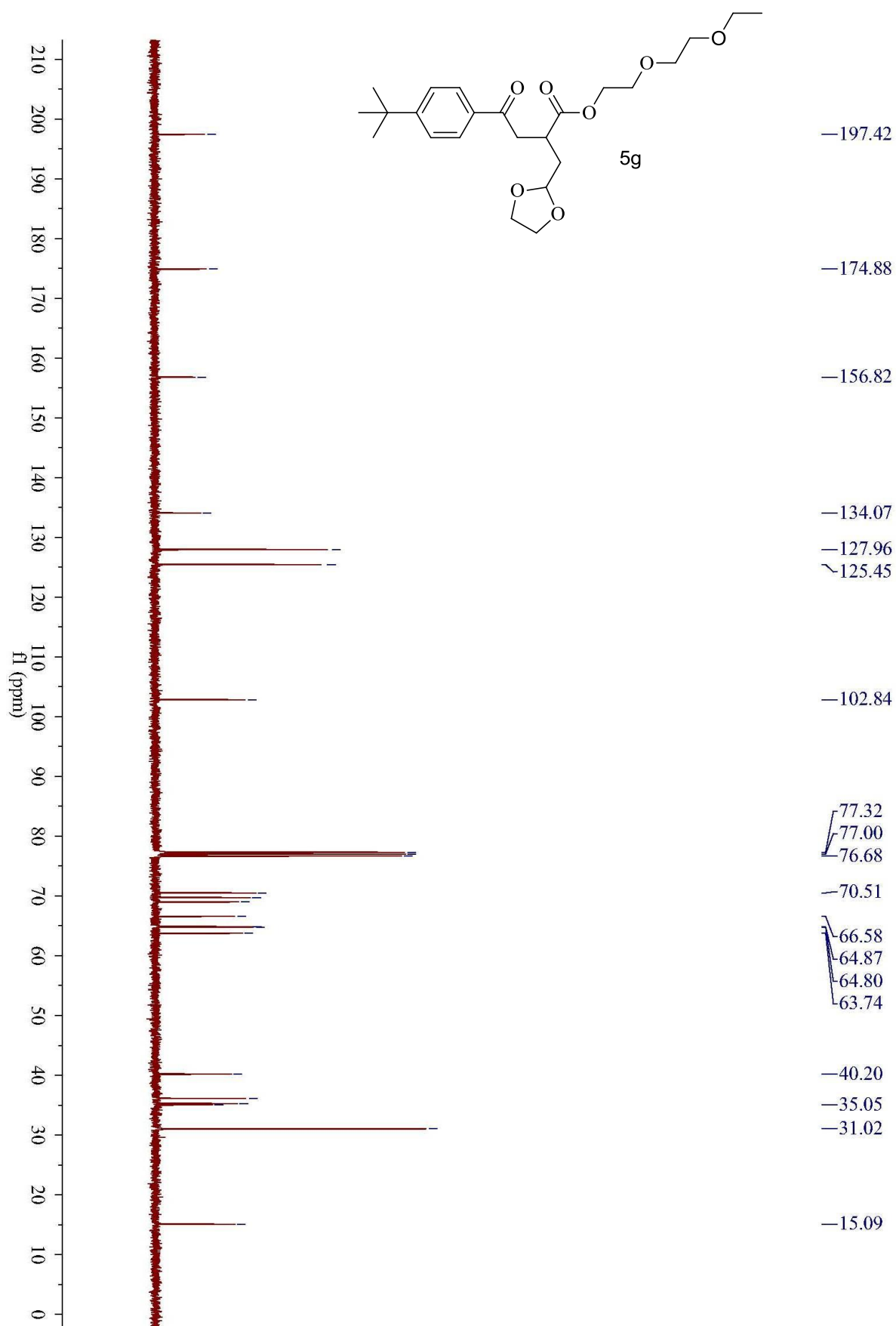


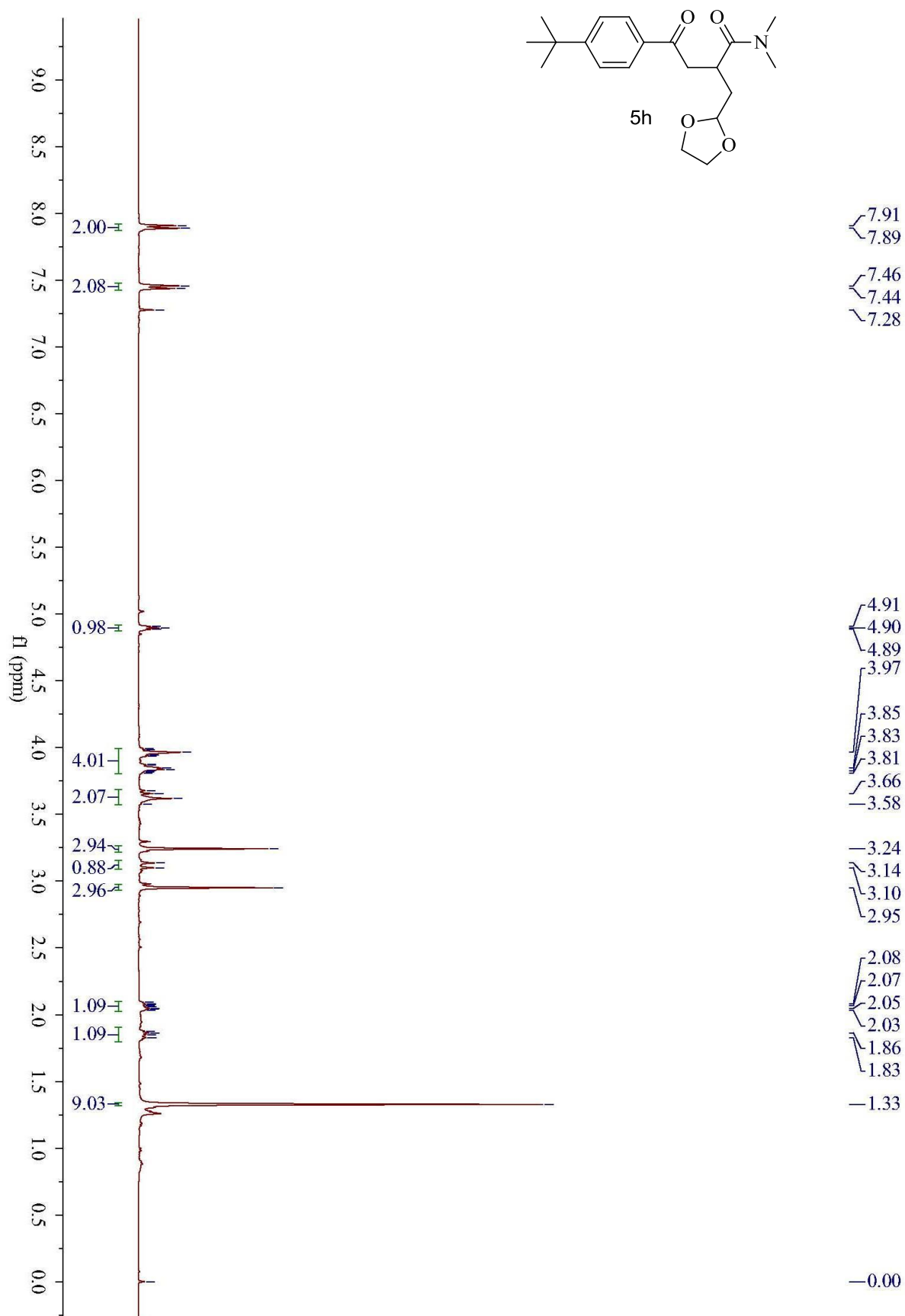


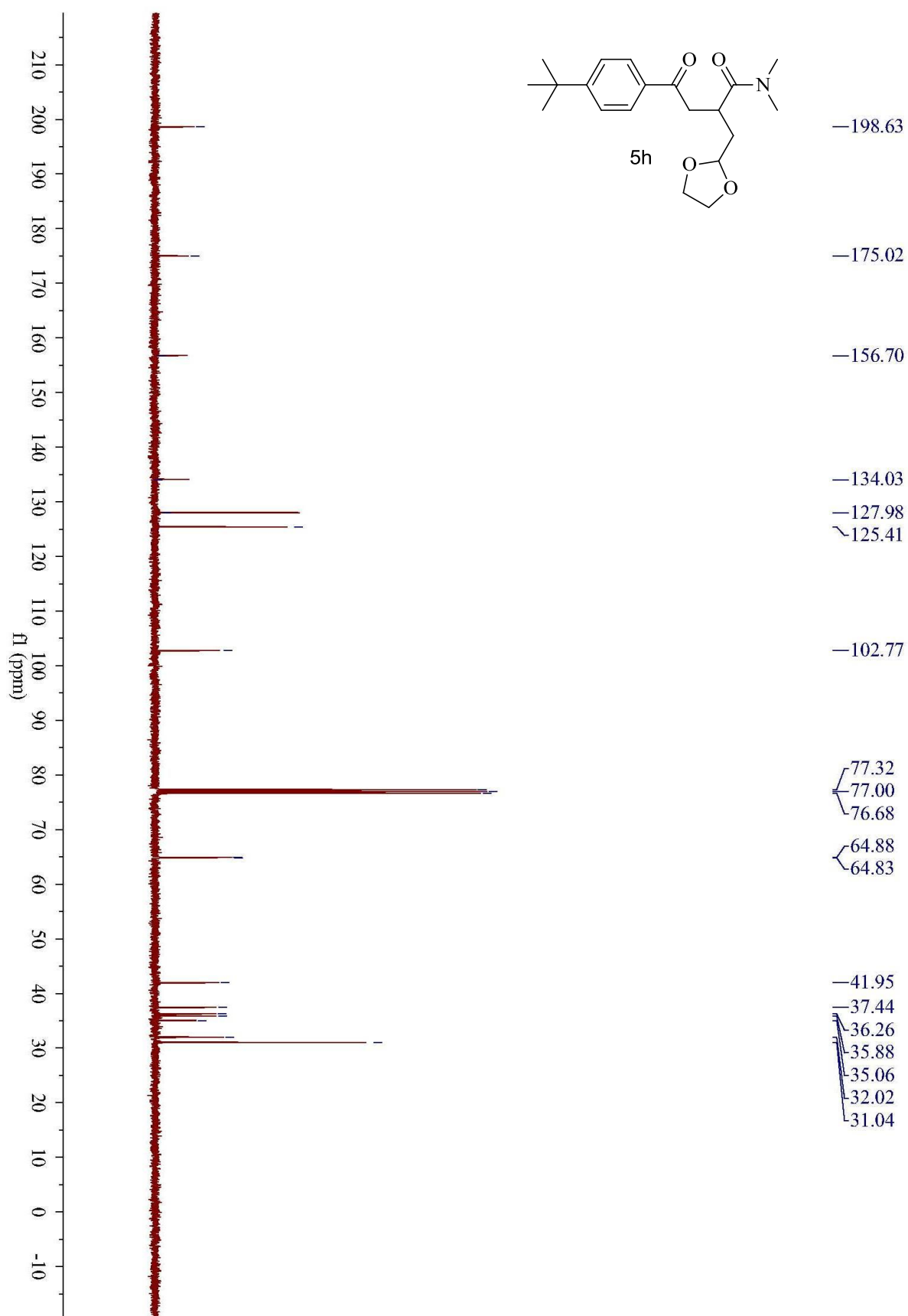


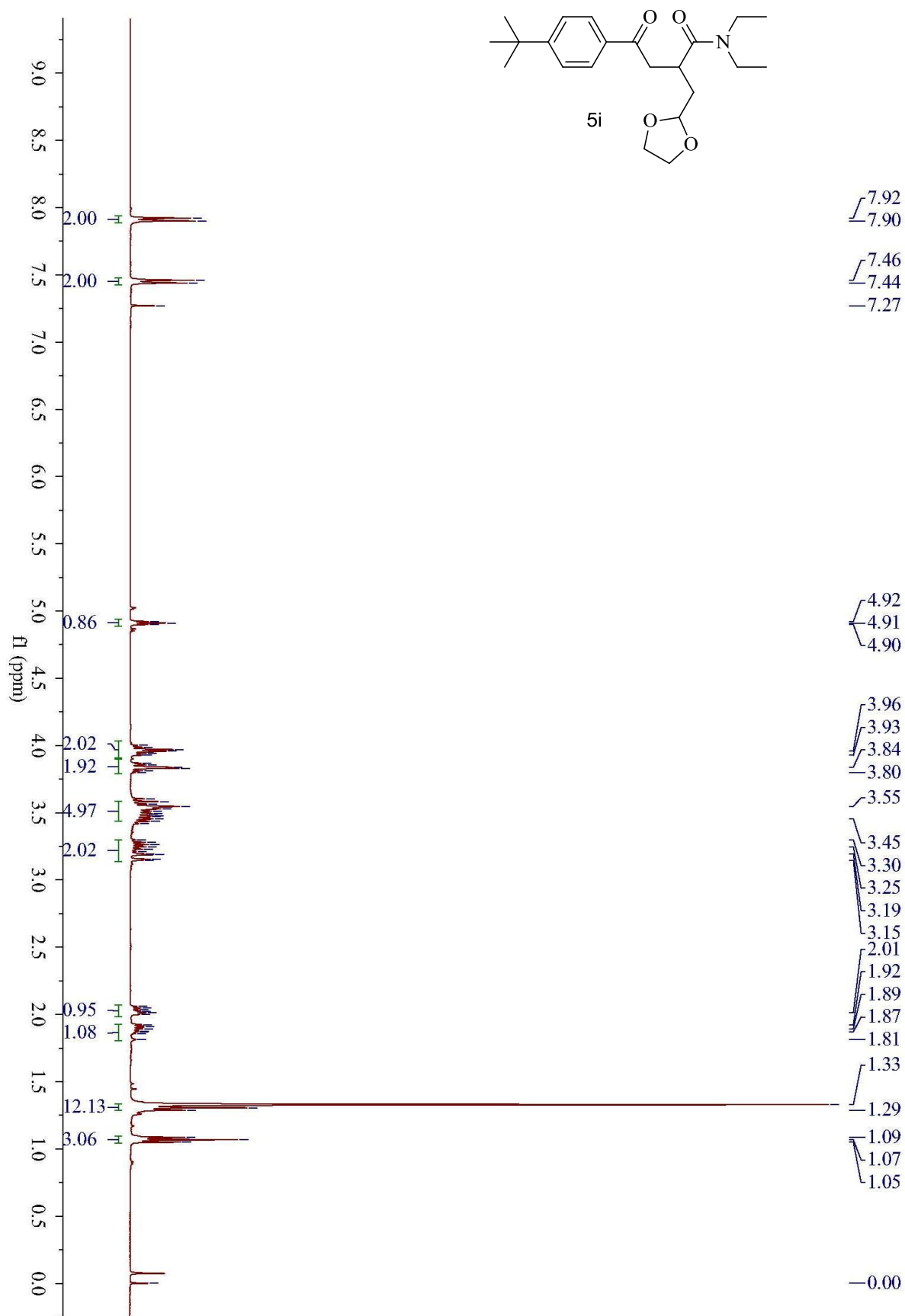


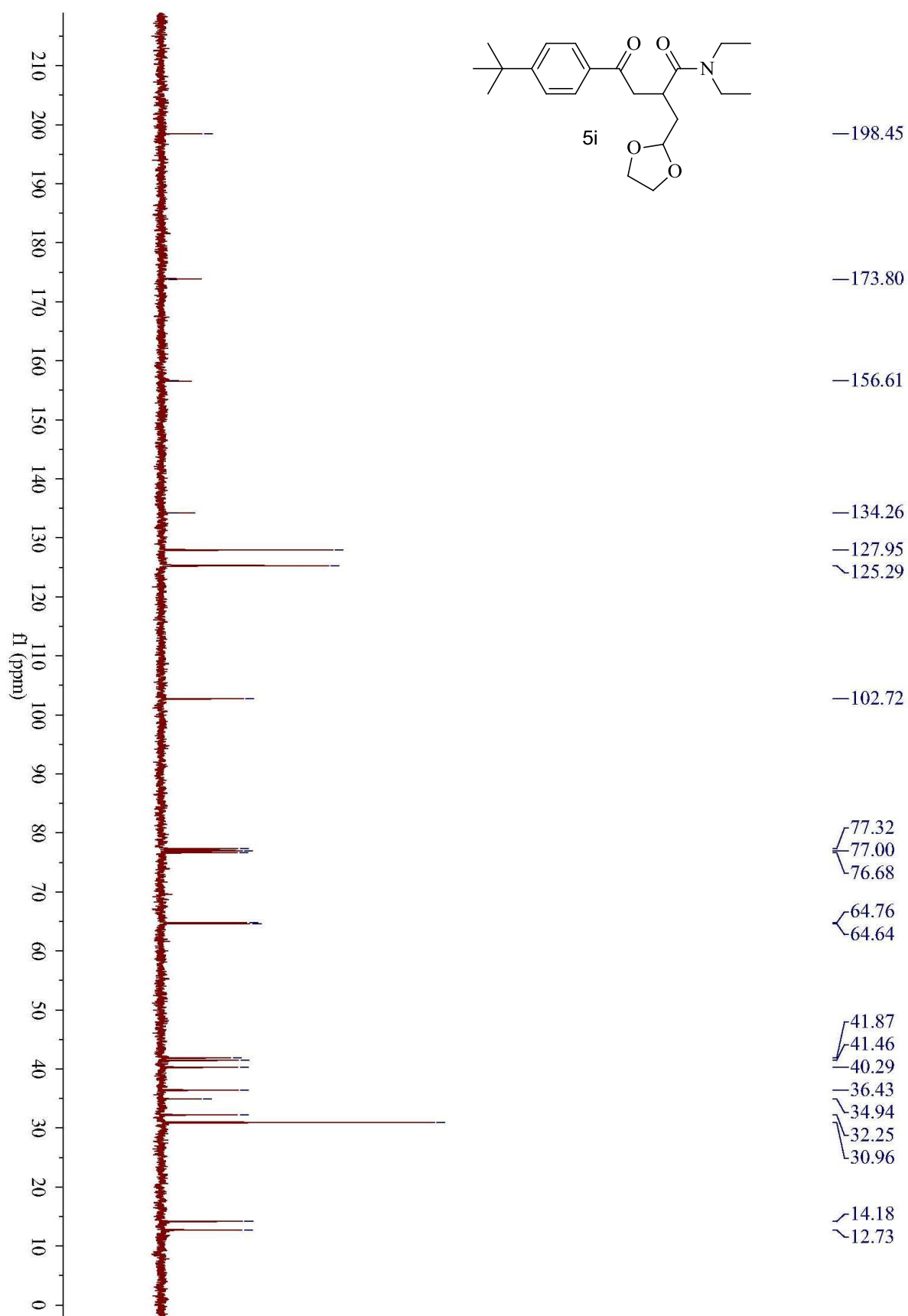


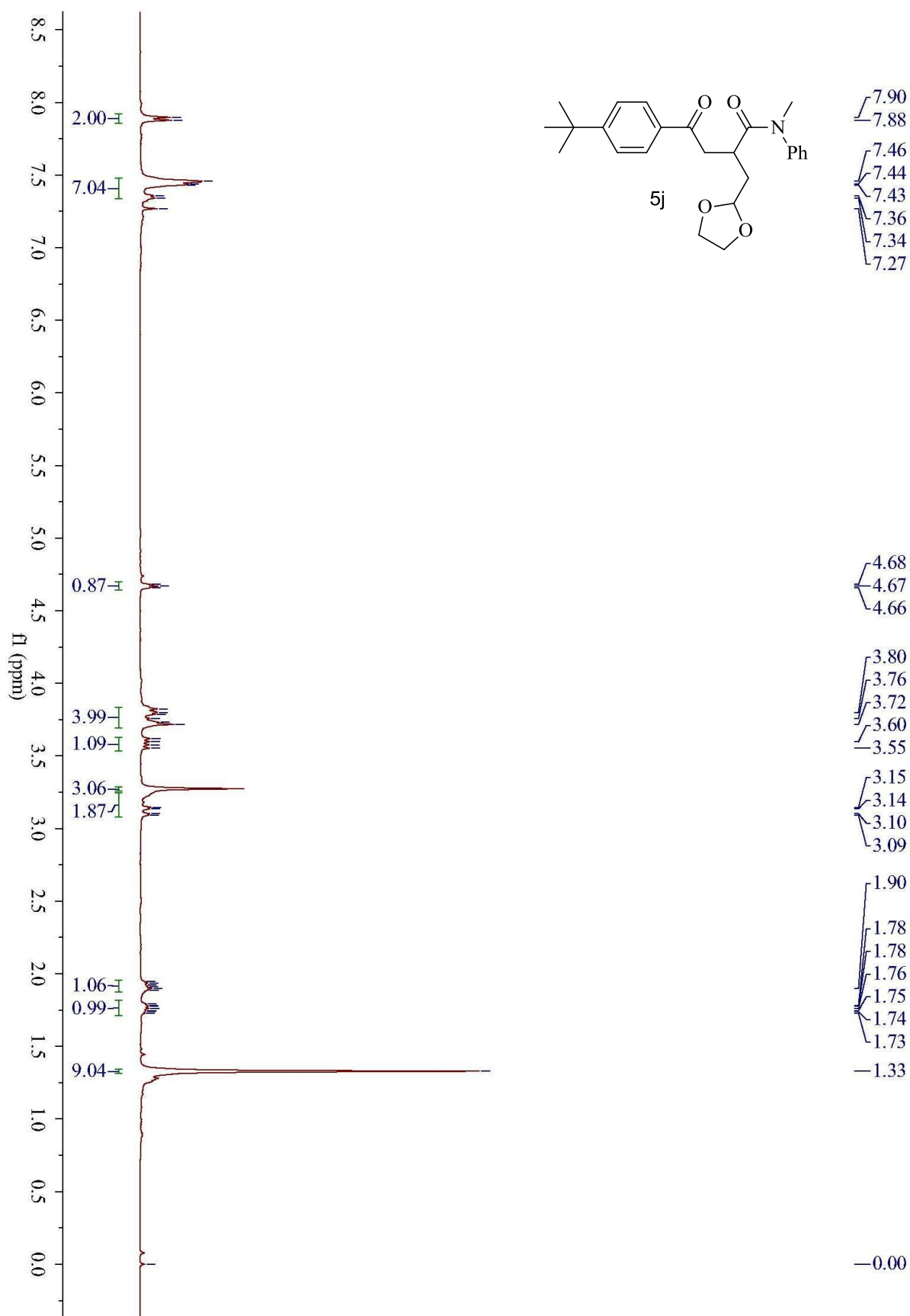


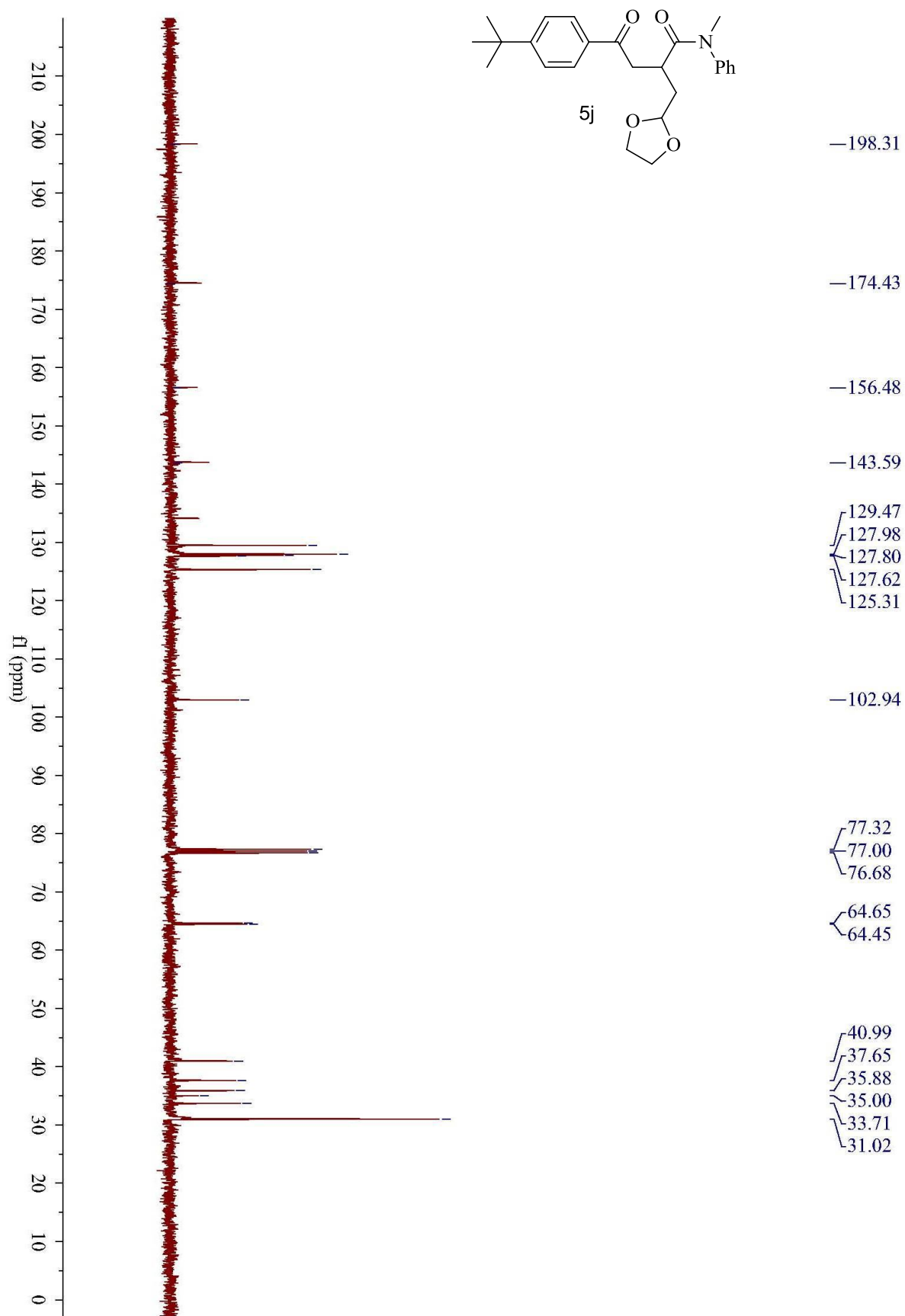


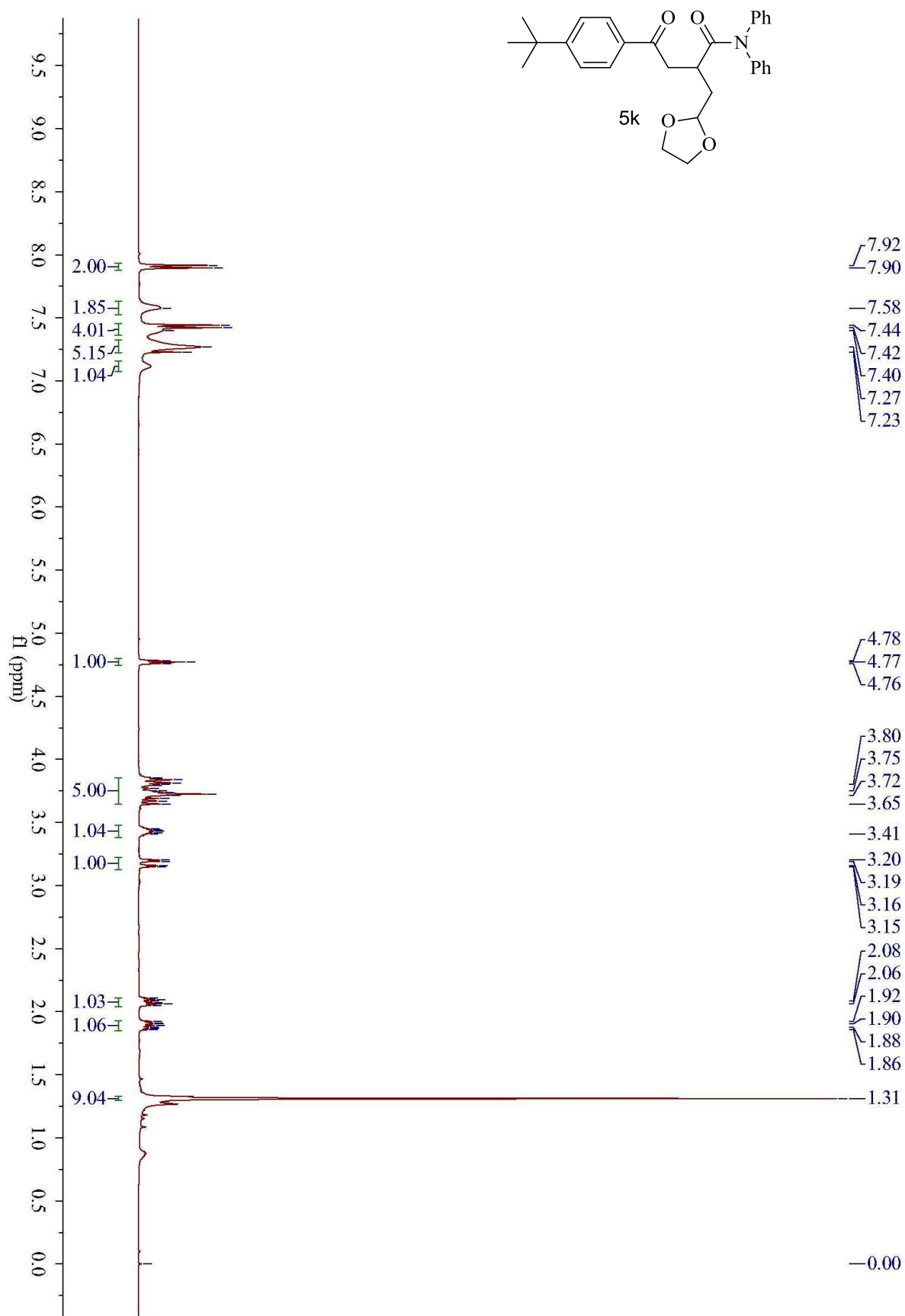


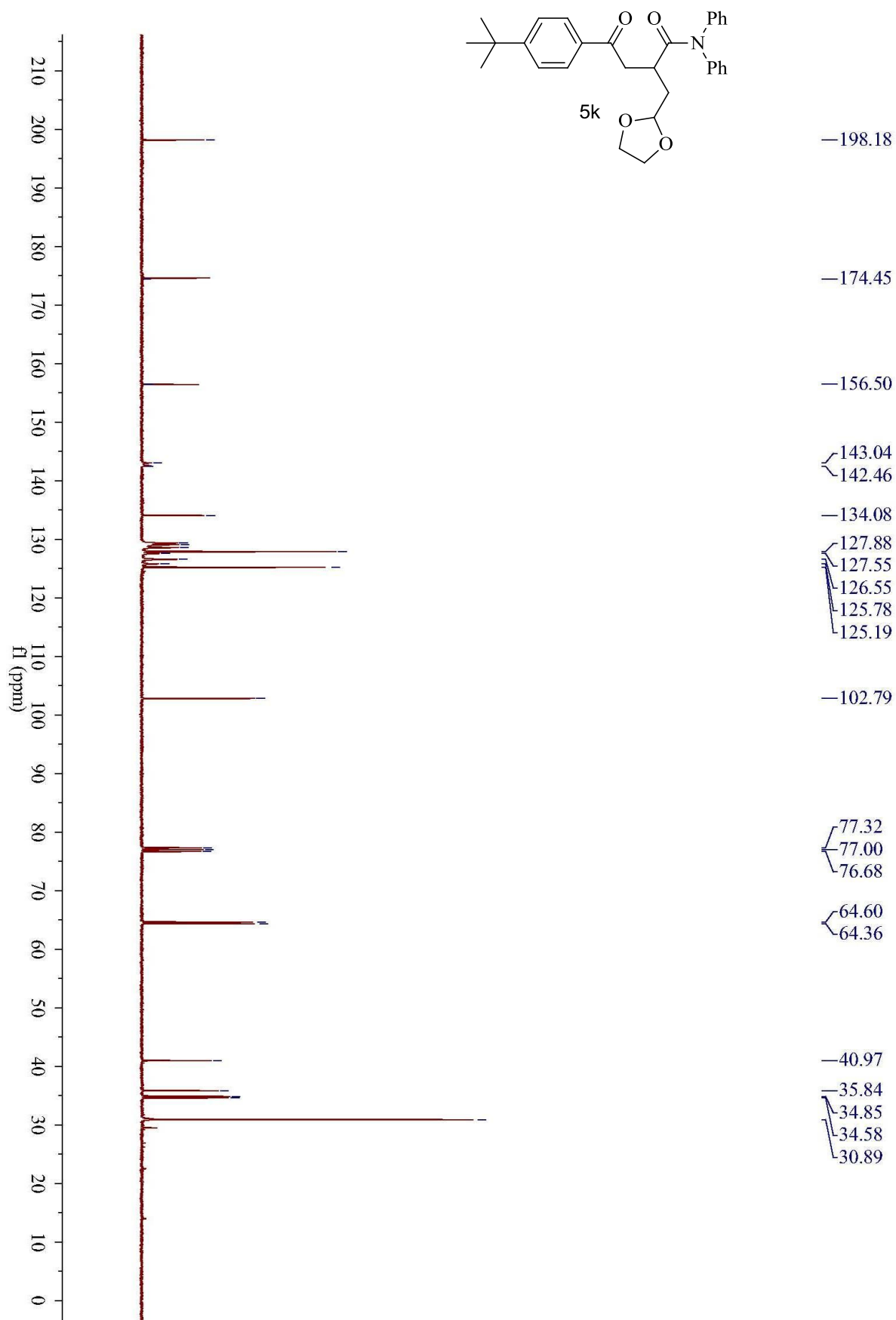


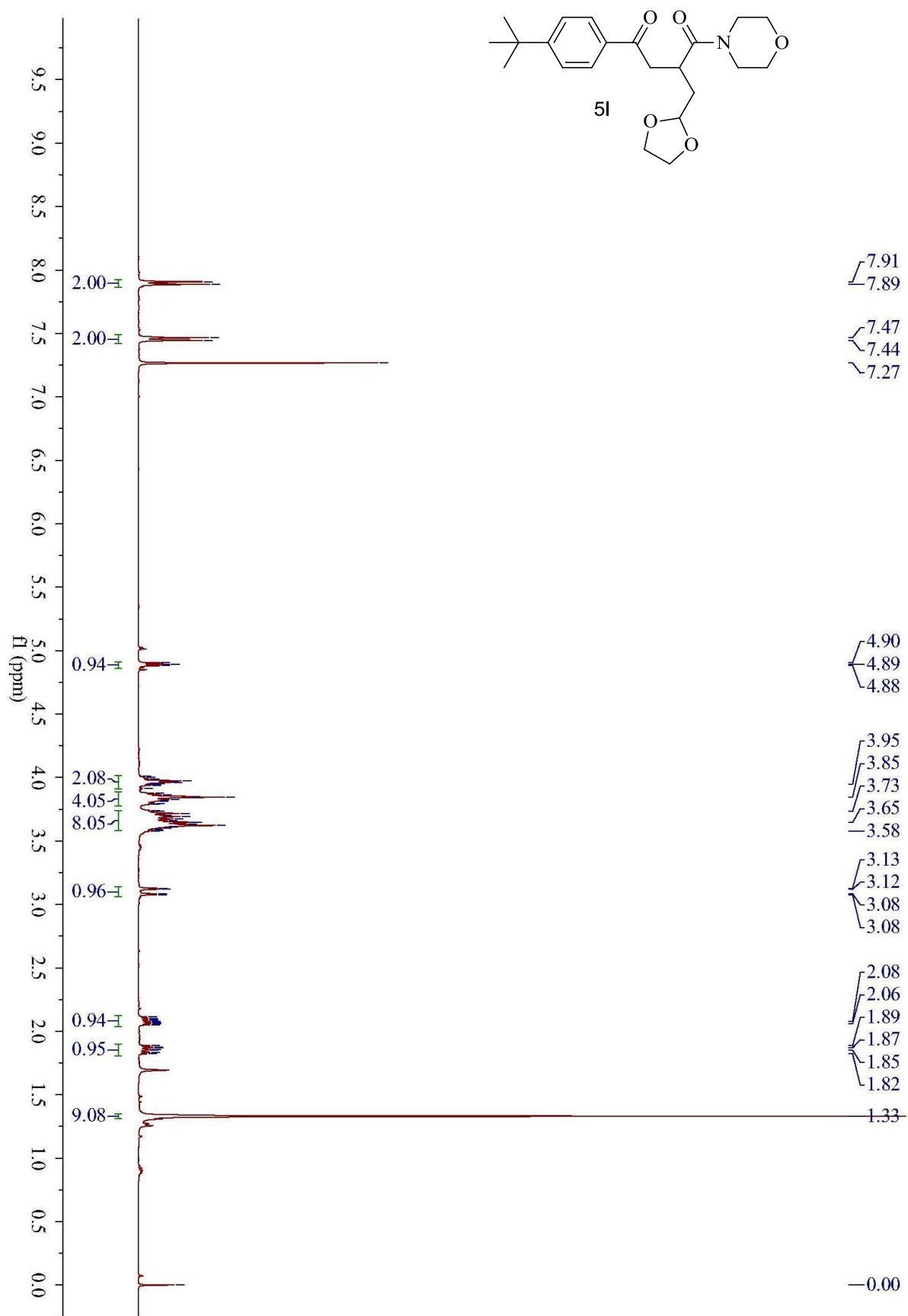


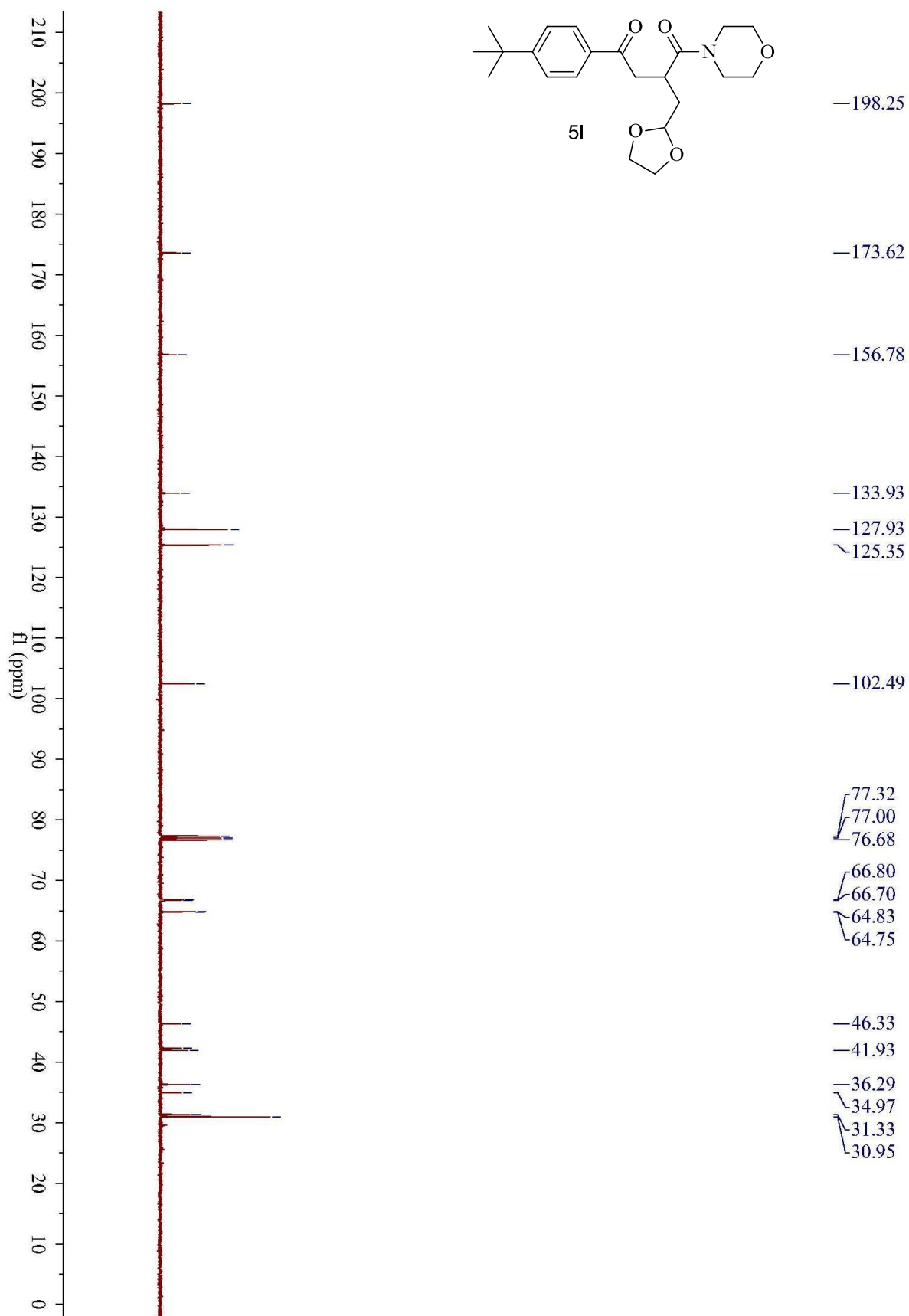


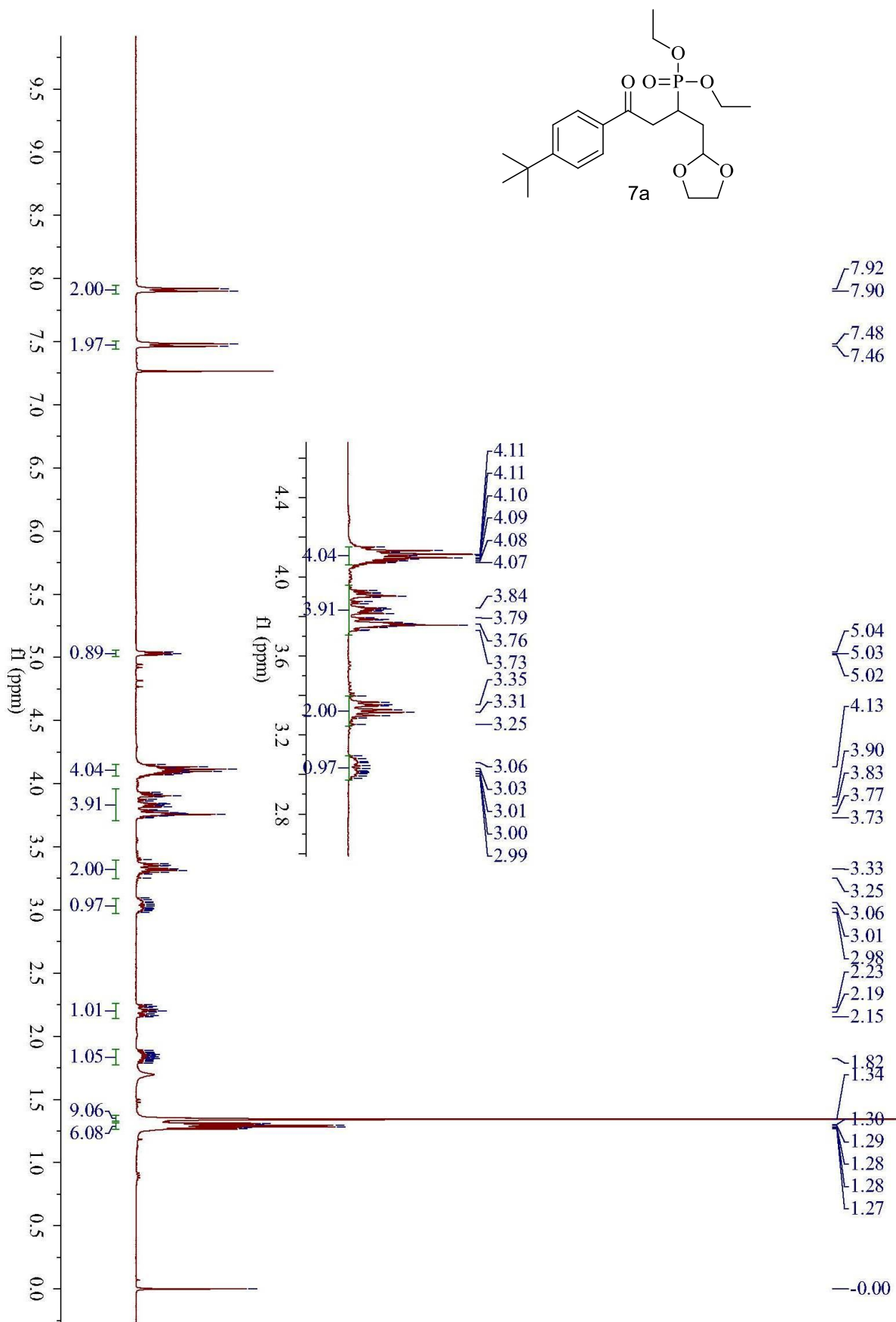


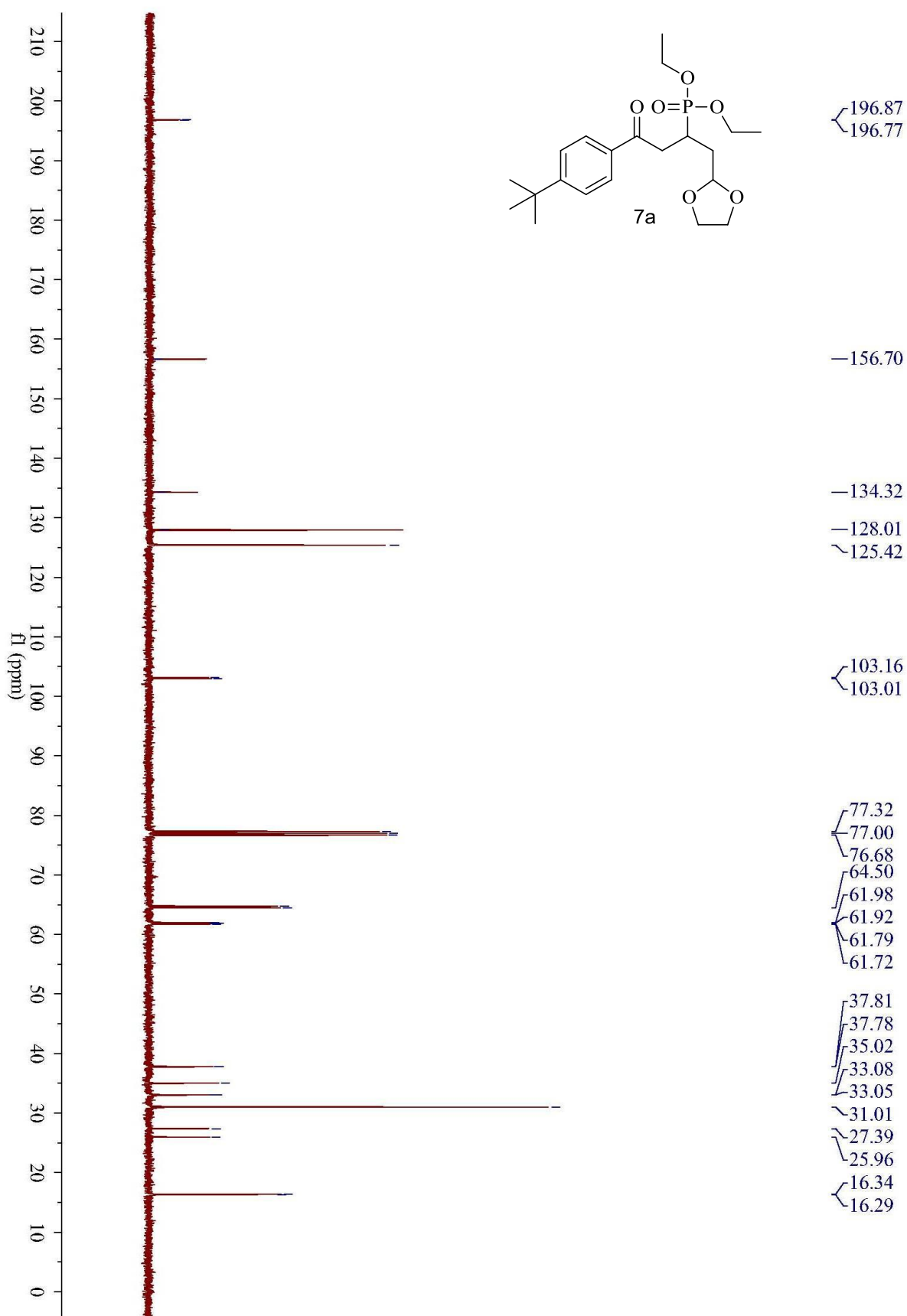


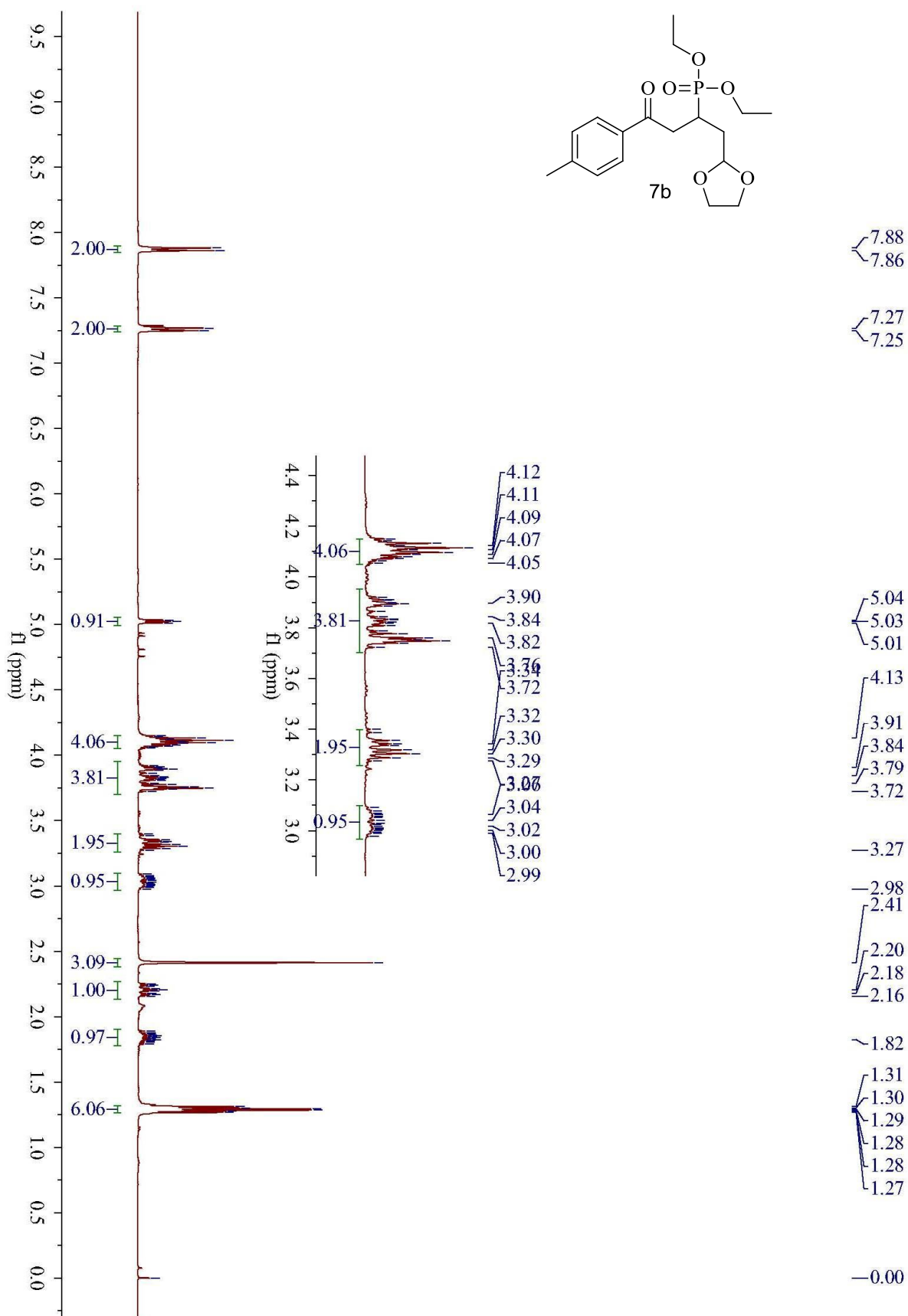


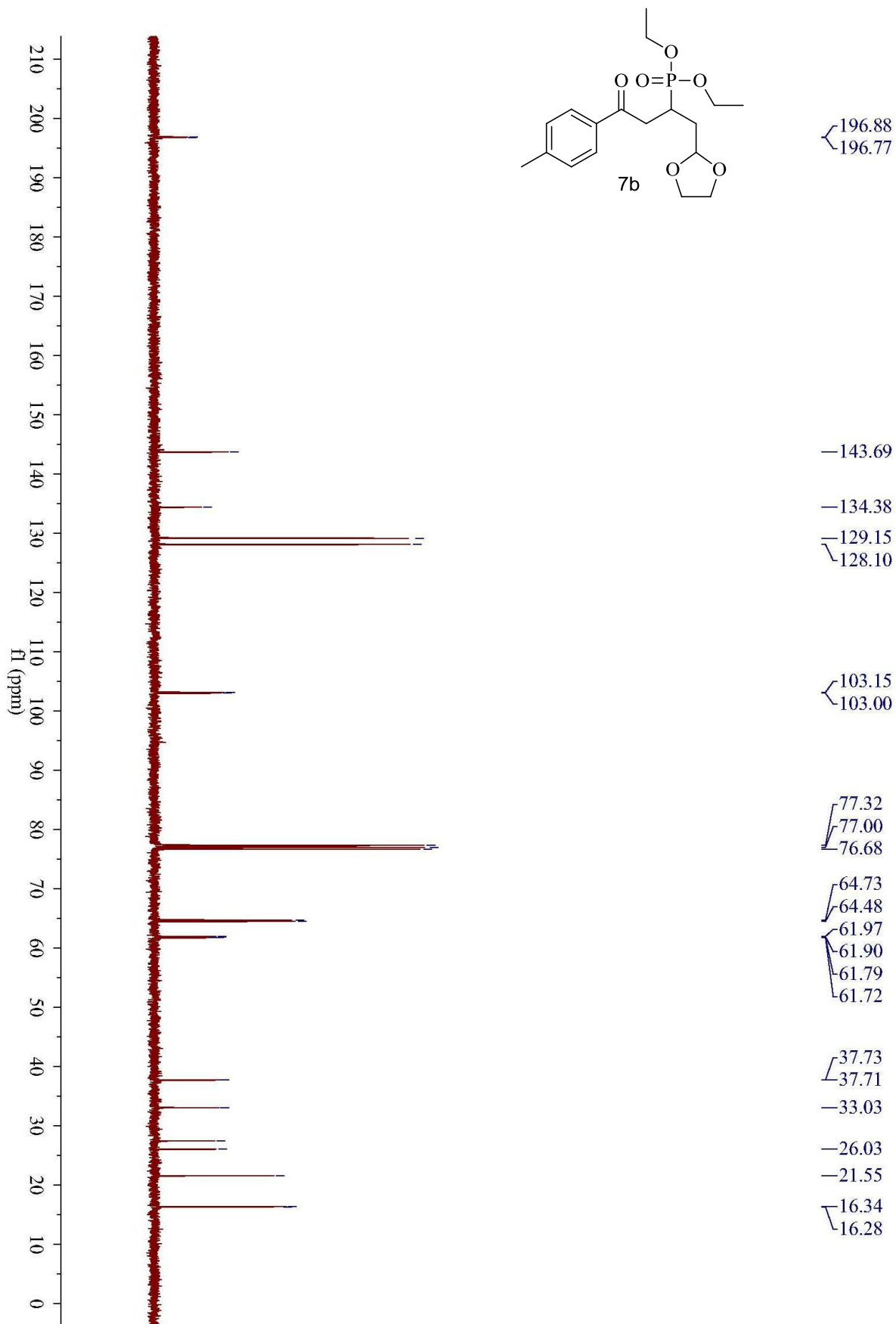


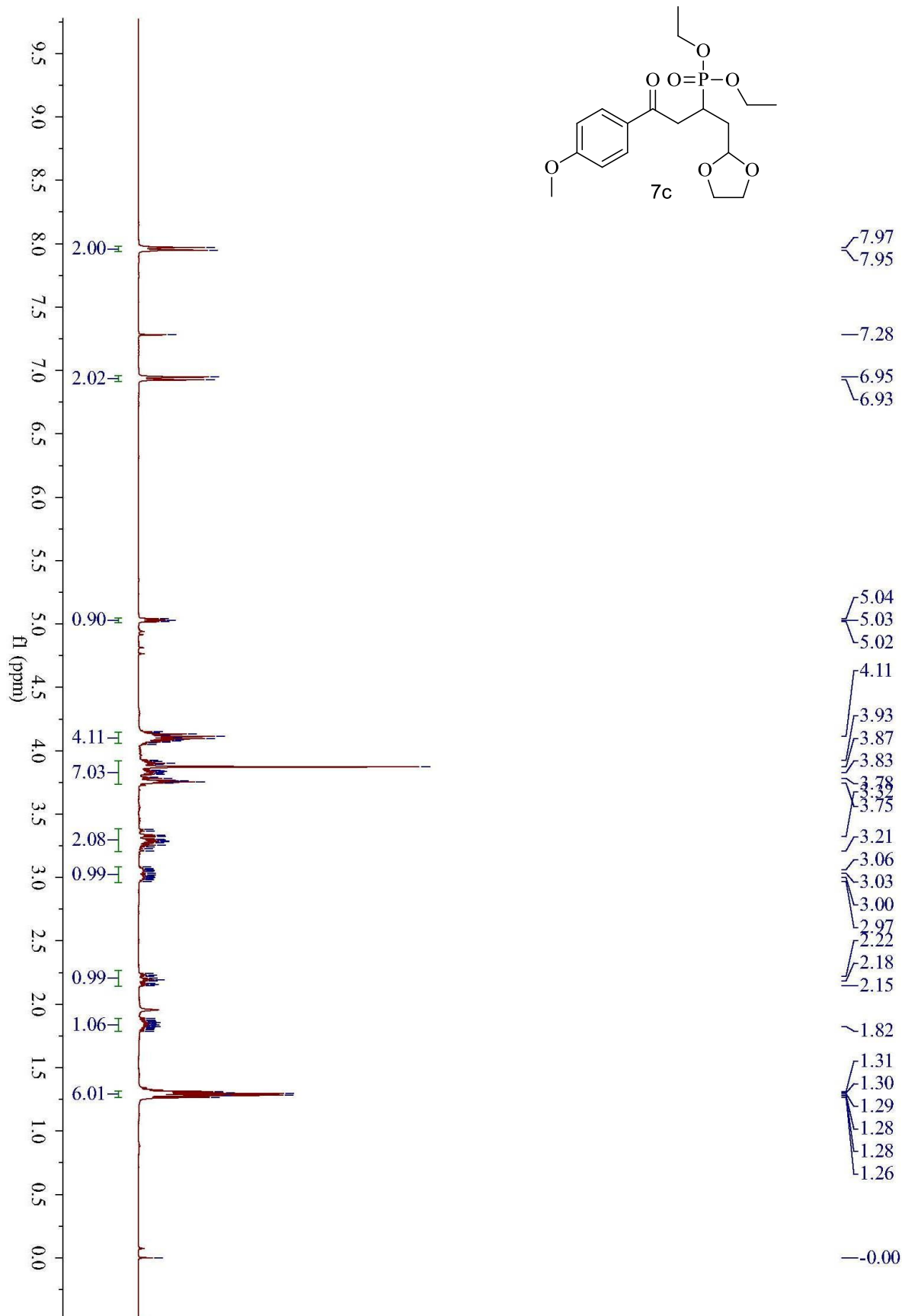


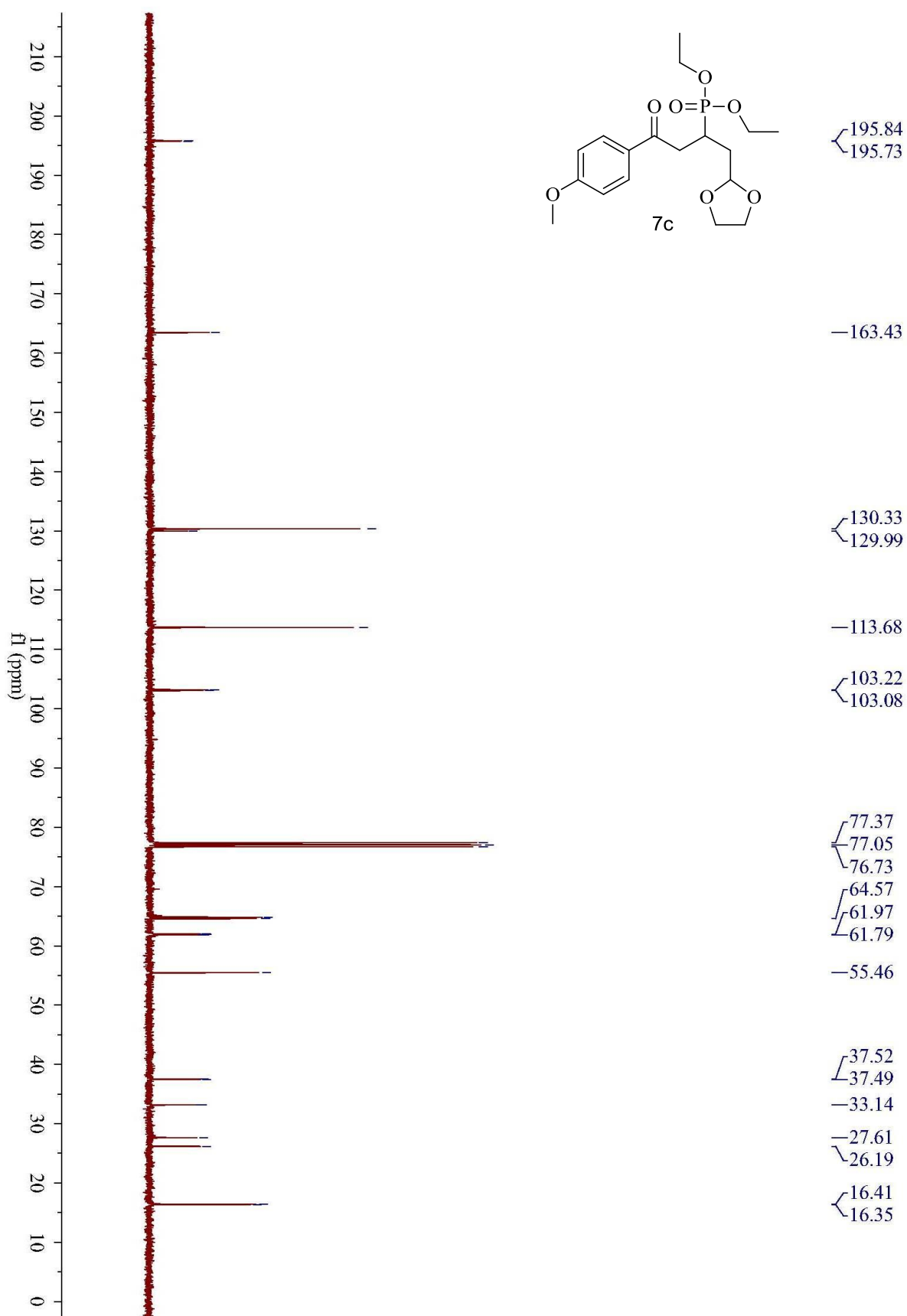


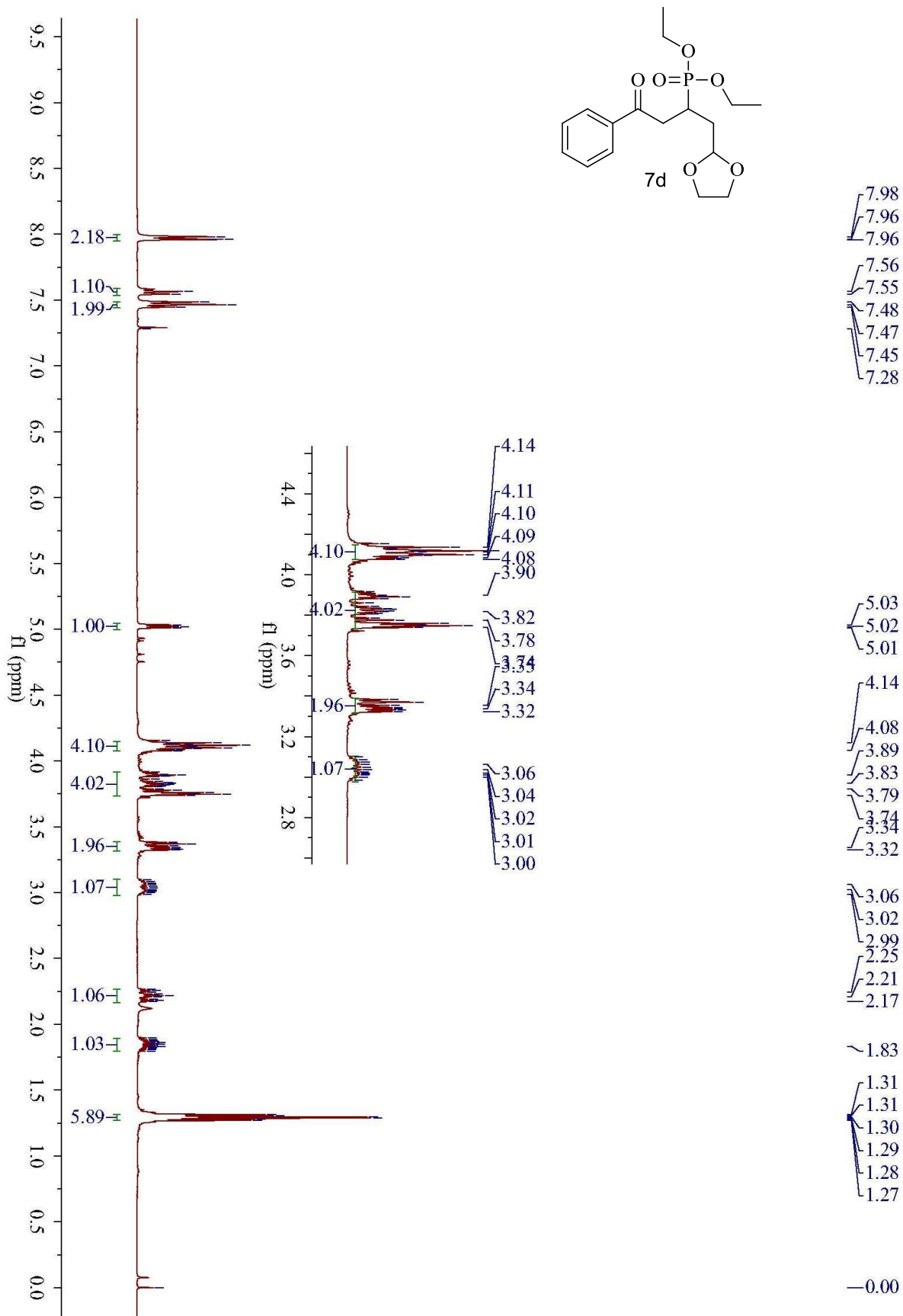


