Direct Remote δ-C(sp^2)-H olefination of β-Aryl Substituted Aliphatic Aldehydes *via* Palladium/Enamine Co-catalysis

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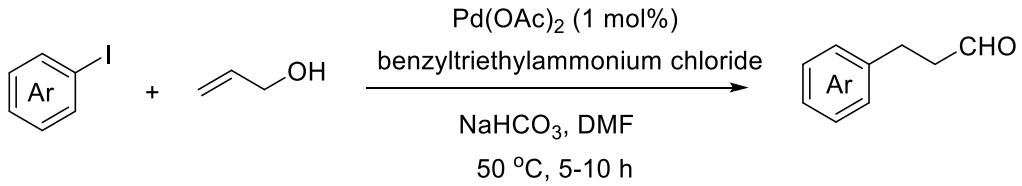
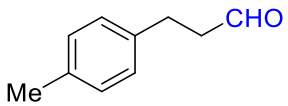
General Information

Unless otherwise noted, all commercially available reagents were purchased from commercial suppliers (Alfa Aesar, Acros, TCI, Innochem, J&K Chemical Co., Accela, Aladdin, Laajoo, 3A chemical, and Sinopharm), and were used directly without further purifications. Hexafluoro-2-propanol (HFIP) was purchased from Chem Greatwall and used as received. HOAc was distilled from P_2O_5. Unless otherwise noted, reactions for C-H functionalization were run under oxygen atmosphere and for synthesis of starting material under nitrogen atmosphere. The reaction vessels used for C–H functionalization were 37 mL pressure tube of Synthware. Purification of products was performed with Sepaflash column chromatography by Santai Technology or preparative thin layer chromatography. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (377 MHz) spectra were recorded in $CDCl_3$ or d6-Acetone (C_3D_6O) solutions using a Bruker AVANCE 400 spectrometer. Calibration was done using tetramethylsilane 0 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR, acetone (2.05 ppm for 1H NMR and 206.7, 29.9 ppm for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, dd = doublet of doublets and td = triplet of doublets. Coupling constants, *J*, were reported in Hertz unit (Hz) HRMS were performed by the Shanghai Mass Spectrometry Center in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument: Thermo Fisher Scientific LTQ FT Ultra, Operation Mode: ESI positive ion mode). Melting points were measured with SWG X-4 digital point apparatus and uncorrected. IR spectra were recorded using Bruker-Vertex 70 instrument.

Preparation and characterization of the aldehydes used as starting material (1b-1i, 1k-1m, 1o-1s, 1u-1v and 1aa)[1a]



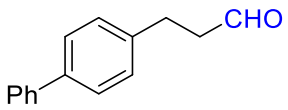
General procedure (A): In a nitrogen-filled glove box, a 100 mL Schlenk tube equipped with a stir bar was charged with substituted iodobenzene (5.0 mmol), $Pd(OAc)_2$ (0.0113g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389g, 1.0 equiv) and $NaHCO_3$ (1.050g, 2.5 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then allyl alcohol (0.4356g, 1.5 equiv.) and DMF (20.0 mL) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 50 °C for 5-10 h. Upon cooling to room temperature, the reaction mixture was filtrated through a pad of silica gel, washed with 50 mL of ethyl acetate and washed twice with water (20.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to provide the corresponding product in 50-80 % yields.



1b

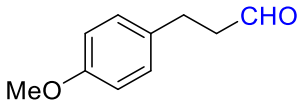
3-(*p*-tolyl)propanal (1b)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 4-iodotoluene (1.0902 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1b** was obtained as colorless liquid. **^{1}H NMR** (400 MHz, acetone-d_6): δ 9.78 (s, 1H), 7.15-7.09 (m, 4H), 2.91 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H),

2.29 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 201.3, 137.9, 135.2, 129.0, 128.2, 45.0, 27.4 and 20.1



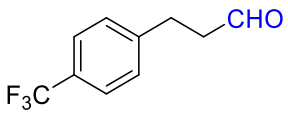
1c

3-([1,1'-biphenyl]-4-yl)propanal (1c)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 4-iodo-1,1'-biphenyl (1.4005 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1c** was obtained as milky white oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.31-7.29 (m, 2H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.6, 140.9, 139.4, 139.3, 128.8, 128.7, 127.4, 127.2, 127.0, 45.3 and 27.4



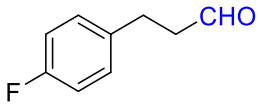
1d

3-(4-methoxyphenyl)propanal (1d)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-iodo-4-methoxybenzene (1.1702 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 3% EtOAc /97% hexane), the product **1d** was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.8, 158.1, 132.4, 129.3, 113.9, 55.2, 45.5 and 27.3



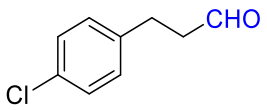
1e

3-(4-(trifluoromethyl)phenyl)propanal (1e)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-iodo-4-(trifluoromethyl)benzene (1.3600 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50°C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1e** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, Acetone-d_6): δ 9.80 (s, 1H), 7.64 (J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 2.88 (t, J = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, Acetone-d_6): δ 200.7, 145.9, 129.1, 127.9 (d, J_{C-F} = 32.4 Hz), 125.9 (d, J_{C-F} = 271.3 Hz), 125.2 (q, J_{C-F} = 3.8 Hz), 44.4 and 27.5; **^{19}F NMR** (377 MHz, Acetone-d_6): δ -62.8



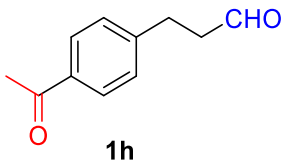
1f

3-(4-fluorophenyl)propanal (1f)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-fluoro-4-iodobenzene (1.1100 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1f** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, Acetone-d_6): δ 9.77 (s, 1H), 7.30-7.25 (m, 2H), 7.06 (d, J = 8.7 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, Acetone-d_6): δ 201.1, 162.5 (d, J_{C-F} = 242.6 Hz), 137.1 (d, J_{C-F} = 3.1 Hz), 130.1 (d, J_{C-F} = 7.8 Hz), 115.0 (d, J_{C-F} = 21.2 Hz), 44.9, 26.9; **^{19}F NMR** (377 MHz, Acetone-d_6): δ -118.8



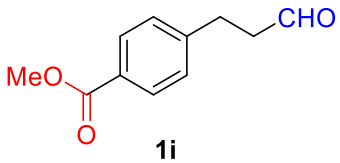
1g

3-(4-chlorophenyl)propanal (1g)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-choloro-4-iodobenzene (1.1923 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1g** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.25 (*J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.1, 138.9, 131.9, 129.9, 128.6, 45.1 and 27.4



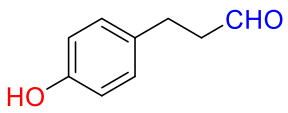
1h

3-(4-acetylphenyl)propanal (1h)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-(4-iodophenyl)ethan-1-one (1.2302 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 5% EtOAc /95% hexane), the product **1h** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.90 (*J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.9, 197.7, 146.2, 135.3, 128.7, 128.6, 44.7, 27.9 and 26.5



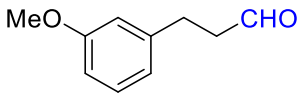
1i

methyl 4-(3-oxopropyl)benzoate (1i)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with methyl 4-iodobenzoate (1.3102 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 8% EtOAc /92% hexane), the product **1i** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.97 (*J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.9, 166.9, 145.9, 129.9, 128.4, 128.3, 52.0, 44.8 and 27.9



1k

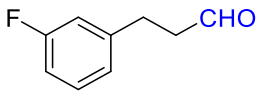
3-(4-hydroxyphenyl)propanal (1k)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 4-iodophenol (1.1000 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1k** was obtained as pale-yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.03 (*J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.18 (br, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.2, 154.2, 132.1, 129.4, 115.5, 45.5 and 27.3



1l

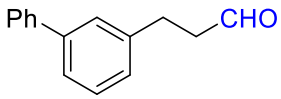
3-(3-methoxyphenyl)propanal (1l)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 3-iodoanisole (1.1702 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel

(Eluent: (3% EtOAc /97% hexane), the product **1l** was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.26 (t, *J* = 8.7 Hz, 1H), 6.82 (m, 3H), 3.82 (s, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.6, 159.8, 141.9, 129.6, 120.6, 114.2, 111.5, 55.2, 45.2, 28.2



1m

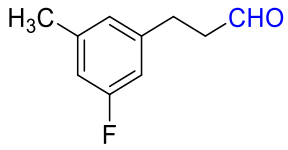
3-(3-fluorophenyl)propanal (1m)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-fluoro-3-iodobenzene (1.1100 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1m** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.30-7.24 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 9.4 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 164.1 (d, J_{C-F} = 245.4 Hz), 142.9 (d, J_{C-F} = 7.3 Hz), 130.1 (d, J_{C-F} = 8.7 Hz), 124.0 (d, J_{C-F} = 2.8 Hz), 115.3 (d, J_{C-F} = 21.8 Hz), 113.3 (d, J_{C-F} = 20.9 Hz), 44.9, 27.8 (d, J_{C-F} = 1.7 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$): δ -113.3



1n

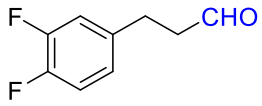
3-([1,1'-biphenyl]-3-yl)propanal (1n)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 3-iodo-1,1'-biphenyl (1.40 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 1% EtOAc /99% hexane), the product **1n** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.55 – 7.53 (m, 2H), 7.41 – 7.37 (m, 4H), 7.33-7.28 (m, 2H), 7.16 – 7.08 (m, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.73 (td, *J* = 7.6, 1.3 Hz, 2H); **^{13}C NMR** (100

MHz, $CDCl_3$): δ 201.4, 141.4, 140.9, 140.8, 128.9, 128.7, 127.2, 127.1, 127.1, 127.0, 125.1, 45.1, 28.0.



1p

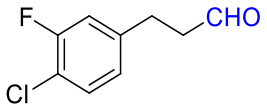
3-(3-fluoro-5-methylphenyl)propanal (1p)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-fluoro-3-iodo-5-methylbenzene (1.1801 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1p** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 6.80 (s, 1H), 6.74 (t, J = 8.8 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 164.1 (d, $J_{C\text{-}F}$ = 242.6 Hz), 142.5 (d, $J_{C\text{-}F}$ = 7.8 Hz), 140.5 (d, $J_{C\text{-}F}$ = 8.1 Hz), 124.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 113.9 (d, $J_{C\text{-}F}$ = 20.7 Hz), 112.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 44.9, 27.7 and 21.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -114.5



1q

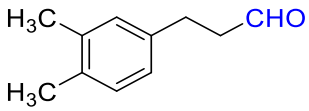
3-(3,4-difluorophenyl)propanal (1q)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1,2-difluoro-4-iodobenzene (1.1999 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1q** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.10-6.98 (m, 2H), 6.93-6.90 (m, 1H), 2.94 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.7, 151.5 (dd, $J_{1C\text{-}F}$ = 247.7 Hz, $J_{2C\text{-}F}$ = 12.8 Hz), 150.2 (dd, $J_{1C\text{-}F}$ = 247.6 Hz, $J_{2C\text{-}F}$ = 12.7 Hz), 137.5 (dd, $J_{1C\text{-}F}$ = 5.6 Hz,

J_{2C-F} = 3.9 Hz), 124.3 (dd, J_{1C-F} = 6.1 Hz, J_{2C-F} = 3.6 Hz), 117.3 (dd, J_{1C-F} = 17.0 Hz, J_{2C-F} = 5.0 Hz), 44.9, 27.2 ; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -137.9 (d, J_{C-F} = 21.6), -141.6 (d, J_{C-F} = 21.6)



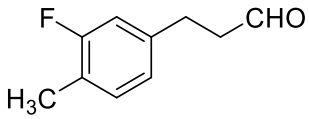
1r

3-(4-chloro-3-fluorophenyl)propanal (1r)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 1-chloro-2-fluoro-4-iodobenzene (0.933 g, 5 mmol), $Pd(OAc)_2$ (0.0113g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1r** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 6.98 (dd, *J* = 10.0, 1.9 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 2.92 (d, *J* = 8.3 Hz, 2H), 2.78 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.5, 159.0 (d, J_{C-F} = 248.1 Hz), 141.4 (d, J_{C-F} = 6.5 Hz), 130.3, 124.7 (d, J_{C-F} = 3.6 Hz), 118.4 (d, J_{C-F} = 18.4 Hz), 116.5 (d, J_{C-F} = 19.6 Hz), 44.5 and 27.1; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -115.7



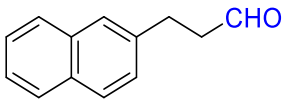
1s

3-(3,4-dimethylphenyl)propanal (1s)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 4-iodo-1,2-dimethylbenzene (1.1603 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1s** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.0, 137.8, 136.8, 134.5, 129.9, 129.7, 125.7, 45.5, 27.7, 19.8 and 19.4



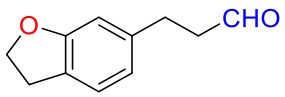
1t

3-(3-fluoro-4-methylphenyl)propanal (1t)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 2-fluoro-4-iodo-1-methylbenzene (1.1801g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 3% EtOAc /97% hexane), the product **1t** was obtained as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.13 (t, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 162.5 (d, J_{C-F} = 244.1 Hz), 140.0 (d, J_{C-F} = 7.5 Hz), 131.5 (d, J_{C-F} = 5.7 Hz), 123.7 (d, J_{C-F} = 3.1 Hz), 122.7 (d, J_{C-F} = 17.0 Hz), 114.9 (d, J_{C-F} = 22.1 Hz), 45.1, 27.5 (d, J_{C-F} = 1.4 Hz), 14.2 (d, J_{C-F} = 3.4 Hz ; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -117.6



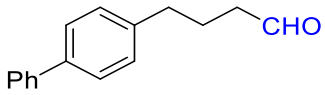
1v

3-(naphthalen-2-yl)propanal (1v)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 2-iodonaphthalene (1.2703 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 10 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **1v** was obtained as pale-yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.77-7.71 (m, 3H), 7.55 (s, 1H), 7.43-7.37 (m, 2H), 7.26 (dd, *J* = 8.4, 1.7, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 3.04 (dt, *J* = 7.6, 1.2 Hz, 2H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.6, 137.9, 133.7, 132.2, 128.3, 127.7, 127.6, 127.0, 126.5,126.2, 125.6, 45.2 and 28.3



1w

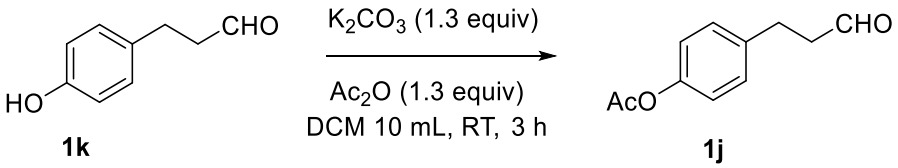
3-(2,3-dihydrobenzofuran-6-yl)propanal (1w)[1a]: This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 5-iodo-2,3-dihydro-1-benzofuran (1.2302 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv.), $NaHCO_3$ (1.050 g, 2.5 equiv.) and allyl alcohol (0.4356 g, 1.5 equiv.) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 3% EtOAc /97% hexane), the product **1w** was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.05 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.59 (t, *J* = 8.7 Hz, 2H), 3.22 (t, *J* = 8.6 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.9, 128.6, 132.2, 127.7, 127.3, 124.9, 109.2, 71.2, 45.8, 29.8 and 27.6



1ab

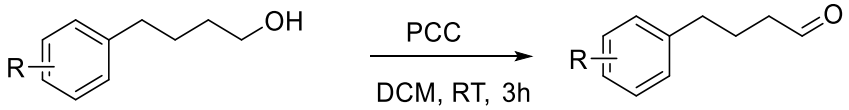
4-([1,1'-biphenyl]-4-yl)butanal (1ab)[1a] : This substrate was prepared using the *general procedure (A)*. The Schlenk tube was charged with 4-iodo-1,1'-biphenyl (1.4006 g, 5 mmol), $Pd(OAc)_2$ (0.0113 g, 0.1 mmol, 1 mol%), benzyltriethylammonium chloride (1.1389 g, 1.0 equiv), $NaHCO_3$ (1.050 g, 2.5 equiv.) and butan-1-ol (0.585 g, 1.5 equiv) in DMF (20.0 mL) and the reaction mixture was stirred at 50 °C for 5 h. After concentration and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /97% hexane), the product **1ab** was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.47 (td, *J* = 7.3, 1.5 Hz, 2H), 1.99 (p, *J* = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.2, 140.9, 140.3, 139.0, 128.8, 128.7, 127.1, 127.1, 126.9, 43.1, 34.6, 23.6. The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[1b].

Synthesis of 4-(3-oxopropyl)phenyl acetate (1k)[2a]

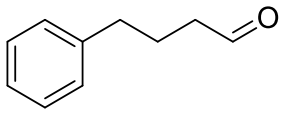


In a 50 mL round bottom flask, 3-(4-hydroxyphenyl)propanal (1.023 g, 3 mmol**),** potassium carbonate (1.3 equiv.) and 10 mL of DCM was added, and then allow the reaction mixture to stir at room temperature for 10 min, thereafter acetic anhydride (1.3 equiv.) was added drop wise and then stir the reaction mixture reaction mixture at room temperature for 3 h. The course of reaction mixture was monitor by TLC (thin layer chromatography). After the completion of reaction potassium carbonate was removed by filtration. After concentration and purification by flash chromatography on silica gel (Eluent: 7% EtOAc /93% hexane), the product **1j** was obtained in a yield of 87% as pale-yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.17 (*J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.4, 169.6, 149.1, 138.0, 129.3, 121.6, 45.1, 27.4 and 21.0.The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[2b].

Synthesis of 4-phenylpropanal derivatives[3]



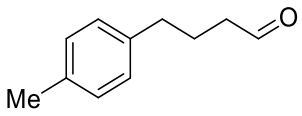
General procedure (B): To a well-stirred solution of substituted 4-phenyl-1-butanol (5 mmol) in dry dichloromethane (15.0 mL) in a 25 mL reaction tube was added Celite (Celite : alcohol = 1:1, wt/wt) and PCC (pyridinium chlorochromate, 2.6945g, 2.5 equiv), and then the reaction mixture was stirred at room temperature for 3 h. After the reaction was finished, the mixture was filtered through a pad of silica gel and washed with 50.0 mL of ethyl acetate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the corresponding product in 60-65 % yields.



1z

Synthesis of 4-phenylbutanal (1z)[3]: This substrate was prepared using the *general procedure (B)* from 4-phenyl-1-butanol (0.8213 g, 5 mmol). After workup and purification of reaction mixture using flash chromatography on silica gel (Eluent: 3% EtOAc /97% hexane) provided **1z** in 64% yield as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.29 (t, *J* = 7.1 Hz, 2H), 7.20-7.15 (m, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.44 (td, *J* = 7.3, 1.5 Hz, 2H), 1.98 (quint, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.3, 141.3, 128.51, 128.50, 126.1, 43.2, 35.0 and 23.7

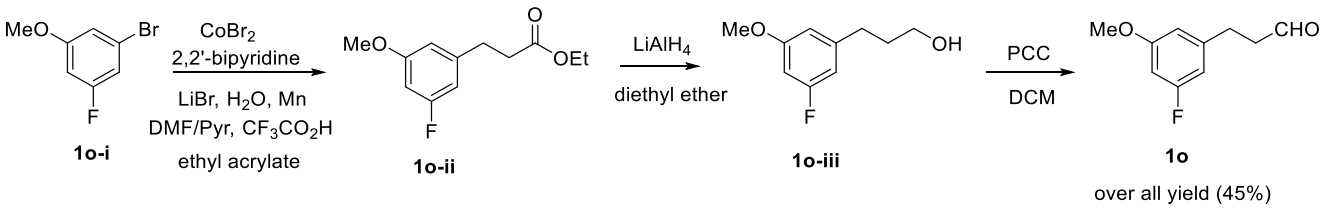
Synthesis of 4-(4-methylphenyl)butan-1-ol (1aa):



1z

Synthesis of 4-phenylbutanal (1aa)[3]: This substrate was prepared using the *general procedure (B)* from 4-(p-tolyl)butan-1-ol (0.8213 g, 5 mmol). After workup and purification of reaction mixture using flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane) provided **1aa** in 67% yield as colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.20-7.14 (m, 4H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.51 (td, *J* = 7.3, 1.8 Hz, 2H), 2.41 (s, 3H), 2.04 (quint, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.5, 138.2, 135.6, 129.2, 128.4, 43.2, 34.6, 23.8 and 21.1

Synthesis of 3-(3-fluoro-5-methoxyphenyl)propanal (1o)[4]

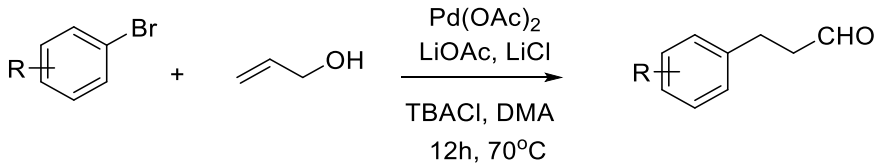


A 50 mL of Schlenk tube was charged with $CoBr_2$ (109 mg, 10 mol %), 2,2'-bipyridine (78 mg, 10 mol%), LiBr (434 mg, 5 mmol,1 equiv.), manganese powder (550 mg, 10 mmol, 2 equiv.) and DMF (9 mL) and pyridine (1 mL). Mn powered was activated with traces of trifluoroacetic acid

(TFA, 100 µL) and water (135 µL) before addition to reaction mixture. Thereafter 1-bromo-3-fluoro-5-methoxybenzene (1.0251g, 5 mmol), ethyl acrylate (0.6674 g, 6 mmol, 1.2 equiv) was added to the reaction mixture stirred at 80 °C until 1-bromo-3-fluoro-5-methoxybenzene was consumed. After the completion of reaction, reaction mixture is poured into a solution of 2N HCl and extracted with DCM. The organic layer is washed with brine and dried over $MgSO_4$. After concentration and purification by flash chromatography on silica gel (Eluent: 6% EtOAc /94% hexane), the product ethyl 3-(3-fluoro-5-methoxyphenyl)propanoate was obtained in (0.791 g, 70%) yield as a viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.54-6.44 (m, 3H), 4.16 (q, J = 7.1 Hz, 2H), 3.8 (s, 3H), 2.92 (t, J = 7.8 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.6, 164.8 (d, J_{C-F} = 245.3 Hz), 160.8 (d, J_{C-F} = 11.4 Hz), 143.6 (d, J_{C-F} = 9.4 Hz), 109.9 (d, J_{C-F} = 2.9 Hz), 107.5 (d, J_{C-F} = 21.6 Hz), 99.5 (d, J_{C-F} = 26.1 Hz), 60.5, 55.4, 35.4, 30.8 (d, J_{C-F} = 2.4 Hz), 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -112.1

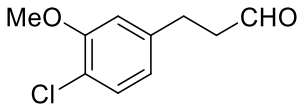
In second next step, 3-(3-fluoro-5-methoxyphenyl)propanoate (0.791 g, 3.5 mmol) was dissolved in diethyl ether (20 mL) and cool down to 0 °C and then $NaBH_4$ (132 mg, 1.2 equiv.) was added in portion wise, After being stirred at 0 °C for 10 min, the reaction was further stirred at room temperature for 4 h. After the completion of reaction (monitor by TCL), reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL). The aqueous and organic layer were separated by extraction of aqueous layer with DCM (2 x 10 mL). The DCM layer was passed over small pad of silica gel, and then organic extracts were dried over anhydrous Na_2SO_4 and concentrate under reduced pressure. The crude product 3-(3-fluoro-5-methoxyphenyl)propan-1-ol was obtained in color less liquid. In final step crude 3-(3-fluoro-5-methoxyphenyl)propan-1-ol compound was oxidized to desired product (**1o**) following *general procedure (B)* with PCC. After concentration and purification by flash chromatography on silica gel (Eluent: 4% EtOAc /96% hexane), the product **1o** was obtained as viscous oil in overall 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 6.53-6.45 (m, 3H), 3.77 (s, 3H), 2.92 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.1, 164.9 (d, J_{C-F} = 244.3 Hz), 161.0 (d, J_{C-F} = 11.7 Hz), 143.5 (d, J_{C-F} = 9.4 Hz), 110.1 (d, J_{C-F} = 2.7 Hz), 107.5 (d, J_{C-F} = 21.6 Hz), 99.5 (d, J_{C-F} = 25.5 Hz), 55.5, 44.8, 28.8 (d, J_{C-F} = 2.5 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$): δ -111.9; **HRMS** (ESI) Calcd for $C_{10}H_{11}FO_2$ $[M + H]^+$ 183.0743, found 183.0663.

Synthesis of 3-phenylpropanal derivatives from bromoarenes[5]



General procedure (C): In a glove box, a 100 mL of Schlenk tube equipped with magnetic stirring bar was charged with bromoarenes derivatives (5 mmol), $Pd(OAc)_2$ (0.1123g, 10 mol%), lithium acetate (0.8248 g, 12.5 mmol, 2.5 equiv.), lithium chloride (0.2073 g, 5 mmol, 1equiv.), tetrabutylammonium chloride (2.7792 g, 10 mmol, 2 equiv.). The tube was fitted with a rubber septum and moved out of the glove box. Then allyl alcohol (0.726 mL, 2.0 equiv.) and DMA (20.0 mL) were added in Schlenk tube through the rubber septum using syringes, and then the septum was replaced with a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 70 °C for 12 h. Upon cooling to room temperature, the reaction mixture was filtrated through a pad of silica gel, washed with 50 mL of ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to provide the corresponding product in 50-60 % yields.

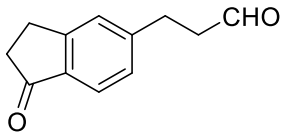
Synthesis of 3-(4-chloro-3-methoxyphenyl)propanal (1u)[5]



1u

This substrate was prepared using the *general procedure (C)* with 4-bromo-1-chloro-2-methoxybenzene (1.1074 g, 5 mmol). After workup and purification of reaction mixture using flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), provide the corresponding product (**1u**) in 51 % yield as viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), δ 6.77 (d, *J* = 1.5 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.88 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 154.8, 140.5, 130.1, 120.9, 120.2, 112.3, 55.9, 45.1 and 27.8. **HRMS** (ESI) Calcd for $C_{10}H_{11}ClO_2$ $[M + H]^+$ 199.0457, found 199.0456.

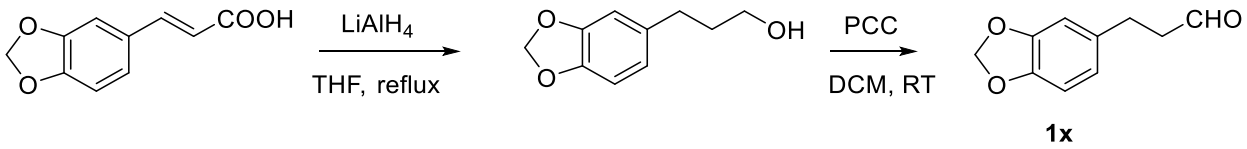
Synthesis of 3-(1-oxo-2,3-dihydro-1H-inden-5-yl)propanal (1y):



1y

This substrate was prepared using the *general procedure (C)* with 5-bromo-2,3-dihydro-1H-inden-1-one (1.0553 g, 5 mmol). After workup and purification of reaction mixture using flash chromatography on silica gel (Eluent: 15% EtOAc /85% hexane), provide the corresponding product (**1y**) in 53 % yield as white solid, m.p. 42-44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.33 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.14 (t, *J* = 6.1 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.5, 200.7, 155.9, 148.0, 135.6, 127.8, 126.5, 123.9, 44.9, 36.4, 28.4, 25.7. The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[5b].

Synthesis of 3-(benzo[d][1,3]dioxol-5-yl)propanal (1x)[6]

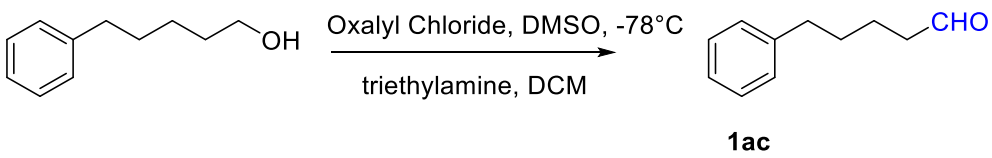


1x

A 150 mL of two neck round bottom flask was charged with $LiAlH_4$ (0.4744g, 12.5 mmol, 2.5 equiv) and 20 mL of THF. The solution was warmed to 50 °C and then (E)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylic acid (0.9609 g, 5 mmol) dissolved in 20 mL of THF was slowly with the help of dropping funnel over the time period of 20 min., thereafter reaction mixture was reflux for 2-3 h. The completion of reaction was monitor by TLC. After completion, reaction mixture was poured to ice cold water and then 5% HCl solution (10 mL) was added and extract with 50 mL of EtOAc. The combined organic layer was washed with saturated solution of $NaHCO_3$ (20 mL) and brine 15 mL. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residual of 3-(benzo[d][1,3]dioxol-5-yl)propan-1-ol was used as such for next step. In next step crude 3-(benzo[d][1,3]dioxol-5-yl)propan-1-ol compound was oxidized to desired product (**1x**) following *general procedure (**B**)* with PCC. After concentration and purification by flash chromatography on silica gel (Eluent: 6% EtOAc /94% hexane), the product **1x** was obtained in (35%) yield as a viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.90 (s, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.5

Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.6, 147.7, 145.9, 134.1, 121.1, 108.8, 108.3, 100.9, 45.6, 27.9. The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[6b].

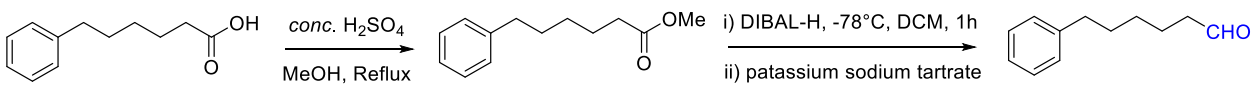
Synthesis of 5-phenylpentanal (1ac)[7]



1ac

Under nitrogen atmosphere, a 150 mL of round bottom flask equipped with stirring bar was cooled down to -78°C, thereafter solution of oxalyl chloride (0.6 mL, 7.13 mmol) in dry DCM (70 mL) was added, and then DMSO (0.47 mL, 6.59 mmol) was added dropwise. After stirring the solution at -78 °C for 30 minutes, 5-phenyl-pentanol (0.9 g, 5.49 mmol) in dry DCM (10 mL) was added dropwise. Thereafter reaction mixture was stirred at -78 °C for 1 h, and then triethyl amine (Et_3N) was added dropwise. The reaction mixture was warmed up to room temperature then concentrated to dryness. The crude product was extracted with 100 mL of diethyl ether (100 mL) and washed with sat. NH_4C1 solution (100 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to dryness. The organic layer was concentrated in rotary evaporator *vacuo* and purified via using flash chromatography; Eluent: (1% EtOAc /99% hexane); Appearance: viscous oil; overall isolated yield: 76%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.28 (ddt, *J* = 7.7, 6.4, 1.0 Hz, 2H), 7.21 – 7.14 (m, 3H), 2.65 – 2.61 (m, 2H), 2.46– 2.42 (m, 2H), 1.68 – 1.64 (m, 4H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.6, 141.9, 128.3, 128.3, 125.8, 43.7, 35.6, 30.8, and 21.6 ; **HRMS** (ESI) Calcd for $C_{11}H_{14}O$ $[M + H]^+$ 163.1042, found 163.1039; The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature.[7]

Synthesis of 6-phenylhexanal[8]

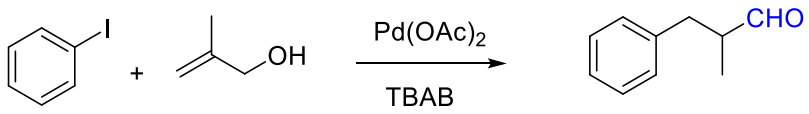


1ad-i **1ad-ii** **1ad**

A 150 mL of round bottom flask equipped with stirring bar and condenser was charged with 6-phenylhexanoic acid (2.7 g, 14.0 mmol), MeOH (70 mL) and catalytic amount of *conc.* H_2SO_4 were refluxed for 5 h. After the completion of reaction, solvent was evaporated and extracted with EtOAc, washed with brine and dry over Na_2SO_4. The organic layer was concentrated in rotary evaporator *vacuo*. Light brownish liquid was obtained in 87% yield which was used without any purification for next step. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.19 – 7.15 (m, 3H), 3.66 (s, 3H), 2.61 (7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.54 (m, 4H), 1.48 – 1.30 (m, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.2, 142.5, 128.3, 128.2, 125.6, 51.4, 35.7, 33.9, 31.1, 28.7 and 24.8 ; **HRMS** (ESI) Calcd for $C_{13}H_{18}O_2$ $[M + H]^+$ 207.1370, found 207.1360; The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature.[8]

In next the solution of methyl 6-phenylhexanoate (1.5 g, 7.3 mmol) in anhydrous DCM (30 mL) was cooled down to -78 °C and then DIBAL-H (9 mL, 1M in Hexane, 1.1 equiv.) was added drop wise. The resulting solution was stirred at -78 °C for 2h and quenched with MeOH (10 mL). The reaction mixture was then poured in DCM and potassium sodium tartrate aqueous and stirred vigorously for 4 h. The reaction mixture was extracted with DCM, washed with brine, dried over Na_2SO_4. The organic layer was concentrated in rotary evaporator *vacuo* and purified *via* using flash chromatography; Eluent: (1% EtOAc /99% hexane); Appearance: viscous oil; overall isolated yield: 71%**. ^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.29 – 7.25 (m, 2H), 7.17 (td, *J* = 6.7, 1.7 Hz, 3H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.41 (td, *J* = 7.4, 1.8 Hz, 2H), 1.69–1.60 (m, 4H), 1.40 – 1.32 (m, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.7, 142.3, 128.3, 128.2, 125.7, 43.8, 35.6, 31.1, 28.7 and 21.9 ; **HRMS** (ESI) Calcd for $C_{12}H_{16}O$ $[M + H]^+$ 177.1230, found177.1229. The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature.[8]

Synthesis of 2-methyl-3-phenylpropanal[9]

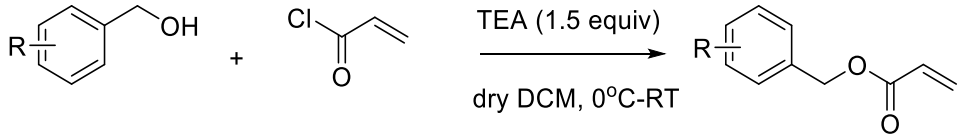


1ae

A 100 mL Schlenk tube equipped with a stir bar was charged with iodobenzene (0.6 mL, 5.0 mmol), 2-methallyl alcohol (1.4 mL, 15 mmol), Pd(OAc)2 (56 mg, 5 mol%), TBAB (1.0 equiv.) and NaHCO3 (1.0 equiv.). The reaction mixture was stirred at 120 °C for 24 h. Upon cooling to

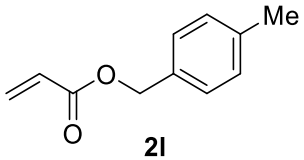
room temperature, the reaction mixture was filtrated through a pad of silica gel, washed with 50 mL of ethyl acetate and washed twice with water (20.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and purified *via* using flash chromatography; Eluent: (1% EtOAc /99% hexane); Appearance: viscous oil; overall isolated yield: 65%**. ^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.71 (d, *J* = 1.5 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 3.08 (dd, *J* = 13.3, 5.6 Hz, 1H), 2.70 – 2.57 (m, 2H), 1.08 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.4, 138.8, 128.9, 128.5, 126.4, 47.9, 36.6 and 13.1.The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature.[9]

Preparation and characterization of acrylates used as starting material (2l-2n, 2j)[10-12]



General procedure (D): To a stirred solution of substituted benzyl chloride (10 mmol) and triethyl amine (TEA) (15 mmol, 1.5 equiv) in dry DCM (15 mL) was added acryloyl chloride (10 mmol) dropwise under nitrogen atmosphere at 0 °C. After being stirred at 0 °C for 30 min., the reaction was further stirred at room temperature till the consumption of starting material (monitored by thin layer chromatography (TLC). After the completion of reaction, the reaction mixture was quenched with H_2O (30 mL) and ammonium chloride (NH_4Cl) aqueous (30 mL). The solvent was dried over dried over anhydrous Na_2SO_4 and concentration under reduced pressure. The residue was purified by flash chromatography on silica gel (Eluent: EtOAc/hexane) to provide the corresponding product in 70-80 % yields.

Synthesis of 4-methylbenzyl acrylate (2l):

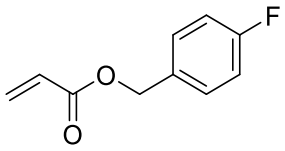


2l

This substrate was prepared using the *general procedure (D)*. To a solution of 4-methylbenzyl alcohol (1.221 g, 10 mmol), and triethyl amine (TEA) (1.897 mL, 15 mmol, 1.5 equiv) in dry DCM (15 mL) was added acryloyl chloride (0.8228 mL, 10 mmol, 1 equiv.) dropwise under nitrogen

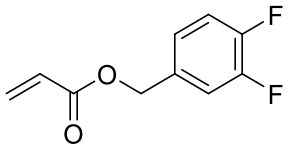
atmosphere at 0 °C. After being stirred at 0 °C for 30 min, the reaction was further stirred at room temperature for 10 h. After the completion of reaction, followed by workup and purification by flash chromatography on silica gel (Eluent: 3% EtOAc /97% hexane), the product **2l** was obtained as transparent viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.54 (dd, *J* = 15.9, 1.5 Hz, 1H), 6.26 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.88 (dd, *J* = 8.9, 1.5 Hz, 1H), 5.25 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 138.1, 133.0, 130.9, 129.3, 128.5, 66.3 and 21.2

Synthesis of 4-fluorobenzyl acrylate (2m):



This substrate was prepared using the *general procedure (D)*. To a solution of 4-fluorobenzyl alcohol (1.261 g, 10 mmol), and triethyl (TEA) (1.897 mL, 15 mmol, 1.5 equiv) in dry DCM (15 mL) was added acryloyl chloride (0.8228 mL, 10 mmol, 1 equiv.) dropwise under nitrogen atmosphere at 0 °C. After being stirred at 0 °C for 30 min, the reaction was further stirred at room temperature for 10 h. After the completion of reaction, followed by workup and purification by flash chromatography on silica gel (Eluent: 5% EtOAc /95% hexane), the product **2m** was obtained as transparent viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.64 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.18 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.86 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.15 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9, 163.9 (d, J_{C-F} = 247.5 Hz), 131.7 (d, J_{C-F} = 3.3 Hz), 131.3, 130.3 (d, J_{C-F} = 8.4 Hz), 128.2, 115.6 (d, J_{C-F} = 21.5 Hz) and 65.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -113.6

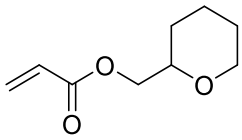
Synthesis of 3,4-difluorobenzyl acrylate (2n):



This substrate was prepared using the *general procedure (D)*. To a solution of 3,4-difluorobenzyl alcohol (1.441 g, 10 mmol), and triethyl (TEA) (1.897 mL, 15 mmol, 1.5 equiv.) in dry DCM (15

mL) was added acryloyl chloride (0.8228 mL, 10 mmol, 1 equiv) dropwise under nitrogen atmosphere at 0 °C. After being stirred at 0 °C for 30 min, the reaction was further stirred at room temperature for 10 h. After the completion of reaction, followed by workup and purification by flash chromatography on silica gel (Eluent: 5% EtOAc /95% hexane), the product **2n** was obtained as transparent viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.09 (m, 3H), 6.48 (d, *J* = 17.4 Hz, 1H), 6.20 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.89 (d, *J* = 10.4 Hz, 1H), 5.14 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7, 151.5 (dd, J_{1C-F} = 248.3 Hz, J_{2C-F} = 7.4 Hz), 151.4 (dd, J_{1C-F} = 248.7 Hz, J_{2C-F} = 7.1 Hz), 133.0 (dd, J_{1C-F} = 3.9 Hz, J_{2C-F} = 5.6 Hz), 131.5, 124.4 (dd, J_{1C-F} = 6.5 Hz, J_{2C-F} = 3.7 Hz), 124.4 (dd, J_{1C-F} = 6.5 Hz, J_{2C-F} = 3.7 Hz), 117.4 (dd, J_{1C-F} = 17.6 Hz, J_{2C-F} = 9.4 Hz), 64.9; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -137.2 (d, J_{C-F} = 21.4), -138.2 (d, J_{C-F} = 21.4); **HRMS** (ESI) Calcd for $C_{10}H_8F_2O_2$ $[M + H]^+$ 199.0565, found 199.0566

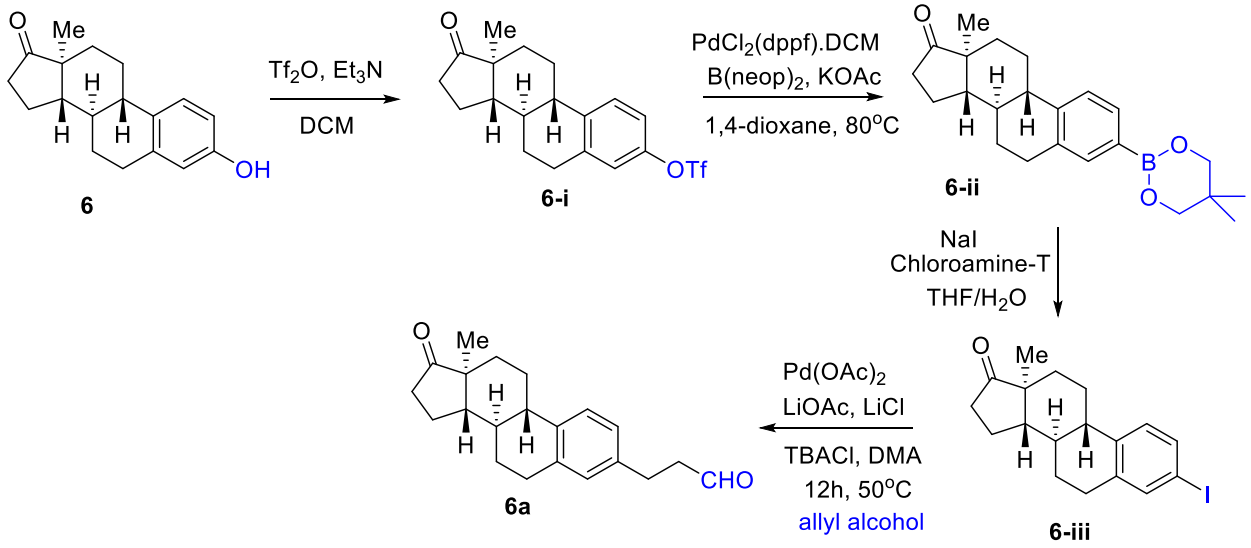
Synthesis of (tetrahydro-2H-pyran-2-yl)methyl acrylate (2j):



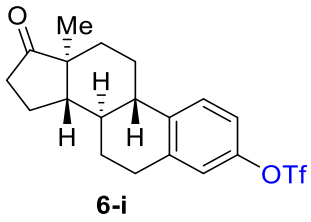
This substrate was prepared using the *general procedure (D)*. To a solution of (tetrahydro-2H-pyran-2-yl)methanol (1.1616 g, 10 mmol), and triethyl (TEA) (1.897 mL, 15 mmol, 1.5 equiv.) in dry DCM (15 mL) was added acryloyl chloride (0.8228 mL, 10 mmol, 1 equiv.) dropwise under nitrogen atmosphere at 0 °C. After being stirred at 0 °C for 30 min., the reaction was further stirred at room temperature for 10 h. After the completion of reaction, followed by workup and purification by flash chromatography on silica gel (Eluent: 2% EtOAc /98% hexane), the product **2j** was obtained as transparent viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.30 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.05 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.70 (dd, *J* = 10.5, 1.6 Hz, 1H), 4.01-3.93 (m, 2H), 3.87-3.83 (m, 1H), 3.46-3.40 (m, 1H), 3.32 (td, , *J* = 11.3, 2.6 Hz, 1H), 1.74-1.71 (m, 1H), 1.46-1.32 (m, 4H), 1.24-1.15 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.8, 130.7, 128.2, 75.2, 68.2, 67.3, 27.7, 25.6, 22.8

Preparation and characterization of starting materials derived from natural products and drug molecules (5a-11a)

Synthesis of *3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)propanal (6a)*:



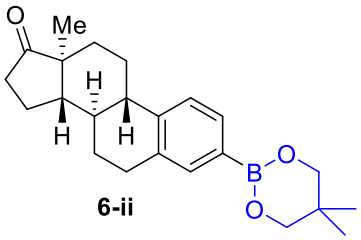
Step 1: Synthesis of *(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate* [13]



A 150 mL round bottom flask equipped with stirring bar was charged with estrone (1.3519 g, 5 mmol), trifluoromethanesulfonic anhydride (1.5001 g, 5 mmol, 1.2 equiv.) and DCM (30 mL). The solution was cooled down to 0 °C and then triethylamine (1.265 mL, 10 mmol, 2 equiv.) dissolved in 15 mL of DCM was added dropwise to the reaction mixture over a time period of 20 min. The solution was stirred for 50 min. at 0 °C followed by room temperature stirred till the consumption of starting material (monitor by TLC). Thereafter, $NaHCO_3$ (35 mL) was added to reaction mixture. The phases were separated and aqueous layer was extracted with DCM (2x20mL). The combine organic layers were washed with brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel; Eluent: (3% EtOAc /97% hexane); Appearance: colorless oil; isolated yield: (1.87 g,

93%). **^{1}H NMR** (400 MHz, $CDCl_3$): 7.34 (d, *J* = 8.6 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 2.97-2.92 (m, 2H), 2.51 (dd, *J* = 19.2, 9.8 Hz, 1H), 2.43-2.38 (m, 1H), 2.33-2.27 (m, 1H), 2.20-1.96 (m, 4H), 1.68-1.41(m, 6H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 220.4, 147.5, 140.2, 139.2, 127.1, 121.1, 118.2, 50.3, 47.8, 44.0, 37.6, 35.7, 31.4, 29.3, 26.0, 25.6, 21.5, 13.8; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -72.95 Hz, The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature.[13]

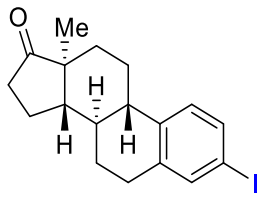
Step 2: Synthesis of *(8R,9S,13S,14S)-3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one*[14]



6-ii

A 150 mL Schlenk tube equipped with stirring bar was charged with triflate (**6-i**) (1.81 g, 4.5 mmol), bis(neopentyl glycolato)diboron (1.524 g, 6.75 mmol, 1.5 equiv), $PdCl_2$(dppf).DCM (186 mg, 5 mol%), KOAc (1.324 g, 13.5 mmol, 3 equiv.), and 1,4-dioxane (30 mL). The solution was stirred at 80 °C for 18 h. The reaction mixture was cooled down to room temperature and filtrated through Celite, washed with EtOAc (100 mL) and then concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography using silica gel; Eluent: (7% EtOAc /93% hexane); Appearance: white solid; isolated yield: (0.842 g, 51%), m.p. 228-230 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.59 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.76 (s, 4H), 2.95-2.93 (m, 2H), 2.54-2.43 (m, 2H), 2.35-2.30 (m, 1H), 2.19-1.94 (m, 4H), 1.66-1.42(m, 6H), 1.01 (s, 6H), 0.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ220.9, 142.4, 135.5, 134.7, 131.3, 124.6, 72.3, 50.6, 48.0, 44.7, 38.0, 35.8, 31.9, 29.2, 26.5, 25.6, 21.8, 21.6, 13.8; The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[14].

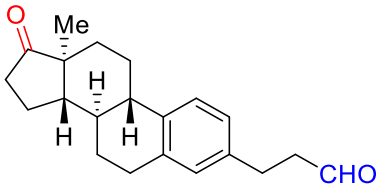
Step 3: Synthesis of *(8R,9S,13S,14S)-3-iodo-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one*[14]



6-iii

To a stirred solution of dioxaborinane derivative **(6-ii)** (0.84 g, 2 mmol) in 1:1 THF:H_2O (10 mL) at 0 °C was added solution of NaI (0.449 g, 3 mmol, 1.5 equiv.) in H_2O (10 mL). Thereafter, Chloroamine-T.3H_2O (1.4 g, 5 mmol, 2.5 equiv.) dissolved in 1:1 THF:H_2O (15 mL) was added dropwise over a time period of 20 min (using dropping funnel) to stirred reaction mixture at 0°C. After stirred the reaction mixture at 25 °C for 36 h, saturated aqueous $Na_2S_2O_3$ (50 mL) was added and reaction mixture was extracted with EtOAc (2x100 mL). The combine organic layers were washed with brine and dried over anhydrous Na_2SO_4. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel; Eluent: (6% EtOAc /94% hexane); Appearance: white solid; isolated yield: (0.487 g, 64%), m.p. 224-227 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.46-7.45 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 2.89-2.85 (m, 2H), 2.53 (dd, *J* = 18.4, 8.9 Hz, 1H), 2.40-2.35 (m, 1H), 2.27-2.22 (m, 1H), 2.19-1.95 (m, 4H), 1.68-1.37 (m, 6H), 0.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 220.7, 139.5, 139.2, 137.7, 134.7, 127.4, 91.2, 50.4, 47.9, 44.1, 37.9, 35.8, 31.5, 28.9, 26.2, 25.6, 21.6, 13.8; The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[14].

Step 4: Synthesis of *3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)propanal*

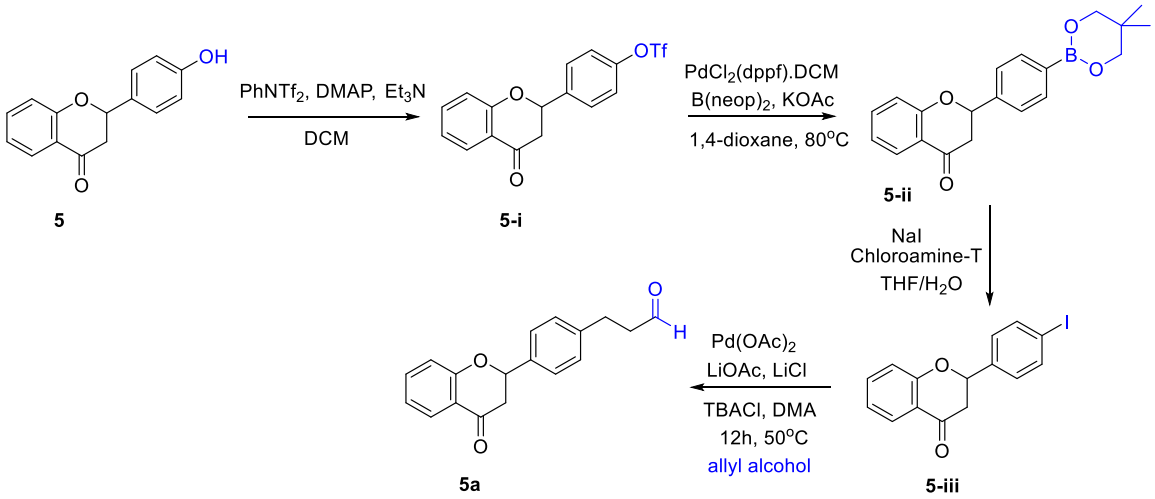


6a

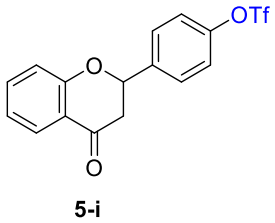
Substrate **(6a)** was prepared using the *general procedure (C)*. The 50 mL Schlenk tube was charged with compound **(6-iii)** (0.456 g, 1.2 mmol), $Pd(OAc)_2$ (27 mg, 10 mol%), lithium acetate (198 mg, 2.5 equiv.), lithium chloride (50 mg, 1equiv.), tetrabutylammonium chloride (667 mg, 2 equiv.), allyl alcohol (174 µL, 2.0 equiv), DMA (10 mL) and then reaction mixture was stirred at 50 °C

for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 15% EtOAc /85% hexane), Appearance: white solid; isolated yield: (0.238 g, 63%), m.p. 127-129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 9.82 (s, 1H), 7.23 (*J* = 8.0 Hz, 1H), 6.99 (*J* = 8.2 Hz, 1H), 6.94 (s, 1H), 2.92-2.89 (m, 4H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.50 (dd, *J* = 18.4, 8.9 Hz, 1H), 2.44-2.39 (m, 1H), 2.30-2.25 (m, 1H), 2.19-1.94 (m, 4H), 1.68-1.41(m, 6H), 0.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 220.8, 201.7, 137.7, 136.6, 128.9, 125.6, 125.5, 50.4, 47.9, 45.2, 44.2, 38.1, 35.8, 31.5, 29.3, 27.5, 26.4, 25.6, 21.5, 13.8; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_2$ $[M + H]^+$ 331.2006, found 331.2005

Synthesis of 3-(4-(4-oxochroman-2-yl)phenyl)propanal (5a):



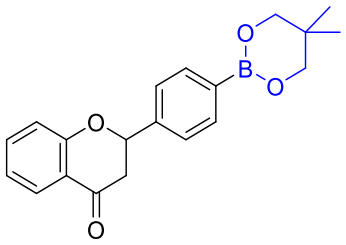
Step 1: Synthesis of *4-(4-oxochroman-2-yl)phenyl trifluoromethanesulfonate*[15]



To a stirred solution of 2-(4-hydroxyphenyl)chroman-4-one (1.442 g, 6 mmol) in DCM (20 mL) at 23 °C was added triethylamine (2.28 mL, 3 equiv), 4-(dimethylamino)pyridine (74 mg, 0.10 equiv) and *N*-phenylbis(trifluoromethanesulfonimide) (2.87 g, 1.2 equiv) and reaction mixture was

stirred at 23 °C for 4 h and concentrated under reduced pressure. The residual was purification by flash chromatography on silica gel: (Eluent: 2% EtOAc /98% hexane), Appearance: white solid; isolated yield: (2.010 g, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.54 (td, *J* = 7.5, 1.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.11-7.05 (m, 2H), 5.53 (dd, *J* = 13.1, 3.1 Hz, 1H), 3.03 (dd, *J* = 16.8, 13.1 Hz, 1H), 2.92 (dd, *J* = 16.8, 3.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.1, 161.1, 149.4, 139.3, 136.4, 128.0, 127.1, 122.0, 121.8, 120.9, 118.0, 78.4, 44.7.

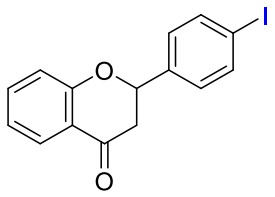
Step 2: Synthesis of *2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)chroman-4-one:*



5-ii

For the synthesis of compound of (**5-ii**), *same procedure was applied as adopted for conversion of (**6-i**) to (**6-ii**) with flavanone triflate* **(5-i)** (1.675 g, 4.5 mmol), bis(neopentyl glycolato)diboron (1.524 g, 6.75 mmol, 1.5 equiv), $PdCl_2$(dppf).DCM (186 mg, 5 mol%), KOAc (1.324g, 13.5 mmol, 3 equiv.), and 1,4-dioxane (30 mL). The solution was stirred at 80 °C for 18 h. After workup and concentration of organic layer under reduced pressure, residual was purified by flash chromatography on silica gel: (Eluent: 6% EtOAc /94% hexane), Appearance: white solid; isolated yield: (1.120 g, 74%), m.p. 135-137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.93 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.53-7.46 (m, 3H), 7.06 (t, *J* = 8.0 Hz, 2H), 5.50 (dd, *J* = 13.4, 2.8 Hz, 1H), 3.78 (s, 4H), 3.08 (dd, *J* = 16.8, 13.3 Hz, 1H), 2.89 (dd, *J* = 16.9, 3.0 Hz, 1H), 1.03 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.0, 161.6, 141.0, 136.2, 134.4, 127.0, 125.2, 121.6, 120.9, 118.2, 79.6, 72.3, 44.7, 31.9, 21.9; **HRMS** (ESI) Calcd for $C_{20}H_{21}BO_4$ $[M + H]^+$ 337.1642, found 337.1622

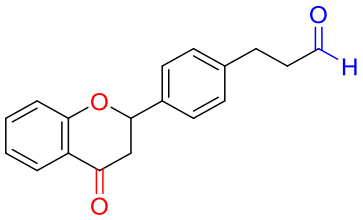
Step 3: Synthesis of *2-(4-iodophenyl)chroman-4-one:*



5-iii

The synthesis of 2-(4-iodophenyl)chroman-4-one (**5-iii**) was carried out using *same procedure was applied as adopted for conversion of (**6-ii**) to (**6-iii**) with flavanone borane derivative* **(5-ii)** (1.009 g, 3 mmol) in 1:1 THF: H_2O (15 mL), NaI (0.675 g, 4.5 mmol, 1.5 equiv) in H_2O (15 mL), Chloroamine-T.$3H_2O$ (2.113 g, 7.5 mmol, 2.5 equiv) dissolved in 1:1 THF: H_2O (20 mL). The reaction mixture was stirred at 25 °C for 36 h. After workup and concentration of organic layer under reduced pressure, residual was purified by flash chromatography on silica gel: (Eluent: 4% EtOAc /96% hexane), Appearance: light yellow solid; isolated yield: (0.315 g, 30%), m.p. 116-118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.77 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.52 (td, *J* = 7.4, 2.0 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.01-7.04 (m, 2H), 5.44 (dd, *J* = 13.0, 3.0 Hz, 1H), 3.03 (dd, *J* = 16.8, 13.1 Hz, 1H), 2.88 (dd, *J* = 16.8, 3.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.5, 161.2, 138.4, 138.0, 136.3, 127.9, 127.1, 121.8, 120.8, 118.1, 94.4, 78.9, 44.5; **HRMS** (ESI) Calcd for $C_{15}H_{11}IO_2$ $[M + H]^+$ 350.9876, found 350.9876

Step 4: Synthesis of *3-(4-(4-oxochroman-2-yl)phenyl)propanal*

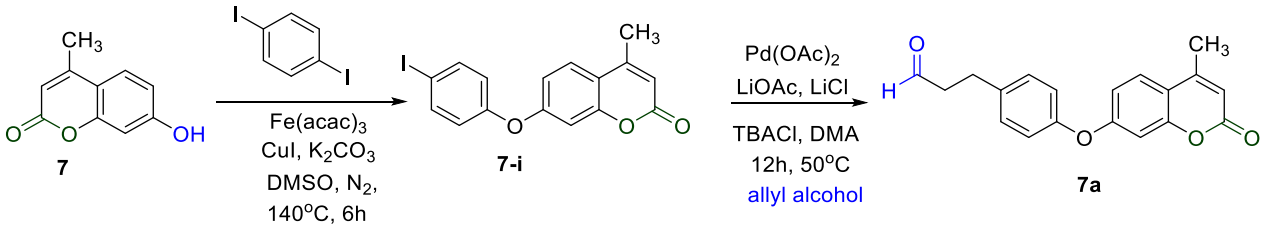


5a

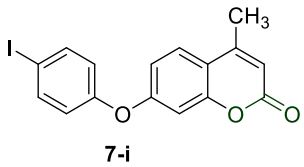
Substrate **(5a)** was prepared using the *general procedure (C)* with compound **5-iii** (0.315 g, 0.9 mmol), $Pd(OAc)_2$ (20 mg, 10 mol%), lithium acetate (148 mg, 2.5 equiv.), lithium chloride (37 mg, 1equiv.), tetrabutylammonium chloride (0.500 g, 2 equiv.), allyl alcohol (131 µL, 2.0 equiv), DMA (5 mL) and then reaction mixture was stirred at 50 °C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 12% EtOAc /88% hexane), Appearance: yellow solid; isolated yield: (0.100 mg, 40%), m.p. 105-107°C; **^{1}H NMR** (400 MHz,

$CDCl_3$): 9.83 (s, 1H), 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.51 (td, *J* = 7.9, 2.0 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 8.1 Hz, 2H), 5.46 (dd, *J* = 13.3, 2.8 Hz, 1H), 3.09 (dd, *J* = 16.8, 13.2 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.88 (dd, *J* = 16.7, 2.9 Hz, 1H), 2.81 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 191.9, 161.5, 141.1, 136.7, 136.2, 128.9, 128.8, 127.0, 126.5, 121.6, 120.9, 118.1, 79.4, 45.1, 44.5, 27.7; **HRMS** (ESI) Calcd for $C_{18}H_{16}O_3[M + H]^+$ 281.1173, found 281.1172.

Synthesis of 3-(4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)phenyl)propanal (7a)

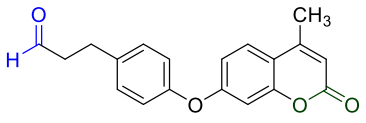


Step 1: Synthesis of 7-(4-iodophenoxy)-4-methyl-2H-chromen-2-one (7-i)[16]



A mixture of 1,4-diiodobenzene (1.64 g, 5 mmol), coumarin **7** (1.057 g, 6 mmol), $Fe(acac)_3$ (353 mg, 20 mol %), CuI (190 mg, 20 mol %), K_2CO_3 (1.38 g, 2 equiv.), and DMSO (20 mL) in a Schlenk tube was stirred under nitrogen atmosphere at 120 °C for 6 h. After the completion of reaction , the mixture was poured into ethyl acetate, then washed with water, extracted with additional ethyl acetate, dried over anhydrous Na_2SO_4, then filtered and evaporated under vacuum, the residue was purified by flash column chromatography on silica gel: (Eluent: 11% EtOAc /89% hexane), Appearance: light yellow solid; isolated yield: (1.039 g, 55%), m.p. 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.84 (dd, *J* = 5.7, 3.1 Hz, 3H), 6.17 (s, 1H), 2.41 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4, 160.0, 155.2, 154.7, 152.0, 138.9, 125.9, 121.9, 115.4, 114.2, 113.0, 105.6, 88.0 and 18.6; **HRMS** (ESI) Calcd for $C_{16}H_{11}IO_3$ $[M + H]^+$ 378.9826, found 378.9827.

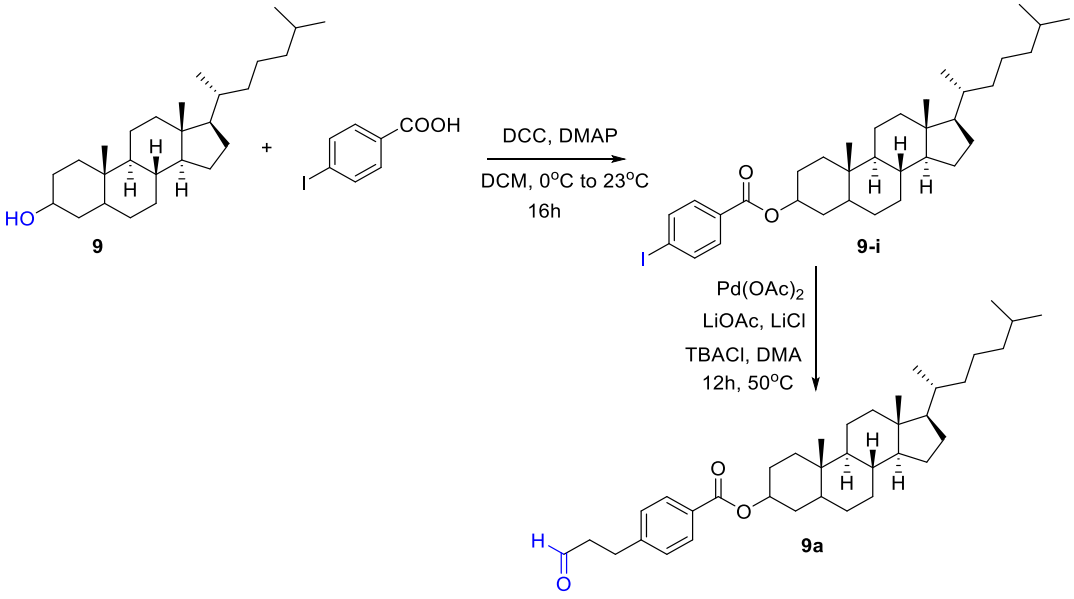
Step 2: Synthesis of 3-(4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)phenyl)propanal (7a):



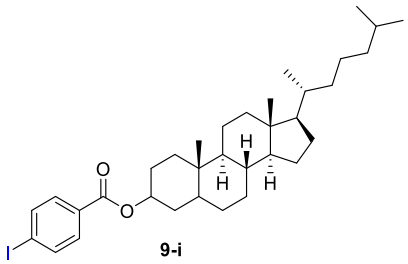
7a

Substrate **(7a)** was prepared using the *general procedure (C)*. The 150 mL Schlenk tube was charged with compound **7-i** (0.378 g, 1.0 mmol), $Pd(OAc)_2$ (23 mg, 10 mol%), lithium acetate (165 mg, 2.5 equiv.), lithium chloride (42 mg, 1 equiv.), tetrabutylammonium chloride (559 mg, 2 equiv.), allyl alcohol (145 µL, 2.0 equiv.), DMA (15 mL) and then reaction mixture was stirred at 50 °C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 14% EtOAc /86% hexane), Appearance: viscous oil; isolated yield: (0.157 g, 51%); m.p. 98-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.18 (s, 1H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.41 (d, *J* = 1.1 Hz, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.2, 161.2, 160.9, 155.0, 153.5, 152.2, 137.2, 130.0, 125.8, 120.4, 115.0, 114.1, 112.8, 105.1, 45.3, 27.4 and 18.7; **HRMS** (ESI) Calcd for $C_{19}H_{16}O_4$ $[M + H]^+$ 309.1121, found 309.1122

Synthesis of (8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-oxopropyl)benzoate (**9a**)



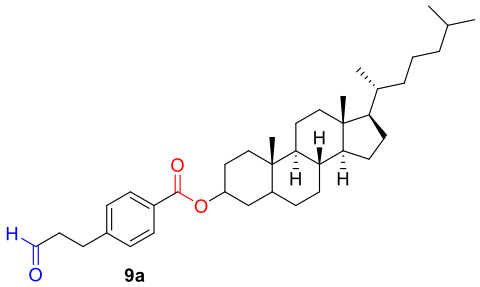
Step 1: Synthesis of *(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-iodobenzoate (9-i)*[17a]



9-i

To a stirred solution of *β*-Cholestanol (1.16 g, 3 mmol) and 4-iodobenzoic acid (1.860 g, 2.5 equiv.) in DCM (20 mL) at 0 °C were added DCC (1.547 g, 2.5 equiv.) and DMAP (0.183 g, 0.5 equiv.) sequentially. After 30 minutes, the ice-cold water-cooling bath was removed and the resulting suspension was stirred vigorously at room temperature for 16 h. Then, reaction mixture was concentration in *vacuo*. The reaction mixture was purification by flash chromatography on silica gel: (Eluent: 1% EtOAc /99% hexane), Appearance: white solid; isolated yield: (0.650 g, 35%), m.p. 183-185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 7.78 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 4.96-4.88 (m, 1H), 1.99-1.91 (m, 2H), 1.84-1.75 (m, 2H), 1.73-1.61 (m, 3H), 1.58-1.48 (m, 4H), 1.38-1.22 (m, 10H), 1.15-1.07 (m, 6H), 1.04-0.97 (m, 3H), 0.91-0.85 (m, 13H), 0.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.6, 137.5, 130.9, 130.4, 100.3, 74.7, 56.4, 56.23, 54.23, 44.7, 42.6, 39.9, 39.5, 36.7, 36.1, 35.8, 35.5, 35.4, 34.0, 31.9, 28.6, 28.2, 27.9, 27.5, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, 12.3, 12.1; **HRMS** (ESI) Calcd for $C_{34}H_{51}IO_2$ $[M + H]^+$ 619.2935, found 619.2940

Step 2: Synthesis of *(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-oxopropyl)benzoate* (9a)

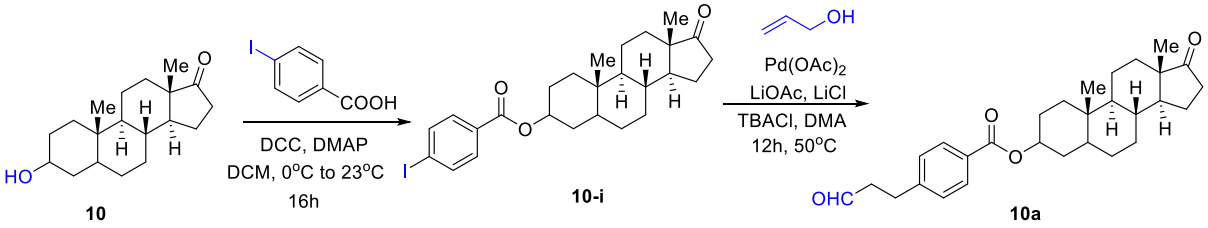


9a

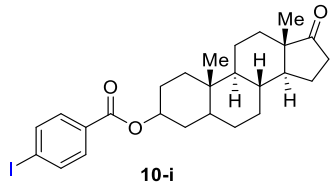
Substrate **(9a)** was prepared using the *general procedure (C)*. The 150 mL Schlenk tube was charged with compound **9-i** (0.619 g, 1.0 mmol), $Pd(OAc)_2$ (23 mg, 10 mol%), lithium acetate (165 mg, 2.5 equiv.), lithium chloride (42 mg, 1equiv.), tetrabutylammonium chloride (559 mg, 2

equiv.), allyl alcohol (145 µL, 2.0 equiv.), DMA (15 mL) and then reaction mixture was stirred at 50 °C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 2% EtOAc /98% hexane), Appearance: white solid; isolated yield: (0.313 g, 57%), m.p. 120-123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 9.82 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.97-4.88 (m, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.98-1.92 (m, 2H), 1.82-1.64 (m, 5H), 1.61-1.48 (m, 4H), 1.37-1.26 (m, 10H), 1.15-0.98 (m, 9H), 0.91-0.85 (m, 13H), 0.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.8, 166.0, 145.5, 129.9, 129.1, 128.2, 74.3, 56.4, 56.23, 54.20, 44.9, 44.7, 42.6, 39.9, 39.5, 36.8, 36.1, 35.8, 35.5, 35.4, 34.1, 31.9, 28.6, 28.2, 27.9, 27.5, 24.2, 23.8, 22.8, 22.6, 22.5, 21.2, 18.6, 12.3, 12.1; **HRMS** (ESI) Calcd for $C_{37}H_{56}O_3$ $[M + H]^+$ 549.4203, found 549.4205

Synthesis of (8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(3-oxopropyl)benzoate (10a)



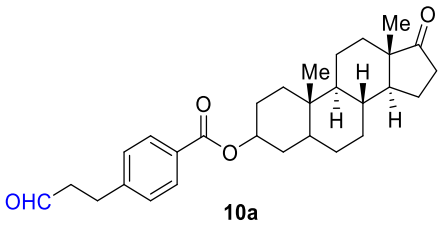
Step 1: Synthesis of (8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H cyclopenta[a]phenanthren-3-yl 4-iodobenzoate (10-i):



The synthesis of compound (**10-i**) was carried out *with androsterone* **(10)** (0.871 g, 3 mmol) and 4-iodobenzoic acid (0.620 g, 2.5 mmol) using *same procedure as adopted for conversion of (9) to (9-i)*. After the completion of reaction followed by workup and purification by flash chromatography on silica gel: (Eluent: 10% EtOAc /90% hexane), provided **10-i** as a gummy viscous oil in (0.780 g, 50%) yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 5.27 (s, 1H), 2.45 (dd, *J* = 19.3, 8.6 Hz, 1H), 2.12-2.02 (m, 1H), 1.97-1.75 (m,

5H), 1.71-1.67 (m, 1H), 1.63-1.48 (m, 6H), 1.38-1.23 (m, 7H), 1.08-0.98 (m, 1H), 0.88 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 221.2, 165.3, 137.7, 131.0, 130.5, 100.4, 70.9, 54.4, 51.4, 47.8, 40.5, 36.0, 35.8, 35.0, 33.1, 32.8, 31.5, 30.7, 28.0, 26.2, 21.7, 20.1, 13.8, 11.4; **HRMS** (ESI) Calcd for $C_{26}H_{33}IO_3$ $[M + H]^+$ 521.1434, found 521.1433

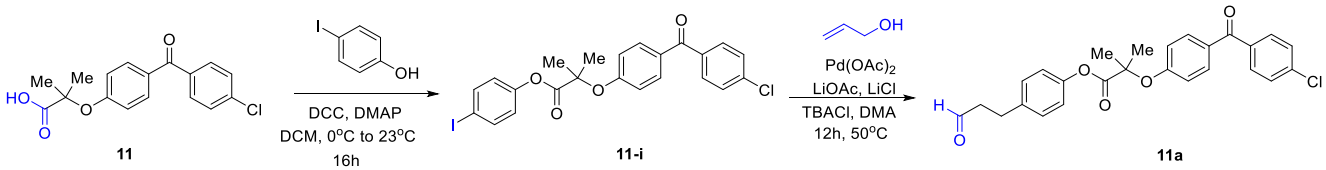
Synthesis of (8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H cyclopenta[a]phenanthren-3-yl 4-(3-oxopropyl)benzoate (10a)



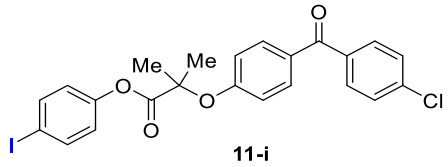
10a

Substrate **(10a)** was prepared using the *general procedure (C)*. The 50 mL Schlenk tube was charged with compound **10-i** (0.625 g, 1.2 mmol), $Pd(OAc)_2$ (27 mg, 10 mol%), lithium acetate (198 mg, 2.5 equiv.), lithium chloride (50 mg, 1equiv.), tetrabutylammonium chloride (667 mg, 2 equiv.), allyl alcohol (174 µL, 2.0 equiv.), DMA (10 mL) and then reaction mixture was stirred at 50°C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 13% EtOAc /87% hexane), Appearance: viscous oil; (0.243g, 45%) isolated yield; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.27 (s, 1H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.46 (dd, *J* = 19.3, 8.6 Hz, 1H), 2.12-2.03 (m, 1H), 1.98-1.78 (m, 4H), 1.77-1.71 (m, 2H), 1.64 -1.47 (m, 6H), 1.41-1.23 (m, 7H), 1.09-0.98 (m, 1H), 0.88 (d, *J* = 2.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 221.3, 200.8, 165.7, 145.6, 129.8, 129.2, 128.3, 70.4, 54.4, 51.4, 47.8, 40.4, 36.0, 35.8, 35.0, 33.1, 32.9, 31.5, 30.7, 28.0, 26.2, 21.7, 20.1, 13.8 and 11.4; **HRMS** (ESI) Calcd for $C_{29}H_{38}O_4$ $[M + H]^+$ 451.2843, found 451.2843

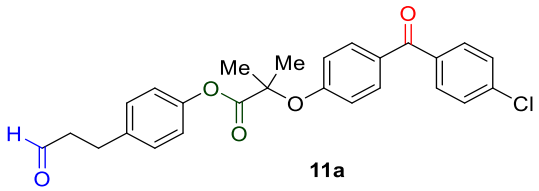
Synthesis of 4-(3-oxopropyl)phenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (11a):



Step 1: Synthesis of 4-iodophenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (11-i)



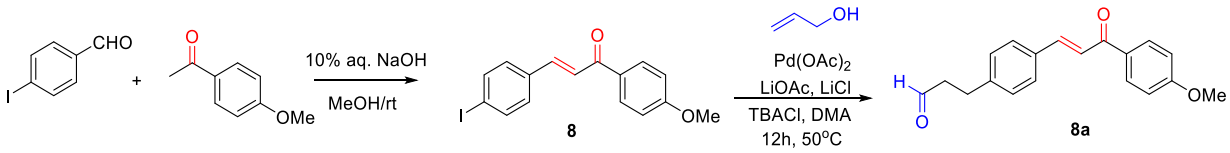
The synthesis of compound (**11-i**) was carried with and 4-iodophenol (0.660 g, 3 mmol) and fenofibric acid **(11)** (0.797 g, 2.5 mmol) using *same procedure as adopted for conversion of (**9**) to (**9-i**)*. After the completion of reaction followed by workup and purification by flash chromatography on silica gel: (Eluent: 5% EtOAc /95% hexane), provided **11-i** as a white solid in (1.0154 g, 65%) yield, m.p. 151-153 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 1.81 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.1, 172.1, 159.3, 150.2, 138.6, 138.4, 136.2, 132.1 131.1, 130.7, 128.5, 123.3, 117.2, 90.3, 79.4 and 25.4; **HRMS** (ESI) Calcd for $C_{23}H_{18}ClIO_4$ $[M + H]^+$ 521.0011, found 521.0011



Substrate **(11a)** was prepared using the *general procedure (C)*. The 50 mL Schlenk tube was charged with compound **11-i** (0.625 g, 1.2 mmol), $Pd(OAc)_2$ (27 mg, 10 mol%), lithium acetate (198 mg, 2.5 equiv.), lithium chloride (50 mg, 1equiv.), tetrabutylammonium chloride (667 mg, 2 equiv.), allyl alcohol (174 µL, 2.0 equiv.), DMA (10 mL) and then reaction mixture was stirred at 50 °C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 8% EtOAc /92% hexane), Appearance: white solid; (0.276 g, 51%) isolated yield; m.p. 99-101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5

Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 1.82 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 194.1, 172.4, 159.5, 148.7, 138.42, 138.37, 136.2, 132.1 131.1, 130.6, 129.3, 128.5, 121.1, 117.3, 79.4, 45.1, 27.3 and 25.4; **HRMS** (ESI) Calcd for $C_{26}H_{23}ClO_5$ $[M + H]^+$ 451.1307, found 451.1306

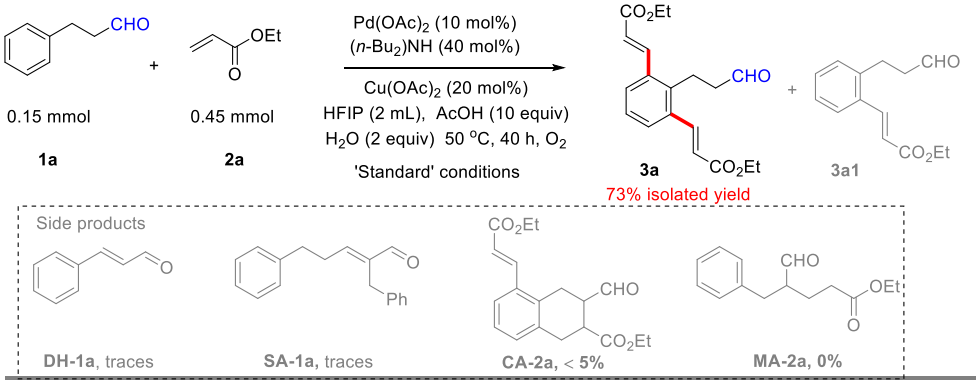
Synthesis of (E)-3-(4-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)propanal (8a):



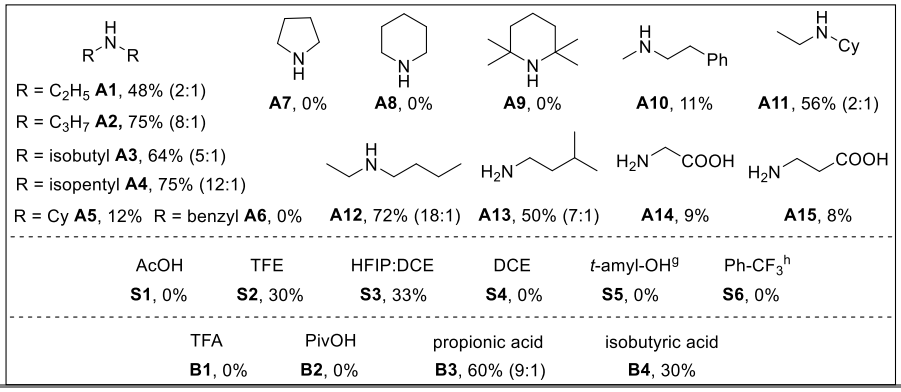
Substrate **(8a)** was prepared using the *general procedure (C)*. The 50 mL Schlenk tube was charged with compound **8** (0.437 g, 1.2 mmol), $Pd(OAc)_2$ (27 mg, 10 mol%), lithium acetate (198 mg, 2.5 equiv.), lithium chloride (50 mg, 1equiv.), tetrabutylammonium chloride (667 mg, 2 equiv.), allyl alcohol (174 µL, 2.0 equiv.), DMA (10 mL) and then reaction mixture was stirred at 50 °C for 5 h. After workup, concentration and purification by flash chromatography on silica gel: (Eluent: 15% EtOAc /85% hexane), Appearance: light yellow solid; (0.201g, 57%) isolated yield; m.p. 88-91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 15.6 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.85 – 2.76 (7.5, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 188.7, 163.4, 143.6, 143.0, 133.2, 131.1, 130.8, 128.9, 128.6, 121.4, 113.8, 55.5, 44.9, 27.9; **HRMS** (ESI) Calcd for $C_{19}H_{18}O_3$ $[M + H]^+$ 295.3501, found 295.3500

Selected results from optimization studies of the olefination of dual remote C-H bonds of *β*-phenyl propionaldehyde 1a with ethyl acrylates 2a

Table S1: Selected optimization studies [a]



Entry	Deviation from 'standard' conditions	Yield [%] of 3a and 3a' (Di : Mono)[b]
1	none	79% (19:1)
2	without $Pd(OAc)_2$	0
3	without $(n\text{-}Bu)_2NH$	0
4	without $Cu(OAc)_2$	5
5	under N_2 atm	26
6	under open air	54 (2:1)
7	without AcOH	10
8	without H_2O	71 (12:1)
9	$Pd(OAc)_2$ / AgOAc instead of $Pd(OAc)_2$ / $Cu(OAc)_2$	14[c,d]
10	$Pd(TFA)_2$ / $Cu(OAc)_2$ instead of $Pd(OAc)_2$ / $Cu(OAc)_2$	54 (5:1)
11	$Cu(OAc)_2$ 50 mol% instead of 20 mol%	61 (14:1)
12	40 °C	76 (15:1)[e]
13	70 °C	20[f]
14	40 mol% amine **A1-A15** was used	listed below
15	**S1-S6** solvents instesd of HFIP(2 mL)	listed below
16	10 equiv of acid **B1-B4** instead of AcOH	listed below

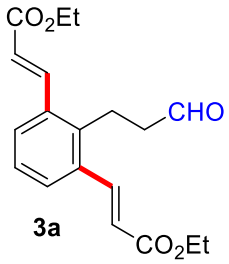


[a] Unless otherwise noted, all reactions were run with **1a** (0.15 mmol) and **2a** (0.45 mmol) in 2 mL solvent for 40 h. [b] Yields & ratio were determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard, [c] 2 equiv. AgOAc, [d] **DH-1a** was observed in 5% yield, [e] 72 h, [f] **CA-2a** was observed in 15% yield, [g] **SA-1a** was observed in 18% yield. [h] **DH-1a** was observed in 30% yield, abbreviation: DH = dehydrogenation product, SA = self Aldol product, CA = cyclic aldehyde product, MA = Michael addition product

General procedure for olefination of dual remote C-H bonds

General procedure (E): In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with *β*-aryl saturated aldehyde derivative (0.15 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then acrylate derivative (0.45 mmol, 3 equiv.), HFIP (2 mL), AcOH (80 µL, 10 equiv.), H_2O (5.5 µL, 2 equiv.) and dibutylamine $(n\text{-Bu})_2NH$ (10 µL, 40 mol %) or $(n\text{-Pr})_2NH$ (9 µL, 40 mol %, see tables 3) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min., then at 50 °C for 40 h (or at 40 °C for 72 h, see tables 2 and 3). After cooling to ambient temperature, the reaction mixture was diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel; Eluent: (EtOAc /hexane). The ratio of di and mono (D:M) olefinated product were determined by ^1H NMR of the crude reaction mixture using dibromometanne as internal standard with respect to benzylic methylene proton signals, which appear as triplet (approximately 3.10 to 3.30 ppm, respectively).

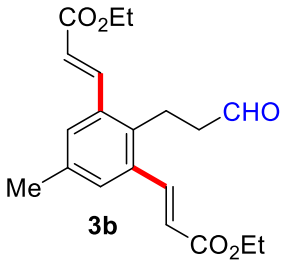
Experimental data for evaluating substrate scope for dual olefination of remote C-H bonds



3a

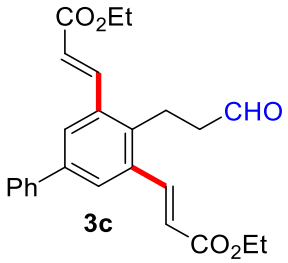
diethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3a): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (15% EtOAc /75% hexane); Appearance: off white solid; isolated yield: 73%; m.p. 87-89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.98 (d, *J* = 15.7 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 4H), 3.21 (t, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100

MHz, $CDCl_3$): δ 199.9, 166.4, 141.4, 138.7, 134.5, 128.7, 127.2, 121.8, 60.7, 44.6, 21.3, 14.3; **IR** (KBr): 2985, 1714, 1627, 1477, 1177, 1026, 985, 970, 792 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{22}O_5$ $[M + H]^+$ 331.1540, found 331.1536



3b

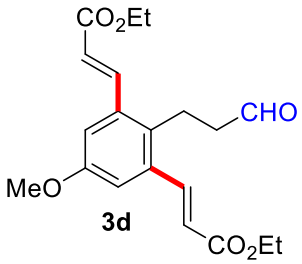
diethyl 3,3'-(5-methyl-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3b): Olefination was done by *general procedure (E)* with 3-(p-tolyl)propanal (0.0222g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (10% EtOAc /80% hexane); Appearance: off white solid; isolated yield: 68%; m.p. 145-146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.96 (d, *J* = 15.7 Hz, 2H), 7.39 (s, 2H), 6.34 (d, *J* = 15.7 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.17 (t, *J* = 8.2 Hz, 2H), 2.63 (t, *J* = 8.2 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.0, 166.4, 141.5, 136.7, 135.9, 134.2, 129.3, 121.4, 60.6, 44.7, 20.86, 20.83, 14.2; **IR** (KBr): 2982, 1714, 1630, 1477, 1182, 1036, 976, 857 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{24}O_5$ $[M + H]^+$ 345.1697, found 345.1692



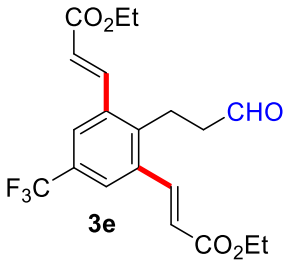
3c

diethyl 3,3'-(4-(3-oxopropyl)-[1,1'-biphenyl]-3,5-diyl)(2E,2'E)-diacrylate (3c): Olefination was done by general *general procedure (E)* with 3-([1,1'-biphenyl]-4-yl)propanal (0.0315 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (12% EtOAc /86% hexane); Appearance: off white solid; isolated yield: 70%; m.p. 136-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.04 (d, *J* = 15.7 Hz, 2H), 7.76 (s, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.2

Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.24 (t, *J* = 8.2 Hz, 2H), 2.70 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 166.4, 141.5, 140.2, 139.5, 137.6, 135.0, 128.9, 128.0, 127.3, 127.0, 122.1, 60.7, 44.6, 21.1, 14.3; **IR** (KBr): 2978, 2931, 1709, 1632, 1447, 1366, 1280, 1179, 1034, 976, 858, 765, 699 cm^{-1}; **HRMS** (ESI) Calcd for $C_{25}H_{26}O_5$ $[M + H]^+$ 407.1853, found 407.1850

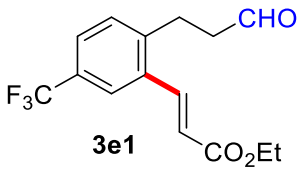


Diethyl 3,3'-(5-methoxy-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3d): Olefination was done by *general procedure (E)* with 3-(4-methoxyphenyl)propanal (0.0246 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (16% EtOAc /84% hexane); Appearance: off white solid; isolated yield: 61%; m.p. 134-136 °C;**^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.95 (d, *J* = 15.7 Hz, 2H), 7.09 (s, 2H), 6.34 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.84 (s, 3H), 3.14 (t, *J* = 8.2 Hz, 2H), 2.62 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.1, 166.3, 158.1, 141.5, 135.5, 131.2, 121.8, 113.9, 60.7, 55.3, 44.9, 20.6, 14.2; **IR** (KBr): 2982, 1714, 1630, 1458, 1285, 1272, 1180, 1035, 975, 869, 842 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{24}O_6$ $[M + H]^+$ 361.1646, found 361.1643



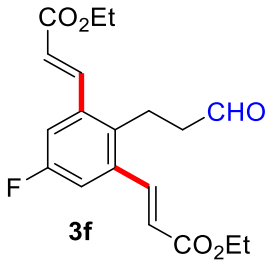
diethyl 3,3'-(2-(3-oxopropyl)-5-(trifluoromethyl)-1,3-phenylene)(2E,2'E)-diacrylate (3e): Olefination was done by *general procedure (E)* with 3-(4-(trifluoromethyl)phenyl)propanal (0.0303 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (18% EtOAc

/80% hexane); Appearance: off white solid; isolated yield: 55%; m.p. 115-118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.98 (d, *J* = 15.7 Hz, 2H), 7.78 (s, 2H), 6.43 (d, *J* = 15.7 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.25 (t, *J* = 8.2 Hz, 2H), 2.70 (t, *J* = 8.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2, 166.0, 142.2, 140.2, 135.5, 129.8 (d, J_{C-F} = 32.6 Hz), 124.9 (d, J_{C-F} = 3.5 Hz), 123.6, 122.1, 61.0, 44.0, 21.5, 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.9; **IR** (KBr): 2979, 2837, 2865, 1726, 1631, 1182, 1120, 976, 861 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{21}F_3O_5$ $[M + H]^+$ 399.1414, found 399.1410



3e1

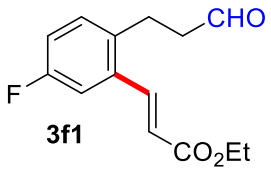
ethyl (E)-3-(2-(3-oxopropyl)-5-(trifluoromethyl)phenyl)acrylate (3e1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /92% hexane); Appearance: light yellow viscous oil; isolated yield: 28%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.94 (d, *J* = 15.7 Hz, 1H), 7.79 (s, 1H), 7.56 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 8.2 Hz, 2H), 2.79 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 166.3, 143.6, 139.9, 133.9, 130.5, 130.0 (q, J_{C-F} = 32.6 Hz), 126.4 (q, J_{C-F} = 3.5 Hz), 125.1 (d, J_{C-F} = 273 Hz), 123.7 (q, J_{C-F} = 3.5 Hz), 122.4, 60.8, 44.4, 25.2, 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.7; **IR** (KBr): 2980, 2837, 1725, 1630, 1441, 978, 863 cm^{-1}; **HRMS** (ESI) Calcd for $C_{15}H_{15}F_3O_3$ $[M + H]^+$ 301.1046, found 301.1043



3f

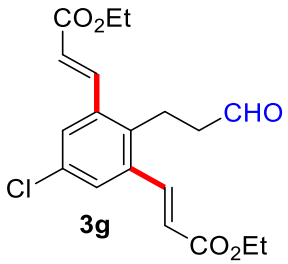
diethyl 3,3'-(5-fluoro-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3f): Olefination was done by *general procedure (E)* with 3-(4-fluorophenyl)propanal (0.0228 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (18% EtOAc /82% hexane); Appearance: off white solid; isolated yield: 56%; m.p. 75-77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.93

(d, J = 15.7 Hz, 2H), 7.26 (d, J = 9.1 Hz, 2H), 6.34 (d, J = 15.7 Hz, 2H), 4.28 (q, J = 7.1 Hz, 4H), 3.16 (t, J = 8.2 Hz, 2H), 2.65 (t, J = 8.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.1, 161.3 (d, J_{C-F} = 246.7 Hz), 140.3 (d, J_{C-F} = 2.2 Hz), 136.4 (d, J_{C-F} = 7.8 Hz), 134.7 (d, J_{C-F} = 3.2 Hz), 122.8, 115.1 (d, J_{C-F} = 22.1 Hz), 60.8, 44.6, 20.8, 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -114.7; **IR** (KBr): 2981, 2731, 1714, 1633, 1180, 975, 857 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{21}FO_5$ $[M + H]^+$ 349.1446, found 349.1442



3f1

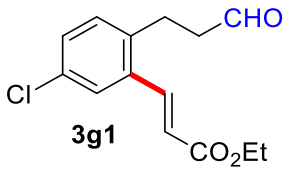
ethyl (E)-3-(5-fluoro-2-(3-oxopropyl)phenyl)acrylate (3f1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: light yellow viscous oil; isolated yield: 19%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.88 (dd, J = 15.8, 1.6 Hz, 1H), 7.26-7.18 (m, 2H), 7.01 (td, J = 8.3, 2.7 Hz, 1H), 6.36 (d, J = 15.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.06 (t, J = 7.5 Hz, 2H), 2.73 (td, J = 7.6, 1.2 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.5, 166.4, 161.5 (d, J_{C-F} = 245.6 Hz), 140.2 (d, J_{C-F} = 2.5 Hz), 135.6 (d, J_{C-F} = 3.1 Hz), 134.8 (d, J_{C-F} = 7.4 Hz), 131.5 (d, J_{C-F} = 8.0 Hz), 121.4, 117.0 (d, J_{C-F} = 21.4 Hz), 113.2 (d, J = 22.1 Hz), 60.7, 45.0, 24.7, 14.2; **^{19}F NMR** (377 MHz, CDCl3): δ -115.5; **IR** (KBr): 2982, 2939, 1714, 1634, 1442, 978, 864 cm^{-1}; **HRMS** (ESI) Calcd for $C_{14}H_{15}FO_3$ $[M + H]^+$ 251.1078, found 251.1078



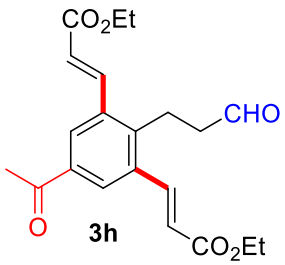
3g

diethyl 3,3'-(5-chloro-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3g): Olefination was done by *general procedure (E)* with 3-(4-chlorophenyl)propanal (0.0253 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (17% EtOAc /83% hexane); Appearance: off

white solid; isolated yield: 40%; m.p. 122-124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.90 (d, *J* = 15.7 Hz, 2H), 7.52 (s, 2H), 6.34 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.15 (t, *J* = 8.2 Hz, 2H), 2.64 (t, *J* = 8.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 166.1, 140.2, 137.1, 136.2, 133.1, 128.2, 123.0, 60.9, 44.3, 20.9, 14.2; **IR** (KBr): 2983, 2736, 1714, 1635, 1182, 976, 853 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{21}ClO_5$ $[M + H]^+$ 365.1150, found 365.1152

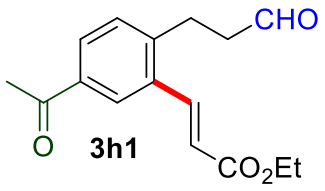


ethyl (E)-3-(5-chloro-2-(3-oxopropyl)phenyl)acrylate (3g1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: light yellow viscous oil; isolated yield: 20%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.86 (d, *J* = 15.7 Hz, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 8.2 Hz, 2H), 2.74 (t, *J* = 8.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.3, 166.4, 140.0, 138.2, 134.8, 132.8, 131.3, 130.0, 126.7, 121.6, 60.8, 44.7, 24.8, 14.3; **HRMS** (ESI) Calcd for $C_{14}H_{15}ClO_3$ $[M + H]^+$ 267.0782, found 267.0784

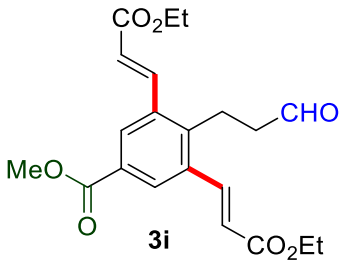


diethyl 3,3'-(5-acetyl-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3h): Olefination was done by *general procedure (E)* with 3-(4-acetylphenyl)propanal (0.0264 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (20% EtOAc /75% hexane); Appearance: off white solid; isolated yield: 49%; m.p. 110-112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.11 (s, 2H), 8.00 (d, *J* = 15.7 Hz, 2H), 6.45 (d, *J* = 15.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.24 (t, *J* = 8.2 Hz, 2H), 2.70 (t, *J* = 8.2 Hz, 2H), 2.64 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100

MHz, $CDCl_3$): δ 199.3, 196.6, 166.1, 143.5, 140.6, 135.9, 135.1, 128.0, 123.1, 60.9, 43.9, 26.5, 21.6, 14.2; **IR** (KBr): 2980, 2778, 1720, 1636, 1603, 1360, 1186, 1040, 980, 868, 844 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{24}O_6$ $[M + H]^+$ 373.1646, found 373.1642

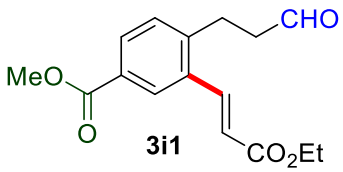


ethyl (E)-3-(5-acetyl-2-(3-oxopropyl)phenyl)acrylate (3h1): The crude product was purified via using flash chromatography; Eluent: (10% EtOAc /85% hexane); Appearance: light yellow viscous oil; isolated yield: 24%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.14 (d, *J* = 1.8 Hz, 1H), 7.94 (d, *J* = 15.7 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 8.2 Hz, 2H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.61(s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.0, 197.1, 166.4, 144.9, 140.4, 135.9, 133.6, 130.2, 129.6, 126.8, 121.7, 60.7, 44.3, 26.5, 25.4, 14.2; **IR** (KBr): 2977, 1731, 1637, 1603, 1360, 1183, 1035, 975, 865, 840 cm^{-1}; **HRMS** (ESI) Calcd for $C_{16}H_{18}O_4$ $[M + H]^+$ 275.1278, found 275.1275

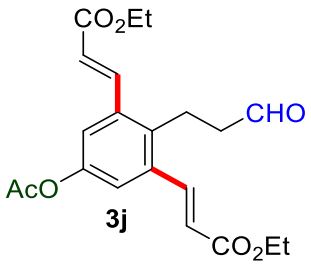


Diethyl 3,3'-(5-(methoxycarbonyl)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3i): Olefination was done by *general procedure (E)* with methyl 4-(3-oxopropyl)benzoate (0.0288g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (22% EtOAc /78% hexane); Appearance: off white solid; isolated yield: 45%; m.p. 98-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.21 (s, 2H), 7.96 (d, *J* = 15.7 Hz, 2H), 6.46 (d, *J* = 15.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.95 (s, 3H), 3.24 (t, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.3, 166.2, 165.9, 143.3, 140.5, 134.9, 129.3, 129.3, 123.0,

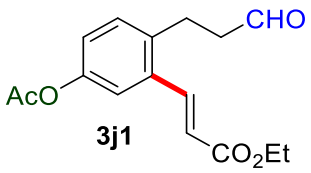
60.9, 52.4, 44.0, 21.5, 14.2; **IR** (KBr): 2983, 1725, 1631, 1601, 1278, 1183, 1033, 979, 868, 770 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{24}O_7$ $[M + H]^+$ 389.1595, found 389.1591



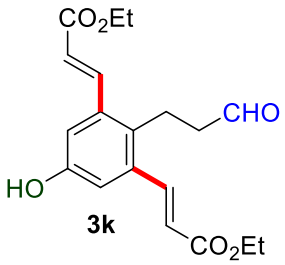
Diethyl 3,3'-(5-(methoxycarbonyl)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3i1): The crude product was purified via using flash chromatography; Eluent: (12% EtOAc /88% hexane); Appearance: light yellow viscous oil; isolated yield: 23%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 7.98-7.95 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.14 (t, *J* = 8.2 Hz, 2H), 2.79 (t, *J* = 8.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.1, 166.5, 166.4, 144.7, 140.3, 133.4, 130.8, 130.1, 129.0, 128.1, 121.6, 60.7, 52.2, 44.4, 25.4, 14.2; **IR** (KBr): 2984, 1726, 1632, 1604, 1282, 1042, 979, 871, 772 cm^{-1}; **HRMS** (ESI) Calcd for $C_{16}H_{18}O_5$ $[M + H]^+$ 291.1227, found 291.1223



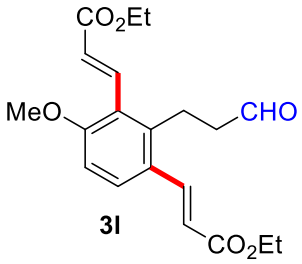
diethyl 3,3'-(5-acetoxy-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3j): Olefination was done by *general procedure (E)* with methyl 4-(3-oxopropyl)phenyl acetate (0.0288g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (25% EtOAc /75% hexane); Appearance: off white solid; isolated yield: 53%; m.p. 135-137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.94 (d, *J* = 15.7 Hz, 2H), 7.29 (s, 2H), 6.34 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.18 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 2.33 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 169.2, 166.2, 149.3, 140.5, 136.3, 135.9, 122.6, 121.6, 60.7, 44.4, 21.0, 20.9, 14.2; **IR** (KBr): 2982, 1763, 1713, 1629, 1213, 1179, 1031, 981, 868 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{24}O_7$ $[M + H]^+$ 389.1595, found 389.1592



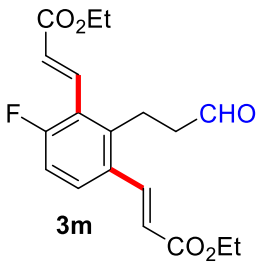
ethyl (E)-3-(5-acetoxy-2-(3-oxopropyl)phenyl)acrylate (3j1): The crude product was purified via using flash chromatography; Eluent: (14% EtOAc /86% hexane); Appearance: light yellow viscous oil; isolated yield: 27%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.91 (d, *J* = 15.7 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.09 (t, *J* = 8.2 Hz, 2H), 2.76 (t, *J* = 8.2 Hz, 2H), 2.32 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.5, 169.4, 166.5, 149.4, 140.4, 137.3, 134.3, 131.0, 123.3, 121.2, 119.7, 60.7, 44.9, 24.8, 21.0, 14.2; **HRMS** (ESI) Calcd for $C_{16}H_{18}O_5$ $[M + H]^+$ 291.1256, found 291.1252



diethyl 3,3'-(5-hydroxy-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3k): Olefination was done by *general procedure (E)* with 3-(4-hydroxyphenyl)propanal (0.0225g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (30% EtOAc /50% hexane); Appearance: off white solid; isolated yield: 55%; m.p. 154-156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.93 (d, *J* = 15.7 Hz, 2H), 7.08 (s, 2H), 6.29 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.11 (t, *J* = 8.2 Hz, 2H), 2.61 (t, *J* = 8.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.6, 166.9, 154.9, 141.7, 135.5, 131.0, 121.5, 115.7, 61.0, 45.0, 20.6, 14.2; **IR** (KBr): 3296, 2980, 1714, 1680, 1627, 1317, 1190, 1031, 974, 868 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{22}O_6$ $[M + H]^+$ 347.1489, found 347.1487

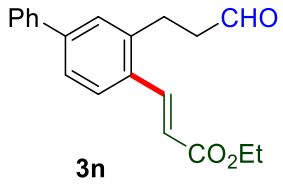


diethyl 3,3'-(4-methoxy-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3l): Olefination was done by *general procedure (E)* with 3-(3-methoxyphenyl)propanal (0.0246g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (17% EtOAc /83% hexane); Appearance: off white solid; isolated yield: 67%; m.p. 96-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.94 (d, *J* = 15.7 Hz, 1H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 15.7 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.90 (s, 3H), 3.21 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 167.2, 166.8, 159.8, 141.4, 140.8, 137.6, 129.1, 126.5, 124.7, 123.0, 119.4, 109.7, 60.5, 55.7, 44.5, 21.7, 14.3; **IR** (KBr):2982, 1704, 1627, 1583, 1479, 1272, 1168, 1036, 976, 818 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{24}O_6$ $[M + H]^+$ 361.1646, found 361.1639



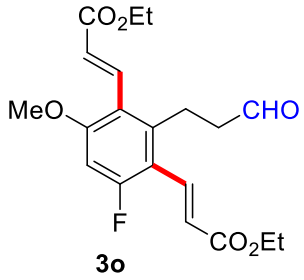
diethyl 3,3'-(4-fluoro-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3m): Olefination was done by *general procedure (E)* with 3-(3-fluorophenyl)propanal (0.0228g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (16% EtOAc /84% hexane); Appearance: off white solid; isolated yield: 65%; m.p. 98-99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.91 (d, *J* = 15.7 Hz, 1H), 7.68 (d, *J* = 15.7 Hz, 1H), 7.52 (dd, *J* = 5.5, 3.2 Hz, 1H), 7.04 (dd, *J* = 8.8, 1.2 Hz, 1H), 6.51 (dd, *J* = 15.7, 1.7 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 4.30-4.25 (m, 4H), 3.19 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 1.36-1.32 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.4,

166.5, 166.3, 161.9 (d, J_{C-F} = 256.5 Hz), 141.3 (d, J_{C-F} = 2.3 Hz), 140.6, 134.7, 130.4 (d, J_{C-F} = 3.6 Hz), 129.4 (d, J_{C-F} = 10.1 Hz), 126.1 (d, J_{C-F} = 12.2 Hz), 122.3 (d, J_{C-F} = 12.1 Hz), 121.5, 114.9 (d, J_{C-F} = 23.9 Hz), 60.8, 60.7, 44.1, 21.7, 14.19, 14.18; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -107.8; **IR** (KBr): 2982, 1715, 1624, 1268, 1159, 1023, 977, 816 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{21}FO_5$ $[M + H]^+$ 349.1446, found 349.1442



3n

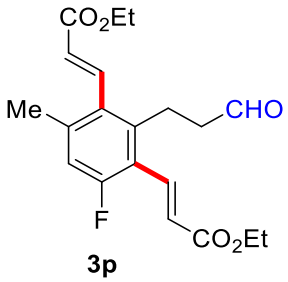
ethyl (E)-3-(3-(3-oxopropyl)-[1,1'-biphenyl]-4-yl)acrylate: The crude product was purified via using flash chromatography; Eluent: (10% EtOAc /90% hexane); Appearance: light yellow viscous oil; isolated yield: 62%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.97 (d, *J* = 15.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.49 – 7.42 (m, 4H), 7.38 – 7.34 (m, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.79 (td, *J* = 7.6, 1.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.7, 166.8, 142.9, 140.8, 140.3, 139.9, 131.8, 128.8, 128.5, 127.8, 127.3, 126.9, 125.6, 119.9, 60.6, 44.9, 25.5, 14.3; **IR** (KBr): 2981, 1710, 1634, 1444, 1364, 1282, 1182, 1036, 978, 859 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{20}O_3$ $[M + H]^+$ 309.1412, found 309.1409. *The appearance of doublet due to one proton at δ 7.64 signify the olefination at position C-6 rather than at C-2.*



3o

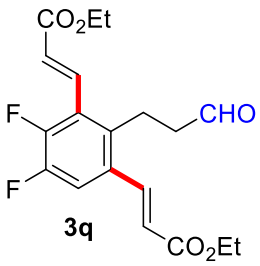
diethyl 3,3'-(4-fluoro-6-methoxy-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3o): Olefination was done by *general procedure (E)* with 3-(3-fluoro-5-methoxyphenyl)propanal (0.0273 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (19% EtOAc /81% hexane); Appearance: viscous oil; isolated yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.69 (d, *J* = 16.1 Hz, 1H), 7.64 (d, *J* = 16.1 Hz, 1H), 6.64 (d, *J* = 12.8 Hz, 1H), 6.51-6.45

(m, 2H), 4.26 (q, J = 7.1 Hz, 4H), 3.88 (s, 3H), 3.19 (t, J = 8.2 Hz, 2H), 2.66 (t, J = 8.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 167.1, 167.0, 161.4, 160.2 (d, J_{C-F} = 11.6 Hz), 142.9, 136.9, 134.9, 124.5, 123.8 (d, J_{C-F} = 13.3 Hz), 119.4, 114.5, 98.4 (d, J_{C-F} = 27.9 Hz), 60.6 (d, J_{C-F} = 3.7 Hz), 55.9, 44.1, 22.2, 14.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -104.5; **IR** (KBr): 2982, 1721, 1626, 1310, 1170, 1098, 1031, 978, 857 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{23}FO_6$ $[M + H]^+$ 379.1551, found 379.1548



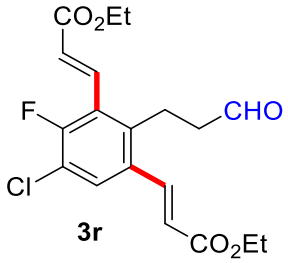
3p

diethyl 3,3'-(4-fluoro-6-methyl-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3p): Olefination was done by *general procedure (E)* with 3-(3-fluoro-5-methylphenyl)propanal (0.0249 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified *via* using flash chromatography; Eluent: (17 % EtOAc /83% hexane); Appearance: light yellow viscous oil; isolated yield: 40%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.75 (d, J = 16.3 Hz, 1H), 7.65 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 11.8 Hz, 1H), 6.55 (dd, J = 16.3, 1.4 Hz, 1H), 5.98 (d, J = 16.3 Hz, 1H), 4.32-4.26 (m, 4H), 3.10 (t, J = 8.2 Hz, 2H), 2.63 (t, J = 8.2 Hz, 2H), 2.32 (s, 3H), 1.38-1.34 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.9, 165.8, 160.8 (d, J_{C-F} = 254.2 Hz), 142.2, 140.4 (d, J_{C-F} = 2.8 Hz), 139.8 (d, J_{C-F} = 9.6 Hz), 134.9, 131.3 (d, J_{C-F} = 3.5 Hz), 126.1, 124.9 (d, J_{C-F} = 13.2 Hz), 119.4 (d, J_{C-F} = 11.6 Hz), 116.4 (d, J_{C-F} = 23.3 Hz), 60.8, 60.7, 44.0, 22.7, 21.3, 14.24, 14.21; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -110.9; **IR** (KBr): 2984, 1718, 1627, 1600, 1306, 1174, 1095, 1033, 977, 855 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{23}FO_5$ $[M + H]^+$ 363.1602, found 363.1595



3q

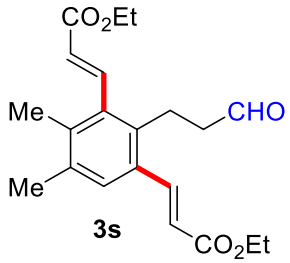
diethyl 3,3'-(4,5-difluoro-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3q): Olefination was done by *general procedure (E)* with 3-(3,4-difluorophenyl)propanal (0.0255 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (18 % EtOAc /82% hexane); Appearance: off white solid; isolated yield: 55%; m.p. 70-73 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.87 (d, *J* = 15.6 Hz, 1H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.35 (dd, *J* = 7.9, 2.7 Hz, 1H), 6.52 (dd, *J* = 16.2, 1.6 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 4.32-4.25 (m, 4H), 3.14 (t, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 8.2 Hz, 2H), 1.37-1.33 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.3, 166.1, 166.0, 151.1 (dd, J_{1C-F} = 258.0 Hz, J_{2C-F} = 14.1), 150.6 (dd, J_{1C-F} = 248.3 Hz, J_{2C-F} = 13.9), 139.6, 136.1 (d, J_{C-F} = 3.5 Hz), 134.0, 130.5 (dd, $J_{1,C-F}$ = 5.6 Hz, $J_{2,C-F}$ = 4.6 Hz,), 127.1 (d, J_{C-F} = 11.5 Hz), 124.4 (d, J_{C-F} = 8.9 Hz), 122.5, 116.0 (d, J_{C-F} = 17.7 Hz), 61.0, 60.8, 44.1, 21.3, 14.18, 14.17; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -133.6 (d, J_{C-F} = 21.2 Hz), δ -138.2 (d, J_{C-F} = 20.8 Hz); **IR** (KBr): 2984, 1720, 1627, 1476, 1313, 1181, 1032, 979, 856 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{20}F_2O_5$ [M + H]$^{+}$ 367.1352, found 367.1350



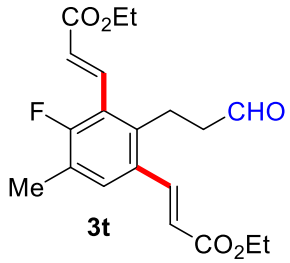
3r

diethyl 3,3'-(5-chloro-4-fluoro-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3r): Olefination was done by *general procedure (E)* with 3-(4-chloro-3-fluorophenyl)propanal (0.02799 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (12 % EtOAc /88% hexane); Appearance: off white solid; isolated yield: 56%; m.p. 105-108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.85 (d, *J* = 15.7 Hz, 1H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 6.50 (dd, *J* = 16.2, 1.9 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 4.28 (qd, *J* = 7.1, 5.0 Hz, 4H), 3.14 (m, 2H), 2.66 (m, 2H), 1.34 (td, *J* = 7.1, 3.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2, 166.1 (d, J_{C-F} = 17.1 Hz), 156.8 (d, J_{C-F} = 257.4 Hz), 139.6 (d, J_{C-F} = 10.5 Hz), 134.1, 131.1 (d, J_{C-F} = 4.5 Hz), 129.3, 127.1 (d, J_{C-F} = 11.5 Hz), 123.9 (d, J_{C-F} = 12.1 Hz), 122.6, 120.7 (d, J_{C-F} = 19.8 Hz), 60.98, 60.89, 43.9, 21.6, 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -110.3; **IR** (KBr): 2981,

1720, 1627, 1456, 1309, 1181, 1035, 981, 858 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{20}ClFO_5$ [M + H]$^+$ 383.1056, found 383.1057

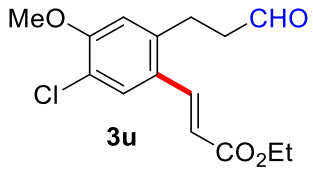


diethyl 3,3'-(4,5-dimethyl-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3s): Olefination was done by *general procedure (E)* with 3-(3,4-dimethylphenyl)propanal (0.0243 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (13 % EtOAc /82% hexane); Appearance: viscous oil; isolated yield: 40%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.92 (d, *J* = 15.7 Hz, 1H), 7.85 (d, *J* = 15.7 Hz, 1H), 7.37 (s, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.94 (d, *J* = 15.7 Hz, 1H), 4.32-4.25 (m, 4H), 3.07 (t, *J* = 8.2 Hz, 2H), 2.59 (t, *J* = 8.2 Hz, 2H), 2.31 (s, 3H), 2.22 (s, 3H), 1.38-1.34 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.3, 166.7, 166.0, 144.0, 141.7, 137.0, 135.8, 135.7, 135.1, 130.8, 128.1, 125.8, 120.2, 60.8, 60.5, 44.6, 22.1, 20.4, 17.5, 14.3, 14.2; **IR** (KBr): 2980, 1709, 1630, 1307, 1270, 1178, 1032, 979, 863 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_5$ [M + H]$^+$ 359.1853, found 359.1849

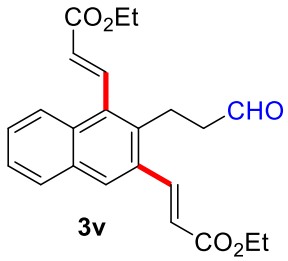


diethyl 3,3'-(4-fluoro-5-methyl-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (3t): Olefination was done by *general procedure (E)* with 3-(3-fluoro-4-methylphenyl)propanal (0.0249 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (15 % EtOAc /85% hexane); Appearance: off white solid; isolated yield: 59%; m.p. 127-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.89 (d, *J* = 15.7 Hz, 1H), 7.68 (d, *J* = 15.7 Hz, 1H), 7.38 (d, *J* = 7.5 Hz,

1H), 6.50 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.29 (d, *J* = 15.7 Hz, 1H), 4.31-4.24 (m, 4H), 3.15 (t, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 1.34 (td, *J* = 7.2, 2.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.6, 166.4, 160.5 (d, J_{C-F} = 255.3 Hz), 140.8, 138.7 (d, J_{C-F} = 2.2 Hz), 135.2, 130.8 (d, J_{C-F} = 6.7 Hz), 129.7 (d, J_{C-F} = 4.2 Hz), 125.8 (d, J_{C-F} = 12.5 Hz), 124.3 (d, J_{C-F} = 20.0 Hz), 121.9 (d, J_{C-F} = Hz), 121.1, 60.7, 60.6, 44.4, 21.5, 14.51, 14.47; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -111.5; **IR** (KBr): 2983, 1716, 1627, 1316, 1187, 1080, 1035, 979, 869 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{23}FO_5$ $[M + H]^+$ 363.1602, found 363.1597

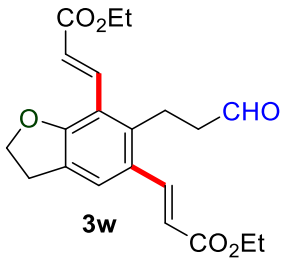


ethyl (E)-3-(5-chloro-4-methoxy-2-(3-oxopropyl)phenyl)acrylate (3u): Olefination was done by *general procedure (E)* with 3-(4-chloro-3-methoxyphenyl)propanal (0.02930 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (13 % EtOAc /87% hexane); Appearance: off white solid; isolated yield: 71%; m.p. 59-61 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.60 (s, 1H), 7.79 (s, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.2, 166.8, 156.1, 140.4, 139.5, 128.4, 126.1, 121.3, 118.9, 113.4, 60.6, 56.2, 45.0, 25.4 and 14.3; **IR** (KBr): 2982, 1706, 1628, 1180, 1040, 976, 860 cm^{-1}; **HRMS** (ESI) Calcd for $C_{15}H_{17}ClO_4$ $[M + H]^+$ 297.0888, found 297.0888



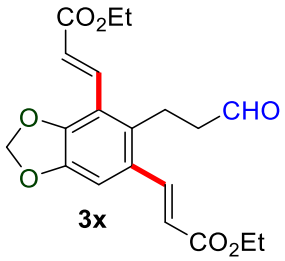
diethyl 3,3'-(2-(3-oxopropyl)naphthalene-1,3-diyl)(2E,2'E)-diacrylate (3v): Olefination was done by *general procedure (E)* with 3-(naphthalen-2-yl)propanal (0.0276 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (16 % EtOAc /84% hexane); Appearance: light

yellow viscous oil; isolated yield: 40 %. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.14 (d, *J* = 15.7 Hz, 1H), 8.05 (d, *J* = 15.7 Hz, 1H), 8.03 (s, 1H), 7.97-7.94 (m, 1H), 7.85-7.83 (m, 1H), 7.52-7.49 (m, 2H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 4.36-4.27 (m, 4H), 3.25 (t, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 1.40-1.35 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.0, 166.4, 165.9, 142.1, 141.9, 134.4, 132.6, 132.0, 131.9, 131.8, 128.7, 127.7, 127.6, 127.2, 126.4, 125.2, 121.9, 60.9, 60.7, 44.3, 22.7, 14.27, 14.25; **HRMS** (ESI) Calcd for $C_{23}H_{24}O_5$ $[M + H]^+$ 381.1697, found 381.1692



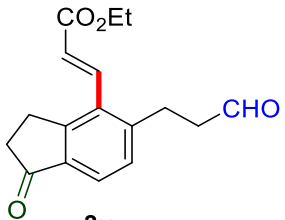
3w

Diethyl 3,3'-(6-(3-oxopropyl)-2,3-dihydrobenzofuran-5,7-diyl)(2E,2'E)-diacrylate (3w): Olefination was done by *general procedure (E)* with 3-(2,3-dihydrobenzofuran-6-yl)propanal (0.0264g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (18 % EtOAc /82% hexane); Appearance: off white solid; isolated yield: 61 %; m.p. 140-143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.96-7.92 (m, 2H)*, 7.0 (s, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 4.61 (t, *J* = 8.6 Hz, 2H), 4.32-4.26 (m, 4H), 3.32 (t, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.38-1.34 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.2, 166.5, 166.3, 159.2, 141.5, 141.0, 134.0, 131.6, 131.3, 128.6, 124.0, 121.0, 108.2, 71.2, 60.8, 60.6, 44.9, 30.9, 21.3, 14.23, 14.21; **IR** (KBr): 2981, 1713, 1627, 1600, 1306, 1178, 1035, 978, 868 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{24}O_6$ $[M + H]^+$ 373.1646, found 373.1642. * = at δ 7.96 two alkene proton merged.



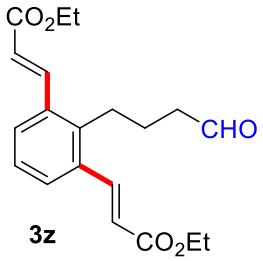
3x

diethyl 3,3'-(5-(3-oxopropyl)benzo[d][1,3]dioxole-4,6-diyl)(2E,2'E)-diacrylate (3x): Olefination was done by *general procedure (E)* with 3-(benzo[d][1,3]dioxol-5-yl)propanal (0.0267 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (30 % EtOAc /70% hexane); Appearance: off white solid; isolated yield: 83%; m.p. 175-177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.92 (d, *J* = 15.7 Hz, 1H), 7.73 (d, *J* = 15.7 Hz, 1H), 7.04 (s, 1H), 6.78 (d, *J* = 15.7 Hz, 1H), 6.23 (d, *J* = 15.7 Hz, 1H), 6.09 (s, 2H), 4.30-4.23 (m, 4H), 3.19 (t, *J* = 8.2 Hz, 2H), 2.65 (t, *J* = 8.2 Hz, 2H), 1.35-1.32 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 167.0, 166.7, 148.7, 146.8, 141.1, 135.4, 133.9, 127.5, 124.2, 119.7, 116.3, 107.4, 101.8, 60.7, 60.6, 45.0, 20.9, 14.3; **IR** (KBr): 2986, 2900, 1711, 1625, 1466, 1312, 1185, 1077, 1036, 977, 867 cm^{-1} ; **HRMS** (ESI) Calcd for $C_{20}H_{22}O_7$ $[M + H]^+$ 375.1438, found 375.1437.



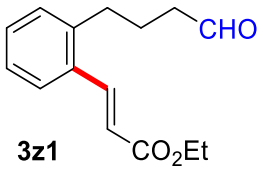
3y

ethyl (E)-3-(1-oxo-5-(3-oxopropyl)-2,3-dihydro-1H-inden-4-yl)acrylate (3y): Olefination was done by *general procedure (E)* with 3-(1-oxo-2,3-dihydro-1H-inden-5-yl)propanal (0.0282 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (16% EtOAc /84% hexane); Appearance: off white solid; isolated yield: 31%; m.p. 127-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.91 (d, *J* = 16.4 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 16.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.21 (t, *J* = 5.7 Hz, 2H), 3.17 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.75-2.72 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.9, 200.0, 166.3, 154.3, 146.8, 139.5, 136.4, 132.0, 129.5, 124.6, 124.5, 60.9, 44.4, 36.4, 26.6, 26.1, 14.3; **IR** (KBr): 2834, 2733, 1710, 1695, 1606, 1120, 978, 864 cm^{-1} ; **HRMS** (ESI) Calcd for $C_{17}H_{18}O_4$ $[M + H]^+$ 287.1278, found 287.1275. *We were unable to isolate di product due to low yield and very close Rf with its side product i.e. cyclic aldehyde (CA).*



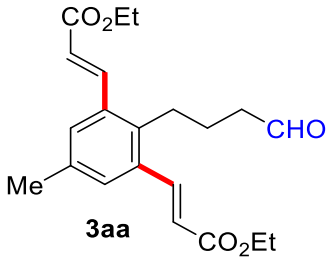
3z

diethyl 3,3'-(2-(4-oxobutyl)-1,3-phenylene)(2E,2'E)-diacrylate (3z): Olefination was done by *general procedure (E)* with 4-phenylbutanal (0.0222 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (14 % EtOAc /86% hexane); Appearance: colorless viscous oil; isolated yield: 19%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 8.05 (d, *J* = 15.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.92-2.89 (m, 2H), 2.55 (dd, *J* = 7.1, 1.1 Hz, 2H), 1.87-1.80 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.3, 166.7, 141.9, 140.1, 134.4, 128.5, 127.0, 121.4, 60.7, 43.2, 28.1, 23.4, 14.3; **IR** (KBr): 2986, 1714, 1626, 1474, 1170, 1031, 986, 977, 765, 701 cm^{-1}; **HRMS** (ESI) Calcd for $C_{20}H_{24}O_5$ $[M + H]^+$ 345.1697, found 345.1692



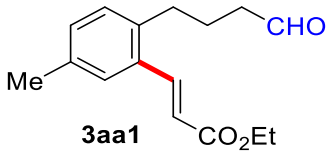
3z1

ethyl (E)-3-(2-(4-oxobutyl)phenyl)acrylate (3z1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: viscous oil; isolated yield: 23%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 8.00 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.20 (t, *J* = 6.8 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.9, 167.1, 141.8, 141.0, 133.2, 130.2, 126.9, 126.8, 120.0, 60.7, 43.2, 32.4, 23.8, 14.4; **HRMS** (ESI) Calcd for $C_{15}H_{18}O_3$ $[M + H]^+$ 247.1254, found 247.1255



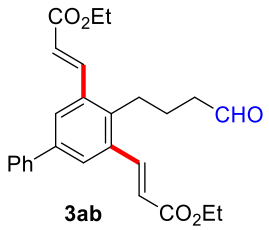
3aa

diethyl 3,3'-(5-methyl-2-(4-oxobutyl)-1,3-phenylene)(2E,2'E)-diacrylate (3aa): Olefination was done by *general procedure (E)* with 4-(p-tolyl)butanal (0.0243g, 0.15 mmol) as the substrate and ethyl acrylate (50µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (17 % EtOAc /88% hexane); Appearance: light yellow viscous oil; isolated yield: 17%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 8.03 (d, *J* = 15.7 Hz, 2H), 7.40 (s, 2H), 6.35 (d, *J* = 15.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.51 (dd, *J* = 6.3, 1.1 Hz, 2H), 2.35 (s, 3H), 1.84-1.77 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.4, 166.7, 142.0, 137.3, 136.5, 134.3, 129.3, 121.1, 60.6, 43.2, 27.7, 23.6, 20.9, 14.3; **IR** (KBr): 2982, 1718, 1620, 1477, 1182, 1035, 976, 760, cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_5$ $[M + H]^+$ 359.1853, found 359.1850



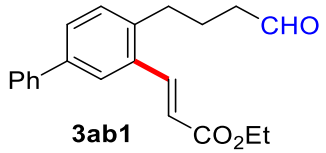
3aa1

ethyl (E)-3-(5-methyl-2-(4-oxobutyl)phenyl)acrylate (3aa1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: light yellow viscous oil; isolated yield: 23%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.98 (d, *J* = 15.7 Hz, 1H), 7.41 (s, 1H), 7.16-7.09 (m, 2H), 6.39 (d, *J* = 15.7 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.50 (dd, *J* = 7.3, 1.3 Hz, 2H), 2.36 (s, 3H), 1.94-1.87 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.9, 167.0, 141.8, 137.9, 136.3, 132.8, 130.9, 130.0, 127.2, 119.5, 60.5, 43.1, 31.9, 23.8, 20.9, 14.3; **HRMS** (ESI) Calcd for $C_{16}H_{20}O_3$ $[M + H]^+$ 261.1320, found 261.1318



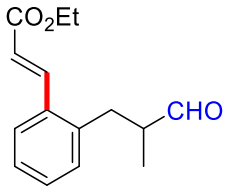
3ab

diethyl 3,3'-(4-(4-oxobutyl)-[1,1'-biphenyl]-3,5-diyl)(2E,2'E)-diacrylate (3ab): Olefination was done by *general procedure (E)* with 4-([1,1'-biphenyl]-4-yl)butanal (0.0336 g, 0.15 mmol) as the substrate and ethyl acrylate (50 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (11 % EtOAc /89% hexane); Appearance: light yellow solid; isolated yield: 20%; m.p. 107-110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.10 (d, *J* = 15.7 Hz, 2H), 7.78 (s, 2H), 7.59 (dt, *J* = 8.1, 1.9 Hz, 2H), 7.46 (td, *J* = 6.7, 1.6 Hz, 2H), 7.41-7.36 (m, 1H), 6.44 (d, *J* = 15.7 Hz, 2H), 4.29 (t, *J* = 7.1 Hz, 4H), 2.99-2.89 (m, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 1.90-1.82 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ; 201.4, 166.6, 141.9, 139.9, 139.7, 139.0, 134.9, 128.9, 127.8, 127.1, 126.9, 121.6, 60.7, 43.2, 27.9, 23.4 and 14.3; **IR** (KBr): 2980, 1718, 1630, 1308, 1172, 1034, 974, 857, 765, 700 cm^{-1}; **HRMS** (ESI) Calcd for $C_{26}H_{28}O_5$ $[M + H]^+$ 421.2010, found 421.2009



3ab1

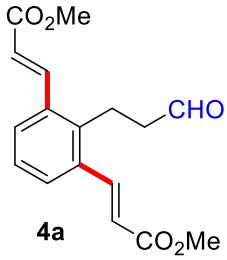
ethyl (E)-3-(4-(4-oxobutyl)-[1,1'-biphenyl]-3-yl)acrylate (3ab1): The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: light yellow viscous oil; isolated yield: 29%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 8.04 (d, *J* = 15.8 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.54 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.47-7.42 (m, 2H), 7.38-7.33 (m, 1H), 7.27(d, *J* = 7.9 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.84 (dd, *J* = 8.6, 6.9 Hz, 2H), 2.52 (td, *J* = 7.2, 1.5 Hz, 2H), 1.99-1.91 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.8, 166.9, 141.7, 140.3, 139.84, 139.82, 133.5, 130.6, 128.83, 128.75, 127.5, 127.0, 125.4, 120.2, 60.6, 43.1, 32.0, 23.6, 14.3; **HRMS** (ESI) Calcd for $C_{21}H_{22}O_3$ $[M + H]^+$ 323.1642, found 323.1642



3ae

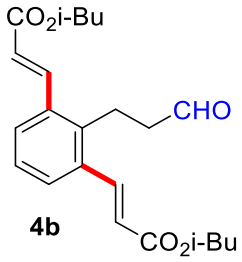
ethyl (E)-3-(2-(2-methyl-3-oxopropyl)phenyl)acrylate : The crude product was purified via using flash chromatography; Eluent: (4% EtOAc /96% hexane); Appearance: light yellow viscous oil; isolated yield: 12%. **^{1}H NMR** (400 MHz, $CDCl_3$): 9.70 (s, 1H), 7.96 (d, *J* = 15.8 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.20 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.25 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.2 Hz, 1H), 2.67– 2.58 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.6, 166.8, 141.5, 138.5, 133.4, 130.8, 130.0, 127.1, 126.9, 120.2, 60.6, 47.8, 33.6, 14.3, 13.3; **HRMS** (ESI) Calcd for $C_{15}H_{18}O_3$ $[M + H]^+$ 247.1256, found 247.1251 The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[17b].

Experimental data for remote C-H di-olefination with acrylates:



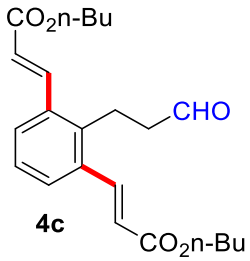
4a

dimethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4a): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201g, 0.15 mmol) as the substrate and methyl acrylate (43 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (15% EtOAc /85% hexane); Appearance: off white solid; isolated yield: 66%; m.p. 65-67°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.00 (d, *J* = 15.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 2H), 3.83 (s, 6H), 3.21 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ199.9, 166.8, 141.6, 138.8, 134.4, 128.7, 127.3, 121.4, 51.8, 44.5, 21.2; **IR** (KBr): 2963, 1716, 1630, 1474, 1170, 971, 867, cm^{-1}; **HRMS** (ESI) Calcd for $C_{17}H_{18}O_5$ $[M + H]^+$ 303.1227, found 303.1223



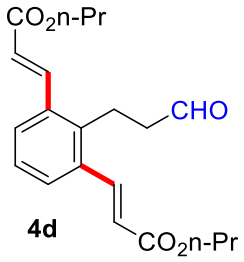
4b

diisobutyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4b): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and isobutyl acrylate (65 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (10% EtOAc /90% hexane); Appearance: off white solid; isolated yield: 71%; m.p. 59-61°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.02 (d, *J* = 15.7 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 2H), 4.02 (d, *J* = 6.7 Hz, 4H), 3.23 (t, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 2.09-1.98 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ199.8, 166.5, 141.4, 138.7, 134.4, 128.7, 127.2, 121.8, 70.8, 44.6, 27.8, 21.2, 19.1; **IR** (KBr): 2959, 1714, 1628, 1472, 1314, 1171, 1011, 973, 865, 806 cm^{-1}; **HRMS** (ESI) Calcd for $C_{23}H_{30}O_5$ $[M + H]^+$ 387.2166, found 387.2160

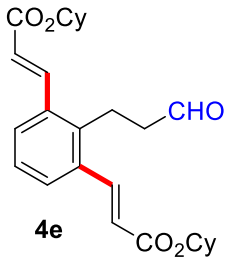


4c

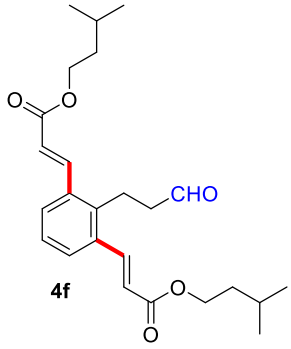
dibutyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4c): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201g, 0.15 mmol) as the substrate and n-butyl acrylate (65µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (9% EtOAc /91% hexane); Appearance: light yellow viscous oil; isolated yield: 70%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 2H), 4.23 (t, *J* = 6.7 Hz, 4H), 3.22 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 1.74-1.67 (m, 4H), 1.50-1.40 (m, 4H), 0.98 (d, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 166.6, 141.4, 138.8, 134.5, 128.7, 127.3, 121.8, 64.7, 44.6, 30.7, 21.3, 19.2, 13.7; **HRMS** (ESI) Calcd for $C_{23}H_{30}O_5$ $[M + H]^+$ 387.2153, found 387.2159



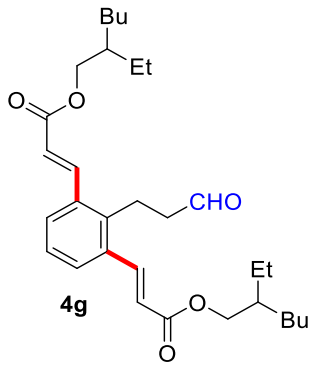
dipropyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4d): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and n-propyl acrylate (57 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (10% EtOAc /90% hexane); Appearance: light yellow viscous oil; isolated yield: 63%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 2H), 4.19 (t, *J* = 6.7 Hz, 4H), 3.22 (t, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 8.2 Hz, 2H), 1.79-1.70 (m, 4H), 1.00 (d, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.8, 166.5, 141.4, 138.7, 134.4, 128.6, 127.2, 121.8, 66.3, 44.5, 22.0, 21.2, 10.4; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_5$ $[M + H]^+$ 359.1853, found 359.1848



dicyclohexyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4e): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and cyclohexyl acrylate (71 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (7% EtOAc /93% hexane); Appearance: light yellow viscous oil; isolated yield: 69%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 2H), 4.94-4.88 (m, 2H), 3.24 (t, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 1.94-1.92 (m, 4H), 1.80-1.77 (m, 4H), 1.60-1.30 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.9, 166.9, 141.1, 138.7, 134.5, 128.6, 127.2, 122.3, 72.9, 44.6, 31.6, 25.4, 23.7, 21.2; **HRMS** (ESI) Calcd for $C_{27}H_{34}O_5$ $[M + H]^+$ 439.2479, found]$^+$ 439.2473

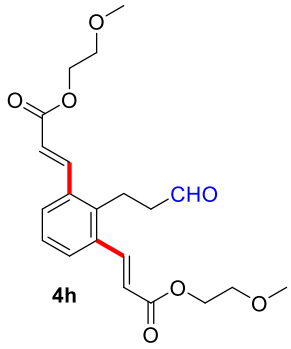


diisopentyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4f): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and isopentyl acrylate (72 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (8% EtOAc /92% hexane); Appearance: light yellow viscous oil; isolated yield: 68%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.98 (d, *J* = 15.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 2H), 4.25 (t, *J* = 6.7 Hz, 4H), 3.20 (t, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 8.2 Hz, 2H), 1.80-1.70 (m, 2H), 1.64 (q, *J* = 6.9 Hz, 4H), 0.96 (d, *J* = 6.6 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.5, 141.3, 138.7, 134.4, 128.6, 127.2, 121.8, 63.4, 44.5, 37.3, 25.1, 22.4, 21.2; **HRMS** (ESI) Calcd for $C_{25}H_{34}O_5$ $[M + H]^+$ 415.2479, found 415.2474

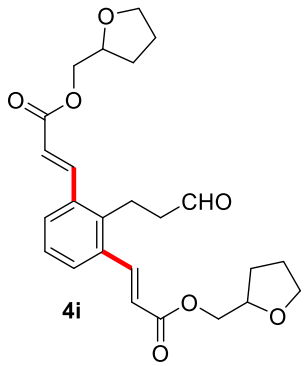


bis(2-ethylhexyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4g): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 2-ethylhexyl acrylate (92 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (7% EtOAc /93% hexane); Appearance: light yellow viscous oil; isolated yield: 72% with amine A_2 or 40.0 % with amine A_1 **^{1}H NMR** (400 MHz, C_3D_6O): δ 9.82 (s, 1H), 8.06 (d, *J* = 15.7 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.7

Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 2H), 4.17-4.09 (m, 4H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6Hz, 2H), 1.70-1.64 (m, 2H), 1.48-1.34 (m, 16H), 0.96-0.90 (m, 12H); **^{13}C NMR** (100 MHz, C_3D_6O): δ 199.8, 166.9, 141.3, 139.3, 134.4, 128.7, 127.3, 121.4, 66.3, 44.3, 38.9, 30.4, 28.8, 23.7, 22.8, 20.9, 13.5, 10.5; **HRMS** (ESI) Calcd for $C_{31}H_{46}O_5$ [M + H]$^+$ 499.3418, found 499.3409

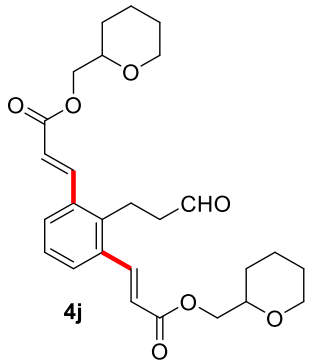


bis(2-methoxyethyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4h): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 2-methoxyethyl acrylate (58 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (47% EtOAc /53% hexane); Appearance: off white solid; isolated yield: 62%; m.p. 67-68°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.01 (d, *J* = 15.7 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 2H), 4.39-4.38 (m, 4H), 3.69-3.67 (d, *J* = 4.6 Hz, 4H), 3.43 (s, 6H), 3.21 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 166.4, 141.9, 138.9, 134.3, 128.7, 127.2, 121.3, 70.4, 63.7, 59.0, 44.5, 21.2; HRMS (ESI) Calcd for $C_{21}H_{26}O_7$ [M + H]$^+$ 391.1751, found 391.1746



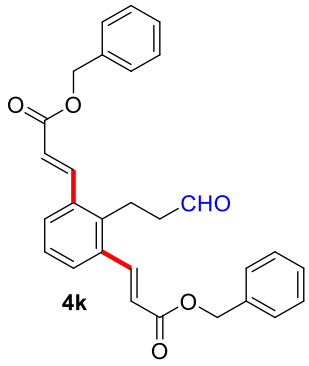
bis((tetrahydrofuran-2-yl)methyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4i): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol)

as the substrate and tetrahydro-2-furanylmethyl acrylate (70 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (45% EtOAc /55% hexane); Appearance: off white solid; isolated yield: 60%; m.p. 53-55°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.02 (d, *J* = 15.7 Hz, 2H), 7.56(d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.41 (d, *J* = 15.7 Hz, 2H), 4.31 (dd, *J* = 10.9, 2.9 Hz, 2H), 4.24-4.12 (m, 4H), 3.95-3.90 (m, 2H), 3.86-3.80 (m, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.09-2.01 (m, 2H), 1.99-1.89 (m, 4H), 1.71-1.62 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.3, 141.9, 138.8, 134.3, 128.7, 127.3, 121.3, 76.5, 68.4, 66.7, 44.5, 28.0, 25.6, 21.2; **HRMS** (ESI) Calcd for $C_{25}H_{30}O_7$ $[M + H]^+$ 443.2064, found 443.2058

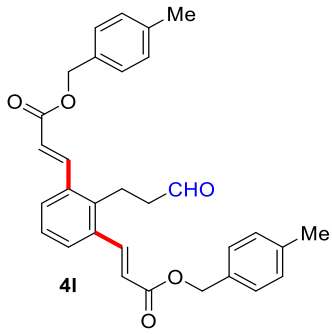


4j

bis((tetrahydro-2H-pyran-2-yl)methyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4j): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and (tetrahydro-2H-pyran-2-yl)methyl acrylate (0.0766 g, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (40% EtOAc /60% hexane); Appearance: colorless viscous oil; isolated yield: 70%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 2H), 4.21 (dd, *J* = 3.3, 3.3 Hz, 2H), 4.14 (dd, *J* = 6.8, 6.8 Hz, 2H), 4.03-3.99 (m, 2H), 3.63-3.58 (m, 2H), 3.47-3.42 (m, 2H), 3.18 (t, *J* = 8.1 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H), 1.89-1.86 (m, 2H), 1.61-150 (m, 8H), 1.41-1.32 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.3, 141.7, 138.8, 134.2, 128.6, 127.1, 121.3, 75.3, 68.3, 67.5, 44.5, 27.7, 25.6, 22.8, 21.0; **HRMS** (ESI) Calcd for $C_{27}H_{34}O_7$ $[M + H]^+$ 471.2377, found 471.2374

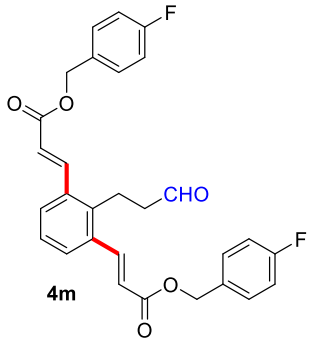


dibenzyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4k): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201g, 0.15 mmol) as the substrate and benzyl acrylate (66 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (17% EtOAc /83% hexane); Appearance: viscous oil; isolated yield: 54%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.07 (d, *J* = 15.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.47-7.38 (m, 10H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 2H), 5.29 (s, 4H), 3.23 (t, *J* = 8.1 Hz, 2H), 2.68 (t, *J* = 8.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.8, 166.2, 142.0, 138.9, 135.8, 134.3, 128.8, 128.6, 128.3, 128.2, 127.3, 121.4, 66.5, 44.5, 21.2; **HRMS** (ESI) Calcd for $C_{29}H_{26}O_5$ $[M + H]^+$ 455.1853, found 455.1845

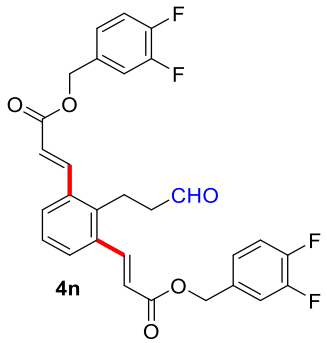


bis(4-methylbenzyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4l): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 4-methylbenzyl acrylate (0.0793 g, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (15% EtOAc /75% hexane); Appearance: viscous oil; isolated yield: 59%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 8.02 (d, *J* = 15.7 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 4H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 4H), 6.37 (d, *J* = 15.7 Hz, 2H), 5.21 (s, 4H), 3.18 (t, *J* = 8.1 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H),

2.36 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.8, 166.2, 141.8, 138.9, 138.2, 134.4, 132.8, 129.2, 128.8, 128.4, 127.2, 121.5, 66.4, 44.5, 21.22, 21.16; **HRMS** (ESI) Calcd for $C_{31}H_{30}O_5$ [M + Na]$^+$ 505.1985, found 505.1980

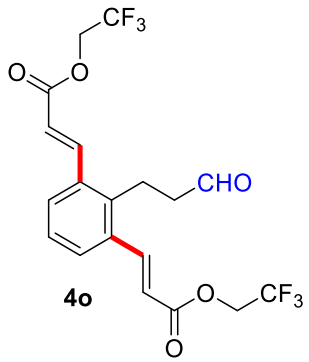


bis(4-fluorobenzyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4m): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 4-fluorobenzyl acrylate (0.0811 g, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (17% EtOAc /83% hexane); Appearance: off white solid; isolated yield: 48%; m.p. 93-95°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 8.03 (d, *J* = 15.5 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.40 (br, 4H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 4H), 6.38 (d, *J* = 15.5 Hz, 2H), 5.21 (s, 4H), 3.19 (t, *J* = 8.1 Hz, 2H), 2.65 (t, *J* = 8.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.1, 162.6 (d, J_{C-F} = 244.6 Hz), 142.0, 139.0, 134.3, 131.7, 130.3 (d, J_{C-F} = 8.2 Hz), 128.8, 127.3, 121.2, 115.5 (d, J_{C-F} = 21.6 Hz), 65.8, 44.6, 21.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -113.4; **IR** (KBr): 2957, 1711, 1623, 1603, 1510, 1223, 1152, 969, 829 cm^{-1}; **HRMS** (ESI) Calcd for $C_{29}H_{24}F_2O_5$ [M + H]$^+$ 491.1665, found 491.1660



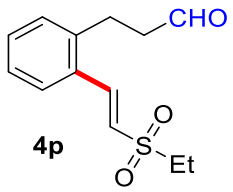
bis(3,4-difluorobenzyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4n): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 3,4-difluorobenzyl acrylate (0.0892 g, 3 equiv., 0.45 mmol) as olefin partner. The

crude product was purified via using flash chromatography; Eluent: (19% EtOAc /81% hexane); Appearance: off white solid; isolated yield: 50%; m.p. 124-127°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.07 (d, *J* = 15.5 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.33-7.20 (m, 4H), 7.18-7.16 (m, 3H), 6.41 (d, *J* = 15.5 Hz, 2H), 5.22 (s, 4H), 3.23 (t, *J* = 8.1 Hz, 2H), 2.69 (t, *J* = 8.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.0, 151.6 (dd, J_{1C-F} = 248.6 Hz, J_{2C-F} = 5.1), 151.5 (dd, J_{1C-F} = 248.6 Hz, J_{2C-F} = 5.1), 142.4, 139.1, 134.3, 132.9 (dd, J_{1C-F} = 5.6 Hz, J_{2C-F} = 3.9 Hz), 128.9, 127.3, 124.4 (dd, J_{1C-F} = 6.5 Hz, J_{2C-F} = 3.7 Hz), 121.0, 117.4 (dd, J_{1C-F} = 17.6 Hz, J_{2C-F} = 8.9 Hz), 65.2, 44.6, 21.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -137.1 (d, J_{C-F} = 20.8 Hz), δ -138.1 (d, J_{C-F} = 20.5 Hz); **IR** (KBr): 2921, 1715, 1625, 1609, 1519, 1318, 1277, 1172, 979, 821 cm^{-1}; **HRMS** (ESI) Calcd for $C_{29}H_{22}F_4O_5$ $[M + H]^+$ 527.1476, found 527.1472



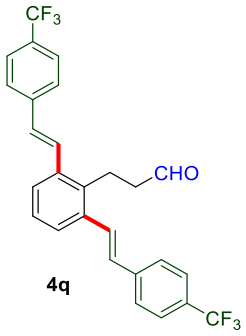
4o

bis(2,2,2-trifluoroethyl) 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (4o): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and 2,2,2-trifluoroethyl acrylate (58 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (13% EtOAc /87% hexane); Appearance: viscous oil; isolated yield: 40%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.12 (d, *J* = 15.5 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 15.5 Hz, 2H), 4.61 (q, *J* = 8.4 Hz, 4H); 3.22 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 164.6, 143.8, 139.5, 134.0, 129.3, 127.5, 122.9 (d, J_{C-F} = 277.2 Hz), 119.5, 60.5 (q, J_{C-F} = 37.0 Hz), 44.6, 21.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -73.7 Hz; **HRMS** (ESI) Calcd for $C_{19}H_{16}F_6O_5$ $[M + H]^+$ 439.0975, found 439.0977.



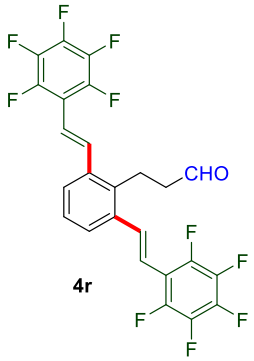
4p

(E)-3-(2-(2-(ethylsulfonyl)vinyl)phenyl)propanal (4p): Olefination was done by *general procedure (E)* with 3-phenylpropanal (0.0201 g, 0.15 mmol) as the substrate and (ethylsulfonyl)ethene (47 µL, 3 equiv., 0.45 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (51% EtOAc /49% hexane); Appearance: brownish viscous oil; isolated yield: 42%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.89 (d, *J* = 15.2 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 15.2 Hz, 1H), 3.15-3.08 (m, 4H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.41 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.3, 142.1, 140.4, 131.3, 130.8, 130.1, 127.1, 125.8, 49.2, 44.7, 25.1, 7.2; **HRMS** (ESI) Calcd for $C_{13}H_{16}O_3S$ $[M + H]^+$ 253.0893, found 253.0889

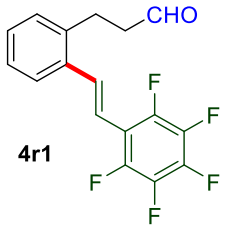


4q

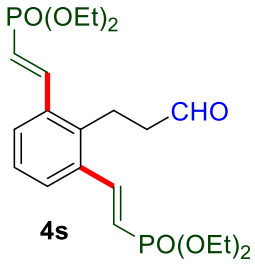
3-(2,6-bis((E)-4-(trifluoromethyl)styryl)phenyl)propanal: The crude product was purified *via* using flash chromatography; Eluent: (2% EtOAc /98% Hexane); Appearance: Light yellow solid; isolated yield: 63%; m.p. 173-175°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 9.82 (s, 1H), 7.63 – 7.53 (m, 10H), 7.48 (d, *J* = 16.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 2H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.73 (t, *J* = 7.8 Hz, 2H);**^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.7, 140.7, 136.6, 136.5, 130.5, 129.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.6, 127.2, 126.7, 126.7, 125.7 (q, $J_{C\text{-}F}$ = 3.9 Hz). 125.5, 122.8, 44.4, 21.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -62.4; **IR** (KBr): 2841, 1721, 1610, 1323, 1168, 1126, 1067, 969, 831cm^{-1}; **HRMS** (ESI) Calcd for $C_{27}H_{20}F_6O$ $[M + H]^+$ 475.1417, found 474.1409



3-(2,6-bis((E)-2-(perfluorophenyl)vinyl)phenyl)propanal: The crude product was purified *via* using flash chromatography; Eluent: (1% EtOAc /99% Hexane); Appearance: off white solid; isolated yield: 21%; m.p. 163-165°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.71 (d, *J* = 16.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 16.4 Hz, 2H), 3.23 – 3.11 (t, *J* = 7.8 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ200.3, 146.1, 143.6, 141.3, 139.1, 136.9, 136.6, 134.8, 134.8 (t, J_{C-F} = 7.6 Hz), 134.7, 127.4, 127.1, 116.0, 112.2, 44.2, 21.4; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -142.6 (d, J_{C-F} = 24.4 Hz), -155.5, -162.4; **IR** (KBr): 2922, 1726, 1520, 1494, 1002, 964 cm^{-1}; **HRMS** (ESI) Calcd for $C_{25}H_{12}F_{10}O$ $[M + H]^+$ 519.0726, found 519.0721

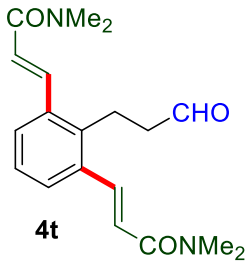


(E)-3-(2-(2-(perfluorophenyl)vinyl)phenyl)propanal: The crude product was purified *via* using flash chromatography; Eluent: (3% EtOAc /97% Hexane); Appearance: off white solid; isolated yield: 21%; m.p. 68-71°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.65 (d, *J* = 16.5 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.29 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 6.87 (d, *J* = 16.5 Hz, 1H), 3.07 (dd, *J* = 8.1, 7.1 Hz, 2H), 2.76 (td, *J* = 7.5, 1.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$):δ 200.9, 146.1, 143.6, 138.7, 136.6, 135.3, 134.5 (t, J_{C-F} = 7.6 Hz), 129.7, 129.1, 127.1, 126.0, 114.8, 114.8, 112.4 (t, J_{C-F} = 7.6 Hz), 44.8, 25.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ -142.75 (d, J_{C-F} = 24.6 Hz), -155.96, -162.55 ; **HRMS** (ESI) Calcd for $C_{17}H_{11}F_5O$ $[M + H]^+$ 327.0730, found 327.0729



4s

tetraethyl ((1E,1'E)-(2-(3-oxopropyl)-1,3-phenylene)bis(ethene-2,1-diyl))bis(phosphonate): The crude product was purified via using flash chromatography; Eluent: (2% MeOH /98% DCM); Appearance: light yellow viscous oil; isolated yield: 48%. **^{1}H NMR** (400 MHz, $CDCl_3$): 9.79 (s, 1H), 7.78 (dd, *J* = 17.3 Hz, 2H), 7.54 (*d*, *J* = 8.0, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.21 (td, *J* = 18.0, 1.9 Hz, 2H), 4.20– 4.12 (m, 8H), 3.18 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.8, 145.5, 145.4, 137.9, 135.2, 135.0, 128.4, 127.2, 119.3, 117.4, 62.0, 61.8, 44.4, 21.1, 16.4, 16.3; **HRMS** (ESI) Calcd for $C_{21}H_{32}O_7P_2$ $[M + H]^+$ 459.1623, found 459.1620



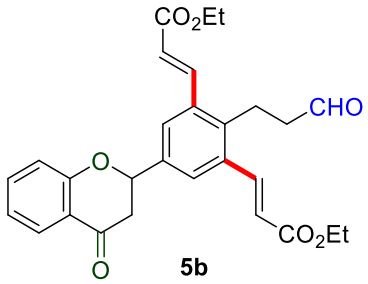
4t

(2E,2'E)-3,3'-(2-(3-oxopropyl)-1,3-phenylene)bis(N,N-dimethylacrylamide): The crude product was purified *via* using flash chromatography; Eluent: (5% MeOH /95% DCM); Appearance: off white solid; isolated yield: 56%; m.p. 173-176°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 9.77 (s, 1H), 7.93 (d, *J* = 15.2 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 15.1 Hz, 2H), 3.33 – 3.18 (m, 8H), 3.07 (s, 6H), 2.65 (t, *J* = 7.9 Hz, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.3, 166.1, 139.4, 138.1, 135.4, 127.9, 126.9, 121.1, 44.2, 37.3, 35.7, 21.5; **IR** (KBr): 2925, 1719, 1647, 1604, 1393, 1137, 978, 795 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{24}N_2O_3$ $[M + H]^+$ 329.1787, found 329.1779

General procedure for late-stage diversification of natural products and drug molecules:

General procedure (F): General procedure for remote C-H olefination of natural products and drug molecules via palladium/enamine co-catalysis is as follows. In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with corresponding aldehyde derivative **5a-11a** (0.10 mmol), $Pd(OAc)_2$ (3.37 mg, 15 mol%), $Cu(OAc)_2$ (5.45 mg, 30 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then ethyl acrylate (45 µL, 0.40 mmol, 4 equiv.), HFIP (2 mL), AcOH (82 µL, 15 equiv.), H_2O (7 µL, 4 equiv.) and dibutylamine (n-Bu)$_2$NH (7 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min., then at 40 °C for 72 h. After cooling to ambient temperature, the reaction mixture was diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel; Eluent: (EtOAc /hexane). The ratio of di and mono (D:M) olefinated product were determined by ^{1}H NMR of the crude reaction mixture using dibromometanne as internal standard with respect to the alkene (CH=CH) proton in the product, which appear as doublet (approximately at 6.3 to 7.0 ppm, respectively).

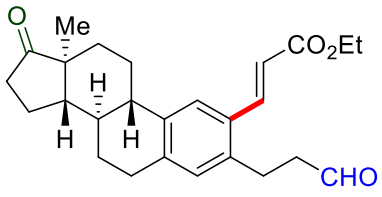
Experimental data of olefinated natural products and drug molecules:



5b

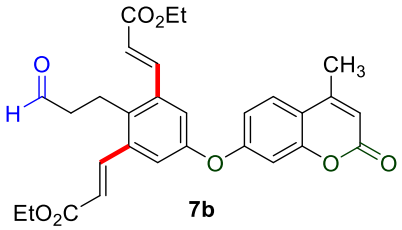
Diethyl 3,3'-(5-(4-oxochroman-2-yl)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (5b): Olefination was done by *general procedure (F)* with substrate **5a** (0.0280 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (16% EtOAc /84% hexane); Appearance: light yellow solid;

isolated yield: 80%; m.p. 168-170°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 9.81 (s, 1H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.94 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.68 (s, 2H), 7.55 (td, *J* = 7.9, 2.0 Hz, 1H), 7.11-7.07 (m, 2H), 6.40 (d, *J* = 15.7 Hz, 2H), 5.50 (dd, *J* = 13.3, 2.8 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 4H), 3.23 (t, *J* = 8.1 Hz, 2H), 3.08 (dd, *J* = 16.8, 13.2 Hz, 1H), 2.91 (dd, *J* = 16.9, 2.9 Hz, 1H), 2.69 (t, *J* = 8.1 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 191.2, 166.2, 161.1, 141.0, 139.2, 138.0, 136.3, 135.2, 127.1, 126.2, 122.5, 121.2, 120.8, 118.0, 78.8, 60.8, 44.5, 44.3, 21.2 and 14.2; **IR** (KBr): 2982, 2843, 1702, 1627, 1606, 1463, 1368, 1180, 1034, 975, 756 cm^{-1} **HRMS** (ESI) Calcd for $C_{28}H_{28}O_7$ $[M + H]^+$ 477.1908, found 477.1908



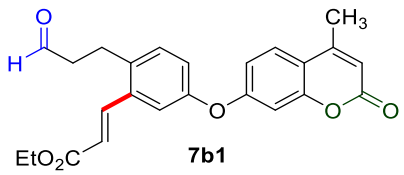
6b1

ethyl (E)-3-((8R,9S,13S,14S)-13-methyl-17-oxo-3-(3-oxopropyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)acrylate (6b1): Olefination was done by *general procedure (F)* with substrate **6a** (0.0310 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified *via* using flash chromatography; Eluent: (20% EtOAc /80% hexane); Appearance: viscous oil; isolated yield: 25% (31% brsm) **^{1}H NMR** (400 MHz, $CDCl_3$): 9.81 (s, 1H), 7.92 (d, *J* = 15.8 Hz, 1H), 7.51 (s, 1H), 6.96 (s, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.91-2.87 (m, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.55-2.48 (m, 2H), 2.31-2.25 (m, 1H), 2.18-2.0 (m, 4H), 1.61-1.46 (m, 6H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 220.6, 200.9, 167.0, 141.6, 139.3, 138.6, 137.3, 130.49, 130.45, 123.8, 119.1, 60.5, 50.5, 47.9, 45.0, 44.1, 38.0, 35.8, 31.5, 29.2, 26.3, 25.7, 24.9, 21.6, 14.3, and 13.8; **HRMS** (ESI) Calcd for $C_{26}H_{32}O_4$ $[M + H]^+$ 409.2373, found 409.2373, brsm = based on recovered starting material.



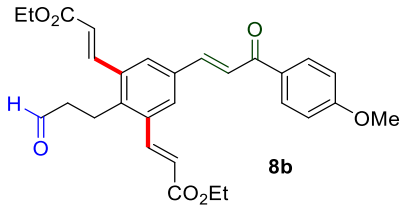
7b

diethyl 3,3'-(5-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (7b): Olefination was done by *general procedure (F)* with substrate **7a** (0.0308 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (25% EtOAc /75% hexane); Appearance: light yellow solid; isolated yield: 20% (24% brsm) m.p. 155-157°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.95 (d, *J* = 15.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.26 (s, 2H), 6.96 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 2H), 6.22 (d, *J* = 1.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 4H), 3.20 (t, *J* = 8.1 Hz, 2H), 2.70 (t, *J* = 8.1 Hz, 2H), 2.44 (d, *J* = 1.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.7, 166.1, 160.6, 160.1, 155.0, 154.3, 152.1, 140.5, 136.6, 135.3, 126.1, 122.8, 119.6, 115.8, 114.4, 113.3, 105.8, 60.8, 44.6, 20.9, 18.7 and 14.2; **IR** (KBr): 2974, 2922, 1718, 1615, 1441, 1417, 1398, 1311, 1272, 1164, 1018, 974, 861 cm^{-1}; **HRMS** (ESI) Calcd for $C_{29}H_{28}O_8$ $[M + H]^+$ 505.1857, found 505.1856; brsm = based on recovered starting material



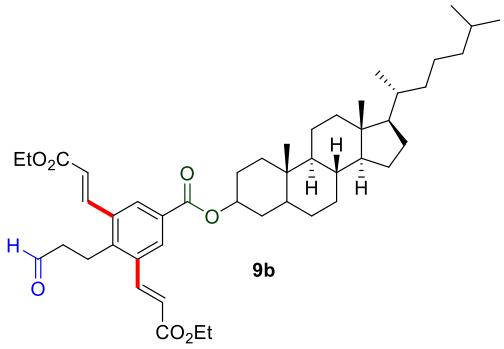
7b1

ethyl (E)-3-(5-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)-2-(3-oxopropyl)phenyl)acrylate (7b1): The crude product was purified via using flash chromatography; Eluent: (20% EtOAc /80% hexane); Appearance: light yellow solid; isolated yield: 40% (47% brsm); m.p. 143-145°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.91 (d, *J* = 15.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.34-7.23 (m, 2H), 7.04 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.20 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.11 (t, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.5, 166.4, 160.7, 160.6, 154.9, 154.2, 152.1, 140.3, 136.4, 135.0, 131.8, 125.9, 121.8, 121.4, 118.1, 115.4, 114.3, 113.1, 105.5 60.7, 45.0, 24.8, 18.7 and 14.2 ; **HRMS** (ESI) Calcd for $C_{24}H_{22}O_6$ $[M + H]^+$ 407.1489, found 407.1488; brsm = based on recovered starting material



8b

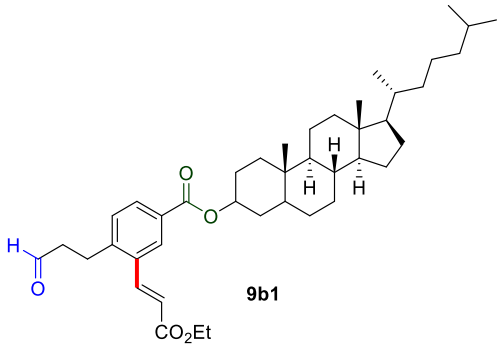
diethyl 3,3'-(5-((E)-3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (8b): The crude product was purified via using flash chromatography; Eluent: (18% EtOAc /82% hexane); Appearance: light yellow solid; isolated yield: 39%; m.p. 137-140°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 15.7 Hz, 2H), 7.76 (d, *J* = 15.3 Hz, 3H)*, 7.58 (d, *J* = 15.7 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 15.7 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.91 (s, 3H), 3.21 (dd, *J* = 8.8, 7.0 Hz, 2H), 2.68 (d, *J* = 7.0 Hz,, 2H), 1.36 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 188.1, 166.2, 163.6, 142.1, 140.9, 140.6, 135.4, 134.2, 130.9, 130.8, 128.1, 122.8, 122.7, 113.9, 60.9, 55.5, 44.2, 21.5, 14.3; **HRMS** (ESI) Calcd for $C_{29}H_{30}O_7$ $[M + H]^+$ 491.1991, found 491.1990; *mean aromatic and alkene peak merged at δ 7.76



9b

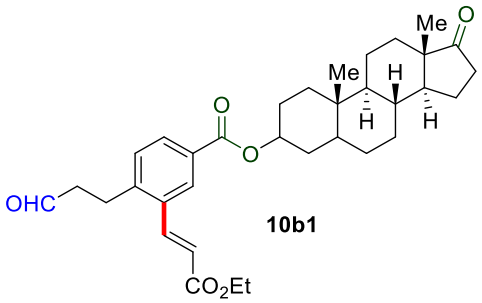
(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-5-((E)-4-ethoxy-4-oxobut-2-en-1-yl)-4-(3-oxopropyl)benzoate (9b): Olefination was done by *general procedure (F)* with substrate **9a** (0.0548 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified via using flash chromatography; Eluent: (22% EtOAc /78% hexane); Appearance: white solid; isolated yield: 11% (15% brsm); m.p. 123-125°C; **^{1}H NMR** (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 8.16 (s, 2H), 7.94 (d, *J* = 15.7 Hz, 2H), 6.44 (d, *J* = 15.7 Hz, 2H), 4.99-4.91 (m, 1H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.21 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.98-1.90 (m, 2H), 1.82-1.79 (m, 2H), 1.71-1.67 (m, 3H),

1.57-1.47 (m, 4H), 1.35-1.28 (m, 15H), 1.15-0.98 (m, 9H), 0.90 – 0.83 (m, 14H), 0.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.5, 166.3, 165.0, 143.1, 140.7, 134.8, 130.0, 129.3, 122.9, 60.9, 56.4, 56.2, 54.2, 44.7, 44.1, 42.6, 39.9, 39.5, 36.7, 36.1, 35.8, 35.5, 35.4, 34.1, 32.0, 31.4, 30.2, 30.1, 29.7, 29.3, 28.6, 28.2, 27.9, 27.5, 27.2, 24.2, 23.8, 22.8, 22.5, 21.5, 21.2, 18.6, 14.3, 12.3, 12.0; **HRMS** (ESI) Calcd for $C_{47}H_{68}O_7$ $[M + H]^+$ 745.5043, found 745.5033; brsm = based on recovered starting material.



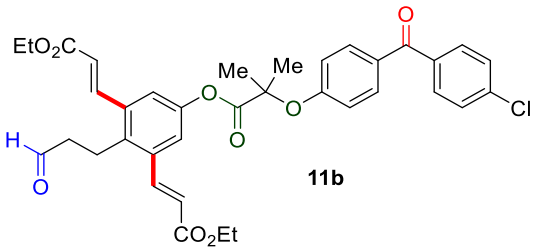
9b1

(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-4-(3 oxopropyl)benzoate (9b1): The crude product was purified via using flash chromatography; Eluent: (14% EtOAc /86% hexane); Appearance: viscous oil; isolated yield: 24% (32% brsm). **^{1}H NMR** (400 MHz, $CDCl_3$): 9.81 (s, 1H), 8.20 (d, *J* = 1.3 Hz, 1H), 7.97-7.91 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 4.98-4.91 (m, 1H), 4.29 (q, *J* = 7.1Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.99-1.92 (m, 2H), 1.84-1.77 (m, 2H), 1.73-1.64 (m, 3H), 1.57-1.48 (m, 4H), 1.38-1.25 (m, 12H), 1.16-1.06 (m, 6H), 1.04-0.99 (m, 3H), 0.91-0.85 (m, 14H), 0.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.1, 166.5, 165.4, 144.4, 140.4, 133.2, 130.9, 129.9, 129.8, 128.0, 121.5, 74.6, 60.7, 56.4, 56.2, 54.2, 44.7, 44.5, 42.5, 39.9, 39.5, 36.7, 36.1, 35.8, 35.5, 35.4, 34.1, 31.9, 28.6, 28.2, 27.9, 27.5, 25.4, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, 14.3, 12.3, 12.0; **IR** (KBr): 2934, 2866, 1716, 1636, 1258, 1178, 1119, 1003, 760 cm^{-1}; **HRMS** (ESI) Calcd for $C_{42}H_{62}O_5N$ $[M + NH_4]^+$ 664.4936, found 664.4933



10b1

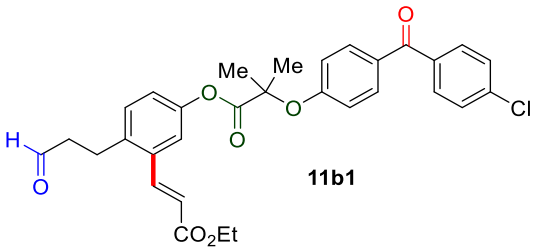
(8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)-4-(3-oxopropyl)benzoate (10b1): Olefination was done by *general procedure (F)* with substrate **10a** (0.0450 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified *via* using flash chromatography; Eluent: (18% EtOAc /82% hexane); Appearance: viscous oil; isolated yield: 33% (47% brsm); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.22 (s, 1H), 7.96-7.91 (m, 2H), 7.33-7.26 (m, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 5.27 (s, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.43 (dd, *J* = 19.2, 8.6 Hz, 1H), 2.10 -2.01 (m, 1H), 1.97-1.67 (m, 6H), 1.66-1.47 (m, 6H), 1.35-1.23 (m, 10H), 1.08-0.99 (m, 1H), 0.87 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 221.2, 200.1, 166.5, 165.2, 144.5, 140.5, 133.4, 130.6, 130.04, 130.02, 128.2, 121.6, 70.9, 60.7, 54.5, 51.4, 47.8, 44.4, 40.5, 36.0, 35.8, 35.0, 33.2, 32.9, 31.5, 30.7, 28.0, 26.2, 25.4, 21.7, 20.1, 14.3, 13.8 and 11.4; **HRMS** (ESI) Calcd for $C_{34}H_{44}O_6$ $[M + H]^+$ 549.3211, found 549.3210; brsm = based on recovered starting material.



11b

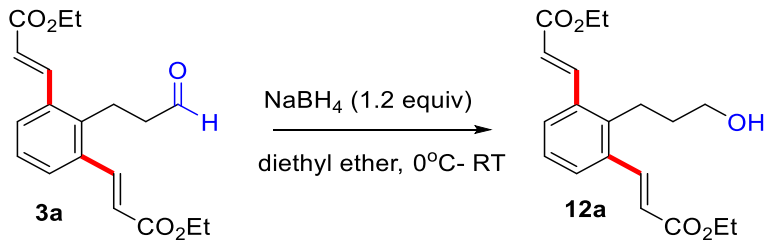
diethyl 3,3'-(5-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate (11b): Olefination was done by *general procedure (F)* with substrate **11a** (0.045 g, 0.10 mmol) and ethyl acrylate (45 µL, 4 equiv., 0.40 mmol) as olefin partner. The crude product was purified *via* using flash chromatography; Eluent: (20% EtOAc /80% hexane); Appearance: light yellow viscous oil; isolated yield: 25% (29% brsm); m.p. 133-135°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.90 (d, *J* = 15.7 Hz, 2H), 7.79 (d, *J* = 8.8

Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.25 (d, *J* = 15.7 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 4H), 3.14 (t, *J* = 6.5 Hz, 2H), 2.62 (t, *J* = 6.5 Hz, 2H), 1.82 (s, 6H), 1.30 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.6, 194.0, 172.2, 166.0, 159.4, 149.1, 140.4, 138.5, 136.8, 136.2, 136.1, 132.1, 131.2, 130.9, 128.6, 122.9, 121.0, 117.5, 79.5, 60.9, 44.4, 25.5, 21.0 and 14.2; **HRMS** (ESI) Calcd for $C_{36}H_{35}ClO_9$ $[M + H]^+$ 647.2042, found 647.2036; brsm = based on recovered starting material.

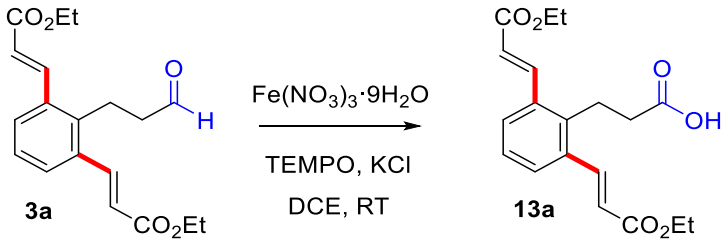


ethyl(E)-3-(5-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-2-(3 oxopropyl)phenyl)acrylate (11b1): The crude product was purified *via* using flash chromatography; Eluent: (12% EtOAc /88% hexane); Appearance: light yellow liquid; isolated yield: 35% (41% brsm); m.p. 118-120°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.88 (d, *J* = 15.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.94 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.83 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.6, 194.1, 172.3, 166.3, 159.4, 149.1, 140.2, 138.4, 137.8, 136.2, 134.5, 132.1, 131.1, 131.1, 130.7, 128.5, 122.7, 121.5, 119.2, 117.3, 79.4, 60.7, 44.8, 25.4, 24.8 and 14.2; **HRMS** (ESI) Calcd for $C_{31}H_{29}ClO_7$ $[M + H]^+$ 549.1675, found 549.1669; brsm = based on recovered starting material.

