Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Contents

General information

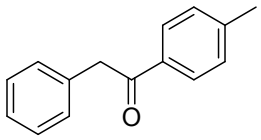
All catalytic reactions were carried out under ambient atmosphere. Chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker “Avance 600” (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ‘‘s”, ‘‘d”, “t” or ‘‘m” for singlet, doublet, triplet or multiplet, respectively. The abbreviation ‘‘br” is given for broadened signals.

Synthesis and characterization of compounds

General procedure

A screw-cap vial equipped with a magnetic stir bar was charged with 0.01 mmol of (7-Dipp)AuCl in 1 ml of dioxane, 0.01 mmol of AgOTf, 15 mmol of H_2O and 1 mmol of acetylene. The vial was transferred to a preaheated oil bath (80°C). After 24 h reaction mixture was cooled, concentrated in vacuum and the product isolated by flash chromatography on a silica gel by elution with hexane-CH_2Cl_2 mixture or recrystallized from hexane/CH_2Cl_2.

*2-phenyl-1-p-tolylethanone (**1a**)*



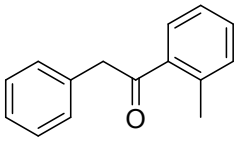
Yield 142 mg, 67%. White solid. M.p. 96-98 °C (lit data: M.p. 104-105 °C).[1]

^{1}H NMR (600 MHz, Chloroform-*d)* δ 7.95 – 7.91 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.24 (m, 5H), 4.26 (s, 2H), 2.41 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 197.4, 144.1, 134.9, 134.2, 129.5, 129.4, 128.9, 128.8, 126.9, 45.5, 21.8.

The NMR data are in agreement with previously reported.[1]

*2-phenyl-1-o-tolylethanone **(2a)***



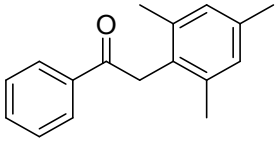
Yield 136 mg, 65%. White solid. M.p. 79-80 °C. (lit data: Colorless oil).[2]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.35 – 7.30 (m, 2H), 7.29 – 7.21 (m, 5H), 4.22 (s, 2H), 2.45 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 201.6, 138.7, 137.8, 134.6, 132.1, 131.4, 129.7, 128.7, 127.0, 125.7, 48.6, 21.4.

The NMR data are in agreement with previously reported.[3]

*2-mesityl-1-phenylethanone (**3b**).*



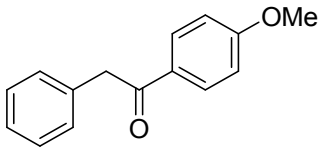
Yield 22 mg, 9.4%. White solid. M.p. 144-145 °C (lit data: M.p. 146.5-148 °C).[4]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.90 (s, 2H), 4.34 (s, 2H), 2.29 (s, 3H), 2.19 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 197.2, 137.3, 137.0, 136.5, 133.3, 129.4, 129.0, 128.8, 128.2, 39.5, 21.1, 20.4.

The NMR data are in agreement with previously reported.[4]

*1-(4-methoxyphenyl)-2-phenylethanone (**4a**)*



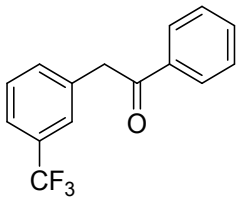
Yield 163 mg, 72%. White solid. M.p. 65-66 °C (lit data: M.p. 66-68 °C).[5]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.30 – 7.23 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 4.24 (s, 2H), 3.86 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 196.3, 163.6, 135.1, 131.1, 129.8, 129.5, 128.7, 126.9, 113.9, 55.6, 45.4.

The NMR data are in agreement with previously reported.[4]

*1-phenyl-2-(3-(trifluoromethyl)phenyl)ethanone (**5a**)*



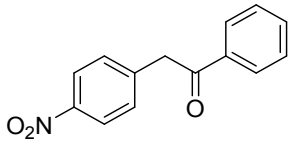
Yield 188.6 mg, 71%. White solid. . M.p. 90-93°C (lit data: M.p. 35-36 °C).[6]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (s, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.48 – 7.44 (m, 2H), 4.36 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 196.7, 136.5, 135.5, 133.6, 133.2, 131.0 (q, *J* = 32.2 Hz), 129.1, 128.9, 128.6, 126.6 – 126.4 (m), 124.5 (q, *J* = 272.8 Hz), 124.0 – 123.88 (m), 45.0.

The NMR data are in agreement with previously reported.[6]

*2-(4-nitrophenyl)-1-phenylethanone (**6a**)*



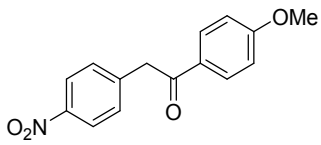
Yield 163 mg, 67.5%. Red solid. M.p. 138-139 °C (lit data: M.p. 141-142 °C).[7]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.42 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 196.1, 147.2, 142.2, 136.3, 133.9, 130.8, 129.0, 128.6, 123.9, 45.1.

The NMR data are in agreement with previously reported.[7]

*1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethanone (**7a**)*



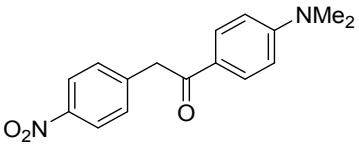
Yield 236 mg, 87%. Yellow needles. M.p. 110-112 °C (lit data: M.p. 114-116 °C).[8]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.35 (s, 2H), 3.88 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 194.6, 164.1, 147.1, 142.6, 130.9, 130.7, 129.3, 123.8, 114.2, 55.7, 44.8.

The NMR data are in agreement with previously reported.[8]

*1-(4-(dimethylamino)phenyl)-2-(4-nitrophenyl)ethanone (**8a**)*



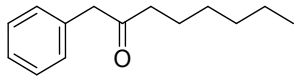
Yield 188 mg, 66%. Orange needles. M.p. .>200 °C (lit data: M.p. 246-247 °C).[9]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 4.30 (s, 2H), 3.07 (s, 6H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 194.0, 153.8, 143.6, 131.0, 130.6, 124.1, 123.8, 110.9, 44.5, 40.2.

The NMR data are in agreement with previously reported.[9]

*1-phenyloctan-2-one (**9b**)*



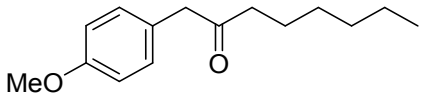
Yield 126.7 mg, 62%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 3.68 (s, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.30 – 1.18 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 208.7, 134.5, 129.5, 128.8, 127.0, 50.3, 42.1, 31.7, 28.9, 23.8, 22.6, 14.1.

The NMR data are in agreement with previously reported.[10]

*1-(4-methoxyphenyl)octan-2-one (**10b**)*



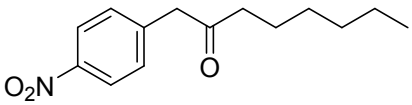
Yield 145 mg, 62%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.11 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 2H), 2.42 (t, J = 7.4 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.28 – 1.20 (m, 6H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 209.2, 158.7, 130.5, 126.6, 114.2, 55.4, 49.4, 41.2, 31. 7, 28.9, 23.9, 22.6, 14.1.

The NMR data are in agreement with previously reported.[11]

*1-(4-nitrophenyl)octan-2-one (**11b**)*



Yield 240 mg, 96%. Yellow crystals. M.p. 46 °C (lit data: orange liquid).[11]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.31 – 1.21 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H).

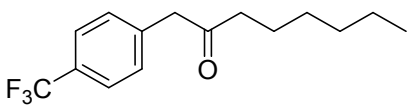
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d)* δ 206.6, 147.2, 141.8, 130.6, 123.9, 49.4, 43.0, 31.7, 28.9, 23.8, 22.6, 14.1.

The NMR data are in agreement with previously reported.[11]

FT-IR (neat, cm^{-1}): 2953, 2930, 2851, 1711, 1521, 1495, 1349, 1112, 1073, 1013, 750, 709.

HRMS calc. for $C_{14}H_{19}NO_3$: $[M-H]^-$ 248.1287; found 248.1292.

*1-(4-(trifluoromethyl)phenyl)octan-2-one (**12b**)*



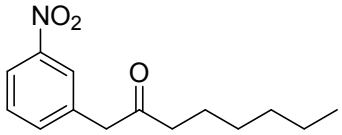
Yield 250 mg, 91%. Yellow oil (lit data: brown liquid).[11]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 3.75 (s, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.30 – 1.21 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 207.4, 138.4, 129.9, 129.4 (q, *J* = 32.5 Hz), 125.6 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 271.9 Hz), 49.5, 42.6, 31.6, 28.86, 23.8, 22.5, 14.0.

The NMR data are in agreement with previously reported.[11].

*1-(3-nitrophenyl)octan-2-one (**13b**)*



Yield 240 mg, 95%. White needles. M.p. 51-53 °C.

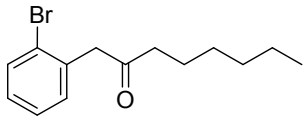
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.5 Hz, 1H), 8.06 (s, 1H), 7.54 – 7.47 (m, 2H), 3.82 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.32 – 1.23 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 206.9, 136.2, 135.9, 129.5, 124.6, 122.2, 100.1, 49.0, 42.9, 31.7, 28.9, 23.8, 22.6, 14.1.

FT-IR (neat, cm^{-1}): 2954, 2928, 2857, 1708, 1521, 1471, 1348, 1126, 1071, 1016, 904, 812, 706.

HRMS calc. for $C_{14}H_{19}NO_3$: $[M-H]^-$ 248.1287; found 248.1294.

*1-(2-bromophenyl)octan-2-one (**14b**)*



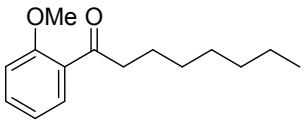
Yield 246 mg, 87%. Yellow oil. (lit data: yellow oil).[10]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 1H), 7.31 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 7.15 – 7.11 (m, 1H), 3.85 (s, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.57 (m, 2H), 1.30 – 1.25 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 207.3, 135.0, 132.9, 131.8, 128.8, 127.7, 125.13, 50.1, 42.7, 31.7, 28.9, 23.8, 22.6, 14.2.

The NMR data are in agreement with previously reported.[10]

*1-(2-methoxyphenyl)octan-1-one (**15a**)*



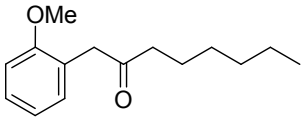
Yield 36 mg, 15.4%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.02 – 6.97 (m, 1H), 6.97 – 6.93 (m, 1H), 3.89 (s, 3H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.31 – 1.21 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 203.6, 158.4, 133.2, 130.2, 120.8, 111.60, 55.61, 43.9, 31.9, 29.5, 24.6, 22.8, 14.2.

The NMR data are in agreement with previously reported.[12]

*1-(2-methoxyphenyl)octan-2-one (**15b**)*



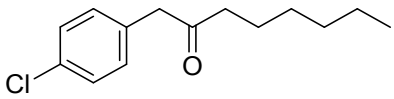
Yield 154 mg, 65.6%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 1H), 7.12 (d, *J* = 7.34 Hz, 1H), 6.92 (t, *J* = 7.40 Hz, 1H), 6.87 (d, *J* = 8.20 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 2H), 2.42 (t, *J* = 7.42 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.29 – 1.19 (m, 6H), 0.87 (t, *J* = 7.04 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 209.3, 157.5, 131.3, 128.5, 123.9, 120.8, 110.6, 55.4, 44.82, 42.1, 31.7, 29.0, 23.9, 22.6, 14.2.

HRMS calc. for $C_{15}H_{22}O_2$: $[M+H]^+$ 235.1692; found 235.1692.

*1-(4-chlorophenyl)octan-2-one (**16b**)*



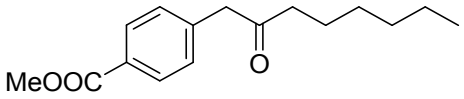
Yield 184 mg, 77%. Colorless oil. (lit data: yellow liquid).[11]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.64 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.29 – 1.20 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 208.0, 133.0, 132.9, 130.9, 128.8, 49.2, 42.3, 31.6, 28.9, 23.8, 22.6, 14.1.

The NMR data are in agreement with previously reported.[11]

*Methyl 4-(2-oxooctyl)benzoate (**17b**)*



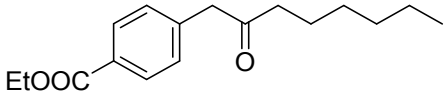
Yield 230 mg, 88%. White solid. M.p. 53-54 °C (lit data: yellow liquid).[11]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.74 (s, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.30 – 1.19 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 207.7, 167.0, 139.7, 130.1, 129.6, 129.0, 52.2, 50.0, 42.5, 31.7, 28.9, 23.8, 22.6, 14.1.

The NMR data are in agreement with previously reported.[11]

*Ethyl 4-(2-oxooctyl)benzoate (**18b**)*



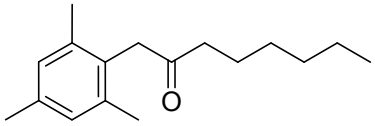
Yield 260 mg, 94%. White solid. M.p. 52 °C

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.23 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.26 – 1.19 (m, 6H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 207.6, 166.4, 139.5, 129.9, 129.5, 129.3, 100.1, 61.0, 49.9, 42.4, 31.6, 28.8, 23.7, 22.5, 14.4, 14.1.

HRMS calc. for $C_{17}H_{24}O_3$: $[M+H]^+$ 277.1798; found 277.1799.

*1-mesityloctan-2-one (**19b**)*



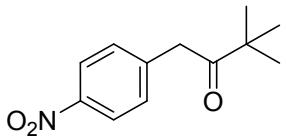
Yield 172.5 mg, 70%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.88 (s, 2H), 3.72 (s, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.27 (s, 3H), 2.20 (s, 6H), 1.61 – 1.55 (m, 2H), 1.30 – 1.24 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 208.9, 136.8, 136.4, 129.3, 129.1, 44.2, 42.1, 31.7, 29.0, 24.0, 22.6, 21.0, 20.5, 14.2.

HRMS calc. for $C_{17}H_{26}O$: $[M+H]^+$ 247.2056; found 247.2053.

*3,3-dimethyl-1-(4-nitrophenyl)butan-2-one (**20b**)*



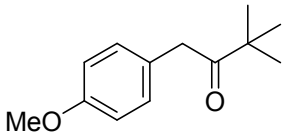
Yield 208 mg, 94%. White solid . M.p. 63-64 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.29 (m, 2H), 3.91 (s, 2H), 1.23 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 211.4, 147.0, 142.7, 130.7, 123.7, 45.0, 43.0, 26.4.

The NMR data are in agreement with previously reported.[13]

*1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (**21b**)*



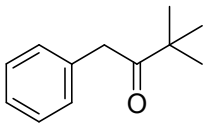
Yield 70 mg, 34%. Colorless oil. (lit data: Colorless oil).[14]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 2H), 1.20 (d, *J* = 1.2 Hz, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d)* δ 213.4, 158.5, 130.6, 127.1, 114.0, 55.4, 44.7, 42.5, 26.6.

The NMR data are in agreement with previously reported.[14]

*3,3-dimethyl-1-phenylbutan-2-one (**22b**)*



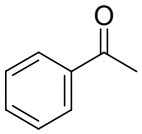
Yield 125 mg, 71%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.18 (d, *J* = 7.3 Hz, 2H), 3.81 (s, 2H), 1.21 (d, *J* = 1.1 Hz, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 213.0, 135.1, 129.7, 128.5, 126.7, 44.8, 43.4, 26.5.

The NMR data are in agreement with previously reported.[3]

*Acetophenone (**23a**)*



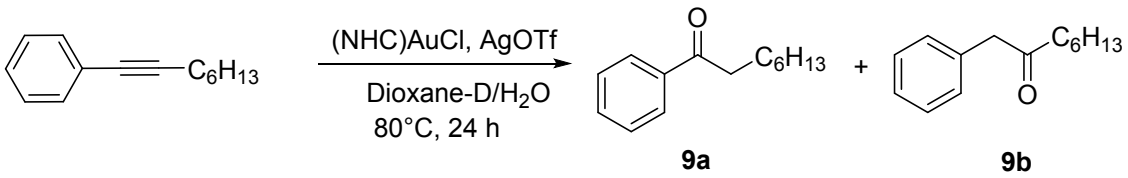
Yield 101 mg, 84%. Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.02 Hz, 2H), 7.56 (t, *J* = 7.40 Hz, 1H), 7.46 (t, *J* = 7.75 Hz, 2H), 2.61 (s, 3H).

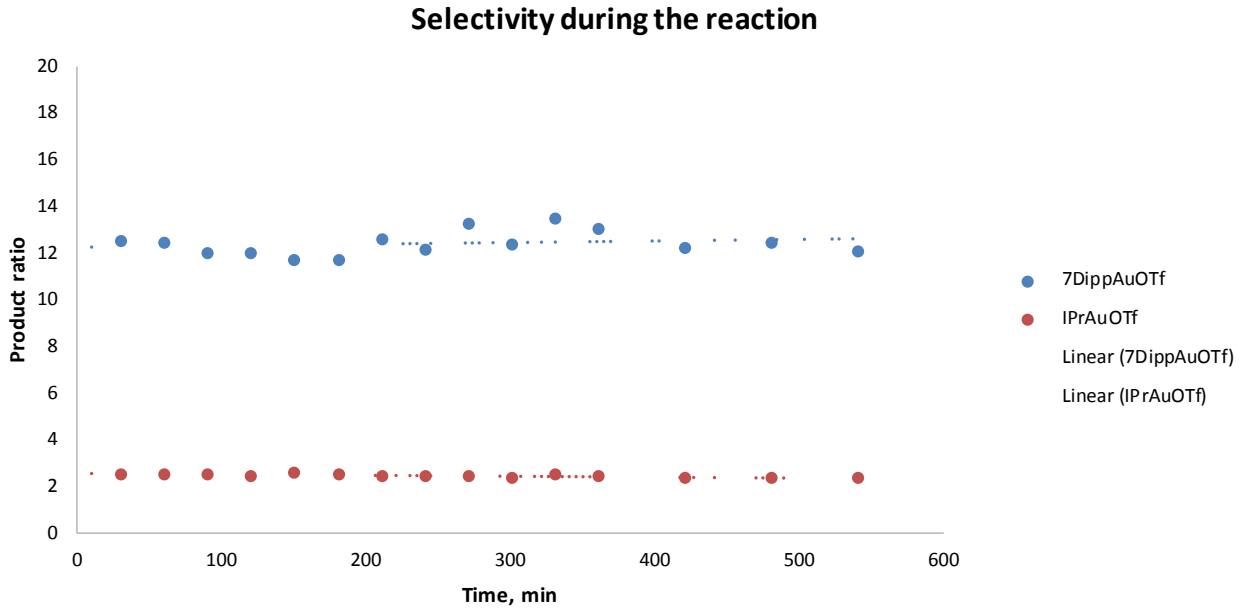
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.7.

The NMR data are in agreement with previously reported.[15]

Kinetic experiments

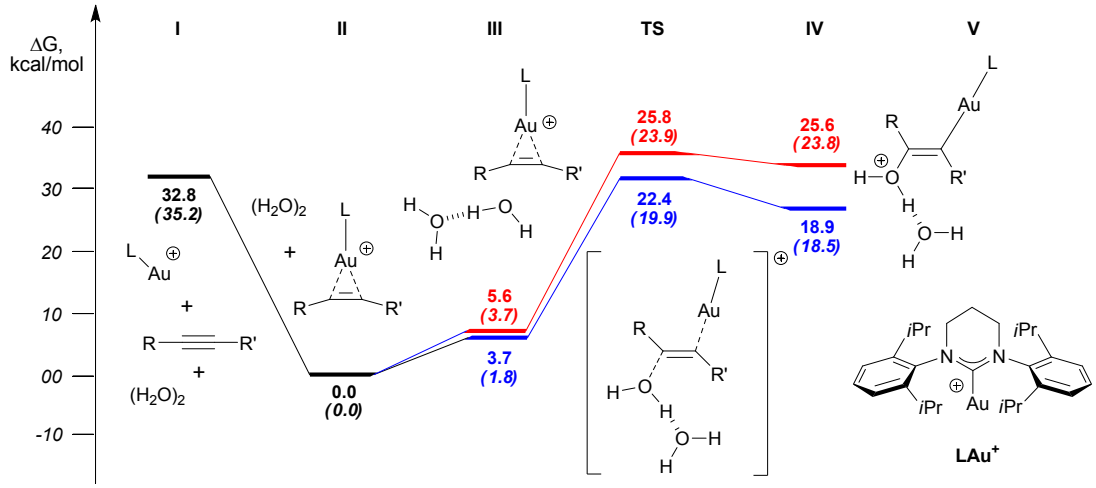


Kinetic experiments were performed in an NMR tube in deuterated 1,4-dioxane under optimized conditions. The mixture composition throughout the reaction was determined by 1H-NMR. From the obtained results the plot of the reaction selectivity (products ratio) over time was obtained.

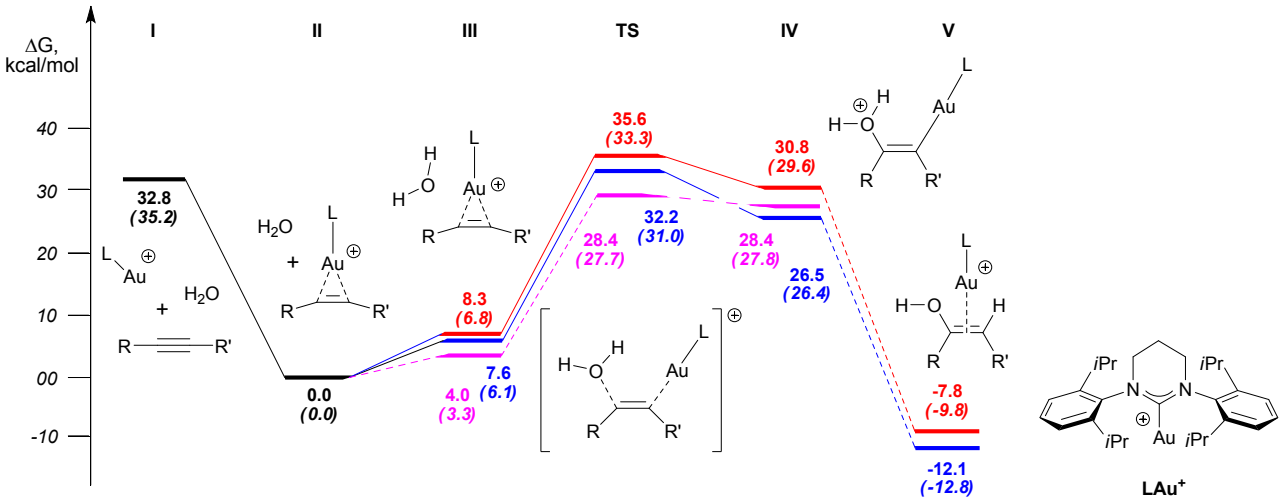


Computational details

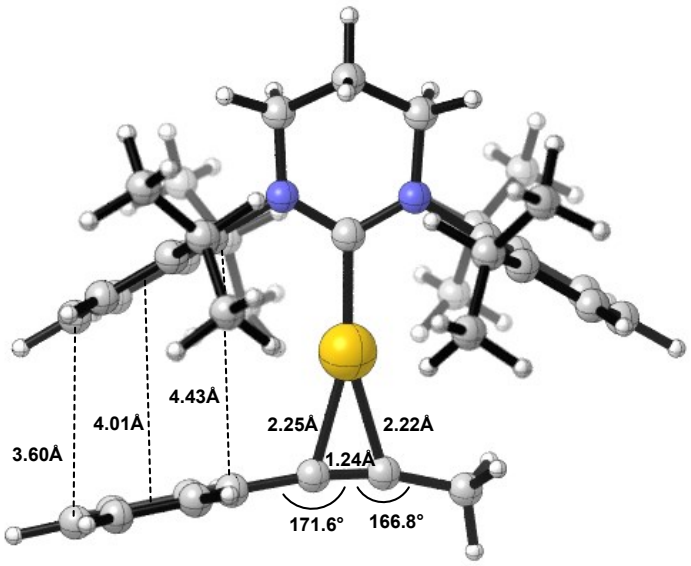
All DFT calculations were performed with the Orca 4.2.1 package.[16] Geometry optimizations were performed at the ωB97X-D3[17] level of theory. Gold was described with a def2-SVP basis set[18] in combination with Stuttgart-Dresden (SDD) pseudopotentials,[18] while all other atoms were described with a def2-SVP basis set. Analytical frequency calculations were performed at the same level of theory to characterize all stationary points as either intermediates (no imaginary frequencies) or transition states (exactly one imaginary frequency). The electronic energy was refined through single point calculations at the ωB97X-D3 level of theory. Gold was described with a def2-TZVPP basis set[18] in combination with SDD pseudopotentials and all other atoms were described with a def2-TZVPP basis set. For representative structures, solvent effects were taken into consideration in the single point calculations through the use of the CPCM solvation model for 1,4-dioxane (ε = 2.25) and water (ε = 80.4) as implemented in Orca.[19] For all calculations the RIJCOSX approximation was employed in combination with def2/J auxiliary basis sets.[20] A larger DFT integration (Grid6) and auxiliary (GridX6) grids and very tight convergence thresholds (VeryTightSCF) were used. The optimized structures were visualized with the CYLview software.[21]



Results summary for water dimer anti-attack (red – Markovnikov, blue – anti-Markovnikov)



Results summary for water syn-attack (red – Markovnikov, blue – anti-Markovnikov); magenta – anti-attack anti-Markovnikov



Selected structural parameters of the intermediate II

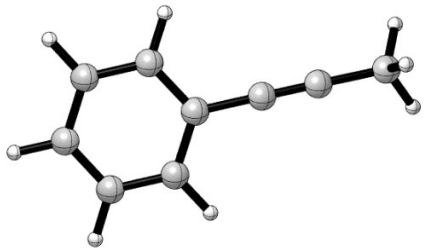
Cartesian coordinates and energies of the optimized structures

Intermediate I-alkyne

E(ωB97X-D3/def2-TZVPP) = –347.736641 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –347.734228 E_h

Lowest frequency = 38.65 cm–1



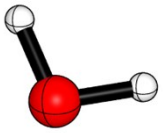
C	-7.423599	-2.446577	1.208146
C	-6.326903	-3.306008	1.277132
C	-7.233560	-1.067983	1.177749
C	-5.035905	-2.779016	1.314317
C	-4.839628	-1.401126	1.284247
C	-5.937557	-0.528440	1.215528
C	-5.741001	0.898147	1.183605
C	-5.584594	2.098602	1.155427
C	-5.397197	3.547098	1.119584
H	-6.270876	4.066517	1.540432
H	-5.259223	3.900490	0.086578
H	-4.512617	3.844300	1.702286
H	-3.829884	-0.985473	1.314050
H	-6.478112	-4.388281	1.301411
H	-4.172780	-3.447511	1.367924
H	-8.437460	-2.853820	1.177176
H	-8.090005	-0.391967	1.123166

Intermediate I-water

E(ωB97X-D3/def2-TZVPP) = –76.442666 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –76.445866 E_h

Lowest frequency = 1645.16 cm–1



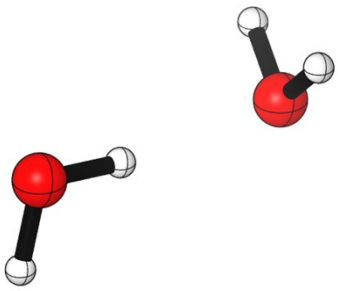
O	-8.275200	-3.447308	-1.335146
H	-7.314830	-3.418811	-1.293169
H	-8.547499	-2.929231	-0.572014

Intermediate I-water-dimer

E(ωB97X-D3/def2-TZVPP) = – -152.893897 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = -152.9008728 E_h

Lowest frequency = 64.43 cm–1



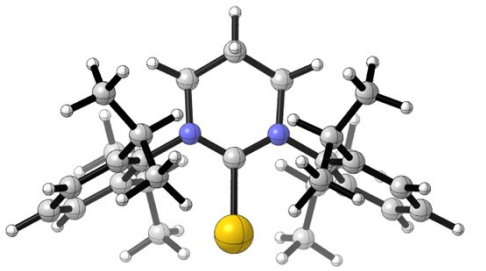
O	0.172365	-0.195997	0.164291
H	1.132474	-0.242987	0.036113
H	-0.098269	-1.117957	0.154687
O	3.015896	0.017087	-0.084190
H	3.118725	0.583212	0.688752
H	3.084829	0.625282	-0.828333

Intermediate I-6-DippAu

E(ωB97X-D3/def2-TZVPP) = –1336.324364 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1336.353664 E_h

Lowest frequency = 19.17 cm–1



C	-1.253004	2.969730	-2.887150
C	-2.265908	1.955833	-2.391609
H	-1.324266	3.068769	-3.978957
C	0.145336	2.532418	-2.495982
H	-1.471857	3.960474	-2.456503
H	0.470598	1.652712	-3.077473
N	0.199186	2.200488	-1.064433
H	0.881249	3.328332	-2.674287
C	-0.870214	1.809102	-0.380214
C	1.495784	2.290693	-0.434721
H	-2.190876	1.006864	-2.950371
H	-3.294553	2.323642	-2.508824
N	-2.058007	1.682230	-0.962666
C	-3.204168	1.228785	-0.209648
C	2.319773	1.149947	-0.416481
C	1.899023	3.532430	0.092740
C	3.591044	1.285615	0.149790
C	3.180978	3.611865	0.643195
C	4.020901	2.502847	0.666674
C	-4.031713	2.191710	0.397722
C	-3.462135	-0.152676	-0.139863
C	-4.584997	-0.560815	0.586926
C	-5.140673	1.727962	1.110667
C	-5.414853	0.367494	1.206095
C	1.874956	-0.200906	-0.962145
C	0.986095	4.751198	0.109928
H	3.530751	4.558621	1.063050

H	5.020896	2.587220	1.097831
H	4.260232	0.421899	0.184533
H	0.848308	-0.092401	-1.348893
C	1.825739	-1.256903	0.148580
C	2.756477	-0.655529	-2.131140
C	1.569535	5.920731	-0.691195
H	0.034885	4.469336	-0.369113
C	0.651416	5.163100	1.548794
H	2.518525	6.276227	-0.260780
H	0.870428	6.770772	-0.695439
H	1.766625	5.638662	-1.736805
H	0.205272	4.325959	2.109922
H	-0.067575	5.996538	1.559172
H	1.548307	5.487813	2.098323
H	2.768223	0.090131	-2.940831
H	2.389584	-1.606519	-2.546019
H	3.798336	-0.814207	-1.812898
H	1.185821	-0.930462	0.984308
H	2.826343	-1.461426	0.559661
H	1.422621	-2.207098	-0.232910
H	-4.817583	-1.625913	0.667668
H	-6.288869	0.027513	1.766578
C	-3.751865	3.686550	0.315118
H	-5.806214	2.443568	1.599872
C	-2.577814	-1.190175	-0.818992
C	-3.389888	4.258586	1.691110
C	-4.922699	4.447781	-0.318815
H	-2.875512	3.832811	-0.335805
C	-1.948058	-2.149841	0.196040
H	-1.747706	-0.659169	-1.311843
C	-3.349776	-1.947262	-1.907039
H	-4.159021	-2.555346	-1.473771
H	-2.682979	-2.627912	-2.458109
H	-3.808935	-1.257415	-2.631489
H	-1.355013	-1.605515	0.948407

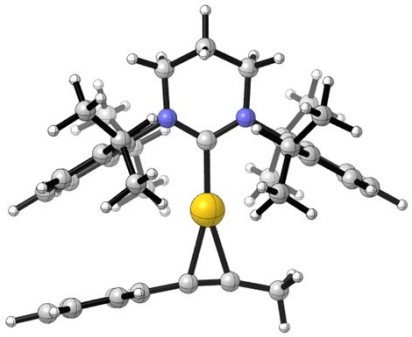
H	-1.280189	-2.864032	-0.309057
H	-2.711036	-2.733665	0.733464
H	-5.824814	4.399802	0.310355
H	-5.185050	4.039073	-1.306618
H	-4.668138	5.510631	-0.446941
H	-2.499477	3.762548	2.110766
H	-4.212768	4.128243	2.410882
H	-3.173291	5.335486	1.622793
Au	-0.686659	1.395896	1.593703

Intermediate II

E(ωB97X-D3/def2-TZVPP) = –1684.142979 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1684.166014 E_h

Lowest frequency = 13.59 cm–1



C	-1.294090	2.893055	-2.943459
C	-2.262621	1.890861	-2.341052
H	-1.408362	2.920047	-4.035886
C	0.130897	2.518665	-2.578253
H	-1.523552	3.904172	-2.568839
H	0.459960	1.618473	-3.126571
N	0.239844	2.273638	-1.136885
H	0.833944	3.324591	-2.832358
C	-0.790240	1.912541	-0.368734
C	1.551419	2.399550	-0.549855
H	-2.182261	0.908131	-2.838301
H	-3.303579	2.225882	-2.451171
N	-1.994915	1.729060	-0.909100
C	-3.092169	1.319011	-0.066137

C	2.389751	1.268938	-0.521820
C	1.950979	3.649496	-0.037885
C	3.665920	1.421141	0.029837
C	3.237344	3.747569	0.501233
C	4.089270	2.647637	0.530824
C	-3.936200	2.311557	0.466741
C	-3.280781	-0.050797	0.197179
C	-4.356864	-0.410797	1.013571
C	-4.994631	1.897424	1.278832
C	-5.207396	0.550013	1.546870
C	1.949513	-0.093145	-1.041855
C	1.033036	4.864648	-0.032748
H	3.582837	4.704605	0.901401
H	5.094043	2.747740	0.947967
H	4.344007	0.564049	0.063887
H	0.913929	0.001427	-1.405171
C	1.933306	-1.134926	0.082771
C	2.810544	-0.550264	-2.225224
C	1.598637	6.008489	-0.882681
H	0.073662	4.563506	-0.482203
C	0.729225	5.322047	1.399564
H	2.556930	6.376341	-0.483948
H	0.899578	6.858472	-0.899550
H	1.773938	5.692536	-1.922395
H	0.290223	4.504335	1.994067
H	0.013107	6.157968	1.398127
H	1.638199	5.664511	1.918755
H	2.793643	0.186366	-3.043184
H	2.446583	-1.510295	-2.621781
H	3.861865	-0.691879	-1.930089
H	1.302453	-0.804214	0.923143
H	2.944908	-1.324379	0.474809
H	1.535493	-2.094693	-0.280635
H	-4.531820	-1.466286	1.238050
H	-6.041222	0.245931	2.183742

C	-3.711773	3.796312	0.218729
H	-5.664473	2.643371	1.714187
C	-2.368103	-1.134645	-0.359426
C	-3.283869	4.506421	1.509082
C	-4.940643	4.461819	-0.410379
H	-2.879291	3.898838	-0.494633
C	-1.726299	-1.959013	0.762063
H	-1.547846	-0.642300	-0.905820
C	-3.117357	-2.028528	-1.354430
H	-3.923538	-2.590093	-0.856610
H	-2.436258	-2.761753	-1.813040
H	-3.576402	-1.436960	-2.161133
H	-1.170815	-1.316003	1.463454
H	-1.022687	-2.695991	0.346832
H	-2.480022	-2.513963	1.342254
H	-5.803534	4.447421	0.273594
H	-5.244806	3.953502	-1.338319
H	-4.729953	5.514693	-0.651635
H	-2.377951	4.045066	1.934608
H	-4.075638	4.458222	2.273712
H	-3.067013	5.568704	1.318459
Au	-0.512489	1.639502	1.644584
C	-0.805979	1.265312	3.841134
C	0.400380	1.470269	3.662005
C	-2.172113	1.019765	4.257780
C	-2.654352	-0.293324	4.360934
C	-3.007220	2.101787	4.573578
C	-3.957441	-0.516871	4.794313
H	-2.002584	-1.131692	4.106436
C	-4.308389	1.867446	5.005393
H	-2.625872	3.121493	4.486164
C	-4.782469	0.560141	5.119199
H	-4.330214	-1.539933	4.882491
H	-4.953773	2.710136	5.262778
H	-5.802794	0.379876	5.466006

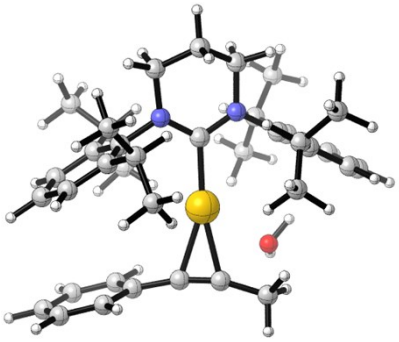
C	1.851991	1.672349	3.783380
H	2.134369	2.675216	3.432768
H	2.148464	1.565343	4.836496
H	2.400717	0.937492	3.177948

Intermediate syn III-aM

E(ωB97X-D3/def2-TZVPP) = –1760.593591 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.617391 E_h

Lowest frequency = 5.13 cm–1



C	-0.717159	3.014225	-2.866051
C	-1.722358	2.115671	-2.173497
H	-0.896711	3.020439	-3.949967
C	0.684112	2.517440	-2.569757
H	-0.831070	4.051700	-2.511357
H	0.877142	1.555234	-3.075243
N	0.867237	2.356185	-1.123292
H	1.444421	3.228056	-2.923294
C	-0.135282	2.101471	-0.275675
C	2.217479	2.456432	-0.636042
H	-1.765035	1.123194	-2.655419
H	-2.735158	2.540191	-2.216887
N	-1.372138	1.954959	-0.758371
C	-2.447764	1.597922	0.134728
C	3.022999	1.301954	-0.643526
C	2.698150	3.712688	-0.219281
C	4.343938	1.432073	-0.197378
C	4.016591	3.783048	0.241982
C	4.833506	2.656880	0.251245

C	-3.191815	2.623747	0.748471
C	-2.722363	0.234342	0.344346
C	-3.767896	-0.088872	1.214453
C	-4.229924	2.245927	1.603236
C	-4.515242	0.904487	1.836060
C	2.512937	-0.046611	-1.136485
C	1.848537	4.975045	-0.288878
H	4.419822	4.740595	0.581785
H	5.866790	2.736840	0.597095
H	5.004978	0.560766	-0.209704
H	1.428401	0.048243	-1.302711
C	2.703127	-1.156253	-0.096889
C	3.160514	-0.417773	-2.477533
C	2.474369	6.014099	-1.227787
H	0.870888	4.696682	-0.711831
C	1.578777	5.564318	1.099391
H	3.443645	6.374373	-0.849366
H	1.813999	6.888854	-1.327471
H	2.646066	5.601692	-2.233781
H	1.047982	4.841013	1.737745
H	0.950153	6.464537	1.023879
H	2.512440	5.852197	1.608316
H	3.007783	0.366177	-3.235320
H	2.736793	-1.356145	-2.866910
H	4.247152	-0.561804	-2.370347
H	2.251347	-0.879543	0.866418
H	3.769944	-1.374144	0.074058
H	2.234108	-2.089588	-0.442940
H	-4.002588	-1.138351	1.409211
H	-5.327948	0.629052	2.512042
C	-2.899099	4.099519	0.514448
H	-4.825411	3.016185	2.100640
C	-1.918090	-0.873950	-0.323376
C	-2.543778	4.820213	1.820730
C	-4.060647	4.790838	-0.209173

