A Synergistic LUMO Lowering Strategy Using Lewis Acid Catalysis in Water to Enable Photoredox Catalytic, Functionalizing C-C Cross-Coupling of Styrenes

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Supporting Information

Table of Contents

1 General Methods

Unless otherwise noted, all commercially available compounds were used as received without further purification.

NMR spectra were recorded on a Varian Mercury plus 300 (300.08 MHz) and Varian Mercury plus 400 (400.00 MHz) using the solvent peak as internal reference ($CDCl_3$: δ H 7.26; δ C 77.0 and C_6D_6: δ H 7.16; δ C 128.4). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet); coupling constants (*J*) are in Hertz (Hz).

ESI-MS spectra were recorded on a BRUKER DALTONICS Esquire 3000 Plus ESI-Ion Trap mass spectrometer or BRUKER DALTONICS Impact II ESI-TOF mass spectrometer. Ionization modes are specified in the descriptions of the corresponding experiments.

All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F_{254}; visualization was accomplished with UV light and/or staining with appropriate stains. Flash chromatography was performed on a BIOTAGE Isolera One using 50 g, 25 g or 10 g SNAP cartridge KP-Sil columns filled with MACHEREY NAGEL silica gel 60 (size 40−63 μm).

GC-FID spectra were recorded on a Thermo Scientific Trace 1310 gas chromatograph equipped with a Thermo Scientific TG-5MS column (5% diphenyl- and 95% dimethylpolysiloxane, 0.25 mm ID, 0.25 μm film thickness, length 30 m) using hydrogen as carrier gas and nitrogen as make-up gas.

Irradiation was performed with twelve OSRAM Oslon SSL royal blue (455 nm) LEDs attached to an aluminum heat sink. The LEDs were operated at approx. 700 mA per LED.

Cyclic voltammetry measurements were performed with a EMSTAT3 Standard PalmSens ES316X965 equipped with a glassy carbon electrode as working electrode and platinum wire as counter electrode. Silver wire was used as pseudo reference electrode and an aq. 0.1 M solution of tetrabutylammonium tetrafluoroborate was applied as supporting electrolyte. Scan rate was set to 100 mV/s. Solutions were degassed with argon prior measurement and experiments were performed under atmosphere of argon. Ferrocene (Fc/Fc^+) was used as an internal reference to determine the reduction and oxidation potentials. The applied solvents are specified within the description of the corresponding experiments.

Stern-Volmer experiments were done with a Shimadzu RF-6000 Spectro Fluorophotometer in 1cm quartz cuvettes.

2 General Procedures

General Procedure A

To a solution of the respective acetophenone (1.0 equiv) in diethylether (0.67 M), bromine (1.0 equiv) was added. The mixture was stirred for approximately one hour (conversion monitored by TLC). The mixture was subsequently poured into an aqueous thiosulfate solution (1 M) and washed three times with water. The organic phase was dried over Na_2SO_4 and after filtration the solvent was removed under reduced pressure. The residue was dissolved in acetone (1 M) and DIPEA (2 equiv) and acetic acid (1.2 equiv) were added. After refluxing the mixture for 12 h the solution was poured into water and extracted with DCM (3×). The combined organic phases were washed with H_2SO_4 (2 M) and a saturated $NaHCO_3$ solution. Following drying over Na_2SO_4 and filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography.

General Procedure B

fac-Ir(ppy)$_3$ (0.5 mol %), Nd(OTf)$_3$ (10 mol %), K_2CO_3 (2.0 equiv) and 2-oxo-2-phenylethyl acetate (1.0 equiv) were added to a Schlenk tube and dissolved in an acetonitrile/water mixture (4:1 *v/v*, 0.25 M). The freshly distilled styrene derivative (1.0 equiv) was added and the mixture was degassed *via* four freeze-pump-thaw cycles. The reaction mixture was subsequently irradiated with blue LEDs for the time indicated. The mixture was poured into water and extracted with DCM (3×). The organic layers were combined and dried over Na_2SO_4. Following filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography.

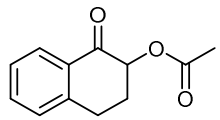
General Procedure C

fac-Ir(ppy)$_3$ (0.5 mol %), Nd(OTf)$_3$ (10 mol %), K_2CO_3 (2.0 equiv) and the respective acetophenone (1.0 equiv) were added in a Schlenk tube and dissolved in an acetonitrile/water mixture (4:1 *v/v*, 0.25 M). Freshly distilled styrene (1.0 equiv) was added and the mixture was degassed *via* four freeze-pump-thaw cycles. The reaction mixture was subsequently irradiated with blue LEDs for the time indicated. The mixture was poured into water and extracted with DCM (3×). The organic layers were combined and dried over Na_2SO_4. Following filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography.

3 Experimental Data

3.1 Experimental Data of α-Acetoxyacetophenone Substrates

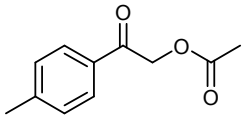
1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl acetate (I)



$C_{12}H_{12}O_3$
204.23 g/mol

According to **general procedure A** using 1.46 g 3,4-dihydronaphthalen-1(2*H*)-one (10.0 mmol, 1.0 equiv). Yield after column chromatography (50 g silica gel, hexanes/ethyl acetate 3-20%): 1.23 g (6.0 mmol, 60%), brownish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 5.54 (dd, *J* = 13.4, 5.2 Hz, 1H), 3.27 – 3.01 (m, 2H), 2.46 – 2.25 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 170.2, 143.0, 133.9, 131.5, 128.6, 127.8, 126.9, 74.5, 29.1, 27.9, 20.8. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{12}H_{12}O_3Na$ 227.0679; Found: 227.0678.

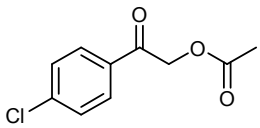
2-Oxo-2-(*p*-tolyl)ethyl acetate (II)



$C_{11}H_{12}O_3$
192.21 g/mol

According to **general procedure A** using 1.34 g 4-methylacetophenone (10.0 mmol, 1.0 equiv). Yield after column chromatography (50 g silica gel, hexanes/ethyl acetate 3-20%): 1.28 g (6.6 mmol, 66%), orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.32 (s, 2H), 2.42 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 170.4, 144.8, 131.7, 129.5, 127.8, 65.9, 21.7, 20.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{11}H_{12}O_3Na$ 215.0679; Found: 215.0678.

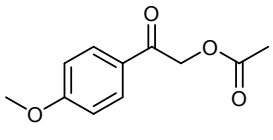
2-(4-Chlorophenyl)-2-oxoethyl acetate (III)



$C_{10}H_9ClO_3$
212.63 g/mol

2.34 g 4-chlorophenacyl bromide (10.0 mmol, 1.0 equiv) was dissolved in 10 ml acetone. 2.59 g DIPEA (20.0 mol, 2.0 equiv) and 0.72 g acetic acid (12.0 mmol, 1.2 equiv) were added. After refluxing the mixture for 12 h the solution was poured into water and extracted with DCM (3×). The combined organic phases were washed with H_2SO_4 (2 M) and a saturated $NaHCO_3$ solution. Following drying over Na_2SO_4 and filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography. Yield after column chromatography (50 g silica gel, hexanes/ethyl acetate 3-18%): 2.11 g (9.9 mmol, 99%), colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 – 7.83 (m, 2H), 7.48 – 7.44 (m, 2H), 5.28 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 170.3, 140.4, 132.5, 129.2, 129.1, 65.8, 20.5. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{10}H_9ClO_3Na$ 235.0132; Found: 235.0118.

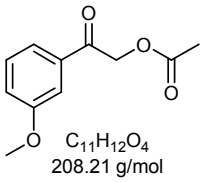
2-(4-Methoxyphenyl)-2-oxoethyl acetate (IV)



$C_{11}H_{12}O_4$
208.21 g/mol

According to **general procedure A** using 1.50 g 4-acetylanisole (10.0 mmol, 1.0 equiv). Yield after column chromatography (50 g silica gel, hexanes/ethyl acetate 3-25%): 0.94 g (4.5 mmol, 45%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.29 (s, 2H), 3.87 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 170.5, 164.0, 130.0, 127.2, 114.0, 65.7, 55.5, 20.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{11}H_{12}O_4Na$ 231.0628; Found: 231.0611.

2-(3-Methoxyphenyl)-2-oxoethyl acetate (V)

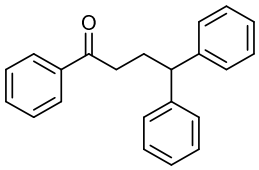


$C_{11}H_{12}O_4$
208.21 g/mol

According to **general procedure A** using 9.16 g 3-acetylanisole (40.0 mmol, 1.0 equiv). Yield after column chromatography (50 g silica gel, hexanes/ethyl acetate 3-25%): 3.81 g (18.3 mmol, 46%), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.35 (m, 3H), 7.16 – 7.12 (m, 1H), 5.31 (s, 2H), 3.85 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 170.4, 159.9, 135.4, 129.8, 120.4, 120.1, 112.0, 66.1, 55.4, 20.5. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{11}H_{12}O_4Na$ 231.0628; Found: 231.0627.

3.2 Experimental Data of Cross-Coupled Products

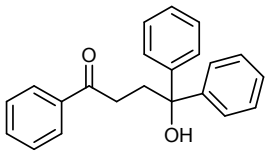
1,4,4-Triphenylbutan-1-one (3)



$C_{22}H_{20}O$
300.40 g/mol

3.9 mg **4CzIPN** (1.0 mol %) and 98 mg 2-oxo-2-phenylethyl acetate (0.50 mmol, 1.0 equiv) were added in a Schlenk tube and dissolved in 3.0 mL of a acetonitrile/water (4:1 *v/v*) mixture. 180 mg 1,1-Diphenylethylene (1.0 mmol, 2.0 equiv) was added and the mixture irradiated with blue LEDs for 2 h. The mixture was poured into water and extracted with DCM (3×). The organic layers were combined and dried over Na_2SO_4. Following filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%) to yield 124 mg **3** (83%, 0.41 mmol) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 – 7.82 (m, 2H), 7.58 – 7.49 (m, 1H), 7.45 – 7.38 (m, 2H), 7.34 – 7.26 (m, 8H), 7.23 – 7.15 (m, 2H), 4.03 (t, *J* = 7.9 Hz, 1H), 2.94 (dd, *J* = 8.1, 6.8 Hz, 2H), 2.57 – 2.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 144.4, 136.9, 132.9, 128.53, 128.49, 128.0, 127.9, 126.3, 50.5, 36.9, 29.8. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{22}H_{20}ONa$ 323.1406; Found: 323.1403.

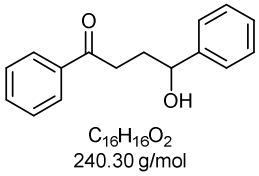
4-Hydroxy-1,4,4-triphenylbutan-1-one (4)



$C_{22}H_{20}O_2$
316.40 g/mol

According to **general procedure B** using 67 mg 1-methoxy-4-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-20%): 142 mg (0.45 mmol, 90%), colorless solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.75 – 7.70 (m, 2H), 7.47 – 7.42 (m, 3H), 7.14 – 7.08 (m, 5H), 7.07 – 6.99 (m, 3H), 6.98 – 6.94 (m, 2H), 2.84 – 2.66 (m, 4H), 2.31 (s, 1H). ^{13}C NMR (101 MHz, C_6D_6) δ 200.1, 147.7, 137.4, 132.7, 128.6, 128.4, 128.3, 127.0, 126.5, 77.5, 36.0, 33.8. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{22}H_{20}O_2Na$ 339.1356; Found: 339.1358.

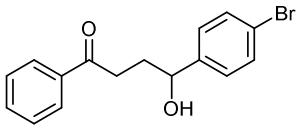
2-Oxo-1,2-diphenylethyl benzoate (8)



$C_{16}H_{16}O_2$
240.30 g/mol

According to **general procedure B** using 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 104 mg (0.43 mmol, 87%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.91 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.34 (m, 4H), 7.30 – 7.27 (m, 1H), 4.84 (dd, *J* = 7.3, 5.3 Hz, 1H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.49 (bs, 1H), 2.26 – 2.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 144.3, 136.8, 133.1, 128.6, 128.5, 128.1, 127.6, 125.7, 73.59, 34.8, 33.0. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{16}O_2Na$ 263.1043; Found: 263.1040.

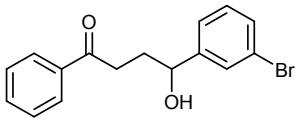
4-(4-Bromophenyl)-4-hydroxy-1-phenylbutan-1-one (12)



$C_{16}H_{15}BrO_2$
319.20 g/mol

According to **general procedure B** using 91 mg 1-bromo-4-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-25%): 127 mg (0.40 mmol, 80%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.29 – 7.26 (m, 4H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.63 (dd, *J* = 7.7, 4.8 Hz, 1H), 2.97 – 2.89 (m, 2H), 2.36 (bs, 1H), 2.05 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 143.4, 136.6, 133.2, 131.5, 128.6, 128.0, 127.5, 121.2, 72.8, 34.5, 32.9. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{15}BrO_2Na$ 341.0148; Found: 341.0145.

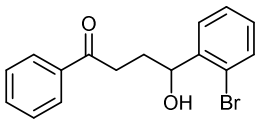
4-(3-Bromophenyl)-4-hydroxy-1-phenylbutan-1-one (13)



$C_{16}H_{15}BrO_2$
319.20 g/mol

According to **general procedure B** using 91 mg 1-bromo-3-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 112 mg (0.35 mmol, 70%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.93 (m, 2H), 7.56 – 7.54 (m, 2H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 1H), 7.30 – 7.28 (m, 1H), 7.22 – 7.18 (m, 1H), 4.80 (dd, *J* = 7.9, 4.5 Hz, 1H), 3.19 – 3.05 (m, 2H), 2.61 (bs, 1H), 2.24 – 2.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 146.8, 136.6, 133.2, 130.5, 130.0, 128.8, 128.6, 128.1, 124.3, 122.6, 72.8, 34.6, 33.0. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{15}BrO_2Na$ 341.0148; Found: 341.0137.

4-(2-Bromophenyl)-4-hydroxy-1-phenylbutan-1-one (14)

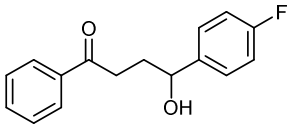


$C_{16}H_{15}BrO_2$
319.20 g/mol

According to **general procedure B** using 91 mg 1-bromo-2-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 115 mg (0.36 mmol, 72%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.96 (m, 2H), 7.62 – 7.50 (m, 3H), 7.48 – 7.44 (m, 2H), 7.36 – 7.32 (m, 1H), 7.13 (td, *J* = 7.6, 1.8 Hz, 1H), 5.17 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.30 – 3.07 (m, 2H), 2.33 – 2.12 (m, 2H).[1] ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 143.3, 136.7, 133.2, 132.7, 128.8, 128.6, 128.1, 127.7, 127.4, 121.8, 72.5, 35.2, 31.4. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{15}BrO_2Na$ 341.0148; Found: 341.0129.

[1] The proton signal of the OH-group is missing in the ^{1}H NMR spectrum.

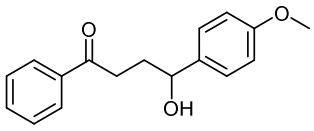
4-(4-Fluorophenyl)-4-hydroxy-1-phenylbutan-1-one (15)



$C_{16}H_{15}FO_2$
258.29 g/mol

According to **general procedure B** using 61 mg 1-fluoro-4-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-20%): 124 mg (0.48 mmol, 96%) colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 – 7.90 (m, 2H), 7.61 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 7.38 – 7.32 (m, 2H), 7.07 – 6.99 (m, 2H), 4.83 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.56 (bs, 1H), 2.22 – 2.14 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$): -115.1. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 162.1 (d, *J* = 245.4 Hz), 140.2, 136.8, 133.2, 128.6, 128.1, 127.4 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.2 Hz), 73.0, 34.7, 33.2. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{15}FO_2Na$ 281.0948; Found: 281.0938.

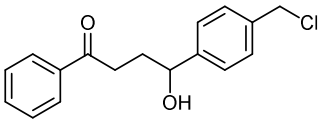
4-Hydroxy-4-(4-methoxyphenyl)-1-phenylbutan-1-one (16)



$C_{17}H_{18}O_3$
270.33 g/mol

According to **general procedure B** using 67 mg 1-methoxy-4-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-20%): 116 mg (0.43 mmol, 86%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.93 (m, 2H), 7.57 – 7.53 (m, 1H), 7.46 – 7.43 (m, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.77 (t, *J* = 6.5 Hz, 1H), 3.82 – 3.77 (m, 3H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.46 (s, 1H), 2.21 – 2.16 (m, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 159.0, 136.8, 136.5, 133.1, 128.5, 128.1, 127.0, 113.8, 73.2, 55.3, 34.8, 33.0. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{18}O_3Na$ 293.1148; Found: 293.1148.

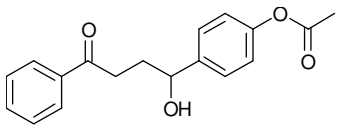
4-(4-(Chloromethyl)phenyl)-4-hydroxy-1-phenylbutan-1-one (17)



$C_{17}H_{17}ClO_2$
288.77 g/mol

According to **general procedure B** using 76 mg 4-(chloromethyl)styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 74 mg (0.26 mmol, 52%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 – 7.85 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 4H), 4.83 (dd, *J* = 7.7, 4.8 Hz, 1H), 4.60 – 4.55 (m, 2H), 3.11 (td, *J* = 6.9, 1.9 Hz, 2H), 2.74 (bs, 1H), 2.28 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 144.7, 136.7, 136.6, 133.1, 128.7, 128.5, 128.0, 126.1, 73.1, 46.0, 34.6, 33.0. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{17}ClO_2Na$ 311.0809; Found: 311.0808.

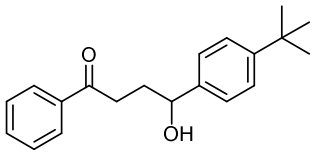
4-(1-Hydroxy-4-oxo-4-phenylbutyl)phenyl acetate (18)



$C_{18}H_{18}O_4$
298.34 g/mol

According to **general procedure B** using 81 mg methyl 4-vinylbenzoate (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 122 mg (0.41 mmol, 82%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.93 (m, 2H), 7.58 – 7.54 (m, 1H), 7.45 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.08 – 7.06 (m, 2H), 4.83 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.12 (td, *J* = 6.9, 1.9 Hz, 2H), 2.58 (s, 1H), 2.29 (s, 3H), 2.20 – 2.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 169.5, 149.9, 142.0, 136.8, 133.2, 128.6, 128.1, 126.9, 121.6, 73.0, 34.7, 33.1, 21.1. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{18}O_4Na$ 321.1097; Found: 321.1089.

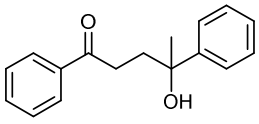
4-(4-(*tert*-Butyl)phenyl)-4-hydroxy-1-phenylbutan-1-one (19)



$C_{20}H_{24}O_2$
296.41 g/mol

According to **general procedure B** using 80 mg 1-(*tert*-butyl)-4-vinylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-20%): 121 mg (0.41 mmol, 82%), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.94 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.38 (m, 3H), 7.38 – 7.31 (m, 3H), 4.80 (dd, *J* = 7.0, 5.8 Hz, 1H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.38 (bs, 1H), 2.25 – 2.16 (m, 2H), 1.35 – 1.31 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 150.5, 141.3, 136.9, 133.0, 128.5, 128.1, 125.5, 125.4, 73.4, 34.8, 34.5, 33.0, 31.3. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{20}H_{24}O_2Na$ 319.1669; Found: 319.1667.

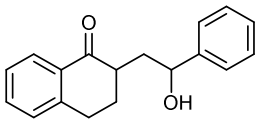
4-Hydroxy-1,4-diphenylpentan-1-one (20)



$C_{17}H_{18}O_2$
254.33 g/mol

According to **general procedure B** using 59 mg prop-1-en-2-ylbenzene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 109 mg (0.43 mmol, 86%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.89 (m, 2H), 7.57 – 7.53 (m, 1H), 7.54 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.30 – 7.27 (m, 1H), 3.12 – 2.84 (m, 2H), 2.70 (bs, 1H), 2.35 – 2.31 (m, 2H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 147.2, 136.7, 133.0, 128.4, 128.2, 128.0, 126.6, 124.8, 74.1, 37.7, 33.7, 31.2. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{18}O_2Na$ 277.1199; Found: 277.1202.

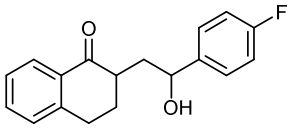
2-(2-Hydroxy-2-phenylethyl)-3,4-dihydronaphthalen-1(2*H*)-one (I-2)[2]



$C_{18}H_{18}O_2$
266.34 g/mol

According to **general procedure C** using 102 mg (0.50 mmol, 1.0 equiv) **I**, 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-25%): 95 mg (0.36 mmol, 72%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 7.93 (m, 1H), 7.50 – 7.19 (m, 8H), 5.05 – 4.87 (m, 1H), 3.82 – 3.53 (m, 1H), 3.14 – 2.91 (m, 2H), 2.83 – 2.61 (m, 1H), 2.50 – 2.36 (m, 1H), 2.30 – 2.09 (m, 1H), 2.03 – 1.87 (m, 1H), 1.74 (dt, *J* = 14.6, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 201.8 (Σ 1C); 145.2, 144.6 (Σ 1C); 144.25, 144.19 (Σ 1C); 133.6, 133.5 (Σ 1C); 132.3; 128.7; 128.41, 128.29 (Σ 2C); 127.7, 127.5 (Σ 1C); 127.4, 127.2 (Σ 1C); 126.7, 126.6 (Σ 1C); 125.8, 125.6 (Σ 2C); 73.4, 72.0 (Σ 1C); 46.5, 44.4 (Σ 1C); 40.9, 39.8 (Σ 1C); 30.4, 30.3 (Σ 1C); 29.1, 28.9 (Σ 1C). HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{18}O_2Na$ 289.1199; Found: 289.1193.

2-(2-(4-Fluorophenyl)-2-hydroxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (I-21)[2]

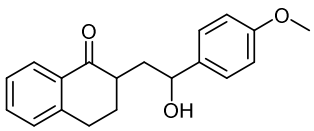


$C_{18}H_{17}FO_2$
284.33 g/mol

According to **general procedure C** using 102 mg (0.50 mmol, 1.0 equiv) **I**, 61 mg 1-fluoro-4-vinylbenzene (**21**) (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 109 mg (0.38 mmol, 77%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 – 8.01 (m, 1H), 7.52 – 7.44 (m, 1H), 7.41 – 7.30 (m, 3H), 7.24 – 7.15 (m, 1H), 7.05 – 6.98 (m, 2H), 5.04 – 4.84 (m, 1H), 4.03 – 3.67 (m, 1H), 3.13 – 2.93 (m, 2H), 2.80 – 2.59 (m, 1H), 2.46 – 2.33 (m, 1H), 2.28 – 2.09 (m, 1H), 2.03 – 1.93 (m, 1H), 1.90 – 1.66 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$): -115.5, -115.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 201.8 (Σ 1C); 162.0 (d, *J* = 246.4 Hz), 161.9 (d, *J* = 246.4 Hz) (Σ 1C); 144.3, 144.2 (Σ 1C); 141.0 (d, *J* = 3.0 Hz), 140.3 (d, *J* = 3.1 Hz) (Σ 1C); 133.7, 133.6 (Σ 1C); 132.2, 132.1 (Σ 1C); 128.68, 128.66 (Σ 1C); 127.7, 127.5 (Σ 1C); 127.4 (d, *J* = 8.1 Hz), 127.2 (d, *J* = 8.1 Hz) (Σ 2C); 126.7, 126.6 (Σ 1C); 115.1 (d, *J* = 21.4 Hz, 2C); 72.8, 71.3 (Σ 1C); 46.6, 44.2 (Σ 1C); 41.2, 39.9 (Σ 1C); 30.5, 30.3 (Σ 1C); 29.1, 28.9 (Σ 1C). HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{17}FO_2Na$ 307.1105; Found: 307.1108.

[2] Non separable diastereomers.

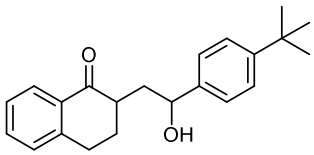
2-(2-Hydroxy-2-(4-methoxyphenyl)ethyl)-3,4-dihydronaphthalen-1(2*H*)-one (I-22)[2]



$C_{19}H_{20}O_3$
296.37 g/mol

According to **general procedure C** using 102 mg **I** (0.50 mmol, 1.0 equiv), 67 mg 4-methoxystyrene (**22**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 132 mg (0.46 mmol, 89%), colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.24 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.12 – 6.95 (m, 2H), 6.88 – 6.73 (m, 3H), 5.07 – 4.77 (m, 1H), 3.66 – 3.44 (m, 1H), 3.35 – 3.33 (m, 3H), 2.60 – 2.47 (m, 2H), 2.46 – 2.36 (m, 2H), 1.77 – 1.65 (m, 1H), 1.60 – 1.38 (m, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ 201.1, 201.0 (Σ 1C); 159.4, 159.3 (Σ 1C); 144.5, 144.4 (Σ 1C); 138.4, 138.0 (Σ 1C); 133.3, 133.2 (Σ 1C); 133.09, 133.07 (Σ 1C); 128.84, 128.80 (Σ 1C); 128.0; 127.6, 127.3 (Σ 2C); 126.8, 126.8 (Σ 1C); 114.1 (Σ 2C); 72.6, 72.0 (Σ 1C); 54.90, 54.88 (Σ 1C); 46.2, 44.8 (Σ 1C); 41.2, 40.6 (Σ 1C); 30.4, 29.9 (Σ 1C); 29.1, 29.0 (Σ 1C). HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{19}H_{20}O_3Na$ 319.1305; Found: 319.1309.

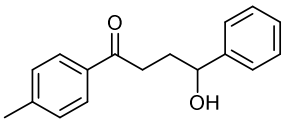
2-(2-(4-(*tert*-Butyl)phenyl)-2-hydroxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (I-23)[2]



$C_{22}H_{26}O_2$
322.45 g/mol

According to **general procedure C** using 102 mg **I** (0.50 mmol, 1.0 equiv), 80 mg 1,3,5-trimethyl-2-vinylbenzene (**23**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-35%): 85 mg (0.26 mmol, 53%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.04 (m, 1H), 7.51 – 7.45 (m, 1H), 7.38 – 7.35 (m, 3H), 7.34 – 7.31 (m, 2H), 7.24 – 7.21 (m, 1H), 5.03 – 4.85 (m, 1H), 3.60 – 3.17 (m, 1H), 3.09 – 2.94 (m, 2H), 2.83 – 2.66 (m, 1H), 2.51 – 2.36 (m, 1H), 2.31 – 2.15 (m, 1H), 2.06 – 1.95 (m, 1H), 1.94 – 1.71 (m, 1H), 1.32 – 1.31 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 201.6 (Σ 1C); 150.3, 150.2 (Σ 1C); 144.2, 144.1 (Σ 1C); 142.1, 141.5 (Σ 1C); 133.6, 133.5 (Σ 1C); 132.32, 132.30 (Σ 1C); 128.67, 128.65 (Σ 1C); 127.7, 127.5 (Σ 1C); 126.7, 126.6 (Σ 1C); 125.5 (Σ 2C); 125.4, 125.3 (Σ 2C); 73.1, 71.9 (Σ 1C); 46.4, 44.4 (Σ 1C); 40.6, 39.6 (Σ 1C); 34.49, 34.47 (Σ 1C); 31.4 (Σ 3C); 30.2, 30.1 (Σ 1C); 29.1, 28.8 (Σ 1C). HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{22}H_{26}O_2Na$ 345.1825; Found: 345.1826.

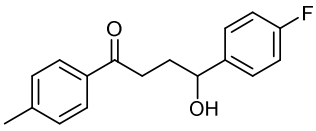
4-Hydroxy-4-phenyl-1-(*p*-tolyl)butan-1-one (II-2)



$C_{17}H_{18}O_2$
254.33 g/mol

According to **general procedure C** using 96 mg (0.50 mmol, 1.0 equiv) **II**, 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/acetone 3-25%): 67 mg (0.26 mmol, 53%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.33 – 7.28 (m, 1H), 7.23 (s, 1H), 4.92 – 4.77 (m, 1H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.66 (bs, 1H), 2.41 (s, 3H), 2.24 – 2.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 144.4, 143.9, 134.3, 129.2, 128.4, 128.2, 127.5, 125.7, 73.6, 34.6, 33.1, 21.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{18}O_2Na$ 277.1199; Found: 277.1186.

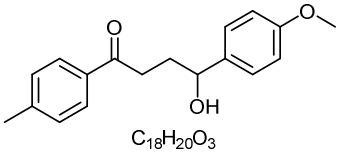
4-(4-Fluorophenyl)-4-hydroxy-1-(*p*-tolyl)butan-1-one (II-21)



$C_{17}H_{17}FO_2$
272.32 g/mol

According to **general procedure C** using 96 mg **II** (0.50 mmol, 1.0 equiv), 61 mg 1-fluoro-4-vinylbenzene (**21**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 127 mg (0.47 mmol, 93%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 4.89 – 4.73 (m, 1H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.66 (bs, 1H), 2.41 (s, 3H), 2.23 – 2.10 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): -115.3. ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 162.1 (d, *J* = 245.3 Hz), 144.0, 140.2 (d, *J* = 3.4 Hz), 134.2, 129.3, 128.2, 127.4 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.3 Hz), 73.0, 34.6, 33.2, 21.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{17}FO_2Na$ 295.1105; Found: 295.1107.

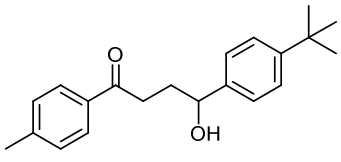
4-Hydroxy-4-(4-methoxyphenyl)-1-(*p*-tolyl)butan-1-one (II-22)



$C_{18}H_{20}O_3$
284.36 g/mol

According to **general procedure C** using 96 mg **II** (0.50 mmol, 1.0 equiv), 67 mg 4-methoxystyrene (**22**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 102 mg (0.36 mmol, 72%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.76 (t, *J* = 6.3 Hz, 1H), 3.79 (s, 3H), 3.06 (t, *J* = 7.0 Hz, 2H), 2.54 (bs, 1H), 2.40 (s, 3H), 2.17 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 159.0, 143.8, 136.5, 134.3, 129.2, 128.2, 127.0, 113.8, 73.2, 55.2, 34.7, 33.1, 21.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{20}O_3Na$ 307.1305; Found: 307.1312.

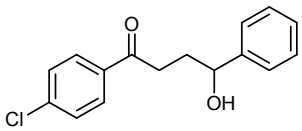
4-(4-(*t*ert-Butyl)phenyl)-4-hydroxy-1-(*p*-tolyl)butan-1-one (II-23)



$C_{21}H_{26}O_2$
310.44 g/mol

According to **general procedure C** using 96 mg **II** (0.50 mmol, 1.0 equiv), 80 mg 1,3,5-trimethyl-2-vinylbenzene (**23**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-20%): 114 mg (0.37 mmol, 73%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.29 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.80 (t, *J* = 6.3 Hz, 1H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.26 – 2.15 (m, 2H), 1.33 (s, 9H).[1] ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 150.5, 143.8, 141.4, 134.4, 129.2, 128.2, 125.5, 125.4, 73.5, 34.8, 34.5, 33.0, 31.3, 21.6. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{21}H_{26}O_2Na$ 333.1825; Found: 333.1828.

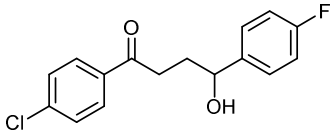
1-(4-Chlorophenyl)-4-hydroxy-4-phenylbutan-1-one (III-2)



$C_{16}H_{15}ClO_2$
274.74 g/mol

According to **general procedure C** using 106 mg (0.50 mmol, 1.0 equiv) **III**, 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 114 mg (0.41 mmol, 83%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.85 (m, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.34 (m, 4H), 7.29 – 7.26 (m, 1H), 4.81 (dd, *J* = 7.4, 5.3 Hz, 1H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.57 (bs, 1H), 2.23 – 2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 144.2, 139.5, 135.0, 129.5, 128.8, 128.5, 127.6, 125.7, 73.4, 34.7, 32.9. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{16}H_{15}ClO_2Na$ 297.0653; Found: 297.0640.

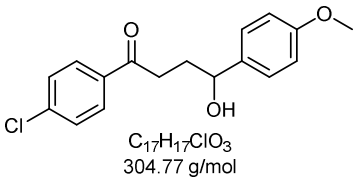
1-(4-Chlorophenyl)-4-(4-fluorophenyl)-4-hydroxybutan-1-one (III-21)



$C_{16}H_{14}ClFO_2$
292.73 g/mol

According to **general procedure C** using 106 mg (0.50 mmol, 1.0 equiv) **III**, 61 mg 1-fluoro-4-vinylbenzene (**21**) (0.50 mmol, 1.0 equiv) and an irradiation time of 3 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 105 mg (0.36 mmol, 72%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.80 (m, 2H), 7.41 (d, *J* = 6.6 Hz, 2H), 7.32 (ddd, *J* = 9.7, 6.1, 3.1 Hz, 2H), 7.05 – 6.99 (m, 2H), 4.80 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.55 (bs, 1H), 2.20 – 2.09 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$): -115.0. ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 162.1 (d, *J* = 245.6 Hz), 140.0 (d, *J* = 3.1 Hz), 139.6, 135.0, 129.5, 128.9, 127.3 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.4 Hz), 72.8, 34.6, 33.0. HRMS (ESI) m/z: $[M - H]^-$: Calcd. for $C_{16}H_{13}ClFO_2$ 291.0583; Found: 291.0577.

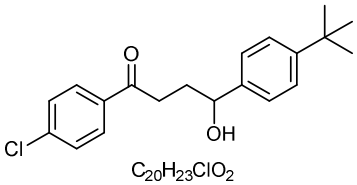
1-(4-Chlorophenyl)-4-hydroxy-4-(4-methoxyphenyl)butan-1-one (III-22)



$C_{17}H_{17}ClO_3$
304.77 g/mol

According to **general procedure C** using 106 mg **III** (0.50 mmol, 1.0 equiv), 67 mg 4-methoxystyrene (**22**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 109 mg (0.36 mmol, 72%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.76 (t, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.27 (s, 1H), 2.20 – 2.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 159.1, 139.5, 136.3, 135.2, 129.5, 128.8, 127.0, 113.9, 73.1, 55.3, 34.8, 32.9. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{17}ClO_3Na$ 327.0758; Found: 327.0761.

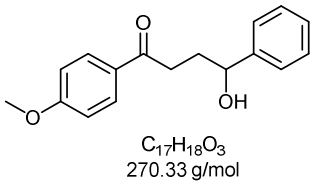
4-(4-(*tert*-Butyl)phenyl)-1-(4-chlorophenyl)-4-hydroxybutan-1-one (III-23)



$C_{20}H_{23}ClO_2$
330.85 g/mol

According to **general procedure C** using 106 mg **III** (0.50 mmol, 1.0 equiv), 80 mg 1,3,5-trimethyl-2-vinylbenzene (**23**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 102 mg (0.31 mmol, 62%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.81 – 4.78 (m, 1H), 3.13 – 3.05 (m, 2H), 2.25 – 2.14 (m, 2H), 2.12 (bs, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 150.6, 141.2, 139.5, 135.2, 129.5, 128.8, 125.5, 125.4, 73.3, 34.8, 34.5, 32.9, 31.3. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{20}H_{23}ClO_2Na$ 353.1279; Found: 353.1277.

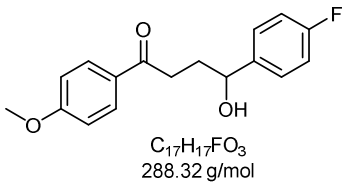
4-Hydroxy-1-(4-methoxyphenyl)-4-phenylbutan-1-one (IV-2)



$C_{17}H_{18}O_3$
270.33 g/mol

According to **general procedure C** using 104 mg **IV** (0.50 mmol, 1.0 equiv), 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 74 mg (0.28 mmol, 55%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.26 (t, *J* = 6.9 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.87 – 4.75 (m, 1H), 3.85 (s, 3H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.80 (bs, 1H), 2.21 – 2.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 163.5, 144.4, 130.3, 129.8, 128.4, 127.4, 125.7, 113.6, 73.6, 55.4, 34.4, 33.2. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{18}O_3Na$ 293.1148; Found: 293.1148.

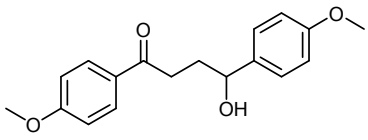
4-(4-Fluorophenyl)-4-hydroxy-1-(4-methoxyphenyl)butan-1-one (IV-21)



$C_{17}H_{17}FO_3$
288.32 g/mol

According to **general procedure C** using 104 mg **IV** (0.50 mmol, 1.0 equiv), 61 mg 1-fluoro-4-vinylbenzene (**21**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 67 mg (0.23 mmol, 47%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 2H), 7.34 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.94 – 6.90 (m, 2H), 4.91 – 4.73 (m, 1H), 3.86 (s, 3H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.26 – 2.05 (m, 2H).[1] ^{19}F NMR (377 MHz, $CDCl_3$): -115.3. ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 163.6, 162.1 (d, *J* = 245.3 Hz), 140.2 (d, *J* = 3.1 Hz), 130.4, 129.7, 127.3 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 21.2 Hz), 113.7, 73.0, 55.5, 34.3, 33.3. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{17}FO_3Na$ 311.1054; Found: 311.1045.

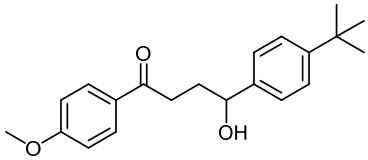
4-Hydroxy-1-(4-methoxyphenyl)-4-(4-methoxyphenyl)butan-1-one (IV-22)



$C_{18}H_{20}O_4$
300.35 g/mol

According to **general procedure C** using 104 mg **IV** (0.50 mmol, 1.0 equiv), 67 mg 4-methoxystyrene (**22**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 82 mg (0.27 mmol, 55%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.96 – 6.86 (m, 4H), 4.79 – 7.76 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.37 (s, 1H), 2.20 – 2.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 163.4, 159.0, 136.6, 130.4, 129.9, 127.0, 113.8, 113.6, 73.2, 55.4, 55.2, 34.5, 33.2. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{20}O_4Na$ 323.1254; Found: 323.1263.

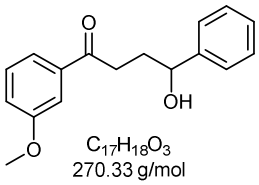
4-(4-(*tert*-Butyl)phenyl)-4-hydroxy-1-(4-methoxyphenyl)butan-1-one (IV-23)



$C_{21}H_{26}O_3$
326.44 g/mol

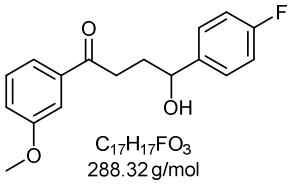
According to **general procedure C** using 104 mg **IV** (0.50 mmol, 1.0 equiv), 80 mg 1,3,5-trimethyl-2-vinylbenzene (**23**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 64 mg (0.20 mmol, 39%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.28 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.79 (t, *J* = 6.2 Hz, 1H), 3.86 (s, 3H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.53 (s, 1H), 2.25 – 2.12 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 163.5, 150.5, 141.5, 130.4, 130.0, 125.5, 125.4, 113.7, 73.5, 55.5, 34.6, 34.5, 33.2, 31.4. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for 349.1774; Found: 349.1792.

4-Hydroxy-1-(3-methoxyphenyl)-4-phenylbutan-1-one (V-2)



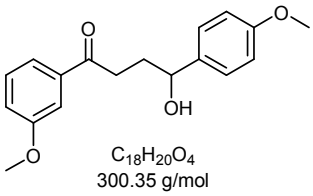
According to **general procedure C** using 104 mg **V** (0.50 mmol, 1.0 equiv), 52 mg styrene (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 5-25%): 105 mg (0.39 mmol, 78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.31 (m, 4H), 7.29 – 7.26 (m, 2H), 7.13 – 7.11 (m, 1H), 4.83 (ddd, *J* = 7.1, 5.2, 1.6 Hz, 1H), 3.85 (s, 3H), 3.10 (td, *J* = 7.0, 1.7 Hz, 2H), 2.47 (bs, 1H), 2.23 – 2.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 159.8, 144.3, 138.2, 129.5, 128.5, 127.6, 125.7, 120.7, 119.6, 112.3, 73.6, 55.4, 34.9, 33.1. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{18}O_3Na$ 293.1148; Found: 293.1150.

4-(4-Fluorophenyl)-4-hydroxy-1-(3-methoxyphenyl)butan-1-one (V-21)



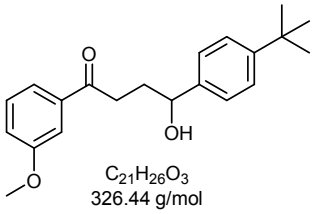
According to **general procedure C** using 104 mg **V** (0.50 mmol, 1.0 equiv), 61 mg 1-fluoro-4-vinylbenzene (**21**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 89 mg (0.31 mmol, 62%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 1H), 7.48 – 7.46 (m, 1H), 7.37 – 7.32 (m, 3H), 7.10 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.04 – 7.00 (m, 2H), 4.80 (t, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 3.09 (t, *J* = 6.9 Hz, 2H), 2.65 (bs, 1H), 2.19 – 2.13 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$): -115.1. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 162.1 (d, *J* = 245.3 Hz), 159.8, 140.1 (d, *J* = 3.0 Hz), 138.1, 129.6, 127.3 (d, *J* = 8.0 Hz), 120.7, 119.6, 115.3 (d, *J* = 21.4 Hz), 112.3, 72.9, 55.4, 34.8, 33.2. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{17}H_{17}FO_3Na$ 311.1054; Found: 311.1044.

4-Hydroxy-1-(3-methoxyphenyl)-4-(4-methoxyphenyl)butan-1-one (V-22)



According to **general procedure C** using 104 mg **V** (0.50 mmol, 1.0 equiv), 67 mg 4-methoxystyrene (**22**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-25%): 83 mg (0.28 mmol, 55%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.46 (m, 1H), 7.37 – 7.26 (m, 3H), 7.09 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.75 (t, *J* = 6.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.06 (t, *J* = 7.0 Hz, 2H), 2.55 (bs, 1H), 2.19 – 2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 159.7, 159.0, 138.1, 136.4, 129.5, 126.9, 120.7, 119.5, 113.8, 112.3, 73.1, 55.3, 55.2, 34.9, 33.1. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{18}H_{20}O_4Na$ 323.1254; Found: 323.1256.

4-(4-(*tert*-Butyl)phenyl)-4-hydroxy-1-(3-methoxyphenyl)butan-1-one (V-23)



According to **general procedure C** using 104 mg **V** (0.50 mmol, 1.0 equiv), 80 mg 1,3,5-trimethyl-2-vinylbenzene (**23**) (0.50 mmol, 1.0 equiv) and an irradiation time of 2 h. Yield after column chromatography (10 g silica gel, hexanes/ethyl acetate 3-20%): 127 mg (0.39 mmol, 78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.48 (m, 1H), 7.40 – 7.30 (m, 5H), 7.10 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.80 (t, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.33 (bs, 1H), 2.25 – 2.13 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 159.8, 150.5, 141.3, 138.2, 129.5, 125.5, 125.4, 120.8, 119.5, 112.3, 73.4, 55.4, 35.0, 34.5, 33.0, 31.3. HRMS (ESI) m/z: $[M + Na]^+$: Calcd. for $C_{21}H_{26}O_3Na$ 349.1774; Found: 349.1780.

