Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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1. General experimental details

Unless otherwise stated, all reactions were performed under an argon atmosphere with exclusion of moisture from reagents and glassware using standard Schlenk techniques for manipulating of air-sensitive compounds. Reaction vessels were three times flame-dried under vacuum and cooled under a stream of argon. All isolated compounds were characterized by ^{1}H NMR and ^{13}C NMR as well as mass spectrometry using EI as ionization method. NMR spectra were recorded using a Bruker AV 300 or 400. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are related to residual solvent peaks. ^{1}H-NMR: $CDCl_3$: 7.26, CD_2Cl_2: 5.32; ^{13}C-NMR: $CDCl_3$: 77.16, CD_2Cl_2: 53.84. Mass spectra were in general recorded on a Finnigan MAT 95-XP (Thermo Electron). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography was performed on a HP 6890 with a HP5 column (Agilent).

Reagents: Unless otherwise stated, commercial reagents were used as received without further purification. Acetone was bought as Extra Dry (99.8%) from Acros.

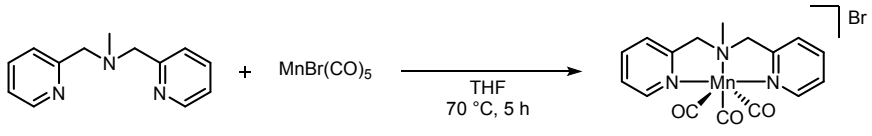
2. Synthesis of Me-dpa (L5)

The title compound was synthesized according to the reported procedure.[1]
Bis(2-pyridylmethyl)amine (dpa) (1g, 5 mmol) was dissolved in 25 mL DCM. A formaldehyde solution (37% in H_2O, 810 mg, 10 mmol) was added dropwise and the solution was further stirred at room temperature overnight. The solution was quenched with 20 mL of NaOH solution (2.5 M in H_2O). After extraction with DCM, the organic phases were reunited and dried with $MgSO_4$. After filtration, the solvent was evaporated. The remaining oil was dissolved in 10 mL Et_2O and filtrated through a syringe filter. The compound was isolated as yellow oil after removing the solvent. Yield: 1 g (99%).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.55 – 8.52 (m, 2H), 7.65 – 7.62 (m, 2H), 7.52 – 7.49 (m, 2H), 7.16 – 7.12 (m, 2H), 3.76 (s, 4H), 2.30 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 159.39, 149.20, 136.55, 123.19, 122.11, 63.74, 42.88.

3. Synthesis of [Mn(Me-dpa)(CO)$_3$]Br

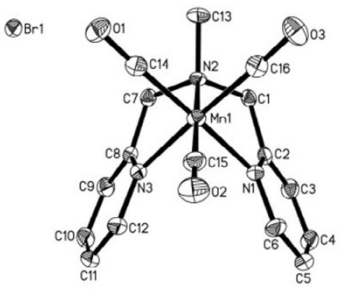
The title compound was synthesized according to the reported procedure with slight modifications.[2]



A flame dried Schlenk flask was charged with Me-dpa (161 mg, 0.8 mmol) dissolved in 20 mL dry THF. $MnBr(CO)_5$ (208 mg, 0.8 mmol) was added under thorough stirring. With the exclusion of light, the yellow solution was heated to 70 °C for 5 h. After cooling down to room temperature, an orange solid precipitates and the solvent was filtered off. The solid was washed repeatedly with Et_2O and after removing the solvent *in vacuo* the complex was isolated as yellow solid. Yield: 277 mg (80%).

^{1}H NMR (300 MHz, CD_2Cl_2) *δ* 8.76 (dd, J = 5.6, 2H), 7.83 – 7.63 (m, 4H), 7.33 – 7.21 (m, 2H), 5.62 (d, 2H), 4.49 (d, 2H), 3.54 (s, 3H).
^{13}C NMR (75 MHz, CD_2Cl_2) *δ* 239.41, 219.67, 160.96, 151.97, 139.83, 125.66, 123.98, 70.43, 57.86.
HRMS (ESI-TOF/MS) calcd. for $C_{16}H_{15}MnN_3O_3$: 352.04884, found: 352.0495.
Selected IR frequencies (ATR, neat) 3024, 2901, 2871, 2736, 2022, 1914, 1607, 783, 773, 631, 535 cm-1.

Crystals have been deposited with the accession number CCDC 1499318 and can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk; Web site: www.ccdc.cam.ac.uk/conts/retrieving.html.[2]



4. Table S1. Metal precursor and acceptor screening

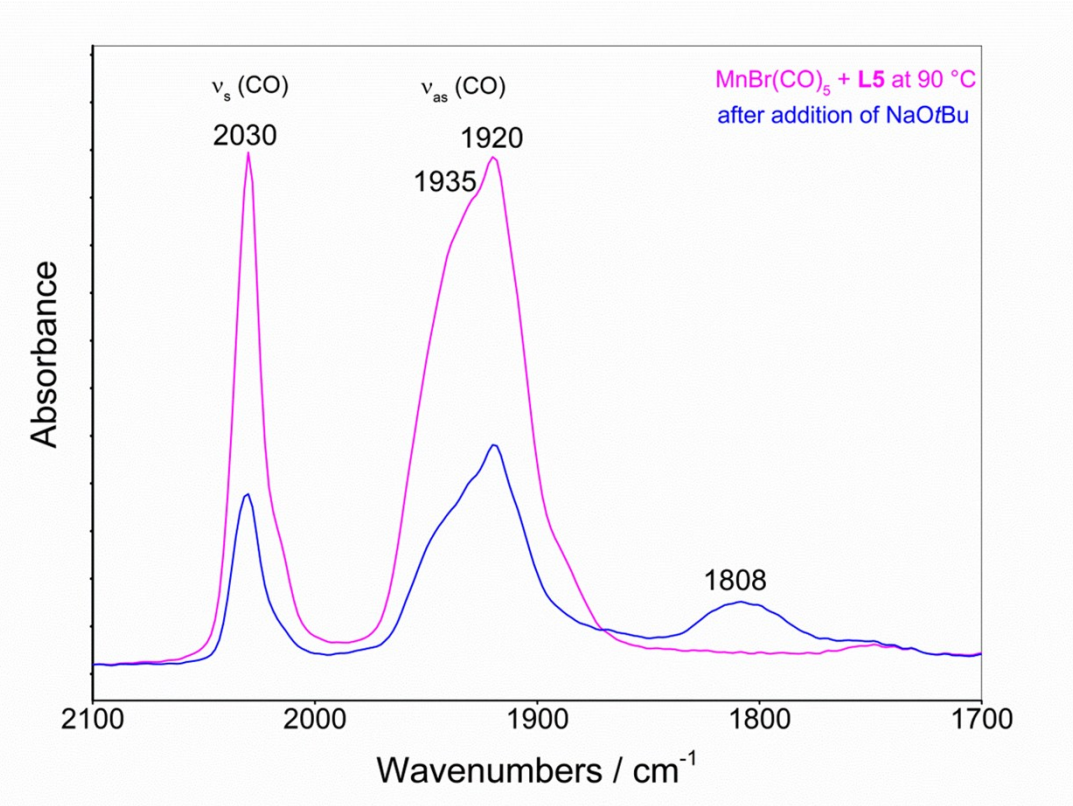
entry[a]	precursor	Precursor loading [mol%]	ligand	Ligand loading [mol%]	base	base loading [mol%]	acceptor	conversion[b] [%]	yield[b] [%]
1	$Mn(CO)_5Br$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	>99	98
2	$Mn_2(CO)_{10}$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	10	10
3	$MnBr_2$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	3	2
4	$Fe_3(CO)_{12}$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	4	3
5	$[Ru(p\text{-cymene})Cl_2]_2$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	95	93
6	$RuCl_3$	0.5	L5	0.5	NaO*t*Bu	0.5	acetone	3	3
7	$Mn(CO)_5Br$	0.5	L5	0.5	NaO*t*Bu	0.5	butanone	2	1
8	$Mn(CO)_5Br$	0.5	L5	0.5	NaO*t*Bu	0.5	pentanone	2	2

[a] All reactions were carried out with 1-phenylethanol (2 mmol), precursor (0.5 mol%), **L5** (0.5 mol%), NaO*t*Bu (0.5 mol%), toluene (3 mL), acceptor (1 mL), 90 °C, 2 h. [b] Conversion and yield was determined by GC using hexadecane as an internal standard.

5. General procedure for the dehydrogenation of alcohols

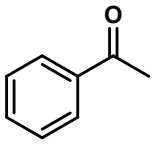
It is essential to ensure that the preformation is carried out with total exclusion of light!
A flame-dried Schlenk tube (25 mL) under an argon atmosphere was charged with $MnBr(CO)_5$ (2.8 mg, 0.01 mmol, 0.5 mol%), and dissolved in 1.5 mL toluene. Me-dpa (2.1 mg, 0.01 mmol, 0.5 mol%, 19.7 M in toluene) was added by syringe and the mixture is heated at 90 °C for 30 min under exclusion of light. To the bright yellow suspension, sodium *tert*-butoxide (0.96 mg, 0.01 mmol, 0.5 mol%) solved in 1 mL of toluene is added to the continuously stirred solution. Subsequently, 2 mmol of substrate and 1 mL of acetone were added. The Schlenk flask is kept at 90 °C for 2 h. After this time, the Schlenk flask was cooled to room temperature and an aliquot was taken for determination of conversion by GC analysis. Purification was accomplished by column chromatography and characterization of the isolated compound by NMR and GC-MS.

6. Figure S1. *In situ* IR spectrum



7. Analytical data of the isolated products

Acetophenone[3]

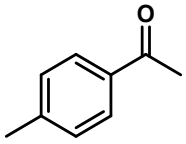


Chemical Formular: C_8H_8O

Molecular Weight: 120.06 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 7.90 (m, 2H), 7.70 – 7.32 (m, 3H), 2.60 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 198.26, 137.27, 133.21, 128.68, 128.42, 26.72.
MS: (EI, 70eV): m/z = 120 ([M]$^+$, 27), 105 (91), 77 (100), 74 (13), 51 (59), 50 (26), 43 (34), 39 (12).
Yield: 98%.

1-(4-Methylphenyl)ethanone[4]

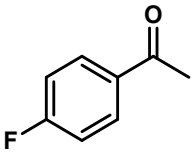


Chemical Formular: $C_9H_{10}O$

Molecular Weight: 134.18 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.31 – 7.19 (m, 2H), 2.57 (s, 3H), 2.41 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.95, 143.97, 134.85, 129.35, 128.55, 26.63, 21.74.
MS: (EI, 70eV): m/z = 134 ([M]$^+$, 25), 119 (100), 91 (85), 89 (22), 65 (41), 63 (24), 51 (13), 50 (11), 43 (44), 39 (23).
Yield: 86%.

1-(4-Fluorophenyl)ethanone[5]

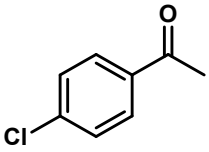


Chemical Formular: C_8H_7FO

Molecular Weight: 138.05 g/mol

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.18 – 7.07 (m, 2H), 2.58 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.63, 165.89 (d, J = 254.7 Hz), 133.71 (d, J = 3.0 Hz), 131.07 (d, J = 9.4 Hz), 115.78 (d, J = 21.9 Hz), 26.68.
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -105.41.
MS: (EI, 70eV): m/z = 138 ([M]$^+$, 25), 123 (100), 95 (93), 94 (10), 75 (60), 74 (18), 69 (15), 51 (11), 50 (20), 43 (51), 42 (13).
Yield: 83%.

1-(4-Chlorophenyl)ethanone[6]



Chemical Formular: C_8H_7ClO

Molecular Weight: 154.59 g/mol

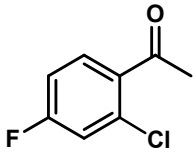
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.47 – 7.38 (m, 2H), 2.58 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.94, 139.67, 135.52, 129.83, 128.99, 26.68.

MS: (EI, 70eV): m/z = 154 ([M]$^+$, 24), 141 (32), 139 (100), 113 (19), 111 (65), 76 (14), 75 (49), 74 (22), 51 (13), 50 (28), 43 (42).

Yield: 87%.

1-(2-Chloro-4-fluorophenyl)ethanone



Chemical Formular: C_8H_6ClFO

Molecular Weight: 172.58 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (m, 1H), 7.16 (m, 1H), 7.04 (m, 1H), 2.64 (d, 3H).

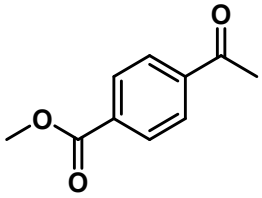
^{13}C NMR (75 MHz, $CDCl_3$) δ 198.36, 163.65 (d, J = 255.5 Hz), 134.97 (d, J = 3.6 Hz), 133.19 (d, J = 10.6 Hz), 131.73 (d, J = 9.5 Hz), 118.01 (d, J = 24.8 Hz), 114.29 (d, J = 21.3 Hz), 30.53

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ -106.42.

MS: (EI, 70eV): m/z = 172 ([M]$^+$, 13), 159 (32), 157 (100), 129 (31), 43 (10).

Yield: 26%.

Methyl 4-acetylbenzoate[3]



Chemical Formular: $C_{10}H_{10}O_3$

Molecular Weight: 178.06 g/mol

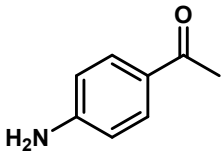
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 – 8.07 (m, 2H), 8.06 – 7.95 (m, 2H), 3.95 (s, 3H), 2.65 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.56, 166.24, 140.23, 133.90, 132.48, 129.84, 128.22, 52.49, 26.91.

MS: (EI, 70eV): m/z = 178 ([M]$^+$, 13), 163 (100), 147 (20), 135 (21), 103 (12), 76 (13), 50 (10), 43 (15).

Yield: 69%.

1-(4-Aminophenyl)ethanone[7]



Chemical Formular: C_8H_9NO

Molecular Weight: 135.17 g/mol

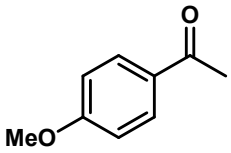
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.84 – 7.72 (m, 2H), 6.72 – 6.60 (m, 2H), 4.21 (br.s, 2H), 2.46 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 196.43, 151.91, 131.13, 128.33, 114.09, 26.42.

MS: (EI, 70eV): m/z = 135 ([M]$^+$, 45), 120 (100), 92 (51), 66 (10), 65 (68), 64 (11), 63 (24), 52 (15), 51 (13), 43 (53), 42 (18), 41 (13), 39 (36), 38 (15).

Yield: 98%.

1-(4-Methoxyphenyl)ethanone[4]

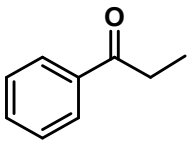


Chemical Formular: $C_9H_{10}O_2$

Molecular Weight: 150.18 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.98 – 7.86 (m, 2H), 6.98 – 6.85 (m, 2H), 3.89 – 3.81 (m, 3H), 2.57 – 2.50 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 196.86, 163.59, 130.67, 130.46, 113.78, 55.55, 26.40.
MS: (EI, 70eV): m/z = 150 ([M]$^+$, 29), 135 (100), 107 (16), 92 (34), 77 (56), 64 (27), 63 (30), 51 (14), 50 (18), 43 (37), 38 (10).
Yield: 95%.

Propiophenone[8]

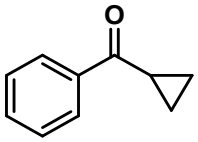


Chemical Formular: $C_9H_{10}O$

Molecular Weight: 134.07 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.02 – 7.91 (m, 2H), 7.61 – 7.38 (m, 3H), 3.00 (q, 2H), 1.22 (t, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 200.92, 137.07, 132.96, 128.65, 128.08, 31.89, 8.36.
MS: (EI, 70eV): m/z = 134 ([M]$^+$, 13), 105 (100), 77 (85), 51 (49), 50 (19), 29 (14).
Yield: 81%.

Cyclopropyl(phenyl)methanone[9]

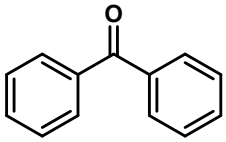


Chemical Formular: $C_{10}H_{10}O$

Molecular Weight: 146.19 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.04 – 7.96 (m, 2H), 7.58 – 7.40 (m, 3H), 2.66 (m, 1H), 1.27 – 1.19 (m, 2H), 1.06 – 0.97 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 200.62, 138.02, 132.74, 128.51, 128.02, 17.16, 11.67.
MS: (EI, 70eV): m/z = 146 ([M]$^+$, 22), 105 (100), 77 (52), 51 (19).
Yield: 49%.

Benzophenone[3]

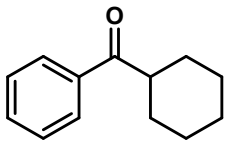


Chemical Formular: $C_{13}H_{10}O$

Molecular Weight: 182.22 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.86 – 7.75 (m, 2H), 7.65 – 7.53 (m, 1H), 7.53 – 7.42 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) *δ* 196.81, 137.72, 132.50, 130.14, 128.37.
MS: (EI, 70eV): m/z = 182 ([M]$^+$, 27), 105 (93), 77 (100), 51 (66), 50 (25).
Yield: 67%.

Cyclohexyl(phenyl)methanone[10]



Chemical Formular: $C_{13}H_{16}O$

Molecular Weight: 188.12 g/mol

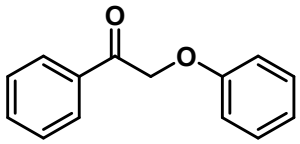
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.84 (m, 2H), 7.60 – 7.39 (m, 3H), 3.26 (tt, 1H), 1.97 – 1.80 (m, 4H), 1.78 – 1.68 (m, 1H), 1.59 – 1.19 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.98, 136.50, 132.82, 128.69, 128.37, 45.76, 29.56, 26.10, 25.99.

MS: (EI, 70eV): m/z = 188 ($[M]^+$, 19), 105 (100), 77 (51), 55 (17), 51 (14), 41 (13).

Yield: 88%.

2-Phenoxy-1-phenylethan-1-one[11]



Chemical Formular: $C_{14}H_{12}O_2$

Molecular Weight: 212.08 g/mol

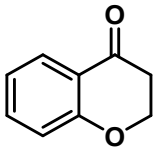
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 2H), 7.67 – 7.57 (m, 1H), 7.55 – 7.45 (m, 2H), 7.35 – 7.26 (m, 2H), 7.03 – 6.92 (m, 3H), 5.28 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.56, 158.02, 133.86, 129.58, 128.84, 128.17, 121.67, 114.83, 70.84.

MS: (EI, 70eV): m/z = 212 ($[M]^+$, 10), 105 (83), 77 (100), 65 (14), 51 (39), 50 (11), 39 (13).

Yield: 25%.

Chroman-4-one[12]



Chemical Formular: $C_9H_8O_2$

Molecular Weight: 148.16 g/mol

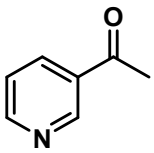
^{1}H NMR (300 MHz, $CDCl_3$) δ .88 (m, 1H), 7.46 (m, 1H), 7.07 – 6.83 (m, 2H), 4.56 – 4.48 (m, 2H), 2.86 – 2.73 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.91, 161.94, 136.07, 127.22, 121.46, 117.97, 67.11, 37.88.

MS: (EI, 70eV): m/z = 148 ($[M]^+$, 31), 120 (61), 92 (100), 65 (12), 64 (32), 63 (48), 62 (16), 53 (11), 51 (11), 50 (18), 42 (10), 39 (14), 38 (14), 29 (11).

Yield: 71%.

1-(pyridine-3-yl)ethan-1-one[13]



Chemical Formular: C_7H_7NO

Molecular Weight: 121.14 g/mol

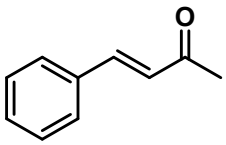
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.76 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.21 (dq, *J* = 8.0, 2.3, 1.8 Hz, 1H), 7.40 (ddd, *J* = 8.0, 4.8, 0.9 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.82, 153.65, 150.05, 135.53, 132.35, 123.72, 26.83.

MS: (EI, 70eV): m/z = 121 ([M]$^+$, 49), 106 (100), 79 (14), 78 (97), 52 (11), 51 (35), 50 (21), 43 (20).

Yield: 37%.

(*E*)-4-Phenylbut-3-en-2-one[14]



Chemical Formular: $C_{10}H_{10}O$

Molecular Weight: 146.19 g/mol

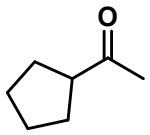
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.47 (m, 3H), 7.47 – 7.33 (m, 3H), 6.71 (d, J = 16.3 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.43, 143.50, 134.54, 130.60, 129.07, 128.35, 127.27, 27.61.

MS: (EI, 70eV): m/z = 146 ([M]$^+$, 60), 145 (65), 132 (10), 131 (100), 103 (99), 102 (15), 77 (50), 51 (30), 50 (10), 43 (18).

Yield: 93%.

1-Cyclopentylethan-1-one[15]



Chemical Formular: $C_7H_{12}O$

Molecular Weight: 112.17 g/mol

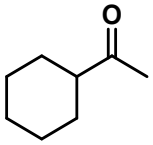
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (m, 1H), 2.17 – 2.08 (m, 3H), 1.84 – 1.47 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 211.77, 52.76, 29.30, 29.22, 26.47.

MS: (EI, 70eV): m/z = 112 ([M]$^+$, 45), 97 (13), 71 (66), 69 (100), 68 (30), 67 (23), 43 (85), 41 (66), 39 (26).

Yield: 85%.

1-Cyclohexylethan-1one[7]



Chemical Formular: $C_8H_{14}O$

Molecular Weight: 126.20 g/mol

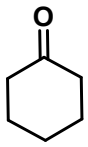
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 – 2.17 (m, 1H), 2.13 – 2.01 (m, 3H), 1.90 – 1.56 (m, 5H), 1.38 – 1.04 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 212.33, 51.50, 28.49, 27.92, 25.92, 25.69.

MS: (EI, 70eV): m/z = 126 ([M]$^+$, 40), 111 (15), 84 (13), 83 (69), 82 (11), 71 (39), 68 (14), 67 (21), 55 (100), 43 (56), 41 (35), 39 (19).

Yield: 96%.

Cyclohexanone[16]

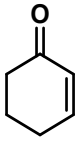


Chemical Formular: $C_6H_{10}O$

Molecular Weight: 98.15 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (m, 4H), 1.94 – 1.56 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 212.53, 42.41, 27.47, 25.43.
MS: (EI, 70eV): m/z = 98 ($[M]^+$, 49), 83 (11), 70 (24), 69 (30), 56 (12), 55 (100), 43 (10), 42 (66), 41 (31), 39 (26).
Yield: 78%.

Cyclohex-2-en-1-one[17]

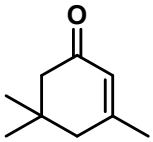


Chemical Formular: C_6H_8O

Molecular Weight: 96.06 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (dt, 1H), 5.90 (dt, 1H), 2.43 – 2.13 (m, 4H), 2.00 – 1.78 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.60, 150.71, 129.76, 38.03, 25.60, 22.66.
MS: (EI, 70eV): m/z = 96 ($[M]^+$, 29), 68 (100), 40 (17), 39 (23).
Yield: 85%.

3,5,5-Trimethylcyclohex-2-en-1-one[18]

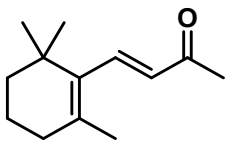


Chemical Formular: $C_9H_{14}O$

Molecular Weight: 138.21 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (m, 1H), 2.19 – 2.10 (m, 4H), 1.90 (m, 3H), 1.00 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 200.02, 160.46, 125.54, 50.83, 45.33, 33.61, 28.40, 28.38, 24.61.
MS: (EI, 70eV): m/z = 138 ($[M]^+$, 12), 82 (100), 67 (10), 54 (17), 53 (13), 41 (21), 39 (45).
Yield: 92%.

β-Ionone[19]

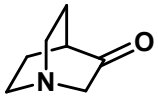


Chemical Formular: $C_{13}H_{22}O$

Molecular Weight: 192.30 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 1H), 6.09 (dd, 1H), 2.27 (s, 3H), 2.09 – 2.00 (m, 2H), 1.74 (q, 3H), 1.66 – 1.55 (m, 2H), 1.49 – 1.41 (m, 2H), 1.05 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 198.83, 143.27, 136.16, 136.04, 131.68, 39.84, 34.17, 33.66, 28.90, 28.54, 27.26, 21.83, 18.99.
MS: (EI, 70eV): m/z = 194 ($[M]^+$, <10), 177 (69), 135 (11), 105 (16), 93 (11), 91 (22), 79 (12), 77 (13), 43 (100), 41 (21), 39 (18).
Yield: 89%.

Chinuclidin-3-on[20]

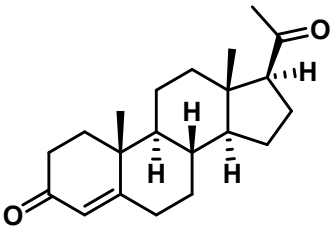


Chemical Formular: $C_7H_{11}NO$

Molecular Weight: 125,08 g/mol

^{1}H NMR (300 MHz, DMSO-d_6) δ 3.53 (s, 2H), 3.15 – 2.95 (m, 4H), 2.42 (q, 1H), 2.09 – 1.82 (m, 4H), 1.24 (s, 1H).
^{13}C NMR (75 MHz, DMSO) δ 60.42, 45.76, 38.40, 22.88.
MS: (EI, 70eV): m/z = 125 ([M]$^+$, 17), 97 (91), 96 (47), 82 (32), 69 (38), 68 (38), 56 (12), 55 (42), 54 (17), 43 (28), 42 (100), 41 (53), 39 (23).
Yield: 88%.

Progesterone[21]

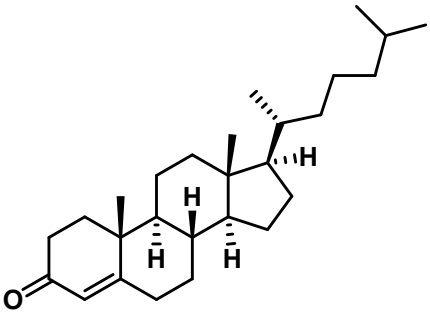


Chemical Formular: $C_{21}H_{30}O$

Molecular Weight: 314.22 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (s, 1H), 2.59 – 2.15 (m, 6H), 2.12 (s, 3H), 2.09 – 1.98 (m, 2H), 1.92 – 1.80 (m, 1H), 1.78 – 1.36 (m, 7H), 1.31 – 0.91 (m, 7H), 0.66 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 209.28, 199.44, 170.93, 123.95, 63.51, 56.03, 53.66, 43.93, 38.68, 38.58, 35.74, 35.56, 33.96, 32.79, 31.90, 31.51, 24.37, 22.85, 21.03, 17.39, 13.35.
MS: (EI, 70eV): m/z = 315 (12), 314 ([M]$^+$, 50), 272 (46), 244 (12), 230 (11), 229 (42), 191 (18), 187 (11), 173 (14), 159 (11), 149 (13), 147 (24), 145 (12), 137 (11), 135 (15), 134 (12), 133 (23), 131 (13), 125 (12), 124 (92), 123 (17), 122 (13), 121 (19), 119 (16), 109 (18), 107 (25), 105 (28), 95 (23), 93 (27), 91 (44), 81 (20), 79 (41), 77 (27), 71 (13), 67 (25), 55 (28), 53 (14), 43 (100), 41 (25).
Yield: 93%.

Cholest-4-en-3-one[14]

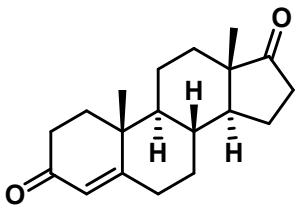


Chemical Formular: $C_{27}H_{44}O$

Molecular Weight: 384.65 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (d, 1H), 2.45 – 2.18 (m, 4H), 2.13 – 0.54 (m, 39H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.48, 171.53, 123.55, 55.91, 55.69, 53.63, 42.20, 39.45, 39.31, 38.42, 35.93, 35.57, 35.51, 35.44, 33.81, 32.78, 31.87, 28.00, 27.83, 24.00, 23.63, 22.64, 22.38, 20.85, 18.46, 17.21, 11.78.
MS: (EI, 70eV): m/z = 385 (11), 384 ([M]$^+$, 39), 369 (12), 342 (18), 261 (26), 260 (17), 230 (12), 229 (48), 149 (21), 148 (16), 147 (23), 137 (11), 135 (21), 134 (12), 133 (19), 125 (11), 124 (100), 123 (19), 122 (11), 121 (19), 119 (16), 109 (20), 107 (24), 105 (23), 95 (30), 93 (26), 91 (28), 81 (26), 79 (31), 77 (15), 71 (11), 69 (19), 67 (24), 57 (25), 55 (42), 43 (53), 41 (36).
Yield: 98%.

Androstenedione[19]



Chemical Formular: $C_{19}H_{26}O_2$

Molecular Weight: 286.42 g/mol

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75 (s, 1H), 2.54 – 2.27 (m, 5H), 2.18 – 1.62 (m, 8H), 1.55 – 1.37 (m, 2H), 1.35 – 1.24 (m, 2H), 1.21 (s, 3H), 1.18 – 0.94 (m, 2H), 0.92 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.29, 170.27, 124.17, 53.84, 50.87, 47.51, 38.65, 35.75, 35.72, 35.18, 33.92, 32.58, 31.30, 30.77, 23.92, 21.76, 20.33, 17.40, 13.72.

