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# Oxidation of Secondary Alcohols Using Solid-supported Hypervalent Iodine

Frederic Ballaschk,[a] and Stefan F. Kirsch[a,b]

[a] Organic Chemistry, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany

[b]sfkirsch@uni-wuppertal.de

## Supplementary Information

# 1. General remarks

The commercial reagents and solvents were used as purchased. The used solvents were, if not explicitly stated, not water-free. TLC was conducted with precoated aluminium sheets (silica gel 60 $F_{254}$) and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate (CAM), basic potassium permanganate ($KMnO_4$), 2,4-dinitrophenylhydrizine (DNPH) and subsequent heating. Flash column chromatography was performed on silica gel (40-60 µm), the eluent used is reported in the respective experiments. Abbreviations of solvents and chemicals are as followed: PE: petroleum ether, CH: Cyclohexane, EA: ethyl acetate, DMF: *N*,*N*-Dimethylformamide, NMP: *N*-Methyl-2-pyrrolidone. IR spectra were measured using ATR-technique in the range of 400-4000 $cm^{-1}$. $^1H$ NMR spectra were recorded with 400 MHz or 600 MHz instruments, $^{13}C$ NMR spectra at 101 MHz or 151 MHz. Chemical shifts are reported in ppm relative to the solvent signal, coupling constants *J* in Hz. Multiplicities were defined by standard abbreviations. Low-resolution mass spectra (LRMS) were recorded using a LC/MS-combination (ESI). High-resolution mass spectra (HRMS) were obtained using ESI ionization (positive) on a Bruker micrOTOF.

# 2. General procedures

**(A) Solid-phase-peptide-synthesis (SPPS)**

**(A1) Solutions:** Aminoacid solution: 0.51M in DMF (Phenylalanine in NMP)
HBTU solution: 0.49M in DMF
DIPEA solution: 2.04M in NMP
piperidine solution: 40% (v/v) in DMF

**(A2) Preparation of the Boc-Gylcine-Merrifield resin**: The resin (200 µmol) was swollen in dichloromethane (2 mL) for 10 minutes in a 10-mL-PP-reactor. The solvent was removed with suction. A solution of TFA (3mL, 25% (v/v) in dichloromethane) was added and the reactor was vortexed for 10 minutes (15 s vortex, 2 min break). The solvent was removed with suction and the resin was washed excessively with dichloromethane.

**(A3) Preparation of the polystyrene-Et-$NH_2$ resin**: The resin (200 µmol) was swollen in dichloromethane (2 mL) for 10 minutes in a 10-mL-PP-reactor. The solvent was removed with suction.

**(A4) Peptide coupling**: The desired aminoacid/DMF solution (1.2 mL, 600 µmol, 0.51M, 3 eq.) was added to the reactor containing the prepared resin. HBTU/DMF solution (1.26 mL, 600 µmol, 0.49M, 3 eq.) and DIPEA/NMP solution (0.9 mL, 600 µmol, 2.04M, 3 eq.) were added

and the mixture was vortexed for 40 minutes (15 s vortex, 2 min break). The solvent was removed with suction and the resin was washed with DMF (3x 2 mL).

**(A5) Fmoc deprotection**: Piperidine/DMF solution (2.4 mL, 9.2 mmol, 40% (v/v), 48 eq.) was added into the reactor. The mixture was vortexed for 3 minutes (15 s vortex, 1 min break) and the solvent was removed with suction. Piperidine/DMF solution (1.2 mL, 4.6 mmol, 40% (v/v), 24 eq.) and DMF (1.2 mL) were added into the reactor and the mixture was further vortexed for 12 minutes (15s vortex, 2 min break). The solvent was removed with suction and the resin was washed with DMF (6x 2 mL)

**(A6) IBX-catalyst coupling**: (*S*)-4-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-5-((3-(tert-butoxycarbonyl)-4-iodophenyl)amino)-5-oxopentanoic acid (**10**) (286 mg, 400 µmol, 2 eq.) was added into the reactor and dissolved with DMF (1 mL). HBTU/DMF solution (1.2 mL, 600 µmol, 0.49M, 3 eq.) and DIPEA/NMP solution (0.6 mL, 1.2 mmol, 2.04M, 6 eq.) were added and the mixture was vortexed for 12 hours (15s vortex, 2 min break). The solvent was removed with suction and the resin was washed with DMF (3x 2 mL).

**(A7) IBS-catalyst coupling**: Sodium 5-carboxy-2-iodobenzenesulfonate (**12**) (210 mg, 600 µmol, 3 eq.), HATU (228 mg, 600 µmol, 3 eq.) and DMSO (3 mL) were added into the reactor. DIPEA/NMP solution (0.9 mL, 600 µmol, 2.04M, 3 eq.) was added and the mixture was vortexed for 12 hours (15 s vortex, 2 min break). The solvent was removed with suction and the resin was washed with DMSO (3x 2mL), DMF (3x 2 mL) and dichloromethane (6x 2 mL).

**(A8) Acetylation**: The resin was swollen in dichloromethane (2 mL) for 10 minutes. The solvent was removed with suction and acetic anhydride (2 mL, 21.6 mmol, 108 eq.). The mixture was vortexed for 1 hour (15s vortex, 2 min break) and subsequently filtered with suction. The resin was washed with DMF (3x 2 mL) and dichloromethane (6x 2 mL).

**(A9) Side chain deprotection**: TFA solution (2 mL, 13 mmol, 50% (v/v) in dichloromethane, 65 eq.) was added to the resin. The reactor was tightly sealed and the reaction was vortexed for 12 h (15s vortex, 2 min break). The solvent was removed with suction and the resin was washed with dichloromethane (3x 2 mL), DMF (3x 2 mL) and again dichloromethane (5x 2 mL)

Theoretical loading is determined using formula (1)

$$(1)\ \text{theo.}\,Loading\ \left(\frac{mmol}{g}\right) = B\left(\frac{mmol}{g}\right) \cdot \frac{1000}{\left(1000 + \left(B\left(\frac{mmol}{g}\right) \cdot (M - 18)\right)\right)}$$

where B equals the loading of starting resin and M equals the molecular weight of the amino acid chain with protective groups.

**(B) Loading determination via UV-VIS**

A sample of the resin, still bearing a Fmoc protection group, is placed in a cuvette. 3 mL of a piperidine/DMF solution (20 v/v%) is added and the mixture is shaken for 10 minutes. The cuvette is placed in the UV-VIS spectrometer and the absorption at 289.8 nm is measured multiple times until the absorption reaches a constant value. This procedure was performed three times. The loading is determined using formula (2)

$$(2)\ Loading\ \left(\frac{mmol}{g}\right) = \frac{Abs_{\ 289nm} \cdot 10^6 \cdot V\ \cdot D}{\varepsilon_{289nm} \cdot m_{Resin} \cdot l}$$

with $Abs_{289nm}$ = Absorption at 289.8 nm; $10^6$ = conversion factor (mmol to mol; g to mg); V = sample volume [L], D = Dilution factor; $\varepsilon_{289nm}$ = Absorption coefficient = 6089 [L $mol^{-1}$ $cm^{-1}$]; m = sample weight [mg] and l = Optical path length [cm].

**(C) Loading determination for the IBS-based resin**

L(-)-Borneol (**13a**)(4.7 mg, 30 µmol, 1 eq.) was dissolved in Acetonitrile (0.2 mL, 0.15M). The preoxidized resin (30 mol%)(swollen in dichloromethane for 10 minutes prior to use) was added and the mixture was stirred at 70 °C for 18 h. The mixture was filtered through a PTFE frit and the filtrate was analysed via GC-FID. The observed conversion was divided by the theoretically possible conversion (30%). Multiplying this factor with the theoretical loading gave the real loading in mmol/g.

**(D) Oxidation of secondary alcohols – Method A**

The secondary alcohol (0.25 mmol, 1 eq.) was dissolved in acetonitrile/water (0.5 mL, 7/3, 0.5M) in a 4-mL-Vial. Oxone (122 mg, 0.4 mmol, 1.6 eq.) and catalyst resin **5c** (12.5 µmol, 5 mol%)(swollen in dichloromethane for 10 minutes prior to use) was added, the vial was tightly sealed and the reaction was shaken for 18 hours at 70 °C. The suspension was filtered through a PTFE frit and the filtrate was evaporated. Purification by flash column chromatography furnished the desired product.

**(E) Oxidation of secondary alcohols – Method B**

The secondary alcohol (0.25 mmol, 1 eq.) was dissolved in acetonitrile (0.5 mL, 0.5M) in a 4-mL-Vial. Oxone (122 mg, 0.4 mmol, 1.6 eq.), *n*$Bu_4NHSO_4$ (34 mg, 0.10 mmol, 40 mol%) and catalyst resin **6** (12.5 µmol, 5 mol%)(swollen in dichloromethane for 10 minutes prior to use) was added, the vial was tightly sealed and the reaction was shaken for 3-72 hours at 70 °C. The suspension was filtered through a PTFE frit and the filtrate was evaporated. Purification by flash column chromatography gave the desired product.

**(F) Oxidation of primary allylic alcohols – Method C**

The primary allylic alcohol (0.25 mmol, 1 eq.) was dissolved in dry acetonitrile (0.5 mL, 0.5M) in a 4-mL-Vial. Oxone (92 mg, 0.3 mmol, 1.2 eq.), *n*$Bu_4NHSO_4$ (34 mg, 0.10 mmol, 40 mol%) and dried sodium sulfate (106 mg, 0.75 mmol, 3 eq.)(dried via heating with a heat-gun under vacuum) and catalyst resin **6** (12.5 µmol, 5 mol%)(swollen in dichloromethane for 10 minutes prior to use) was added, the vessel was tightly sealed and the reaction was shaken for 18 hours at 70 °C under argon. The suspension was filtered through a PTFE frit and the filtrate was evaporated. Purification by flash column chromatography gave the desired product.

## 3. Experimental procedures

2-Iodo-5-nitrobenzoic acid (**7'**). 2-Iodobenzoic acid (3.00 g, 12.1 mmol, 1 eq.) was cooled to 0 °C in a round-bottom flask. At 0 °C, a mixture of nitric acid/sulfuric acid (18 mL, 3:1) was added carefully. After stirring for 15 minutes at 0 °C, the temperature was raised to ambient temperature and stirred for another 30 minutes. Finally, the mixture was heated to 130 °C for 60 to 90 minutes (CAUTION!! Nitrous gases!!) with a reflux condenser and two washing bottles, the second one filled with aqueous NaOH solution (1M). The mixture is cooled below 100 °C and then slowly poured into ice. The grey precipitate is collected and resuspensed in 25 mL water. Potassium iodide (2.61 g, 15.7 mmol, 1.3 eq.), dissolved in 15 mL water, is added slowly to the suspension. The reaction is heated to 100 °C for another 60 to 90 minutes, before cooling to room temperature. Saturated $Na_2S_2O_3$ solution is added until discoloration of the solution. The pH of the solution was adjusted to <1 with concentrated hydrochloric acid. A fluffy off-white solid precipitated, which was collected by filtration, washed with an excessive amount of water and which was finally recrystallized from water to yield 2-iodo-5-nitrobenzoic acid (**7'**) (2.32 g, 7.92 mmol, 65%) as yellow needles. $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 13.91 (s, 1H), 8.40 (d, *J* = 2.8 Hz, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.01 (dd, *J* = 8.6, 2.8 Hz, 1H), $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 166.4, 147.3, 142.4, 138.1, 126.0, 124.0, 103.6. The analytical data are in agreement with previously reported ones.[1]

*tert*-Butyl 2-iodo-5-nitrobenzoate (**7**). 2-Iodo-5-nitrobenzoic acid (**7'**) (2.60 g, 8.87 mmol, 1 eq.) was dissolved in *tert*-butanol (60 mL, 0.15M). After the addition of di-*tert*-butyl dicarbonate (4.81 g, 22.2 mmol, 2.5 eq.) and DMAP (325 mg, 2.66 mmol, 0.3 eq.), the reaction was heated to 70 °C for 3-4 hours. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (CH:EA 100:0 → 90:10) yielding *tert*-butyl 2-iodo-5-nitrobenzoate (**7**)(3.09 g, 8.84 mmol, 99%) as yellow solid. TLC: $R_f$ = 0.23 (CH:EA 95:5)[UV], $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 8.46 (d, *J* = 2.7 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 7.93 (dd, *J* = 8.6, 2.7 Hz, 1H), 1.65 (s, 9H), $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 164.4, 147.9, 142.4, 139.0, 125.8, 125.0, 101.9, 84.3, 28.2. The analytical data are in agreement with previously reported ones.[2]

*tert*-Butyl 5-amino-2-iodobenzoate (**8**). *tert*-Butyl 2-iodo-5-nitrobenzoate (**7**)(4.50 g, 12.6 mmol, 1 eq.) was dissolved in ethyl acetate (42 mL, 0.3M) in an autoclave. Palladium on charcoal (1.33 g, 5 w/w%, 1.26 mmol, 10 mol%) was added and the apparatus was purged with hydrogen gas for 5 minutes. The autoclave was sealed, the pressure was raised to 100 psi and the reaction was stirred for 18 hours at room temperature. The suspension was filtered over a

Celite pad, eluted with ethyl acetate and the filtrate was evaporated under reduced pressure. Purification by flash column chromatography (PE:$Et_2O$ 40:60 → 30:70) furnished *tert*-butyl 5-amino-2-iodobenzoate (**8**)(7.28 g, 10.3 mmol, 82%) as a 45% mixture with diethyl ether. TLC: $R_f$ = 0.33 (PE:$Et_2O$ 30:70)[UV, Ninhydrin]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.61 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.9 Hz, 1H), 1.60 (s, 9H); $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 166.4, 146.5, 141.4, 138.1, 119.1, 117.2, 82.6, 78.3, 28.3; IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3469, 3375, 3000, 2977, 2930, 1706, 1622, 1592, 1243, 1143, 1009, 818; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}NO_2$ 320.0142; Found 320.0141.

(*S*)-*tert*-Butyl 5-(2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5-methoxy-5-oxopentanamido)-2-iodobenzoate (**9**). *tert*-Butyl 5-amino-2-iodobenzoate (**8**)(1.70 g, 3.36 mmol, 1 eq.) and (*S*)-4-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5-methoxy-5-oxopentanoic acid (1.74 g, 4.53 mmol, 1.35 eq.) were dissolved in dry DMF (5.6 mL, 0.6M). At 0 °C, HATU (1.91 g, 5.03 mmol, 1.5 eq.) and DIPEA (1.18 mL, 6.71 mmol, 2 eq.) were added and the reaction was warmed to ambient temperature overnight. The mixture was diluted with ethyl acetate and saturated sodium bicarbonate solution. The phases were separated and the aqueous phase was extracted twice with ethyl acetate. The combined organic phases were washed with saturated sodium chloride solution, dried over sodium sulfate, filtered and evaporated under reduced pressure. Purification by flash column chromatography (PE:EA 90:10 → 60:40) gave the desired product (2.09 g, 3.05 mmol, 91%) as white solid. TLC: $R_f$ = 0.47 (PE:EA 50:50)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.73 (s, 1H), 7.83 – 7.80 (m, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.41 – 7.35 (m, 3H), 7.31 – 7.25 (m, 2H), 5.86 (d, *J* = 7.7 Hz, 1H), 4.42 (d, *J* = 6.4 Hz, 2H), 4.38 (s, 1H), 4.19 (t, *J* = 6.9 Hz, 1H), 3.68 (s, 3H), 2.67 – 2.38 (m, 2H), 2.29 – 1.97 (m, 2H), 1.61 (s, 9H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 174.3, 169.8, 165.9, 143.7, 143.6, 141.4, 141.4, 138.2, 137.8, 127.9, 127.2, 127.2, 125.1, 123.4, 121.7, 120.2, 86.8, 83.1, 67.5, 52.2, 47.2, 30.5, 28.3, 28.0; IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3302, 3064, 2970, 2932, 1682, 1581, 1368, 1254, 1159, 738; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{33}IN_2NaO_7$: 707.1225; Found: 707.1231.

(*S*)-4-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-5-((3-(tert-butoxycarbonyl)-4-iodophenyl)amino)-5-oxopentanoic acid (**10**). (*S*)-*tert*-butyl 5-(2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5-methoxy-5-oxopentanamido)-2-iodobenzoate (**9**)(3.51 g, 5.13 mmol, 1 eq.) was dissolved in THF (17 mL, 0.3M) and cooled to 0 °C. Lithium hydroxide monohydrate (258 mg, 6.15 mmol, 1.2 eq.), dissolved in 17 mL water, was slowly added under vigorous stirring. The mixture was warmed to room temperature overnight, before adjusting the

pH to 10 with aqueous sodium hydroxide solution (10M). The aqueous solution was extracted three times with diethyl ether. After acidification with aqueous hydrochloric acid (6M) to pH 1-3, the mixture was extracted three times with ethyl acetate. The combined organic phases were dried over sodium sulfate, filtered and evaporated under reduced pressure. The crude product (2.50 g, 3.73 mmol, 73%) could be used without further purification. $^{1}$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.21 (s, 1H), 7.89 (s, 1H), 7.73 (t, *J* = 7.8 Hz, 3H), 7.57 – 7.48 (m, 2H), 7.39 – 7.26 (m, 5H), 5.97 (d, *J* = 8.7 Hz, 1H), 4.57 (q, *J* = 7.8, 7.4 Hz, 1H), 4.44 – 4.32 (m, 2H), 4.15 (t, *J* = 6.8 Hz, 1H), 2.63 – 2.41 (m, 2H), 2.25 – 1.98 (m, 2H), 1.57 (s, 9H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 176.3, 170.2, 165.9, 157.2, 143.6, 143.5, 141.4, 138.0, 137.9, 128.0, 127.3, 125.1, 123.4, 121.9, 120.2, 87.0, 83.1, 67.9, 54.6, 47.1, 30.0, 28.2, 28.1; IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3302, 3093, 3064, 3043, 2970, 2931, 1690, 1531, 1254, 1159, 739; HRMS (ESI) m/z: [M+Na] calcd for $C_{31}H_{31}IN_2NaO_7$: 693.1068; Found: 693.1069.

4-Amino-3-sulfobenzoic acid (**11**). Sulfuric acid (foaming, 25%, 8 mL) is cooled to 0 °C. 4-aminobenzoic acid (4.00 g, 29.2 mmol, 1 eq.) is added portion wise. The reaction is heated to 180 °C for 2 h. Afterwards, the solution is cooled below 100 °C, poured into 26 g of ice with external cooling and stirred for another 30 min. The precipitate is filtered through a Büchner funnel and washed with low amounts of ice water. The product is dried in vacuum to yield 4-amino-3-sulfobenzoic acid (4.95 g, 22.8 mmol, 78%) as grey solid, which was used for the next step without further purification. $^{1}$H-NMR (400 MHz, $d^6$-DMSO): δ [ppm] = 8.14 (d, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.4, 2.0 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H).; $^{13}$C-NMR (101 MHz, $d^6$-DMSO): δ [ppm] = 167.1, 144.2, 132.3, 131.6, 129.6, 120.4, 117.8; HRMS (ESI) m/z: [M-H] calc'd for $C_7H_6NO_5S$: 215.9972; Found: 215.9983.

Sodium 5-carboxy-2-iodobenzenesulfonate (**12**). 4-amino-3-sulfobenzoic acid (**11**) (4.10 g, 18.9 mmol, 1 eq.) was suspensed in water (42 ml, 0.45M) and an aqueous sodium hydroxide solution (1.89 ml, 10M, 18.9mmol, 1 eq.) was added. The mixture was cooled to 0 °C before Sulfuric acid (96%, 21.1 ml, 378 mmol, 20 eq.) was added through a dropping funnel under external cooling. After complete addition, the reaction was cooled to -10 °C. Sodium nitrite (1.43 g, 20.8 mmol, 1.1 eq.), dissolved in 17 ml water, was slowly added dropwise with the temperature below 5 °C during addition. The reaction was stirred for another 60 min at -2 °C, before urea (2.27 g, 37.8 mmol, 2 eq.) was added in small portions. Stirring at -2 °C was continued for another hour before the reaction mixture was poured into sodium iodide solution (4.24 g, 28.3 mmol, 1.5 eq.), dissolved in 13 mL water at 0 °C. After stirring at room temperature for 12 h, the reaction was quenched with sat. sodium sulfite solution (aq.) until

complete discoloration occurred. The resulting suspension was stirred for 30 min at 0 °C and the precipitate is filtered through a Buchner funnel, washed with ice water and acetone to give a brown powder. Treatment with boiling acetone (1 mL/100 mg substrate) and subsequent filtration furnished sodium 5-carboxy-2-iodobenzenesulfonate (3.12 g, 8.91 mmol, 47%) as off-white powder. $^{1}$H-NMR (600 MHz, d$^{6}$-DMSO): δ [ppm] = 13.02 (s, 1H), 8.45 (d, J = 2.1 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.51 (dd, J = 8.0, 2.1 Hz, 1H).; $^{13}$C-NMR (151 MHz, d$^{6}$-DMSO): δ [ppm] = 166.8, 150.6, 141.3, 130.1, 129.9, 128.5, 99.6. IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3474, 3377, 3086, 3074, 1692, 1242, 1215, 754, 728, 606; HRMS (ESI) m/z: [M-Na] calcd for $C_7H_4IO_5S$: 326.8830; Found: 326.8828.

**Synthesis of 4 using SPPS.** Boc-Glycine-Merrifield resin (100 mg, 200 µmol, 2 mmol/g, 1 eq.) and (*S*)-4-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-5-((3-(tert-butoxycarbonyl)-4-iodophenyl)amino)-5-oxopentanoic acid (**10**) (268 mg, 400 µmol, 2 eq.) were submitted to SPPS using the following sequence: (**A2**) → ((**A4**)+(**A5**))$_m$ →(**A6**)+(**A5**) → ((**A4**)+(**A5**))$_n$ → (**A8**) → (**A9**), which afforded the desired modified resin with a loading of 0.46 mmol/g for **4 (**m = 4; n = 0).

**Synthesis of 5a**, **5b and 5c using SPPS.** Polystyrene-Et-$NH_2$ resin (169 mg, 200 µmol, 1.18 mmol/g, 1 eq.) and (*S*)-4-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)-5-((3-(tert-butoxycarbonyl)-4-iodophenyl)amino)-5-oxopentanoic acid (**10**) (268 mg, 400 µmol, 2 eq.) were submitted to SPPS using the following sequence: (**A3**) → ((**A4**)+(**A5**))$_m$ →(**A6**)+(**A5**) → ((**A4**)+(**A5**))$_n$ → (**A8**) → (**A9**), which afforded the modified resin with a loading of 0.40 mmol/g for **5a** (m = 0; n = 0), 0.34 mmol/g for **5b** (m = 2; n = 0) and 0.30 mmol/g for **5c** (m = 4, n = 0) using method **B**.

**Synthesis of 6' using SPPS.** Polystyrene-Et-$NH_2$ resin (169 mg, 200 µmol, 1.18 mmol/g, 1 eq.) and sodium 5-carboxy-2-iodobenzenesulfonate (**12**) (210 mg, 600 µmol, 3 eq.) were submitted to SPPS using the following sequence: (**A3**) → ((**A4**)+(**A5**))$_n$ →(**A7**), which afforded the modified resin **6'** (n = 1).

**Synthesis of 6.** The modified resin (**6'**) (200 µmol, 1 eq.) was swollen in dry dichloromethane (3 mL) for 10 minutes. A magnetic stir bar, *n*$Bu_4NHSO_5$ (826 mg, 1.00 mol, 43%, 5 eq.) and methanesulfonic acid (65µL, 1.00 mmol, 5 eq.) were added and the mixture was stirred at room temperature for 5 hours. Subsequent removal of the solvent and excessive washing with dichloromethane gave the oxidized resin, which was submitted for loading determination using method **C** (loading: 0.50 mmol/g).

(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (**14a**). L-(-)-Borneol (**13a**) (39 mg, 0.25 mmol) gave (1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (**14b**)(30 mg, 0.20 mmol, 79%) using general procedure **D** and (34.5 mg, 0.23 mmol, 91%) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (PE:EA 90:10) as white solid. TLC: $R_f$ = 0.43 (PE:EA 90:10) [CAM, DNPH]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.34 (dt, *J* = 18.2, 3.9 Hz, 1H), 2.08 (t, *J* = 4.5 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.83 (d, *J* = 18.2 Hz, 1H), 1.70 – 1.64 (m, 1H), 1.40 (ddd, *J* = 13.2, 9.4, 4.5 Hz, 1H), 1.33 (ddd, *J* = 13.2, 9.4, 3.9 Hz, 1H), 0.95 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H); $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 219.7, 57.8, 46.9, 43.5, 43.2, 30.1, 27.2, 19.9, 19.3, 9.4. The analytical data are in agreement with previously reported ones.[3]

Nonan-5-one (**14b**). Nonan-5-ol (**13b**) (36 mg, 0.25 mmol) gave nonan-5-one (**14b**) (25 mg, 0.18 mmol, 70%) using general procedure **D** and (28 mg, 0.20 mmol, 79%) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (PE:EA 95:5) as colorless oil.

Large-Scale: Nonan-5-ol (**13b**)(7.21 g, 50.0 mmol, 1 eq.) was dissolved in acetonitrile (100 mL, 0.5M) in a 500-mL-RBF equipped with a mechanical stirrer. *n*$Bu_4NHSO_4$ (6.79 g, 20.0 mmol, 40 mol%) and catalyst resin **6** (892 mg, 500 µmol, 1 mol%) was added and the reaction was stirred for 5 hours at 70 °C. The suspension was filtered through a Buchner funnel, washed with acetonitrile and the filtrate was evaporated. Purification by flash column chromatography (CH:EA 95:5) gave the desired product (5.67 g, 39.9 mmol, 80%) as colorless oil. The filter cake was washed multiple times with water, methanol and dichloromethane to reisolate the used catalyst (848 mg).

TLC: $R_f$ = 0.5 (PE:EA 90:10)[DNPH]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.38 (t, *J* = 7.5 Hz, 4H), 1.54 (dt, *J* = 15.0, 7.6 Hz, 4H), 1.30 (dq, *J* = 14.7, 7.4 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 6H); $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 211.8, 42.7, 26.2, 22.5, 14.0. The analytical data are in agreement with previously reported ones.[4]

(+)-Fenchone (**14c**). (+)-Fenchol (**13c**) (39 mg, 0.25 mmol) gave (+)-fenchone (**14c**)(23 mg, 0.15 mmol, 63%) using general procedure **D** and (32 mg, 0.21 mmol, 85%) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (PE:EA 90:10) as colorless oil. TLC: $R_f$ = 0.37 (PE:EA 90:10) [CAM, DNPH]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.15 – 2.11 (m, 1H), 1.78 (tdd, *J* = 8.7, 7.4, 6.3, 3.6 Hz, 2H), 1.75 – 1.67 (m, 1H), 1.56 (dd, *J* = 12.7, 3.6 Hz, 1H), 1.52 (dd, *J* = 10.3, 1.8 Hz, 1H), 1.38 (tdd, *J* = 8.4, 7.2, 4.2 Hz,

1H), 1.14 (s, 3H), 1.03 (s, 6H); $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 223.5, 54.3, 47.5, 45.5, 41.8, 32.0, 25.1, 23.5, 21.9, 14.8. The analytical data are in agreement with previously reported ones.[5]

Menthone (**14d**). (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol (**13d**)(39 mg, 0.25 mmol) gave menthone (**14d**)(12 mg, 80 µmol, 32%) as diastereomeric mixture using general procedure **D** and (25 mg, 0.16 mmol, 65%) using general procedure **E** after 24 h reaction time, followed by flash column chromatography (PE:EA 95:5) as colorless oil. TLC: $R_f$ = 0.49 (PE:EA 90:10)[DNPH]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.38 – 2.25 (m, 1H), 2.16 – 1.65 (m, 6H), 1.51 – 1.22 (m, 2H), 1.03 – 0.97 (m, 3H), 0.94 – 0.89 (m, 3H), 0.86 – 0.81 (m, 3H).;$^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 214.6, 212.5, 57.3, 56.1, 51.0, 48.2, 35.6, 34.5, 34.1, 29.6, 28.0, 27.1, 27.0, 26.1, 22.4, 21.6, 21.3, 21.0, 20.0, 18.9. The analytical data are in agreement with previously reported ones.[6]

Cyclooctanone (**14e**). Cyclooctanol (**13e**)(32 mg, 0.25 mmol) gave cyclooctanone (**14e**) (23 mg, 0.18 mmol, 71%) using general procedure **D** and (26 mg, 0.21 mmol, 83%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as colorless oil. TLC: $R_f$ = 0.51 (PE:EA 70:30) [UV], $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.42 – 2.37 (m, 4H), 1.90 – 1.83 (m, 4H), 1.57 – 1.50 (m, 4H), 1.40 – 1.34 (m, 2H); $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 218.3, 42.1, 27.3, 25.8, 24.9. The analytical data are in agreement with previously reported ones.[7]

Adamantan-2-one (**14f**). Adamantan-2-ol (**13f**) (38 mg, 0.25 mmol) gave adamantan-2-one (**14f**) (12 mg, 0.08 mmol, 32%) in acetone (0.5 mL, 0.5M) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (CH:EA 90:10) as white solid. TLC: $R_f$ = 0.29 (CH:EA 90:10) [DNPH], $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.55 (br s, 2H), 2.11 – 1.90 (m, 12H).; $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 218.3, 47.0, 39.3, 36.3, 27.5. The analytical data are in agreement with previously reported ones.[6]

3,4-Dihydronaphthalen-1(2*H*)-one (**14g**). 1,2,3,4-Tetrahydronaphthalen-1-ol (**13g**) (37 mg, 0.25 mmol) yielded 3,4-dihydronaphthalen-1(2*H*)-one (**14g**)(30 mg, 0.21 mmol, 82%) using general procedure **D** and (31 mg, 0.21 mmol, 85%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as yellow oil. TLC: $R_f$ = 0.48 (PE:EA 70:30)[UV], $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.03 (dd, J = 7.8, 1.1 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.33 – 7.23 (m, 2H), 2.97 (t, J = 6.1 Hz, 2H), 2.70 – 2.59 (m, 2H), 2.21 – 2.07 (m, 2H);

$^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 198.4, 144.6, 133.5, 132.8, 128.9, 127.3, 126.8, 39.3, 29.9, 23.4. The analytical data are in agreement with previously reported ones.[8]

2-Bromo-2,3-dihydro-1*H*-inden-1-one (**14h**). *trans*-2-Bromo-2,3-dihydro-1*H*-inden-1-ol (**13h**) (53 mg, 0.25 mmol) gave 2-bromo-2,3-dihydro-1*H*-inden-1-one (**14h**)(44 mg, 0.21 mmol, 84%) using general procedure **D** and (44 mg, 0.21 mmol, 84%) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (PE:EA 80:20) as yellow oil. TLC: $R_f$ = 0.38 (PE:EA 70:30) [UV], $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.84 (d, J = 7.7 Hz, 1H), 7.66 (td, J = 7.7, 1.2 Hz, 1H), 7.49 – 7.39 (m, 2H), 4.65 (dd, J = 7.5, 3.2 Hz, 1H), 3.83 (dd, J = 18.1, 7.5 Hz, 1H), 3.42 (dd, J = 18.1, 3.2 Hz, 1H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 199.6, 151.2, 136.1, 133.7, 128.4, 126.6, 125.2, 44.2, 38.1. The analytical data are in agreement with previously reported ones.[9]

Benzophenone (**14i**). Diphenylmethanol (**13i**) (46 mg, 0.25 mmol) gave benzophenone (**14i**) (44.6 mg, 244 µmol, 98%) using general procedure **E** for 3 h after flash chromatography (CH:EA 95:5) as white solid. TLC: $R_f$ = 0.45 (CH:EA 90:10) [UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.83 – 7.76 (m, 4H), 7.59 (tt, J = 7.1, 1.3 Hz, 2H), 7.51 – 7.45 (m, 4H). $^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 196.8, 137.7, 132.5, 130.1, 128.4. The analytical data are in agreement with previously reported ones.[10]

4-(4-Methoxyphenyl)butan-2-one (**14ja**). 4-(4-Methoxyphenyl)butan-2-ol (**13ja**) (45 mg, 0.25 mmol) gave 4-(4-Methoxyphenyl)butan-2-one (**14ja**)(33 mg, 0.19 mmol, 75%) using general procedure **D** and (38 mg, 0.22 mmol, 86%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as colorless oil. TLC: $R_f$ = 0.38 (PE:EA 75:25) [UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.11 – 7.08 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.13 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 208.2, 158.1, 133.1, 129.3, 114.0, 55.4, 45.6, 30.2, 29.0. The analytical data are in agreement with previously reported ones.[11]

4-(4-(Benzyloxy)phenyl)butan-2-one (**14jb**). 4-(4-(benzyloxy)phenyl)-butan-2-ol (**13jb**) (64 mg, 0.25 mmol) gave 4-(4-(benzyloxy)phenyl)butan-2-one (**14jb**) (37 mg, 0.19 mmol, 58%) using general procedure **D** and (50 mg, 0.20 mmol, 79%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as yellowish solid. TLC: $R_f$ = 0.38 (PE:EA 70:30)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.45 – 7.29 (m, 5H), 7.13 – 7.07 (m, 2H), 6.92 – 6.87 (m, 2H), 5.04 (s, 2H), 2.87 – 2.82 (m, 2H), 2.76 – 2.69 (m, 2H), 2.13 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 208.2, 157.4, 137.3, 133.5, 129.4, 128.7, 128.0, 127.6,

115.1, 70.2, 45.6, 30.2, 29.1. The analytical data are in agreement with previously reported ones.[12]

4-(3-Oxobutyl)phenyl benzoate (**14jc**). 4-(3-hydroxybutyl)phenyl benzoate (**13jc**) (68 mg, 0.25 mmol) gave 4-(3-oxobutyl)phenyl benzoate (**14jc**)(46 mg, 0.16 mmol, 69%) using general procedure **D** and (57 mg, 0.21 mmol, 85%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as white solid. TLC: $R_f$ = 0.49 (PE:EA 70:30)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.23 – 8.17 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.26 – 7.22 (m, 2H), 7.15 – 7.11 (m, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.15 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 207.7, 165.4, 149.4, 138.8, 133.7, 130.3, 129.7, 129.5, 128.7, 121.8, 45.2, 30.2, 29.2. The analytical data are in agreement with previously reported ones.[13]

Benzyl (4-(3-oxobutyl)phenyl) carbonate (**14jd**). Benzyl (4-(3-hydroxybutyl)phenyl) carbonate (**13jd**) (75 mg, 0.25 mmol) gave benzyl (4-(3-oxobutyl)phenyl) carbonate (**14jd**)(61 mg, 0.21 mmol, 82%) using general procedure **D** and (64 mg, 0.22 mmol, 86%) using general procedure **E** after flash column chromatography (PE:EA 85:15) as white solid. TLC: $R_f$ = 0.50 (PE:EA 70:30)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.46 – 7.36 (m, 5H), 7.21 – 7.16 (m, 2H), 7.11 – 7.06 (m, 2H), 5.26 (s, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 207.7, 153.9, 149.6, 139.0, 135.0, 129.5, 128.9, 128.8, 128.7, 121.1, 70.5, 45.2, 30.2, 29.2. IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3040, 2993, 2950, 2931, 2894, 1746, 1704, 1509, 1253, 1016, 921, 700; HRMS (FD) m/z: $[M]^+$ calcd for $C_{18}H_{18}O_4$: 298.1205; Found: 298,1193.