Synthetic procedures and experimental data for post-synthetic modification of compound (3a):

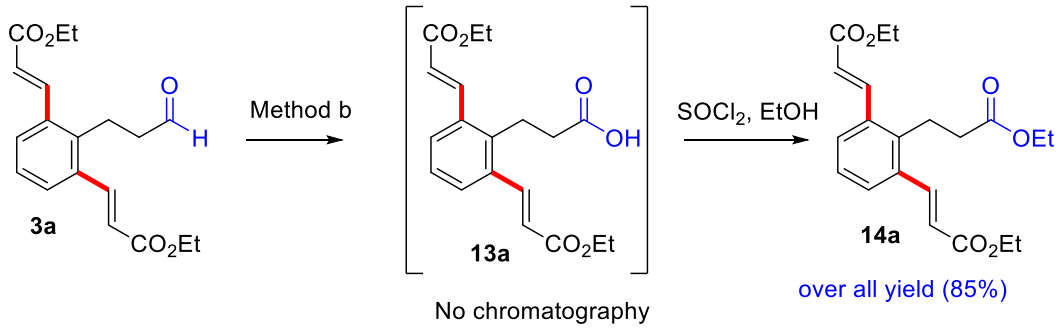


Synthesis of diethyl 3,3'-(2-(3-hydroxypropyl)-1,3-phenylene)(2E,2'E)-diacrylate 12a (Figure 5, method a): To a stirred ice cold solution of diethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate **3a** (66 mg, 0.2 mmol) in diethyl ether (10 mL) was added $NaBH_4$ (9 mg, 1.2 equiv.) in portion wise, After being stirred at 0 °C for 10 min, the reaction was further stirred at room temperature for 4 h. After the completion of reaction (monitor by TCL), reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous and organic layer were separated by extraction of aqueous layer with DCM (2 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrate under reduced pressure. The resulting crude product was purified via using flash chromatography; (Eluent: 30% EtOAc / 70% hexane); Appearance: colorless viscous oil; isolated yield: 89%; m.p. 56-57°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.09 (d, *J* = 15.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 3.70 (t, *J* = 6.2 Hz, 2H), 3.00 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 1H), 1.82-1.75 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 142.2, 140.8, 134.3, 128.4, 126.6, 120.9, 61.6, 60.6, 34.0, 25.1, 14.2; **IR** (KBr): 3528, 3222, 2987, 2939, 2885, 1716, 1698, 1626, 1177, 984, 863 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{24}O_5$ $[M + H]^+$ 333.1697, found 333.1691

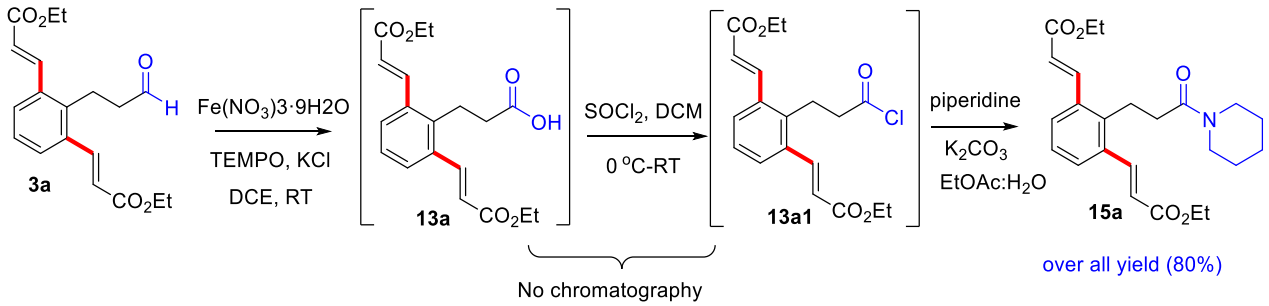


Synthesis of 3-(2,6-bis((E)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)propanoic acid 13a (Figure 5, method b)[18]: A 38 mL Schlenk tube was charged with diethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate **3a** (66 mg, 0.2 mmol), $Fe(NO_3)_3·9H_2O$ (8 mg, 10 mol%), TEMPO (6 mg, 20 mol%), KCl (4 mg, 20 mmol), and DCE (2 mL). The tube was evacuated and filled with O_2 with three times. The reaction mixture was the stirred vigorously at room temperature for 24 h. After the completion of reaction, crude reaction mixture was filtered through a short pad of silica and eluted with additional 20 mL of EtOAC: MeOH (1:1) solvent. The filtrate was then concentrated in vacuo. The residual was purified via flash chromatography; Eluent: (40% EtOAc /60% hexane); Appearance: off white solid; isolated yield: 92%; m.p. 118-120 °C; **^{1}H NMR** (400

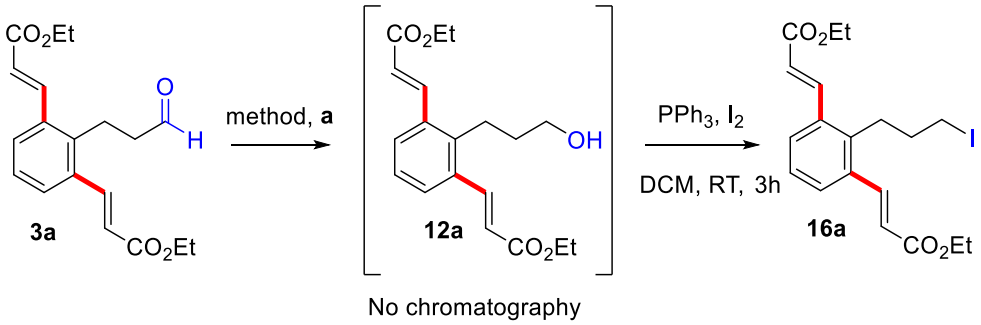
MHz, $CDCl_3$): 9.98 (s, 1H), 8.08 (d, *J* = 15.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 2H), 4.28(q, *J* = 7.2 Hz, 4H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.2, 166.7, 141.8, 138.9, 134.5, 128.6, 127.2, 121.6, 60.7, 35.0, 24.0, 14.2; **IR** (KBr): 3239, 2984, 1740, 1708, 1685, 1627, 1327, 1149, 971, 806 cm^{-1} ; **HRMS** (ESI) Calcd for $C_{19}H_{22}O_6$ $[M + H]^+$ 347.1489, found 347.1483



Synthesis of diethyl 3,3'-(2-(3-ethoxy-3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate 14a (Figure 5, method c) The crude diethyl 3-(2,6-bis((E)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)propanoic acid (**13a)** obtained from corresponding aldehyde **3a** (66 mg, 0.2 mmol) using method (**b**) was dissolved in 5 mL of EtOH and cooled down to 0 °C, then thionyl chloride (60 µL, 5 equiv.) dissolved in 5 mL DCM was added dropwise. The reaction mixture was stirred at room temperature for 3 h. After the completion of reaction, reaction mixture was concentrated in vacuo and residual was purified via flash chromatography; Eluent: (25% EtOAc /75% hexane); Appearance: white solid; overall isolated yield: 85%; m.p. 82-84°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.03 (d, *J* = 15.7 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 2H), 4.28(q, *J* = 7.2 Hz, 4H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 8.4 Hz, 2H), 2.48 (t, *J* = 8.4 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.8, 166.5, 141.7, 138.9, 134.6, 128.6, 127.2, 121.7, 60.7, 60.6, 35.1, 24.1, 14.3, 14.1; **IR** (KBr): 2984, 1725, 1708, 1622, 1316, 1187, 1160, 1042, 973, 860 cm^{-1} ; **HRMS** (ESI) Calcd for $C_{21}H_{26}O_6$ $[M + H]^+$ 375.1802, found 375.1797

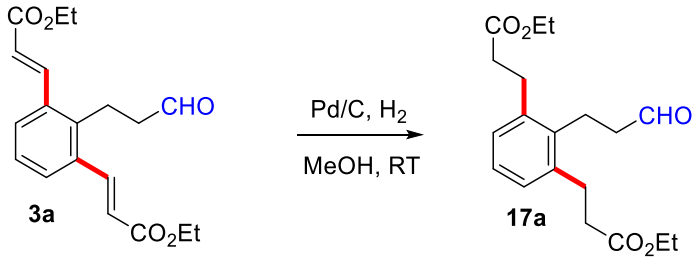


Synthesis of diethyl 3,3'-(2-(3-oxo-3-(piperidin-1-yl)propyl)-1,3-phenylene)(2E,2'E)-diacrylate 15a (Figure 5, method d): The crude diethyl 3-(2,6-bis((E)-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl)propanoic acid (**13a)** obtained from corresponding aldehyde **3a** (66 mg, 0.2 mmol) using method (**b**) was dissolved in 5 mL of DCM and cooled down to 0 °C, then thionyl chloride (60 µL, 5 equiv.) dissolved in 5 mL DCM was added dropwise. The reaction mixture was stirred at room temperature for 3 h. After the completion of reaction, reaction mixture was concentrated in vacuo and crude compound diethyl 3,3'-(2-(3-chloro-3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate **(13a1)** was used as such for next step. This crude compound (**13a1)** was dissolved in 5 mL of EtOAc and added dropwise to stirred biphasic ice-cold solution of piperidine (95 µL, 5 equiv) dissolved 5 mL EtOAc and potassium carbonate (28 mg, 5 equiv) dissolved in 5 mL of water. The reaction mixture was stirred for 4 h at room temperature. After the completion of reaction, the aqueous and organic layers were separated by extraction of aqueous layer with EtOAc (2 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrate under reduced pressure. The resulting crude product was purified via using flash chromatography; Eluent: (45% EtOAc /65% hexane); Appearance: white solid; overall isolated yield: 80%; m.p. 87-89°C; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.03 (d, *J* = 15.7 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 4H), 3.53 (br, 2H), 3.31 (br, 2H), 3.22 (t, *J* = 8.4 Hz, 2H), 2.46 (t, *J* = 8.4 Hz, 2H), 1.62 (br, 2H), 1.51 (br, 4H), 1.34 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.3, 166.4, 141.7, 139.7, 134.6, 128.6, 127.0, 121.6, 60.6, 46.5, 42.7, 34.0, 26.3, 25.4, 24.8, 24.4, 14.3; **IR** (KBr): 2981, 2935, 2856, 1706, 1642, 1620, 1316, 1163, 1041, 985, 793 cm^{-1}; **HRMS** (ESI) Calcd for $C_{24}H_{31}NO_5$ $[M + H]^+$ 414.2275, found 414.2270



diethyl 3,3'-(2-(3-iodopropyl)-1,3-phenylene)(2E,2'E)-diacrylate 17a (Figure 5 method e)[19]

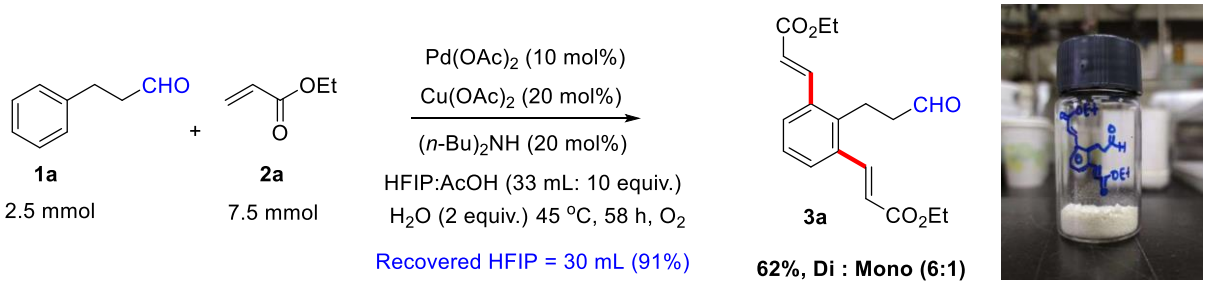
A 50 mL round bottom flask equipped with magnetic stirring bar was charged with triphenylphosphine (76 mg, 1.5 equiv.), I_2 (76 mg, 1.5 equiv.) and 5 mL of DCM was allowed to stir at room temperature for 10 min, thereafter imidazole (34 mg, 2.5 equiv.) was added and again stir the reaction mixture for another 15 min. Finally crude diethyl 3,3'-(2-(3-hydroxypropyl)-1,3-phenylene)(2E,2'E)-diacrylate (**12a)** obtained from corresponding aldehyde **3a** (66 mg, 0.2 mmol) using method (**a**) was dissolved in 5 mL of DCM and added slowly to the reaction mixture. After the completion of reaction (3 h), reaction mixture was quenched with saturated sodium metabisulfite (10 mL). This mixture was extracted with ethyl acetate (2 x 5 mL) and combine organic layer was dried over anhydrous Na_2SO4. The organic layer was concentrated and purified via using flash chromatography; Eluent: (5% EtOAc /95% hexane); Appearance: viscous oil; overall isolated yield: 64%; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.07 (d, *J* = 15.7 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 4H), 3.28 (t, *J* = 6.7 Hz, 2H), 3.02 (t, *J* = 8.1 Hz, 2H), 2.06-1.99 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 141.7, 139.2, 134.6, 128.5, 127.1, 121.5, 60.7, 34.5, 29.9, 14.4, 5.5; **IR** (KBr): 2979, 1713, 1631, 1366, 1269, 1165, 1036, 981, 803 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{23}IO_4$ $[M + H]^+$ 443.0714, found 443.0713



diethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)dipropionate 17a (Figure 5, method f): A 50 mL round bottom flask containing stirring bar charged with diethyl 3,3'-(2-(3-oxopropyl)-1,3-phenylene)(2E,2'E)-diacrylate **3a** (66 mg, 0.2 mmol) , Pd/C (10 mol%) and MeOH (5 mL). The flask was sealed with septum, and then evacuated and backfilled with hydrogen for three times. The reaction mixture was stirred at room temperature for 12 h. After the completion of reaction, crude reaction mixture was filtered through a short pad of silica and eluted with additional 20 mL of ethyl acetate. The filtrate was then concentrated in vacuo. The residual was purified via using flash chromatography; Eluent: (4% EtOAc /96% hexane); Appearance: viscous oil; isolated yield: 51%. **^{1}H NMR** (400 MHz, $CDCl_3$): 9.87 (s, 1H), 7.14-7.04 (m, 3H), 4.16 (q, *J* = 7.2 Hz, 4H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 4H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 4H), 1.24 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 200.9, 172.7, 138.8, 136.3, 127.3, 126.7, 60.5, 44.6, 35.5, 27.8, 20.6, 14.1; **HRMS** (ESI) Calcd for $C_{19}H_{26}O_5$ $[M + H]^+$ 335.1853, found 335.1847

Synthetic procedure for scale up reaction for synthesis of (3a):

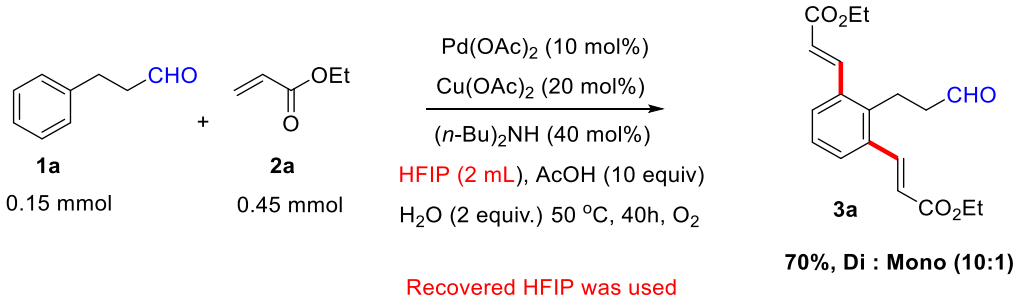
In glove box, a 150 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-phenylpropanal **1a** (0.335 mL, 2.5 mmol), $Pd(OAc)_2$ (58 mg, 10 mol%), $Cu(OAc)_2$ (136 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then ethyl acrylate (0.8 mL, 0.45 mmol, 3 equiv), HFIP (33 mL), AcOH (1.32 mL, 10 equiv), H_2O (91 µL, 2 equiv) and dibutylamine $(n\text{-Bu})_2NH$ (85 µL, 20 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 45 °C for 58 h. After cooling to ambient temperature, the reaction mixture was filtered through a pad of silica gel and washed with additional 30 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel; Eluent: (15% EtOAc /85% hexane); Appearance: off white solid; isolated yield: 62%, Di:Mono (6:1)



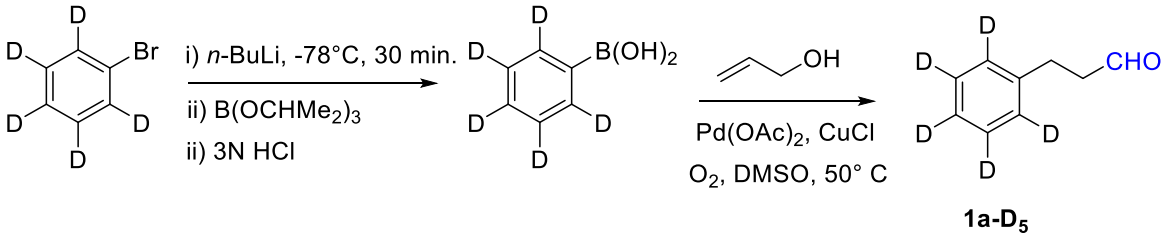
Note: *Near about 30 mL (91%) HFIP solvent (out of 33 mL) was recovered after rotary evaporator vacuo.*

Reaction with recovered HFIP for synthesis of 3a:

To further demonstrate the practical utility of protocol, a reaction was performed under the developed reaction condition with recovered HFIP solvent. To our delight, an isolated yield of **3a** 70% was obtained with Di: Mono (10:1) selectivity.



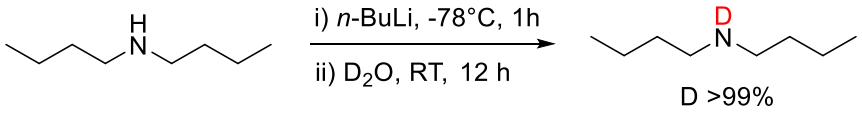
Synthetic procedure for Synthesis of [$^2H_5$]Hydrocinnamaldehyde (1a-D_5)[20]



Under nitrogen atmosphere, a 250 mL of round bottom flask equipped with stirring bar was charged with bromobenzene-D_5 (2.9 mL 20 mmol), dry THF (40 mL) and cooled down to -78°C. Thereafter, *n*-butyl lithium (12.5 mL, 2M, 25 mmol) was added dropwise and stirred the

reaction mixture for 30 min. at -78°C and then tri-isopropyl borate (6.3 mL, 30 mmol) was added dropwise. The solution was allowed to warm at room temperature and stirred for 2 h. After that the reaction was quenched with dilute HCl (20%, 50 mL) and stirred the reaction mixture for another 3h at room temperature. The solution was extracted with diethyl ether (2 x 50 mL). The organic layer was washed twice with water followed by brine and concentrated over rotary evaporation. To the reaction mixture hexane was added and white solid D_5-phenylboronic acid (2.0 g) compound was obtained in 75% yield which was used for further step without purification. In next step D_5-phenylboronic acid (0.635 g, 5 mmol), $Pd(OAc)_2$ (56 mg, 5 mol%), CuCl (50 mg, 10 mol%) and allyl alcohol (0.6 mL, 8 mmol) were charged in dry 150 mL dry Schlenk tube containing 16 mL of dry solvent (DMSO/HOAc=1/1, v/v). The reaction mixture was stirred at 50°C for 30 h. After the reaction was completed, the reaction mixture was diluted with 20 mL of saturated NaCl solution. The mixture was extracted with Et_2O (150 mL), washed with saturated $NaHCO_3$ (3 x 20 mL), saturated NaCl (3 x 20 mL) and dried over sodium sulfate. The solvent was removed, and the residue was purified by flash chromatography on silica gel: (Eluent: 1% EtOAc /99% hexane), provide the corresponding [$^2H_5$] Hydrocinnamaldehyde in 65 % yields as light-yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.5, 140.1, 128.3, 128.0, 127.8, 127.6, 45.2, and 27.9 The observed ^{1}H and ^{13}C NMR values were in consistent with previously reported literature[20]

Synthesis of deuterated di-butyl amine:

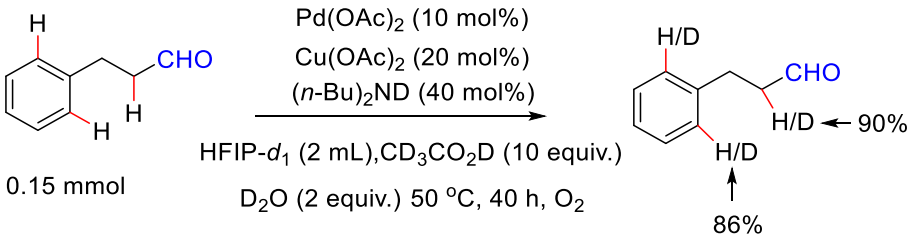


An oven-dried 100 mL round bottom flask was charged with di-butyl amine (3.23 mL, 20 mmol) and dry THF (30 mL) was cooled down at -78 °C and then *n*-butyl lithium (12.0 mL, 2.5M, 30 mmol) was added dropwise. The reaction mixture was stirred at -78 °C for 1h and then quenched with D_2O (2 mL). Thereafter, reaction mixture was stirred at room temperature for 2 h. After completion of reaction, reaction mixture was extracted with EtOAc (100 mL), washed with saturated brine, dried over sodium sulfate. The solvent was removed under reduced pressure which

gave pure deuterated di-butyl amine (88%) yield with > 99% D. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.59 (td, *J* = 7.2, 0.8 Hz, 4H), 1.55 – 1.41 (m, 4H), 1.40 – 1.25 (m, 4H), 0.92 (td, *J* = 7.2, 0.8 Hz, 6H); **HRMS** (ESI) Calcd for $C_8H_{18}DN$ $[M + H]^+$ 131.1580, found 131.1570, *We have also confirmed the incorporation of D by comparing ^{1}H NMR spectra of (n-Bu)$_2$N-D spectra with (n-Bu)$_2$N-H*.

General procedure for H/D Exchange experiments with aldehyde (1a):

H/D Exchange experiments with Pd(OAc)$_2$ (Procedure 1) : In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-phenylpropanal **1a** (20.13 µL, 0.15 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then HFIP-d_1 (2 mL), CD_3CO_2D (80 µL, 10 equiv.), D_2O (5.5 µL, 2 equiv.), and deuterated dibutylamine $(n\text{-Bu})_2ND$ (10 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 50 °C for 40 h. After cooling to ambient temperature, the reaction mixture was diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and analyzed by ^{1}H NMR to determine the H/D exchange.



Scheme S1 : H/D experiment with $Pd(OAc)_2$

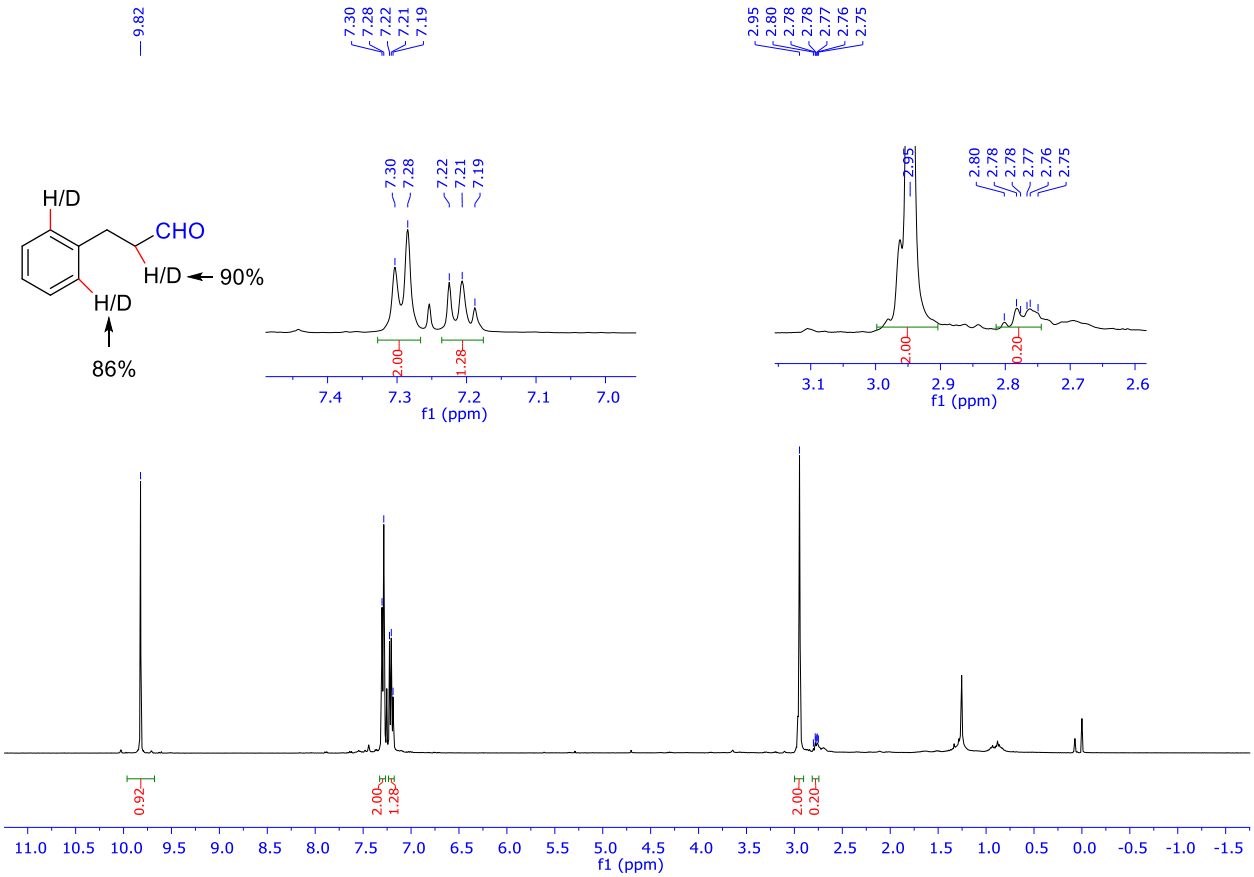
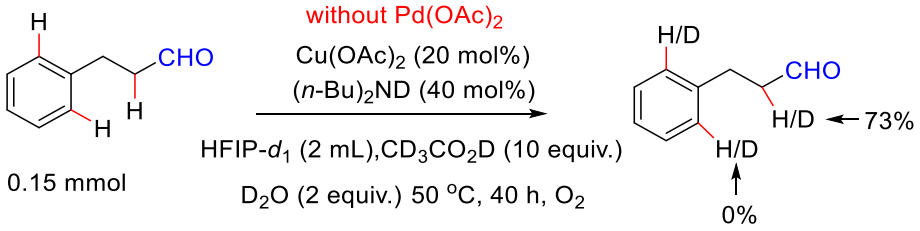


Figure S1: Crude ^{1}H NMR spectra of (***1a***) observed from H/D exchange experiment with $Pd(OAc)_2$

H/D Exchange experiments without Pd(OAc)$_2$: The above procedure (1) was followed without the addition of Pd(OAc)$_2$



Scheme S2 : H/D experiment without Pd(OAc)$_2$

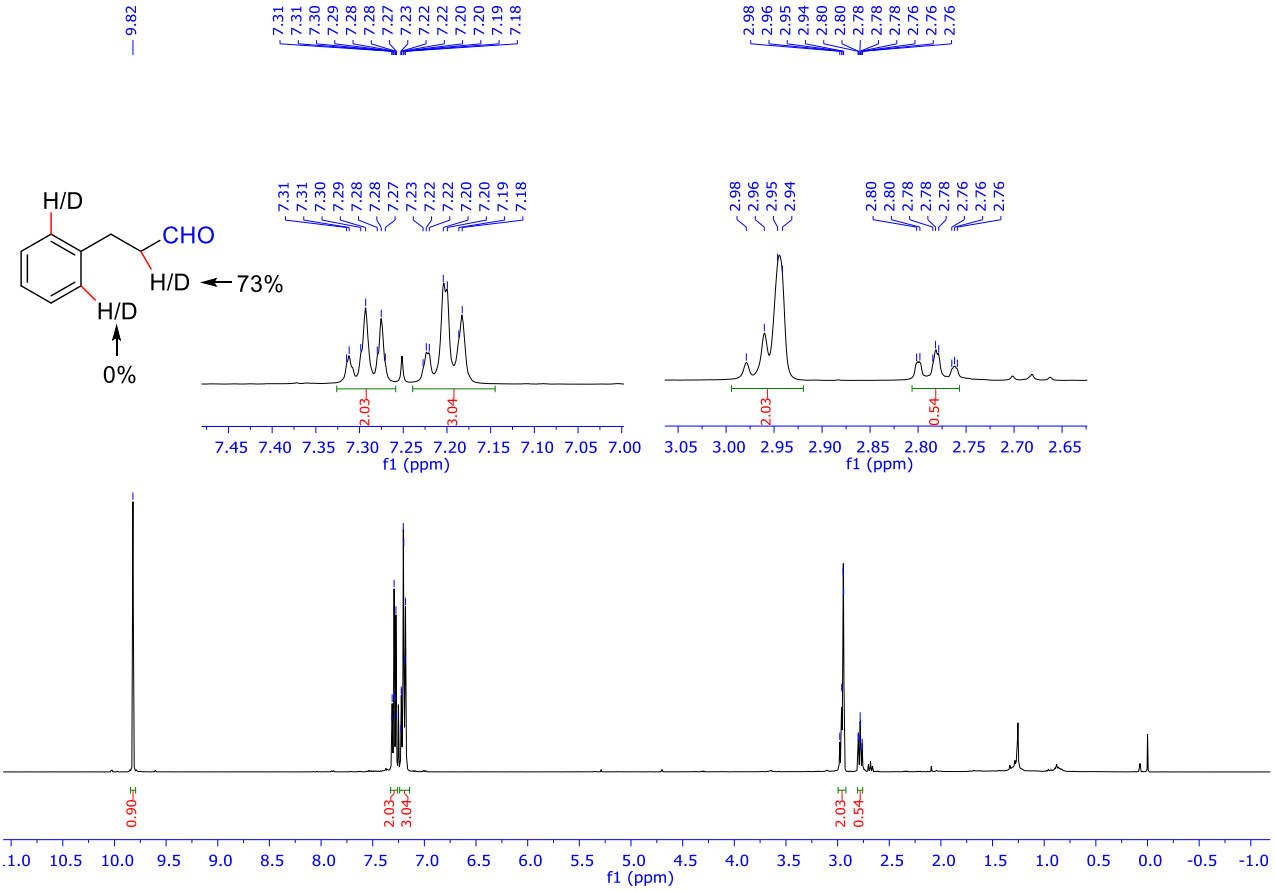
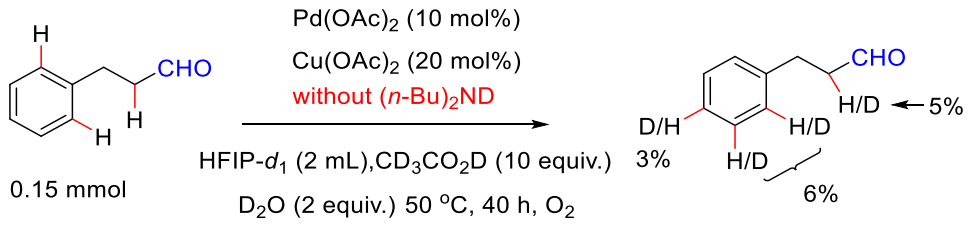


Figure S2: Crude ^{1}H NMR spectra of (***1a***) observed from H/D exchange experiment without Pd (OAc)$_2$

H/D Exchange experiments without amine: The above procedure (**1**) was followed without the addition of (*n*-Bu)$_2$ND



Scheme S3 : H/D experiment without amine

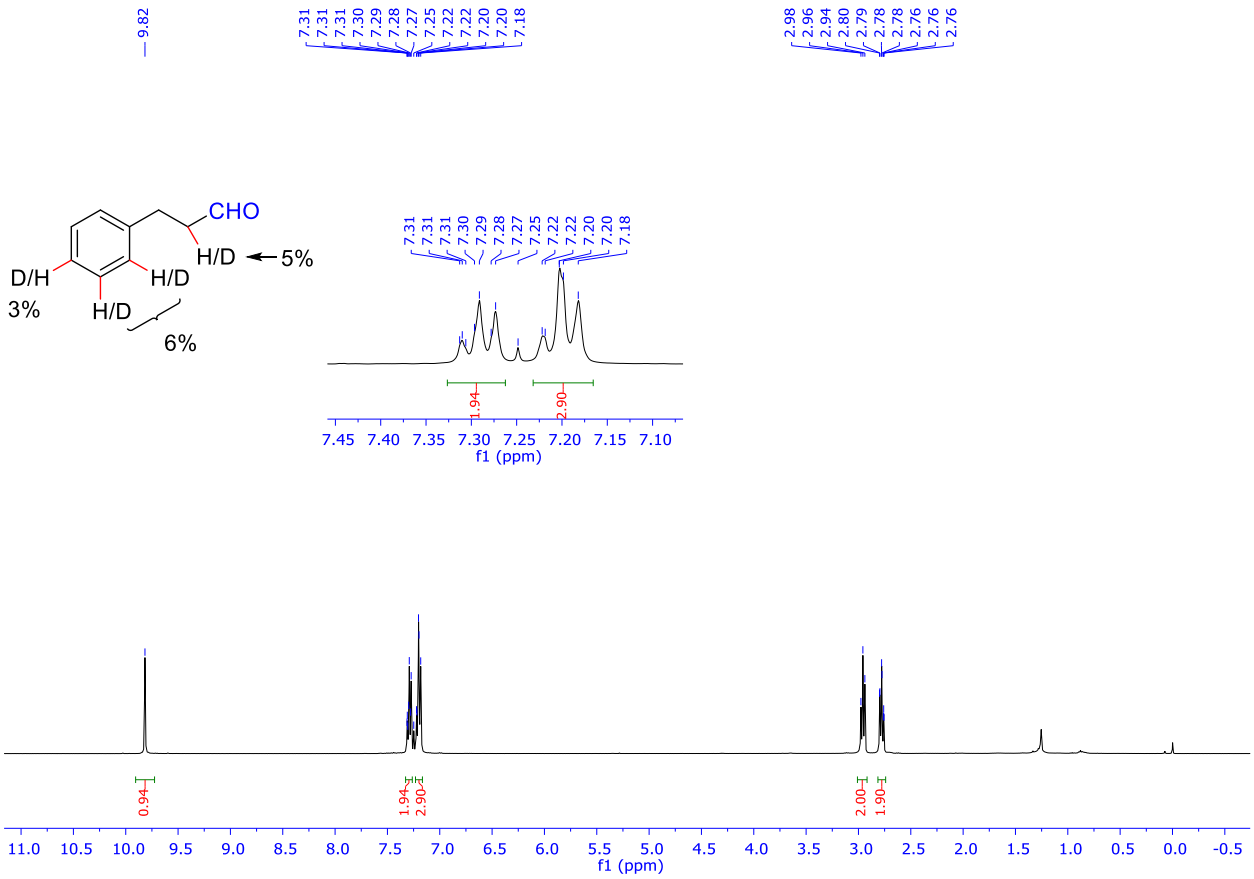


Figure S3: Crude ^{1}H NMR spectra of (***1a***) observed from H/D exchange experiment without amine

Remark: ortho and meta proton difficult to distinguish

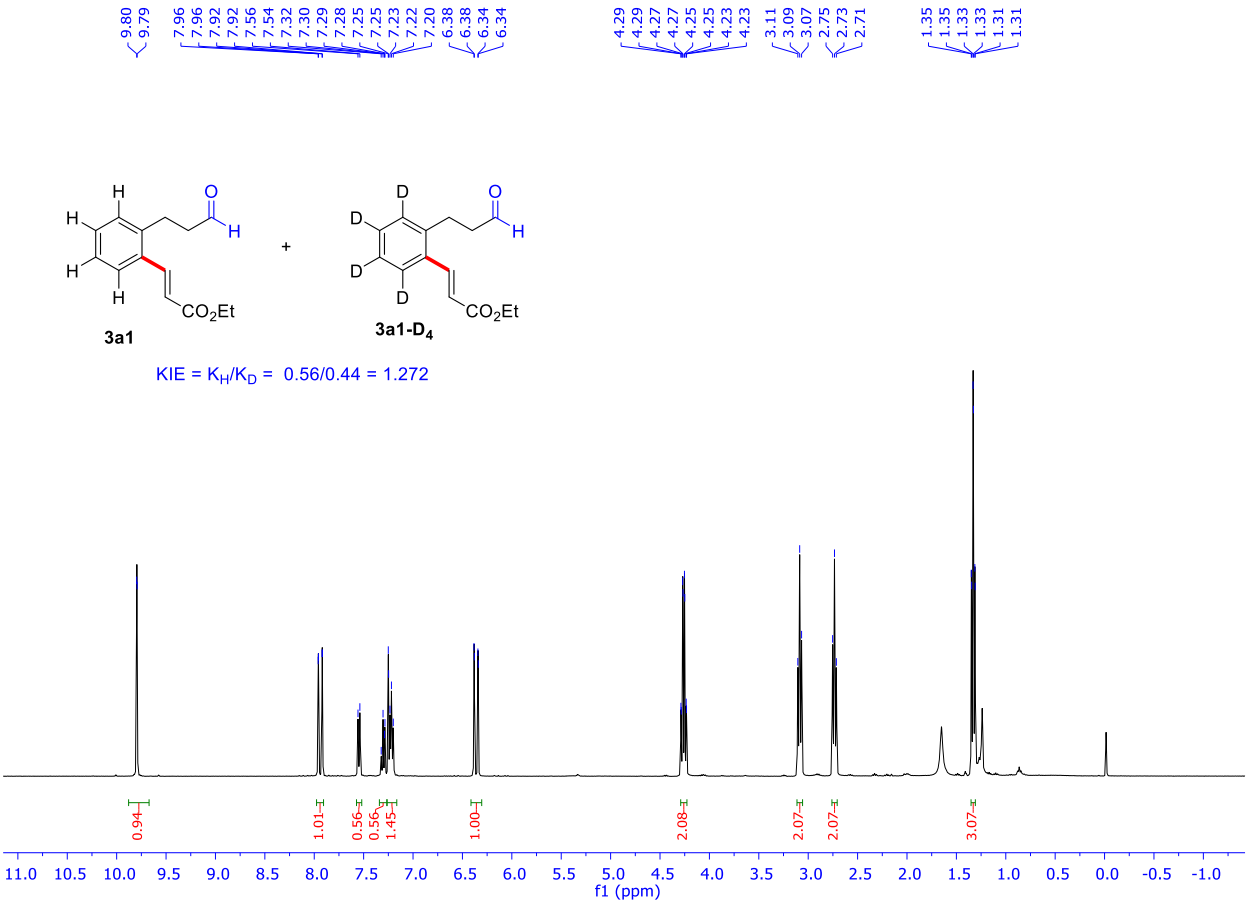
Experimental procedure for measurement of kinetic isotopic effect (KIE) values with 1a-D_5

Intermolecular competition under standard reaction condition:

In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-phenylpropanal **1a** (10.6 mg, 0.075 mmol) and 3-phenylpropanal **1a-*d*$_5$** (10.44 mg, 0.075 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then HFIP (2 mL), AcOH (80 µL, 10 equiv), H_2O (5.5 µL, 2 equiv.) and dibutylamine (n-Bu)$_2$NH (10 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 50 °C for 6 h. The reaction was cooled in an ice-bath and subsequently diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel (Eluent: 10% EtOAc /90% hexane) to afford **3a1/3a1-D$_4$** (mono) and (Eluent: 15% EtOAc /85% hexane) **3a/3a-D$_3$** (di) for which a deuterium content of 44.0% (for mono) and 27% (for di) was determined by ^{1}H NMR spectroscopy). k_H/k_D was calculated by considering both mono and di product which found to be 1.29.

Kinetic Isotopic Effects:

Intermolecular Reactions


9.80
9.79
7.96
7.96
7.92
7.92
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7.32
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3.11
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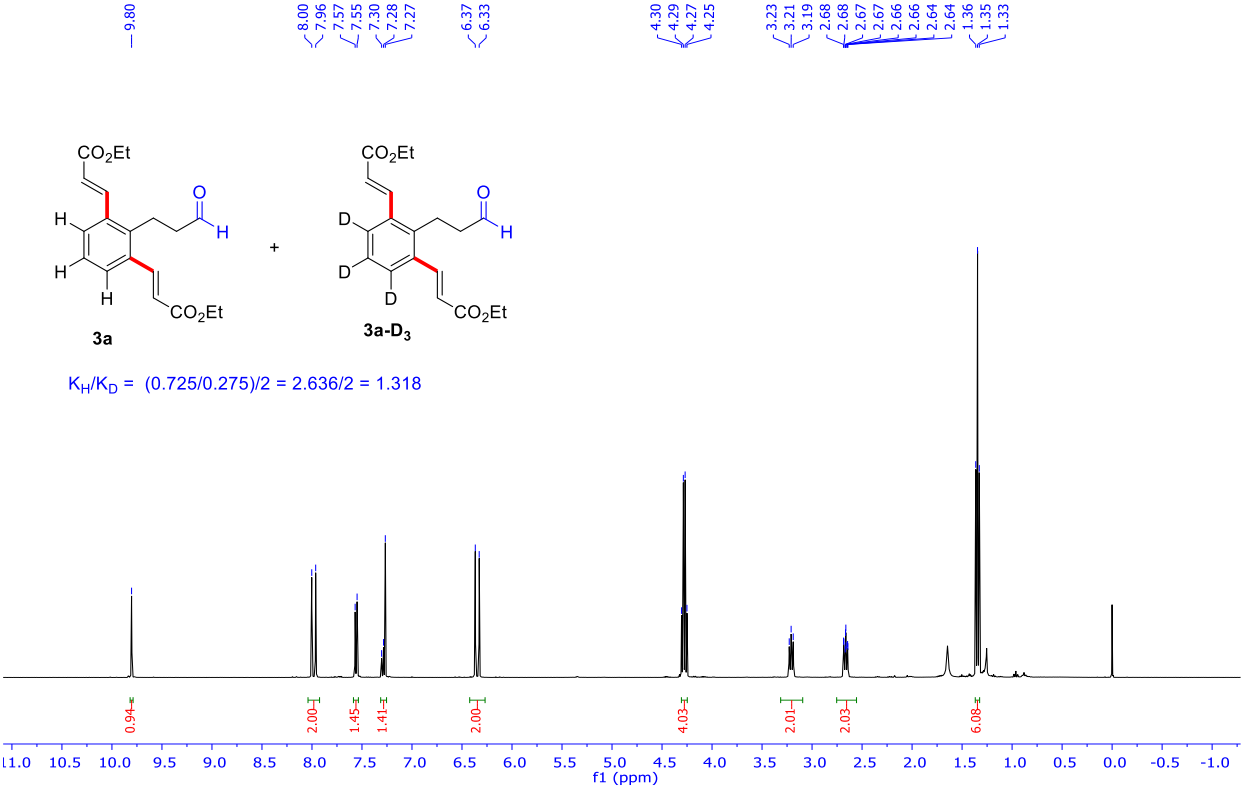
2.73
2.71
1.35
1.35
1.33
1.33
1.31
1.31
3a1
3a1-D4
KIE = KH/KD = 0.56/0.44 = 1.272
0.94
1.01
0.56
0.56
1.45
1.00
2.08
2.07
2.07
3.07
f1 (ppm)


9.80
8.00
7.96
7.57
7.55
7.30
7.28
7.27
6.37
6.33
4.30
4.29
4.27
4.25
3.23
3.21
3.19
2.68
2.68
2.67
2.67
2.66
2.66
2.64
2.64
1.36
1.35
1.33
3a
3a-D3
KH/KD = (0.725/0.275)/2 = 2.636/2 = 1.318
0.94
2.00
1.45
1.41
2.00
4.03
2.01
2.03
6.08
f1 (ppm)

KIE based on mono and di products:

KIE = $K_{H/D\ (mono)}$ + $K_{H/D\ (di)}$ = 1.272 +1.318

KIE = 2 $K_{H/D}$ = 2.59

KIE = $K_{H/D}$ = 2.59/2 = 1.295

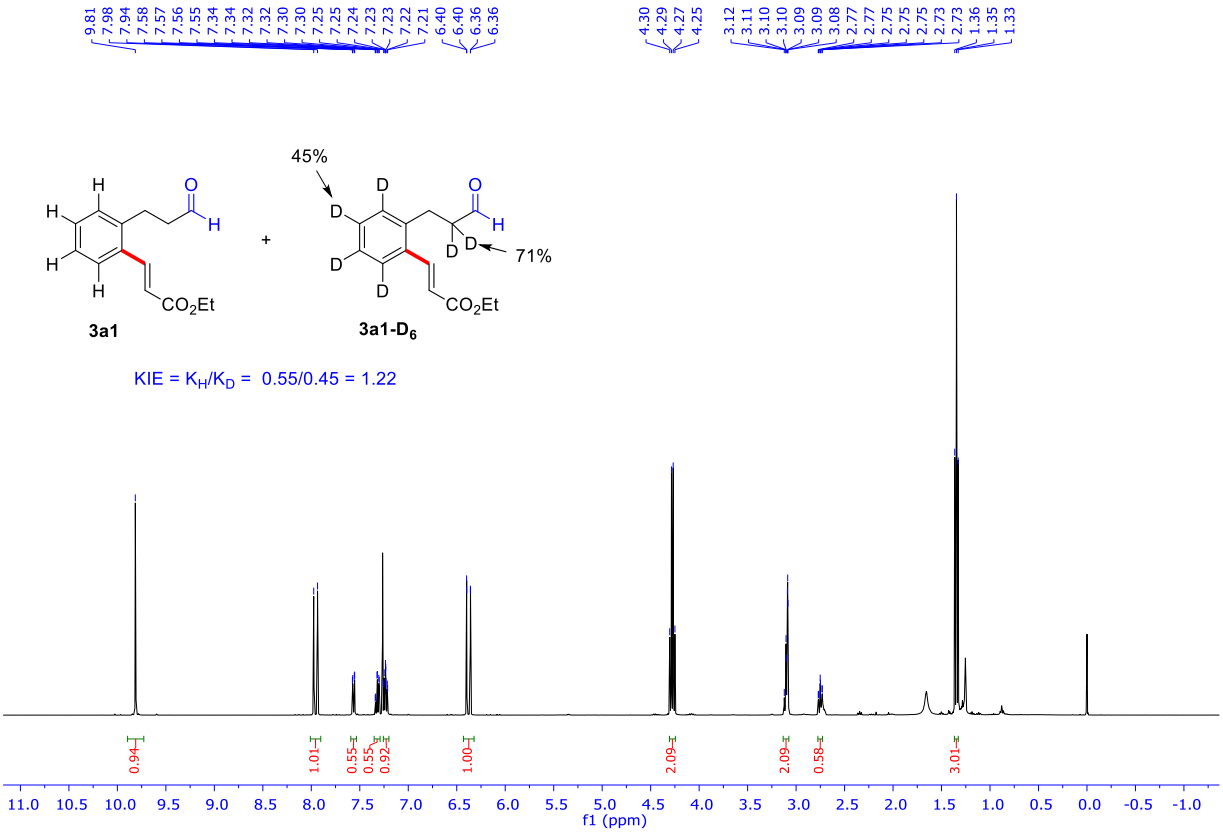
KIE = **$K_{H/D}$ = 1.29**

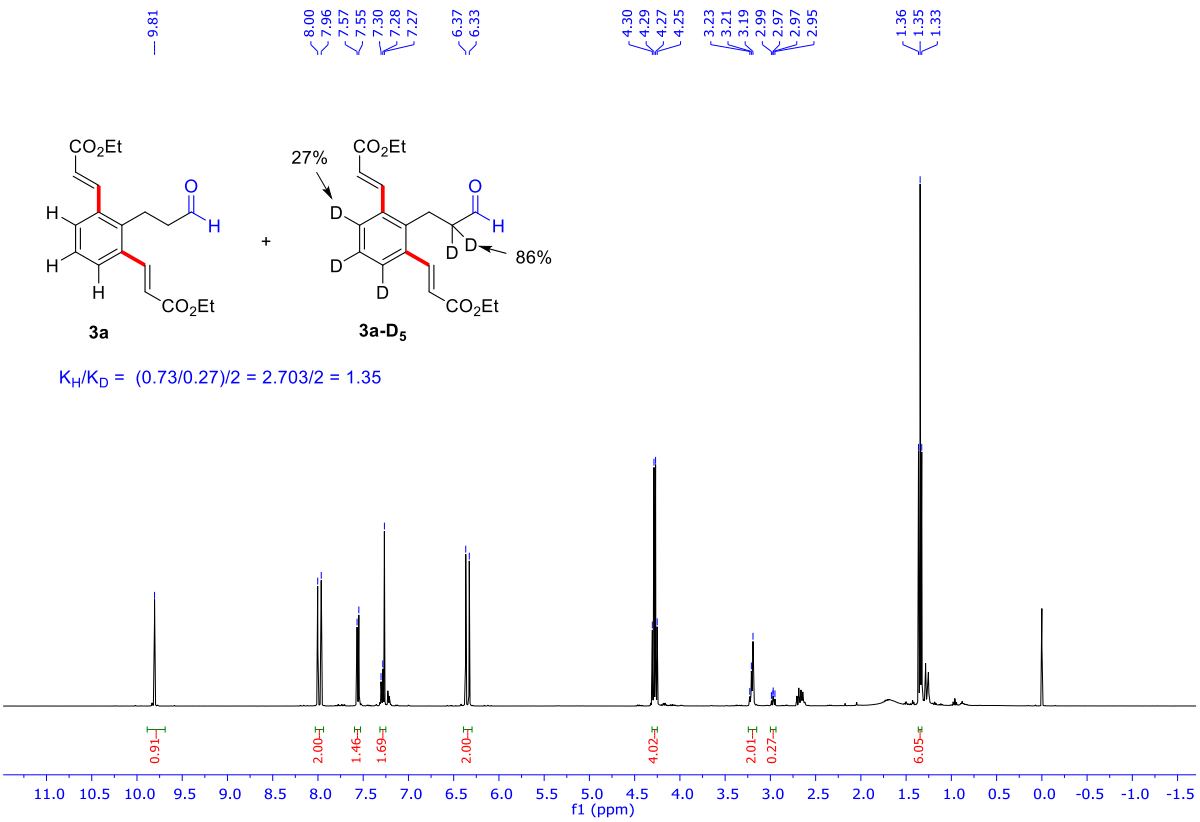
Intermolecular competition with all deuterated reagent:

In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-phenylpropanal **1a** (10.6 mg, 0.075 mmol) and 3-phenylpropanal **1a-*d*$_5$** (10.44 mg, 0.075 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then HFIP-d_1 (2 mL), CD_3CO_2D (80 µL, 10 equiv), D_2O (5.5 µL, 2 equiv.) and deuterated dibutylamine (n-Bu)$_2$ND (10 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 50 °C for 6 h. The reaction was cooled in an ice-bath and subsequently diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo* and purified by flash column chromatography using silica gel (Eluent: 10% EtOAc /90% hexane) to afford **3a1/3a1-D$_6$** (mono) and (Eluent: 15% EtOAc /85% hexane) **3a/3a-D$_5$** (di) for which a deuterium content of 45.0% (for mono) and 27% (for di) was determined by ^{1}H NMR spectroscopy). k_H/k_D was calculated by considering both mono and di product which found to be 1.29.

Kinetic Isotopic Effects:

Intermolecular Reactions


9.81
7.98
7.94
7.58
7.57
7.56
7.55
7.34
7.34
7.32
7.32
7.30
7.30
7.25
7.25
7.24
7.23
7.23
7.22
7.21
6.40
6.36
6.36
4.30
4.29
4.27
4.25
3.12
3.11
3.10
3.10
3.09
3.09
3.08
2.77
2.77
2.75
2.75
2.75
2.73
2.73
1.36
1.35
1.33
45%
71%
3a1
3a1-D6
KIE = KH/KD = 0.55/0.45 = 1.22
0.94
1.01
0.55
0.55
0.92
1.00
2.09
2.09
0.58
3.01
f1 (ppm)


9.81
8.00
7.96
7.57
7.55
7.30
7.28
7.27
6.37
6.33
4.30
4.29
4.27
4.25
3.23
3.21
3.19
2.99
2.97
2.97
2.95
1.36
1.35
1.33
27%
86%
3a
3a-D5
KH/KD = (0.73/0.27)/2 = 2.703/2 = 1.35
0.91
2.00
1.46
1.69
2.00
4.02
2.01
0.27
6.05
f1 (ppm)

KIE based on mono and di products under deuterated condition:

$KIE = K_{H/D\ (mono)} + K_{H/D\ (di)} = 1.22 + 1.35$

$KIE = 2\ K_{H/D} = 2.57$

$KIE = K_{H/D} = 2.57/2 = 1.29$

$KIE = \mathbf{K_{H/D} = 1.29}$

From the above *intermolecular competition* reactions, similar KIE value was observed under deuterated (1.29) and non-deuterated (1.29) reaction conditions.

General procedure for the Parallel KIE experiments[21]

In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-phenylpropanal **1a** (10.6 mg, 0.075 mmol), or 3-phenylpropanal **1a-*d*$_5$** (10.44 mg, 0.075 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then HFIP (2 mL), AcOH (80 µL, 10 equiv), H_2O (5.5 µL, 2 equiv) and dibutylamine $(n\text{-}Bu)_2NH$ (10 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 50 °C for the indicated time: 1 h, 2 h, 3 h, 4h, 5 h and 6h (six parallel runs). After cooling rapidly in ice cold water, the reaction mixture was diluted with 10 mL of DCM and passed through small pad of silica gel and washed with additional10 mL of DCM. The solvents were removed under vacuum. The yield of the mono-olefinated and di-olefinated products was determined by ^{1}H NMR analysis of the crude using dibromomethane as internal standard by integration of the benzylic methylene proton signals which appear as triplet due to two protons (approximately 3.2 ppm, respectively). The resulting data was analyzed using Microsoft Excel. For (**3a1+3a)**, $y = 5.2286x + 7.5333$, $R^2 = 0.9747$, for (**3a1-d$_4$ + 3a-d$_3$)**, $y = 4.3143x + 0.7333$, $R_2 = 0.967$. KIE value (1.21) was determined by comparing the relative initial rates.

Time (h)	Mono + Di NMR Yield (**3a1 + 3a**)%	Mono + Di NMR Yield (**3a1-d_4 + 3a-d_3**)%
1	11+1 = 12	5+0 = 5
2	14+3 = 17	8+1 = 9
3	17+7 = 24	12+2 = 14
4	20+11 = 31	14+3 = 17
5	20+12 = 34	19+6 = 25
6	21+16 = 37	18+7 = 25

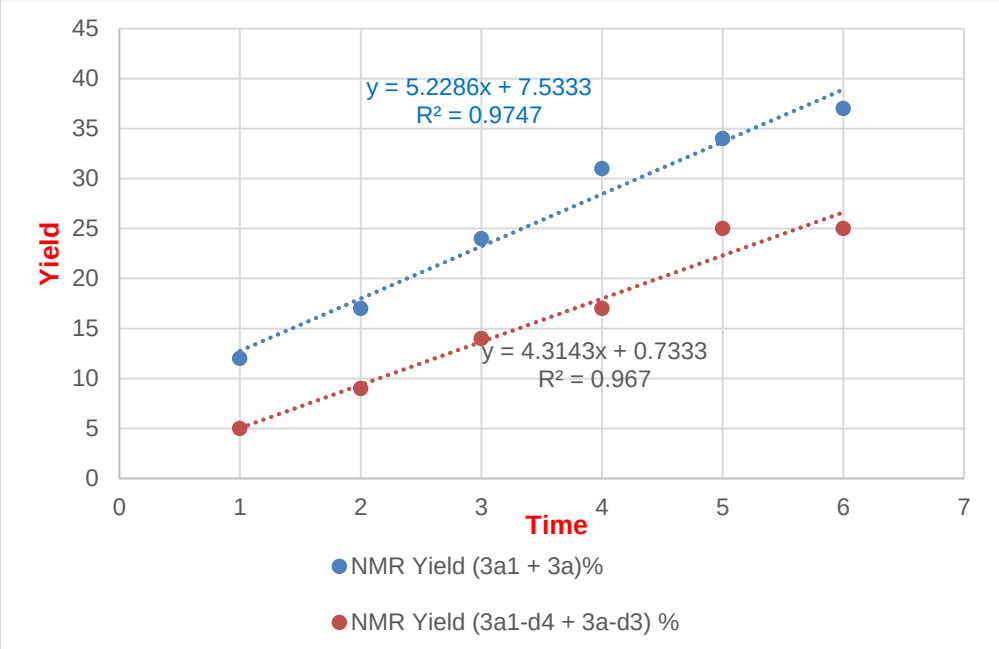
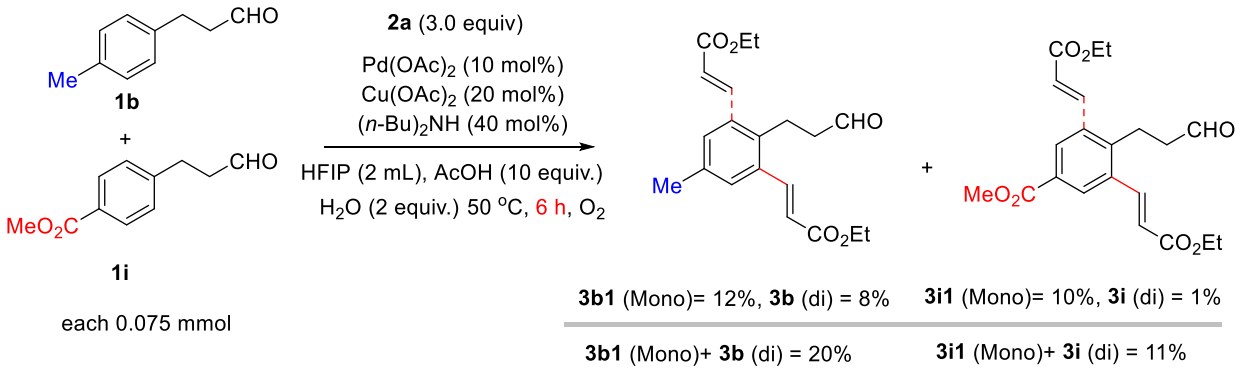


Figure S4: Initial rate data for the formation of (3a1+3a) and (3a1-d_4 + 3a-d_3)

Intermolecular competition experiment between 3-(p-tolyl)propanal (1b) and methyl 4-(3-oxopropyl)benzoate (1i):



Scheme S4: Competitive reaction between electron rich and electron poor substrate

In glove box, a 37 mL Schlenk tube was equipped with a magnetic stir bar was charged with 3-(p-tolyl)propanal **1b** (11.16 mg, 0.075 mmol) and methyl 4-(3-oxopropyl)benzoate**1i** (14.42 mg, 0.075 mmol), $Pd(OAc)_2$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (5.5 mg, 20 mol%). The tube was fitted with a rubber septum and moved out of the glove box. Then HFIP (2 mL), AcOH (80 µL, 10 equiv), H_2O (5.5 µL, 2 equiv.) and dibutylamine $(n\text{-}Bu)_2NH$ (10 µL, 40 mol %) were added to the Schlenk tube through the rubber septum using syringes. The tube was evacuated and filled with O_2 with three times and then the septum was replaced with a Teflon screwcap under O_2 flow. The reaction mixture was stirred at room temperature for 10 min, then at 50 °C for 6 h. The reaction was cooled in an ice-bath and subsequently diluted with 10 mL of DCM and filtered through a pad of silica gel and washed with additional 10 mL of ethyl acetate. The organic layer was concentrated in *vacuo*.The yield of the mono-olefinated and di-olefinated products were determined by ^1H NMR analysis of the crude using dibromomethane as internal standard by integration of the alkene proton signals which appear as doublet due to one protons (approximately 6.5 ppm, respectively).

	Me	*vs*	CO_2Me	Yield
Mono	**3b1** = 12%		**3i1** = 10%	12:10
Di	**3b** = 8%		**3i** = 1%	8:1
Mono+Di				20:11

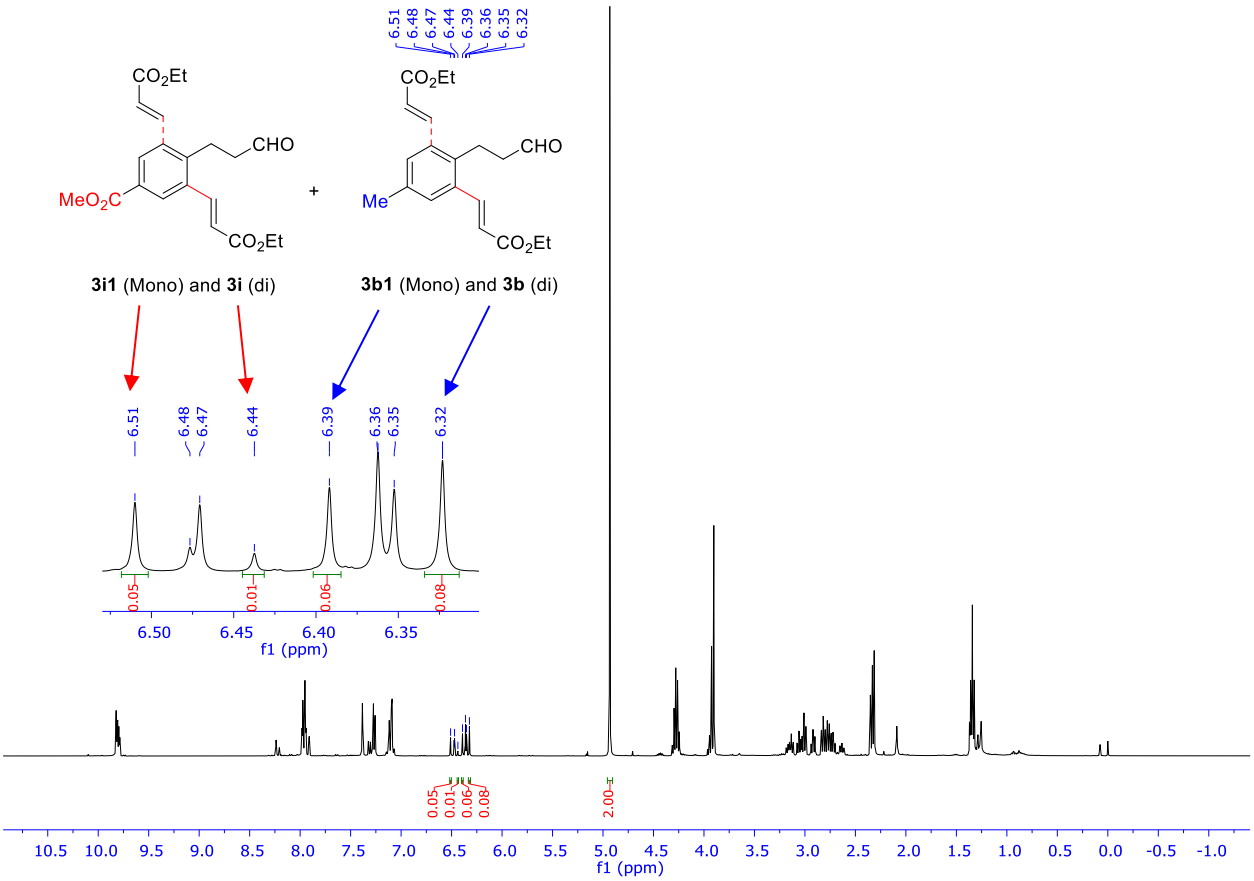
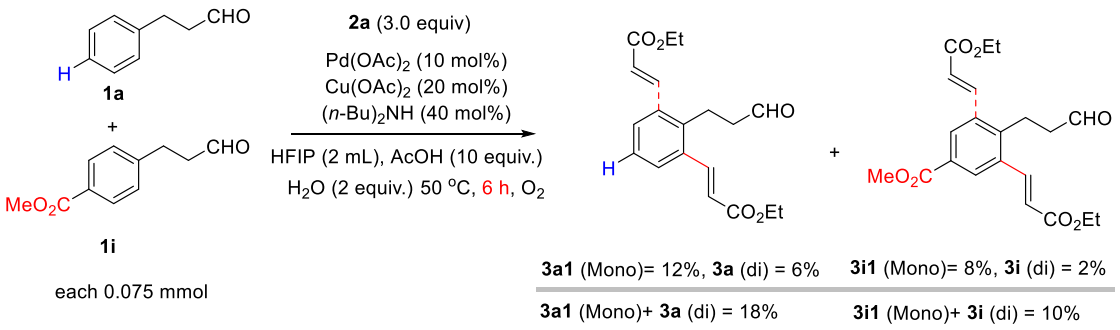


Figure S5: ^{1}H NMR spectra of crude reaction mixture after 6h

Intermolecular competition experiment between 3-phenyl propanal (1a) and methyl 4-(3-oxopropyl)benzoate (1i):

Under similar reaction condition as mention above, a intermolecular competition experiment was carried out between 3-phenyl propanal **1a** (10.06 mg, 0.075 mmol) and methyl 4-(3-oxopropyl)benzoate **1i** (14.42 mg, 0.075 mmol).



Scheme S5: Competitive reaction between electron neutral and electron poor substrate

	H	*vs*	CO_2Me	Yield
Mono	**3a1** = 12%		**3i1** = 8%	12:8
Di	**3a** = 6%		**3i** = 2%	6:2
Mono+Di				18:10

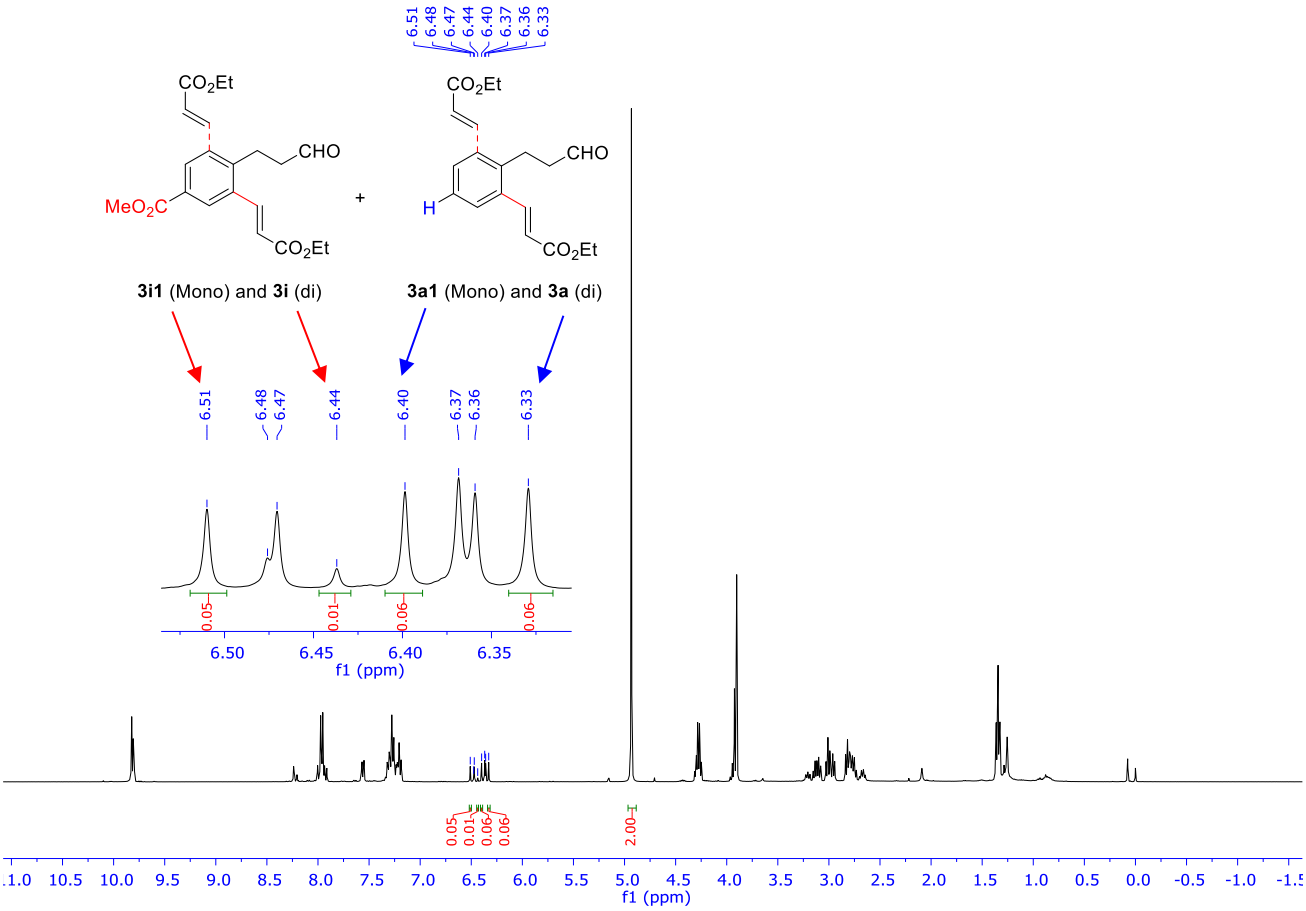


Figure S6: ^{1}H NMR spectra of crude reaction mixture after **6h**

Conclusion: The intermolecular competition between electron rich or neutral and electron poor substrates suggests that substrates bearing electron donating group in *meta* position of the CH functionalization site are more reactive with respect to mono-product, di-products even combining both mono and di-product. These results could indicate that the C-H activation step might occur through an electrophilic type mechanism.

Control Experiments:

To ascertain the role of electrophilic palladation some control experiment has been performed under standard reaction conditions. The reaction of 3-phenylpropanal **1a**, without ethyl acrylate (**2a**) showed the formation of dehydrogenated product (**1ag)** 8% yield with some unreacted starting material. This observation compliance with the previous report[22], where electrophilic palladation of the nucleophilic enamine gave intermediate **I**, which undergoes *β*-hydride elimination followed by hydrolysis to give **1ag**. The control experiments without di-butyl amine (**A**) ruled out the possibility dehydrogenation *via* keto-Enol tautomerization pathway.[23] The reaction without $Pd(OAc)_2$ also diminished the involvement of palladium promoted dehydrogenation. These observations support the involvement of electrophilic palladation at the α C atom.

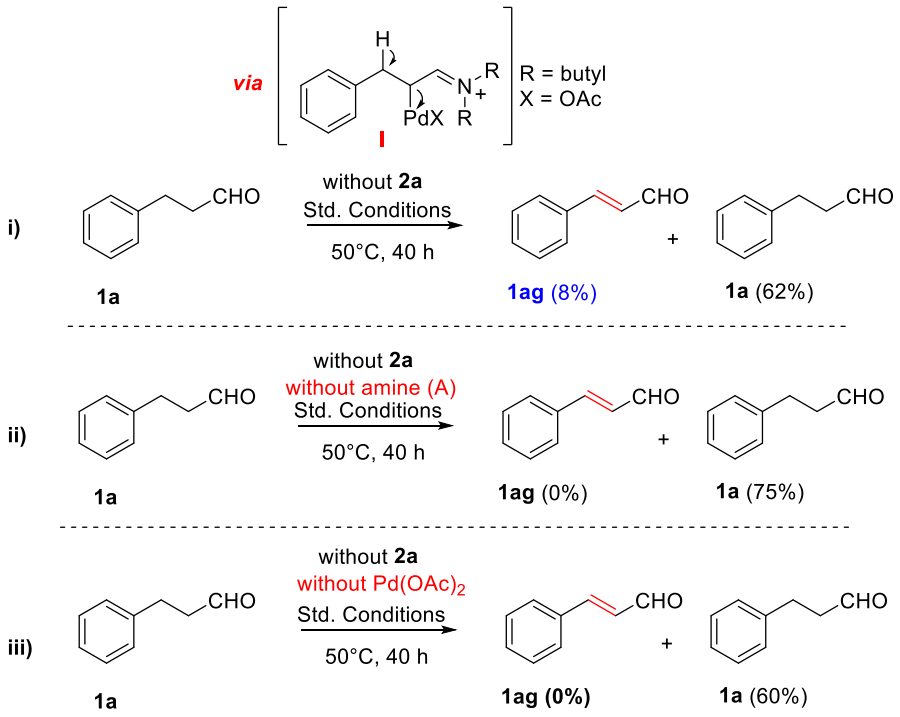


Figure S7: Control experiments under std. reaction condition

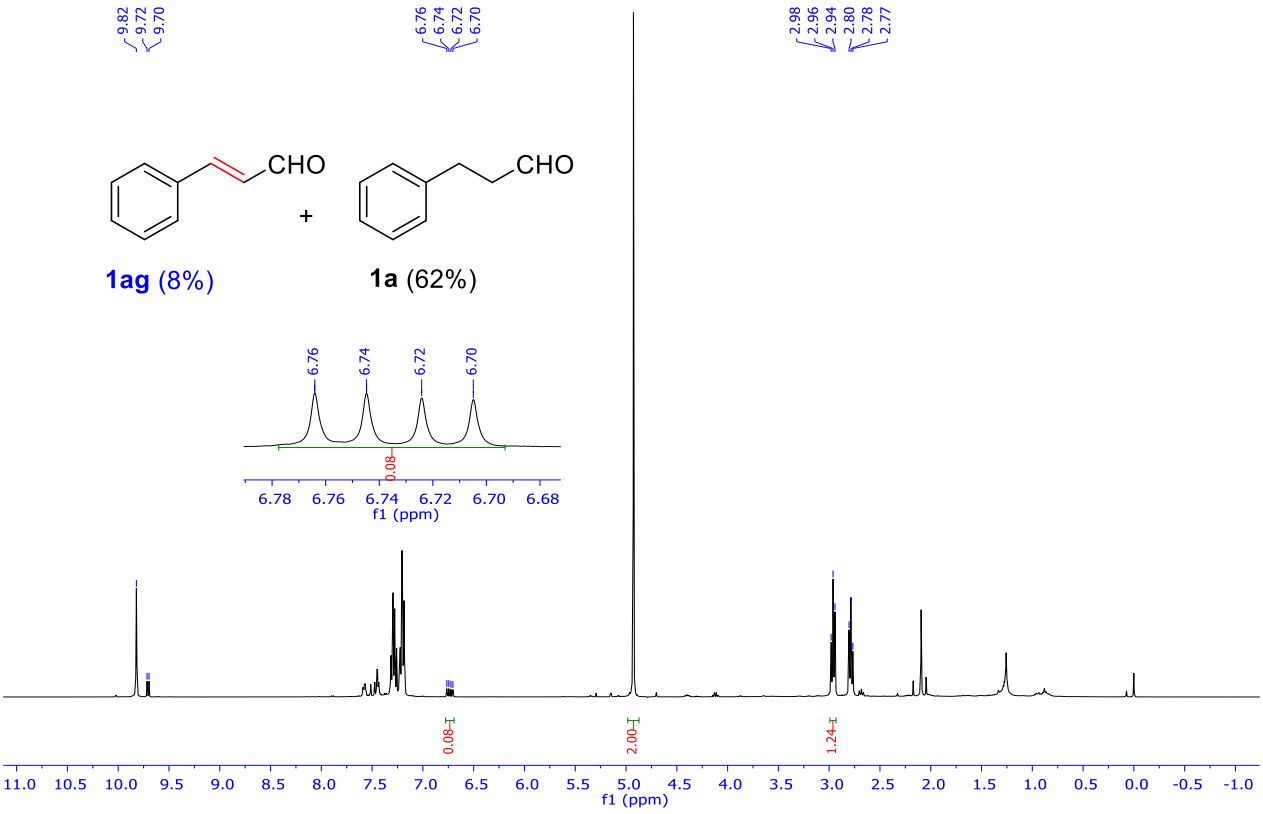


Figure S8: ^{1}H NMR spectra of crude reaction mixture under std. reaction condition without **2a**

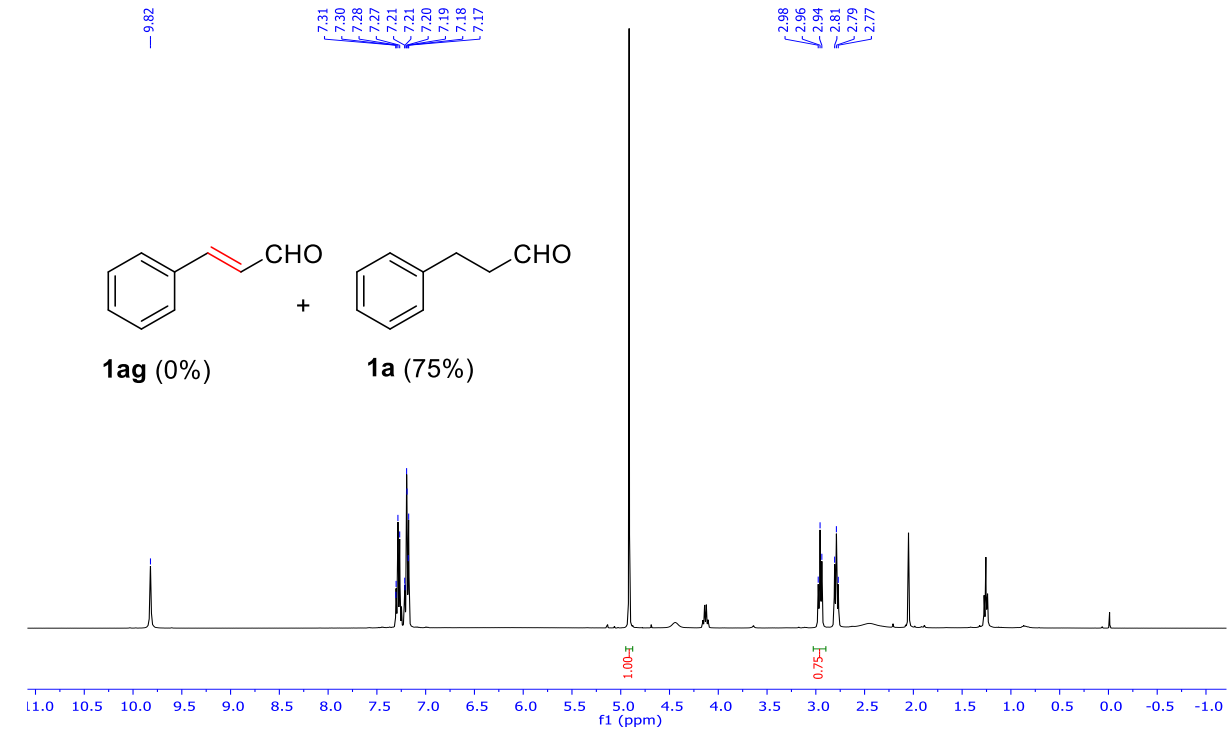


Figure S9: ^{1}H NMR spectra of crude reaction mixture under std. reaction condition without **2a** and **amine.**

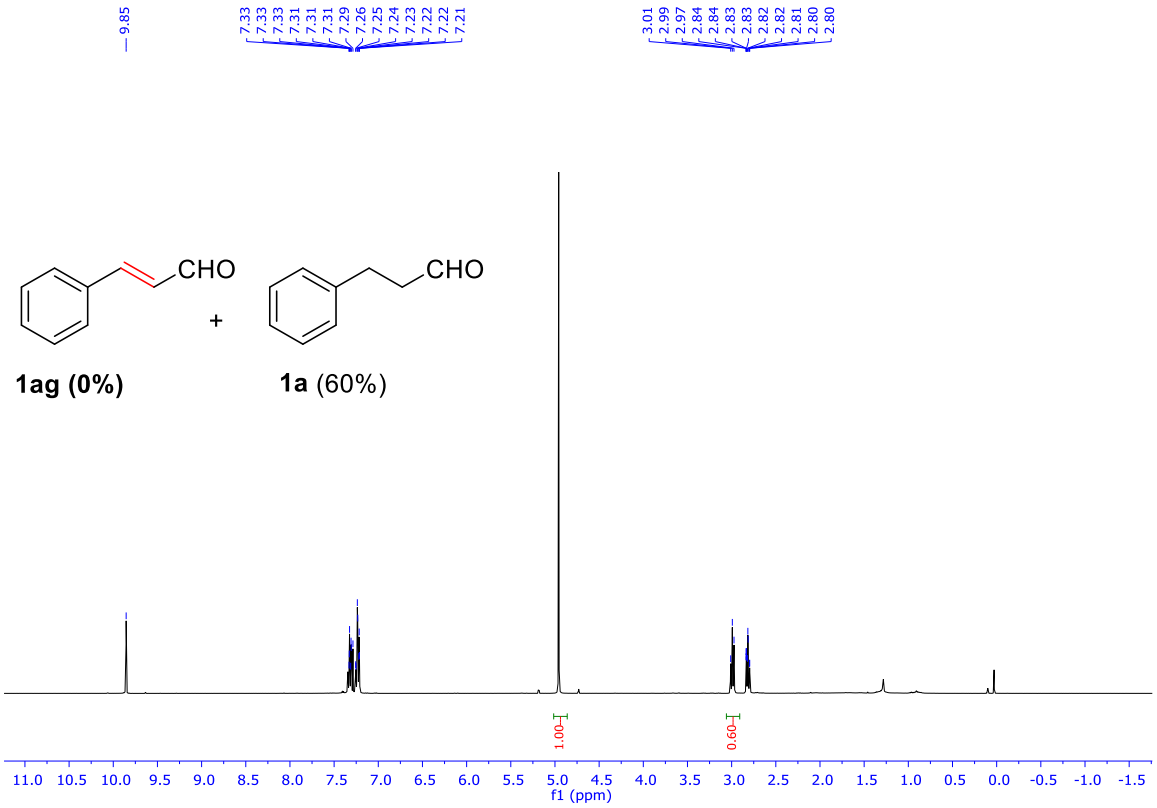
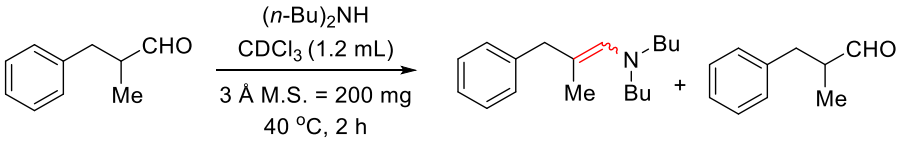


Figure S10: ^{1}H NMR spectra of crude reaction mixture under std. reaction condition without **2a** and $Pd(OAc)_2$

General procedure for synthesis of Enamine:



Scheme S5a: Synthesis of enamine **1af**

Method g: Molecular sieves (3 Å, 200 mg) were added to a solution of aldehyde (0.15 mmol) in $CDCl_3$ (1.2 mL) at room temperature. The solution was cooled to 0 °C, then the secondary amine (1.2 equiv.) was added and the reaction mixture was stirred at 40 °C for 2-3 h. Conversion of the aldehyde to the enamine was chwcked by ^{1}H NMR spectra of 0.6 mL aliquots sampled from the reaction mixture, filtered, and diluted with $CDCl_3$ in an NMR tube. The internal standared dimromomethanewas added to check to calculate the yield.

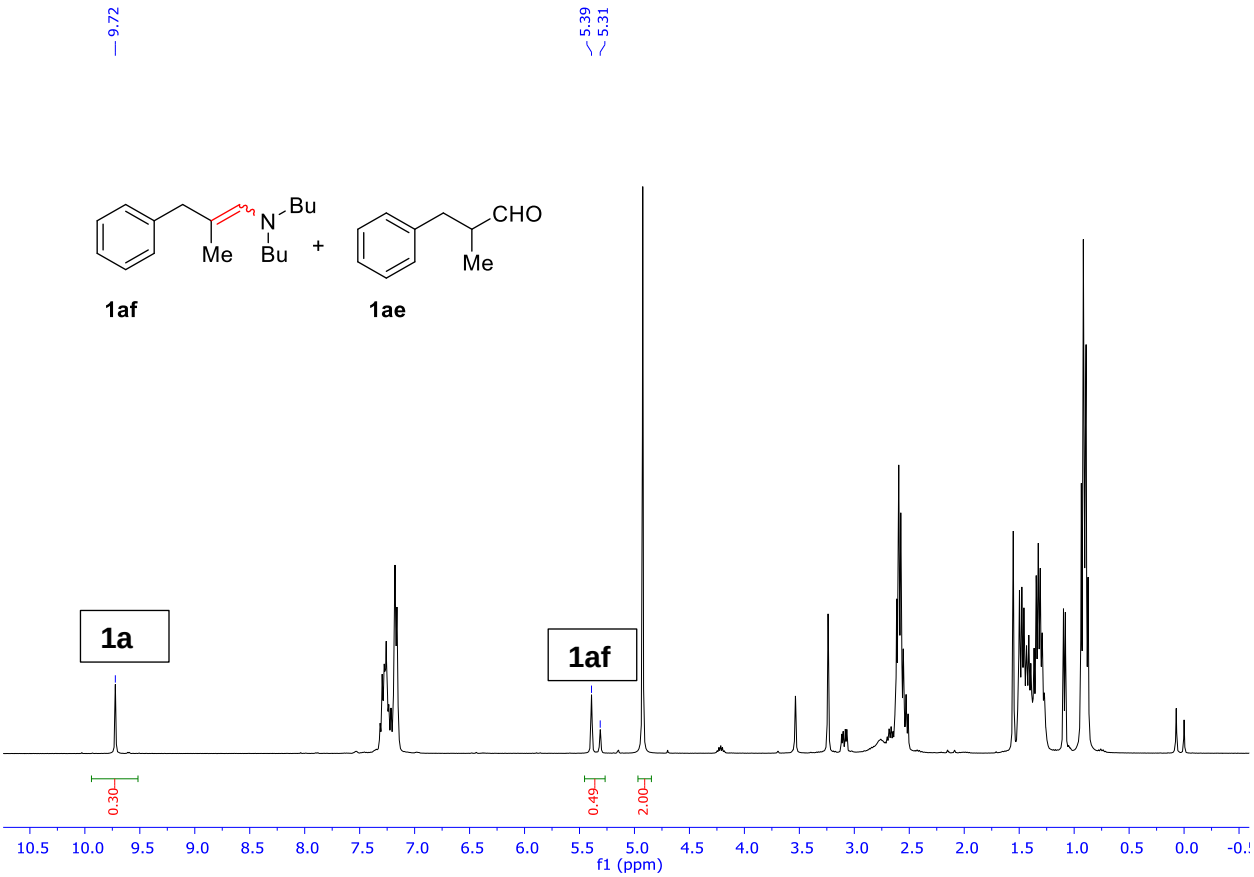
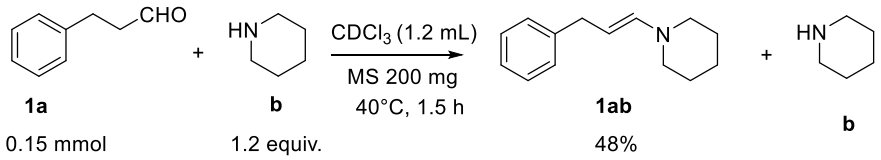


Figure S11: ^{1}H NMR spectra of crude reaction mixture of reaction **1ae** and **(*n*-Bu)$_2$NH** after 2h.

Enamine formation under various reaction conditions:

Enamine formation in $CDCl_3$ solvent (without Pd, $Cu(OAc)_2$ and AcOH):



Scheme S6: Enamine formation of **1a** with **b** in $CDCl_3$ solvent

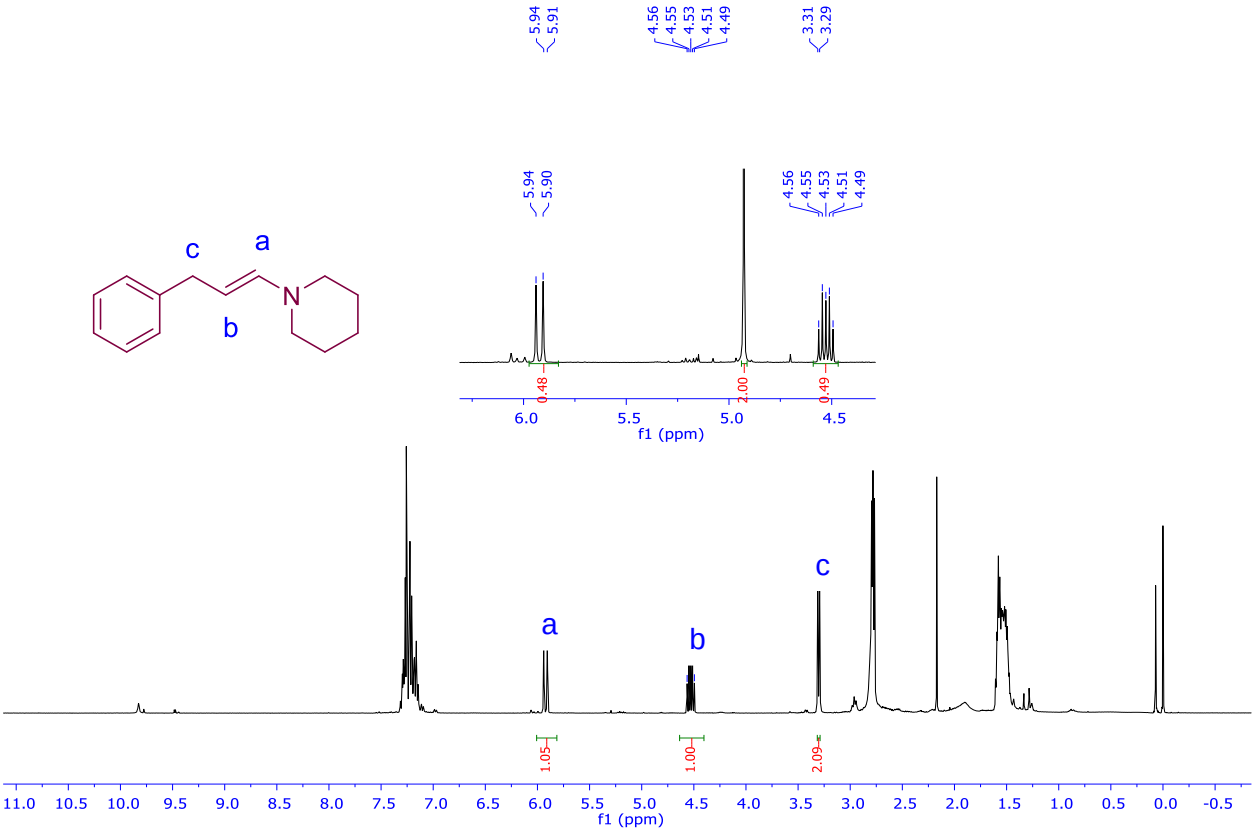
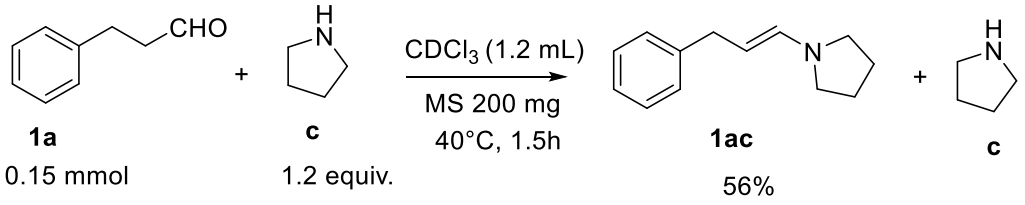


Figure S12: Crude ^1H NMR spectra of reaction **1a** and **b** in $CDCl_3$



Scheme S7: Enamine formation of **1a** with **c** in $CDCl_3$ solvent

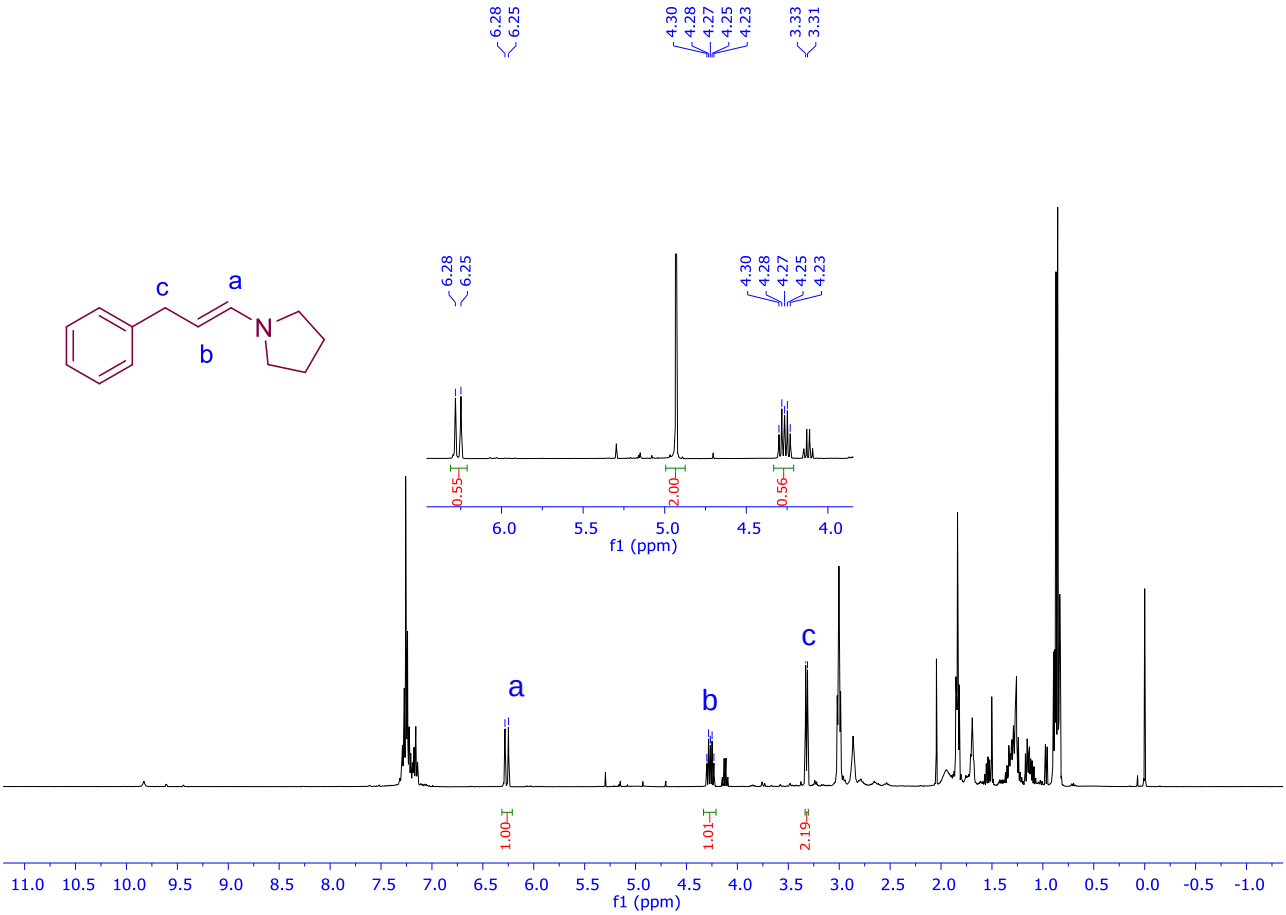
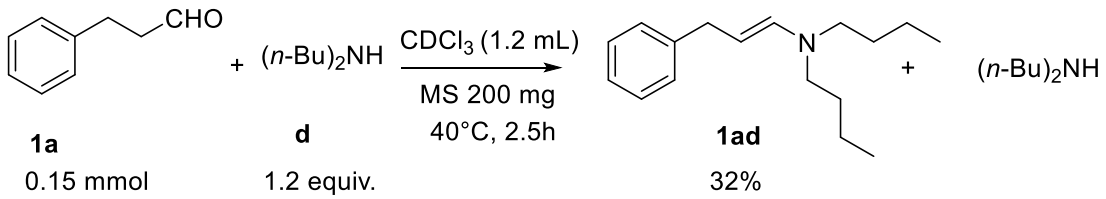


Figure S13: Crude ^1H NMR spectra of reaction **1a** and **c** in $CDCl_3$



Scheme S8: Enamine formation of **1a** with **d** in $CDCl_3$ solvent

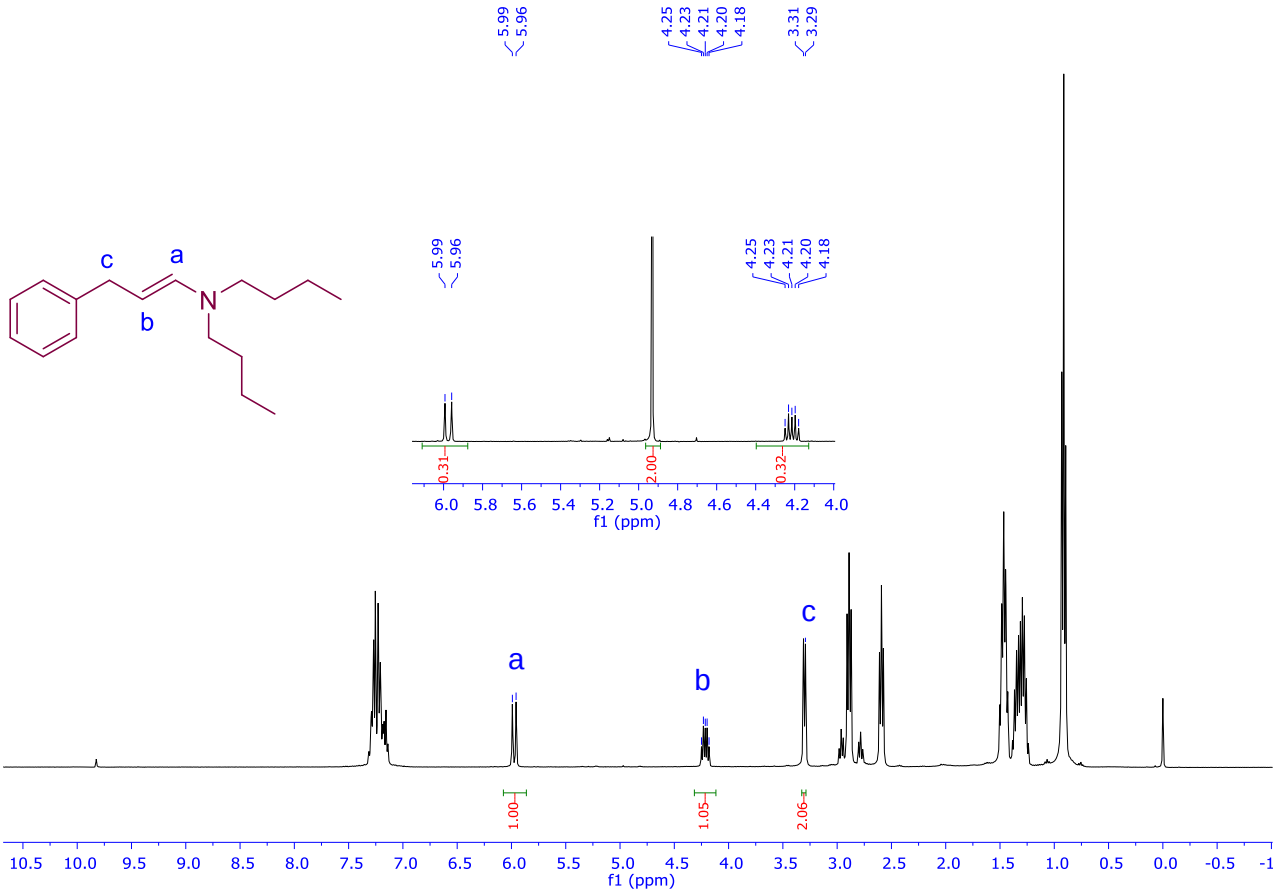
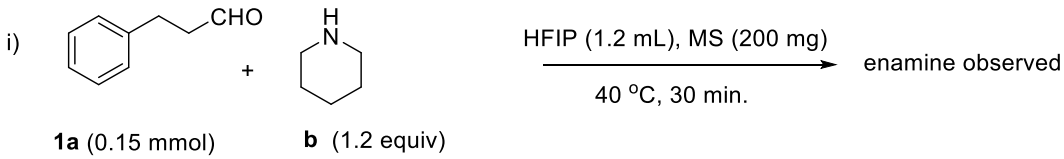


Figure S14: Crude ^{1}H NMR spectra of reaction **1a** and **d** in $CDCl_3$

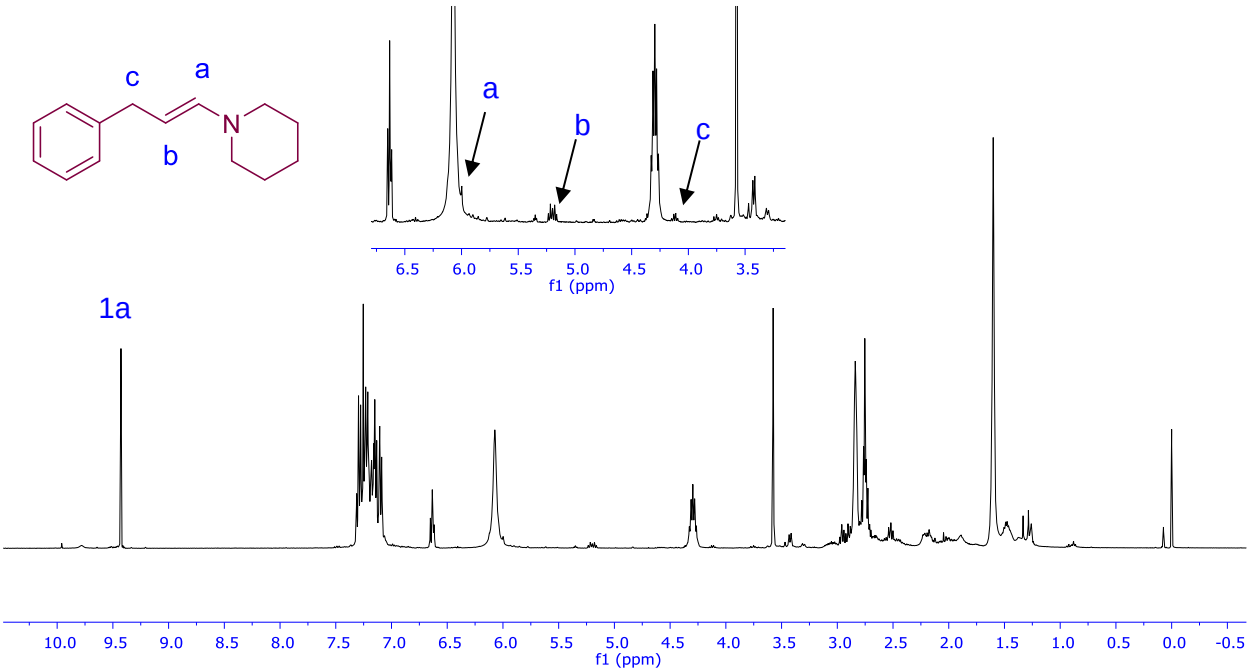
From the above experiments (Scheme S6-S8) it can be concluded that enamine formation is not the problem associated with inactiveness of cyclic amine (A7, A8) compare to acyclic amine (A).

Enamine formation in HFIP solvent (without Pd, $Cu(OAc)_2$, AcOH):

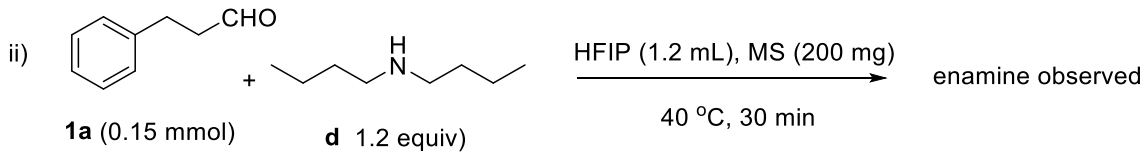


1a (0.15 mmol) **b** (1.2 equiv)

Scheme S9: Enamine formation of **1a** with **b** in HFIP solvent



Crude ^{1}H NMR spectra of reaction 1a and b in HFIP



Scheme S10: Enamine formation of **1a** with **d** in HFIP solvent

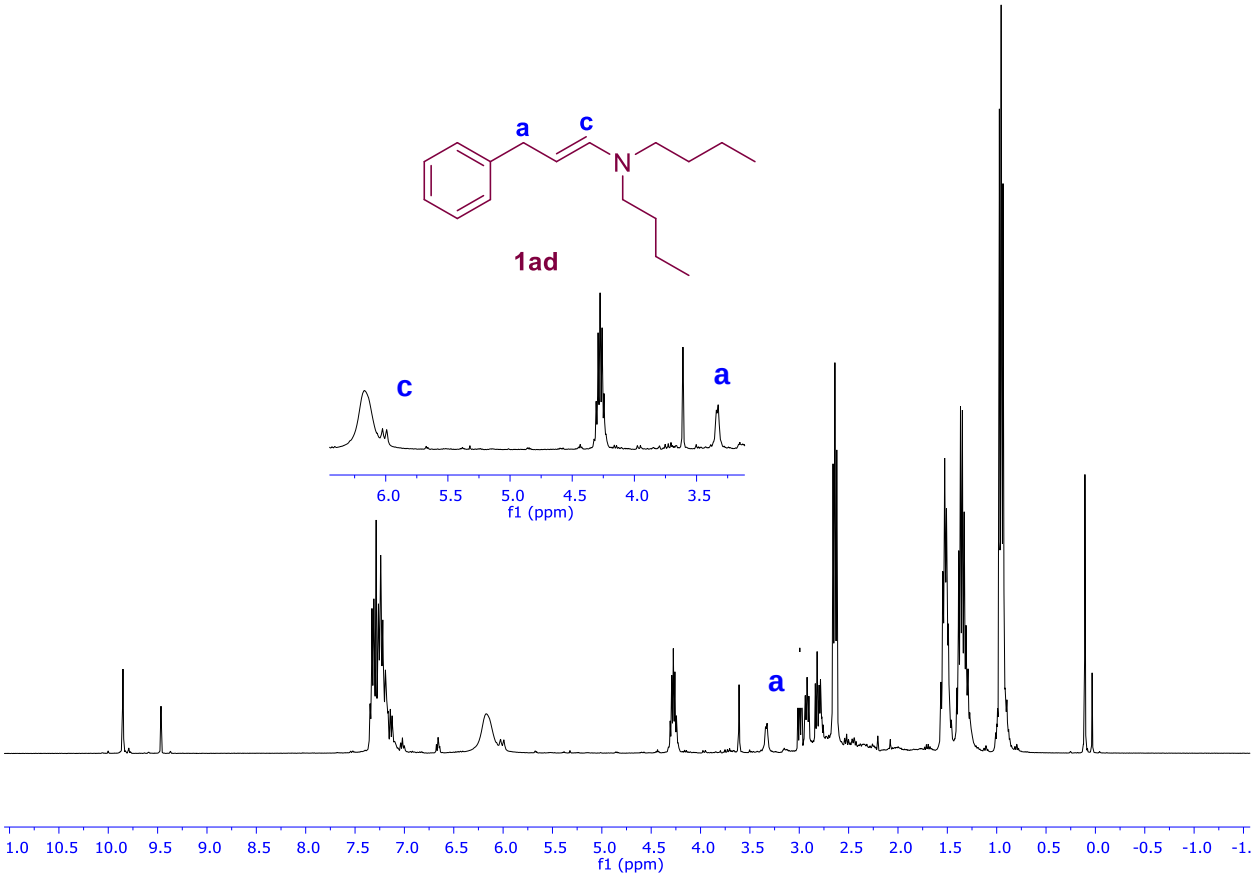
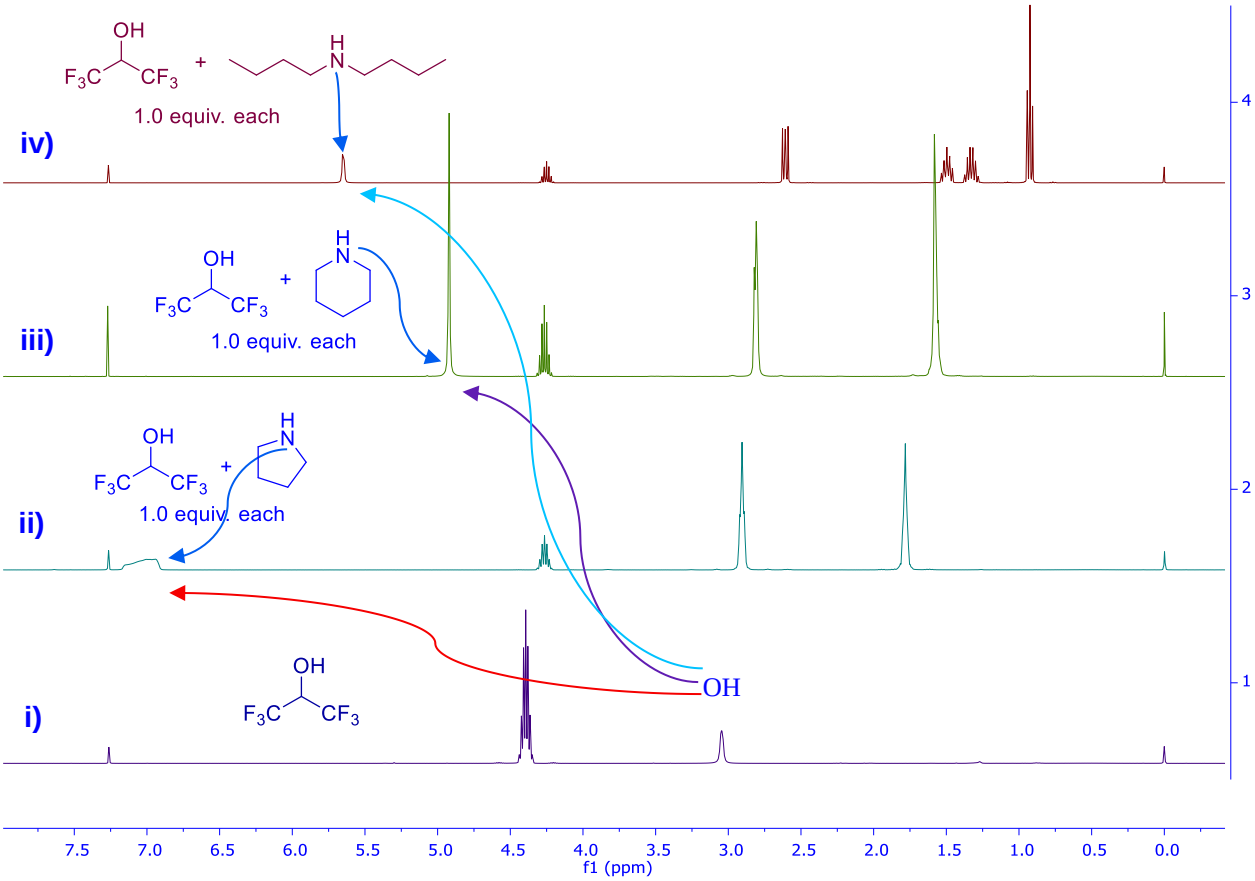


Figure S16: Crude ^{1}H NMR spectra of reaction **1a** and **d** in HFIP

The low detection of enamine in HFIP solvent (Scheme S9-S10) may be due to decrease in nucleophilicity of amine due to strong hydrogen bonding interation between amine and HFIP (see experiment in Figure S17).[24]

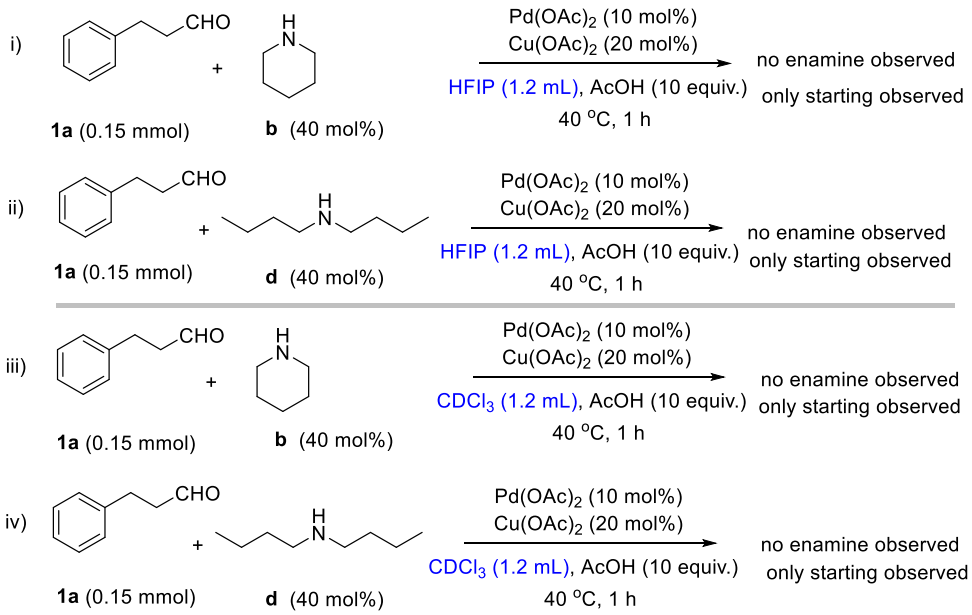
^{1}H NMR Interation of amine and HFIP:



Scheme S17: ^{1}H-NMR of i) HFIP and mixtures of HFIP with different amine (ii) to (iv) in $CDCl_3$

The shifting of OH and NH proton of HFIP and amine (scheme S17) towards downfield shift (deshieled) supporting the H-bonding between the basic amine moiety and the exceptionally good hydrogen bond donor HFIP.[25] This H-bonding interaction decrease the nucleophilicity of amine, that might be the reason associated with low detection of enamine in HFIP solvent (Scheme S9-S10). In other words, we can that this hydrogen bonding maintains the equilibrium between enamine formation and C-H activation step.

Enamine formation under standard reaction condition in HFIP and $CDCl_3$ solvents



Scheme S11: Enamine formation of **1a** with different amine under various reaction condition

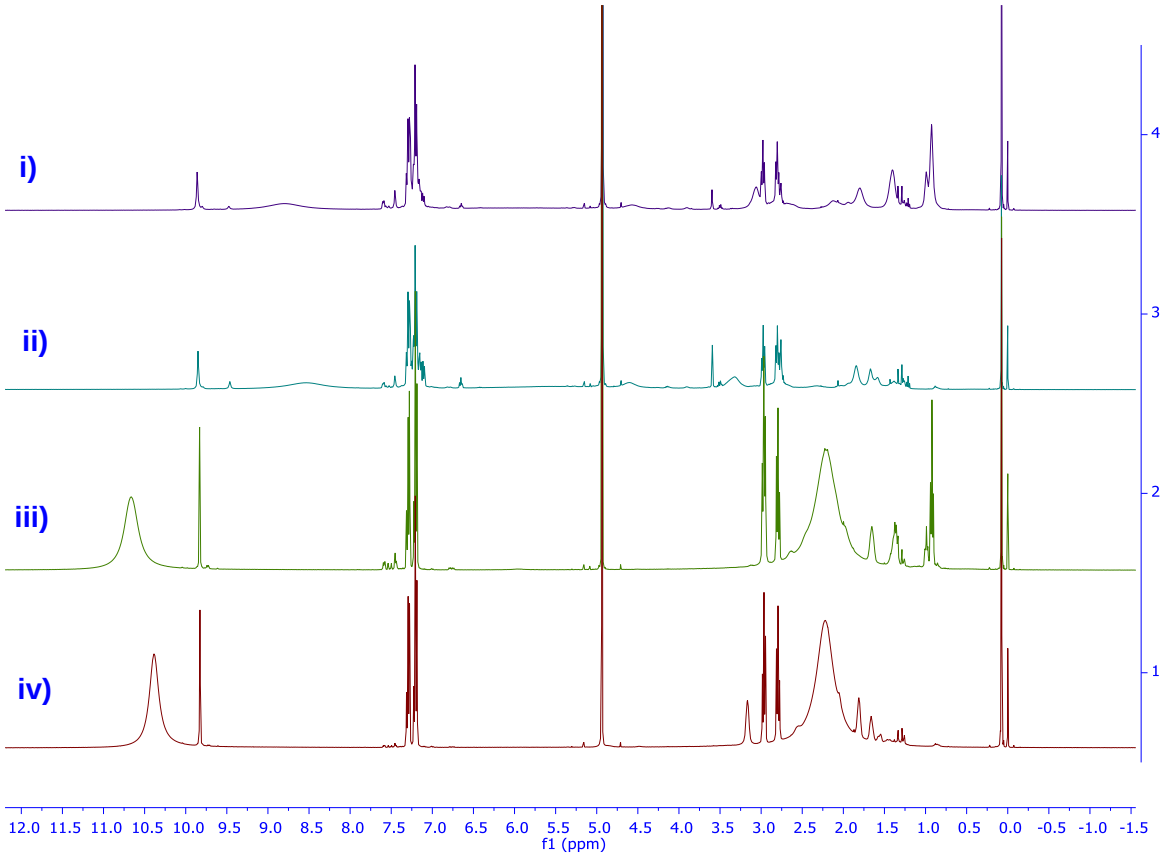
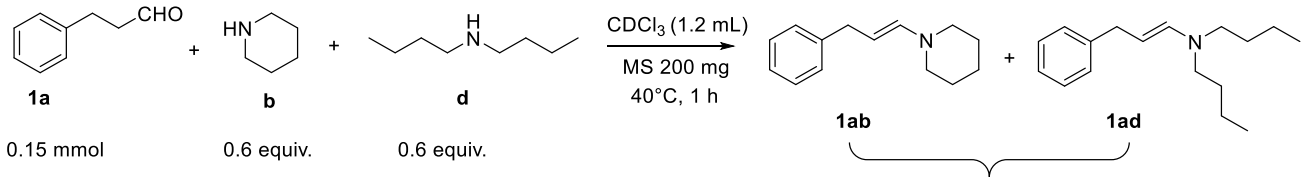


Figure S18: Crude ^1H NMR spectra of enamine formation of above reactions (i-iv)

No enamine formation has been detected under standard reaction condition in HFIP and $CDCl_3$ solvent (Scheme S11, Figure 18) that mean enamine formation is highly reversible in nature.

Intermolecular competition experiment between 3-phenyl propanal (1a), cyclic amine and acyclic amine:



Scheme S12: Intermolecular competition between **1a**, **b**, and **d**

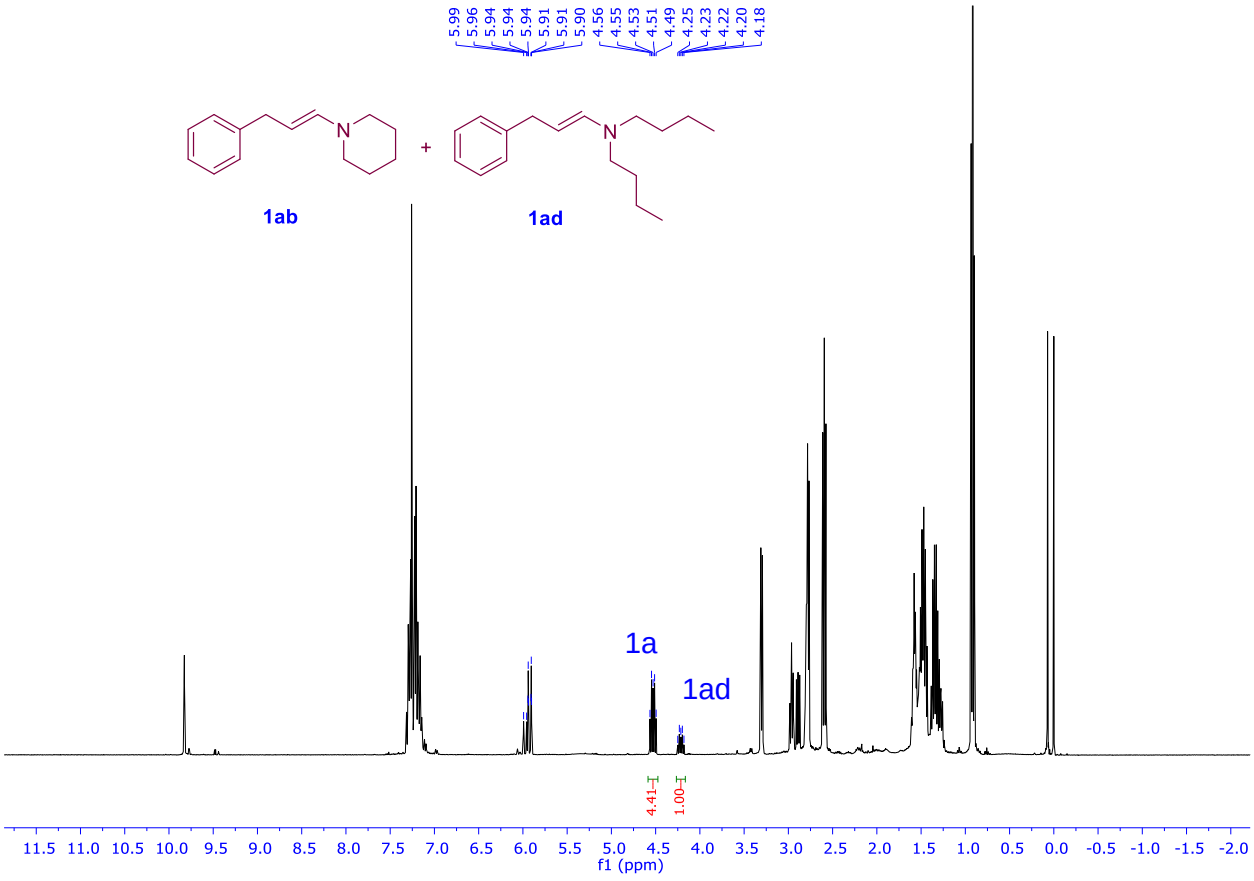
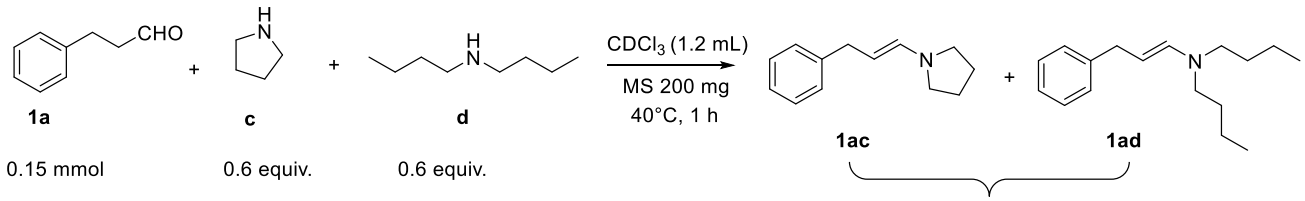


Figure S19: Crude ^{1}H NMR spectra of reaction **1a**, **b** and **d**



Scheme S13: Intermolecular competition between **1a**, **c**, and **d**

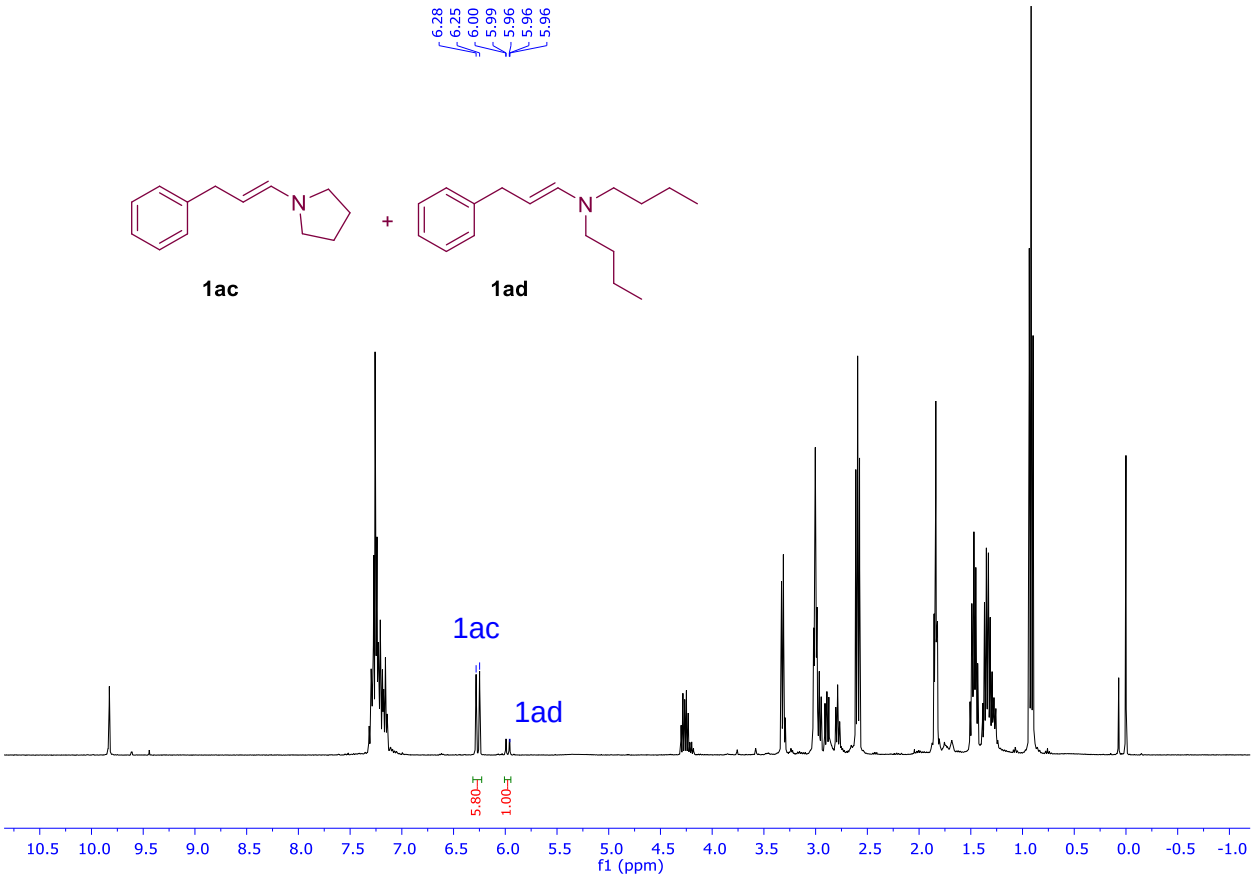
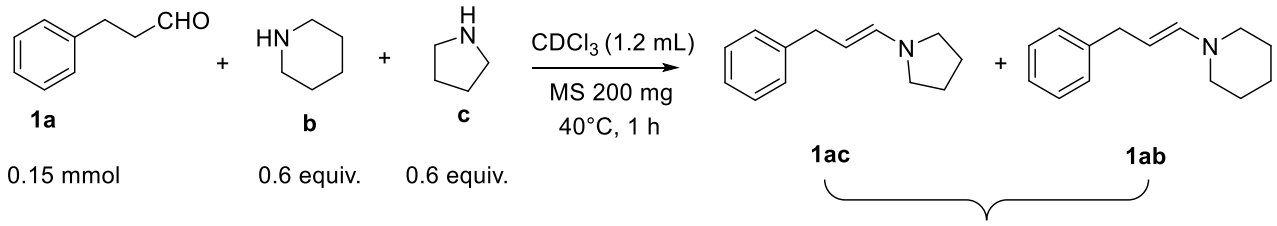


Figure S20: Crude ^{1}H NMR spectra of reaction **1a**, **c** and **d**



Scheme S14: Intermolecular competition between **1a**, **b**, and **c**

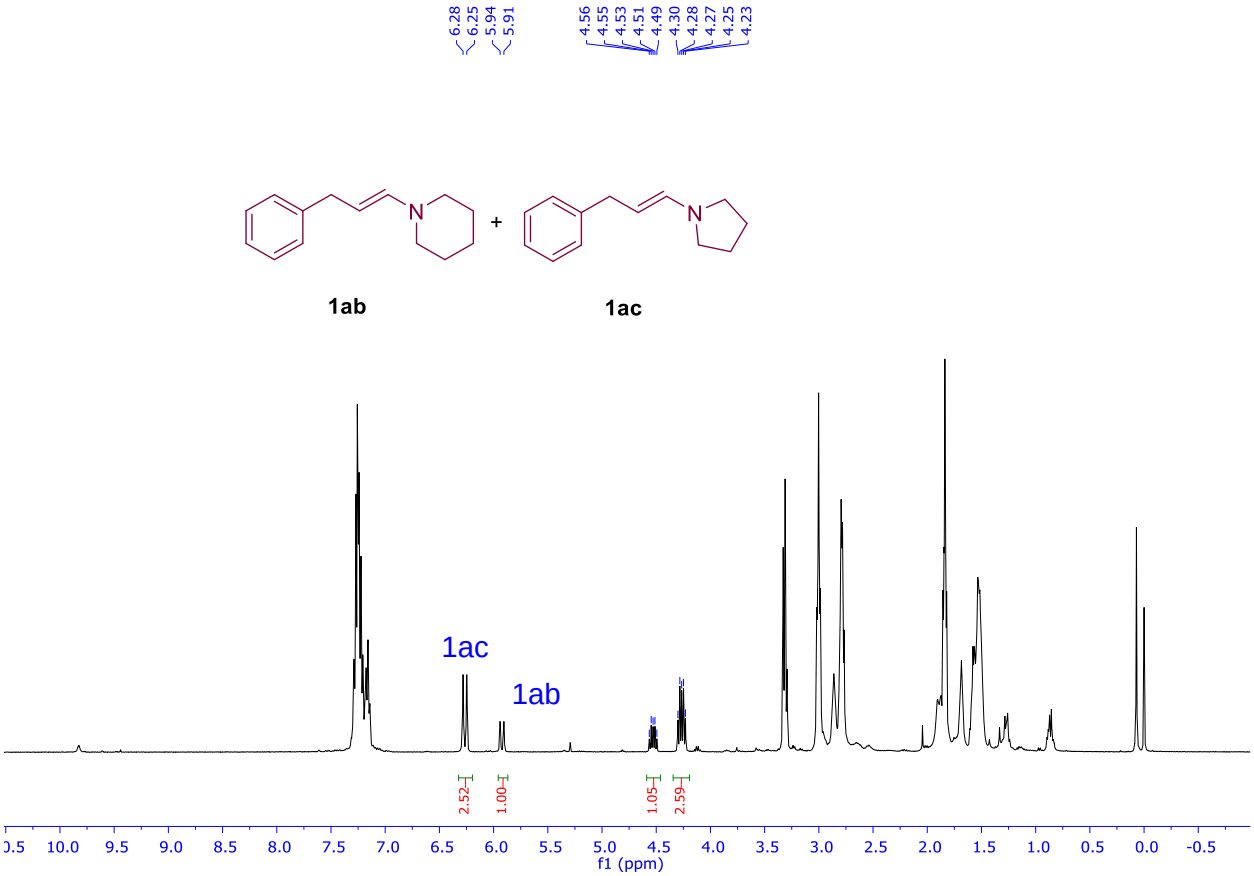
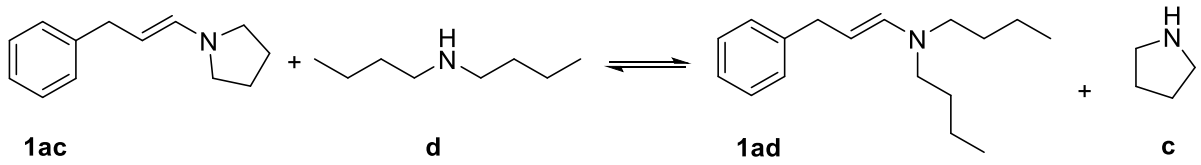


Figure S21: Crude ^{1}H NMR spectra of reaction **1a**, **b** and **c**

From the above competitive experiments (Scheme S12-S14), it can be concluded that cyclic amine (A7, A8) are more nucleophilic in nature and showed more enamine formation compared to acyclic amine (A) likely owing the less steric hindrance character.[26]

Amine-enamine exchange experiments:

Amine-enamine exchange experiment was performed according to literature report.[26] The enamine (**1ac**, **1ab** and **1ad**) was synthesized according to above method **g** (Scheme S**5a**) and used as such for amine-enamine experiments.



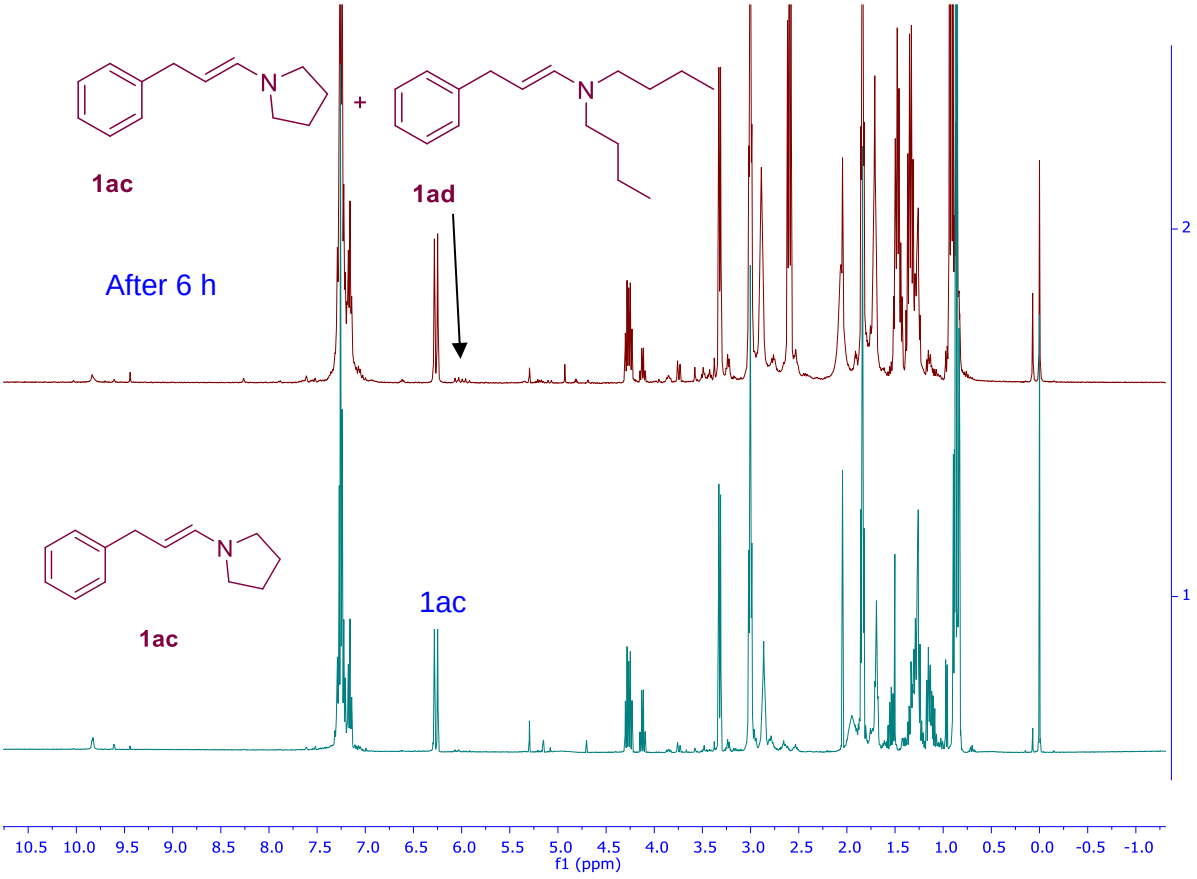


Figure S22: Crude ^{1}H NMR spectra of Amine-enamine exchange reaction with **1ac** and **d** after 6h

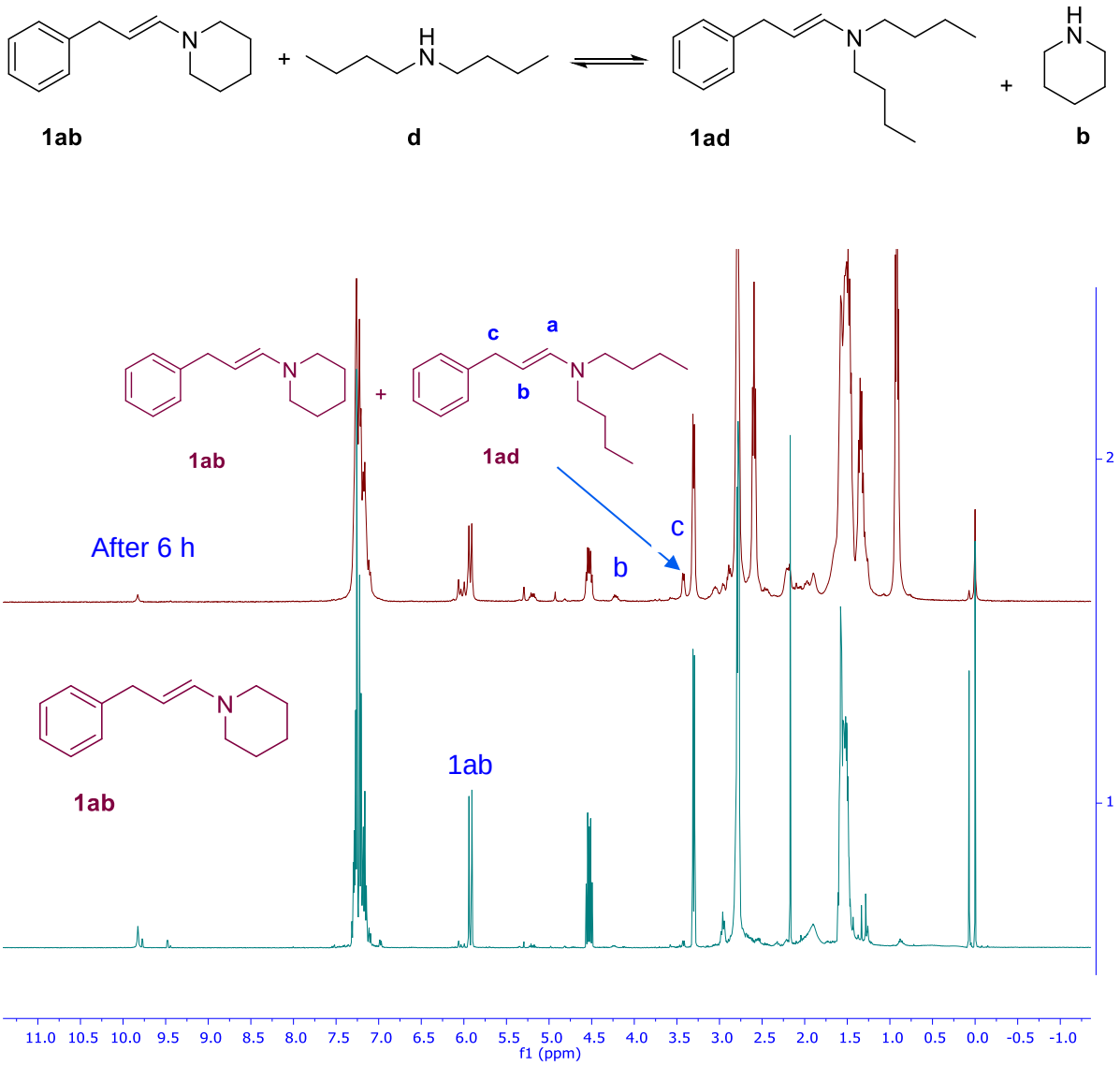


Figure S23: Crude ^{1}H NMR spectra of Amine-enamine exchange reaction with **1ab** and **d** after 6h

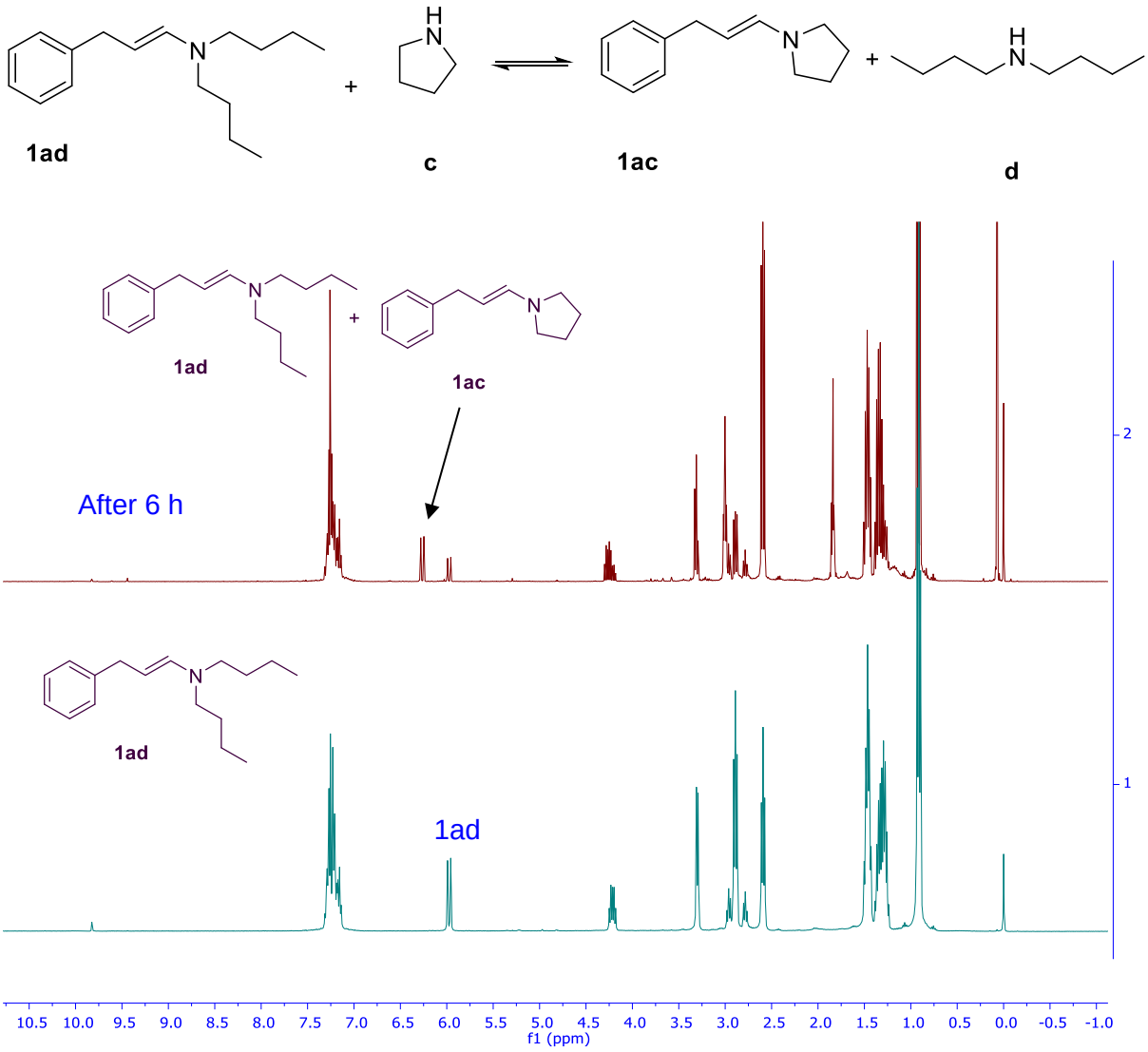
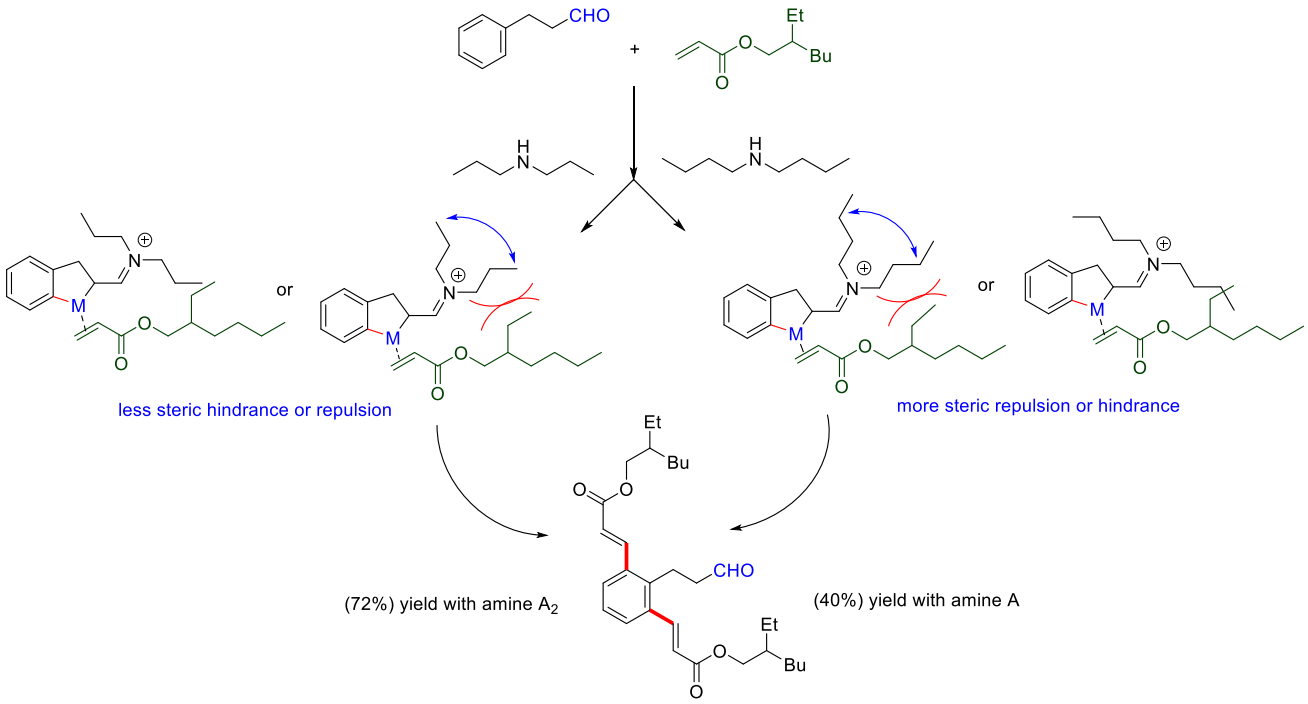


Figure S24: Crude ^{1}H NMR spectra of Amine-enamine exchange reaction with **1ad** and **c** after 6h

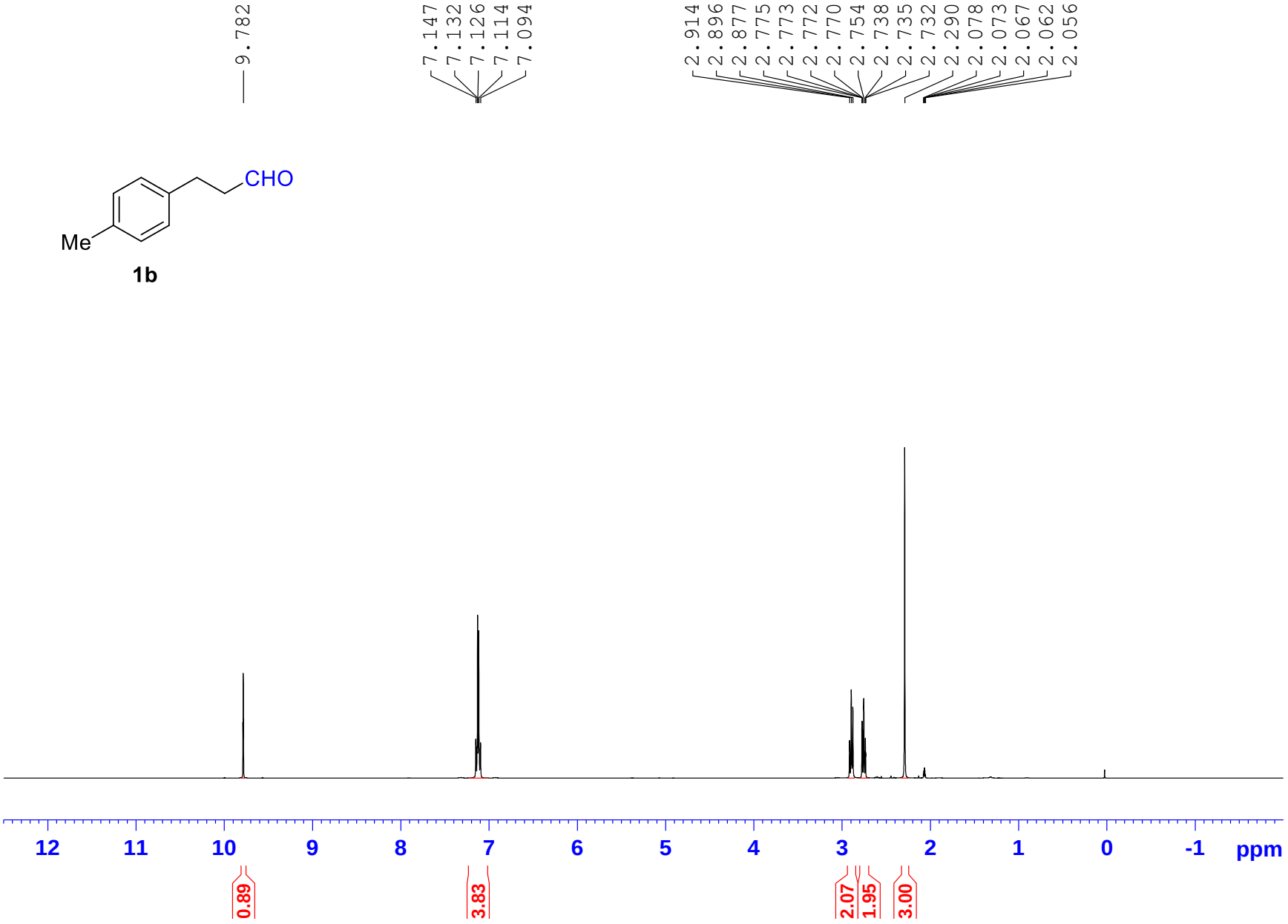
The above results of amine-enamine exchange experiments compliance with the previous report[26], where cyclic amine found to be more stable compare to acyclic amine. Overall cyclic amine (A7 and A8) are more nucleophilic and gave more stable enamine compare to acyclic amine (A) which effect the equilibrium between amine and enamine and might not give desired product (Table 1, entry 16).

General depiction regarding effect of steric hinderance on olefin migratory insertion step

Effect of steric hinderance in C-H insertion step



Under optimal reaction condition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7.126
7.114
7.094
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2.896
2.877
2.775
2.773
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2.770
2.754
2.738
2.735
2.732
2.290
2.078
2.073
2.067
2.062
2.056
CHO
Me
1b
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.89
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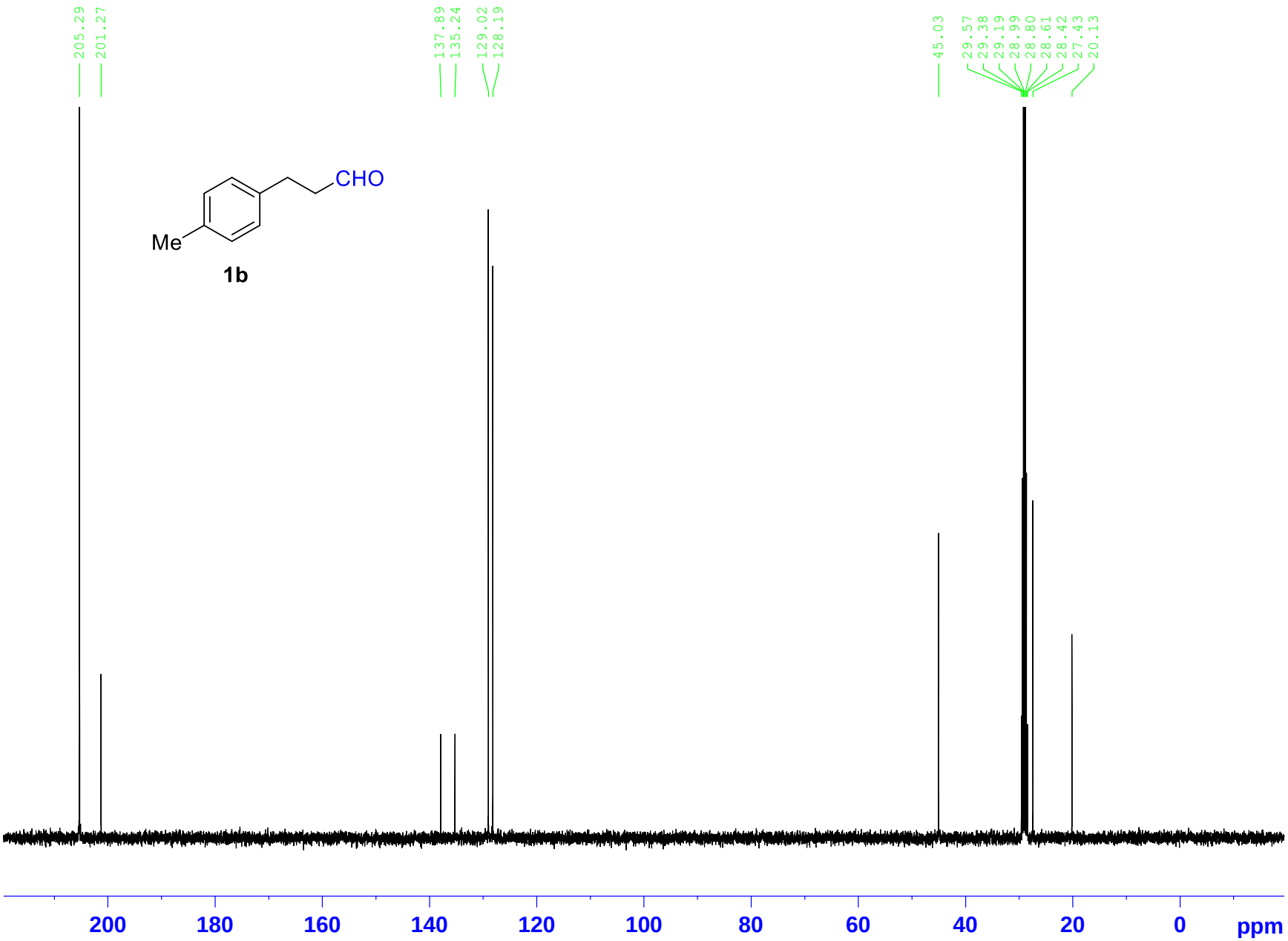
2.07
1.95
3.00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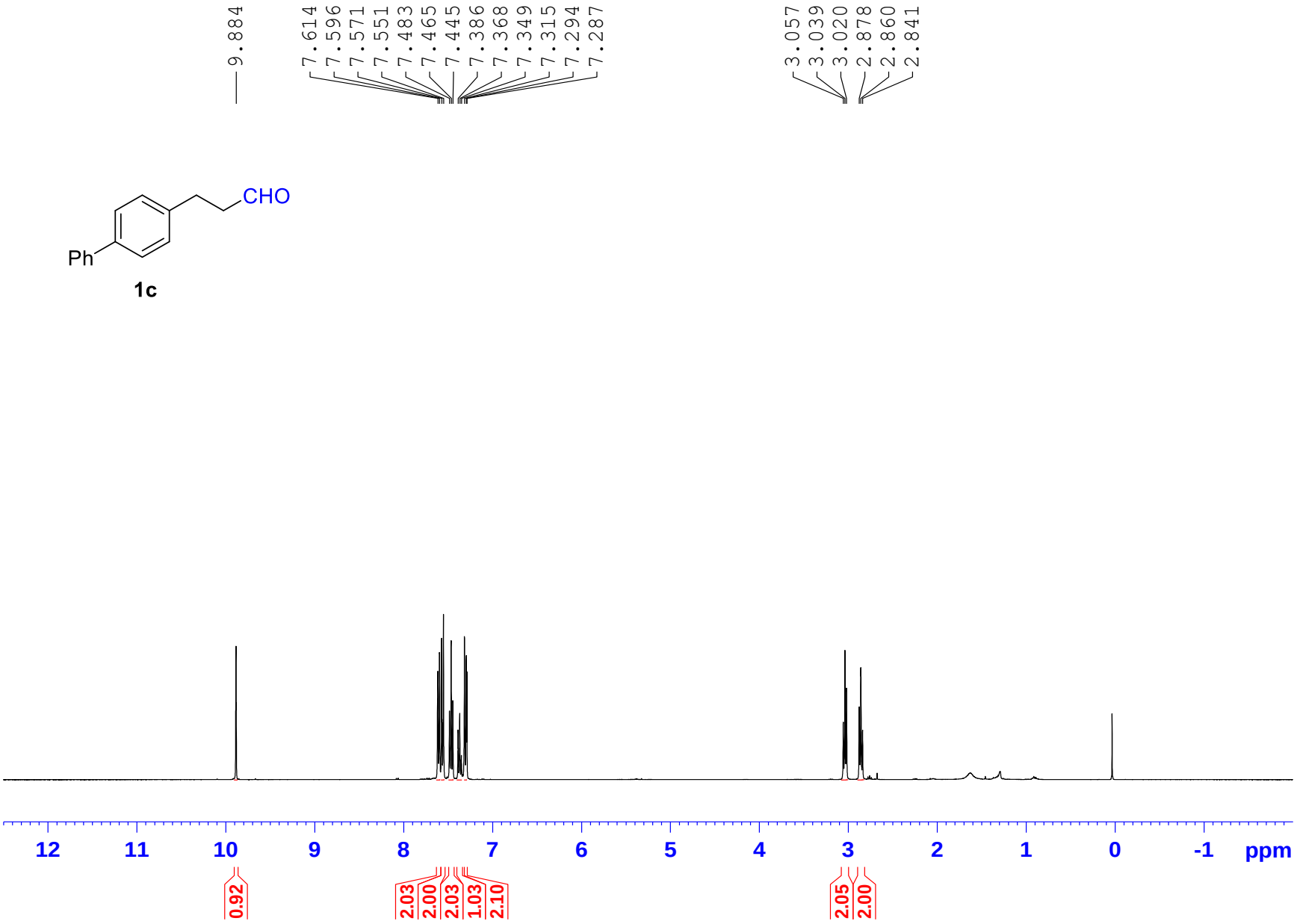
201.27
137.89
135.24
129.02
128.19
45.03
29.57
29.38
29.19
28.99
28.80
28.61
28.42
27.43
20.13
CHO
Me
1b
200
180
160
140
120
100
80
60
40
20
0
ppm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7.596
7.571
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7.483
7.465
7.445
7.386
7.368
7.349
7.315
7.294
7.287
3.057
3.039
3.020
2.878
2.860
2.841
CHO
Ph
1c
12
11
10
9
8
7
6
5
4
3
2
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-1
ppm
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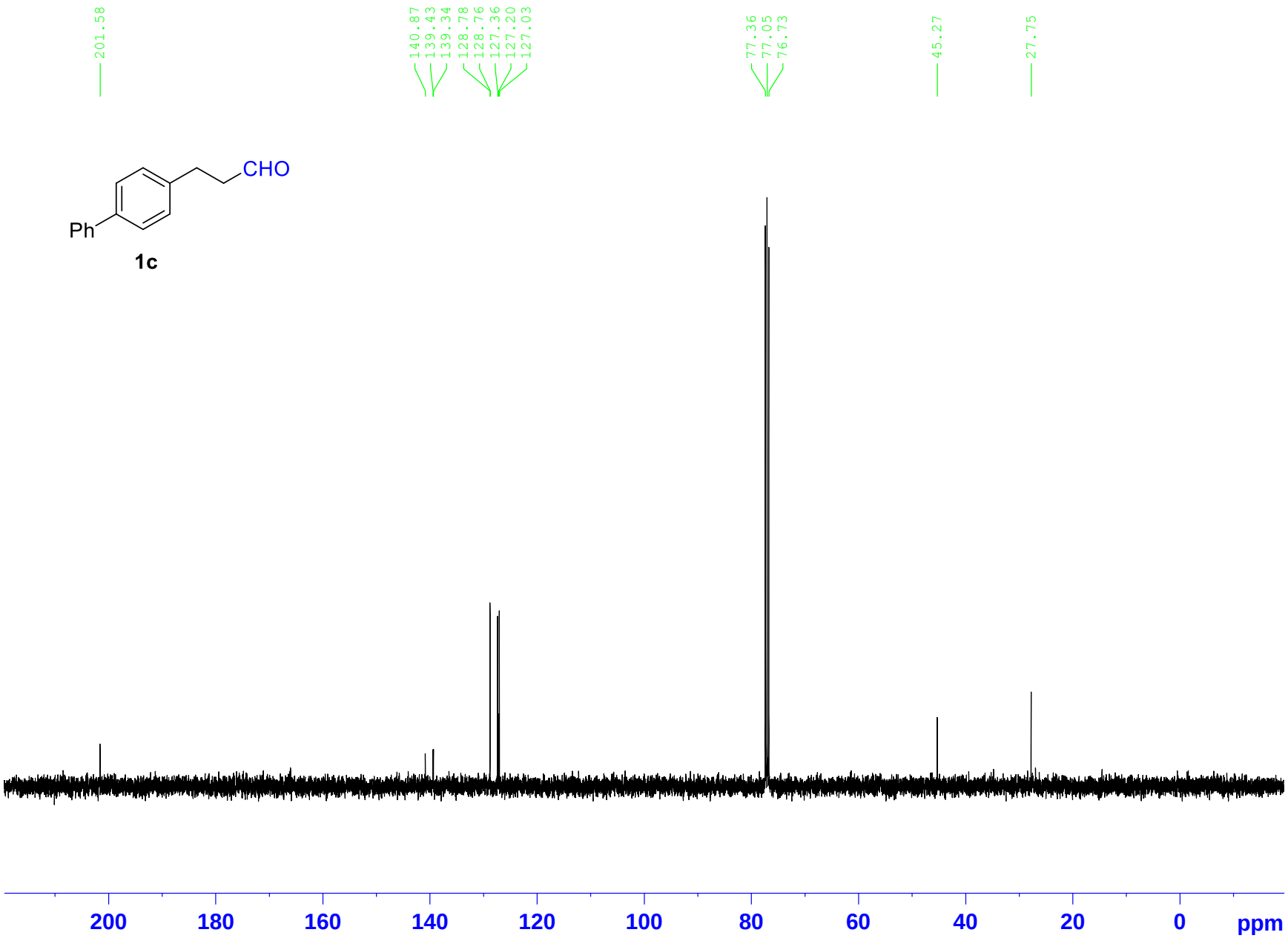
2.00
2.03
1.03
2.10
2.05
2.00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128.78
128.76
127.36
127.20
127.03
77.36
77.05
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45.27
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CHO
Ph
1c
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180
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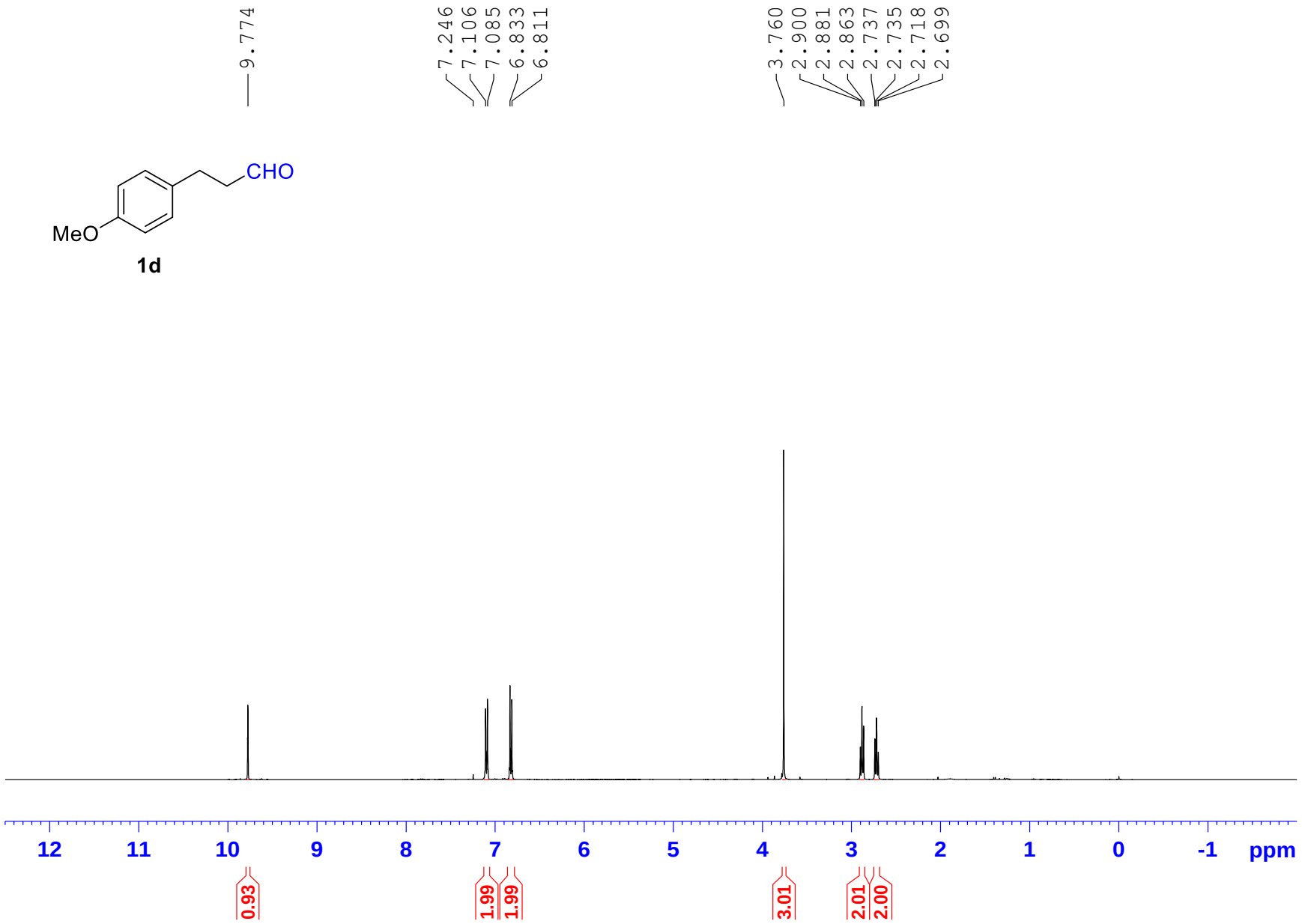
140
120
100
80
60
40
20
0
ppm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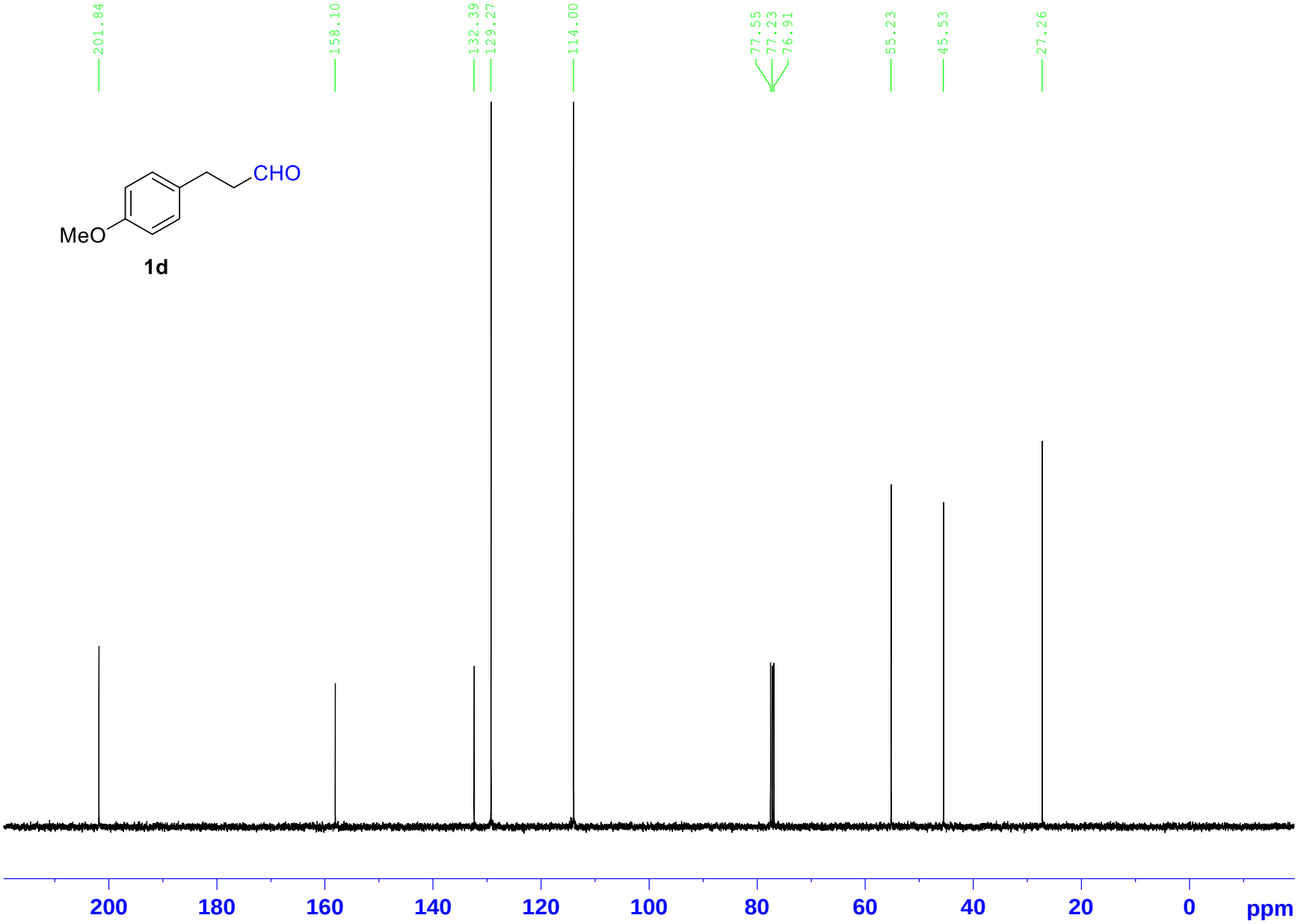
7.106
7.085
6.833
6.811
3.760
2.900
2.881
2.863
2.737
2.735
2.718
2.699
CHO
MeO
1d
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.93
1.99
1.99
3.01
2.01
2.00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129.27
114.00
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77.23
76.91
55.23
45.53
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MeO
1d
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140
120
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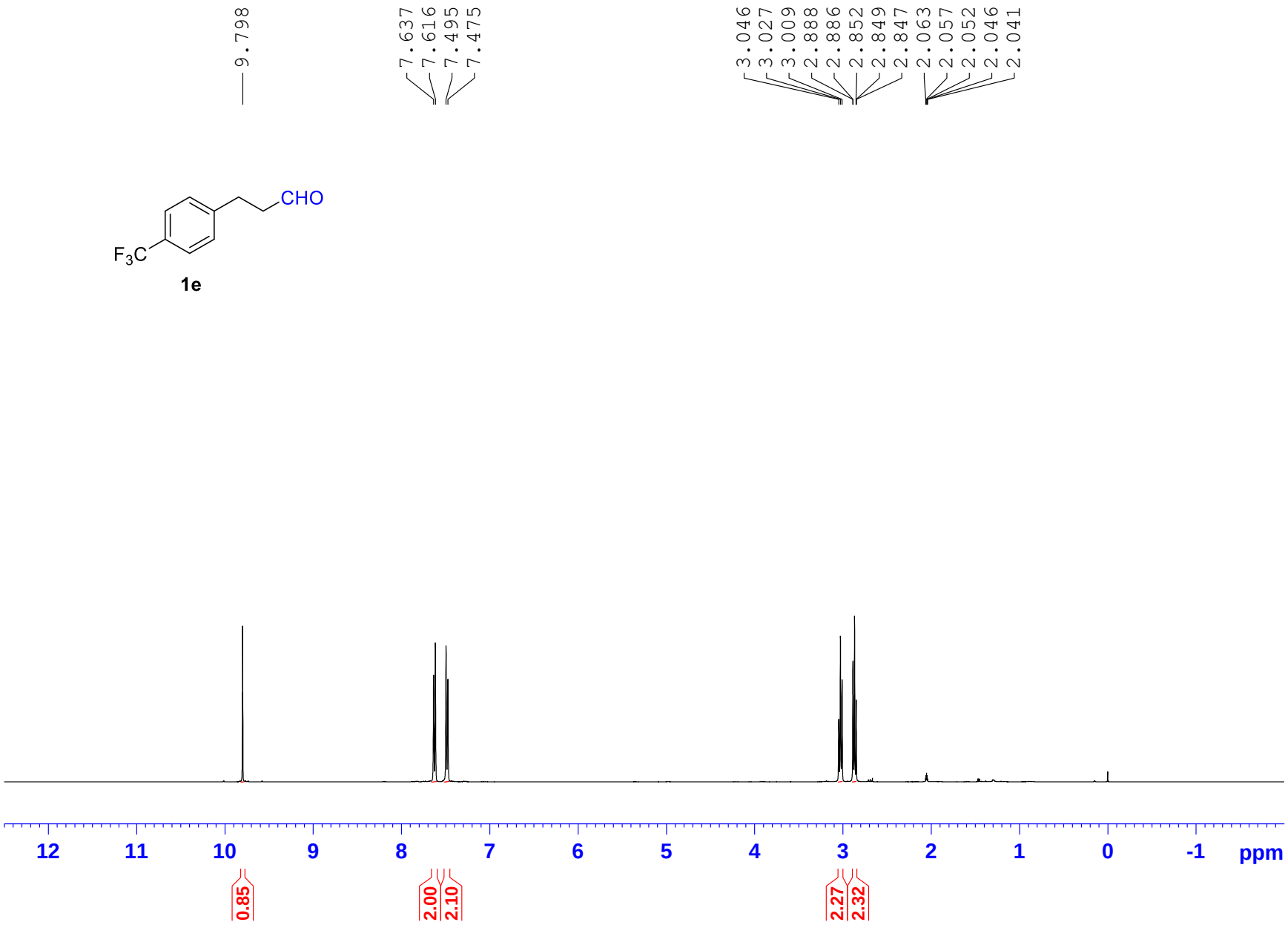
80
60
40
20
0
ppm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2.886
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2.847
2.063
2.057
2.052
2.046
2.041
CHO
F3C
1e
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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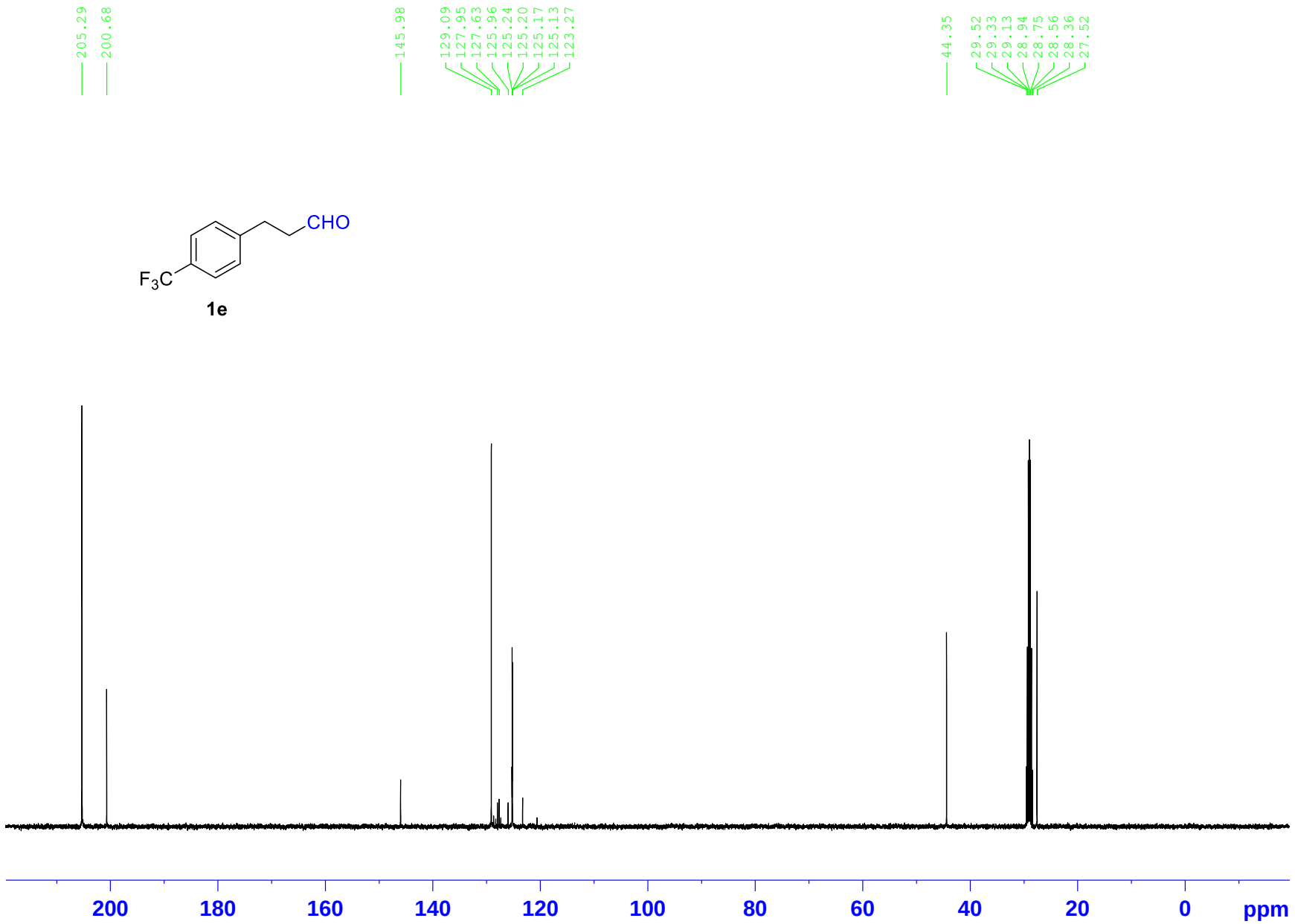
2.10
2.27
2.32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125.17
125.13
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29.52
29.33
29.13
28.94
28.75
28.56
28.36
27.52
CHO
F3C
1e
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160
140
120
100
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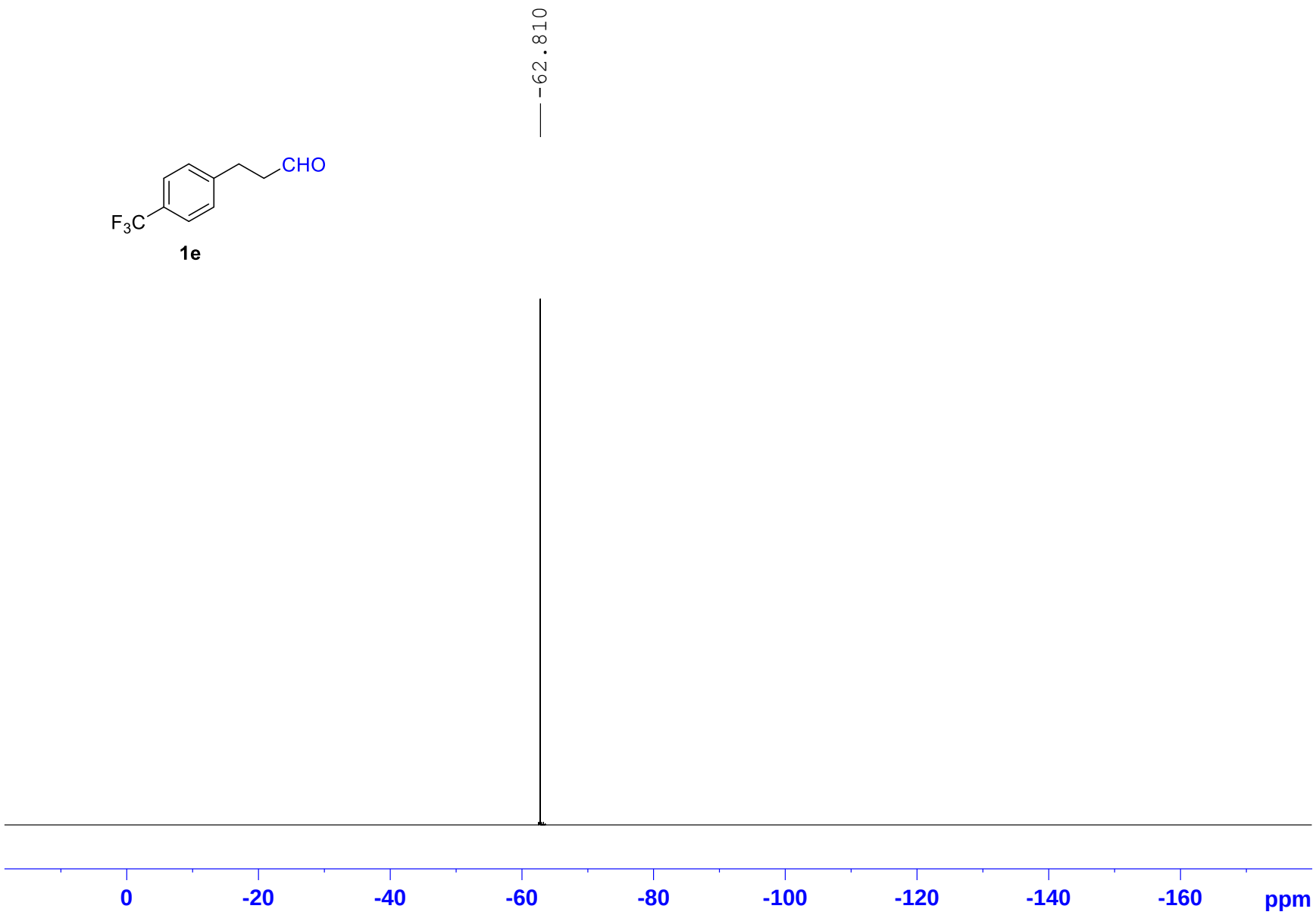
60
40
20
0
ppm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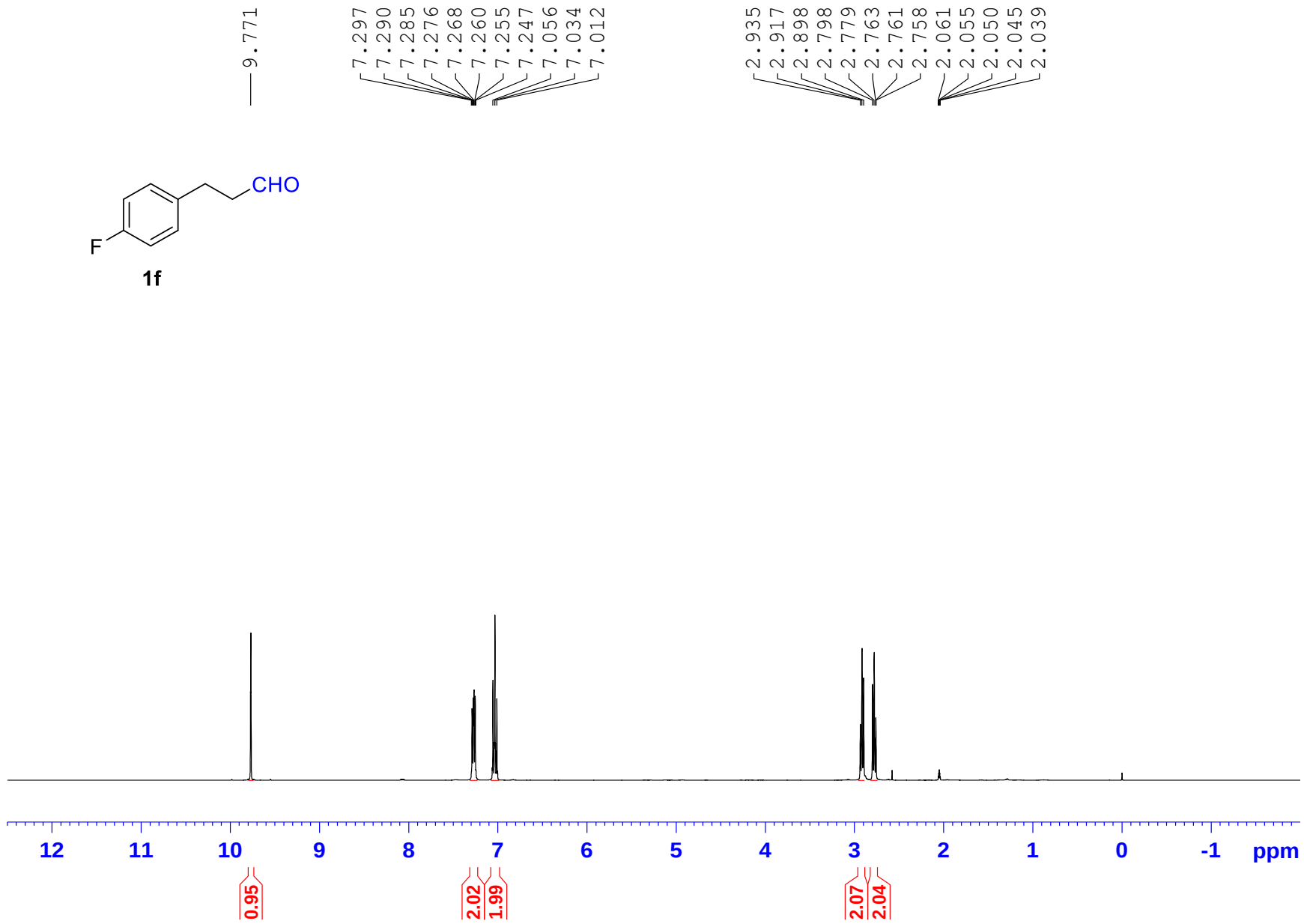
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2.039
CHO
F
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11
10
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8
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5
4
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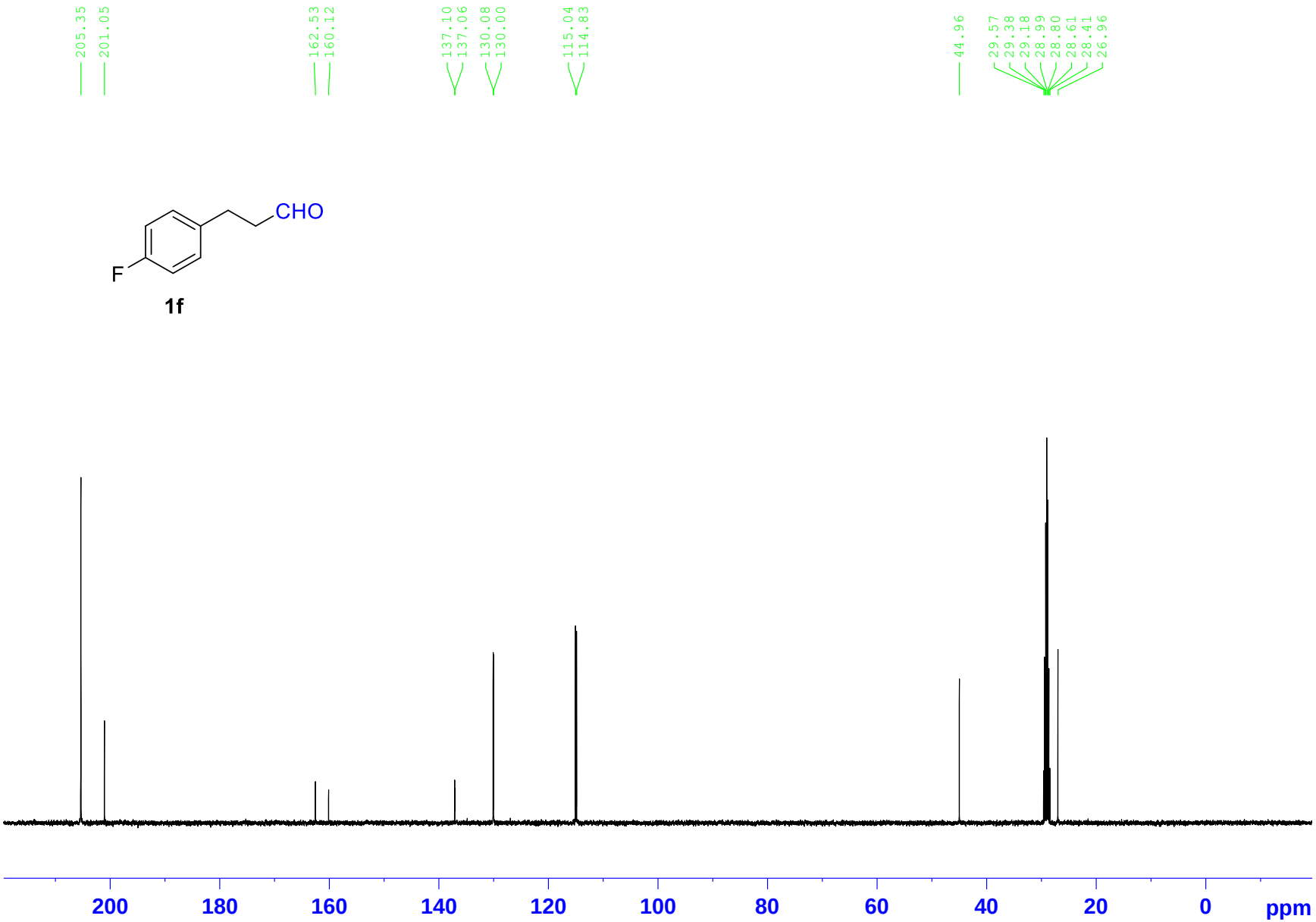
2.07
2.04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130.00
115.04
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29.18
28.99
28.80
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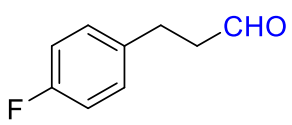