H	-2.015351	4.167496	-0.139509
C	-1.028005	-1.604384	0.688545
H	-1.243681	-0.405391	-1.057134
C	-2.818682	-1.846951	-1.094311
H	-3.460699	-2.433604	-0.418778
H	-2.211603	-2.562895	-1.669238
H	-3.476366	-1.314968	-1.798422
H	-0.327166	-0.909313	1.178564
H	-0.435179	-2.387689	0.191633
H	-1.628648	-2.087233	1.475559
H	-4.977996	4.775429	0.399915
H	-4.293428	4.299345	-1.166402
H	-3.817102	5.843746	-0.418027
H	-1.720135	4.310535	2.345305
H	-3.403414	4.864717	2.508052
H	-2.230248	5.856134	1.619679
Au	0.140123	2.050952	1.771060
C	-0.311090	1.792746	3.966857
C	0.714612	2.478665	3.903772
C	-1.487104	1.027152	4.325990
C	-1.486174	-0.369658	4.197454
C	-2.606324	1.680328	4.862093
C	-2.590797	-1.104292	4.615324
H	-0.608676	-0.870350	3.782070
C	-3.705520	0.936490	5.280907
H	-2.602478	2.768458	4.956602
C	-3.698141	-0.453324	5.161177
H	-2.582951	-2.193235	4.526786
H	-4.573151	1.445085	5.707472
H	-4.560144	-1.034201	5.498442
C	1.938122	3.226147	4.223023
H	2.024275	4.140675	3.622786
H	1.921258	3.498245	5.288024
H	2.801642	2.578971	4.017914
H	3.424156	1.021056	1.909066

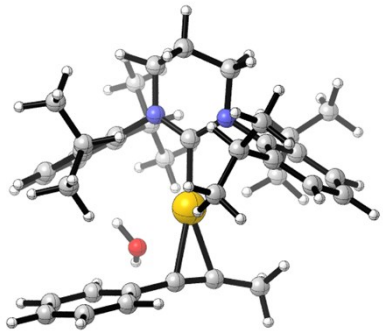
H	3.372806	-0.080991	2.962634
O	2.938213	0.734937	2.694302

Intermediate syn-III-M

E(ωB97X-D3/def2-TZVPP) = –1760.593680 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.617448 E_h

Lowest frequency = 15.01 cm–1



C	-1.365263	3.183105	-2.739758
C	-2.223108	1.990328	-2.365308
H	-1.452666	3.392299	-3.814750
C	0.077898	2.884794	-2.381966
H	-1.714259	4.078262	-2.199234
H	0.510763	2.131607	-3.063595
N	0.168877	2.397664	-1.000613
H	0.706035	3.783929	-2.458215
C	-0.848521	1.846604	-0.329155
C	1.463043	2.501123	-0.371005
H	-1.975723	1.119072	-2.996666
H	-3.292936	2.196941	-2.501834
N	-2.010787	1.645566	-0.955818
C	-3.110541	1.028006	-0.260084
C	2.347245	1.410975	-0.471642
C	1.798780	3.687057	0.308762
C	3.592486	1.525780	0.154602
C	3.055402	3.750228	0.917725
C	3.944017	2.681836	0.843596
C	-3.965585	1.833325	0.518921
C	-3.310483	-0.356364	-0.419372

C	-4.410851	-0.931092	0.228862
C	-5.030086	1.203382	1.171444
C	-5.255972	-0.161569	1.024288
C	1.981751	0.124202	-1.199717
C	0.841740	4.866536	0.416769
H	3.346981	4.653347	1.460219
H	4.923127	2.753212	1.323199
H	4.301841	0.695680	0.100137
H	1.030580	0.293487	-1.729380
C	1.742245	-1.018415	-0.205658
C	3.028005	-0.255525	-2.252734
C	1.448309	6.142626	-0.177806
H	-0.058192	4.624294	-0.170375
C	0.384346	5.080215	1.865249
H	2.325669	6.480614	0.395499
H	0.712863	6.961476	-0.166451
H	1.772538	5.989945	-1.218702
H	-0.092815	4.173652	2.270212
H	-0.344858	5.902614	1.926440
H	1.232045	5.332472	2.521454
H	3.205542	0.567804	-2.960961
H	2.696034	-1.133789	-2.826672
H	3.994787	-0.515235	-1.794292
H	0.925719	-0.775538	0.493949
H	2.647175	-1.226754	0.387255
H	1.468587	-1.944953	-0.733087
H	-4.612180	-1.999166	0.107612
H	-6.106364	-0.630682	1.525052
C	-3.798058	3.345157	0.606877
H	-5.704654	1.793833	1.795414
C	-2.392369	-1.222470	-1.273179
C	-3.976832	3.888749	2.024781
C	-4.749968	4.043129	-0.375021
H	-2.767678	3.587022	0.302347
C	-1.867837	-2.441119	-0.506112

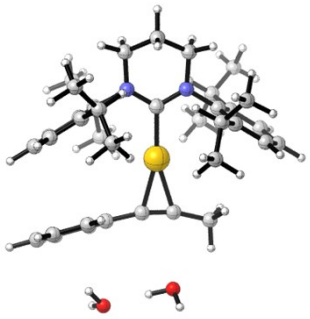
H	-1.512759	-0.614806	-1.538428
C	-3.086949	-1.637957	-2.576703
H	-3.951771	-2.290007	-2.377104
H	-2.393130	-2.193868	-3.225667
H	-3.457547	-0.767437	-3.138964
H	-1.372606	-2.137858	0.427472
H	-1.144330	-2.999009	-1.119684
H	-2.678865	-3.141766	-0.249972
H	-5.801401	3.855482	-0.105920
H	-4.610516	3.692535	-1.409080
H	-4.589404	5.131983	-0.363646
H	-3.294202	3.398804	2.734092
H	-5.003974	3.751977	2.396382
H	-3.770747	4.969277	2.042667
Au	-0.575939	1.420715	1.667106
C	-0.641762	1.402702	3.942921
C	0.458274	0.960397	3.602881
C	-1.828924	1.963187	4.553780
C	-3.025955	1.232551	4.597719
C	-1.768533	3.253560	5.101982
C	-4.150497	1.796705	5.192071
H	-3.049469	0.237716	4.148687
C	-2.900901	3.807254	5.691492
H	-0.831901	3.814295	5.060679
C	-4.091130	3.080320	5.736511
H	-5.083129	1.228863	5.232059
H	-2.854657	4.810252	6.121101
H	-4.977855	3.517228	6.201926
C	1.814709	0.400428	3.531862
H	2.468578	1.032728	2.913642
H	2.232748	0.337280	4.546725
H	1.792693	-0.607617	3.095104
H	-2.872076	-1.080402	1.987521
H	-2.203915	-2.087170	2.917602
O	-2.148743	-1.172131	2.622758

Intermediate anti-III-aM

E(ωB97X-D3/def2-TZVPP) = –1837.049888 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1837.076734 E_h

Lowest frequency = 8.46 cm–1



C	-0.533896	3.046944	-3.091688
C	-1.727393	2.451275	-2.365428
H	-0.737897	3.109385	-4.169423
C	0.698169	2.194877	-2.846410
H	-0.358274	4.074362	-2.733708
H	0.637444	1.242474	-3.401132
N	0.850326	1.912026	-1.416138
H	1.610828	2.706052	-3.184184
C	-0.156065	1.952033	-0.540176
C	2.168536	1.559989	-0.946096
H	-2.036586	1.495353	-2.823697
H	-2.595618	3.123640	-2.401790
N	-1.393676	2.224952	-0.956433
C	-2.453998	2.328341	0.016999
C	2.563784	0.211225	-1.007122
C	3.006782	2.570041	-0.433790
C	3.839713	-0.115283	-0.537106
C	4.273830	2.190364	0.018547
C	4.688923	0.863339	-0.032300
C	-2.769920	3.604760	0.520190
C	-3.124718	1.165440	0.436467
C	-4.133318	1.310856	1.394870
C	-3.792053	3.696829	1.467307

C	-4.467981	2.561089	1.901387
C	1.649688	-0.882158	-1.542014
C	2.582862	4.030407	-0.352962
H	4.951936	2.948475	0.418864
H	5.685033	0.589979	0.323602
H	4.176683	-1.154826	-0.566892
H	0.707290	-0.409826	-1.859557
C	1.290267	-1.892571	-0.447798
C	2.258229	-1.568179	-2.770591
C	3.410920	4.905705	-1.302047
H	1.531371	4.094982	-0.674091
C	2.644708	4.556096	1.085423
H	4.470014	4.933669	-1.001572
H	3.038092	5.941375	-1.299184
H	3.373202	4.533502	-2.337121
H	2.032184	3.941537	1.764614
H	2.272181	5.590280	1.136217
H	3.674915	4.558942	1.473984
H	2.514103	-0.838371	-3.553810
H	1.555448	-2.299180	-3.198487
H	3.181148	-2.110794	-2.513102
H	0.829956	-1.394927	0.420852
H	2.180106	-2.434584	-0.091271
H	0.578086	-2.639629	-0.830359
H	-4.671388	0.428328	1.749893
H	-5.263723	2.651370	2.644698
C	-2.017569	4.853264	0.083370
H	-4.062131	4.673668	1.877699
C	-2.799534	-0.213520	-0.118611
C	-1.209157	5.442840	1.243972
C	-2.949980	5.890504	-0.550097
H	-1.290190	4.552970	-0.685154
C	-2.454429	-1.208799	0.993508
H	-1.903334	-0.118546	-0.752021
C	-3.942071	-0.726552	-1.003601

H	-4.870198	-0.850150	-0.423666
H	-3.689710	-1.704507	-1.441130
H	-4.159415	-0.029740	-1.827467
H	-1.631962	-0.830725	1.621594
H	-2.141735	-2.174300	0.568122
H	-3.315715	-1.401881	1.651669
H	-3.670908	6.290324	0.179811
H	-3.527919	5.458332	-1.381173
H	-2.372662	6.741202	-0.942853
H	-0.519248	4.695071	1.666346
H	-1.866241	5.793182	2.055337
H	-0.611035	6.303021	0.906038
Au	0.201952	1.565833	1.445250
C	0.013542	1.236359	3.630354
C	1.207361	1.054345	3.366259
C	-1.302581	1.373177	4.220733
C	-2.032623	0.228059	4.569044
C	-1.831499	2.644880	4.481930
C	-3.275296	0.357412	5.183878
H	-1.613563	-0.759768	4.365309
C	-3.071094	2.765904	5.105709
H	-1.262925	3.533508	4.199554
C	-3.793961	1.624437	5.458050
H	-3.840707	-0.536734	5.457020
H	-3.478628	3.758437	5.311967
H	-4.766150	1.722900	5.946778
O	1.785078	1.291393	6.311962
C	2.648833	0.795194	3.401121
H	2.897679	-0.125083	2.854741
H	2.904657	0.700366	4.467769
H	3.208876	1.626763	2.951651
H	0.900729	1.180514	6.704185
H	2.227485	1.885474	6.924931
O	-0.764767	1.269027	7.489341
H	-1.371085	1.852743	7.017967

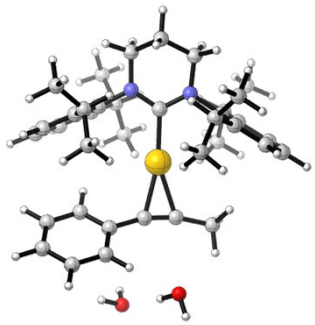
H	-1.264251	0.454797	7.609418

Intermediate anti-III-M

E(ωB97X-D3/def2-TZVPP) = –1837.050822 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1837.076924 E_h

Lowest frequency = 7.51 cm–1



C	-0.877085	3.018442	-3.019079
C	-1.783733	1.949118	-2.440186
H	-1.050066	3.115643	-4.099705
C	0.571611	2.656322	-2.751999
H	-1.110692	3.994144	-2.562044
H	0.884586	1.790395	-3.361569
N	0.760182	2.342374	-1.332645
H	1.246582	3.487081	-3.001424
C	-0.213294	1.886661	-0.540401
C	2.095616	2.489687	-0.807767
H	-1.706612	1.008587	-3.013645
H	-2.837664	2.260124	-2.468494
N	-1.434067	1.688509	-1.039591
C	-2.472871	1.120653	-0.217040
C	2.959092	1.377804	-0.831321
C	2.492898	3.745507	-0.309758
C	4.260674	1.558910	-0.353158
C	3.803792	3.871610	0.159821
C	4.682560	2.792793	0.130953
C	-3.370924	1.986213	0.435601
C	-2.582229	-0.281102	-0.139269
C	-3.638829	-0.808480	0.610758

C	-4.415337	1.407292	1.162179
C	-4.553530	0.025667	1.244719
C	2.521045	0.010416	-1.339958
C	1.540351	4.931072	-0.235965
H	4.146097	4.832850	0.552209
H	5.706547	2.914386	0.491991
H	4.959972	0.718574	-0.361786
H	1.448360	0.069054	-1.582042
C	2.671144	-1.062876	-0.256468
C	3.259009	-0.374993	-2.627730
C	2.057122	6.136983	-1.028609
H	0.586088	4.622564	-0.691127
C	1.239547	5.299746	1.222381
H	2.993239	6.532515	-0.604580
H	1.318571	6.953046	-1.011598
H	2.253315	5.878681	-2.080560
H	0.840925	4.436794	1.779395
H	0.494621	6.108527	1.273892
H	2.144514	5.644076	1.746893
H	3.125855	0.387060	-3.411126
H	2.883120	-1.333563	-3.017162
H	4.341031	-0.486800	-2.456145
H	2.108442	-0.792225	0.651034
H	3.724127	-1.210389	0.029513
H	2.287340	-2.030845	-0.612180
H	-3.756940	-1.892561	0.688757
H	-5.384486	-0.407450	1.807510
C	-3.224354	3.501312	0.394229
H	-5.134812	2.050426	1.674931
C	-1.612945	-1.219788	-0.844854
C	-2.815224	4.048982	1.768328
C	-4.492451	4.186069	-0.129988
H	-2.407746	3.739882	-0.305069
C	-0.911672	-2.157071	0.143454
H	-0.827853	-0.604803	-1.311180

C	-2.311000	-2.001557	-1.964743
H	-3.069682	-2.689386	-1.559590
H	-1.584140	-2.604329	-2.531009
H	-2.820914	-1.328973	-2.671537
H	-0.380859	-1.591008	0.925474
H	-0.177366	-2.788094	-0.379950
H	-1.624788	-2.831593	0.642319
H	-5.340395	4.056946	0.560479
H	-4.796971	3.783169	-1.108231
H	-4.327924	5.267999	-0.244832
H	-1.861912	3.614112	2.108356
H	-3.571444	3.818504	2.535550
H	-2.692853	5.142173	1.732204
Au	0.204131	1.573726	1.447865
C	0.158197	1.427364	3.661109
C	1.356653	1.389345	3.354346
C	-1.098614	1.602896	4.363178
C	-2.274339	0.963983	3.949877
C	-1.113767	2.460939	5.476060
C	-3.459016	1.180264	4.649933
H	-2.263659	0.307039	3.075243
C	-2.305287	2.672831	6.163363
H	-0.175375	2.917086	5.801492
C	-3.478631	2.036223	5.750560
H	-4.374428	0.679981	4.326486
H	-2.320940	3.342911	7.026466
H	-4.411737	2.208857	6.292456
C	2.820330	1.333037	3.316786
H	3.172244	0.366575	2.930131
H	3.144670	1.468731	4.360900
H	3.233268	2.135036	2.687993
H	1.470731	1.222756	6.550074
H	2.425311	2.291667	7.086769
O	2.019953	1.980667	6.272123
O	0.207634	-0.016236	7.012796

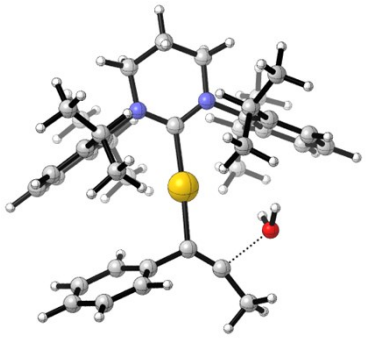
H	0.089593	-0.772459	6.428274
H	-0.660533	0.403673	7.038224

Intermediate syn-TS-aM

E(ωB97X-D3/def2-TZVPP) = –1760.554803 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.579141 E_h

Lowest frequency = –161.52 cm–1



C	-0.799696	2.988089	-2.993733
C	-1.767255	2.002274	-2.367533
H	-0.968647	3.046329	-4.077730
C	0.626262	2.557261	-2.706827
H	-0.974208	3.996084	-2.583175
H	0.882583	1.636183	-3.259875
N	0.798941	2.328132	-1.269699
H	1.346704	3.328726	-3.012944
C	-0.194839	1.940942	-0.460155
C	2.128956	2.488675	-0.742697
H	-1.764661	1.041832	-2.912237
H	-2.797200	2.386005	-2.393502
N	-1.418126	1.762069	-0.964133
C	-2.475308	1.269757	-0.111824
C	2.983923	1.370312	-0.697665
C	2.540907	3.765221	-0.312102
C	4.285088	1.562297	-0.218377
C	3.849596	3.902474	0.166464
C	4.718564	2.815066	0.204685
C	-3.286279	2.193416	0.575019
C	-2.671221	-0.120588	-0.013645

C	-3.718440	-0.574804	0.793843
C	-4.314947	1.686348	1.373243
C	-4.535101	0.317831	1.478287
C	2.538235	-0.020360	-1.128340
C	1.606668	4.966858	-0.314375
H	4.200163	4.882012	0.502513
H	5.739887	2.944246	0.569708
H	4.975629	0.715847	-0.179326
H	1.469036	0.033021	-1.384825
C	2.670199	-1.025109	0.021577
C	3.291118	-0.485119	-2.380818
C	2.179299	6.145713	-1.108035
H	0.671064	4.660321	-0.806204
C	1.244132	5.373652	1.119234
H	3.097383	6.543095	-0.648256
H	1.451251	6.969798	-1.146588
H	2.423022	5.859431	-2.142364
H	0.793931	4.530887	1.668307
H	0.517806	6.200215	1.119191
H	2.131742	5.711757	1.677715
H	3.167197	0.227623	-3.210345
H	2.919981	-1.465362	-2.715889
H	4.370937	-0.586359	-2.190914
H	2.083489	-0.705100	0.898481
H	3.717938	-1.155187	0.334580
H	2.293768	-2.014067	-0.278278
H	-3.897673	-1.649029	0.887792
H	-5.350319	-0.055530	2.102487
C	-3.070154	3.698397	0.500365
H	-4.955784	2.376015	1.928170
C	-1.780252	-1.129061	-0.725249
C	-2.674049	4.260877	1.871046
C	-4.298411	4.419858	-0.068054
H	-2.229479	3.886504	-0.186176
C	-0.969373	-1.953160	0.281534

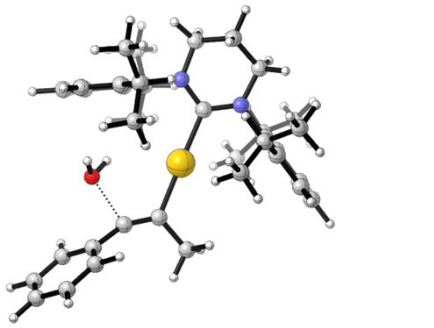
H	-1.055852	-0.566517	-1.334903
C	-2.582758	-2.026199	-1.674936
H	-3.284319	-2.672395	-1.125055
H	-1.912629	-2.684154	-2.249053
H	-3.172280	-1.433026	-2.390222
H	-0.365813	-1.302597	0.934170
H	-0.287642	-2.643017	-0.239010
H	-1.623269	-2.560601	0.926580
H	-5.166599	4.328907	0.602969
H	-4.592982	4.011668	-1.046949
H	-4.093185	5.493518	-0.195252
H	-1.752754	3.787860	2.245820
H	-3.459576	4.080621	2.621385
H	-2.503570	5.346871	1.815339
Au	0.118105	1.712966	1.559291
C	0.286971	1.633186	3.642677
C	1.378901	1.776172	4.284307
C	-1.039576	1.541588	4.335967
C	-1.870664	0.437172	4.113697
C	-1.470208	2.571743	5.180580
C	-3.102331	0.352904	4.757152
H	-1.552619	-0.354974	3.431253
C	-2.715124	2.490932	5.803165
H	-0.837595	3.450075	5.332805
C	-3.530486	1.378893	5.599405
H	-3.737990	-0.519071	4.587535
H	-3.046538	3.302758	6.455036
H	-4.501977	1.313905	6.094503
C	2.255166	1.891302	5.436915
H	2.781052	2.854202	5.473127
H	1.571623	1.831602	6.302821
H	2.978120	1.068053	5.500210
H	2.991722	2.708310	2.384627
H	2.948219	1.193239	2.269877
O	3.030230	1.902731	2.923697

Intermediate syn-TS-M

E(ωB97X-D3/def2-TZVPP) = –1760.551570 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.574215 E_h

Lowest frequency = –198.96 cm–1



C	-1.065794	2.993191	-3.240127
C	-2.013650	1.889826	-2.807872
H	-1.077469	3.097294	-4.333859
C	0.338299	2.671861	-2.762593
H	-1.398558	3.956175	-2.819025
H	0.779087	1.846380	-3.349045
N	0.329057	2.302492	-1.343110
H	1.006844	3.537107	-2.876644
C	-0.741503	1.839911	-0.691135
C	1.582567	2.432959	-0.639909
H	-1.804533	0.952068	-3.353105
H	-3.060200	2.155594	-3.012291
N	-1.882701	1.652959	-1.366975
C	-3.055064	1.176234	-0.681389
C	2.466389	1.338443	-0.629207
C	1.883810	3.650508	-0.000936
C	3.676122	1.485880	0.055781
C	3.107093	3.746616	0.668304
C	3.995759	2.676949	0.697553
C	-3.951639	2.116075	-0.135676
C	-3.288467	-0.210825	-0.609239
C	-4.460069	-0.644438	0.023241
C	-5.110116	1.631368	0.483403
C	-5.367926	0.264855	0.556409

C	2.130260	0.008572	-1.289262
C	0.926578	4.834136	0.003598
H	3.370819	4.677129	1.178089
H	4.946907	2.772188	1.226499
H	4.380925	0.650795	0.090473
H	1.179479	0.131079	-1.832060
C	1.904787	-1.077353	-0.230669
C	3.191282	-0.408291	-2.312925
C	1.534671	6.056244	-0.694291
H	0.028236	4.542432	-0.563151
C	0.465861	5.168068	1.427795
H	2.431403	6.419054	-0.168063
H	0.811095	6.885339	-0.724778
H	1.831508	5.825087	-1.728807
H	0.008455	4.289430	1.910685
H	-0.280284	5.977628	1.417100
H	1.306401	5.497865	2.058569
H	3.343251	0.368731	-3.077698
H	2.893585	-1.336779	-2.823454
H	4.164982	-0.597890	-1.835234
H	1.131618	-0.771636	0.492091
H	2.827552	-1.281804	0.334686
H	1.584450	-2.021454	-0.697743
H	-4.670293	-1.714839	0.094387
H	-6.281337	-0.094486	1.036221
C	-3.687952	3.614515	-0.179003
H	-5.831982	2.336226	0.905270
C	-2.323783	-1.230190	-1.197998
C	-3.462638	4.177315	1.229881
C	-4.799517	4.366951	-0.919102
H	-2.753900	3.771414	-0.738145
C	-1.826420	-2.220740	-0.141192
H	-1.440779	-0.683809	-1.563653
C	-2.958664	-1.953524	-2.392228
H	-3.819539	-2.563525	-2.076112

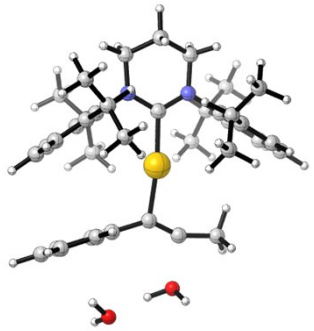
H	-2.233217	-2.627343	-2.872948
H	-3.320711	-1.241964	-3.149891
H	-1.340647	-1.701503	0.700458
H	-1.090105	-2.911497	-0.578730
H	-2.647039	-2.832875	0.264191
H	-5.759727	4.304958	-0.383670
H	-4.956901	3.963452	-1.930961
H	-4.545063	5.433273	-1.014480
H	-2.623458	3.668642	1.731884
H	-4.360602	4.065978	1.859138
H	-3.225997	5.251227	1.186428
Au	-0.653007	1.494595	1.344703
C	-1.597824	1.141843	4.164887
C	-0.564959	1.302756	3.415773
C	-2.322430	1.233598	5.398680
C	-2.954861	0.120423	5.982664
C	-2.324845	2.472001	6.066047
C	-3.568622	0.248590	7.220402
H	-2.962832	-0.831443	5.448634
C	-2.927226	2.586574	7.315155
H	-1.842767	3.333960	5.598618
C	-3.548615	1.477713	7.887962
H	-4.062793	-0.611920	7.676205
H	-2.918802	3.544544	7.839702
H	-4.027991	1.569794	8.865555
C	0.795609	1.502304	4.073043
H	1.224178	2.459861	3.743684
H	0.750823	1.489241	5.171974
H	1.481793	0.712901	3.735004
H	-3.760235	1.287209	2.692898
H	-2.855070	0.162699	2.190229
O	-3.212655	0.551175	3.004614

Intermediate anti-TS-aM

E(ωB97X-D3/def2-TZVPP) = –1837.026473 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = —1837.052539 E_h

Lowest frequency = –285.18 cm–1



C	-0.529494	2.972022	-3.148696
C	-1.738831	2.435942	-2.402057
H	-0.729114	2.993362	-4.228937
C	0.682432	2.103762	-2.861342
H	-0.329805	4.009342	-2.834248
H	0.593376	1.123635	-3.362126
N	0.833103	1.898794	-1.418008
H	1.605429	2.571193	-3.232763
C	-0.176614	1.982278	-0.546893
C	2.149775	1.579178	-0.924681
H	-2.078503	1.476269	-2.830671
H	-2.586407	3.133204	-2.461057
N	-1.410595	2.246012	-0.987577
C	-2.474305	2.369568	-0.019907
C	2.551301	0.231684	-0.898993
C	2.981709	2.621270	-0.471226
C	3.825954	-0.059812	-0.402424
C	4.248107	2.277546	0.010796
C	4.669117	0.951553	0.045146
C	-2.763335	3.647043	0.495503
C	-3.155358	1.215148	0.405217
C	-4.135850	1.367268	1.391135
C	-3.755214	3.746327	1.474121
C	-4.432018	2.616999	1.923122
C	1.646452	-0.897809	-1.370175
C	2.549074	4.080564	-0.485055

H	4.919973	3.062563	0.367159
H	5.665048	0.704846	0.420868
H	4.166515	-1.098031	-0.366024
H	0.705876	-0.450934	-1.727147
C	1.279698	-1.836035	-0.215945
C	2.272801	-1.658735	-2.544791
C	3.357728	4.890544	-1.506043
H	1.492859	4.114395	-0.793573
C	2.625136	4.706722	0.911552
H	4.422401	4.936718	-1.227985
H	2.984633	5.924424	-1.566050
H	3.301200	4.449412	-2.512804
H	2.051524	4.116920	1.644543
H	2.214871	5.727668	0.899185
H	3.663706	4.775638	1.270968
H	2.536151	-0.979684	-3.370093
H	1.578457	-2.419150	-2.933673
H	3.194596	-2.179504	-2.241782
H	0.800489	-1.284387	0.608466
H	2.169767	-2.341764	0.190513
H	0.581712	-2.615353	-0.558366
H	-4.676564	0.489661	1.754558
H	-5.199153	2.712112	2.695504
C	-2.013578	4.890135	0.039947
H	-3.997649	4.723719	1.900179
C	-2.857364	-0.164538	-0.163742
C	-1.205144	5.502861	1.188265
C	-2.953557	5.911867	-0.608136
H	-1.287376	4.578890	-0.725735
C	-2.471189	-1.160997	0.933074
H	-1.985623	-0.072018	-0.830869
C	-4.034371	-0.675249	-1.003077
H	-4.939531	-0.797104	-0.387337
H	-3.800670	-1.653904	-1.449599
H	-4.282010	0.021329	-1.818465

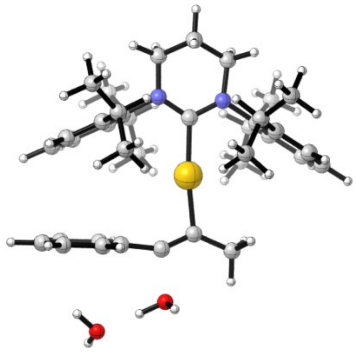
H	-1.613044	-0.789807	1.515119
H	-2.193885	-2.132180	0.495802
H	-3.301318	-1.338679	1.634558
H	-3.676406	6.316012	0.117699
H	-3.529905	5.462859	-1.431404
H	-2.383376	6.760994	-1.014735
H	-0.519321	4.760844	1.626633
H	-1.860852	5.872540	1.992094
H	-0.604469	6.353955	0.832133
Au	0.110261	1.678468	1.465982
C	0.140106	1.352202	3.544871
C	1.342246	1.130118	3.891765
C	-1.172585	1.416868	4.207191
C	-1.917457	0.247581	4.408273
C	-1.693248	2.645755	4.632920
C	-3.157132	0.305617	5.042166
H	-1.516952	-0.710183	4.067864
C	-2.929122	2.696831	5.277901
H	-1.124136	3.561990	4.458266
C	-3.664899	1.527928	5.486277
H	-3.730380	-0.612715	5.193218
H	-3.323892	3.659491	5.612392
H	-4.635183	1.571730	5.986510
O	1.425892	0.761513	5.884219
C	2.776218	0.935785	3.650979
H	2.958618	0.970142	2.566386
H	3.098786	-0.041004	4.034687
H	3.374243	1.726984	4.125460
H	0.557458	0.803951	6.362746
H	1.984444	1.398282	6.346685
O	-0.776617	1.003676	7.362445
H	-1.439762	1.597385	6.983448
H	-1.264191	0.197222	7.564124

Intermediate anti-TS-M

E(ωB97X-D3/def2-TZVPP) = –1837.021376 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1837.048261 E_h

Lowest frequency = –306.46 cm–1



C	-0.939319	3.034565	-3.018269
C	-1.831855	2.029422	-2.315846
H	-1.198848	3.092567	-4.084401
C	0.511992	2.626935	-2.851941
H	-1.096433	4.038164	-2.589715
H	0.737921	1.715313	-3.433210
N	0.806545	2.388586	-1.437472
H	1.192101	3.413403	-3.208845
C	-0.106943	1.993518	-0.542421
C	2.183744	2.529221	-1.032232
H	-1.845220	1.066292	-2.856453
H	-2.870737	2.386325	-2.267402
N	-1.369871	1.808060	-0.941842
C	-2.356122	1.325951	-0.007388
C	3.018853	1.396488	-1.058670
C	2.650049	3.797805	-0.637965
C	4.354455	1.564347	-0.680137
C	3.992591	3.911089	-0.265526
C	4.839094	2.807504	-0.288862
C	-3.132144	2.260491	0.703983
C	-2.540496	-0.062535	0.134307
C	-3.543325	-0.501352	1.003596
C	-4.112630	1.769546	1.570012
C	-4.325553	0.403293	1.711422

C	2.519287	0.020440	-1.478067
C	1.737066	5.014071	-0.562807
H	4.385399	4.881688	0.048529
H	5.887537	2.917859	-0.001578
H	5.029843	0.704842	-0.693369
H	1.427041	0.082829	-1.603463
C	2.778046	-1.029806	-0.392627
C	3.116786	-0.397316	-2.827895
C	2.278110	6.198675	-1.370541
H	0.766972	4.732272	-1.001206
C	1.469873	5.401976	0.896877
H	3.222283	6.581590	-0.952799
H	1.556923	7.030362	-1.362171
H	2.467757	5.922687	-2.419162
H	1.049350	4.553298	1.459781
H	0.756733	6.238874	0.955367
H	2.397020	5.713542	1.403641
H	2.909467	0.349820	-3.609518
H	2.700140	-1.361552	-3.158098
H	4.210578	-0.509858	-2.764511
H	2.341425	-0.719497	0.569712
H	3.854391	-1.200950	-0.236509
H	2.329075	-1.995027	-0.672268
H	-3.714428	-1.574249	1.126592
H	-5.109298	0.040682	2.380953
C	-2.934512	3.764055	0.571444
H	-4.728655	2.471538	2.138377
C	-1.684289	-1.087333	-0.596818
C	-2.437605	4.370683	1.889258
C	-4.207450	4.461637	0.075967
H	-2.148298	3.936293	-0.180026
C	-0.831597	-1.893013	0.391346
H	-0.986562	-0.538668	-1.248419
C	-2.529274	-2.001997	-1.492156
H	-3.202616	-2.640668	-0.898868

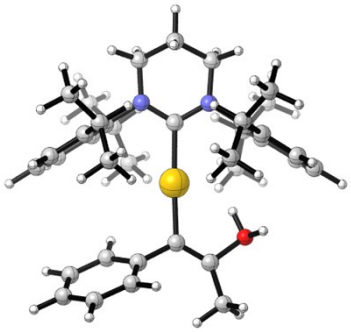
H	-1.885183	-2.668546	-2.086163
H	-3.153177	-1.422022	-2.189268
H	-0.206395	-1.228990	1.009419
H	-0.166736	-2.587807	-0.144430
H	-1.459623	-2.493616	1.068842
H	-5.023212	4.388893	0.812681
H	-4.571594	4.019526	-0.864336
H	-4.020089	5.531557	-0.102033
H	-1.497170	3.895967	2.211941
H	-3.177254	4.234708	2.694771
H	-2.256397	5.450923	1.779572
Au	0.489471	1.726351	1.416479
C	0.367572	1.397286	4.191168
C	1.311387	1.555957	3.331354
C	-1.048358	1.181632	4.470728
C	-1.593227	-0.105450	4.364340
C	-1.846722	2.238570	4.931264
C	-2.915236	-0.335181	4.737357
H	-0.967769	-0.920789	3.993879
C	-3.168079	2.005331	5.303687
H	-1.419867	3.241785	5.005675
C	-3.699526	0.715820	5.216482
H	-3.337333	-1.339421	4.652712
H	-3.786524	2.830833	5.663690
H	-4.735592	0.533786	5.512946
C	2.794657	1.670612	3.494632
H	3.303467	0.943302	2.845699
H	3.111280	1.503362	4.533656
H	3.131734	2.664678	3.163154
H	0.359776	0.945642	6.570774
H	1.274472	2.181600	6.257568
O	1.055883	1.293623	5.945993
O	-0.851962	0.477147	7.578577
H	-0.864455	-0.425532	7.915921
H	-1.739387	0.635699	7.229797

Intermediate syn-IV-aM

E(ωB97X-D3/def2-TZVPP) = –1760.565958 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.592076 E_h

Lowest frequency = 13.88 cm–1



C	-0.754790	2.978141	-3.074281
C	-1.736962	1.973306	-2.498048
H	-0.886306	3.052969	-4.162582
C	0.667900	2.559821	-2.746056
H	-0.954021	3.977523	-2.653355
H	0.955485	1.654786	-3.310127
N	0.789883	2.302569	-1.308968
H	1.386924	3.348049	-3.011059
C	-0.232030	1.899424	-0.541418
C	2.087579	2.468554	-0.707191
H	-1.704244	1.020509	-3.055109
H	-2.768803	2.348058	-2.558184
N	-1.434563	1.720903	-1.086730
C	-2.507070	1.251079	-0.239943
C	2.955127	1.358932	-0.638161
C	2.442960	3.729292	-0.187923
C	4.211957	1.546743	-0.051589
C	3.710601	3.864239	0.393368
C	4.592965	2.787626	0.452065
C	-3.294907	2.194241	0.447992
C	-2.712635	-0.135606	-0.112943
C	-3.744153	-0.565811	0.727176
C	-4.309489	1.710491	1.278335
C	-4.535628	0.345898	1.416566

C	2.560836	-0.019993	-1.149633
C	1.497376	4.921812	-0.210500
H	4.021709	4.837503	0.783926
H	5.587578	2.916933	0.886427
H	4.908711	0.706890	0.009650
H	1.500499	0.022857	-1.442792
C	2.674985	-1.078289	-0.046443
C	3.371410	-0.404454	-2.393873
C	2.048235	6.063322	-1.073411
H	0.551409	4.588118	-0.663445
C	1.167553	5.392943	1.211582
H	2.995684	6.456550	-0.672410
H	1.332431	6.898482	-1.108609
H	2.238347	5.736320	-2.107022
H	0.735848	4.575420	1.811482
H	0.432835	6.211873	1.188498
H	2.061958	5.769877	1.733588
H	3.261650	0.344156	-3.193565
H	3.036705	-1.375867	-2.787936
H	4.445596	-0.490813	-2.166693
H	2.083093	-0.798146	0.839441
H	3.717554	-1.228288	0.274627
H	2.299518	-2.049198	-0.401957
H	-3.927839	-1.636694	0.847442
H	-5.335493	-0.009592	2.070551
C	-3.067776	3.696285	0.343638
H	-4.931868	2.416459	1.834049
C	-1.837191	-1.163852	-0.815998
C	-2.688180	4.290821	1.705897
C	-4.283358	4.409121	-0.262282
H	-2.216383	3.864777	-0.334905
C	-1.005739	-1.958612	0.198200
H	-1.125939	-0.618668	-1.456537
C	-2.658399	-2.087615	-1.723661
H	-3.346664	-2.720461	-1.141879

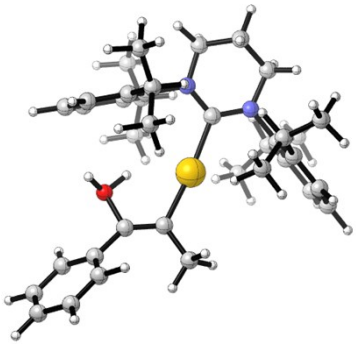
H	-1.998892	-2.760041	-2.293636
H	-3.263181	-1.514502	-2.442707
H	-0.395027	-1.289231	0.824998
H	-0.329177	-2.658876	-0.315494
H	-1.646881	-2.551211	0.869583
H	-5.165290	4.328746	0.392266
H	-4.557397	3.983396	-1.239909
H	-4.074551	5.480443	-0.404330
H	-1.787682	3.807549	2.118053
H	-3.494332	4.157243	2.443780
H	-2.489955	5.370278	1.619536
Au	0.046949	1.674299	1.498821
C	0.368922	1.651796	3.537518
C	1.583858	1.795832	4.053868
C	-0.842311	1.584974	4.395339
C	-1.763976	0.542982	4.204570
C	-1.133597	2.576984	5.343173
C	-2.924402	0.473986	4.969467
H	-1.565001	-0.217684	3.443828
C	-2.306474	2.515360	6.095840
H	-0.448841	3.419951	5.473959
C	-3.200186	1.460701	5.916930
H	-3.624679	-0.350860	4.816206
H	-2.524977	3.299621	6.824987
H	-4.117045	1.412250	6.509206
C	2.199438	1.840357	5.404491
H	2.688584	2.805798	5.613612
H	1.406942	1.695966	6.150339
H	2.945615	1.040680	5.526809
H	3.097728	2.681423	2.873462
H	2.191538	1.613721	2.142348
O	2.677570	1.807604	2.997695

Intermediate syn-IV-M

E(ωB97X-D3/def2-TZVPP) = –1760.561284 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.585541 E_h

