Reactions catalyzed by a binuclear copper complex: selective oxidation of alkenes to carbonyls with O_2

Yuxia Liu,[a] Dong Xue,[a] Chaoqun Li,[a] Jianliang Xiao,[ab] Chao Wang*[a]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China. E-mail: c.wang@snnu.edu.cn

[b] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

SUPPORTING INFORMATION

Table of Contents

Warning: all the oxidation reactions described here should be carried out with caution due to its potential fire and explosion hazards**.**

1. General information

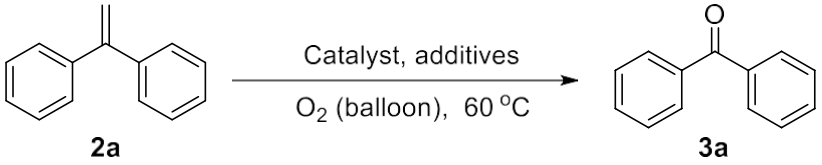
Experiments involving air or moisture sensitive reagents were performed under an atmosphere of purified N_2 using standard Schlenk techniques. Solvents used in these experiments were reagent grade or better. MeCN, DCM were refluxed over CaH_2 and toluene, THF and Et_2O were refluxed over Na/benzophenone and distilled under purified N_2 atmosphere. Solvents (ethyl acetate, petroleum ether) used for column chromatography were of technical grade and used after distillation. Chemicals employed in the synthesis of ligands and substrates were purchased from commercial suppliers and used without further purification. Copper salts were purchased from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was conducted with TLC Silica gel 60 F254 (Qingdao Haiyang) and plates were revealed under UV irradiation, iodine, potassium permanganate or ninhydrin. Flash column chromatography was performed using Qingdao Haiyang Silica Gel 60. ^{1}H NMR spectra were recorded on a Bruker Advance 400 (400 MHz) NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or $CDCl_3$ (δ 7.26 ppm). Multiplicities are given as: brs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet), td (triplets of doublet) or m (multiplet). ^{13}C NMR spectra were recorded on a Bruker Advance 400 (100 MHz) NMR spectrometer and reported in ppm relative to $CDCl_3$ (δ 77.0 ppm). Coupling constants were reported as a *J* value in Hz. HRMS data were recorded on Bruker Apex IV FTMS (ESI). IR spectra were recorded on a Bruker Tensor 27 spectrometer. Alkene substrates were synthesized according to literature.[1-3] The binuclear metal complex **1** was synthesized according to our previous method.[4-5]

2. Optimization of reaction conditions for aerobic cleavage of alkenes

General procedure: In a Schlenk tube equipped with a magnetic stir bar, **2a** (0.5 mmol, 90 mg), **1** (0.0025 mmol, 3 mg), TBAC (0.005 mmol, 2.8 mg, if added), and additive were added. Solvent (0.5 mL) was introduced by a syringe, and the reaction tube was degassed and charged with oxygen gas (3 times), and kept under an oxygen

atmosphere by using an oxygen balloon. The tube was gradually heated to 60 °C and allowed to react for 12 h. After stirring at 60 °C for 12 h, the solvent was removed via rotary evaporation at ambient temperature. The resulting mixture was diluted with water and extracted with DCM (3 x 15 mL). The organic layers were combined, washed with brine, and dried over Na_2SO_4. After filtration, the solvent was then removed via rotary evaporation and the crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (vol/vol: 1:50) to afford compound **3a**.

Table S1 Optimization of reaction conditions for aerobic cleavage of **2a**[a]



Entry	Catalyst	Catalyst loading (mol%)	TBAC (mol%)	$NaBF_4$ (mol%)	Solvent	Yield (%)[b]
1	-	0	0	0	THF (fresh)[c]	0
2	**1**	0.5	0	0	THF (fresh)	45
3	**1**	0.5	1	0	THF (fresh)	70
4	**1**	0.5	1	10	THF (fresh)	75
5	**1**	0.5	1	30	THF (fresh)	90
6	**1**	0.5	1	50	THF (fresh)	90
7	**1**	0.5	1	30	THF (not distilled)	67
8	**1**	0.5	1	30	Toluene	trace
9	**1**	0.5	1	30	DMF	trace
10	**1**	0.5	1	30	CH_3OH	trace
11	**1**	0.5	1	30	DCM	trace
12	**1**	0.5	1	30	Dioxane	17
13	**1**	0.5	1	30	Glycol dimethylether	28
14	**1**	0.5	1	30	Diglyme	67
15	**1**	0.5	1	30	MeCN	trace
16	CuCl	0.5	0	0	THF (fresh)	0
17	CuCl	0.5	0	0	THF+H_2O (1:1)	0
18	CuCl	0.5	1	30	THF (fresh)	0
19	CuCl	0.5	1	30	THF+H_2O (1: 1)	0
20	$CuCl_2$	0.5	0	0	THF (fresh)	0
21	$CuCl_2$	0.5	0	0	THF+H_2O (1:1)	0
22	$CuCl_2$	0.5	1	30	THF (fresh)	0
23	$CuCl_2$	0.5	1	30	THF+H_2O (1: 1)	0
24[d]	**1**	0.5	1	30	THF (fresh)	36
25[e]	**1**	0.5	1	30	THF (fresh)	0

[a] Reaction conditions: **2a (**0.5 mmol), additives, solvent (0.5 mL), O_2 balloon, 60 °C, 12 h. [b] Isolated yield. [c] "Fresh" means that THF was distilled over sodium under Ar. [d] The reaction was carried out under air. [e] The reaction was carried out under argon.

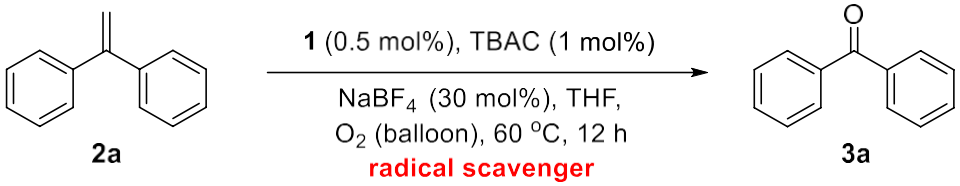
3. General procedure for aerobic cleavage of 2

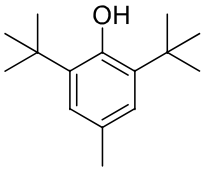
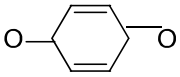
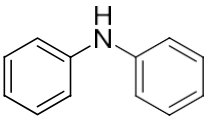
In a Schlenk tube equipped with a magnetic stirring bar, **2** (0.5 mmol), catalyst **1** (0.0025 mmol, 3.0 mg), TBAC (0.005 mmol, 2.8 mg), and $NaBF_4$ (0.15 mmol, 16.2 mg), was injected freshly distilled THF (0.5 mL) by syringe. The reaction tube was then degassed with oxygen gas (3 times) and kept under oxygen atmosphere by using an oxygen balloon. The tube was gradually heated to 60 °C and allowed to react for 12 hours. After stirring at 60 °C for 12 h, the solvent was removed via rotary evaporation at ambient temperature. The resulting mixture was diluted with water and extracted with DCM (3 x 15 mL). The organic layers were combined, washed with brine, and dried over Na_2SO_4. After filtration, the solvent was then removed via rotary evaporation and the crude product purified by column chromatography on silica gel using ethyl acetate/petroleum ether to afford the carbonyl product.

4. Mechanistic investigations

4.1 Radical trapping experiments

Table S2. Effect of the radical scavengers in **1** catalyzed aerobic cleavage of **2a**

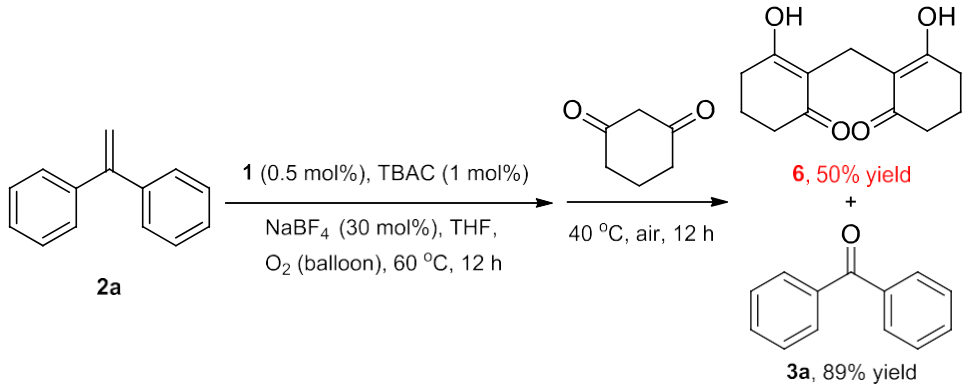


Radical scavenger	n (radical scavenger/**1**)	Yield of **3a** (%)	Recovered **2a** (%)
	1	N.R.[a]	-
	5	N.R.	>90
	10	N.R.	-
TEMPO	5	N.R.	>90
	10	N.R.	-
	5	N.R.	>90
	10	N.R.	-
	5	N.R.	>90
	10	N.R.	-

[a] N.R. = No reaction

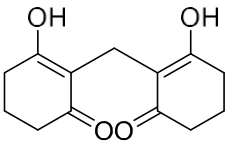
General procedure for Table S2: In a Schlenk tube equipped with a magnetic stir bar, **2a** (0.5 mmol, 90 mg), **1** (0.0025 mmol, 3.0 mg), TBAC (0.005 mmol, 2.8 mg), and $NaBF_4$ (0.15 mmol, 16.2 mg) were added. The tube was sealed, degassed with Ar (3 times) and left under inert atmosphere. Freshly distilled THF (1.0 mL) was added by syringe and the reaction mixture was stirred under Ar atmosphere for 30 min at 25 °C. Next, the corresponding amount of radical scavenger was added and the tube was degassed with oxygen and kept under oxygen atmosphere by using an oxygen balloon. The reaction mixture was then heated up to 60 °C and allowed to react overnight. No **3a** was formed as indicated by TLC. **2a** was recovered by column chromatography on silica gel.

4.2 Evidence for the formation of formaldehyde



In a Schlenk tube equipped with a magnetic stir bar, catalyst **1** (0.0025 mmol, 3.0 mg), TBAC (0.005 mmol, 2.8 mg), and $NaBF_4$ (0.15 mmol, 16.2 mg) were added. The tube was sealed, degassed (3 times) and left under inert atmosphere. Freshly distilled THF (1.0 mL) was added by syringe and the reaction mixture was stirred under Ar atmosphere for 30 min at 25 °C. Next, **2a** (0.5 mmol, 90 mg) was added by syringe and the tube was degassed and charged with oxygen gas and kept under oxygen atmosphere by using an oxygen balloon. The tube was gradually heated to 60 °C and allowed to react for overnight. After cooling to room temperature, the mixture was degassed to remove oxygen gas by the freeze-pump-thaw procedure with Ar. 1,3-Cyclohexanedione (1 mmol, 112 mg) was then added to the reaction tube, and the mixture was stirred under an air atmosphere for 12 h at 40 °C. After the reaction, saturated $NaHCO_3$ (10 mL) was added, and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic phases were washed with brine (1 x 10 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification via flash column chromatography (petroleum ether/acetone, 4:l) yielded 59 mg of **6** (50% yield) as a white solid and 81 mg of **3a** (89% yield). The formation of **6** from 1,3-cyclohexanedione and formaldehyde has been reported previously.[6-7]

2,2'-methylenebis(3-hydroxycyclohex-2-enone) (6)[7]

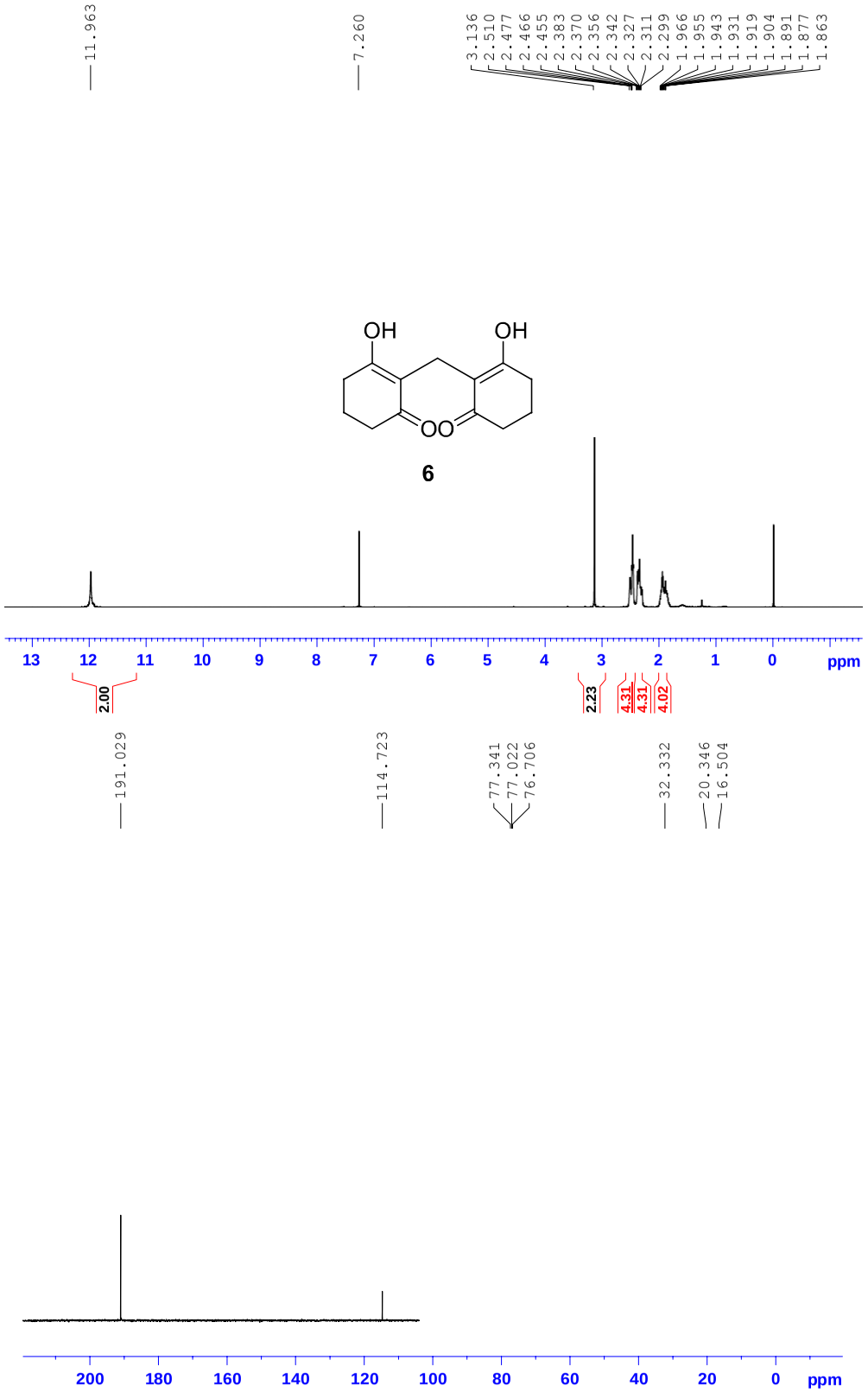


6

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 12.96 (brs, 2 H), 3.14 (s, 2 H), 2.51-2.46 (m, 4 H), 2.38-2.30 (m, 4 H), 1.97-1.86 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm):

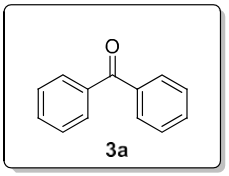
191.0, 114.7, 32.3, 20.3, 16.5.

^{1}H NMR and ^{13}C NMR spectra of 6:



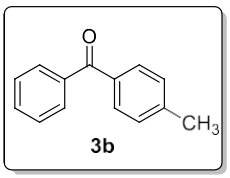
5. Analytic data of products

Benzophenone (3a)[8]



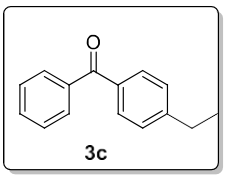
Compound **3a** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 49-50 °C. Yield: **90%** (81 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 4.0 Hz, 4H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.7, 137.5, 132.3, 130.0, 128.2. **IR** (KBr, plate), ν (cm^{-1}): 1651, 1594, 1572, 1448, 1318, 1277, 1073, 997, 939, 916, 814, 763, 703, 635, 436. **HRMS** (ESI) m/z calc. for $C_{14}H_{10}F_3O$ $[M+Na]^+$ 205.0623; found 205.0613.

Phenyl (p-tolyl)methanone (3b)[8]



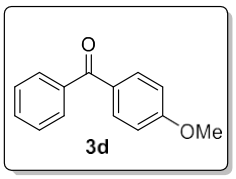
Compound **3b** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **85%** (83 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.4, 143.2, 137.9, 134.9, 132.1, 130.3, 129.9, 128.9, 128.2, 21.6. **IR** (KBr, plate), ν (cm^{-1}): 1657, 1604, 1449, 1407, 1313, 1277, 1178, 1148, 1071, 1024, 922, 837, 787, 731, 699, 601, 472. **HRMS** (ESI) m/z calc. for $C_{14}H_{12}NaO$ $[M+Na]^+$ 219.0780; found 219.0771.

(4-Ethylphenyl)(phenyl)methanone (3c)[9]



Compound **3c** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **70%** (74 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.80 (d, *J* = 6.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.5, 149.4, 138.0, 135.1, 132.1, 130.4, 129.9, 128.2, 127.8, 28.9, 15.2. **IR** (KBr, plate), ν (cm^{-1}): 1657, 1604, 1449, 1414, 1312, 1278, 1179, 1071, 922, 848, 701, 602. **HRMS** (ESI) m/z calc. for $C_{15}H_{14}NaO$ $[M+Na]^+$ 233.0948; found 233.0947.

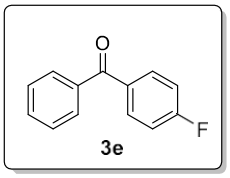
(4-Methoxyphenyl)(phenyl)methanone (3d)[10]



3d

Compound **3d** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. White solid. Yield: **71%** (75 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.6, 163.3, 138.3, 132.6, 131.9, 130.2, 129.7, 128.2, 113.6, 55.5. **IR** (KBr, plate), ν (cm^{-1}): 1644, 1599, 1505, 1449, 1414, 1309, 1285, 1252, 1174, 1148, 1112, 1028, 923, 845, 795, 740, 699, 608. **HRMS** (ESI) m/z calc. for $C_{14}H_{12}NaO_2$ $[M+Na]^+$ 235.0735; found 235.0741.