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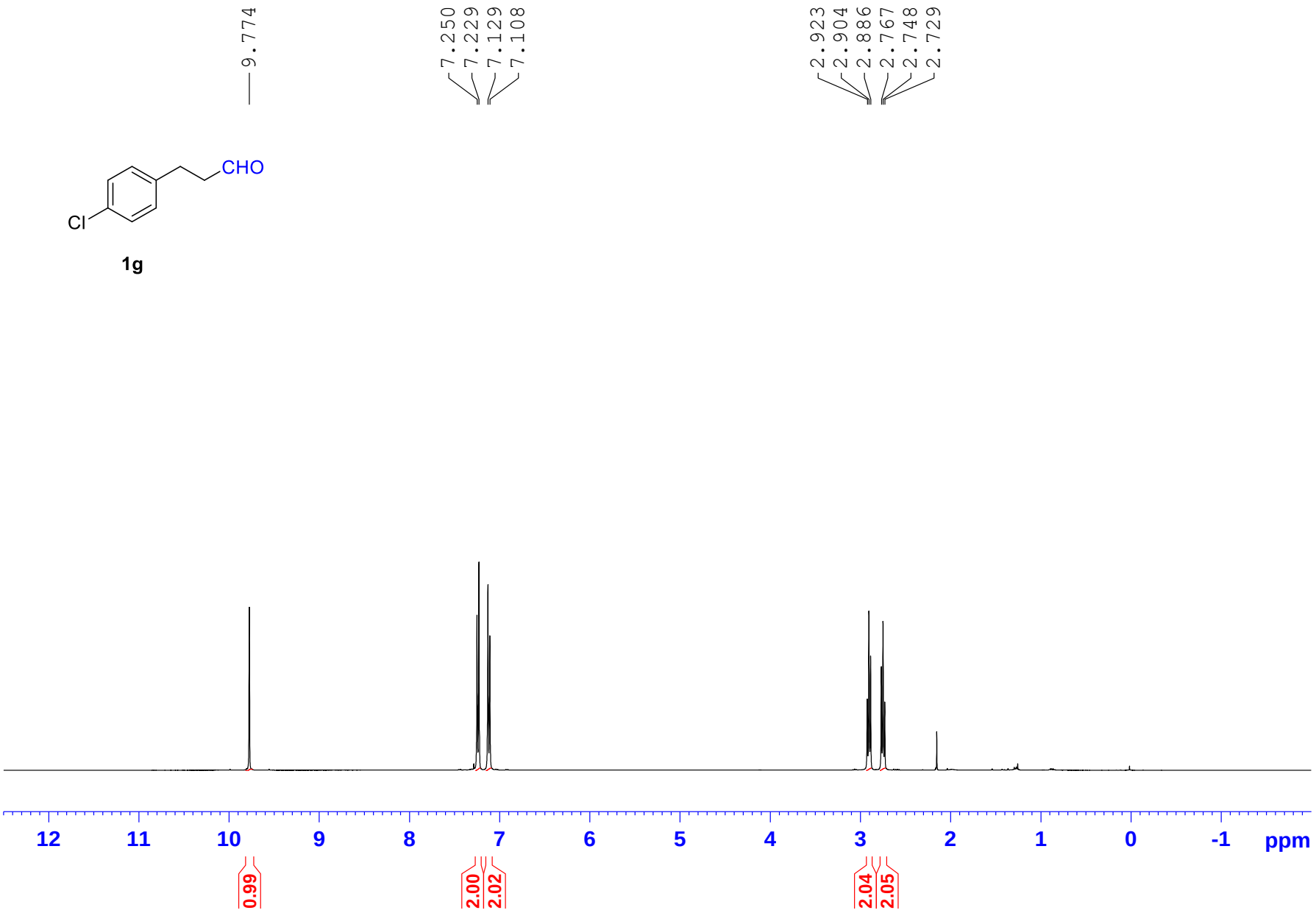
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Cl
1g
12
11
10
9
8
7
6
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4
3
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1
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ppm
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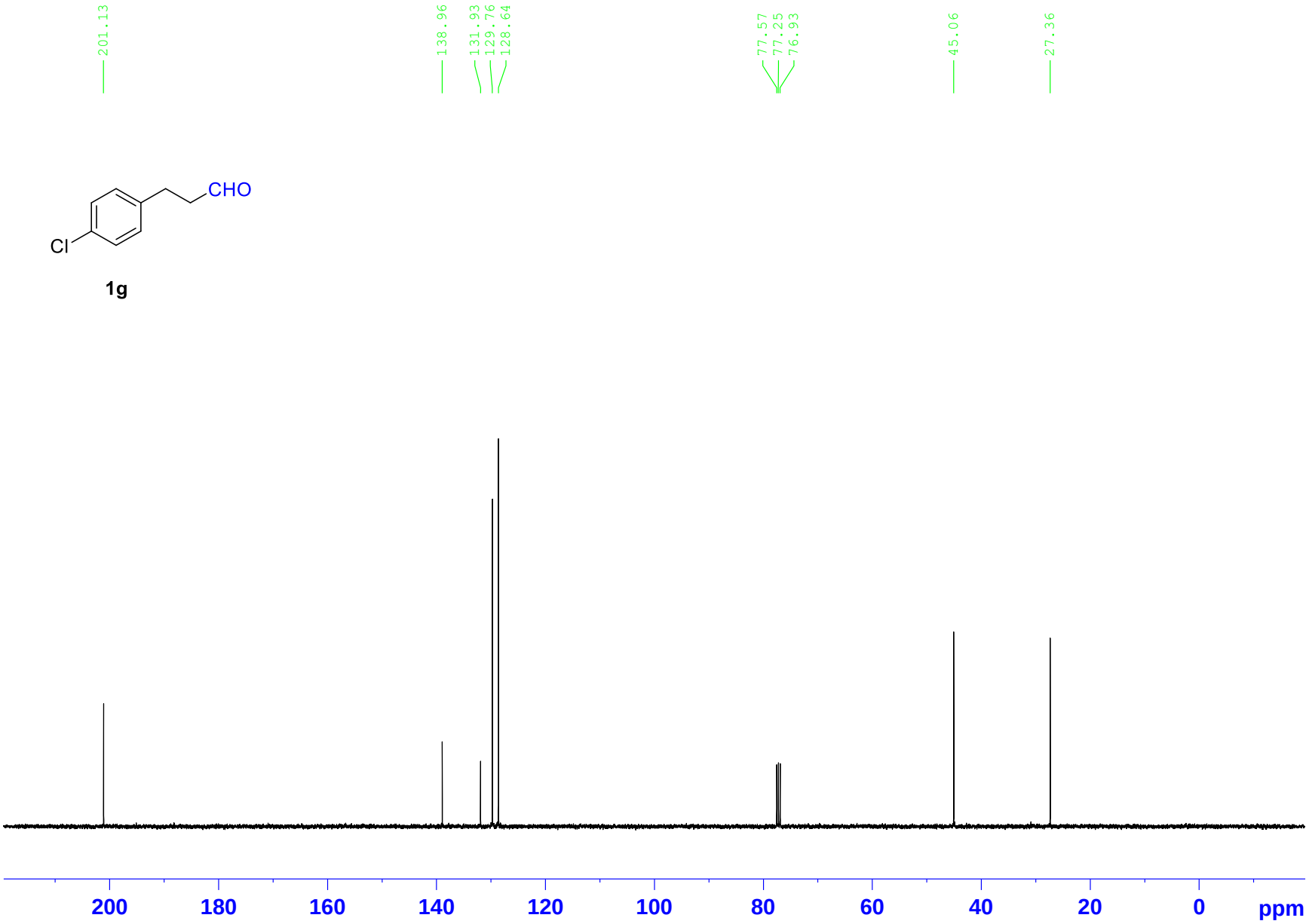
2.02
2.04
2.05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20
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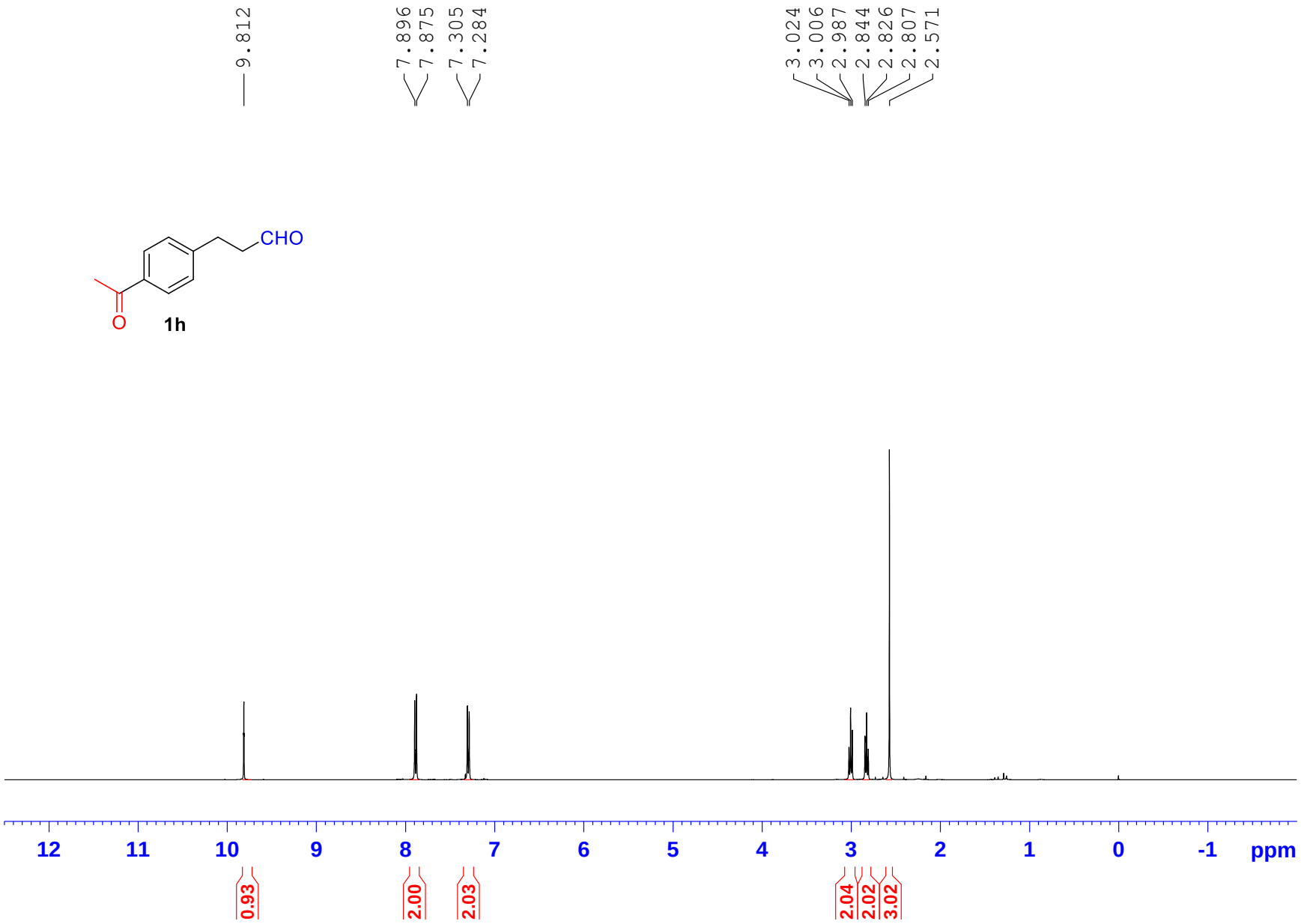
ppm

1g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CHO
O
1h
12
11
10
9
8
7
6
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2
1
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ppm
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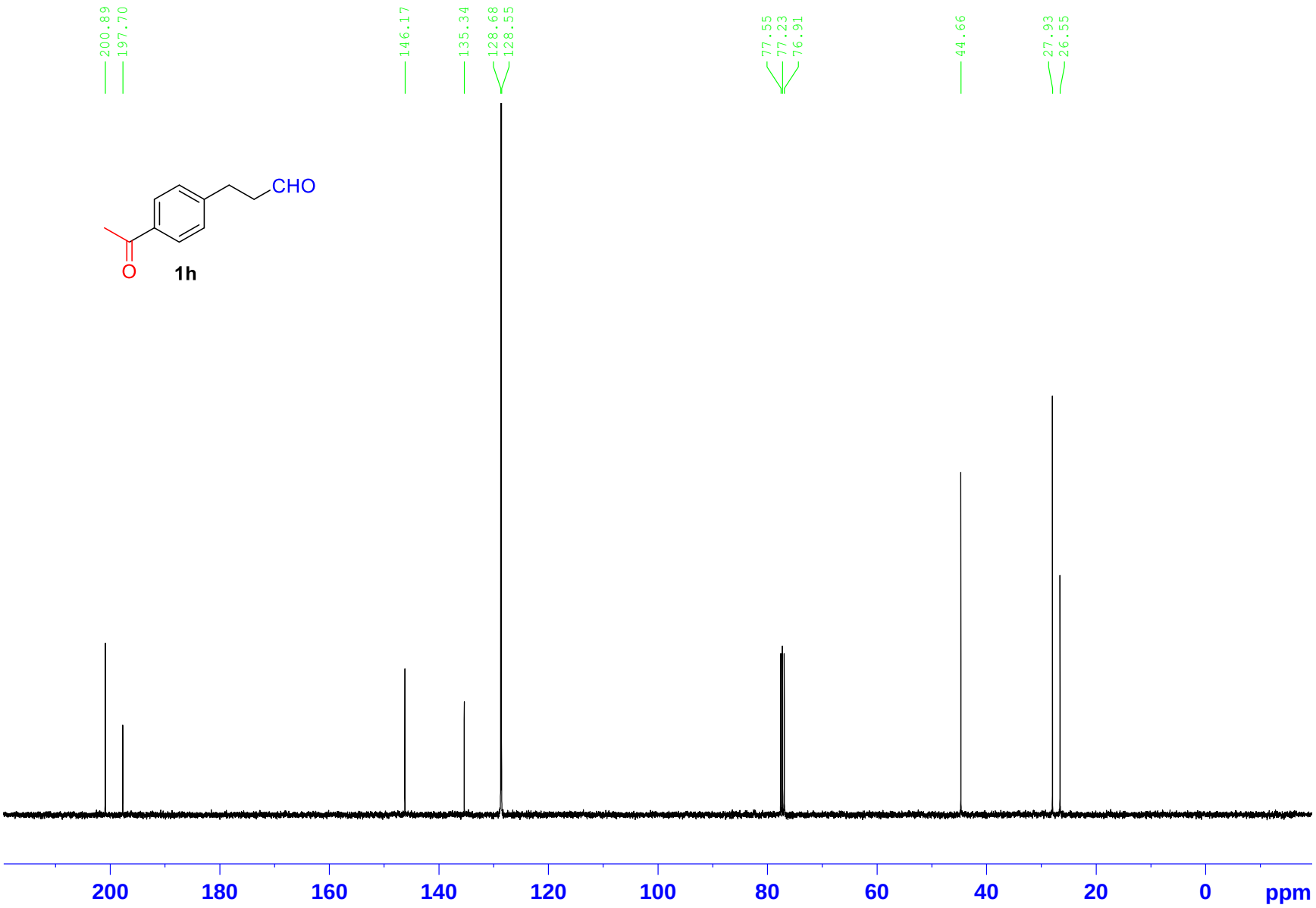
2.04
2.02
3.02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O
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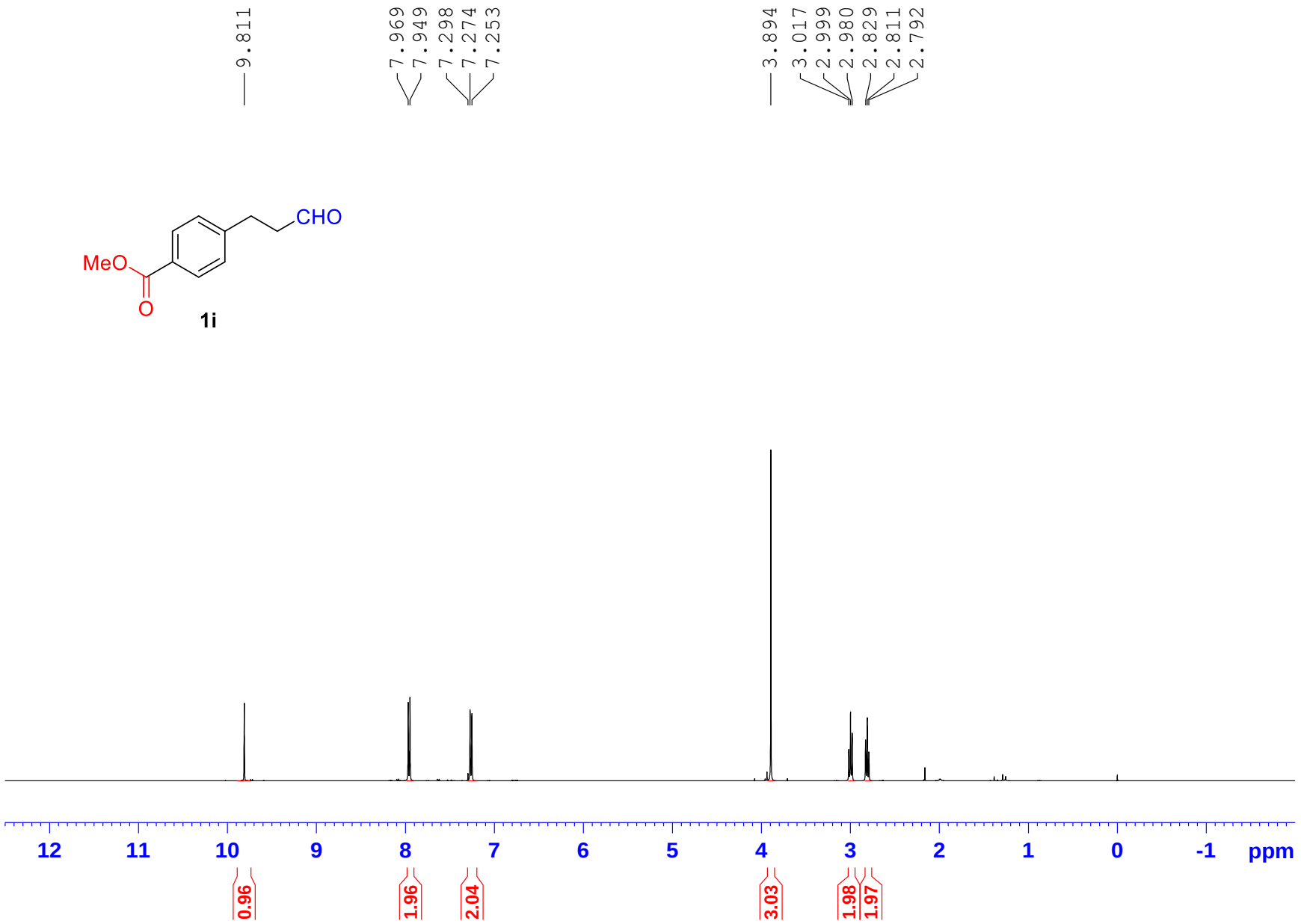
120
100
80
60
40
20
0
ppm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2.792
CHO
MeO
O
1i
12
11
10
9
8
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6
5
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2
1
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-1
ppm
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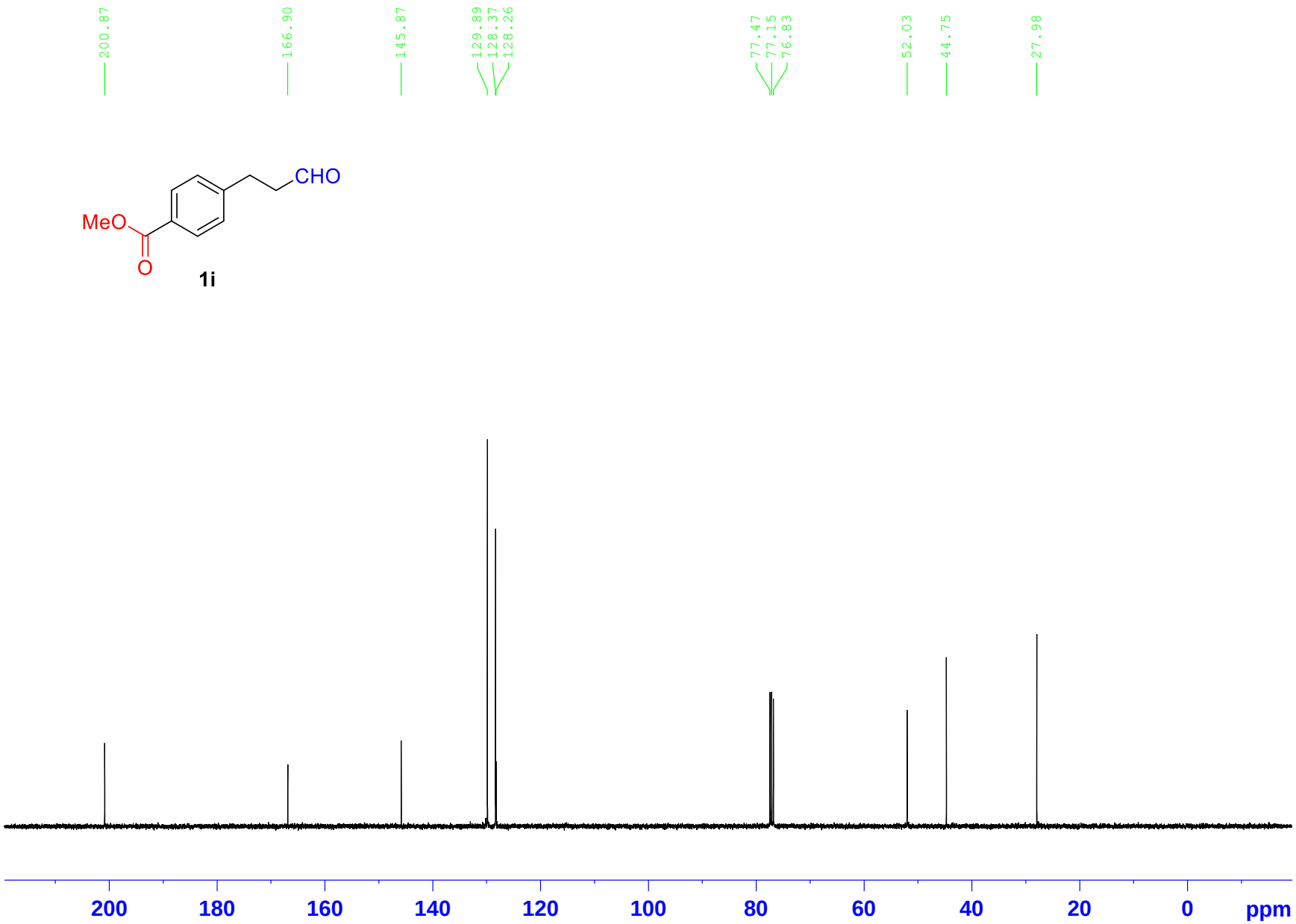
1.97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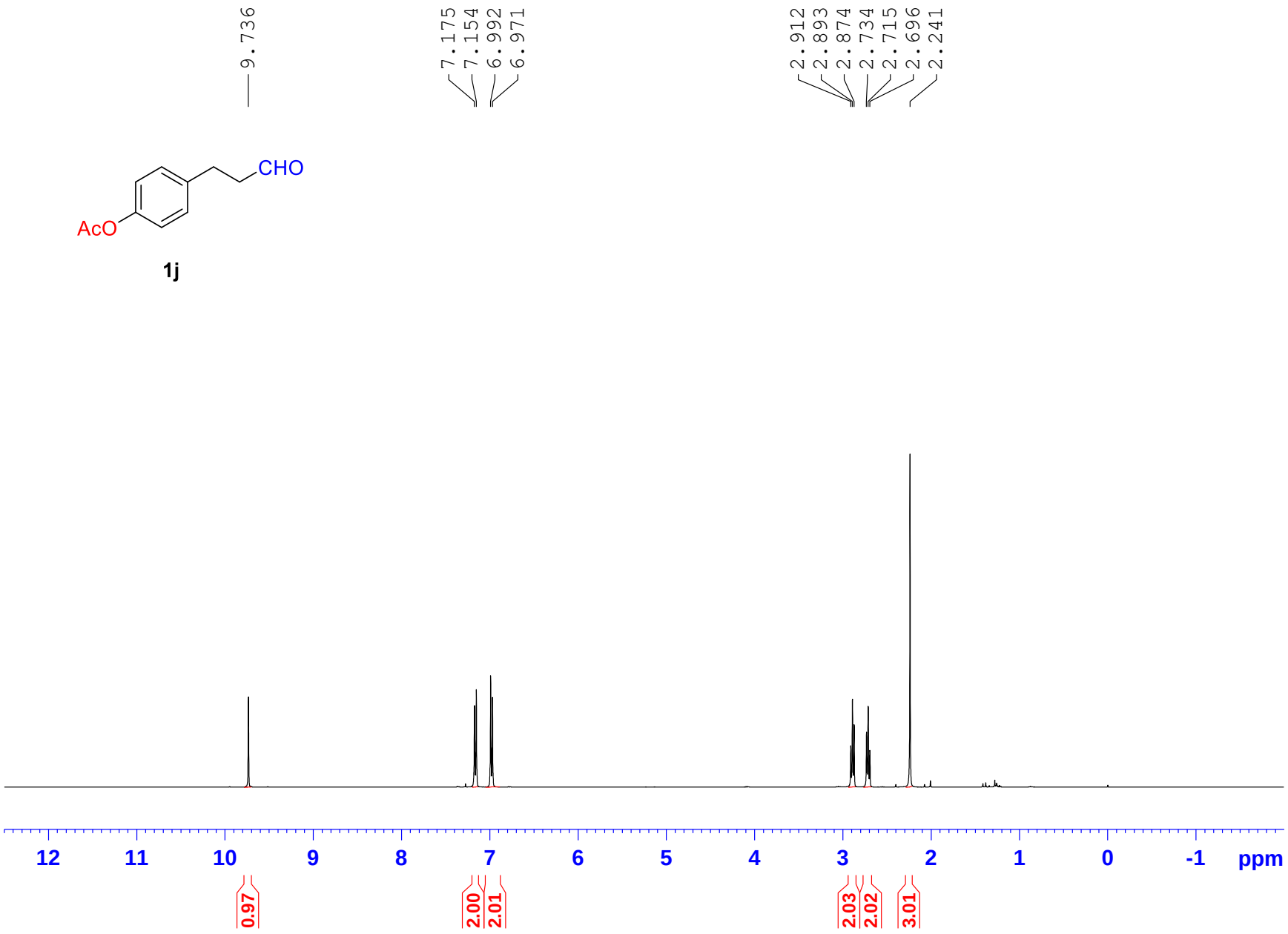
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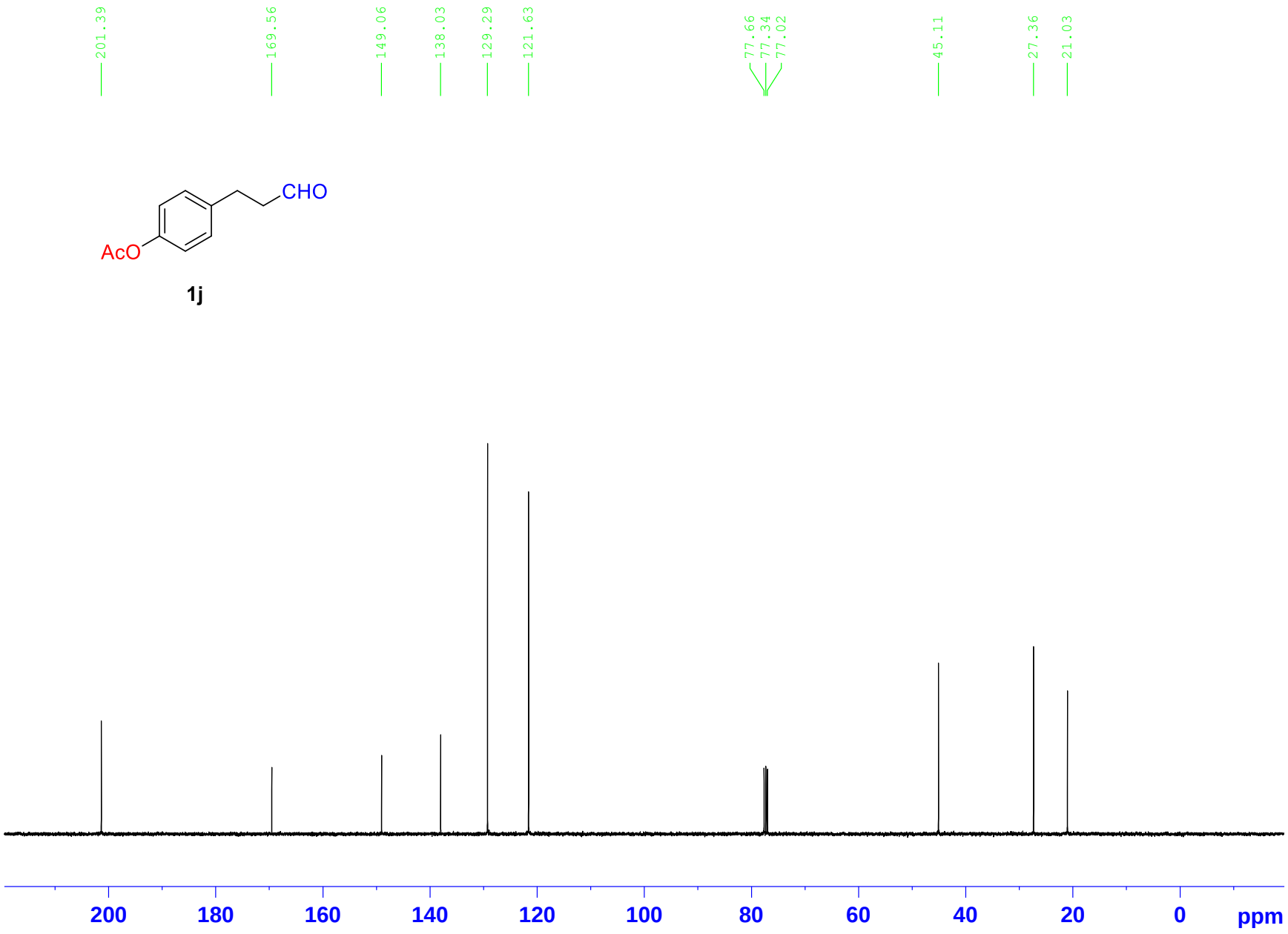
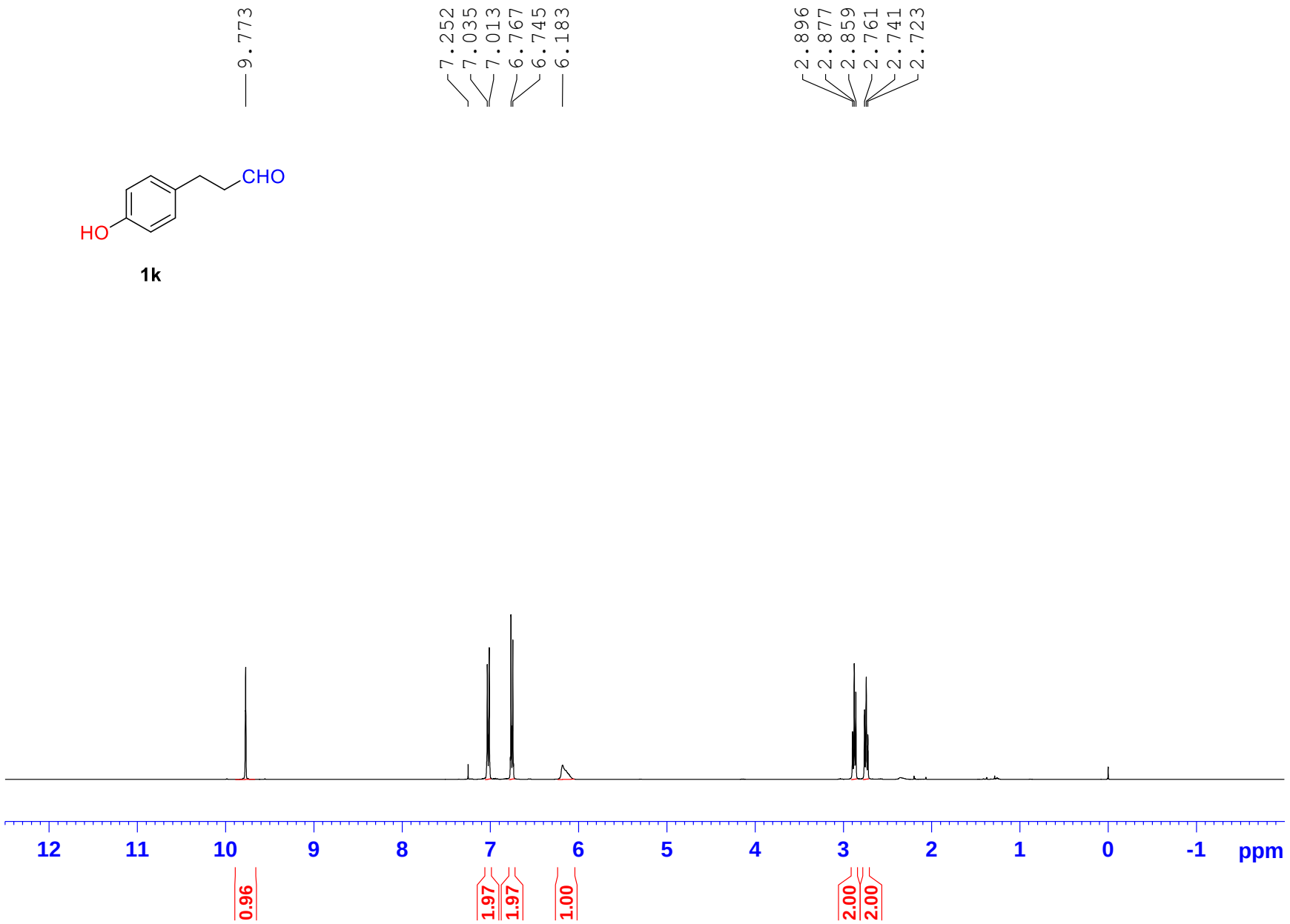
2.696
2.241
CHO
AcO
1j
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
2.00
2.01
2.03
2.02
3.01


201.39
169.56
149.06
138.03
129.29
121.63
77.66
77.34
77.02
45.11
27.36
21.03
CHO
AcO
200
180
160
140
120
100
80
60
40
20
0
ppm

1j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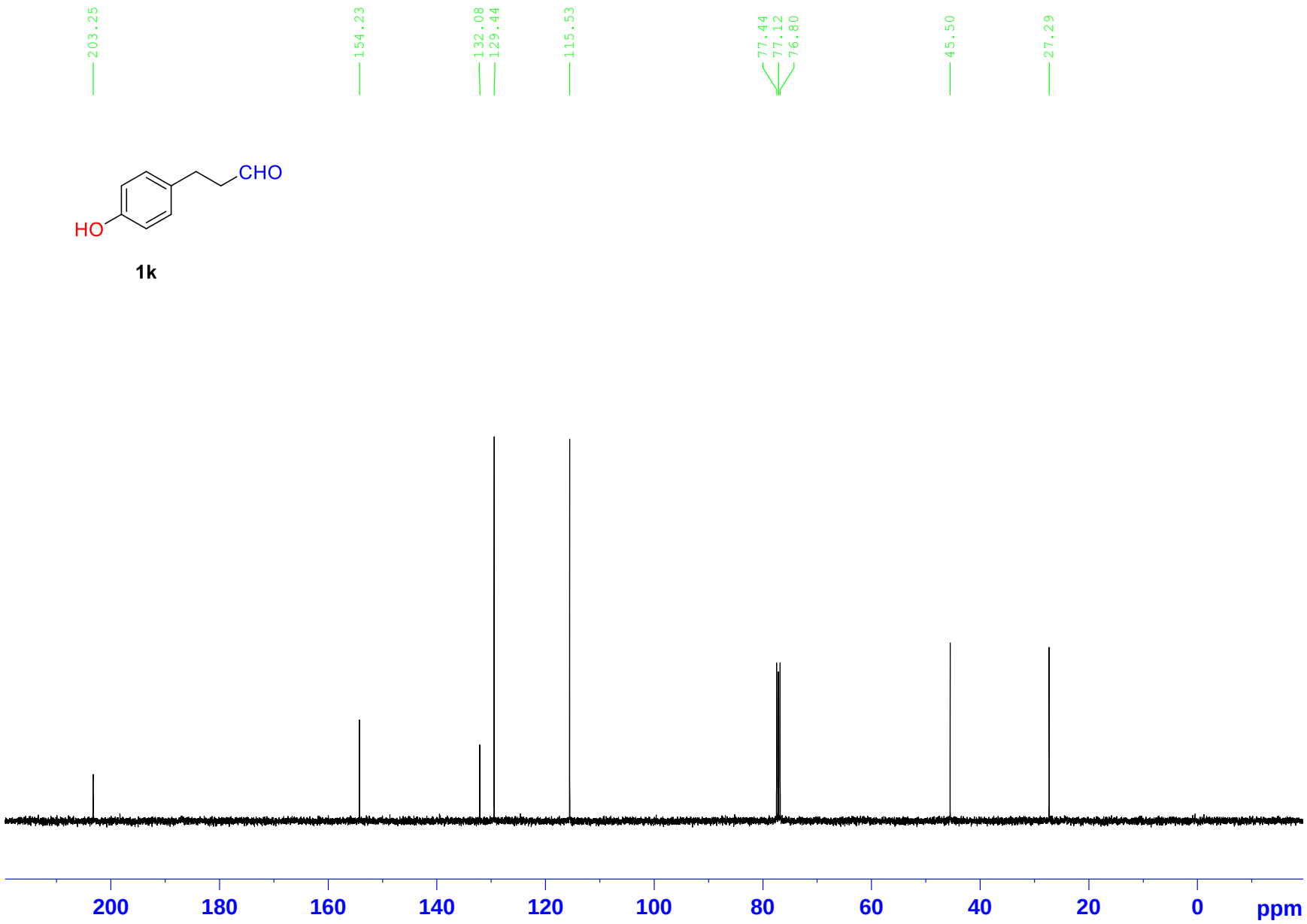
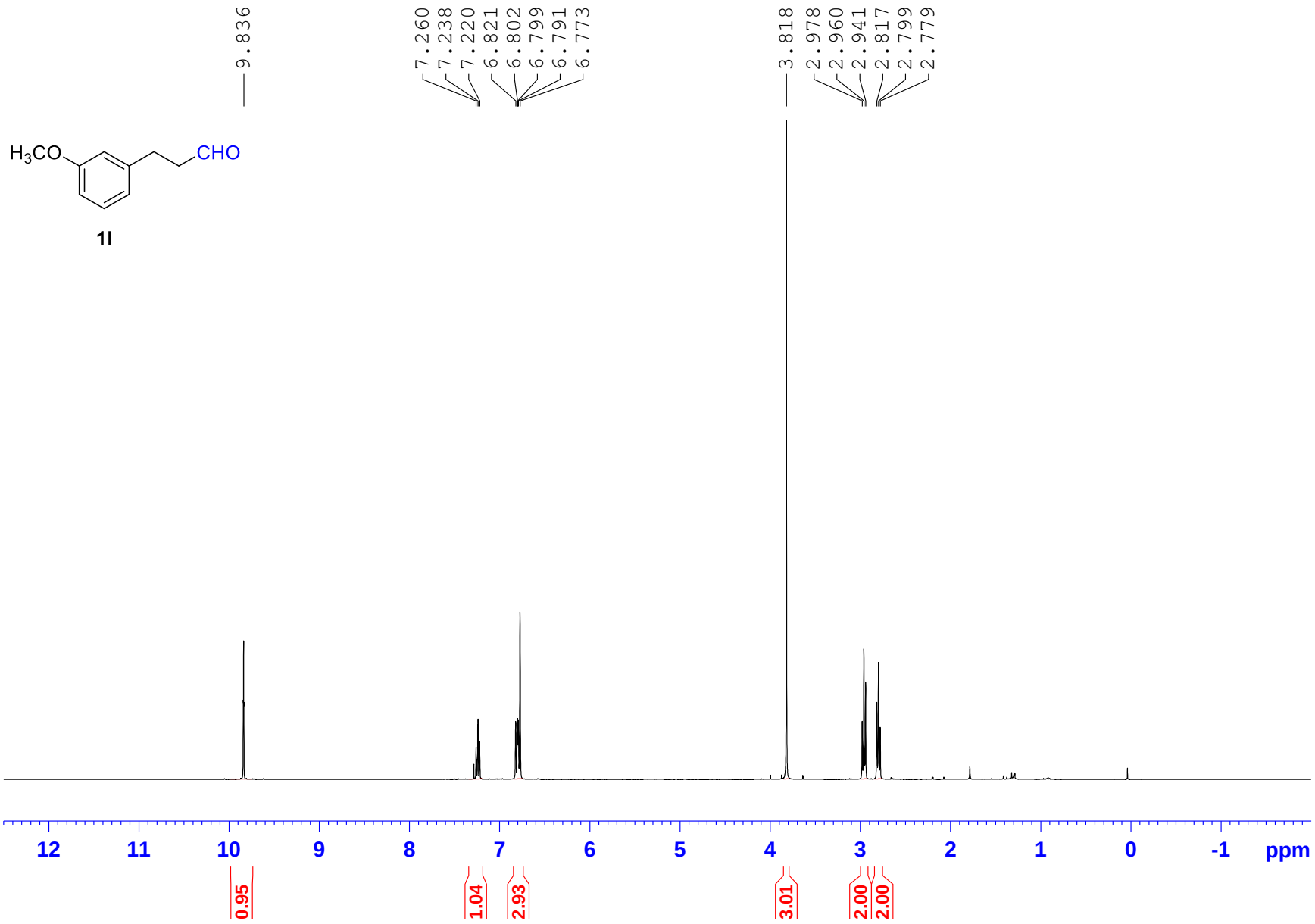
7.252
7.035
7.013
6.767
6.745
6.183
2.896
2.877
2.859
2.761
2.741
2.723
CHO
HO
1k
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.96
1.97
1.97
1.00
2.00
2.00


203.25
154.23
132.08
129.44
115.53
77.44
77.12
76.80
45.50
27.29
CHO
HO
1k
200
180
160
140
120
100
80
60
40
20
0
ppm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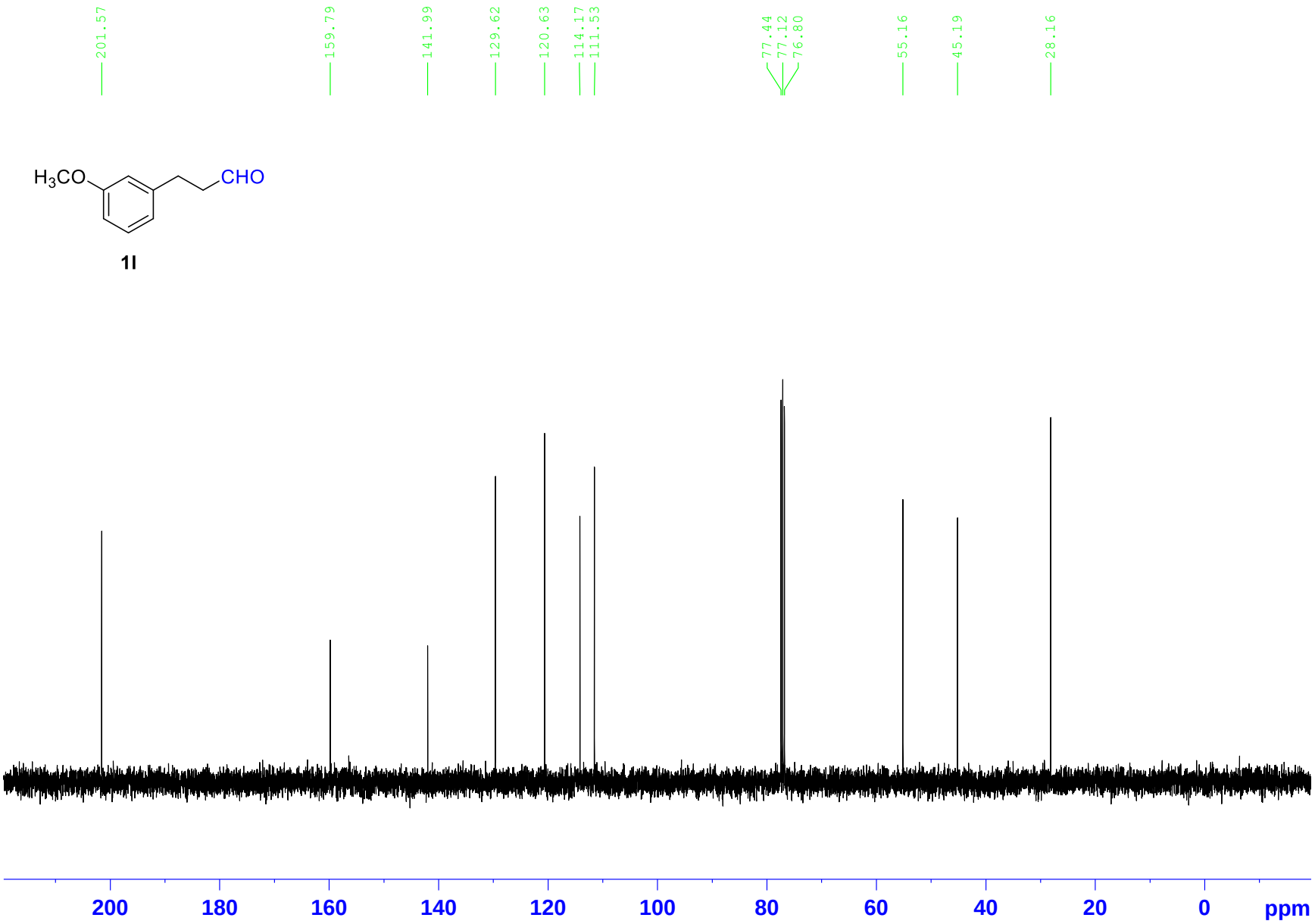
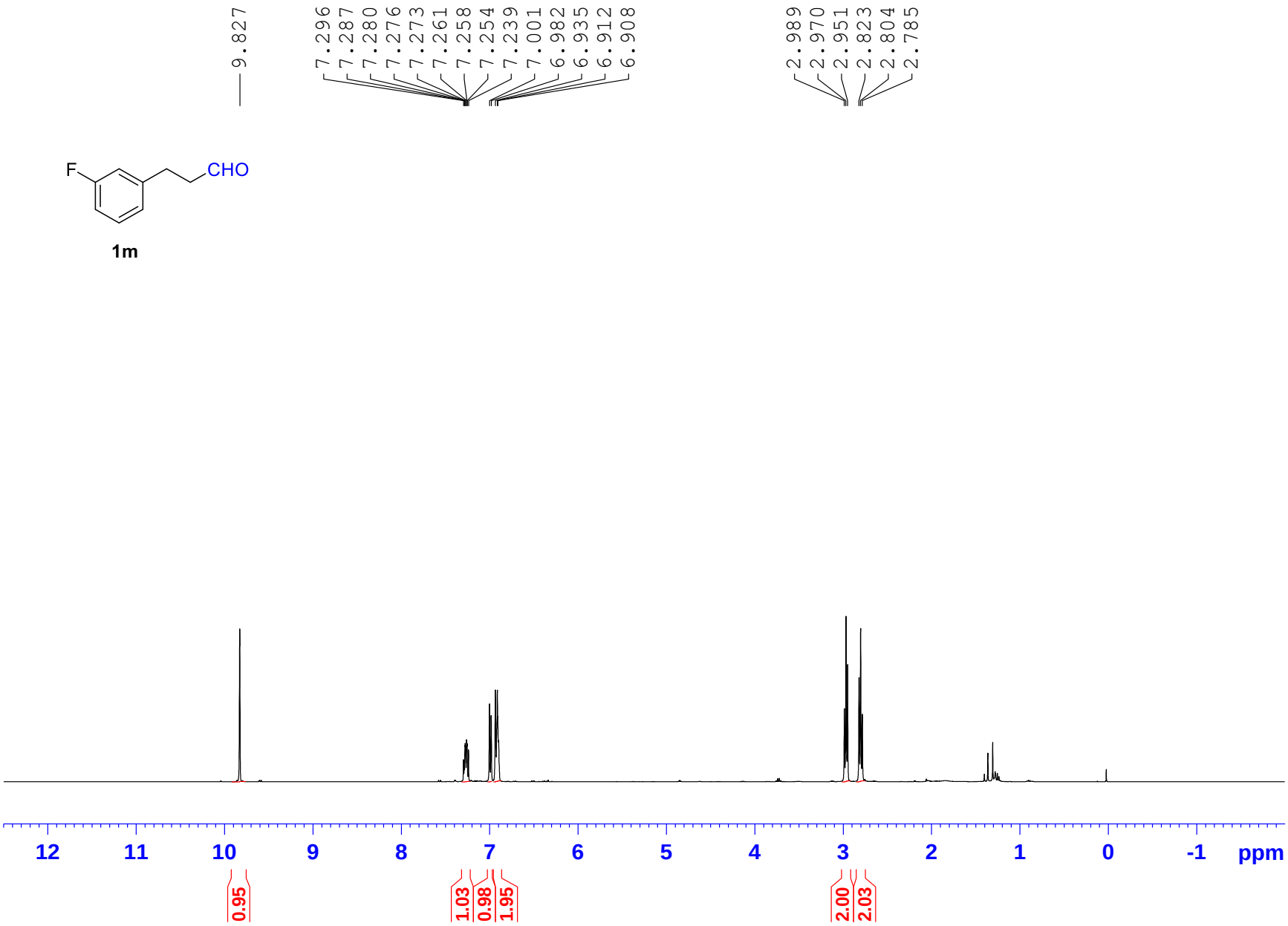
7.260
7.238
7.220
6.821
6.802
6.799
6.791
6.773
3.818
2.978
2.960
2.941
2.817
2.799
2.779
H3CO
CHO
1l
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
1.04
2.93
3.01
2.00
2.00


201.57
159.79
141.99
129.62
120.63
114.17
111.53
77.44
77.12
76.80
55.16
45.19
28.16
H3CO
CHO
200
180
160
140
120
100
80
60
40
20
0
ppm

1l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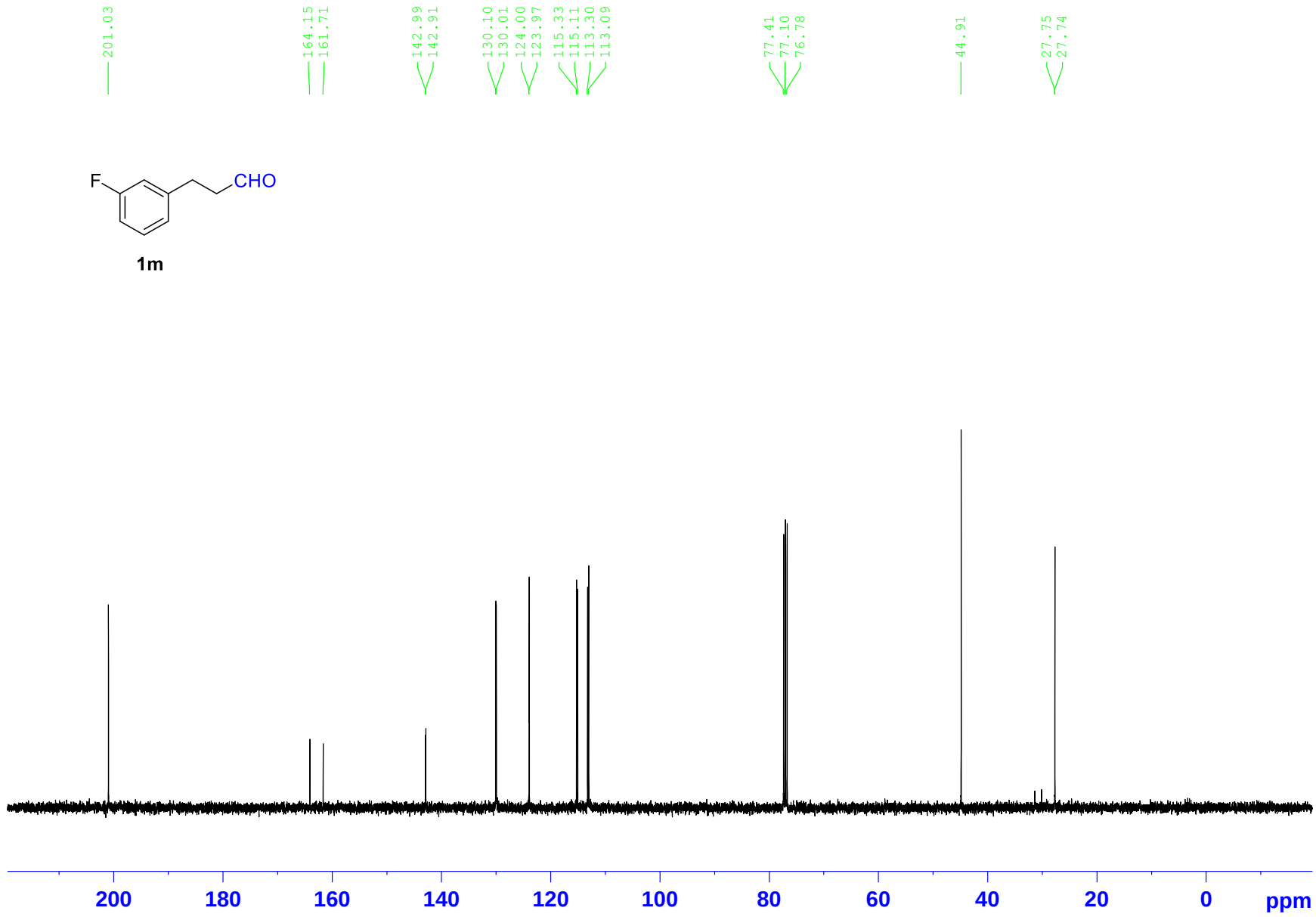
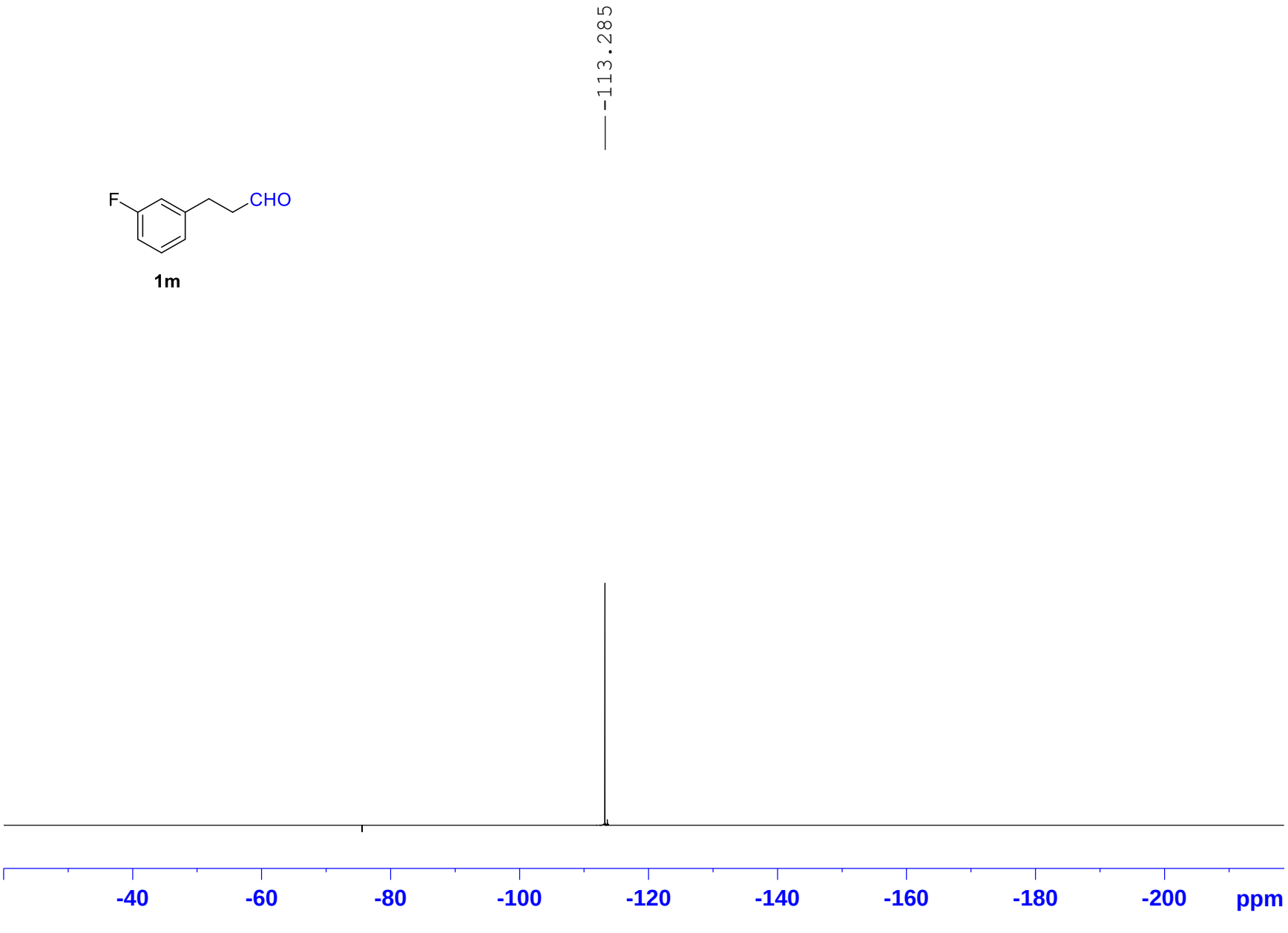
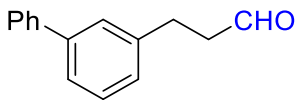
7.296
7.287
7.280
7.276
7.273
7.261
7.258
7.254
7.239
7.001
6.982
6.935
6.912
6.908
2.989
2.970
2.951
2.823
2.804
2.785
F
CHO
1m
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
1.03
0.98
1.95
2.00
2.03


201.03
164.15
161.71
142.99
142.91
130.10
130.01
124.00
123.97
115.33
115.11
113.30
113.09
77.41
77.10
76.78
44.91
27.75
27.74
F
CHO
1m
200
180
160
140
120
100
80
60
40
20
0
ppm

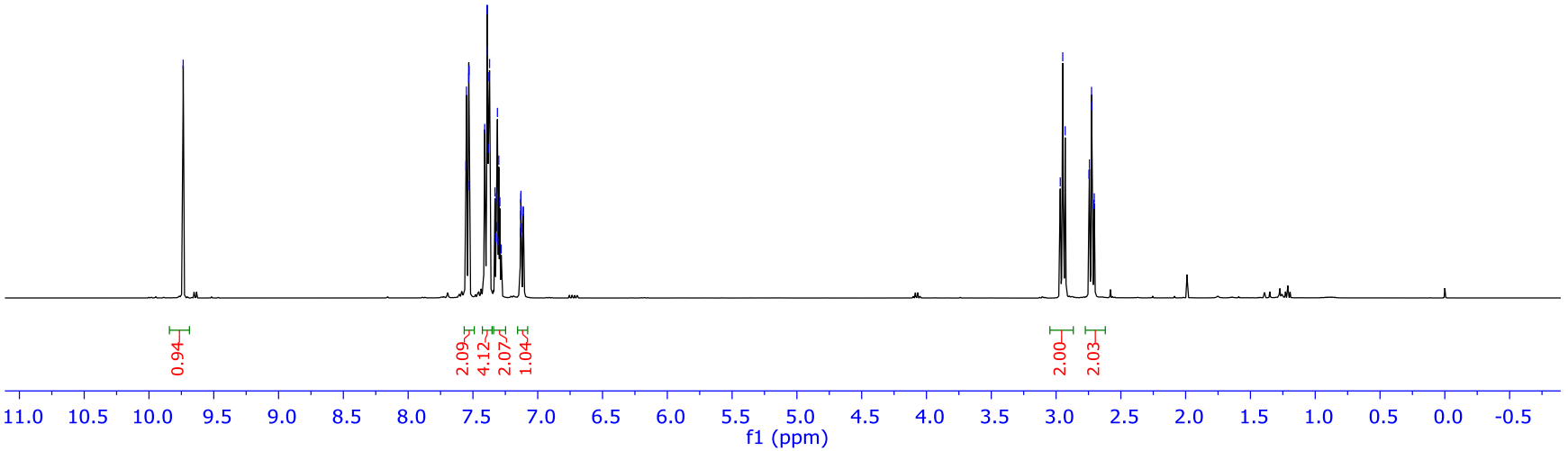

-113.285
F
CHO
1m
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

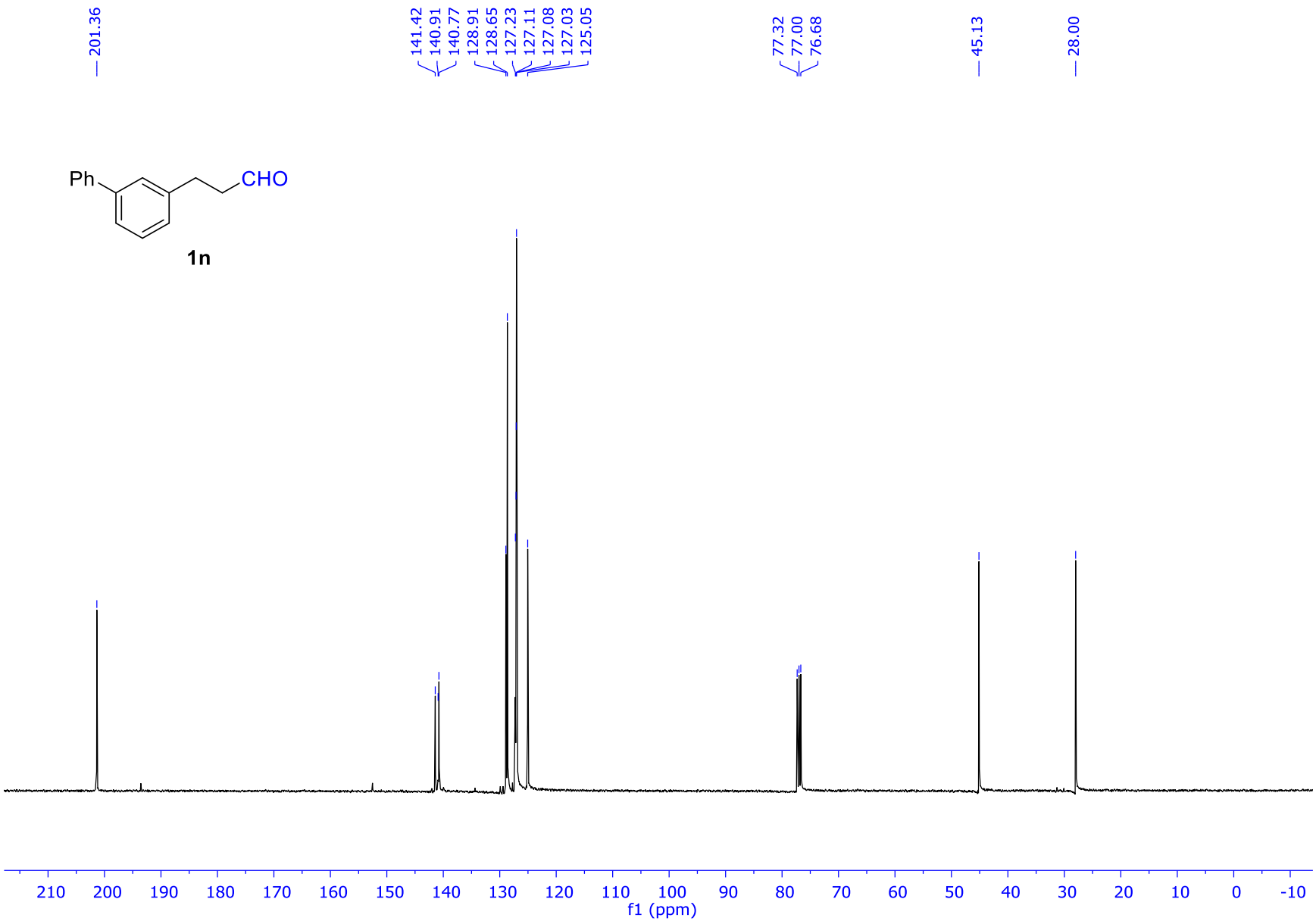

9.74
7.55
7.55
7.54
7.53
7.53
7.41
7.39
7.39
7.38
7.38
7.37
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.13
7.13
7.13
7.13
7.13
7.11
7.11

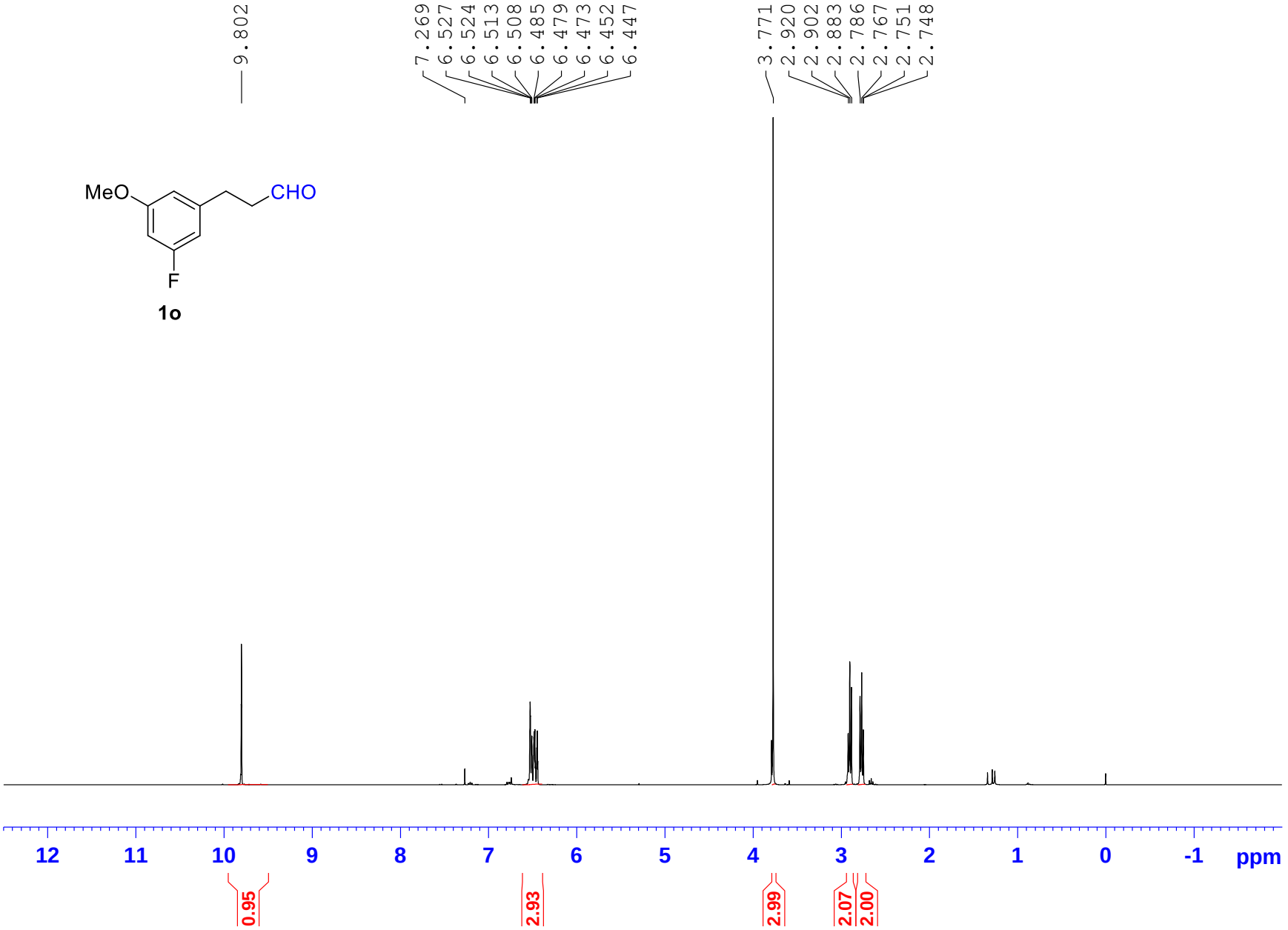

2.97
2.95
2.93
2.75
2.74
2.73
2.72
2.71
2.70

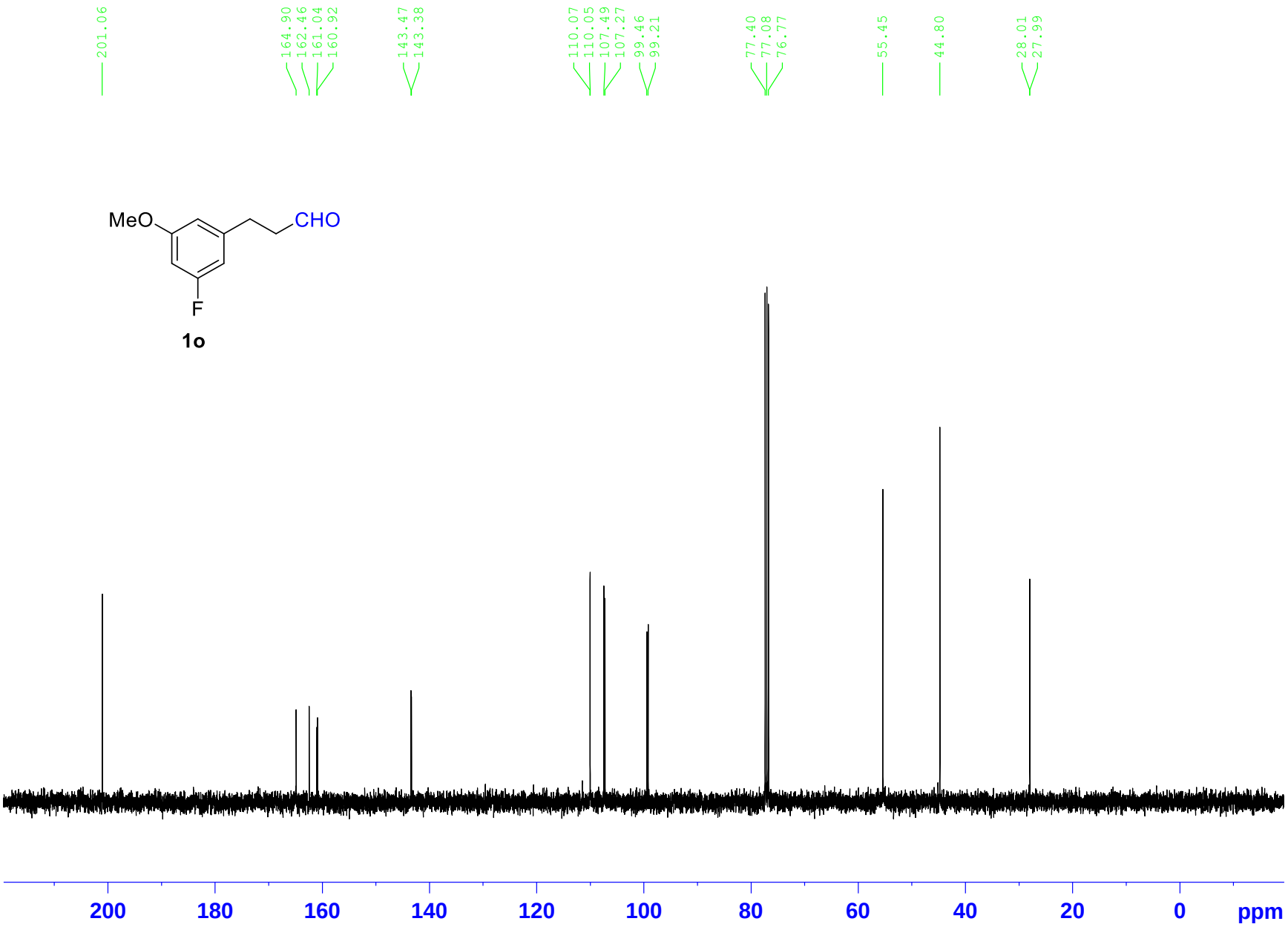

Ph
CHO

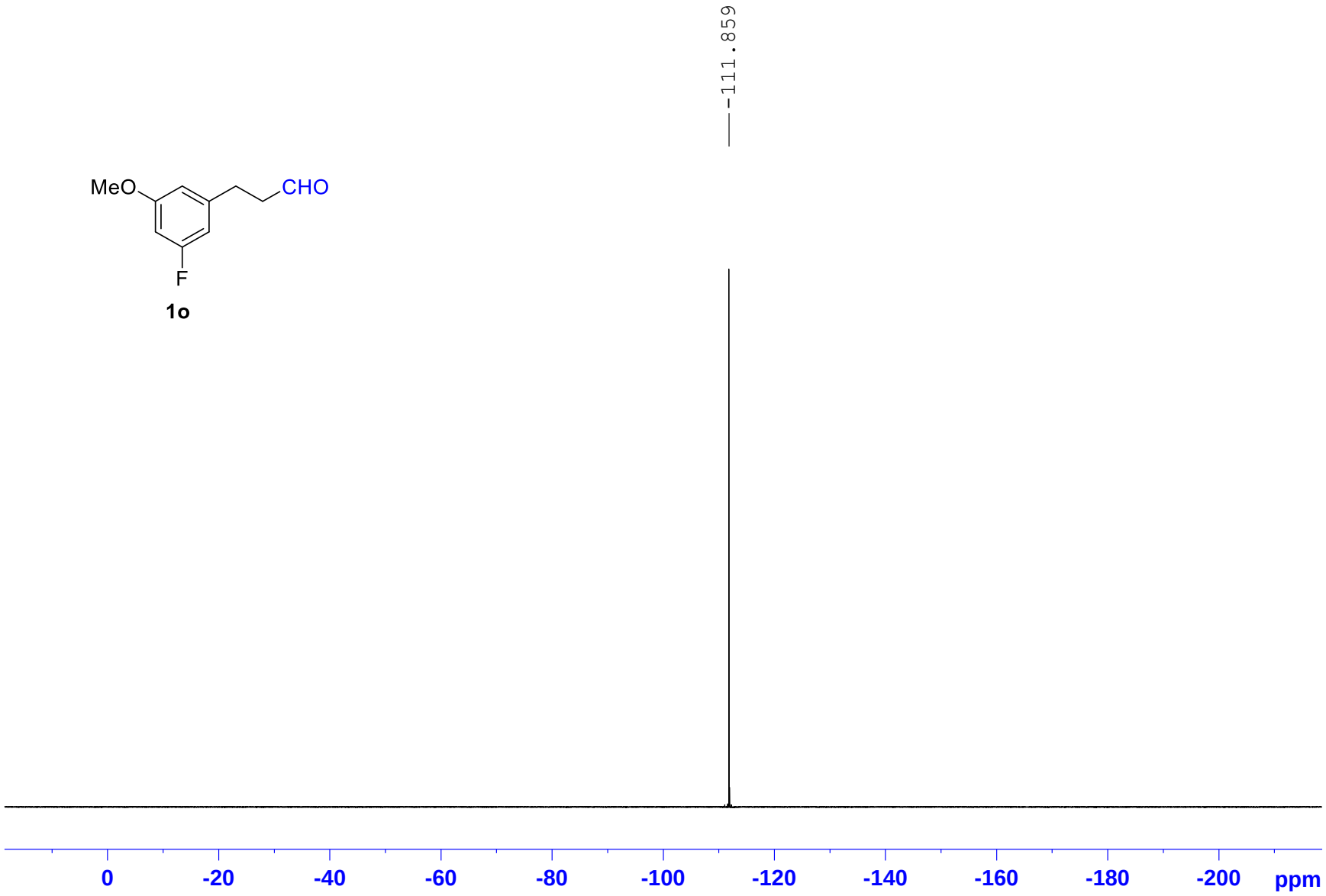
1n

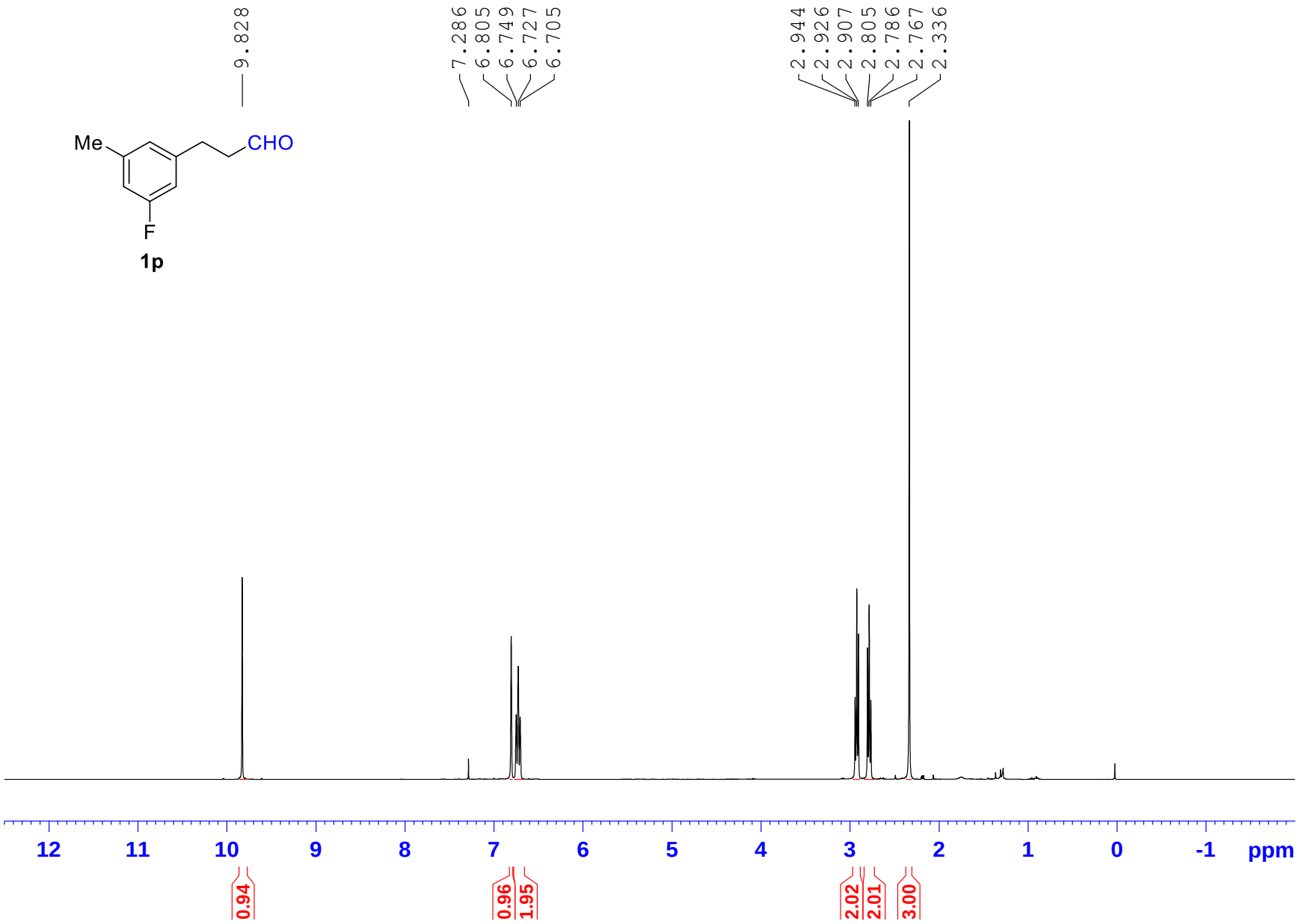

0.94
2.09
4.12
2.07
1.04
2.00
2.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

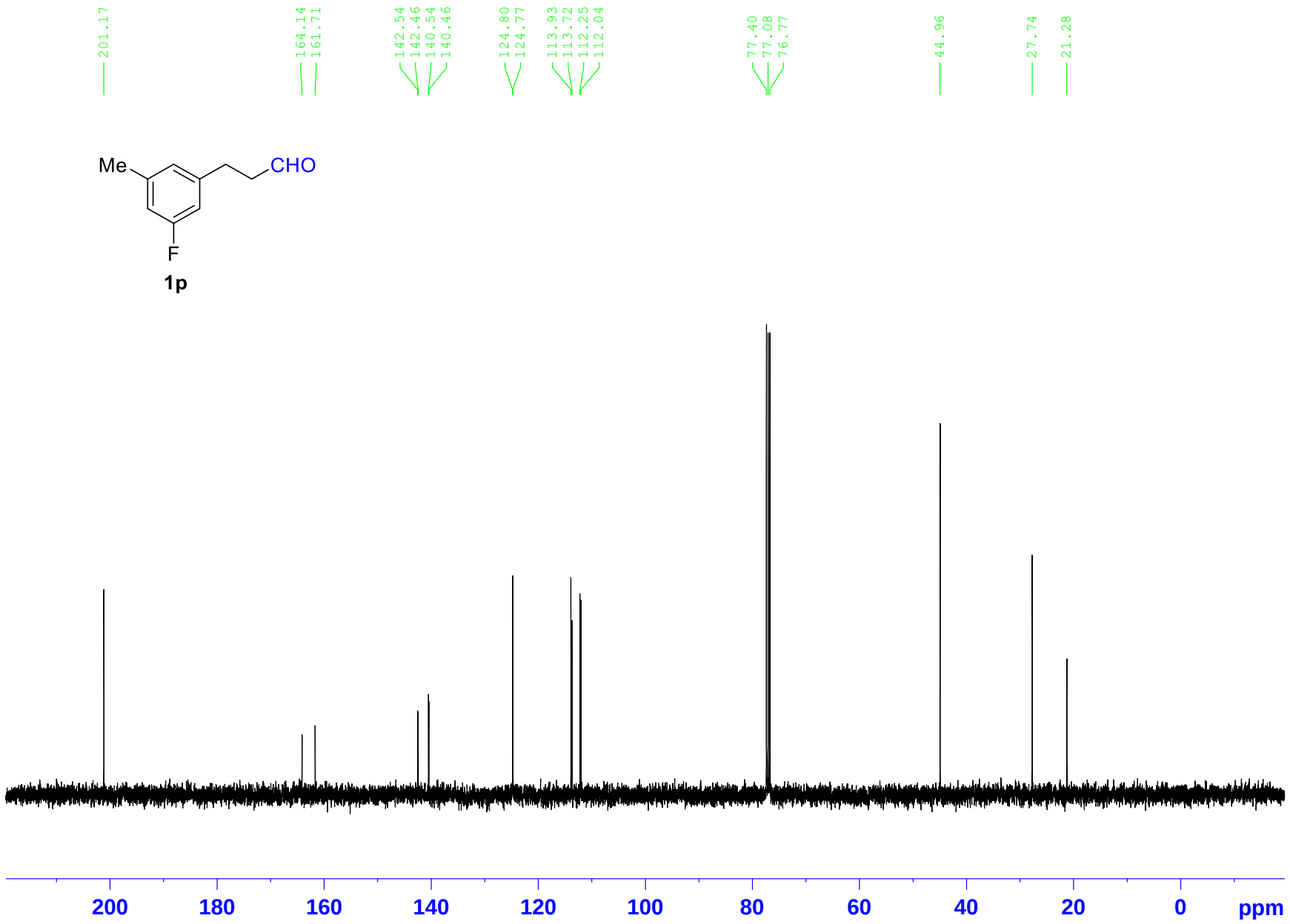

201.36
141.42
140.91
140.77
128.91
128.65
127.23
127.11
127.08
127.03
125.05
77.32
77.00
76.68
45.13
28.00
Ph
CHO
1n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

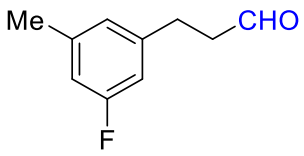

9.802
7.269
6.527
6.524
6.513
6.508
6.485
6.479
6.473
6.452
6.447
3.771
2.920
2.902
2.883
2.786
2.767
2.751
2.748
MeO
CHO
F
1o
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
2.93
2.99
2.07
2.00


201.06
164.90
162.46
161.04
160.92
143.47
143.38
110.07
110.05
107.49
107.27
99.46
99.21
77.40
77.08
76.77
55.45
44.80
28.01
27.99
MeO
CHO
F
1o
200
180
160
140
120
100
80
60
40
20
0
ppm

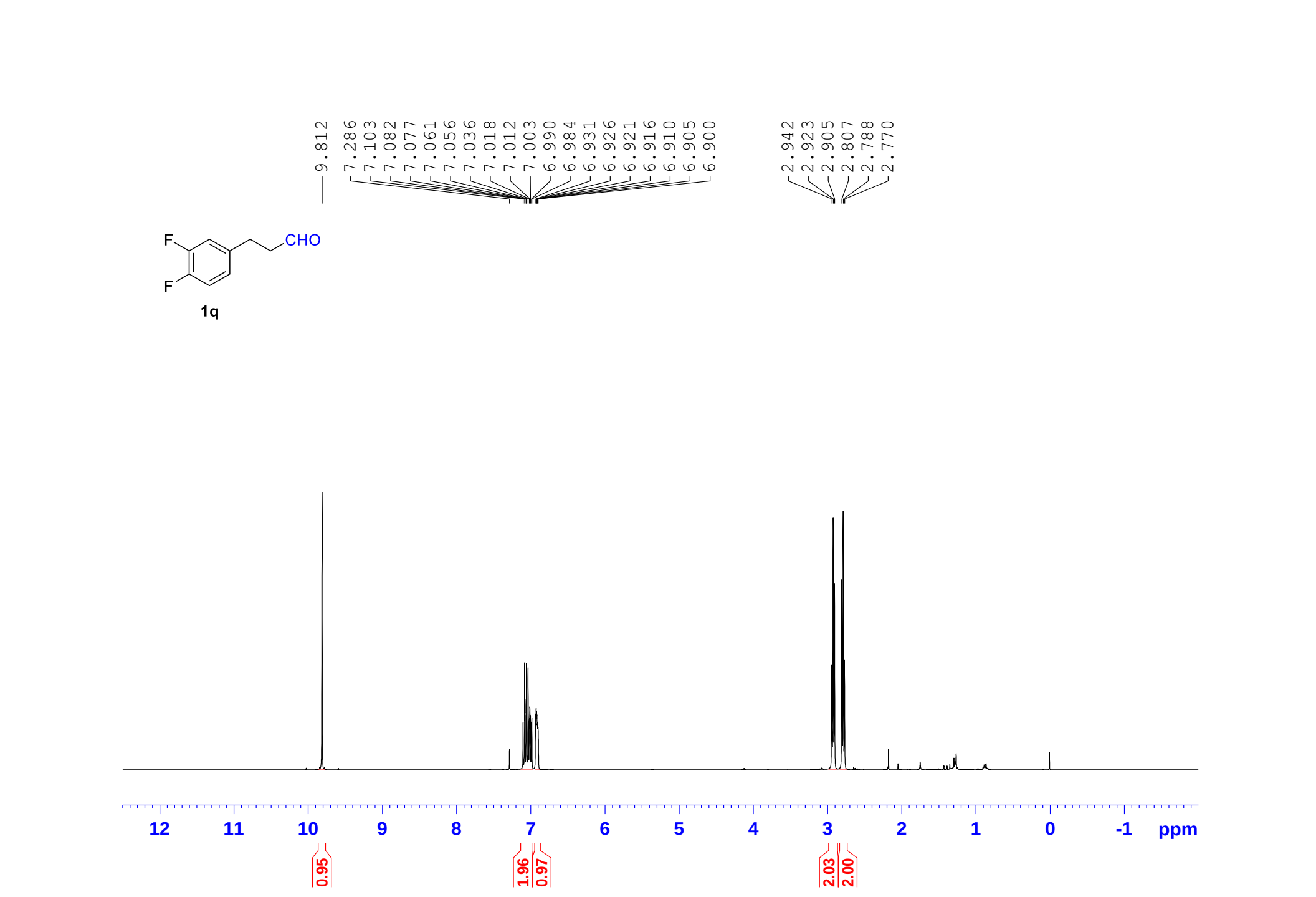

-111.859
MeO
CHO
F
1o
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


9.828
7.286
6.805
6.749
6.727
6.705
2.944
2.926
2.907
2.805
2.786
2.767
2.336
Me
CHO
F
1p
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.94
0.96
1.95
2.02
2.01
3.00


201.17
164.14
161.71
142.54
142.46
140.54
140.46
124.80
124.77
113.93
113.72
112.25
112.04
77.40
77.08
76.77
44.96
27.74
21.28
Me
CHO
F
1p
200
180
160
140
120
100
80
60
40
20
0
ppm



1p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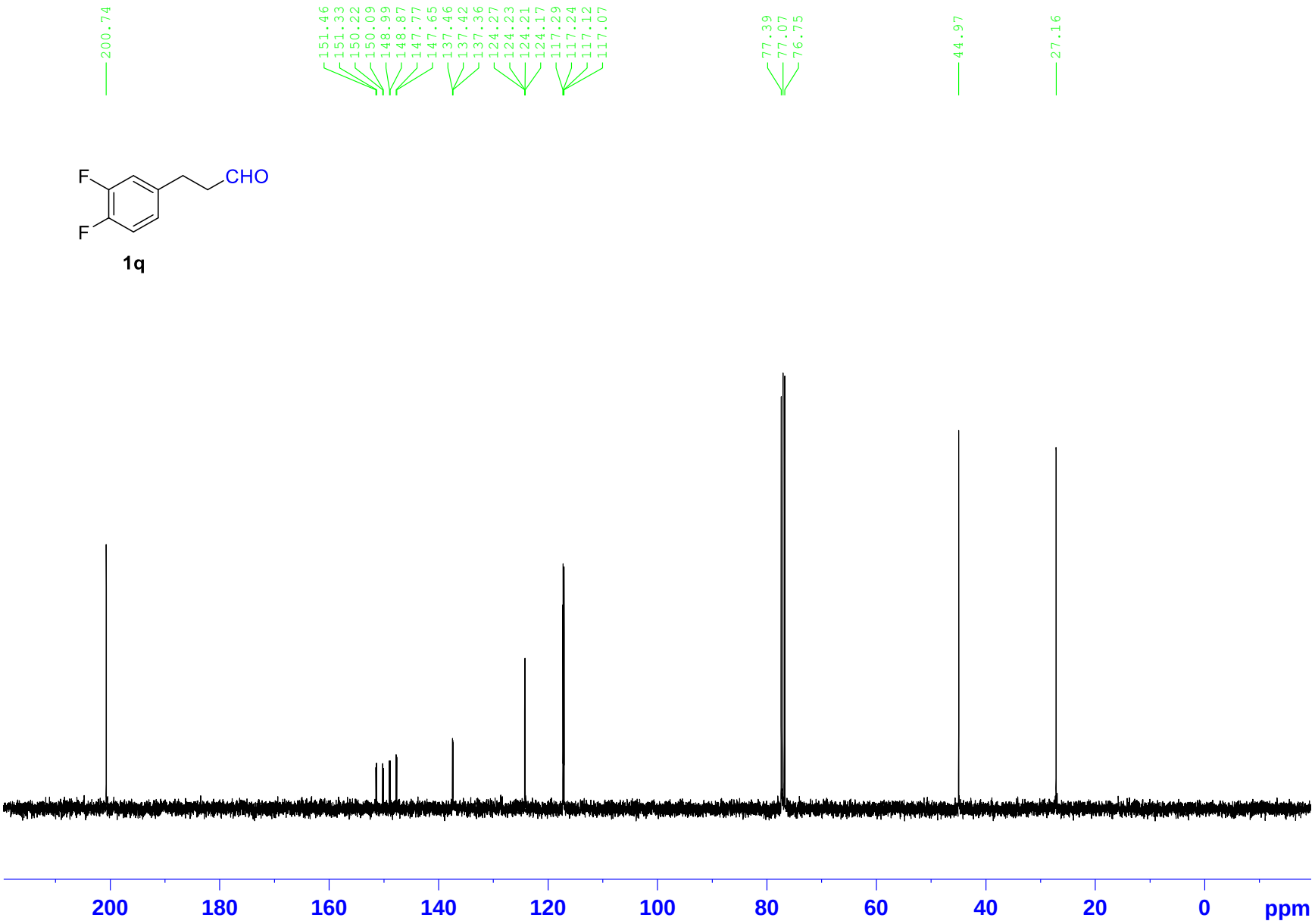
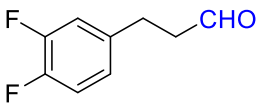
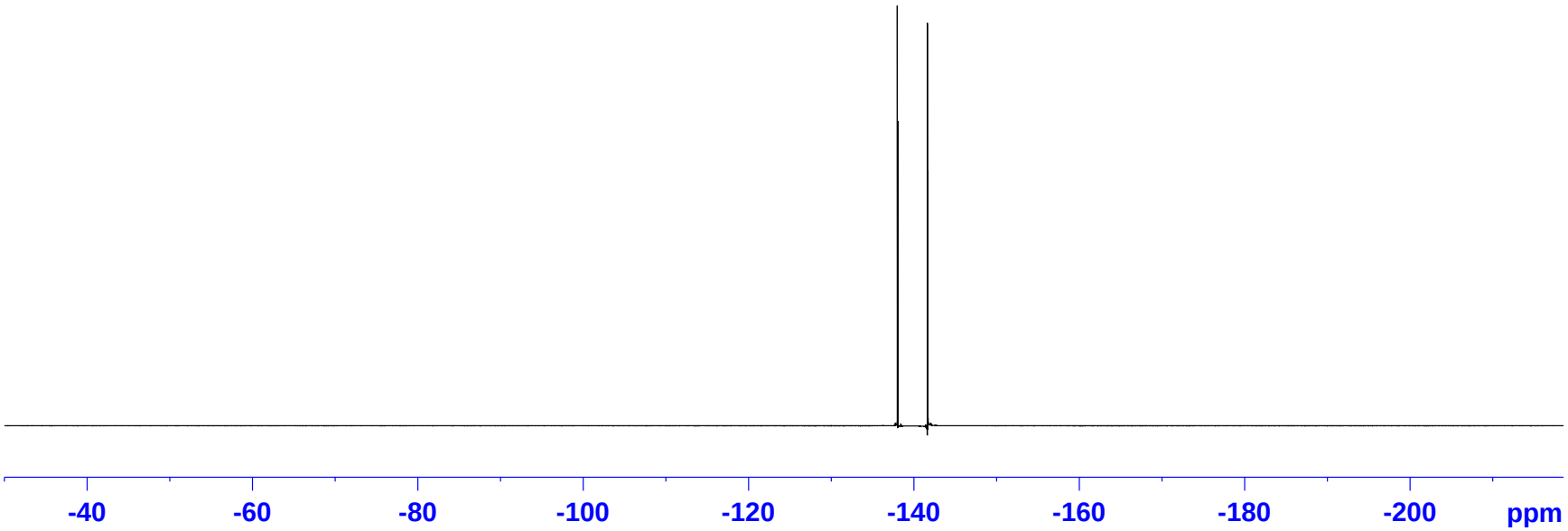
7.286
7.103
7.082
7.077
7.061
7.056
7.036
7.018
7.012
7.003
6.990
6.984
6.931
6.926
6.921
6.916
6.910
6.905
6.900
2.942
2.923
2.905
2.807
2.788
2.770
F
F
CHO
1q
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
1.96
0.97
2.03
2.00

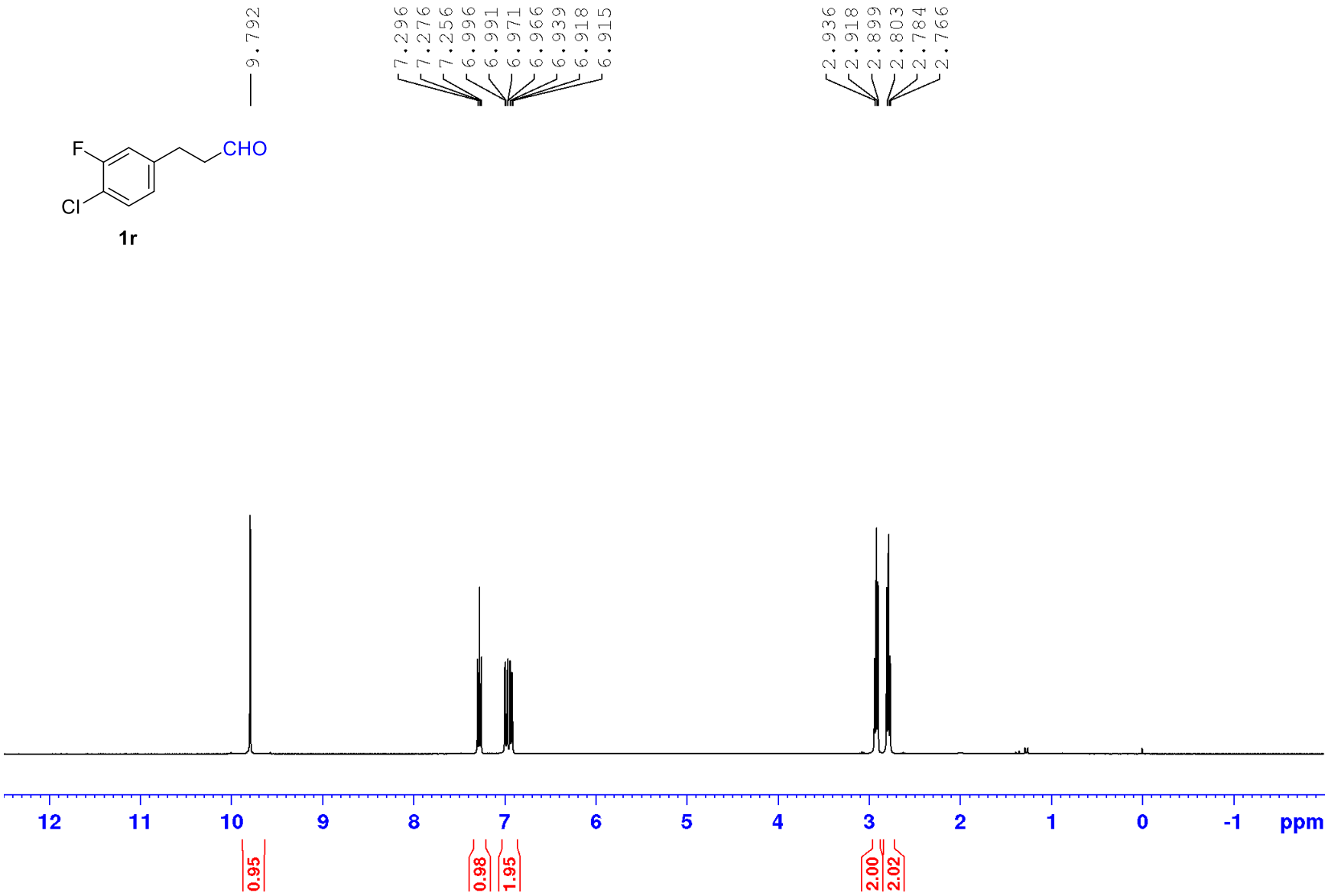

200.74
151.46
151.33
150.22
150.09
148.99
148.87
147.77
147.65
137.46
137.42
137.36
124.27
124.23
124.21
124.17
117.29
117.24
117.12
117.07
77.39
77.07
76.75
44.97
27.16
F
F
CHO
1q
200
180
160
140
120
100
80
60
40
20
0
ppm



1q

-137.975
-138.032
-141.611
-141.669

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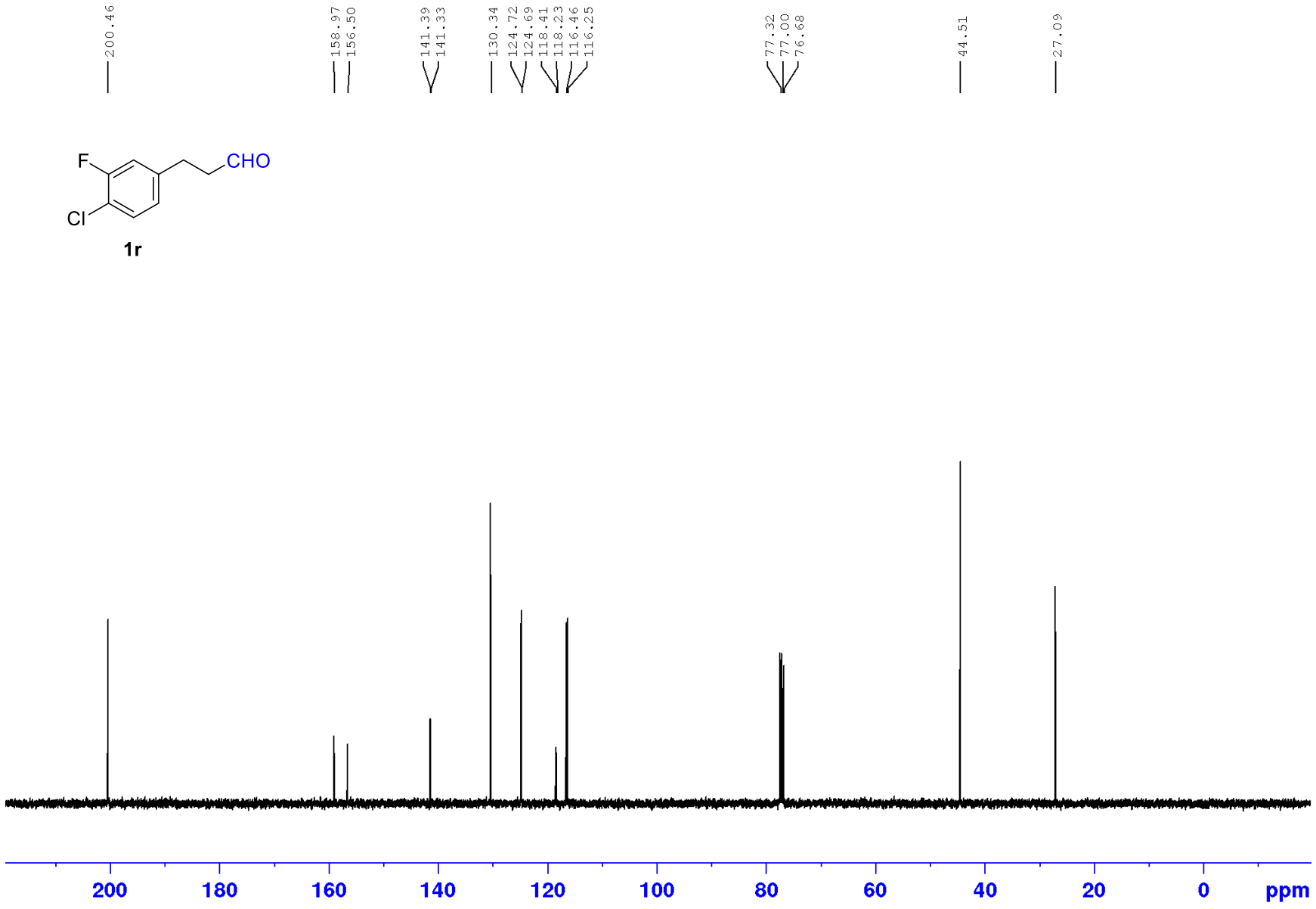
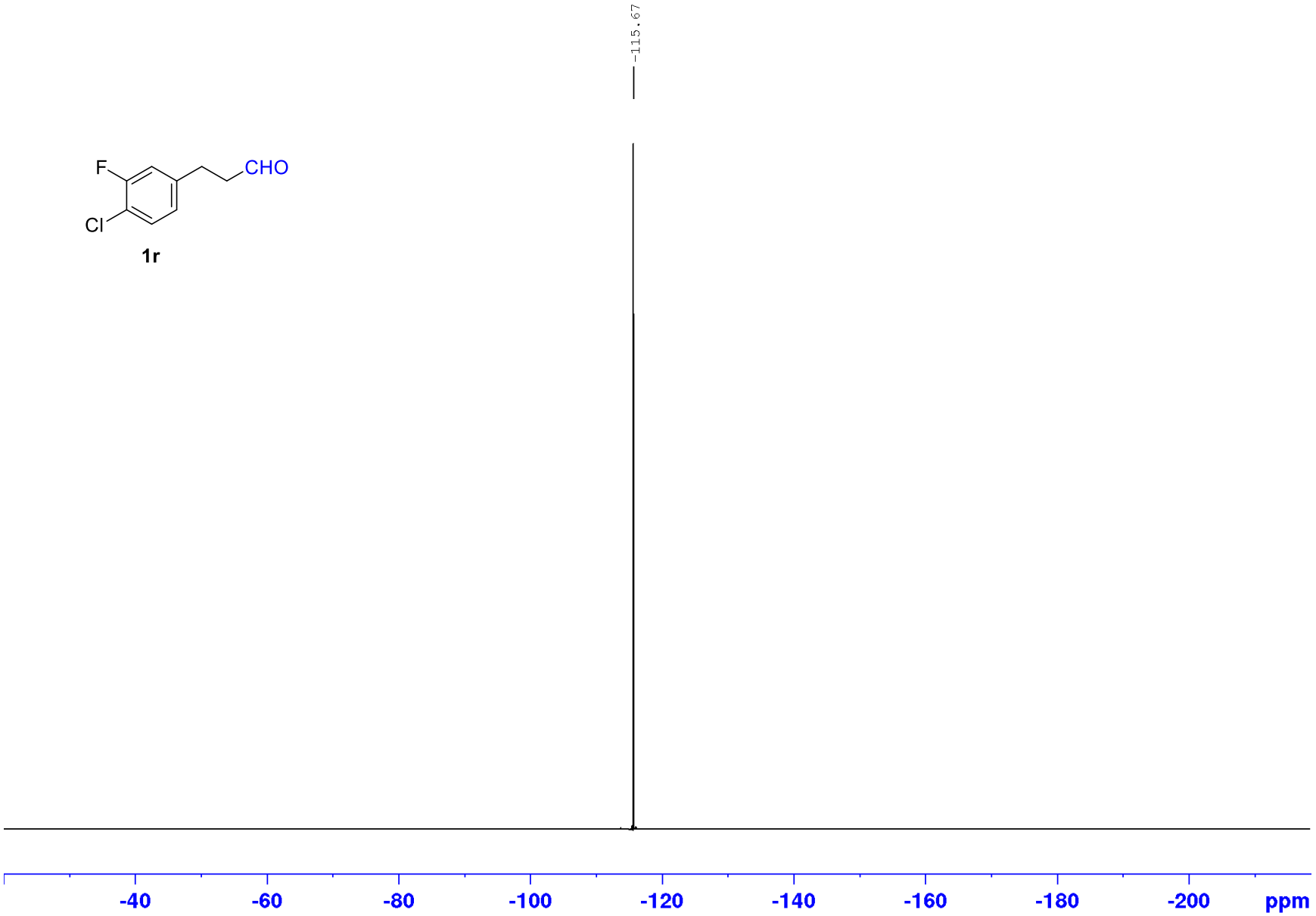
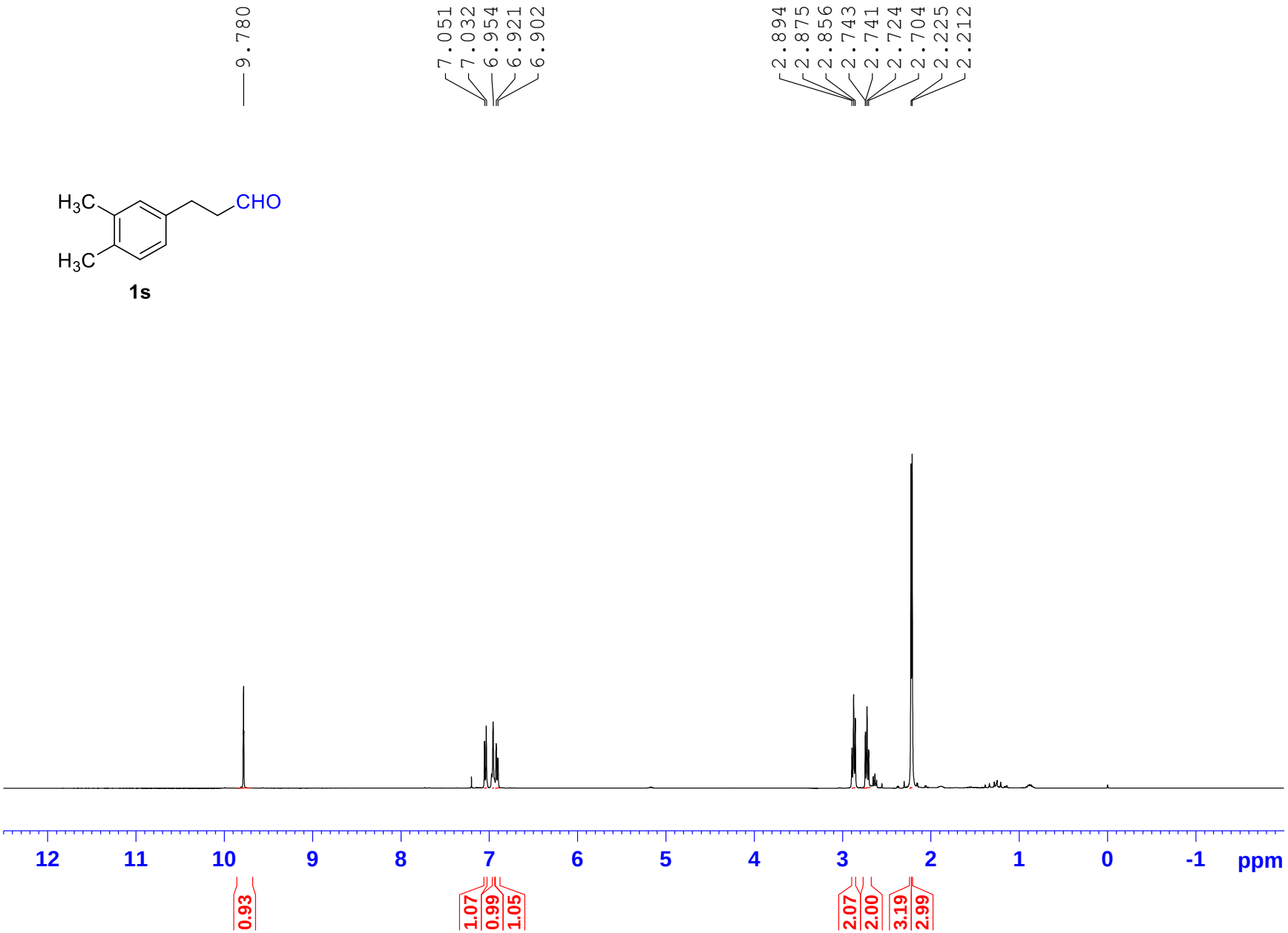
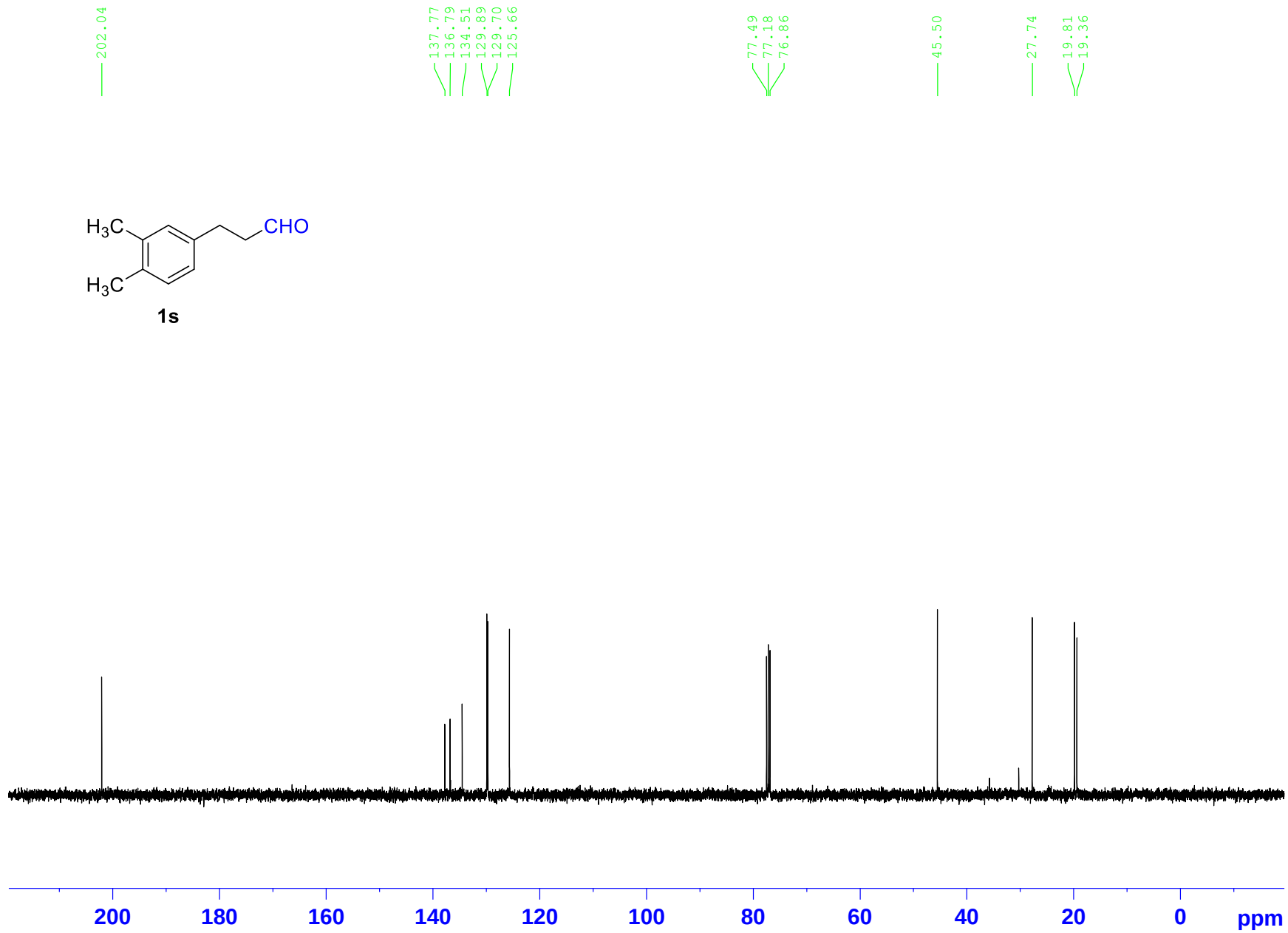
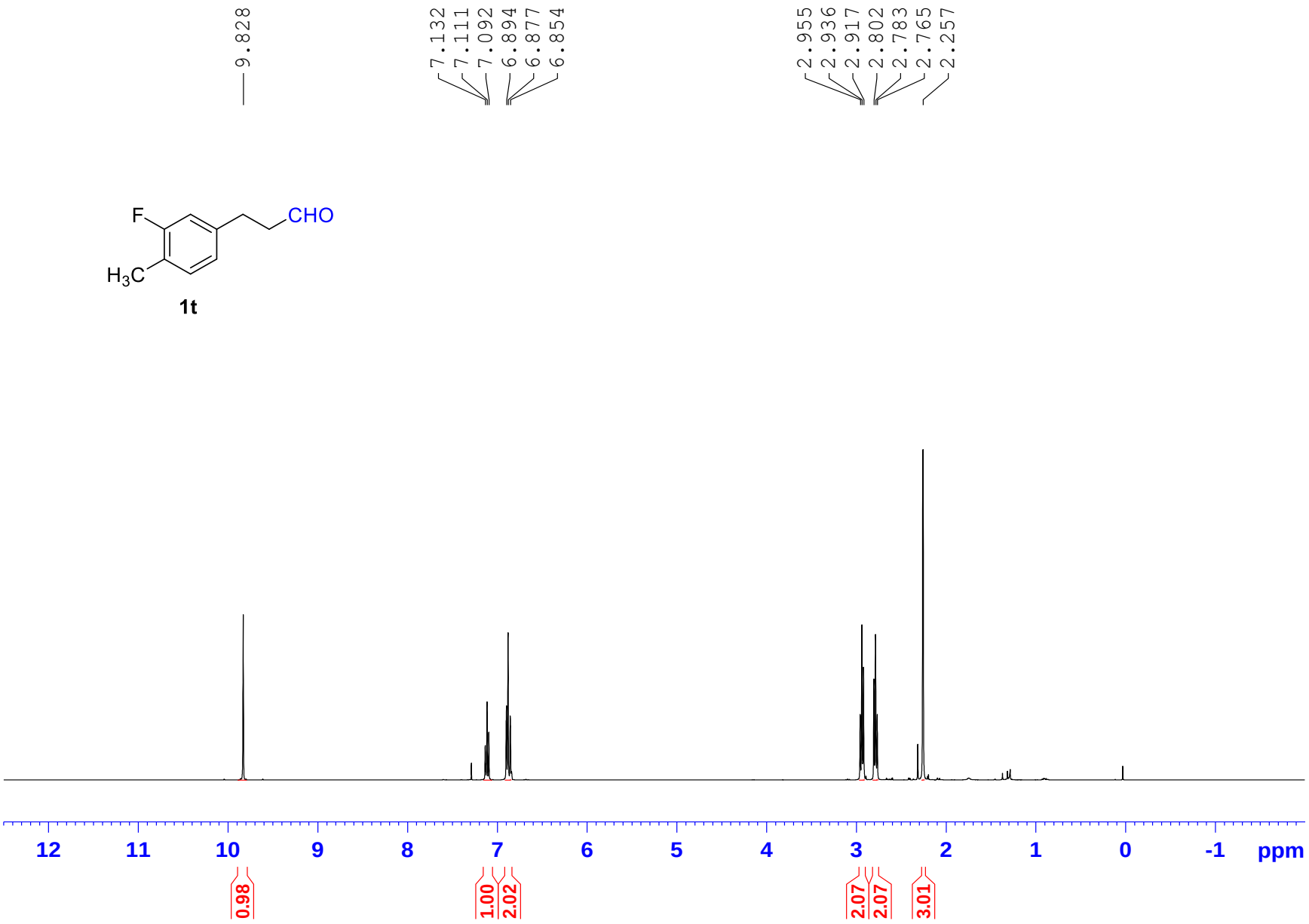
7.296
7.276
7.256
6.996
6.991
6.971
6.966
6.939
6.918
6.915
2.936
2.918
2.899
2.803
2.784
2.766
F
CHO
Cl
1r
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
0.98
1.95
2.00
2.02

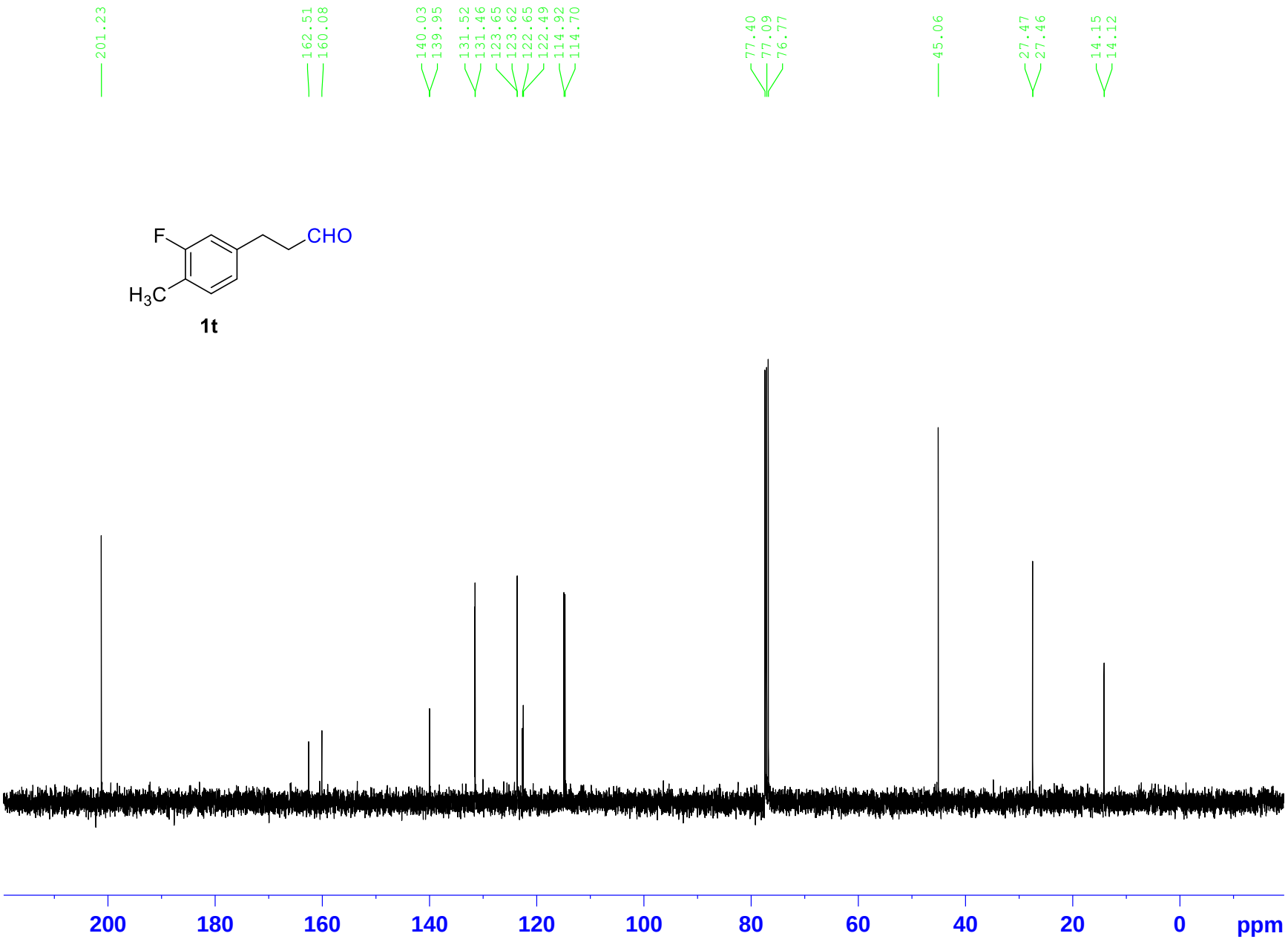

200.46
158.97
156.50
141.39
141.33
130.34
124.72
124.69
118.41
118.23
116.46
116.25
77.32
77.00
76.68
44.51
27.09
F
CHO
Cl
1r
200
180
160
140
120
100
80
60
40
20
0
ppm


-115.67
F
CHO
Cl
1r
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

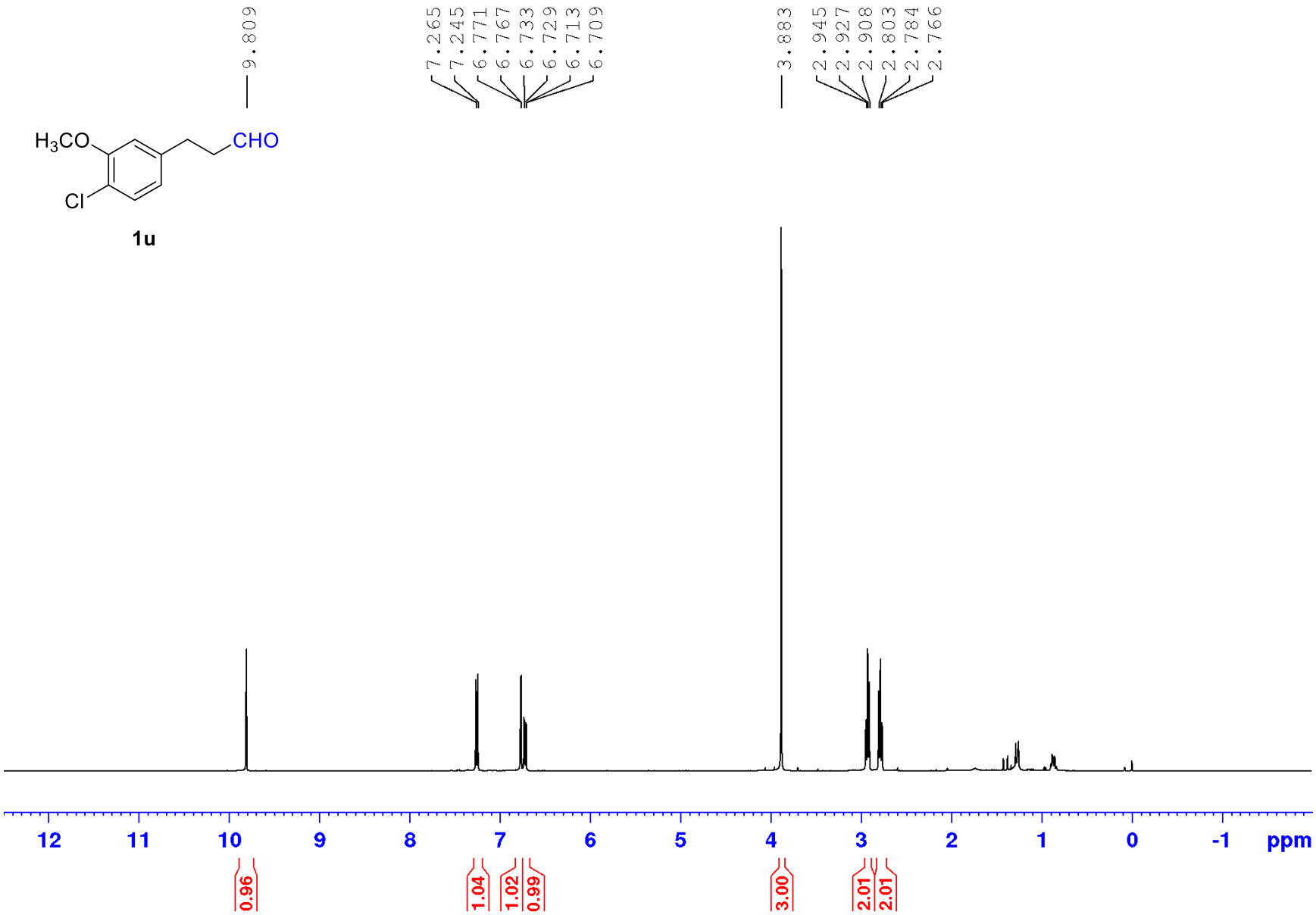

9.780
7.051
7.032
6.954
6.921
6.902
2.894
2.875
2.856
2.743
2.741
2.724
2.704
2.225
2.212
H3C
CHO
H3C
1s
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.93
1.07
0.99
1.05
2.07
2.00
3.19
2.99

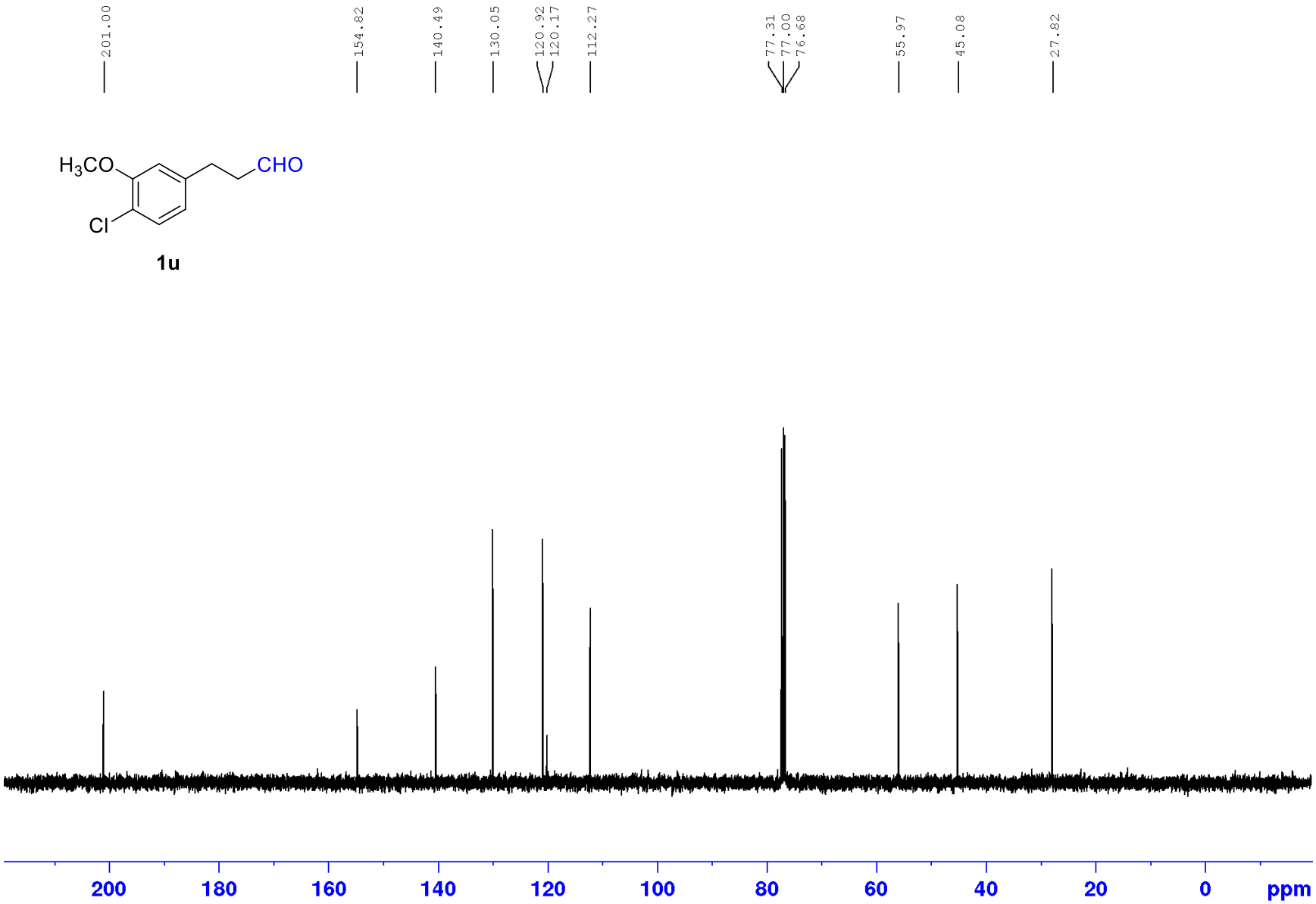

202.04
137.77
136.79
134.51
129.89
129.70
125.66
77.49
77.18
76.86
45.50
27.74
19.81
19.36
H3C
CHO
H3C
1s
200
180
160
140
120
100
80
60
40
20
0
ppm

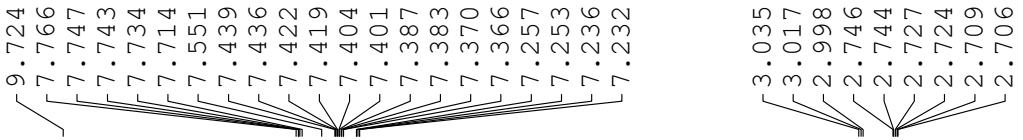

9.828
7.132
7.111
7.092
6.894
6.877
6.854
2.955
2.936
2.917
2.802
2.783
2.765
2.257
F
CHO
H3C
1t
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
1.00
2.02
2.07
2.07
3.01

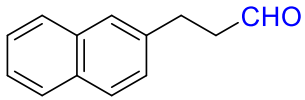

201.23
162.51
160.08
140.03
139.95
131.52
131.46
123.65
123.62
122.65
122.49
114.92
114.70
77.40
77.09
76.77
45.06
27.47
27.46
14.15
14.12
F
CHO
H3C
1t
200
180
160
140
120
100
80
60
40
20
0
ppm


-117.584
F
CHO
H3C
1t
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

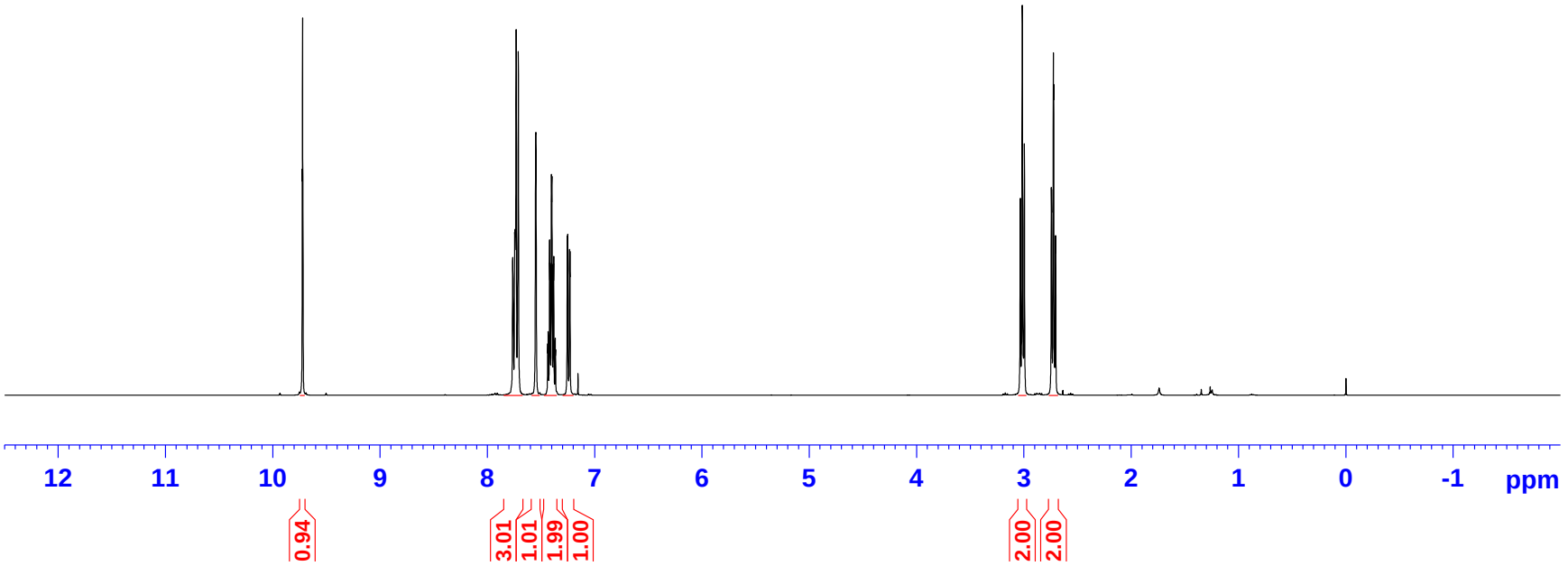

9.809
7.265
7.245
6.771
6.767
6.733
6.729
6.713
6.709
3.883
2.945
2.927
2.908
2.803
2.784
2.766
H3CO
CHO
Cl
1u
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.96
1.04
1.02
0.99
3.00
2.01
2.01

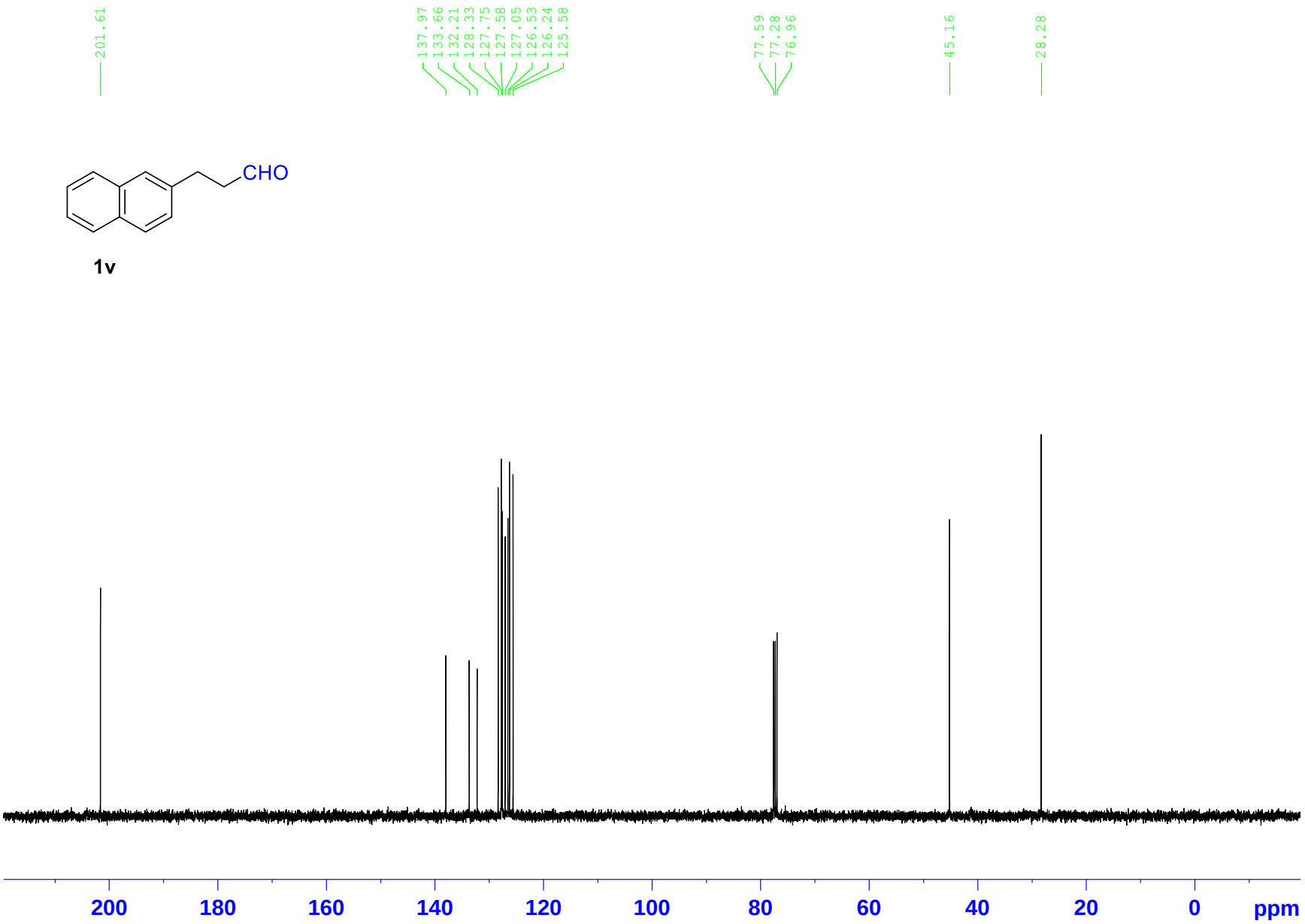

201.00
154.82
140.49
130.05
120.92
120.17
112.27
77.31
77.00
76.68
55.97
45.08
27.82
H3CO
CHO
Cl
1u
200
180
160
140
120
100
80
60
40
20
0
ppm

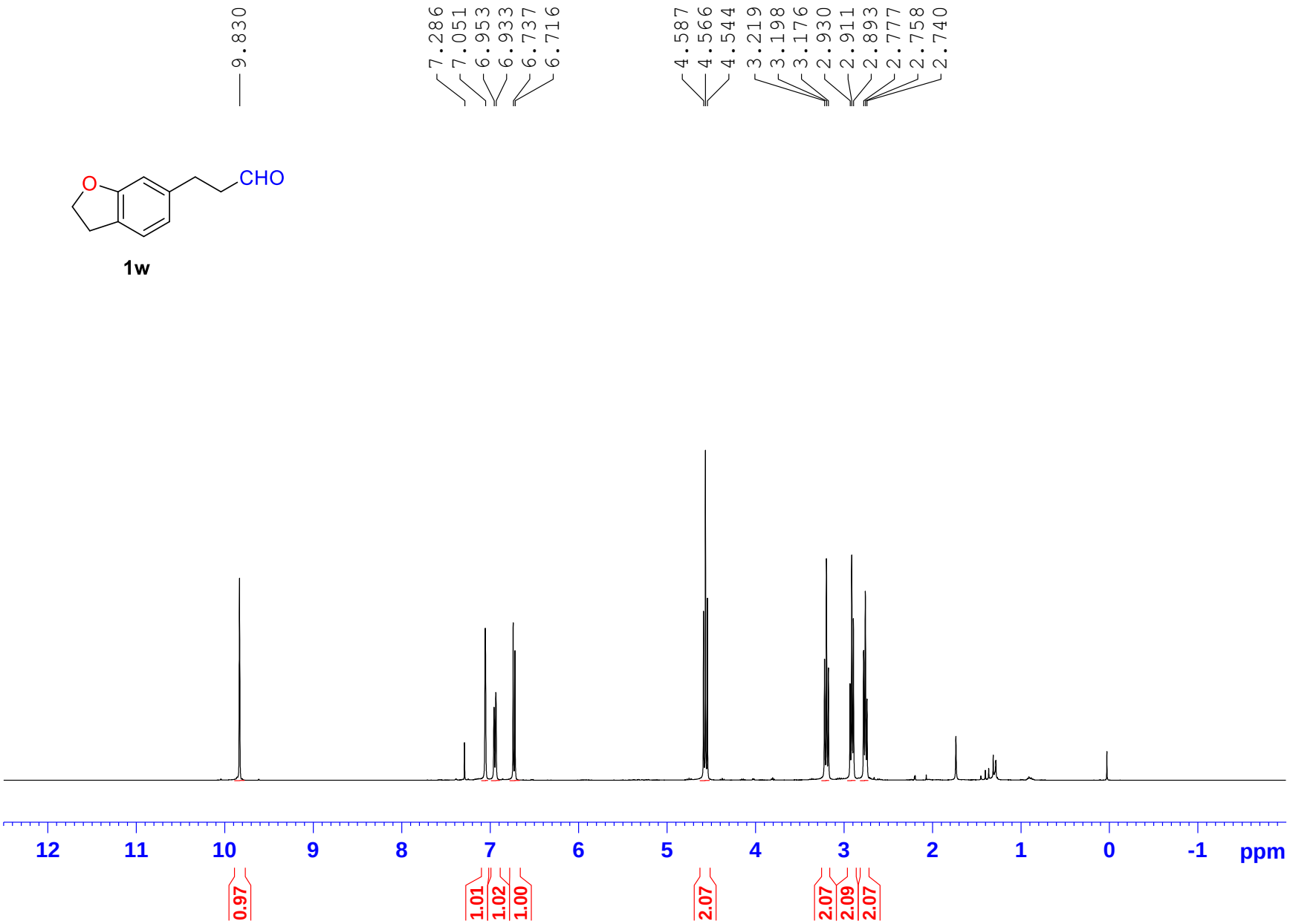

9.724
7.766
7.747
7.743
7.734
7.714
7.551
7.439
7.436
7.422
7.419
7.404
7.401
7.387
7.383
7.370
7.366
7.257
7.253
7.236
7.232
3.035
3.017
2.998
2.746
2.744
2.727
2.724
2.709
2.706

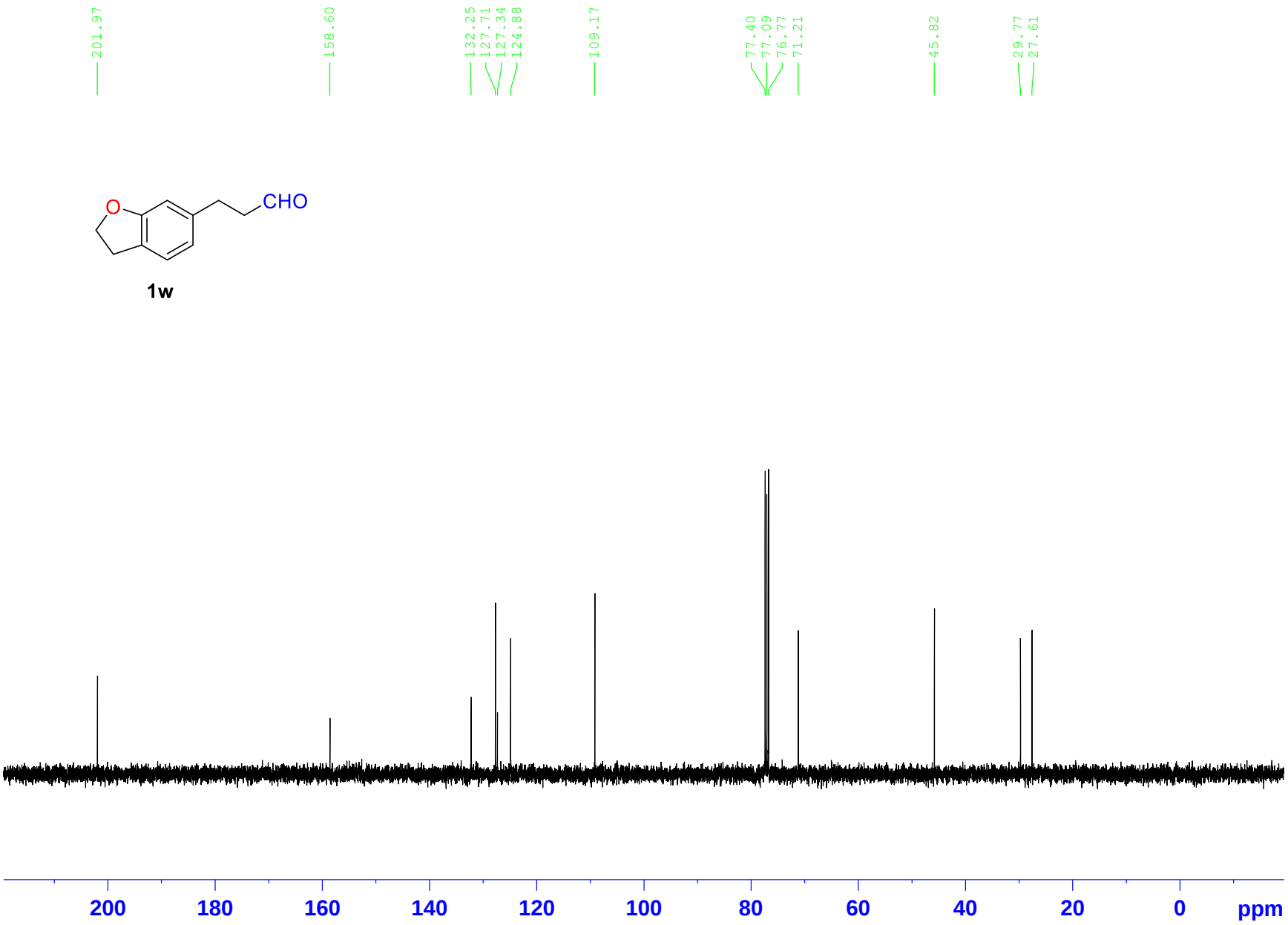

CHO

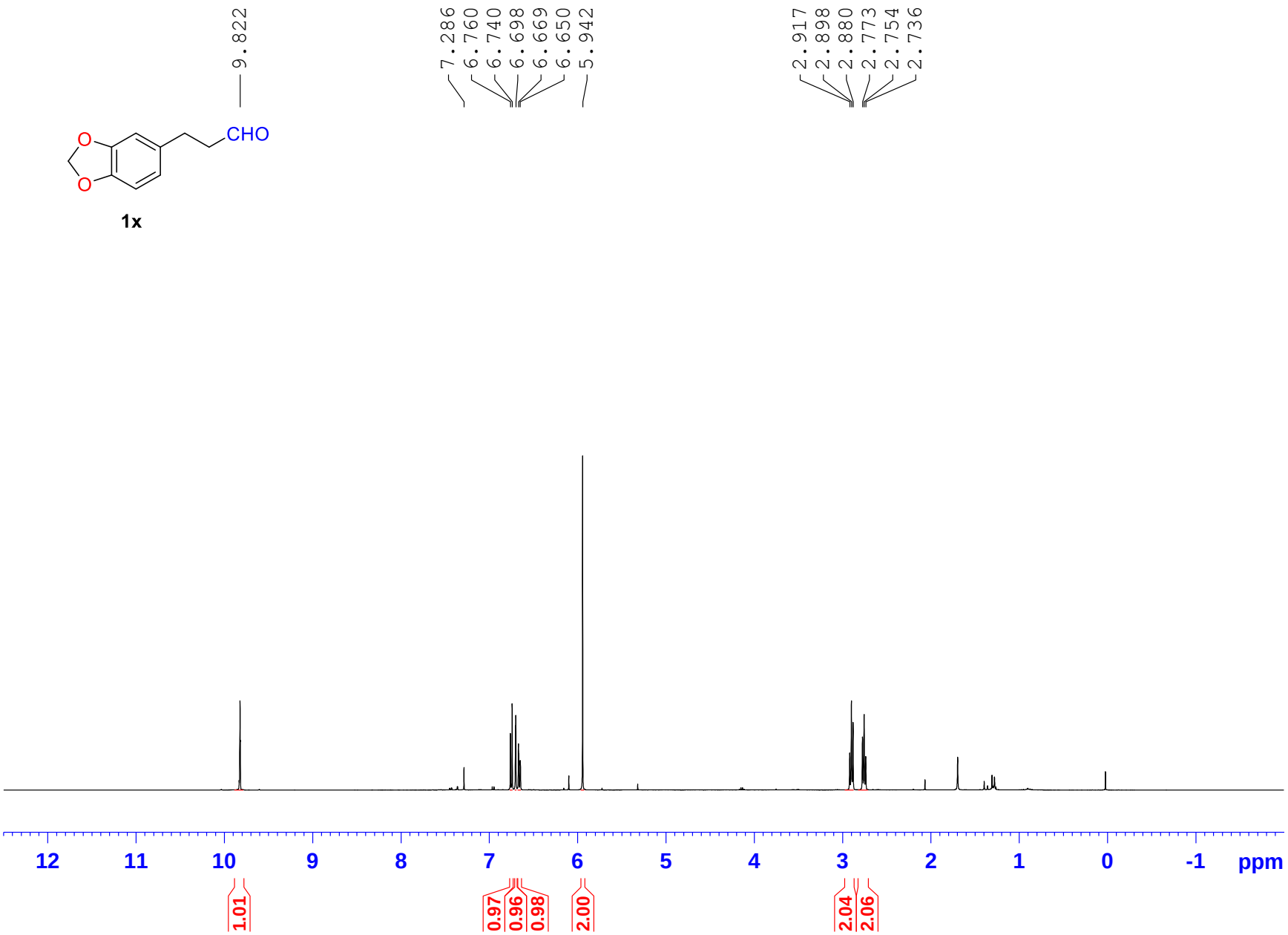
1v

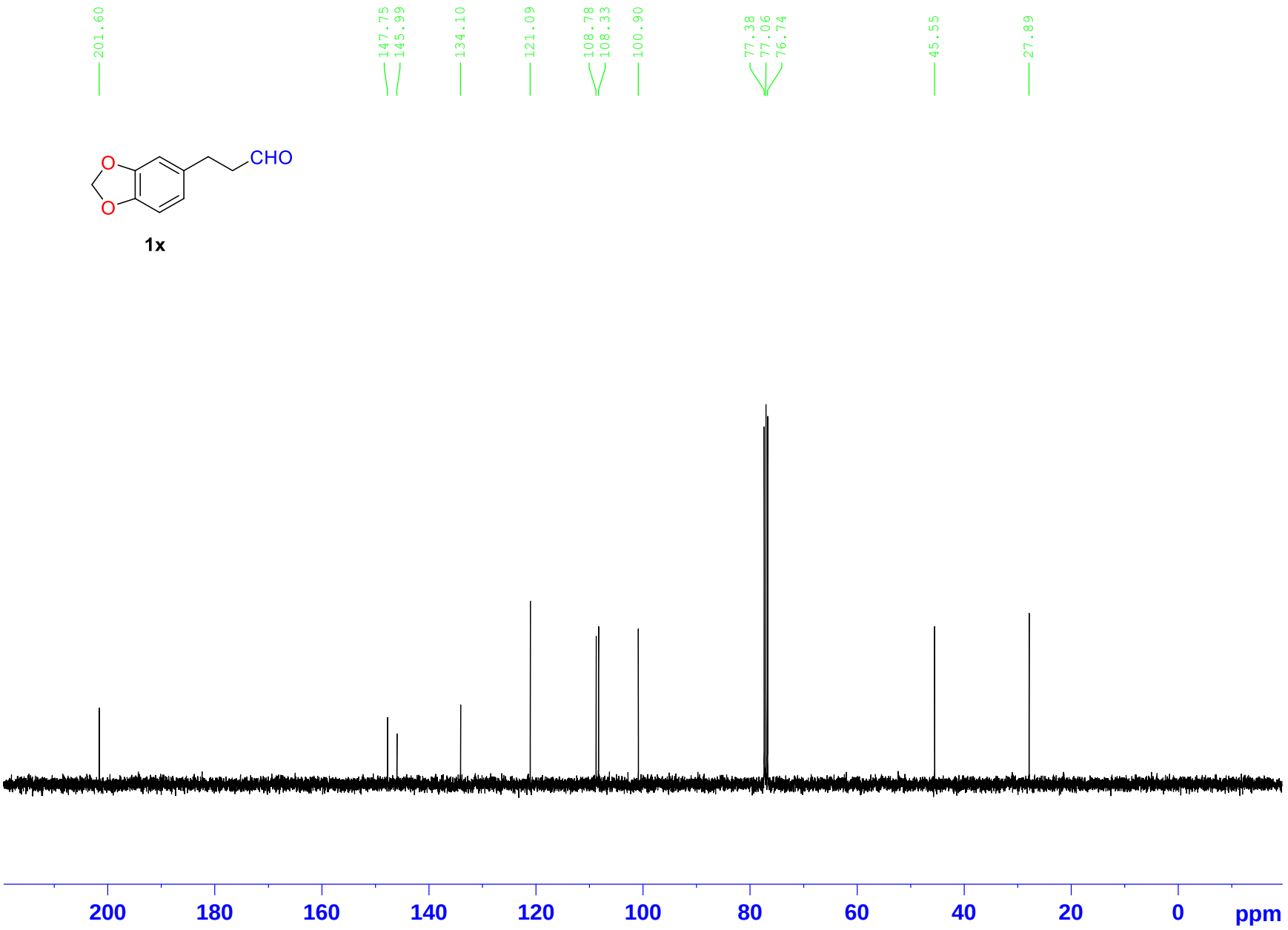

12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.94
3.01
1.01
1.99
1.00
2.00
2.00


201.61
137.97
133.66
132.21
128.33
127.75
127.58
127.05
126.53
126.24
125.58
77.59
77.28
76.96
45.16
28.28
CHO
1v
200
180
160
140
120
100
80
60
40
20
0
ppm

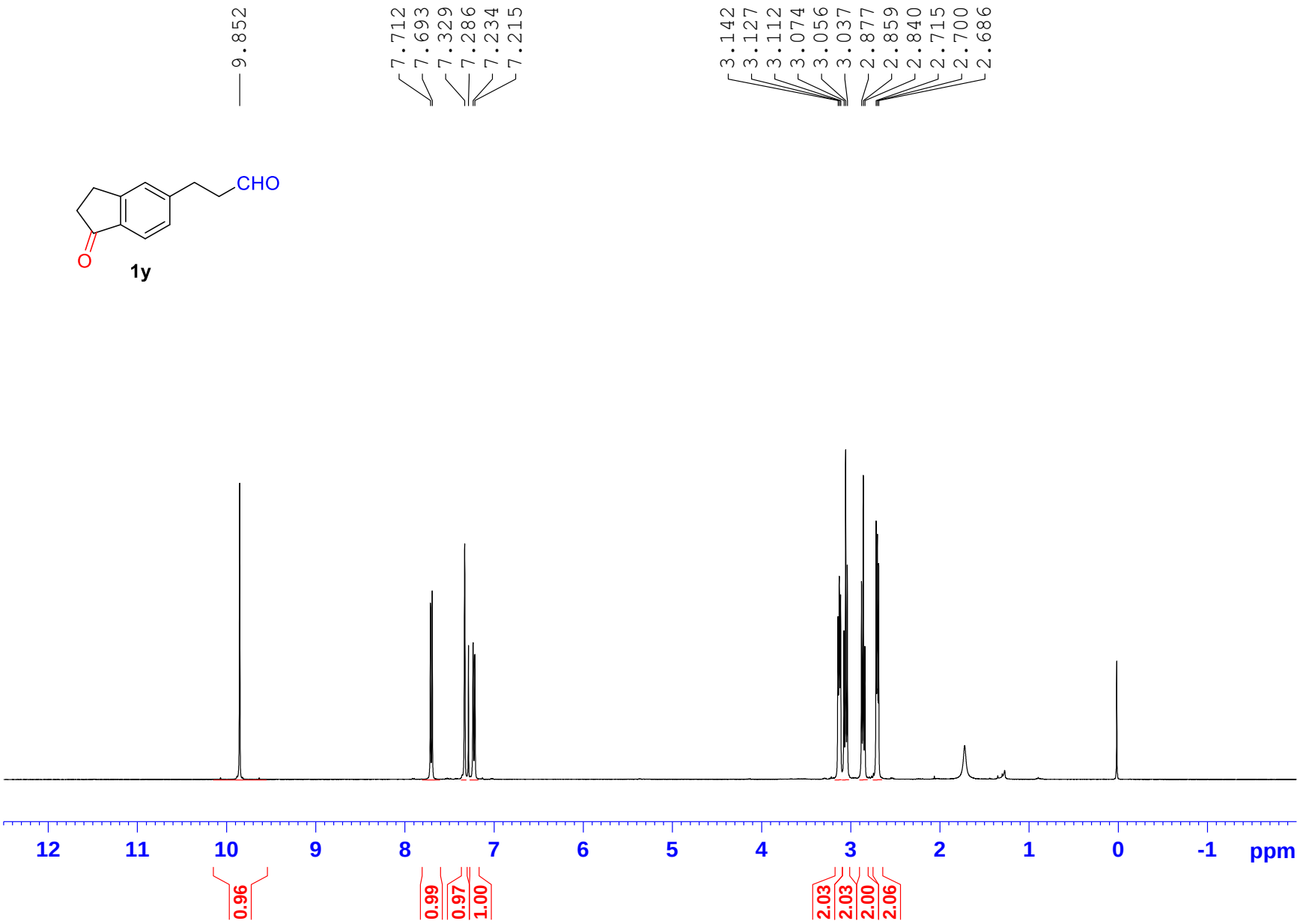

9.830
7.286
7.051
6.953
6.933
6.737
6.716
4.587
4.566
4.544
3.219
3.198
3.176
2.930
2.911
2.893
2.777
2.758
2.740
O
CHO
1w
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
1.01
1.02
1.00
2.07
2.07
2.09
2.07

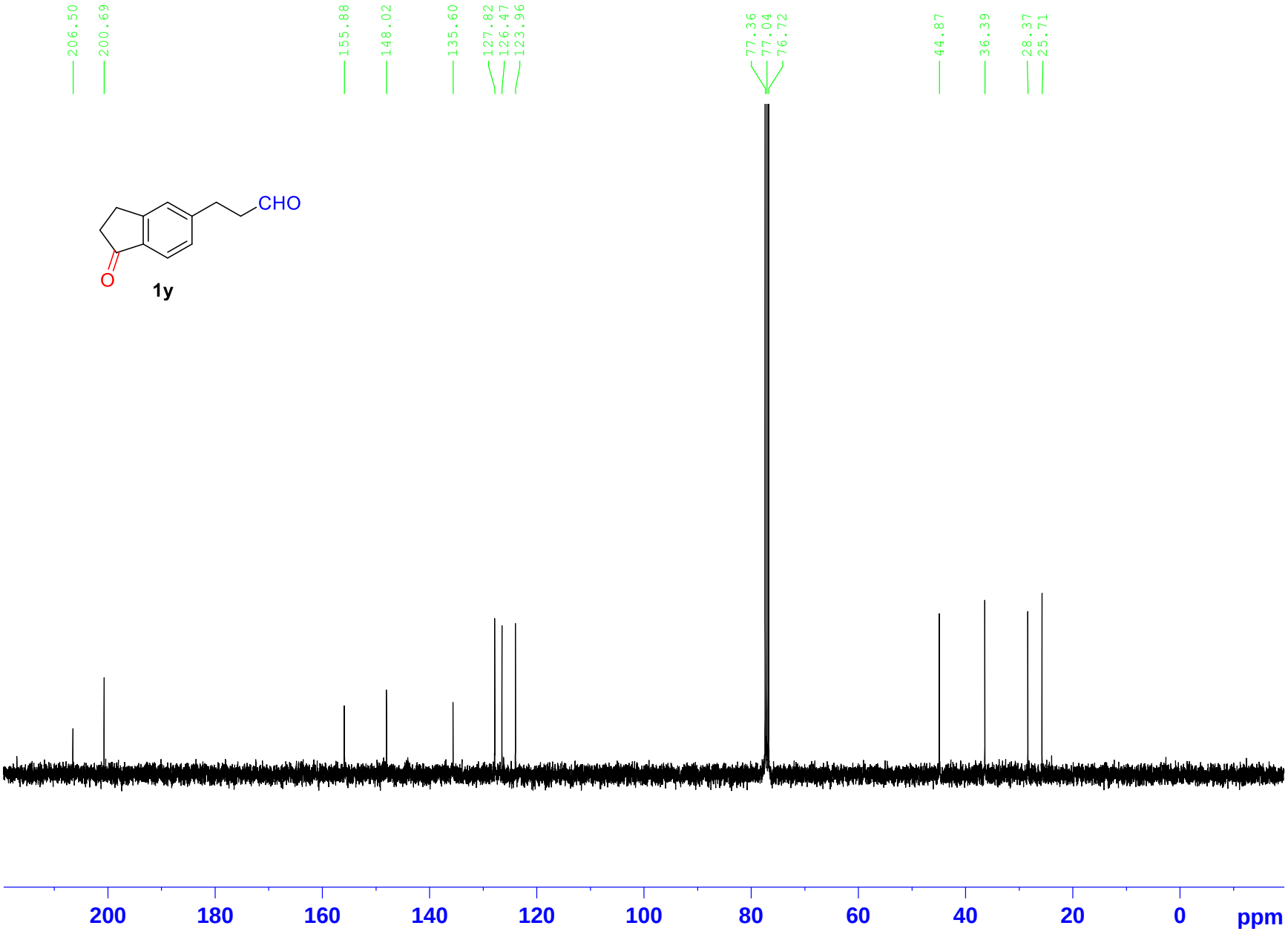

201.97
158.60
132.25
127.71
127.34
124.88
109.17
77.40
77.09
76.77
71.21
45.82
29.77
27.61
O
CHO
1w
200
180
160
140
120
100
80
60
40
20
0
ppm

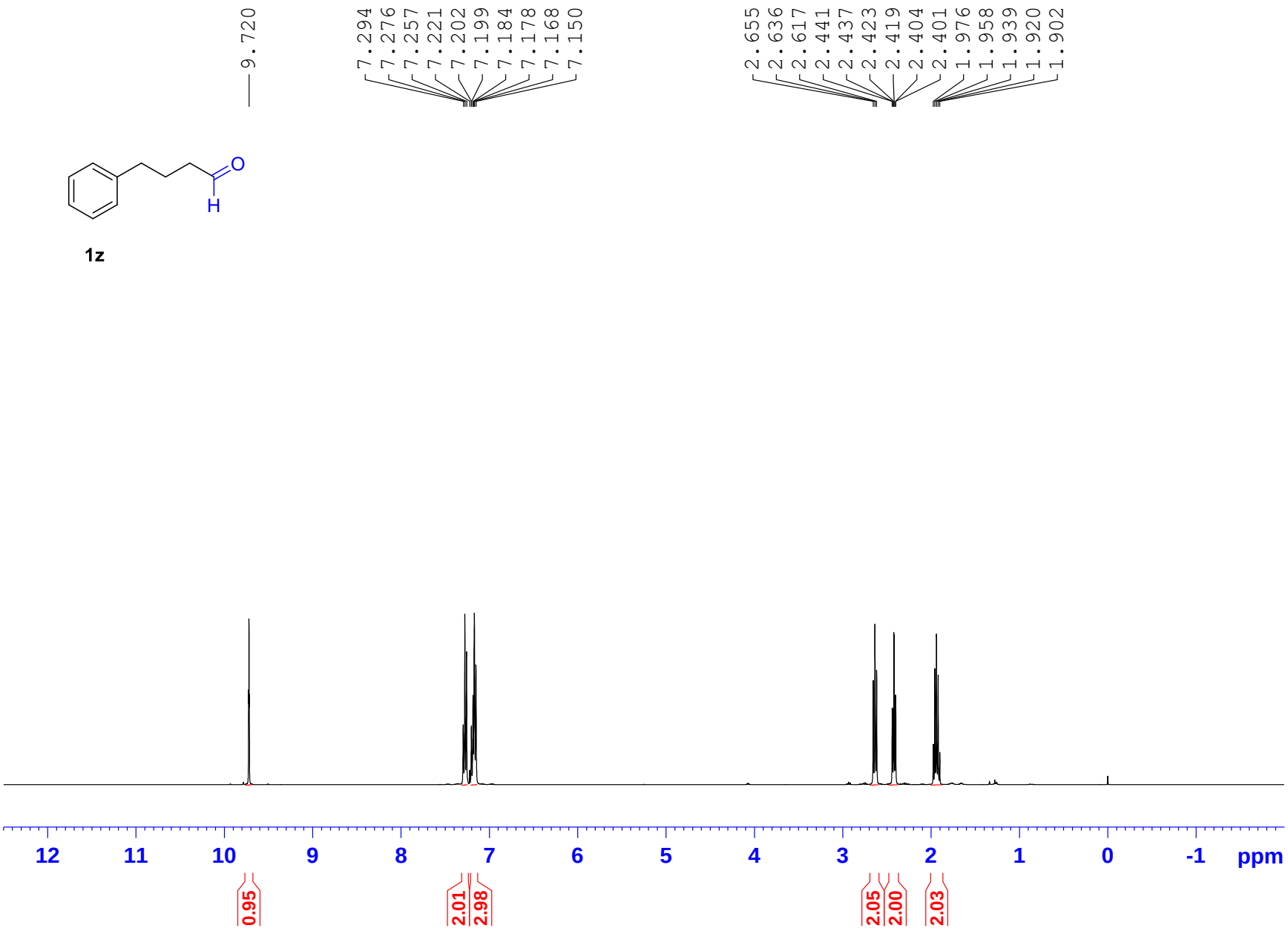

9.822
7.286
6.760
6.740
6.698
6.669
6.650
5.942
2.917
2.898
2.880
2.773
2.754
2.736
O
O
CHO
1x
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
0.97
0.96
0.98
2.00
2.04
2.06

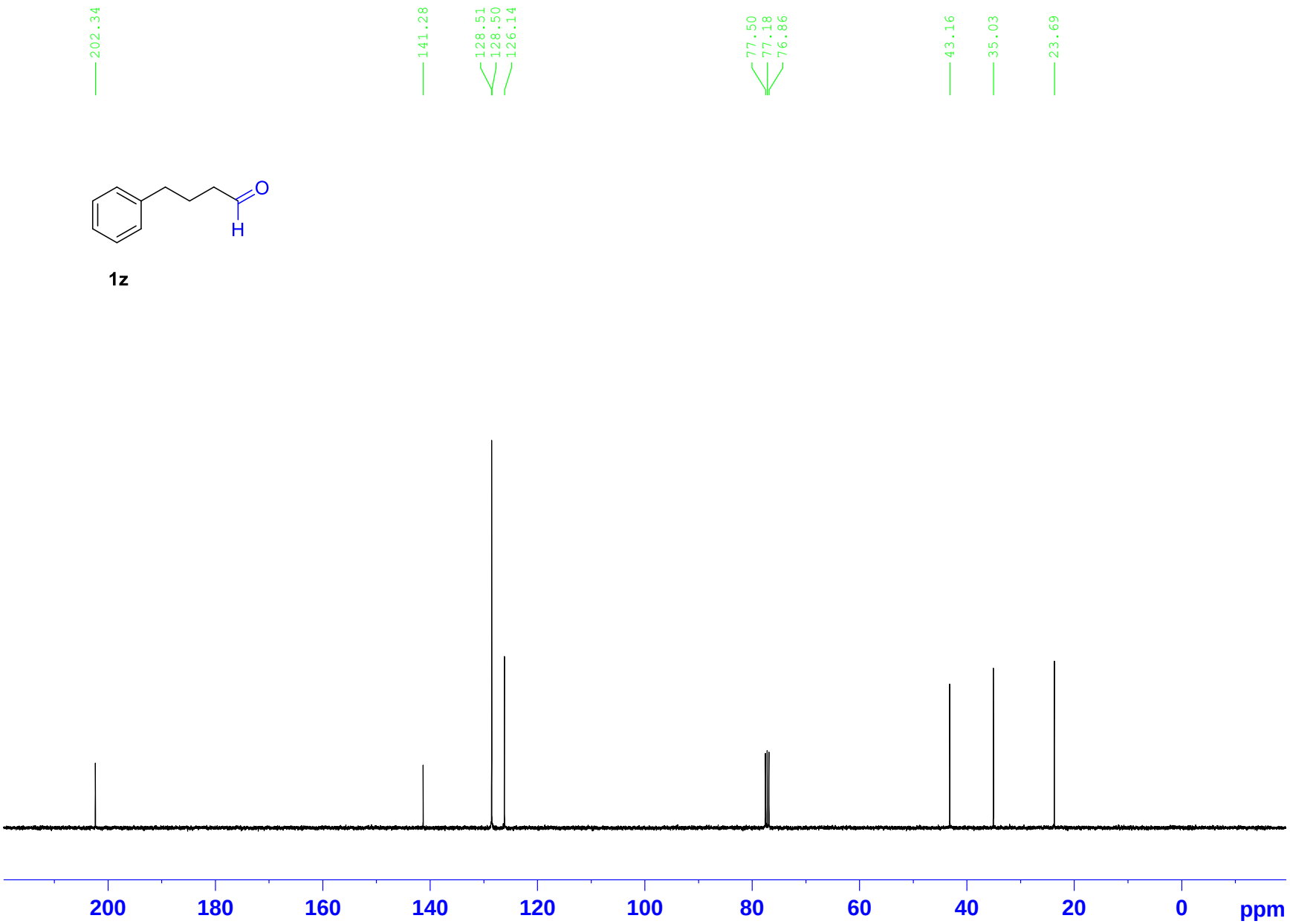

201.60
147.75
145.99
134.10
121.09
108.78
108.33
100.90
77.38
77.06
76.74
45.55
27.89
O
O
CHO
200
180
160
140
120
100
80
60
40
20
0
ppm