3.3 Cyclic Voltammograms

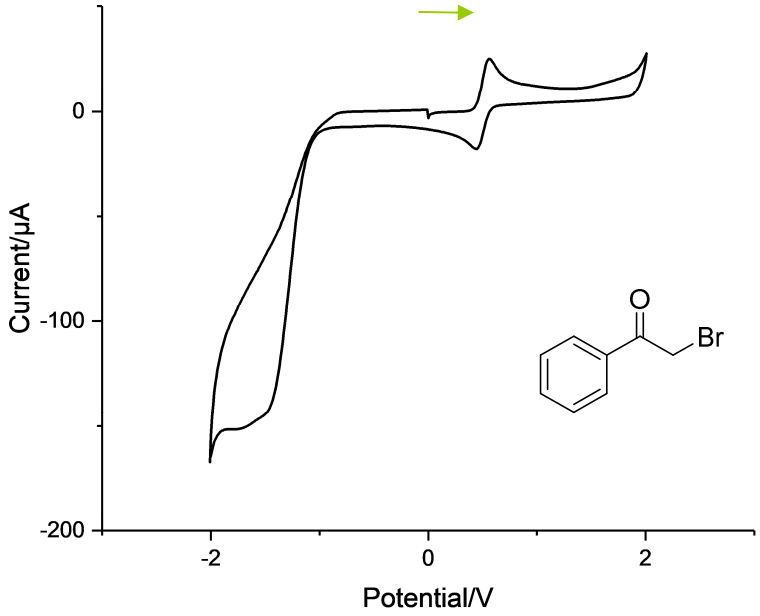


Figure S1: Cyclic voltammogram of 2-bromo-1-phenylethan-1-one in MeCN and ferrocene as internal standard. Measured in *positive* direction first.

$$E^{red} = -1.45 \text{ V } vs \text{ SCE}$$

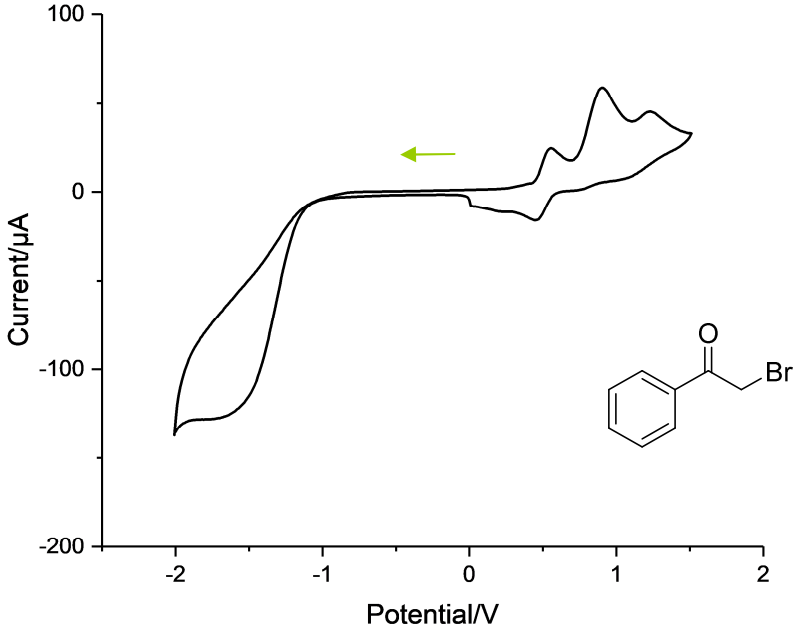


Figure S2: Cyclic voltammogram of 2-bromo-1-phenylethan-1-one in MeCN and ferrocene as internal standard. Measured in *negative* direction first.

$$E^{ox} (Br^{\bullet}/Br^{-}) = 0.66 \text{ V } vs \text{ SCE}$$

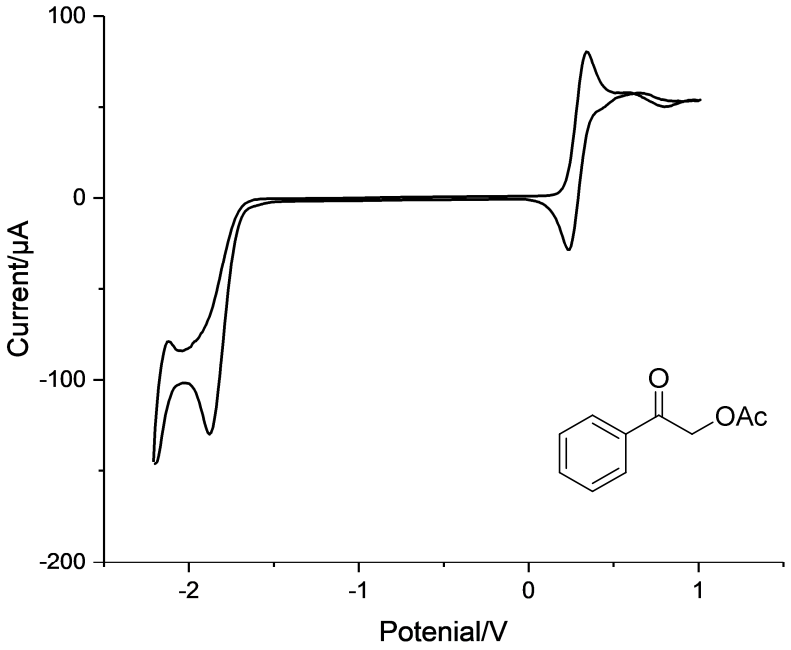


Figure S3: Cyclic voltammogram of 2-oxo-2-phenylethyl acetate (**1**) in **MeCN** and ferrocene as internal standard.

E^{red} = -1.72 V *vs* SCE

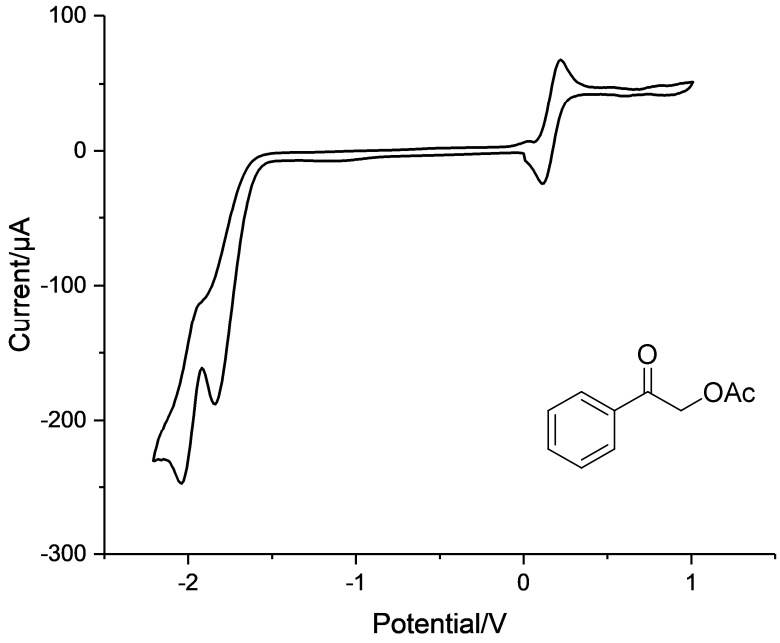


Figure S4: Cyclic voltammogram of 2-oxo-2-phenylethyl acetate (**1**) in **MeCN/H_2O 4:1** and ferrocene as internal standard.

E^{red} = -1.54 V *vs* SCE

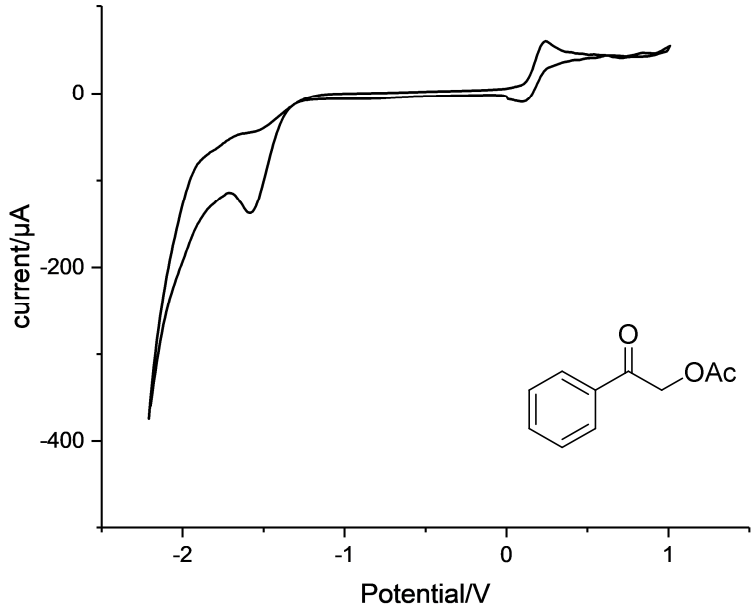


Figure S5: Cyclic voltammogram of 2-oxo-2-phenylethyl acetate (**1**) in **MeCN/H_2O 4:1** and **10 mol% Nd(OTf)$_3$** and ferrocene as internal standard.

E^{red} = -1.27 V *vs* SCE

3.4 Stern-Volmer Quenching Experiments

All fluorescence measurements were performed in a quartz cuvette (d = 1 cm) with an excitation wavelength of 380 nm and a slit width of 5 nm. All samples were degassed prior to use by bubbling argon through the solution inside the cuvette for 10 min.

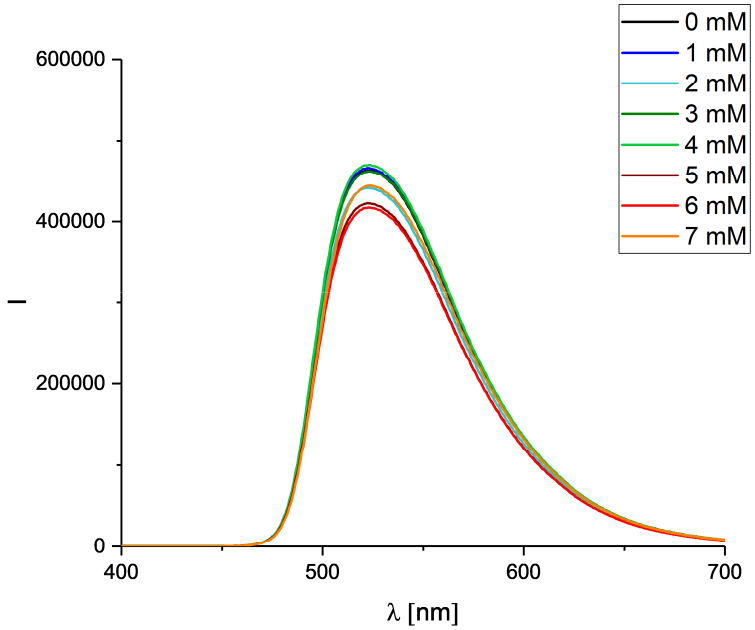


Figure S6: Quenching Study A: Fluorescence of *fac*-Ir(ppy)$_3$ (50 µM) with 2-oxo-2-phenylethyl acetate (**1**) (0-7 mM) in MeCN.

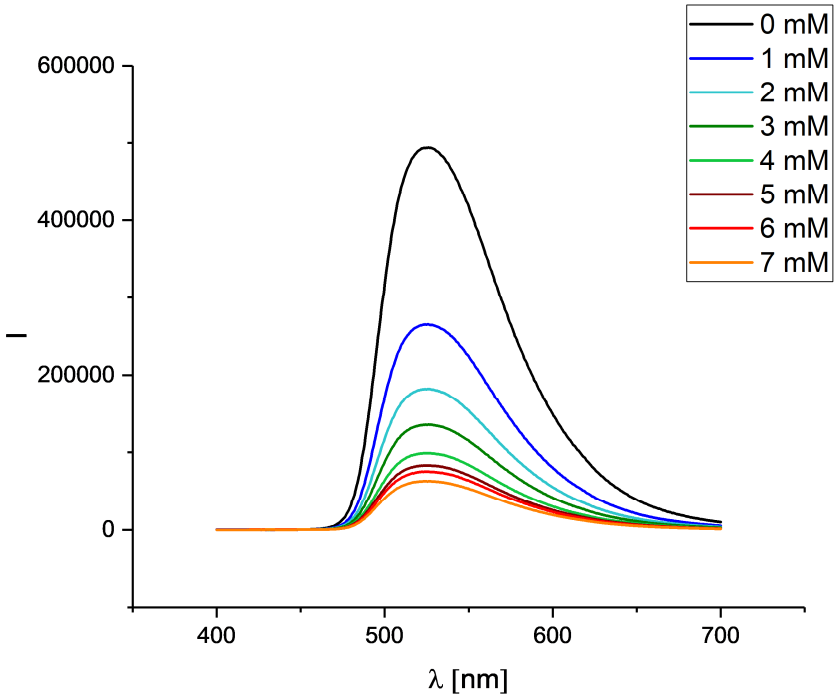


Figure S7: Quenching Study B: Fluorescence of *fac*-Ir(ppy)$_3$ (50 µM) with 2-oxo-2-phenylethyl acetate (**1**) (0-7 mM) in MeCN/H_2O (*v*/*v* = 4:1).

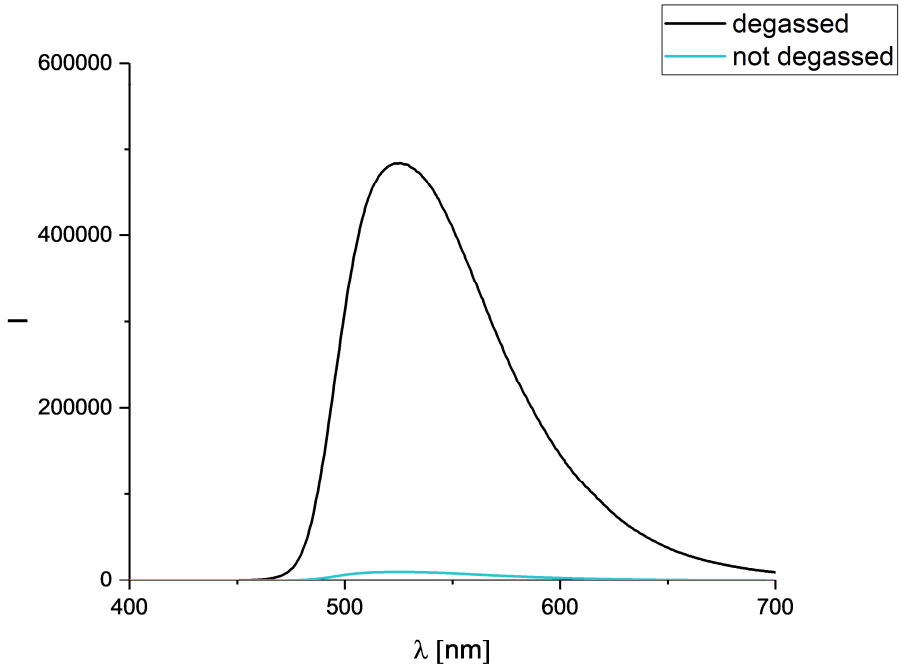


Figure S8: Quenching Study C: Fluorescence of *fac*-Ir(ppy)$_3$ (50 µM) in MeCN/H_2O (*v*/*v* = 4:1) with and without degassing.

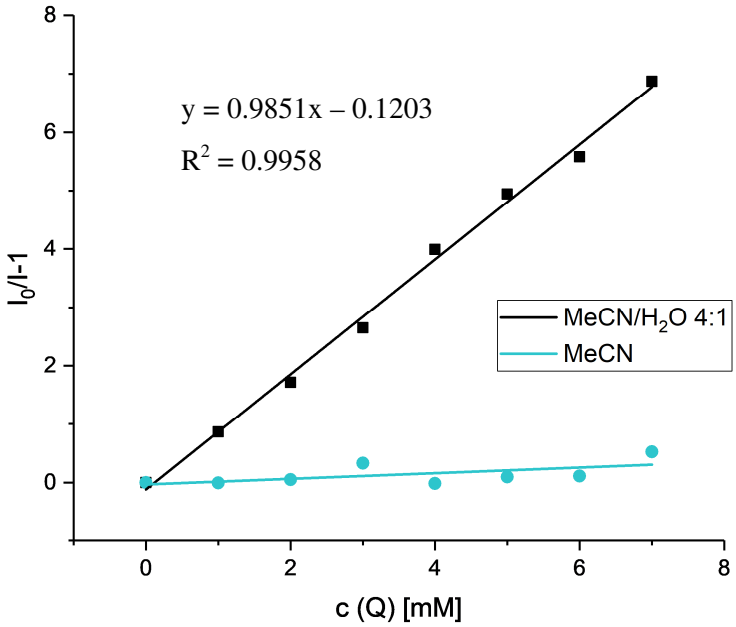
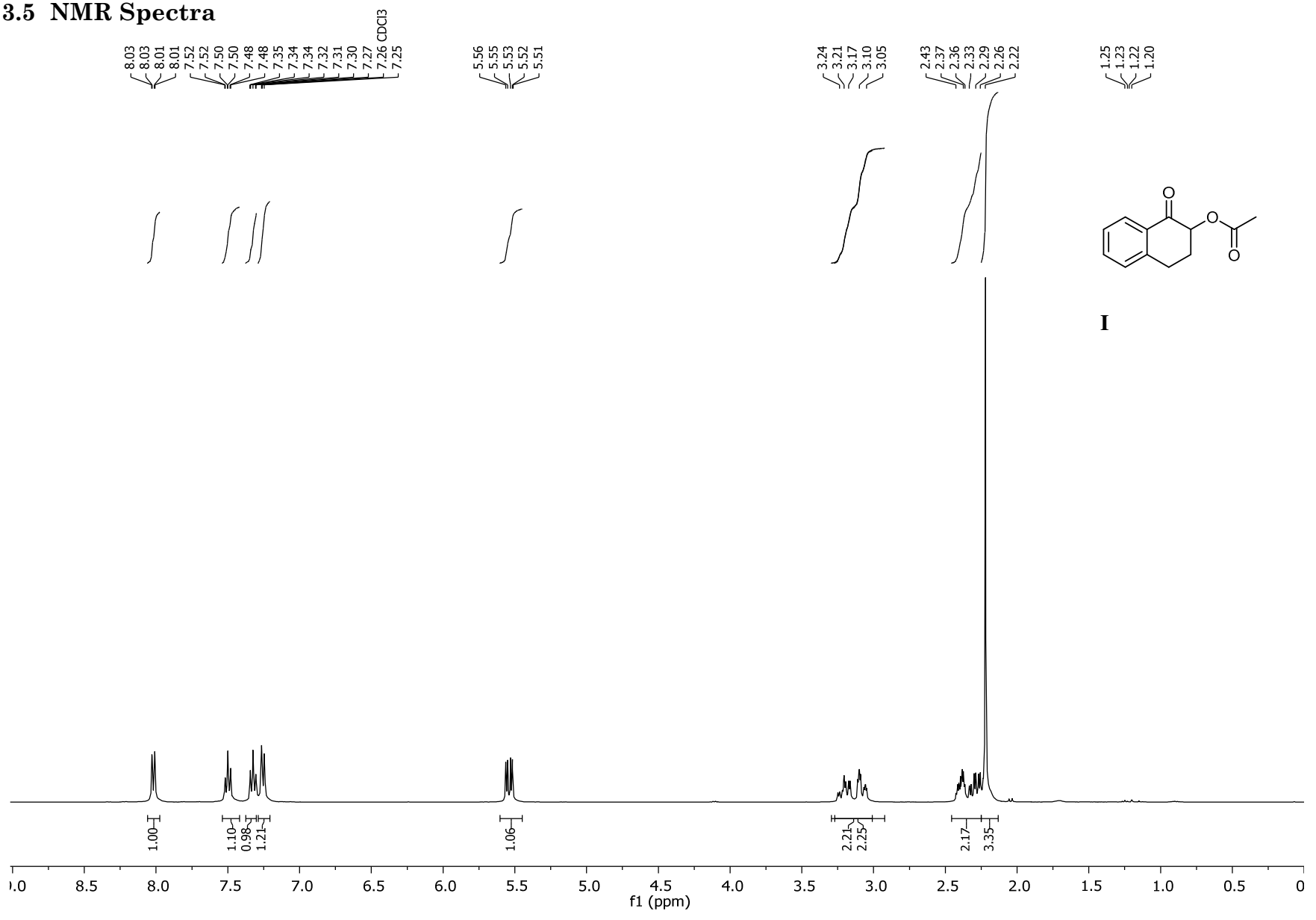
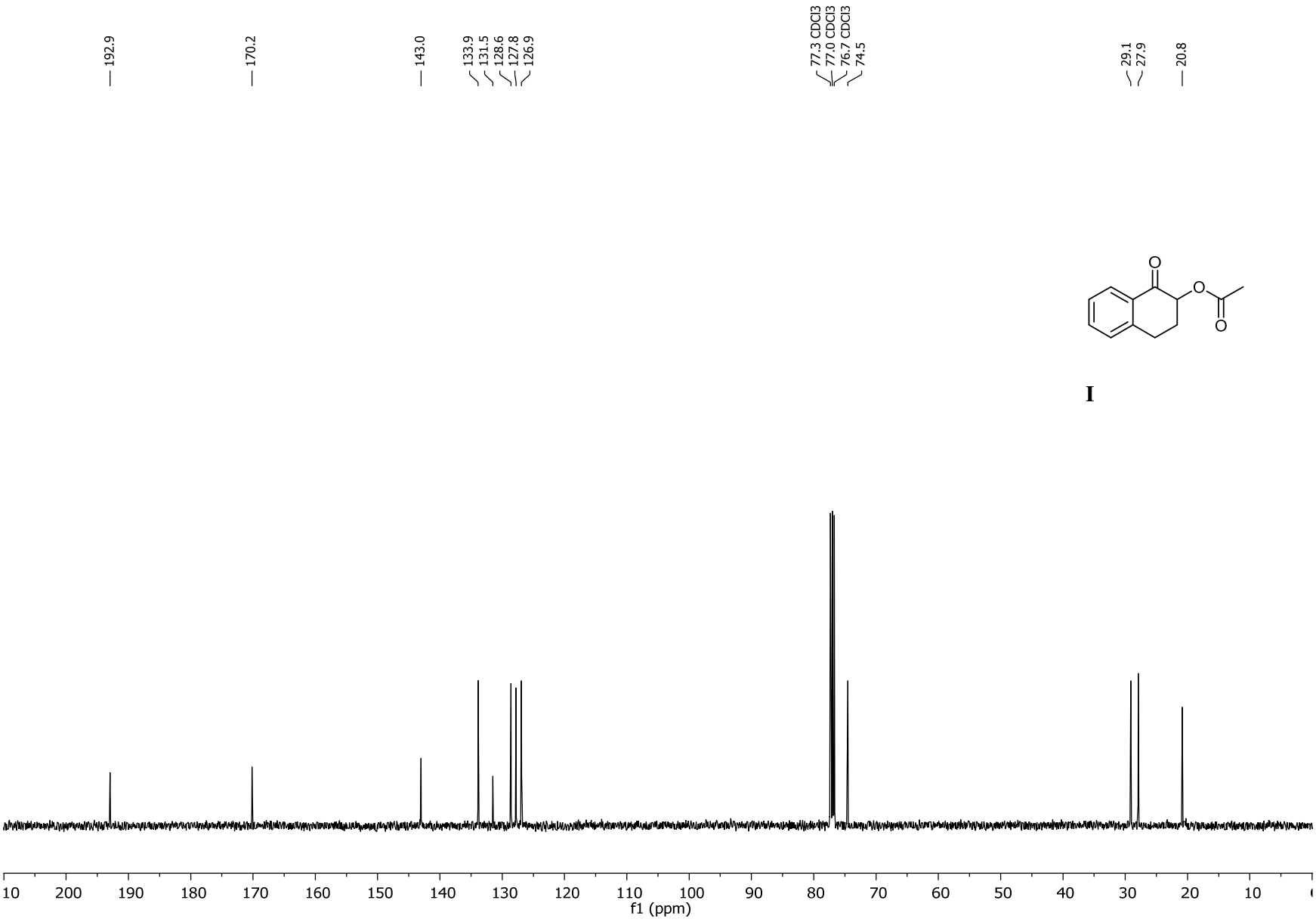


Figure S9: Stern-Volmer-Plot: A linear fit was made for both **quenching study A** and **quenching study B**.

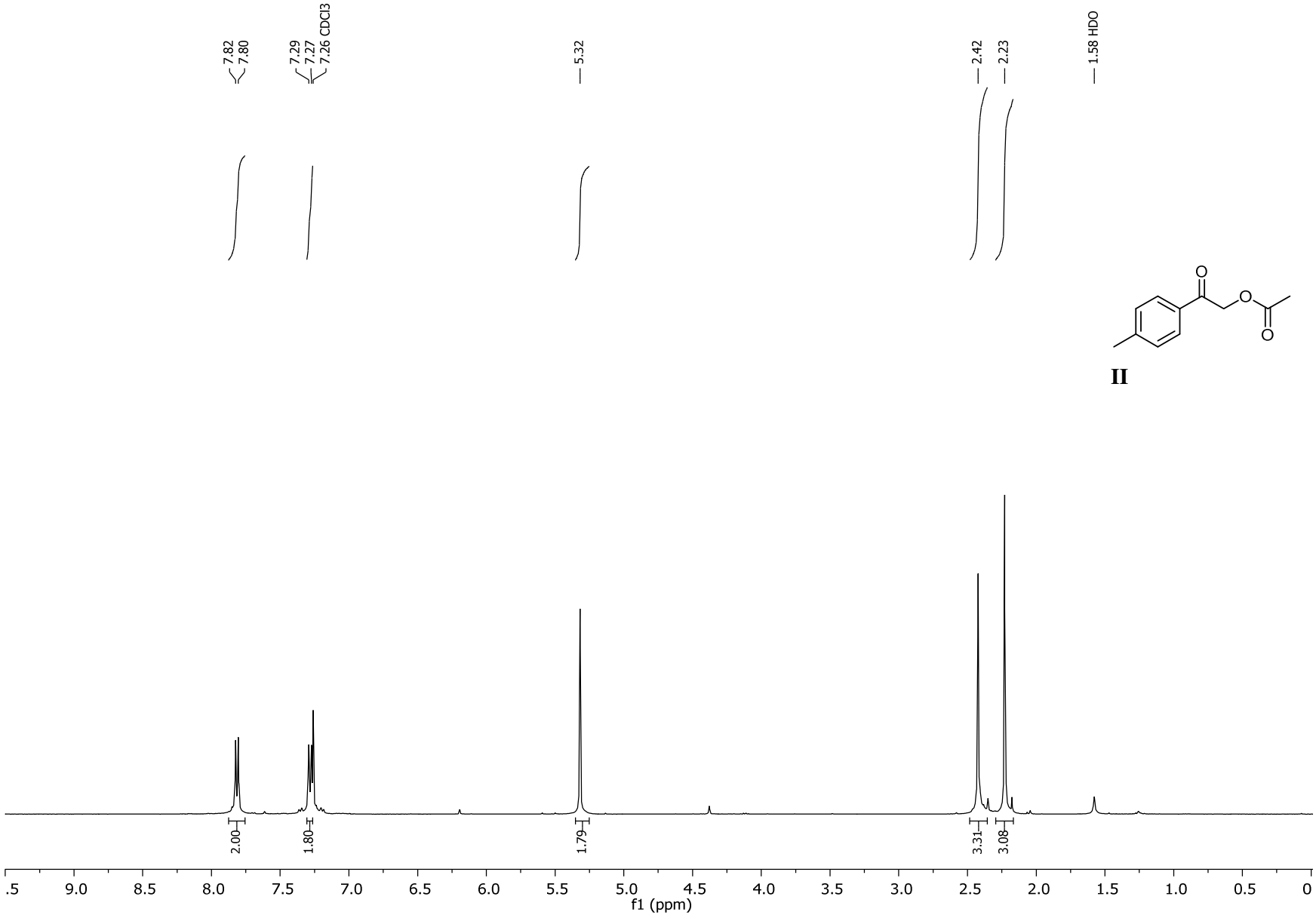
3.5 NMR Spectra



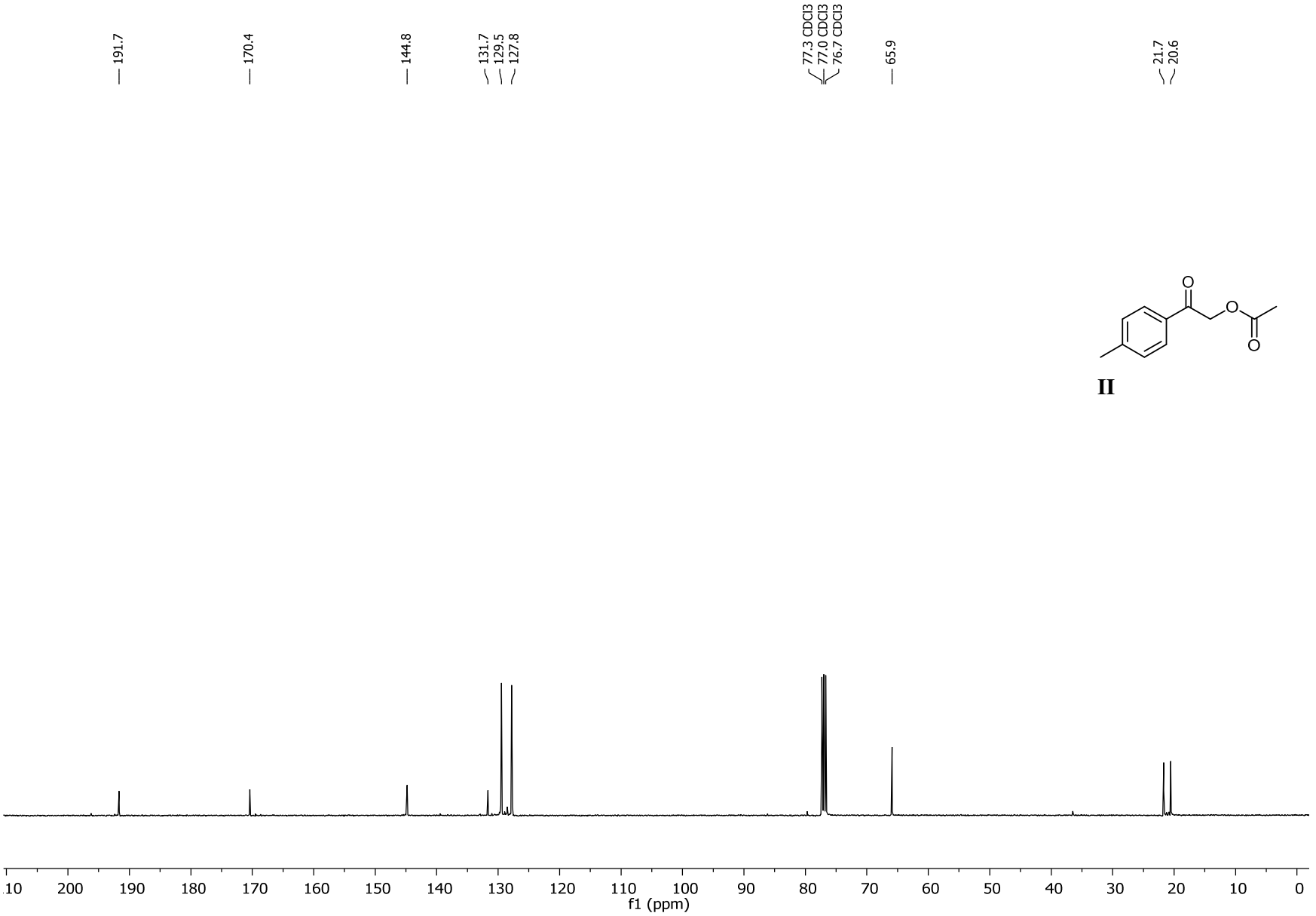
I


192.9
170.2
143.0
133.9
131.5
128.6
127.8
126.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
74.5
29.1
27.9
20.8
O
O
O
f1 (ppm)

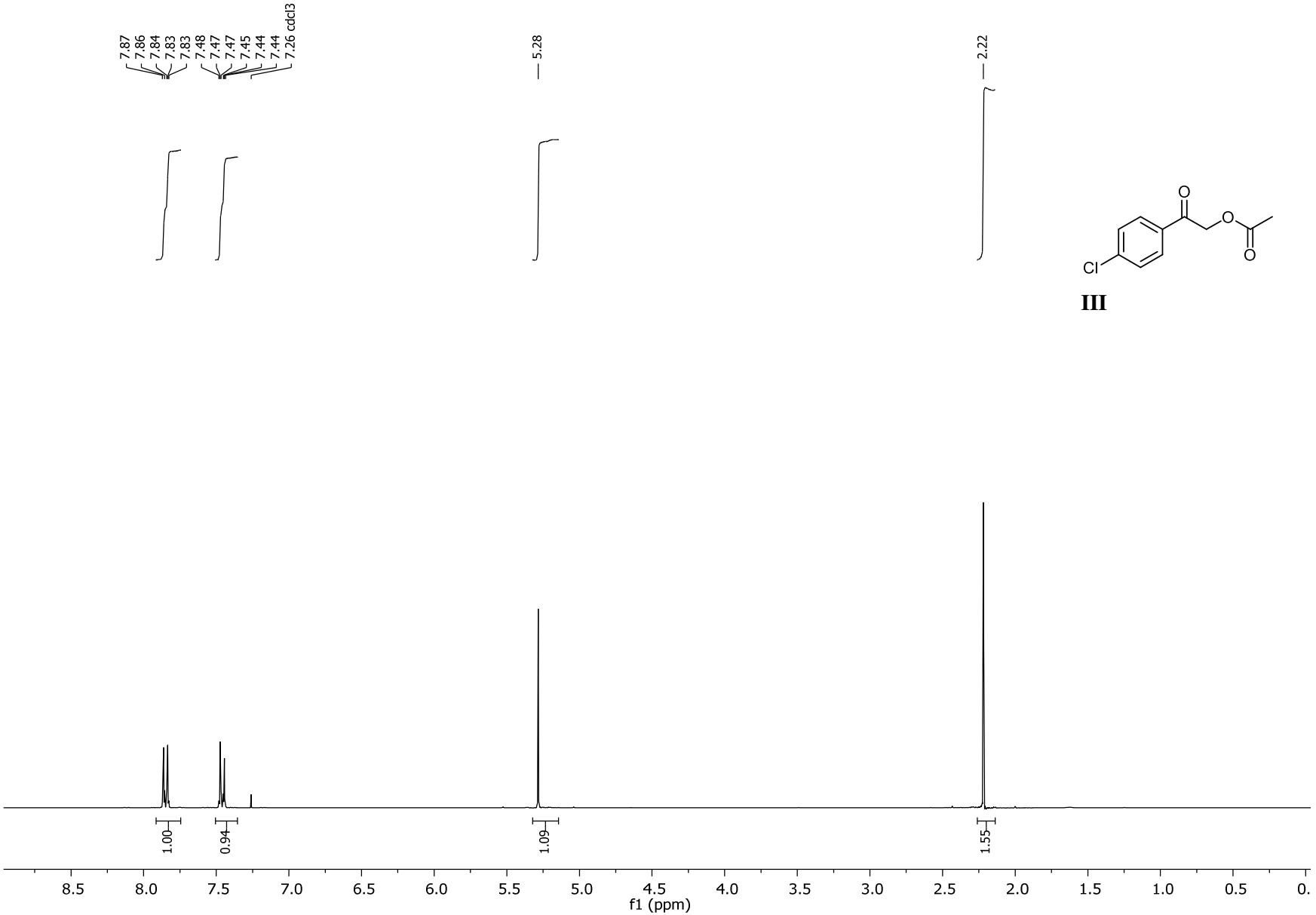
I


7.82
7.80
7.29
7.27
7.26 CDCl3
5.32
2.42
2.23
1.58 HDO
2.00
1.80
1.79
3.31
3.08
f1 (ppm)

II

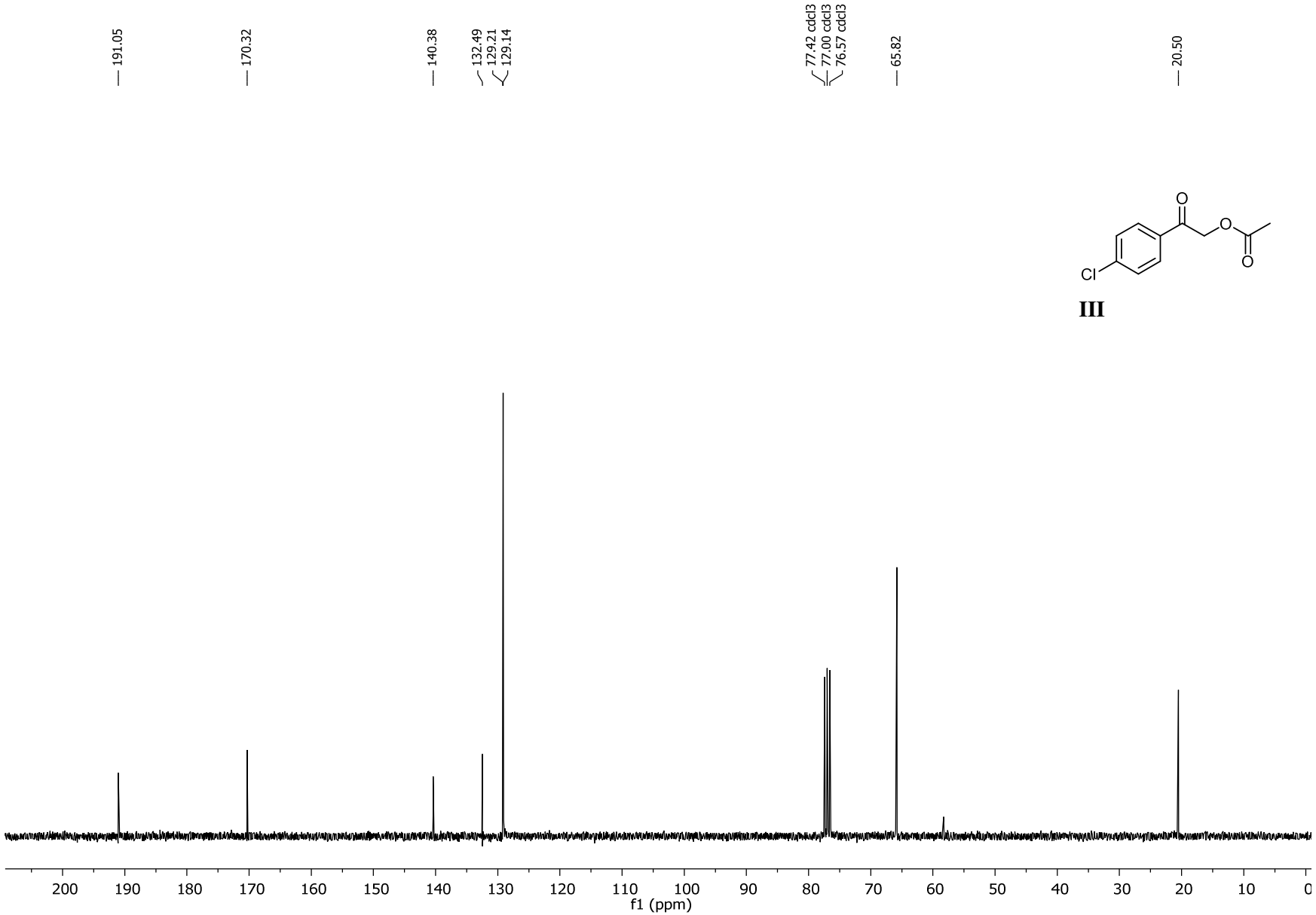

191.7
170.4
144.8
131.7
129.5
127.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
65.9
21.7
20.6
f1 (ppm)

II

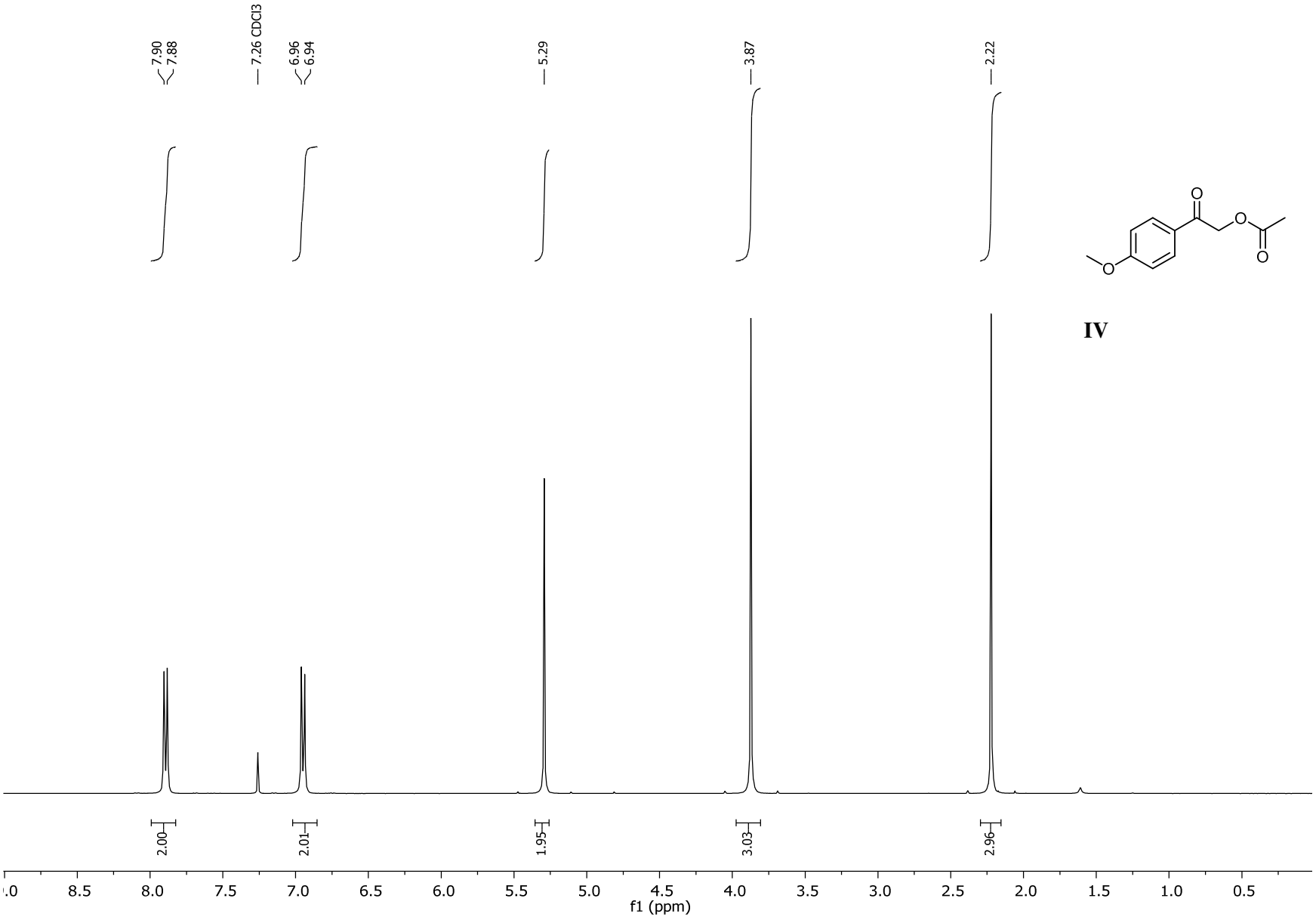

7.87
7.86
7.84
7.83
7.83
7.48
7.47
7.47
7.45
7.44
7.44
7.26 cdcl3
5.28
2.22
1.00
0.94
1.09
1.55
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

