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Supporting Information

Synthesis of 1,4-Diketones via Palladium/Photo-Cocatalyzed Dehydrogenative Cross-Coupling

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Table of Contents

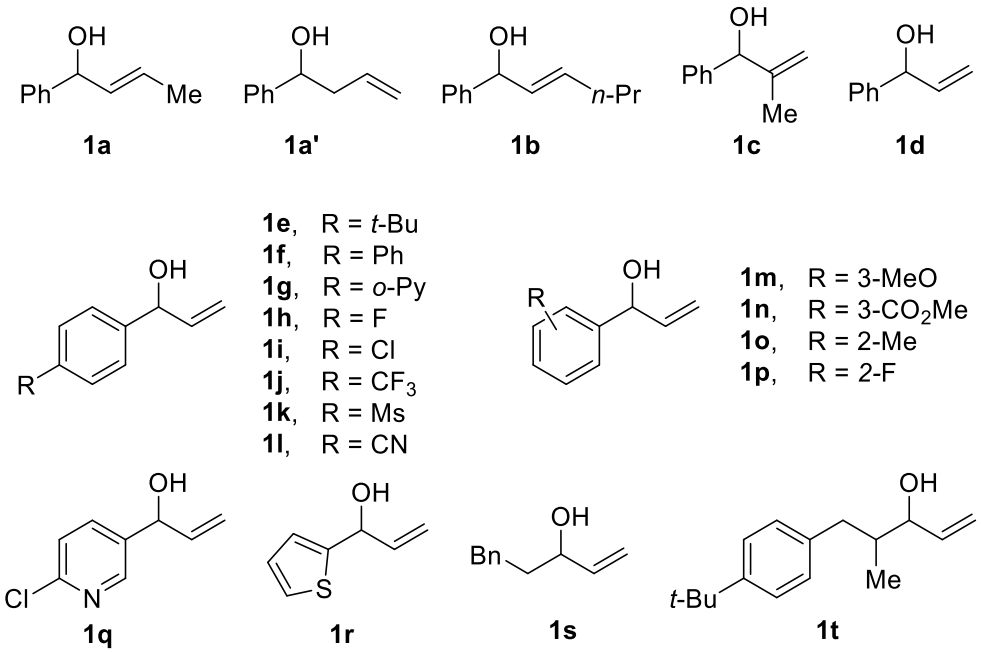
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$ at 400 and 101 MHz. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling ($F^{19}CPD$) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ ($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ ($CDCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

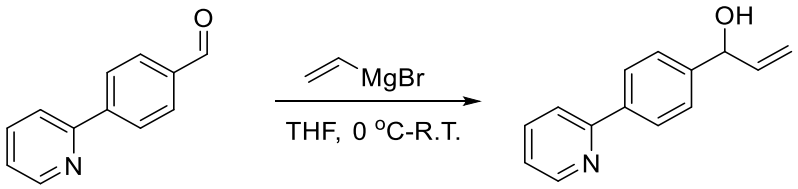
Unless otherwise noted, all reagents and starting materials were purchased from Aldrich, Strem, Alfa Aesar Energy-chemical, or Adamas-beta used without further purification. TBADT (tetrabutyl ammonium decatungstate) were synthesized according to the reported method[1].

Procedures for Synthesis of Starting Materials

Starting aldehydes were purchased from Aldrich, Energy, Alfa Aesar or Adamas-beta. Allylic alcohols **1a-f** and **1h-t** were synthesized according to the reported methods[2].



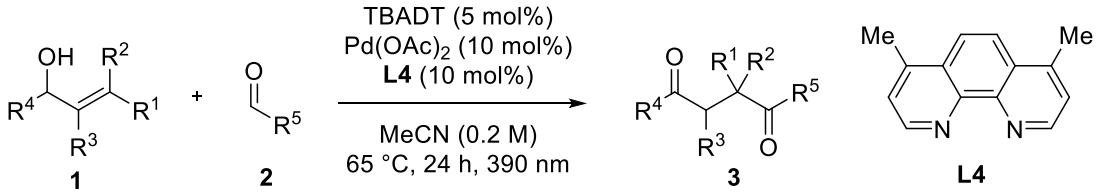
Procedure for the preparation of 1-(4-(Pyridin-2-yl)phenyl)prop-2-en-1-ol (1g)



A round bottomed flask was charged with 4-(pyridin-2-yl)benzaldehyde (3.66g, 20 mmol, 1 equiv) in THF (40 mL), flushed with nitrogen, and cooled to 0 ℃. Vinylmagnesium bromide (24 mL, 24 mmol, 1.2 equiv, 1 M in THF) was added slowly to the solution. The reaction was warmed to room temperature within 1 hour, before it was quenched with water. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) to afford the *1-(4-(pyridin-2-yl)phenyl)prop-2-en-1-ol* (**1g**) in 82% yield (3.46 g) as a white solid. mp 61-

63 °C **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.67 (d, *J* = 4.8, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.07 (ddd, *J* = 17.0, 10.3, 6.0 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.25 (d, *J* = 6.0 Hz, 1H), 5.20 (d, *J* = 10.4, 1H), 2.74 – 2.49 (br s, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 157.3, 149.8, 143.6, 140.3, 138.8, 136.9, 127.2 (2C), 126.8 (2C), 122.3, 120.7, 115.4, 75.1 ppm. **HRMS** (ESI) m/z calculated for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1070, found: 212.1073.

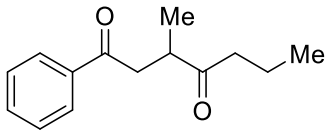
General Procedure for Palladium/TBADT-Cocatalyzed Dehydrogenative Cross-Coupling



TBADT (tetrabutylammonium decatungstate) (33.2 mg, 0.01 mmol, 5 mol%), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), Ligand **L4** (4.2 mg, 0.02 mmol, 10 mol%), aldehydes **2** (if solid, 0.6 mmol, 3.0 equiv), allylic alcohols **1** (if solid, 0.2 mmol, 1.0 equiv) were placed in a tube equipped with a stir bar. The tube was evacuated and filled with argon (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) was added under argon atmosphere. Next, aldehydes (if liquid, 0.6 mmol, 3.0 equiv) and allylic alcohols (if liquid, 0.2 mmol, 1.0 equiv) were added, sequentially. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction maintain 65 °C) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate) to afford the desired products **3**.

Characterization Data of 1, 4-Diketones

3-Methyl-1-phenylheptane-1,4-dione (3aa)



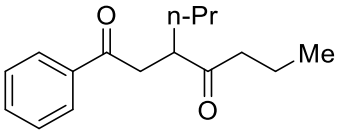
The title compound **3aa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil. Yield: 75% (32.7 mg), starting from (*E*)-*1-phenylbut-2-en-1-ol* (**1a**); yield: 52% (22.7 mg), starting from *(Z)-1-phenylbut-2-en-1-ol* (*cis*-**1a**); yield: 34% (14.9 mg), starting from *1-phenylbut-3-en-1-ol* (**1a'**).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.54 (dd, *J* = 17.9, 8.9 Hz, 1H), 3.27 – 3.16 (m, 1H), 2.91 (dd, *J* = 17.9, 4.4 Hz, 1H), 2.69 – 2.52 (m, 2H), 1.70 – 1.58 (m, 2H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 213.8, 198.8, 136.8, 133.3, 128.7 (2C), 128.2 (2C), 43.5, 42.0, 41.2, 17.2, 17.1, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1382.

1-Phenyl-3-propylheptane-1,4-dione (3ba)



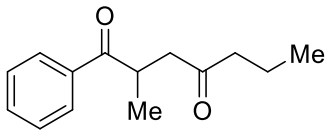
The title compound **3ba** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (25.6 mg, 52%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.94 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.52 (dd, *J* = 17.9, 9.8 Hz, 1H), 3.24 – 3.15 (m, 1H), 2.97 (dd, *J* = 17.9, 3.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.60 – 2.50 (m, 1H), 1.73 – 1.53 (m, 4H), 1.44 – 1.32 (m, 2H), 0.98 – 0.89 (m, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 213.8, 199.1, 136.8, 133.3, 128.7 (2C), 128.2 (2C), 46.3, 44.7, 40.3, 34.0, 20.6, 17.0, 14.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$: 269.1512, found: 269.1512.

2-Methyl-1-phenylheptane-1,4-dione (3ca)



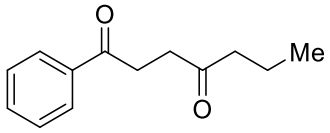
The title compound **3ca** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (32.7 mg, 75%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.98 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.03 – 3.94 (m, 1H), 3.13 (dd, *J* = 17.9, 8.6 Hz, 1H), 2.52 (dd, *J* = 17.9, 5.0 Hz, 1H), 2.46 – 2.36 (m, 2H), 1.63 – 1.55 (m, 2H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.7, 203.6, 136.1, 133.1, 128.7 (2C), 128.6 (2C), 46.2, 45.0, 36.2, 17.9, 17.3, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1385.

1-Phenylheptane-1,4-dione (3da)



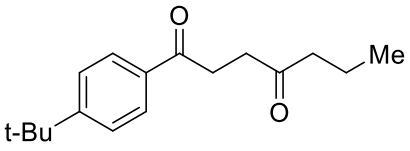
The title compound **3da** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (29.0 mg, 71%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.98 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.28 (t, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.61 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 198.8, 136.8, 133.2, 128.7 (2C), 128.2 (2C), 45.0, 36.3, 32.5, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found: 205.1228.

1-(4-(*tert*-Butyl)phenyl)heptane-1,4-dione (3ea)



The title compound **3ea** was isolated through column chromatography (silica gel,

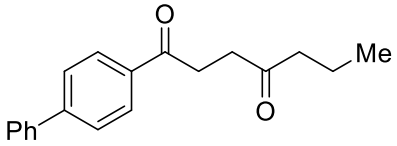
petroleum ether/ethyl acetate 4:1) as a pale yellow oil (38.5 mg, 74%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.92 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 3.26 (t, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.33 (s, 9H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.9, 198.5, 156.9, 134.2, 128.1 (2C), 125.6 (2C), 45.0, 36.4, 35.2, 32.4, 31.2 (3C), 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{24}O_2Na$ $[M+Na]^+$: 283.1669, found: 283.1674.

1-([1,1'-Biphenyl]-4-yl)heptane-1,4-dione (3fa)



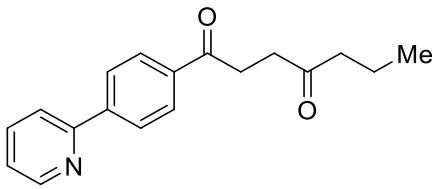
The title compound **3fa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (50.5 mg, 90%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.05 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.31 (t, *J* = 6.3 Hz, 2H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.62 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 198.4, 145.9, 140.0, 135.5, 129.0 (2C), 128.8 (2C), 128.3, 127.4 (2C), 127.3 (2C), 45.0, 36.4, 32.5, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{20}O_2Na$ $[M+Na]^+$: 303.1356, found: 303.1355.

1-(4-(Pyridin-2-yl)phenyl)heptane-1,4-dione (3ga)



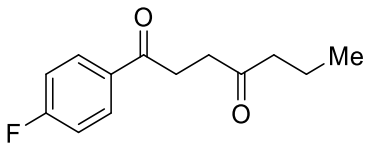
The title compound **3ga** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (42.8 mg, 76%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.70 (d, *J* = 4.9 Hz, 1H), 8.10 – 7.94 (m, 4H), 7.78 – 7.61 (m, 2H), 7.25 – 7.15 (m, 1H), 3.30 (t, *J* = 5.8 Hz, 2H), 2.85 (t, *J* = 5.7 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.58 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 198.5, 156.2, 150.0, 143.7, 137.0, 136.8, 128.7 (2C), 127.1 (2C), 123.0, 121.1, 45.0, 36.3, 32.6, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{19}NO_2Na$ $[M+Na]^+$: 304.1308, found: 304.1309.

1-(4-Fluorophenyl)heptane-1,4-dione (3ha)



The title compound **3ha** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (29.3 mg, 66%).

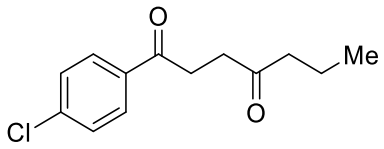
^{1}H NMR (400 MHz, Chloroform-d) δ = 8.00 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.11 (dd, *J* = 8.6 Hz, 8.6 Hz, 2H), 3.23 (t, *J* = 6.1 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.58 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.7, 197.2, 165.9 (d, J_{C-F} = 254.6 Hz), 133.2 (d, J_{C-F} = 3.0 Hz), 130.8 (d, J_{C-F} = 9.4 Hz, 2C), 115.8 (d, J_{C-F} = 21.9 Hz, 2C), 45.0, 36.3, 32.3, 17.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –105.26 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{16}FO_2$ $[M+H]^+$: 223.1129, found: 223.1133.

1-(4-Chlorophenyl)heptane-1,4-dione (3ia)



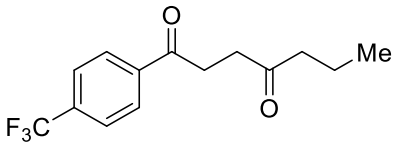
The title compound **3ia** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (29.6 mg, 62%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.91 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.22 (t, *J* = 6.1 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.60 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.6, 197.6, 139.7, 135.2, 129.6 (2C), 129.0 (2C), 45.0, 36.3, 32.4, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{16}ClO_2$ $[M+H]^+$: 239.0833, found: 239.0840.

1-(4-(Trifluoromethyl)phenyl)heptane-1,4-dione (3ja)



The title compound **3ja** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (27.8 mg, 51%).

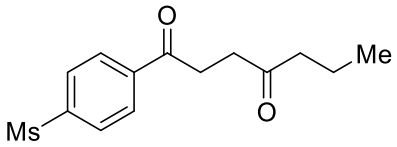
^{1}H NMR (400 MHz, Chloroform-d) δ = 8.08 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 3.28 (t, *J* = 6.1 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.60 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.5, 198.0, 139.5, 134.5 (q, J_{C-F} = 32.5 Hz), 128.5 (2C), 125.8 (q, J_{C-F} = 3.7 Hz, 2C), 123.7 (q, J_{C-F} = 272.7 Hz), 44.9, 36.3, 32.7, 17.5, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = – 63.1 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{16}F_3O_2$ $[M+H]^+$: 273.1097, found: 273.1104.

1-(4-(Methylsulfonyl)phenyl)heptane-1,4-dione (3ka)



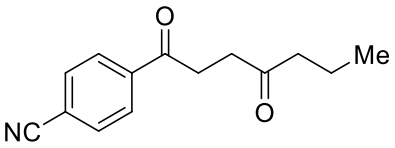
The title compound **3ka** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (26.0 mg, 46%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.14 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 2H), 3.27 (t, *J* = 6.0 Hz, 2H), 3.07 (s, 3H), 2.89 (t, *J* = 6.2 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.60 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.4, 197.8, 144.2, 140.8, 129.1 (2C), 127.9 (2C), 44.9, 44.5, 36.3, 32.8, 17.4, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O_4S$ $[M+H]^+$: 283.0999, found: 283.1006.

4-(4-Oxoheptanoyl)benzonitrile (3la)



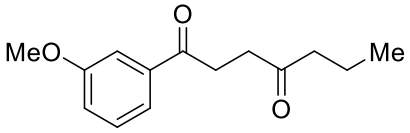
The title compound **3la** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (18.8 mg, 41%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.06 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 3.25 (t, *J* = 6.0 Hz, 2H), 2.88 (t, *J* = 6.2 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.59 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.4, 197.6, 139.8, 132.6 (2C), 128.6 (2C), 118.1, 116.5, 44.9, 36.3, 32.7, 17.4, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1176, found: 230.1179.

1-(3-Methoxyphenyl)heptane-1,4-dione (3ma)



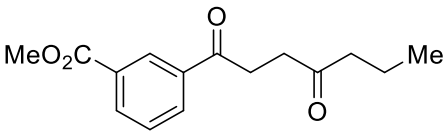
The title compound **3ma** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (27.6 mg, 59%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.57 (d, *J* = 7.7 Hz, 1H), 7.48 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.84 (s, 3H), 3.26 (t, *J* = 6.3 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.60 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 198.7, 159.9, 138.1, 129.7, 120.9, 119.8, 112.3, 55.5, 45.0, 36.3, 32.6, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{18}O_3Na$ $[M+Na]^+$: 257.1148, found: 257.1152.

Methyl 3-(4-oxoheptanoyl)benzoate (3na)



The title compound **3na** was isolated through column chromatography (silica gel,

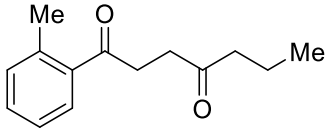
petroleum ether/ethyl acetate 4:1) as a pale yellow oil (31.5 mg, 60%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.62 (s, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 3.94 (s, 3H), 3.30 (t, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 6.2 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.59 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.6, 198.0, 166.4, 137.0, 134.0, 132.3, 130.8, 129.4, 129.0, 52.5, 45.0, 36.3, 32.6, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1097, found: 285.1090.

1-(*o*-Tolyl)heptane-1,4-dione (3oa)



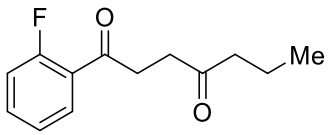
The title compound **3oa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (18.8 mg, 43%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.73 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.30 – 7.19 (m, 2H), 3.17 (t, *J* = 6.0 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.47 (s, 3H), 1.68 – 1.62 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 202.9, 138.1, 137.9, 132.0, 131.4, 128.6, 125.8, 44.9, 36.6, 35.3, 21.3, 17.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1384.

1-(2-Fluorophenyl)heptane-1,4-dione (3pa)



The title compound **3pa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (19.5 mg, 44%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.86-7.84 (m, 1H), 7.56 – 7.45 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.13 (dd, *J* = 11.2, 8.3 Hz, 1H), 3.30 – 3.24 (m, 2H), 2.83 (t, *J* = 6.1 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.60 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

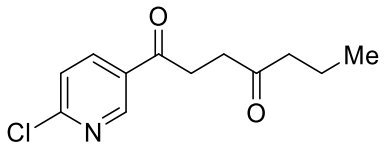
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.7, 197.1 (d, J_{C-F} = 4.2 Hz), 162.2 (d, J_{C-F} = 255.2 Hz), 134.7 (d, J_{C-F} = 8.9 Hz), 130.7 (d, J_{C-F} = 2.8 Hz), 125.4 (d, J_{C-F} = 13.1 Hz),

124.5 (d, J_{C-F} = 3.0 Hz), 116.8 (d, J_{C-F} = 23.6 Hz), 44.9, 37.4 (d, J_{C-F} = 8.2 Hz), 36.4 (d, J_{C-F} = 2.7 Hz), 17.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –109.0 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{16}FO_2$ $[M+H]^+$: 223,1129, found: 223,1130.

1-(6-Chloropyridin-3-yl)heptane-1,4-dione (3qa)



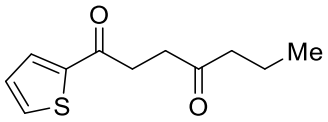
The title compound **3qa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (20.6 mg, 43%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.96 (d, *J* = 2.3 Hz, 1H), 8.19 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 3.22 (t, *J* = 6.0 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.67 – 1.59 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.3, 196.6, 155.8, 150.0, 138.2, 131.0, 124.6, 44.8, 36.1, 32.7, 17.4, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{12}H_{15}ClNO_2$ $[M+H]^+$: 240.0786, found: 240.0793.

1-(Thiophen-2-yl)heptane-1,4-dione (3ra)



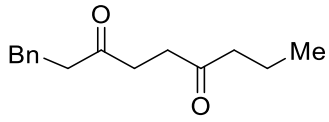
The title compound **3ra** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (20.6 mg, 49%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.76 (d, *J* = 3.8 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.12 (t, *J* = 4.0 Hz, 1H), 3.22 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 1.66 – 1.60 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.6, 191.8, 143.9, 133.6, 132.1, 128.2, 45.0, 36.3, 33.0, 17.4, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{11}H_{14}O_2SNa$ $[M+Na]^+$: 233.0607, found: 233.0608.

1-Phenylnonane-3,6-dione (3sa)



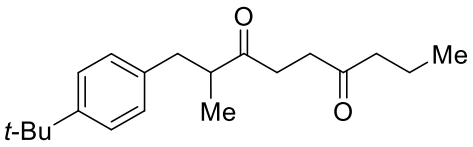
The title compound **3sa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (20.6 mg, 29%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.24 (t, *J* = 7.9 Hz, 2H), 7.19 – 7.12 (m, 3H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.67 – 2.60 (m, 4H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.55 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 208.7, 141.2, 128.6 (2C), 128.4 (2C), 126.2, 44.8, 44.5, 36.3, 36.1, 29.8, 17.4, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1536, found: 233.1538.

1-(4-(*tert*-Butyl)phenyl)-2-methylnonane-3,6-dione (3ta)



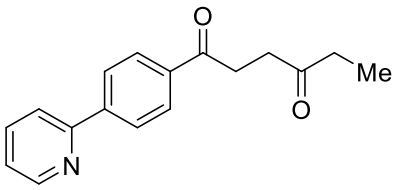
The title compound **3ta** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a pale yellow oil (17.0 mg, 28%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.29 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 3.01 – 2.95 (m, 1H), 2.89 – 2.83 (m, 1H), 2.79 – 2.74 (m, 1H), 2.70 – 2.63 (m, 1H), 2.60 – 2.50 (m, 3H), 2.43 – 2.40 (m, 2H), 1.64 – 1.57 (m, 2H), 1.30 (s, 9H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 213.0, 209.8, 149.1, 136.7, 128.7 (2C), 125.4 (2C), 48.2, 44.9, 38.6, 36.0, 35.3, 34.5, 31.5 (3C), 17.4, 16.5, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{31}O_2$ $[M+H]^+$: 303.2319, found: 303.2325.

1-(4-(Pyridin-2-yl)phenyl)hexane-1,4-dione (3ab)



The title compound **3ab** was isolated through column chromatography (silica gel,

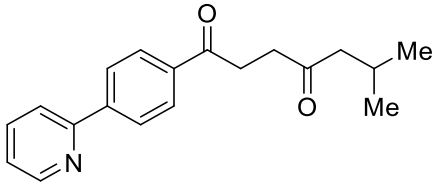
petroleum ether/ethyl acetate 4:1) as a pale yellow oil (31.0 mg, 58%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.7 Hz, 1H), 8.12 – 7.96 (m, 4H), 7.78 – 7.63 (m, 2H), 7.29 – 7.23 (m, 1H), 3.33 (t, *J* = 6.3 Hz, 2H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.57 (q, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 210.3, 198.5, 156.2, 150.0, 143.7, 137.0, 136.8, 128.7 (2C), 127.1 (2C), 123.0, 121.2, 36.2, 35.9, 32.7, 8.0 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1338.

6-Methyl-1-(4-(pyridin-2-yl)phenyl)heptane-1,4-dione (3ac)



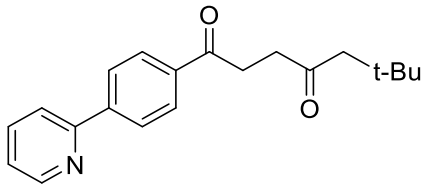
The title compound **3ac** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (38.4 mg, 65%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.7 Hz, 1H), 8.13 – 7.98 (m, 4H), 7.80 – 7.74 (m, 2H), 7.28 (t, *J* = 4.7 Hz, 1H), 3.31 (t, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 6.3 Hz, 2H), 2.41 (d, *J* = 7.0 Hz, 2H), 2.23 – 2.15 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.5, 198.4, 156.2, 150.0, 143.7, 137.0, 136.8, 128.7 (2C), 127.1 (2C), 123.0, 121.2, 52.1, 36.9, 32.5, 24.8, 22.7 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1645, found: 296.1650.

6,6-Dimethyl-1-(4-(pyridin-2-yl)phenyl)heptane-1,4-dione (3ad)



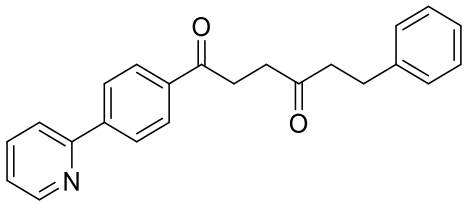
The title compound **3ad** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (50.7 mg, 82%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.7 Hz, 1H), 8.11 – 7.98 (m, 4H), 7.81 – 7.76 (m, 2H), 7.28 (t, *J* = 2.7 Hz, 1H), 3.27 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 6.3 Hz, 2H), 2.42 (s, 2H), 1.04 (d, *J* = 3.1 Hz, 9H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.4, 198.5, 156.2, 150.0, 143.7, 137.0, 136.9, 128.7 (2C), 127.1 (2C), 123.0, 121.2, 55.2, 38.8, 32.6, 31.2, 29.9 (3C). ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{24}NO_2$ $[M+H]^+$: 310.1802, found: 310.1801.

6-Phenyl-1-(4-(pyridin-2-yl)phenyl)hexane-1,4-dione (3ae)



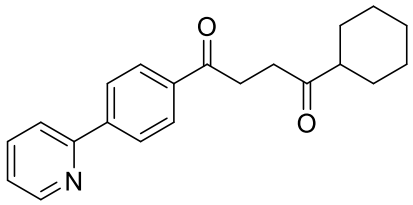
The title compound **3ae** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (30.2 mg, 44%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.73 (d, *J* = 4.8 Hz, 1H), 8.14 – 8.04 (m, 4H), 7.81 – 7.77 (m, 2H), 7.32 – 7.26 (m, 3H), 7.23 – 7.17 (m, 3H), 3.33 (t, *J* = 6.3 Hz, 2H), 2.99 – 2.93 (m, 2H), 2.91 – 2.84 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 208.7, 198.3, 156.2, 150.0, 143.7, 141.2, 137.1, 136.7, 128.7 (2C), 128.6 (2C), 128.4 (2C), 127.2 (2C), 126.2, 123.1, 121.2, 44.6, 36.5, 32.7, 29.9 ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{22}NO_2$ $[M+H]^+$: 344.1645, found: 344.1648.

1-Cyclohexyl-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3af)



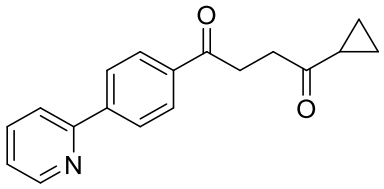
The title compound **3af** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (19.3 mg, 30%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.73 (d, *J* = 4.7 Hz, 1H), 8.13 – 8.03 (m, 4H), 7.82 – 7.76 (m, 2H), 7.32 – 7.26 (m, 1H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.53 – 2.43 (m, 1H), 1.97 – 1.90 (m, 2H), 1.84 – 1.77 (m, 2H), 1.47 – 1.35 (m, 2H), 1.35 – 1.17 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 212.9, 198.6, 156.3, 150.0, 143.7, 137.0, 136.9, 128.7 (2C), 127.2 (2C), 123.0, 121.2, 51.1, 34.4, 32.6, 28.7 (2C), 26.0, 25.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{24}NO_2$ $[M+H]^+$: 322.1802, found: 322.1805.

1-Cyclopropyl-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3ag)



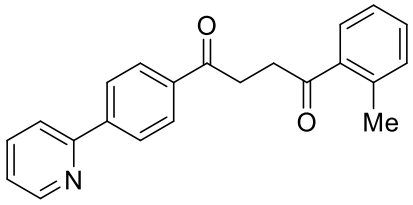
The title compound **3ag** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (23.5 mg, 42%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.7 Hz, 1H), 8.12 – 8.06 (m, 4H), 7.79 – 7.77 (m, 2H), 7.31 – 7.27 (m, 1H), 3.32 (t, *J* = 6.4 Hz, 2H), 3.06 (t, *J* = 6.4 Hz, 2H), 2.08 – 2.01 (m, 1H), 1.09 – 1.05 (m, 2H), 0.94 – 0.90 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.5, 198.5, 156.2, 150.0, 143.7, 137.0, 136.9, 128.7 (2C), 127.1 (2C), 123.0, 121.2, 36.9, 32.6, 20.9, 11.0 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found: 280.1338.

1-(4-(Pyridin-2-yl)phenyl)-4-(o-tolyl)butane-1,4-dione (3ah)



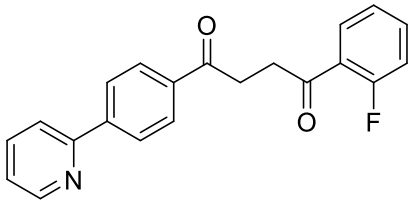
The title compound **3ah** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (42.2 mg, 64%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.69 (d, *J* = 4.7 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.80 – 7.76 (m, 1H), 7.75 – 7.72 (m, 2H), 7.28 – 7.17 (m, 3H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.33 (t, *J* = 6.1 Hz, 2H), 2.47 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 202.7, 198.4, 156.2, 150.0, 143.7, 138.2, 137.9, 137.1, 136.9, 132.0, 131.5, 128.7, 128.7 (2C), 127.2 (2C), 125.8, 123.1, 121.2, 35.4, 33.1, 21.4 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{19}NO_2Na$ $[M+Na]^+$: 352.1308, found: 352.1315.

1-(2-Fluorophenyl)-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3ai)



The title compound **3ai** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (28.0 mg, 42%).

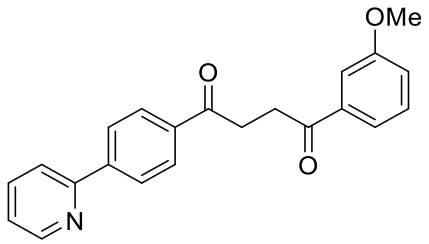
^{1}H NMR (400 MHz, Chloroform-d) δ = 8.73 (d, *J* = 4.8 Hz, 1H), 8.14 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.94 – 7.89 (m, 1H), 7.95 – 7.89 (m, 1H), 7.56 – 7.50 (m, 1H), 7.31 – 7.14 (m, 4H), 3.51 – 3.46 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.3, 197.1 (d, J_{C-F} = 3.8 Hz), 162.3 (d, J_{C-F} = 255.2 Hz), 156.2, 150.0, 143.7, 137.1, 136.9, 134.8 (d, J_{C-F} = 8.9 Hz), 130.8 (d, J_{C-F} = 2.3 Hz), 128.8 (2C), 127.2 (2C), 125.6 (d, J_{C-F} = 13.1 Hz), 124.6 (d, J_{C-F} = 3.6 Hz), 123.0, 121.2, 116.8 (d, J_{C-F} = 23.6 Hz), 37.5 (d, J_{C-F} = 8.1 Hz), 32.9 (d, J_{C-F} = 2.2 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –108.9 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{17}FNO_2$ $[M+H]^+$: 334.1238, found: 334.1242.

1-(3-Methoxyphenyl)-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3aj)



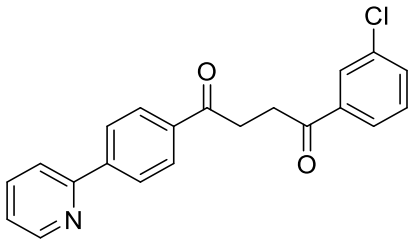
The title compound **3aj** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (25.6 mg, 37%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.74 (d, *J* = 4.7 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.82 – 7.75 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.13 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.86 (s, 3H), 3.53 – 3.45 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.7, 198.5, 160.0, 156.3, 150.1, 143.8, 138.3, 137.1, 136.9, 129.8, 128.8 (2C), 127.2 (2C), 123.1, 121.2, 121.0, 119.9, 112.4, 55.6, 32.9 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{20}NO_3$ $[M+H]^+$: 346.1438, found: 346.1443.

1-(3-Chlorophenyl)-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3ak)



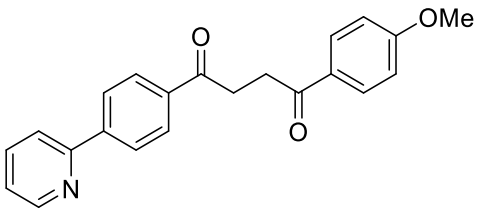
The title compound **3ak** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (21.0 mg, 30%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.73 (d, *J* = 4.7 Hz, 1H), 8.15 – 8.10 (m, 4H), 8.02 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.51 (t, *J* = 6.3 Hz, 2H), 3.44 (t, *J* = 6.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.2, 197.6, 156.2, 150.1, 143.9, 138.5, 137.1, 136.8, 135.1, 133.2, 130.1, 128.8 (2C), 128.4, 127.2 (2C), 126.4, 123.1, 121.2, 32.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{17}ClNO_2$ $[M+H]^+$: 350.0942, found: 350.0946.

1-(4-Methoxyphenyl)-4-(4-(pyridin-2-yl)phenyl)butane-1,4-dione (3al)



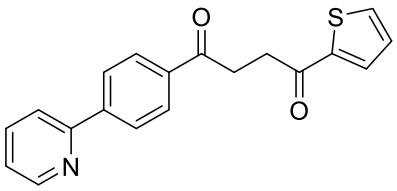
The title compound **3al** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (22.1 mg, 32%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.7 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.81 – 7.75 (m, 2H), 7.28 (t, *J* = 4.0 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.51 – 3.45 (m, 1H), 3.45 – 3.40 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.7, 197.3, 163.6, 156.2, 150.0, 143.7, 137.0, 136.9, 130.5 (2C), 129.9, 128.7 (2C), 127.1 (2C), 123.0, 121.1, 113.8 (2C), 55.6, 32.9, 32.3 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{20}NO_3$ $[M+H]^+$: 346.1438, found: 346.1439.

1-(4-(Pyridin-2-yl)phenyl)-4-(thiophen-2-yl)butane-1,4-dione (3am)



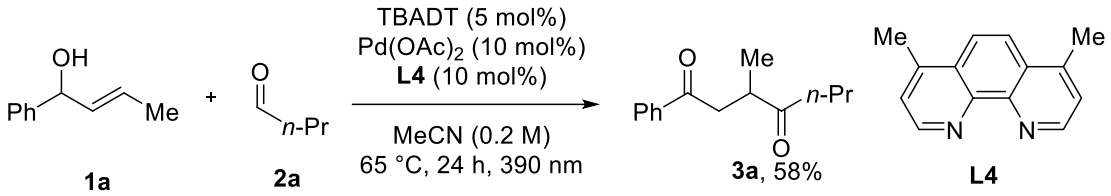
The title compound **3am** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 4:1) as a pale yellow oil (25.1 mg, 39%).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, *J* = 4.8 Hz, 1H), 8.14 – 8.09 (m, 4H), 7.84 (d, *J* = 3.8 Hz, 1H), 7.79 (d, *J* = 4.2 Hz, 2H), 7.65 (d, *J* = 4.9 Hz, 1H), 7.29 (t, *J* = 4.4 Hz, 1H), 7.15 (t, *J* = 4.4 Hz, 1H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 6.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 198.2, 191.8, 156.2, 150.0, 144.0, 143.8, 137.1, 136.8, 133.7, 132.2, 128.7 (2C), 128.3, 127.2 (2C), 123.1, 121.2, 33.3, 32.9 ppm.

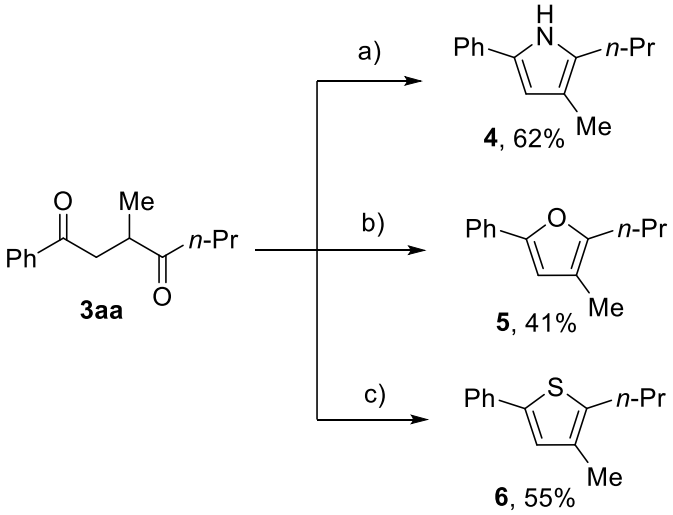
HRMS (ESI) m/z calculated for $C_{19}H_{15}NO_2SNa$ $[M+Na]^+$: 344.0716, found: 344.0722.

Procedures for 1 mmol Scale Synthesis of 3a



TBADT (tetrabutylammonium decatungstate) (166 mg, 0.05 mmol, 5 mol%), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol, 10 mol%), Ligand **L4** (21 mg, 0.1 mmol, 10 mol%), The tube was evacuated and filled with argon (three cycles). To these solids, dry MeCN (5 mL, 0.2 M) was added under argon atmosphere. Next, aldehydes **2a** (216 mg, 3.0 mmol, 3.0 equiv) and allylic alcohols **1a** (148 mg, 1.0 mmol, 1.0 equiv) were added, sequentially. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction maintain 65 °C) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) to afford the desired products **3a** as a pale yellow oil (127 mg, 58%).

Procedures for Derivatizations of the Cross-Coupling Product



a) NH_4OAc, AcOH, Reflux, 20 h; b) TfOH, CH_3CN, 85 °C;
c) Lawesson reagent (1.5 equiv), THF, 55 °C, 24 h.

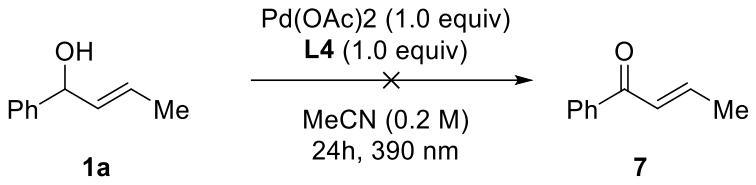
Procedure **a)**: A mixture of the 1,4-diketone **3aa** (0.40 mmol, 87.2 mg, 1.0 equiv), ammonium acetate (2.4 mmol, 186 mg, 6.0 equiv), and acetic acid (0.1 M, 4 mL) was heated under reflux for 20 h. After cooling down, the reaction mixture was poured into ice-water. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 1:1) to afford *3-methyl-5-phenyl-2-propyl-1H-pyrrole* (**4**) in 62% yield (49.4 mg) as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ = 7.43 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.09 (s, 3H), 1.69 – 1.62 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 133.2, 130.2, 129.3, 128.9 (2C), 125.5, 123.3 (2C), 116.2, 108.0, 28.2, 23.4, 14.0, 11.1 ppm. **HRMS** (ESI) m/z calculated for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434, found: 200.1436.

Procedure **b)**: To a dry Schlenk tube that charged with nitrogen, 1,4-diketone **3aa** (0.40 mmol, 87.2 mg, 1.0 equiv) was added, CH_3CN (0.1 M, 4.0 mL) was injected through a syringe. Subsequently, triflic acid (60 mg, 0.40 mmol, 1.0 equiv) was added to the mixture, and the resulting solution was stirred at 85 ºC for 1 h. Next, the resulting solution was cooled to room temperature, and solvent was evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether 20:1) to afford *3-methyl-5-phenyl-2-propylfuran* (**5**) in 41%

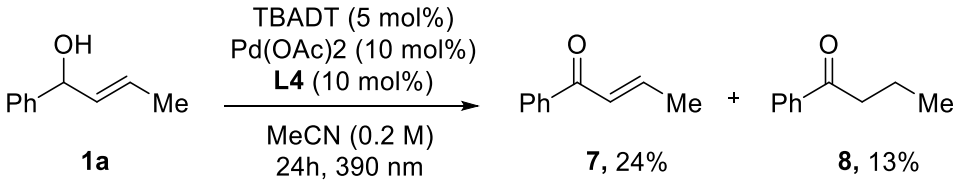
yield (31.1 mg) as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ = 7.61 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.45 (s, 1H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.00 (s, 3H), 1.74 – 1.64 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 151.5, 150.9, 131.4, 128.7 (2C), 126.6, 123.3 (2C), 116.2, 108.4, 28.1, 22.1, 13.9, 10.1 ppm. **HRMS** (ESI) m/z calculated for $C_{14}H_{17}O$ $[M+H]^+$: 201.1274, found: 201.1276.

Procedure **c)**: To a dry Schlenk tube charged with nitrogen, the 1,4-diketone **3aa** (0.40 mmol, 87.2 mg, 1.0 equiv), THF (8.0 mL), and lawesson reagent (242 mg, 0.60 mmol, 1.5 equiv) were added successively. Subsequently, the resulting solution was stirred at 55 ºC for 24 h, before it was cooled to room temperature. After evaporating the volatiles under vacuum, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford *3-methyl-5-phenyl-2-propylthiophene* (**6**) in 55% yield (47.6 mg) as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ = 7.60 – 7.57 (m, 2H), 7.39 – 7.35 (m, 2H), 7.29 – 7.24 (m, 1H), 7.06 (s, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 1.77 – 1.69 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.5, 138.8, 134.9, 133.7, 128.9 (2C), 126.9, 126.1, 125.4 (2C), 30.2, 24.8, 14.0, 13.9 ppm. **HRMS** (ESI) m/z calculated for $C_{14}H_{17}S$ $[M+H]^+$: 217.1045, found: 217.1049.