MS: (EI, 70eV): m/z = 287 (12), 286 ([M]$^+$, 59), 244 (35), 201 (19), 174 (10), 173 (14), 163 (14), 162 (12), 159 (12), 150 (21), 149 (23), 148 (36), 147 (12), 146 (11), 145 (20), 136 (12), 135 (13), 134 (12), 133 (17), 131 (20), 129 (14), 128 (10), 124 (65), 123 (20), 122 (22), 121 (21), 120 (11), 119 (30), 117 (19), 115 (16), 109 (34), 108 (16), 107 (51), 106 (19), 105 (53), 103 (12), 97 (31), 95 (18), 94 (19), 93 (46), 92 (17), 91 (100), 81 (31), 80 (20), 79 (93), 78 (20), 77 (64), 68 (12), 67 (63), 66 (14), 65 (30), 55 (89), 53 (43), 43 (19), 42 (17), 41 (87), 39 (38), 29 (37).

Yield: 94%.

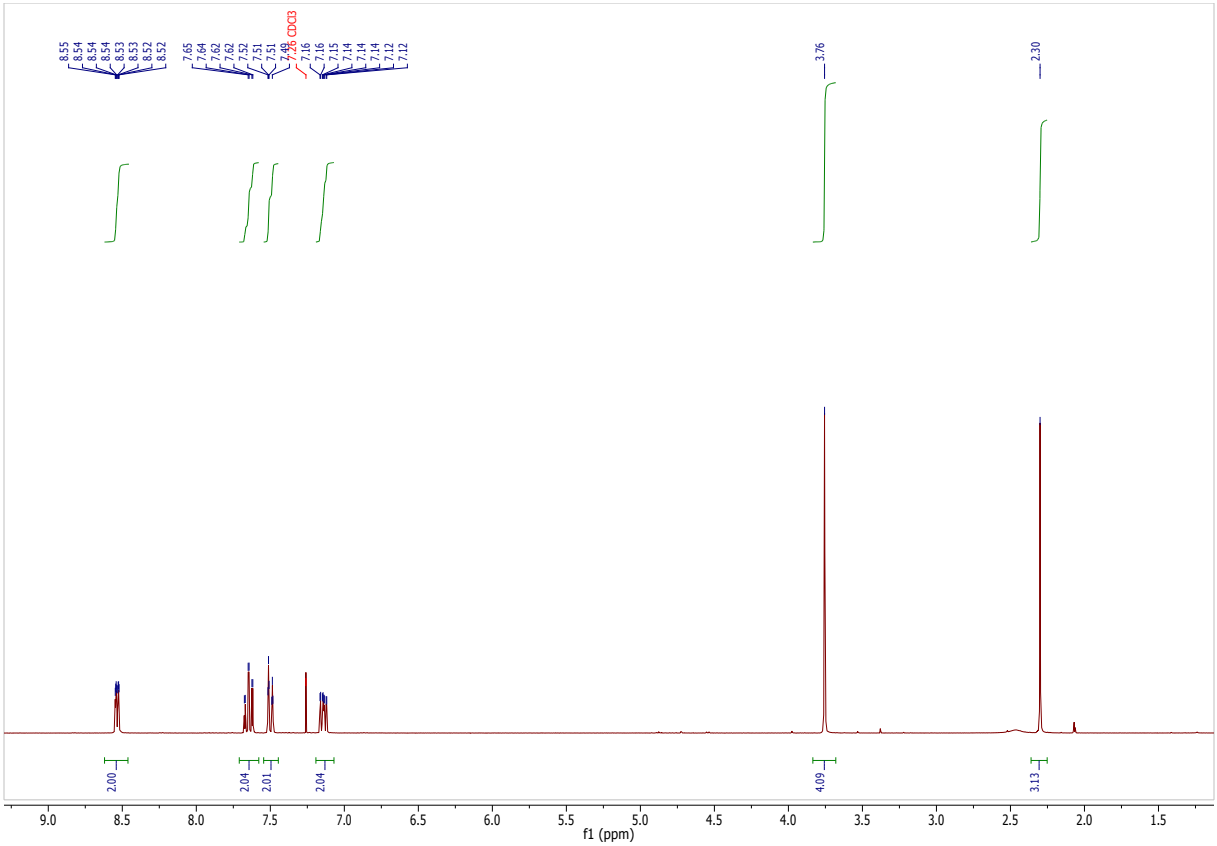


Figure SI 2.[1]H-NMR of Me-dpa.

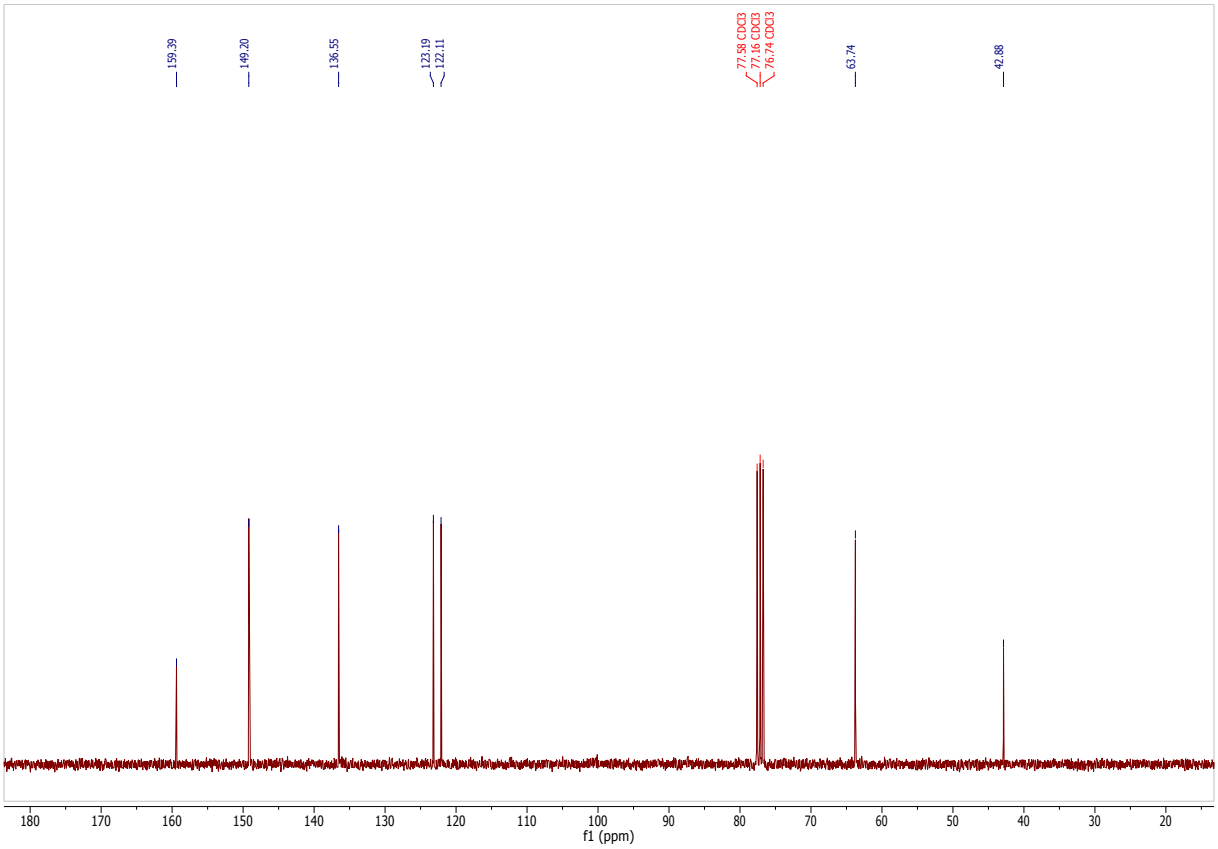


Figure SI 3.[13]C-NMR of Me-dpa.

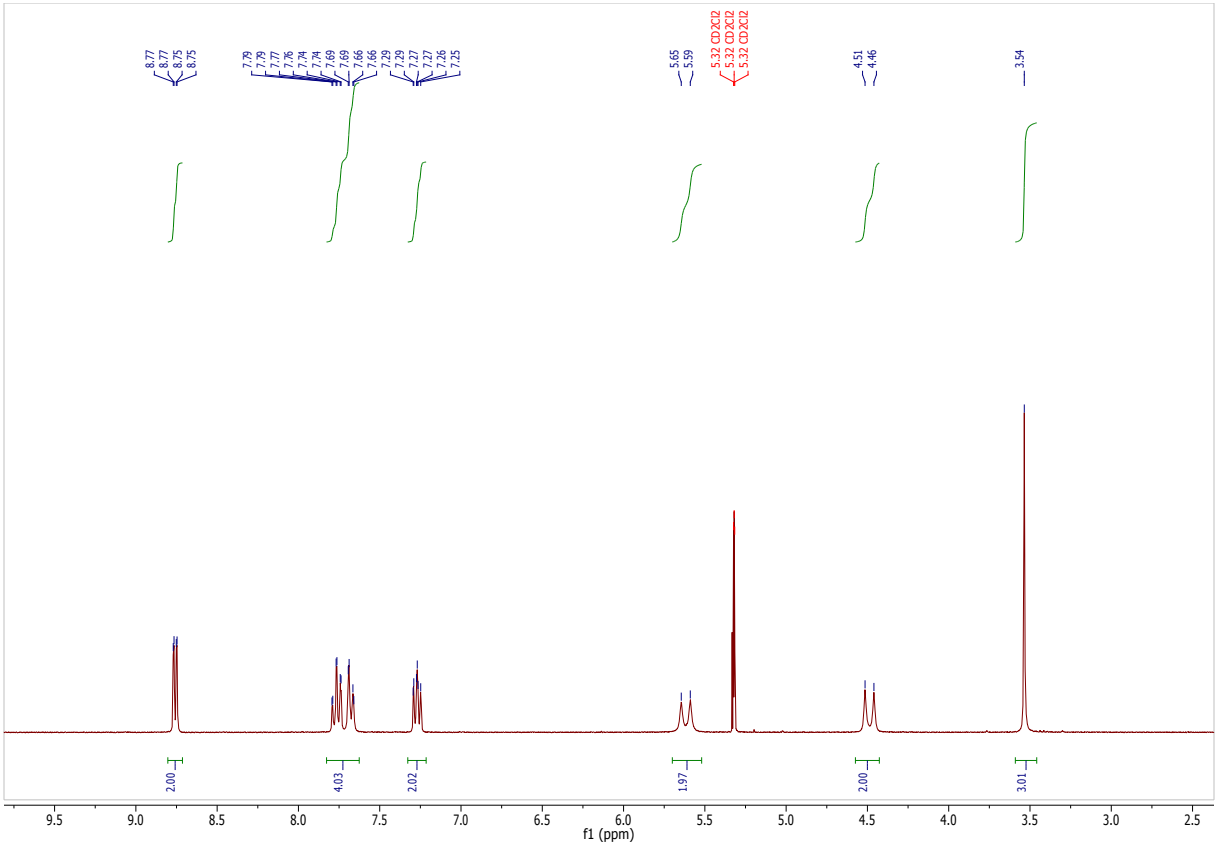


Figure SI 4. ^{1}H-NMR of complex [Mn(Me-dpa)(CO)$_3$]Br.

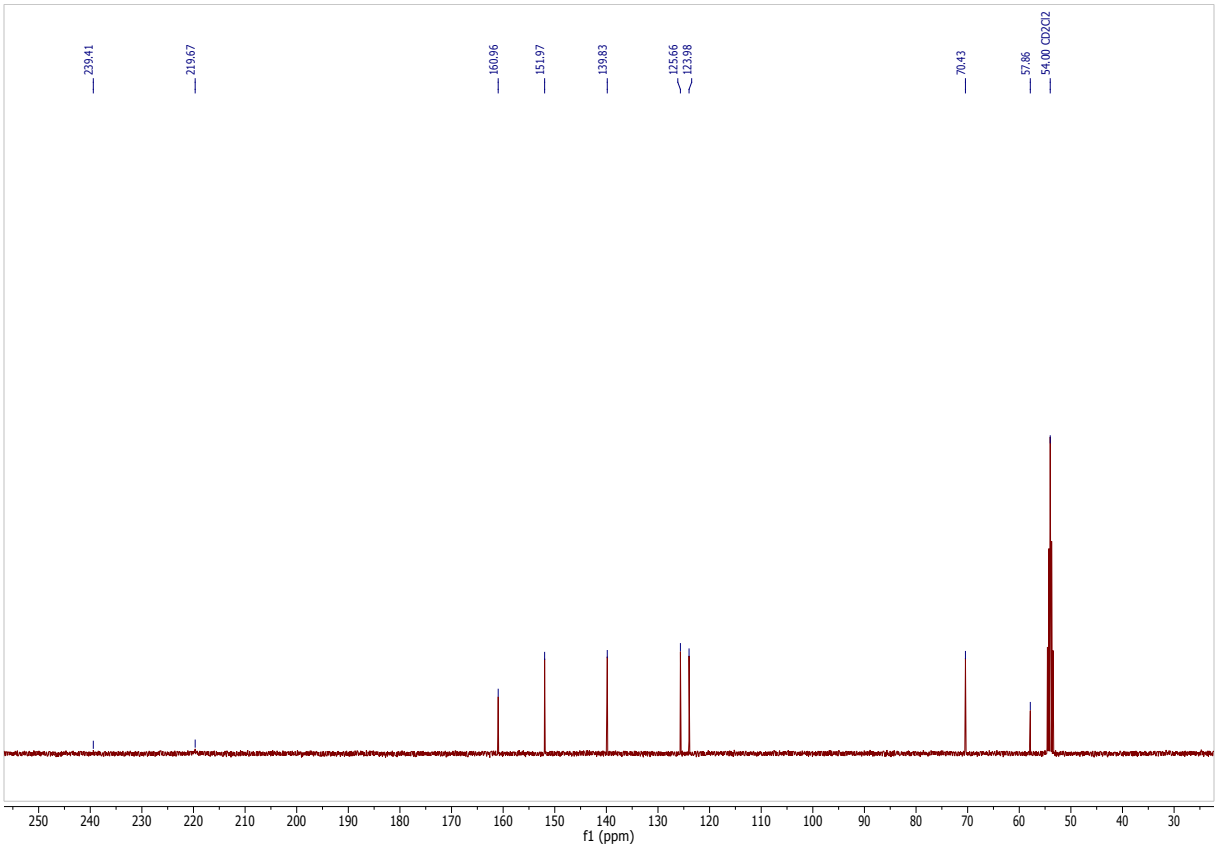


Figure SI 5. ^{13}C-NMR of complex [Mn(Me-dpa)(CO)$_3$]Br.

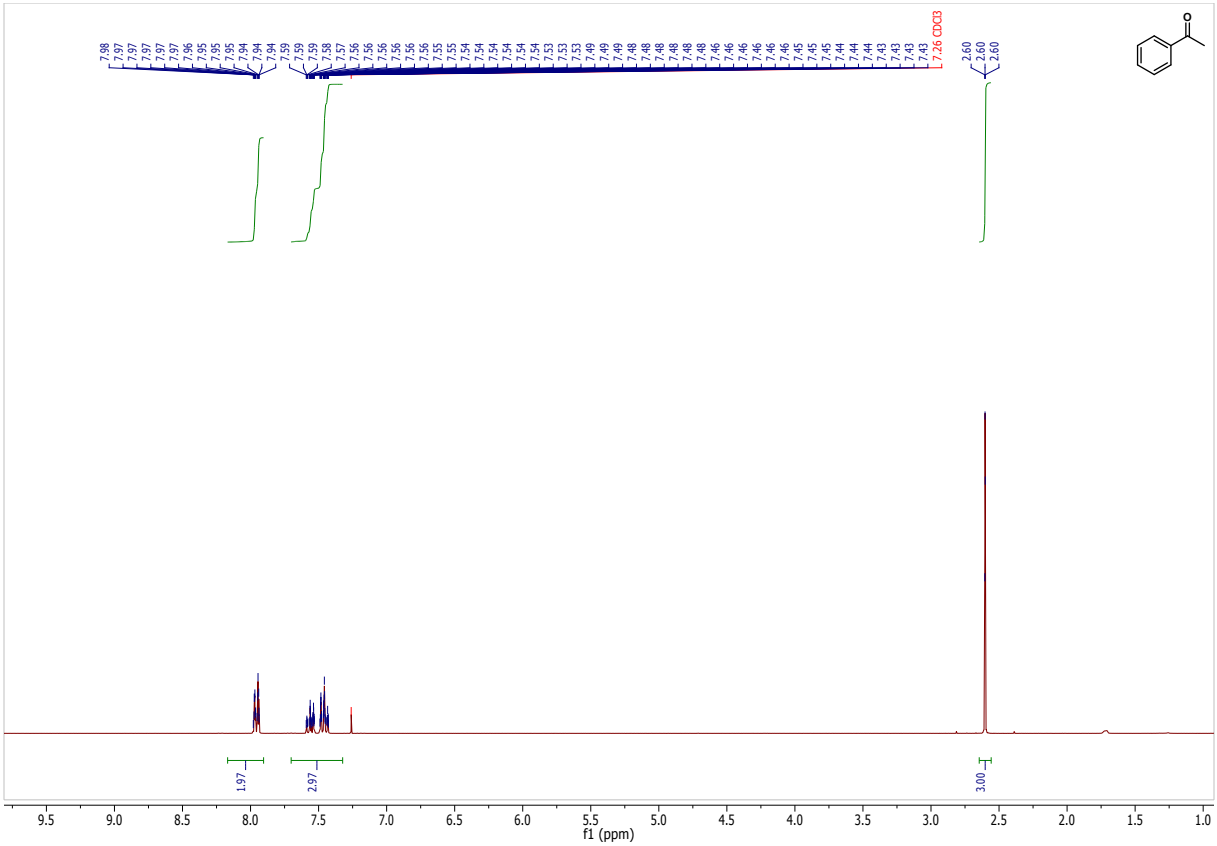


Figure SI 6. ^{1}H-NMR of acetophenone.

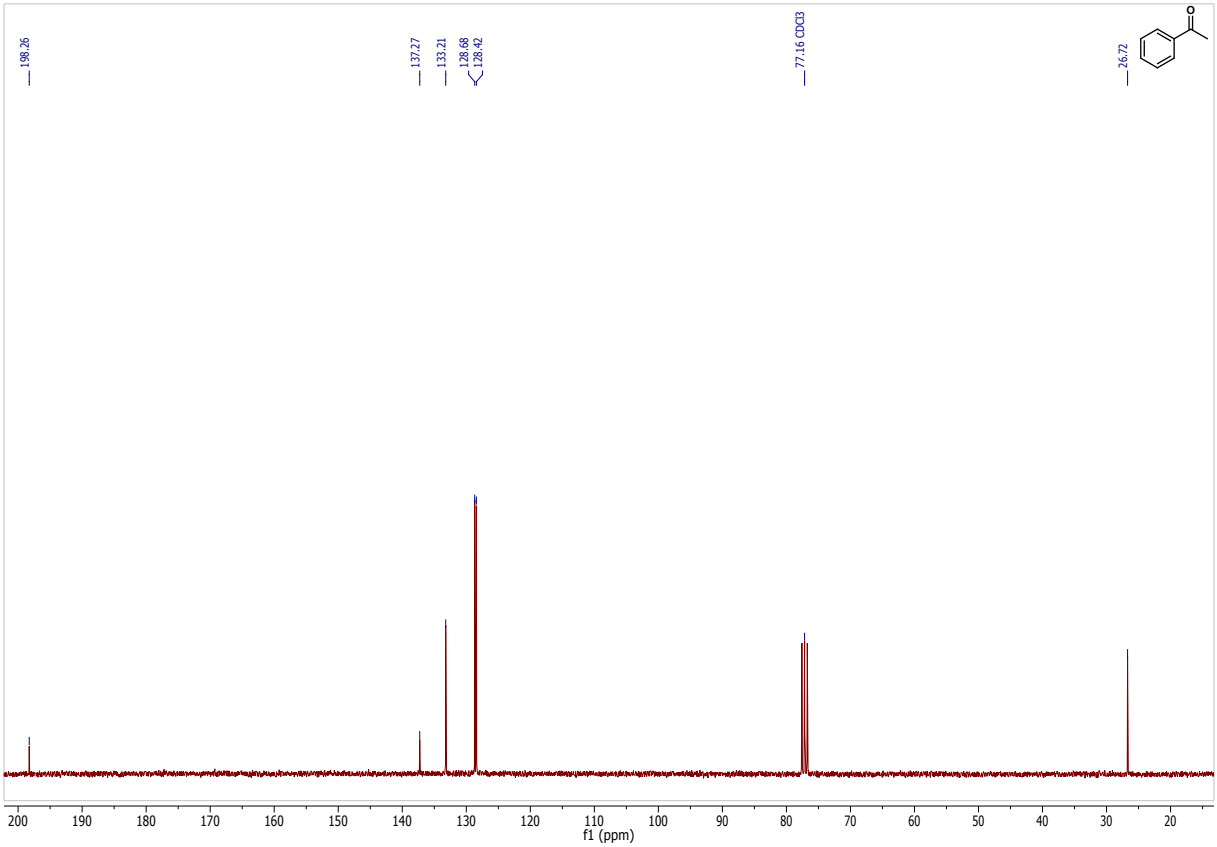


Figure SI 7. ^{13}C-NMR of acetophenone.

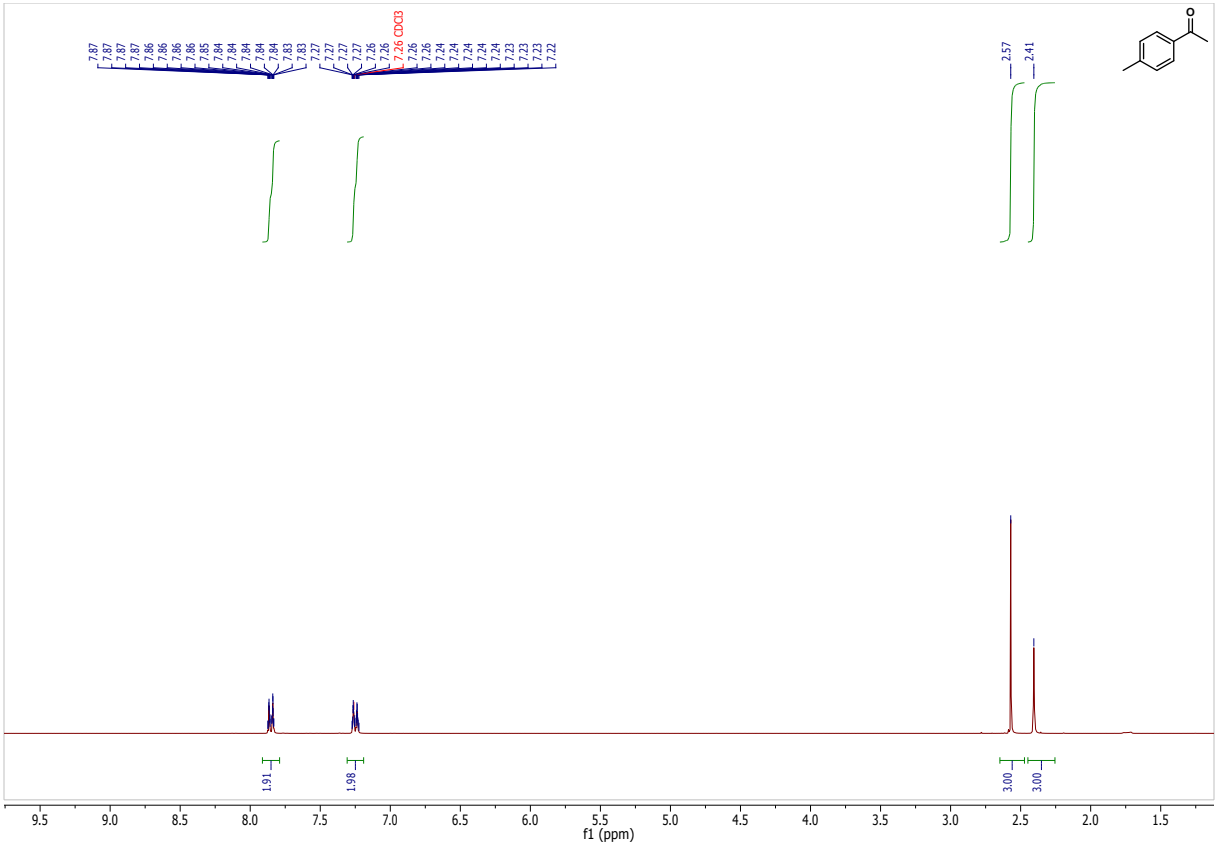


Figure SI 8. ^{1}H-NMR of 1-(4-methylphenyl)ethanone.

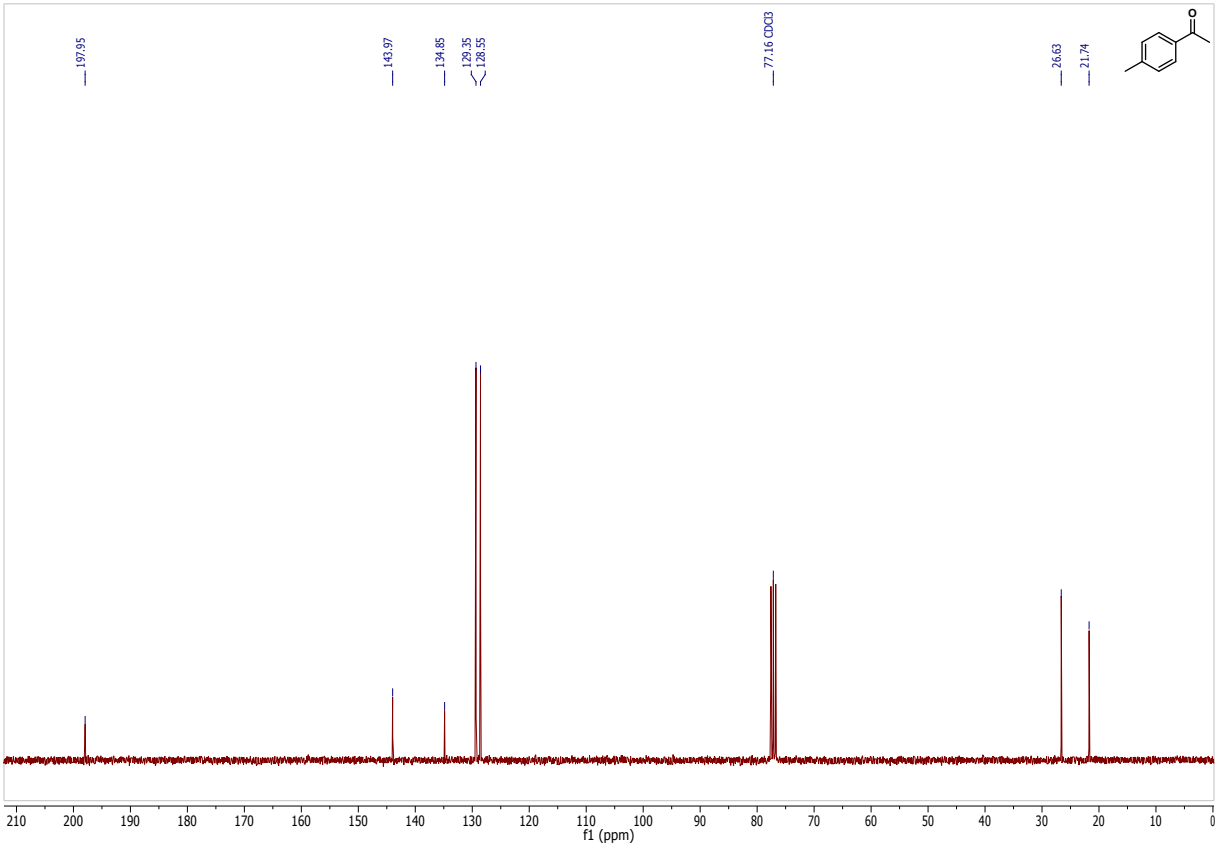


Figure SI 9. ^{13}C-NMR of 1-(4-methylphenyl)ethanone.