O
O
O
Cl

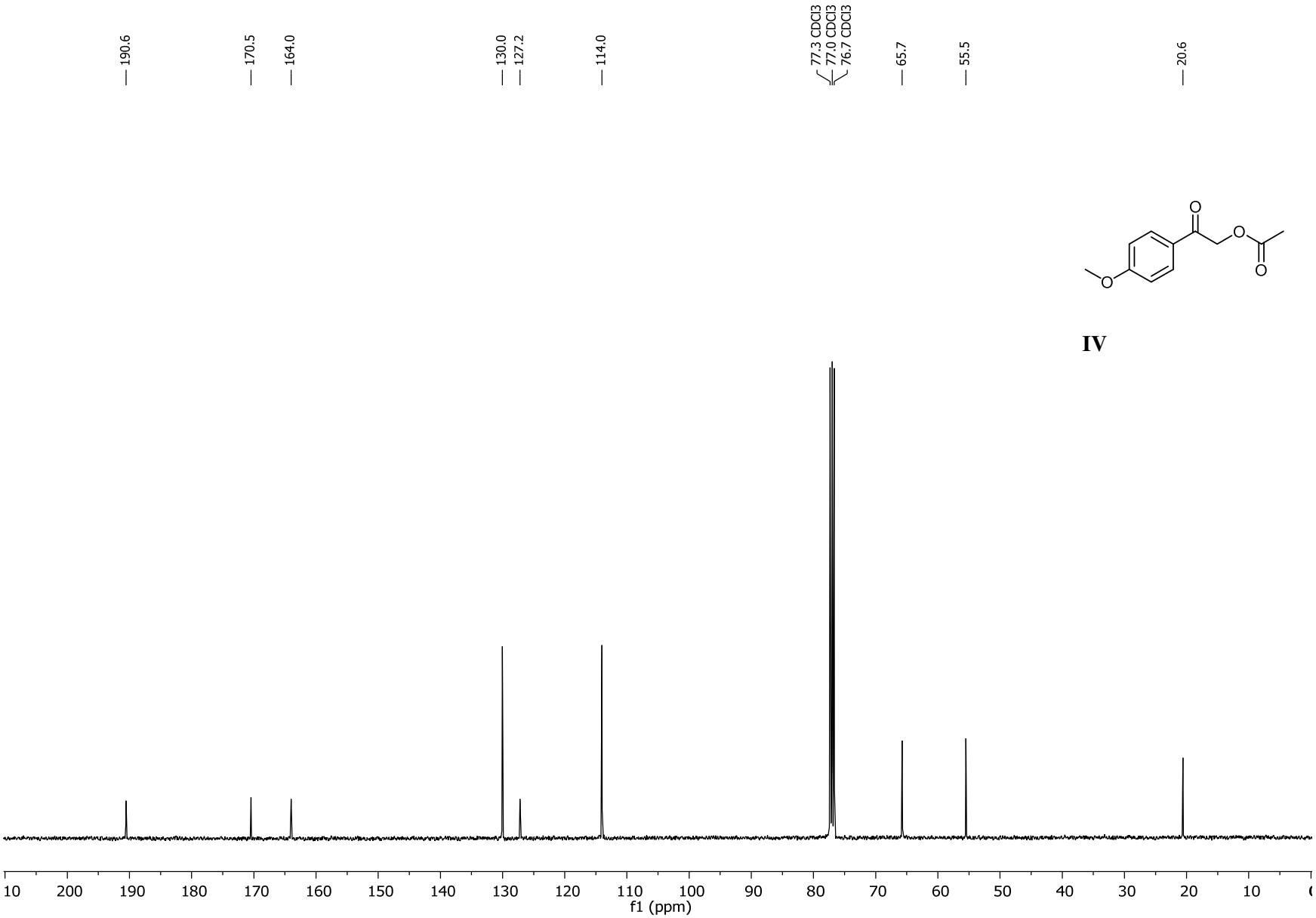
III


191.05
170.32
140.38
132.49
129.21
129.14
77.42 cdcl3
77.00 cdcl3
76.57 cdcl3
65.82
20.50
Cl
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

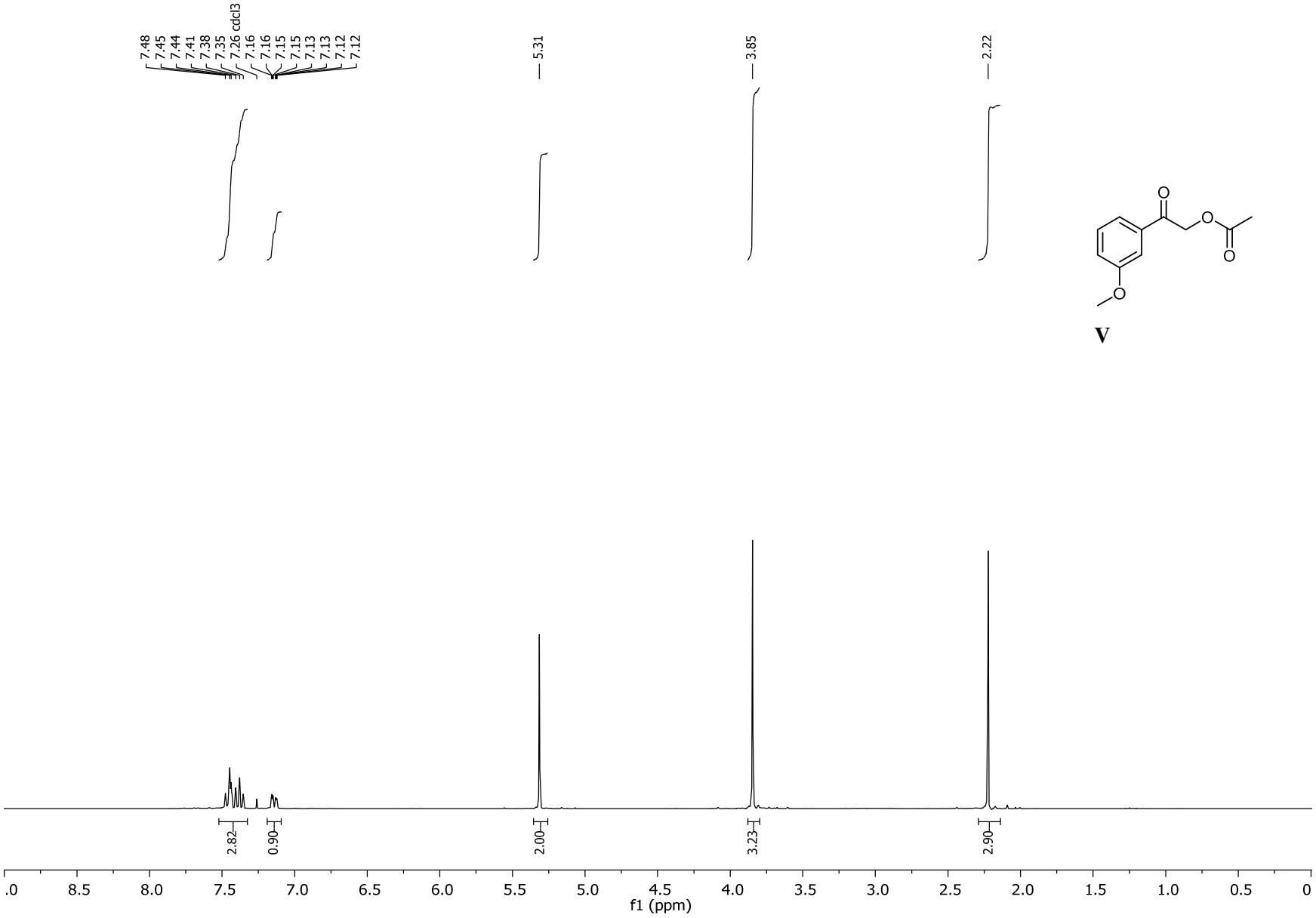
III



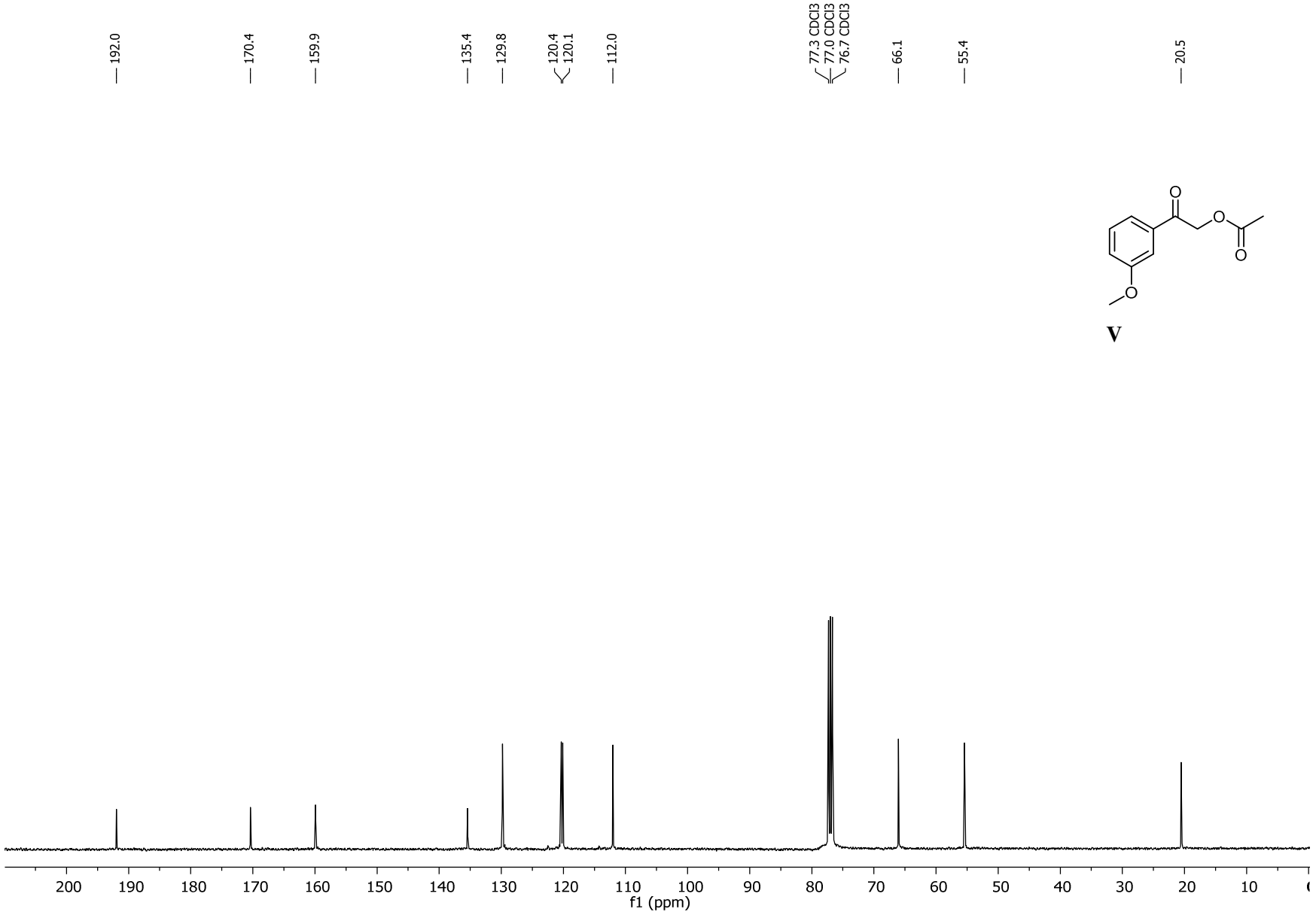
IV


190.6
170.5
164.0
130.0
127.2
114.0
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
65.7
55.5
20.6
O
O
O
O
f1 (ppm)

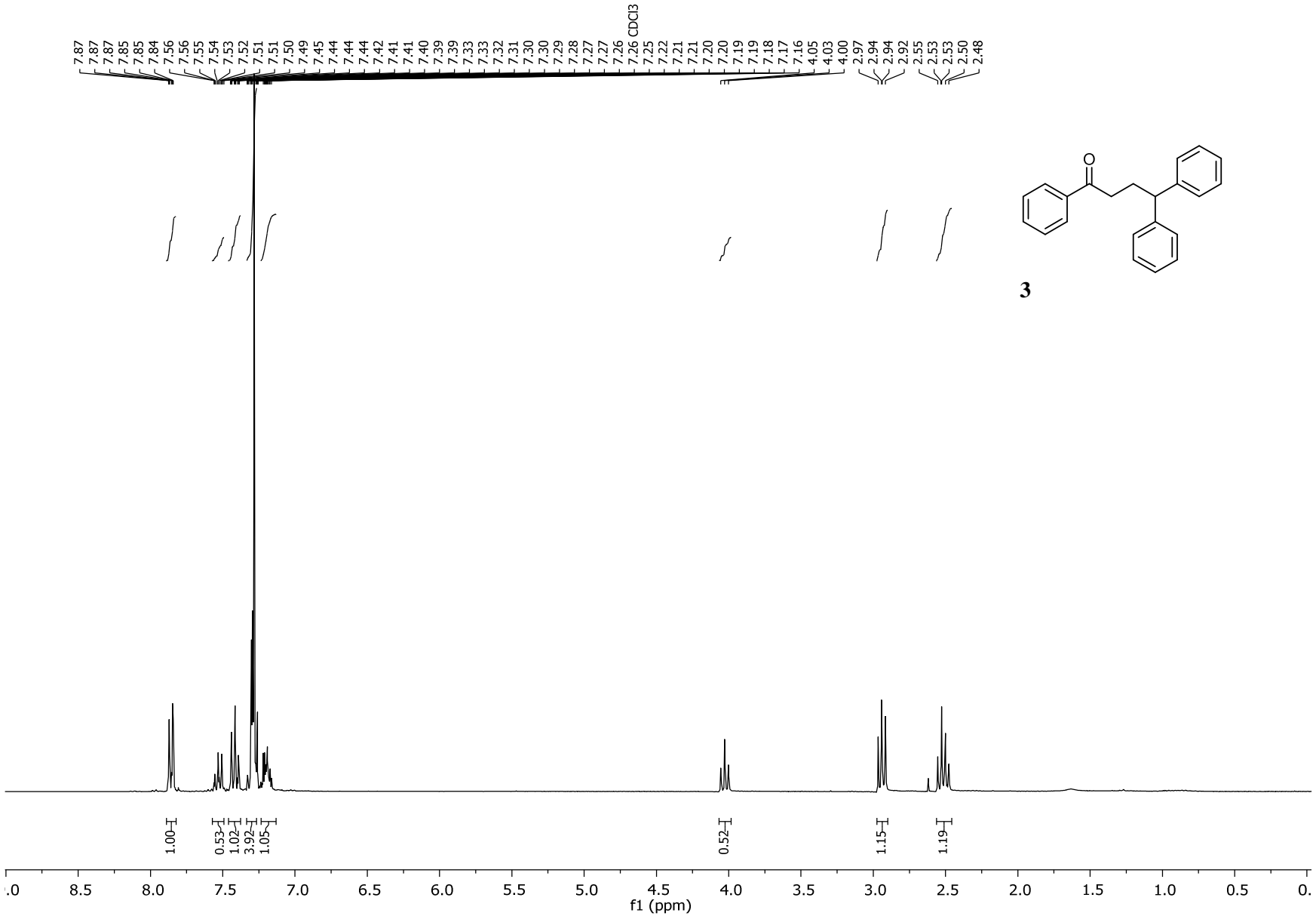
IV

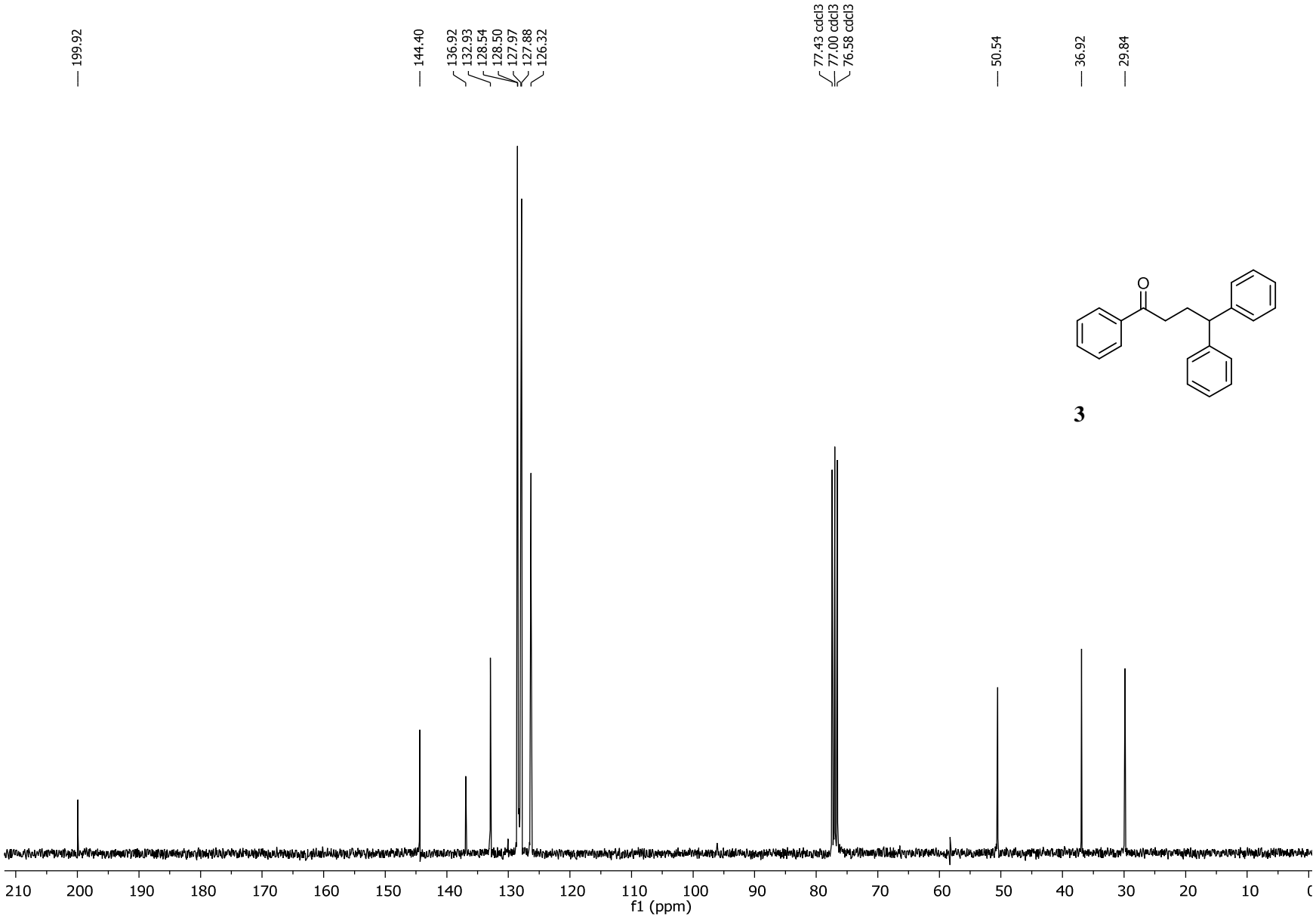

7.48
7.45
7.44
7.41
7.38
7.35
7.26 cdcl3
7.16
7.16
7.15
7.15
7.13
7.13
7.12
7.12
5.31
3.85
2.22
2.82
0.90
2.00
3.23
2.90
f1 (ppm)

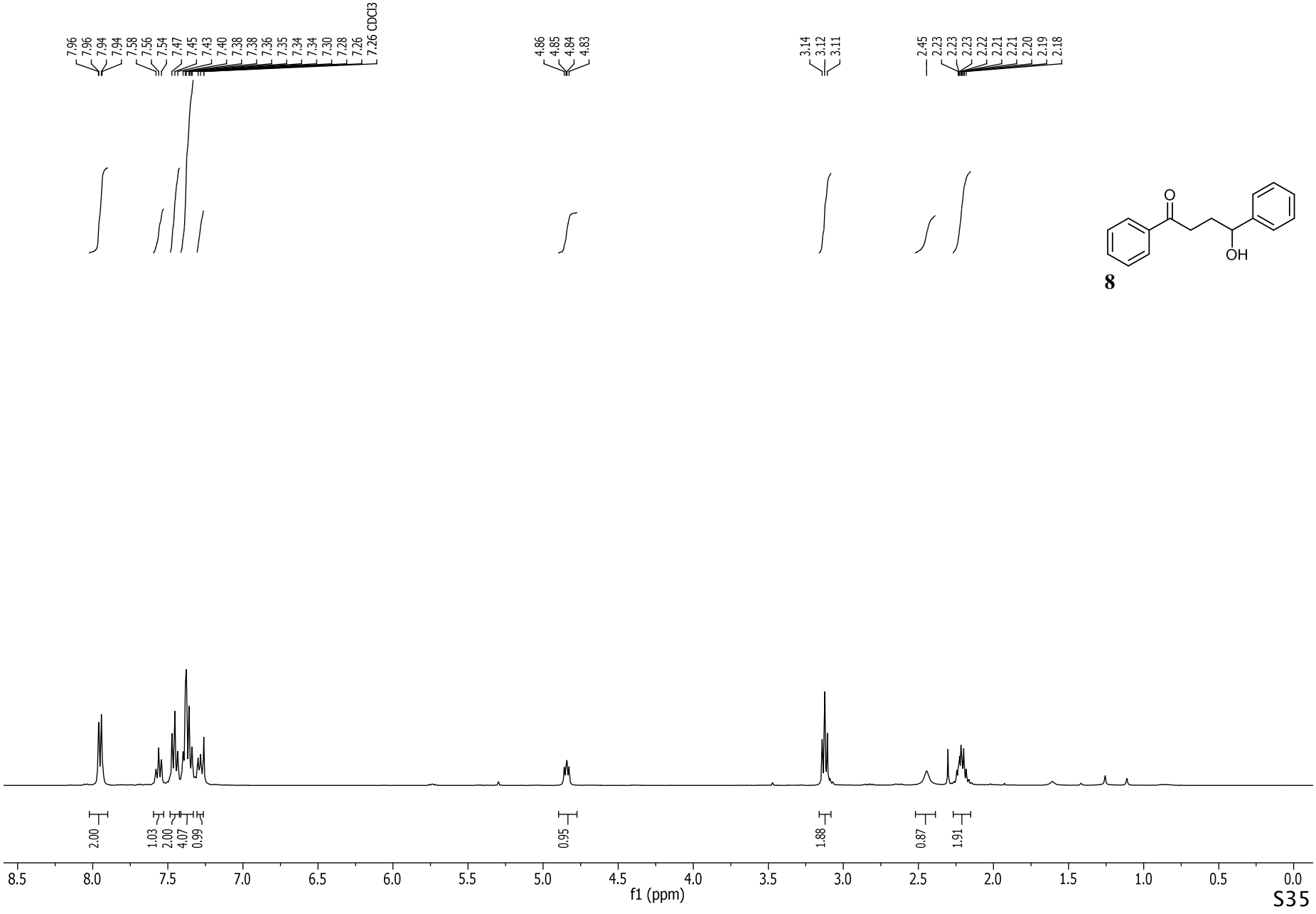
V


192.0
170.4
159.9
135.4
129.8
120.4
120.1
112.0
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
66.1
55.4
20.5
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

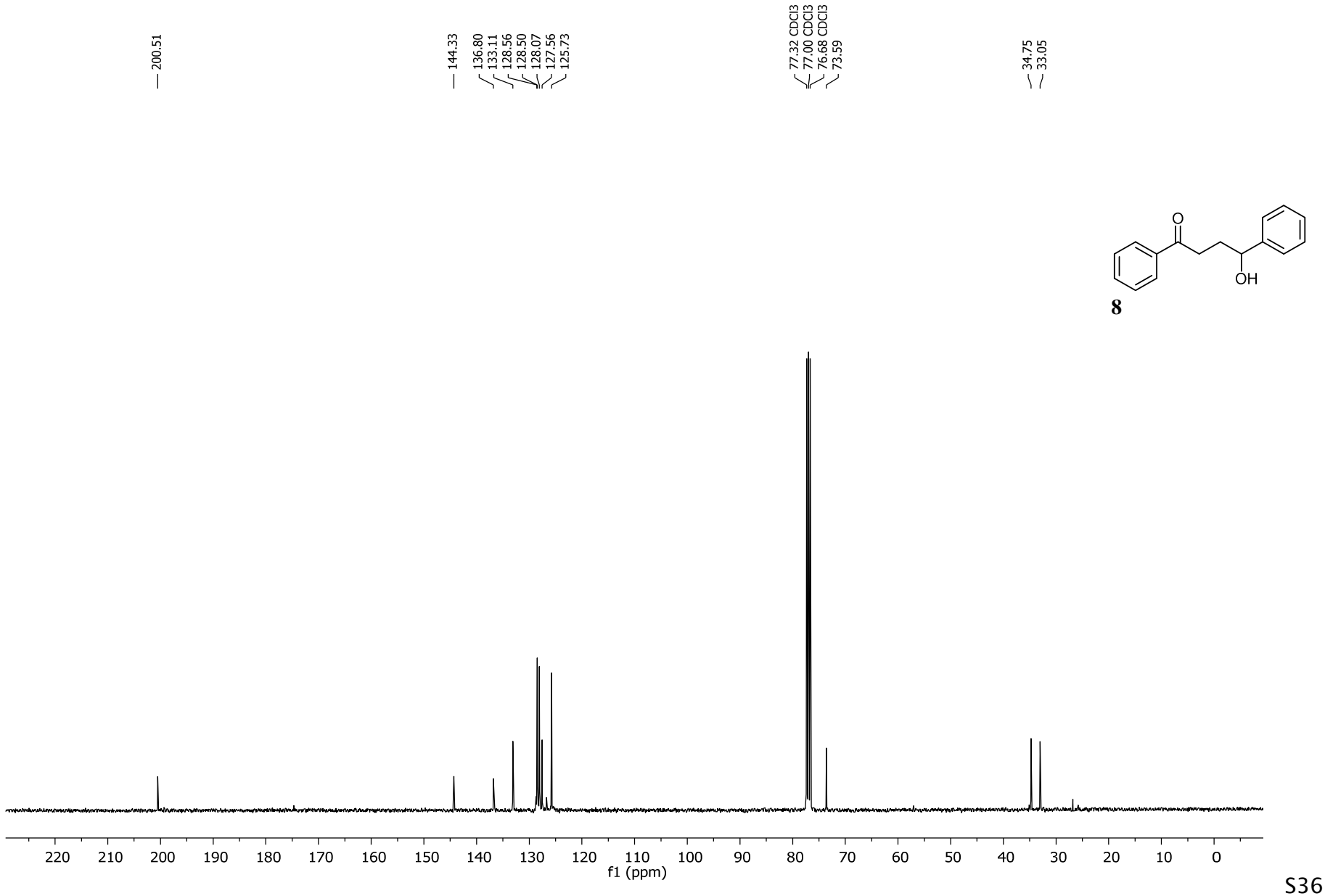
V

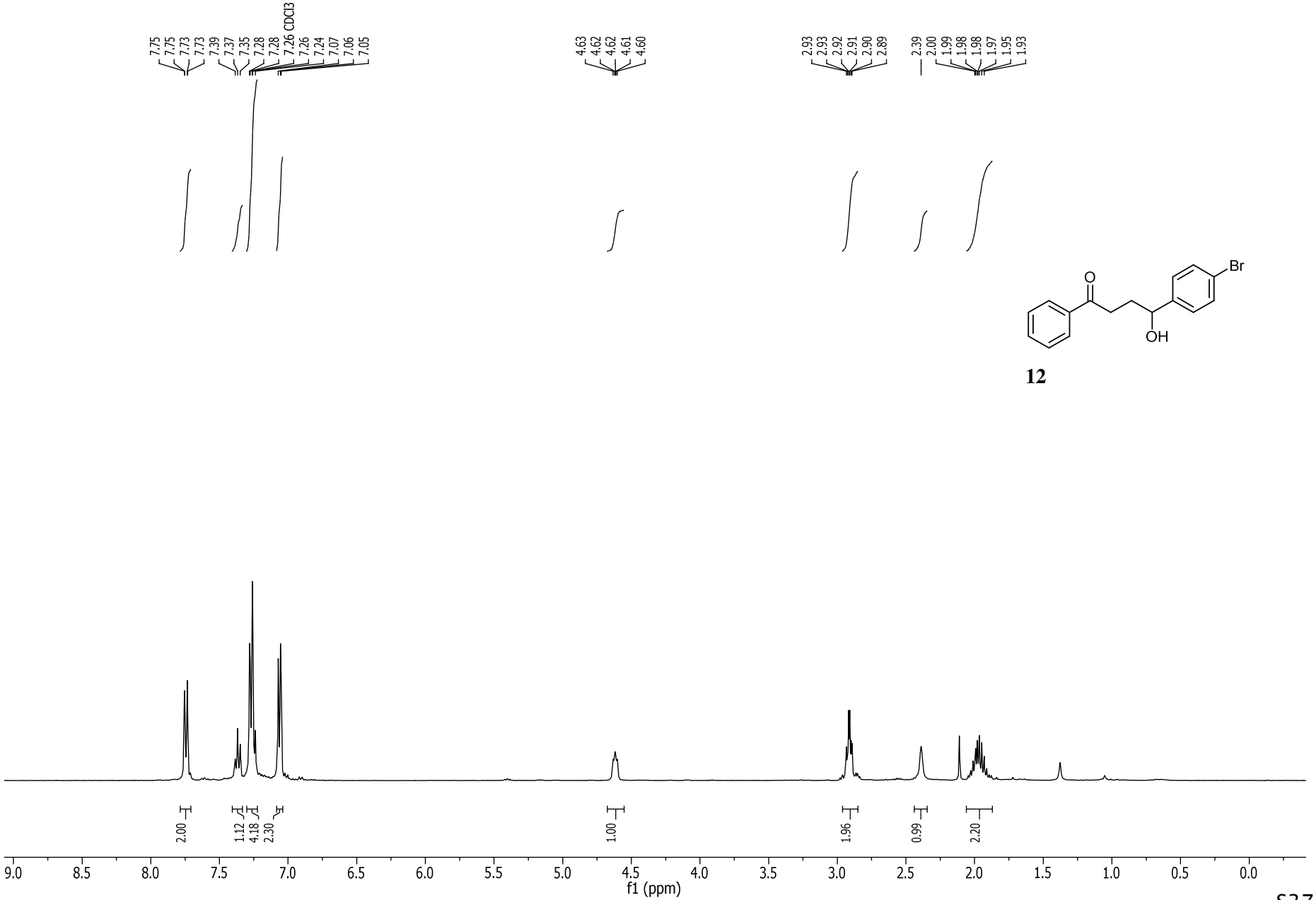

7.87
7.87
7.87
7.85
7.85
7.84
7.56
7.56
7.55
7.54
7.53
7.52
7.51
7.51
7.50
7.49
7.45
7.44
7.44
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
CDCl3
7.25
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.16
4.05
4.03
4.00
2.97
2.94
2.94
2.92
2.55
2.53
2.53
2.50
2.48
O
3
1.00
0.53
1.02
3.92
1.05
0.52
1.15
1.19
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
f1 (ppm)


199.92
144.40
136.92
132.93
128.54
128.50
127.97
127.88
126.32
77.43 cdcl3
77.00 cdcl3
76.58 cdcl3
50.54
36.92
29.84
O
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

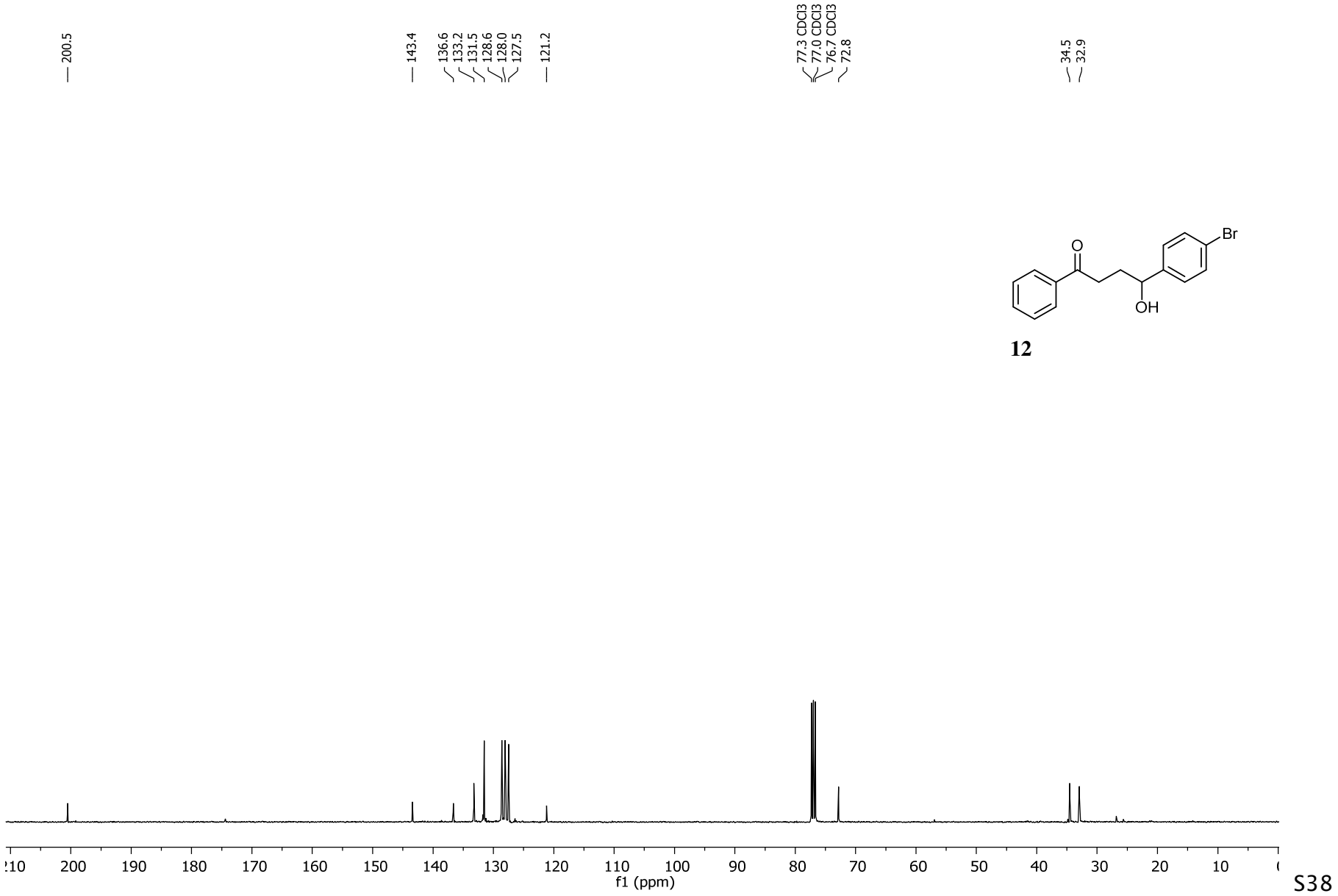

7.96
7.96
7.94
7.94
7.58
7.56
7.54
7.47
7.45
7.43
7.40
7.38
7.38
7.36
7.35
7.34
7.34
7.30
7.28
7.26
7.26 CDCl3
4.86
4.85
4.84
4.83
3.14
3.12
3.11
2.45
2.23
2.23
2.23
2.22
2.21
2.21
2.20
2.19
2.18
O
OH
2.00
1.03
2.00
4.07
0.99
0.95
1.88
0.87
1.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

8

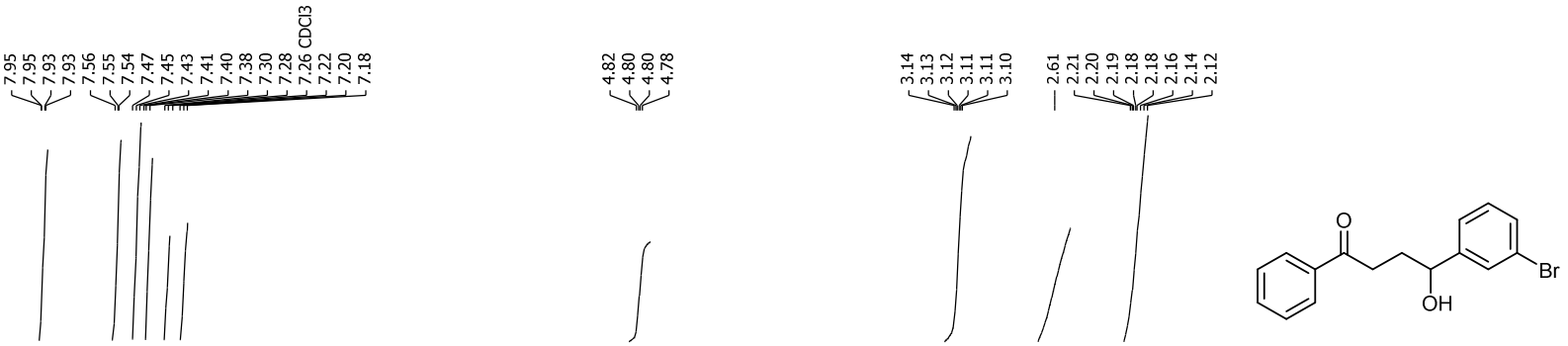

200.51
144.33
136.80
133.11
128.56
128.50
128.07
127.56
125.73
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.59
34.75
33.05
O
OH
8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.75
7.75
7.73
7.73
7.39
7.37
7.35
7.28
7.28
CDCl3
7.26
7.26
7.24
7.07
7.06
7.05
4.63
4.62
4.62
4.61
4.60
2.93
2.93
2.92
2.91
2.90
2.89
2.39
2.00
1.99
1.98
1.98
1.97
1.95
1.93
O
Br
OH
2.00
1.12
4.18
2.30
1.00
1.96
0.99
2.20
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
f1 (ppm)

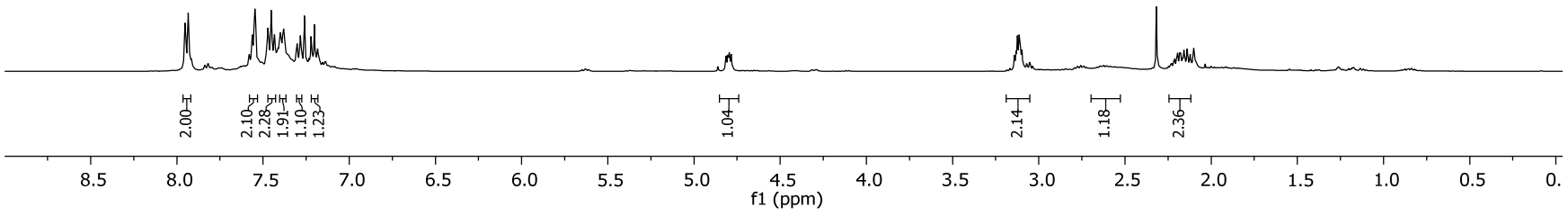
12

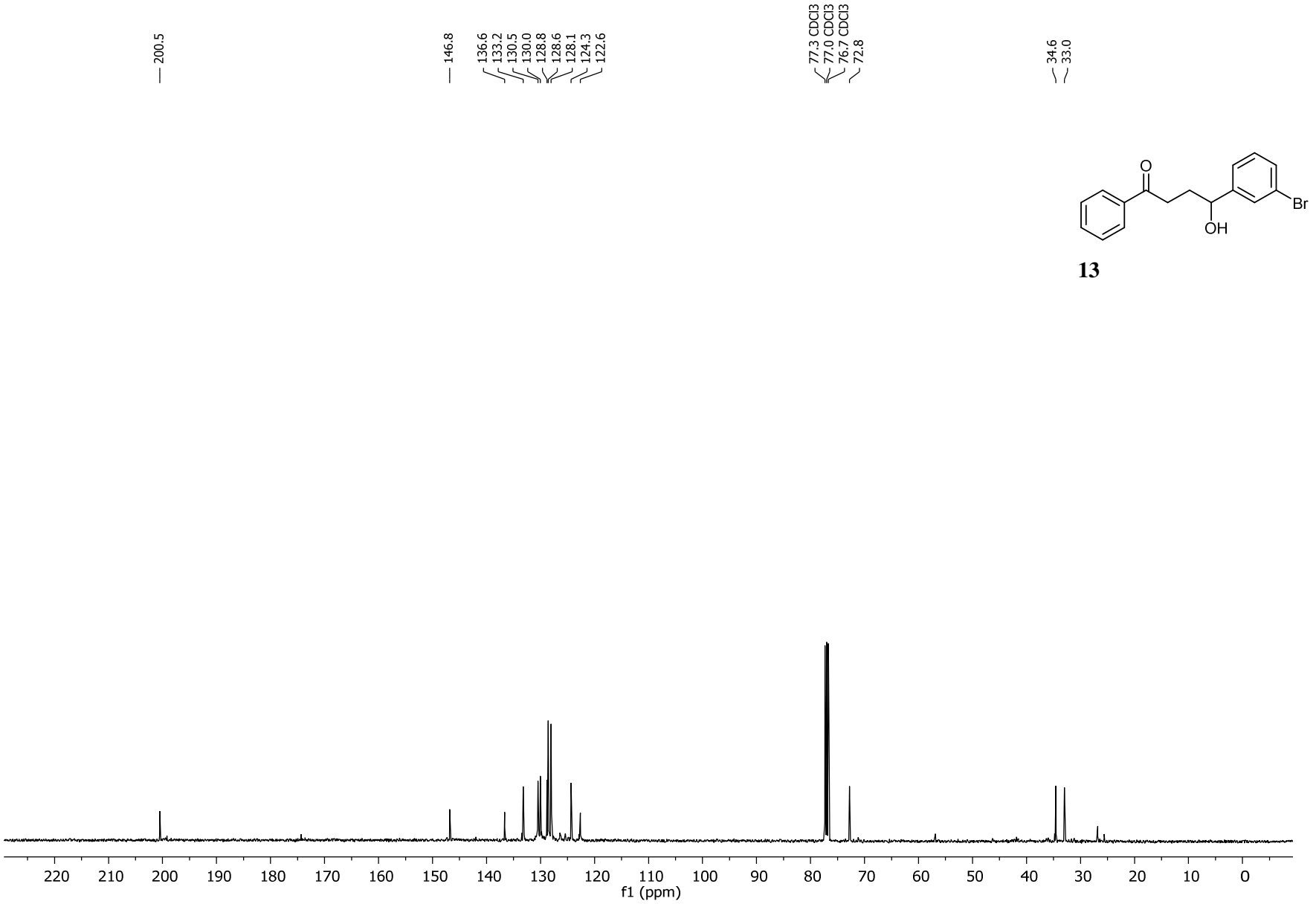

200.5
143.4
136.6
133.2
131.5
128.6
128.0
127.5
121.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
72.8
34.5
32.9
O
Br
OH
f1 (ppm)

12

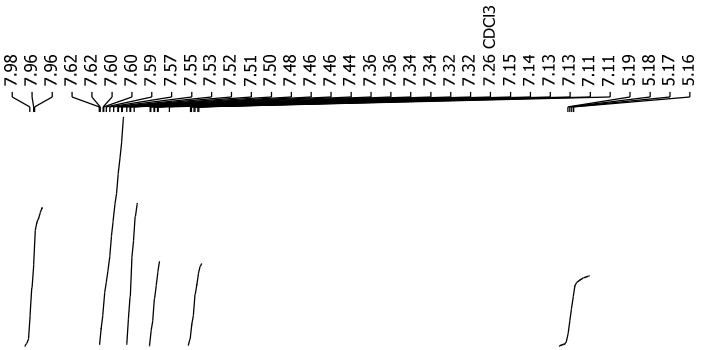

7.95
7.95
7.93
7.93
7.56
7.55
7.54
7.47
7.45
7.43
7.41
7.40
7.38
7.30
7.28
7.26 CDCl3
7.22
7.20
7.18
4.82
4.80
4.80
4.78
3.14
3.13
3.12
3.11
3.11
3.10
2.61
2.21
2.20
2.19
2.18
2.18
2.16
2.14
2.12
O
Br
OH

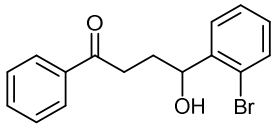
13


2.00
2.10
2.28
1.91
1.10
1.23
1.04
2.14
1.18
2.36
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.
f1 (ppm)

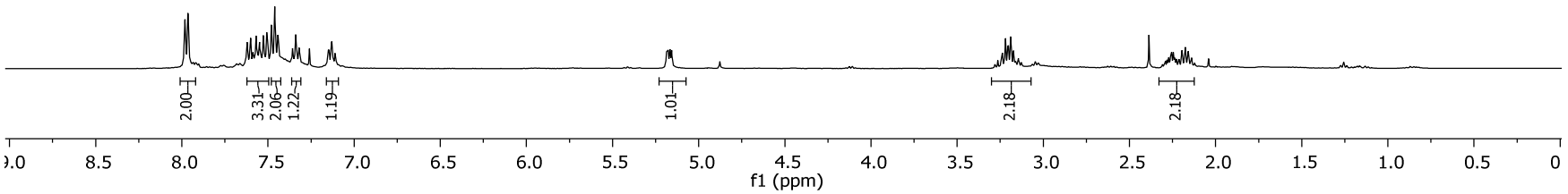

200.5
146.8
136.6
133.2
130.5
130.0
128.8
128.6
128.1
124.3
122.6
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
72.8
34.6
33.0
O
Br
OH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