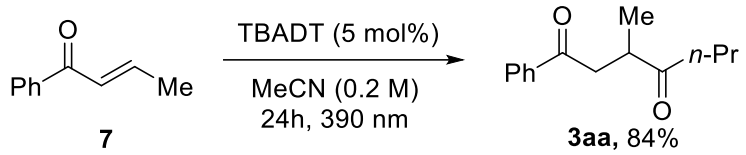
Control Experiments



$Pd(OAc)_2$ (45 mg, 0.2 mmol, 1.0 equiv), Ligand **L4** (42 mg, 0.2 mmol, 1.0 equiv), allylic alcohols **1a** (29.6 mg, 0.2 mmol, 1.0 equiv) were placed in a tube equipped with a stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) was added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction maintain 65 °C) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The formation of **7** was not observed.



TBADT (tetrabutyl ammonium decatungstate) (66.4 mg, 0.02 mmol, 5 mol%), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol, 10 mol%), Ligand **L4** (8.4 mg, 0.04 mmol, 10 mol%), allylic alcohols **1a** (59.2 mg, 0.4 mmol, 1.0 equiv) were placed in a tube equipped with a stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (2 mL, 0.2 M) was added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction maintain 65 °C) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate) to afford *(E)-1-phenylbut-2-en-1-one (**6**)* as a colorless oil (14.2 mg, 24%) and *1-phenylbutan-1-one (**8**)* as a colorless oil (7.6 mg, 13%). The NMR data of **7**[3] or **8**[4] are consistent with the reported literature.



7 **3aa,** 84%

TBADT (tetrabutyl ammonium decatungstate) (33.2 mg, 0.01 mmol, 5 mol%), *(E)-1-phenylbut-2-en-1-one* (**7**) (29.2 mg, 0.2 mmol, 1.0 equiv) were placed in a tube equipped with a stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) was added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away to keep the reaction maintain 65 °C) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate) to afford *3-methyl-1-phenylheptane-1,4-dione* (**3aa**) as a colorless oil (36.7 mg, 84%) .

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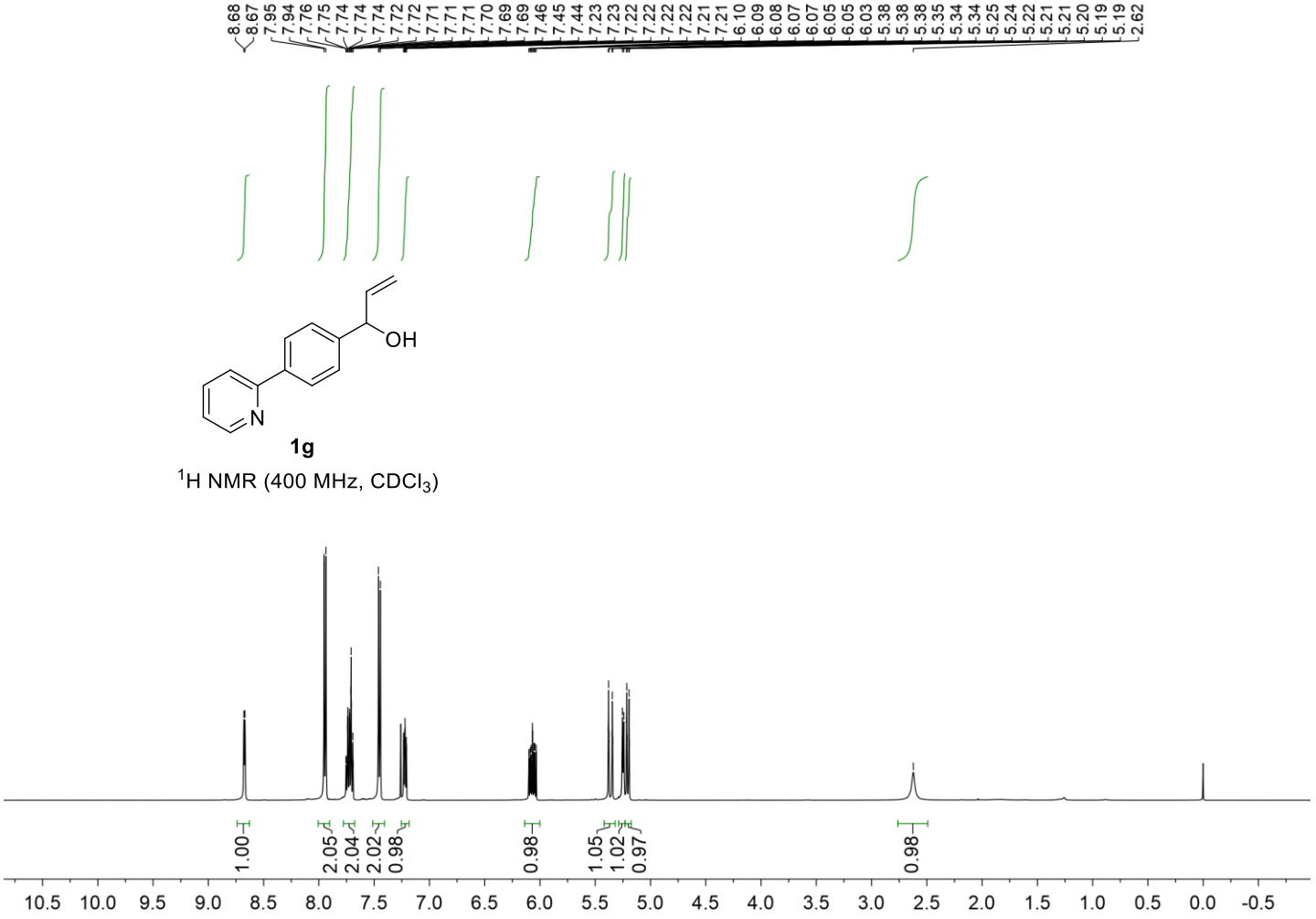
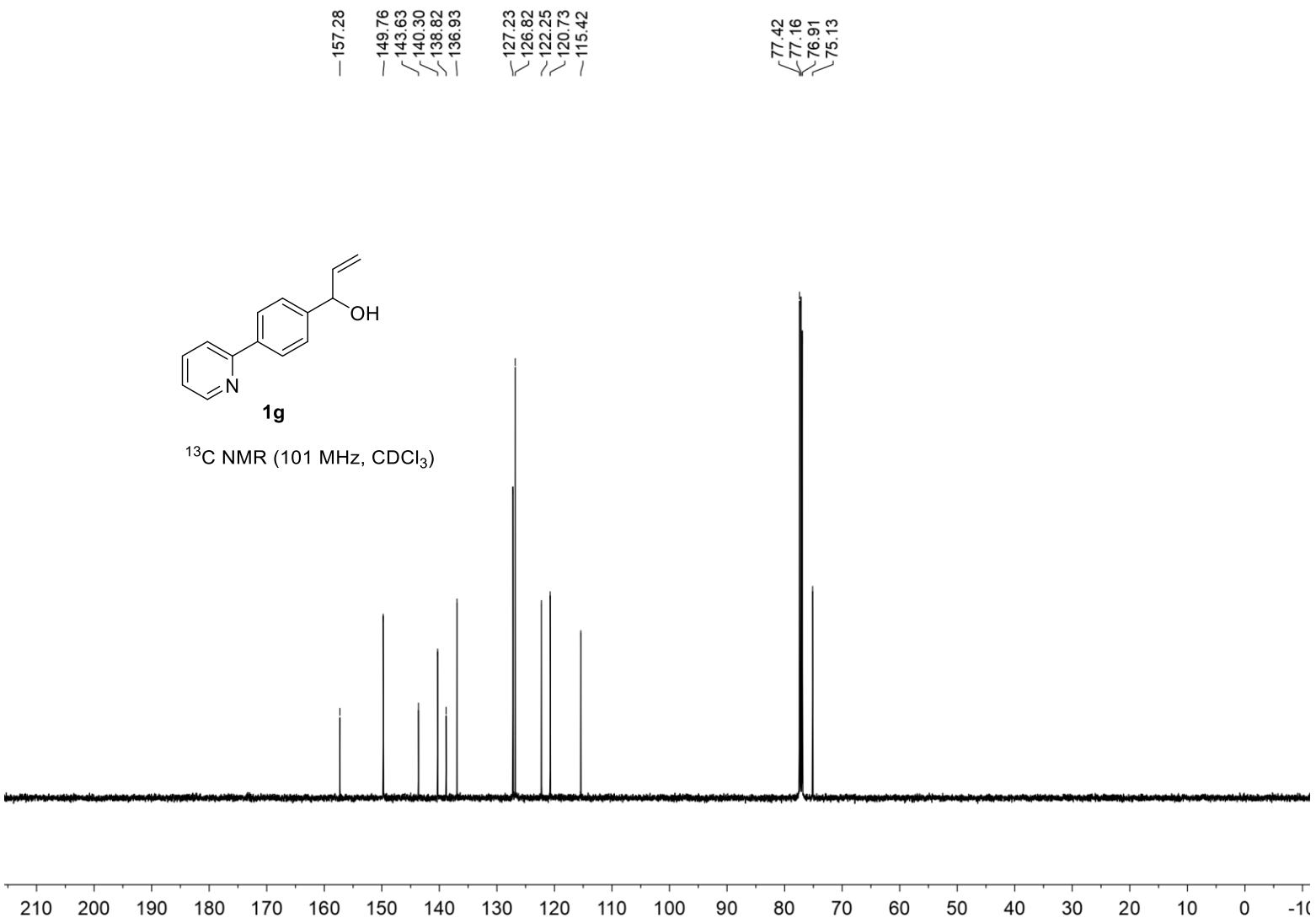
^{1}H, ^{13}C and ^{19}F-Spectra

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149.76
143.63
140.30
138.82
136.93
127.23
126.82
122.25
120.73
115.42
77.42
77.16
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N
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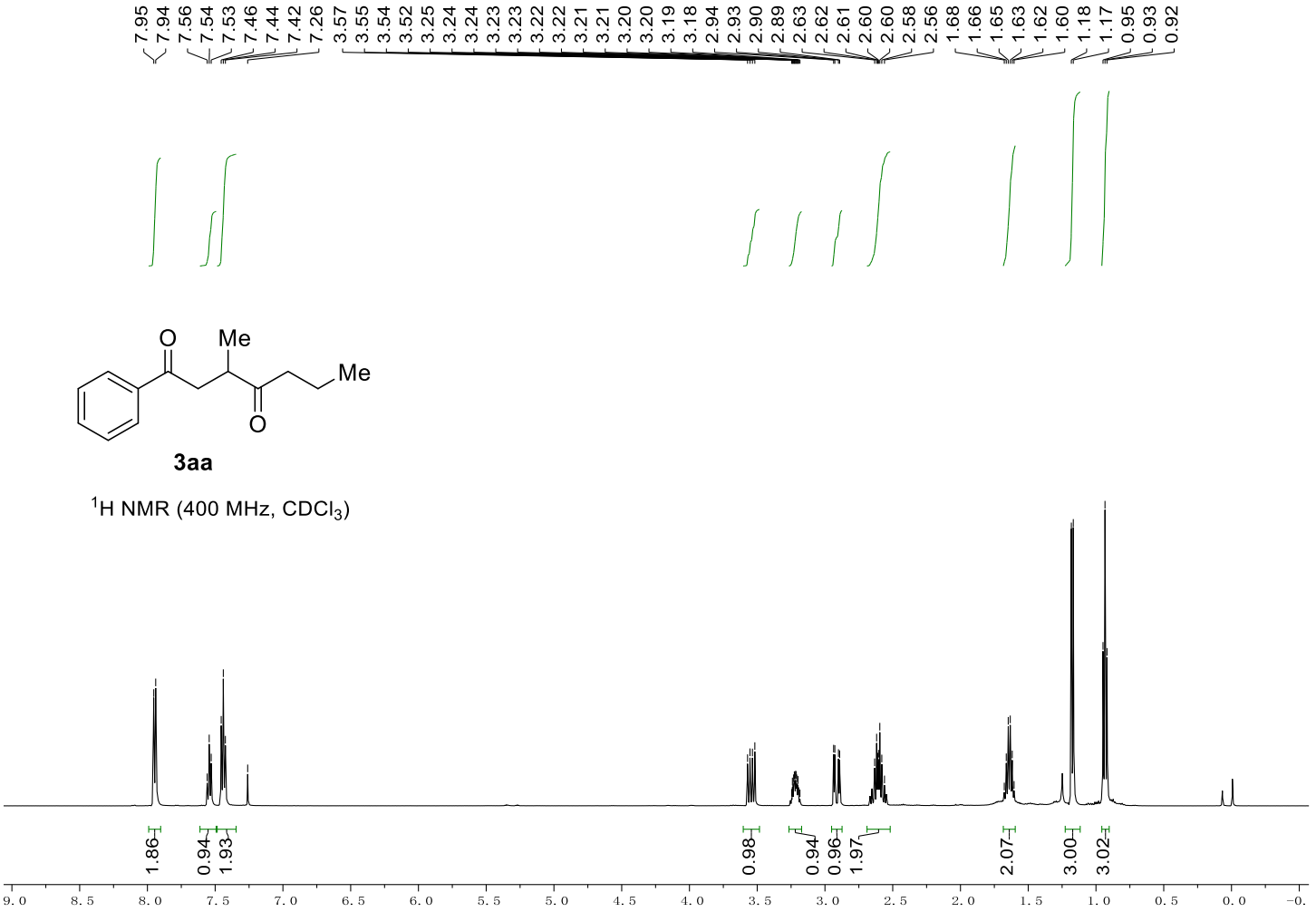
7.95
7.94
7.56
7.54
7.53
7.46
7.44
7.42
7.26
3.57
3.55
3.54
3.52
3.25
3.24
3.24
3.23
3.23
3.22
3.22
3.21
3.21
3.20
3.20
3.19
3.18
2.94
2.93
2.90
2.89
2.63
2.62
2.61
2.60
2.60
2.58
2.56
1.68
1.66
1.65
1.63
1.62
1.60
1.18
1.17
0.95
0.93
0.92
O
Me
Me
O
3aa
1H NMR (400 MHz, CDCl3)
1.86
0.94
1.93
0.98
0.94
0.96
1.97
2.07
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
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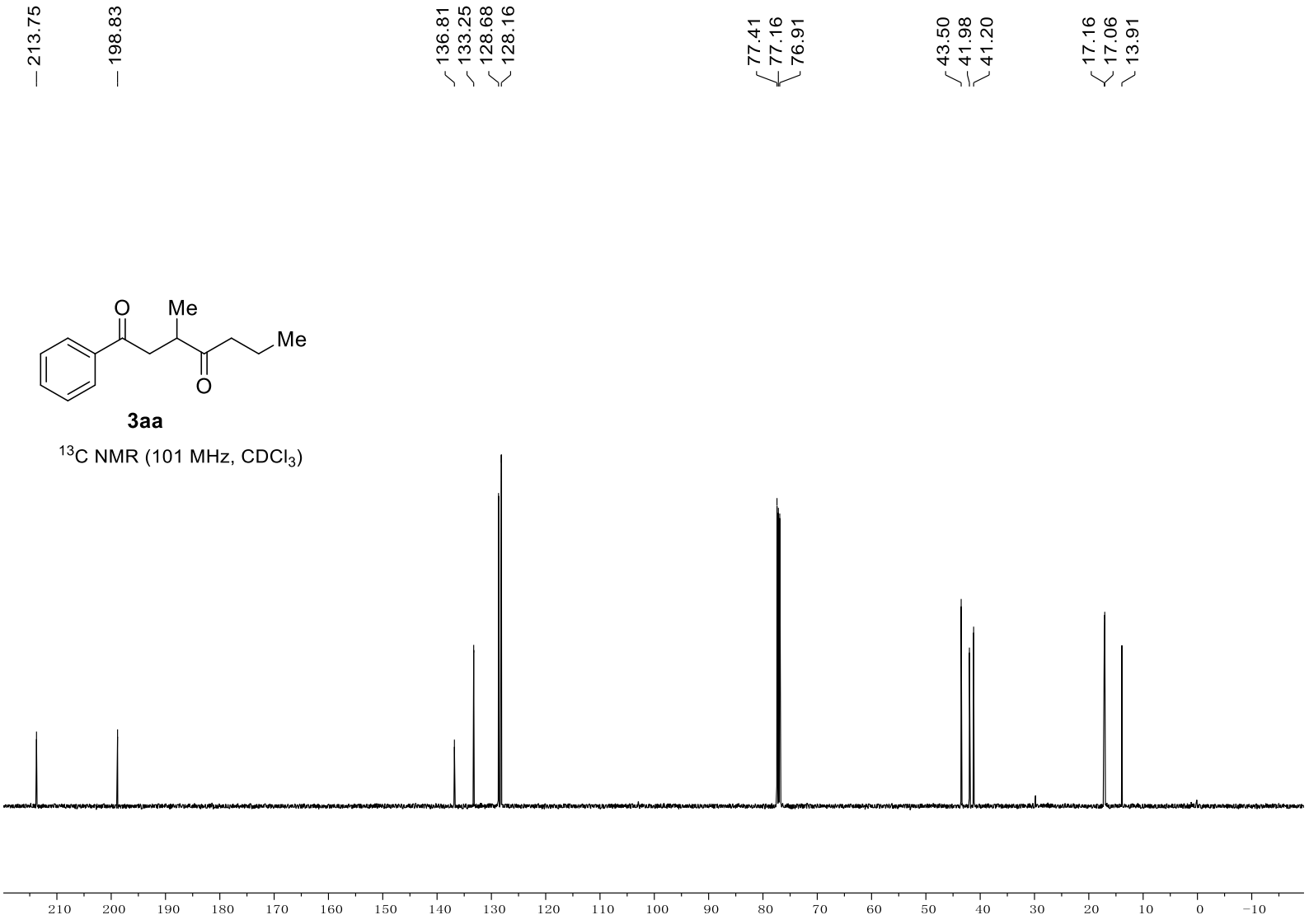
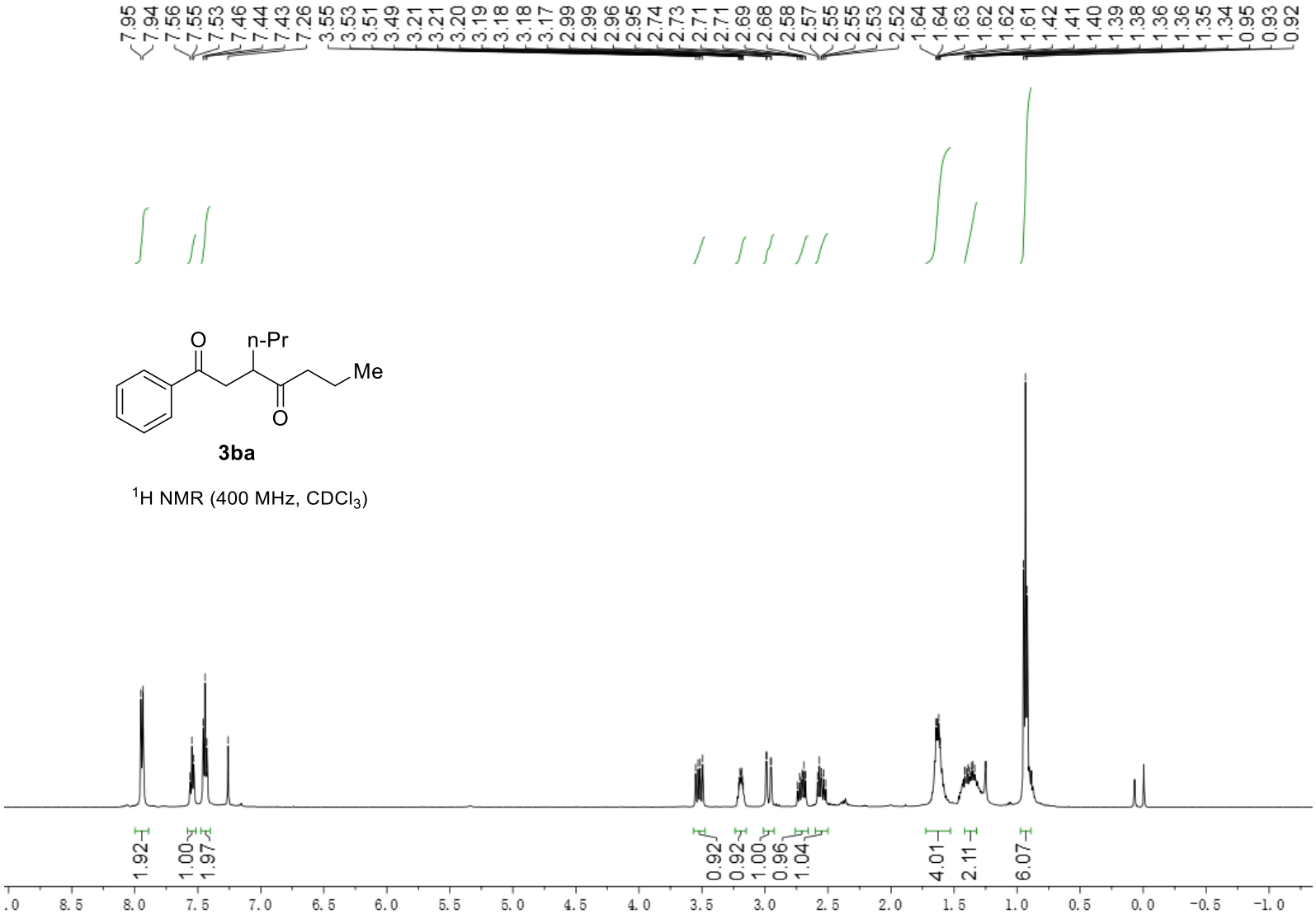
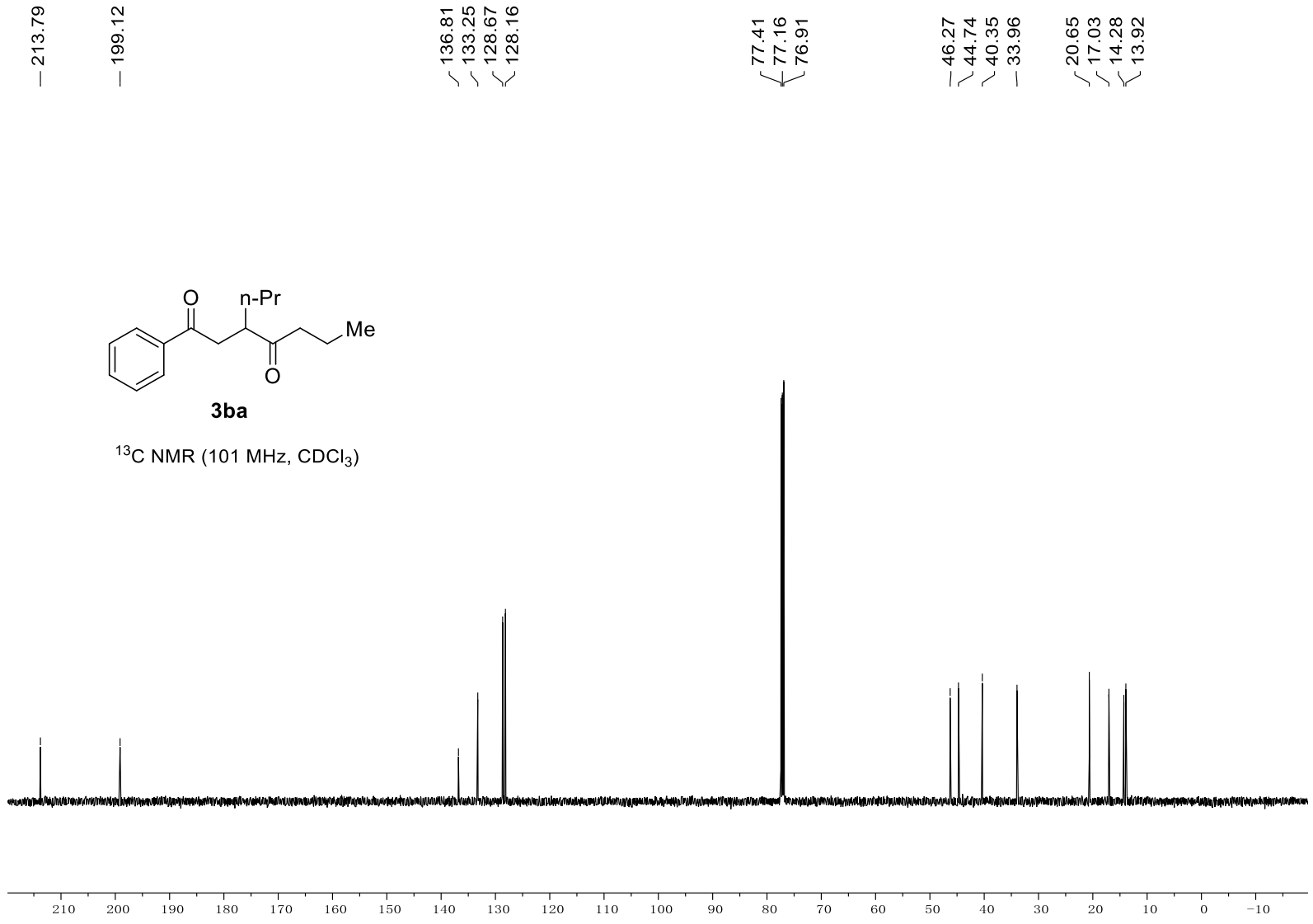

213.75
198.83
136.81
133.25
128.68
128.16
77.41
77.16
76.91
43.50
41.98
41.20
17.16
17.06
13.91
O
Me
Me
O
3aa
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



3ba

^{1}H NMR (400 MHz, $CDCl_3$)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199.12
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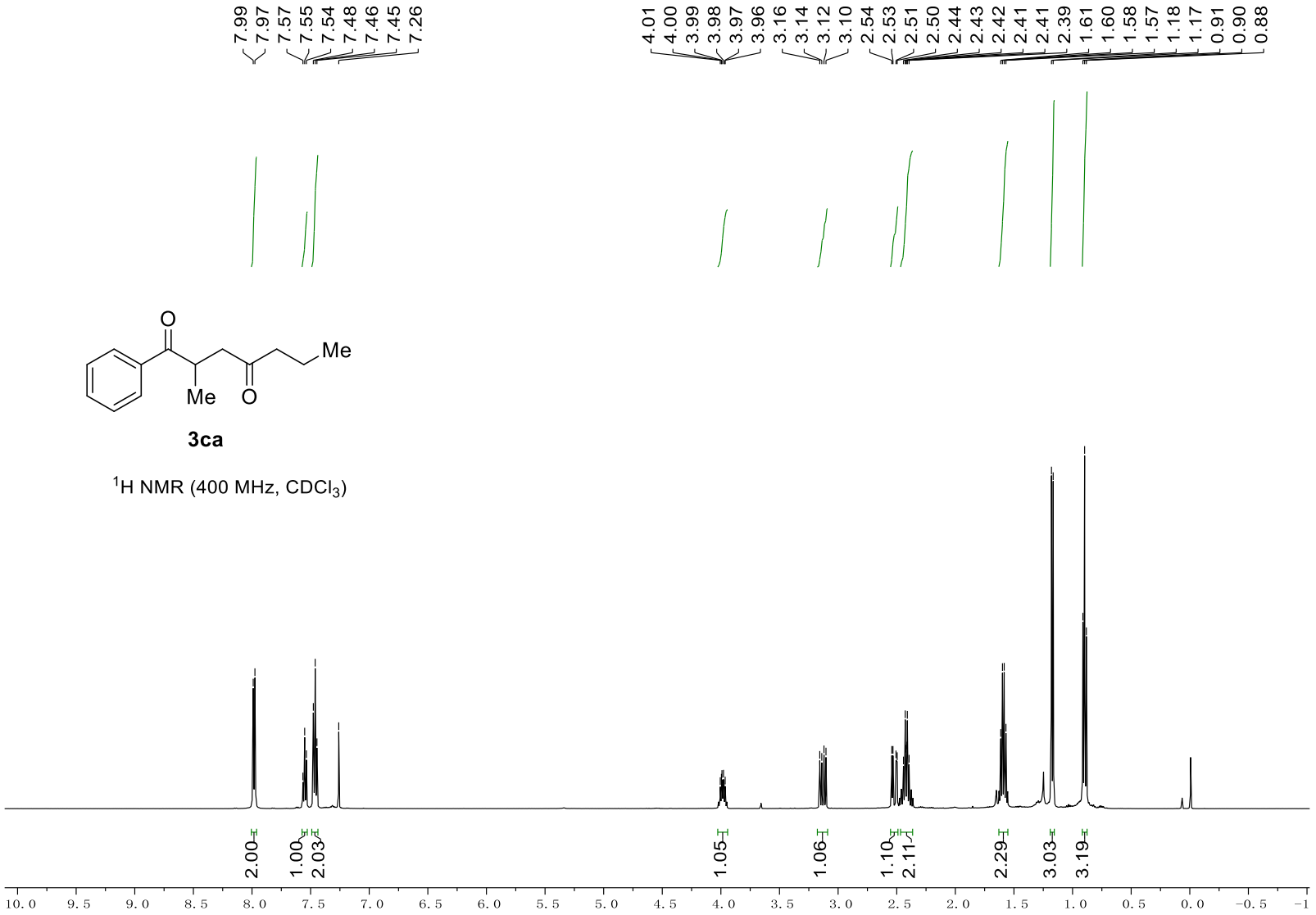
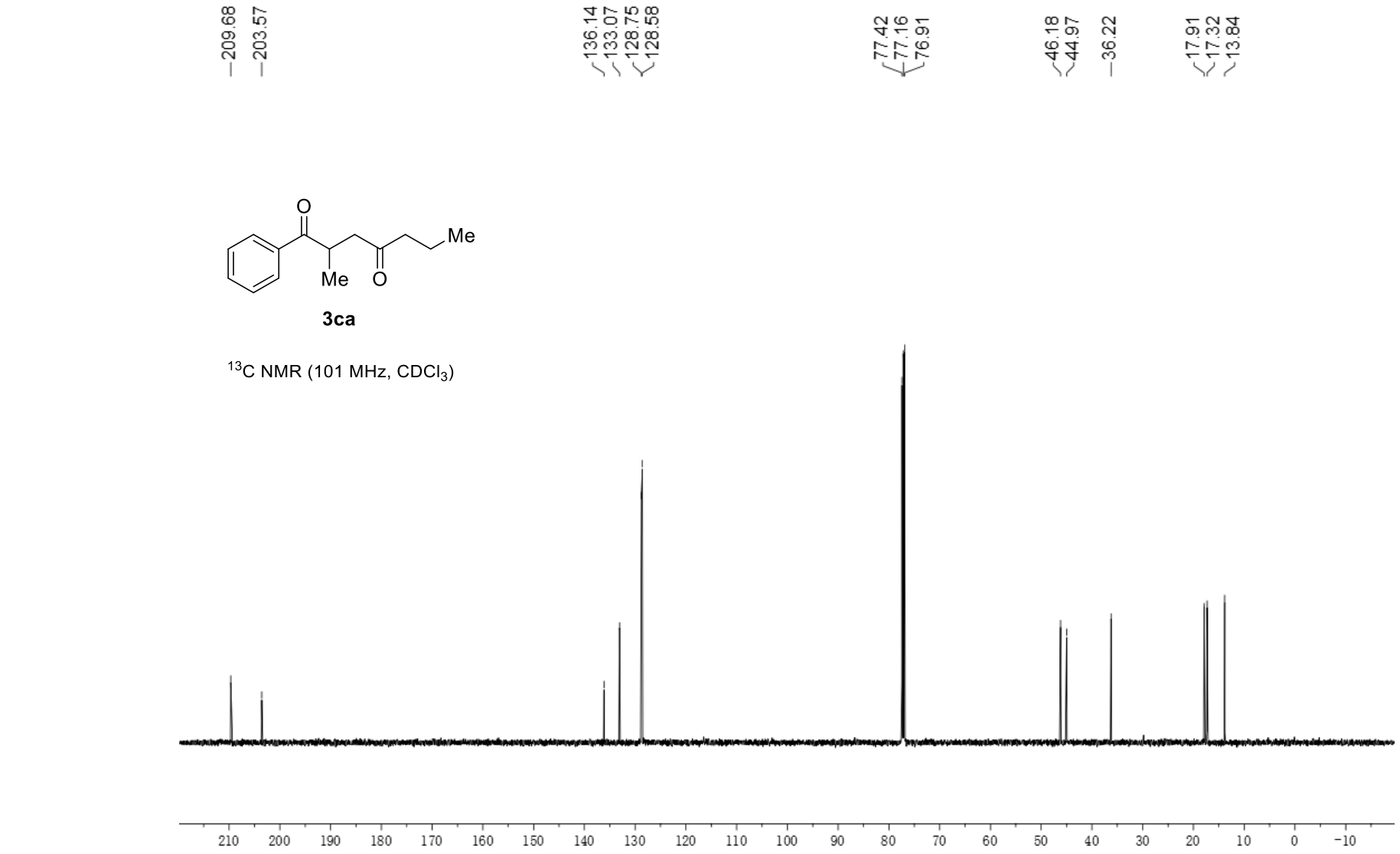
133.25
128.67
128.16
77.41
77.16
76.91
46.27
44.74
40.35
33.96
20.65
17.03
14.28
13.92
O
n-Pr
Me
O
3ba
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



3ca

^{1}H NMR (400 MHz, $CDCl_3$)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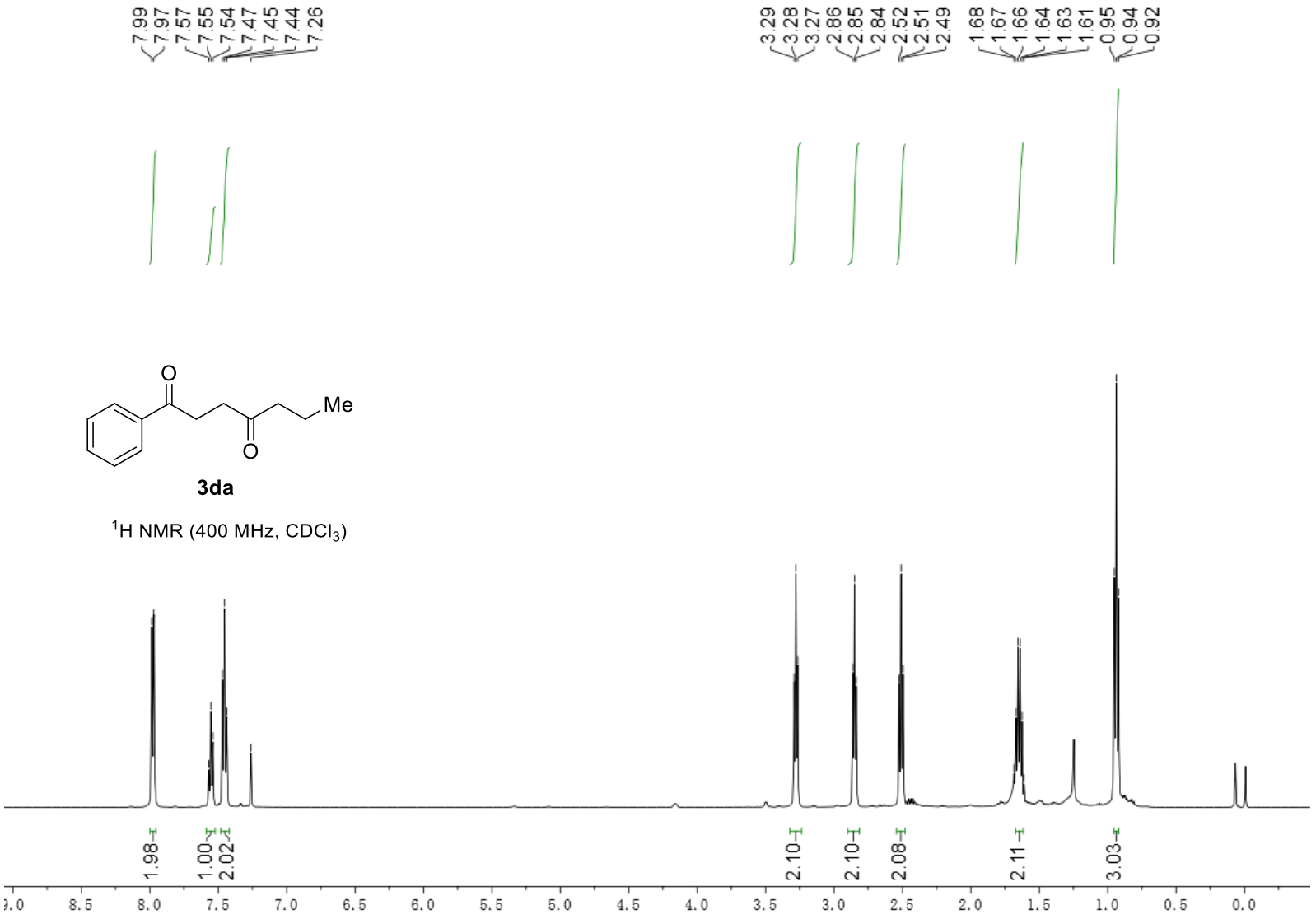
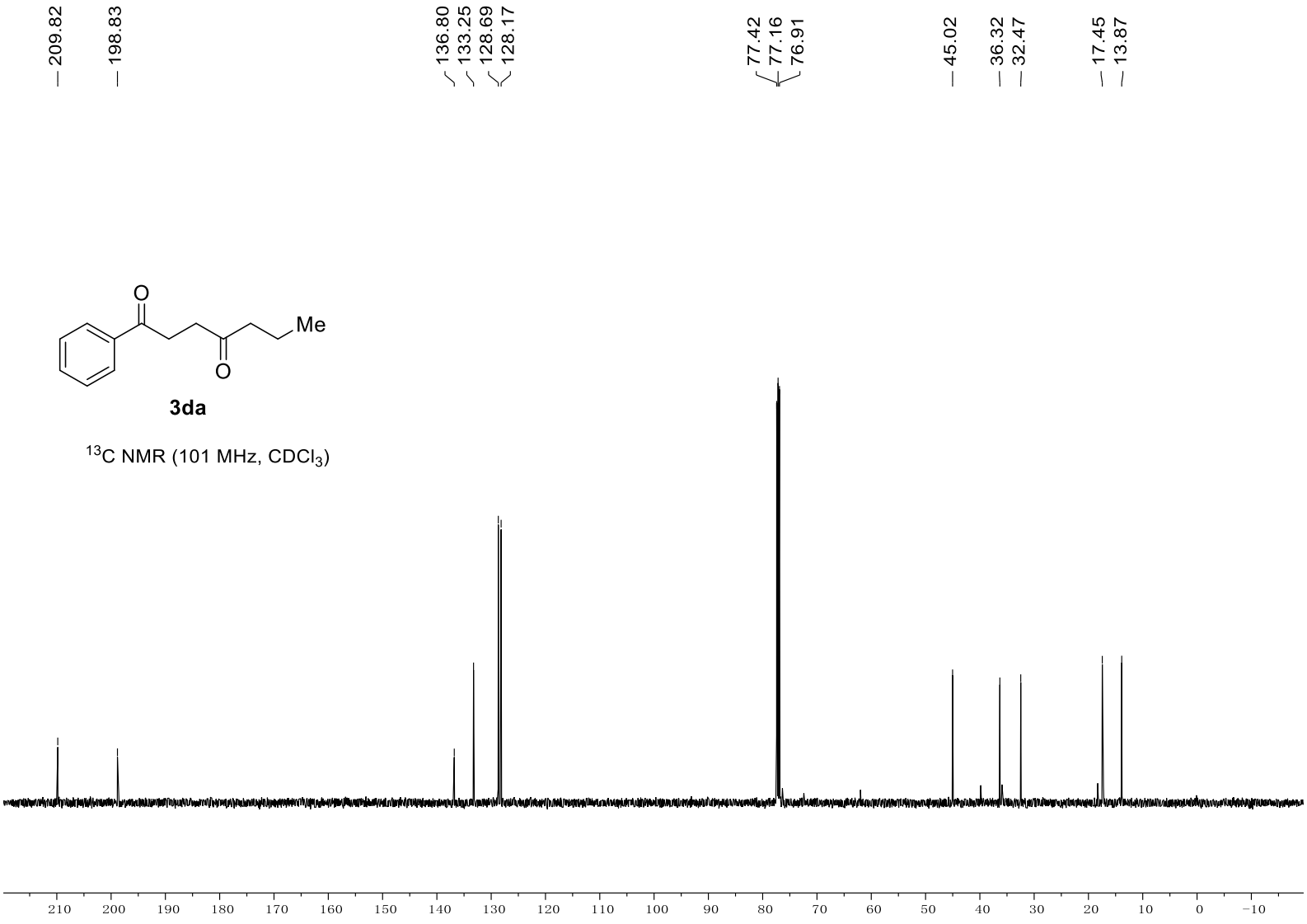
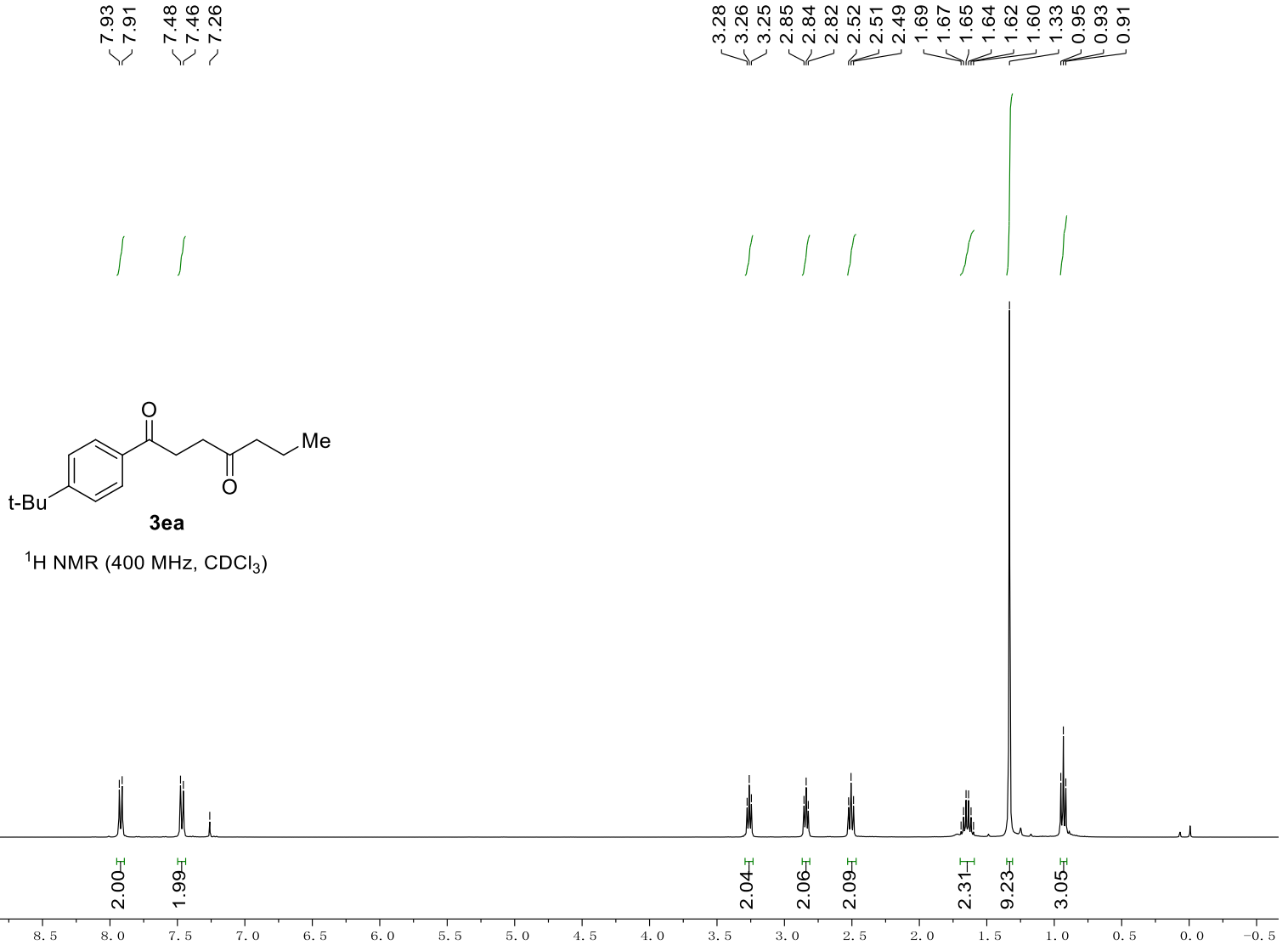
128.58
77.42
77.16
76.91
46.18
44.97
36.22
17.91
17.32
13.84
O
Me
Me
O
3ca
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