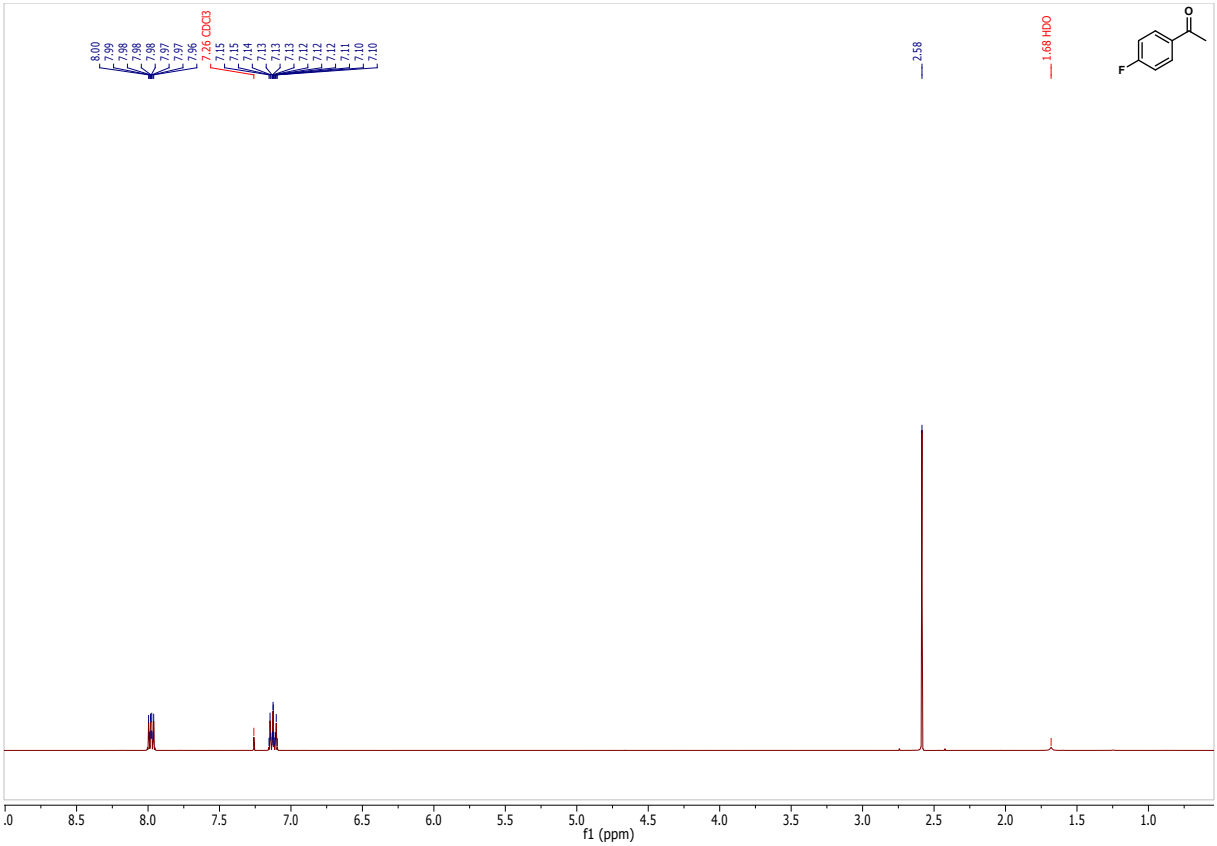


Figure SI 10.[1]H-NMR of 1-(4-fluorophenyl)ethanone.

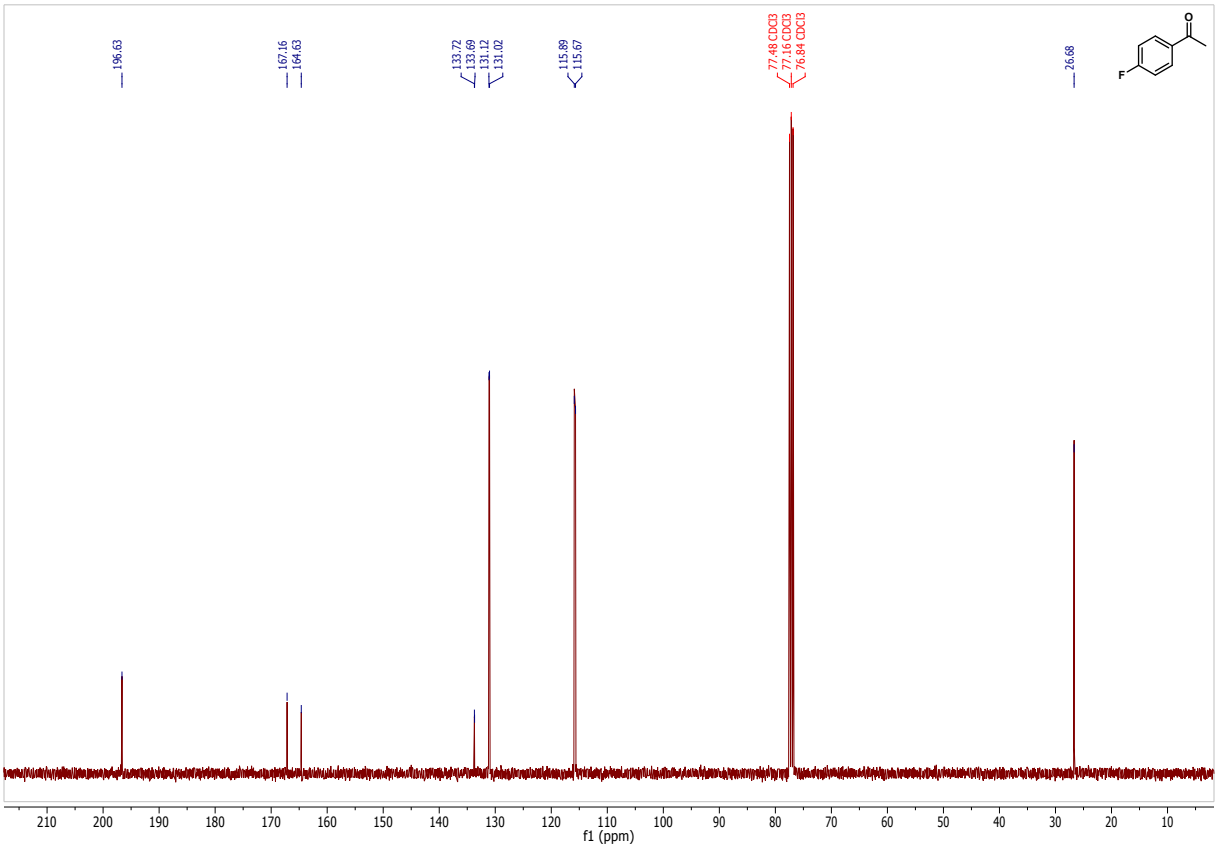


Figure SI 11. [13]C-NMR 1-(4-fluorophenyl)ethanone.

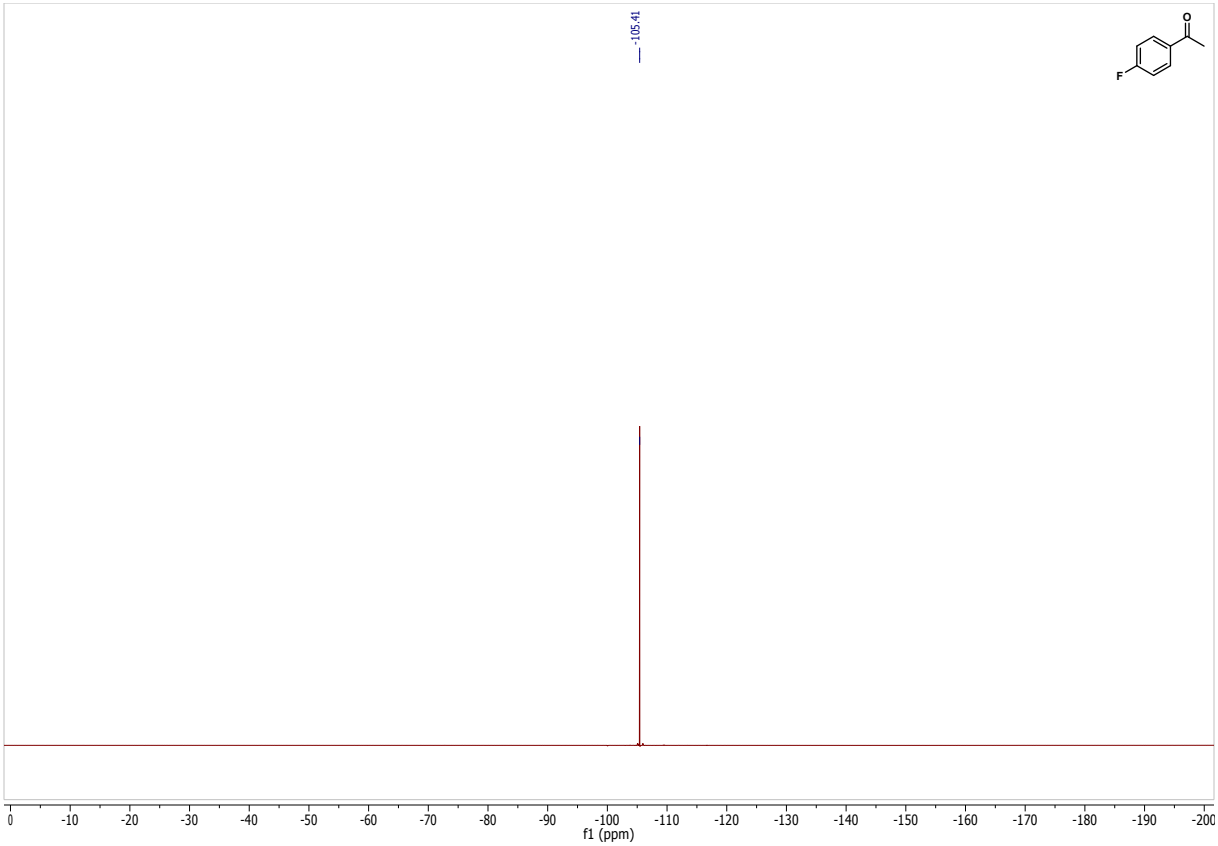


Figure SI 12. $^{19}F\{^{1}H\}$-NMR 1-(4-fluorophenyl)ethanone.

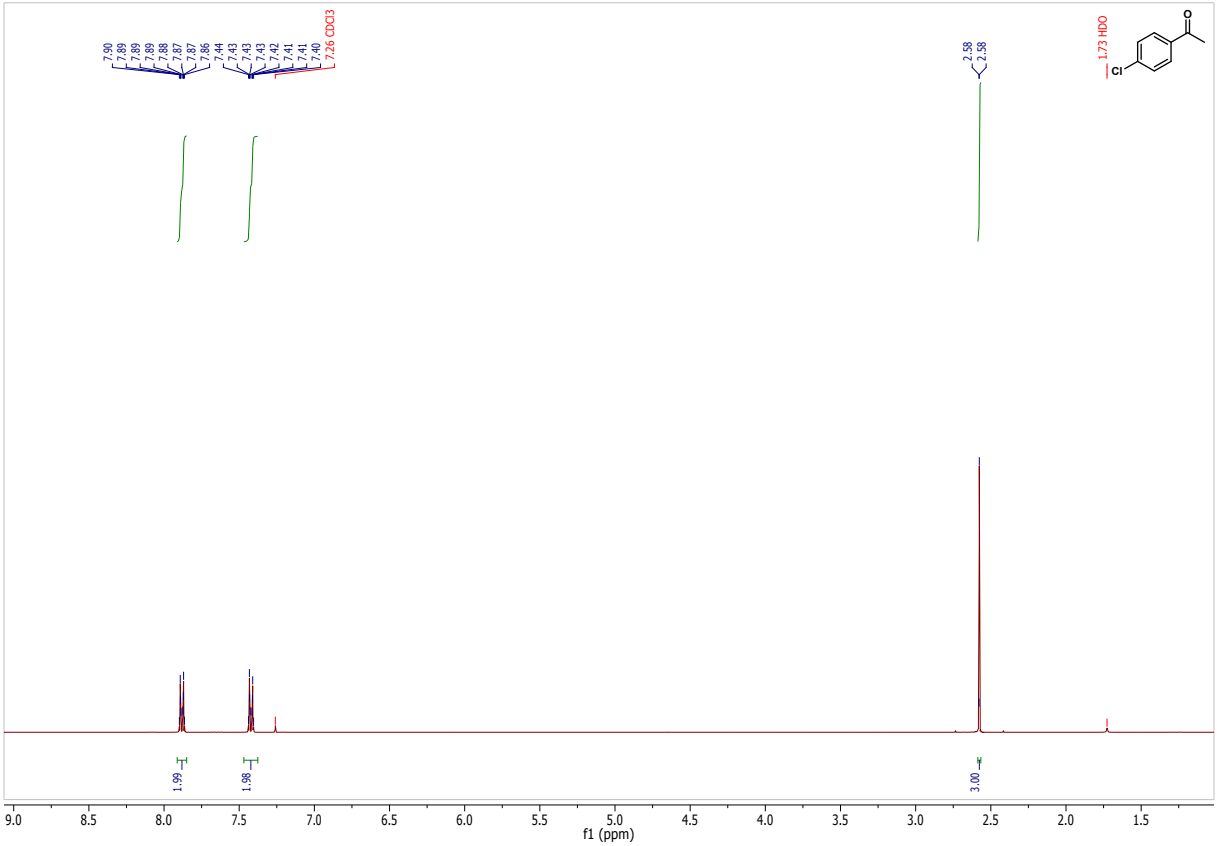


Figure SI 13. ^{1}H-NMR of 1-(4-chlorophenyl)ethanone.

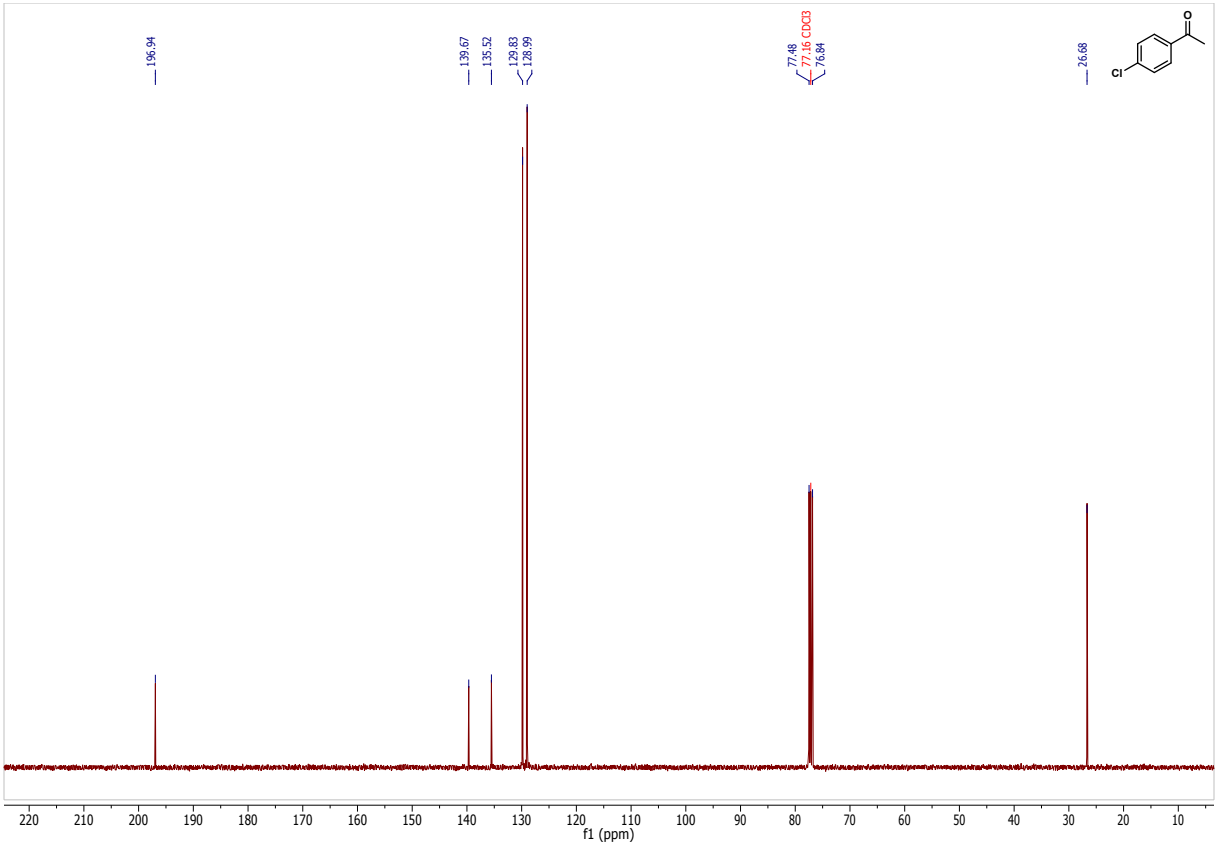


Figure SI 14. ^{13}C-NMR 1-(4-chlorophenyl)ethanone.

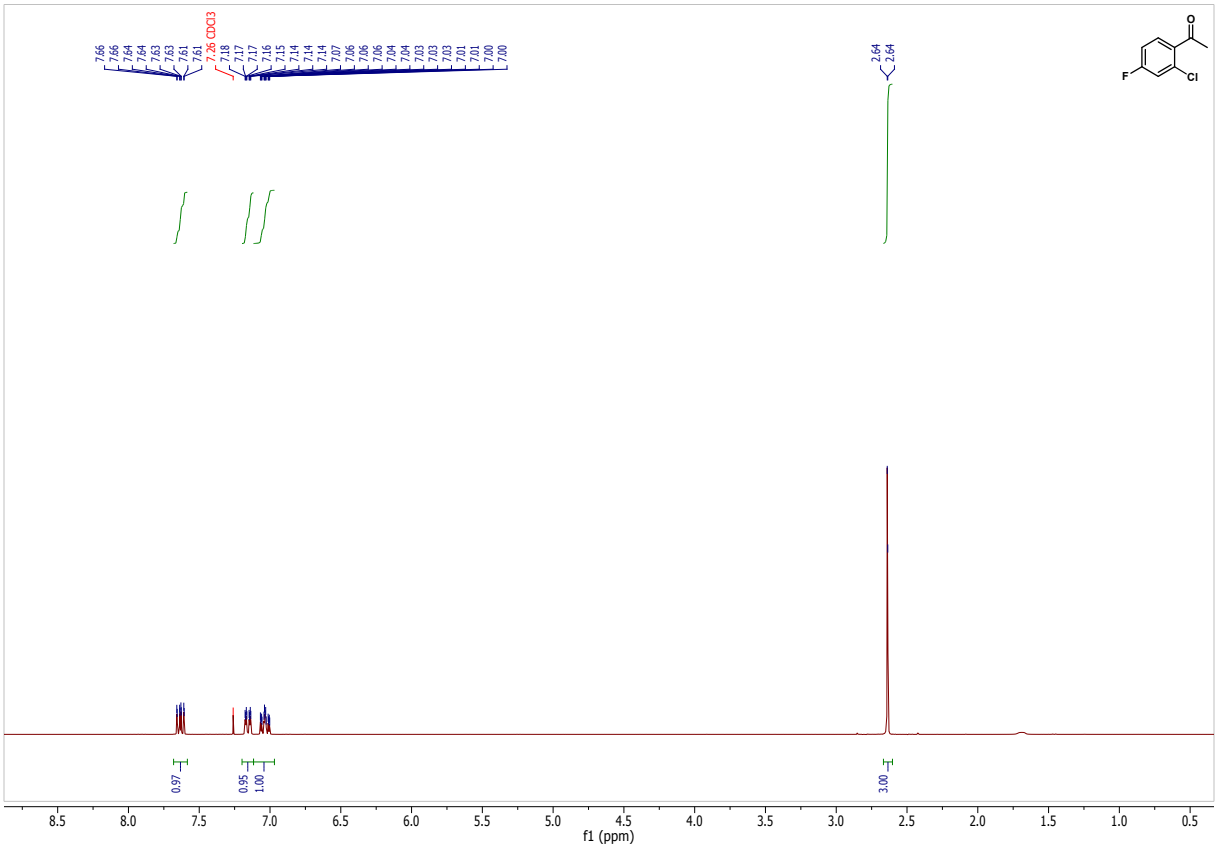


Figure SI 15. ^{1}H-NMR of 1-(2-chloro-4-flourophenyl)ethanone.

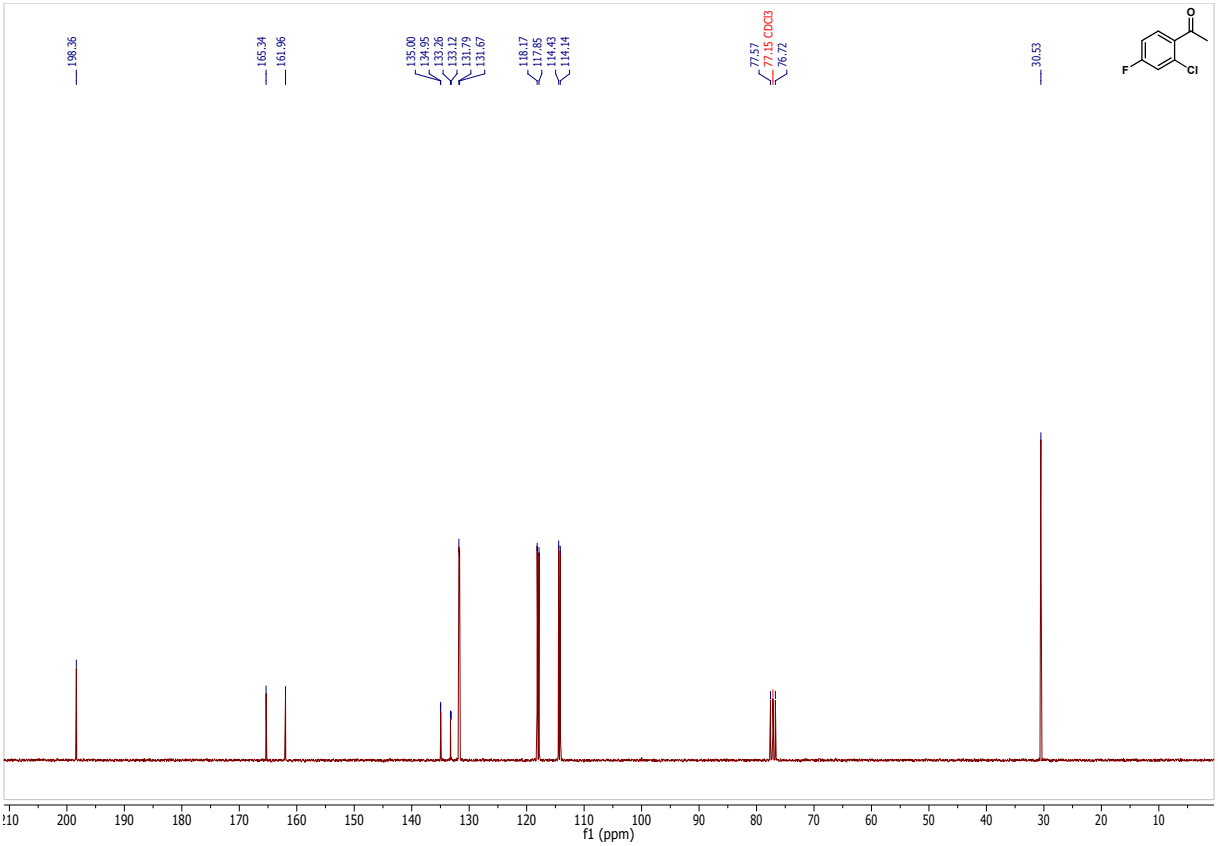


Figure SI 16. ^{13}C-NMR 1-(2-chloro-4-flourophenyl)ethanone.

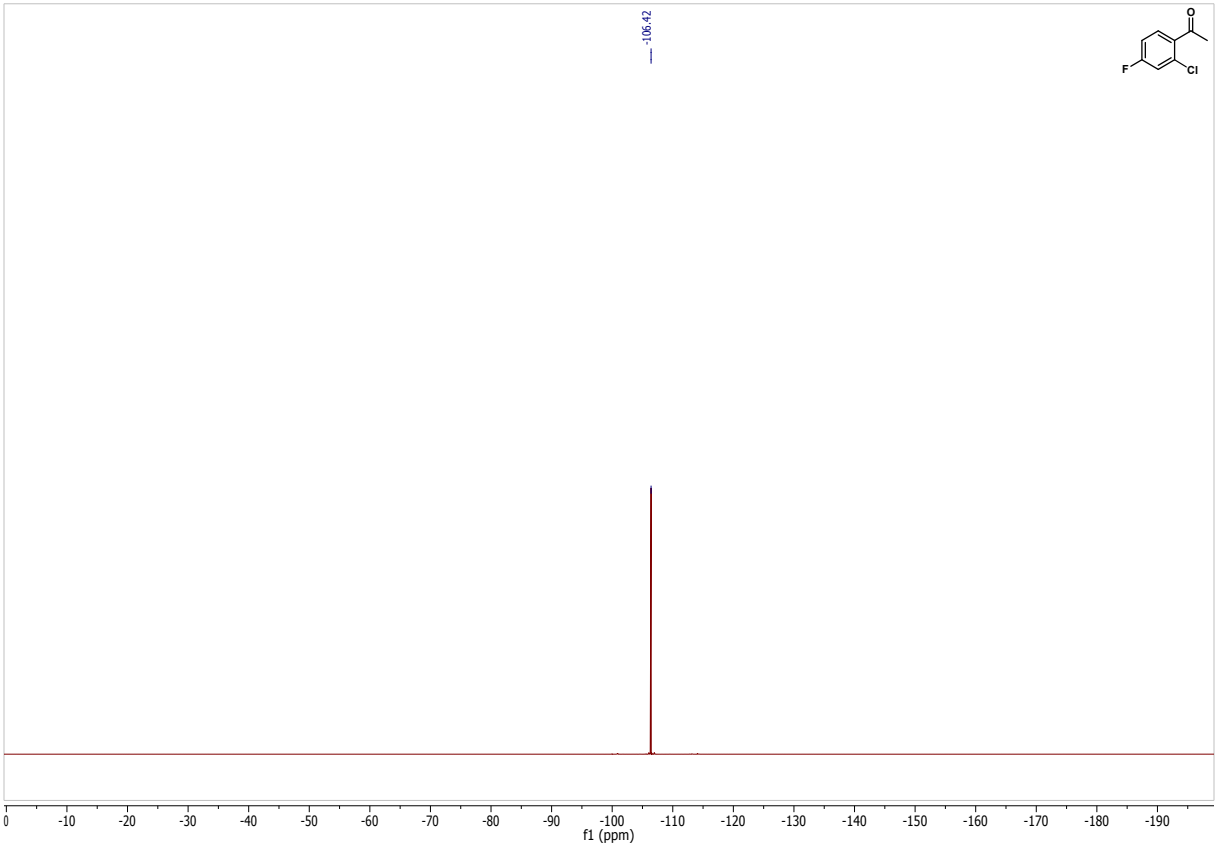


Figure SI 17. ^{19}F{^{1}H}-NMR 1-(2-chloro-4-fluorophenyl)ethanone.

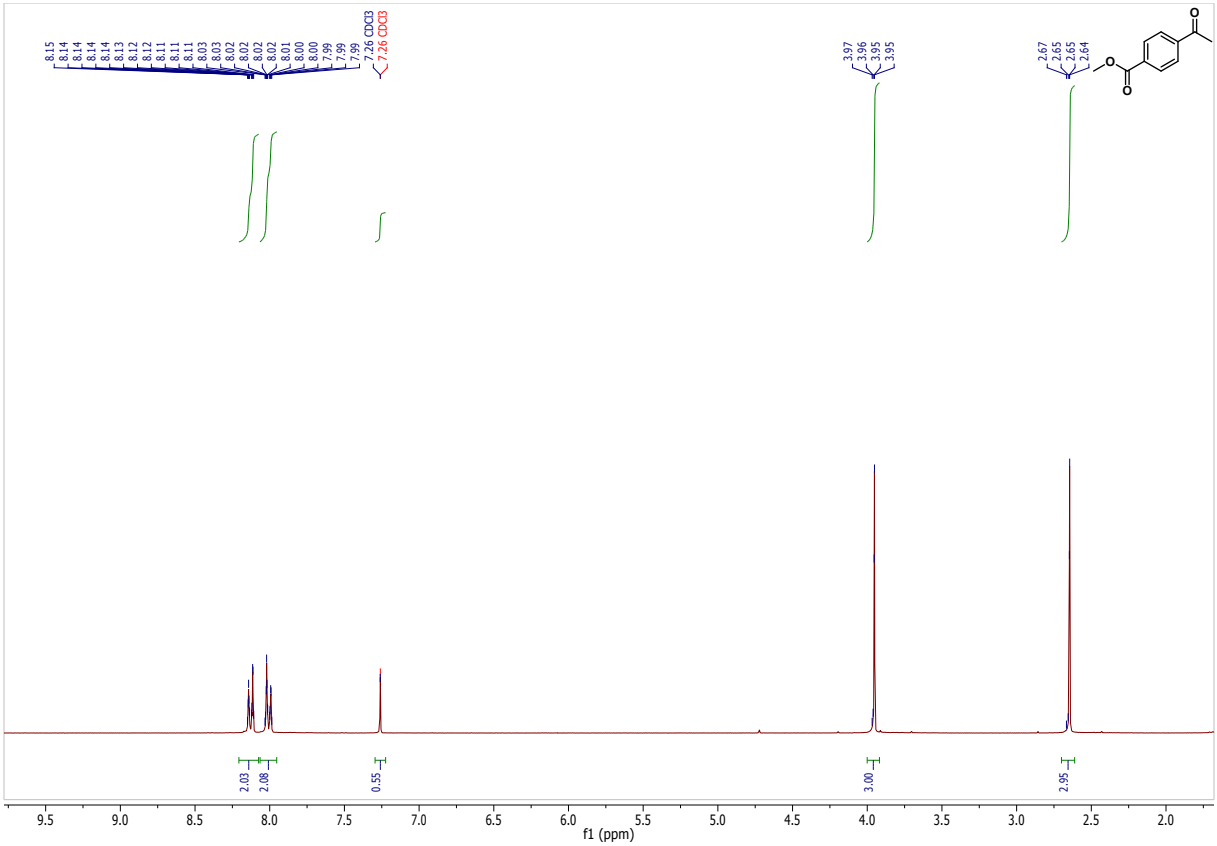


Figure SI 18. ^{1}H-NMR of methyl-4-acetylbenzoate.