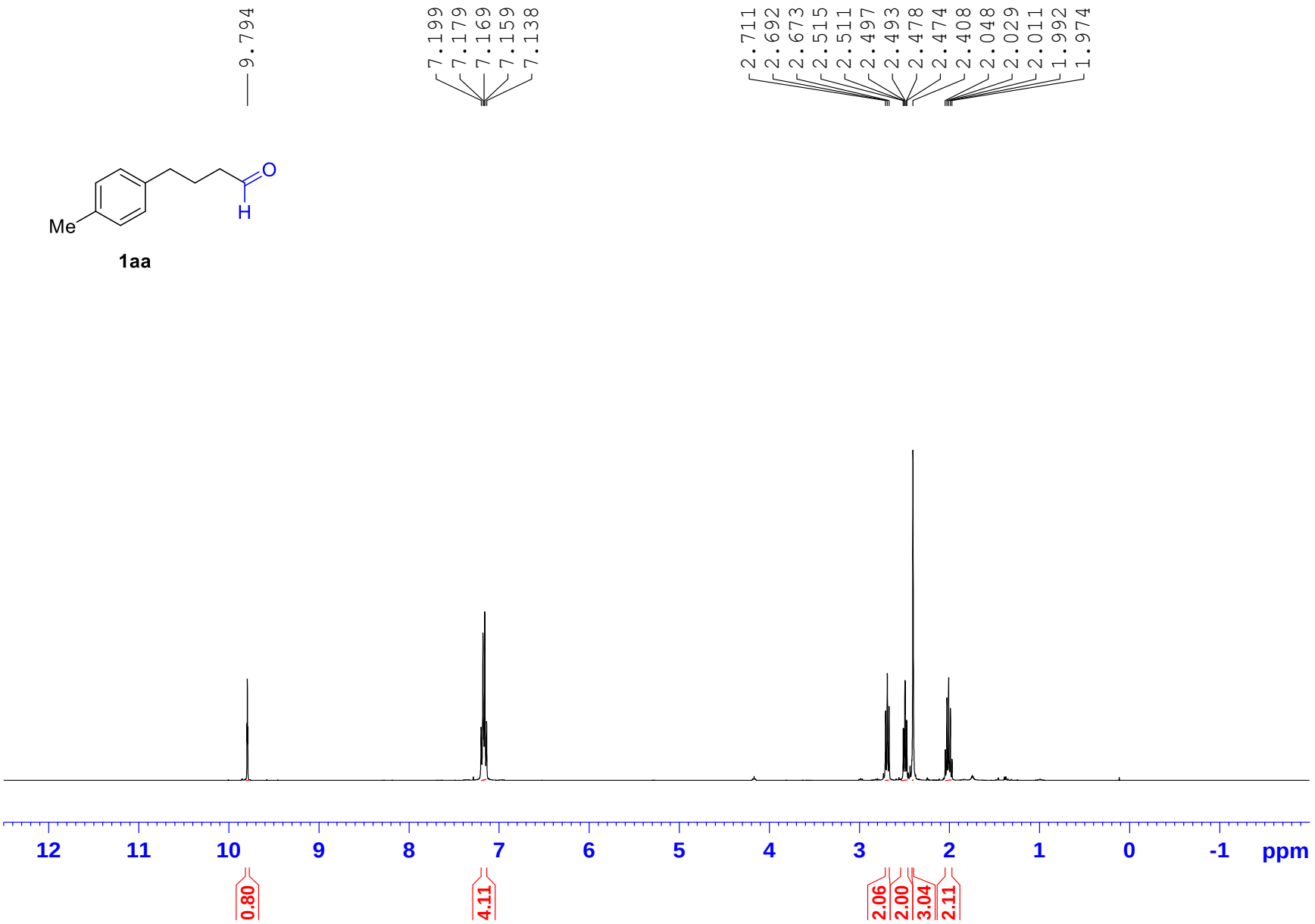
1x

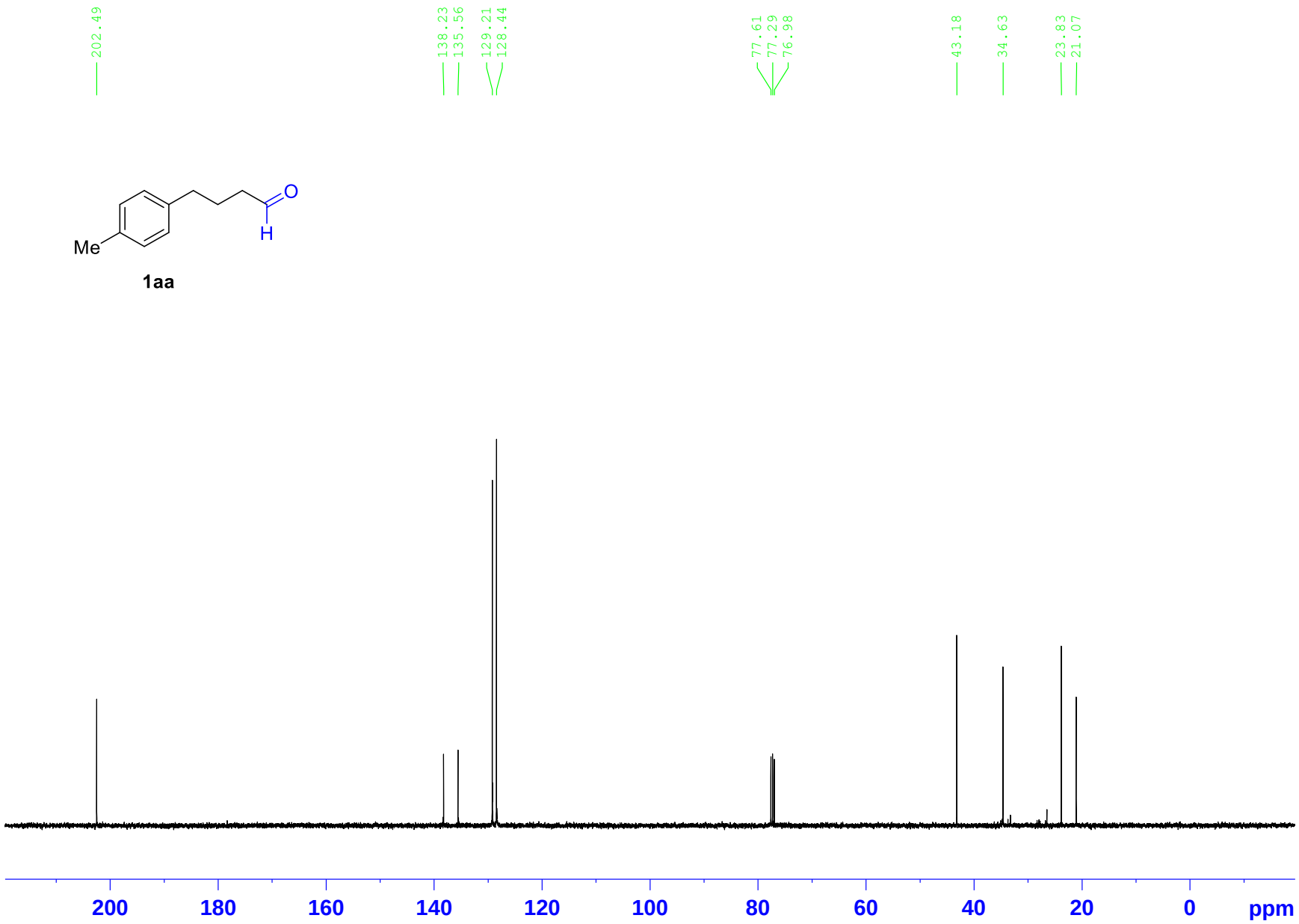

9.852
7.712
7.693
7.329
7.286
7.234
7.215
3.142
3.127
3.112
3.074
3.056
3.037
2.877
2.859
2.840
2.715
2.700
2.686
CHO
O
1y
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.96
0.99
0.97
1.00
2.03
2.03
2.00
2.06


206.50
200.69
155.88
148.02
135.60
127.82
126.47
123.96
77.36
77.04
76.72
44.87
36.39
28.37
25.71
CHO
O
1y
200
180
160
140
120
100
80
60
40
20
0
ppm

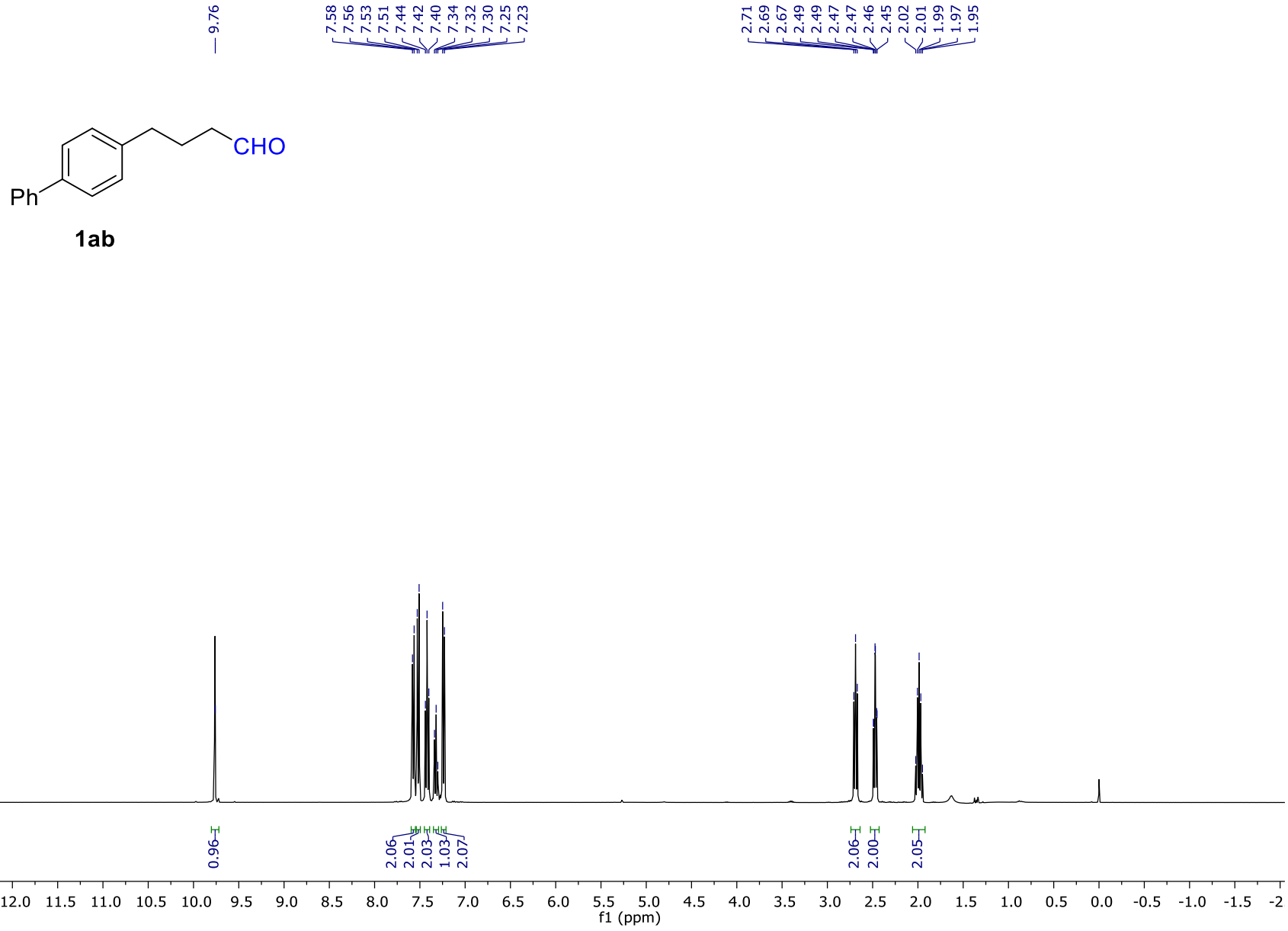

9.720
7.294
7.276
7.257
7.221
7.202
7.199
7.184
7.178
7.168
7.150
2.655
2.636
2.617
2.441
2.437
2.423
2.419
2.404
2.401
1.976
1.958
1.939
1.920
1.902
O
H
1z
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
2.01
2.98
2.05
2.00
2.03

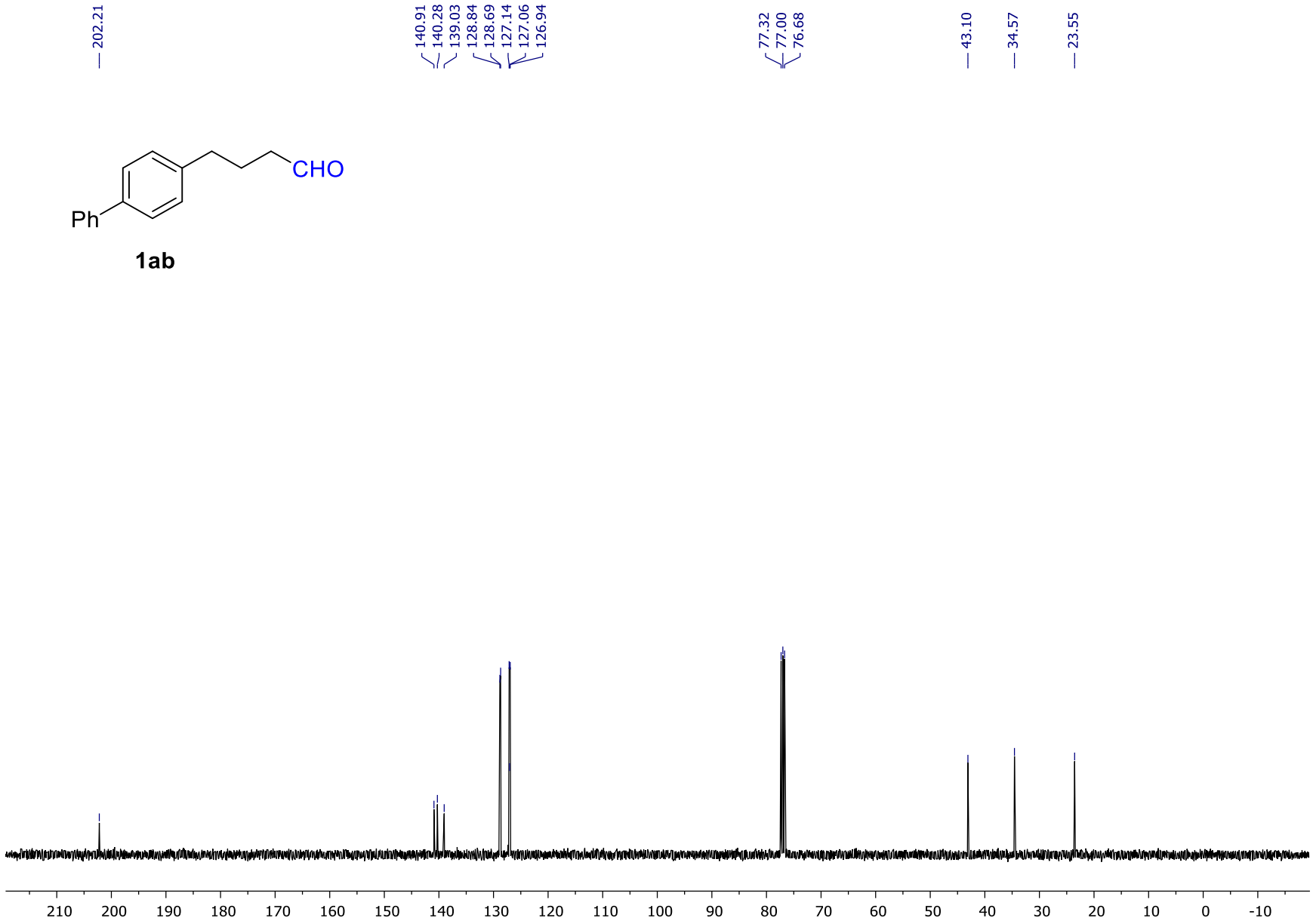

202.34
141.28
128.51
128.50
126.14
77.50
77.18
76.86
43.16
35.03
23.69
O
H
1z
200
180
160
140
120
100
80
60
40
20
0
ppm

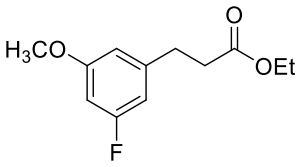

9.794
7.199
7.179
7.169
7.159
7.138
2.711
2.692
2.673
2.515
2.511
2.497
2.493
2.478
2.474
2.408
2.048
2.029
2.011
1.992
1.974
O
H
Me
1aa
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.80
4.11
2.06
2.00
3.04
2.11


202.49
138.23
135.56
129.21
128.44
77.61
77.29
76.98
43.18
34.63
23.83
21.07
O
H
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

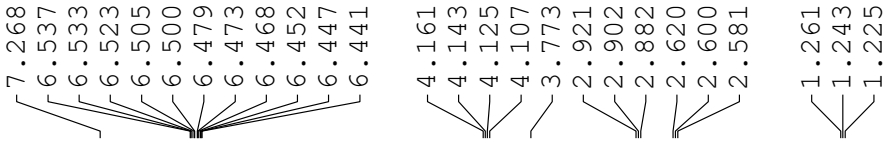
1aa

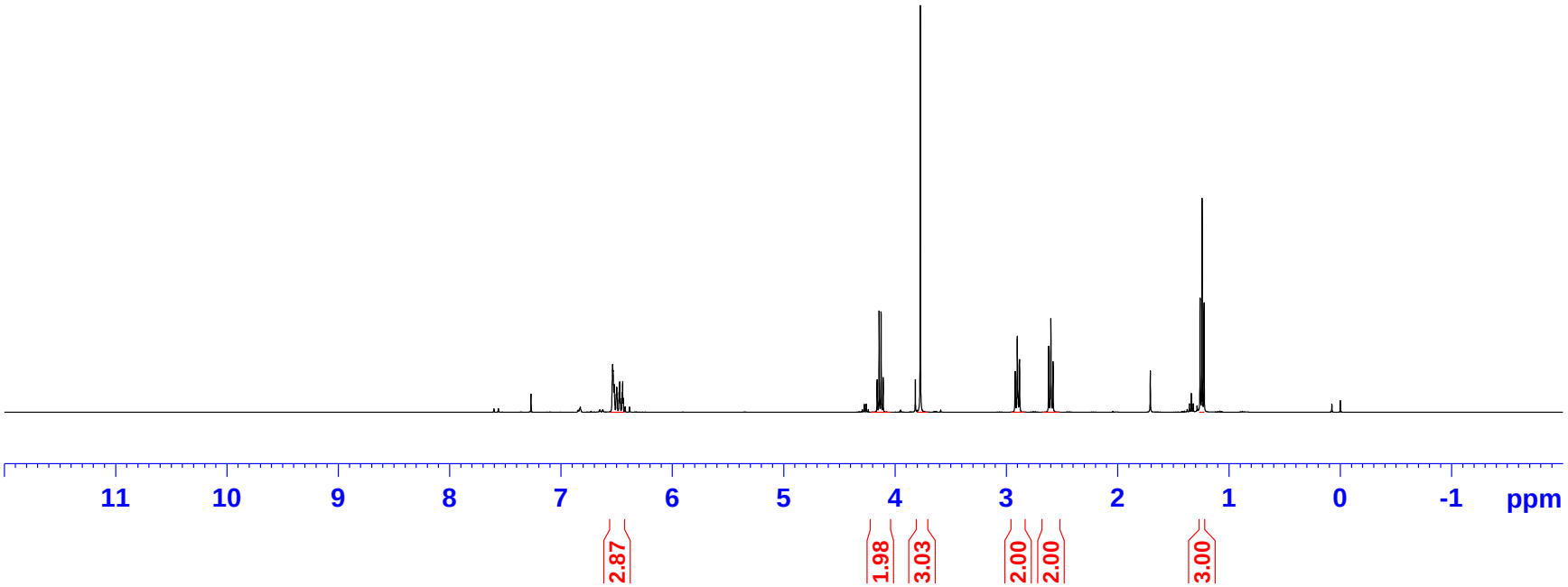

9.76
7.58
7.56
7.53
7.51
7.44
7.42
7.40
7.34
7.32
7.30
7.25
7.23
2.71
2.69
2.67
2.49
2.49
2.47
2.47
2.46
2.45
2.02
2.01
1.99
1.97
1.95
CHO
Ph
1ab
0.96
2.06
2.01
2.03
1.03
2.07
2.06
2.00
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)

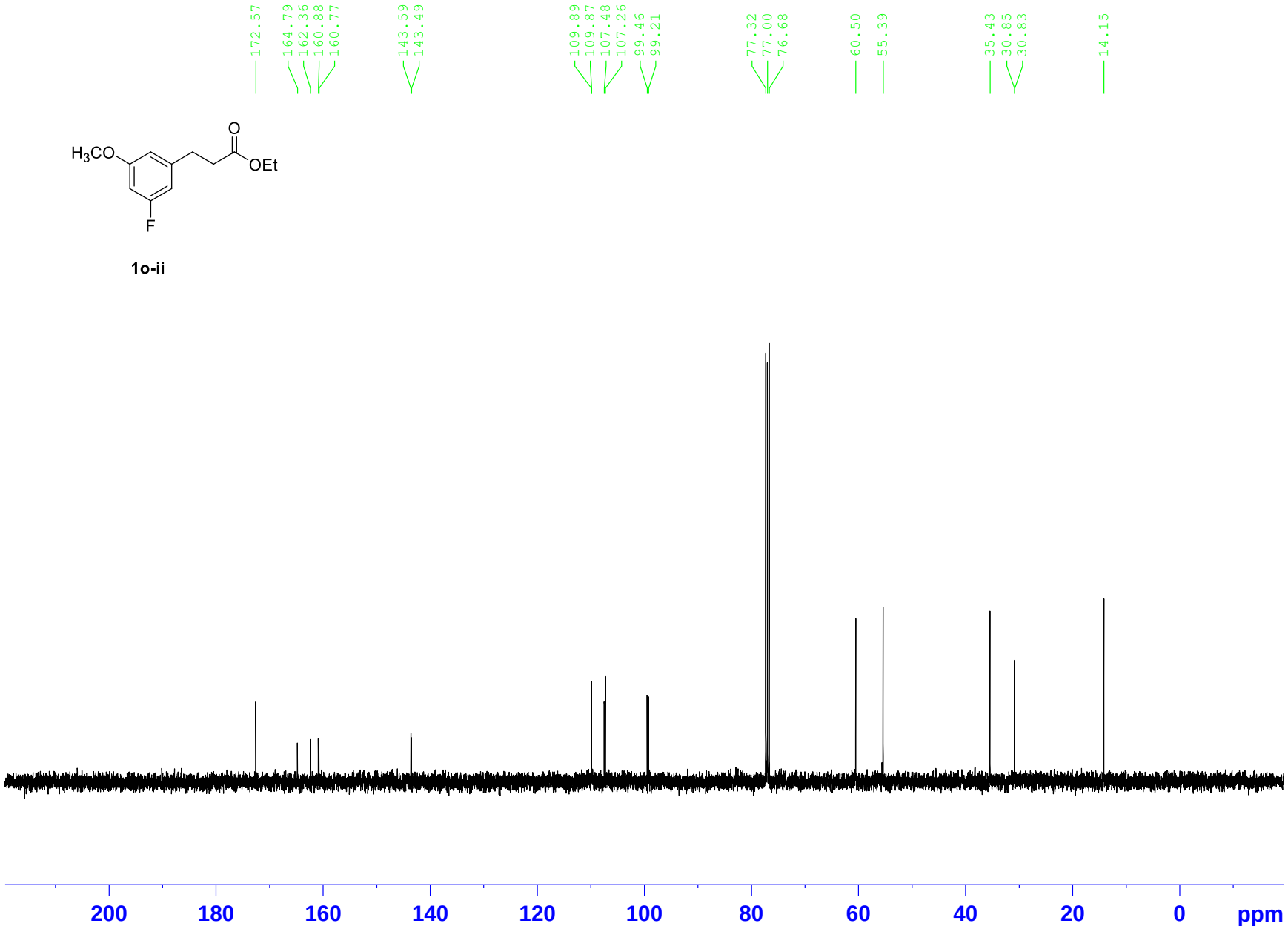

202.21
140.91
140.28
139.03
128.84
128.69
127.14
127.06
126.94
77.32
77.00
76.68
43.10
34.57
23.55
CHO
Ph
1ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

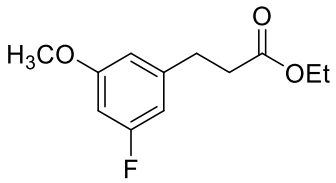

H3CO
O
OEt
F

1o-ii

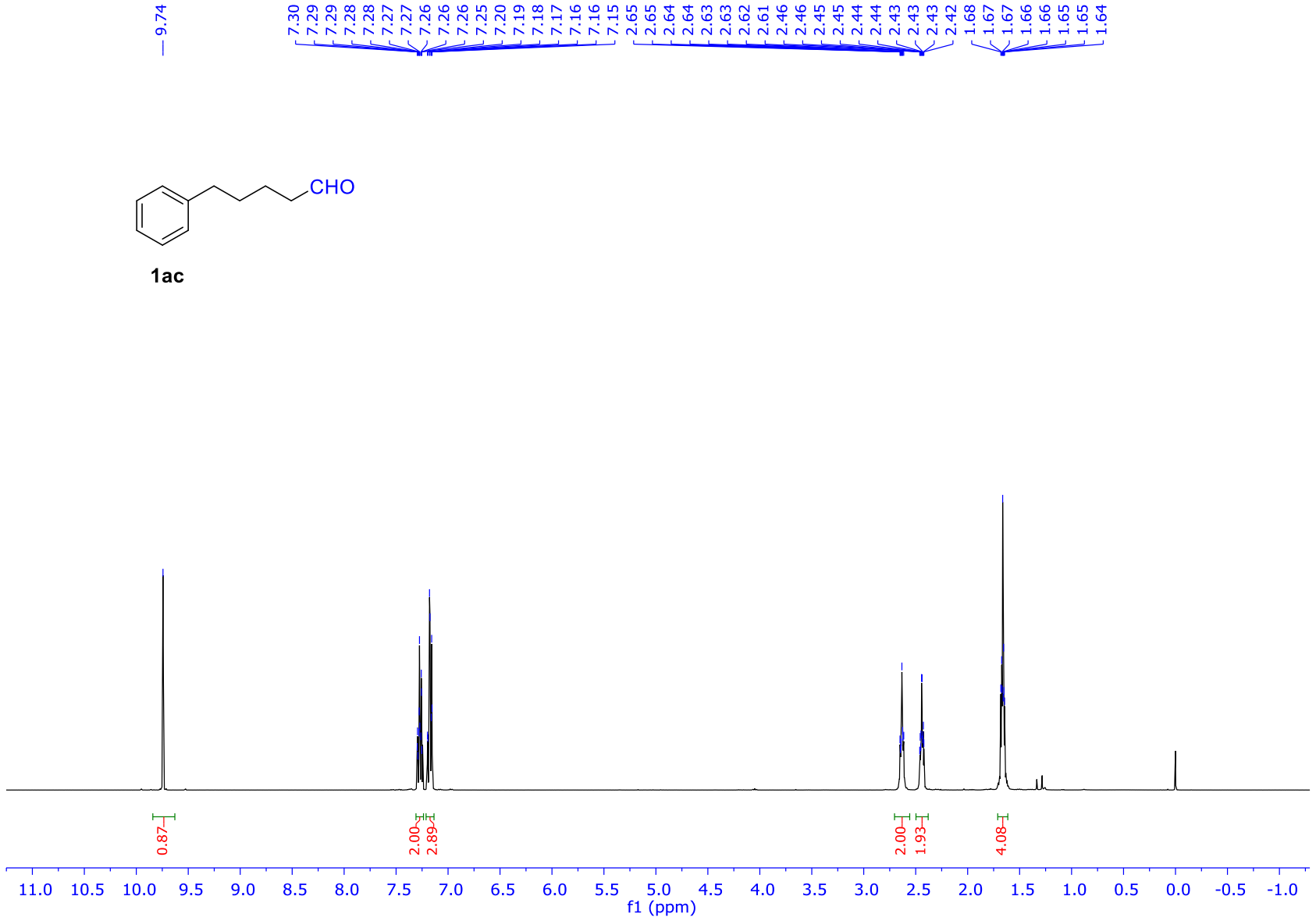

7.268
6.537
6.533
6.523
6.505
6.500
6.479
6.473
6.468
6.452
6.447
6.441
4.161
4.143
4.125
4.107
3.773
2.921
2.902
2.882
2.620
2.600
2.581
1.261
1.243
1.225


11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.87
1.98
3.03
2.00
2.00
3.00

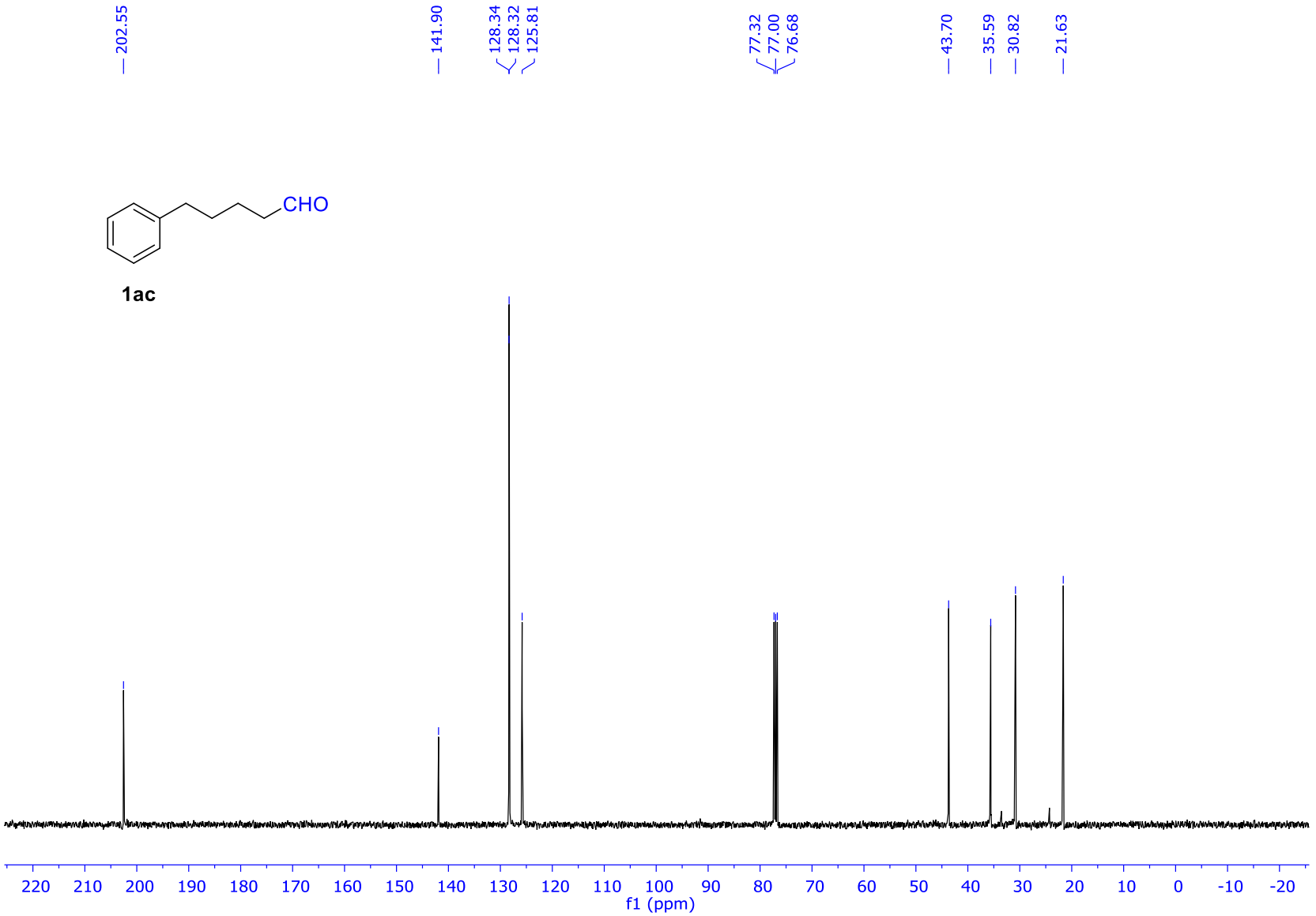

172.57
164.79
162.36
160.88
160.77
143.59
143.49
109.89
109.87
107.48
107.26
99.46
99.21
77.32
77.00
76.68
60.50
55.39
35.43
30.85
30.83
14.15
H3CO
O
OEt
F
1o-ii
200
180
160
140
120
100
80
60
40
20
0
ppm

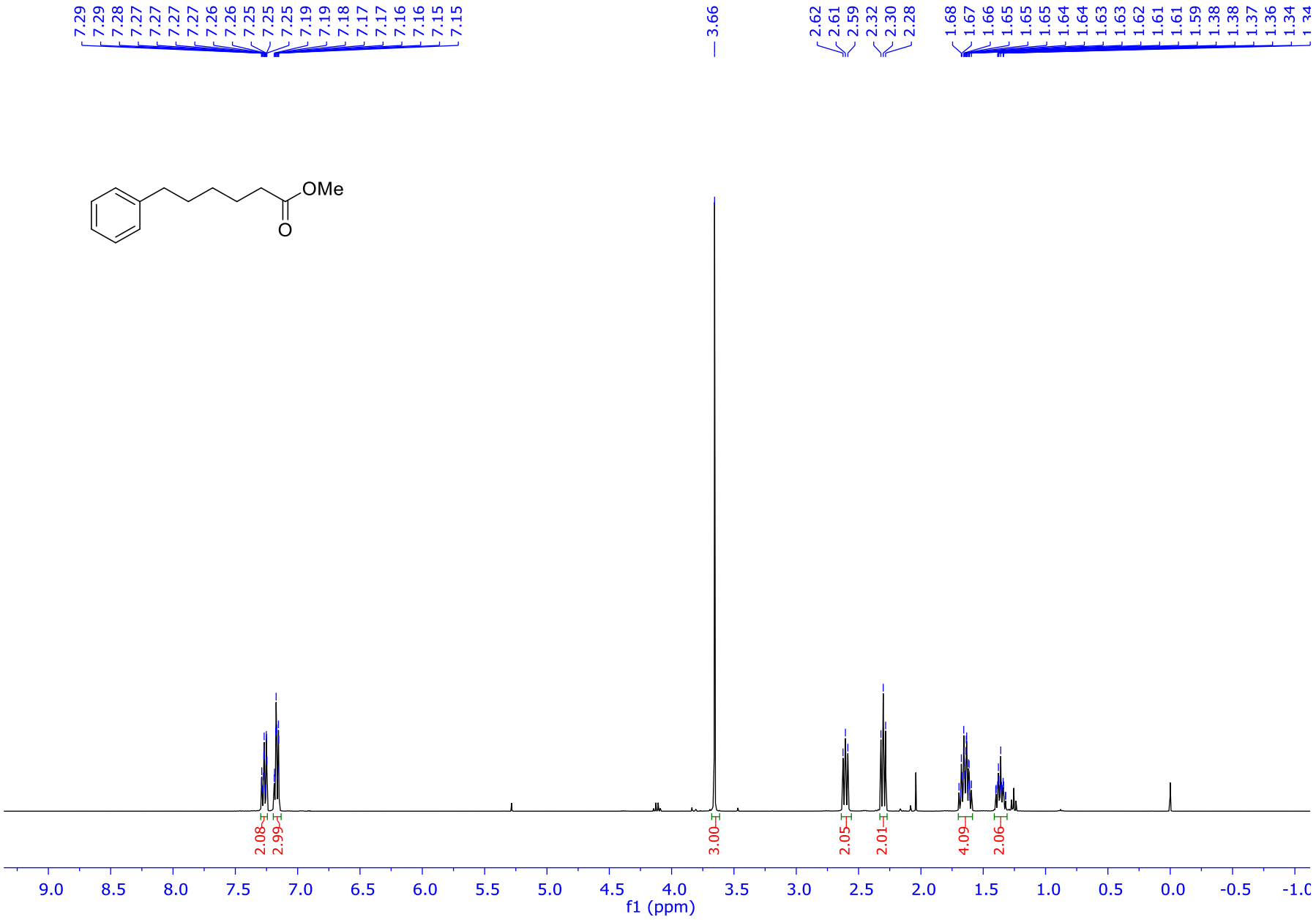


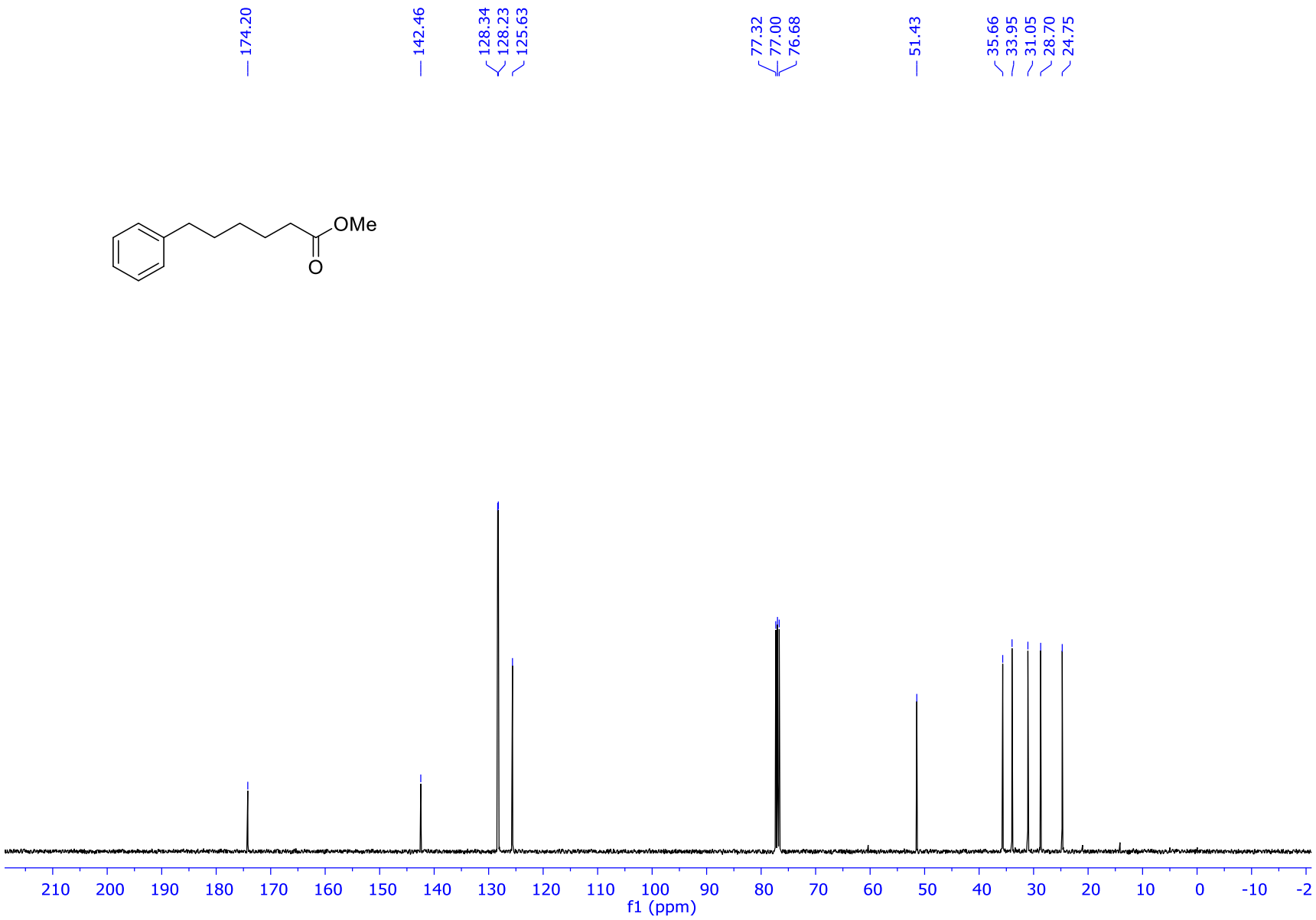
1o-ii


9.74
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.20
7.19
7.18
7.17
7.16
7.16
7.15
2.65
2.65
2.64
2.64
2.63
2.63
2.62
2.61
2.46
2.46
2.45
2.45
2.44
2.44
2.43
2.43
2.42
1.68
1.67
1.67
1.66
1.66
1.65
1.65
1.64
CHO
0.87
2.00
2.89
2.00
1.93
4.08
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)

1ac


202.55
141.90
128.34
128.32
125.81
77.32
77.00
76.68
43.70
35.59
30.82
21.63
CHO
1ac
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)


7.29
7.29
7.28
7.27
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
3.66
2.62
2.61
2.59
2.32
2.30
2.28
1.68
1.67
1.66
1.65
1.65
1.65
1.64
1.64
1.63
1.63
1.62
1.61
1.61
1.59
1.38
1.38
1.37
1.36
1.34
OMe
O
2.08
2.99
3.00
2.05
2.01
4.09
2.06
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)


174.20
142.46
128.34
128.23
125.63
77.32
77.00
76.68
51.43
35.66
33.95
31.05
28.70
24.75
OMe
O
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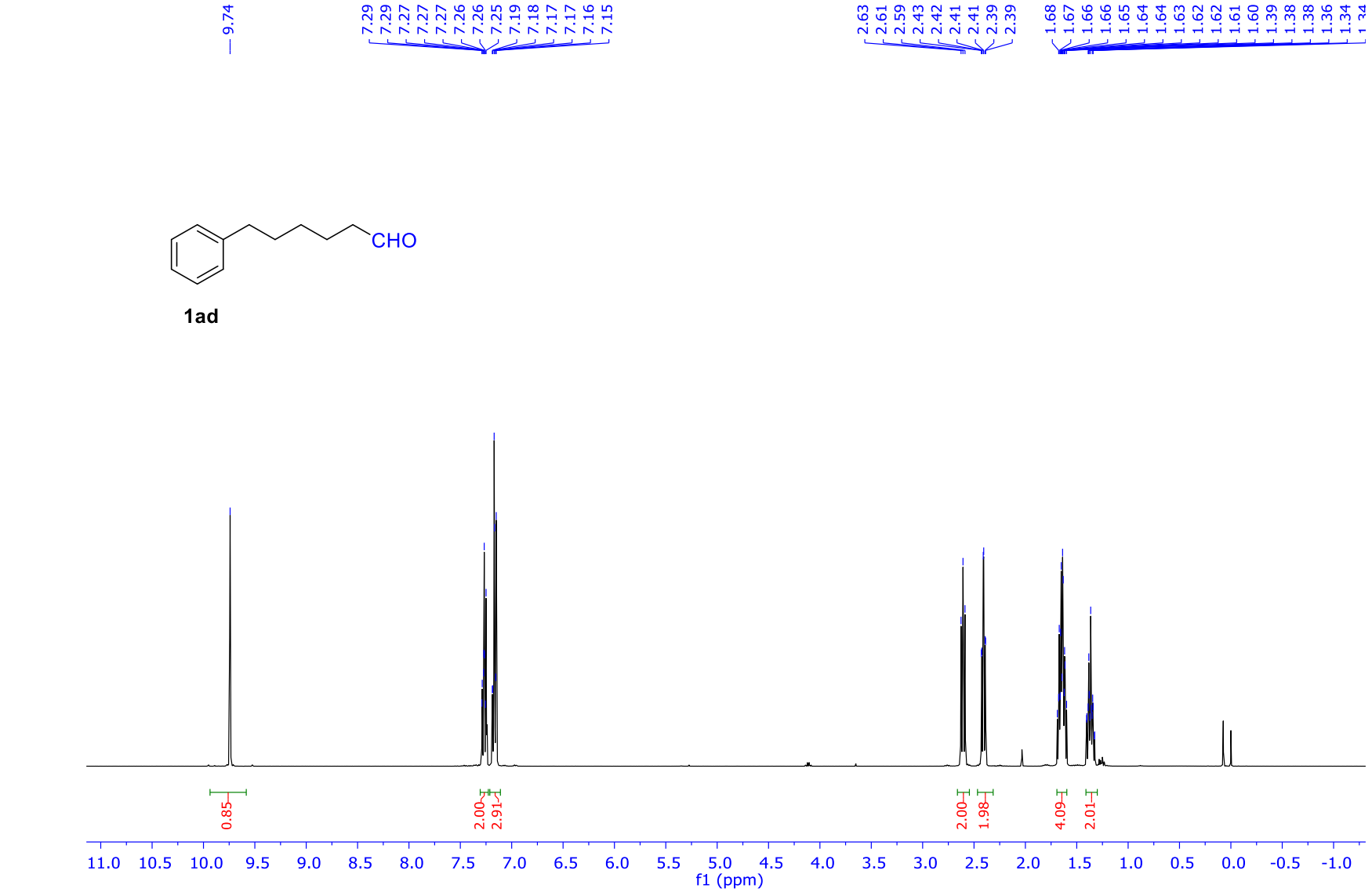
f1 (ppm)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7.29
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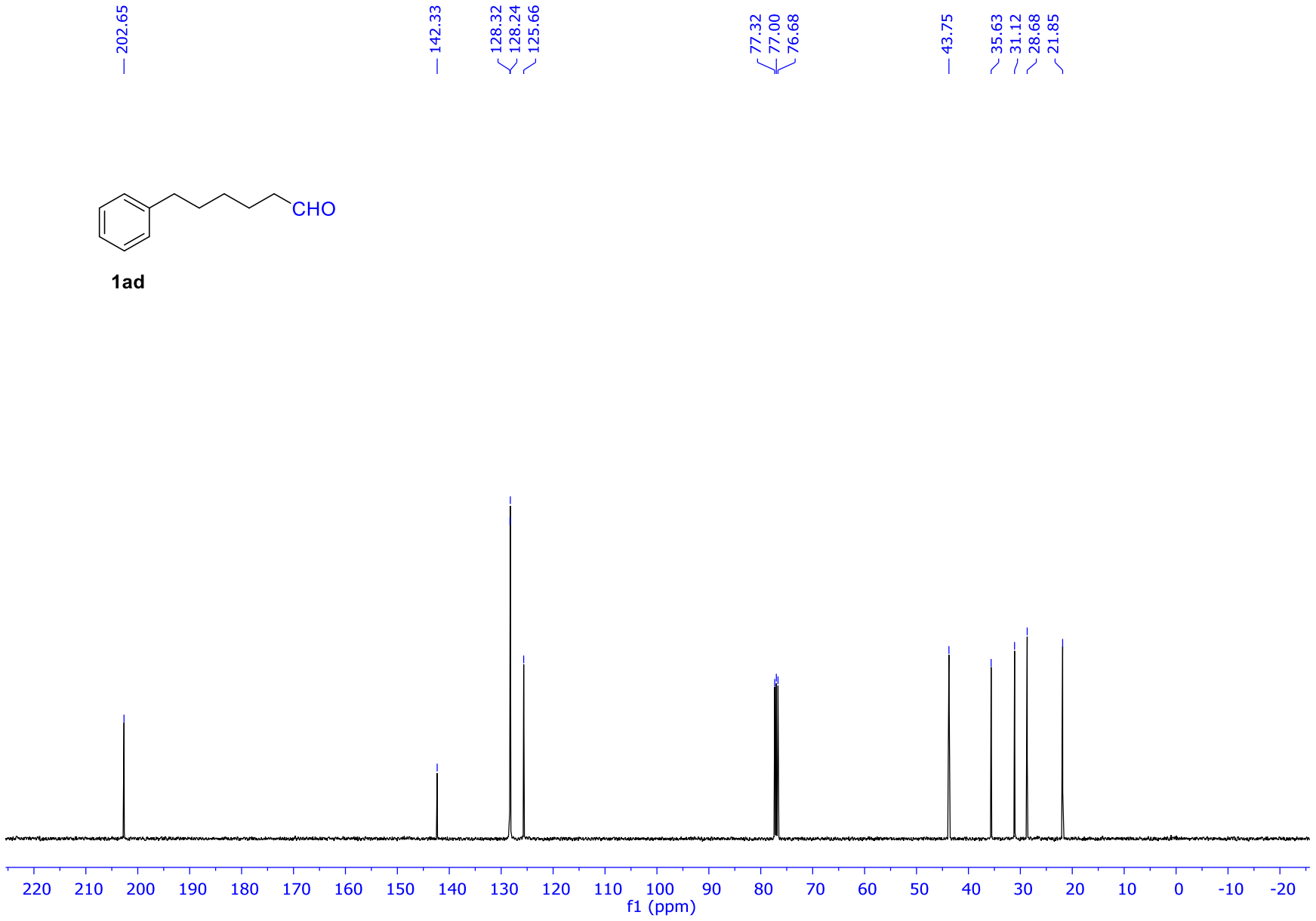
7.19
7.18
7.17
7.17
7.16
7.15
2.63
2.61
2.59
2.43
2.42
2.41
2.41
2.39
2.39
1.68
1.67
1.66
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.61
1.60
1.39
1.38
1.36
1.34
CHO
1ad
0.85
2.00
2.91
2.00
1.98
4.09
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.32
77.00
76.68
43.75
35.63
31.12
28.68
21.85
CHO
1ad
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)


9.71
9.71
7.31
7.31
7.30
7.29
7.29
7.29
7.27
7.27
7.27
7.27
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15


3.11
3.09
3.07
3.06
2.70
2.69
2.69
2.68
2.68
2.67
2.67
2.66
2.66
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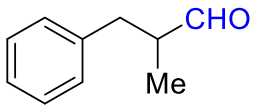
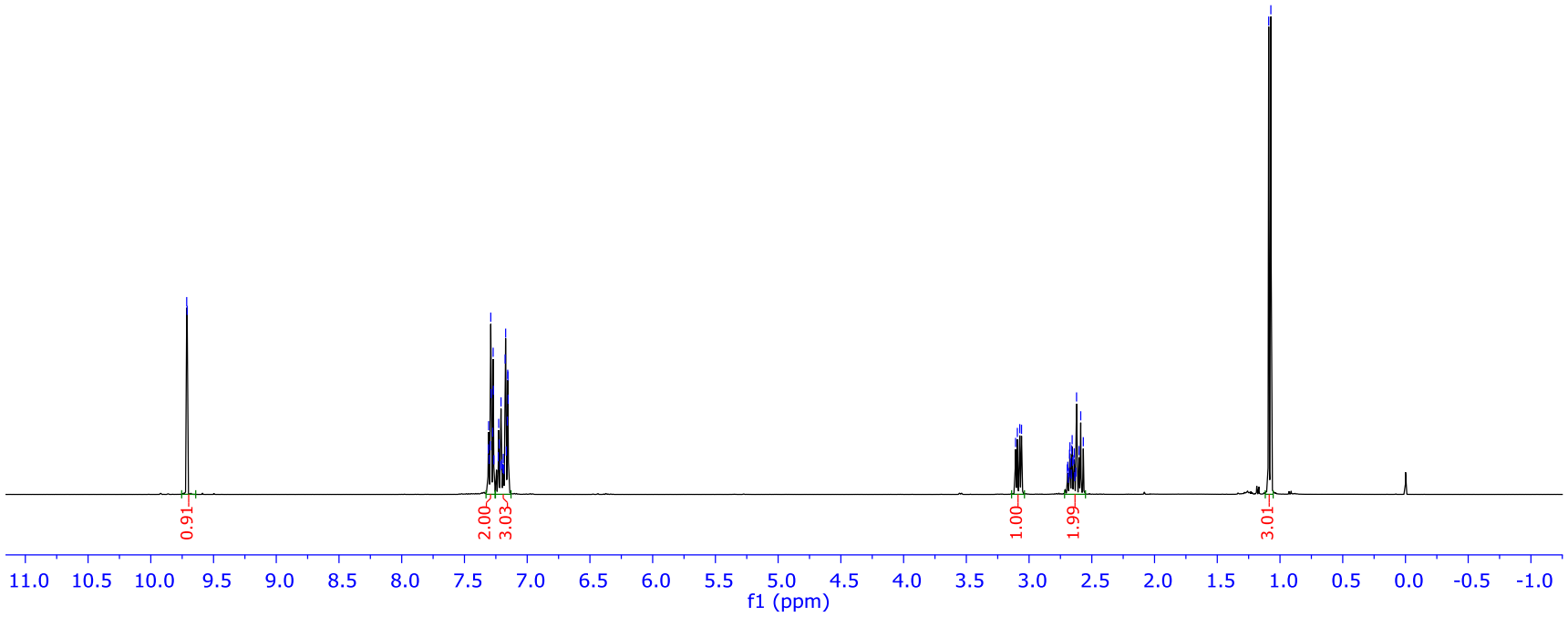
2.60
2.59
2.57
1.09
1.07


CHO
Me

1ae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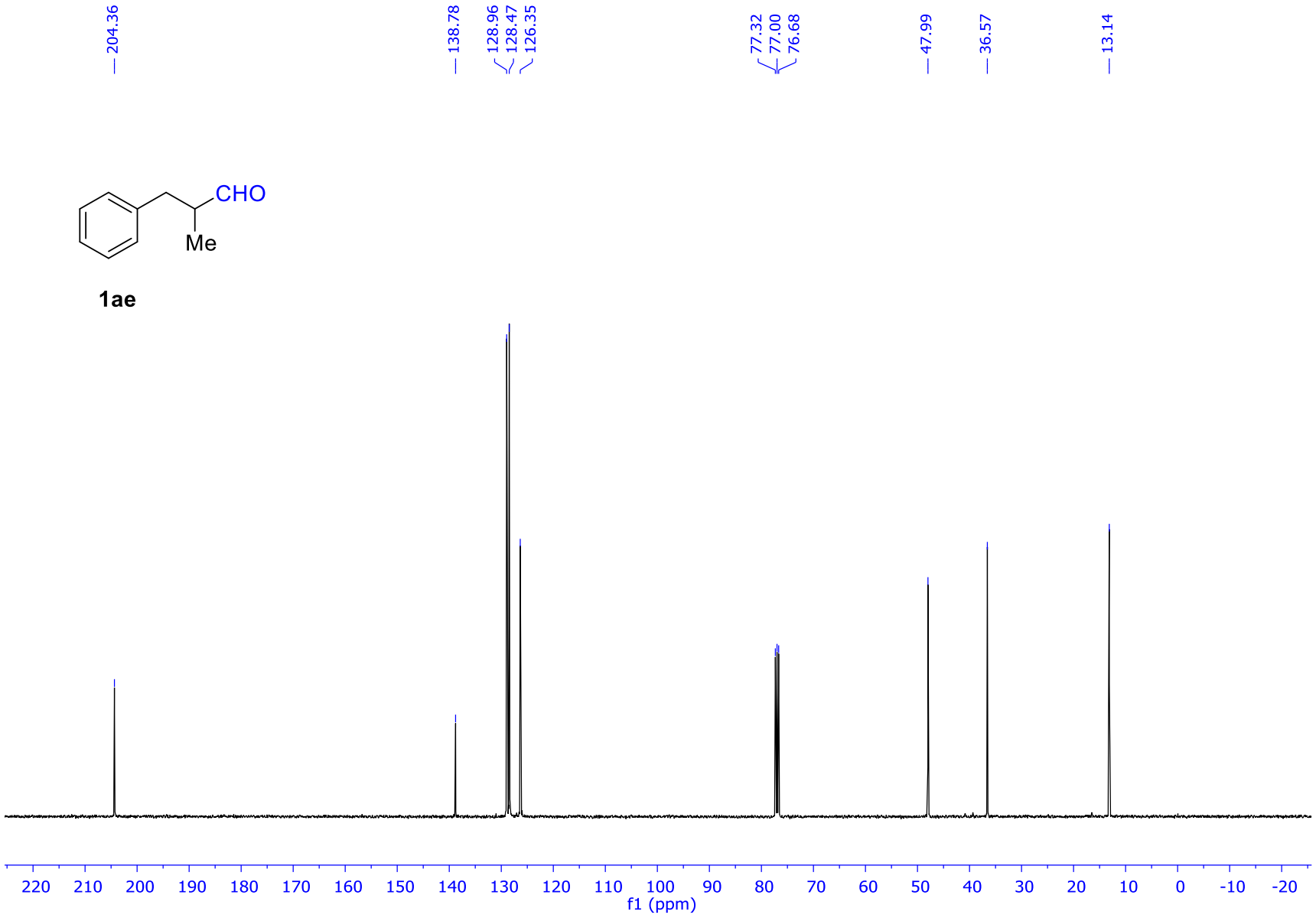
3.03
1.00
1.99
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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128.47
126.35
77.32
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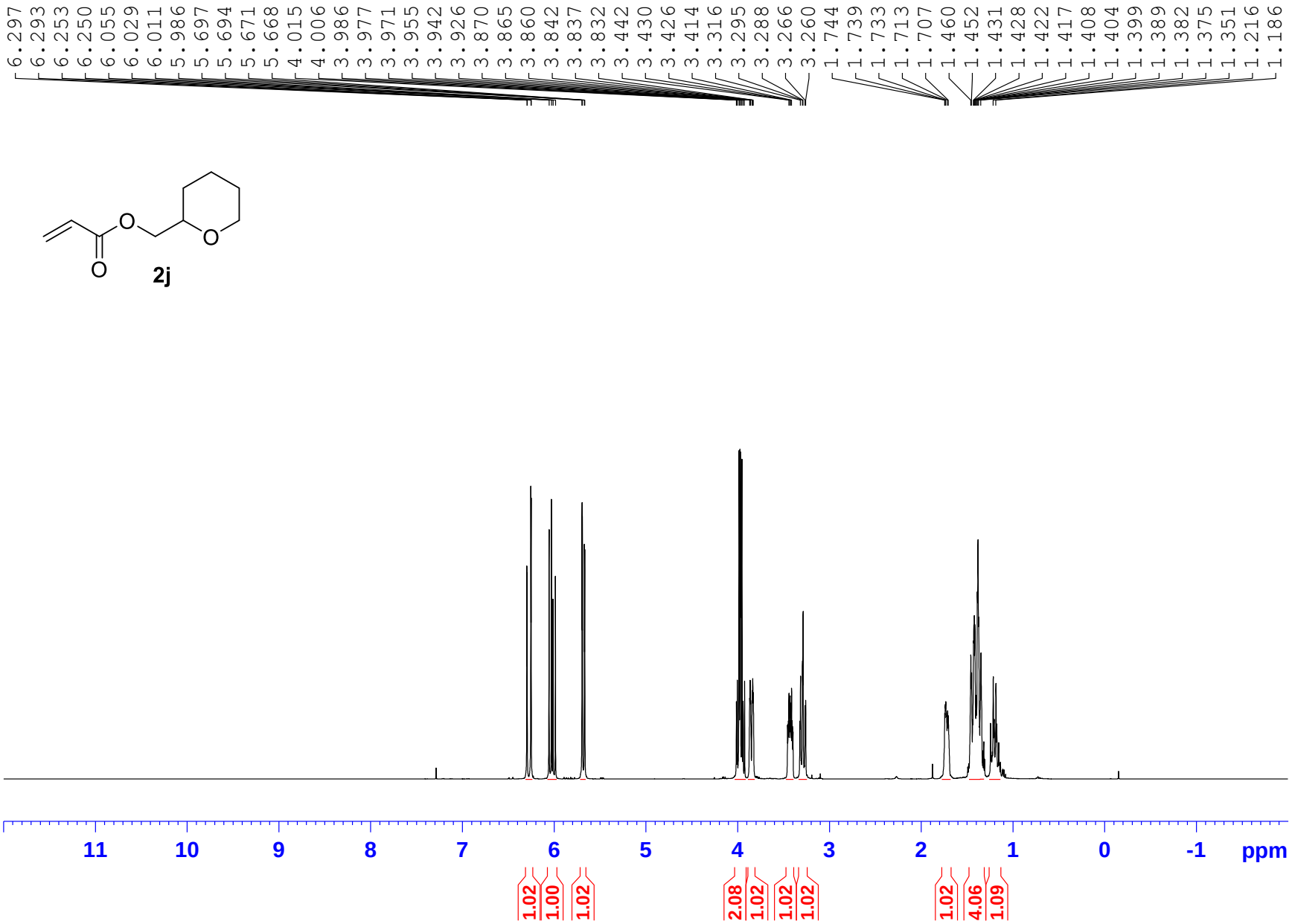
76.68
47.99
36.57
13.14
CHO
Me
1ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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6.250
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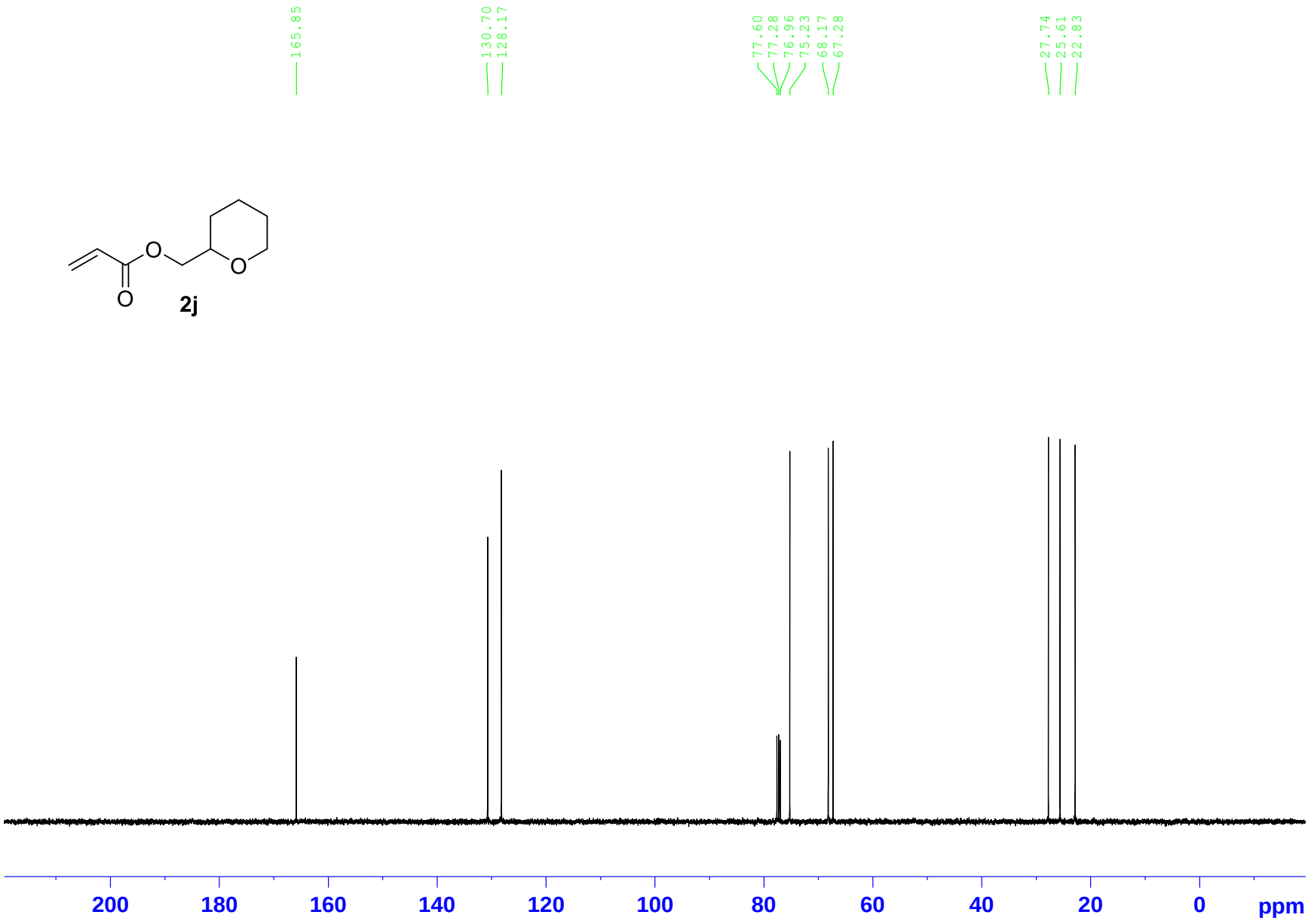
6.029
6.011
5.986
5.697
5.694
5.671
5.668
4.015
4.006
3.986
3.977
3.971
3.955
3.942
3.926
3.870
3.865
3.860
3.842
3.837
3.832
3.442
3.430
3.426
3.414
3.316
3.295
3.288
3.266
3.260
1.744
1.739
1.733
1.713
1.707
1.460
1.452
1.431
1.428
1.422
1.417
1.408
1.404
1.399
1.389
1.382
1.375
1.351
1.216
1.186
O
O
O
2j
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.00
1.02
2.08
1.02
1.02
1.02
1.02
4.06
1.09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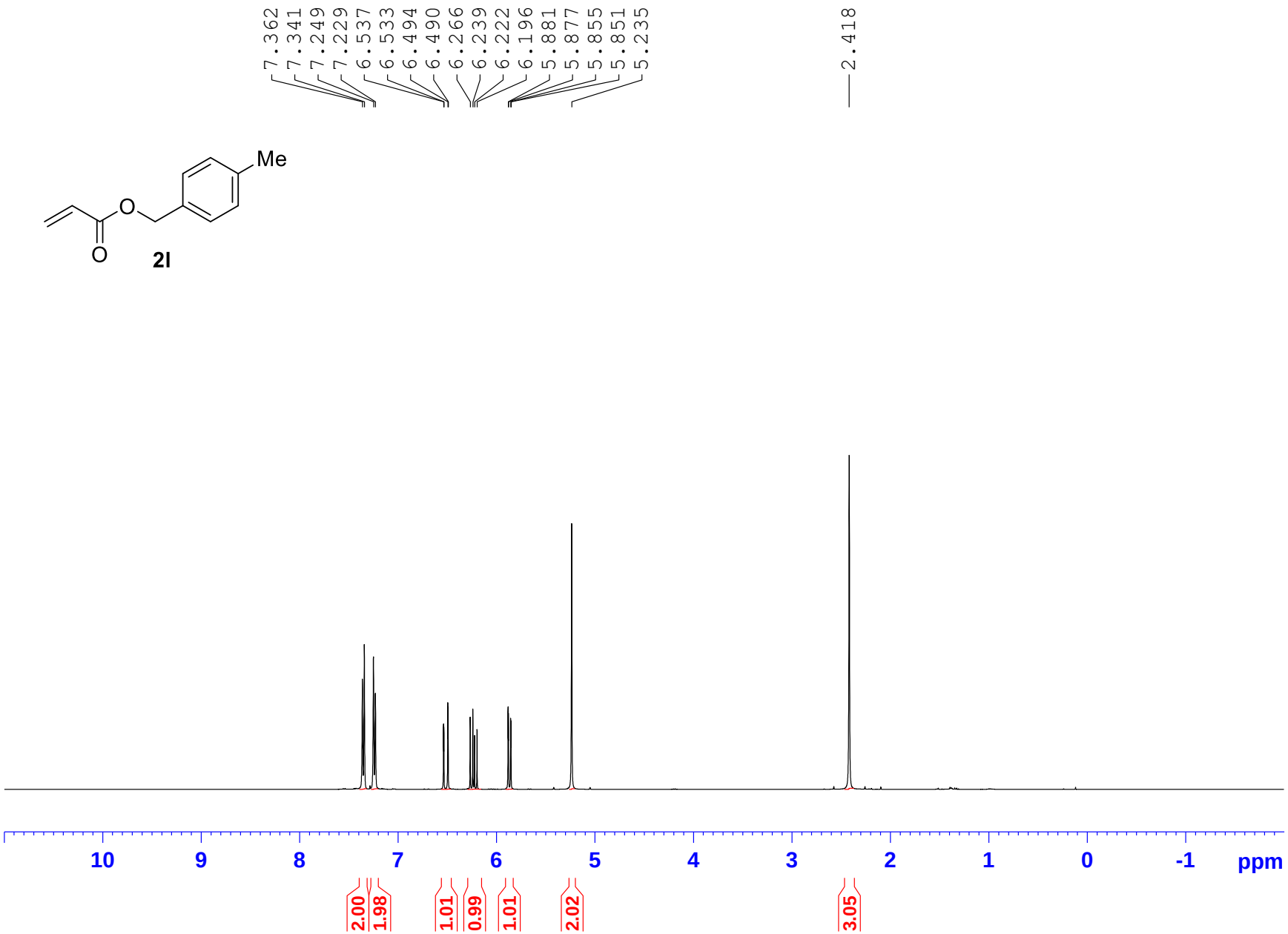
130.70
128.17
77.60
77.28
76.96
75.23
68.17
67.28
27.74
25.61
22.83
O
O
O
2j
200
180
160
140
120
100
80
60
40
20
0
ppm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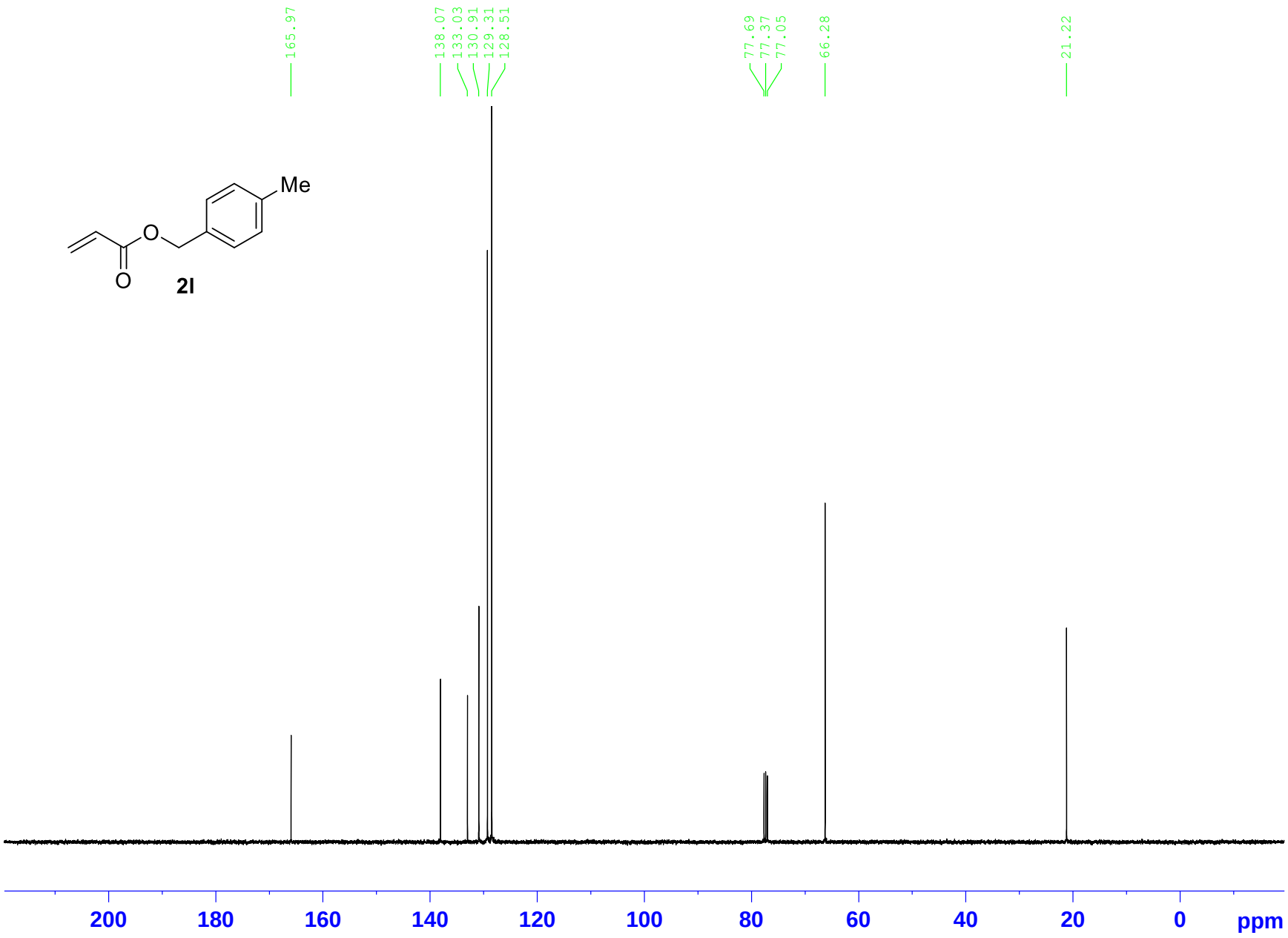
7.249
7.229
6.537
6.533
6.494
6.490
6.266
6.239
6.222
6.196
5.881
5.877
5.855
5.851
5.235
2.418
Me
O
O
2l
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
1.98
1.01
0.99
1.01
2.02
3.05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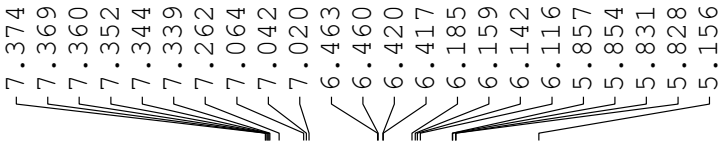
138.07
133.03
130.91
129.31
128.51
77.69
77.37
77.05
66.28
21.22
Me
O
O
2l
200
180
160
140
120
100
80
60
40
20
0
ppm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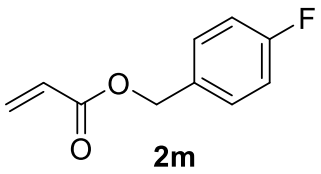
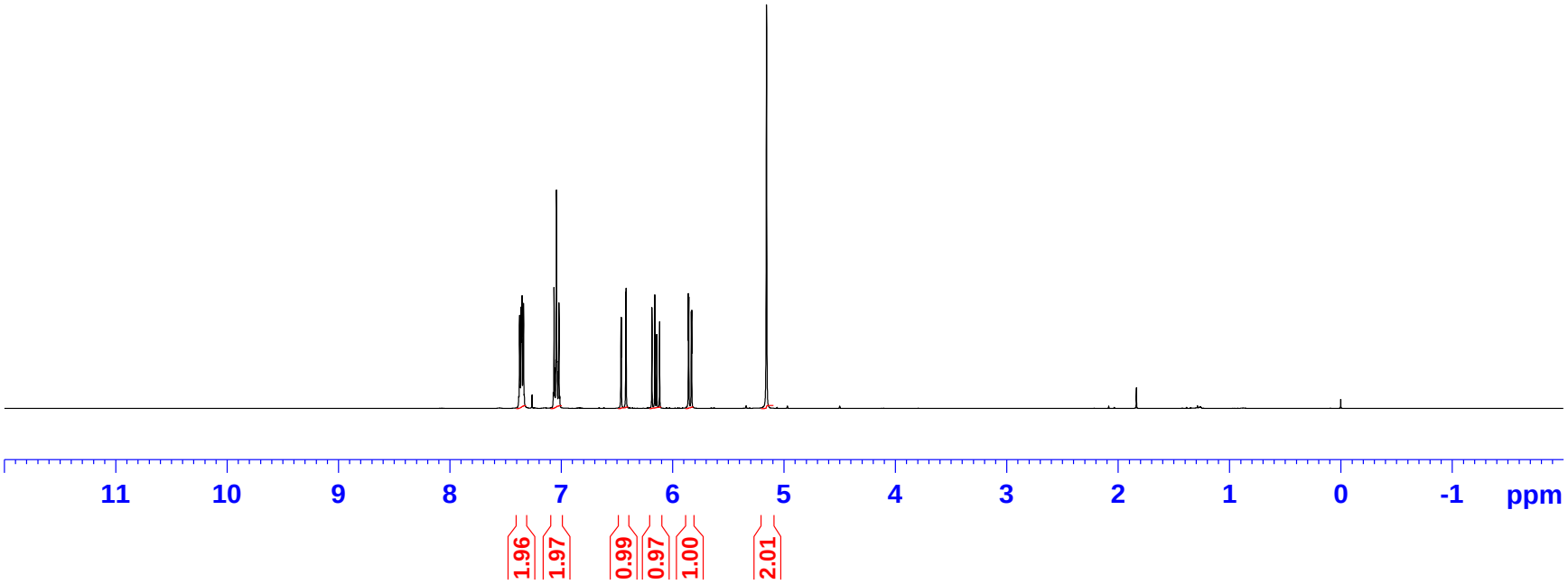
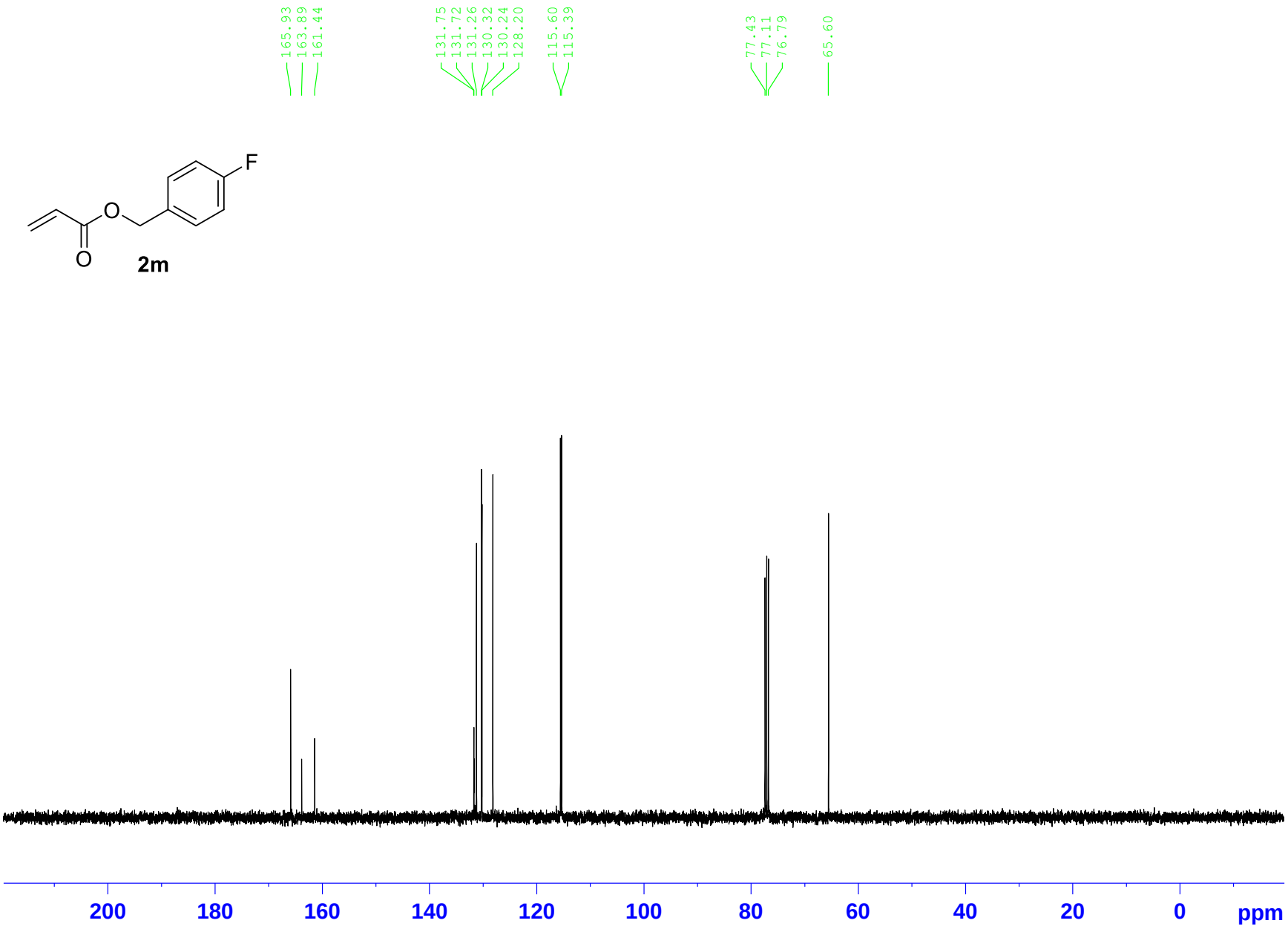
7.344
7.339
7.262
7.064
7.042
7.020
6.463
6.460
6.420
6.417
6.185
6.159
6.142
6.116
5.857
5.854
5.831
5.828
5.156


F
O
O

2m


11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.96
1.97
0.99
0.97
1.00
2.01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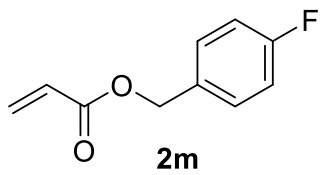
131.72
131.26
130.32
130.24
128.20
115.60
115.39
77.43
77.11
76.79
65.60
F
O
O
2m
200
180
160
140
120
100
80
60
40
20
0
ppm



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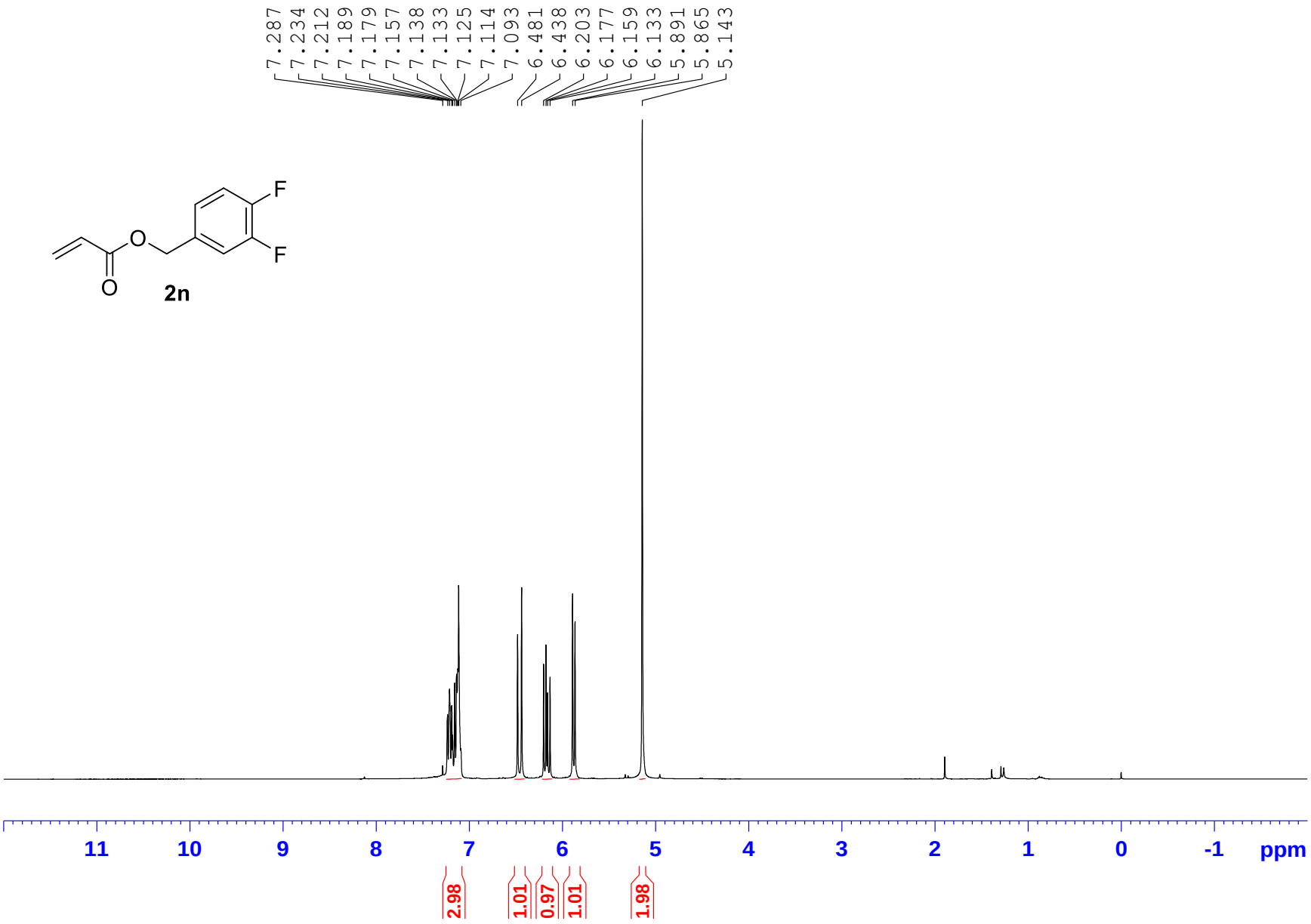
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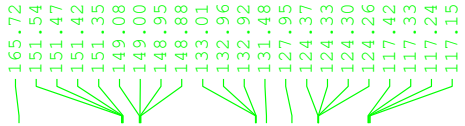
7.157
7.138
7.133
7.125
7.114
7.093
6.481
6.438
6.203
6.177
6.159
6.133
5.891
5.865
5.143
F
F
O
O
2n
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.98
1.01
0.97
1.01
1.98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132.92
131.48
127.95
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124.30
124.26
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117.24
117.15
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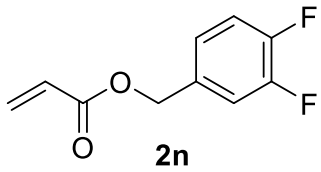
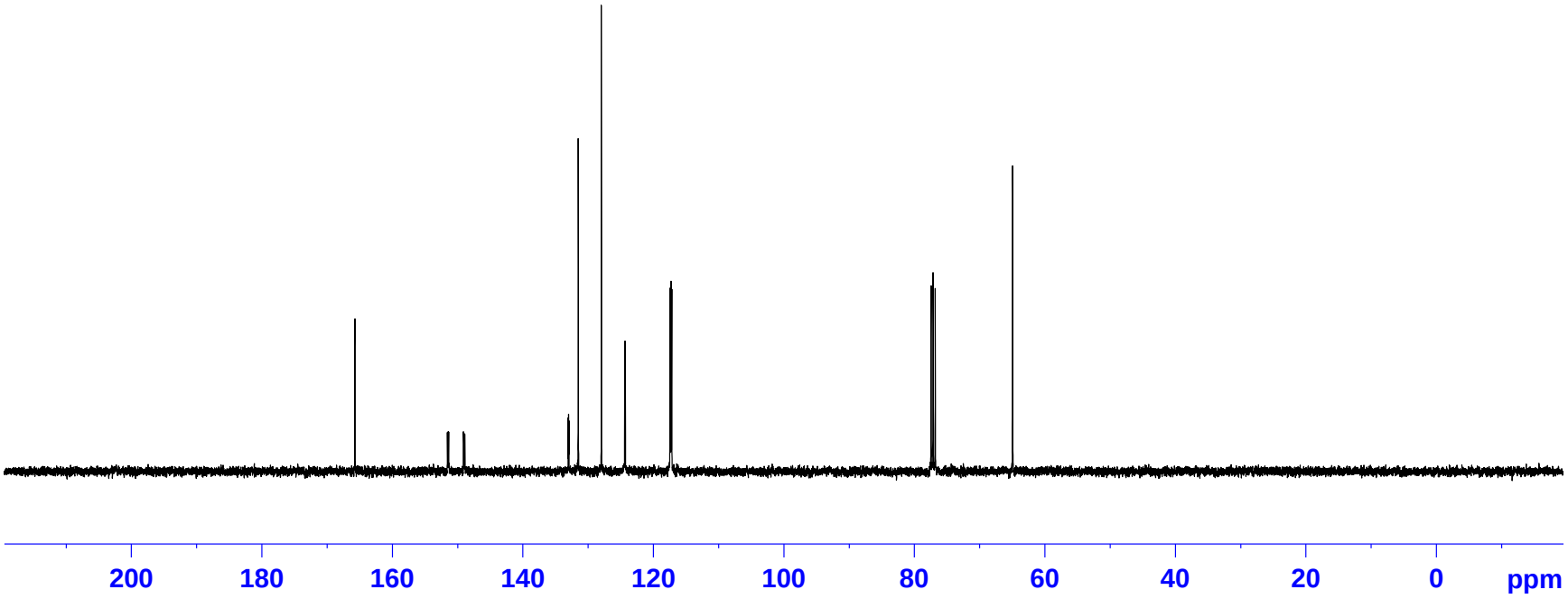
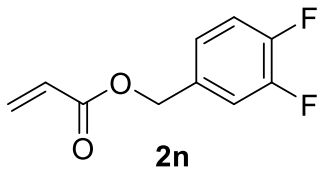
77.09
76.77
64.91


F
F
O
O

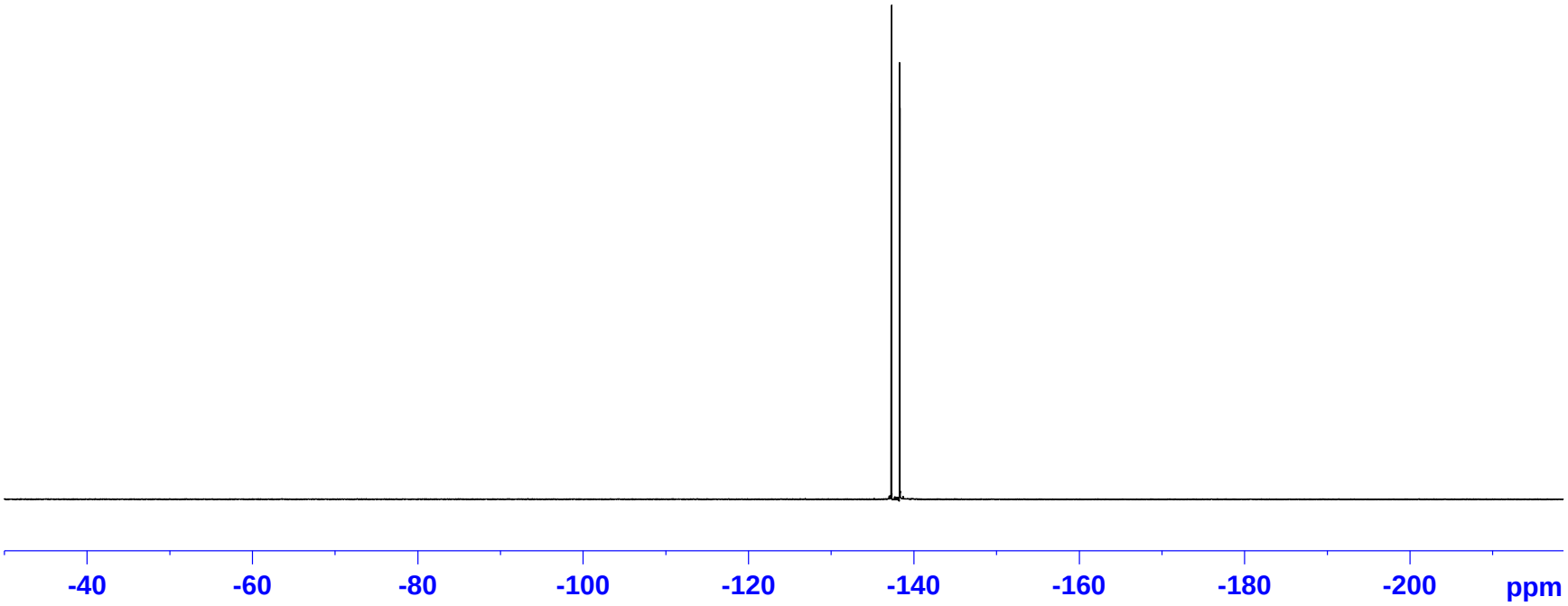
2n

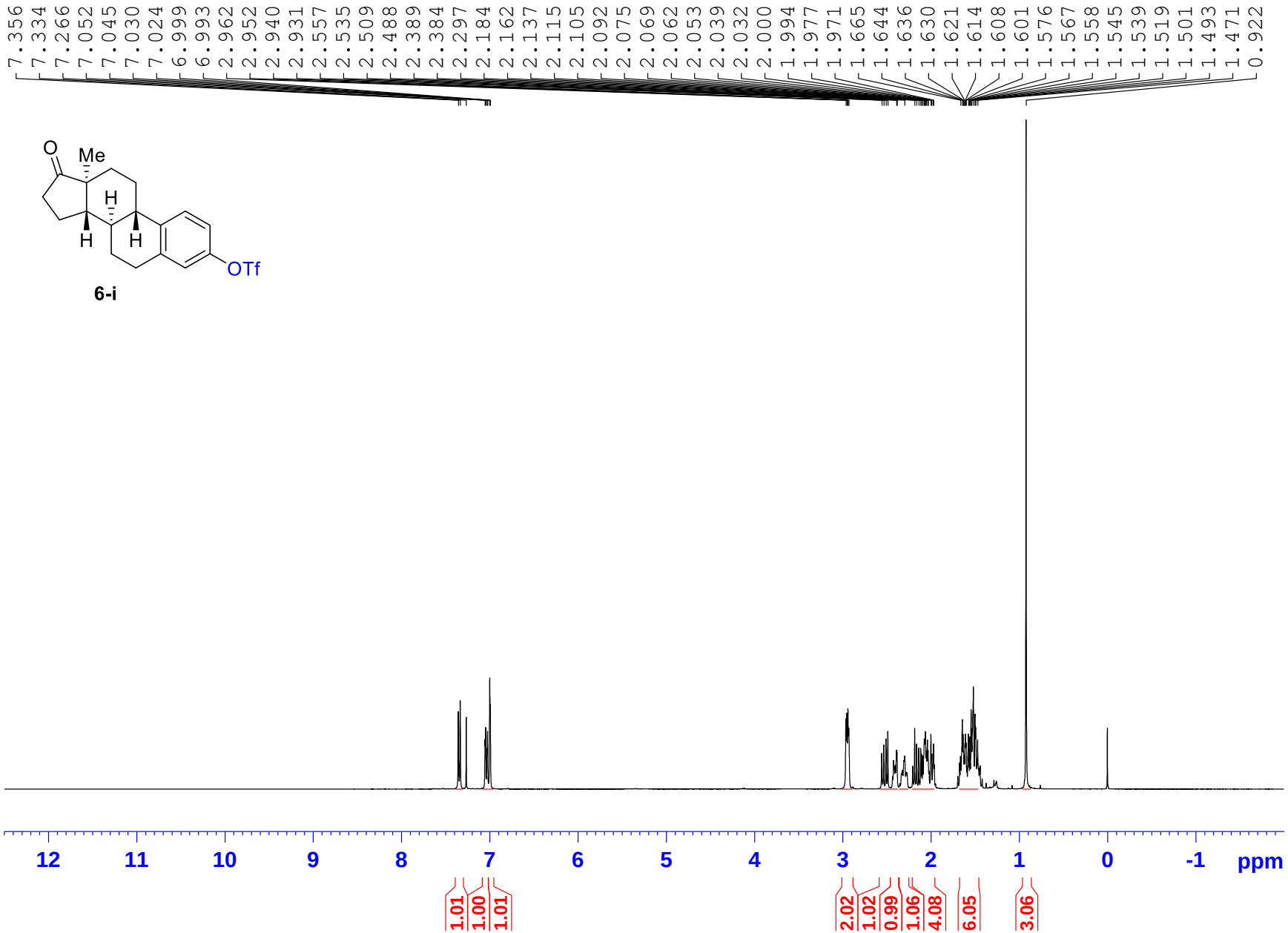

200
180
160
140
120
100
80
60
40
20
0
ppm



2n

-137.223
-137.280
-138.249
-138.305

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2.931
2.557
2.535
2.509
2.488
2.389
2.384
2.297
2.184
2.162
2.137
2.115
2.105
2.092
2.075
2.069
2.062
2.053
2.039
2.032
2.000
1.994
1.977
1.971
1.665
1.644
1.636
1.630
1.621
1.614
1.608
1.601
1.576
1.567
1.558
1.545
1.539
1.519
1.501
1.493
1.471
0.922
O
Me
H
H
H
OTf
6-i
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.00
1.01
2.02
1.02
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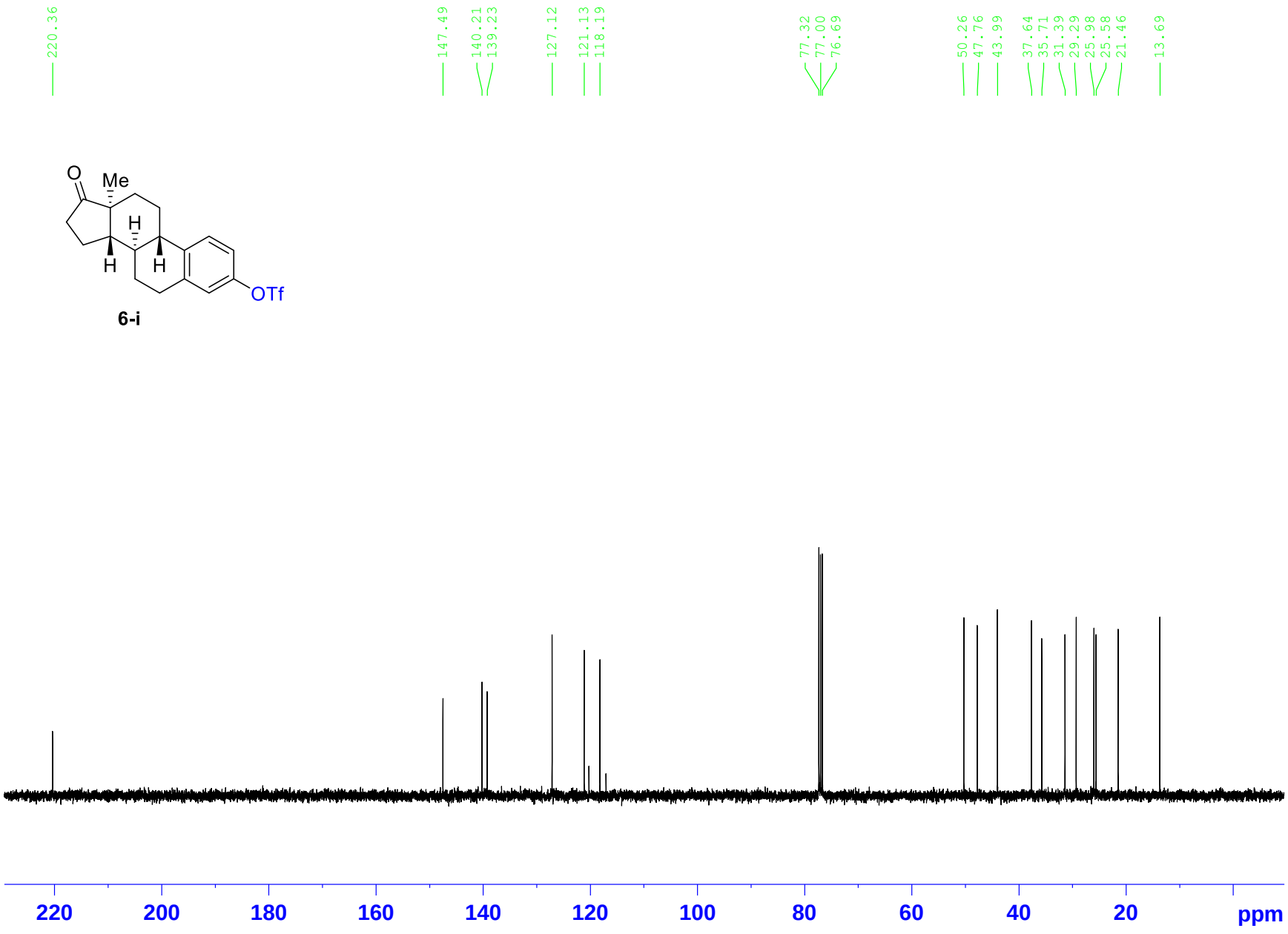
4.08
6.05
3.06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121.13
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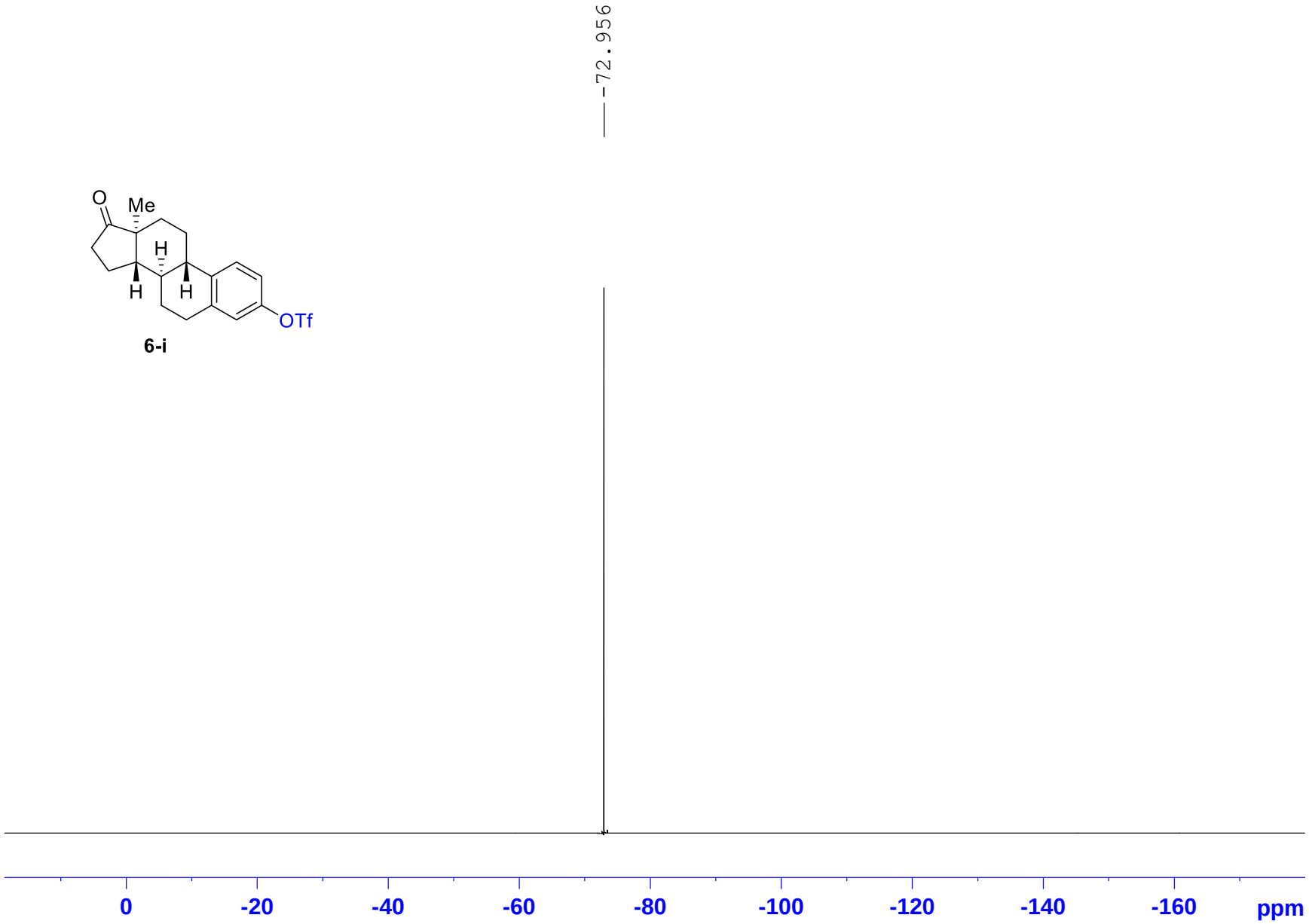
77.32
77.00
76.69
50.26
47.76
43.99
37.64
35.71
31.39
29.29
25.98
25.58
21.46
13.69
O
Me
H
H
H
OTf
6-i
220
200
180
160
140
120
100
80
60
40
20
ppm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OTf
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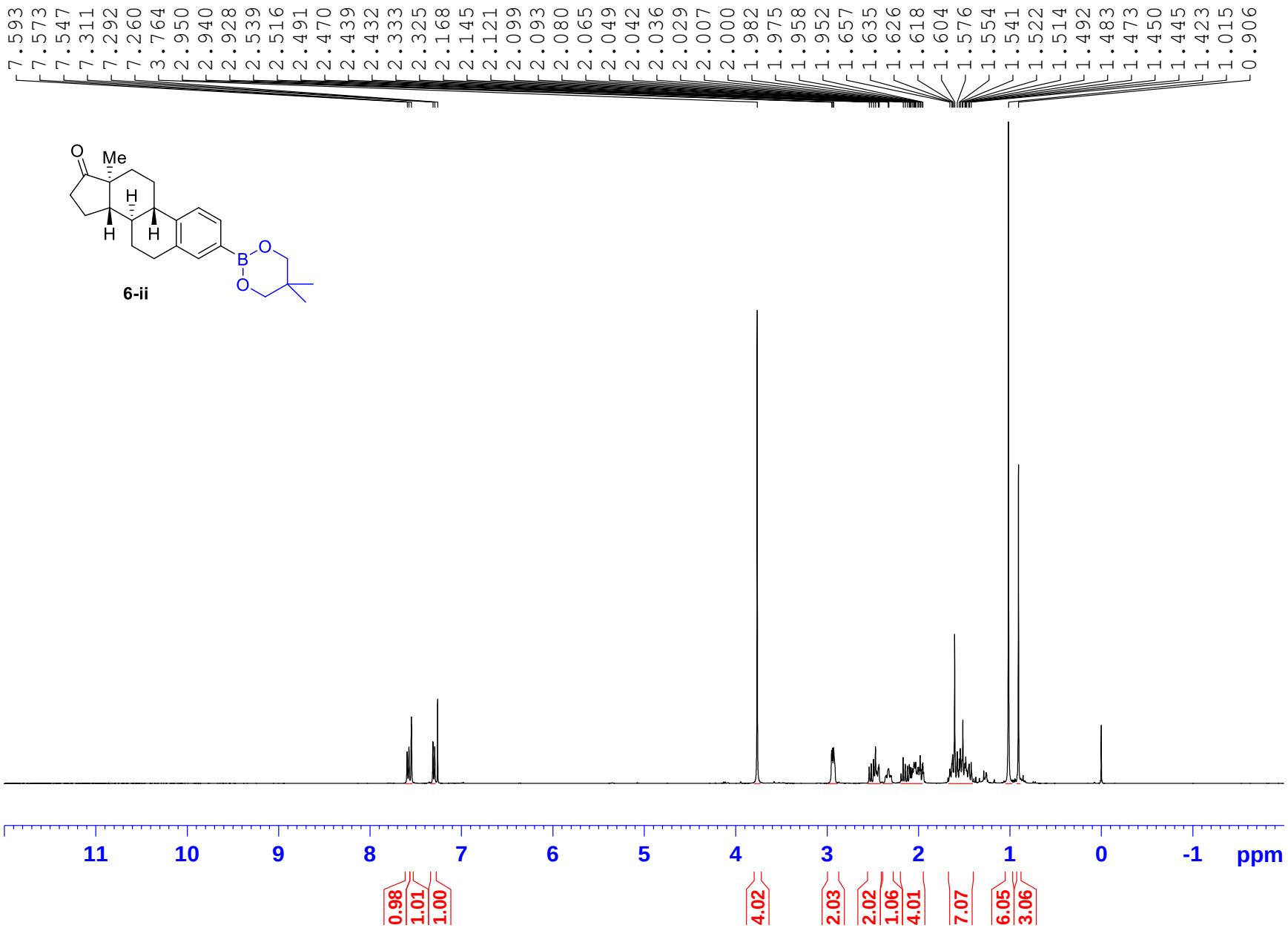
ppm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7.260
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2.491
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2.439
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2.333
2.325
2.168
2.145
2.121
2.099
2.093
2.080
2.065
2.049
2.042
2.036
2.029
2.007
2.000
1.982
1.975
1.958
1.952
1.657
1.635
1.626
1.618
1.604
1.576
1.554
1.541
1.522
1.514
1.492
1.483
1.473
1.450
1.445
1.423
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0.906
O
Me
H
H
H
B
O
O
6-ii
11
10
9
8
7
6
5
4
3
2
1
0
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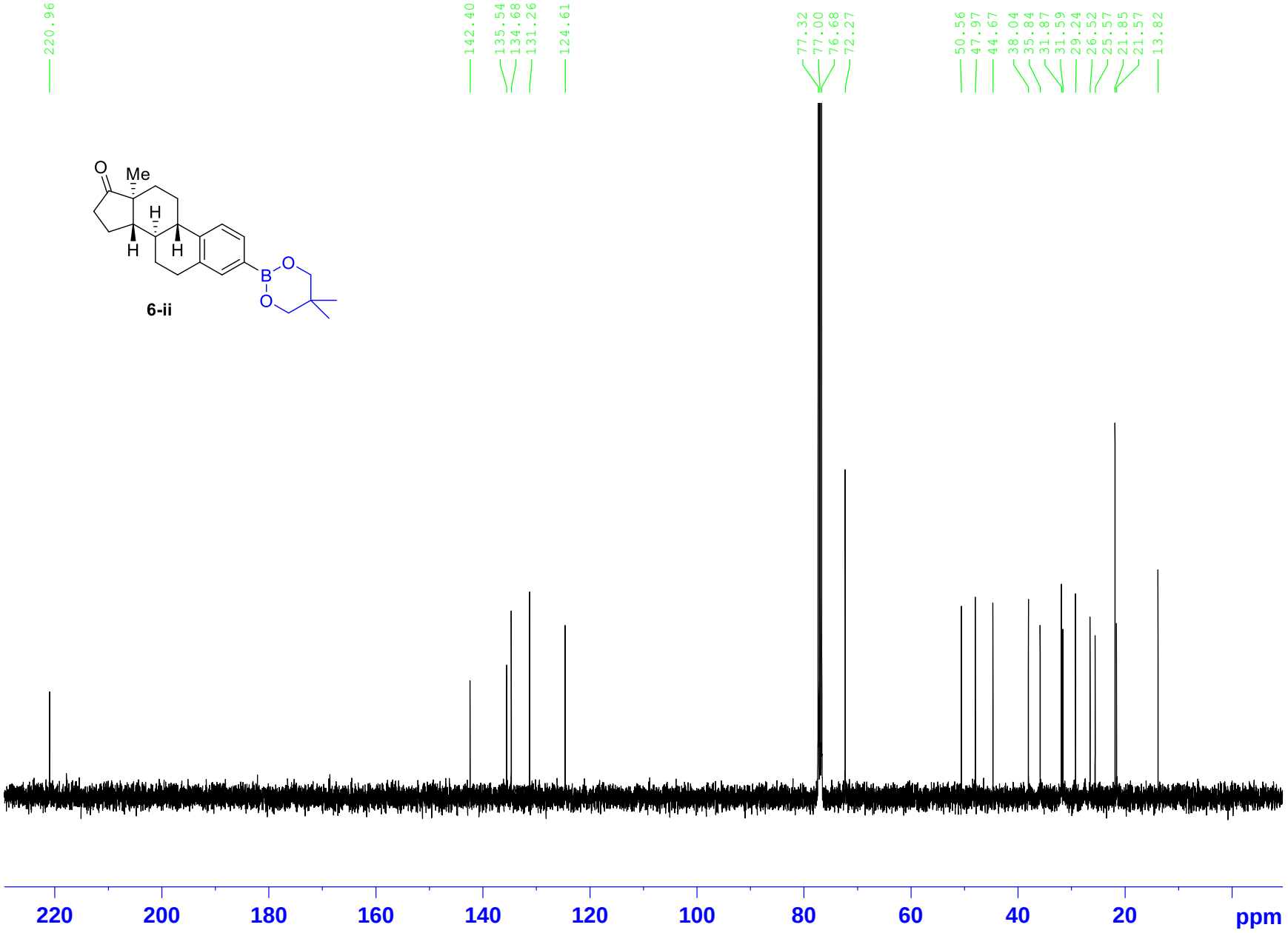
1.00
4.02
2.03
2.02
1.06
4.01
7.07
6.05
3.06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124.61
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77.00
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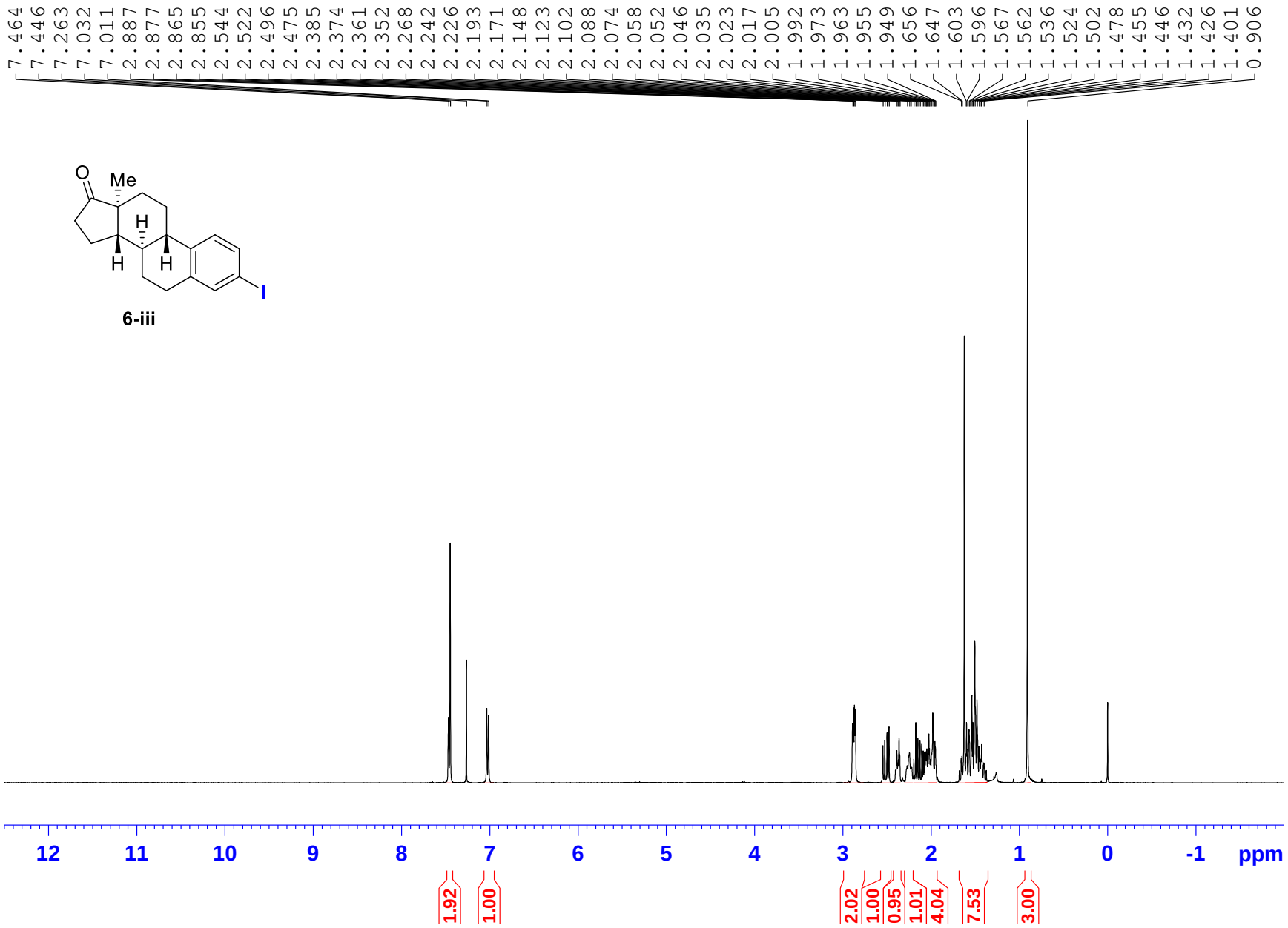
72.27
50.56
47.97
44.67
38.04
35.84
31.87
31.59
29.24
26.52
25.57
21.85
21.57
13.82
O
Me
H
H
H
B
O
O
6-ii
220
200
180
160
140
120
100
80
60
40
20
ppm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2.374
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2.242
2.226
2.193
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2.123
2.102
2.088
2.074
2.058
2.052
2.046
2.035
2.023
2.017
2.005
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1.973
1.963
1.955
1.949
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1.603
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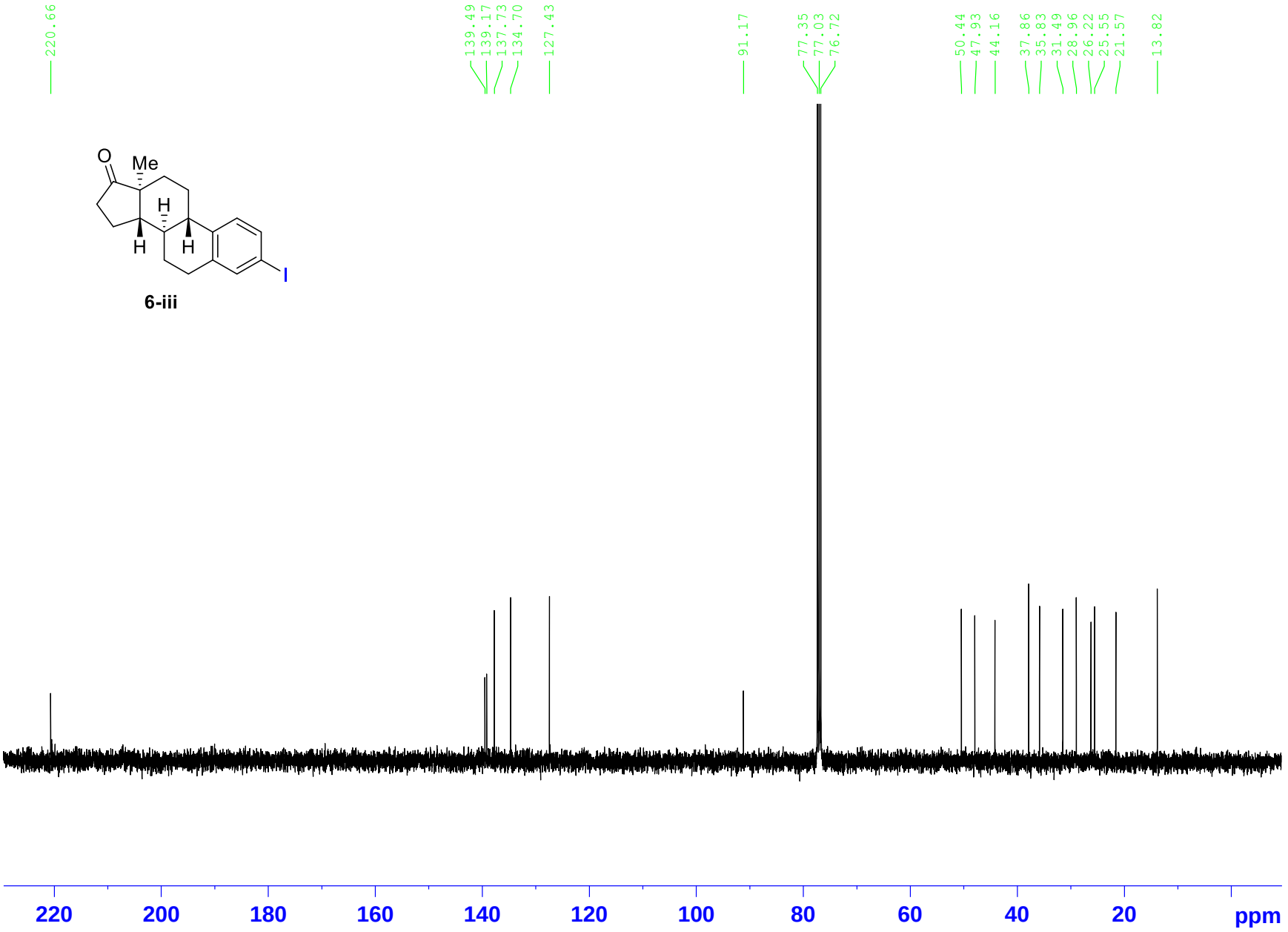
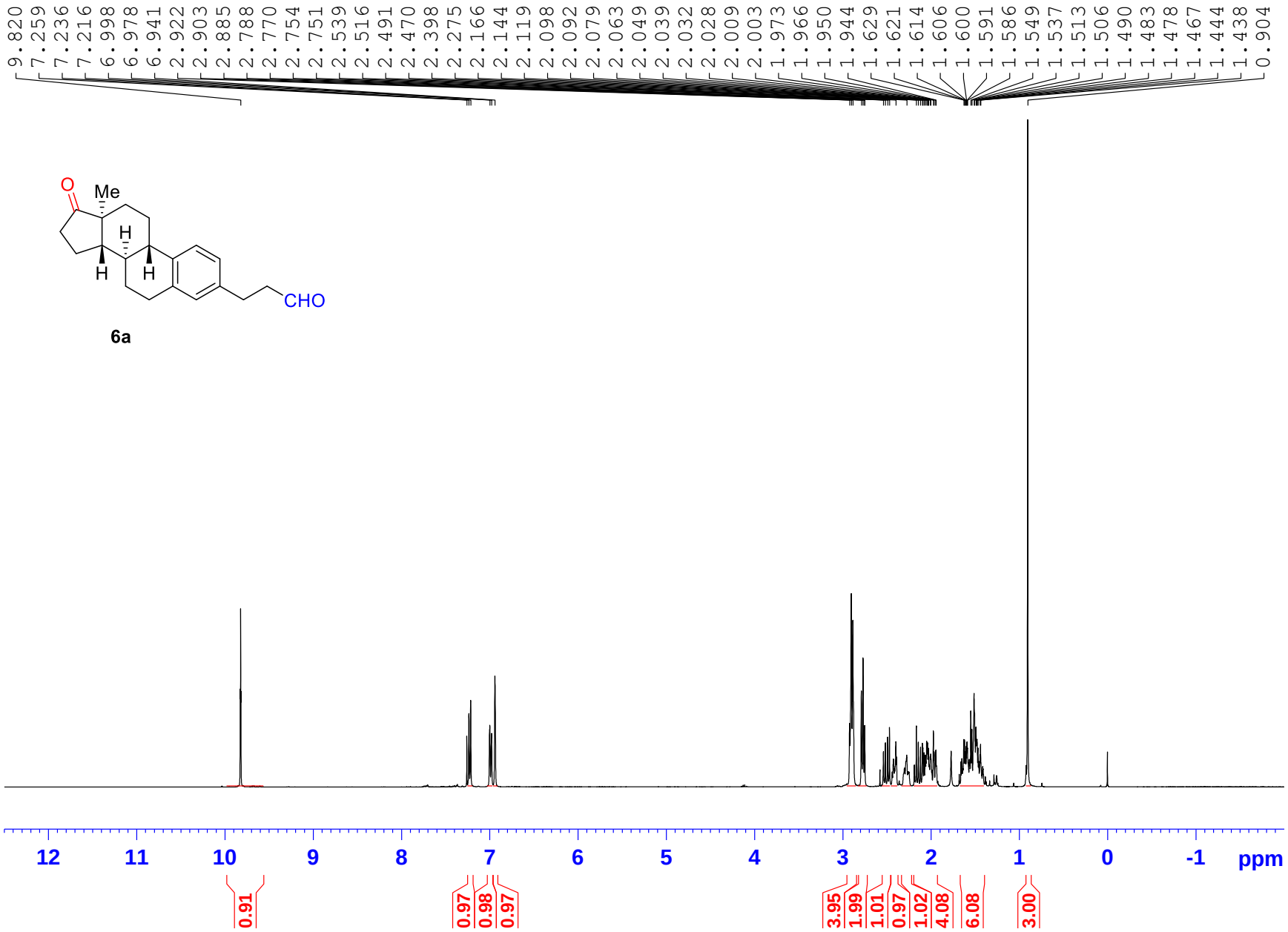
1.567
1.562
1.536
1.524
1.502
1.478
1.455
1.446
1.432
1.426
1.401
0.906
O
Me
H
H
H
I
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.92
1.00
2.02
1.00
0.95
1.01
4.04
7.53
3.00

6-iii


220.66
139.49
139.17
137.73
134.70
127.43
91.17
77.35
77.03
76.72
50.44
47.93
44.16
37.86
35.83
31.49
28.96
26.22
25.55
21.57
13.82
O
Me
H
H
H
I
220
200
180
160
140
120
100
80
60
40
20
ppm

6-iii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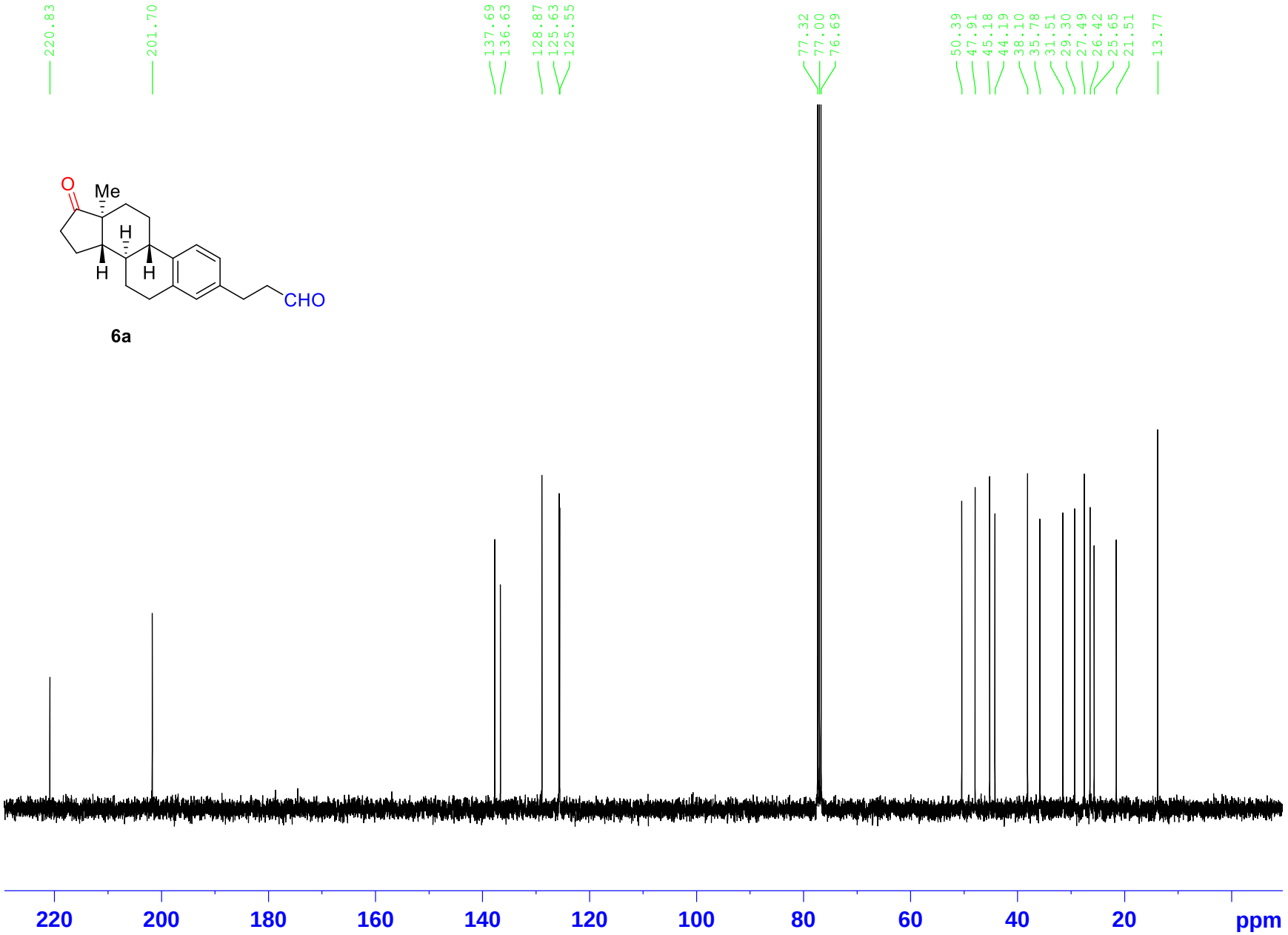
7.259
7.236
7.216
6.998
6.978
6.941
2.922
2.903
2.885
2.788
2.770
2.754
2.751
2.539
2.516
2.491
2.470
2.398
2.275
2.166
2.144
2.119
2.098
2.092
2.079
2.063
2.049
2.039
2.032
2.028
2.009
2.003
1.973
1.966
1.950
1.944
1.629
1.621
1.614
1.606
1.600
1.591
1.586
1.549
1.537
1.513
1.506
1.490
1.483
1.478
1.467
1.444
1.438
0.904
O
Me
H
H
H
CHO
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.91
0.97
0.98
0.97
3.95
1.99
1.01
0.97
1.02
4.08
6.08
3.00

6a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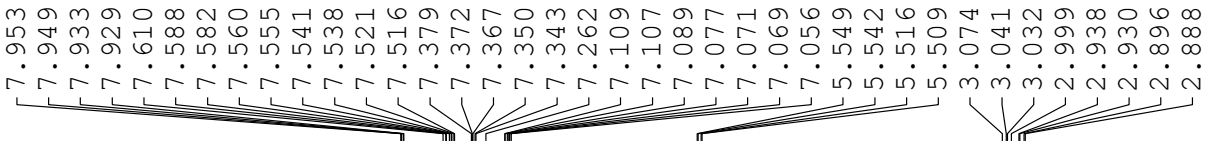
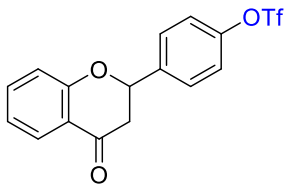
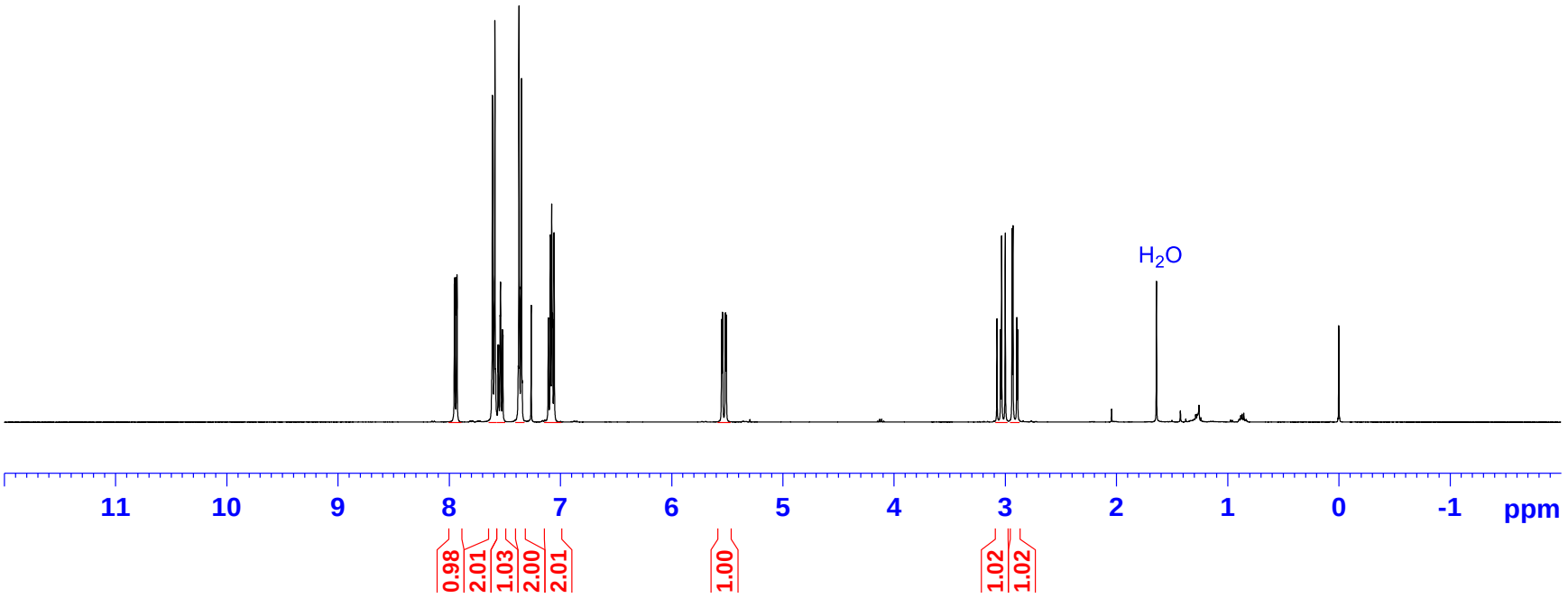
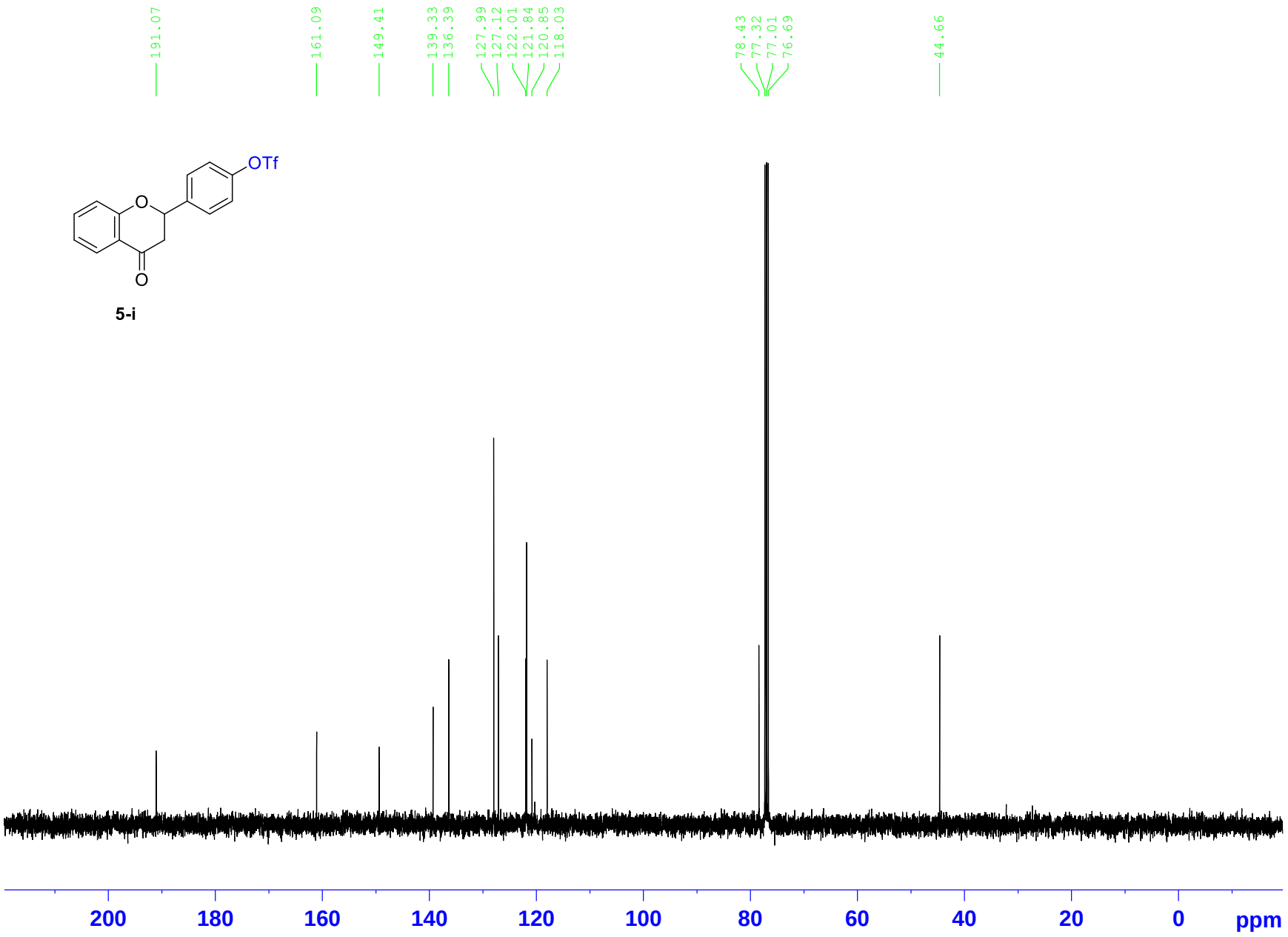
201.70
137.69
136.63
128.87
125.63
125.55
77.32
77.00
76.69
50.39
47.91
45.18
44.19
38.10
35.78
31.51
29.30
27.49
26.42
25.65
21.51
13.77
O
Me
H
H
H
CHO
6a
220
200
180
160
140
120
100
80
60
40
20
ppm

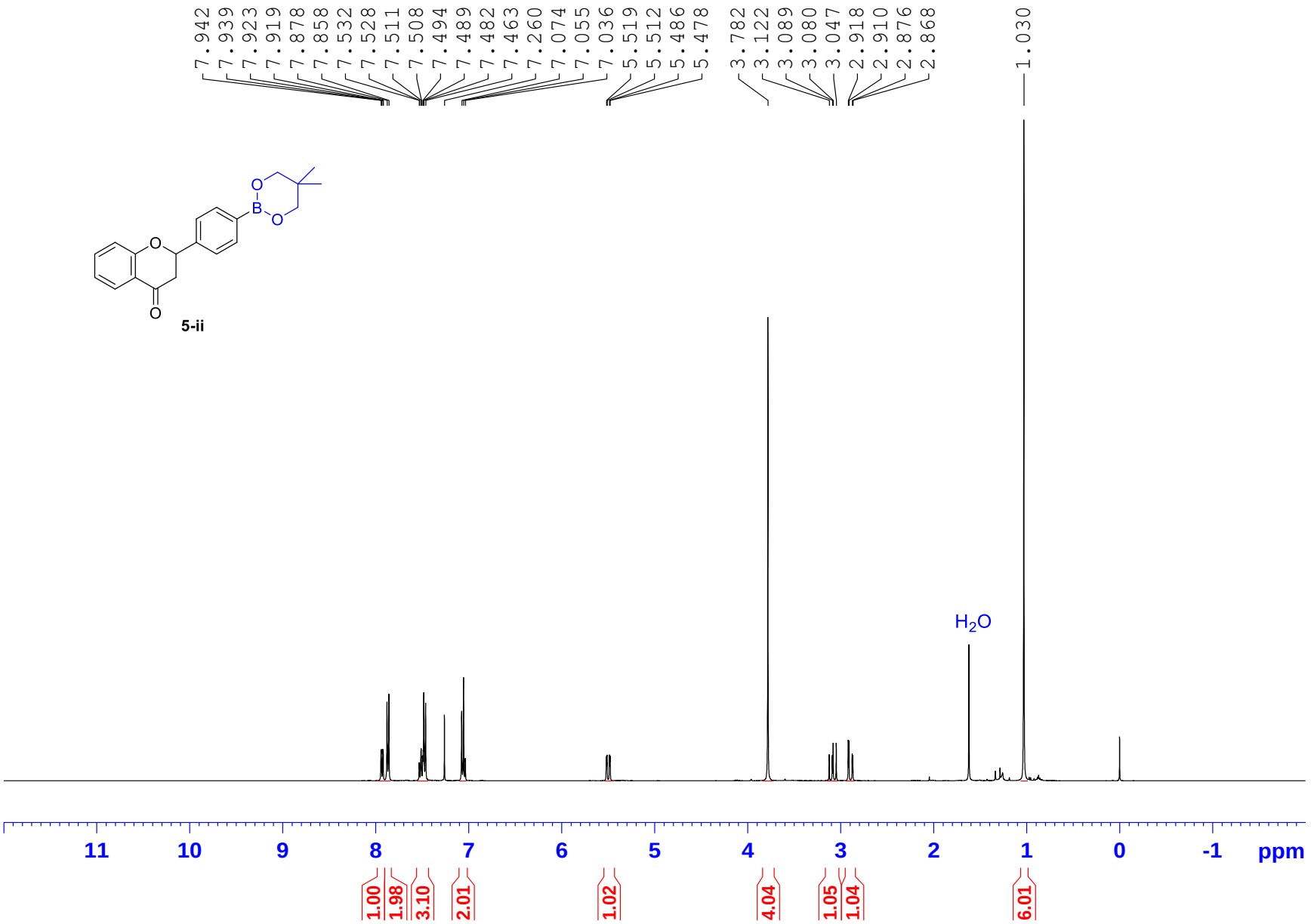

7.953
7.949
7.933
7.929
7.610
7.588
7.582
7.560
7.555
7.541
7.538
7.521
7.516
7.379
7.372
7.367
7.350
7.343
7.262
7.109
7.107
7.089
7.077
7.071
7.069
7.056
5.549
5.542
5.516
5.509
3.074
3.041
3.032
2.999
2.938
2.930
2.896
2.888

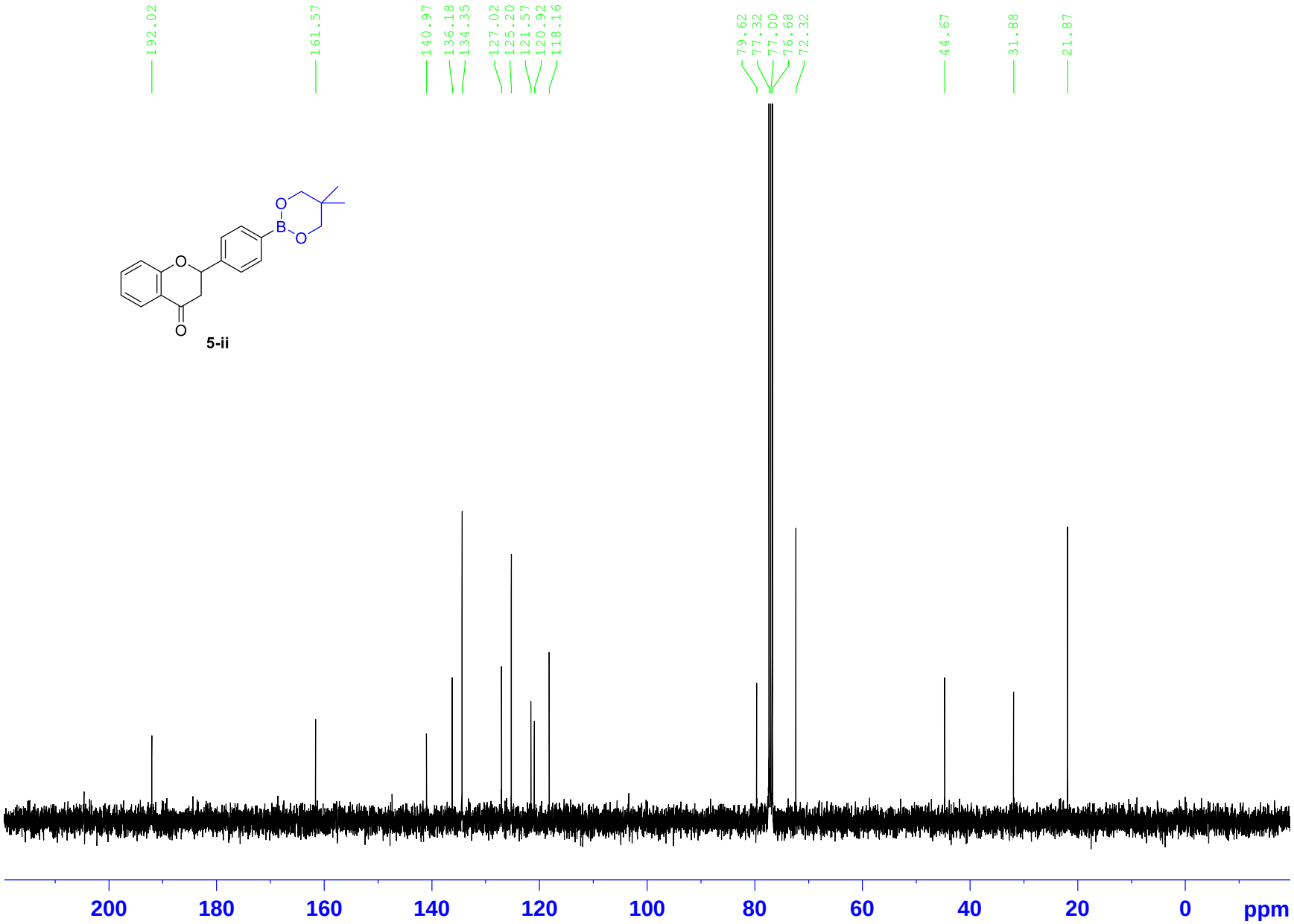

OTf
O
O

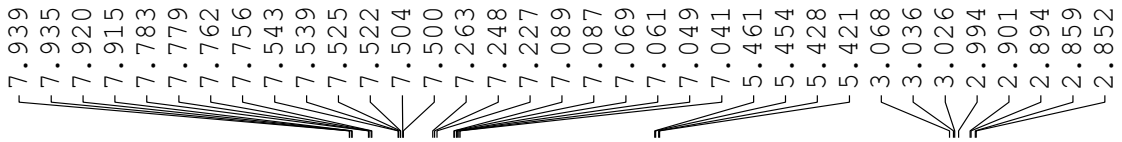
5-i

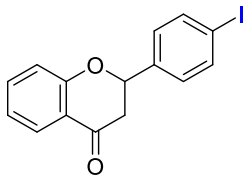

H2O
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
2.01
1.03
2.00
2.01
1.00
1.02
1.02


191.07
161.09
149.41
139.33
136.39
127.99
127.12
122.01
121.84
120.85
118.03
78.43
77.32
77.01
76.69
44.66
OTf
O
O
5-i
200
180
160
140
120
100
80
60
40
20
0
ppm

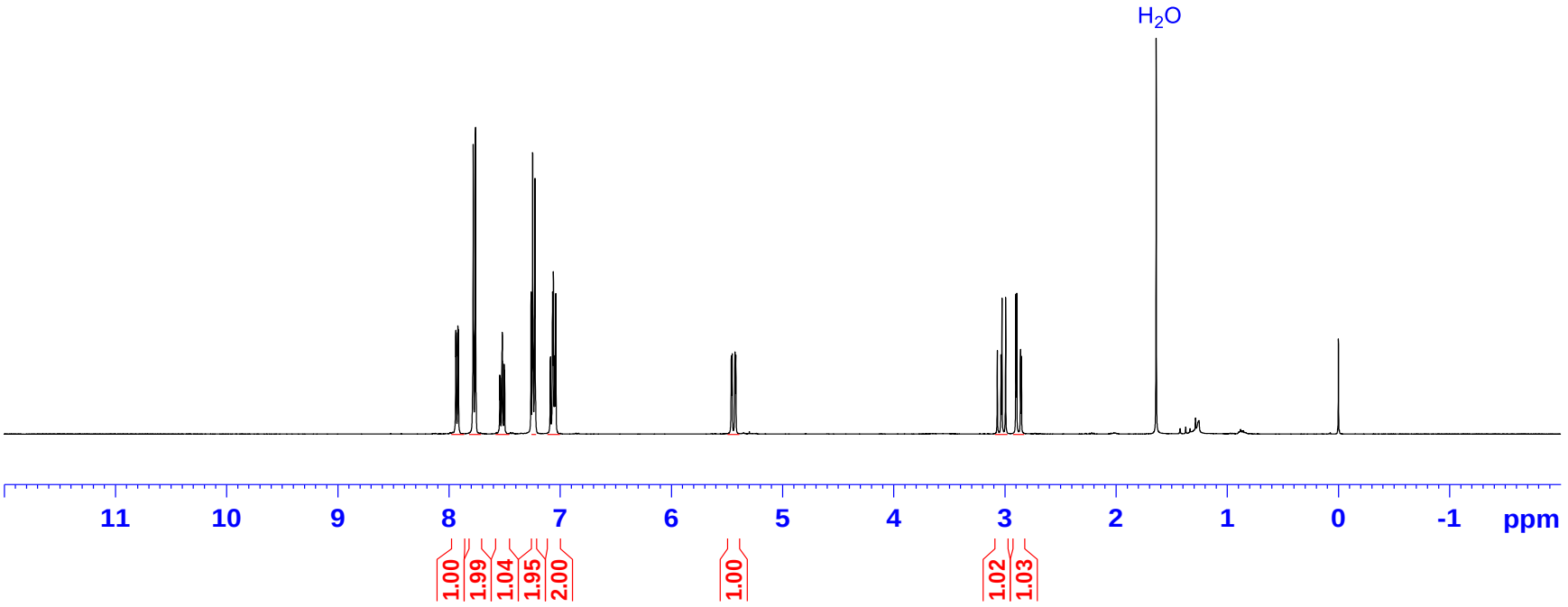

7.942
7.939
7.923
7.919
7.878
7.858
7.532
7.528
7.511
7.508
7.494
7.489
7.482
7.463
7.260
7.074
7.055
7.036
5.519
5.512
5.486
5.478
3.782
3.122
3.089
3.080
3.047
2.918
2.910
2.876
2.868
1.030
O
B
O
O
O
5-ii
H2O
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.98
3.10
2.01
1.02
4.04
1.05
1.04
6.01

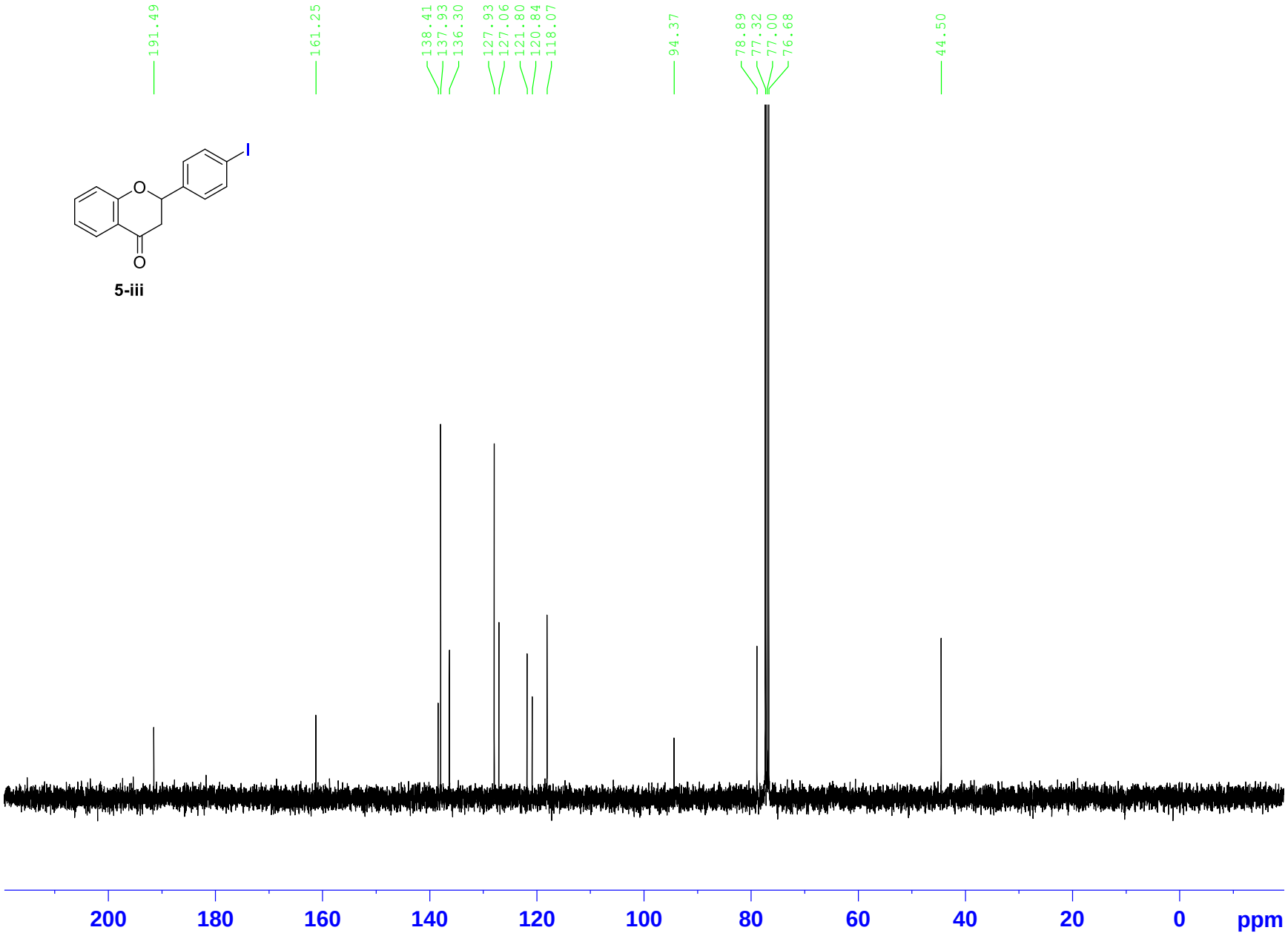

192.02
161.57
140.97
136.18
134.35
127.02
125.20
121.57
120.92
118.16
79.62
77.32
77.00
76.68
72.32
44.67
31.88
21.87
O
B
O
O
O
5-ii
200
180
160
140
120
100
80
60
40
20
0
ppm

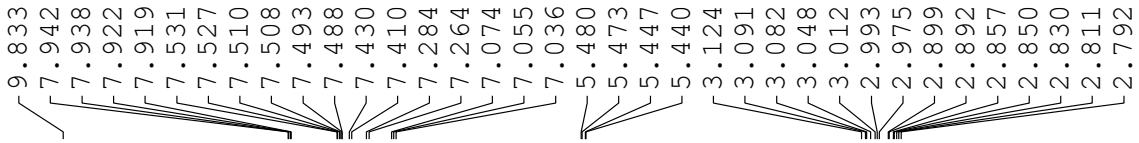

7.939
7.935
7.920
7.915
7.783
7.779
7.762
7.756
7.543
7.539
7.525
7.522
7.504
7.500
7.263
7.248
7.227
7.089
7.087
7.069
7.061
7.049
7.041
5.461
5.454
5.428
5.421
3.068
3.036
3.026
2.994
2.901
2.894
2.859
2.852

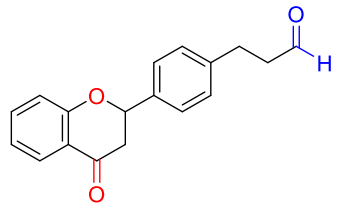

I
O
O

5-iii

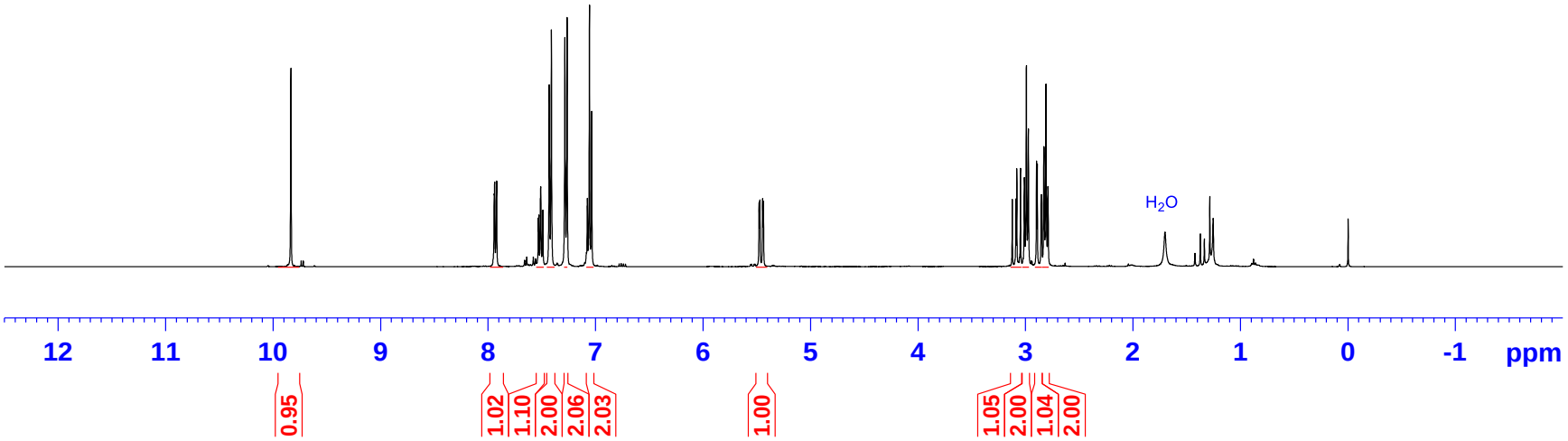

H2O
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.99
1.04
1.95
2.00
1.00
1.02
1.03

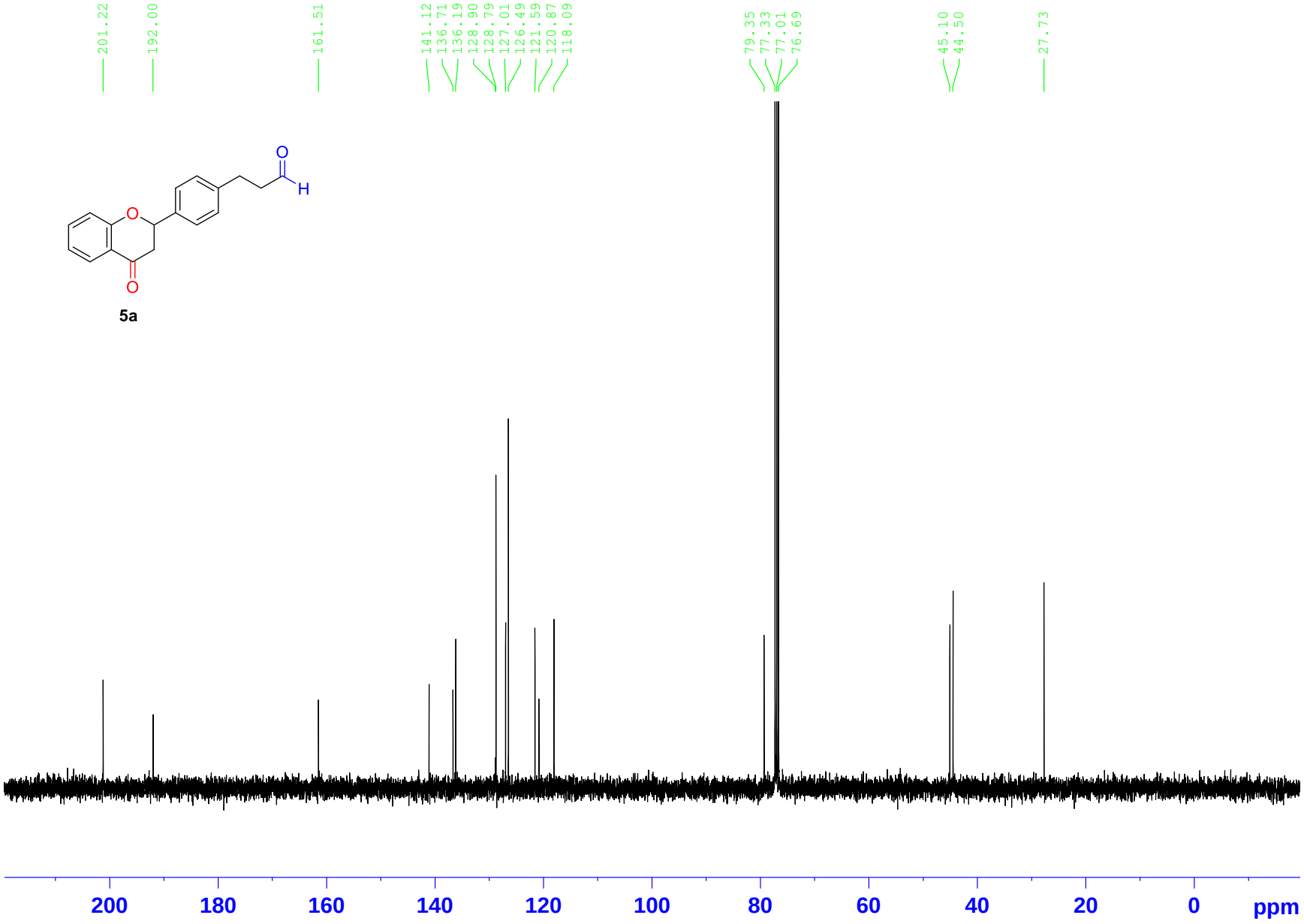

191.49
161.25
138.41
137.93
136.30
127.93
127.06
121.80
120.84
118.07
94.37
78.89
77.32
77.00
76.68
44.50
I
O
O
5-iii
200
180
160
140
120
100
80
60
40
20
0
ppm

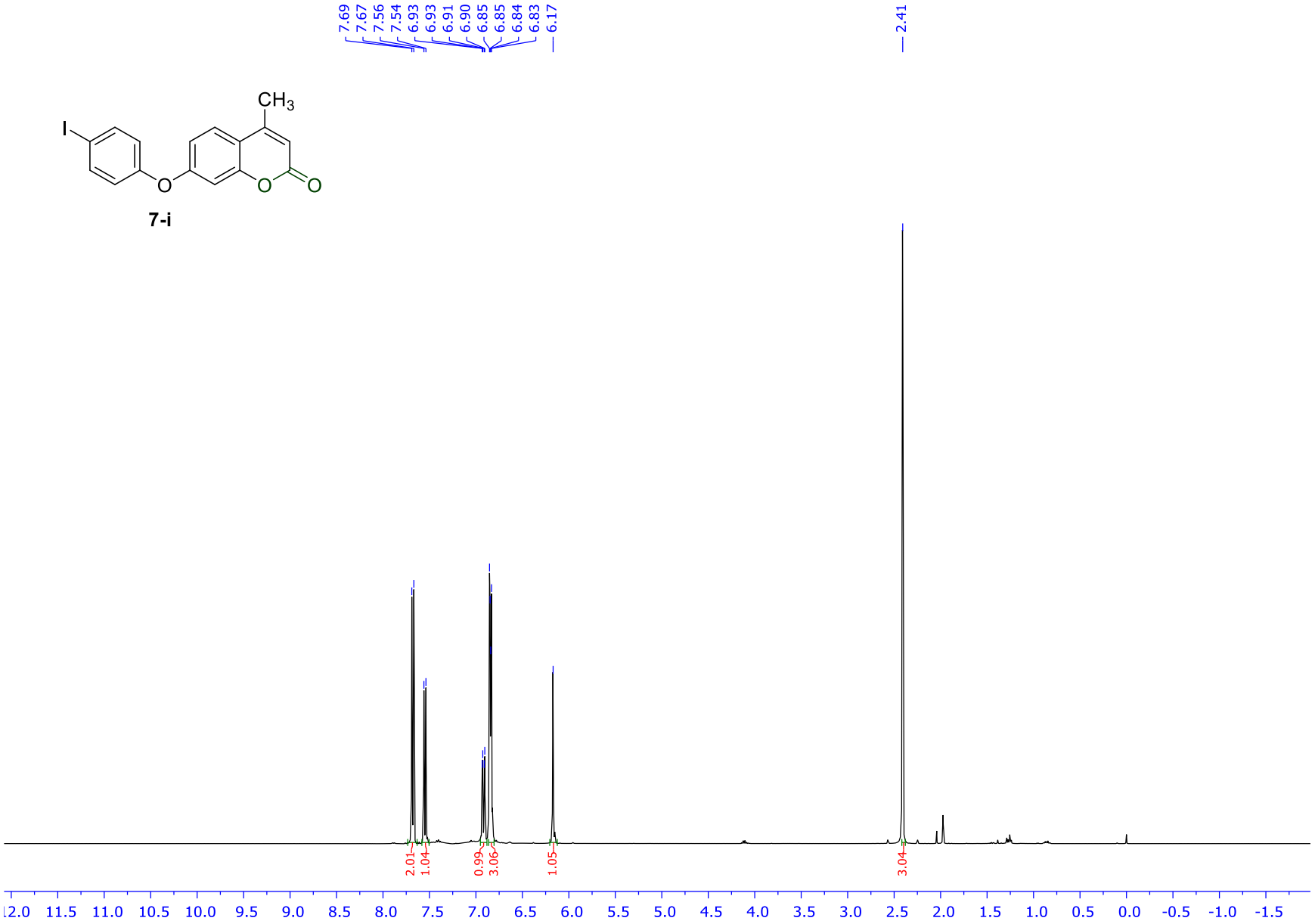

9.833
7.942
7.938
7.922
7.919
7.531
7.527
7.510
7.508
7.493
7.488
7.430
7.410
7.284
7.264
7.074
7.055
7.036
5.480
5.473
5.447
5.440
3.124
3.091
3.082
3.048
3.012
2.993
2.975
2.899
2.892
2.857
2.850
2.830
2.811
2.792

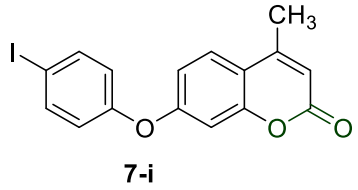

O
H
O
O

5a


H2O
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
1.02
1.10
2.00
2.06
2.03
1.00
1.05
2.00
1.04
2.00

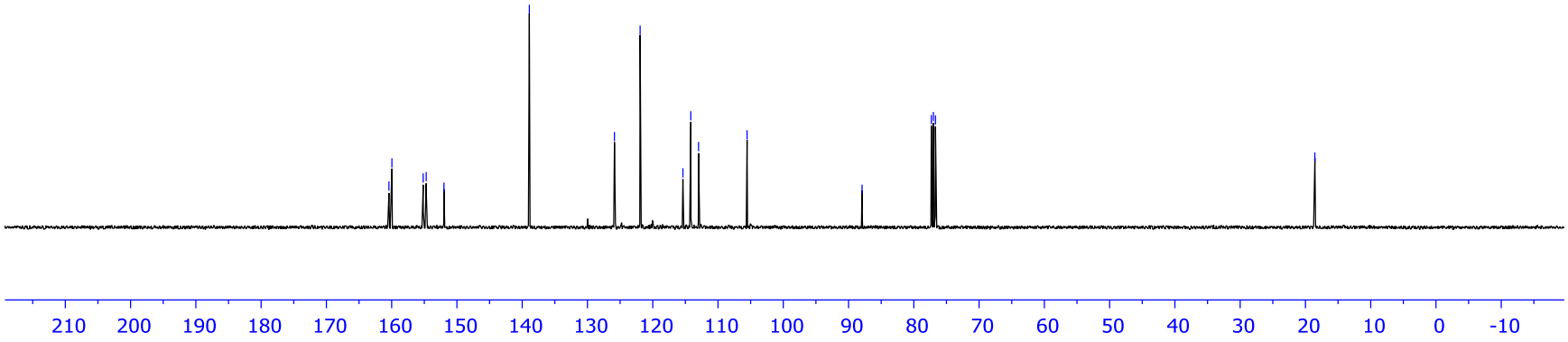

201.22
192.00
161.51
141.12
136.71
136.19
128.90
128.79
127.01
126.49
121.59
120.87
118.09
79.35
77.33
77.01
76.69
45.10
44.50
27.73
O
H
O
O
5a
200
180
160
140
120
100
80
60
40
20
0
ppm

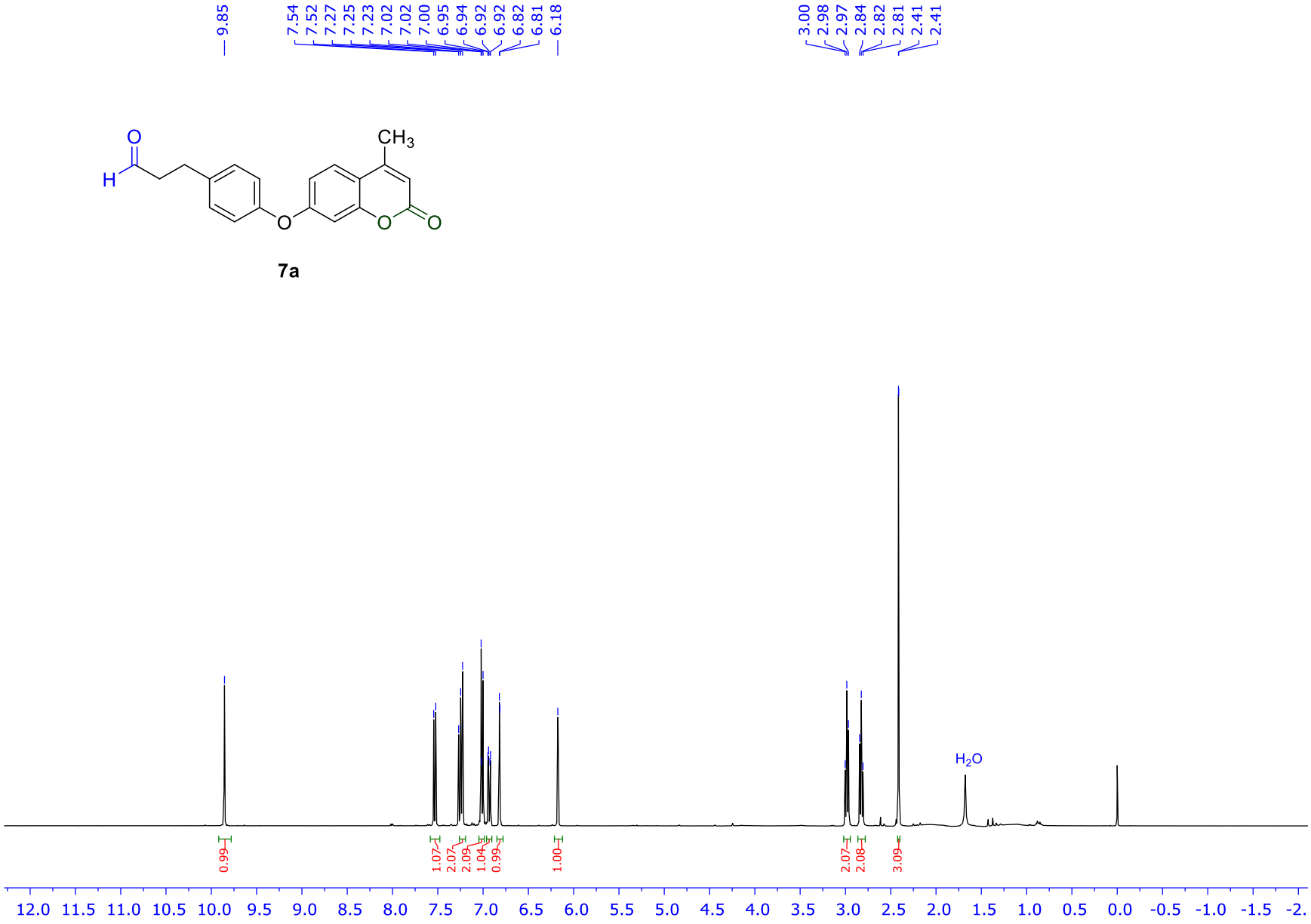

7.69
7.67
7.56
7.54
6.93
6.93
6.91
6.90
6.85
6.85
6.84
6.83
6.17
2.41
CH3
I
O
O
O
7-i
2.01
1.04
0.99
3.06
1.05
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5



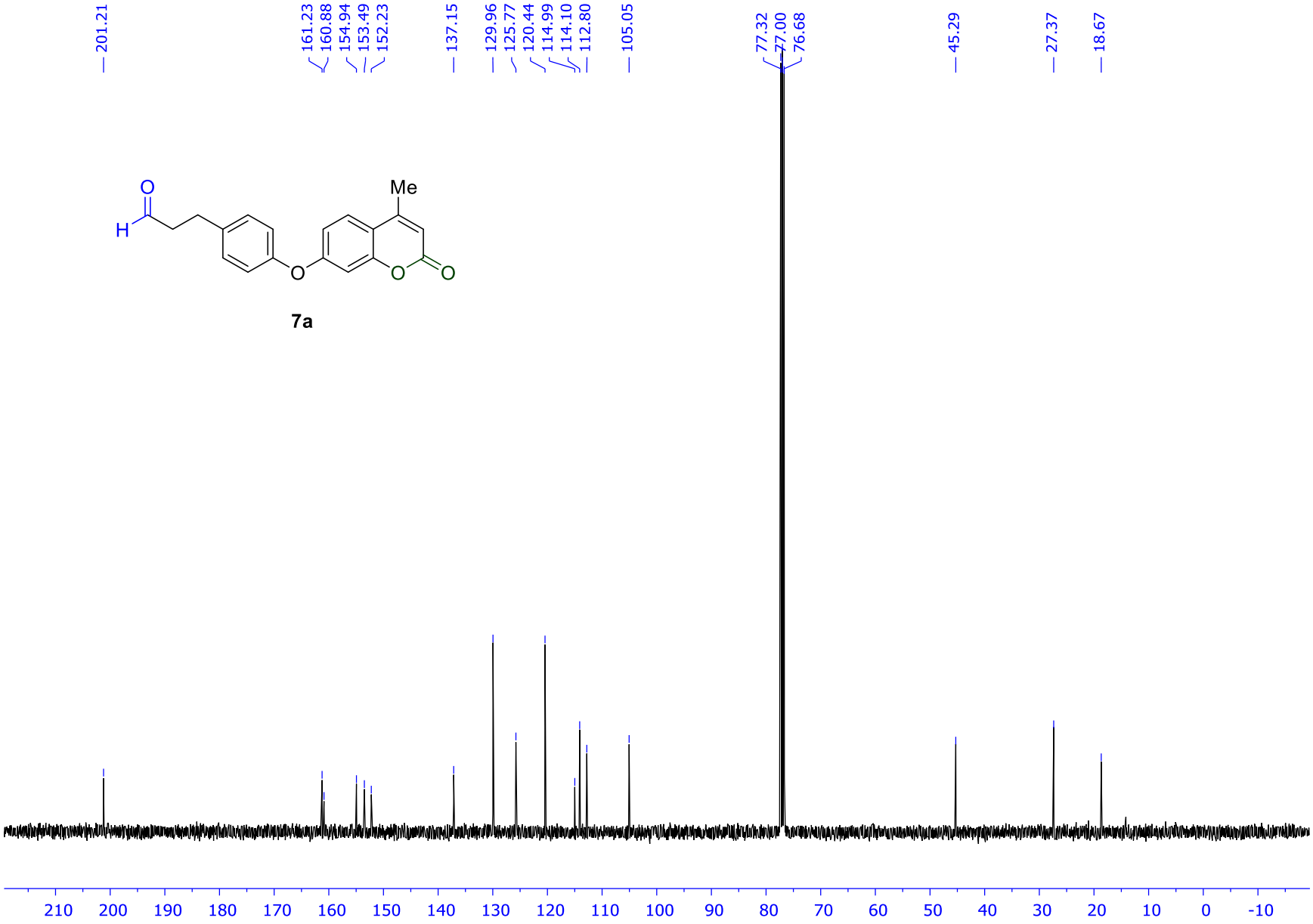
7-i

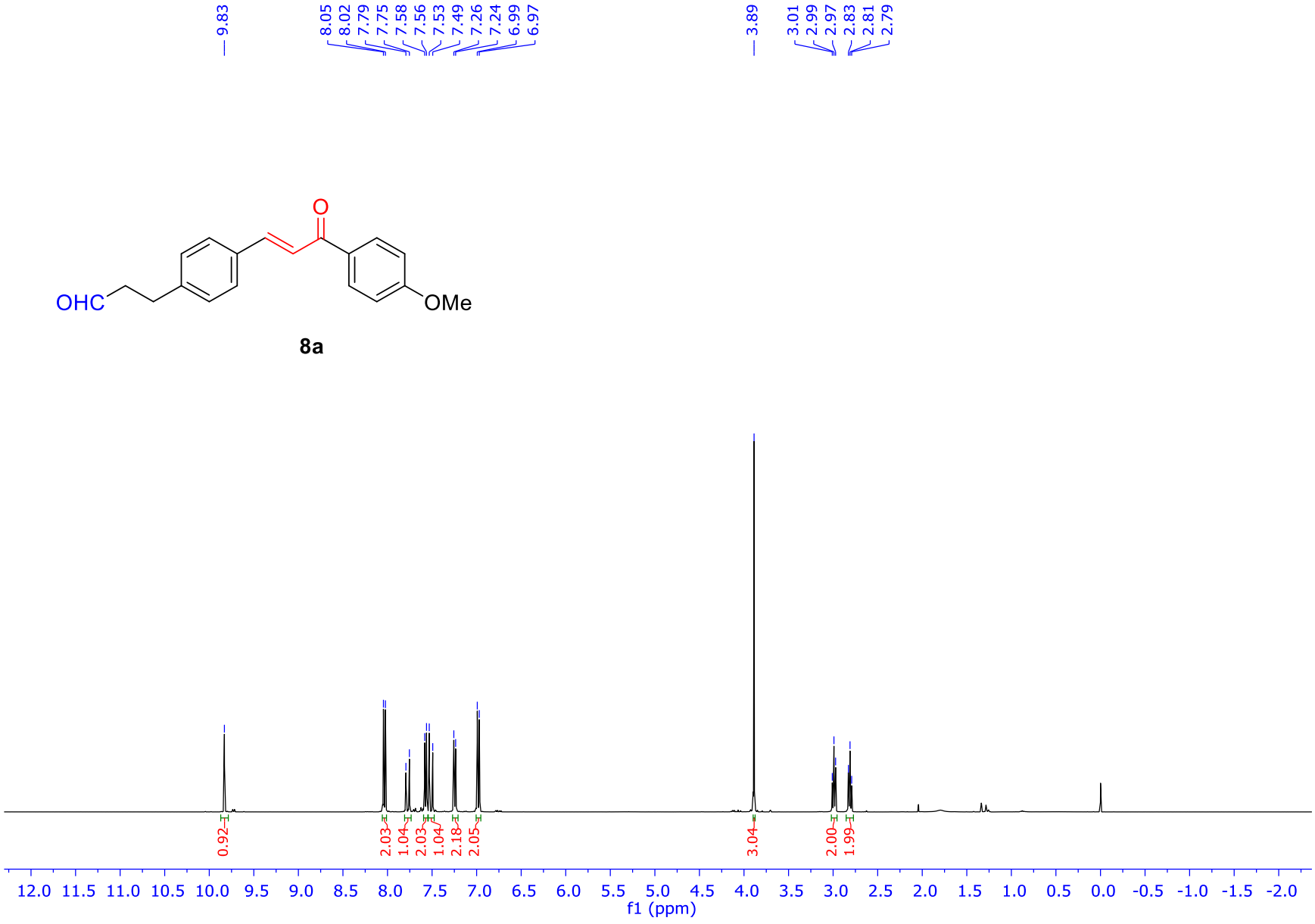
160.42
159.96
155.17
154.71
151.99
138.91
125.87
121.93
115.38
114.17
112.98
105.55
87.93
77.32
77.00
76.68
18.56

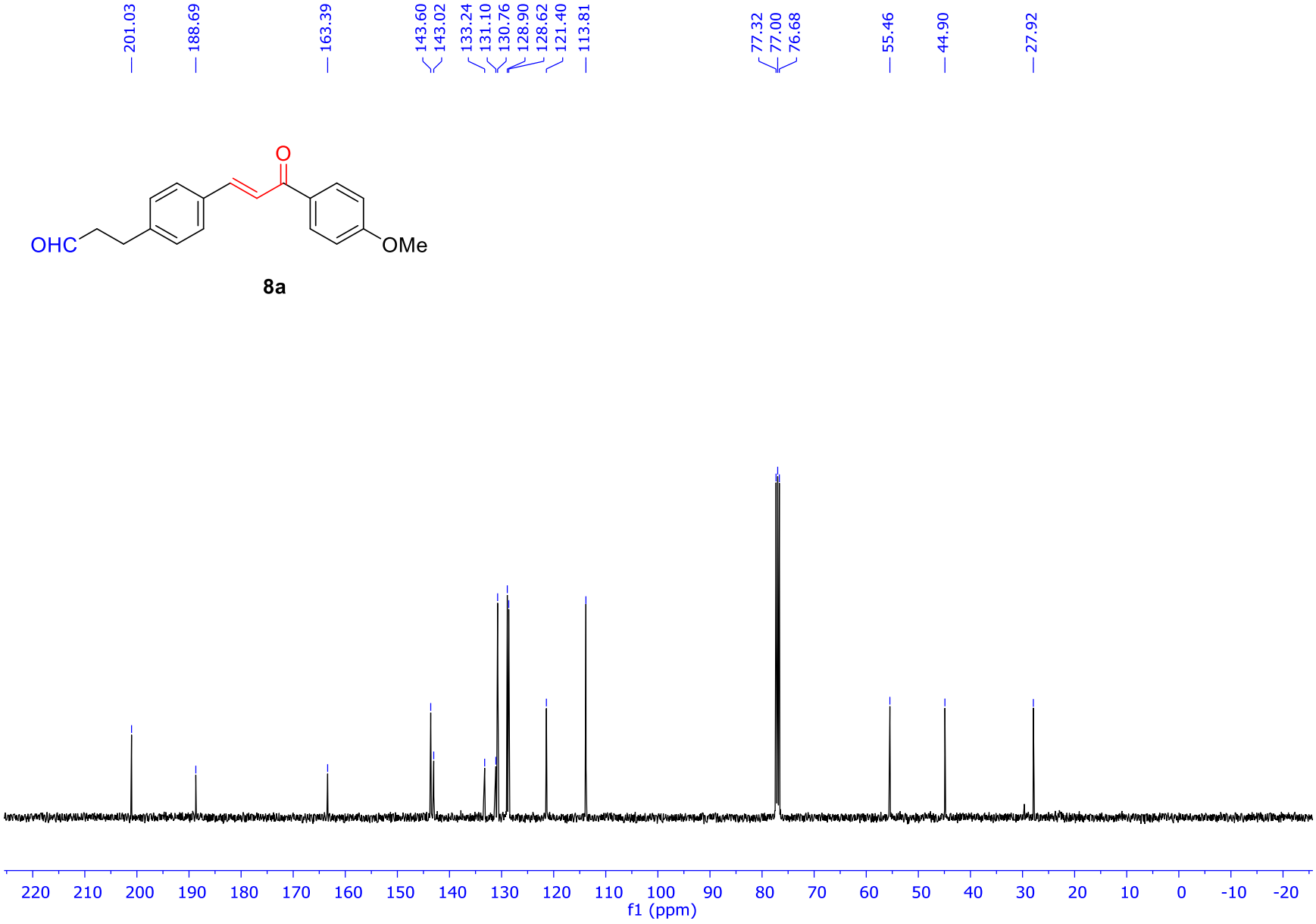


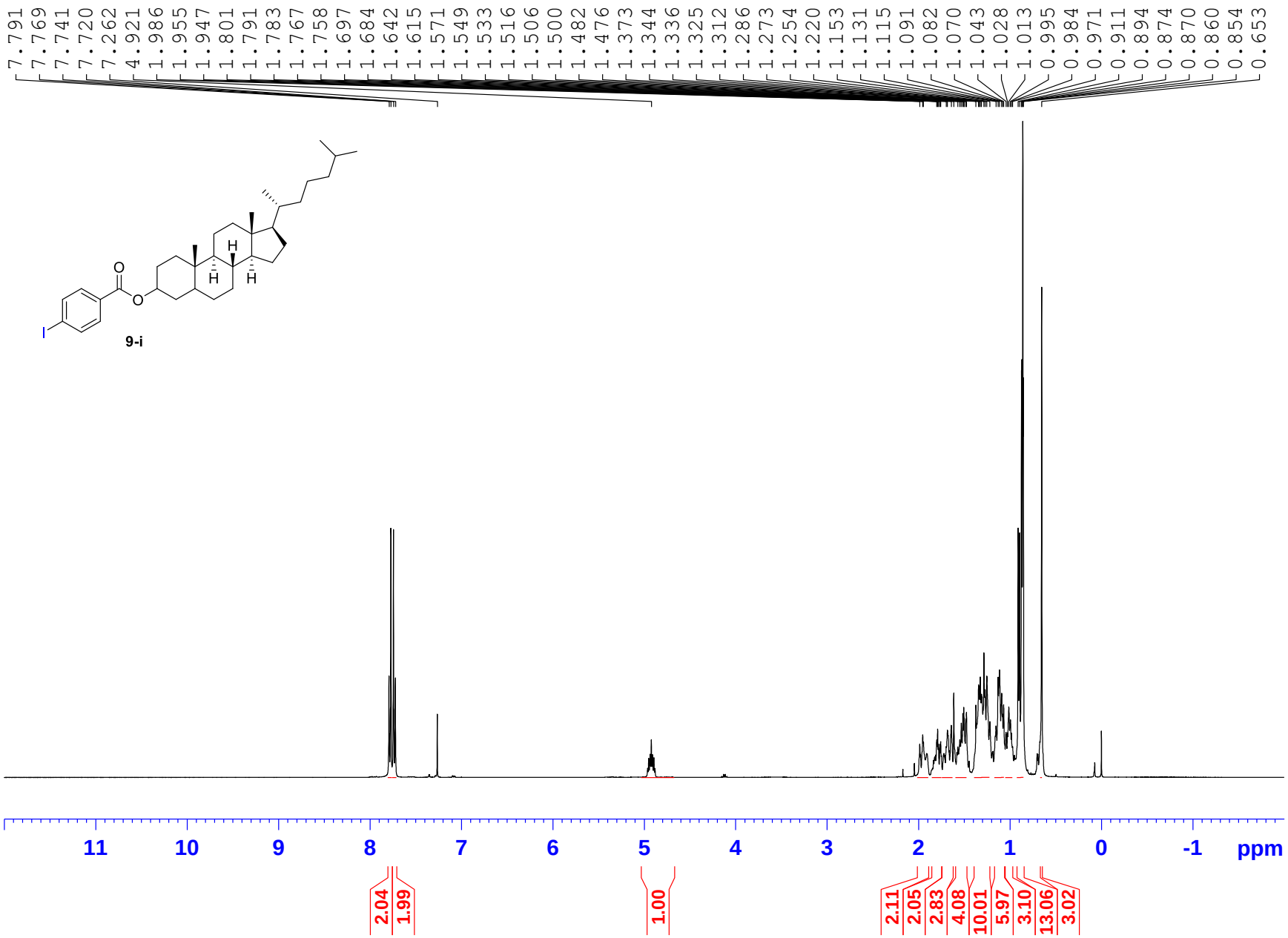

9.85
7.54
7.52
7.27
7.25
7.23
7.02
7.02
7.00
6.95
6.94
6.92
6.92
6.82
6.81
6.18
3.00
2.98
2.97
2.84
2.82
2.81
2.41
2.41
O
H
CH3
O
O
O
H2O
0.99
1.07
2.07
2.09
1.04
0.99
1.00
2.07
2.08
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.