(4-Fluorophenyl)(phenyl)methanone (3e)[10]

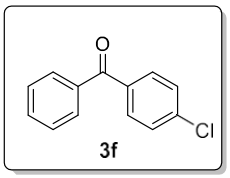


3e

Compound **3e** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **88%** (88 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.86-7.82 (m, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6

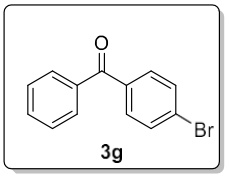
Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.2, 165.3 (d, *J* = 252.7 Hz), 137.5, 133.8 (d, *J* = 3.1 Hz), 132.6 (d, *J* = 9.1 Hz), 132.4, 129.8, 115.4 (d, *J* = 21.6 Hz). **IR** (KBr, plate), ν (cm^{-1}): 1645, 1596, 1502, 1445, 1407, 1302, 1282, 1262, 1227, 1151, 1096, 1020, 962, 939, 922, 850, 795, 735, 696, 597, 500. **HRMS** (ESI) m/z calc. for $C_{13}H_9FNaO$ $[M+Na]^+$ 223.0529; found 223.0520.

(4-Chlorophenyl)(phenyl)methanone (3f)[10]



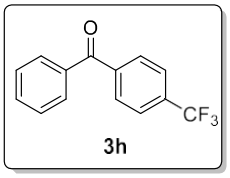
Compound **3f** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 70-71 °C. Yield: **77%** (83 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.78-7.75 (m, 4H), 7.62-7.58 (m, 1H), 7.51-7.45 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.5, 138.9, 137.3, 135.9, 132.6, 131.5, 129.9, 128.6, 128.4. **IR** (KBr, plate), ν (cm^{-1}): 1650, 1581, 1482, 1441, 1397, 1281, 1147, 1086, 921, 842, 788, 728, 695, 663, 503, 475. **HRMS** (ESI) m/z calc. for $C_{13}H_9ClNaO$ $[M+Na]^+$ 239.0234; found 239.0220.

(4-Bromophenyl)(phenyl)methanone (3g)[8]



Compound **3g** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 76-77 °C. Yield: **78%** (101 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.78 (d, *J* = 7.8 Hz, 2H), 7.69-7.59 (m, 5H), 7.49 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.6, 137.2, 136.3, 132.7, 131.6, 129.9, 128.4, 127.5. **IR** (KBr, plate), ν (cm^{-1}): 1648, 1580, 1393, 1282, 1066, 1008, 941, 919, 842, 788, 725, 695, 655, 468. **HRMS** (ESI) m/z calc. for $C_{13}H_9BrNaO$ $[M+Na]^+$ 282.9728; found 282.9715.

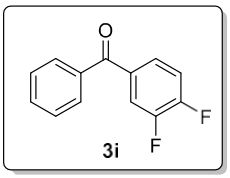
(4- Trifluoromethyl)phenyl)(phenyl)methanone (3h)[10]



3h

Compound **3h** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 109-110 °C. Yield: **82%** (103 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.5, 140.8, 136.8, 133.6 (q, *J* = 32.5 Hz), 133.1, 130.15, 130.11, 128.5, 125.4 (q, *J* = 3.6 Hz), 126.4 (q, *J* = 270.9 Hz). **IR** (KBr, plate), ν (cm^{-1}): 1651, 1596, 1573, 1408, 1330, 1281, 1171, 1113, 1065, 1016, 940, 921, 857, 797, 750, 696, 653, 598, 466. **HRMS** (ESI) m/z calc. for $C_{14}H_{10}F_3O$ $[M+Na]^+$ 211.0188; found 211.0181.

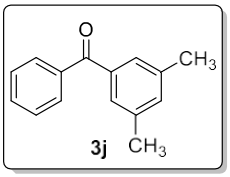
(3,4-Difluorophenyl)(phenyl)methanone (3i)[11]



3i

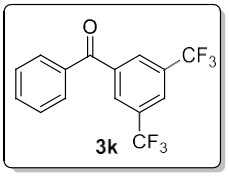
Compound **3i** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **78%** (85 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, *J* = 7.1 Hz, 2H), 7.70-7.57 (m, 1H), 7.63-7.58 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.30-7.24 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 194.0, 153.2 (dd, *J* = 254.7, 12.7 Hz), 150.1 (dd, *J* = 249.4, 12.9 Hz), 136.9, 134.5 (t, *J* = 4.0 Hz), 132.8, 129.8, 128.5, 127.1 (dd, *J* = 7.1, 3.5 Hz), 119.3 (dd, *J* = 18.2, 1.2 Hz), 117.3 (d, *J* = 17.7 Hz). **IR** (KBr, plate), ν (cm^{-1}): 1651, 1607, 1513, 1424, 1320, 1288, 1202, 1105, 898, 858, 836, 795, 769, 726, 698, 595, 453. **HRMS** (ESI) m/z calc. for $C_{13}H_8F_2NaO$ $[M+Na]^+$ 241.0435; found 241.0421.

(3,5-Dimethylphenyl) (phenyl) methanone (3j)[12]



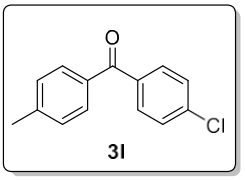
Compound **3j** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **78%** (82 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.79 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (s, 2H), 7.22 (s, 1H), 2.37 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 197.1, 137.89, 137.87, 134.0, 132.2, 130.0, 128.2, 127.8, 21.2. **IR** (KBr, plate), ν (cm^{-1}): 1658, 1598, 1450, 1320, 1231, 866, 812, 725, 697, 663. **HRMS** (ESI) m/z calc. for $C_{15}H_{14}NaO$ $[M+Na]^+$ 233.0938; found 233.0925.

(3,5-Bis(trifluoromethyl)phenyl)(phenyl)methanone (3k)[13]



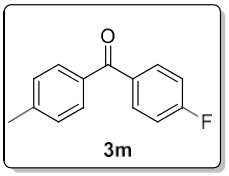
Compound **3k** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **80%** (127 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.24 (s, 2H), 8.10 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 193.6, 139.4, 135.9, 133.6, 132.1 (q, *J* = 33.7 Hz), 130.0, 129.8 (d, *J* = 3.2 Hz), 128.9, 125.6 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 271.3 Hz). **IR** (KBr, plate), ν (cm^{-1}): 1674, 1618, 1599, 1451, 1380, 1283, 1137, 910, 848, 797, 722, 685, 660, 624. **HRMS** (ESI) m/z calc. for $C_{15}H_8F_6NaO$ $[M+Na]^+$ 341.0371; found 341.0354.

(4-Chlorophenyl)(p-tolyl)methanone (3l)[14]



Compound **3l** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 118-120 °C. Yield: **87%** (100 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 195.2, 143.5, 138.6, 136.3, 134.6, 131.3, 130.2, 129.1, 128.6, 21.7. **IR** (KBr, plate), ν (cm^{-1}): 1644, 1604, 1583, 1479, 1398, 1373, 1285, 1182, 1144, 1086, 1013, 964, 927, 853, 820, 799, 747, 675, 557, 503, 457. **HRMS** (ESI) m/z calc. for $C_{14}H_{12}ClO$ $[M+H]^+$ 231.0571; found 231.0556.

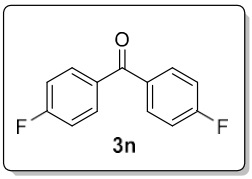
(4-Fluorophenyl)(p-tolyl)methanone (3m)[15]



3m

Compound **3m** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 89-90 °C. Yield: **89%** (95 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.84-7.81 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.29 (d *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 195.0, 165.2 (d, *J* = 252.3 Hz), 143.3, 134.8, 134.1 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 8.9 Hz), 130.1, 129.0, 115.3 (d, *J* = 21.7 Hz), 21.6. **IR** (KBr, plate), ν (cm^{-1}): 1649, 1601, 1501, 1406, 1285, 1221, 1152, 1098, 967, 929, 851, 825, 814, 753, 677, 579, 493, 471. **HRMS** (ESI) m/z calc. for $C_{14}H_{12}FO$ $[M+H]^+$ 215.0866; found 215.0856.

Bis(4-fluorophenyl)methanone (3n)[15]

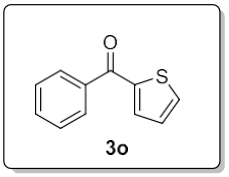


3n

Compound **3n** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid, m. p. 97-100 °C. Yield: **85%** (93 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.83-7.80 (m, 4H), 7.17 (t, *J* = 8.4 Hz, 4H); **^{13}C NMR**

(100 MHz, $CDCl_3$) δ (ppm): 193.8, 165.4 (d, *J* = 252.7 Hz), 133.7 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 9.2 Hz), 115.5 (d, *J* = 21.9 Hz). **IR** (KBr, plate), ν (cm^{-1}): 1649, 1598, 1504, 1408, 1300, 1261, 1229, 1150, 1099, 1020, 929, 854, 812, 764, 674, 577, 495. **HRMS** (ESI) m/z calc. for $C_{13}H_8F_2NaO$ $[M+Na]^+$ 241.0441; found 241.0448.

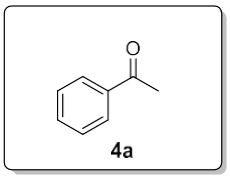
Phenyl(thiophen-2-yl)methanone (3o)[14]



3o

Compound **3o** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **95%** (89 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.61-7.57 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39-7.37 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 190.0, 141.3, 138.6, 133.9, 129.4, 128.6, 128.4, 126.2. **IR** (KBr, plate), ν (cm^{-1}): 1650, 1598, 1511, 1446, 1409, 1262, 1022, 858, 801, 716, 701, 671. **HRMS** (ESI) m/z calc. for $C_{11}H_8NaOS$ $[M+Na]^+$ 211.0188; found 211.0181.

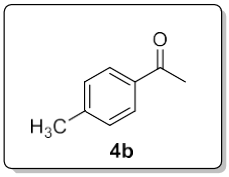
Acetophenone (4a)[8]



4a

Compound **4a** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **90%** (54 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.96 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 198.1, 137.2, 133.1, 128.6, 128.3, 26.6.

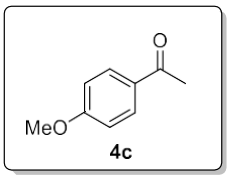
1-*p*-Tolylethanone (4b)[16]



4b

Compound **4b** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **78%** (53 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 197.7, 143.7, 134.6, 129.1, 128.3, 26.4, 21.5.

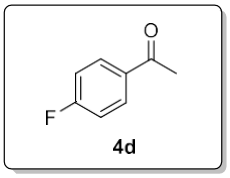
1-(4-Methoxyphenyl)ethanone (4c)[16]



4c

Compound **4c** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **69%** (52 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 8.8 Hz, 2H), 6.91 (t, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 196.7, 163.4, 130.5, 113.6, 55.3, 26.2.

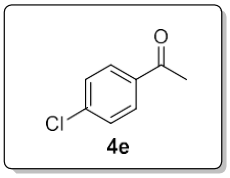
1-(4-Fluorophenyl)ethanone (4d)[8]



4d

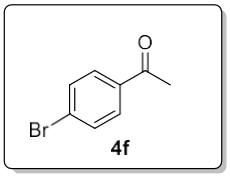
Compound **4d** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **87%** (60 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.96 (q, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 8.8 Hz, 2H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.4, 165.7 (d, *J* = 253.4 Hz), 133.5 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 9.1 Hz), 115.5 (d, *J* = 21.7 Hz), 26.4.

1-(4-Chlorophenyl)ethanone (4e)[8]



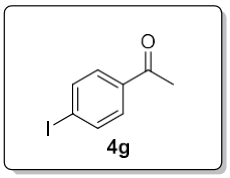
Compound **4e** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid. Yield: **86%** (66 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 8.8 Hz, 2H), 2.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.7, 139.5, 135.4, 129.6, 128.8, 26.5.

1-(4-Bromophenyl)ethanone (4f)[8]



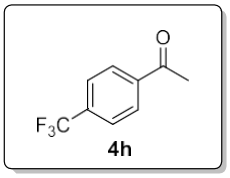
Compound **4f** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. White solid. Yield: **78%** (78 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.81 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 2.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 197.0, 135.8, 131.9, 129.8, 128.3, 26.5.

1-(4-Iodophenyl)ethenone (4g)[17]



Compound **4g** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **85%** (96 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 197.3, 137.9, 136.3, 129.7, 101.1, 26.4.

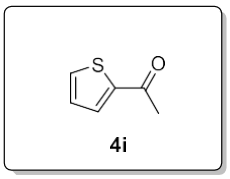
1-(4-(Trifluoromethyl)phenyl)ethenone (4h)[18]



4h

Compound **4h** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **89%** (71 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 196.9, 139.7, 134.3 (q, *J* = 32.5 Hz), 128.6, 125.6 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 270.9 Hz), 26.7.

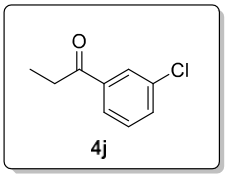
1-(Thiophen-2-yl)ethanone (4i)[16]



4i

Compound **4i** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **76%** (48 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.04-8.03 (m, 1H), 7.54-7.53 (m, 1H), 7.32-7.30 (m, 1H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 192.2, 142.6, 132.3, 127.0, 126.4, 27.5.

1-(3-Chlorophenyl)propan-1-one (4j)[19]

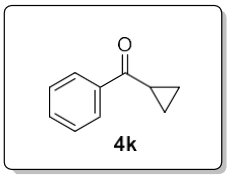


4j

Compound **4j** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. White solid. Yield: **54%** (35 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.93 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 199.4, 138.4, 134.9, 132.8, 129.9, 128.1, 126.0, 31.9, 8.1. **IR** (KBr, plate), ν (cm^{-1}): 1677, 1446, 1413, 1352, 1303, 1268, 1203, 1066, 997, 979, 741, 706,

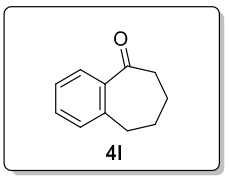
686, 632, 573, 475, 418. **HRMS** (ESI) m/z calc. for C_9H_9ClNaO $[M+Na]^+$ 191.0234; found 191.0223.

Cyclopropyl(phenyl)methanone (4k)[8]



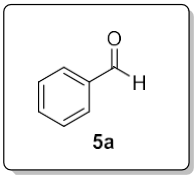
Compound **4k** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **82%** (60 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 2.71-2.65 (m, 1H), 1.27-1.23 (m, 2H), 1.06-1.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 200.6, 138.0, 132.7, 128.5, 128.0, 17.1, 11.6. **IR** (KBr, plate), ν (cm^{-1}): 3062, 3008, 1668, 1596, 1577, 1450, 1387, 1225, 1035, 993, 868, 781, 708, 646. **HRMS** (ESI) m/z calc. for $C_{10}H_{10}NaO$ $[M+Na]^+$ 169.0623; found 169.0612.

6,7,8,9-Tetrahydro-5H-benzo*[7]*annulen-5-one (4l)[20]



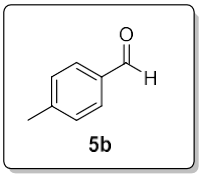
Compound **4l** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **60%** (48 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.93 (t, *J* = 6.2 Hz, 2H), 2.73 (t, *J* = 5.8 Hz, 2H); 1.91-1.78 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 206.1, 141.3, 138.8, 132.1, 129.6, 128.5, 126.6, 40.8, 32.5, 25.2, 20.9. **IR** (KBr, plate), ν (cm^{-1}): 1678, 1600, 1451, 1289, 1259, 1218, 1094, 1030, 958, 771, 738, 554, 465. **HRMS** (ESI) m/z calc. for $C_{11}H_{12}NaO$ $[M+Na]^+$ 183.0780; found 183.0771.

Benzaldehyde (5a)[8]



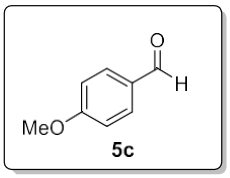
Compound **5a** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **70%** (47 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 10.02 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 192.4, 136.4, 134.4, 129.7, 129.0.

4-Methylbenzaldehyde (5b)[8]



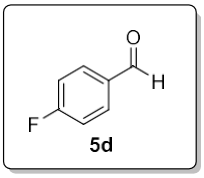
Compound **5b** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **75%** (45 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.96 (s, 1 H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 192.0, 145.5, 134.2, 129.8, 129.7, 21.9.

4-Methoxybenzaldehyde (5c)[8]



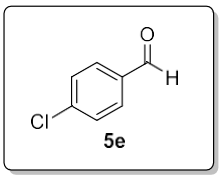
Compound **5c** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. Oil. Yield: **80%** (54 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.84 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 190.7, 164.5, 131.8, 129.8, 114.2, 55.4.

4-Fluorobenzaldehyde (5d)[8]



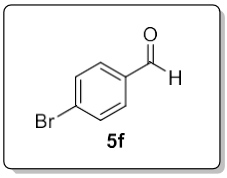
Compound **5d** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **78%** (48 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.94 (s, 1H), 7.88 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 190.4, 166.5 (d, *J* = 255.1 Hz), 132.9 (d, *J* = 2.6 Hz), 132.2 (d, *J* = 9.8 Hz), 116.3 (d, *J* = 22.0 Hz).

4-Chlorobenzaldehyde (5e)[8]



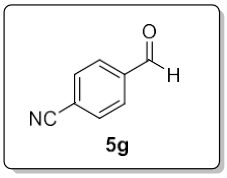
Compound **5e** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **88%** (62 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.98 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 190.8, 141.0, 134.7, 130.9, 129.5.

4-Bromobenzaldehyde (5f)[8]



Compound **5f** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **78%** (72 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.97 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 191.1, 135.1, 132.4, 131.0, 129.8.

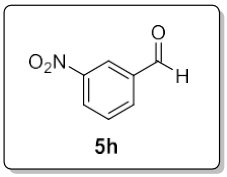
4-Formylbenzonitrile (5g)[21]



5g

Compound **5g** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **89%** (58 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 10.09 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 190.6, 138.7, 132.9, 129.9, 117.7, 117.6.

