Supporting Information

Catalyst-free Tandem Halogenation/Semipinacol Rearrangement of Allyl Alcohols with Sodium Halide in Water

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1. General information

All solvent and reagents were commercially available and used without further purification unless specified otherwise. Reactions were monitored by thin layer chromatography (TLC), which carried out on GF254 plates. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 400 or 500, 376 and 101 or 126 MHz respectively, using $CDCl_3$ as a solvent. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants, *J*, are reported in Hertz (Hz). HRMS were recorded on a LCMS-IT-TOF. The products were purified by column chromatography on silica gel with petroleum ether/ EA (100:1 to 40:1).

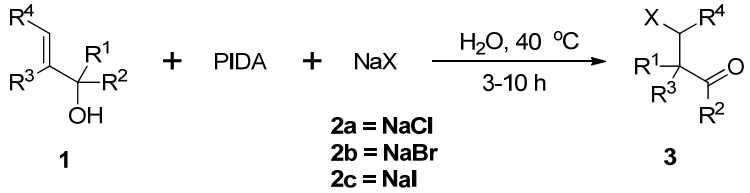
Allyl alcohols substrates[1]were prepared according to literature.

Reference

[1] H. Li, F. M. Zhang, Y. Q. Tu, *chem. sci.* 2011, **2**, 1839.

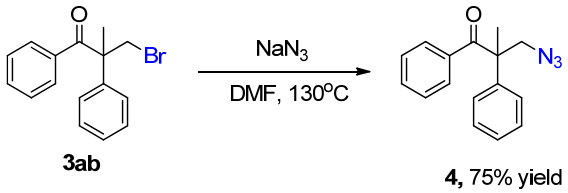
2. Experimental Procedures

2.1 Preparation of the product 3

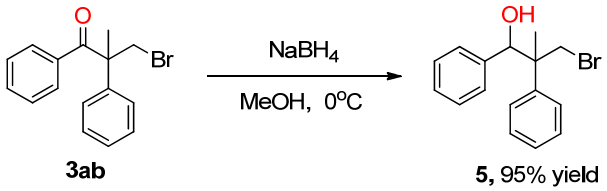


To a 10 mL round-bottom flask equipped with a magnetic stirrer bar, were added **1** (0.1 mmol, 1.0 equiv), PIDA (0.2 mmol, 2.0 equiv) and NaBr (0.4 mmol, 4.0 equiv). Then water (1 mL) was added, and the mixture was then stirred at 40°C. Then the reaction was monitored by TLC and till **1** was consumed up. Afterwards, the reaction mixture was cooled down, quenched with saturated $NaHCO_3$ (10 mL), followed by extraction with ethyl acetate (3 x 5 mL) and washed with brine, dried over Na_2SO_4, filtered and then concentrated in vacuum. The residue was then purified by column chromatography on silica gel (PE/EA, ~300 mL) to afford the desired product **3**.

2.2 Transformations of the product 3ab

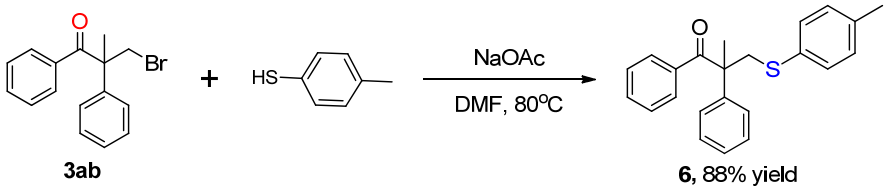


To a solution of **3ab** (0.1 mmol, 1.0 equiv) in DMF (1 mL), NaN_3 (0.3 mmol, 3.0 equiv) was added. The mixture was stirred at 130°C until complete conversion monitored by TLC. Then H_2O (1 mL) was added. The solution was extracted with EA and washed with brine, dried over Na_2SO_4, filtered and then concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EA = 40/1, v/v) to afford the product **4** in 75 % yield.



3ab **5,** 95% yield

To a solution of **3ab** (0.1 mmol, 1.0 equiv) in MeOH (1 mL), $NaBH_4$ (0.2 mmol, 2.0 equiv) was added at 0 ℃. The mixture was stirred at 0°C for 0.5 h. Then H_2O (1 mL) was added. The solution was extracted with EA and washed with brine, dried over Na_2SO_4, filtered and then concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EA = 20/1, v/v) to afford the product **5** in 95 % yield.

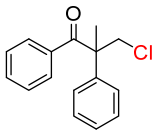


3ab **6,** 88% yield

To a solution of **3ab** (0.1 mmol, 1.0 equiv) in DMF (1 mL), 4-methylthiophenol (0.7 mmol, 7.0 equiv) and NaOAc (2.1 mmol, 21.0 equiv) was added. The mixture was stirred at 80°C overnight. Then H_2O (1 mL) was added. The solution was extracted with EA and washed with brine, dried over Na_2SO_4, filtered and then concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EA = 40/1, v/v) to afford the product **6** in 88 % yield.

3. Characterization of Products

3-chloro-2-methyl-1,2-diphenylpropan-1-one (**3aa)**



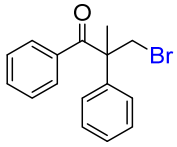
Brown oil, 20.2 mg, yield 78%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.46-7.31 (m, 8H), 7.27-7.21 (m, 2H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.88 (d, *J* = 11.0 Hz, 1H), 1.80 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 201.51, 140.25, 136.15, 132.08, 129.41, 129.18, 128.11, 127.89, 126.51, 55.64, 53.27, 21.58.

HRMS (ESI^{+}): calcd. For $C_{16}H_{15}OClNa^{+}$ [M+Na]$^{+}$ 281.0704; found 281.0695.

3-bromo-2-methyl-1,2-diphenylpropan-1-one (**3ab)**



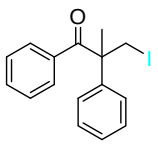
Brown oil, 26.7 mg, yield 89%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.45-7.37 (m, 5H), 7.37-7.31 (m, 3H), 7.27-7.21 (m, 2H), 4.07 (d, *J* = 10.2 Hz, 1H), 3.78 (d, *J* = 10.2 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 201.29, 140.48, 136.21, 132.06, 129.40, 129.21, 128.12, 127.94, 126.43, 54.98, 43.13, 22.86.

HRMS (ESI^{+}): calcd. For $C_{16}H_{15}OBrH^{+}$ [M+H]$^{+}$ 303.0379; found 303.0366.

3-iodo-2-methyl-1,2-diphenylpropan-1-one (**3ac)**



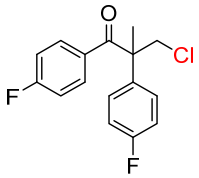
Brown oil, 28.4 mg, yield 81%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47-7.34 (m, 8H), 7.29-7.23 (m, 2H), 3.90 (d, *J* = 10.0 Hz, 1H), 3.68 (d, *J* = 10.0 Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.72, 140.74, 136.28, 131.97, 129.43, 129.20, 128.08, 127.89, 126.31, 54.08, 25.05, 19.28.

HRMS (ESI^{+}): calcd. For $C_{16}H_{15}OINa^{+}$ [M+Na]$^{+}$ 373.0060; found 373.0063.

3-chloro-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3ba)**



Brown oil, 24.5 mg, yield 83%.

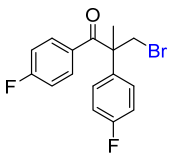
^{1}H NMR (400 MHz, Chloroform-d) δ 7.54-7.43 (m, 2H), 7.33-7.25 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 4.10 (d, *J* = 11.1 Hz, 1H), 3.86 (d, *J* = 11.1 Hz, 1H), 1.79 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-d) δ -105.62, -113.80.

^{13}C NMR (101 MHz, Chloroform-d) δ 199.66, 166.16, 163.58 (d, *J* = 9.1 Hz), 161.07, 135.94 (d, *J* = 3.3 Hz), 132.18 (d, *J* = 9.3 Hz), 131.87 (d, *J* = 3.2 Hz), 128.26 (d, *J* = 8.1 Hz), 116.23 (d, *J* = 21.4 Hz), 115.35 (d, *J* = 21.6 Hz), 55.04, 53.30, 21.68.

HRMS (ESI^{+}): calcd. For $C_{16}H_{13}OF_2ClH^{+}$ [M+H]$^{+}$ 295.0696; found 295.0708.

3-bromo-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3bb)**



Brown oil, 29.5 mg, yield 87%.

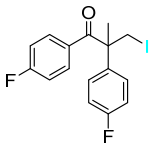
^{1}H NMR (400 MHz, Chloroform-d) δ 7.53-7.44 (m, 2H), 7.33-7.24 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.93 (t, *J* = 8.6 Hz, 2H), 4.00 (d, *J* = 10.4 Hz, 1H), 3.75 (d, *J* = 10.3 Hz, 1H), 1.81 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-d) δ -105.71, -113.69.

^{13}C NMR (101 MHz, Chloroform-d) δ 199.40, 166.13, 163.57 (d, *J* = 5.4 Hz), 161.08, 136.23 (d, *J* = 3.6 Hz), 132.14 (d, *J* = 9.3 Hz), 131.99 (d, *J* = 3.3 Hz), 128.17 (d, *J* = 8.1 Hz), 116.23 (d, *J* = 21.4 Hz), 115.32 (d, *J* = 21.4 Hz), 54.40, 43.13, 22.92.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OF_2BrH^+$ $[M+H]^+$ 339.0191; found 339,0196.

3-iodo-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3bc)**



Brown oil, 30.5 mg, yield 79%.

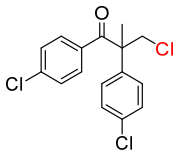
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55-7.41 (m, 2H), 7.35-7.23 (m, 2H), 7.15-7.05 (m, 2H), 6.99-6.86 (m, 2H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.62 (d, *J* = 10.1 Hz, 1H), 1.78 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-d) δ -105.75, -113.62.

^{13}C NMR (101 MHz, Chloroform-d) δ 198.76, 166.09, 163.52 (d, *J* = 7.4 Hz), 161.02, 136.57 (d, *J* = 3.3 Hz), 132.22 (d, *J* = 8.9 Hz), 131.99 (d, *J* = 3.0 Hz), 128.01 (d, *J* = 8.1 Hz), 116.27 (d, *J* = 21.6 Hz), 115.32 (d, *J* = 21.9 Hz), 53.52, 25.07, 19.45.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OF_2INa^+$ $[M+Na]^+$ 408.9871; found 408.9860.

3-chloro-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3ca)**



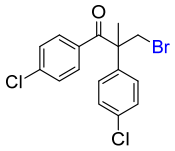
Brown oil, 24.2 mg, yield 74%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.35-7.28 (m, 4H), 7.19-7.15 (m, 4H), 4.01 (d, *J* = 11.1 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 1.71 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.83, 138.84, 138.57, 134.14, 133.79, 130.92, 129.48, 128.59, 127.93, 55.24, 53.01, 21.47.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OCl_3Na^+$ [M+Na]$^+$ 348.9924; found 348.9927.

3-bromo-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3cb)**



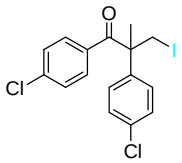
Brown oil, 26.0 mg, yield 70%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.33 (m, 4H), 7.26-7.22 (m, 4H), 3.98 (d, *J* = 10.4 Hz, 1H), 3.75 (d, *J* = 10.4 Hz, 1H), 1.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.58, 138.84, 138.79, 134.16, 133.88, 130.90, 129.50, 128.58, 127.83, 54.59, 42.78, 22.72.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OCl_2BrH^+$ [M+H]$^+$ 370.9600; found 370.9595.

3-iodo-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3cc)**



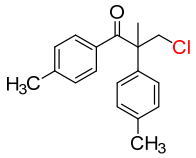
Brown oil, 19.7 mg, yield 47%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.33 (m, 4H), 7.28-7.20 (m, 4H), 3.80 (d, *J* = 10.2 Hz, 1H), 3.61 (d, *J* = 10.2 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 198.94, 139.18, 138.72, 134.10, 133.94, 130.94, 129.51, 128.56, 127.67, 53.73, 24.88, 18.78.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OCl_2INa^+$ [M+Na]$^+$ 440.9280; found 440.9273.

3-chloro-2-methyl-1,2-di-p-tolylpropan-1-one (**3da)**



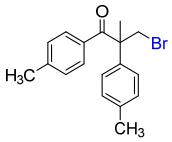
Brown oil, 21.2 mg, yield 74%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 (d, *J* = 8.4, 1.9 Hz, 2H), 7.23-7.16 (m, 4H), 7.04 (d, 2H), 4.14 (d, *J* = 10.9 Hz, 1H), 3.85 (d, *J* = 9.1 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 201.20, 142.79, 137.53, 137.46, 133.35, 129.83, 129.71, 128.78, 126.36, 55.19, 53.56, 21.65, 21.50, 21.11.

HRMS (ESI$^+$): calcd. For $C_{18}H_{19}OClNa^+$ [M+Na]$^+$ 309.1017; found 309.1002.

3-bromo-2-methyl-1,2-di-p-tolylpropan-1-one (**3db)**



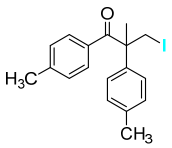
Brown oil, 26.5 mg, yield 80%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.23-7.15 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.04 (d, *J* = 10.2 Hz, 1H), 3.75 (d, *J* = 10.2 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.94, 142.75, 137.70, 137.58, 133.40, 129.85, 129.70, 128.78, 126.27, 54.52, 43.58, 22.94, 21.50, 21.12.

HRMS (ESI$^+$): calcd. For $C_{18}H_{19}OBrH^+$ [M+H]$^+$ 331.0692; found 331.0696.

3-iodo-2-methyl-1,2-di-p-tolylpropan-1-one (**3dc)**



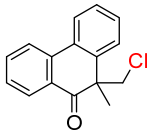
Brown oil, 12.1 mg, yield 32%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.23-7.14 (m, 4H), 7.03 (d, *J* = 8.1 Hz, 2H), 3.85 (d, *J* = 10.0 Hz, 1H), 3.62 (d, *J* = 10.0 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 1.77 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.35, 142.68, 137.95, 137.55, 133.45, 129.85, 129.75, 128.75, 126.14, 53.61, 25.15, 21.49, 21.12, 19.97.

HRMS (ESI^{+}): calcd. For $C_{18}H_{19}OINa^{+}$ [M+Na]$^{+}$ 401.0373; found 403.0354.

10-(chloromethyl)-10-methylphenanthren-9(10*H*)-one (**3ea)**



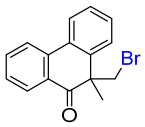
White solid, 24.4 mg, yield 95%.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.14 (d, *J* = 7.8, 1.5 Hz, 1H), 8.10-8.02 (m, 2H), 7.70 (t, *J* = 7.6, 7.0, 1.4 Hz, 1H), 7.52-7.38 (m, 4H), 4.24 (d, *J* = 10.8 Hz, 1H), 3.86 (d, *J* = 10.8 Hz, 1H), 1.56 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.48, 139.50, 137.02, 134.86, 130.22, 129.31, 128.62, 128.42, 128.03, 127.89, 126.73, 124.14, 123.10, 52.53, 50.73, 25.30.

HRMS (ESI^{+}): calcd. For $C_{16}H_{13}OClNa^{+}$ [M+Na]$^{+}$ 279.0547; found 279.0546.

10-(bromomethyl)-10-methylphenanthren-9(10*H*)-one (**3eb)**



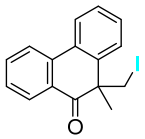
White solid, 29.5 mg, yield 98%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 1H), 8.02-7.93 (m, 2H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.46-7.32 (m, 4H), 4.05 (d, *J* = 10.0 Hz, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 1.53 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.40, 140.02, 137.00, 134.88, 130.02, 129.35, 128.49, 128.43, 128.10, 127.92, 126.64, 124.10, 123.10, 51.92, 39.23, 26.39.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OBrH^+$ $[M+H]^+$ 301.0223; found 301.0218.

10-(iodomethyl)-10-methylphenanthren-9(10*H*)-one (**3ec)**



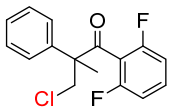
White solid, 32.7 mg, yield 94%.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (d, *J* = 7.8, 1.5 Hz, 1H), 8.07-8.02 (m, 2H), 7.70 (t, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.48-7.41 (m, 4H), 3.95 (d, *J* = 9.7 Hz, 1H), 3.49 (d, *J* = 9.7 Hz, 1H), 1.63 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.68, 140.98, 136.98, 134.88, 129.70, 129.42, 128.42, 128.29, 128.18, 127.92, 126.56, 124.05, 123.10, 51.37, 27.30, 13.73.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OINa^+$ $[M+Na]^+$ 370.9903; found 370.9889.

3-chloro-1-(2,6-difluorophenyl)-2-methyl-2-phenylpropan-1-one (**3fa)**



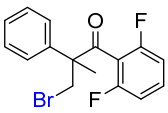
Brown oil, 24.4 mg, yield 83%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38-7.30 (m, 5H), 7.26-7.21 (m, 1H), 6.78 (t, *J* = 8.1 Hz, 2H), 3.92 (d, *J* = 10.2 Hz, 1H), 3.78 (d, *J* = 10.3 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.63, 159.52 (d, *J* = 8.1 Hz), 157.03 (d, *J* = 8.0 Hz), 136.90, 131.43 (t, *J* = 9.8 Hz), 128.97, 128.60, 128.24, 128.01, 127.15, 111.59 (d, *J* = 25.6 Hz), 57.66, 51.23, 19.02.

HRMS (ESI$^+$): calcd. For $C_{16}H_{13}OF_2ClNa^+$ $[M+Na]^+$ 317.0515; found 317.0506.

3-bromo-1-(2,6-difluorophenyl)-2-methyl-2-phenylpropan-1-one (**3fb)**



Brown oil, 29.8 mg, yield 88%.

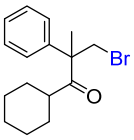
^{1}H NMR (400 MHz, Chloroform-d) δ 7.40-7.20 (m, 6H), 6.79 (m, 2H), 4.15 (d, *J* = 10.4 Hz, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 1.83 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-d) δ -109.77.

^{13}C NMR (101 MHz, Chloroform-d) δ 199.29, 159.50 (d, *J* = 8.0 Hz), 157.01 (d, *J* = 7.9 Hz), 137.20, 131.44 (t, *J* = 9.8 Hz), 128.59, 128.33 (d, *J* = 18.9 Hz), 128.03, 127.11, 126.53, 111.59 (d, *J* = 25.4 Hz), 57.00, 40.54, 20.21.

HRMS (ESI^{+}): calcd. For $C_{16}H_{13}OF_2BrNa^{+}$ [M+Na]$^{+}$ 361.0010; found 360.9999.

3-bromo-1-cyclohexyl-2-methyl-2-phenylpropan-1-one (**3gb)**



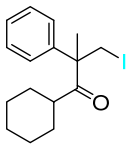
Brown oil, 27.5 mg, yield 89%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42-7.34 (m, 2H), 7.34-7.28 (m, 1H), 7.26-7.21 (m, 2H), 3.70 (d, *J* = 10.3 Hz, 1H), 3.61 (d, *J* = 10.3 Hz, 1H), 2.49-2.35 (m, 1H), 1.74 (s, 3H), 1.72-1.66 (m, 1H), 1.63-1.58 (m, 1H), 1.59-1.50 (m, 2H), 1.39-1.31 (m, 2H), 1.29-1.24 (m, 1H), 1.15-1.08 (m, 2H), 0.99-0.85 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 212.45, 139.16, 128.75, 127.82, 126.68, 55.75, 47.25, 30.53, 25.55, 25.45, 21.93, 18.12.

HRMS (ESI^{+}): calcd. For $C_{16}H_{21}OBrNa^{+}$ [M+Na]$^{+}$ 331.0668; found 331.0660.

3-iodo-1-cyclohexyl-2-methyl-2-phenylpropan-1-one (**3gc)**



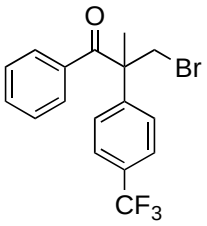
Brown oil, 27.4 mg, yield 77%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42-7.36 (m, 2H), 7.36-7.32 (m, 1H), 7.30-7.25 (m, 2H), 3.93 (d, *J* = 10.5 Hz, 1H), 3.79 (d, *J* = 10.5 Hz, 1H), 2.48-2.37 (m, 1H), 1.78 (s, 3H), 1.74-1.68 (m, 1H), 1.64-1.54 (m, 3H), 1.43-1.27 (m, 3H), 1.18-1.10 (m, 2H), 1.01-0.90 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 213.28, 138.64, 128.74, 127.81, 126.79, 56.49, 47.01, 41.75, 30.54, 30.48, 25.57, 25.54, 25.46, 19.91.

HRMS (ESI^{+}): calcd. For $C_{16}H_{21}OINa^{+}$ [M+Na]$^{+}$ 379.0529; found 379.0512.

3-bromo-2-methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one **(3hb)**



White solid, 24.0 mg, yield 65%.

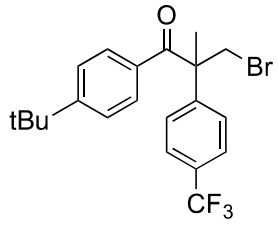
^{1}H NMR (400 MHz, Chloroform-d) δ 7.54-7.46 (m, 4H), 7.45-7.36 (m, 3H), 7.35-7.32 (m, 2H), 4.05 (d, *J* = 10.3 Hz, 1H), 3.77 (d, *J* = 10.3 Hz, 1H), 1.80 (s, 3H).

^{19}F NMR (376 MHz, Chloroform-d) δ -63.25.

^{13}C NMR (101 MHz, Chloroform-d) δ 200.43, 139.78, 139.33, 129.53, 129.45, 128.29, 126.35, 125.23, 125.20, 125.16, 125.12, 55.19, 42.22, 22.66.

HRMS (ESI^{+}): calcd. For $C_{17}H_{14}OF_3BrNa^{+}$ [M+Na]$^{+}$ 393.0072; found 393.0070.

3-bromo-1-(4-(*tert*-butyl)phenyl)-2-methyl-2-(4-(trifluoromethyl)phenyl)propan-1-one **(3ib)**



White solid, 23.0 mg, yield 54%.

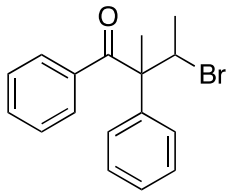
^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 (q, *J* = 8.5 Hz, 4H), 7.45-7.41 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.08 (d, *J* = 10.2 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 1.79 (s, 3H), 1.33 (s, 9H).

^{19}F NMR (376 MHz, Chloroform-d) δ -63.23.

^{13}C NMR (101 MHz, Chloroform-d) δ 200.57, 151.40, 139.66, 136.55, 129.45, 126.35, 125.92, 125.14, 125.11, 54.83, 41.97, 34.58, 31.26, 22.84.

HRMS (ESI^{+}): calcd. For $C_{21}H_{22}OF_3BrNa^{+}$ [M+Na]$^{+}$ 449.0698; found 449.0715.

3-bromo-2-methyl-1,2-diphenylbutan-1-one (**3jb**)



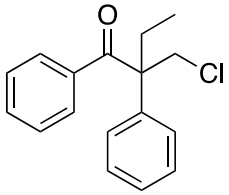
Colorless oil, 27.0 mg, yield 85%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45-7.39 (m, 4H), 7.38-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.20 (m, 2H), 5.14-4.97 (m, 1H), 1.81 (d, *J* = 6.5 Hz, 4H), 1.76 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 202.10, 141.17, 137.77, 131.67, 128.86, 128.07, 127.79, 126.87, 60.09, 58.60, 23.33, 17.40.

HRMS (ESI^{+}): calcd. For $C_{17}H_{17}OBrNa^{+}$ [M+Na]$^{+}$ 339.0355; found 339.0356.

2-(chloromethyl)-1,2-diphenylbutan-1-one (**3ka**)



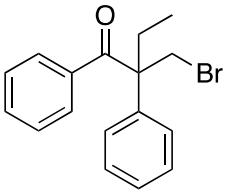
Colorless oil, 22.3 mg, yield 82%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44-7.37 (m, 4H), 7.37-7.26 (m, 4H), 7.25-7.19 (m, 2H), 4.24 (d, *J* = 11.5 Hz, 1H), 4.03 (d, *J* = 11.5 Hz, 1H), 2.68-2.45 (m, 1H), 2.35-2.18 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.06, 140.23, 136.51, 132.10, 129.23, 129.04, 128.11, 128.09, 127.76, 126.96, 59.32, 49.83, 24.98, 7.96.

HRMS (ESI$^+$): calcd. For $C_{17}H_{17}ClONa^+$ $[M+Na]^+$ 295.0860; found 295.0858.

2-(bromomethyl)-1,2-diphenylbutan-1-one (**3kb**)



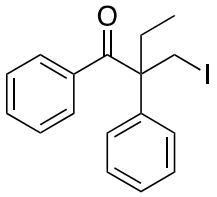
Colorless oil, 29.8 mg, yield 94%.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.35 (m, 5H), 7.35-7.30 (m, 3H), 7.27-7.19 (m, 2H), 4.12 (d, *J* = 10.7 Hz, 1H), 4.01-3.86 (m, 1H), 2.66-2.45 (m, 1H), 2.39-2.21 (m, 1H), 0.75 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 201.83, 140.40, 136.53, 132.09, 129.28, 129.06, 128.12, 127.81, 126.92, 58.69, 40.49, 26.08, 7.89.

HRMS (ESI$^+$): calcd. For $C_{17}H_{17}OBrNa^+$ $[M+Na]^+$ 339.0355; found 339.0352.

2-(iodomethyl)-1,2-diphenylbutan-1-one (**3kc**)



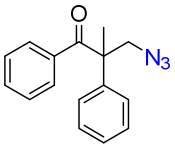
Colorless oil, 23.6 mg, yield 65%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43-7.33 (m, 5H), 7.33-7.28 (m, 2H), 7.28-7.25 (m, 1H), 7.25-7.18 (m, 2H), 3.93 (d, *J* = 10.5, 2.1 Hz, 1H), 3.79 (d, *J* = 10.5, 1.7 Hz, 1H), 2.53-2.40 (m, 1H), 2.33-2.12 (m, 1H), 0.71 (t, *J* = 7.5, 2.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 200.90, 140.77, 136.60, 132.01, 129.36, 129.05, 128.08, 127.80, 126.88, 57.87, 28.12, 17.70, 7.76.

HRMS (ESI$^+$): calcd. For $C_{17}H_{17}IONa^+$ $[M+Na]^+$ 387.0216; found 387.0219.

3-azido-2-methyl-1,2-diphenylpropan-1-one (**4)**



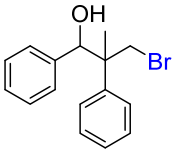
Colorless oil, 19.9 mg, yield 75%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51-7.46 (m, 2H), 7.43-7.37 (m, 3H), 7.37-7.31 (m, 3H), 7.28-7.21 (m, 2H), 3.87 (d, *J* = 12.2 Hz, 1H), 3.62 (d, *J* = 12.1 Hz, 1H), 1.75 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 201.80, 140.43, 135.77, 132.16, 129.58, 129.24, 128.10, 127.87, 126.47, 60.95, 55.21, 21.16.

HRMS (ESI$^+$): calcd. For $C_{16}H_{15}N_3ONa^+$ $[M+Na]^+$ 288.1107; found 288.1094.

3-bromo-2-methyl-1,2-diphenylpropan-1-ol (**5)**



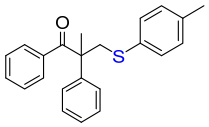
Colorless oil, 29.0 mg, yield 95%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.31 (m, 4H), 7.26-7.17 (m, 4H), 6.96-6.91 (m, 2H), 4.98-4.88 (m, 1H), 3.87 (s, 2H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 140.73, 140.01, 128.05, 127.90, 127.77, 127.61, 127.14, 79.67, 47.63, 42.89, 20.50.

HRMS (ESI$^+$): calcd. For $C_{16}H_{17}OBrNa^+$ $[M+Na]^+$ 327.0355; found 327.0352.

2-methyl-1, 2-diphenyl-3-(p-tolylthio)propan-1-one (**6)**



White solid, 30.5 mg, yield 88%.

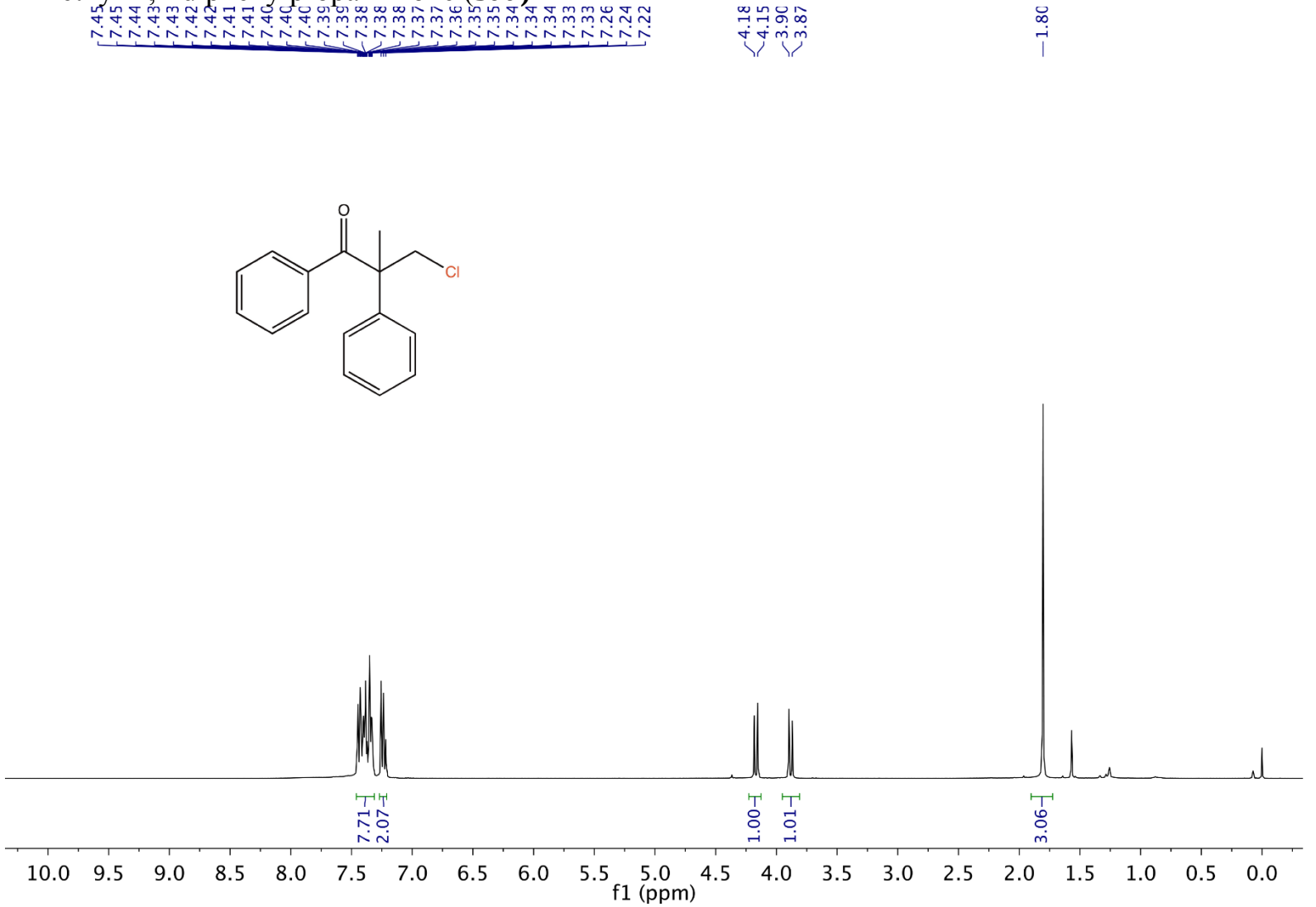
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48-7.42 (m, 2H), 7.39-7.34 (m, 4H), 7.33-7.27 (m, 2H), 7.25-7.19 (m, 2H), 7.12-7.07 (m, 2H), 7.01-6.96 (m, 2H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.50 (d, *J* = 12.7 Hz, 1H), 2.27 (s, 3H), 1.78 (s, 3H).