4-(3-Oxobutyl)phenyl trifluoromethanesulfonate (**14je**). 4-(3-hydroxybutyl)phenyl trifluoromethanesulfonate (**13je**) (75 mg, 0.25 mmol) gave 4-(3-oxobutyl)phenyl trifluoromethanesulfonate (**14je**)(48 mg, 0.16 mmol, 63%) using general procedure **D** and (61 mg, 0.21 mmol, 82%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as yellow oil. TLC: $R_f$ = 0.21 (PE:EA 90:10)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.27 – 7.24 (m, 2H), 7.19 – 7.15 (m, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 207.1, 148.1, 141.9, 130.3 121.4, 118.9 (q, J = 320.9 Hz), 44.8, 30.2, 29.0; $^{19}$F-NMR (376 MHz, $CDCl_3$) δ = -72.9; IR (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3007, 2930, 1716, 1501, 1417, 1204, 1132, 882, 605; HRMS (FD) m/z: $[M]^+$ calcd for $C_{11}H_{11}O_4F_2S$: 296.0330; Found: 296.0330.

2,2-Dimethyl-1-phenylpropan-1-one (**14k**). 2,2-Dimethyl-1-phenylpropan-1-ol (**13k**) (41 mg, 0.25 mmol) gave 2,2-dimethyl-1-phenylpropan-1-one (**14k**)(31 mg, 0.19 mmol, 76%) using general procedure **D** and (40 mg, 0.24 mmol, 98%) using general procedure **E** after flash column chromatography (PE:EA 90:10) as yellow oil. TLC: $R_f$ = 0.50 (PE:EA 90:10) [UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.70 – 7.66 (m, 2H), 7.48 – 7.37 (m, 3H), 1.35 (s, 9H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 209.4, 138.8, 130.9, 128.2, 127.9, 44.3, 28.2. The analytical data are in agreement with previously reported ones.[6]

3-Chloro-1-phenylpropan-1-one (**14l**). 3-Chloro-1-phenylpropan-1-ol (**13l**) (43 mg, 0.25 mmol) gave 3-chloro-1-phenylpropan-1-one (**14l**) (35 mg, 0.21 mmol, 82%) using general procedure **D** and (36 mg, 0.21 mmol, 84%) using general procedure **E** after flash column chromatography (PE:EA 80:20) as yellow solid. TLC: $R_f$ = 0.35 (PE:EA 70:30) [UV], $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.98 – 7.92 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.45 (m, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 196.8, 136.5, 133.7, 128.9, 128.2, 41.4, 38.8. The analytical data are in agreement with previously reported ones.[14]

Benzil (**14m**). Benzoin (53 mg, 0.25 mmol) gave benzil (**14m**)(38 mg, 0.18 mmol, 71%) using general procedure **D** and (47 mg, 0.22 mmol, 90%) using general procedure **E** after flash column chromatography (PE:EA 90:10) as yellow solid. Using 1,2-diphenylethane-1,2-diol (**13m**) (54 mg, 0.25 mmol) and oxone (245 mg, 0.80 mmol, 3.2 eq.), benzil (51 mg, 0.24 mmol, 97%) was obtained using general procedure **E** after flash column chromatography (PE:EA 90:10). TLC: $R_f$ = 0.30 (PE:EA 90:10) [UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.01 – 7.95 (m, 4H), 7.69 – 7.62 (m, 2H), 7.55 – 7.48 (m, 4H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 194.7, 135.0, 133.2, 130.0, 129.1. The analytical data are in agreement with previously reported ones.[15]

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (**14n**). 4,4'-Dimethoxybenzoin (**13n**) (68 mg, 0.25 mmol) gave 1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (**14n**) (60 mg, 0.22 mmol, 89%) using general procedure **E** after flash column chromatography (CH:EA 80:20) as yellow solid. TLC: $R_f$ = 0.16 (CH:EA 90:10)[UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.97 – 7.89 (m, 4H), 6.97 – 6.93 (m, 4H), 3.86 (s, 6H).;$^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 193.6, 165.0, 132.4, 126.4, 114.4, 55.7. The analytical data are in agreement with previously reported ones.[16]

Methyl 2-oxo-2-phenylacetate (**14o**). Methyl 2-hydroxy-2-phenylacetate (**13o**) (41 mg, 0.25 mmol) gave methyl 2-oxo-2-phenylacetate (**14o**)(27 mg, 0.16 mmol, 66%) using general

procedure **E** after 3 h reaction time, followed by flash column chromatography (CH:EA 90:10) as slightly yellow oil. TLC: $R_f$ = 0.50 (CH:EA 70:30)[UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 8.04 – 7.98 (m, 2H), 7.69 – 7.63 (m, 1H), 7.55 – 7.47 (m, 2H), 3.97 (s, 3H).;$^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 186.2, 164.2, 135.1, 132.6, 130.2, 129.0, 52.9. The analytical data are in agreement with previously reported ones.[17]

4,4-Dimethyldihydrofuran-2,3-dione (**14p**). 3-Hydroxy-4,4-dimethyldihydrofuran-2(3*H*)-one (**13o**) (33 mg, 0.25 mmol) gave 4,4-dimethyldihydrofuran-2,3-dione (**14p**)(21 mg, 0.16 mmol, 66%) using general procedure **E** after 3 h reaction time, followed by flash column chromatography (CH:EA 50:50) as white solid. TLC: $R_f$ = 0.25 (CH:EA 50:50)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.44 (s, 2H), 1.31 (s, 6H).;$^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 198.1, 160.5, 42.0, 22.3. The analytical data are in agreement with previously reported ones.[18]

Cyclohexyl(phenyl)methanone (**14q**). Cyclohexyl(phenyl)methanol (**13q**) (47 mg, 0.25 mmol) gave cyclohexyl(phenyl)methanone (**14q**)(44.5 mg, 236 µmol, 95%) using general procedure **D** and (45.2 mg, 240 µmol, 96%) using general procedure **E** after flash column chromatography (PE:EA 90:10) as off-white solid. TLC: $R_f$ = 0.60 (PE:EA 75:25) [UV], $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.98 – 7.91 (m, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 3.26 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.94 – 1.80 (m, 4H), 1.78 – 1.69 (m, 1H), 1.60 – 1.23 (m, 5H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 203.9, 136.5, 132.8, 128.7, 128.3, 45.8, 29.5, 26.1, 26.0. The analytical data are in agreement with previously reported ones.[19]

(+)-Estrone methyl ether (**14r**). 3-Methoxyestradiol (**13r**) (72 mg, 0.25 mmol) gave (+)-estrone methyl ether (**14r**)(43 mg, 0.15 mmol, 61%) using general procedure **E** after flash column chromatography (CH:EA 60:40) as white solid. TLC: $R_f$ = 0.40 (CH:EA 70:30)[UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.21 (d, J = 8.6 Hz, 1H), 6.73 (dd, J = 8.6, 2.7 Hz, 1H), 6.65 (d, J = 2.5 Hz, 1H), 3.78 (s, 3H), 2.95 – 2.86 (m, 2H), 2.54 – 2.47 (m, 1H), 2.43 – 2.37 (m, 1H), 2.29 – 2.22 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 1.99 (m, 2H), 1.98 – 1.93 (m, 1H), 1.67 – 1.40 (m, 6H), 0.91 (s, 3H). $^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 220.9, 157.7, 137.8, 132.2, 126.4, 114.0, 111.7, 55.3, 50.6, 48.1, 44.1, 38.5, 36.0, 31.7, 29.8, 26.7, 26.1, 21.7, 14.0. The analytical data are in agreement with previously reported ones.[20]

5β -Cholestan-3-one (**14s**). 5β -Cholestan-3α-ol (**13s**)(97 mg, 0.25 mmol) gave 5β -Cholestan-3-one (**14s**)(75 mg, 0.19 mmol, 78%) using general procedure **E** in toluene (0.5 mL) after flash column chromatography (CH:EA 95:5). TLC: $R_f$ = 0.20 (CH:EA 95:5)[UV]; $^1$H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.43 – 2.20 (m, 3H), 2.11 – 1.94 (m, 3H), 1.88 – 1.76 (m, 1H), 1.74

– 1.65 (m, 1H), 1.61 – 0.92 (m, 28H), 0.86 (d, J = 1.7 Hz, 3H), 0.85 (d, J = 1.7 Hz, 3H), 0.76 – 0.68 (m, 1H), 0.67 (s, 3H);$^{13}$C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 212.2, 56.4, 54.0, 46.9, 44.9, 42.7, 40.1, 39.7, 38.7, 38.3, 36.3, 35.9, 35.8, 35.6, 31.9, 29.1, 28.4, 28.1, 24.4, 24.0, 22.9, 22.7, 21.6, 18.8, 12.2, 11.6. The analytical data are in agreement with previously reported ones.[21]

Cyclohexanone (**14t**). Cyclohexanol (**13t**) (25 mg, 0.25 mmol) gave Cyclohexanone (**14t**)(18 mg, 0.19 mmol, 75%)(determined as GC-FID yield, calibrated with stock solutions of **13t**/**14t**) using general procedure **E**, which was not isolated.

Cinnamaldehyde (**16a**). (E)-3-phenylprop-2-en-1-ol (**15a**) (33.5 mg, 250 µmol) gave cinnamaldehyde (**16a**) (12.0 mg, 90.8 µmol, 36%) using general procedure **F** after flash column chromatography (CH:EA 95:5) as yellow oil. TLC: $R_f$ = 0.45 (CH:EA 80:20)[UV]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 9.72 (d, J = 7.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.48 (d, J = 15.9 Hz, 1H), 7.44 (dd, J = 5.1, 2.0 Hz, 3H), 6.73 (dd, J = 15.9, 7.7 Hz, 1H).;$^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 193.8, 152.8, 134.2, 131.4, 129.3, 128.8, 128.6. The analytical data are in agreement with previously reported ones.[22]

(1*R*)-(-)-Myrtenal (**16b**). (1*R*)-(-)-Myrtenol (**15b**) (38.1 mg, 250 µmol) gave (1*R*)-(-)-Myrtenal (**16b**) (12.6 mg, 83.9 µmol, 33%) using general procedure **F** after flash column chromatography (CH:EA 90:10) as colorless oil. TLC: $R_f$ = 0.50 (CH:EA 80:20)[$KMnO_4$]; $^1$H-NMR (600 MHz, $CDCl_3$): δ [ppm] = 9.44 (s, 1H), 6.72 – 6.67 (m, 1H), 2.87 (td, J = 5.7, 1.5 Hz, 1H), 2.63 – 2.47 (m, 3H), 2.22 – 2.16 (m, 1H), 1.34 (s, 3H), 1.05 (d, J = 9.2 Hz, 1H), 0.74 (s, 3H).;$^{13}$C-NMR (151 MHz, $CDCl_3$): δ [ppm] = 191.4, 151.7, 147.8, 40.9, 38.3, 37.7, 33.2, 31.3, 25.8, 21.1. The analytical data are in agreement with previously reported ones.[23]

# 4. References


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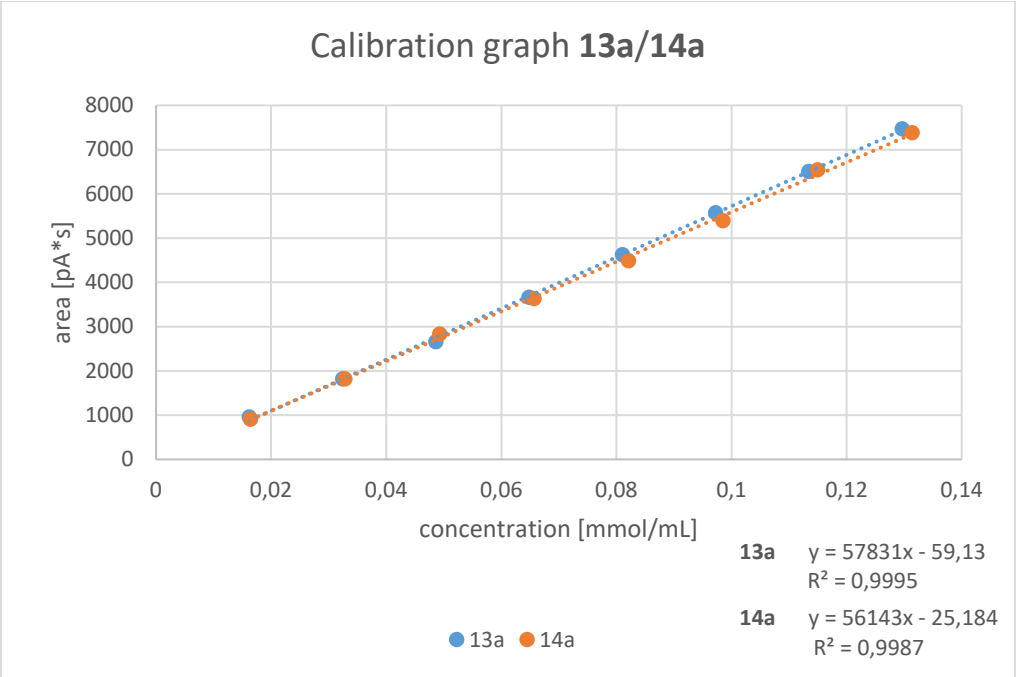
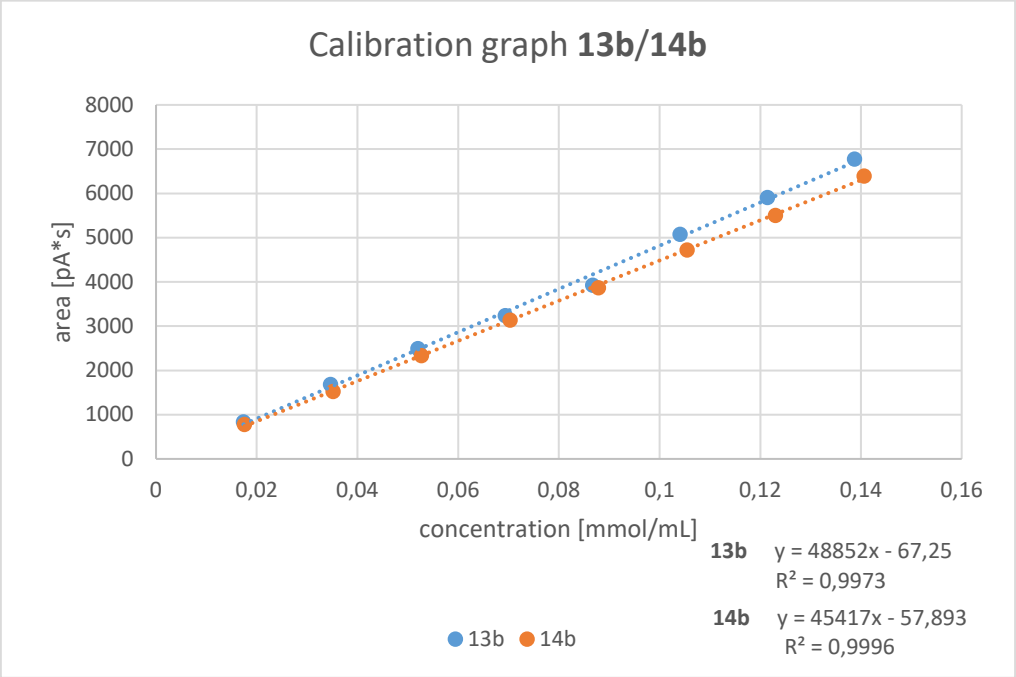
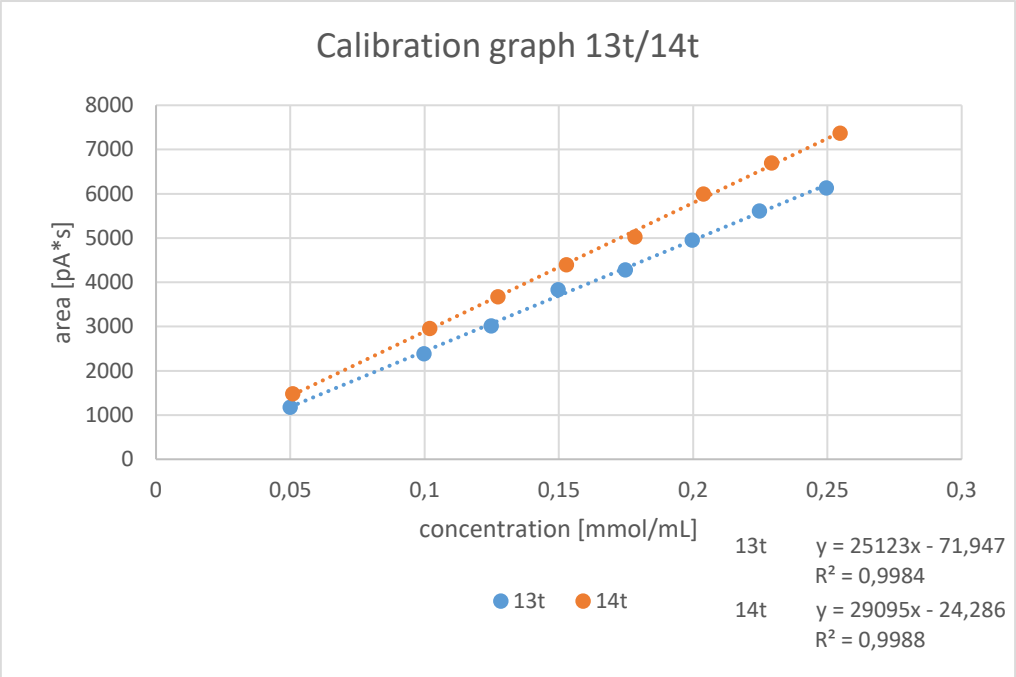
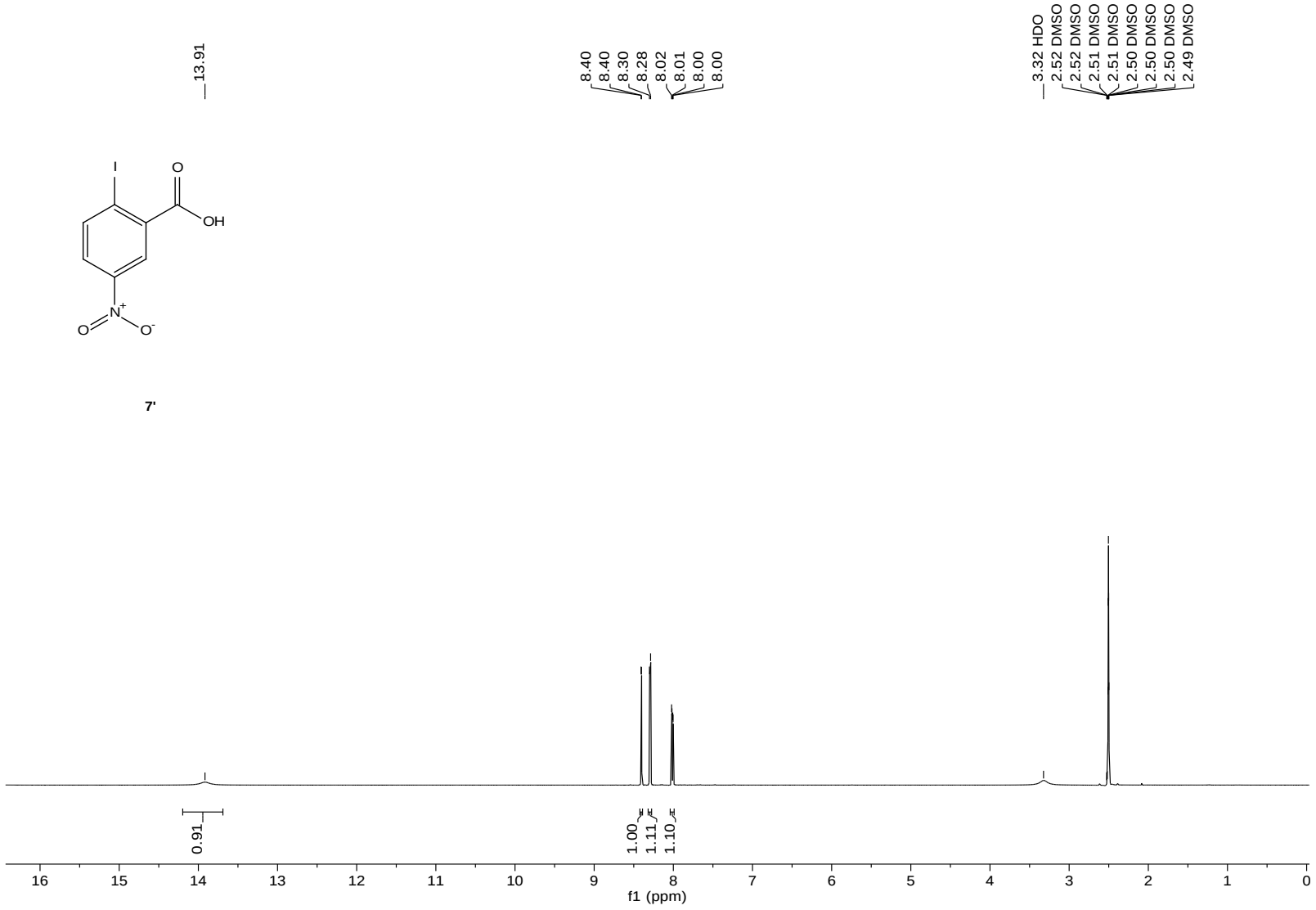
# 5. Calibration graphs



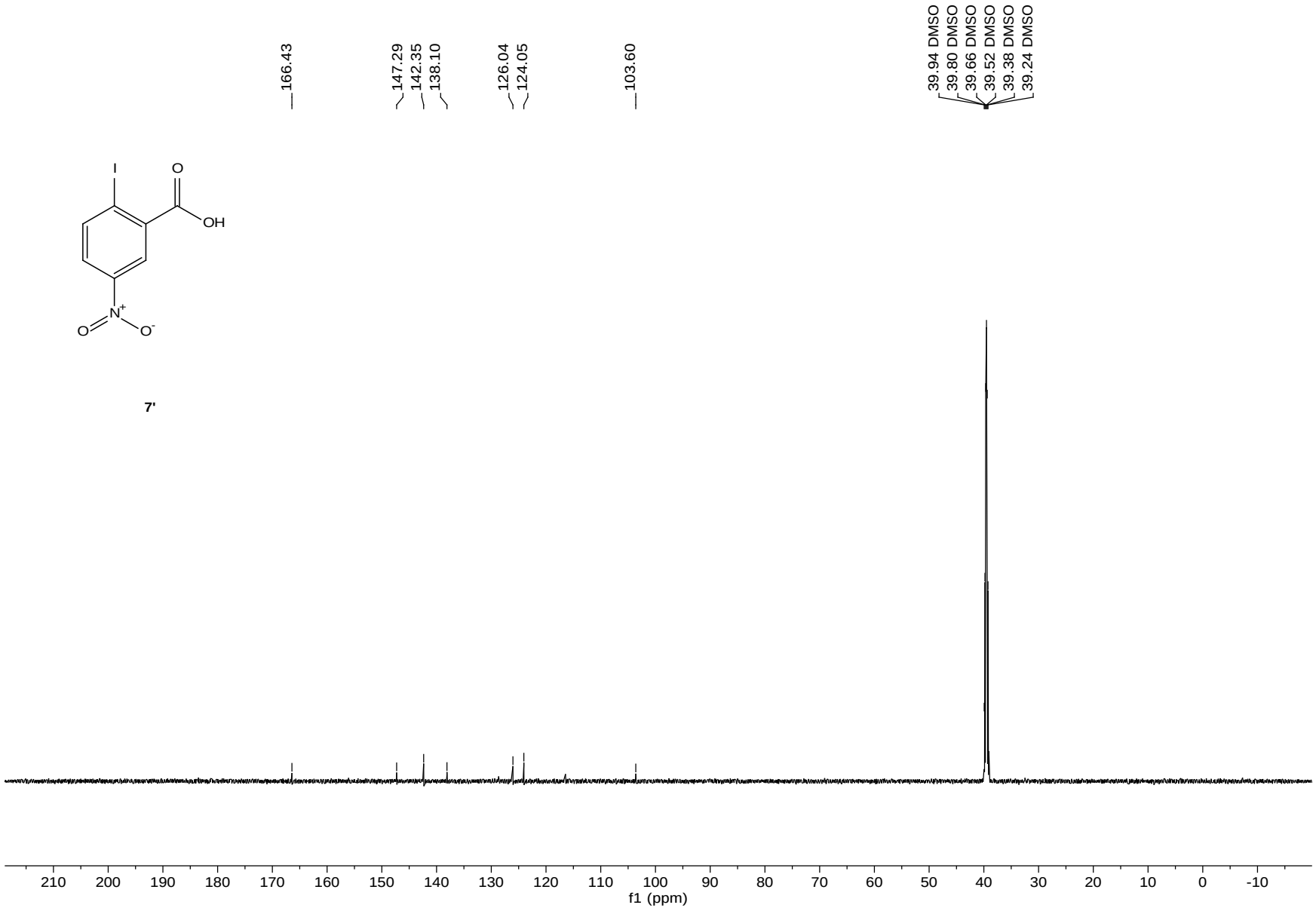



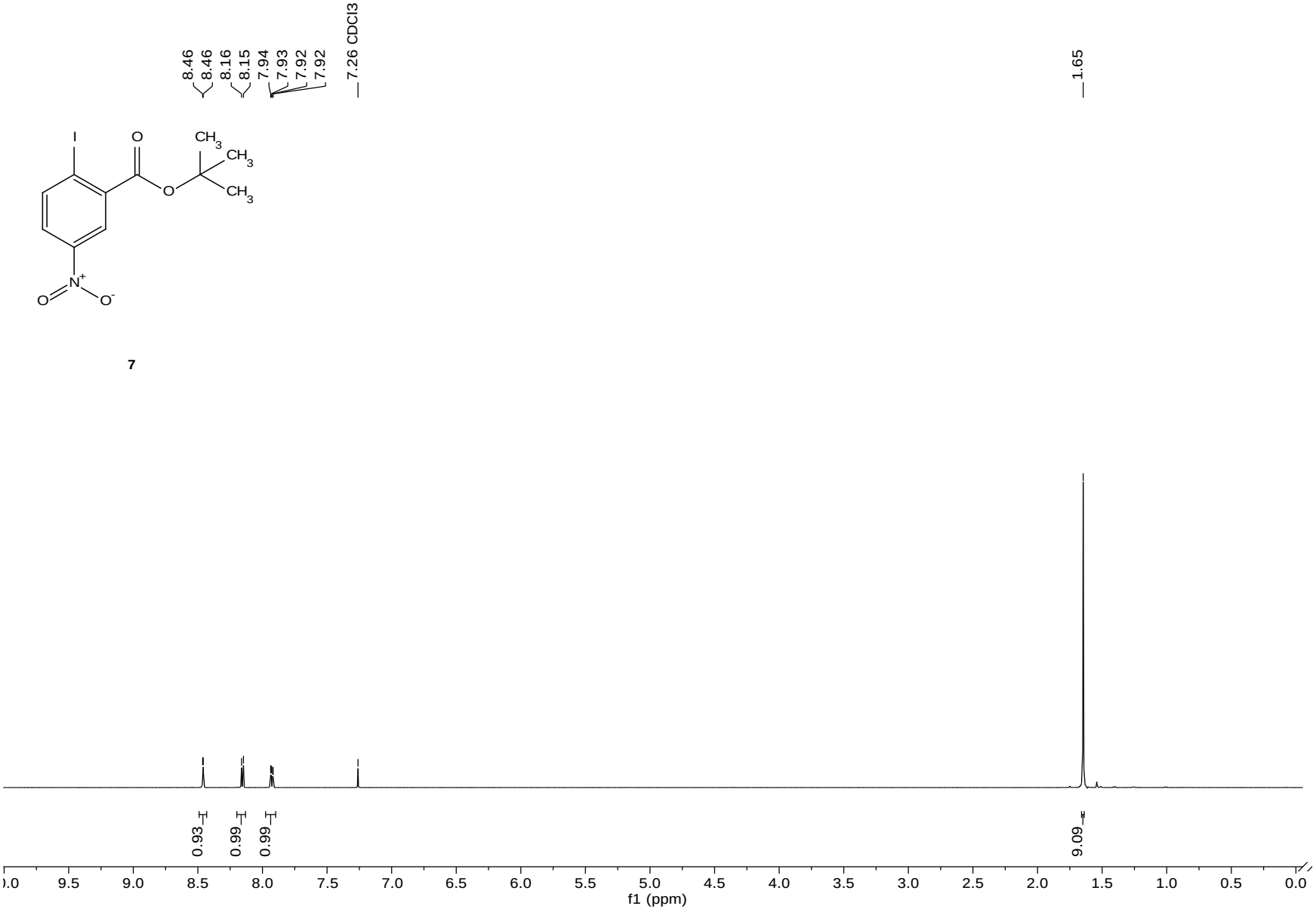

Calibration graph 13t/14t
8000
7000
6000
5000
4000
3000
2000
1000
0
area [pA*s]
0
0,05
0,1
0,15
0,2
0,25
0,3
concentration [mmol/mL]
13t
14t
13t y = 25123x - 71,947
R² = 0,9984
14t y = 29095x - 24,286
R² = 0,9988

# 6. Spectra

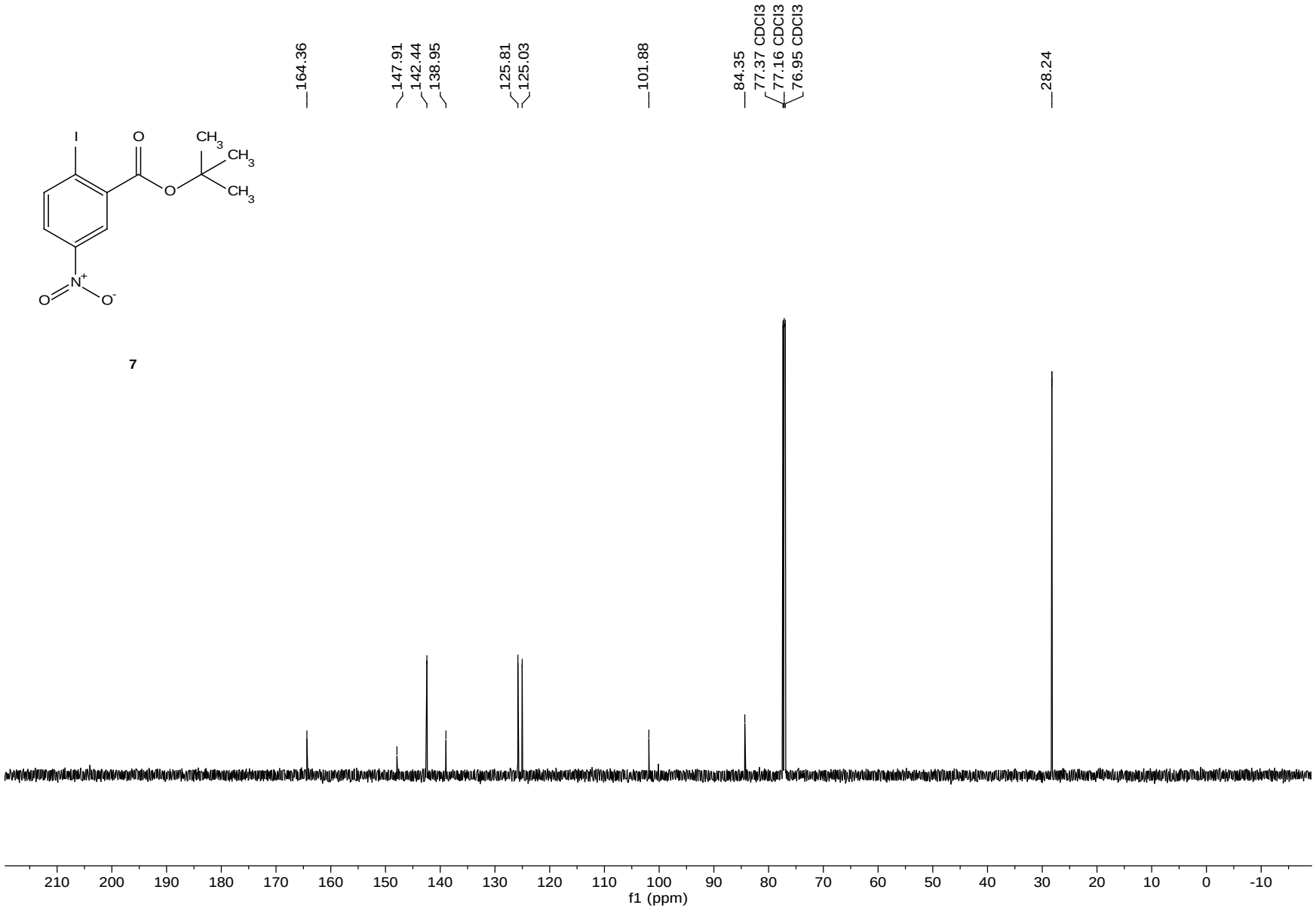

13.91
8.40
8.40
8.30
8.28
8.02
8.01
8.00
8.00
3.32 HDO
2.52 DMSO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
I
O
OH
N+
O
O-
0.91
1.00
1.11
1.10
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