3da

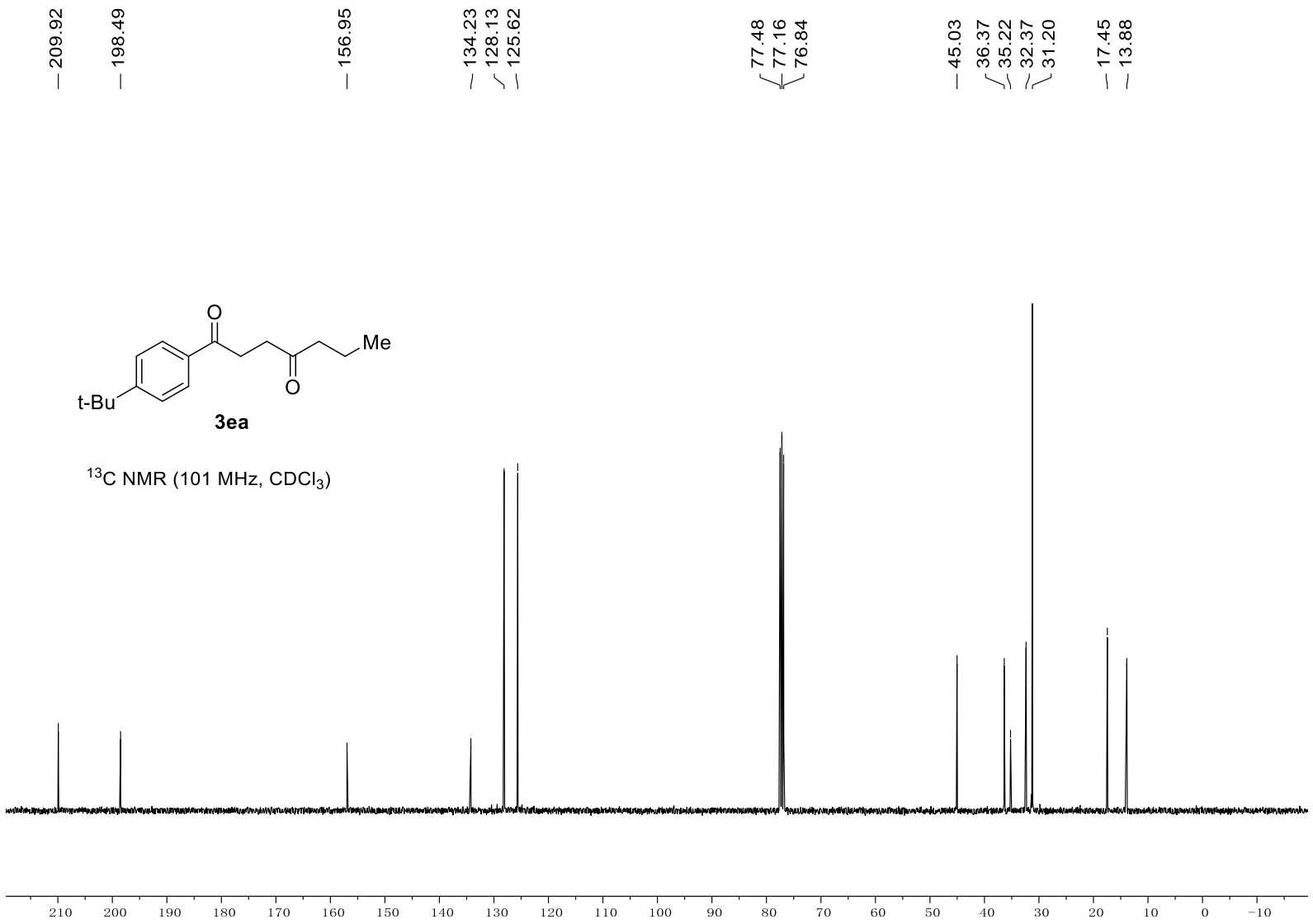
^{1}H NMR (400 MHz, $CDCl_3$)

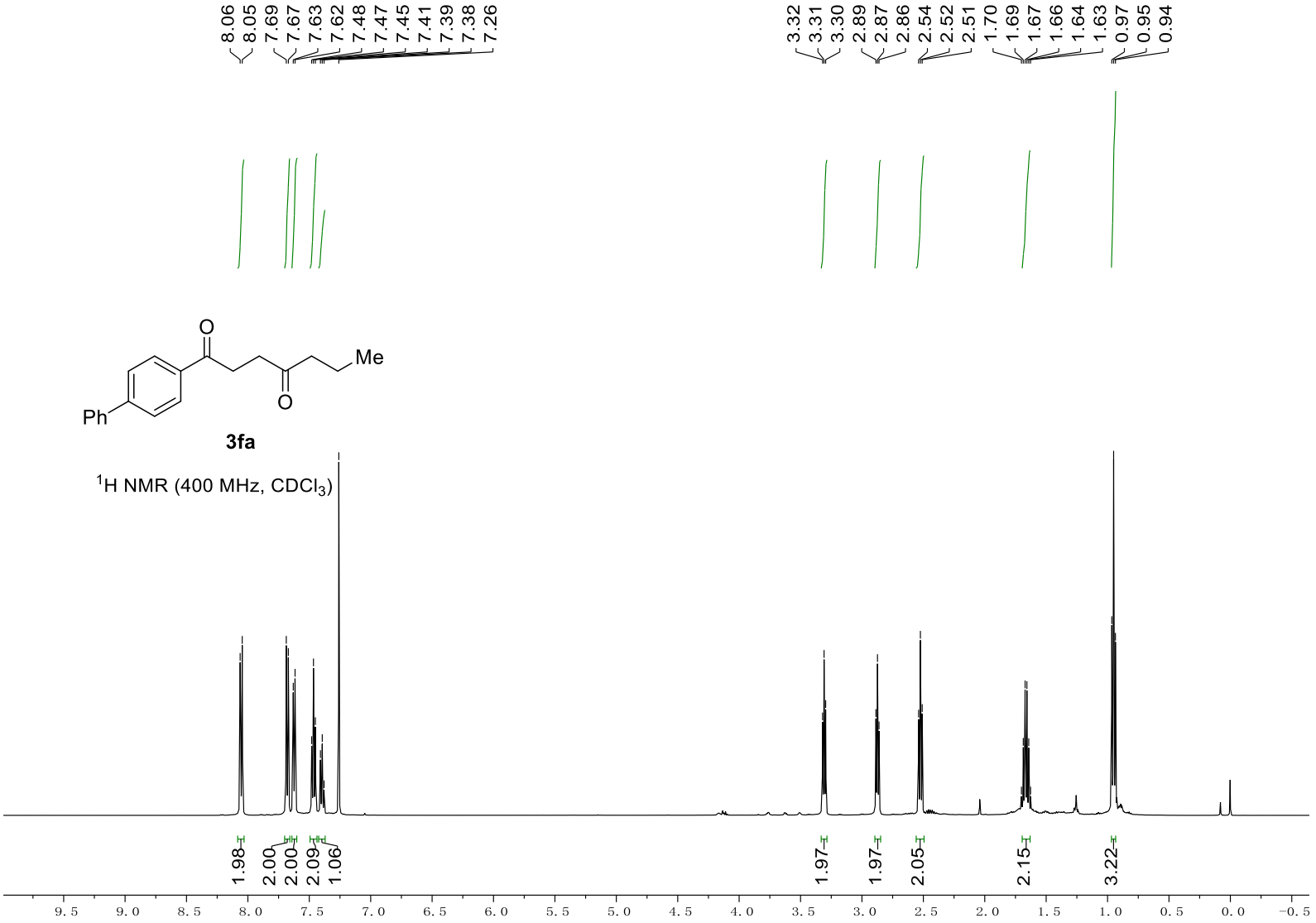

209.82
198.83
136.80
133.25
128.69
128.17
77.42
77.16
76.91
45.02
36.32
32.47
17.45
13.87
O
O
Me
3da
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

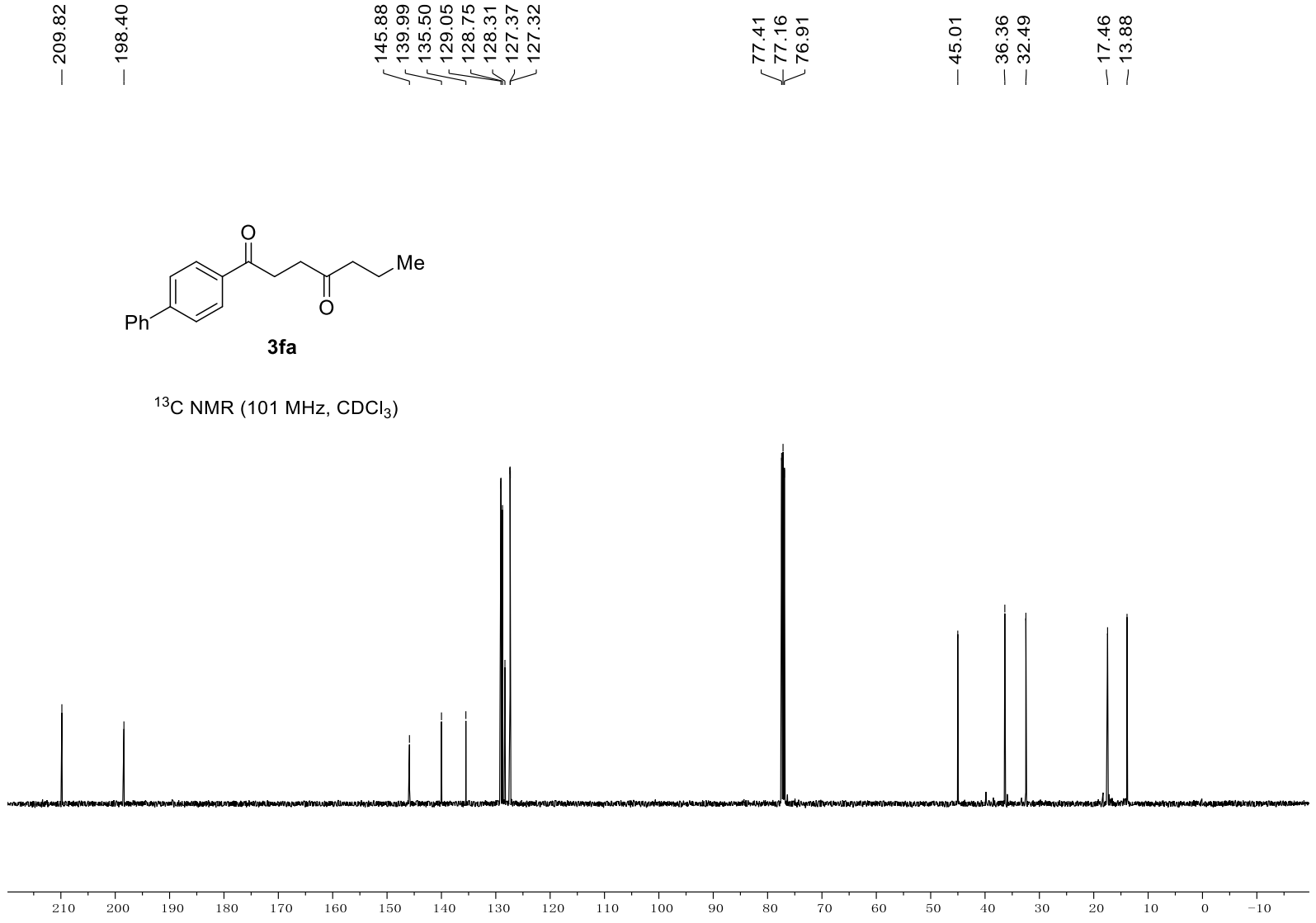


3ea

^{1}H NMR (400 MHz, $CDCl_3$)

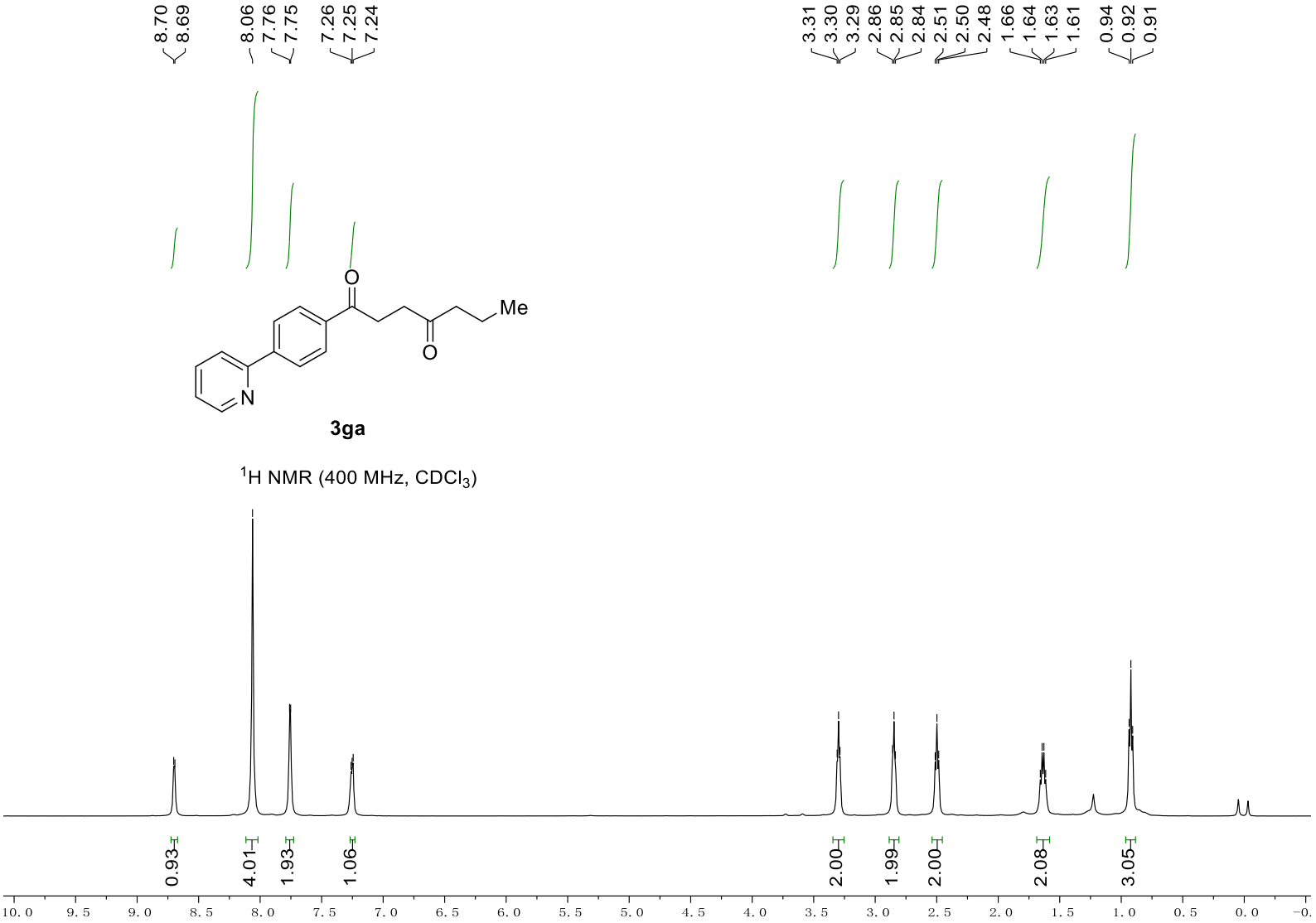

209.92
198.49
156.95
134.23
128.13
125.62
77.48
77.16
76.84
45.03
36.37
35.22
32.37
31.20
17.45
13.88
O
O
Me
t-Bu
3ea
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


8.06
8.05
7.69
7.67
7.63
7.62
7.48
7.47
7.45
7.41
7.39
7.38
7.26
3.32
3.31
3.30
2.89
2.87
2.86
2.54
2.52
2.51
1.70
1.69
1.67
1.66
1.64
1.63
0.97
0.95
0.94
O
Me
O
Ph
3fa
1H NMR (400 MHz, CDCl3)
1.98
2.00
2.00
2.09
1.06
1.97
1.97
2.05
2.15
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5



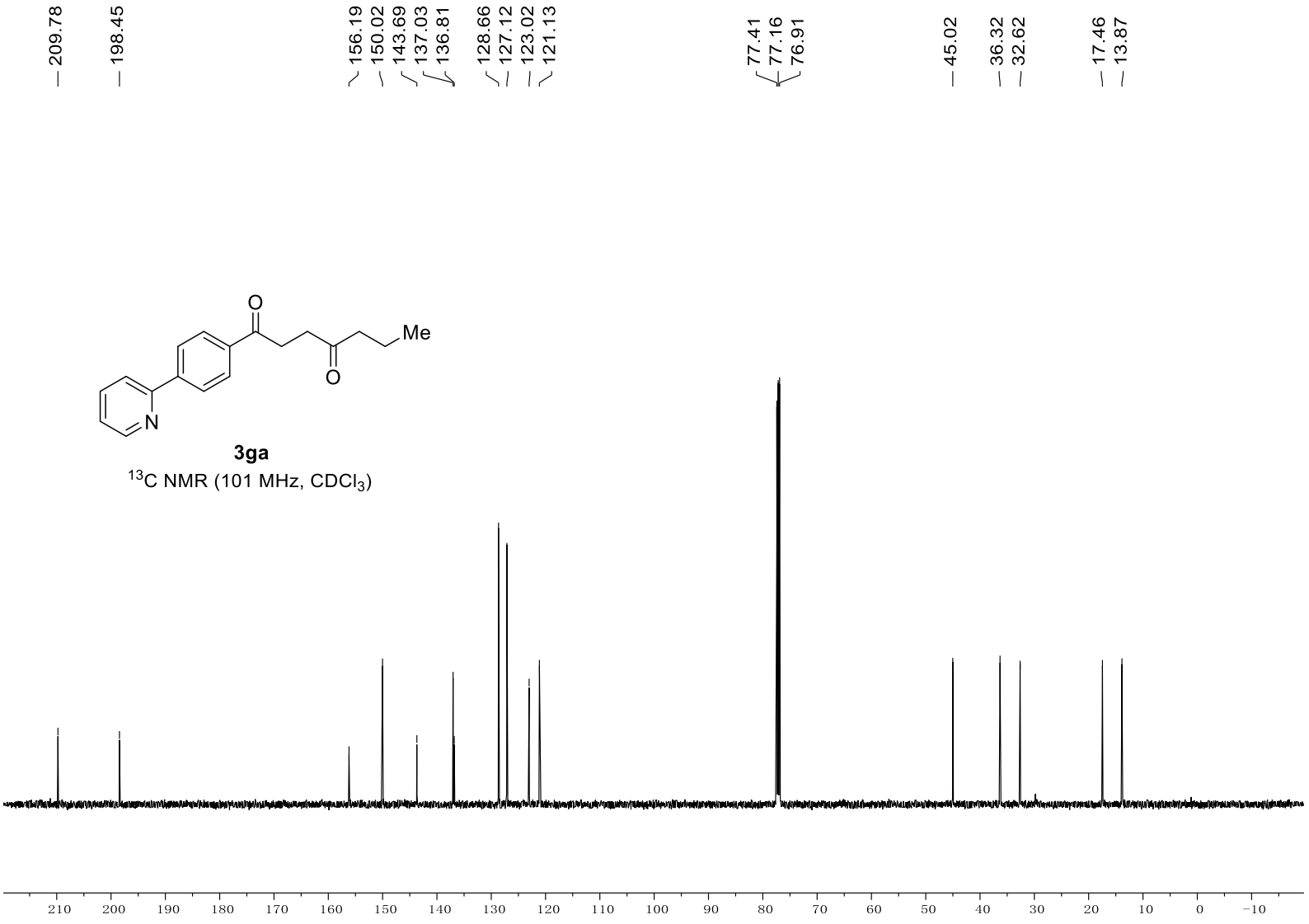
3fa

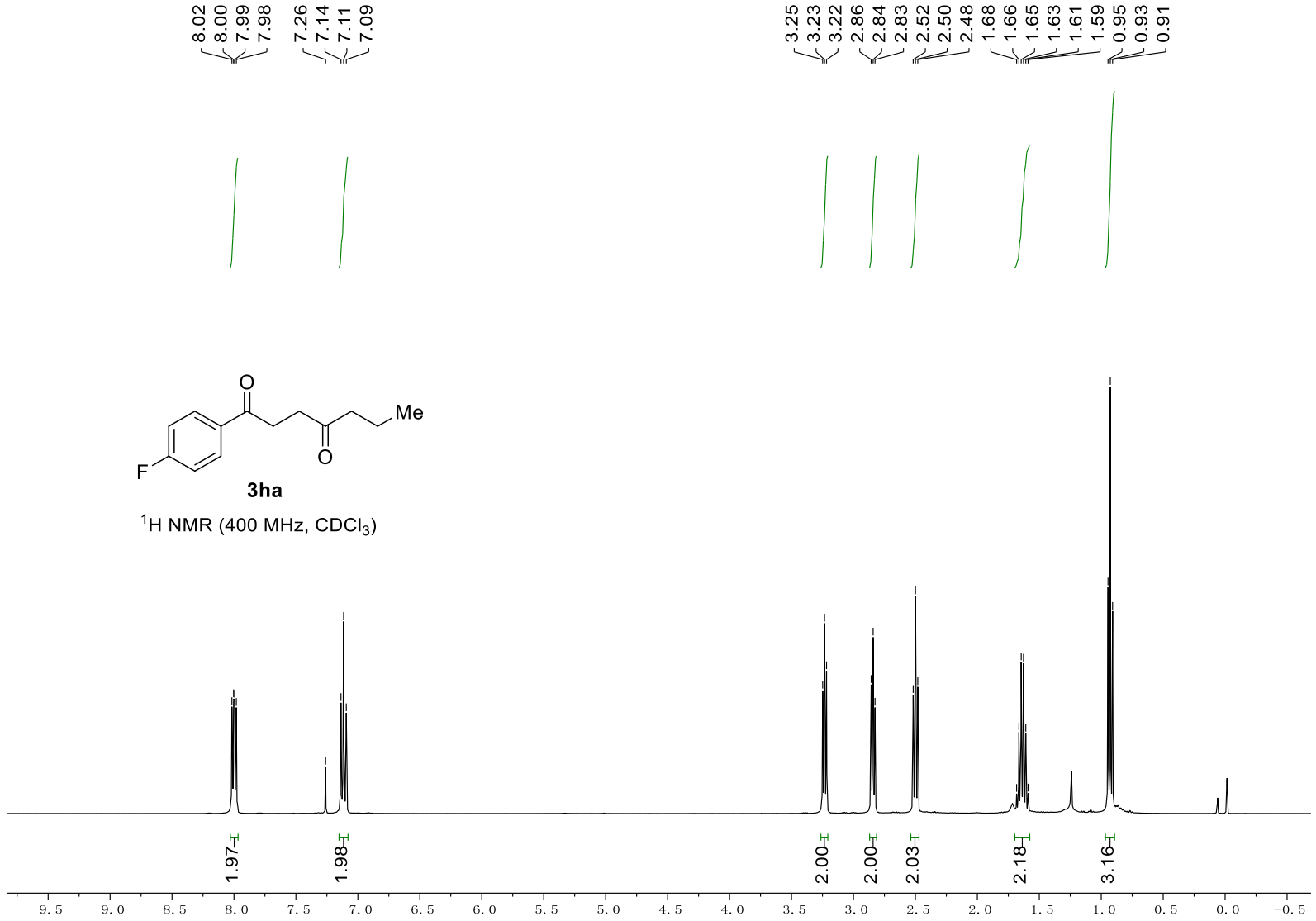
^{13}C NMR (101 MHz, $CDCl_3$)



3ga

^{1}H NMR (400 MHz, $CDCl_3$)

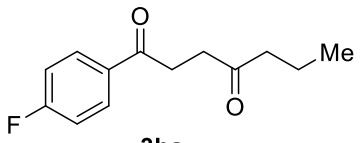

209.78
198.45
156.19
150.02
143.69
137.03
136.81
128.66
127.12
123.02
121.13
77.41
77.16
76.91
45.02
36.32
32.62
17.46
13.87
O
O
Me
N
3ga
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



3ha

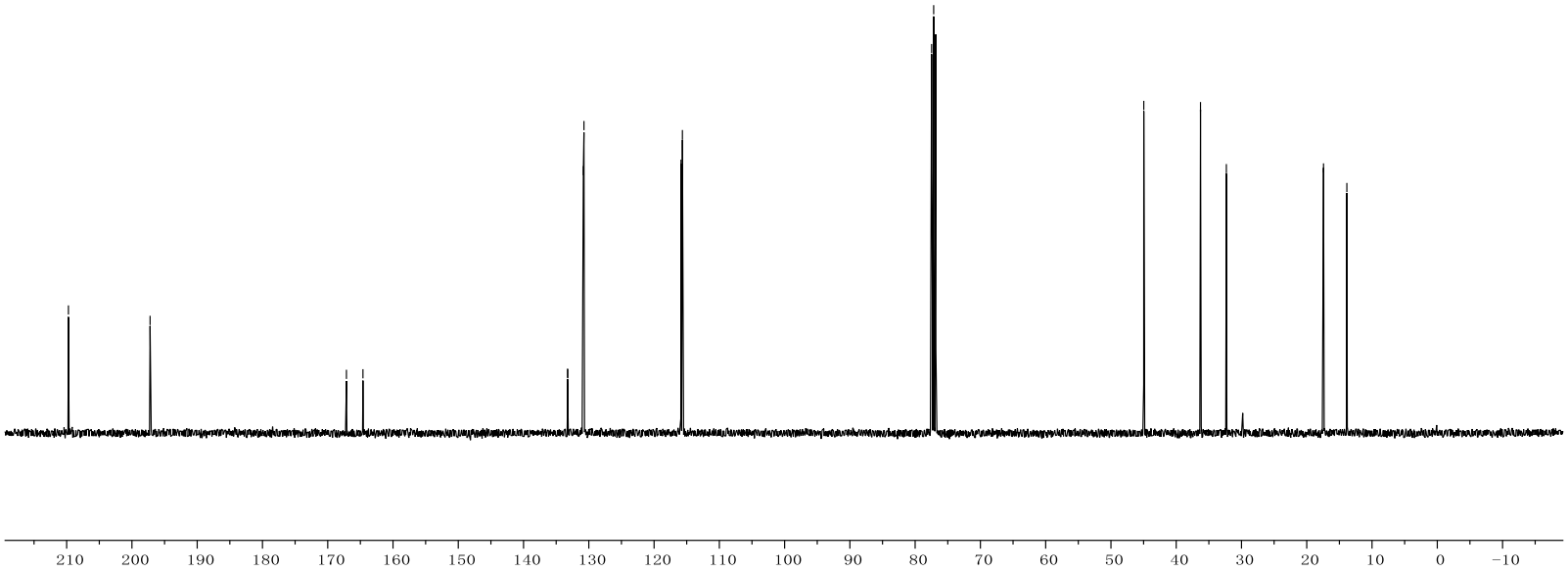
^{1}H NMR (400 MHz, $CDCl_3$)

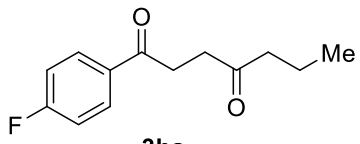
209.73
197.22
167.13
164.60
133.25
133.22
130.84
130.74
115.88
115.66
77.48
77.16
76.84
44.97
36.28
32.32
17.43
13.86



3ha

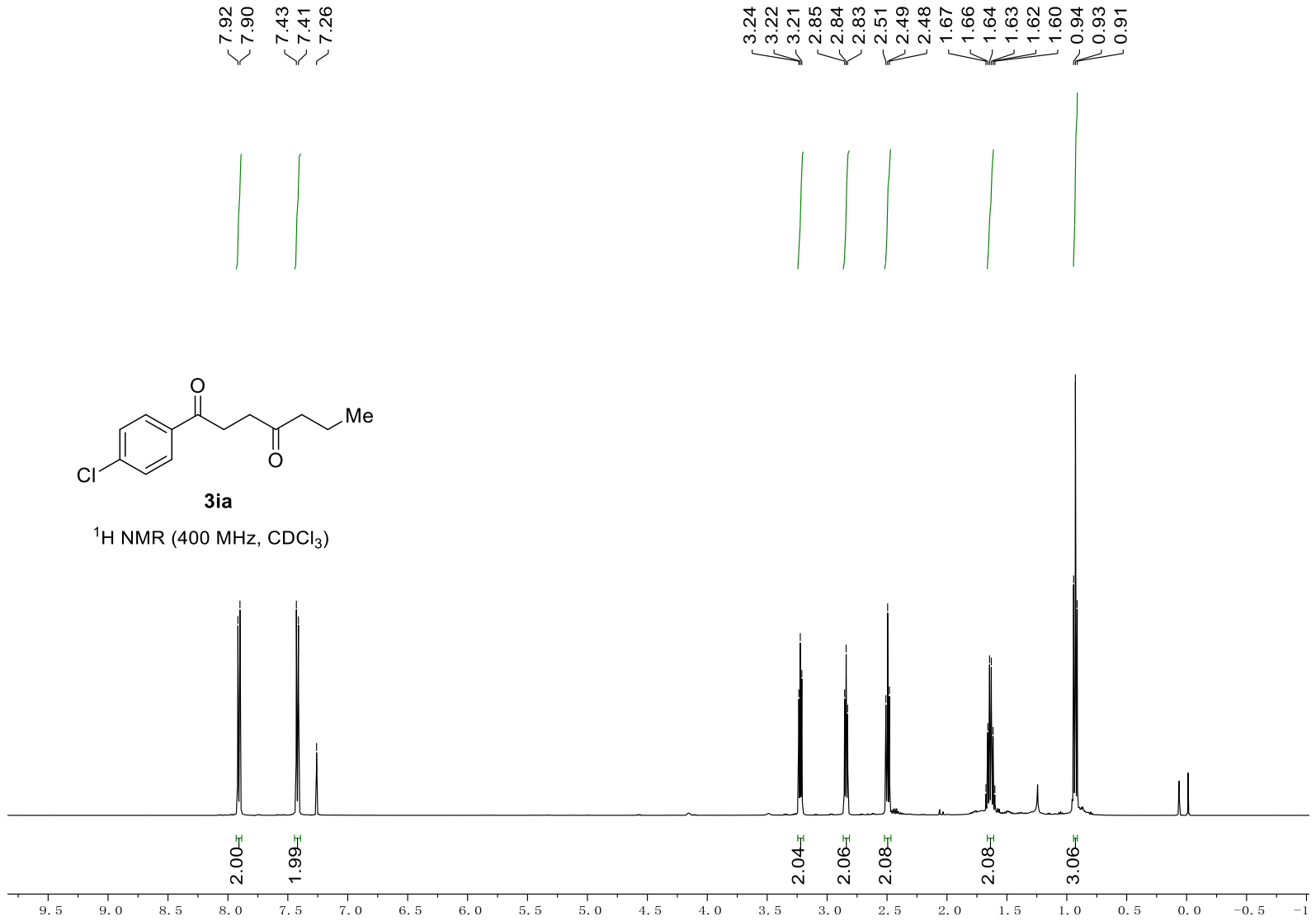
^{13}C NMR (101 MHz, $CDCl_3$)





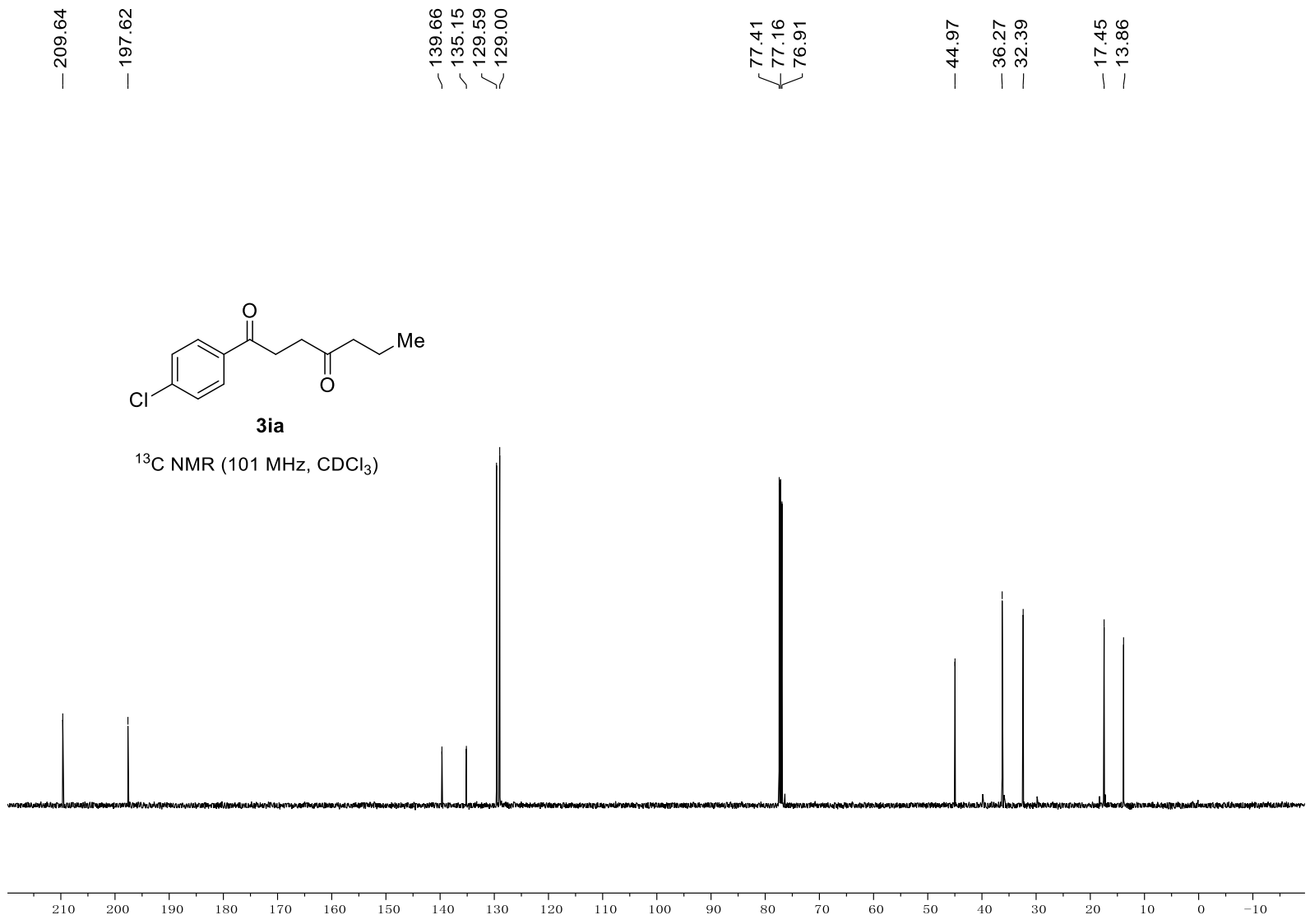
3ha

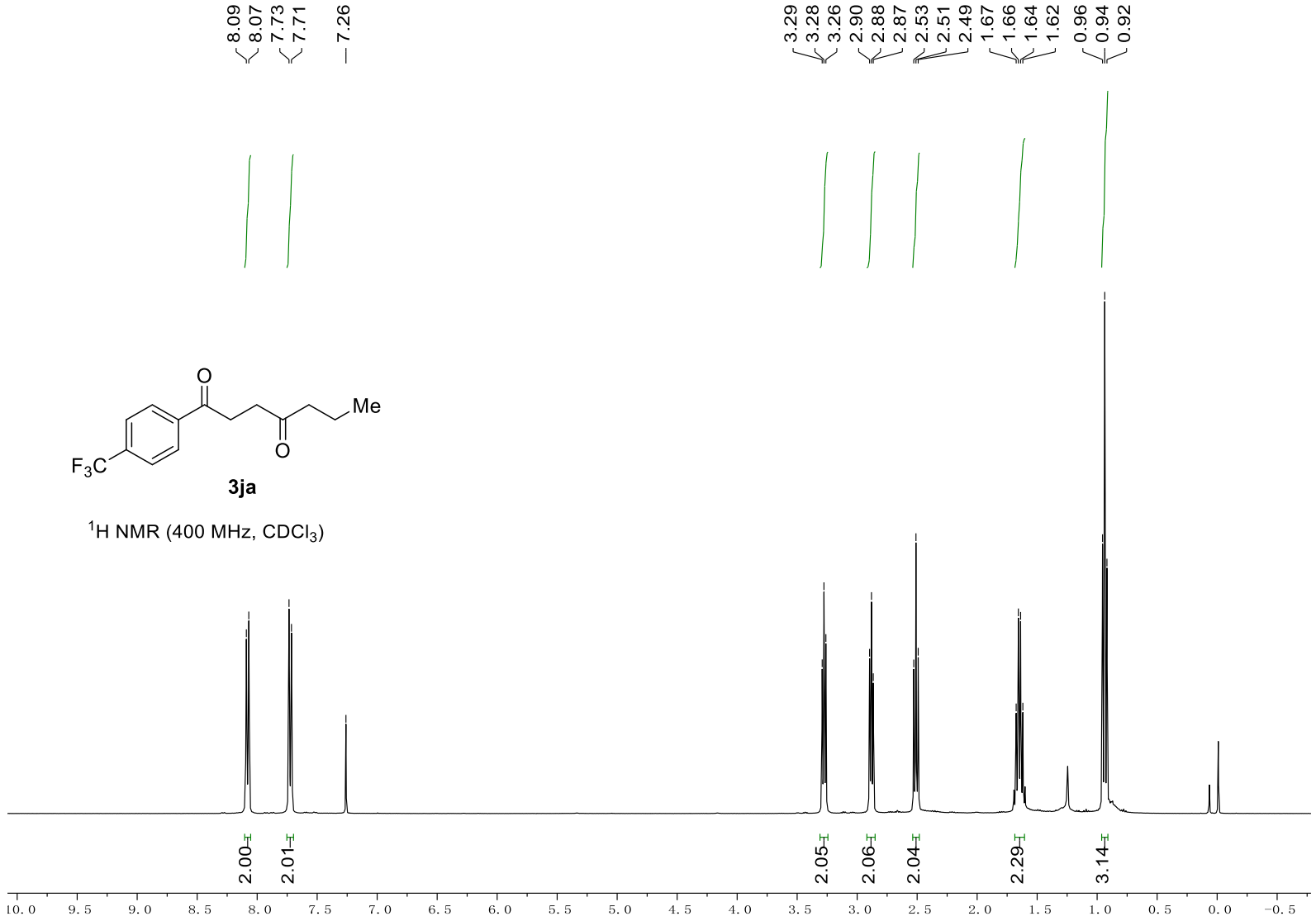
^{19}FNMR (376 MHz, $CDCl_3$)