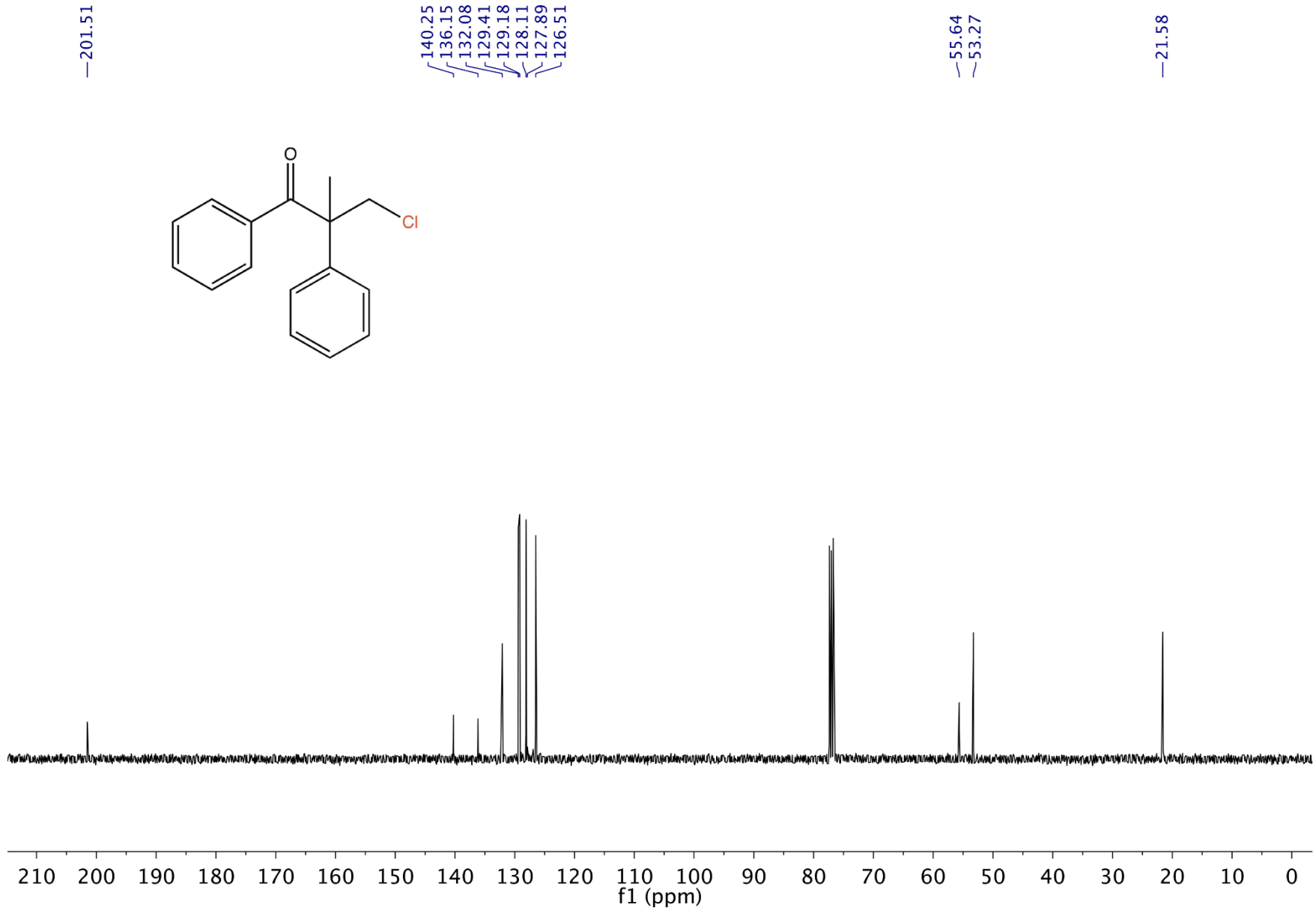
^{13}C NMR (101 MHz, Chloroform-d) δ 202.33, 142.04, 136.31, 136.17, 133.94, 131.84, 130.63, 129.80, 129.57, 129.52, 129.05, 128.55, 128.02, 127.49, 127.08, 126.41, 55.68, 47.21, 23.01, 20.99.

HRMS (ESI$^+$): calcd. For $C_{23}H_{22}OSH^+$ $[M+H]^+$ 347.1464; found 347.1451.

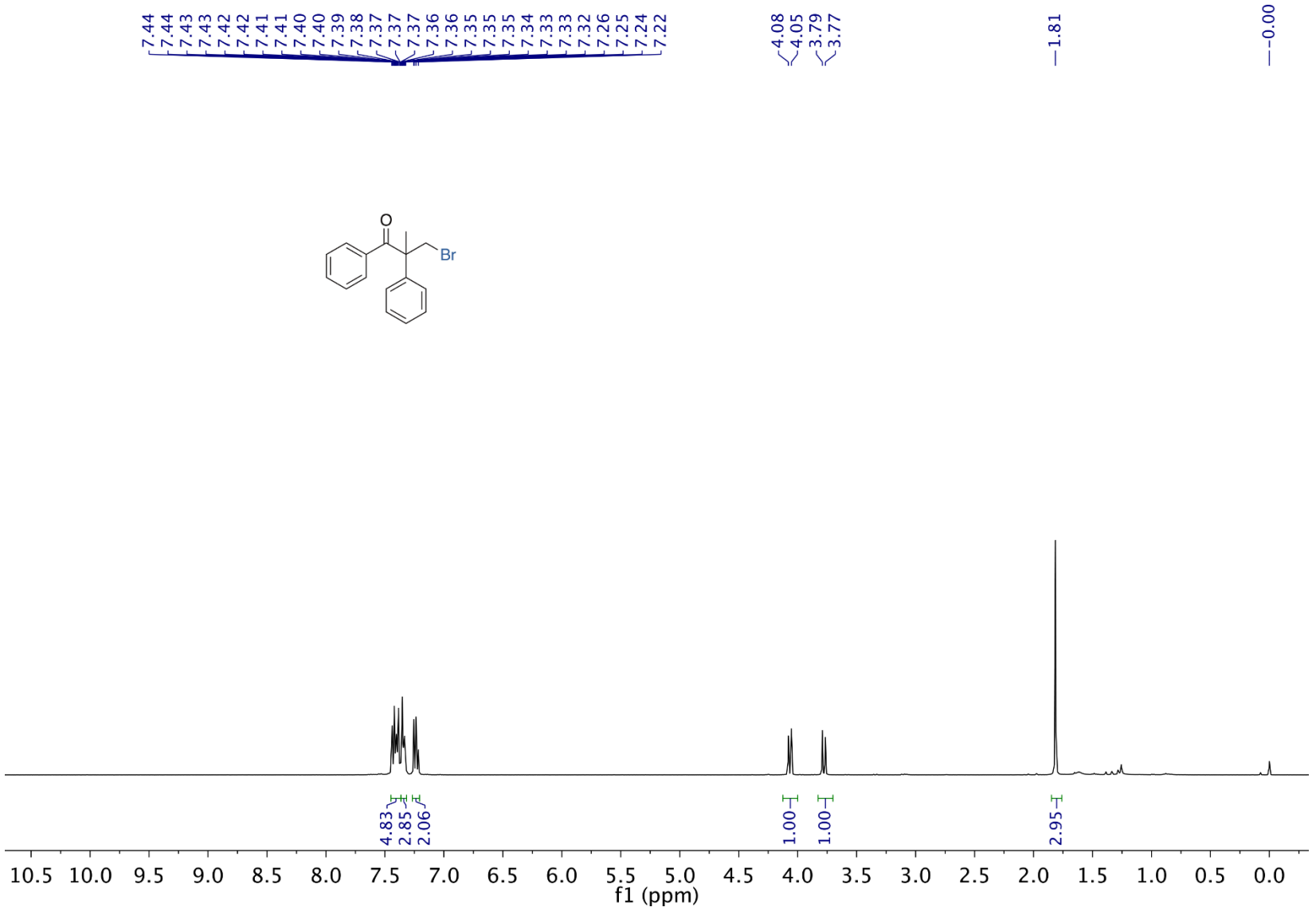
4. ^{1}H, ^{19}F and ^{13}C-NMR Spectra

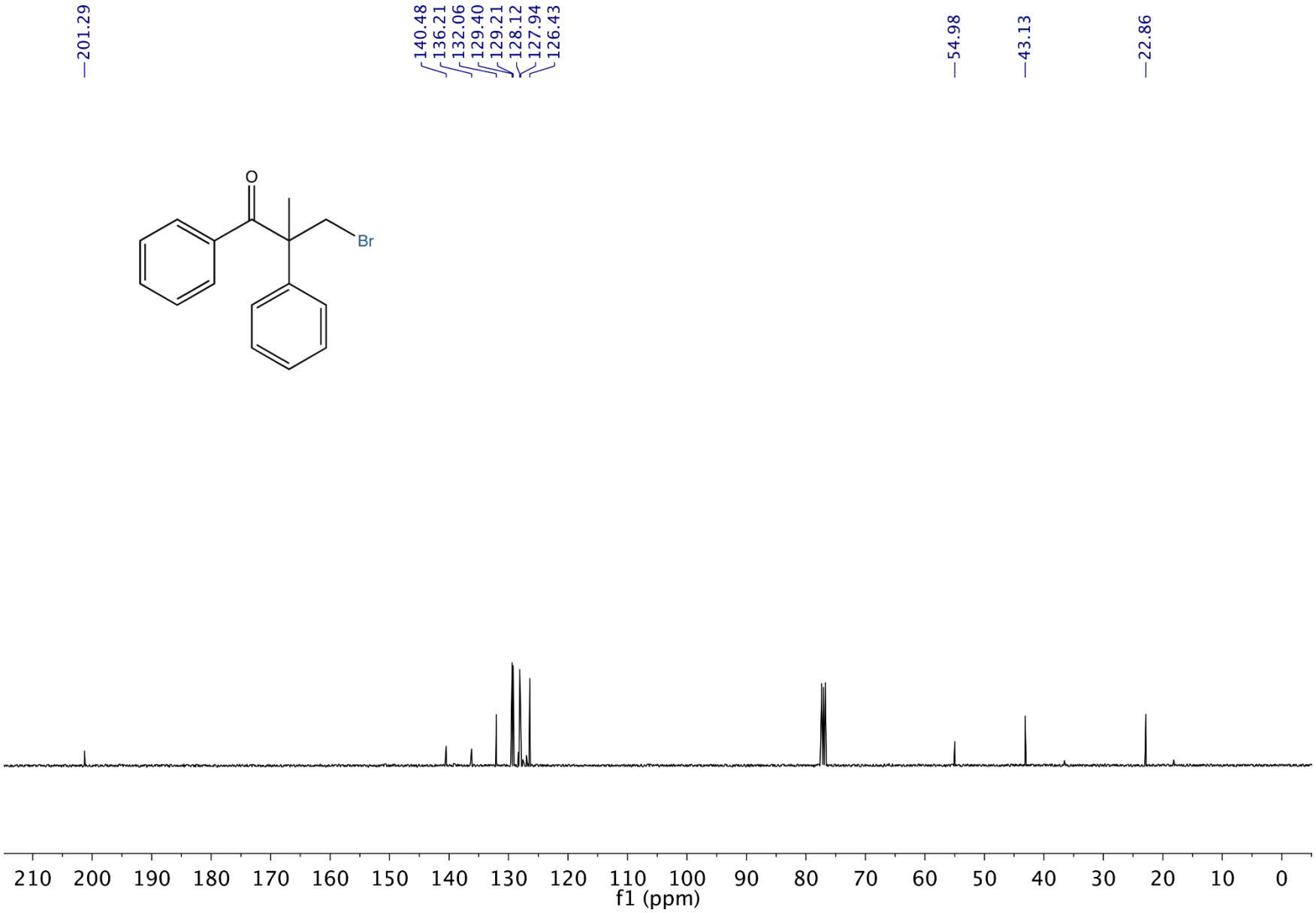
3-chloro-2-methyl-1,2-diphenylpropan-1-one (**3aa)**



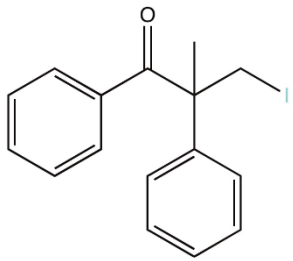

201.51
140.25
136.15
132.08
129.41
129.18
128.11
127.89
126.51
55.64
53.27
21.58
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

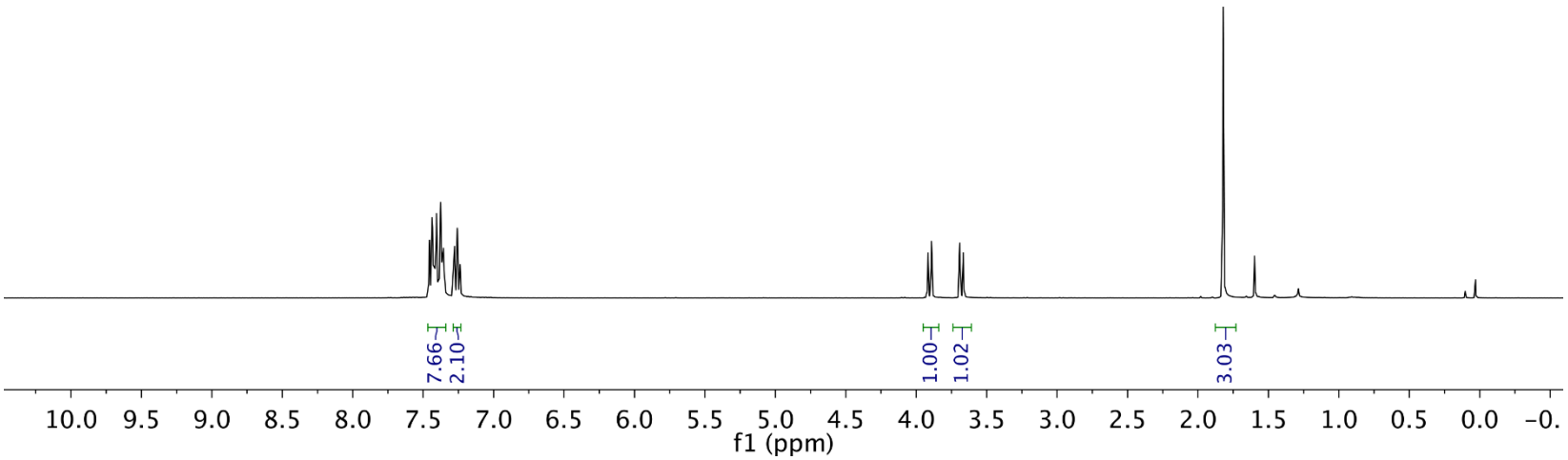
3-bromo-2-methyl-1,2-diphenylpropan-1-one (**3ab)**

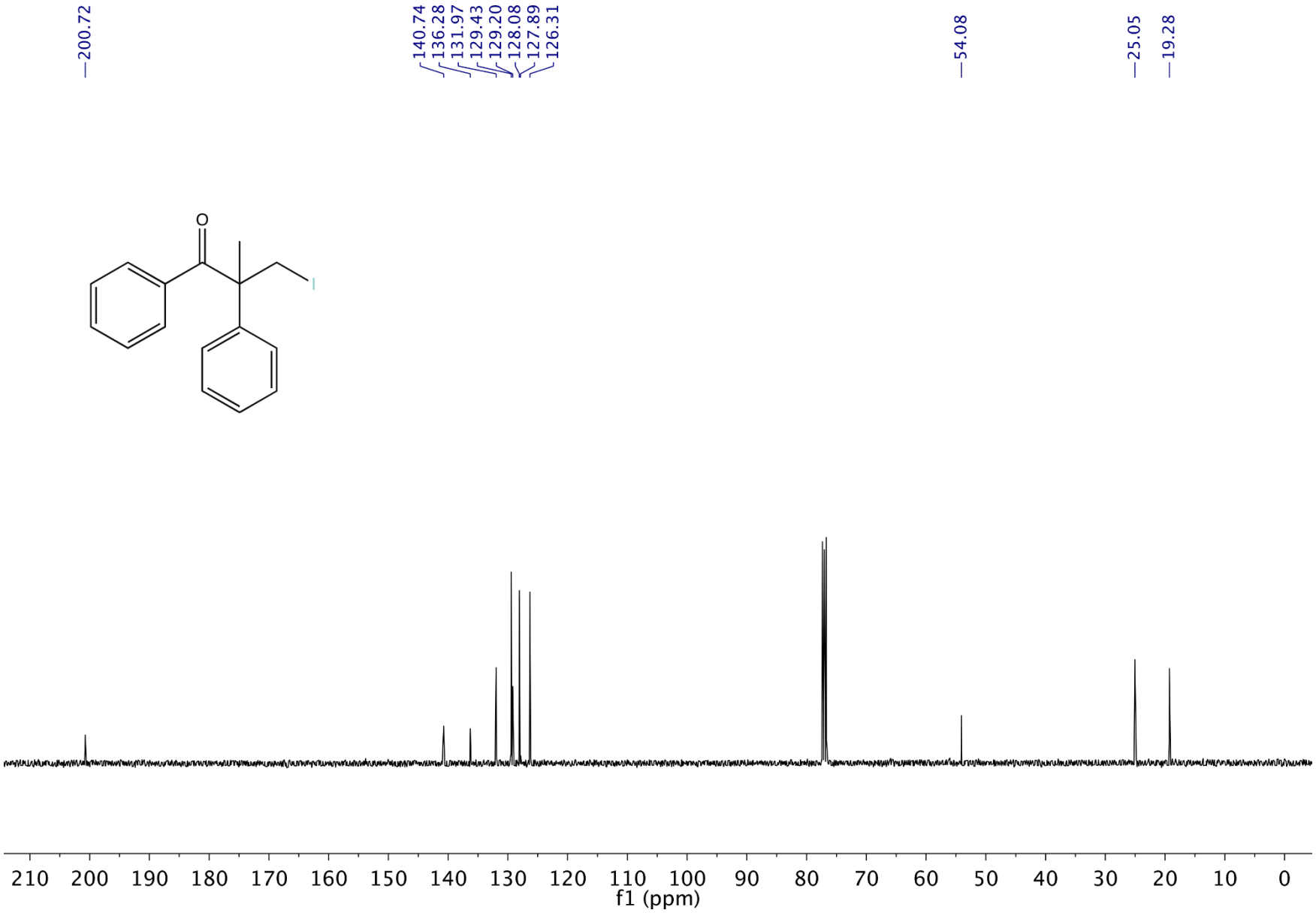



201.29
140.48
136.21
132.06
129.40
129.21
128.12
127.94
126.43
54.98
43.13
22.86
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3-iodo-2-methyl-1,2-diphenylpropan-1-one (**3ac)**

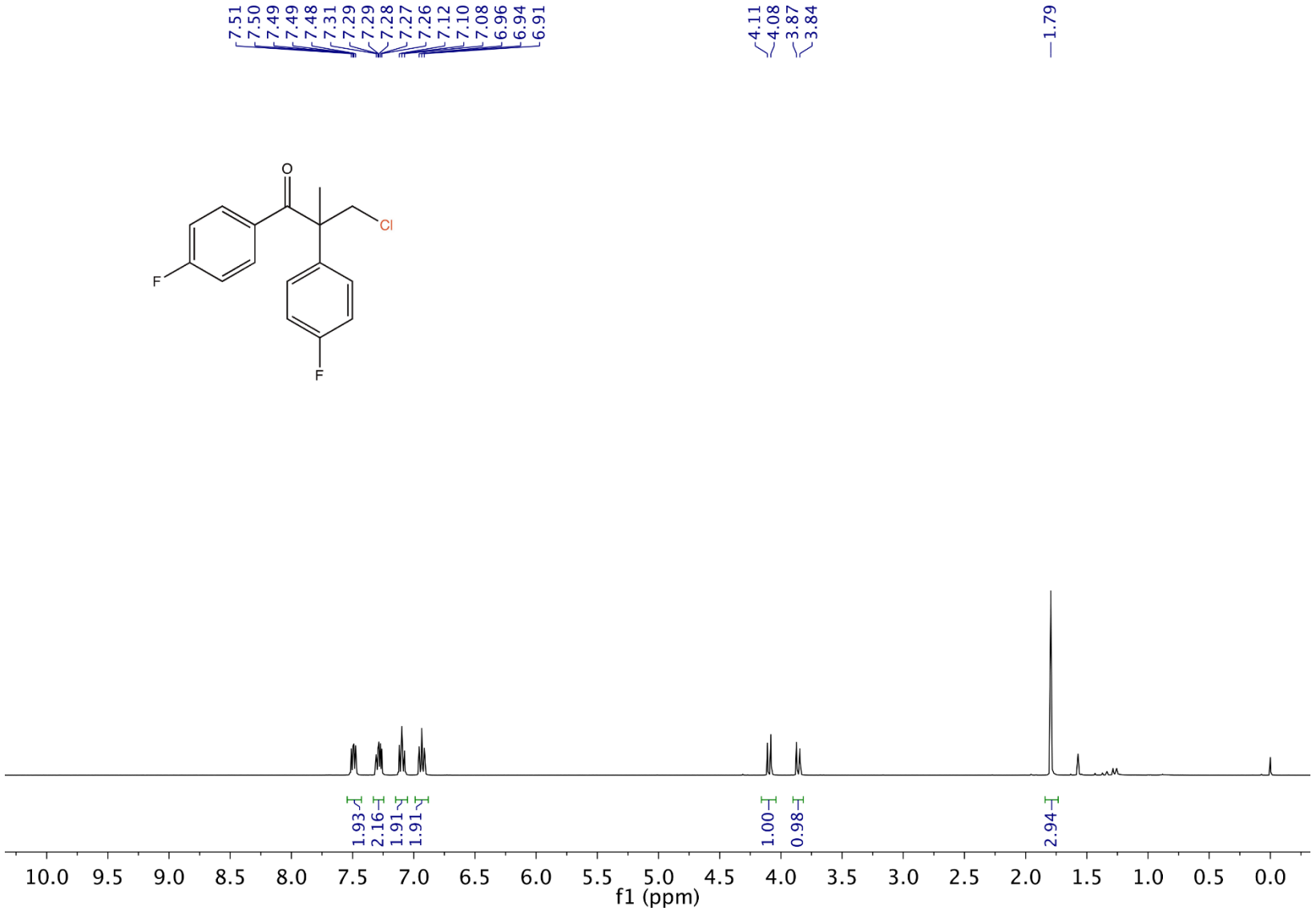


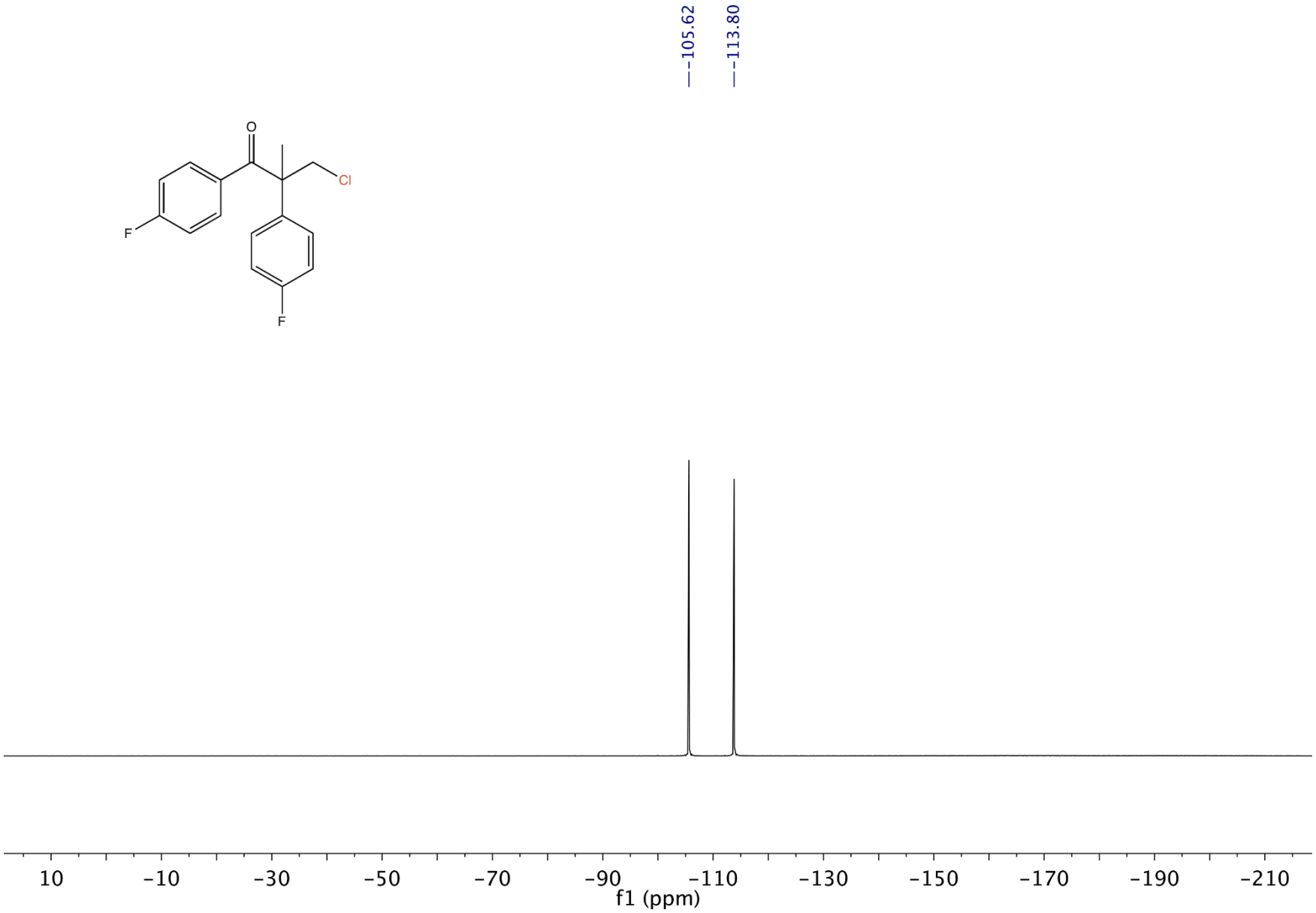


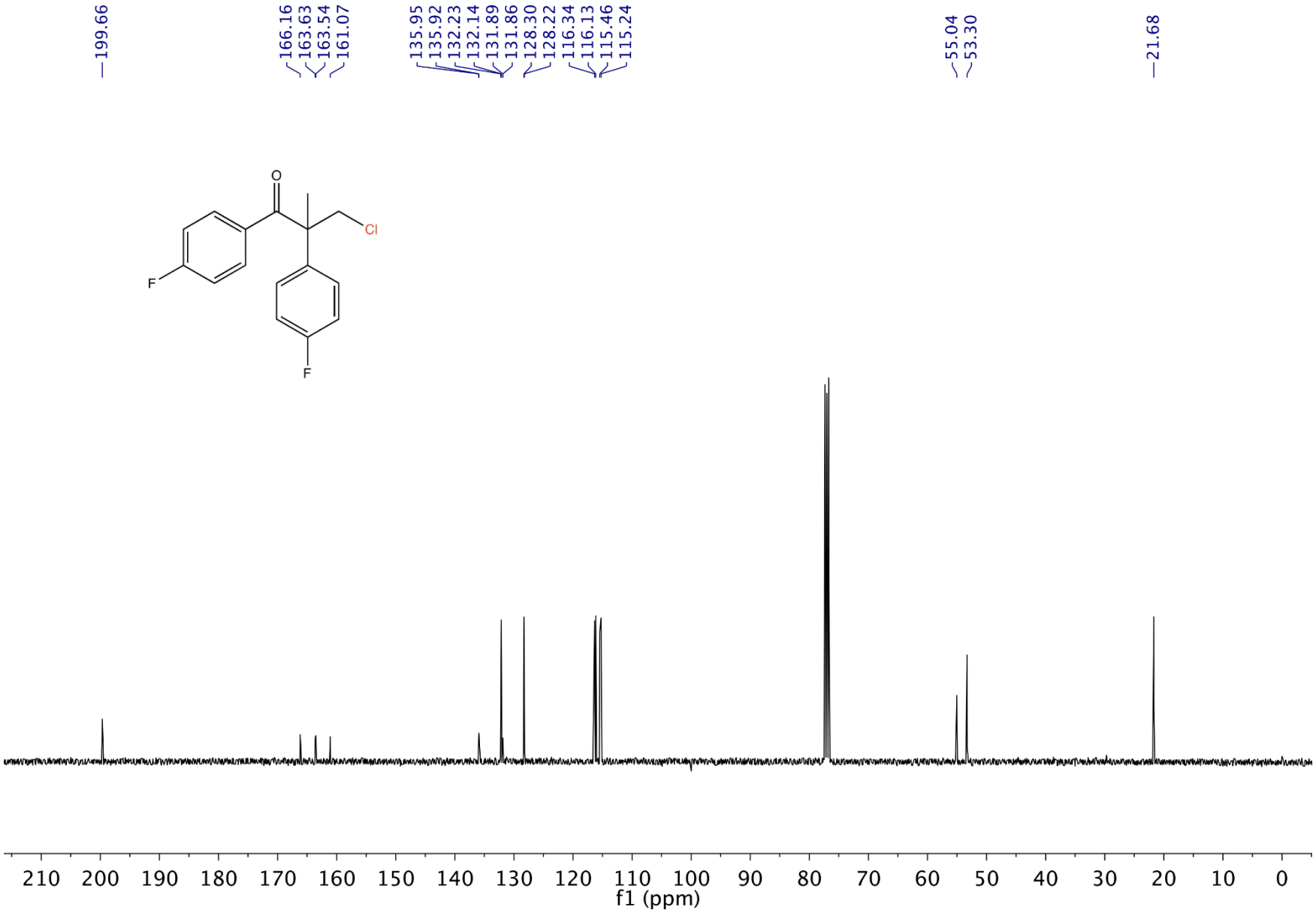

200.72
140.74
136.28
131.97
129.43
129.20
128.08
127.89
126.31
54.08
25.05
19.28
O
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

VI

3-chloro-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3ba)**

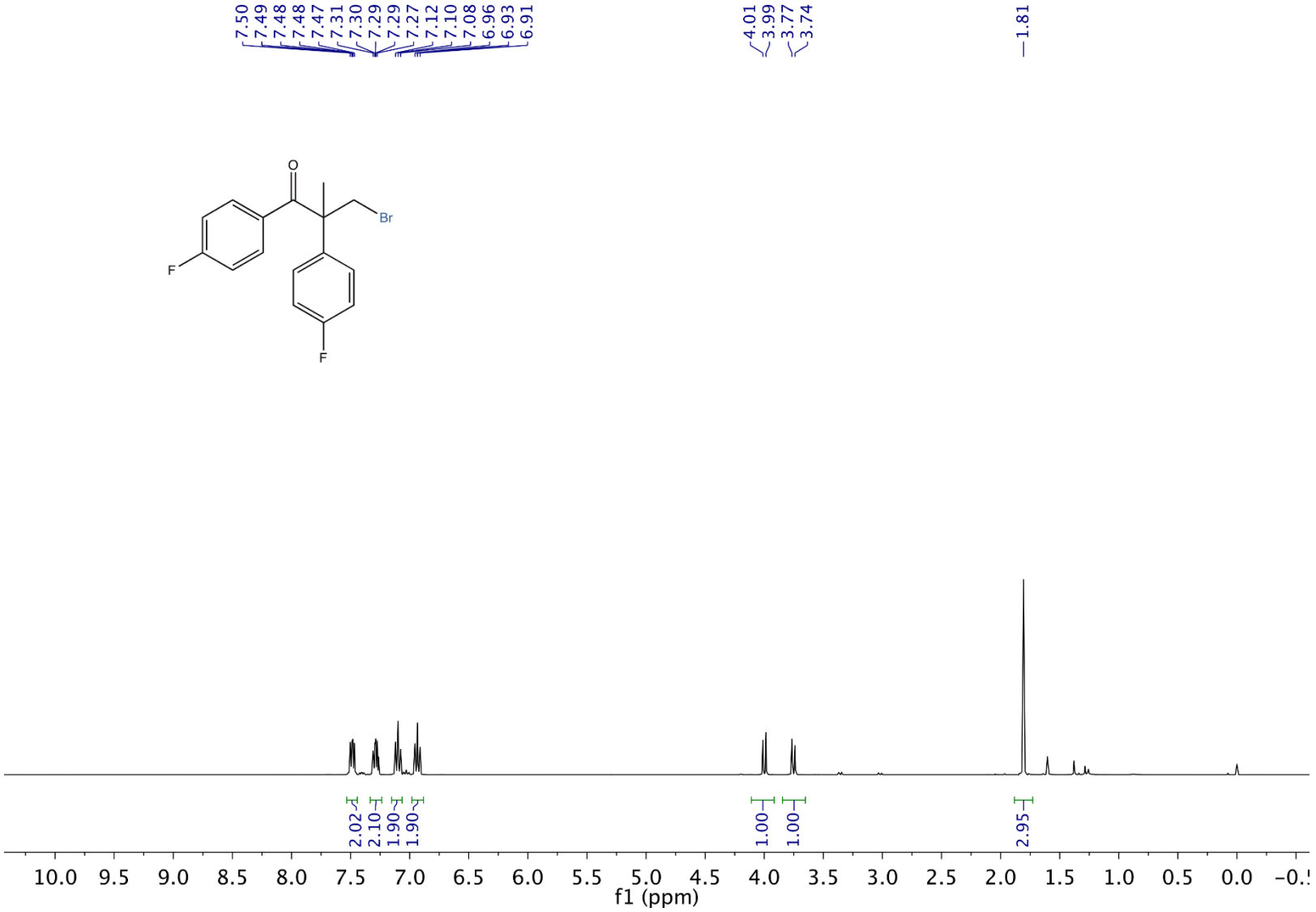



-105.62
-113.80
O
Cl
F
F
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

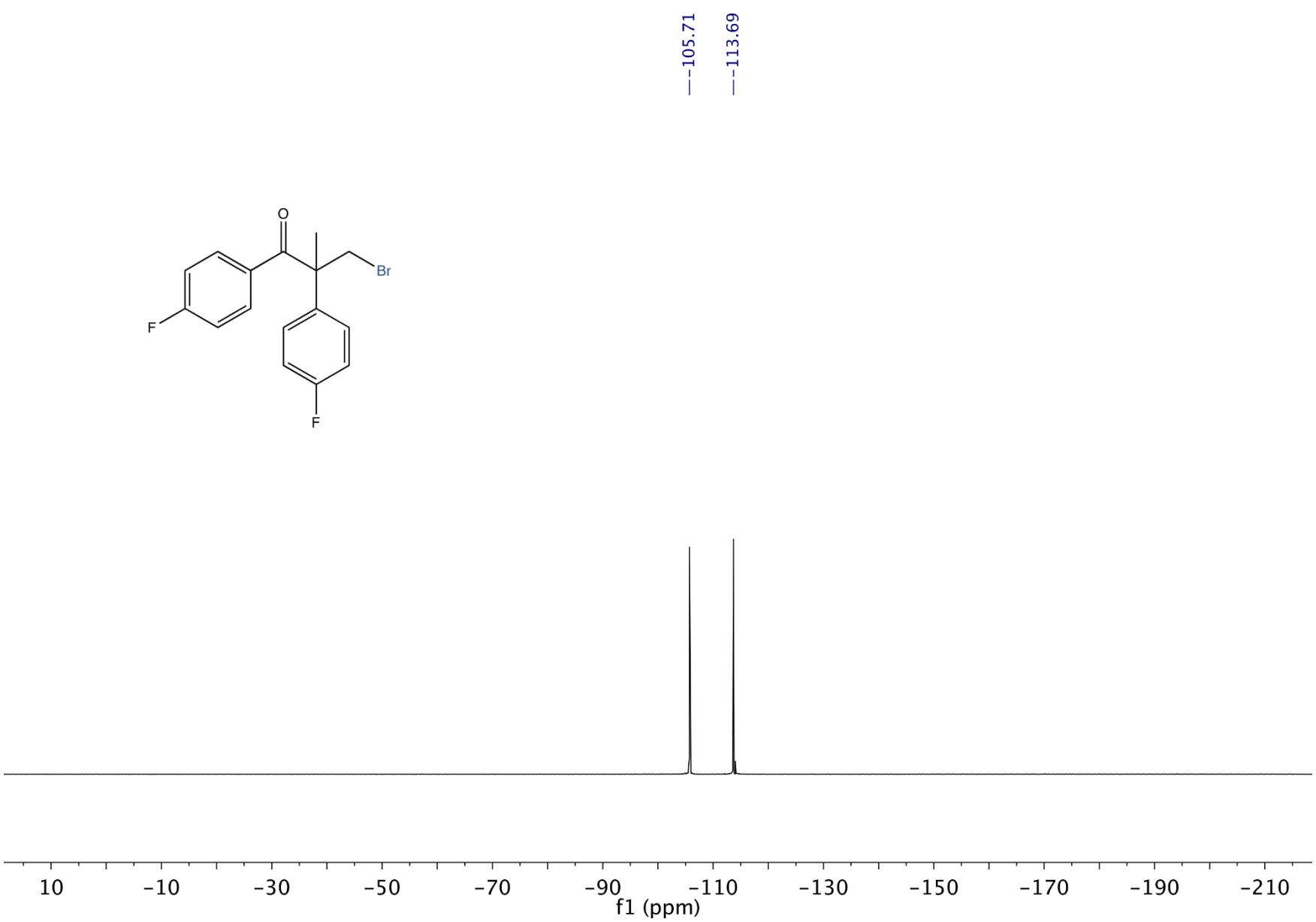

199.66
166.16
163.63
163.54
161.07
135.95
135.92
132.23
132.14
131.89
131.86
128.30
128.22
116.34
116.13
115.46
115.24
55.04
53.30
21.68
O
Cl
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