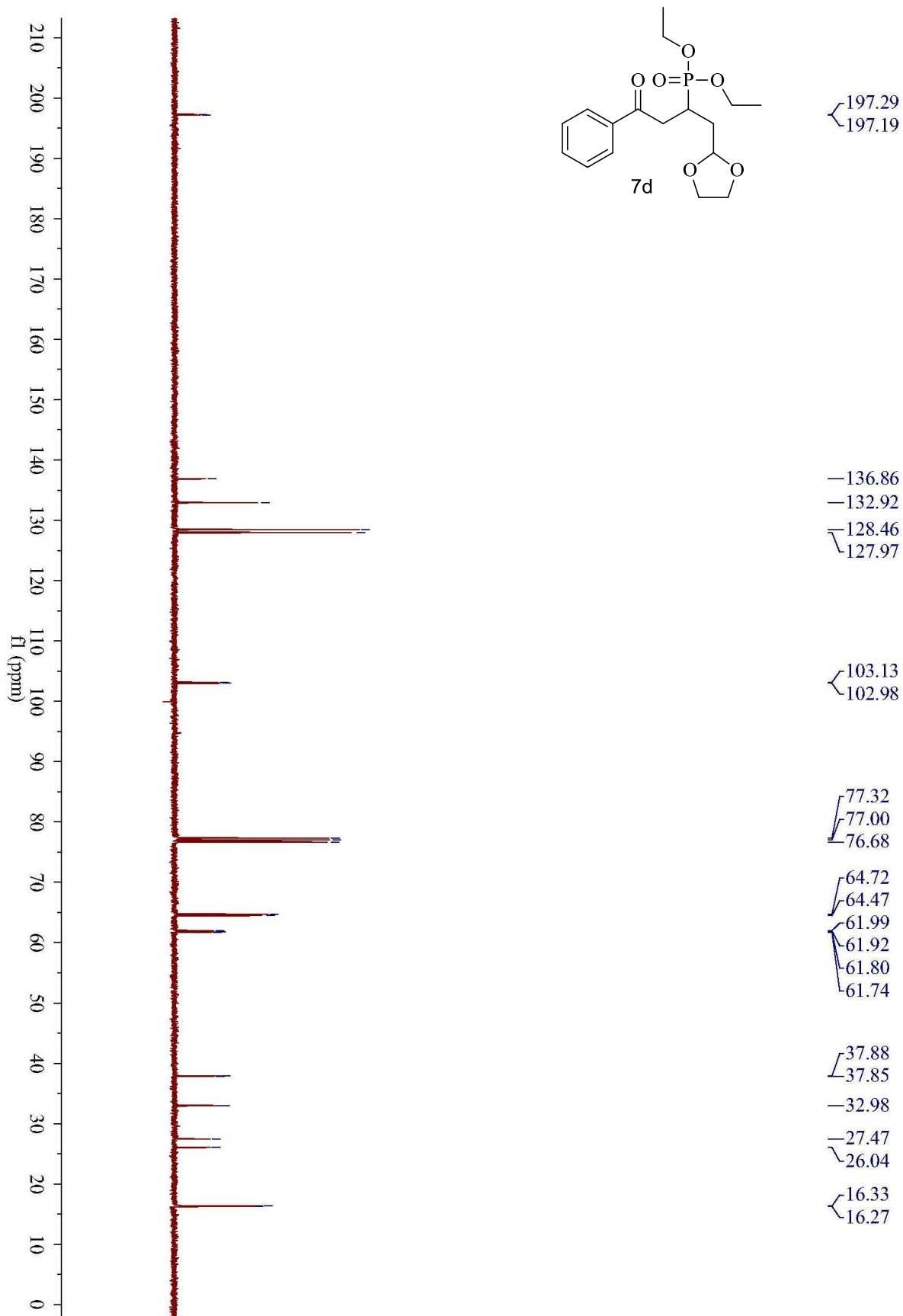


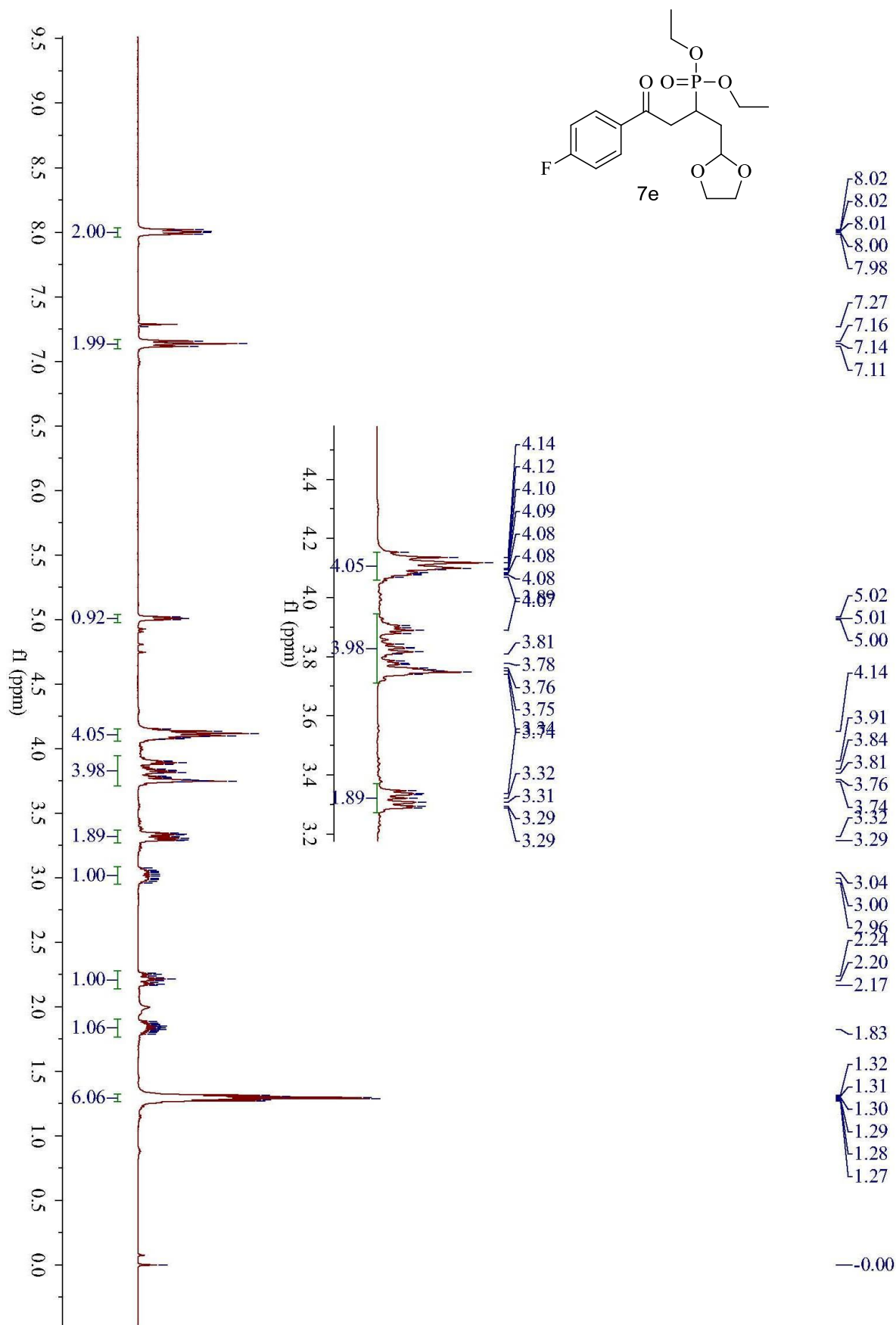


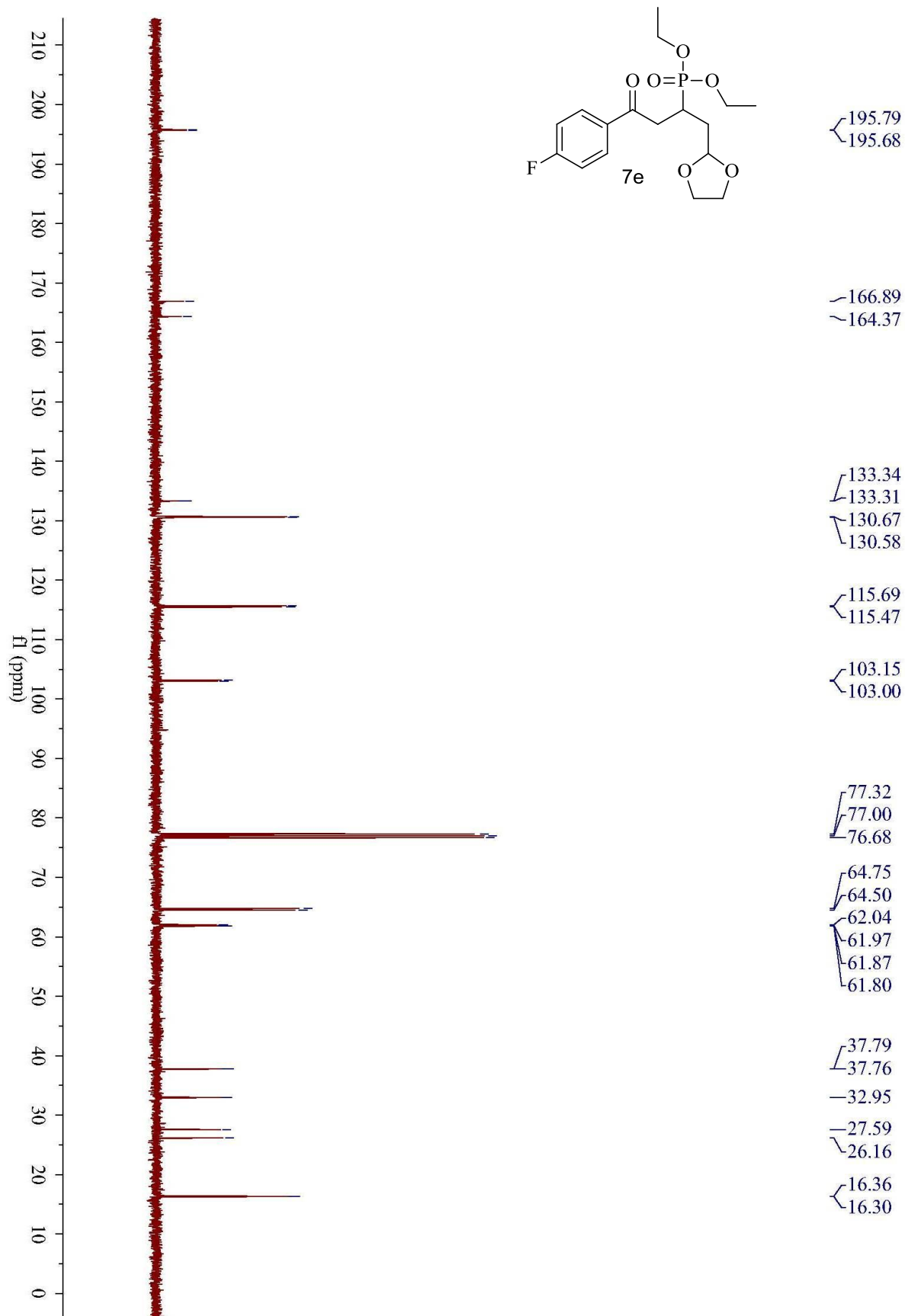


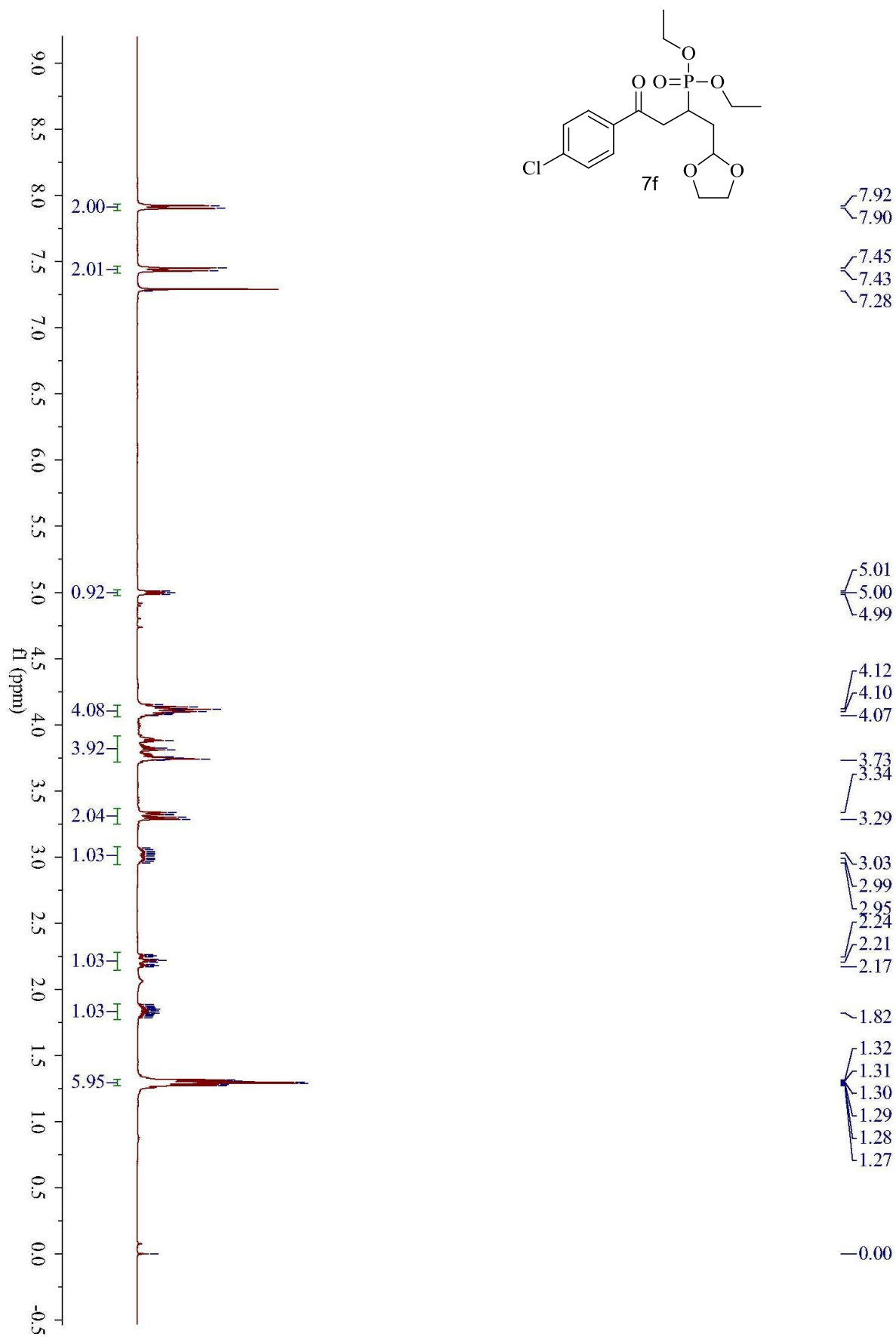


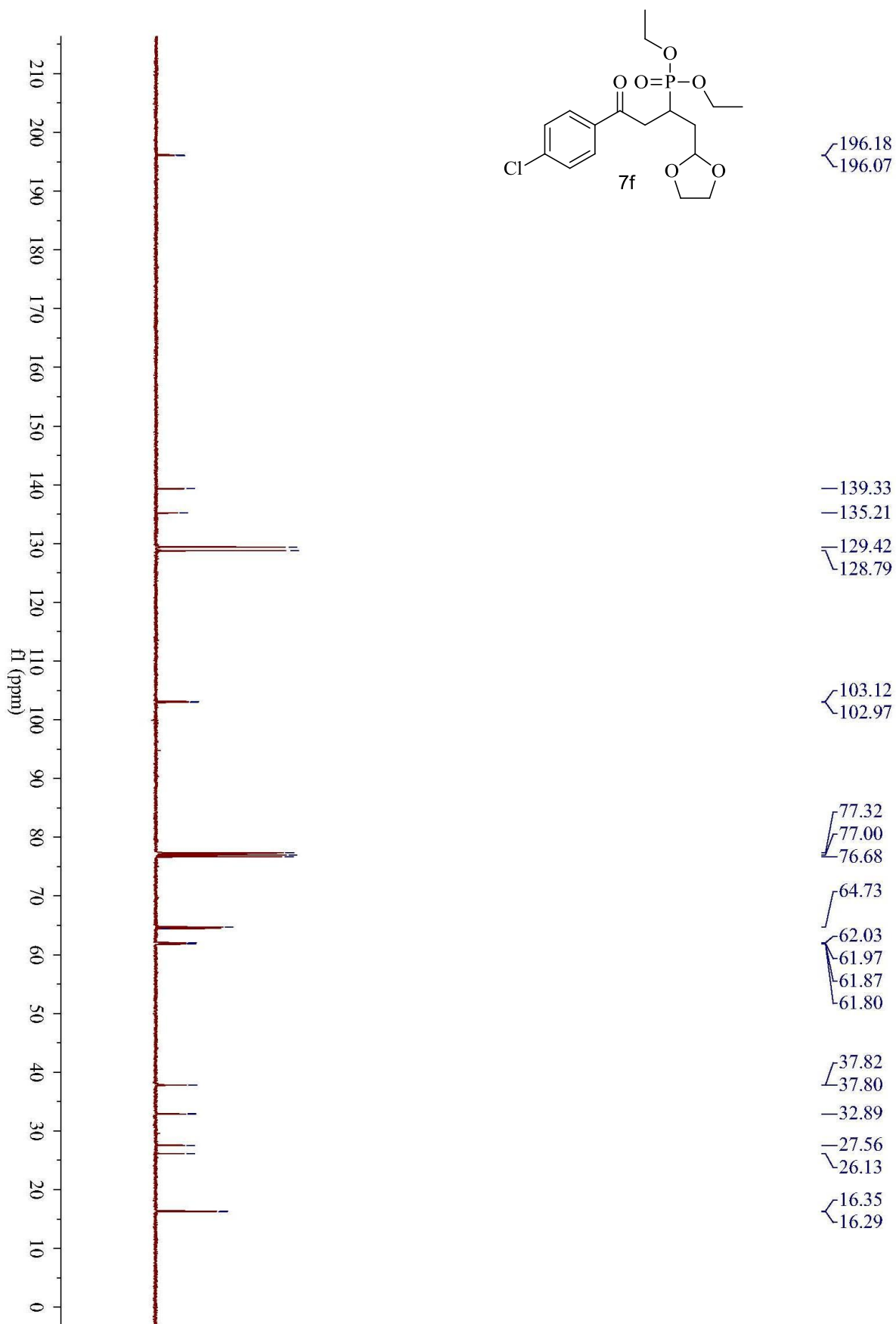


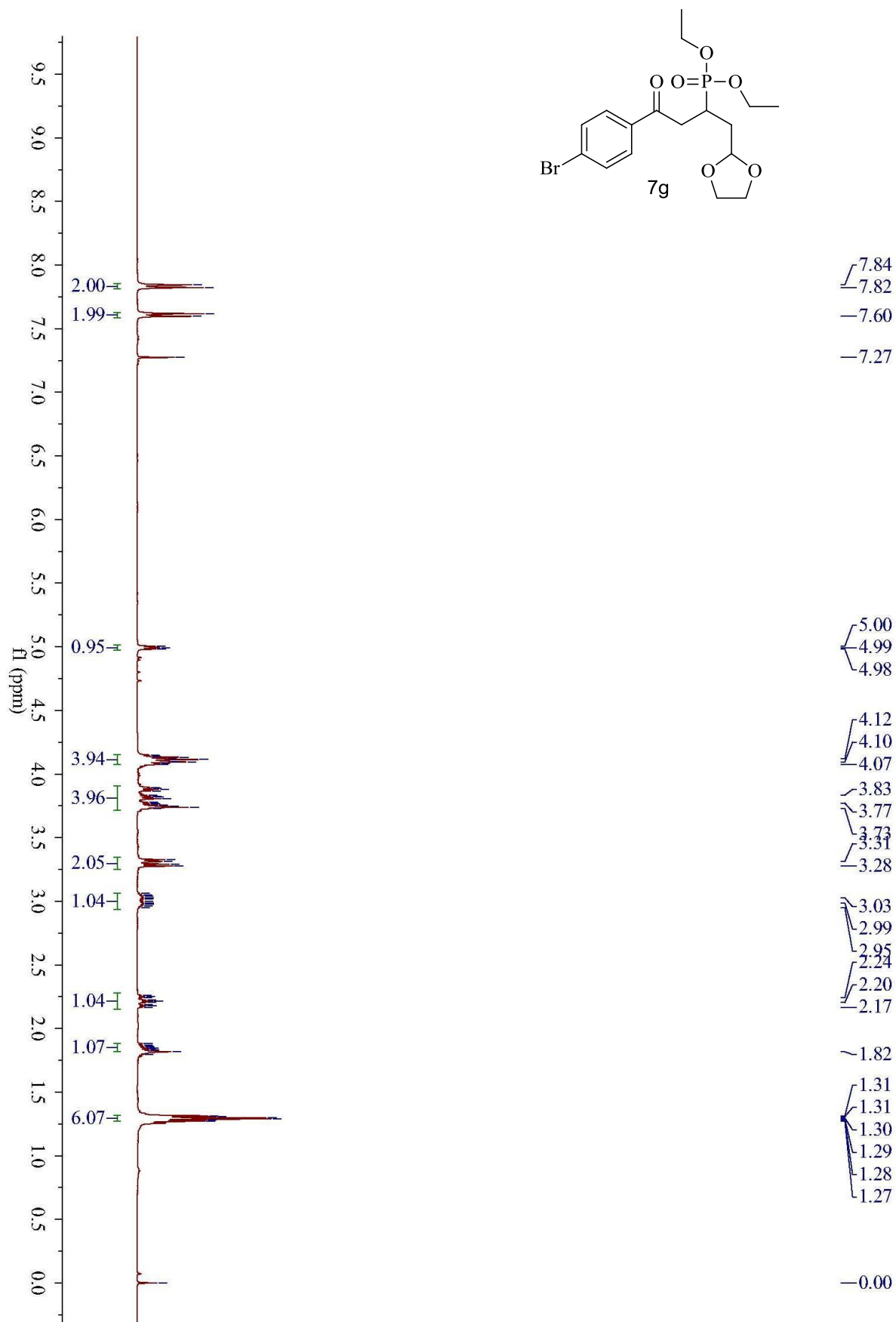


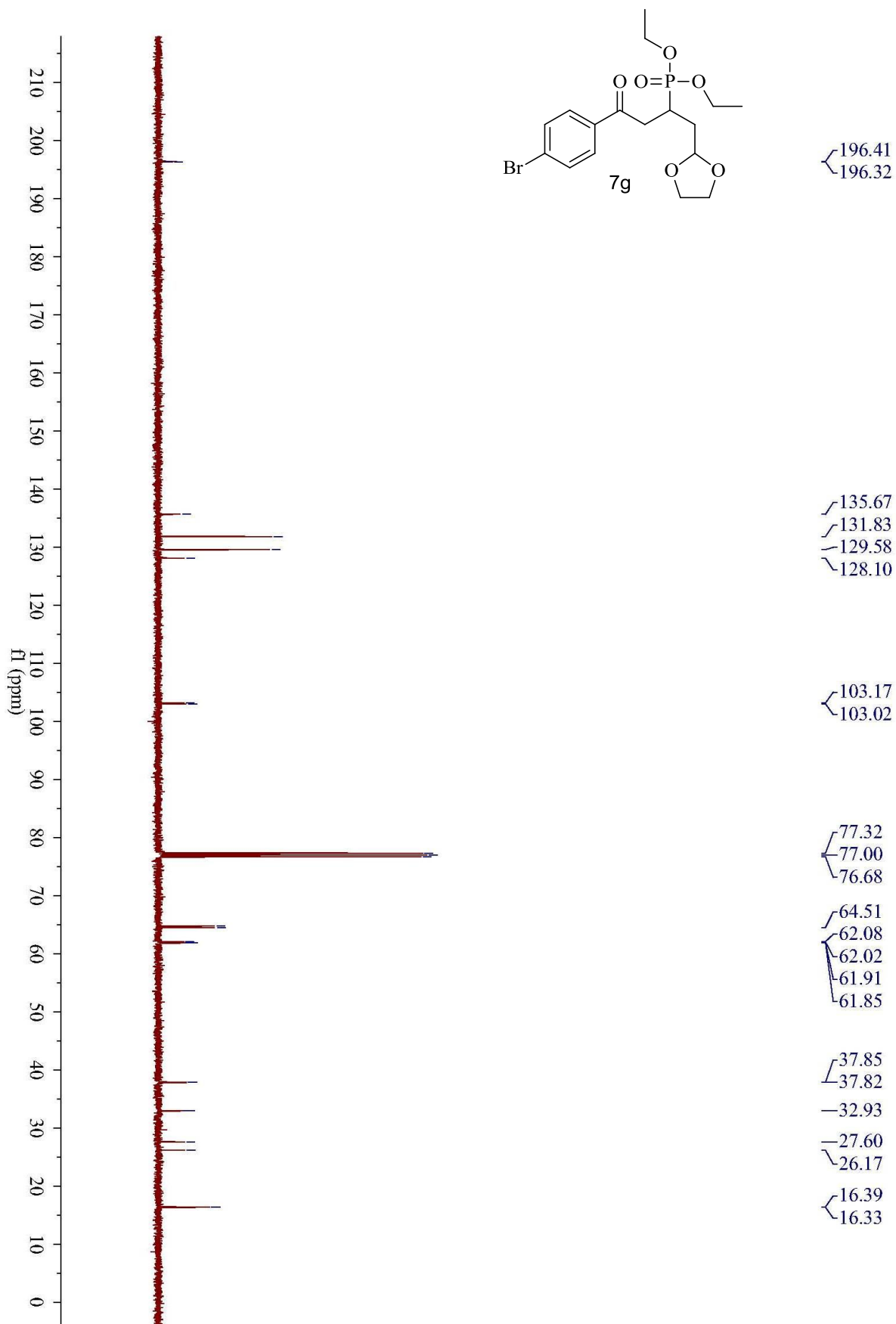


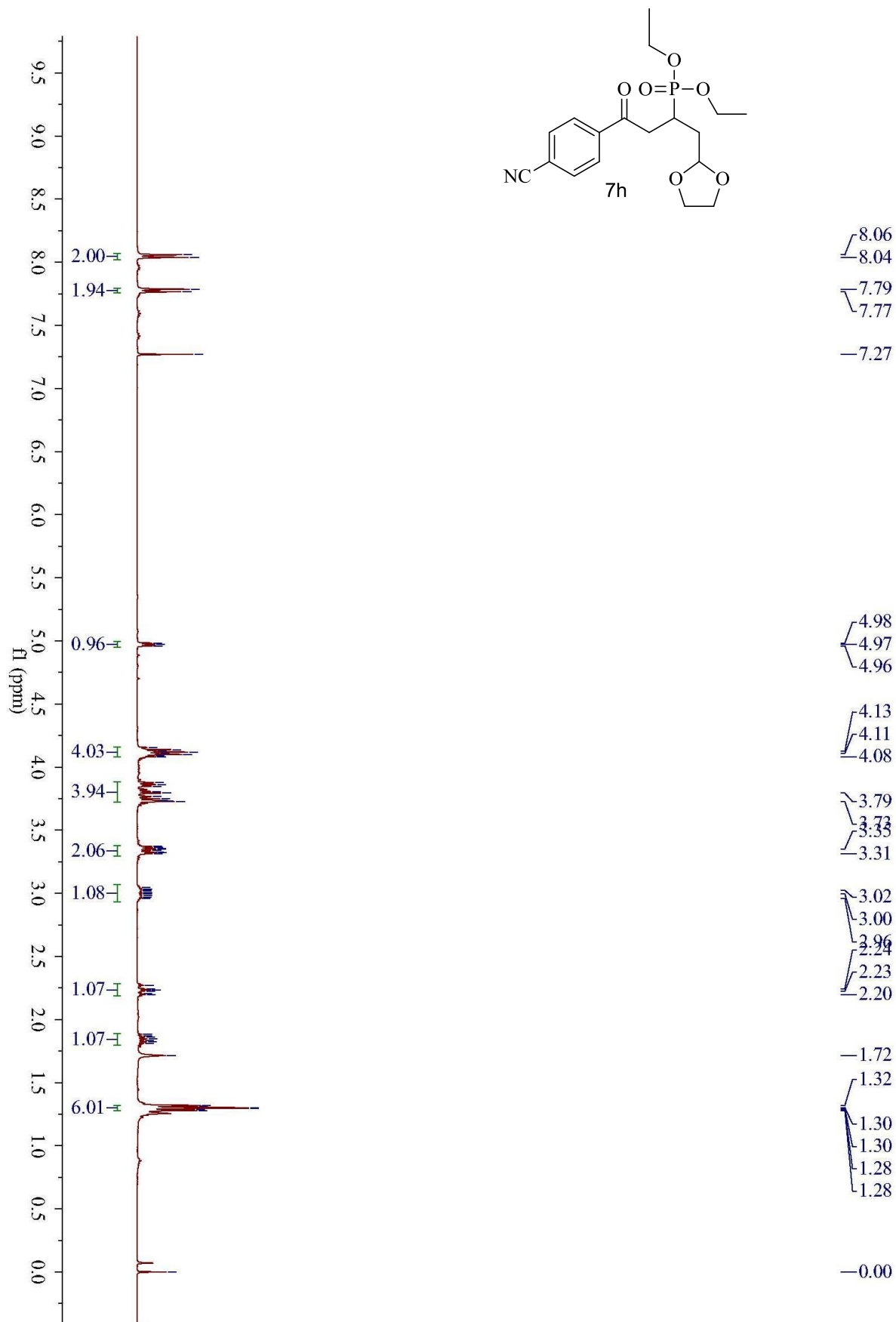


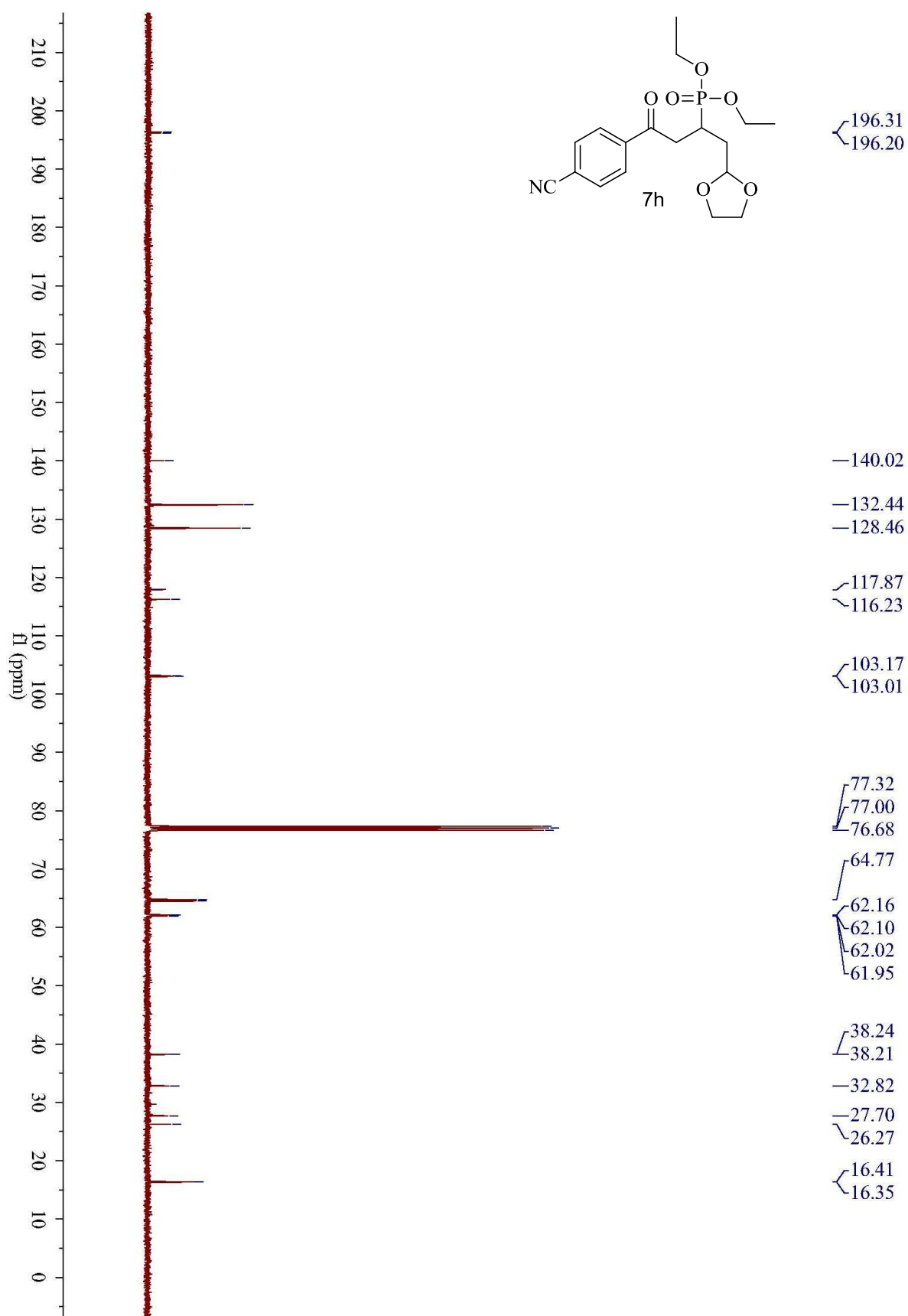


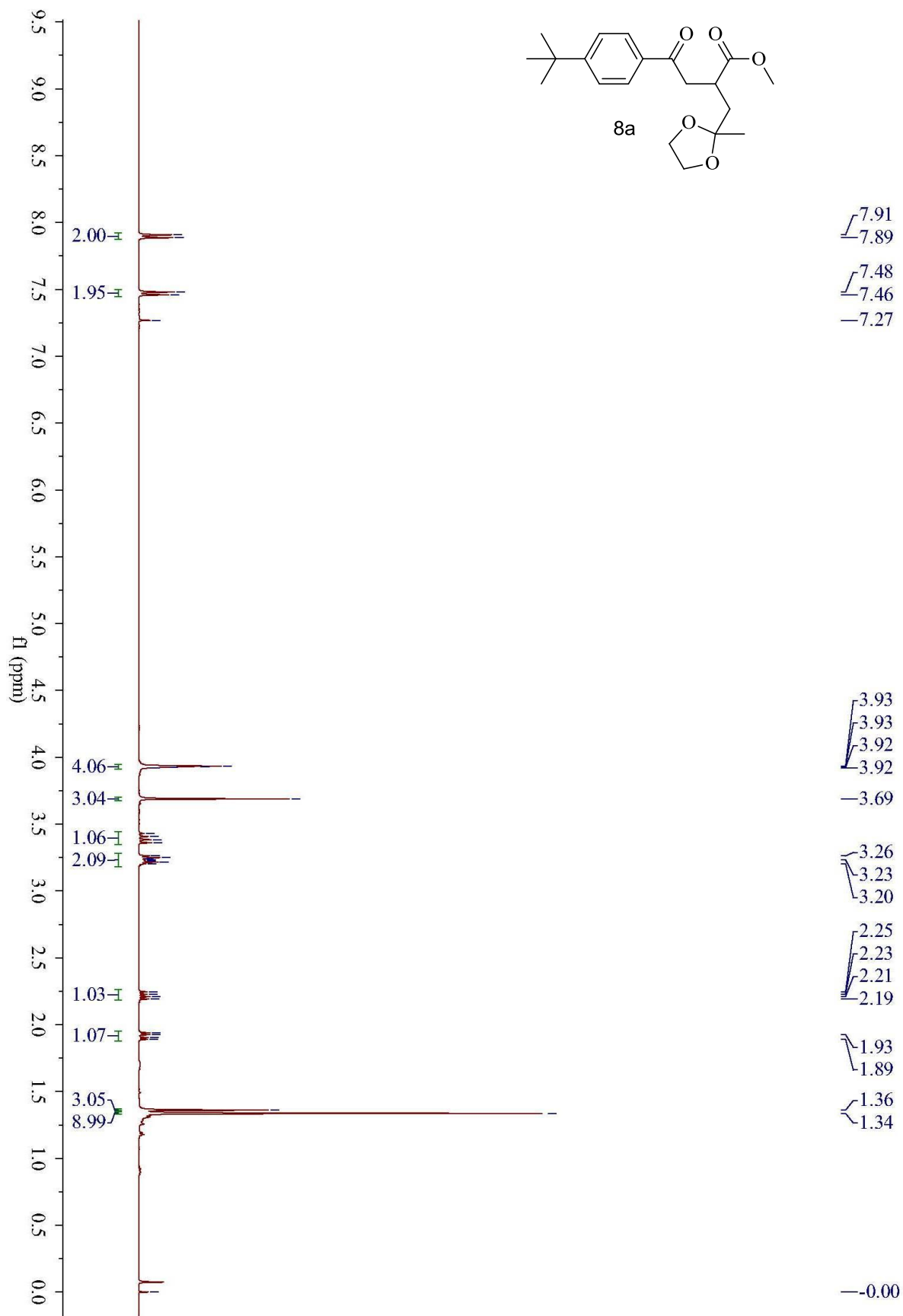


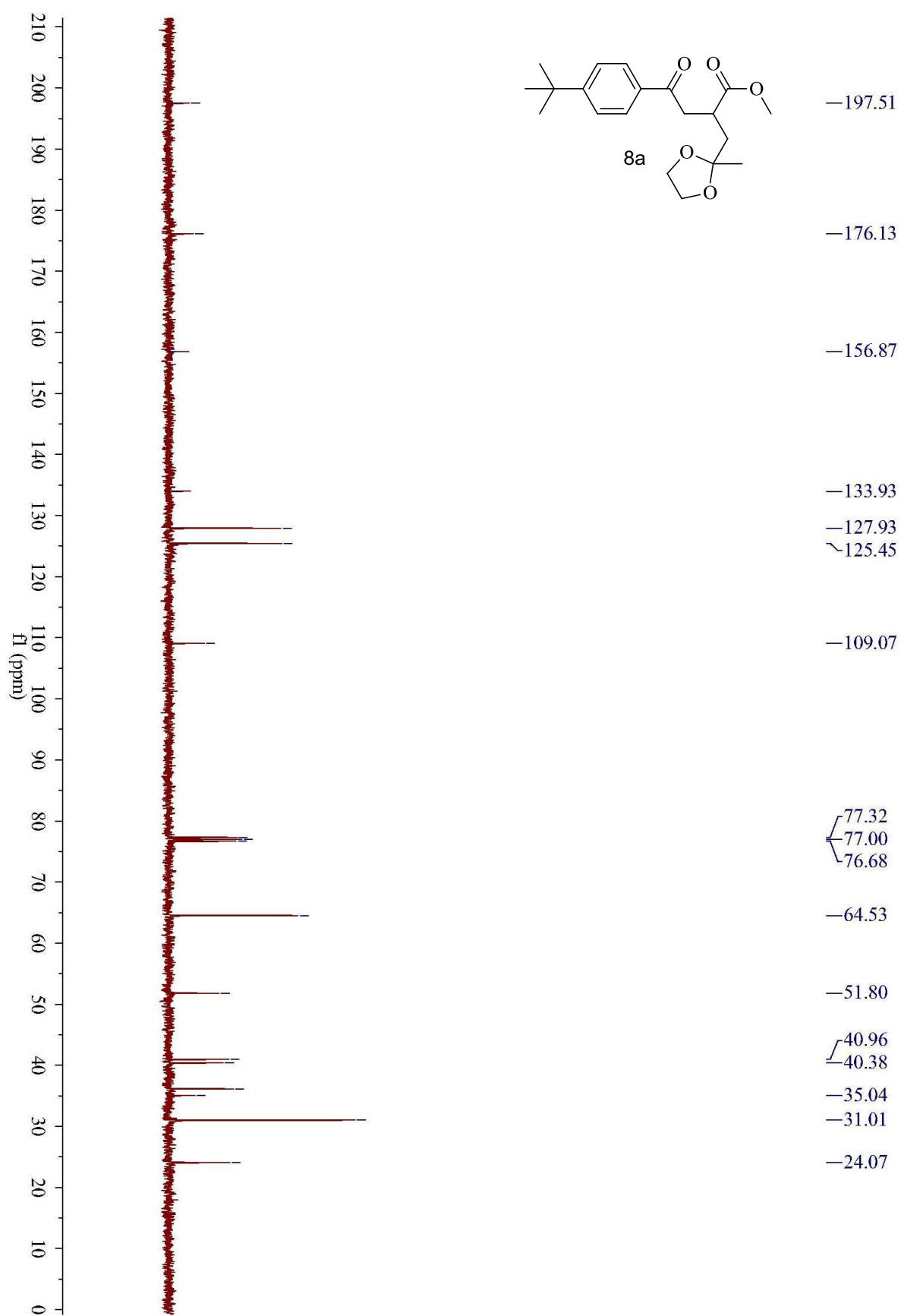


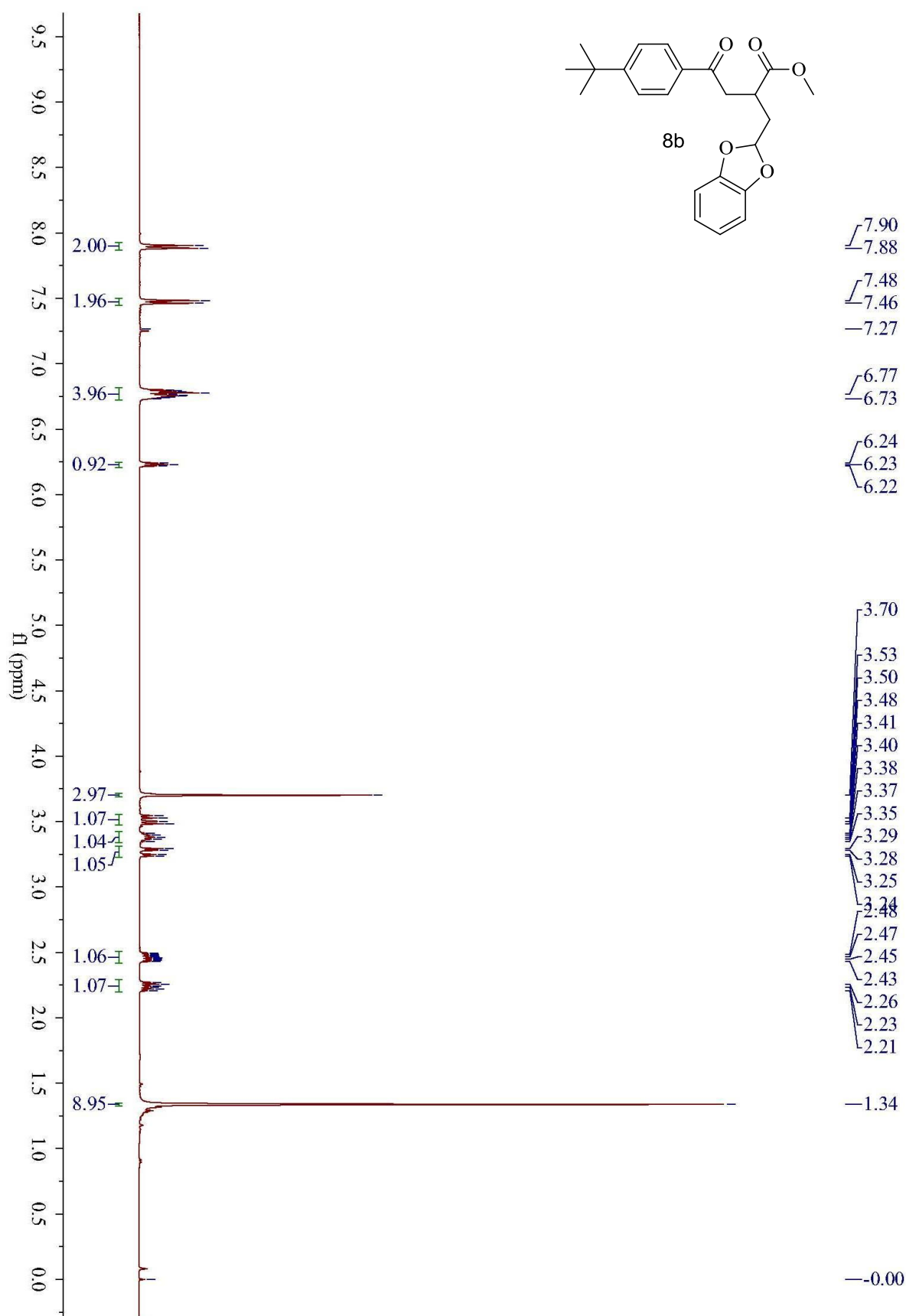


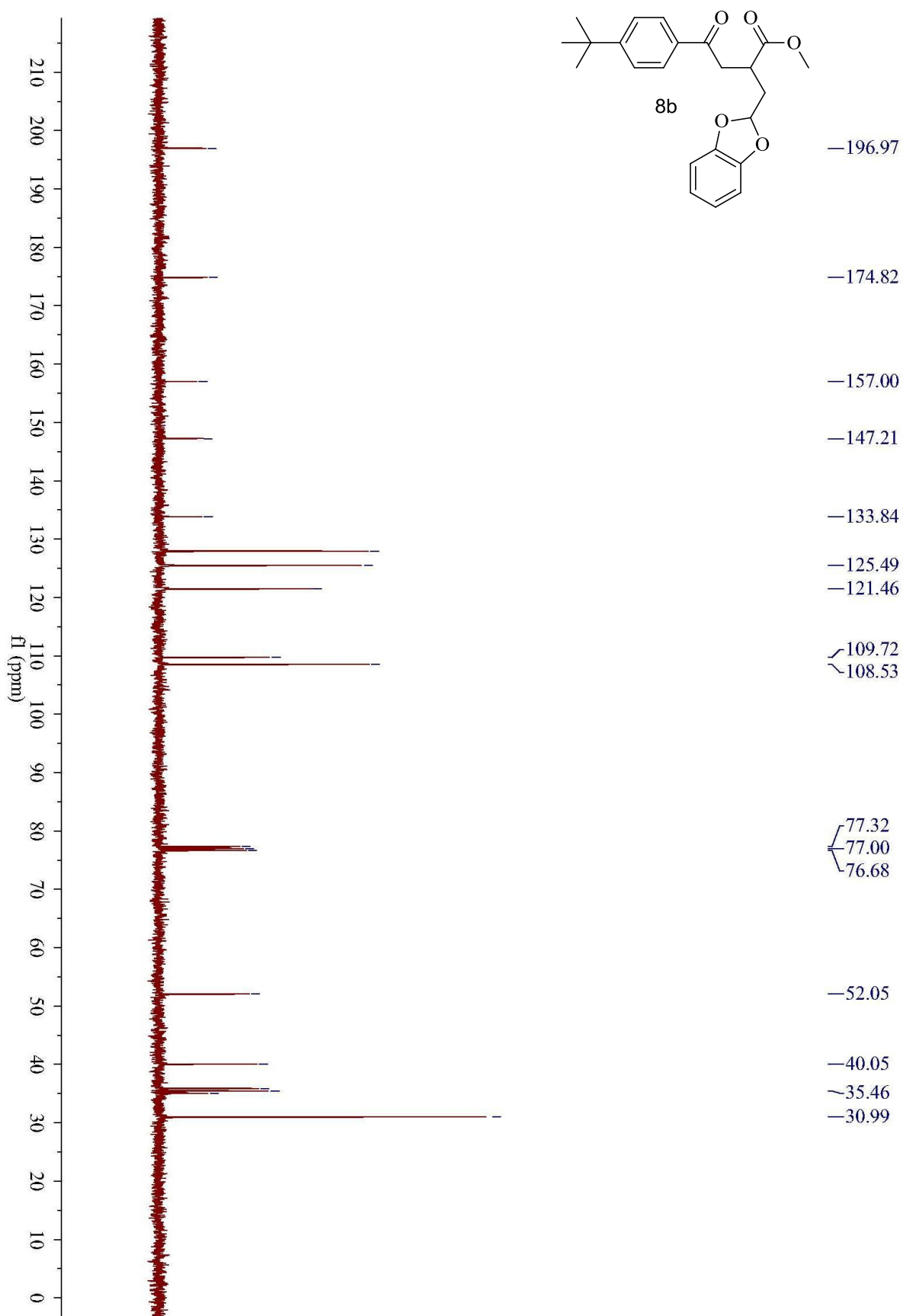


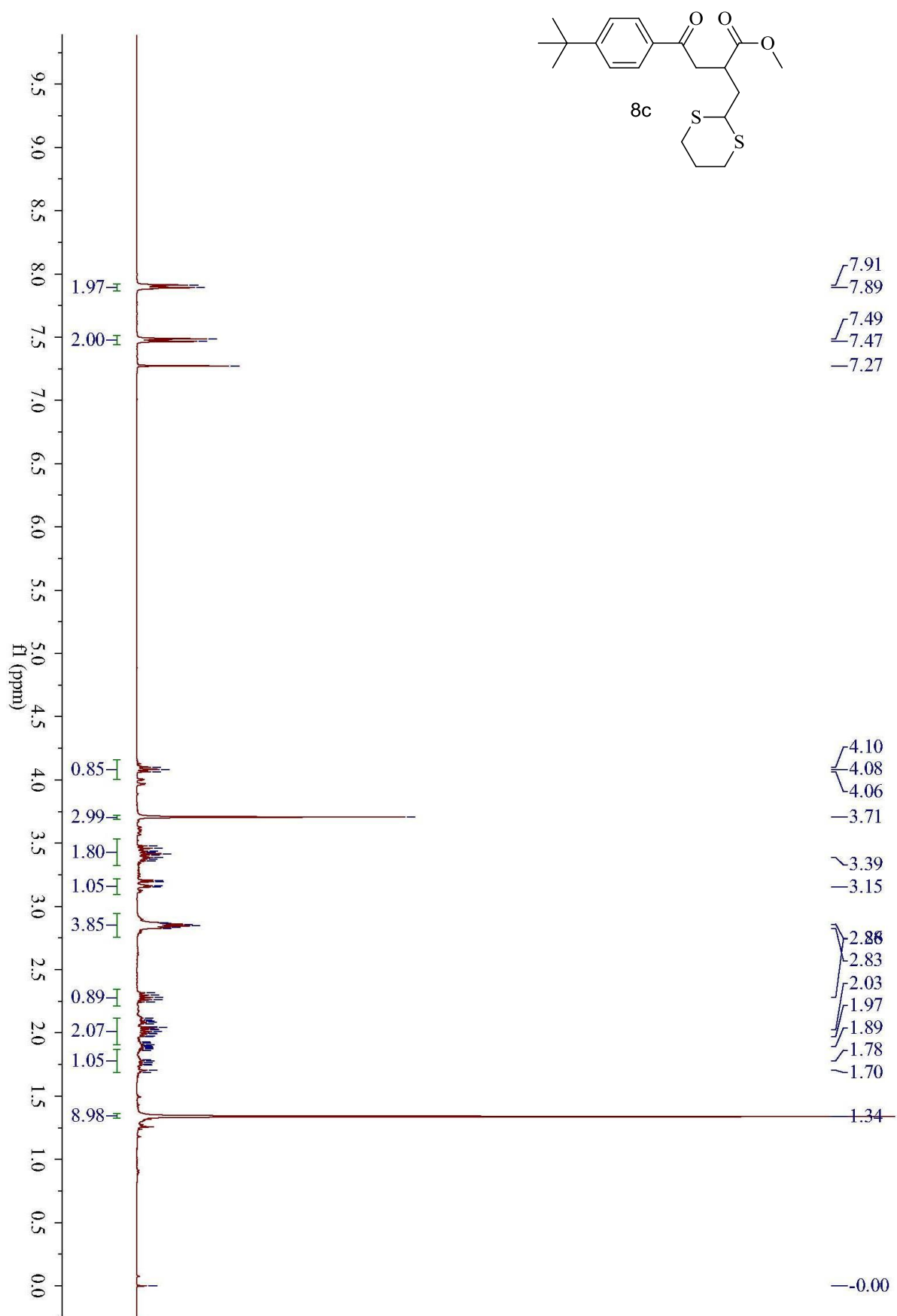


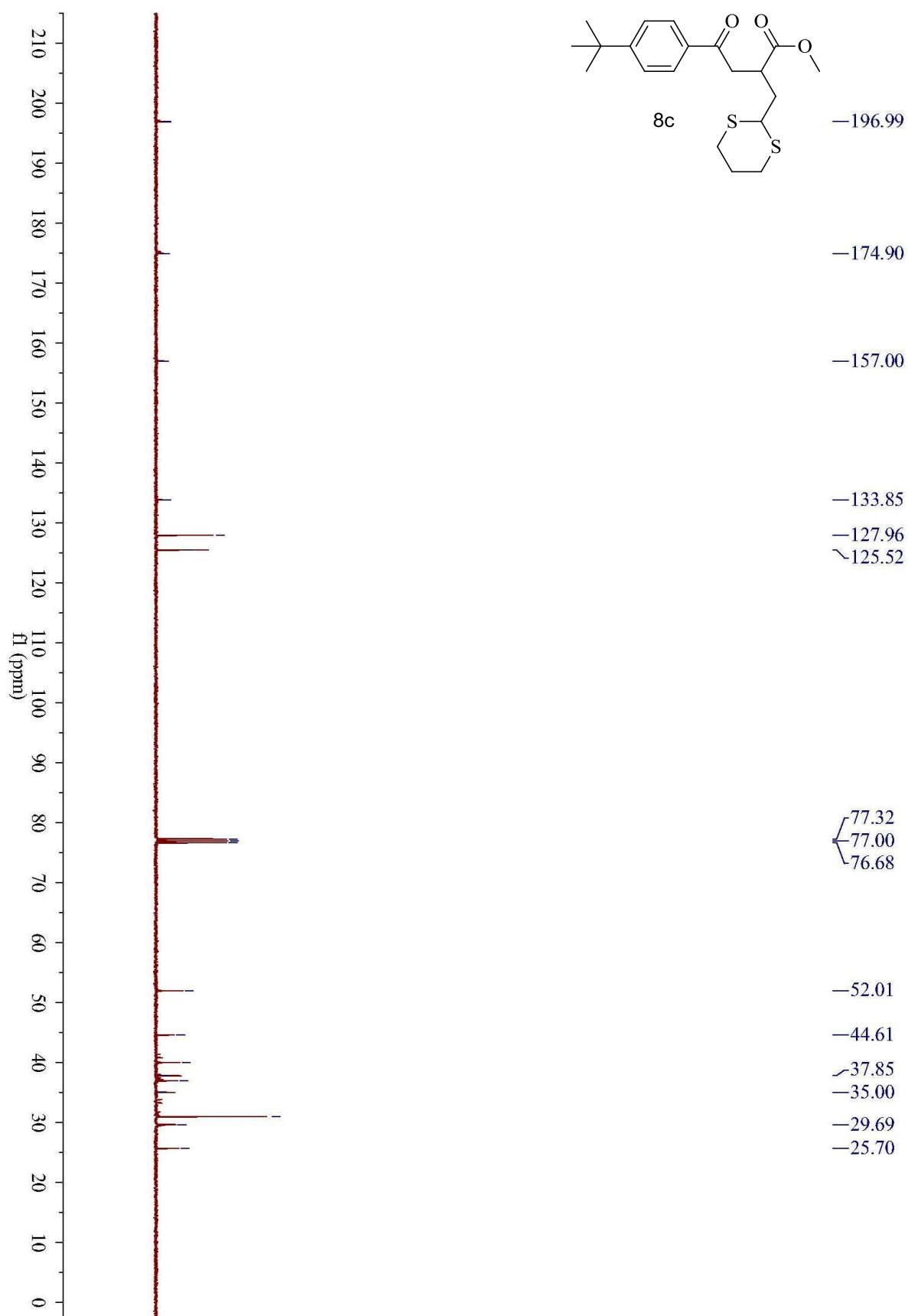


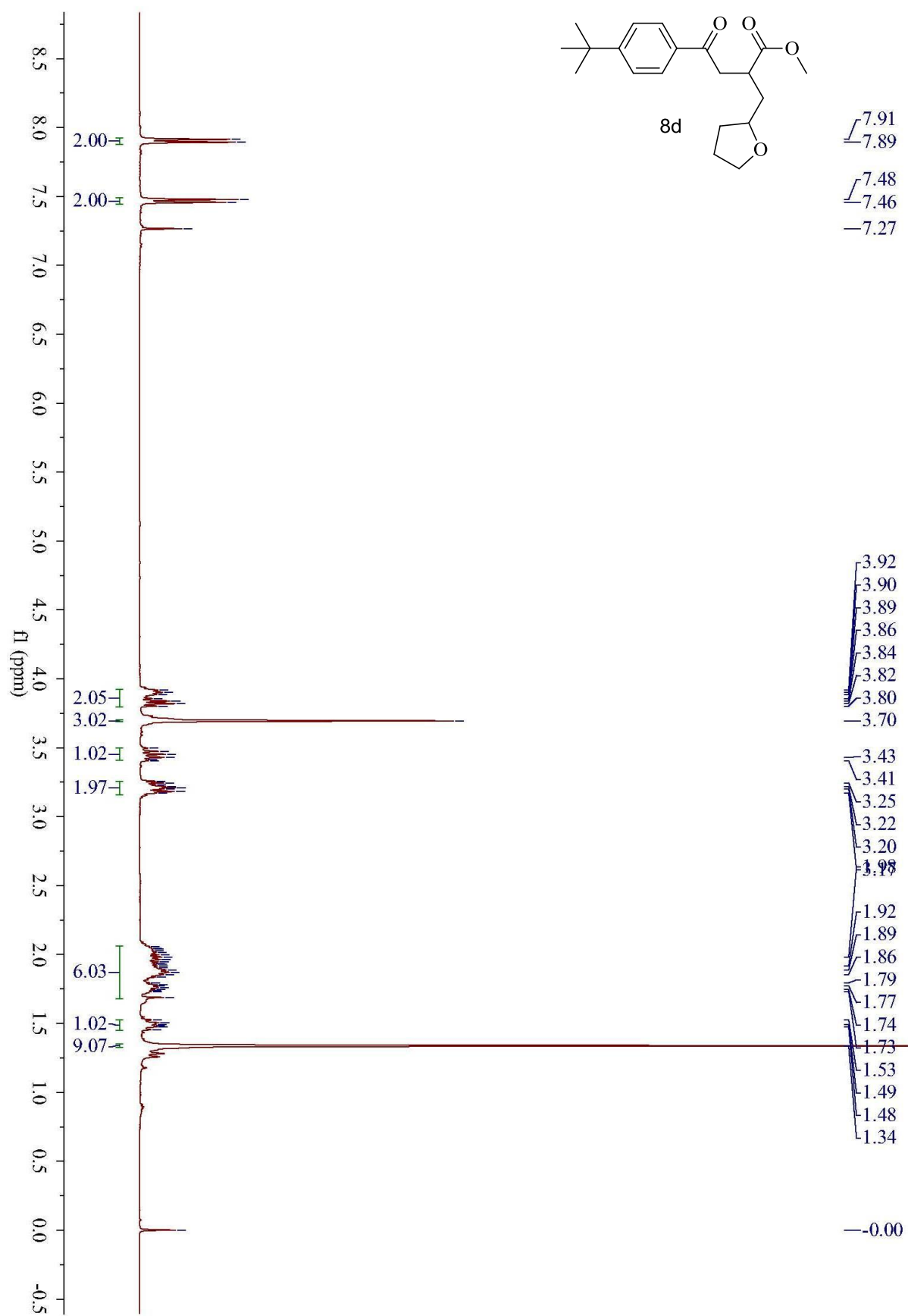


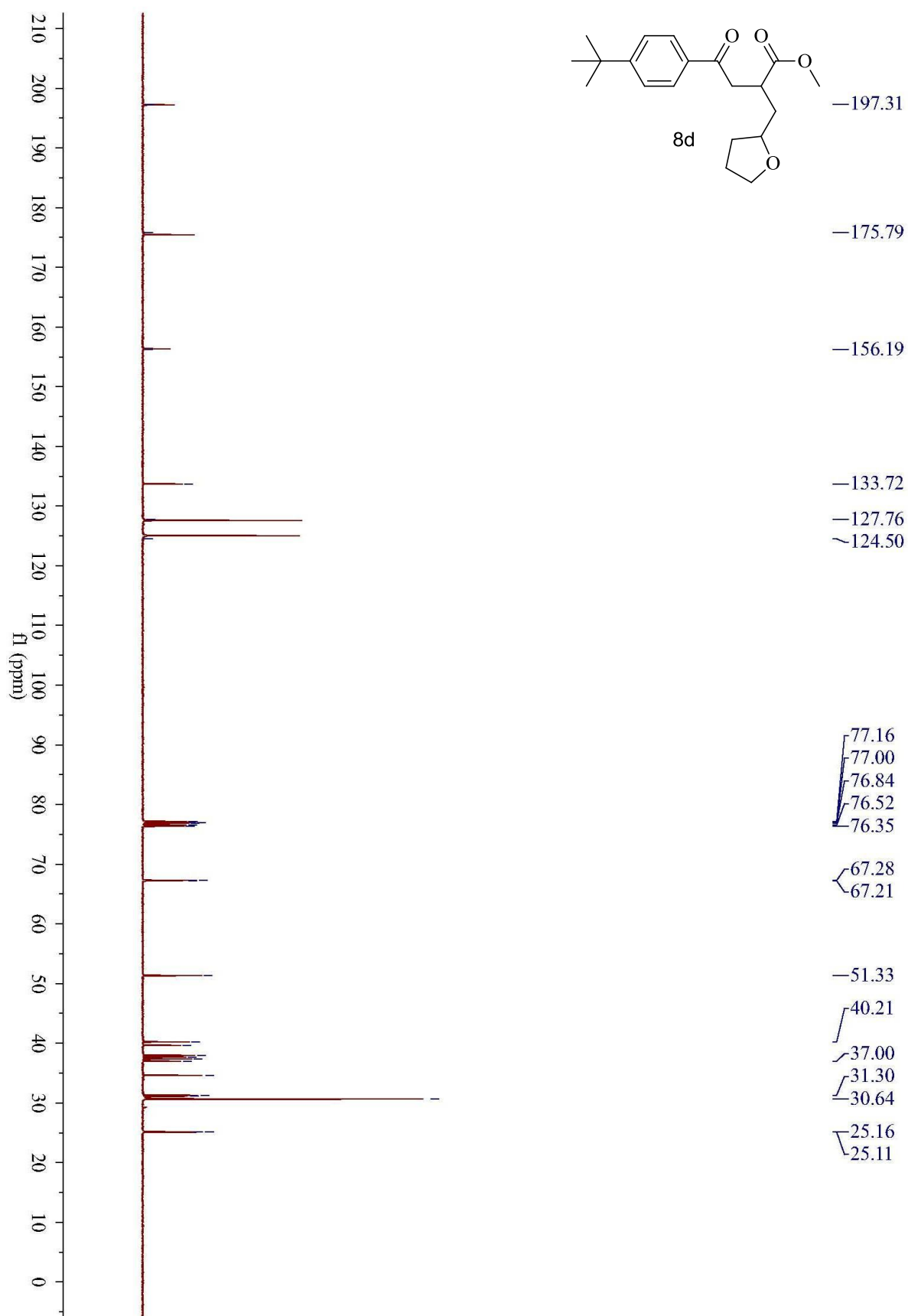