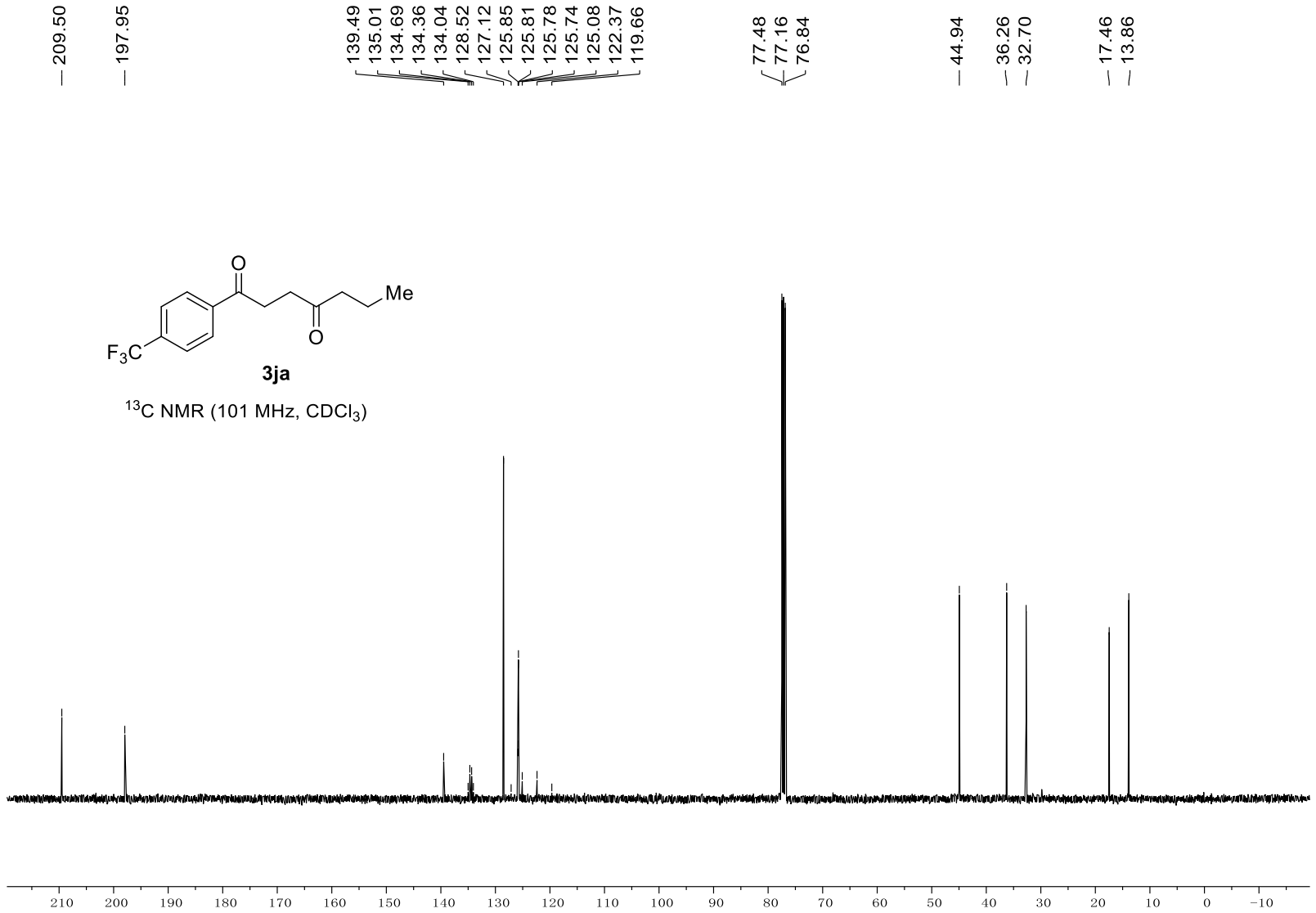


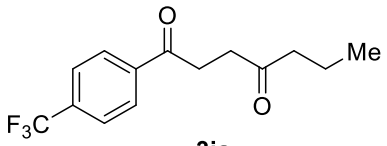
3ia

^{1}H NMR (400 MHz, $CDCl_3$)


209.64
197.62
139.66
135.15
129.59
129.00
77.41
77.16
76.91
44.97
36.27
32.39
17.45
13.86
O
O
Me
Cl
3ia
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

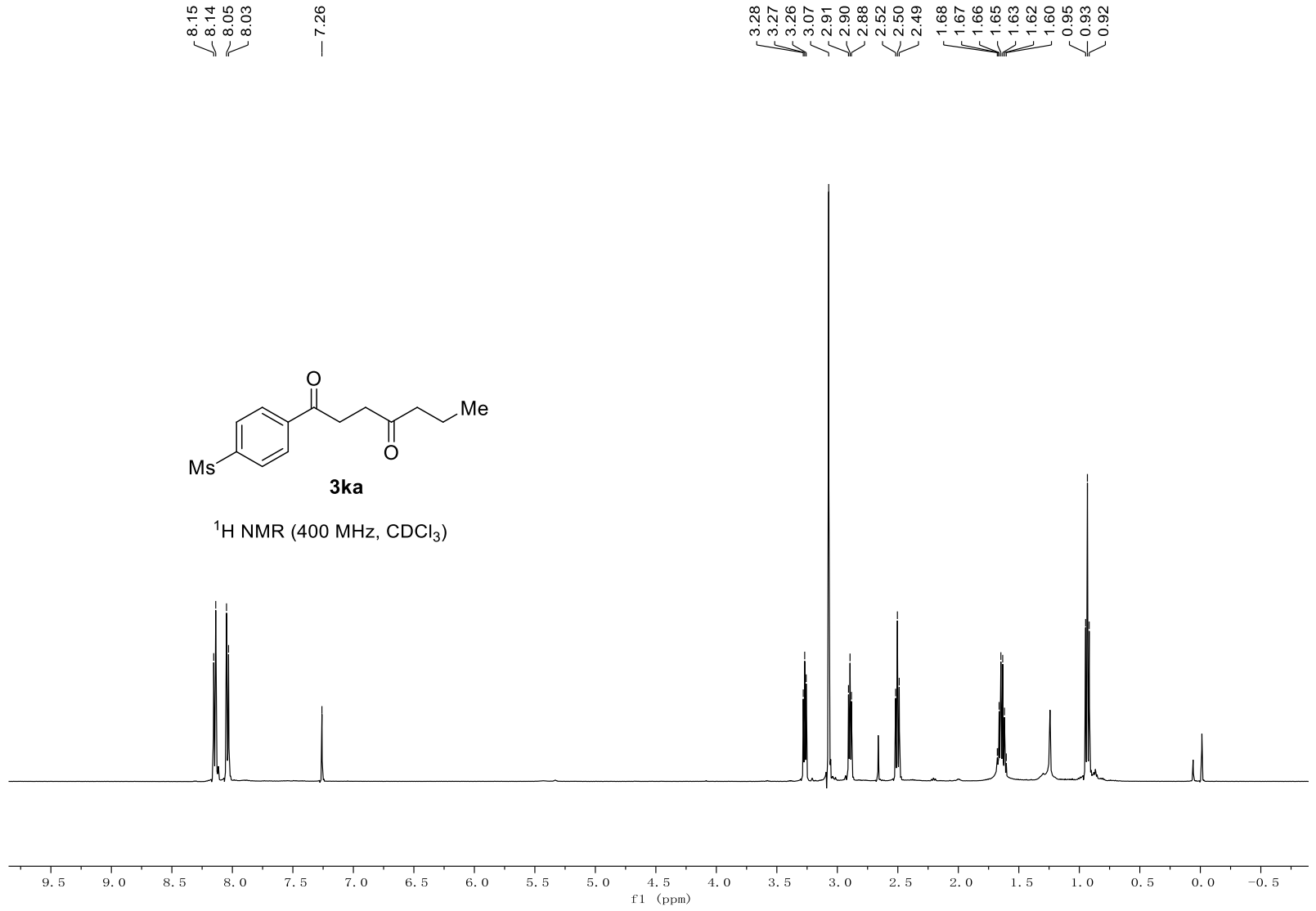

8.09
8.07
7.73
7.71
7.26
3.29
3.28
3.26
2.90
2.88
2.87
2.53
2.51
2.49
1.67
1.66
1.64
1.62
0.96
0.94
0.92
O
Me
O
F3C
3ja
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.05
2.06
2.04
2.29
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5

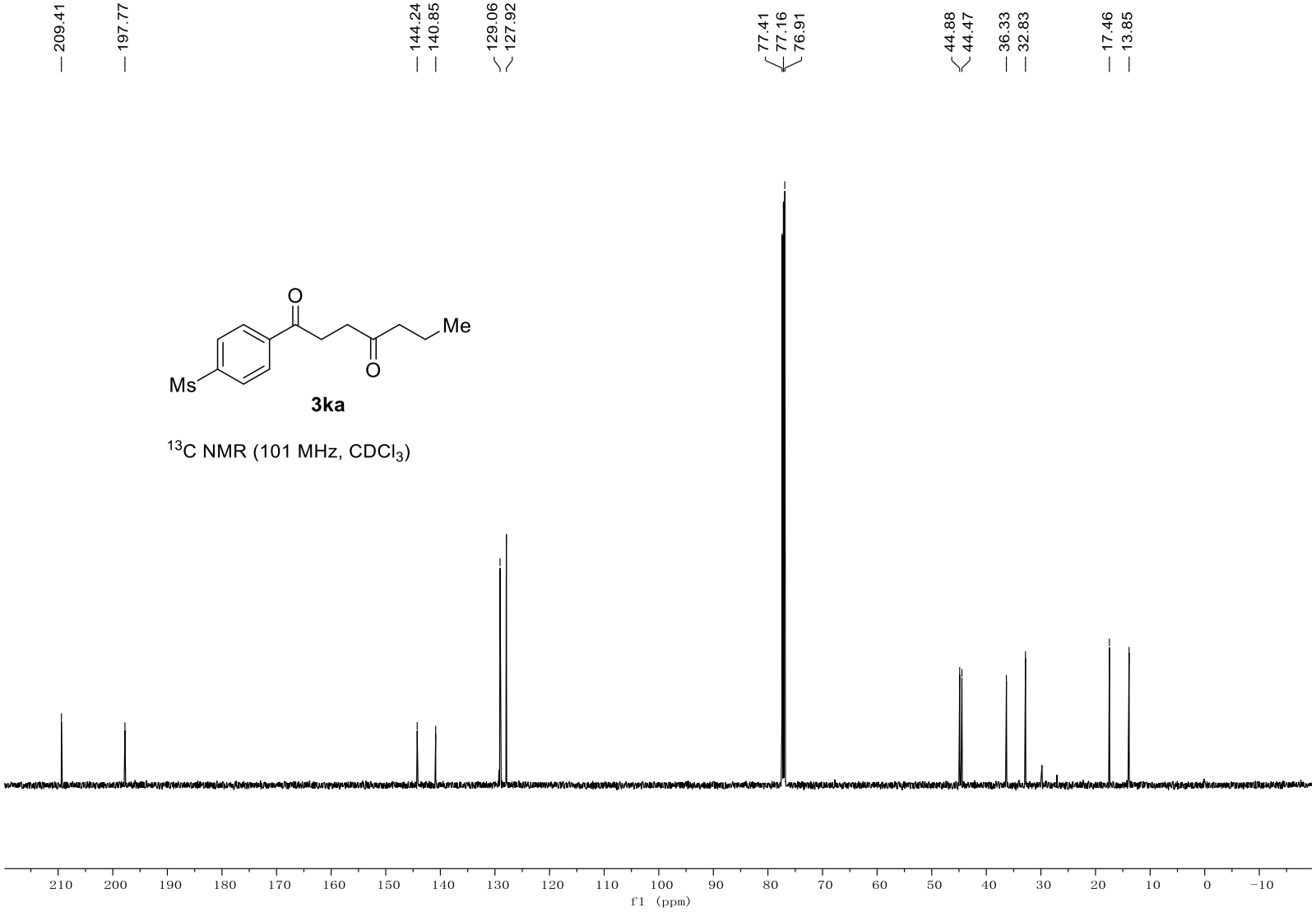

209.50
197.95
139.49
135.01
134.69
134.36
134.04
128.52
127.12
125.85
125.81
125.78
125.74
125.08
122.37
119.66
77.48
77.16
76.84
44.94
36.26
32.70
17.46
13.86
O
O
Me
F3C
3ja
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

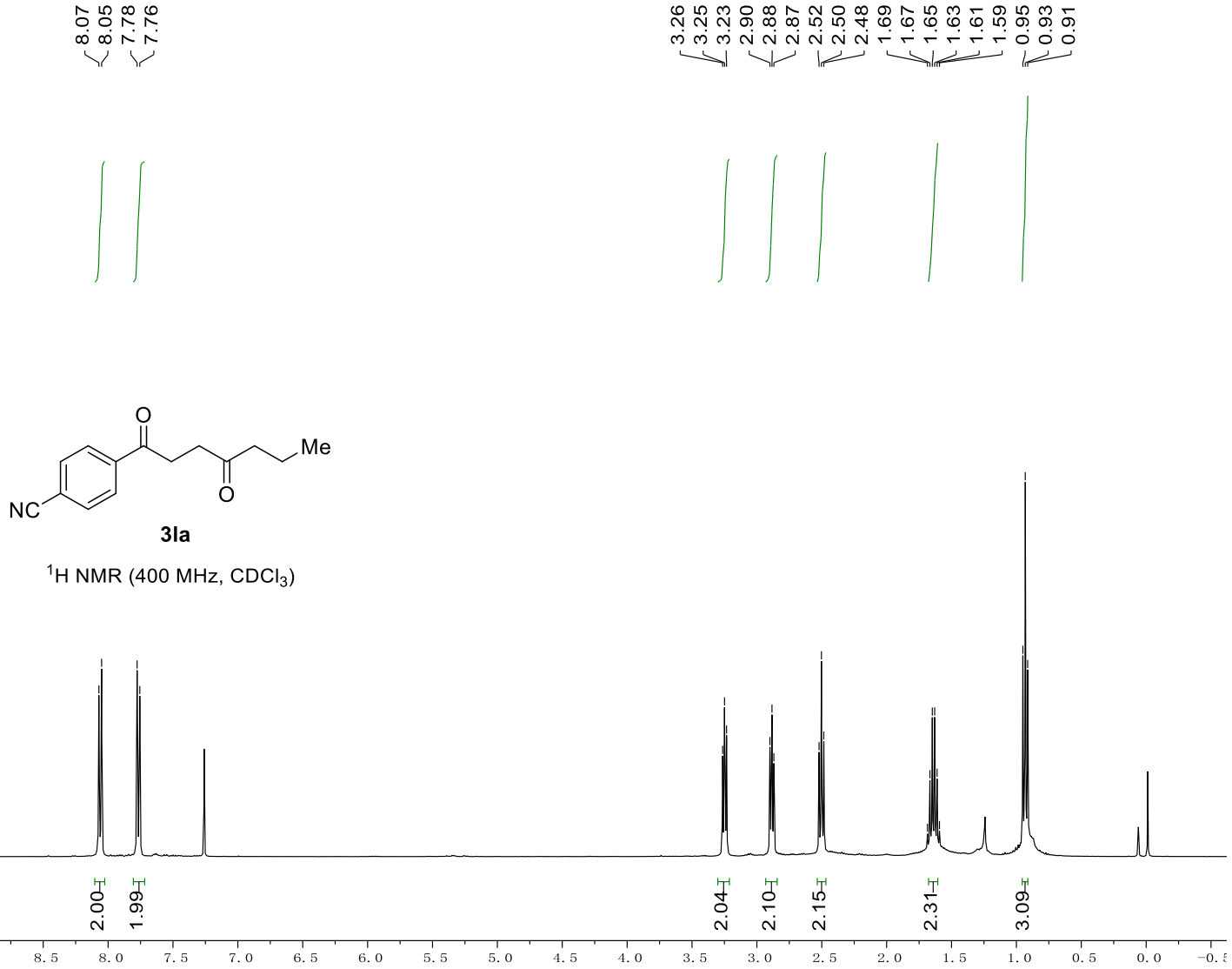


3ja

^{19}FNMR (376 MHz, $CDCl_3$)

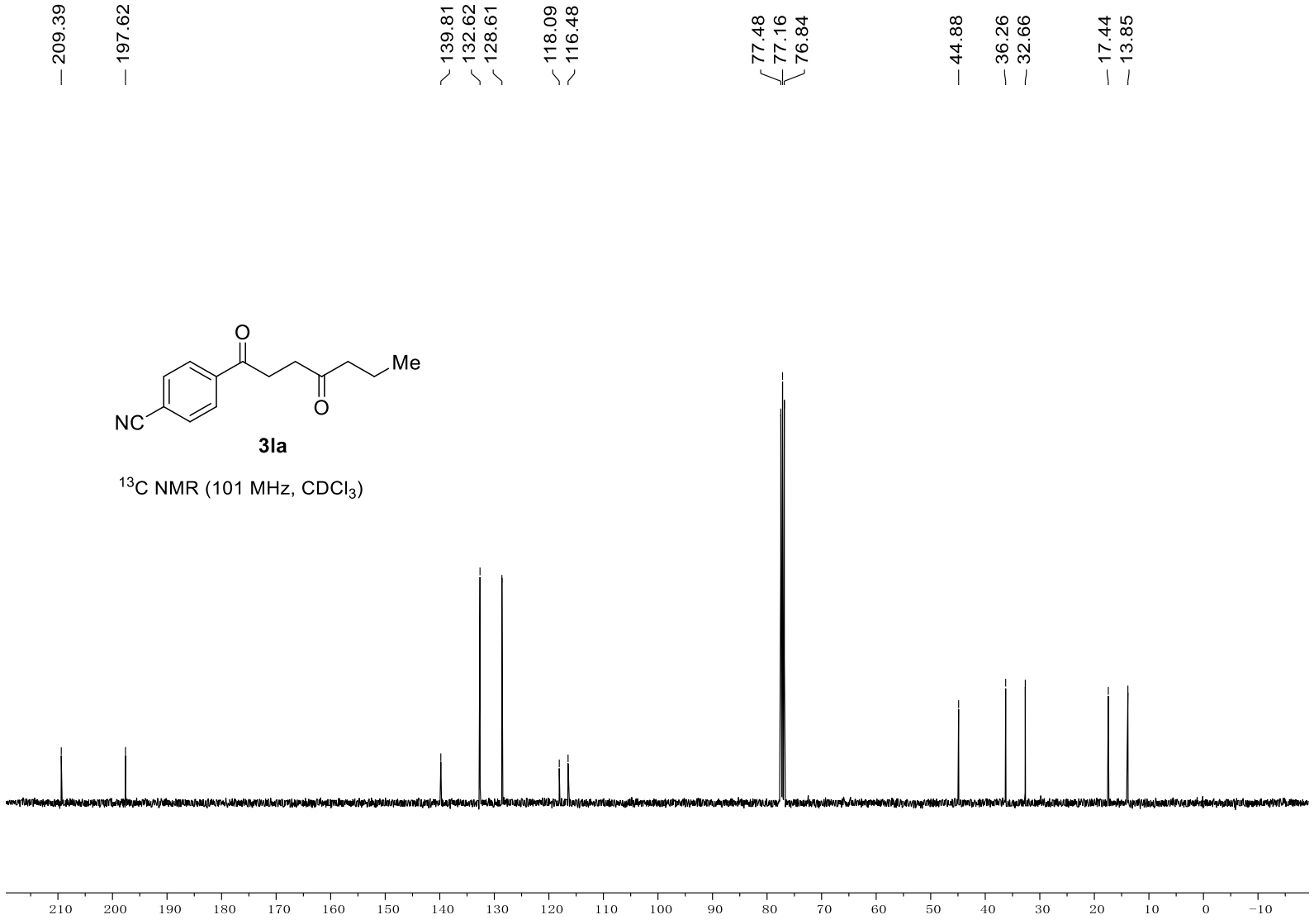

8.15
8.14
8.05
8.03
7.26
3.28
3.27
3.26
3.07
2.91
2.90
2.88
2.52
2.50
2.49
1.68
1.67
1.66
1.65
1.63
1.62
1.60
0.95
0.93
0.92
O
O
Me
Ms
3ka
^{1}H NMR (400 MHz, $CDCl_3$)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

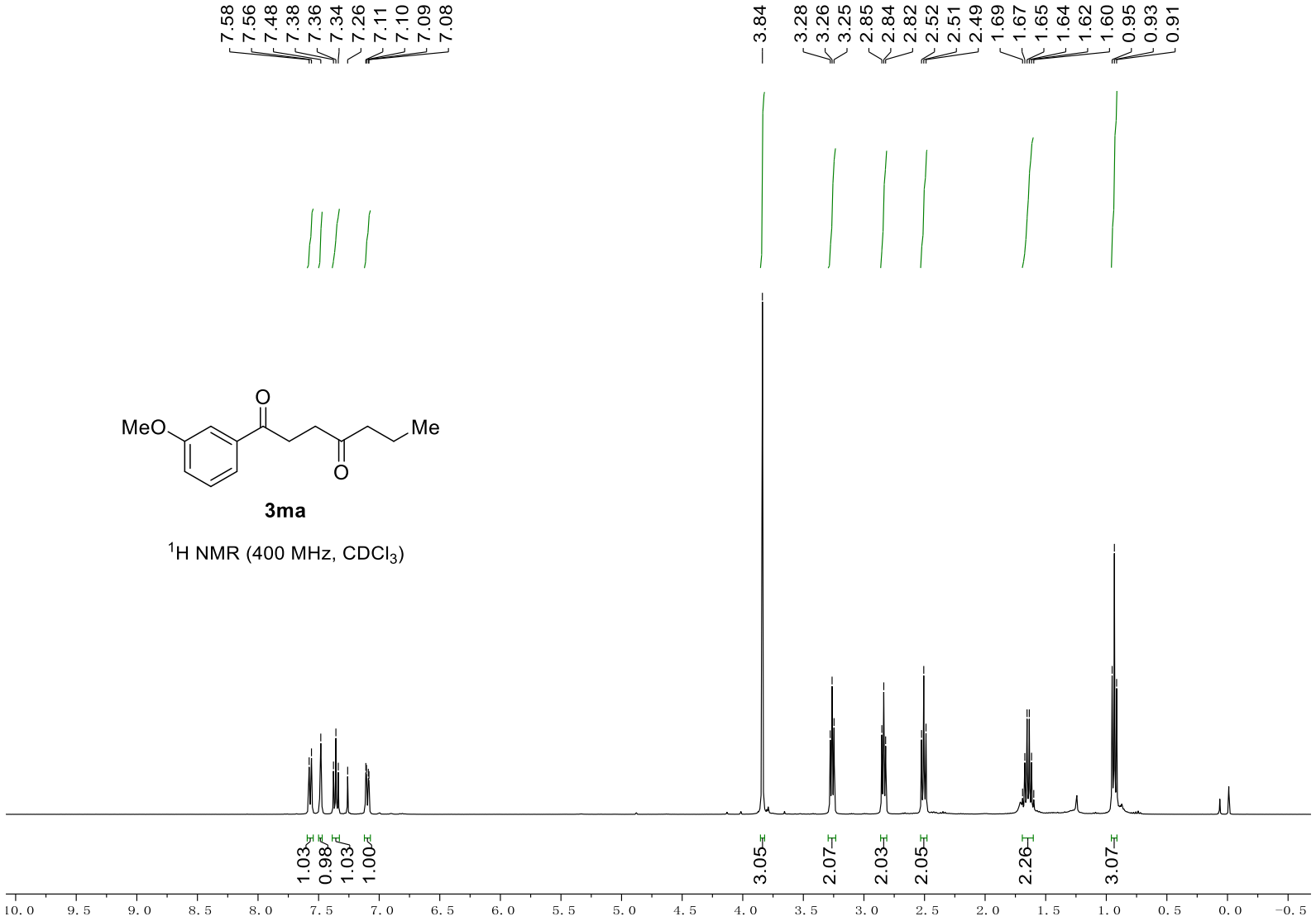

209.41
197.77
144.24
140.85
129.06
127.92
77.41
77.16
76.91
44.88
44.47
36.33
32.83
17.46
13.85
O
O
Me
Ms
3ka
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



3Ia

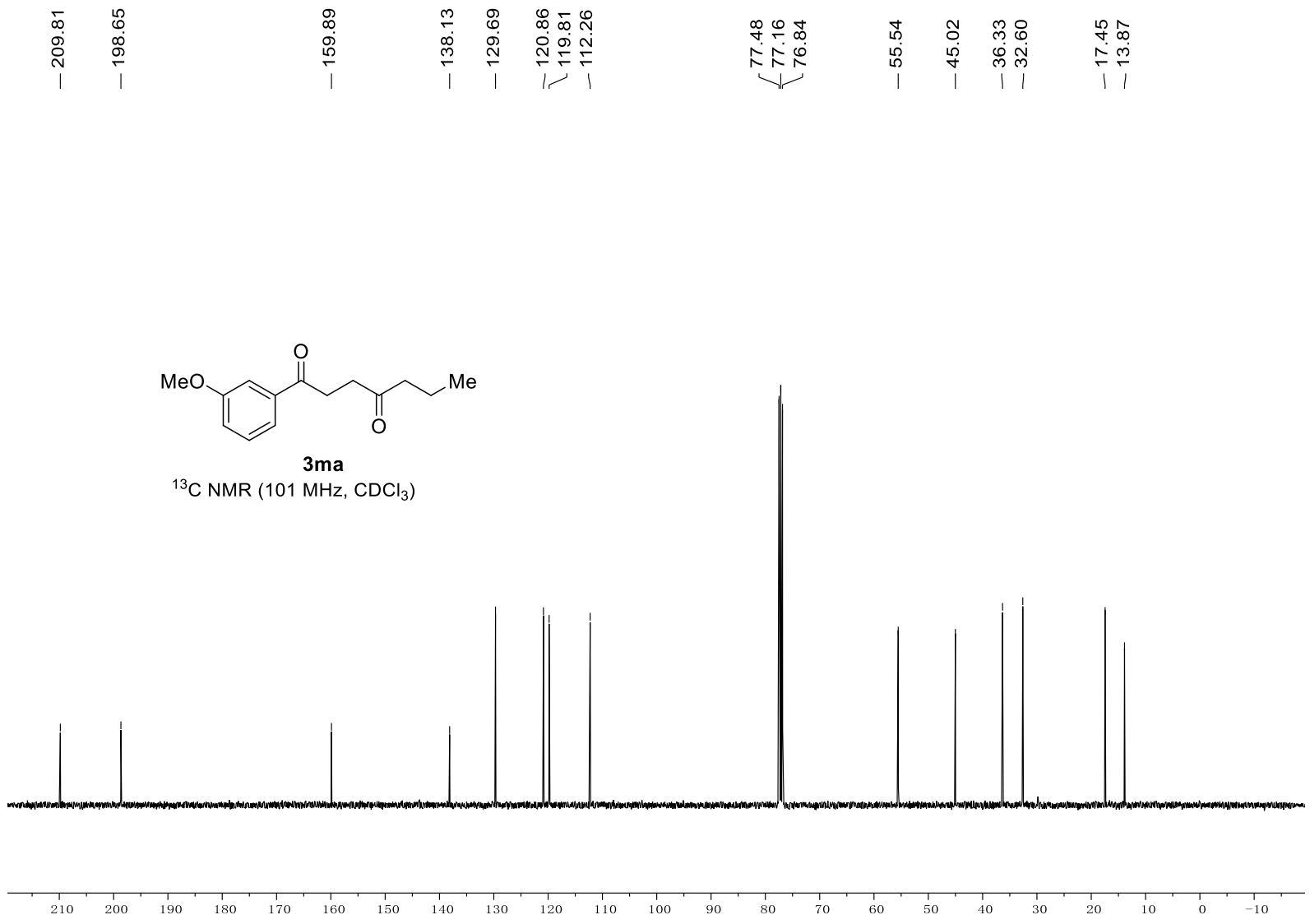
^{1}H NMR (400 MHz, $CDCl_3$)

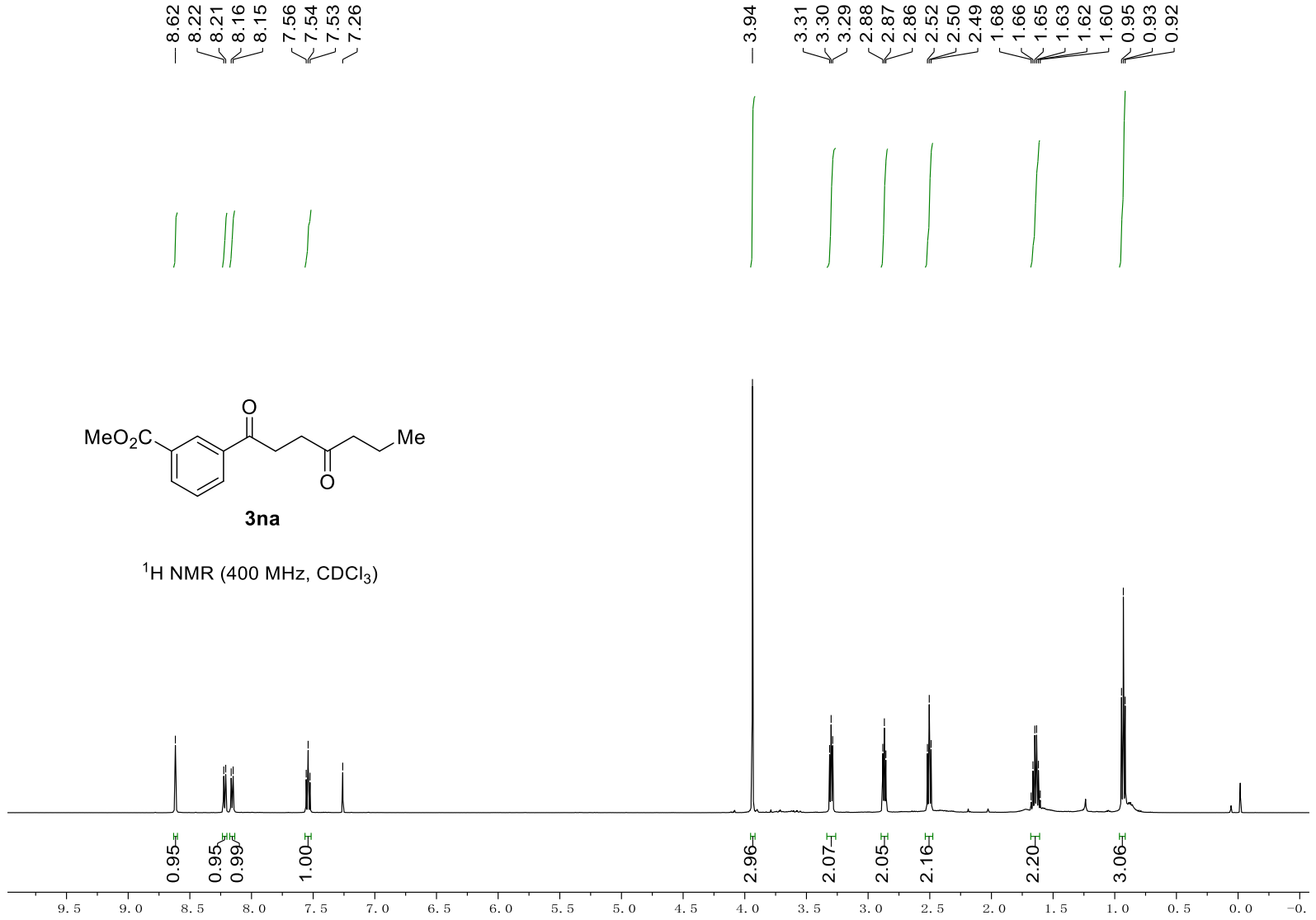

209.39
197.62
139.81
132.62
128.61
118.09
116.48
77.48
77.16
76.84
44.88
36.26
32.66
17.44
13.85
O
Me
O
NC
3la
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

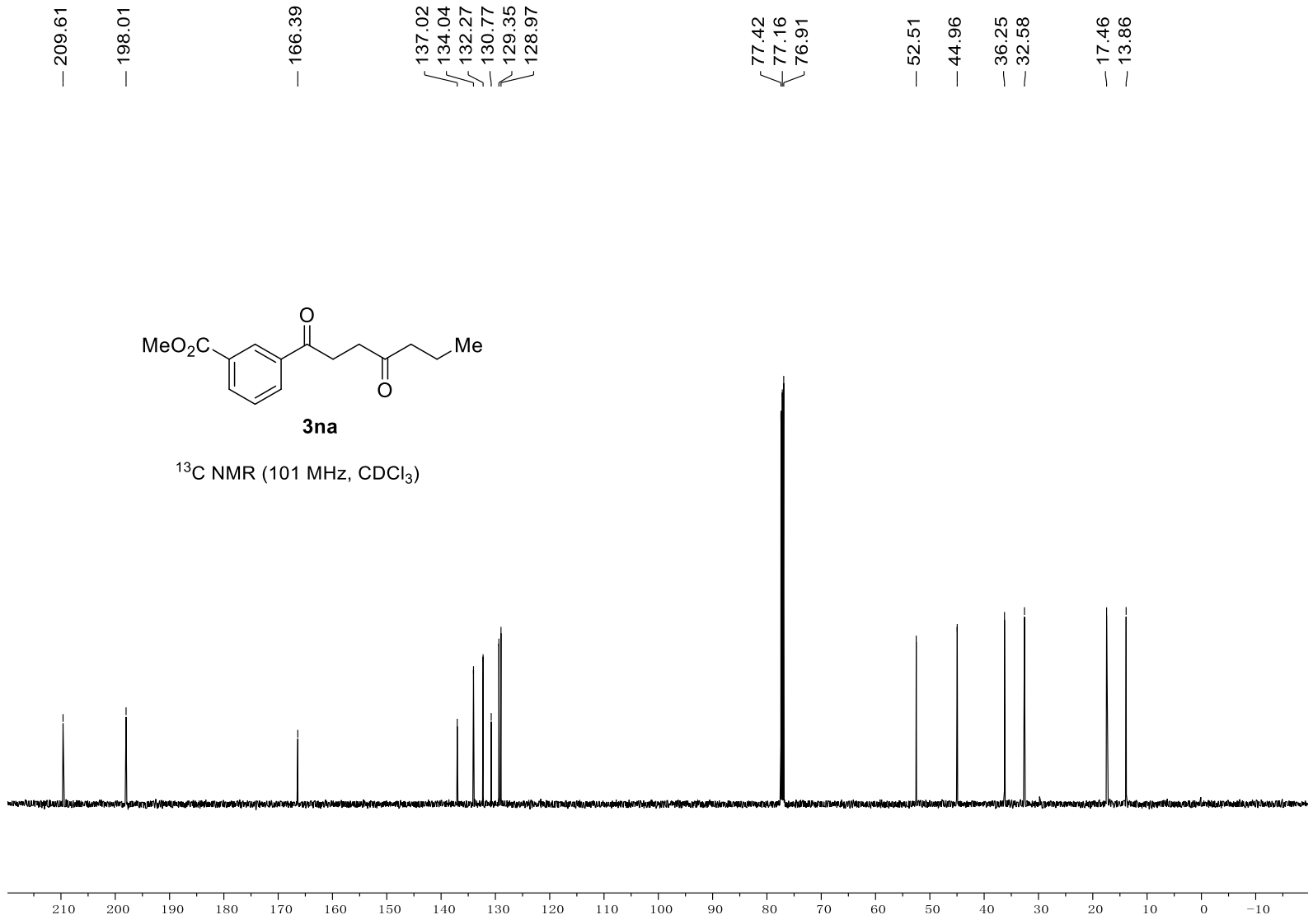


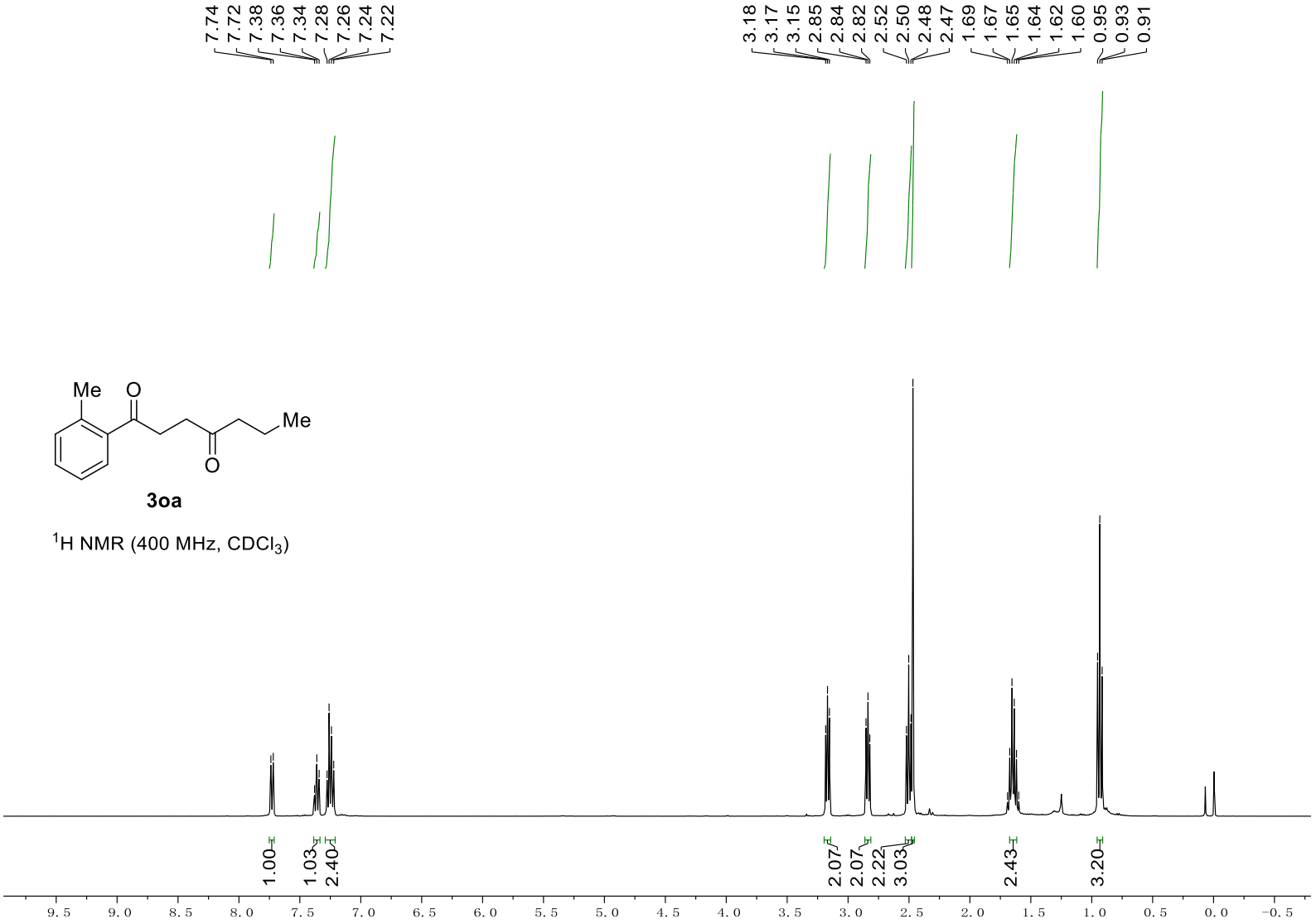
3ma

^{1}H NMR (400 MHz, $CDCl_3$)


209.81
198.65
159.89
138.13
129.69
120.86
119.81
112.26
77.48
77.16
76.84
55.54
45.02
36.33
32.60
17.45
13.87
MeO
O
O
Me
3ma
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

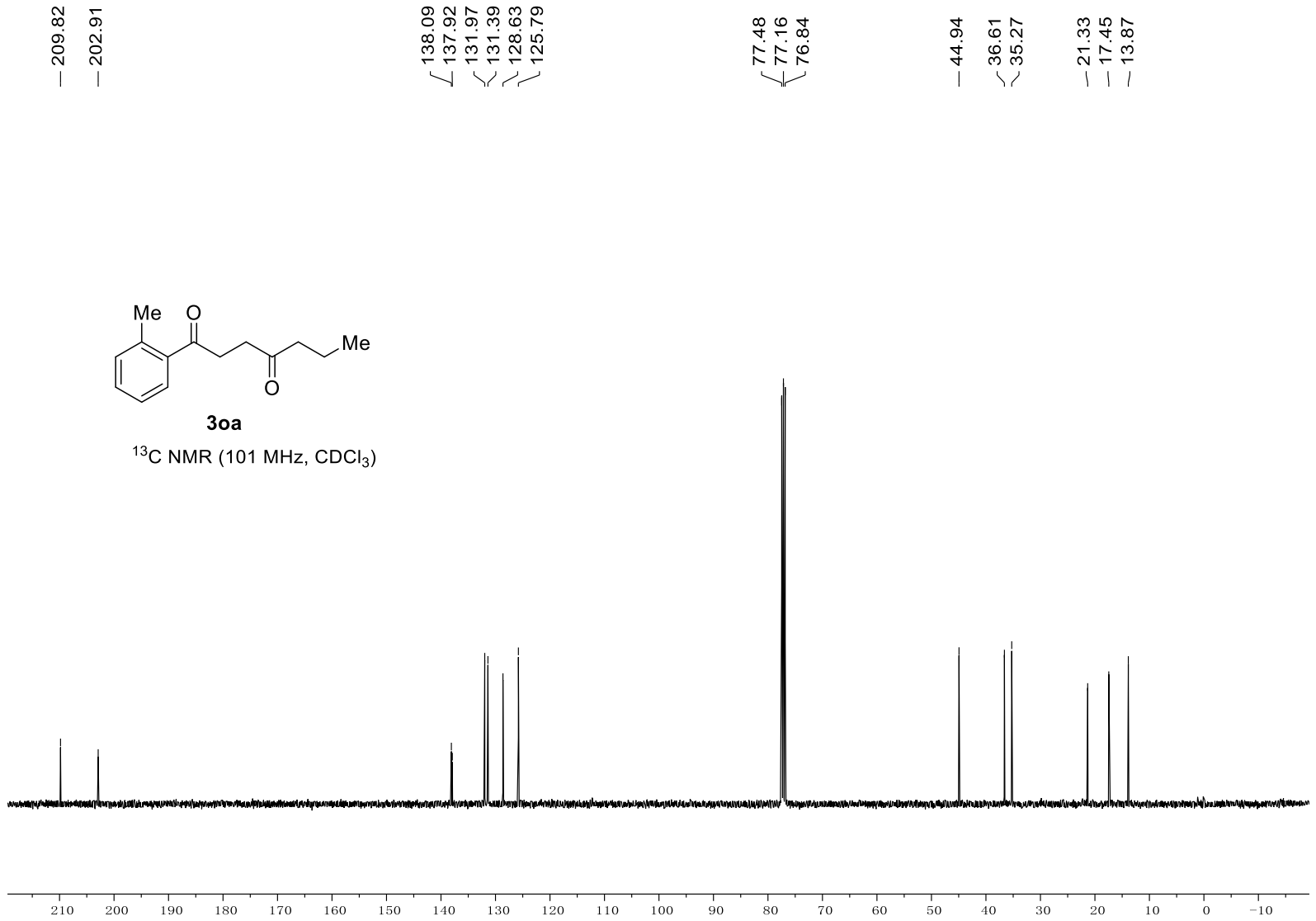

8.62
8.22
8.21
8.16
8.15
7.56
7.54
7.53
7.26
3.94
3.31
3.30
3.29
2.88
2.87
2.86
2.52
2.50
2.49
1.68
1.66
1.65
1.63
1.62
1.60
0.95
0.93
0.92
MeO2C
O
O
Me
3na
1H NMR (400 MHz, CDCl3)
0.95
0.95
0.99
1.00
2.96
2.07
2.05
2.16
2.20
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.