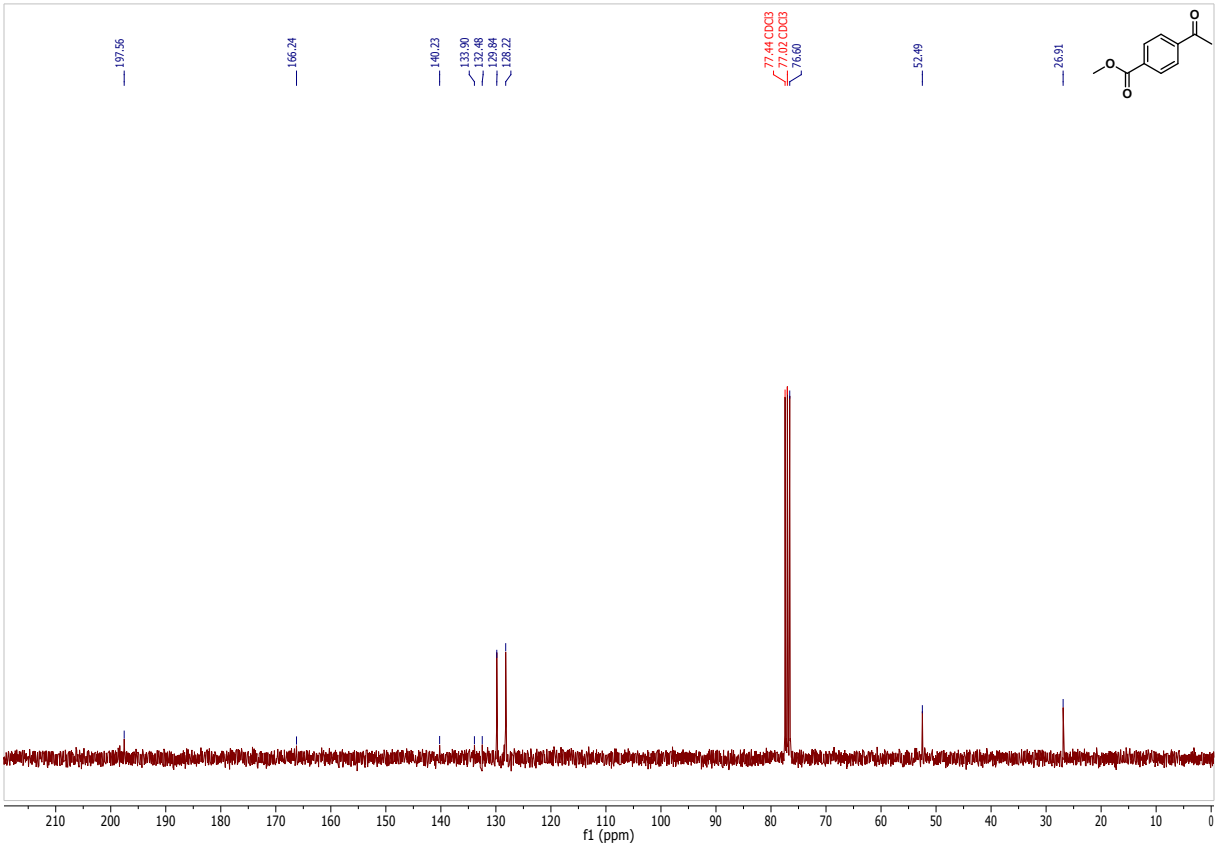


Figure SI 19. ^{13}C-NMR of methyl-4-acetylbenzoate

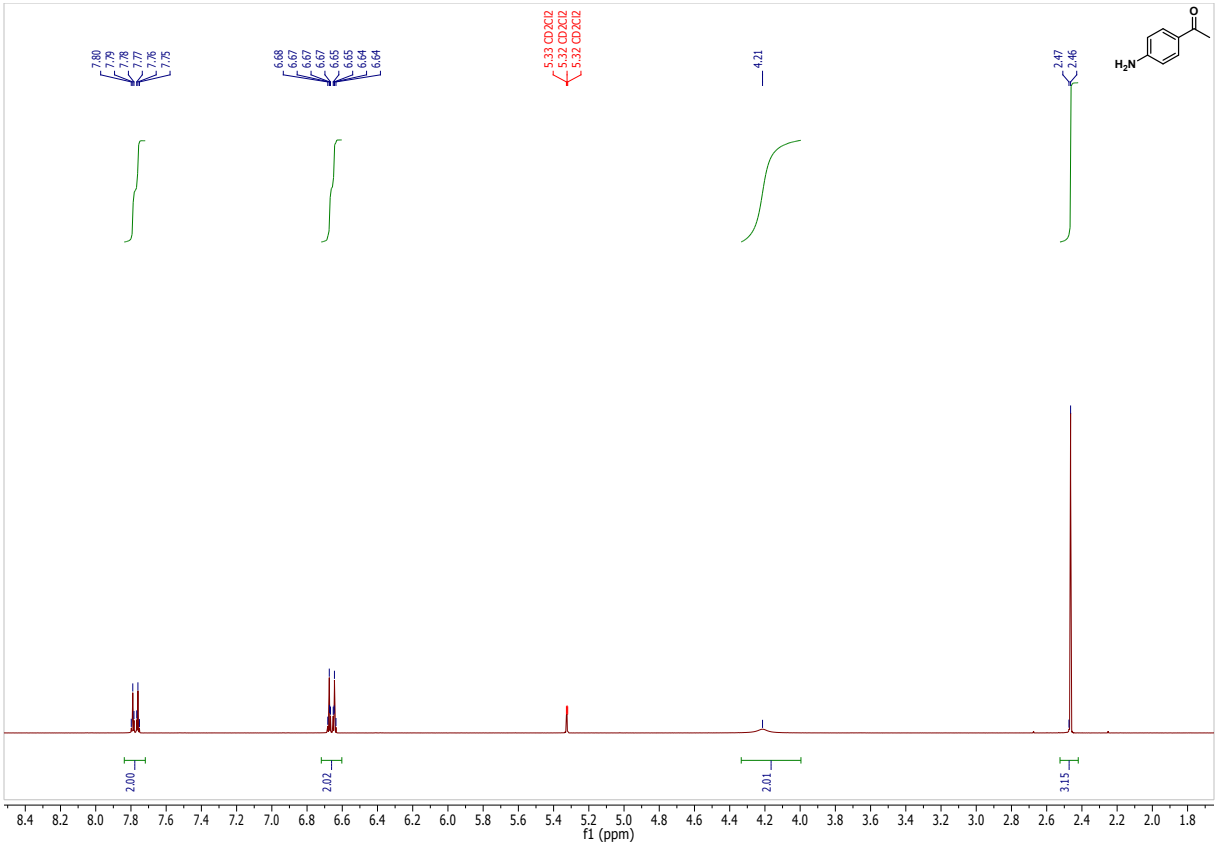


Figure SI 20. ^{1}H-NMR of 1-(4-aminophenyl)ethanone.

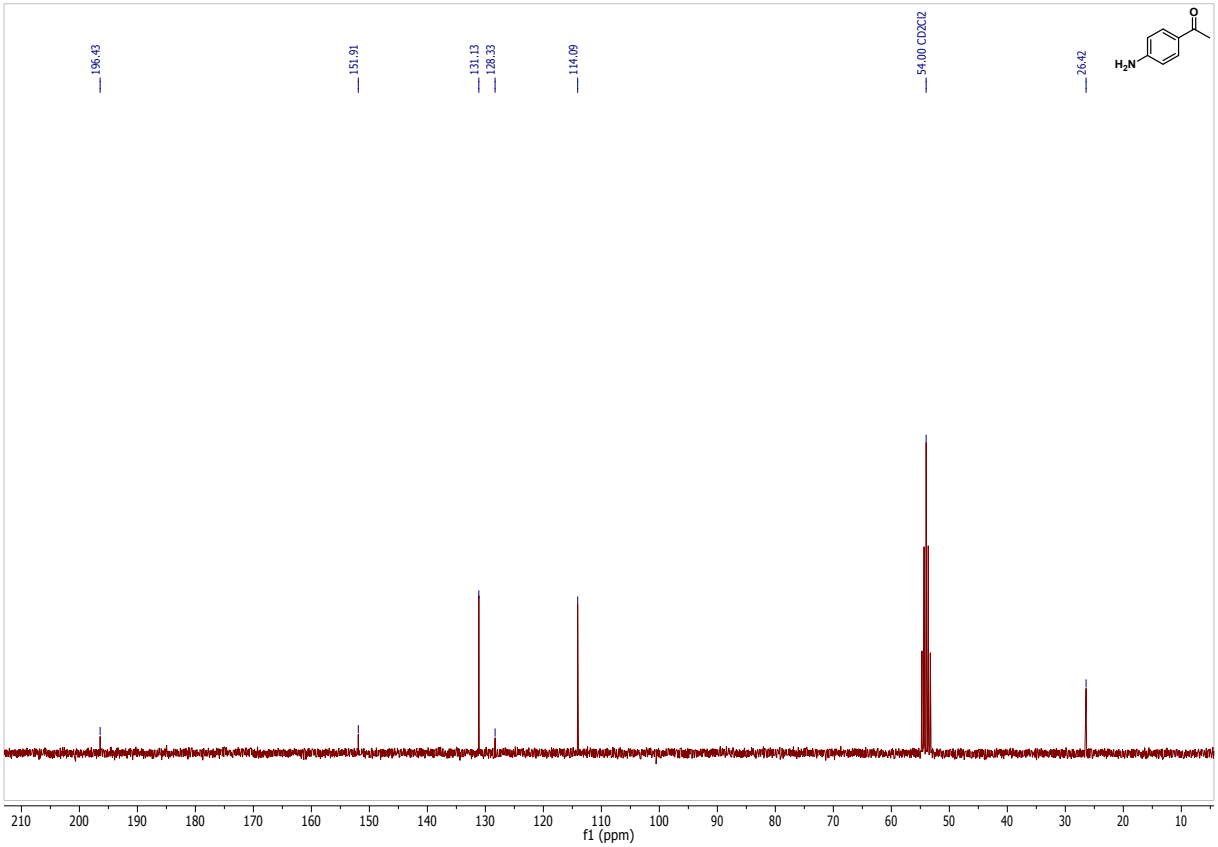


Figure SI 21. ^{13}C-NMR of 1-(4-aminophenyl)ethanone.

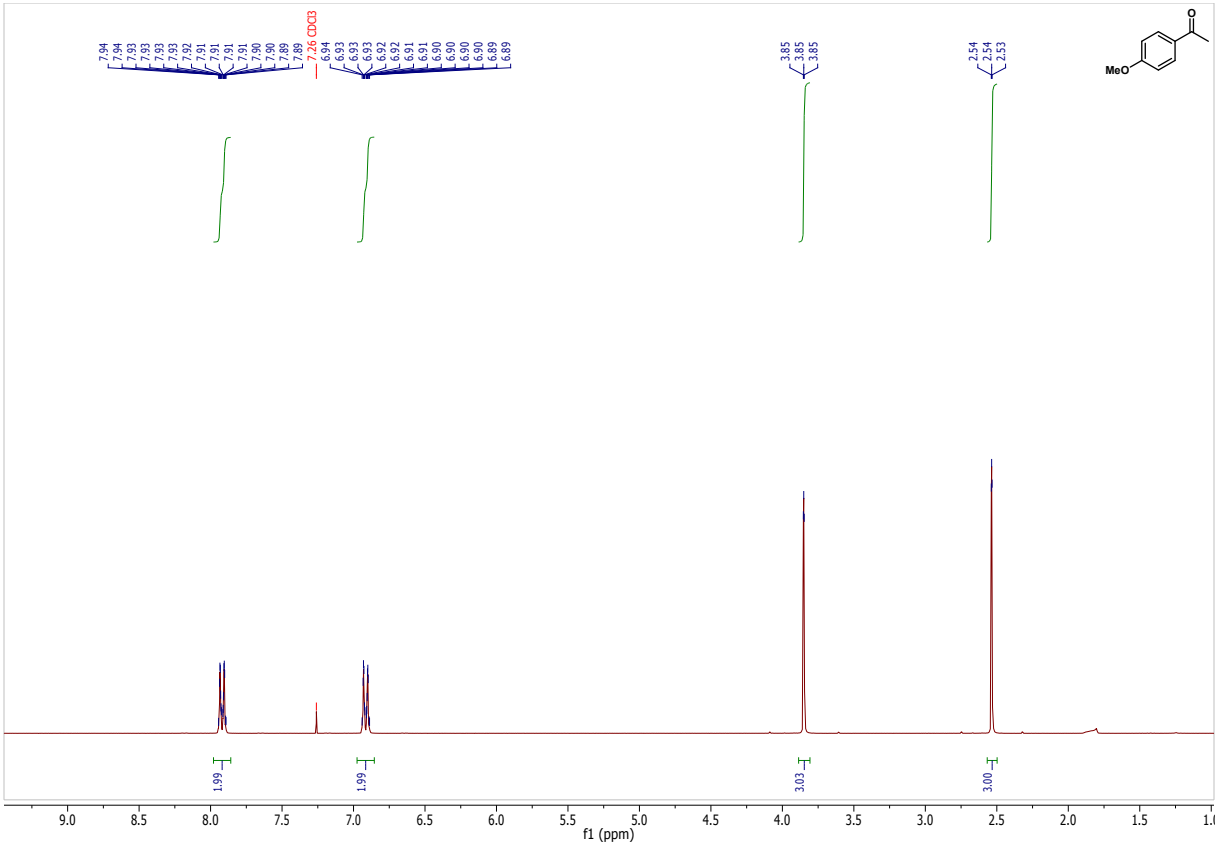


Figure SI 22. ^{1}H-NMR of 1-(4-methoxyphenyl)ethanone.

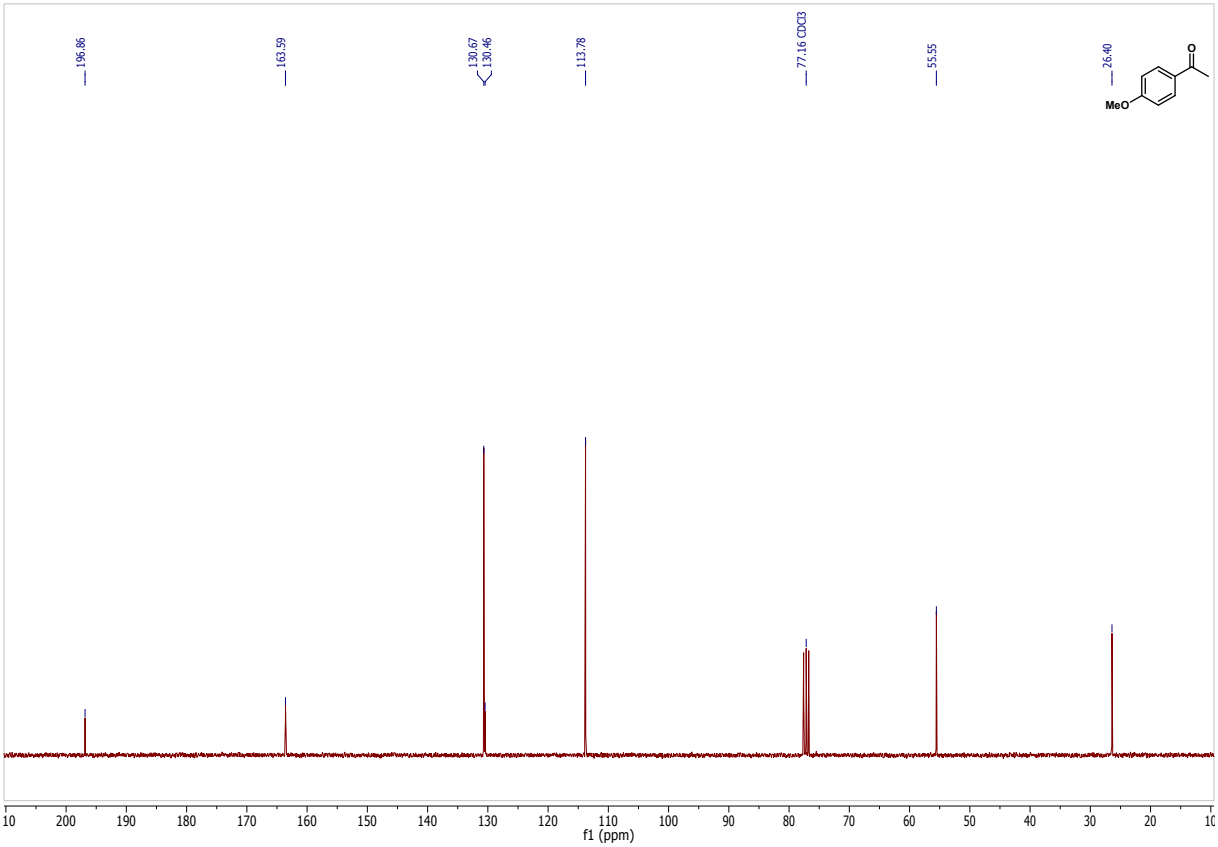


Figure SI 23. ^{13}C-NMR 1-(4-methoxyphenyl)ethanone.

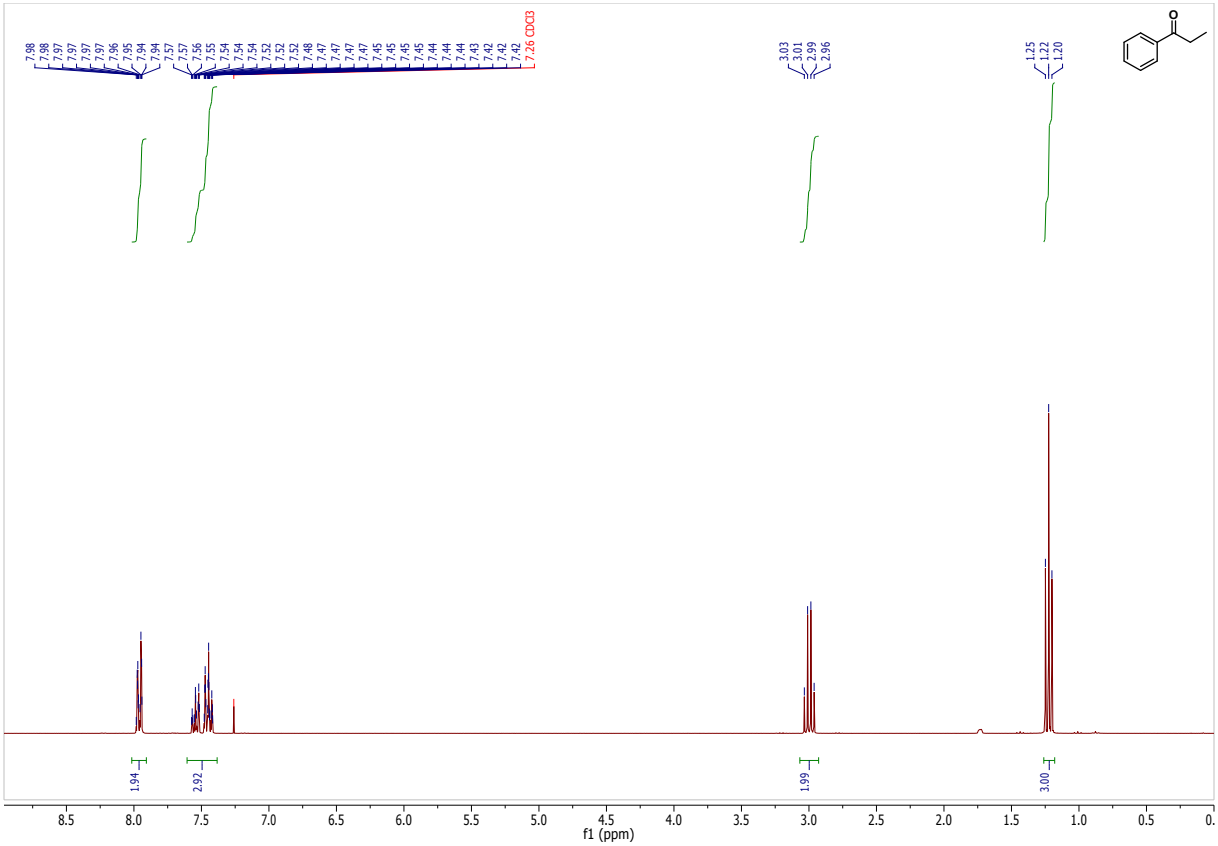


Figure SI 24. ^{1}H-NMR of propiophenone.

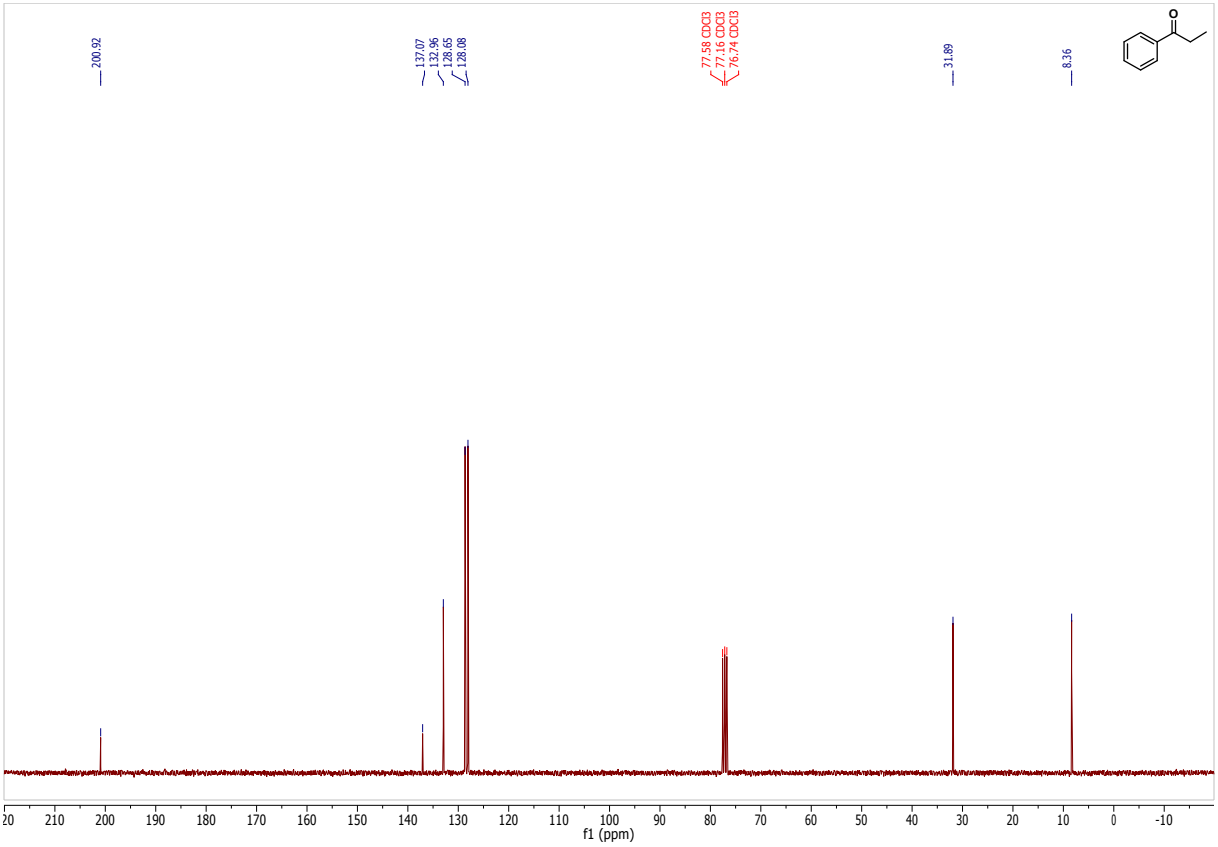


Figure SI 25. ^{13}C-NMR of propiophenone.

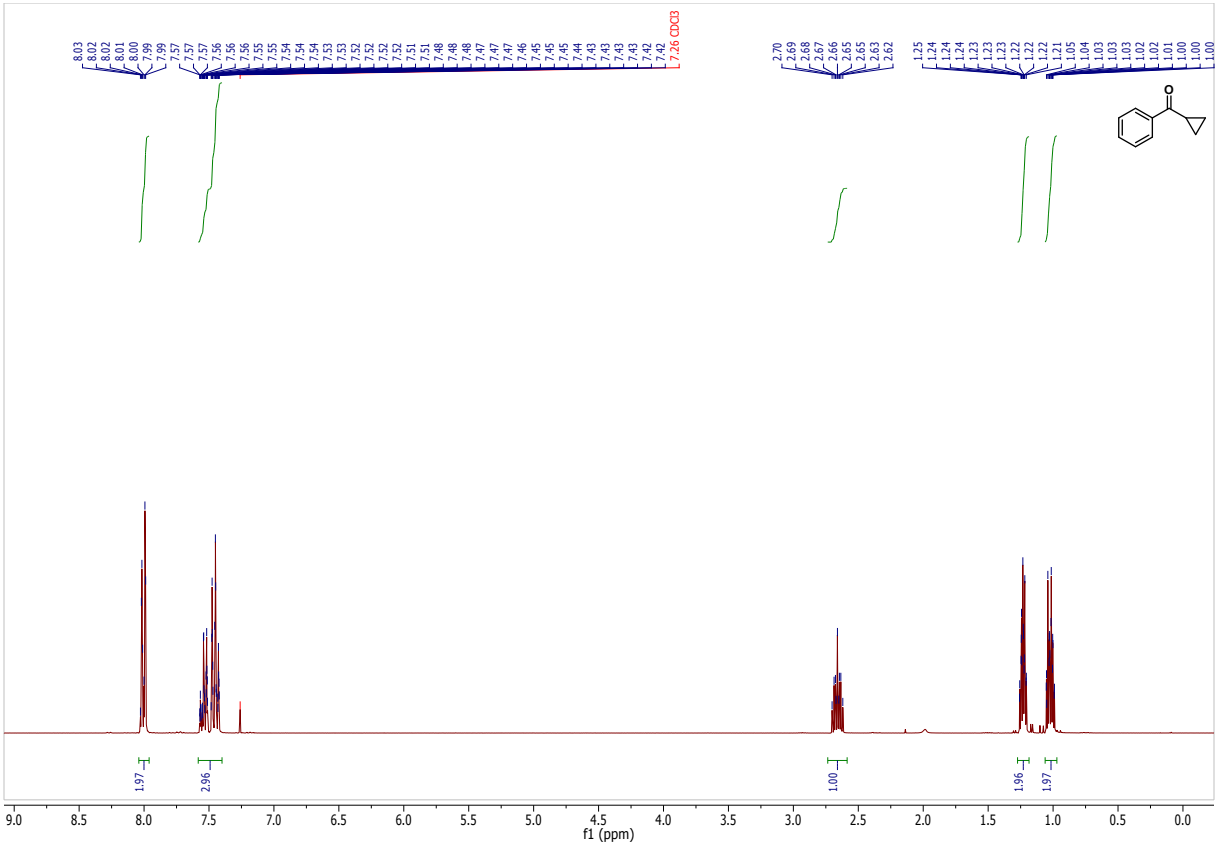


Figure SI 26. ^{1}H-NMR of cyclopropyl(phenyl)methanone.

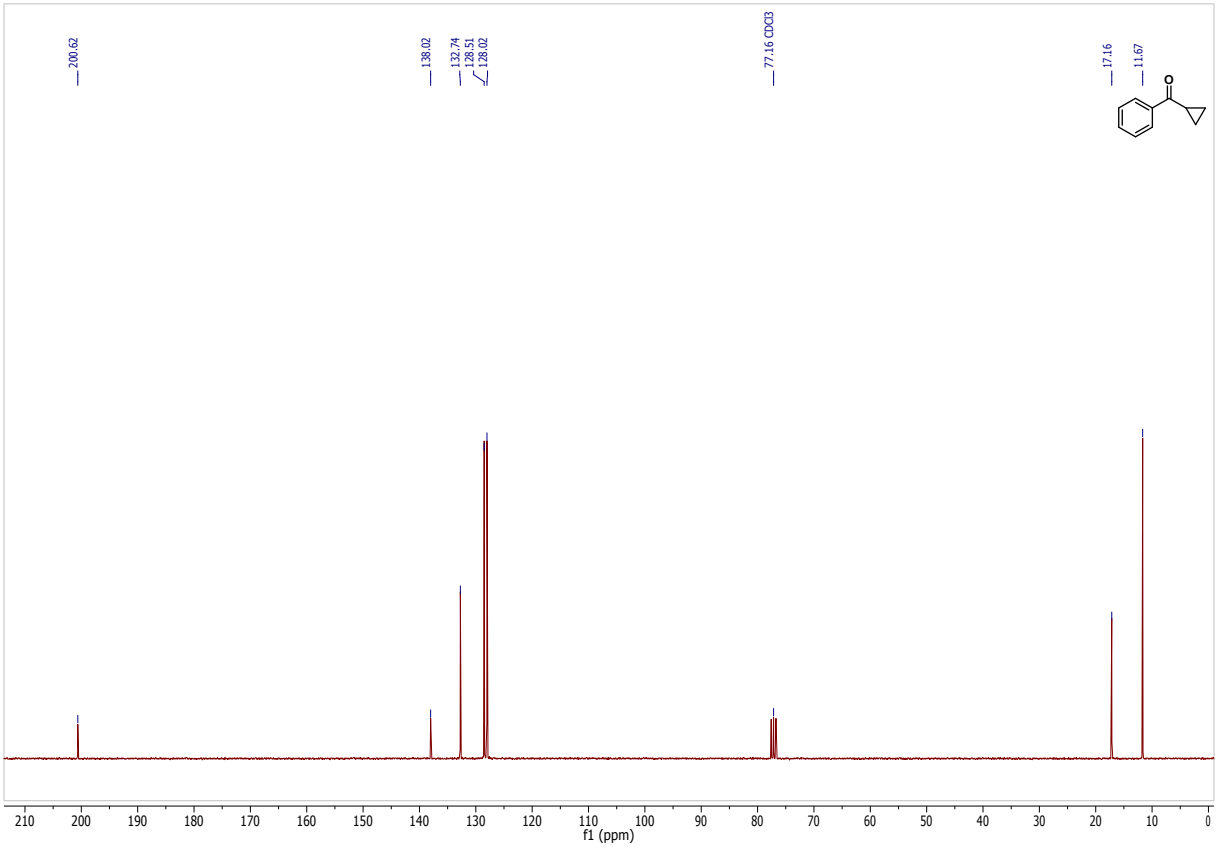


Figure SI 27. ^{13}C-NMR of cyclopropyl(phenyl)methanone.