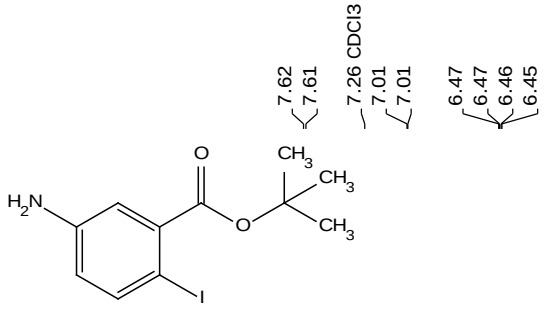
7'


166.43
147.29
142.35
138.10
126.04
124.05
103.60
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
I
O
OH
N+
O
O-
7'
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)


8.46
8.46
8.16
8.15
7.94
7.93
7.92
7.92
7.26 CDCl3
1.65
I
O
CH3
CH3
CH3
O
N+
O
O-
0.93
0.99
0.99
9.09
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
f1 (ppm)

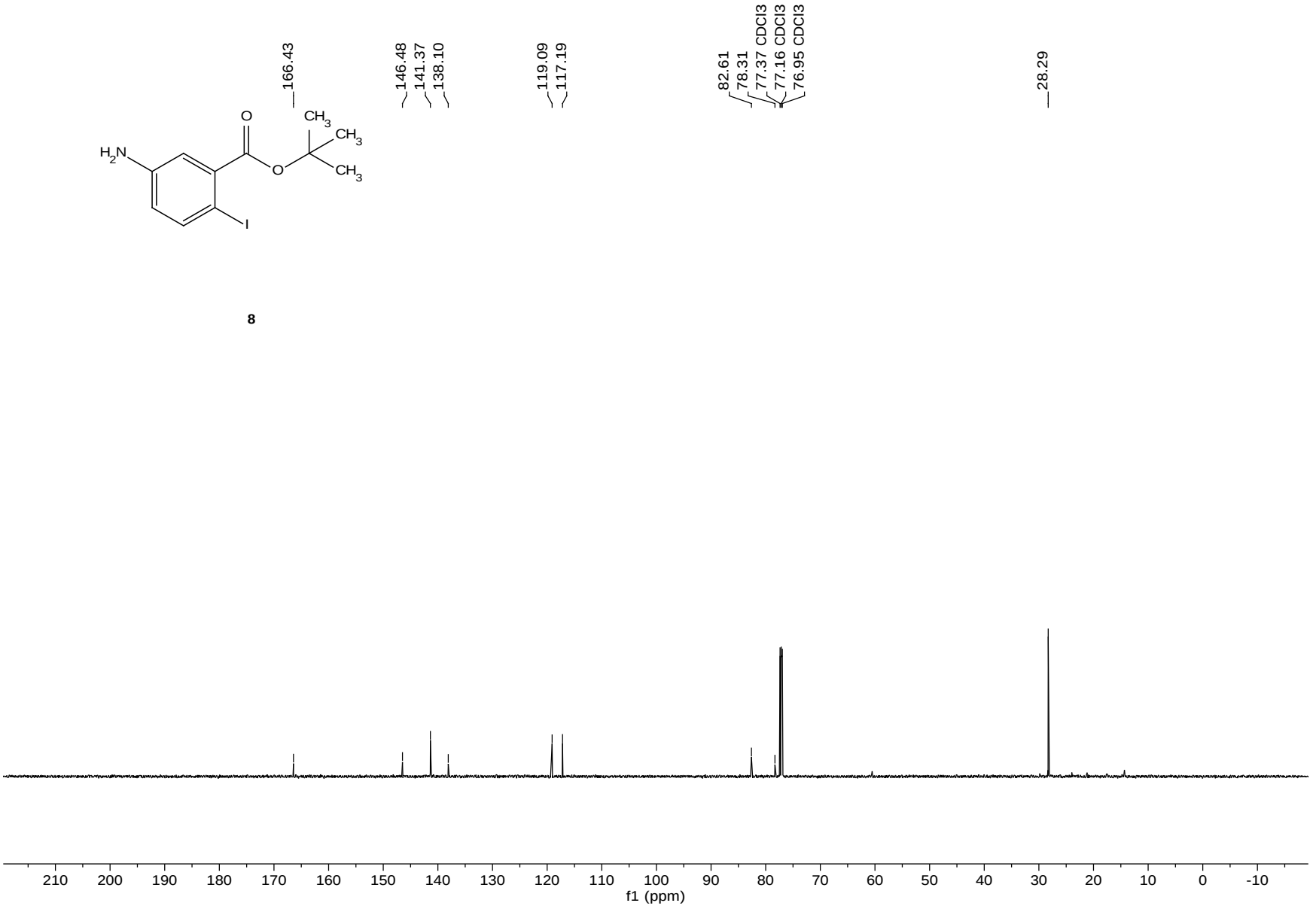
**7**


164.36
147.91
142.44
138.95
125.81
125.03
101.88
84.35
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
28.24
I
O
CH3
CH3
CH3
O
N+
O
O-
7
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)


O
CH3
CH3
CH3
H2N
O
I

**8**

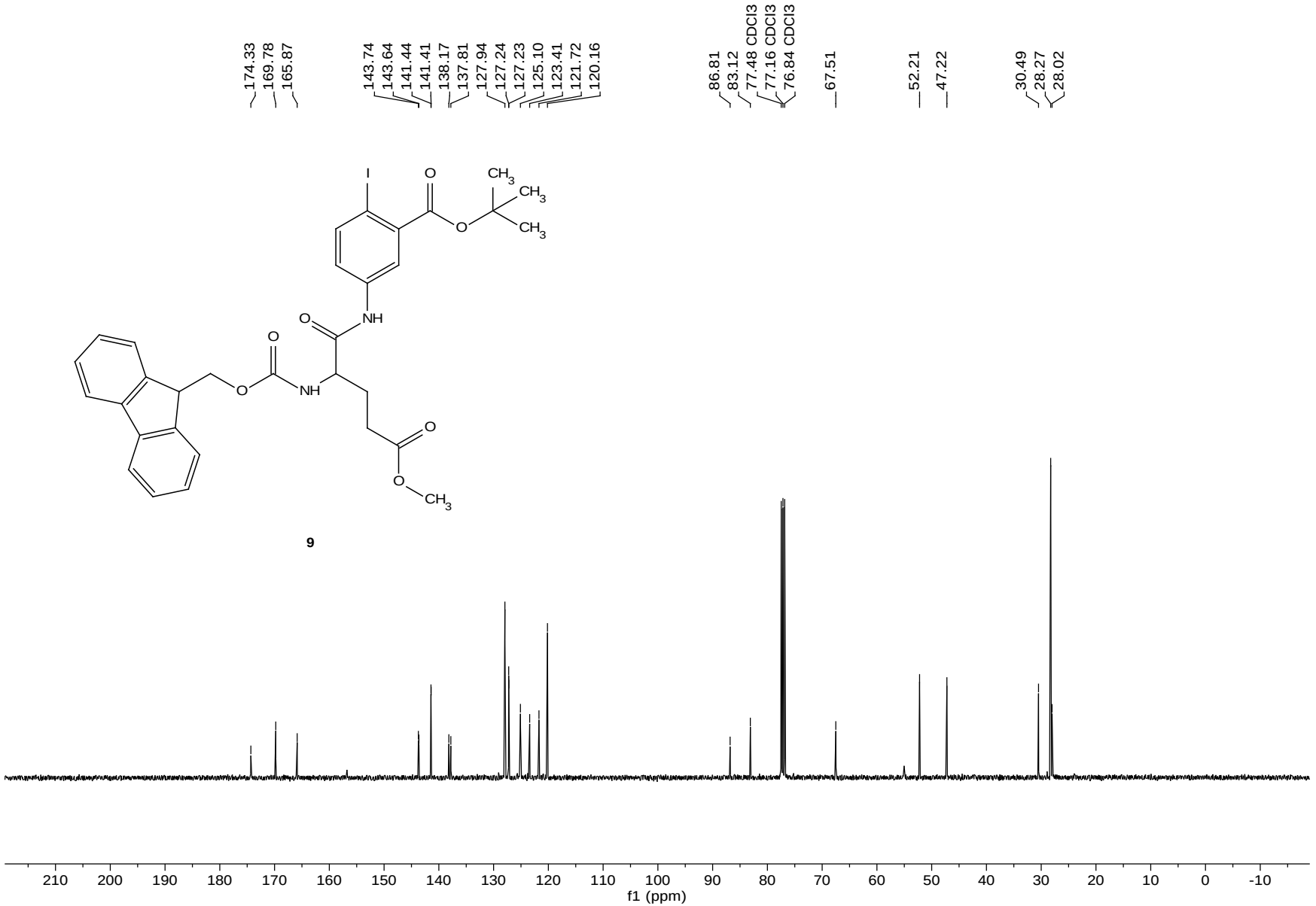

7.62
7.61
7.26 CDCl3
7.01
7.01
6.47
6.47
6.46
6.45
1.60
1.00
1.01
1.02
9.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.43
146.48
141.37
138.10
119.09
117.19
82.61
78.31
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
28.29
O
CH3
CH3
CH3
H2N
O
I
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)

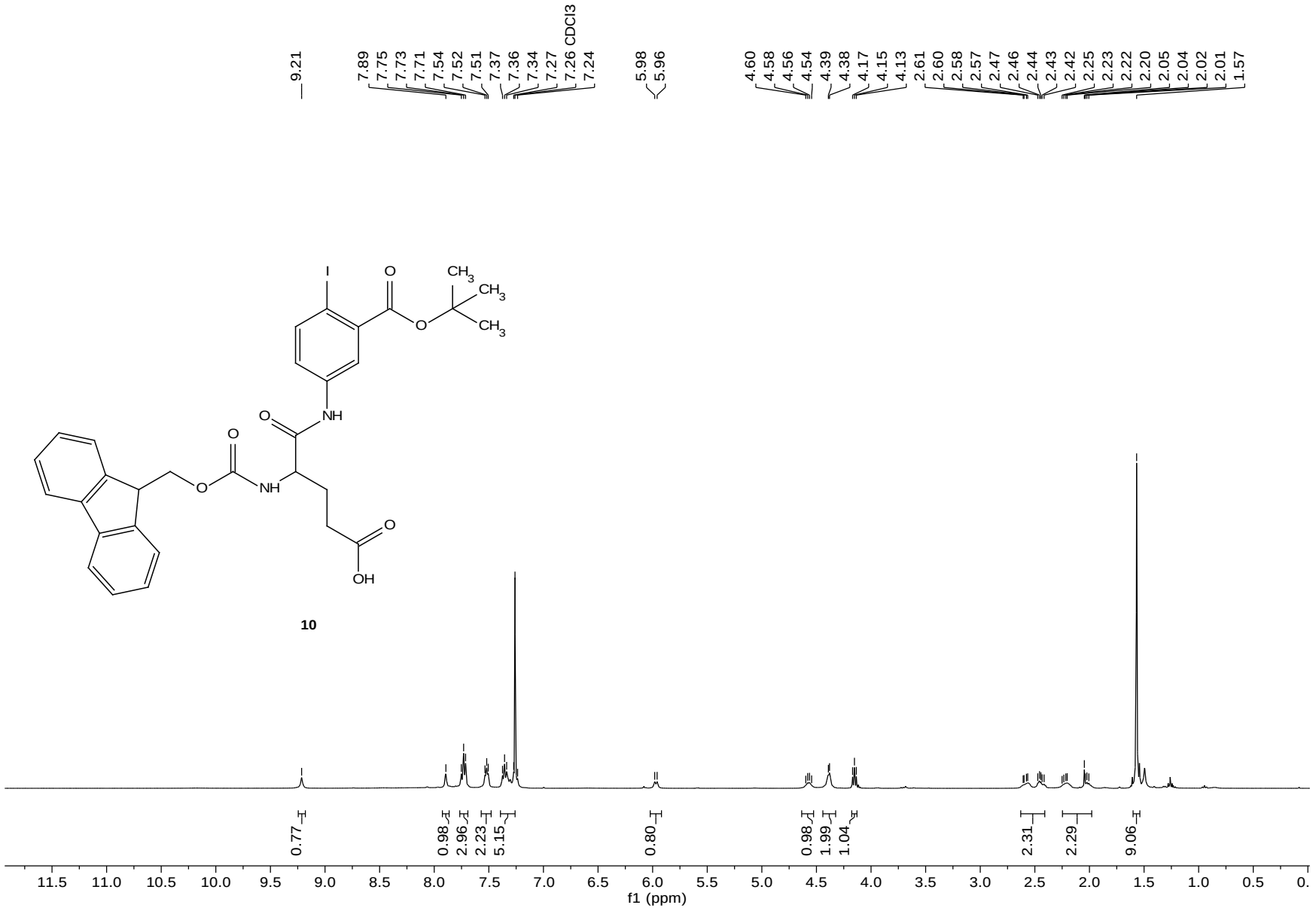
**8**


8.73
7.83
7.82
7.81
7.80
7.75
7.73
7.57
7.55
7.54
7.42
7.41
7.39
7.39
7.38
7.36
7.29
7.27
7.26 CDCl3
5.87
5.85
4.43
4.41
4.38
4.21
4.19
4.17
3.68
2.63
2.61
2.59
2.48
2.47
2.45
2.42
2.22
2.21
2.05
2.03
2.02
2.00
1.61
I
O
CH3
CH3
CH3
O
O
NH
O
O
NH
O
O
O
CH3
0.82
1.78
2.06
2.05
2.97
2.25
0.95
2.06
0.88
1.09
3.08
2.15
2.21
9.00
f1 (ppm)

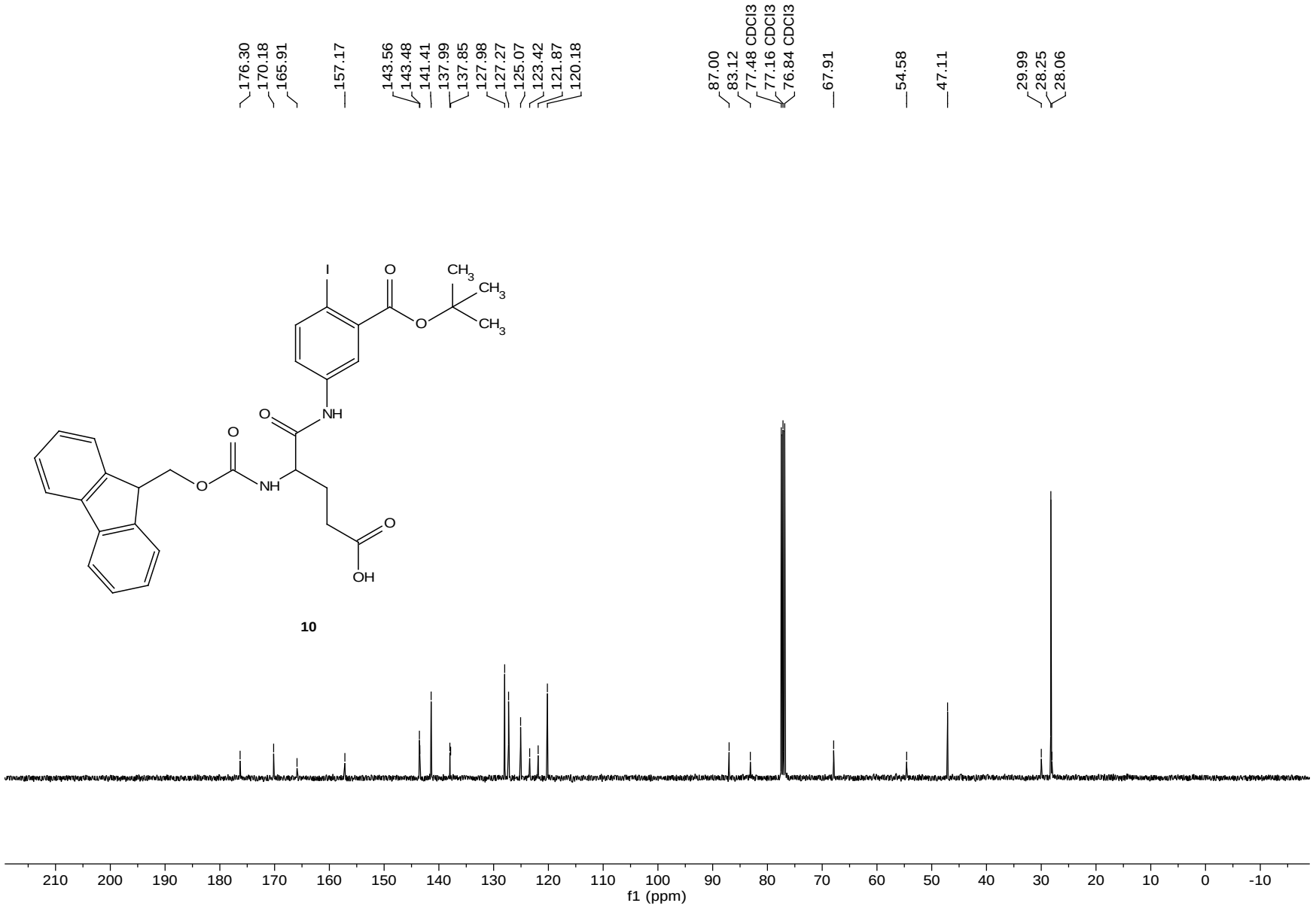
**9**

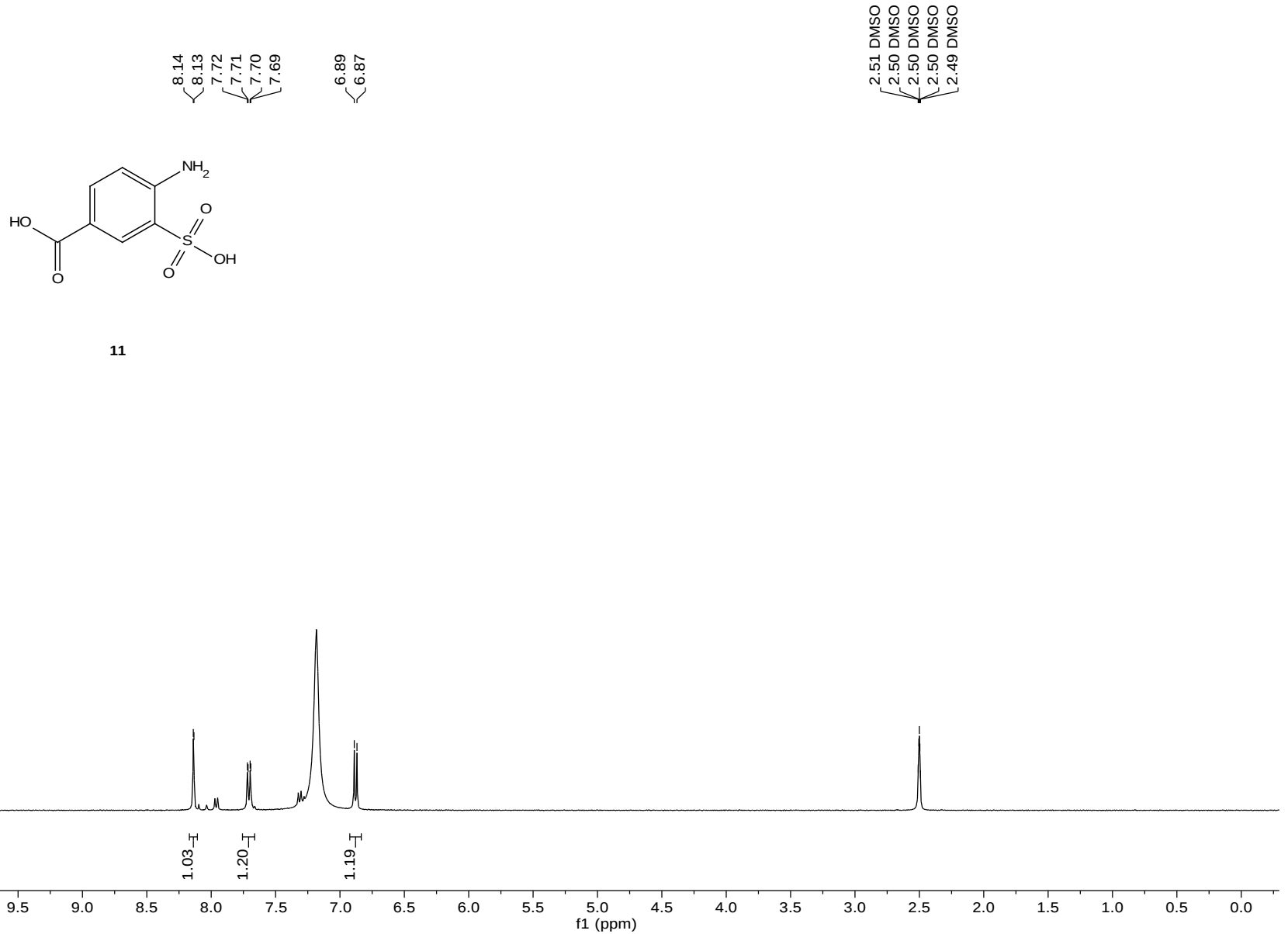

174.33
169.78
165.87
143.74
143.64
141.44
141.41
138.17
137.81
127.94
127.24
127.23
125.10
123.41
121.72
120.16
86.81
83.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.51
52.21
47.22
30.49
28.27
28.02
I
O
CH3
CH3
CH3
O
NH
O
O
NH
O
O
O
CH3
f1 (ppm)

**9**

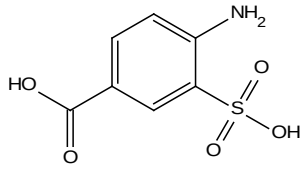

9.21
7.89
7.75
7.73
7.71
7.54
7.52
7.51
7.37
7.36
7.34
7.27
CDCl3
7.24
5.98
5.96
4.60
4.58
4.56
4.54
4.39
4.38
4.17
4.15
4.13
2.61
2.60
2.58
2.57
2.47
2.46
2.44
2.43
2.42
2.25
2.23
2.22
2.20
2.05
2.04
2.02
2.01
1.57
I
O
CH3
CH3
CH3
O
O
NH
O
O
NH
O
OH
0.77
0.98
2.96
2.23
5.15
0.80
0.98
1.99
1.04
2.31
2.29
9.06
11.5
11.0
10.5
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.
f1 (ppm)

**10**


176.30
170.18
165.91
157.17
143.56
143.48
141.41
137.99
137.85
127.98
127.27
125.07
123.42
121.87
120.18
87.00
83.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.91
54.58
47.11
29.99
28.25
28.06
I
O
CH3
CH3
CH3
O
O
NH
O
O
NH
O
OH
10
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)

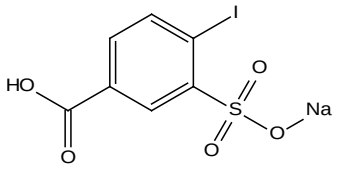

8.14
8.13
7.72
7.71
7.70
7.69
6.89
6.87
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
NH2
HO
O
S
O
O
OH
1.03
1.20
1.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**11**


NH2
HO
O
S
O
O
OH

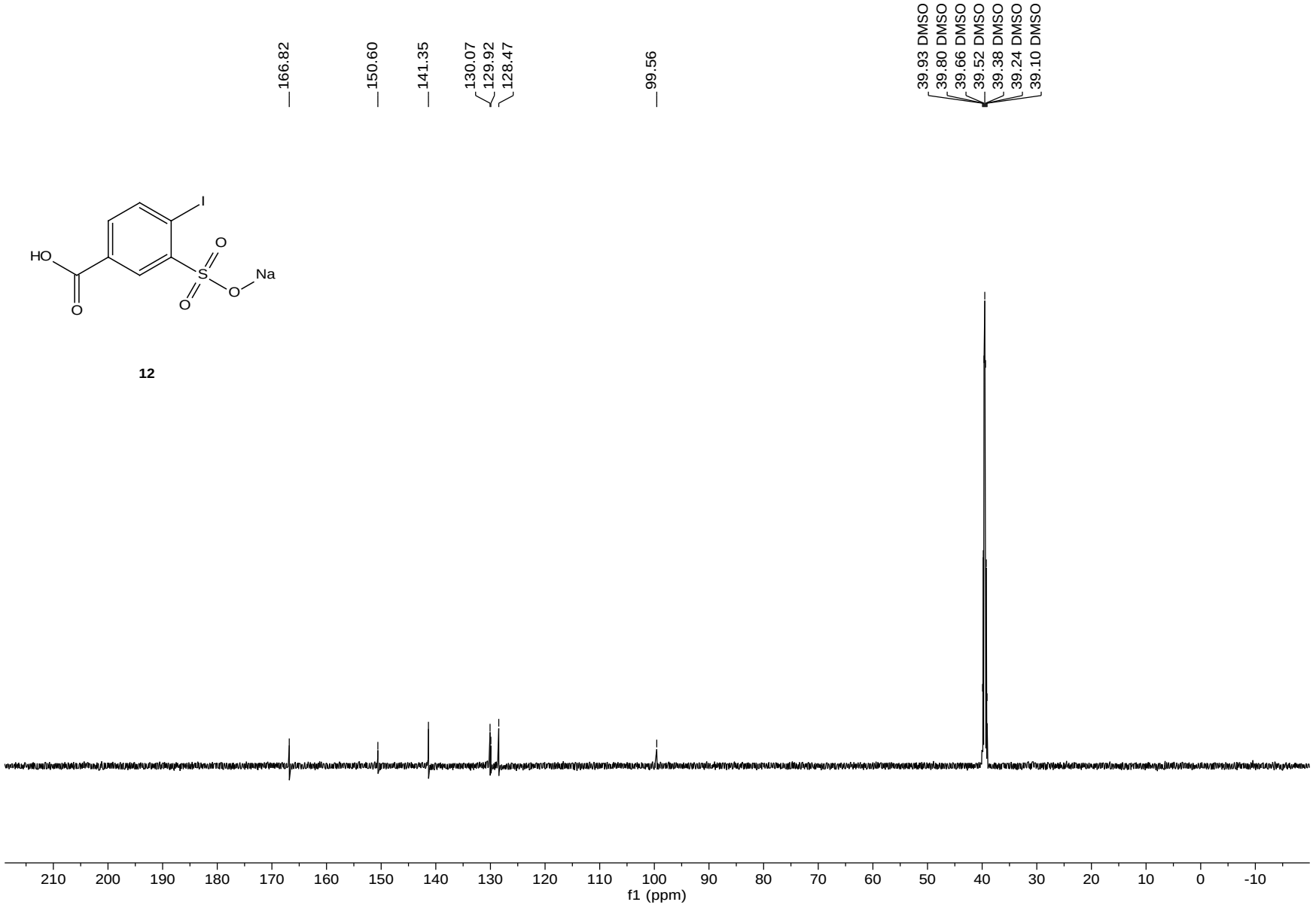
**11**


167.10
144.23
132.32
131.59
129.60
120.42
117.79
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

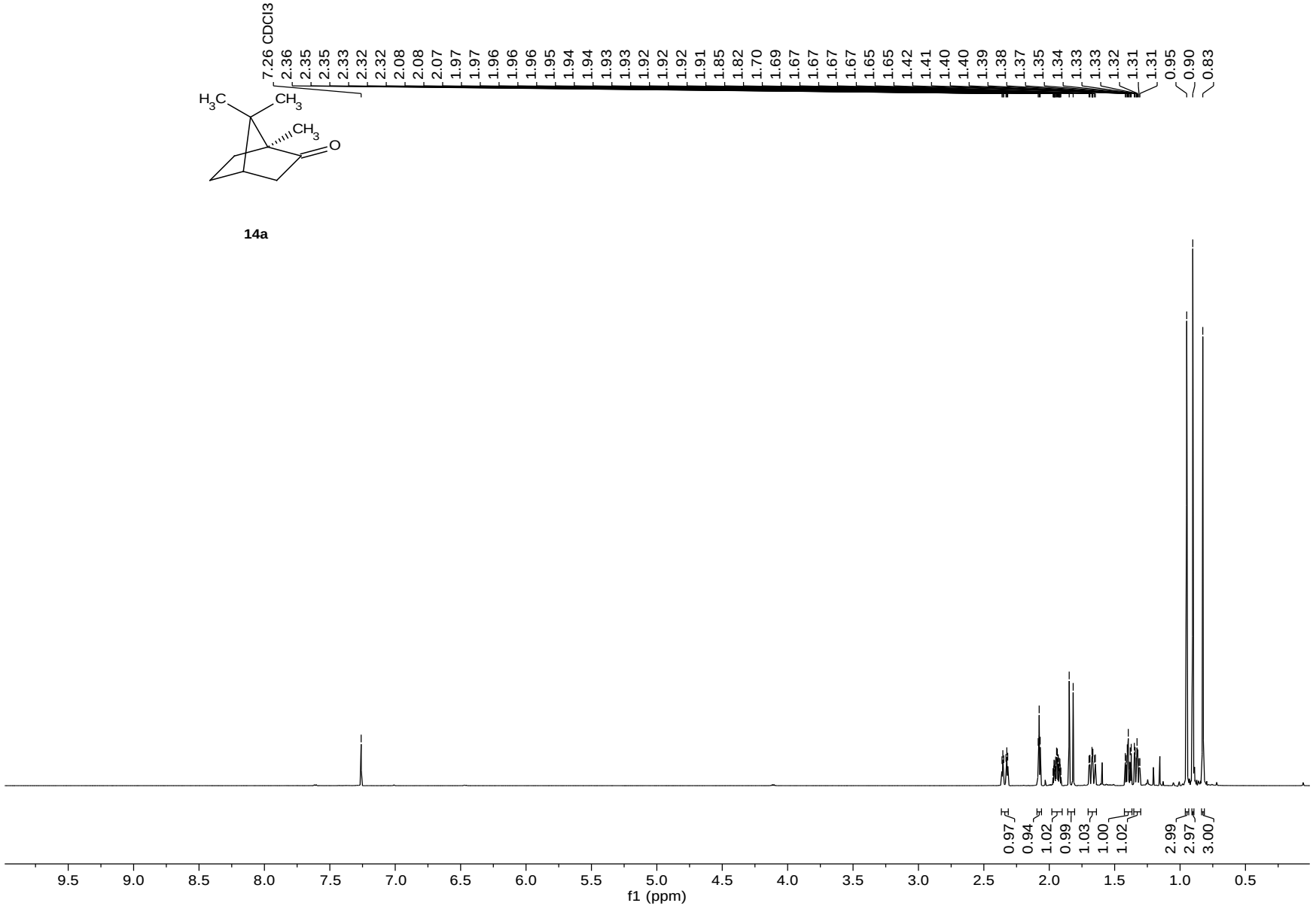

HO
O
S
O
O
O
Na
I

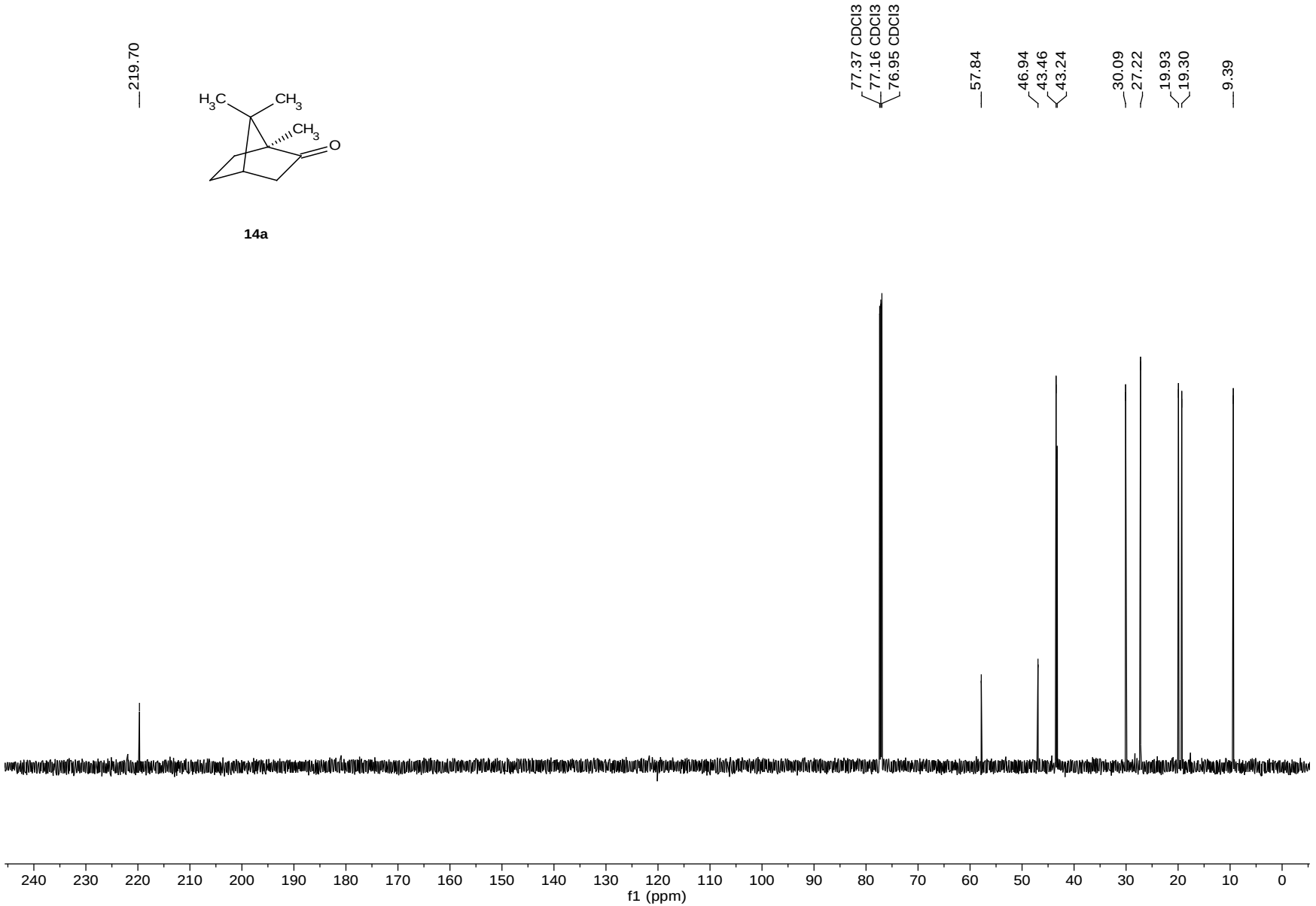
**12**

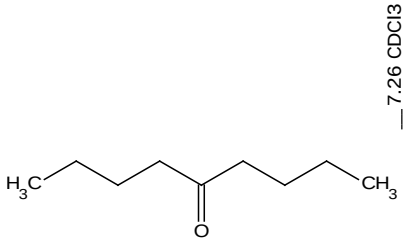

13.02
8.45
8.45
8.03
8.01
7.52
7.51
7.50
7.50
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
0.75
1.00
1.11
1.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