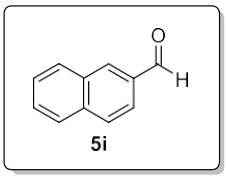
3-Nitrobenzaldehyde (5h)[22]



5h

Compound **5h** was obtained following the general procedure for oxidation of **2**, reaction time: 12 h. Oil. Yield: **82%** (62 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 10.1 (s, 1H), 8.71 (d, *J* = 2.0 Hz, 1H), 8.71-8.47 (m, 1H), 8.23 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 189.7, 137.4, 134.6, 130.4, 128.6, 124.5.

2-Naphthaldehyde (5i)[8]



5i

Compound **5i** was obtained following the general procedure for oxidation of **2**, reaction time: 24 h. White solid, m. p. 53-55 °C. Yield: **65%** (51 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 10.17 (s, 1H), 8.35 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.98-7.90 (m, 3H), 7.67-7.58 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 192.3, 136.5, 134.5, 134.2, 132.7, 129.5, 129.1, 128.1, 127.1, 122.8. **IR** (KBr, plate), ν (cm^{-1}): 3062, 2846, 2829, 1693, 1623, 1462, 1344, 1261, 1165, 1114, 1023, 1012, 961, 907, 871,

833, 775, 750, 627, 599, 480. **HRMS** (ESI) m/z calc. for $C_{11}H_9O$ $[M+H]^+$ 157.0647; found 157.0641.

6. References:

1 S. Serra, *Tetrahedron: Asymmetry*, 2011, **22**, 619.

2 T. Wang, Y. Hu and S. Zhang, *Org. Biomol. Chem.*, 2010, **8**, 2312.

3 T. W. Liwosz and S. R. Chemler, *Chem. Eur. J.*, 2013, **19**, 12771.

4 Y. Liu, C. Wang, D. Xue, M. Xiao, J. Liu, C. Li and J. Xiao, *Chem. Eur. J.*, 2017, **23**, 3062.

5 Y. Liu, C. Wang, D. Xue, M. Xiao, C. Li and J. Xiao, *Chem. Eur. J.*, 2017, **23**, 3051.

6 J.-J. Yu, L.-M. Wang, J.-Q. Liu, F.-L. Guo, Y. Liu and N. Jiao, *Green Chem.*, 2010, **12**, 216.

7 A. B. Smith, B. D. Dorsey, M. Ohba, A. T. Lupo and M. S. Malamas, *J. Org. Chem.*, 1988, **53**, 4314.

8 A. Gonzalez-de-Castro and J. Xiao, *J. Am. Chem. Soc.*, 2015, **137**, 8206.

9 R. Kulasekharan, M. V. S. N. Maddipatla, A. Parthasarathy and V. Ramamurthy, *J. Org. Chem.*, 2013, **78**, 942.

10 C. Liu, M. Achtenhagen and M. Szostak, *Org. Lett.*, 2016, **18**, 2375.

11 C. He, X. Zhang, R. Huang, J. Pan, J. Li, X. Ling, Y. Xiong and X. Zhu, *Tetrahedron Lett.*, 2014, **55**, 4458.

12 X. Qi, L.-B. Jiang, H.-P. Li and X.-F. Wu, *Chem. Eur. J.*, 2015, **21**, 17650.

13 L. Chu, J. M. Lipshultz and D. W. C. MacMillan, *Angew. Chem. Int. Ed.*, 2015, **54**, 7929.

14 W.-M. Cheng, R. Shang, H.-Z. Yu and Y. Fu, *Chem. Eur. J.*, 2015, **21**, 13191.

15 Y. Hao, J. Jiang, Y. Wang and Z. Jin, *Catal. Commun.*, 2015, **71**, 106.

16 D. A. Chaudhari and R. A. Fernandes, *J. Org. Chem.*, 2016, **81**, 2113.

17 S. Chakraborty, P. E. Piszel, W. W. Brennessel and W. D. Jones, *Organometallics*, 2015, **34**, 5203.

18 W. Liu, H. Wang and C.-J. Li, *Org. Lett.*, 2016, **18**, 2184.

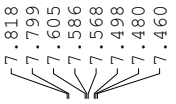
19 Y. Mori and M. Seki, *Adv. Synth. Catal.*, 2007, **349**, 2027.

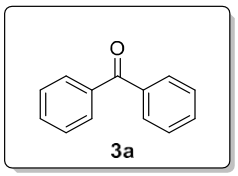
20 S. Zhang, C. Miao, C. Xia and W. Sun, *Chemcatchem*, 2015, **7**, 1865.

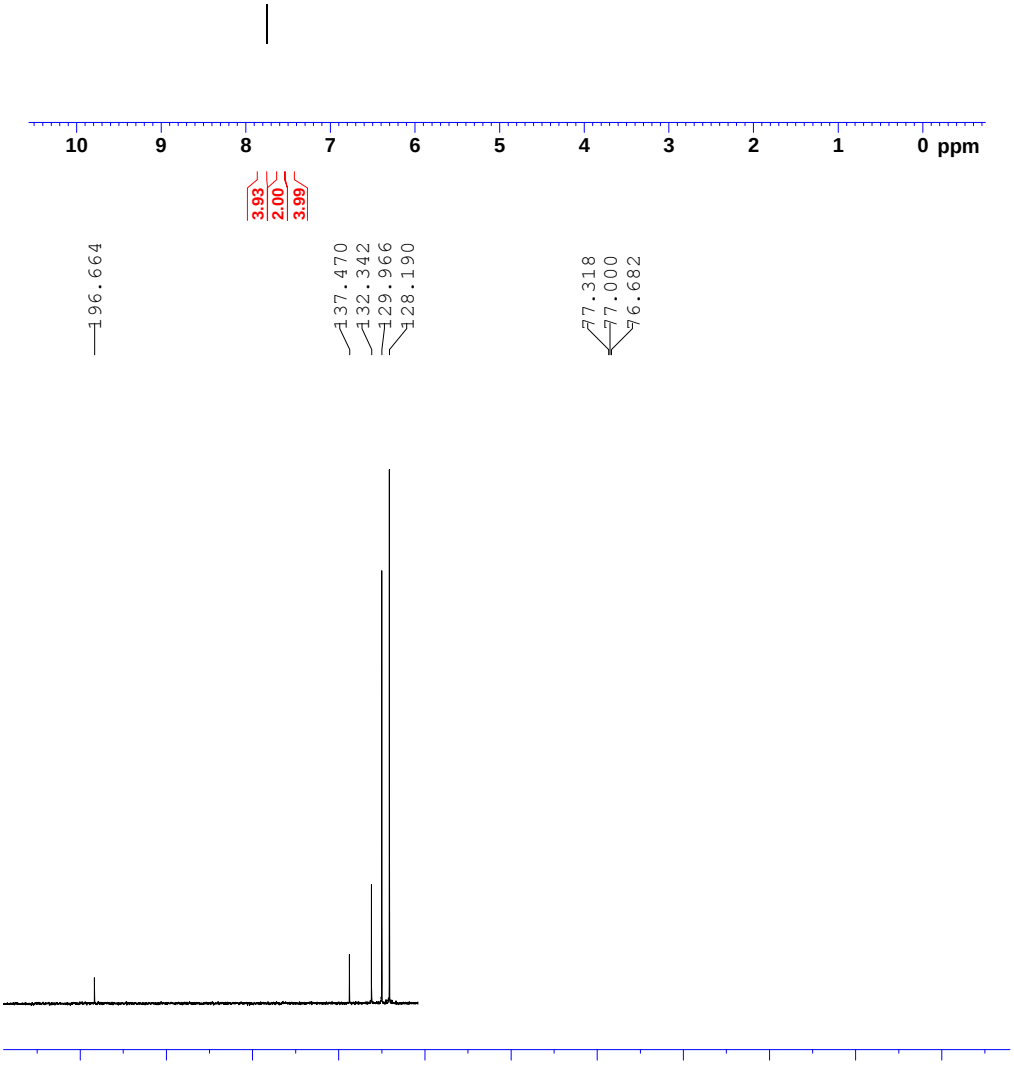
21 Q. Xing, H. Lv, C. Xia and F. Li, *Chem. Commun.*, 2016, **52**, 489.

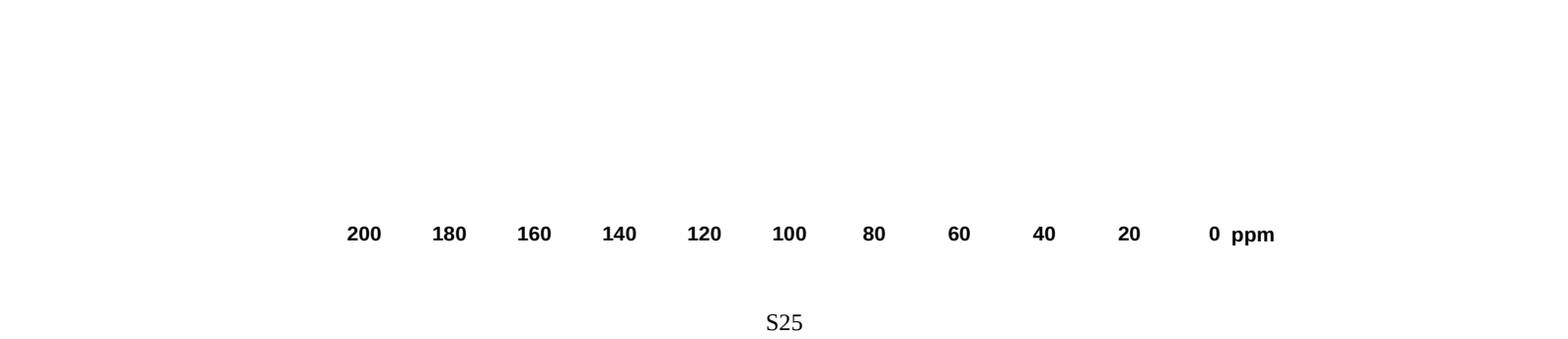
22 Y. Lin, L. Zhu, Y. Lan and Y. Rao, *Chem. Eur. J.*, 2015, **21**, 14937.

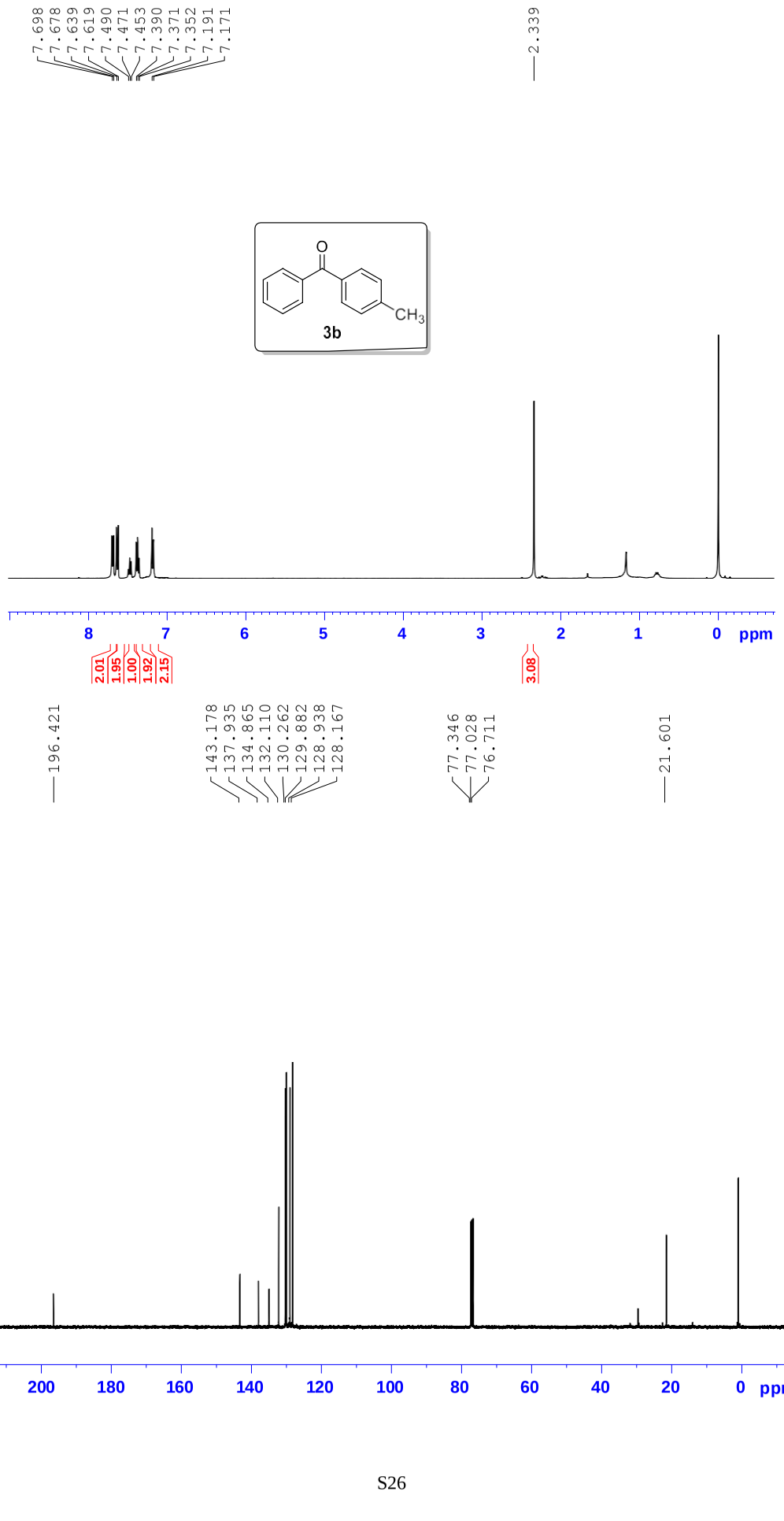
7. Traces of ^{1}H NMR and ^{13}C NMR spectra