Lowest frequency = 11.82 cm–1



C	-1.071340	2.917422	-3.294716
C	-2.029628	1.848622	-2.799672
H	-1.117578	2.990338	-4.390059
C	0.342748	2.583088	-2.853502
H	-1.370016	3.899037	-2.891291
H	0.747901	1.728346	-3.423463
N	0.370821	2.265895	-1.421966
H	1.023583	3.429854	-3.020234
C	-0.684952	1.846194	-0.724635
C	1.632022	2.431535	-0.738343
H	-1.861221	0.892041	-3.325898
H	-3.075857	2.134902	-2.977176
N	-1.852776	1.651625	-1.357991
C	-3.003445	1.226670	-0.602926
C	2.515821	1.338249	-0.677375
C	1.932565	3.677625	-0.155962
C	3.724151	1.516794	0.002419
C	3.157205	3.805141	0.505717
C	4.044641	2.737548	0.585663
C	-3.826698	2.201281	-0.003308
C	-3.273817	-0.152848	-0.488536
C	-4.399233	-0.542474	0.247614
C	-4.938015	1.760335	0.727946
C	-5.228842	0.402266	0.847614
C	2.172353	-0.021785	-1.268440
C	0.973432	4.859727	-0.199321

H	3.420933	4.757842	0.972430
H	4.994762	2.856758	1.111412
H	4.426644	0.683168	0.082257
H	1.259788	0.095080	-1.874605
C	1.848429	-1.026104	-0.155468
C	3.272627	-0.545741	-2.196022
C	1.573627	6.050462	-0.955720
H	0.070959	4.542782	-0.746073
C	0.522956	5.257277	1.211798
H	2.478628	6.432597	-0.458233
H	0.851041	6.879237	-1.009061
H	1.854600	5.777092	-1.984349
H	0.064869	4.403035	1.735927
H	-0.219405	6.069277	1.171164
H	1.368745	5.608891	1.823127
H	3.513611	0.179194	-2.988356
H	2.957640	-1.485132	-2.675085
H	4.201599	-0.759984	-1.645151
H	1.042899	-0.651405	0.496074
H	2.727771	-1.213000	0.480533
H	1.527905	-1.991590	-0.576768
H	-4.635665	-1.604763	0.349595
H	-6.114145	0.078545	1.401754
C	-3.551007	3.693138	-0.117855
H	-5.601932	2.495992	1.190425
C	-2.390769	-1.210237	-1.135452
C	-3.351715	4.337898	1.258461
C	-4.649378	4.402081	-0.920042
H	-2.606891	3.814747	-0.668799
C	-1.846530	-2.207292	-0.107708
H	-1.520443	-0.696163	-1.570761
C	-3.137789	-1.920499	-2.272058
H	-3.988636	-2.504729	-1.887449
H	-2.470631	-2.616767	-2.802523
H	-3.537078	-1.203211	-3.005325

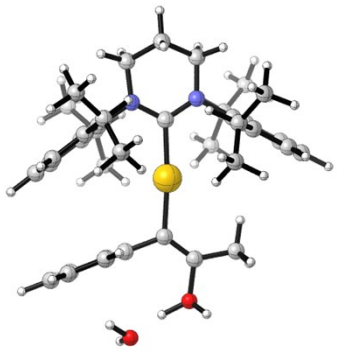
H	-1.286654	-1.696550	0.691475
H	-1.161858	-2.920527	-0.590439
H	-2.651003	-2.794662	0.361702
H	-5.620049	4.360398	-0.401329
H	-4.786150	3.948996	-1.913816
H	-4.396076	5.463354	-1.062770
H	-2.549345	3.835408	1.821887
H	-4.270429	4.302418	1.865167
H	-3.075004	5.397233	1.149383
Au	-0.598842	1.600981	1.340114
C	-1.888674	1.049400	3.947946
C	-0.762046	1.503265	3.401361
C	-2.487185	1.010281	5.292052
C	-3.111951	-0.146425	5.784336
C	-2.434580	2.156445	6.099337
C	-3.660054	-0.155776	7.063877
H	-3.157350	-1.046386	5.165408
C	-2.971112	2.137018	7.384206
H	-1.979981	3.070529	5.710324
C	-3.583518	0.981922	7.868315
H	-4.141976	-1.060621	7.441155
H	-2.920071	3.033586	8.006411
H	-4.009380	0.969099	8.874192
C	0.337500	2.064277	4.265290
H	0.419306	3.152949	4.113349
H	0.196684	1.874912	5.340355
H	1.305573	1.638702	3.961837
H	-3.673037	0.851489	2.835394
H	-2.335907	0.423529	2.087665
O	-2.820918	0.382982	2.961750

Intermediate anti-IV-aM

E(ωB97X-D3/def2-TZVPP) = –1837.031603 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1837.061006 E_h

Lowest frequency = 6.80 cm–1



C	-0.521573	2.992766	-3.126668
C	-1.733398	2.433745	-2.401812
H	-0.712734	3.040972	-4.207649
C	0.689503	2.120073	-2.851221
H	-0.327676	4.022124	-2.783573
H	0.607837	1.155327	-3.382586
N	0.827550	1.874614	-1.413437
H	1.614674	2.600599	-3.200590
C	-0.183639	1.940818	-0.539971
C	2.141273	1.530818	-0.930580
H	-2.062998	1.481839	-2.855452
H	-2.584925	3.126826	-2.454055
N	-1.414422	2.216936	-0.989806
C	-2.485058	2.330561	-0.029773
C	2.537487	0.182147	-0.963581
C	2.981549	2.548545	-0.439097
C	3.813851	-0.136294	-0.489508
C	4.249614	2.178856	0.018643
C	4.665123	0.851167	-0.006347
C	-2.775310	3.600926	0.501951
C	-3.174671	1.173745	0.373386
C	-4.162730	1.314451	1.353281
C	-3.773410	3.689802	1.475298
C	-4.457853	2.556765	1.902917
C	1.618848	-0.921873	-1.467175
C	2.555665	4.009170	-0.383314
H	4.927878	2.945623	0.402068
H	5.662666	0.584467	0.350957

H	4.148973	-1.176887	-0.498126
H	0.690240	-0.450567	-1.823306
C	1.222604	-1.871706	-0.332467
C	2.239209	-1.672861	-2.650842
C	3.381524	4.870367	-1.346617
H	1.504237	4.064466	-0.704391
C	2.613576	4.555778	1.047217
H	4.441391	4.903882	-1.048643
H	3.007783	5.905809	-1.360463
H	3.342417	4.481148	-2.375466
H	2.004802	3.940857	1.729418
H	2.231534	5.587349	1.083161
H	3.645052	4.572899	1.433150
H	2.523294	-0.982903	-3.460147
H	1.532063	-2.410118	-3.060887
H	3.146995	-2.219937	-2.351760
H	0.749352	-1.321560	0.496105
H	2.098984	-2.401975	0.072773
H	0.511271	-2.630201	-0.694130
H	-4.710408	0.433146	1.697053
H	-5.230851	2.643494	2.670648
C	-2.019430	4.848264	0.068728
H	-4.015301	4.662102	1.913404
C	-2.873242	-0.199167	-0.209280
C	-1.224980	5.450534	1.232044
C	-2.950858	5.876091	-0.581951
H	-1.283308	4.543548	-0.689774
C	-2.490730	-1.204617	0.880545
H	-1.997194	-0.098135	-0.869086
C	-4.043503	-0.702930	-1.062030
H	-4.952721	-0.835662	-0.454423
H	-3.803865	-1.675092	-1.519691
H	-4.287755	0.003097	-1.870394
H	-1.634791	-0.834685	1.466585
H	-2.210302	-2.171948	0.436603

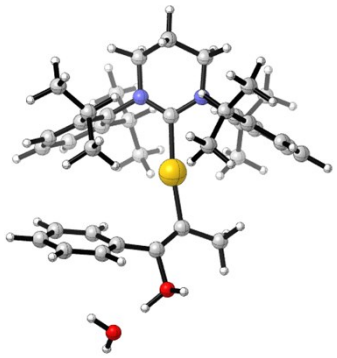
H	-3.324126	-1.389310	1.576577
H	-3.686430	6.269755	0.137003
H	-3.512826	5.436141	-1.419975
H	-2.375981	6.731283	-0.969107
H	-0.546891	4.702556	1.672096
H	-1.890890	5.815602	2.029840
H	-0.618621	6.303251	0.889184
Au	0.094877	1.651177	1.491830
C	0.203227	1.426722	3.539475
C	1.342003	1.289640	4.205599
C	-1.115890	1.467221	4.218650
C	-1.867433	0.295519	4.399145
C	-1.650786	2.683739	4.673049
C	-3.104409	0.333753	5.042119
H	-1.473593	-0.653042	4.024123
C	-2.885190	2.719141	5.325336
H	-1.091178	3.608345	4.506686
C	-3.615254	1.543077	5.518846
H	-3.677130	-0.588890	5.169056
H	-3.286046	3.674888	5.673294
H	-4.584086	1.573037	6.022653
O	1.311212	1.121174	5.688129
C	2.762404	1.208176	3.759660
H	2.800996	1.291069	2.666009
H	3.218593	0.249315	4.052377
H	3.375155	2.025138	4.179379
H	0.406490	1.139729	6.276674
H	2.012977	1.624962	6.126173
O	-0.612297	1.174377	7.209456
H	-1.314554	1.763388	6.877822
H	-1.041802	0.313876	7.311627

Intermediate anti-IV-M

E(ωB97X-D3/def2-TZVPP) = –1837.021832 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1837.052481 E_h

Lowest frequency = 10.01 cm–1



C	-0.962505	3.058840	-2.941697
C	-1.828065	1.967326	-2.343964
H	-1.191295	3.182657	-4.009285
C	0.498183	2.698389	-2.755773
H	-1.177693	4.020304	-2.446835
H	0.780268	1.845812	-3.399200
N	0.760067	2.358168	-1.355850
H	1.156329	3.536305	-3.026497
C	-0.159182	1.860942	-0.515687
C	2.123542	2.503836	-0.912576
H	-1.777755	1.045853	-2.951056
H	-2.884308	2.270707	-2.308413
N	-1.401349	1.669132	-0.973262
C	-2.399378	1.061824	-0.132880
C	2.990736	1.399622	-1.008534
C	2.545963	3.751962	-0.418287
C	4.313469	1.573929	-0.590177
C	3.877824	3.874320	-0.012134
C	4.755142	2.797776	-0.098664
C	-3.274221	1.892940	0.591509
C	-2.509342	-0.340605	-0.119531
C	-3.547222	-0.904862	0.629586
C	-4.296205	1.280466	1.320865
C	-4.439568	-0.103542	1.332561
C	2.532969	0.047047	-1.537611
C	1.593119	4.931284	-0.277193
H	4.237765	4.829871	0.378355

H	5.794858	2.914582	0.216734
H	5.013099	0.736086	-0.652576
H	1.446639	0.104746	-1.705731
C	2.760163	-1.068200	-0.512169
C	3.188419	-0.279769	-2.884979
C	2.110600	6.185943	-0.988913
H	0.642218	4.650567	-0.755891
C	1.280850	5.205049	1.199232
H	3.034865	6.567388	-0.527247
H	1.363280	6.992916	-0.938330
H	2.327050	5.989421	-2.050181
H	0.867222	4.308585	1.688244
H	0.546097	6.019277	1.297919
H	2.188118	5.500122	1.750297
H	3.005731	0.513719	-3.626163
H	2.790039	-1.222729	-3.290673
H	4.279557	-0.393295	-2.786184
H	2.262238	-0.833370	0.441512
H	3.830927	-1.225054	-0.308626
H	2.351344	-2.021349	-0.880774
H	-3.666581	-1.991571	0.653336
H	-5.258409	-0.563766	1.892285
C	-3.122260	3.407684	0.617391
H	-4.994983	1.898525	1.890826
C	-1.551674	-1.241981	-0.886473
C	-2.657069	3.883966	1.999205
C	-4.402863	4.125781	0.176038
H	-2.329902	3.674540	-0.098542
C	-0.806107	-2.194437	0.054034
H	-0.790313	-0.599693	-1.354641
C	-2.267938	-1.999820	-2.010566
H	-3.010835	-2.707052	-1.609228
H	-1.547737	-2.578294	-2.610037
H	-2.800087	-1.313059	-2.686948
H	-0.259441	-1.636257	0.830561

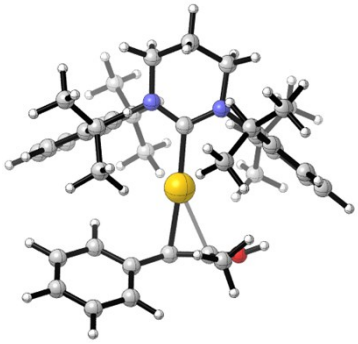
H	-0.079966	-2.801648	-0.507970
H	-1.495102	-2.890717	0.557496
H	-5.230058	3.956464	0.883191
H	-4.738967	3.784341	-0.815091
H	-4.237390	5.212580	0.121446
H	-1.711853	3.398226	2.289172
H	-3.402851	3.647396	2.774785
H	-2.498381	4.973519	2.005252
Au	0.423280	1.471937	1.441537
C	0.533087	1.484458	4.420618
C	1.248536	1.252384	3.325683
C	-0.910690	1.695244	4.671963
C	-1.844146	0.744774	4.241545
C	-1.365061	2.818831	5.384136
C	-3.197460	0.900802	4.538940
H	-1.498204	-0.123640	3.675340
C	-2.717494	2.970547	5.684366
H	-0.656054	3.591245	5.698151
C	-3.636942	2.005031	5.266928
H	-3.910463	0.146574	4.201235
H	-3.057837	3.853441	6.231368
H	-4.697786	2.121600	5.501555
C	2.731927	0.984675	3.373111
H	2.964168	0.072849	2.803012
H	3.147229	0.859972	4.385421
H	3.275356	1.796932	2.863124
H	0.653221	1.348457	6.588814
H	1.824728	2.271890	5.865994
O	1.266108	1.488922	5.755502
O	-0.236349	1.207959	7.729513
H	-0.302649	0.362188	8.190258
H	-1.136814	1.467697	7.481191

Intermediate syn-V-aM

E(ωB97X-D3/def2-TZVPP) = –1760.632608 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.657693 E_h

Lowest frequency = 14.34 cm–1



C	-0.731585	3.064639	-2.900151
C	-1.735498	2.080246	-2.329745
H	-0.877729	3.163993	-3.984496
C	0.680227	2.593593	-2.599612
H	-0.892084	4.061631	-2.458028
H	0.919264	1.674594	-3.162924
N	0.820386	2.332490	-1.164201
H	1.425613	3.350726	-2.880384
C	-0.194630	1.905884	-0.404944
C	2.122172	2.497839	-0.564047
H	-1.760683	1.147691	-2.920036
H	-2.752509	2.498558	-2.343079
N	-1.406338	1.755671	-0.937872
C	-2.464836	1.180650	-0.141961
C	2.960468	1.376651	-0.412561
C	2.496618	3.784216	-0.128308
C	4.191757	1.571557	0.225677
C	3.736507	3.925818	0.501508
C	4.575575	2.829301	0.683028
C	-3.318806	2.035333	0.580387
C	-2.615295	-0.219767	-0.137386
C	-3.669210	-0.756288	0.608962
C	-4.362693	1.447250	1.300388
C	-4.540762	0.067963	1.312690
C	2.586406	-0.004009	-0.934611
C	1.580198	4.989454	-0.292063

H	4.054439	4.910312	0.854101
H	5.546187	2.960356	1.168118
H	4.870167	0.723721	0.352108
H	1.508619	0.004672	-1.161302
C	2.816528	-1.108177	0.102378
C	3.332315	-0.301418	-2.242580
C	2.298361	6.182845	-0.928868
H	0.766174	4.697935	-0.971507
C	0.924676	5.368284	1.040961
H	3.068372	6.603723	-0.263801
H	1.580998	6.988559	-1.145428
H	2.790292	5.901998	-1.872498
H	0.362397	4.520979	1.464043
H	0.222034	6.204543	0.905701
H	1.678664	5.681085	1.781185
H	3.148639	0.473930	-3.002199
H	3.014674	-1.269569	-2.658598
H	4.420029	-0.349180	-2.076448
H	2.325520	-0.876148	1.059606
H	3.887148	-1.265619	0.306062
H	2.415876	-2.064791	-0.264085
H	-3.815596	-1.839340	0.635395
H	-5.366730	-0.371233	1.877673
C	-3.123514	3.544713	0.630335
H	-5.047920	2.081432	1.868475
C	-1.675204	-1.149875	-0.892985
C	-2.735561	3.999426	2.043806
C	-4.359029	4.297774	0.121587
H	-2.283278	3.798434	-0.035687
C	-0.879310	-2.039029	0.070006
H	-0.942459	-0.526346	-1.429337
C	-2.423223	-1.979570	-1.943170
H	-3.131317	-2.681452	-1.475878
H	-1.717393	-2.574512	-2.542929
H	-2.998335	-1.339614	-2.629833

H	-0.294682	-1.435626	0.783632
H	-0.178301	-2.681073	-0.485120
H	-1.540002	-2.699059	0.653222
H	-5.229479	4.136553	0.776340
H	-4.643136	3.976856	-0.892302
H	-4.167627	5.381067	0.093596
H	-1.824392	3.490284	2.397072
H	-3.530069	3.774750	2.772458
H	-2.554216	5.084792	2.067790
Au	0.145774	1.431677	1.563833
C	0.367005	0.761653	3.680915
C	1.577644	1.417988	3.487762
C	-0.820643	1.267110	4.434593
C	-2.097947	0.830459	4.049115
C	-0.710609	2.114919	5.544525
C	-3.232073	1.252952	4.734612
H	-2.206567	0.158935	3.190933
C	-1.849380	2.548210	6.222918
H	0.271631	2.422963	5.909047
C	-3.112894	2.123450	5.818298
H	-4.216100	0.900278	4.416611
H	-1.743222	3.209684	7.086110
H	-4.002616	2.457721	6.357230
C	1.875637	2.859702	3.777900
H	0.964070	3.460862	3.871463
H	2.445474	2.925355	4.718656
H	2.499406	3.280459	2.973507
H	3.327442	1.194328	2.748266
H	0.429400	-0.328790	3.565225
O	2.630445	0.658258	3.153042

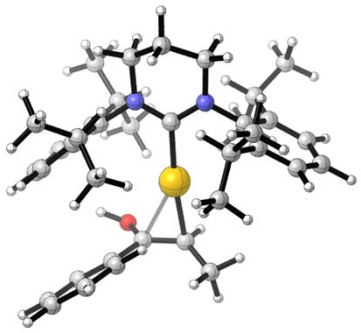
Intermediate V-M

E(ωB97X-D3/def2-TZVPP) = –1760.626405 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(1,4-dioxane)) = –1760.649926 E_h

E(ωB97X-D3/def2-TZVPP+CPCM(water)) = –1760.676292 E_h

Lowest frequency = 10.78 cm–1



C	-1.301410	3.131779	-2.877910
C	-2.174085	1.970753	-2.432878
H	-1.394277	3.283253	-3.962132
C	0.146386	2.850288	-2.518343
H	-1.639450	4.060386	-2.389408
H	0.580414	2.085454	-3.185622
N	0.258844	2.390109	-1.129340
H	0.766782	3.752274	-2.620052
C	-0.749160	1.870319	-0.428883
C	1.564816	2.482853	-0.523178
H	-1.955894	1.064903	-3.025552
H	-3.242600	2.193159	-2.561468
N	-1.938742	1.689048	-1.014865
C	-3.019195	1.159245	-0.219306
C	2.445395	1.392322	-0.649590
C	1.914654	3.661334	0.161940
C	3.707278	1.506230	-0.058533
C	3.190370	3.725828	0.729740
C	4.078693	2.660752	0.621873
C	-3.870603	2.069735	0.435095
C	-3.157713	-0.234907	-0.085466
C	-4.142001	-0.703649	0.794320
C	-4.814731	1.553479	1.326769
C	-4.942586	0.180576	1.515064
C	2.062732	0.107224	-1.371494
C	0.954879	4.832291	0.321874
H	3.495372	4.626320	1.269466

H	5.071376	2.731373	1.072482
H	4.414401	0.676014	-0.134193
H	1.072207	0.257768	-1.830206
C	1.925861	-1.057696	-0.384482
C	3.044252	-0.225495	-2.499996
C	1.476682	6.093640	-0.376951
H	0.002015	4.558332	-0.158752
C	0.647083	5.090262	1.801550
H	2.416546	6.447598	0.074927
H	0.744047	6.911754	-0.300688
H	1.672647	5.912301	-1.444783
H	0.274405	4.175375	2.290456
H	-0.117518	5.874551	1.911234
H	1.541893	5.417583	2.353447
H	3.138101	0.608132	-3.212513
H	2.707813	-1.113875	-3.055591
H	4.050499	-0.446158	-2.111155
H	1.181066	-0.832560	0.395403
H	2.881892	-1.272932	0.118166
H	1.606582	-1.974294	-0.903713
H	-4.292908	-1.781066	0.906319
H	-5.693880	-0.203981	2.209678
C	-3.790678	3.570049	0.182932
H	-5.466769	2.234300	1.879339
C	-2.317644	-1.213073	-0.895015
C	-3.184041	4.321480	1.370610
C	-5.157035	4.140127	-0.215335
H	-3.113178	3.727282	-0.669340
C	-1.773097	-2.374836	-0.060469
H	-1.446495	-0.660733	-1.283275
C	-3.123737	-1.724626	-2.098263
H	-3.987507	-2.322161	-1.767021
H	-2.500845	-2.363978	-2.742403
H	-3.515583	-0.897618	-2.710112
H	-1.210492	-2.018849	0.814752

H	-1.103663	-2.999781	-0.670380
H	-2.578077	-3.032552	0.303194
H	-5.882467	4.082610	0.611220
H	-5.584131	3.597092	-1.072397
H	-5.065566	5.200463	-0.495407
H	-2.174644	3.947263	1.599632
H	-3.801709	4.203729	2.274214
H	-3.104356	5.397461	1.152493
Au	-0.476335	1.232146	1.516199
C	-1.309359	0.152472	3.542266
C	0.066112	0.361372	3.495453
C	-2.320989	0.999144	4.238200
C	-3.347502	0.349193	4.940704
C	-2.283111	2.399118	4.234579
C	-4.311621	1.085279	5.624601
H	-3.380303	-0.742689	4.974625
C	-3.242810	3.131797	4.925562
H	-1.514752	2.924027	3.663554
C	-4.260794	2.477942	5.620095
H	-5.101397	0.565593	6.171836
H	-3.199572	4.223452	4.915383
H	-5.015256	3.055660	6.159326
C	0.861854	1.292879	4.377948
H	1.745232	1.674426	3.846892
H	0.281688	2.149728	4.739480
H	1.221713	0.737986	5.259001
H	-2.677550	-0.938010	2.784761
H	0.610761	-0.523219	3.137666
O	-1.757908	-1.025365	3.081928

References

1. B. Zhao and X. Lu, *Tetrahedron Lett.*, 2006, **47**, 6765-6768.
2. G. M. Anstead, C. S. Peterson, K. G. Pinney, S. R. Wilson and J. A. Katzenellenbogen, *J. Med. Chem.*, 1990, **33**, 2726-2734.
3. K. Huang, G. Li, W.-P. Huang, D.-G. Yu and Z.-J. Shi, *Chem. Commun.*, 2011, **47**, 7224-7226.
4. P. J. Wagner, M. A. Meador, B. Zhou and B. S. Park, *J. Am. Chem. Soc.*, 1991, **113**, 9630-9639.
5. B. Zhao and X. Lu, *Org. Lett.*, 2006, **8**, 5987-5990.
6. S. Inaba and R. D. Rieke, *J. Org. Chem.*, 1985, **50**, 1373-1381.
7. D. B. Denney, D. Z. Denney and S. D. Pastor, *Phosphorus Sulfur Relat. Elem.*, 1985, **22**, 191-197.
8. A. R. Hajipour, A. Zarei, L. Khazdooz and A. E. Ruoho, *Synth. Commun.*, 2009, **39**, 2702-2722.
9. M. J. Gallagher, M. J. Gallagher, H. Noerdin and H. Noerdin, *Aust. J. Chem.*, 1985, **38**, 997-1005.
10. L. Ackermann and L. T. Kaspar, *J. Org. Chem.*, 2007, **72**, 6149-6153.
11. L.-Z. Yuan, G. Zhao, A. Hamze, M. Alami and O. Provot, *Adv. Synth. Catal.*, 2017, **359**, 2682-2691.
12. S. H. Lee, A. Kundu, S. H. Han, N. K. Mishra, K. S. Kim, M. H. Choi, A. K. Pandey, J. S. Park, H. S. Kim and I. S. Kim, *ACS Omega*, 2018, **3**, 2661-2672.
13. T. Hering, D. P. Hari and B. König, *J. Org. Chem.*, 2012, **77**, 10347-10352.
14. T. C. Stephens and G. Pattison, *Org. Lett.*, 2017, **19**, 3498-3501.
15. Y. Yuan, X. Shi and W. Liu, *Synlett*, 2011, **2011**, 559-564.
16. a) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73-78; b) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, e1327.
17. Y.-S. Lin, G.-D. Li, S.-P. Mao and J.-D. Chai, *J. Chem. Theory Comput.*, 2013, **9**, 263-272.
18. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
19. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.
20. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
21. C. Y. Legault, CYLview, 1.0b, Université de Sherbrooke, 2009, http://www.cylview.org.

Spectra

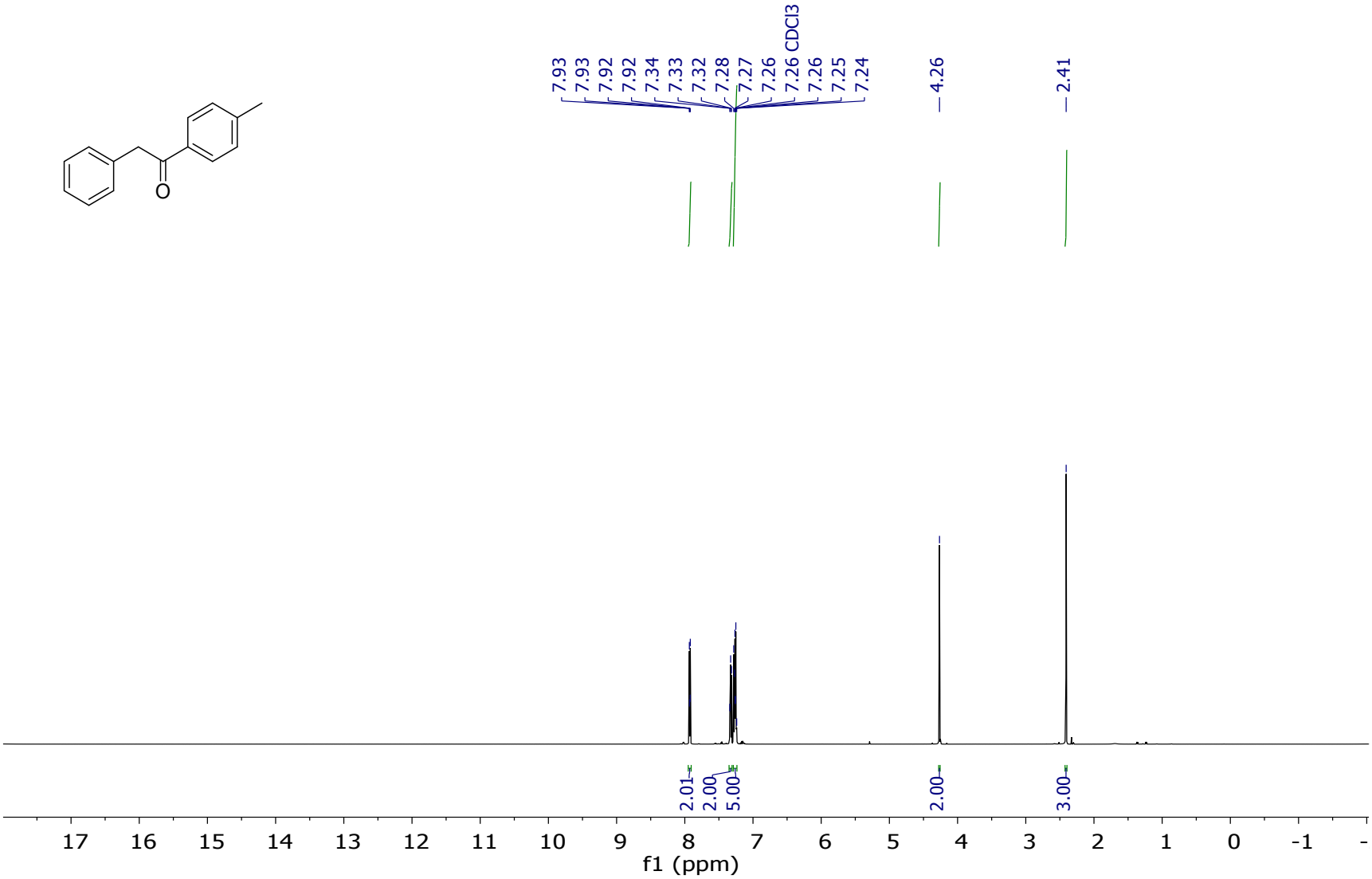


Figure S1. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-phenyl-1-p-tolylethanone (1a).

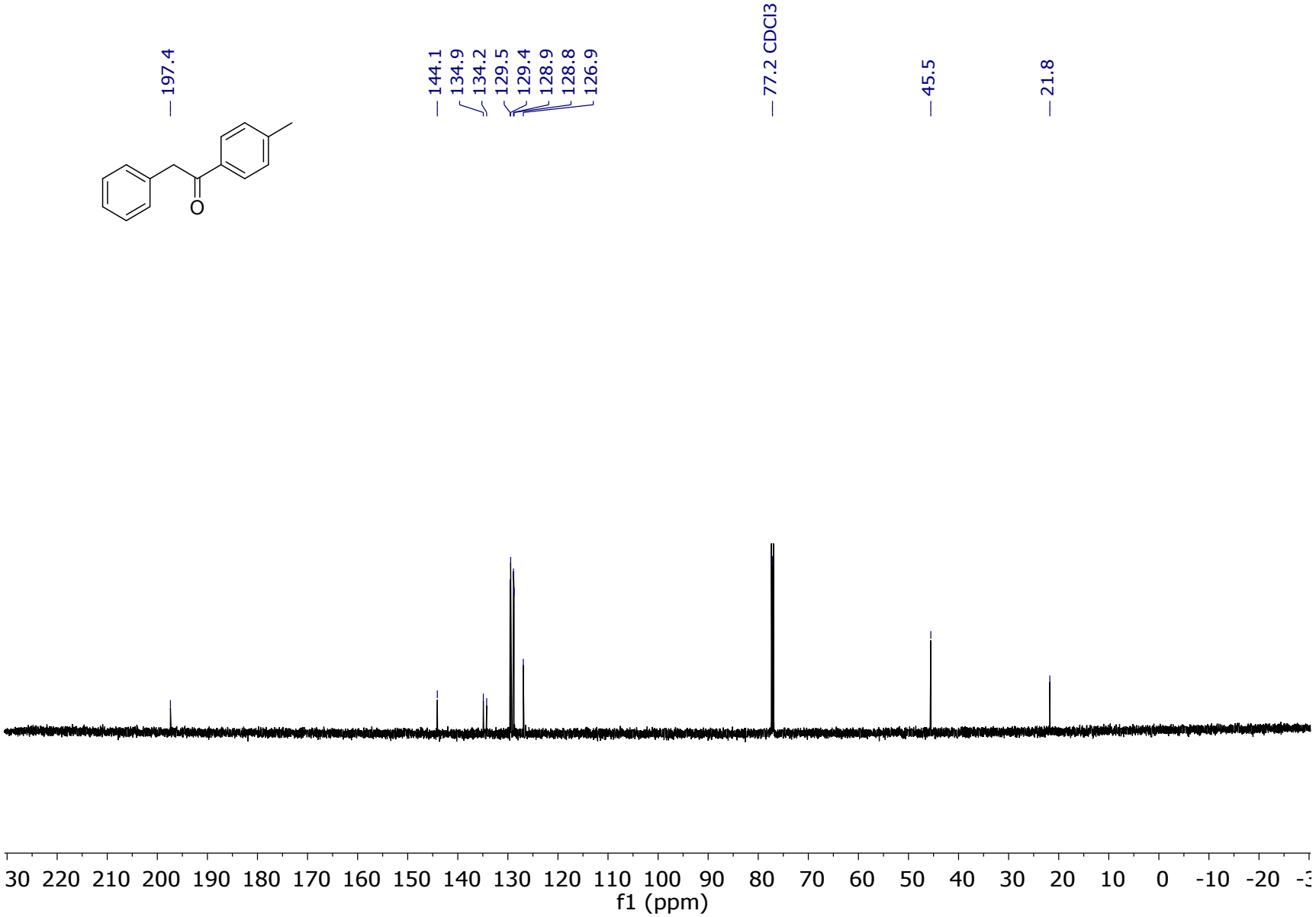


Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 2-phenyl-1-p-tolylethanone (1a).

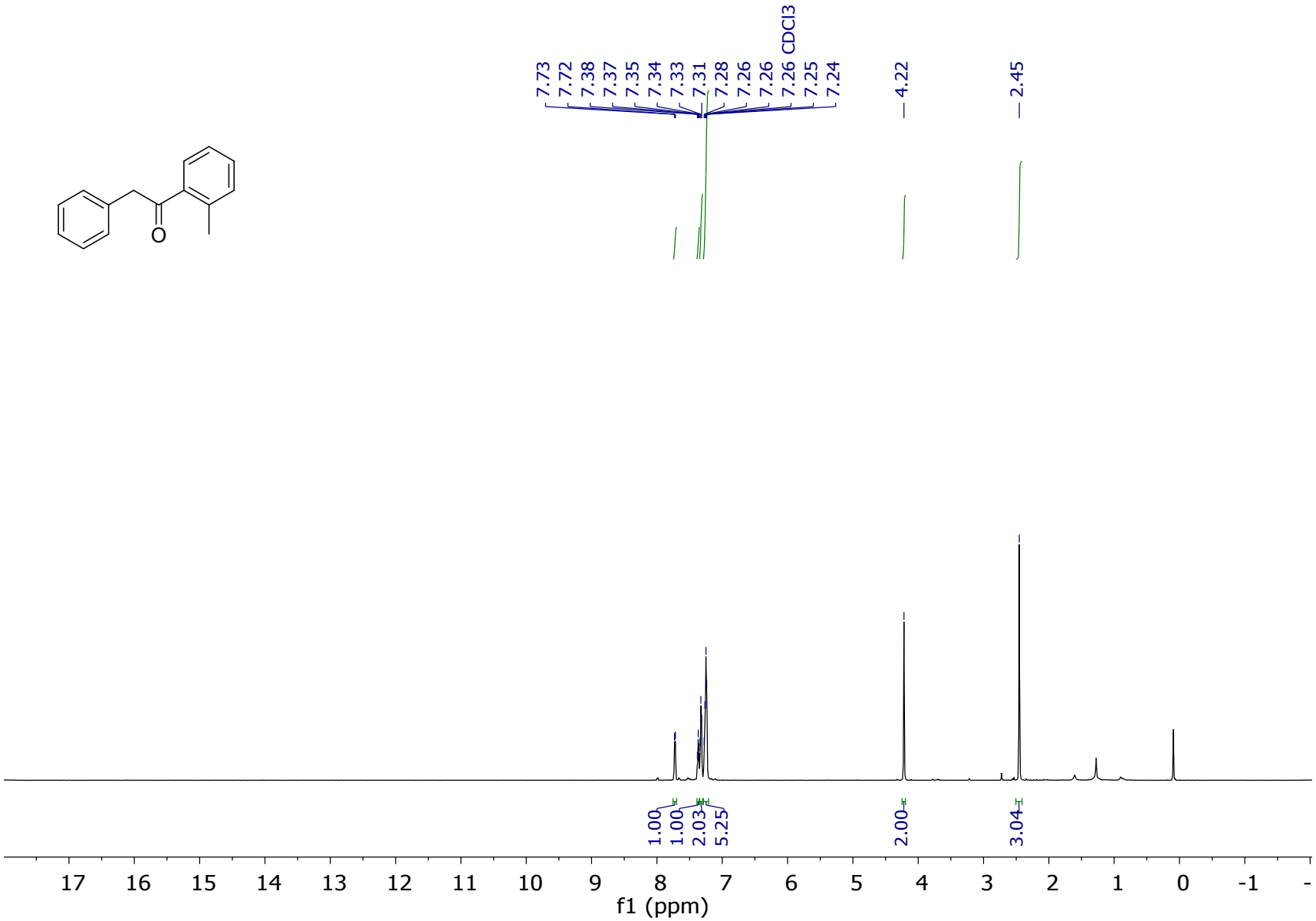


Figure S3. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-phenyl-1-o-tolylethanone (2a).

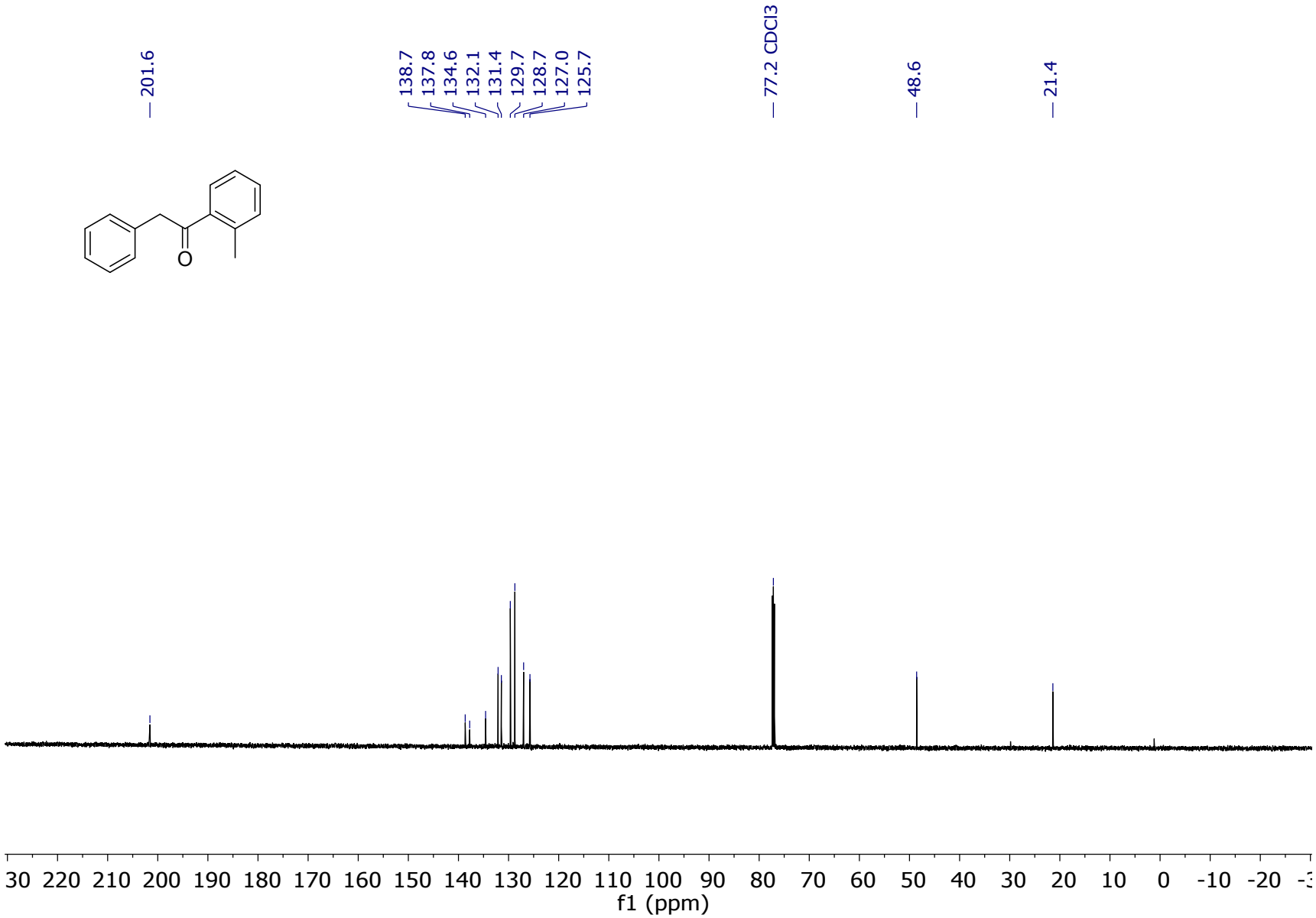


Figure S4. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 2-phenyl-1-o-tolylethanone (2a).