166.82
150.60
141.35
130.07
129.92
128.47
99.56
39.93 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
HO
O
S
O
O
O
Na
I
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)

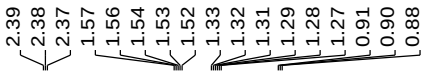
**12**

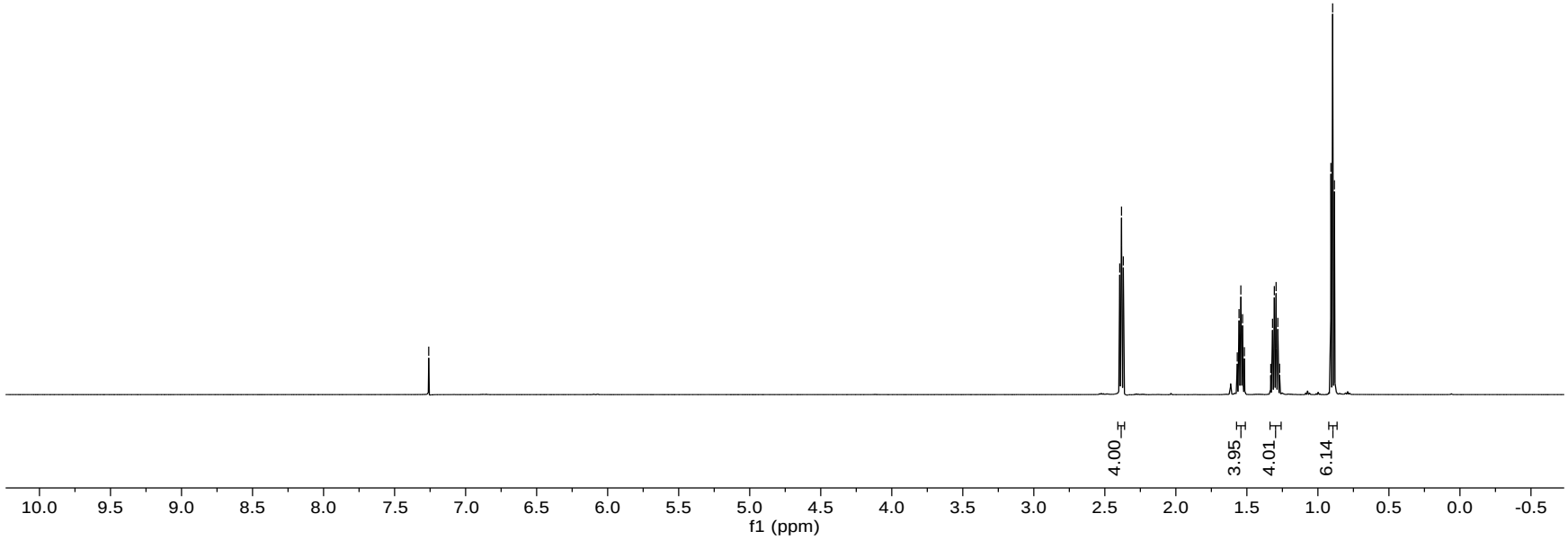

7.26 CDCl3
2.36 2.35 2.35 2.33 2.32 2.32 2.08 2.08 2.07 1.97 1.97 1.96 1.96 1.96 1.95 1.94 1.94 1.93 1.93 1.92 1.92 1.92 1.91 1.85 1.82 1.70 1.69 1.67 1.67 1.67 1.67 1.65 1.65 1.42 1.41 1.40 1.40 1.39 1.38 1.37 1.35 1.34 1.33 1.33 1.32 1.31 1.31 0.95 0.90 0.83
H3C
CH3
CH3
O
14a
0.97 0.94 1.02 0.99 1.03 1.00 1.02 2.99 2.97 3.00
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
f1 (ppm)

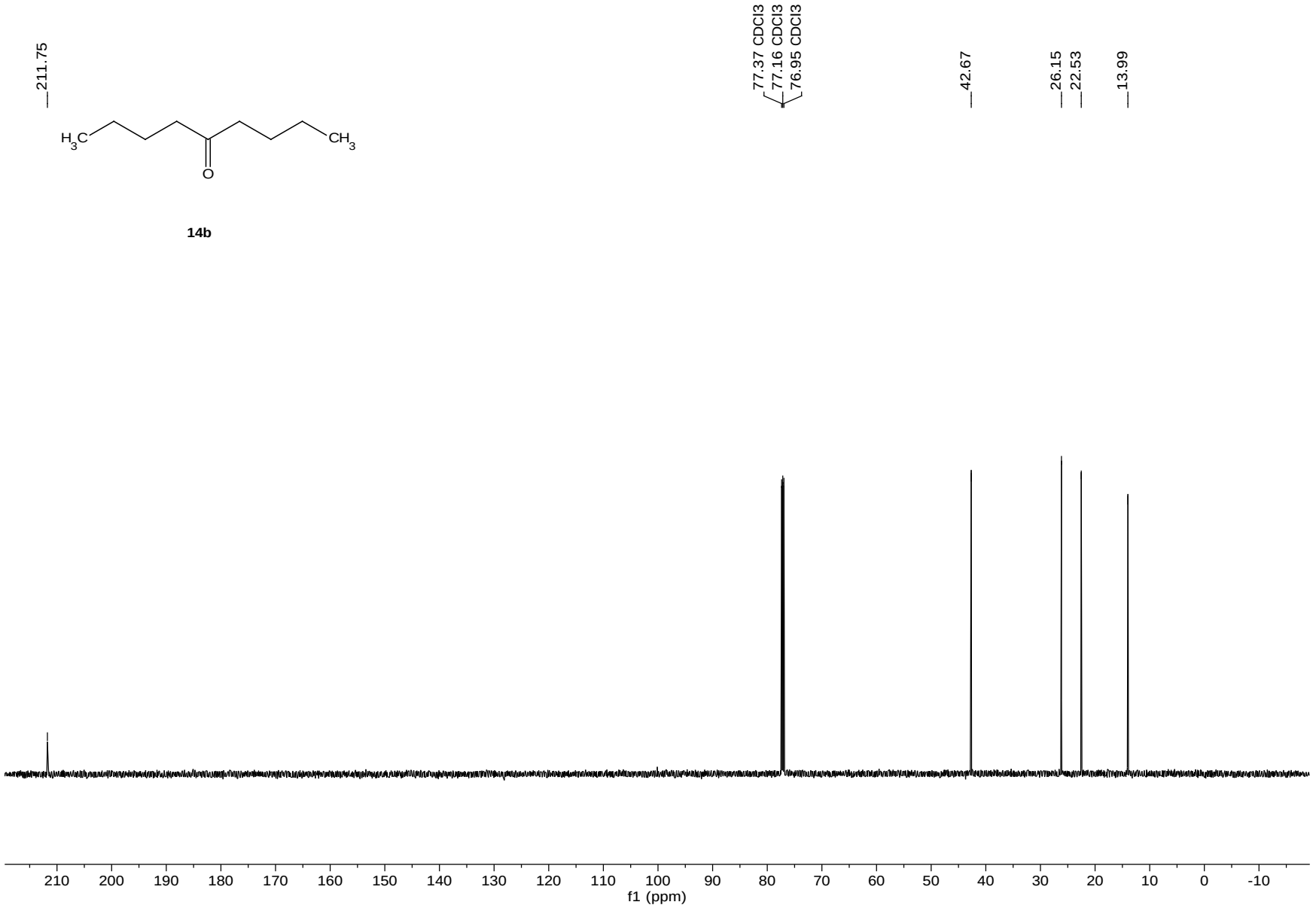

219.70
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
57.84
46.94
43.46
43.24
30.09
27.22
19.93
19.30
9.39
H3C
CH3
CH3
O
14a
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

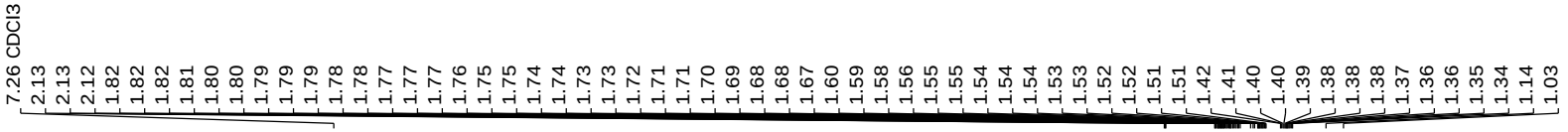

7.26 CDCl3
H3C
CH3
O

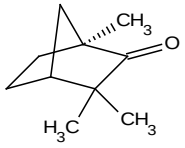
**14b**


2.39
2.38
2.37
1.57
1.56
1.54
1.53
1.52
1.33
1.32
1.31
1.29
1.28
1.27
0.91
0.90
0.88

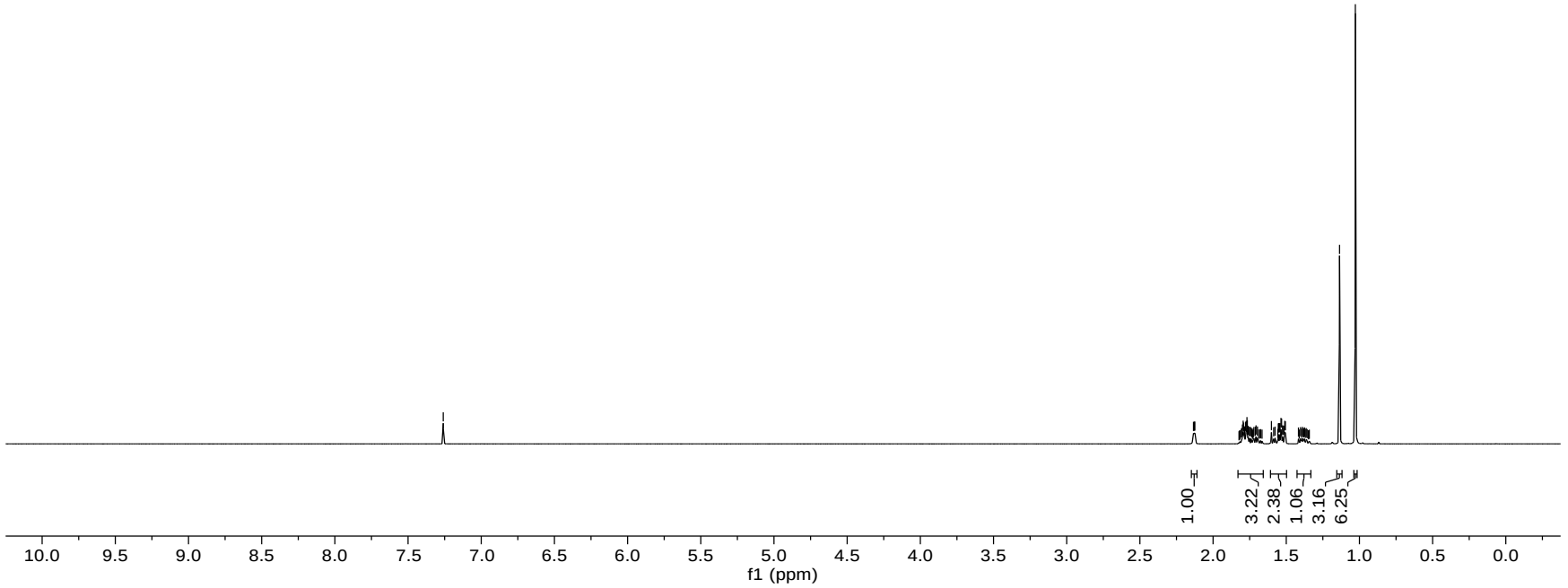

4.00
3.95
4.01
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

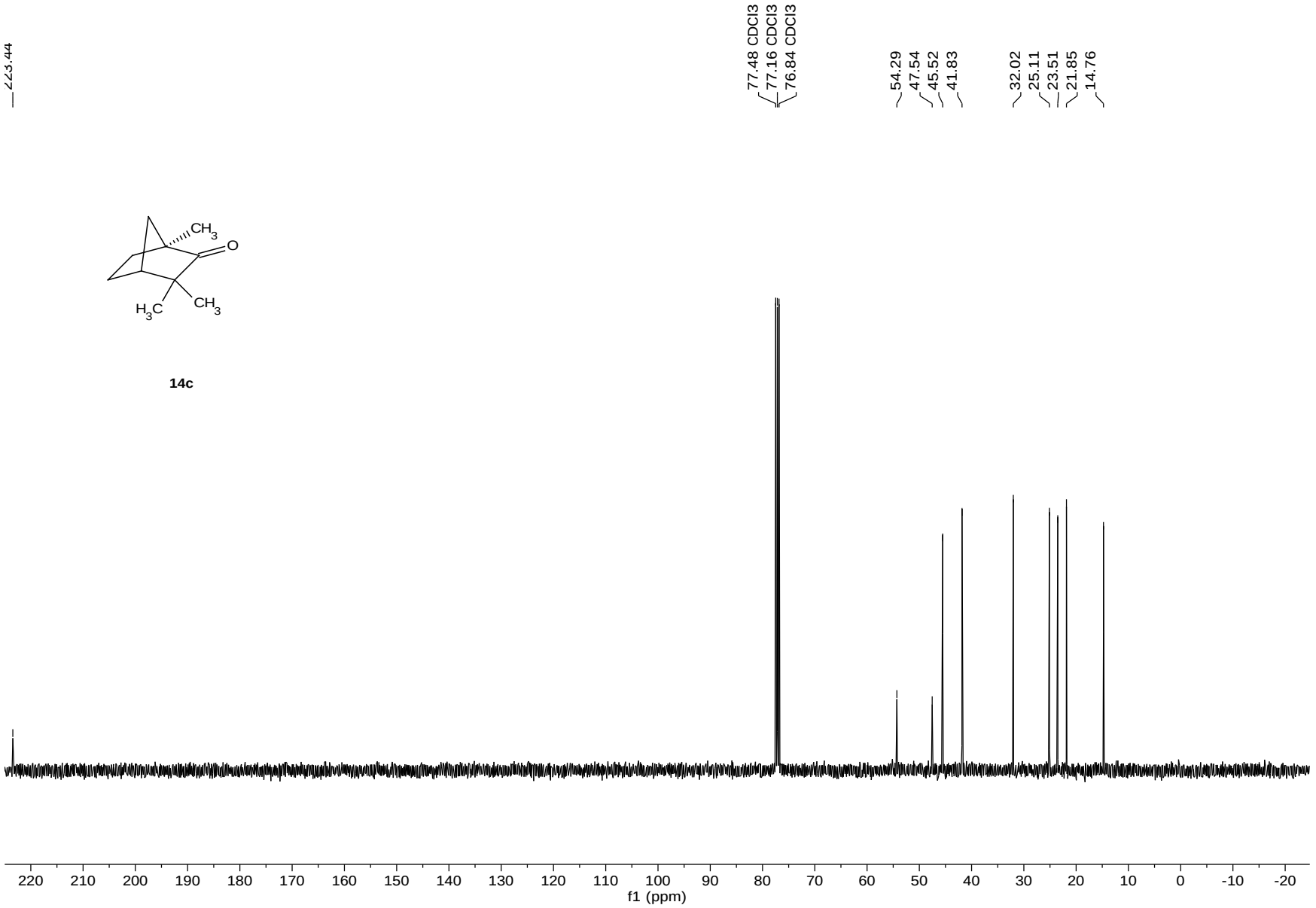

211.75
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
42.67
26.15
22.53
13.99
H3C
CH3
O
14b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

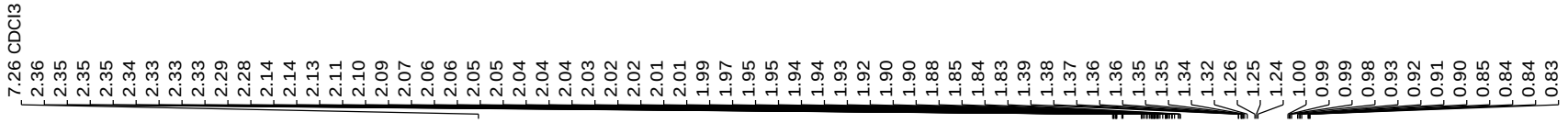

7.26 CDCl3
2.13
2.13
2.12
1.82
1.82
1.82
1.81
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.77
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.68
1.67
1.60
1.59
1.58
1.56
1.55
1.55
1.54
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.42
1.41
1.40
1.40
1.39
1.38
1.38
1.38
1.37
1.36
1.36
1.35
1.34
1.14
1.03

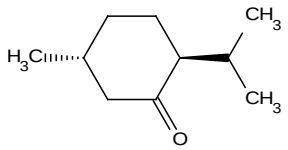

CH3
O
H3C
CH3

**14c**

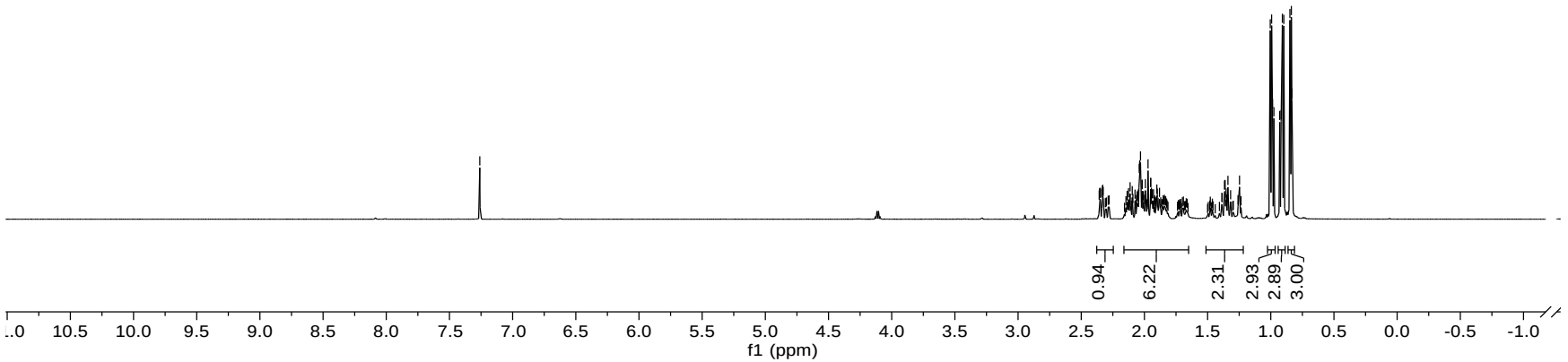

1.00
3.22
2.38
1.06
3.16
6.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

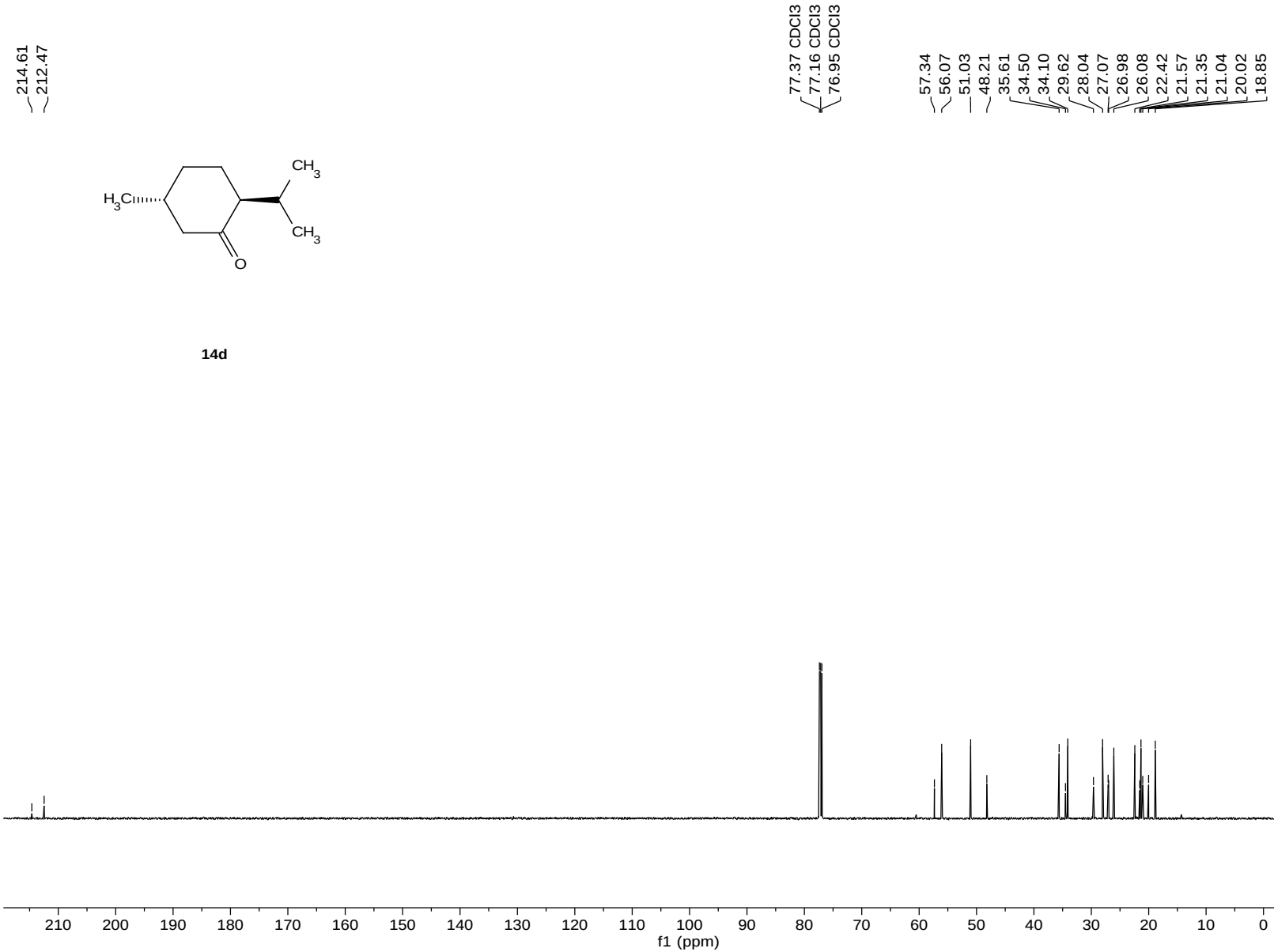

227.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
54.29
47.54
45.52
41.83
32.02
25.11
23.51
21.85
14.76
CH3
O
H3C
CH3
14c
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.26 CDCl3
2.36 2.35 2.35 2.35 2.34 2.33 2.33 2.33 2.29 2.28 2.14 2.14 2.13 2.11 2.10 2.09 2.07 2.06 2.06 2.05 2.05 2.04 2.04 2.04 2.03 2.02 2.02 2.01 2.01 1.99 1.97 1.95 1.95 1.94 1.94 1.93 1.92 1.90 1.90 1.88 1.85 1.84 1.83 1.39 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.32 1.26 1.25 1.24 1.00 0.99 0.99 0.98 0.93 0.92 0.91 0.90 0.85 0.84 0.84 0.83

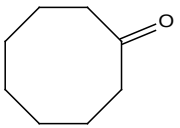

H3C
CH3
CH3
O

**14d**


0.94
6.22
2.31
2.93
2.89
3.00
10.5 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 -1.0
f1 (ppm)

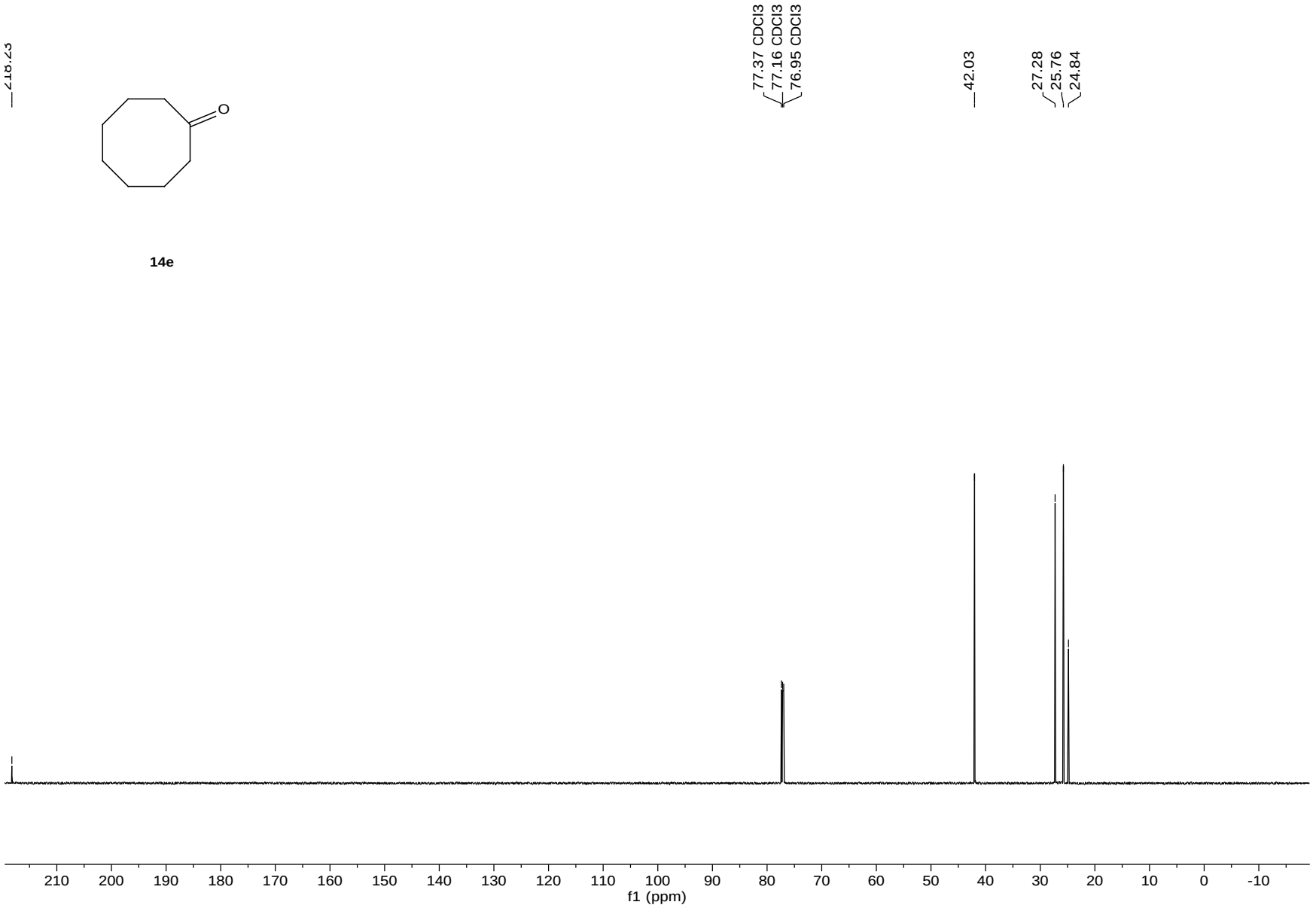

214.61
212.47
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
57.34
56.07
51.03
48.21
35.61
34.50
34.10
29.62
28.04
27.07
26.98
26.08
22.42
21.57
21.35
21.04
20.02
18.85
CH3
H3C
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

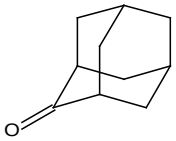
**14d**


O

**14e**

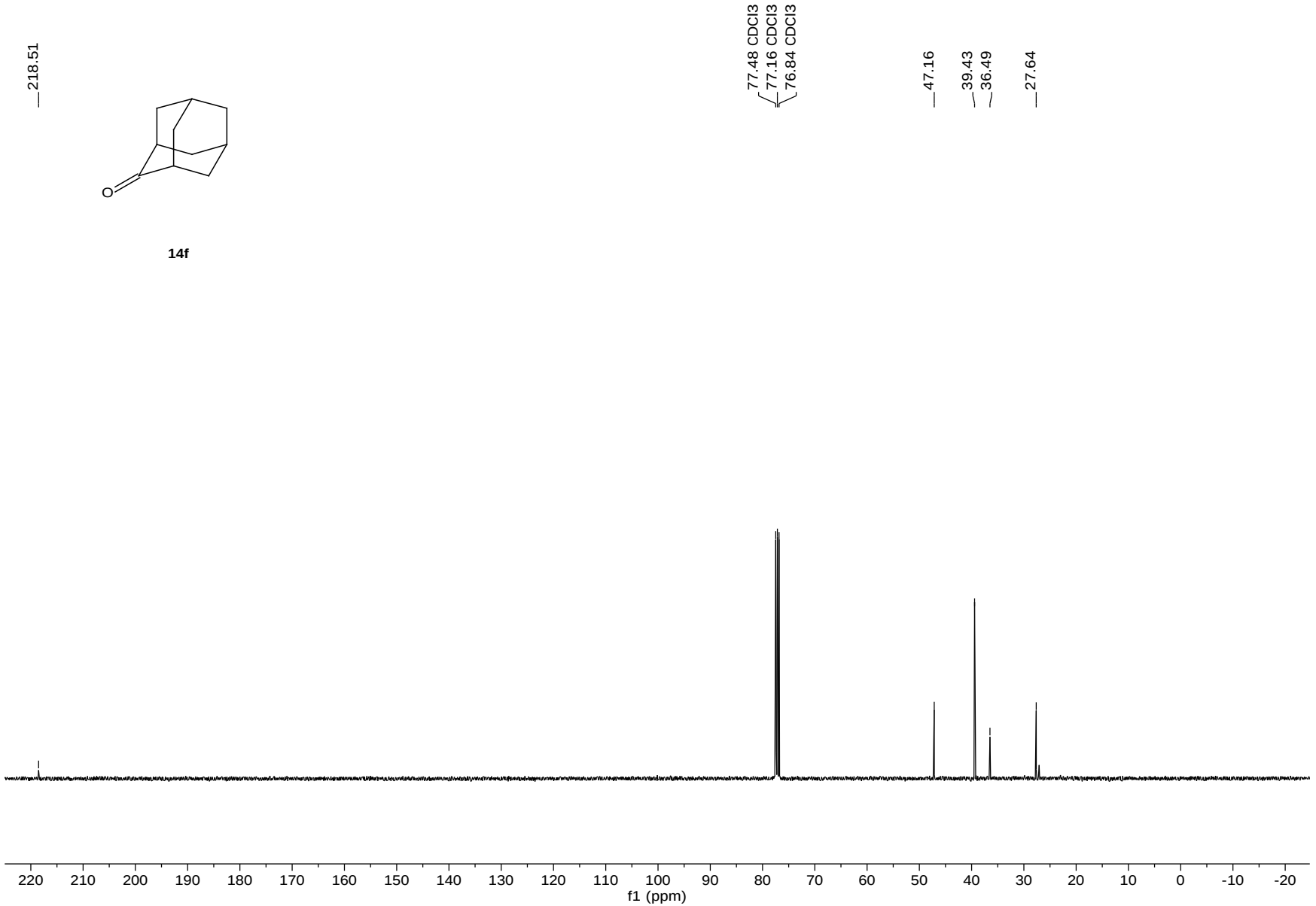

7.26 CDCl3
2.39
2.38
2.38
2.37
2.36
1.86
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.53
1.53
1.52
1.51
1.51
1.50
1.49
1.35
1.35
3.94
3.92
3.95
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
14e
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
42.03
27.28
25.76
24.84
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)