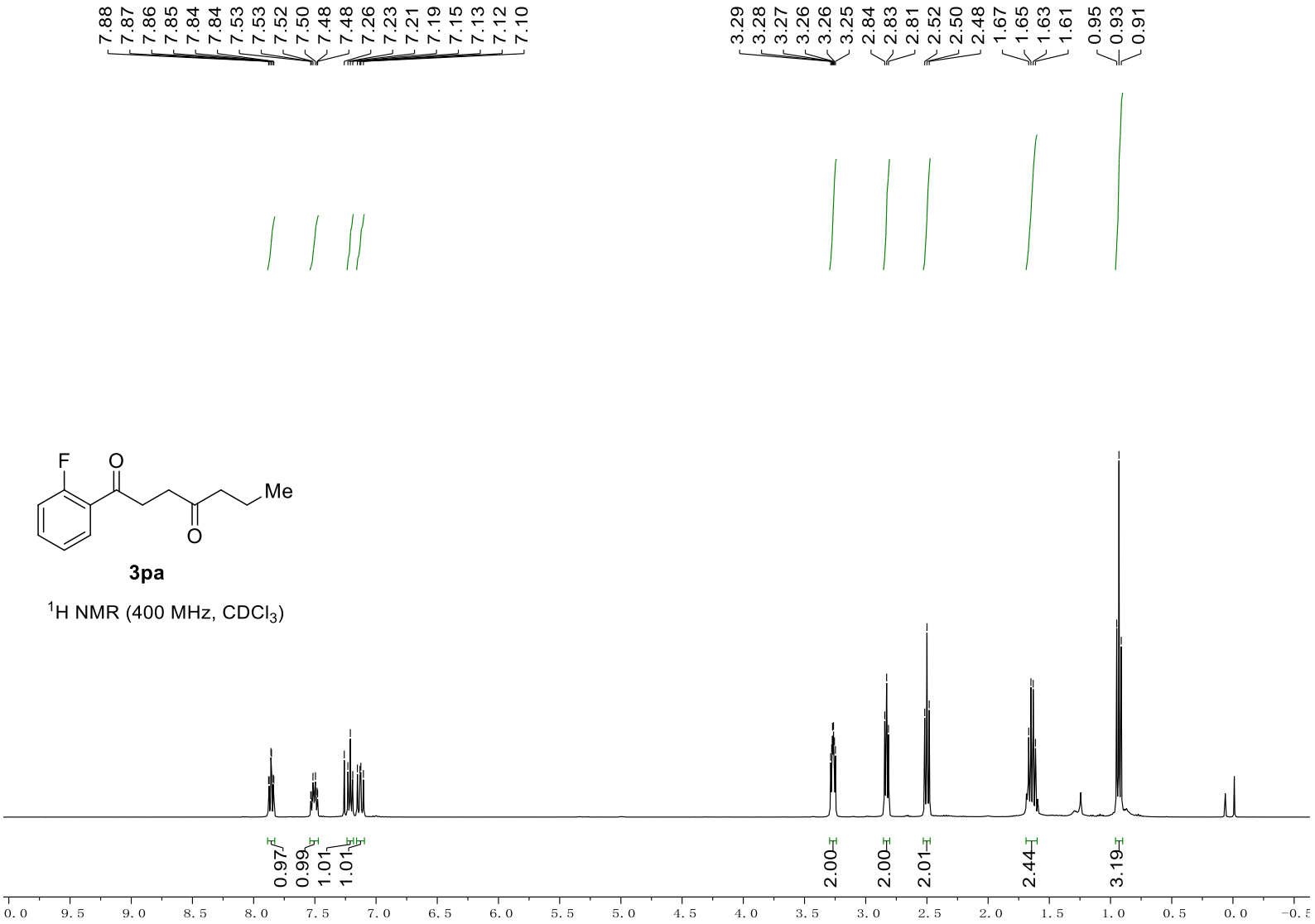

209.61
198.01
166.39
137.02
134.04
132.27
130.77
129.35
128.97
77.42
77.16
76.91
52.51
44.96
36.25
32.58
17.46
13.86
MeO2C
O
O
Me
3na
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

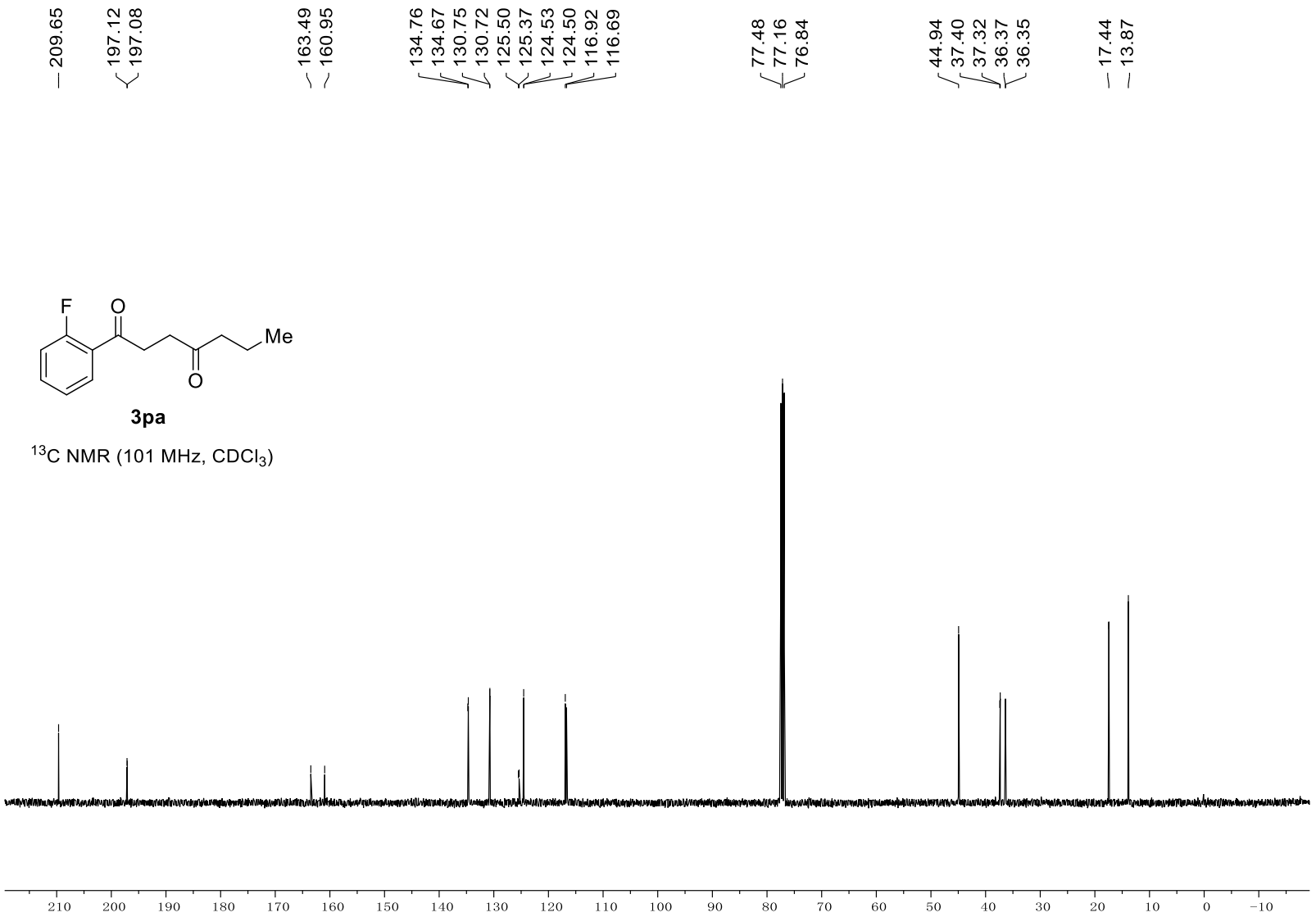


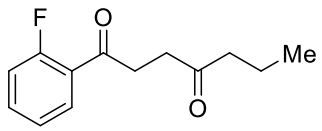
3oa

^{1}H NMR (400 MHz, $CDCl_3$)


209.82
202.91
138.09
137.92
131.97
131.39
128.63
125.79
77.48
77.16
76.84
44.94
36.61
35.27
21.33
17.45
13.87
Me
O
Me
O
3oa
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

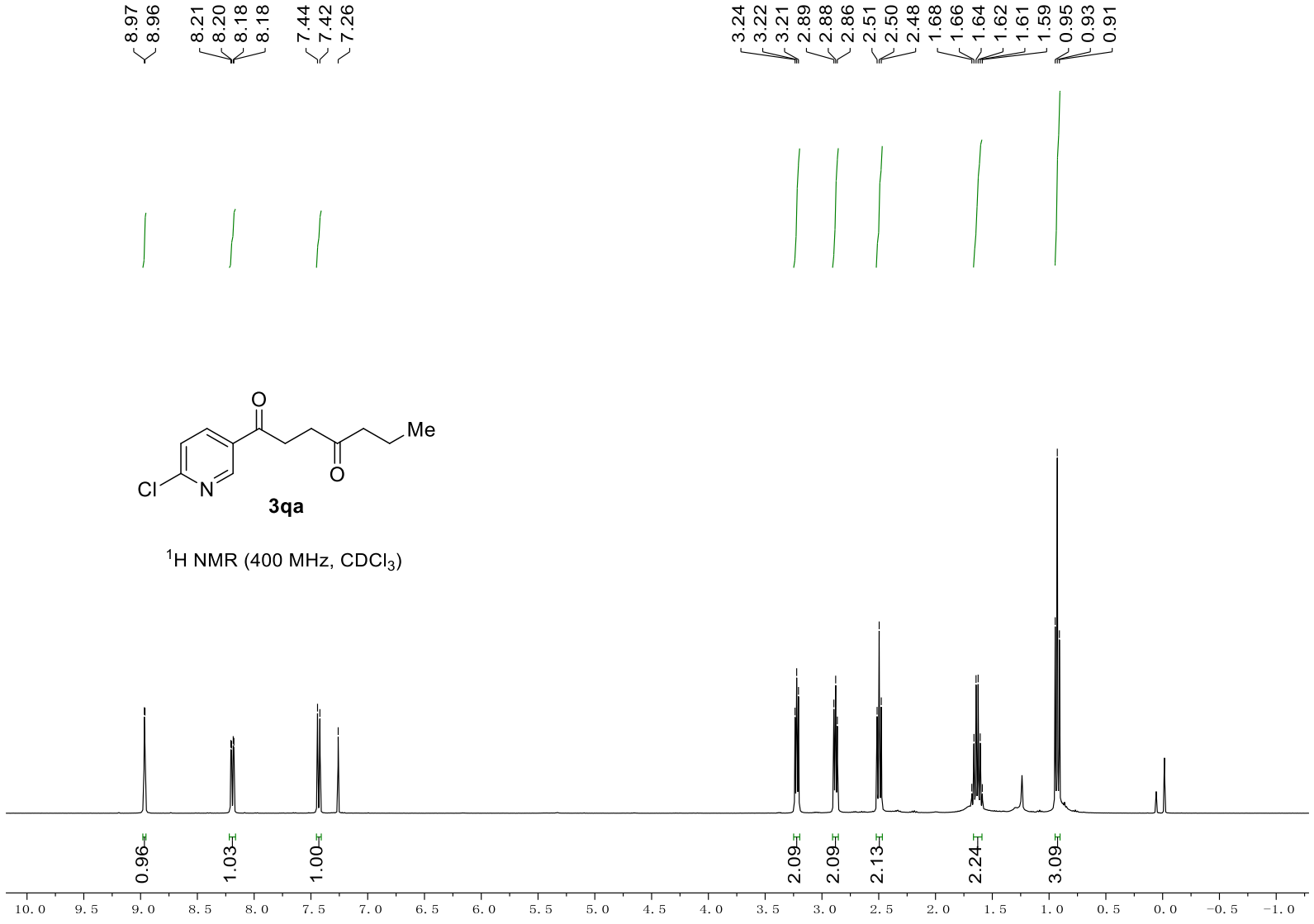

7.88
7.87
7.86
7.85
7.84
7.84
7.53
7.53
7.52
7.50
7.48
7.48
7.26
7.23
7.21
7.19
7.15
7.13
7.12
7.10
3.29
3.28
3.27
3.26
3.26
3.25
2.84
2.83
2.81
2.52
2.50
2.48
1.67
1.65
1.63
1.61
0.95
0.93
0.91
F
O
O
Me
3pa
1H NMR (400 MHz, CDCl3)
0.97
0.99
1.01
1.01
2.00
2.00
2.01
2.44
3.19
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


209.65
197.12
197.08
163.49
160.95
134.76
134.67
130.75
130.72
125.50
125.37
124.53
124.50
116.92
116.69
77.48
77.16
76.84
44.94
37.40
37.32
36.37
36.35
17.44
13.87
F
O
Me
O
3pa
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



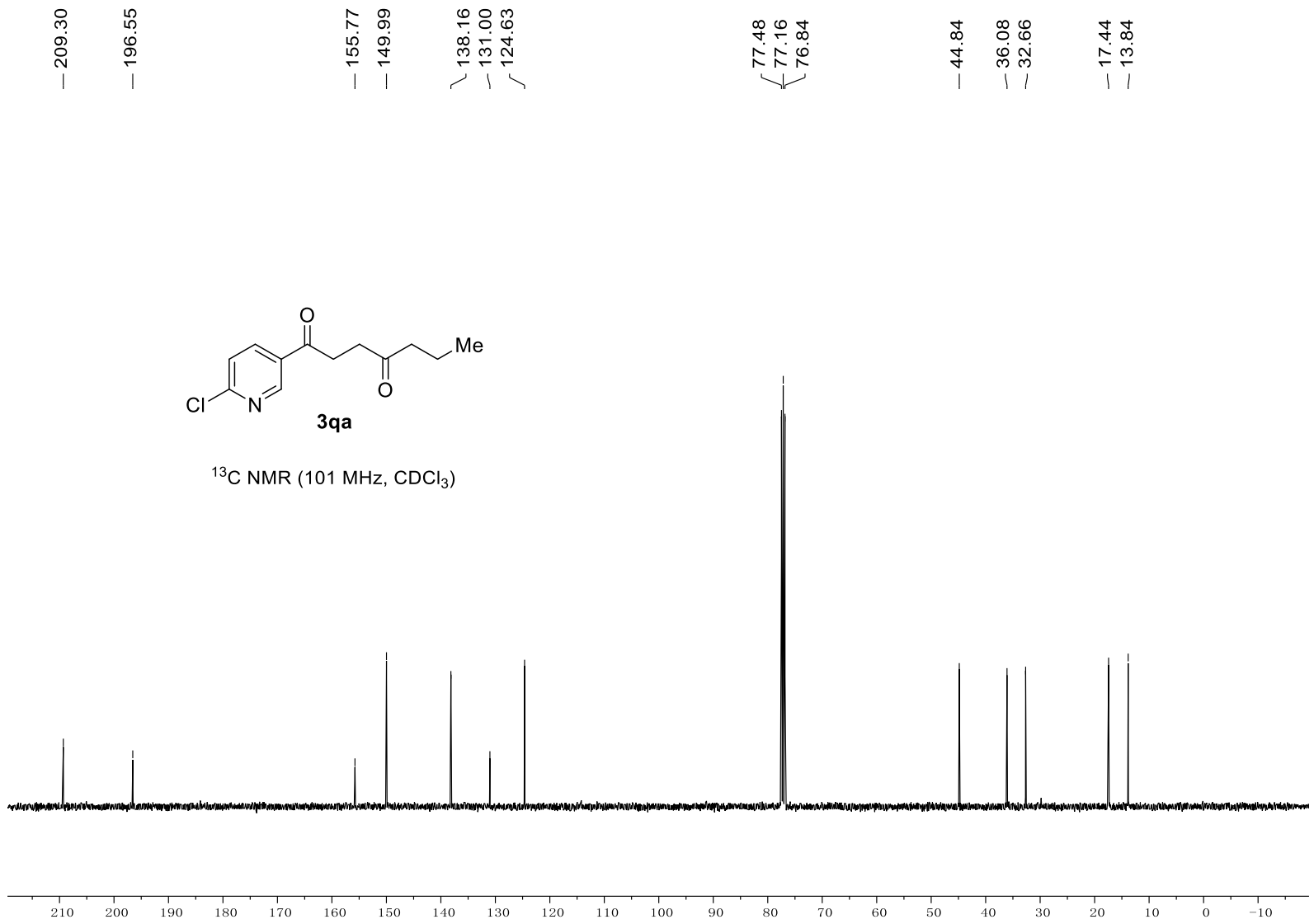
3pa

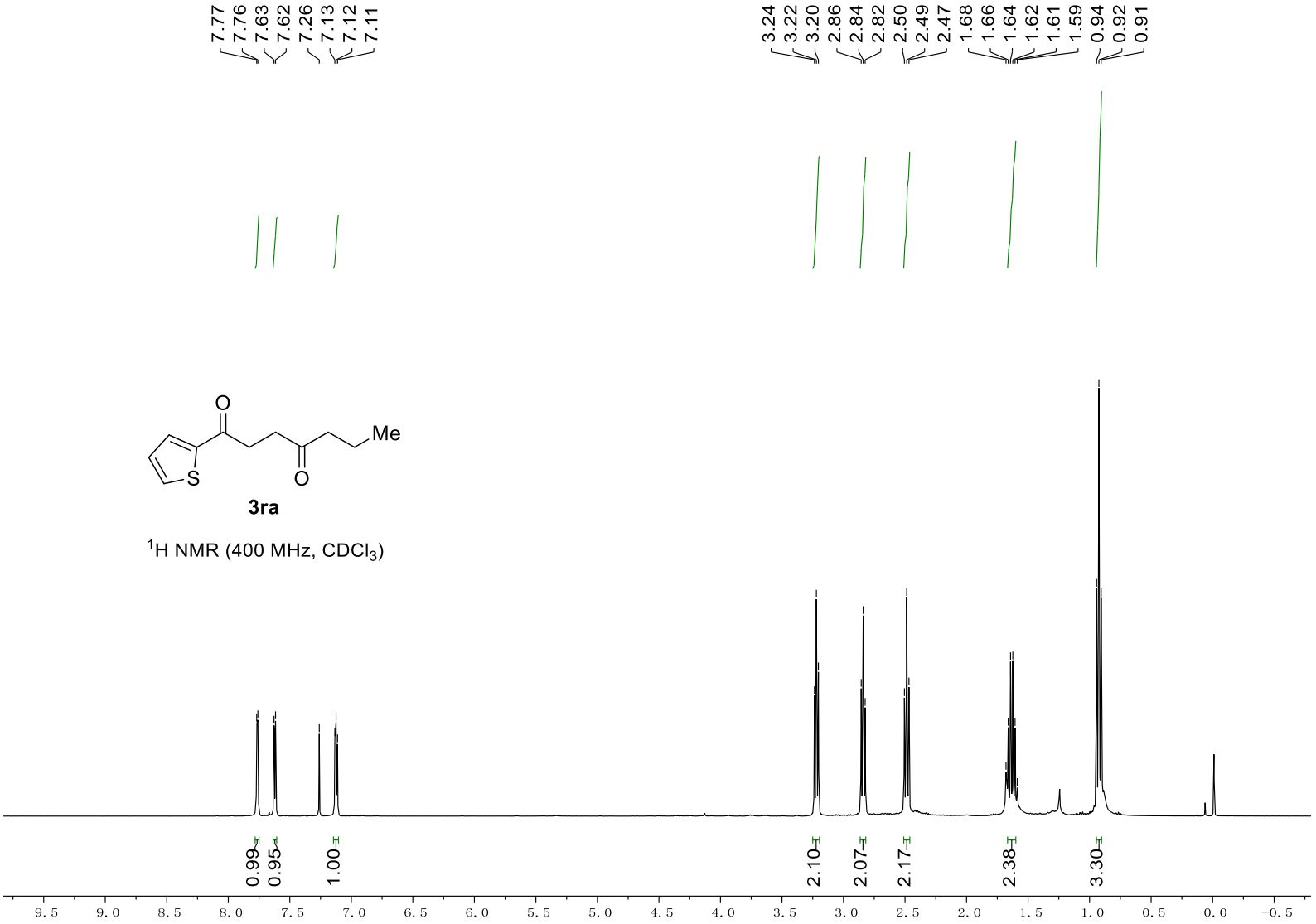
^{19}F NMR (376 MHz, $CDCl_3$)



3qa

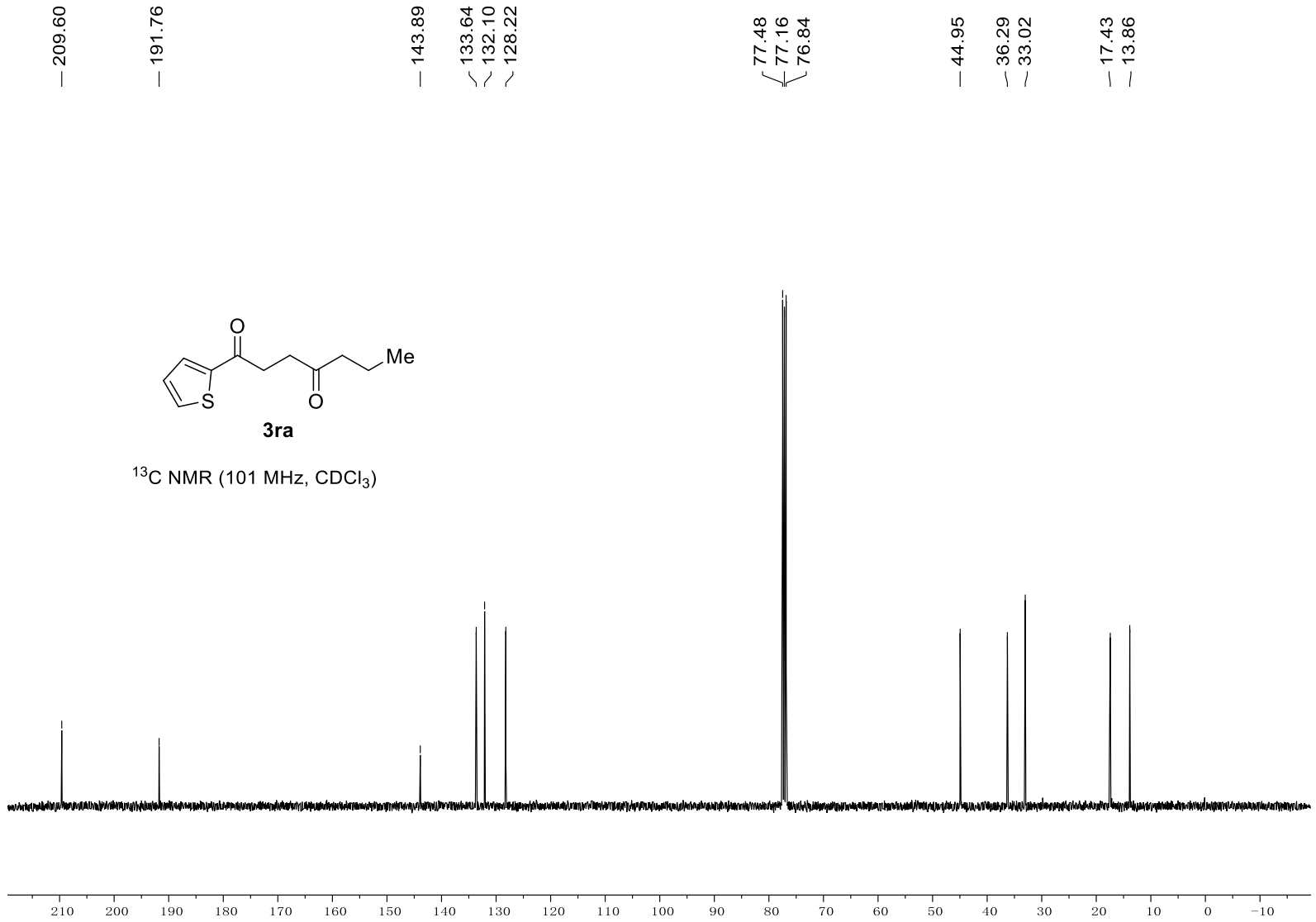
^{1}H NMR (400 MHz, $CDCl_3$)

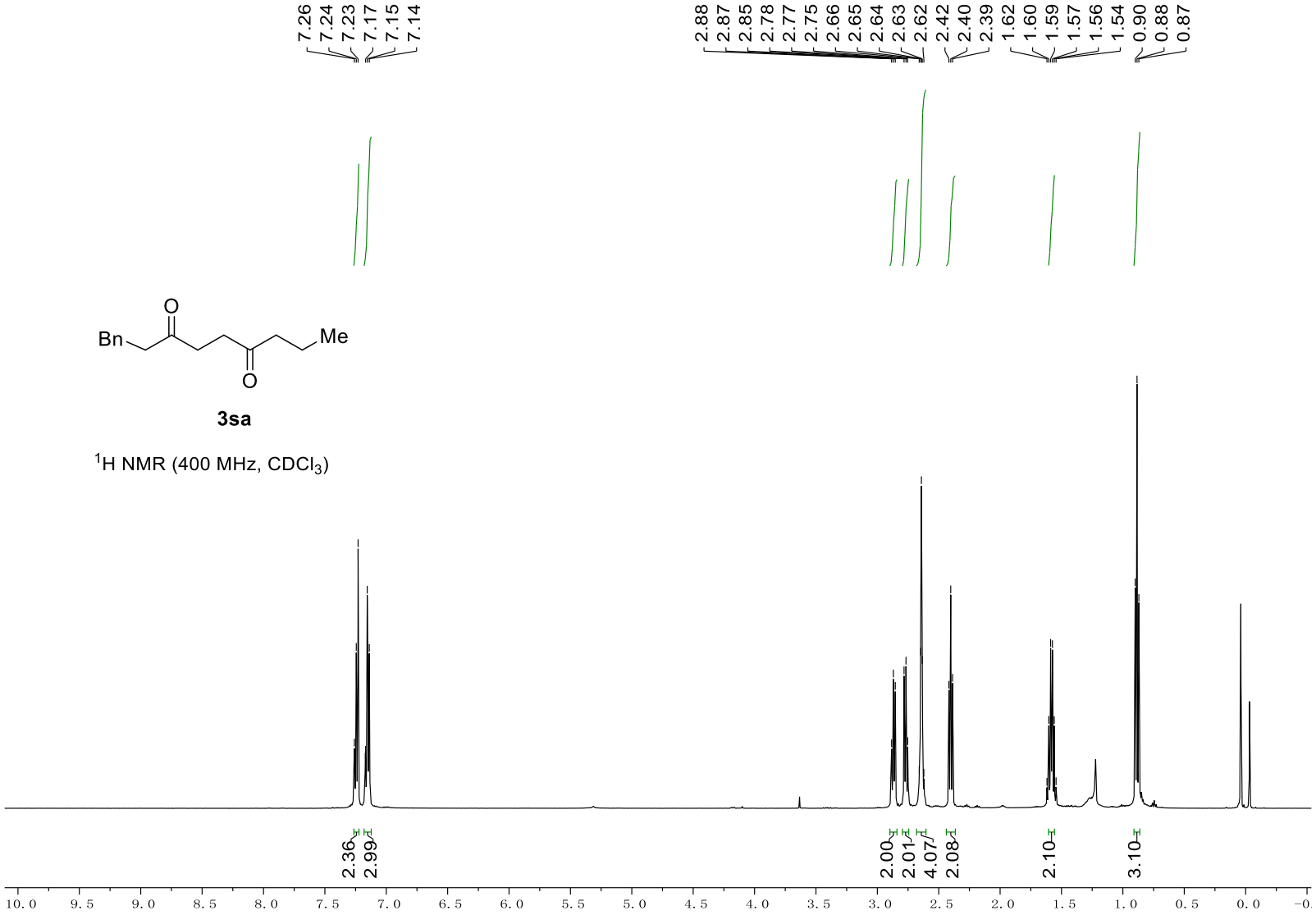

209.30
196.55
155.77
149.99
138.16
131.00
124.63
77.48
77.16
76.84
44.84
36.08
32.66
17.44
13.84
O
Me
O
Cl
N
3qa
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



3ra

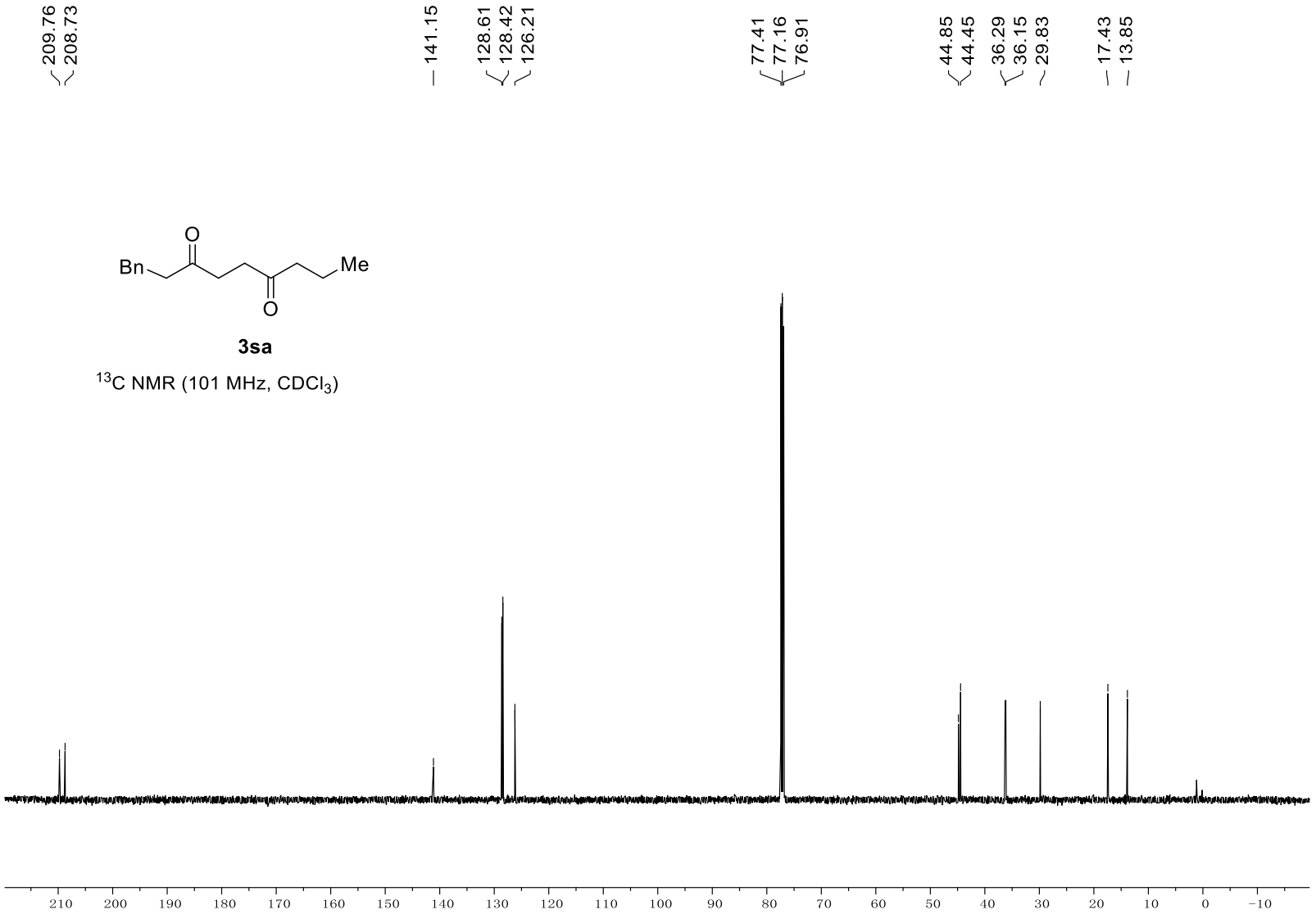
^{1}H NMR (400 MHz, $CDCl_3$)

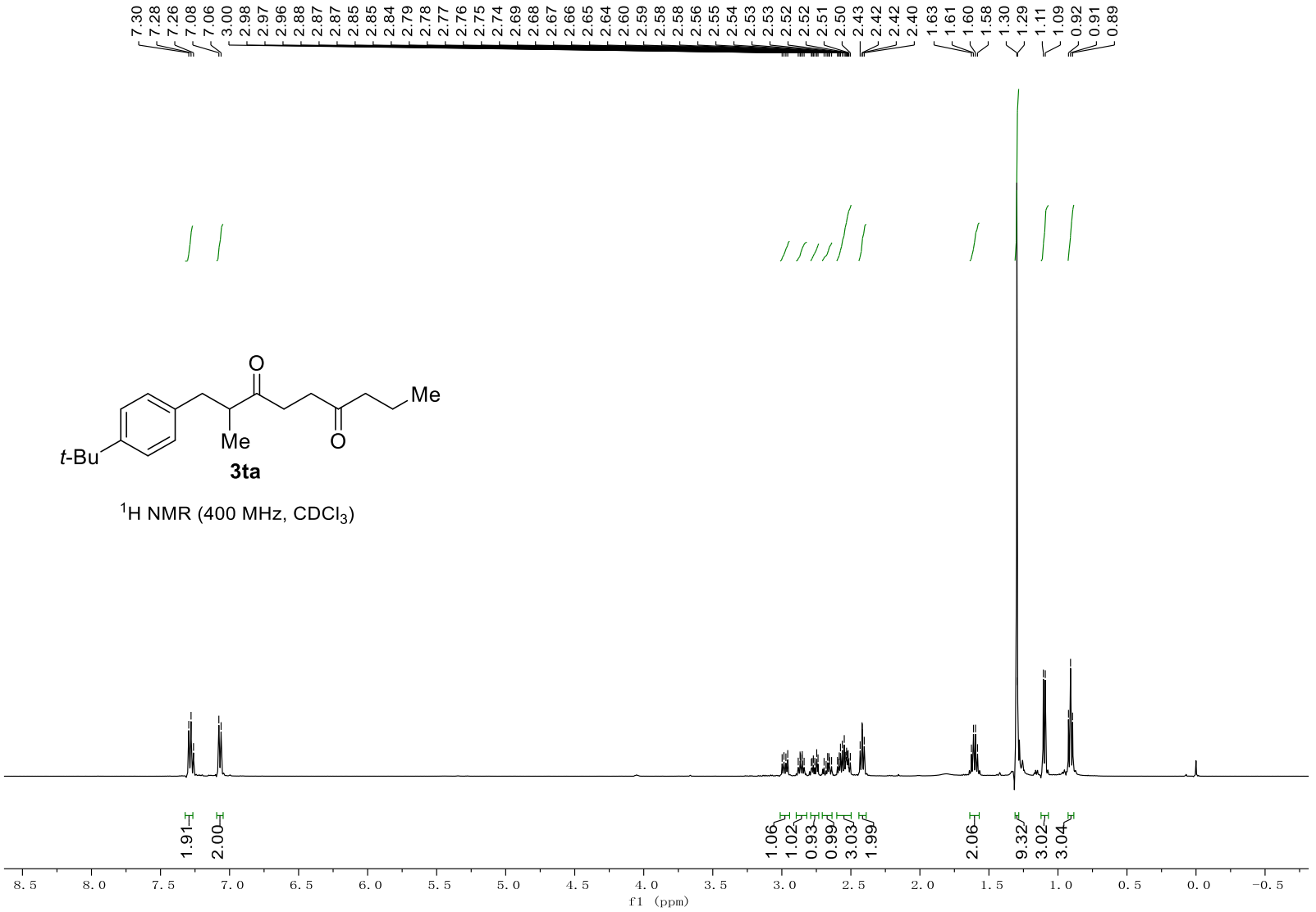

209.60
191.76
143.89
133.64
132.10
128.22
77.48
77.16
76.84
44.95
36.29
33.02
17.43
13.86
O
Me
S
O
3ra
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