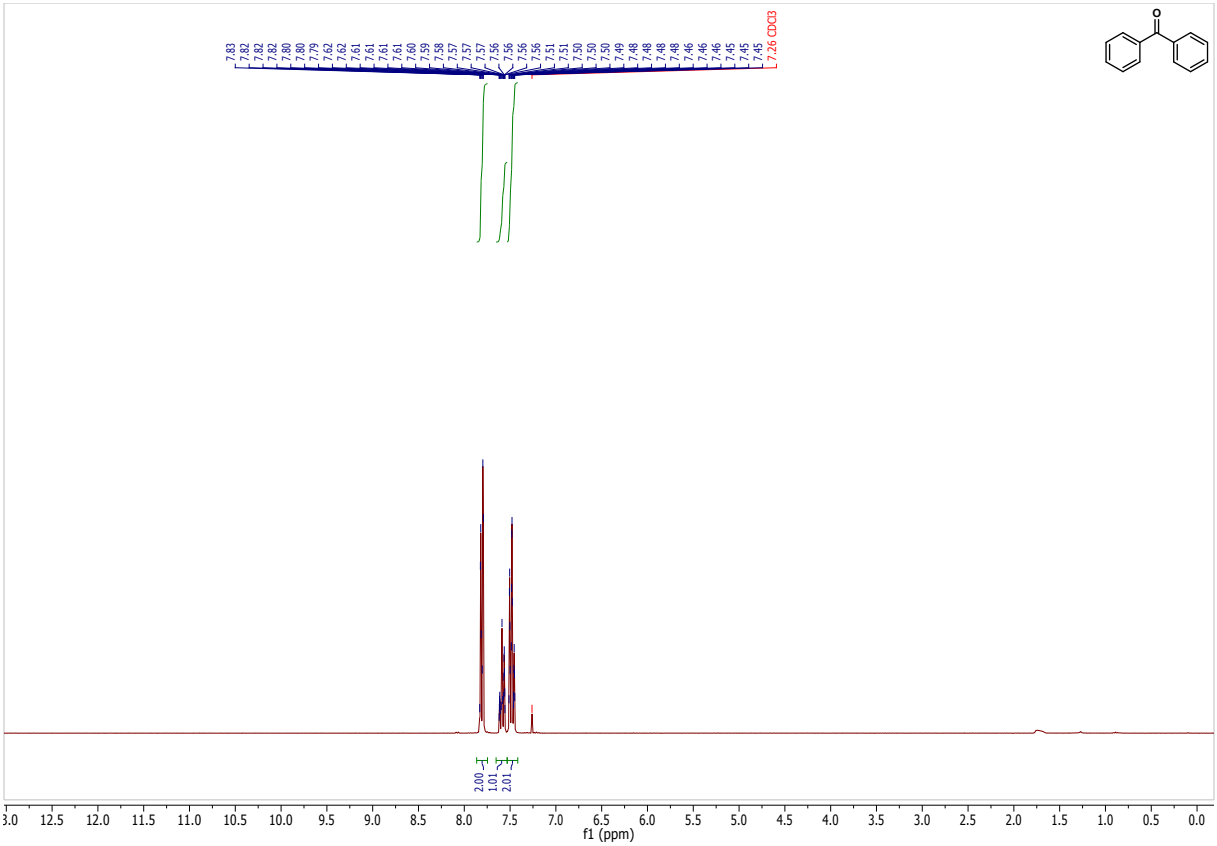


Figure SI 28. ^{1}H-NMR of benzophenone.

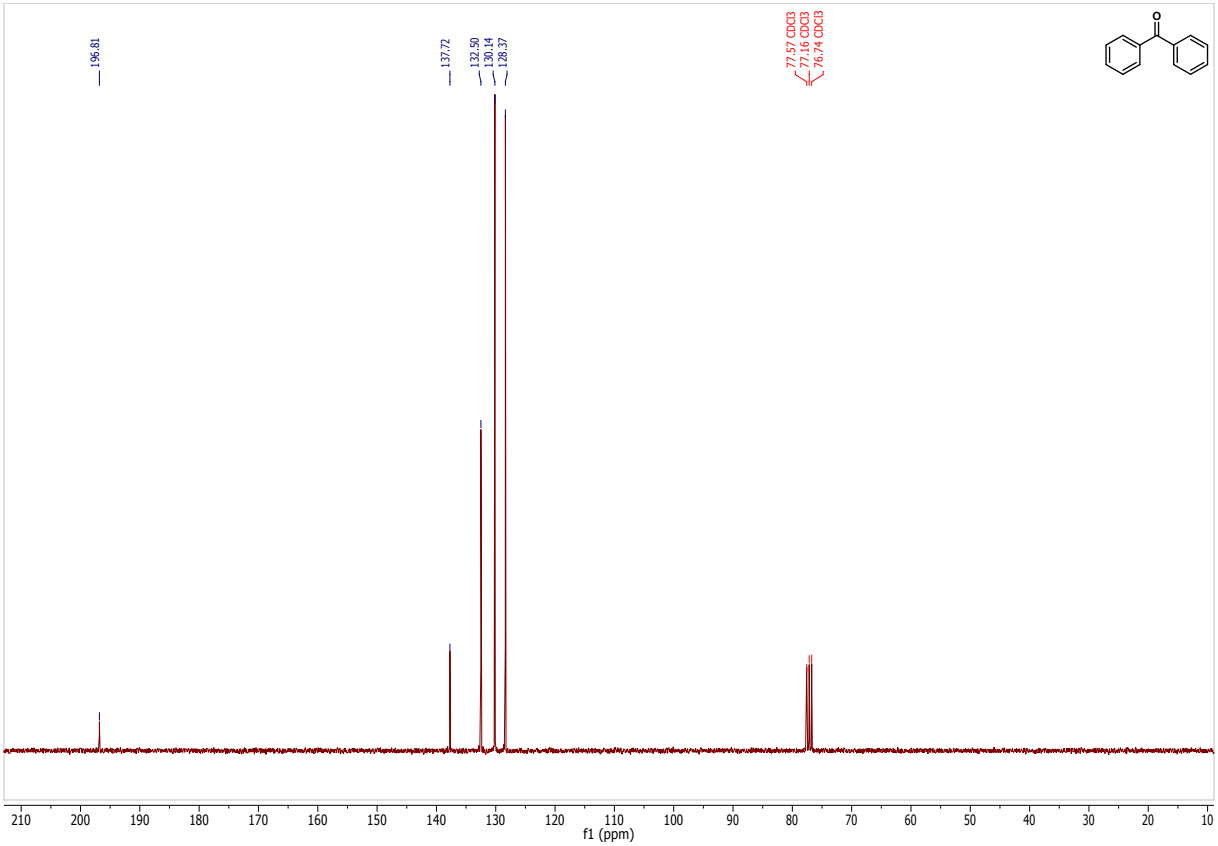


Figure SI 29. ^{13}C-NMR of benzophenone.

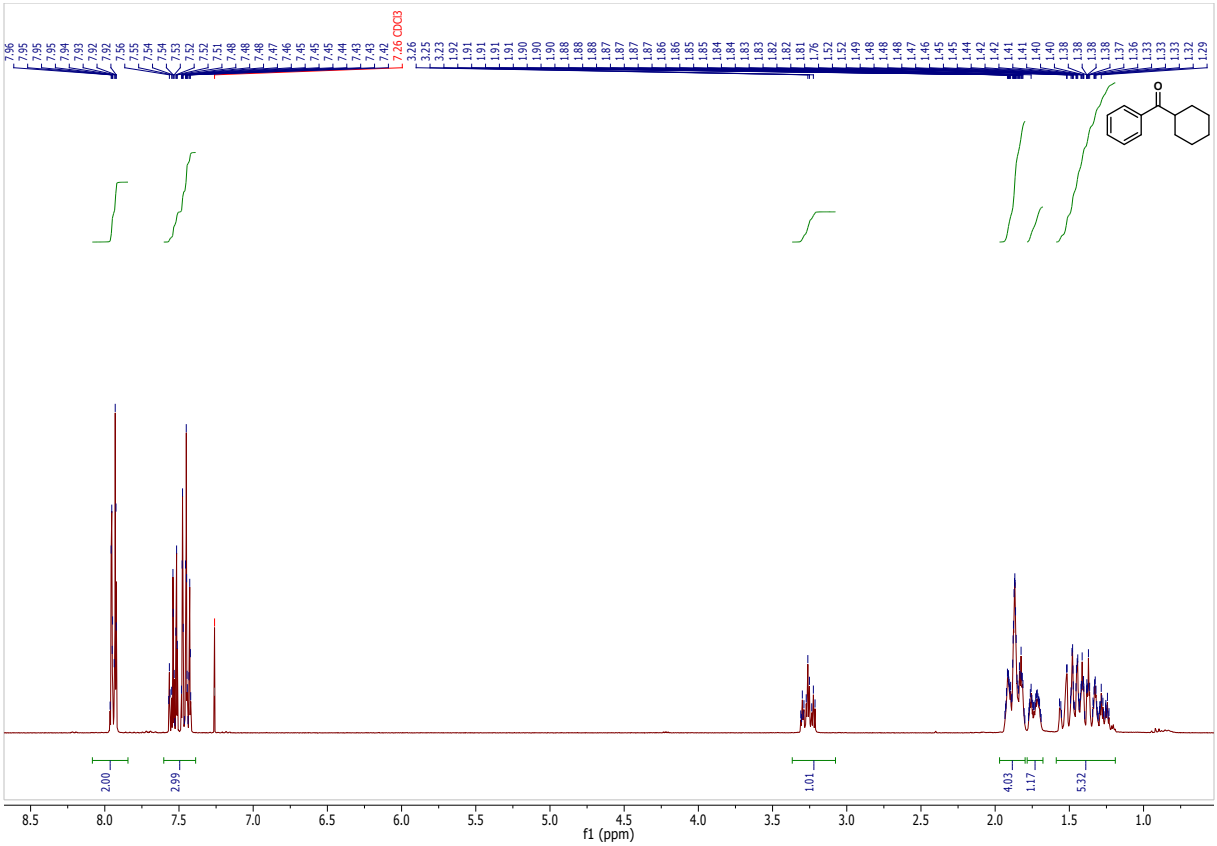


Figure SI 30. ^{1}H-NMR of cyclohexyl(phenyl)methanone.

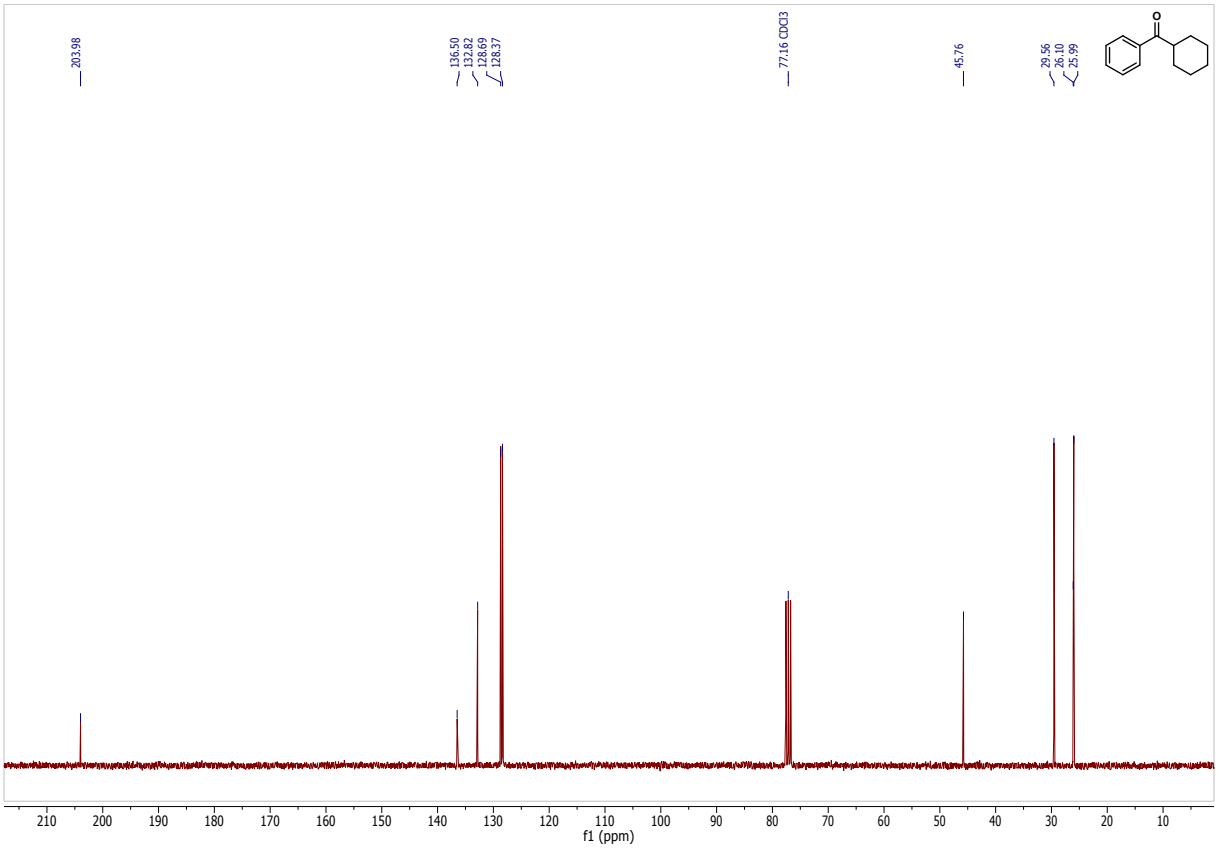


Figure SI 31. ^{13}C-NMR of cyclohexyl(phenyl)methanone.

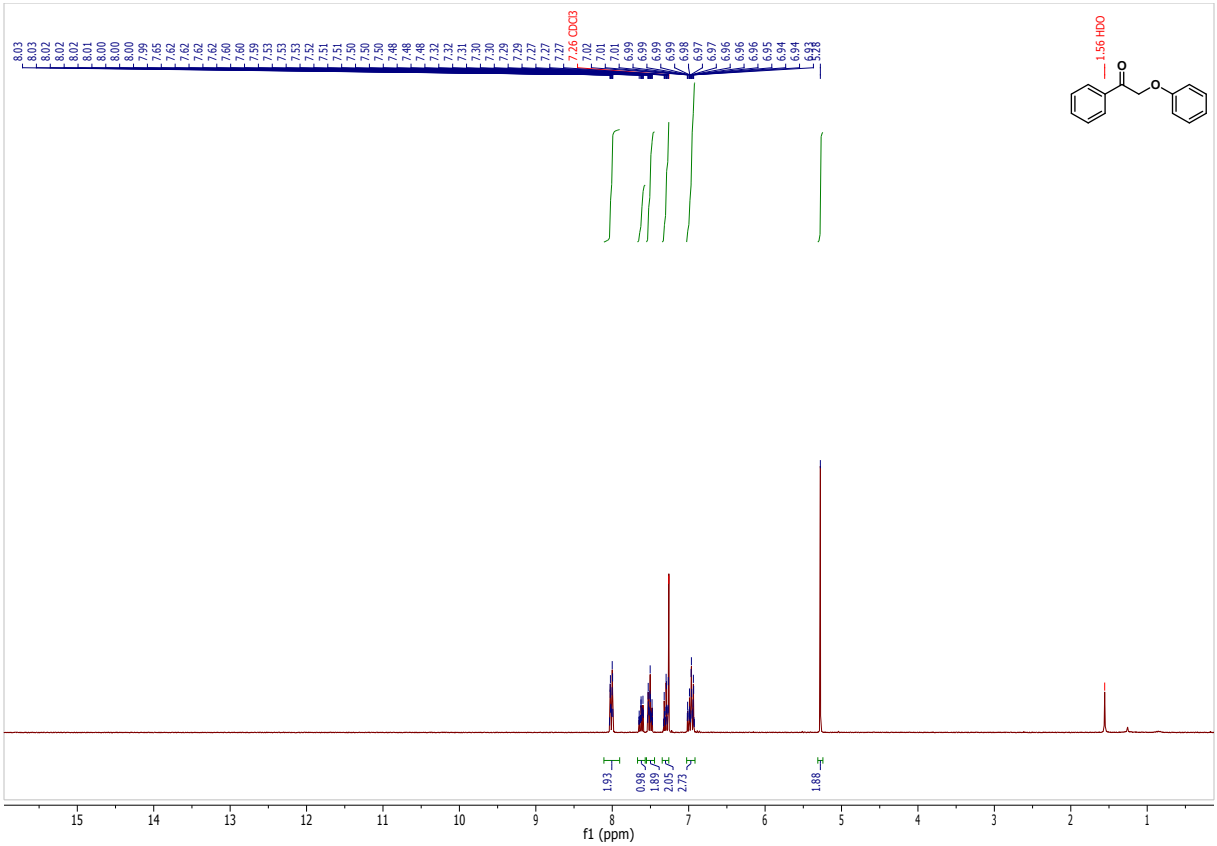


Figure SI 32. ^{1}H-NMR of 2-phenoxy-1-phenylethan-1-one.

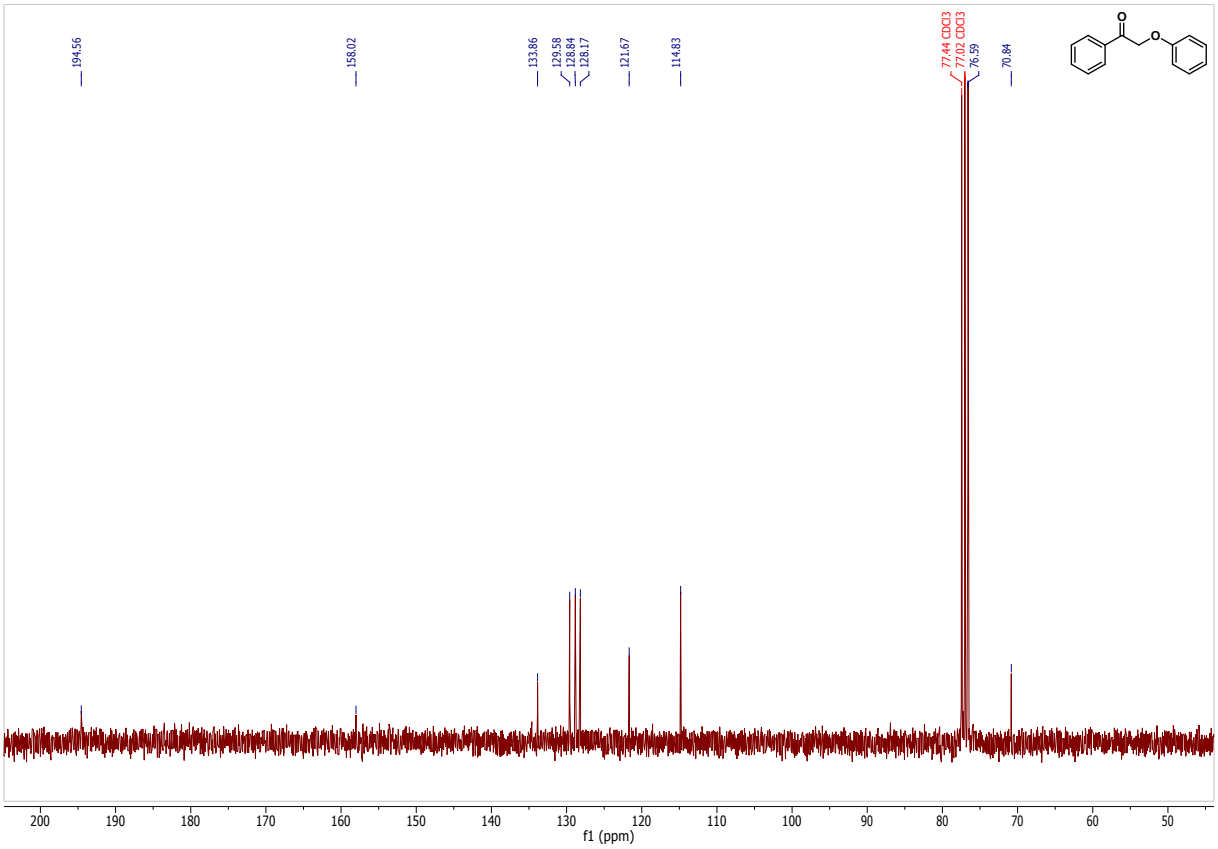


Figure SI 33. ^{13}C-NMR of 2-phenoxy-1-phenylethan-1-one.

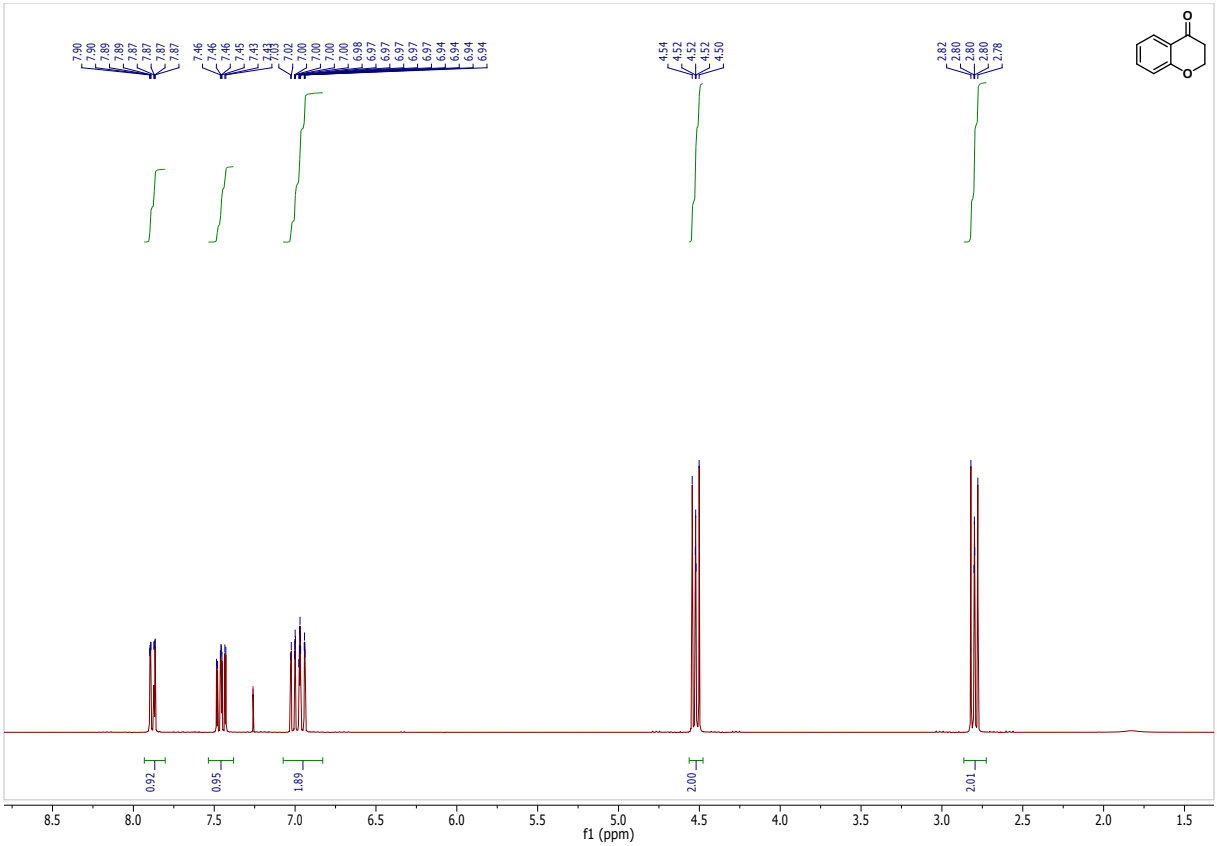


Figure SI 34. ^{1}H-NMR of chroman-4-one.

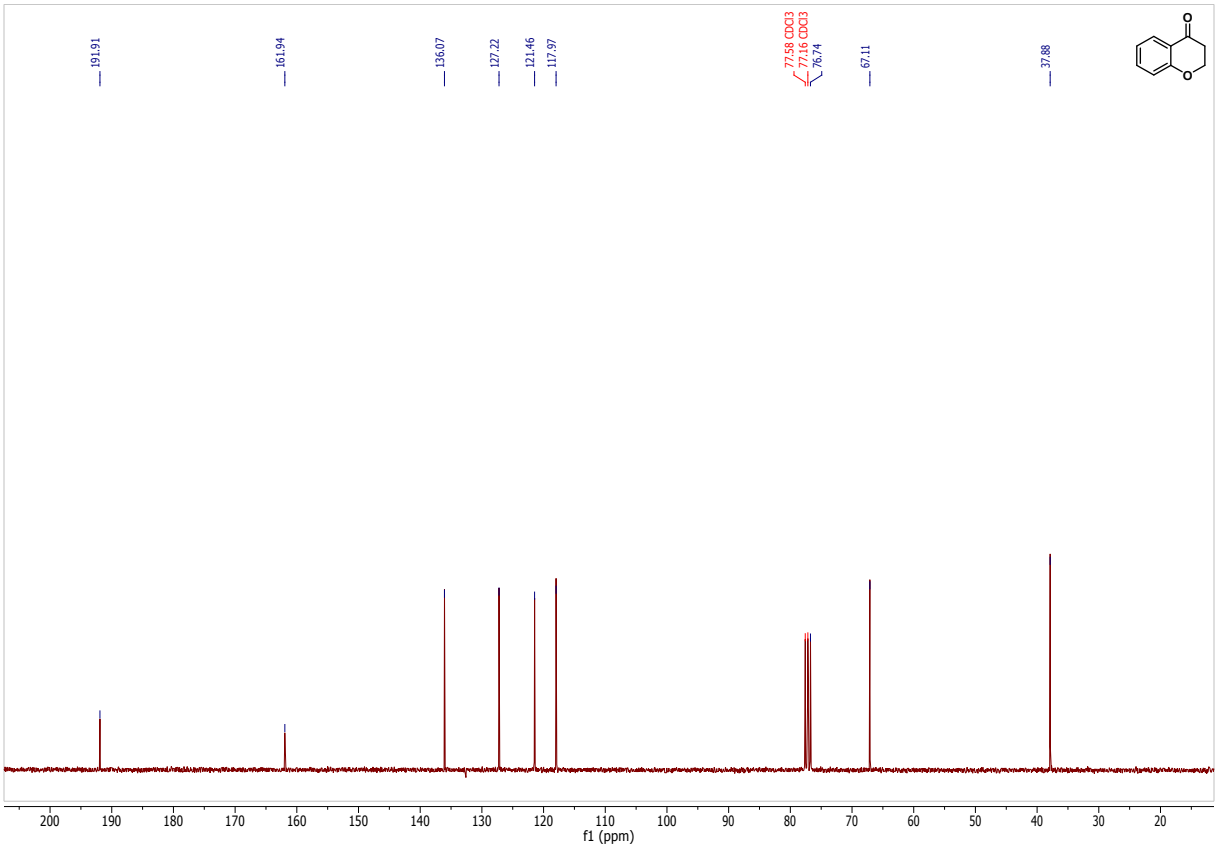


Figure SI 35. ^{13}C-NMR of chroman-4-one.

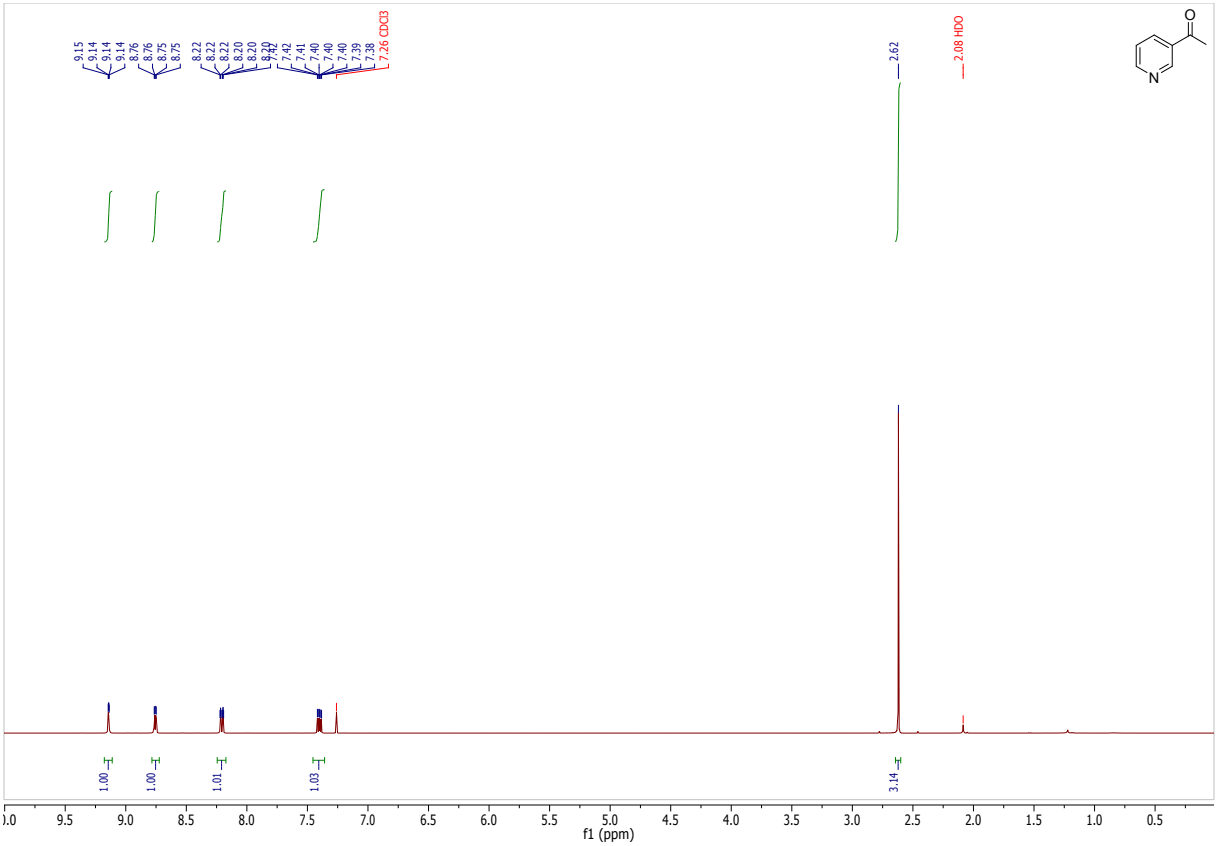


Figure SI 36. ^{1}H-NMR of 1-(pyridine-3-yl)ethan-1-one.