IX

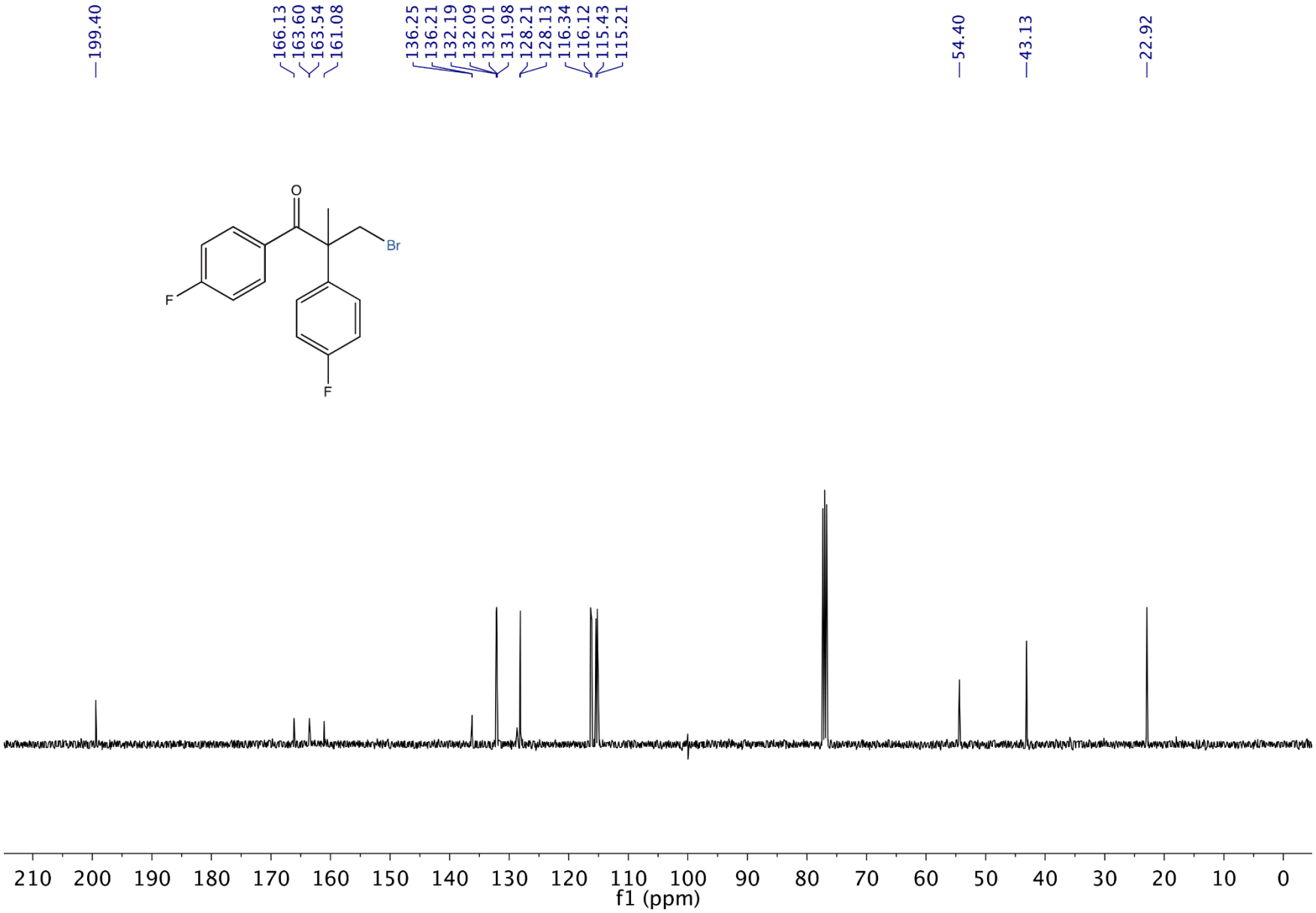
3-bromo-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3bb)**



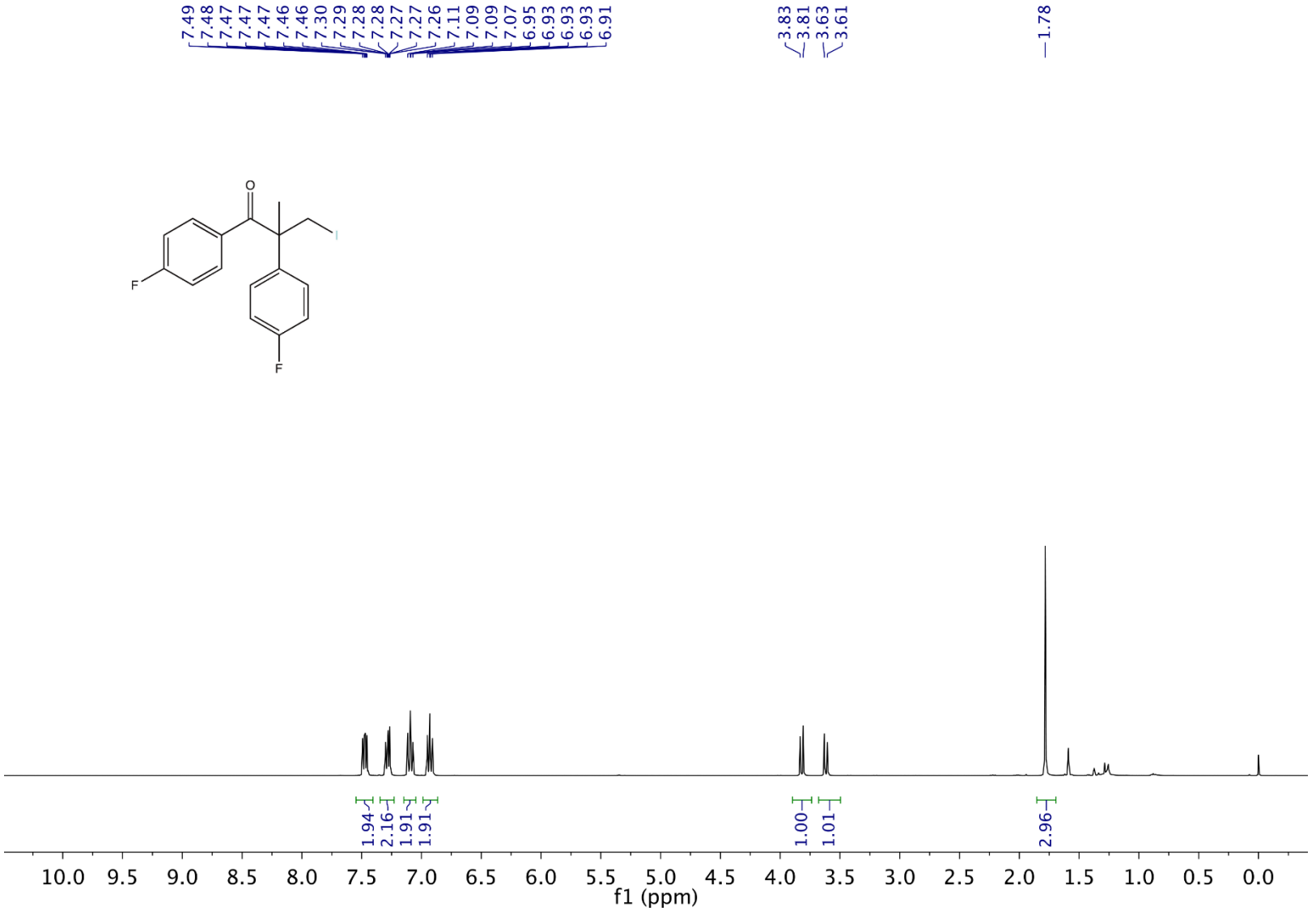
X


-105.71
-113.69
O
Br
F
F
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

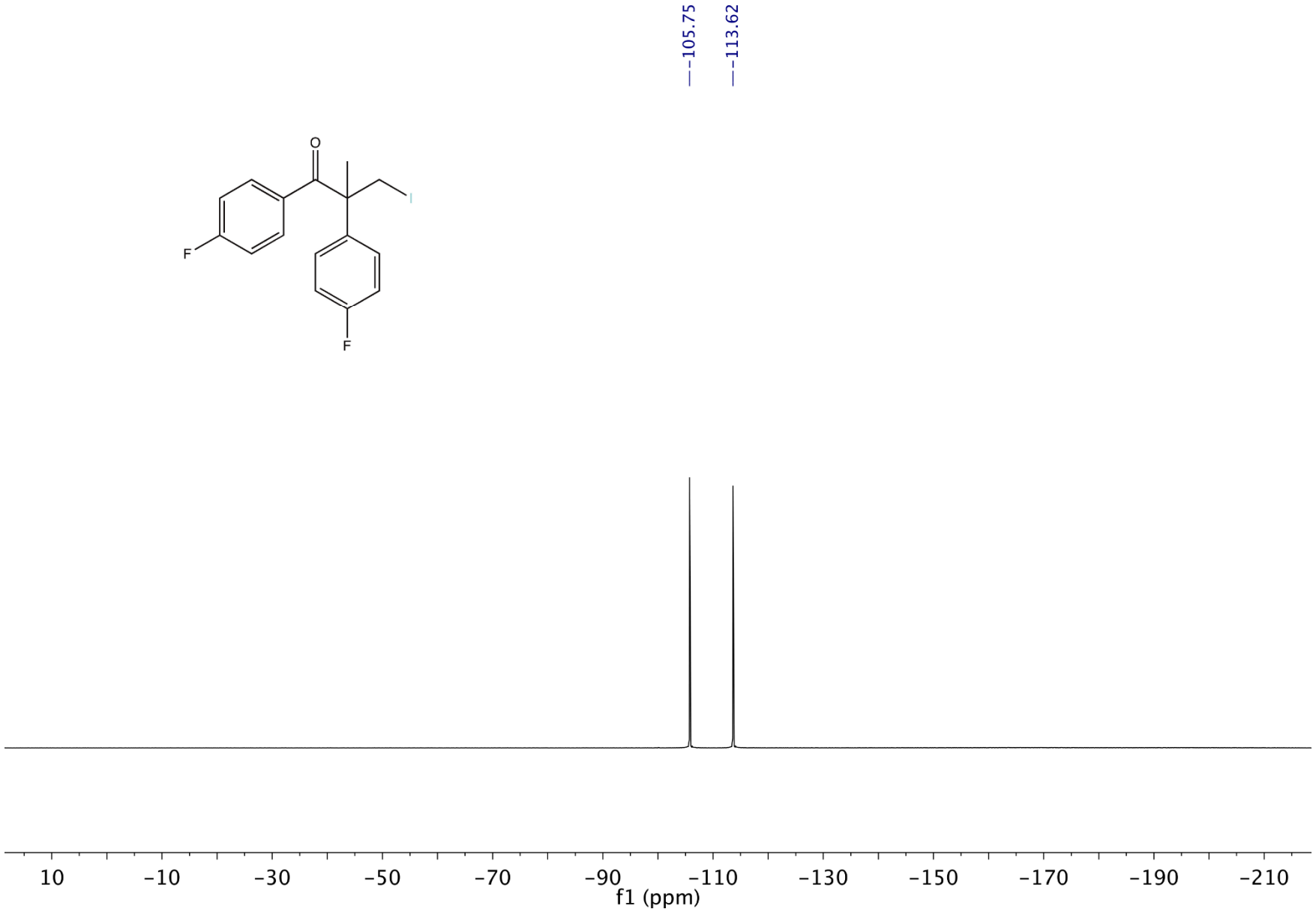
XI

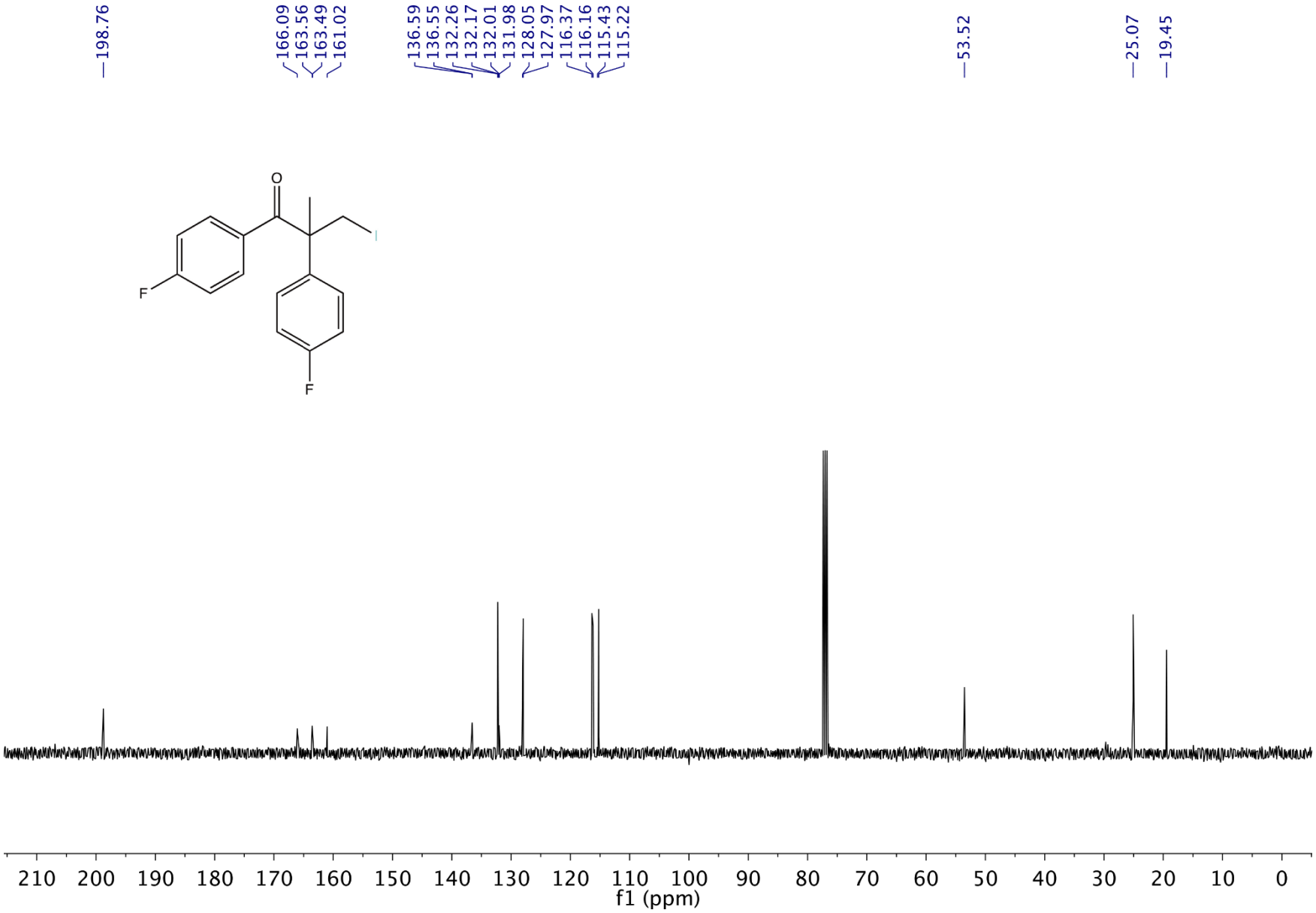

199.40
166.13
163.60
163.54
161.08
136.25
136.21
132.19
132.09
132.01
131.98
128.21
128.13
116.34
116.12
115.43
115.21
54.40
43.13
22.92
O
Br
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3-iodo-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (**3bc)**

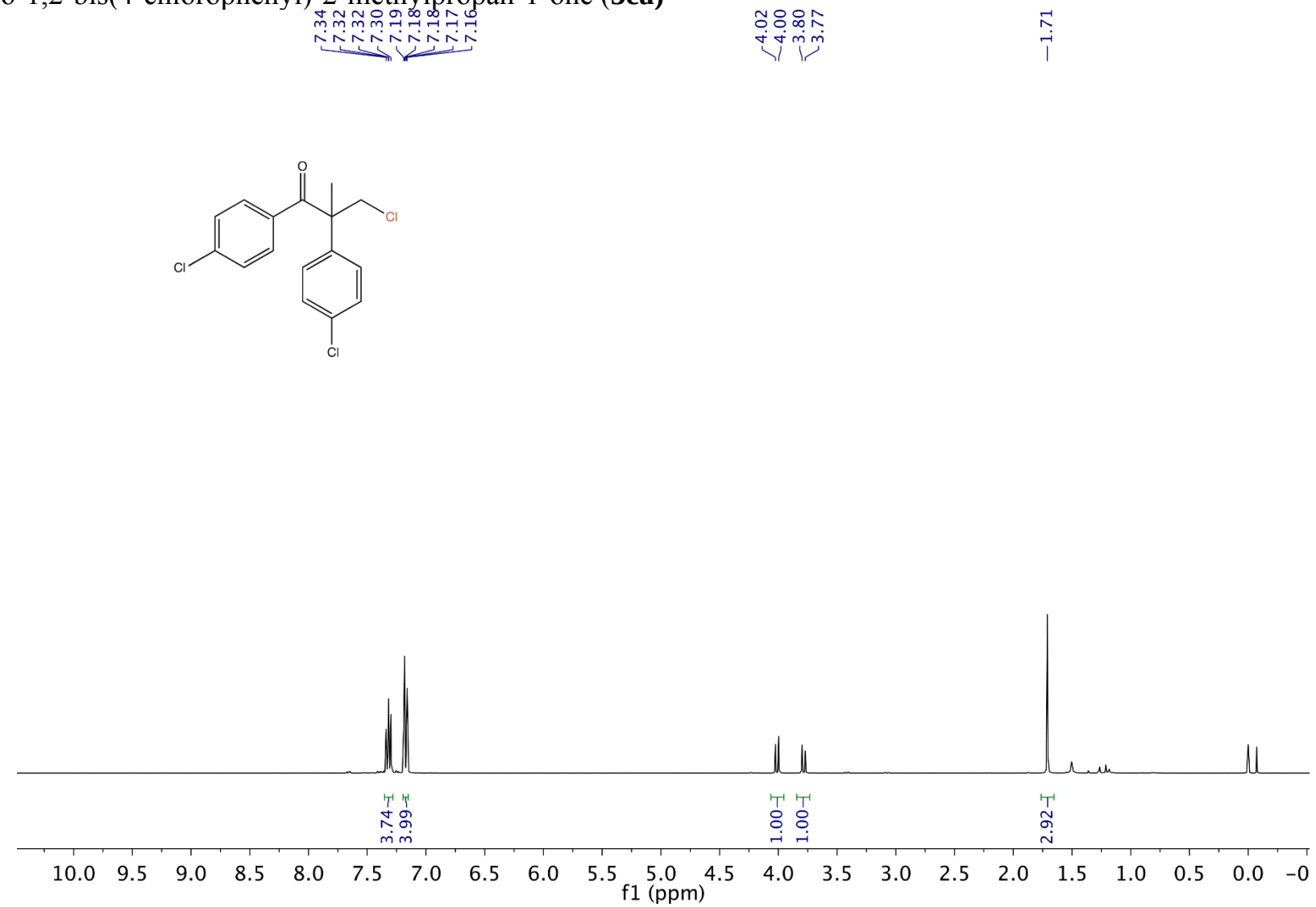


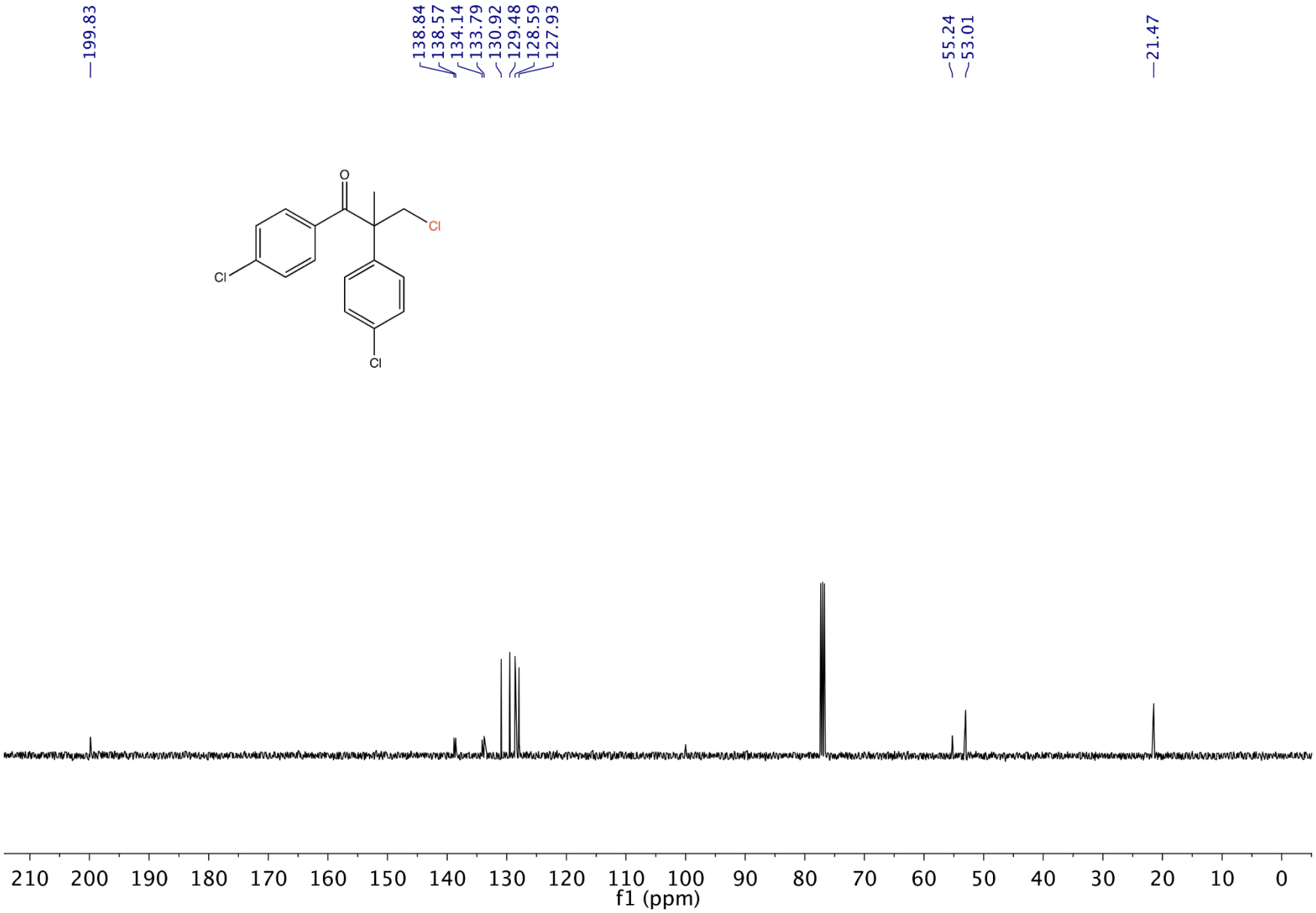
O
F
F


−105.75
−113.62
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

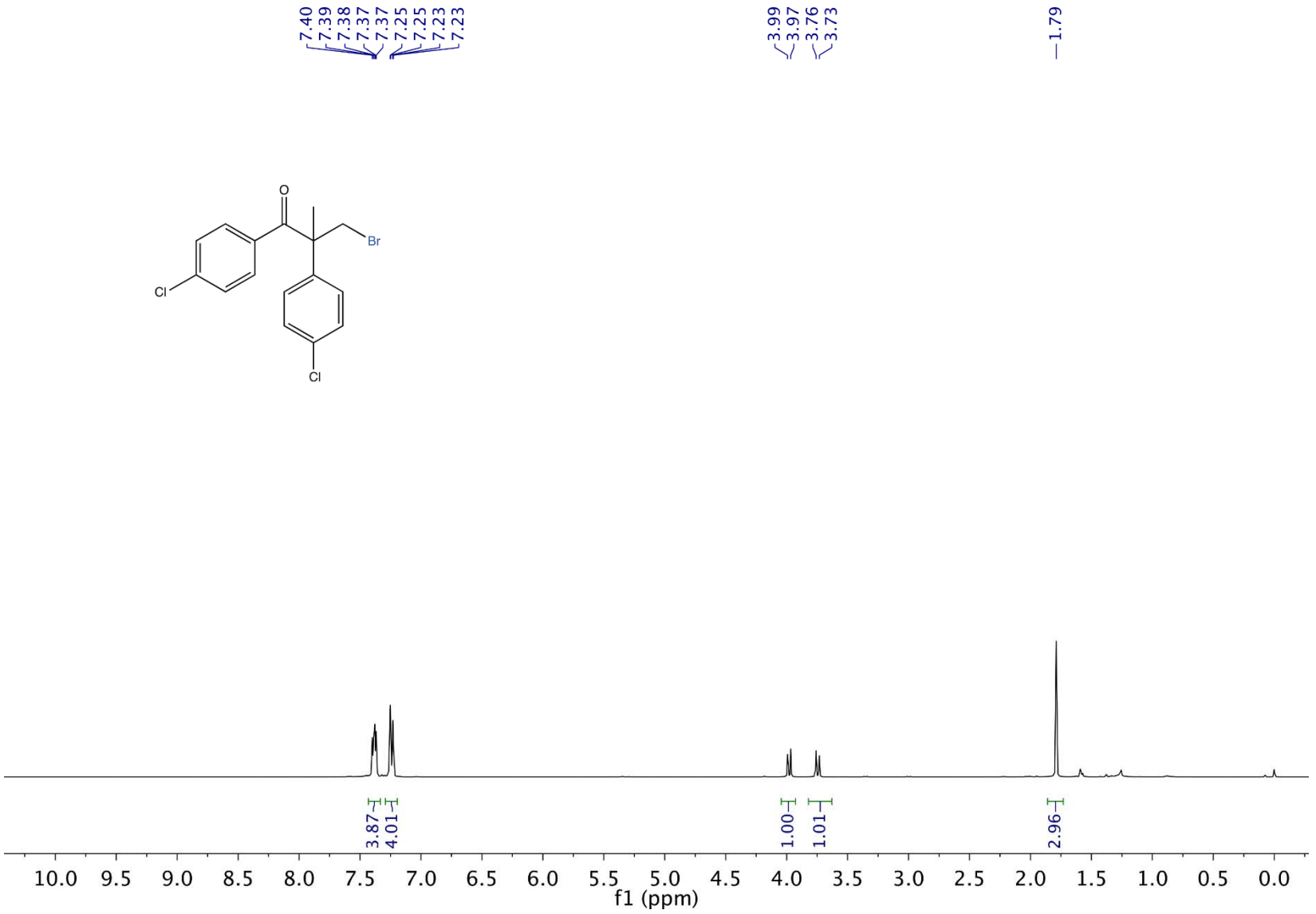

198.76
166.09
163.56
163.49
161.02
136.59
136.55
132.26
132.17
132.01
131.98
128.05
127.97
116.37
116.16
115.43
115.22
53.52
25.07
19.45
O
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

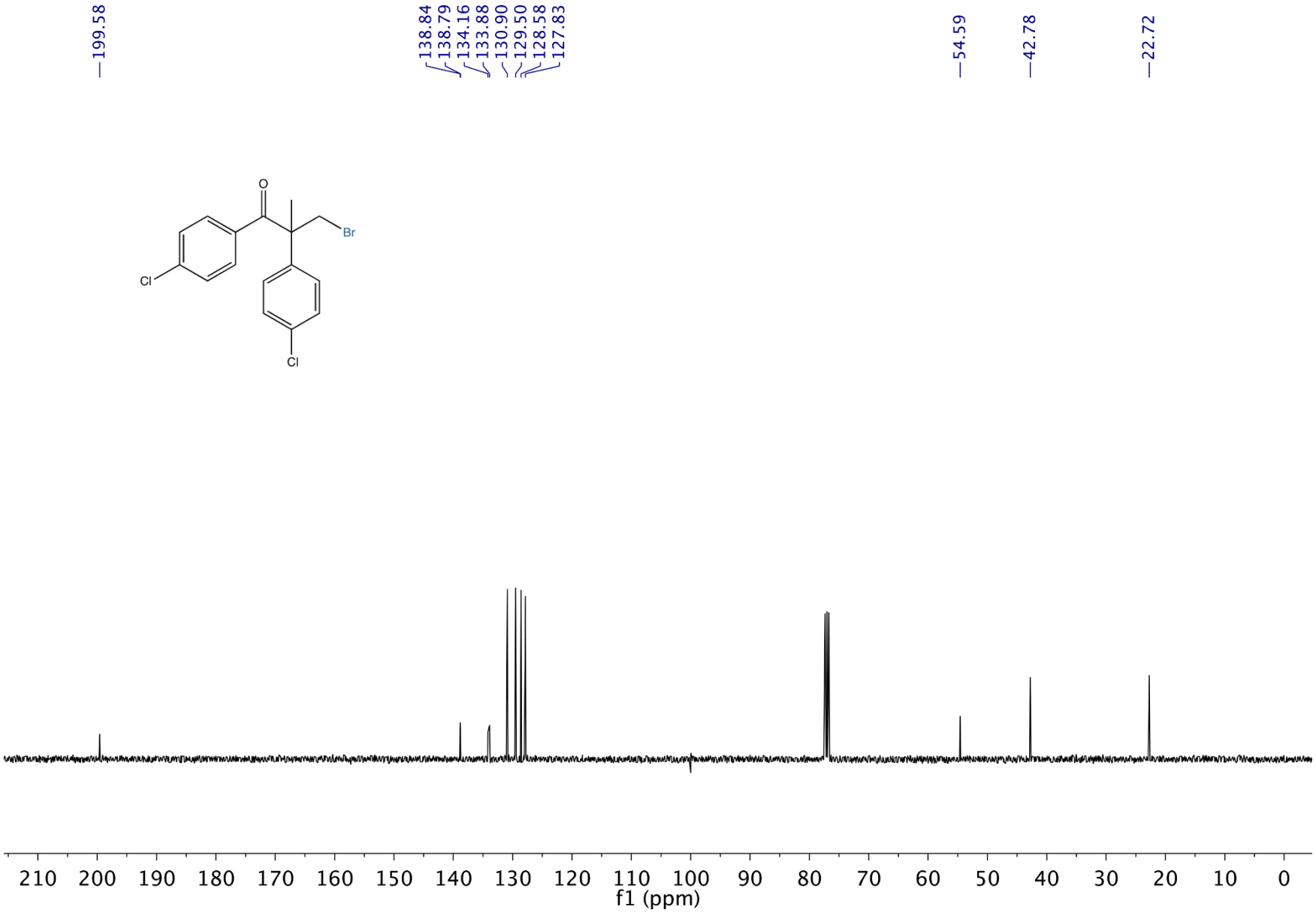
3-chloro-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3ca)**