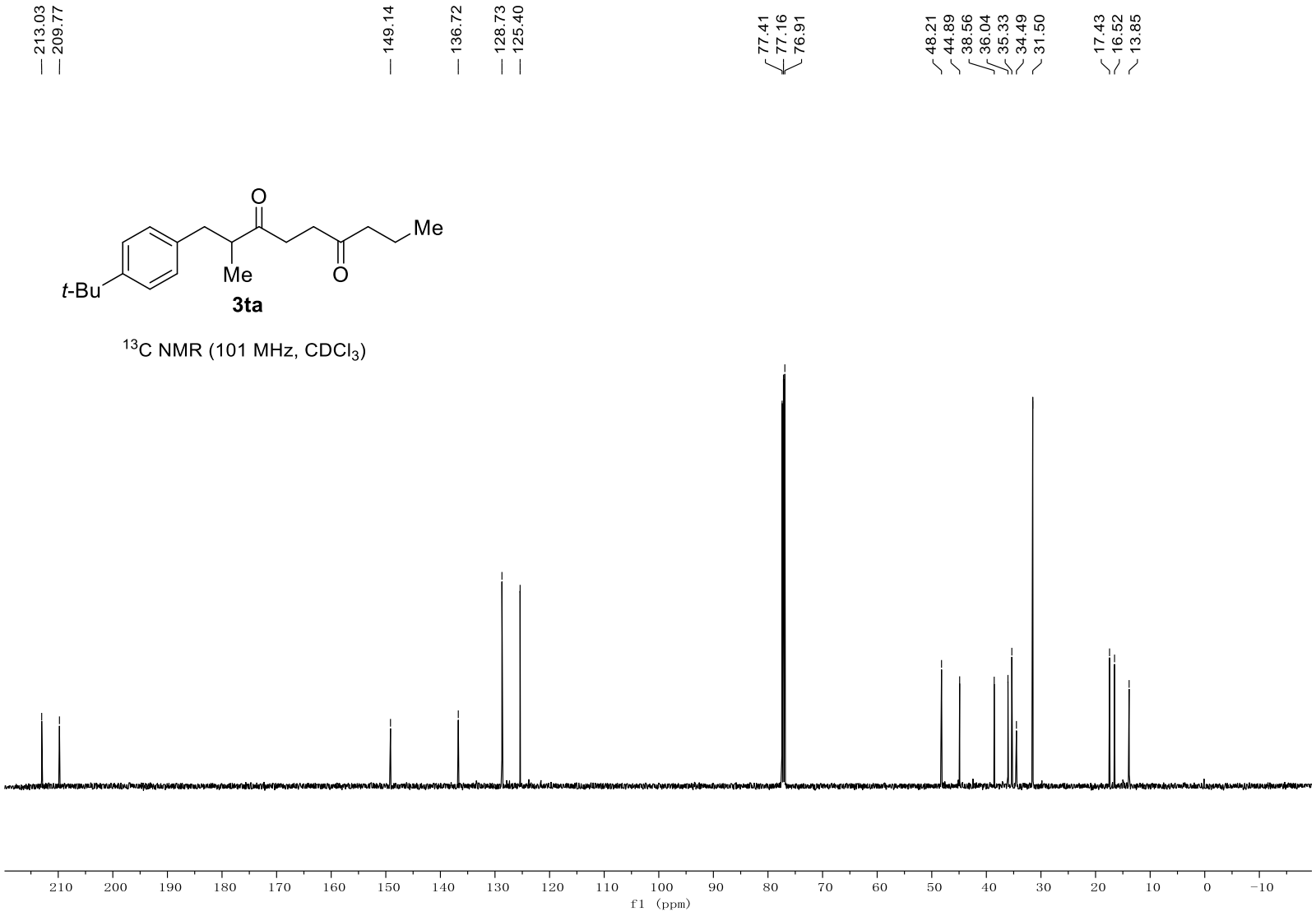


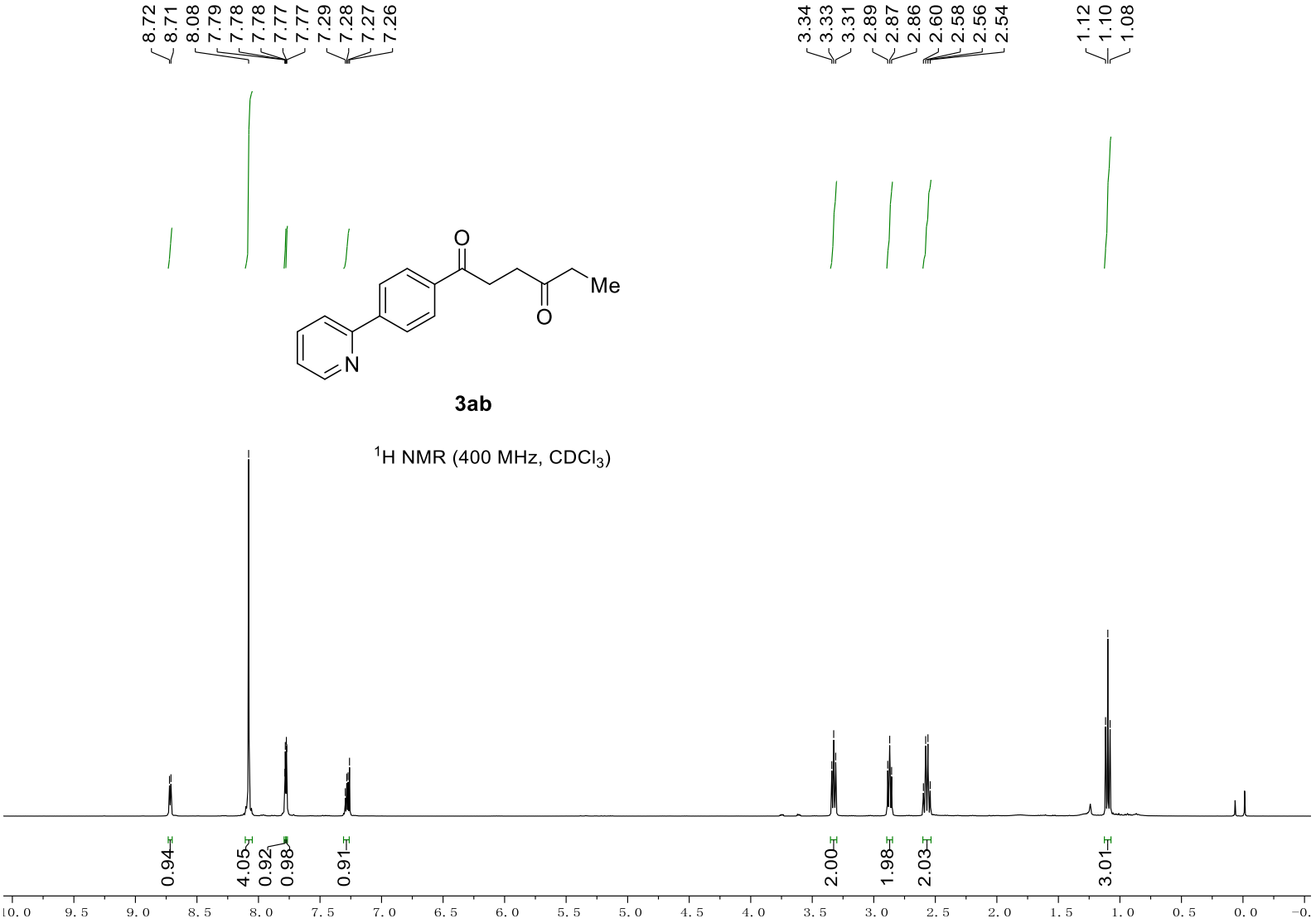
3sa

^{1}H NMR (400 MHz, $CDCl_3$)


209.76
208.73
141.15
128.61
128.42
126.21
77.41
77.16
76.91
44.85
44.45
36.29
36.15
29.83
17.43
13.85
O
Bn
Me
O
3sa
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

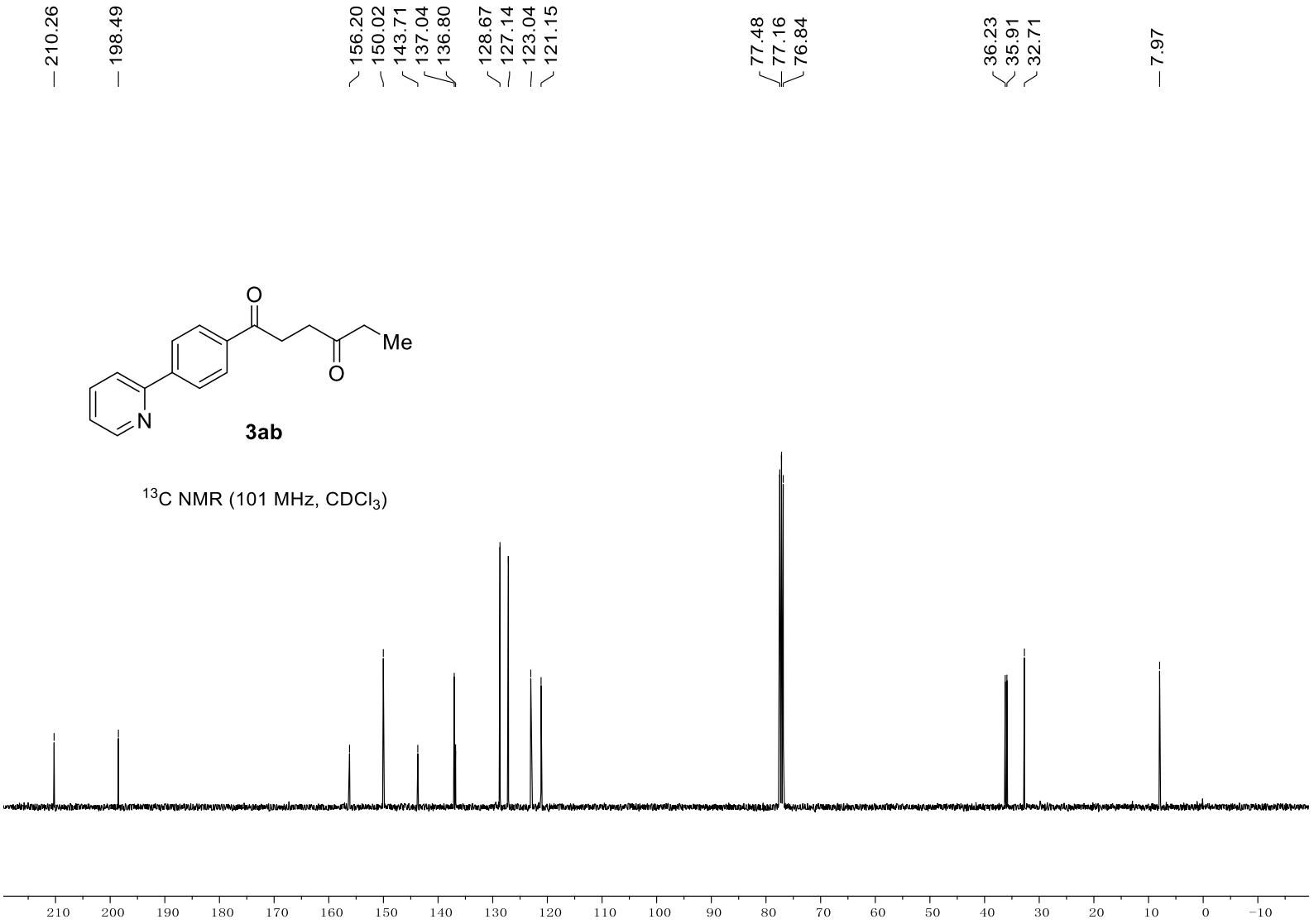

7.30
7.28
7.26
7.08
7.06
3.00
2.98
2.97
2.96
2.88
2.87
2.87
2.85
2.85
2.84
2.79
2.78
2.77
2.76
2.75
2.74
2.69
2.68
2.67
2.66
2.65
2.64
2.60
2.59
2.58
2.58
2.56
2.55
2.54
2.53
2.53
2.52
2.52
2.51
2.50
2.43
2.42
2.42
2.40
1.63
1.61
1.60
1.58
1.30
1.29
1.11
1.09
0.92
0.91
0.89
O
Me
Me
O
t-Bu
3ta
1H NMR (400 MHz, CDCl3)
1.91
2.00
1.06
1.02
0.93
0.99
3.03
1.99
2.06
9.32
3.02
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

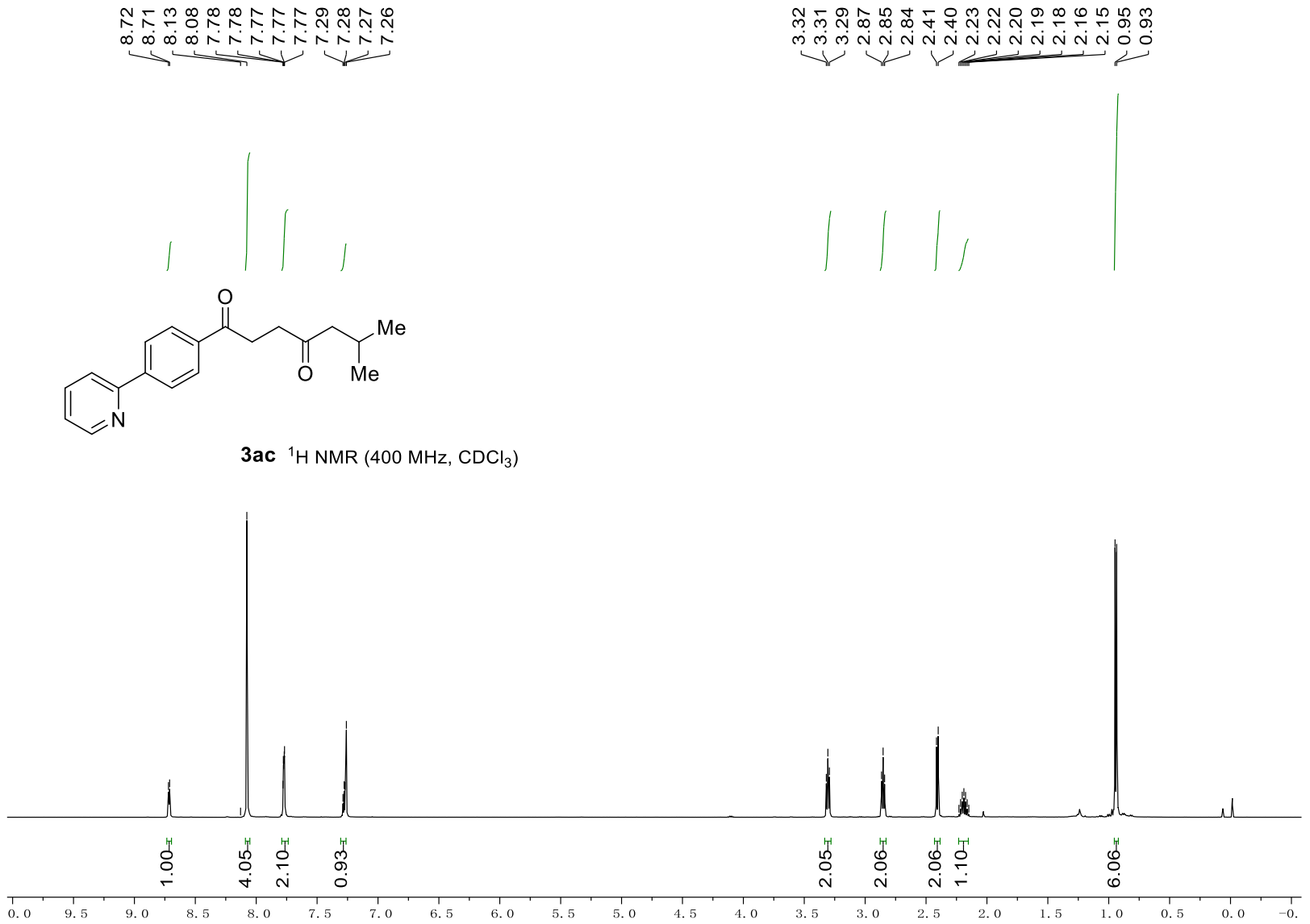

213.03
209.77
149.14
136.72
128.73
125.40
77.41
77.16
76.91
48.21
44.89
38.56
36.04
35.33
34.49
31.50
17.43
16.52
13.85
O
Me
Me
O
t-Bu
3ta
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



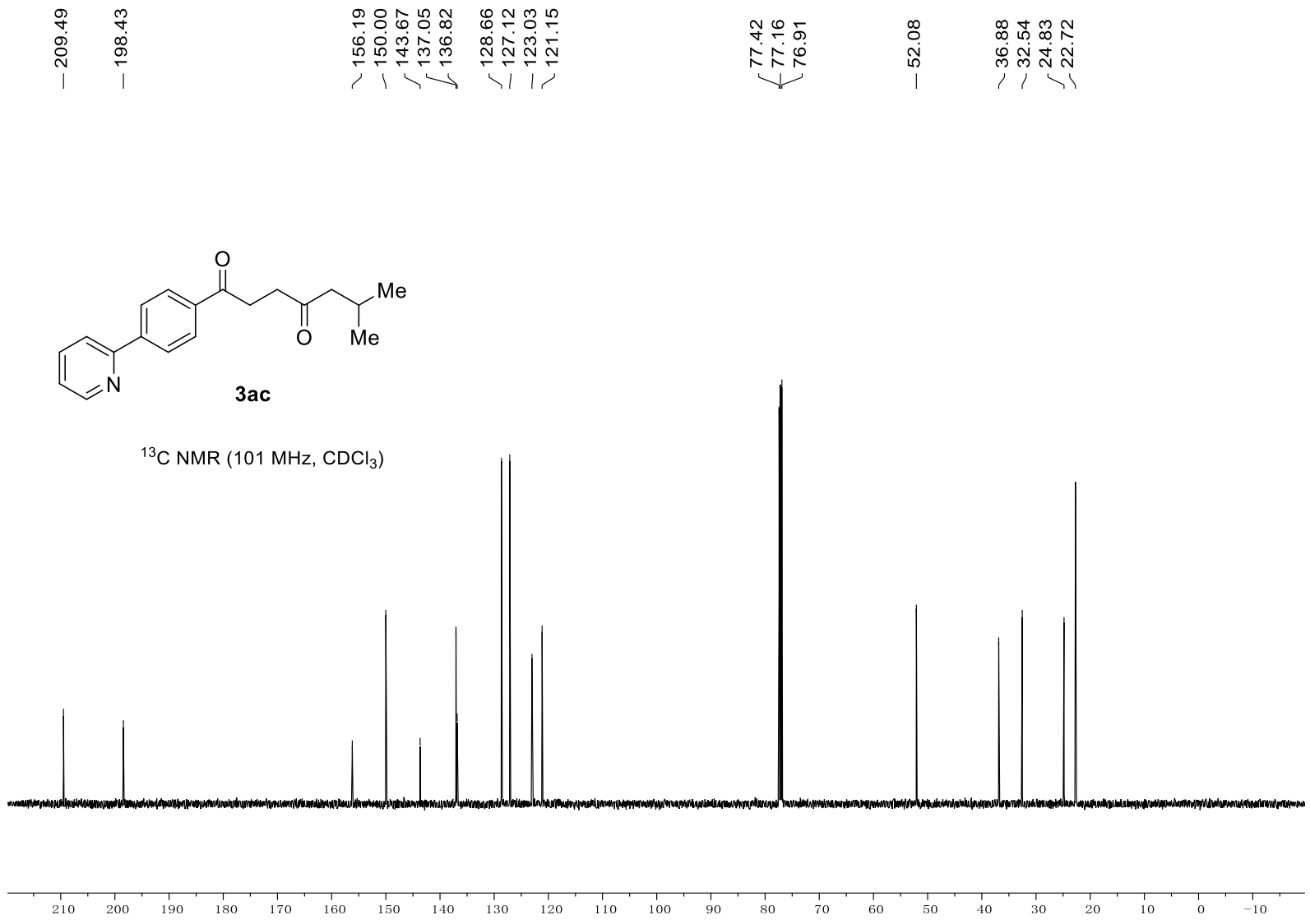
3ab

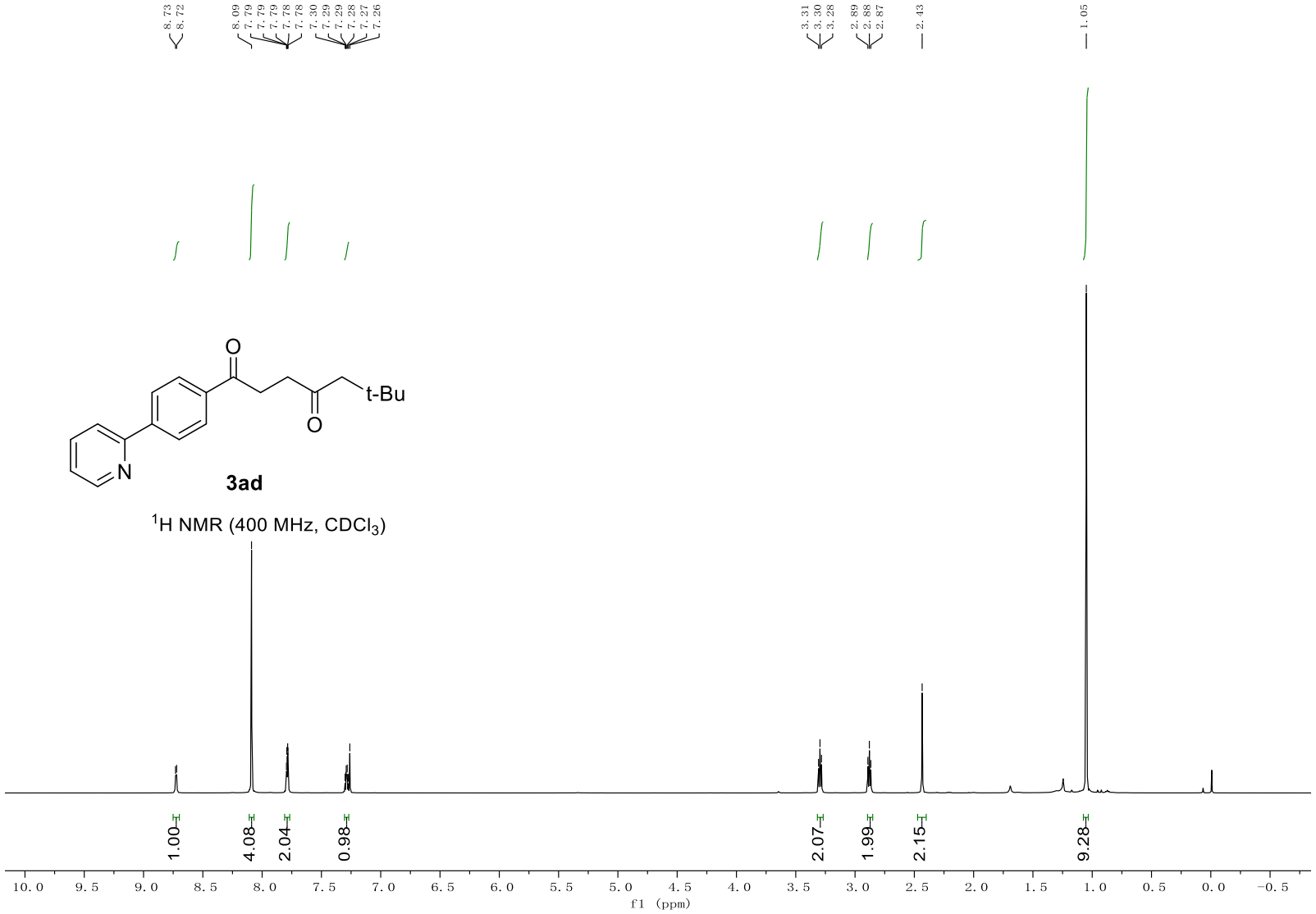
^{1}H NMR (400 MHz, $CDCl_3$)

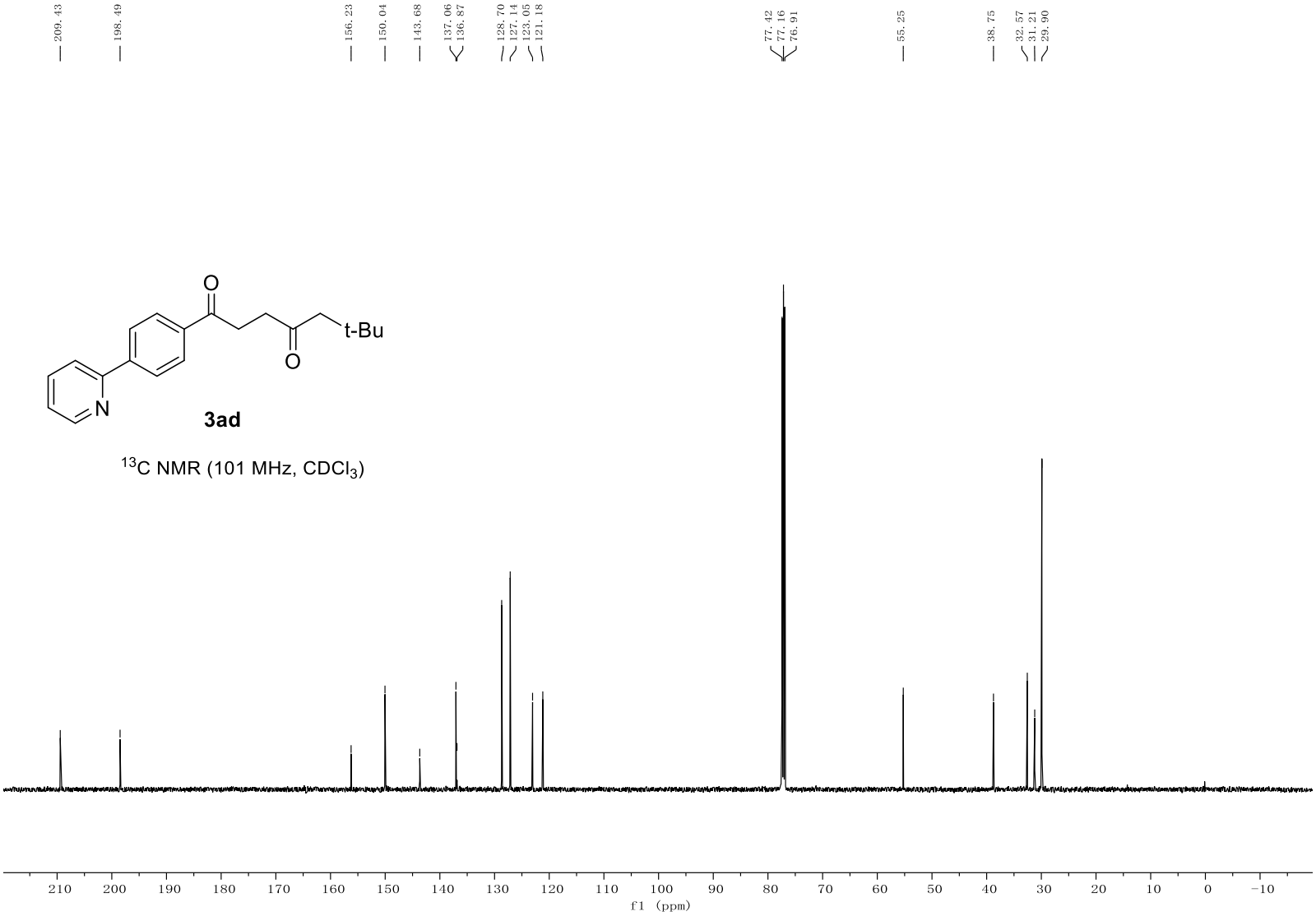

210.26
198.49
156.20
150.02
143.71
137.04
136.80
128.67
127.14
123.04
121.15
77.48
77.16
76.84
36.23
35.91
32.71
7.97
O
O
Me
N
3ab
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

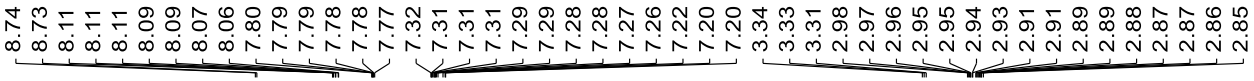


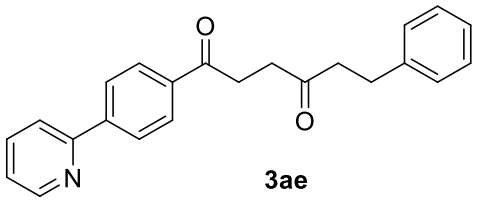
3ac ^{1}H NMR (400 MHz, $CDCl_3$)


209.49
198.43
156.19
150.00
143.67
137.05
136.82
128.66
127.12
123.03
121.15
77.42
77.16
76.91
52.08
36.88
32.54
24.83
22.72
O
Me
O
Me
N
3ac
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


8.73
8.72
8.09
7.79
7.79
7.79
7.78
7.78
7.30
7.29
7.29
7.28
7.27
7.26
3.31
3.30
3.28
2.89
2.88
2.87
2.43
1.05
O
O
t-Bu
N
3ad
1H NMR (400 MHz, CDCl3)
1.00
4.08
2.04
0.98
2.07
1.99
2.15
9.28
f1 (ppm)

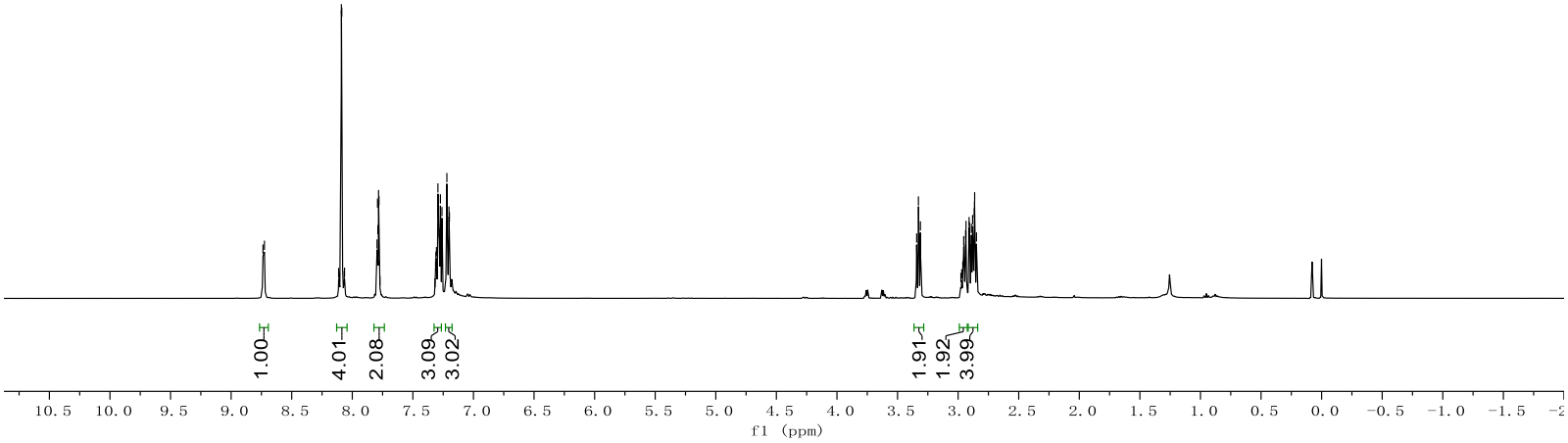

209.43
198.49
156.23
150.04
143.68
137.06
136.87
128.70
127.14
123.05
121.18
77.42
77.16
76.91
55.25
38.75
32.57
31.21
29.90
O
O
t-Bu
N
3ad
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



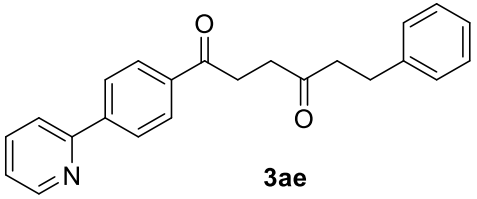


3ae

^{1}H NMR (400 MHz, $CDCl_3$)

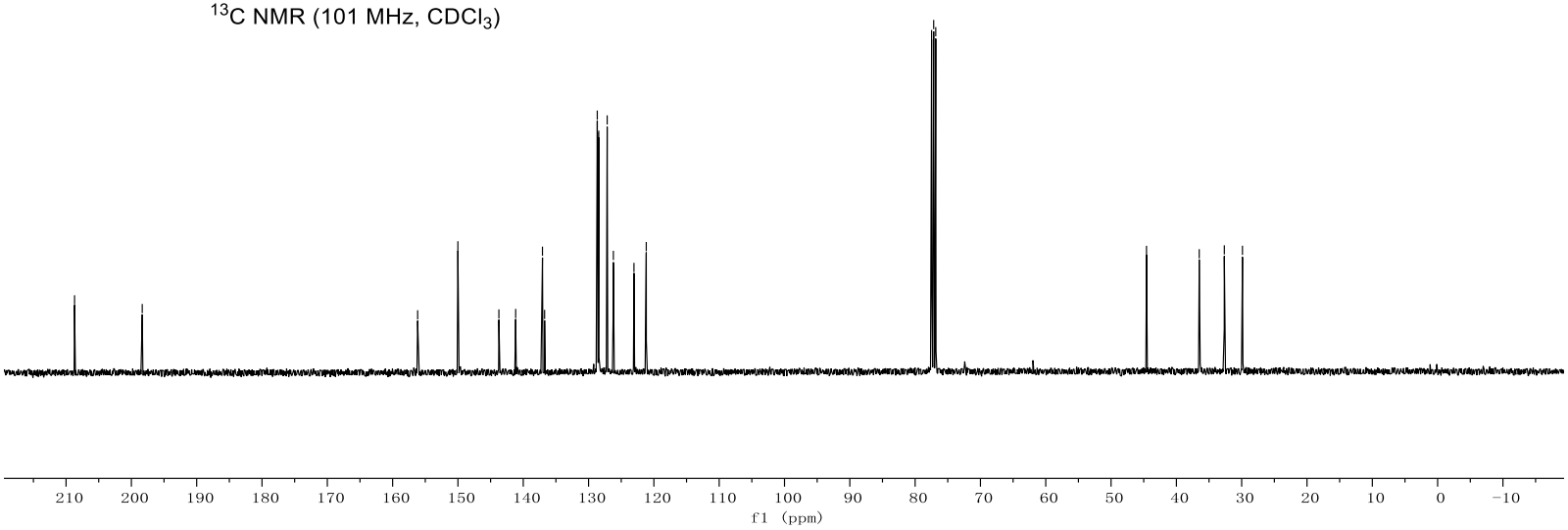


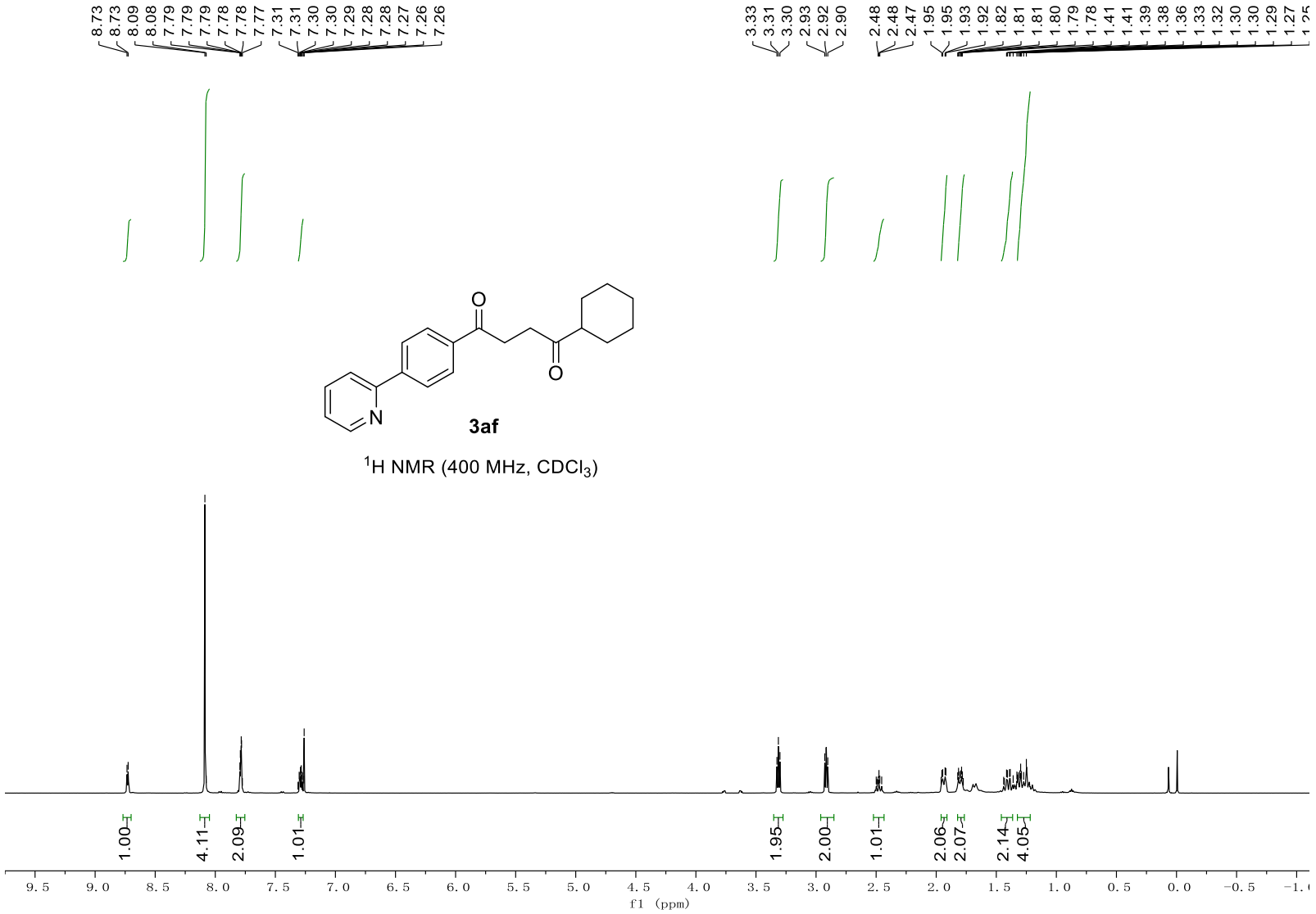
208.70
198.34
156.17
150.01
143.73
141.16
137.06
136.73
128.67
128.60
128.44
127.15
126.20
123.05
121.17
77.48
77.16
76.84
44.57
36.50
32.66
29.88