7a


201.21
161.23
160.88
154.94
153.49
152.23
137.15
129.96
125.77
120.44
114.99
114.10
112.80
105.05
77.32
77.00
76.68
45.29
27.37
18.67
O
H
Me
O
O
O
7a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


9.83
8.05
8.02
7.79
7.75
7.58
7.56
7.53
7.49
7.26
7.24
6.99
6.97
3.89
3.01
2.99
2.97
2.83
2.81
2.79
O
OHC
OMe
8a
0.92
2.03
1.04
2.03
1.04
2.18
2.05
3.04
2.00
1.99
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 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


201.03
188.69
163.39
143.60
143.02
133.24
131.10
130.76
128.90
128.62
121.40
113.81
77.32
77.00
76.68
55.46
44.90
27.92
O
OHC
OMe
8a
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)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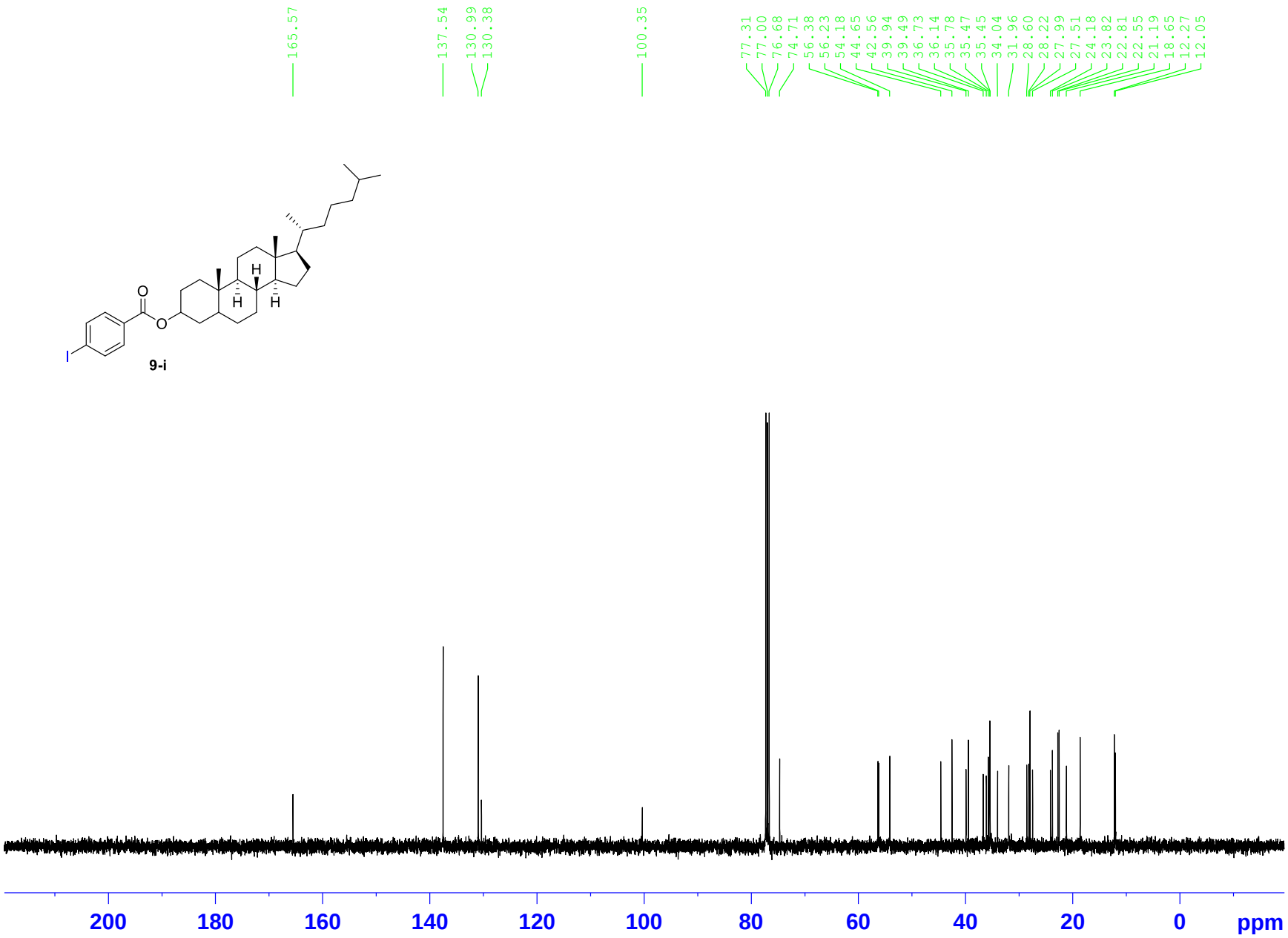
7.769
7.741
7.720
7.262
4.921
1.986
1.955
1.947
1.801
1.791
1.783
1.767
1.758
1.697
1.684
1.642
1.615
1.571
1.549
1.533
1.516
1.506
1.500
1.482
1.476
1.373
1.344
1.336
1.325
1.312
1.286
1.273
1.254
1.220
1.153
1.131
1.115
1.091
1.082
1.070
1.043
1.028
1.013
0.995
0.984
0.971
0.911
0.894
0.874
0.870
0.860
0.854
0.653
O
O
H
H
H
I
9-i
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.04
1.99
1.00
2.11
2.05
2.83
4.08
10.01
5.97
3.10
13.06
3.02


165.57
137.54
130.99
130.38
100.35
77.31
77.00
76.68
74.71
56.38
56.23
54.18
44.65
42.56
39.94
39.49
36.73
36.14
35.78
35.47
35.45
34.04
31.96
28.60
28.22
27.99
27.51
24.18
23.82
22.81
22.55
21.19
18.65
12.27
12.05
O
O
H
H
H
I
9-i
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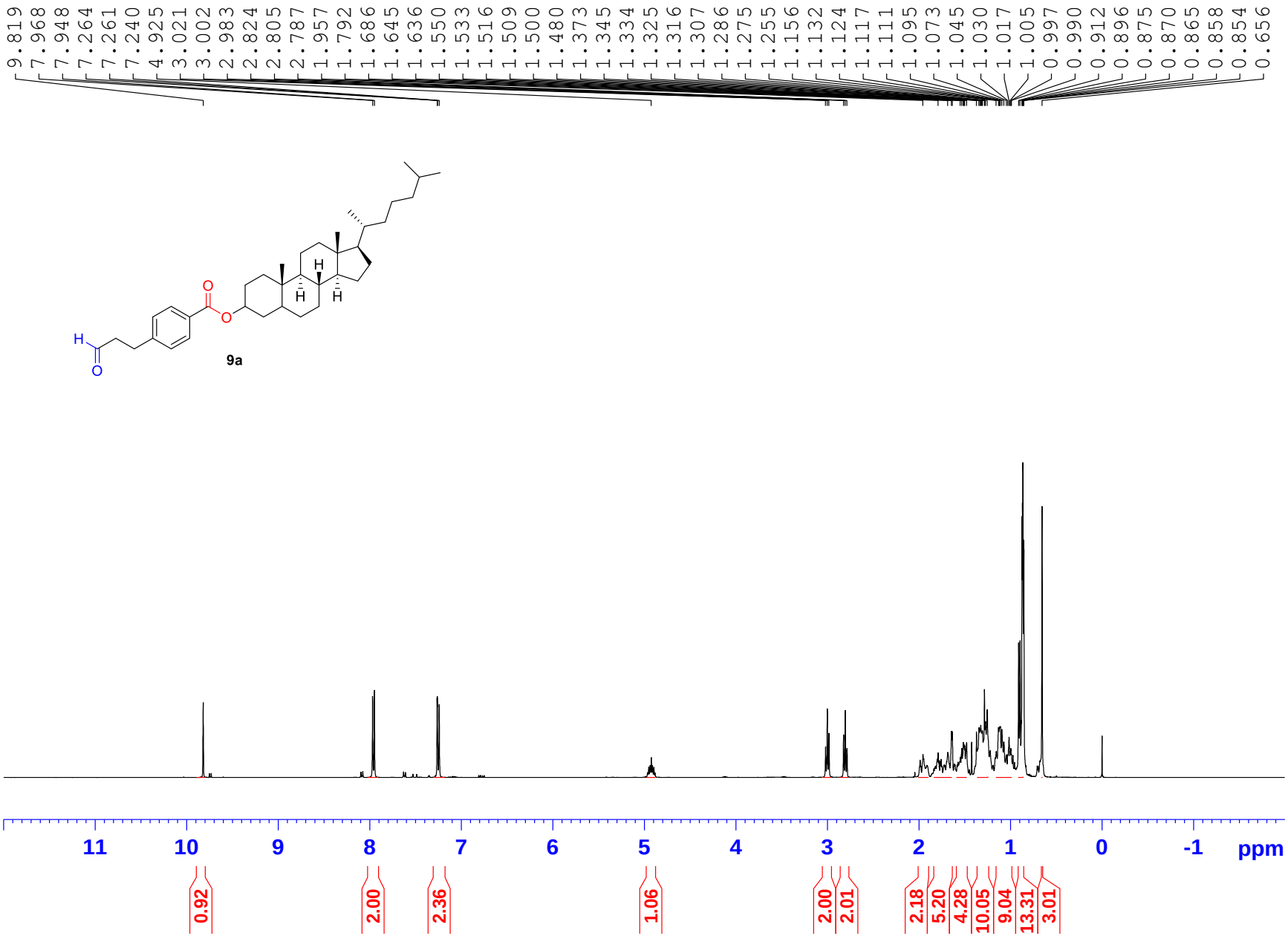
160
140
120
100
80
60
40
20
0
ppm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3.002
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2.805
2.787
1.957
1.792
1.686
1.645
1.636
1.550
1.533
1.516
1.509
1.500
1.480
1.373
1.345
1.334
1.325
1.316
1.307
1.286
1.275
1.255
1.156
1.132
1.124
1.117
1.111
1.095
1.073
1.045
1.030
1.017
1.005
0.997
0.990
0.912
0.896
0.875
0.870
0.865
0.858
0.854
0.656
9a
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.92
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4.28
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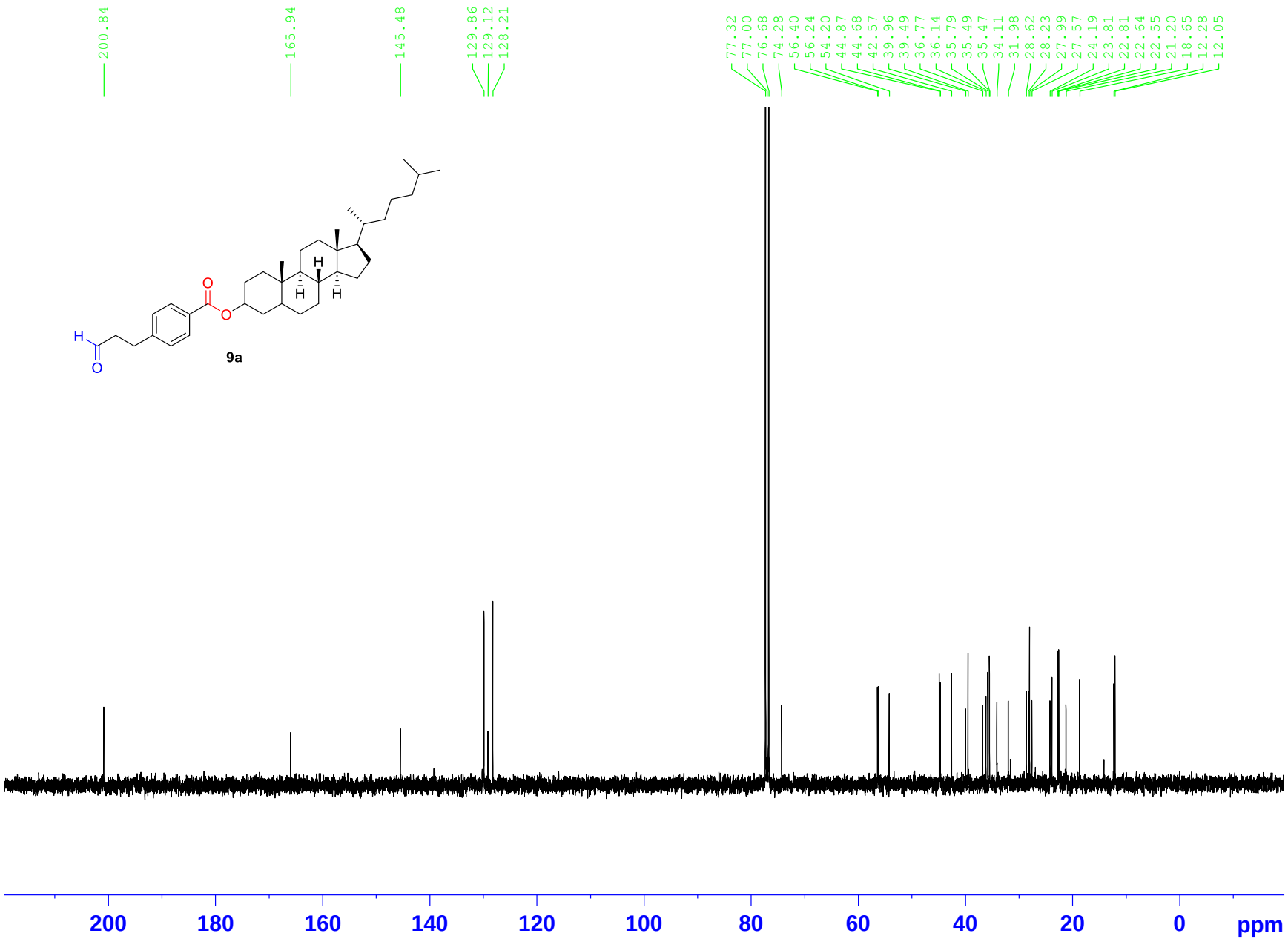
9.04
13.31
3.01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54.20
44.87
44.68
42.57
39.96
39.49
36.77
36.14
35.79
35.49
35.47
34.11
31.98
28.62
28.23
27.99
27.57
24.19
23.81
22.81
22.64
22.55
21.20
18.65
12.28
12.05
H
O
O
O
H
H
H
9a
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120
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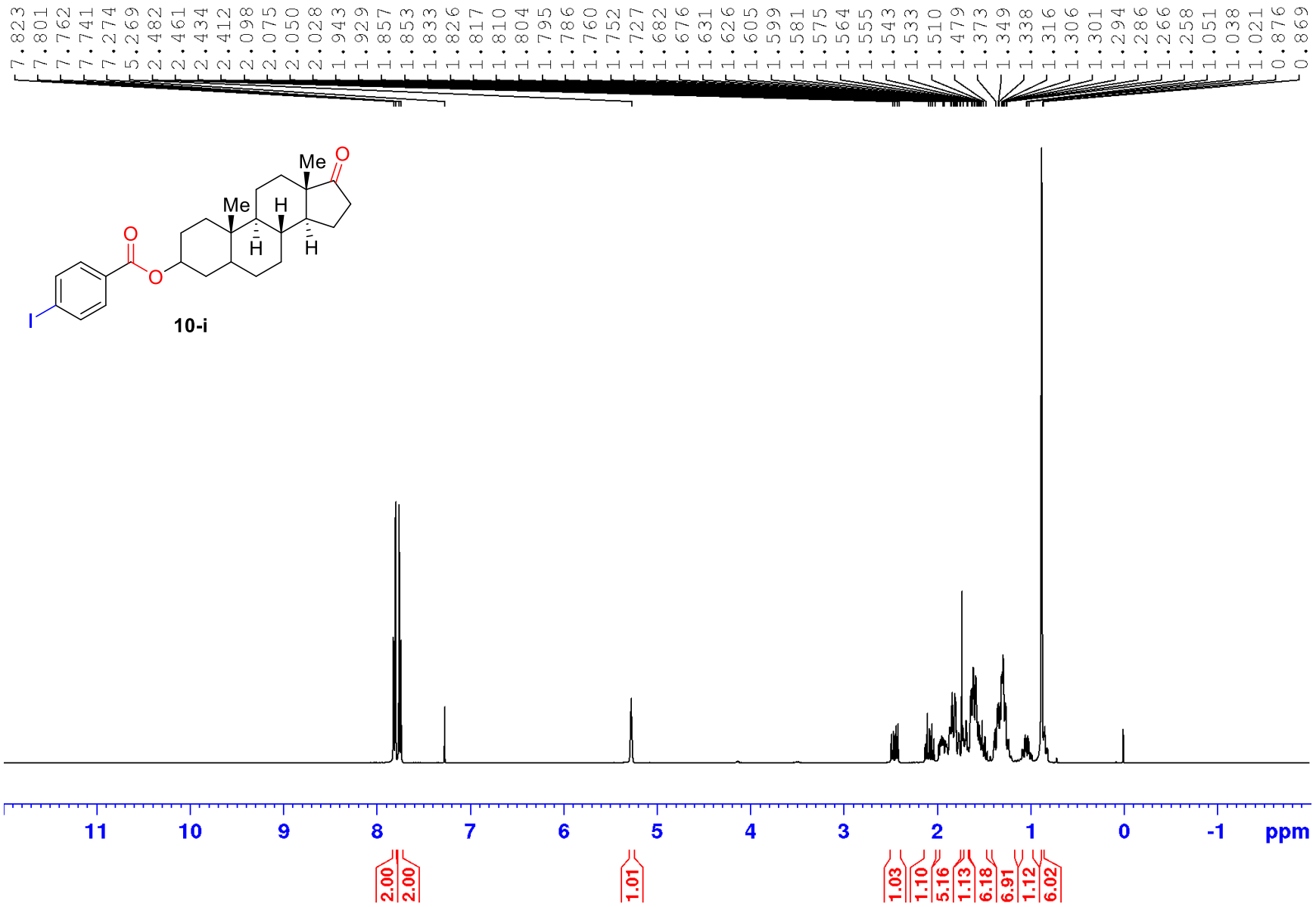
40
20
0
ppm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2.412
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2.075
2.050
2.028
1.943
1.929
1.857
1.853
1.833
1.826
1.817
1.810
1.804
1.795
1.786
1.760
1.752
1.727
1.682
1.676
1.631
1.626
1.605
1.599
1.581
1.575
1.564
1.555
1.543
1.533
1.510
1.479
1.373
1.349
1.338
1.316
1.306
1.301
1.294
1.286
1.266
1.258
1.051
1.038
1.021
0.876
0.869
Me
O
Me
H
O
H
H
O
I
10-i
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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2.00
1.01
1.03
1.10
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1.13
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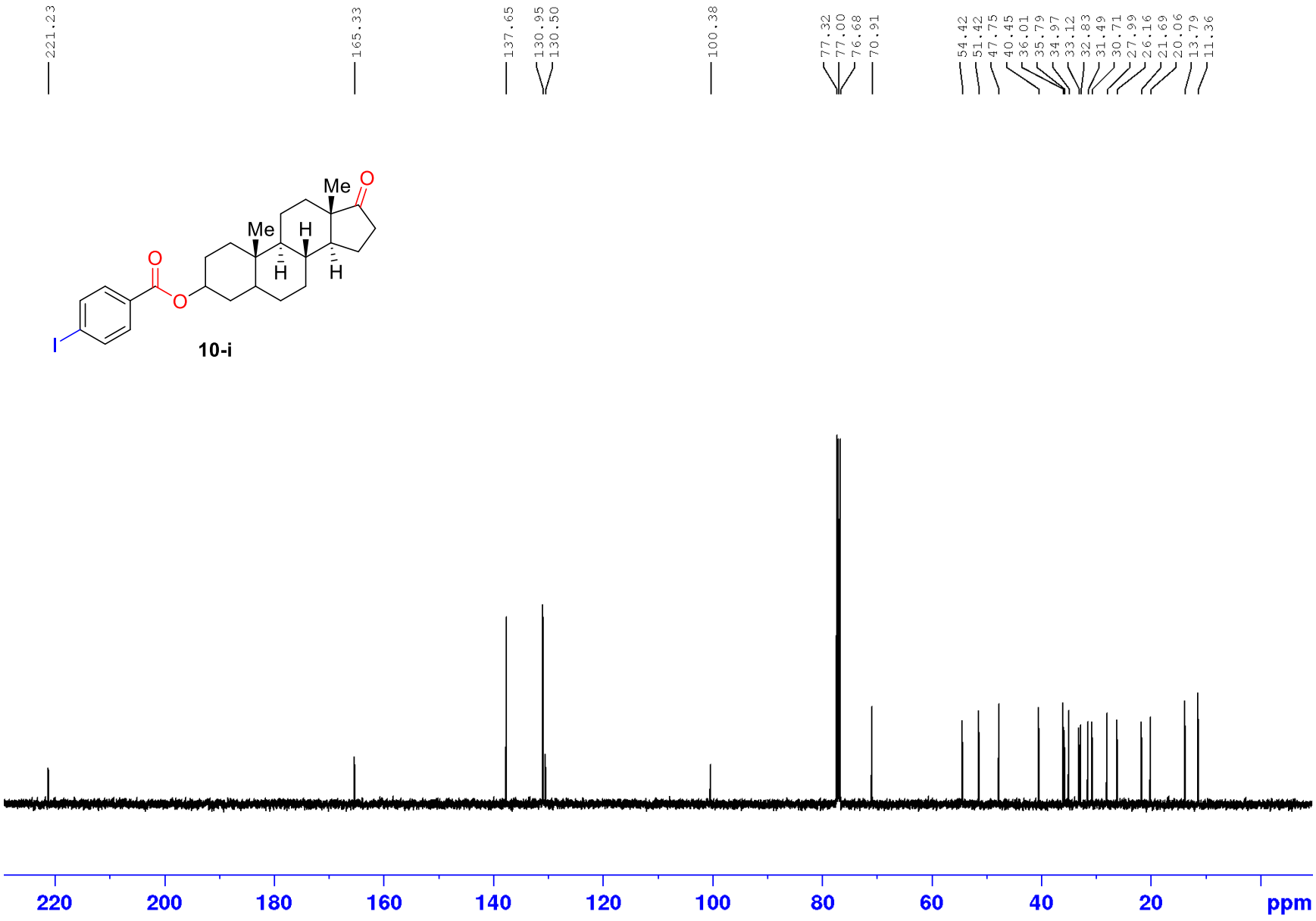
6.91
1.12
6.02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165.33
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77.00
76.68
70.91
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51.42
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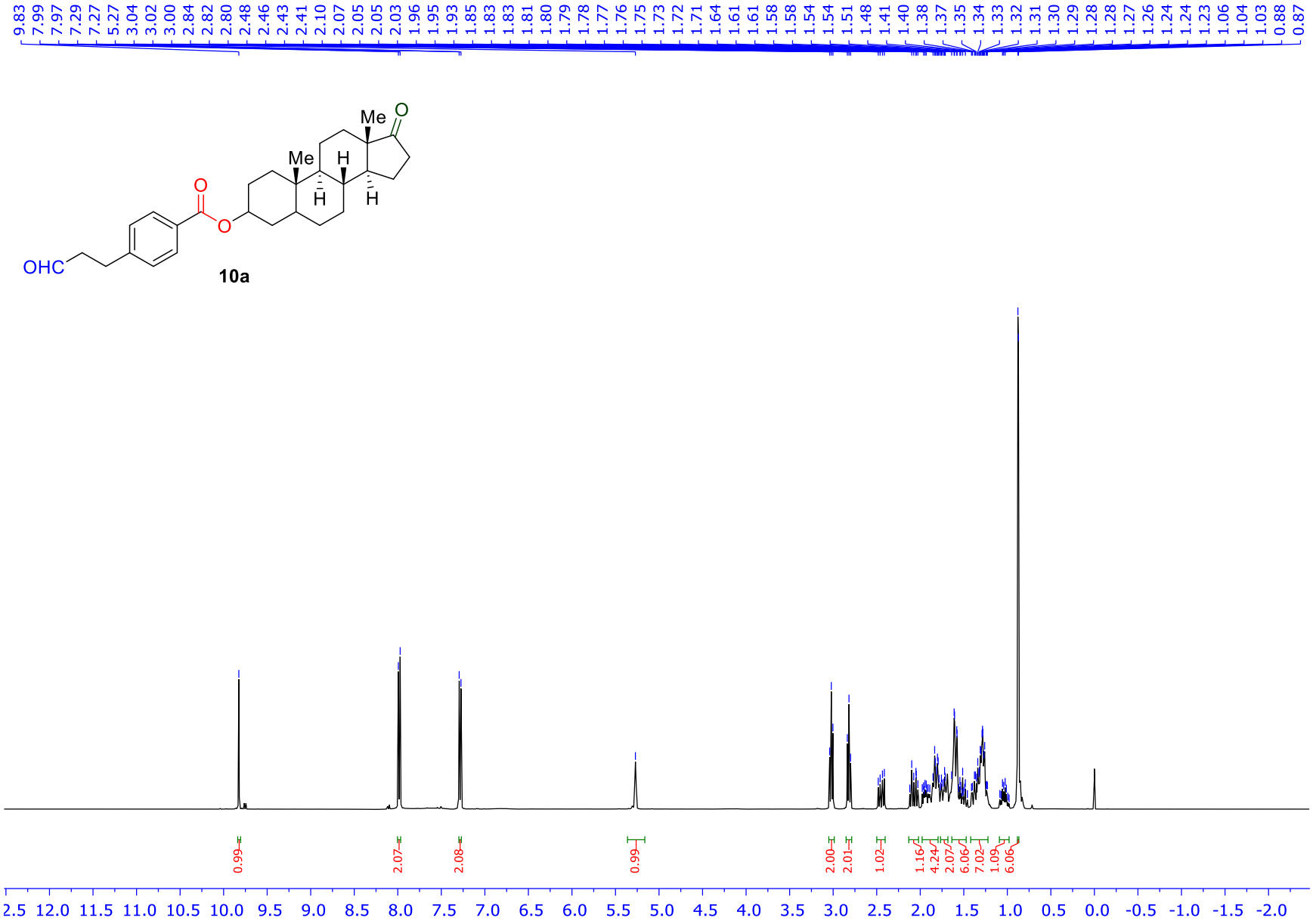
40.45
36.01
35.79
34.97
33.12
32.83
31.49
30.71
27.99
26.16
21.69
20.06
13.79
11.36
Me
O
Me
H
H
H
O
O
I
10-i
220
200
180
160
140
120
100
80
60
40
20
ppm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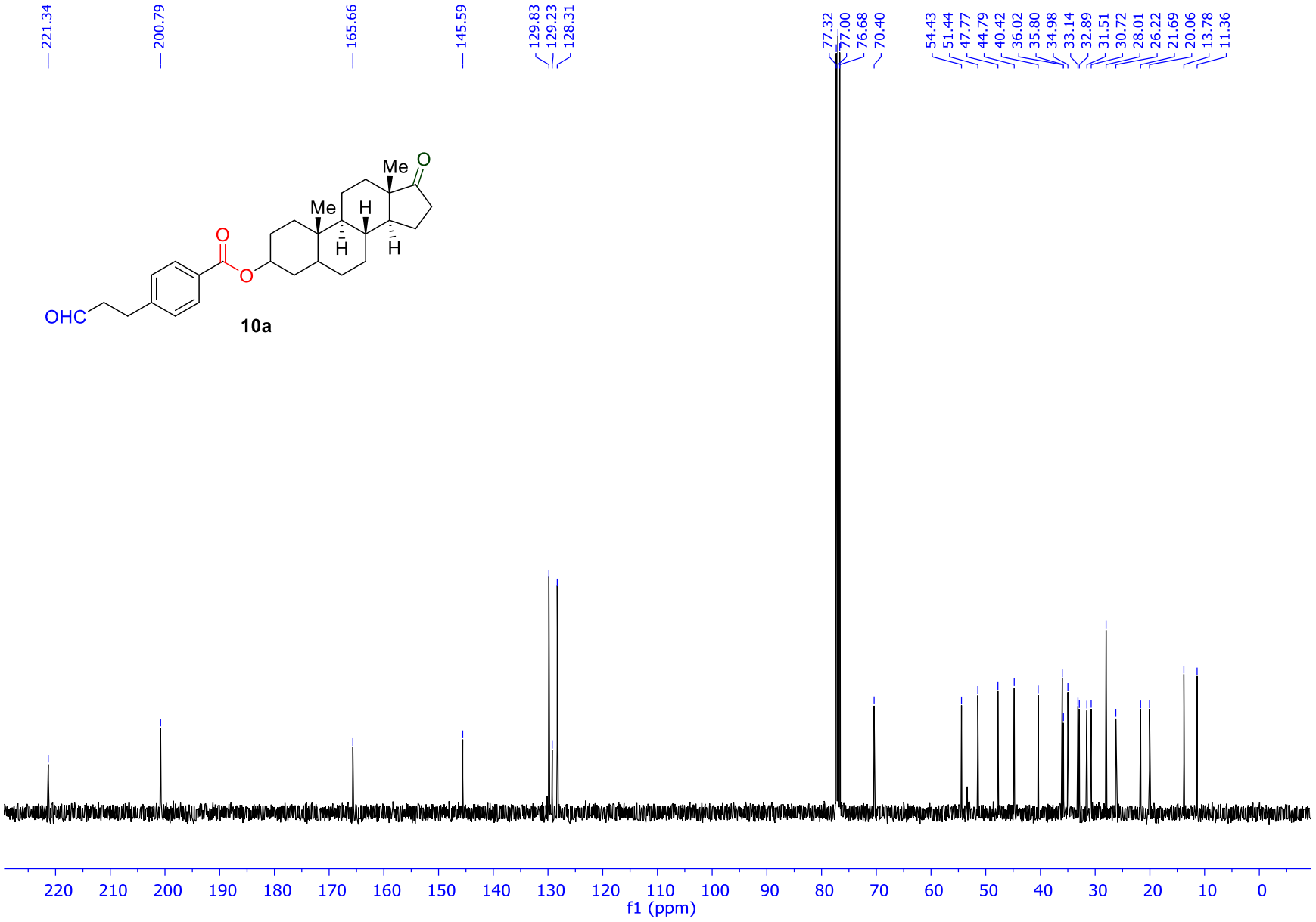
Me
O
Me
H
H
H
O
O
OHC
10a
0.99
2.07
2.08
0.99
2.00
2.01
1.02
1.16
4.24
2.07
6.06
7.02
1.09
6.06
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0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200.79
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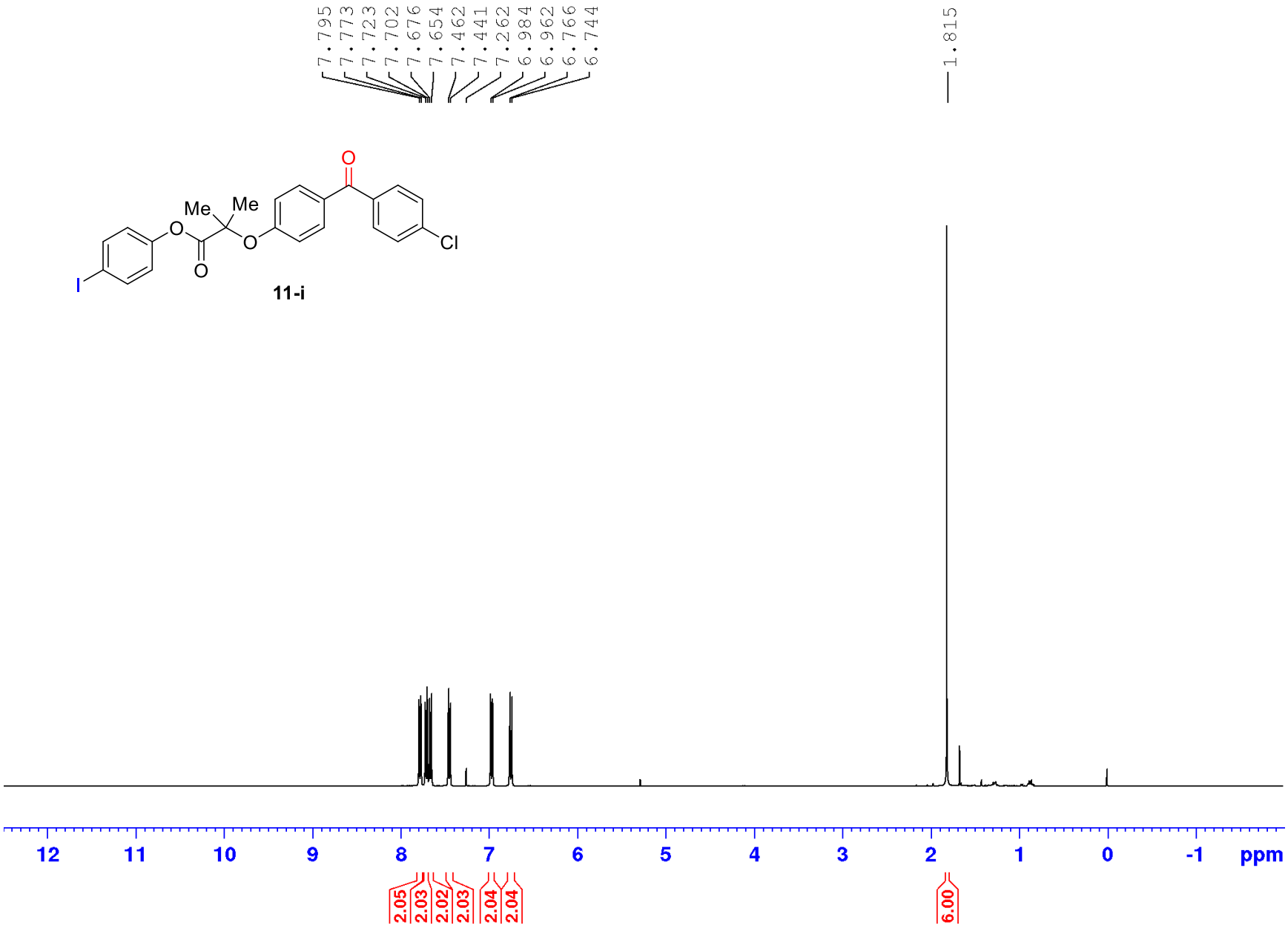
129.23
128.31
77.32
77.00
76.68
70.40
54.43
51.44
47.77
44.79
40.42
36.02
35.80
34.98
33.14
32.89
31.51
30.72
28.01
26.22
21.69
20.06
13.78
11.36
Me
O
Me
H
H
H
O
O
OHC
10a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.723
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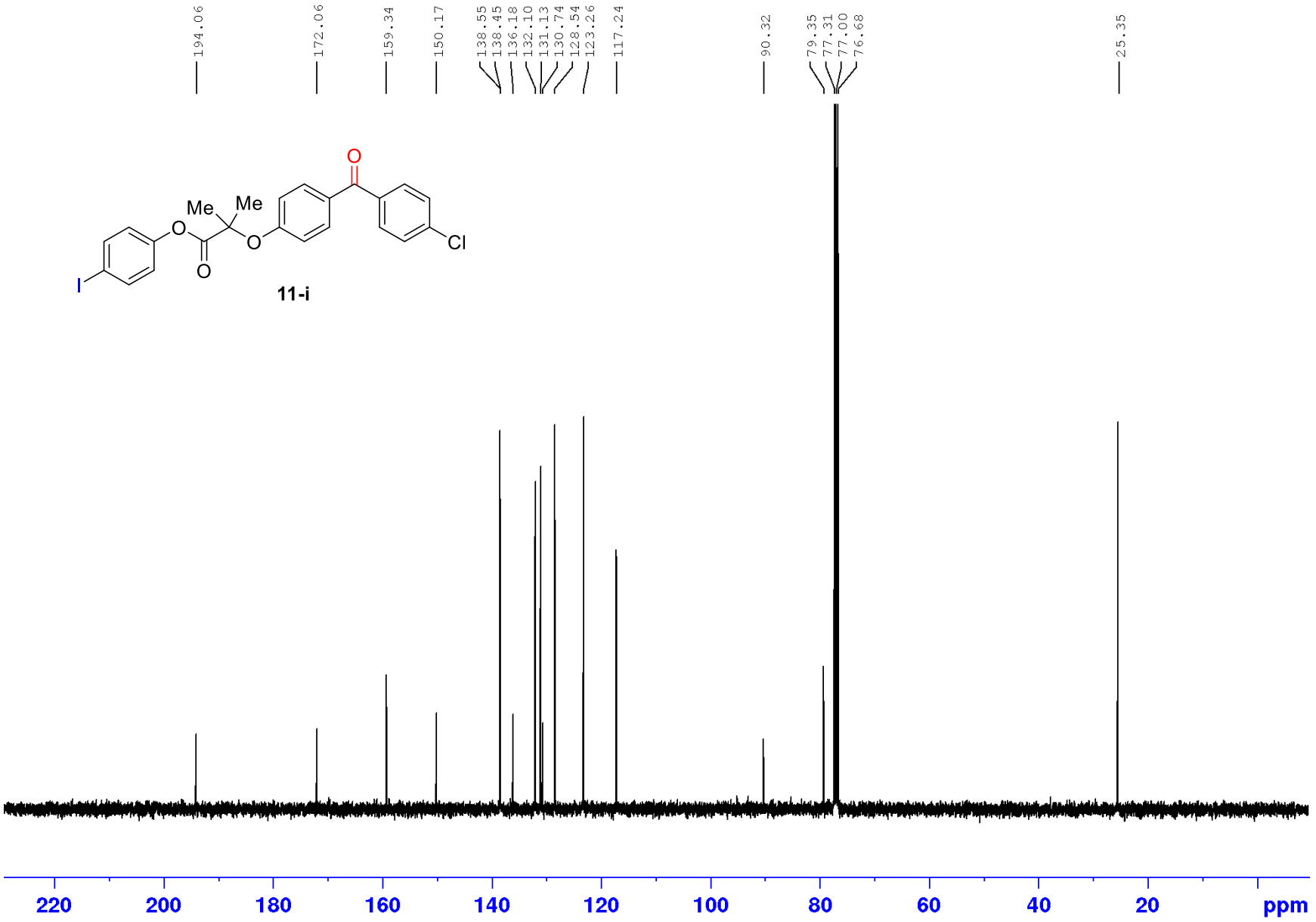
7.654
7.462
7.441
7.262
6.984
6.962
6.766
6.744
1.815
Me
Me
O
O
O
O
Cl
I
11-i
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.05
2.03
2.02
2.03
2.04
2.04
6.00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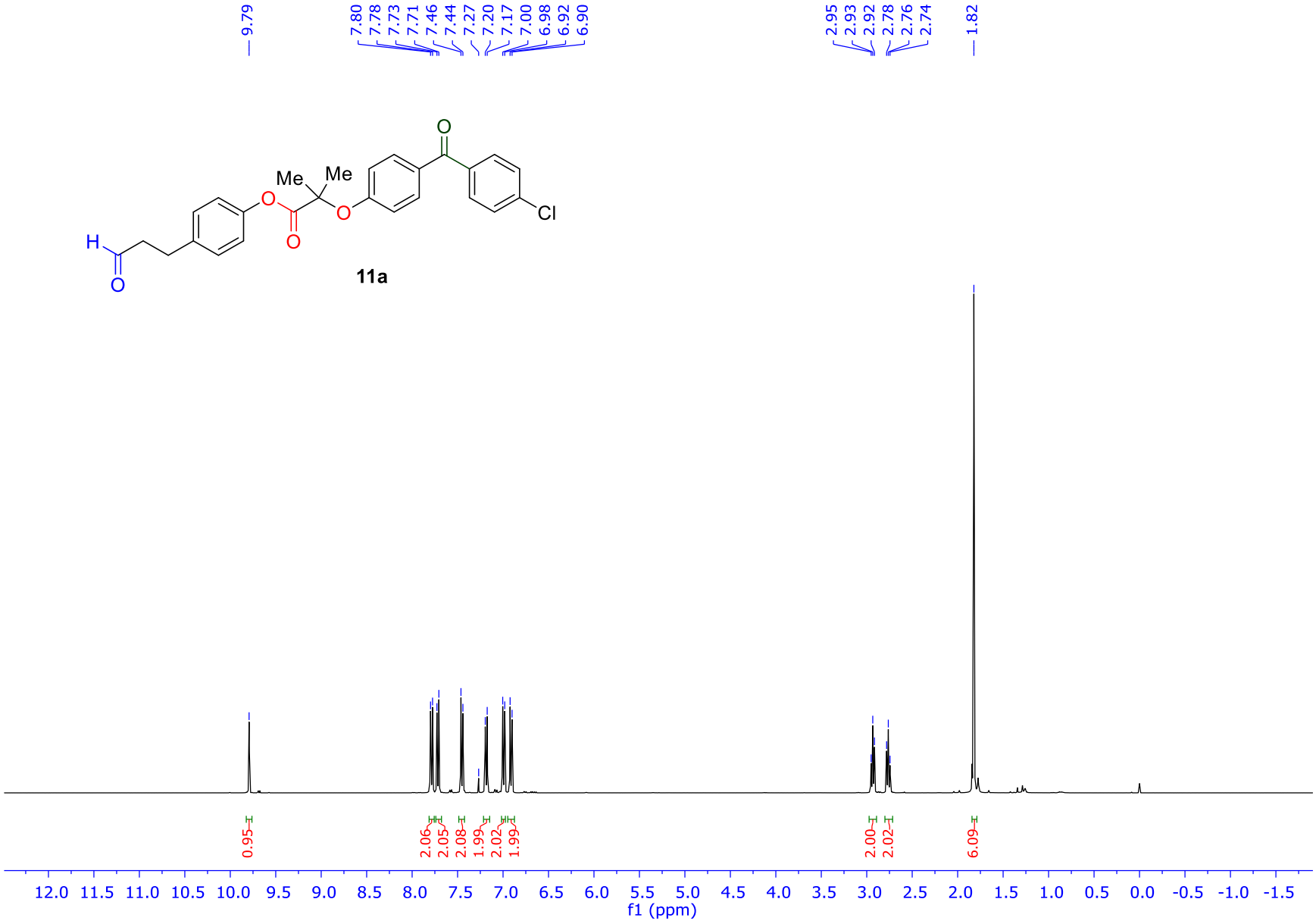
172.06
159.34
150.17
138.55
138.45
136.18
132.10
131.13
130.74
128.54
123.26
117.24
90.32
79.35
77.31
77.00
76.68
25.35
Me
Me
O
O
O
O
Cl
I
11-i
220
200
180
160
140
120
100
80
60
40
20
ppm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7.80
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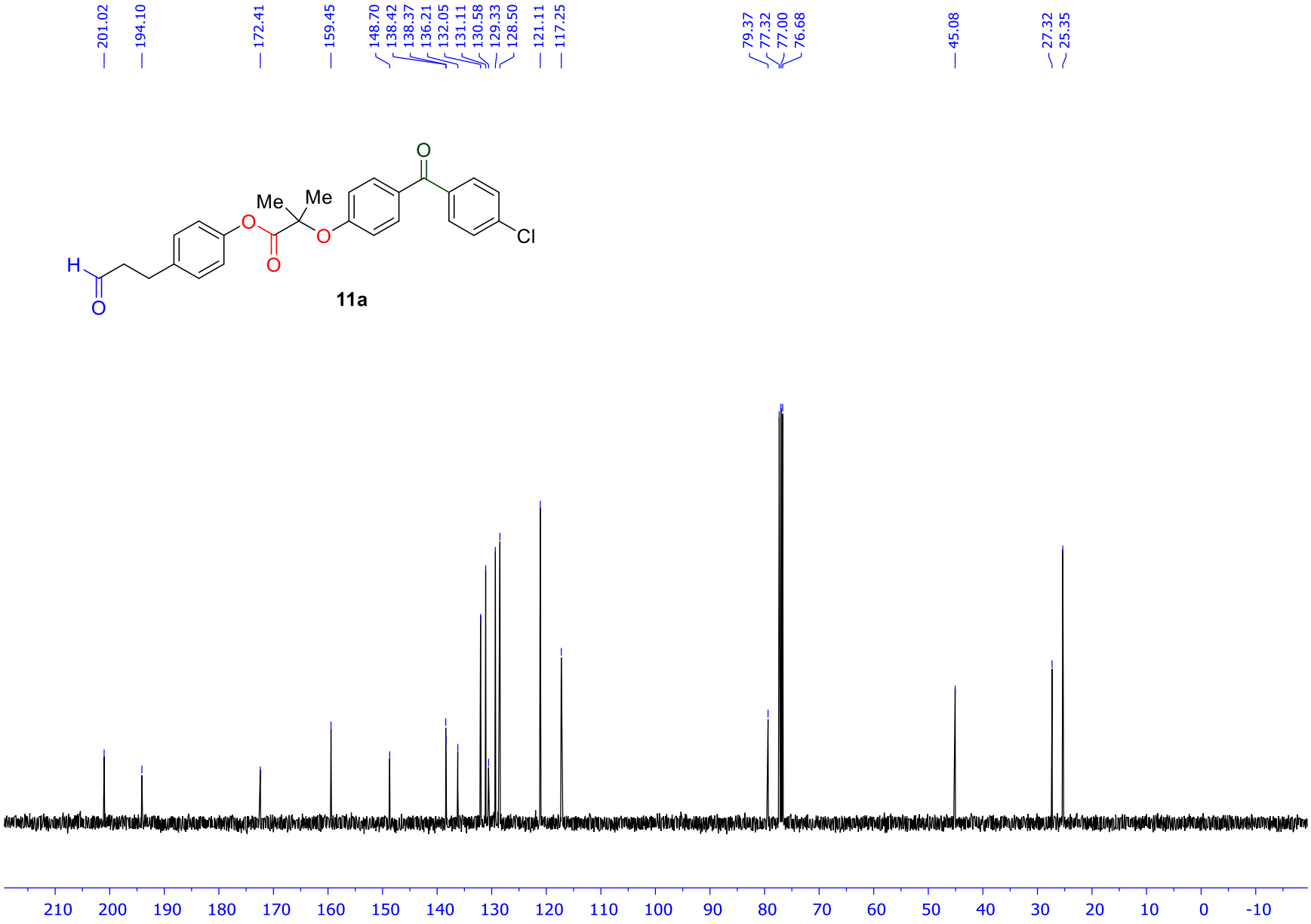
7.73
7.71
7.46
7.44
7.27
7.20
7.17
7.00
6.98
6.92
6.90
2.95
2.93
2.92
2.78
2.76
2.74
1.82
O
Me
Me
O
O
O
Cl
H
O
11a
0.95
2.06
2.05
2.08
1.99
2.02
1.99
2.00
2.02
6.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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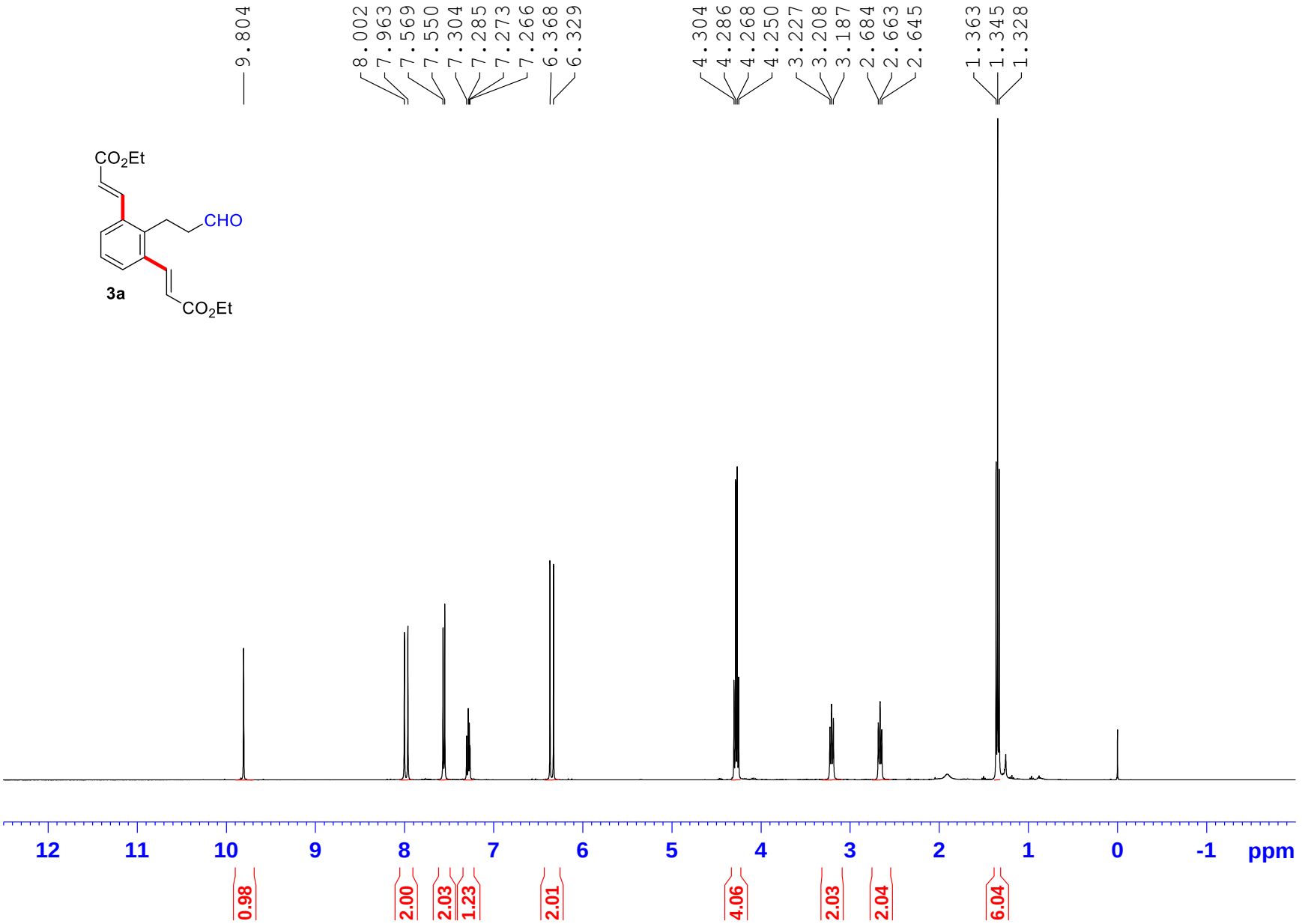
194.10
172.41
159.45
148.70
138.42
138.37
136.21
132.05
131.11
130.58
129.33
128.50
121.11
117.25
79.37
77.32
77.00
76.68
45.08
27.32
25.35
Me
Me
O
O
O
O
H
O
Cl
11a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Copies of ^{1}H NMR and ^{13}C NMR spectra of all olefinated compounds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7.304
7.285
7.273
7.266
6.368
6.329
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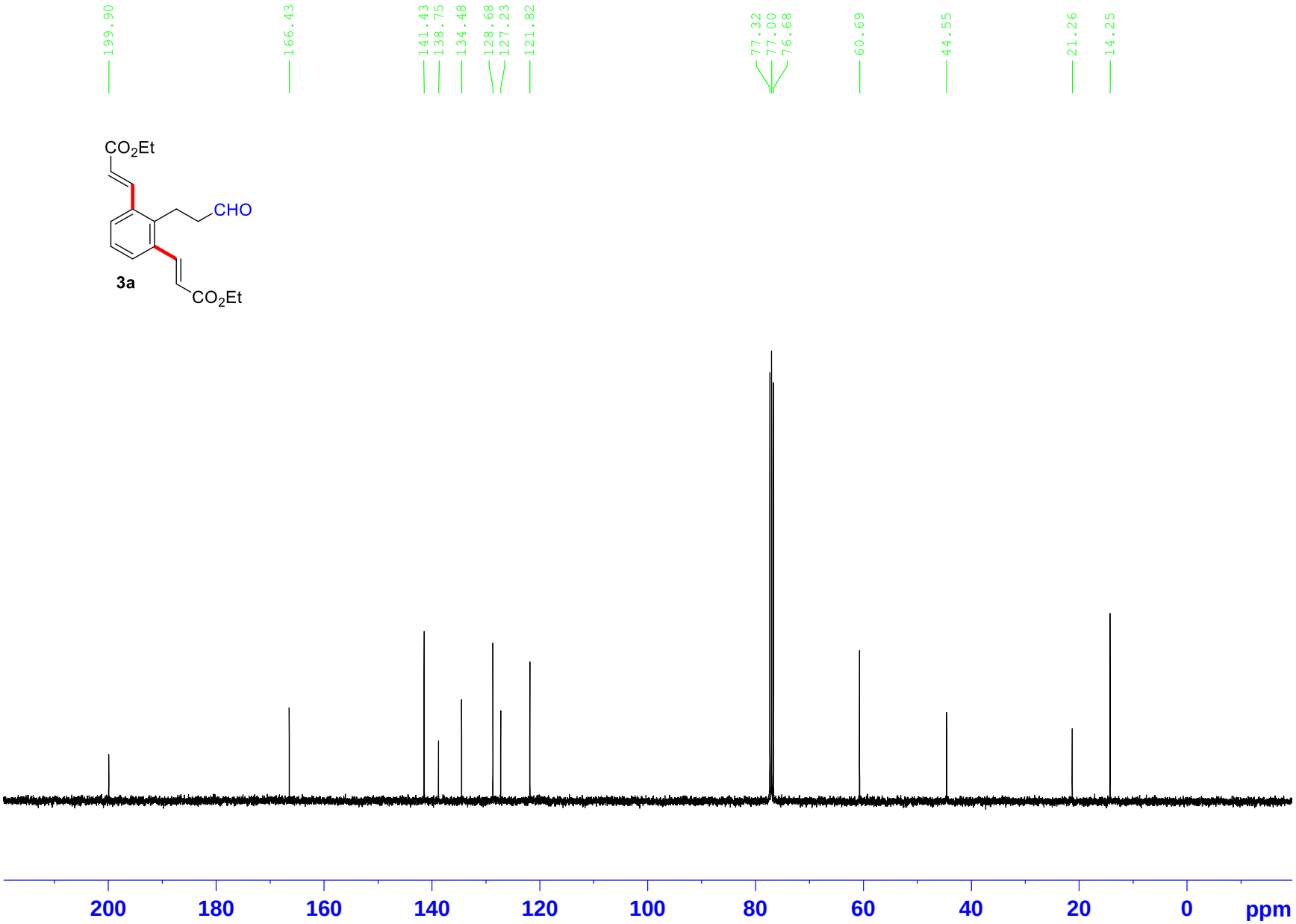
4.268
4.250
3.227
3.208
3.187
2.684
2.663
2.645
1.363
1.345
1.328
CO2Et
CHO
CO2Et
3a
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
2.00
2.03
1.23
2.01
4.06
2.03
2.04
6.04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141.43
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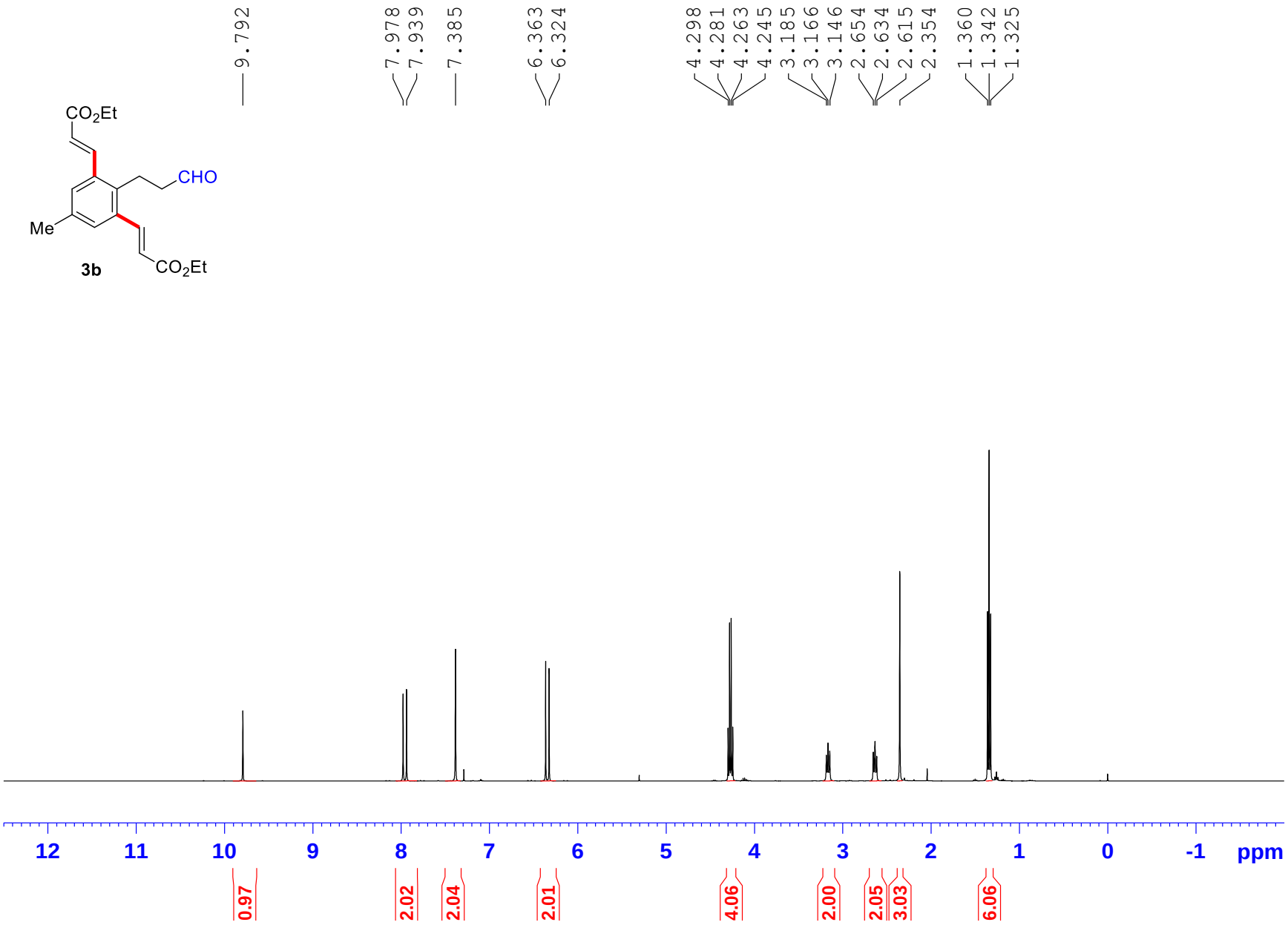
134.48
128.68
127.23
121.82
77.32
77.00
76.68
60.69
44.55
21.26
14.25
CO2Et
CHO
CO2Et
3a
200
180
160
140
120
100
80
60
40
20
0
ppm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7.385
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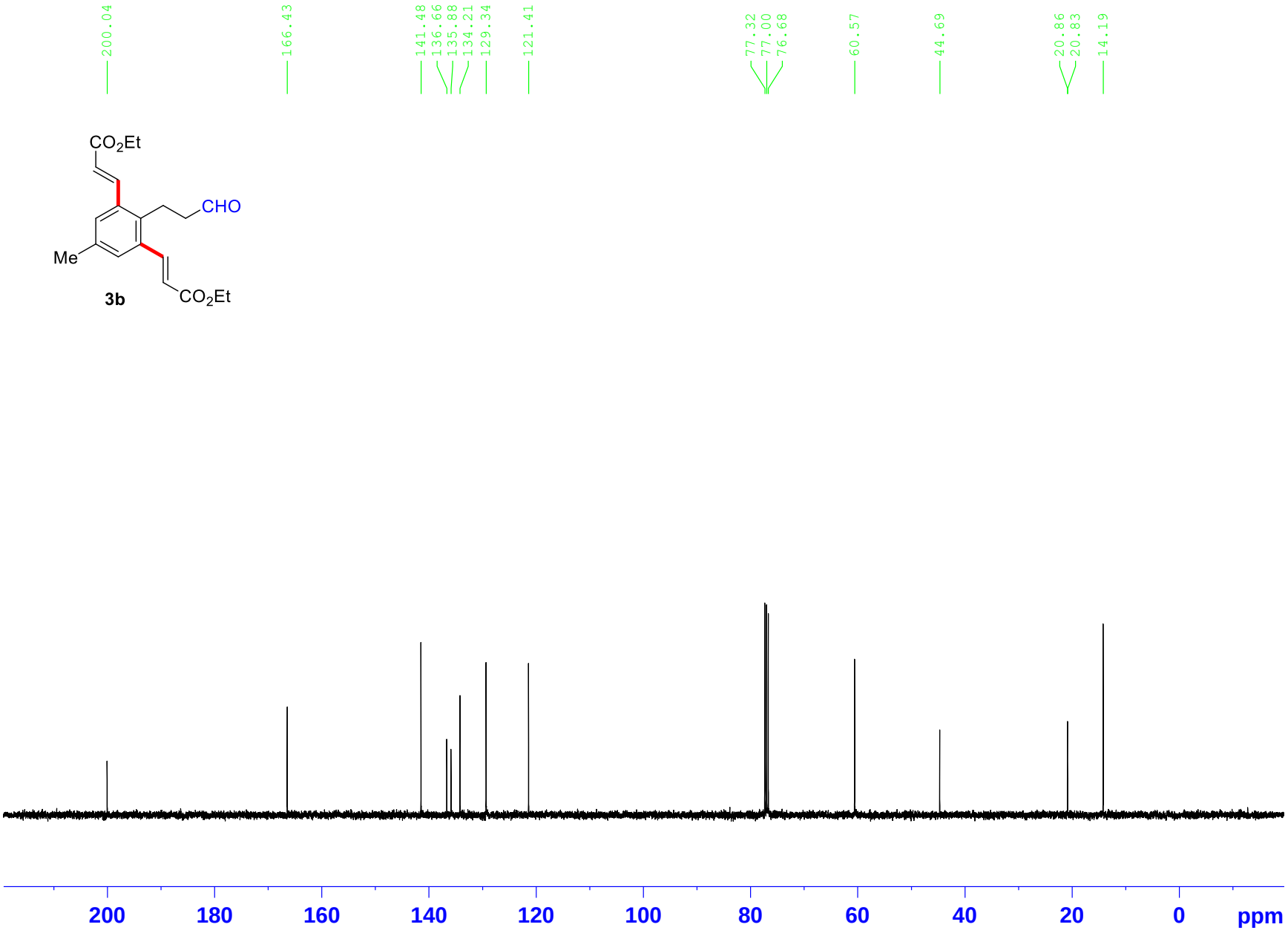
4.281
4.263
4.245
3.185
3.166
3.146
2.654
2.634
2.615
2.354
1.360
1.342
1.325
CO2Et
CHO
Me
CO2Et
3b
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
2.02
2.04
2.01
4.06
2.00
2.05
3.03
6.06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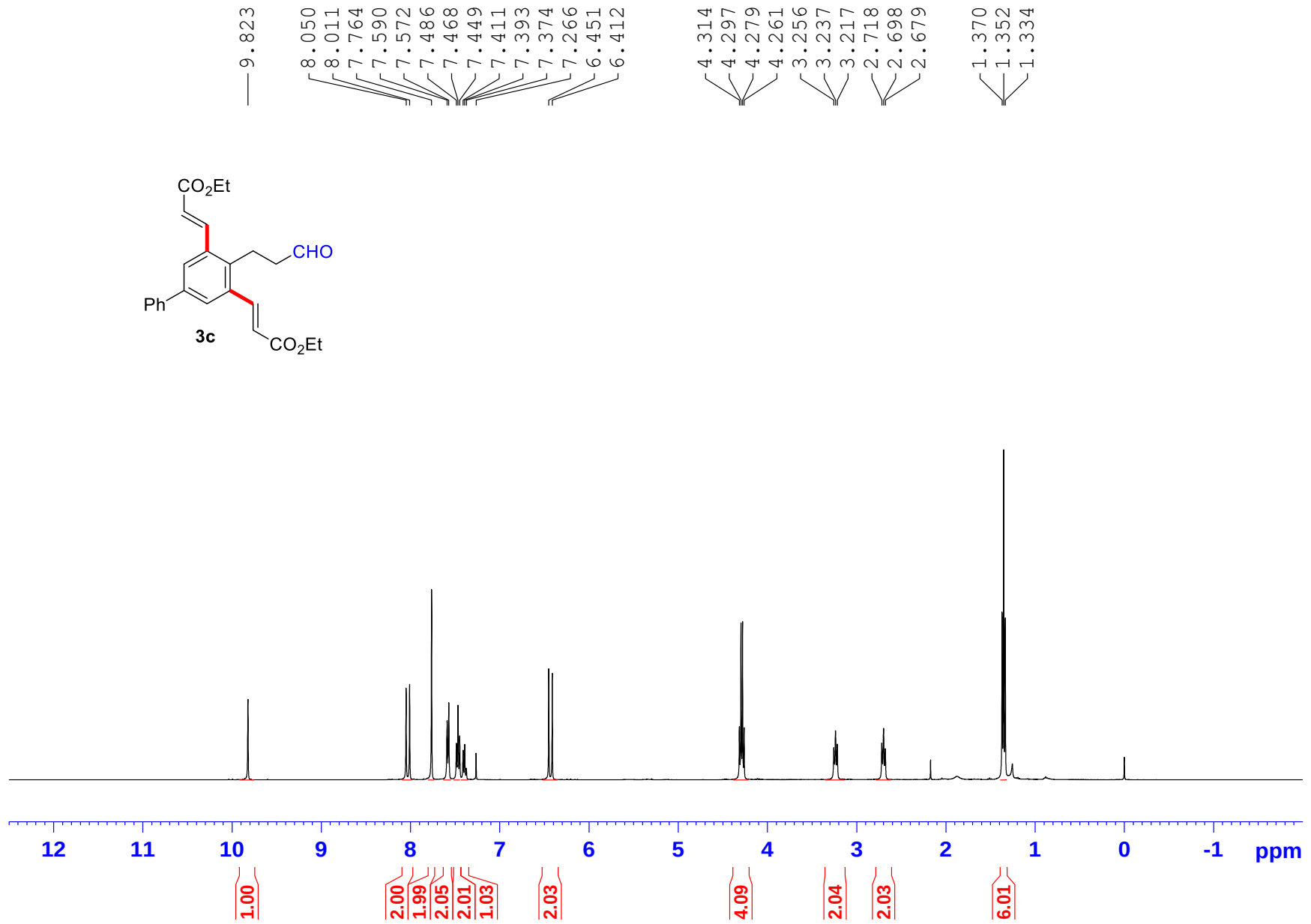
135.88
134.21
129.34
121.41
77.32
77.00
76.68
60.57
44.69
20.86
20.83
14.19
CO2Et
CHO
Me
CO2Et
3b
200
180
160
140
120
100
80
60
40
20
0
ppm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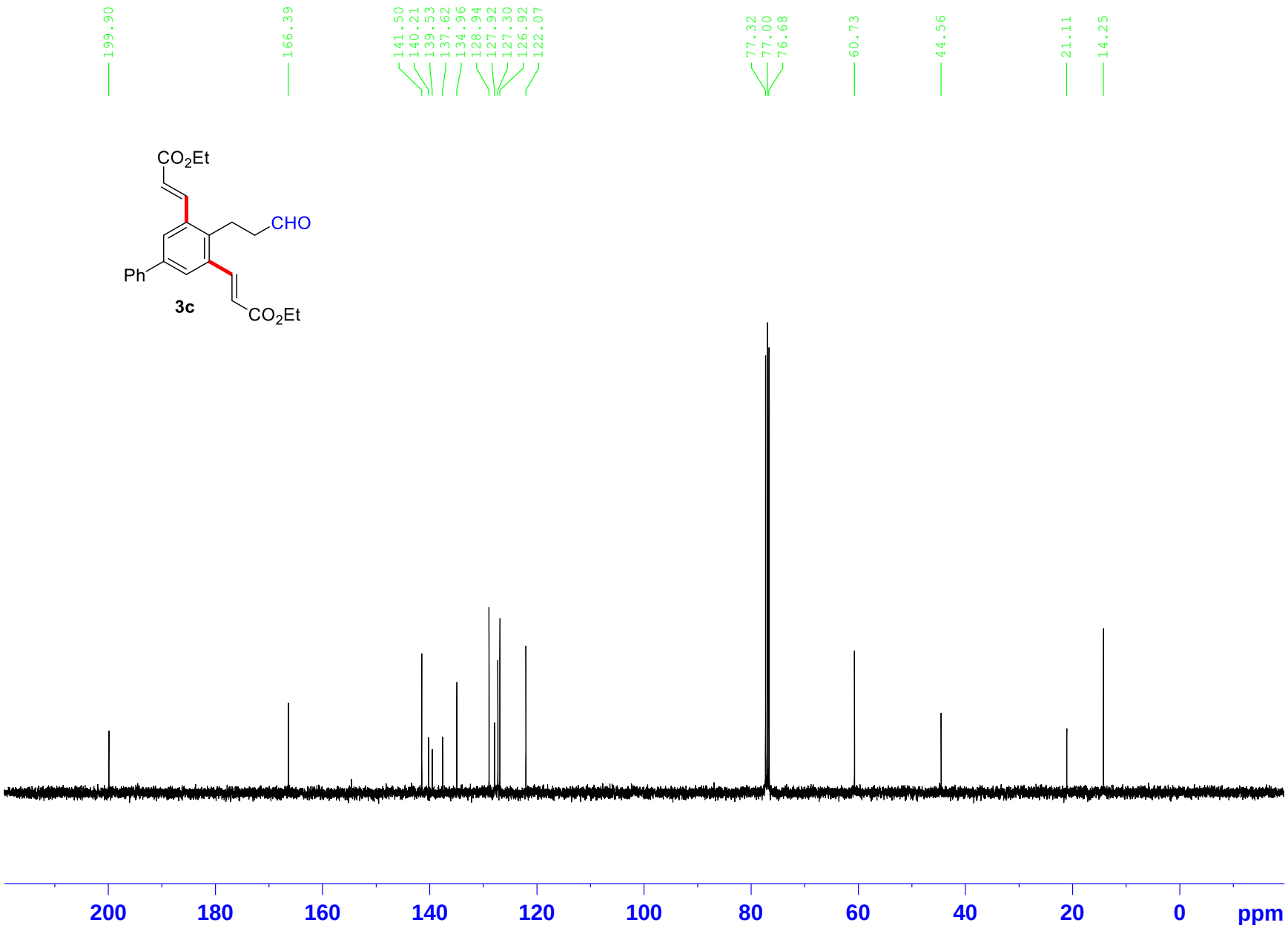
8.050
8.011
7.764
7.590
7.572
7.486
7.468
7.449
7.411
7.393
7.374
7.266
6.451
6.412
4.314
4.297
4.279
4.261
3.256
3.237
3.217
2.718
2.698
2.679
1.370
1.352
1.334
CO2Et
CHO
Ph
CO2Et
3c
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
2.00
1.99
2.05
2.01
1.03
2.03
4.09
2.04
2.03
6.01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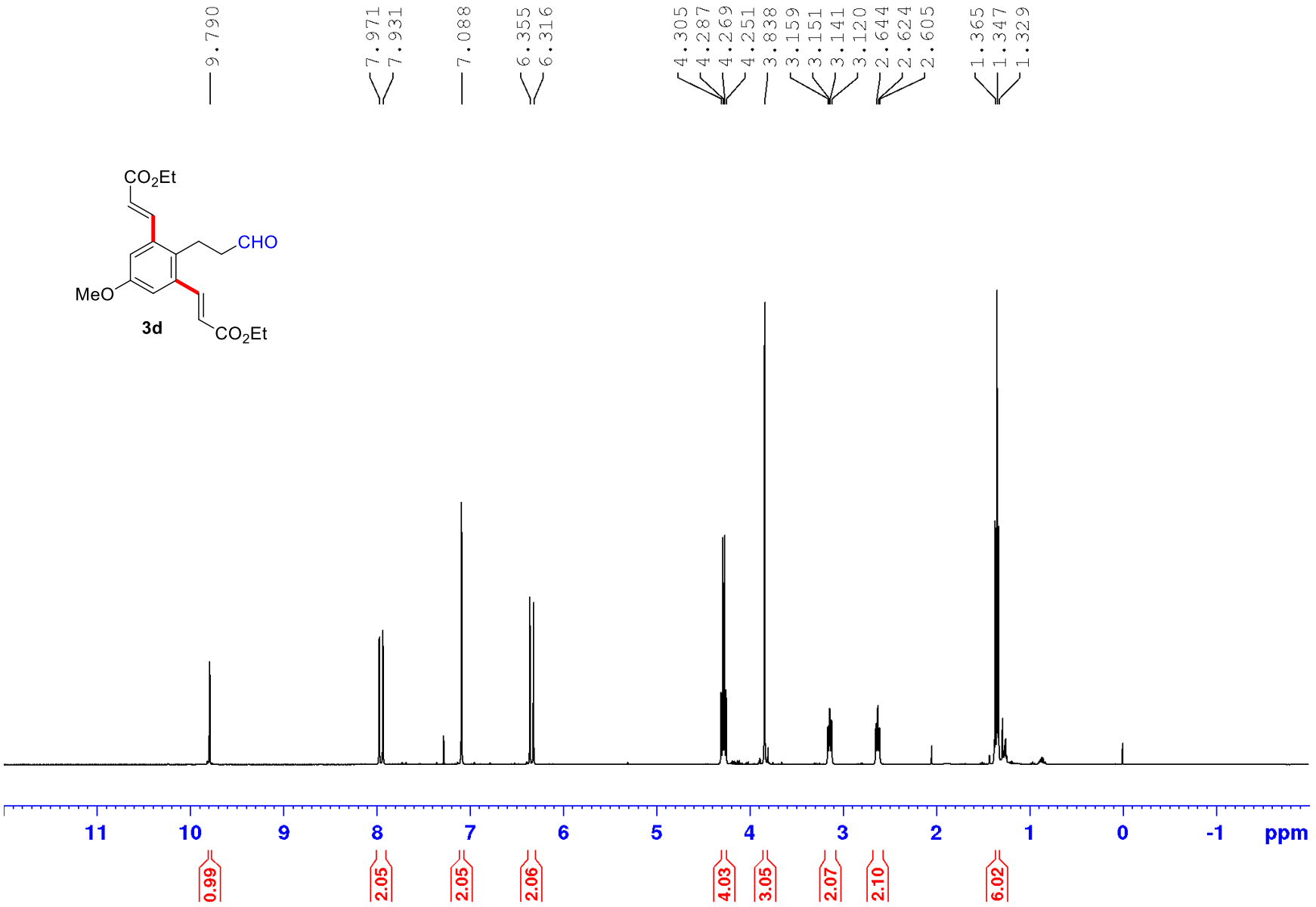
141.50
140.21
139.53
137.62
134.96
128.94
127.92
127.30
126.92
122.07
77.32
77.00
76.68
60.73
44.56
21.11
14.25
CO2Et
CHO
Ph
CO2Et
3c
200
180
160
140
120
100
80
60
40
20
0
ppm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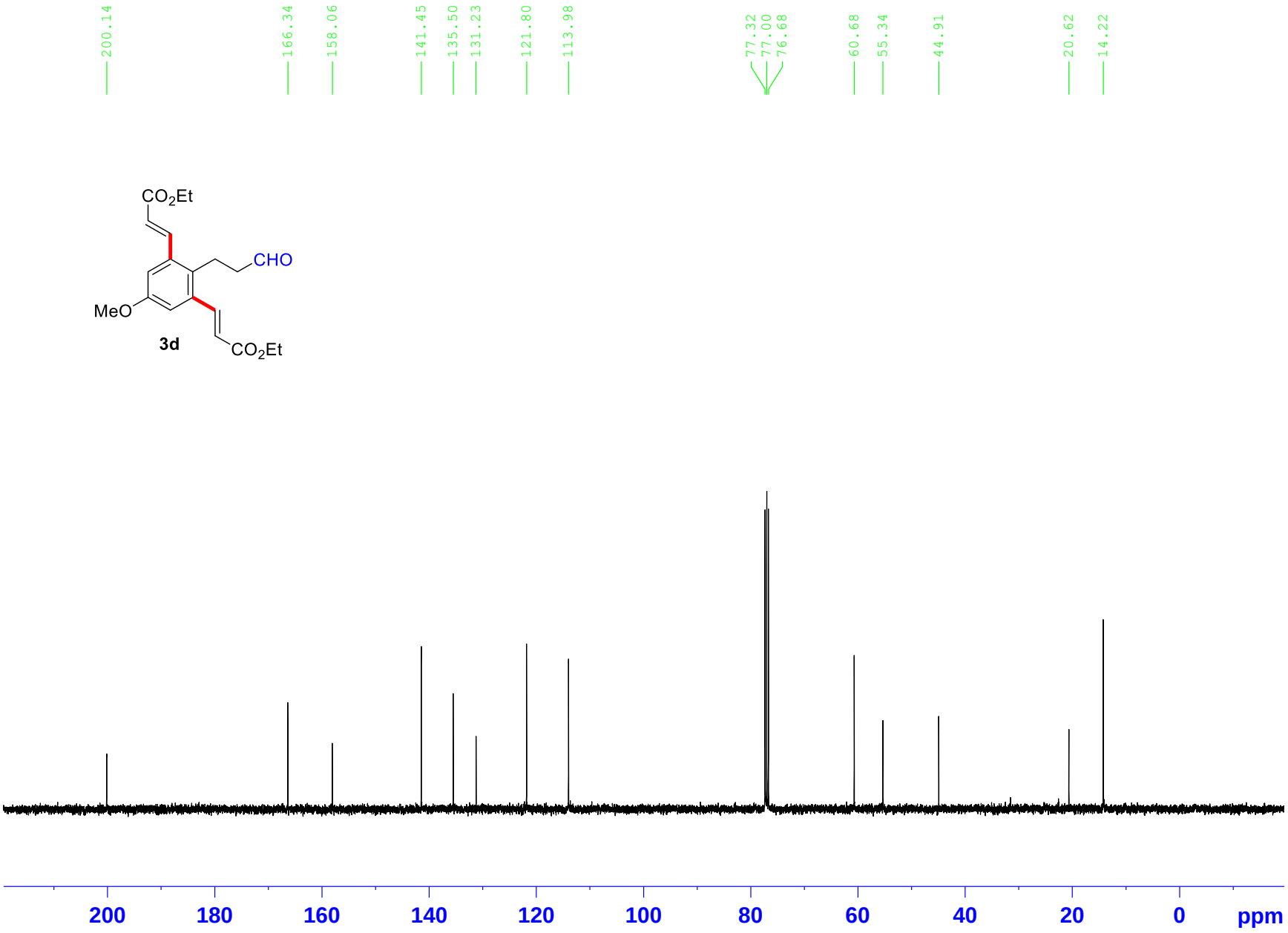
7.088
6.355
6.316
4.305
4.287
4.269
4.251
3.838
3.159
3.151
3.141
3.120
2.644
2.624
2.605
1.365
1.347
1.329
CO2Et
CHO
MeO
CO2Et
3d
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.99
2.05
2.05
2.06
4.03
3.05
2.07
2.10
6.02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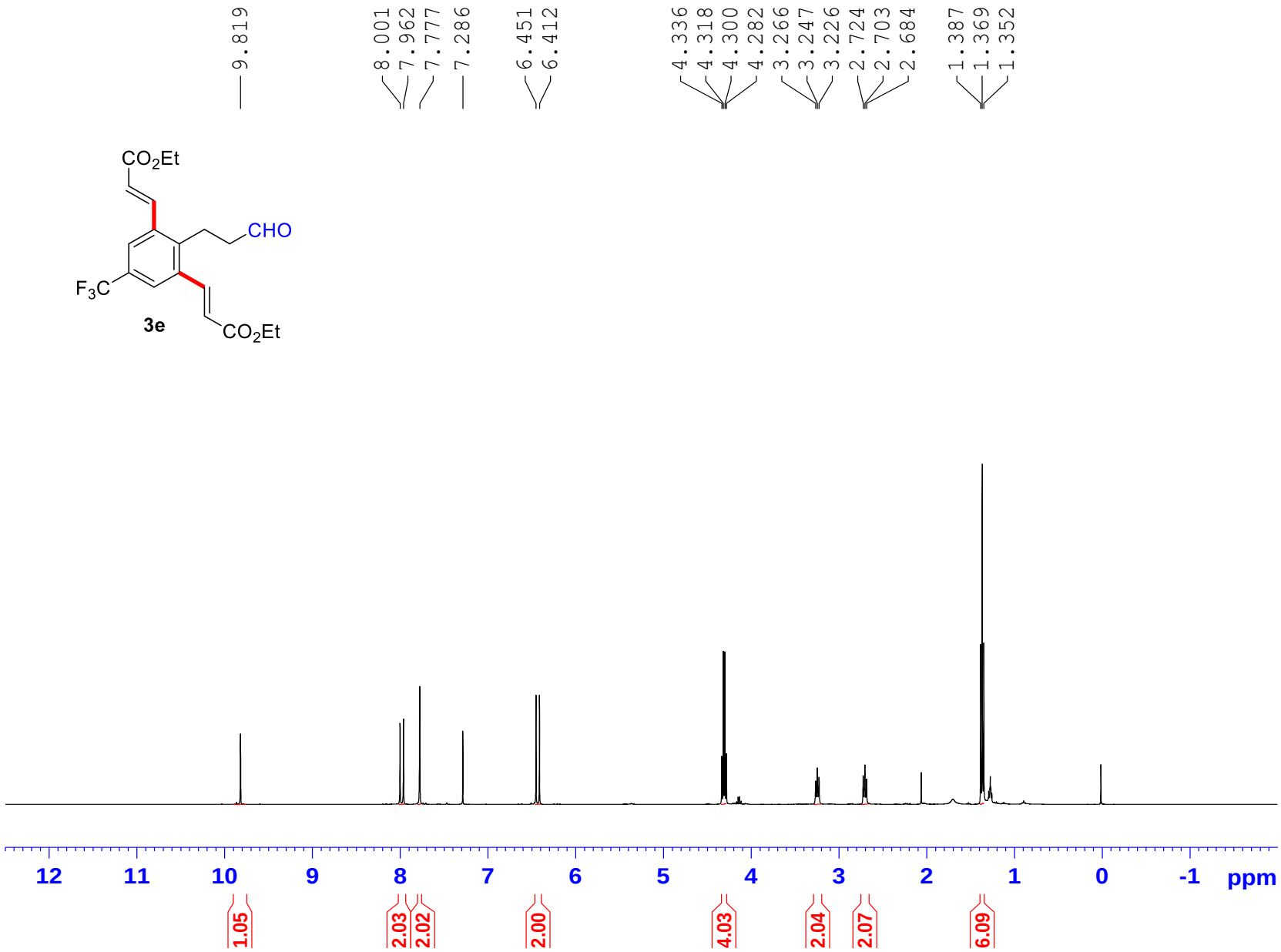
158.06
141.45
135.50
131.23
121.80
113.98
77.32
77.00
76.68
60.68
55.34
44.91
20.62
14.22
CO2Et
CHO
MeO
CO2Et
3d
200
180
160
140
120
100
80
60
40
20
0
ppm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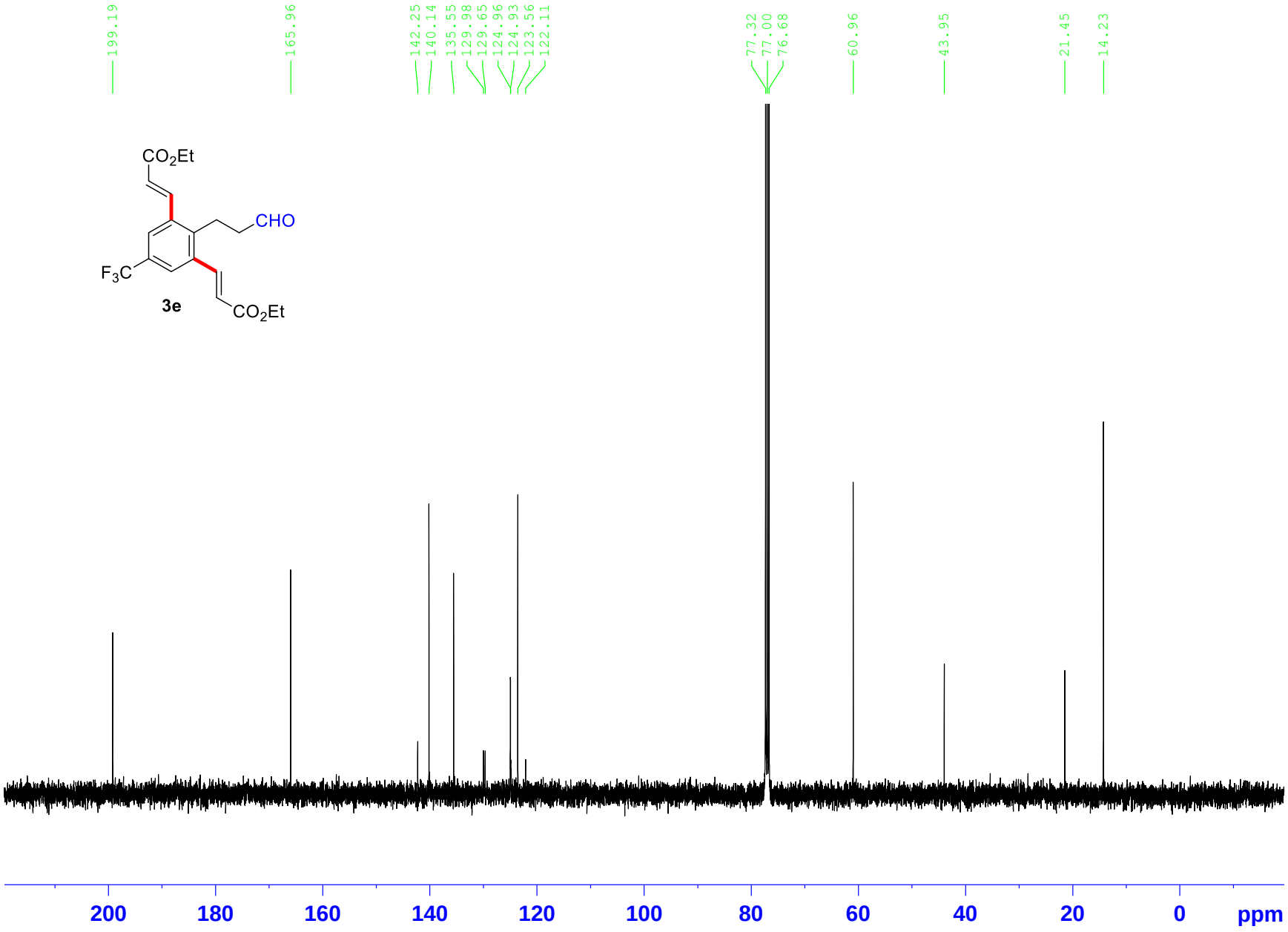
8.001
7.962
7.777
7.286
6.451
6.412
4.336
4.318
4.300
4.282
3.266
3.247
3.226
2.724
2.703
2.684
1.387
1.369
1.352
CO2Et
CHO
F3C
CO2Et
3e
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.05
2.03
2.02
2.00
4.03
2.04
2.07
6.09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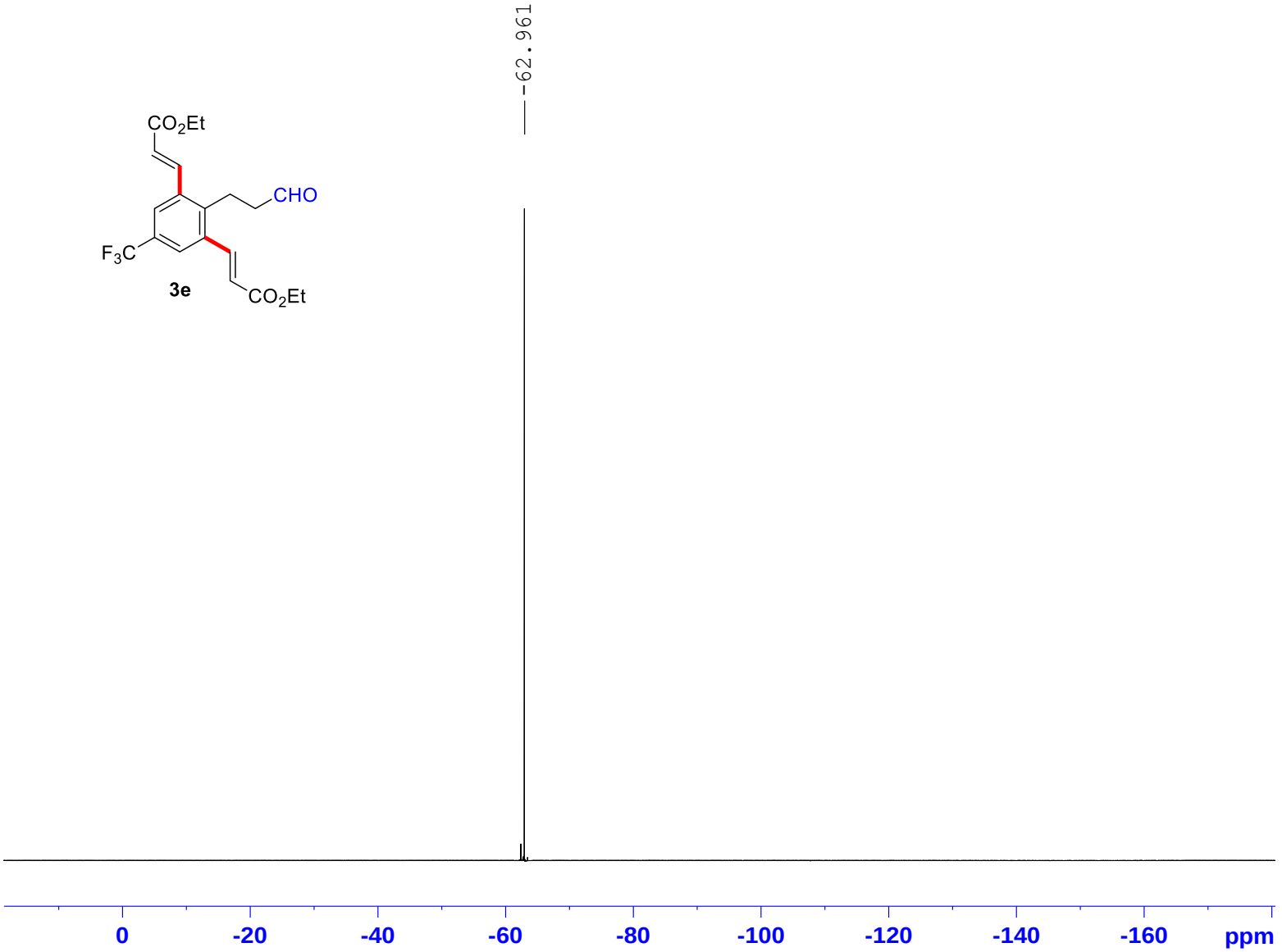
142.25
140.14
135.55
129.98
129.65
124.96
124.93
123.56
122.11
77.32
77.00
76.68
60.96
43.95
21.45
14.23
CO2Et
CHO
F3C
CO2Et
3e
200
180
160
140
120
100
80
60
40
20
0
ppm


-62.961
CO2Et
CHO
F3C
3e
CO2Et
0
-20
-40
-60
-80
-100
-120
-140
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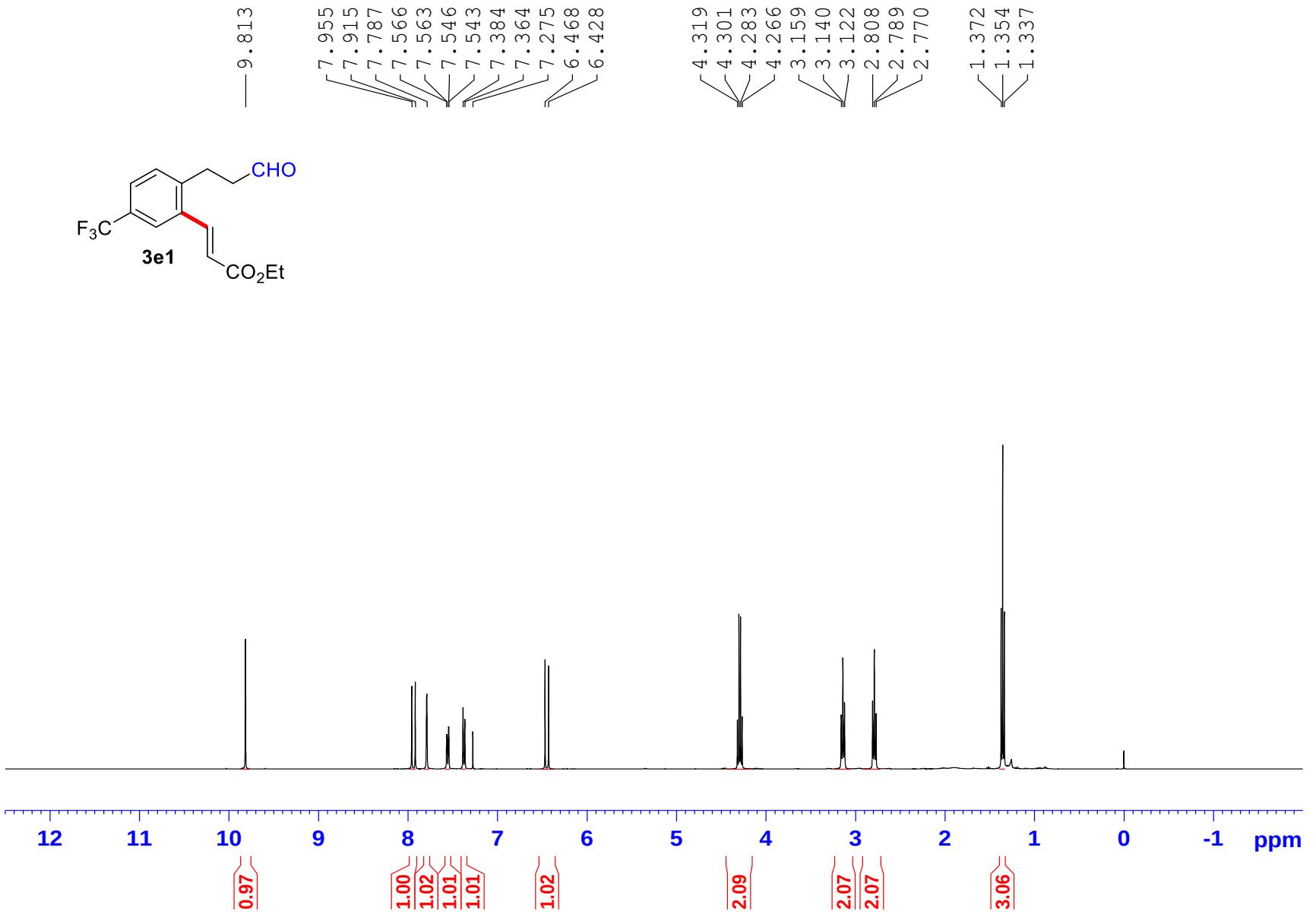
ppm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6.468
6.428
4.319
4.301
4.283
4.266
3.159
3.140
3.122
2.808
2.789
2.770
1.372
1.354
1.337
CHO
F3C
3e1
CO2Et
12
11
10
9
8
7
6
5
4
3
2
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1.02
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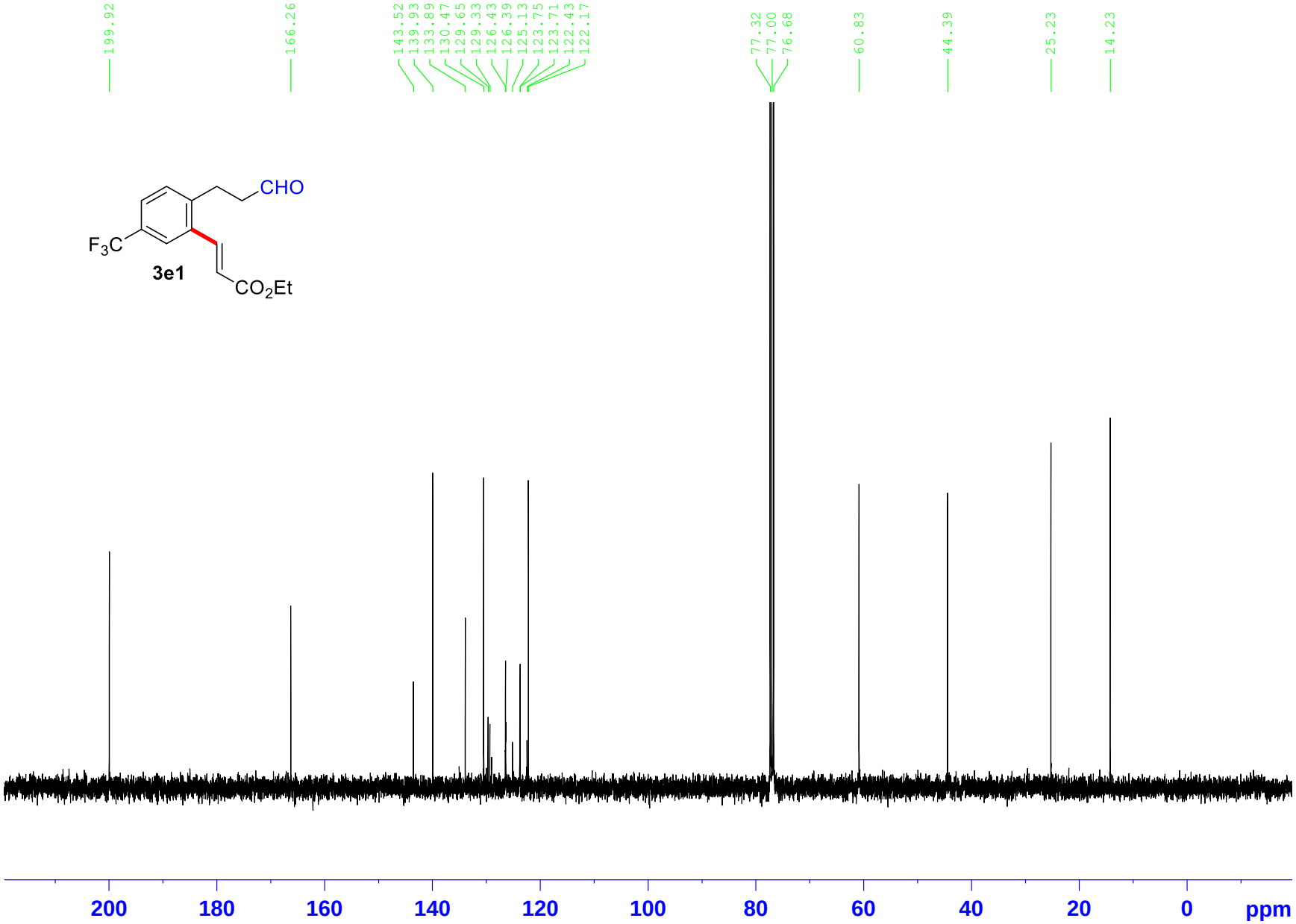
3.06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123.75
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122.43
122.17
77.32
77.00
76.68
60.83
44.39
25.23
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CO2Et
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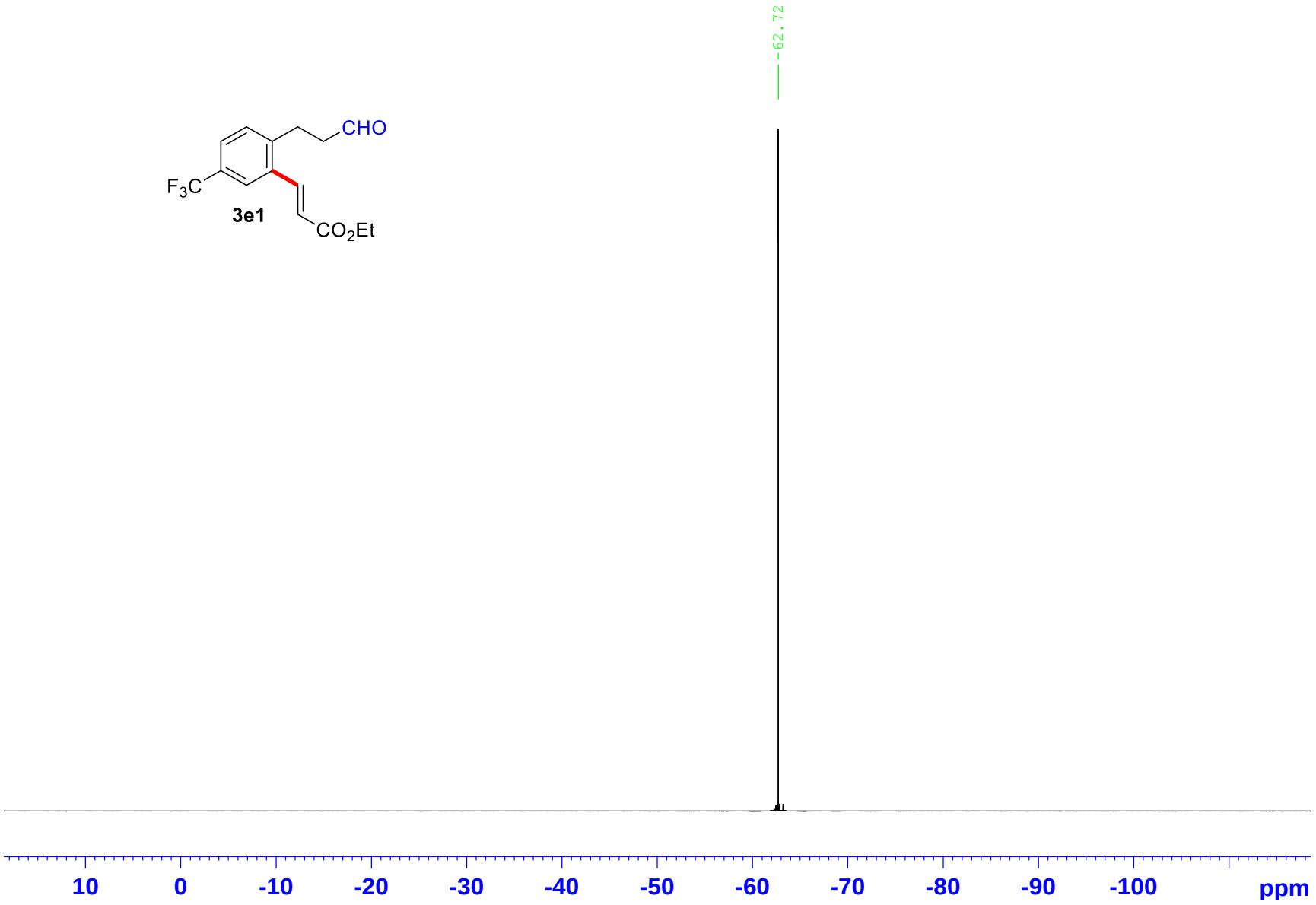
20
0
ppm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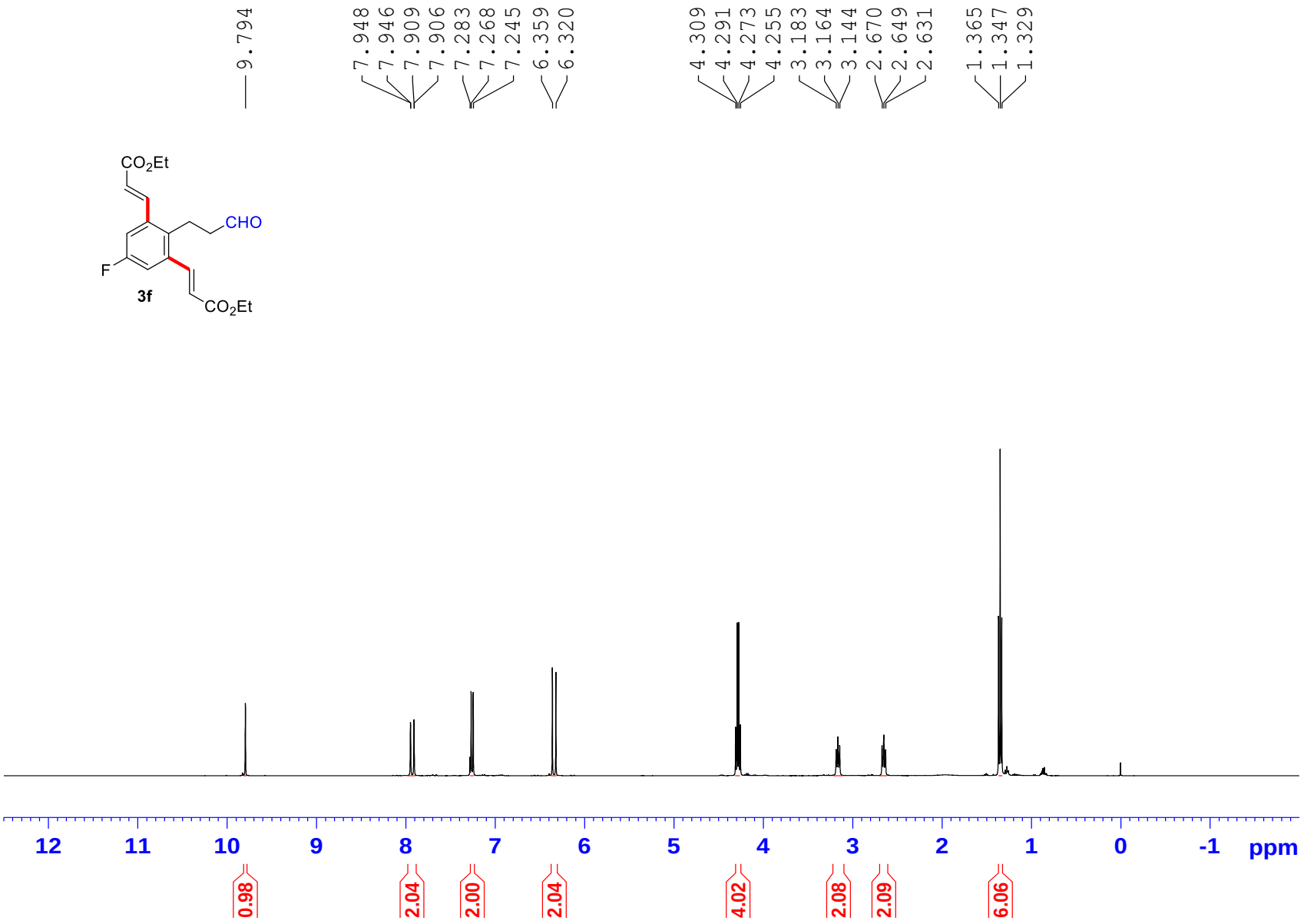
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4.273
4.255
3.183
3.164
3.144
2.670
2.649
2.631
1.365
1.347
1.329
CO2Et
CHO
F
CO2Et
3f
12
11
10
9
8
7
6
5
4
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2.04
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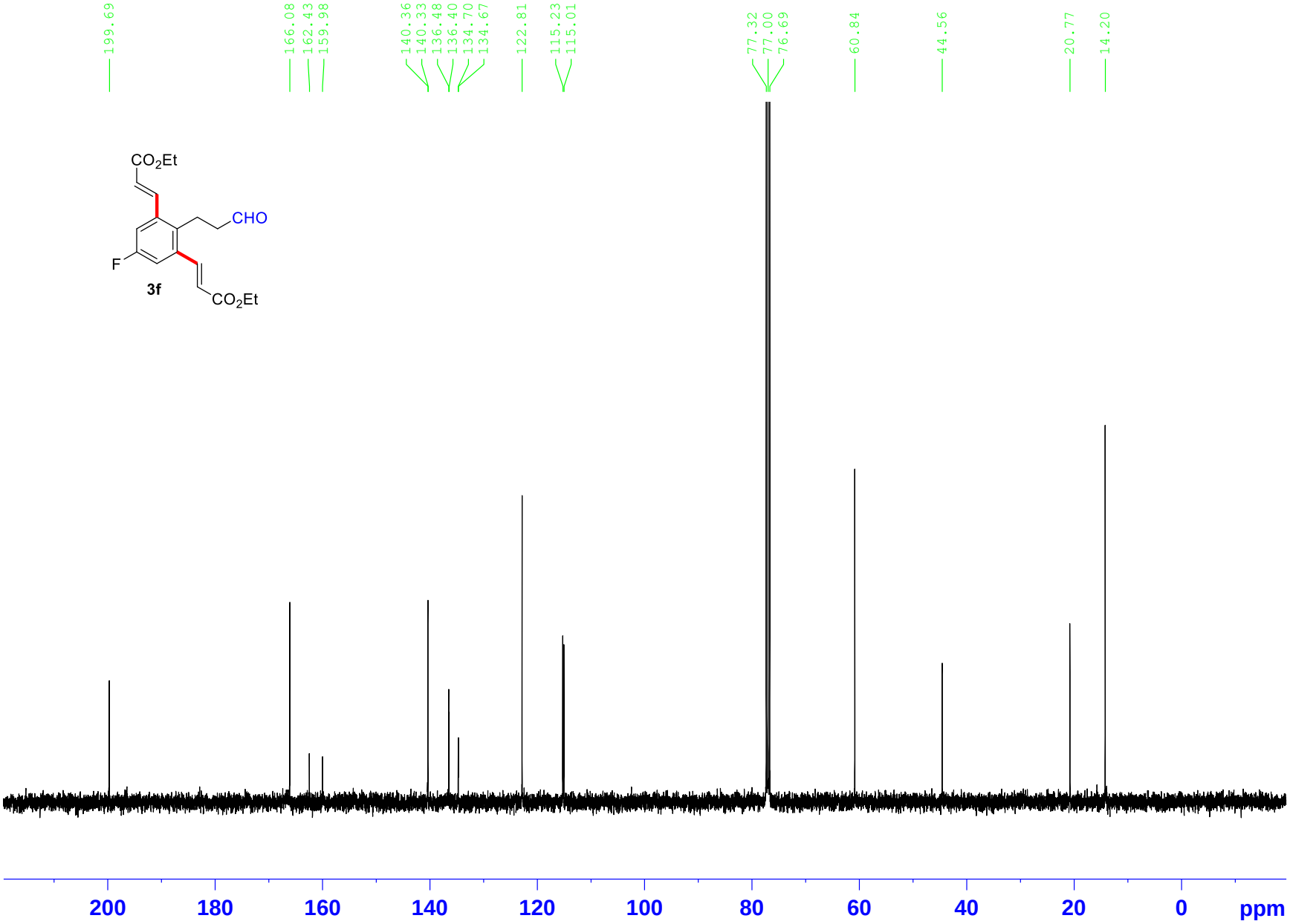
2.09
6.06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136.40
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122.81
115.23
115.01
77.32
77.00
76.69
60.84
44.56
20.77
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CHO
F
3f
CO2Et
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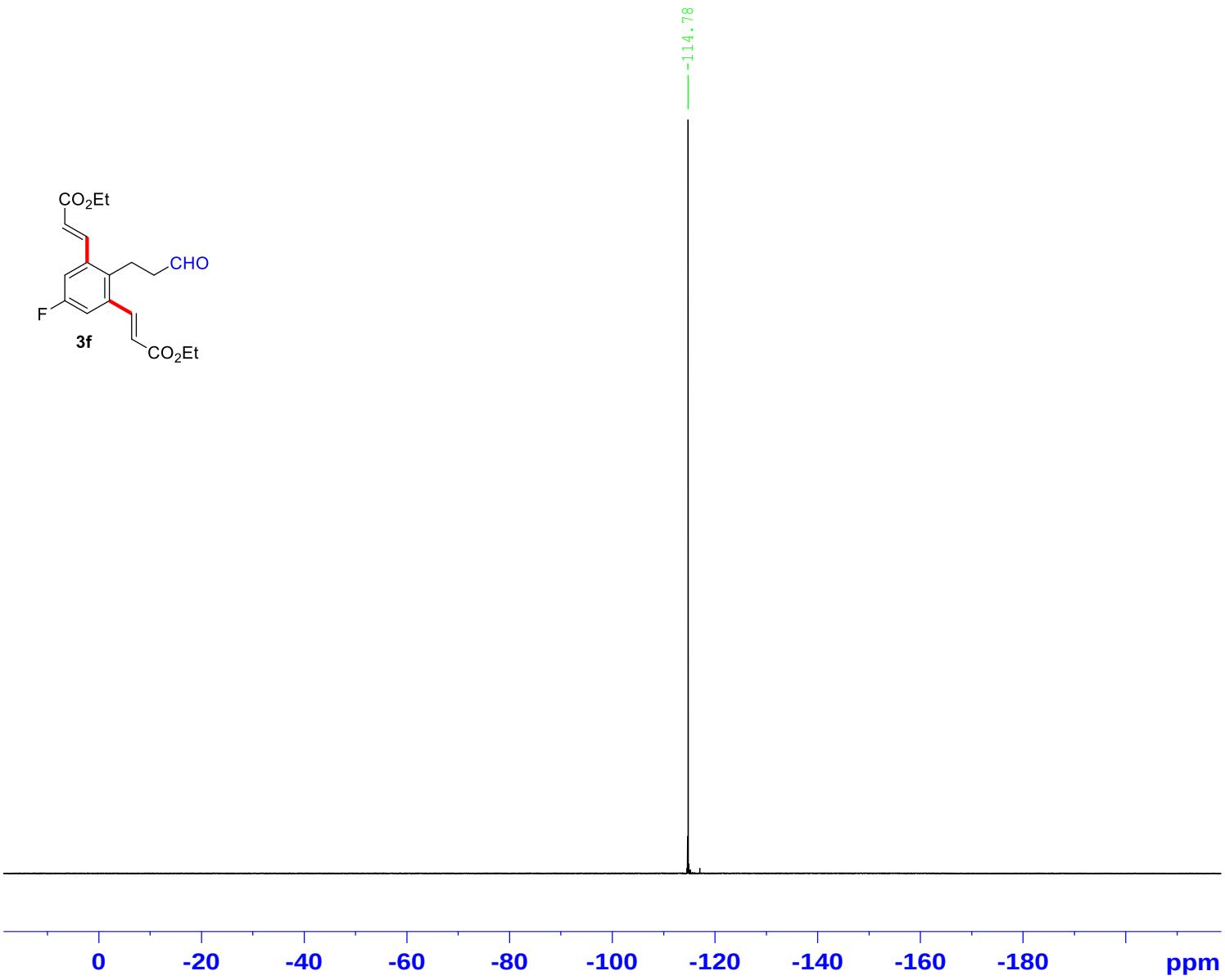
ppm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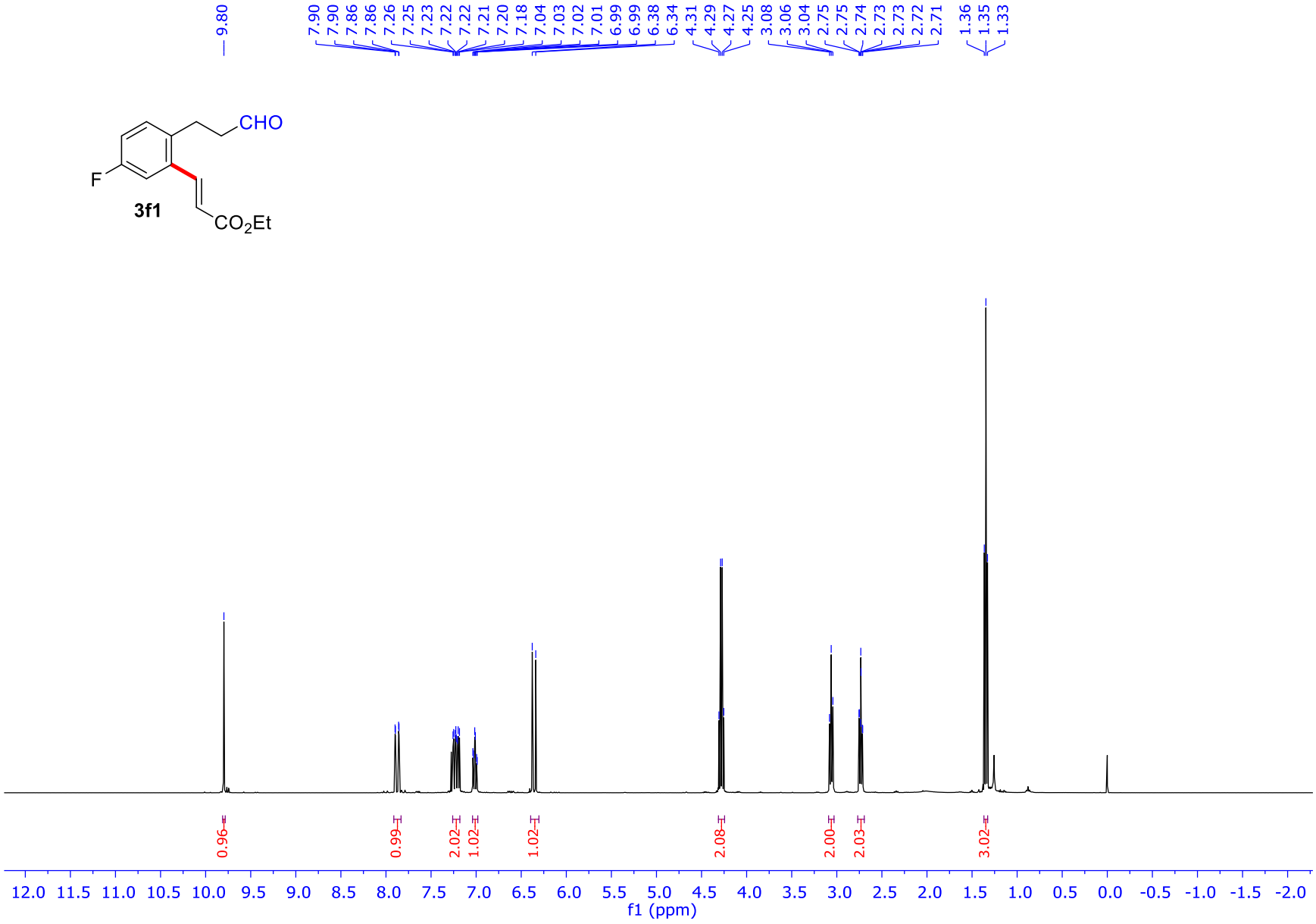
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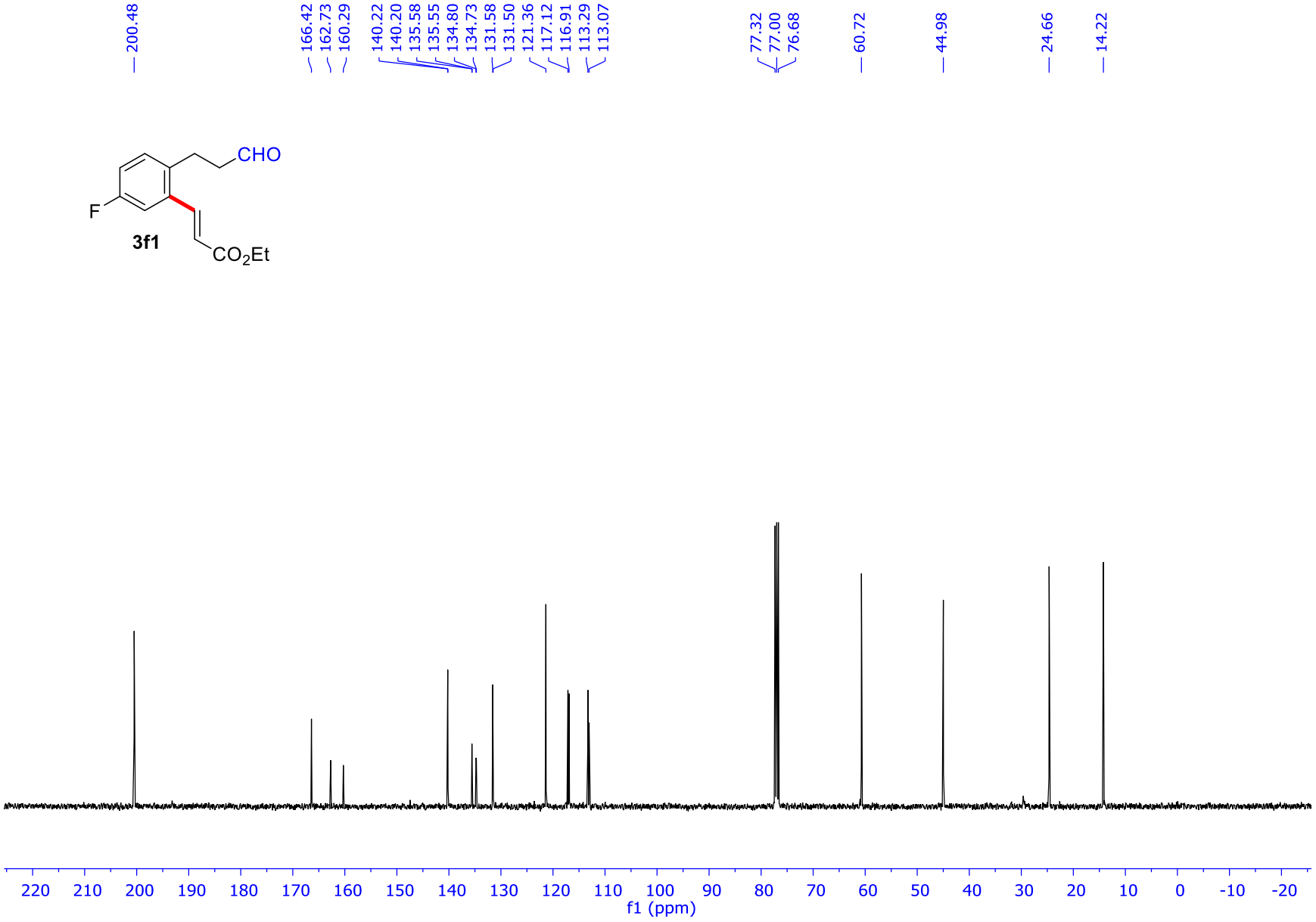
7.23
7.22
7.22
7.21
7.20
7.18
7.04
7.03
7.02
7.01
6.99
6.99
6.38
6.34
4.31
4.29
4.27
4.25
3.08
3.06
3.04
2.75
2.75
2.74
2.73
2.73
2.72
2.71
1.36
1.35
1.33
CHO
F
3f1
CO2Et
0.96
0.99
2.02
1.02
1.02
2.08
2.00
2.03
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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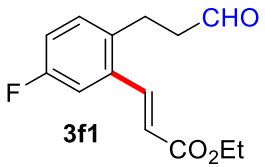
134.73
131.58
131.50
121.36
117.12
116.91
113.29
113.07
77.32
77.00
76.68
60.72
44.98
24.66
14.22
CHO
F
3f1
CO2Et
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


CHO
F
CO2Et

3f1

-115.49
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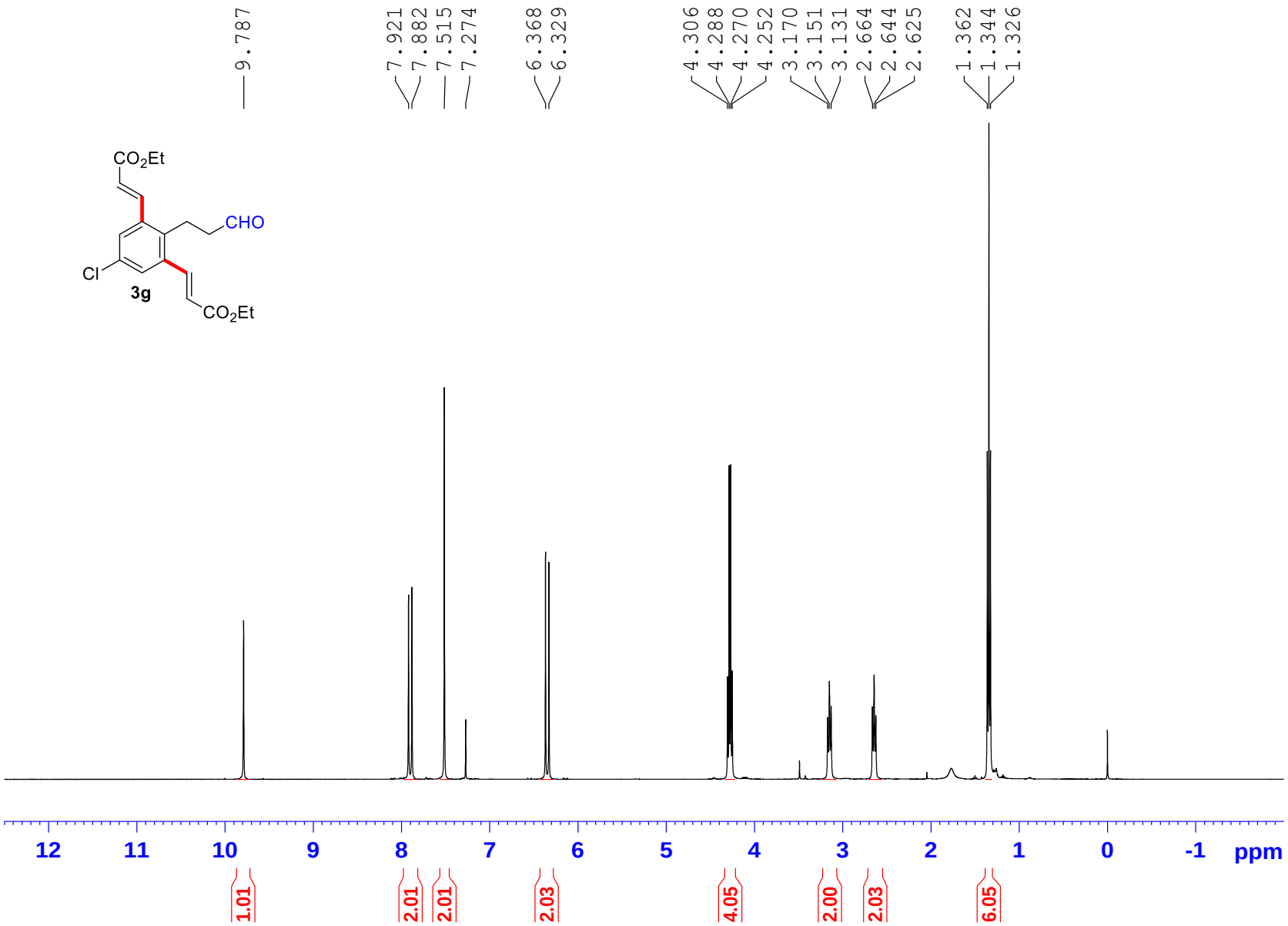
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)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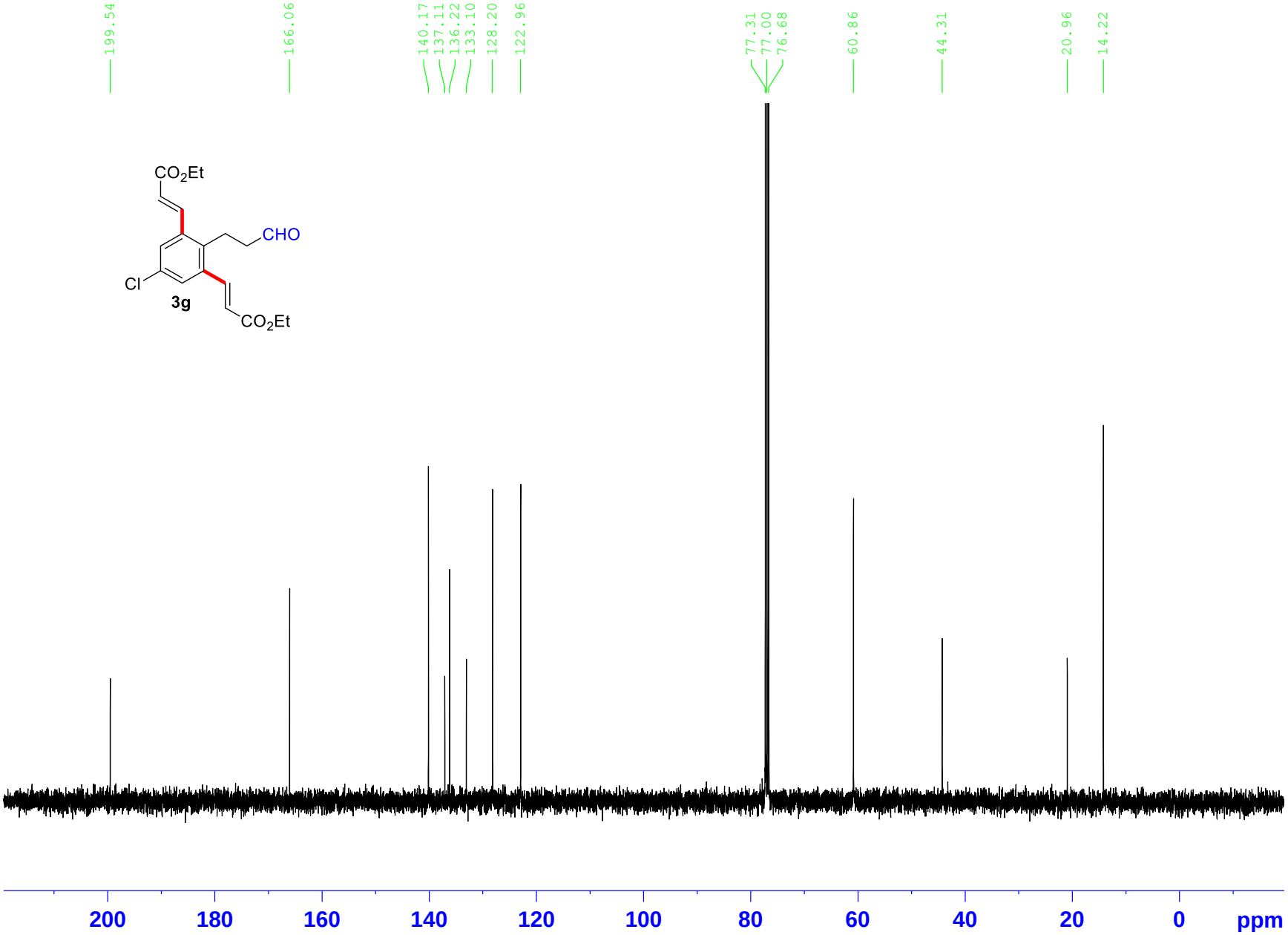
4.288
4.270
4.252
3.170
3.151
3.131
2.664
2.644
2.625
1.362
1.344
1.326
CO2Et
CHO
Cl
3g
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
2.01
2.01
2.03
4.05
2.00
2.03
6.05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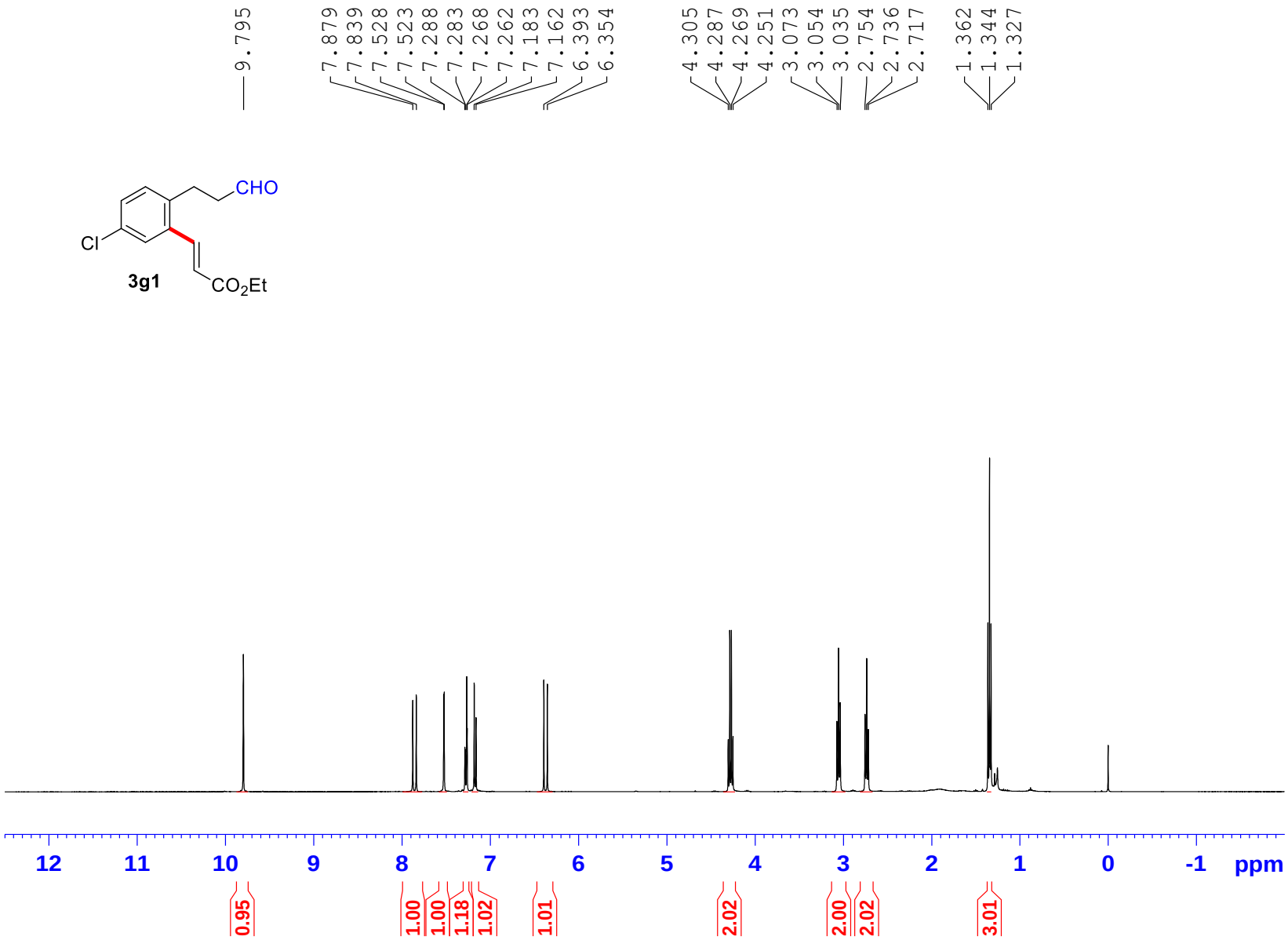
128.20
122.96
77.31
77.00
76.68
60.86
44.31
20.96
14.22
CO2Et
CHO
Cl
3g
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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7.268
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7.162
6.393
6.354
4.305
4.287
4.269
4.251
3.073
3.054
3.035
2.754
2.736
2.717
1.362
1.344
1.327
CHO
Cl
3g1
CO2Et
12
11
10
9
8
7
6
5
4
3
2
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-1
ppm
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1.01
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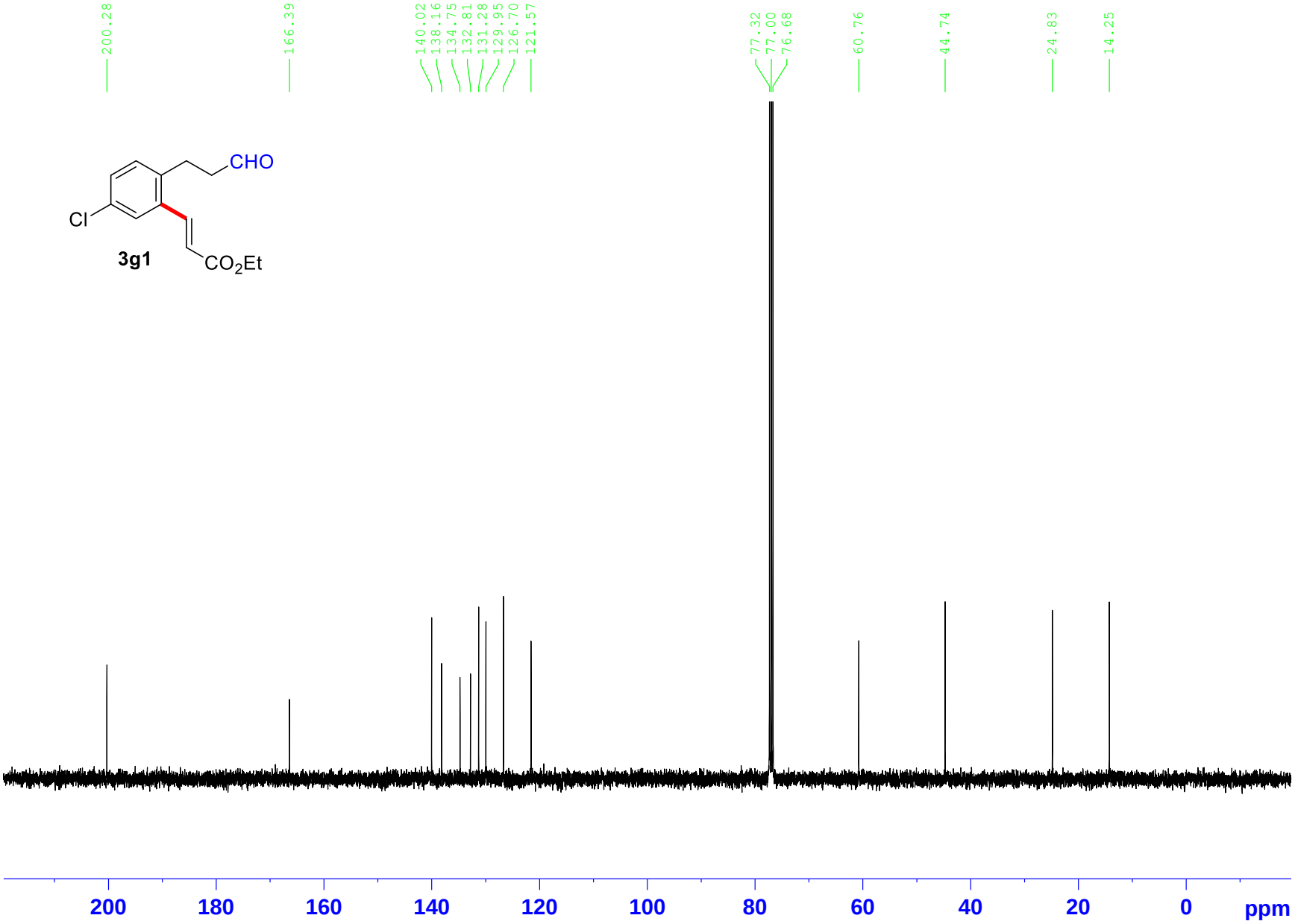
2.00
2.02
3.01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129.95
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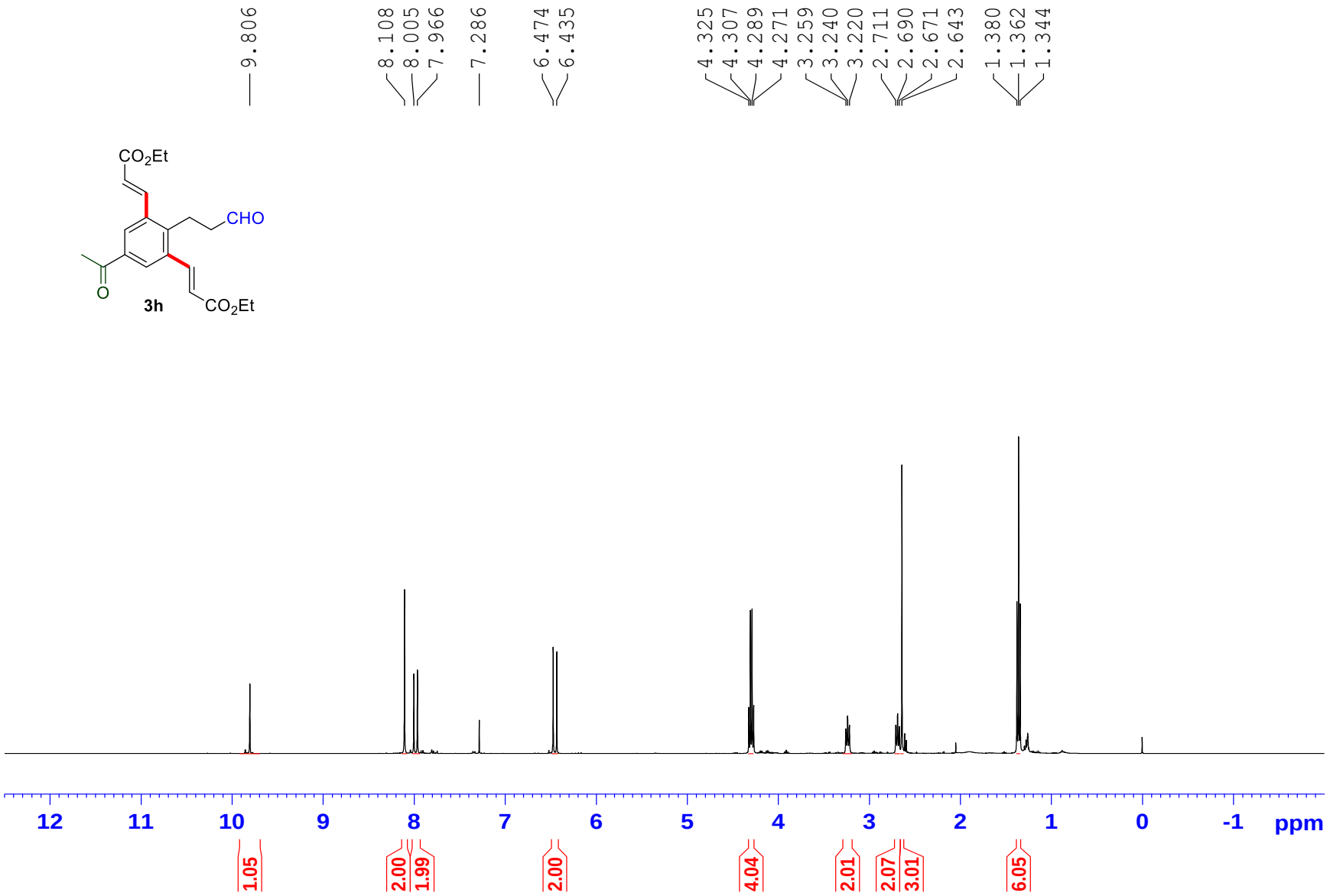
121.57
77.32
77.00
76.68
60.76
44.74
24.83
14.25
CHO
Cl
3g1
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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4.325
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4.271
3.259
3.240
3.220
2.711
2.690
2.671
2.643
1.380
1.362
1.344
CO2Et
CHO
O
3h
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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2.00
1.99
2.00
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2.07
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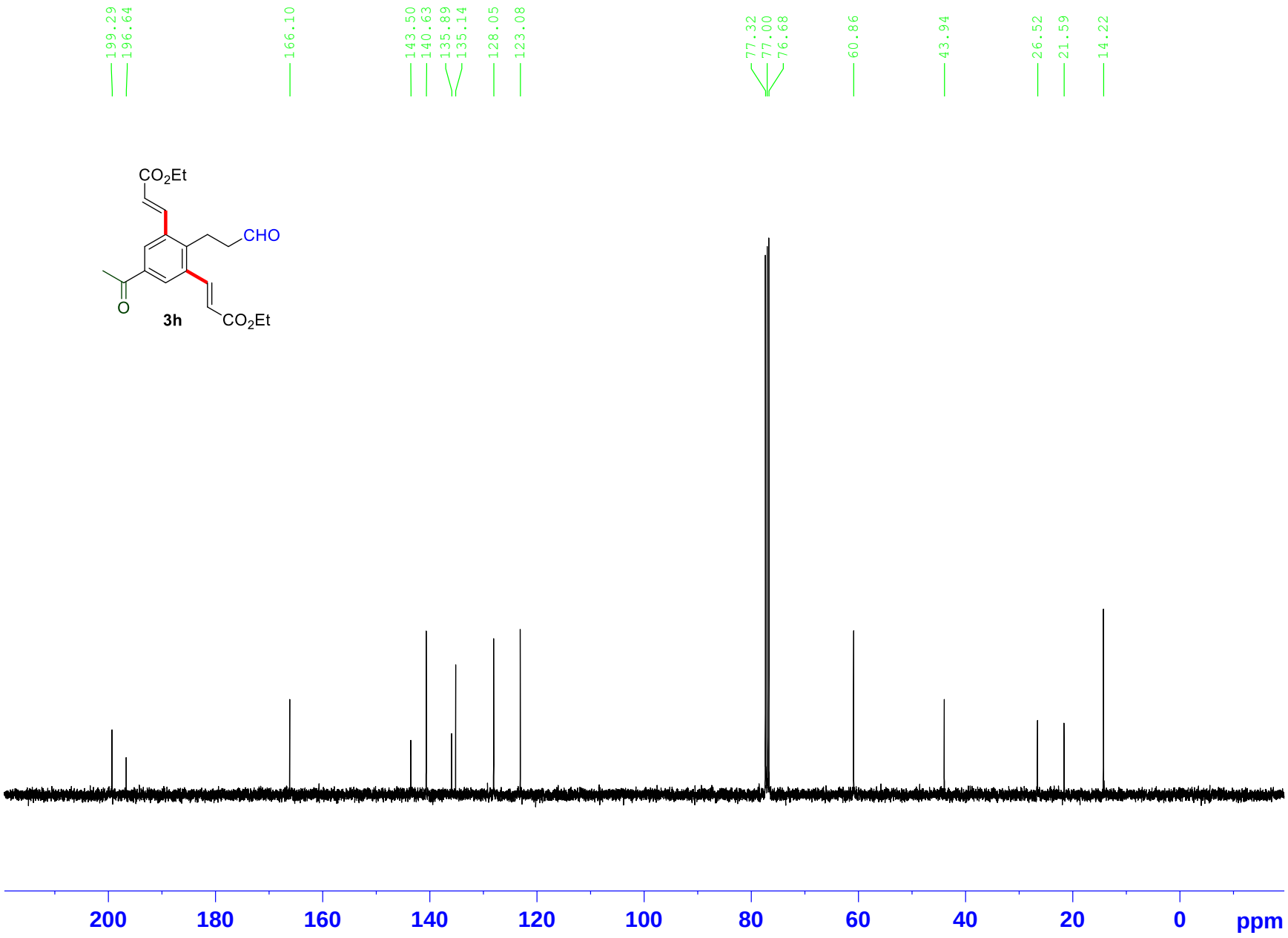
6.05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135.14
128.05
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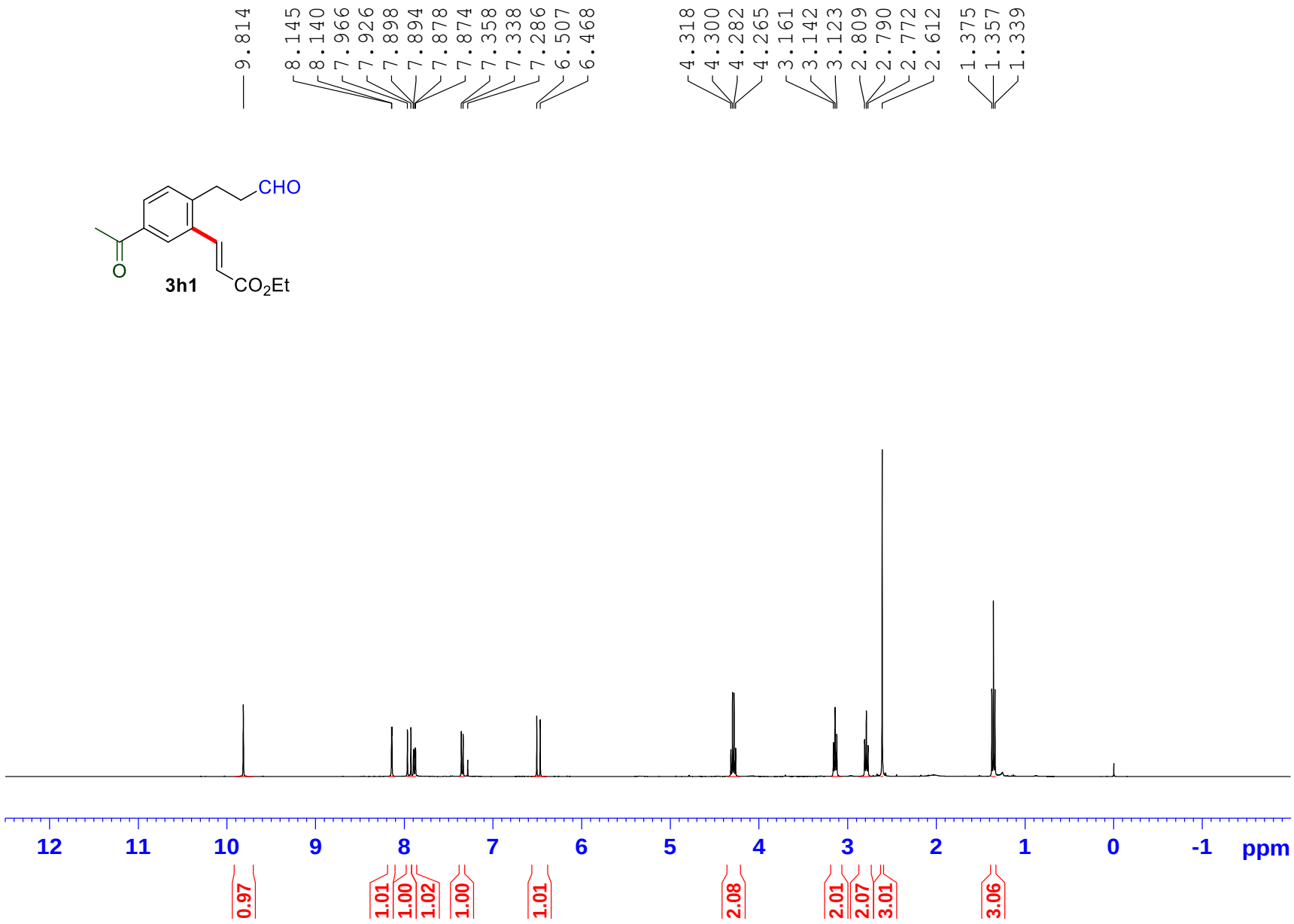
77.32
77.00
76.68
60.86
43.94
26.52
21.59
14.22
CO2Et
CHO
O
3h
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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7.338
7.286
6.507
6.468
4.318
4.300
4.282
4.265
3.161
3.142
3.123
2.809
2.790
2.772
2.612
1.375
1.357
1.339
CHO
O
3h1
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.00
1.02
1.00
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2.08
2.01
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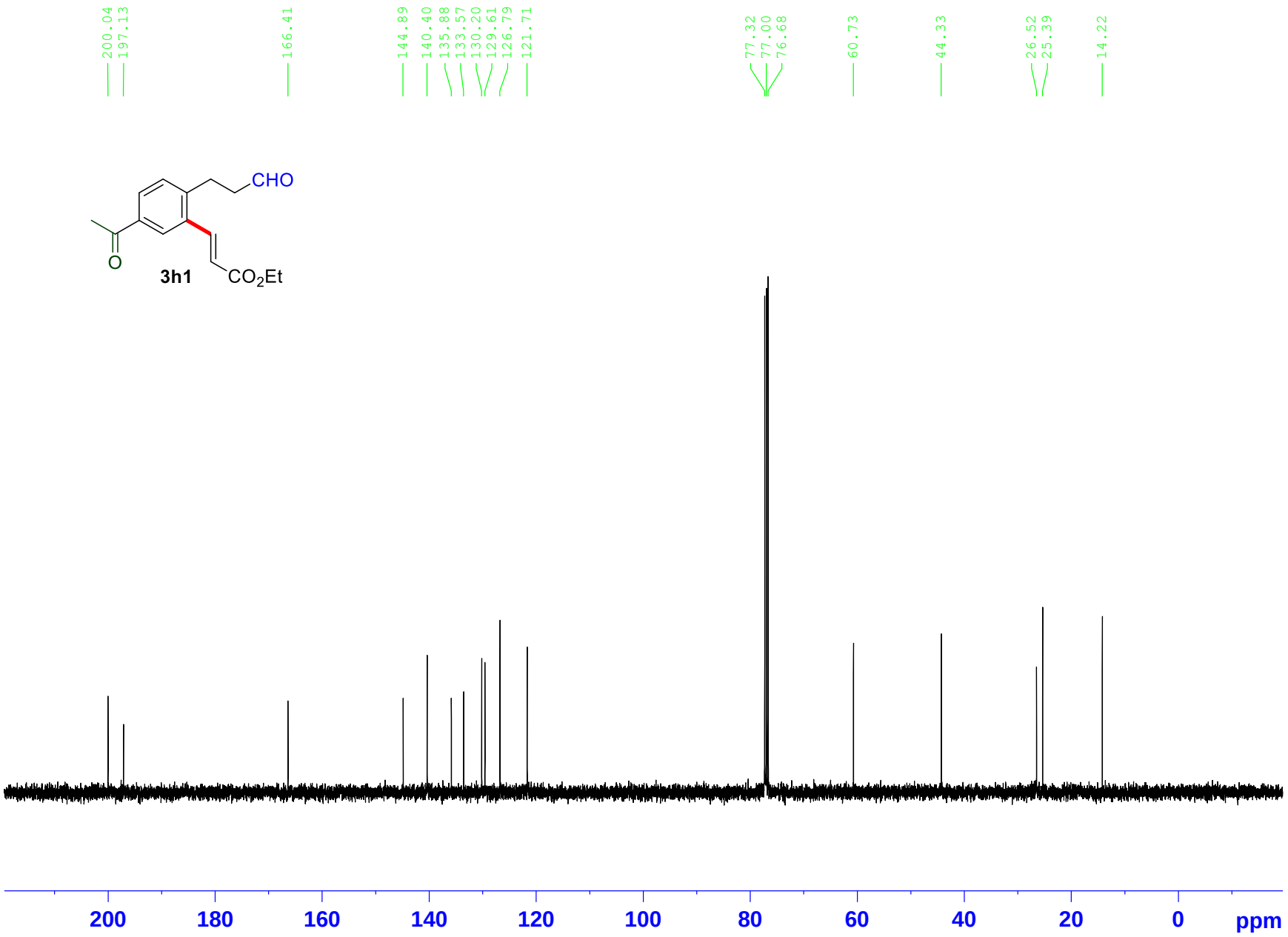
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77.32
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76.68
60.73
44.33
26.52
25.39
14.22
CHO
O
3h1
CO2Et
200
180
160
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120
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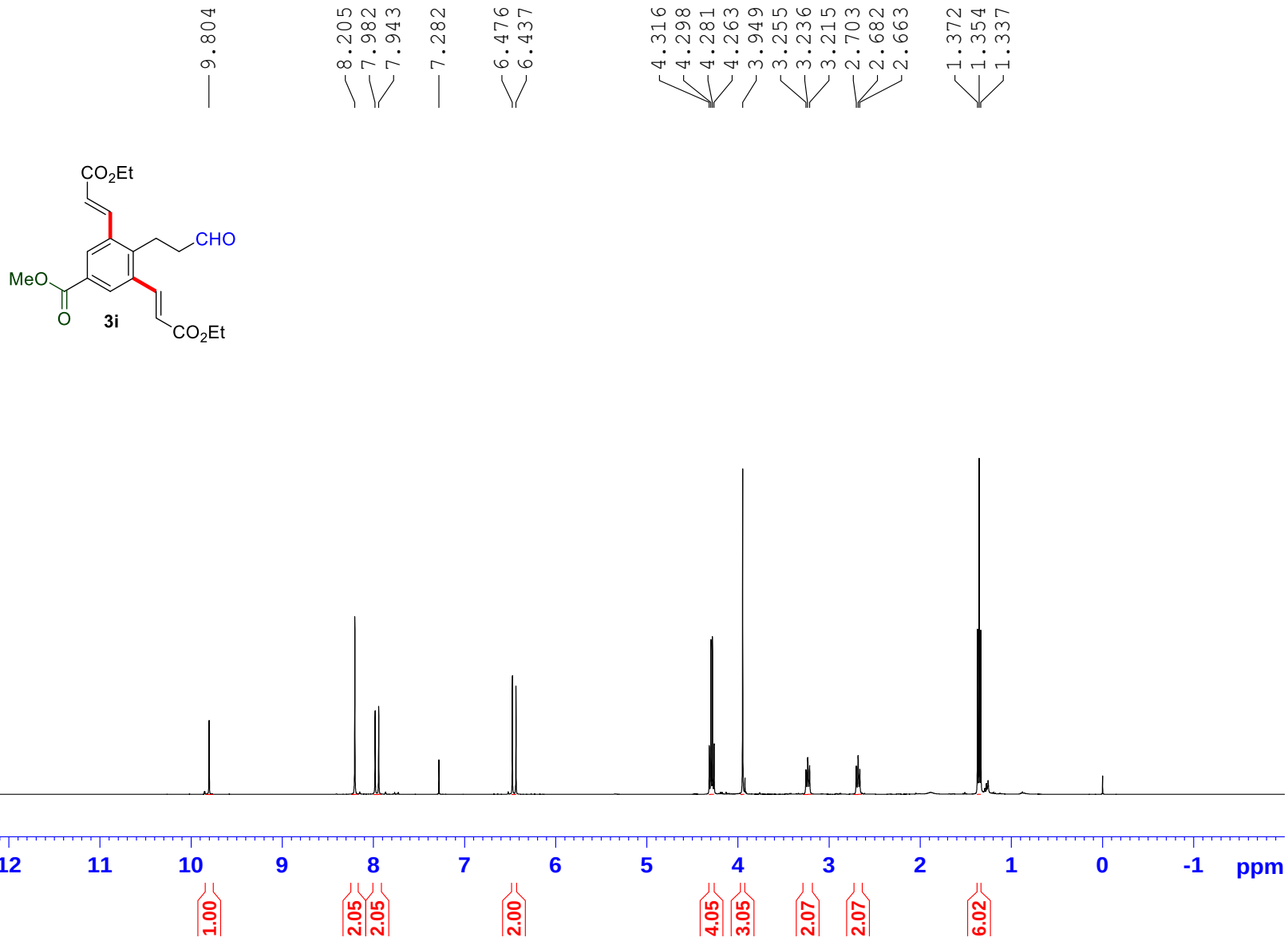
40
20
0
ppm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4.263
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3.255
3.236
3.215
2.703
2.682
2.663
1.372
1.354
1.337
CO2Et
CHO
MeO
O
3i
CO2Et
12
11
10
9
8
7
6
5
4
3
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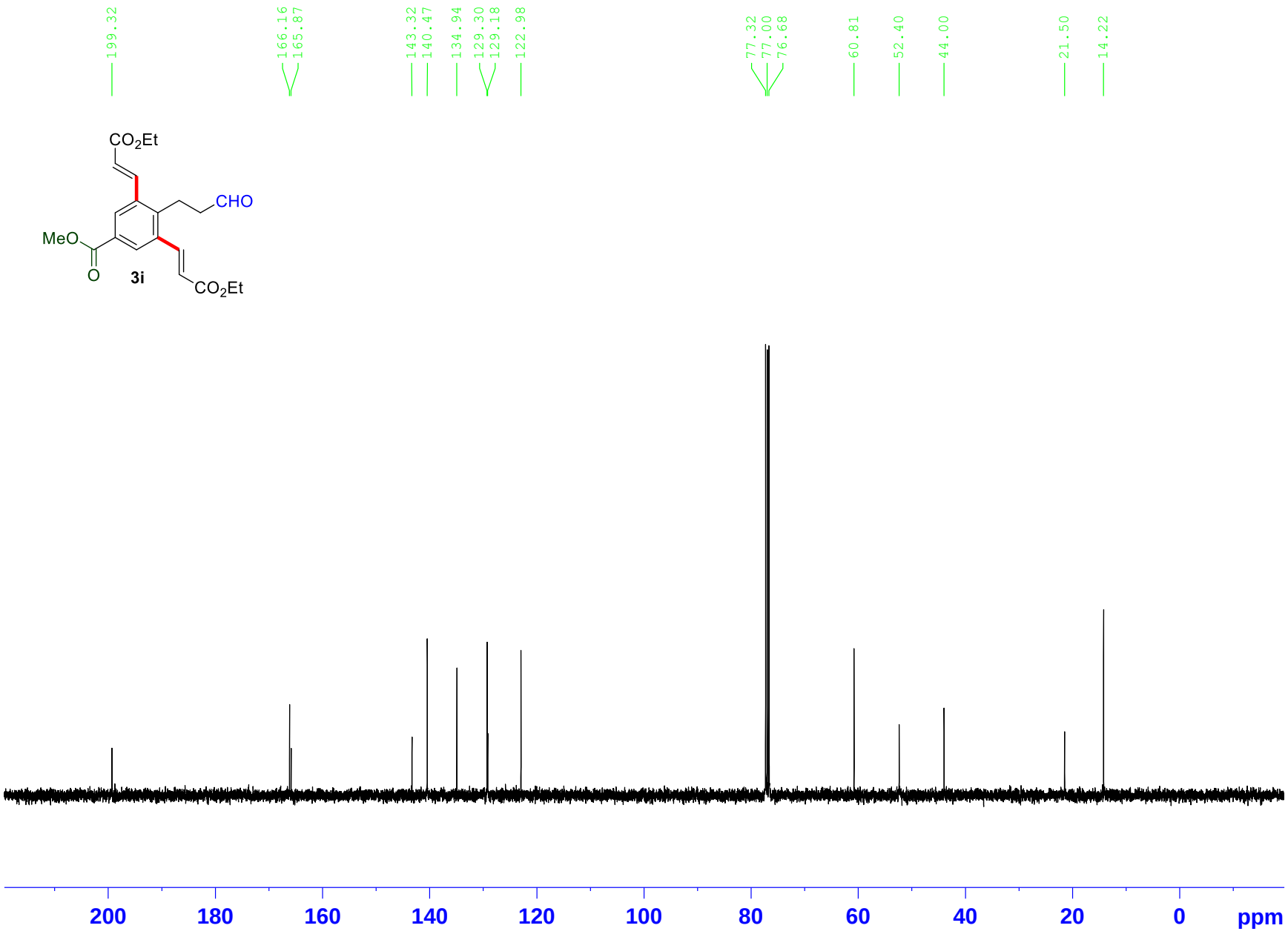
6.02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77.32
77.00
76.68
60.81
52.40
44.00
21.50
14.22
CO2Et
CHO
MeO
O
3i
CO2Et
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120
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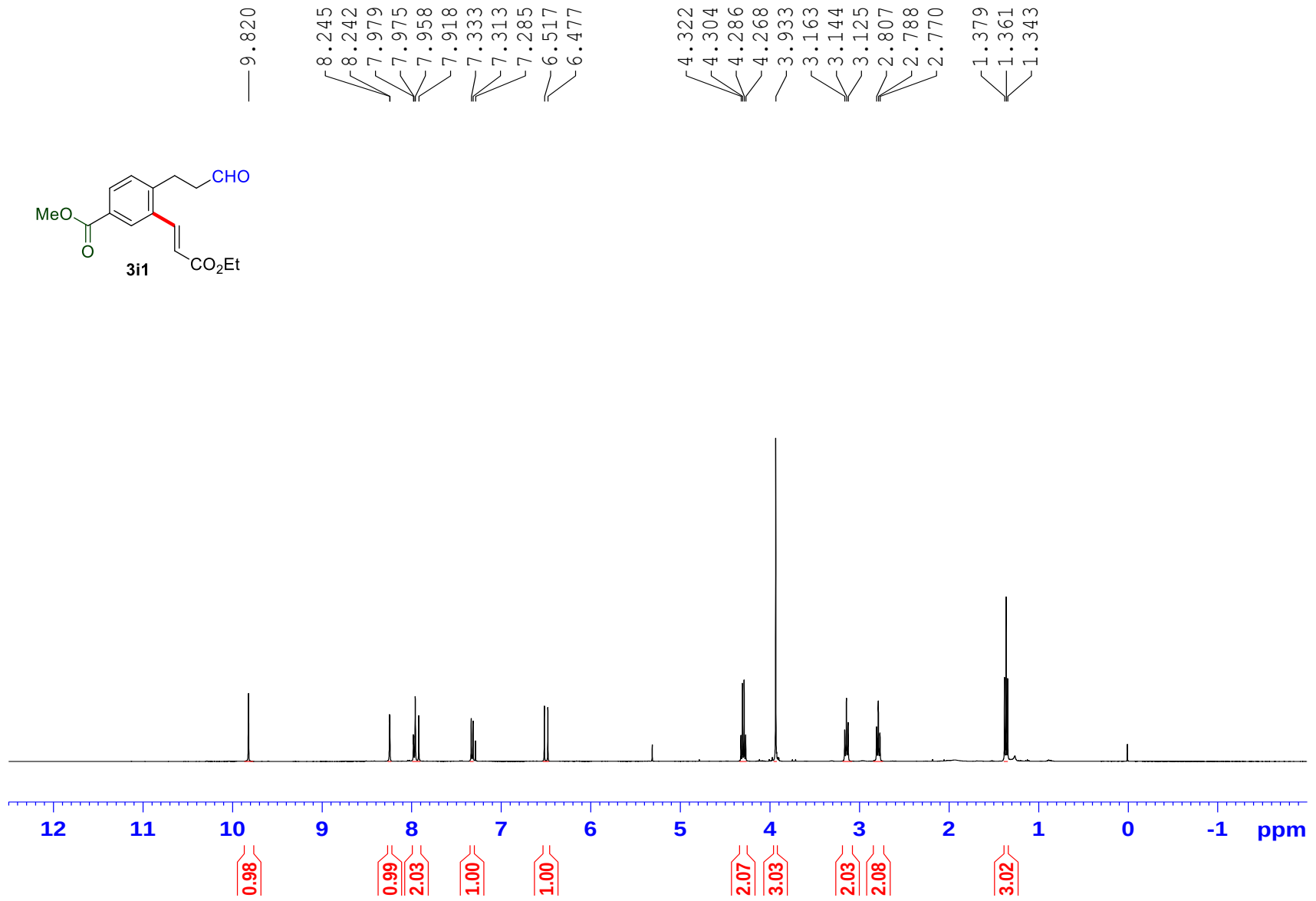
ppm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4.304
4.286
4.268
3.933
3.163
3.144
3.125
2.807
2.788
2.770
1.379
1.361
1.343
CHO
MeO
O
CO2Et
3i1
12
11
10
9
8
7
6
5
4
3
2
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2.07
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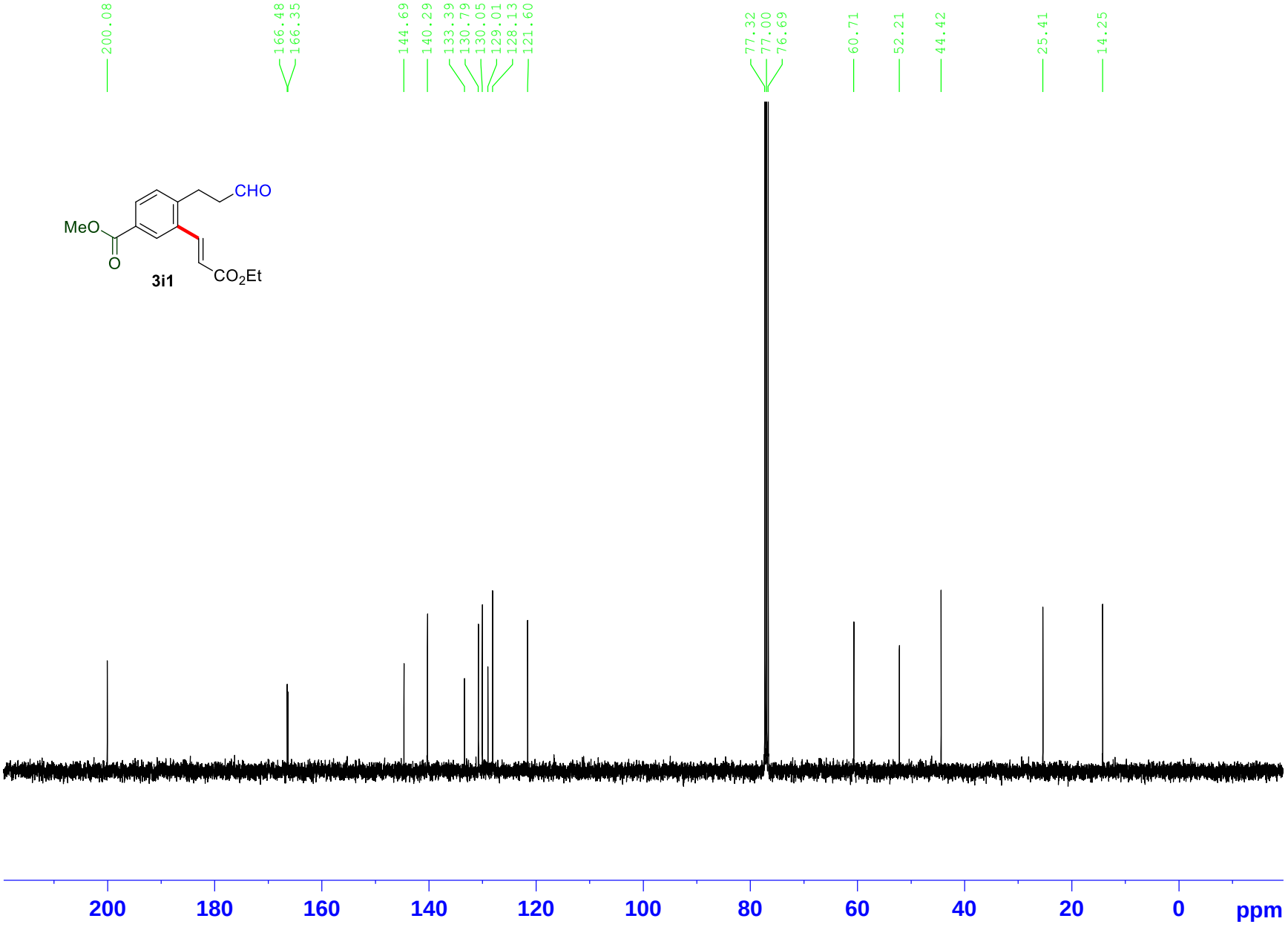
2.08
3.02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130.05
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128.13
121.60
77.32
77.00
76.69
60.71
52.21
44.42
25.41
14.25
CHO
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O
CO2Et
3i1
200
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120
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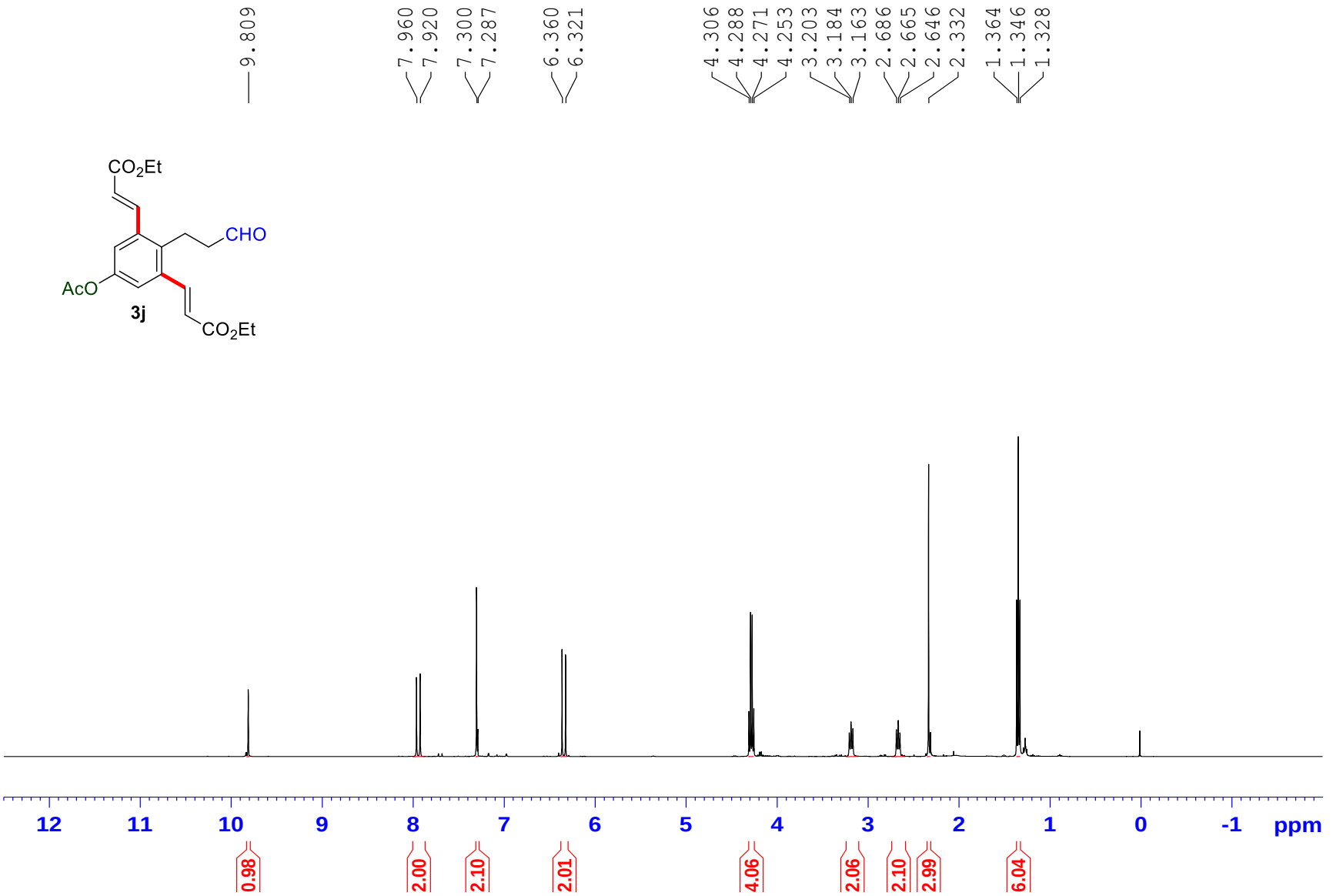
0
ppm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4.271
4.253
3.203
3.184
3.163
2.686
2.665
2.646
2.332
1.364
1.346
1.328
CO2Et
CHO
AcO
CO2Et
3j
12
11
10
9
8
7
6
5
4
3
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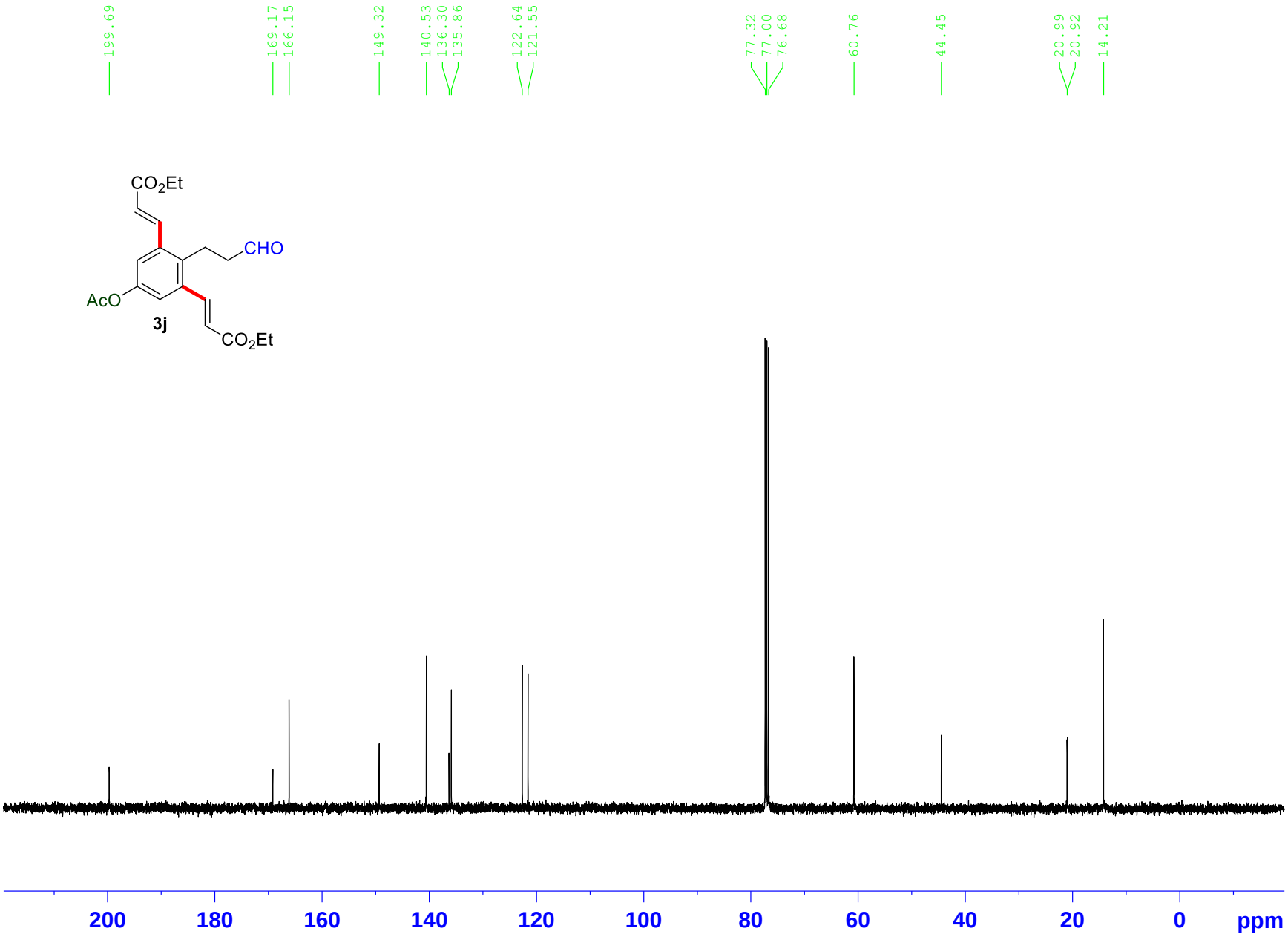
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77.32
77.00
76.68
60.76
44.45
20.99
20.92
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CO2Et
CHO
AcO
3j
CO2Et
200
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120
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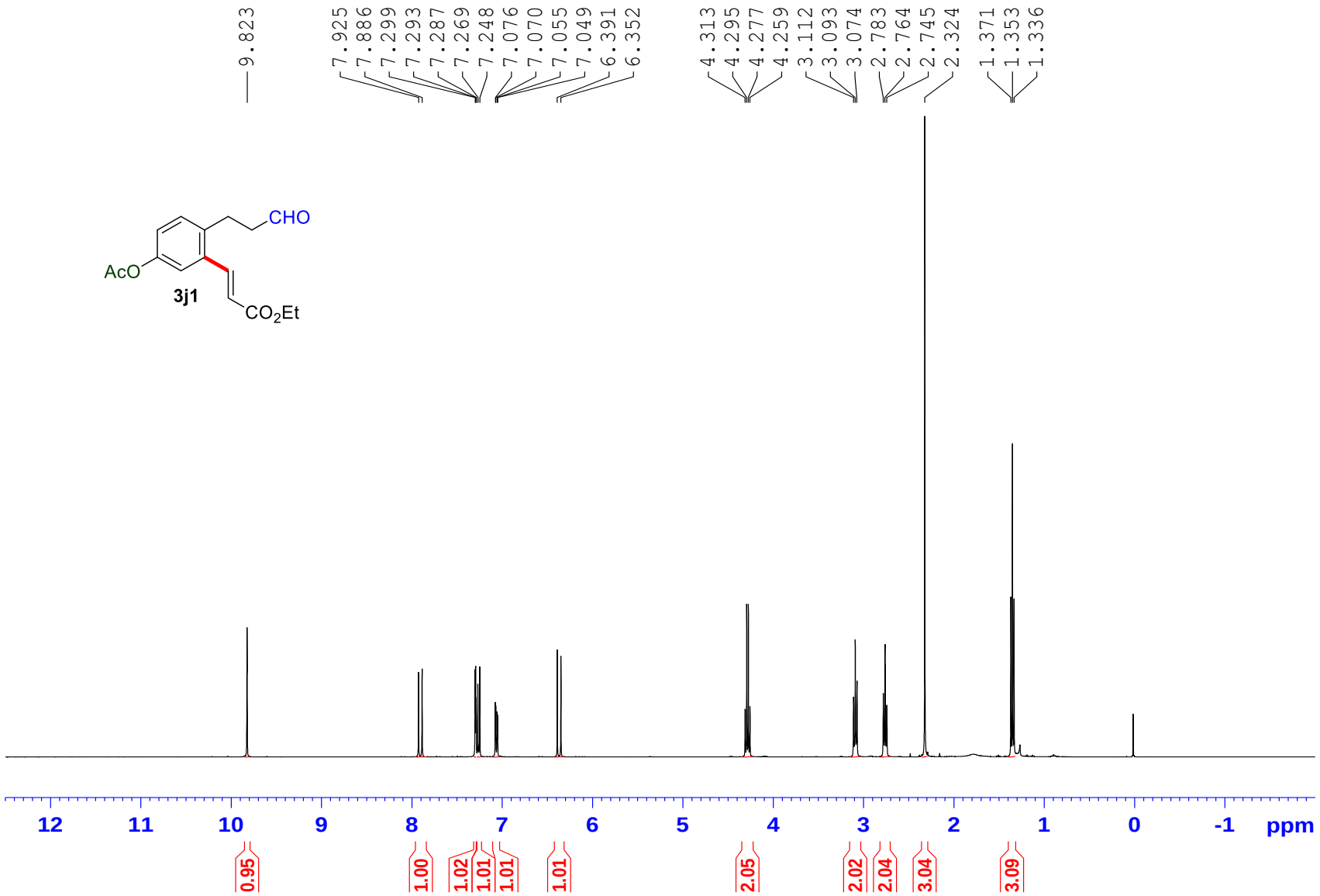
40
20
0
ppm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6.391
6.352
4.313
4.295
4.277
4.259
3.112
3.093
3.074
2.783
2.764
2.745
2.324
1.371
1.353
1.336
CHO
AcO
3j1
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
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1.01
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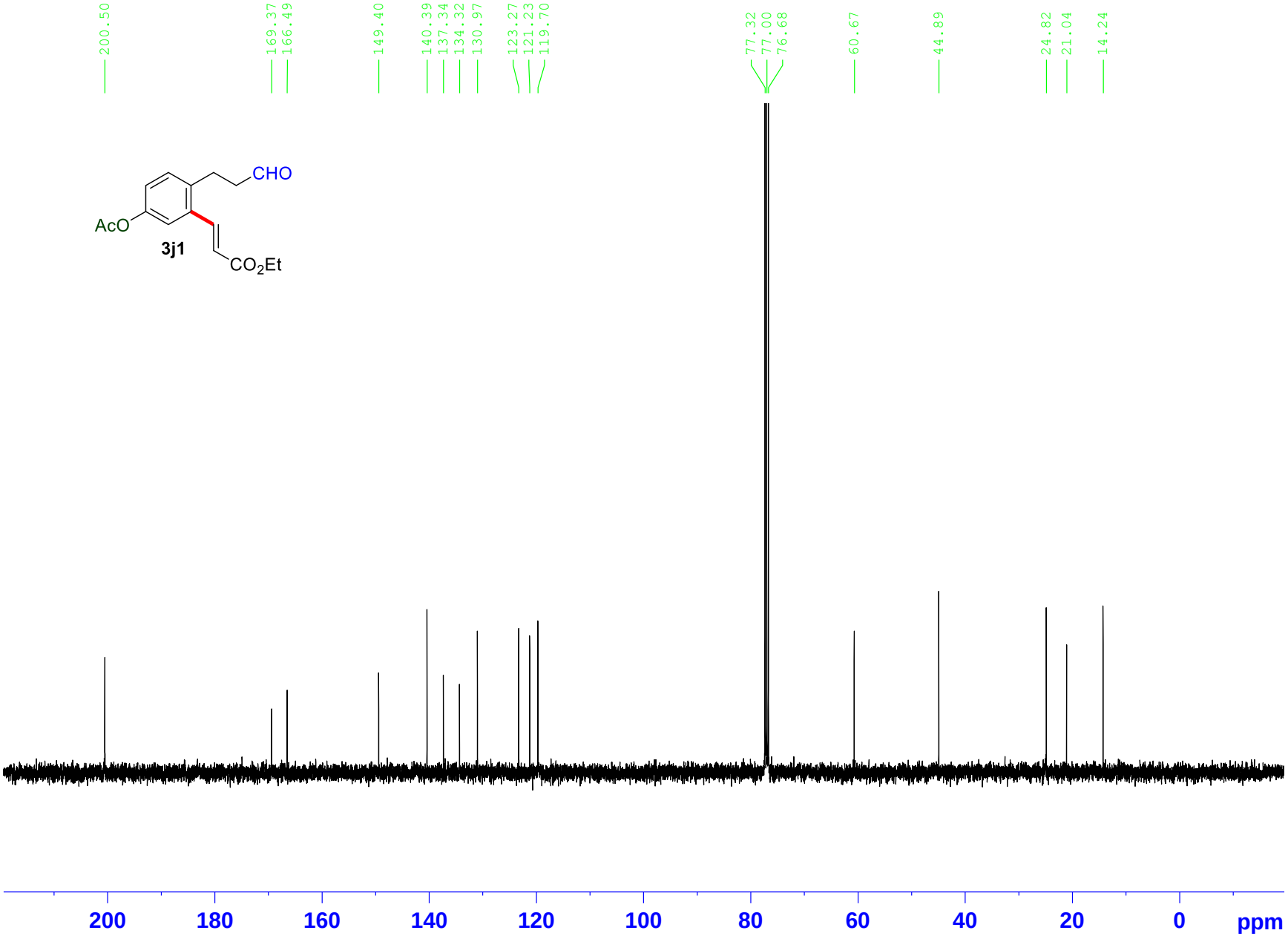
2.04
3.04
3.09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137.34
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130.97
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119.70
77.32
77.00
76.68
60.67
44.89
24.82
21.04
14.24
CHO
AcO
3j1
CO2Et
200
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120
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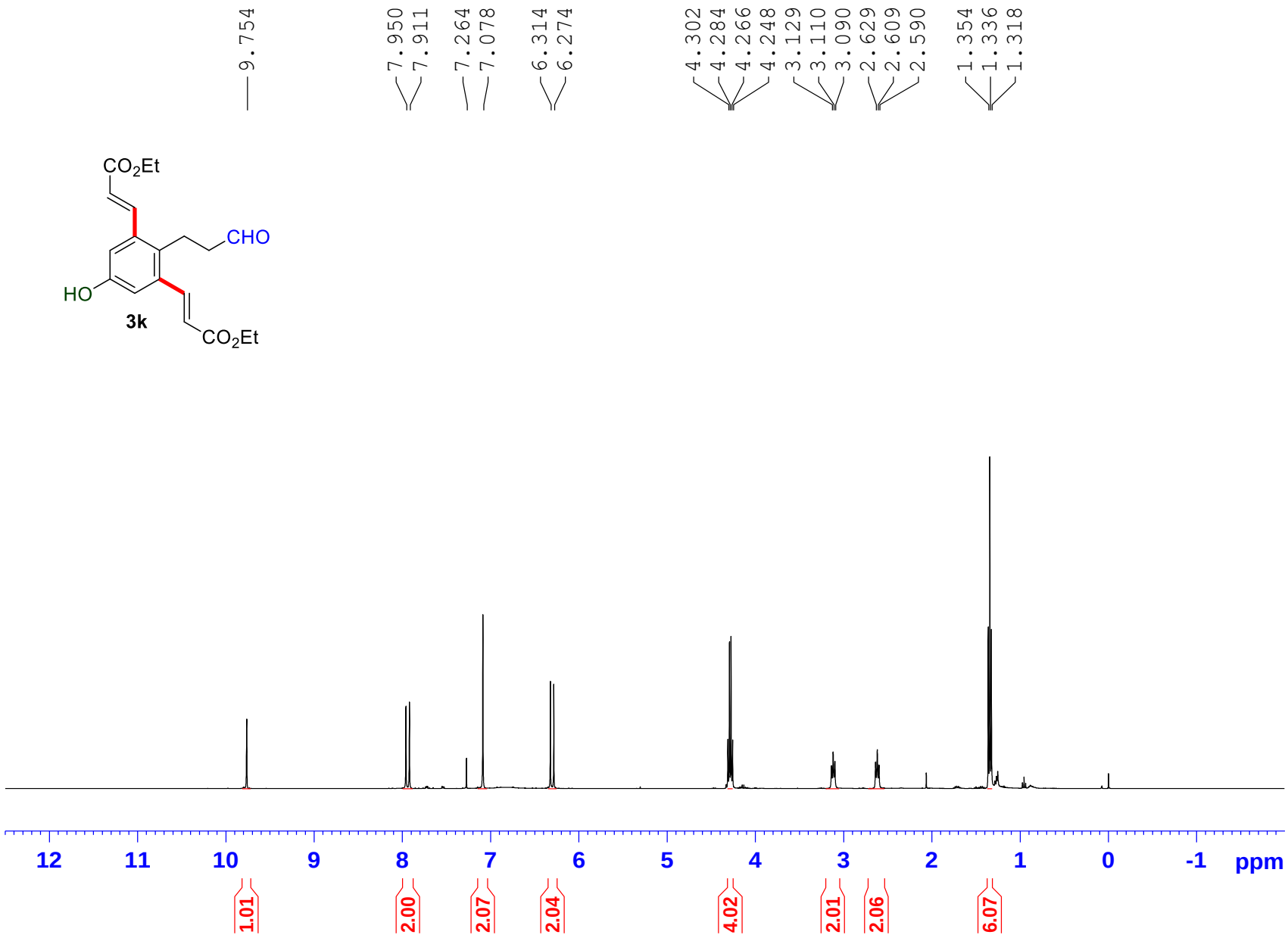
80
60
40
20
0
ppm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4.266
4.248
3.129
3.110
3.090
2.629
2.609
2.590
1.354
1.336
1.318
CO2Et
CHO
HO
CO2Et
3k
12
11
10
9
8
7
6
5
4
3
2
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-1
ppm
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2.07
2.04
4.02
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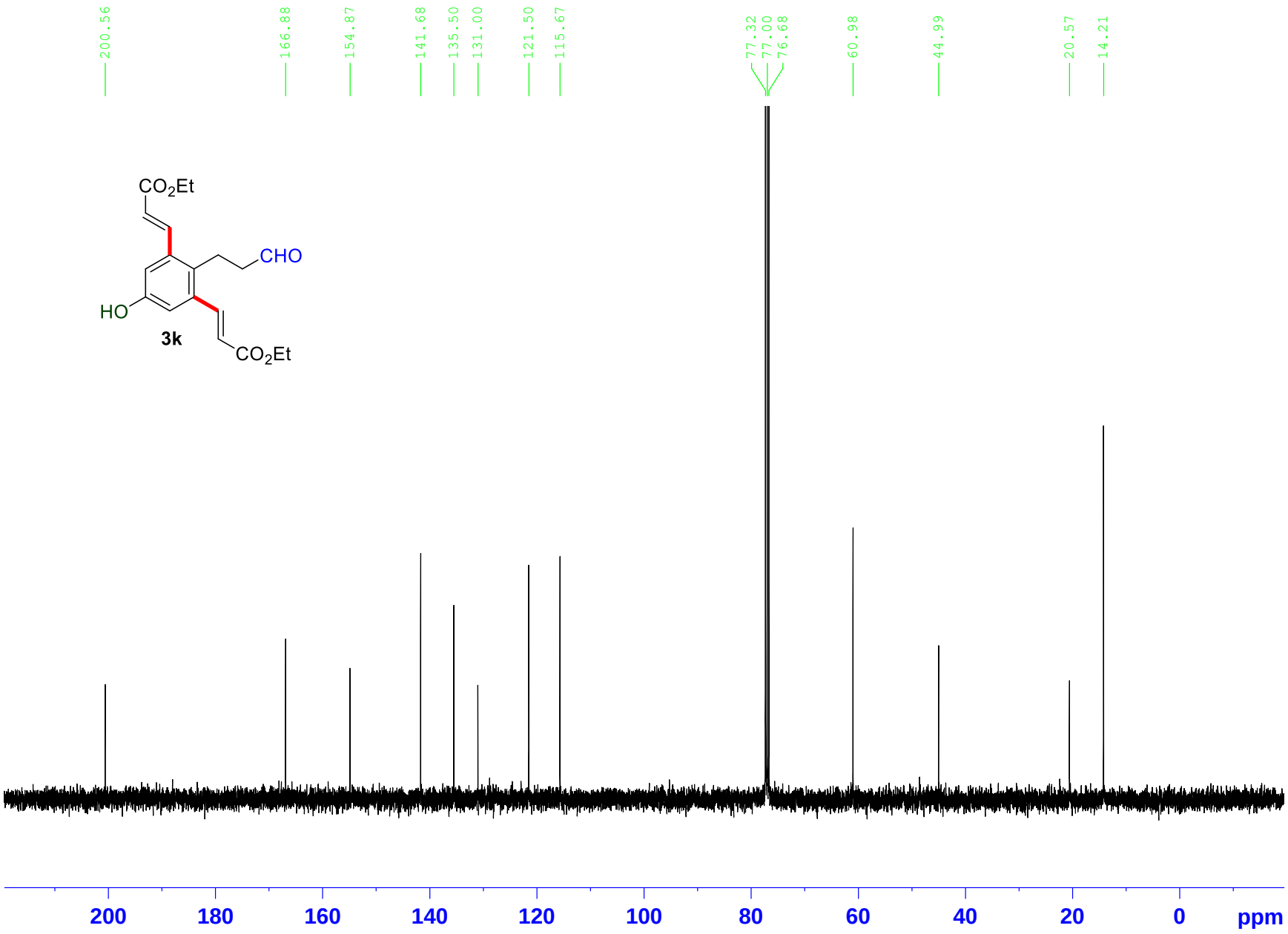
2.06
6.07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115.67
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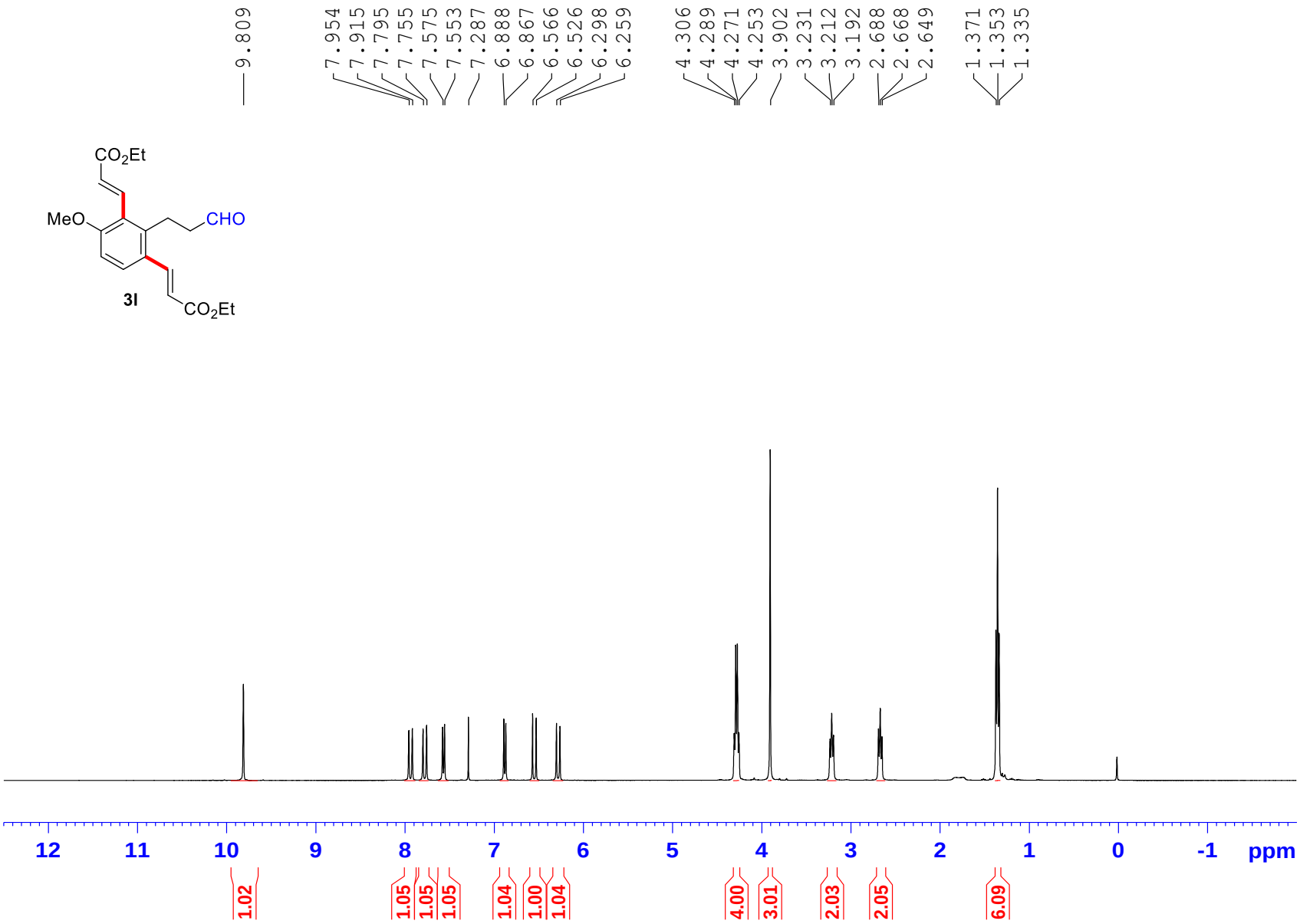
77.00
76.68
60.98
44.99
20.57
14.21
CO2Et
CHO
HO
3k
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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7.287
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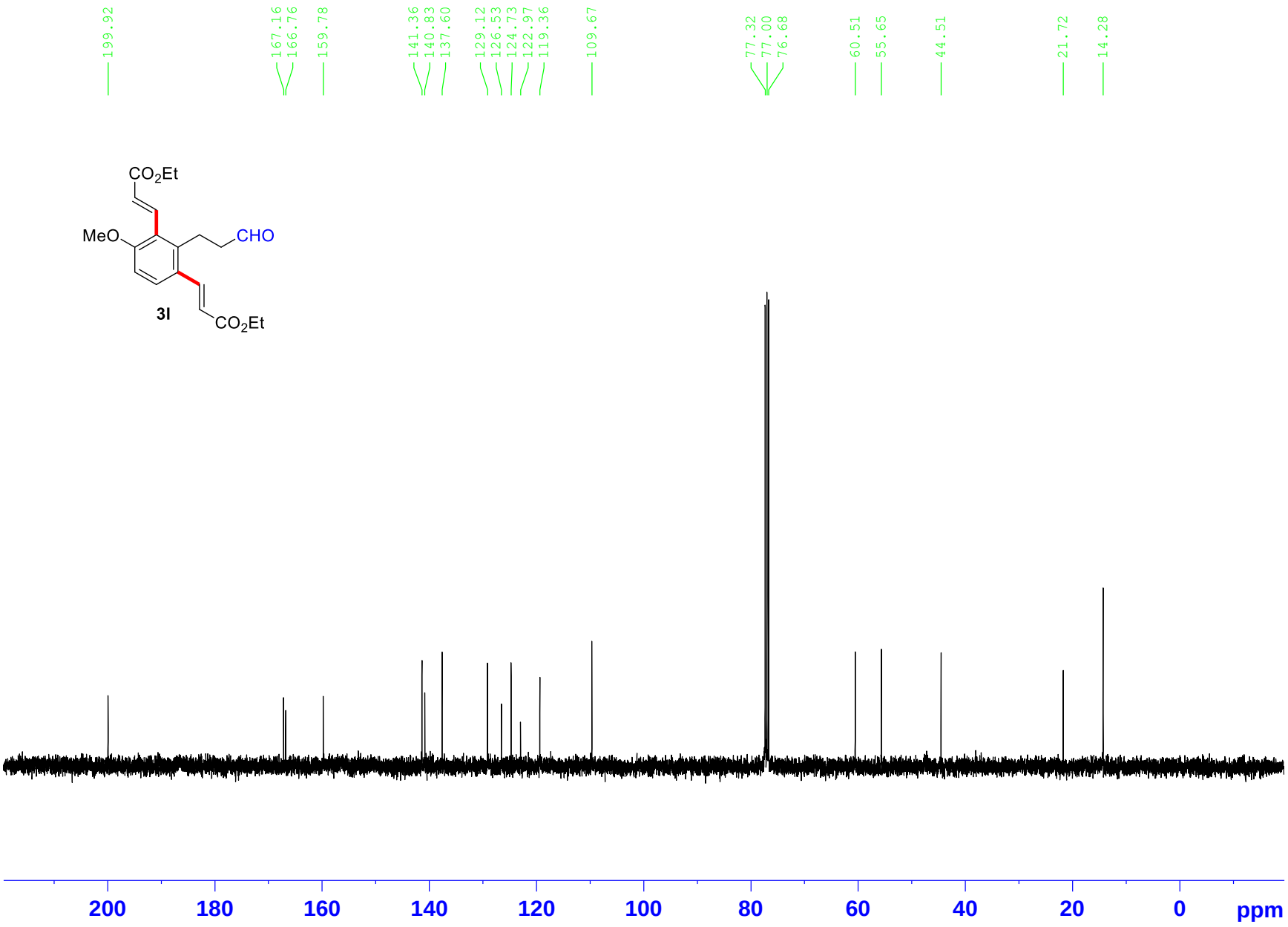
6.526
6.298
6.259
4.306
4.289
4.271
4.253
3.902
3.231
3.212
3.192
2.688
2.668
2.649
1.371
1.353
1.335
CO2Et
MeO
CHO
3l
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.05
1.05
1.05
1.04
1.00
1.04
4.00
3.01
2.03
2.05
6.09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137.60
129.12
126.53
124.73
122.97
119.36
109.67
77.32
77.00
76.68
60.51
55.65
44.51
21.72
14.28
CO2Et
MeO
CHO
3l
CO2Et
200
180
160
140
120
100
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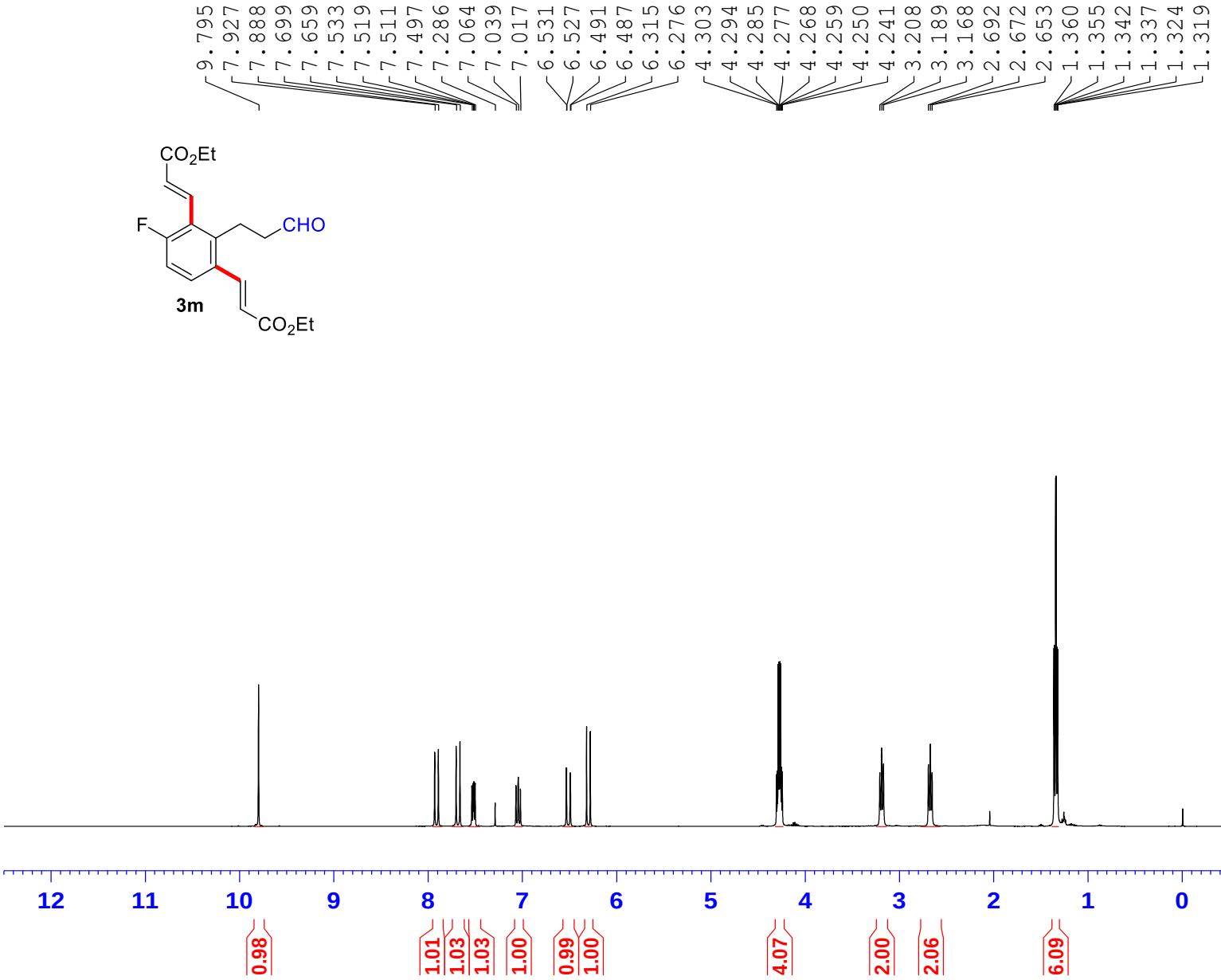
40
20
0
ppm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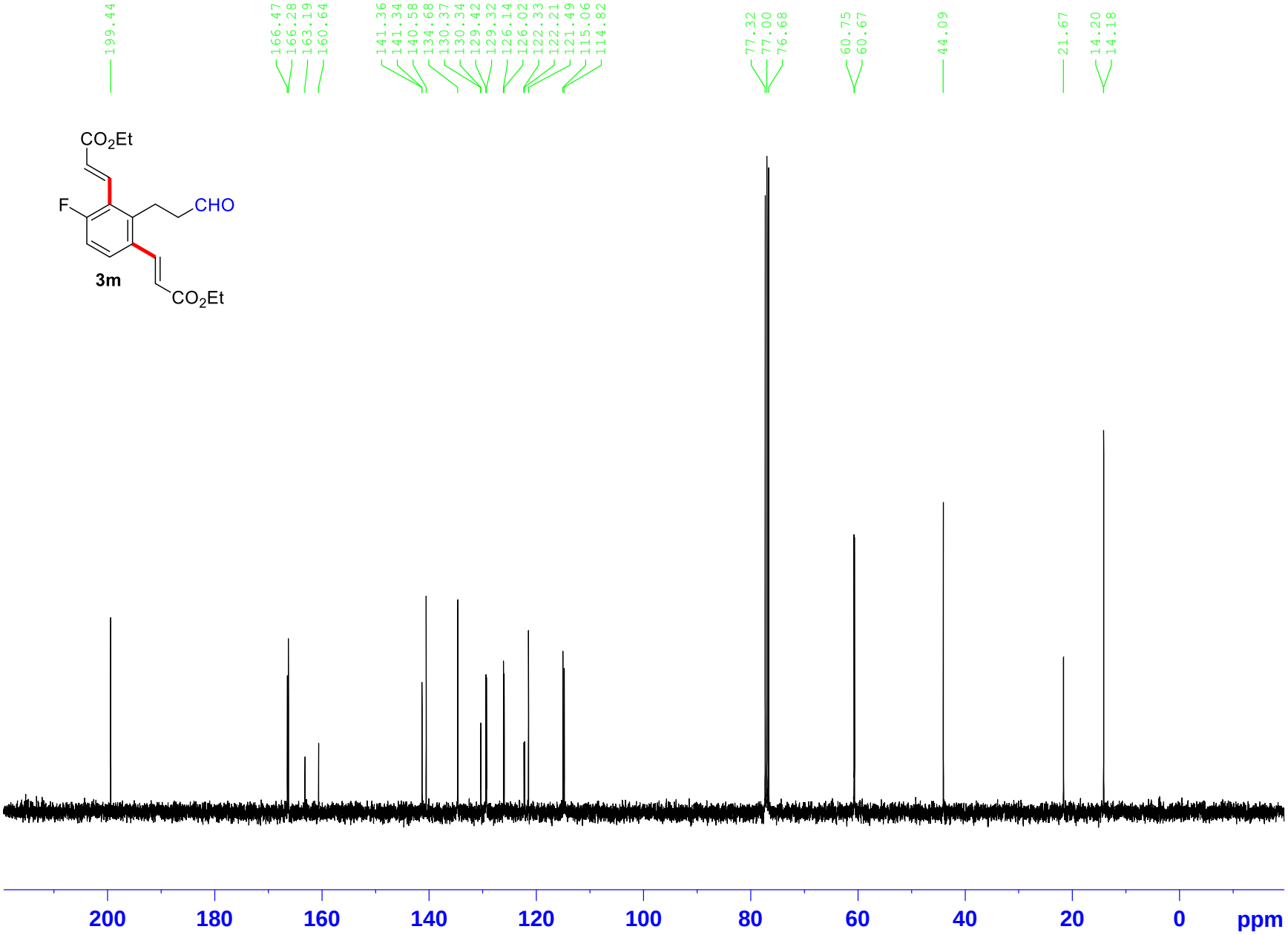
7.511
7.497
7.286
7.064
7.039
7.017
6.531
6.527
6.491
6.487
6.315
6.276
4.303
4.294
4.285
4.277
4.268
4.259
4.250
4.241
3.208
3.189
3.168
2.692
2.672
2.653
1.360
1.355
1.342
1.337
1.324
1.319
CO2Et
F
CHO
3m
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
1.01
1.03
1.03
1.00
0.99
1.00
4.07
2.00
2.06
6.09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166.47
166.28
163.19
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141.36
141.34
140.58
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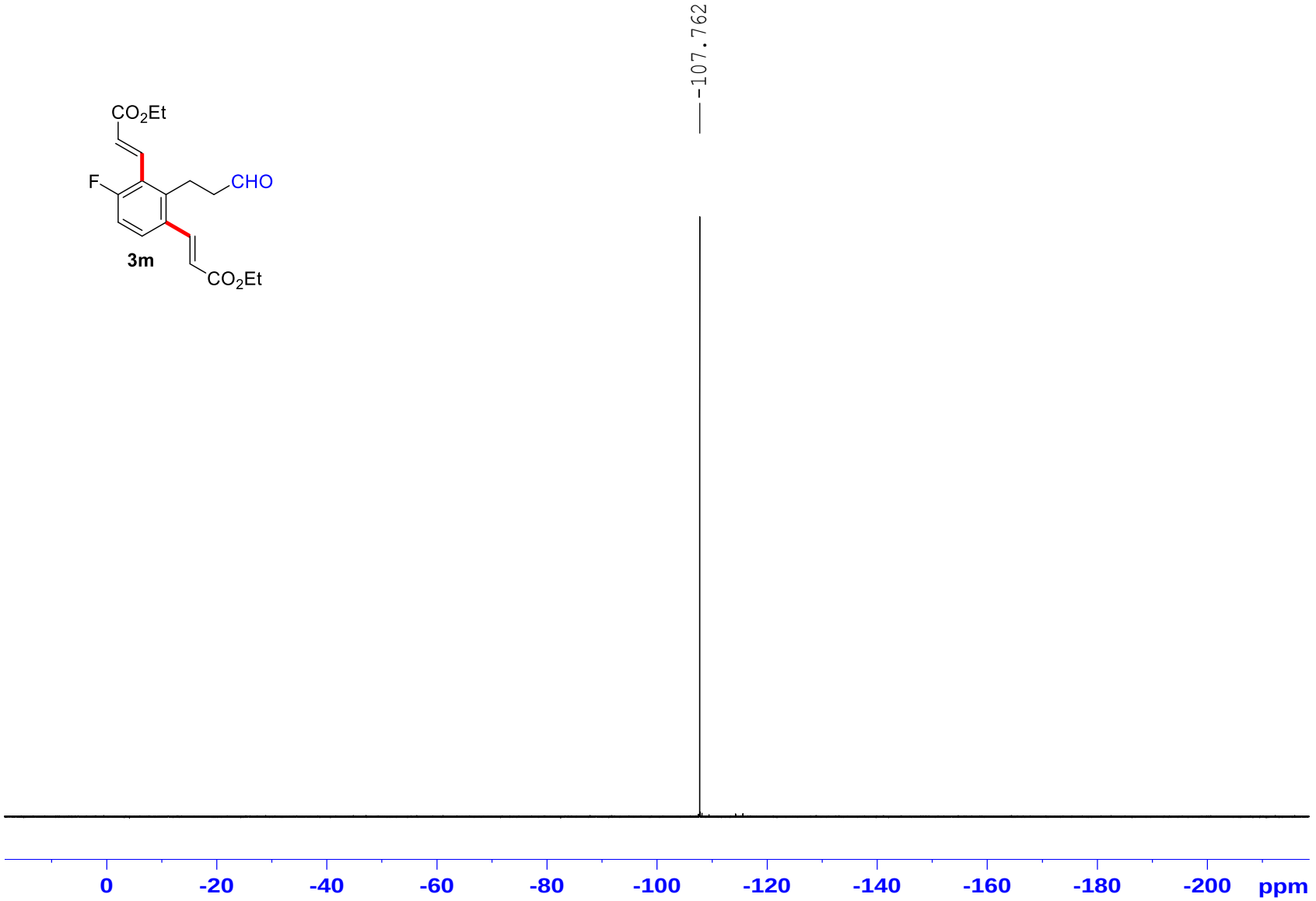
130.37
130.34
129.42
129.32
126.14
126.02
122.33
122.21
121.49
115.06
114.82
77.32
77.00
76.68
60.75
60.67
44.09
21.67
14.20
14.18
CO2Et
F
CHO
3m
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm