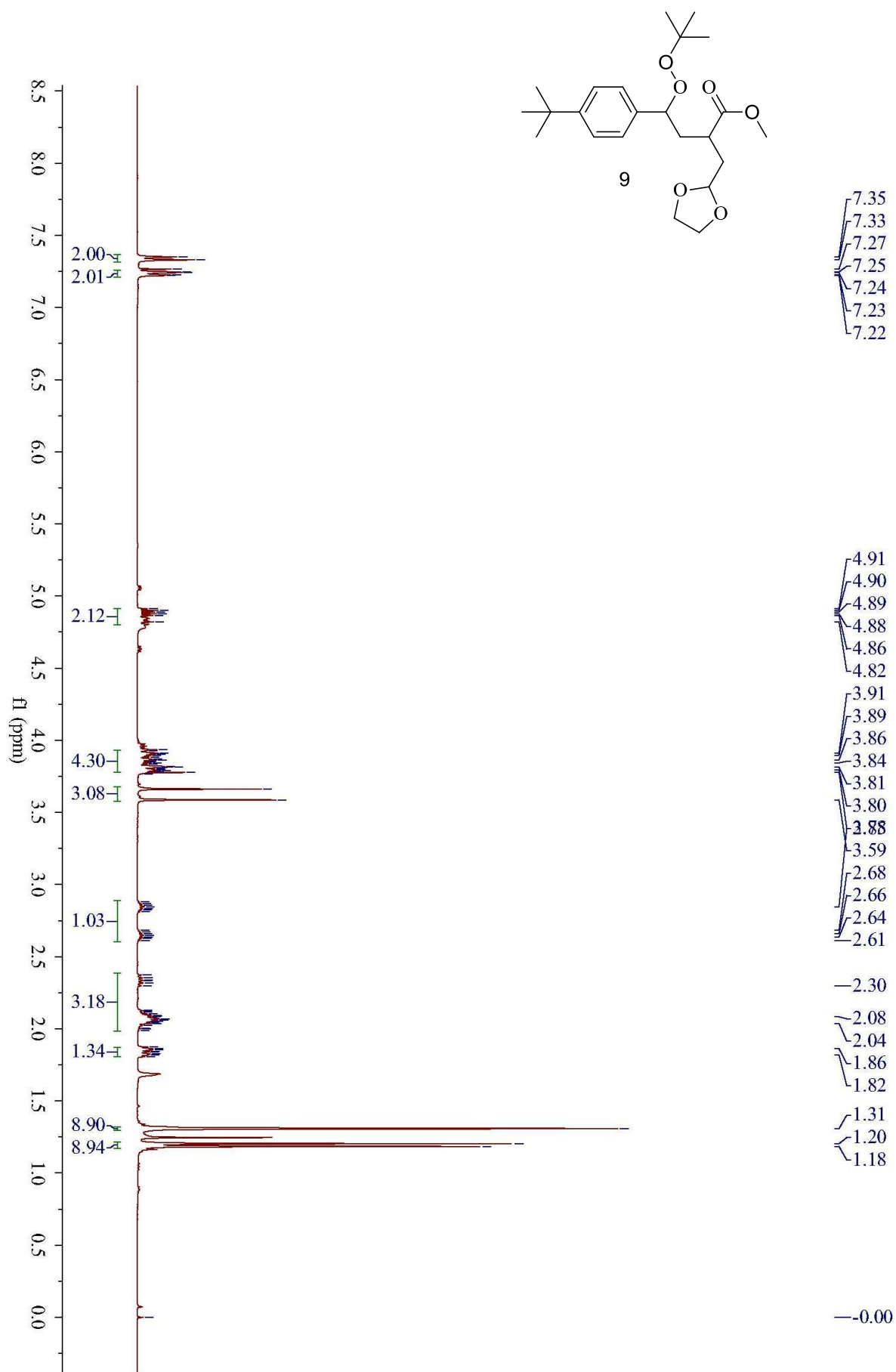


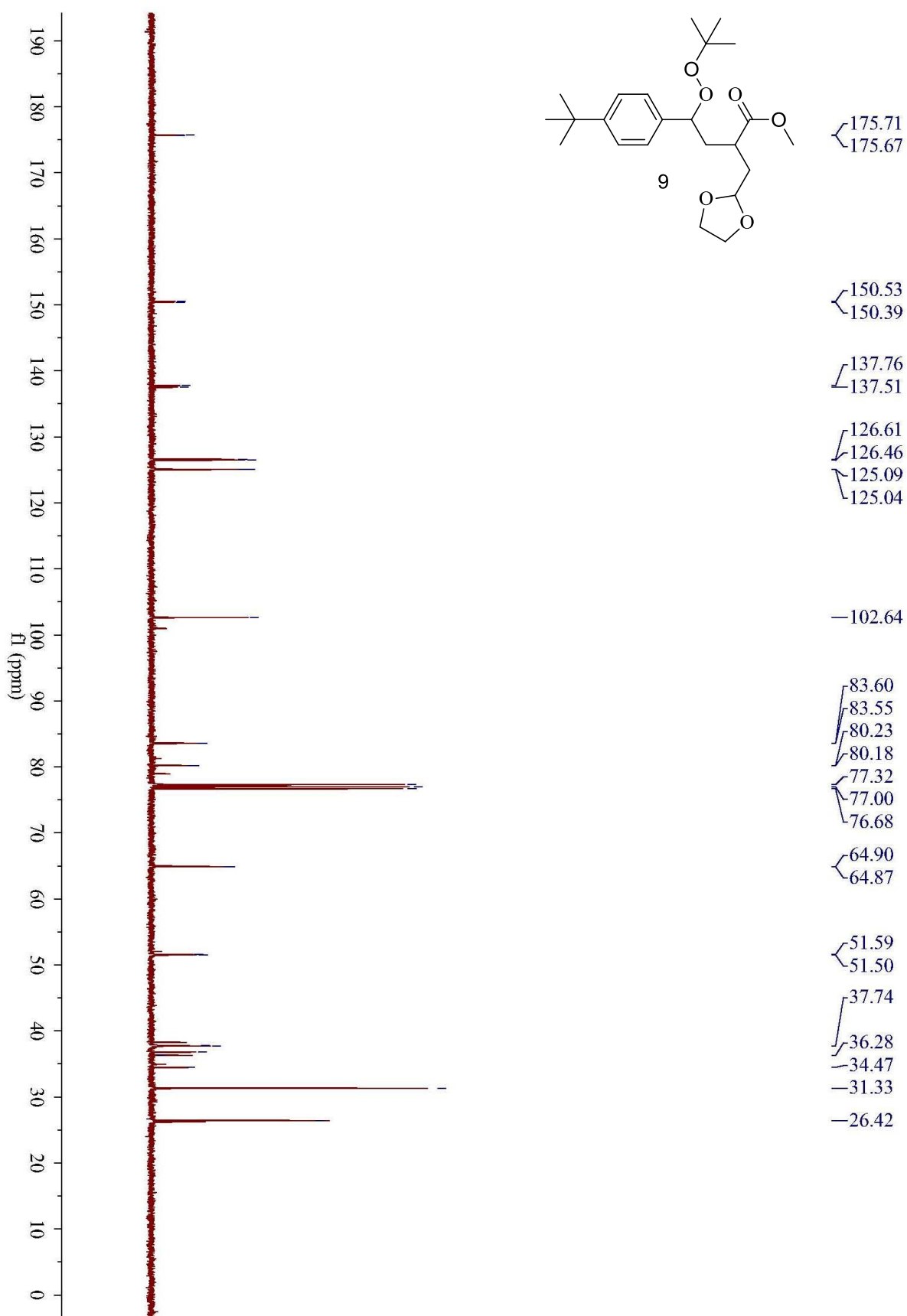


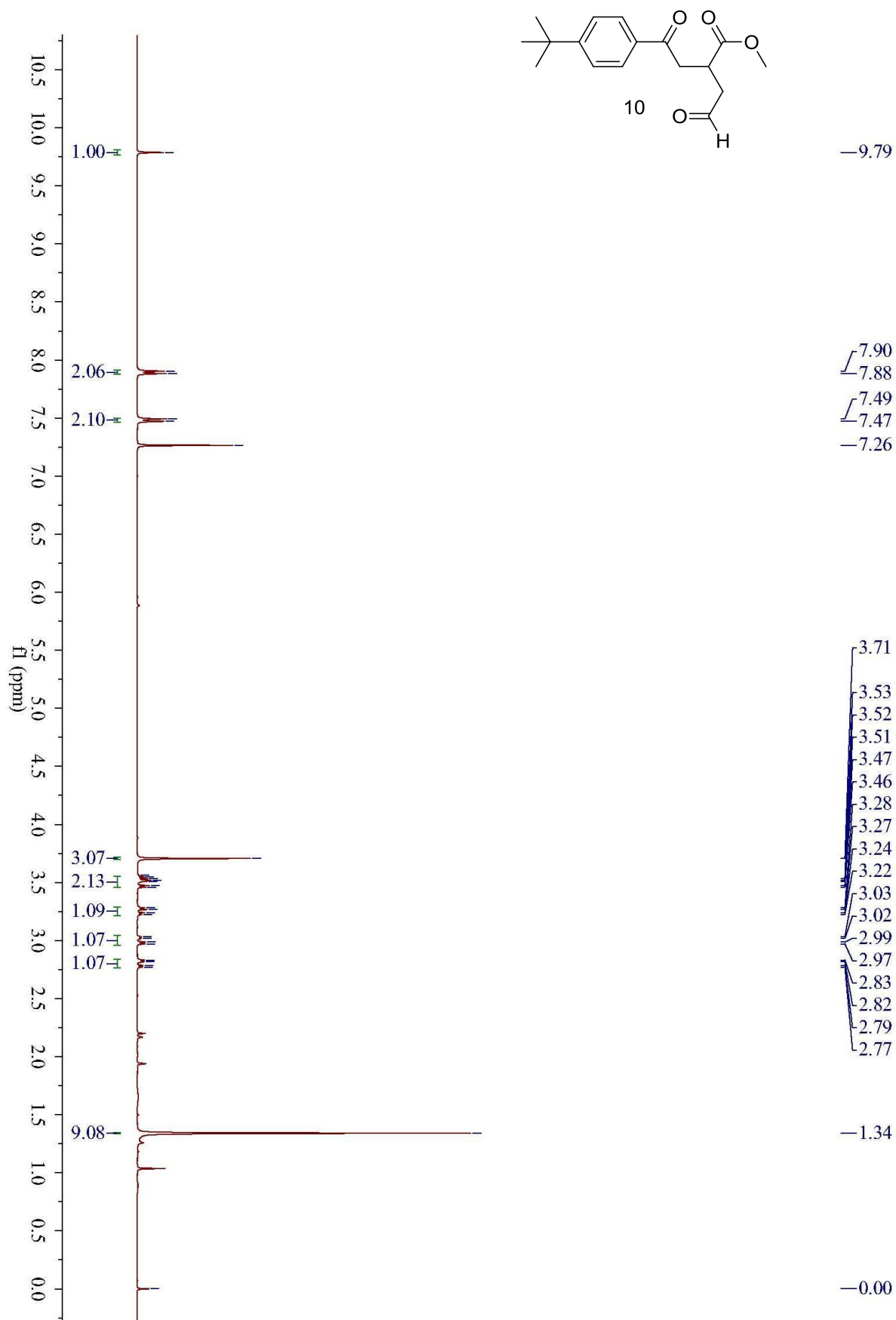


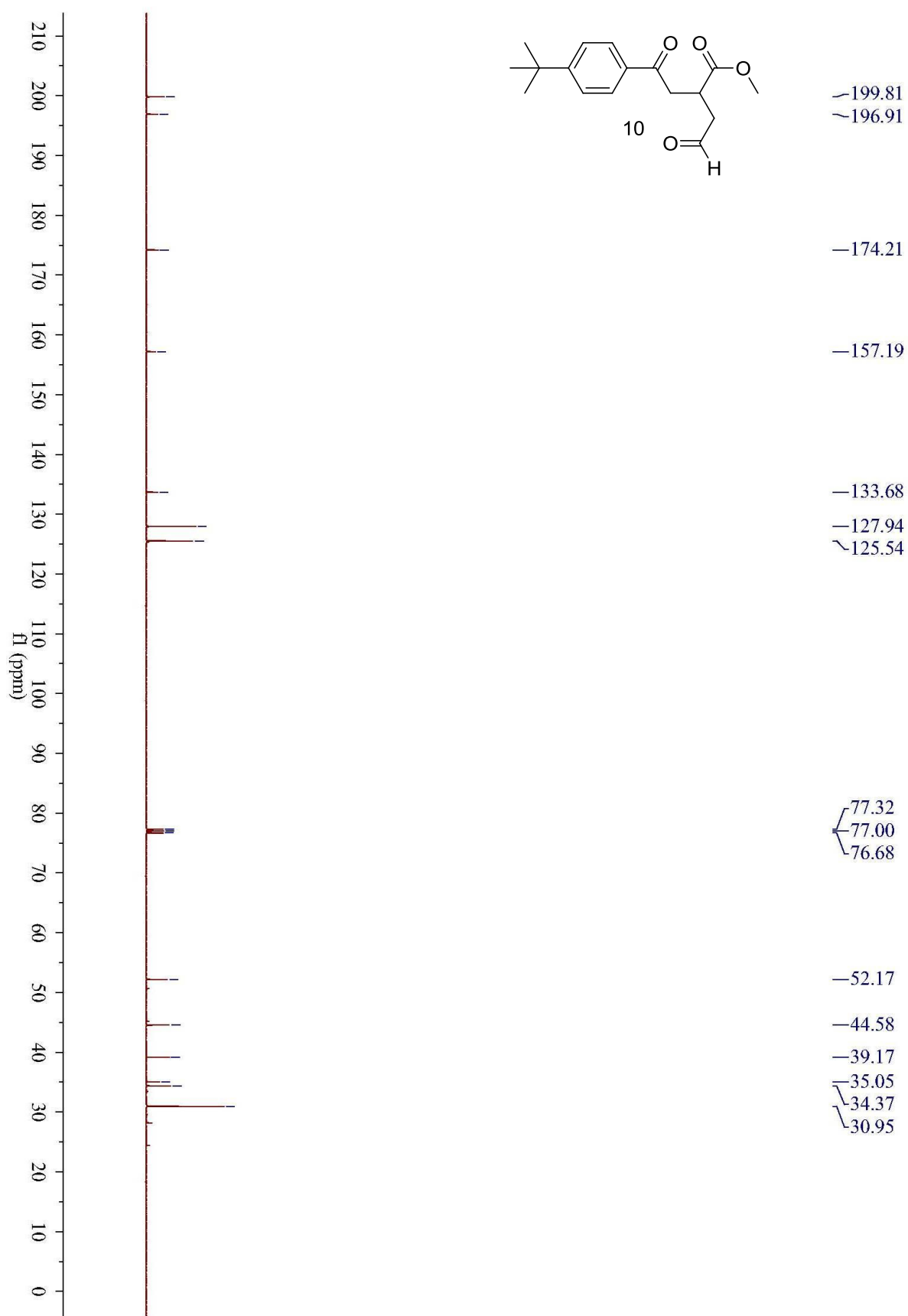


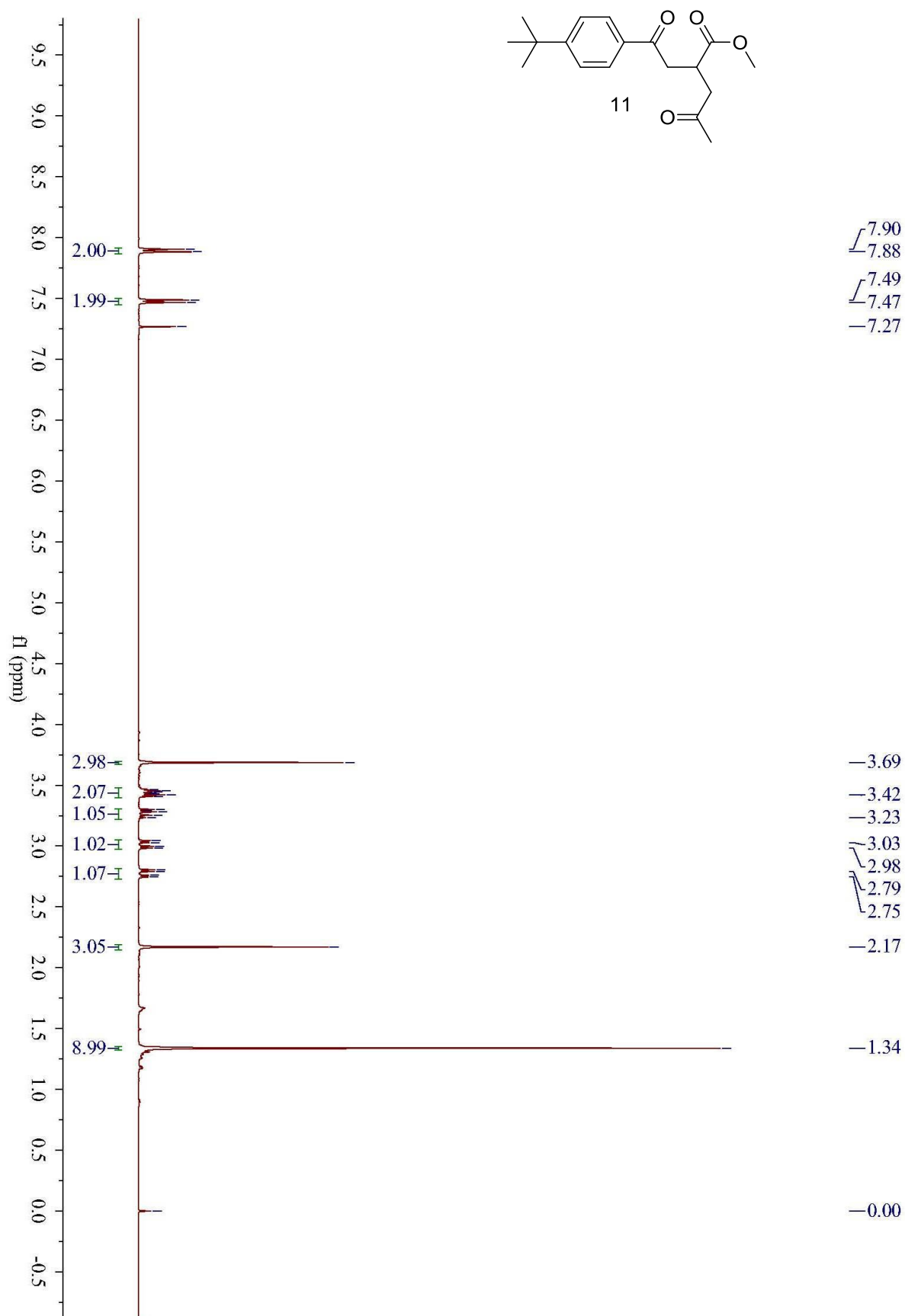


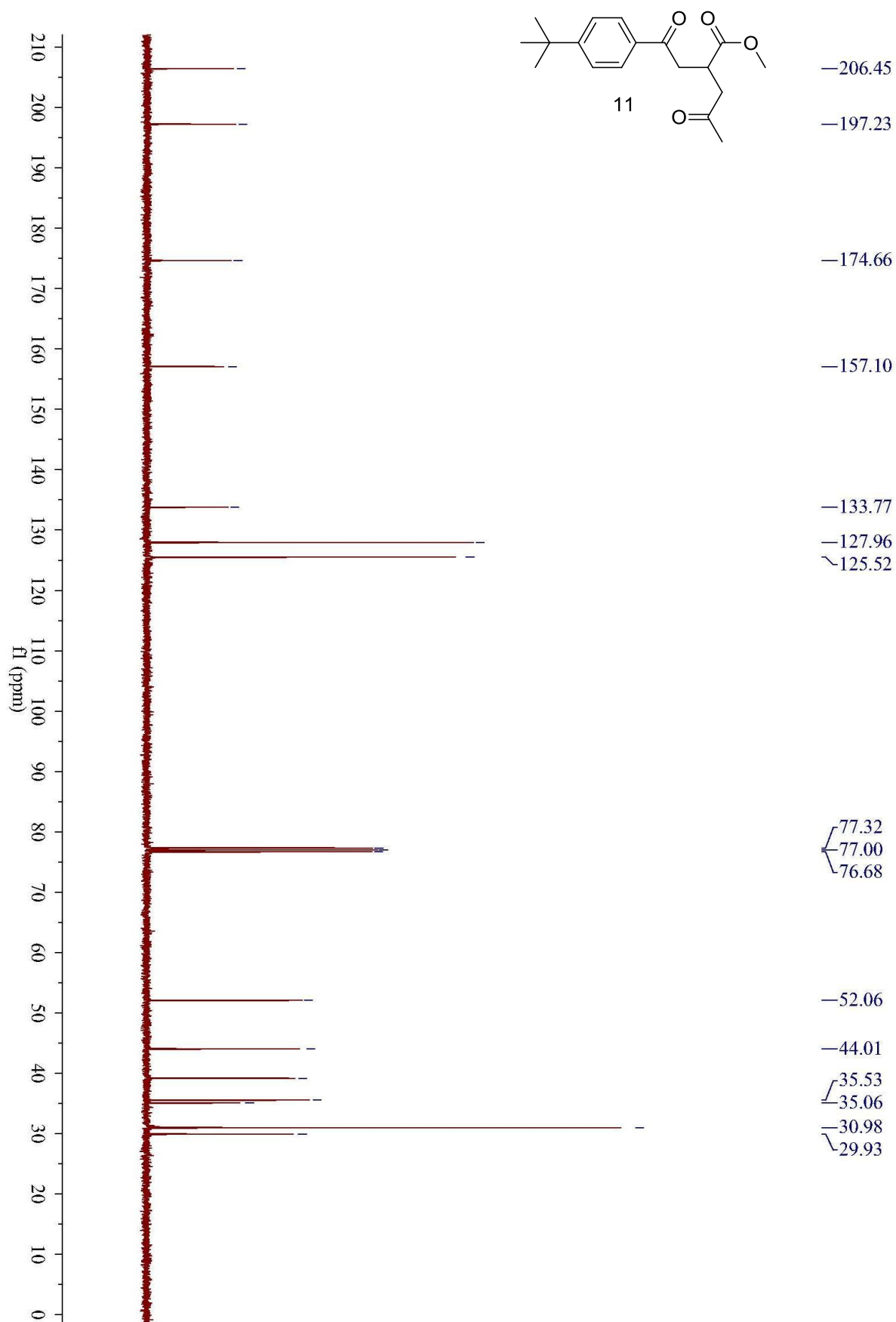


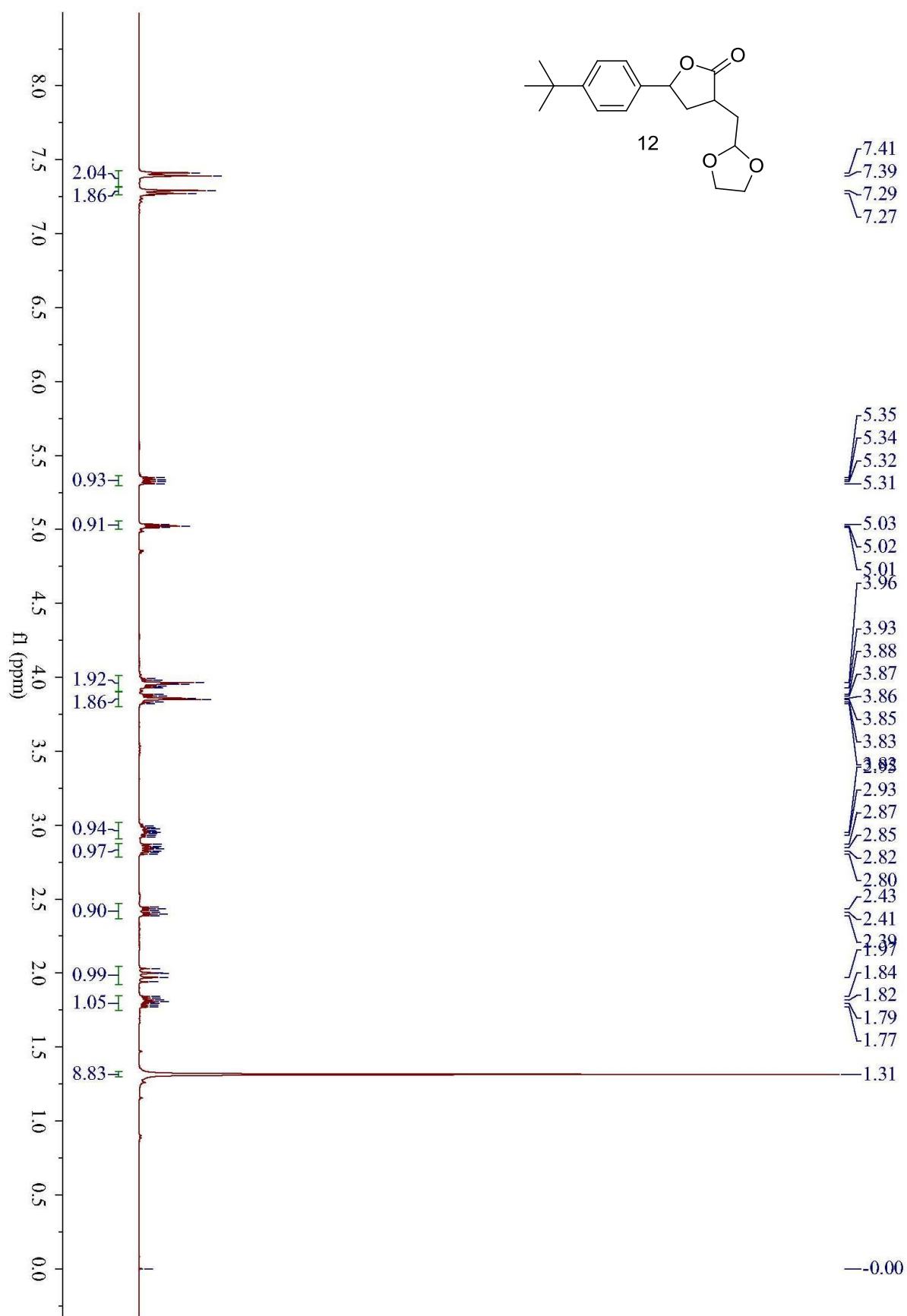


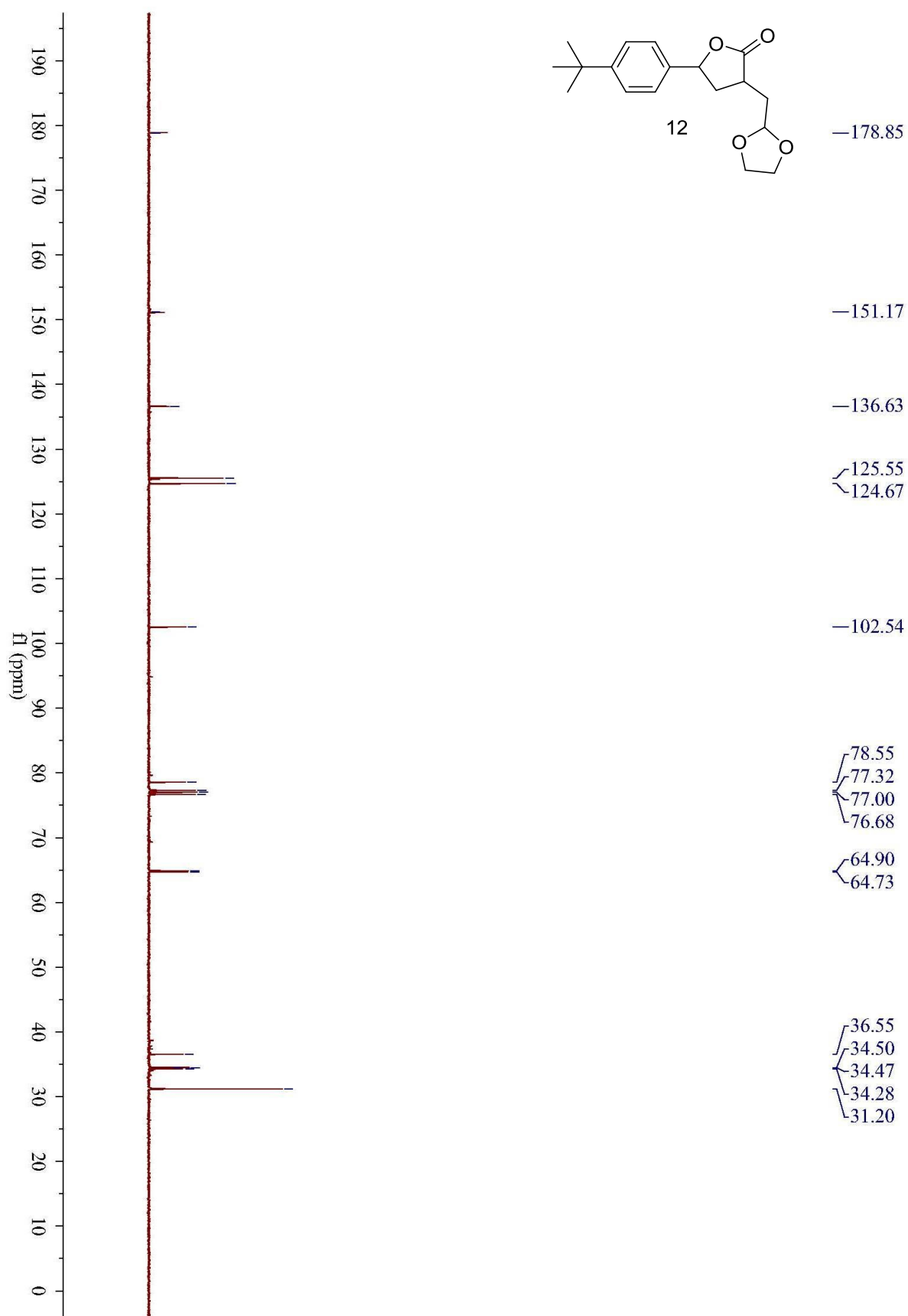


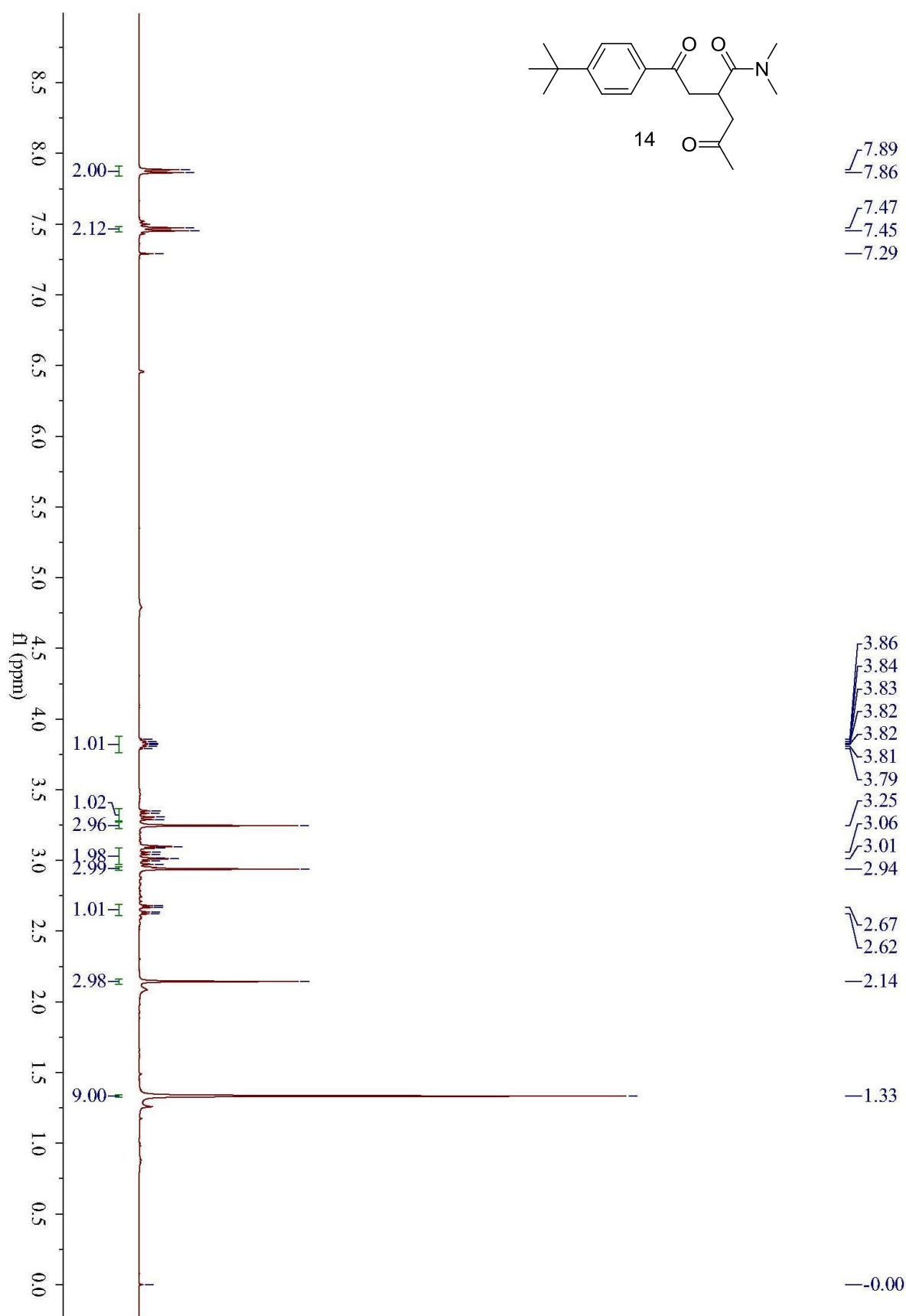


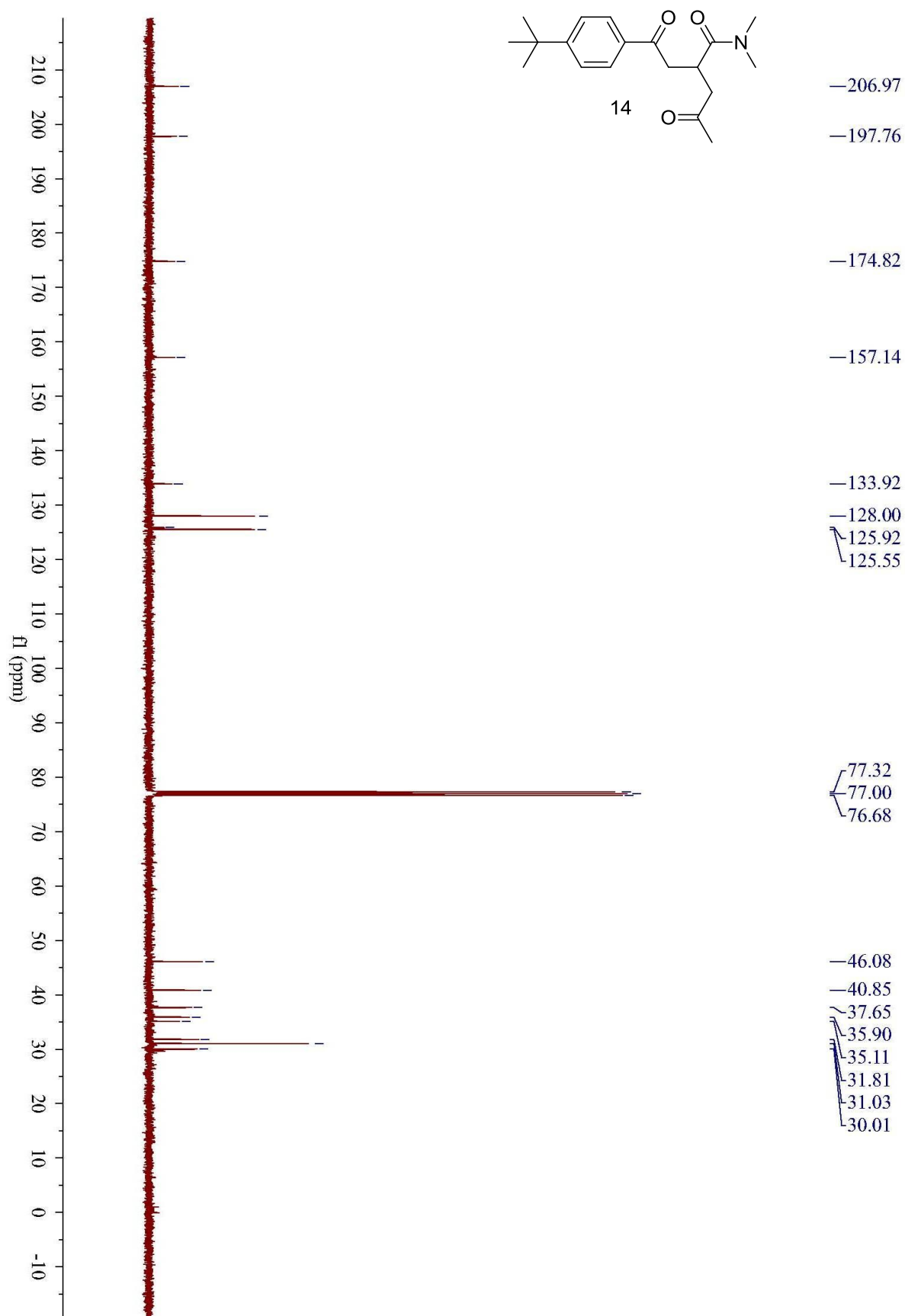


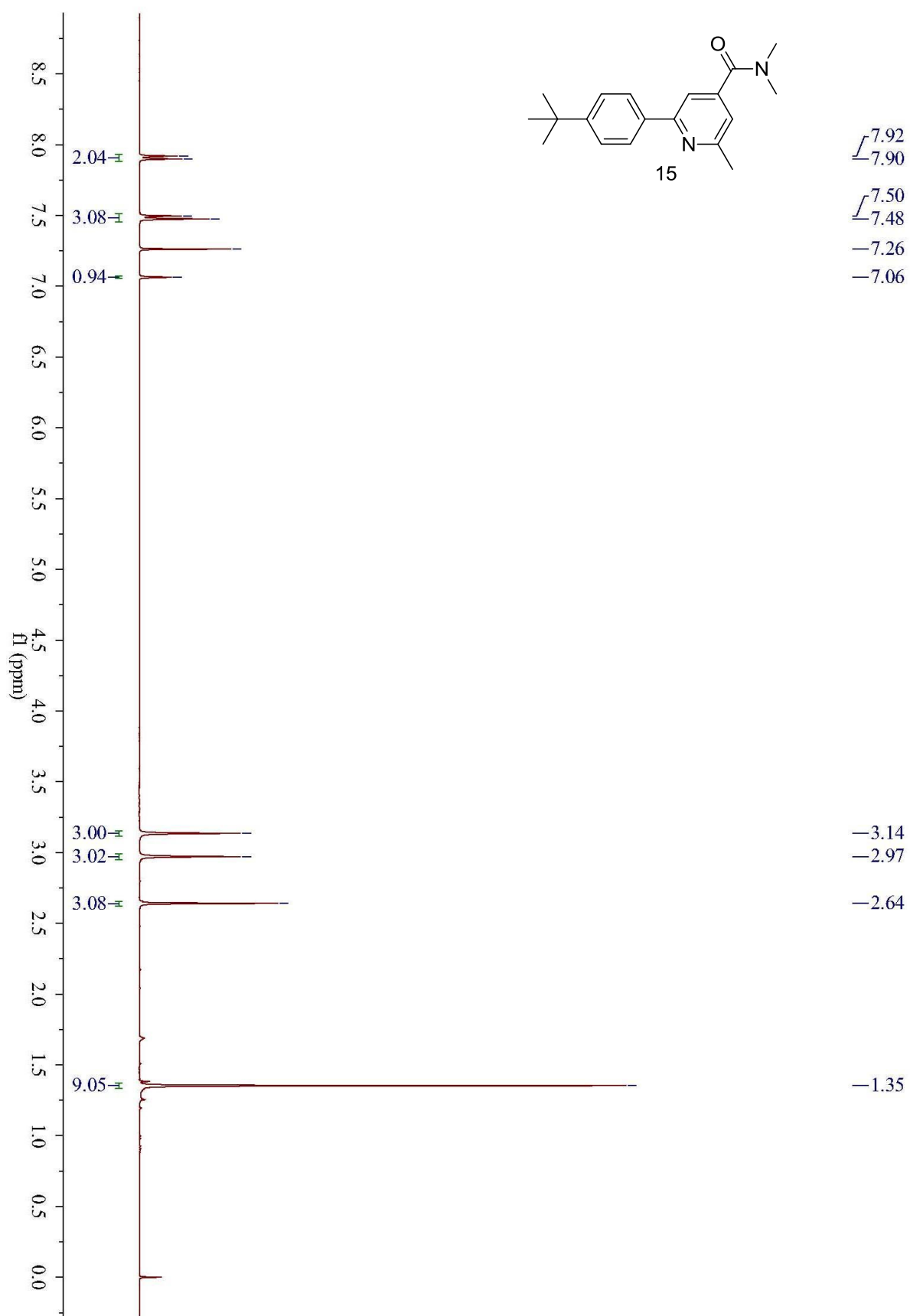


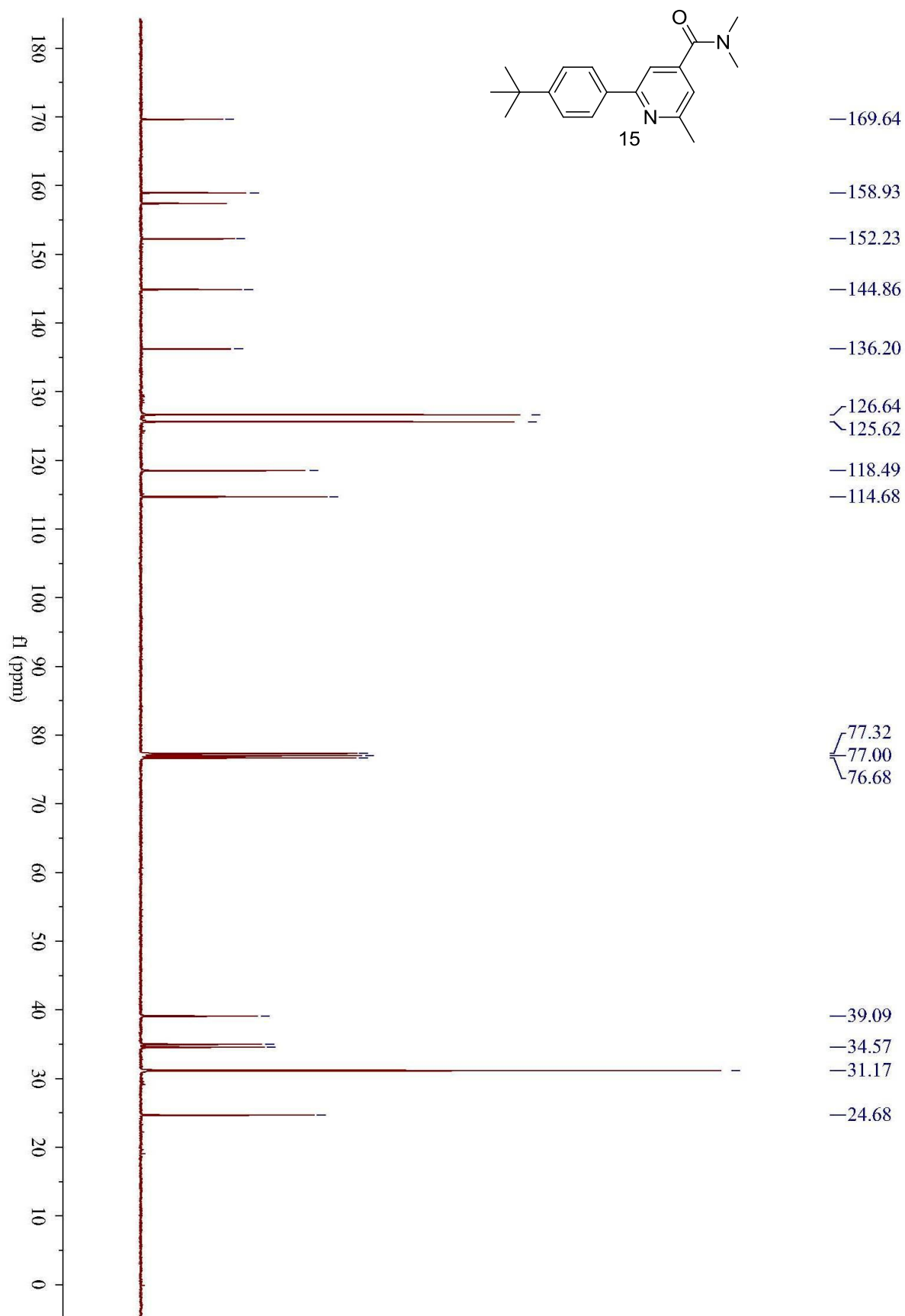












XRD data of the compound .

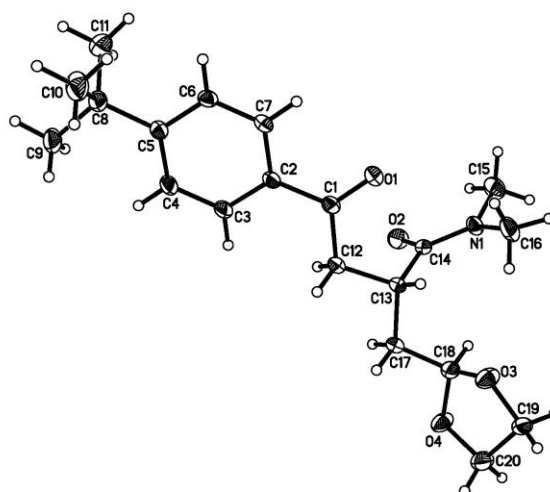


Figure S1. ORTEP structural drawing of **5h**.

Table S2. Crystallography data for **5h**

complex	5h
Empirical formula	C ₂₀ H ₂₉ NO ₄
Formula weight(g mol ⁻¹)	347.44