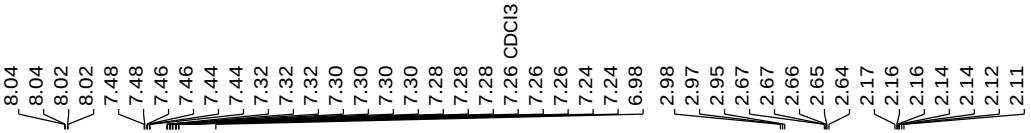

O

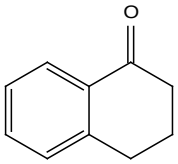
**14f**


7.26 CDCl3
2.55
2.10
2.10
2.07
2.02
1.98
1.93
1.85
12.13
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 -1.0
f1 (ppm)

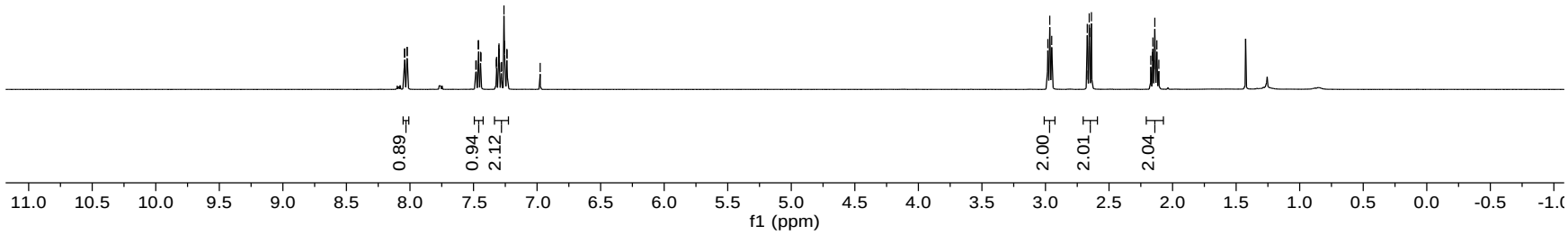

218.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
47.16
39.43
36.49
27.64
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

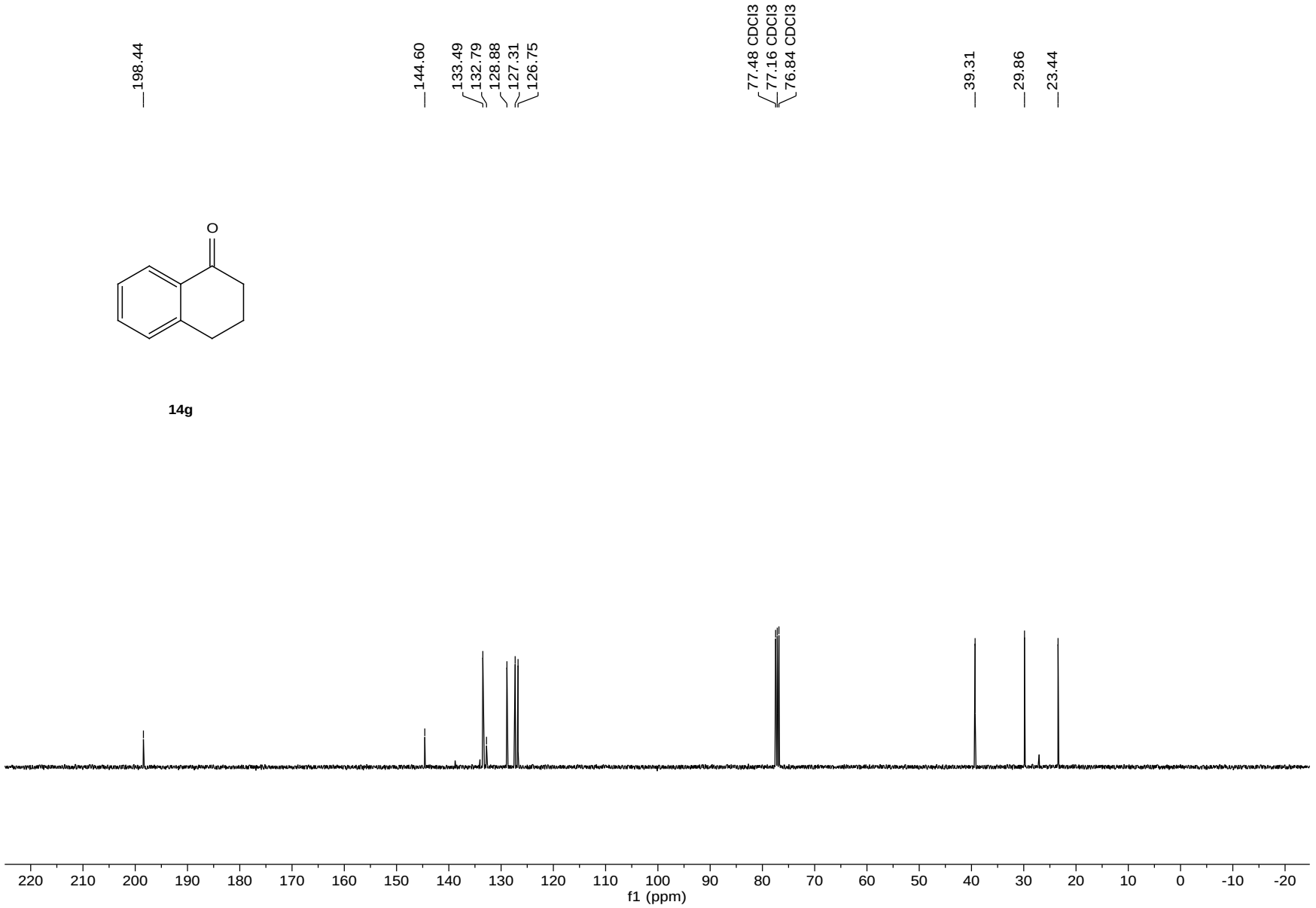
**14f**

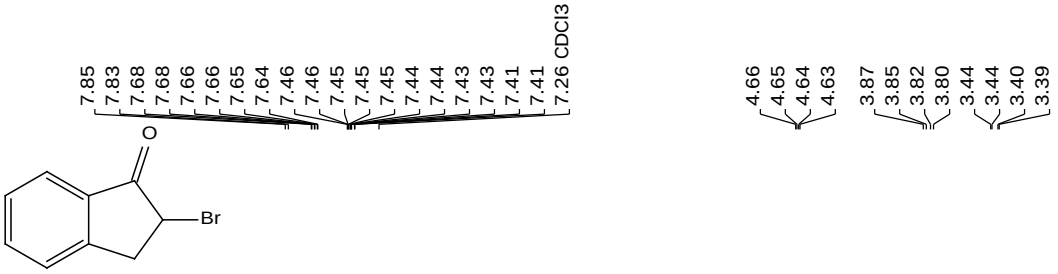

8.04
8.04
8.02
8.02
7.48
7.48
7.46
7.46
7.44
7.44
7.32
7.32
7.30
7.30
7.30
7.30
7.28
7.28
7.28
CDCl3
7.26
7.26
7.26
7.24
7.24
6.98
2.98
2.97
2.95
2.67
2.67
2.66
2.65
2.64
2.17
2.16
2.16
2.14
2.14
2.12
2.11


O

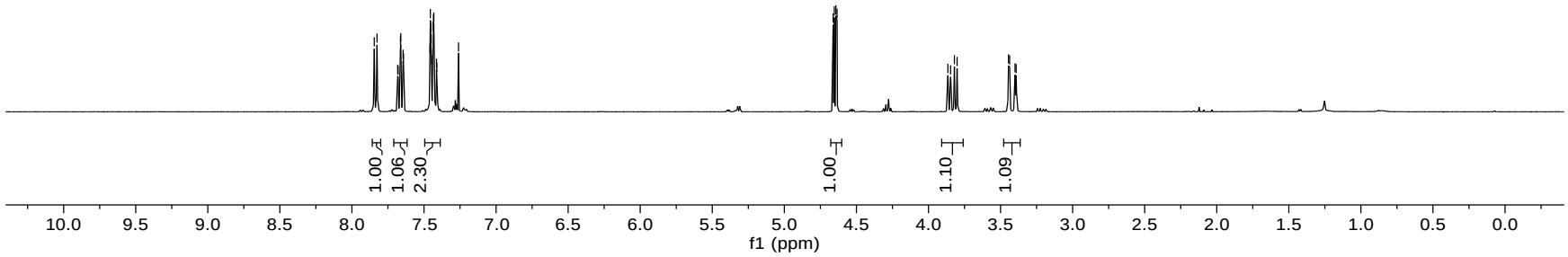
**14g**

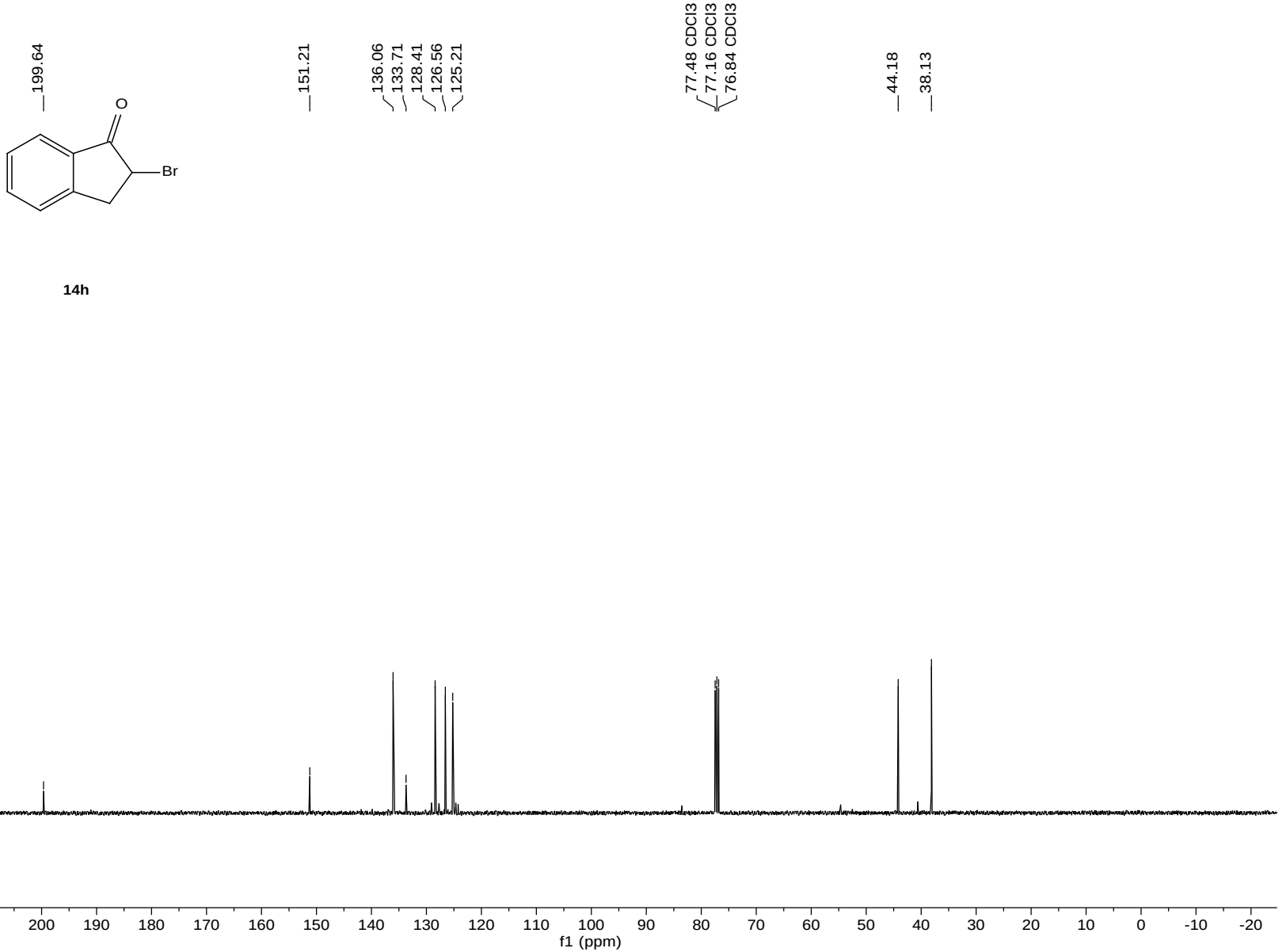

0.89
0.94
2.12
2.00
2.01
2.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


198.44
144.60
133.49
132.79
128.88
127.31
126.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.31
29.86
23.44
O
14g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

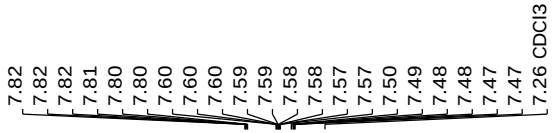

7.85
7.83
7.68
7.68
7.66
7.66
7.65
7.64
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.41
7.41
7.26 CDCl3
4.66
4.65
4.64
4.63
3.87
3.85
3.82
3.80
3.44
3.44
3.40
3.39
O
Br

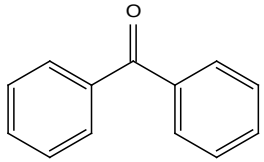
**14h**


1.00
1.06
2.30
1.00
1.10
1.09
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
f1 (ppm)

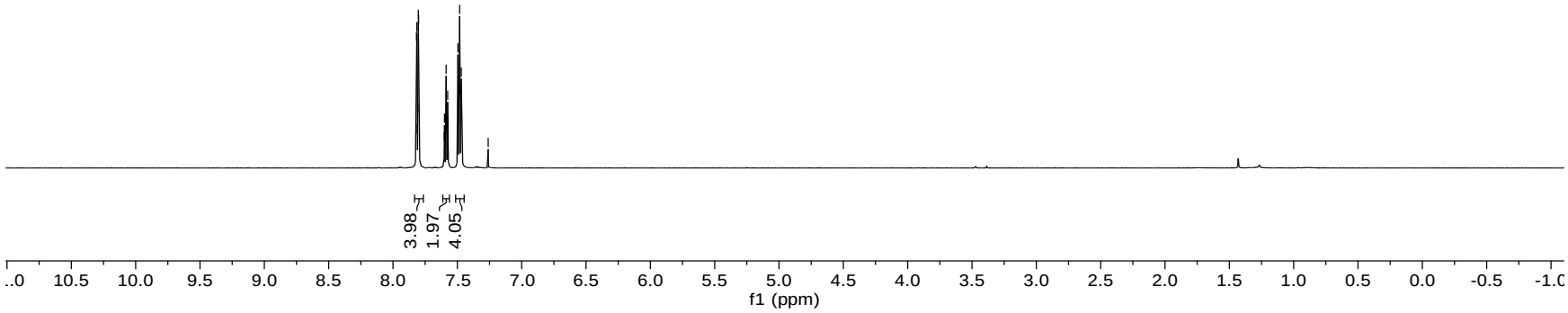

199.64
151.21
136.06
133.71
128.41
126.56
125.21
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.18
38.13
O
Br
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

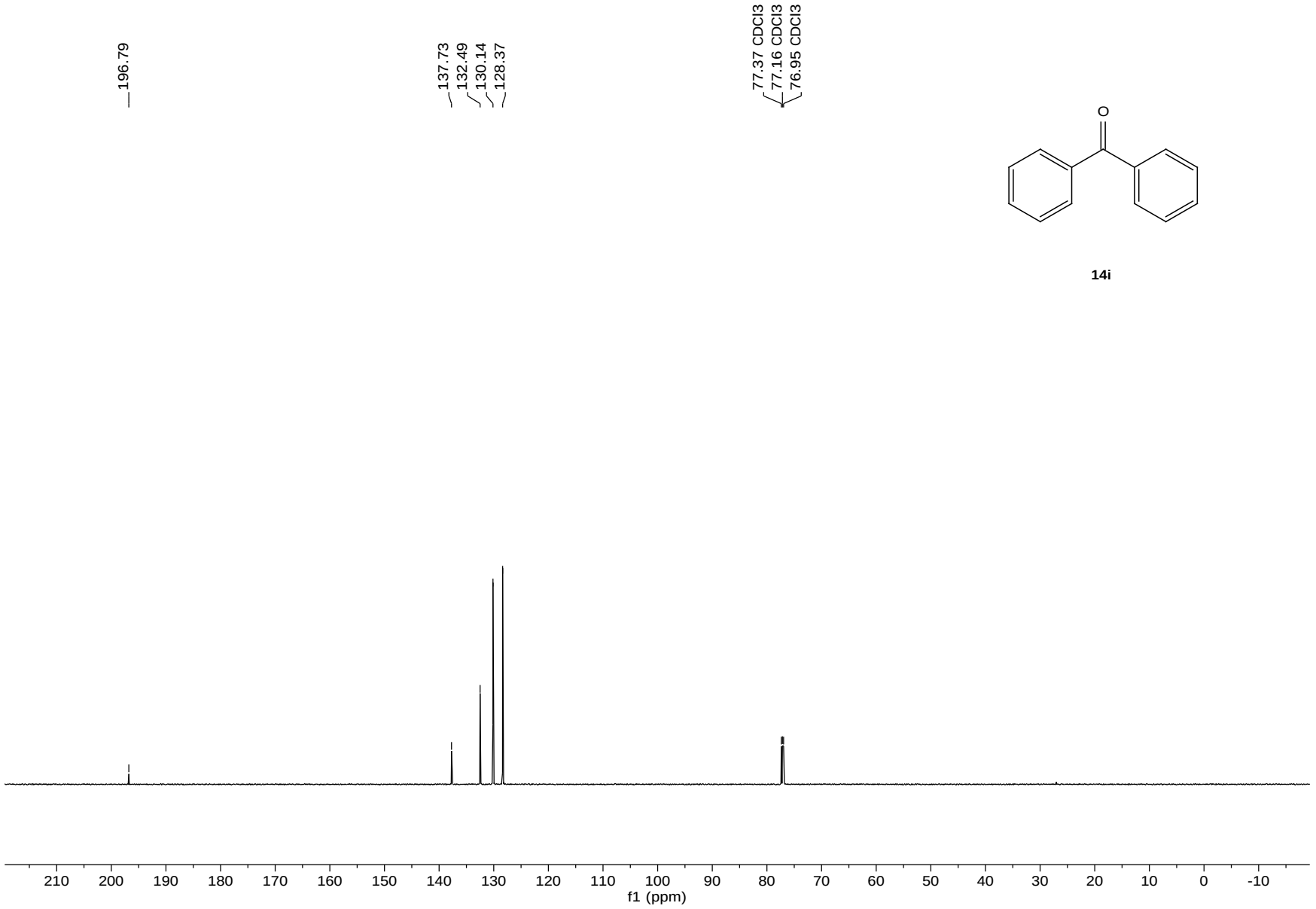
**14h**

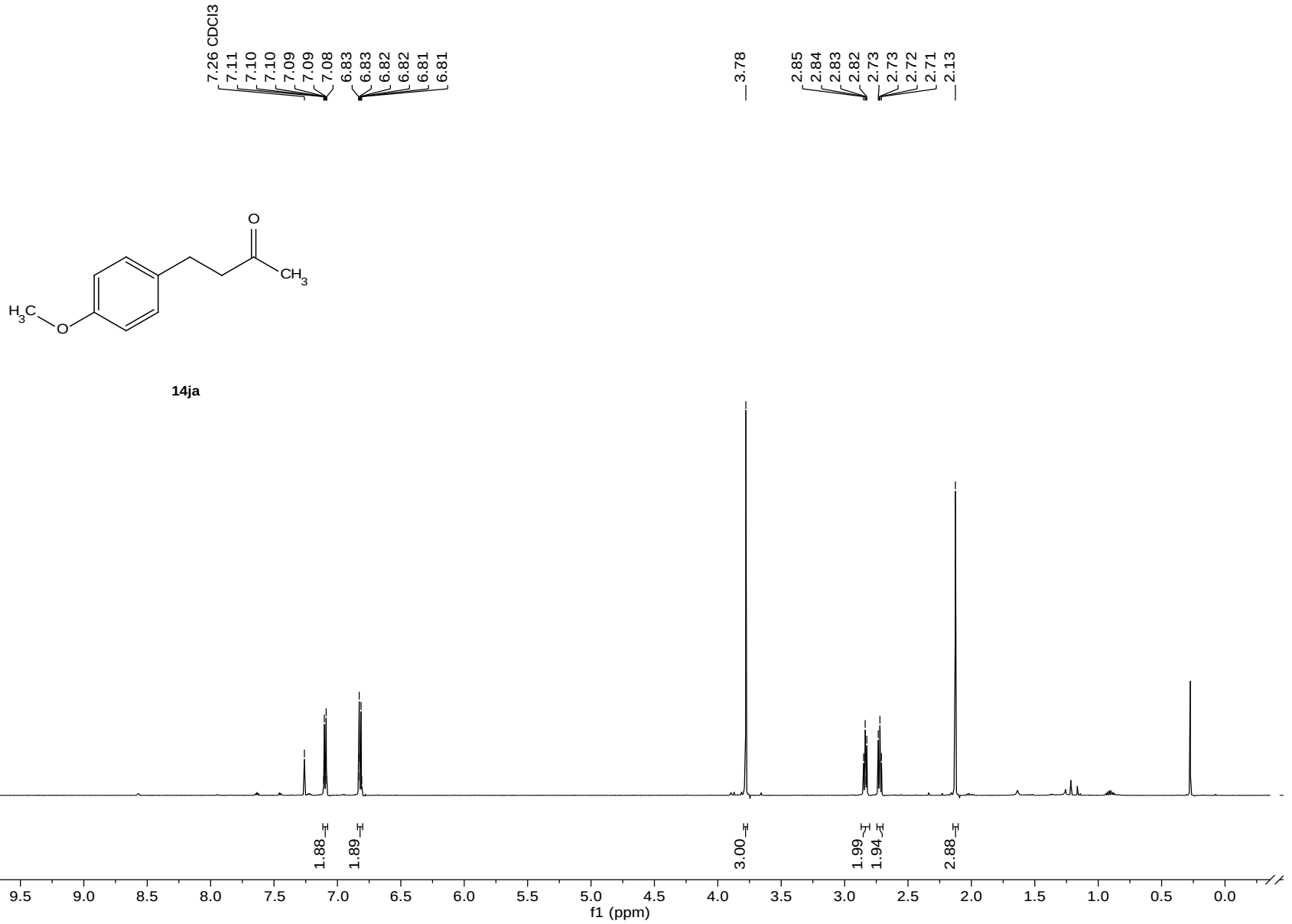

7.82
7.82
7.82
7.81
7.80
7.80
7.60
7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.57
7.50
7.49
7.48
7.48
7.47
7.47
7.26 CDCl3

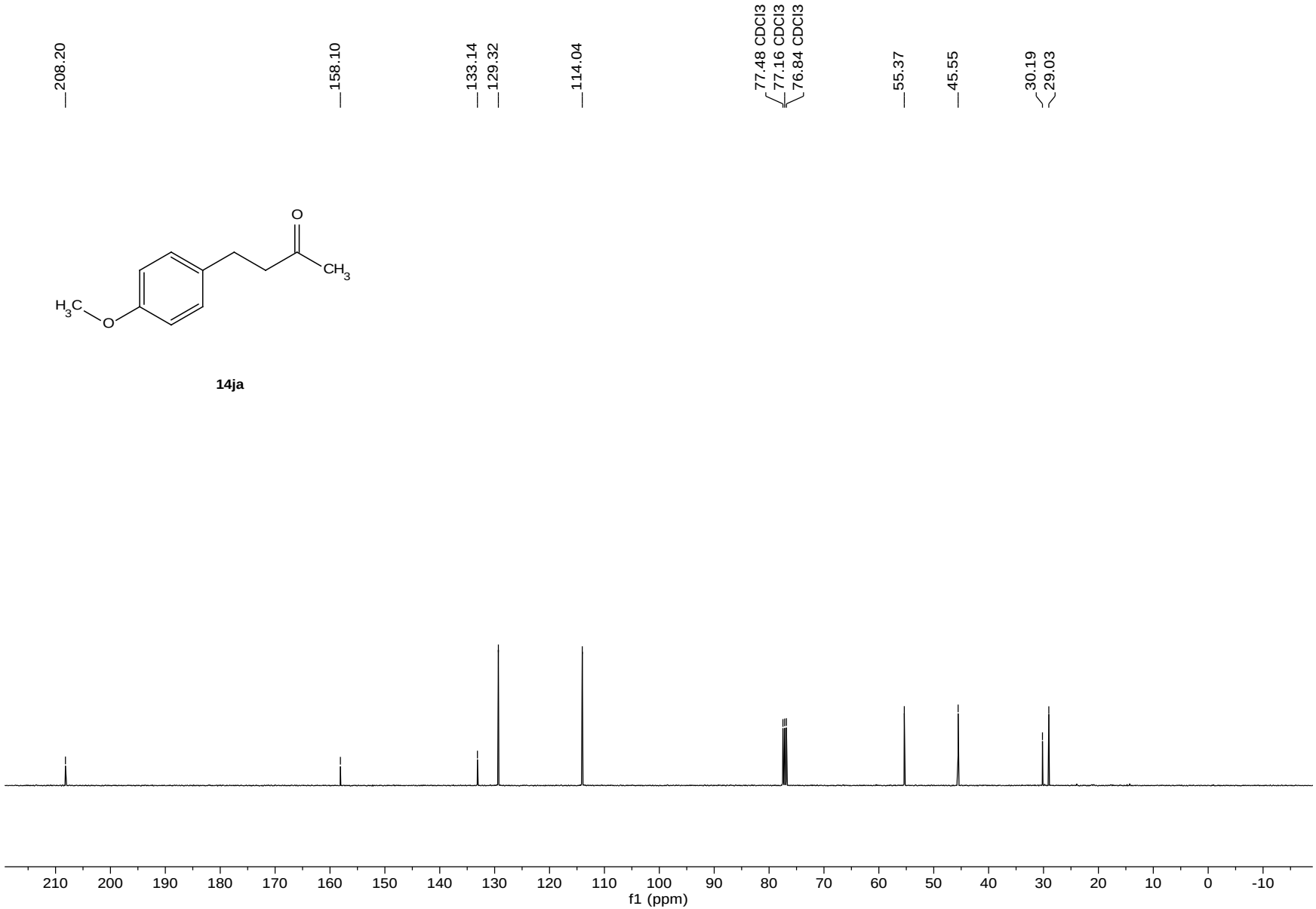

O

**14i**


3.98
1.97
4.05
10.5
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
f1 (ppm)

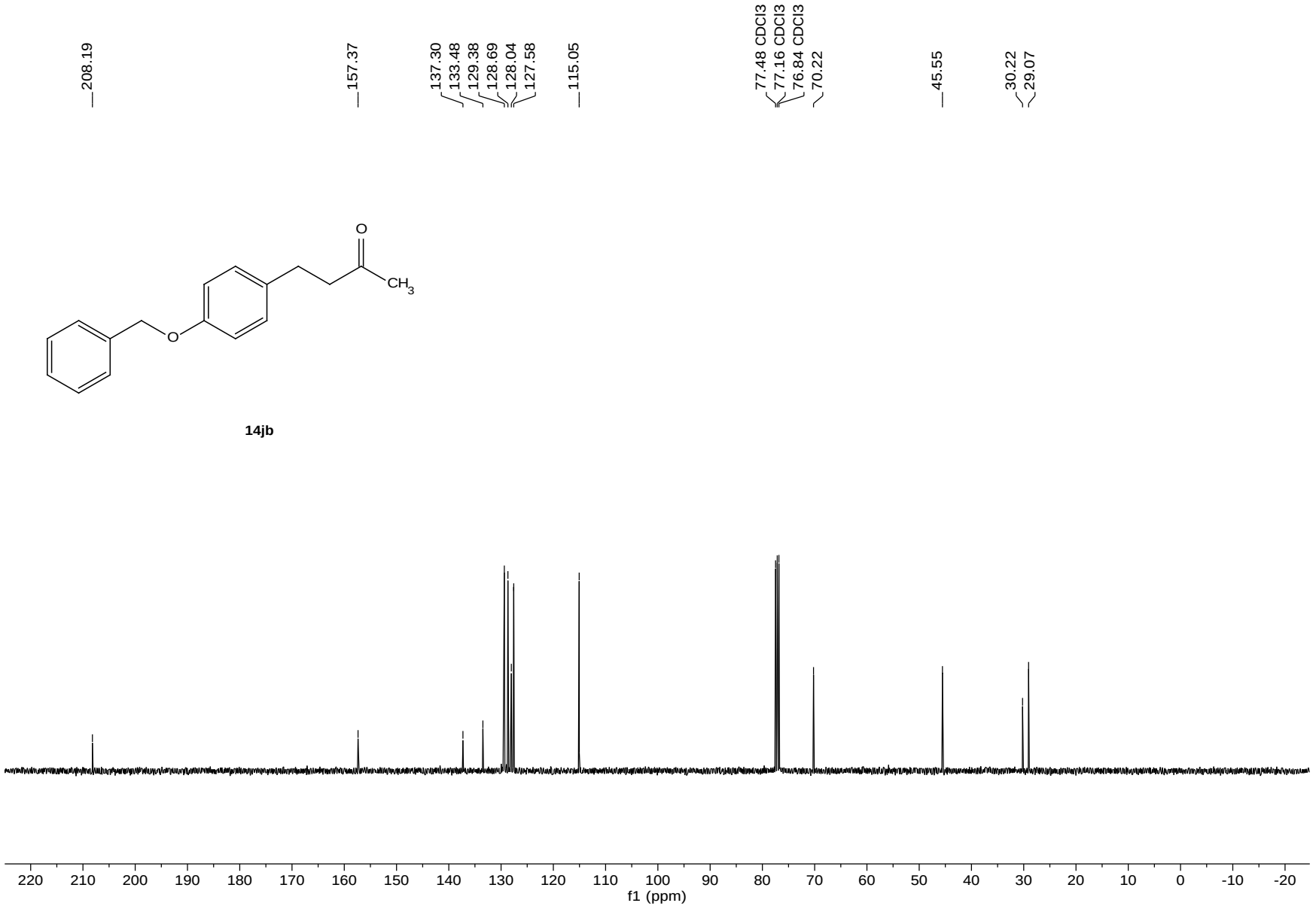

196.79
137.73
132.49
130.14
128.37
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
O
14i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26 CDCl3
7.11
7.10
7.10
7.09
7.09
7.08
6.83
6.83
6.82
6.82
6.81
6.81
3.78
2.85
2.84
2.83
2.82
2.73
2.73
2.72
2.71
2.13
O
CH3
H3C
O
14ja
1.88
1.89
3.00
1.99
1.94
2.88
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
f1 (ppm)

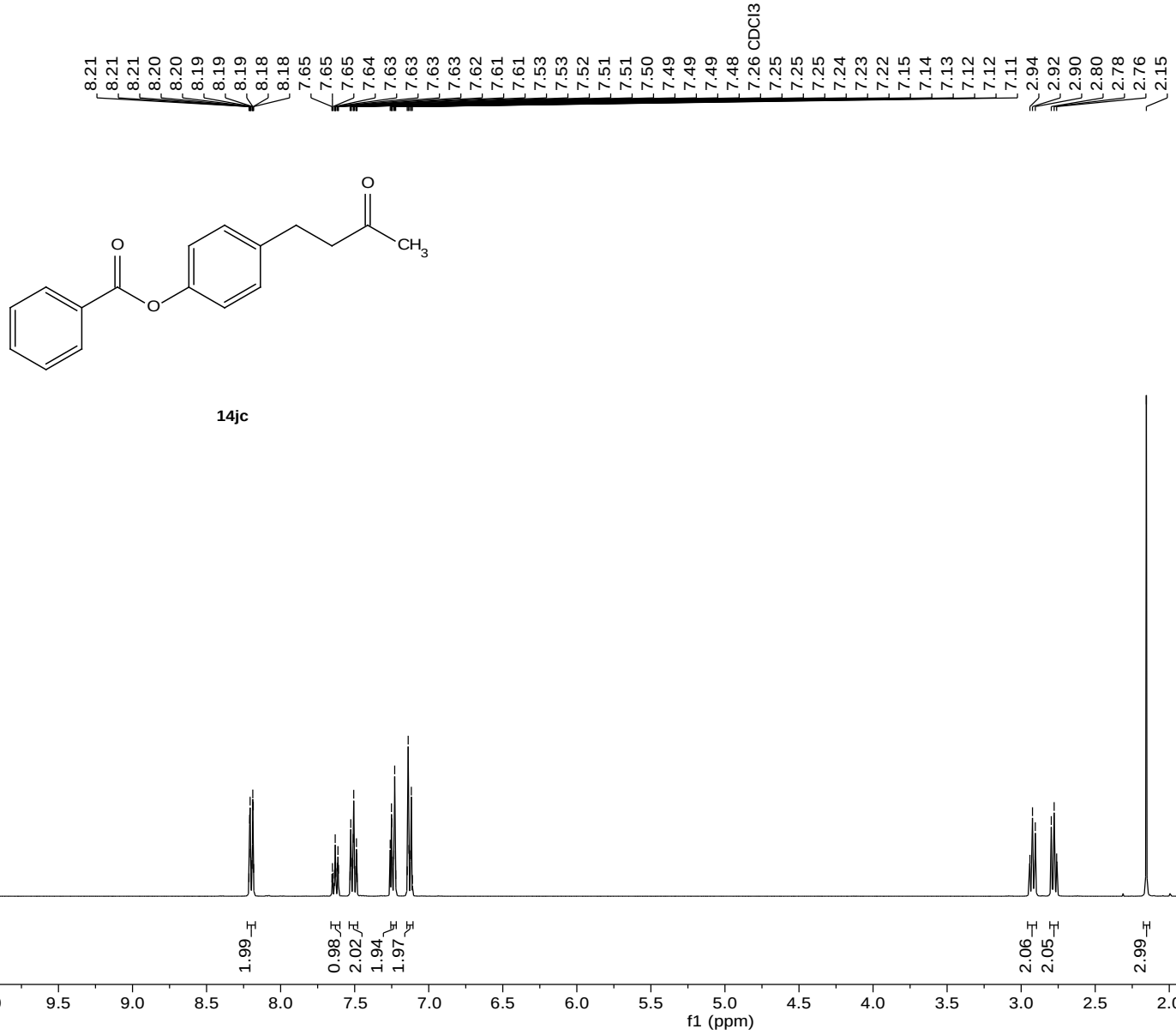

208.20
158.10
133.14
129.32
114.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.37
45.55
30.19
29.03
O
CH3
H3C
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