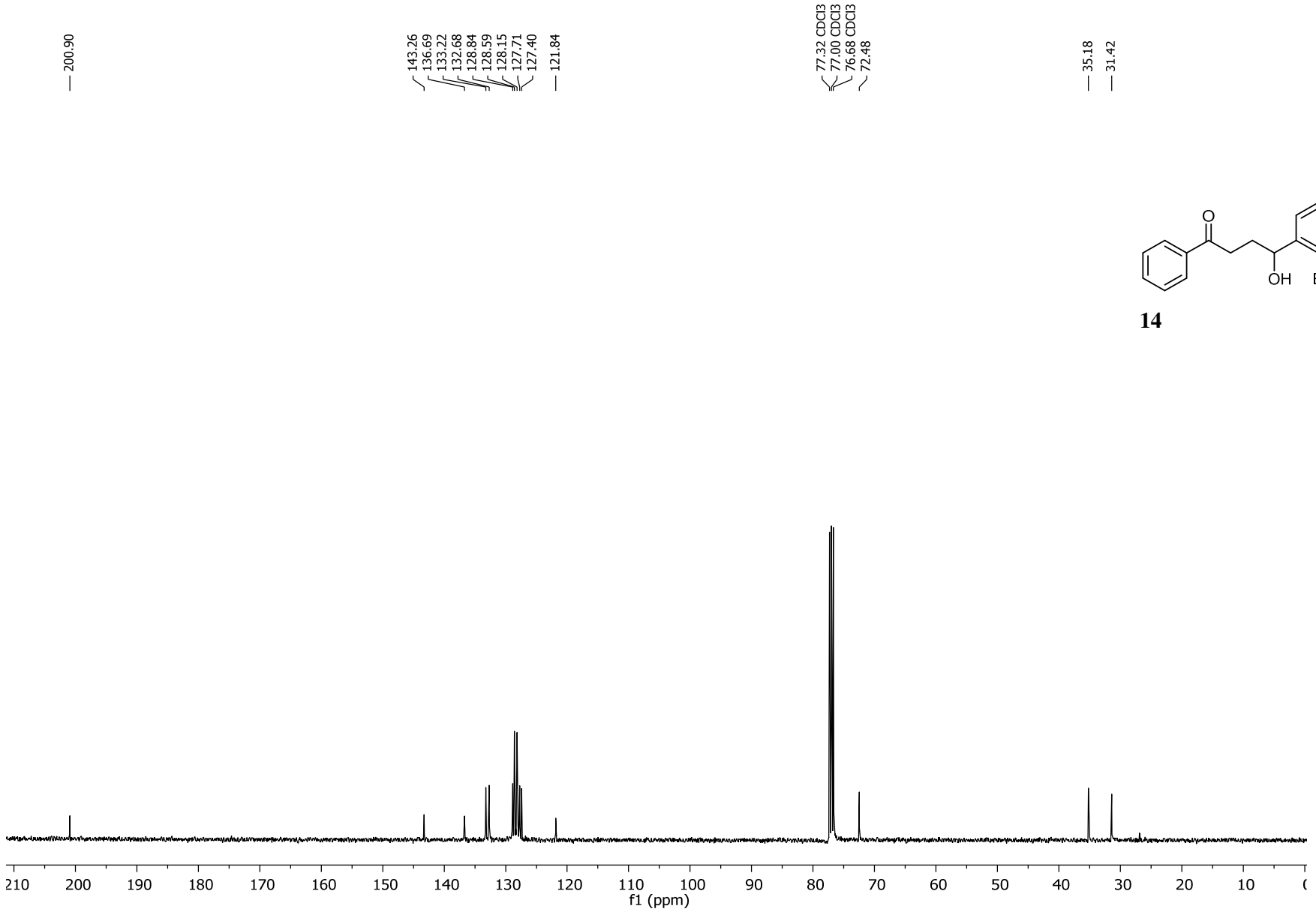
13


7.98
7.96
7.96
7.62
7.62
7.60
7.60
7.59
7.57
7.55
7.53
7.52
7.51
7.50
7.48
7.46
7.46
7.44
7.36
7.36
7.34
7.34
7.32
7.32
7.26 CDCl3
7.15
7.14
7.13
7.13
7.11
7.11
5.19
5.18
5.17
5.16
3.26
3.24
3.22
3.20
3.19
3.17
3.13
2.31
2.29
2.27
2.25
2.25
2.23
2.21
2.20
2.18
2.16
2.14

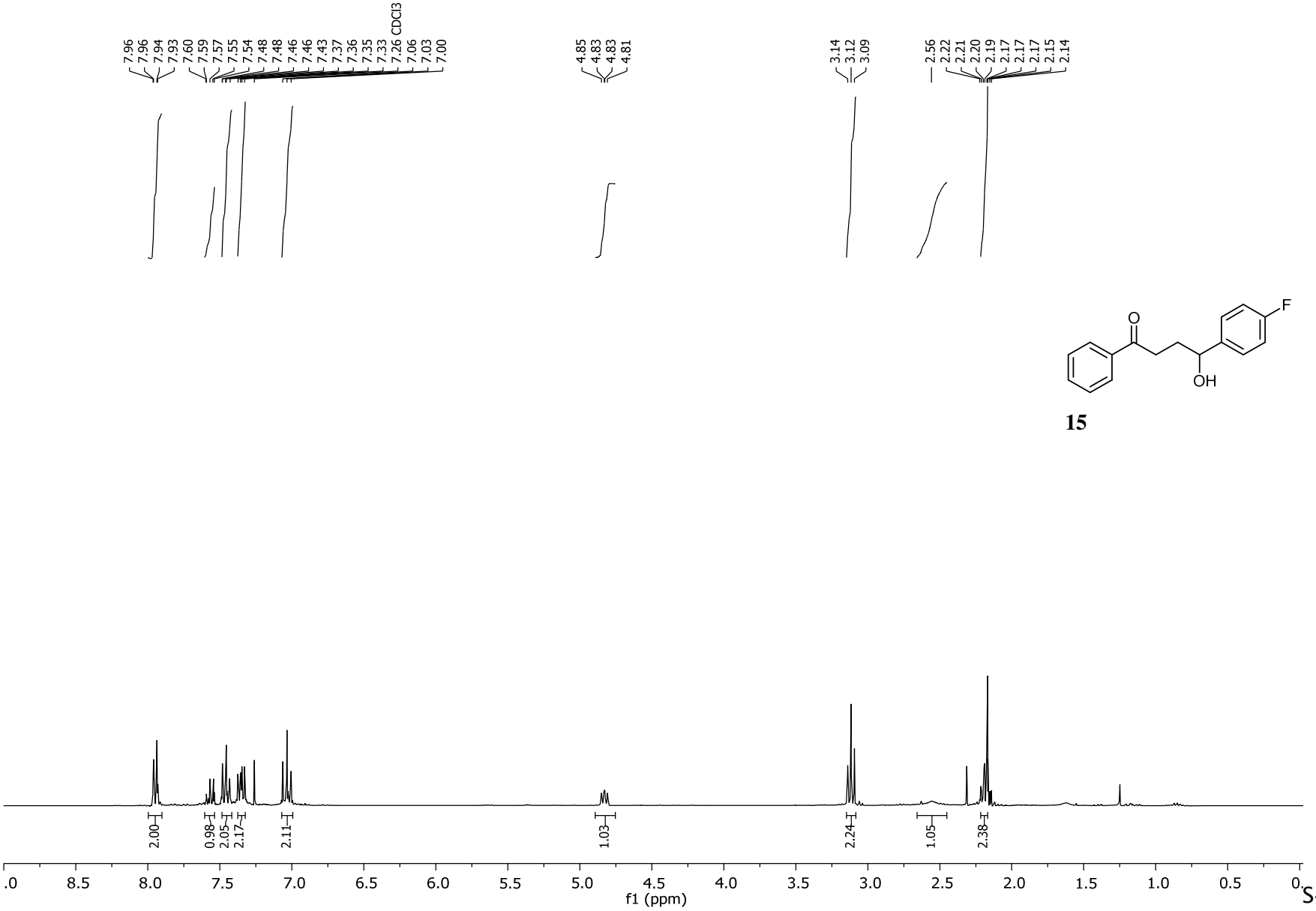

O
OH
Br

14


2.00
3.31
2.06
1.22
1.19
1.01
2.18
2.18
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
f1 (ppm)

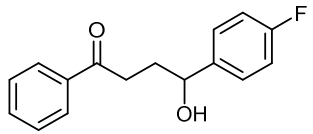

200.90
143.26
136.69
133.22
132.68
128.84
128.59
128.15
127.71
127.40
121.84
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.48
35.18
31.42
O
OH
Br
f1 (ppm)

14

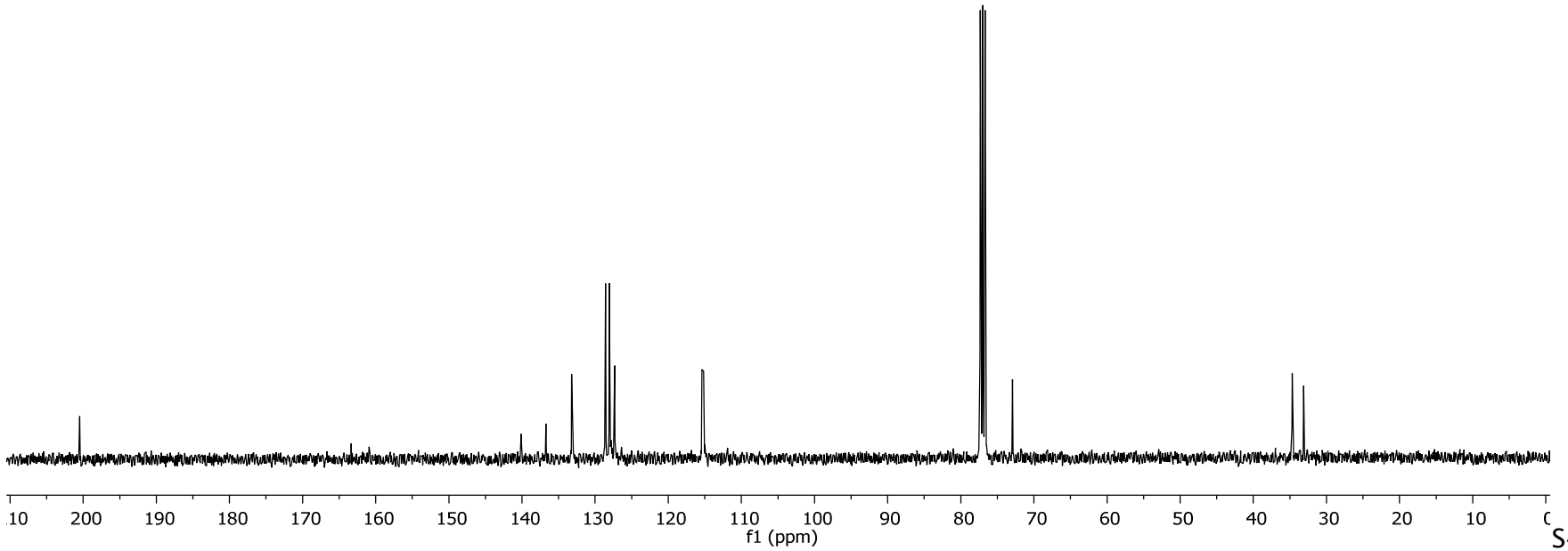

7.96
7.96
7.94
7.93
7.60
7.59
7.57
7.55
7.54
7.48
7.48
7.46
7.46
7.43
7.37
7.36
7.35
7.33
7.26 CDCl3
7.06
7.03
7.00
4.85
4.83
4.83
4.81
3.14
3.12
3.09
2.56
2.22
2.21
2.20
2.19
2.17
2.17
2.15
2.14
O
F
OH
2.00
0.98
2.05
2.17
2.11
1.03
2.24
1.05
2.38
f1 (ppm)

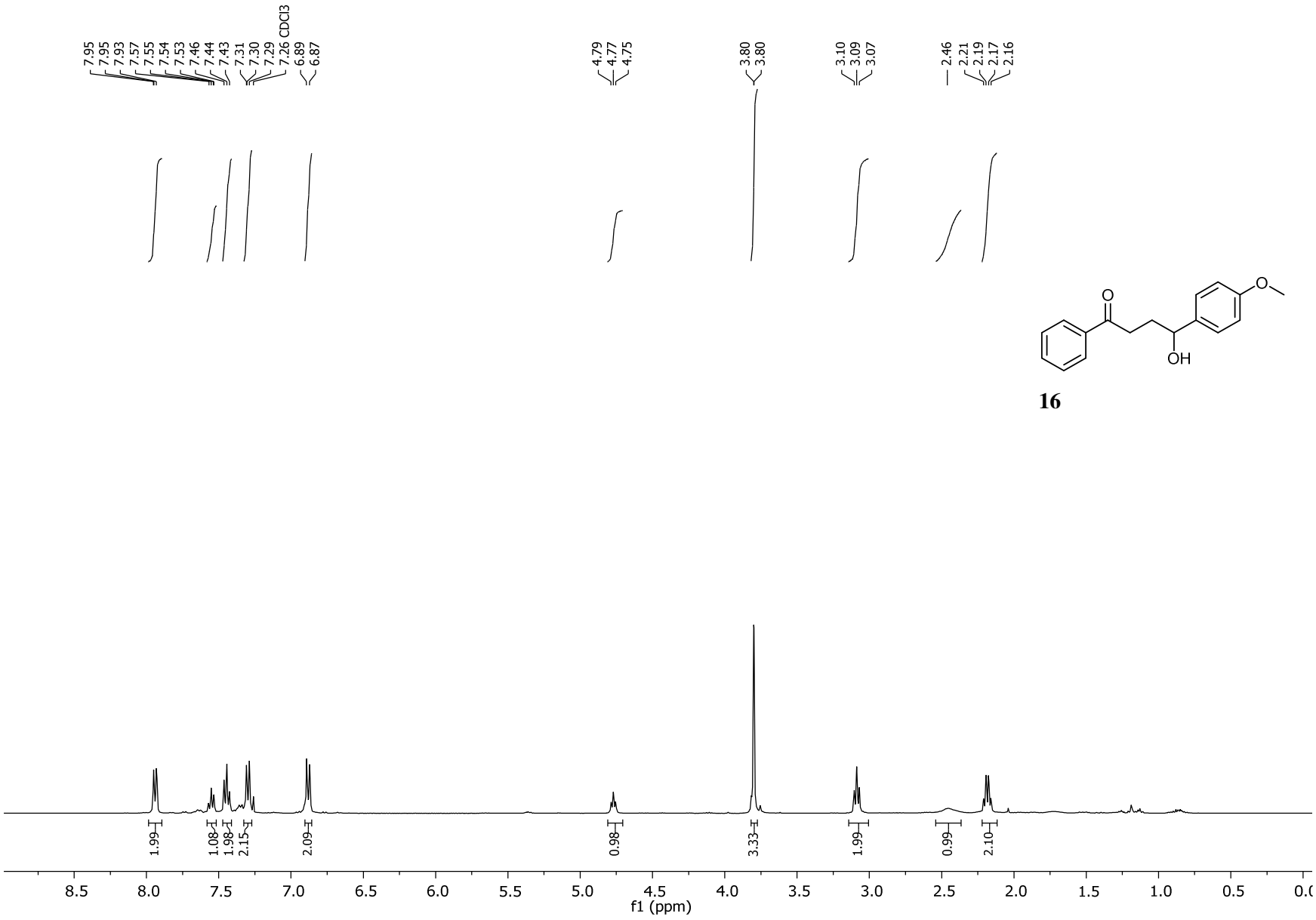
15


200.5
163.3
160.9
140.1
136.7
133.2
128.6
128.1
127.4
127.3
115.4
115.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
72.9
34.7
33.1

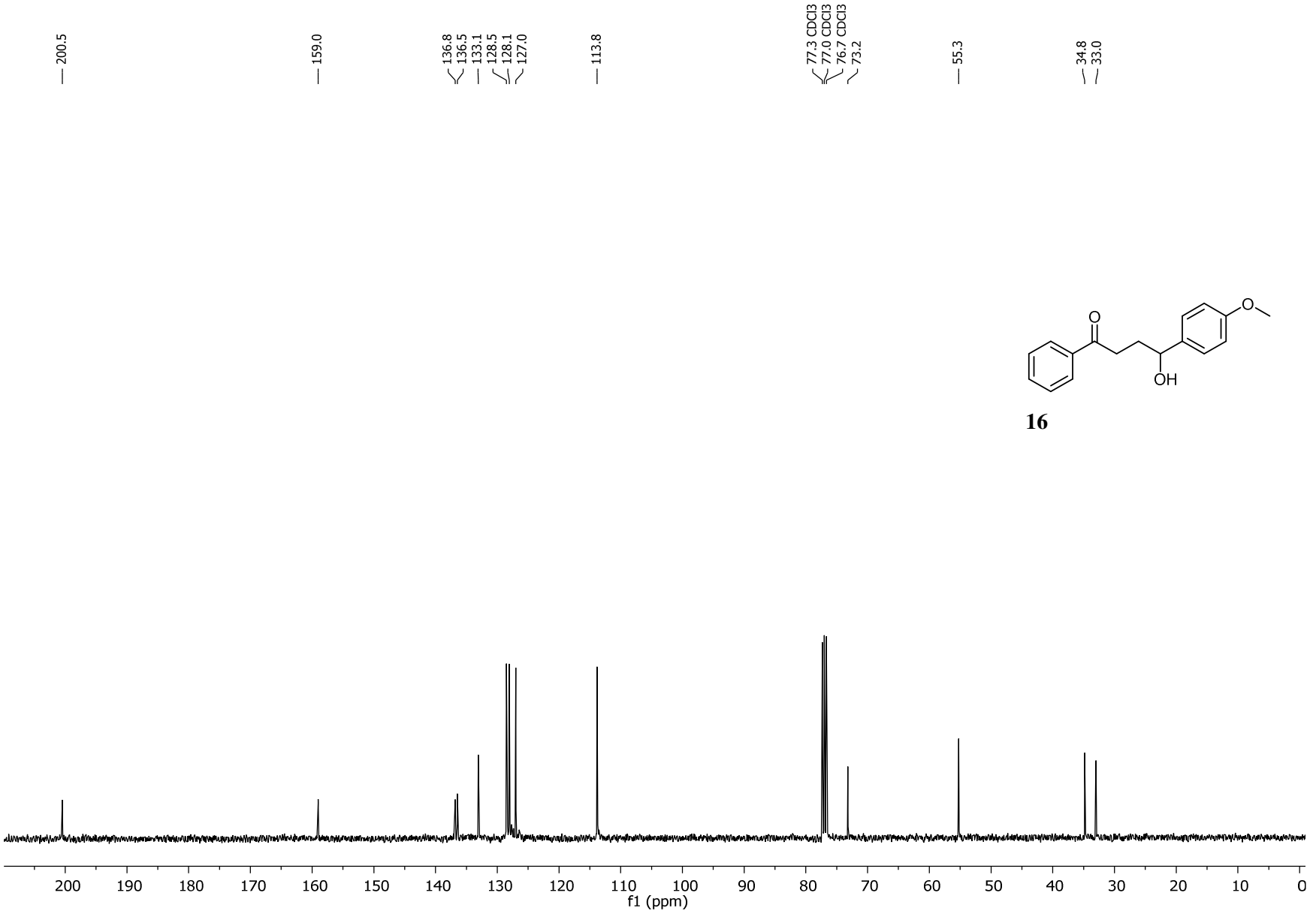

O
F
OH

15

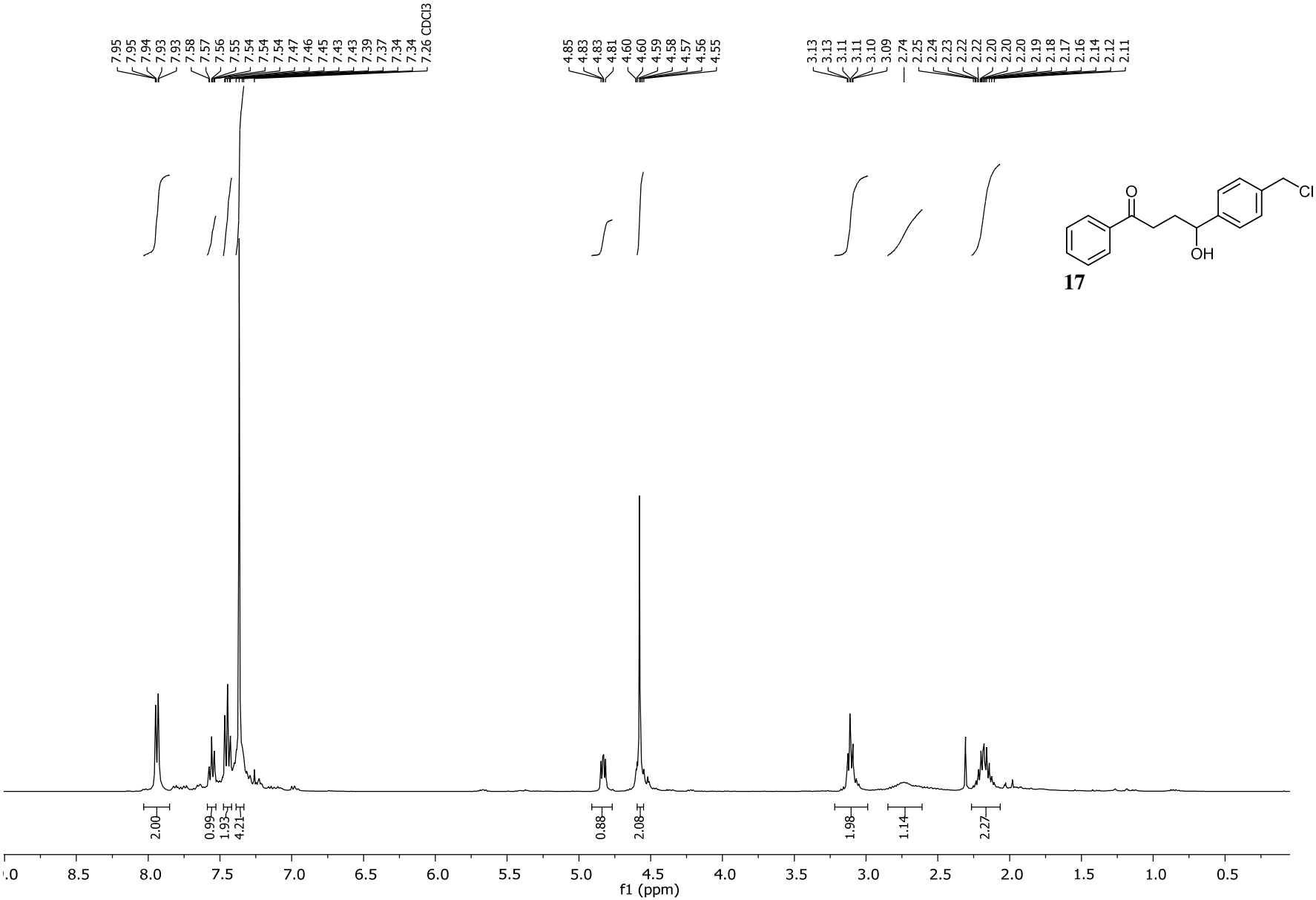

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

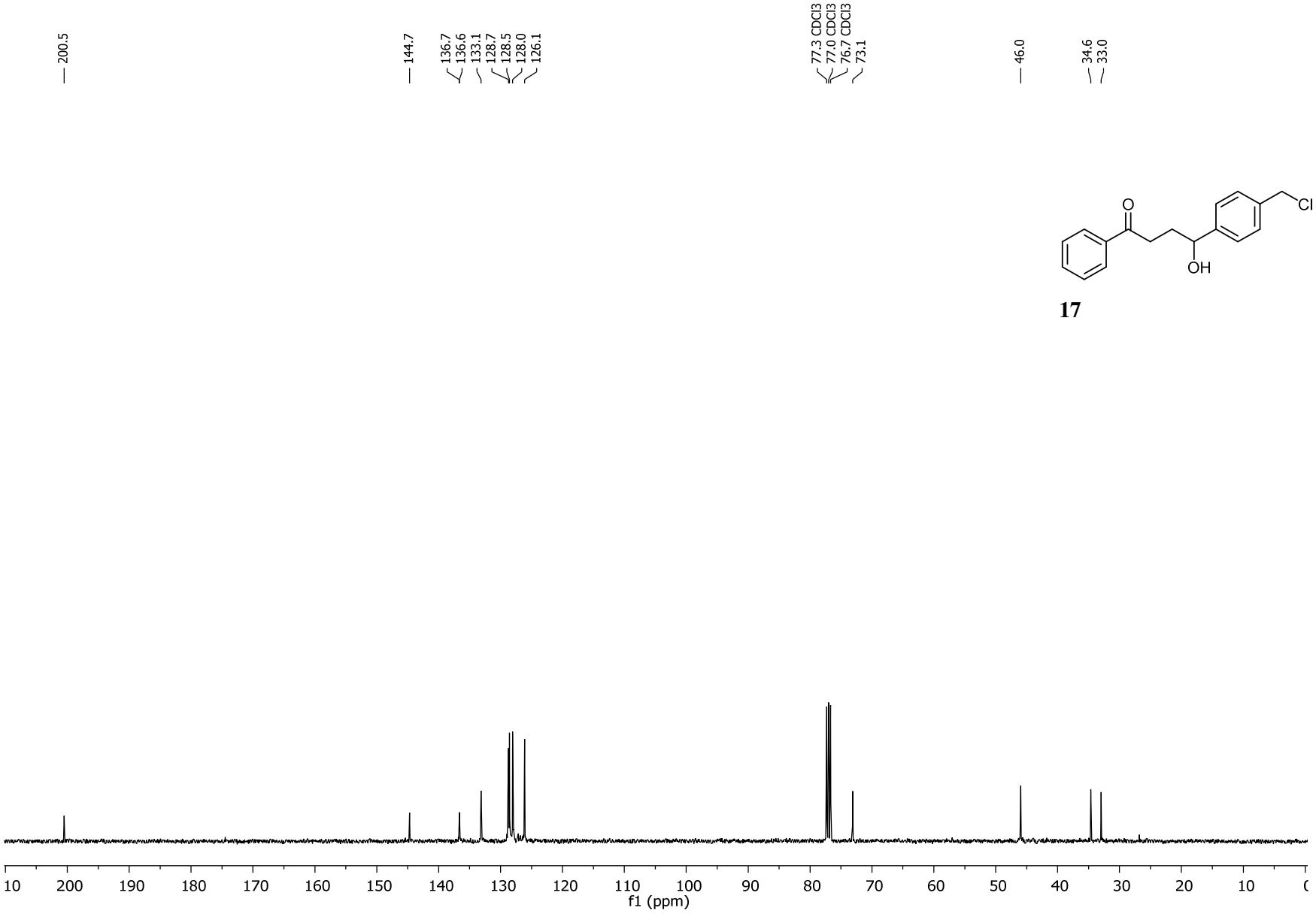

7.95
7.95
7.93
7.57
7.55
7.54
7.53
7.46
7.44
7.43
7.31
7.30
7.29
7.26 CDCl3
6.89
6.87
4.79
4.77
4.75
3.80
3.80
3.10
3.09
3.07
2.46
2.21
2.19
2.17
2.16
O
O
OH
1.99
1.08
1.98
2.15
2.09
0.98
3.33
1.99
0.99
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

16

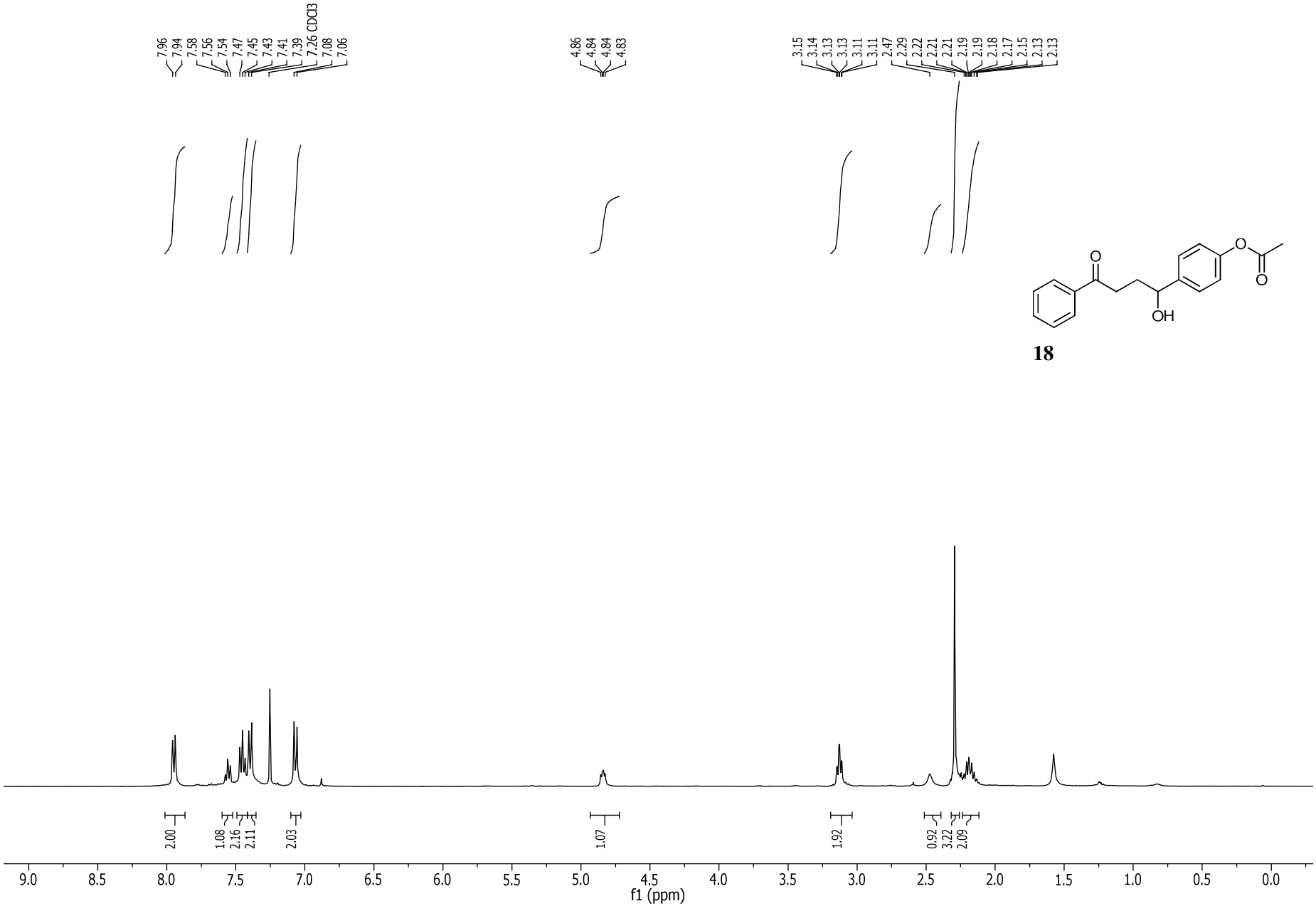

200.5
159.0
136.8
136.5
133.1
128.5
128.1
127.0
113.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.2
55.3
34.8
33.0
O
O
OH
f1 (ppm)

16

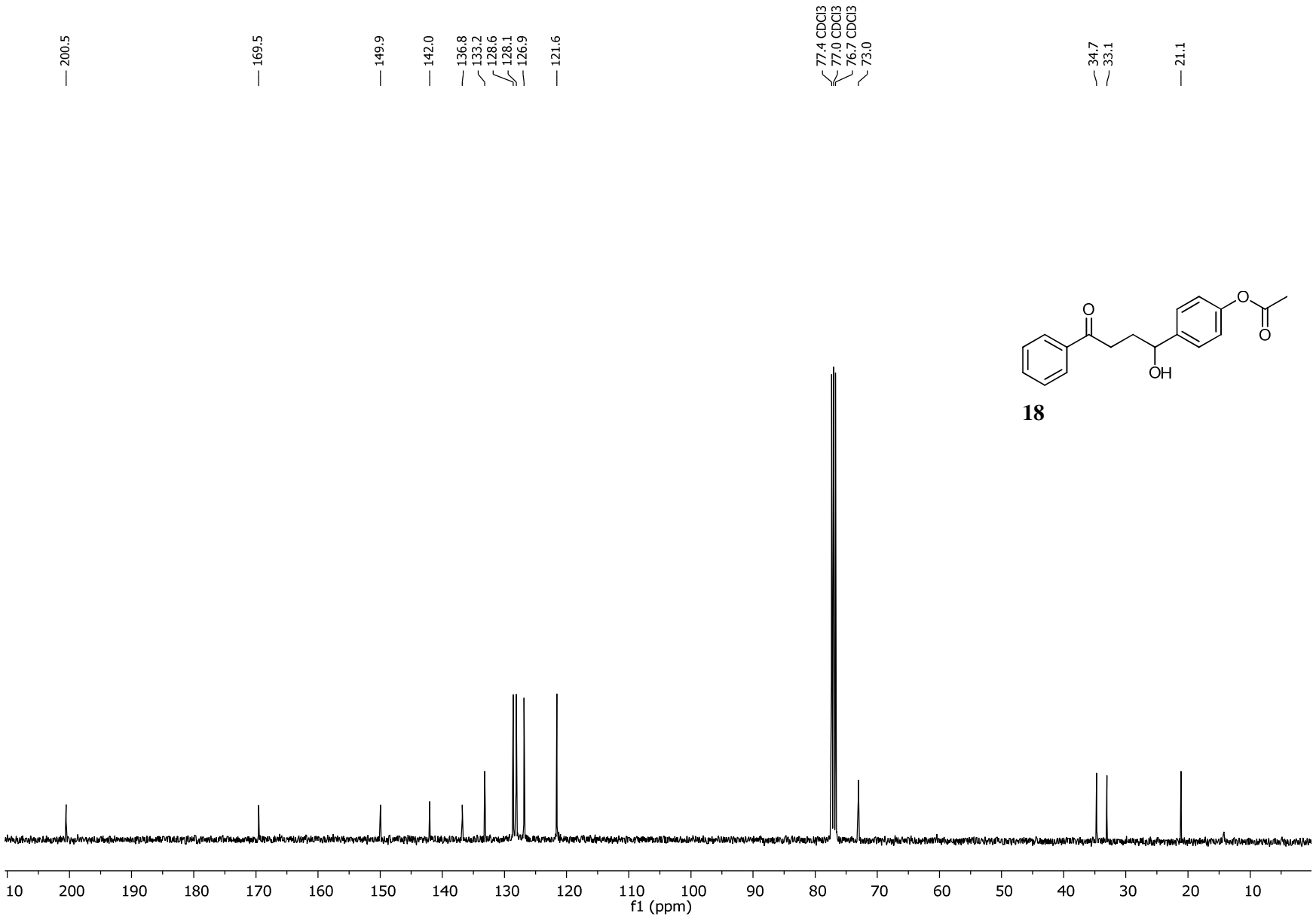

7.95
7.95
7.94
7.93
7.93
7.58
7.57
7.56
7.55
7.54
7.54
7.54
7.47
7.46
7.45
7.43
7.43
7.39
7.37
7.34
7.34
7.26 CDCl3
4.85
4.83
4.83
4.81
4.60
4.60
4.59
4.58
4.57
4.56
4.55
3.13
3.13
3.11
3.11
3.10
3.09
2.74
2.25
2.24
2.23
2.22
2.22
2.20
2.20
2.20
2.19
2.18
2.17
2.16
2.14
2.12
2.11
O
Cl
OH
17
2.00
0.99
1.93
4.21
0.88
2.08
1.98
1.14
2.27
f1 (ppm)

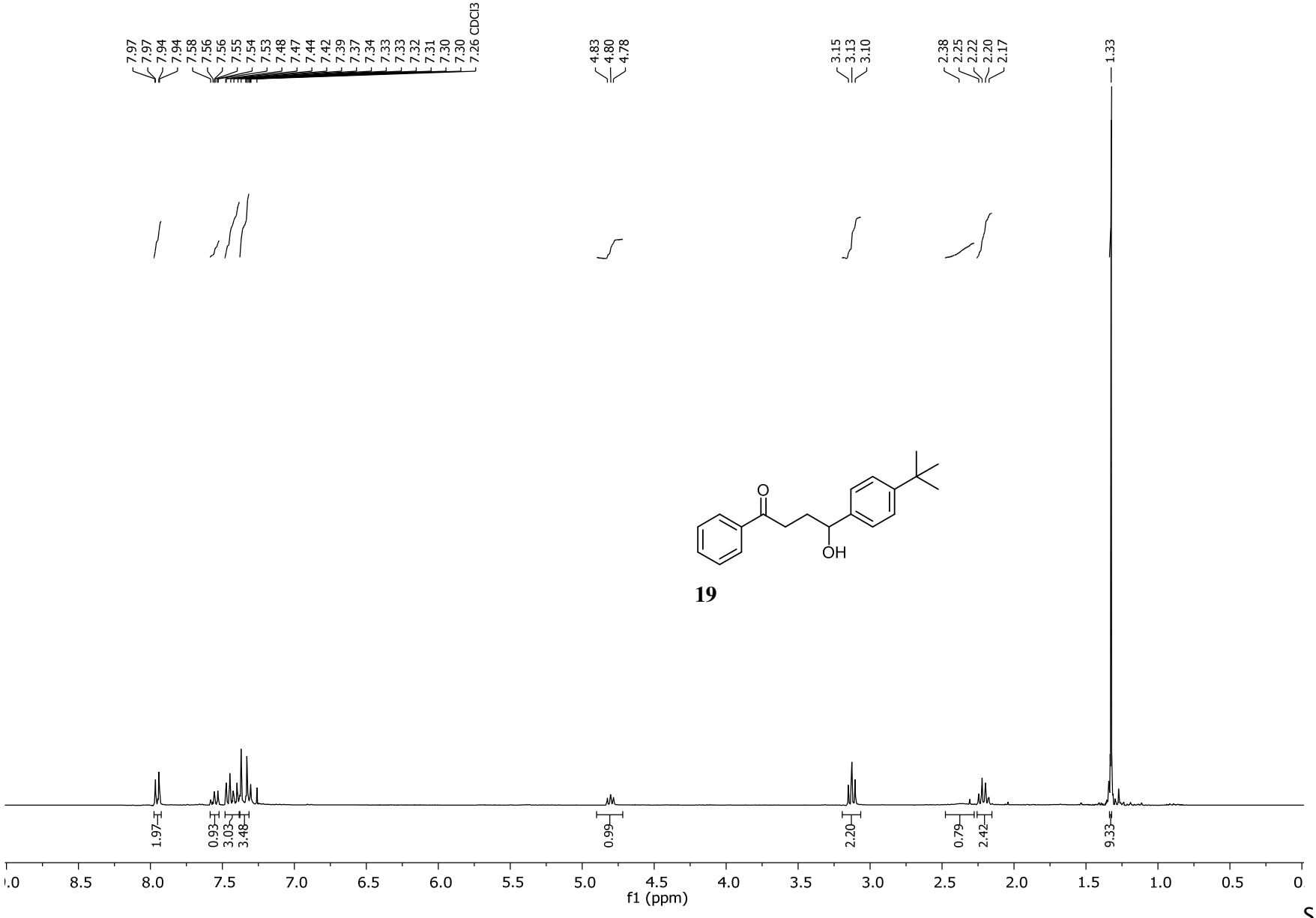

200.5
144.7
136.7
136.6
133.1
128.7
128.5
128.0
126.1
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.1
46.0
34.6
33.0
O
Cl
OH
f1 (ppm)

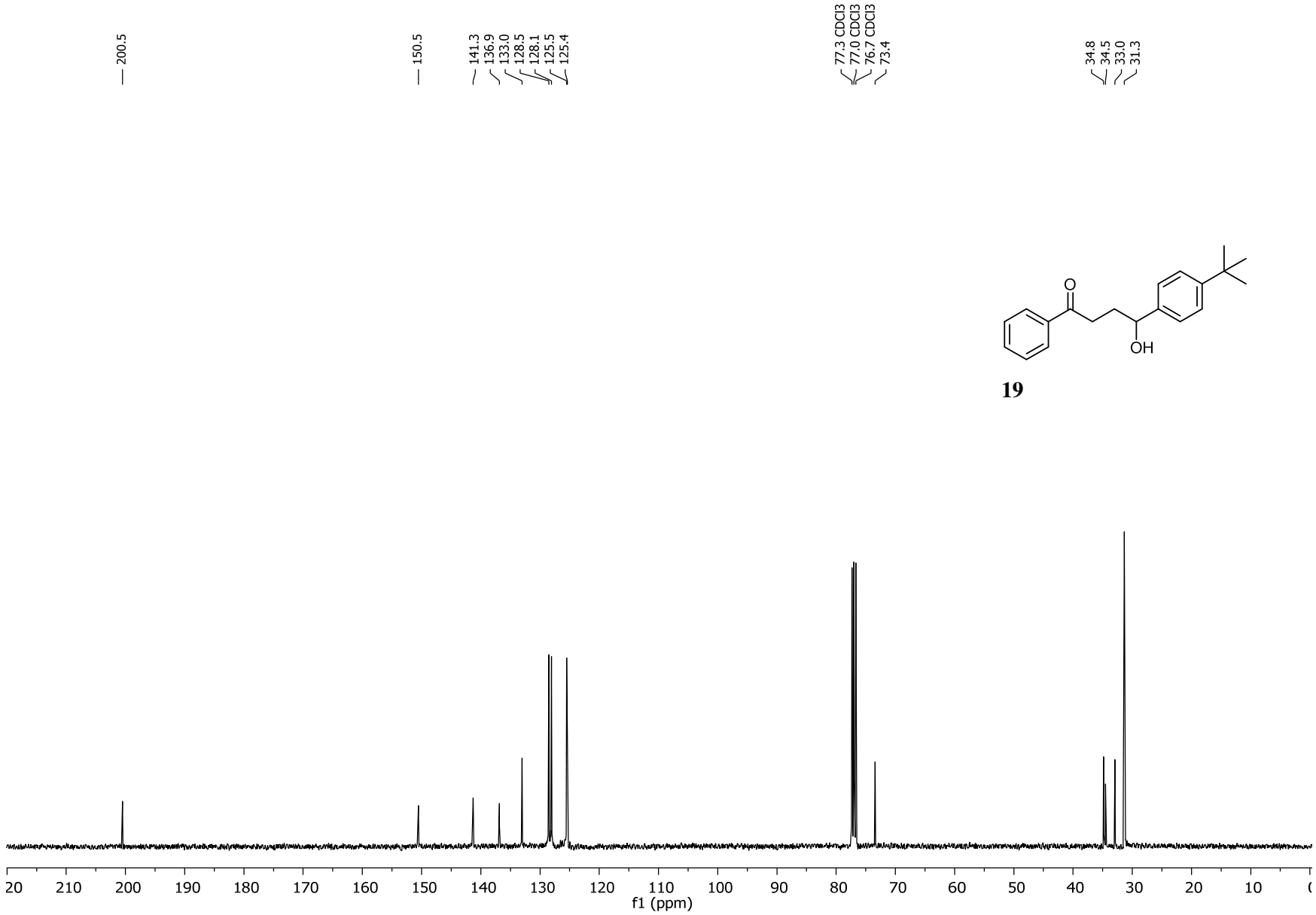
17


7.96
7.94
7.58
7.56
7.54
7.47
7.45
7.43
7.41
7.39
7.26 CDCl3
7.08
7.06
4.86
4.84
4.84
4.83
3.15
3.14
3.13
3.13
3.11
3.11
2.47
2.29
2.22
2.21
2.21
2.19
2.19
2.18
2.17
2.15
2.13
2.13
O
O
O
OH
2.00
1.08
2.16
2.11
2.03
1.07
1.92
0.92
3.22
2.09
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
f1 (ppm)