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	triclinic
space group	P -1
Unit cell dimensions	a = 8.7953(7) Å
	b = 10.2914(8) Å
	c = 12.3417(10) Å
	α = 106.950(2) °
	β = 105.261(2) °
	γ = 105.466(7) °
Volume (Å ³)	957.29(13)
Z	2
ρ(g cm ⁻³)	1.205
F(000)	376
Crystal size(mm ³)	0.45 x 0.21 x 0.20
Theta range for data collection	2.23 ° to 32.16 °
Limiting indices	-13 < h < 13

	-15 < = k < = 15
	-18 < = l < = 18
Reflections collected / unique	28894 / 6692
Data / restraints / parameters	6692 / 0 / 231
GOF	1.078
$R1, wR2[I > 2\sigma(I)]$	$R1 = 0.0885$ $wR2 = 0.1724$
$R1, wR2(\text{all data})$	$R1 = 0.1397$ $wR2 = 0.1949$
Largest diff. peak and hole(e Å ³)	0.376 and -0.240

Table S3. Bond lengths [Å] and angles [°] for **5h**

O1- C1 1.2178(19)	O2- C14 1.226(2)	O3- C18 1.405(2)	O3 -C19 1.417(2)
O4 -C20 1.410(2)	O4 -C18 1.419(2)	N1- C14 1.349(2)	N1 -C16 1.450(2)
N1- C15 1.455(2)	C1 -C2 1.492(2)	C1 -C12 1.504(2)	C2- C7 1.390(2)
C2 -C3 1.393(2)	C3 -C4 1.389(2)	C3- H3 0.9300	C4 C5 1.386(2)
C4- H4 0.9300	C5 -C6 1.398(2)	C5 -C8 1.526(2)	C6 -C7 1.380(2)
C6 -H6 0.9300	C7 -H7 0.9300	C8 -C9 1.529(2)	C8 -C10 1.533(3)
C8- C11 1.534(3)	C9 -H9A 0.9600	C9- H9B 0.9600	C9 -H9C 0.9600
C10- H10A 0.9600	C10- H10B 0.9600	C10- H10C 0.9600	C11- H11A 0.9600
C11 -H11B 0.9600	C11 -H11C 0.9600	C12 -C13 1.530(2)	C12- H12A 0.9700
C12- H12B 0.9700	C13 -C14 1.529(2)	C13 -C17 1.537(2)	C13- H13 0.9800
C15- H15A 0.9600	C15- H15B 0.9600	C15- H15C 0.9600	C16- H16A 0.9600
C16- H16B 0.9600	C16- H16C 0.9600	C17- C18 1.498(2)	C17 -H17A 0.9700