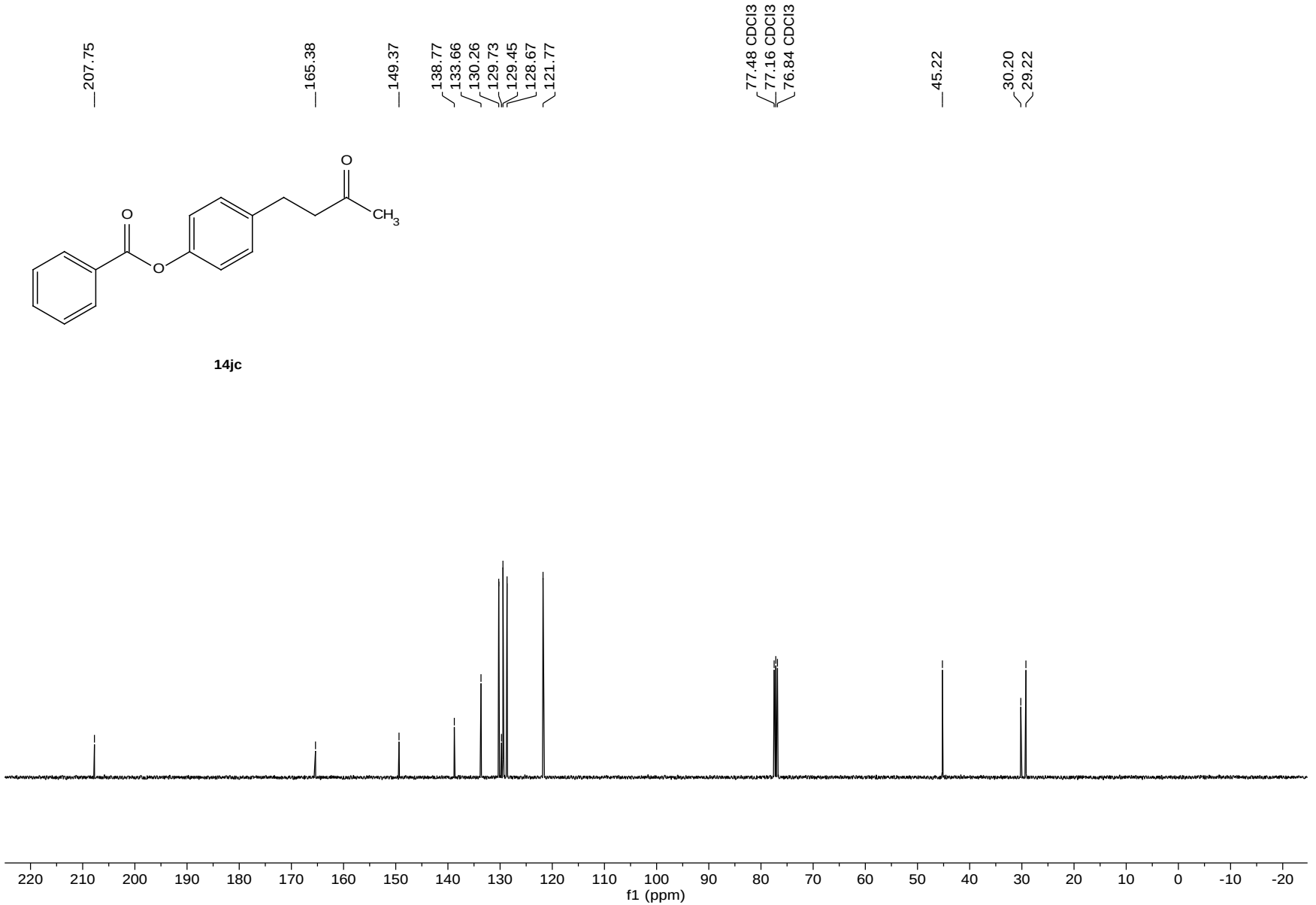
**14ja**

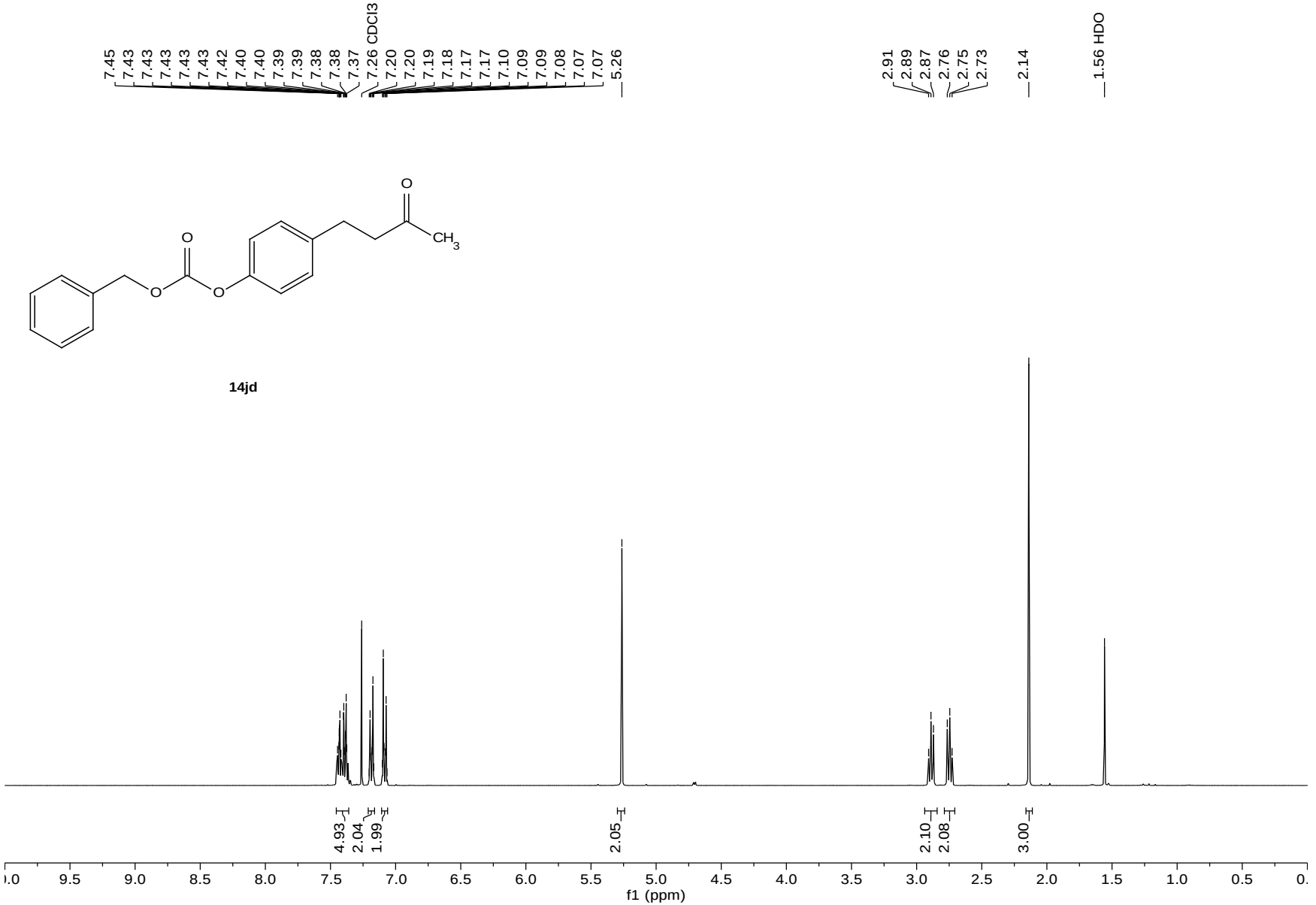

7.44
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.40
7.38
7.38
7.37
7.36
7.34
7.34
7.33
7.32
7.26 CDCl3
7.11
7.11
7.10
7.09
6.92
6.91
6.91
6.90
6.89
5.04
2.86
2.85
2.83
2.74
2.73
2.71
2.71
2.13
O
CH3
O
14jb
5.08
1.96
2.00
2.06
1.98
2.01
2.82
f1 (ppm)

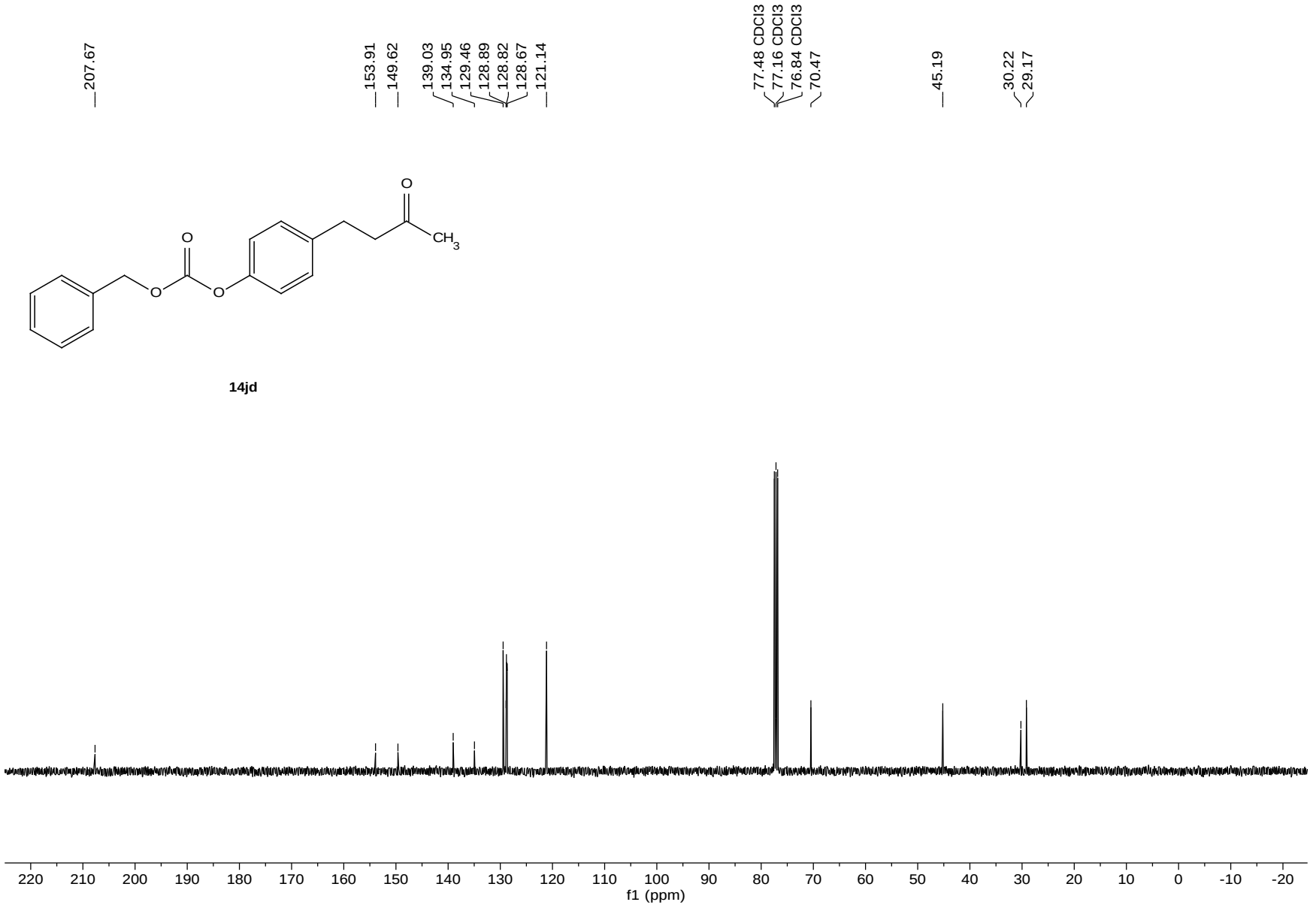

208.19
157.37
137.30
133.48
129.38
128.69
128.04
127.58
115.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.22
45.55
30.22
29.07
O
CH3
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

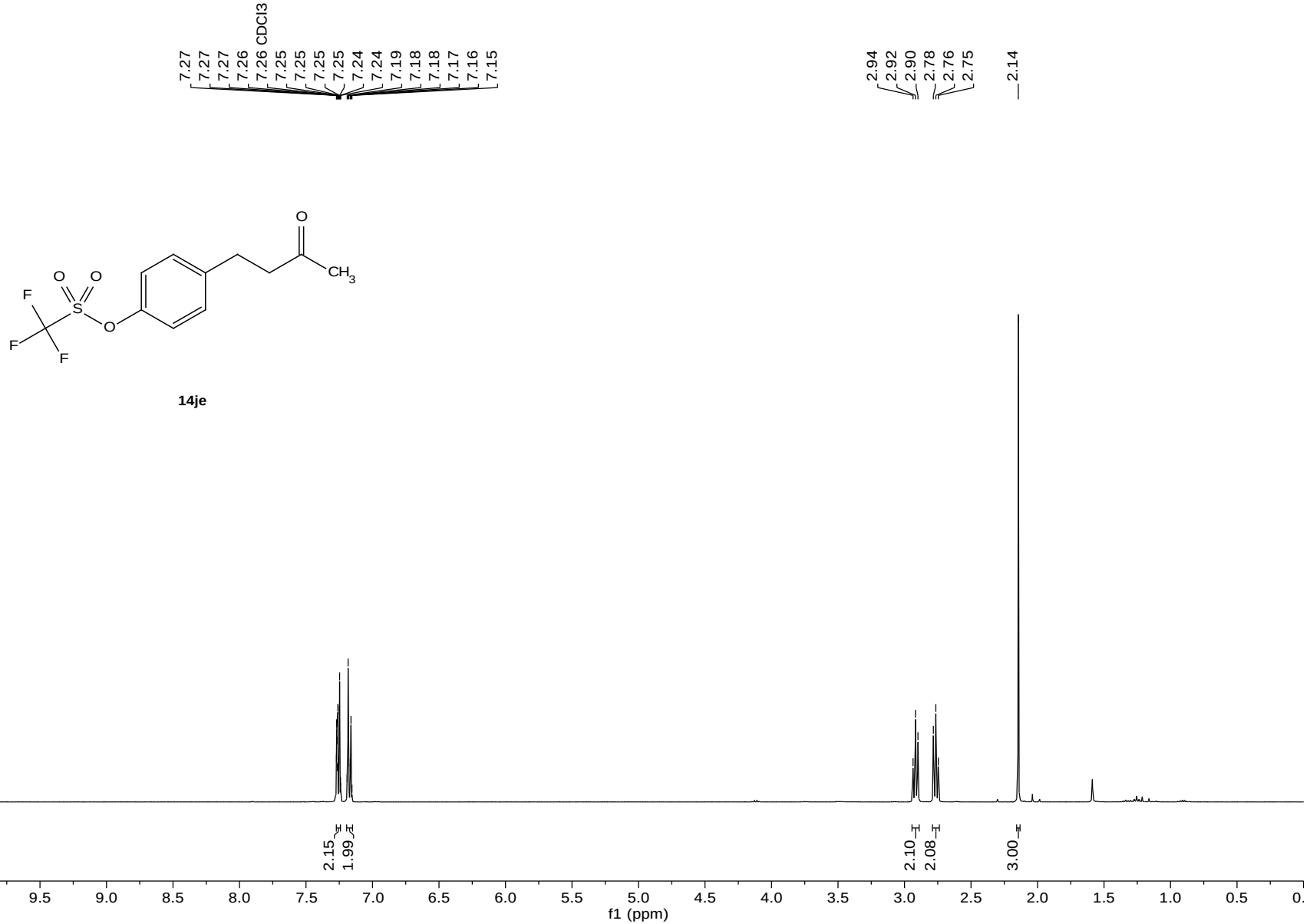
**14jb**


8.21 8.21 8.21 8.20 8.20 8.19 8.19 8.19 8.18 8.18 7.65 7.65 7.65 7.64 7.63 7.63 7.63 7.63 7.62 7.61 7.61 7.53 7.53 7.52 7.51 7.51 7.50 7.49 7.49 7.49 7.48 7.26 CDCl3 7.25 7.25 7.25 7.24 7.23 7.22 7.15 7.14 7.13 7.12 7.12 7.11 2.94 2.92 2.90 2.80 2.78 2.76 2.15
O
O
O
CH3
14jc
1.99
0.98
2.02
1.94
1.97
2.06
2.05
2.99
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
f1 (ppm)

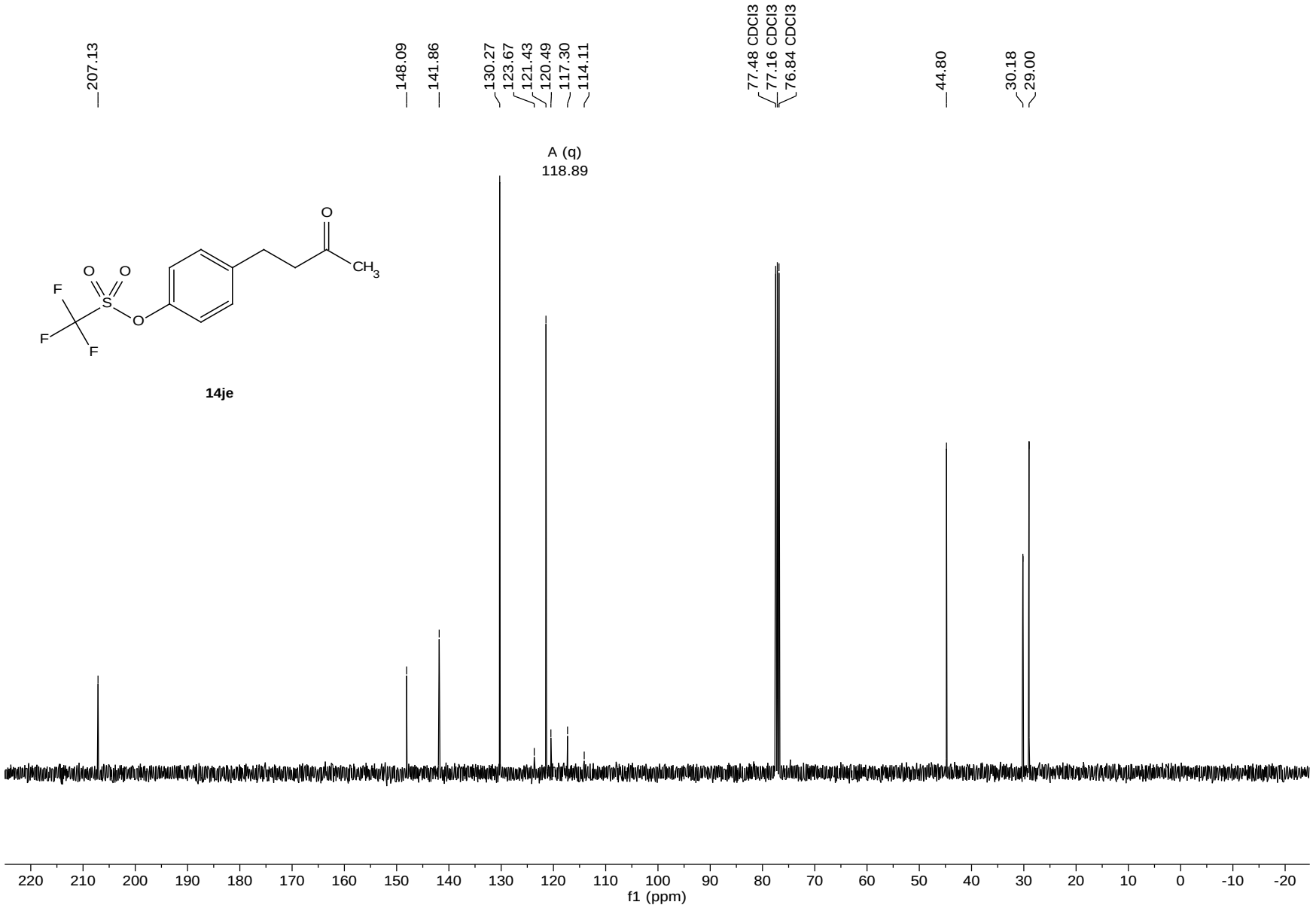

207.75
165.38
149.37
138.77
133.66
130.26
129.73
129.45
128.67
121.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.22
30.20
29.22
O
O
O
CH3
14jc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

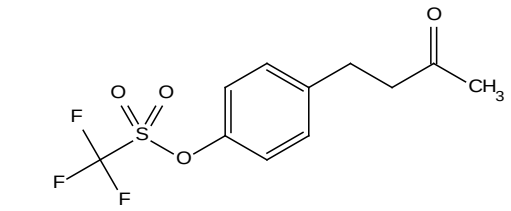

7.45
7.43
7.43
7.43
7.43
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.26 CDCl3
7.20
7.20
7.19
7.18
7.17
7.17
7.10
7.09
7.09
7.08
7.07
7.07
5.26
2.91
2.89
2.87
2.76
2.75
2.73
2.14
1.56 HDO
O
O
O
O
CH3
14jd
4.93
2.04
1.99
2.05
2.10
2.08
3.00
f1 (ppm)


207.67
153.91
149.62
139.03
134.95
129.46
128.89
128.82
128.67
121.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.47
45.19
30.22
29.17
O
O
O
O
CH3
14jd
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.27
7.27
7.27
7.26
7.26 CDCl3
7.25
7.25
7.25
7.25
7.24
7.24
7.19
7.18
7.18
7.17
7.16
7.15
2.94
2.92
2.90
2.78
2.76
2.75
2.14
O
O
O
F
S
O
F
F
CH3
2.15
1.99
2.10
2.08
3.00
f1 (ppm)

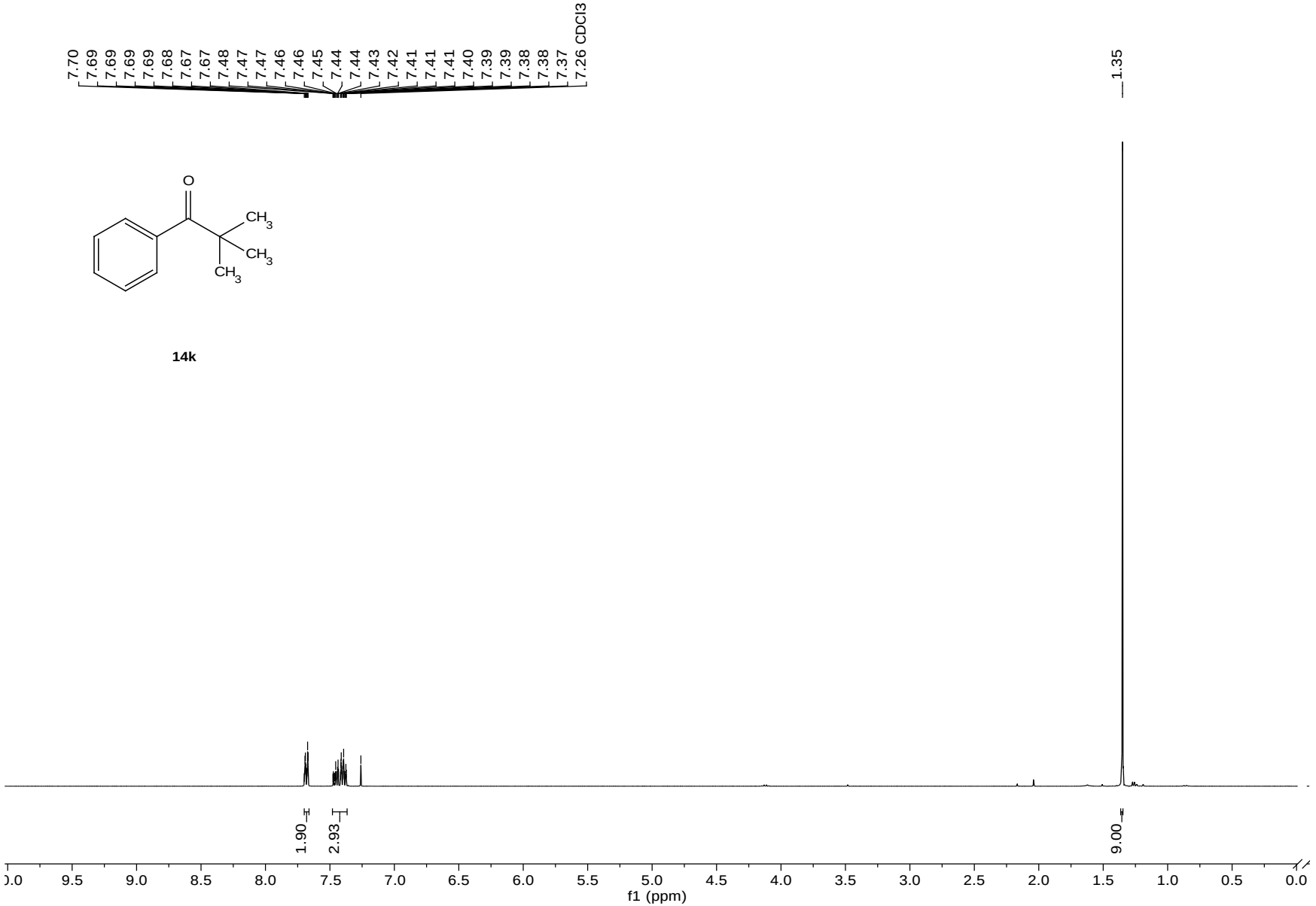
**14je**


207.13
148.09
141.86
130.27
123.67
121.43
120.49
117.30
114.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.80
30.18
29.00
A (q)
118.89
O
O
O
F
S
O
F
F
CH3
14je
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

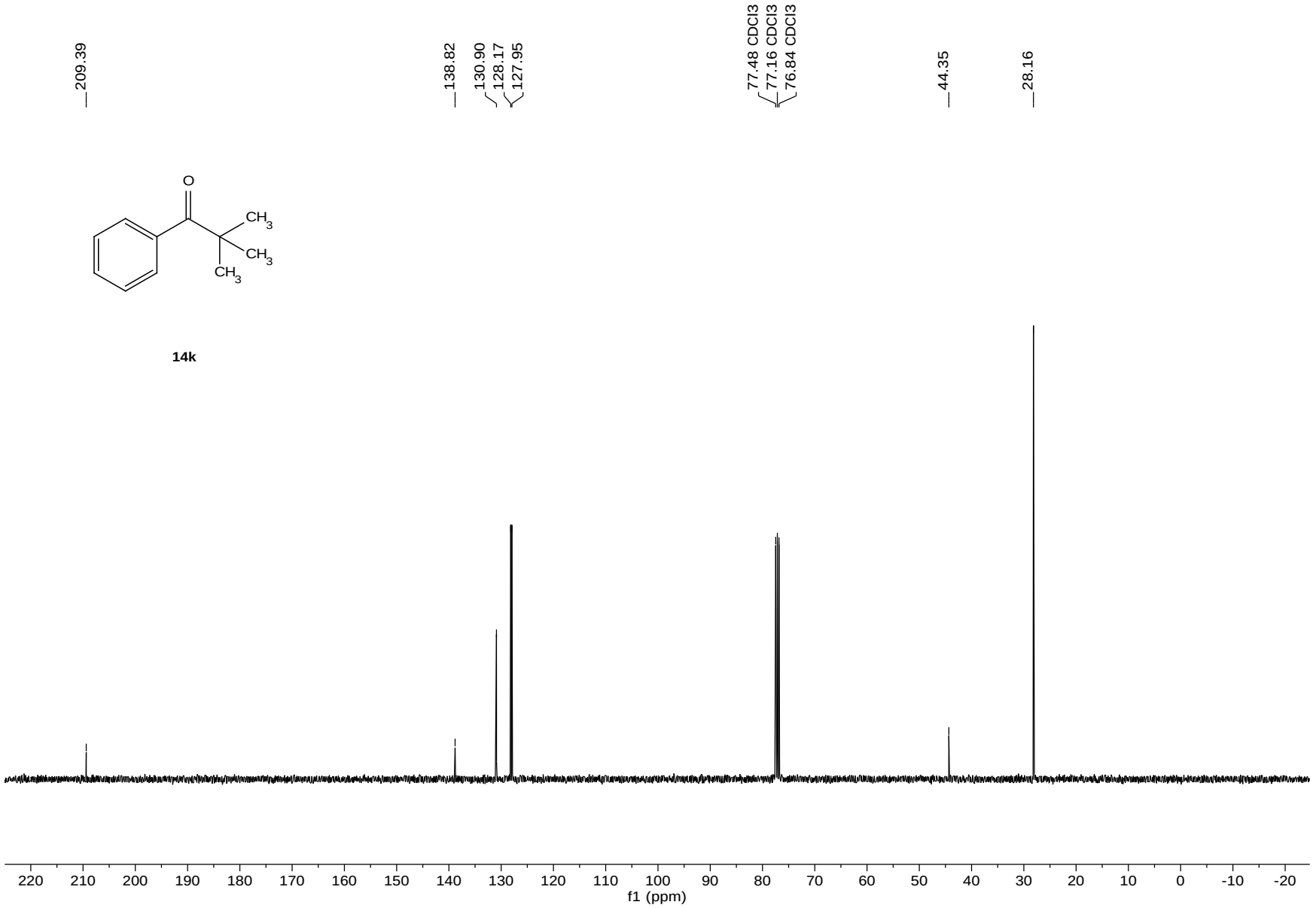

O
O
O
F
S
O
F
F
CH3

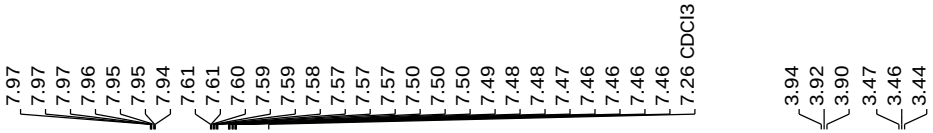
**14je**

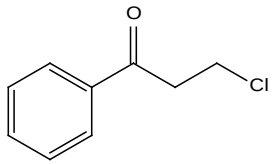

-72.92
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.70
7.69
7.69
7.69
7.69
7.68
7.67
7.67
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.26 CDCl3
1.35
O
CH3
CH3
CH3
1.90
2.93
9.00
f1 (ppm)