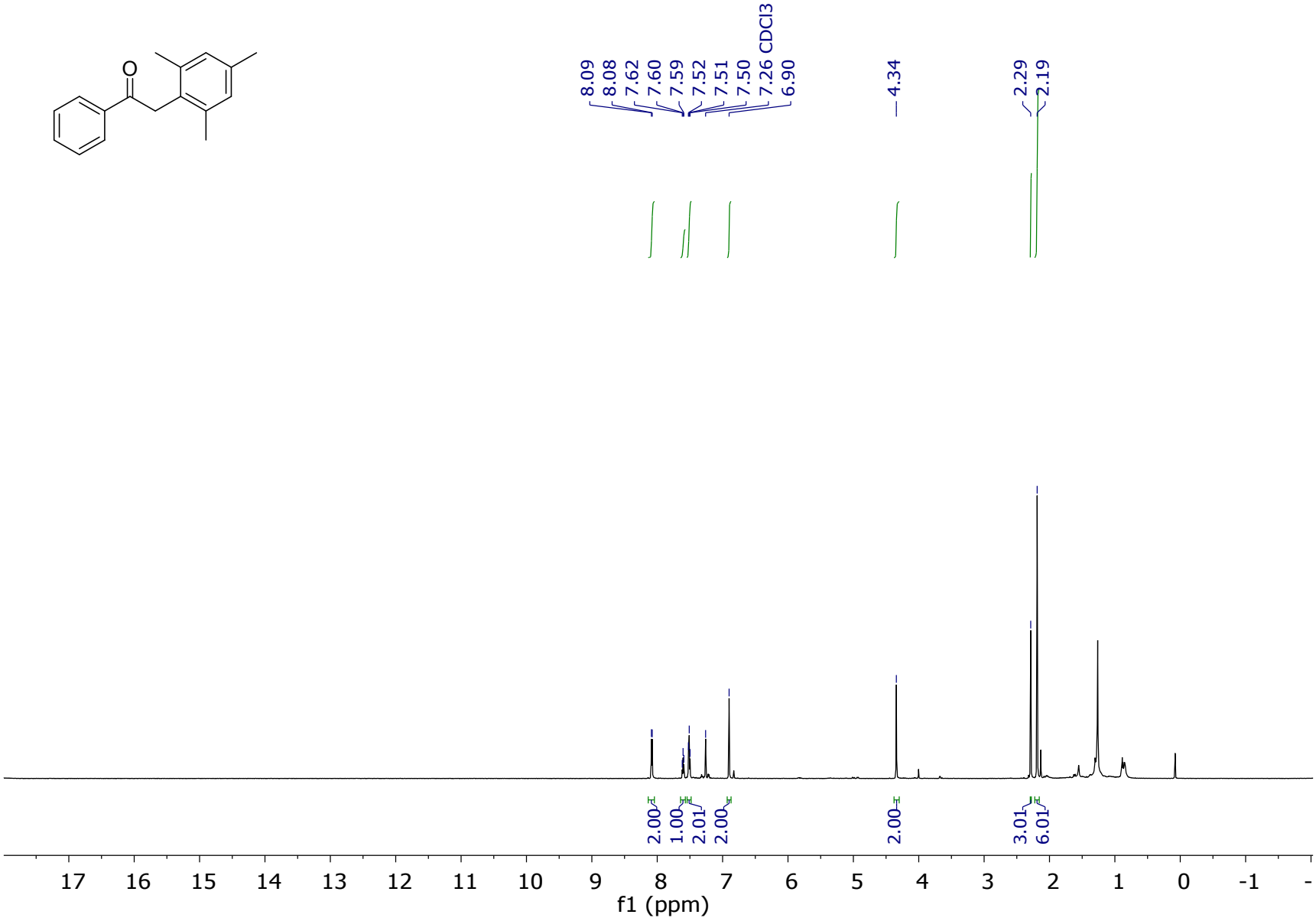


Figure S5. ^{1}H NMR (600 MHz, Chloroform-d) of 2-mesityl-1-phenylethanone (3b).

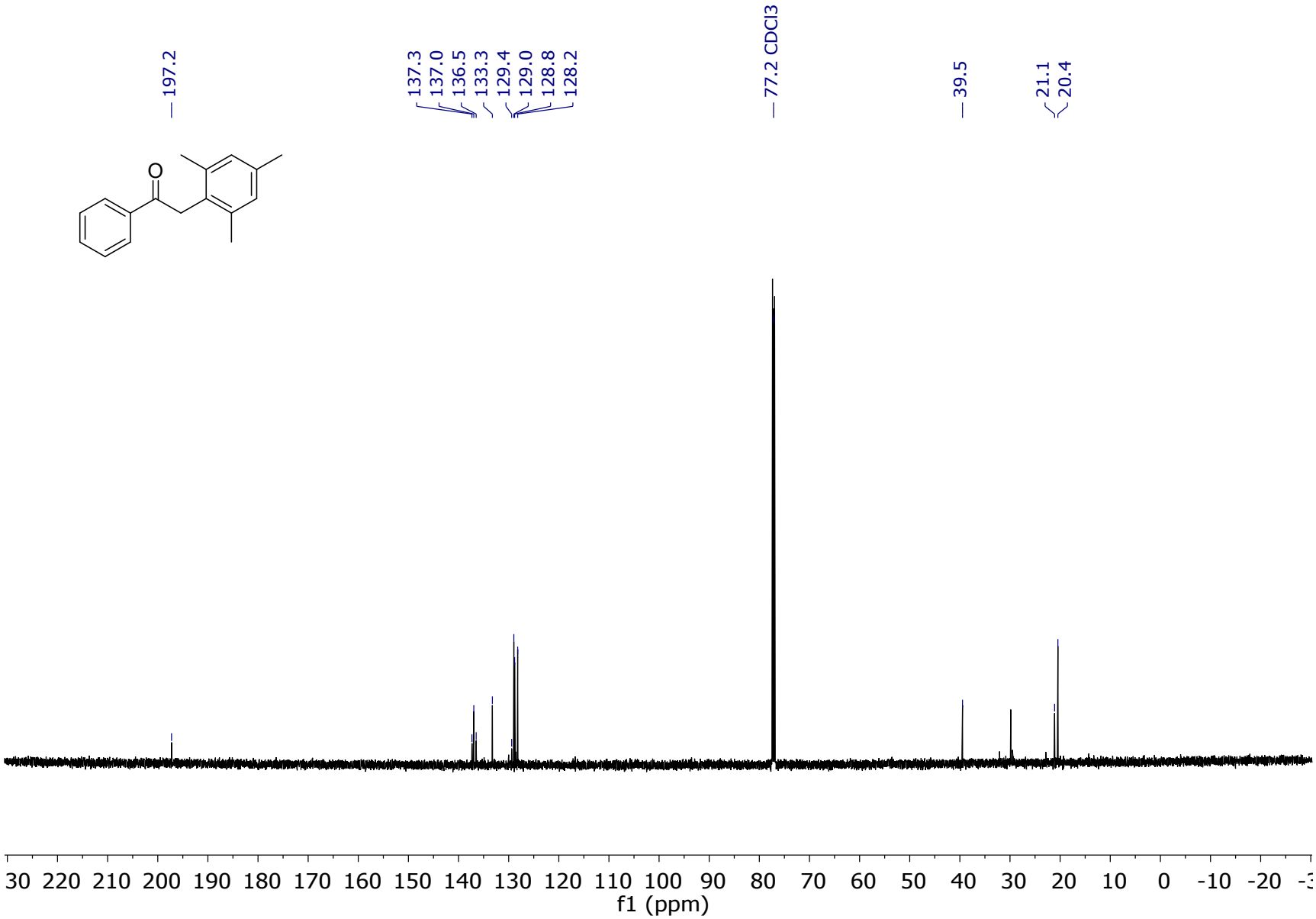


Figure S6. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-mesityl-1-phenylethanone (3b).

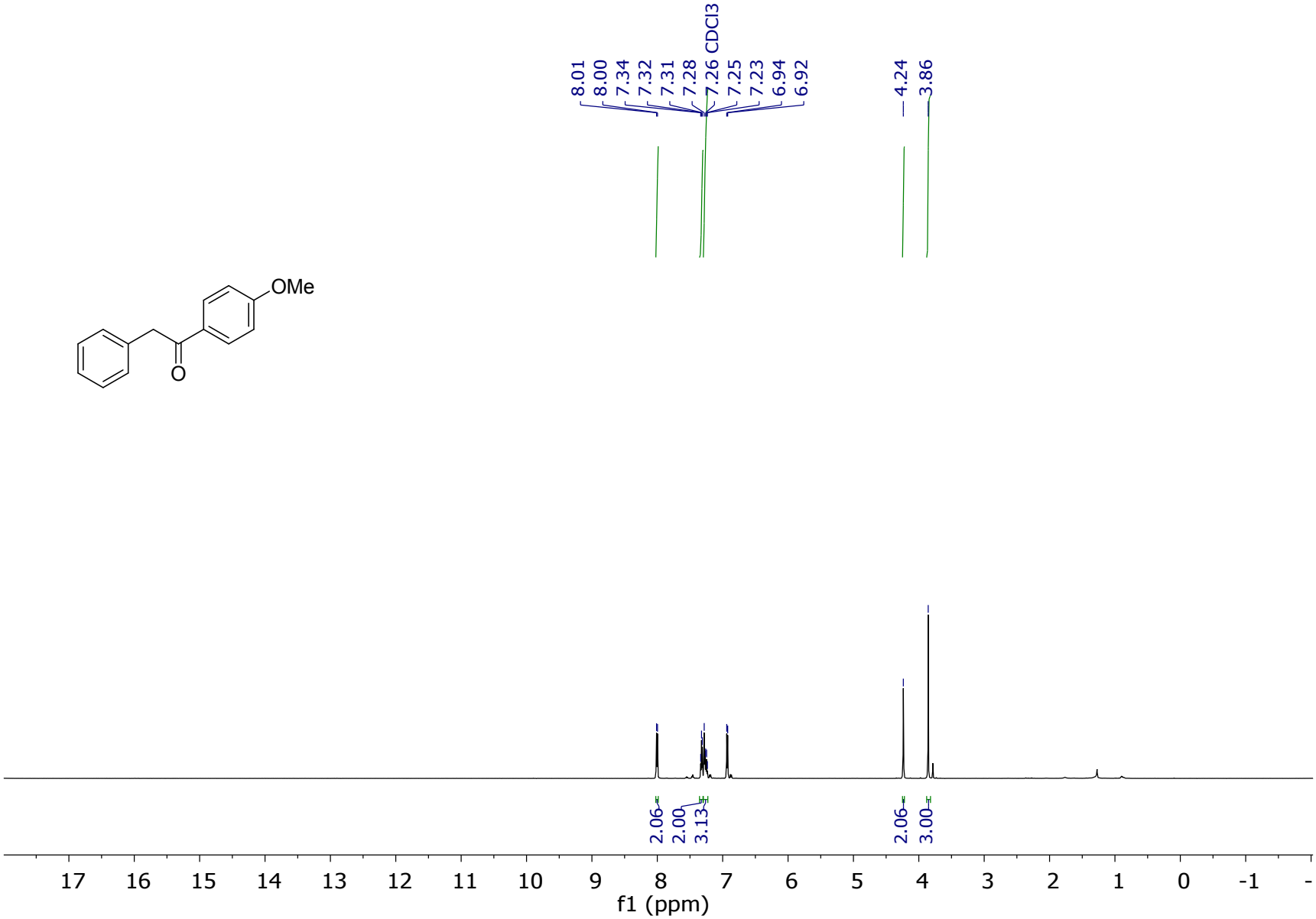


Figure S7. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-2-phenylethanone (4a).

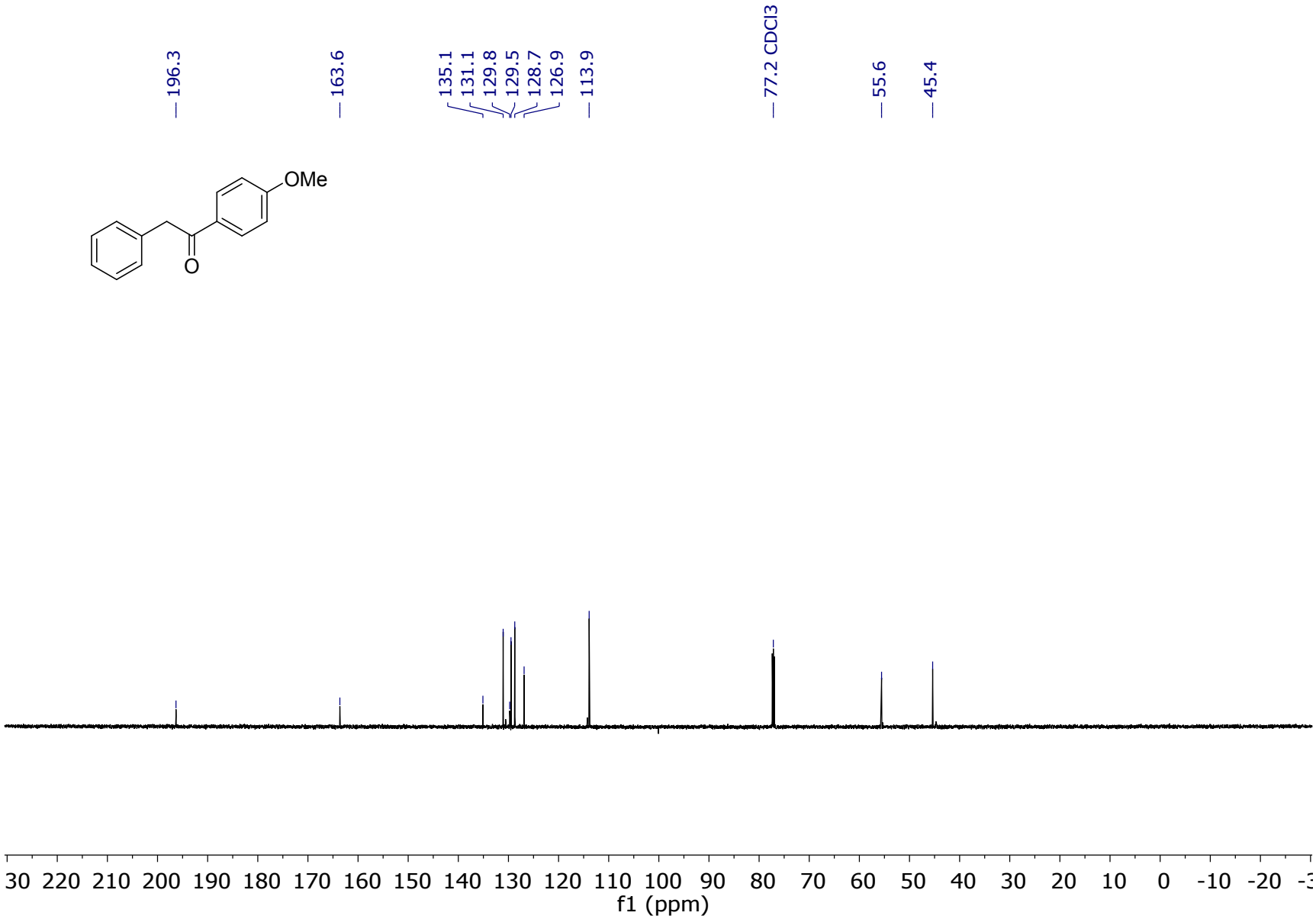


Figure S8. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-2-phenylethanone (4a).

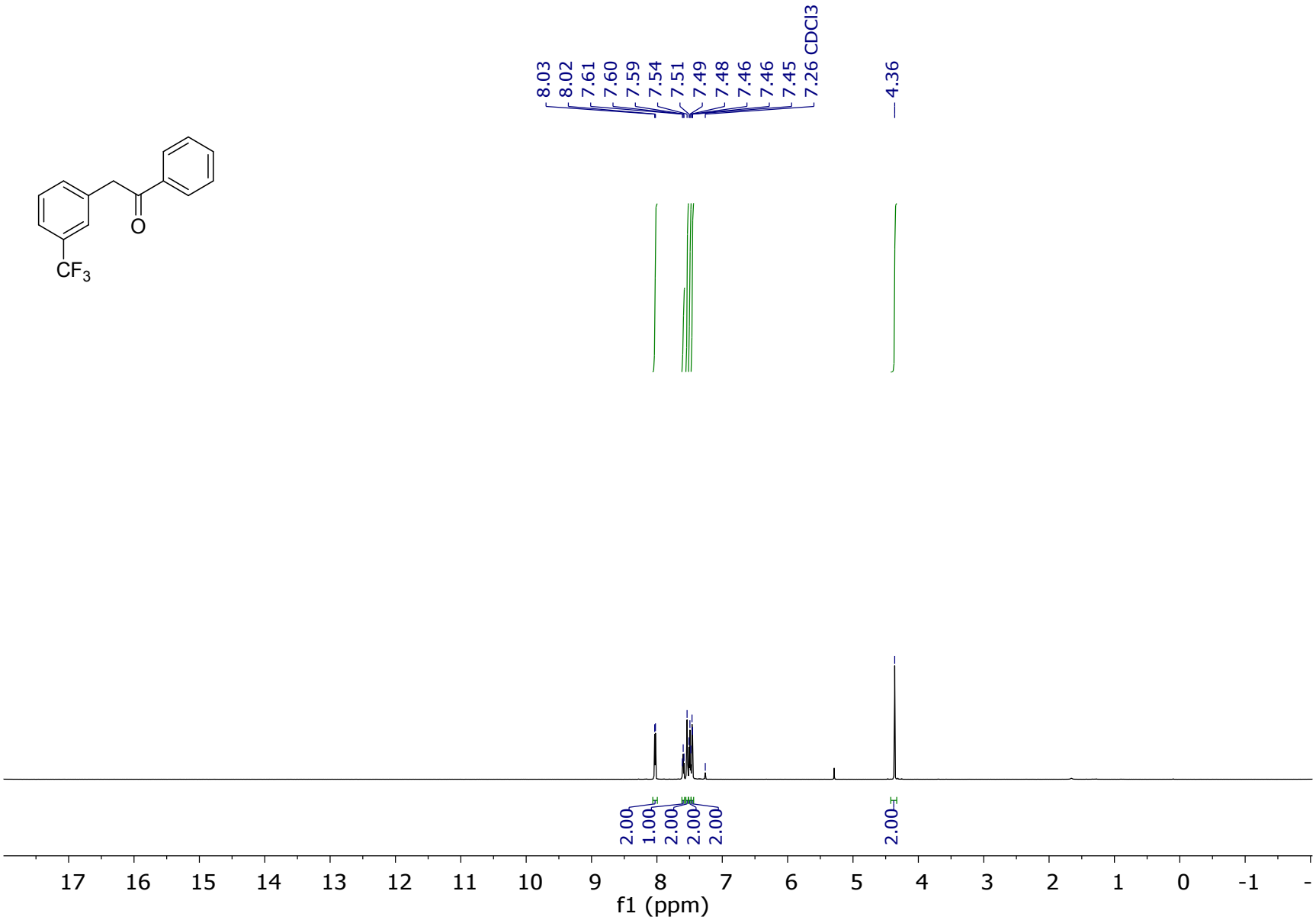


Figure S9. ^{1}H NMR (600 MHz, Chloroform-d) of 1-phenyl-2-(3-(trifluoromethyl)phenyl)ethanone (5a).

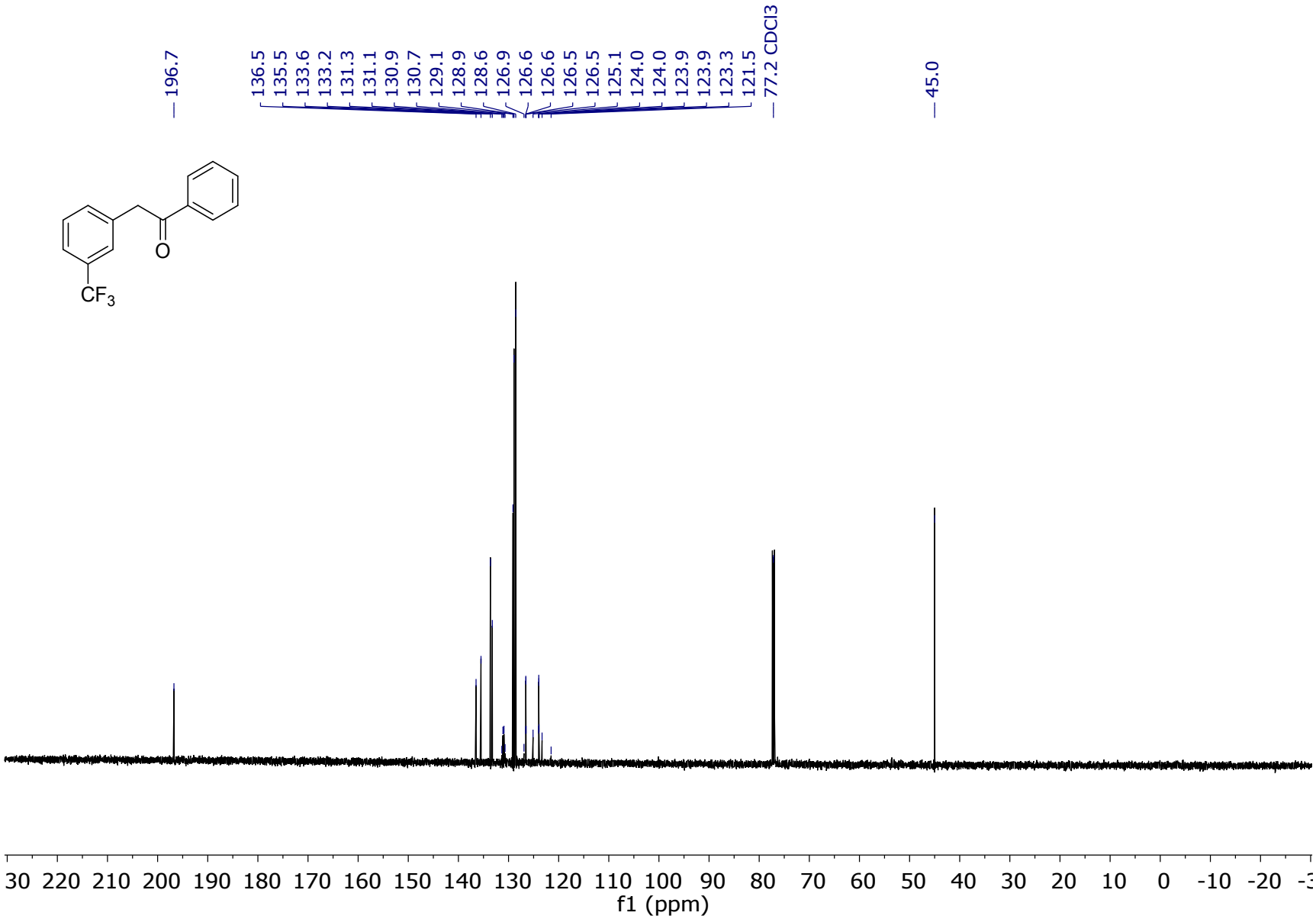


Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-phenyl-2-(3-(trifluoromethyl)phenyl)ethanone (5a).

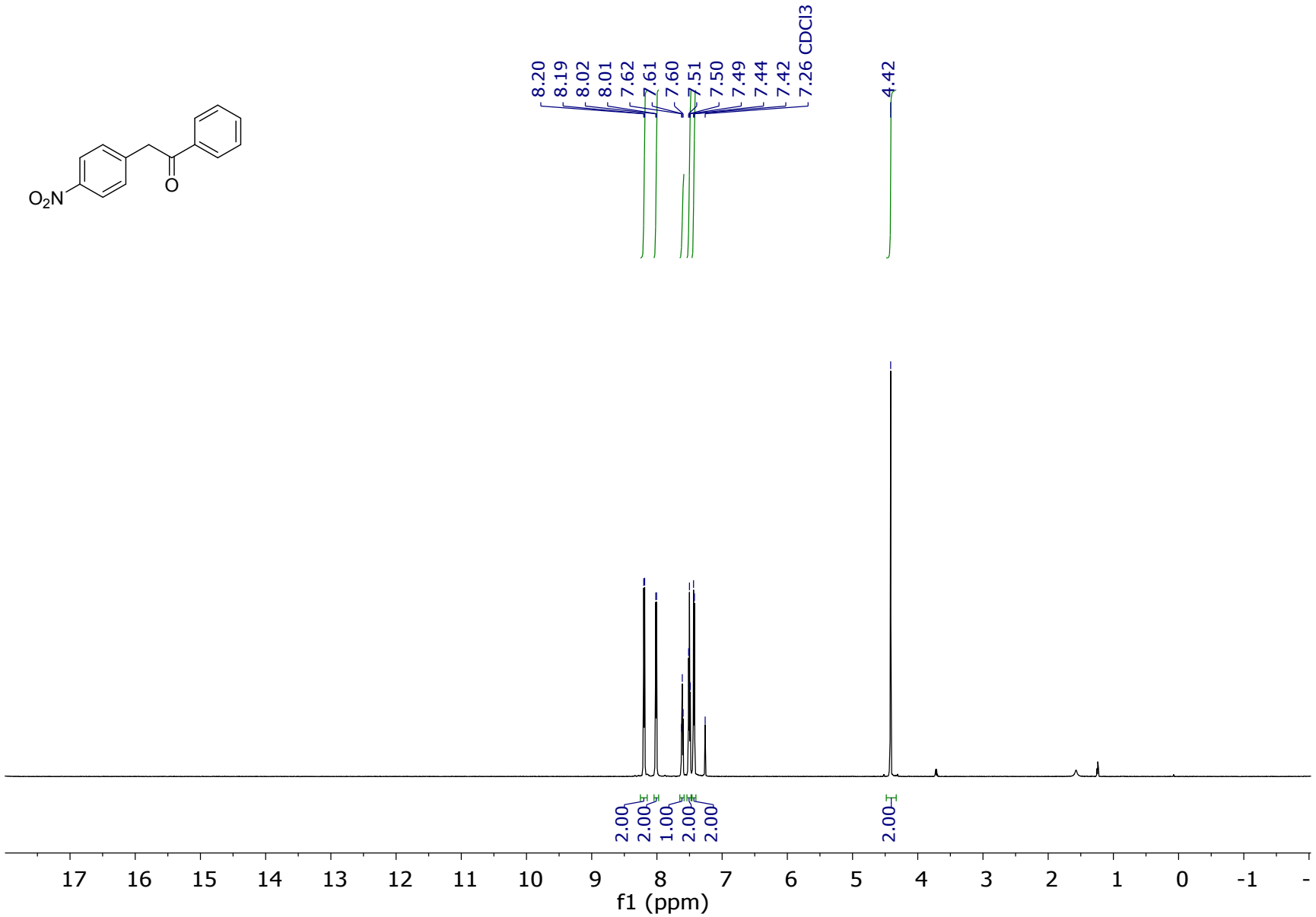


Figure S11. ^{1}H NMR (600 MHz, Chloroform-d) of 2-(4-nitrophenyl)-1-phenylethanone (6a).

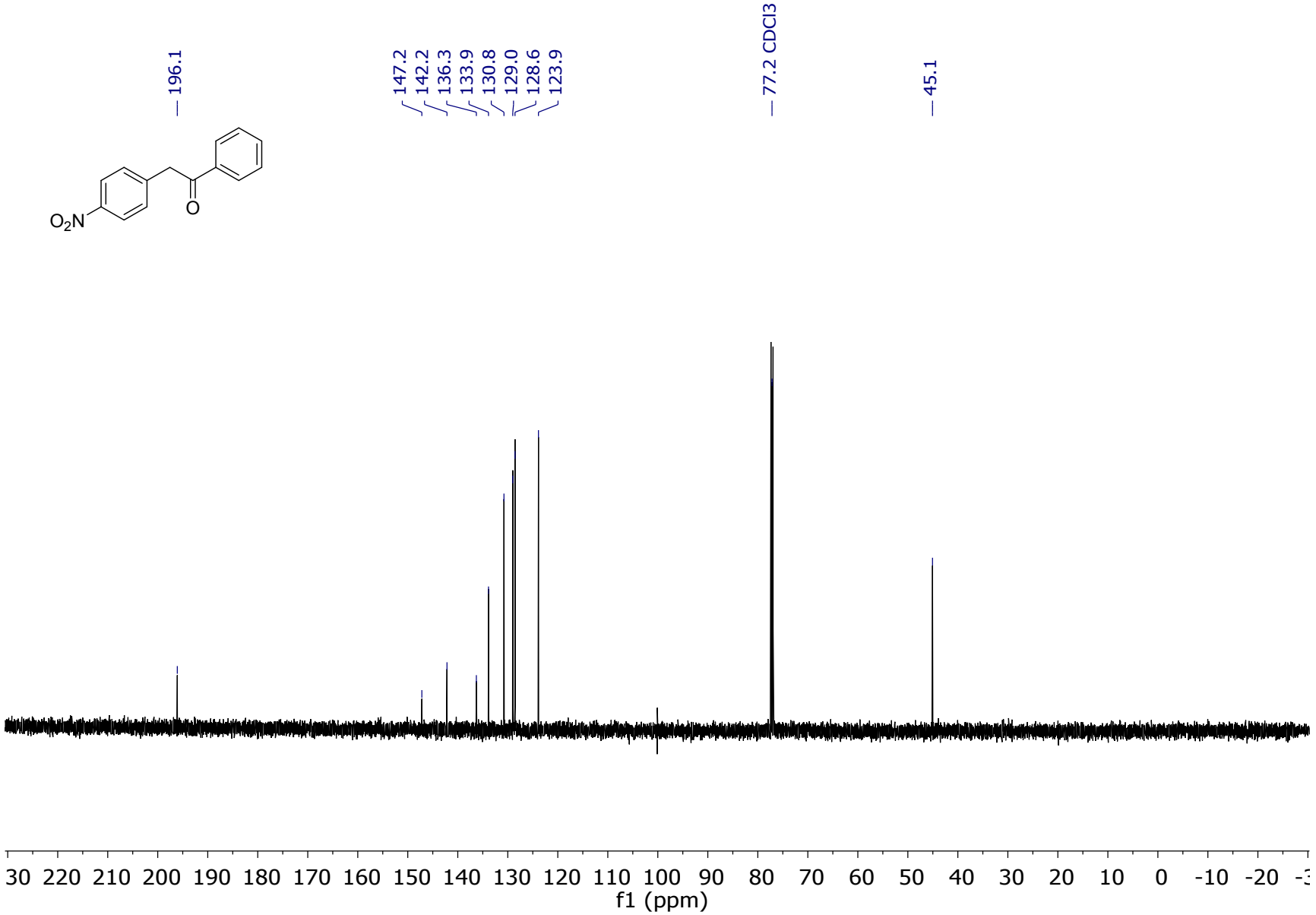


Figure S12. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-(4-nitrophenyl)-1-phenylethanone (6a).

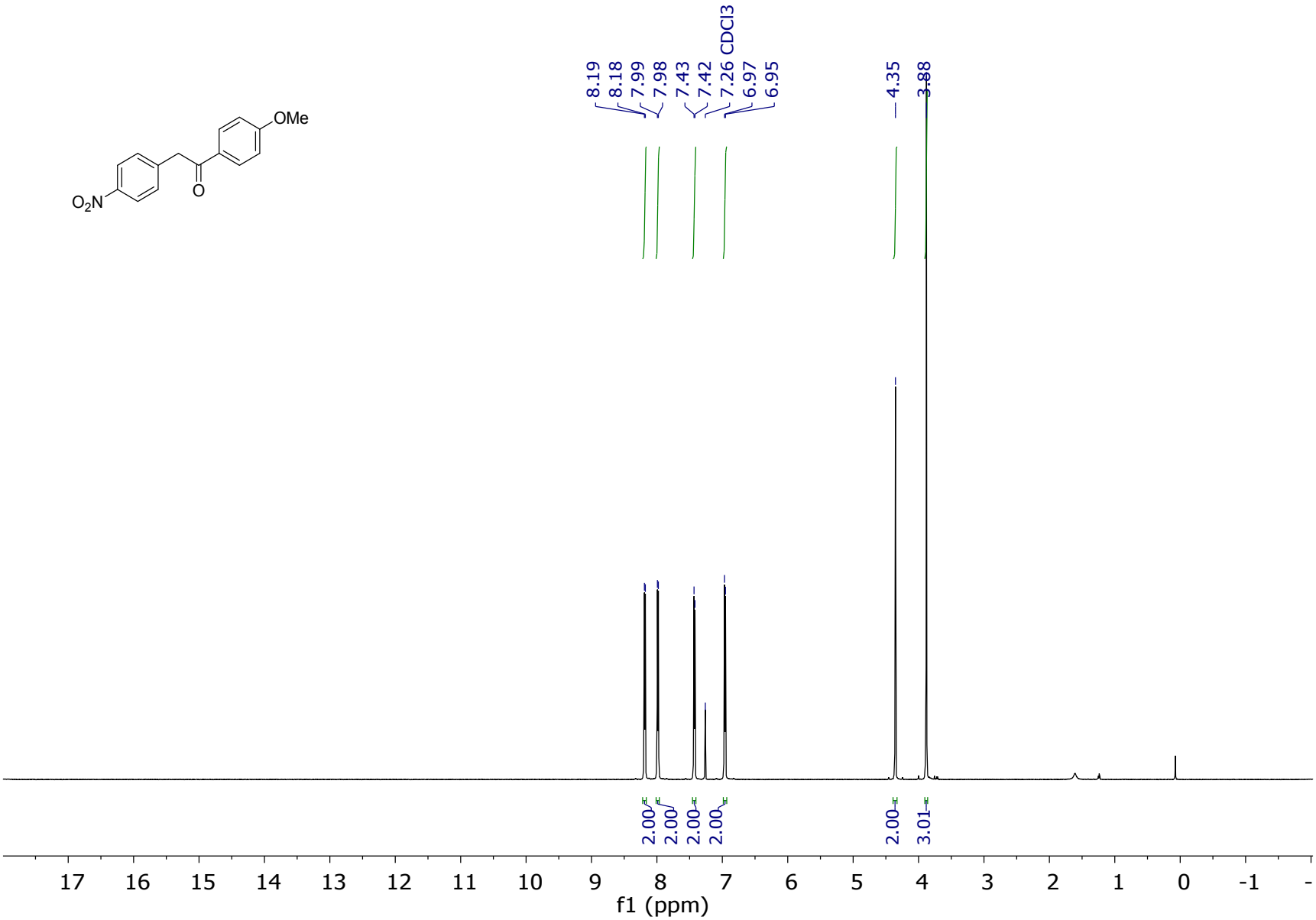


Figure S13. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethanone (7a).

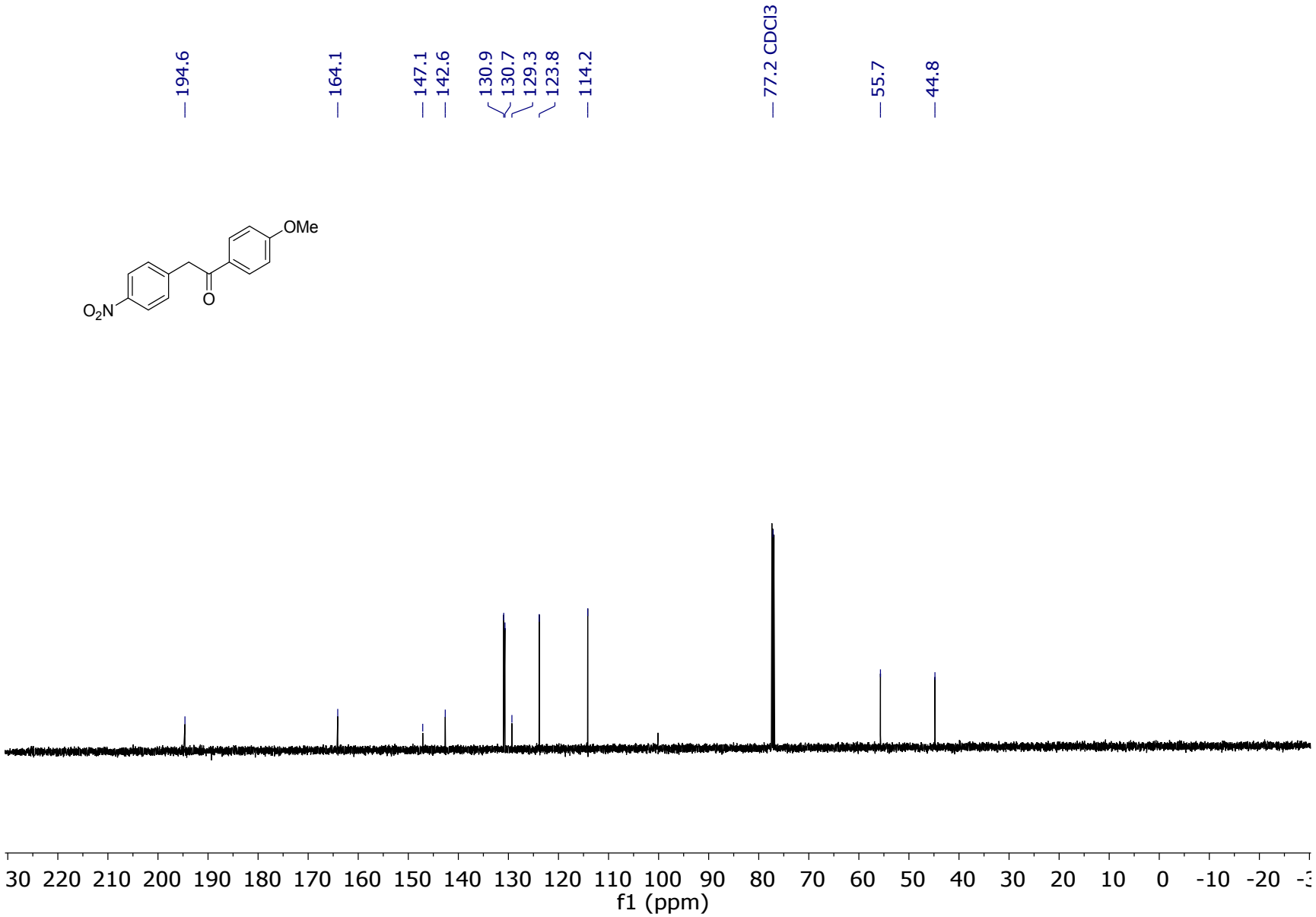


Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethanone (7a).