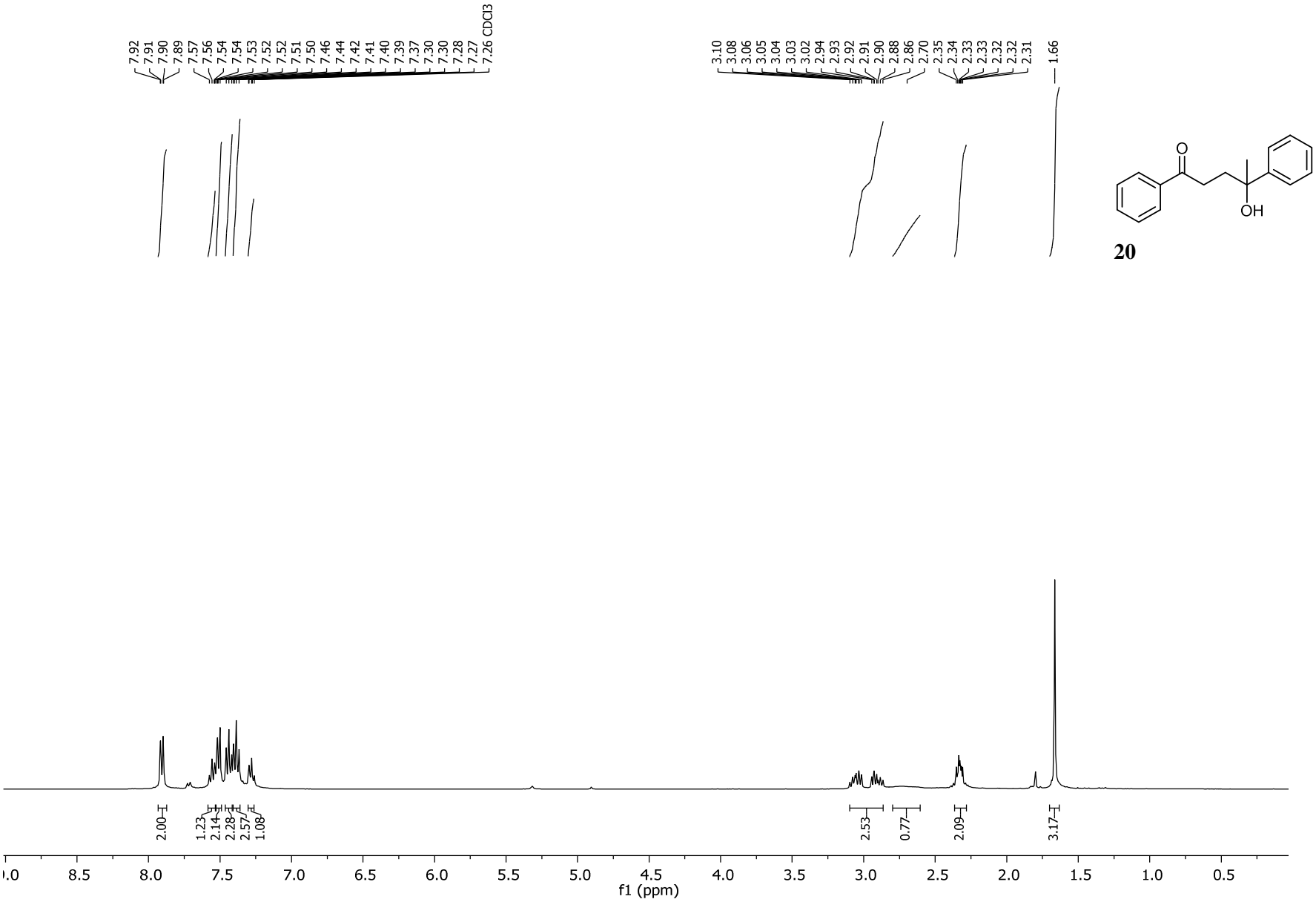
18

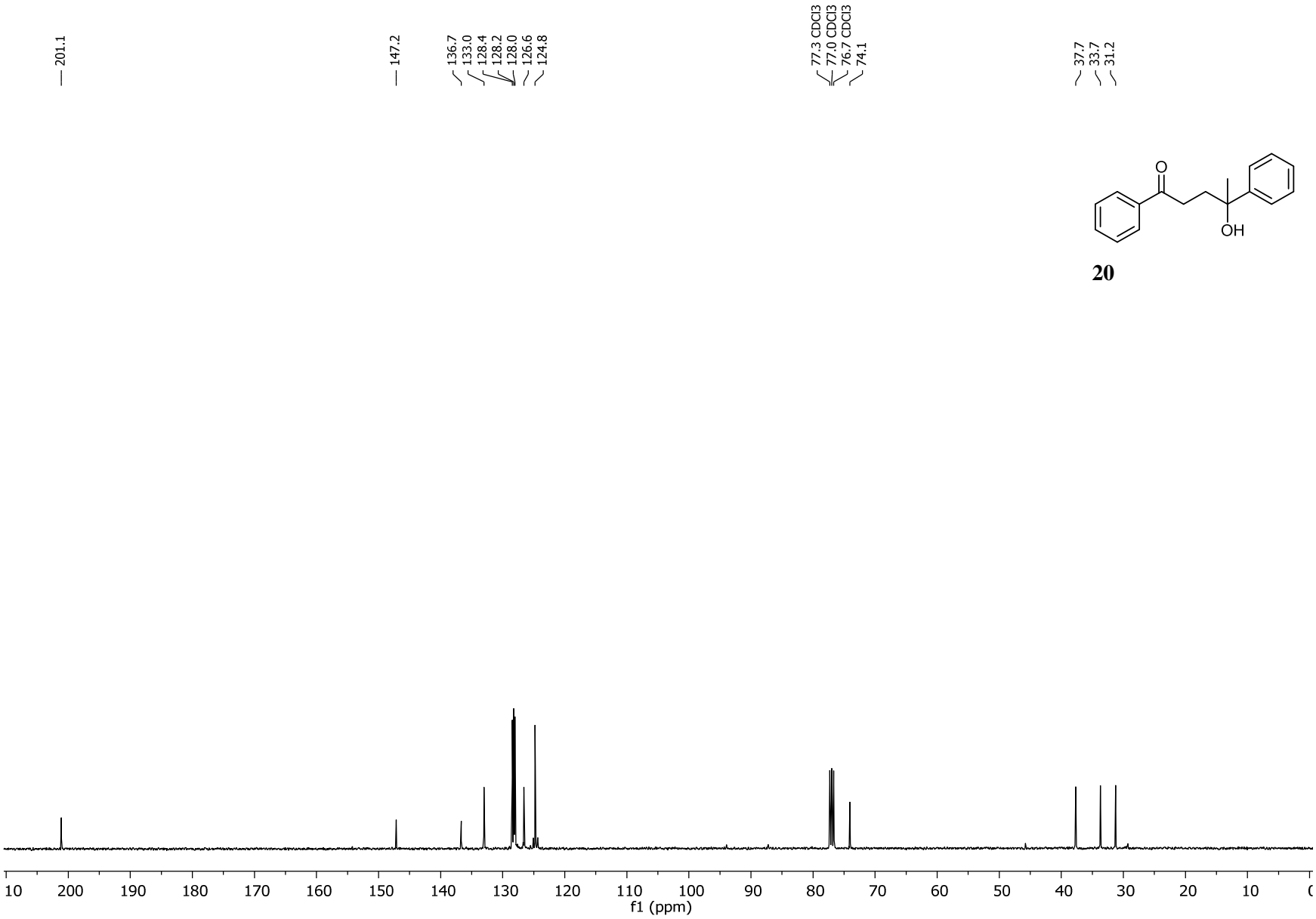

200.5
169.5
149.9
142.0
136.8
133.2
128.6
128.1
126.9
121.6
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
73.0
34.7
33.1
21.1
O
O
O
OH
18
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.97
7.97
7.94
7.94
7.58
7.56
7.56
7.55
7.54
7.53
7.48
7.47
7.44
7.42
7.39
7.37
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.26 CDCl3
4.83
4.80
4.78
3.15
3.13
3.10
2.38
2.25
2.22
2.20
2.17
1.33
O
OH
19
1.97
0.93
3.03
3.48
0.99
2.20
0.79
2.42
9.33
f1 (ppm)

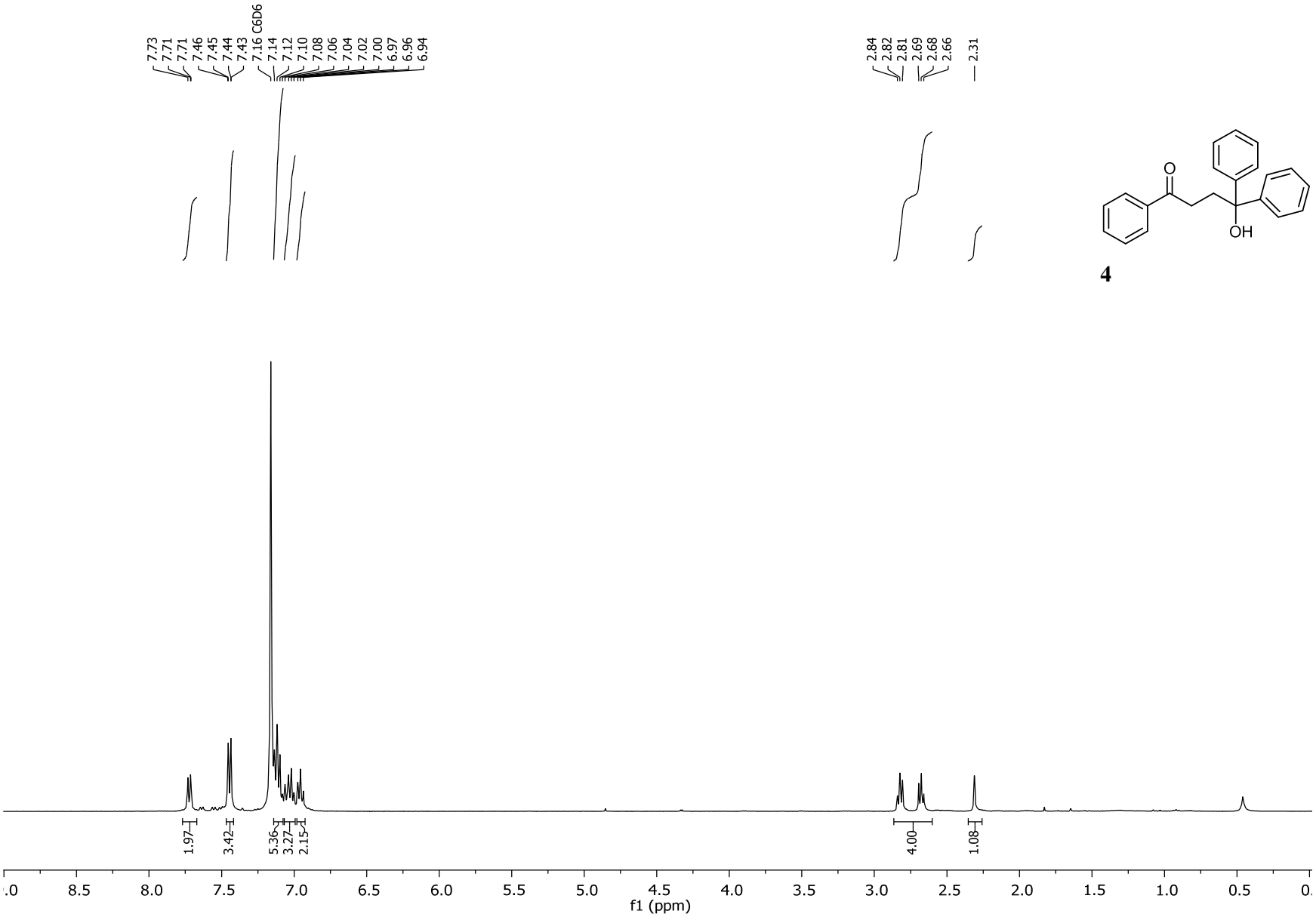

200.5
150.5
141.3
136.9
133.0
128.5
128.1
125.5
125.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.4
34.8
34.5
33.0
31.3
O
OH
f1 (ppm)

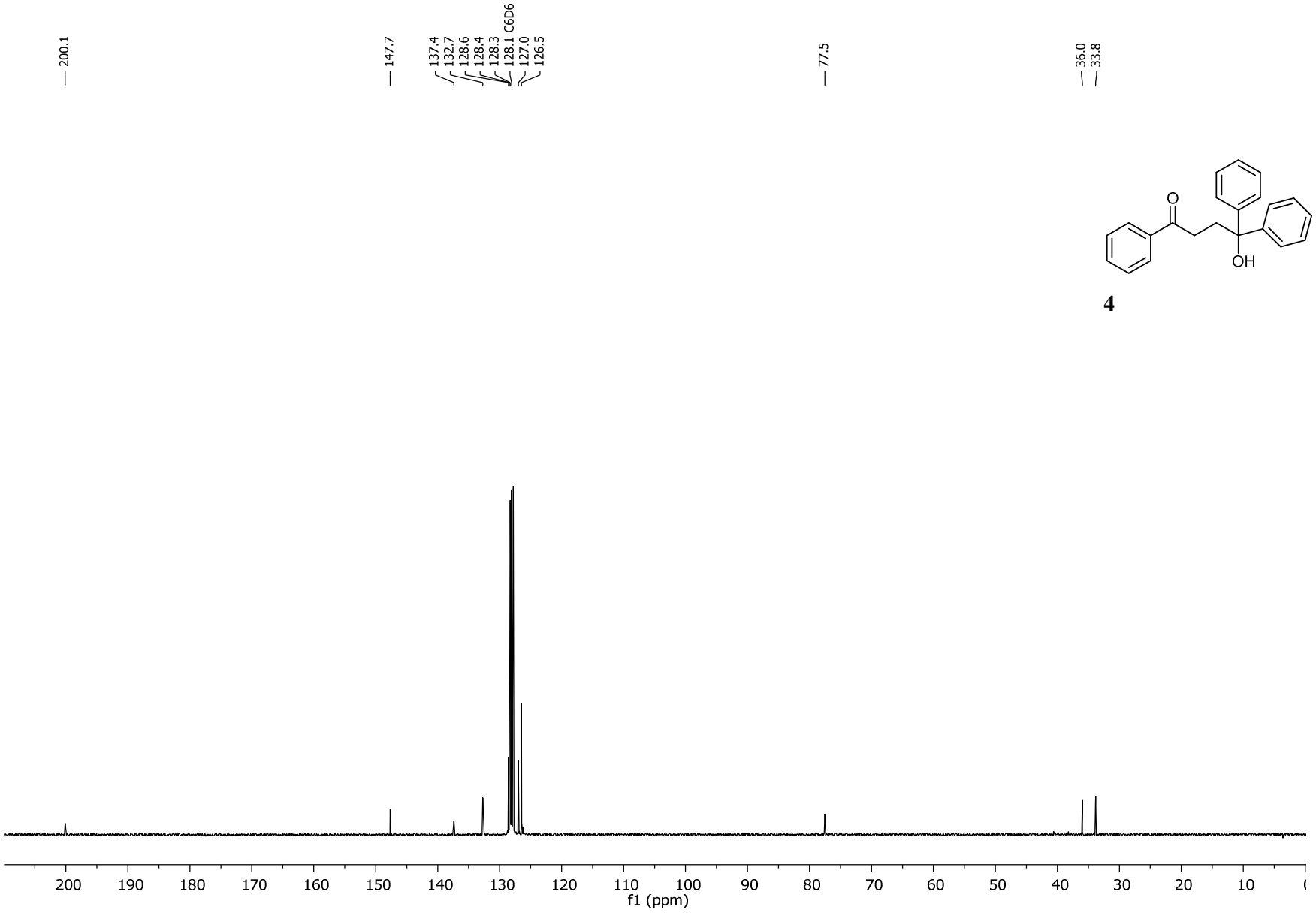
19

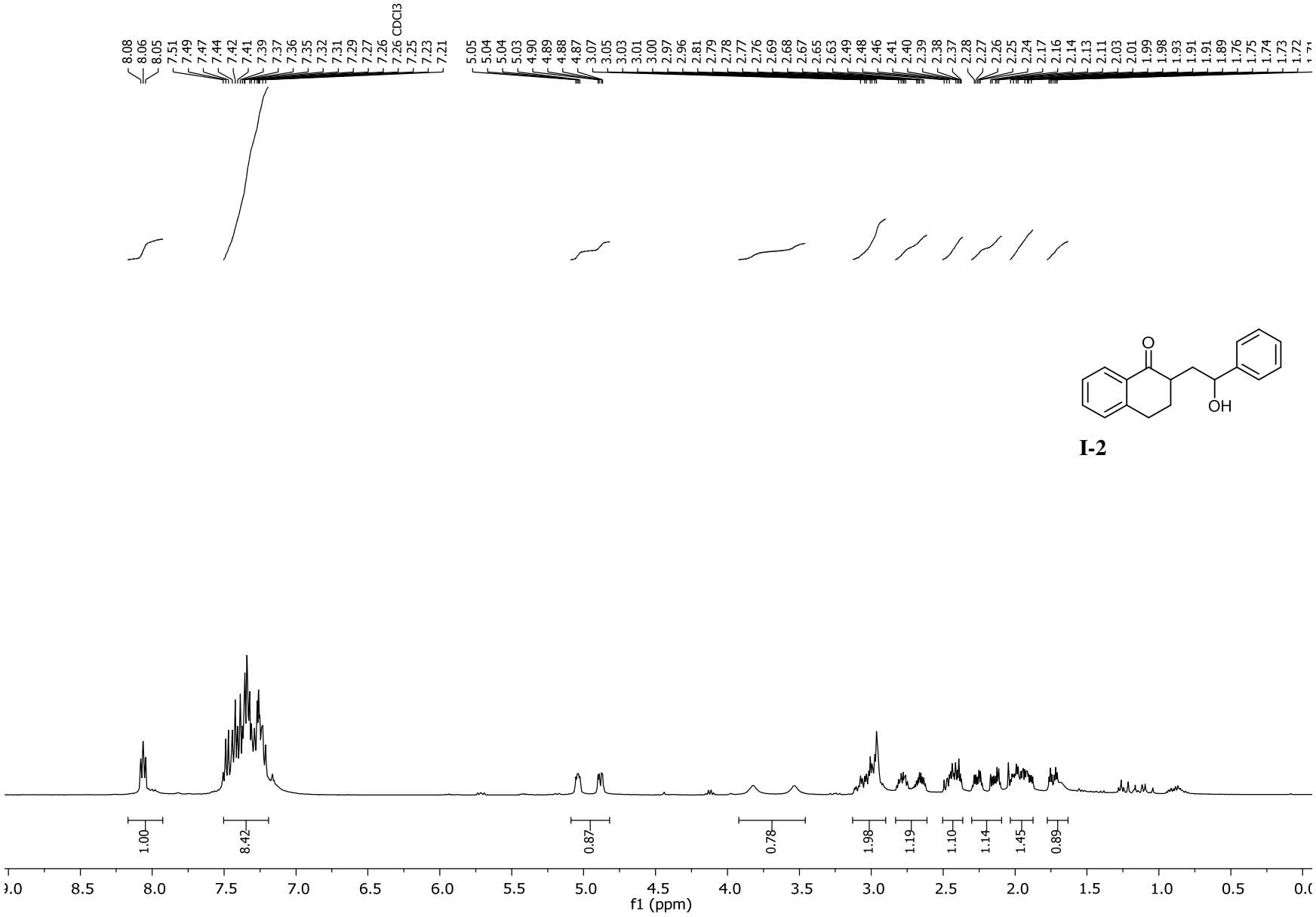

7.92
7.91
7.90
7.89
7.57
7.56
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.46
7.44
7.42
7.41
7.40
7.39
7.37
7.30
7.28
7.27
7.26 CDCl3
3.10
3.08
3.06
3.05
3.04
3.03
3.02
2.94
2.93
2.92
2.91
2.90
2.88
2.86
2.70
2.35
2.34
2.33
2.32
2.32
2.31
1.66
O
OH
20
2.00
1.23
2.14
2.28
2.57
1.08
2.53
0.77
2.09
3.17
f1 (ppm)


201.1
147.2
136.7
133.0
128.4
128.2
128.0
126.6
124.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
74.1
37.7
33.7
31.2
O
OH
f1 (ppm)

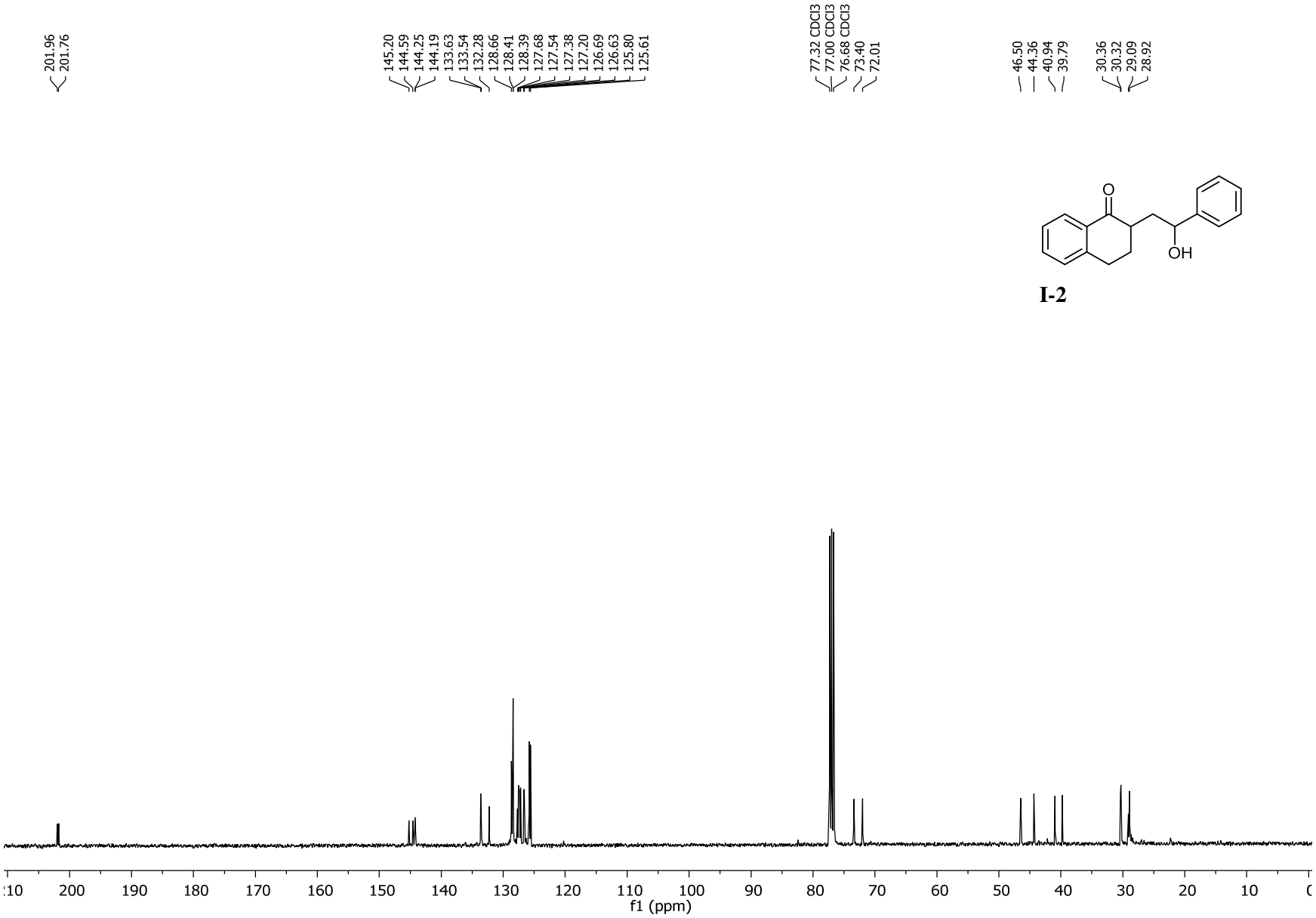
20


7.73
7.71
7.71
7.46
7.45
7.44
7.43
7.16 C6D6
7.14
7.12
7.10
7.08
7.06
7.04
7.02
7.00
6.97
6.96
6.94
2.84
2.82
2.81
2.69
2.68
2.66
2.31
O
OH
4
1.97
3.42
5.36
3.27
2.15
4.00
1.08
f1 (ppm)

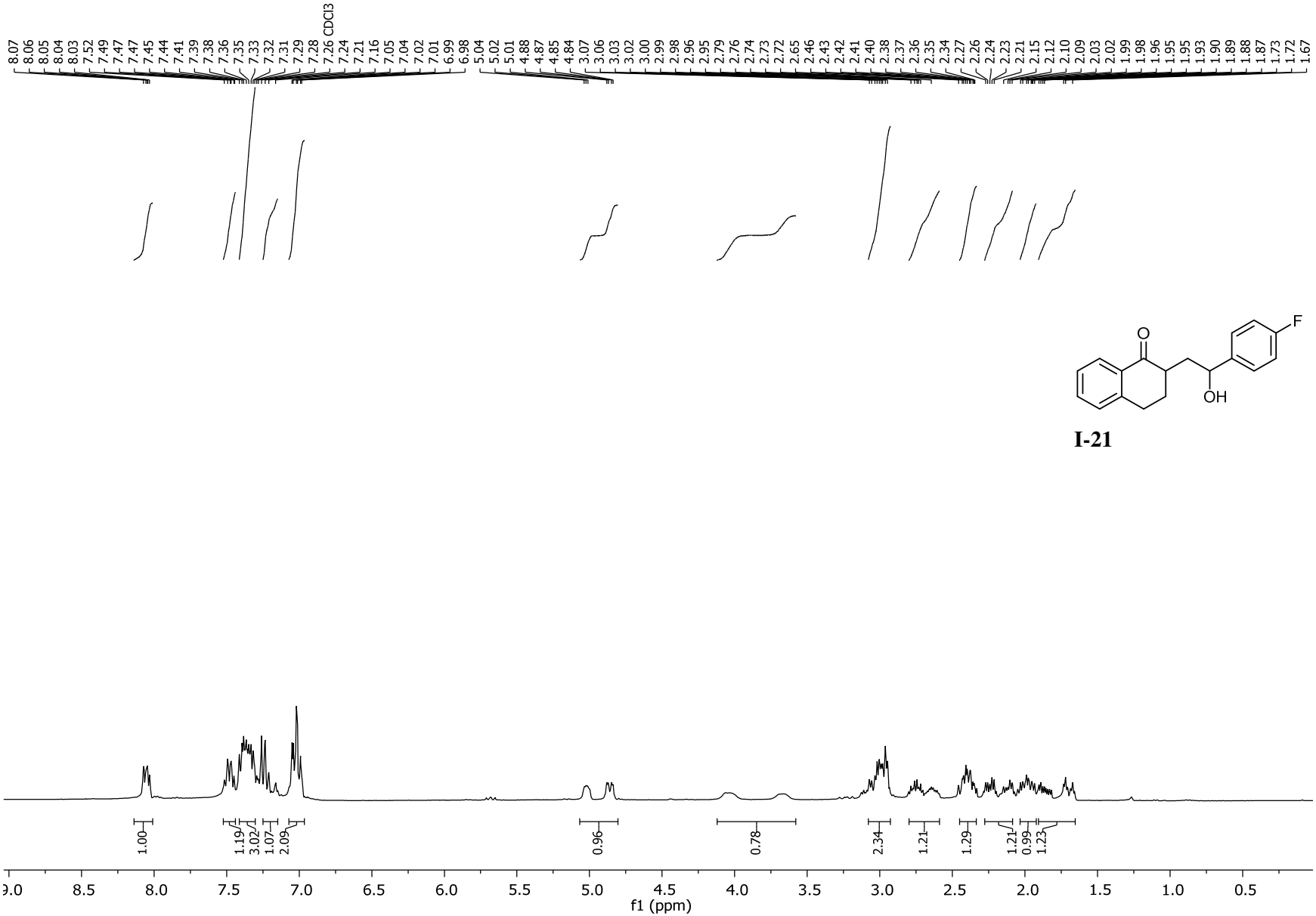

200.1
147.7
137.4
132.7
128.6
128.4
128.3
128.1 C6D6
127.0
126.5
77.5
36.0
33.8
O
OH
4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.08
8.06
8.05
7.51
7.49
7.47
7.44
7.42
7.41
7.39
7.37
7.36
7.35
7.32
7.31
7.29
7.27
7.26
CDCl3
7.25
7.23
7.21
5.05
5.04
5.04
5.03
4.90
4.89
4.88
4.87
3.07
3.05
3.03
3.01
3.00
2.97
2.96
2.81
2.79
2.78
2.77
2.76
2.69
2.68
2.67
2.65
2.63
2.49
2.48
2.46
2.41
2.40
2.39
2.38
2.37
2.28
2.27
2.26
2.25
2.24
2.17
2.16
2.14
2.13
2.11
2.03
2.01
1.99
1.98
1.93
1.91
1.91
1.89
1.76
1.75
1.74
1.73
1.72
O
OH
1.00
8.42
0.87
0.78
1.98
1.19
1.10
1.14
1.45
0.89
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
f1 (ppm)

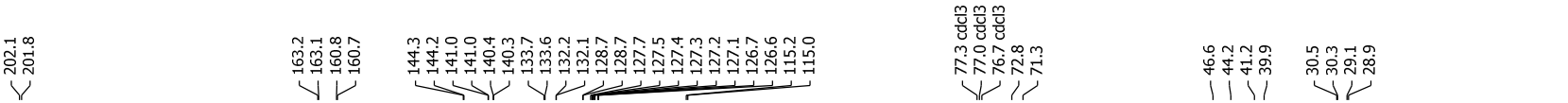
I-2

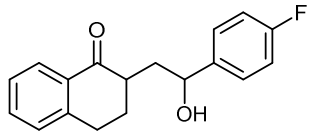

201.96
201.76
145.20
144.59
144.25
144.19
133.63
133.54
132.28
128.66
128.41
128.39
127.68
127.54
127.38
127.20
126.69
126.63
125.80
125.61
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.40
72.01
46.50
44.36
40.94
39.79
30.36
30.32
29.09
28.92
O
OH
f1 (ppm)

I-2

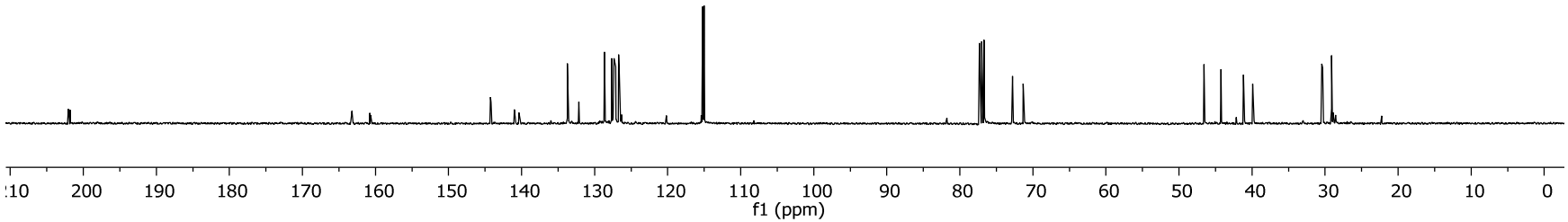

8.07 8.06 8.05 8.04 8.03 7.52 7.49 7.47 7.47 7.45 7.44 7.41 7.39 7.38 7.36 7.35 7.33 7.32 7.31 7.29 7.28 CDCl3 7.26 7.24 7.21 7.16 7.05 7.04 7.02 7.01 6.99 6.98
5.04 5.02 5.01 4.88 4.87 4.85 4.84 3.07 3.06 3.03 3.02 3.00 2.99 2.98 2.96 2.95 2.79 2.76 2.74 2.73 2.72 2.65 2.46 2.43 2.42 2.41 2.40 2.38 2.37 2.36 2.35 2.34 2.27 2.26 2.24 2.23 2.21 2.15 2.12 2.10 2.09 2.03 2.02 1.99 1.98 1.96 1.95 1.95 1.93 1.90 1.89 1.88 1.87 1.73 1.72 1.67
O
F
OH
1.00 1.19 3.02 1.07 2.09 0.96 0.78 2.34 1.21 1.29 1.21 0.99 1.23
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
f1 (ppm)

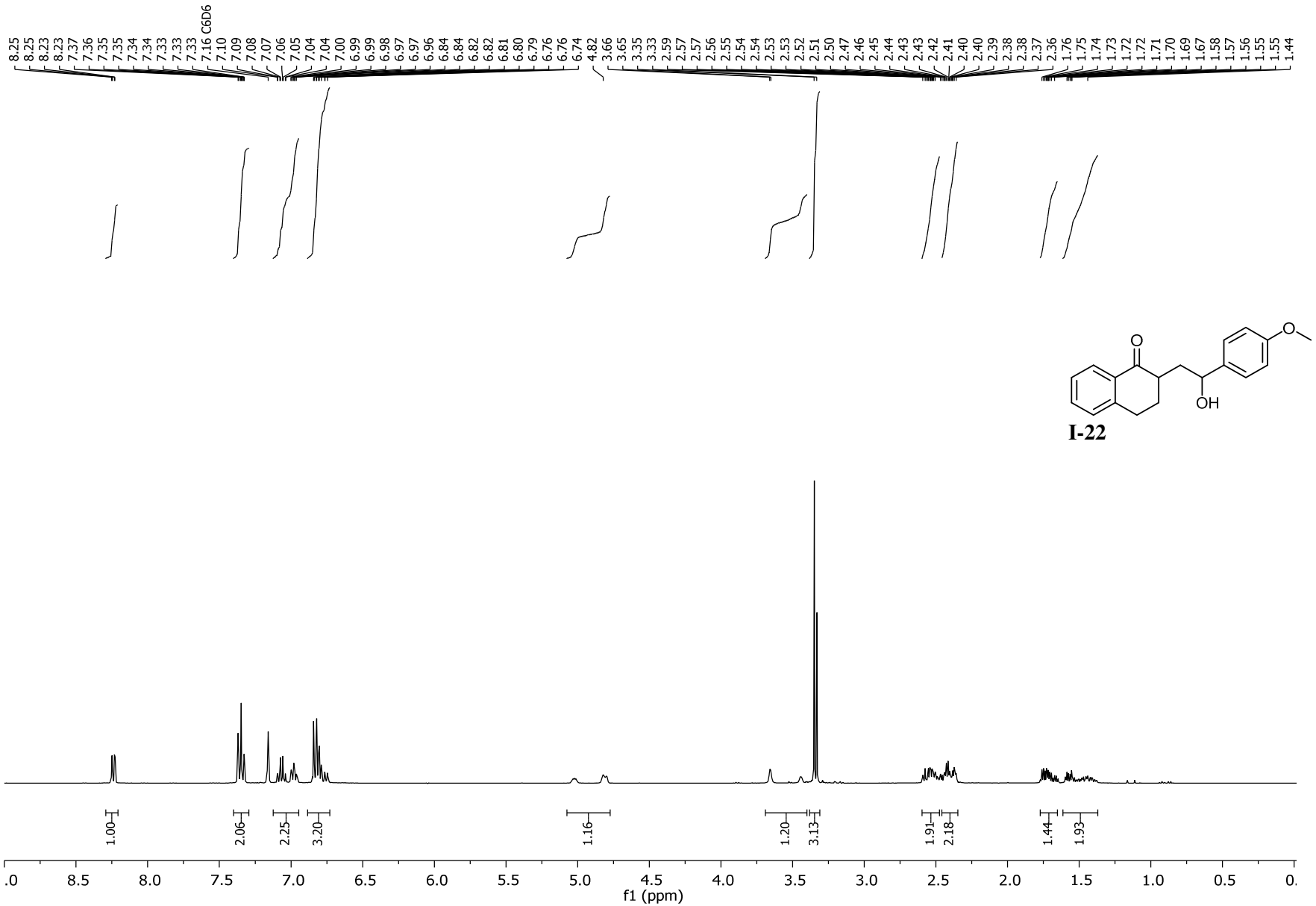
I-21


202.1
201.8
163.2
163.1
160.8
160.7
144.3
144.2
141.0
141.0
140.4
140.3
133.7
133.6
132.2
132.1
128.7
128.7
127.7
127.5
127.4
127.3
127.2
127.1
126.7
126.6
115.2
115.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
72.8
71.3
46.6
44.2
41.2
39.9
30.5
30.3
29.1
28.9

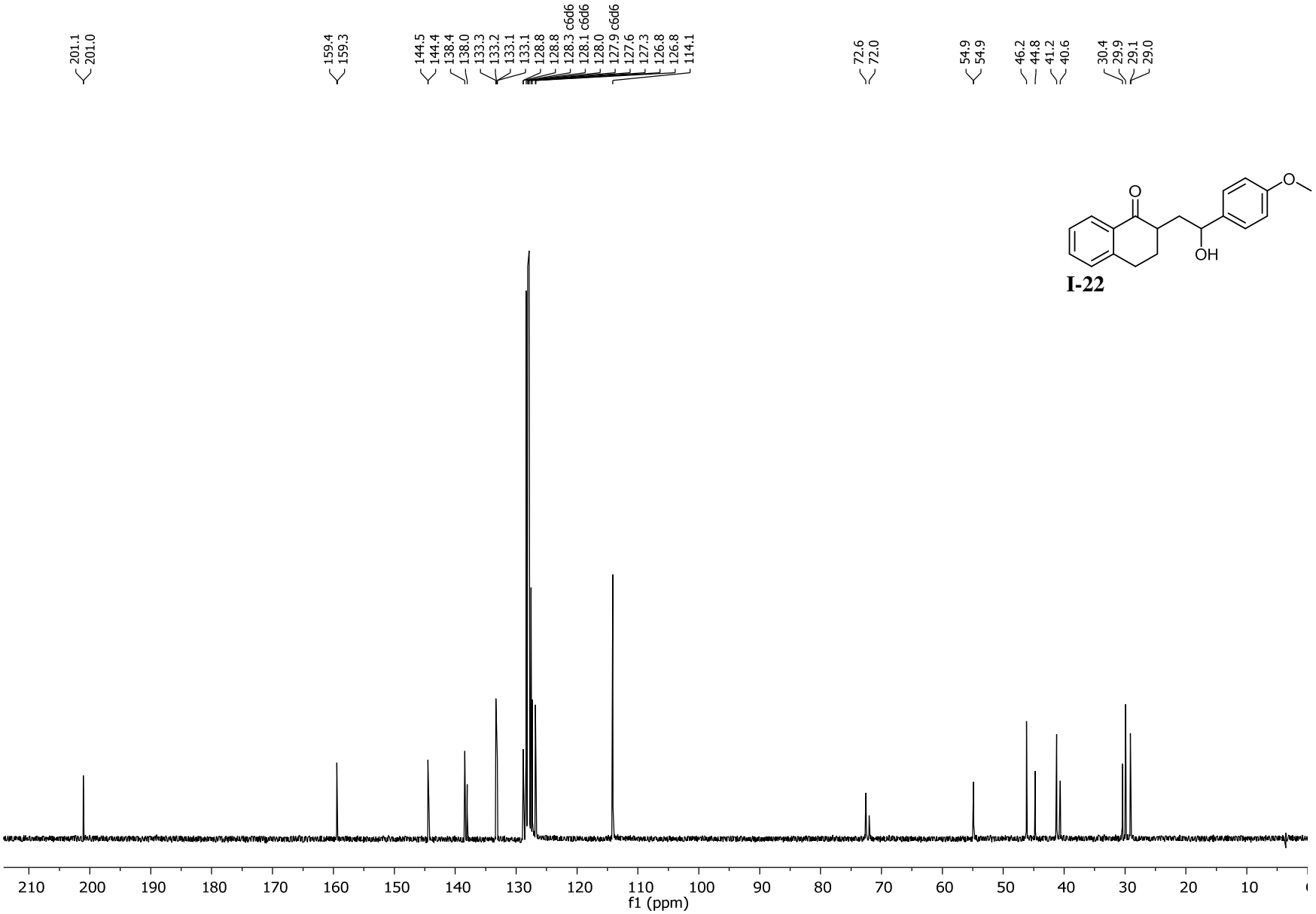

O
F
OH

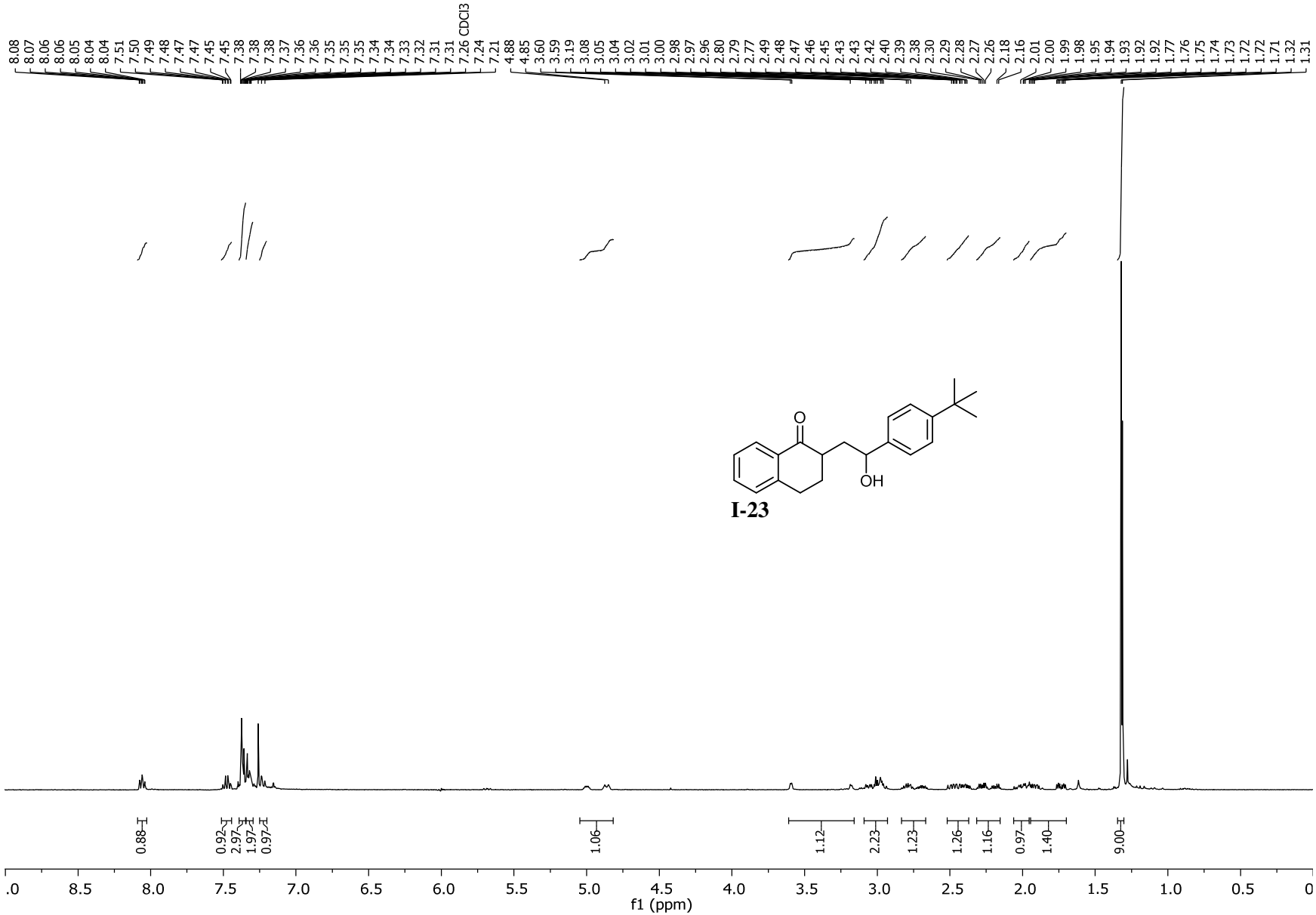
I-21

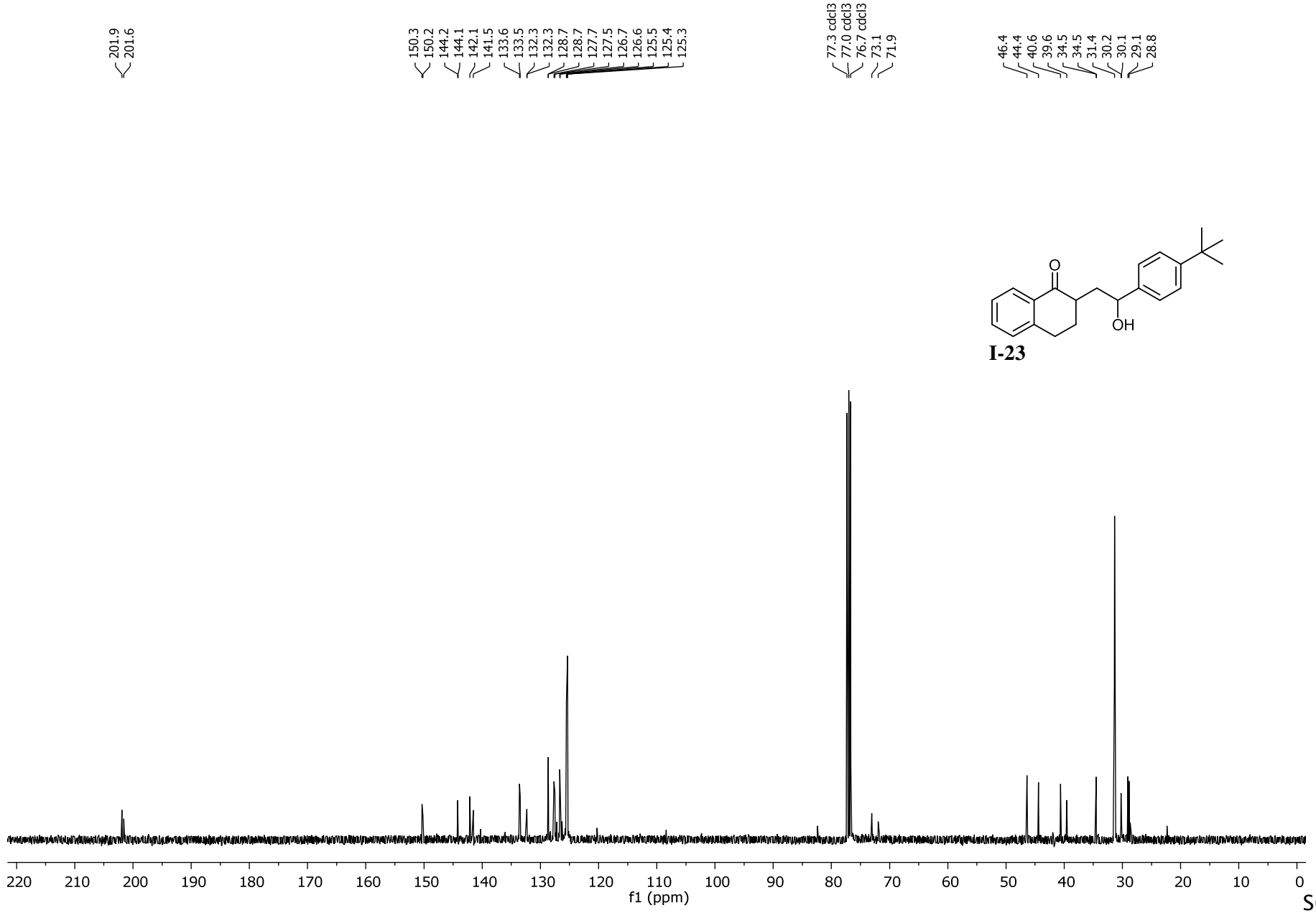

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

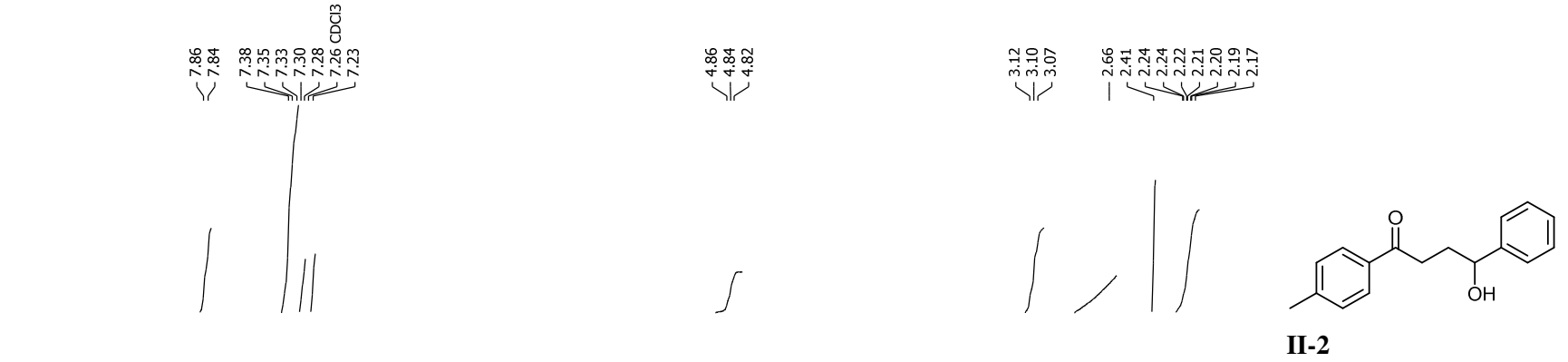

8.25 8.25 8.23 8.23 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.16 C6D6 7.10 7.09 7.08 7.07 7.06 7.05 7.04 7.04 7.00 6.99 6.99 6.98 6.97 6.97 6.96 6.84 6.84 6.82 6.82 6.81 6.80 6.79 6.76 6.76 6.74 4.82 3.66 3.65 3.35 3.33 2.59 2.57 2.57 2.56 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.50 2.47 2.46 2.45 2.44 2.43 2.43 2.42 2.41 2.40 2.40 2.39 2.38 2.38 2.37 2.36 1.76 1.75 1.74 1.73 1.72 1.72 1.71 1.70 1.69 1.67 1.58 1.57 1.56 1.55 1.55 1.44
O
O
OH
1.00 2.06 2.25 3.20 1.16 1.20 3.13 1.91 2.18 1.44 1.93
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
f1 (ppm)