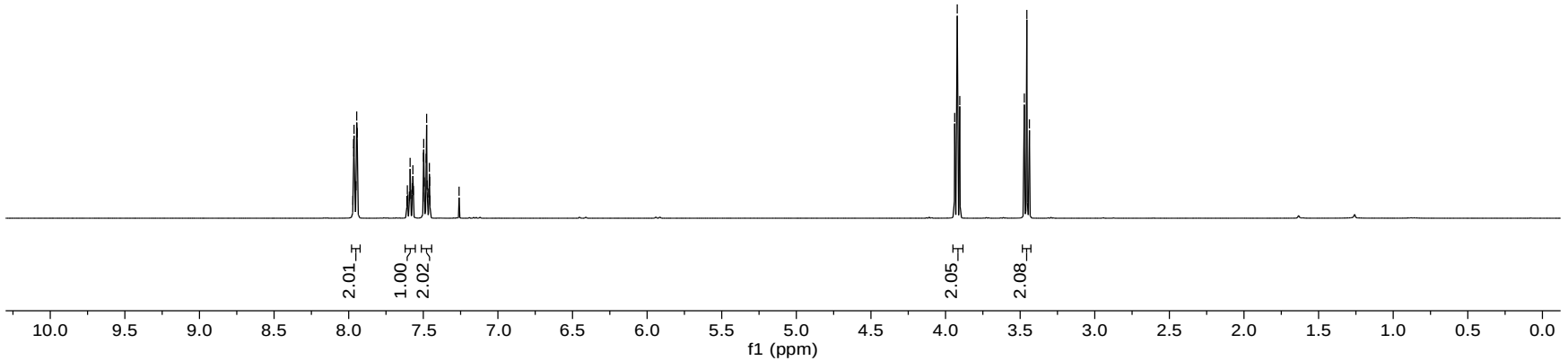
**14k**

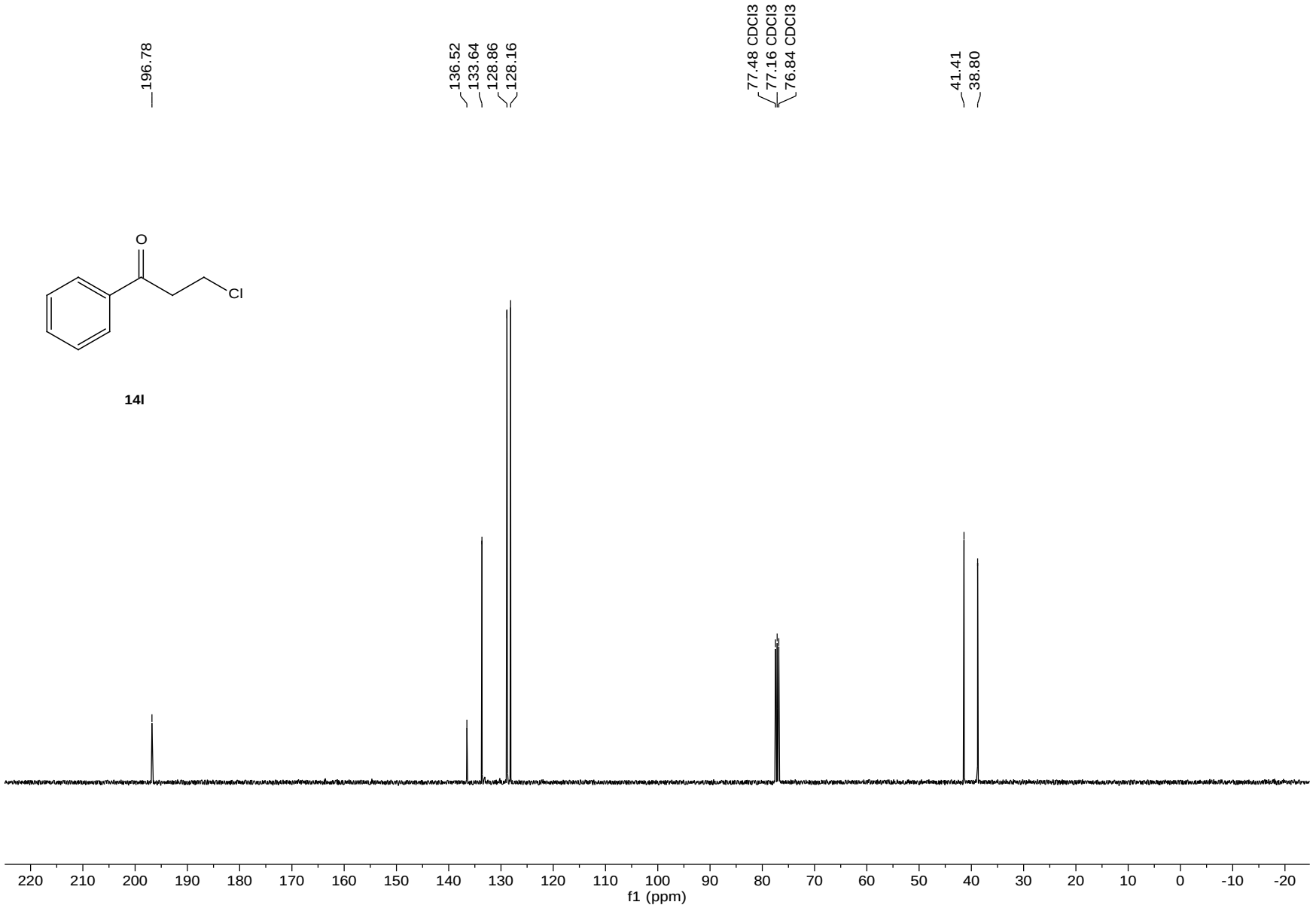

209.39
138.82
130.90
128.17
127.95
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.35
28.16
O
CH3
CH3
CH3
14k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.97
7.97
7.97
7.96
7.95
7.95
7.94
7.61
7.61
7.60
7.59
7.59
7.58
7.57
7.57
7.57
7.50
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.46
7.46
7.26 CDCl3
3.94
3.92
3.90
3.47
3.46
3.44


O
Cl

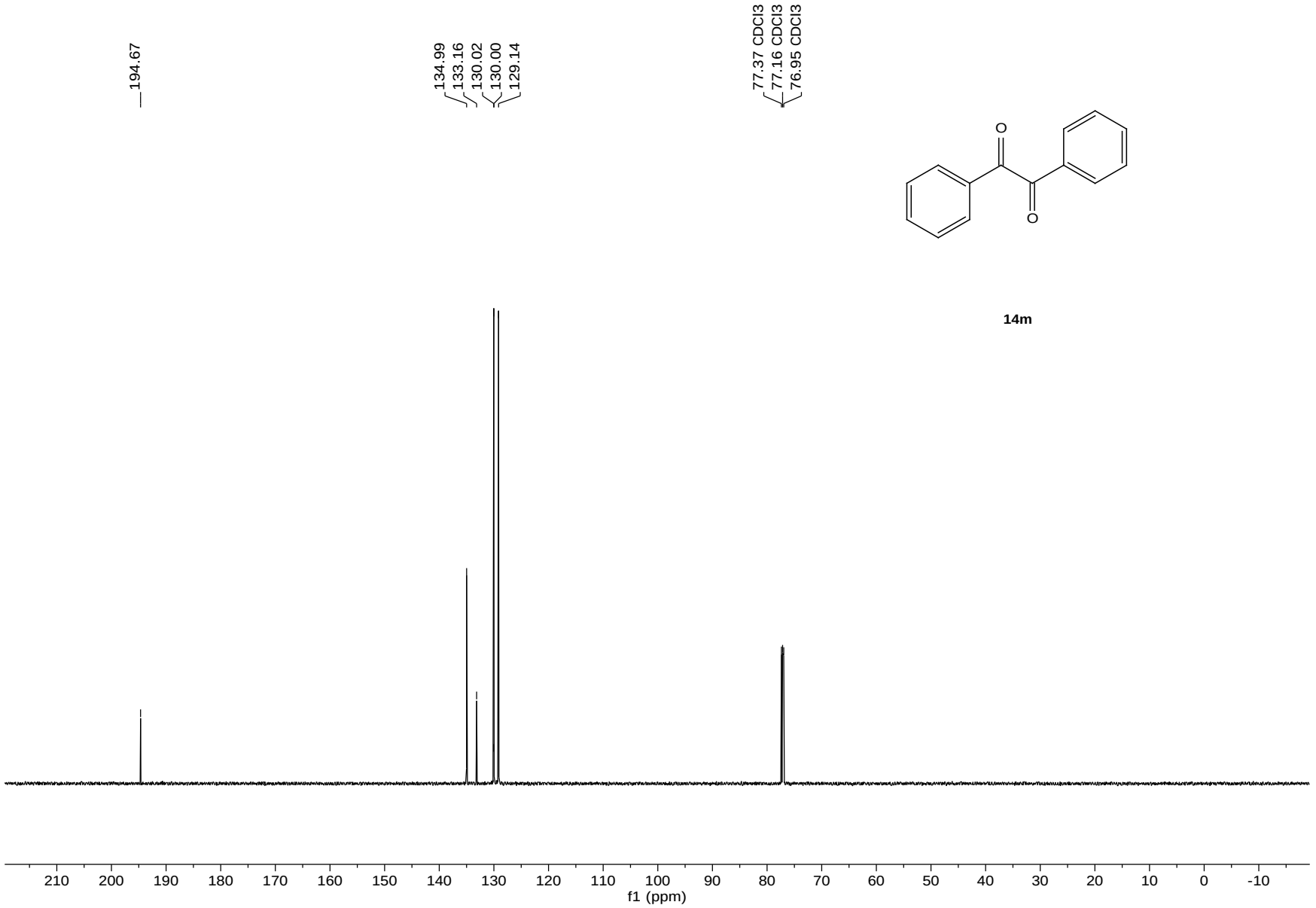
**14l**


2.01
1.00
2.02
2.05
2.08
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
f1 (ppm)


196.78
136.52
133.64
128.86
128.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.41
38.80
O
Cl
14l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

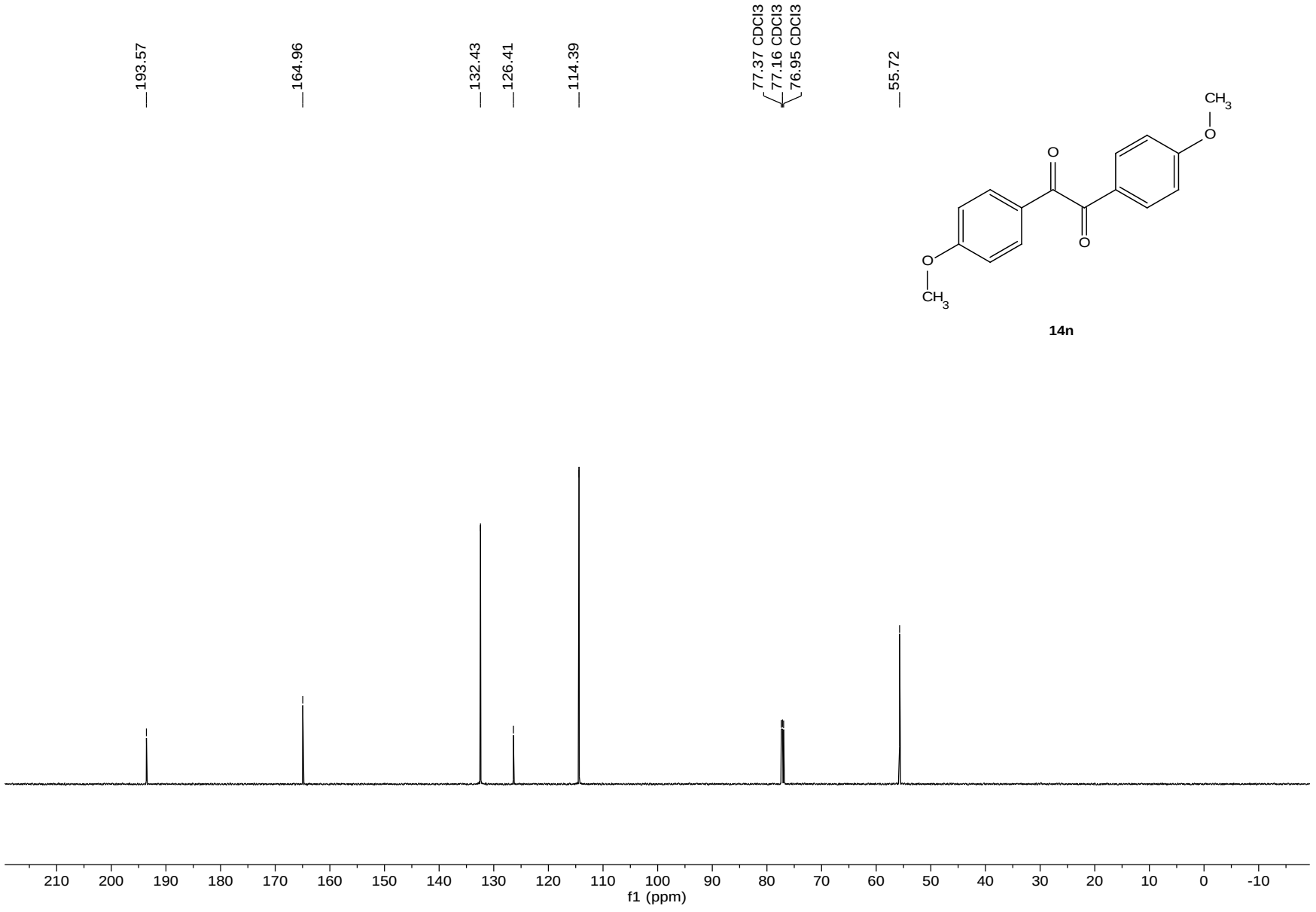

7.99
7.98
7.97
7.97
7.97
7.66
7.65
7.64
7.52
7.52
7.51
7.50
7.26 CDCl3
O
O
3.95
2.00
4.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**14m**

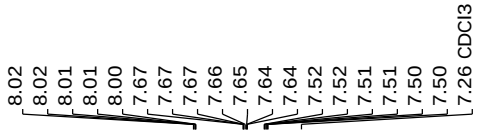

194.67
134.99
133.16
130.02
130.00
129.14
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
O
O
14m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

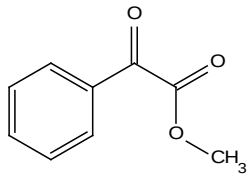

7.94
7.93
7.93
7.92
7.92
7.92
7.26 CDCl3
6.96
6.96
6.95
6.95
6.94
6.94
3.86
O
O
O
O
CH3
CH3
3.84
3.84
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

**14n**

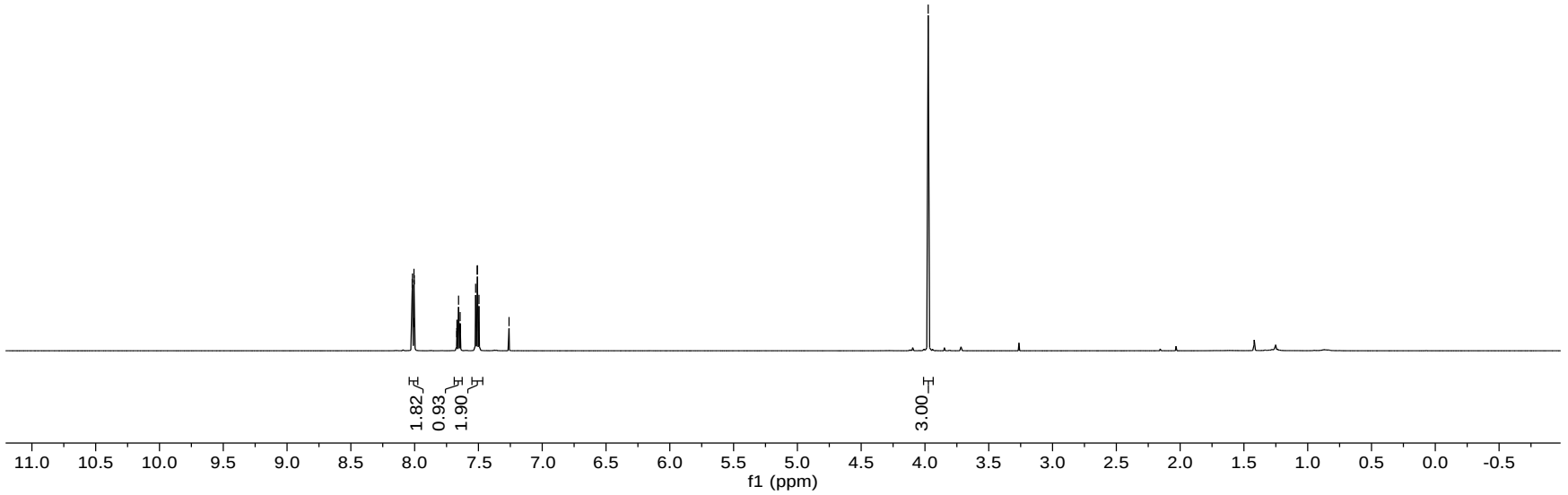

193.57
164.96
132.43
126.41
114.39
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
55.72
O
O
O
O
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

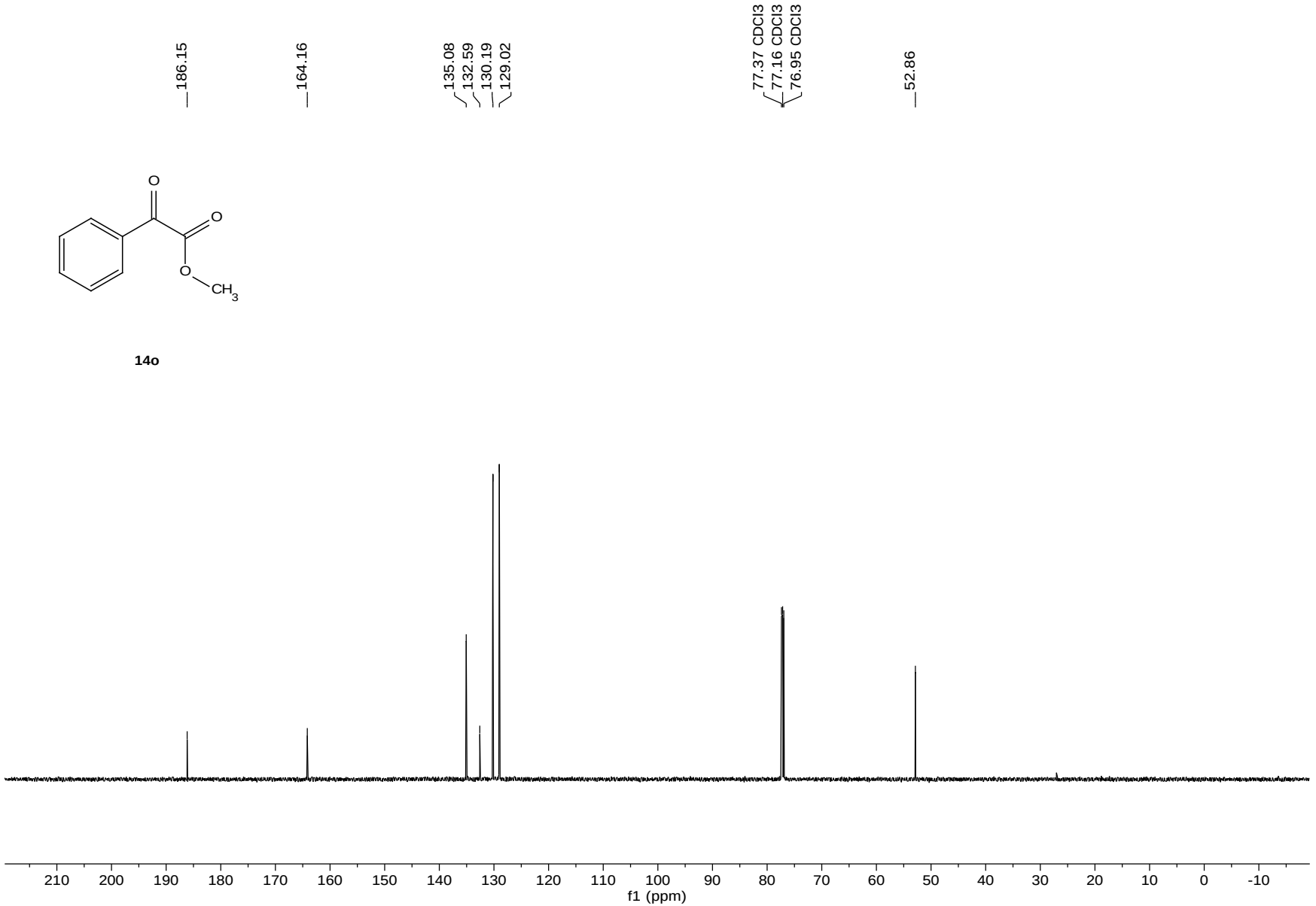
**14n**


8.02
8.02
8.01
8.01
8.00
7.67
7.67
7.67
7.66
7.65
7.64
7.64
7.52
7.52
7.51
7.51
7.50
7.50
7.26 CDCl3
3.97

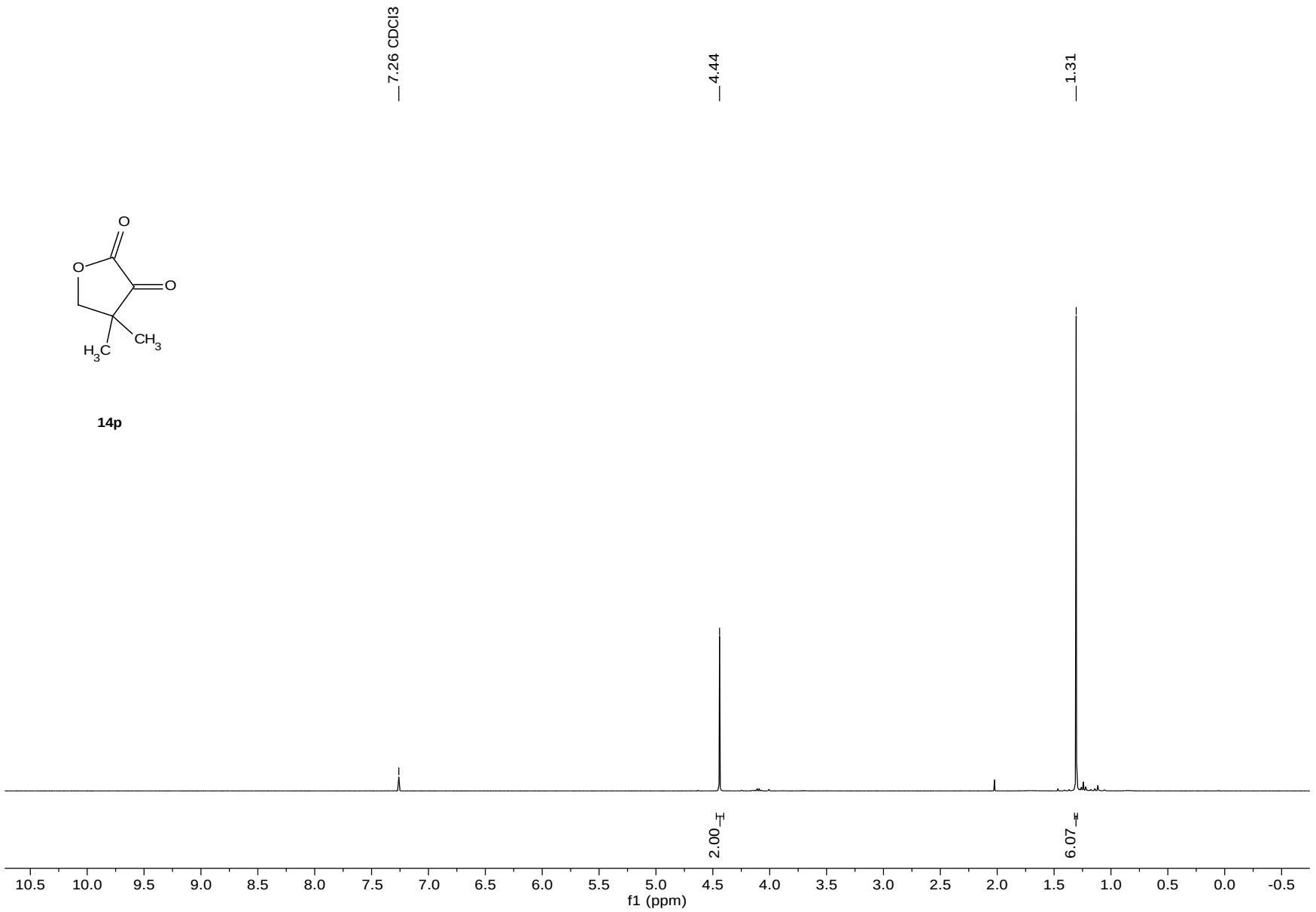

O
O
O
CH3

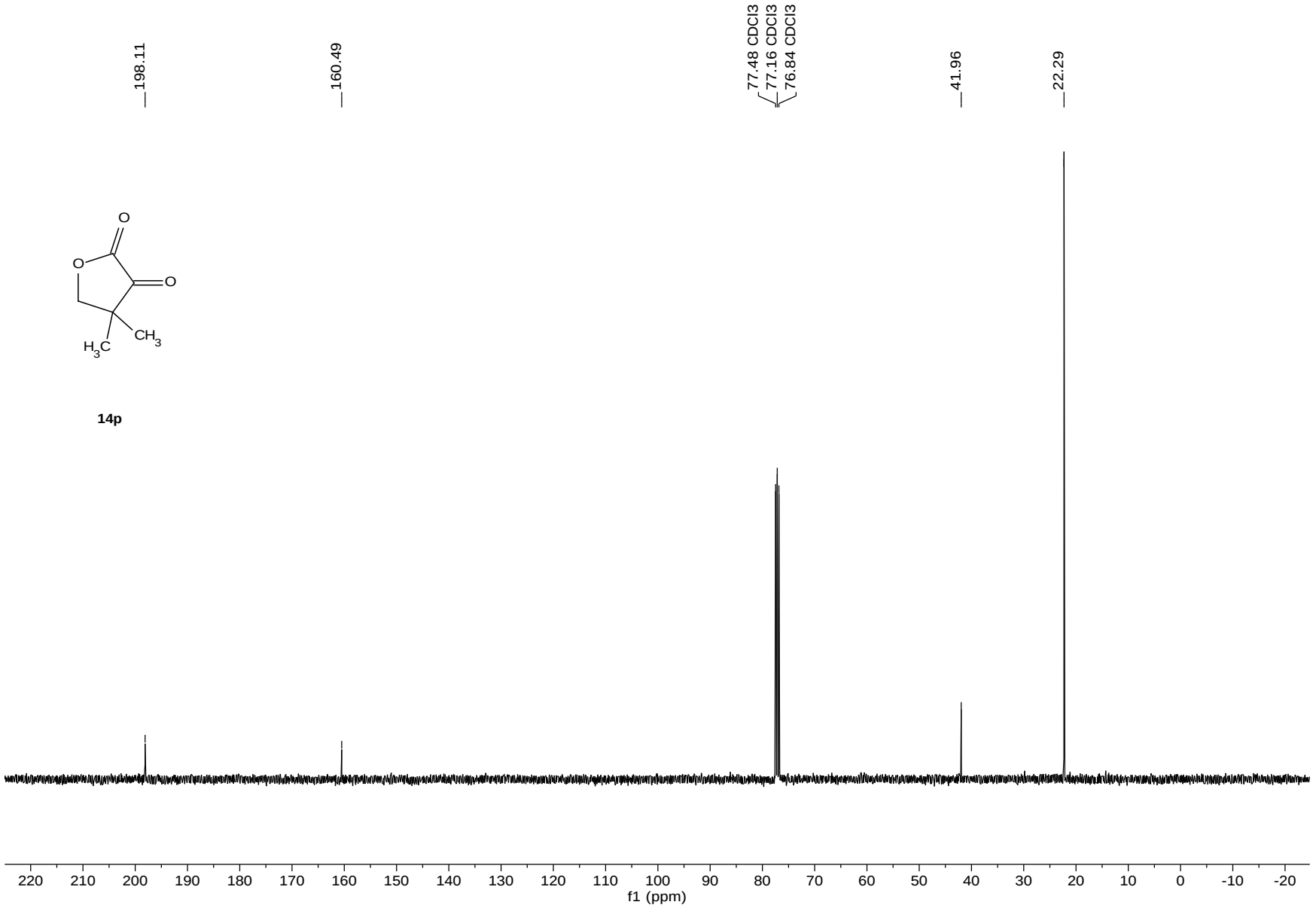
**14o**

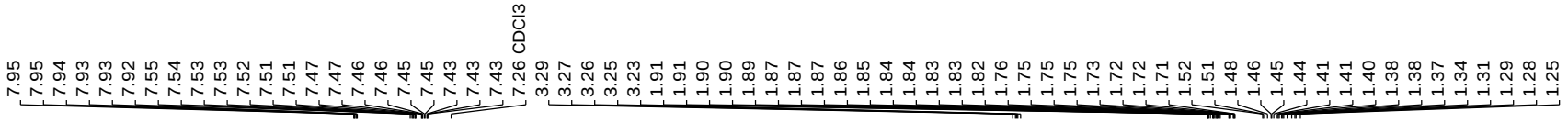

1.82
0.93
1.90
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

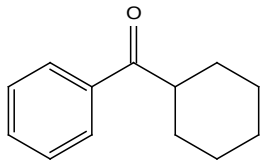

186.15
164.16
135.08
132.59
130.19
129.02
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
52.86
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**14o**

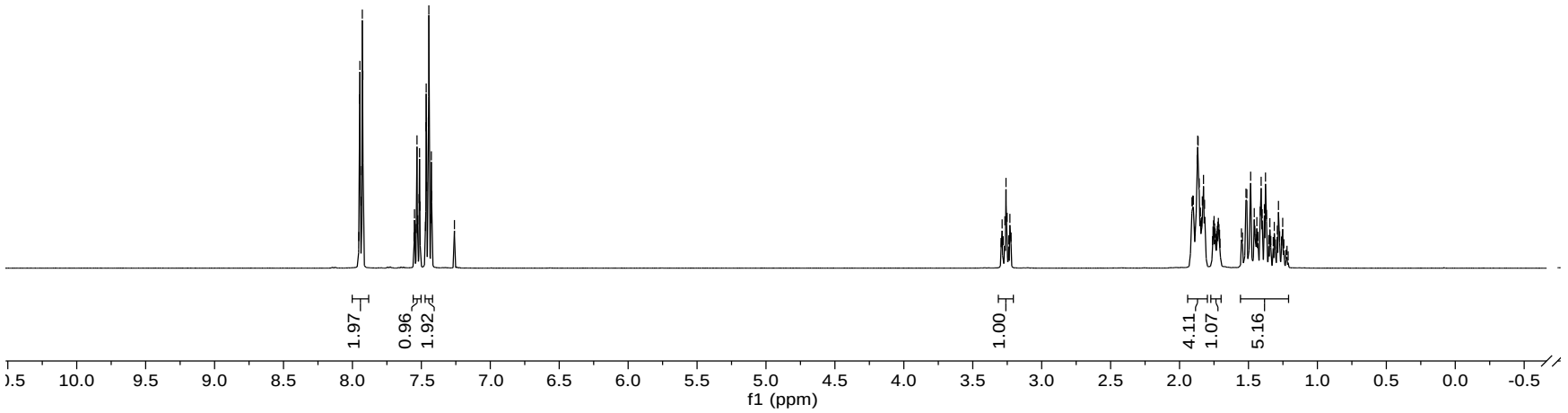

7.26 CDCl3
4.44
1.31
O
O
O
H3C
CH3
14p
2.00
6.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

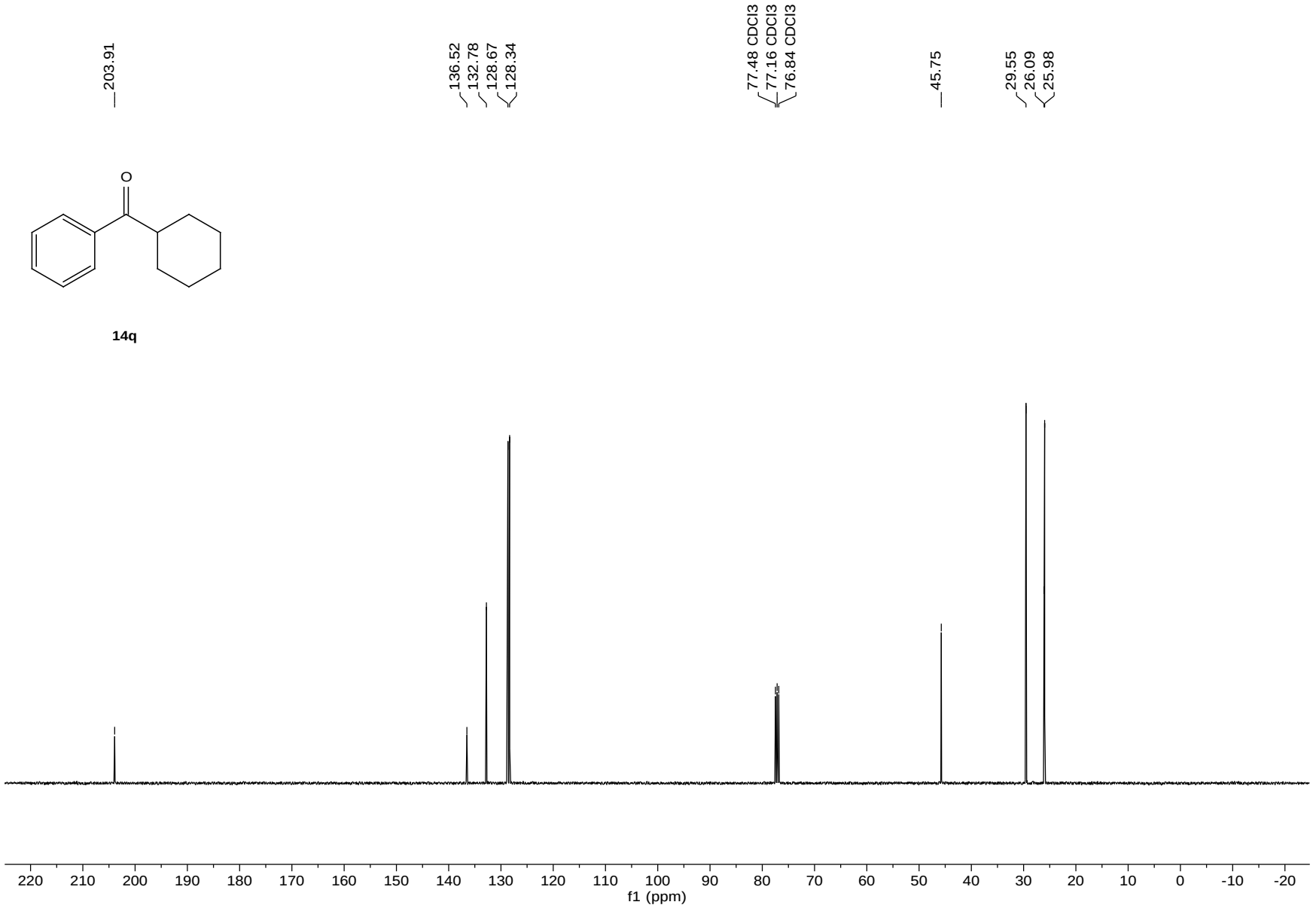

198.11
160.49
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
41.96
22.29
O
O
O
H3C
CH3
14p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