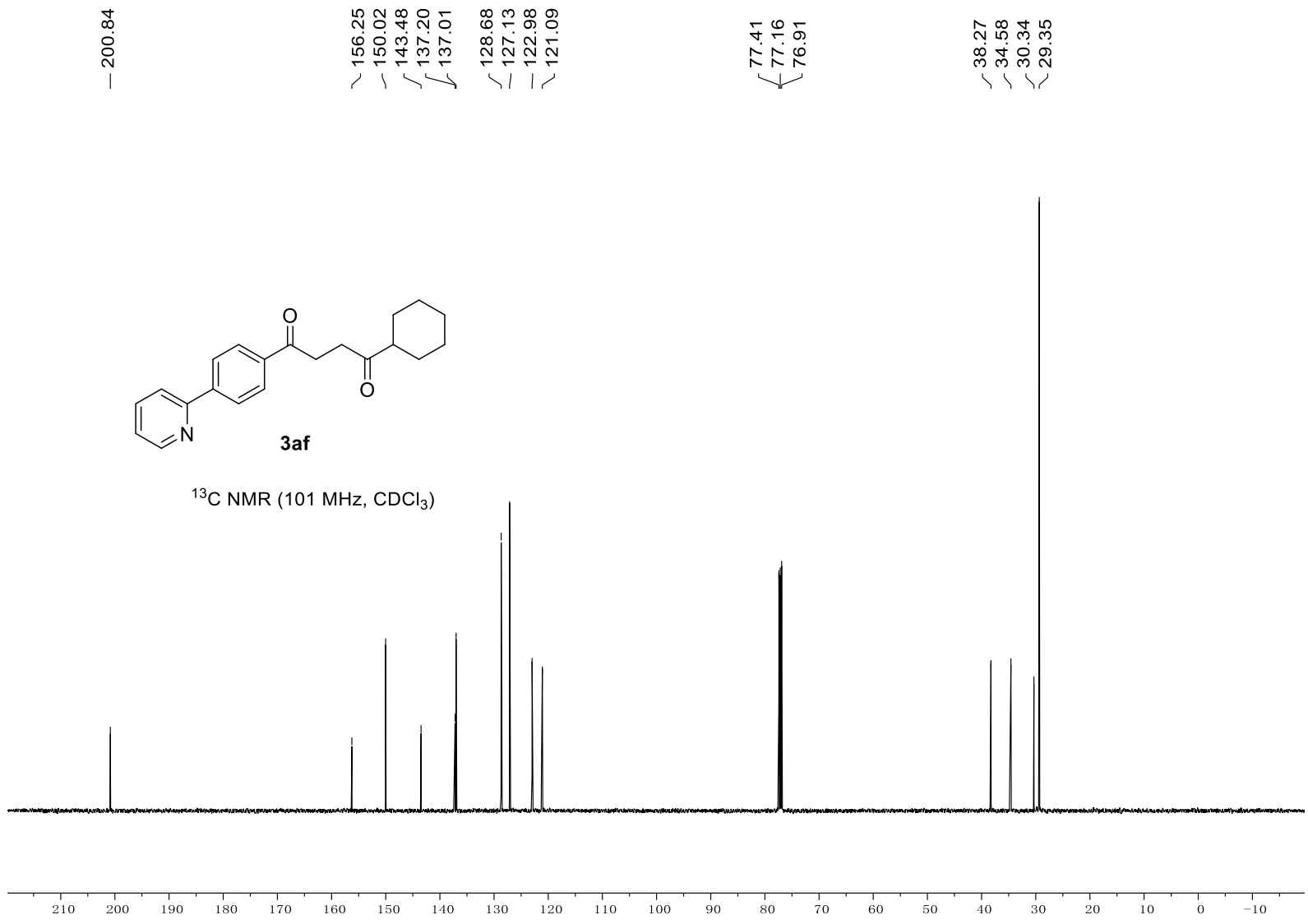


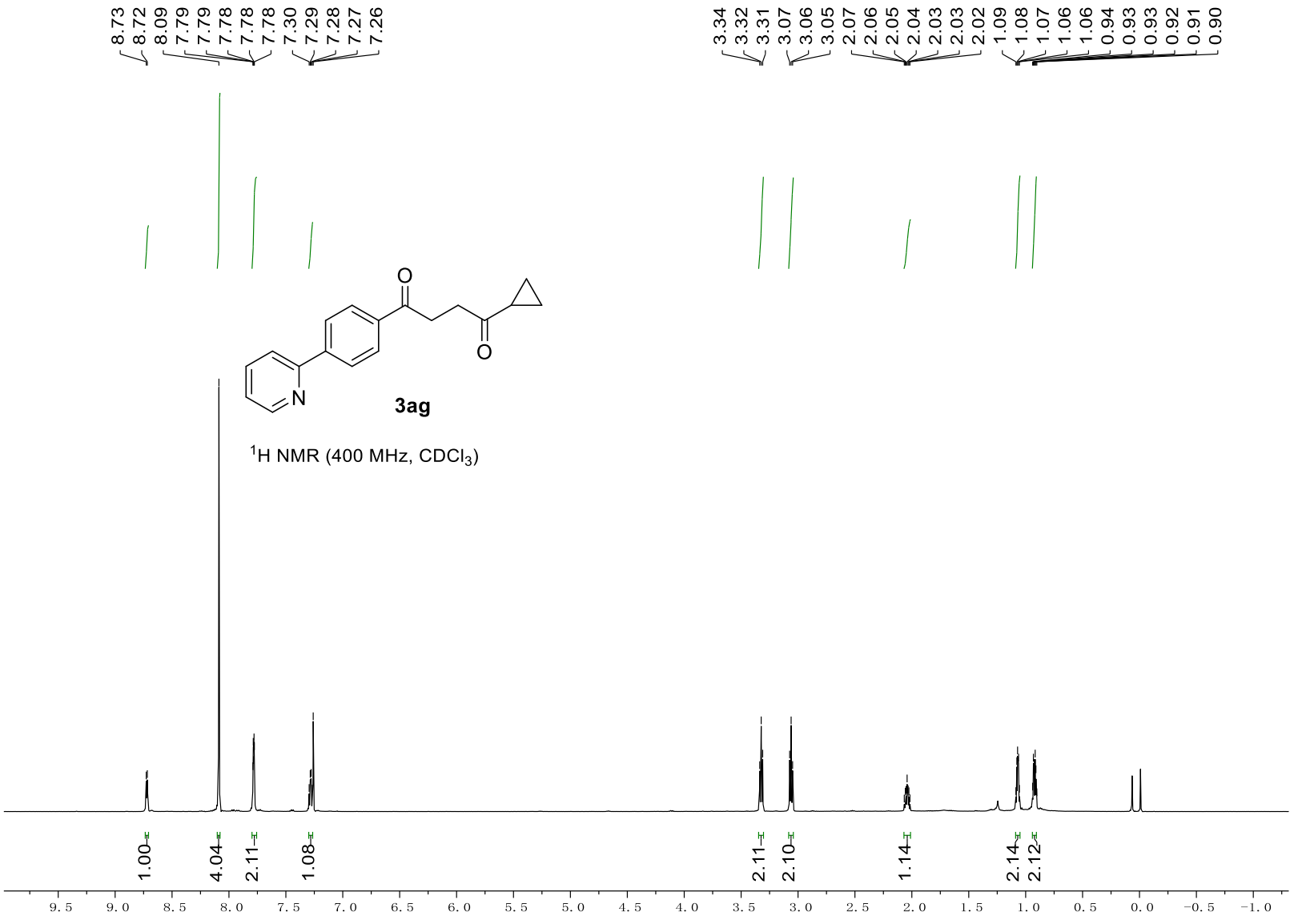
3ae

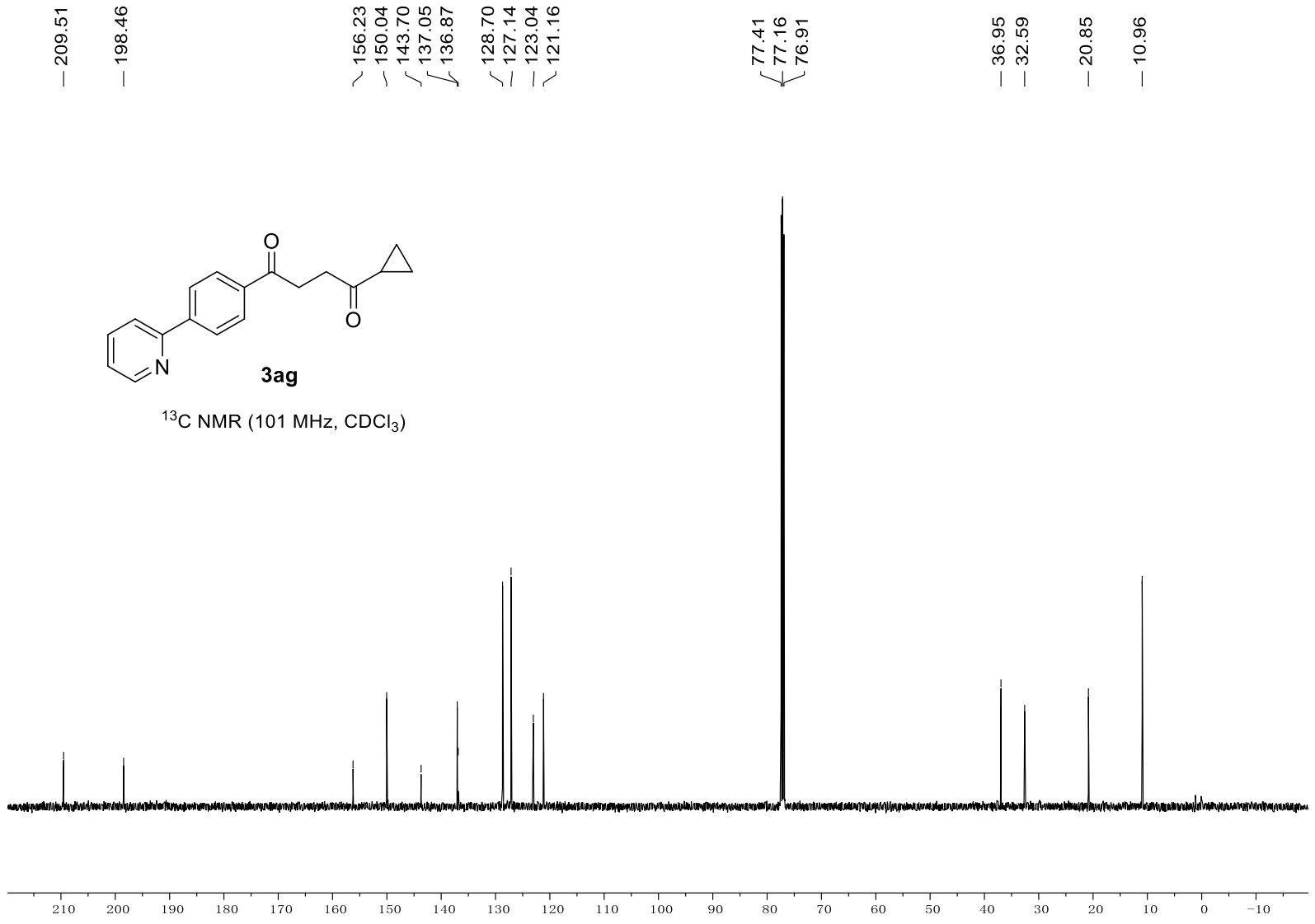
^{13}C NMR (101 MHz, $CDCl_3$)

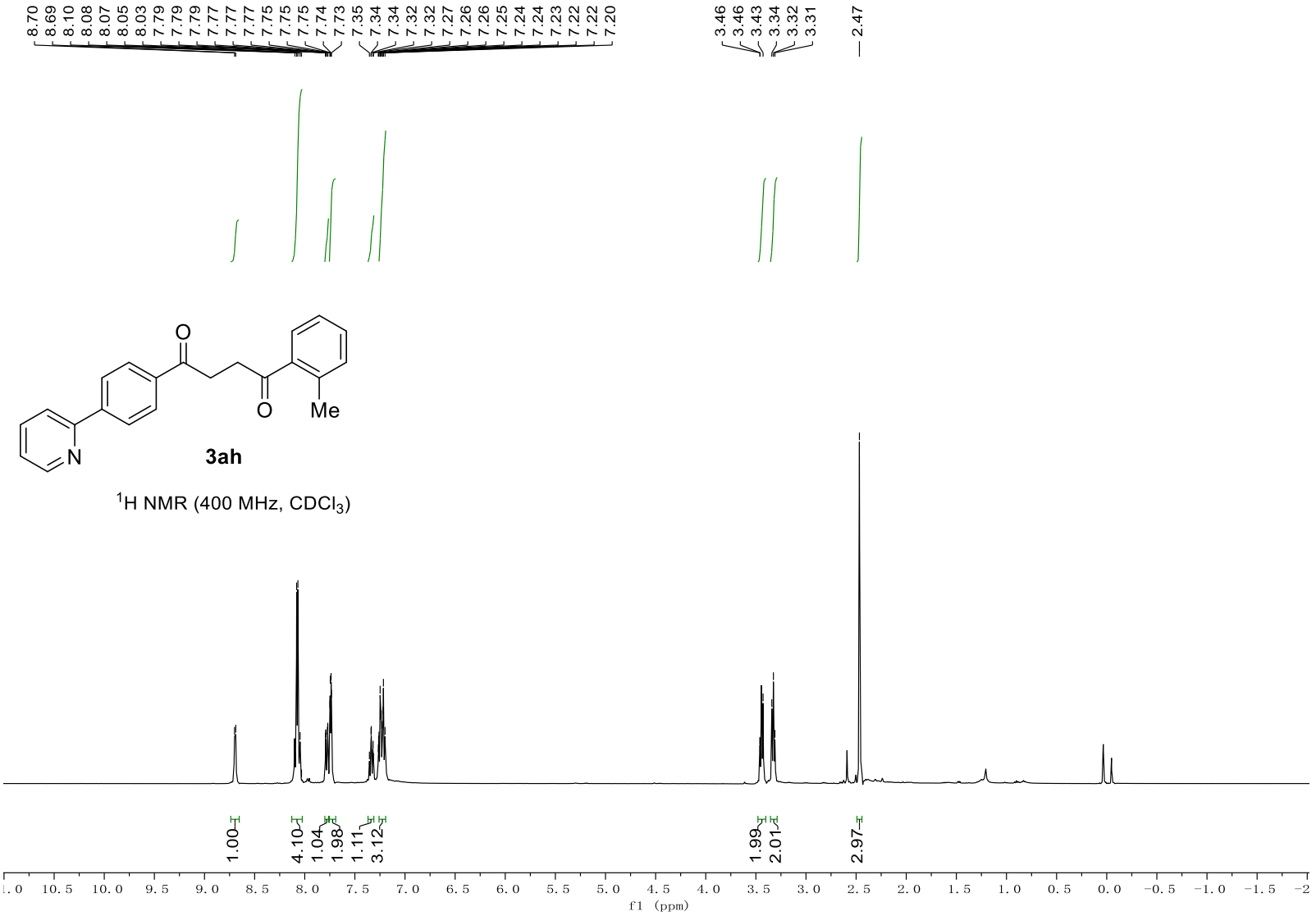


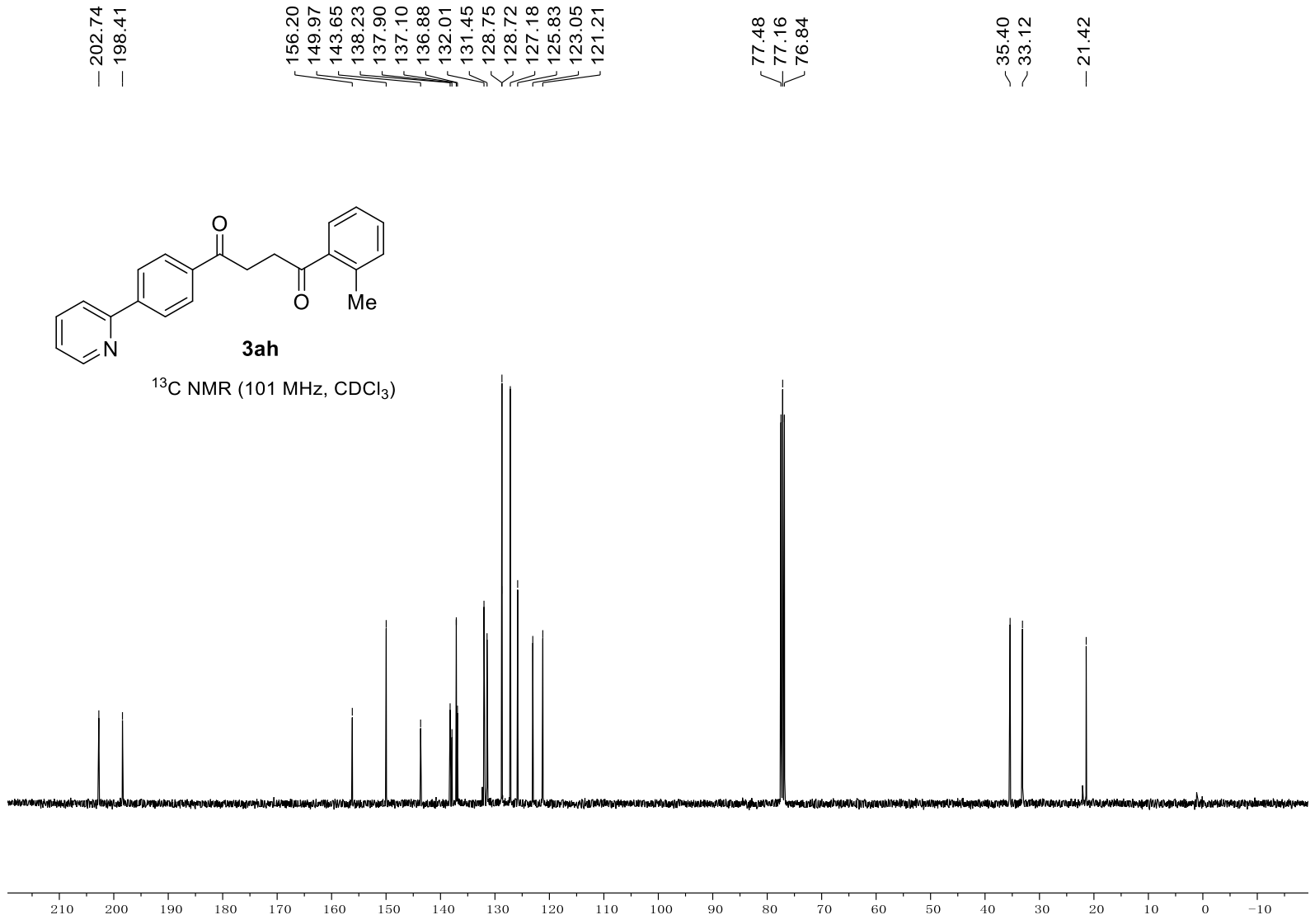

8.73
8.73
8.09
8.08
7.79
7.79
7.79
7.78
7.78
7.77
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
3.33
3.31
3.30
2.93
2.92
2.90
2.48
2.48
2.47
1.95
1.95
1.93
1.92
1.82
1.81
1.81
1.80
1.79
1.78
1.41
1.41
1.39
1.38
1.36
1.33
1.32
1.30
1.30
1.29
1.27
O
O
N
3af
1H NMR (400 MHz, CDCl3)
1.00
4.11
2.09
1.01
1.95
2.00
1.01
2.06
2.07
2.14
4.05
f1 (ppm)

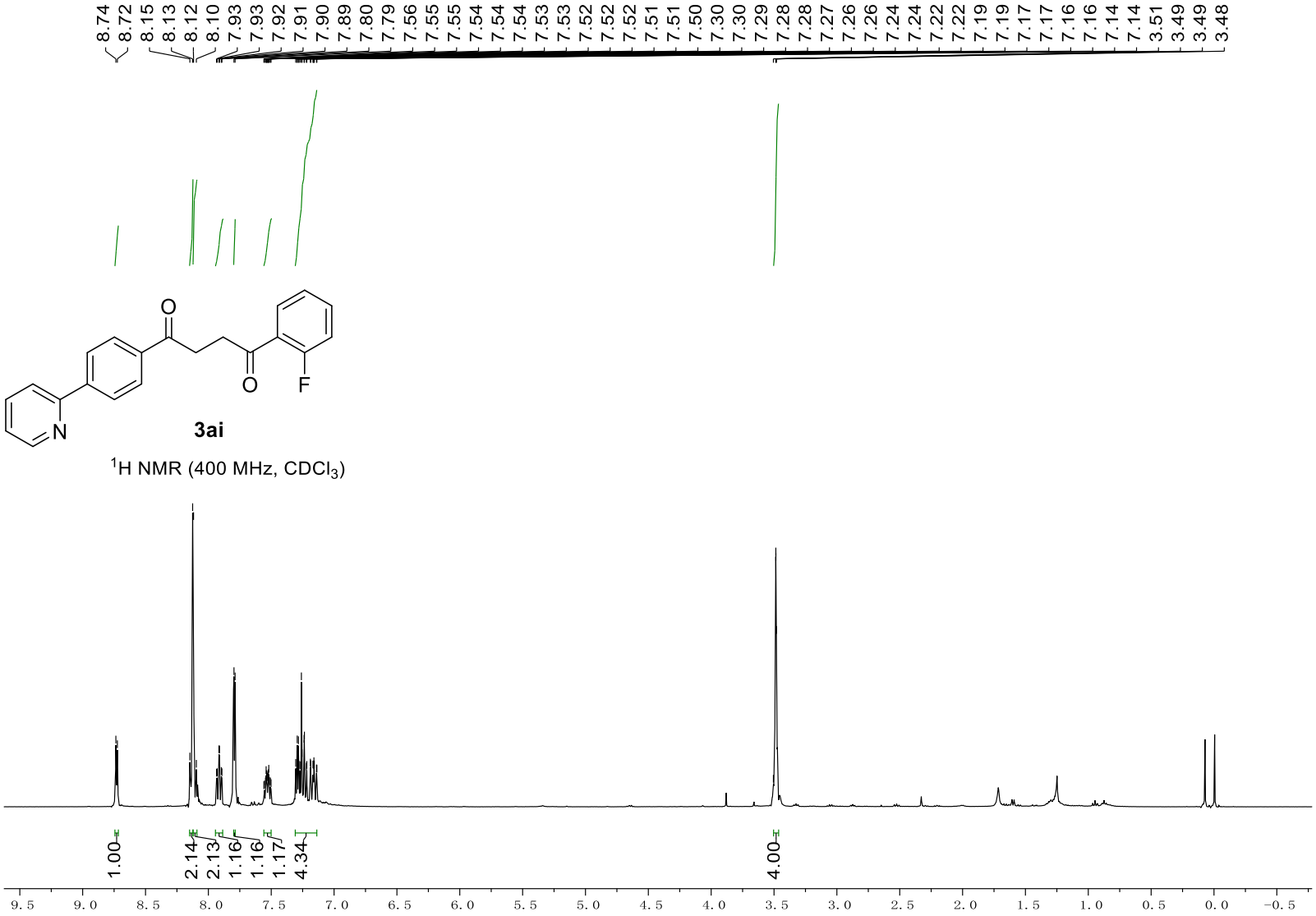

200.84
156.25
150.02
143.48
137.20
137.01
128.68
127.13
122.98
121.09
77.41
77.16
76.91
38.27
34.58
30.34
29.35
O
O
N
3af
^{13}C NMR (101 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

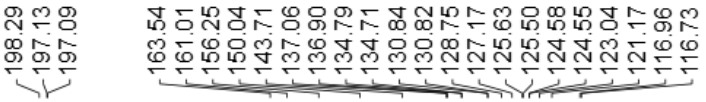

8.73
8.72
8.09
7.79
7.79
7.78
7.78
7.78
7.30
7.29
7.28
7.27
7.26
3.34
3.32
3.31
3.07
3.06
3.05
2.07
2.06
2.05
2.04
2.03
2.03
2.02
1.09
1.08
1.07
1.06
1.06
0.94
0.93
0.93
0.92
0.91
0.90
O
O
N
3ag
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
4.04
2.11
1.08
2.11
2.10
1.14
2.14
2.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0

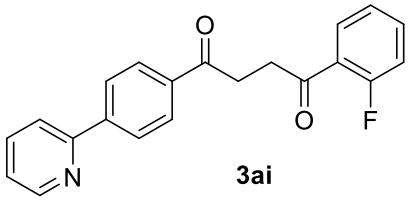

209.51
198.46
156.23
150.04
143.70
137.05
136.87
128.70
127.14
123.04
121.16
77.41
77.16
76.91
36.95
32.59
20.85
10.96
O
O
N
3ag
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


8.70
8.69
8.10
8.08
8.07
8.05
8.03
7.79
7.79
7.79
7.77
7.77
7.77
7.75
7.75
7.75
7.74
7.73
7.35
7.34
7.34
7.32
7.32
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.20
3.46
3.46
3.43
3.34
3.32
3.31
2.47
O
O
Me
N
3ah
1H NMR (400 MHz, CDCl3)
1.00
4.10
1.04
1.98
1.11
3.12
1.99
2.01
2.97
f1 (ppm)


202.74
198.41
156.20
149.97
143.65
138.23
137.90
137.10
136.88
132.01
131.45
128.75
128.72
127.18
125.83
123.05
121.21
77.48
77.16
76.84
35.40
33.12
21.42
O
O
Me
N
3ah
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

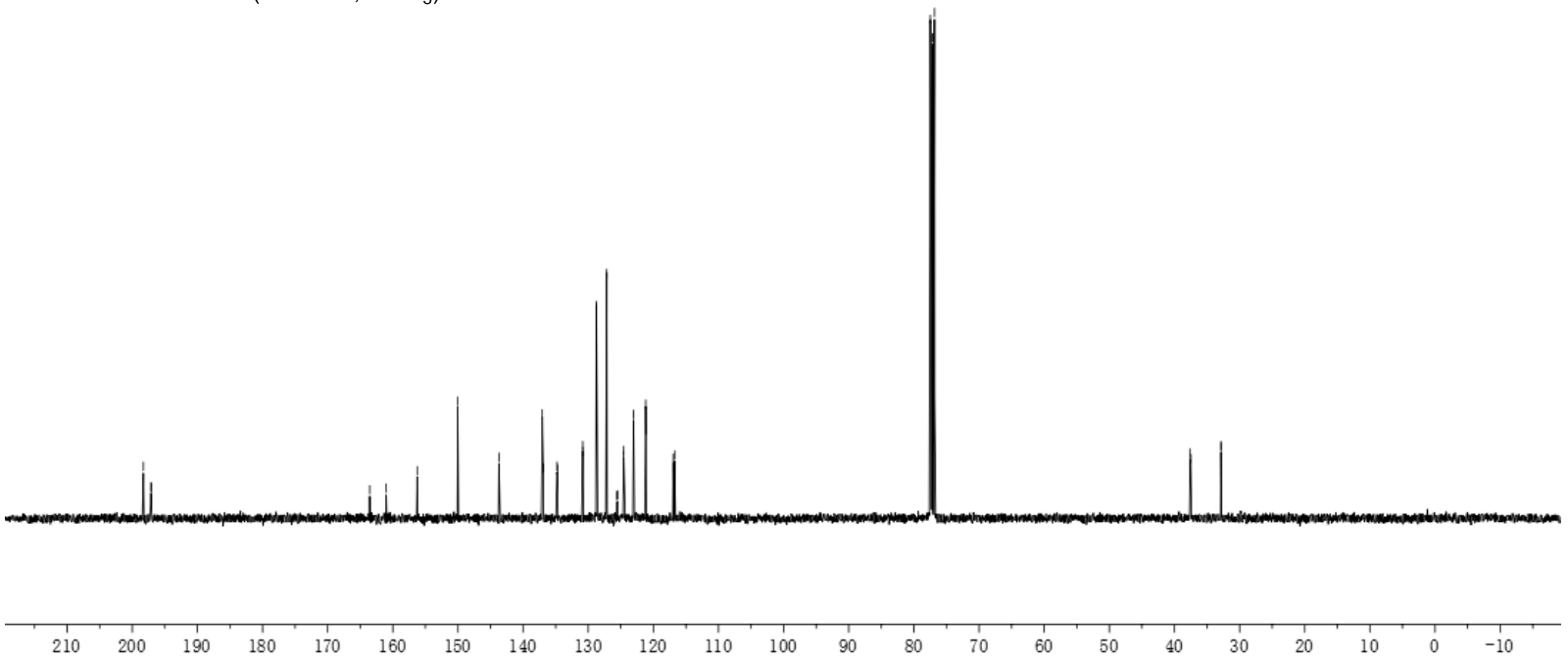

8.74
8.72
8.15
8.13
8.12
8.10
7.93
7.93
7.92
7.91
7.90
7.89
7.80
7.79
7.56
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.24
7.22
7.22
7.19
7.19
7.17
7.17
7.16
7.16
7.14
7.14
3.51
3.49
3.49
3.48
O
O
F
N
3ai
1H NMR (400 MHz, CDCl3)
1.00
2.14
2.13
1.16
1.16
1.17
4.34
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5

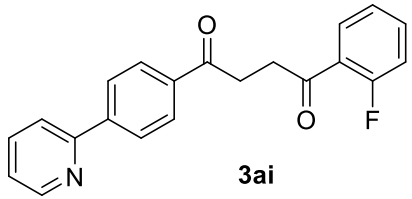




3ai

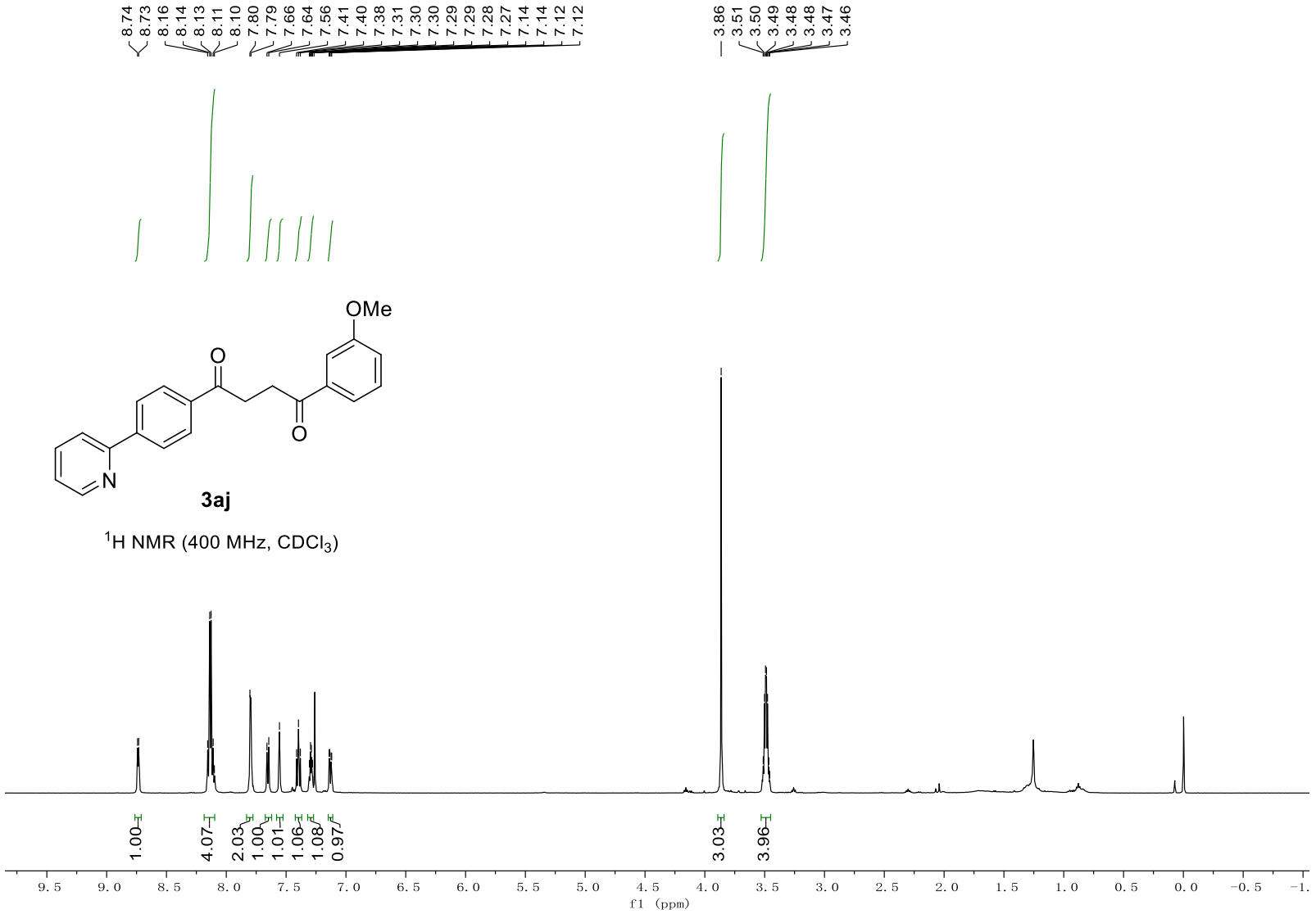
^{13}C NMR (101 MHz, $CDCl_3$)

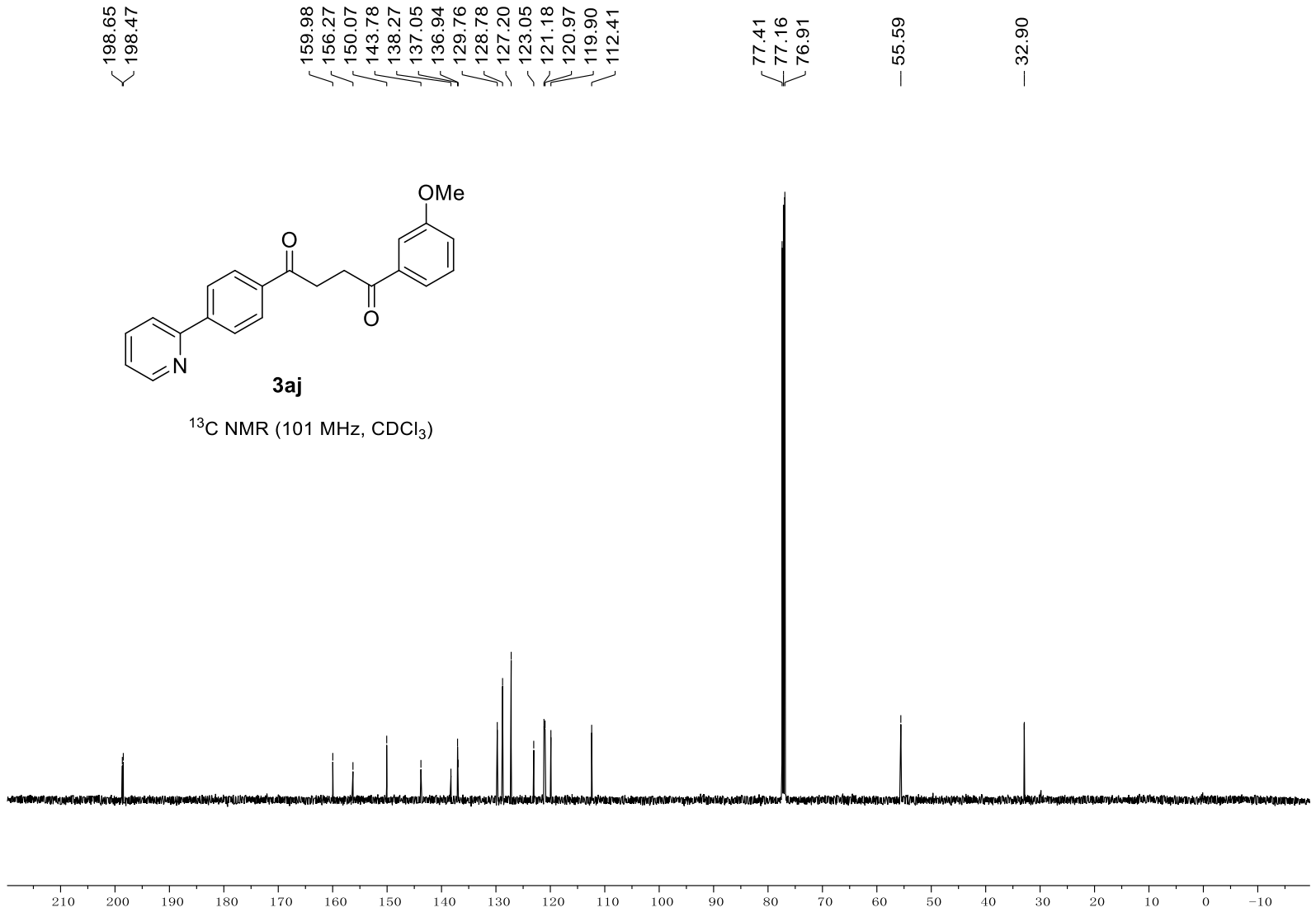


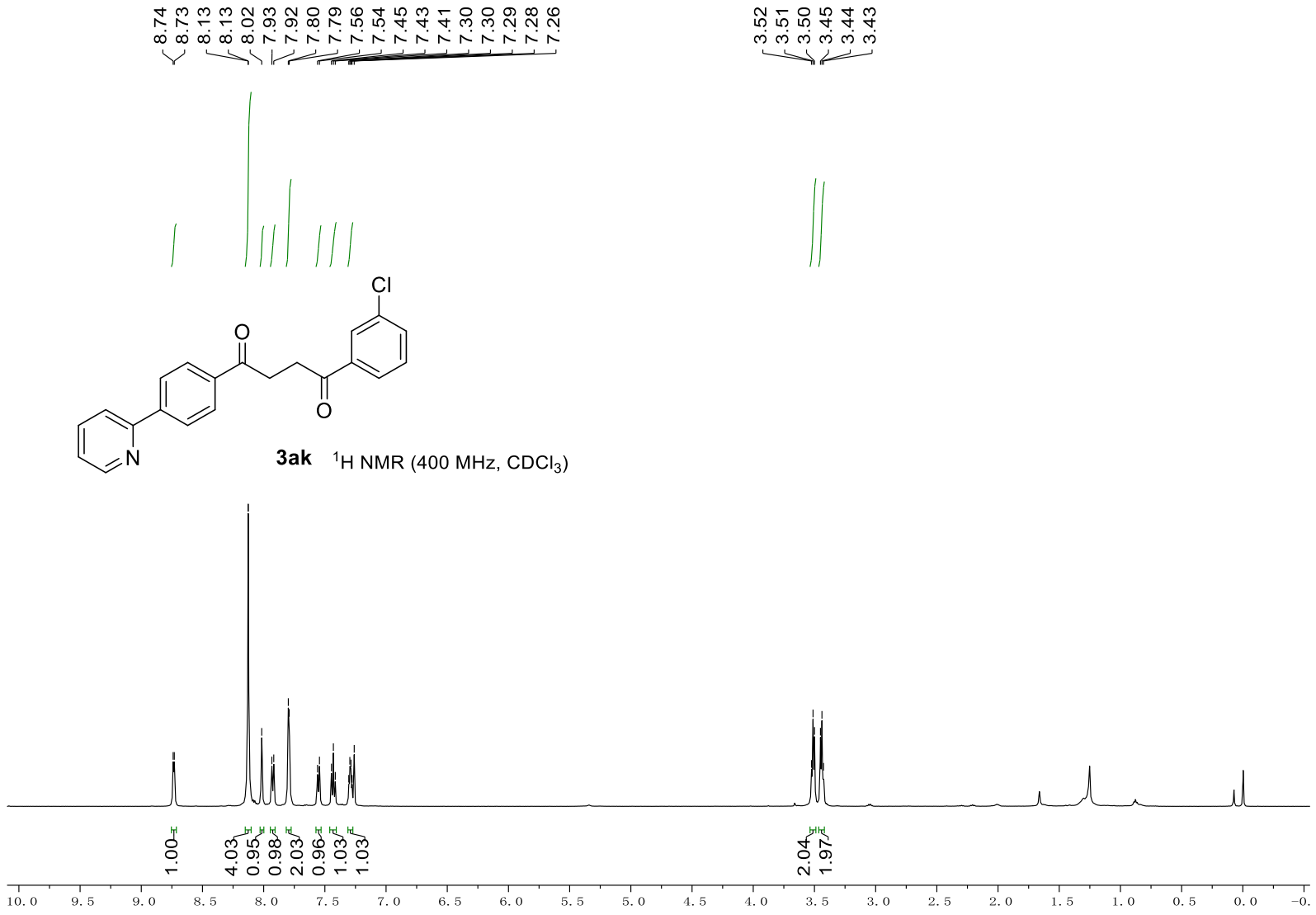


3ai

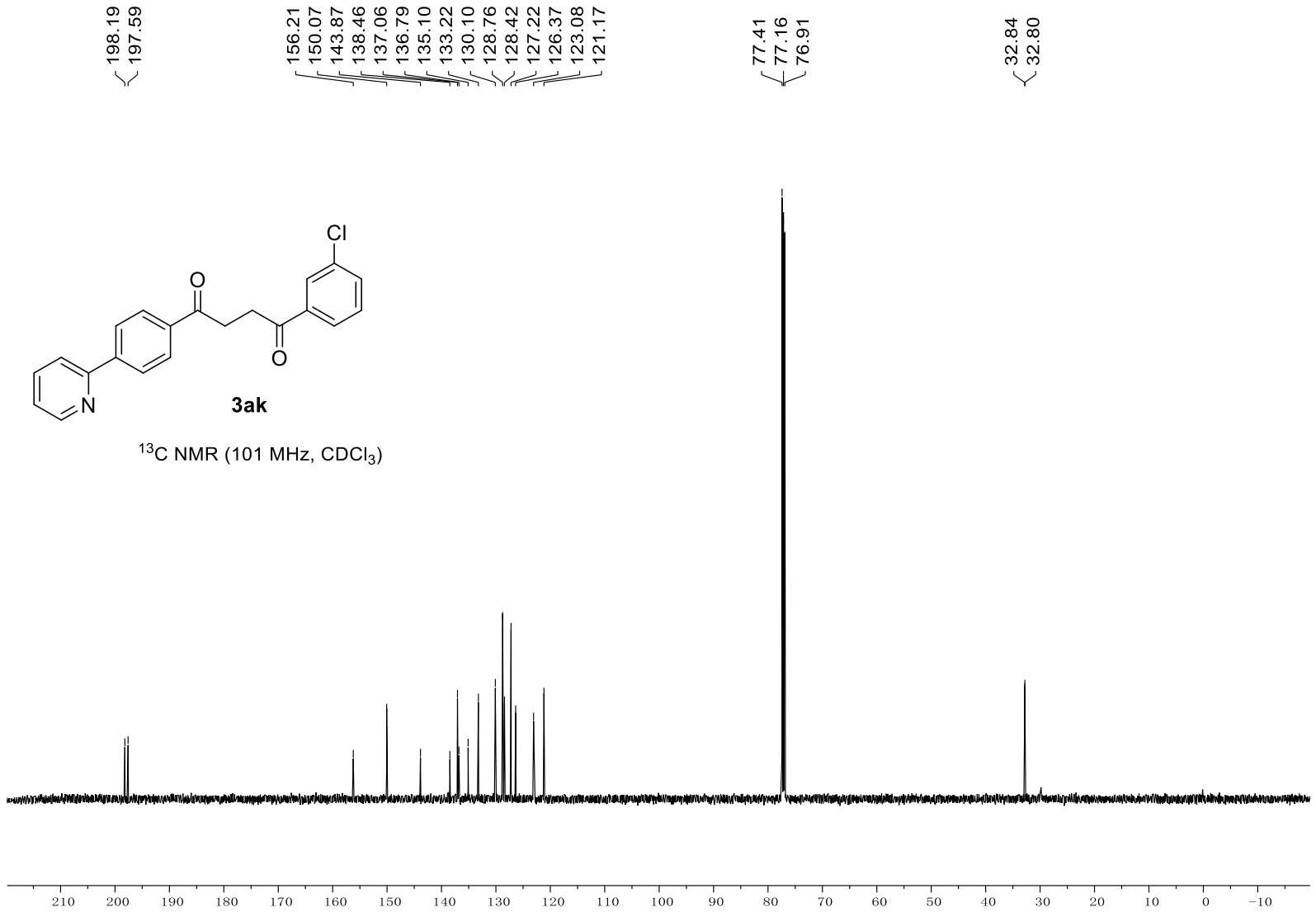
^{19}F NMR (376 MHz, $CDCl_3$)