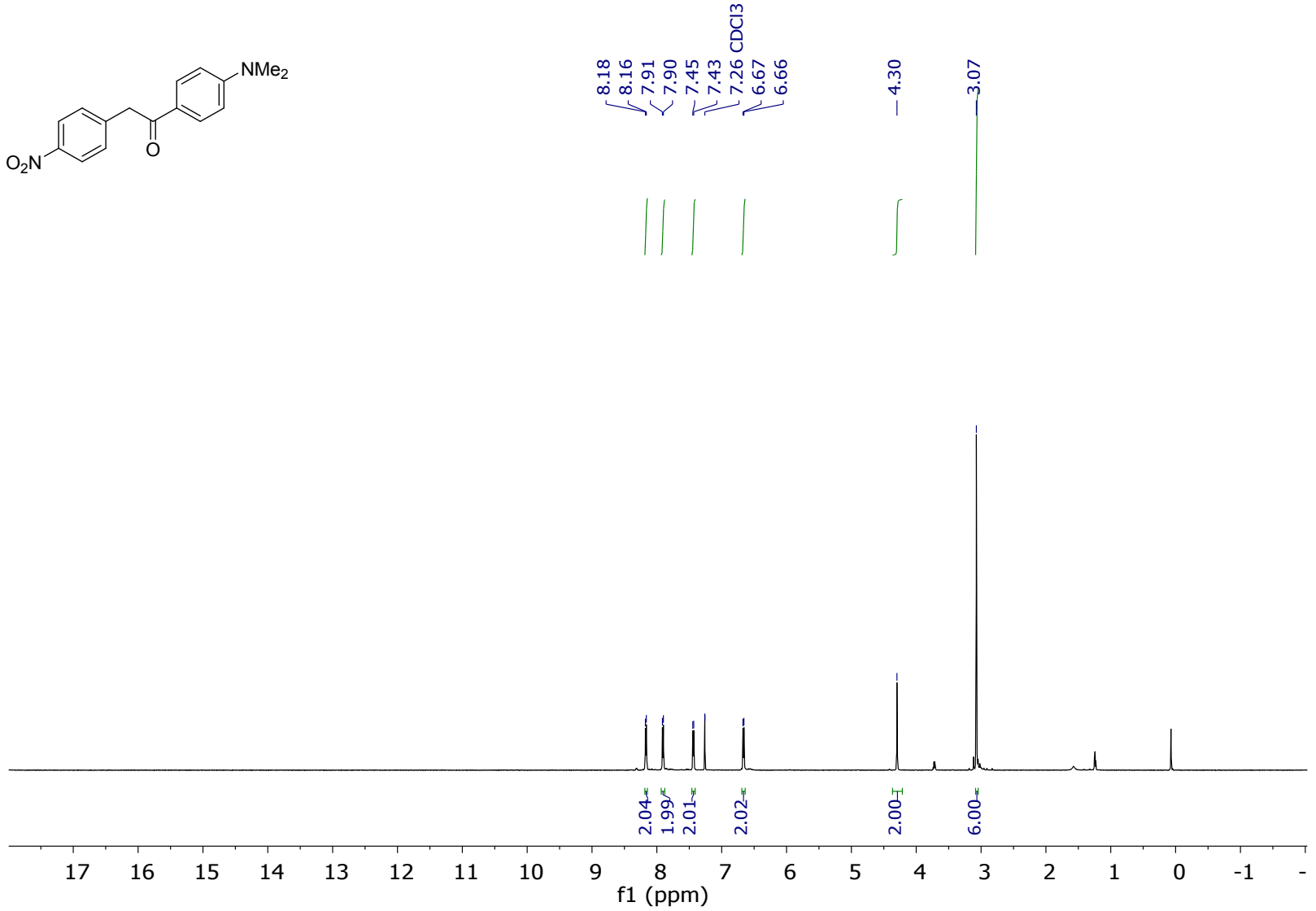


Figure S15. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-(dimethylamino)phenyl)-2-(4-nitrophenyl)ethanone (8a).

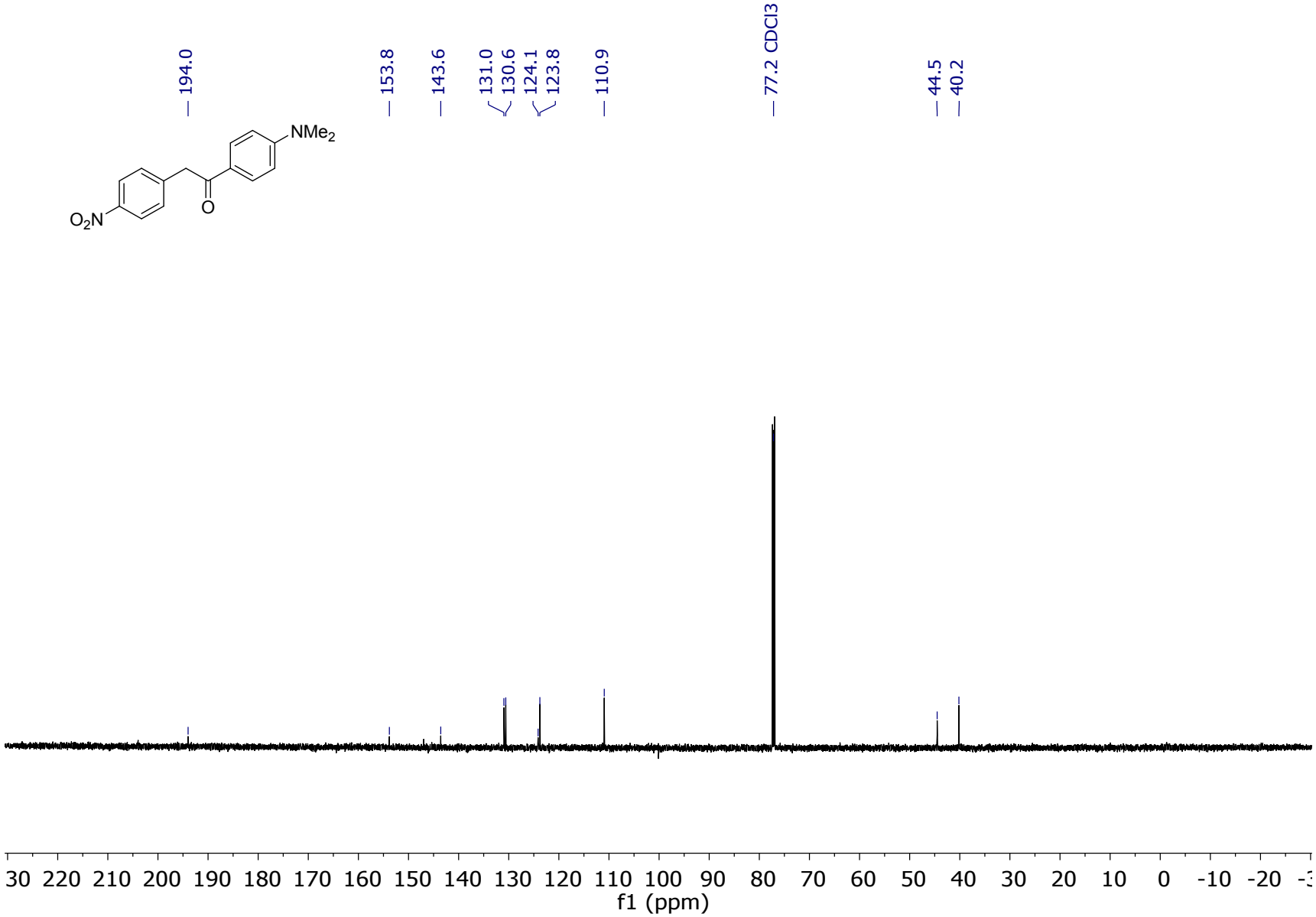


Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-(dimethylamino)phenyl)-2-(4-nitrophenyl)ethanone (8a).

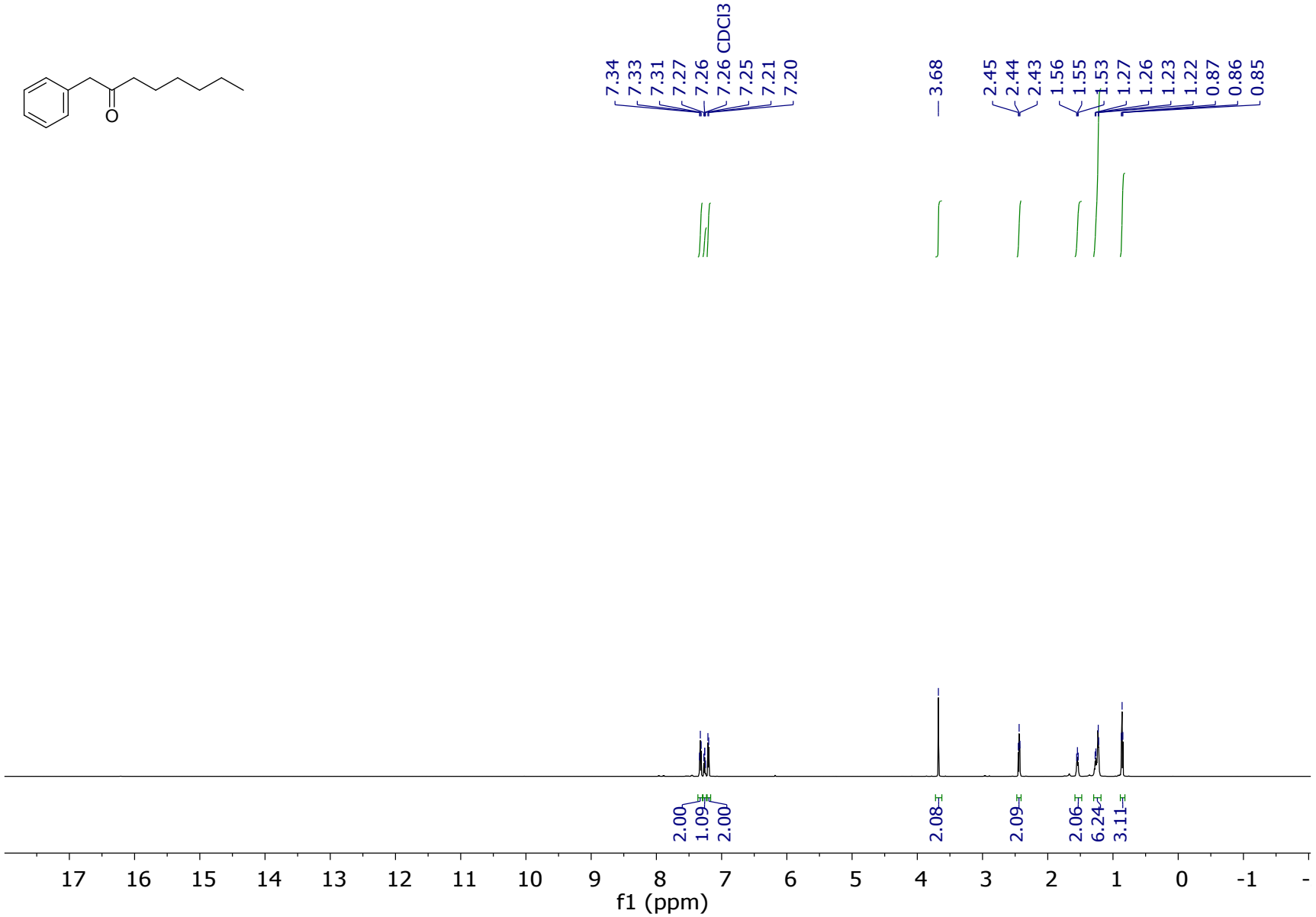


Figure S17. ^{1}H NMR (600 MHz, Chloroform-d) of 1-phenyloctan-2-one (9b).

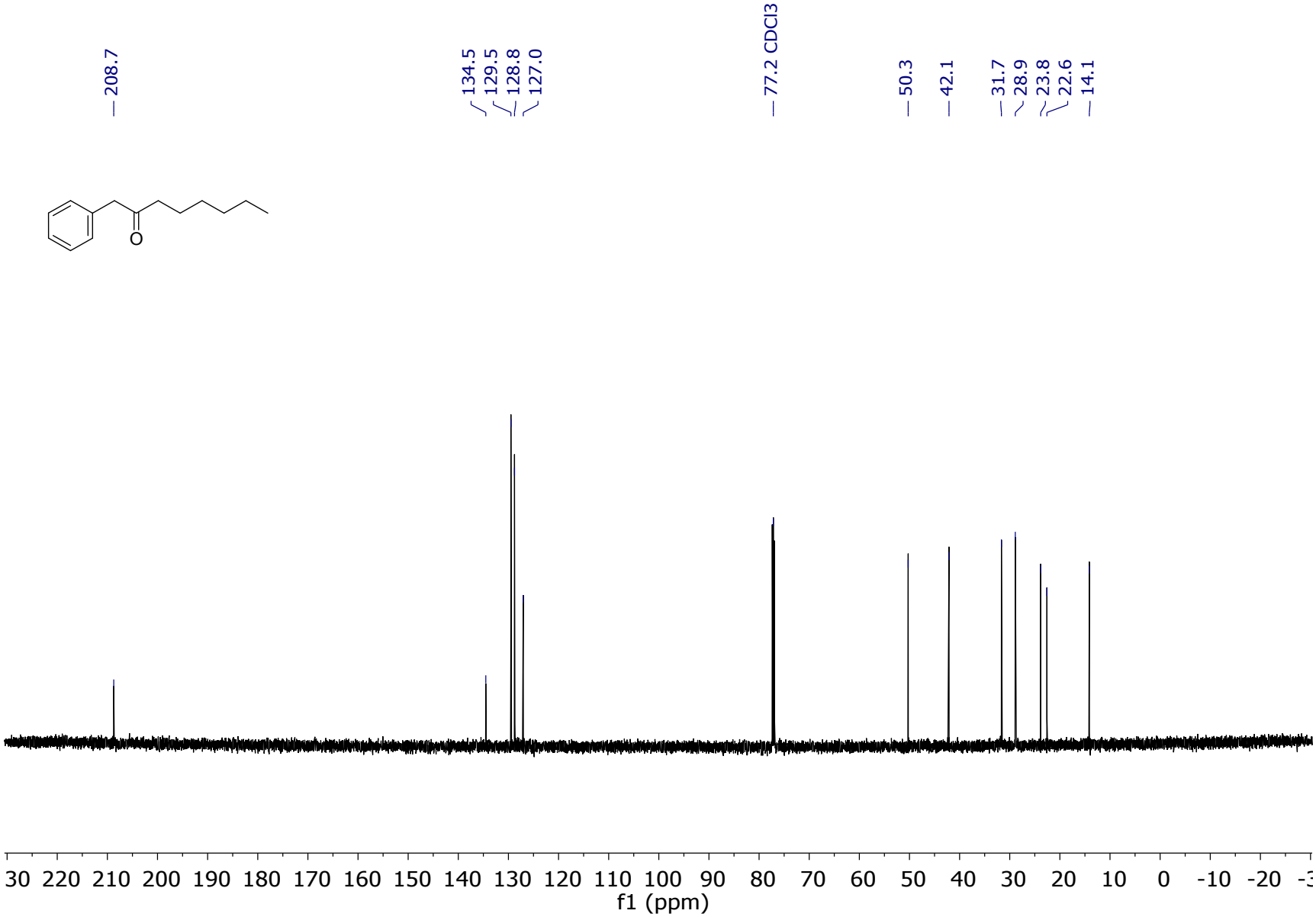


Figure S18. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-phenyloctan-2-one (9b).

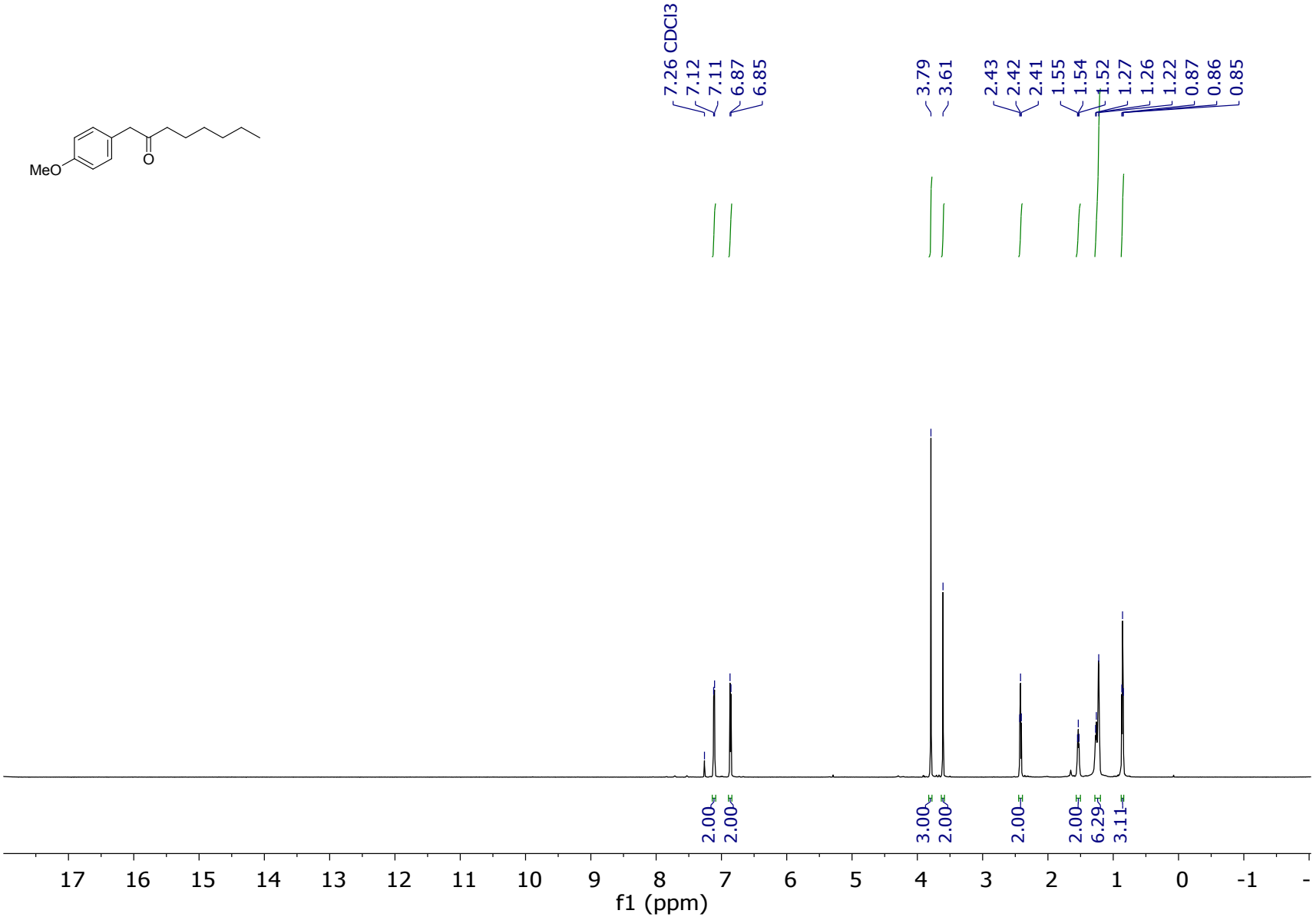


Figure S19. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-methoxyphenyl)octan-2-one (10b).

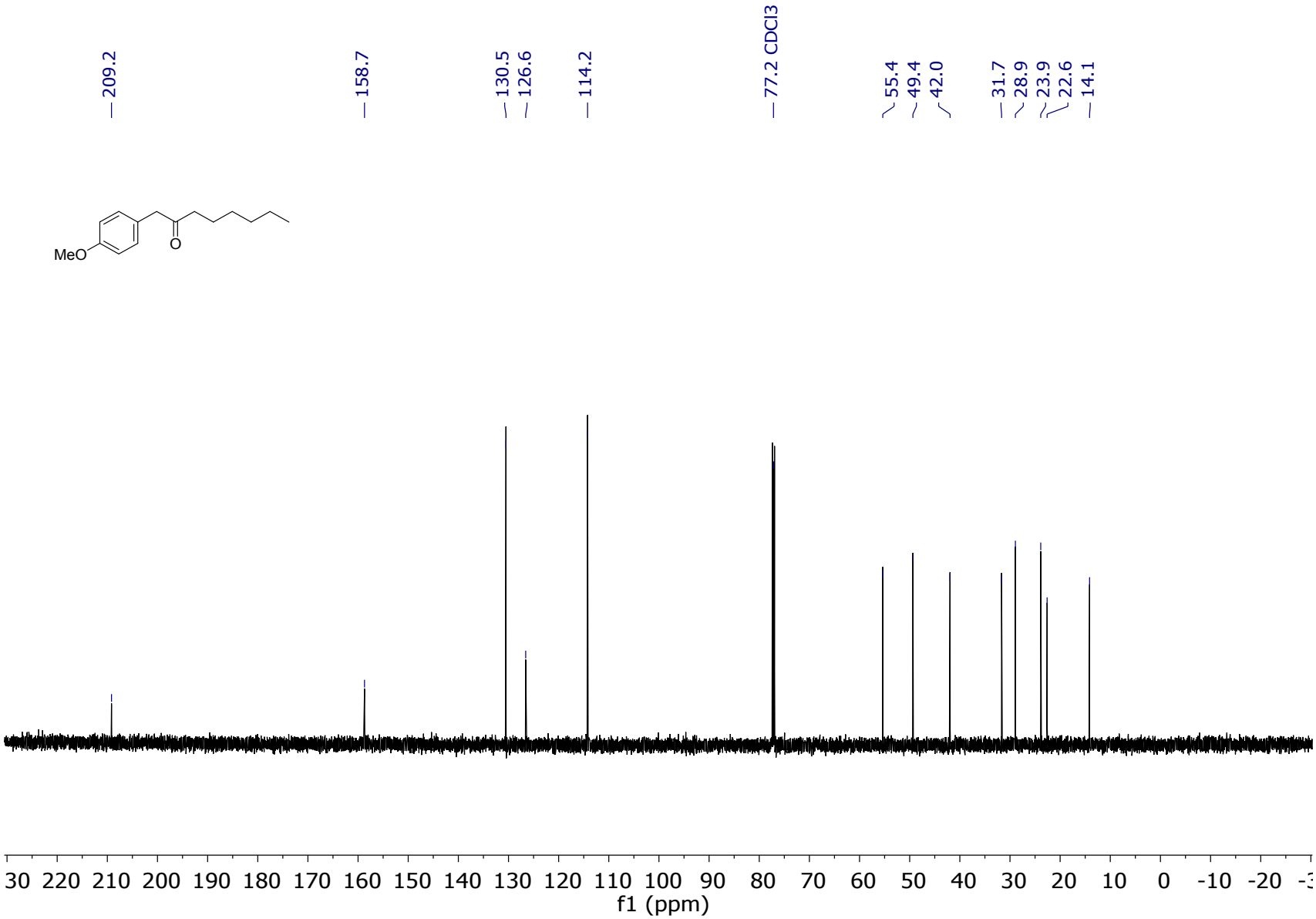


Figure S20. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-methoxyphenyl)octan-2-one (10b).

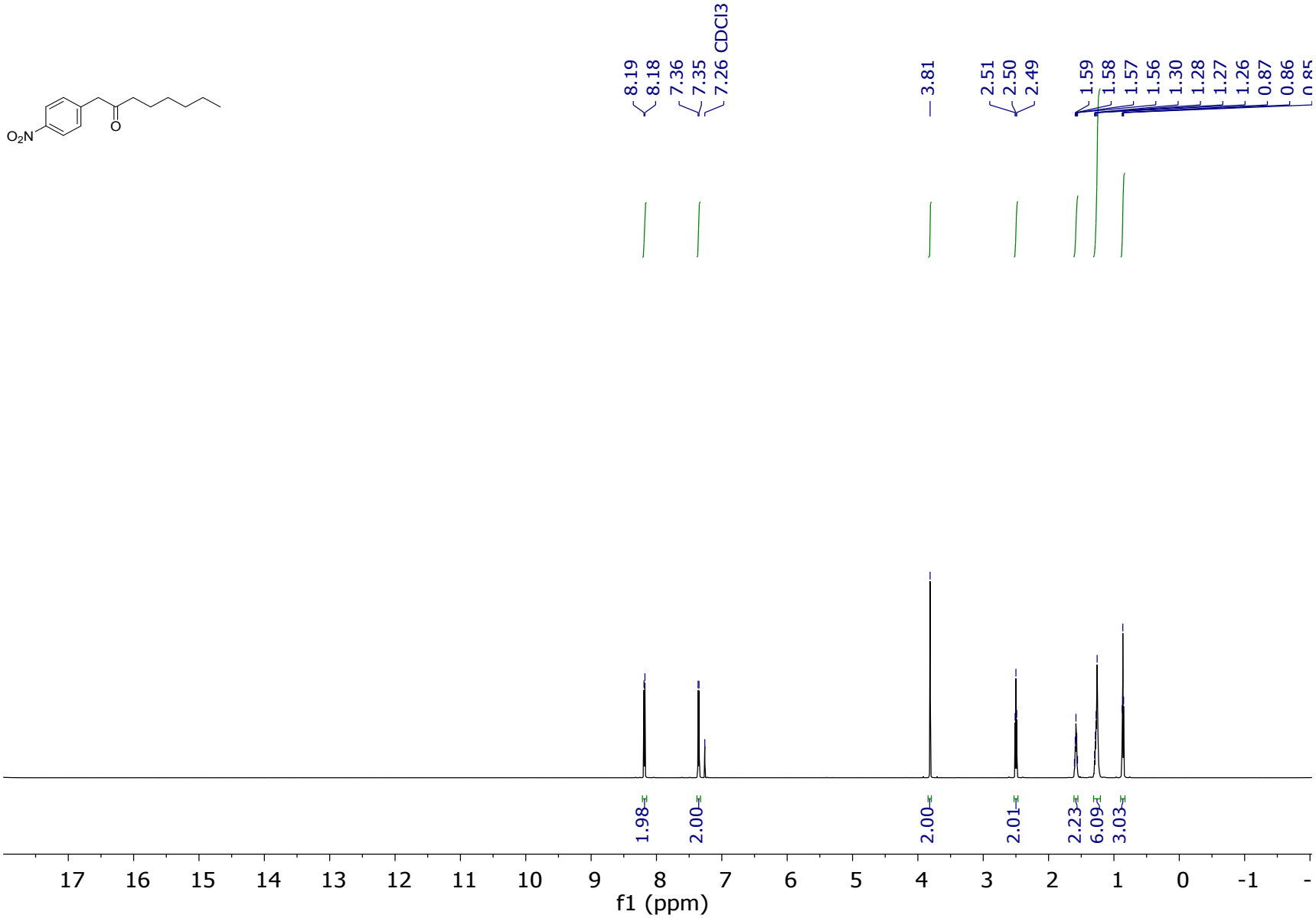


Figure S21. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-nitrophenyl)octan-2-one (11b).

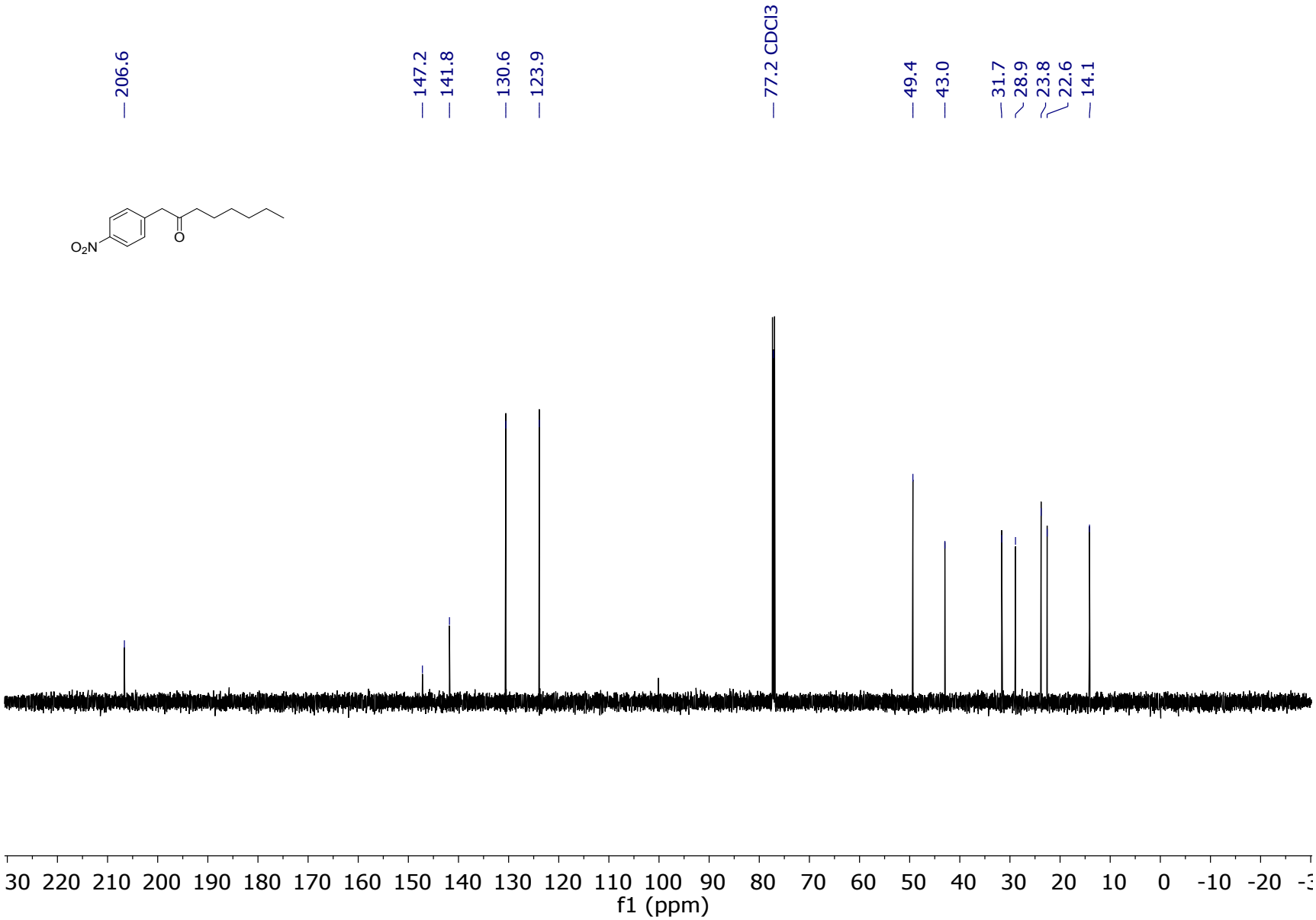


Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-nitrophenyl)octan-2-one (11b).

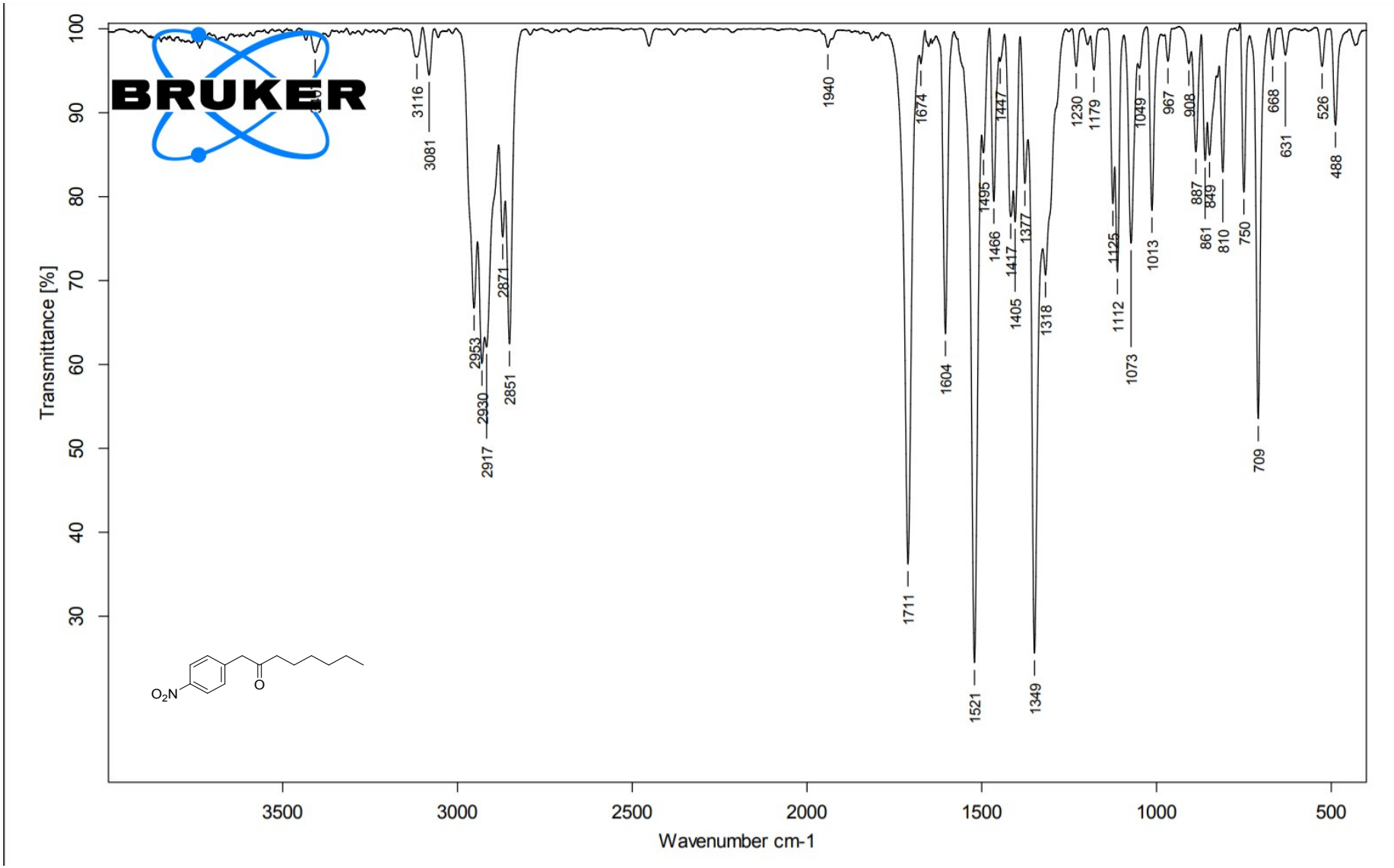


Figure S23. FT-IR spectra of 1-(4-nitrophenyl)octan-2-one (11b).

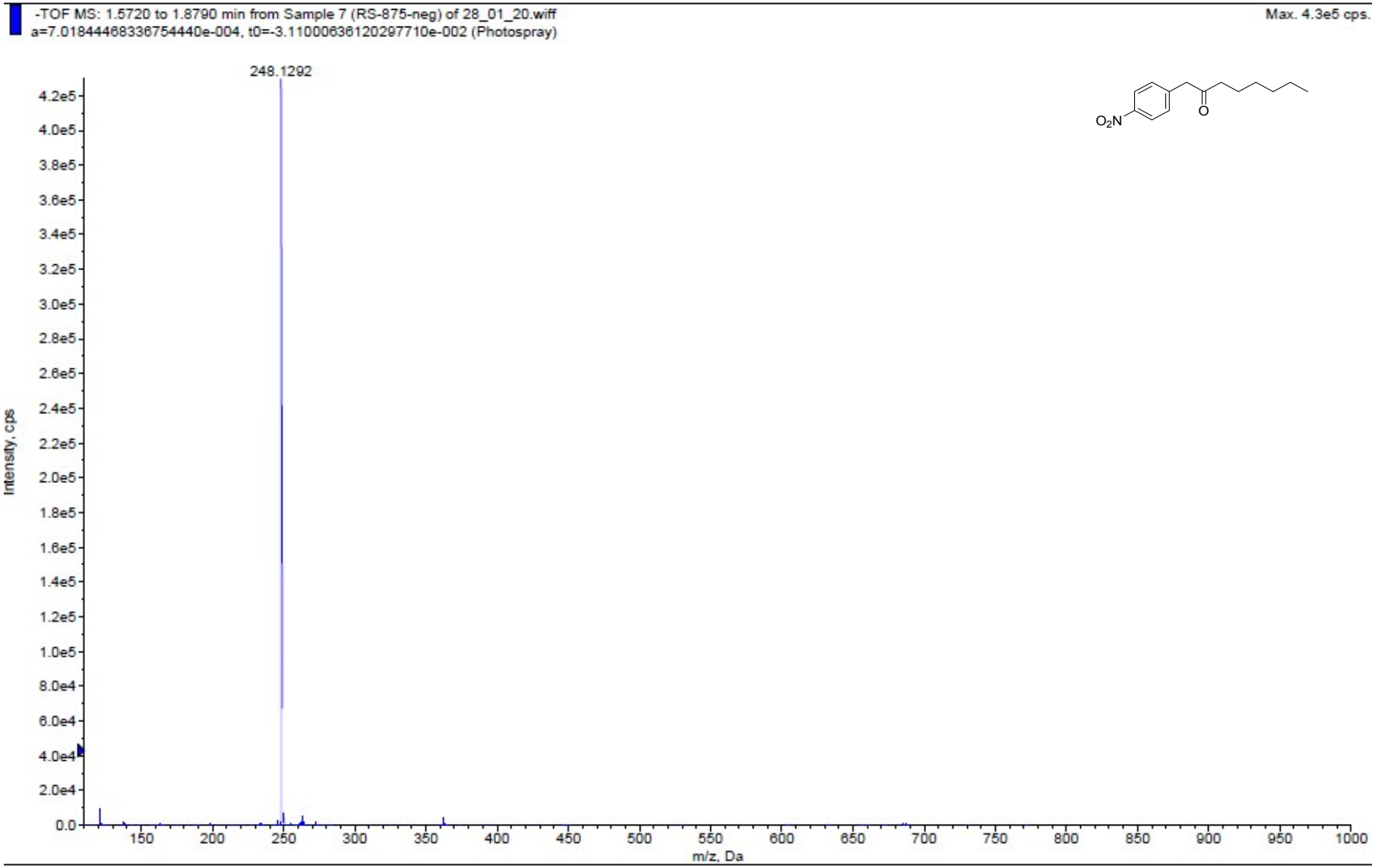


Figure S24. HRMS spectra of 1-(4-nitrophenyl)octan-2-one (11b).