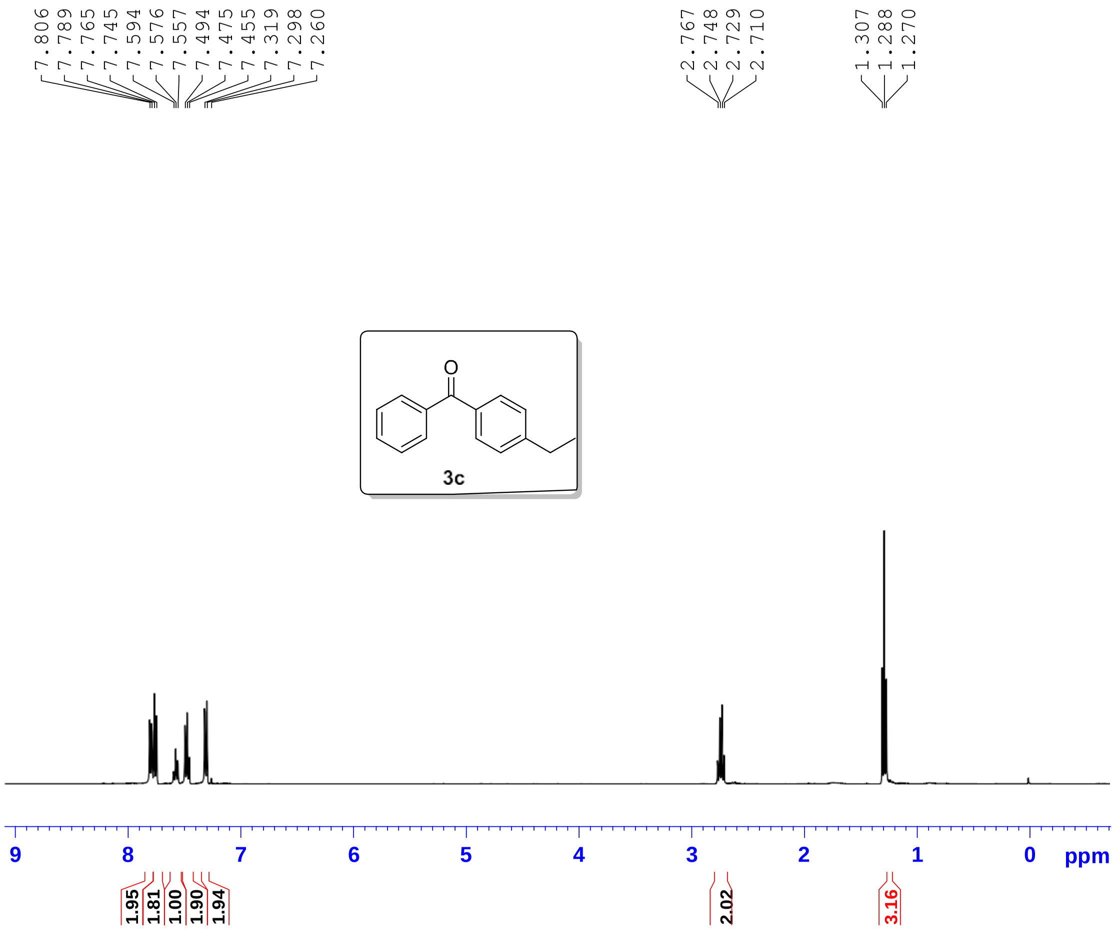


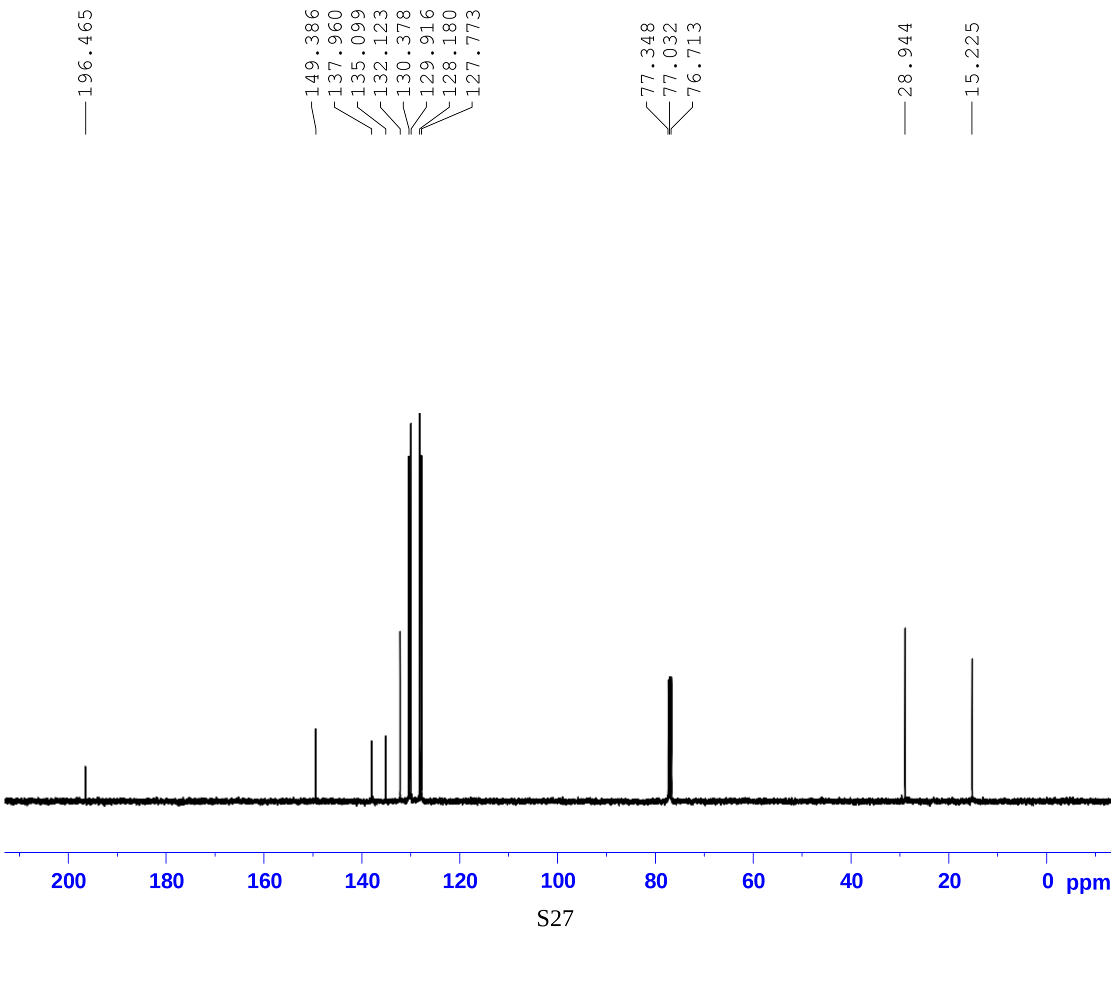


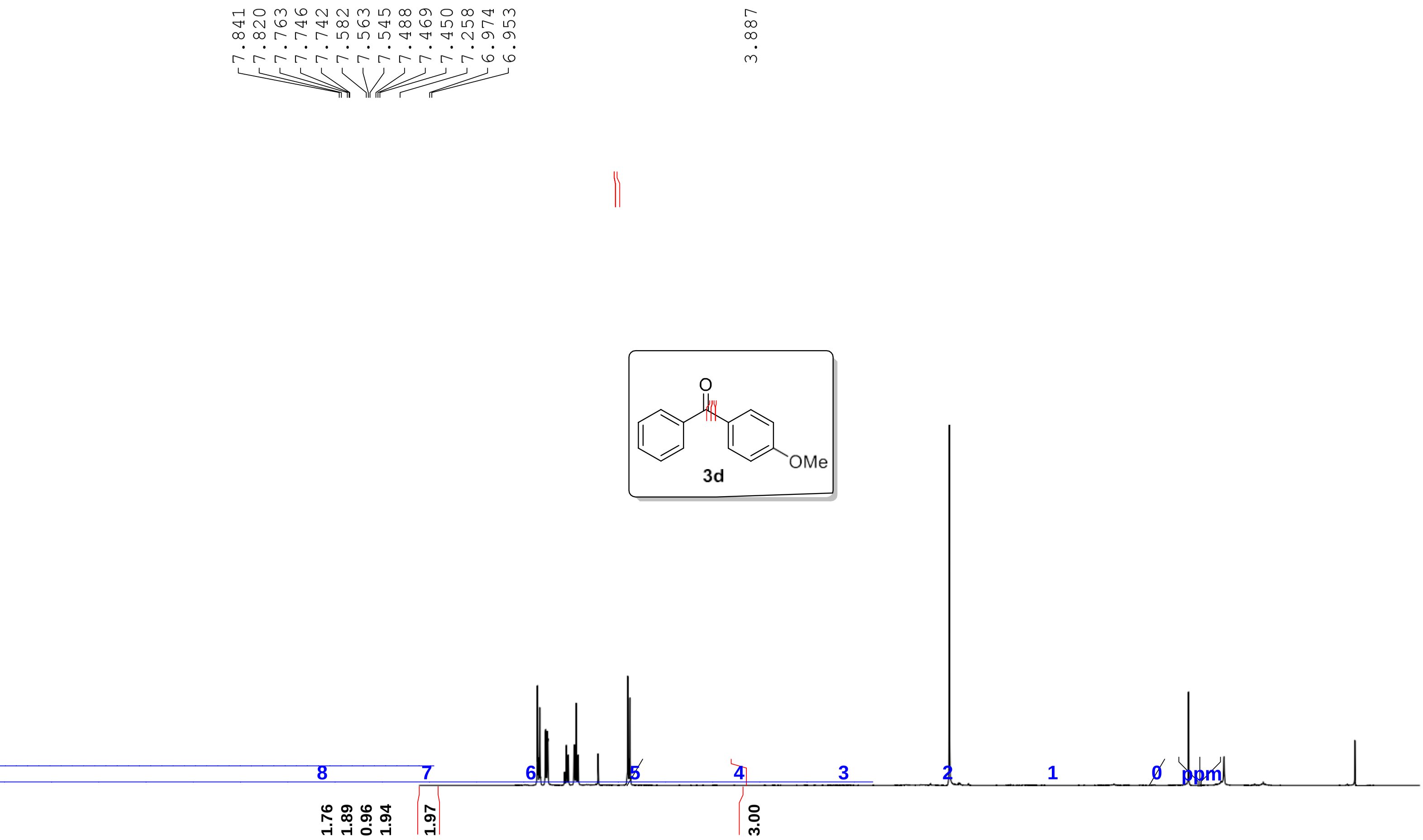


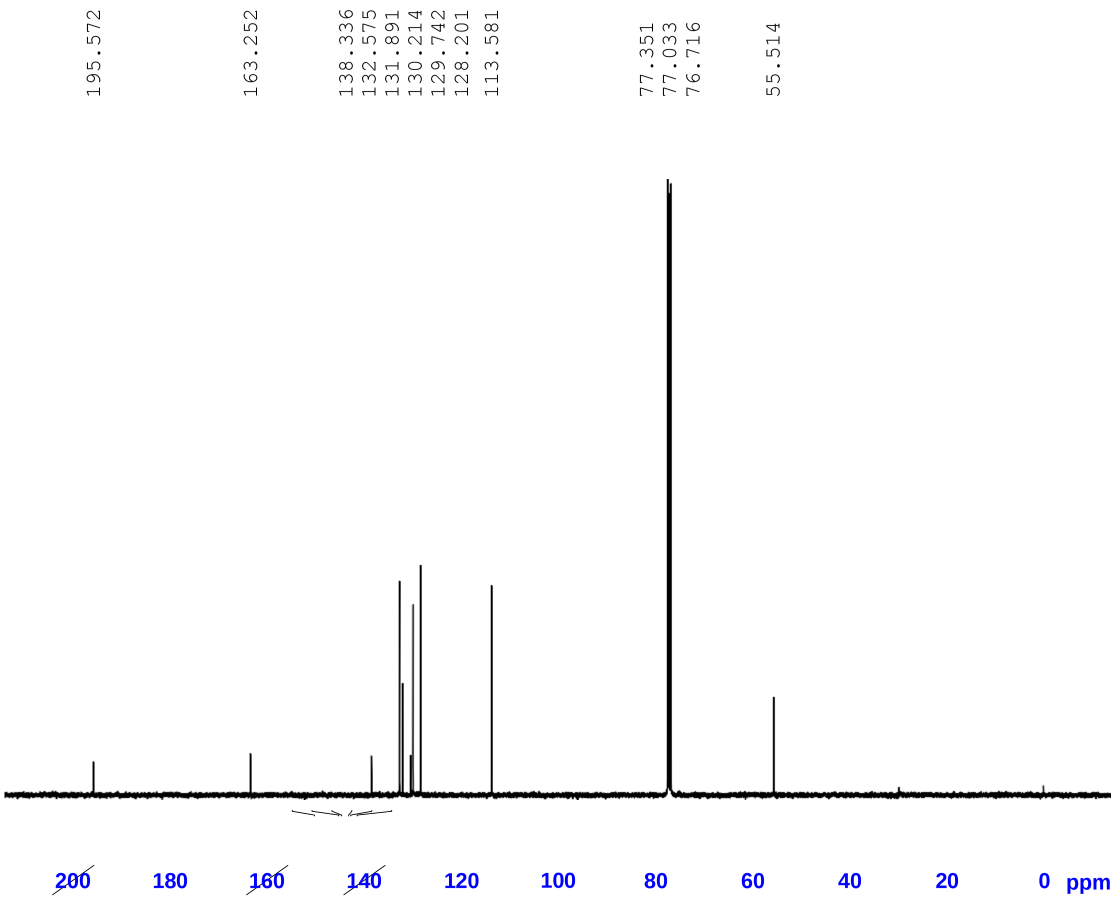

200
180
160
140
120
100
80
60
40
20
0
ppm

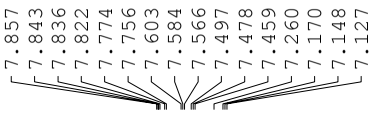

7.698
7.678
7.639
7.619
7.490
7.471
7.453
7.390
7.371
7.352
7.191
7.171
2.339
O
CH3
3b
8
7
6
5
4
3
2
1
0
ppm
2.01
1.95
1.00
1.92
2.15
3.08
196.421
143.178
137.935
134.865
132.110
130.262
129.882
128.938
128.167
77.346
77.028
76.711
21.601
200
180
160
140
120
100
80
60
40
20
0
ppm

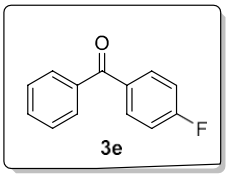

7.806
7.789
7.765
7.745
7.594
7.576
7.557
7.494
7.475
7.455
7.319
7.298
7.260
2.767
2.748
2.729
2.710
1.307
1.288
1.270
O
3c
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.81
1.00
1.90
1.94
2.02
3.16


196.465
149.386
137.960
135.099
132.123
130.378
129.916
128.180
127.773
77.348
77.032
76.713
28.944
15.225
200
180
160
140
120
100
80
60
40
20
0
ppm

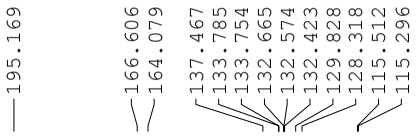

7.841
7.820
7.763
7.746
7.742
7.582
7.563
7.545
7.488
7.469
7.450
7.258
6.974
6.953
3.887
O
OMe
3d
8
7
6
5
4
3
2
1
0
ppm
1.76
1.89
0.96
1.94
1.97
3.00

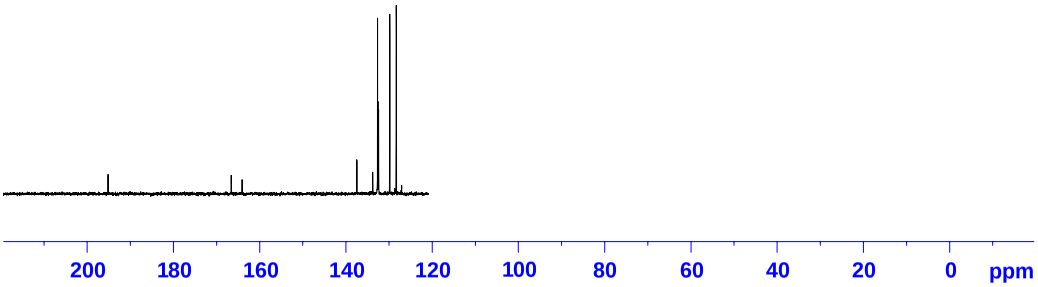

195.572
163.252
138.336
132.575
131.891
130.214
129.742
128.201
113.581
77.351
77.033
76.716
55.514
200
180
160
140
120
100
80
60
40
20
0
ppm

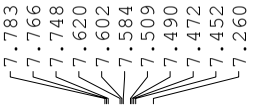

7.857
7.843
7.836
7.822
7.774
7.756
7.603
7.584
7.566
7.497
7.478
7.459
7.260
7.170
7.148
7.127

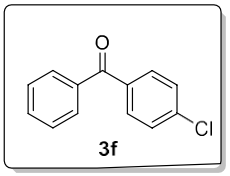

O
F
3e

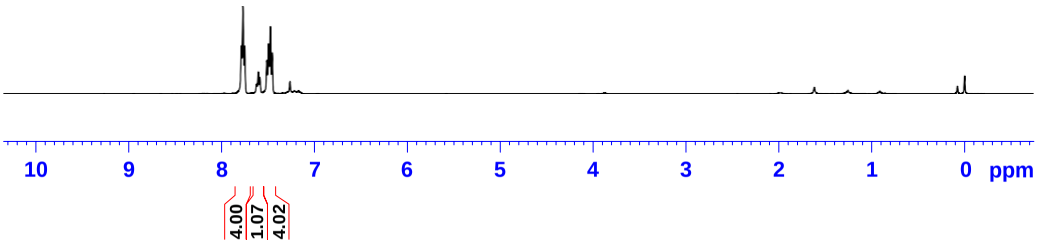
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.00
1.07
2.10
2.11

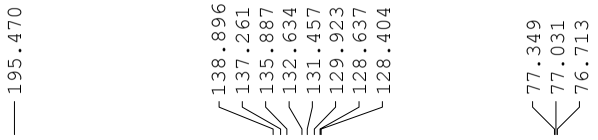

195.169
166.606
164.079
137.467
133.785
133.754
132.665
132.574
132.423
129.828
128.318
115.512
115.296
77.351
77.033
76.715

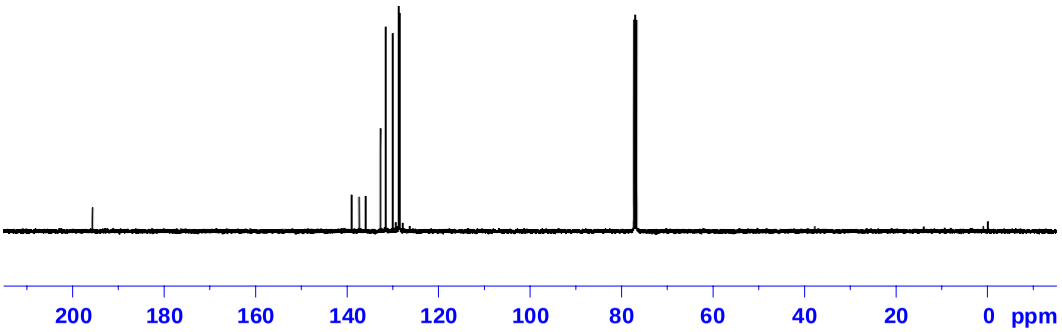

200
180
160
140
120
100
80
60
40
20
0
ppm

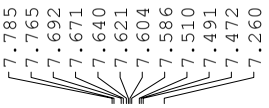

7.783
7.766
7.748
7.620
7.602
7.584
7.509
7.490
7.472
7.452
7.260

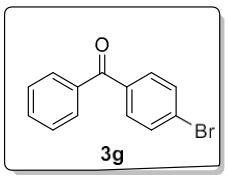

O
Cl
3f

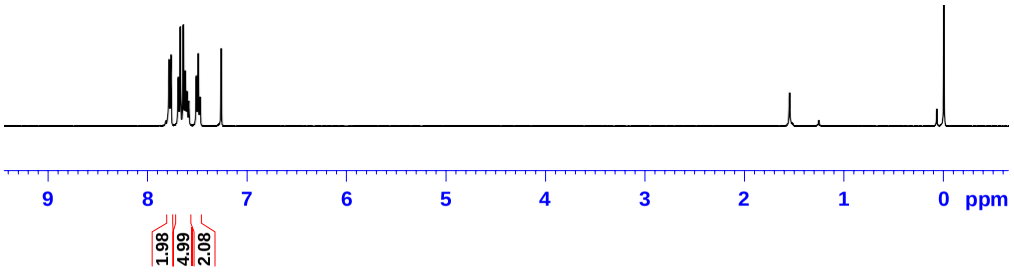

10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
1.07
4.02

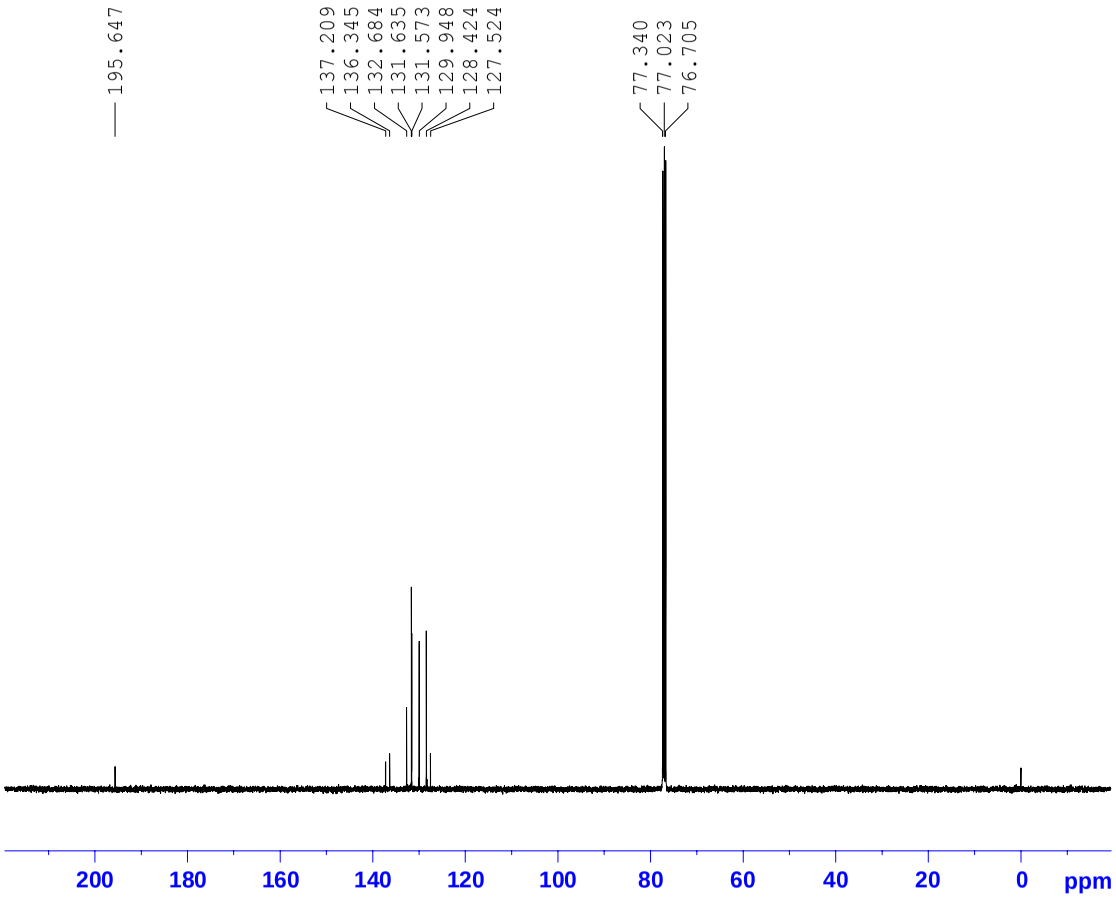

195.470
138.896
137.261
135.887
132.634
131.457
129.923
128.637
128.404
77.349
77.031
76.713