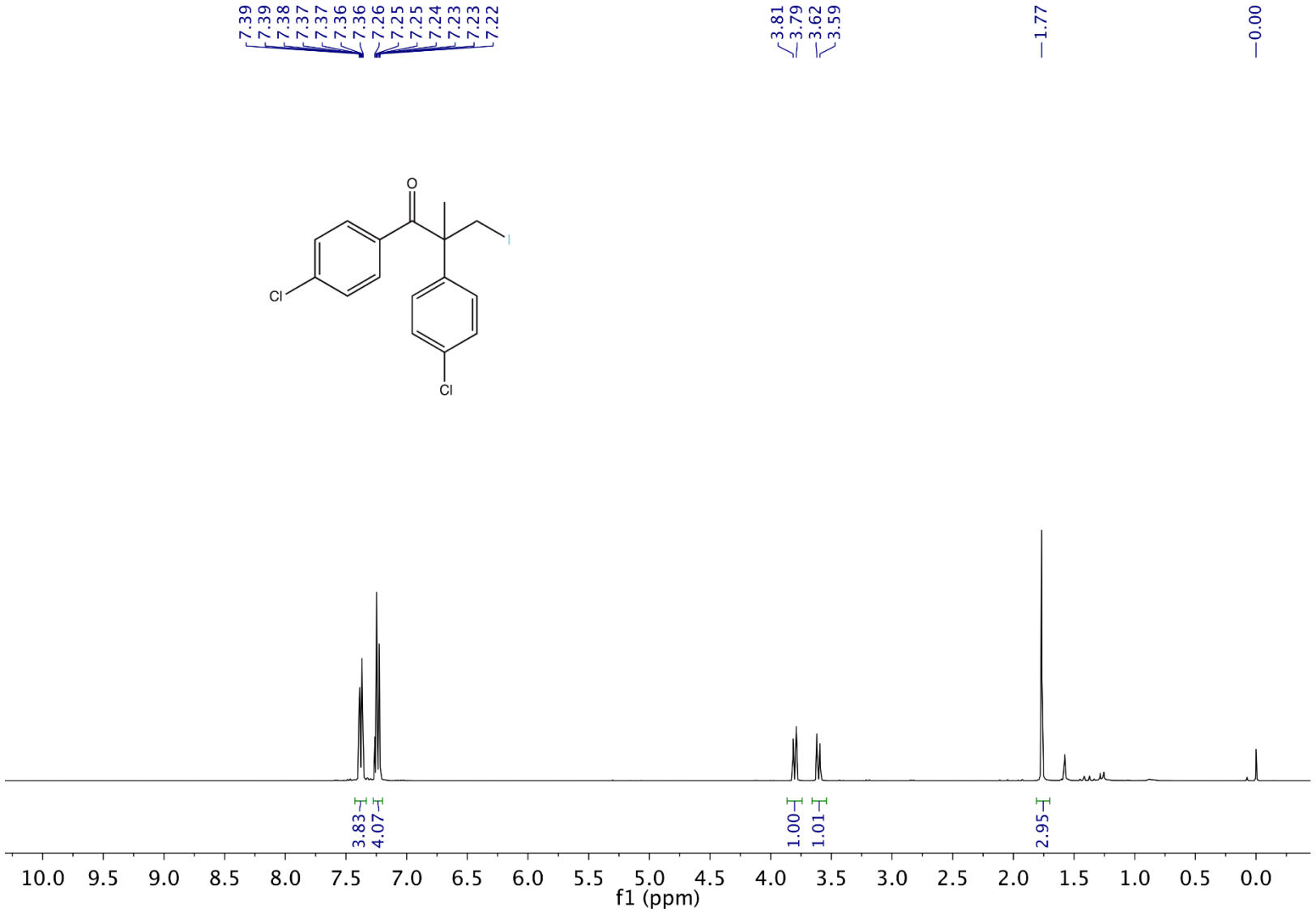

199.83
138.84
138.57
134.14
133.79
130.92
129.48
128.59
127.93
55.24
53.01
21.47
O
Cl
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

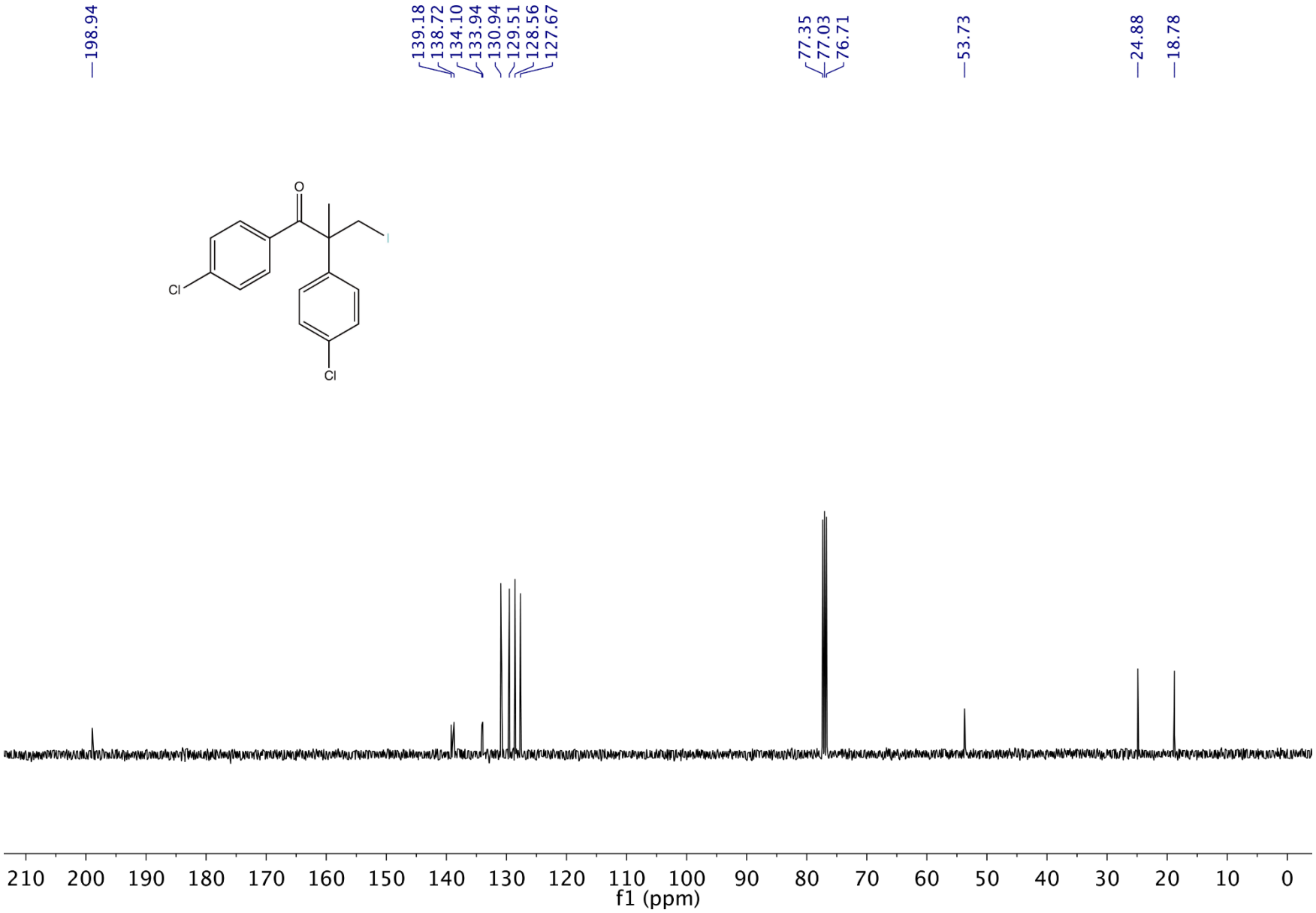
3-bromo-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3cb)**



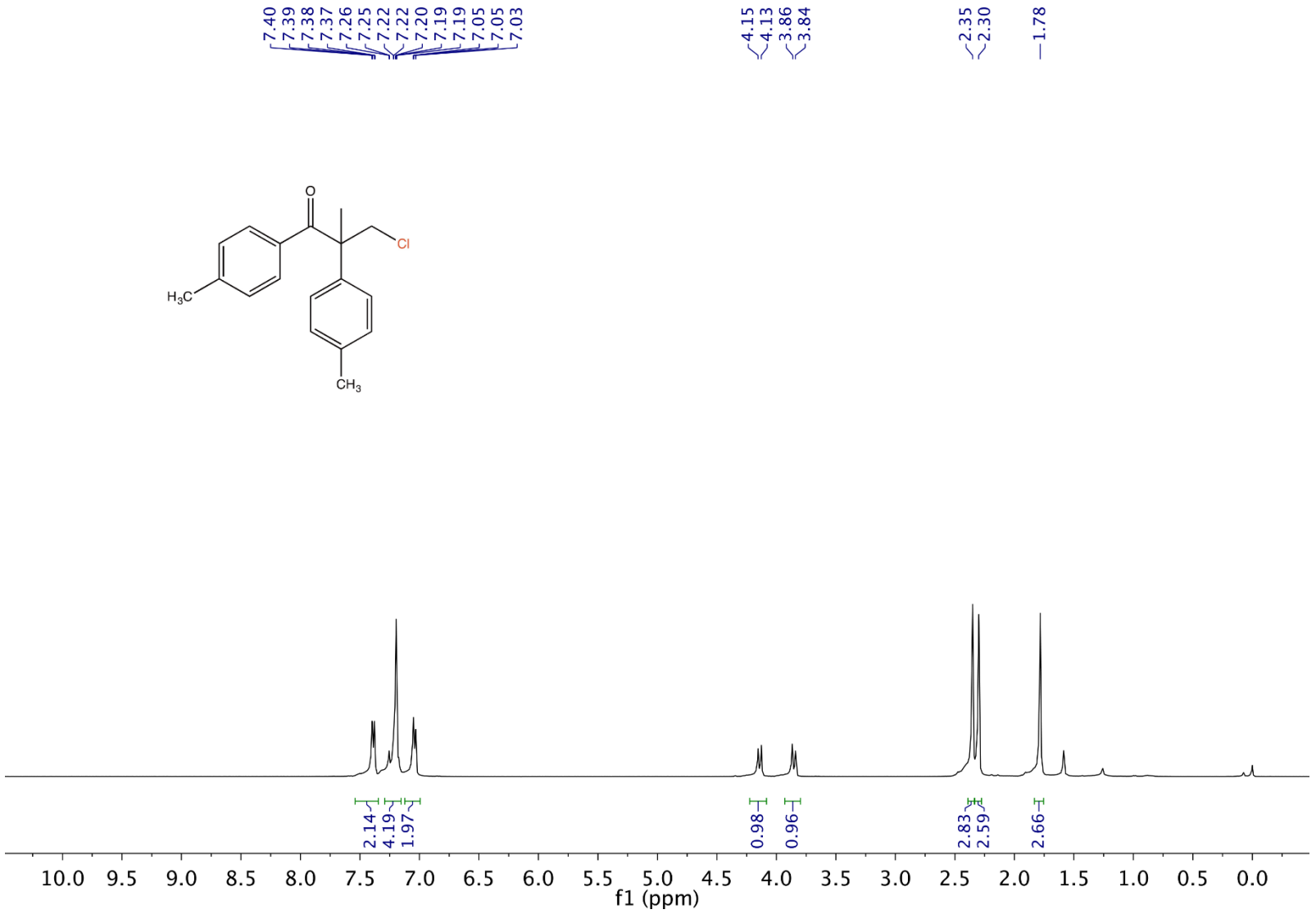

199.58
138.84
138.79
134.16
133.88
130.90
129.50
128.58
127.83
54.59
42.78
22.72
O
Br
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

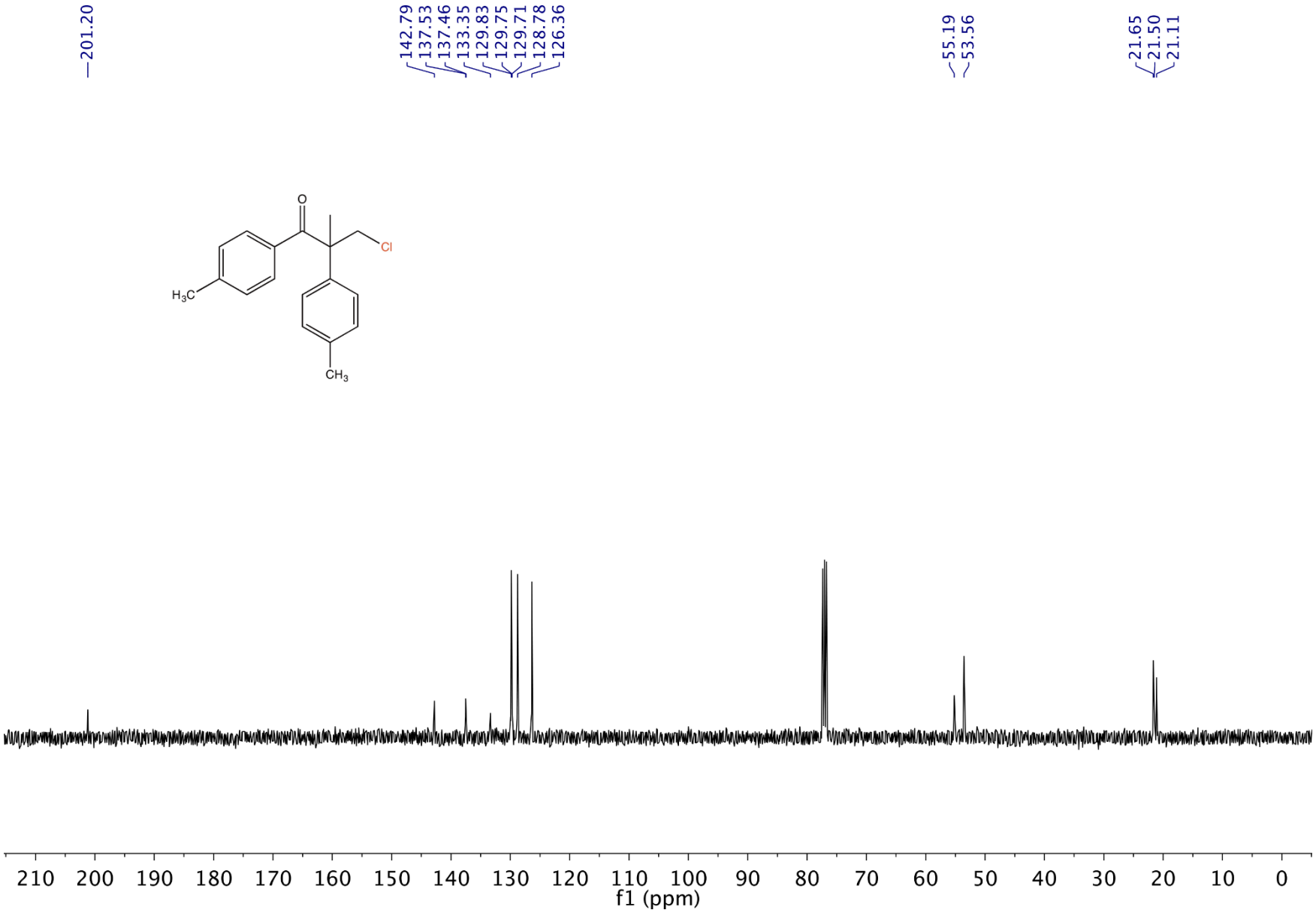
3-iodo-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (**3cc)**



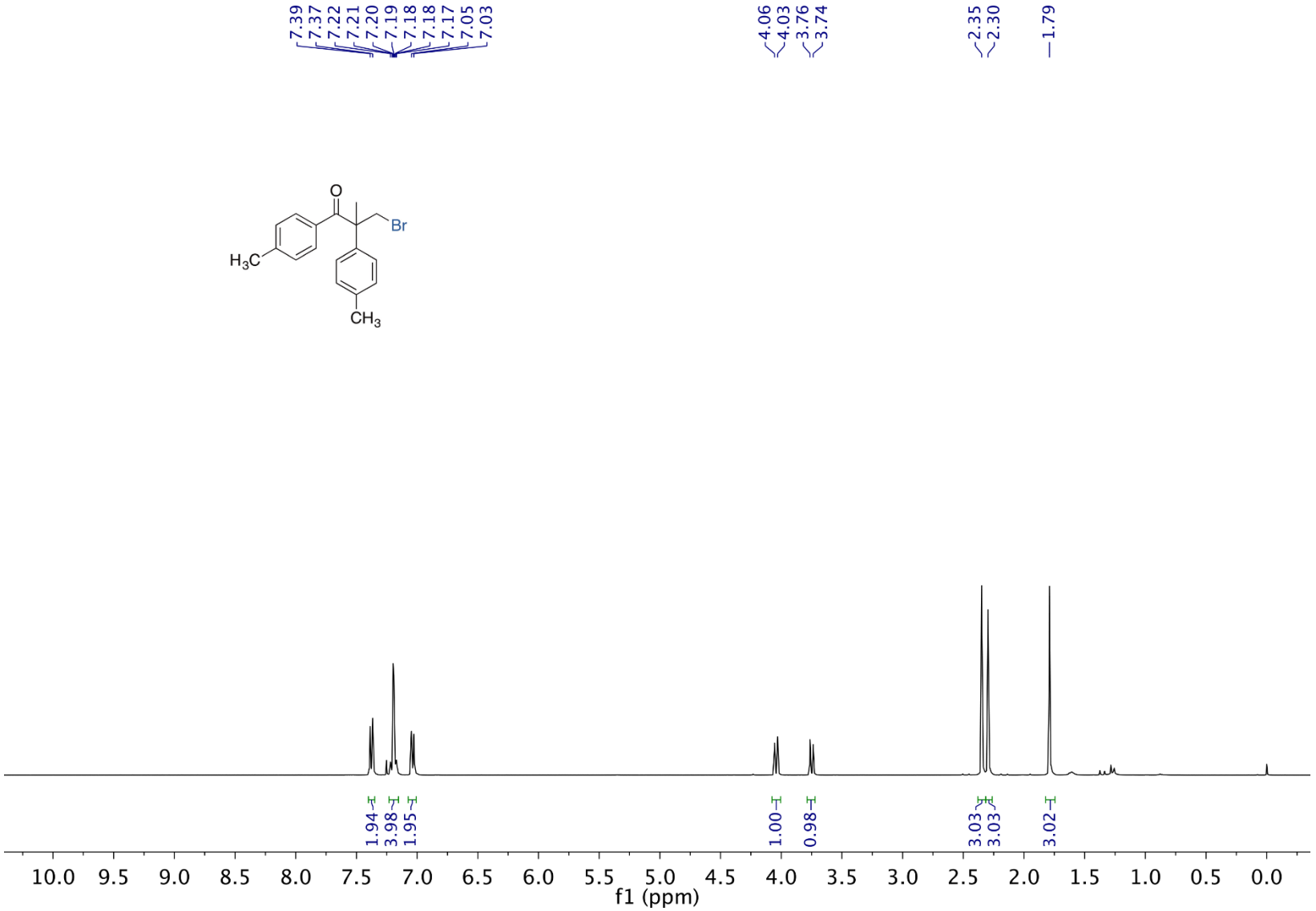

198.94
139.18
138.72
134.10
133.94
130.94
129.51
128.56
127.67
77.35
77.03
76.71
53.73
24.88
18.78
O
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

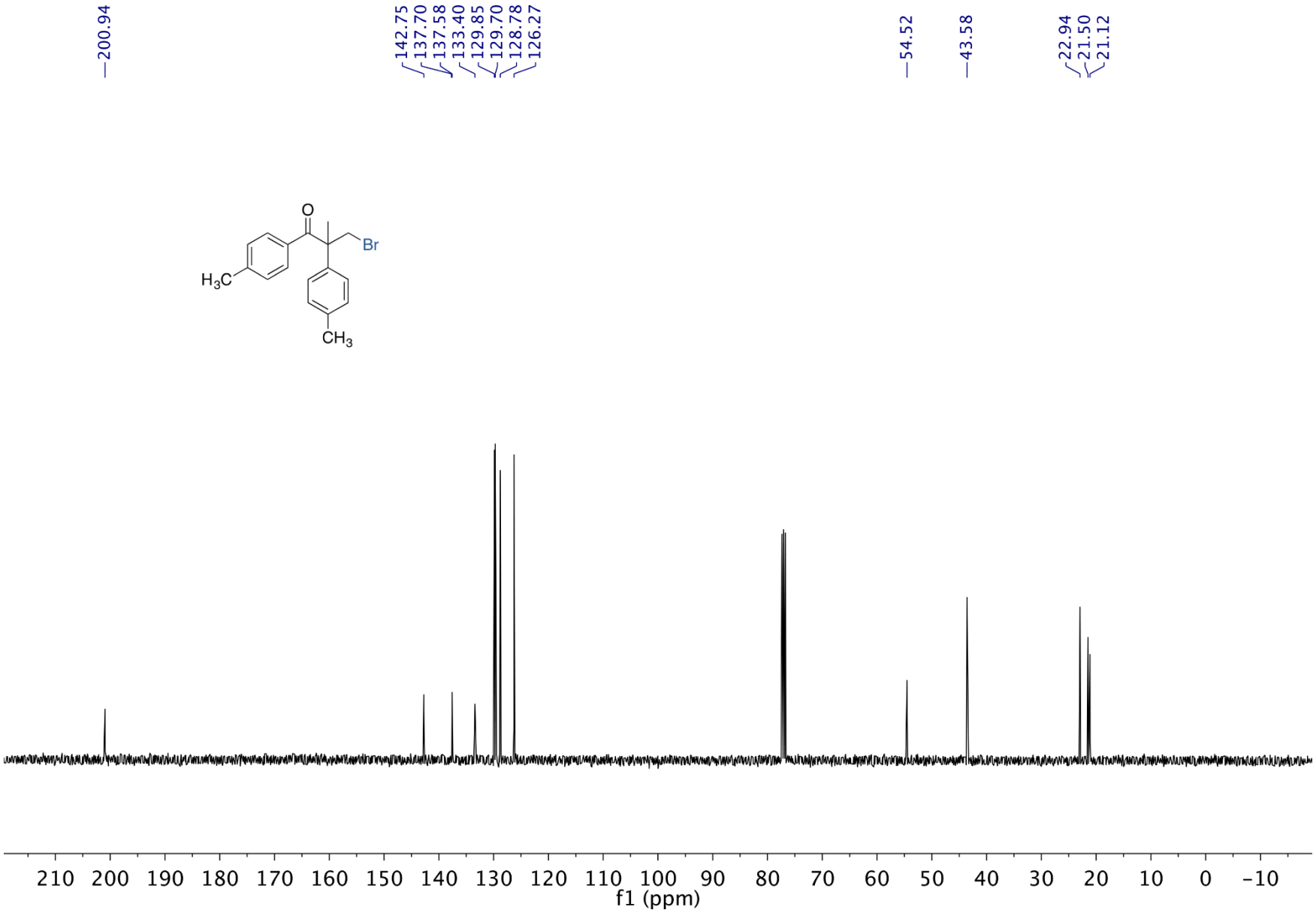
3-chloro-2-methyl-1,2-di-p-tolylpropan-1-one (**3da)**



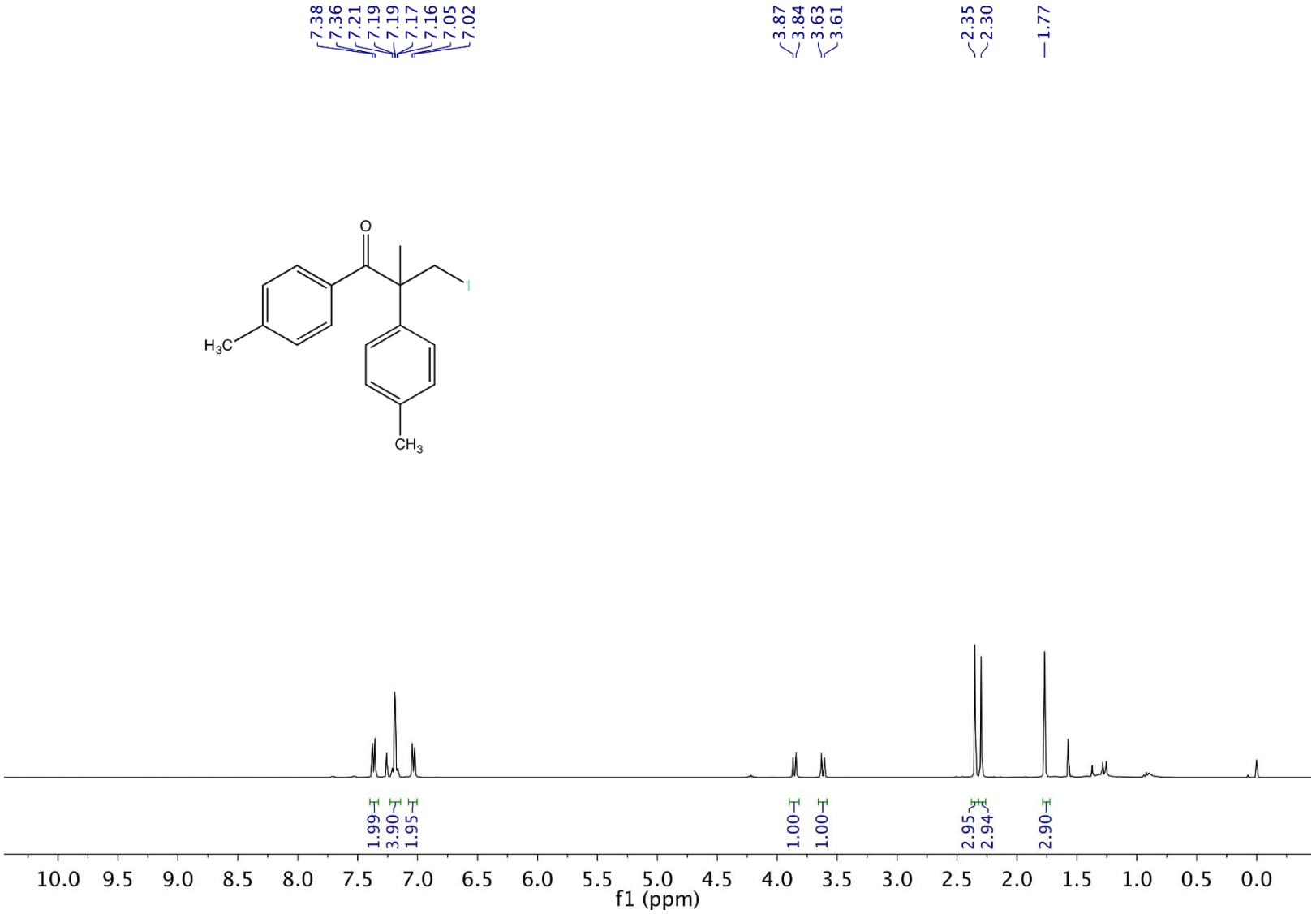

201.20
142.79
137.53
137.46
133.35
129.83
129.75
129.71
128.78
126.36
55.19
53.56
21.65
21.50
21.11
O
Cl
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

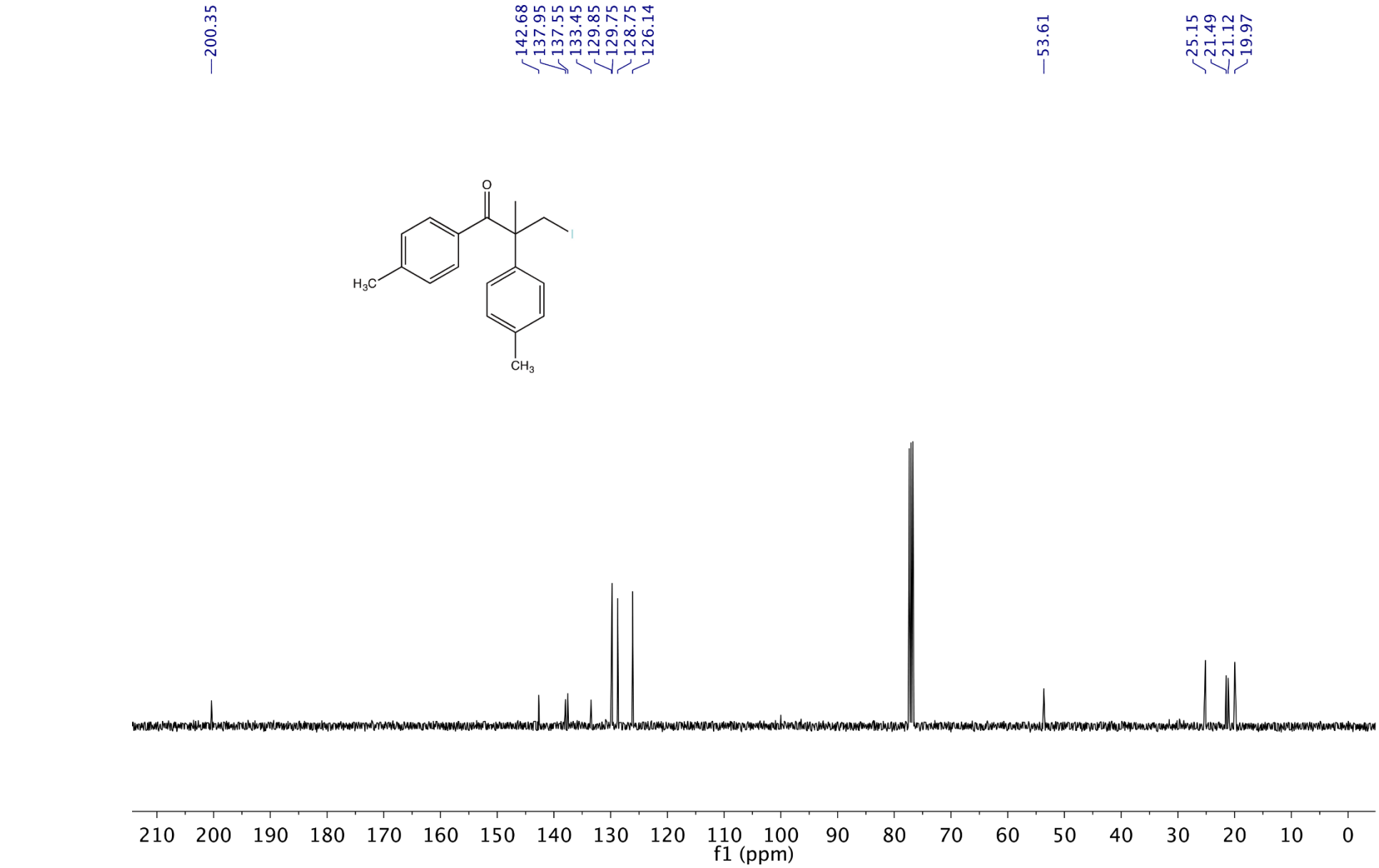
3-bromo-2-methyl-1,2-di-p-tolylpropan-1-one (**3db)**



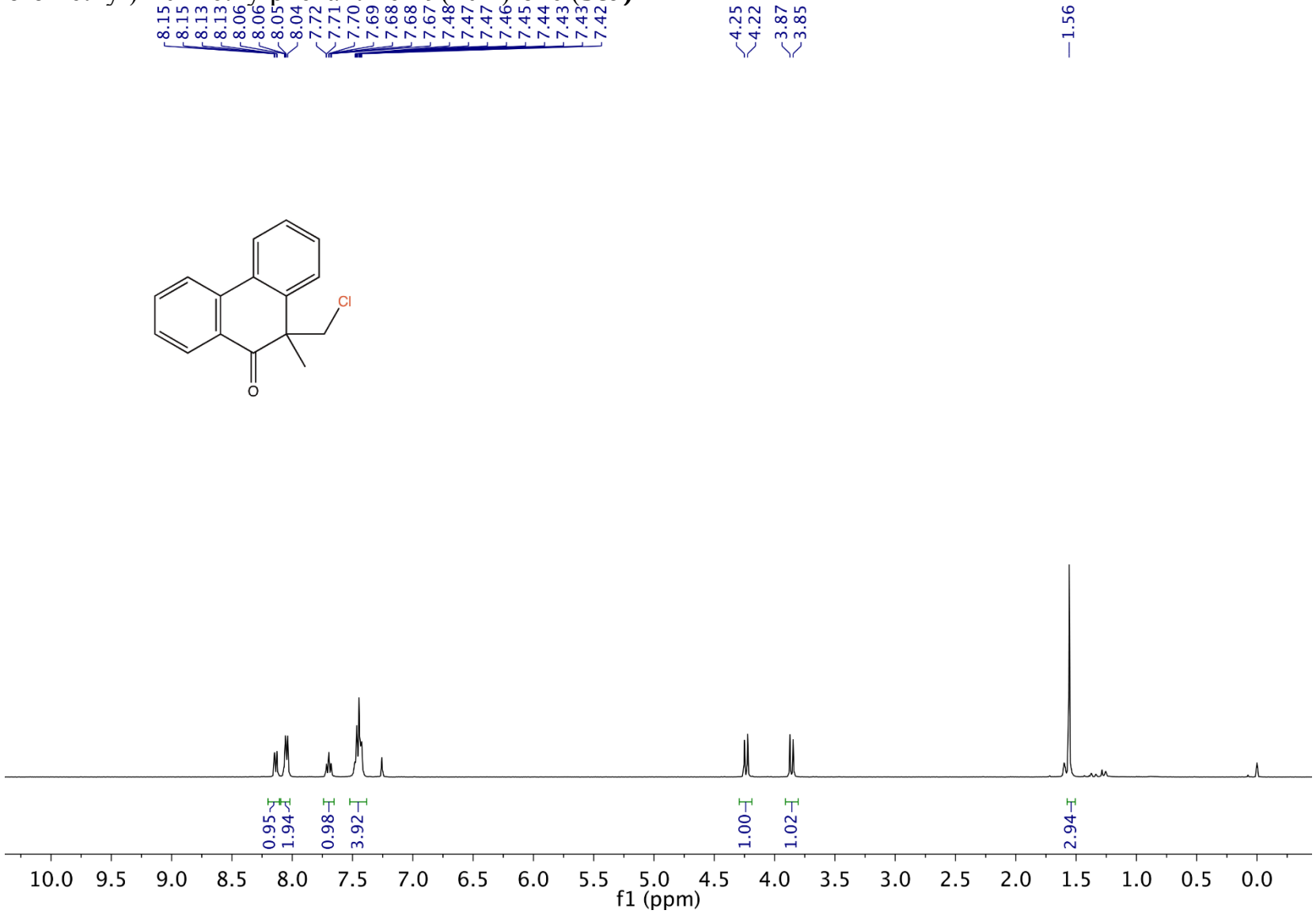

200.94
142.75
137.70
137.58
133.40
129.85
129.70
128.78
126.27
54.52
43.58
22.94
21.50
21.12
O
Br
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