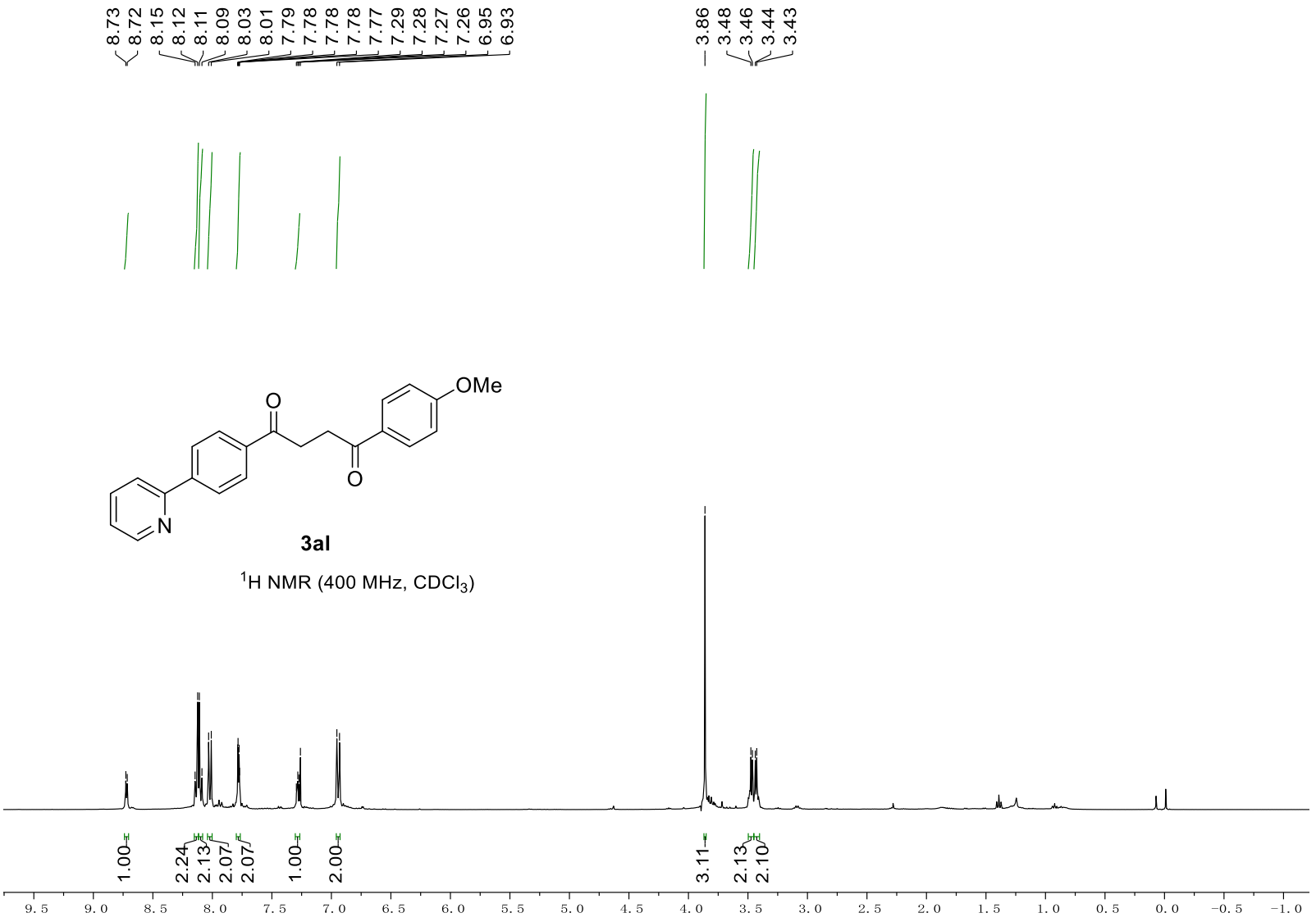

8.74
8.73
8.16
8.14
8.13
8.11
8.10
7.80
7.79
7.66
7.64
7.56
7.41
7.40
7.38
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.14
7.14
7.12
7.12
3.86
3.51
3.50
3.49
3.48
3.48
3.47
3.46
OMe
O
O
N
3aj
1H NMR (400 MHz, CDCl3)
1.00
4.07
2.03
1.00
1.01
1.06
1.08
0.97
3.03
3.96
f1 (ppm)


198.65
198.47
159.98
156.27
150.07
143.78
138.27
137.05
136.94
129.76
128.78
127.20
123.05
121.18
120.97
119.90
112.41
77.41
77.16
76.91
55.59
32.90
OMe
O
O
N
3aj
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

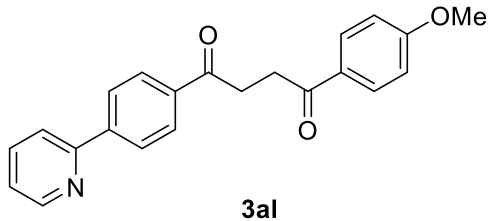


3ak ^{1}H NMR (400 MHz, $CDCl_3$)


198.19
197.59
156.21
150.07
143.87
138.46
137.06
136.79
135.10
133.22
130.10
128.76
128.42
127.22
126.37
123.08
121.17
77.41
77.16
76.91
32.84
32.80
Cl
O
O
N
3ak
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

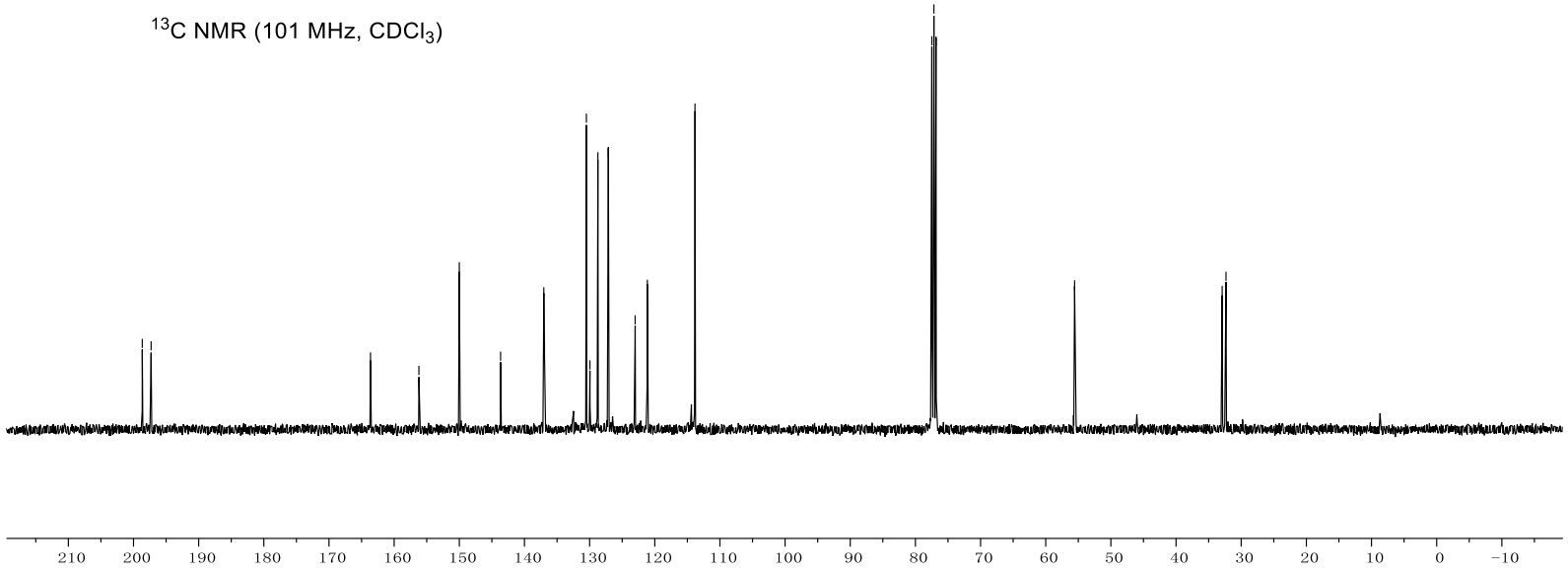

8.73
8.72
8.15
8.12
8.11
8.09
8.03
8.01
7.79
7.78
7.78
7.78
7.77
7.29
7.28
7.27
7.26
6.95
6.93
3.86
3.48
3.46
3.44
3.43
OMe
O
O
N
3al
1H NMR (400 MHz, CDCl3)
1.00
2.24
2.13
2.07
2.07
1.00
2.00
3.11
2.13
2.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0

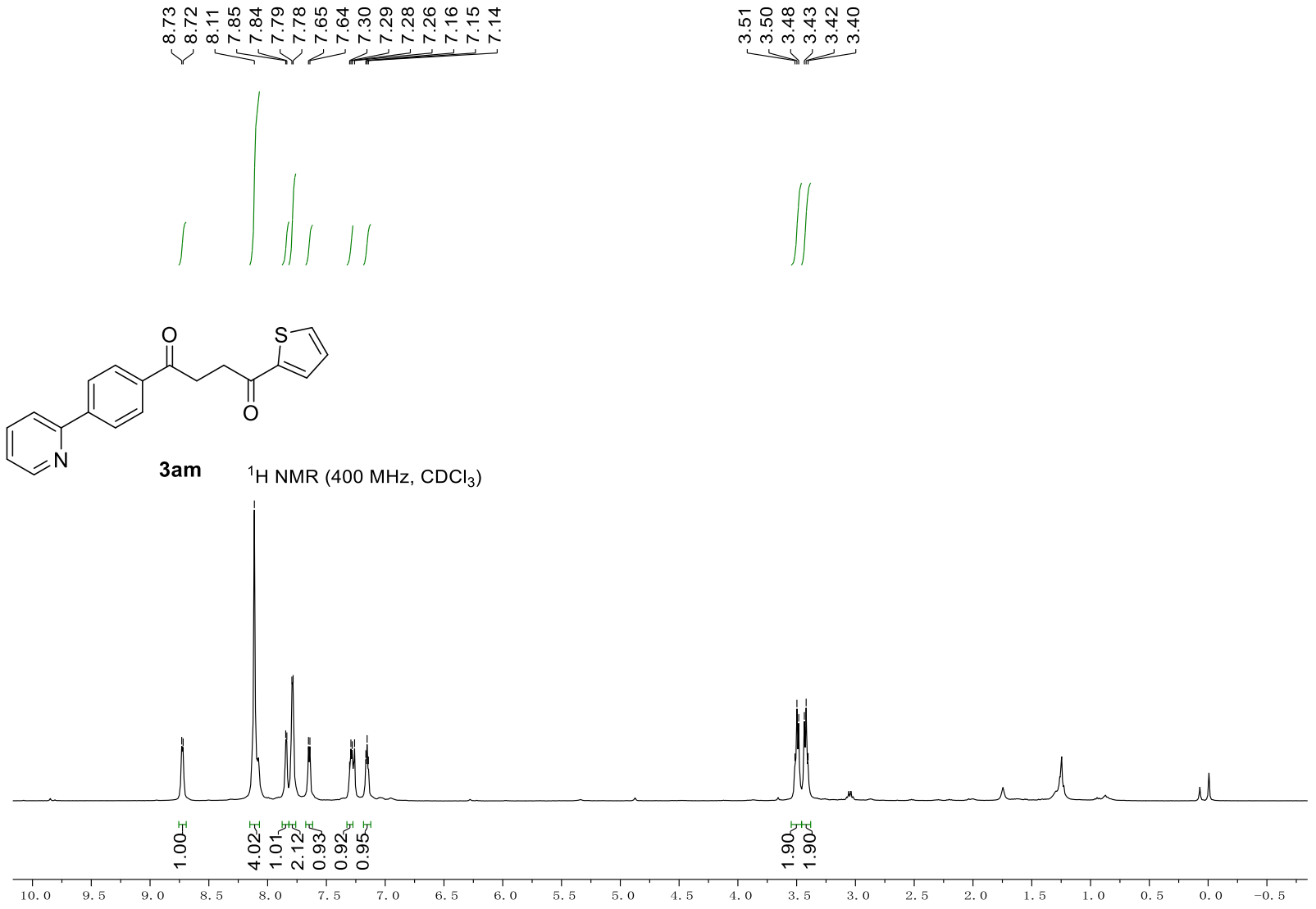
198.66
197.30
163.63
156.20
150.00
143.66
137.03
136.93
130.50
129.95
128.73
127.13
123.01
121.14
113.83
77.48
77.16
76.84
55.57
32.92
32.33

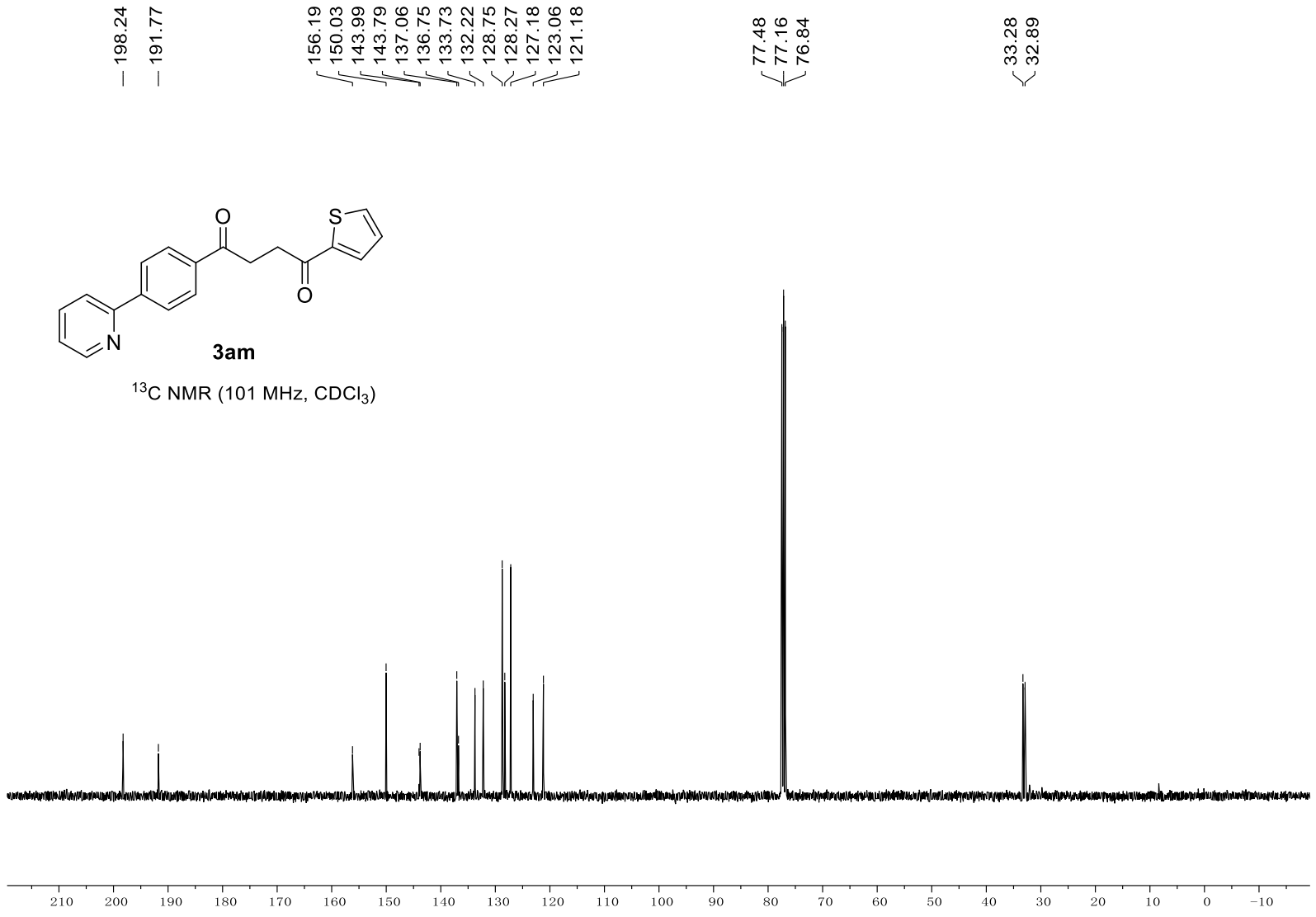


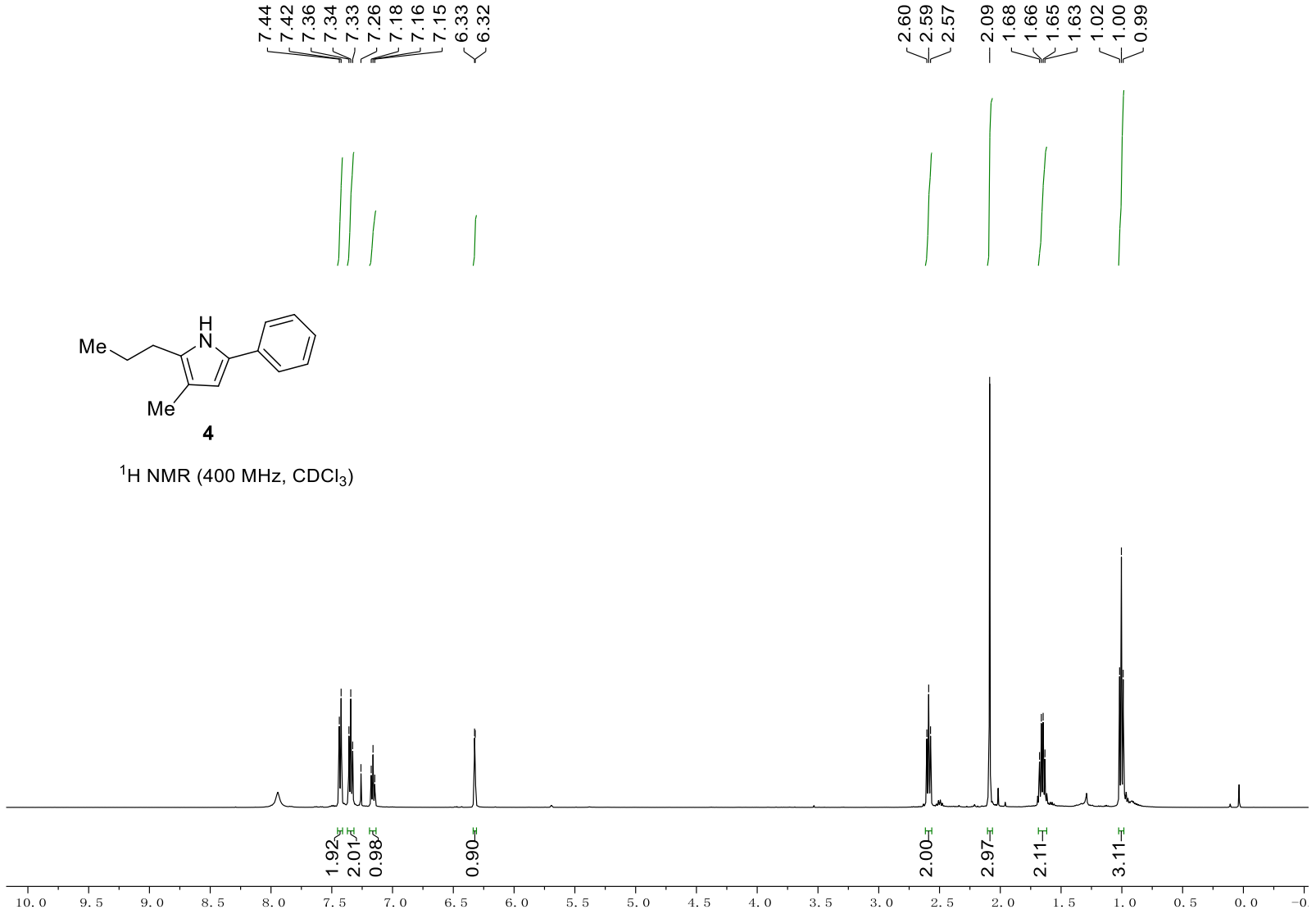
3al

^{13}C NMR (101 MHz, $CDCl_3$)



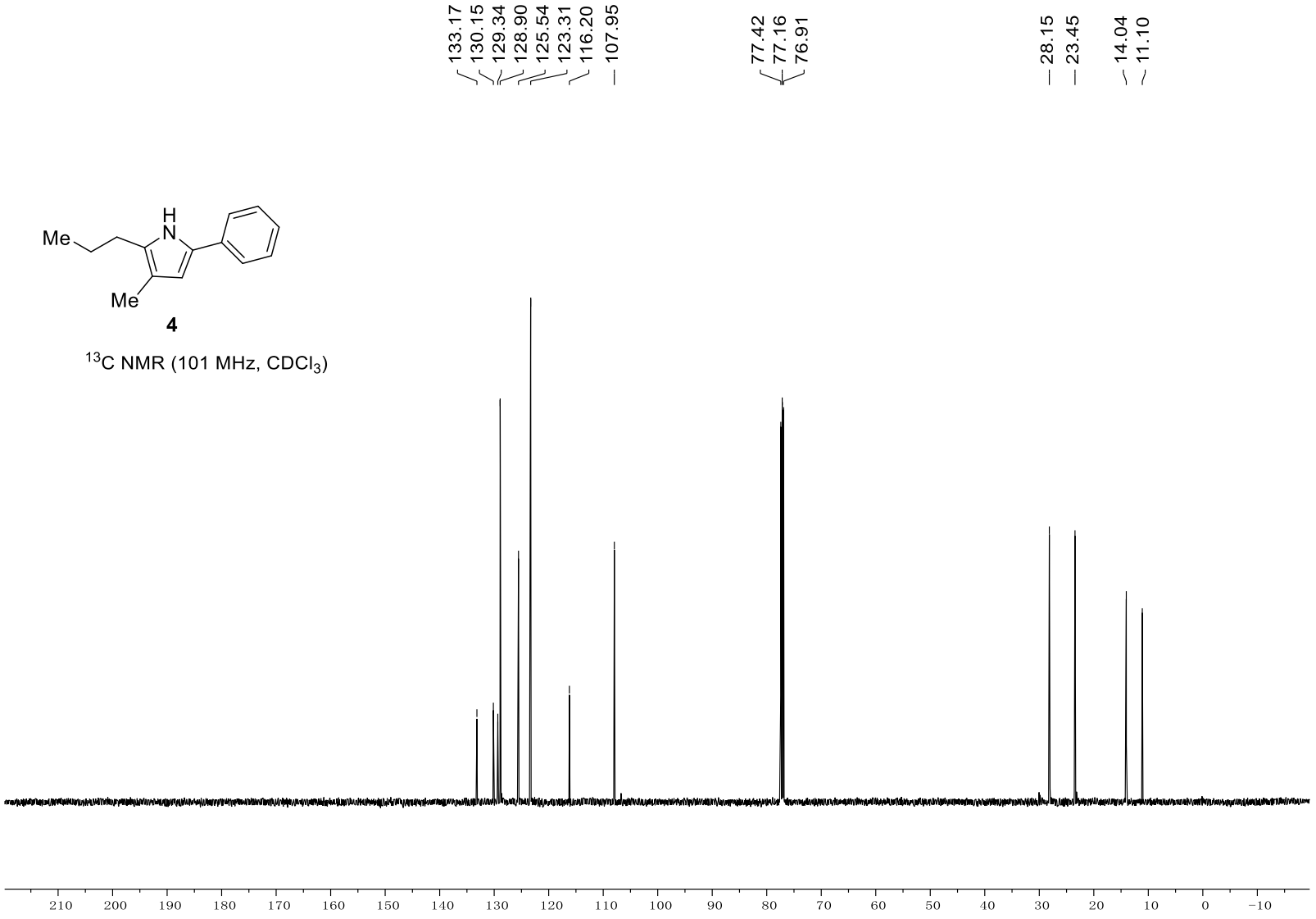

8.73
8.72
8.11
7.85
7.84
7.79
7.78
7.65
7.64
7.30
7.29
7.28
7.26
7.16
7.15
7.14
3.51
3.50
3.48
3.43
3.42
3.40
O
S
O
N
3am
1H NMR (400 MHz, CDCl3)
1.00
4.02
1.01
2.12
0.93
0.92
0.95
1.90
1.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

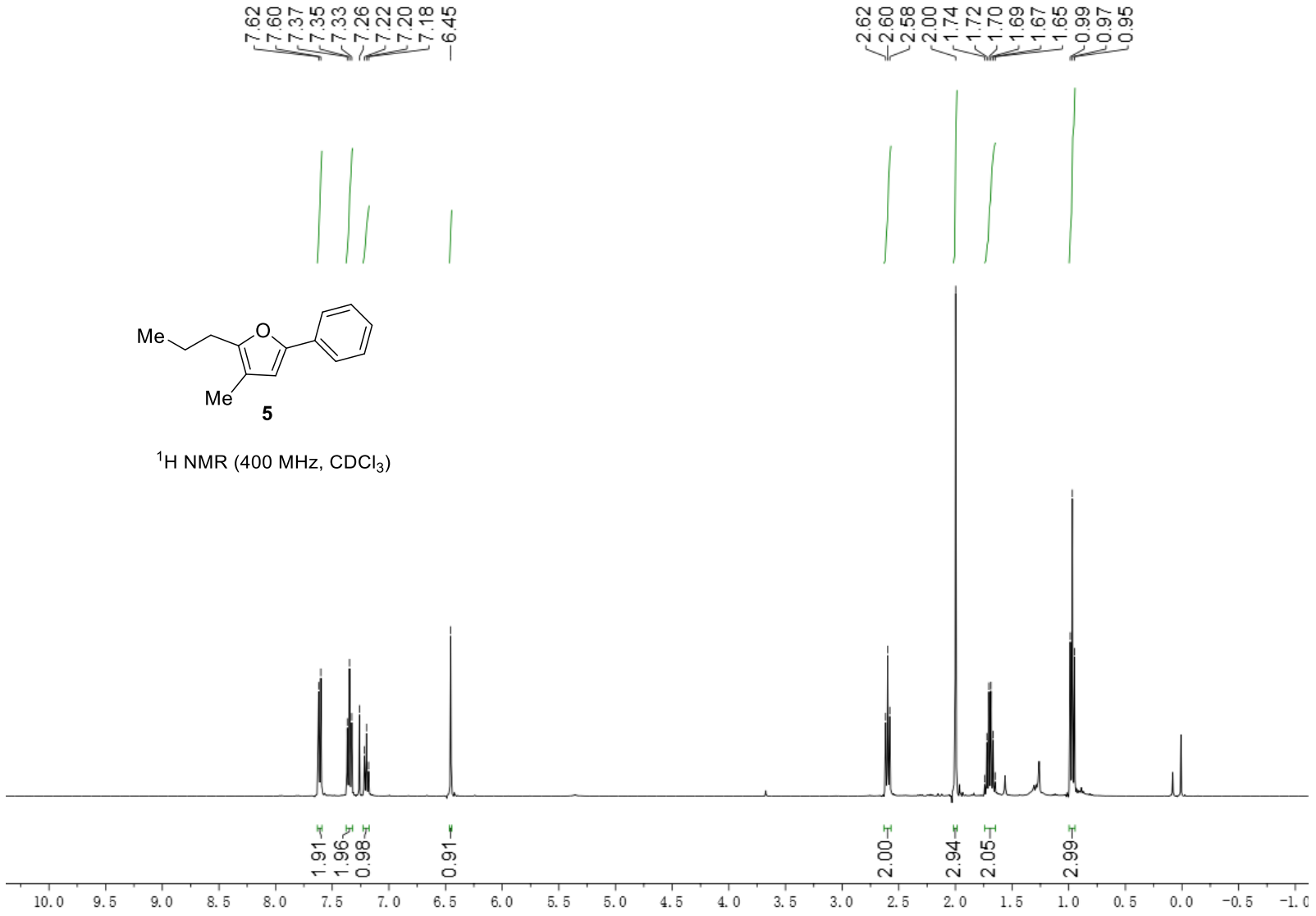

198.24
191.77
156.19
150.03
143.99
143.79
137.06
136.75
133.73
132.22
128.75
128.27
127.18
123.06
121.18
77.48
77.16
76.84
33.28
32.89
O
S
O
N
3am
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

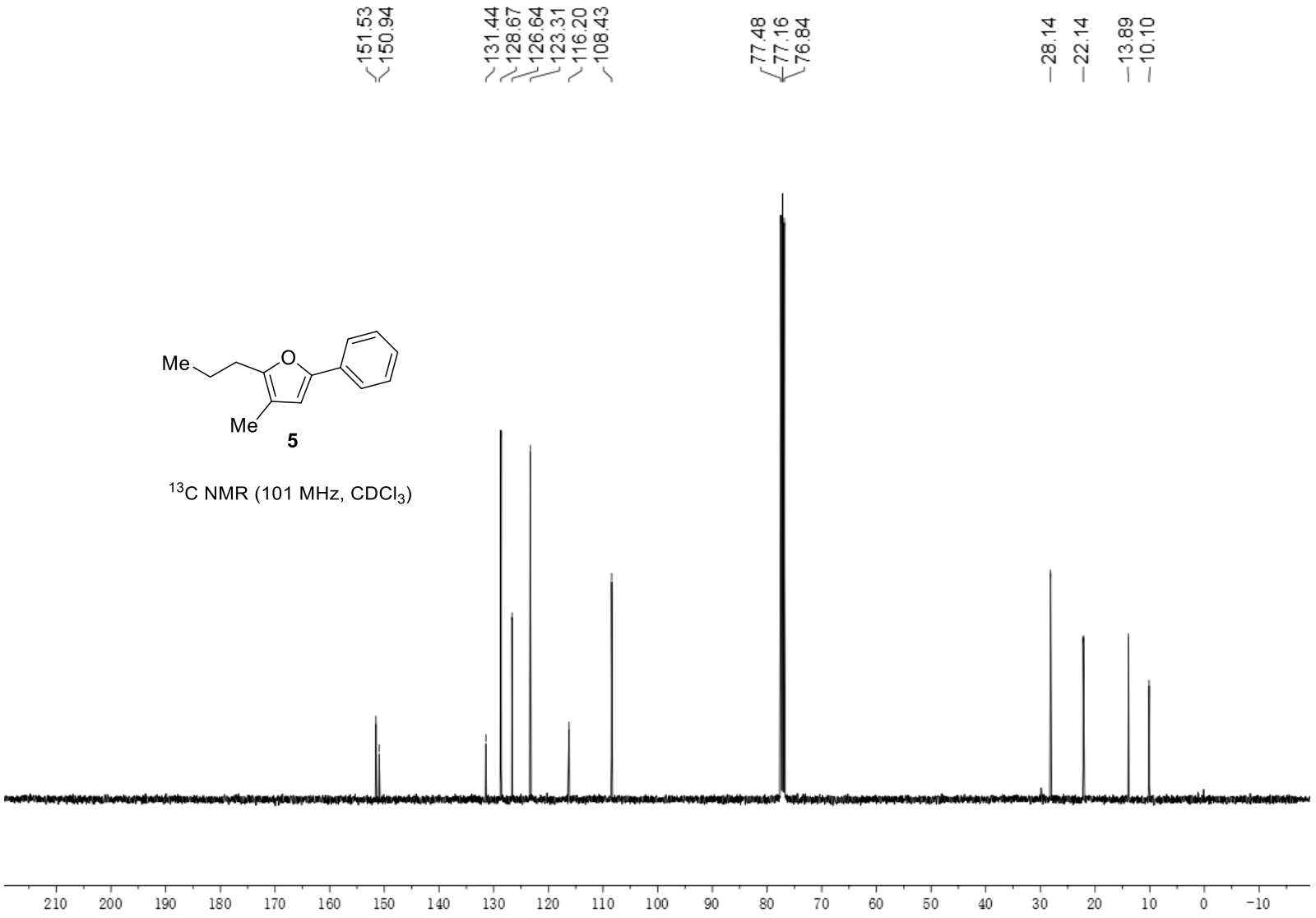


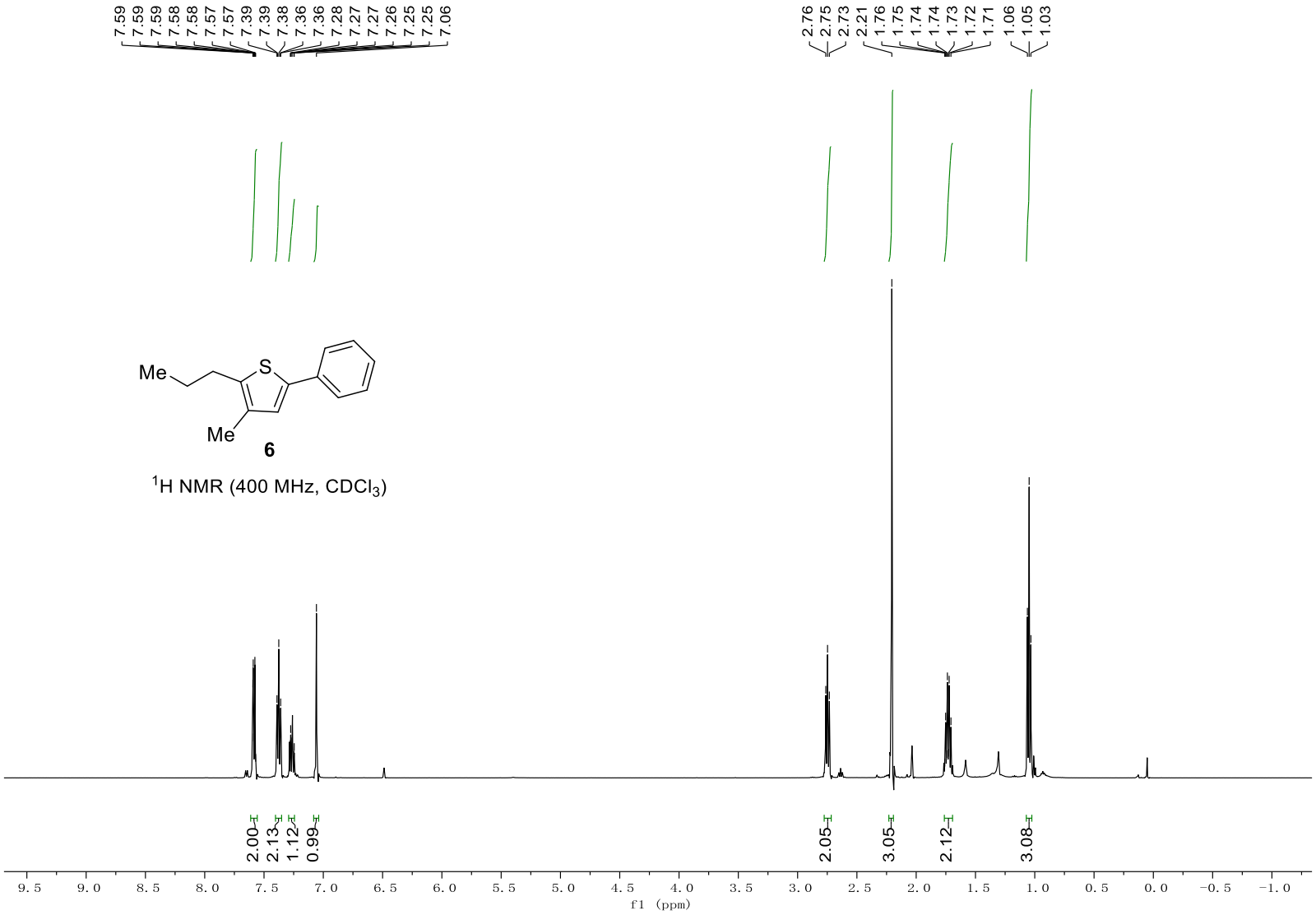
4

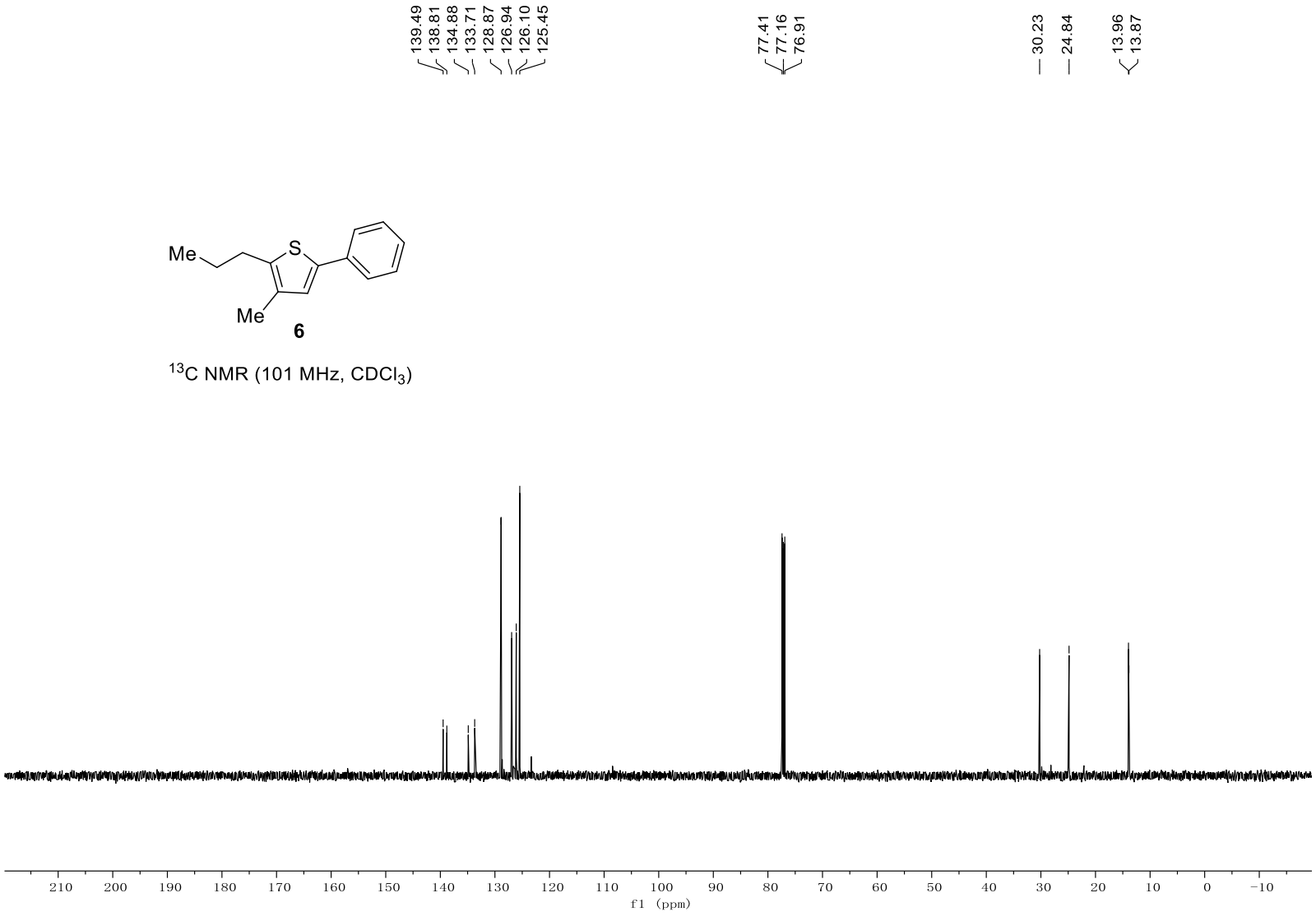
^{1}H NMR (400 MHz, $CDCl_3$)


133.17
130.15
129.34
128.90
125.54
123.31
116.20
107.95
77.42
77.16
76.91
28.15
23.45
14.04
11.10
Me
H
N
Me
4
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10


7.62
7.60
7.37
7.35
7.33
7.26
7.22
7.20
7.18
6.45
2.62
2.60
2.58
2.00
1.74
1.72
1.70
1.69
1.67
1.65
0.99
0.97
0.95
Me
O
Me
5
1H NMR (400 MHz, CDCl3)
1.91
1.96
0.98
0.91
2.00
2.94
2.05
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


151.53
150.94
131.44
128.67
126.64
123.31
116.20
108.43
77.48
77.16
76.84
28.14
22.14
13.89
10.10
Me
O
Me
5
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.39
7.39
7.38
7.36
7.36
7.28
7.27
7.27
7.26
7.25
7.25
7.06
2.76
2.75
2.73
2.21
1.76
1.75
1.74
1.74
1.73
1.72
1.71
1.06
1.05
1.03
Me
S
Me
6
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
2.13
1.12
0.99
2.05
3.05
2.12
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


139.49
138.81
134.88
133.71
128.87
126.94
126.10
125.45
77.41
77.16
76.91
30.23
24.84
13.96
13.87
Me
S
Me
6
^{13}C NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)