CO2Et
F
CHO
3m
CO2Et
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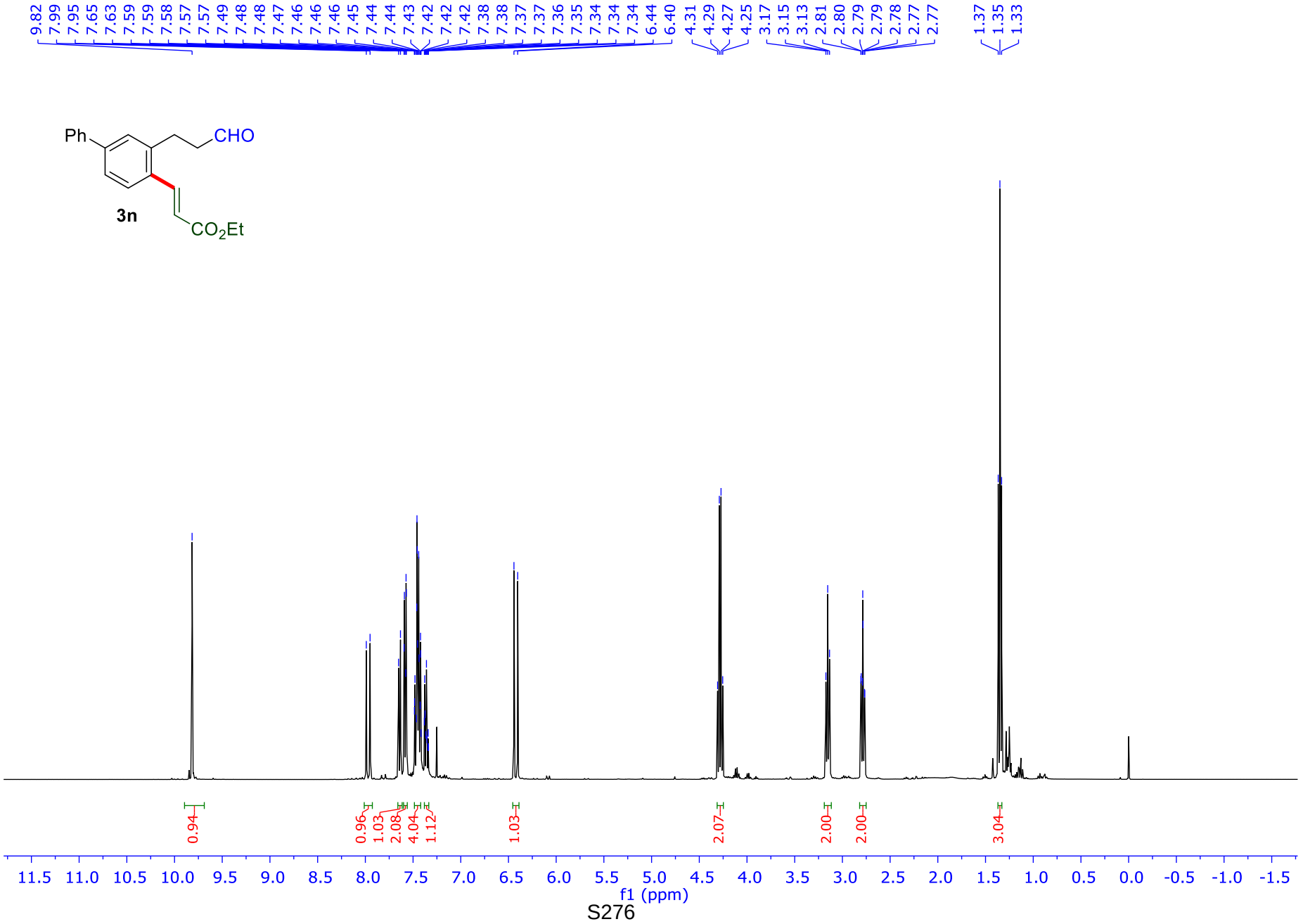
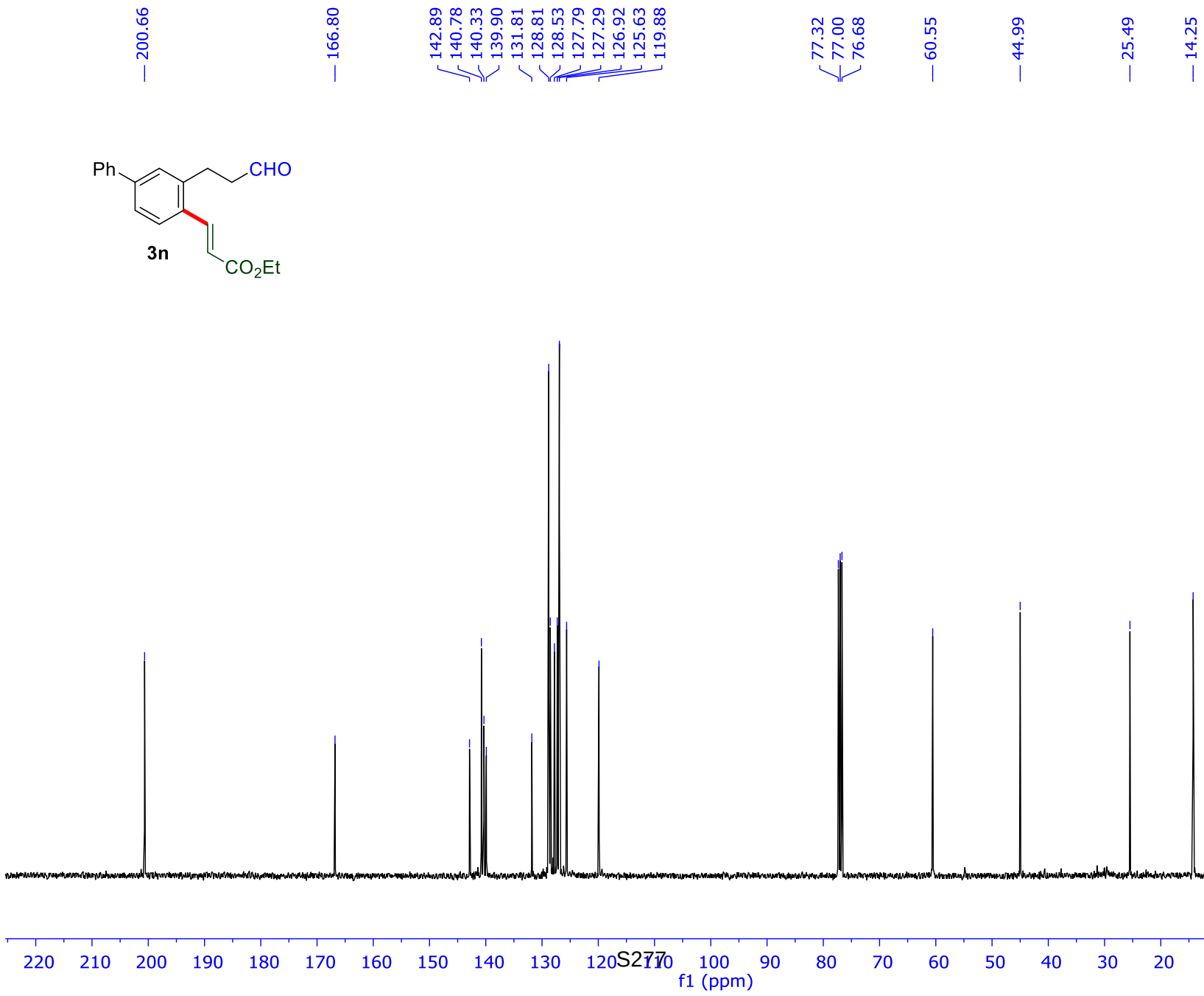
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


9.82 7.99 7.95 7.65 7.63 7.59 7.59 7.58 7.57 7.57 7.49 7.48 7.48 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.42 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.34 7.34 6.44 6.40 4.31 4.29 4.27 4.25 3.17 3.15 3.13 2.81 2.80 2.79 2.79 2.78 2.77 2.77 1.37 1.35 1.33
Ph
CHO
3n
CO2Et
0.94 0.96 1.03 2.08 4.04 1.12 1.03 2.07 2.00 2.00 3.04
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 -1.0 -1.5
f1 (ppm)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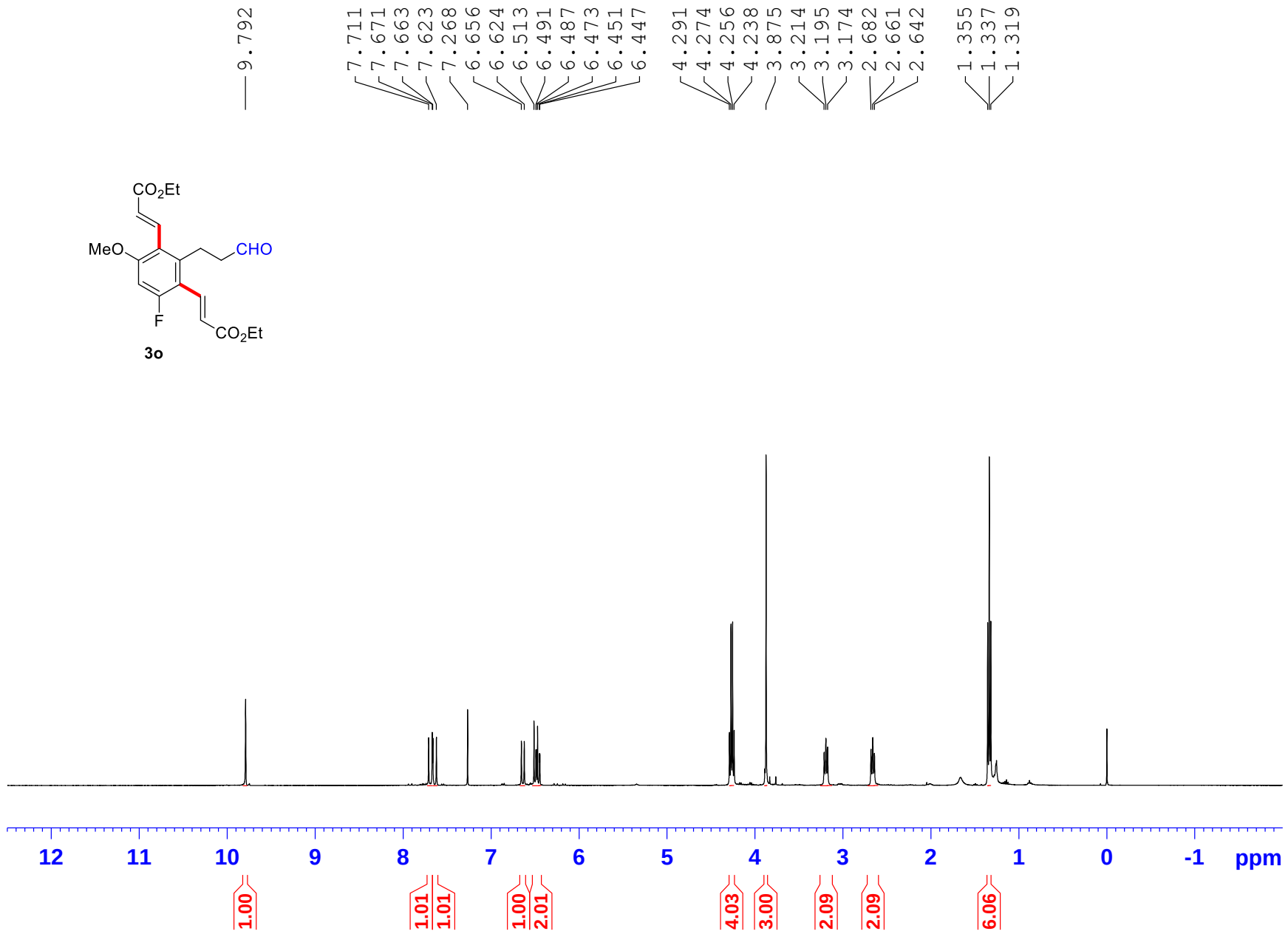
140.78
140.33
139.90
131.81
128.81
128.53
127.79
127.29
126.92
125.63
119.88
77.32
77.00
76.68
60.55
44.99
25.49
14.25
Ph
CHO
3n
CO2Et
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.663
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7.268
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6.624
6.513
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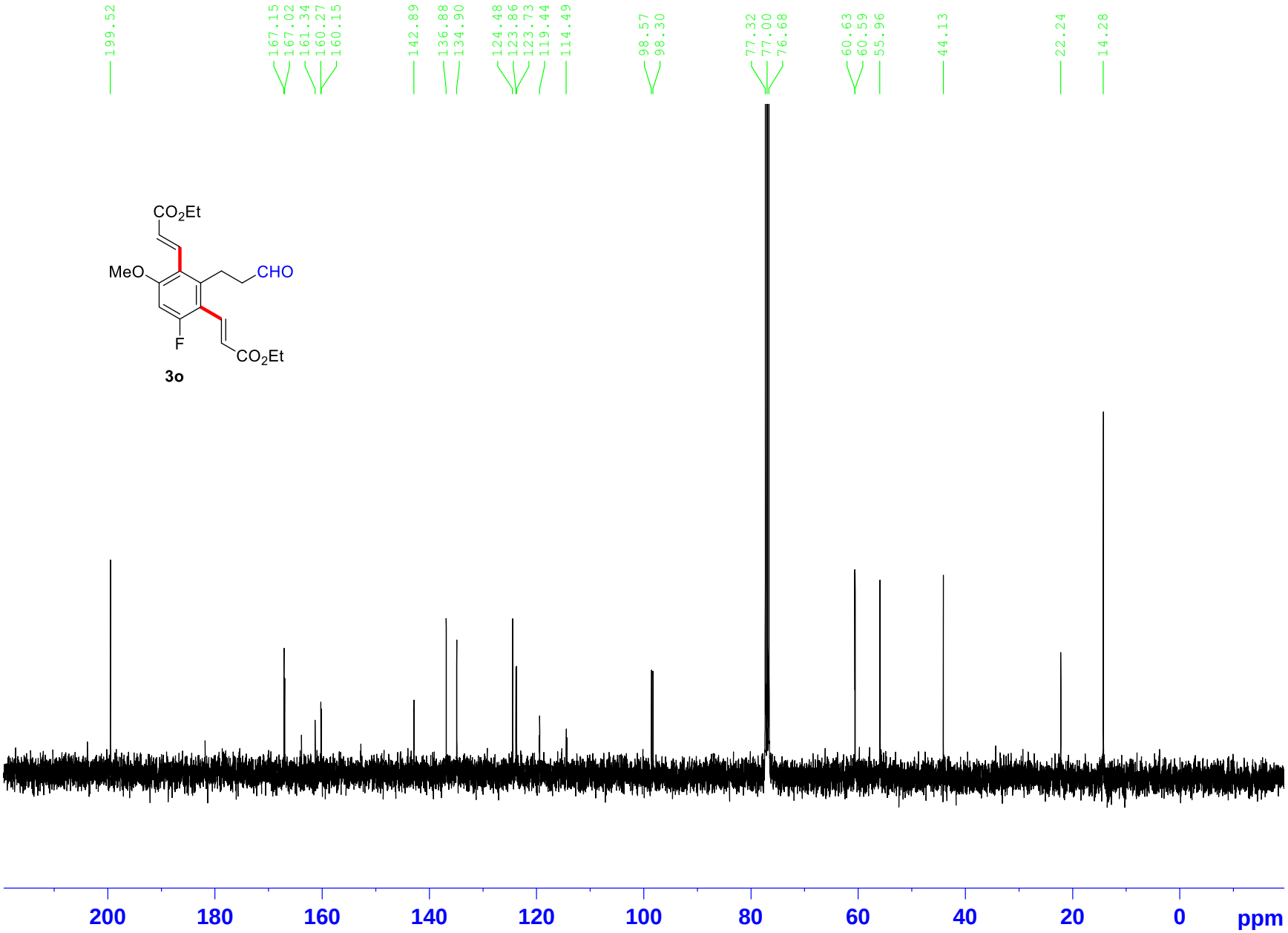
6.487
6.473
6.451
6.447
4.291
4.274
4.256
4.238
3.875
3.214
3.195
3.174
2.682
2.661
2.642
1.355
1.337
1.319
CO2Et
MeO
CHO
F
CO2Et
3o
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.01
1.01
1.00
2.01
4.03
3.00
2.09
2.09
6.06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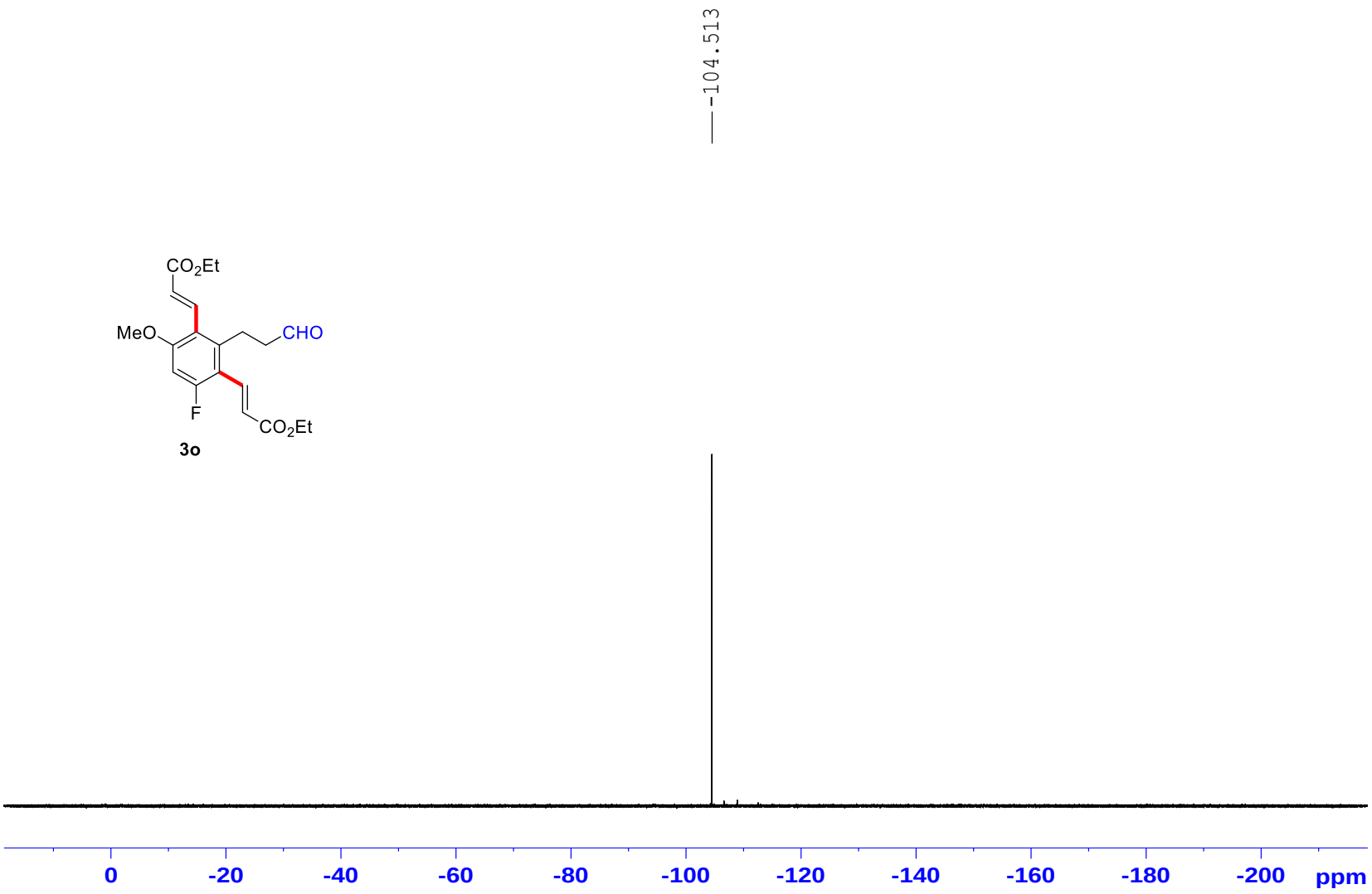
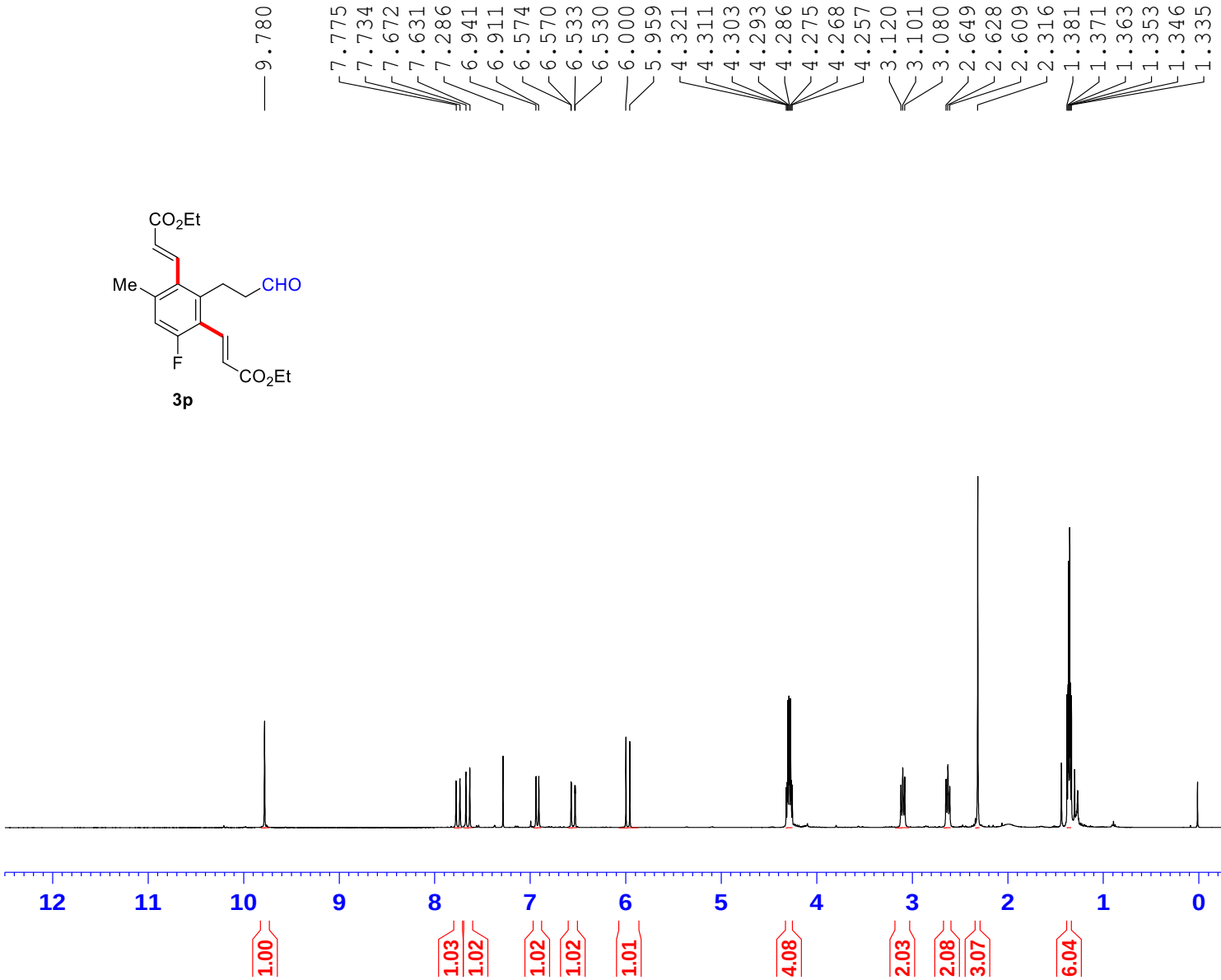
167.15
167.02
161.34
160.27
160.15
142.89
136.88
134.90
124.48
123.86
123.73
119.44
114.49
98.57
98.30
77.32
77.00
76.68
60.63
60.59
55.96
44.13
22.24
14.28
CO2Et
MeO
CHO
F
CO2Et
3o
200
180
160
140
120
100
80
60
40
20
0
ppm


-104.513
CO2Et
MeO
CHO
F
CO2Et
3o
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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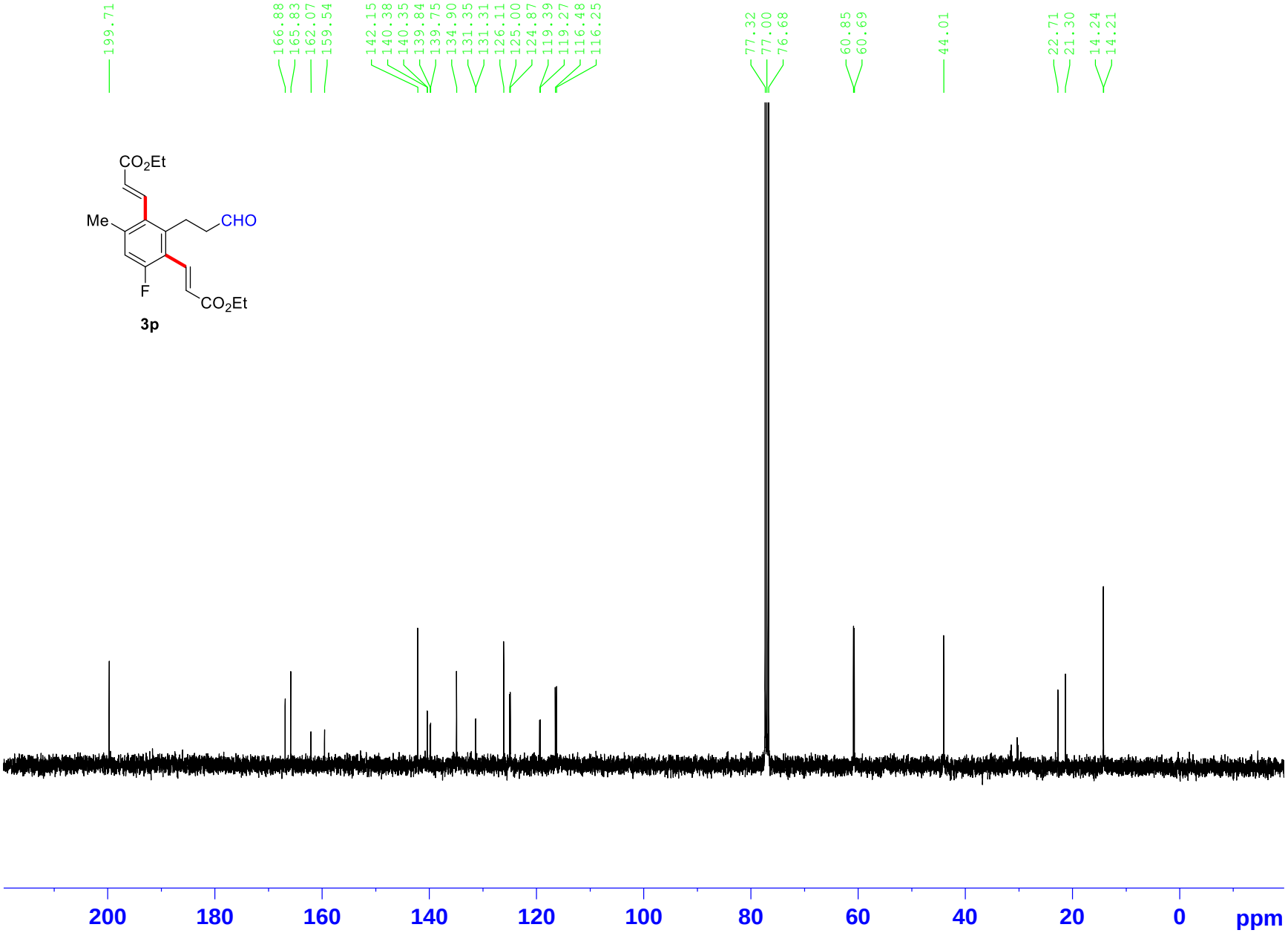
6.911
6.574
6.570
6.533
6.530
6.000
5.959
4.321
4.311
4.303
4.293
4.286
4.275
4.268
4.257
3.120
3.101
3.080
2.649
2.628
2.609
2.316
1.381
1.371
1.363
1.353
1.346
1.335
CO2Et
Me
CHO
F
CO2Et
3p
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.03
1.02
1.02
1.02
1.01
4.08
2.03
2.08
3.07
6.04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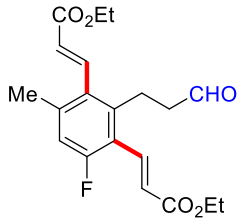
134.90
131.35
131.31
126.11
125.00
124.87
119.39
119.27
116.48
116.25
77.32
77.00
76.68
60.85
60.69
44.01
22.71
21.30
14.24
14.21
CO2Et
Me
CHO
F
CO2Et
3p
200
180
160
140
120
100
80
60
40
20
0
ppm


CO2Et
Me
CHO
F
CO2Et

3p

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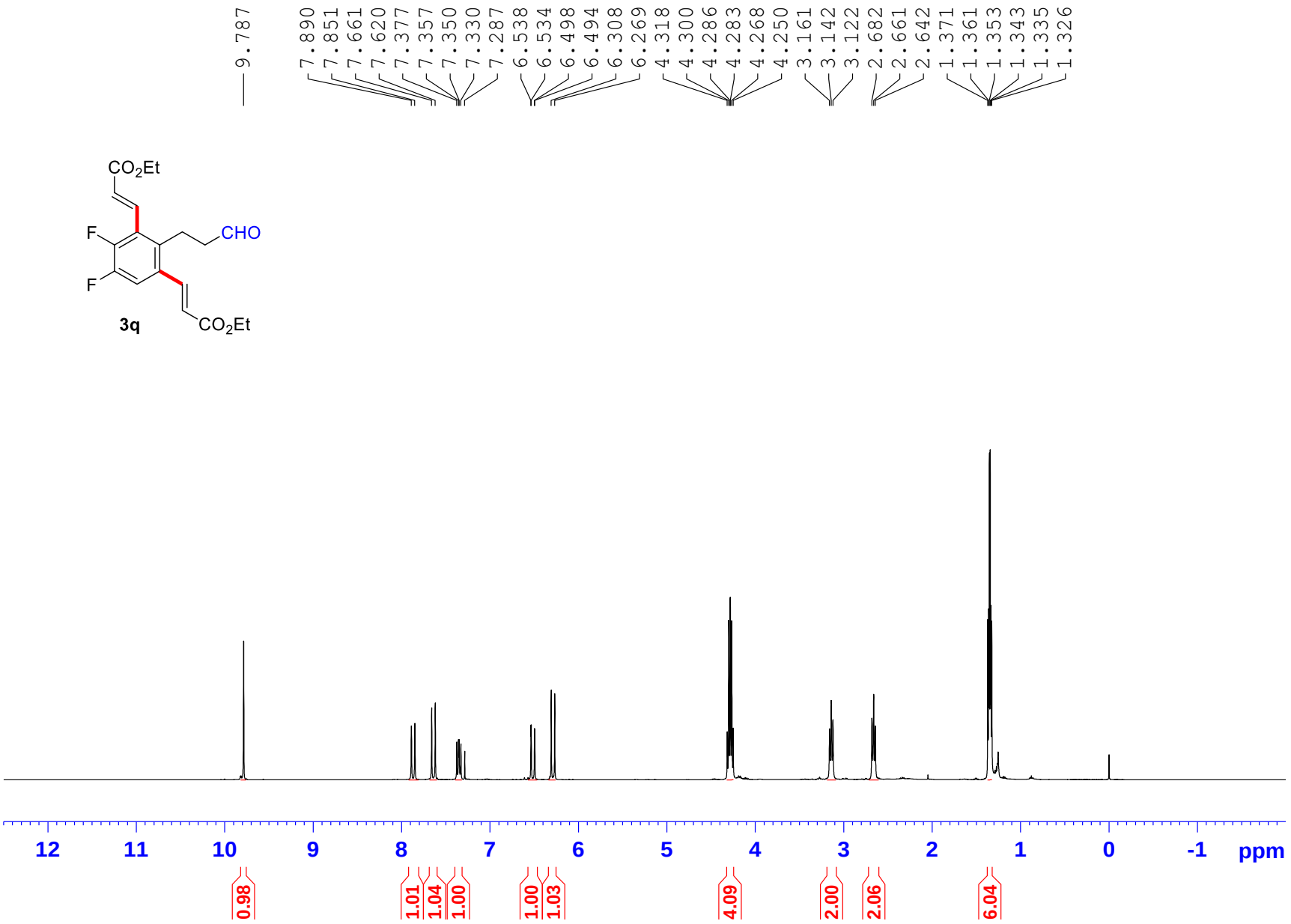
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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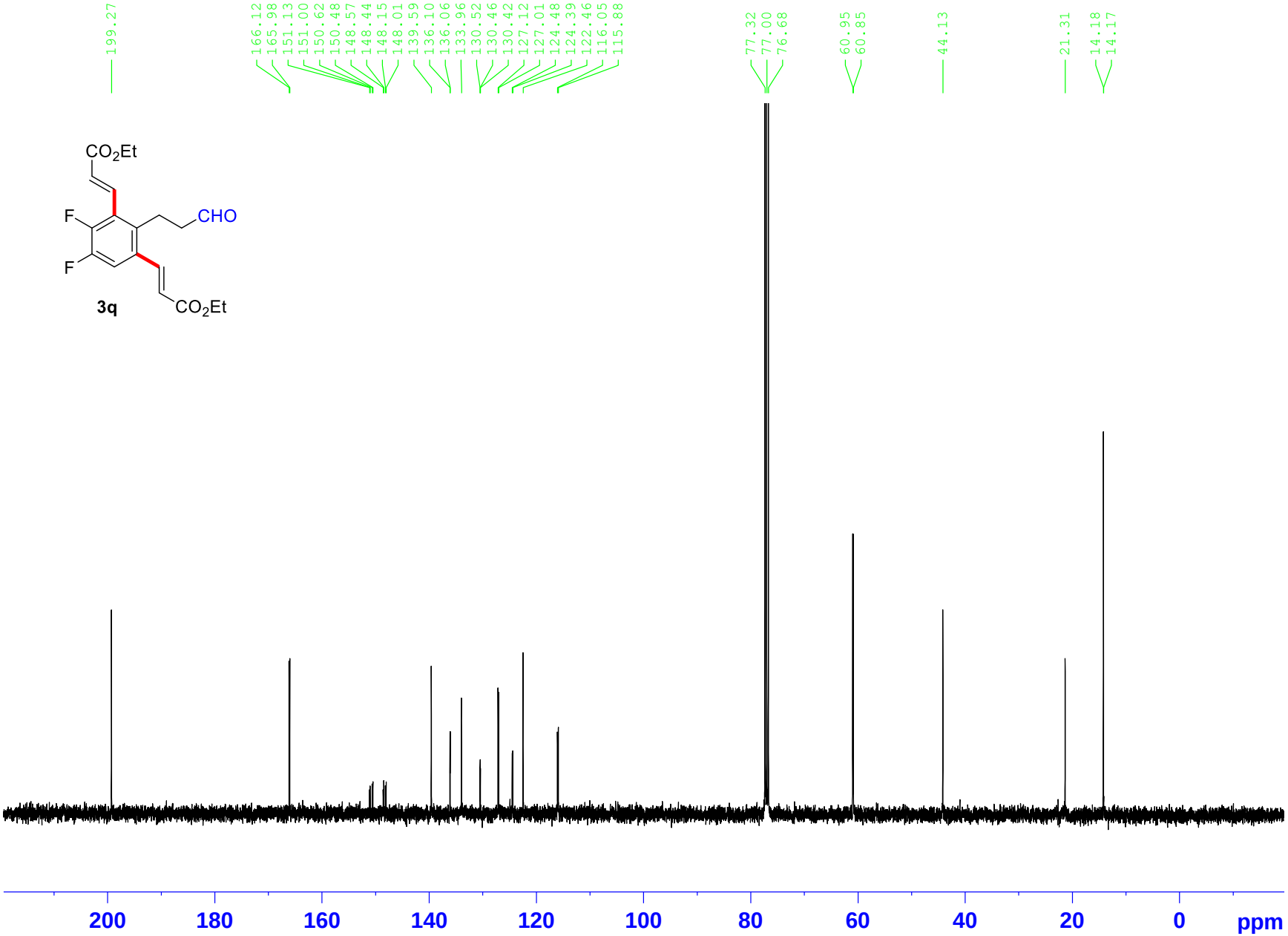
7.620
7.377
7.357
7.350
7.330
7.287
6.538
6.534
6.498
6.494
6.308
6.269
4.318
4.300
4.286
4.283
4.268
4.250
3.161
3.142
3.122
2.682
2.661
2.642
1.371
1.361
1.353
1.343
1.335
1.326
CO2Et
F
F
CHO
CO2Et
3q
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
1.01
1.04
1.00
1.00
1.03
4.09
2.00
2.06
6.04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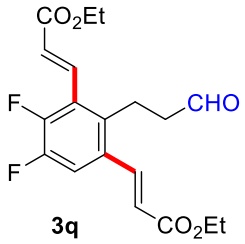
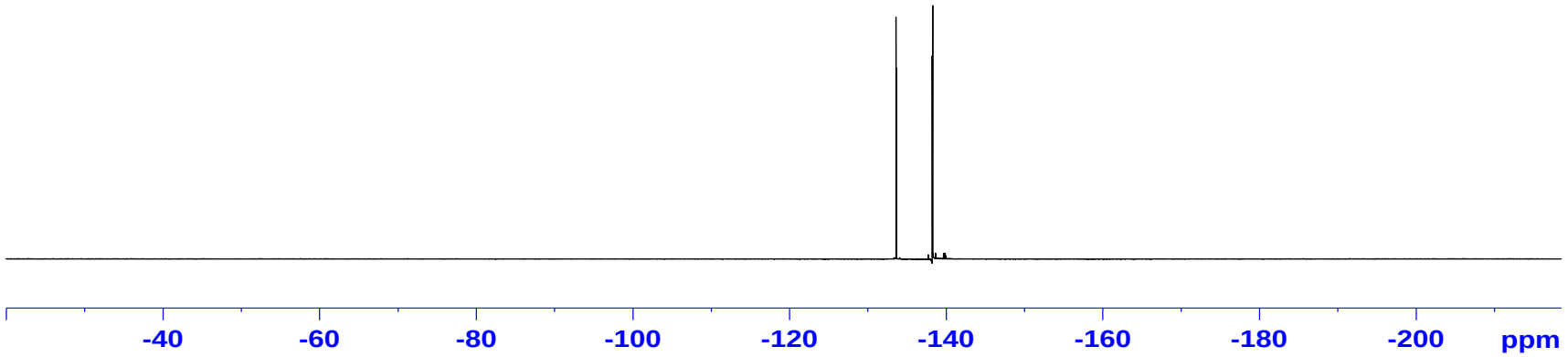
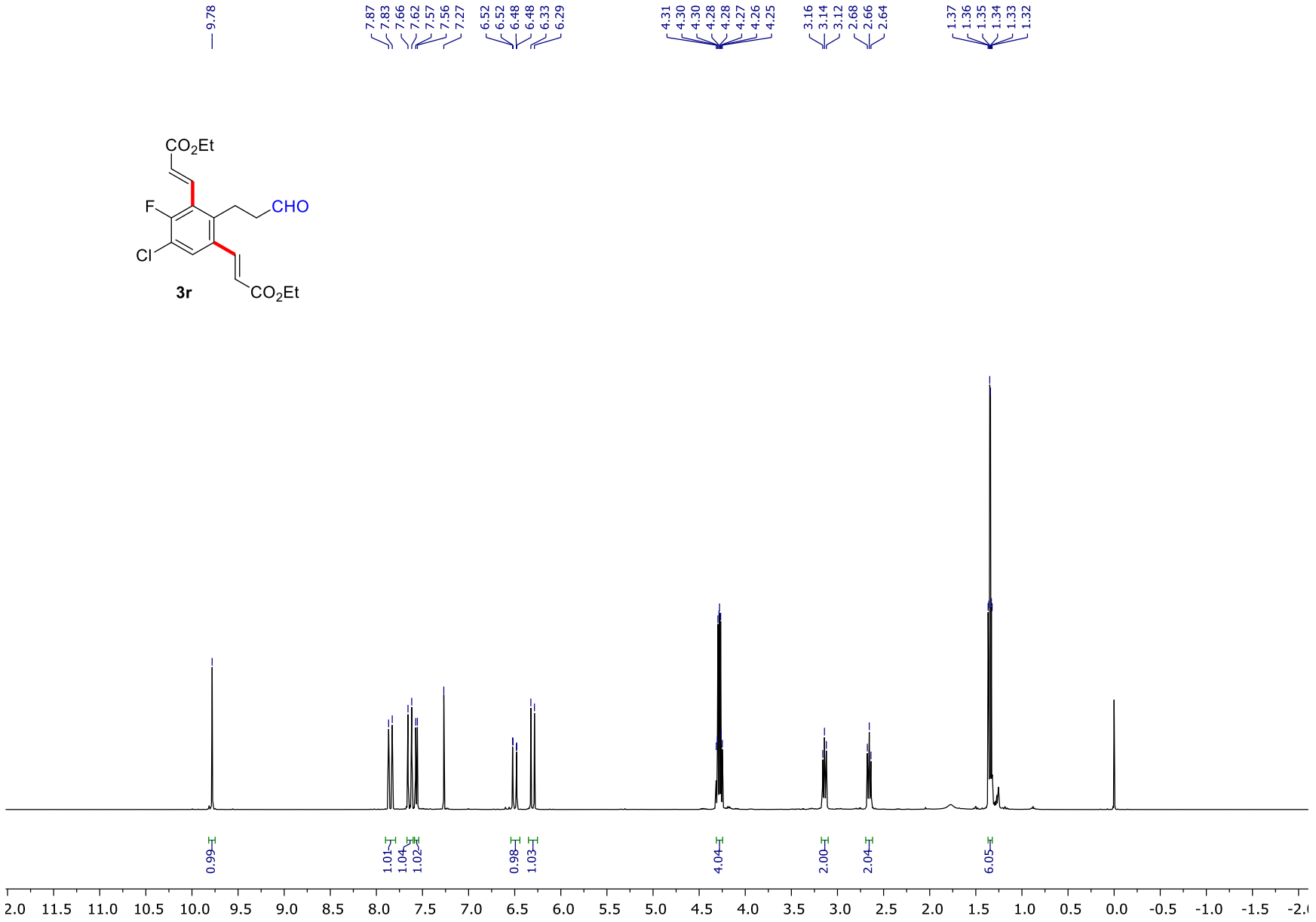
150.62
150.48
148.57
148.44
148.15
148.01
139.59
136.10
136.06
133.96
130.52
130.46
130.42
127.12
127.01
124.48
124.39
122.46
116.05
115.88
77.32
77.00
76.68
60.95
60.85
44.13
21.31
14.18
14.17
CO2Et
F
F
CHO
CO2Et
3q
200
180
160
140
120
100
80
60
40
20
0
ppm



3q

-133.621
-133.678
-138.242
-138.297

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7.83
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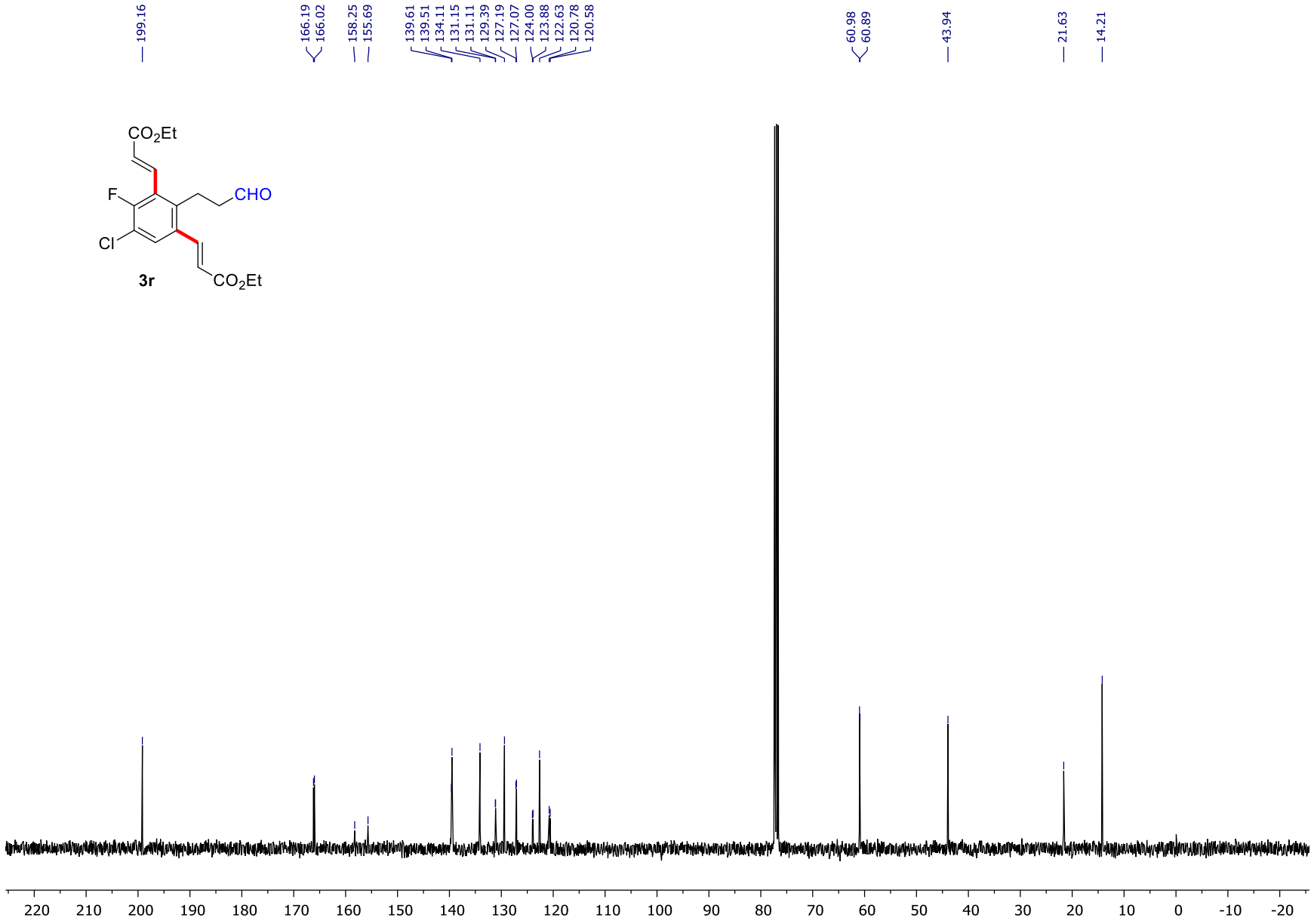
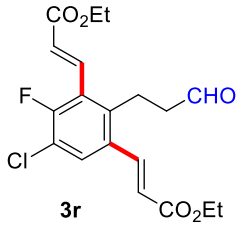
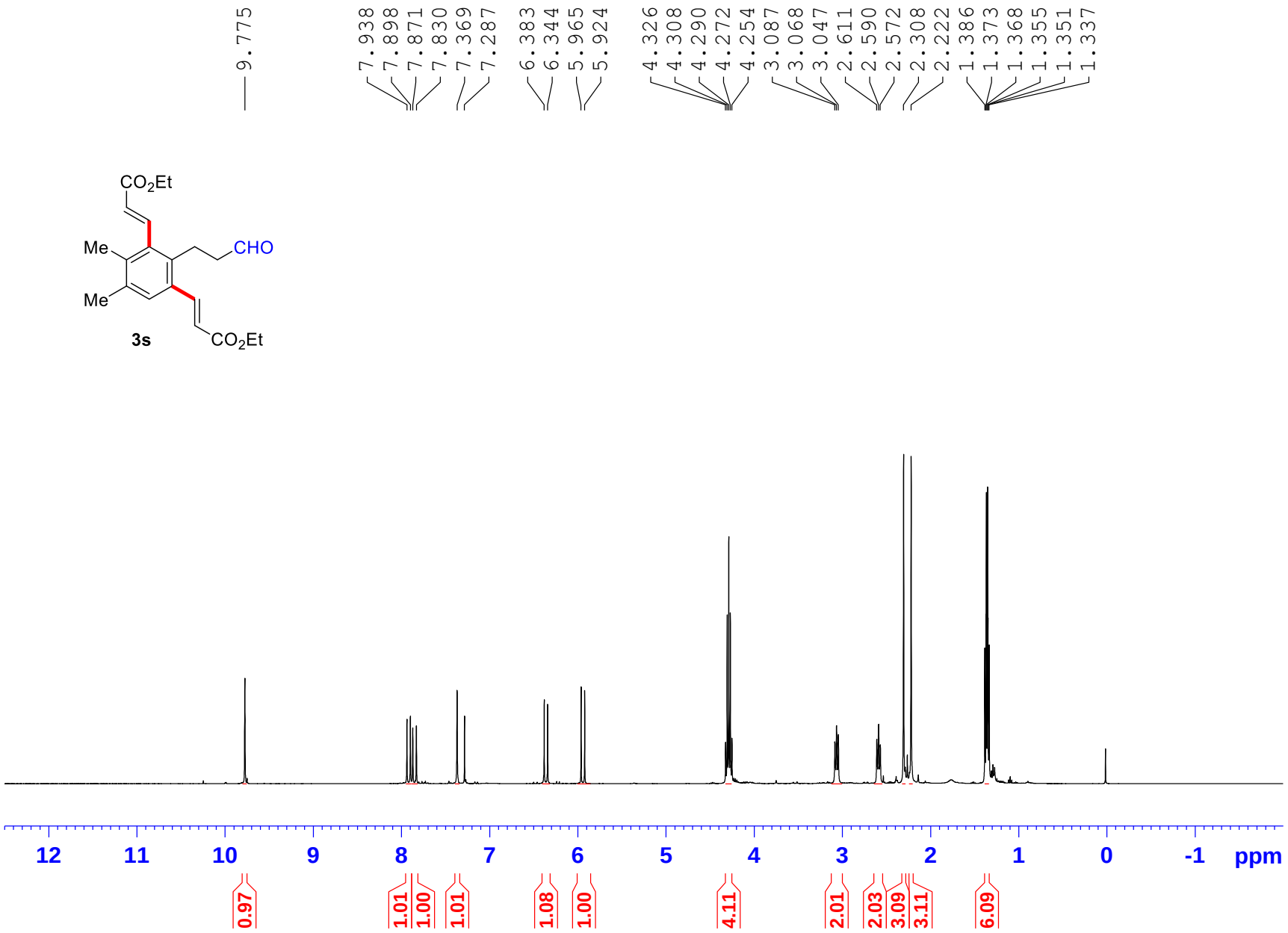
7.57
7.56
7.27
6.52
6.52
6.48
6.48
6.33
6.29
4.31
4.30
4.30
4.28
4.28
4.27
4.26
4.25
3.16
3.14
3.12
2.68
2.66
2.64
1.37
1.36
1.35
1.34
1.33
1.32
CO2Et
F
CHO
Cl
CO2Et
3r
0.99
1.01
1.04
1.02
0.98
1.03
4.04
2.00
2.04
6.05
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5


199.16
166.19
166.02
158.25
155.69
139.61
139.51
134.11
131.15
131.11
129.39
127.19
127.07
124.00
123.88
122.63
120.78
120.58
60.98
60.89
43.94
21.63
14.21
CO2Et
F
CHO
Cl
CO2Et
3r
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


CO2Et
F
CHO
Cl
CO2Et

3r

-110.32
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)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7.898
7.871
7.830
7.369
7.287
6.383
6.344
5.965
5.924
4.326
4.308
4.290
4.272
4.254
3.087
3.068
3.047
2.611
2.590
2.572
2.308
2.222
1.386
1.373
1.368
1.355
1.351
1.337
CO2Et
Me
CHO
Me
CO2Et
3s
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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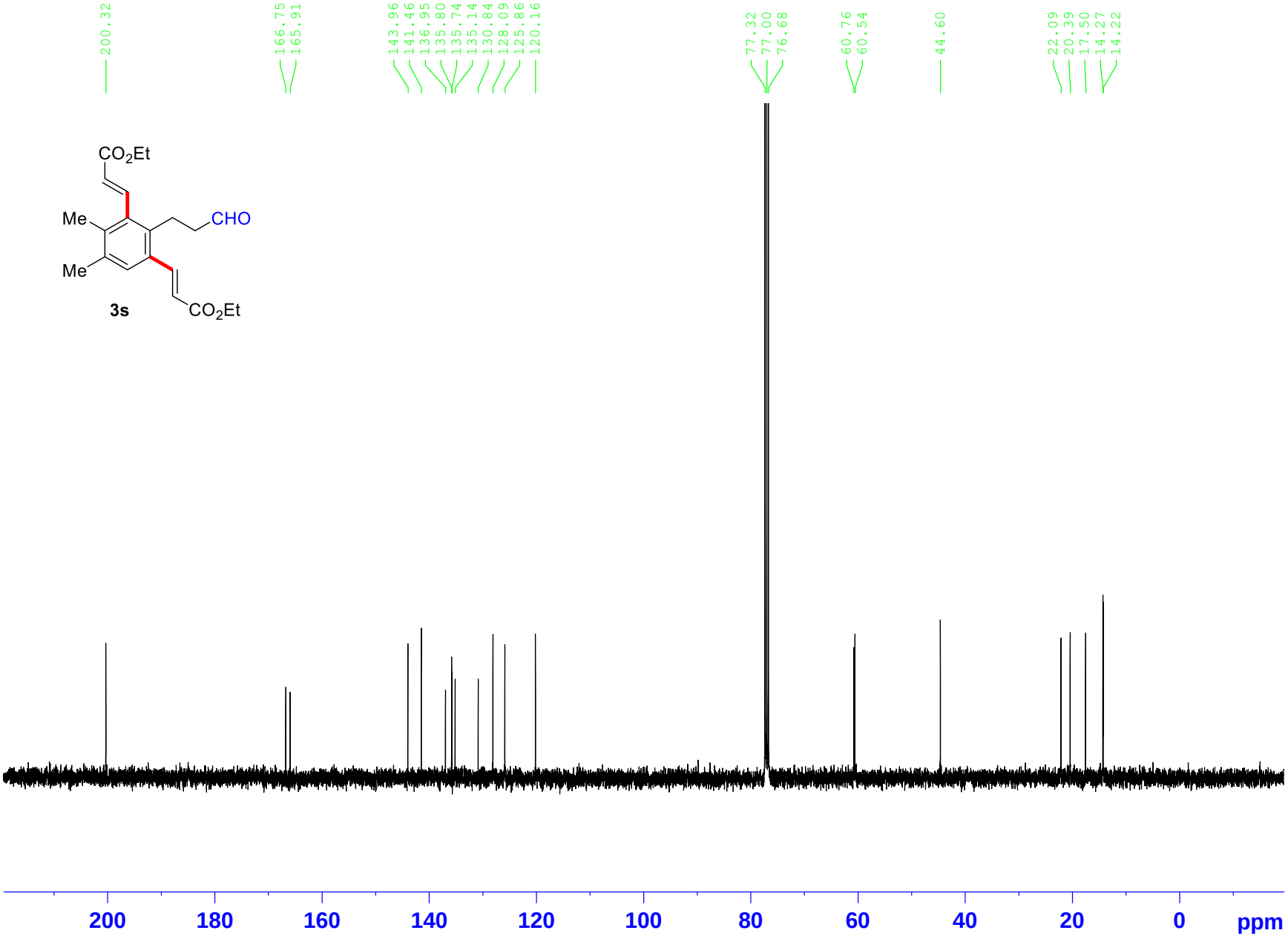
1.00
1.01
1.08
1.00
4.11
2.01
2.03
3.09
3.11
6.09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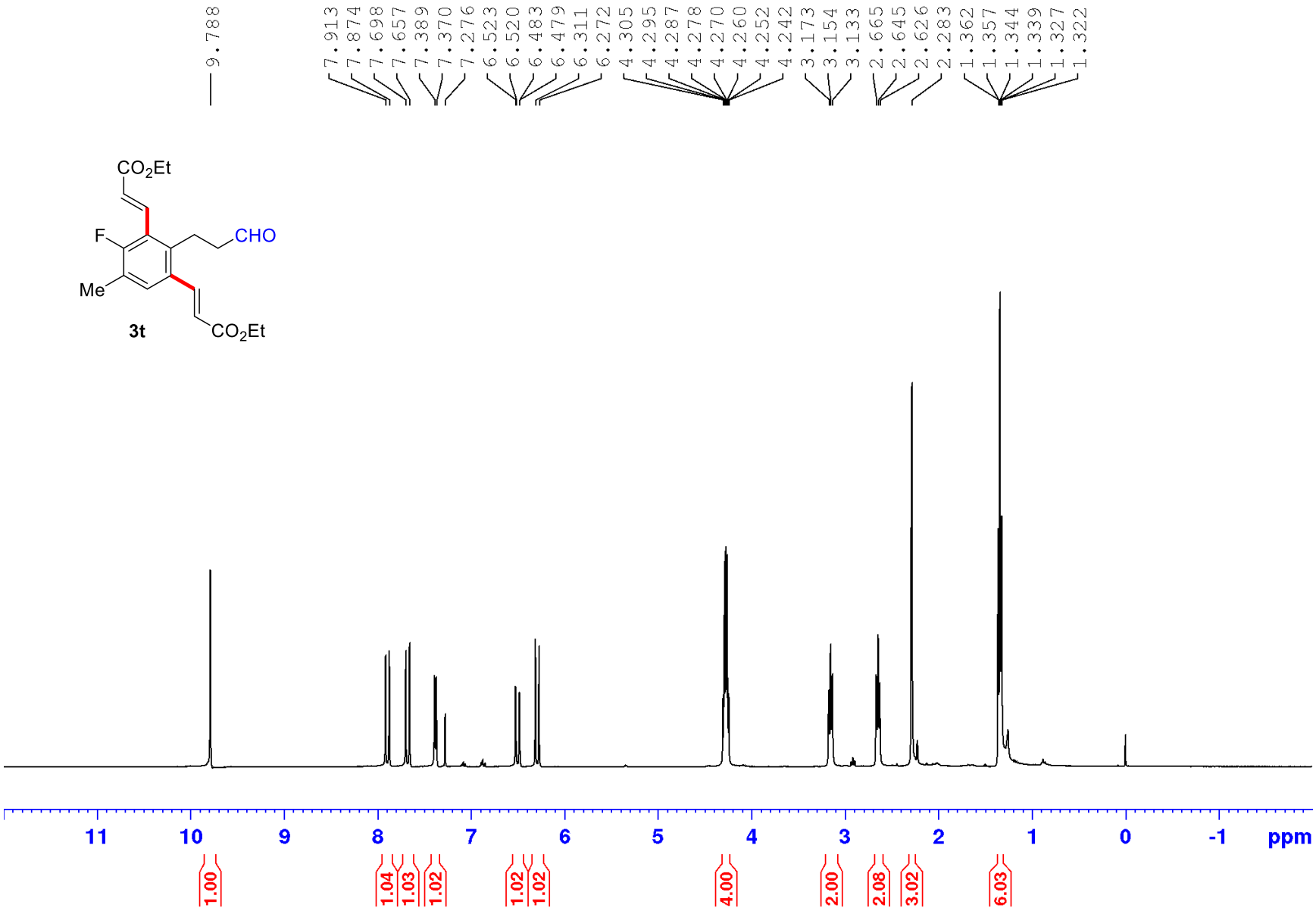
165.91
143.96
141.46
136.95
135.80
135.74
135.14
130.84
128.09
125.86
120.16
77.32
77.00
76.68
60.76
60.54
44.60
22.09
20.39
17.50
14.27
14.22
CO2Et
Me
Me
CHO
CO2Et
3s
200
180
160
140
120
100
80
60
40
20
0
ppm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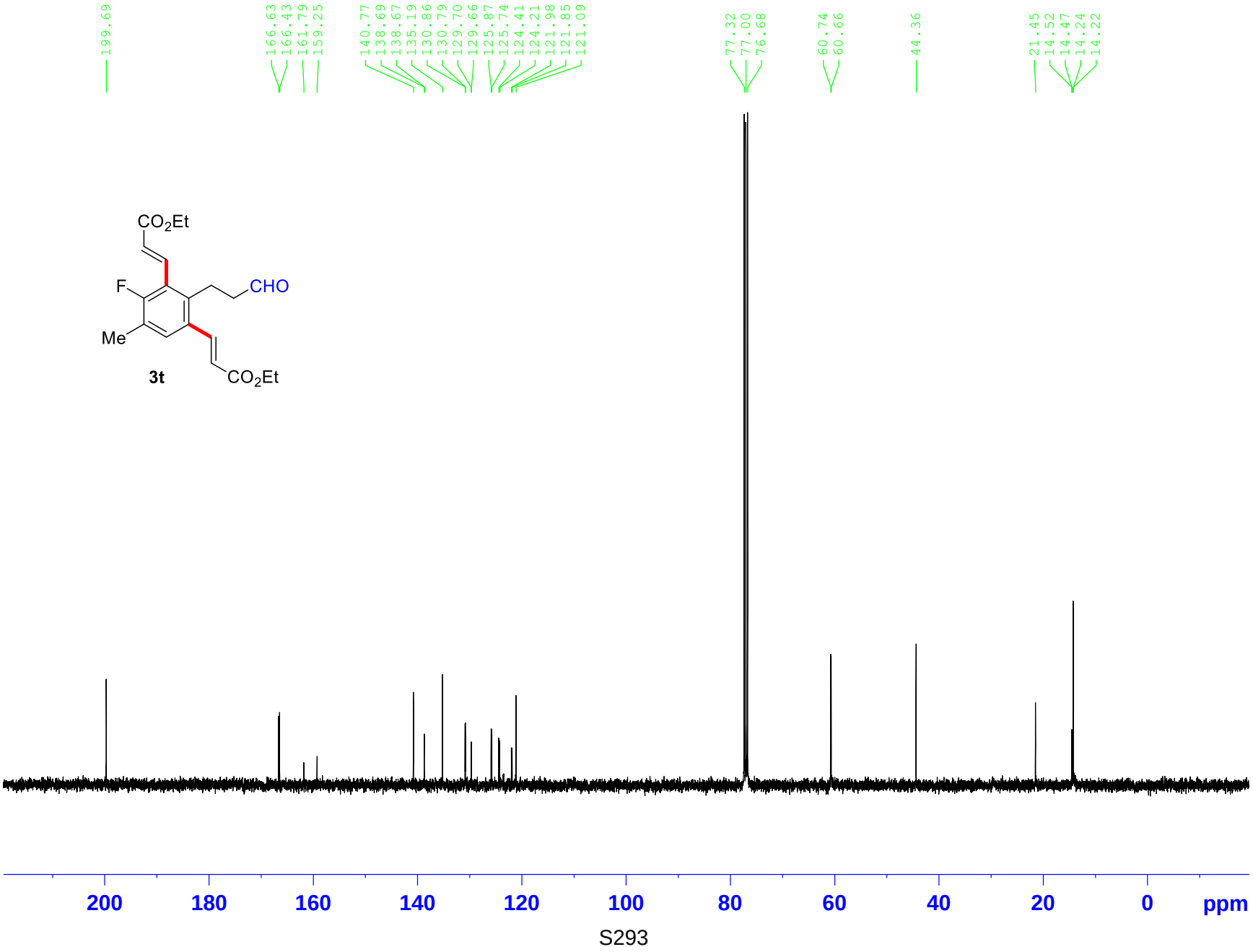
7.389
7.370
7.276
6.523
6.520
6.483
6.479
6.311
6.272
4.305
4.295
4.287
4.278
4.270
4.260
4.252
4.242
3.173
3.154
3.133
2.665
2.645
2.626
2.283
1.362
1.357
1.344
1.339
1.327
1.322
CO2Et
F
CHO
Me
CO2Et
3t
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.04
1.03
1.02
1.02
1.02
4.00
2.00
2.08
3.02
6.03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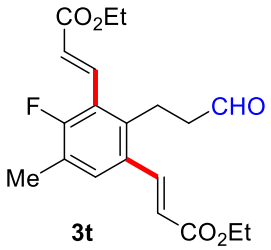
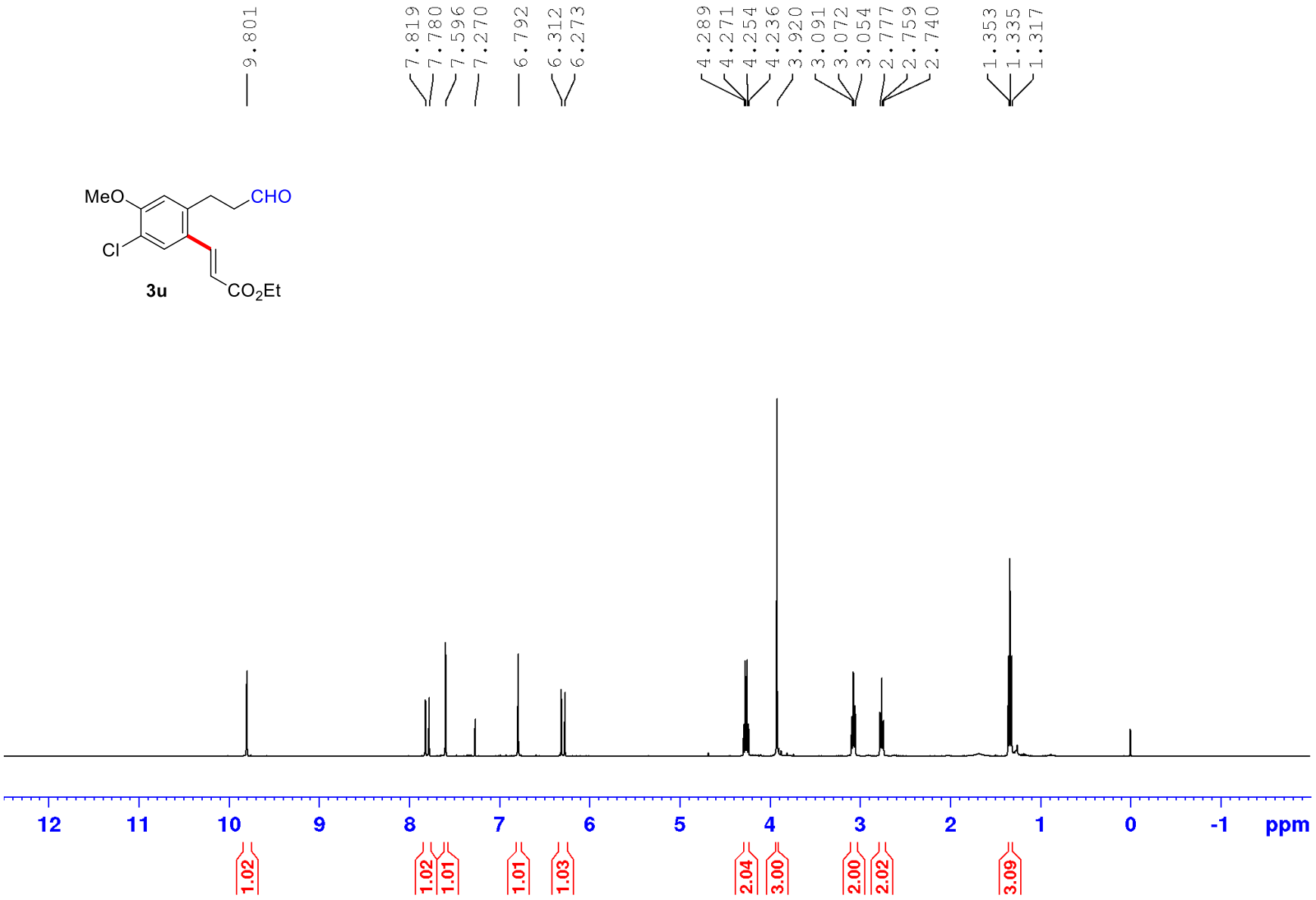
166.63
166.43
161.79
159.25
140.77
138.69
138.67
135.19
130.86
130.79
129.70
129.66
125.87
125.74
124.41
124.21
121.98
121.85
121.09
77.32
77.00
76.68
60.74
60.66
44.36
21.45
14.52
14.47
14.24
14.22
CO2Et
F
CHO
Me
CO2Et
3t
200
180
160
140
120
100
80
60
40
20
0
ppm



3t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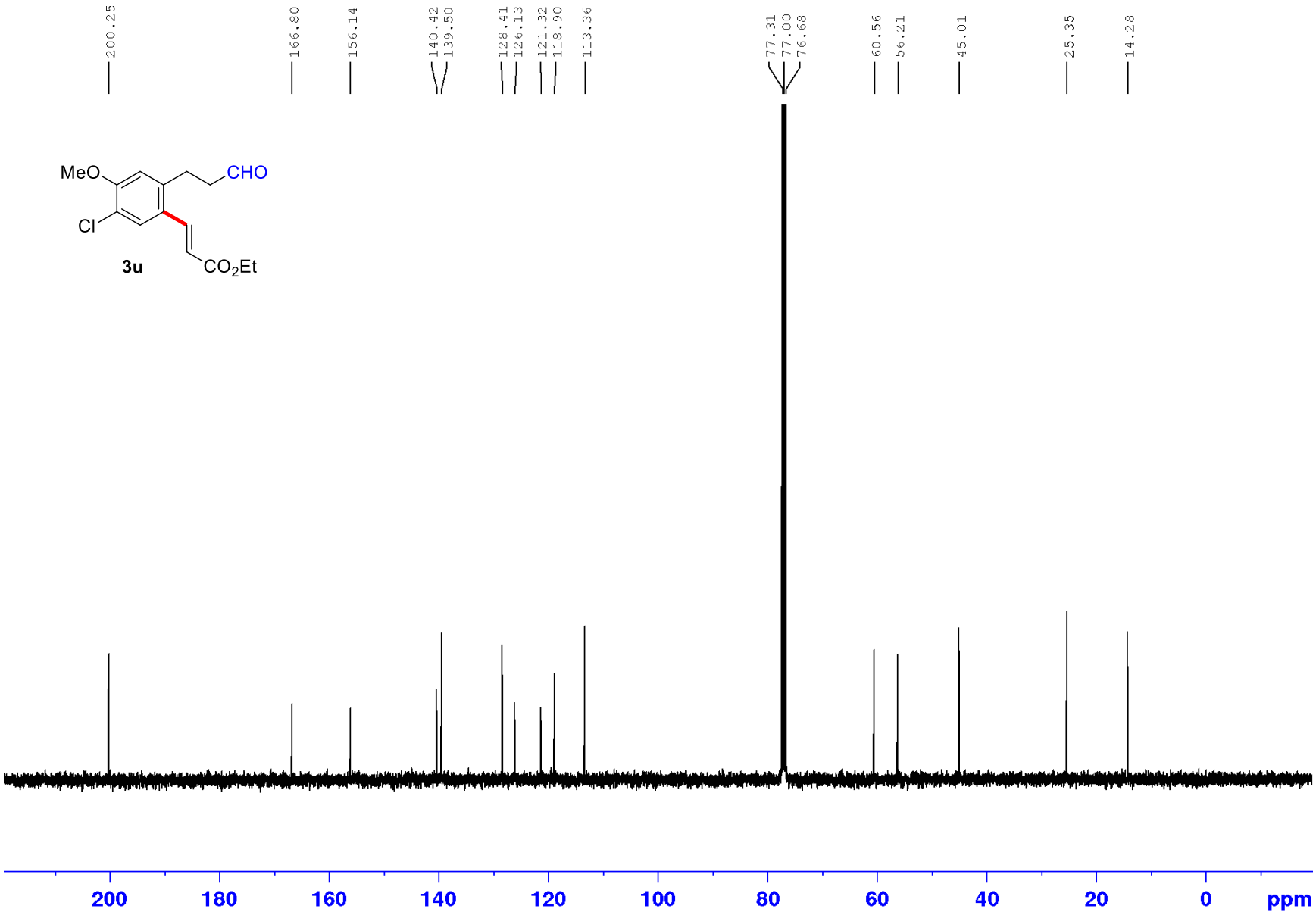
7.819
7.780
7.596
7.270
6.792
6.312
6.273
4.289
4.271
4.254
4.236
3.920
3.091
3.072
3.054
2.777
2.759
2.740
1.353
1.335
1.317
MeO
CHO
Cl
3u
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
1.02
1.01
1.01
1.03
2.04
3.00
2.00
2.02
3.09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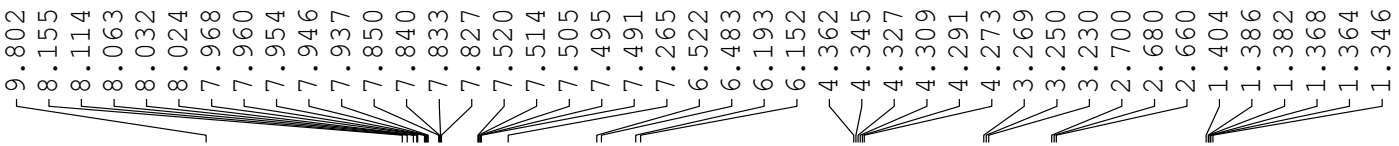
166.80
156.14
140.42
139.50
128.41
126.13
121.32
118.90
113.36
77.31
77.00
76.68
60.56
56.21
45.01
25.35
14.28
MeO
CHO
Cl
CO2Et
3u
200
180
160
140
120
100
80
60
40
20
0
ppm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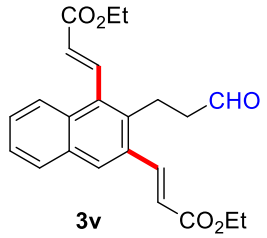
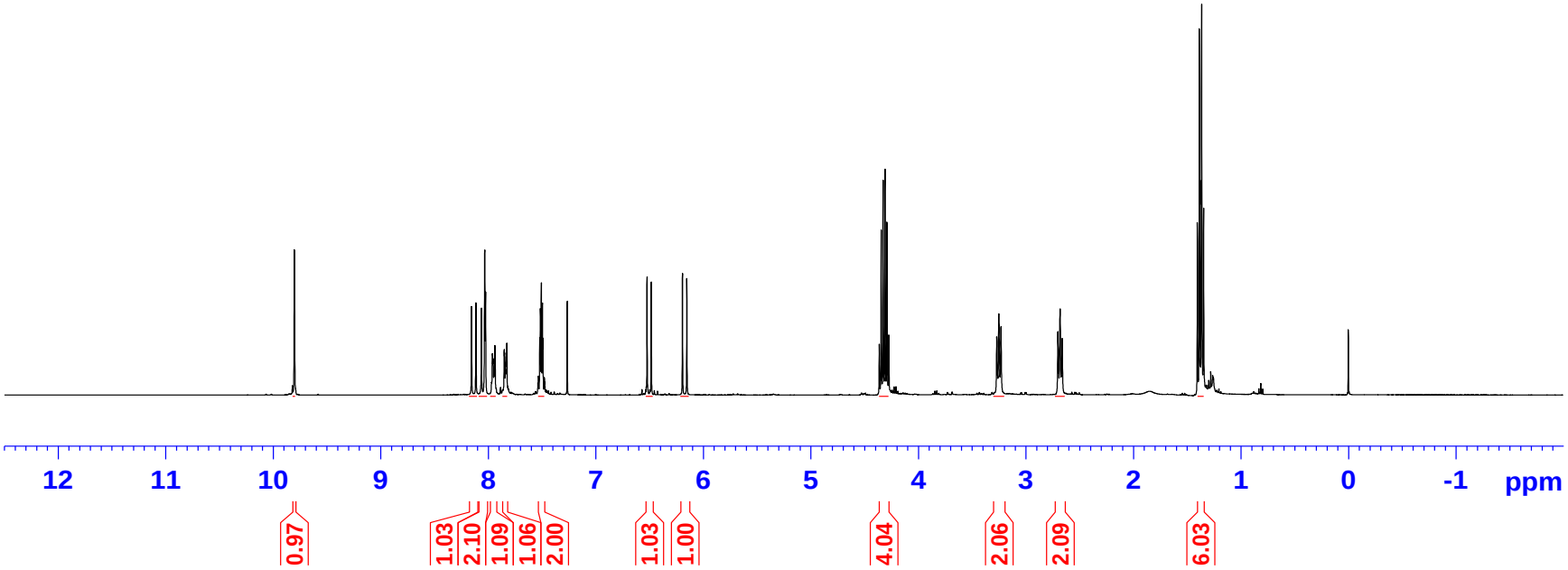
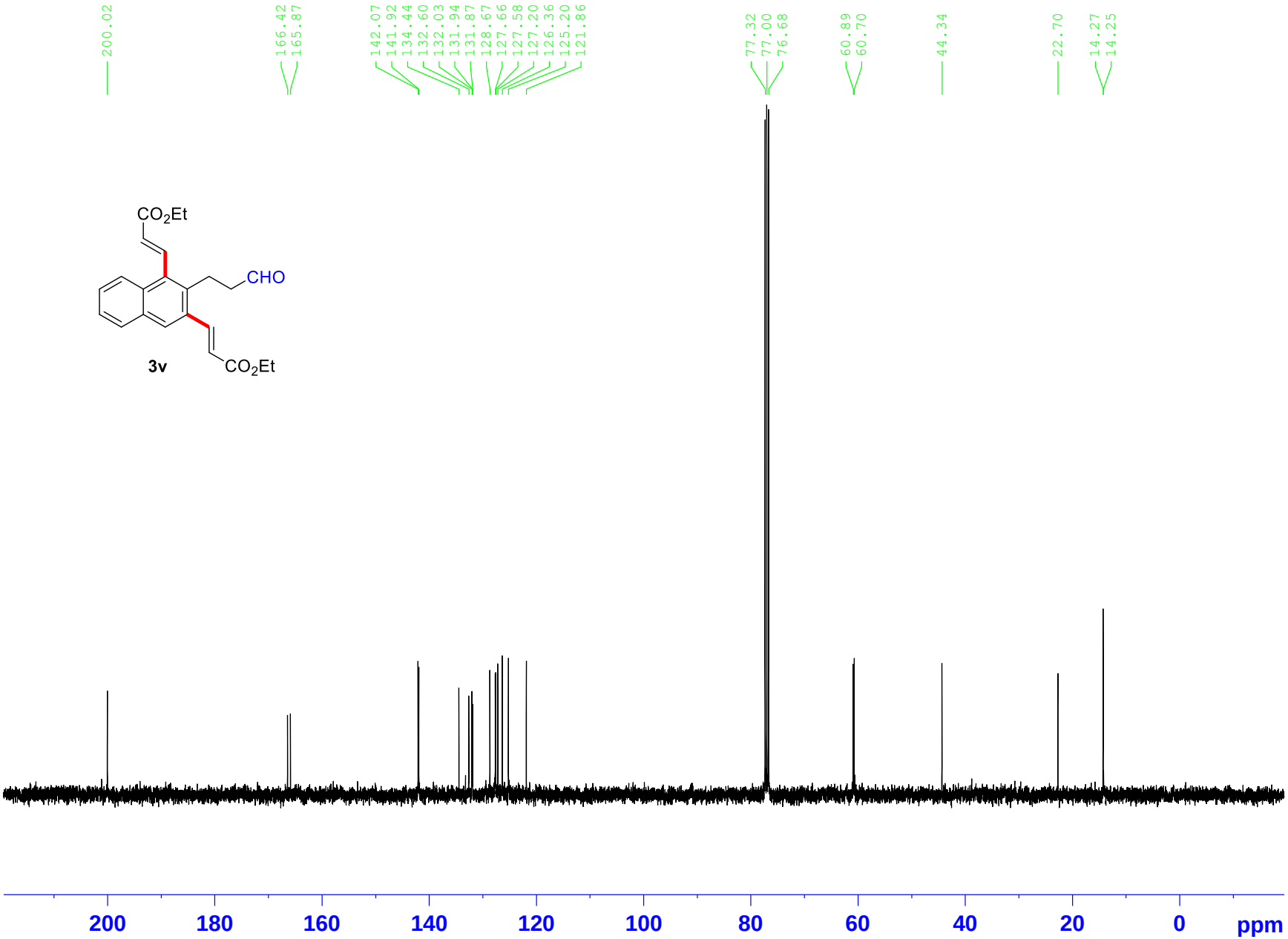
8.155
8.114
8.063
8.032
8.024
7.968
7.960
7.954
7.946
7.937
7.850
7.840
7.833
7.827
7.520
7.514
7.505
7.495
7.491
7.265
6.522
6.483
6.193
6.152
4.362
4.345
4.327
4.309
4.291
4.273
3.269
3.250
3.230
2.700
2.680
2.660
1.404
1.386
1.382
1.368
1.364
1.346


CO2Et
CHO
CO2Et

3v


12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
1.03
2.10
1.09
1.06
2.00
1.03
1.00
4.04
2.06
2.09
6.03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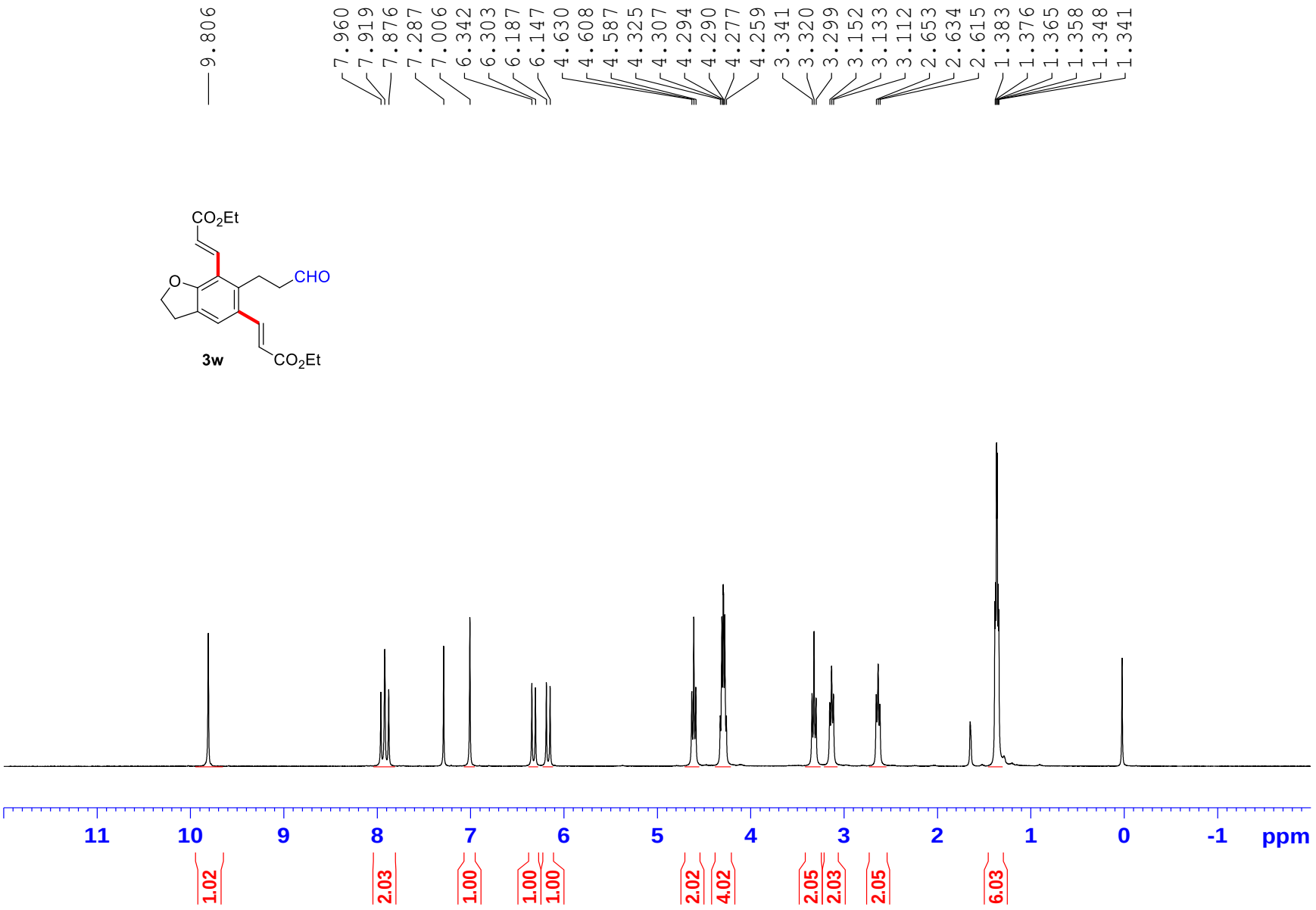
166.42
165.87
142.07
141.92
134.44
132.60
132.03
131.94
131.87
128.67
127.66
127.58
127.20
126.36
125.20
121.86
77.32
77.00
76.68
60.89
60.70
44.34
22.70
14.27
14.25
CO2Et
CHO
CO2Et
3v
200
180
160
140
120
100
80
60
40
20
0
ppm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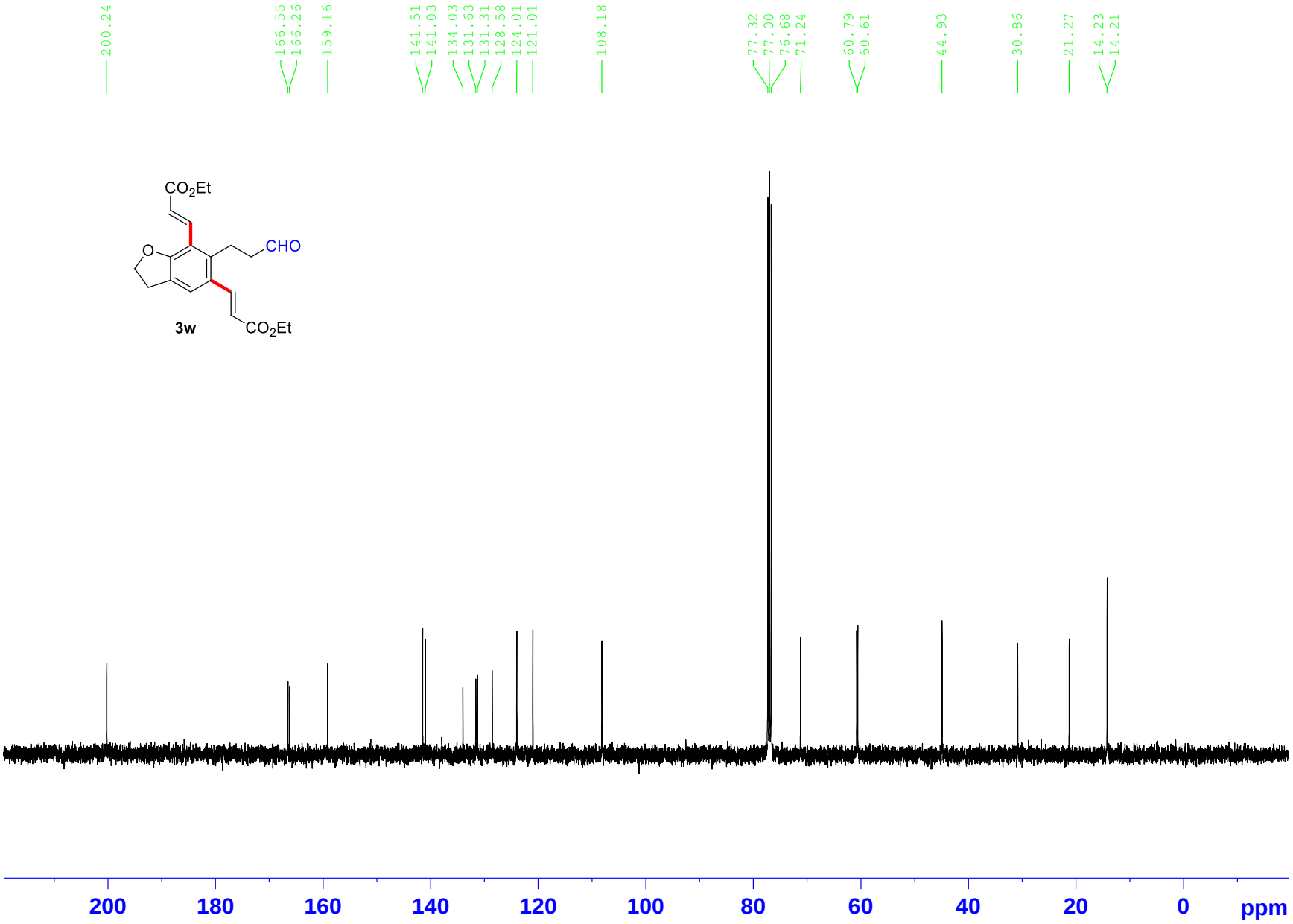
7.876
7.287
7.006
6.342
6.303
6.187
6.147
4.630
4.608
4.587
4.325
4.307
4.294
4.290
4.277
4.259
3.341
3.320
3.299
3.152
3.133
3.112
2.653
2.634
2.615
1.383
1.376
1.365
1.358
1.348
1.341
CO2Et
CHO
O
CO2Et
3w
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.02
2.03
1.00
1.00
1.00
2.02
4.02
2.05
2.03
2.05
6.03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166.55
166.26
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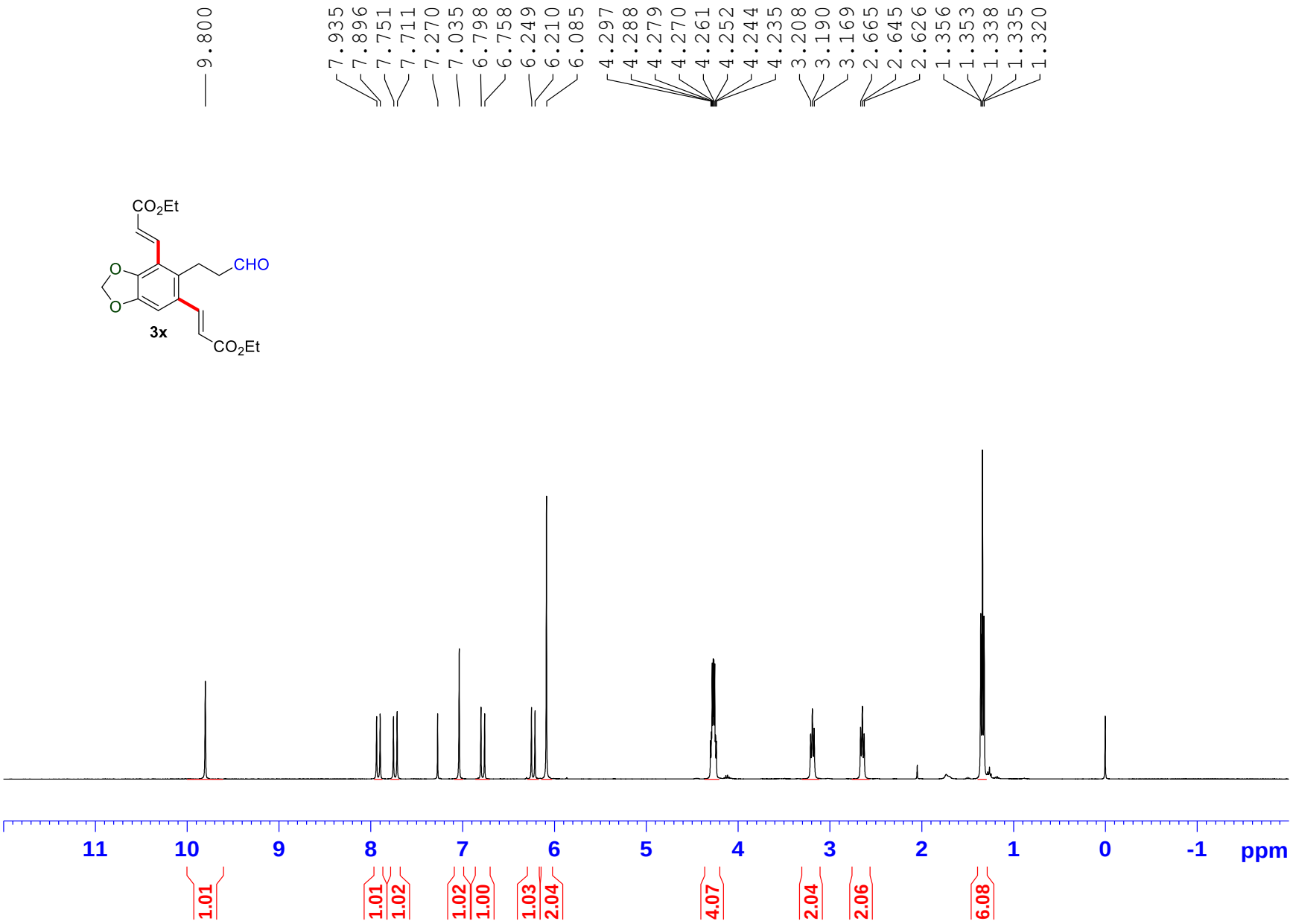
141.03
134.03
131.63
131.31
128.58
124.01
121.01
108.18
77.32
77.00
76.68
71.24
60.79
60.61
44.93
30.86
21.27
14.23
14.21
CO2Et
CHO
O
CO2Et
3w
200
180
160
140
120
100
80
60
40
20
0
ppm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7.751
7.711
7.270
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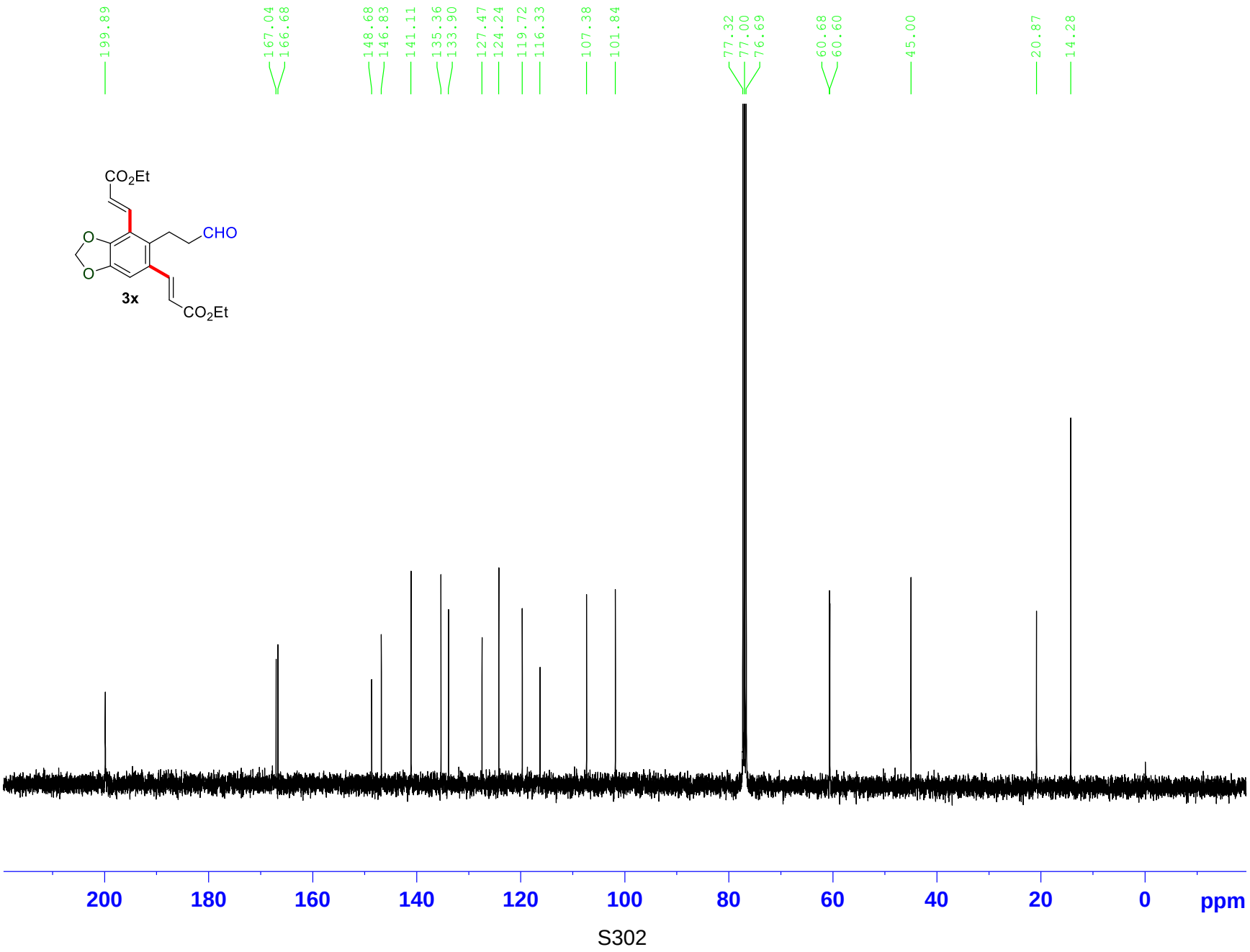
6.798
6.758
6.249
6.210
6.085
4.297
4.288
4.279
4.270
4.261
4.252
4.244
4.235
3.208
3.190
3.169
2.665
2.645
2.626
1.356
1.353
1.338
1.335
1.320
CO2Et
CHO
O
O
3x
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
1.01
1.02
1.02
1.00
1.03
2.04
4.07
2.04
2.06
6.08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166.68
148.68
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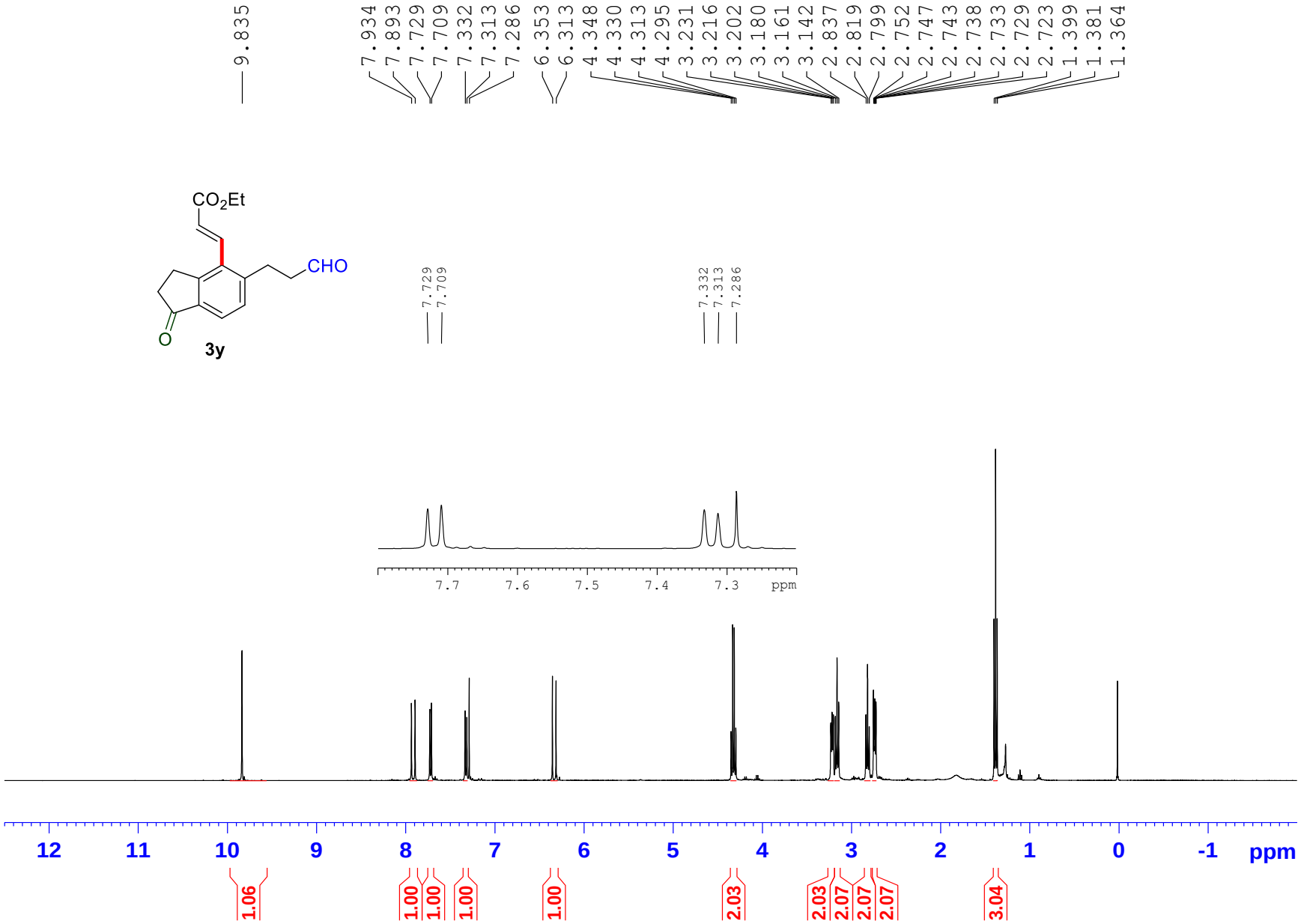
141.11
135.36
133.90
127.47
124.24
119.72
116.33
107.38
101.84
77.32
77.00
76.69
60.68
60.60
45.00
20.87
14.28
CO2Et
CHO
O
O
3x
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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7.729
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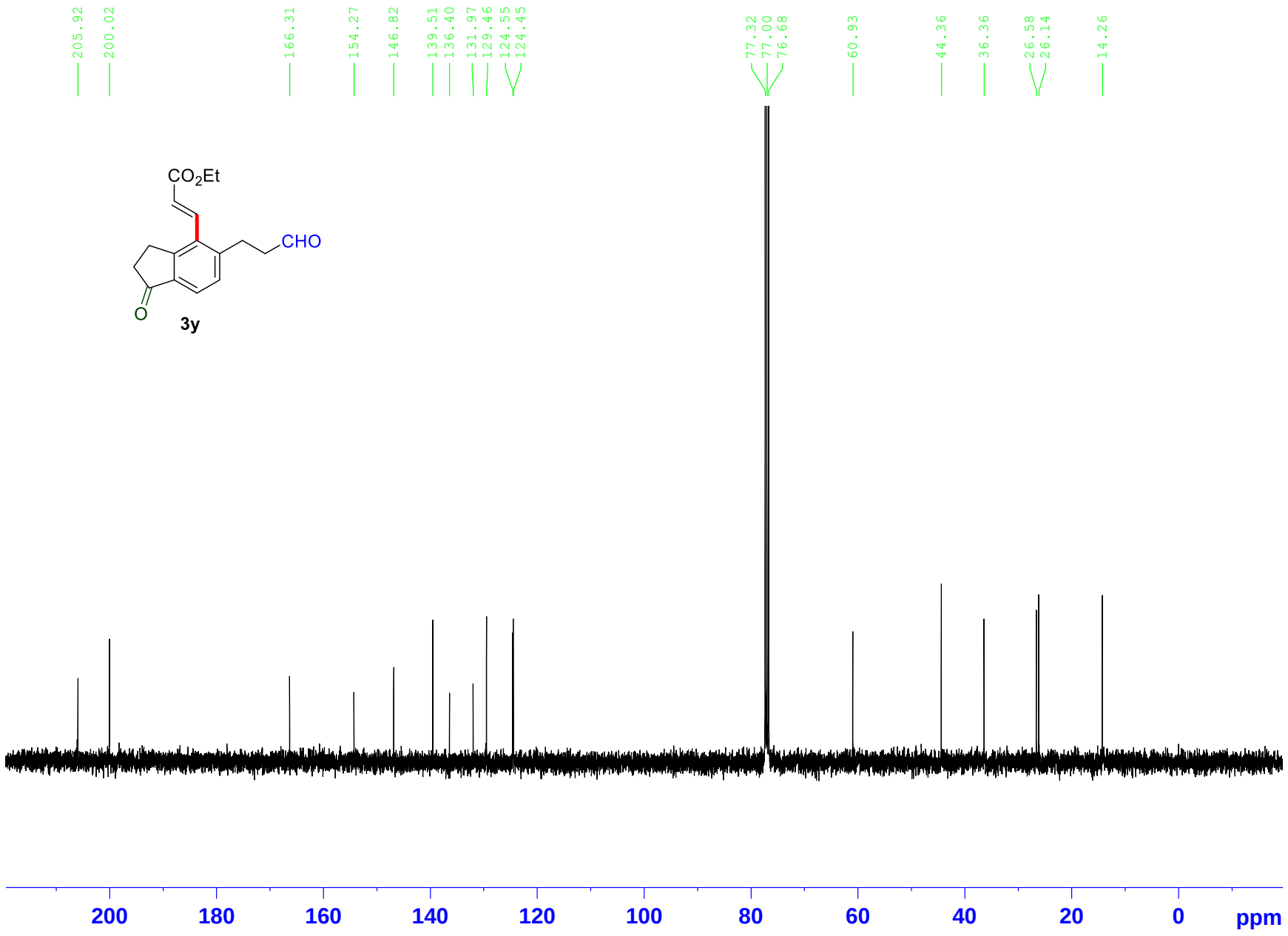
7.313
7.286
6.353
6.313
4.348
4.330
4.313
4.295
3.231
3.216
3.202
3.180
3.161
3.142
2.837
2.819
2.799
2.752
2.747
2.743
2.738
2.733
2.729
2.723
1.399
1.381
1.364
CO2Et
CHO
O
3y
7.729
7.709
7.332
7.313
7.286
7.7
7.6
7.5
7.4
7.3
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.06
1.00
1.00
1.00
1.00
2.03
2.03
2.07
2.07
2.07
3.04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200.02
166.31
154.27
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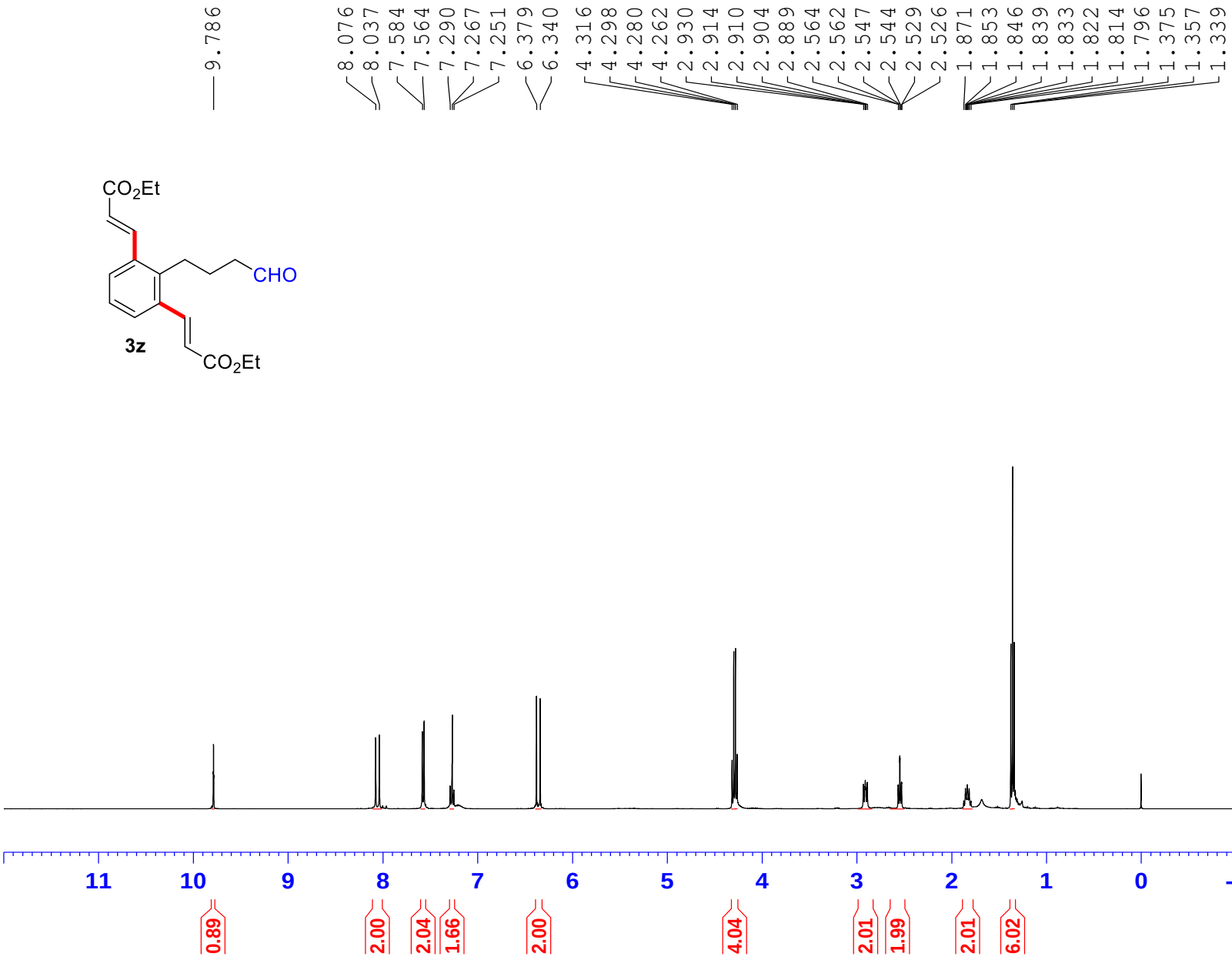
139.51
136.40
131.97
129.46
124.55
124.45
77.32
77.00
76.68
60.93
44.36
36.36
26.58
26.14
14.26
CO2Et
CHO
O
3y
200
180
160
140
120
100
80
60
40
20
0
ppm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8.037
7.584
7.564
7.290
7.267
7.251
6.379
6.340
4.316
4.298
4.280
4.262
2.930
2.914
2.910
2.904
2.889
2.564
2.562
2.547
2.544
2.529
2.526
1.871
1.853
1.846
1.839
1.833
1.822
1.814
1.796
1.375
1.357
1.339
CO2Et
CHO
3z
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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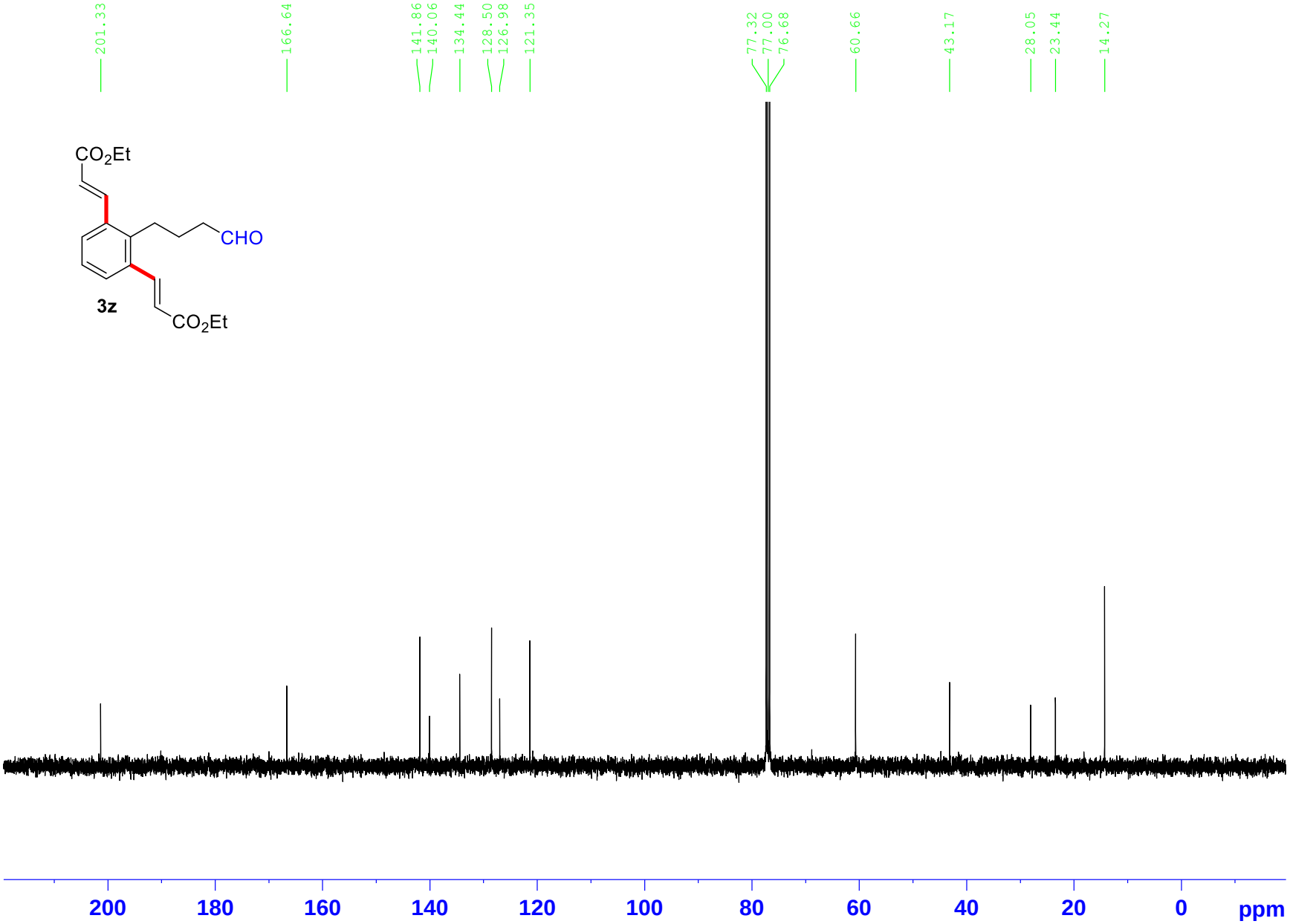
1.66
2.00
4.04
2.01
1.99
2.01
6.02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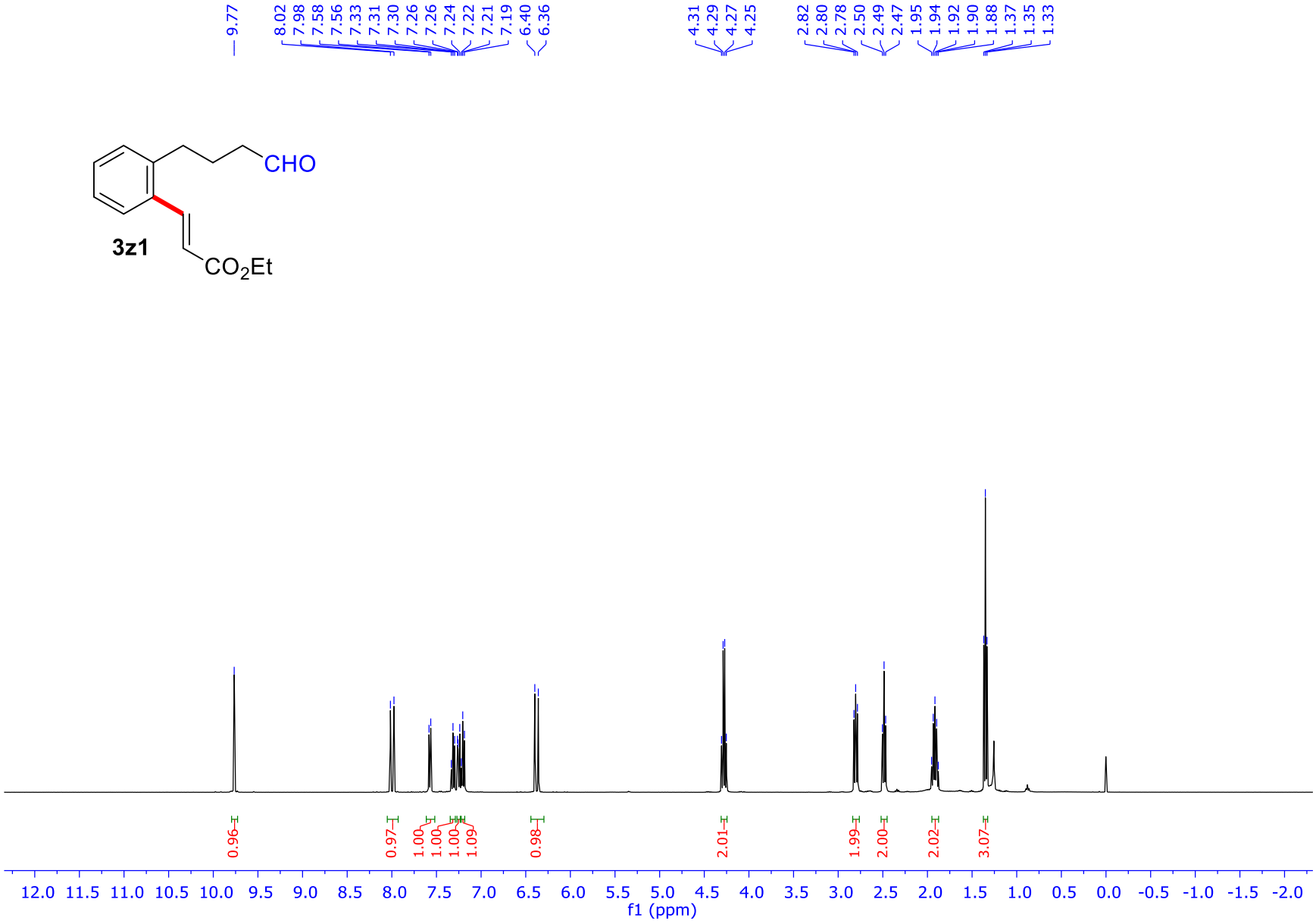
141.86
140.06
134.44
128.50
126.98
121.35
77.32
77.00
76.68
60.66
43.17
28.05
23.44
14.27
CO2Et
CHO
3z
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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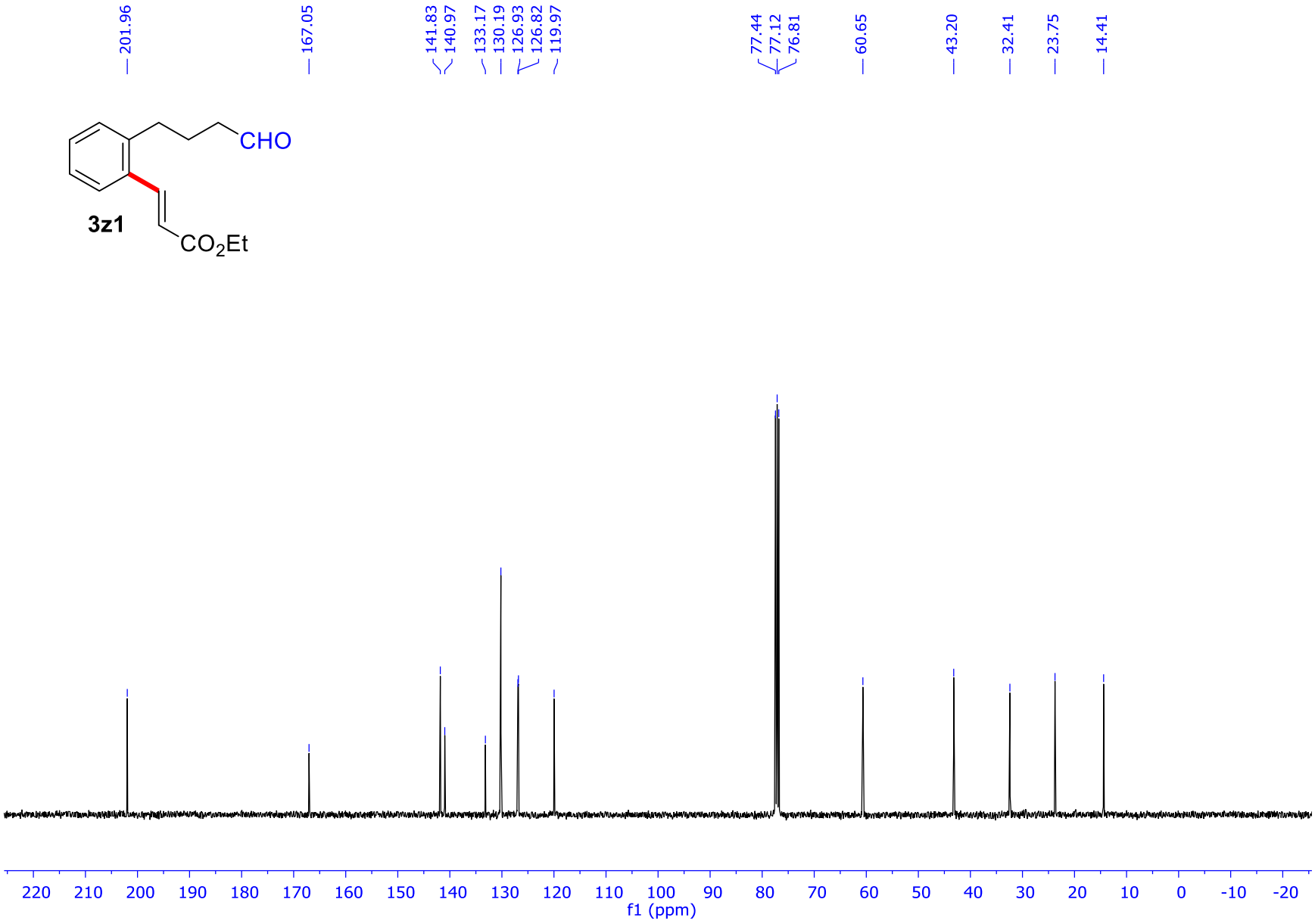
8.02
7.98
7.58
7.56
7.33
7.31
7.30
7.26
7.26
7.24
7.22
7.21
7.19
6.40
6.36
4.31
4.29
4.27
4.25
2.82
2.80
2.78
2.50
2.49
2.47
1.95
1.94
1.92
1.90
1.88
1.37
1.35
1.33
CHO
3z1
CO2Et
0.96
0.97
1.00
1.00
1.09
0.98
2.01
1.99
2.00
2.02
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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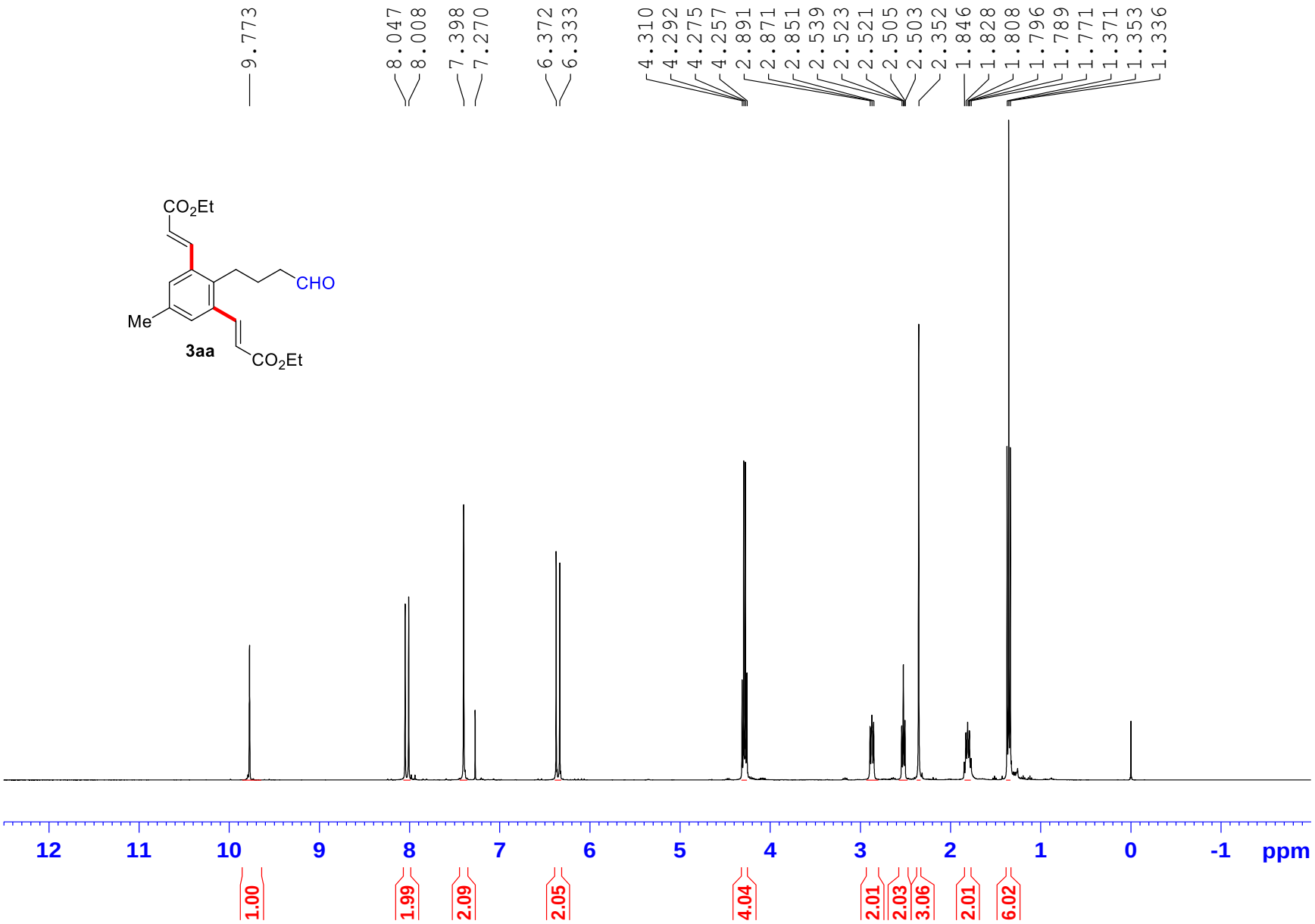
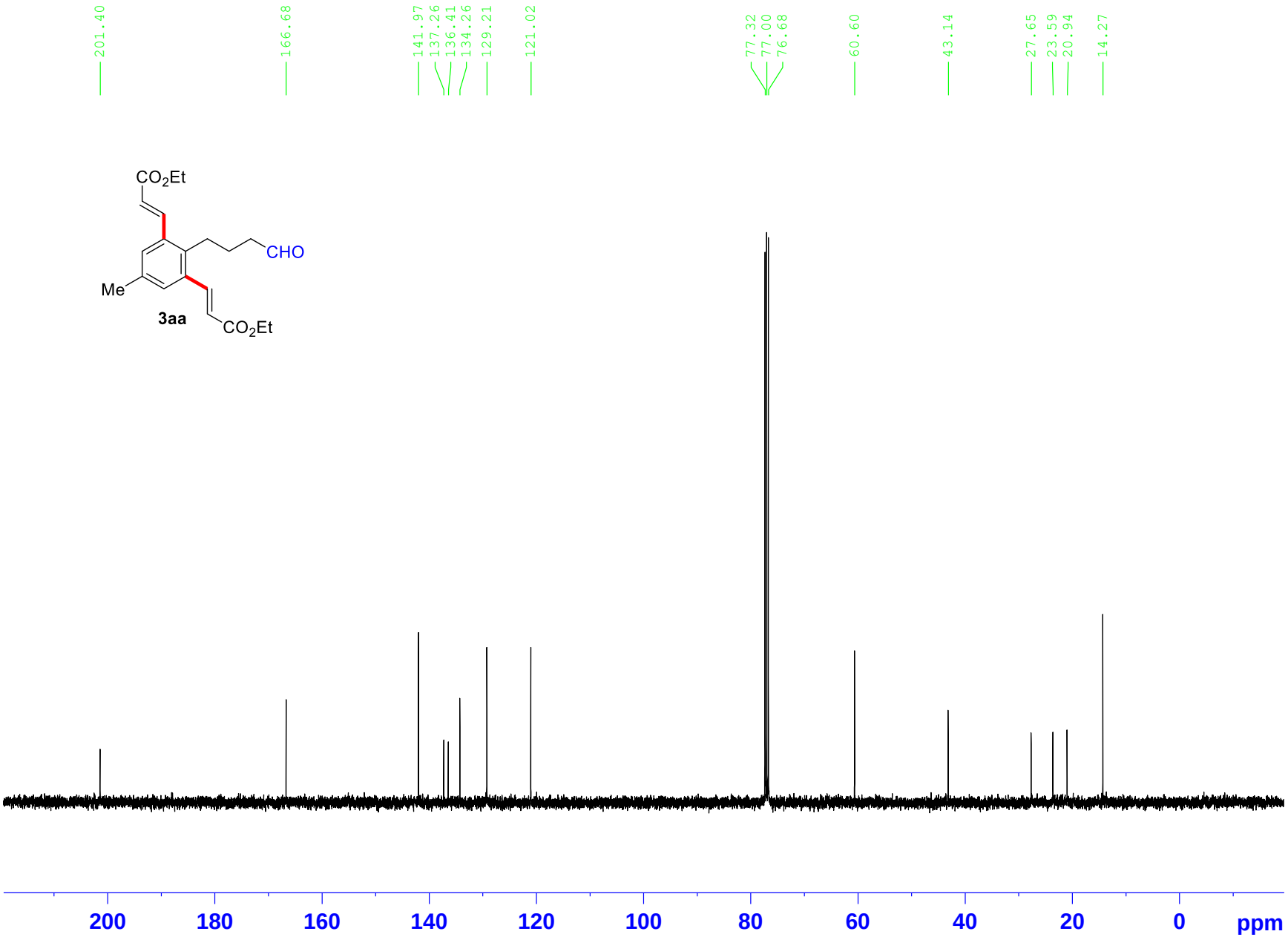
167.05
141.83
140.97
133.17
130.19
126.93
126.82
119.97
77.44
77.12
76.81
60.65
43.20
32.41
23.75
14.41
CHO
3z1
CO2Et
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