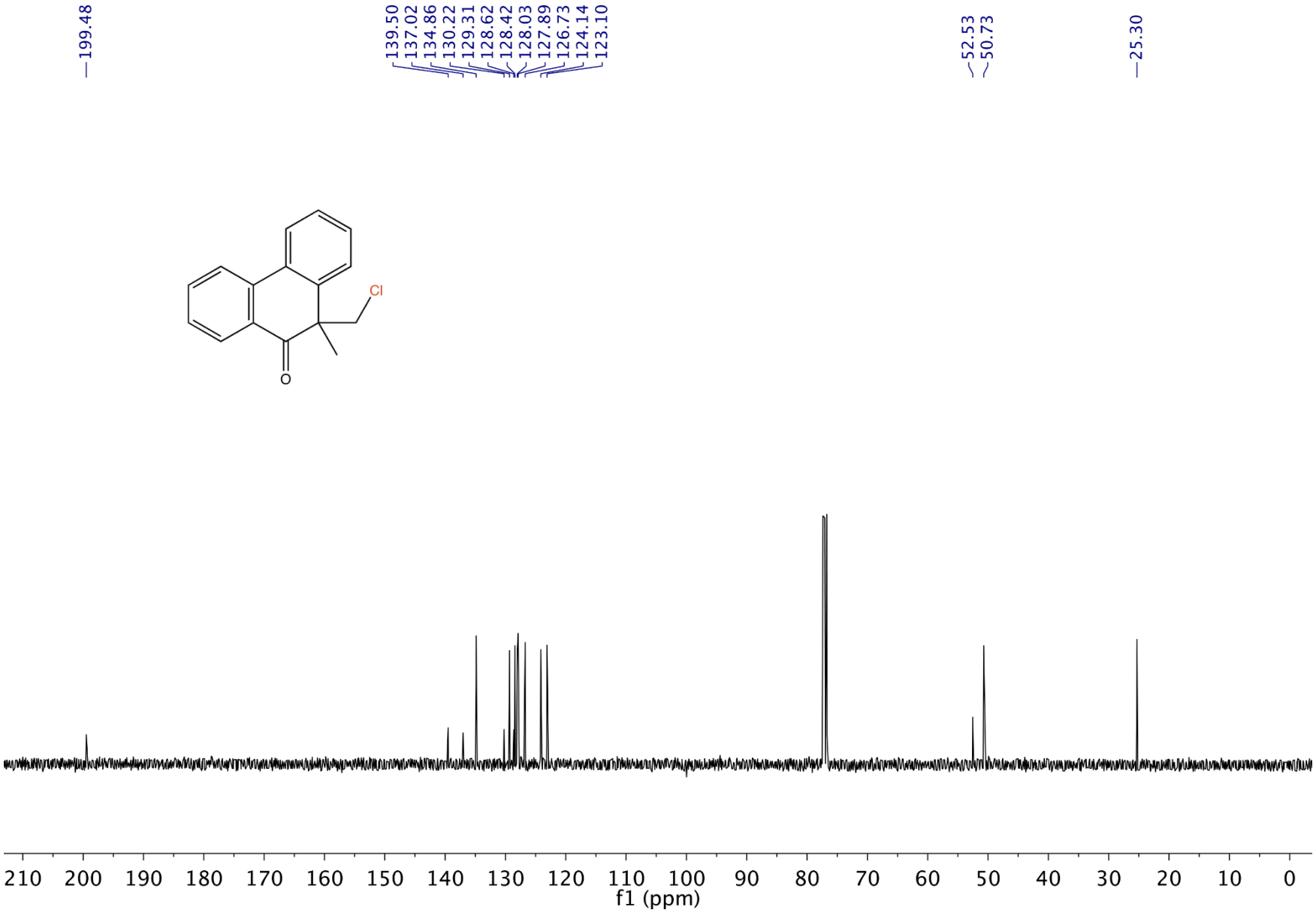
3-iodo-2-methyl-1,2-di-p-tolylpropan-1-one (**3dc)**




200.35
142.68
137.95
137.55
133.45
129.85
129.75
128.75
126.14
53.61
25.15
21.49
21.12
19.97
O
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

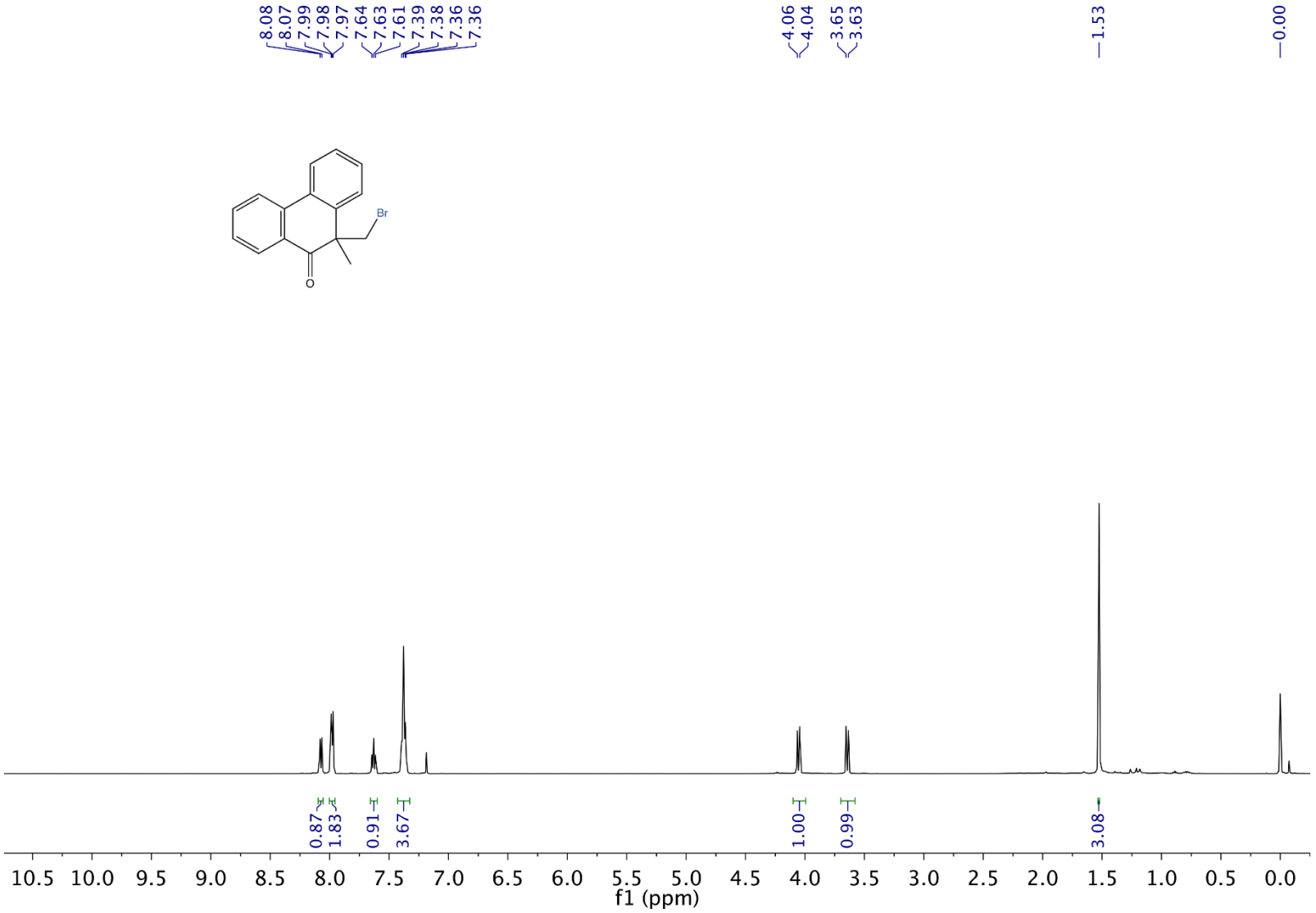
10-(chloromethyl)-10-methylphenanthren-9(10*H*)-one (**3ea)**

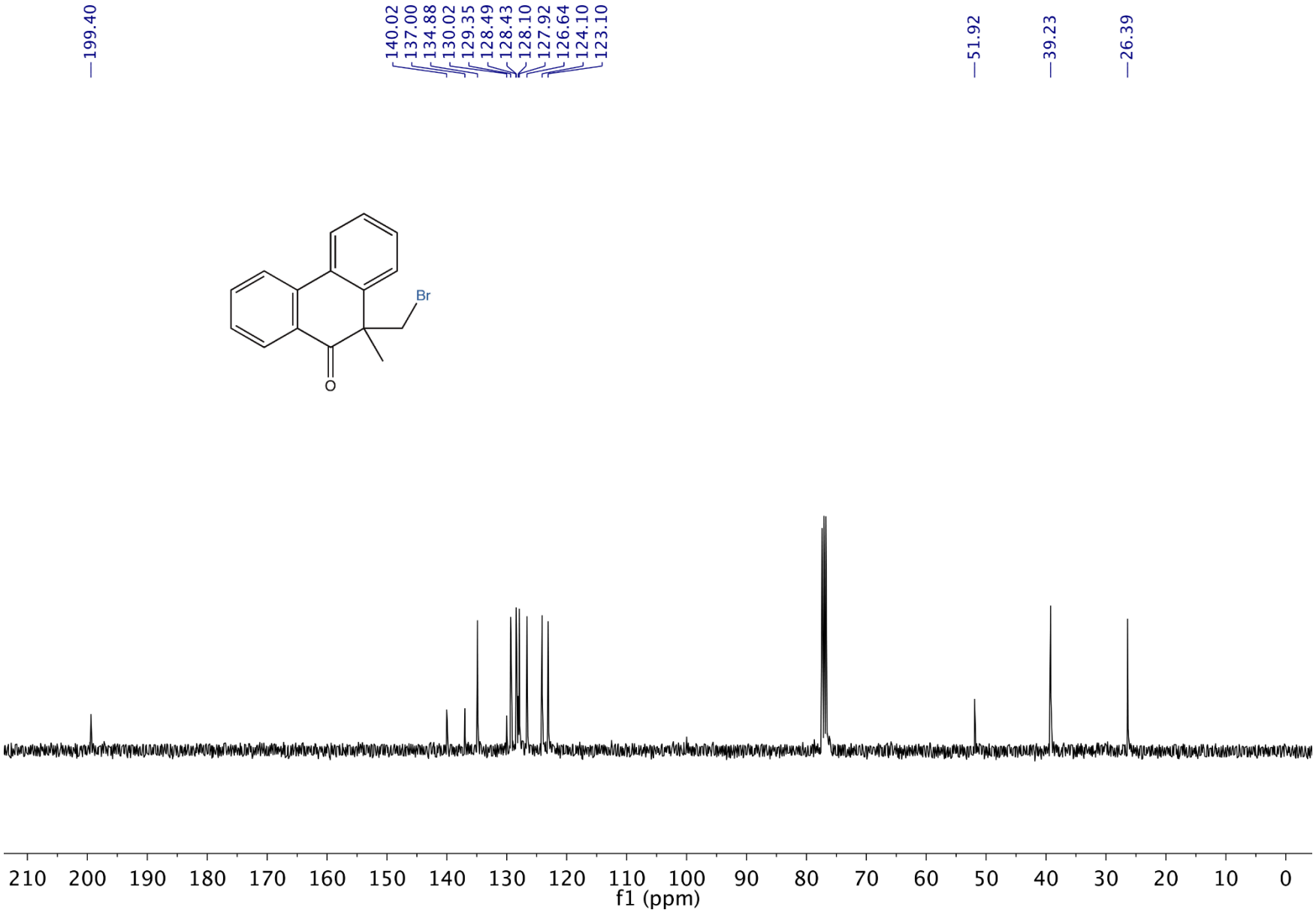



199.48
139.50
137.02
134.86
130.22
129.31
128.62
128.42
128.03
127.89
126.73
124.14
123.10
52.53
50.73
25.30
Cl
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

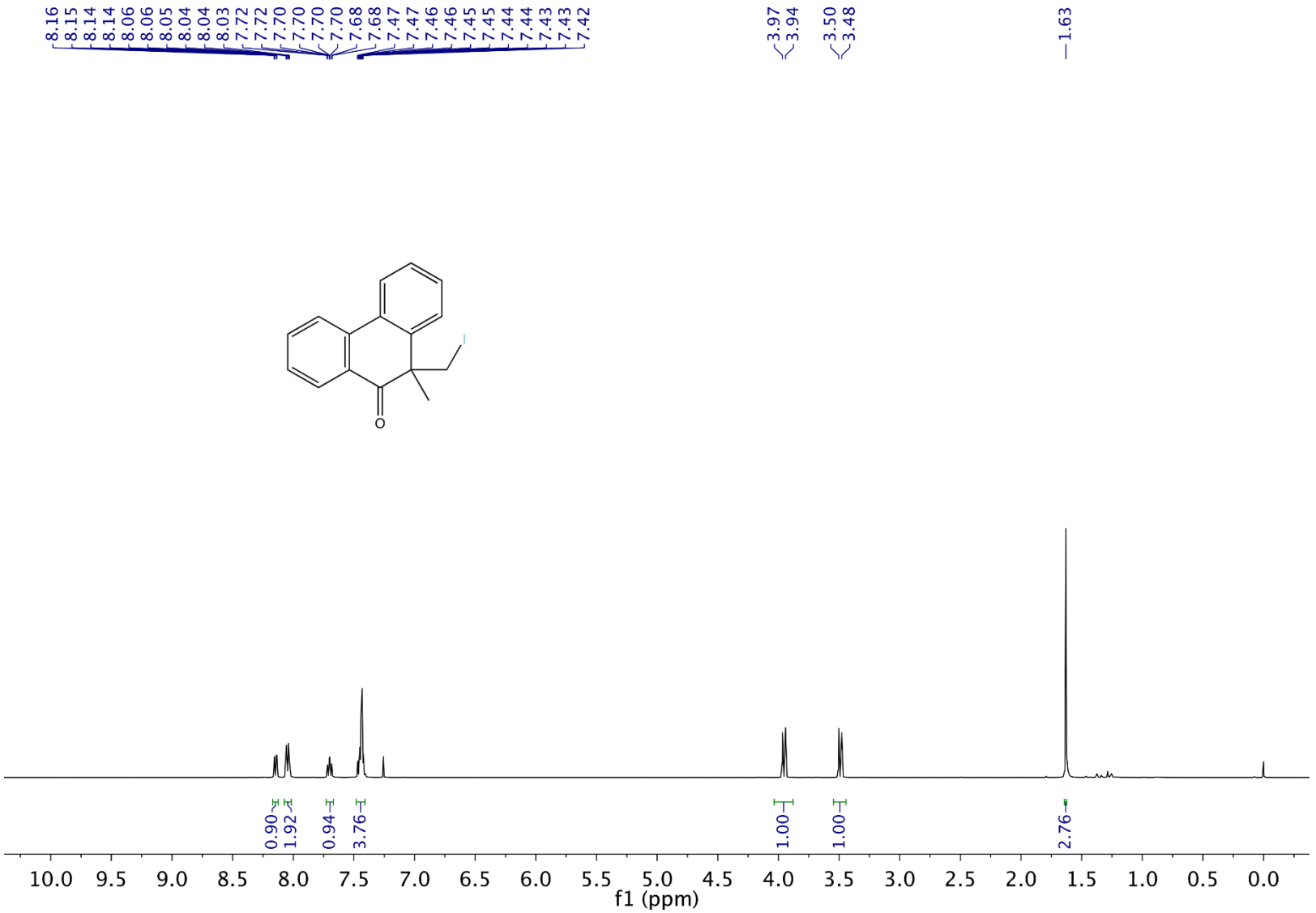
XXIX

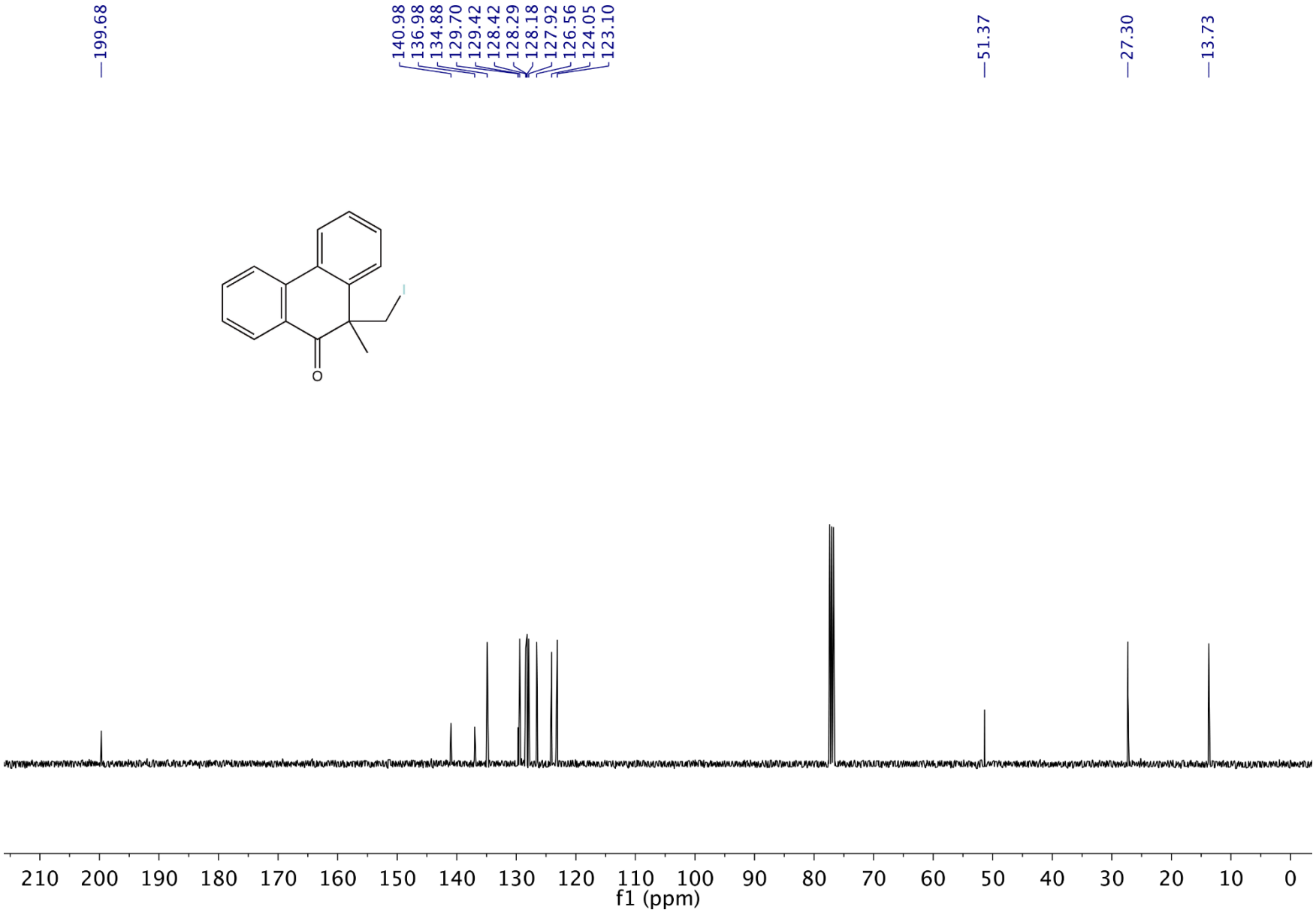
10-(bromomethyl)-10-methylphenanthren-9(10*H*)-one (**3eb)**



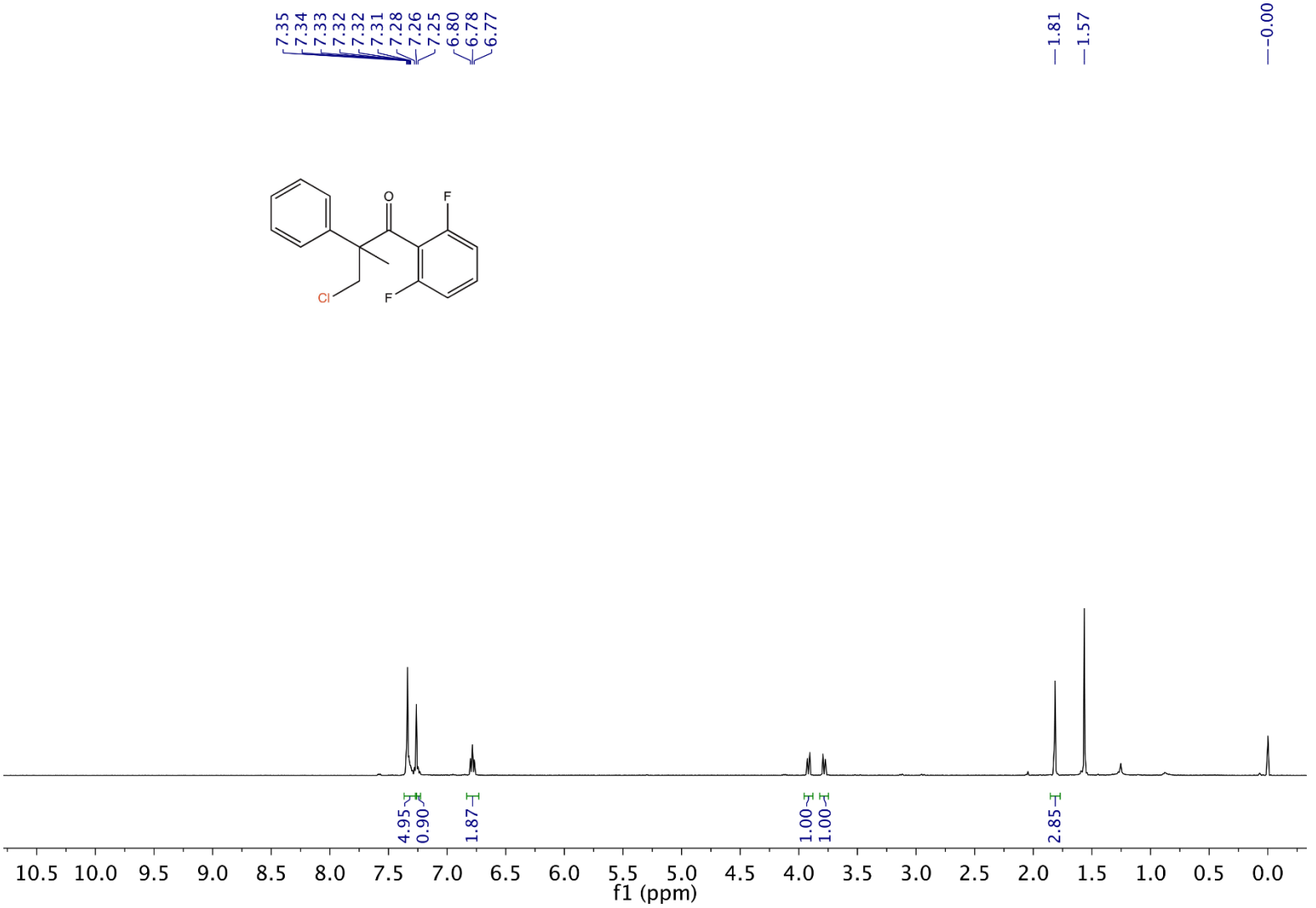

199.40
140.02
137.00
134.88
130.02
129.35
128.49
128.43
128.10
127.92
126.64
124.10
123.10
51.92
39.23
26.39
Br
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

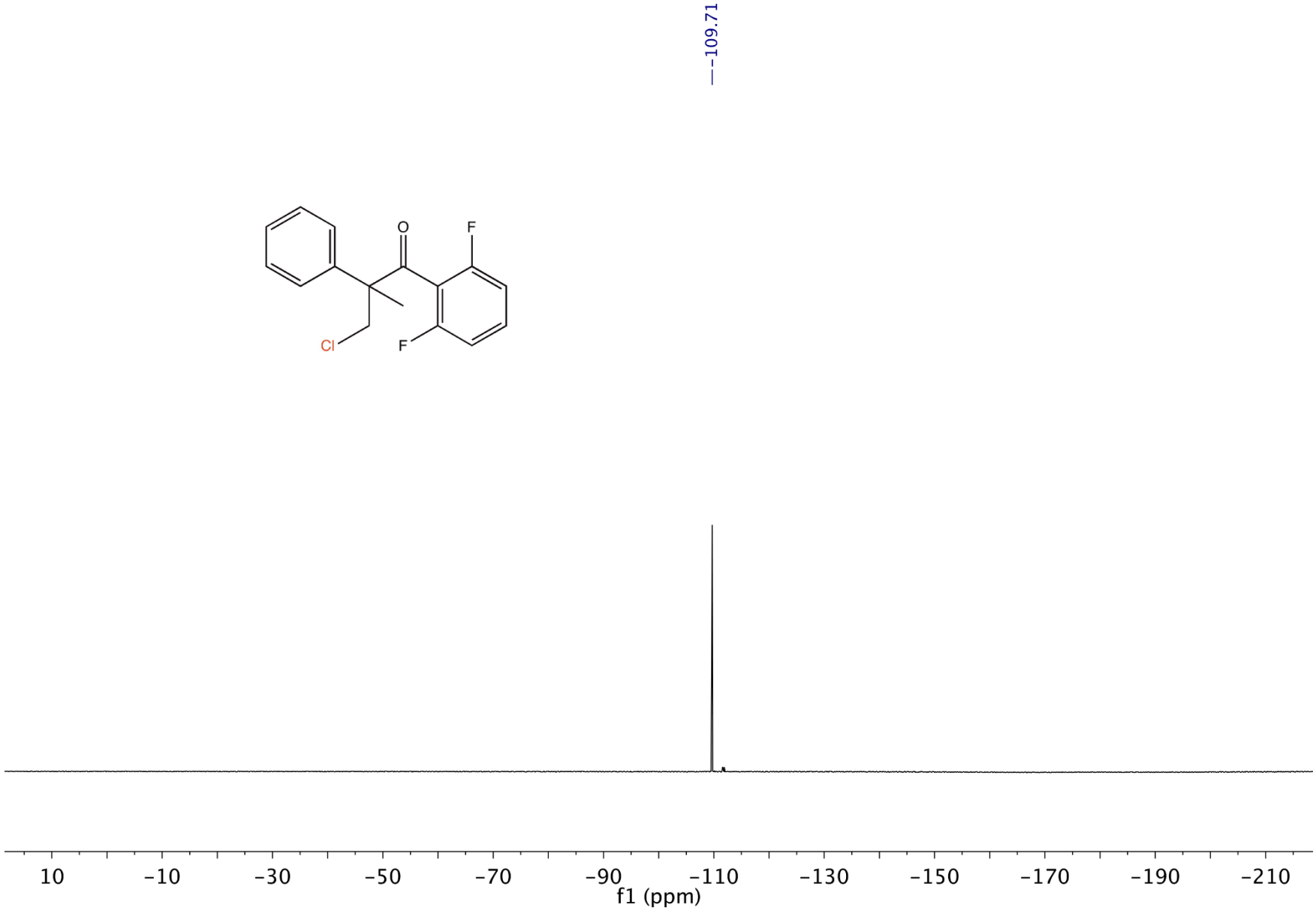
10-(iodomethyl)-10-methylphenanthren-9(10*H*)-one (**3ec)**

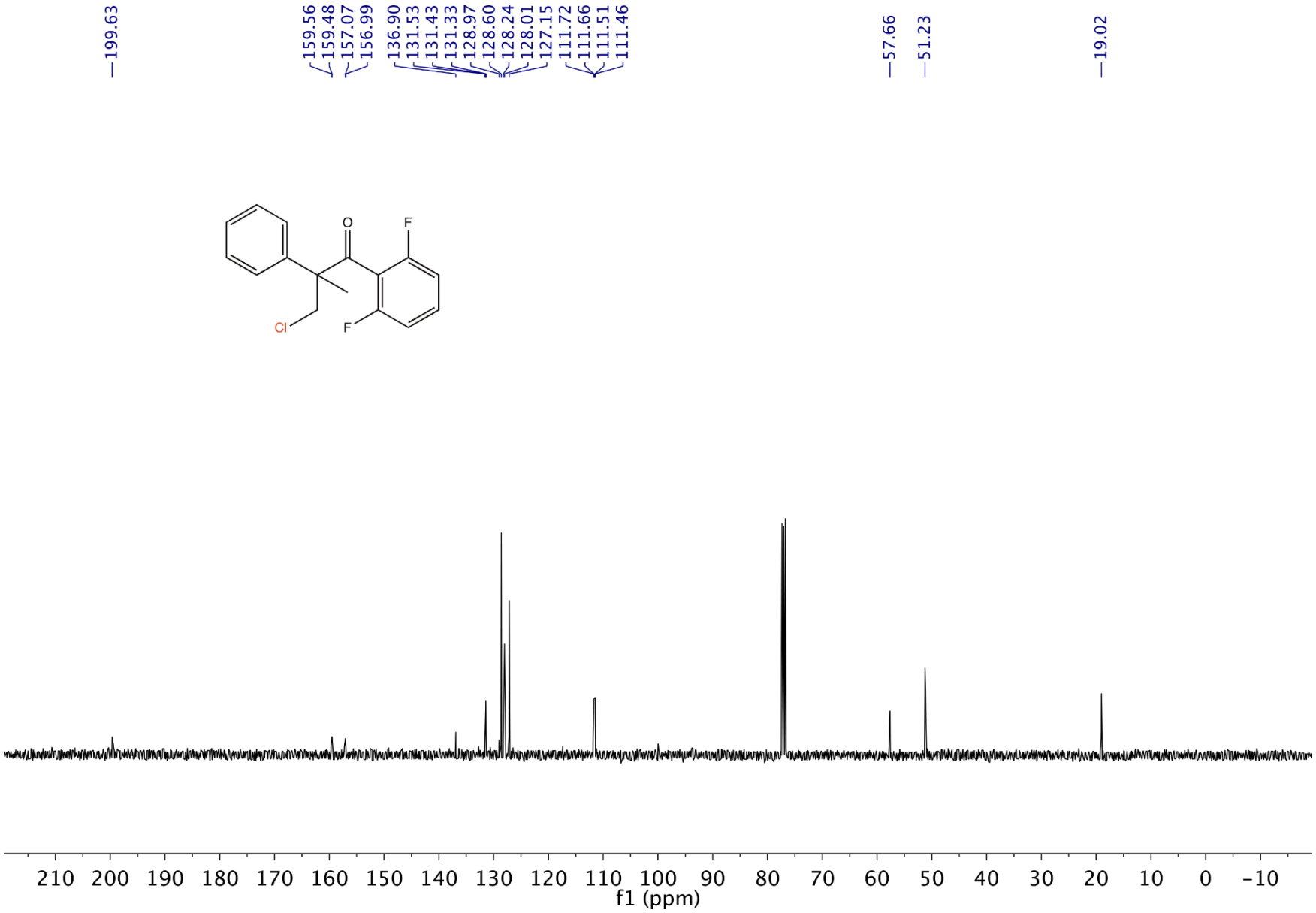



199.68
140.98
136.98
134.88
129.70
129.42
128.42
128.29
128.18
127.92
126.56
124.05
123.10
51.37
27.30
13.73
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

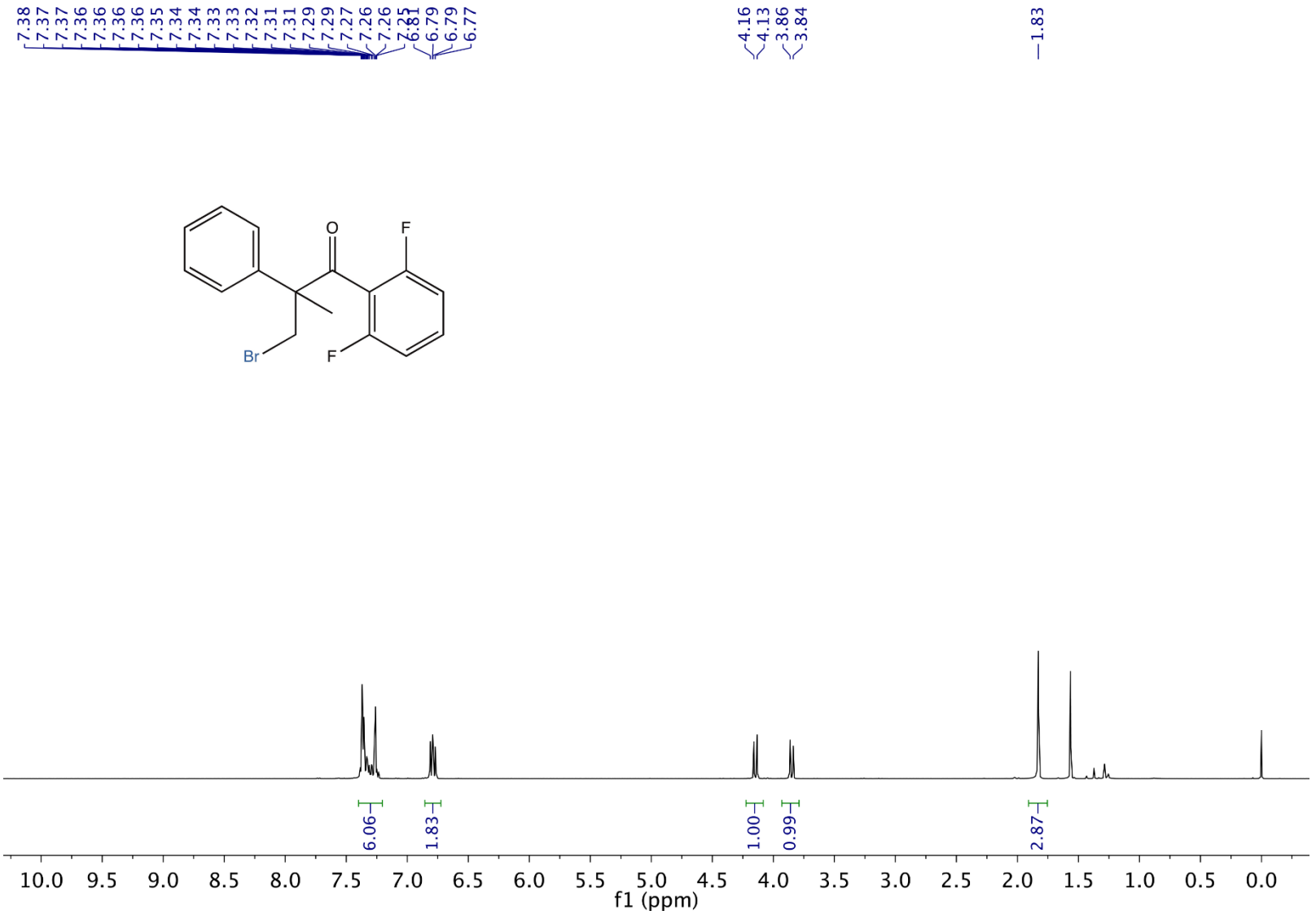
3-chloro-1-(2,6-difluorophenyl)-2-methyl-2-phenylpropan-1-one (**3fa)**