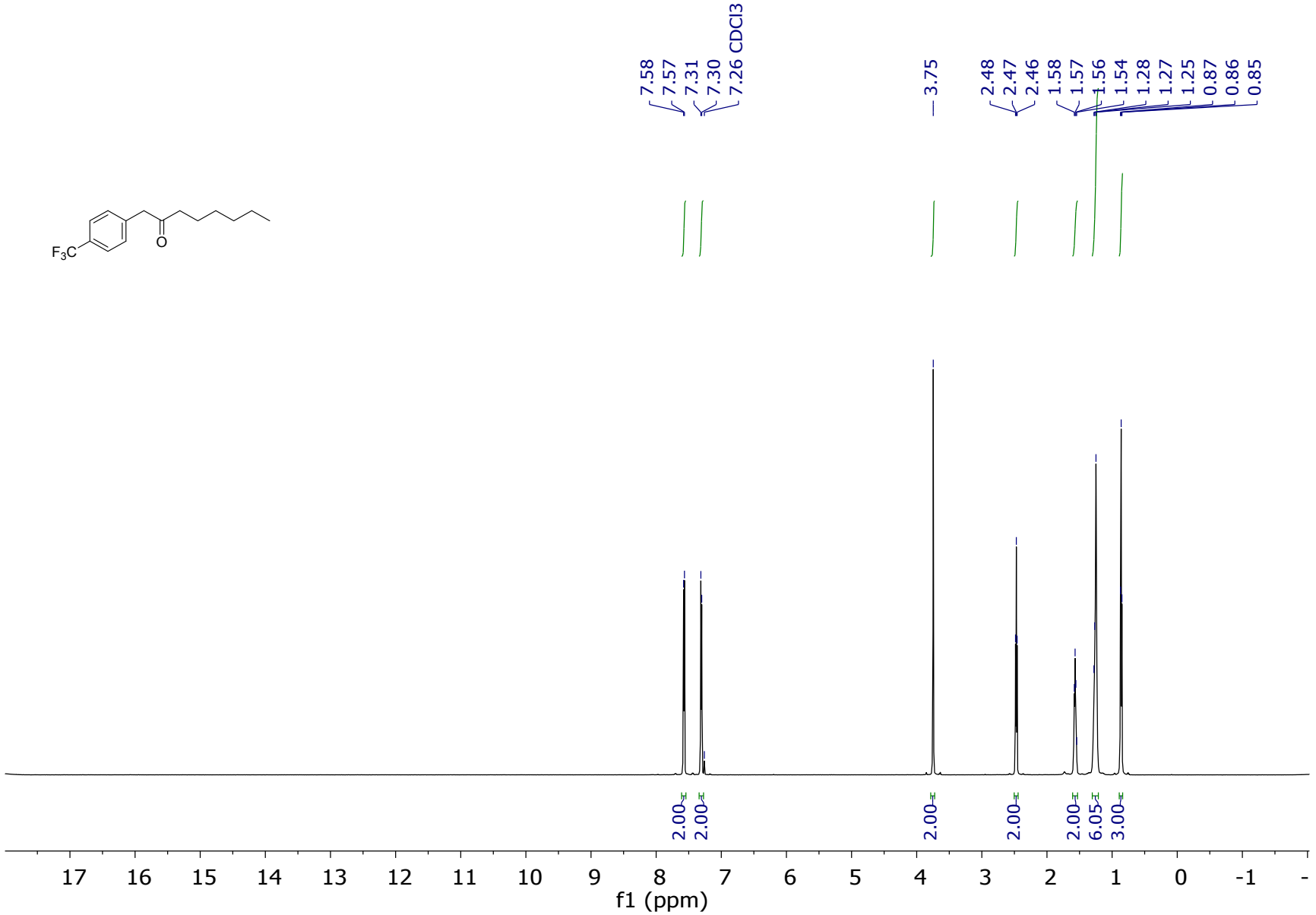


Figure S25. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-(trifluoromethyl)phenyl)octan-2-one (12b).

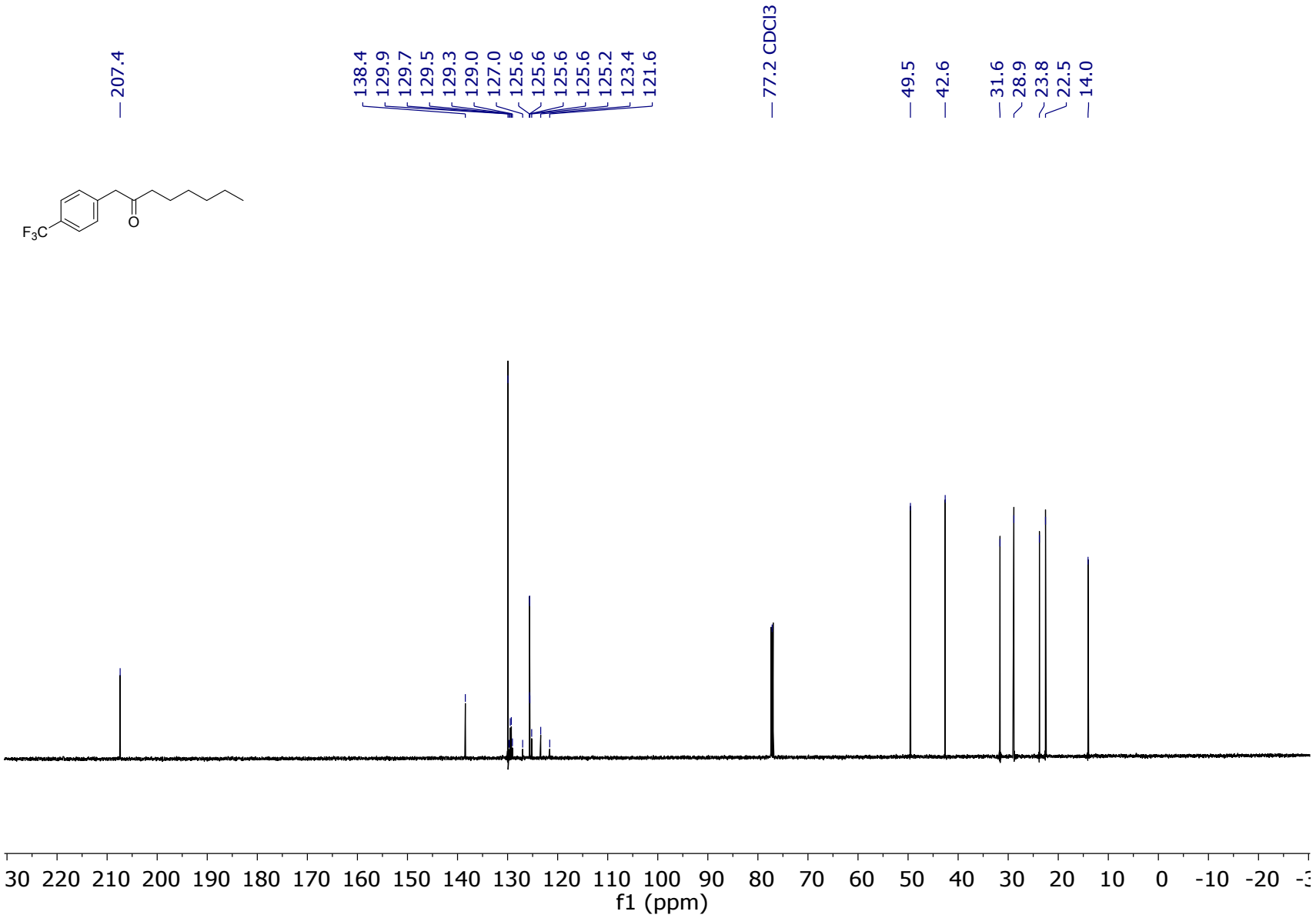


Figure S26. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-(trifluoromethyl)phenyl)octan-2-one (12b).

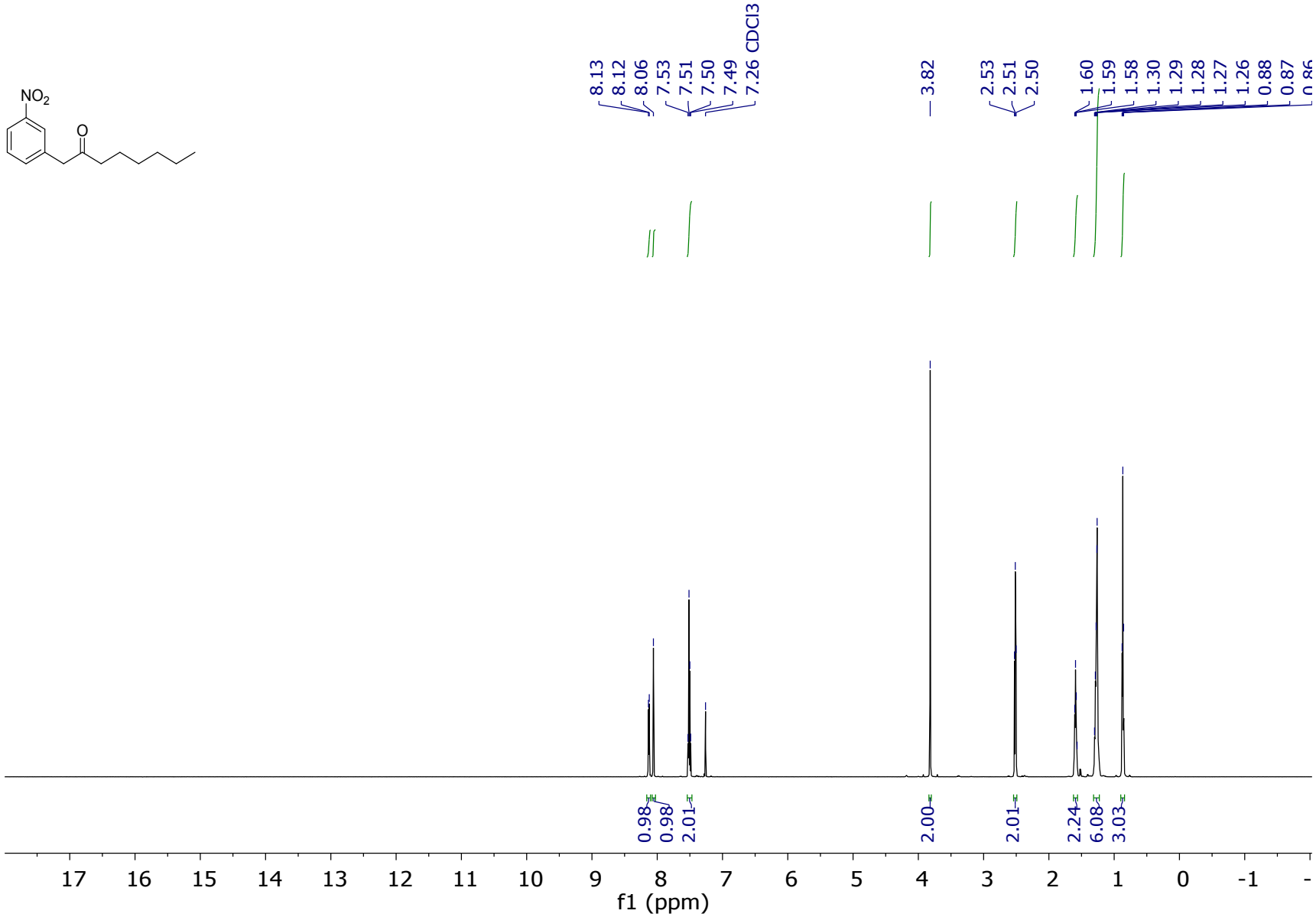


Figure S27. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(3-nitrophenyl)octan-2-one (13b).

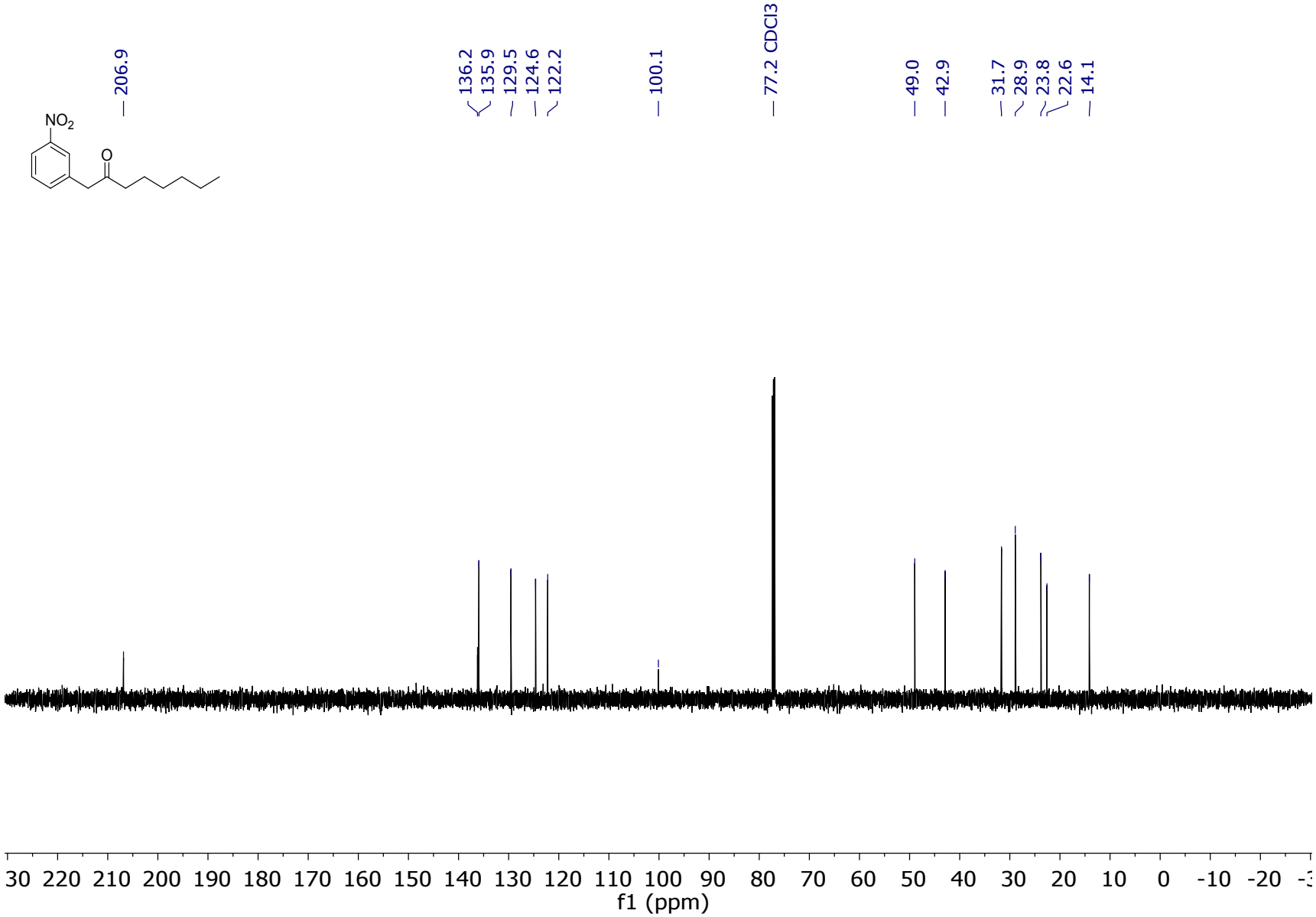


Figure S28. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(3-nitrophenyl)octan-2-one (13b).

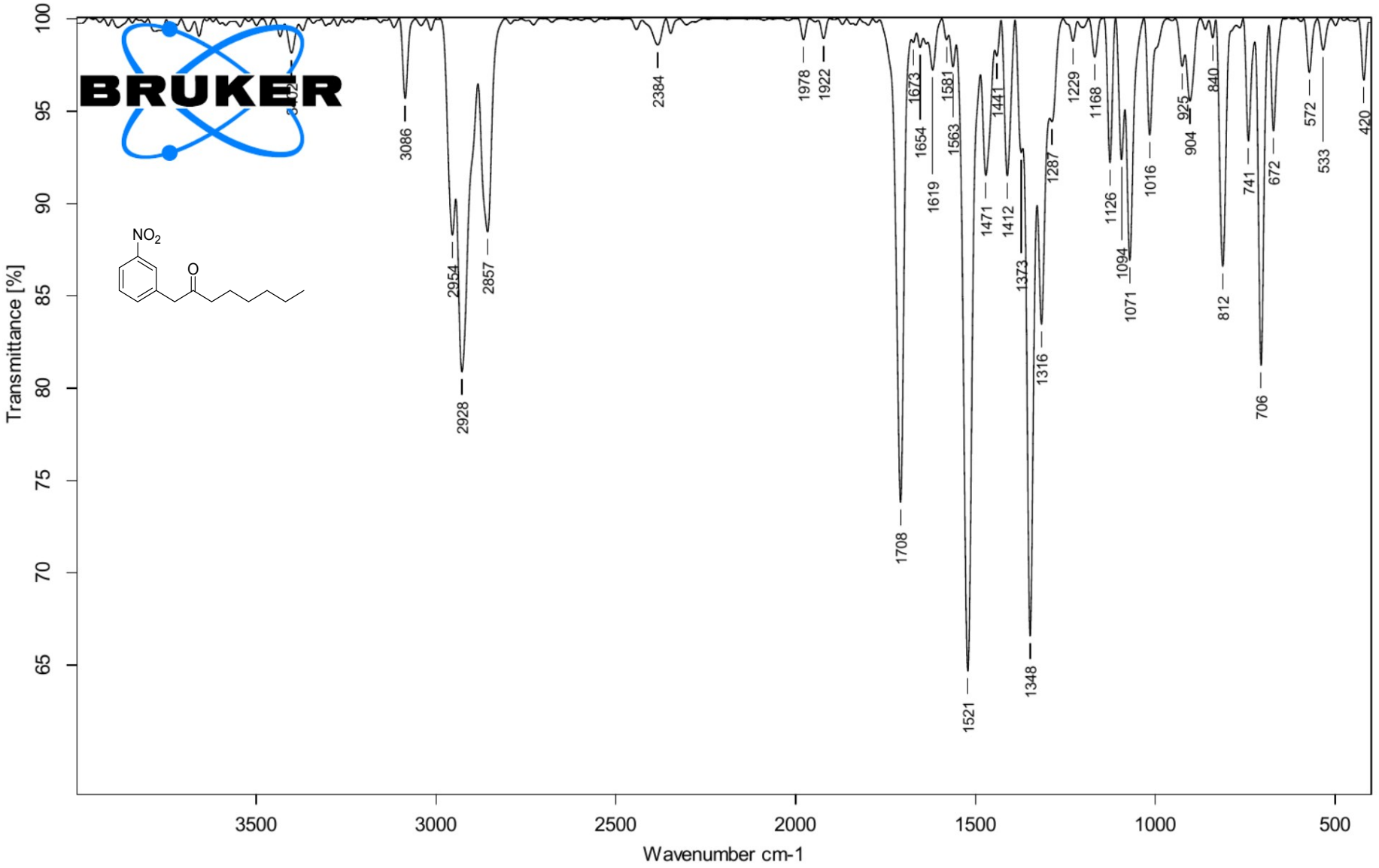


Figure S29. FT-IR spectra of 1-(3-nitrophenyl)octan-2-one (13b).

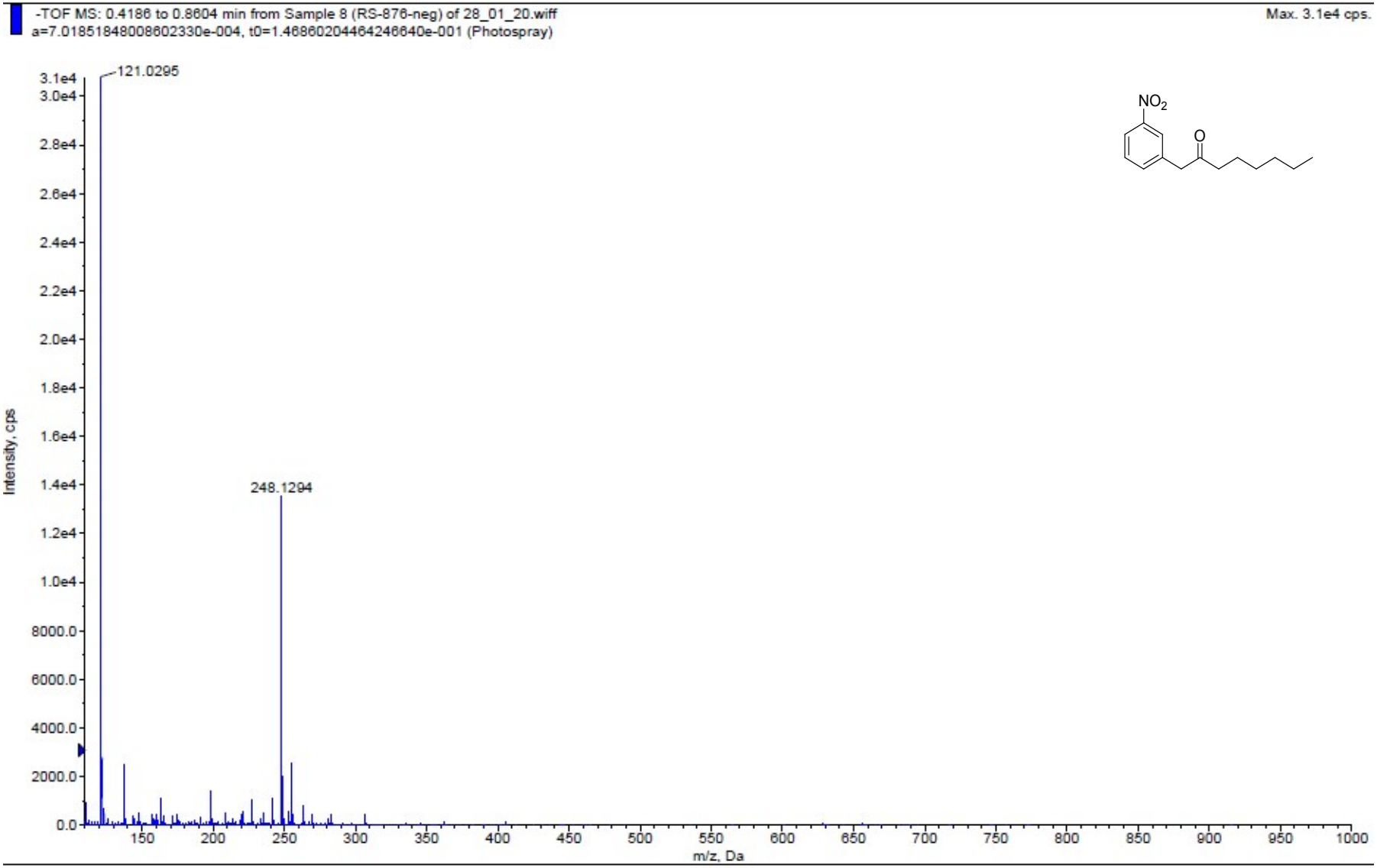


Figure S30. HRMS spectra of 1-(3-nitrophenyl)octan-2-one (13b).

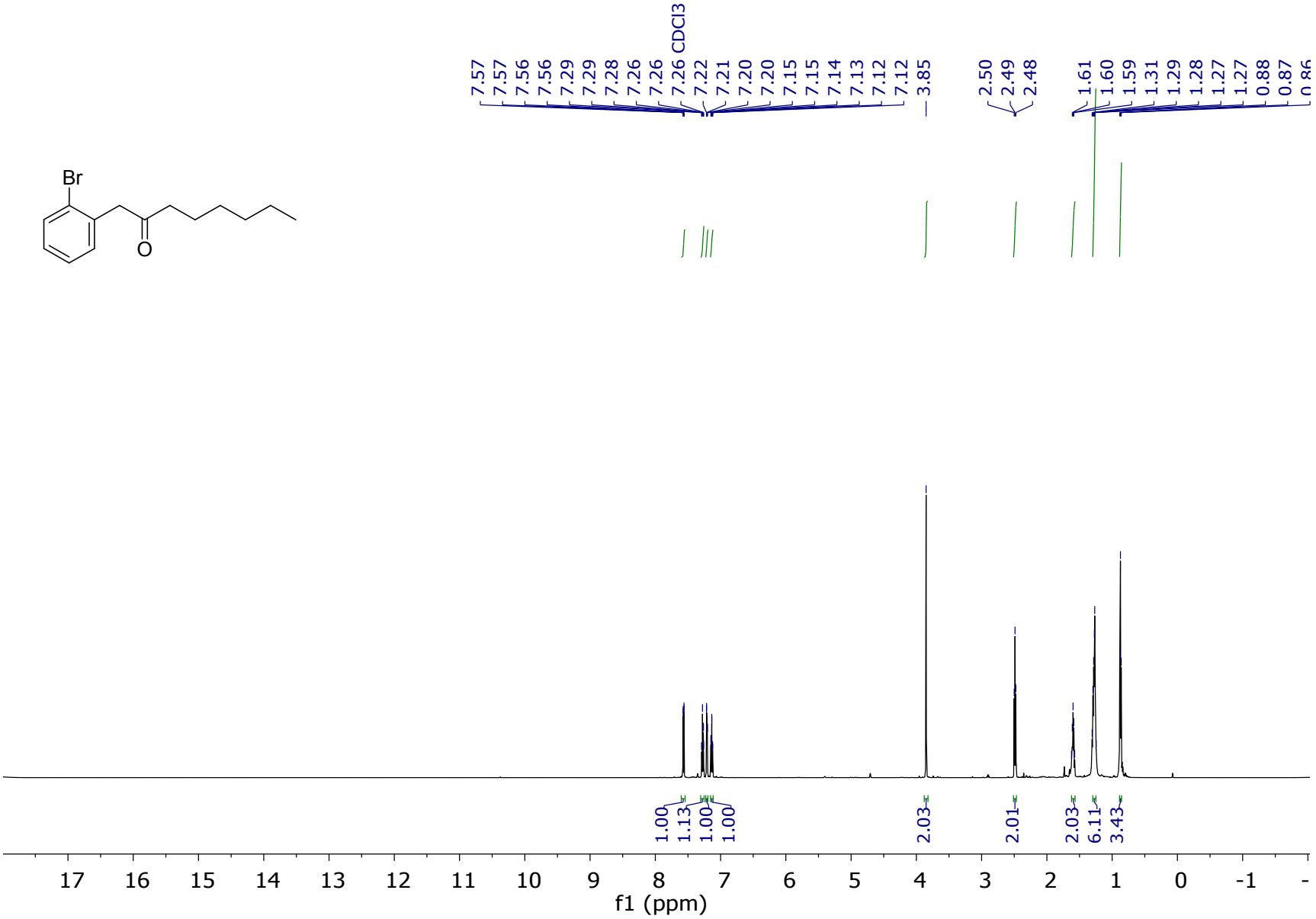


Figure S31. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(2-bromophenyl)octan-2-one (14b).

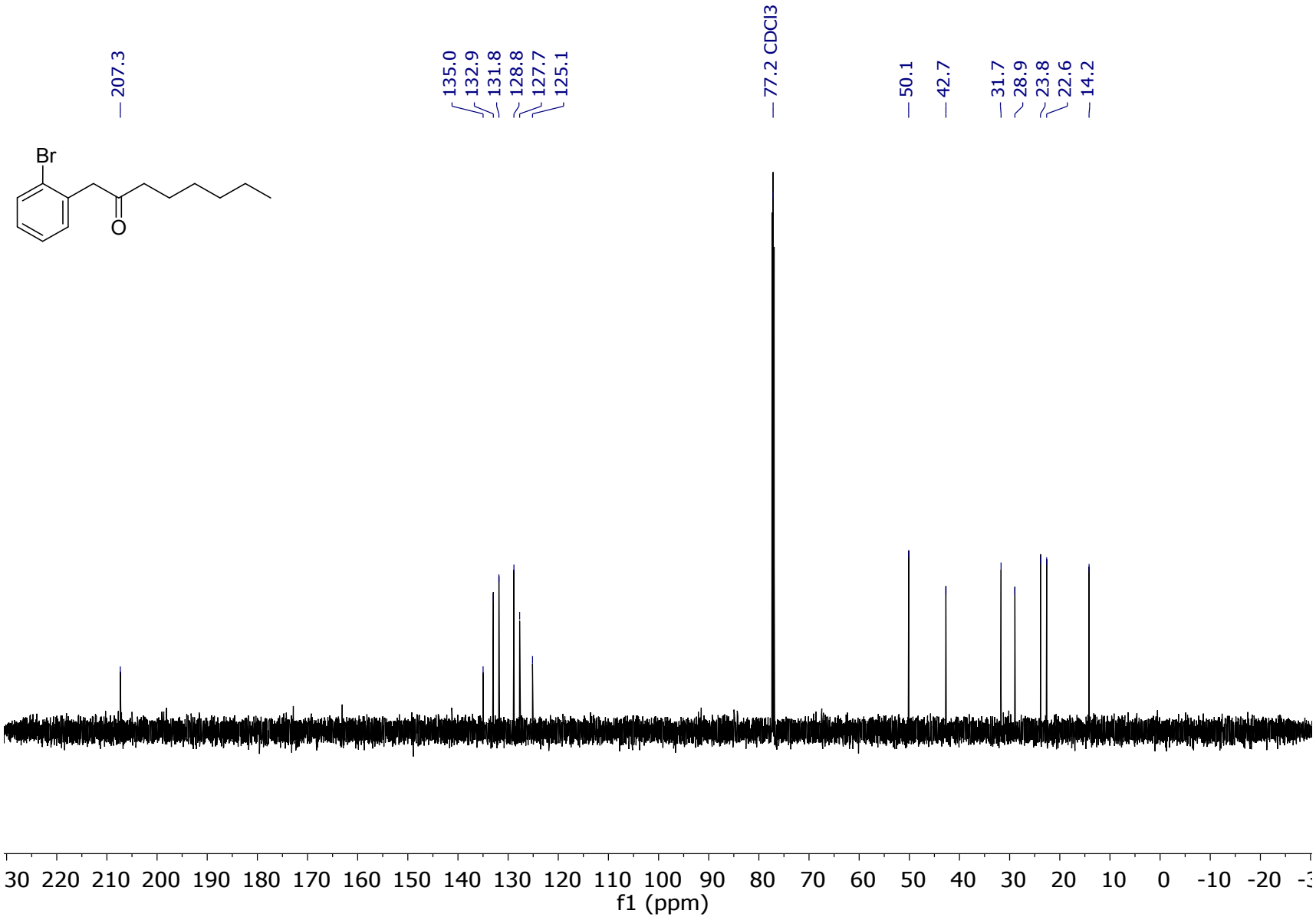


Figure S32. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(2-bromophenyl)octan-2-one (14b).

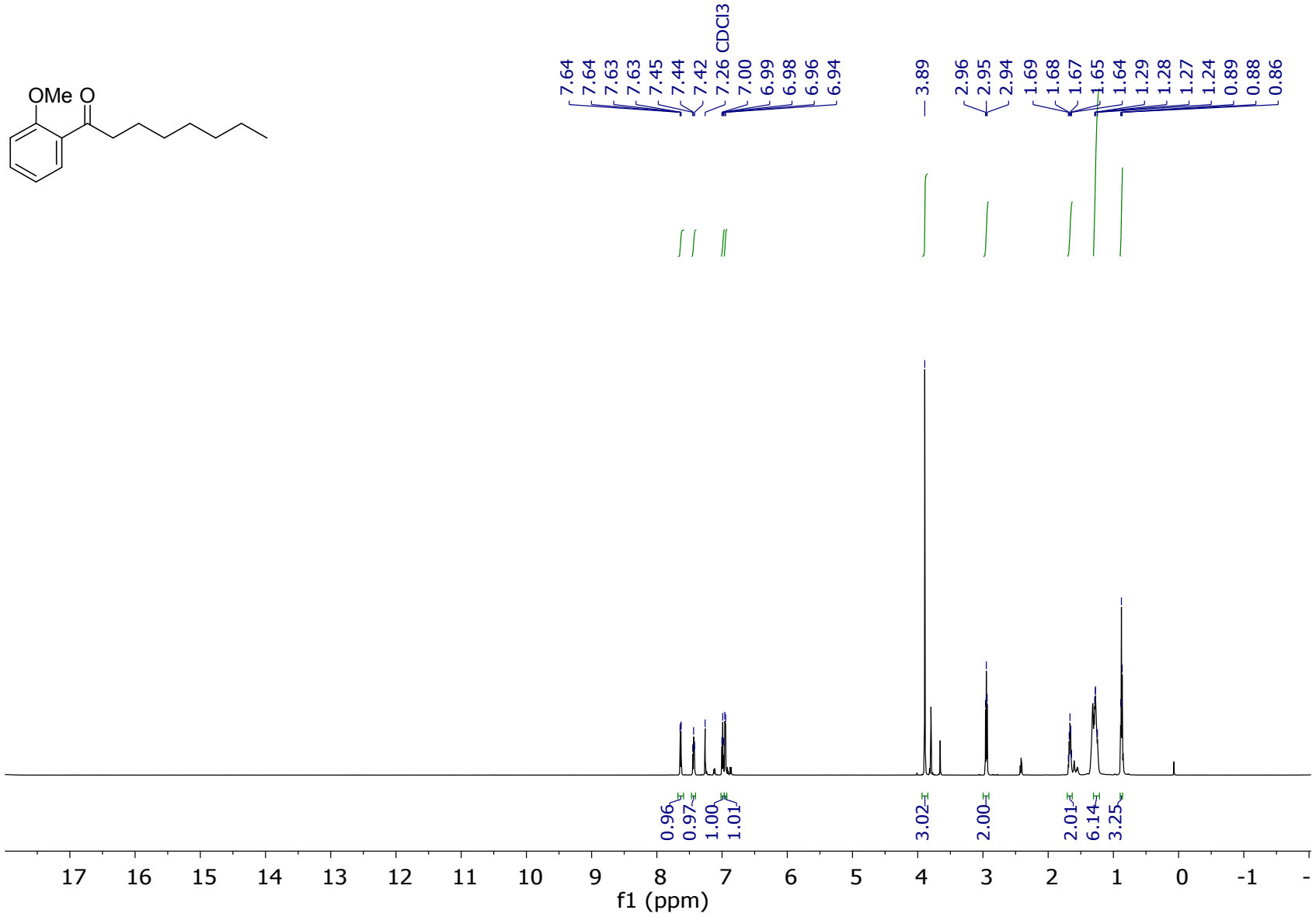


Figure S36. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(2-methoxyphenyl)octan-1-one (15a).

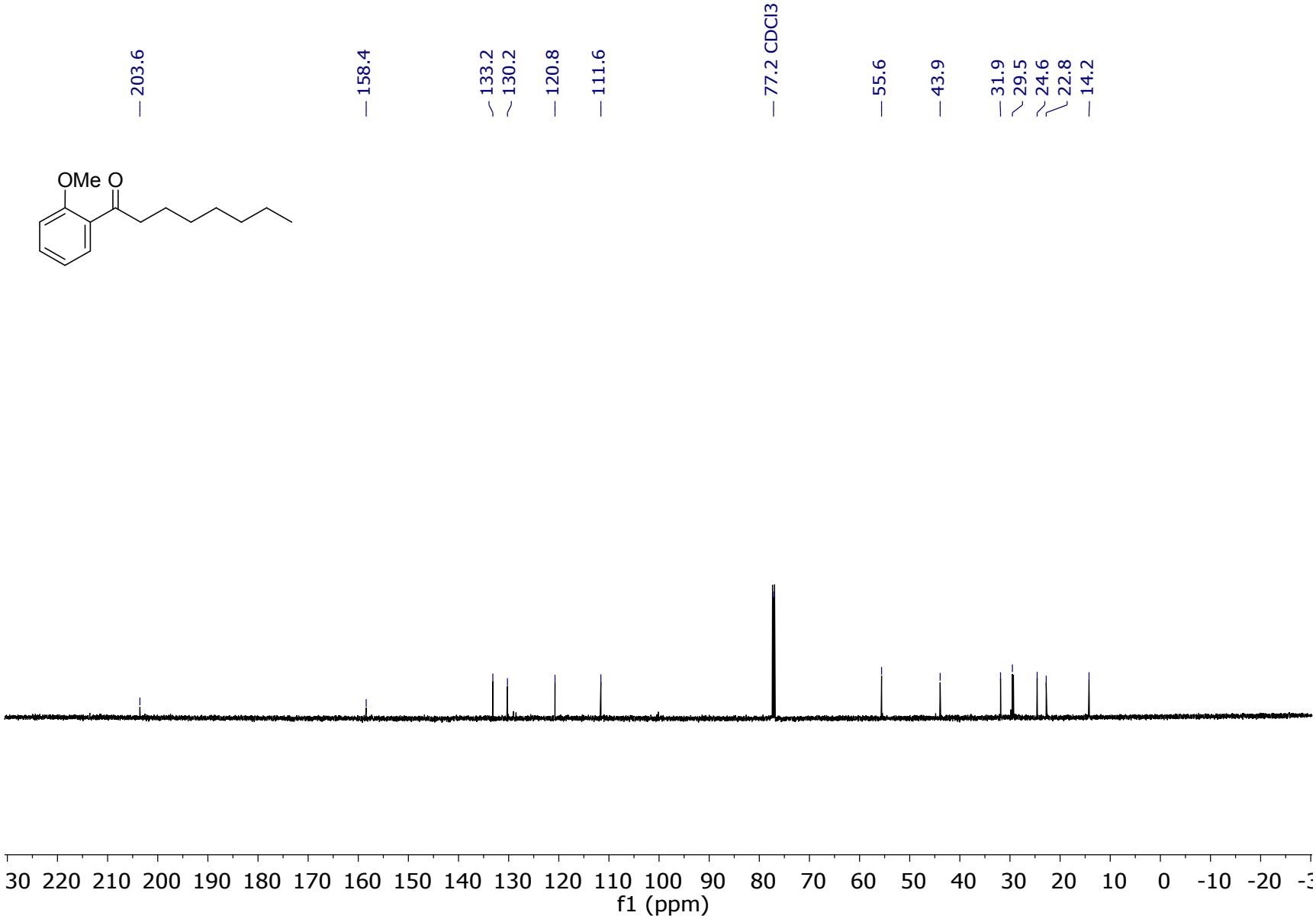


Figure S37. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(2-methoxyphenyl)octan-1-one (15a).

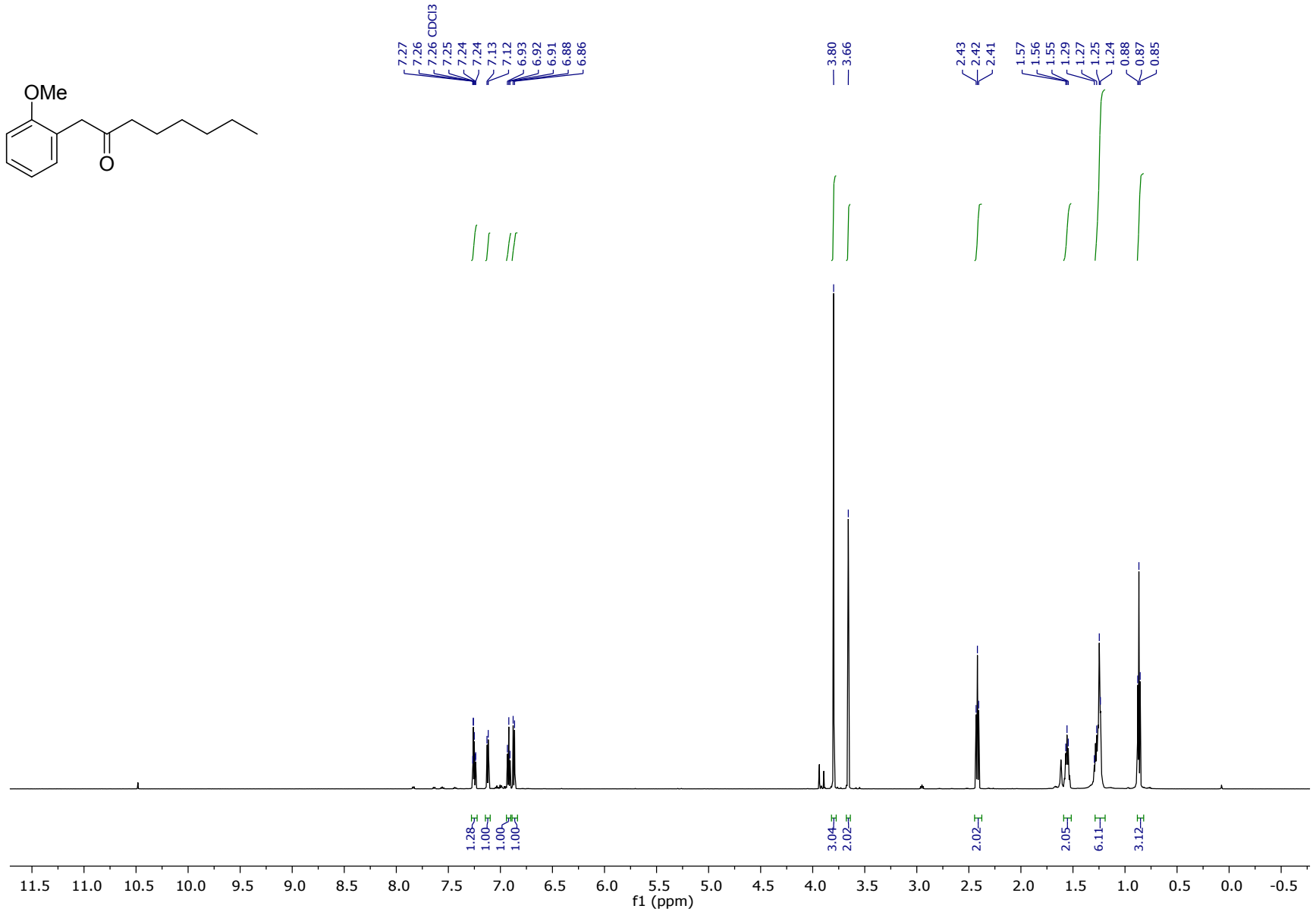


Figure S33. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(2-methoxyphenyl)octan-2-one (15b).