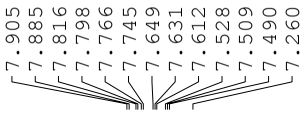

200
180
160
140
120
100
80
60
40
20
0
ppm

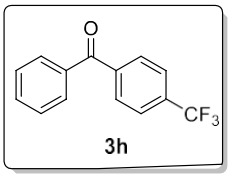

7.785
7.765
7.692
7.671
7.640
7.621
7.604
7.586
7.510
7.491
7.472
7.260

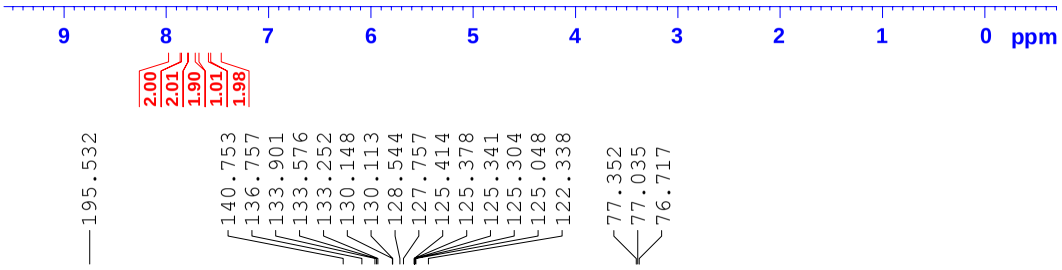

O
Br
3g

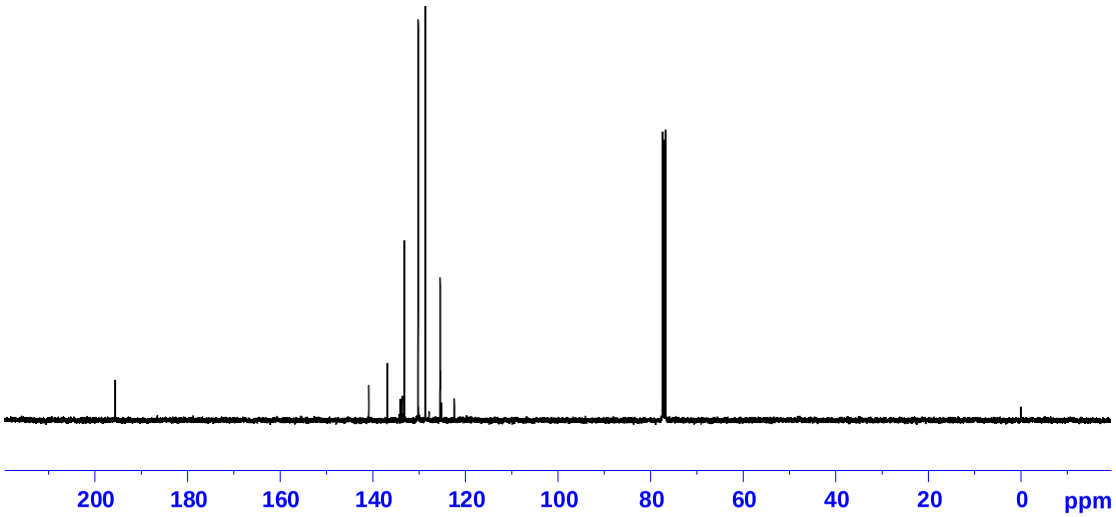

9
8
7
6
5
4
3
2
1
0
ppm
1.98
4.99
2.08

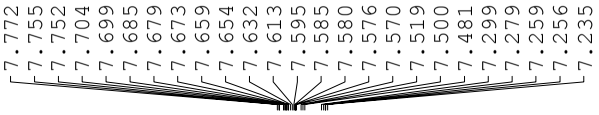

195.647
137.209
136.345
132.684
131.635
131.573
129.948
128.424
127.524
77.340
77.023
76.705
200
180
160
140
120
100
80
60
40
20
0
ppm

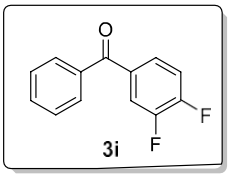

7.905
7.885
7.816
7.798
7.766
7.745
7.649
7.631
7.612
7.528
7.509
7.490
7.260

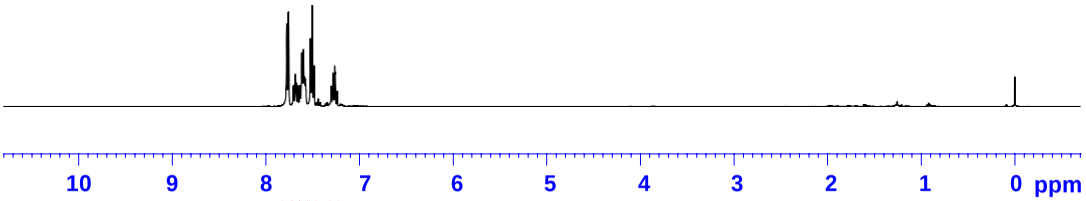

O
CF3
3h

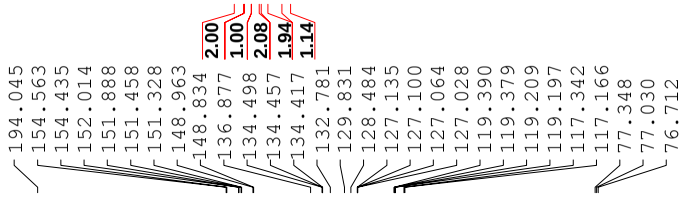

9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
1.90
1.01
1.98
195.532
140.753
136.757
133.901
133.576
133.252
130.148
130.113
128.544
127.757
125.414
125.378
125.341
125.304
125.048
122.338
77.352
77.035
76.717

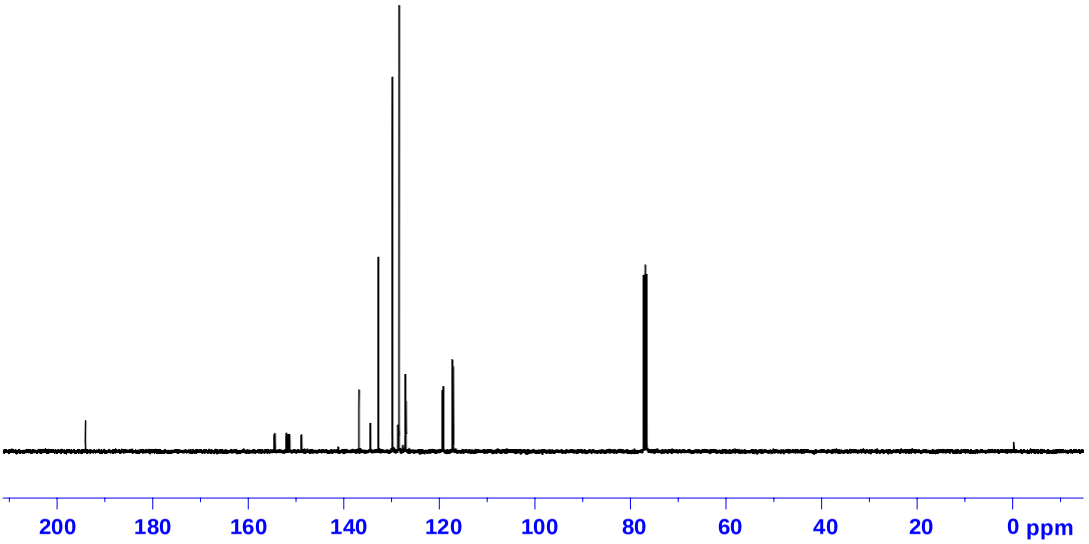

200
180
160
140
120
100
80
60
40
20
0
ppm

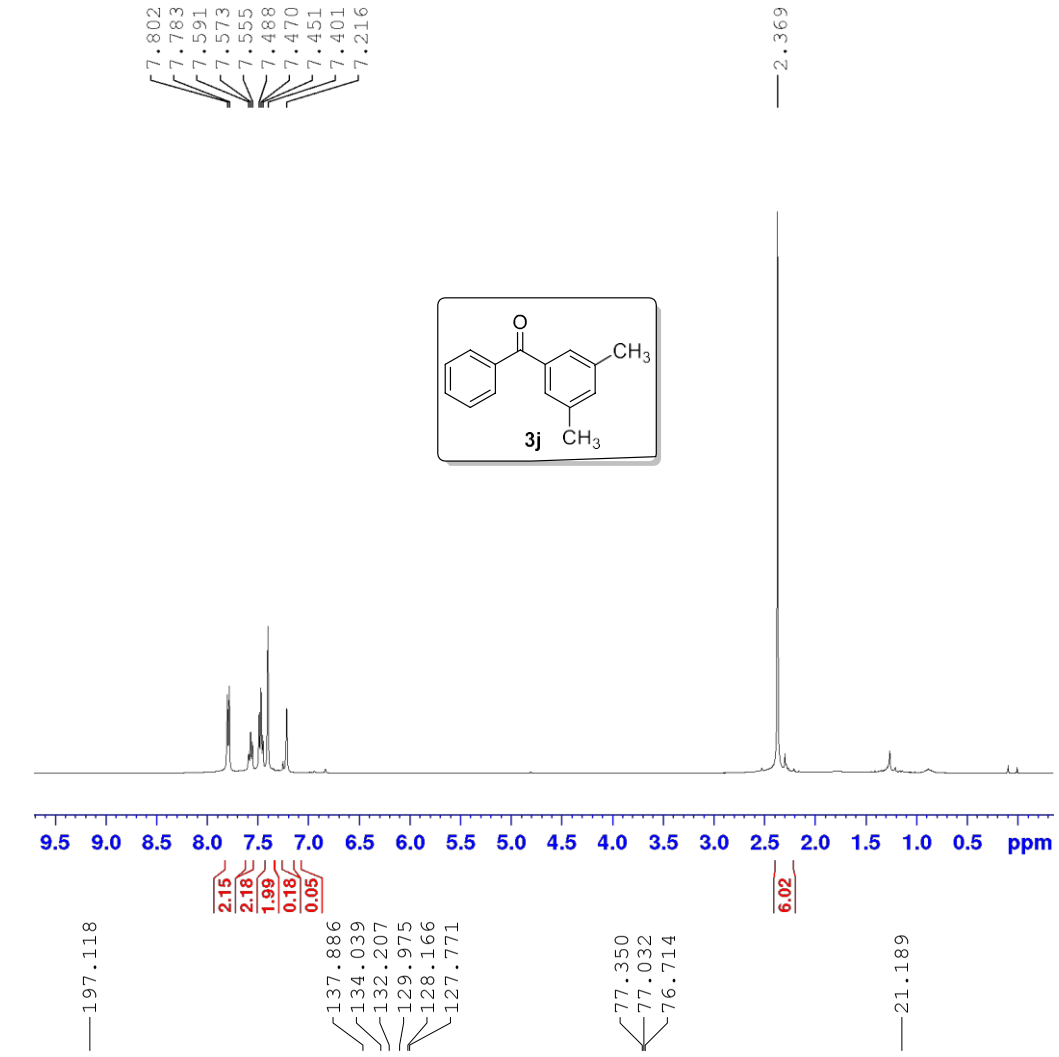

7.772
7.755
7.752
7.704
7.699
7.685
7.679
7.673
7.659
7.654
7.632
7.613
7.595
7.585
7.580
7.576
7.570
7.519
7.500
7.481
7.299
7.279
7.259
7.256
7.235

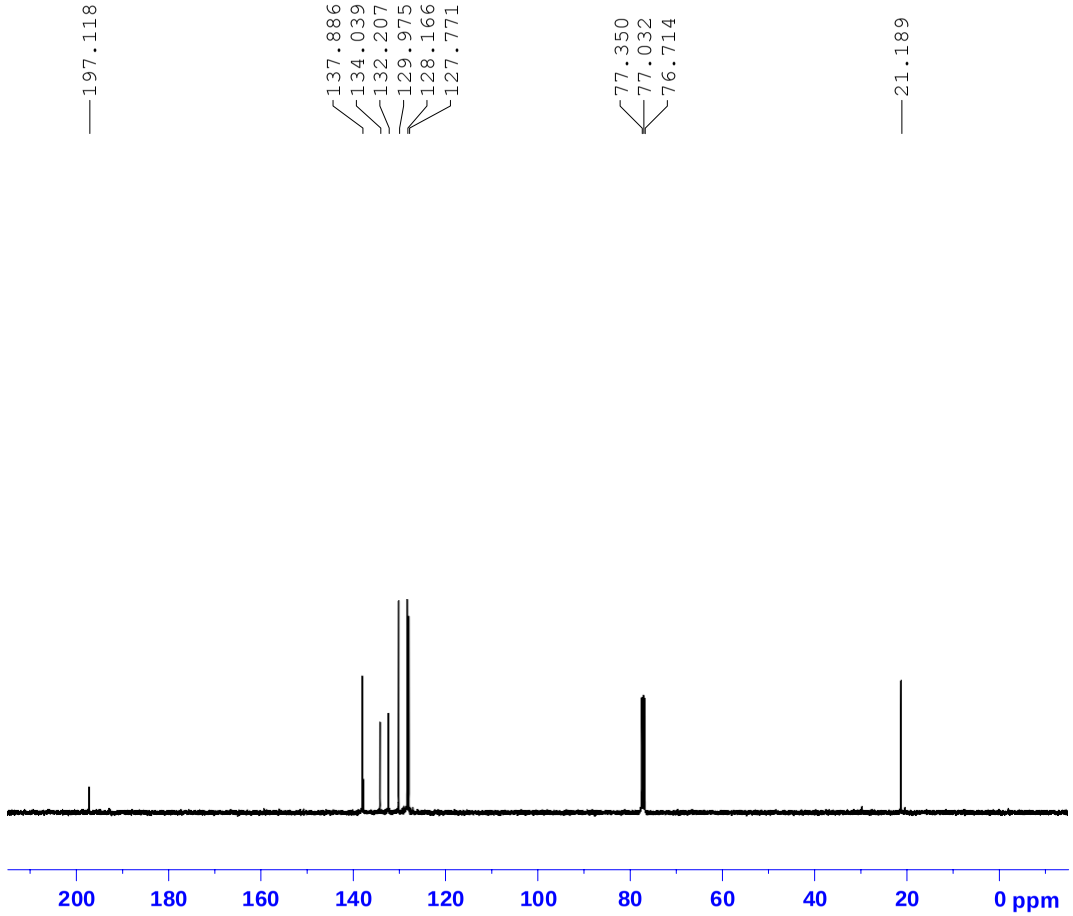

O
F
F
3i

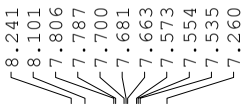

10
9
8
7
6
5
4
3
2
1
0 ppm

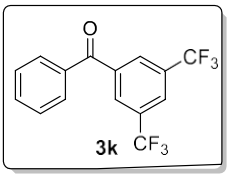

2.00
1.00
2.08
1.94
1.14
194.045
154.563
154.435
152.014
151.888
151.458
151.328
148.963
148.834
136.877
134.498
134.457
134.417
132.781
129.831
128.484
127.135
127.100
127.064
127.028
119.390
119.379
119.209
119.197
117.342
117.166
77.348
77.030
76.712

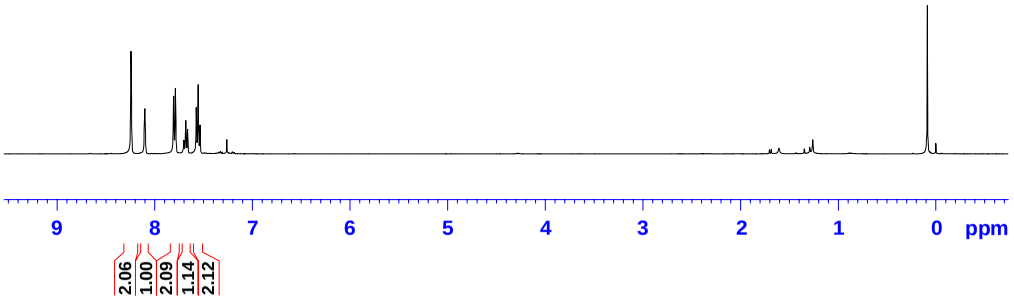

200
180
160
140
120
100
80
60
40
20
0 ppm

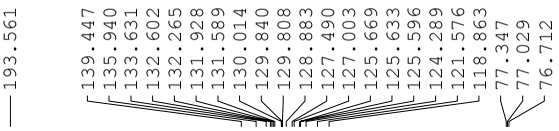

7.802
7.783
7.591
7.573
7.555
7.488
7.470
7.451
7.401
7.216
2.369
O
CH3
3j
CH3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.15
2.18
1.99
0.18
0.05
6.02

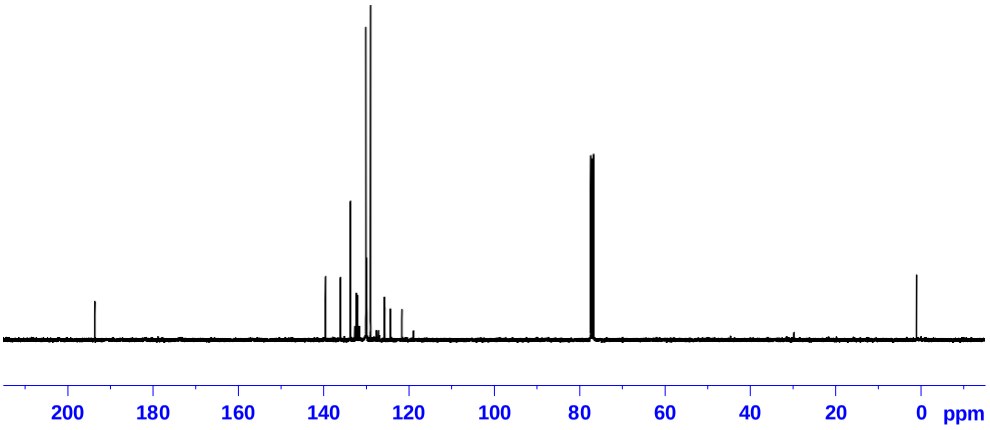

197.118
137.886
134.039
132.207
129.975
128.166
127.771
77.350
77.032
76.714
21.189
200 180 160 140 120 100 80 60 40 20 0 ppm