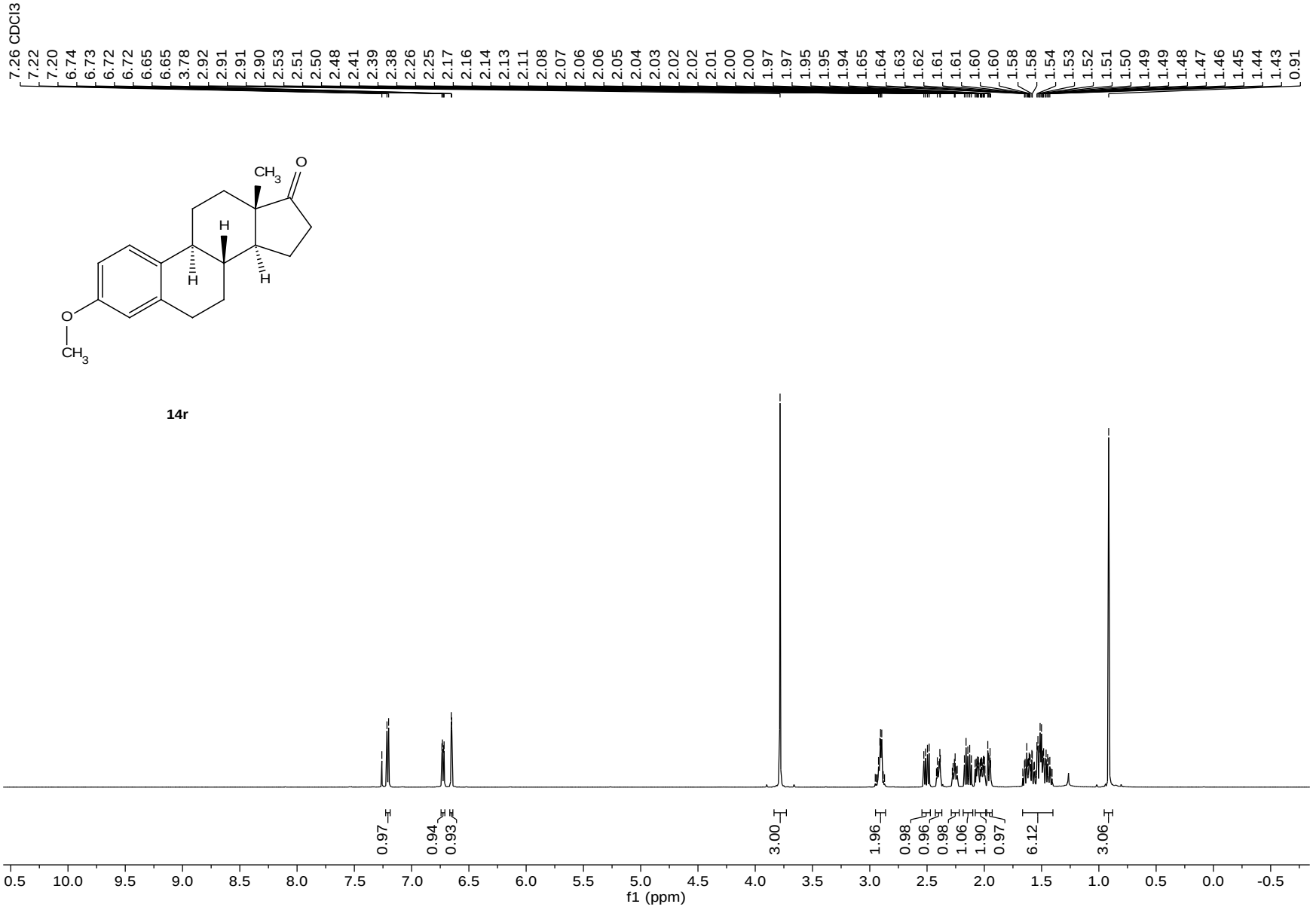

7.95
7.95
7.94
7.93
7.93
7.92
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.47
7.47
7.46
7.46
7.45
7.45
7.43
7.43
7.43
7.26 CDCl3
3.29
3.27
3.26
3.25
3.23
1.91
1.91
1.90
1.90
1.89
1.87
1.87
1.87
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.76
1.75
1.75
1.75
1.73
1.72
1.72
1.71
1.52
1.51
1.48
1.46
1.45
1.44
1.41
1.41
1.40
1.38
1.38
1.37
1.34
1.31
1.29
1.28
1.25

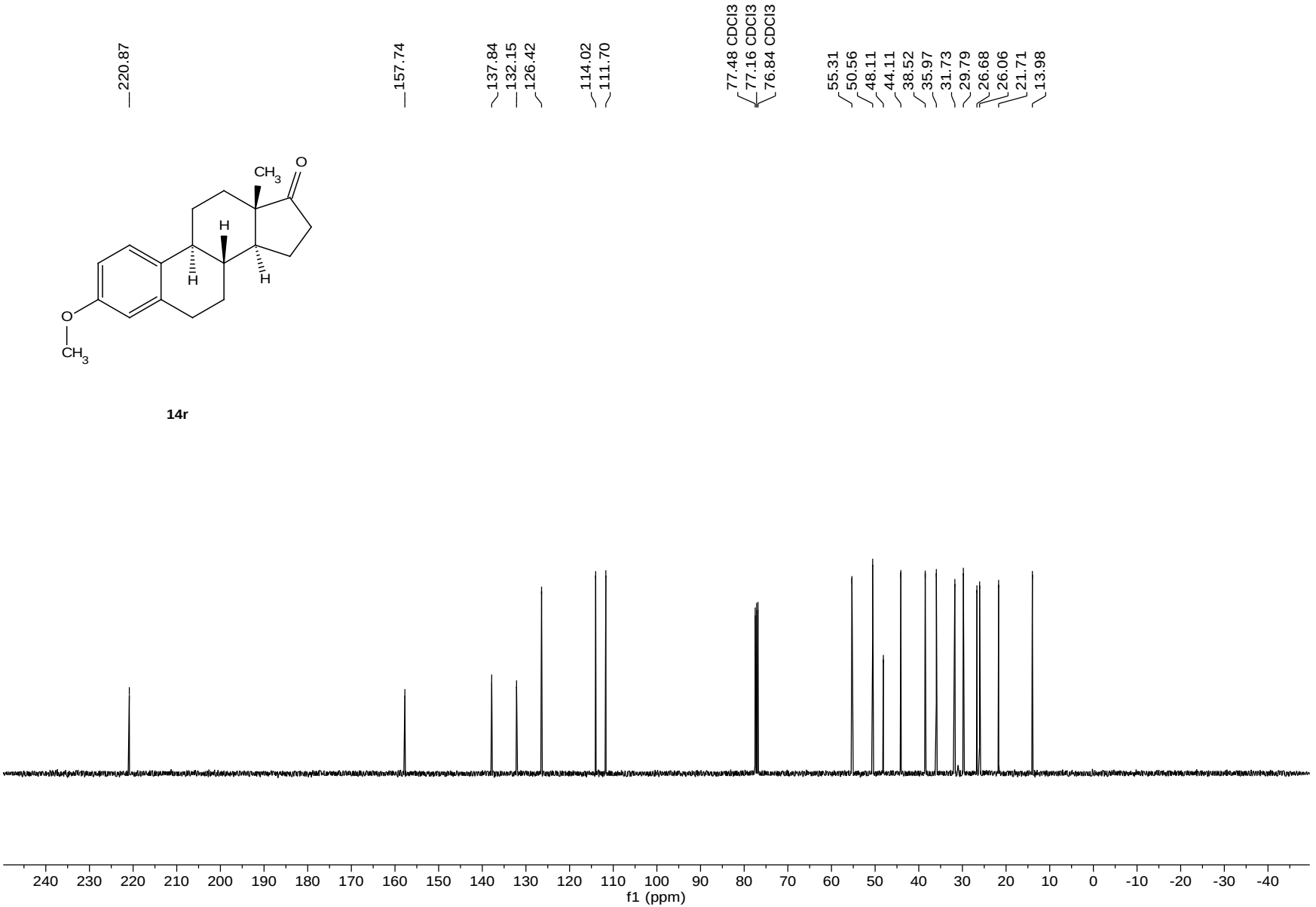

O

**14q**

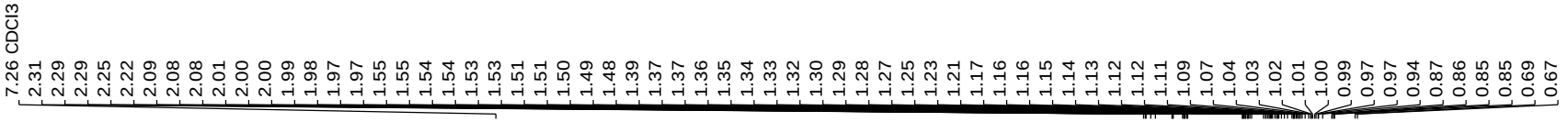

1.97
0.96
1.92
1.00
4.11
1.07
5.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

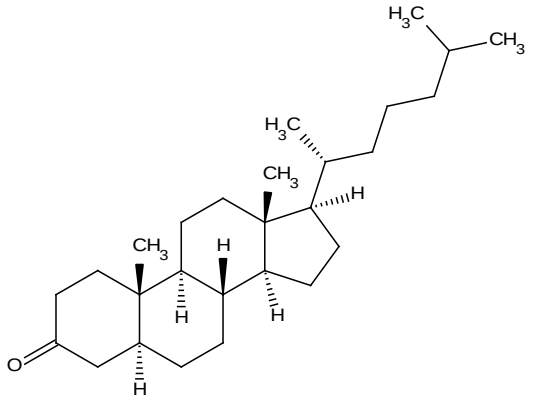

203.91
136.52
132.78
128.67
128.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
45.75
29.55
26.09
25.98
O
14q
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.26 CDCl3
7.22 7.20 6.74 6.73 6.72 6.72 6.65 6.65 3.78 2.92 2.91 2.91 2.90 2.53 2.51 2.50 2.48 2.41 2.39 2.38 2.26 2.25 2.17 2.16 2.14 2.13 2.11 2.08 2.07 2.06 2.06 2.05 2.04 2.03 2.02 2.02 2.01 2.00 2.00 1.97 1.97 1.95 1.95 1.94 1.65 1.64 1.63 1.62 1.61 1.61 1.60 1.60 1.58 1.58 1.54 1.53 1.52 1.51 1.50 1.49 1.49 1.48 1.47 1.46 1.45 1.44 1.43 0.91
CH3
O
H
H
H
O
CH3
14r
0.97
0.94
0.93
3.00
1.96
0.98
0.96
0.98
1.06
1.90
0.97
6.12
3.06
0.5 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
f1 (ppm)

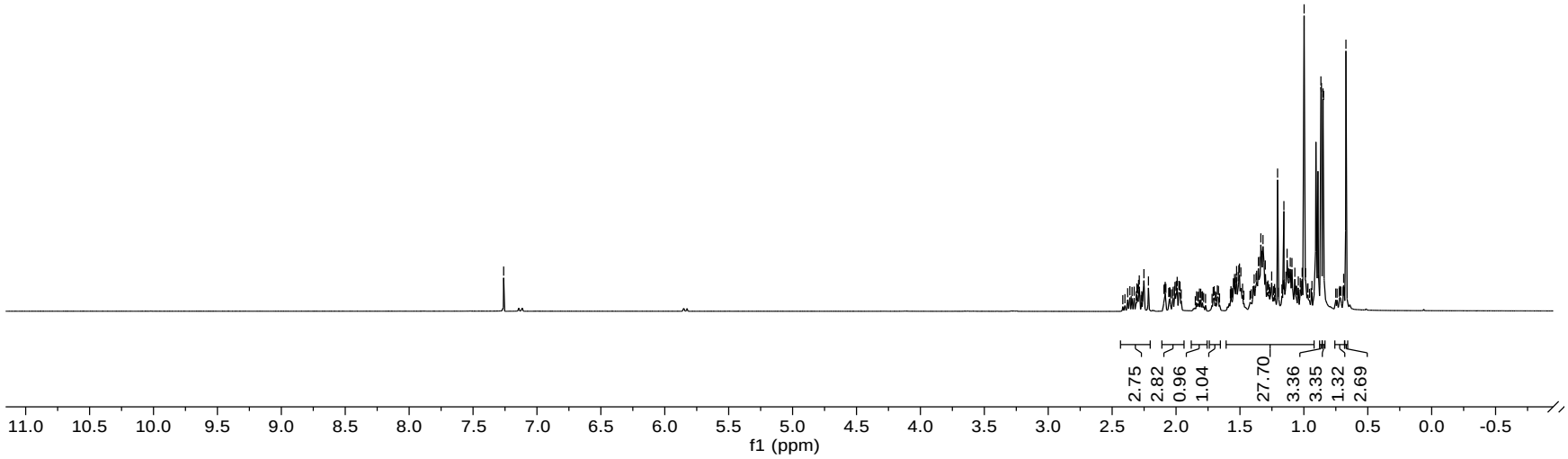

220.87
157.74
137.84
132.15
126.42
114.02
111.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.31
50.56
48.11
44.11
38.52
35.97
31.73
29.79
26.68
26.06
21.71
13.98
CH3
O
H
H
H
O
CH3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

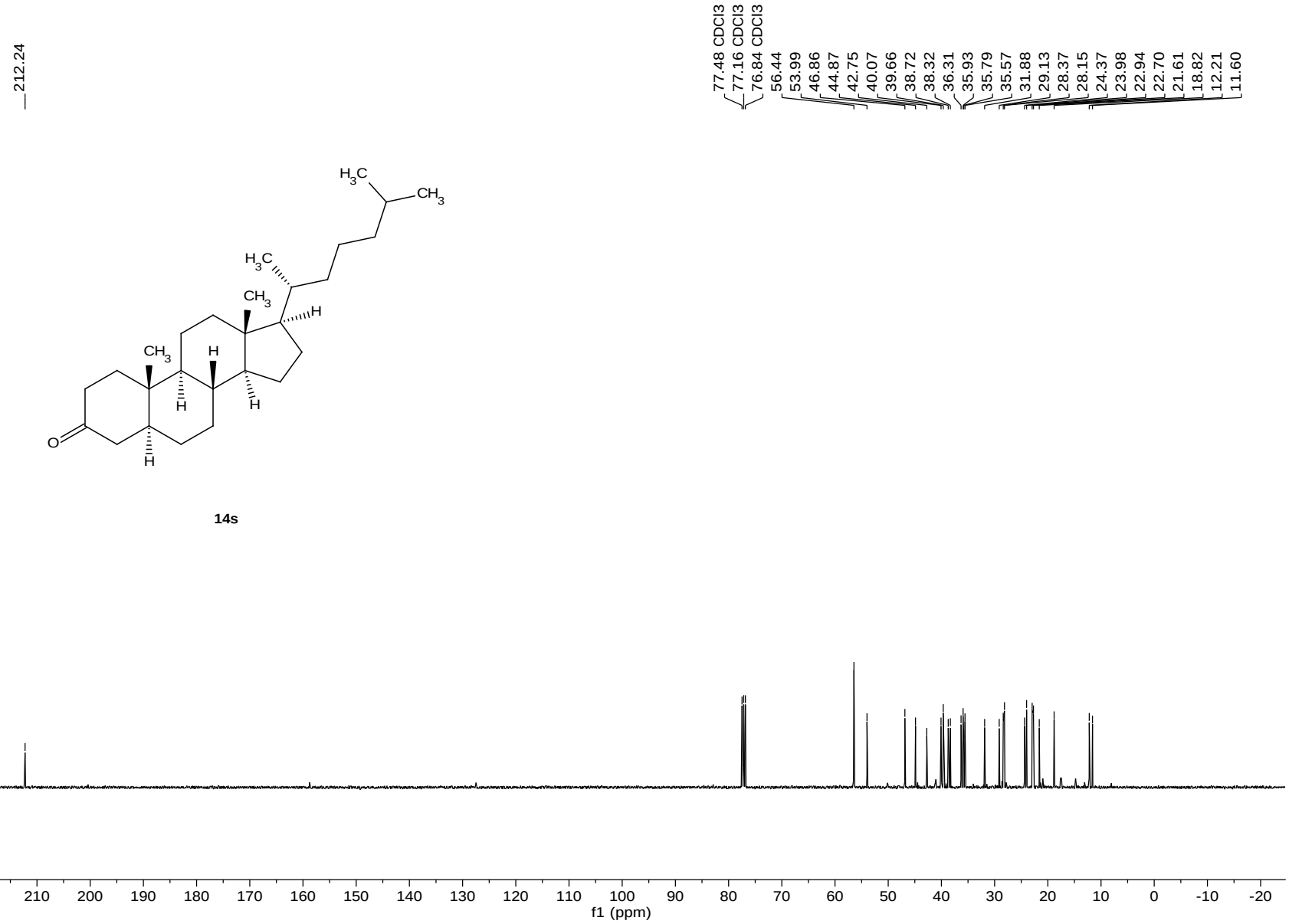
**14r**


7.26 CDCl3
2.31 2.29 2.29 2.25 2.22 2.09 2.08 2.08 2.01 2.00 2.00 1.99 1.98 1.97 1.97 1.55 1.55 1.54 1.54 1.53 1.53 1.51 1.51 1.50 1.49 1.48 1.39 1.37 1.37 1.36 1.35 1.34 1.33 1.32 1.30 1.29 1.28 1.27 1.25 1.23 1.21 1.17 1.16 1.16 1.15 1.14 1.13 1.12 1.12 1.11 1.09 1.07 1.04 1.03 1.02 1.01 1.00 0.99 0.97 0.97 0.94 0.87 0.86 0.85 0.85 0.69 0.67

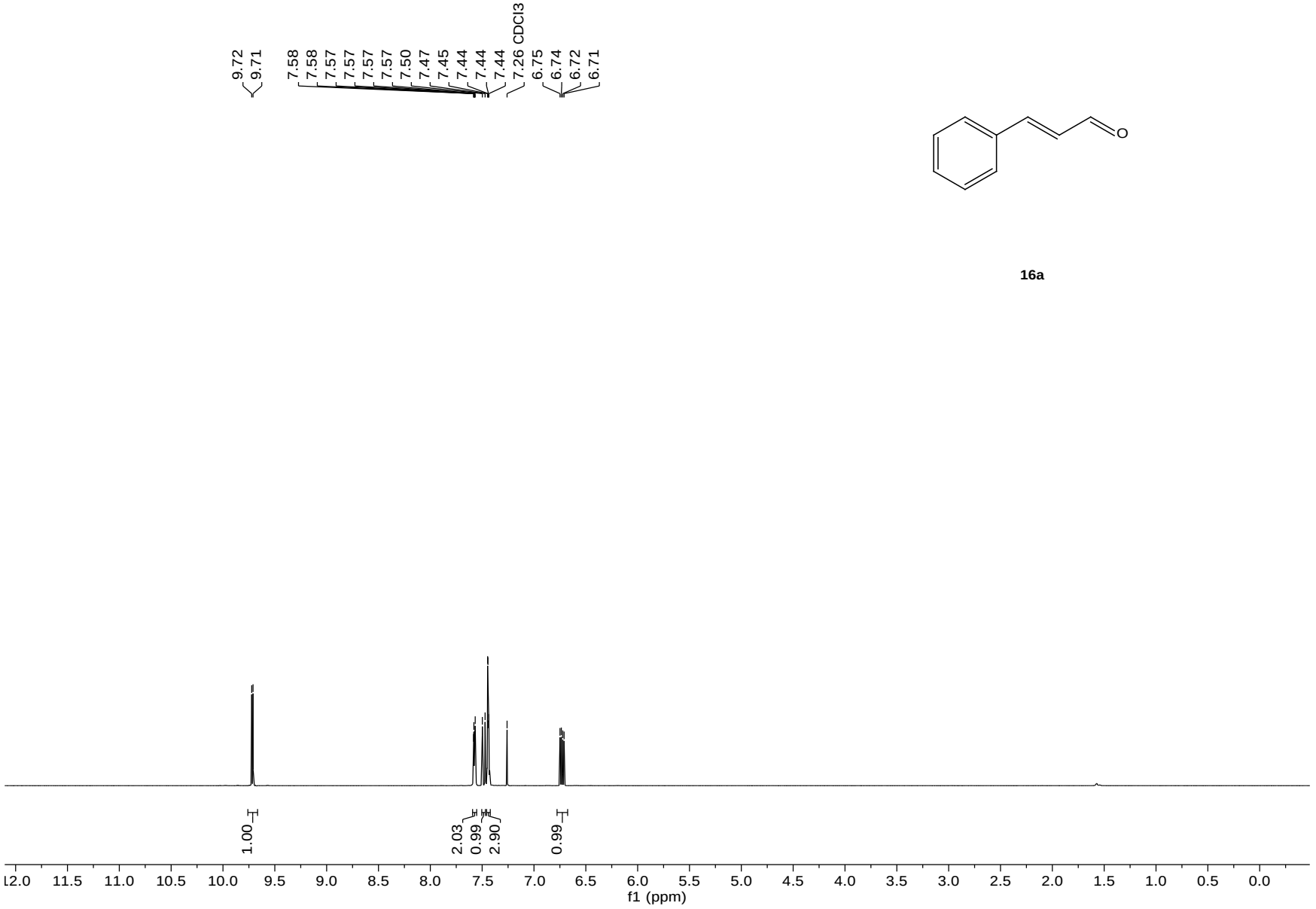

H3C
CH3
H3C
CH3
H
CH3
H
H
H
O
H

**14s**

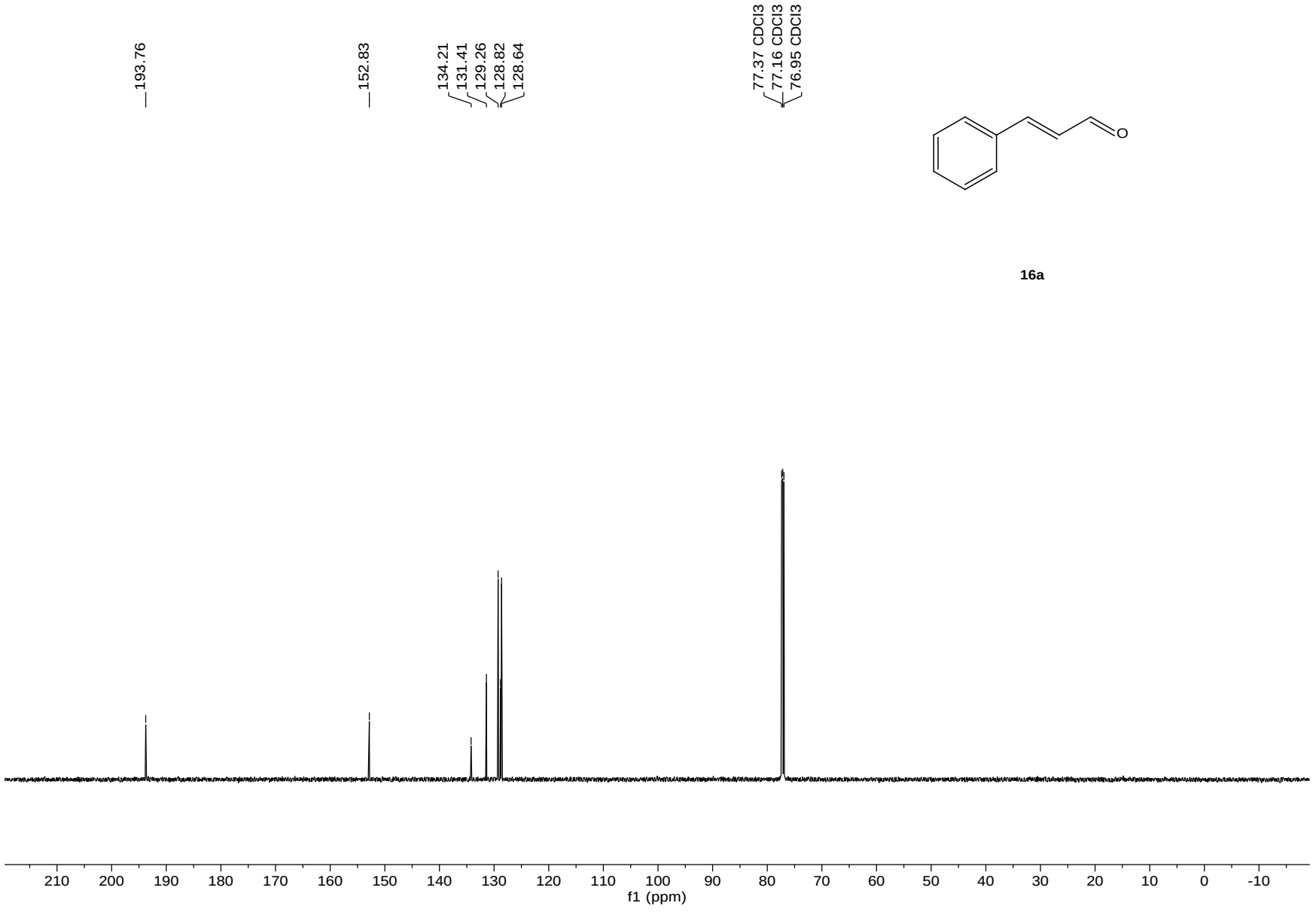

2.75
2.82
0.96
1.04
27.70
3.36
3.35
1.32
2.69
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

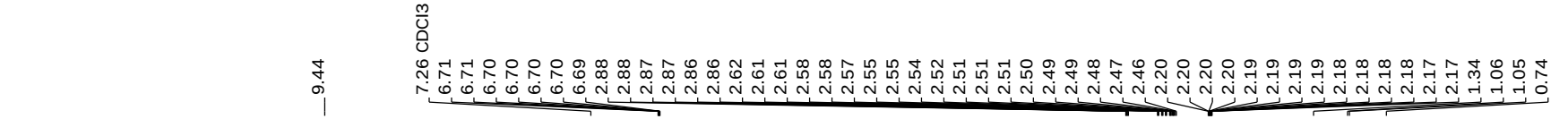

212.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.44
53.99
46.86
44.87
42.75
40.07
39.66
38.72
38.32
36.31
35.93
35.79
35.57
31.88
29.13
28.37
28.15
24.37
23.98
22.94
22.70
21.61
18.82
12.21
11.60
H3C
CH3
H3C
CH3
H
CH3
H
H
H
H
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

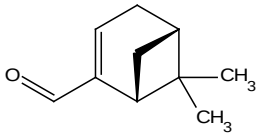
**14s**


9.72
9.71
7.58
7.58
7.57
7.57
7.57
7.57
7.50
7.47
7.45
7.44
7.44
7.44
7.26 CDCl3
6.75
6.74
6.72
6.71
O
1.00
2.03
0.99
2.90
0.99
12.0
11.5
11.0
10.5
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
f1 (ppm)

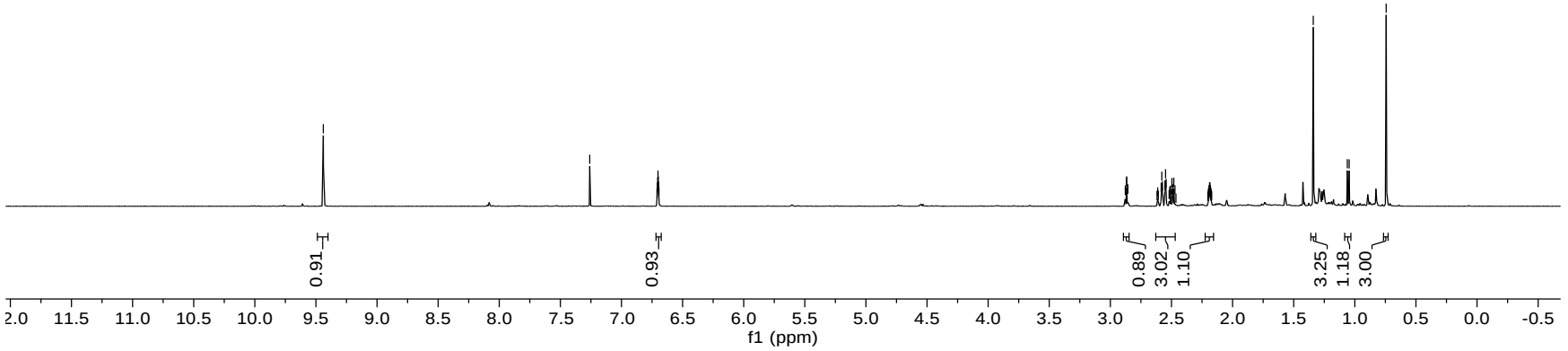
**16a**

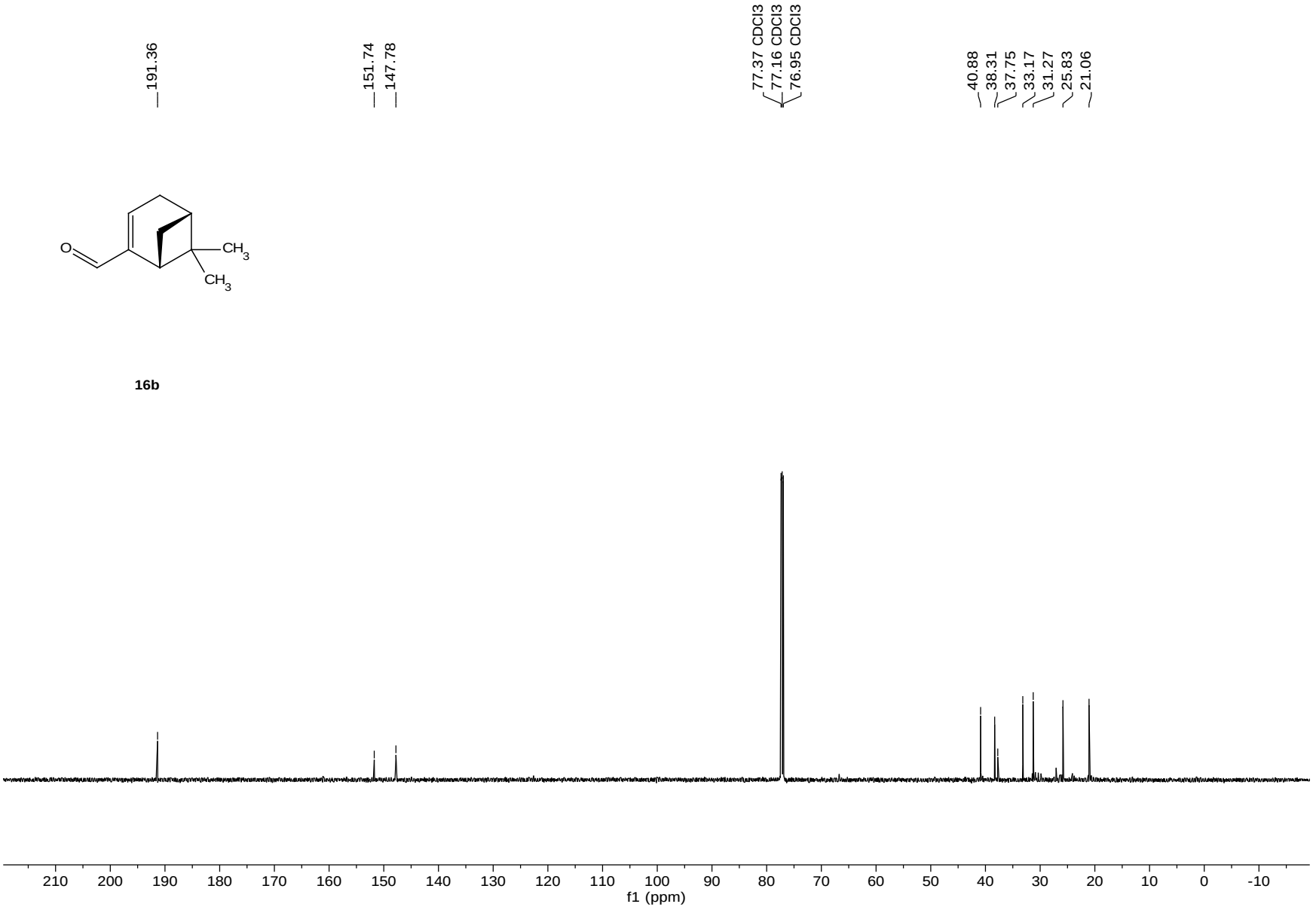

193.76
152.83
134.21
131.41
129.26
128.82
128.64
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
O
16a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.44
7.26 CDCl3
6.71
6.71
6.70
6.70
6.70
6.70
6.69
2.88
2.88
2.87
2.87
2.86
2.86
2.62
2.61
2.61
2.58
2.58
2.57
2.55
2.55
2.54
2.52
2.51
2.51
2.51
2.50
2.49
2.49
2.48
2.47
2.46
2.20
2.20
2.20
2.19
2.19
2.19
2.19
2.18
2.18
2.18
2.18
2.17
2.17
1.34
1.06
1.05
0.74


O
CH3
CH3

**16b**


0.91
0.93
0.89
3.02
1.10
3.25
1.18
3.00
12.0
11.5
11.0
10.5
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
f1 (ppm)


191.36
151.74
147.78
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
40.88
38.31
37.75
33.17
31.27
25.83
21.06
O
CH3
CH3
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)

**16b**