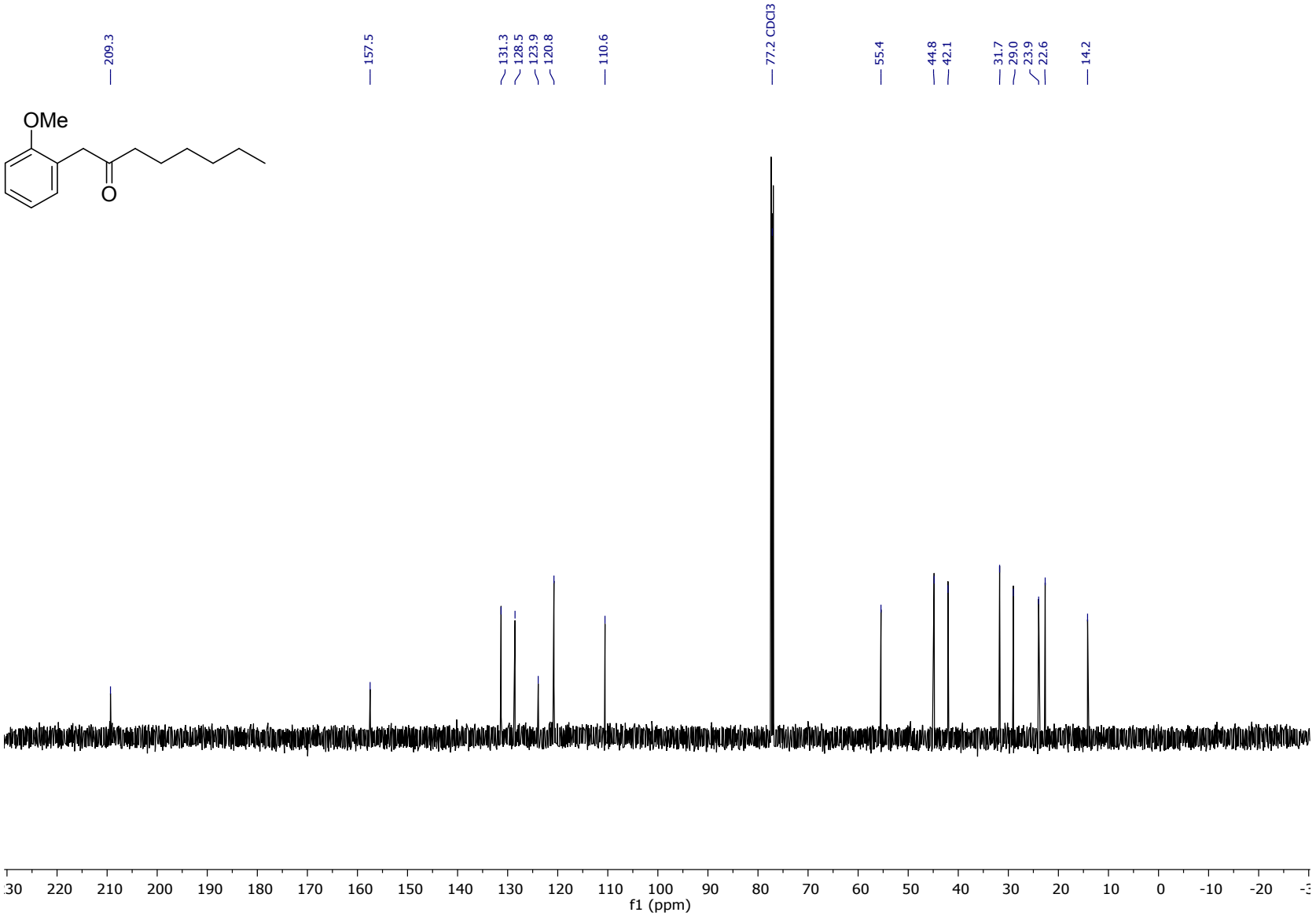


Figure S34. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(2-methoxyphenyl)octan-2-one (15b).

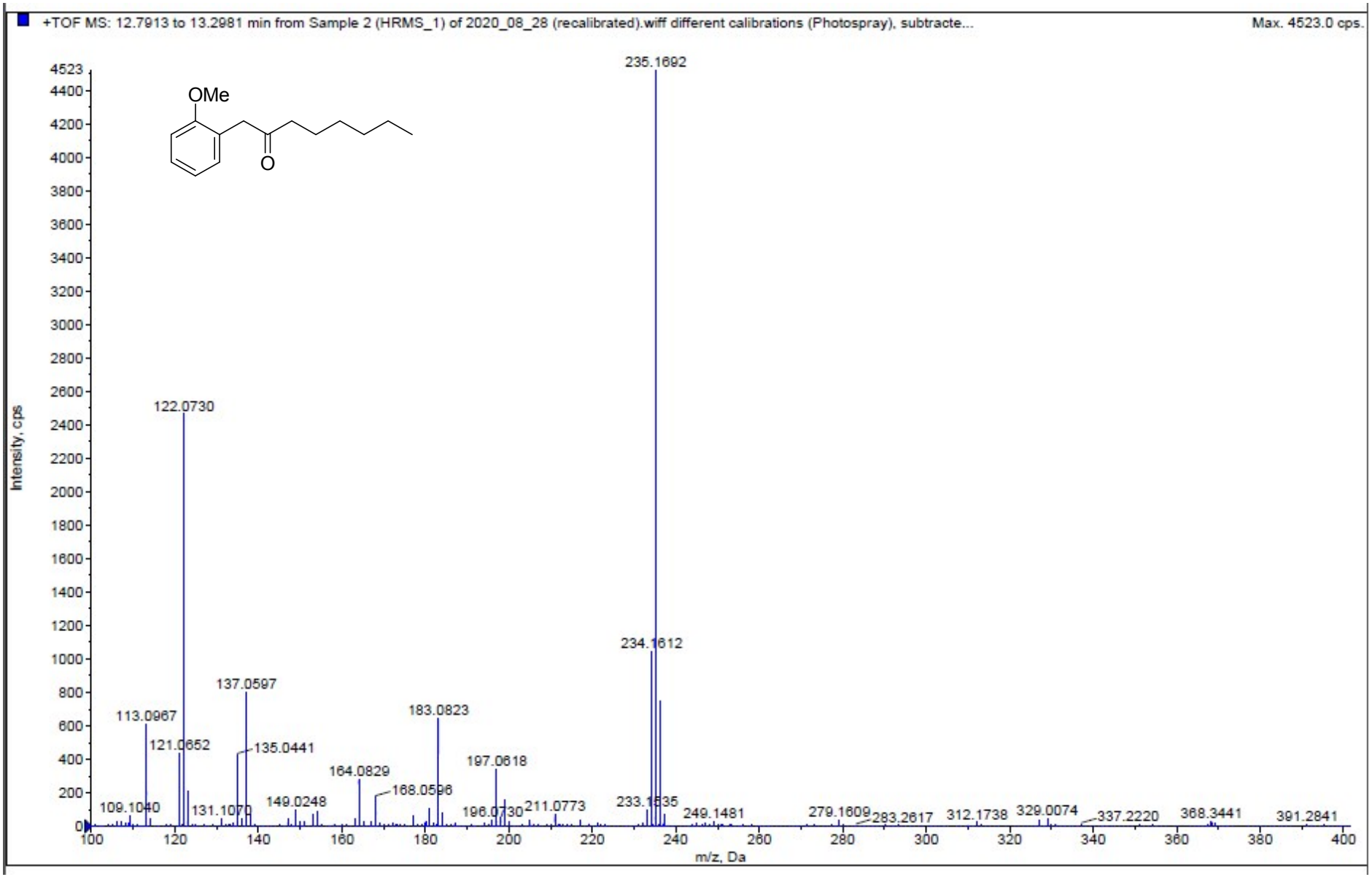


Figure S35. HRMS spectra of 1-(2-methoxyphenyl)octan-2-one (15b).

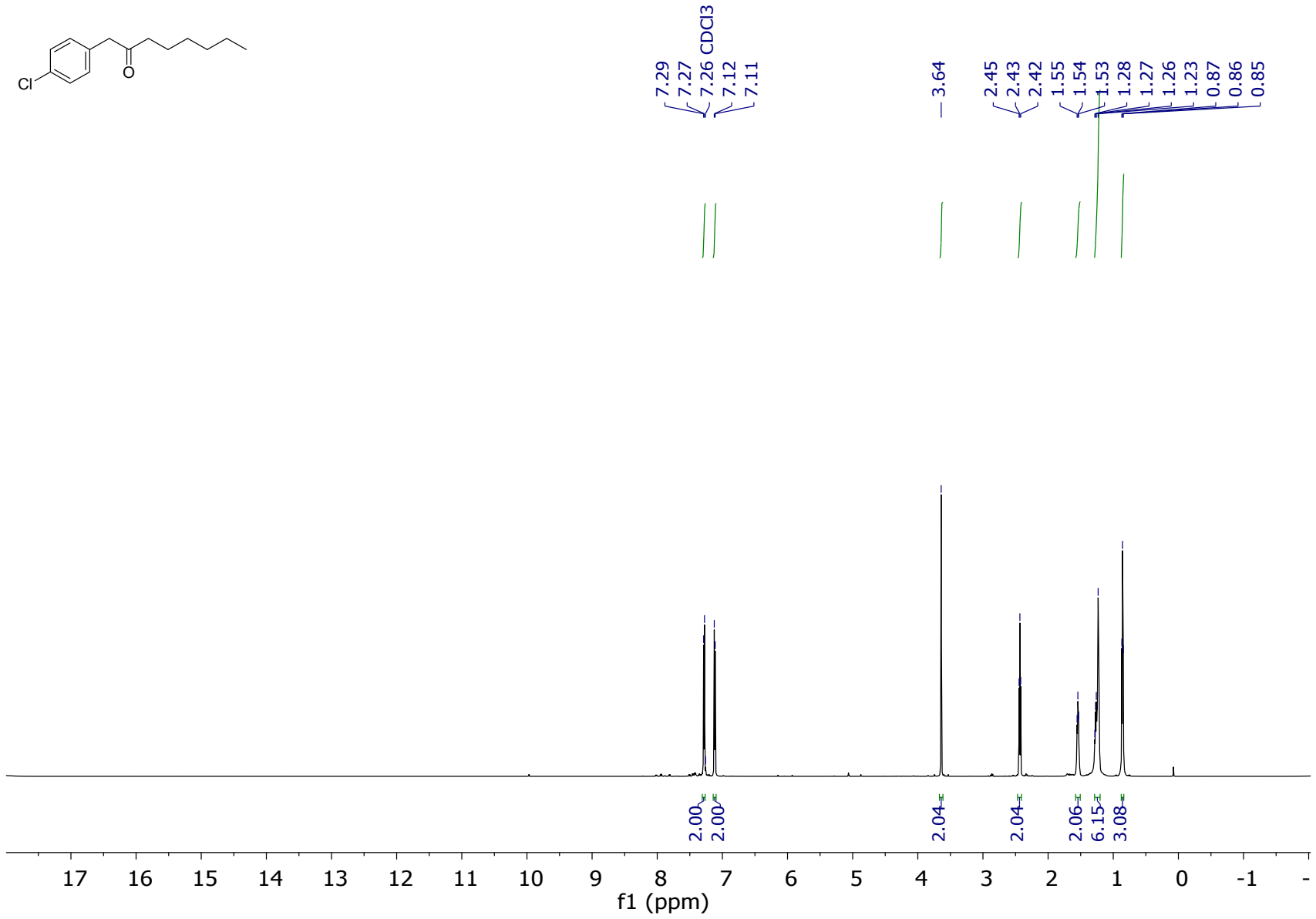


Figure S43. ^{1}H NMR (600 MHz, Chloroform-d)of 1-(4-chlorophenyl)octan-2-one (16b).

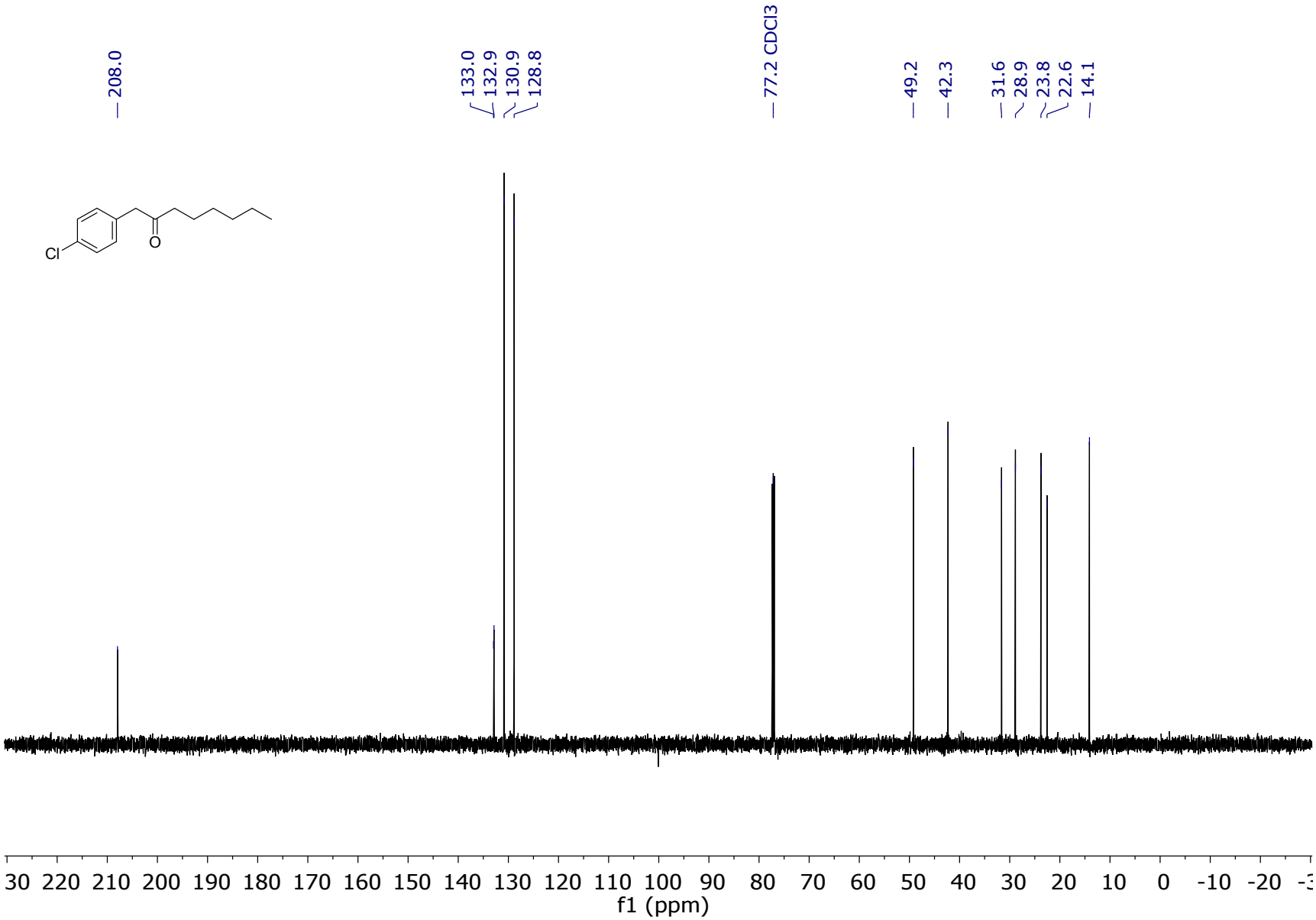


Figure S44. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-chlorophenyl)octan-2-one (16b).

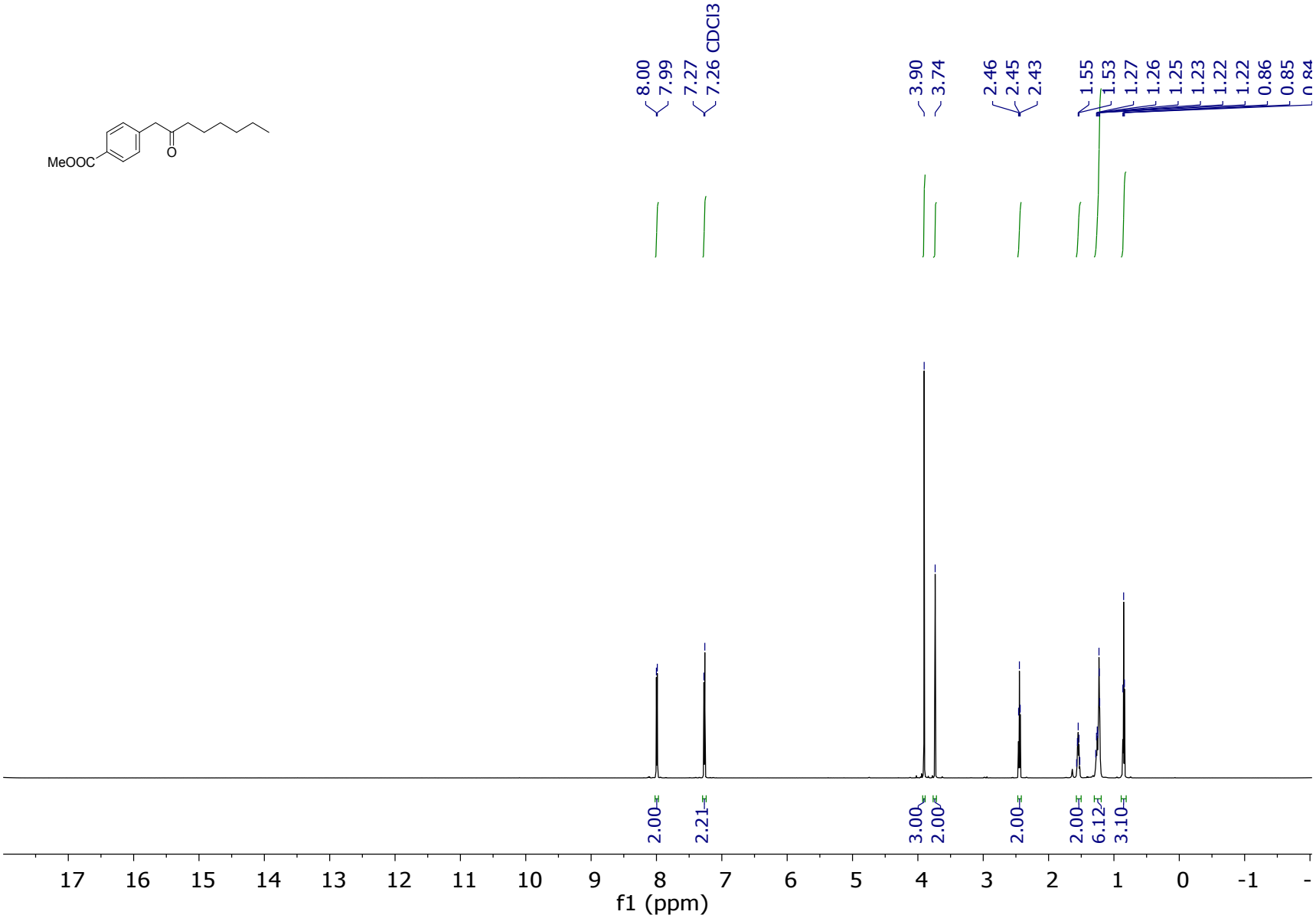


Figure S38. ^{1}H NMR (600 MHz, Chloroform-d) of methyl 4-(2-oxooctyl)benzoate (17b).

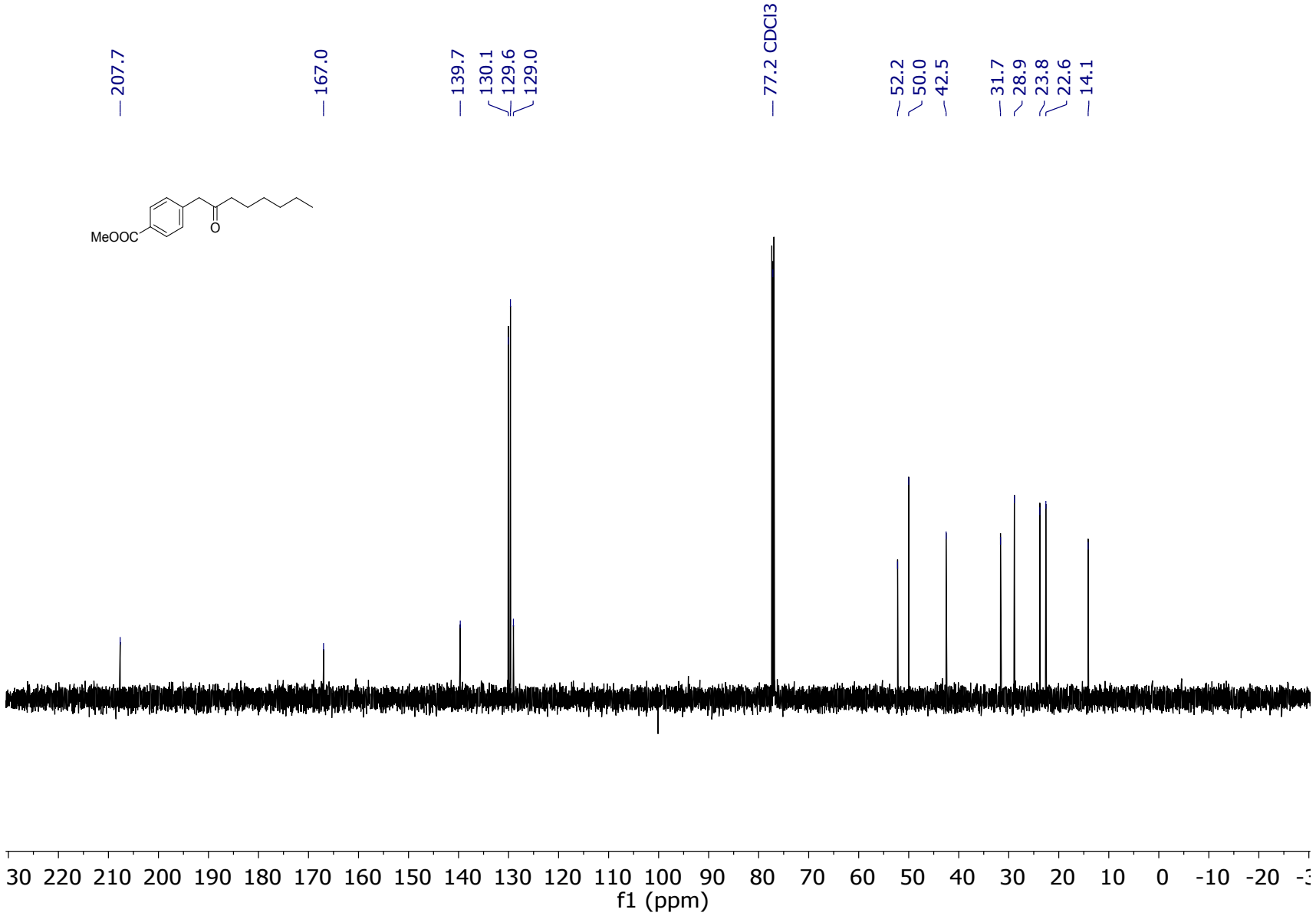


Figure S39. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of methyl 4-(2-oxooctyl)benzoate (17b).

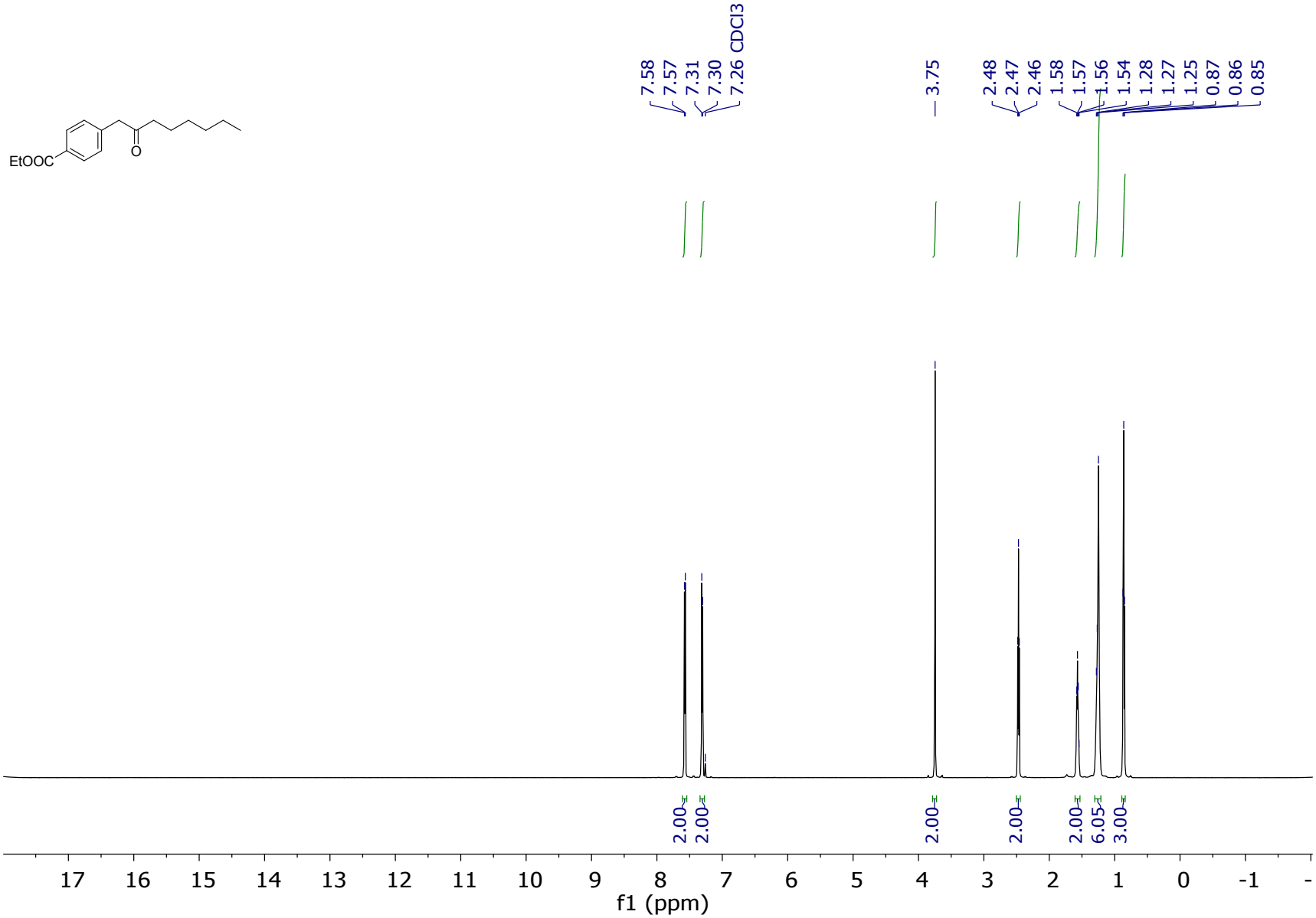


Figure S40. ^{1}H NMR (600 MHz, Chloroform-d) of ethyl 4-(2-oxooctyl)benzoate (18b).

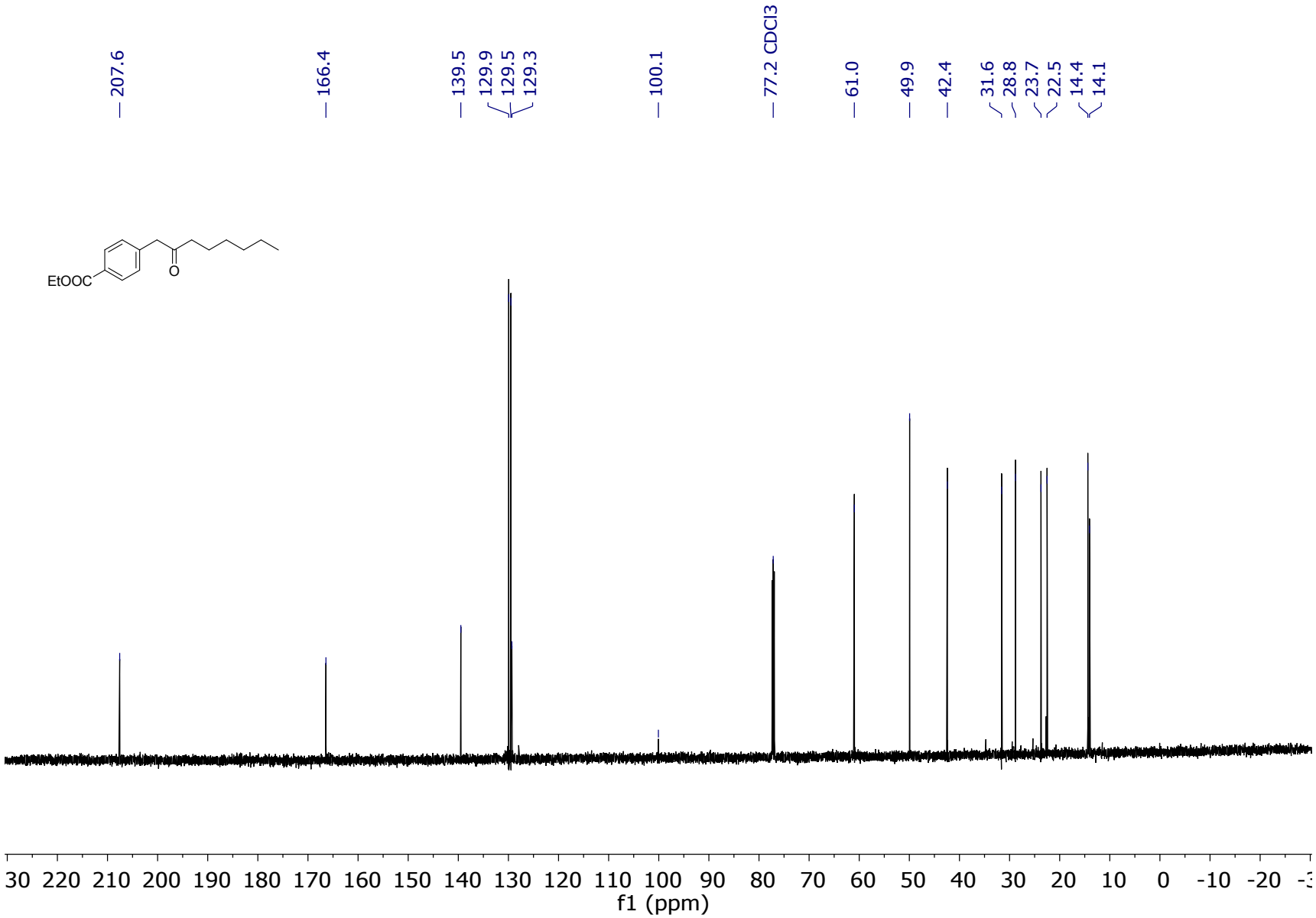


Figure S41. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of ethyl 4-(2-oxooctyl)benzoate (18b).

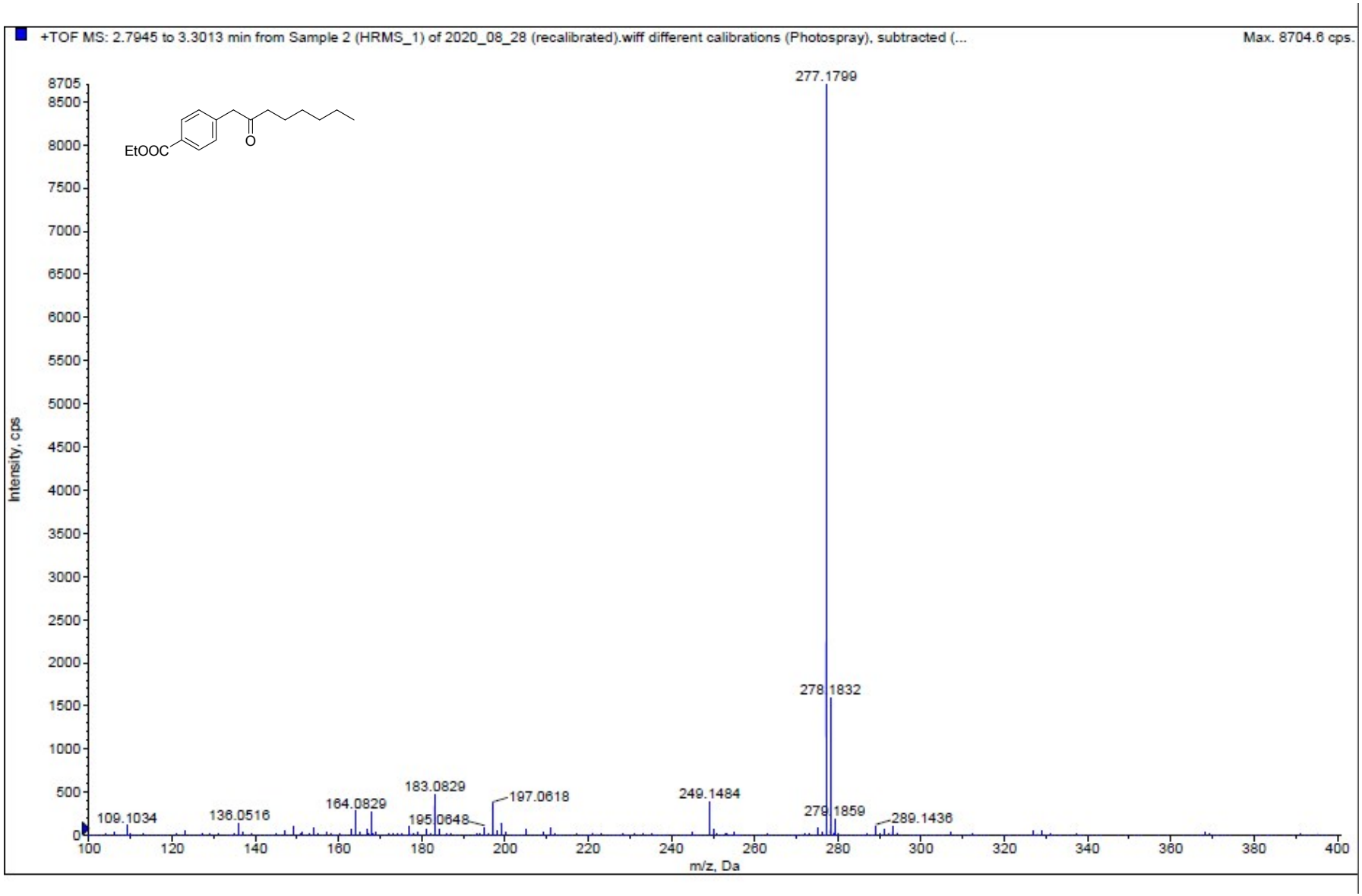


Figure S42. HRMS spectra of ethyl 4-(2-oxooctyl)benzoate (18b).

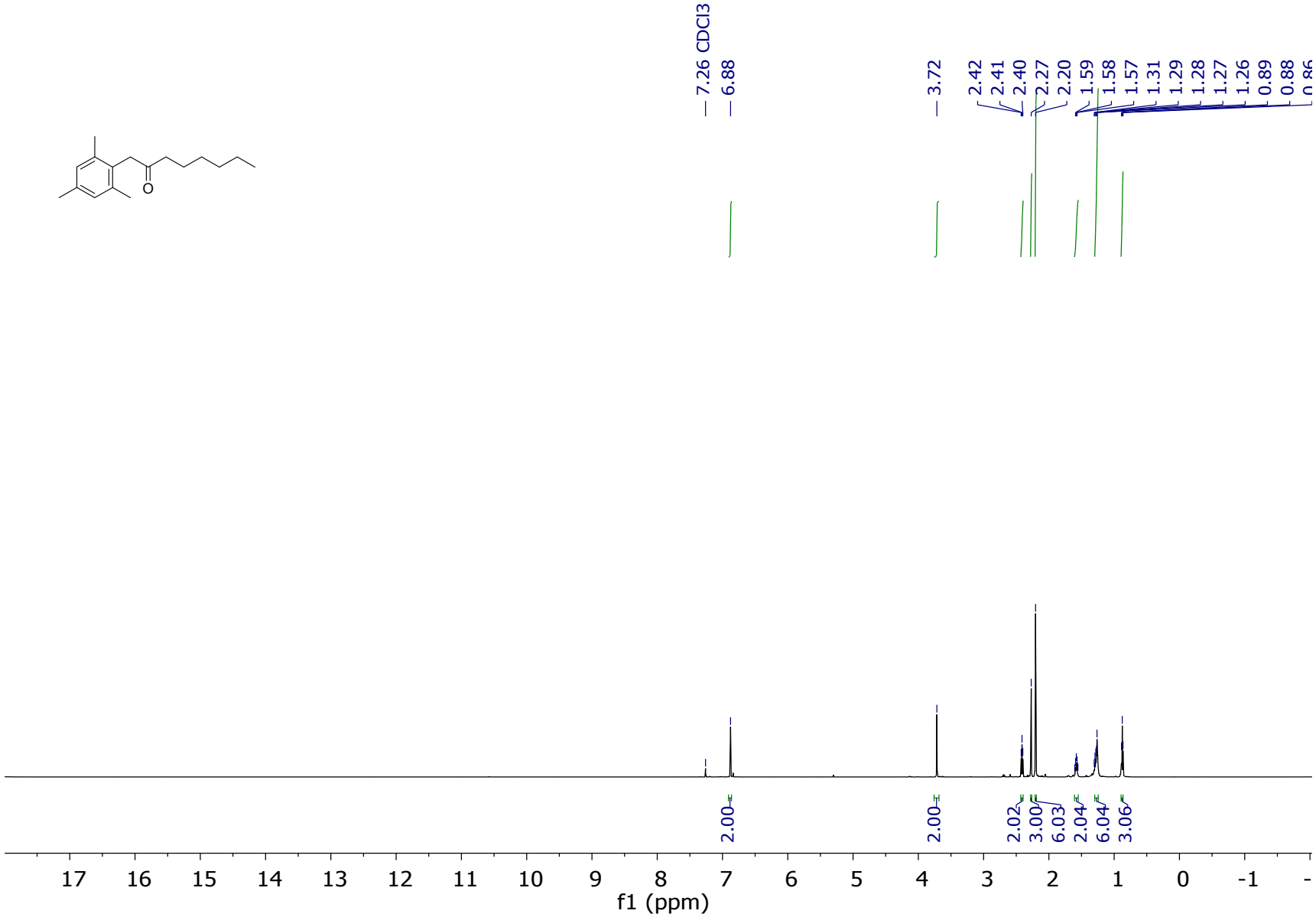


Figure S45. ^{1}H NMR (600 MHz, Chloroform-d) of 1-mesityloctan-2-one (19b).