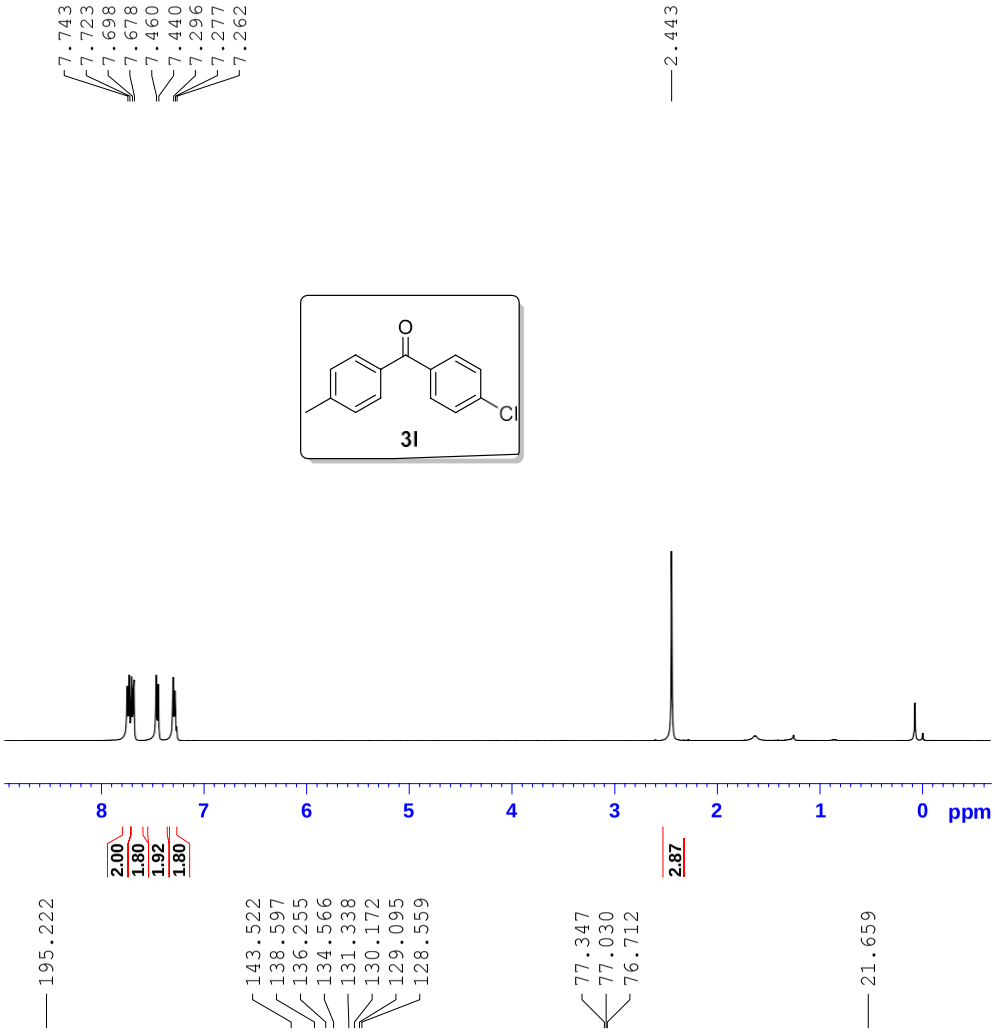

8.241
8.101
7.806
7.787
7.700
7.681
7.663
7.573
7.554
7.535
7.260

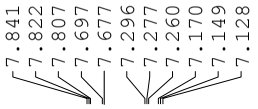

O
CF3
CF3
3k

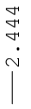

9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.00
2.09
1.14
2.12

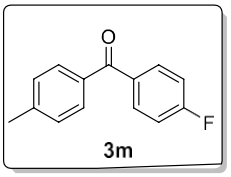

193.561
139.447
135.940
133.631
132.602
132.265
131.928
131.589
130.014
129.840
129.808
128.883
127.490
127.003
125.669
125.633
125.596
124.289
121.576
118.863
77.347
77.029
76.712

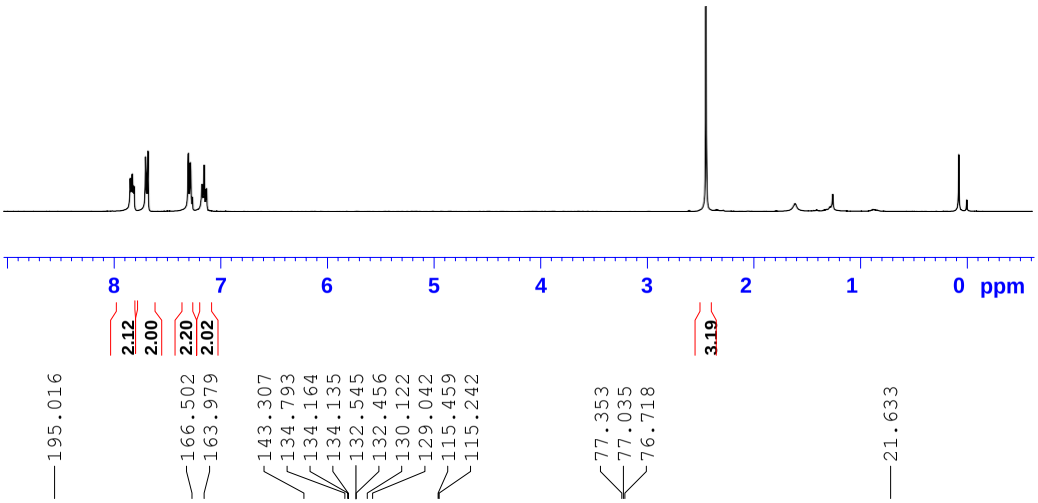

200
180
160
140
120
100
80
60
40
20
0
ppm


7.743
7.723
7.698
7.678
7.460
7.440
7.296
7.277
7.262
2.443
O
Cl
3l
8
7
6
5
4
3
2
1
0
ppm
2.00
1.80
1.92
1.80
2.87
195.222
143.522
138.597
136.255
134.566
131.338
130.172
129.095
128.559
77.347
77.030
76.712
21.659
200
180
160
140
120
100
80
60
40
20
ppm

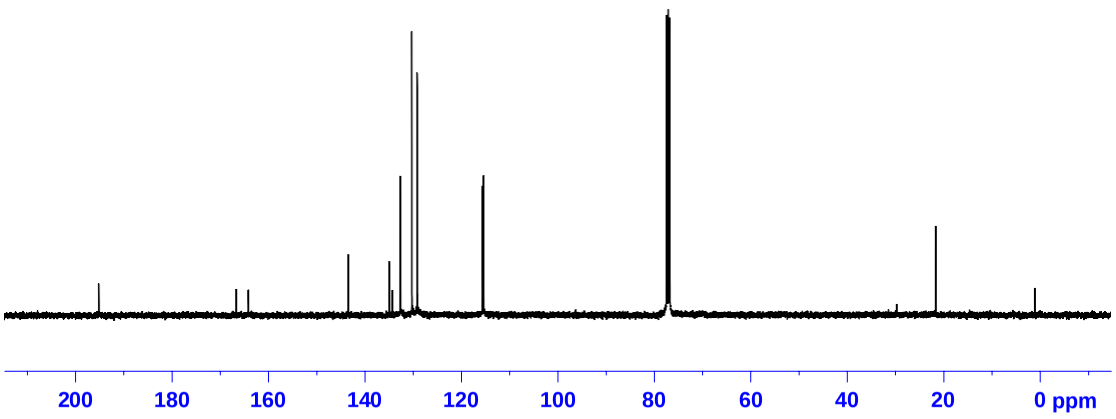

7.841
7.822
7.807
7.697
7.677
7.296
7.277
7.260
7.170
7.149
7.128

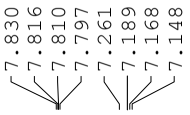

2.444

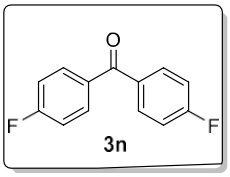

O
F
3m

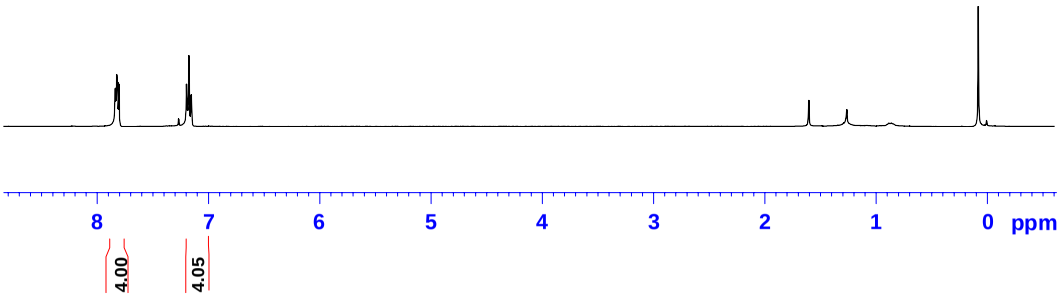

8
7
6
5
4
3
2
1
0 ppm
2.12
2.00
2.20
2.02
3.19

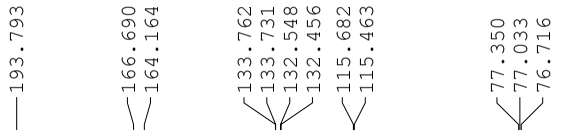
195.016
166.502
163.979
143.307
134.793
134.164
134.135
132.545
132.456
130.122
129.042
115.459
115.242
77.353
77.035
76.718
21.633