I-22

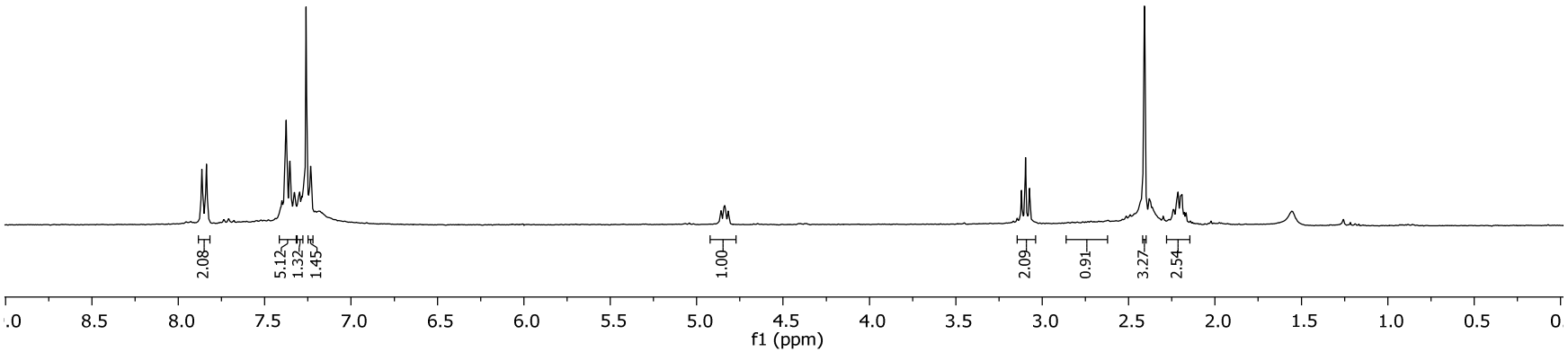

201.1
201.0
159.4
159.3
144.5
144.4
138.4
138.0
133.3
133.2
133.1
133.1
128.8
128.8
128.3 c6d6
128.1 c6d6
128.0
127.9 c6d6
127.6
127.3
126.8
126.8
114.1
72.6
72.0
54.9
54.9
46.2
44.8
41.2
40.6
30.4
29.9
29.1
29.0
O
O
OH
I-22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

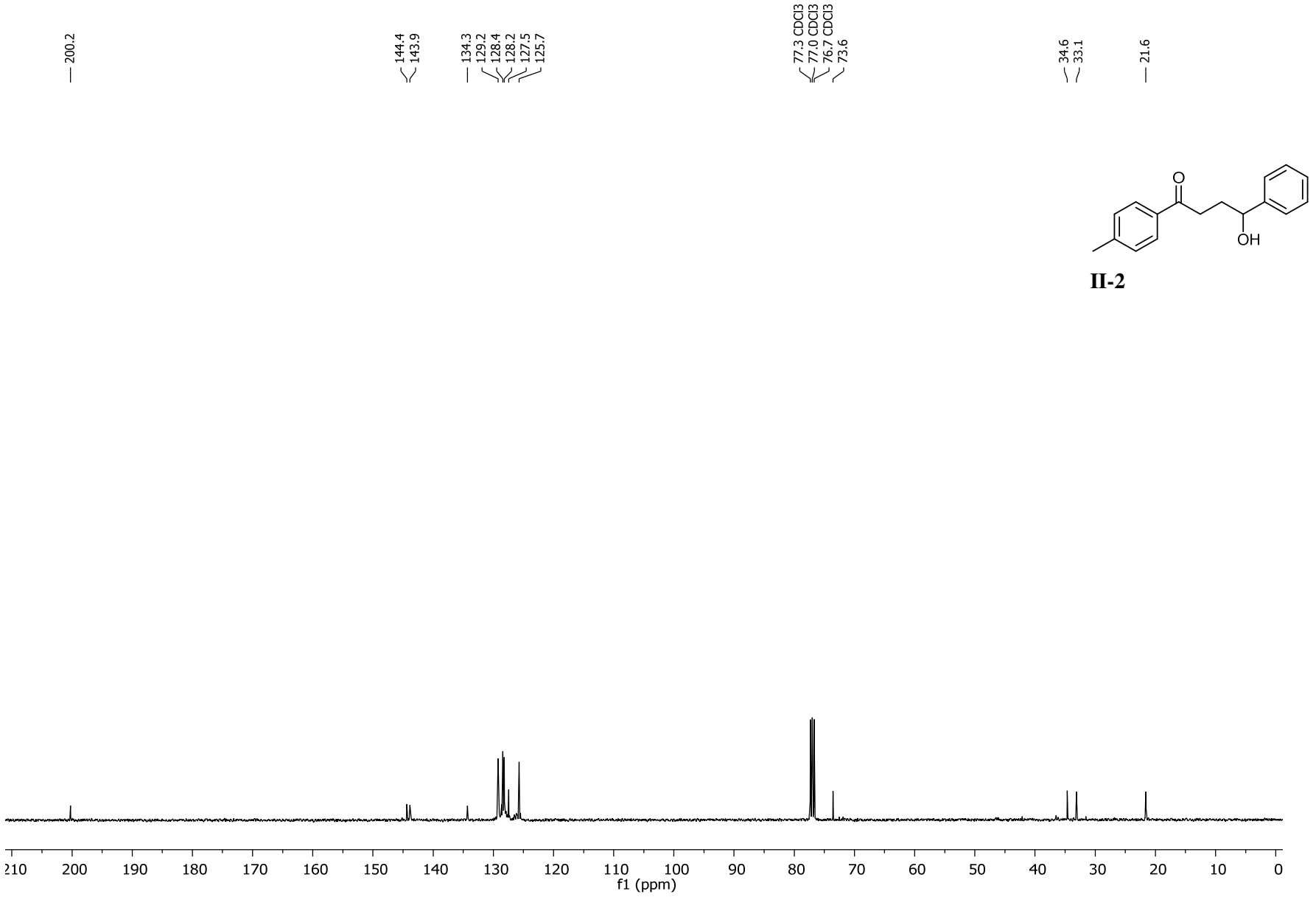

8.08 8.07 8.06 8.06 8.05 8.04 8.04 7.51 7.50 7.49 7.48 7.47 7.47 7.45 7.45 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.26 CDCl3 7.24 7.21 4.88 4.85 3.60 3.59 3.19 3.08 3.05 3.04 3.02 3.01 3.00 2.98 2.97 2.96 2.80 2.79 2.77 2.49 2.48 2.47 2.46 2.45 2.43 2.42 2.40 2.39 2.38 2.30 2.29 2.28 2.27 2.26 2.18 2.16 2.01 2.00 1.99 1.98 1.95 1.94 1.93 1.92 1.92 1.77 1.76 1.75 1.74 1.73 1.72 1.72 1.71 1.32 1.31
O
OH
I-23
0.88 0.92 2.97 1.97 0.97 1.06 1.12 2.23 1.23 1.26 1.16 0.97 1.40 9.00
.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
f1 (ppm)


201.9
201.6
150.3
150.2
144.2
144.1
142.1
141.5
133.6
133.5
132.3
132.3
128.7
128.7
127.7
127.5
126.7
126.6
125.5
125.4
125.3
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
73.1
71.9
46.4
44.4
40.6
39.6
34.5
34.5
31.4
30.2
30.1
29.1
28.8
O
OH
I-23
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

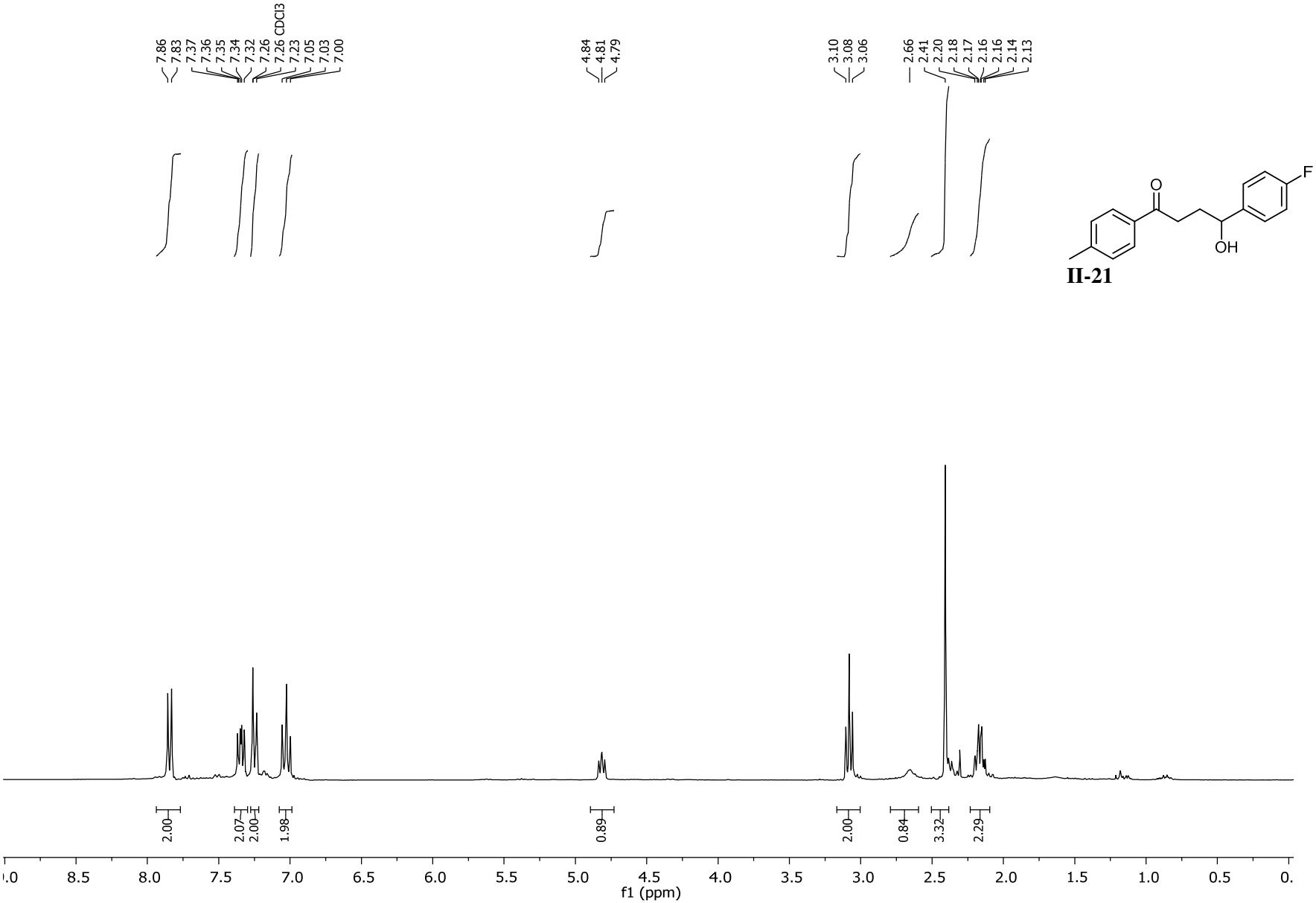

7.86
7.84
7.38
7.35
7.33
7.30
7.28
7.26 CDCl3
7.23
4.86
4.84
4.82
3.12
3.10
3.07
2.66
2.41
2.24
2.22
2.21
2.20
2.19
2.17
O
OH

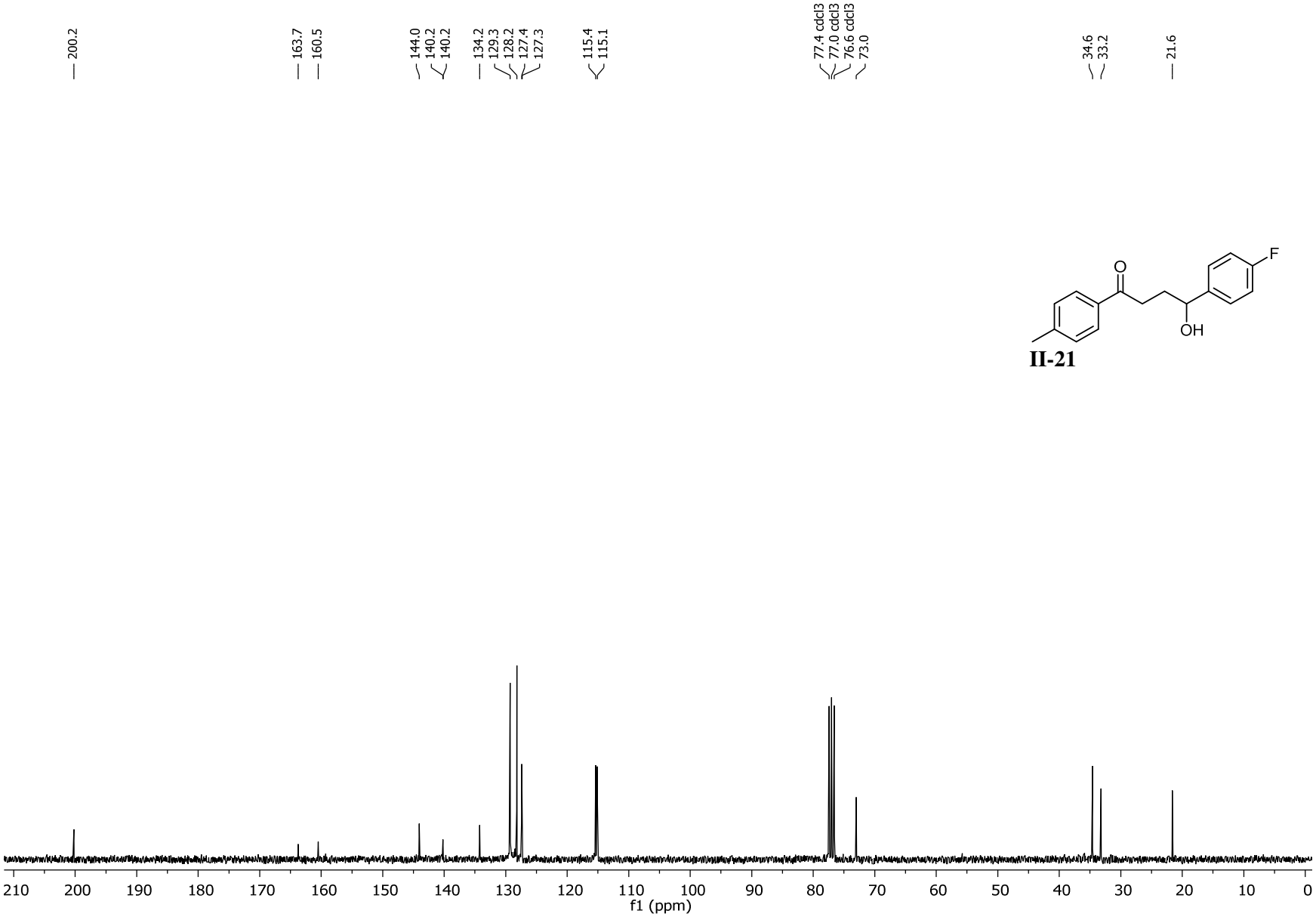
II-2

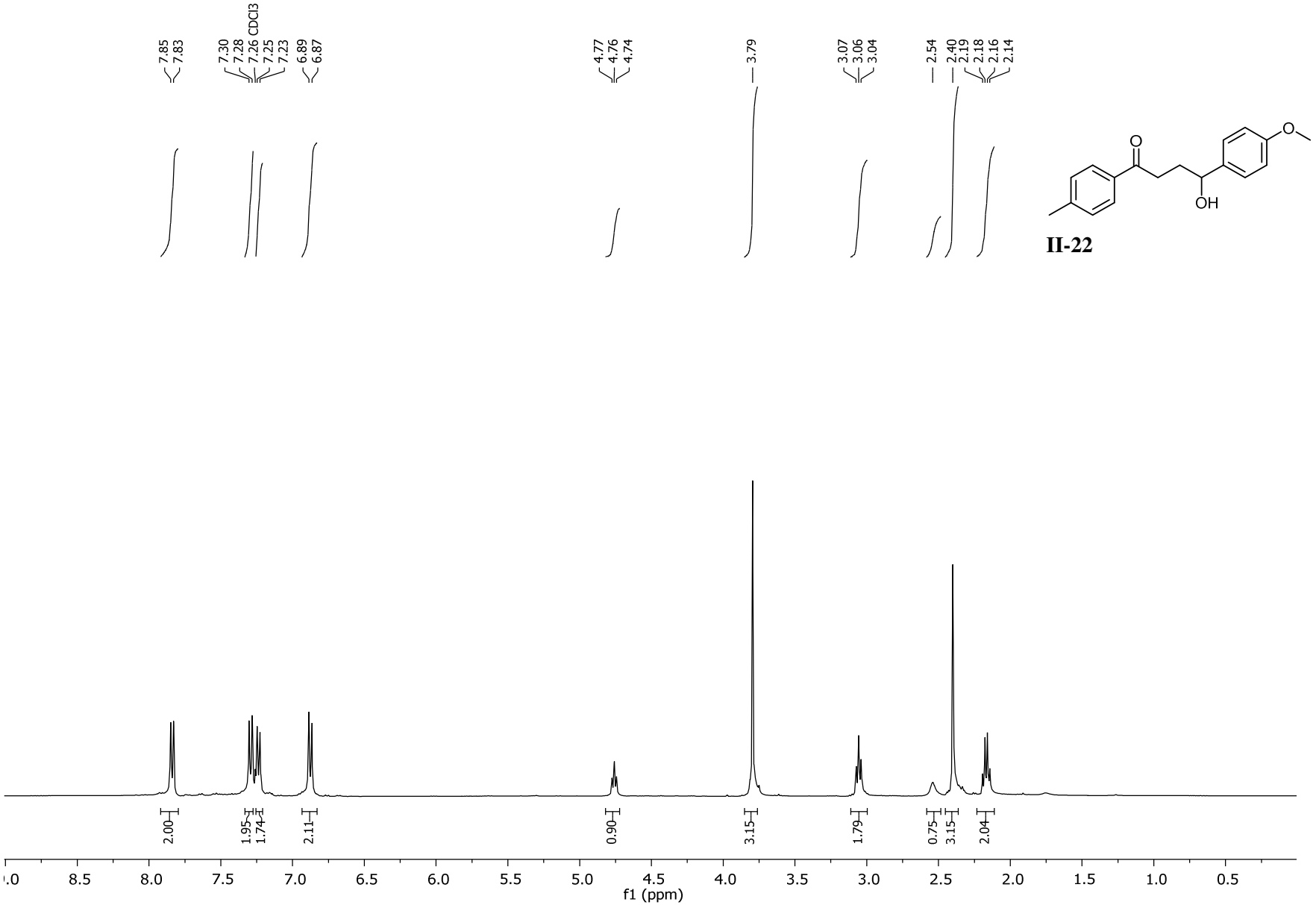

2.08
5.12
1.32
1.45
1.00
2.09
0.91
3.27
2.54
f1 (ppm)

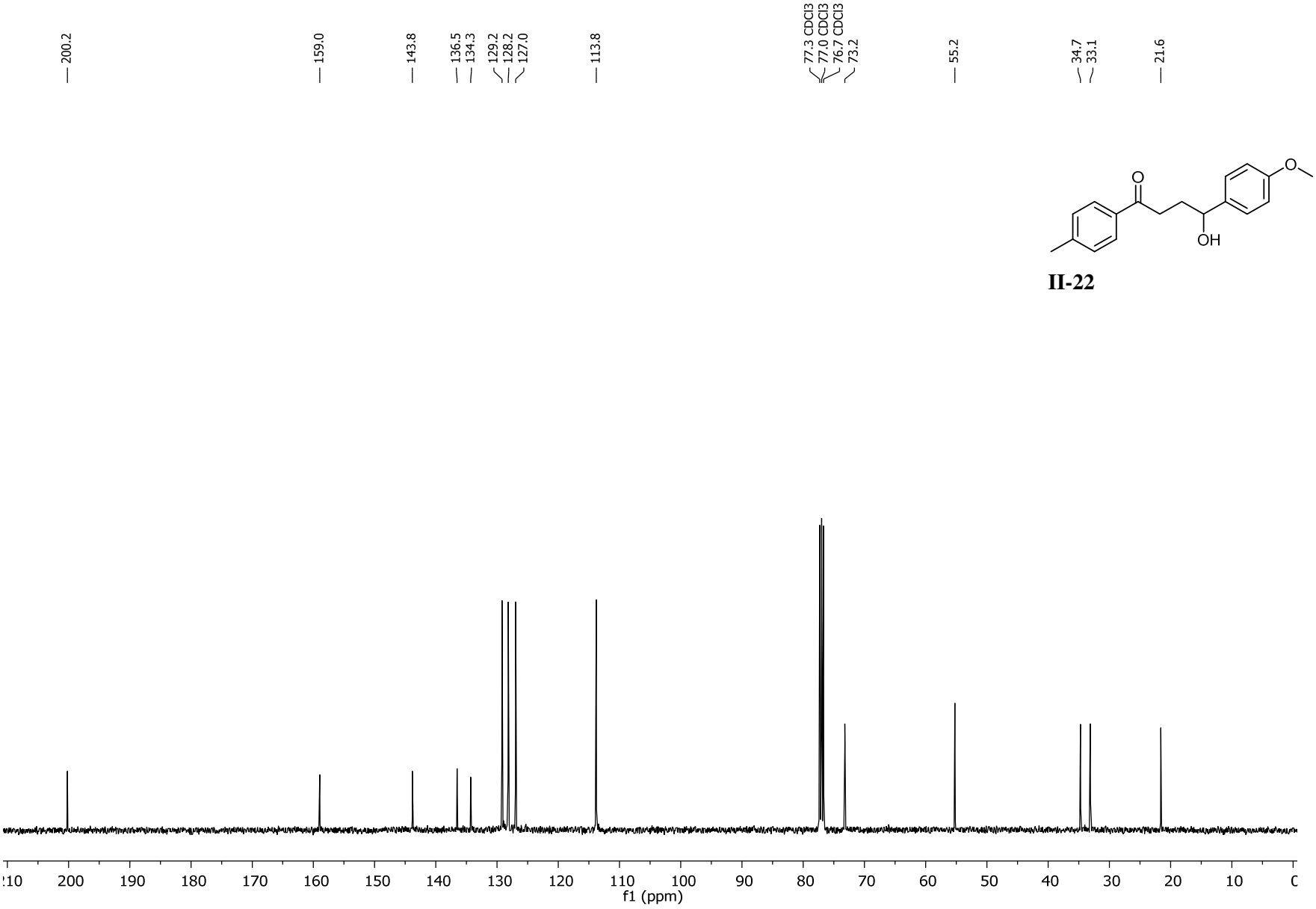

200.2
144.4
143.9
134.3
129.2
128.4
128.2
127.5
125.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.6
34.6
33.1
21.6
O
OH
f1 (ppm)

II-2

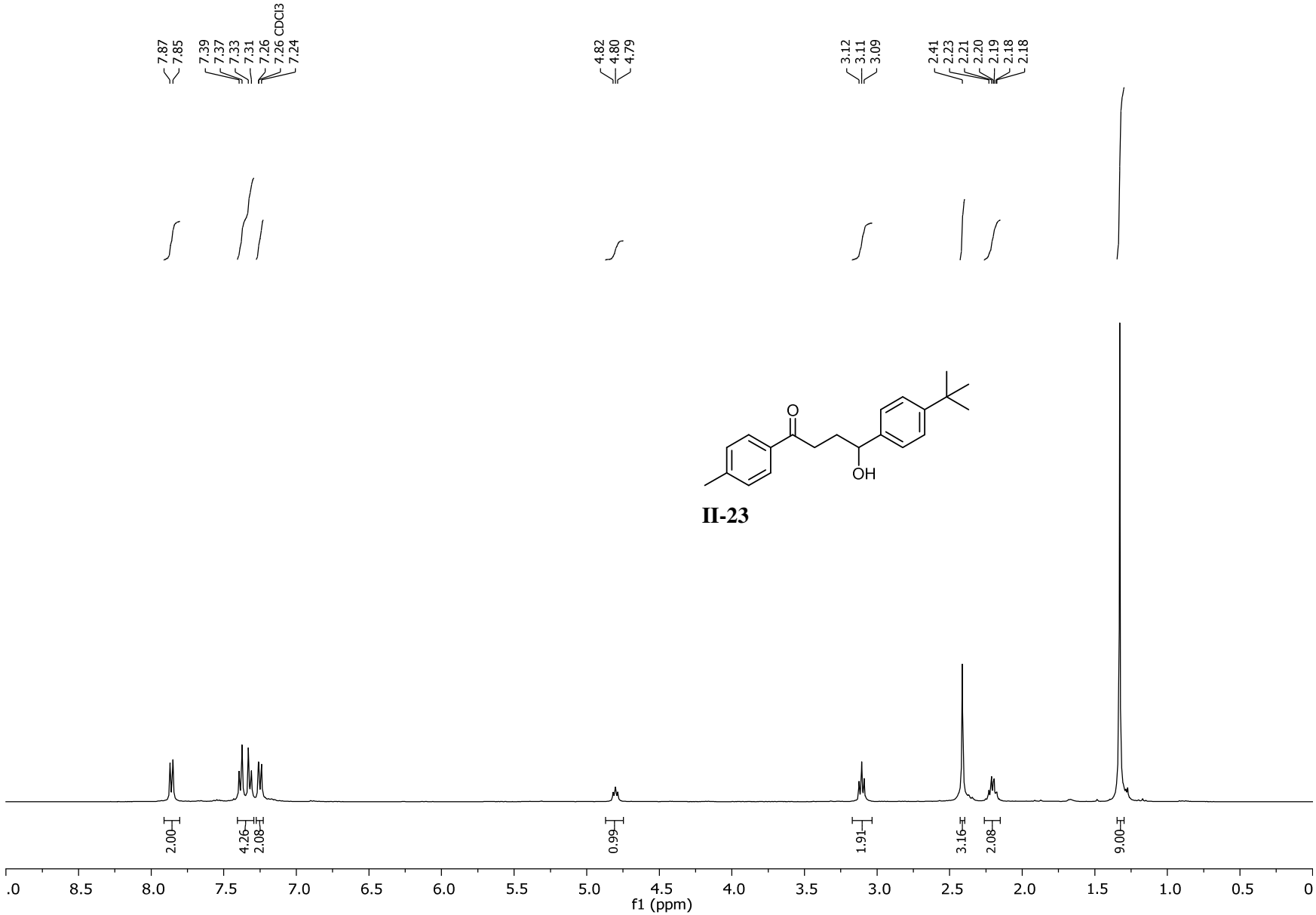

7.86
7.83
7.37
7.36
7.35
7.34
7.32
7.26
7.26 CDCl3
7.23
7.05
7.03
7.00
4.84
4.81
4.79
3.10
3.08
3.06
2.66
2.41
2.20
2.18
2.17
2.16
2.16
2.14
2.13
F
O
OH
II-21
2.00
2.07
2.00
1.98
0.89
2.00
0.84
3.32
2.29
f1 (ppm)


200.2
163.7
160.5
144.0
140.2
140.2
134.2
129.3
128.2
127.4
127.3
115.4
115.1
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
73.0
34.6
33.2
21.6
O
F
OH
II-21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

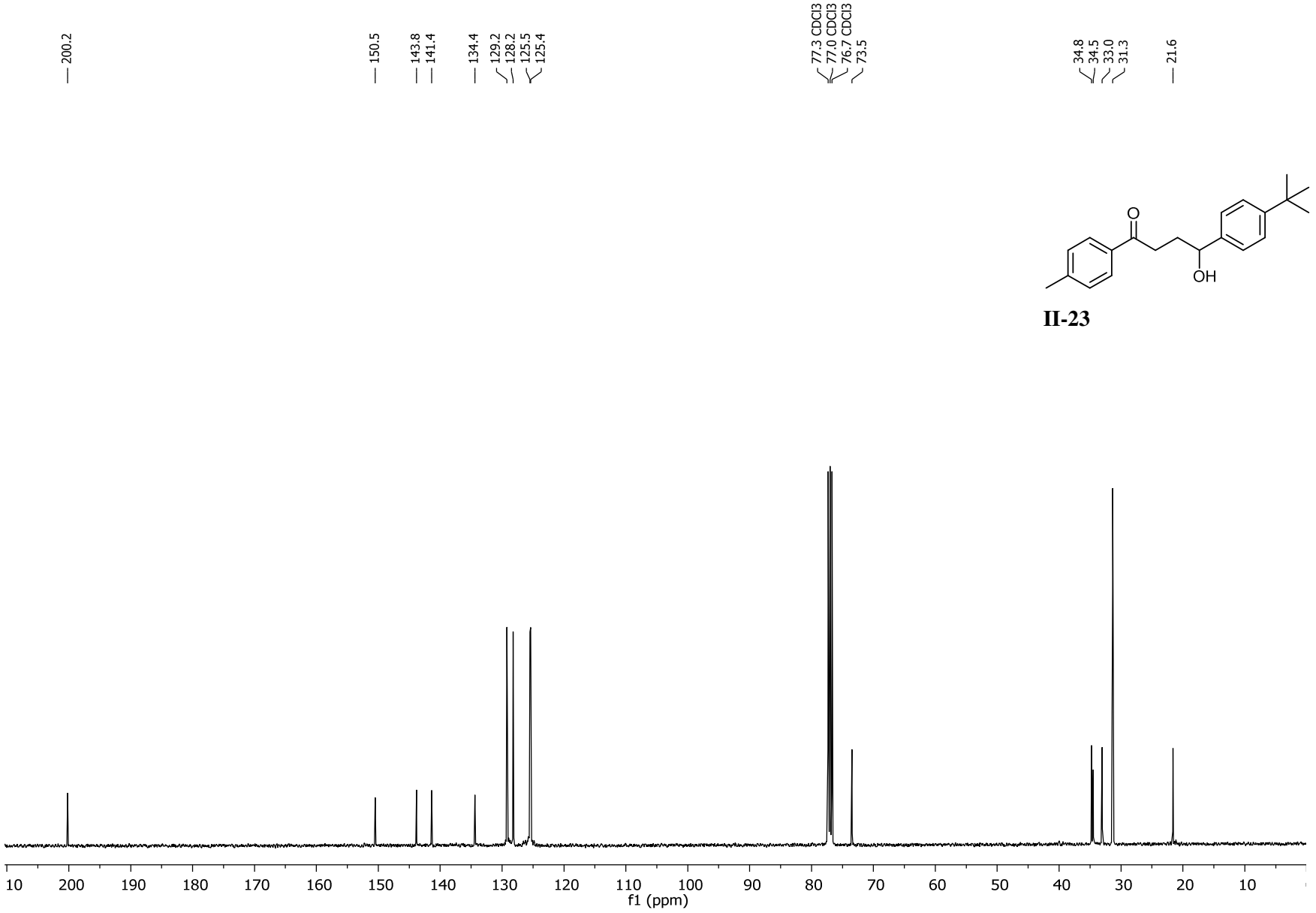

7.85
7.83
7.30
7.28
7.26 CDCl3
7.25
7.23
6.89
6.87
4.77
4.76
4.74
3.79
3.07
3.06
3.04
2.54
2.40
2.19
2.18
2.16
2.14
O
O
OH
II-22
2.00
1.95
1.74
2.11
0.90
3.15
1.79
0.75
3.15
2.04
f1 (ppm)


200.2
159.0
143.8
136.5
134.3
129.2
128.2
127.0
113.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.2
55.2
34.7
33.1
21.6
O
O
OH
f1 (ppm)

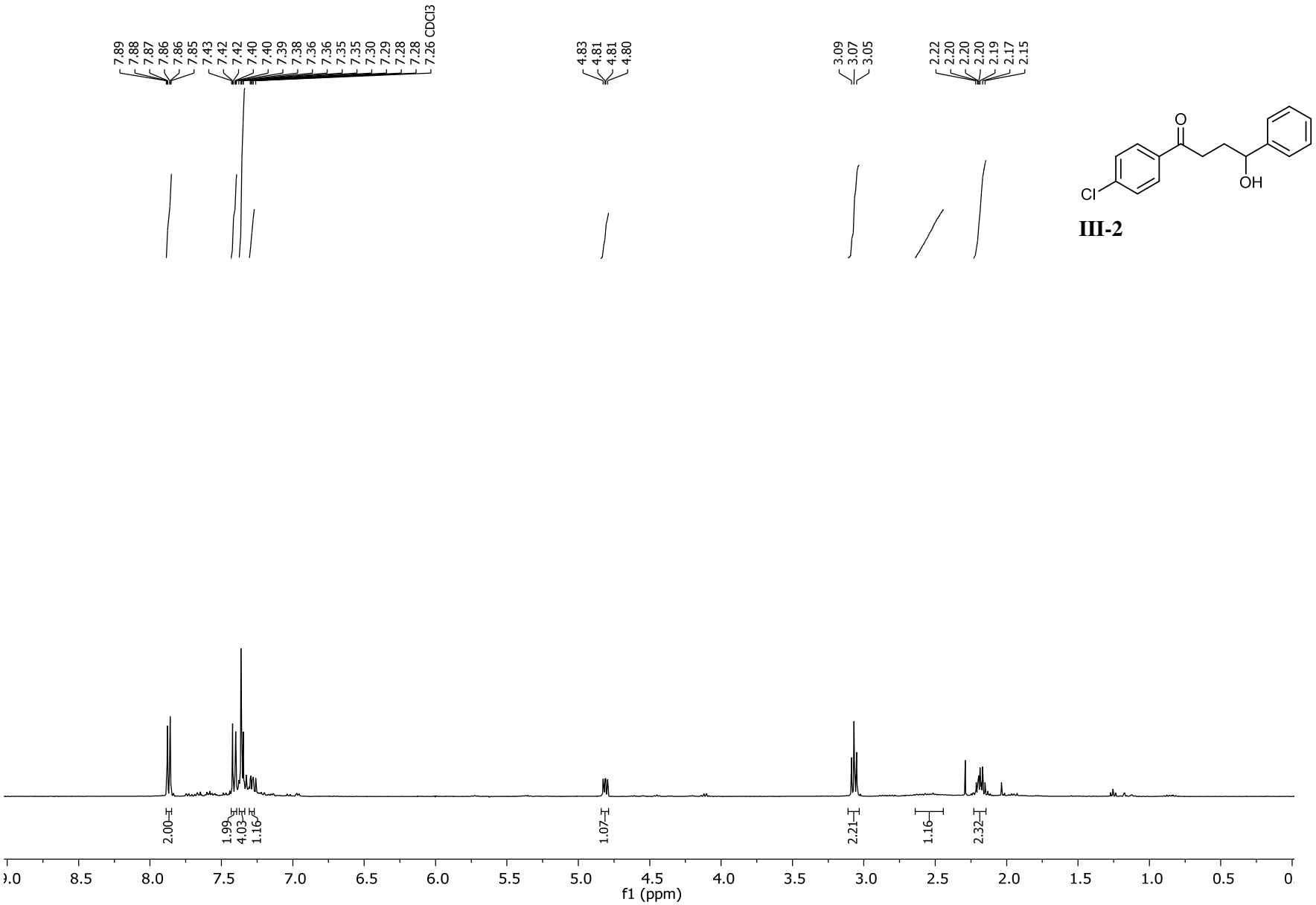
II-22

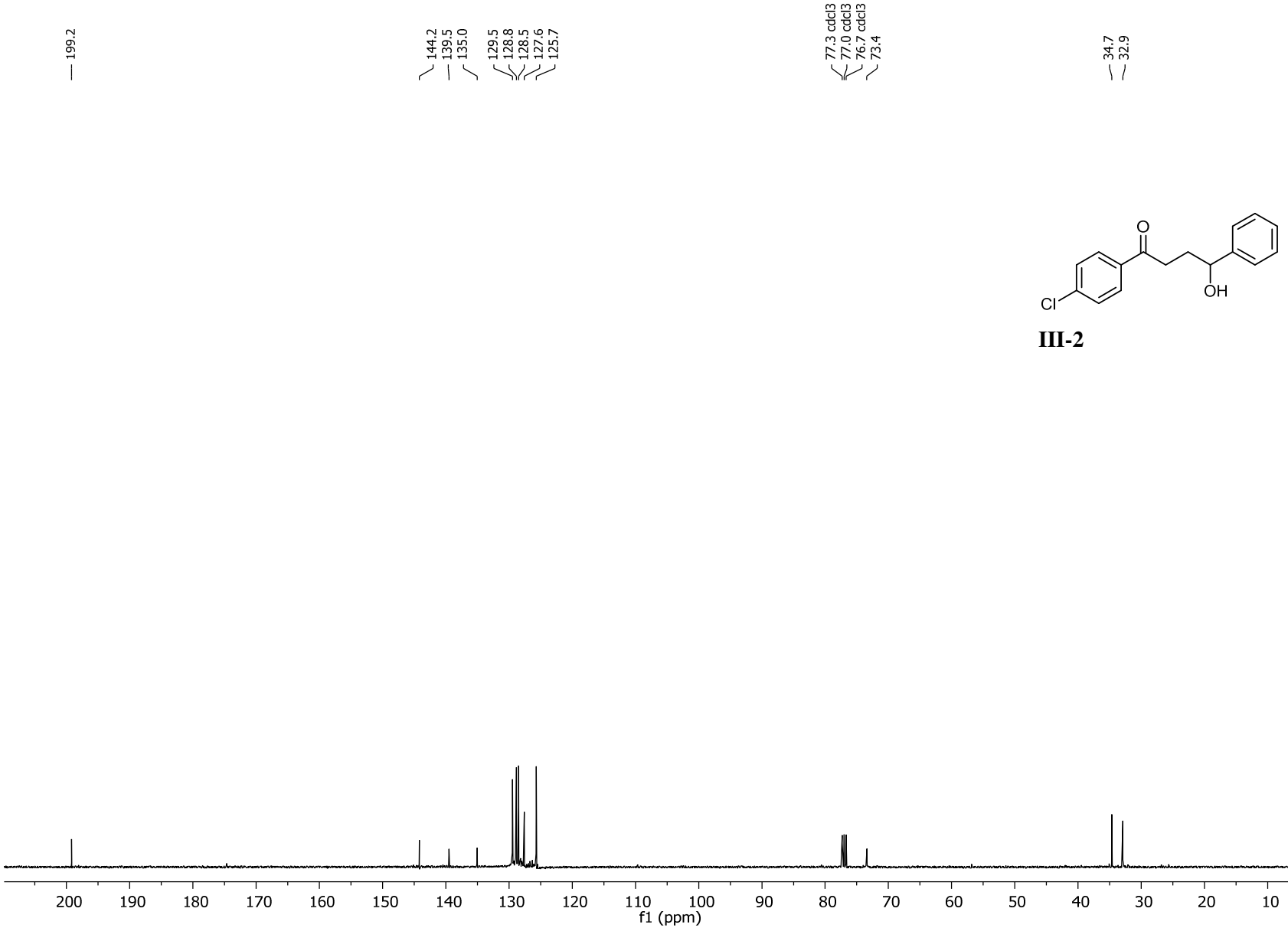

7.87
7.85
7.39
7.37
7.33
7.31
7.26
7.26 CDCl3
7.24
4.82
4.80
4.79
3.12
3.11
3.09
2.41
2.23
2.21
2.20
2.19
2.18
2.18
O
OH
2.00
4.26
2.08
0.99
1.91
3.16
2.08
9.00
f1 (ppm)