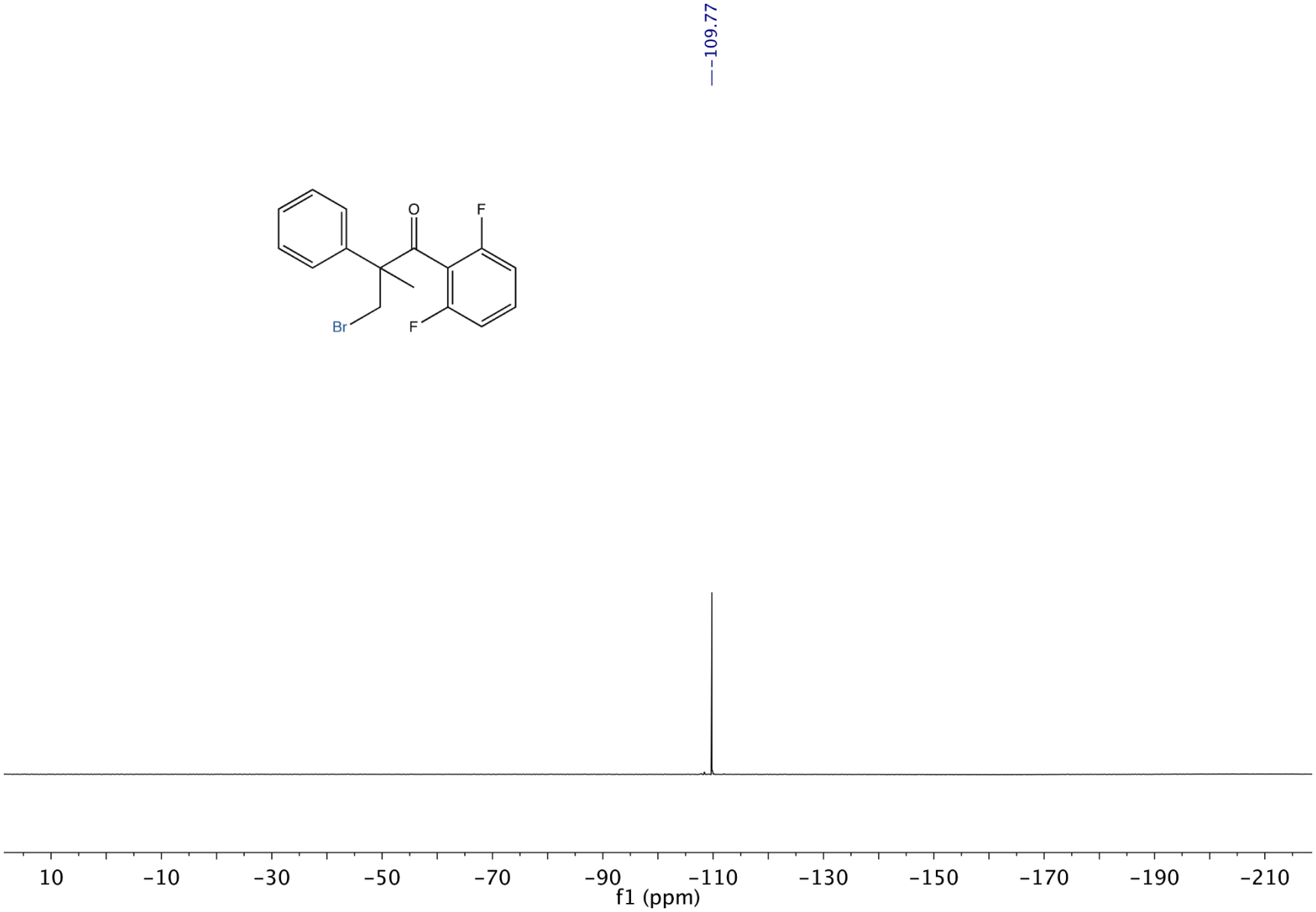

−109.71
O
F
Cl
F
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)

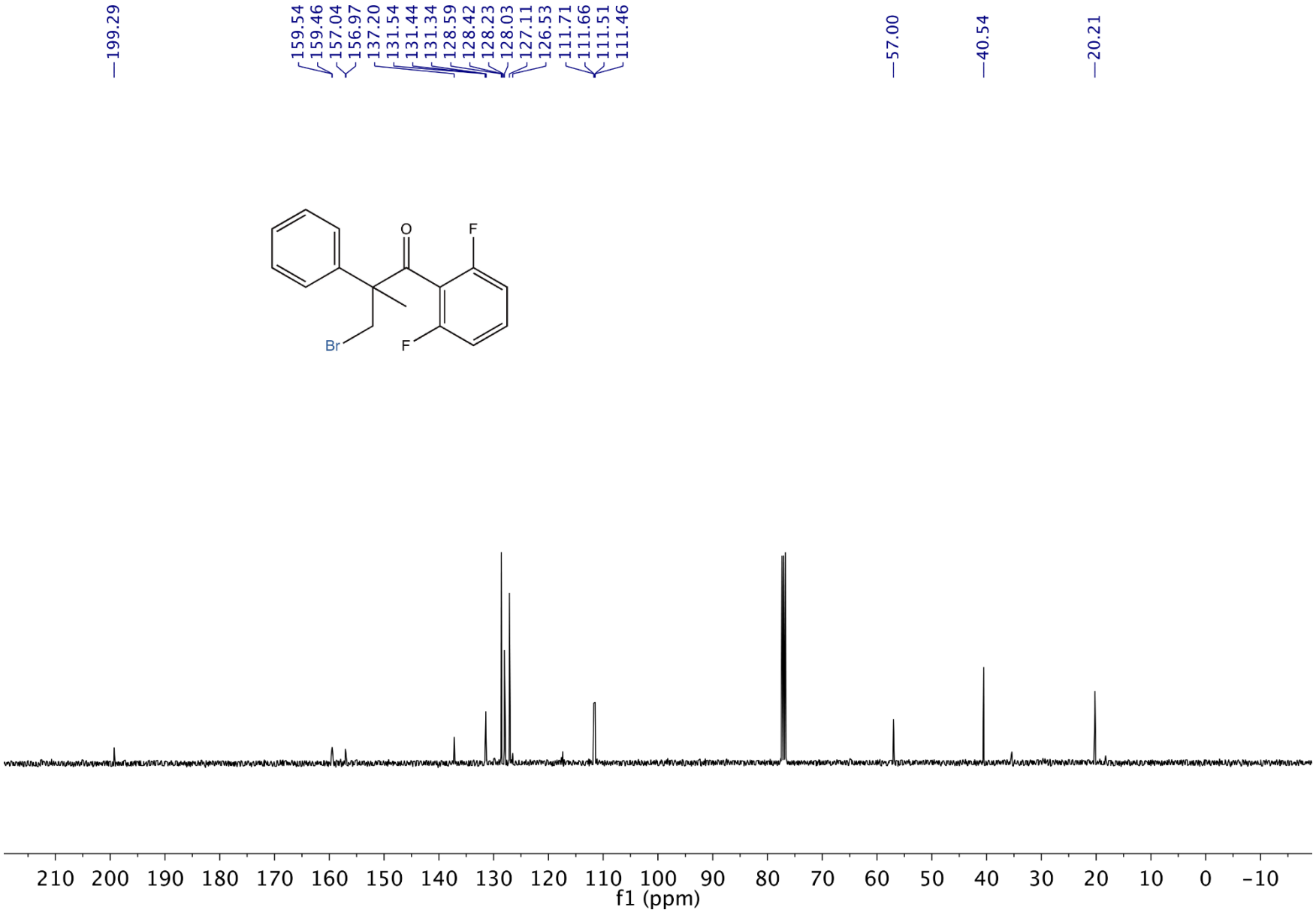

199.63
159.56
159.48
157.07
156.99
136.90
131.53
131.43
131.33
128.97
128.60
128.24
128.01
127.15
111.72
111.66
111.51
111.46
57.66
51.23
19.02
O
F
Cl
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3-bromo-1-(2,6-difluorophenyl)-2-methyl-2-phenylpropan-1-one (**3fb)**

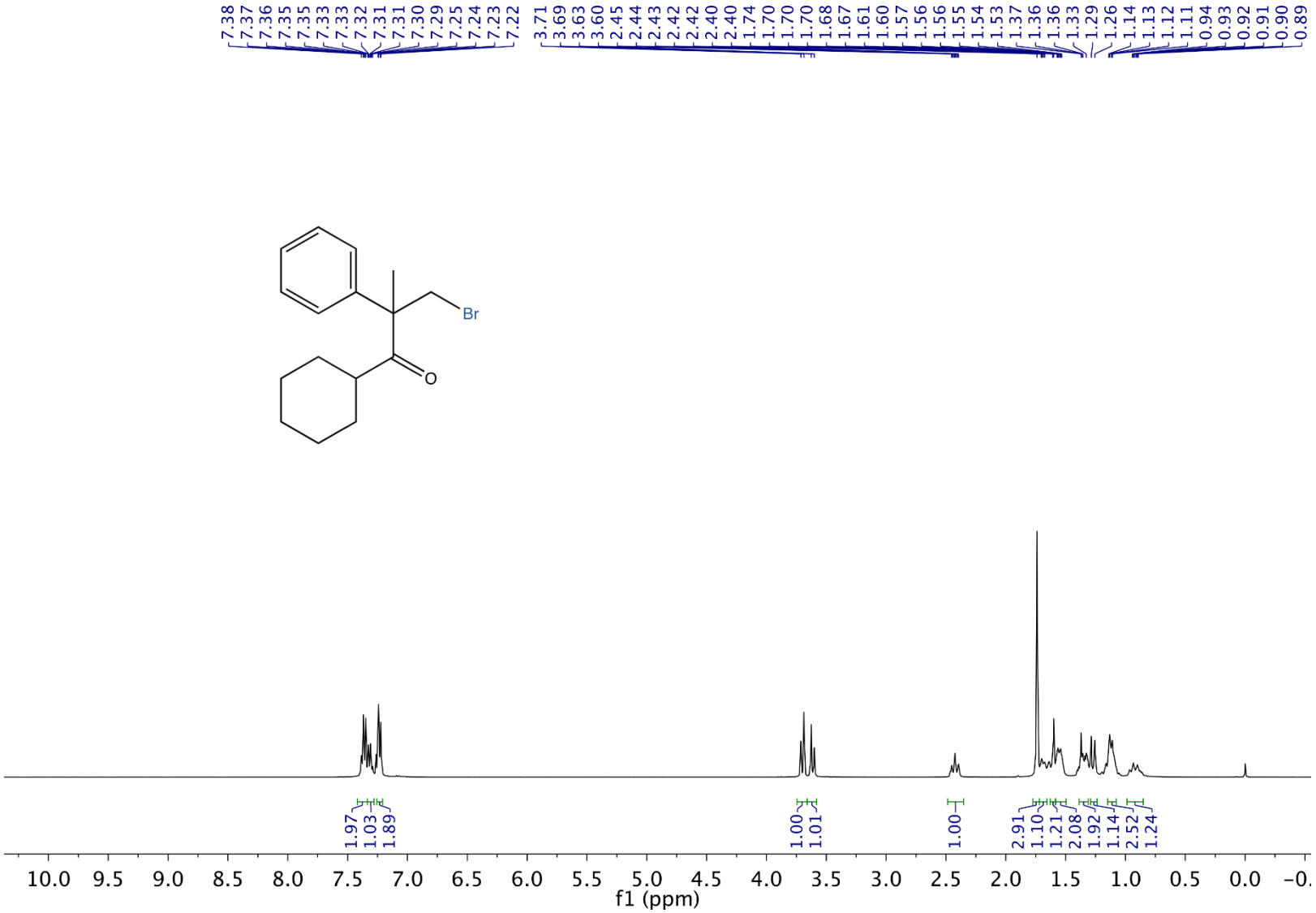


O
F
Br
F

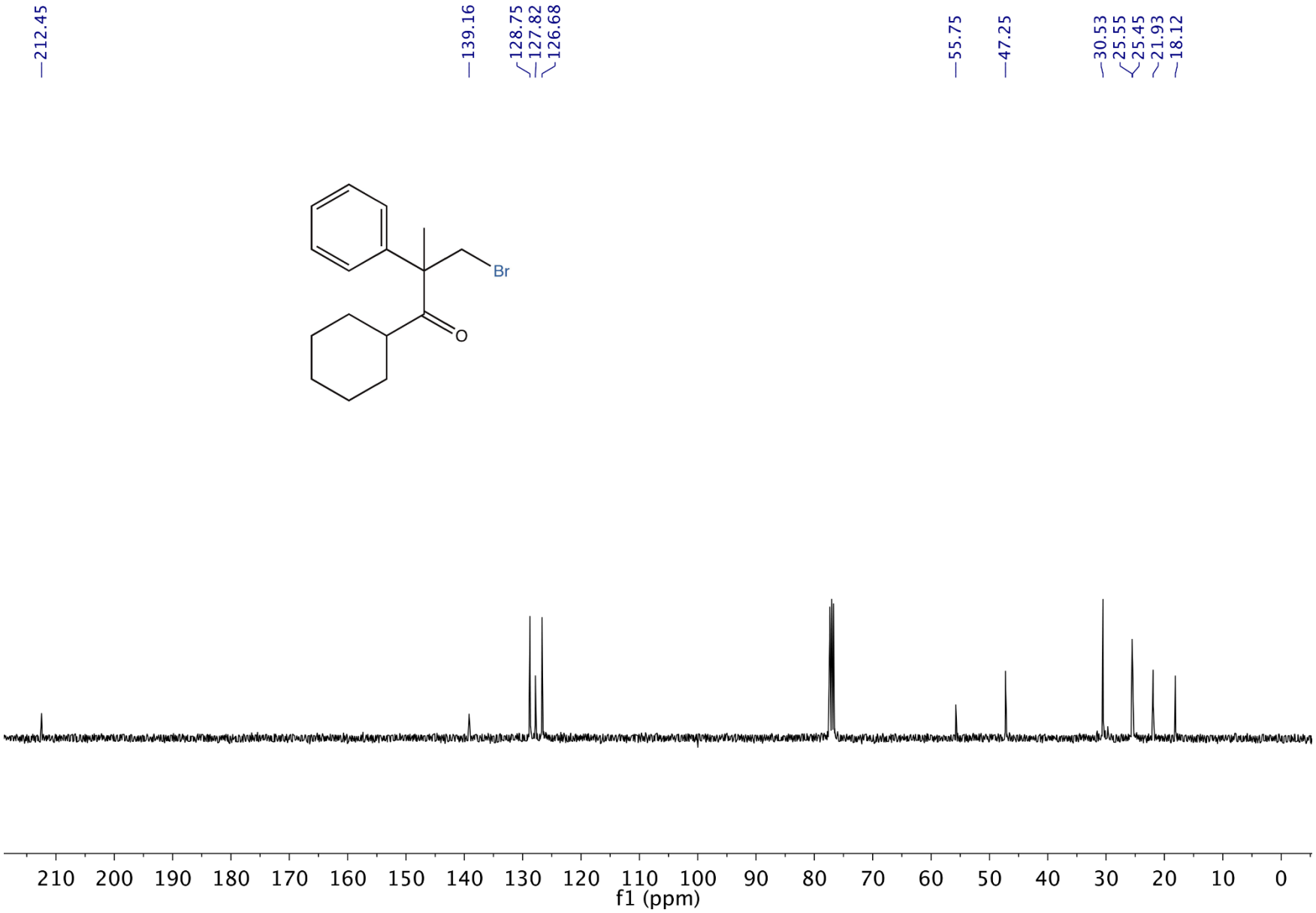

−109.77
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
f1 (ppm)


199.29
159.54
159.46
157.04
156.97
137.20
131.54
131.44
131.34
128.59
128.42
128.23
128.03
127.11
126.53
111.71
111.66
111.51
111.46
57.00
40.54
20.21
O
F
Br
F
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)

3-bromo-1-cyclohexyl-2-methyl-2-phenylpropan-1-one (**3gb)**

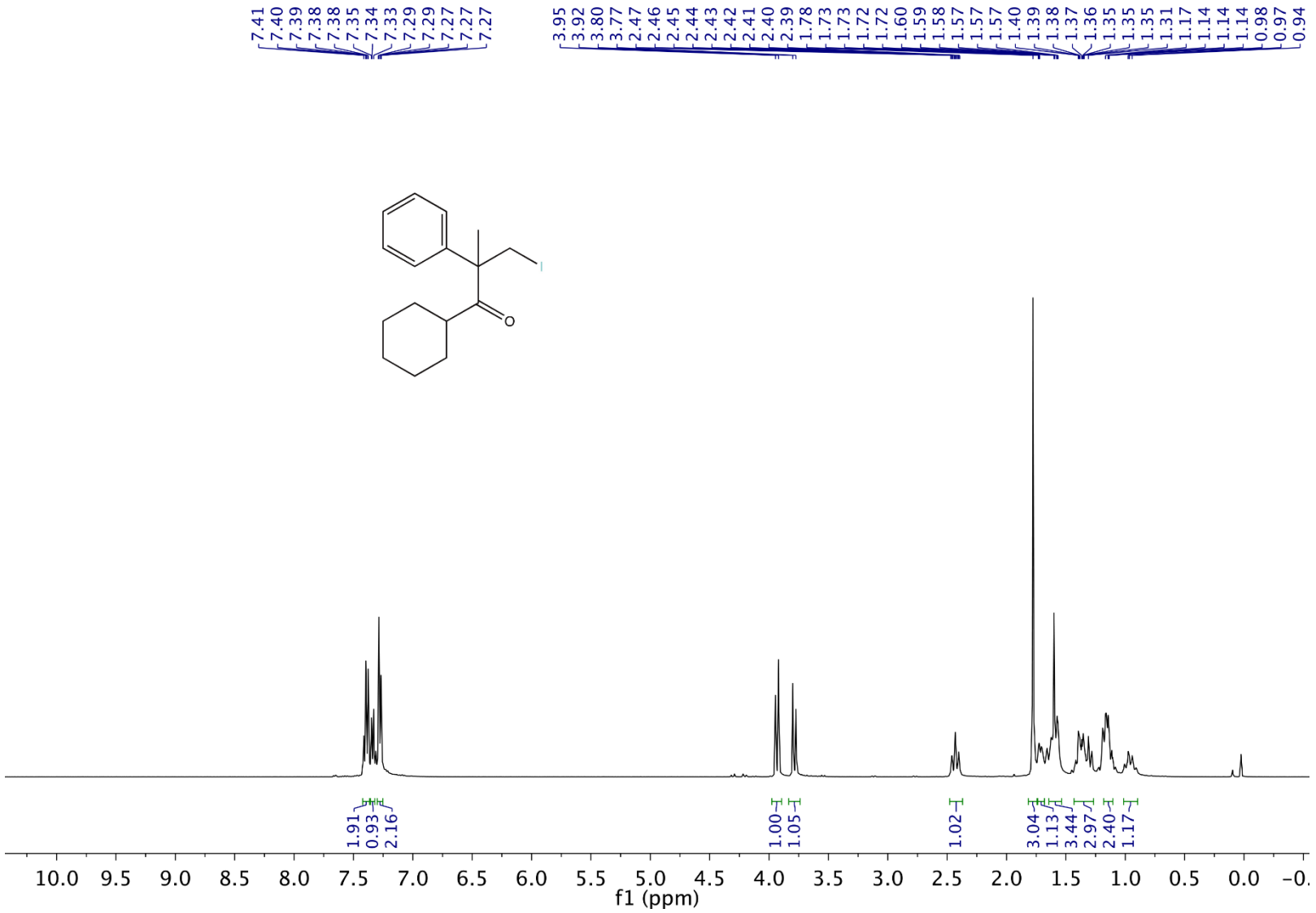


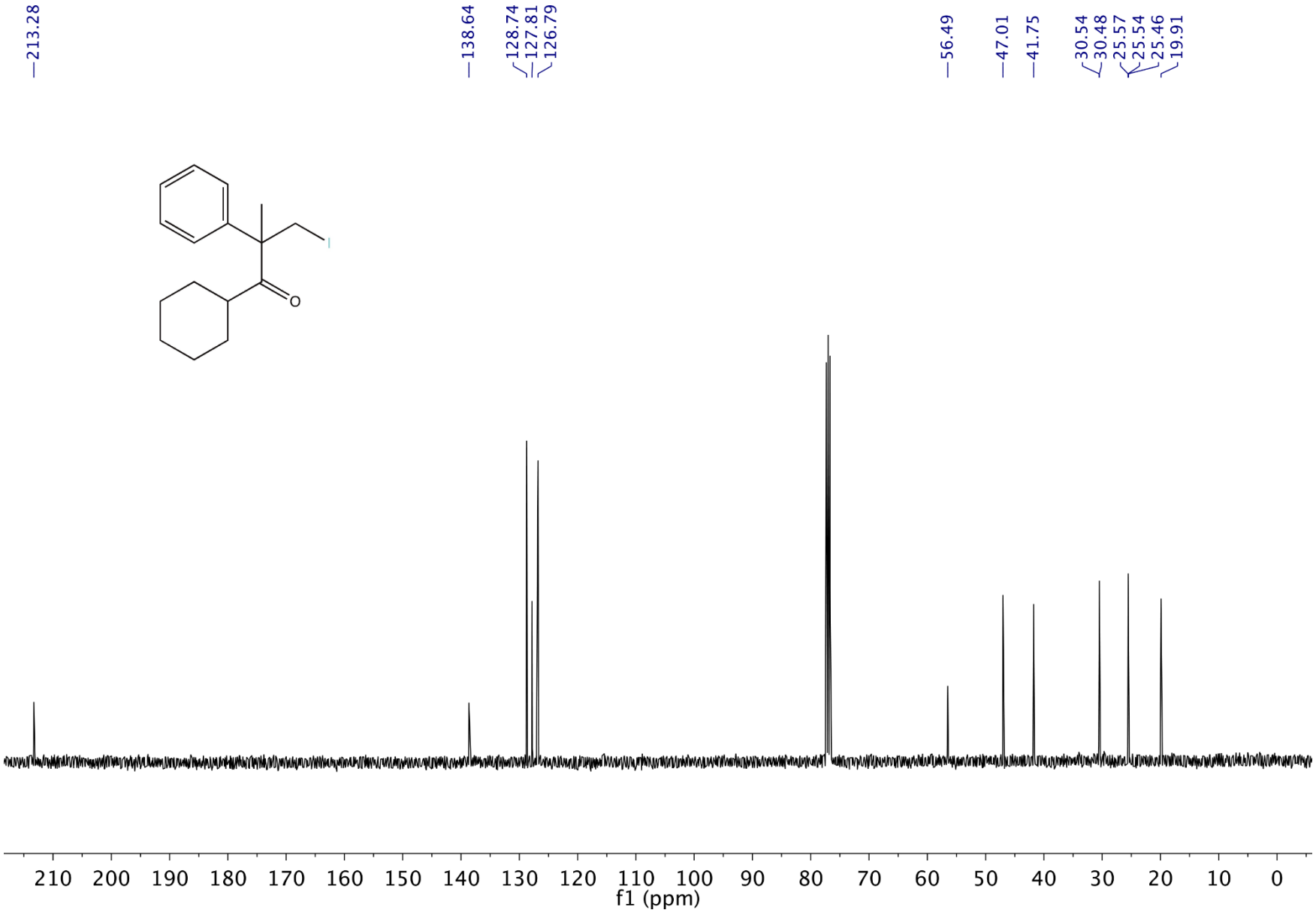
XL


212.45
139.16
128.75
127.82
126.68
55.75
47.25
30.53
25.55
25.45
21.93
18.12
Br
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

XLI

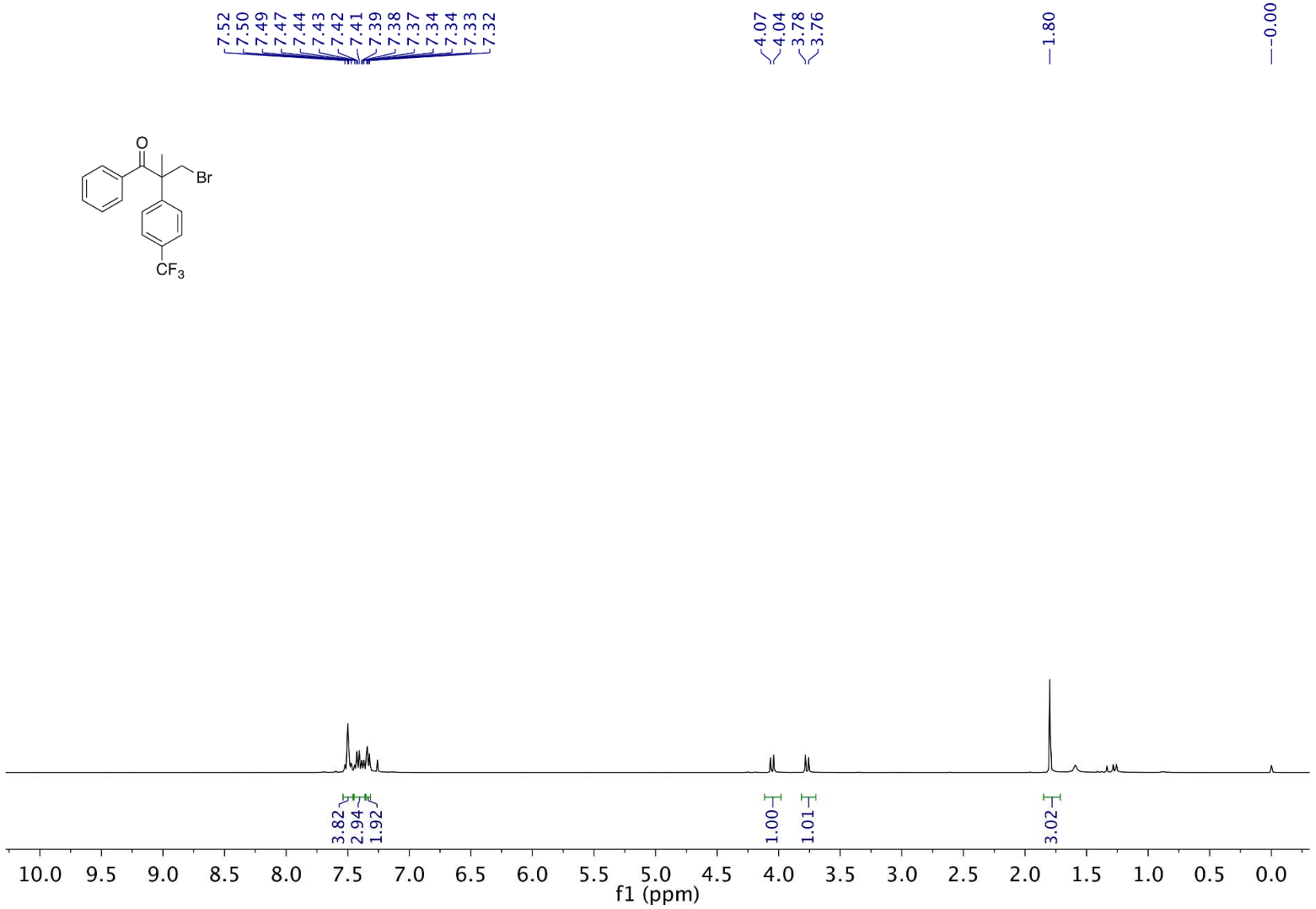
3-iodo-1-cyclohexyl-2-methyl-2-phenylpropan-1-one (**3gc)**

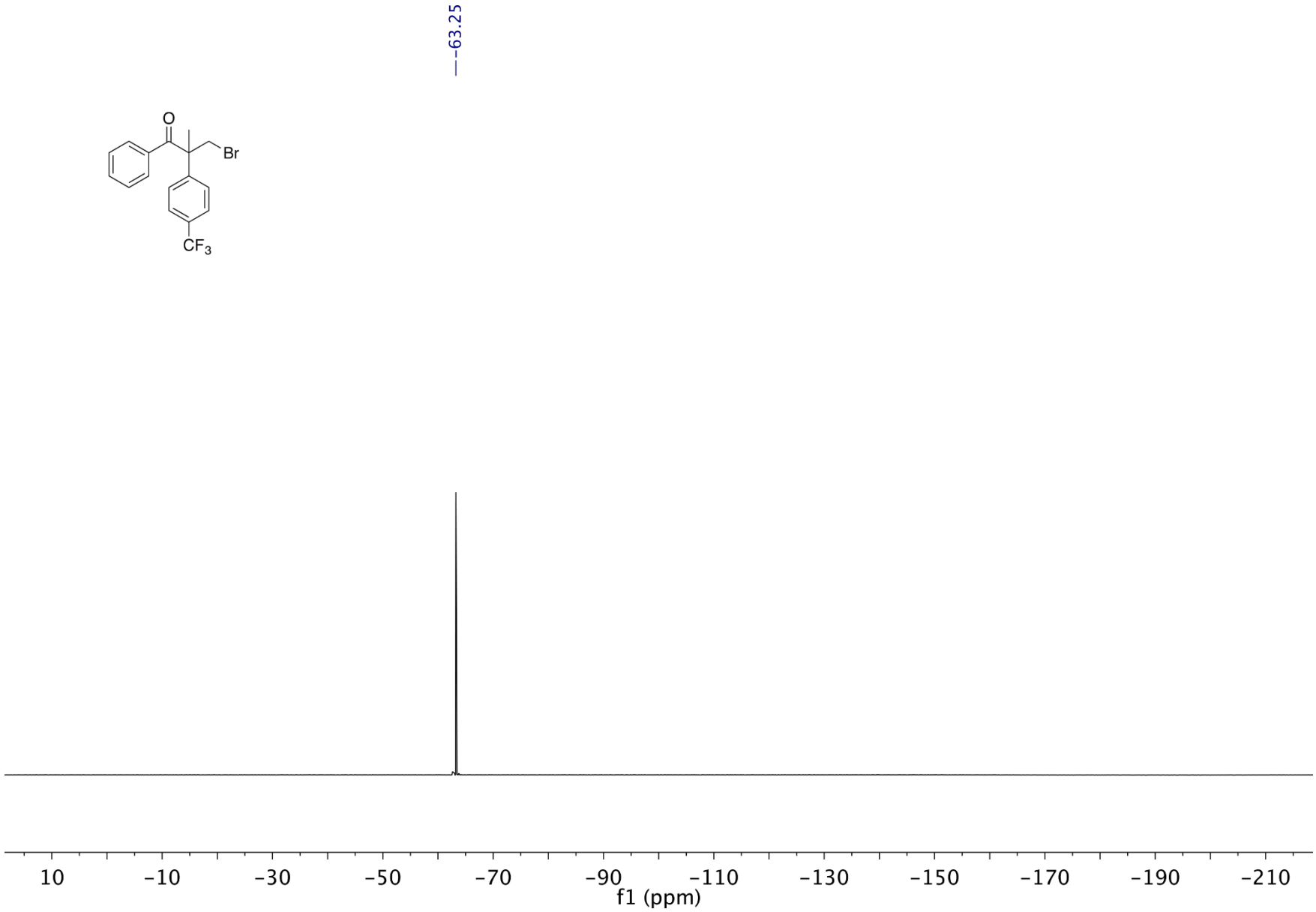



213.28
138.64
128.74
127.81
126.79
56.49
47.01
41.75
30.54
30.48
25.57
25.54
25.46
19.91
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