C17 -H17B 0.9700	C18- H18 0.9800	C19- C20 1.503(3)	C19 -H19A 0.9700
C19- H19B 0.9700	C20 -H20A 0.9700	C20 -H20B 0.9700	C18- O3 -C19 105.70(13)
C20- O4 -C18 108.72(14)	C14- N1 -C16 124.88(14)	C14- N1 -C15 118.33(15)	C16 -N1- C15 115.69(14)
O1 -C1- C2 120.84(15)	O1- C1- C12 121.13(15)	C2- C1 -C12 118.02(13)	C7- C2 -C3 118.09(15)
C7- C2 -C1 119.22(14)	C3- C2- C1 122.69(14)	C4 -C3- C2 120.87(15)	C4- C3- H3 119.6
C2 -C3- H3 119.6	C5- C4 -C3 121.21(15)	C5- C4 -H4 119.4	C3 -C4 -H4 119.4
C4 -C5 -C6 117.53(15)	C4 -C5 -C8 123.09(14)	C6- C5- C8 119.38(14)	C7- C6 -C5 121.53(15)

C7- C6 -H6 119.2	C5 -C6 -H6 119.2	C6 -C7 -C2 120.76(14)	C6 -C7- H7 119.6
C2 -C7 -H7 119.6	C5- C8 -C9 112.19(15)	C5- C8- C10 109.09(16)	C9 -C8 -C10 108.13(16)