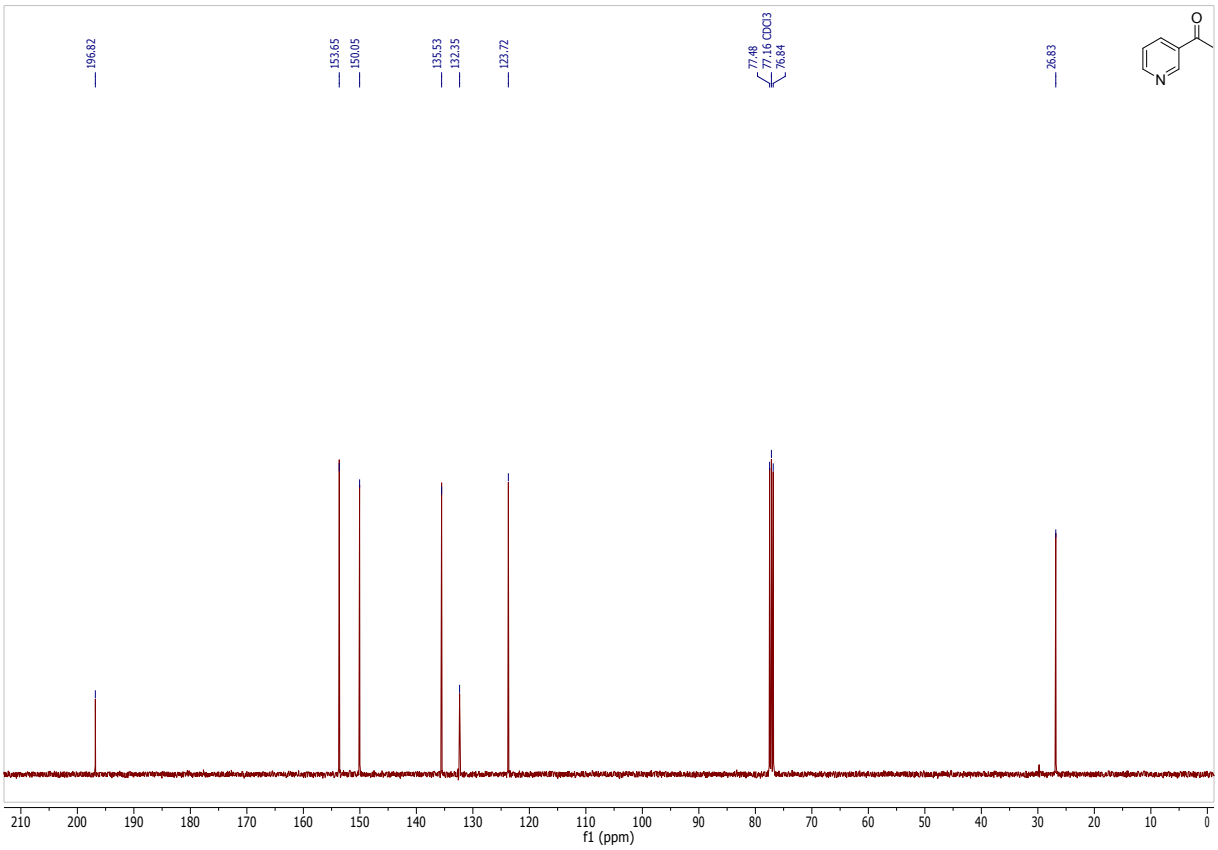


Figure SI 37. ^{13}C-NMR of 1-(pyridine-3-yl)ethan-1-one.

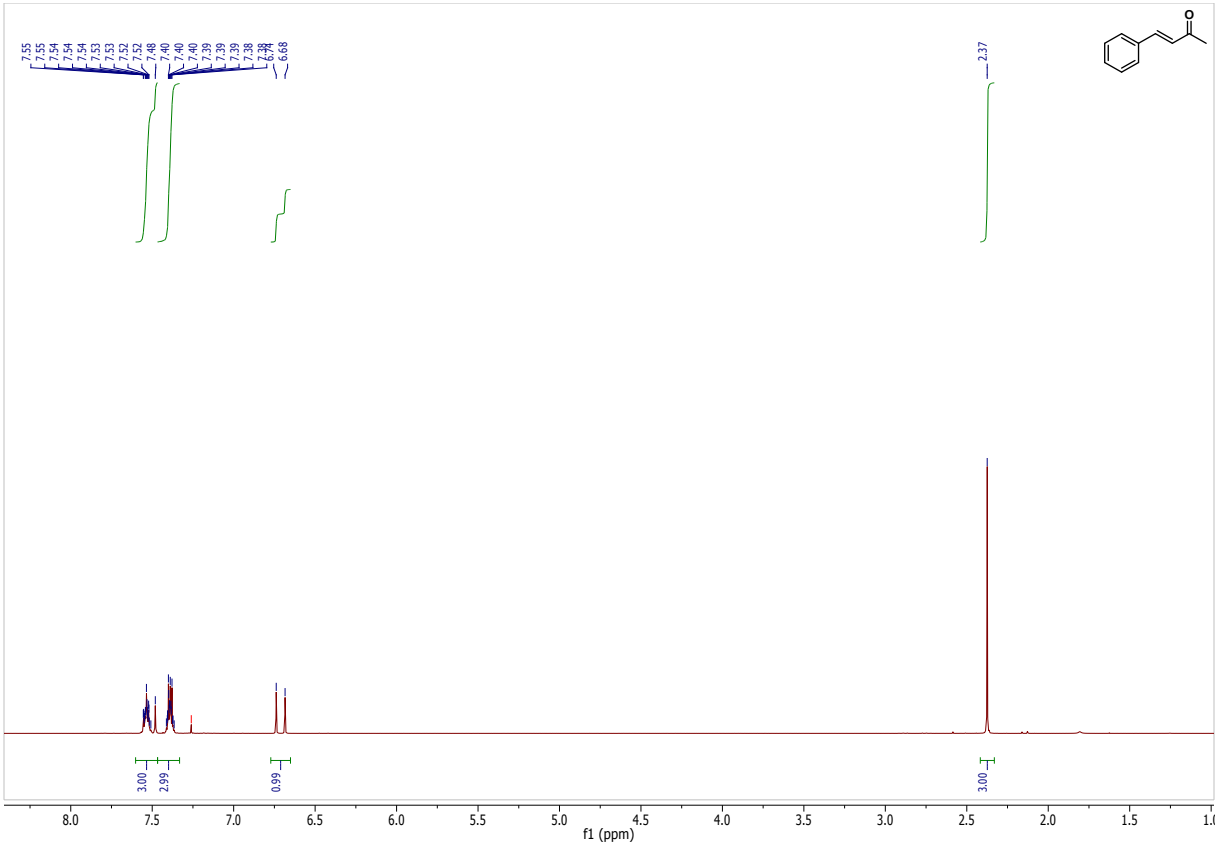


Figure SI 38. ^{1}H-NMR of (*E*)-4-phenylbut-3-en-2-one.

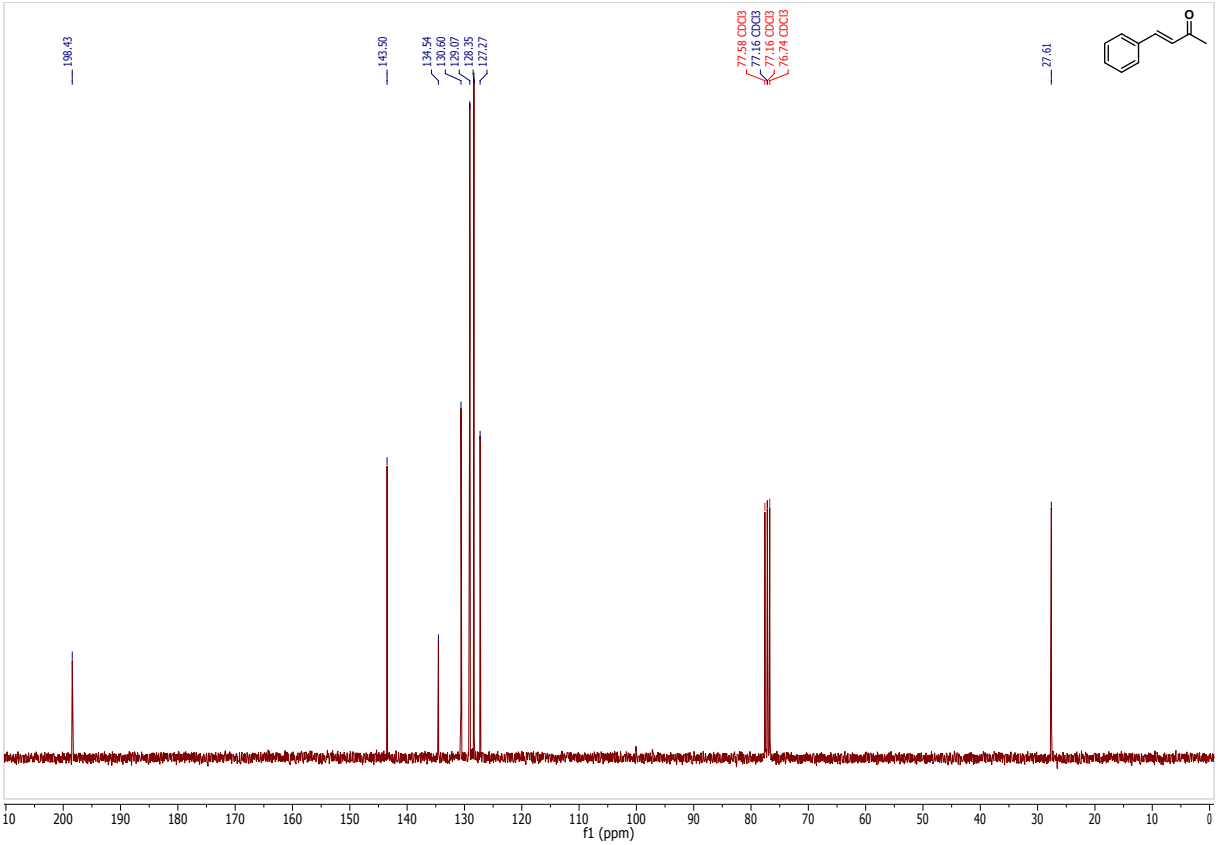


Figure SI 39. ^{13}C-NMR of (*E*)-4-phenylbut-3-en-2-one.

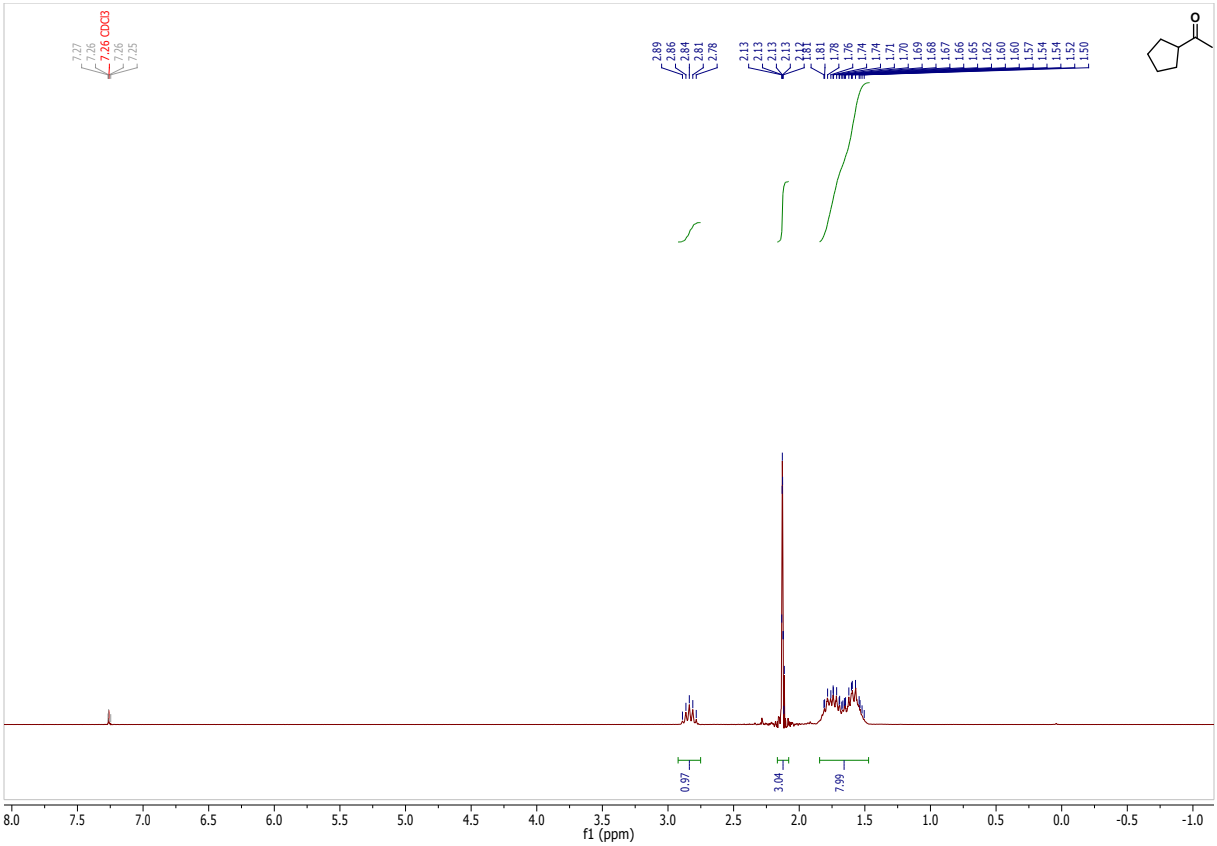


Figure SI 40. ^{1}H-NMR of cyclopentylmethylketone.

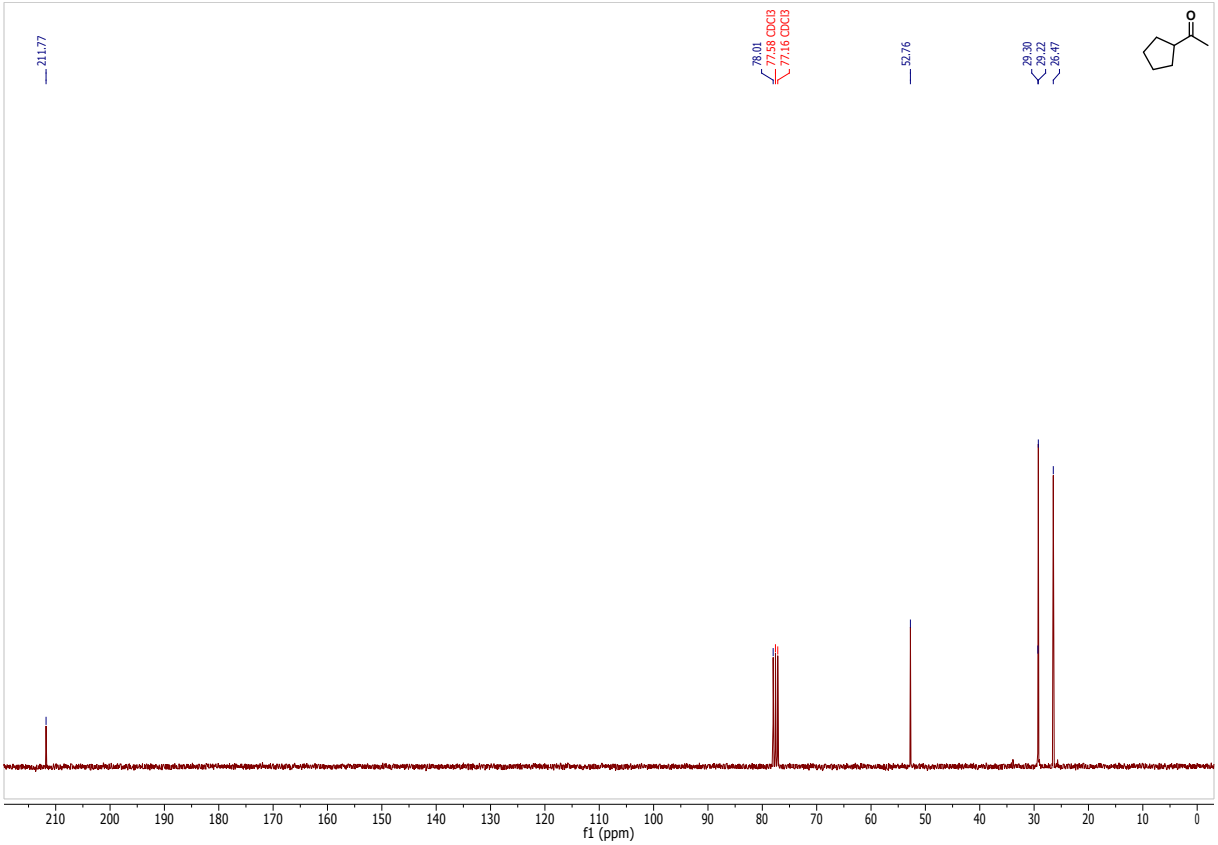


Figure SI 41. ^{13}C-NMR of cyclopentylmethylketone.

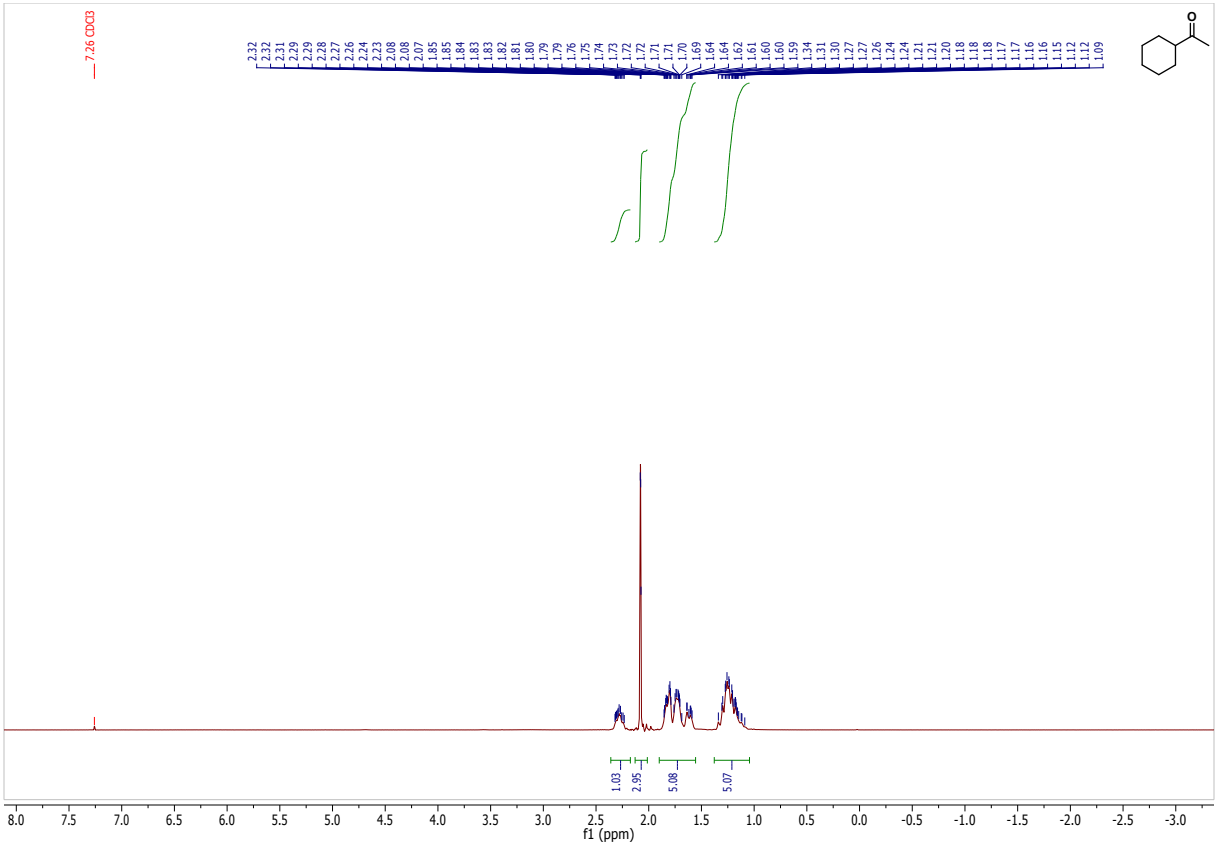


Figure SI 42. ^{1}H-NMR of cyclohexylmethylketone.

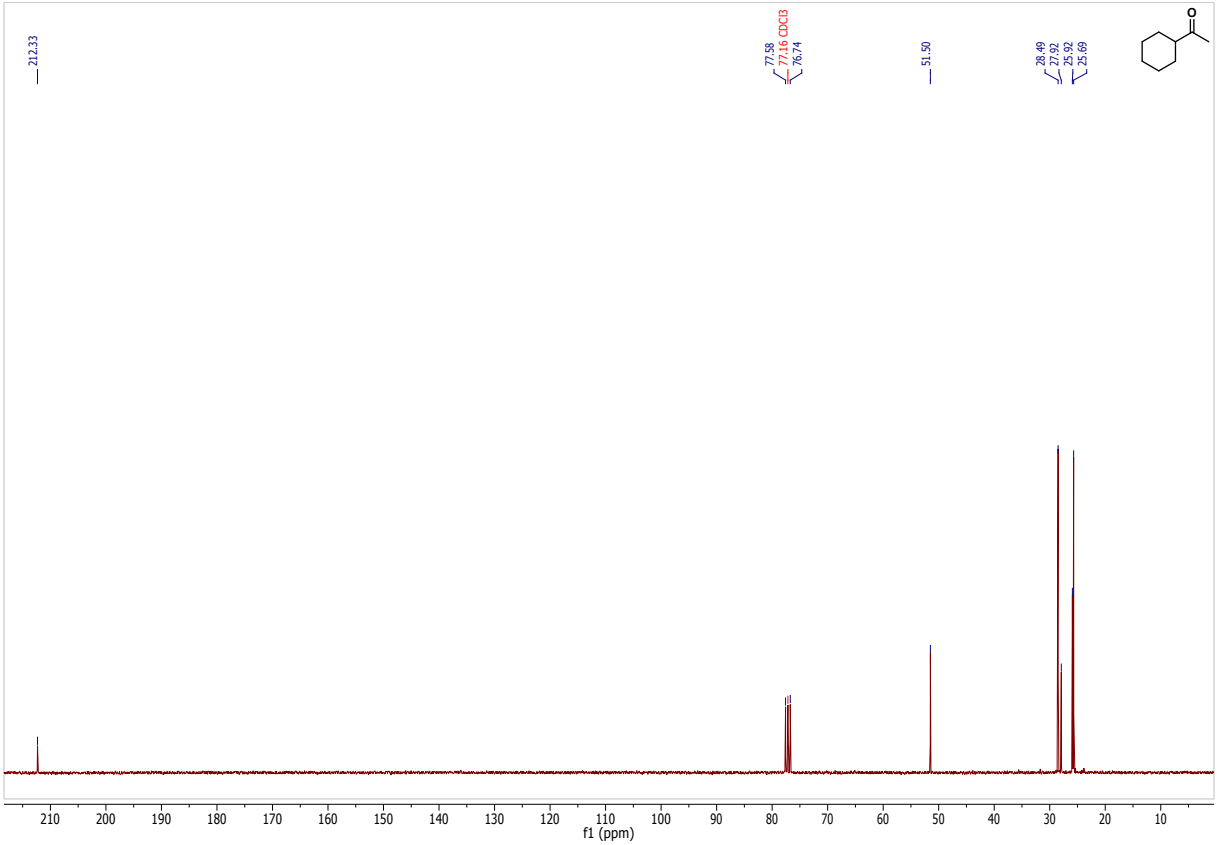


Figure SI 43. ^{13}C-NMR of cyclohexylmethylketone.

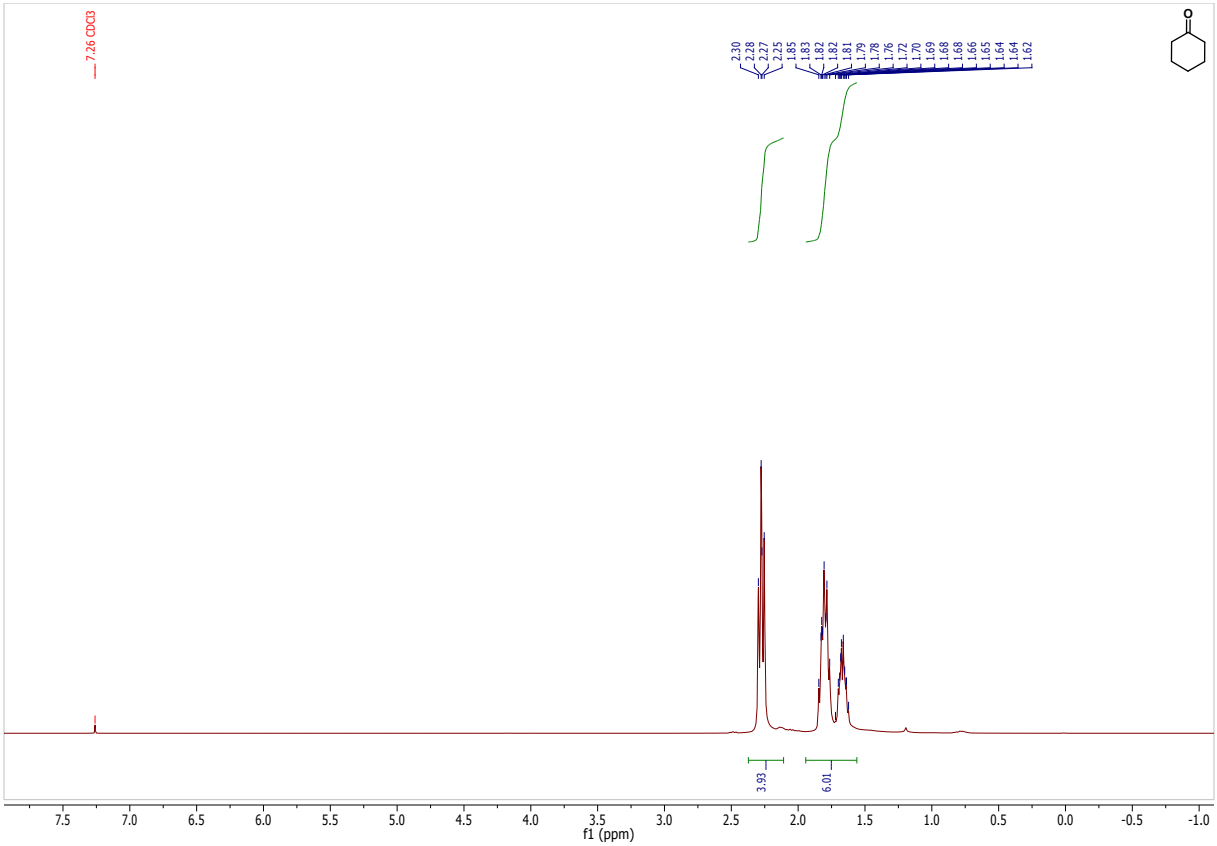


Figure SI 44. ^{1}H-NMR of cyclohexanone.