II-23

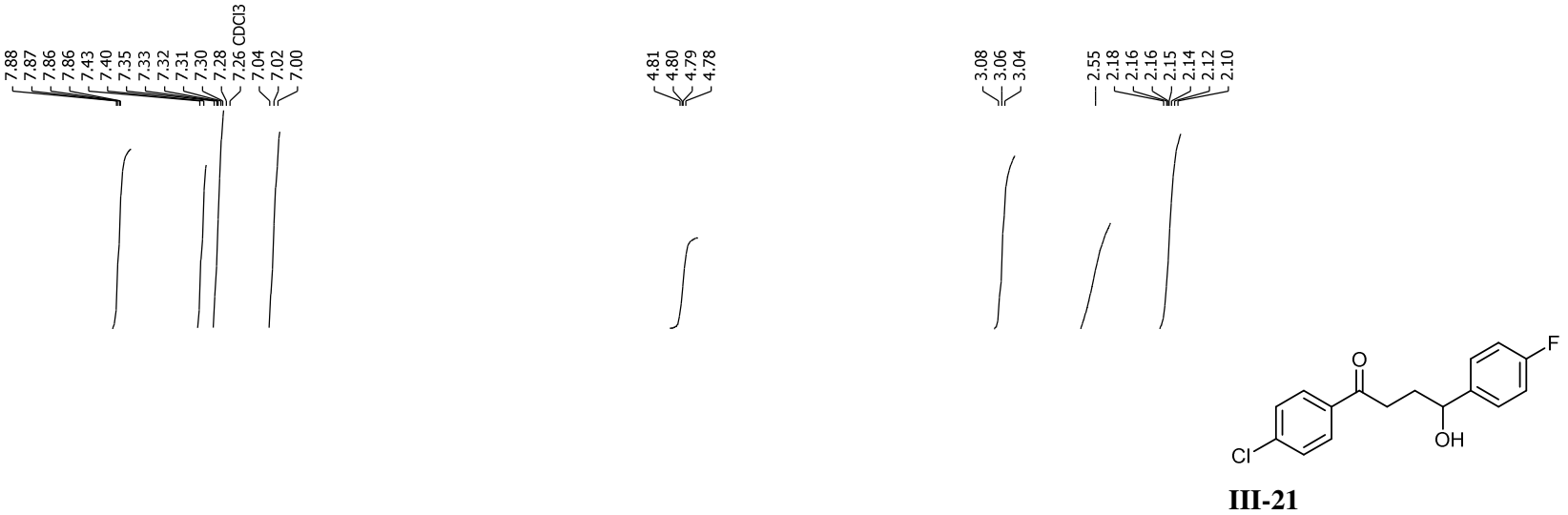

200.2
150.5
143.8
141.4
134.4
129.2
128.2
125.5
125.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.5
34.8
34.5
33.0
31.3
21.6
O
OH
f1 (ppm)

II-23

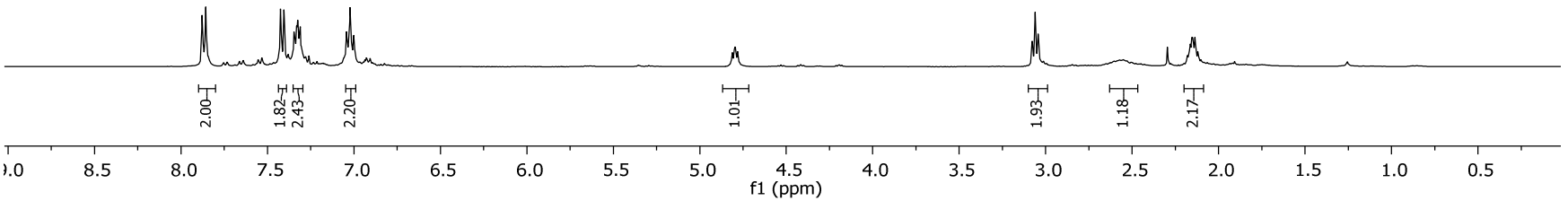

7.89
7.88
7.87
7.86
7.86
7.85
7.43
7.42
7.42
7.40
7.40
7.39
7.38
7.36
7.36
7.35
7.35
7.30
7.29
7.28
7.28
7.26 CDCl3
4.83
4.81
4.81
4.80
3.09
3.07
3.05
2.22
2.20
2.20
2.20
2.19
2.17
2.15
O
OH
Cl
III-2
2.00
1.99
4.03
1.16
1.07
2.21
1.16
2.32
f1 (ppm)

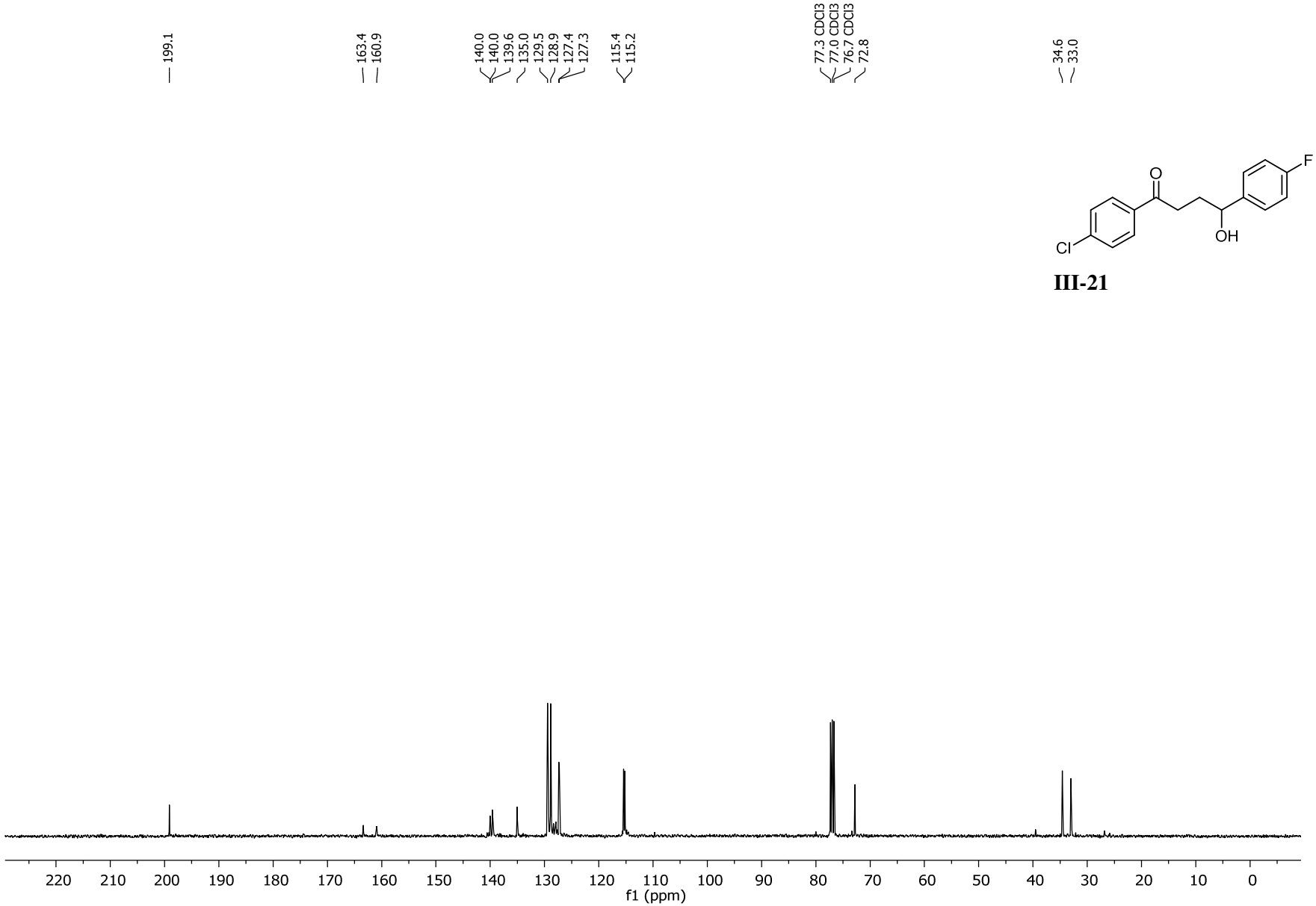

199.2
144.2
139.5
135.0
129.5
128.8
128.5
127.6
125.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
73.4
34.7
32.9
O
OH
Cl
f1 (ppm)

III-2

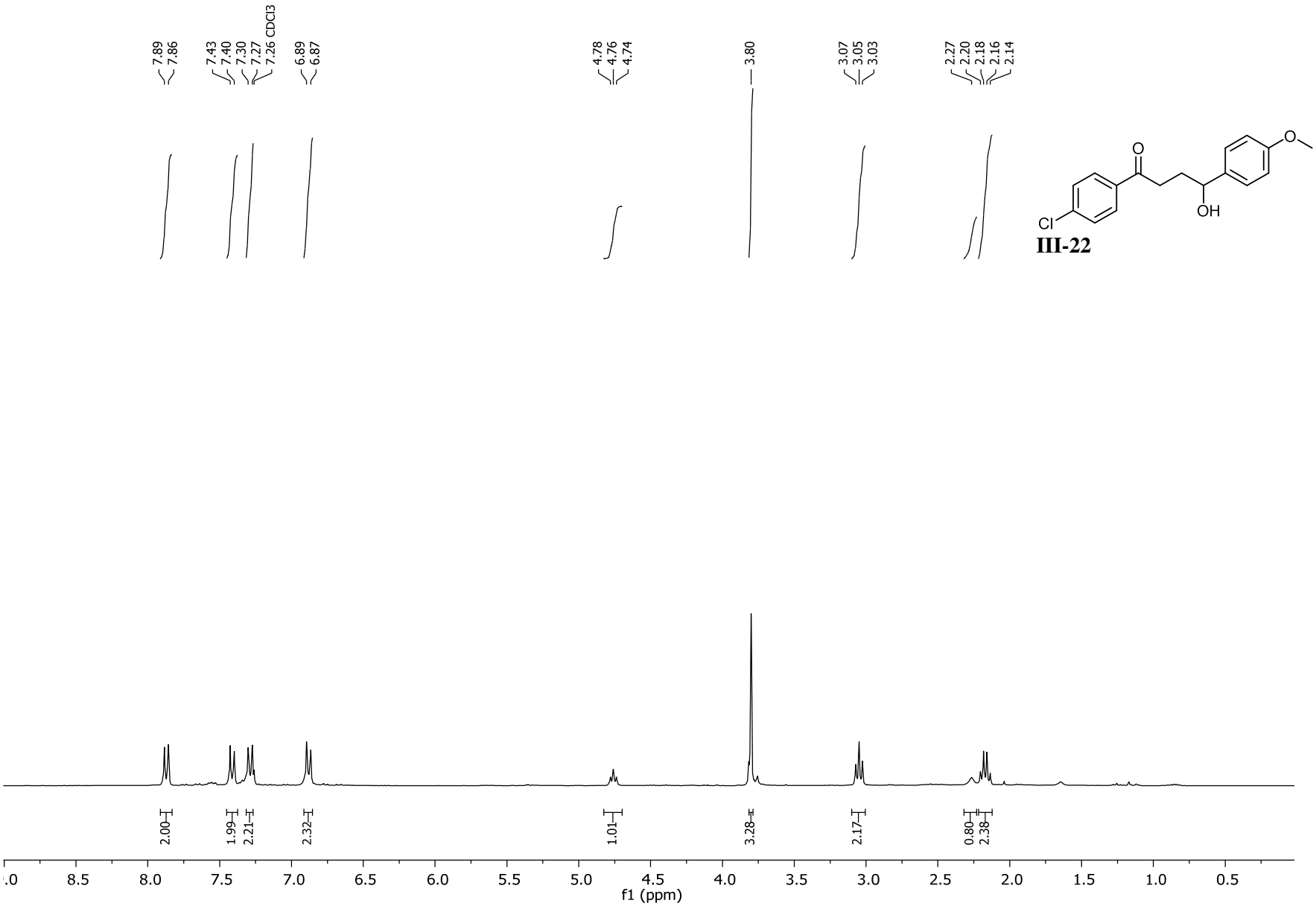

7.88
7.87
7.86
7.86
7.43
7.40
7.35
7.33
7.32
7.31
7.30
7.28
7.26 CDCl3
7.04
7.02
7.00
4.81
4.80
4.79
4.78
3.08
3.06
3.04
2.55
2.18
2.16
2.16
2.15
2.14
2.12
2.10
O
F
Cl
OH

III-21

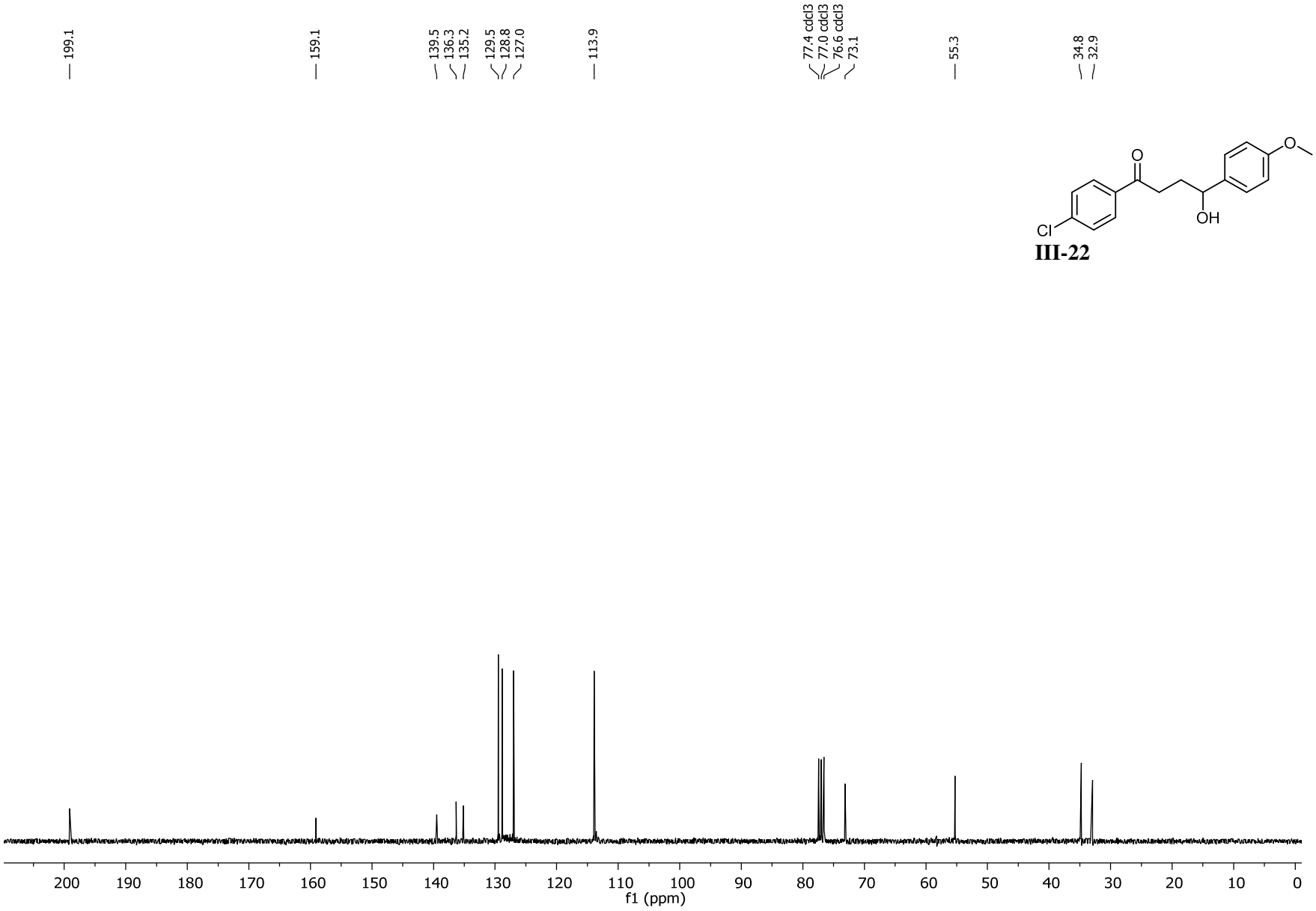

2.00
1.82
2.43
2.20
1.01
1.93
1.18
2.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

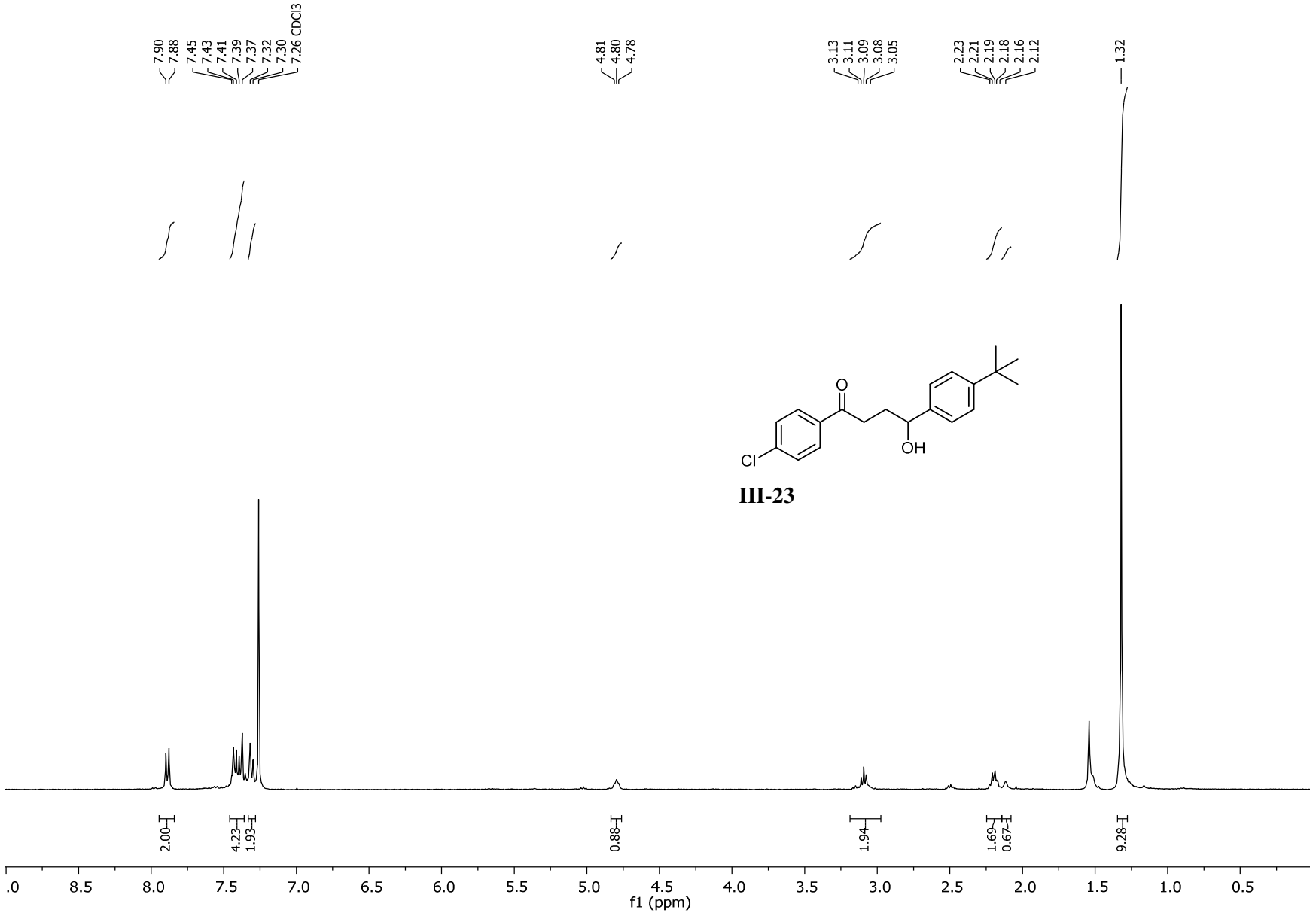

199.1
163.4
160.9
140.0
140.0
139.6
135.0
129.5
128.9
127.4
127.3
115.4
115.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
72.8
34.6
33.0
O
F
Cl
OH
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

III-21

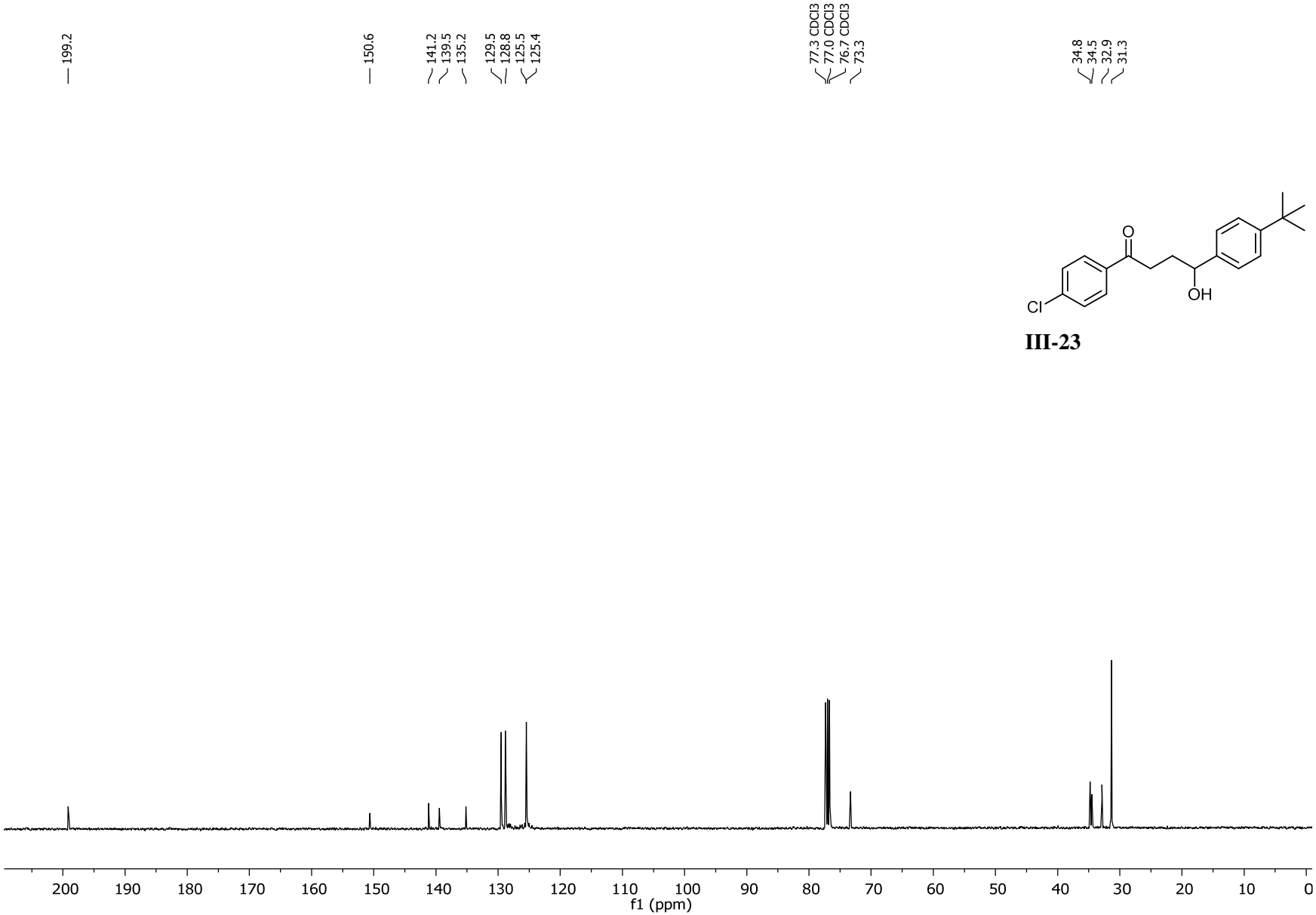

7.89
7.86
7.43
7.40
7.30
7.27
7.26 CDCl3
6.89
6.87
4.78
4.76
4.74
3.80
3.07
3.05
3.03
2.27
2.20
2.18
2.16
2.14
O
O
OH
Cl
2.00
1.99
2.21
2.32
1.01
3.28
2.17
0.80
2.38
f1 (ppm)

III-22

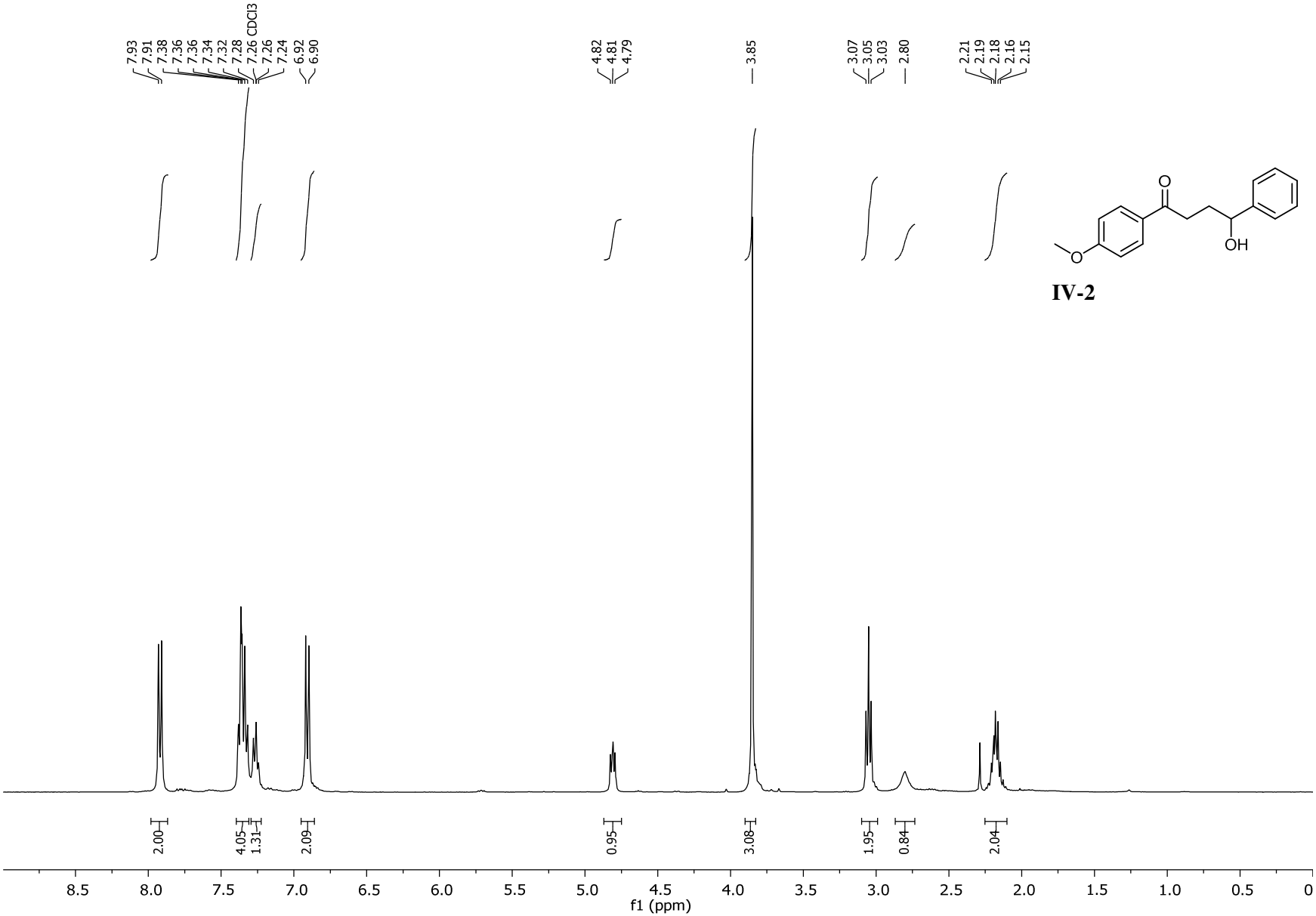

199.1
159.1
139.5
136.3
135.2
129.5
128.8
127.0
113.9
77.4 cdcl3
77.0 cdcl3
76.6 cdcl3
73.1
55.3
34.8
32.9
O
O
OH
Cl
III-22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

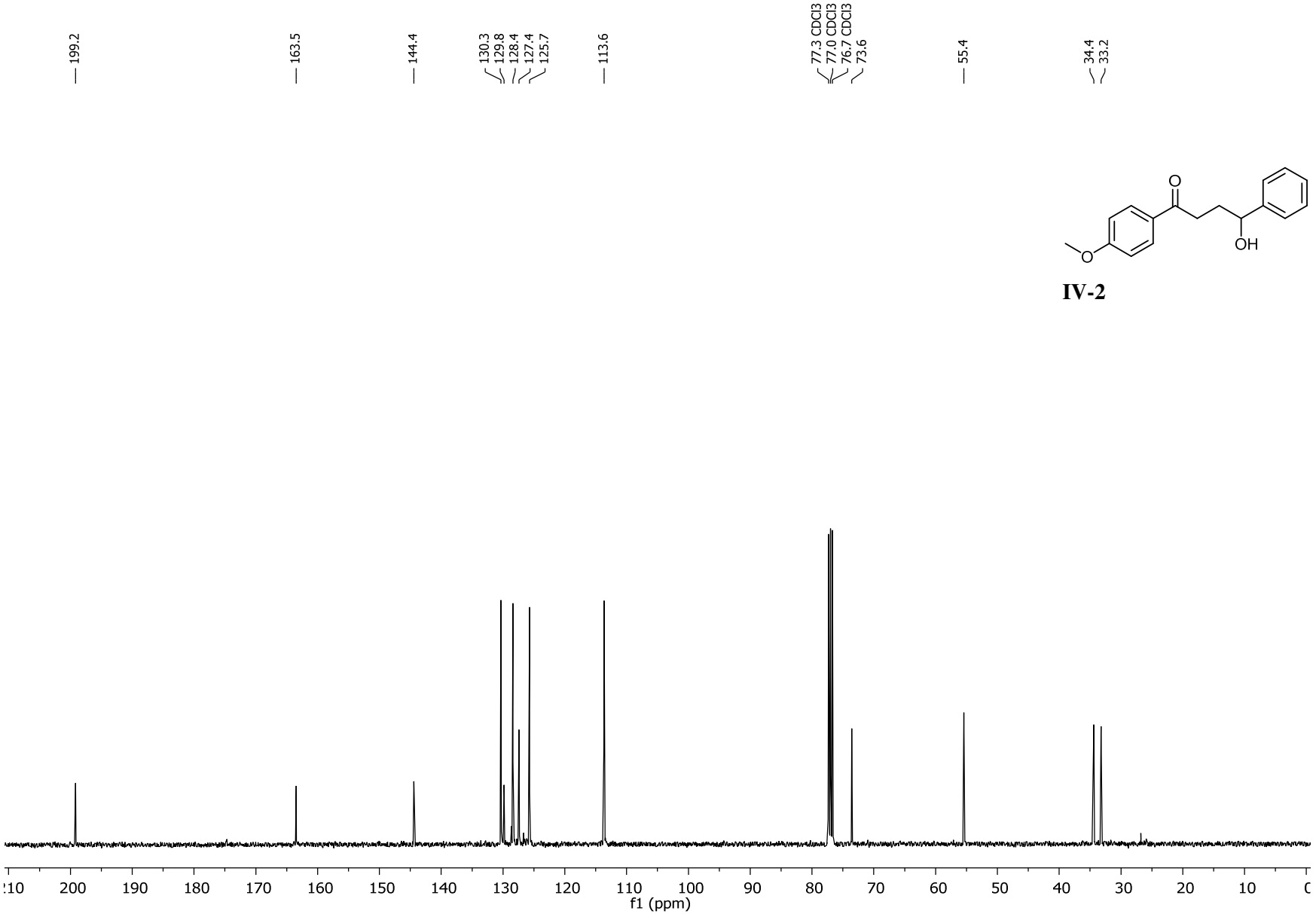

7.90
7.88
7.45
7.43
7.41
7.39
7.37
7.32
7.30
7.26 CDCl3
4.81
4.80
4.78
3.13
3.11
3.09
3.08
3.05
2.23
2.21
2.19
2.18
2.16
2.12
1.32
O
OH
Cl
2.00
4.23
1.93
0.88
1.94
1.69
0.67
9.28
f1 (ppm)

III-23

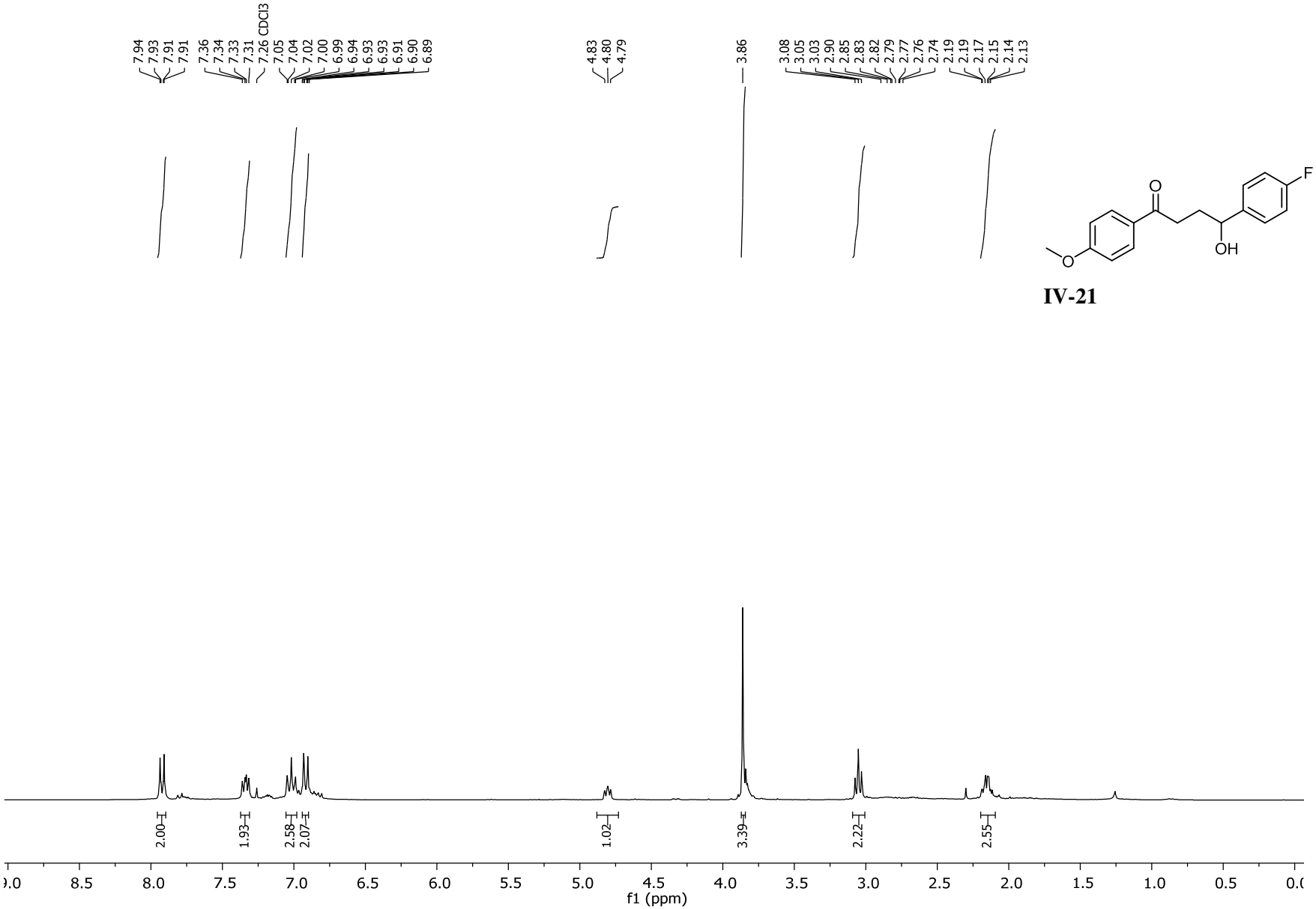

199.2
150.6
141.2
139.5
135.2
129.5
128.8
125.5
125.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.3
34.8
34.5
32.9
31.3
O
OH
Cl
f1 (ppm)

III-23

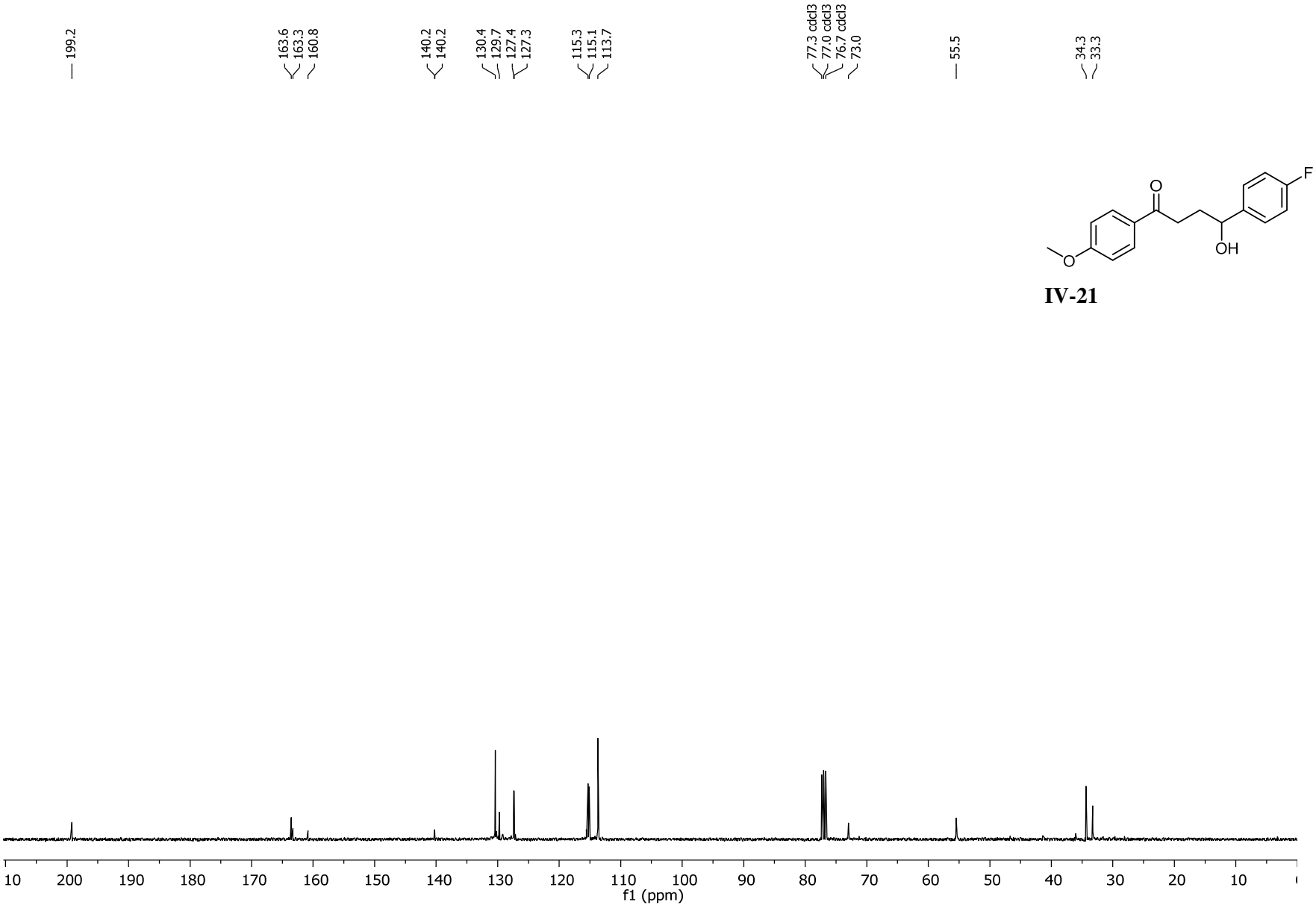

7.93
7.91
7.38
7.36
7.36
7.34
7.32
7.28
7.26 CDCl3
7.26
7.24
6.92
6.90
4.82
4.81
4.79
3.85
3.07
3.05
3.03
2.80
2.21
2.19
2.18
2.16
2.15
O
OH
O
IV-2
2.00
4.05
1.31
2.09
0.95
3.08
1.95
0.84
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


199.2
163.5
144.4
130.3
129.8
128.4
127.4
125.7
113.6
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.6
55.4
34.4
33.2
O
OH
O
f1 (ppm)

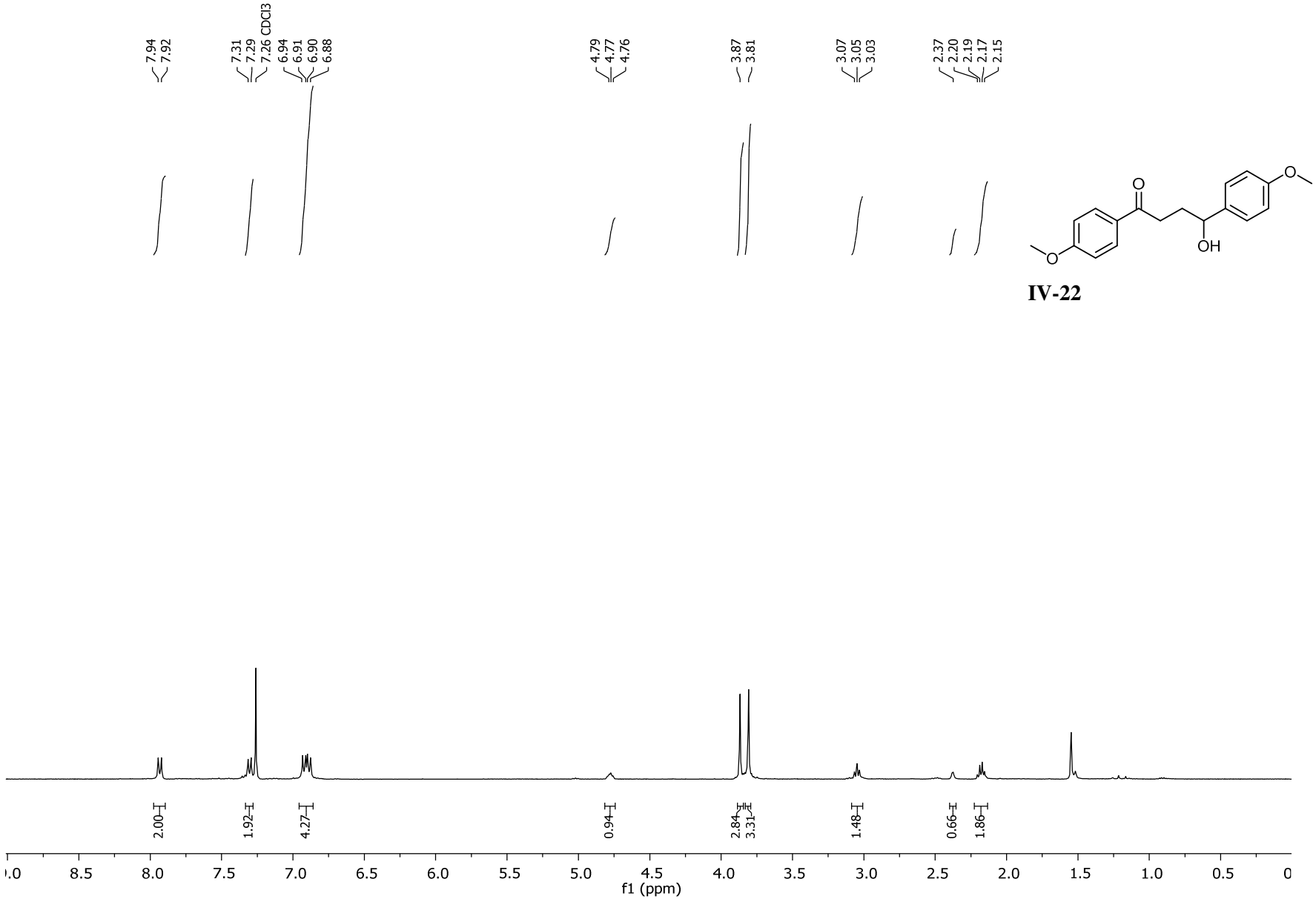
IV-2


7.94
7.93
7.91
7.91
7.36
7.34
7.33
7.31
7.26 CDCl3
7.05
7.04
7.02
7.00
6.99
6.94
6.93
6.93
6.91
6.90
6.89
4.83
4.80
4.79
3.86
3.08
3.05
3.03
2.90
2.85
2.83
2.82
2.79
2.77
2.76
2.74
2.19
2.19
2.17
2.15
2.14
2.13
F
O
OH
O
2.00
1.93
2.58
2.07
1.02
3.39
2.22
2.55
f1 (ppm)