C5- C8- C11 109.12(15)	C9 -C8- C11 108.47(16)	C10- C8- C11 109.82(17)	C8 -C9 -H9A 109.5
C8- C9- H9B 109.5	H9A- C9 -H9B 109.5	C8 -C9- H9C 109.5	H9A- C9 -H9C 109.5
H9B -C9 -H9C 109.5	C8- C10 -H10A 109.5	C8- C10 -H10B 109.5	H10A- C10 -H10B 109.5
C8 -C10- H10C 109.5	H10A -C10- H10C 109.5	H10B- C10 -H10C 109.5	C8- C11- H11A 109.5
C8 -C11 -H11B 109.5	H11A- C11- H11B 109.5	C8 -C11- H11C 109.5	H11A- C11 -H11C 109.5
H11B- C11 -H11C 109.5	C1 -C12- C13 114.30(13)	C1- C12 -H12A 108.7	C13 -C12- H12A 108.7
C1 -C12- H12B 108.7	C13- C12- H12B 108.7	H12A- C12- H12B 107.6	C14 -C13- C12 108.44(13)
C14 -C13- C17 109.99(14)	C12- C13 -C17 107.91(13)	C14 -C13 -H13 110.1	C12 -C13 -H13 110.1
C17 -C13- H13 110.1	O2- C14 -N1 121.66(15)	O2 -C14- C13 119.26(14)	N1 -C14 -C13 119.04(14)