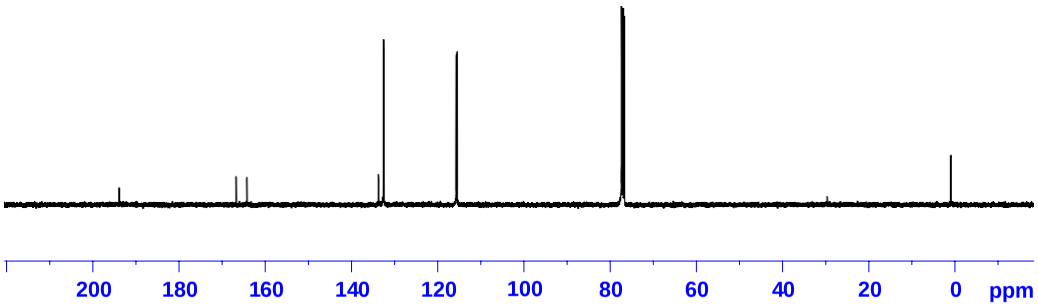

200
180
160
140
120
100
80
60
40
20
0 ppm

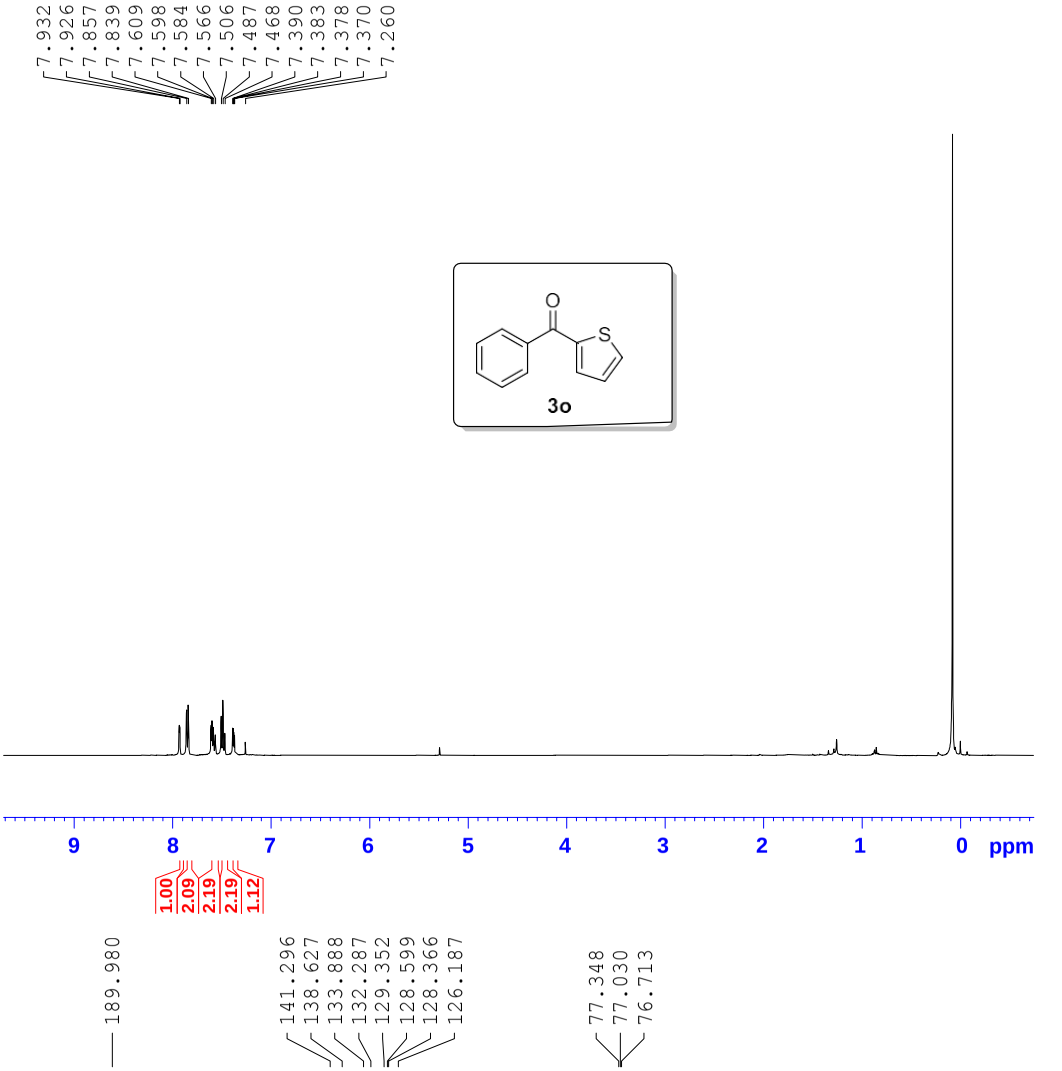

7.830
7.816
7.810
7.797
7.261
7.189
7.168
7.148

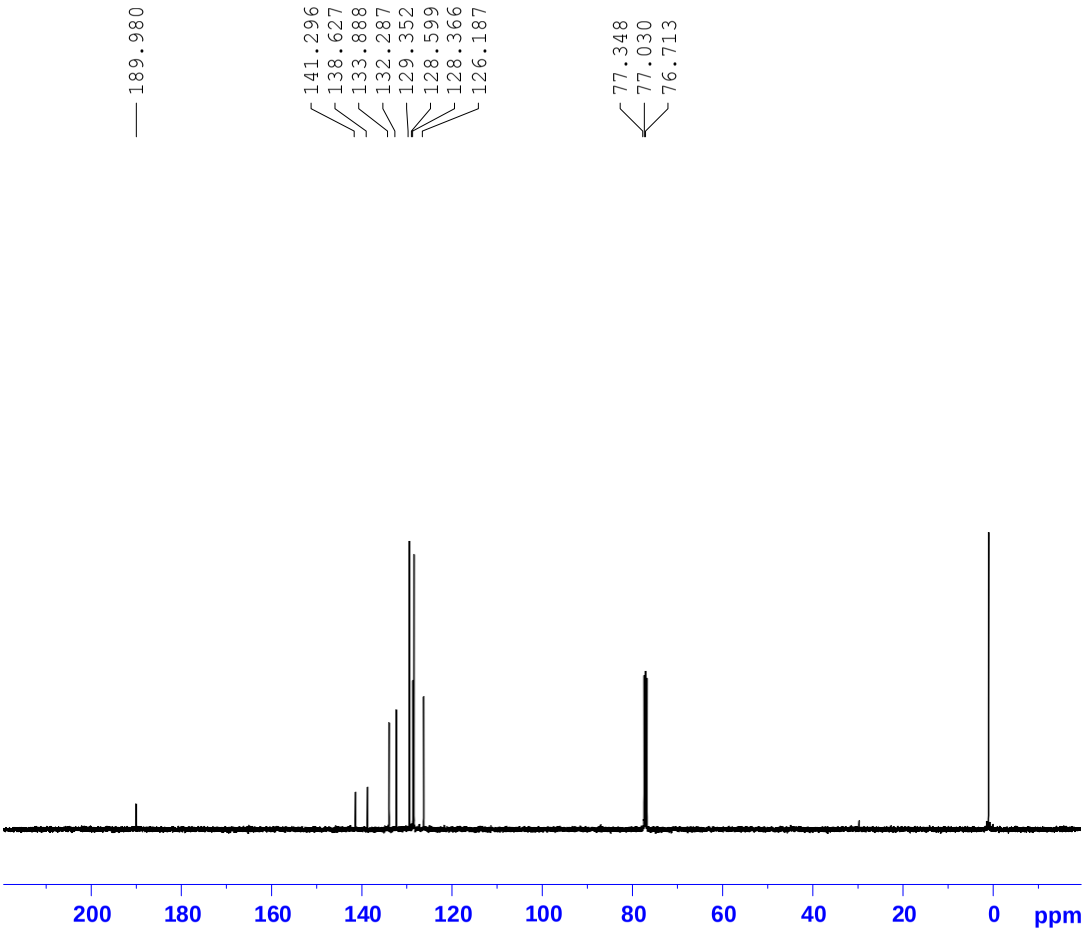

O
F
F
3n

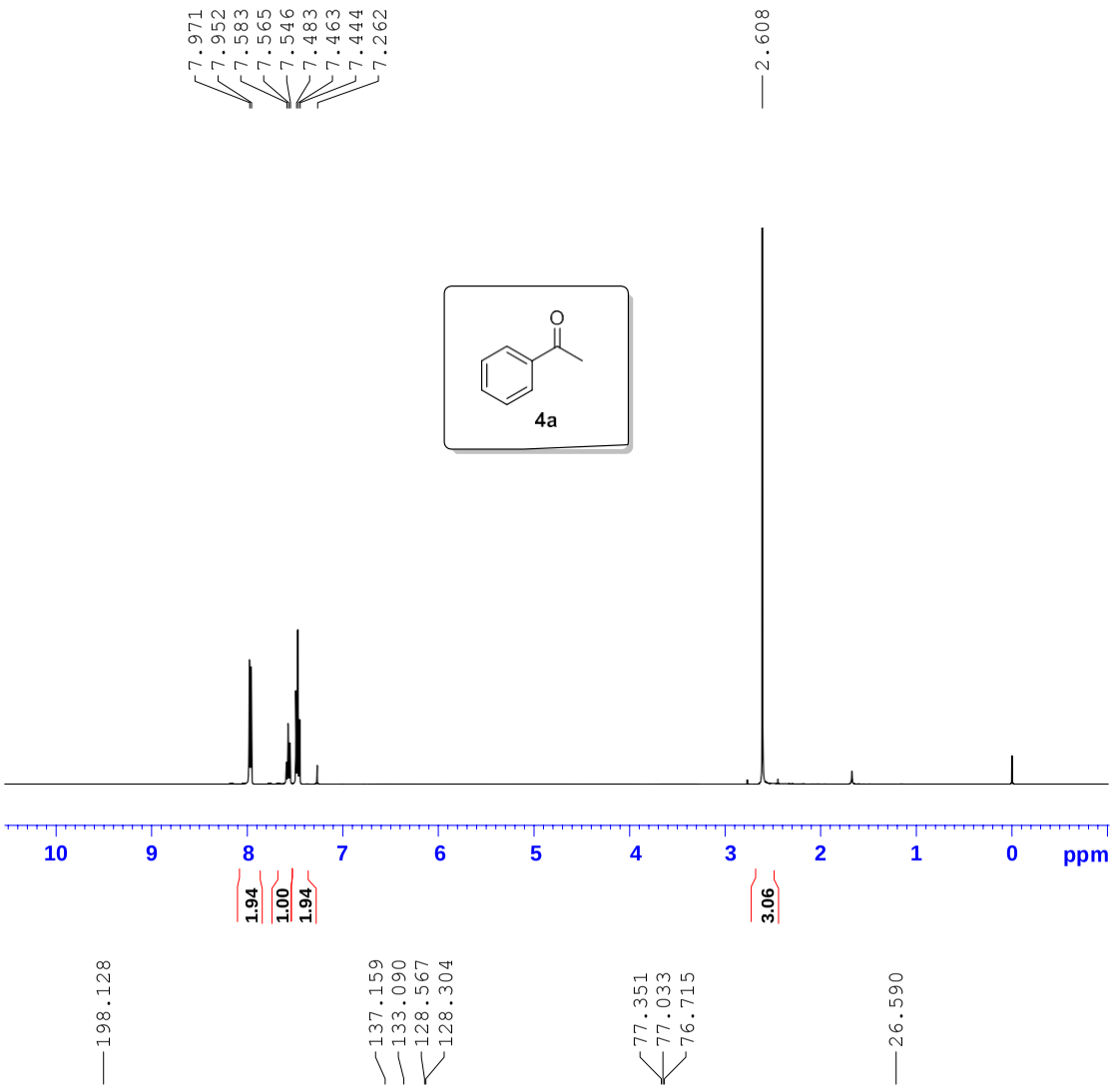

8
7
6
5
4
3
2
1
0
ppm
4.00
4.05

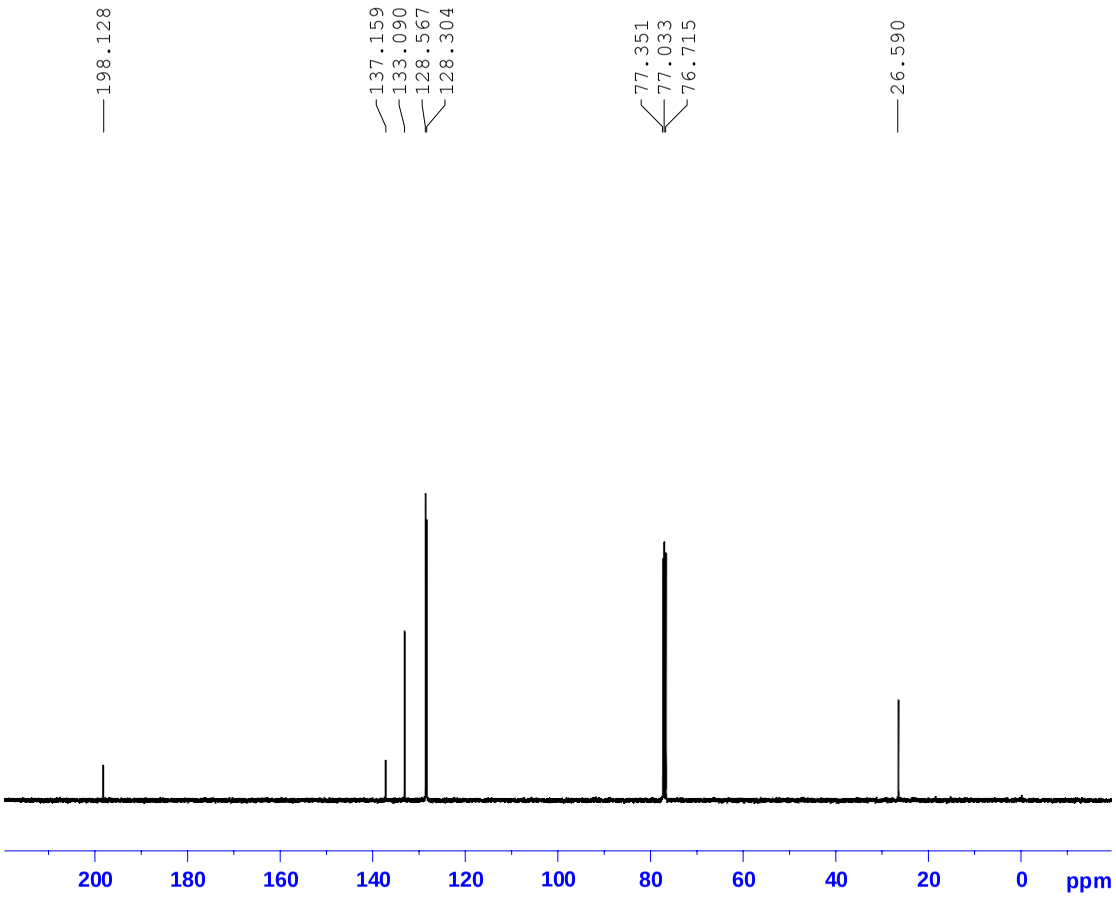

193.793
166.690
164.164
133.762
133.731
132.548
132.456
115.682
115.463
77.350
77.033
76.716

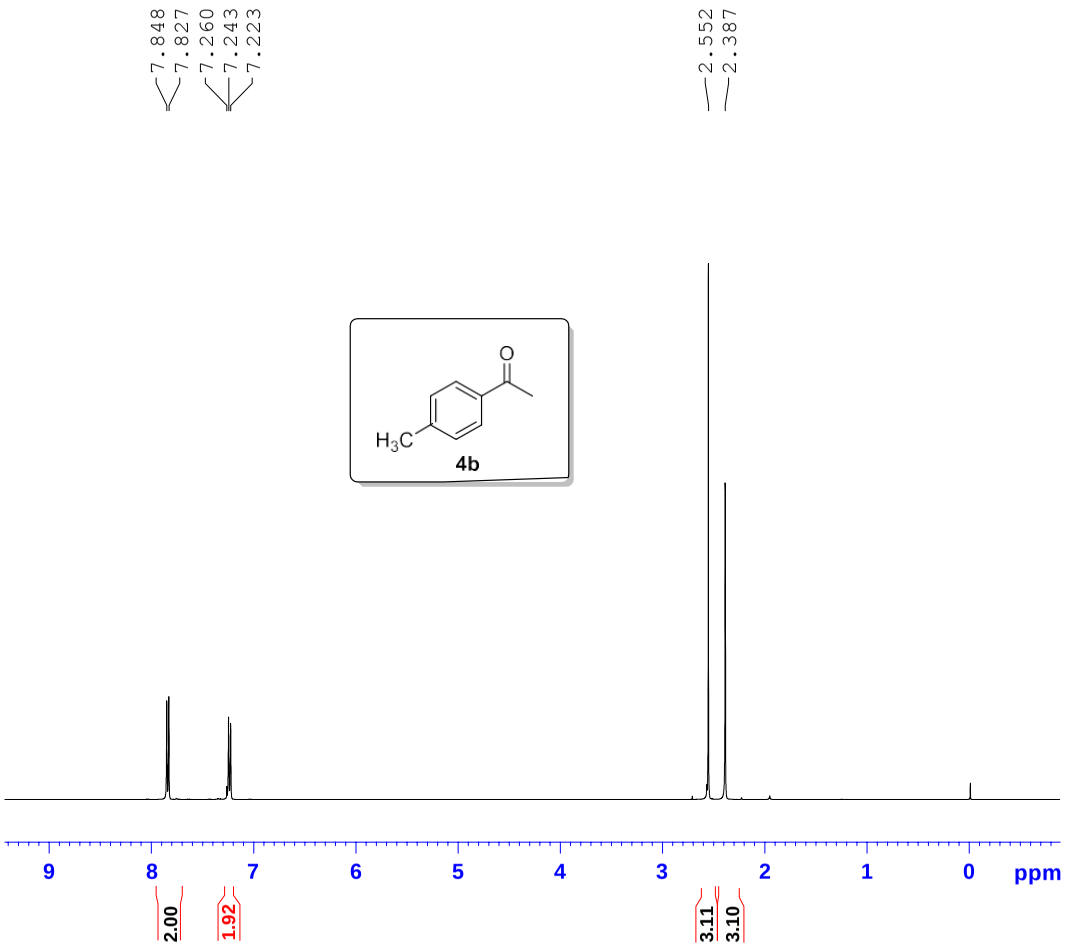

200
180
160
140
120
100
80
60
40
20
0
ppm

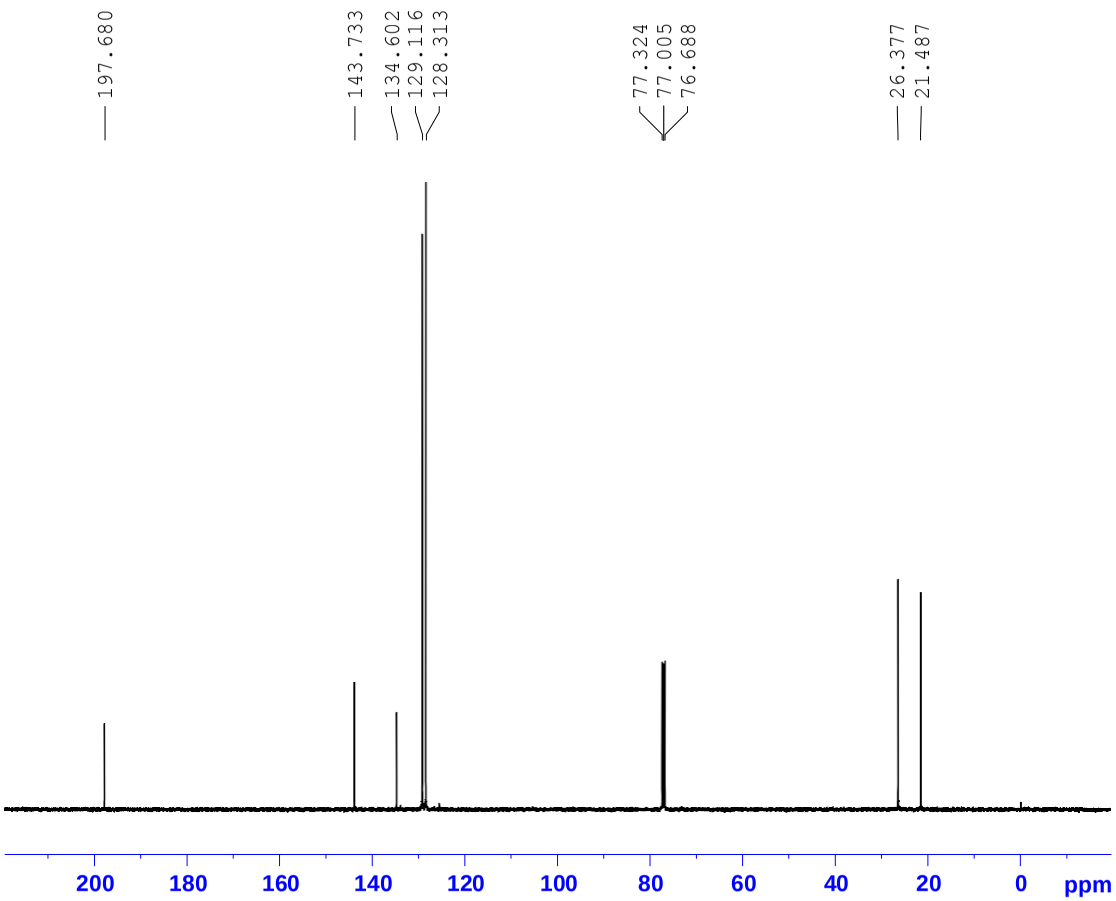

7.932
7.926
7.857
7.839
7.609
7.598
7.584
7.566
7.506
7.487
7.468
7.390
7.383
7.378
7.370
7.260
O
S
3o
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.09
2.19
2.19
1.12

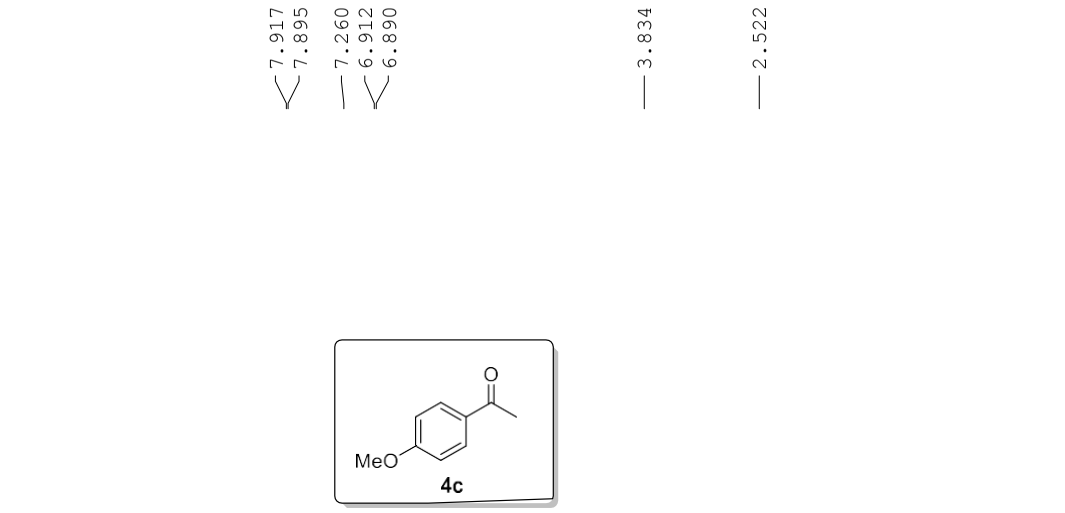

189.980
141.296
138.627
133.888
132.287
129.352
128.599
128.366
126.187
77.348
77.030
76.713
200
180
160
140
120
100
80
60
40
20
0
ppm

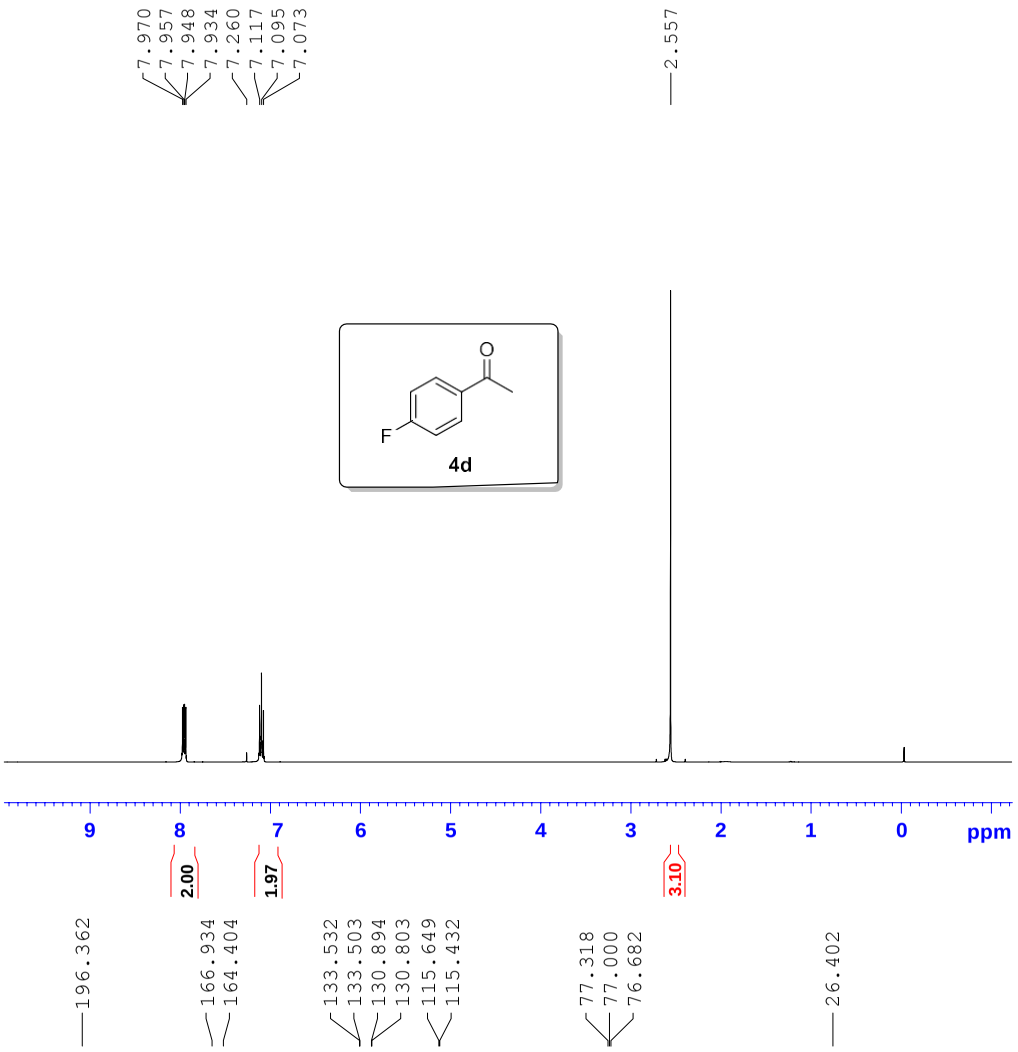

7.971
7.952
7.583
7.565
7.546
7.483
7.463
7.444
7.262
2.608
4a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.00
1.94
3.06