9.773
8.047
8.008
7.398
7.270
6.372
6.333
4.310
4.292
4.275
4.257
2.891
2.871
2.851
2.539
2.523
2.521
2.505
2.503
2.352
1.846
1.828
1.808
1.796
1.789
1.771
1.371
1.353
1.336
CO2Et
CHO
Me
3aa
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.99
2.09
2.05
4.04
2.01
2.03
3.06
2.01
6.02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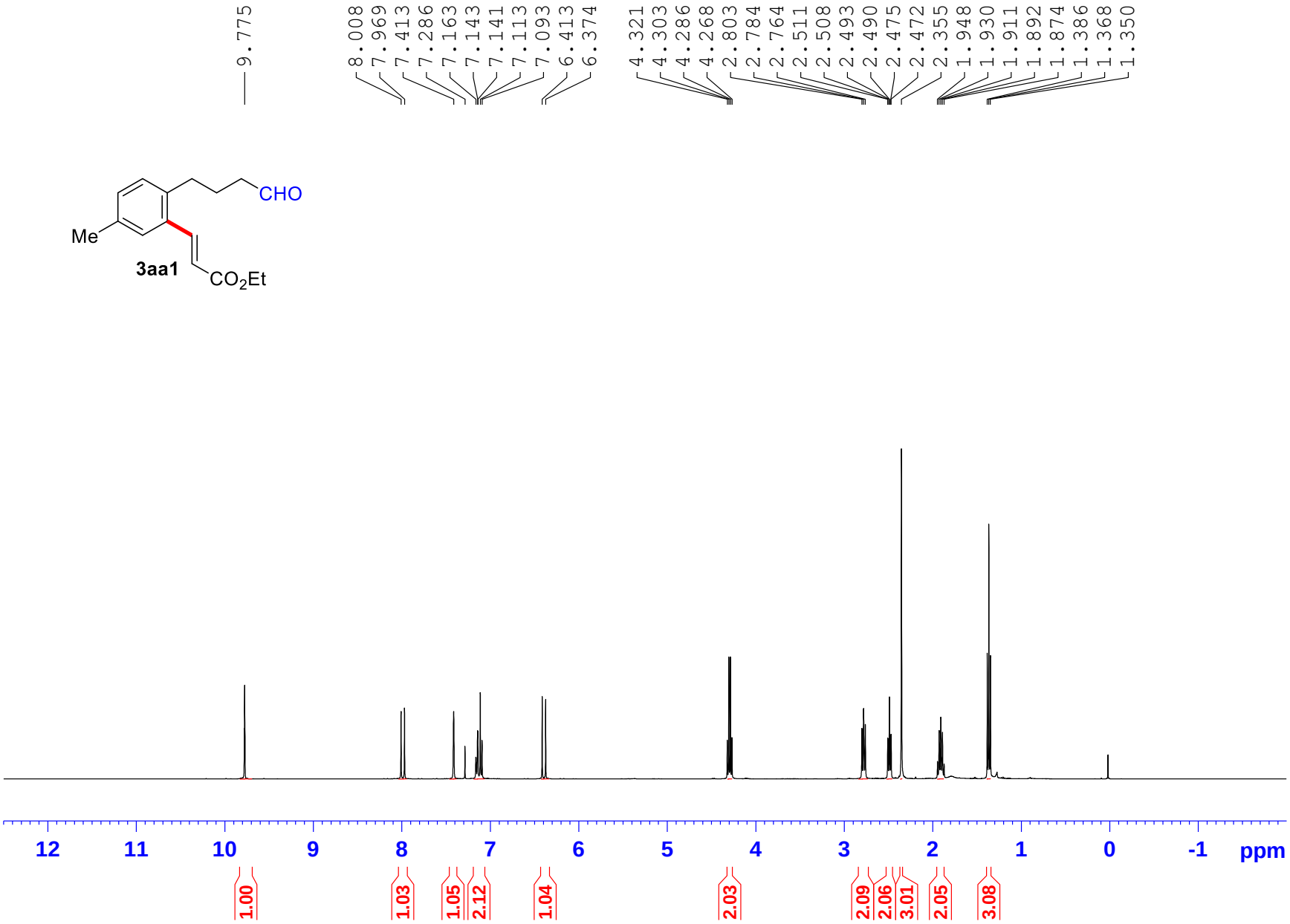
141.97
137.26
136.41
134.26
129.21
121.02
77.32
77.00
76.68
60.60
43.14
27.65
23.59
20.94
14.27
CO2Et
CHO
Me
CO2Et
3aa
200
180
160
140
120
100
80
60
40
20
0
ppm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7.969
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7.143
7.141
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7.093
6.413
6.374
4.321
4.303
4.286
4.268
2.803
2.784
2.764
2.511
2.508
2.493
2.490
2.475
2.472
2.355
1.948
1.930
1.911
1.892
1.874
1.386
1.368
1.350
CHO
Me
3aa1
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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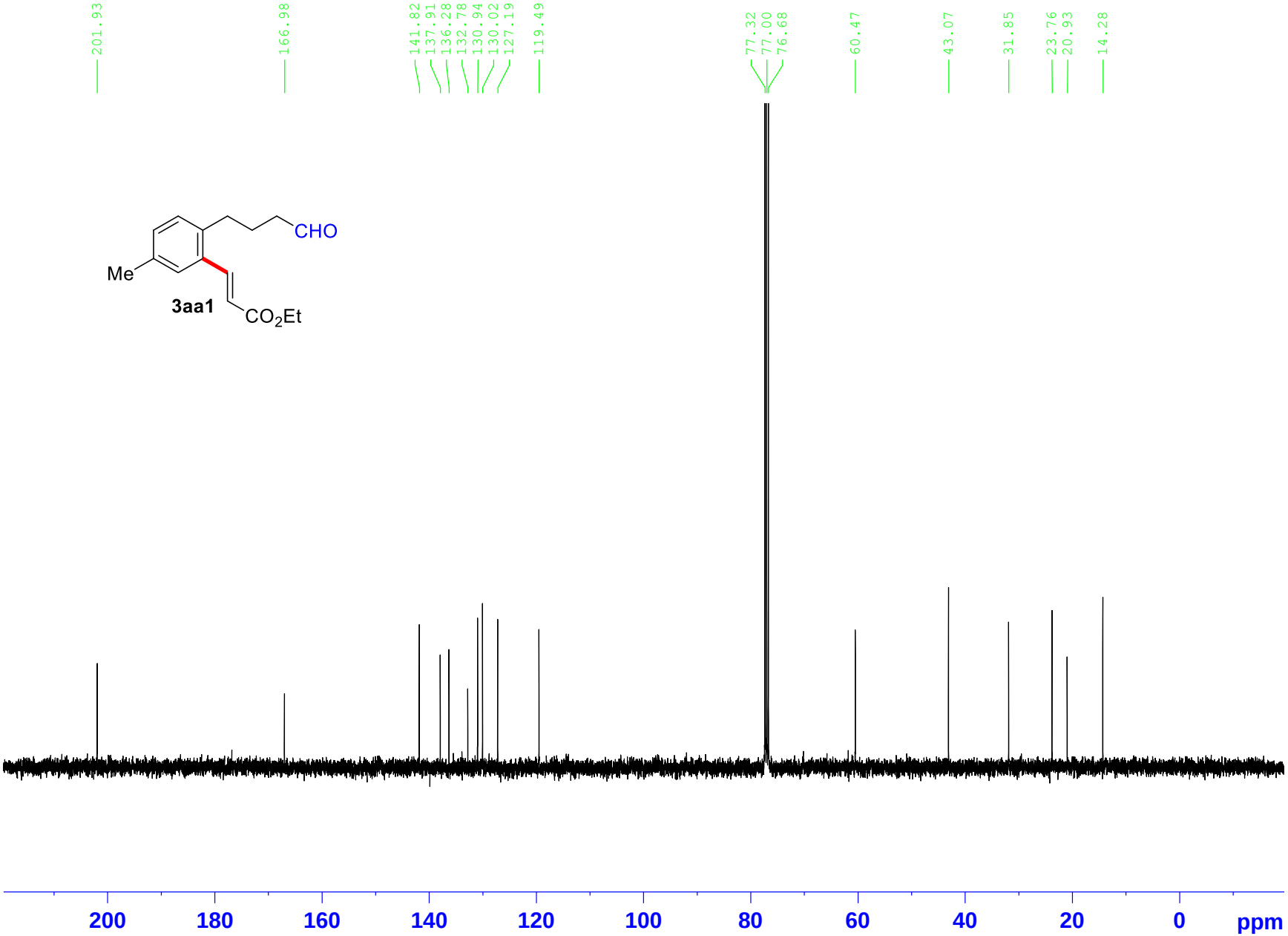
1.03
1.05
2.12
1.04
2.03
2.09
2.06
3.01
2.05
3.08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166.98
141.82
137.91
136.28
132.78
130.94
130.02
127.19
119.49
77.32
77.00
76.68
60.47
43.07
31.85
23.76
20.93
14.28
CHO
Me
3aa1
CO2Et
200
180
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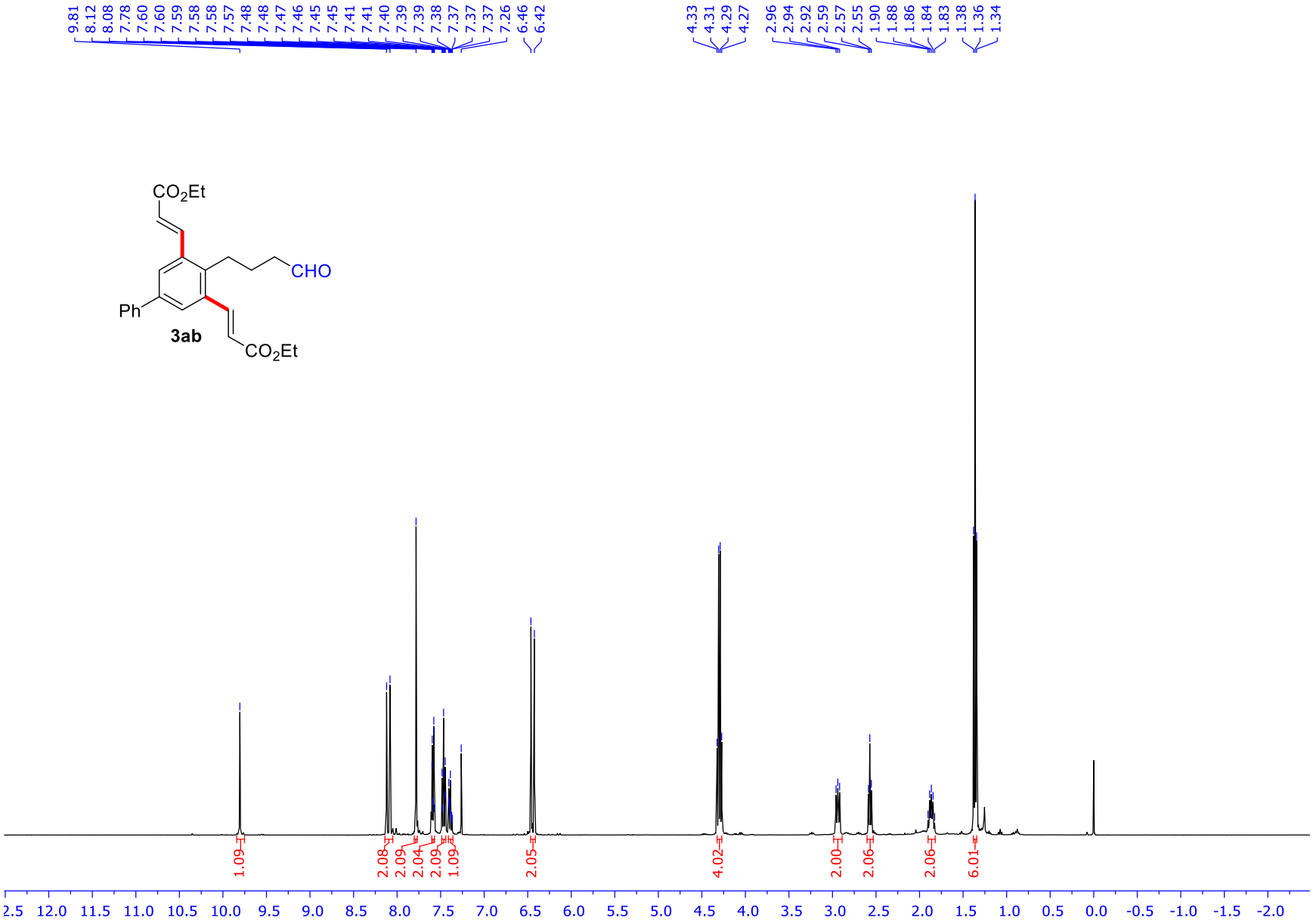
120
100
80
60
40
20
0
ppm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8.08
7.78
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7.58
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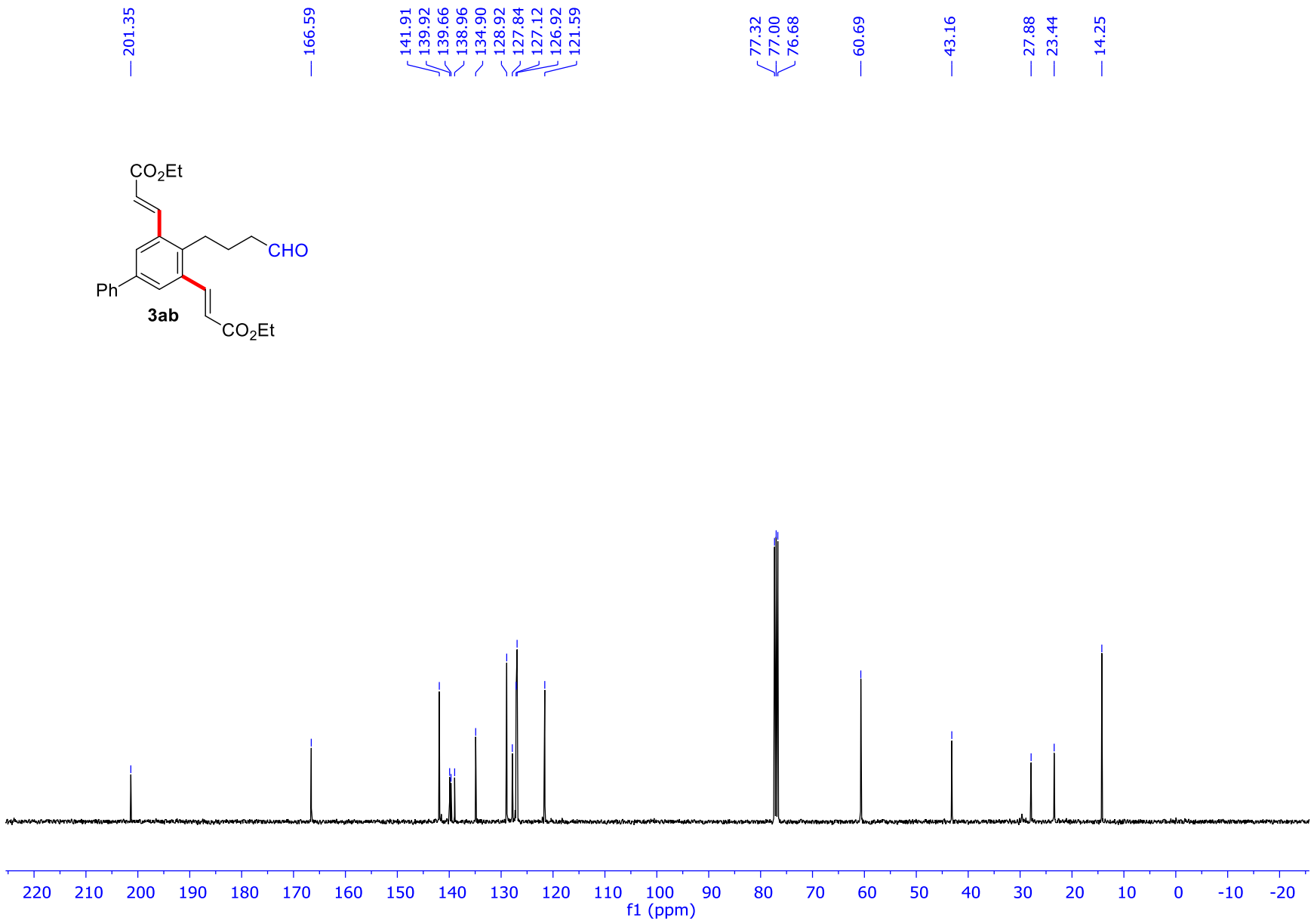
7.57
7.48
7.48
7.47
7.46
7.45
7.45
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.26
6.46
6.42
4.33
4.31
4.29
4.27
2.96
2.94
2.92
2.59
2.57
2.55
1.90
1.88
1.86
1.84
1.83
1.38
1.36
1.34
CO2Et
CHO
Ph
3ab
CO2Et
1.09
2.08
2.09
2.04
2.09
1.09
2.05
4.02
2.00
2.06
2.06
6.01
2.5 12.0 11.5 11.0 10.5 10.0 9.5 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 -1.0 -1.5 -2.0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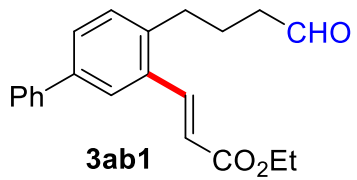
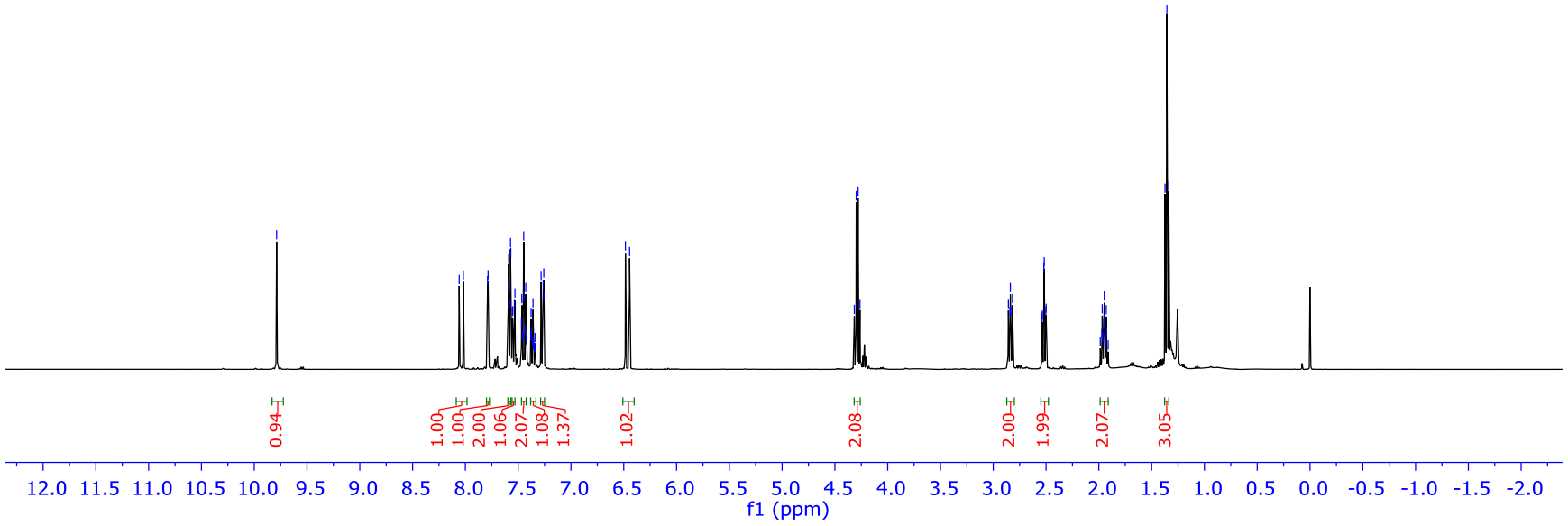
139.92
139.66
138.96
134.90
128.92
127.84
127.12
126.92
121.59
77.32
77.00
76.68
60.69
43.16
27.88
23.44
14.25
CO2Et
CHO
Ph
3ab
CO2Et
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


9.79
8.06
8.02
7.79
7.78
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.28
7.26
7.26
7.26
6.48
6.44
4.32
4.30
4.28
4.26
2.86
2.84
2.84
2.83
2.82
2.54
2.54
2.52
2.52
2.50
2.50
1.99
1.97
1.97
1.96
1.95
1.95
1.95
1.94
1.93
1.93
1.93
1.91
1.37
1.36
1.34


CHO
Ph
CO2Et

3ab1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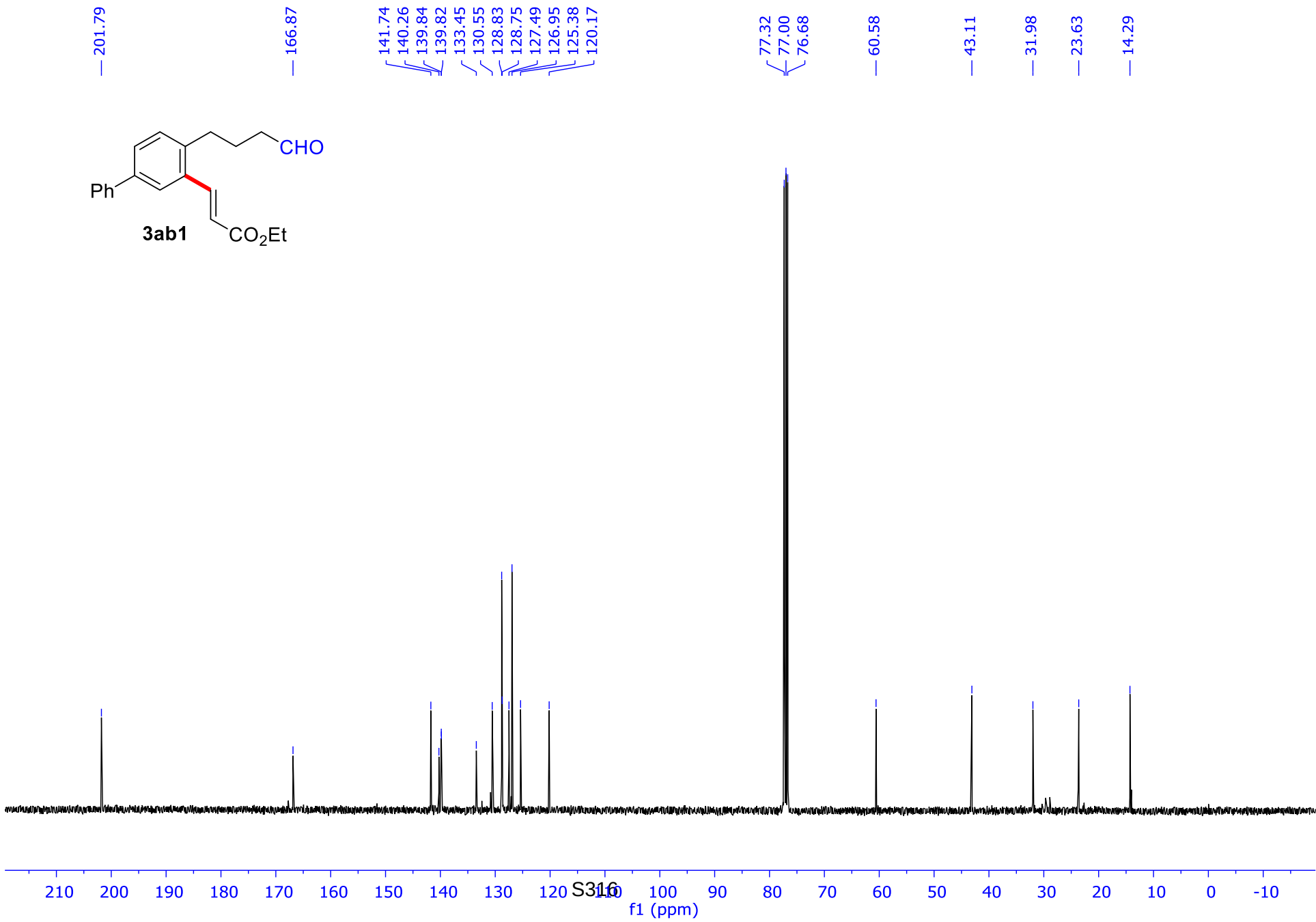
1.00
1.00
2.00
1.06
2.07
1.08
1.37
1.02
2.08
2.00
1.99
2.07
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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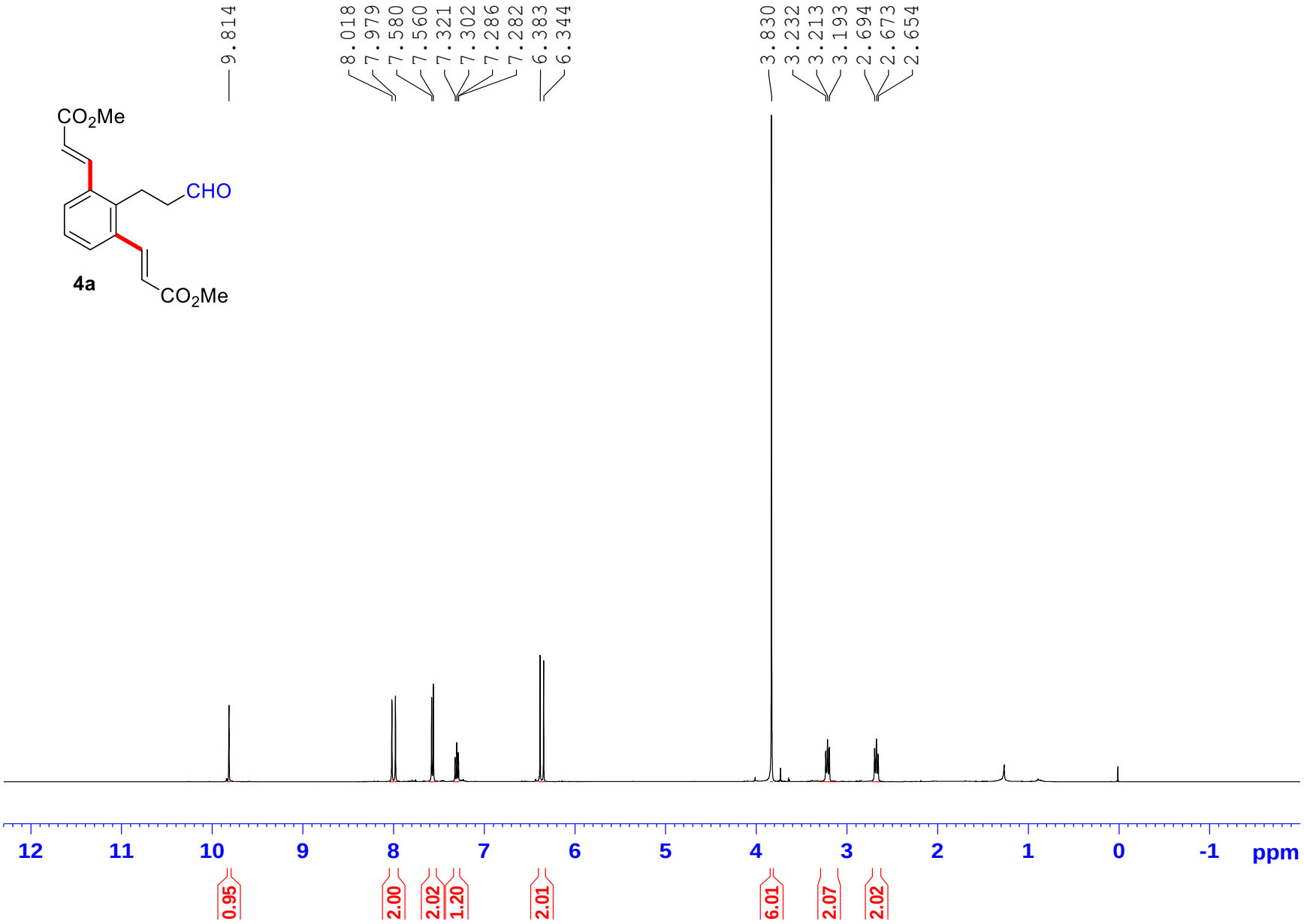
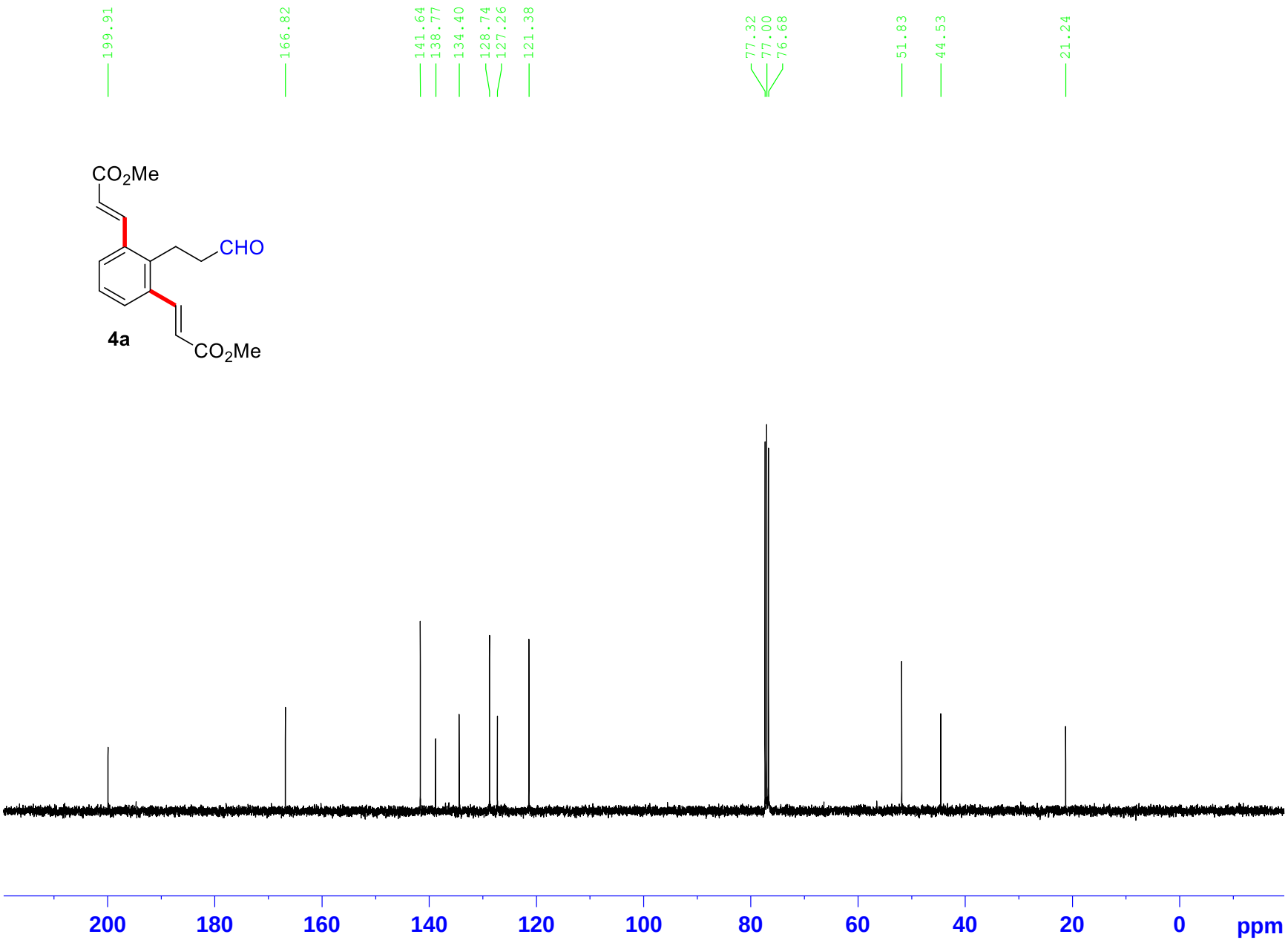
166.87
141.74
140.26
139.84
139.82
133.45
130.55
128.83
128.75
127.49
126.95
125.38
120.17
77.32
77.00
76.68
60.58
43.11
31.98
23.63
14.29
CHO
Ph
CO2Et
3ab1
f1 (ppm)


9.814
8.018
7.979
7.580
7.560
7.321
7.302
7.286
7.282
6.383
6.344
3.830
3.232
3.213
3.193
2.694
2.673
2.654
CO2Me
CHO
CO2Me
4a
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
2.00
2.02
1.20
2.01
6.01
2.07
2.02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166.82
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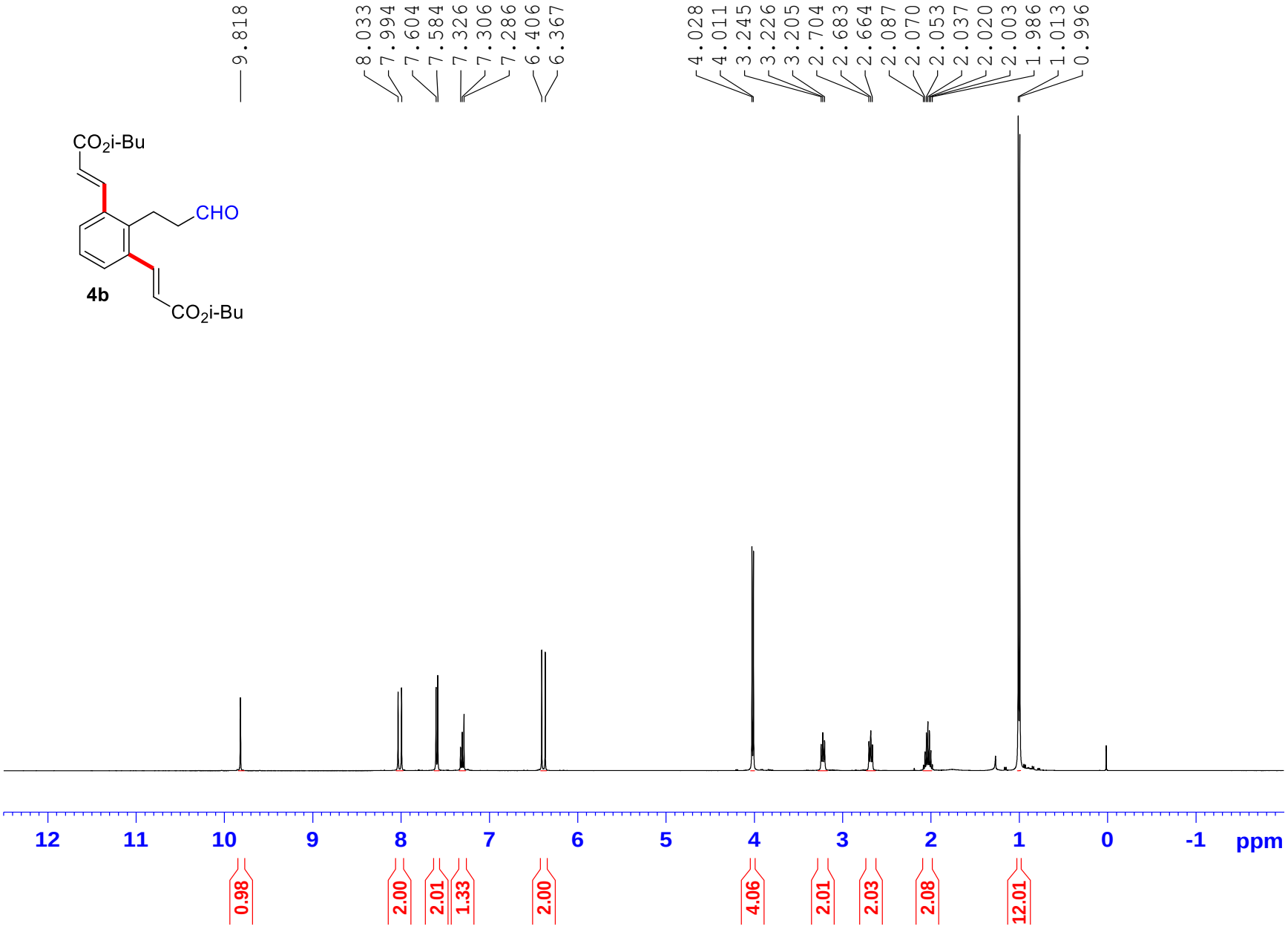
138.77
134.40
128.74
127.26
121.38
77.32
77.00
76.68
51.83
44.53
21.24
CO2Me
CHO
CO2Me
4a
200
180
160
140
120
100
80
60
40
20
0
ppm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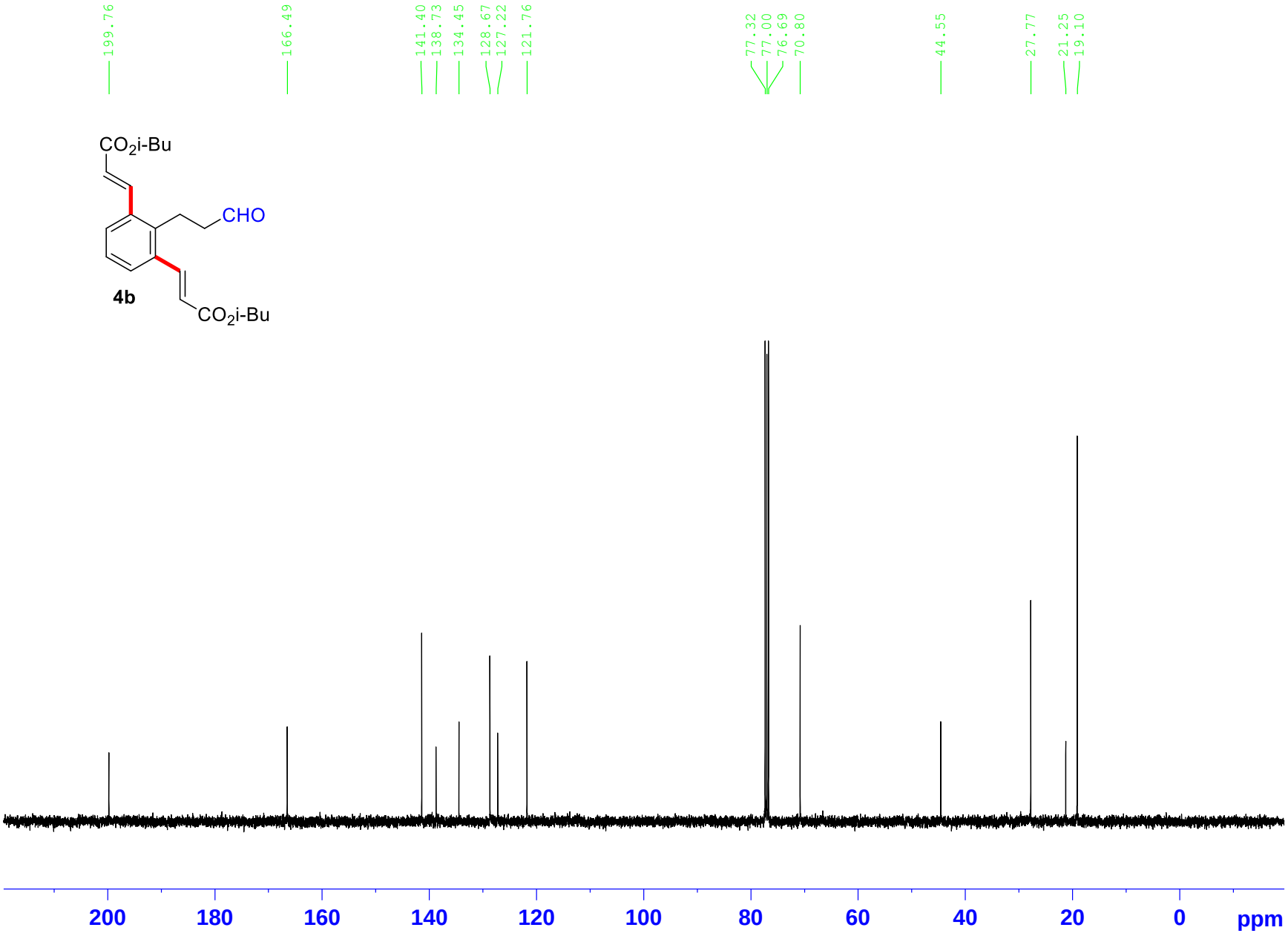
8.033
7.994
7.604
7.584
7.326
7.306
7.286
6.406
6.367
4.028
4.011
3.245
3.226
3.205
2.704
2.683
2.664
2.087
2.070
2.053
2.037
2.020
2.003
1.986
1.013
0.996
CO2i-Bu
CHO
CO2i-Bu
4b
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
2.00
2.01
1.33
2.00
4.06
2.01
2.03
2.08
12.01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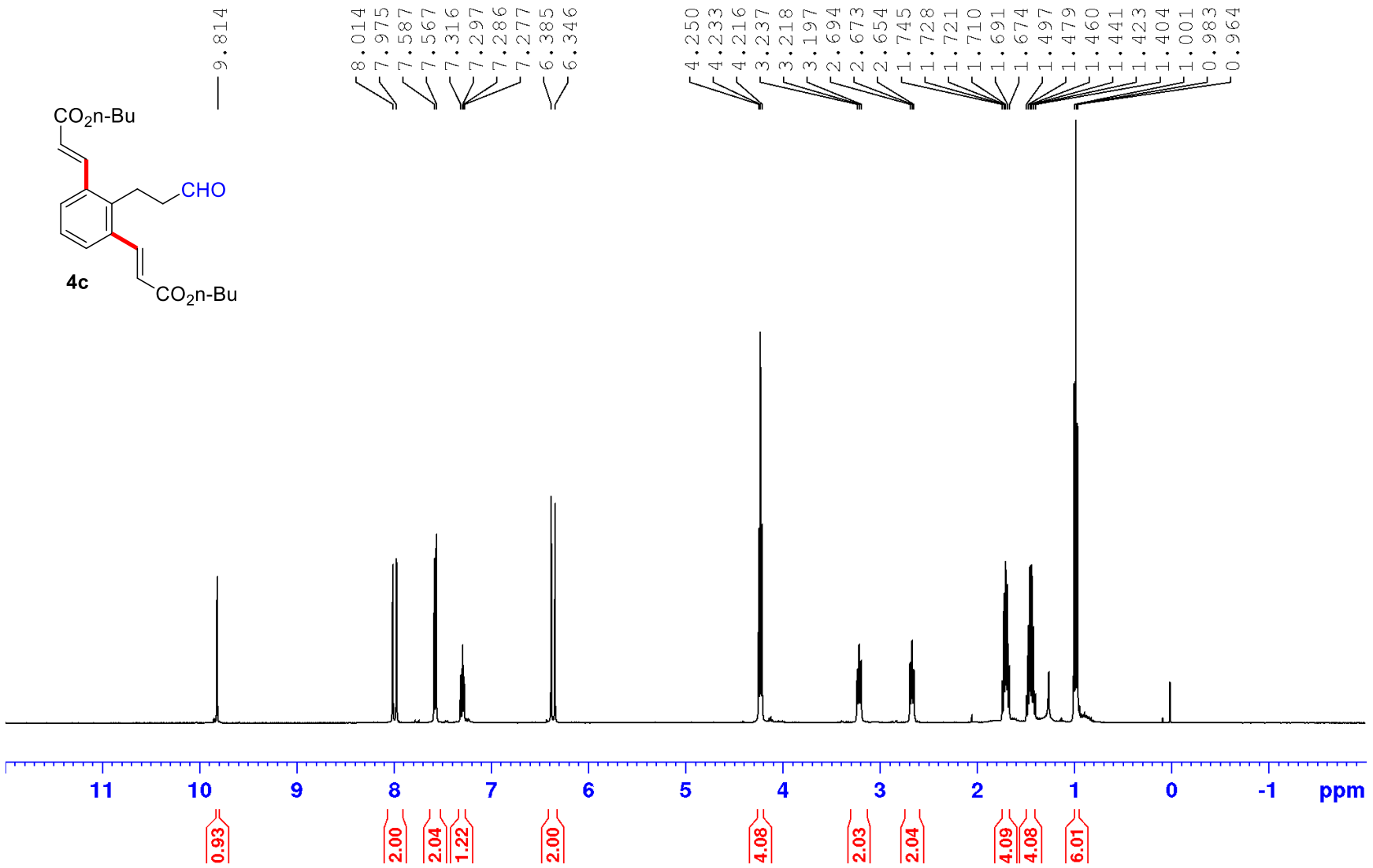
128.67
127.22
121.76
77.32
77.00
76.69
70.80
44.55
27.77
21.25
19.10
CO2i-Bu
CHO
4b
CO2i-Bu
200
180
160
140
120
100
80
60
40
20
0
ppm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8.014
7.975
7.587
7.567
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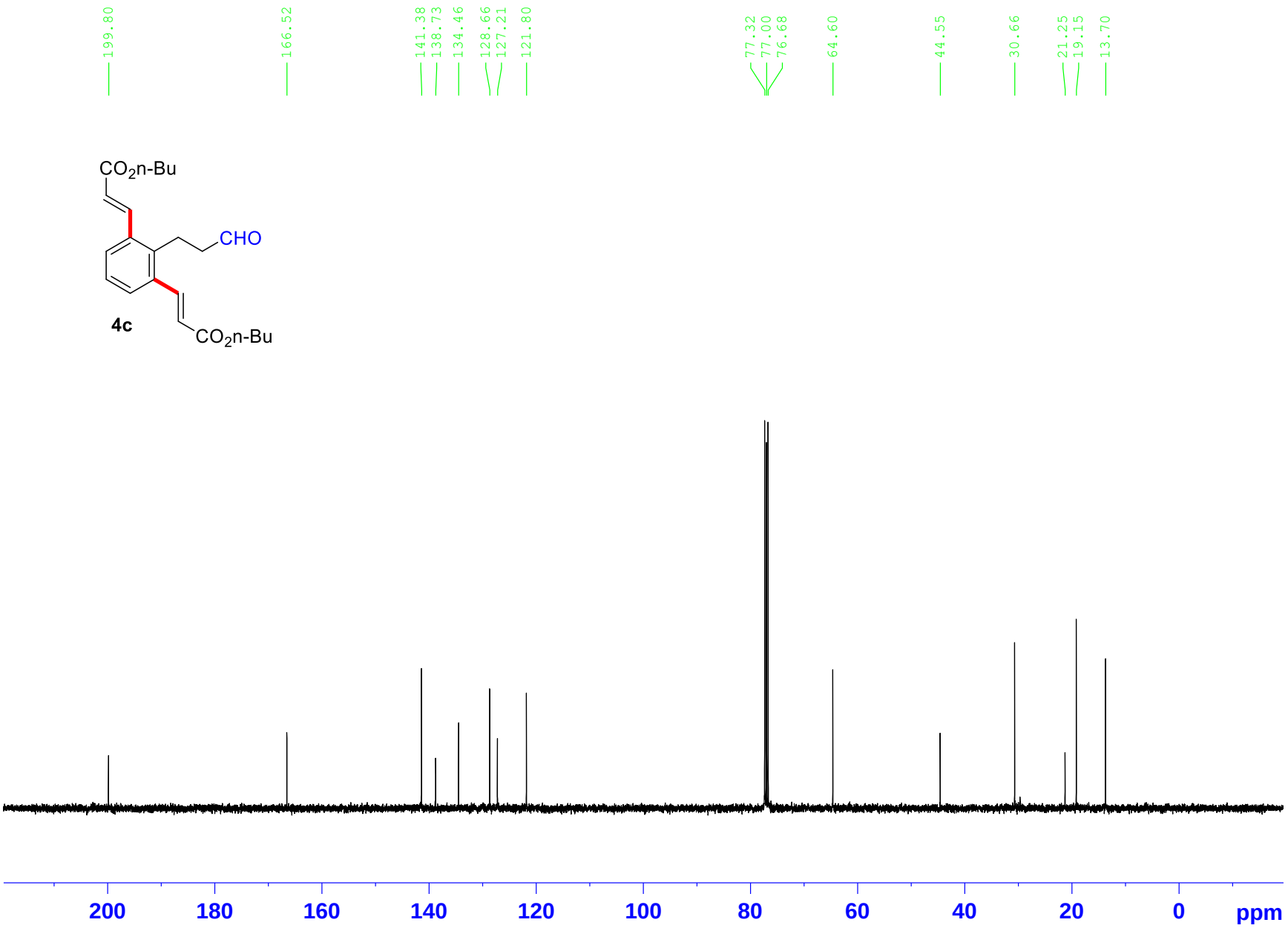
7.297
7.286
7.277
6.385
6.346
4.250
4.233
4.216
3.237
3.218
3.197
2.694
2.673
2.654
1.745
1.728
1.721
1.710
1.691
1.674
1.497
1.479
1.460
1.441
1.423
1.404
1.001
0.983
0.964
CO2n-Bu
CHO
CO2n-Bu
4c
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.93
2.00
2.04
1.22
2.00
4.08
2.03
2.04
4.09
4.08
6.01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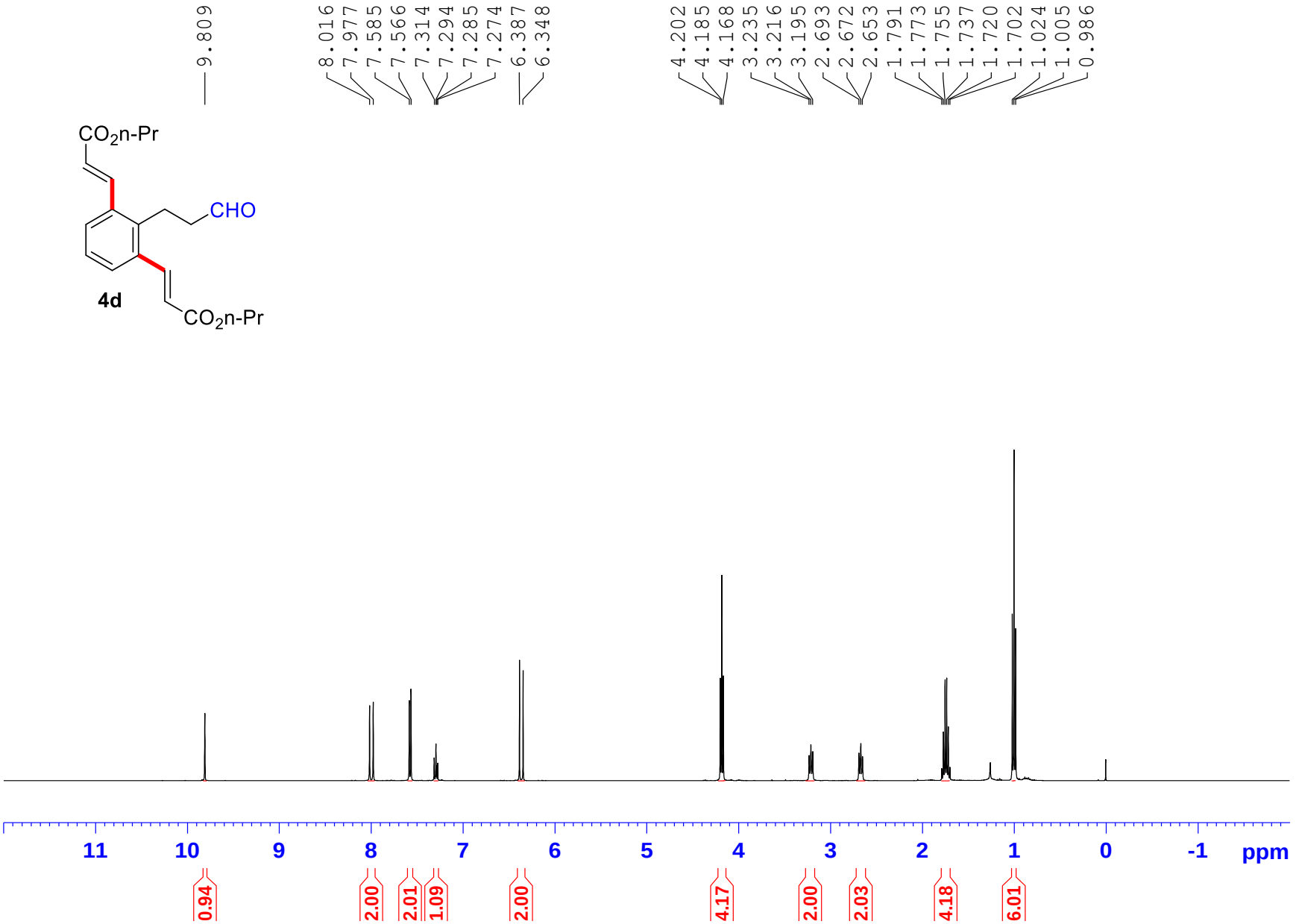
134.46
128.66
127.21
121.80
77.32
77.00
76.68
64.60
44.55
30.66
21.25
19.15
13.70
CO2n-Bu
CHO
CO2n-Bu
4c
200
180
160
140
120
100
80
60
40
20
0
ppm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7.566
7.314
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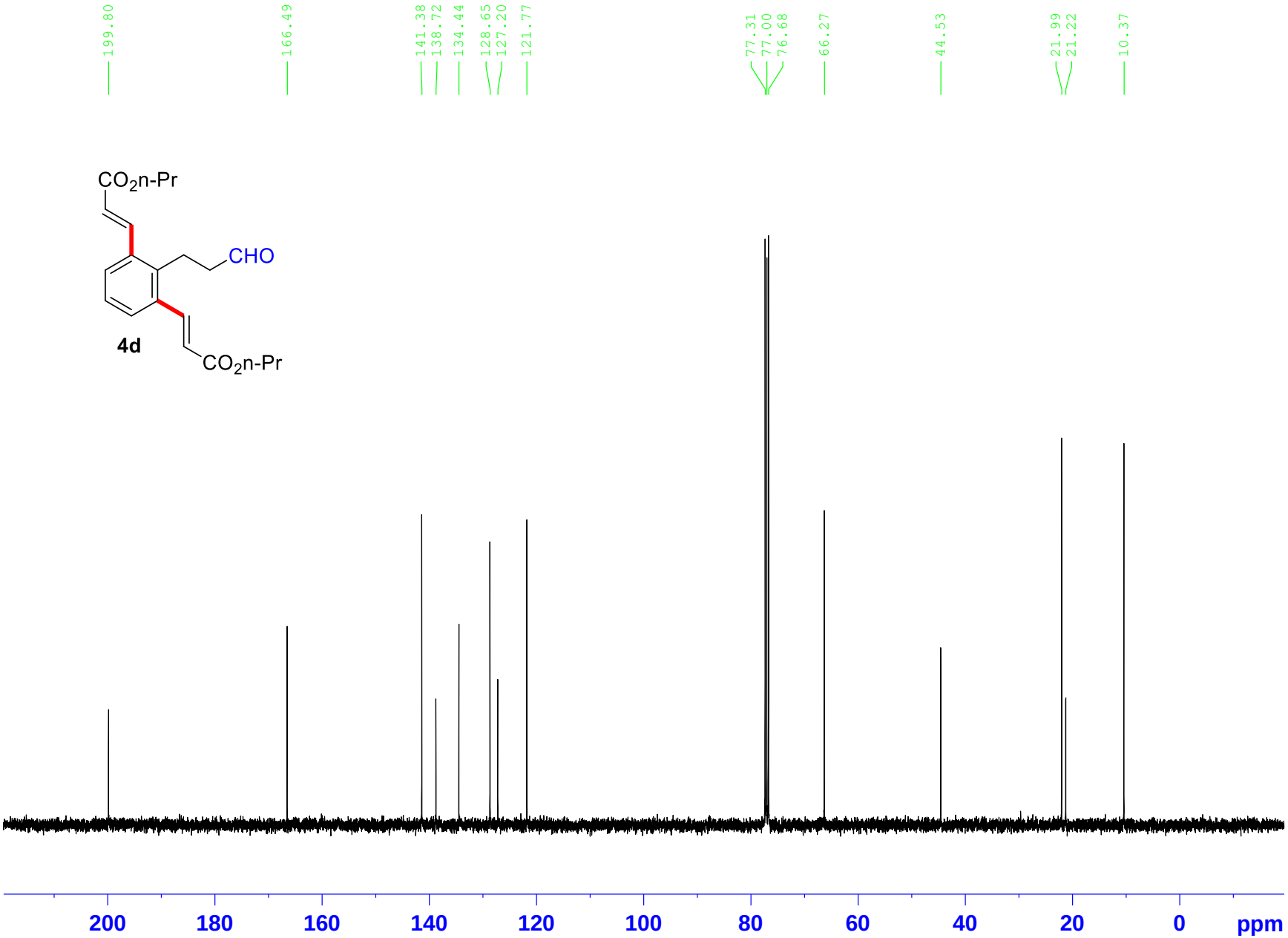
7.285
7.274
6.387
6.348
4.202
4.185
4.168
3.235
3.216
3.195
2.693
2.672
2.653
1.791
1.773
1.755
1.737
1.720
1.702
1.024
1.005
0.986
CO2n-Pr
CHO
CO2n-Pr
4d
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.94
2.00
2.01
1.09
2.00
4.17
2.00
2.03
4.18
6.01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138.72
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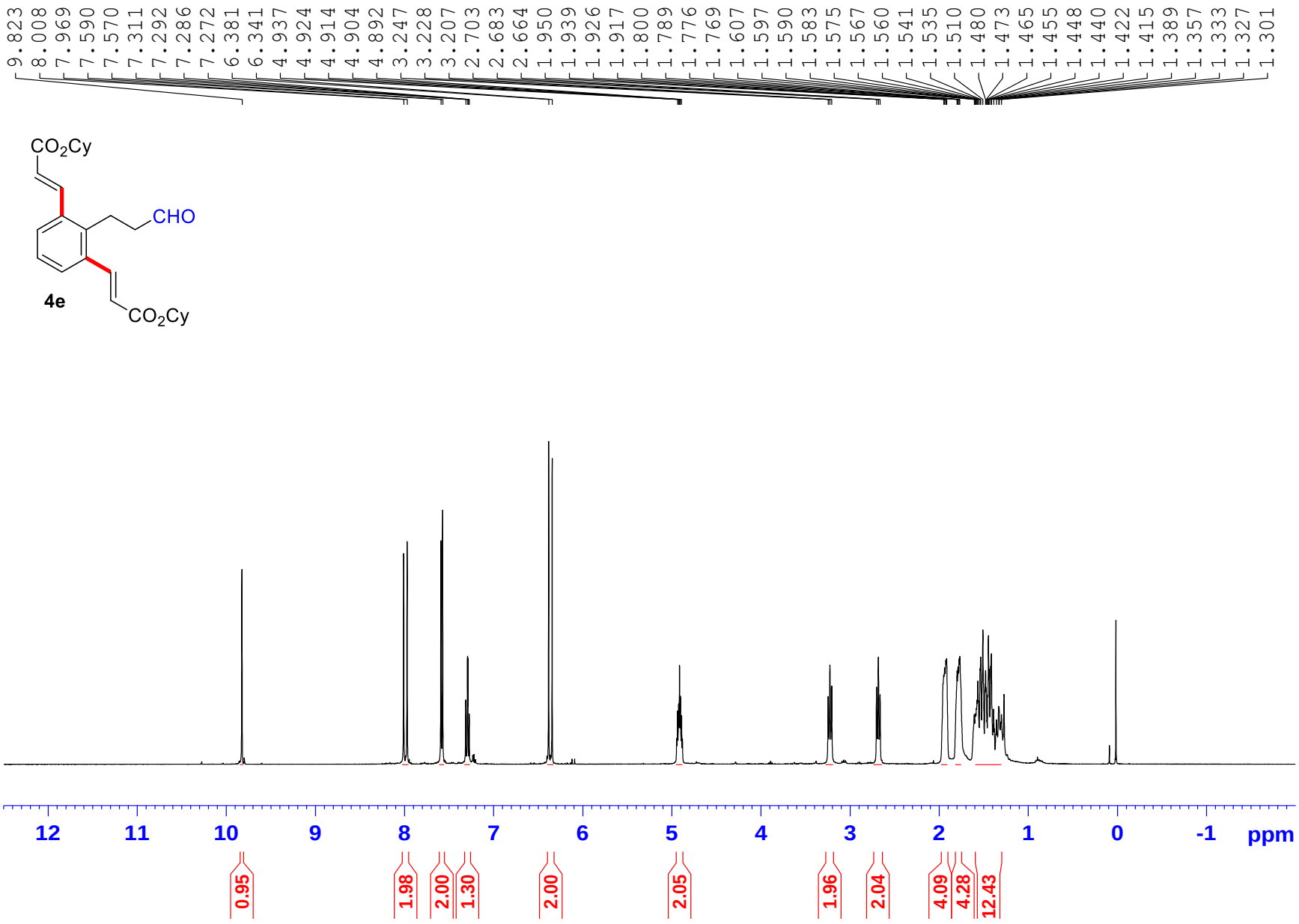
128.65
127.20
121.77
77.31
77.00
76.68
66.27
44.53
21.99
21.22
10.37
CO2n-Pr
CHO
CO2n-Pr
4d
200
180
160
140
120
100
80
60
40
20
0
ppm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7.570
7.311
7.292
7.286
7.272
6.381
6.341
4.937
4.924
4.914
4.904
4.892
3.247
3.228
3.207
2.703
2.683
2.664
1.950
1.939
1.926
1.917
1.800
1.789
1.776
1.769
1.607
1.597
1.590
1.583
1.575
1.567
1.560
1.541
1.535
1.510
1.480
1.473
1.465
1.455
1.448
1.440
1.422
1.415
1.389
1.357
1.333
1.327
1.301
CO2Cy
CHO
CO2Cy
4e
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.95
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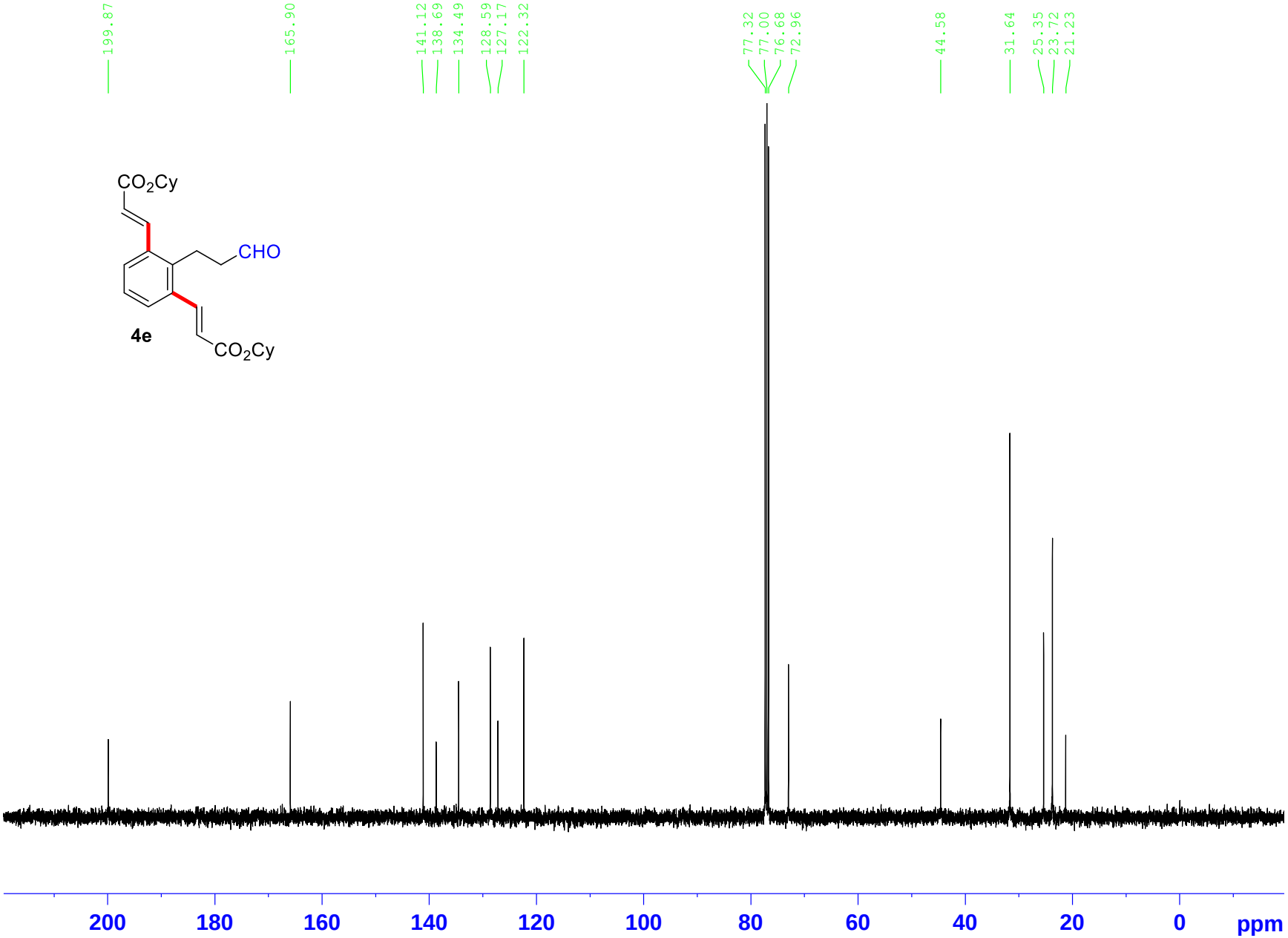
2.00
1.30
2.00
2.05
1.96
2.04
4.09
4.28
12.43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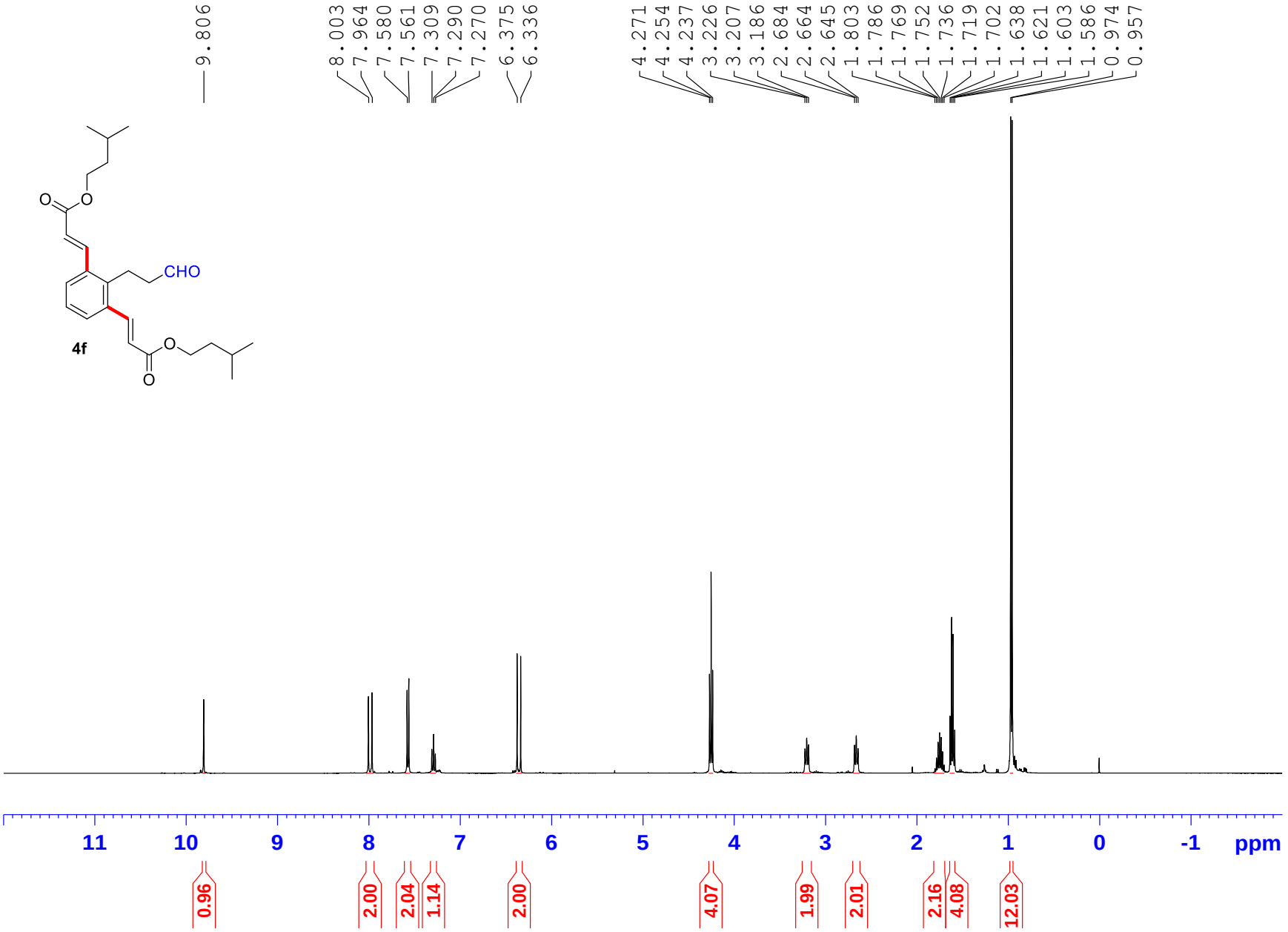
128.59
127.17
122.32
77.32
77.00
76.68
72.96
44.58
31.64
25.35
23.72
21.23
CO2Cy
CHO
4e
CO2Cy
200
180
160
140
120
100
80
60
40
20
0
ppm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6.375
6.336
4.271
4.254
4.237
3.226
3.207
3.186
2.684
2.664
2.645
1.803
1.786
1.769
1.752
1.736
1.719
1.702
1.638
1.621
1.603
1.586
0.974
0.957
CHO
4f
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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2.04
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2.00
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1.99
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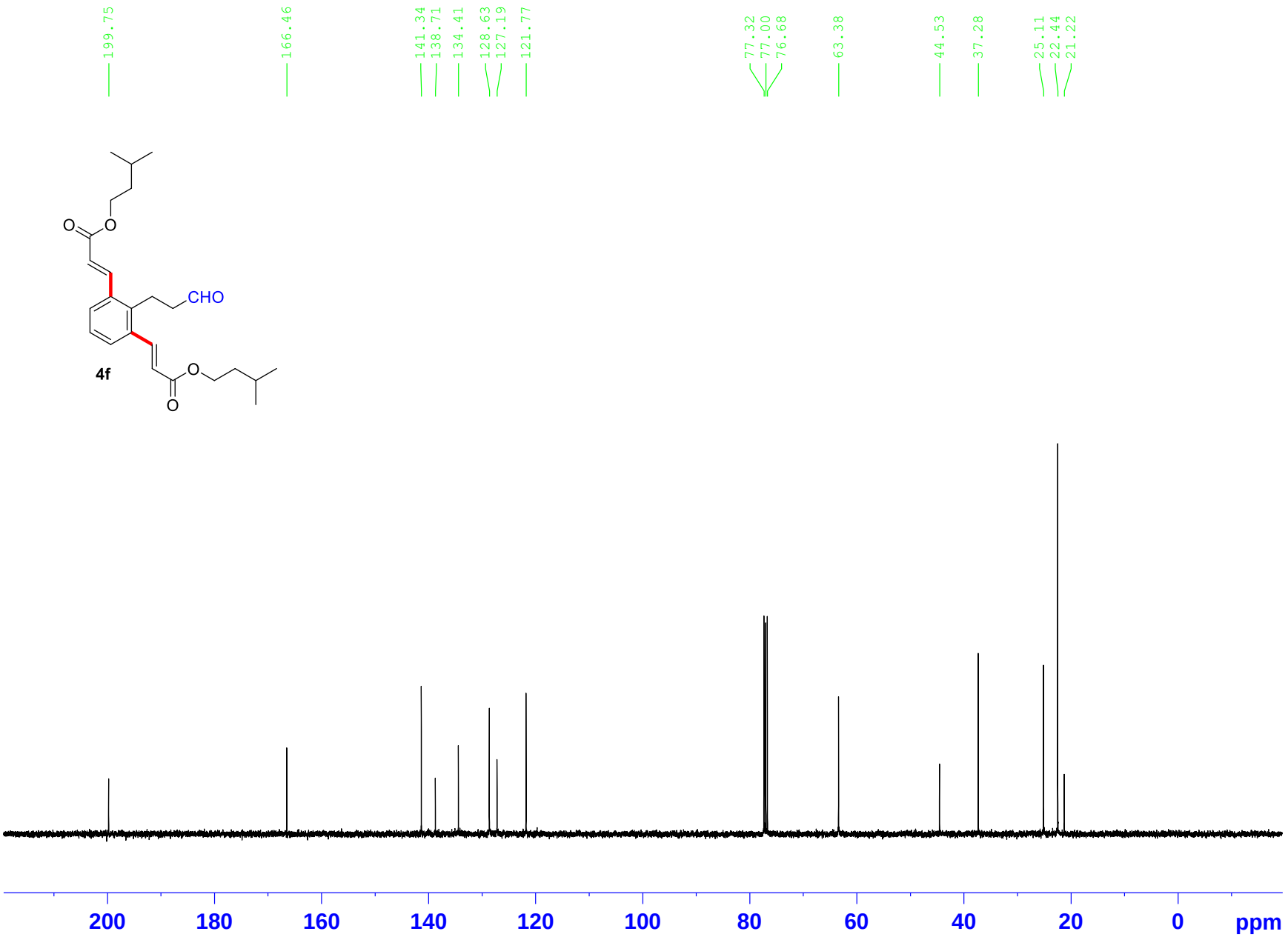
2.16
4.08
12.03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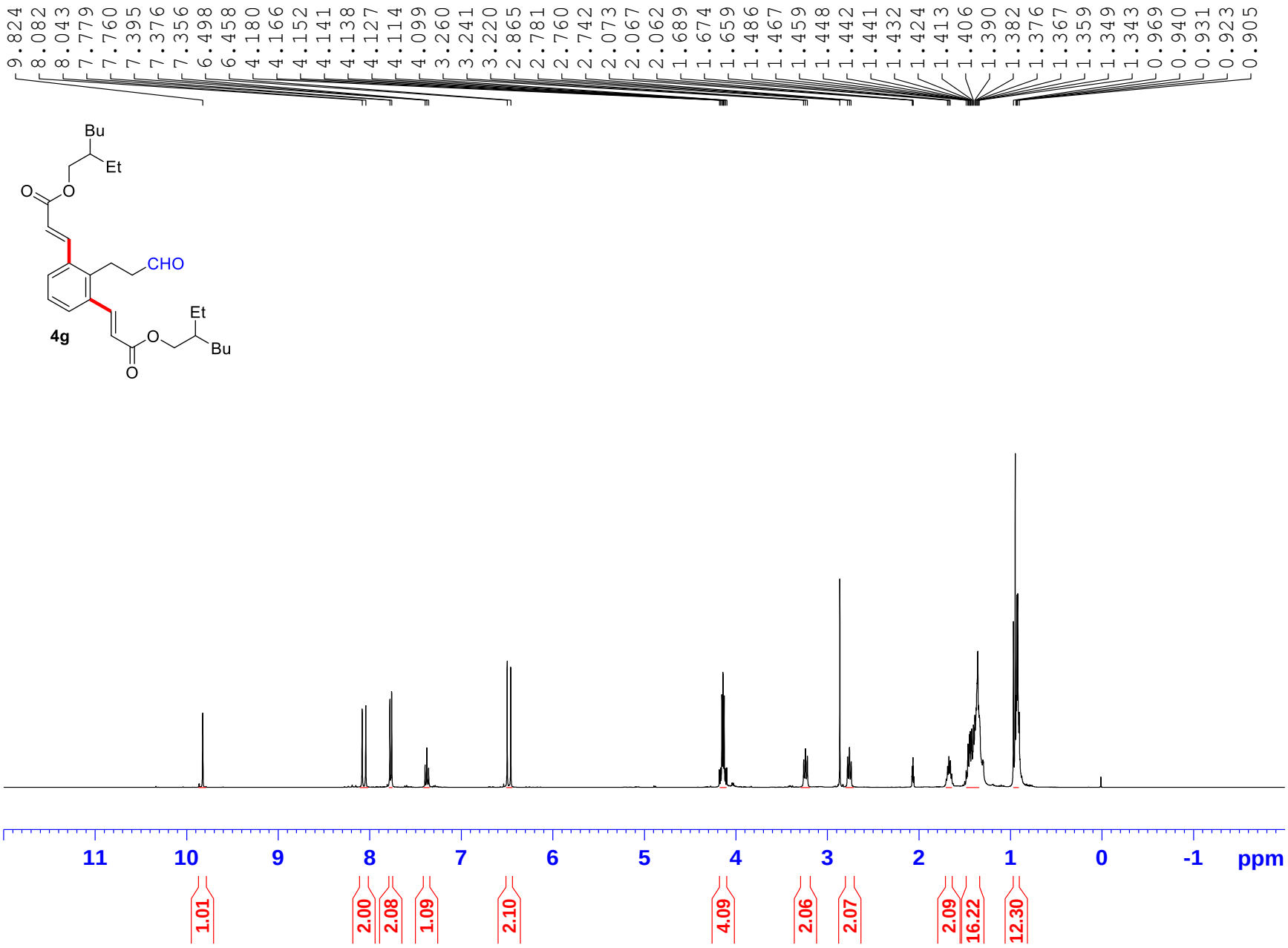
128.63
127.19
121.77
77.32
77.00
76.68
63.38
44.53
37.28
25.11
22.44
21.22
CHO
4f
200
180
160
140
120
100
80
60
40
20
0
ppm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8.043
7.779
7.760
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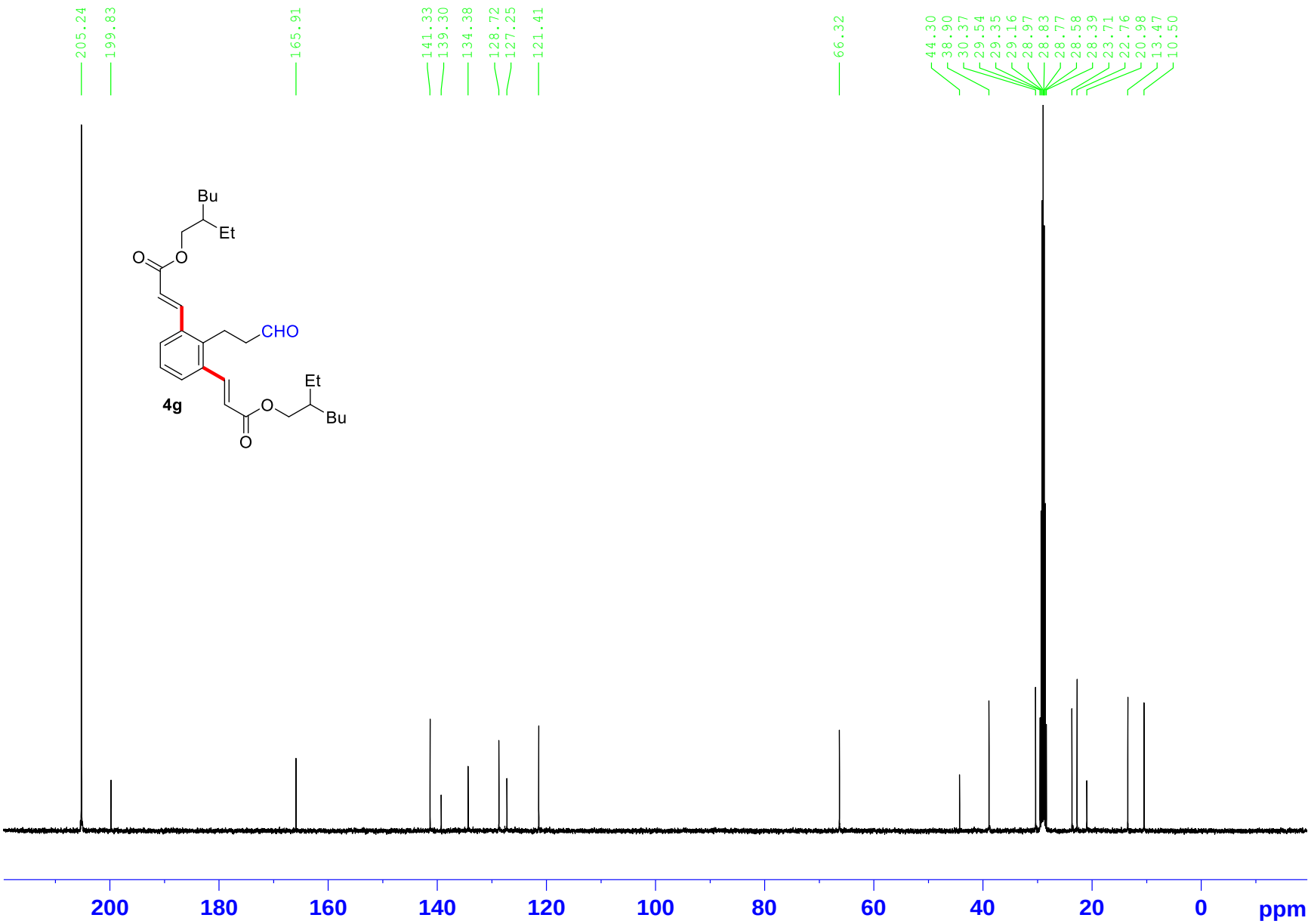
7.376
7.356
6.498
6.458
4.180
4.166
4.152
4.141
4.138
4.127
4.114
4.099
3.260
3.241
3.220
2.865
2.781
2.760
2.742
2.073
2.067
2.062
1.689
1.674
1.659
1.486
1.467
1.459
1.448
1.442
1.441
1.432
1.424
1.413
1.406
1.390
1.382
1.376
1.367
1.359
1.349
1.343
0.969
0.940
0.931
0.923
0.905
Bu
Et
O
O
CHO
Et
Bu
O
O
4g
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.01
2.00
2.08
1.09
2.10
4.09
2.06
2.07
2.09
16.22
12.30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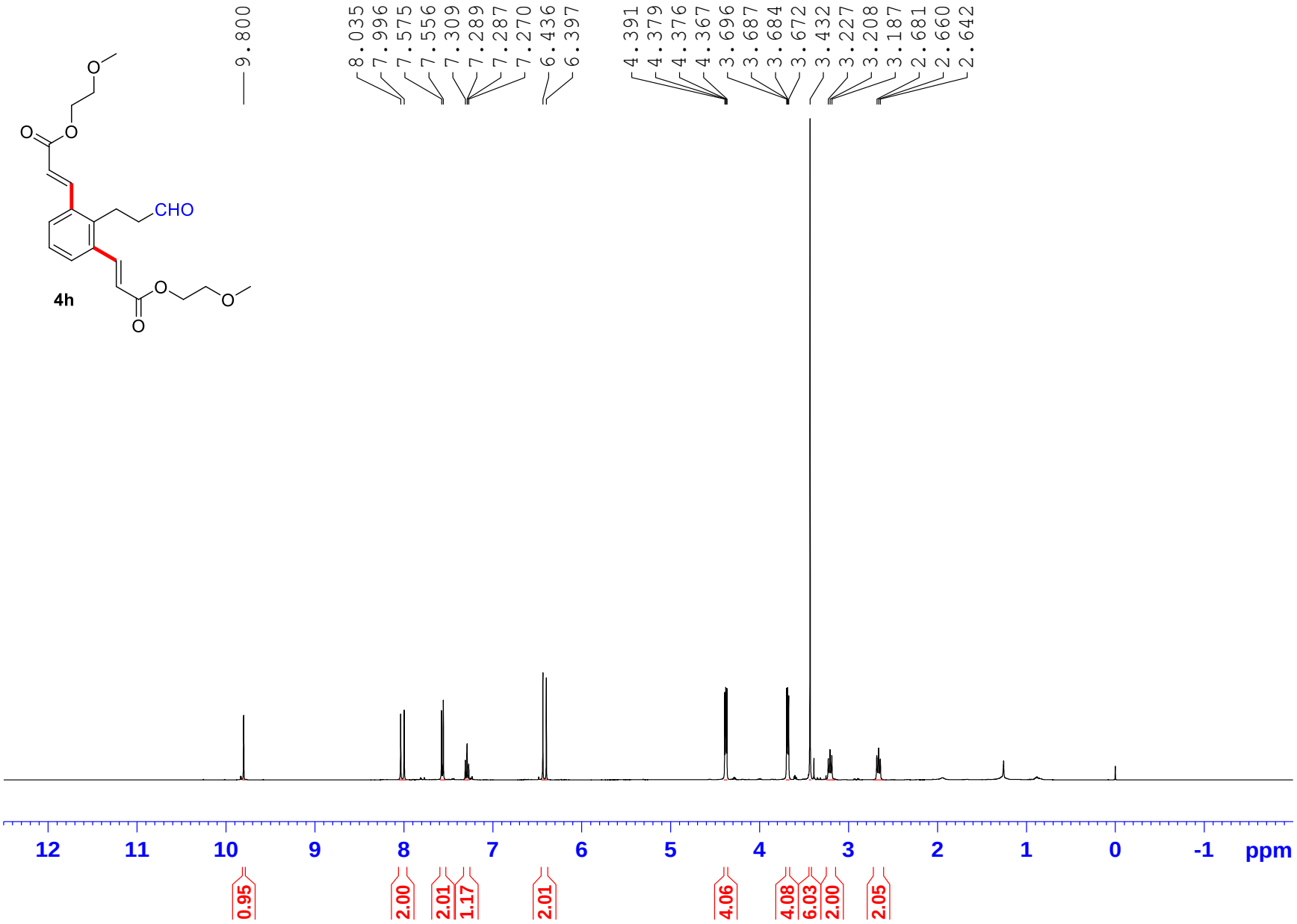
141.33
139.30
134.38
128.72
127.25
121.41
66.32
44.30
38.90
30.37
29.54
29.35
29.16
28.97
28.83
28.77
28.58
28.39
23.71
22.76
20.98
13.47
10.50
Bu
Et
O
O
CHO
Et
Bu
O
O
4g
200
180
160
140
120
100
80
60
40
20
0
ppm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7.287
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6.436
6.397
4.391
4.379
4.376
4.367
3.696
3.687
3.684
3.672
3.432
3.227
3.208
3.187
2.681
2.660
2.642
CHO
4h
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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2.00
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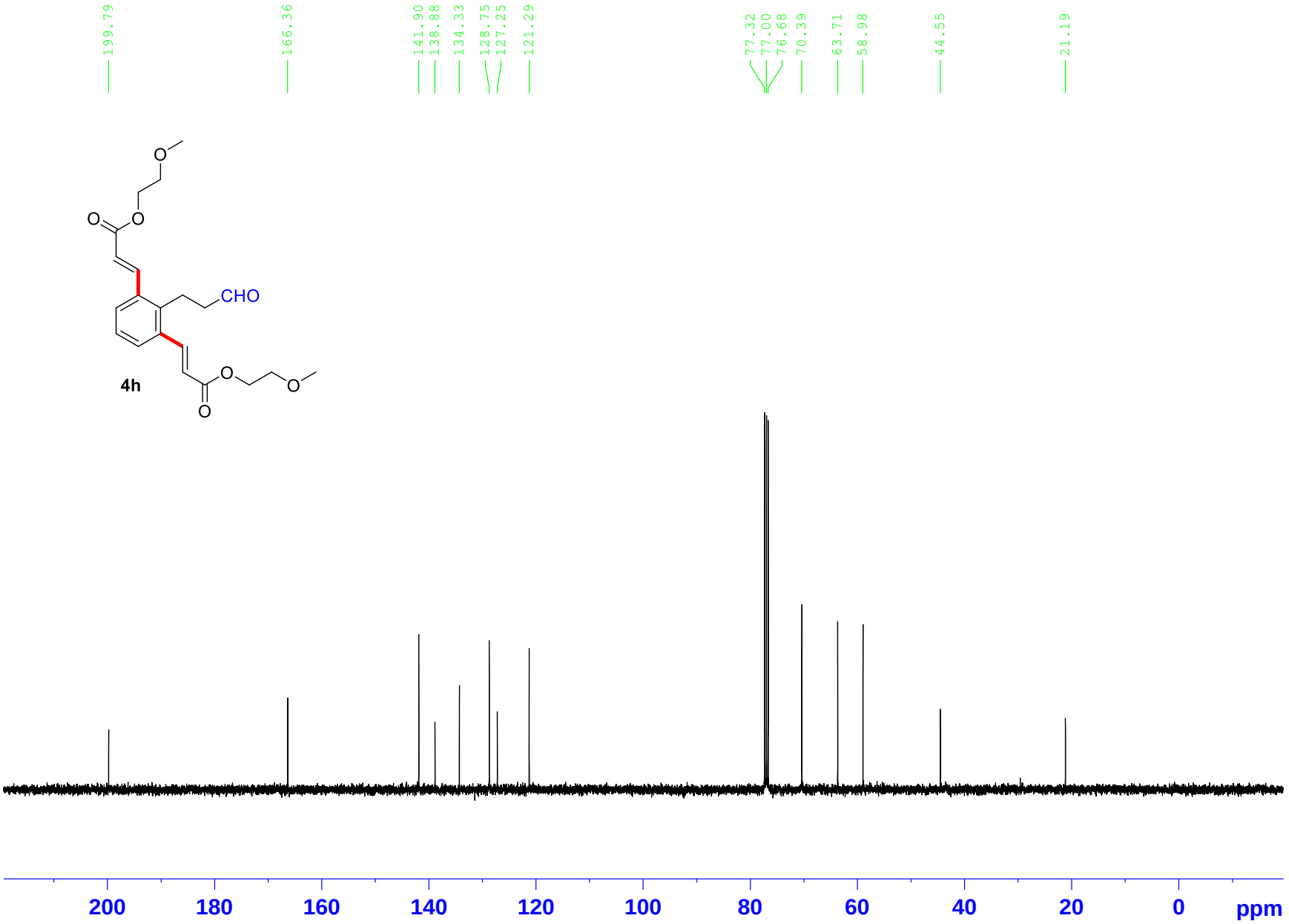
1.17
2.01
4.06
4.08
6.03
2.00
2.05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128.75
127.25
121.29
77.32
77.00
76.68
70.39
63.71
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21.19
CHO
4h
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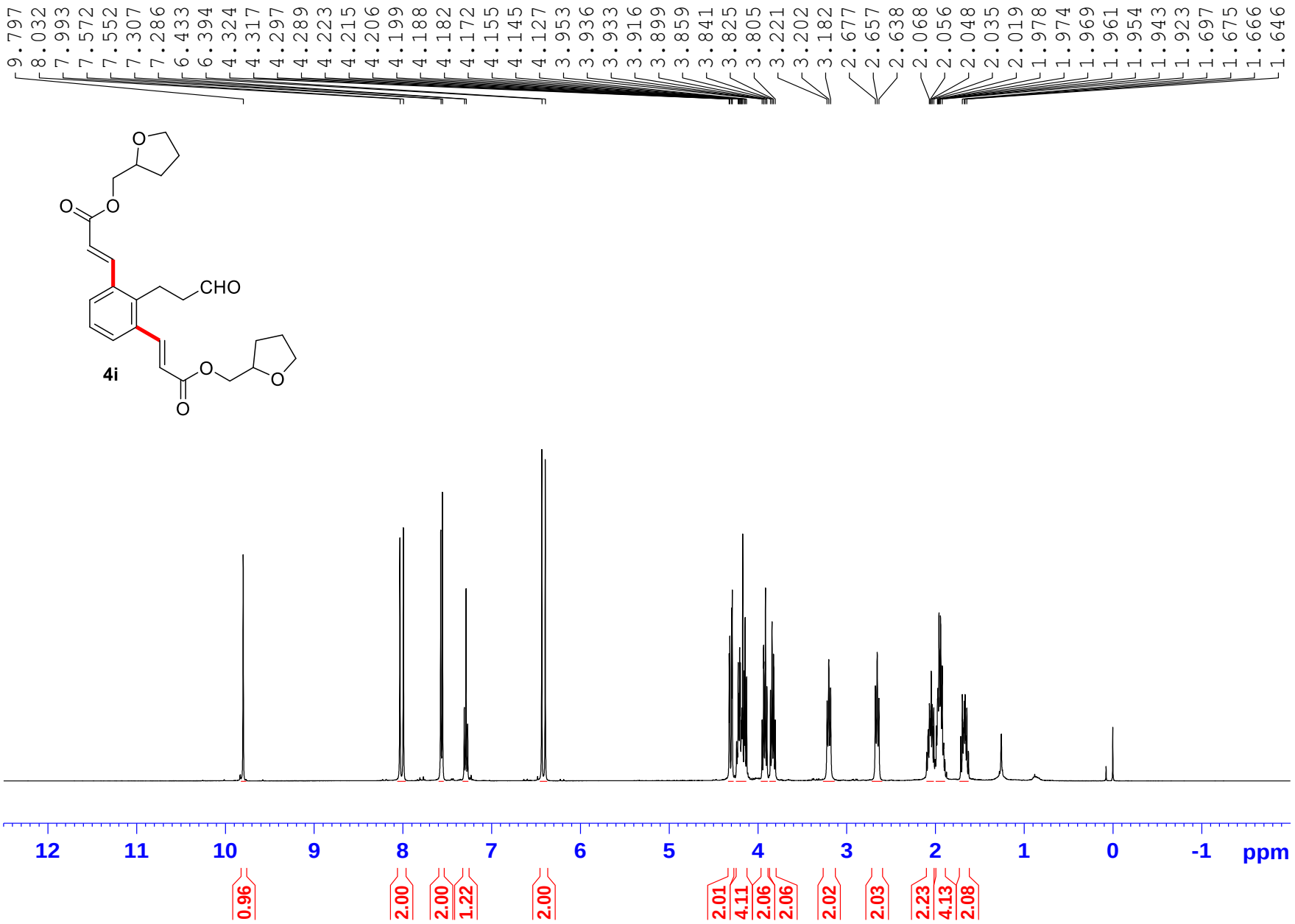
160
140
120
100
80
60
40
20
0
ppm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6.433
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4.289
4.223
4.215
4.206
4.199
4.188
4.182
4.172
4.155
4.145
4.127
3.953
3.936
3.933
3.916
3.899
3.859
3.841
3.825
3.805
3.221
3.202
3.182
2.677
2.657
2.638
2.068
2.056
2.048
2.035
2.019
1.978
1.974
1.969
1.961
1.954
1.943
1.923
1.697
1.675
1.666
1.646
O
O
O
CHO
O
O
O
4i
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.96
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2.02
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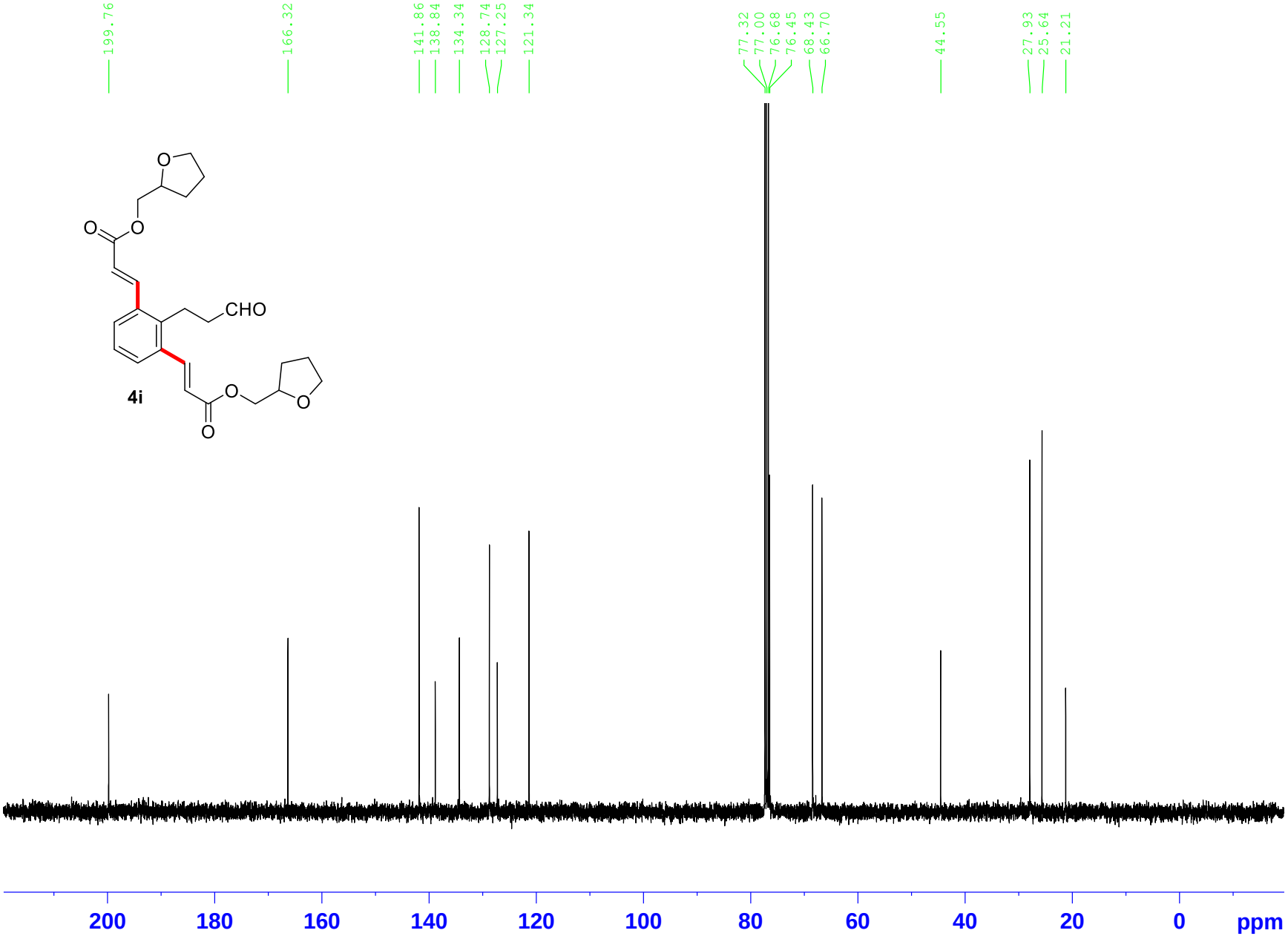
2.23
4.13
2.08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66.70
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CHO
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120
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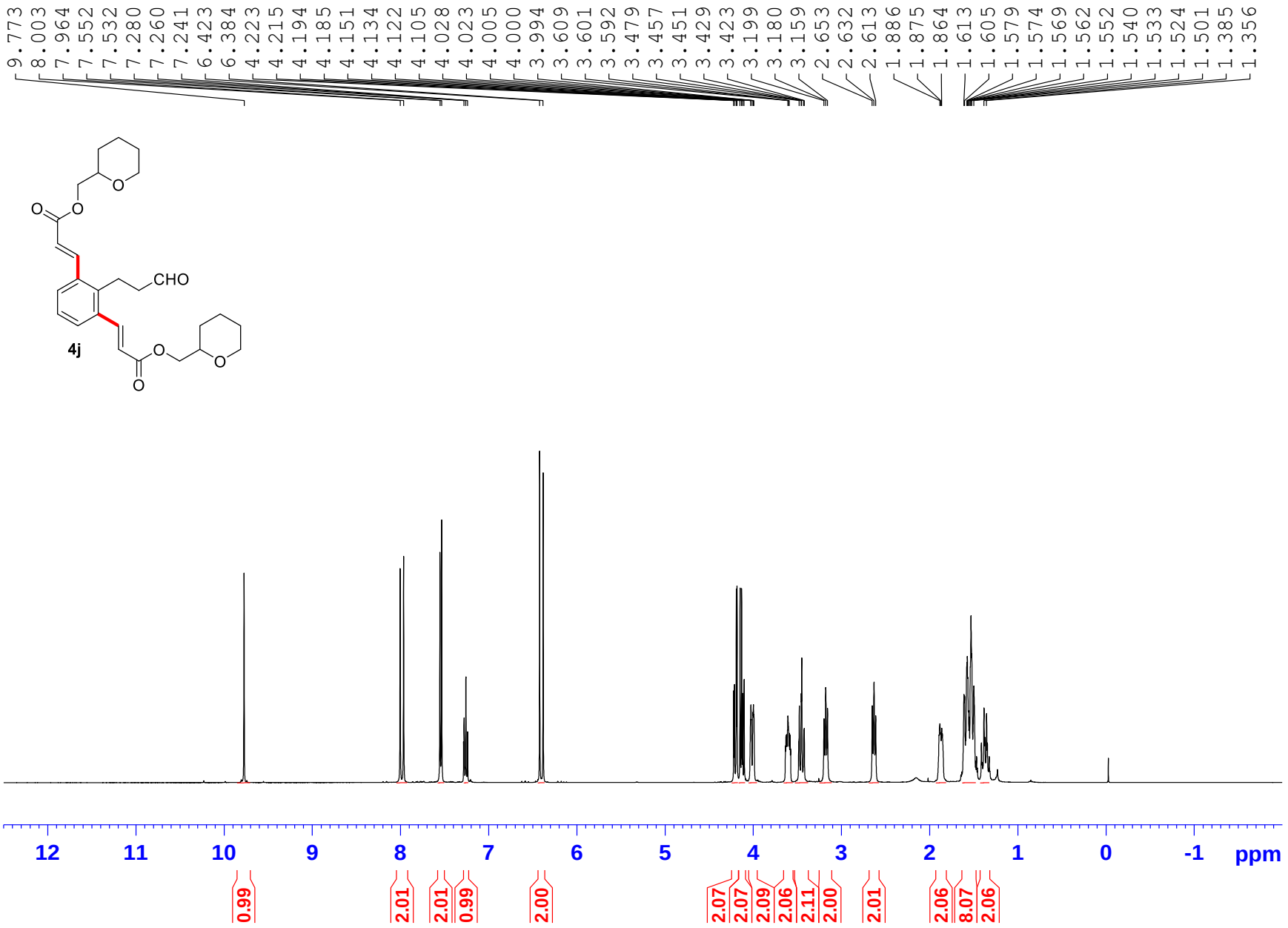
20
0
ppm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7.241
6.423
6.384
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4.215
4.194
4.185
4.151
4.134
4.122
4.105
4.028
4.023
4.005
4.000
3.994
3.609
3.601
3.592
3.479
3.457
3.451
3.429
3.423
3.199
3.180
3.159
2.653
2.632
2.613
1.886
1.875
1.864
1.613
1.605
1.579
1.574
1.569
1.562
1.552
1.540
1.533
1.524
1.501
1.385
1.356
CHO
4j
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.99
2.01
2.01
0.99
2.00
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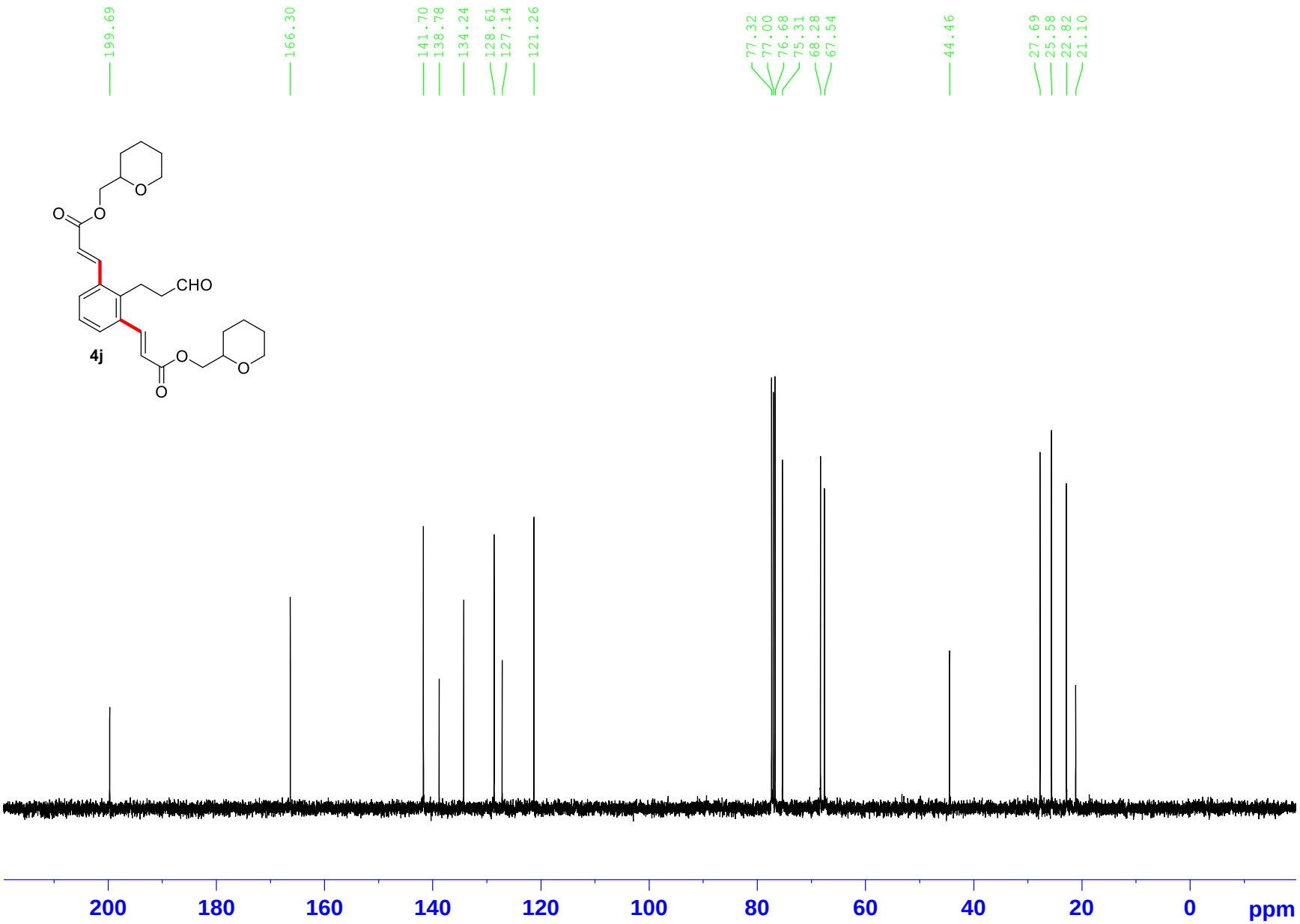
2.07
2.09
2.06
2.11
2.00
2.01
2.06
8.07
2.06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121.26
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77.00
76.68
75.31
68.28
67.54
44.46
27.69
25.58
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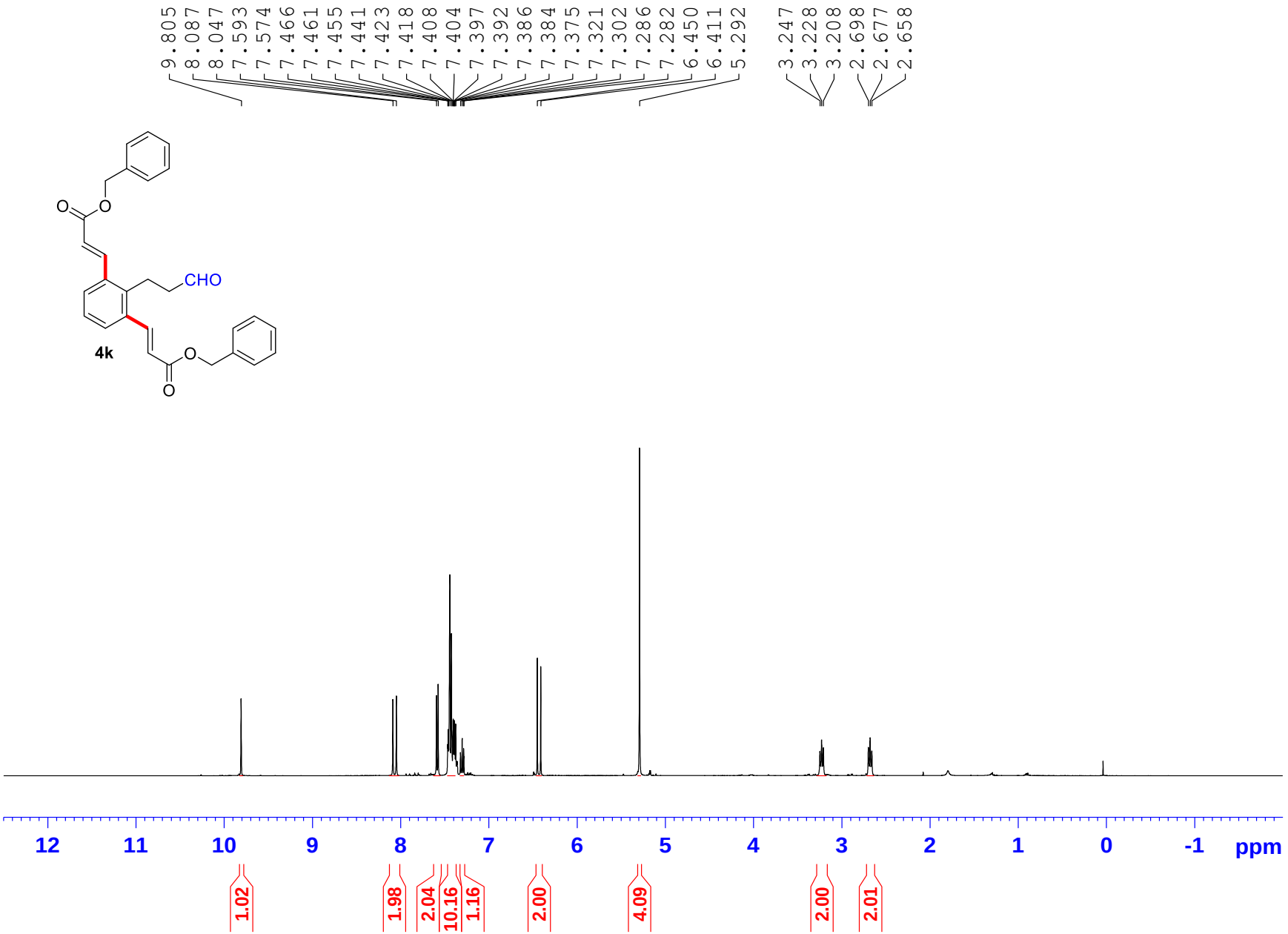
21.10
CHO
4j
200
180
160
140
120
100
80
60
40
20
0
ppm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7.455
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7.423
7.418
7.408
7.404
7.397
7.392
7.386
7.384
7.375
7.321
7.302
7.286
7.282
6.450
6.411
5.292
3.247
3.228
3.208
2.698
2.677
2.658
CHO
4k
12
11
10
9
8
7
6
5
4
3
2
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0
-1
ppm
1.02
1.98
2.04
10.16
1.16
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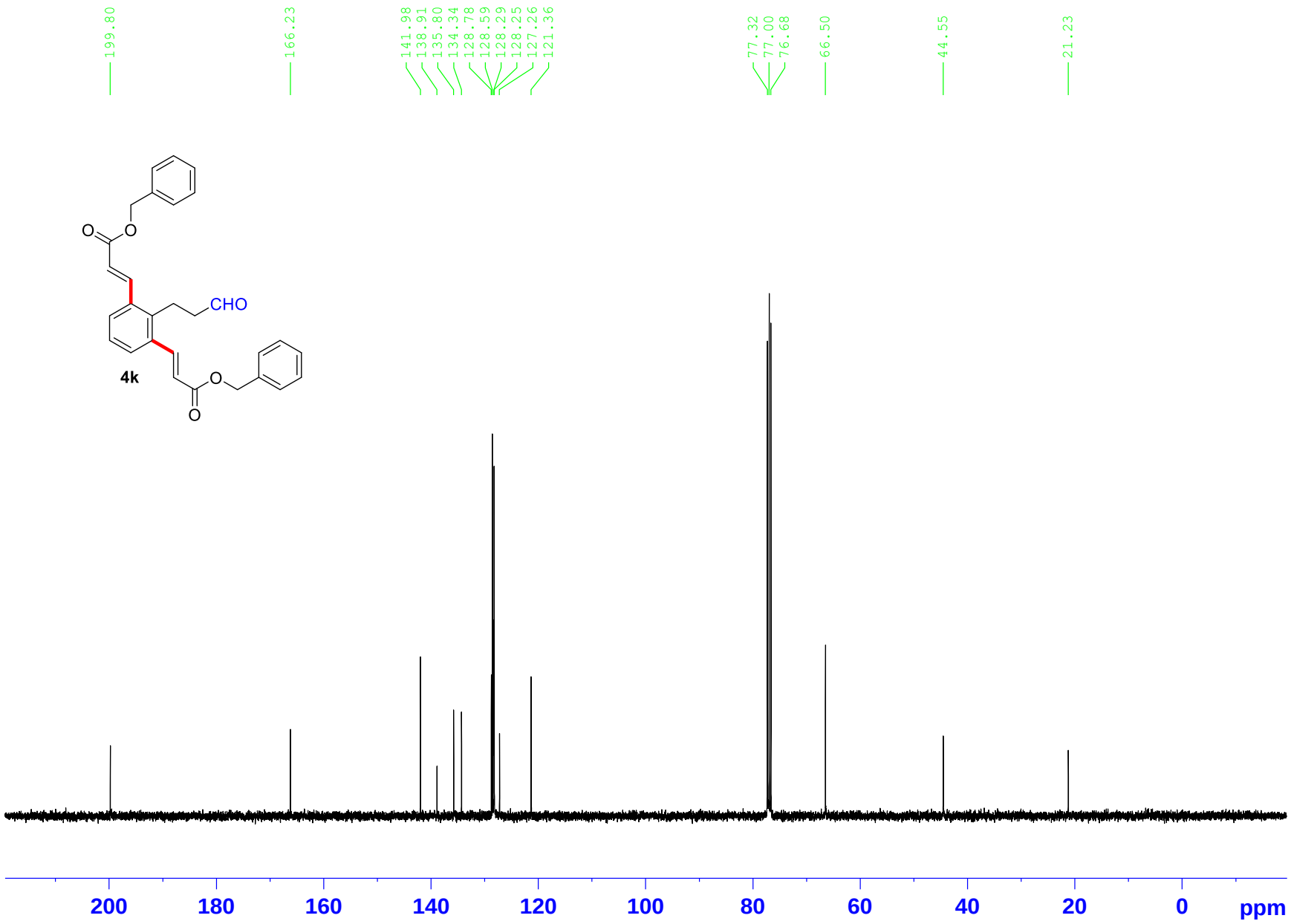
4.09
2.00
2.01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141.98
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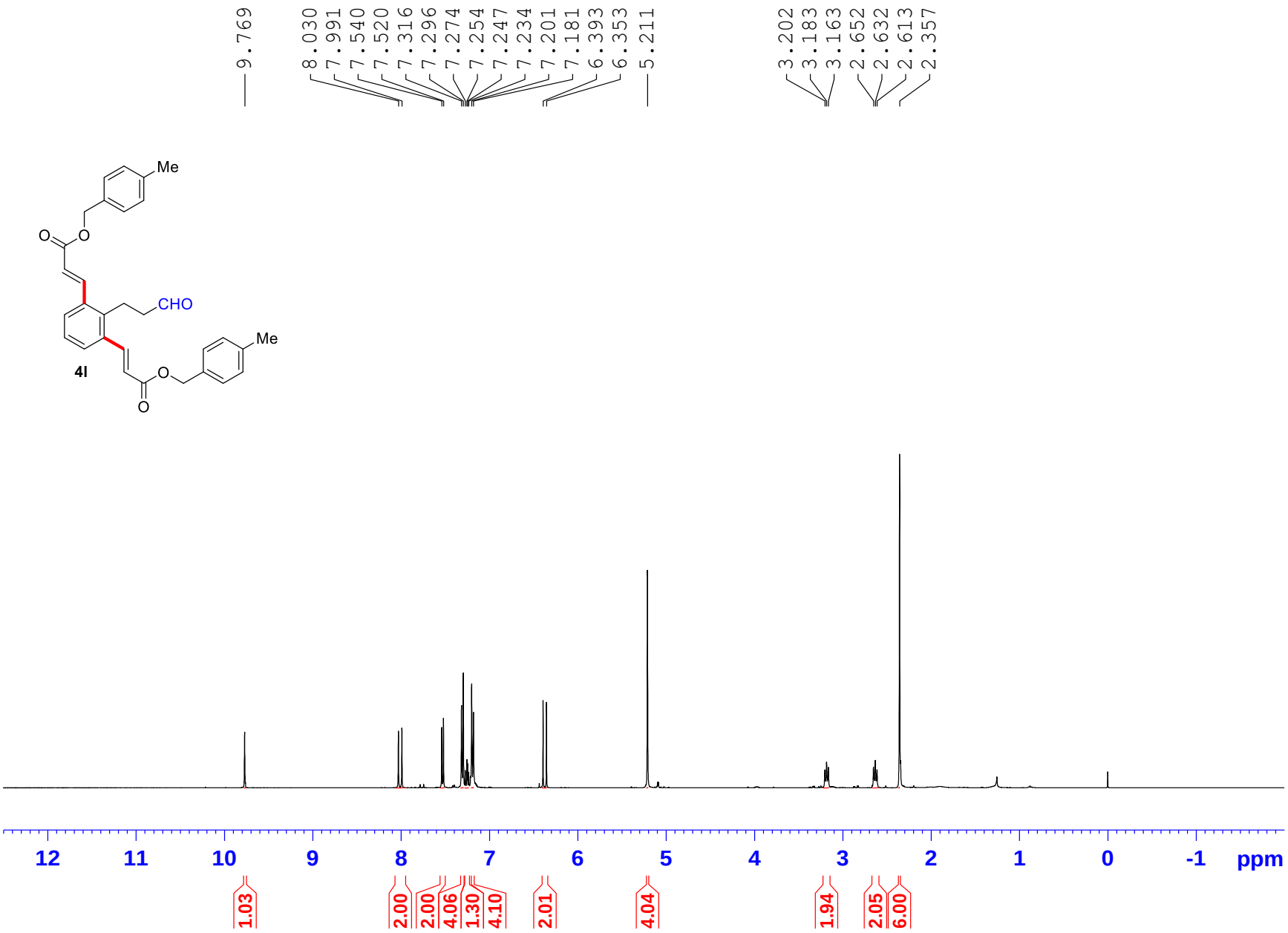
135.80
134.34
128.78
128.59
128.29
128.25
127.26
121.36
77.32
77.00
76.68
66.50
44.55
21.23
CHO
4k
200
180
160
140
120
100
80
60
40
20
0
ppm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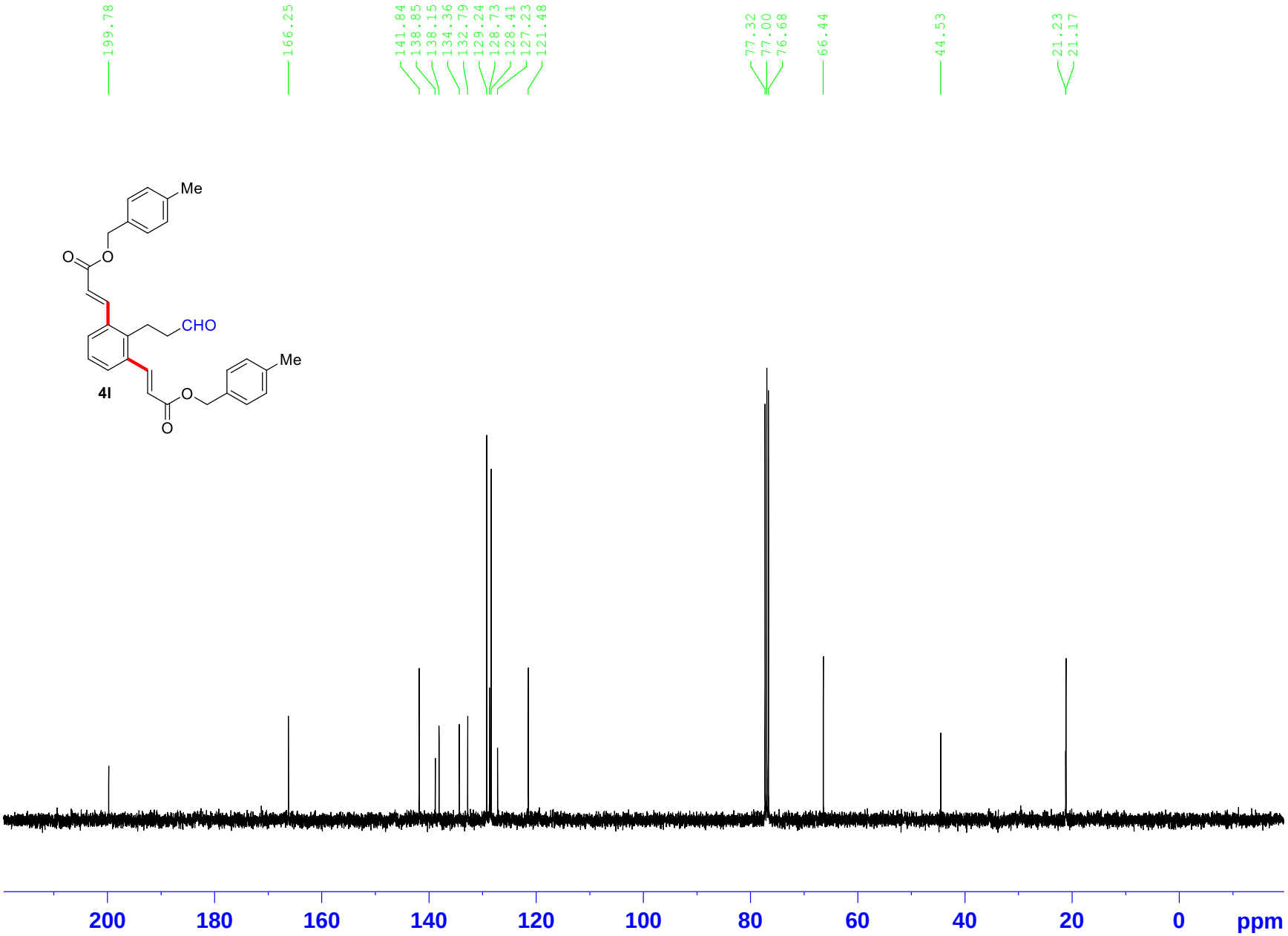
7.274
7.254
7.247
7.234
7.201
7.181
6.393
6.353
5.211
3.202
3.183
3.163
2.652
2.632
2.613
2.357
Me
O
O
CHO
Me
4l
O
O
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.03
2.00
2.00
4.06
1.30
4.10
2.01
4.04
1.94
2.05
6.00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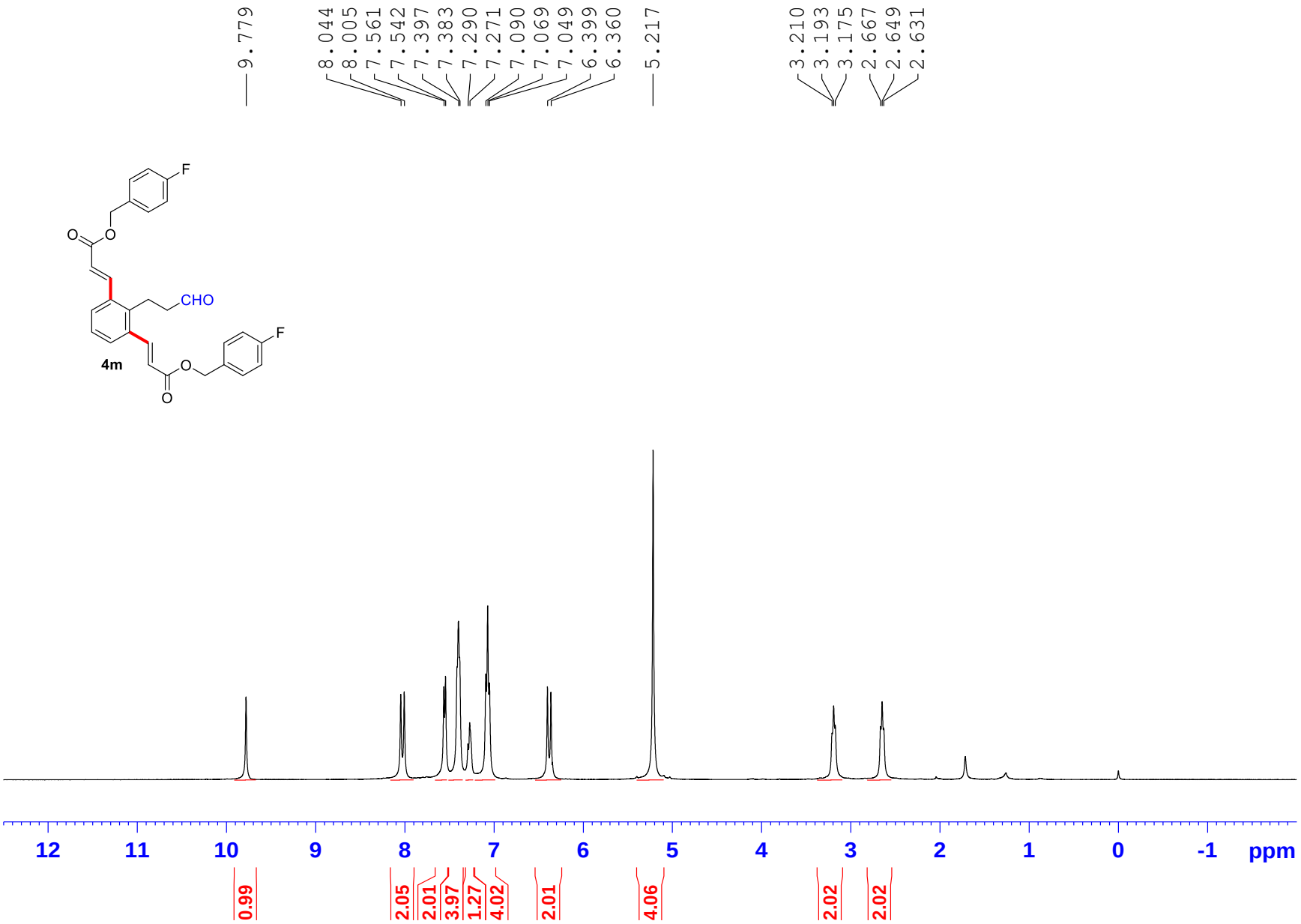
132.79
129.24
128.73
128.41
127.23
121.48
77.32
77.00
76.68
66.44
44.53
21.23
21.17
Me
O
O
CHO
Me
O
O
4l
200
180
160
140
120
100
80
60
40
20
0
ppm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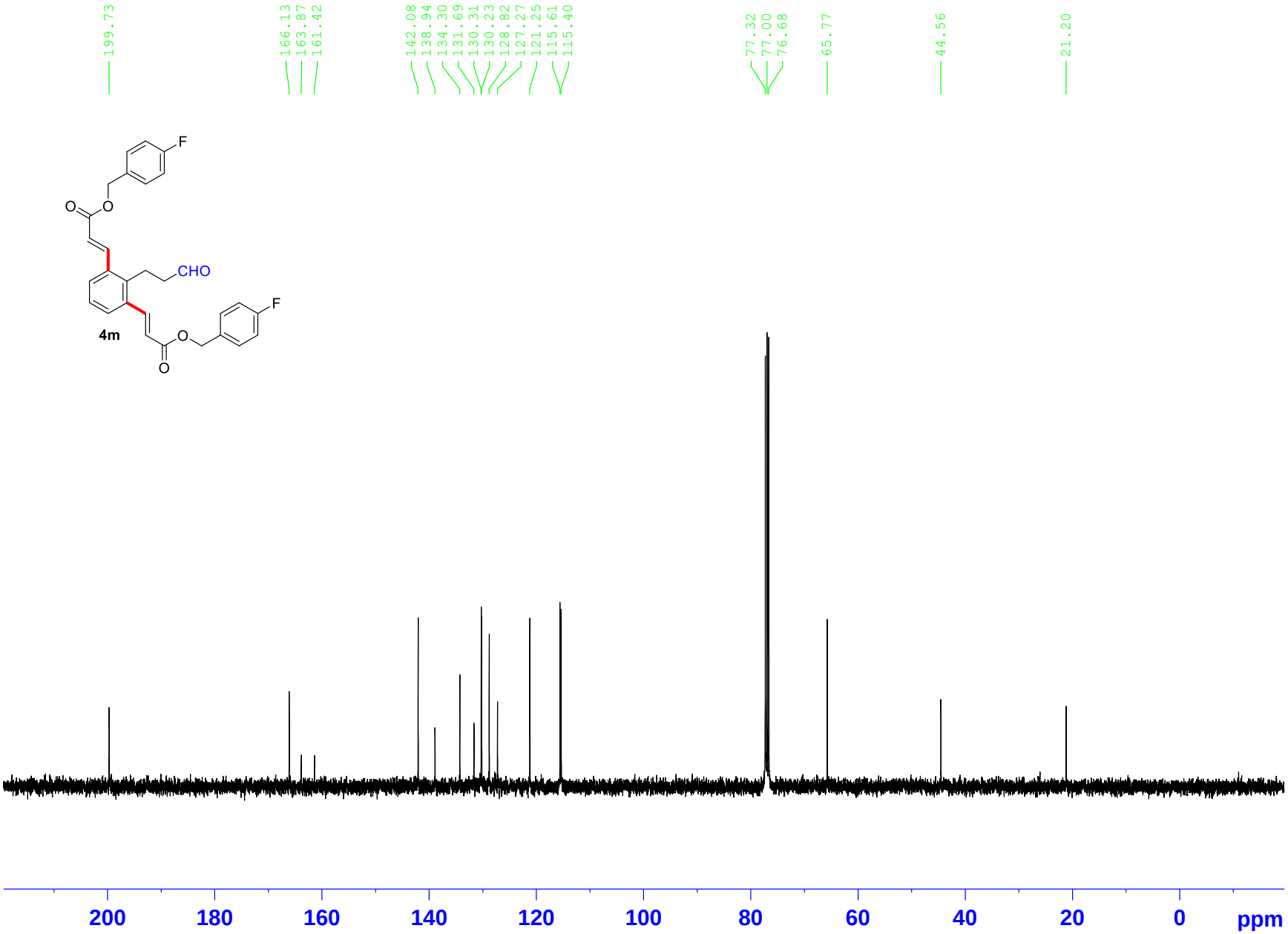
7.542
7.397
7.383
7.290
7.271
7.090
7.069
7.049
6.399
6.360
5.217
3.210
3.193
3.175
2.667
2.649
2.631
F
O
O
CHO
F
4m
O
O
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.99
2.05
2.01
3.97
1.27
4.02
2.01
4.06
2.02
2.02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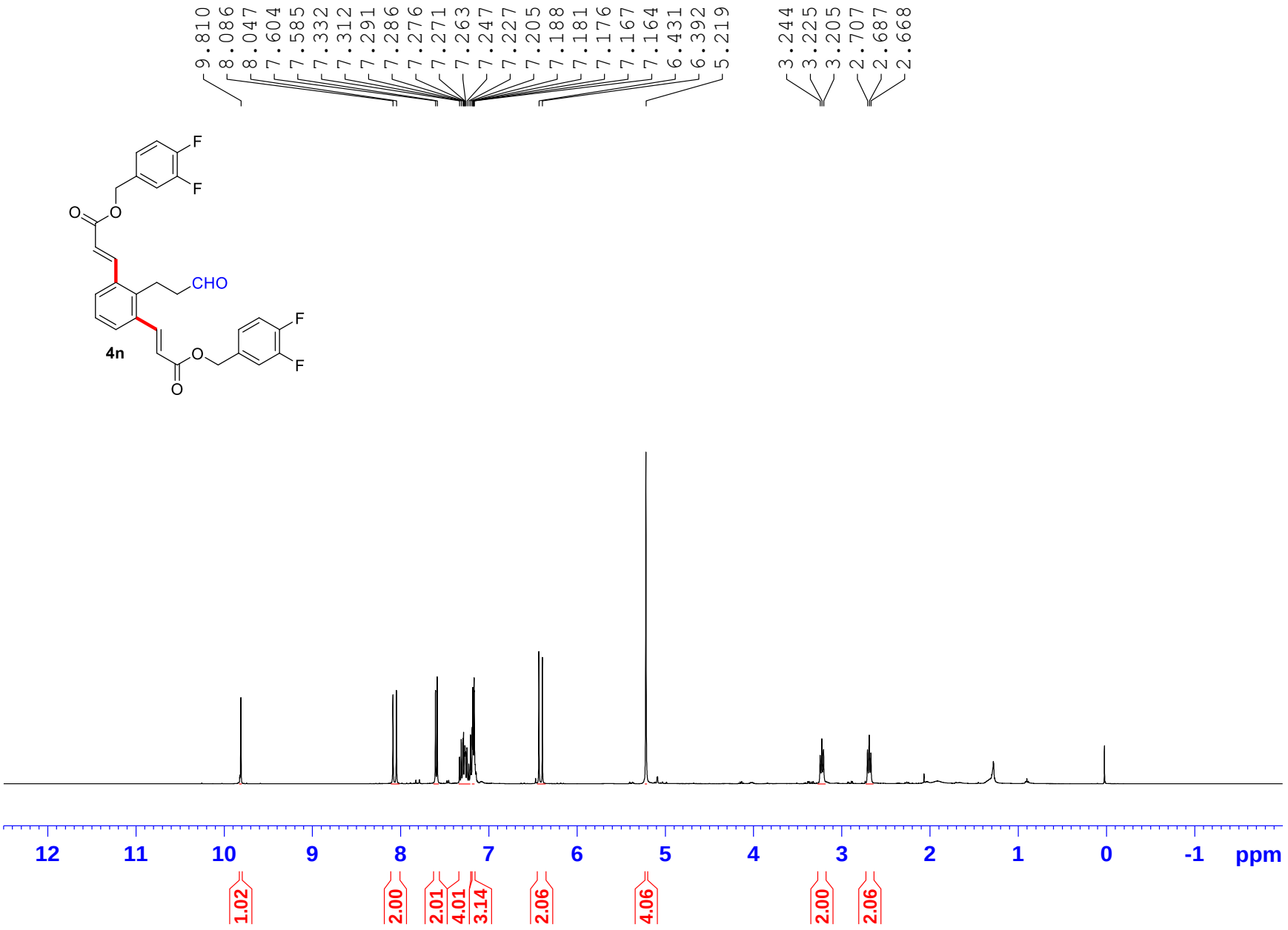
161.42
142.08
138.94
134.30
131.69
130.31
130.23
128.82
127.27
121.25
115.61
115.40
77.32
77.00
76.68
65.77
44.56
21.20
F
O
O
CHO
F
4m
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm


-113.433
F
O
O
CHO
F
4m
O
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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7.291
7.286
7.276
7.271
7.263
7.247
7.227
7.205
7.188
7.181
7.176
7.167
7.164
6.431
6.392
5.219
3.244
3.225
3.205
2.707
2.687
2.668
F
F
O
O
CHO
F
F
4n
O
O
12
11
10
9
8
7
6
5
4
3
2
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-1
ppm
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4.01
3.14
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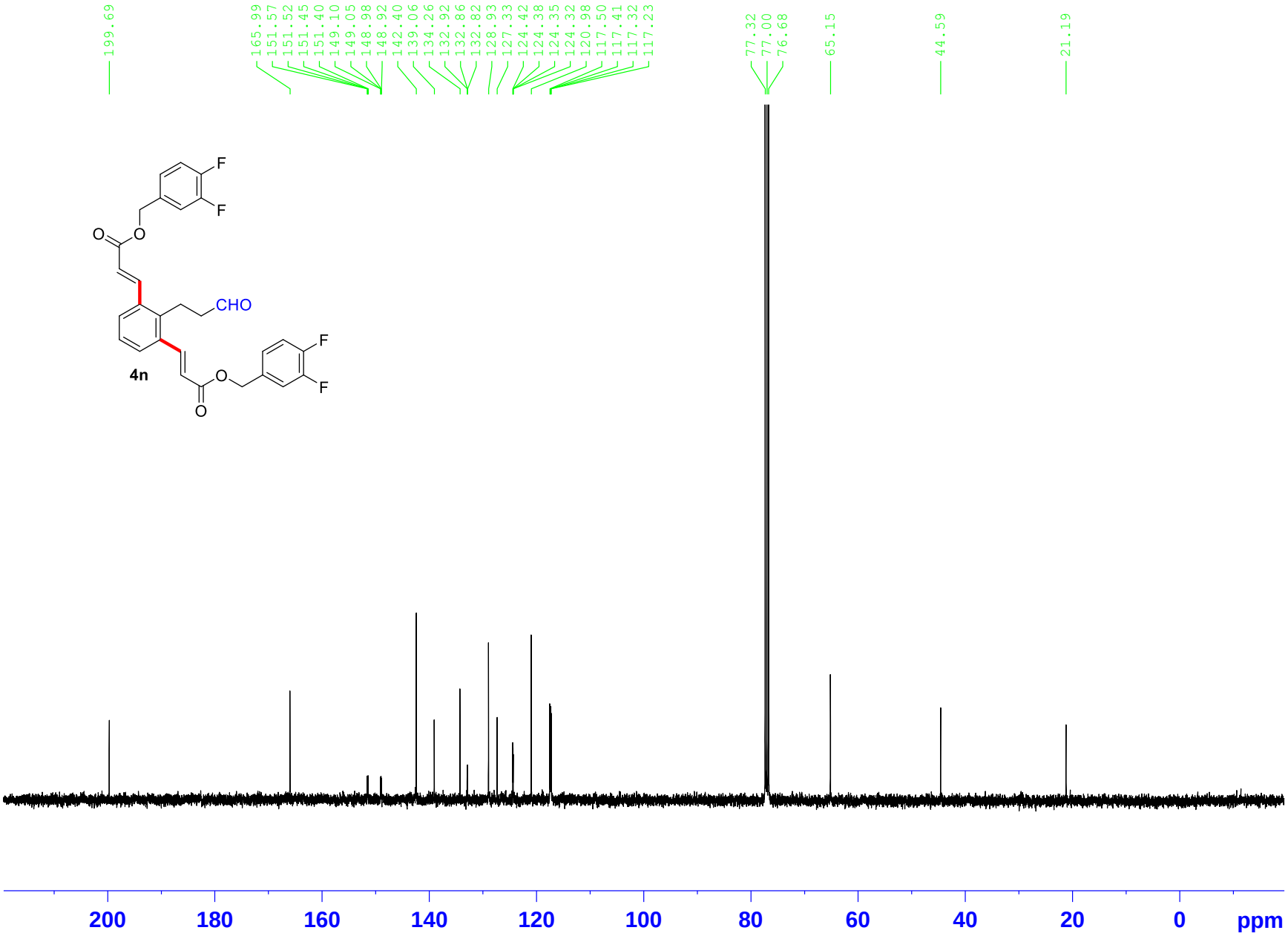
4.06
2.00
2.06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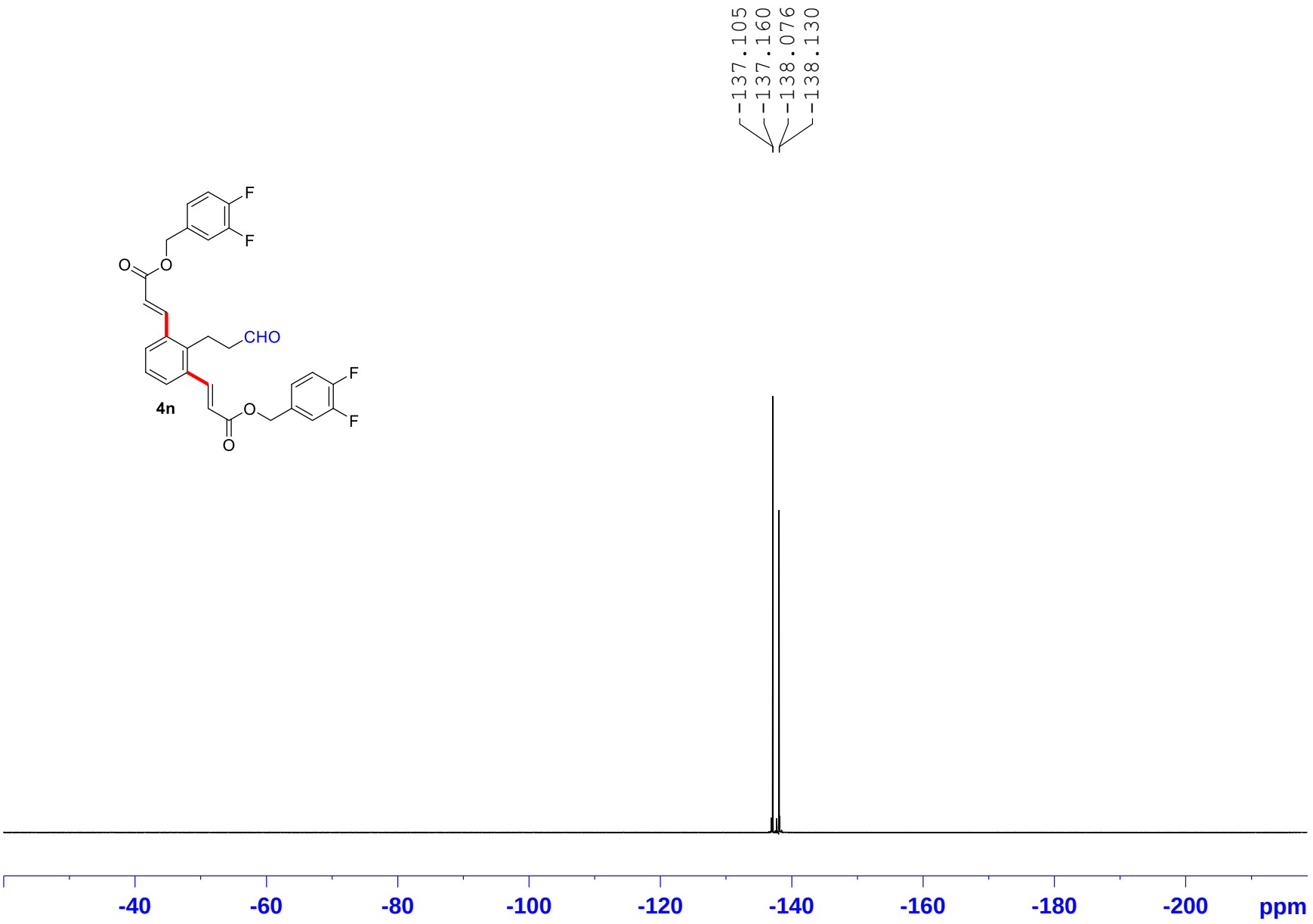
151.45
151.40
149.10
149.05
148.98
148.92
142.40
139.06
134.26
132.92
132.86
132.82
128.93
127.33
124.42
124.38
124.35
124.32
120.98
117.50
117.41
117.32
117.23
77.32
77.00
76.68
65.15
44.59
21.19
F
F
O
O
CHO
F
F
4n
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm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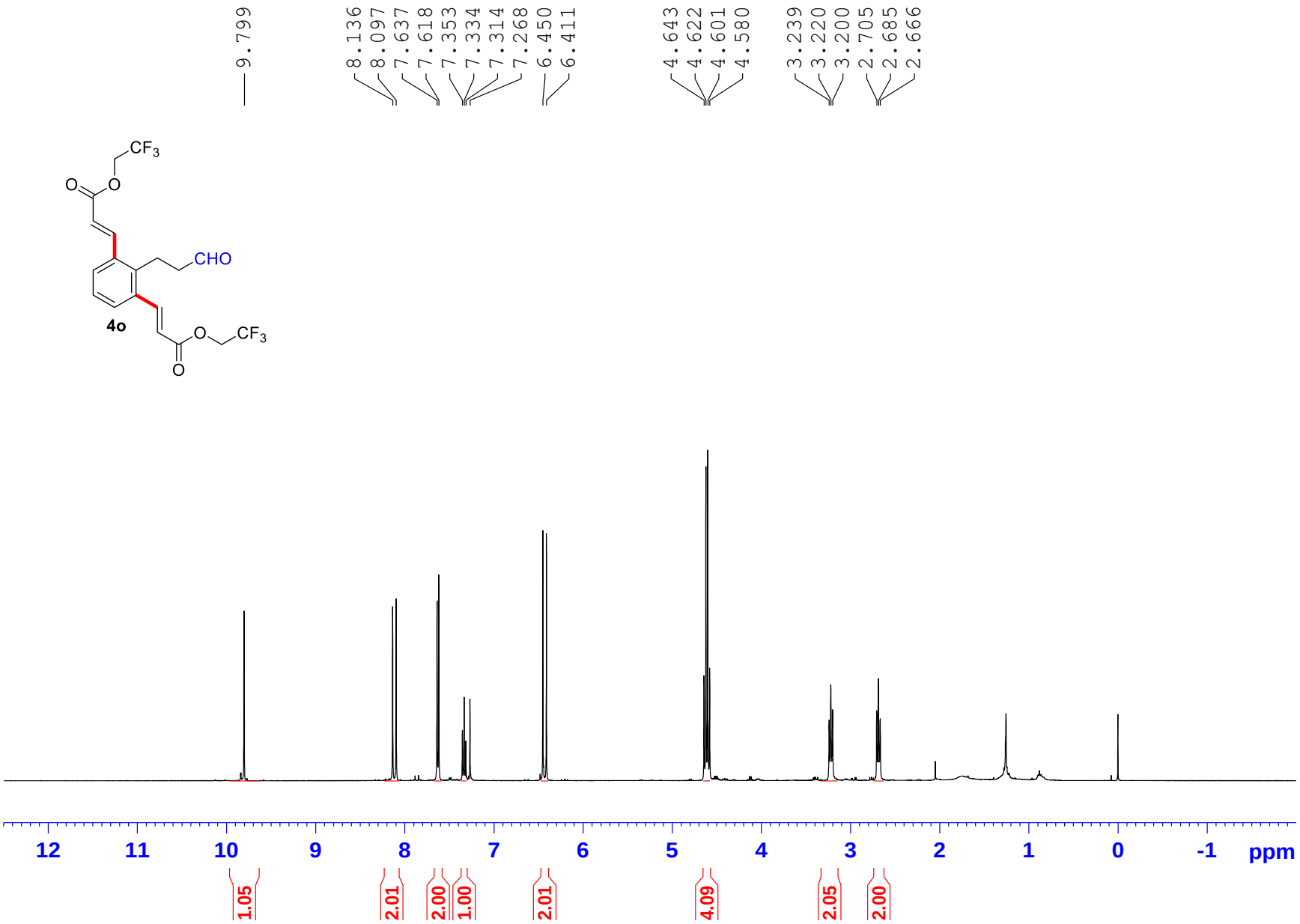
-137.160
-138.076
-138.130
F
F
O
O
CHO
F
F
O
O
4n
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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8.136
8.097
7.637
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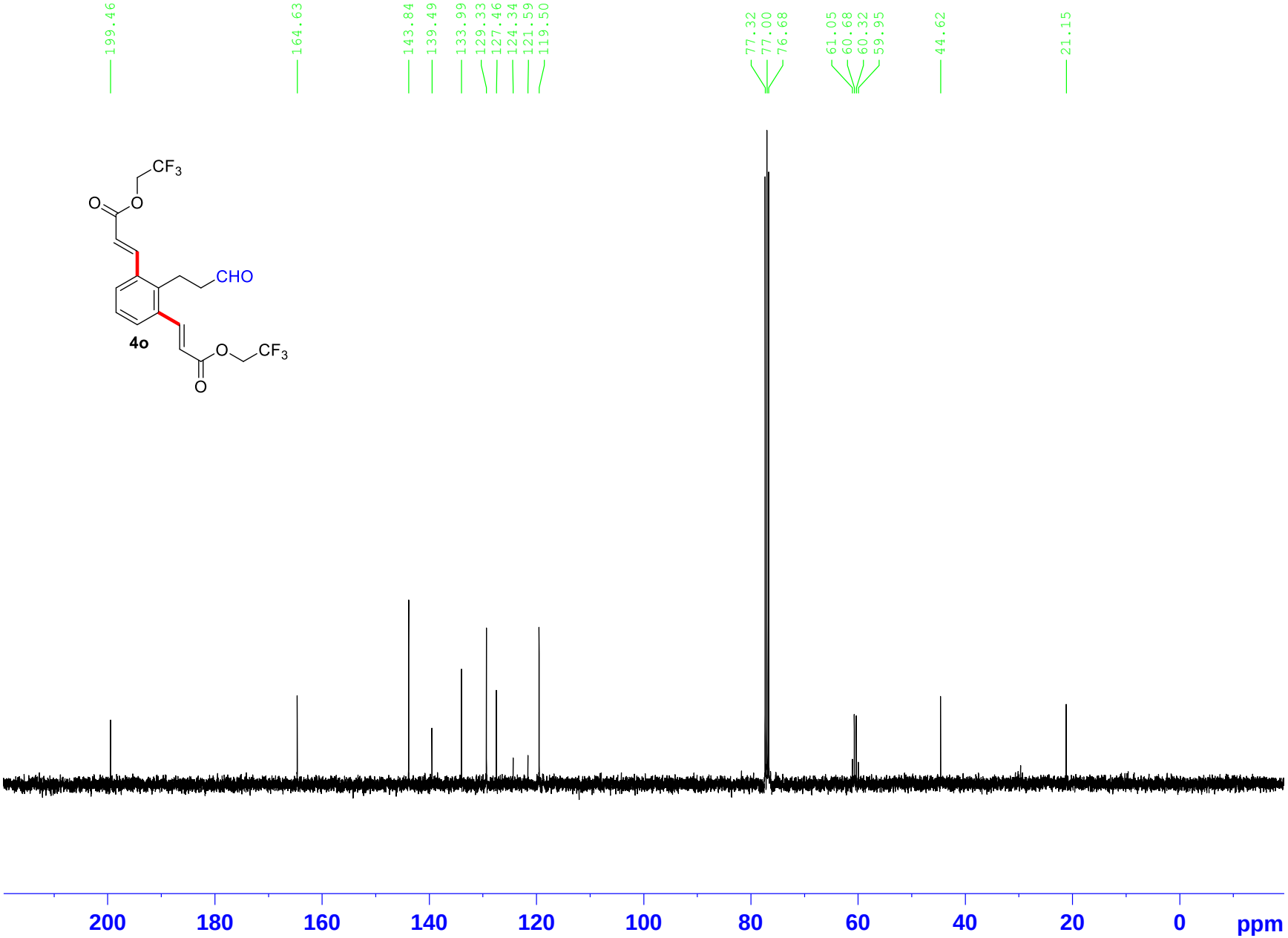
7.353
7.334
7.314
7.268
6.450
6.411
4.643
4.622
4.601
4.580
3.239
3.220
3.200
2.705
2.685
2.666
CF3
O
O
CHO
4o
O
CF3
O
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.05
2.01
2.00
1.00
2.01
4.09
2.05
2.00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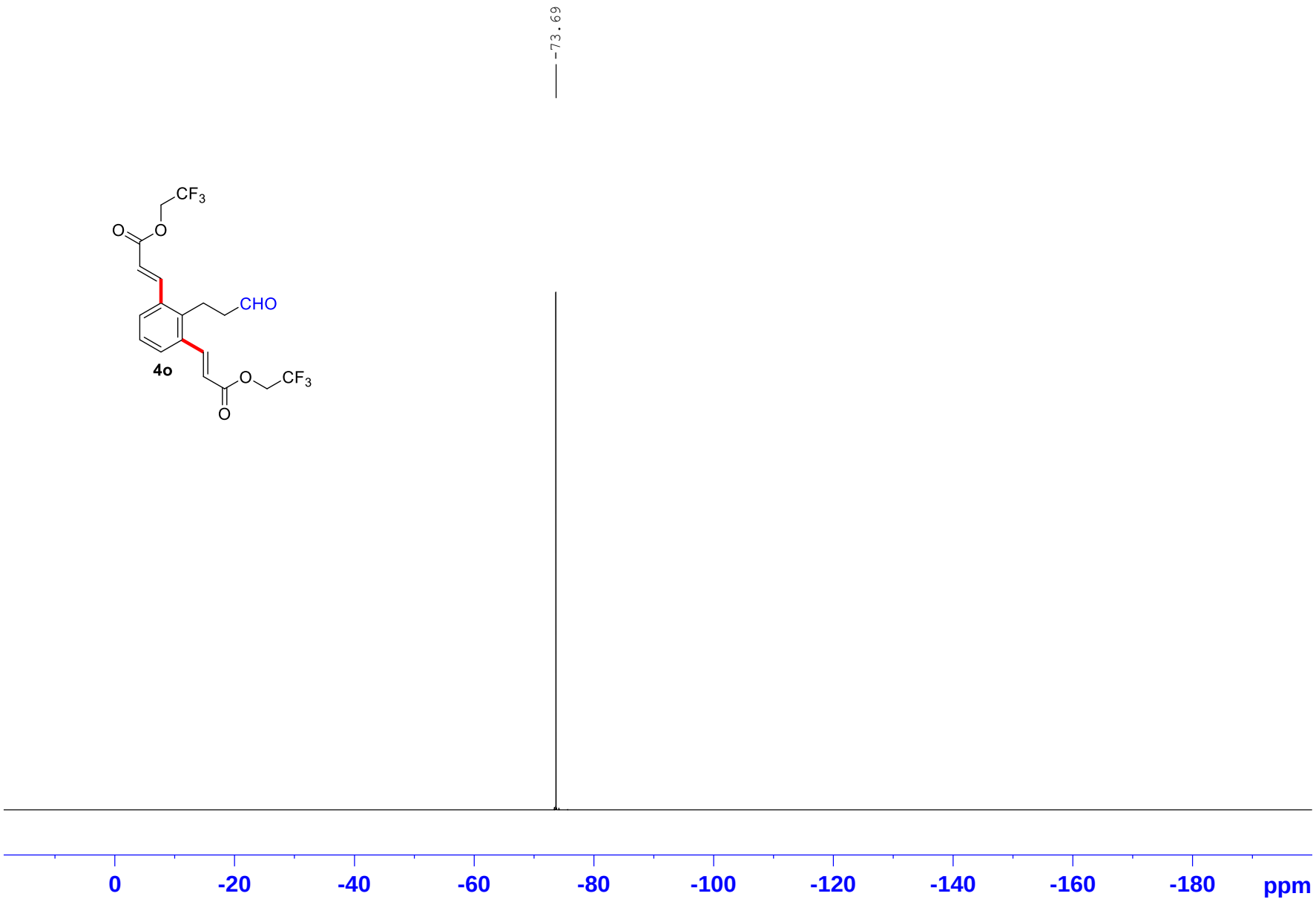
129.33
127.46
124.34
121.59
119.50
77.32
77.00
76.68
61.05
60.68
60.32
59.95
44.62
21.15
CF3
O
O
CHO
4o
O
CF3
O
200
180
160
140
120
100
80
60
40
20
0
ppm


-73.69
CF3
O
O
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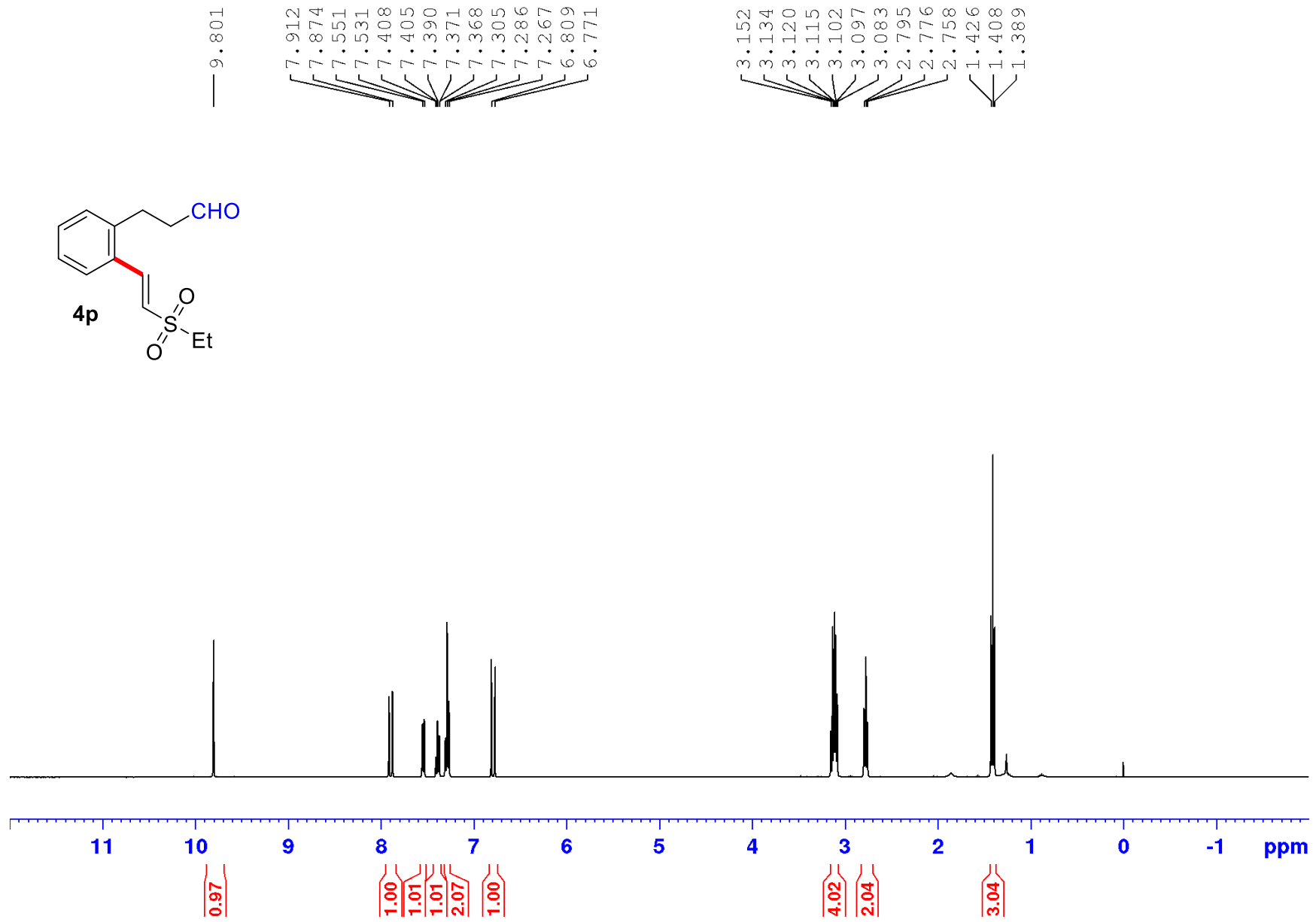
4o
O
CF3
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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7.368
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7.286
7.267
6.809
6.771
3.152
3.134
3.120
3.115
3.102
3.097
3.083
2.795
2.776
2.758
1.426
1.408
1.389
CHO
4p
O
S
O
Et
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.97
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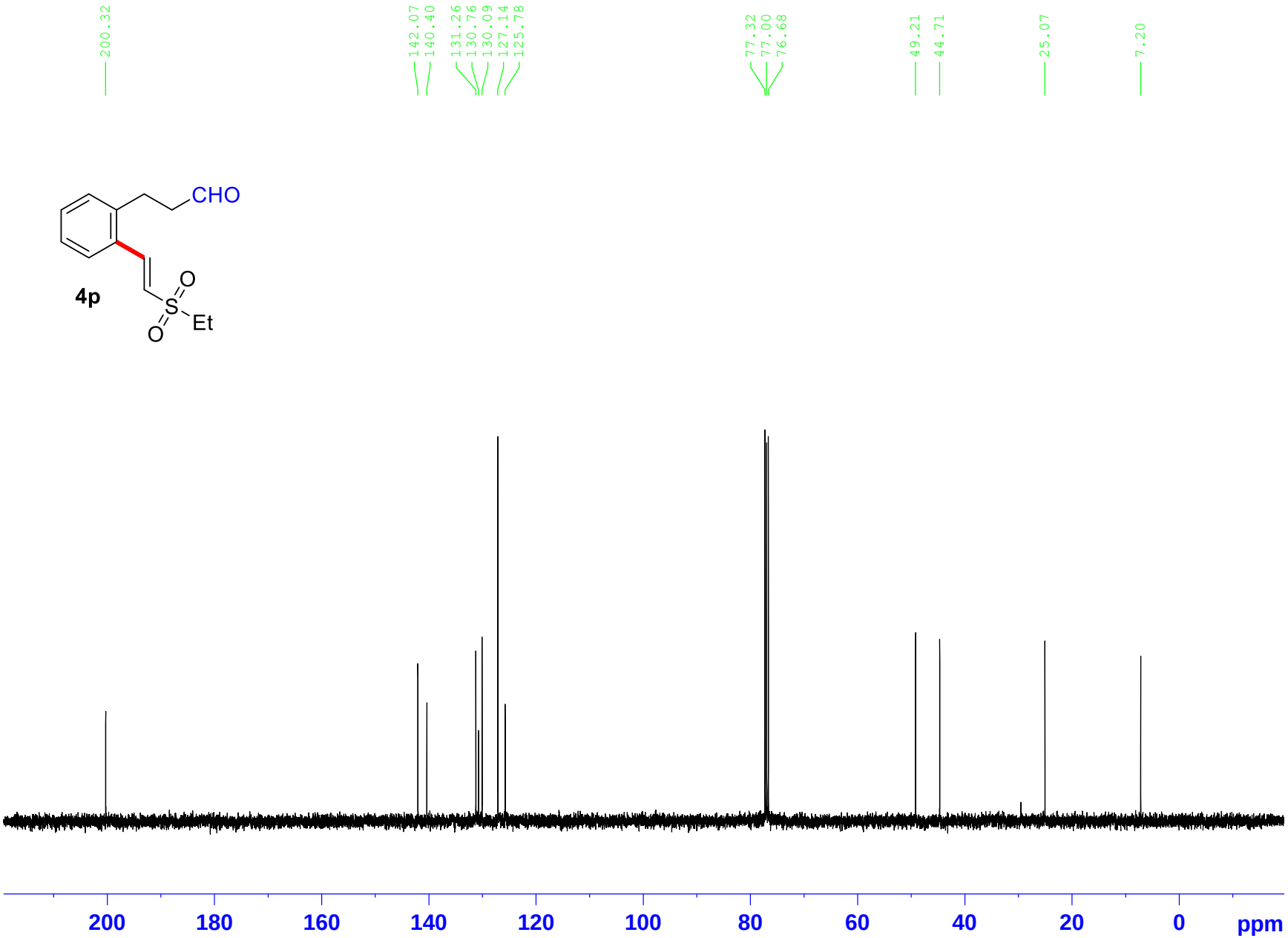
1.01
1.01
2.07
1.00
4.02
2.04
3.04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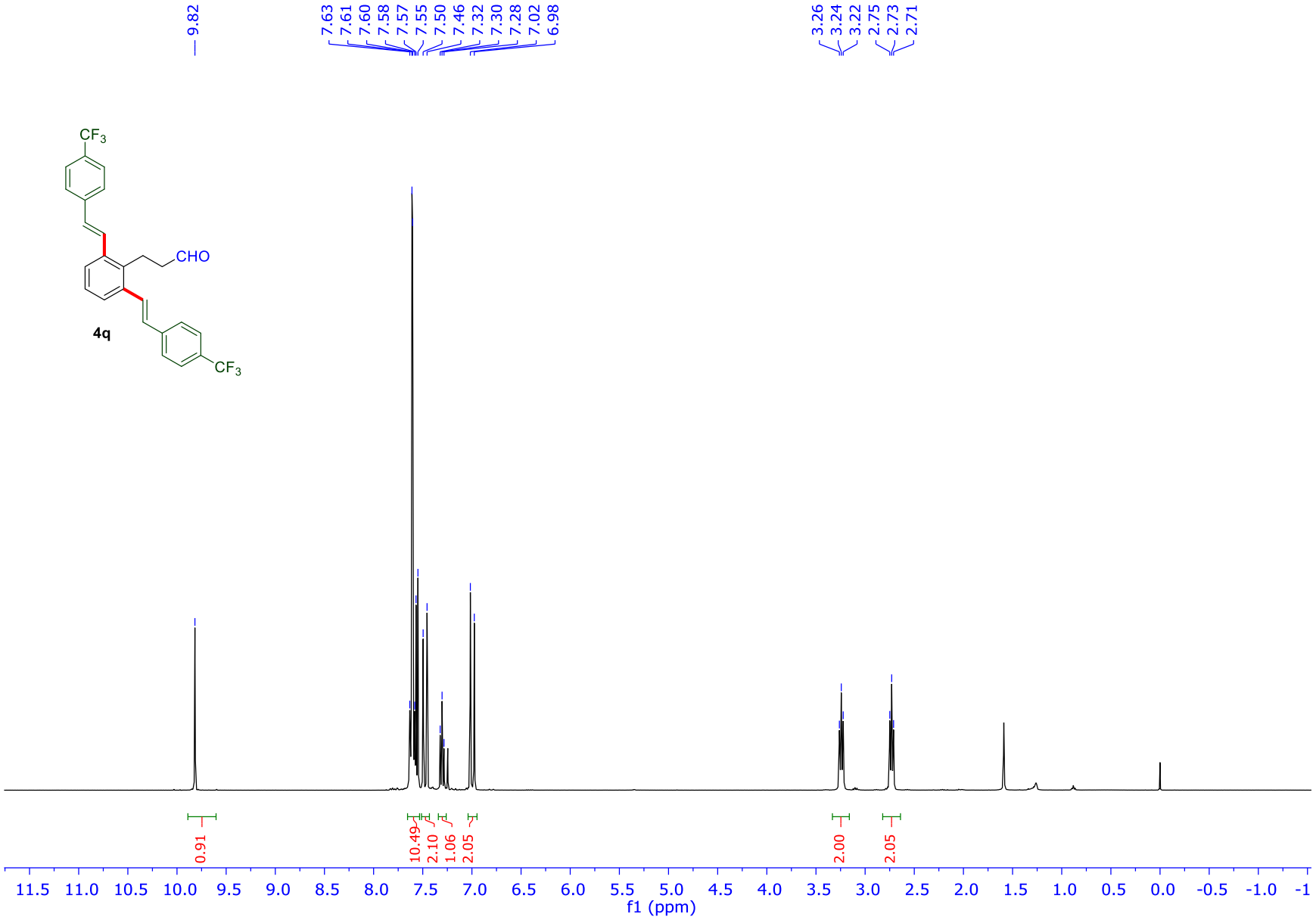
142.07
140.40
131.26
130.76
130.09
127.14
125.78
77.32
77.00
76.68
49.21
44.71
25.07
7.20
CHO
4p
O
S
O
Et
200
180
160
140
120
100
80
60
40
20
0
ppm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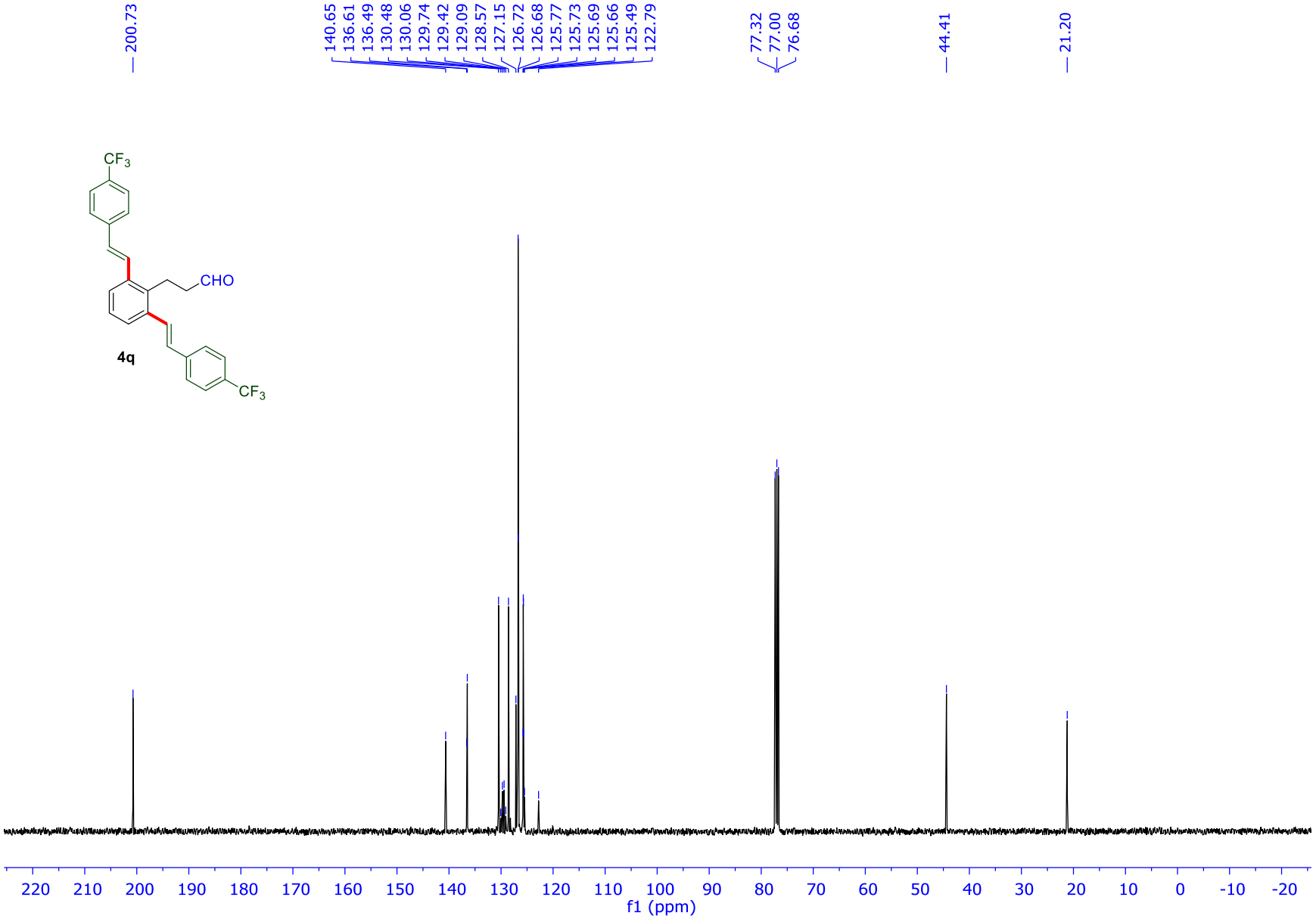
7.61
7.60
7.58
7.57
7.55
7.50
7.46
7.32
7.30
7.28
7.02
6.98
3.26
3.24
3.22
2.75
2.73
2.71
CF3
CHO
4q
CF3
0.91
10.49
2.10
1.06
2.05
2.00
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)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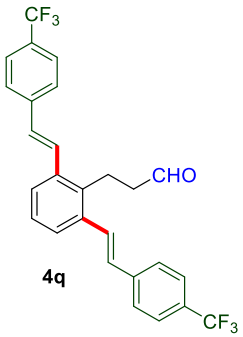
140.65
136.61
136.49
130.48
130.06
129.74
129.42
129.09
128.57
127.15
126.72
126.68
125.77
125.73
125.69
125.66
125.49
122.79
77.32
77.00
76.68
44.41
21.20
CF3
CHO
4q
CF3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


CF3
CHO
CF3

4q

-62.36
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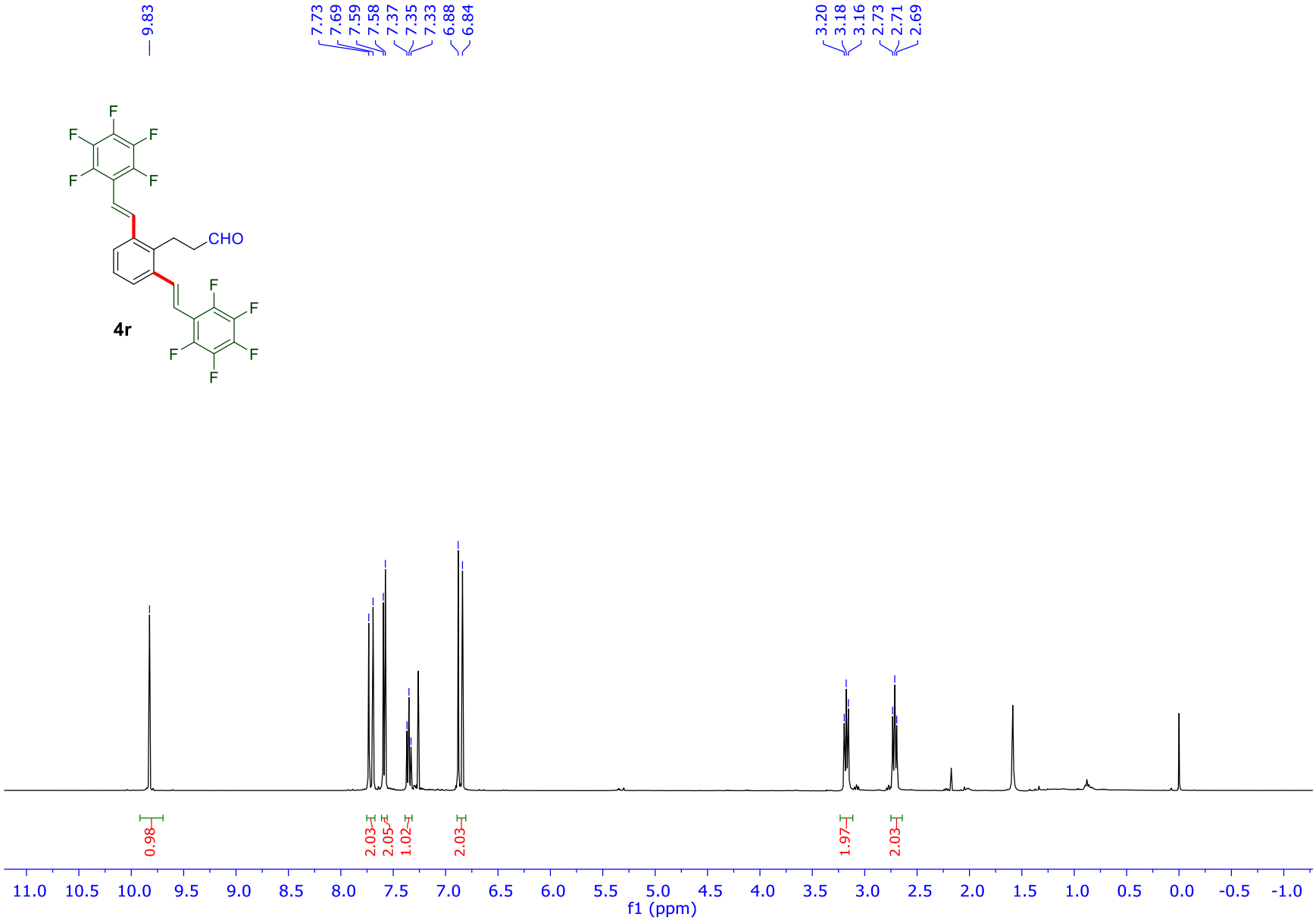
f1 (ppm)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7.73
7.69
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7.58
7.37
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7.33
6.88
6.84
3.20
3.18
3.16
2.73
2.71
2.69
F
F
F
F
F
CHO
F
F
F
F
F
4r
0.98
2.03
2.05
1.02
2.03
1.97
2.03
11.0
10.5
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
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2.5
2.0
1.5
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0.0
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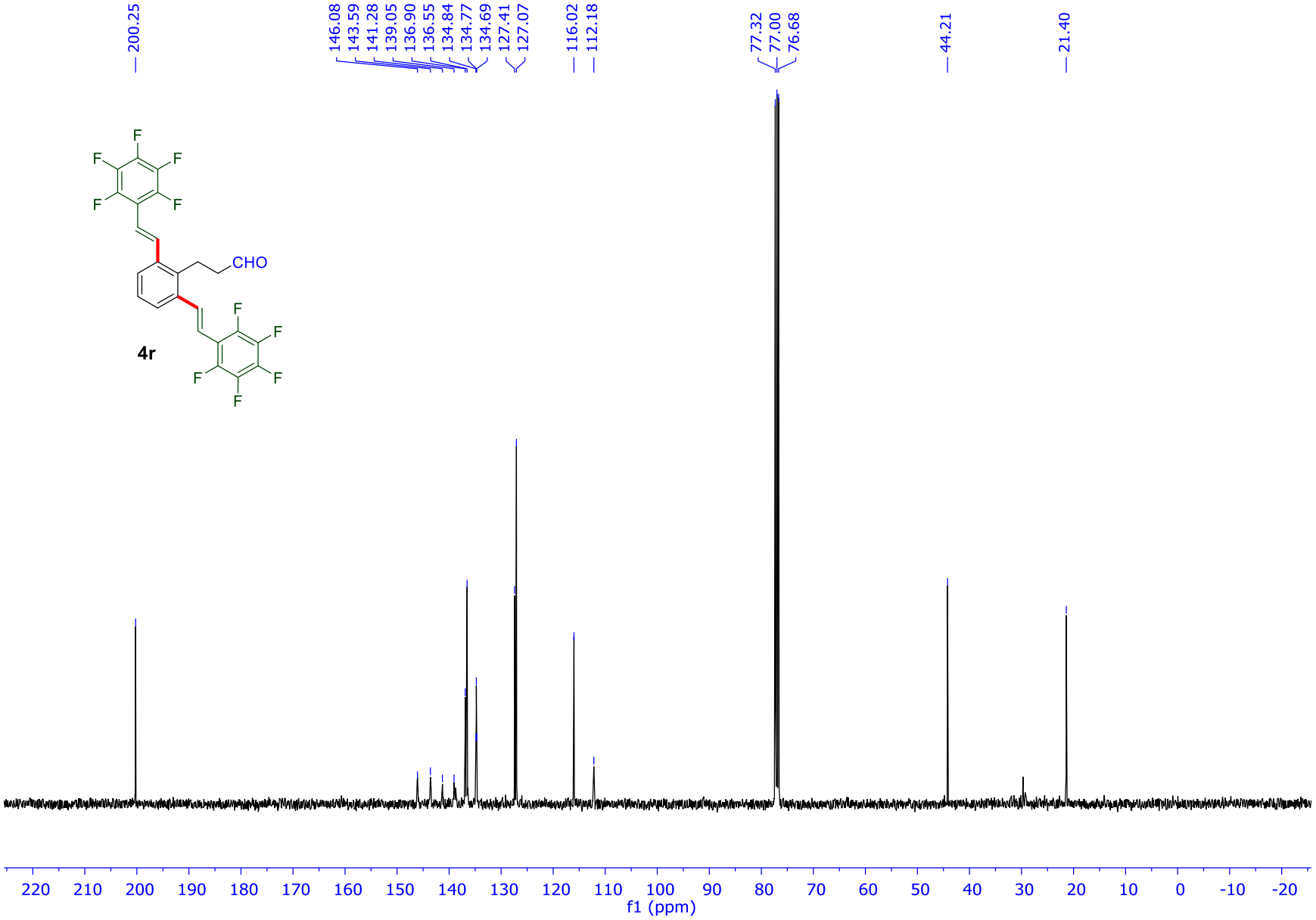
f1 (ppm)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143.59
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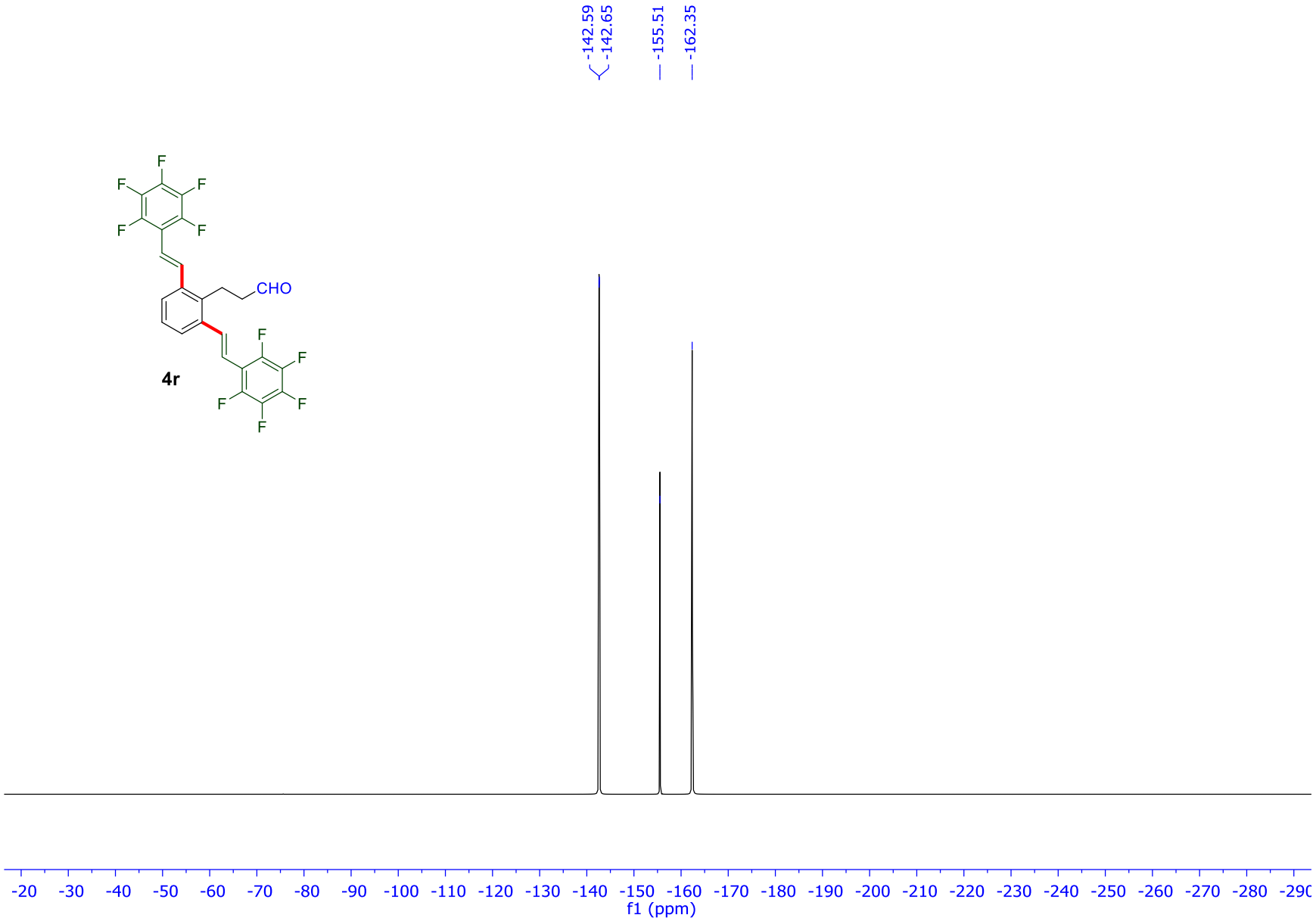
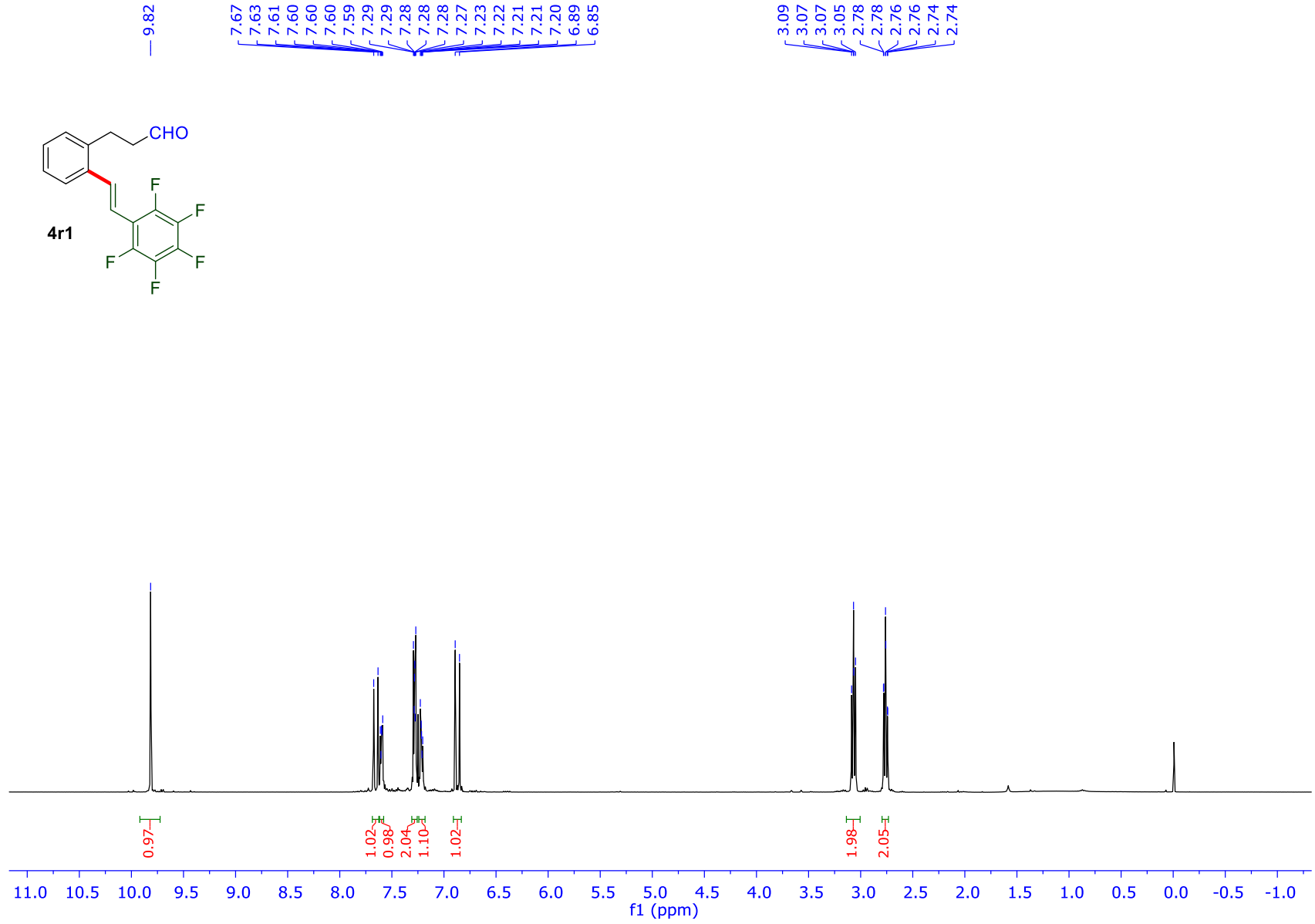
134.84
134.77
134.69
127.41
127.07
116.02
112.18
77.32
77.00
76.68
44.21
21.40
CHO
4r
f1 (ppm)