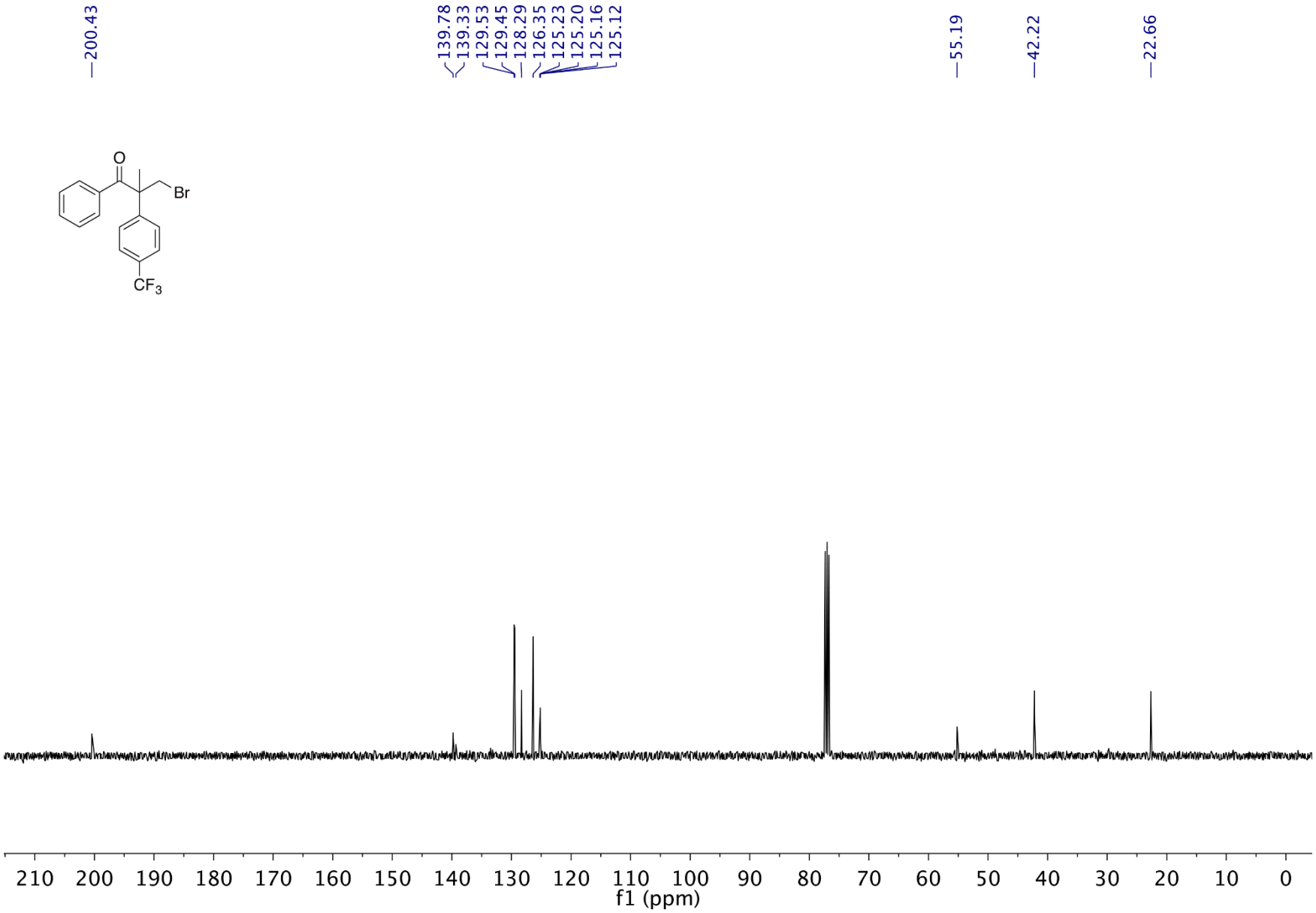
XLIII

3-bromo-2-methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one **(3hb)**



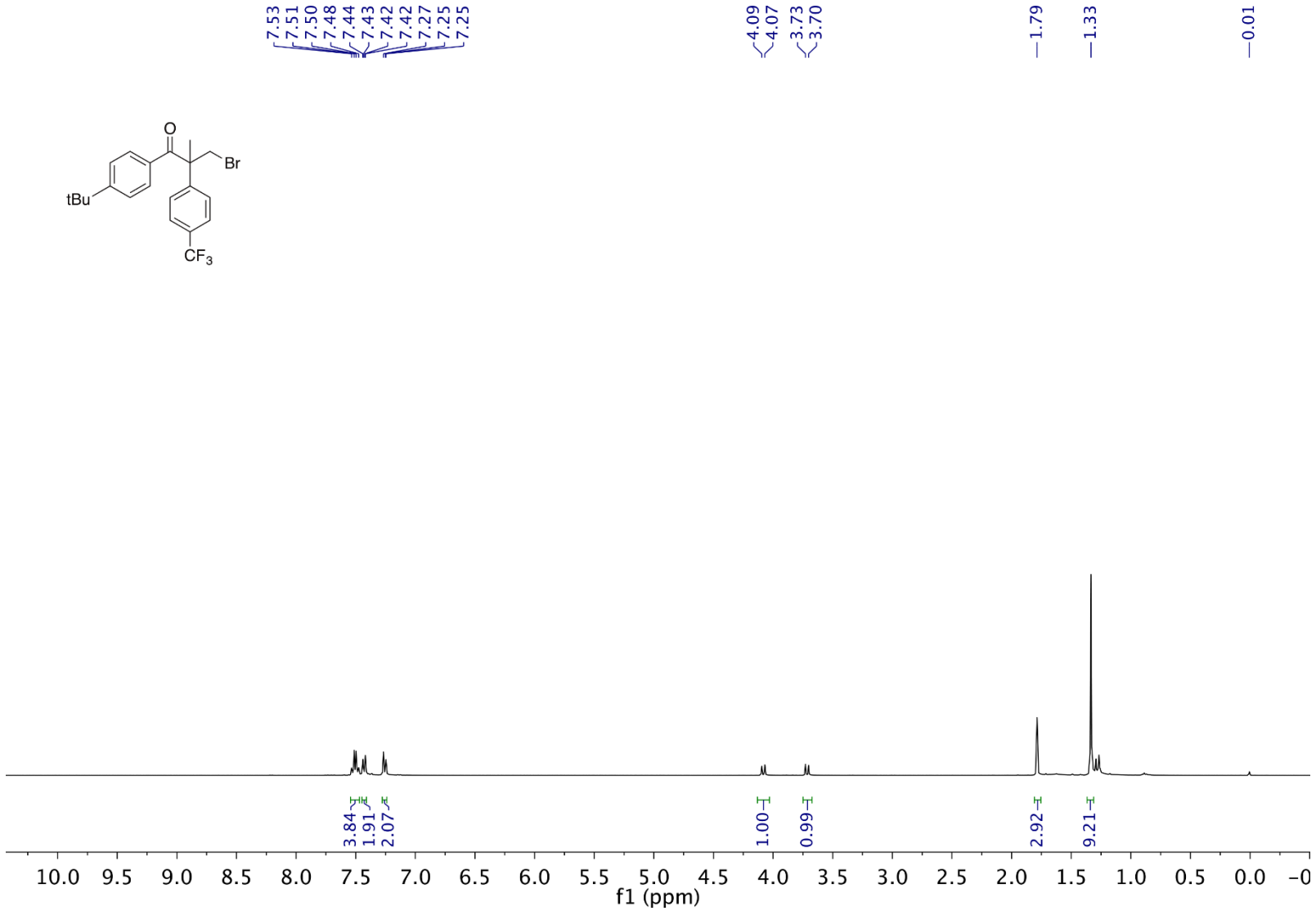


XLV

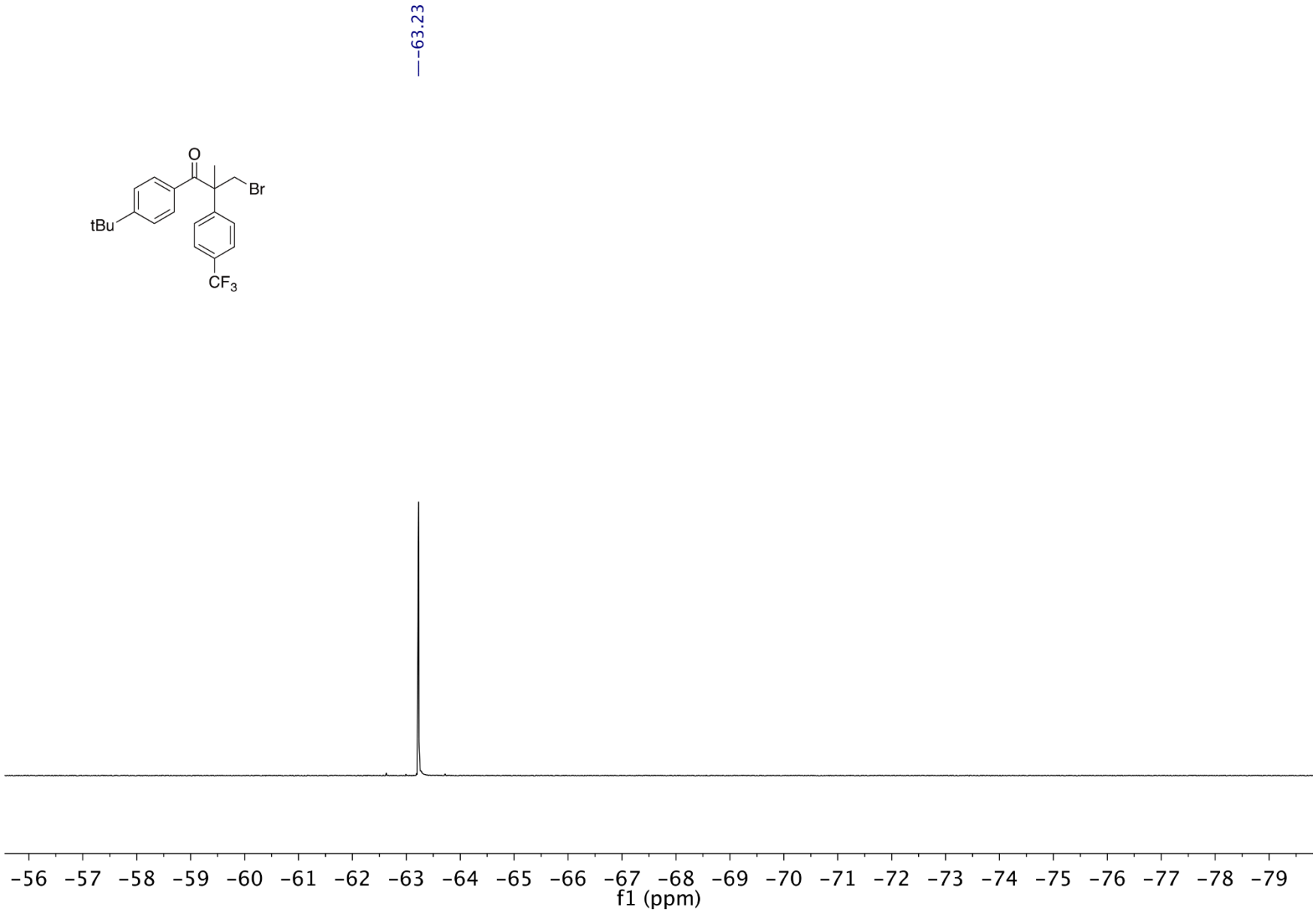

200.43
139.78
139.33
129.53
129.45
128.29
126.35
125.23
125.20
125.16
125.12
55.19
42.22
22.66
O
Br
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

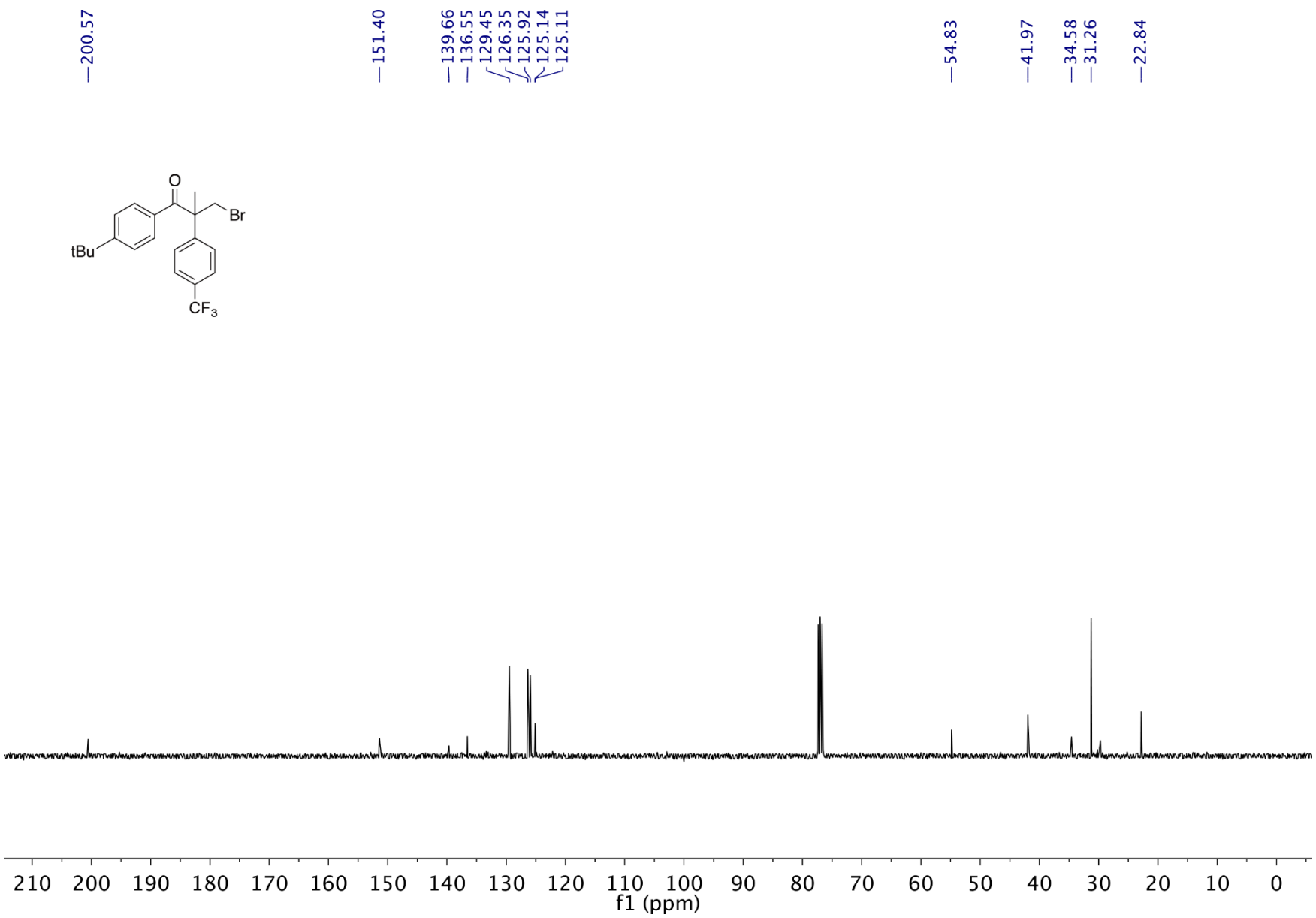
XLVI

3-bromo-1-(4-(*tert*-butyl)phenyl)-2-methyl-2-(4-(trifluoromethyl)phenyl)prop-an-1-one **(3ib)**



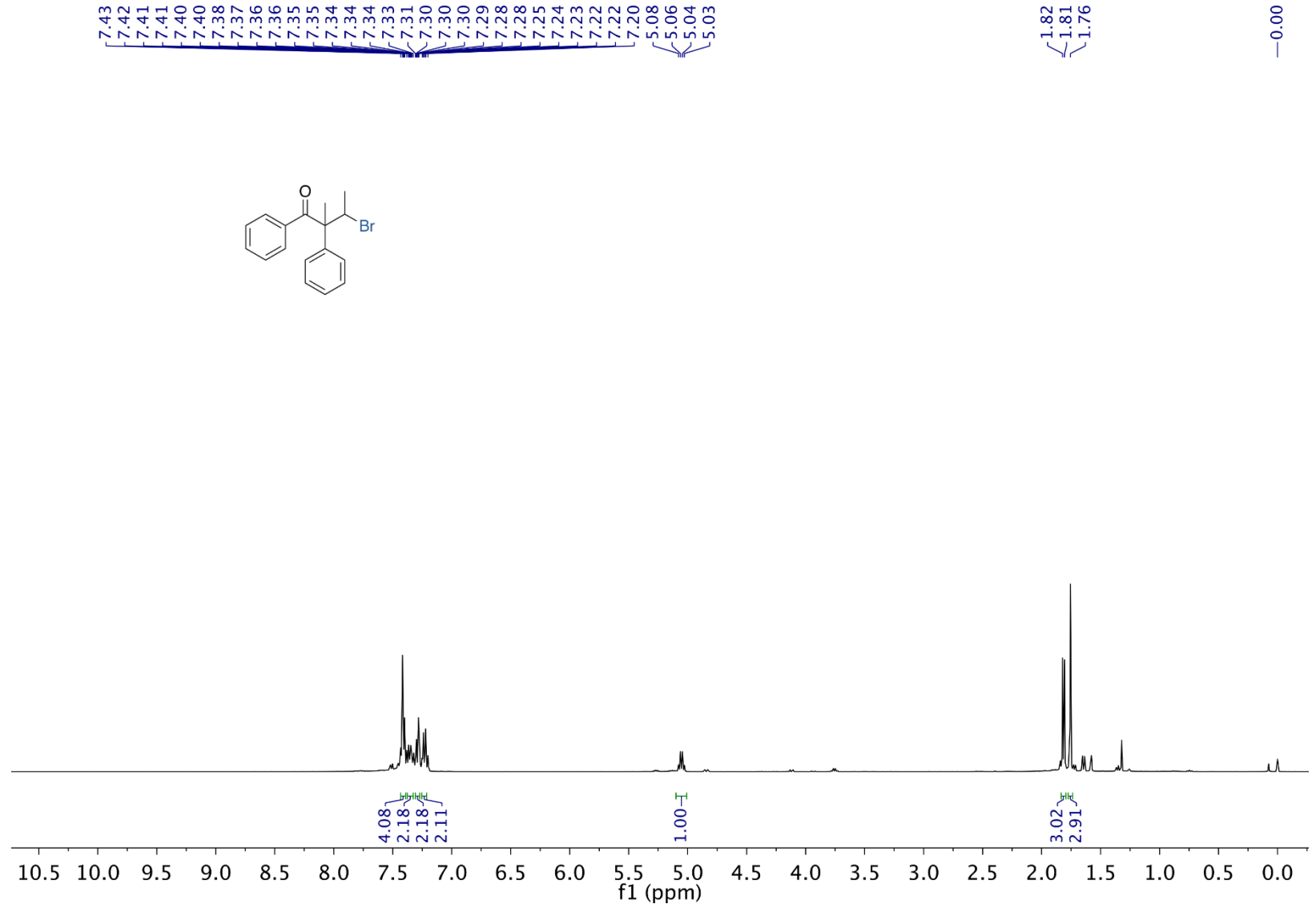
O
Br
tBu
CF3

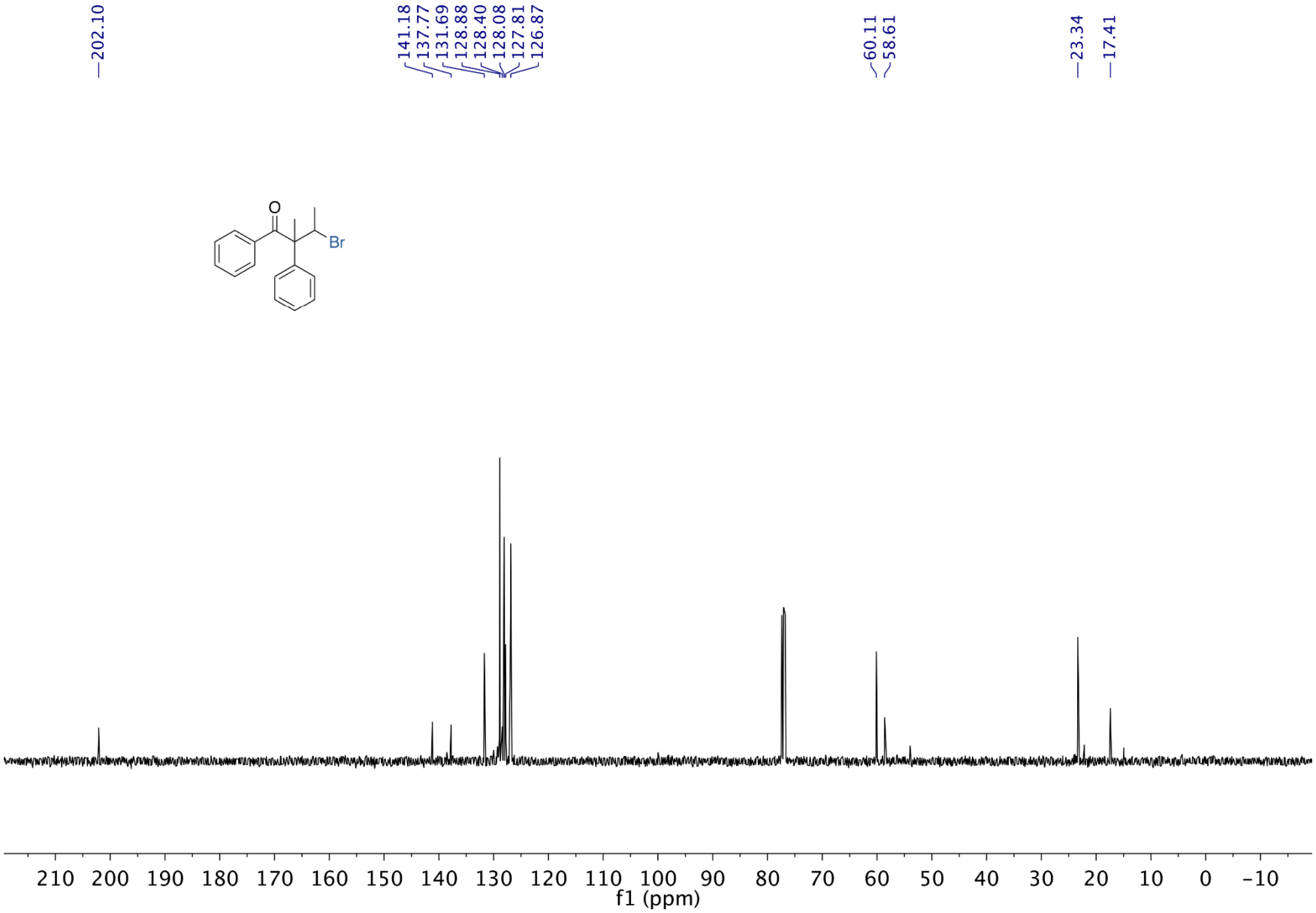

−63.23
−56 −57 −58 −59 −60 −61 −62 −63 −64 −65 −66 −67 −68 −69 −70 −71 −72 −73 −74 −75 −76 −77 −78 −79
f1 (ppm)


200.57
151.40
139.66
136.55
129.45
126.35
125.92
125.14
125.11
54.83
41.97
34.58
31.26
22.84
O
Br
tBu
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

XLIX

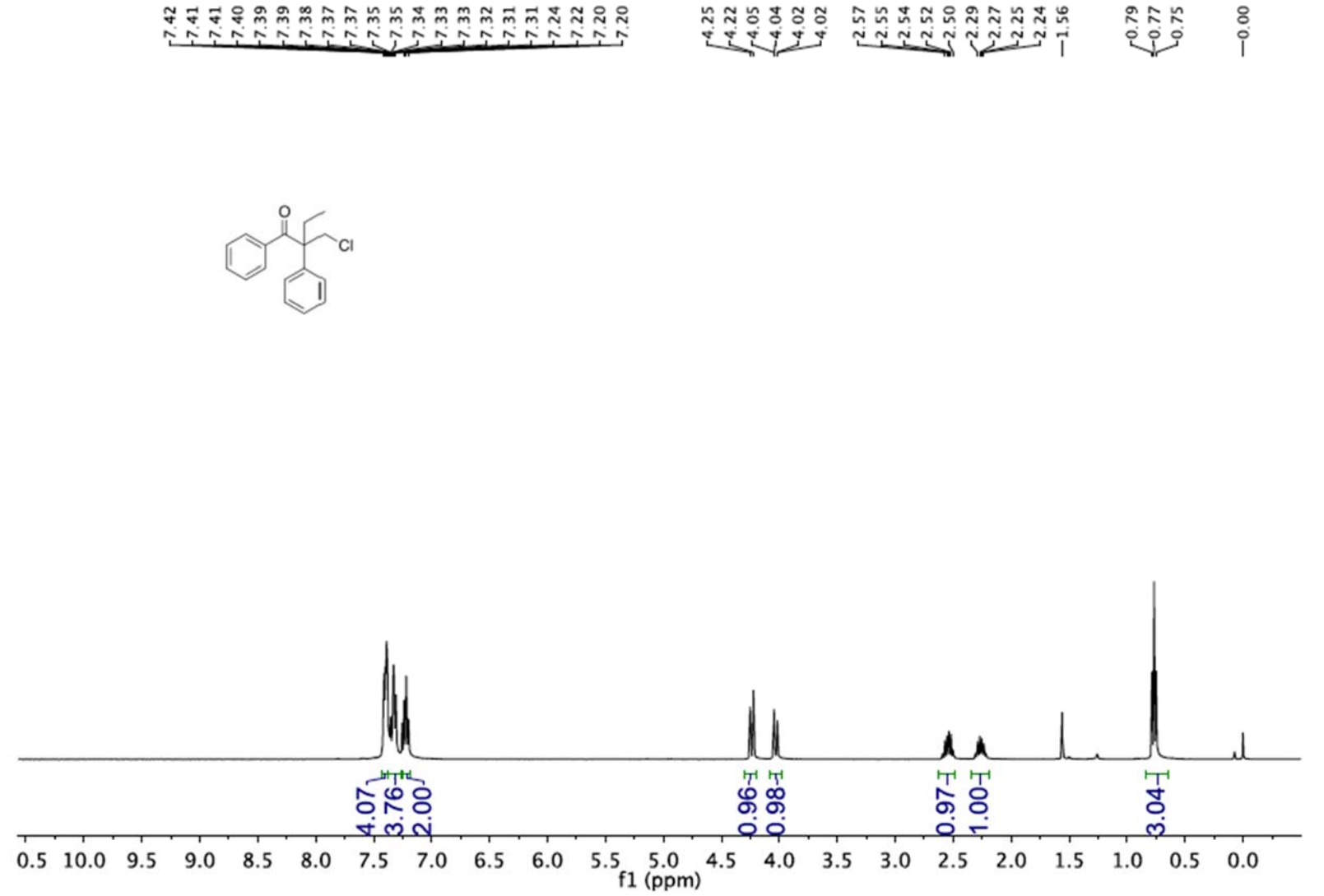
3-bromo-2-methyl-1,2-diphenylbutan-1-one (**3jb**)

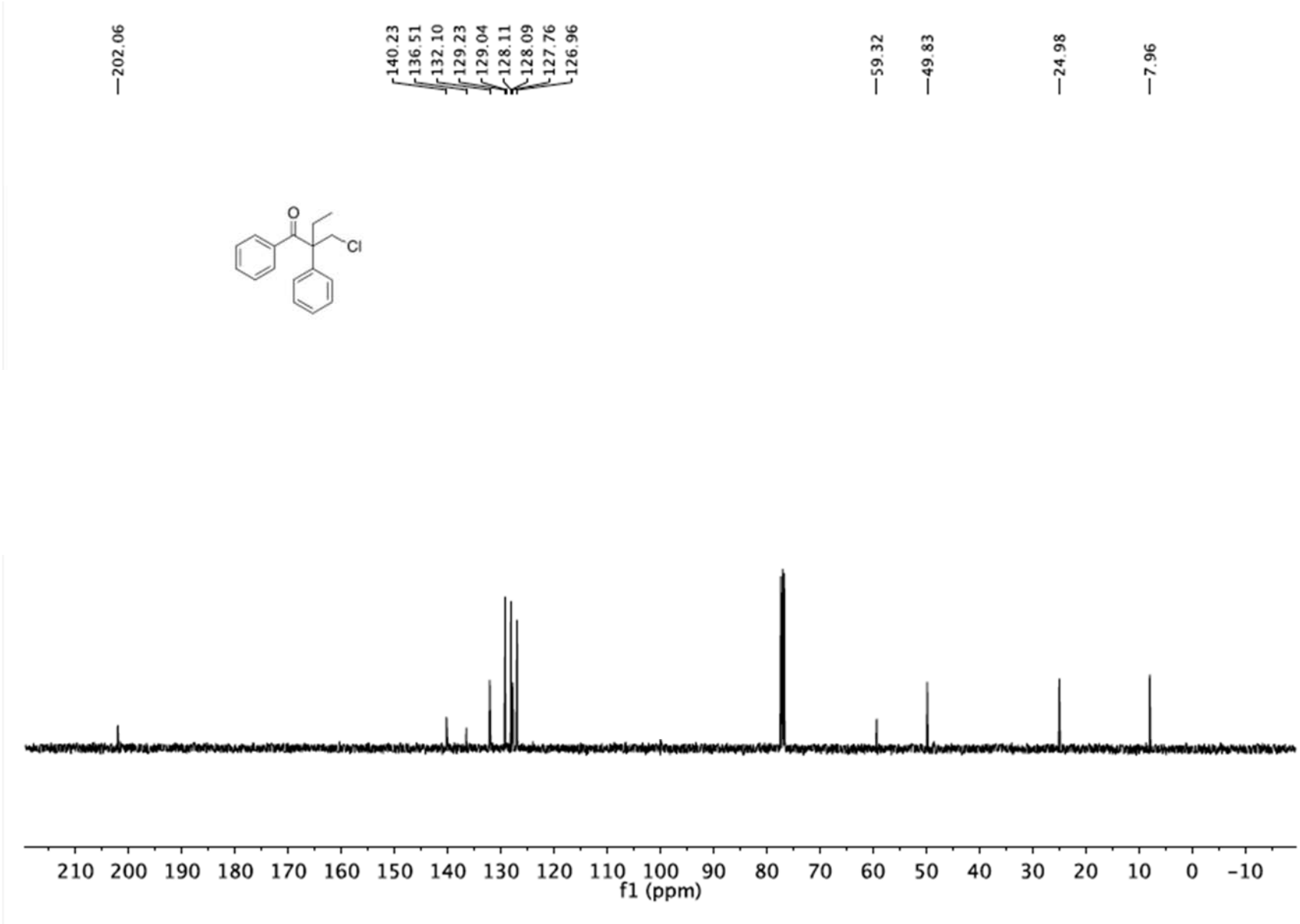



202.10
141.18
137.77
131.69
128.88
128.40
128.08
127.81
126.87
60.11
58.61
23.34
17.41
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

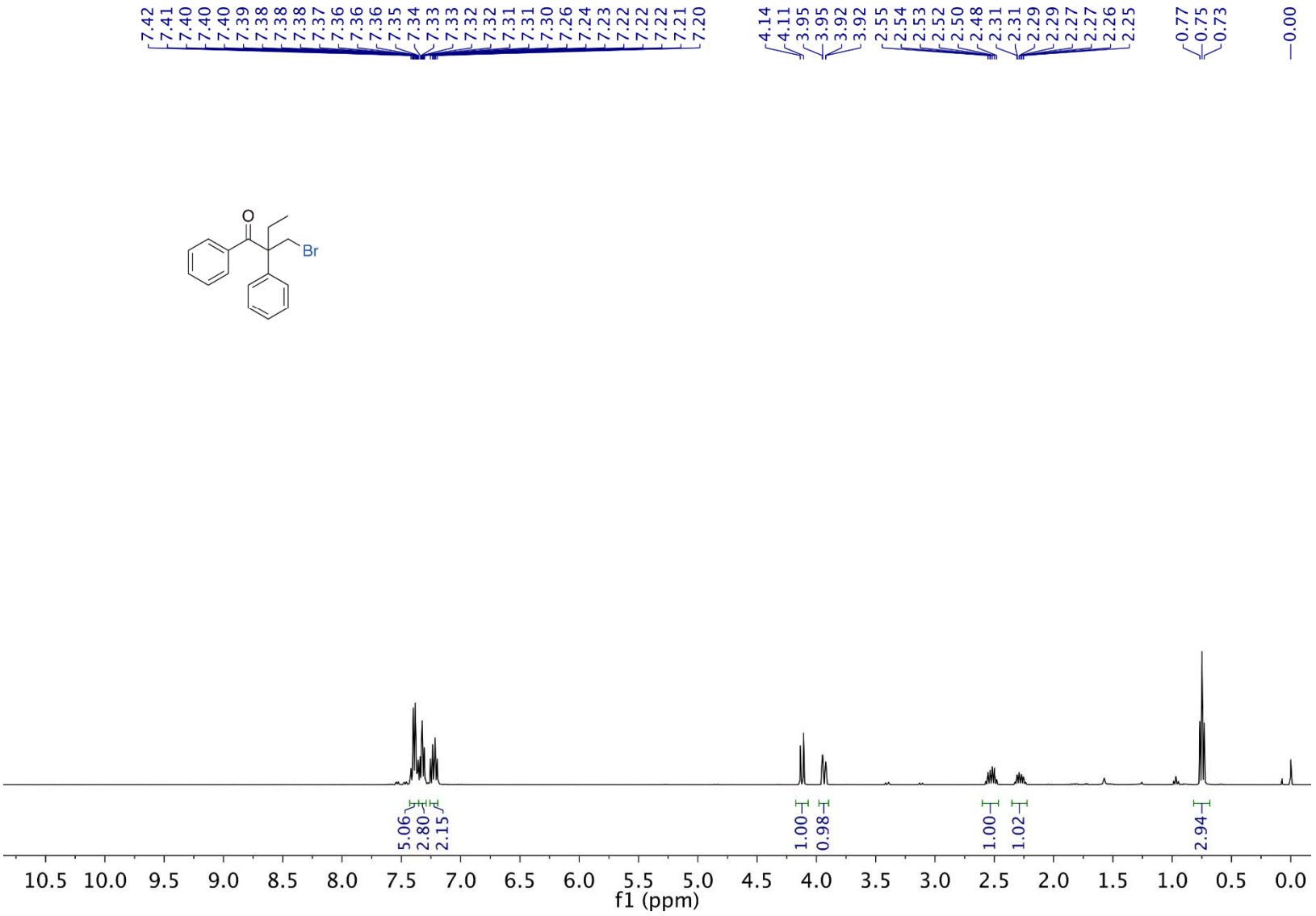
LI

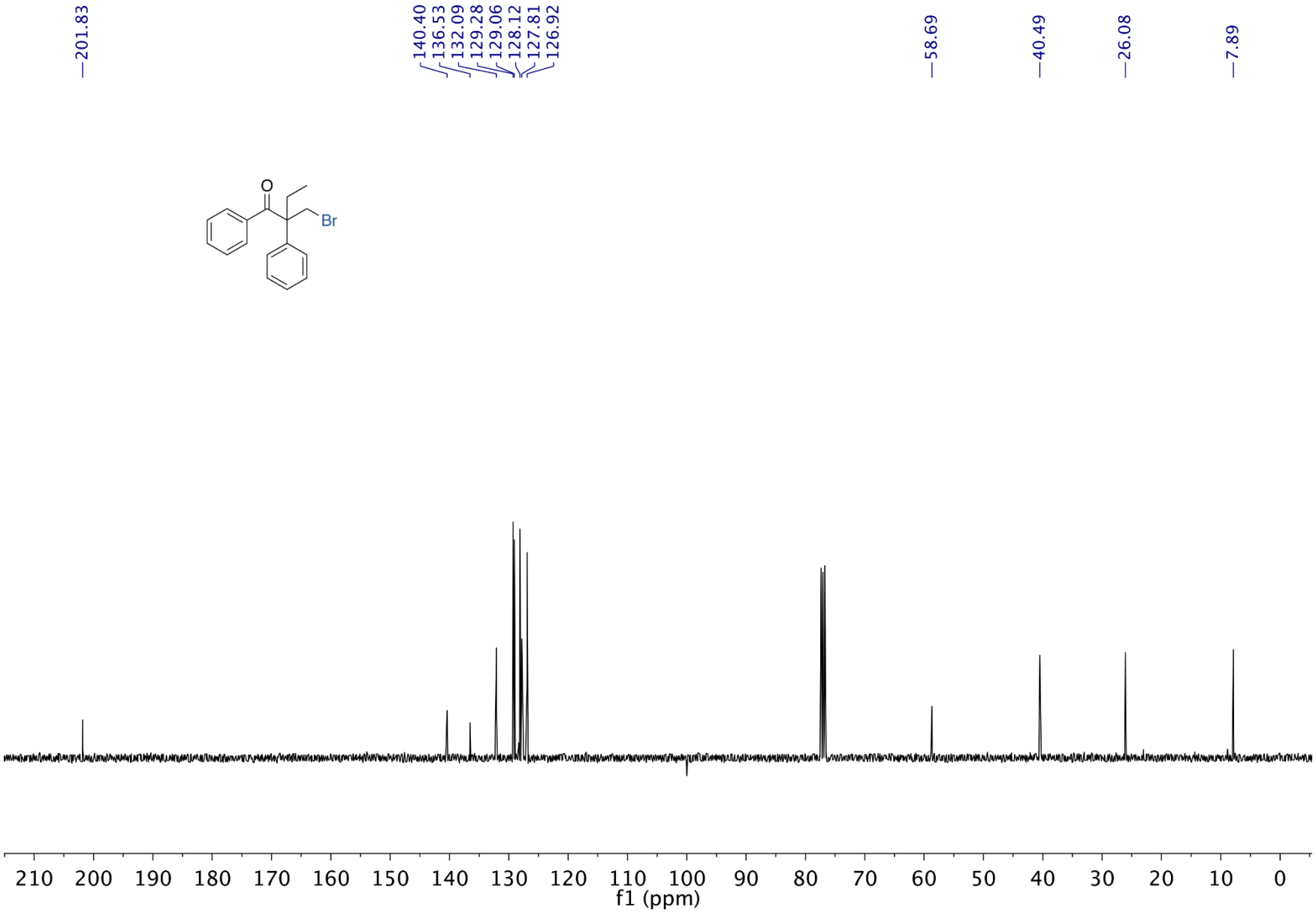
2-(chloromethyl)-1,2-diphenylbutan-1-one (**3ka**)