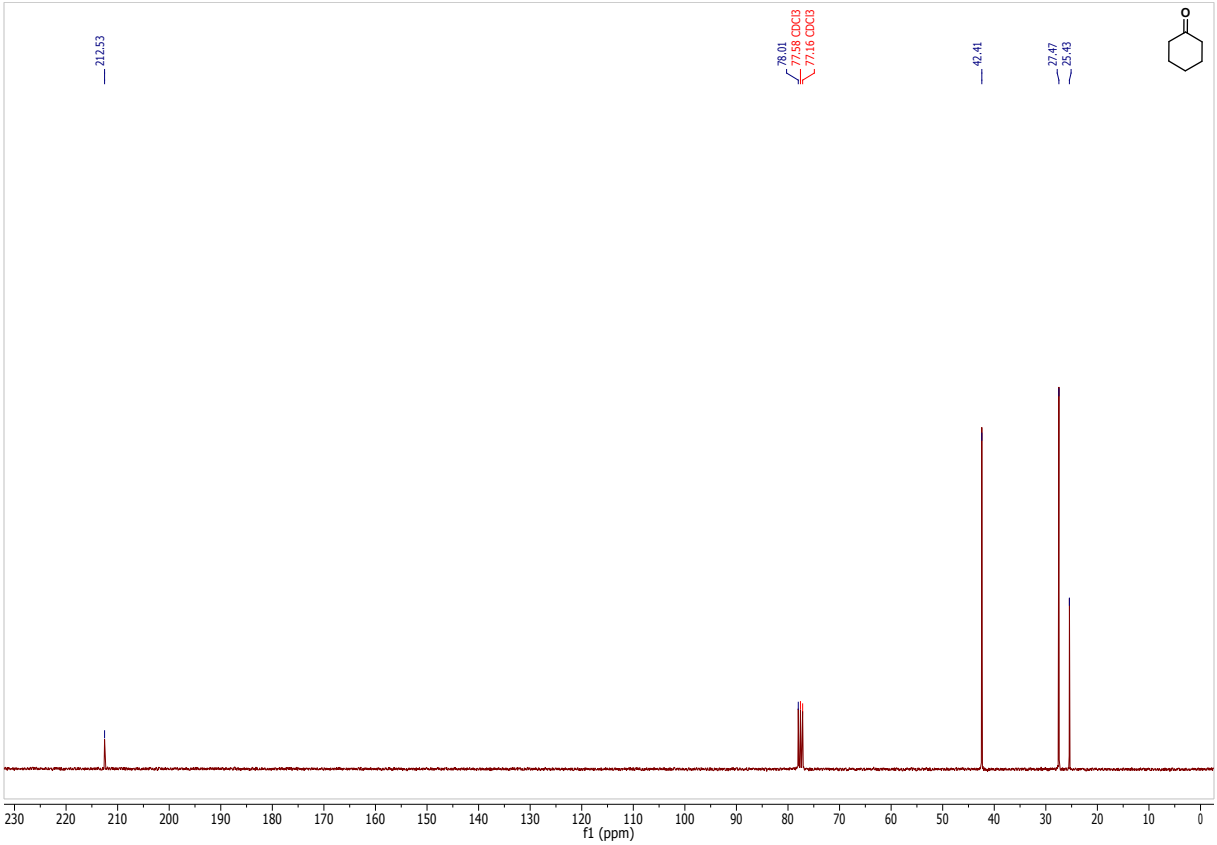


Figure SI 45. ^{13}C-NMR of cyclohexanone.

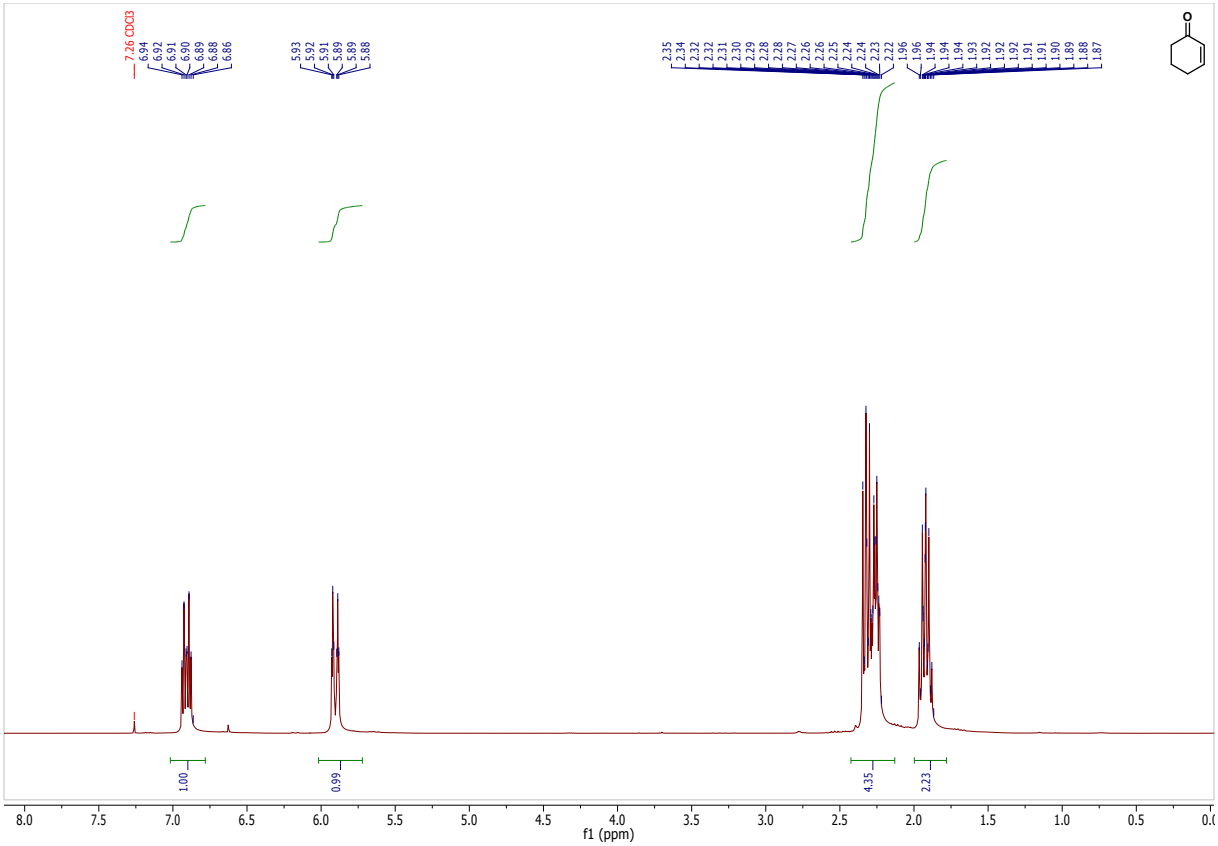


Figure SI 46. ^{1}H-NMR of cyclohex-2-en-1-one.

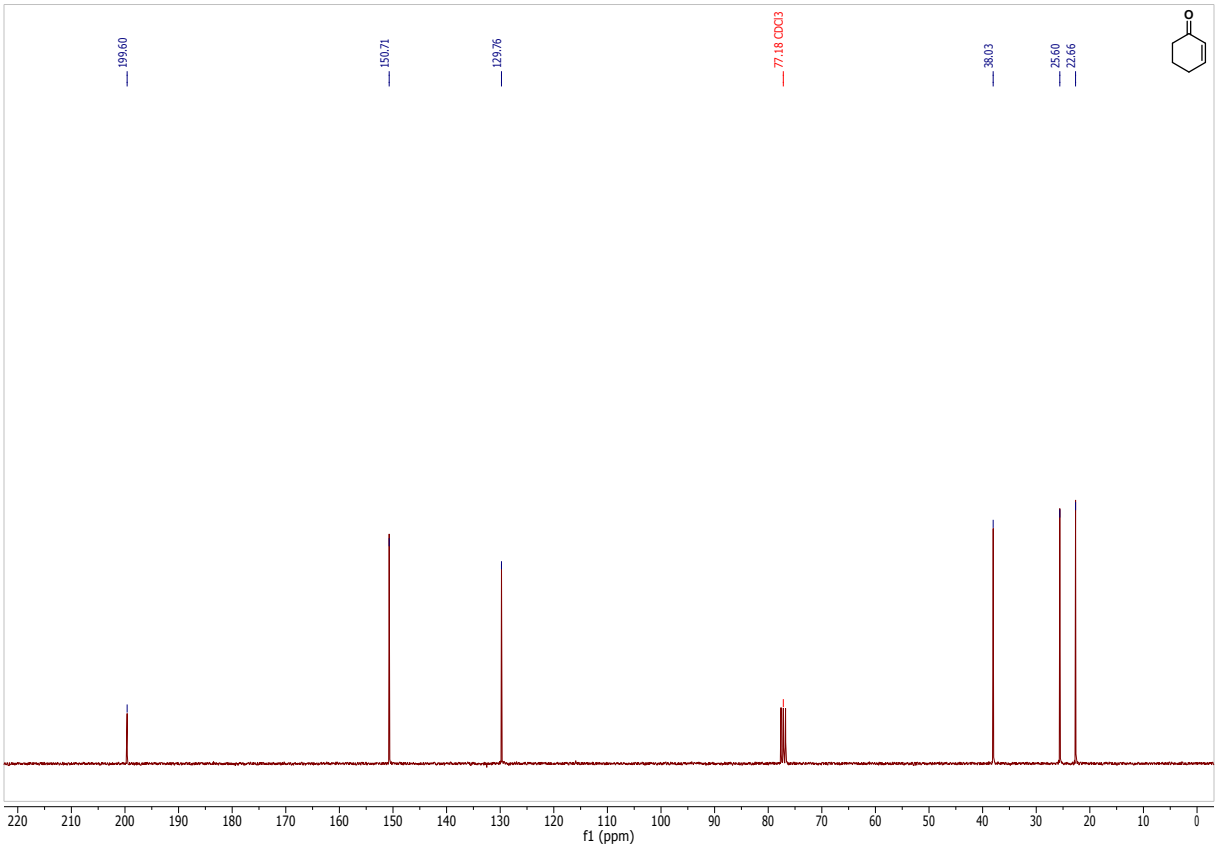


Figure SI 47. ^{13}C-NMR of cyclohex-2-en-1-one.

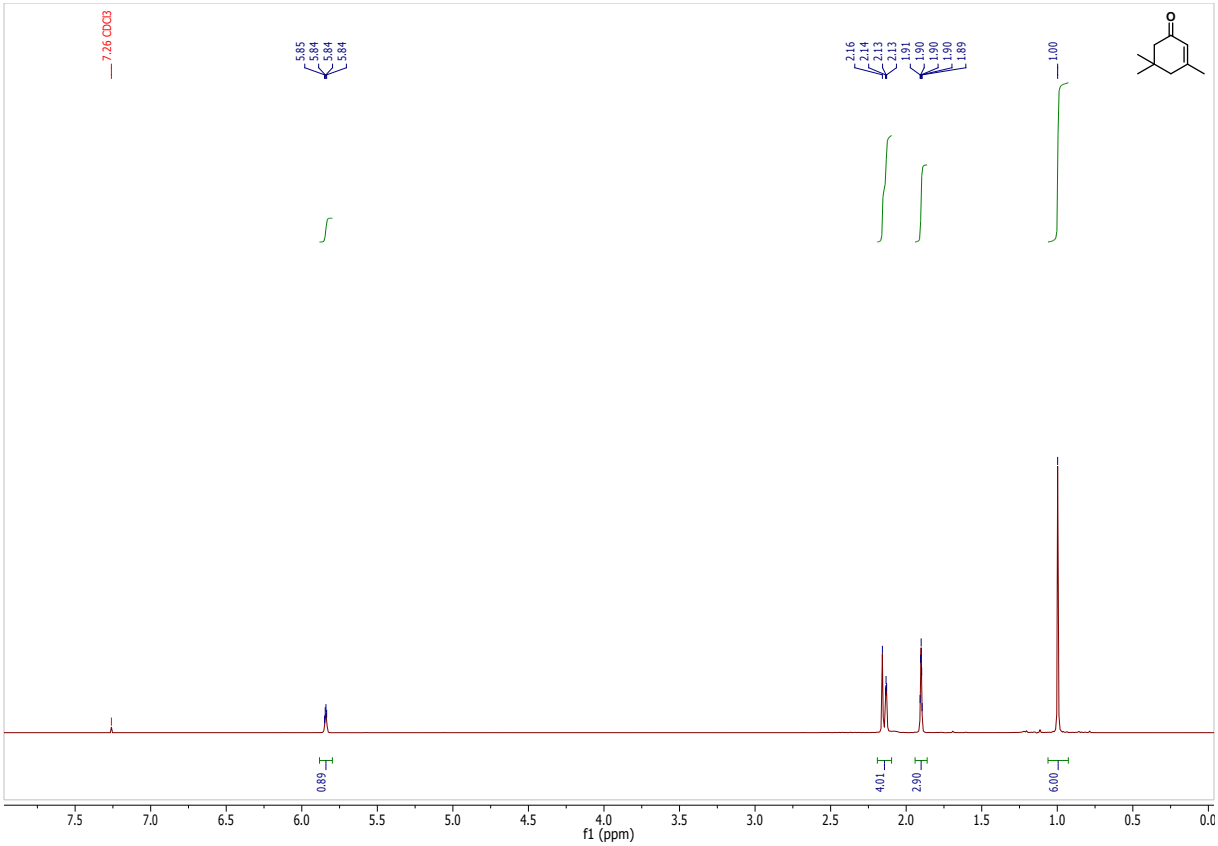


Figure SI 48. ^{1}H-NMR of 3,5,5-trimethylcyclohex-2-en-1-one.

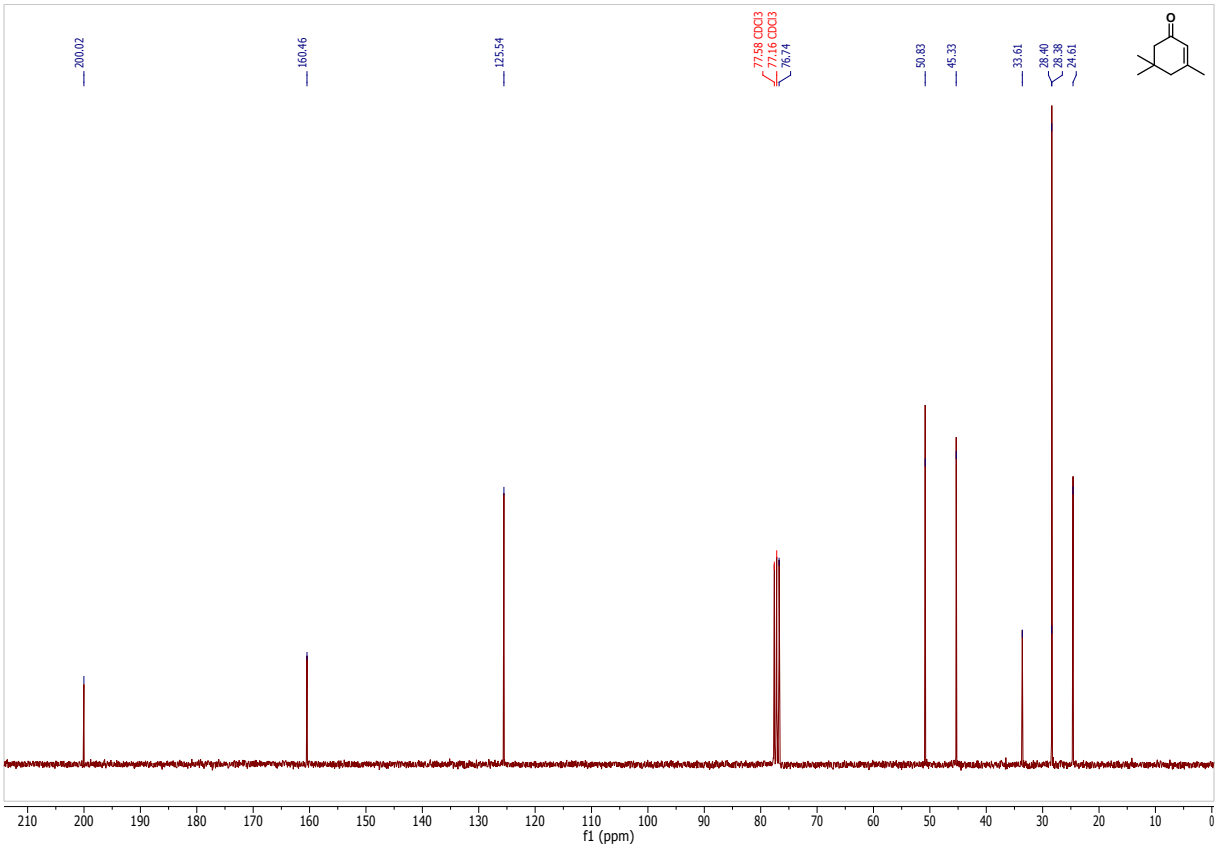


Figure SI 49. ^{13}C-NMR of 3,5,5-trimethylcyclohex-2-en-1-one.

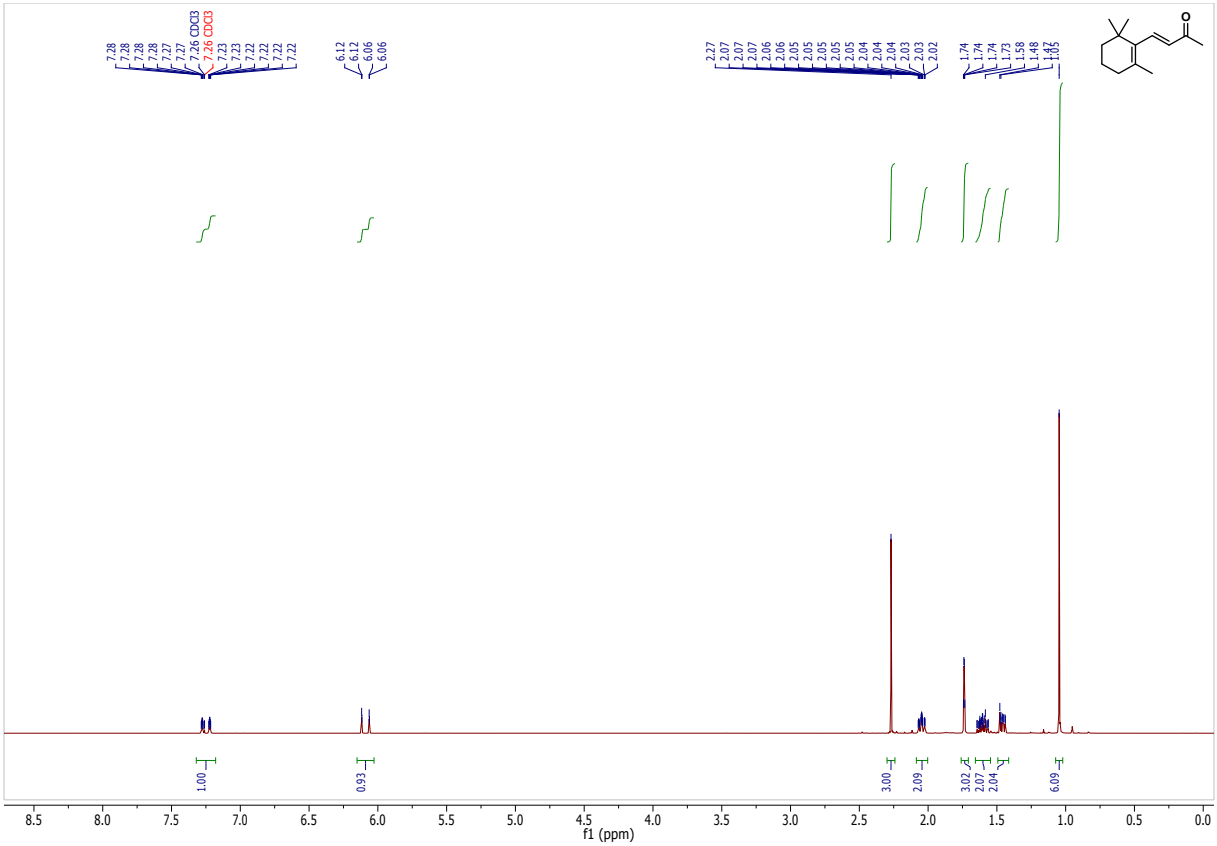


Figure SI 50. ^{1}H-NMR of β-Ionone.

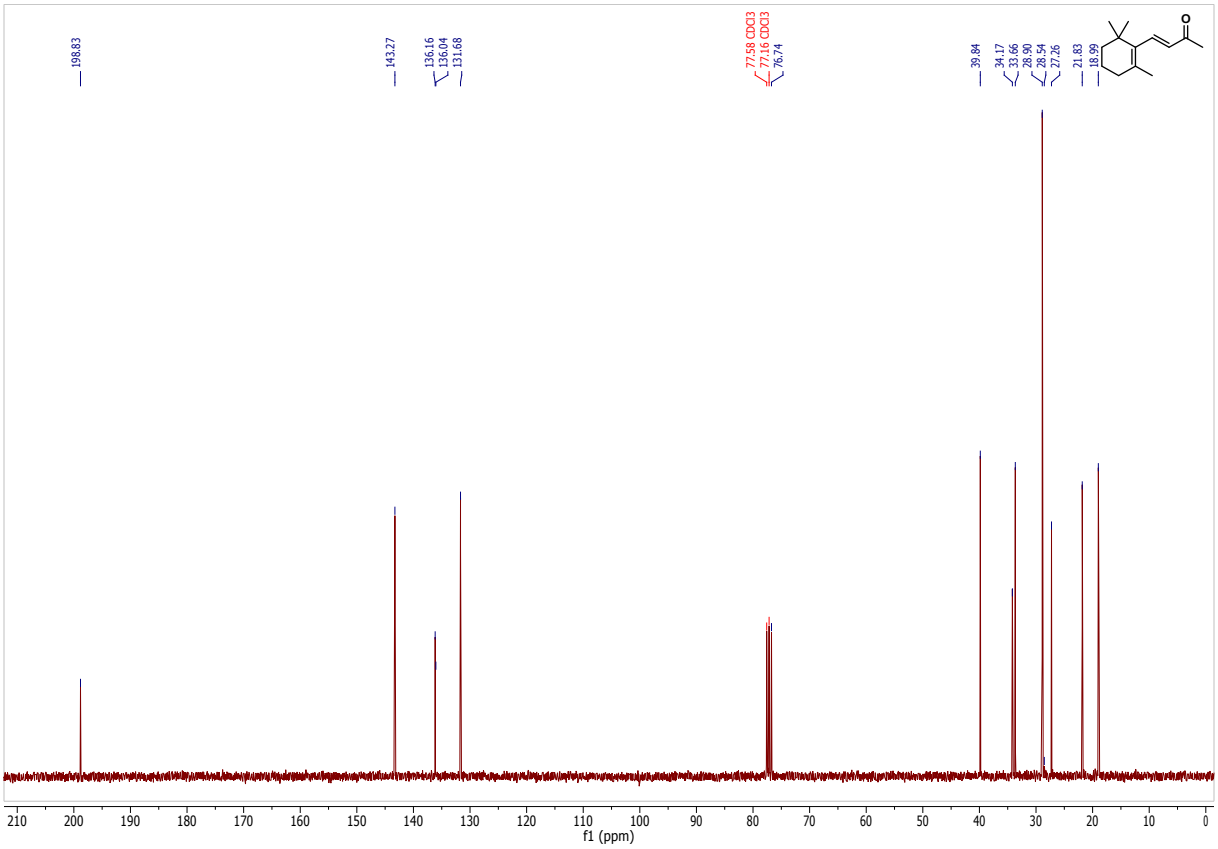


Figure SI 51. ^{13}C-NMR of β-Ionone.

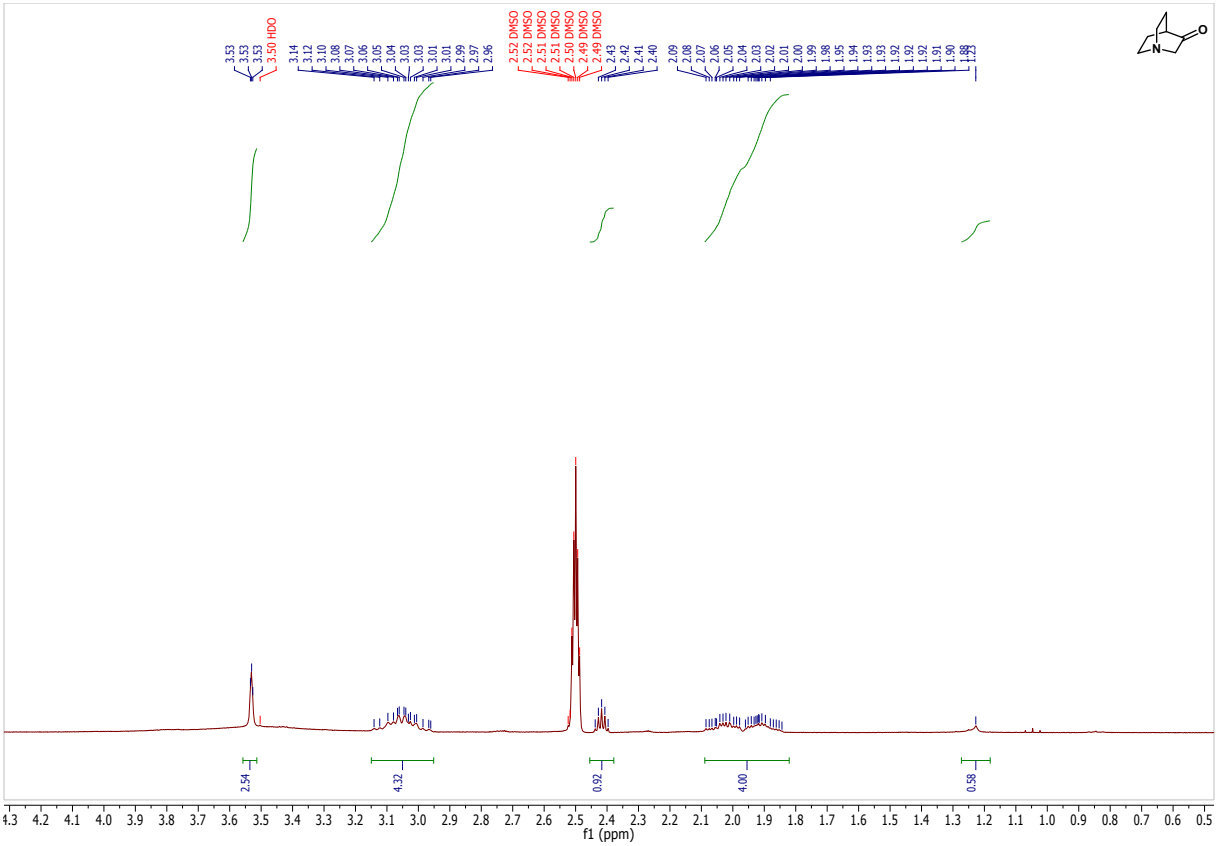


Figure SI 52. ^{1}H-NMR of chinuclidin-3-on.

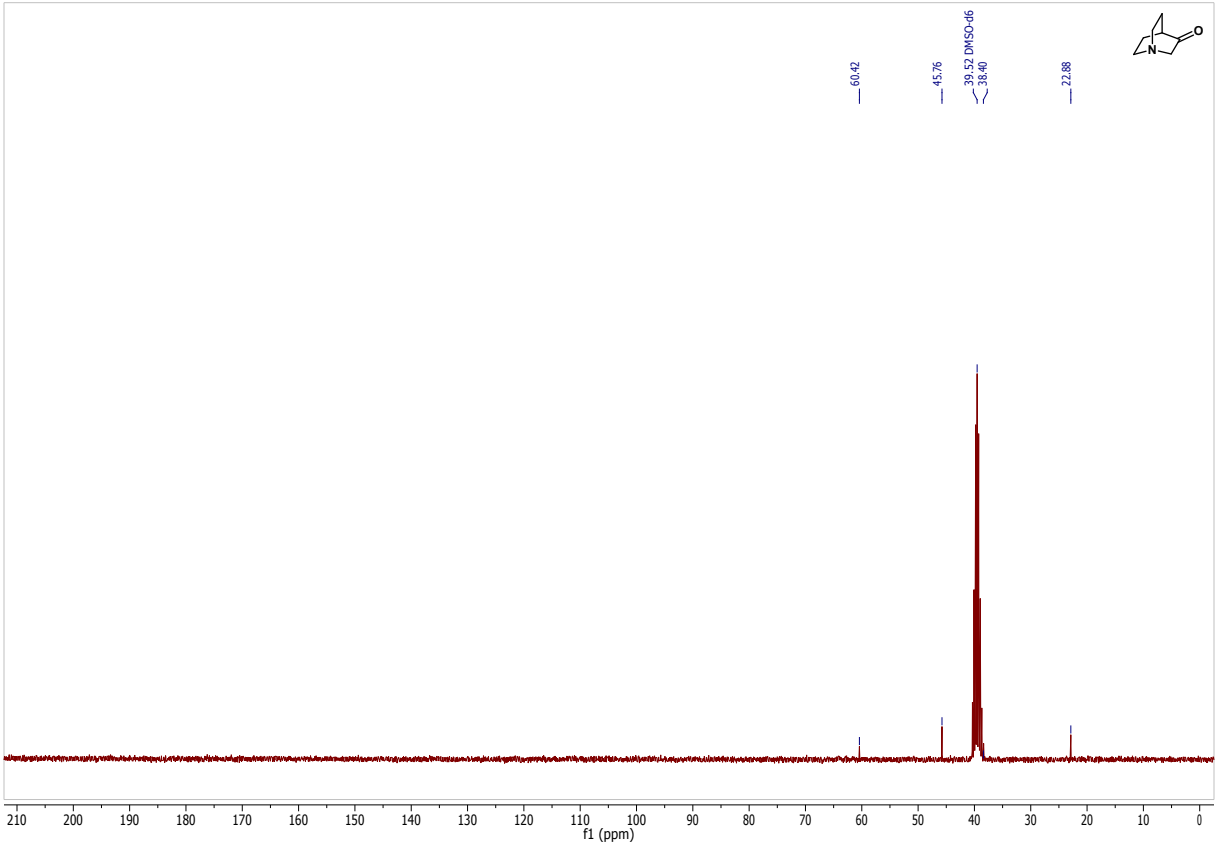


Figure SI 53. ^{13}C-NMR of chinuclidin-3-on.