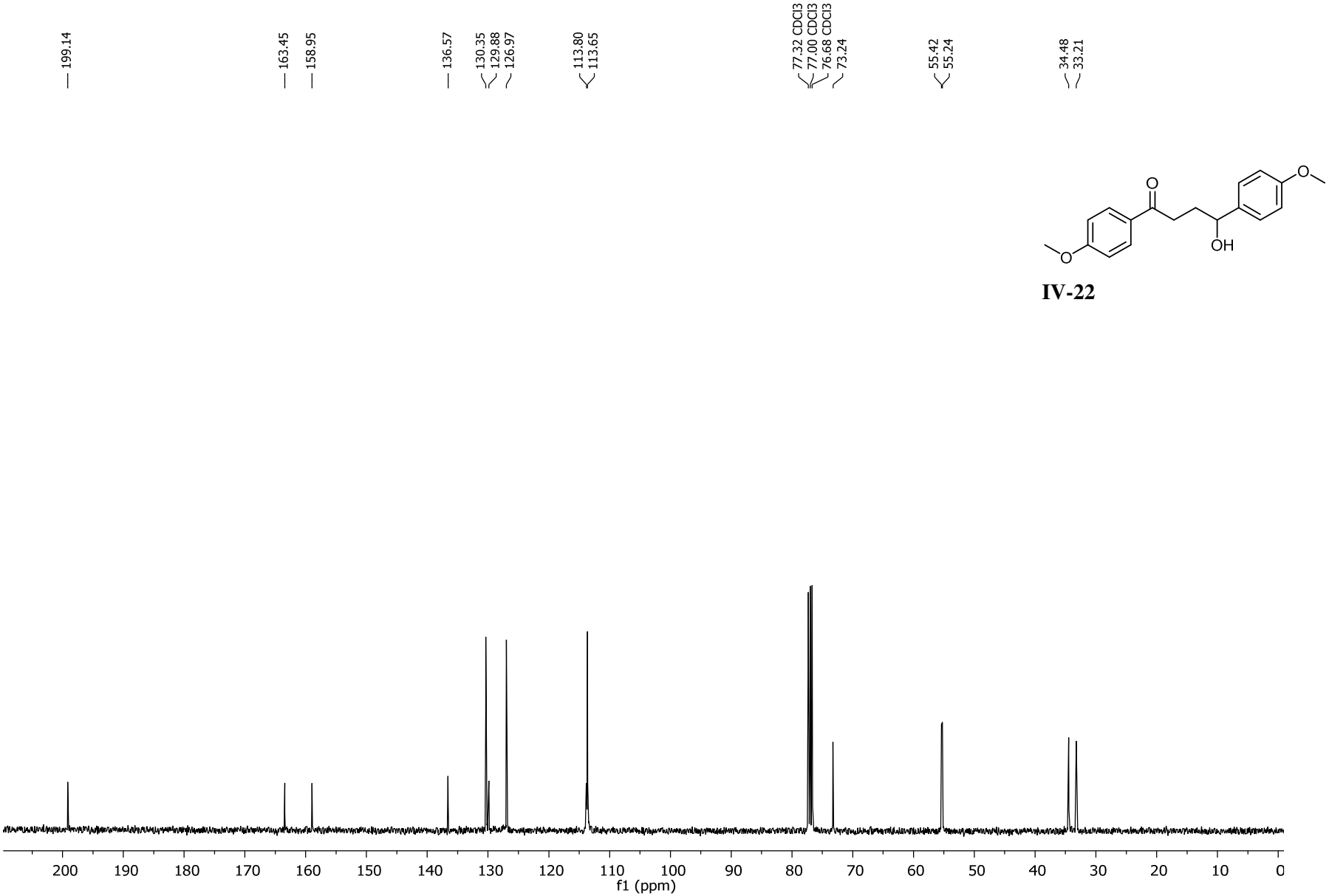
IV-21


199.2
163.6
163.3
160.8
140.2
140.2
130.4
129.7
127.4
127.3
115.3
115.1
113.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
73.0
55.5
34.3
33.3
O
F
OH
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

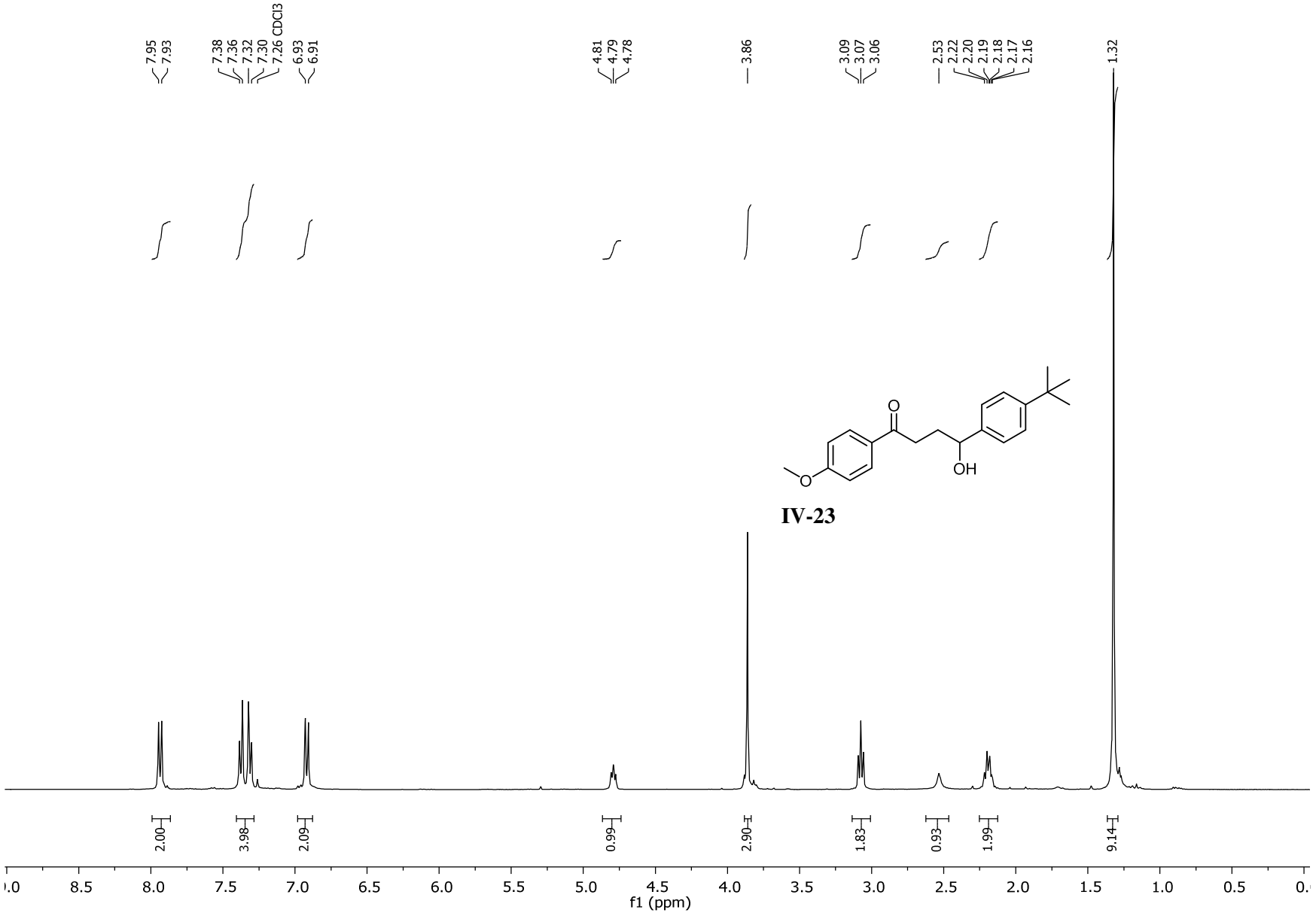
IV-21


7.94
7.92
7.31
7.29
7.26 CDCl3
6.94
6.91
6.90
6.88
4.79
4.77
4.76
3.87
3.81
3.07
3.05
3.03
2.37
2.20
2.19
2.17
2.15
O
O
OH
O
2.00
1.92
4.27
0.94
2.84
3.31
1.48
0.66
1.86
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
f1 (ppm)

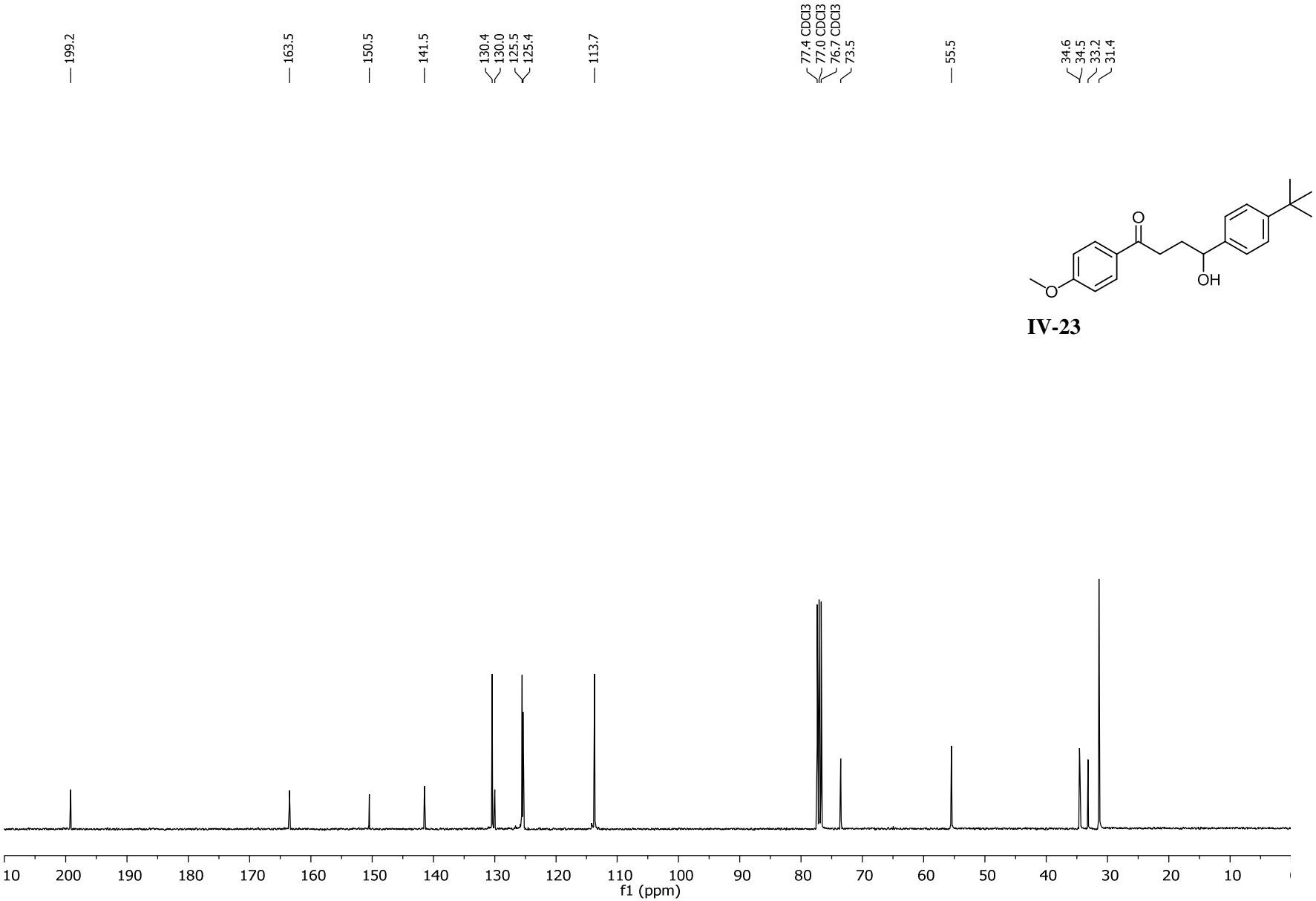
IV-22


199.14
163.45
158.95
136.57
130.35
129.88
126.97
113.80
113.65
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.24
55.42
55.24
34.48
33.21
O
O
OH
O
f1 (ppm)

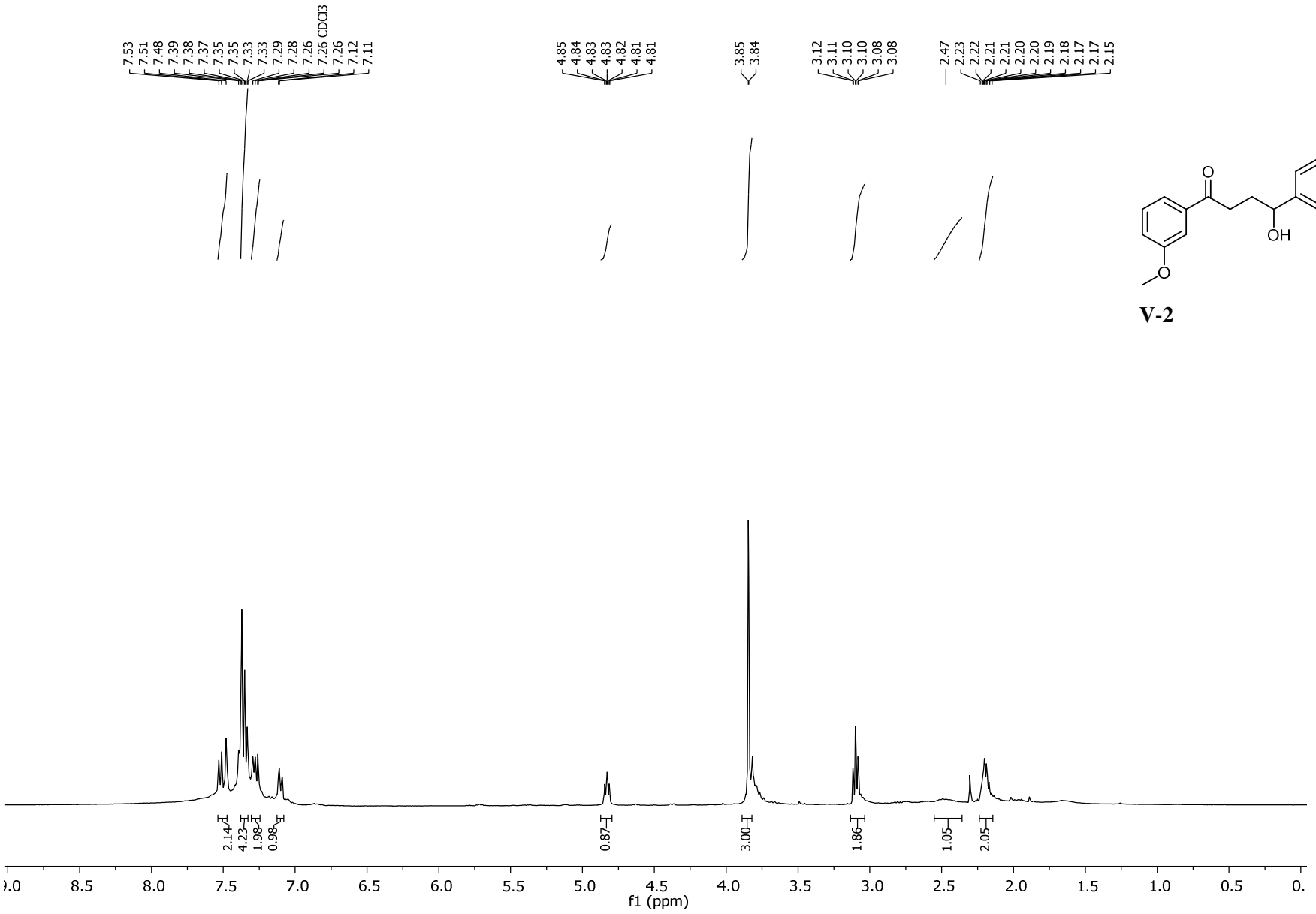
IV-22


7.95
7.93
7.38
7.36
7.32
7.30
7.26 CDCl3
6.93
6.91
4.81
4.79
4.78
3.86
3.09
3.07
3.06
2.53
2.22
2.20
2.19
2.18
2.17
2.16
1.32
O
OH
O
2.00
3.98
2.09
0.99
2.90
1.83
0.93
1.99
9.14
f1 (ppm)

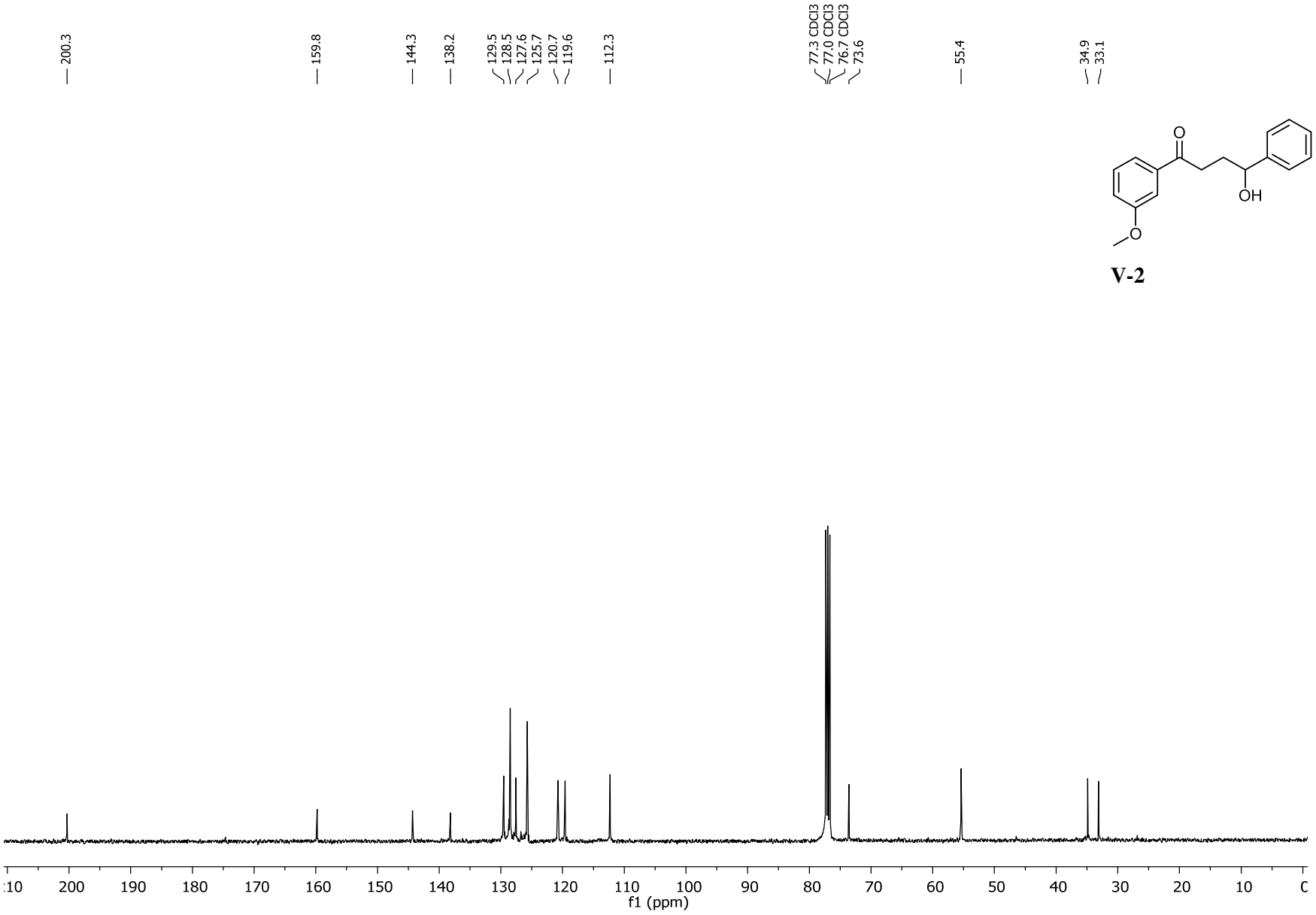
IV-23


199.2
163.5
150.5
141.5
130.4
130.0
125.5
125.4
113.7
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
73.5
55.5
34.6
34.5
33.2
31.4
O
OH
O
f1 (ppm)

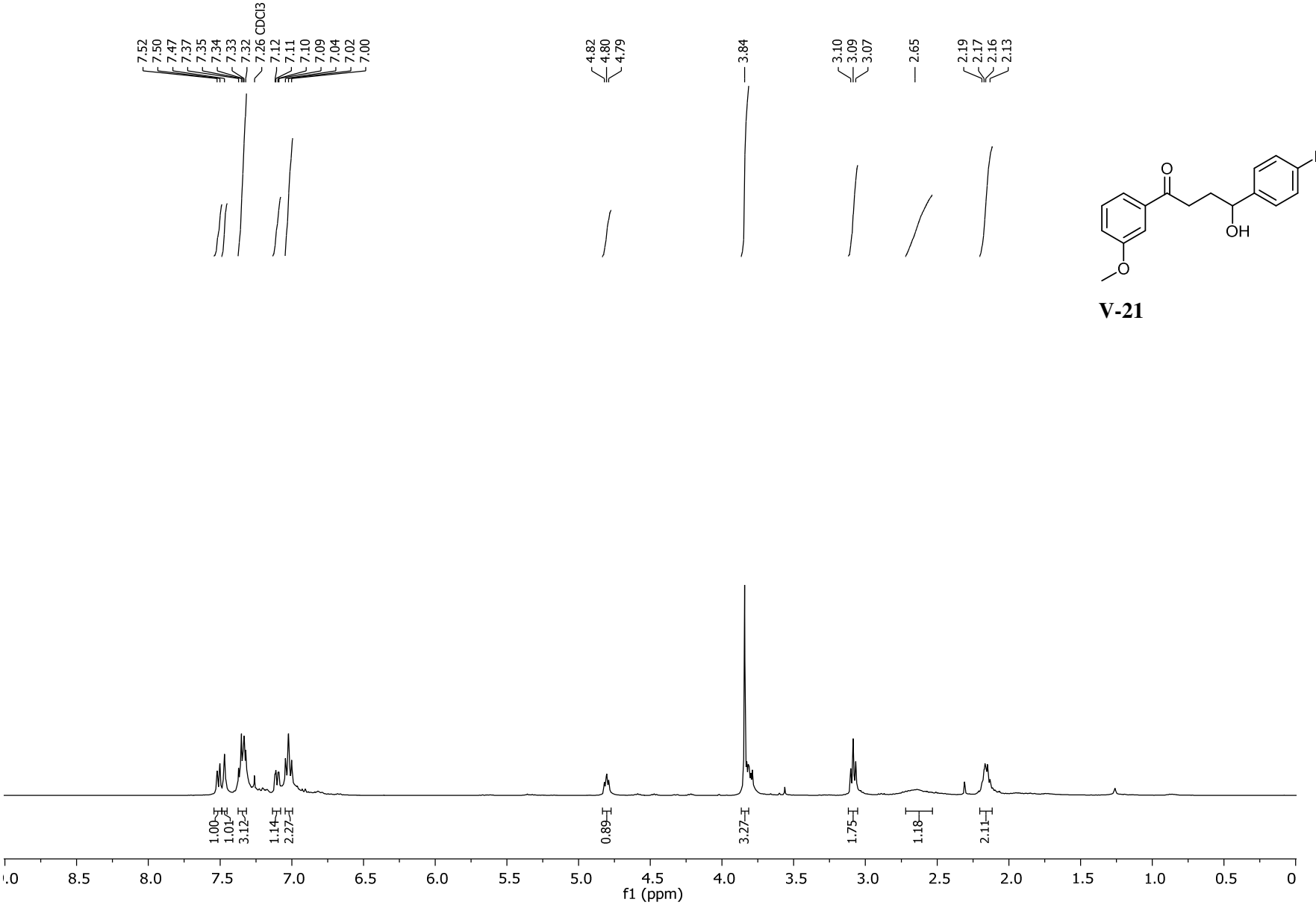
IV-23


7.53
7.51
7.48
7.39
7.38
7.37
7.35
7.35
7.33
7.33
7.29
7.28
7.26
7.26 CDCl3
7.26
7.12
7.11
4.85
4.84
4.83
4.83
4.82
4.81
4.81
3.85
3.84
3.12
3.11
3.10
3.10
3.08
3.08
2.47
2.23
2.22
2.21
2.21
2.20
2.20
2.19
2.18
2.17
2.17
2.15
O
OH
O
2.14
4.23
1.98
0.98
0.87
3.00
1.86
1.05
2.05
f1 (ppm)

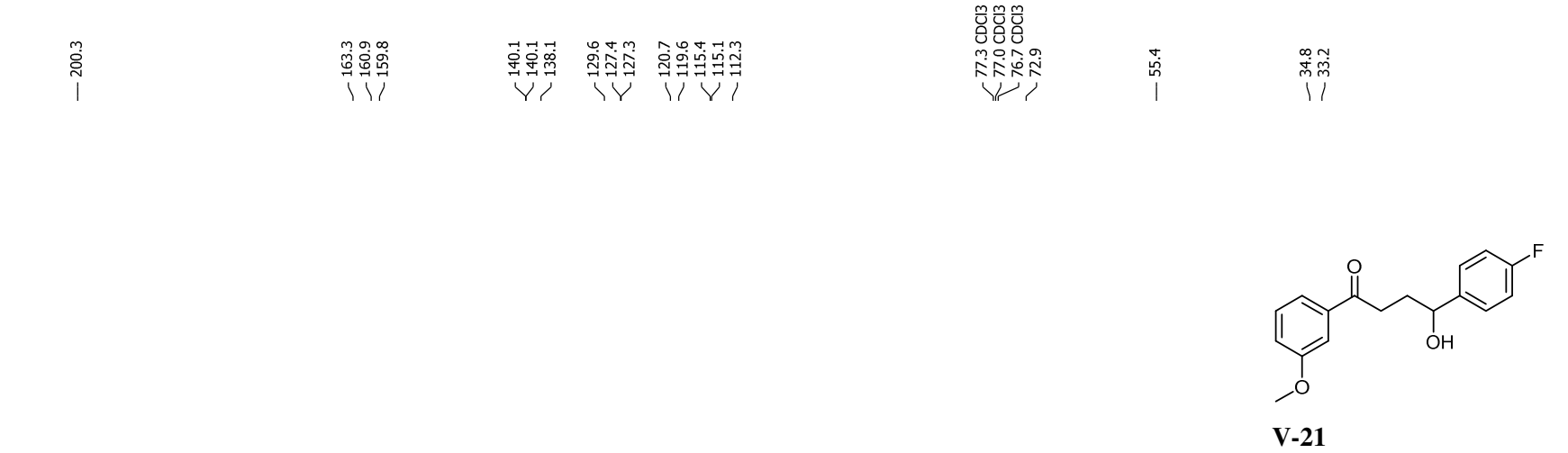
V-2

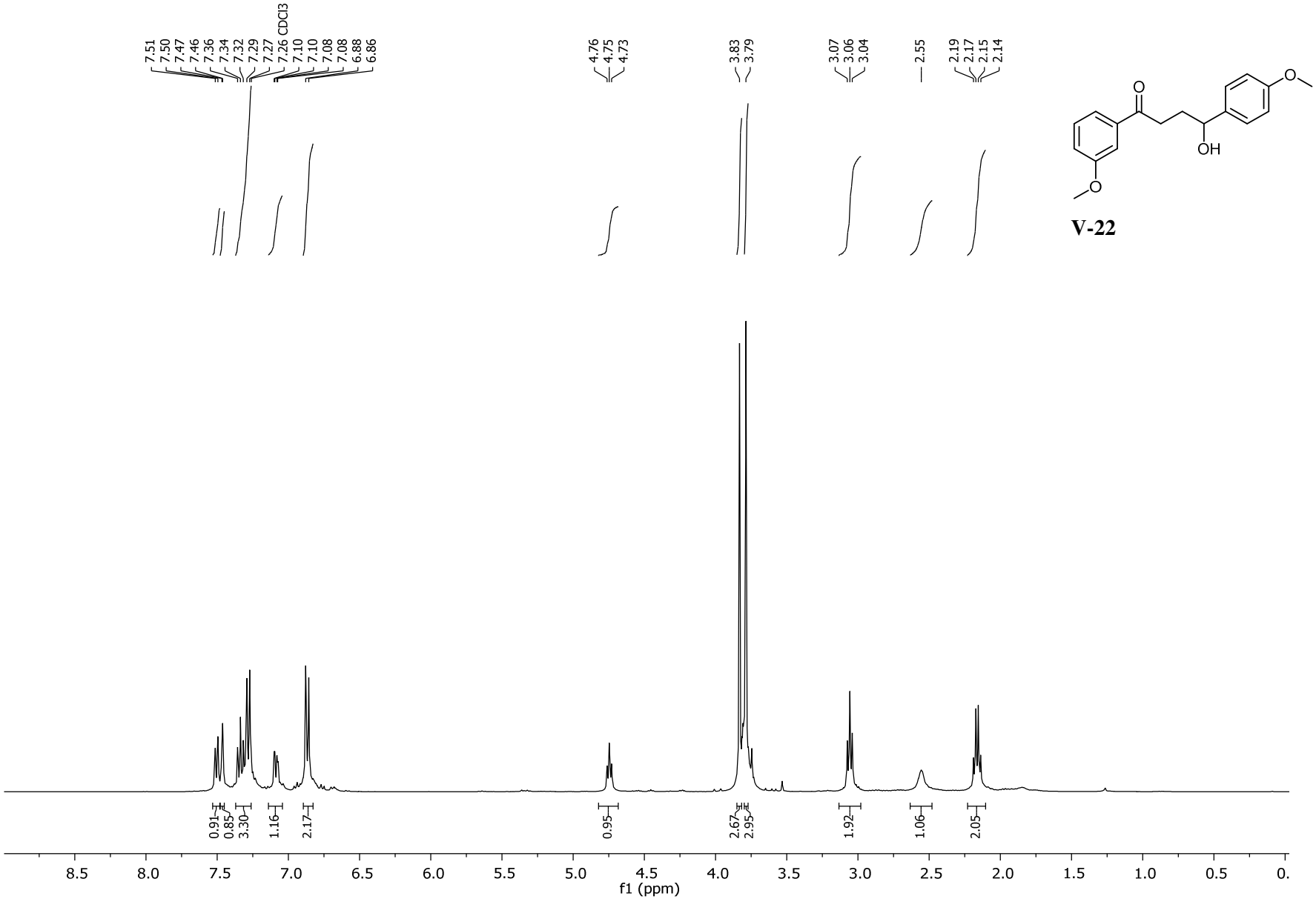

200.3
159.8
144.3
138.2
129.5
128.5
127.6
125.7
120.7
119.6
112.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.6
55.4
34.9
33.1
O
OH
O
f1 (ppm)

V-2

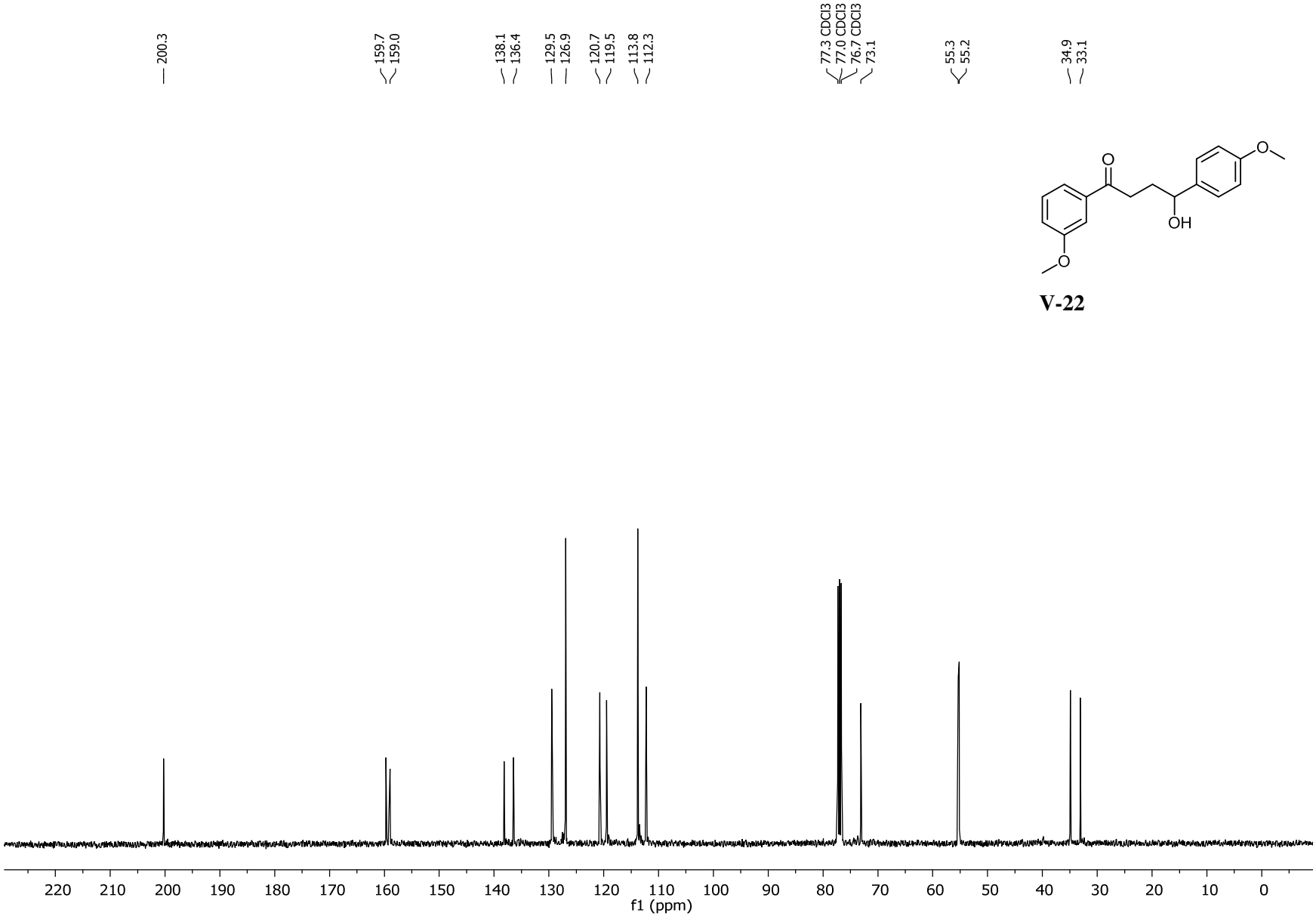

7.52
7.50
7.47
7.37
7.35
7.34
7.33
7.32
7.26 CDCl3
7.12
7.11
7.10
7.09
7.04
7.02
7.00
4.82
4.80
4.79
3.84
3.10
3.09
3.07
2.65
2.19
2.17
2.16
2.13
O
F
OH
O
1.00
1.01
3.12
1.14
2.27
0.89
3.27
1.75
1.18
2.11
f1 (ppm)

V-21

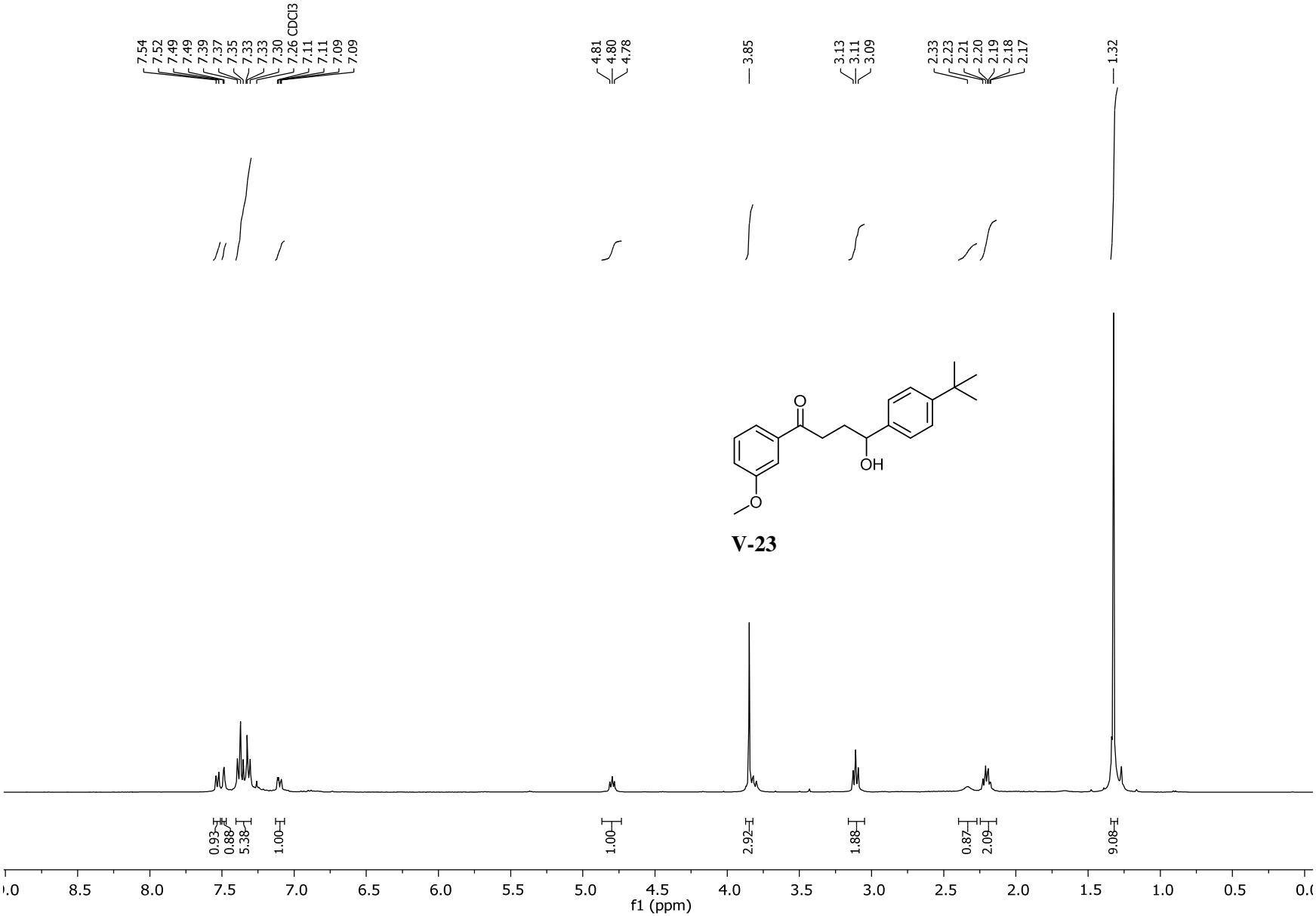

200.3
163.3
160.9
159.8
140.1
140.1
138.1
129.6
127.4
127.3
120.7
119.6
115.4
115.1
112.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
72.9
55.4
34.8
33.2
F
O
OH
O
V-21
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.51
7.50
7.47
7.46
7.36
7.34
7.32
7.29
7.27
CDCl3
7.26
7.10
7.10
7.08
7.08
6.88
6.86
4.76
4.75
4.73
3.83
3.79
3.07
3.06
3.04
2.55
2.19
2.17
2.15
2.14
O
O
OH
O
0.91
0.85
3.30
1.16
2.17
0.95
2.67
2.95
1.92
1.06
2.05
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.
f1 (ppm)

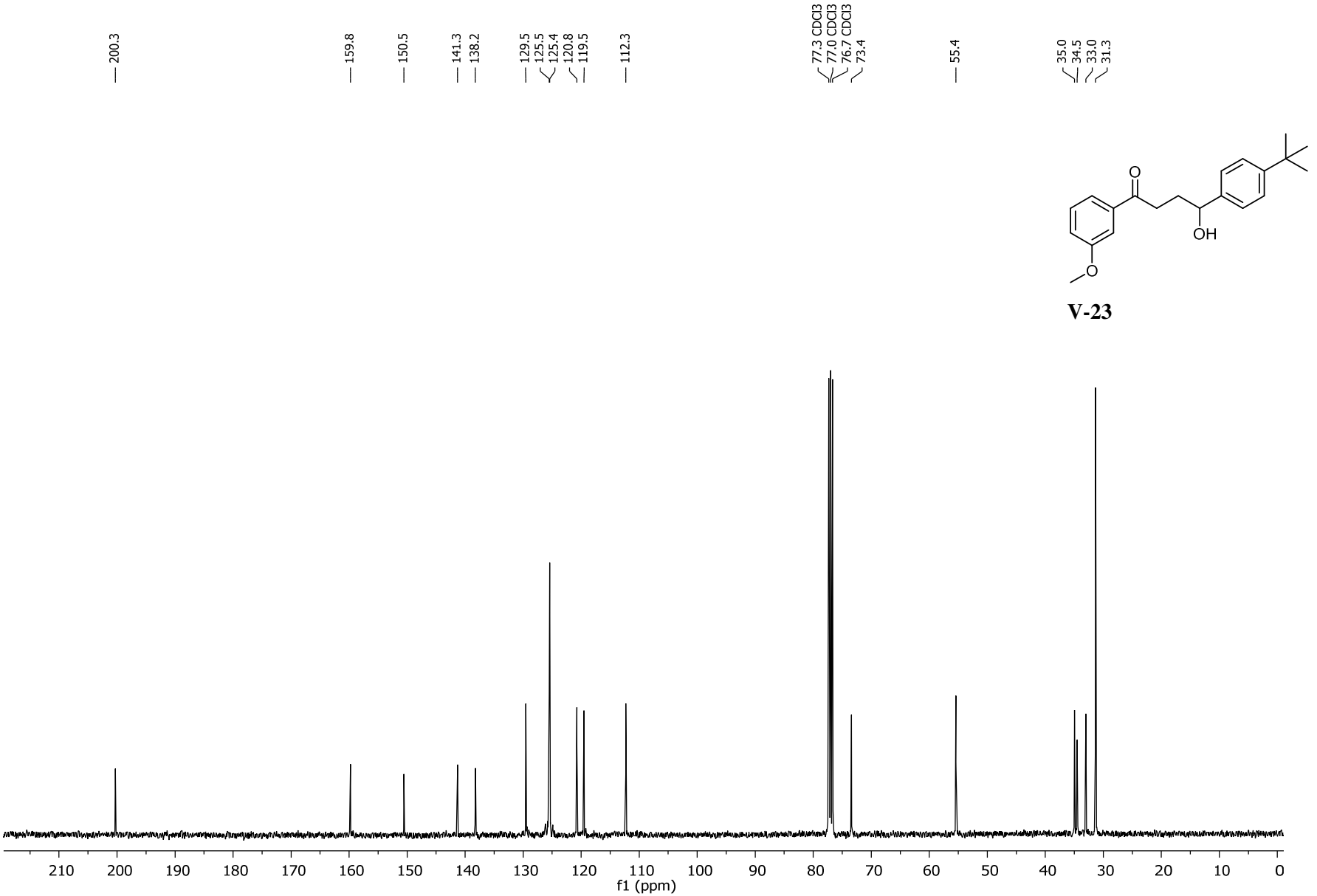
V-22


200.3
159.7
159.0
138.1
136.4
129.5
126.9
120.7
119.5
113.8
112.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.1
55.3
55.2
34.9
33.1
O
OH
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

V-22


7.54
7.52
7.49
7.49
7.39
7.37
7.35
7.33
7.33
7.30
7.26 CDCl3
7.11
7.11
7.09
7.09
4.81
4.80
4.78
3.85
3.13
3.11
3.09
2.33
2.23
2.21
2.20
2.19
2.18
2.17
1.32
O
OH
O
0.93
0.88
5.38
1.00
1.00
2.92
1.88
0.87
2.09
9.08
f1 (ppm)

V-23


200.3
159.8
150.5
141.3
138.2
129.5
125.5
125.4
120.8
119.5
112.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
73.4
55.4
35.0
34.5
33.0
31.3
O
OH
O
f1 (ppm)

V-23