202.06
140.23
136.51
132.10
129.23
129.04
128.11
128.09
127.76
126.96
59.32
49.83
24.98
7.96
O
Cl
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)

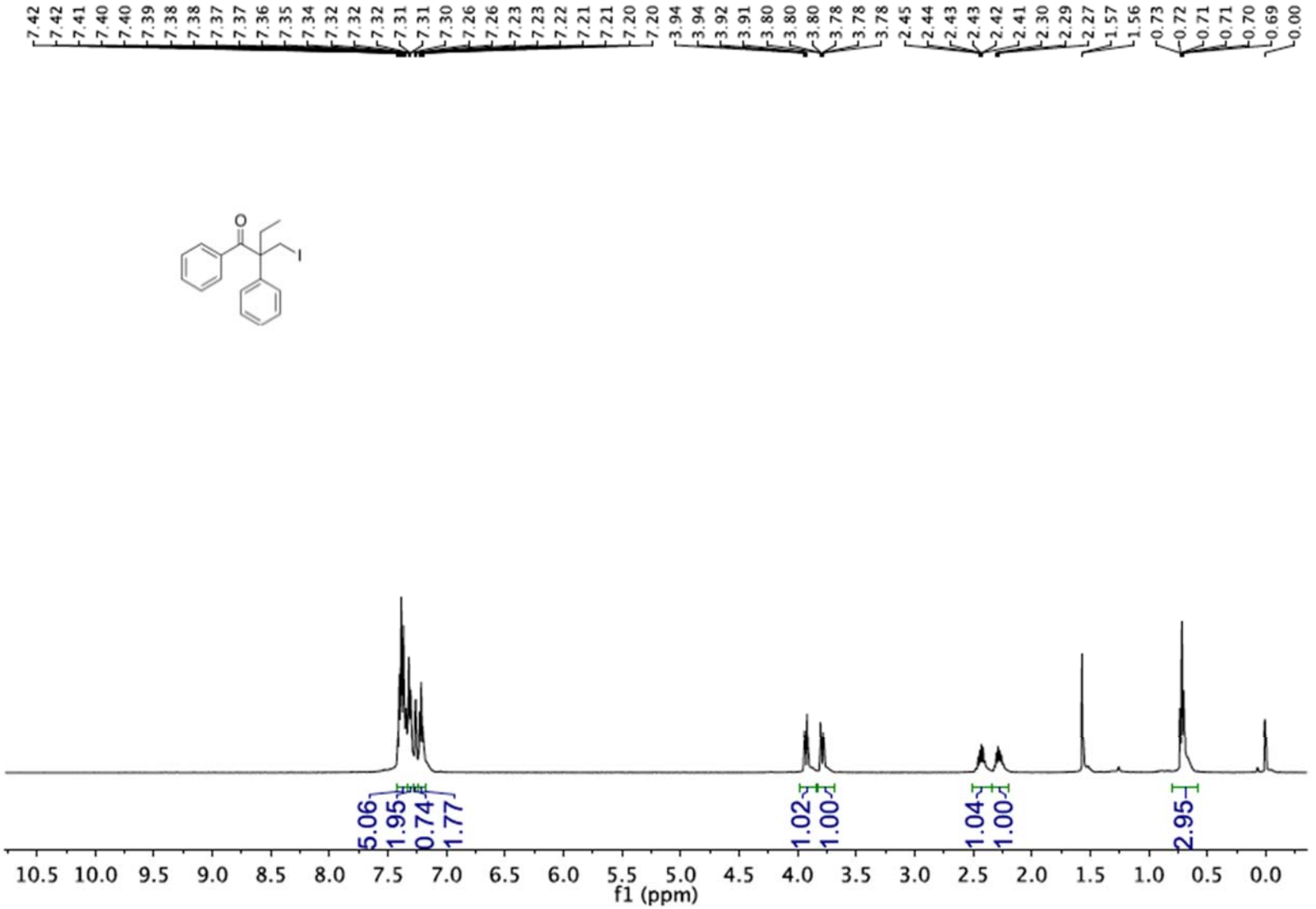
2-(bromomethyl)-1,2-diphenylbutan-1-one (**3kb**)

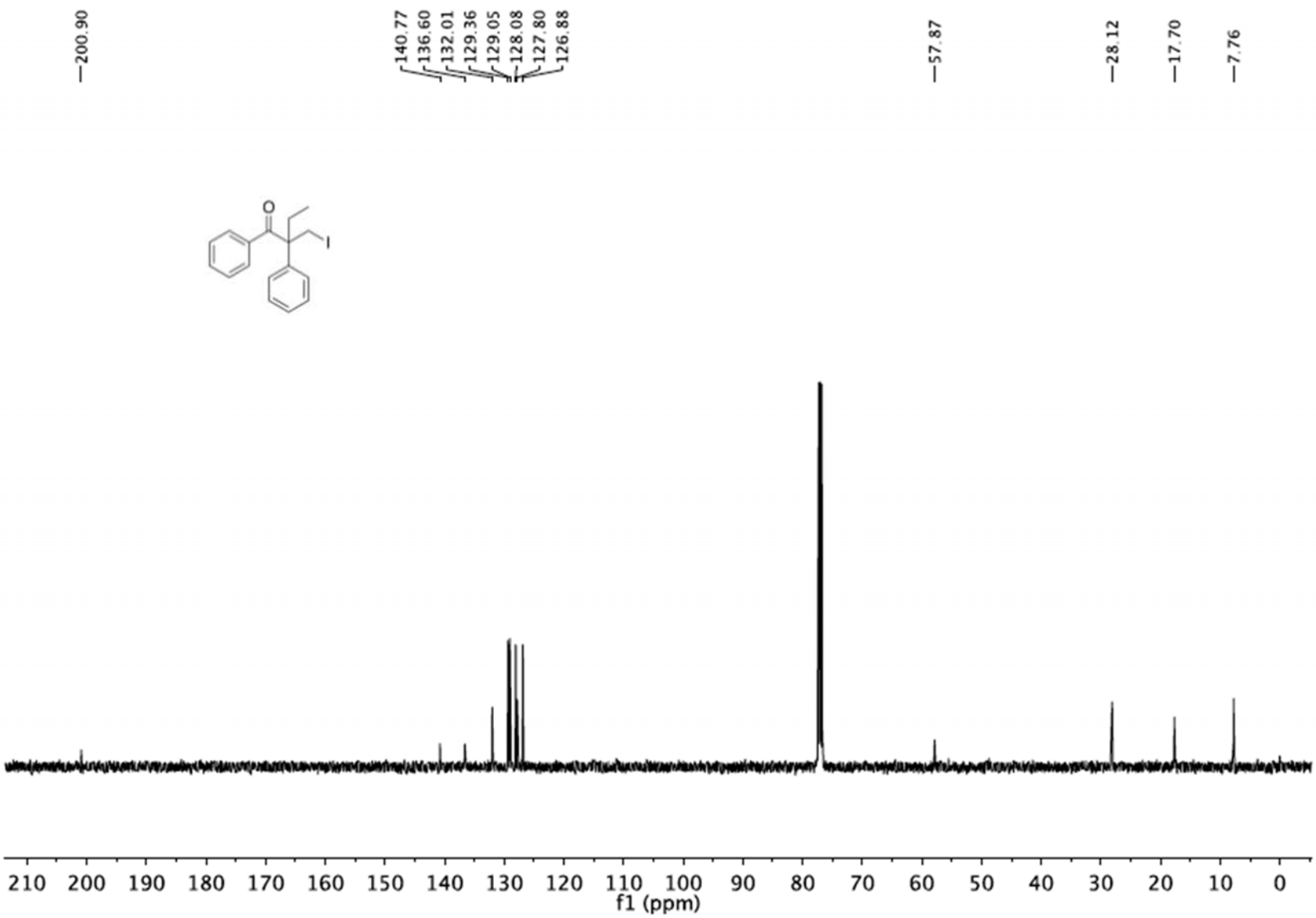



201.83
140.40
136.53
132.09
129.28
129.06
128.12
127.81
126.92
58.69
40.49
26.08
7.89
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

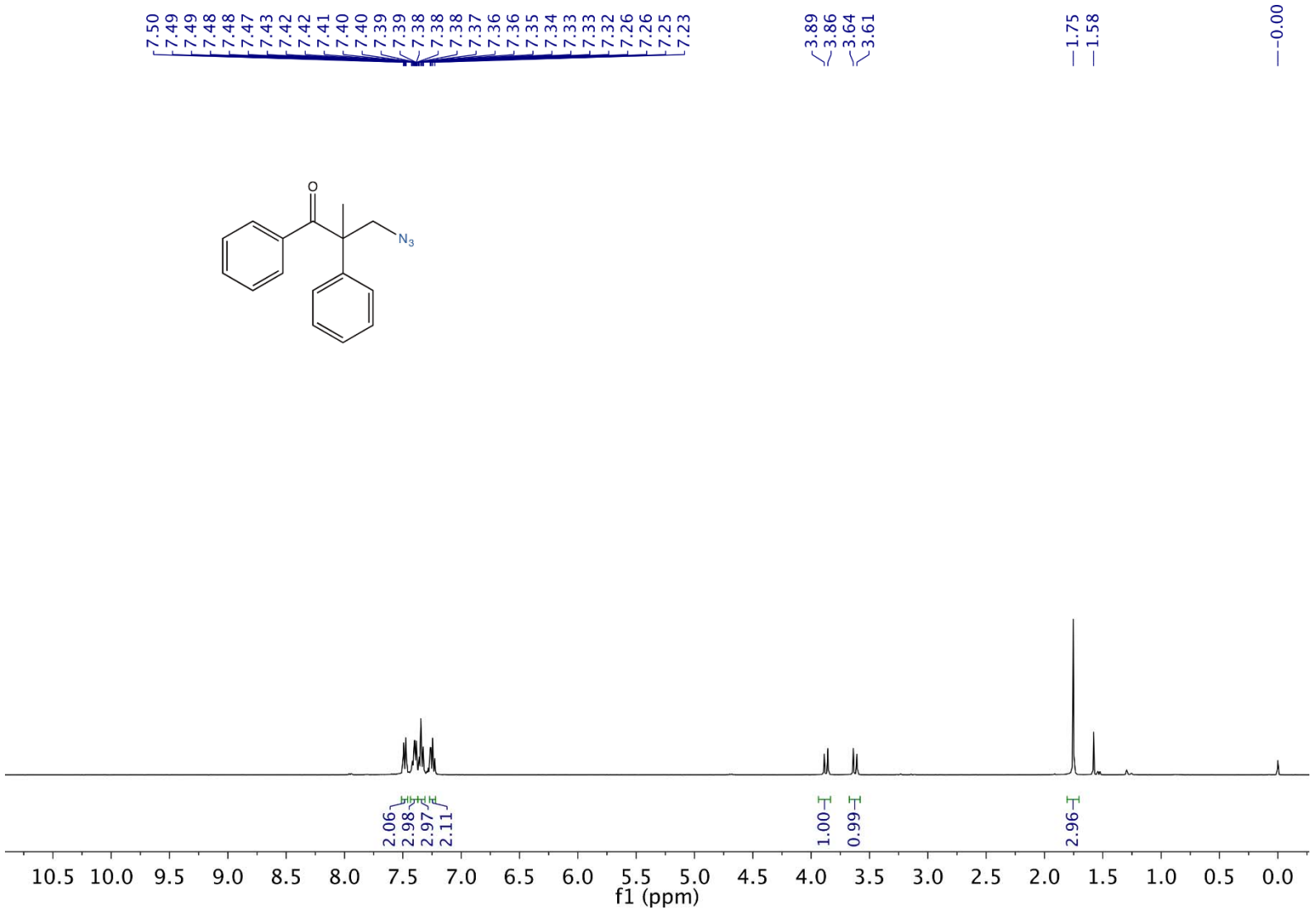
LV

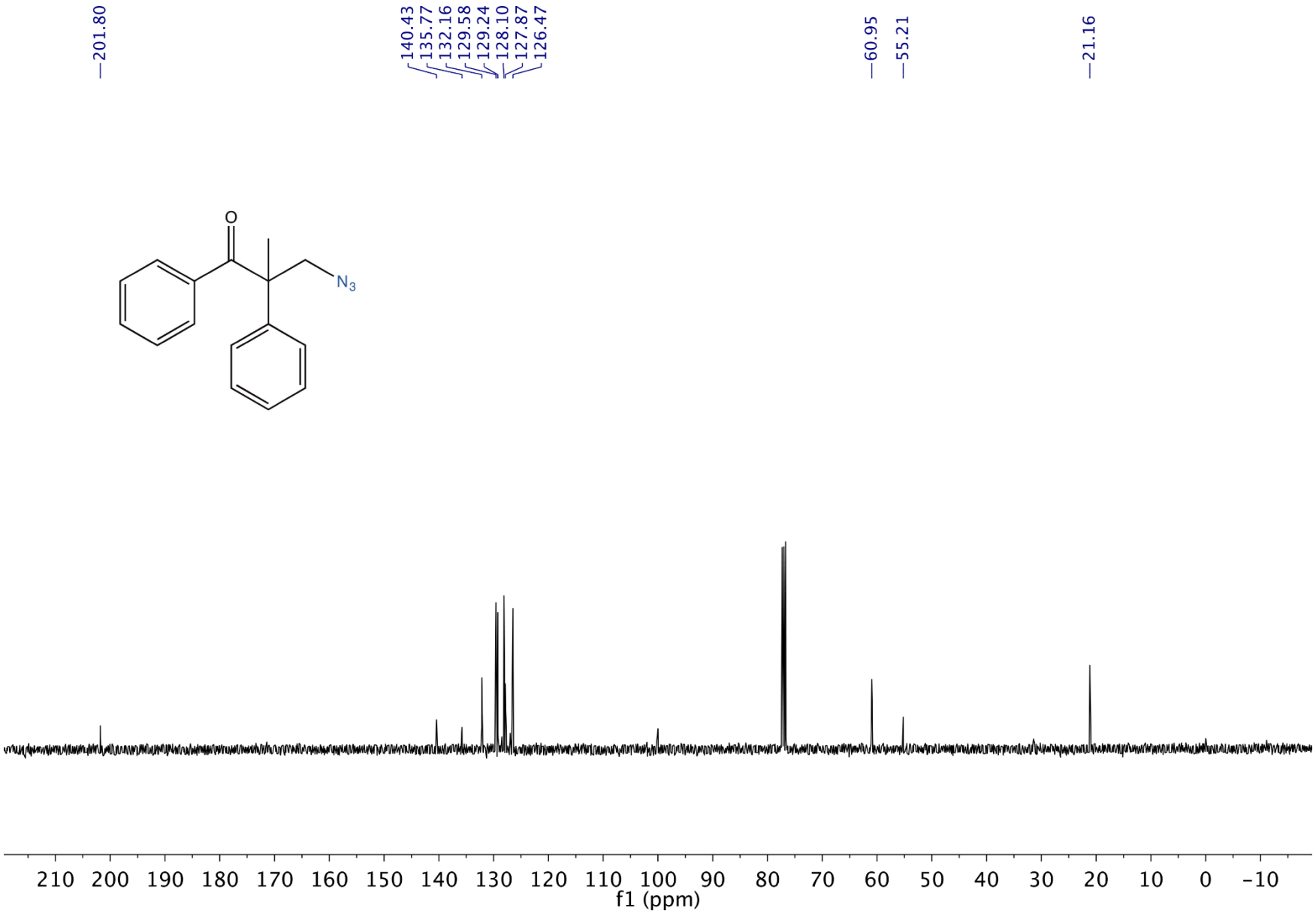
2-(iodomethyl)-1,2-diphenylbutan-1-one (**3kc**)




200.90
140.77
136.60
132.01
129.36
129.05
128.08
127.80
126.88
57.87
28.12
17.70
7.76
O
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

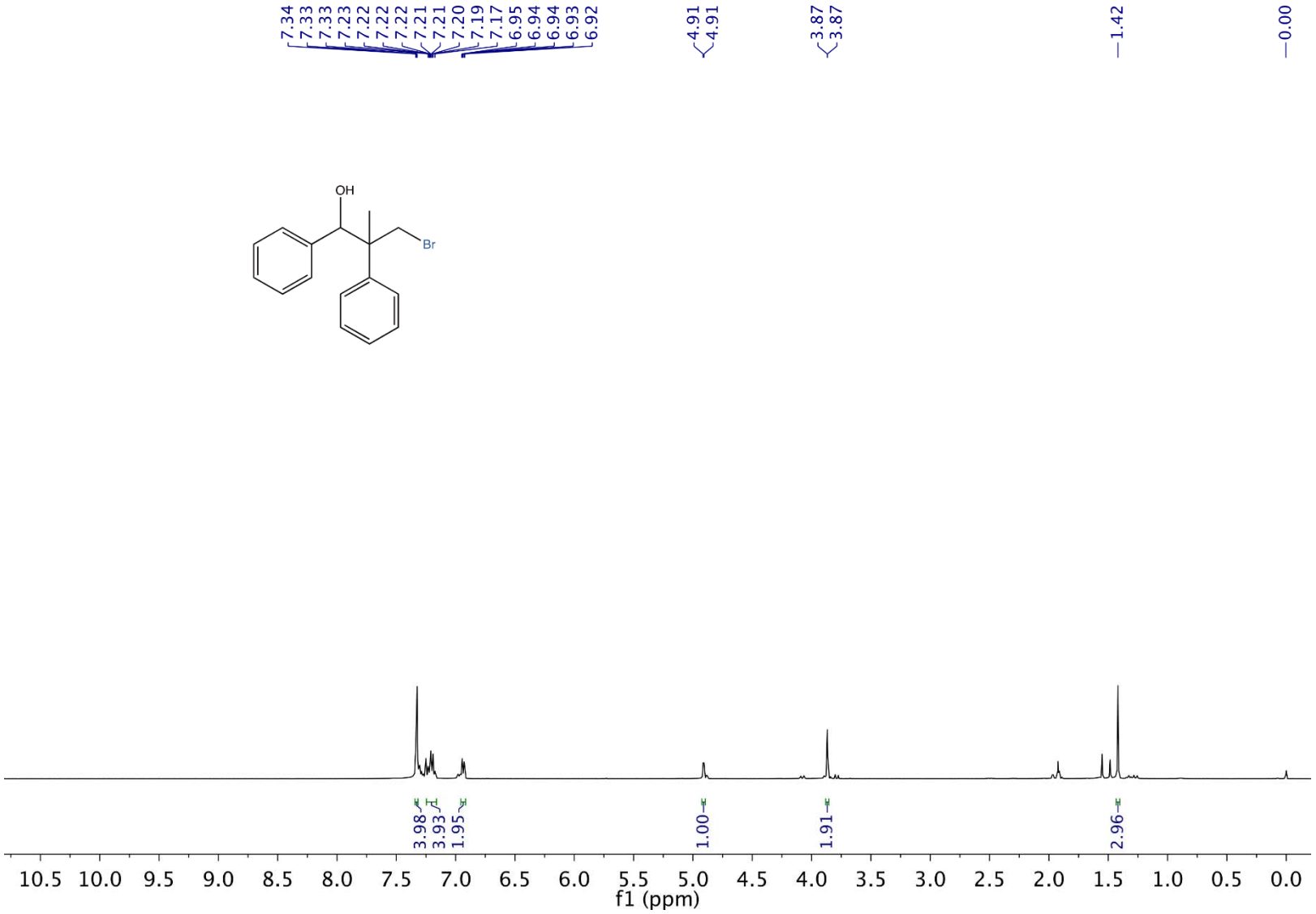
3-azido-2-methyl-1,2-diphenylpropan-1-one (**4**)

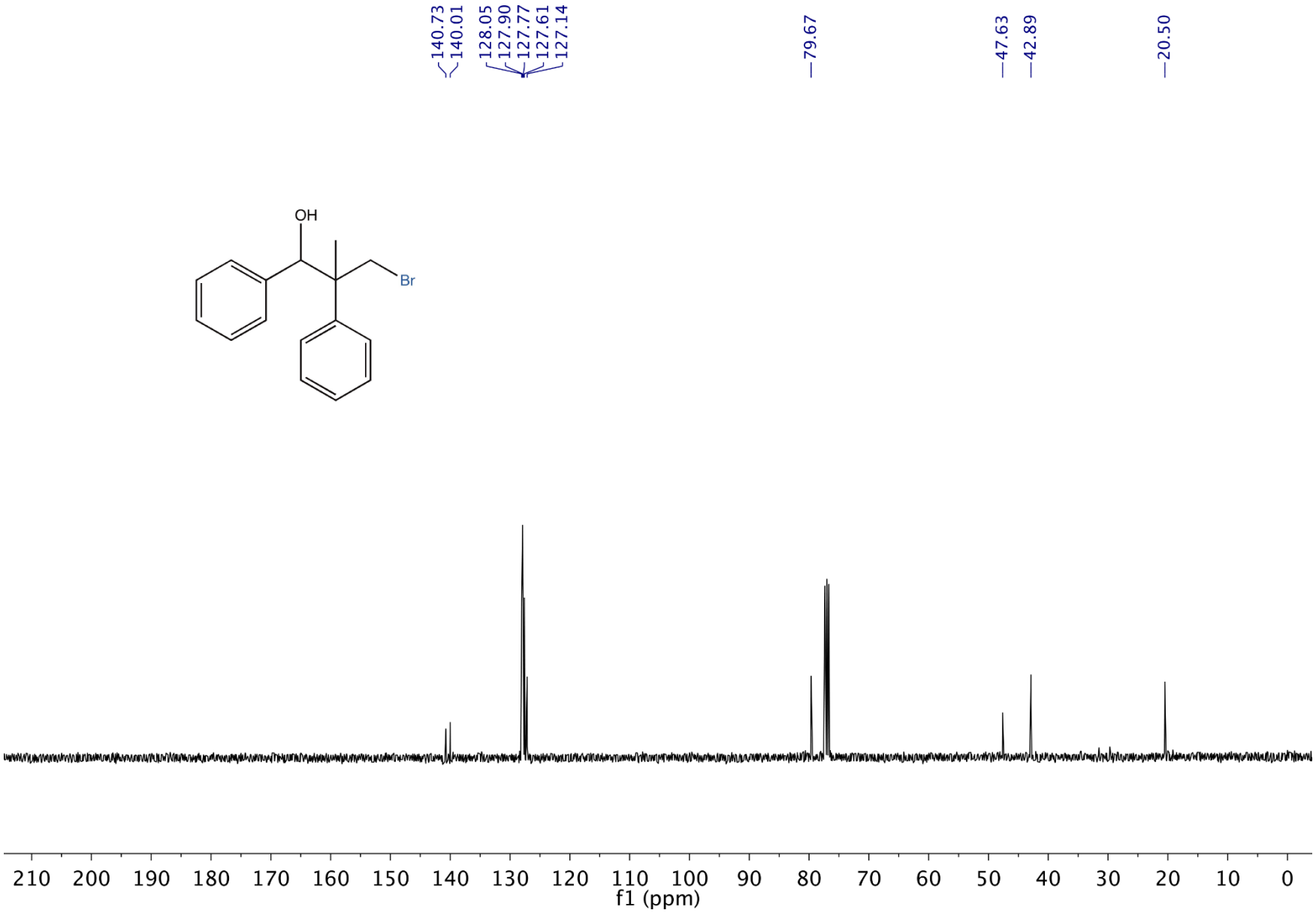



201.80
140.43
135.77
132.16
129.58
129.24
128.10
127.87
126.47
60.95
55.21
21.16
O
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

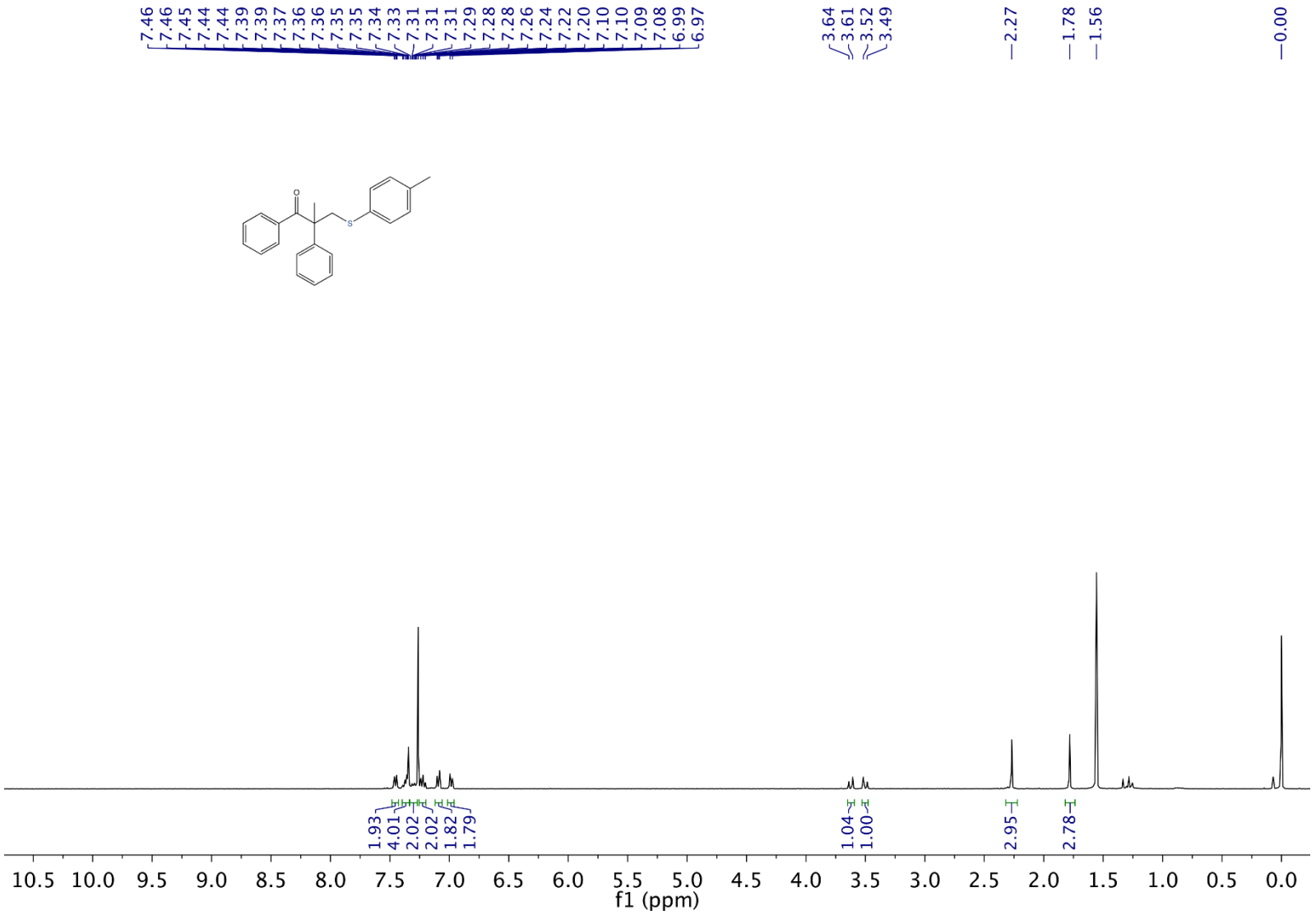
LIX

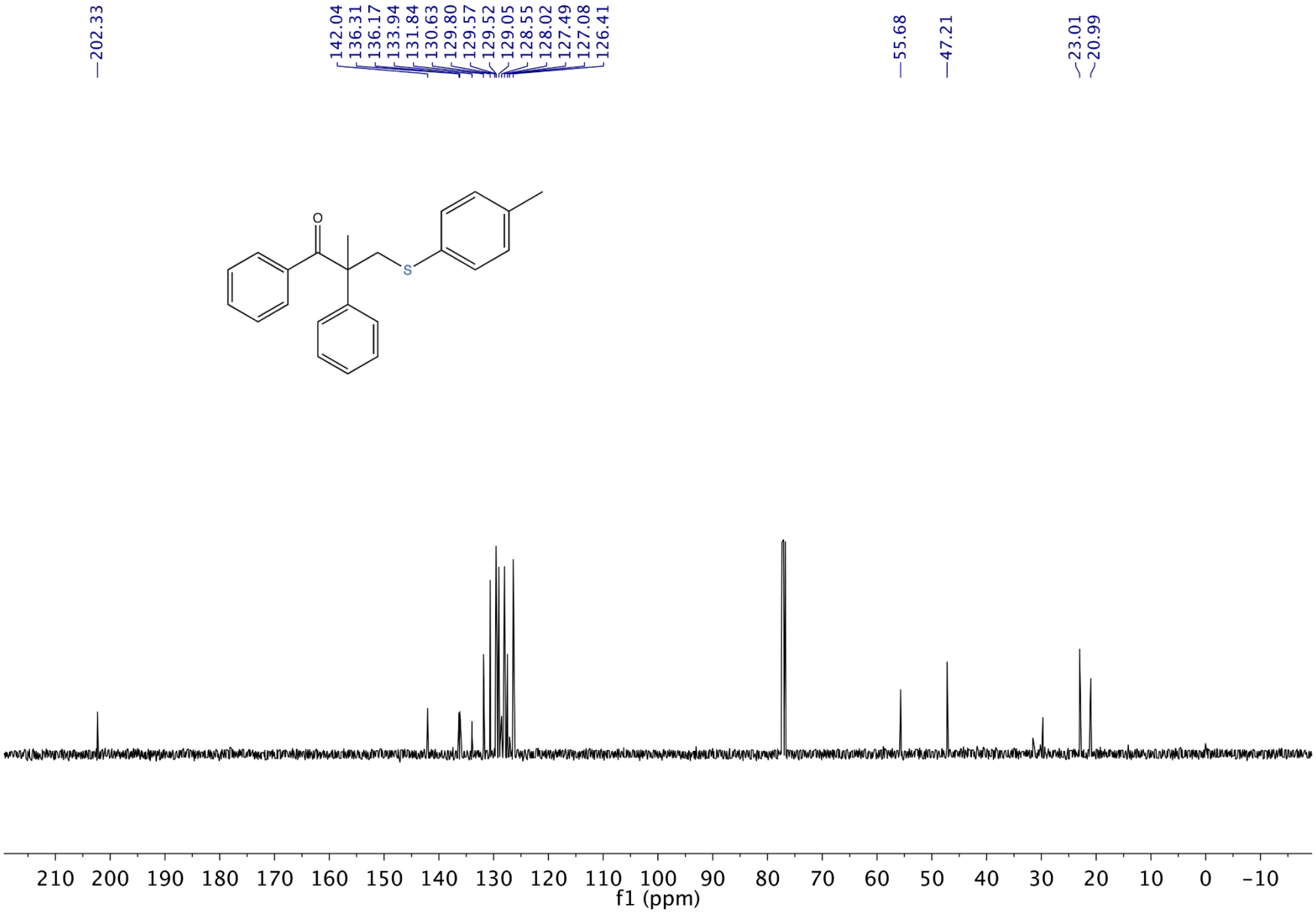
3-bromo-2-methyl-1,2-diphenylpropan-1-ol (**5)**




140.73
140.01
128.05
127.90
127.77
127.61
127.14
79.67
47.63
42.89
20.50
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-methyl-1,2-diphenyl-3-(p-tolylthio)propan-1-one (**6)**




202.33
142.04
136.31
136.17
133.94
131.84
130.63
129.80
129.57
129.52
129.05
128.55
128.02
127.49
127.08
126.41
55.68
47.21
23.01
20.99
O
S
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)