N1- C15 -H15A 109.5	N1 -C15- H15B 109.5	H15A- C15 -H15B 109.5	N1 -C15- H15C 109.5
H15A- C15- H15C 109.5	H15B- C15- H15C 109.5	N1 -C16 -H16A 109.5	N1- C16- H16B 109.5
H16A- C16 -H16B 109.5	N1- C16 -H16C 109.5	H16A- C16- H16C 109.5	H16B -C16 -H16C 109.5
C18 -C17 -C13 114.75(13)	C18 -C17 -H17A 108.6	C13- C17- H17A 108.6	C18 -C17 H-17B 108.6
C13 -C17- H17B 108.6	H17A- C17- H17B 107.6	O3 -C18 -O4 106.57(14)	O3 -C18 -C17 111.76(16)
O4- C18 -C17 109.75(14)	O3- C18 -H18 109.6	O4 -C18 -H18 109.6	C17- C18- H18 109.6
O3- C19- C20 103.55(14)	O3 -C19- H19A 111.1	C20- C19- H19A 111.1	O3- C19 -H19B 111.1
C20- C19 -H19B 111.1	H19A -C19 -H19B 109.0	O4 -C20- C19 104.46(15)	O4 -C20- H20A 110.9
C19- C20- H20A 110.9	O4 -C20 -H20B 110.9	C19 -C20- H20B 110.9	H20A- C20 -H20B 108.9

Adducts detected by LC-MS