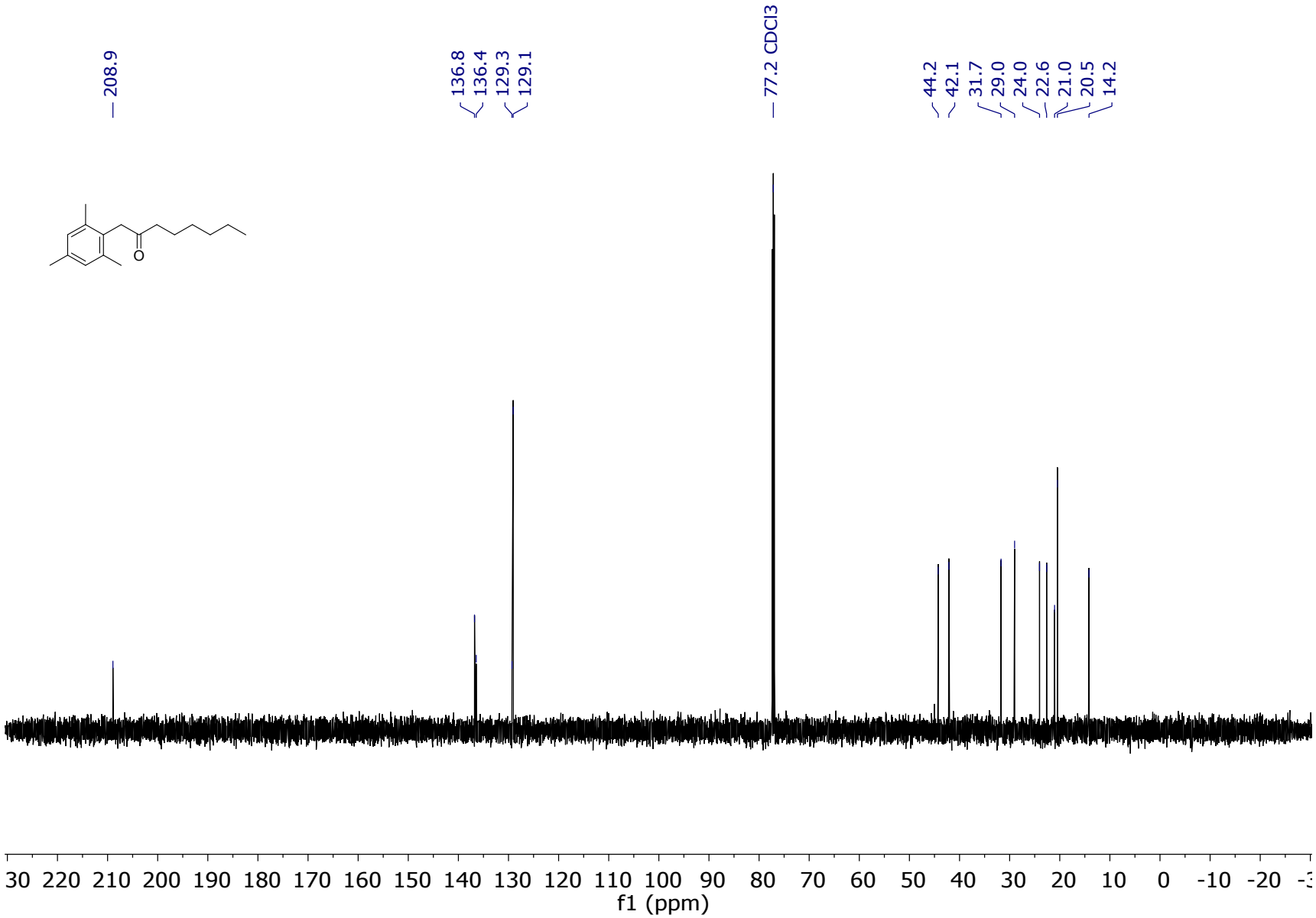


Figure S46. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-mesityloctan-2-one (19b).

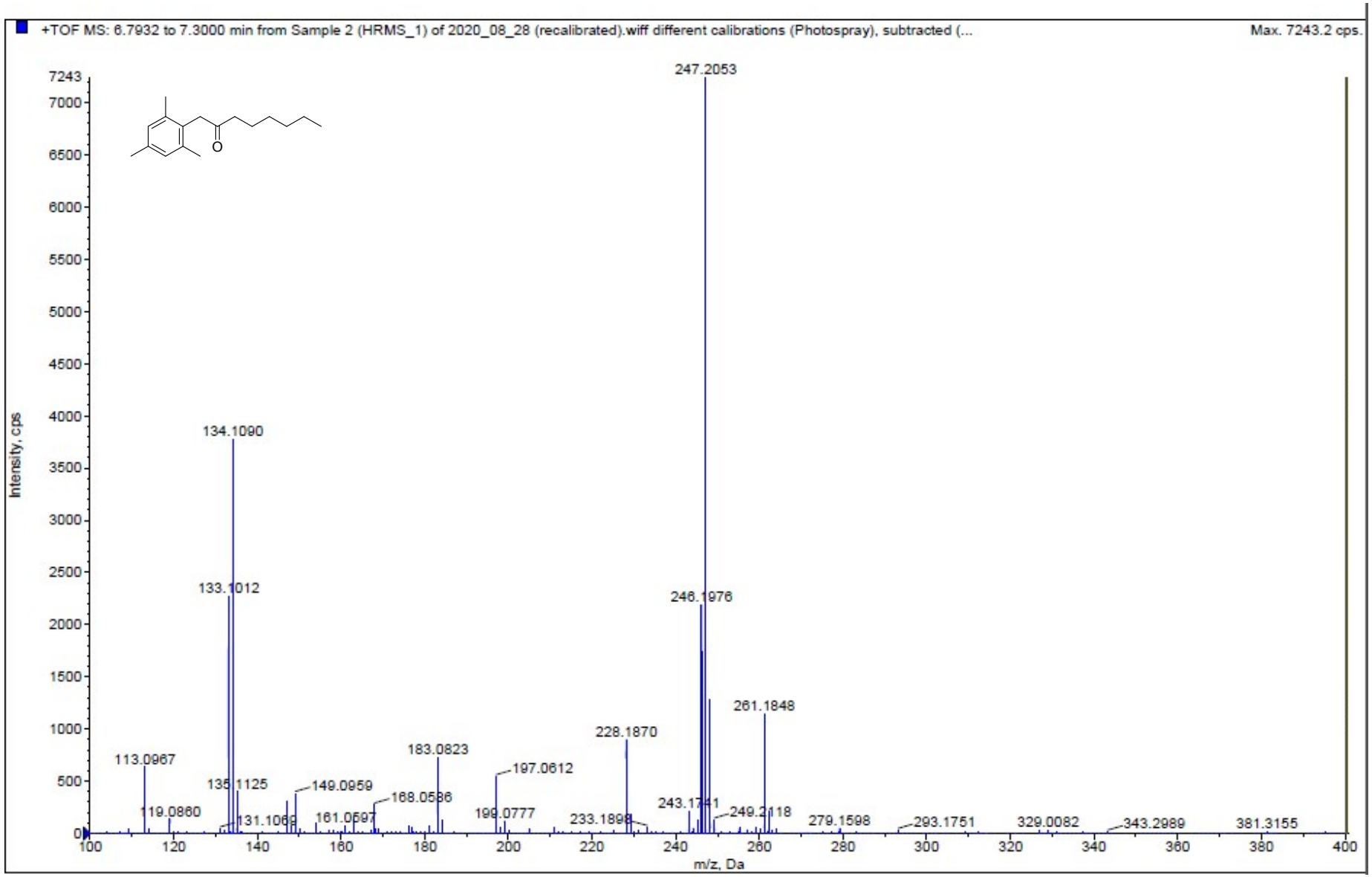


Figure S47. HRMS spectra of 1-mesityloctan-2-one (19b).

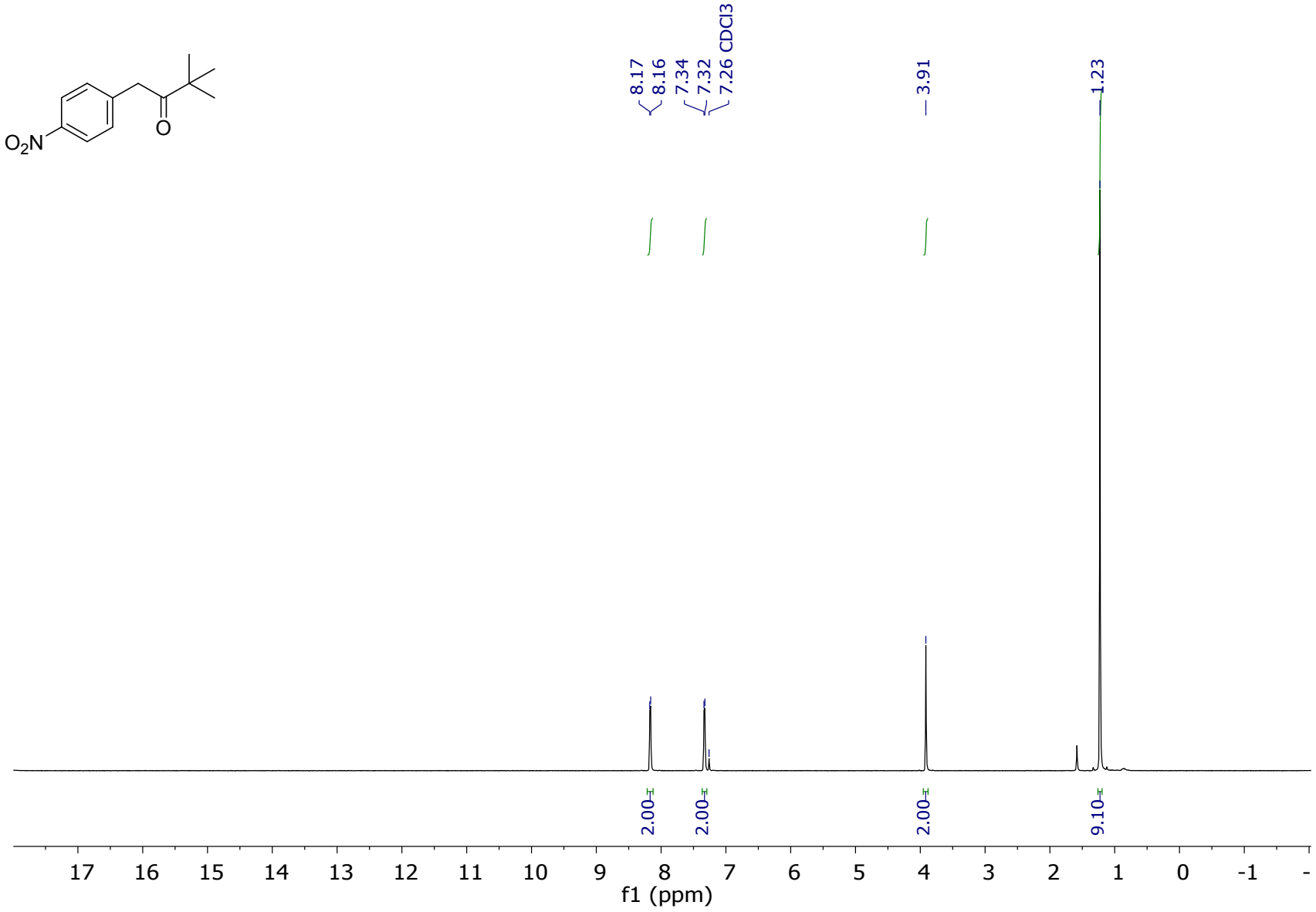


Figure S48. ^{1}H NMR (600 MHz, Chloroform-d) of 3,3-dimethyl-1-(4-nitrophenyl)butan-2-one (20b).

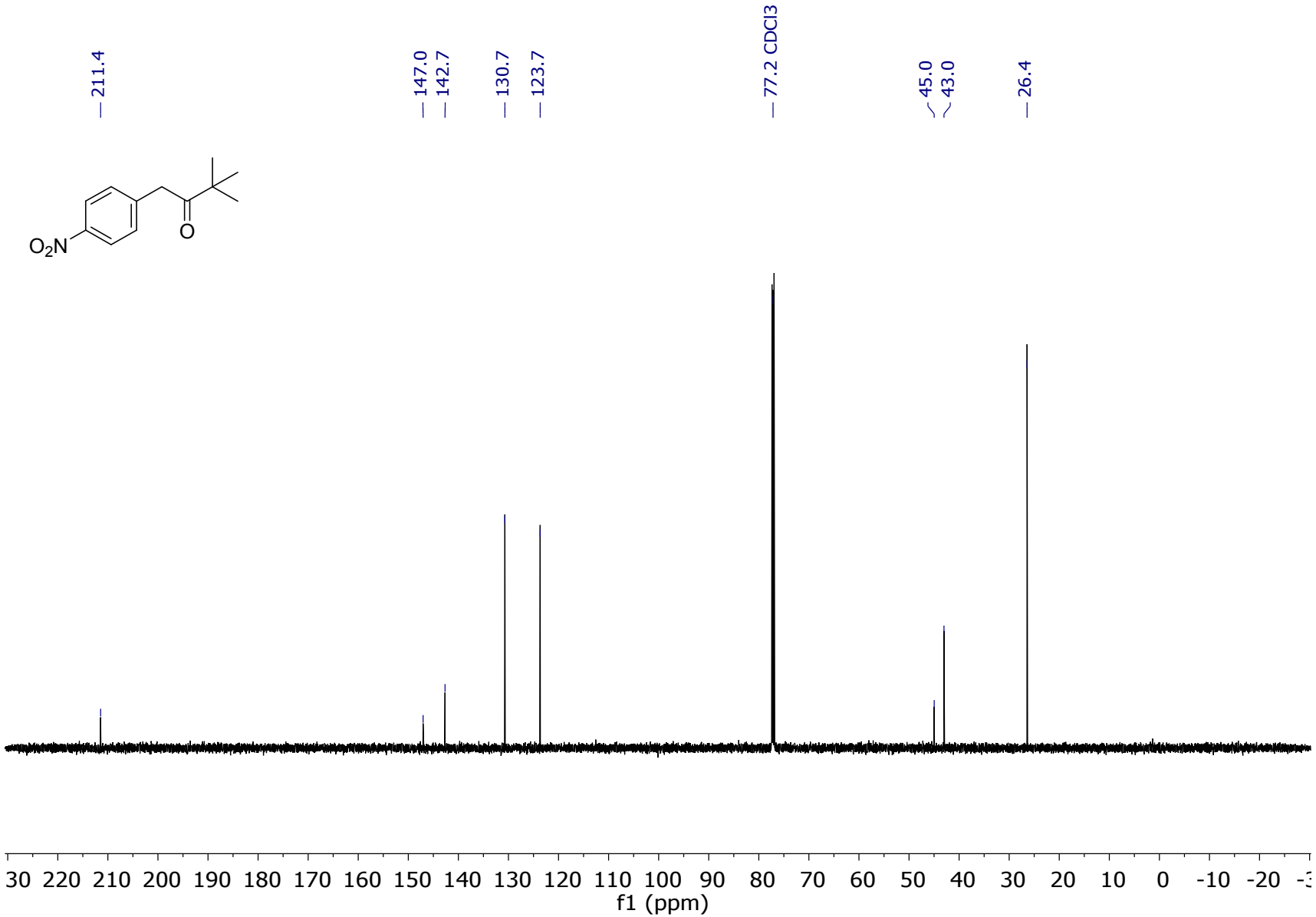


Figure S49. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 3,3-dimethyl-1-(4-nitrophenyl)butan-2-one (20b).

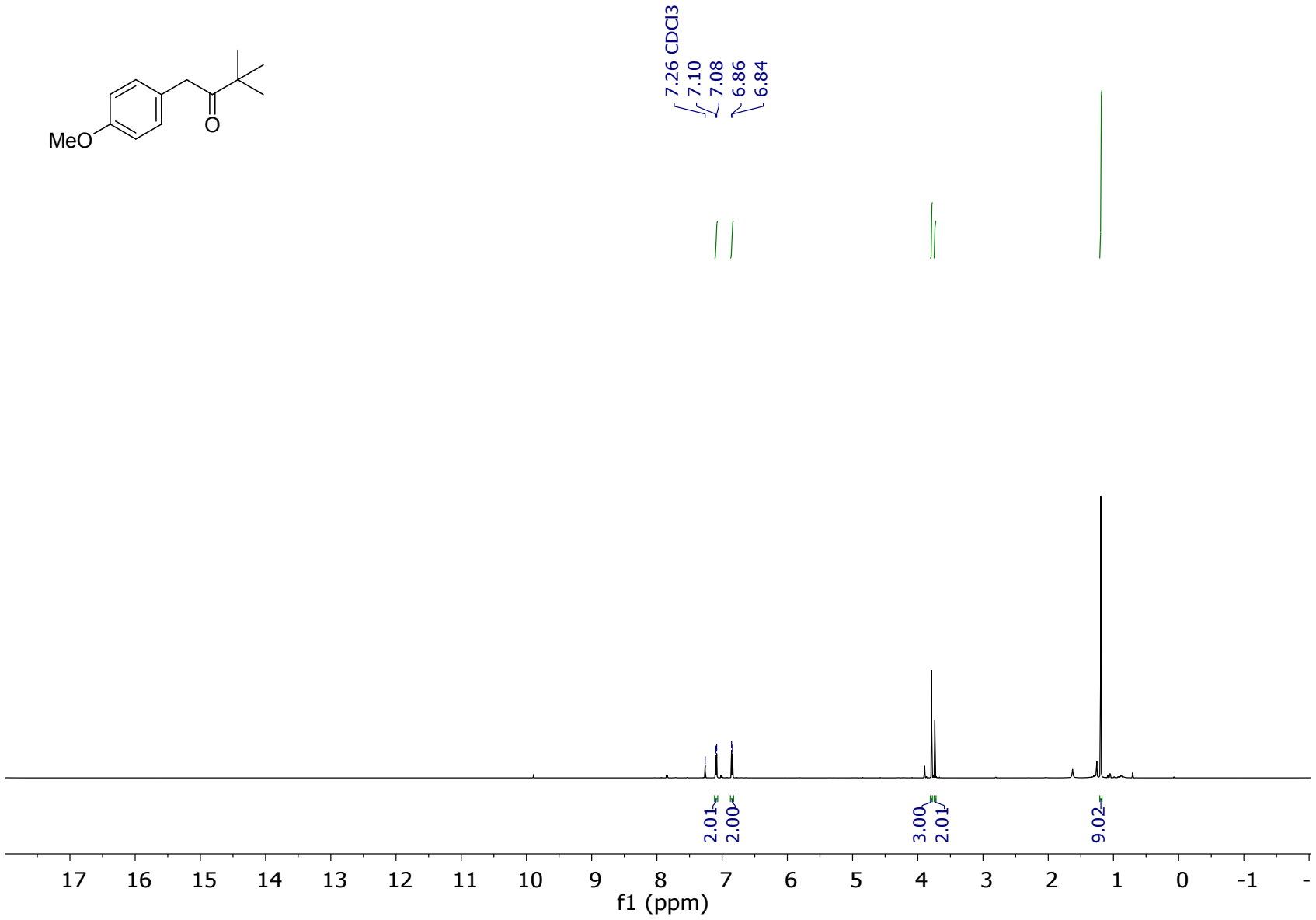


Figure S50. ^{1}H NMR (600 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (21b).

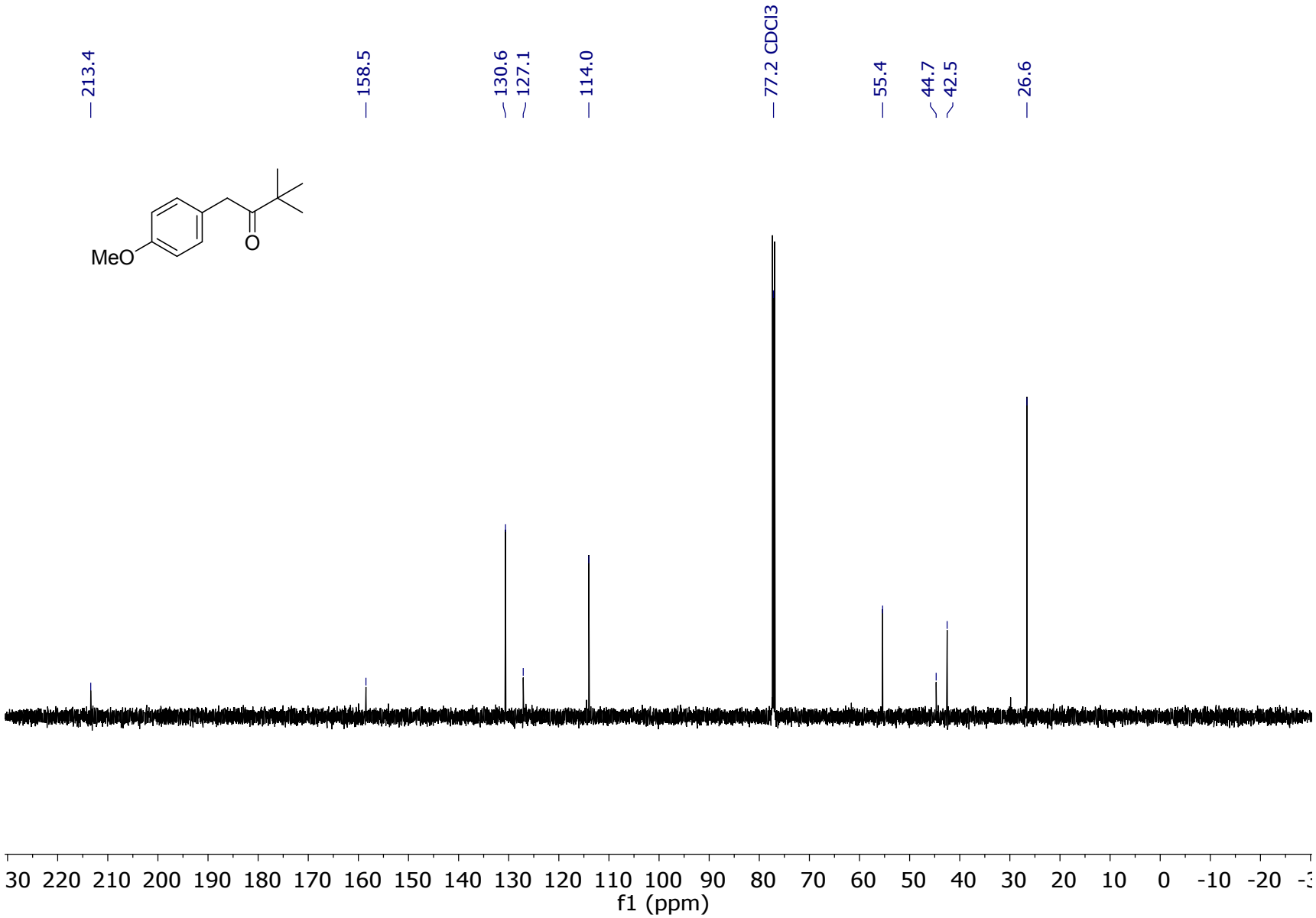


Figure S51. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (21b).

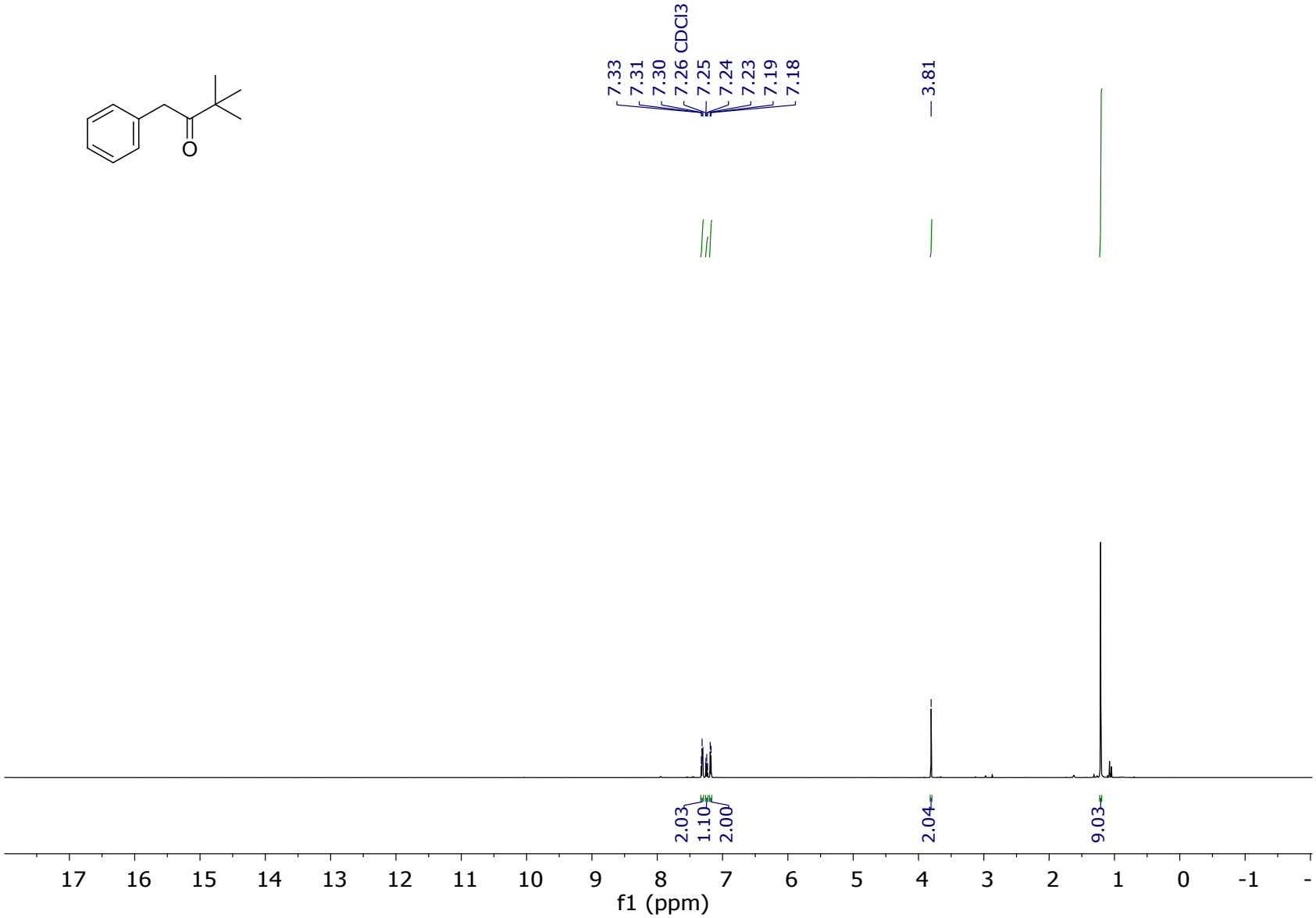


Figure S52. ^{1}H NMR (600 MHz, Chloroform-d) of 3,3-dimethyl-1-phenylbutan-2-one (22b).

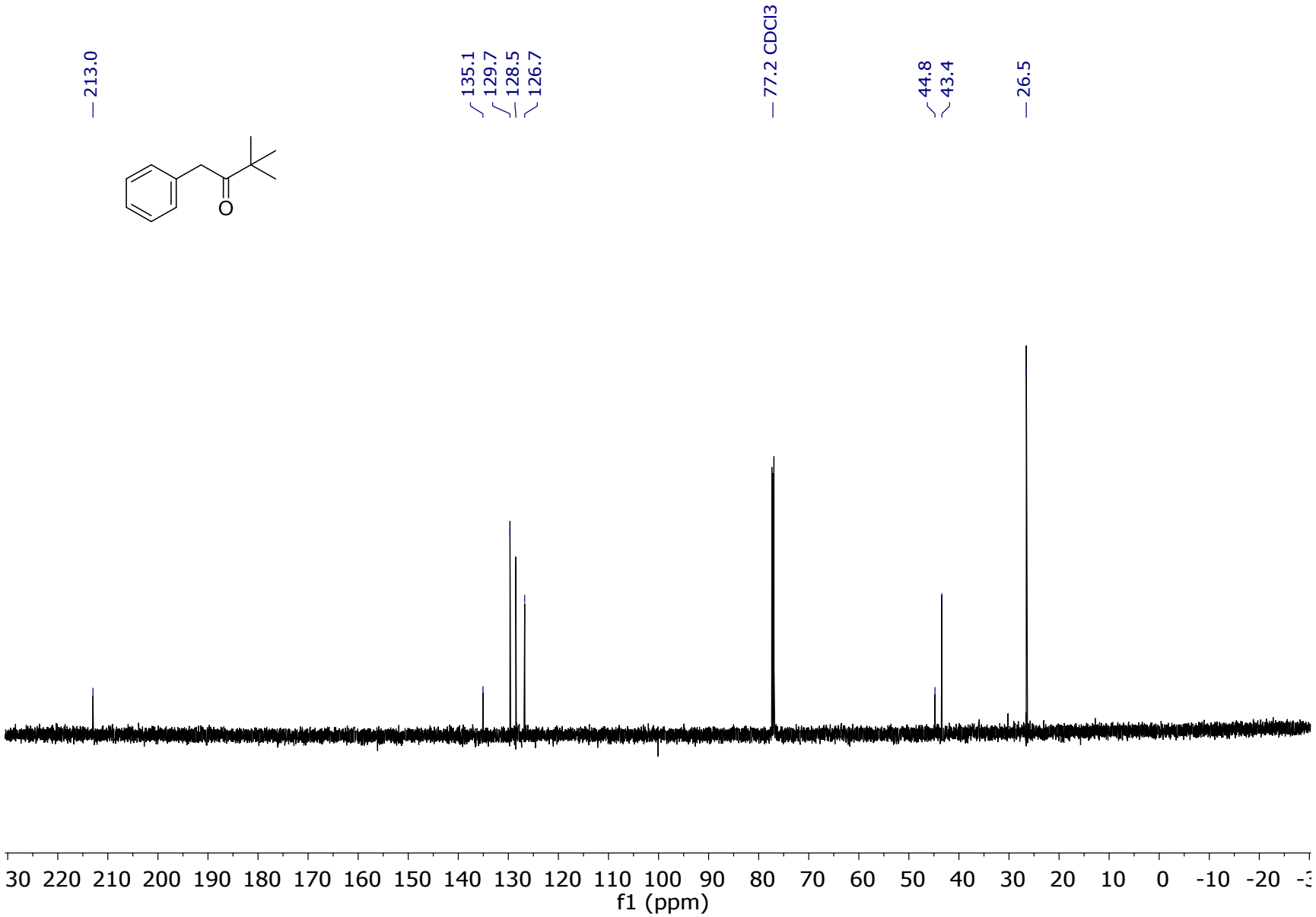


Figure S53. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 3,3-dimethyl-1-phenylbutan-2-one (22b).

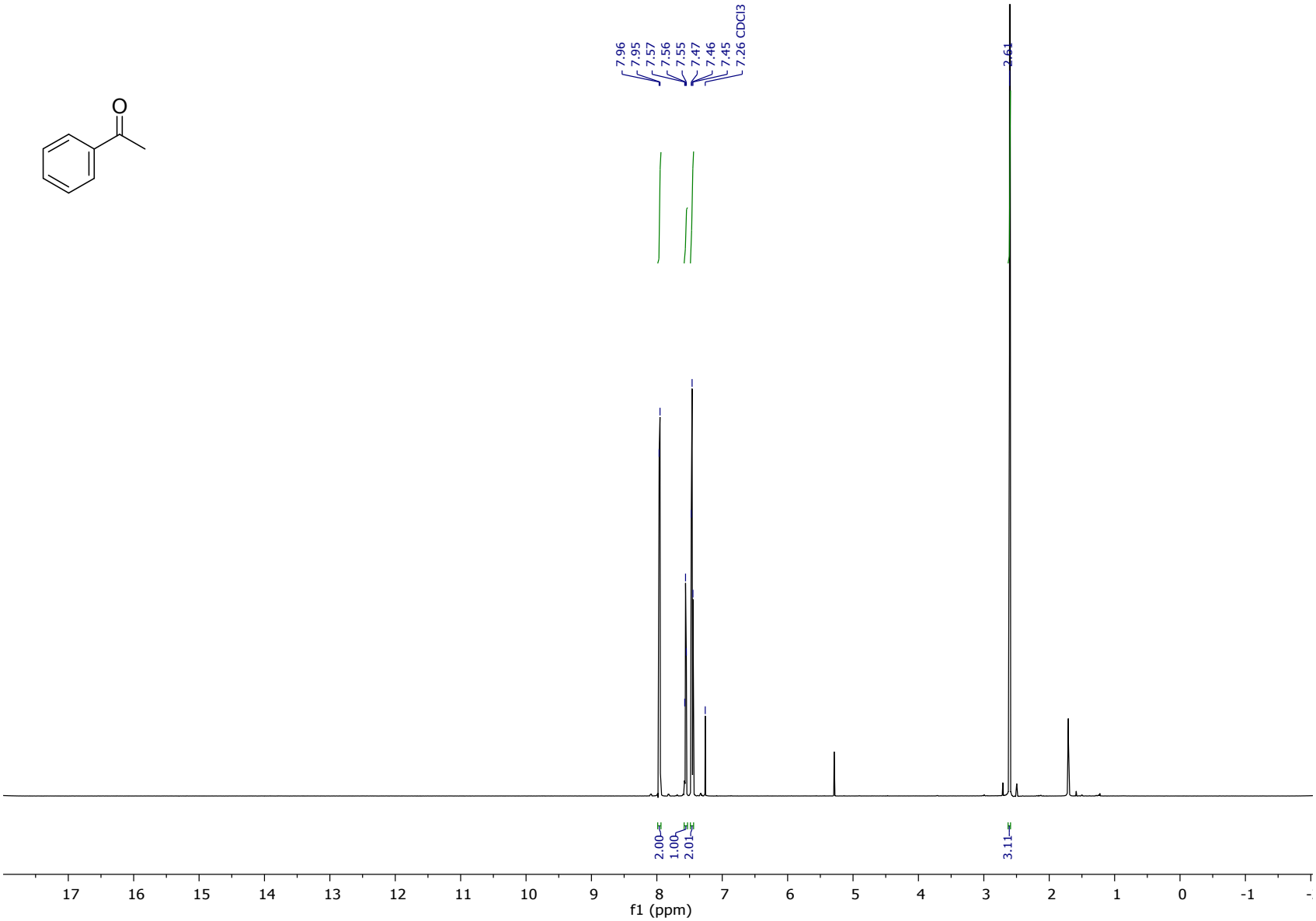


Figure S54. ^{1}H NMR (600 MHz, Chloroform-d) of acetophenone (23a).

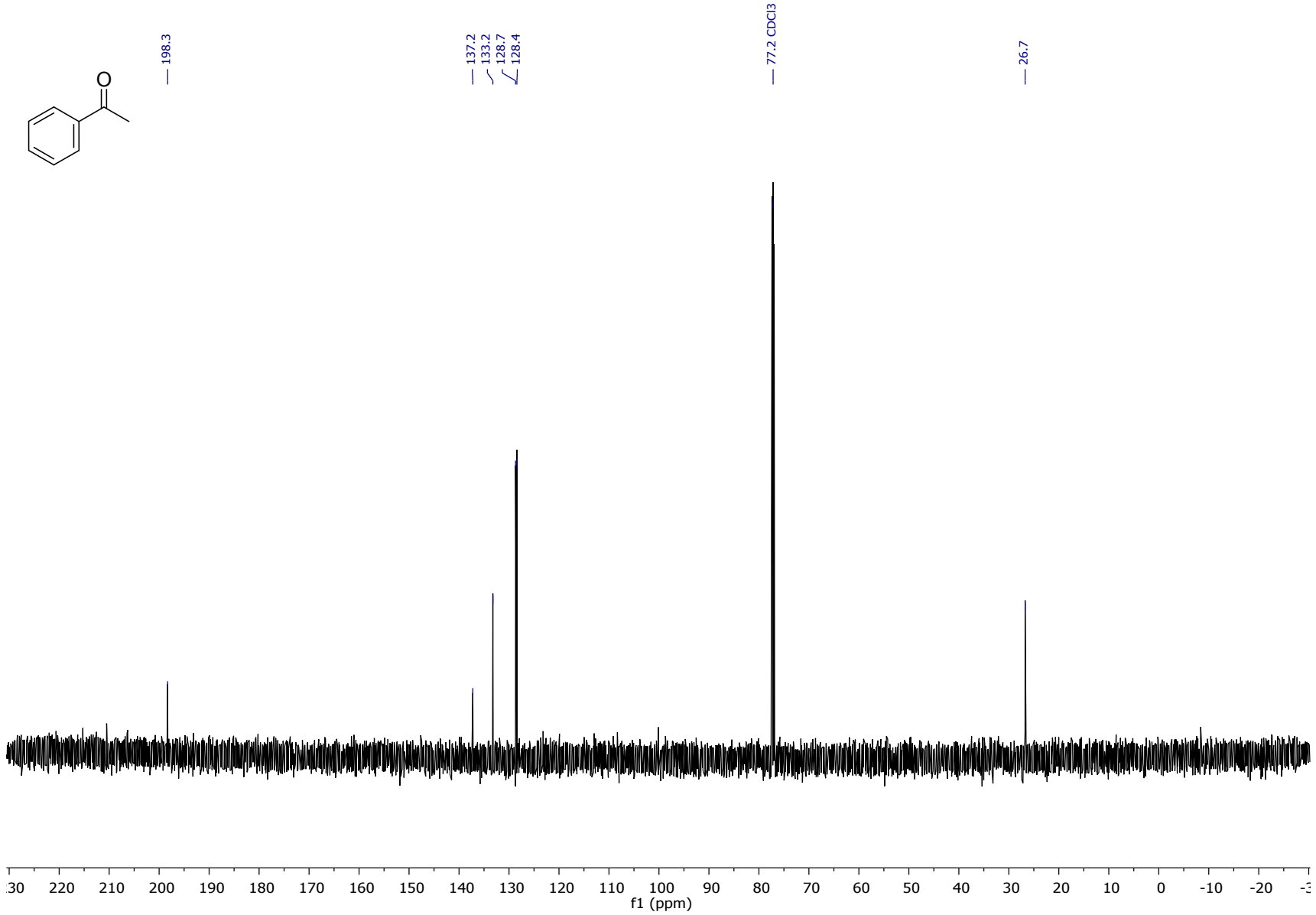


Figure S55. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of acetophenone (23a).