-142.59
-142.65
-155.51
-162.35
F
F
F
F
F
CHO
F
F
F
F
F
4r
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)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7.67
7.63
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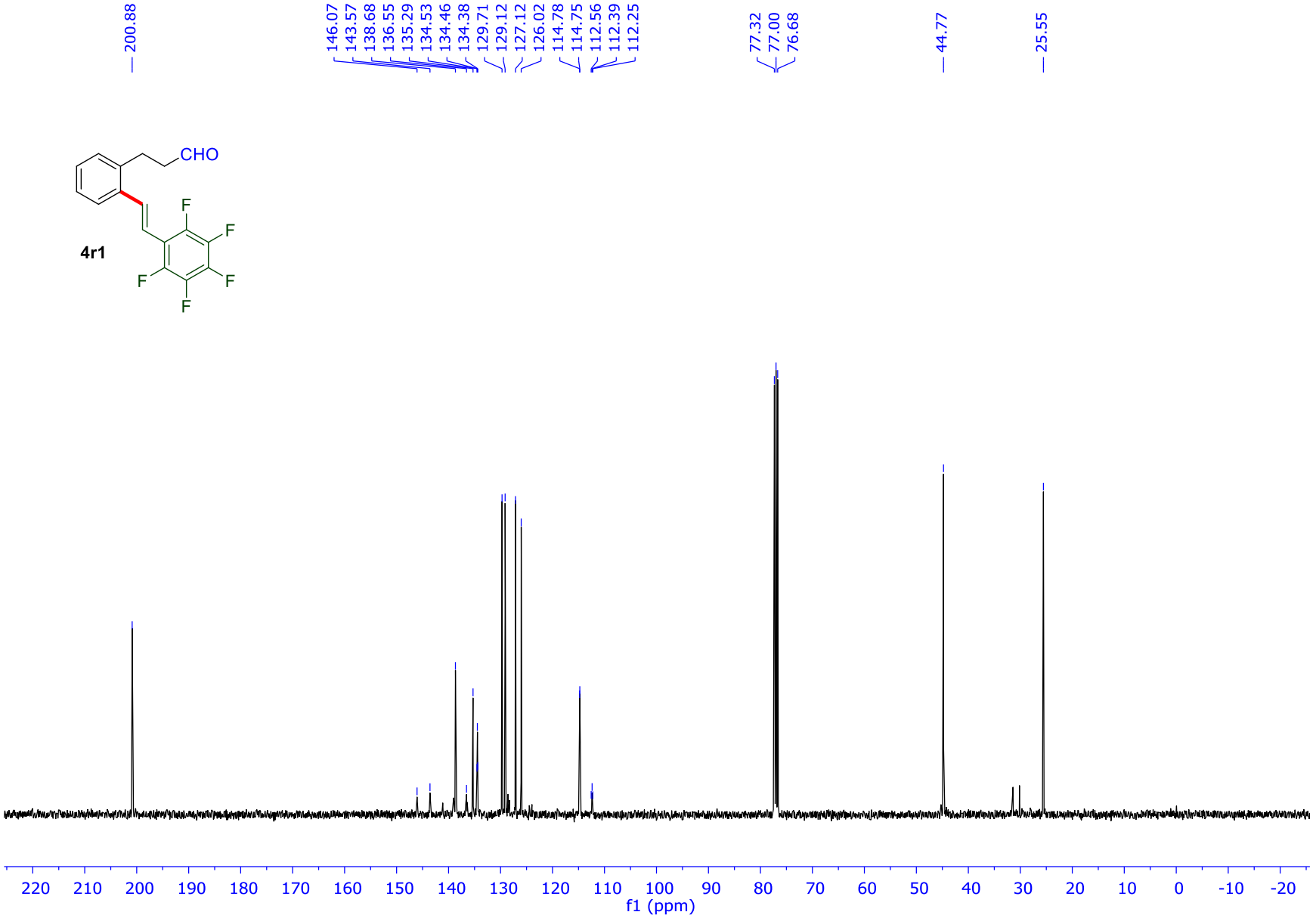
7.60
7.60
7.60
7.59
7.29
7.29
7.28
7.28
7.28
7.27
7.23
7.22
7.21
7.21
7.20
6.89
6.85
3.09
3.07
3.07
3.05
2.78
2.78
2.76
2.76
2.74
2.74
CHO
F
F
F
F
F
4r1
0.97
1.02
0.98
2.04
1.10
1.02
1.98
2.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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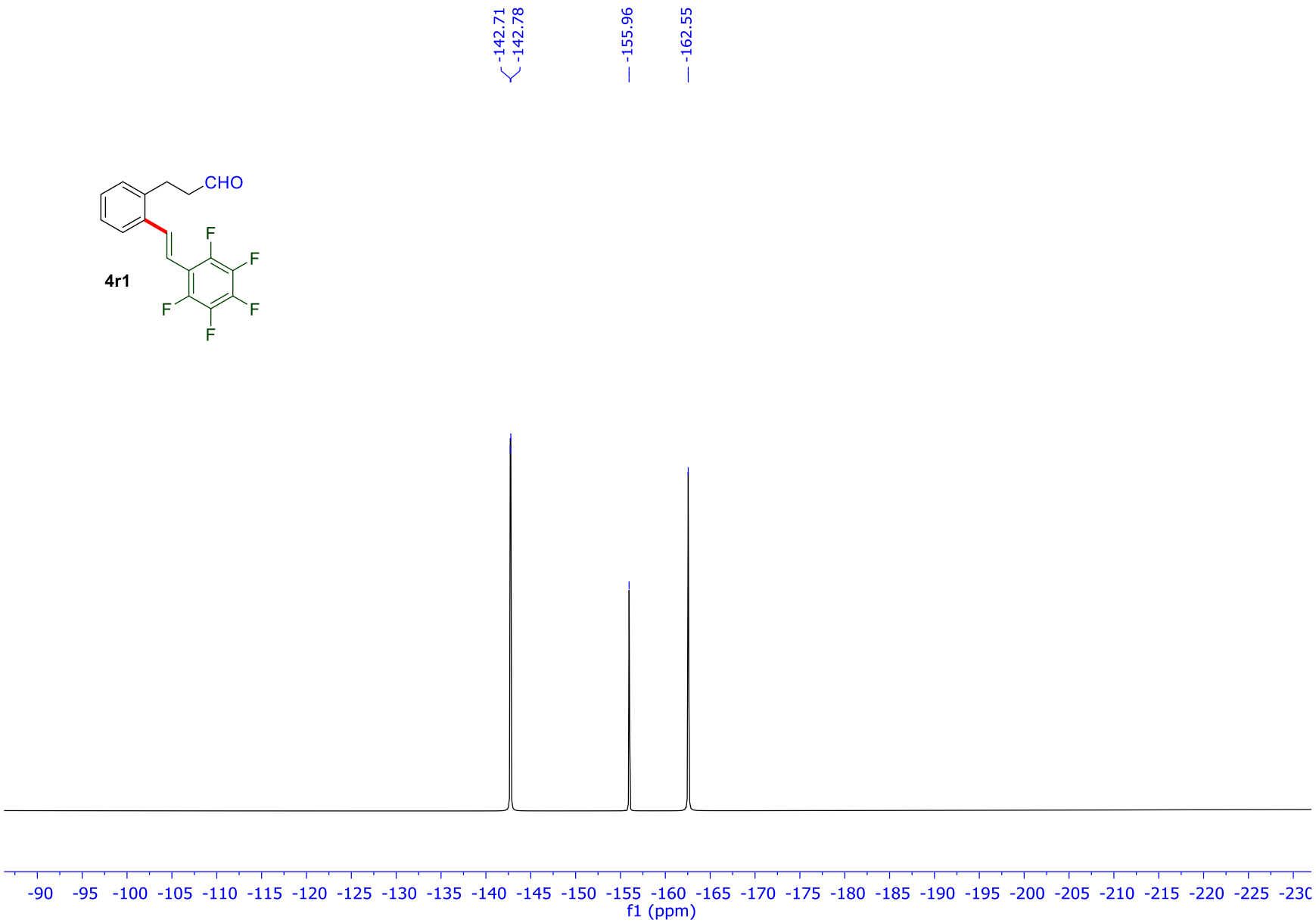
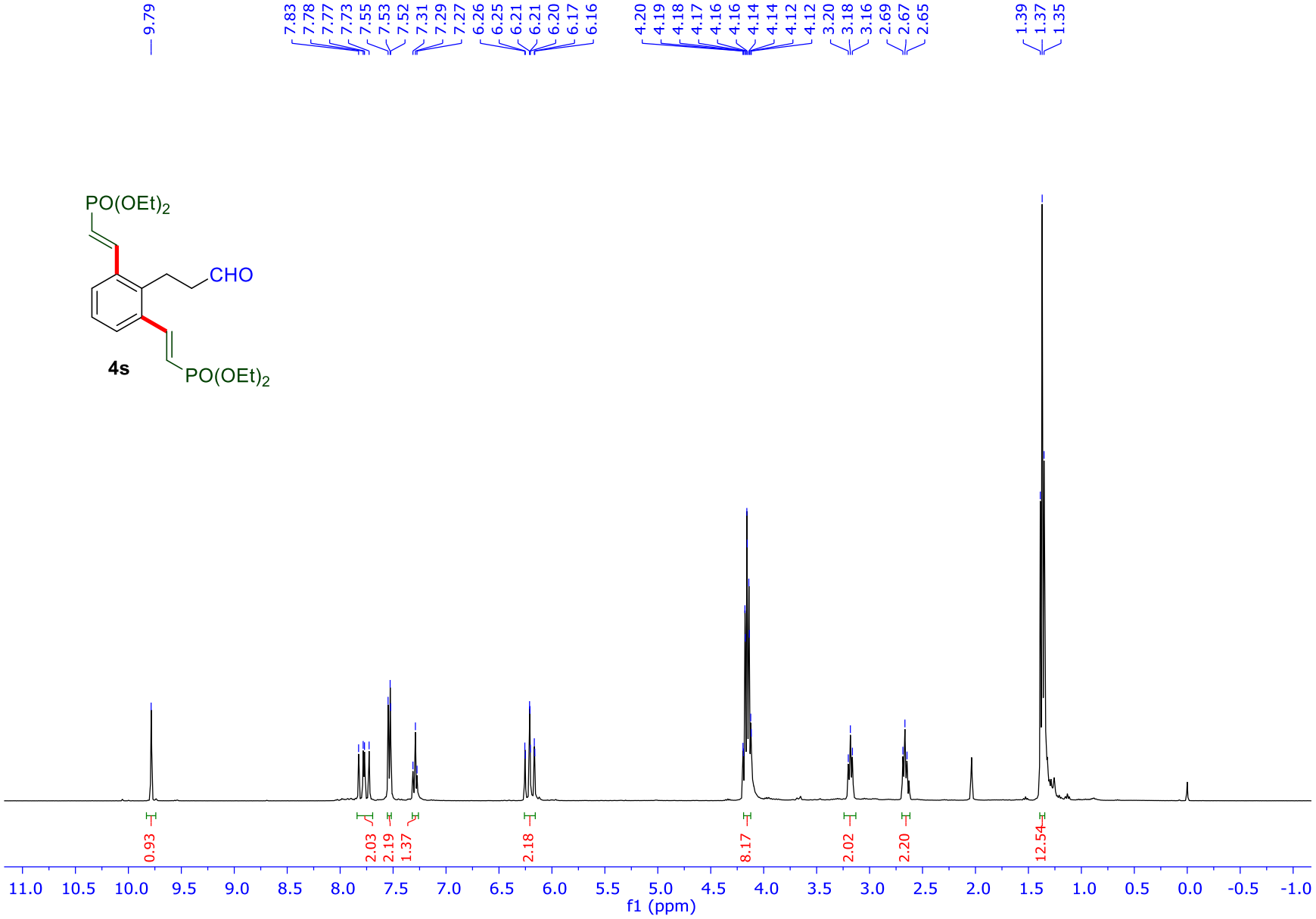
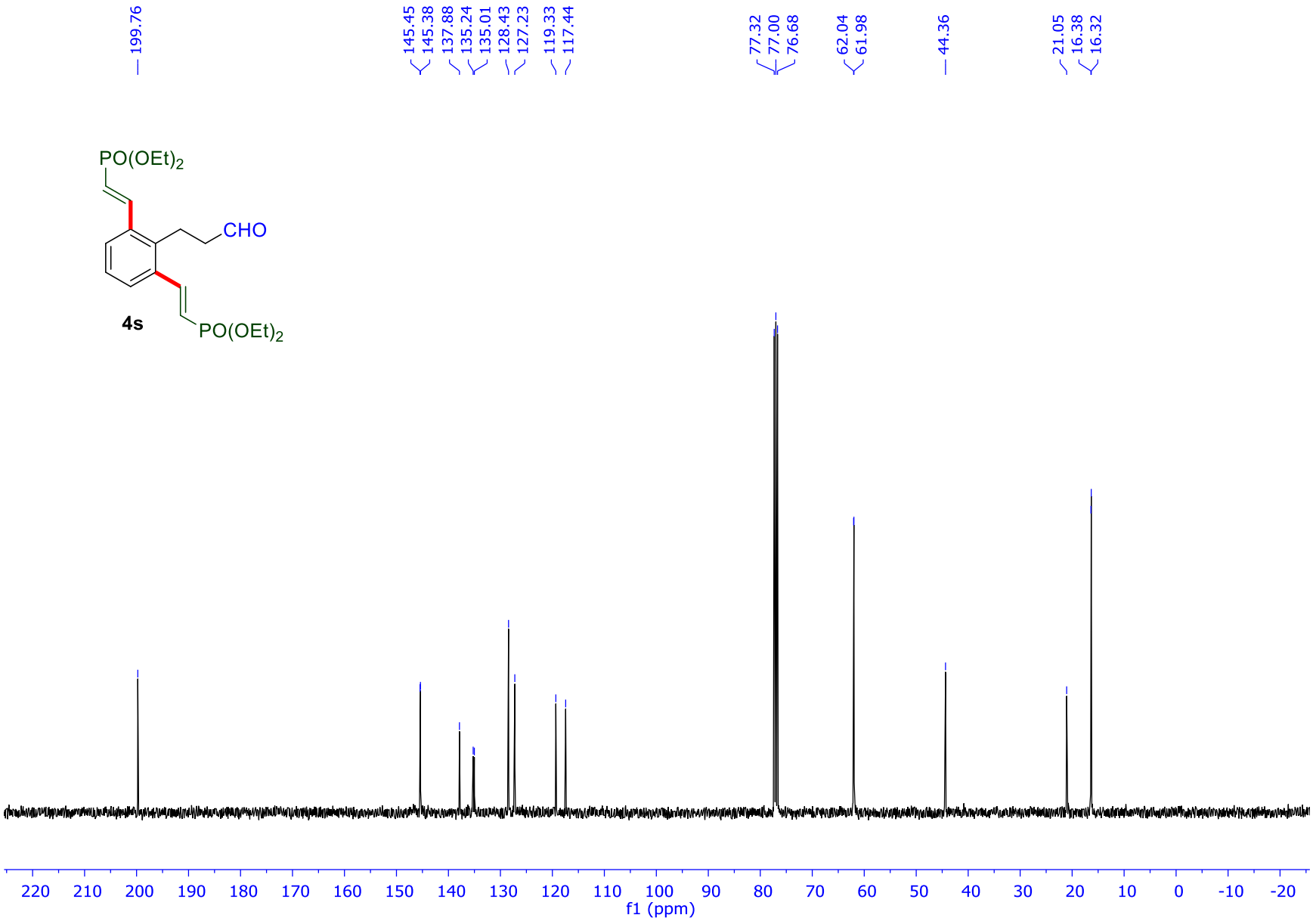
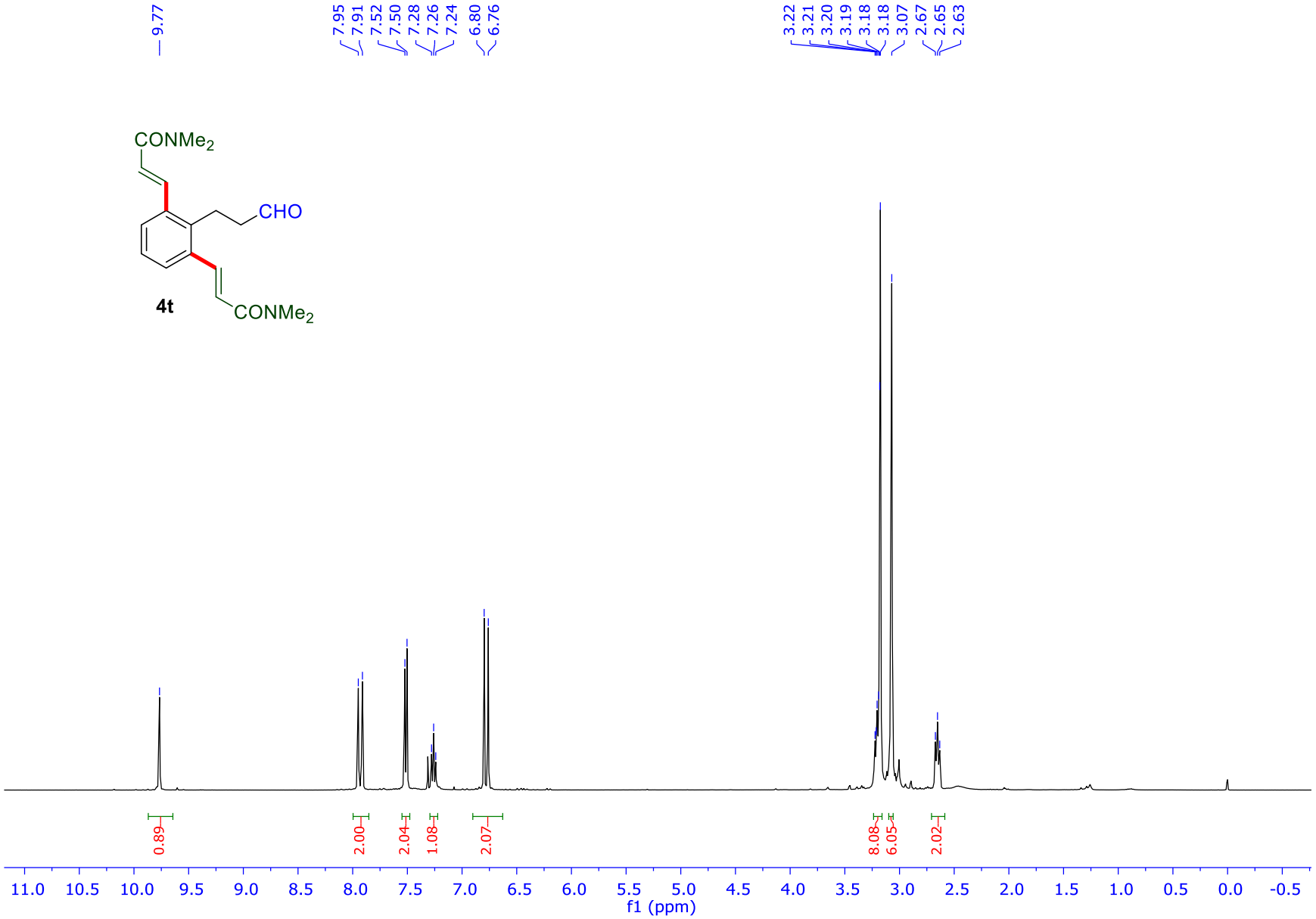
134.53
134.46
134.38
129.71
129.12
127.12
126.02
114.78
114.75
112.56
112.39
112.25
77.32
77.00
76.68
44.77
25.55
CHO
F
F
F
F
F
4r1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


-142.71
-142.78
-155.96
-162.55
CHO
F
F
F
F
F
4r1
-90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230
f1 (ppm)


9.79
7.83
7.78
7.77
7.73
7.55
7.53
7.52
7.31
7.29
7.27
6.26
6.25
6.21
6.21
6.20
6.17
6.16
4.20
4.19
4.18
4.17
4.16
4.16
4.14
4.14
4.12
4.12
3.20
3.18
3.16
2.69
2.67
2.65
1.39
1.37
1.35
PO(OEt)2
CHO
PO(OEt)2
4s
0.93
2.03
2.19
1.37
2.18
8.17
2.02
2.20
12.54
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)


199.76
145.45
145.38
137.88
135.24
135.01
128.43
127.23
119.33
117.44
77.32
77.00
76.68
62.04
61.98
44.36
21.05
16.38
16.32
PO(OEt)2
CHO
PO(OEt)2
4s
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)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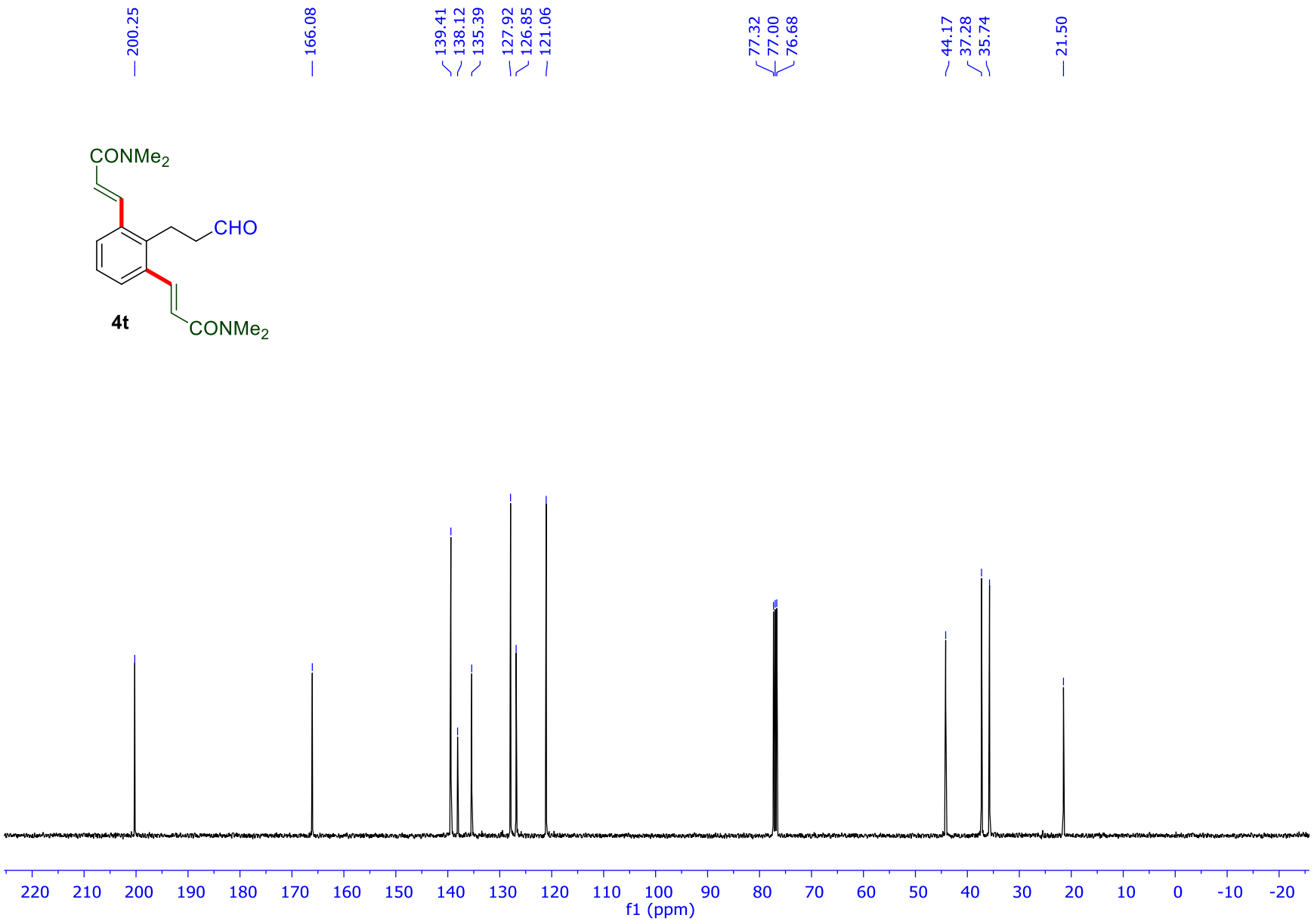
7.95
7.91
7.52
7.50
7.28
7.26
7.24
6.80
6.76
3.22
3.21
3.20
3.19
3.18
3.18
3.07
2.67
2.65
2.63
CONMe2
CHO
CONMe2
4t
0.89
2.00
2.04
1.08
2.07
8.08
6.05
2.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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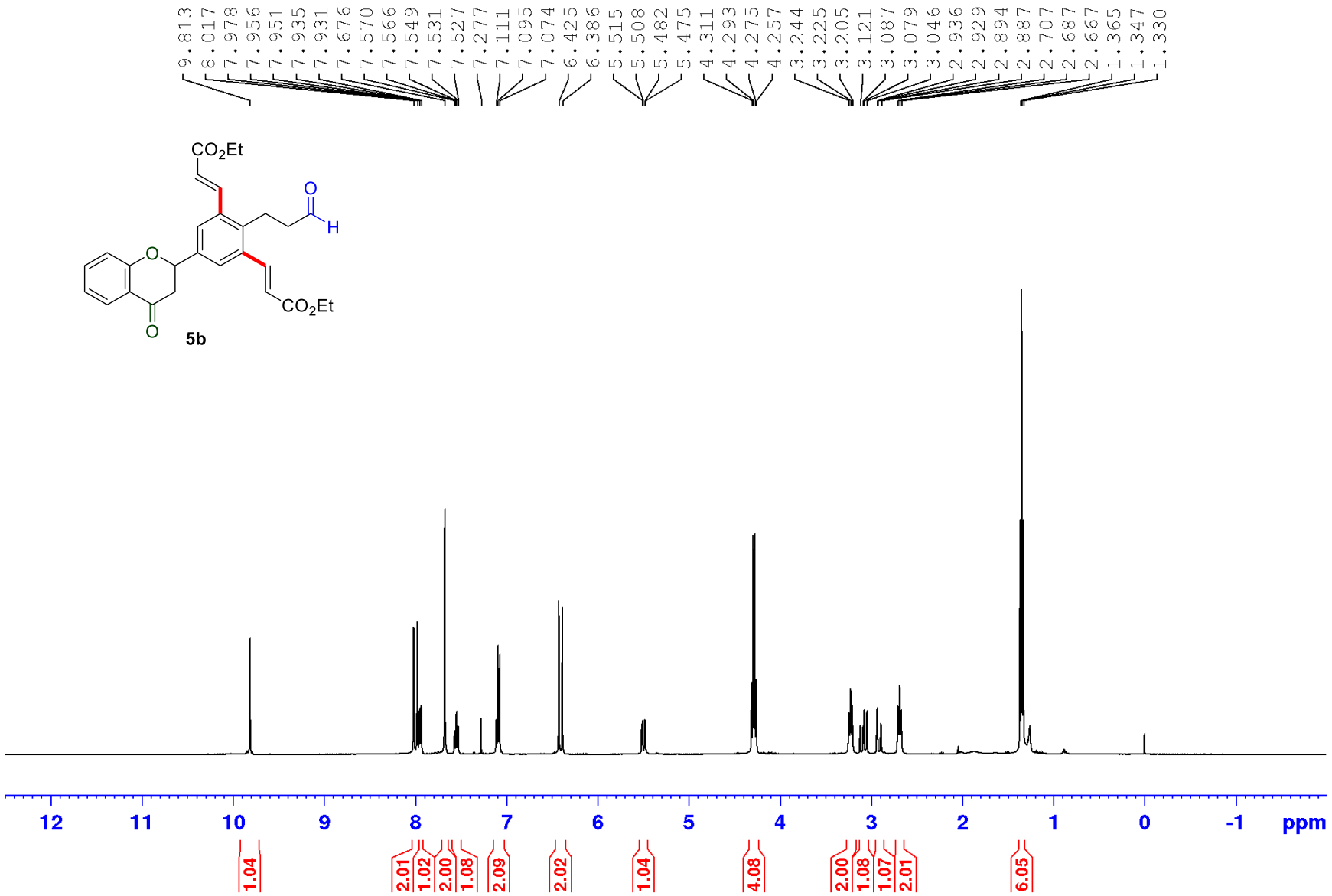
166.08
139.41
138.12
135.39
127.92
126.85
121.06
77.32
77.00
76.68
44.17
37.28
35.74
21.50
CONMe2
CHO
CONMe2
4t
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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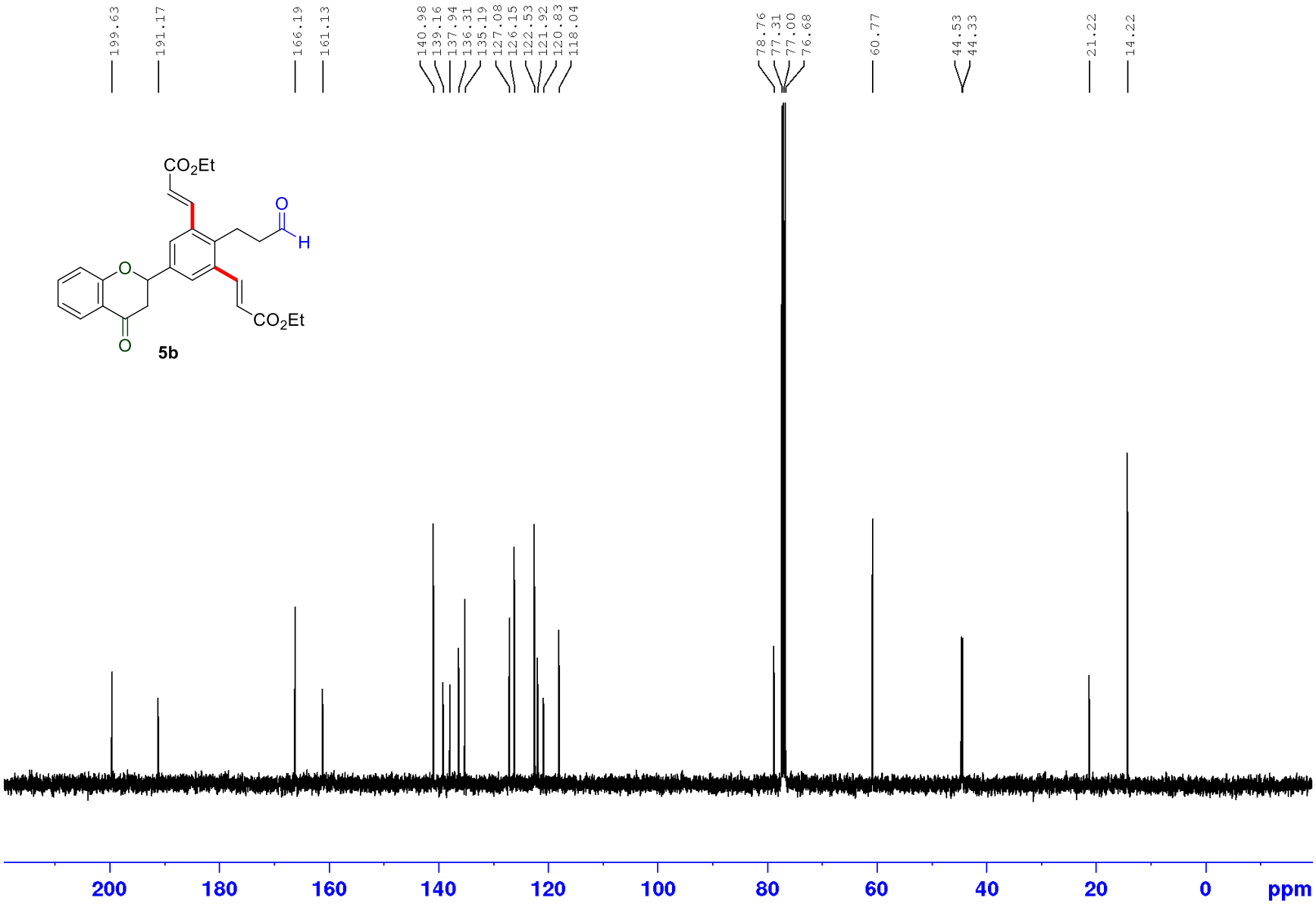
8.017
7.978
7.956
7.951
7.935
7.931
7.676
7.570
7.566
7.549
7.531
7.527
7.277
7.111
7.095
7.074
6.425
6.386
5.515
5.508
5.482
5.475
4.311
4.293
4.275
4.257
3.244
3.225
3.205
3.121
3.087
3.079
3.046
2.936
2.929
2.894
2.887
2.707
2.687
2.667
1.365
1.347
1.330
CO2Et
O
H
O
CO2Et
O
5b
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.04
2.01
1.02
2.00
1.08
2.09
2.02
1.04
4.08
2.00
1.08
1.07
2.01
6.05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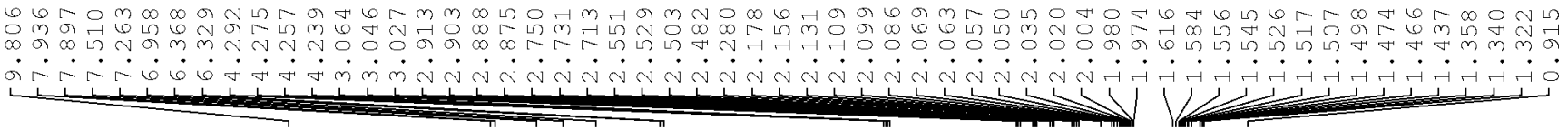
191.17
166.19
161.13
140.98
139.16
137.94
136.31
135.19
127.08
126.15
122.53
121.92
120.83
118.04
78.76
77.31
77.00
76.68
60.77
44.53
44.33
21.22
14.22
CO2Et
O
H
O
CO2Et
O
5b
200
180
160
140
120
100
80
60
40
20
0
ppm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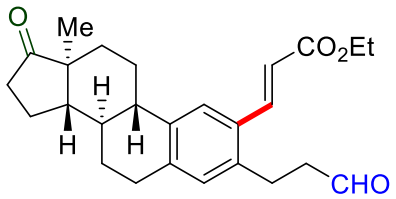
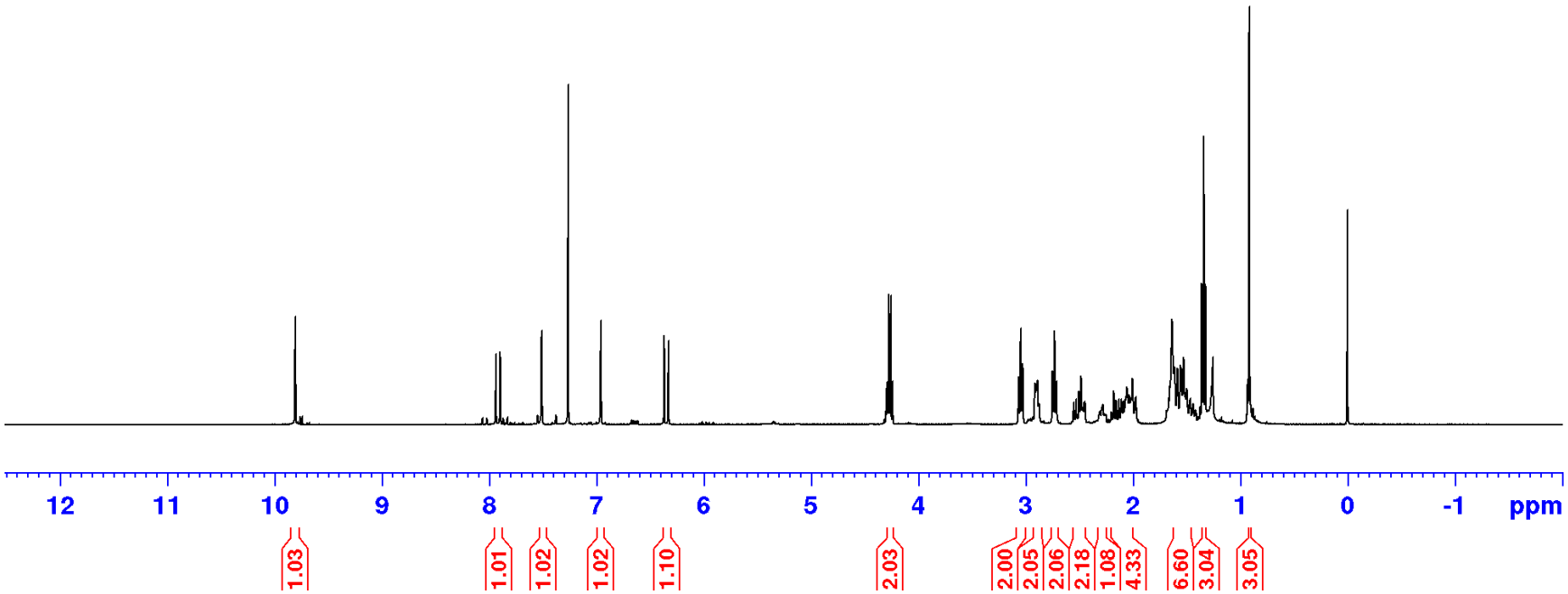
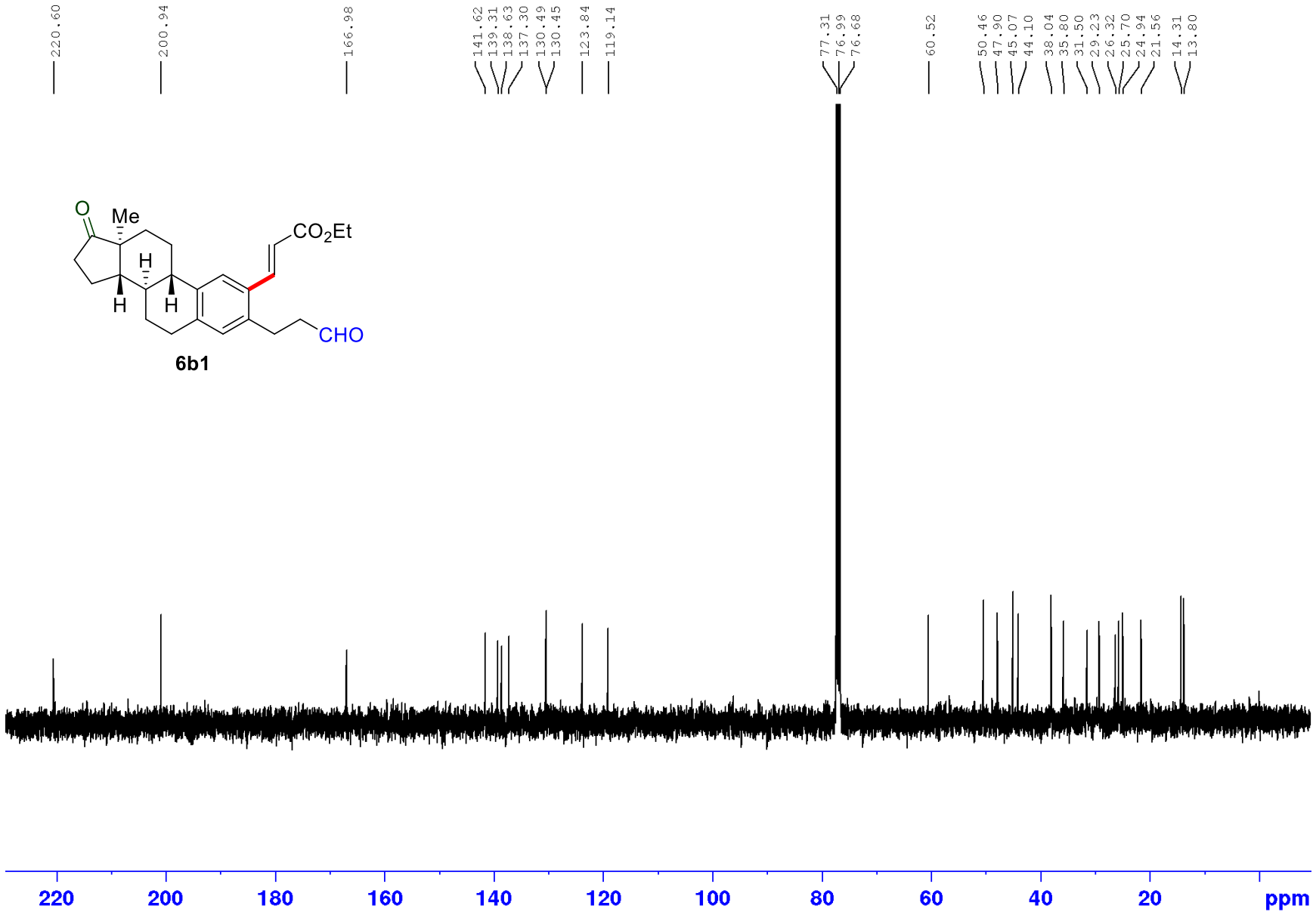
7.510
7.263
6.958
6.368
6.329
4.292
4.275
4.257
4.239
3.064
3.046
3.027
2.913
2.903
2.888
2.875
2.750
2.731
2.713
2.551
2.529
2.503
2.482
2.280
2.178
2.156
2.131
2.109
2.099
2.086
2.069
2.063
2.057
2.050
2.035
2.020
2.004
1.980
1.974
1.616
1.584
1.556
1.545
1.526
1.517
1.507
1.498
1.474
1.466
1.437
1.358
1.340
1.322
0.915


O
Me
H
H
H
CO2Et
CHO

6b1


12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.03
1.01
1.02
1.02
1.10
2.03
2.00
2.05
2.06
2.18
1.08
4.33
6.60
3.04
3.05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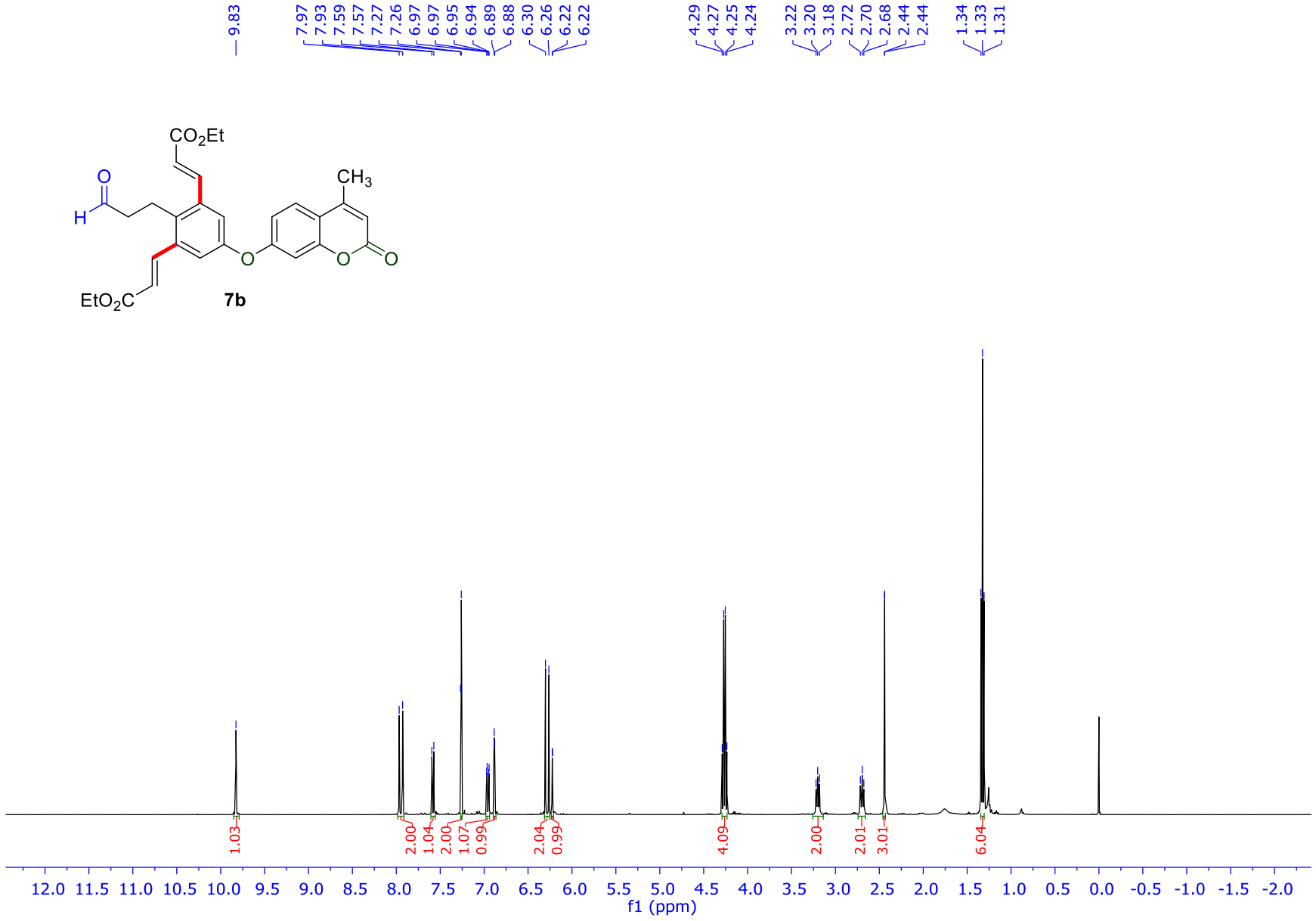
200.94
166.98
141.62
139.31
138.63
137.30
130.49
130.45
123.84
119.14
77.31
76.99
76.68
60.52
50.46
47.90
45.07
44.10
38.04
35.80
31.50
29.23
26.32
25.70
24.94
21.56
14.31
13.80
O
Me
H
H
H
CO2Et
CHO
6b1
220
200
180
160
140
120
100
80
60
40
20
ppm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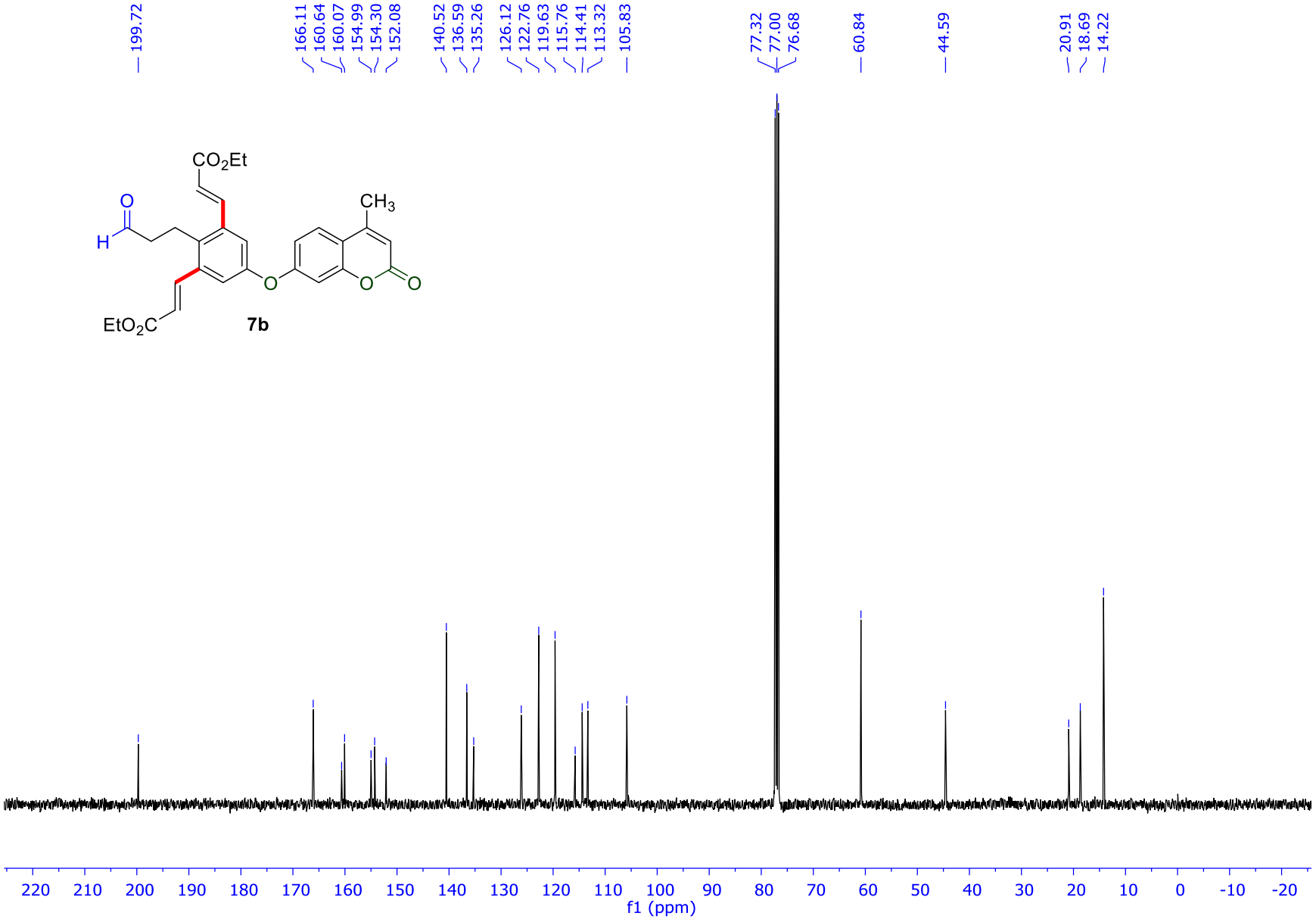
7.97
7.93
7.59
7.57
7.27
7.26
6.97
6.97
6.95
6.94
6.89
6.88
6.30
6.26
6.22
6.22
4.29
4.27
4.25
4.24
3.22
3.20
3.18
2.72
2.70
2.68
2.44
2.44
1.34
1.33
1.31
CO2Et
O
H
CH3
O
O
O
EtO2C
7b
1.03
2.00
1.04
2.00
1.07
0.99
2.04
0.99
4.09
2.00
2.01
3.01
6.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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 -1.0 -1.5 -2.0
f1 (ppm)


199.72
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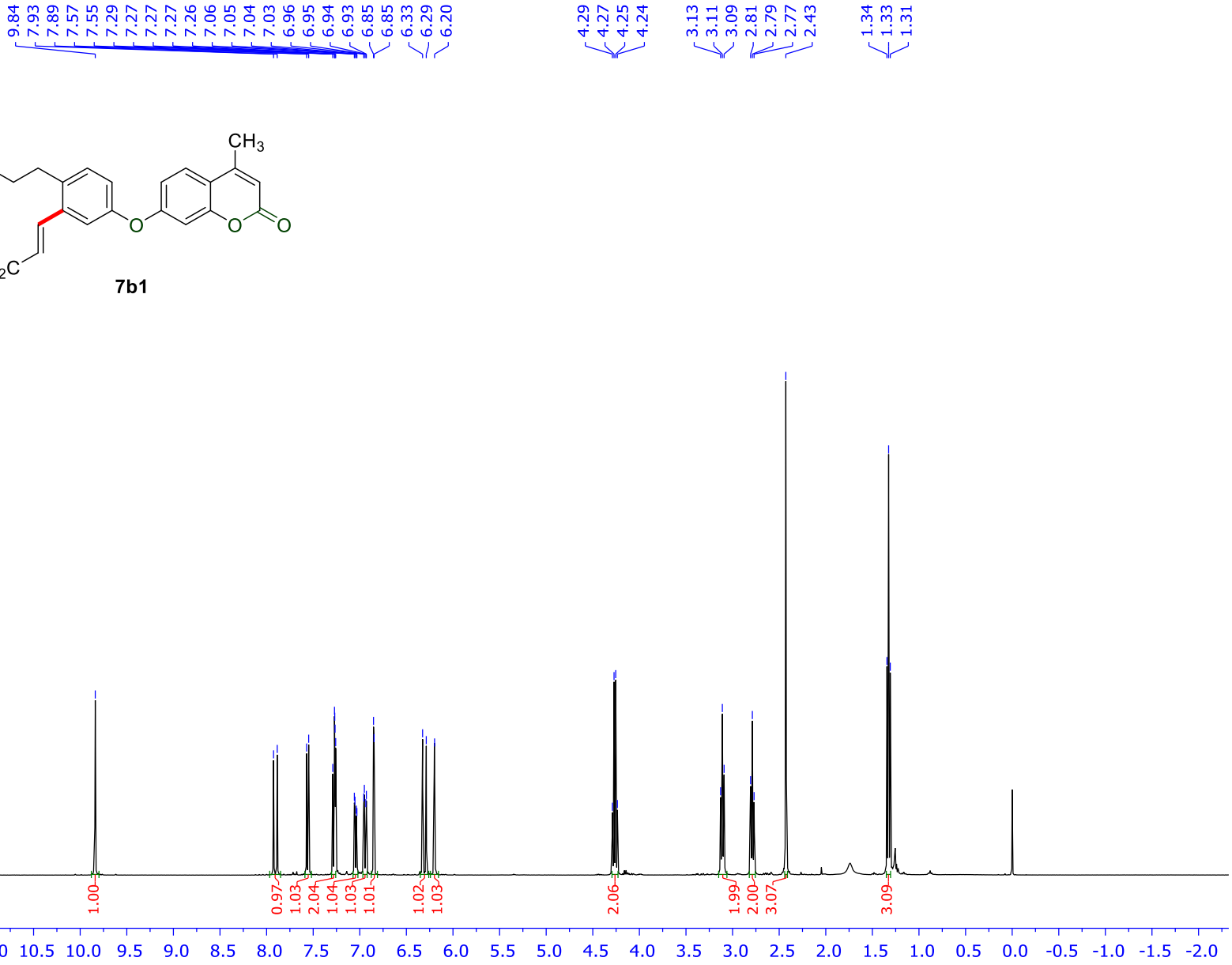
160.64
160.07
154.99
154.30
152.08
140.52
136.59
135.26
126.12
122.76
119.63
115.76
114.41
113.32
105.83
77.32
77.00
76.68
60.84
44.59
20.91
18.69
14.22
CO2Et
O
H
CH3
O
O
O
EtO2C
7b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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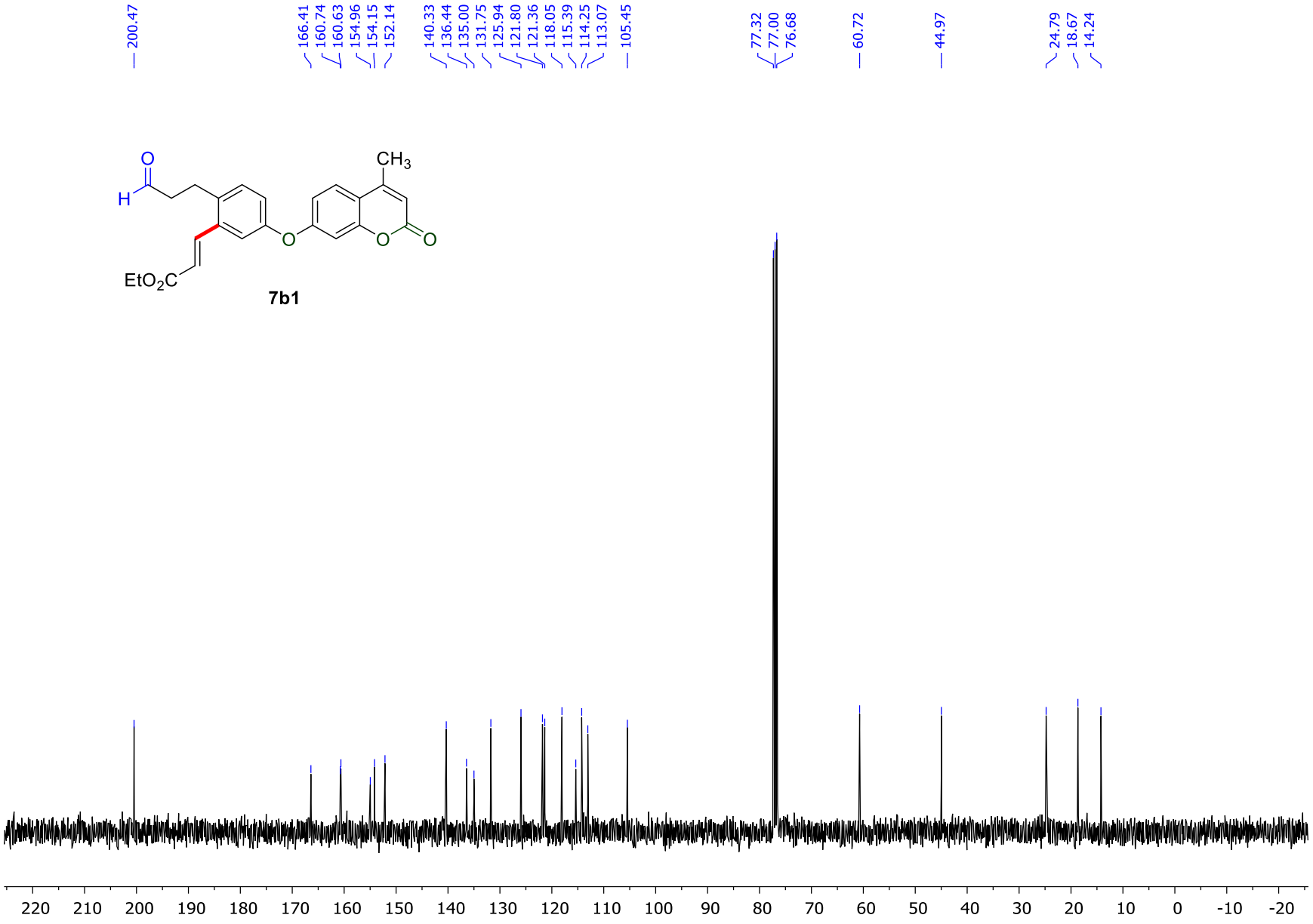
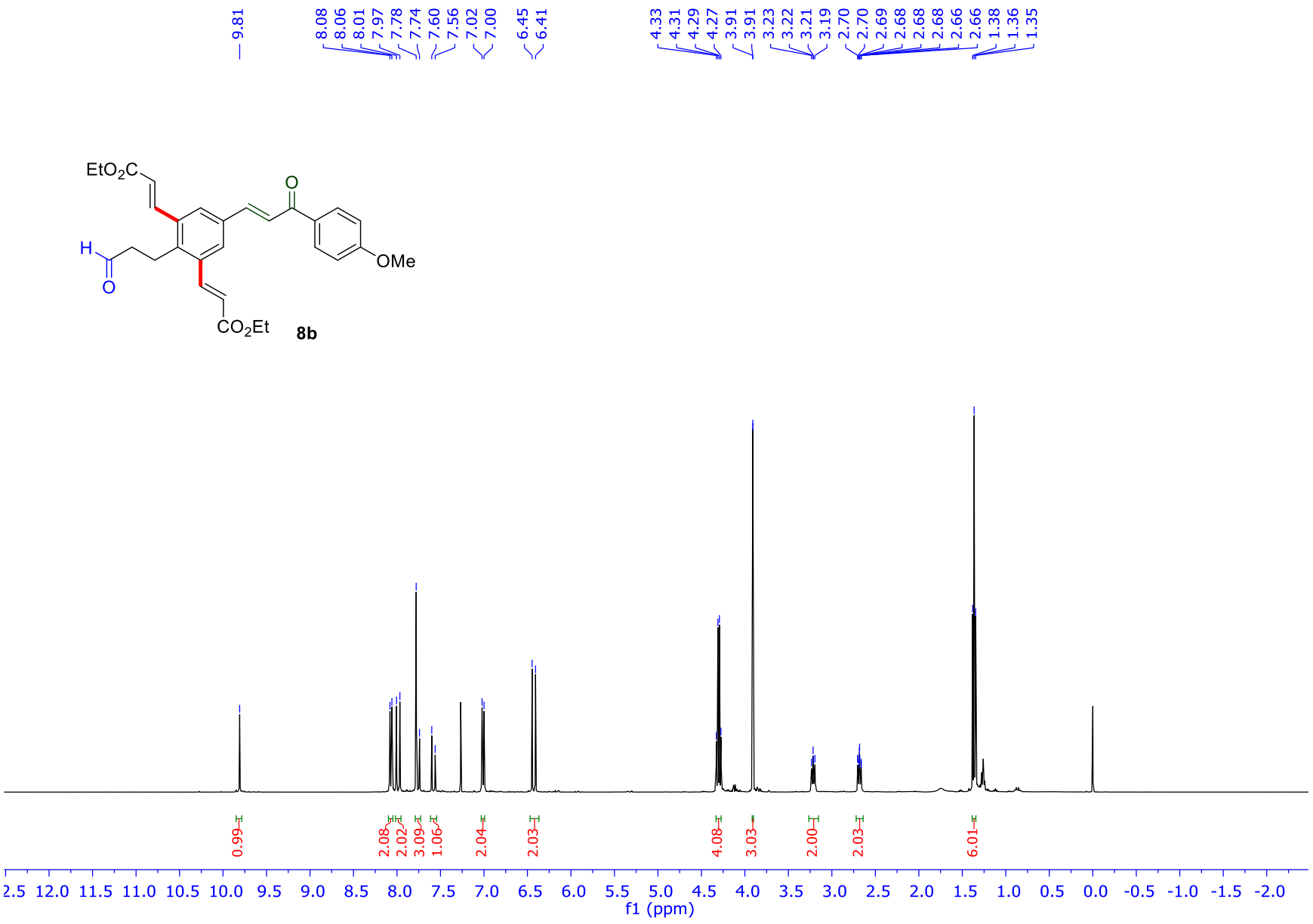
7.93
7.89
7.57
7.55
7.29
7.27
7.27
7.27
7.26
7.06
7.05
7.04
7.03
6.96
6.95
6.94
6.93
6.85
6.85
6.33
6.29
6.20
4.29
4.27
4.25
4.24
3.13
3.11
3.09
2.81
2.79
2.77
2.43
1.34
1.33
1.31
O
H
CH3
O
O
O
EtO2C
1.00
0.97
1.03
2.04
1.04
1.03
1.01
1.02
1.03
2.06
1.99
2.00
3.07
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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 -1.0 -1.5 -2.0

7b1


200.47
166.41
160.74
160.63
154.96
154.15
152.14
140.33
136.44
135.00
131.75
125.94
121.80
121.36
118.05
115.39
114.25
113.07
105.45
77.32
77.00
76.68
60.72
44.97
24.79
18.67
14.24
O
H
CH3
O
O
O
EtO2C
7b1
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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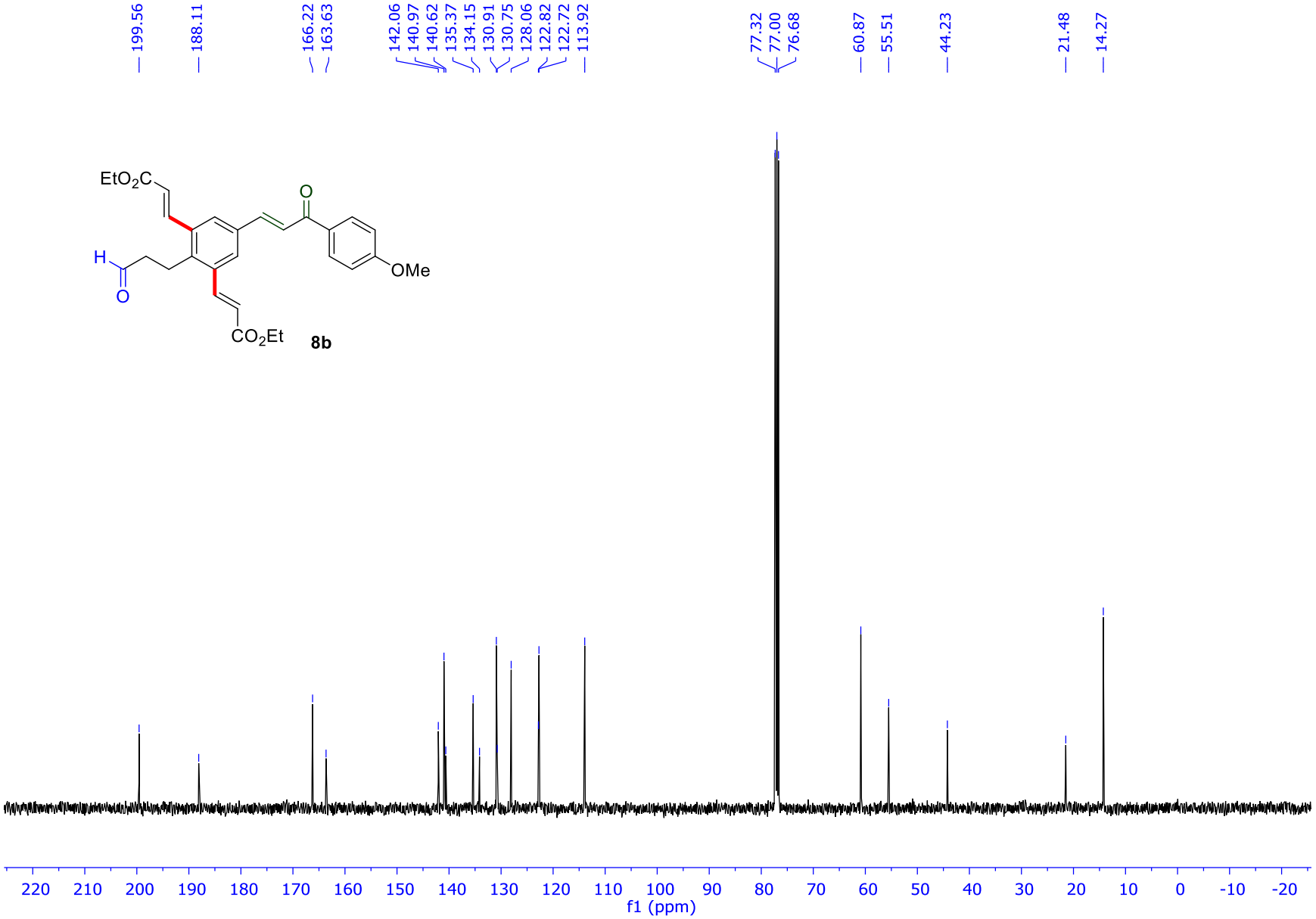
8.08
8.06
8.01
7.97
7.78
7.74
7.60
7.56
7.02
7.00
6.45
6.41
4.33
4.31
4.29
4.27
3.91
3.23
3.22
3.21
3.19
2.70
2.70
2.69
2.68
2.68
2.68
2.66
2.66
1.38
1.36
1.35
EtO2C
O
H
O
OMe
CO2Et
8b
0.99
2.08
2.02
3.09
1.06
2.04
2.03
4.08
3.03
2.00
2.03
6.01
f1 (ppm)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166.22
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140.97
140.62
135.37
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130.91
130.75
128.06
122.82
122.72
113.92
77.32
77.00
76.68
60.87
55.51
44.23
21.48
14.27
EtO2C
O
H
O
OMe
CO2Et
8b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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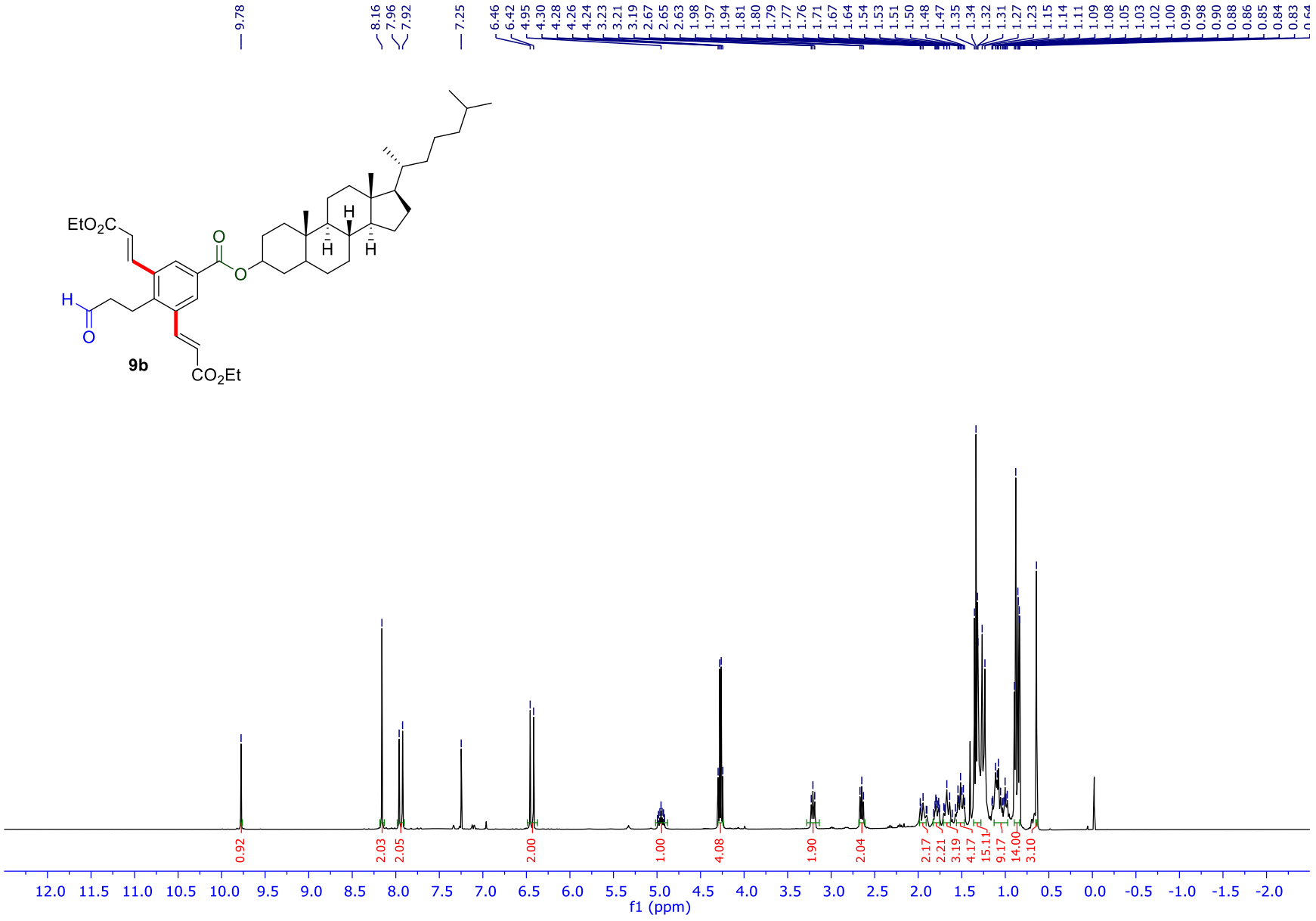
-10
-20
f1 (ppm)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6.42
4.95
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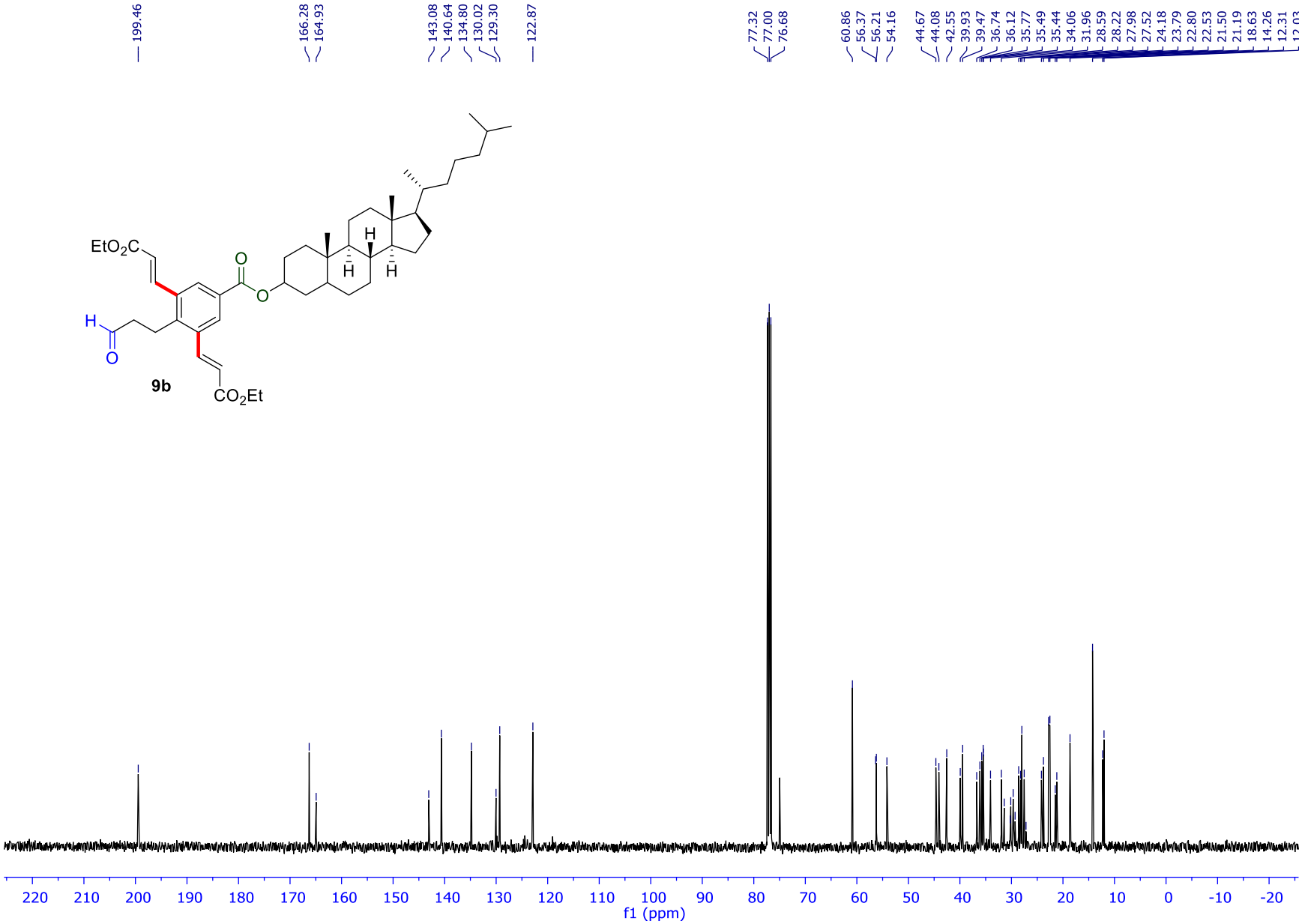
4.28
4.26
4.24
3.23
3.21
3.19
2.67
2.65
2.63
1.98
1.97
1.94
1.81
1.80
1.79
1.77
1.76
1.71
1.67
1.64
1.54
1.53
1.51
1.50
1.48
1.47
1.35
1.34
1.32
1.31
1.27
1.23
1.15
1.14
1.11
1.09
1.08
1.05
1.03
1.02
1.00
0.99
0.98
0.90
0.88
0.86
0.85
0.84
0.83
EtO2C
O
O
H
O
H
H
H
9b
CO2Et
0.92
2.03
2.05
2.00
1.00
4.08
1.90
2.04
2.17
2.21
3.19
4.17
15.11
9.17
14.00
3.10
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 -1.0 -1.5 -2.0
f1 (ppm)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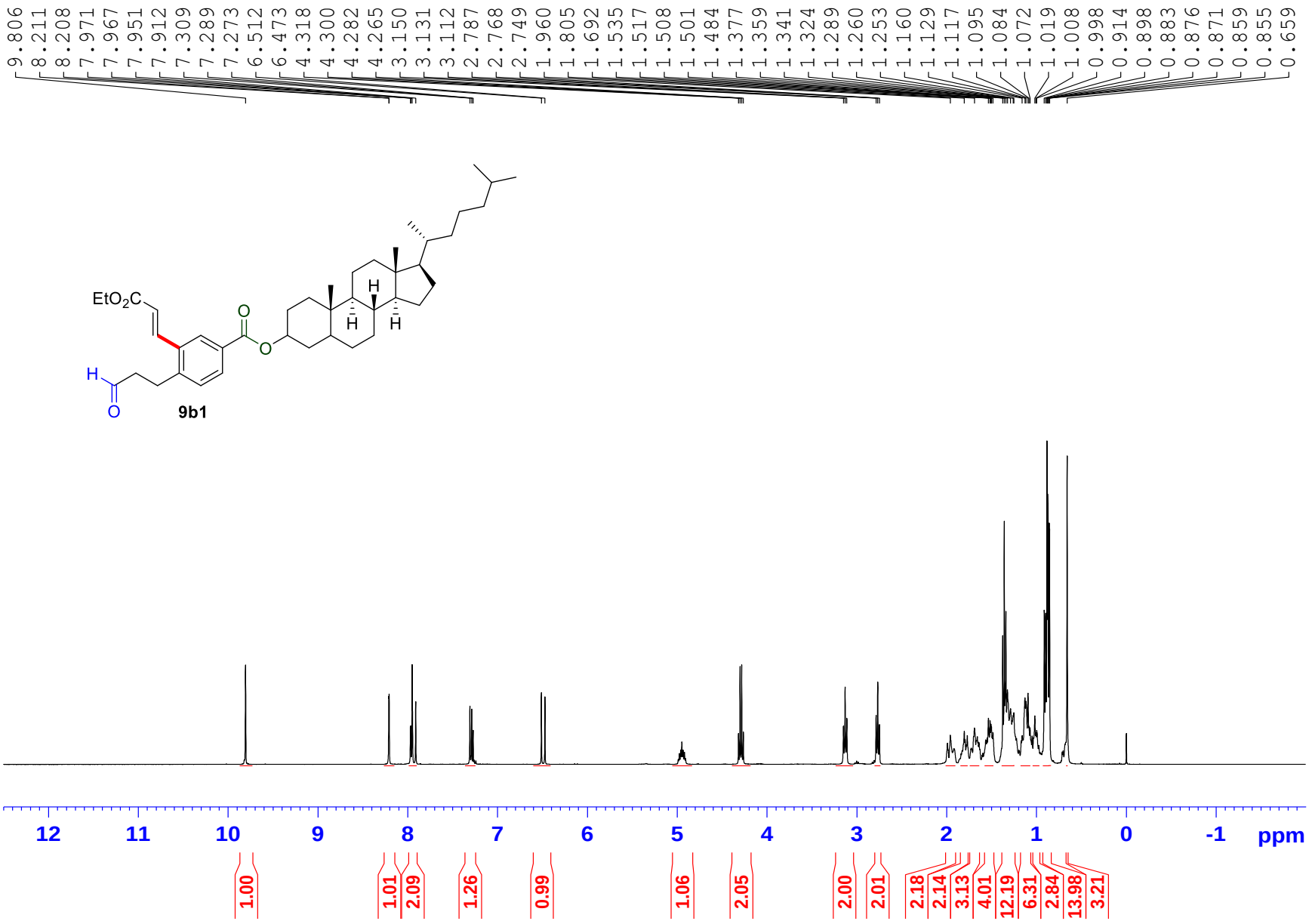
77.00
76.68
60.86
56.37
56.21
54.16
44.67
44.08
42.55
39.93
39.47
36.74
36.12
35.77
35.49
35.44
34.06
31.96
28.59
28.22
27.98
27.52
24.18
23.79
22.80
22.53
21.50
21.19
18.63
14.26
12.31
EtO2C
O
O
H
O
H
H
H
9b
CO2Et
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.273
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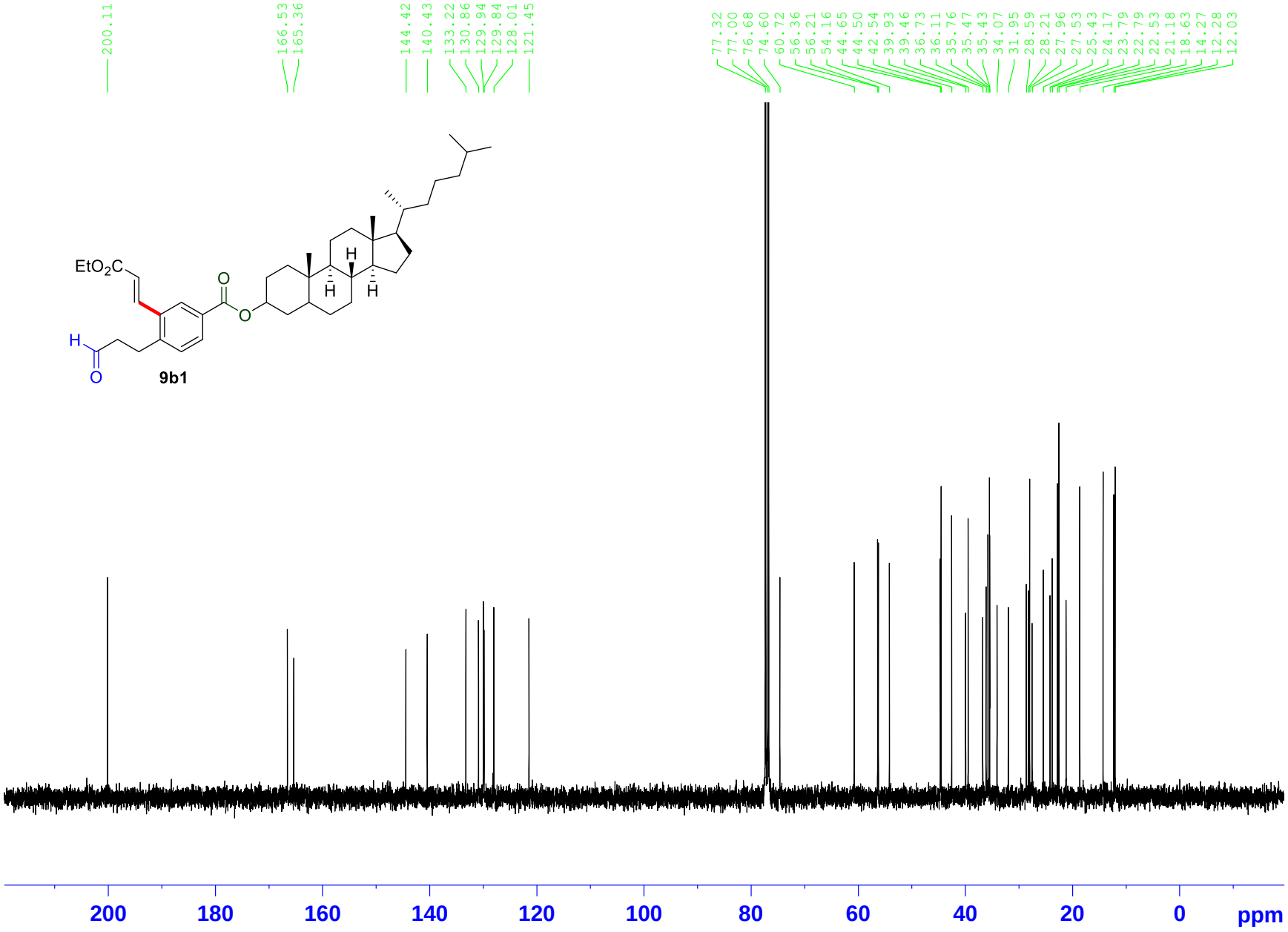
6.473
4.318
4.300
4.282
4.265
3.150
3.131
3.112
2.787
2.768
2.749
1.960
1.805
1.692
1.535
1.517
1.508
1.501
1.484
1.377
1.359
1.341
1.324
1.289
1.260
1.253
1.160
1.129
1.117
1.095
1.084
1.072
1.019
1.008
0.998
0.914
0.898
0.883
0.876
0.871
0.859
0.855
0.659
EtO2C
O
O
H
O
H
H
H
9b1
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.01
2.09
1.26
0.99
1.06
2.05
2.00
2.01
2.18
2.14
3.13
4.01
12.19
6.31
2.84
13.98
3.21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165.36
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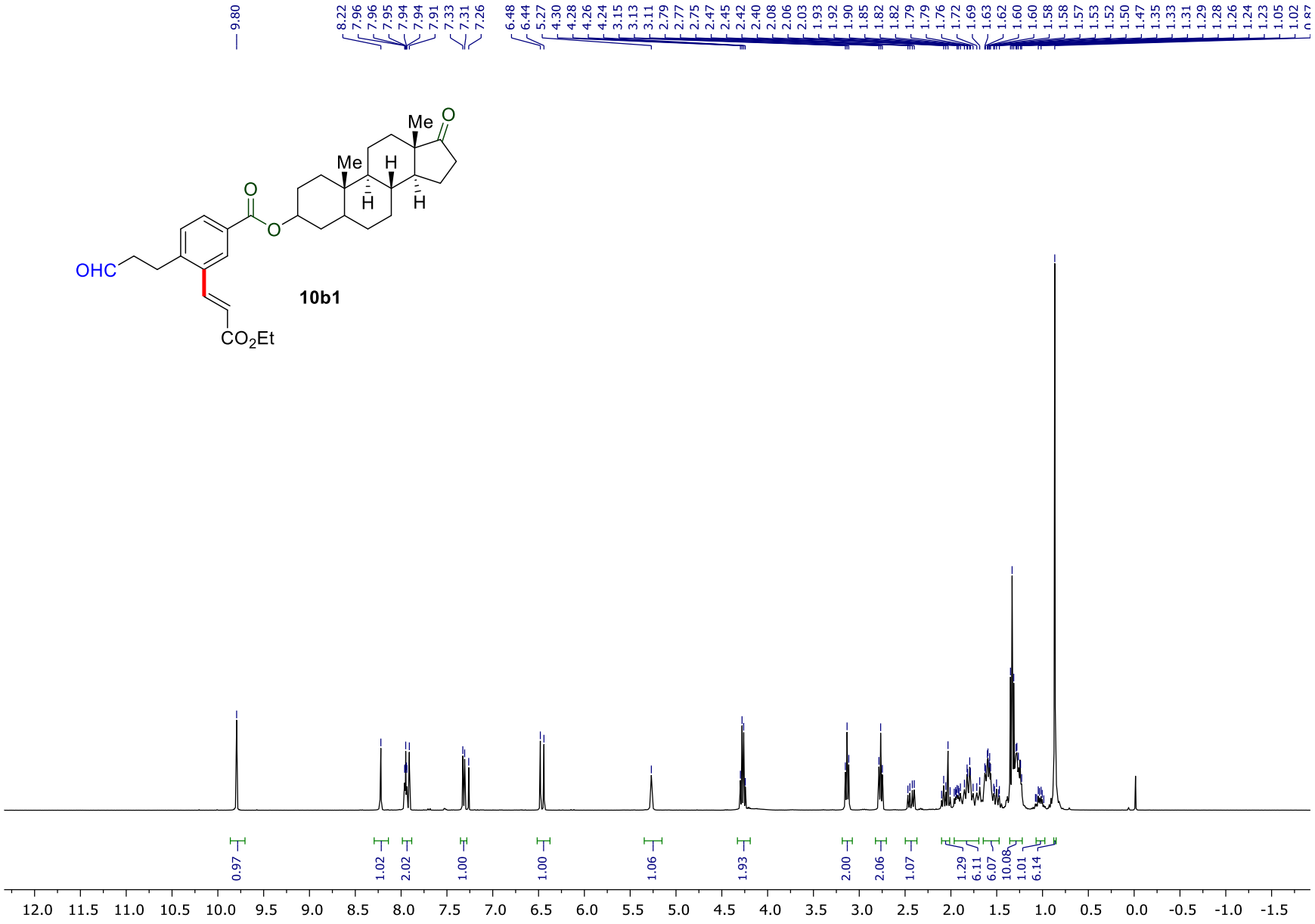
133.22
130.86
129.94
129.84
128.01
121.45
77.32
77.00
76.68
74.60
60.72
56.36
56.21
54.16
44.65
44.50
42.54
39.93
39.46
36.73
36.11
35.76
35.47
35.43
34.07
31.95
28.59
28.21
27.96
27.53
25.43
24.17
23.79
22.79
22.53
21.18
18.63
14.27
12.28
12.03
EtO2C
O
O
H
O
H
H
H
9b1
200
180
160
140
120
100
80
60
40
20
0
ppm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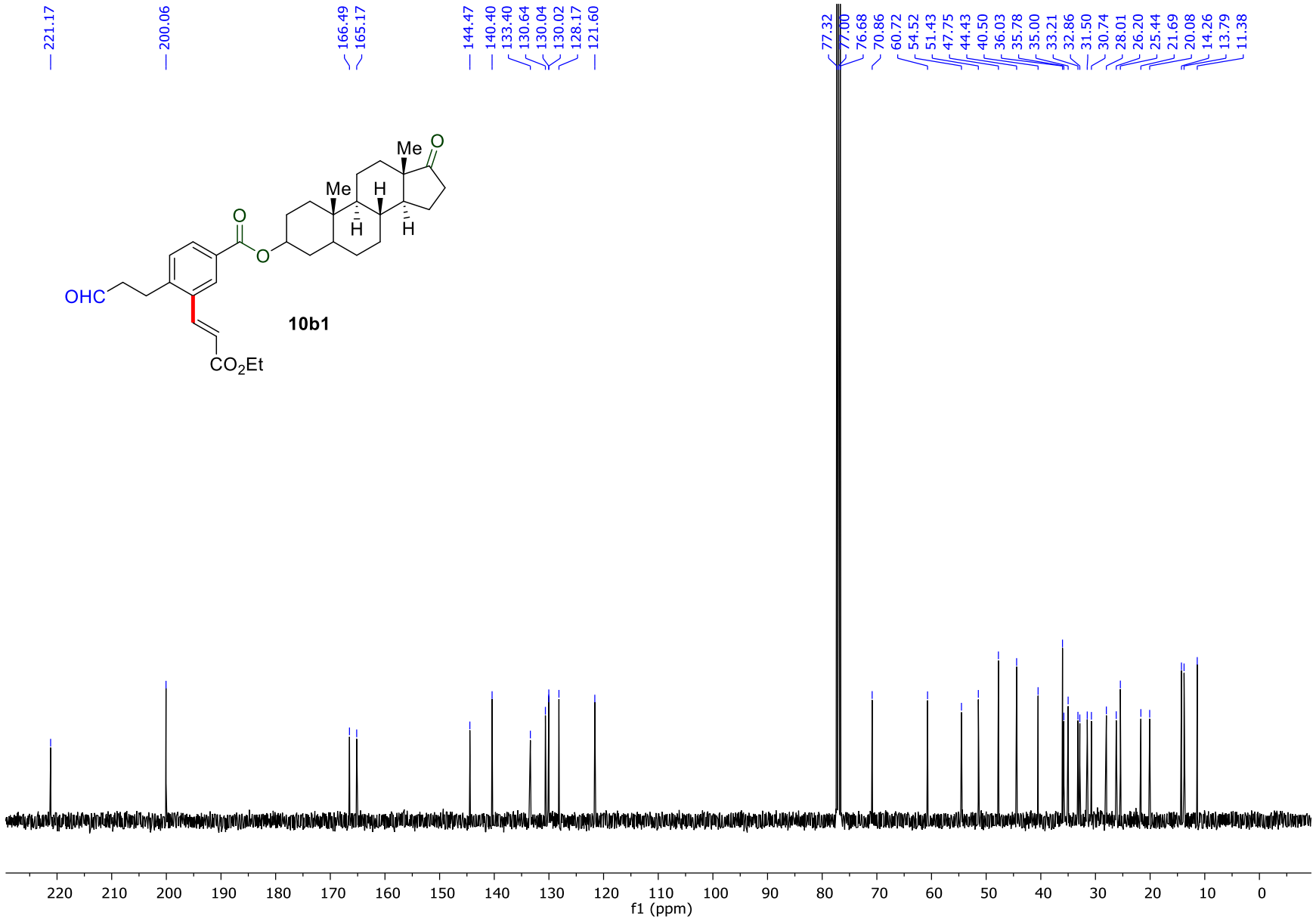
8.22
7.96
7.96
7.95
7.94
7.94
7.91
7.33
7.31
7.26
6.48
6.44
5.27
4.30
4.28
4.26
4.24
3.15
3.13
3.11
2.79
2.77
2.75
2.47
2.45
2.42
2.40
2.08
2.06
2.03
1.93
1.92
1.90
1.85
1.82
1.82
1.79
1.79
1.76
1.72
1.69
1.63
1.62
1.60
1.60
1.58
1.58
1.57
1.53
1.52
1.50
1.47
1.35
1.33
1.31
1.29
1.28
1.26
1.24
1.23
1.05
1.02
Me
O
Me
H
H
H
O
O
OHC
CO2Et
10b1
0.97
1.02
2.02
1.00
1.00
1.06
1.93
2.00
2.06
1.07
1.29
6.11
6.07
10.08
1.01
6.14
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
-1.0
-1.5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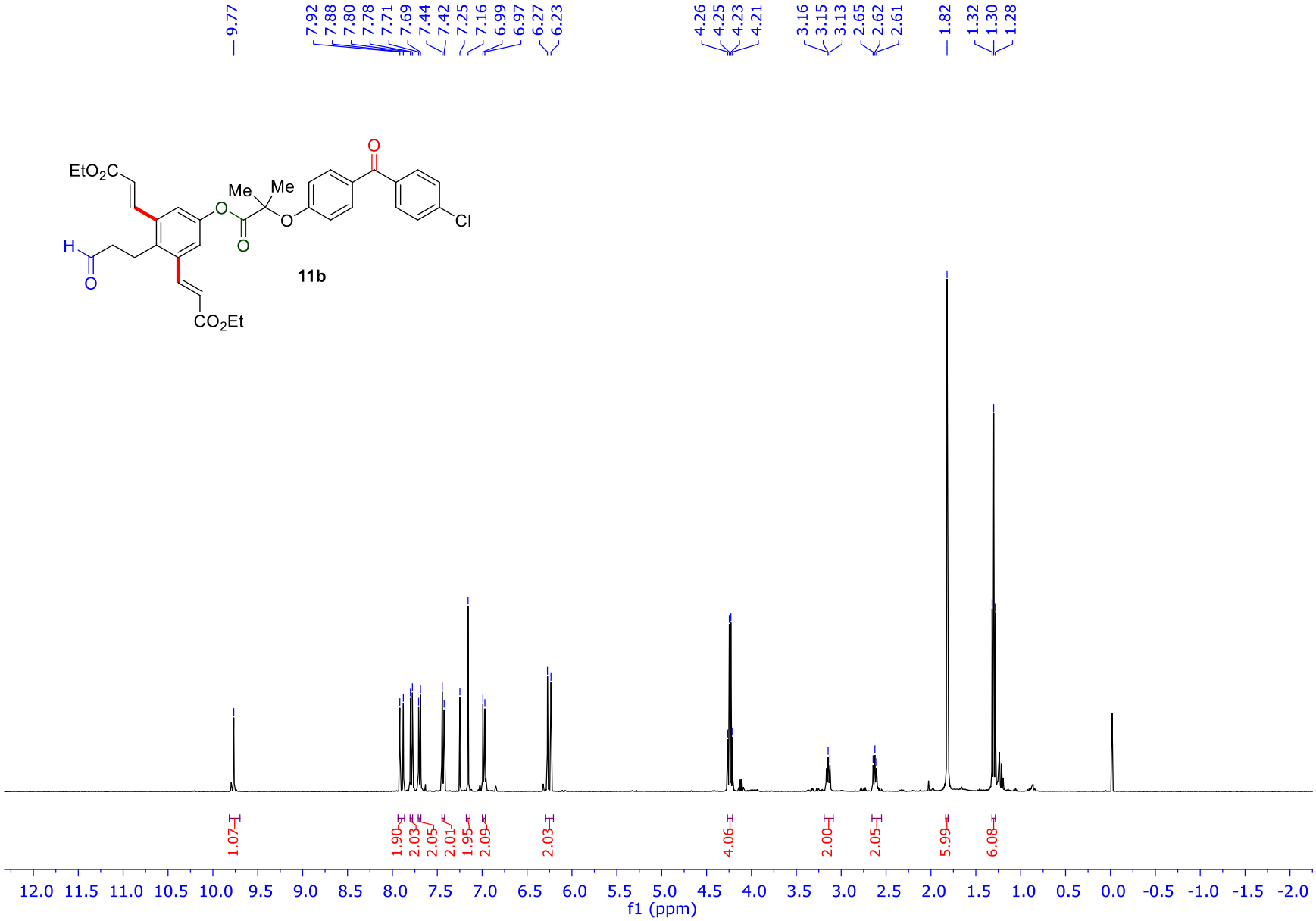
200.06
166.49
165.17
144.47
140.40
133.40
130.64
130.04
130.02
128.17
121.60
77.32
77.00
76.68
70.86
60.72
54.52
51.43
47.75
44.43
40.50
36.03
35.78
35.00
33.21
32.86
31.50
30.74
28.01
26.20
25.44
21.69
20.08
14.26
13.79
11.38
Me
O
Me
H
O
H
H
O
OHC
CO2Et
10b1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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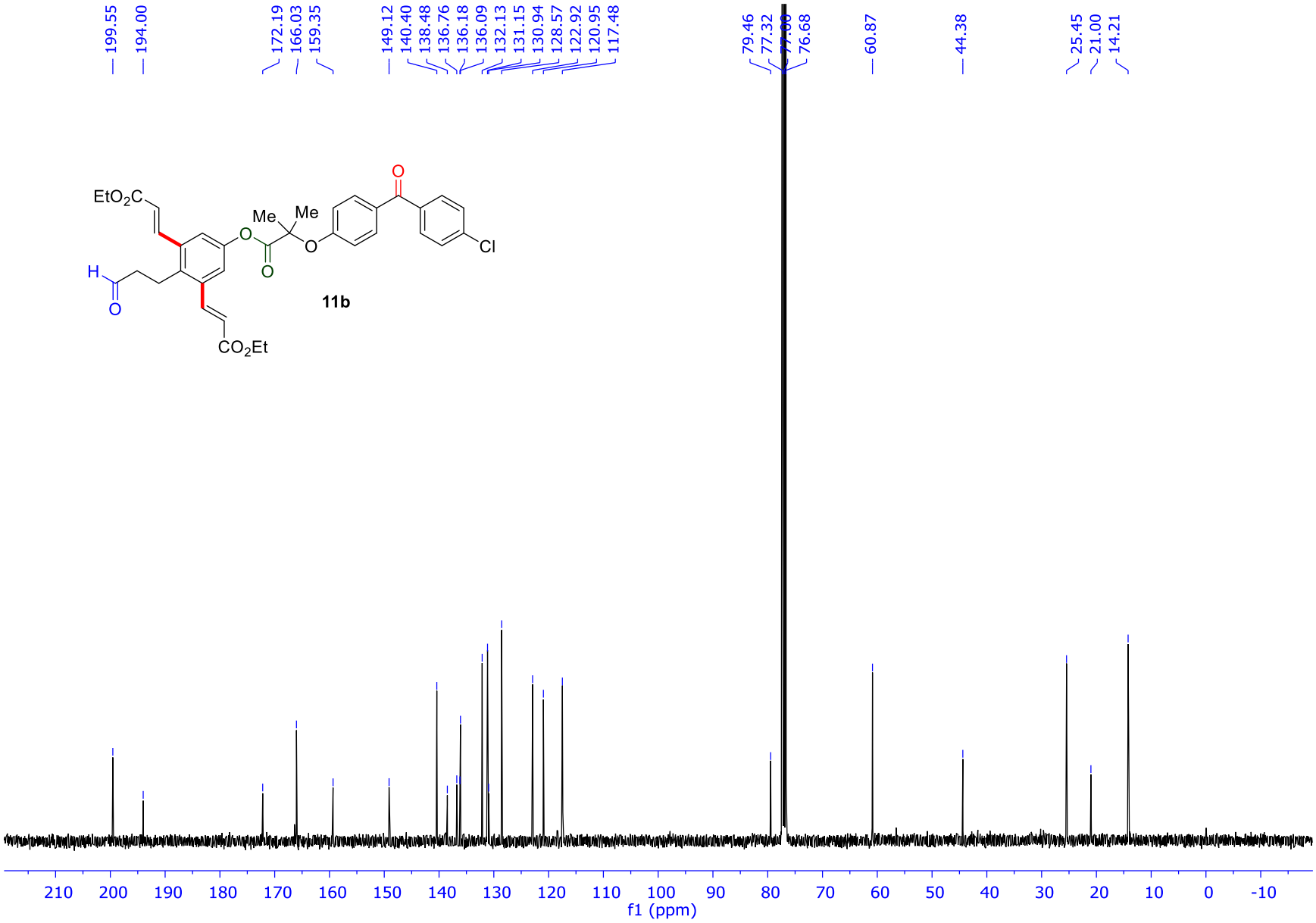
7.92
7.88
7.80
7.78
7.71
7.69
7.44
7.42
7.25
7.16
6.99
6.97
6.27
6.23
4.26
4.25
4.23
4.21
3.16
3.15
3.13
2.65
2.62
2.61
1.82
1.32
1.30
1.28
EtO2C
Me
Me
O
O
O
O
Cl
H
O
CO2Et
11b
1.07
1.90
2.03
2.05
2.01
1.95
2.09
2.03
4.06
2.00
2.05
5.99
6.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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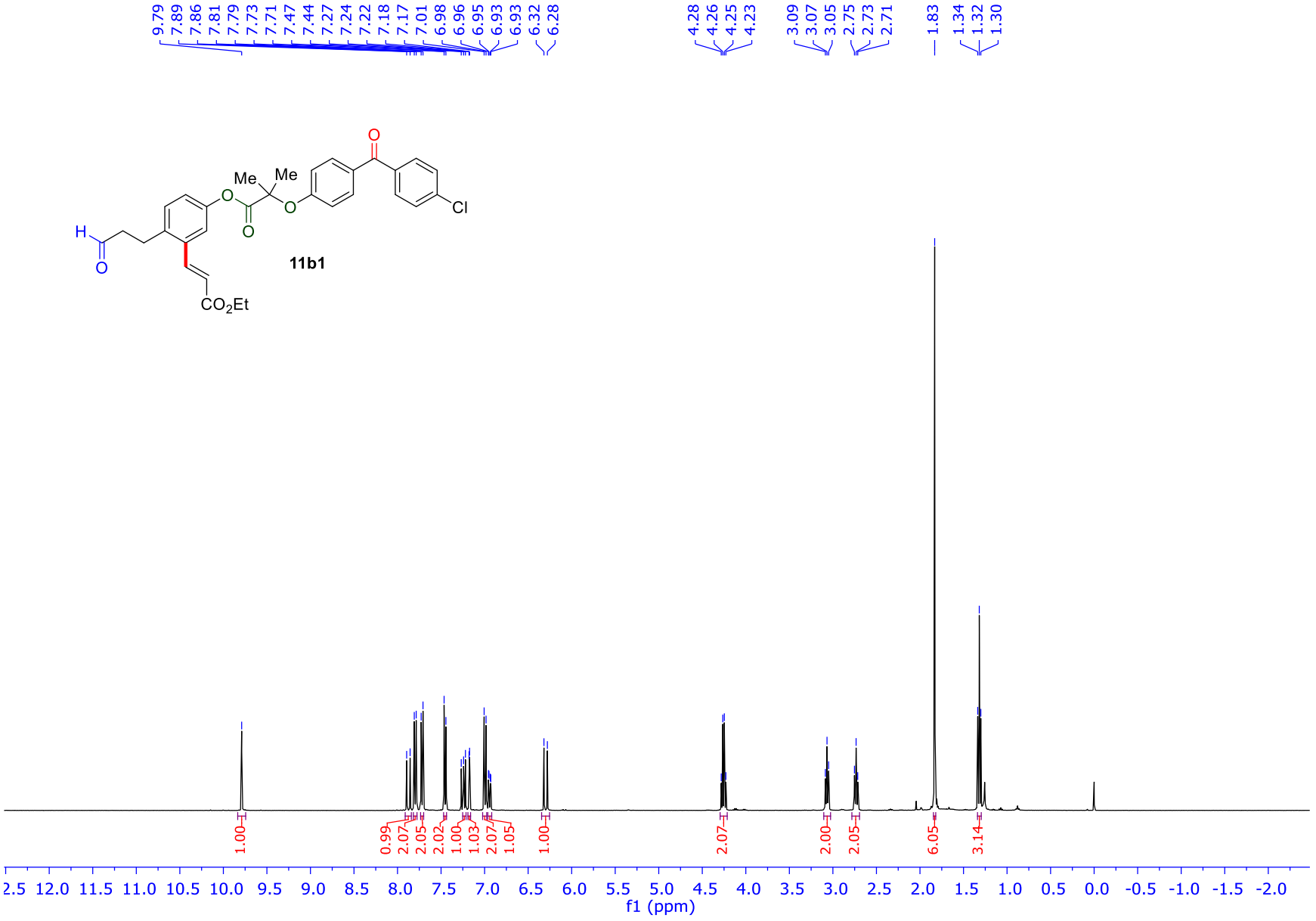
166.03
159.35
149.12
140.40
138.48
136.76
136.18
136.09
132.13
131.15
130.94
128.57
122.92
120.95
117.48
79.46
77.32
77.00
76.68
60.87
44.38
25.45
21.00
14.21
EtO2C
Me
Me
O
O
O
O
Cl
H
O
CO2Et
11b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.86
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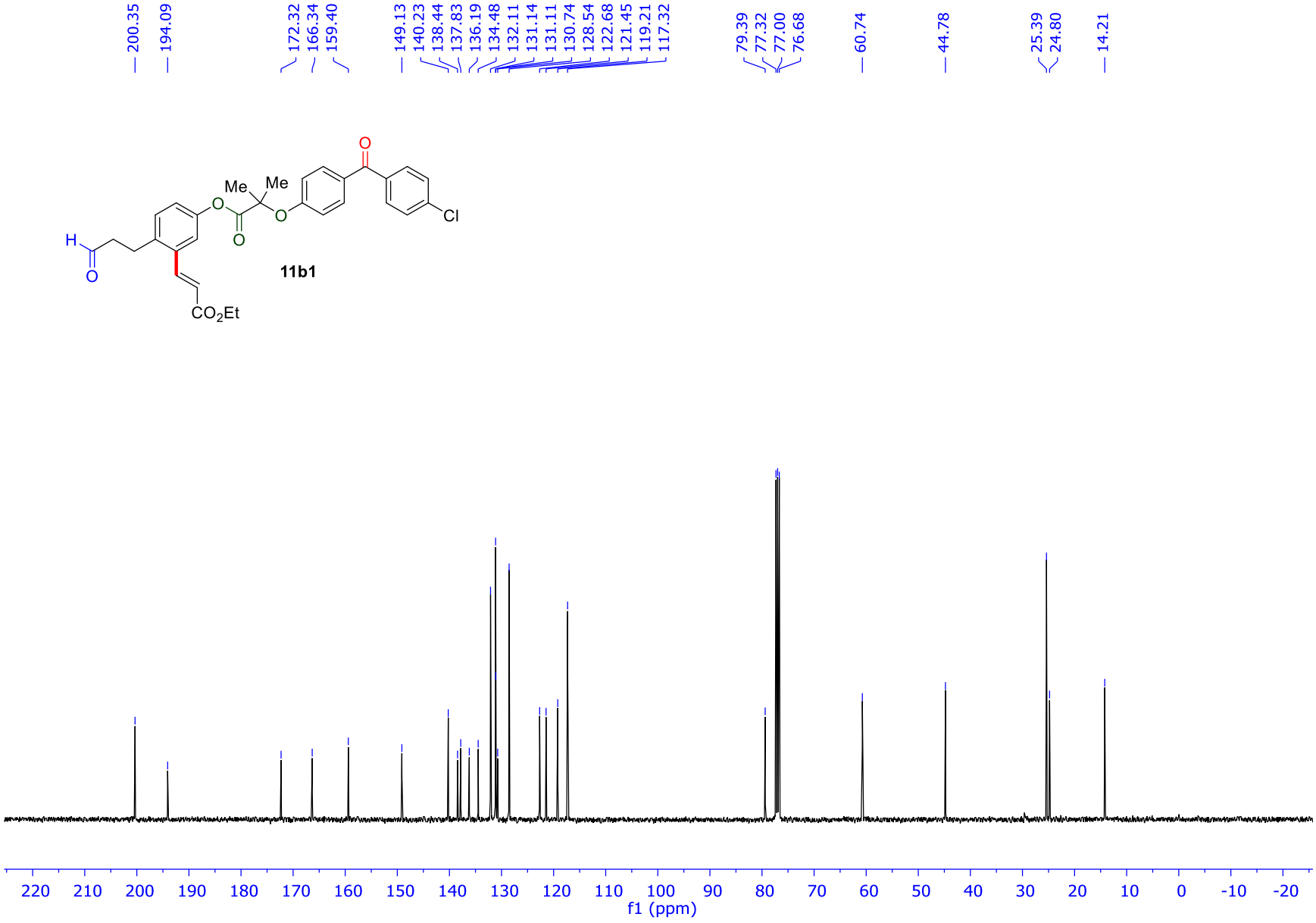
7.79
7.73
7.71
7.47
7.44
7.27
7.24
7.22
7.18
7.17
7.01
6.98
6.96
6.95
6.93
6.93
6.32
6.28
4.28
4.26
4.25
4.23
3.09
3.07
3.05
2.75
2.73
2.71
1.83
1.34
1.32
1.30
Me
Me
O
O
O
O
O
Cl
H
O
CO2Et
11b1
1.00
0.99
2.07
2.05
2.02
1.00
1.03
2.07
1.05
1.00
2.07
2.00
2.05
6.05
3.14
2.5 12.0 11.5 11.0 10.5 10.0 9.5 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 -1.0 -1.5 -2.0
f1 (ppm)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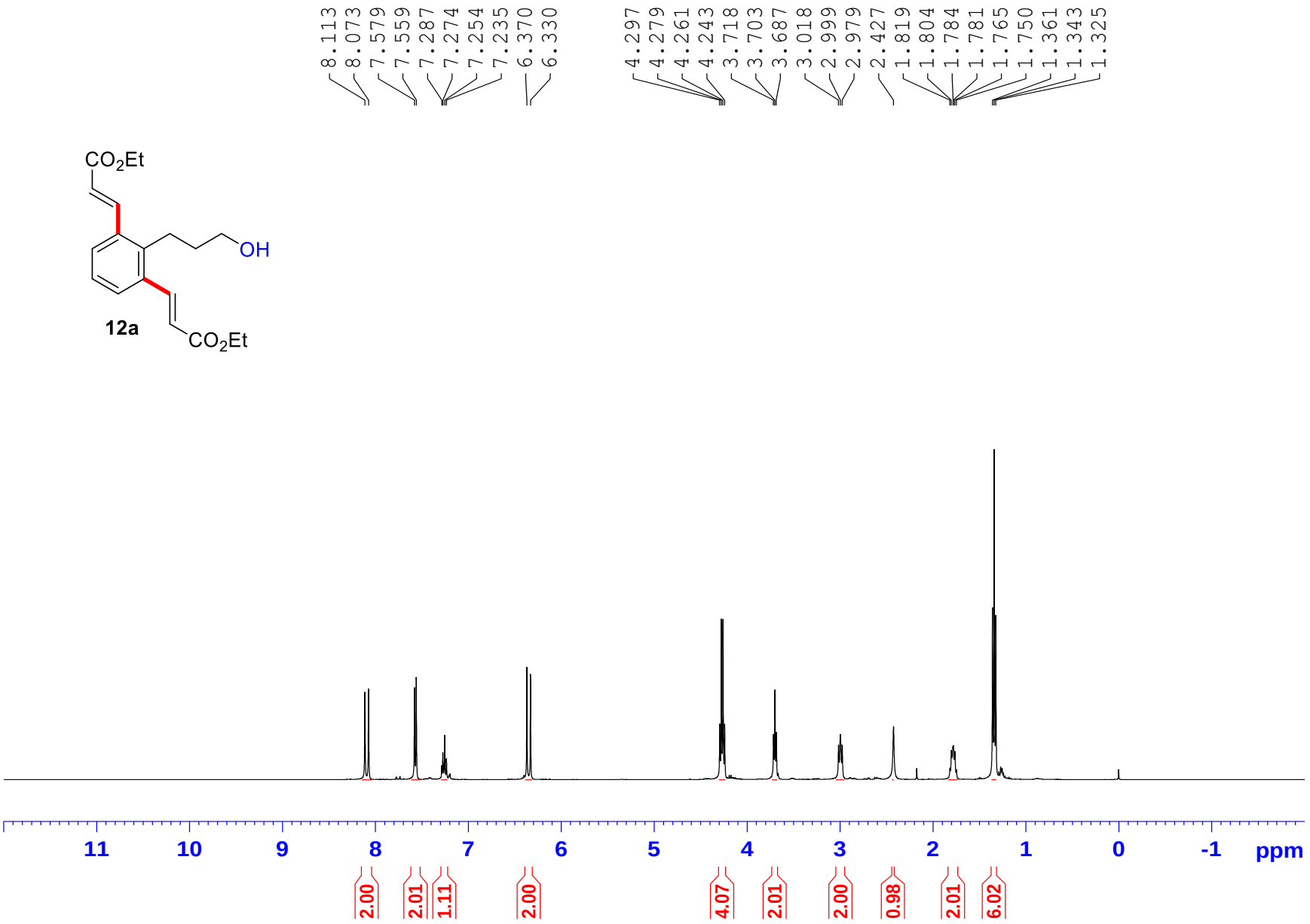
194.09
172.32
166.34
159.40
149.13
140.23
138.44
137.83
136.19
134.48
132.11
131.14
131.11
130.74
128.54
122.68
121.45
119.21
117.32
79.39
77.32
77.00
76.68
60.74
44.78
25.39
24.80
14.21
Me
Me
O
O
O
O
H
O
Cl
CO2Et
11b1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

Post synthetic product spectra’s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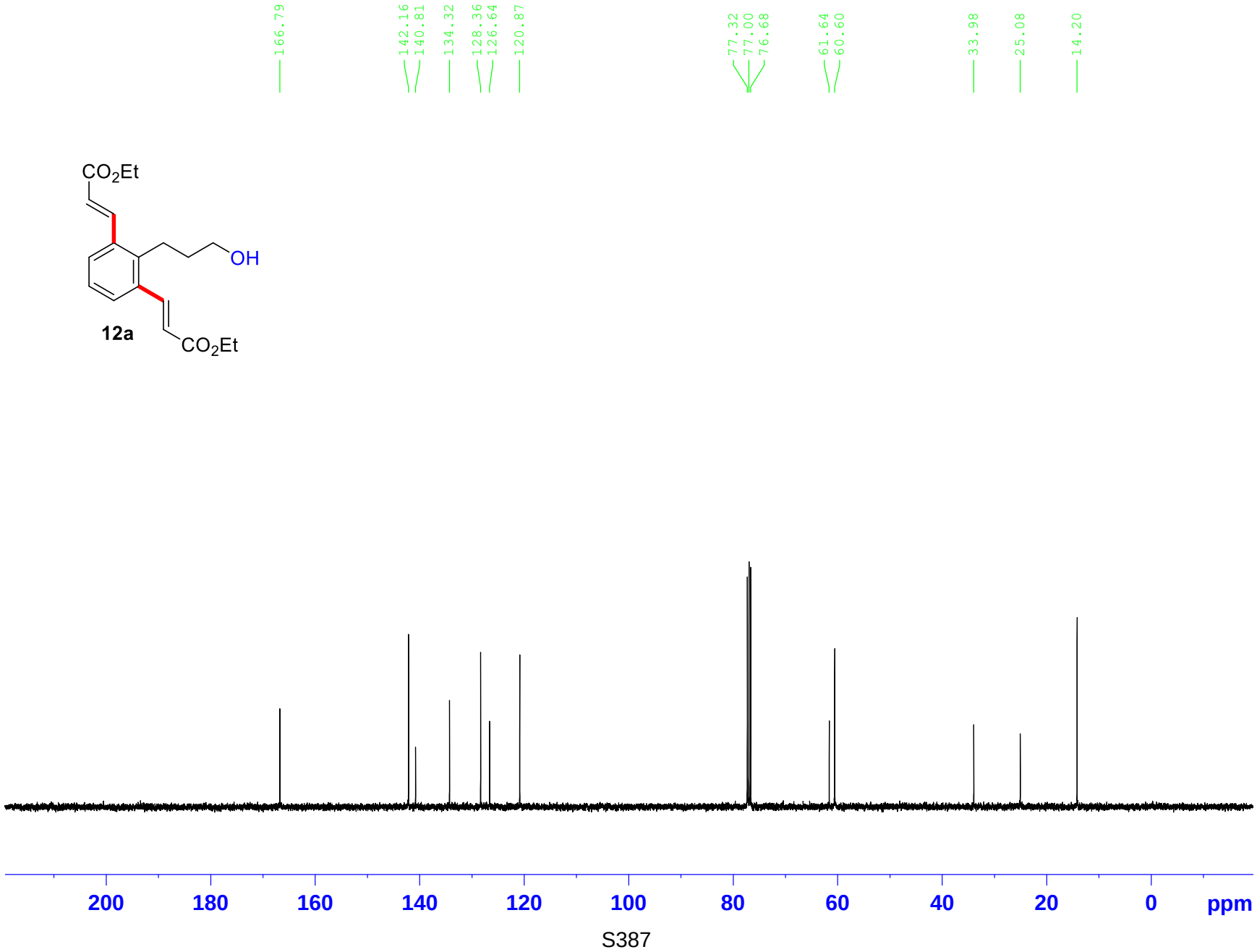
7.287
7.274
7.254
7.235
6.370
6.330
4.297
4.279
4.261
4.243
3.718
3.703
3.687
3.018
2.999
2.979
2.427
1.819
1.804
1.784
1.781
1.765
1.750
1.361
1.343
1.325
CO2Et
OH
12a
CO2Et
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
2.01
1.11
2.00
4.07
2.01
2.00
0.98
2.01
6.02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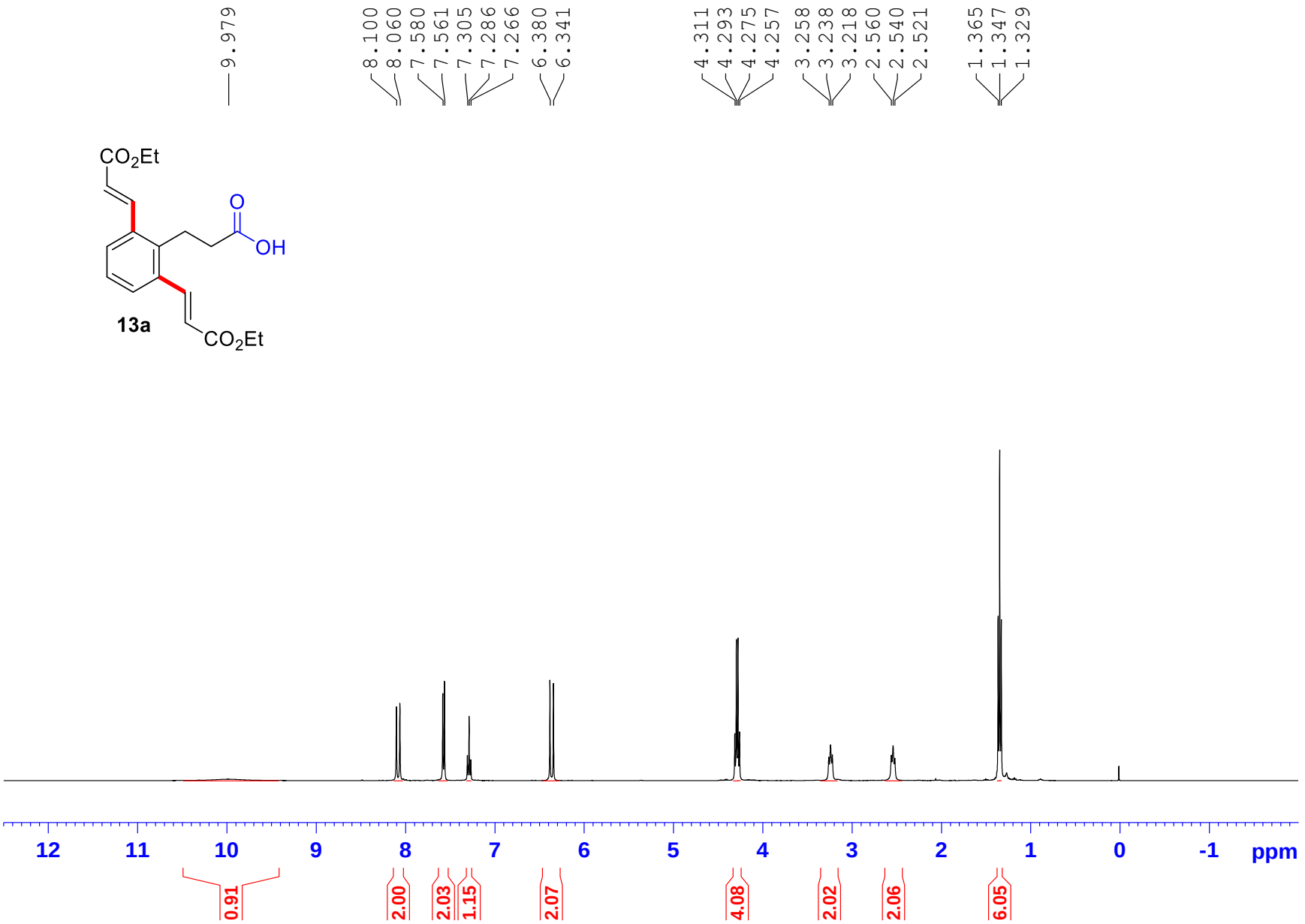
142.16
140.81
134.32
128.36
126.64
120.87
77.32
77.00
76.68
61.64
60.60
33.98
25.08
14.20
CO2Et
OH
CO2Et
12a
200
180
160
140
120
100
80
60
40
20
0
ppm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7.266
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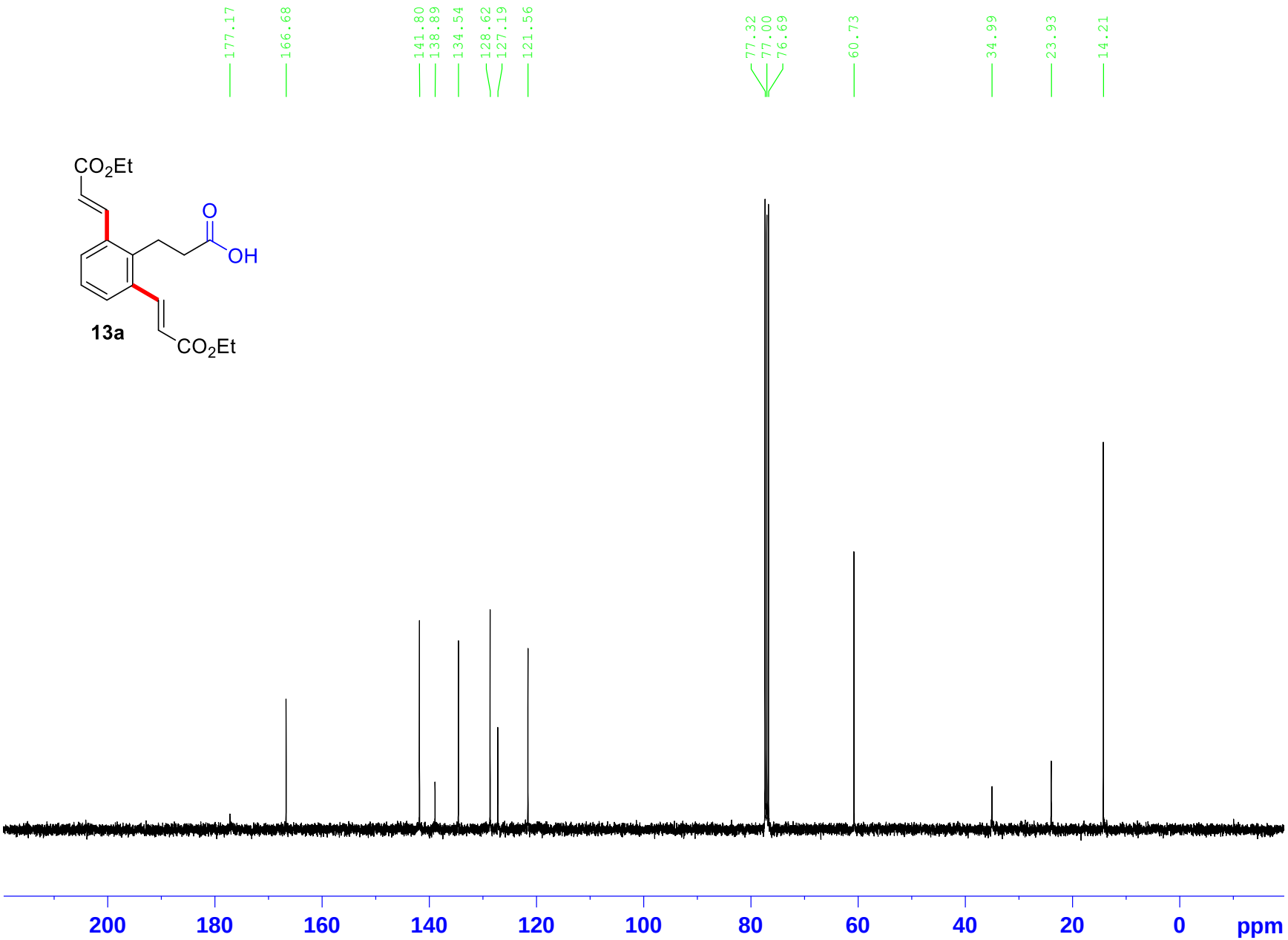
6.341
4.311
4.293
4.275
4.257
3.258
3.238
3.218
2.560
2.540
2.521
1.365
1.347
1.329
CO2Et
O
OH
13a
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
0.91
2.00
2.03
1.15
2.07
4.08
2.02
2.06
6.05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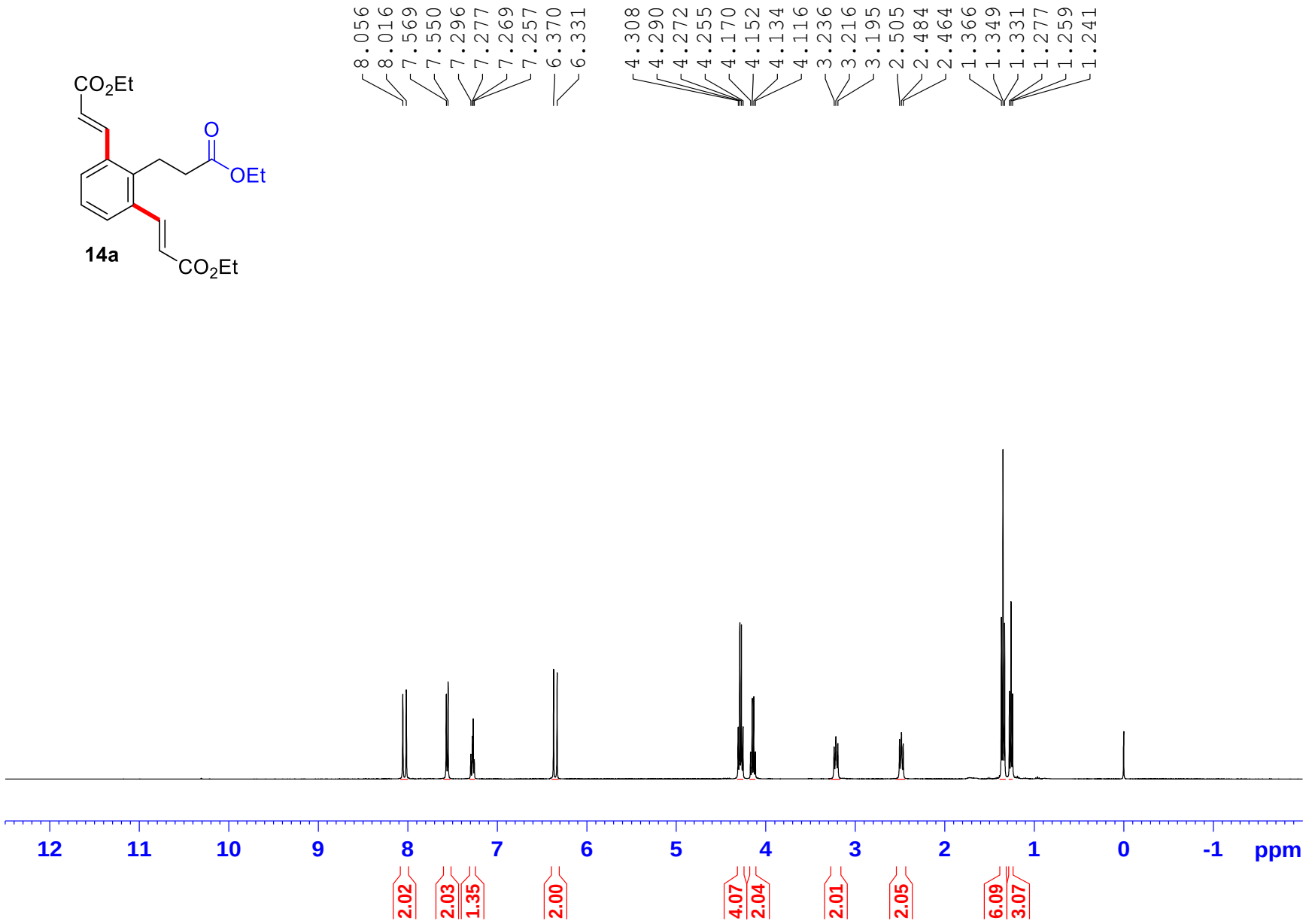
128.62
127.19
121.56
77.32
77.00
76.69
60.73
34.99
23.93
14.21
CO2Et
O
OH
13a
CO2Et
200
180
160
140
120
100
80
60
40
20
0
ppm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8.016
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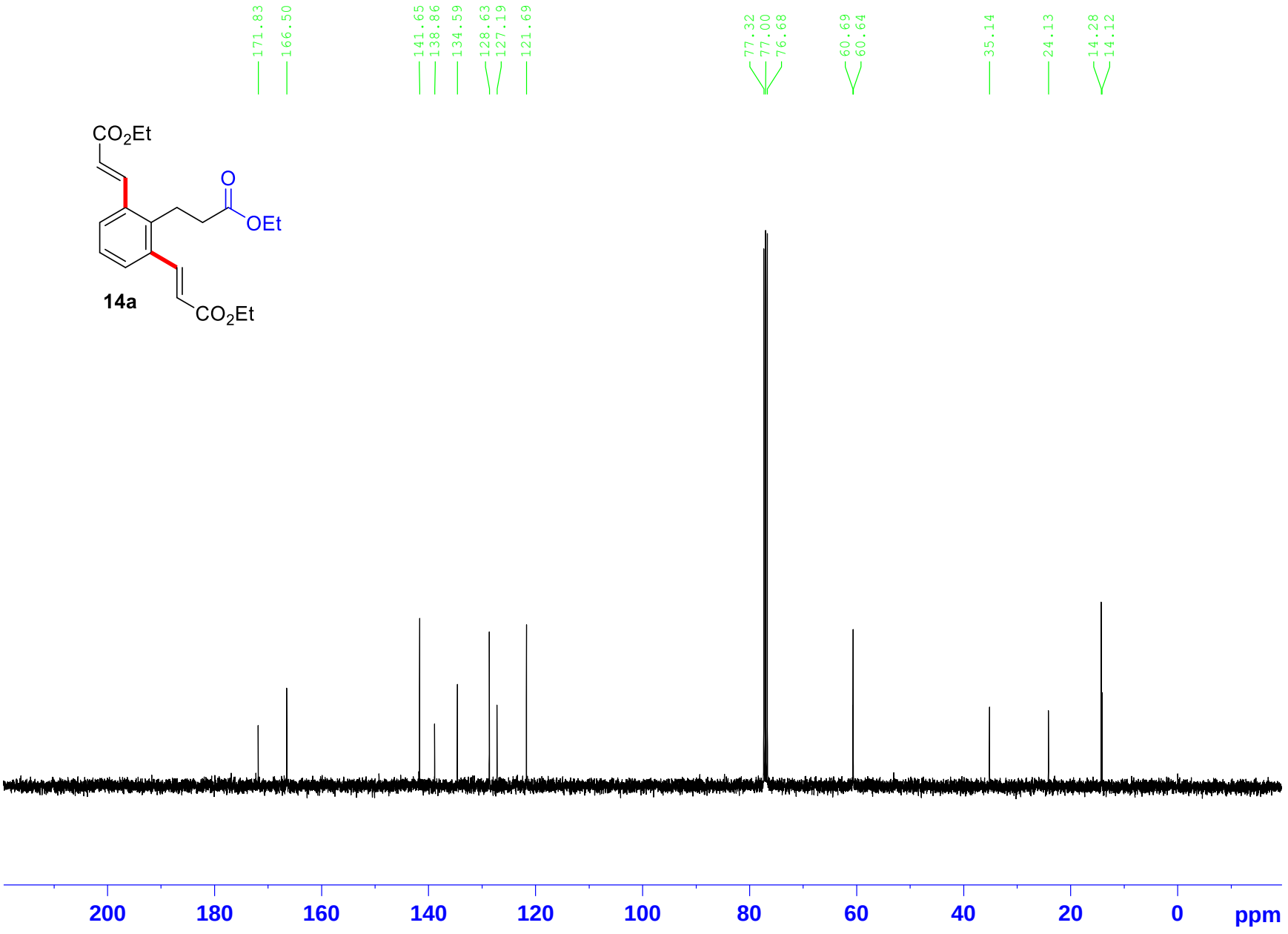
7.277
7.269
7.257
6.370
6.331
4.308
4.290
4.272
4.255
4.170
4.152
4.134
4.116
3.236
3.216
3.195
2.505
2.484
2.464
1.366
1.349
1.331
1.277
1.259
1.241
CO2Et
O
OEt
14a
CO2Et
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.02
2.03
1.35
2.00
4.07
2.04
2.01
2.05
6.09
3.07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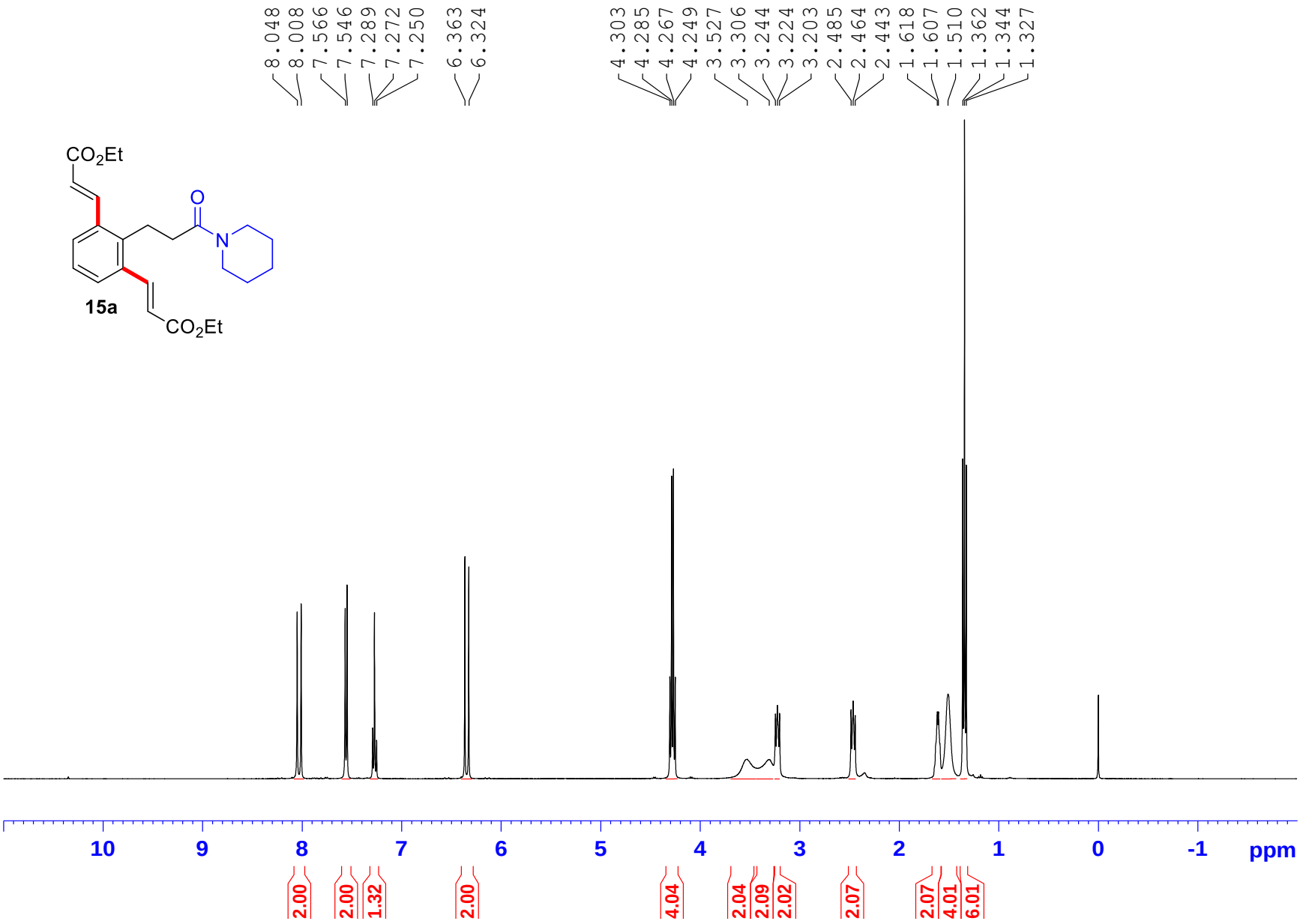
128.63
127.19
121.69
77.32
77.00
76.68
60.69
60.64
35.14
24.13
14.28
14.12
CO2Et
O
OEt
CO2Et
14a
200
180
160
140
120
100
80
60
40
20
0
ppm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7.566
7.546
7.289
7.272
7.250
6.363
6.324
4.303
4.285
4.267
4.249
3.527
3.306
3.244
3.224
3.203
2.485
2.464
2.443
1.618
1.607
1.510
1.362
1.344
1.327
CO2Et
O
N
15a
CO2Et
10
9
8
7
6
5
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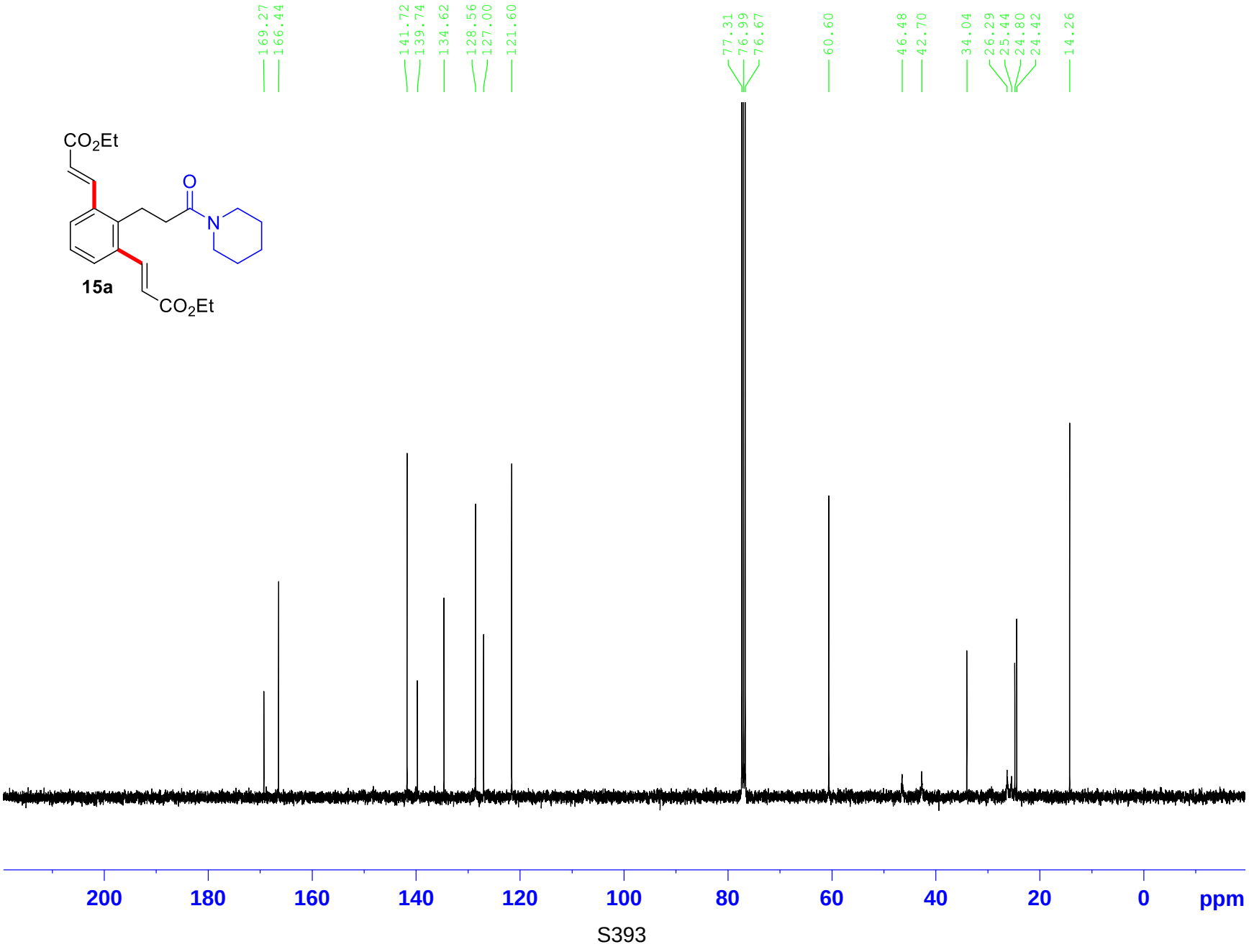
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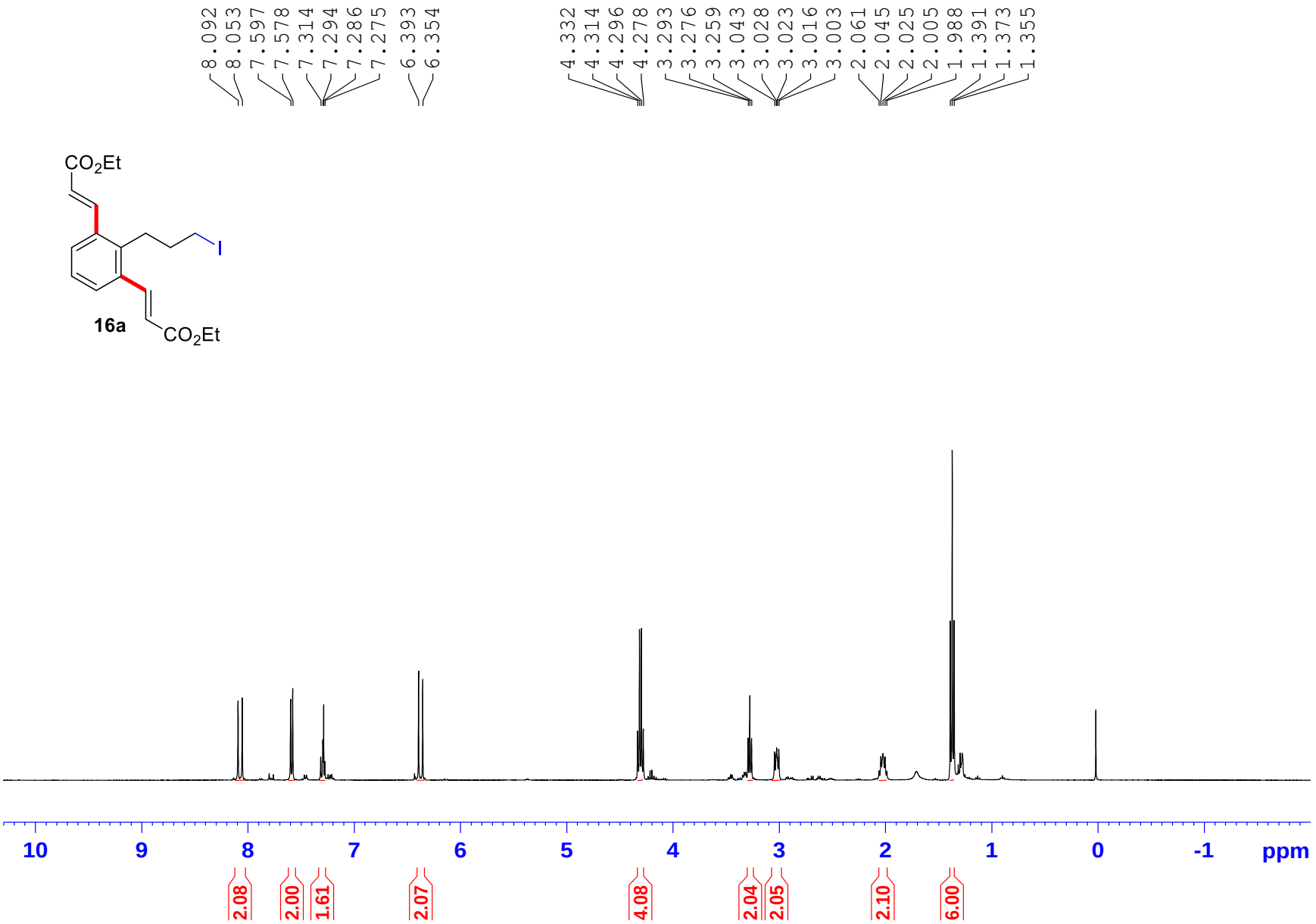
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8
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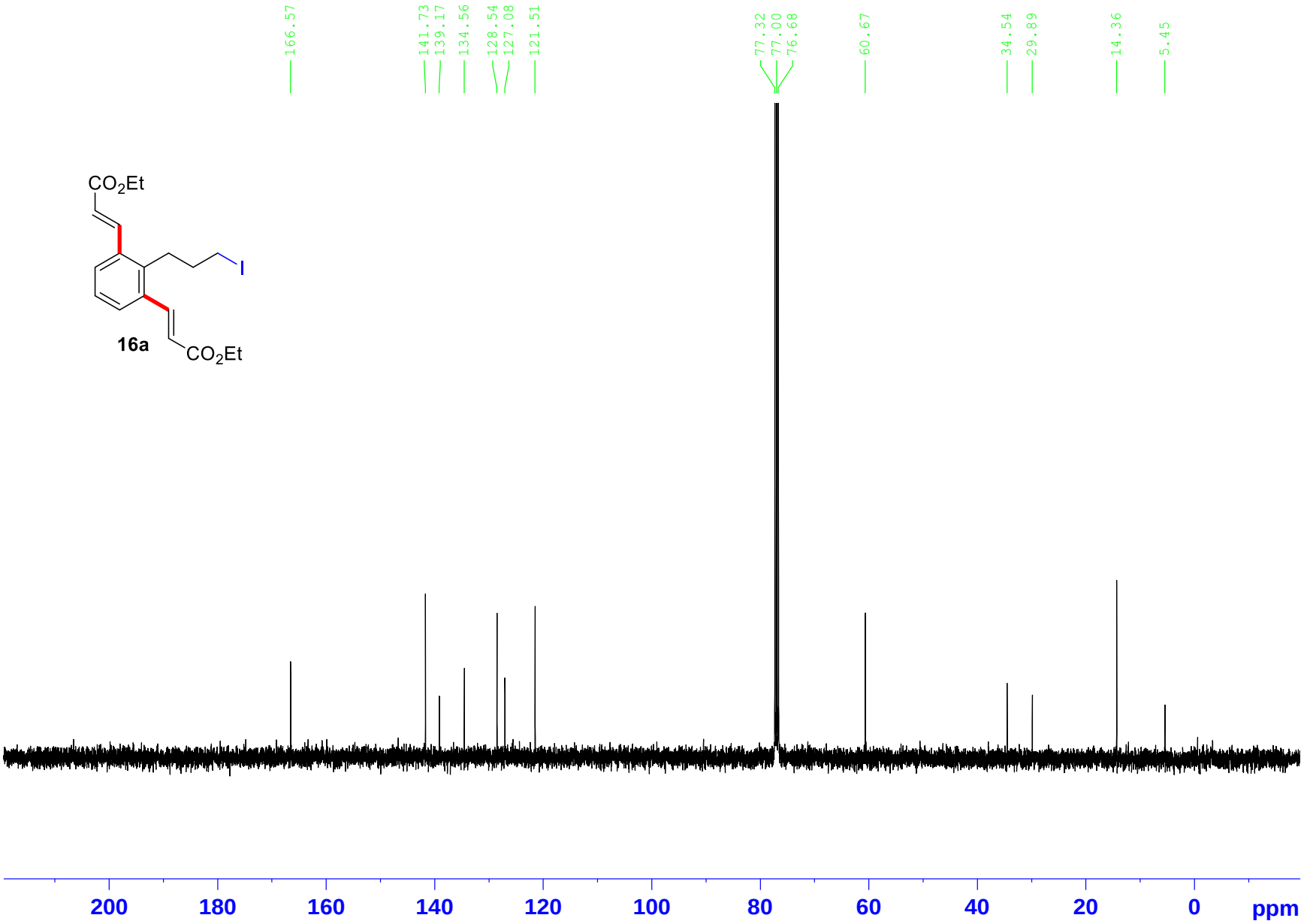
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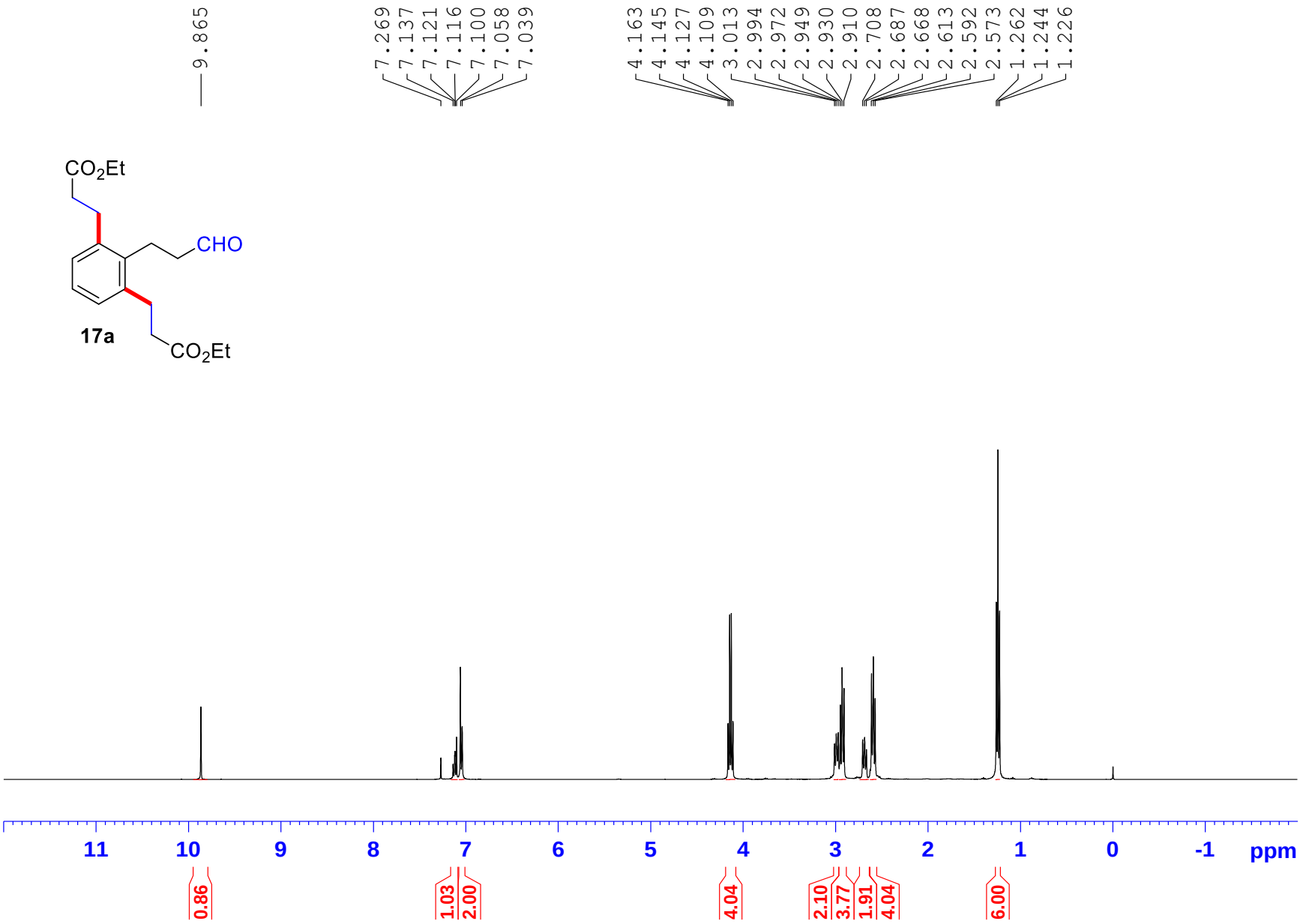
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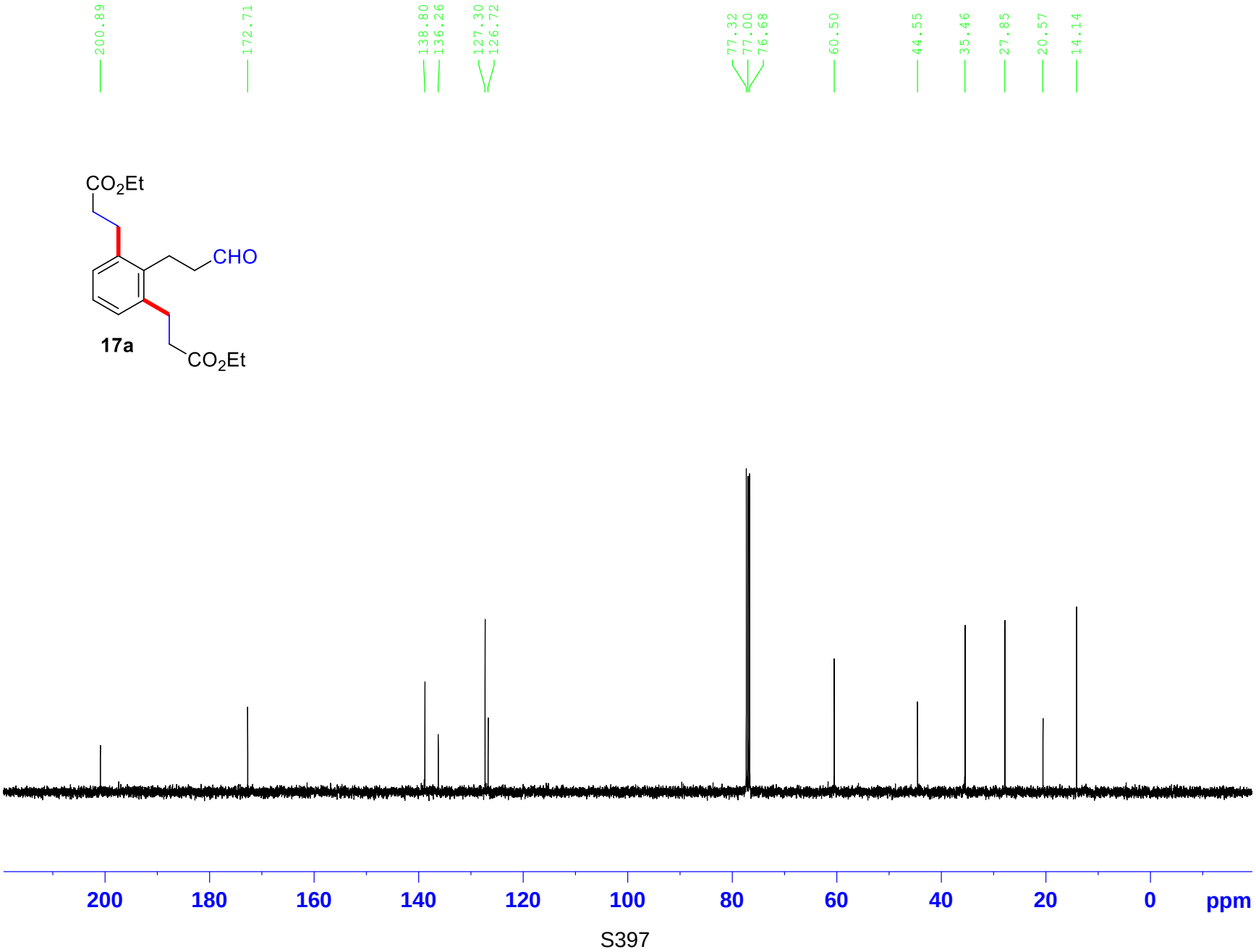
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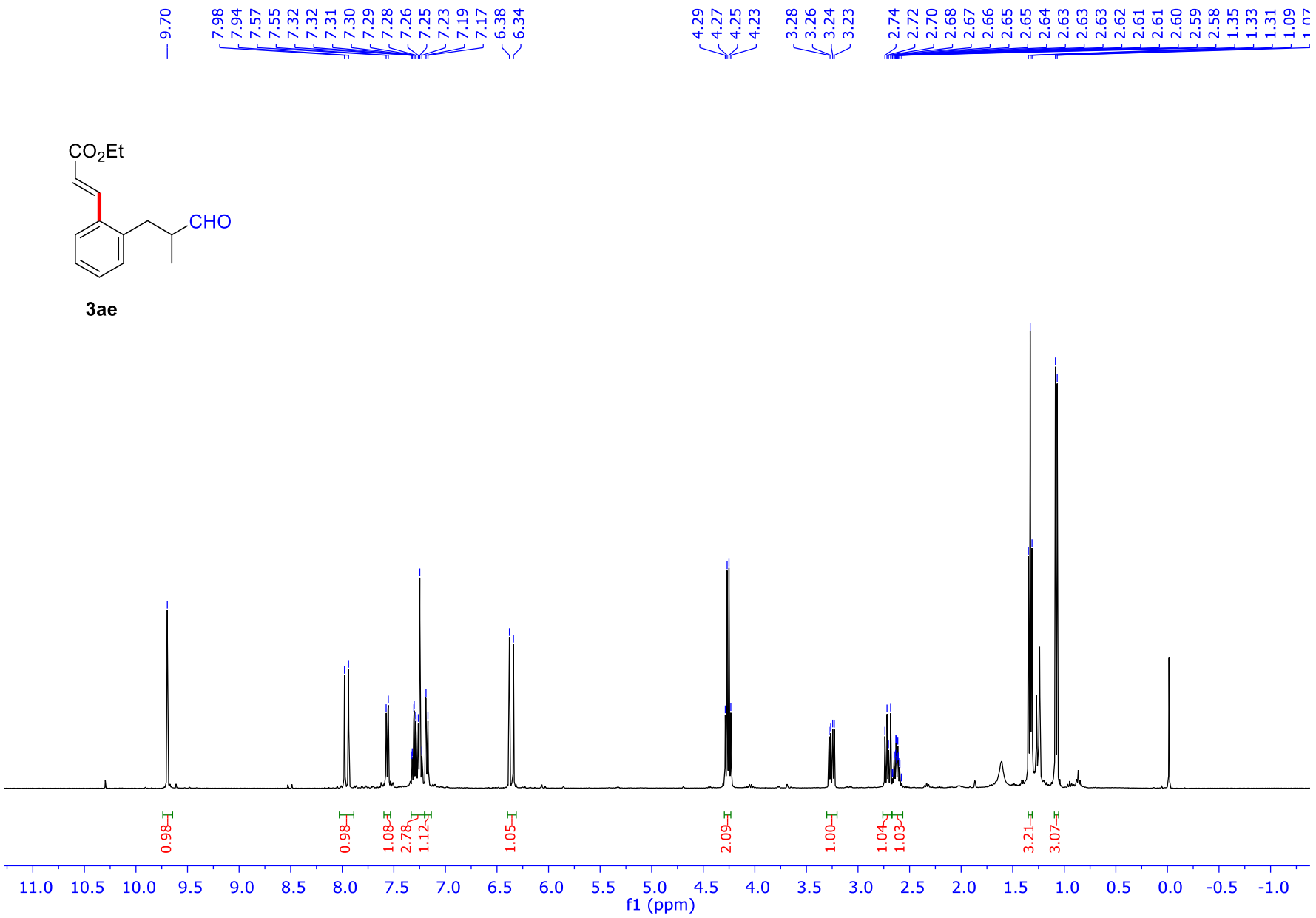
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1.00
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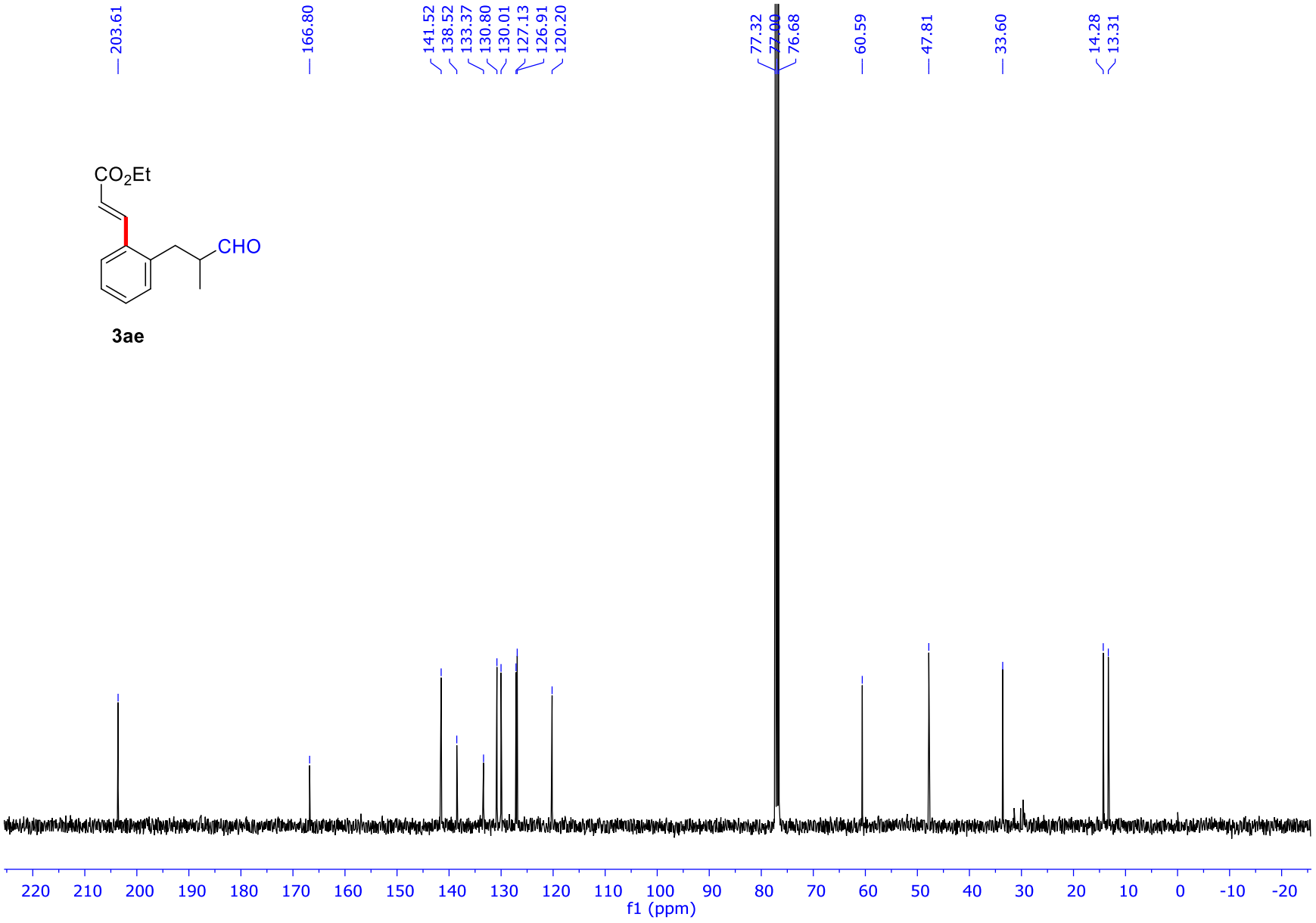
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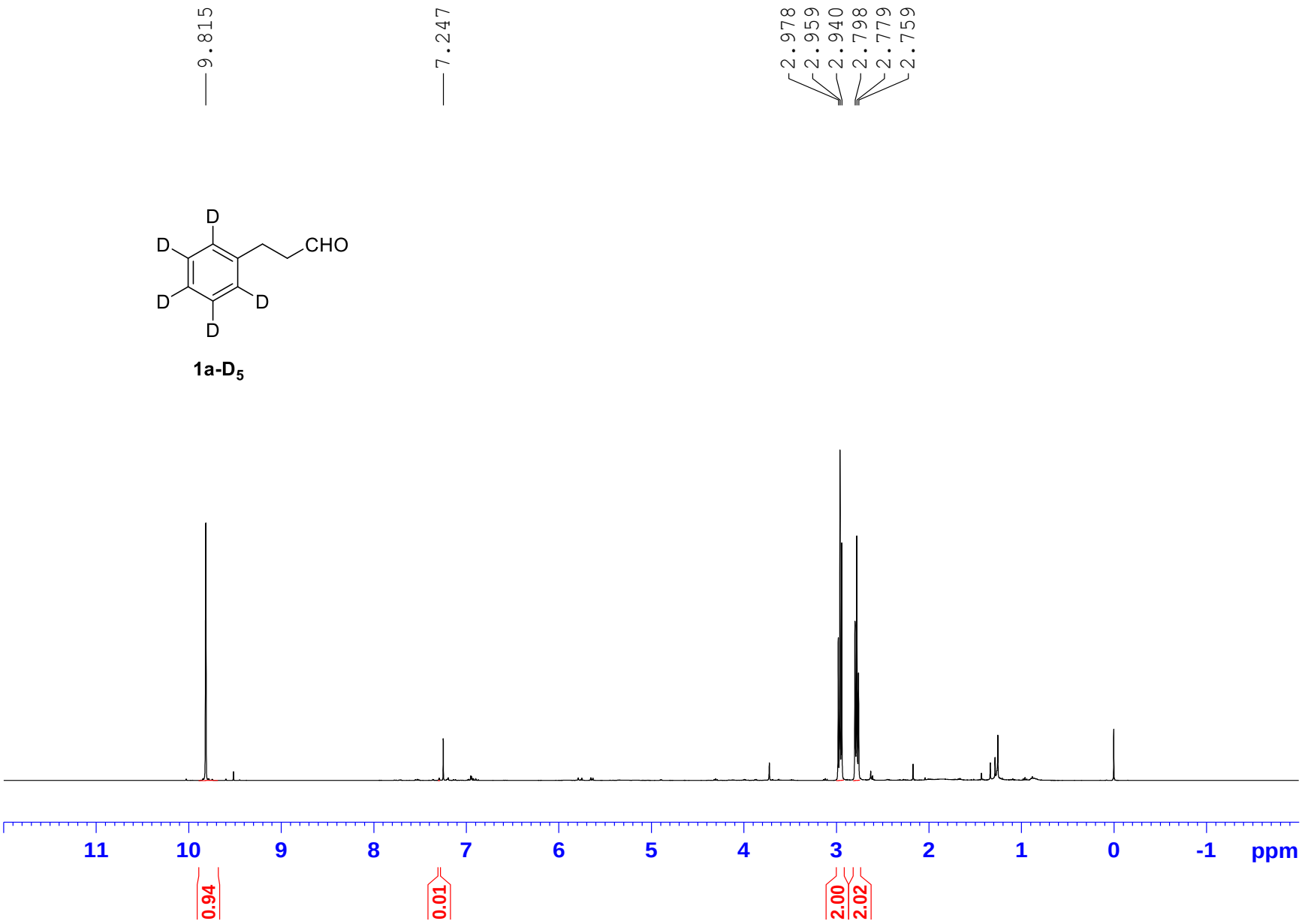
f1 (ppm)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9
8
7
6
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4
3
2
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0
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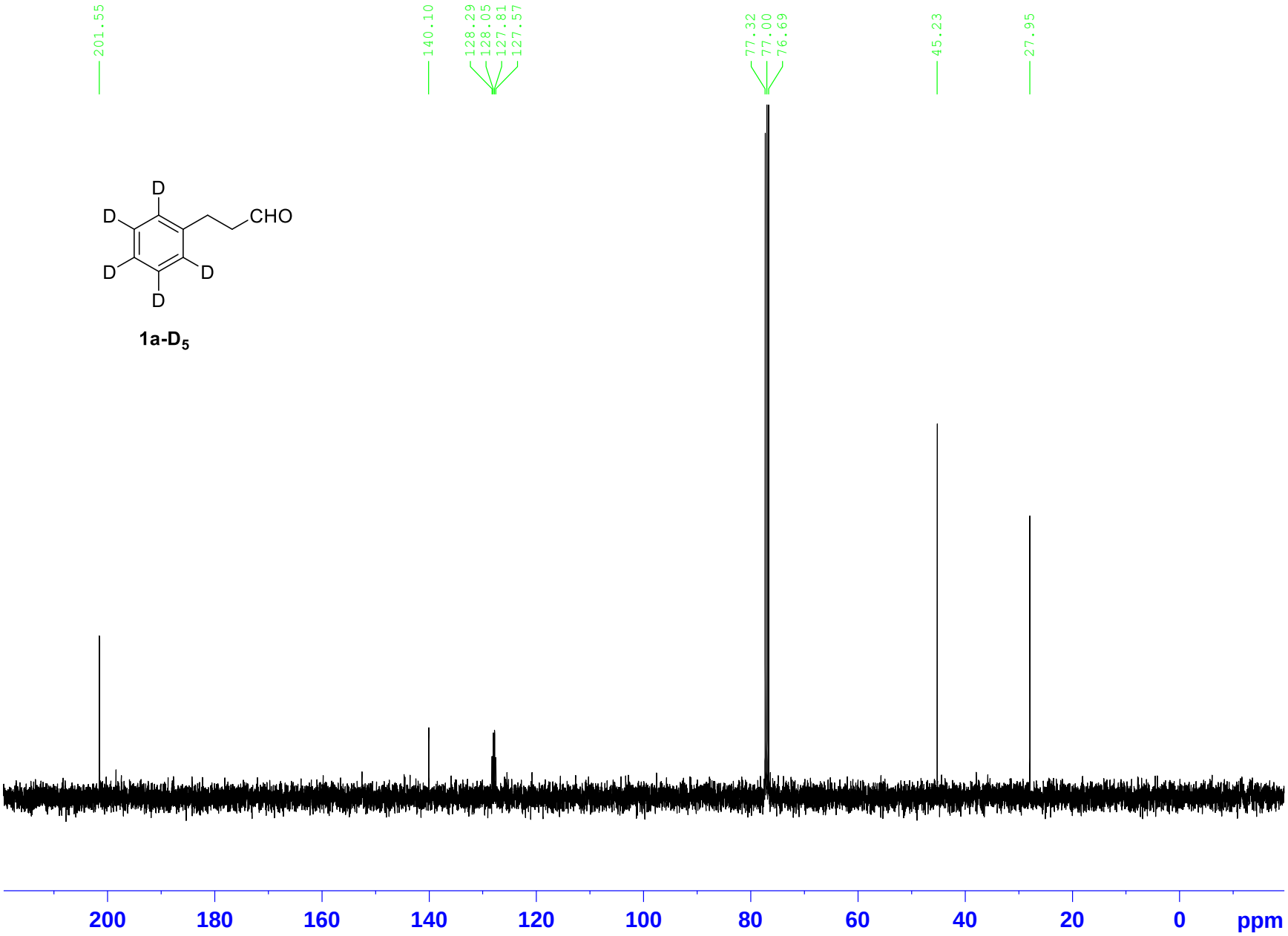
2.02

1a-D_5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CHO
200
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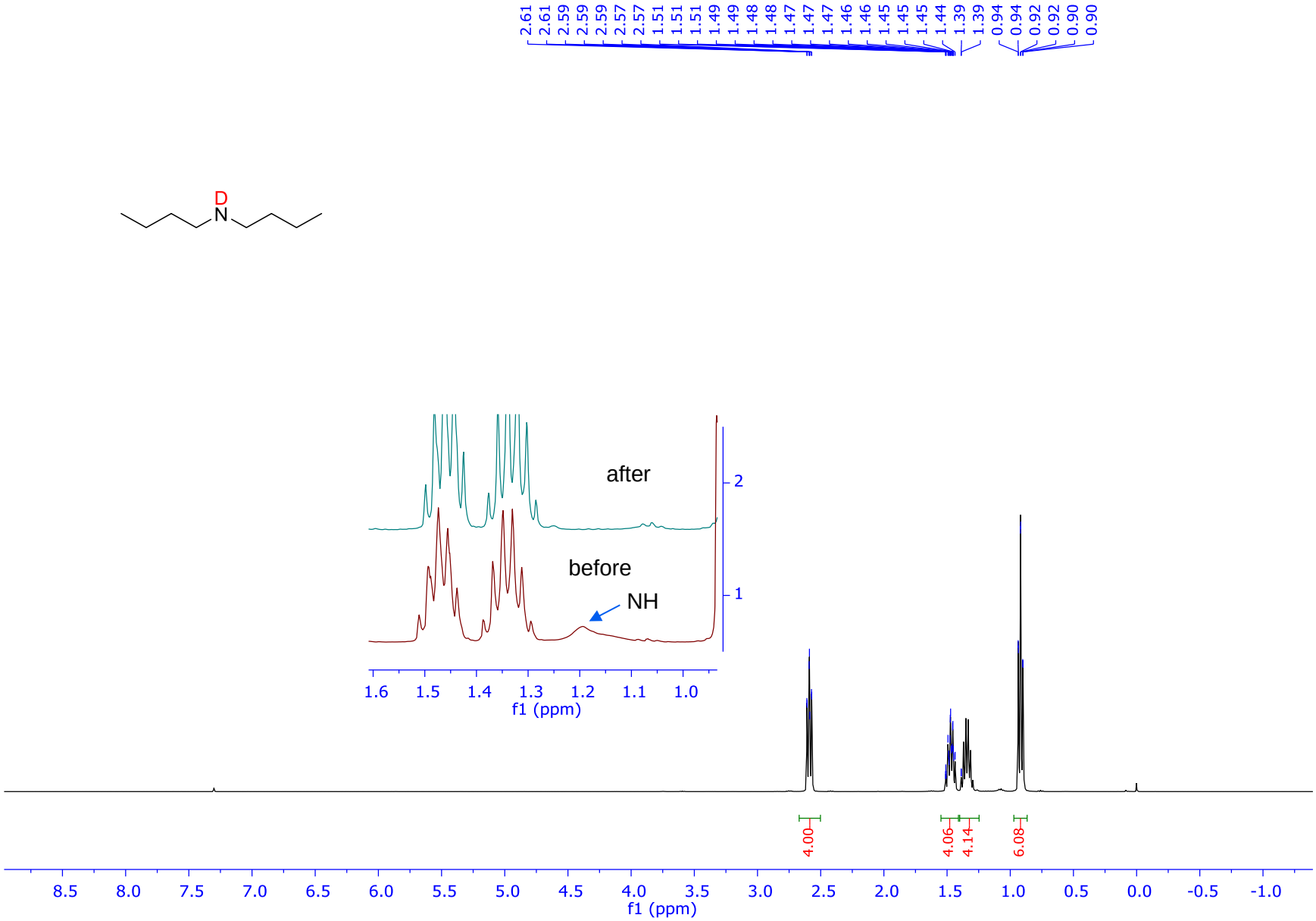
60
40
20
0
ppm

1a-D_5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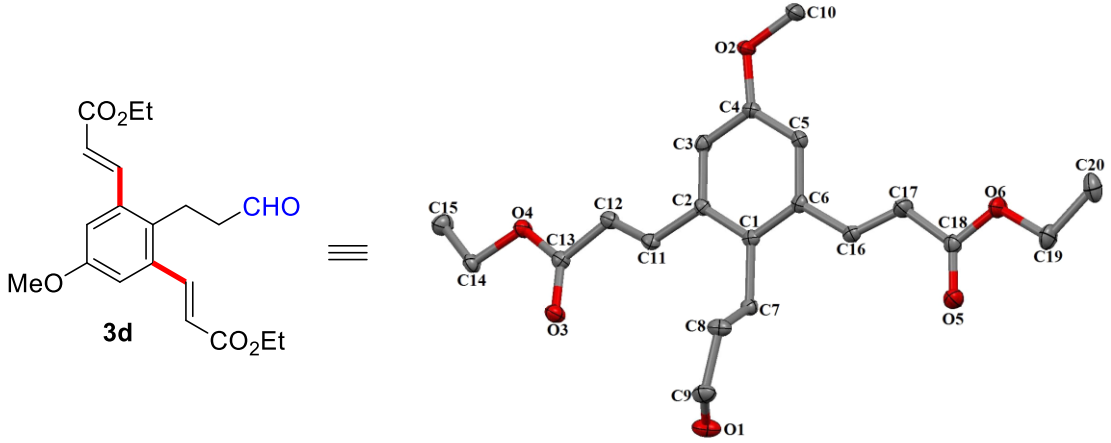
D
N
after
before
NH
2
1
1.6 1.5 1.4 1.3 1.2 1.1 1.0
f1 (ppm)
4.00
4.06
4.14
6.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



X-ray structure of compound ***3d***. Hydrogen atoms have been omitted for clarity. The thermal ellipsoid was drawn at the 50% probability level. (**CCDC 1964780**)

Table S1 Crystal data and structure refinement for compound **3d**

Identification code	Full
Empirical formula	C20 H24 O6
Formula weight	360.39
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 21.9046(9) Å, α= 90° b = 4.7807(2) Å, β= 94.293(2)° c = 17.8266(8) Å, γ = 90°
Volume	1861.55(14)Å^3
Z	4
Density (calculated)	1.286 Mg/m^3
Absorption coefficient	0.095 mm^{-1}
F(000)	768
Crystal size	0.18 x 0.16 x 0.16 mm^3
Theta range for data collection	2.54 to 27.57°
Index ranges	-28<=h<=28, -6<=k<=6, -23<=l<=23
Reflections collected	37246
Independent reflections	4270 [R(int) = 0.1663]
Completeness to theta = 27.57°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9850 and 0.9832
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4270 / 0 / 236
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1036
R indices (all data)	R1 = 0.0661, wR2 = 0.1100
Extinction coefficient	0.007(2)
Largest diff. peak and hole	0.314 and -0.250 e.Å^{-3}

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