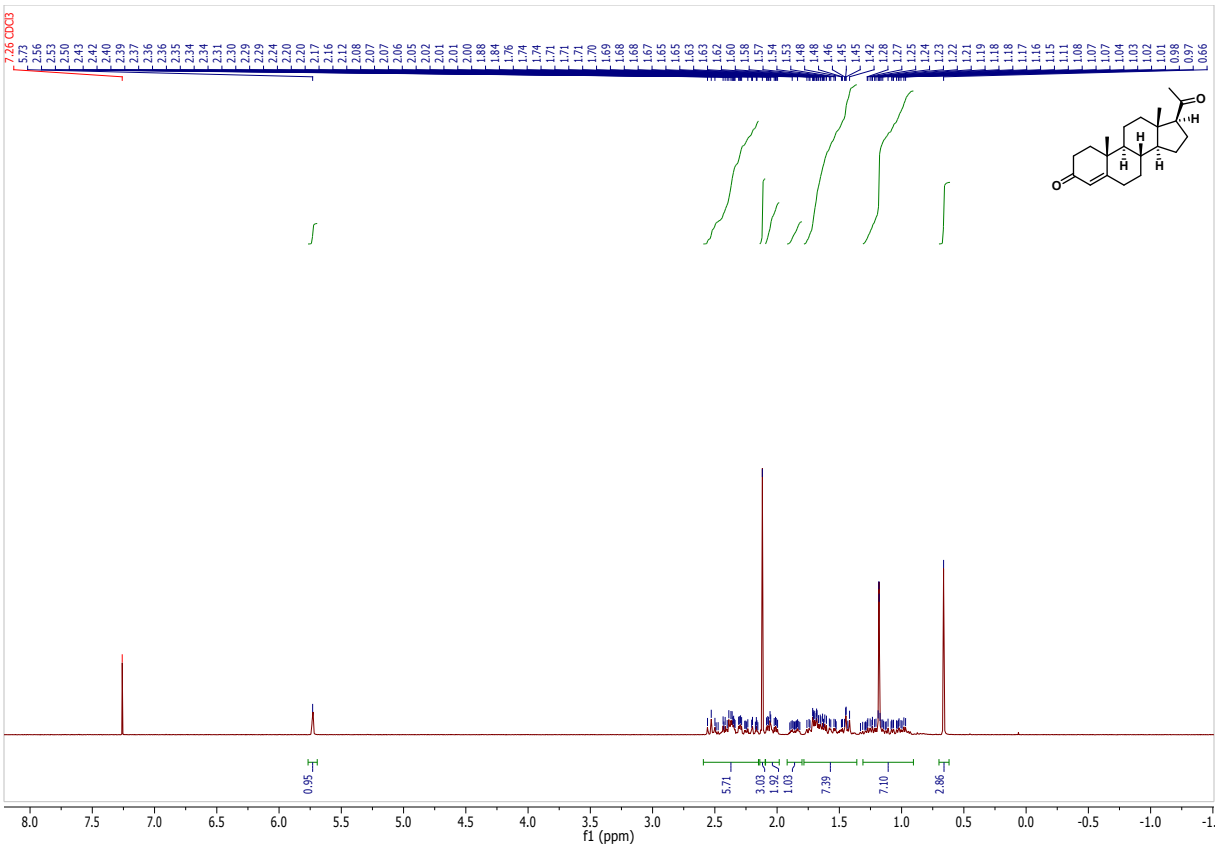


Figure SI 54. ^{1}H-NMR of progesterone.

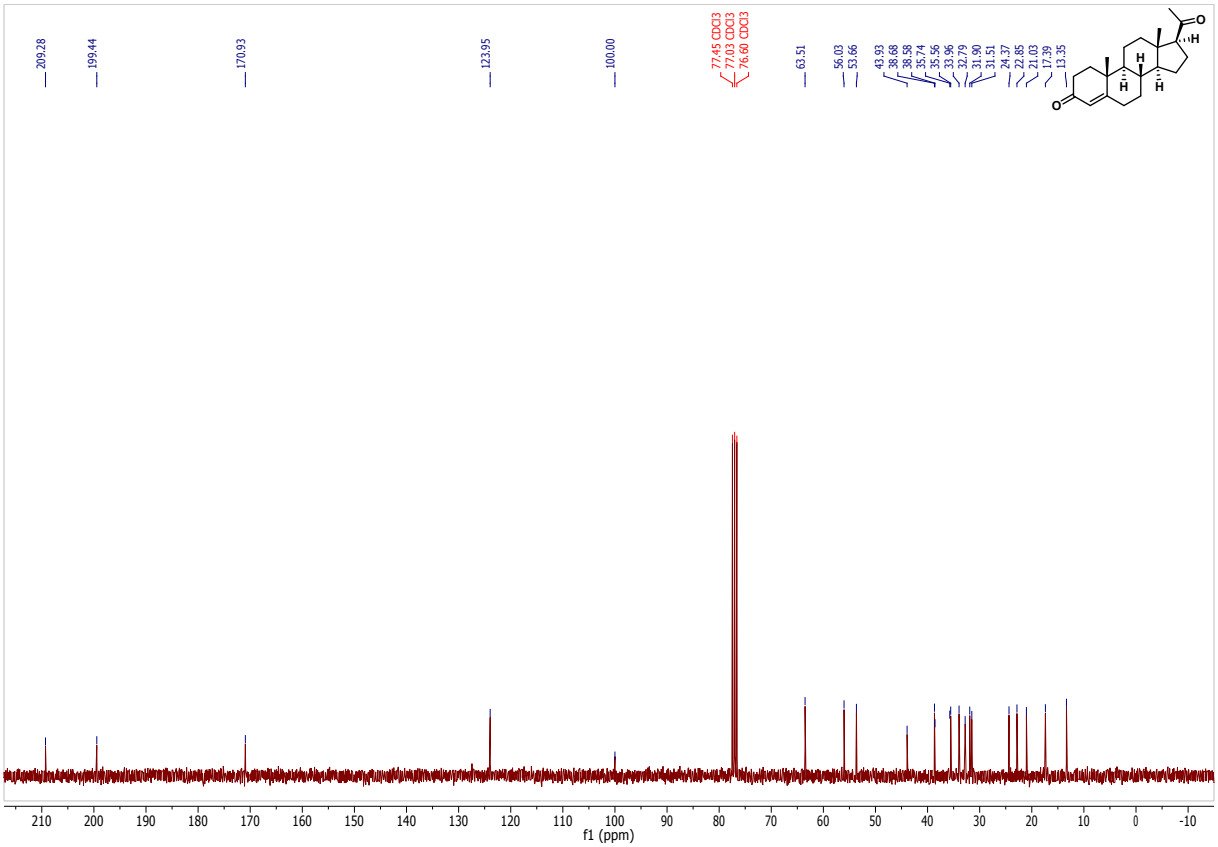


Figure SI 55. ^{13}C-NMR of progesterone.

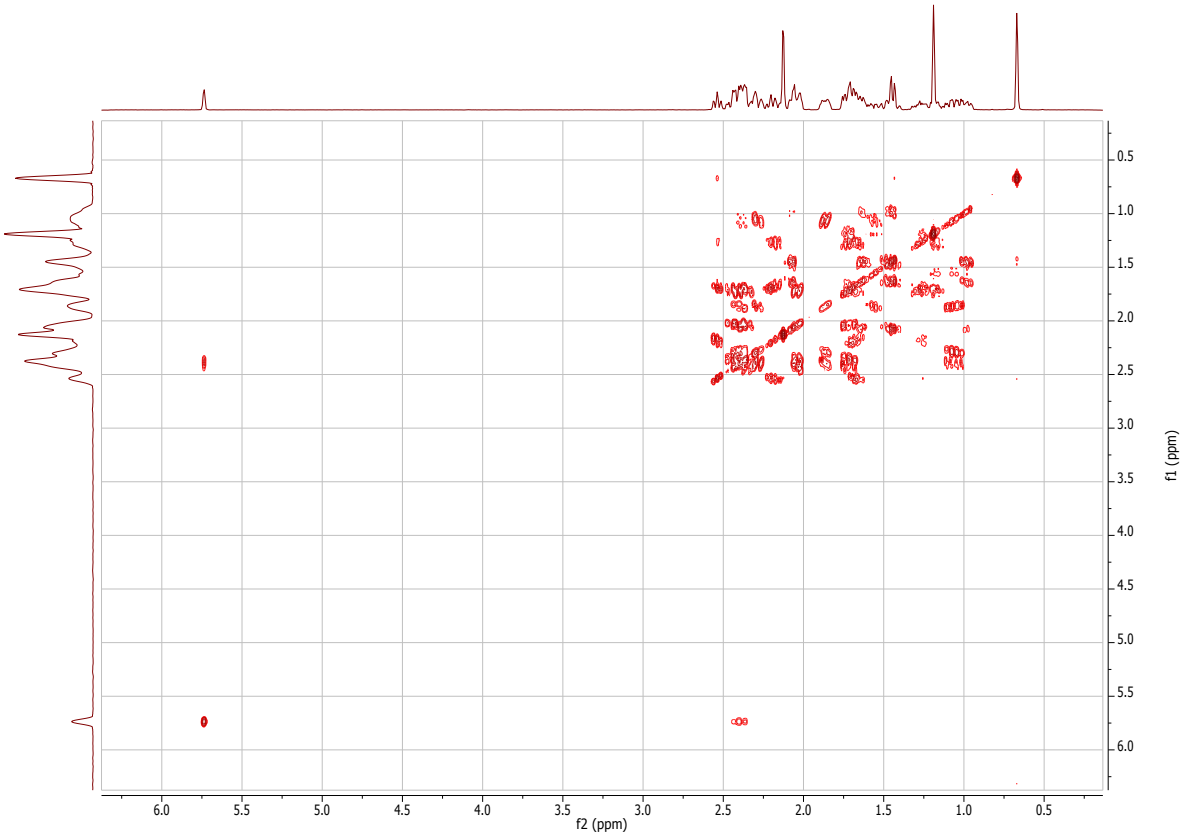


Figure SI 56. ^{1}H-^{1}H-COSY of progesterone.

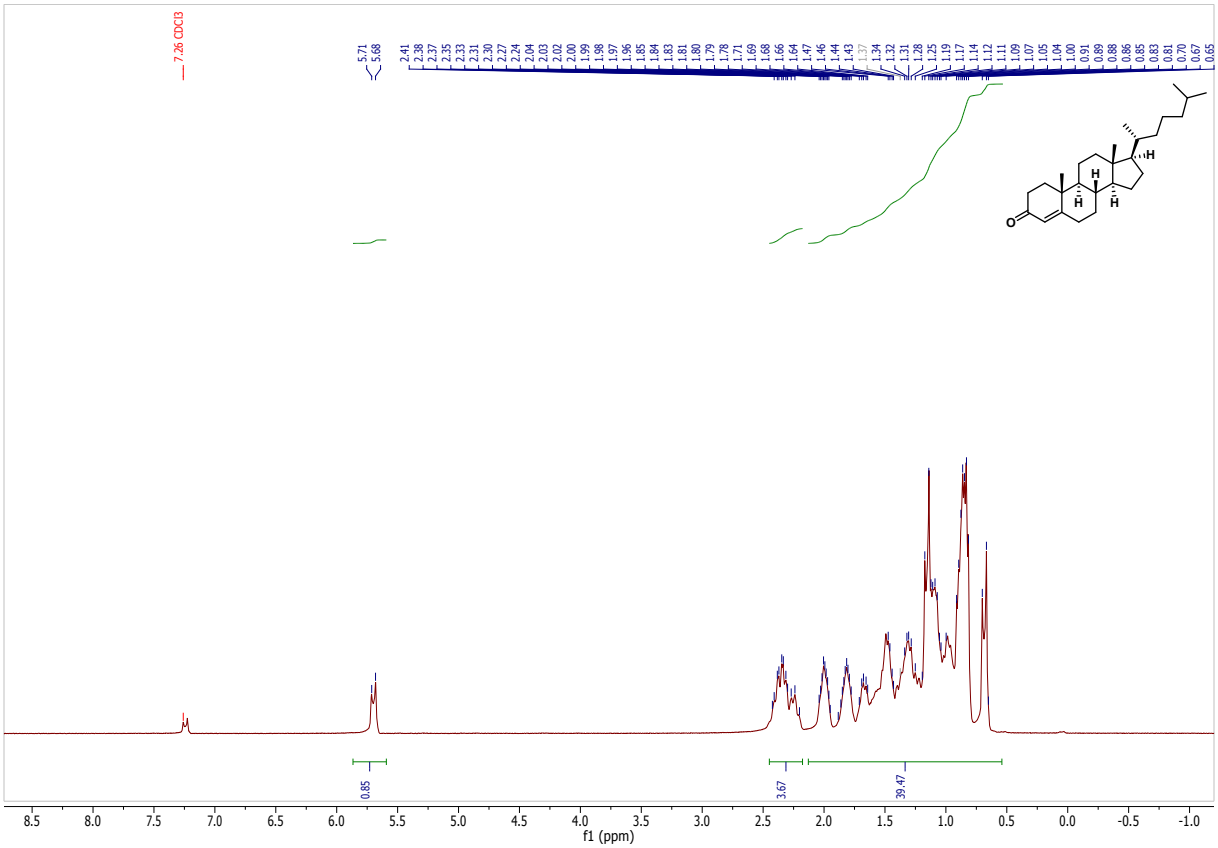


Figure SI 57. ^{1}H-NMR of cholest-4-en-3-one.

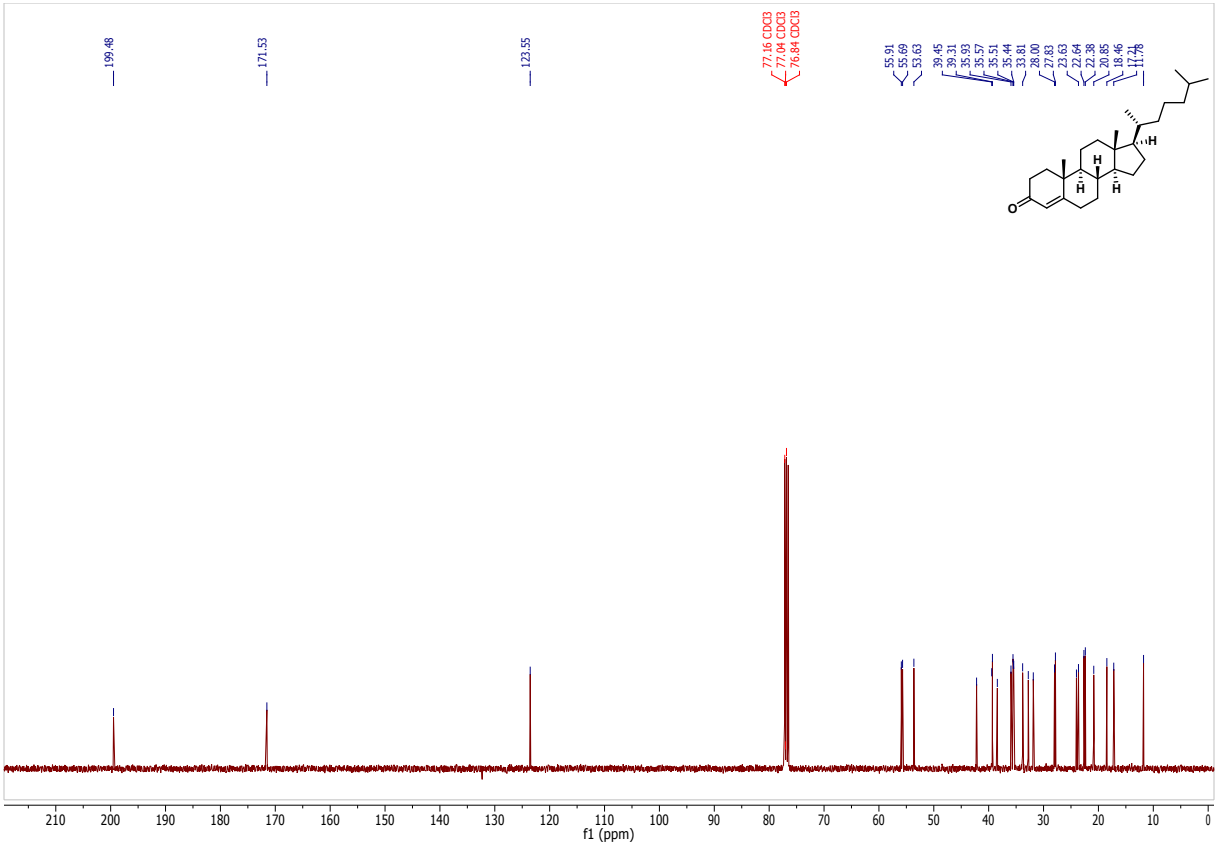


Figure SI 58. ^{13}C-NMR of cholest-4-en-3-one.

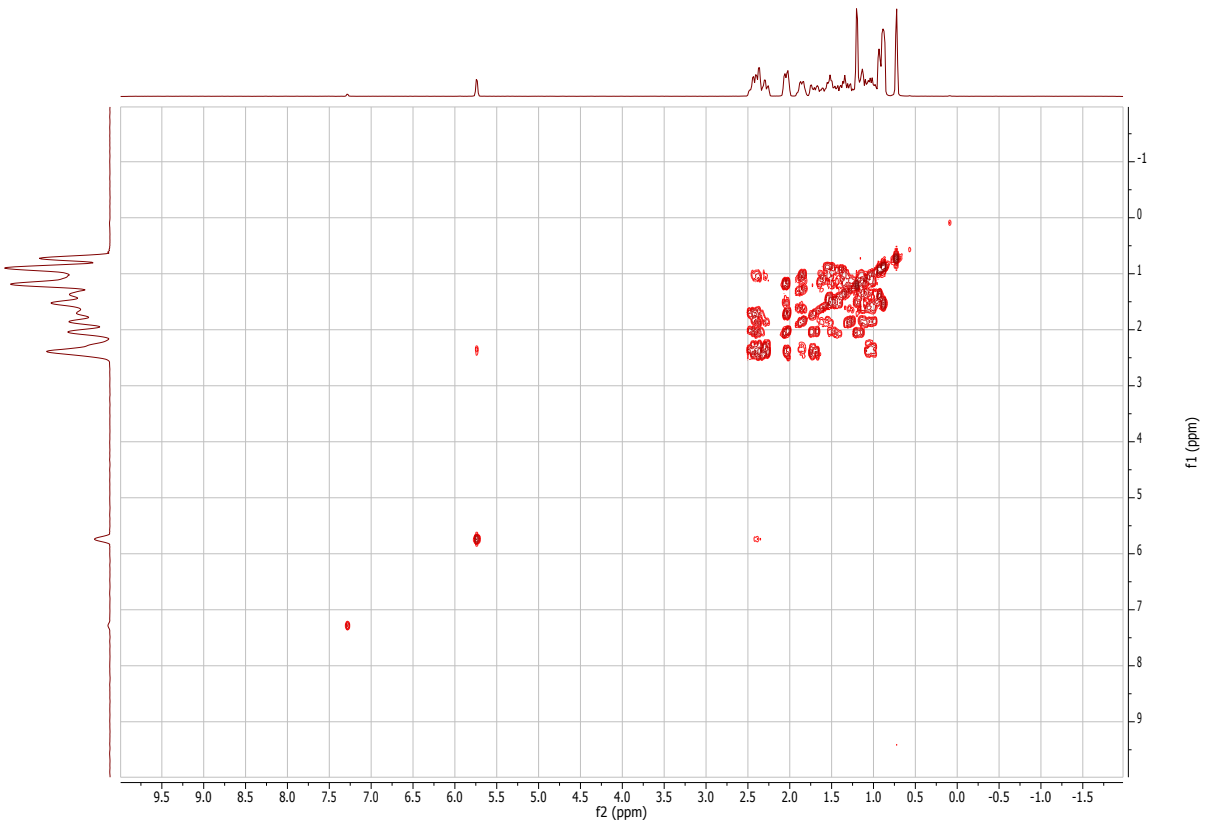


Figure SI 59. ^{1}H-^{1}H-COSY of cholest-4-en-3-one.

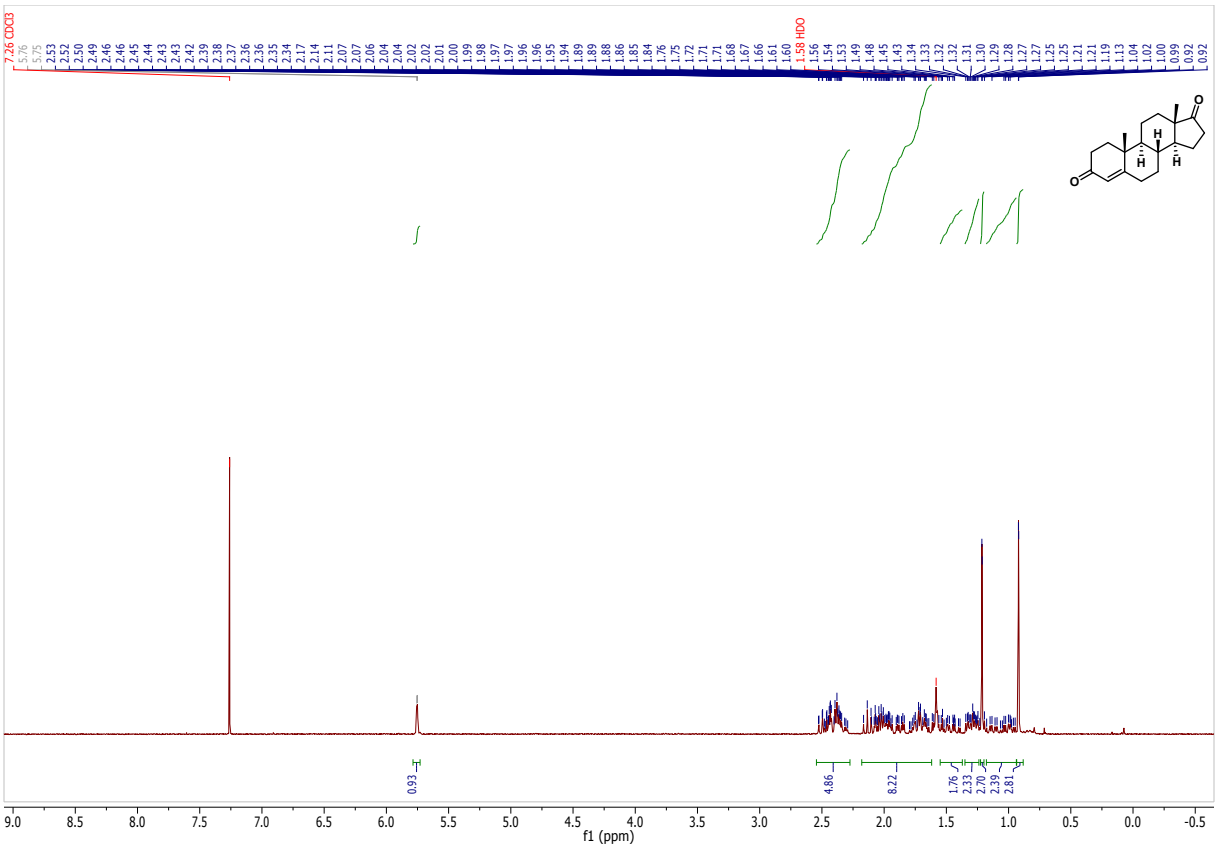


Figure SI 60. ^{1}H-NMR of androstenedione.

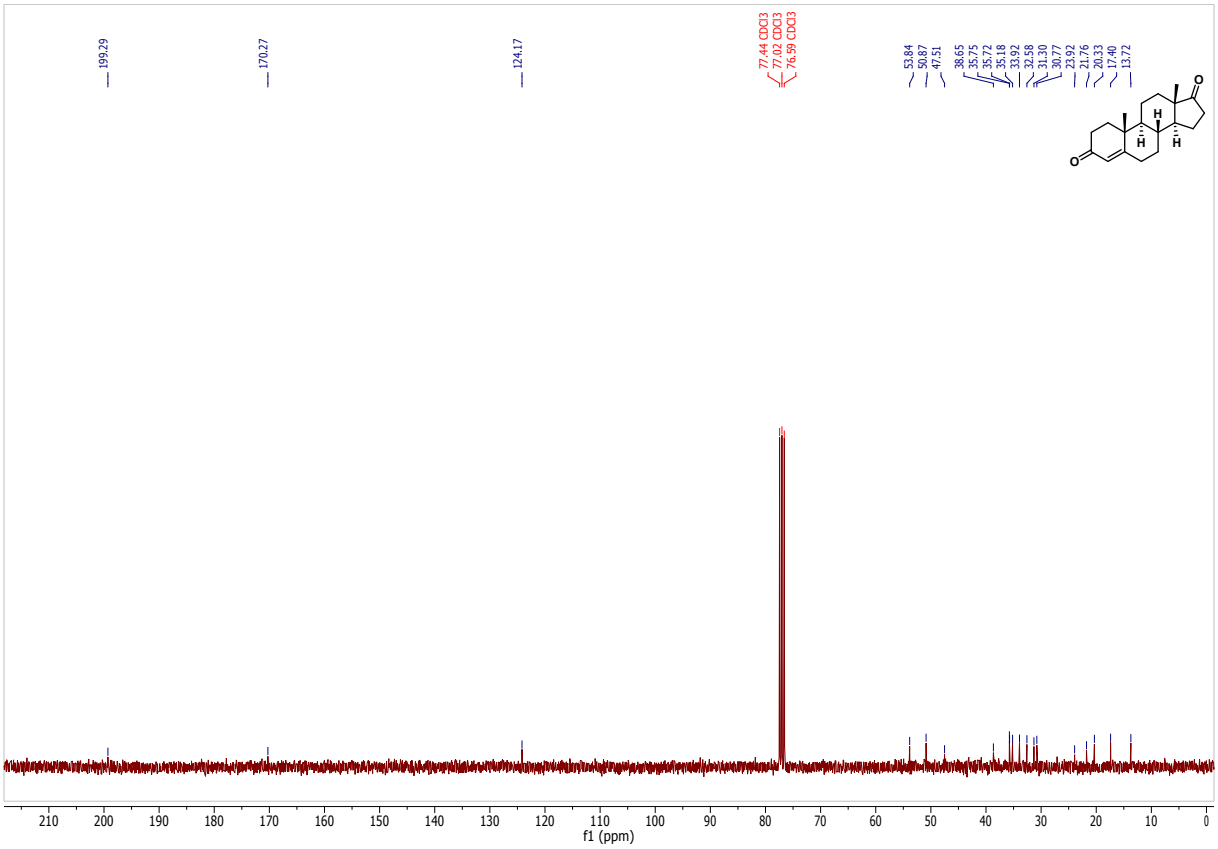


Figure SI 61. ^{13}C-NMR of androstenedione.

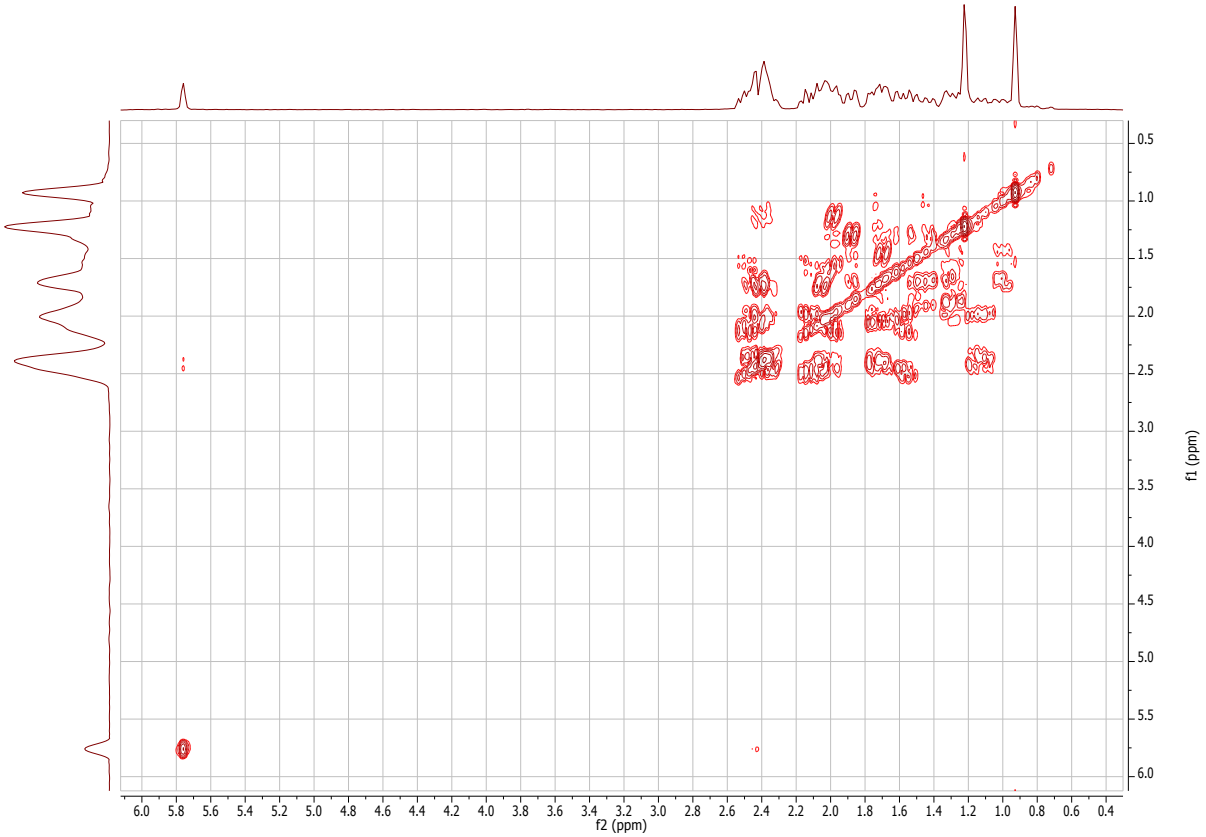


Figure SI 62. ^{1}H-^{1}H-COSY of androstenedione.

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