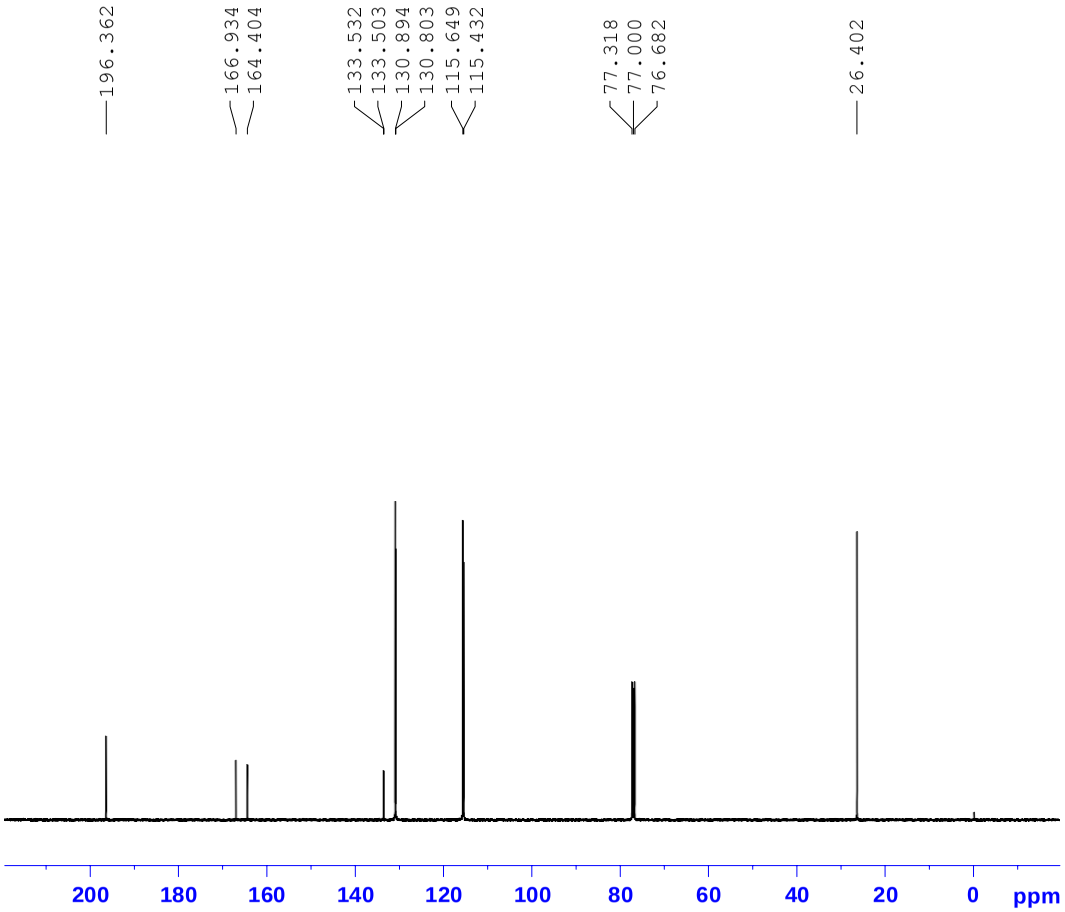

198.128
137.159
133.090
128.567
128.304
77.351
77.033
76.715
26.590
200
180
160
140
120
100
80
60
40
20
0
ppm

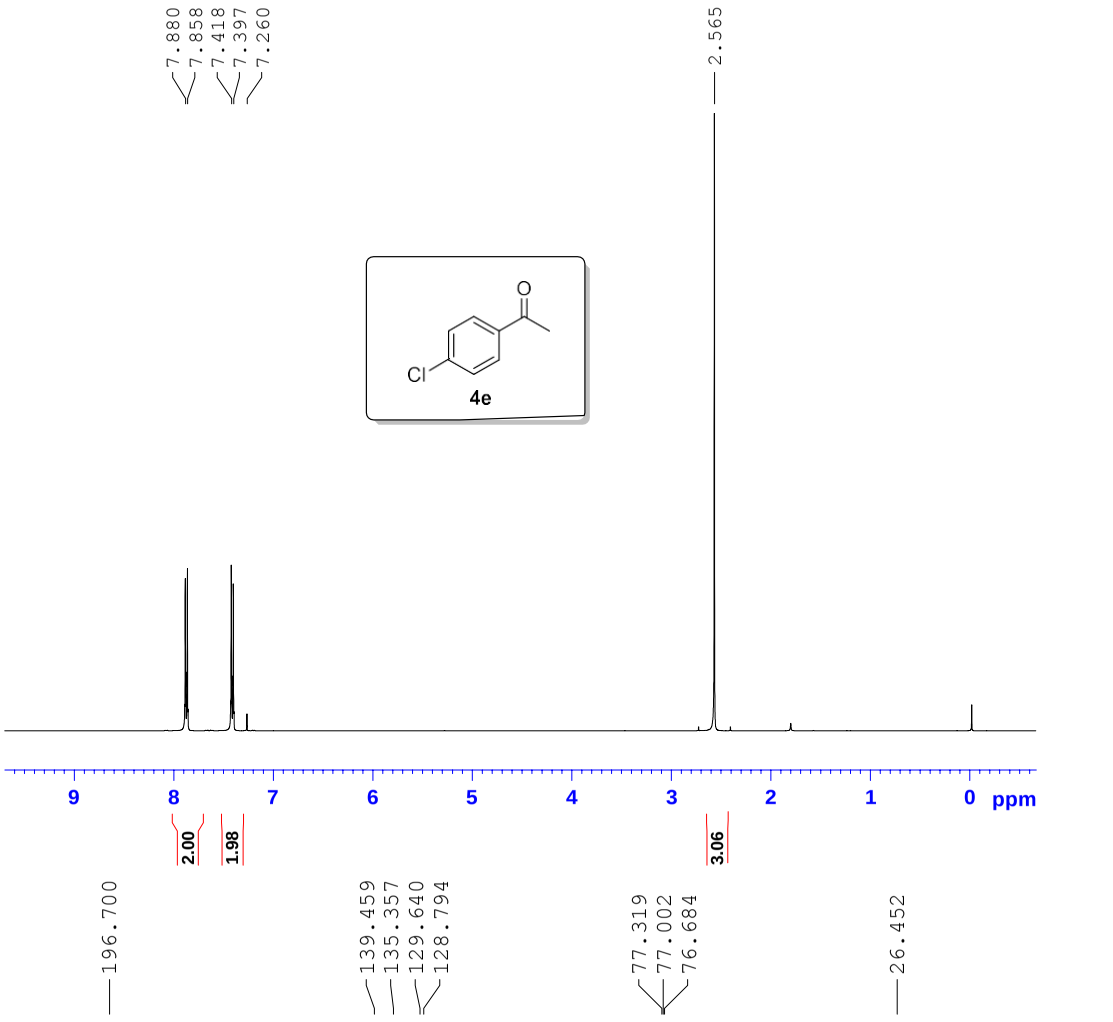

7.848
7.827
7.260
7.243
7.223
2.552
2.387
O
H3C
4b
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.92
3.11
3.10

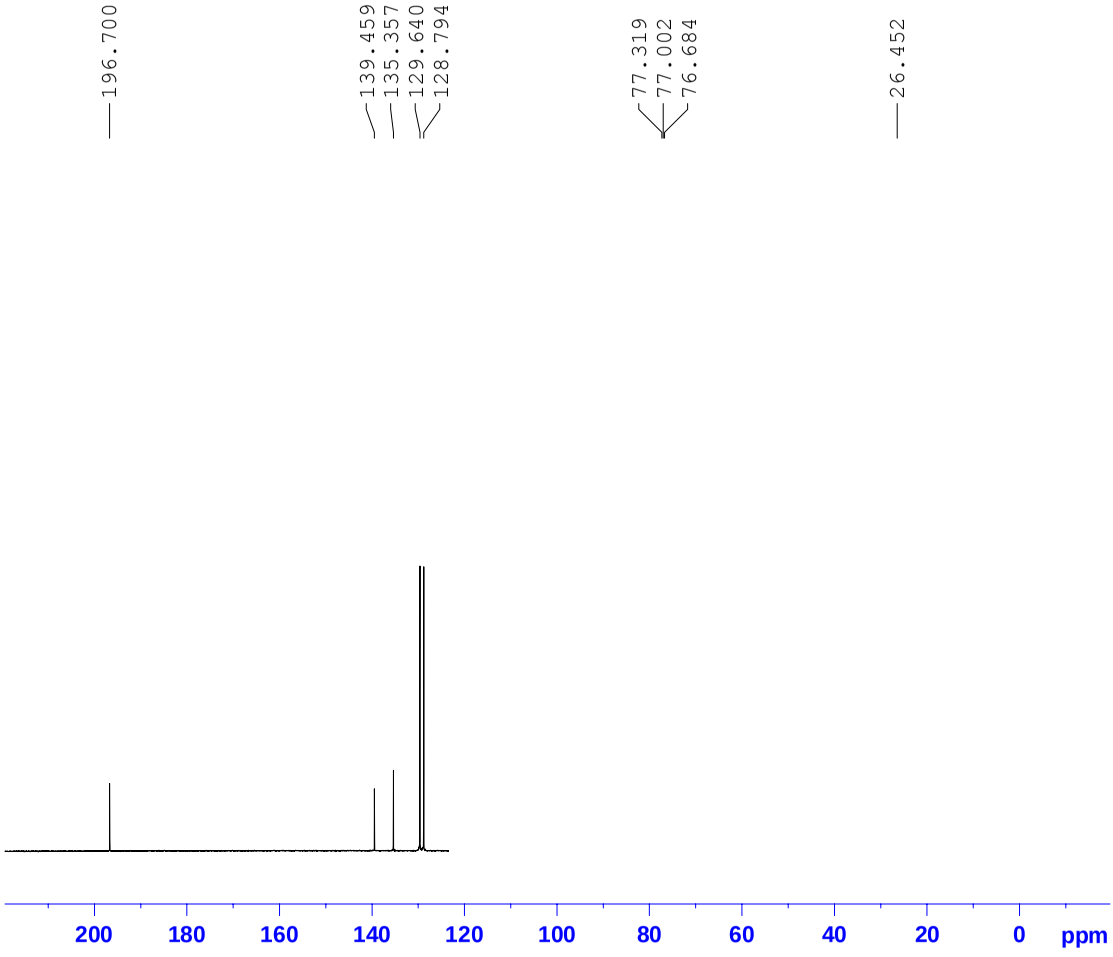

197.680
143.733
134.602
129.116
128.313
77.324
77.005
76.688
26.377
21.487
200
180
160
140
120
100
80
60
40
20
0
ppm

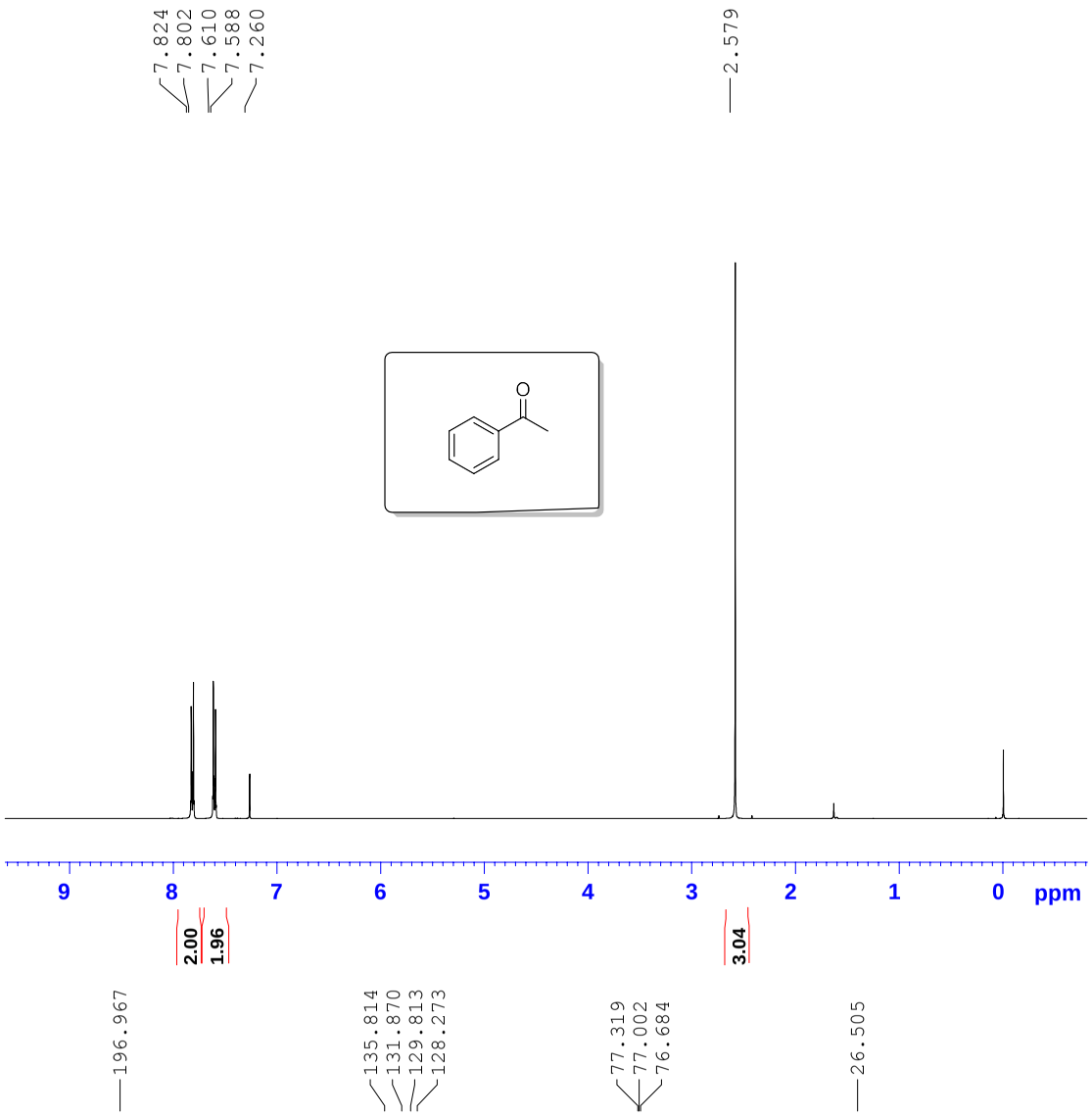

7.917
7.895
7.260
6.912
6.890
3.834
2.522
O
MeO
4c
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
3.07
3.15
196.661
163.389
130.476
113.575
77.323
77.005
76.688
55.344
26.210
200
180
160
140
120
100
80
60
40
20
0
ppm

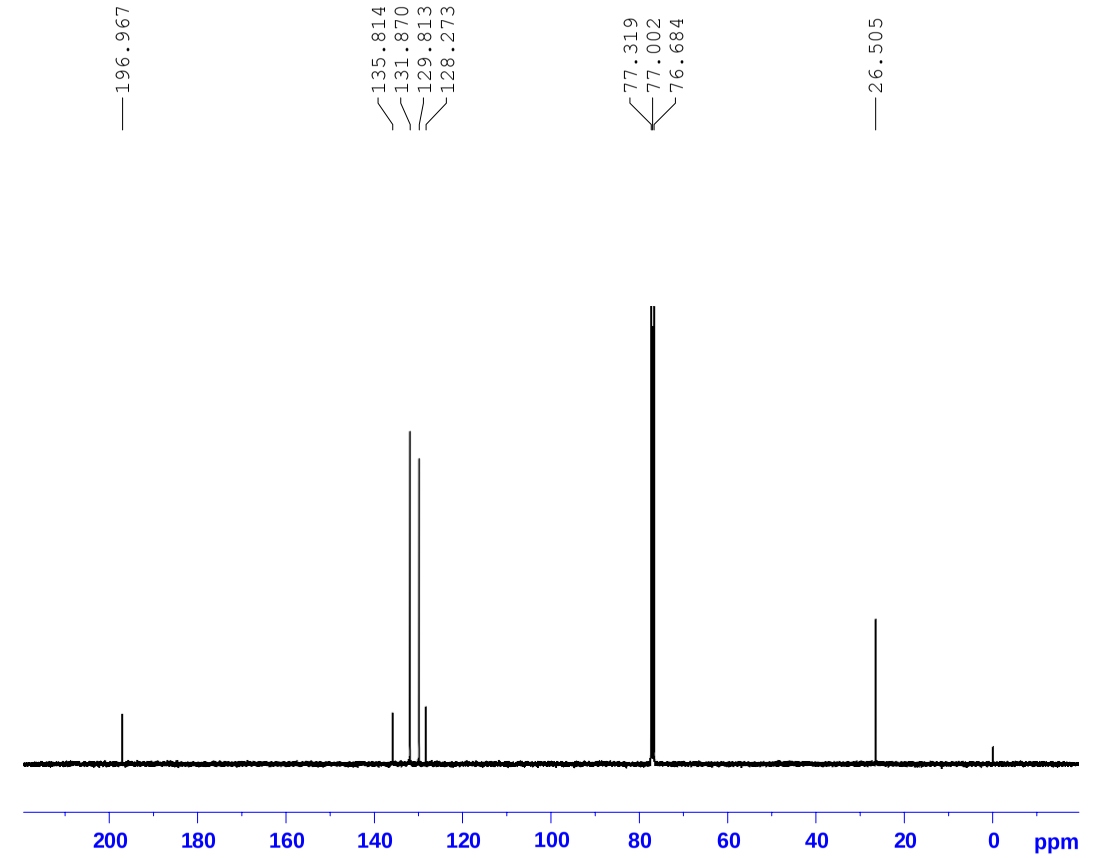

7.970
7.957
7.948
7.934
7.260
7.117
7.095
7.073
2.557
O
F
4d
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.97
3.10

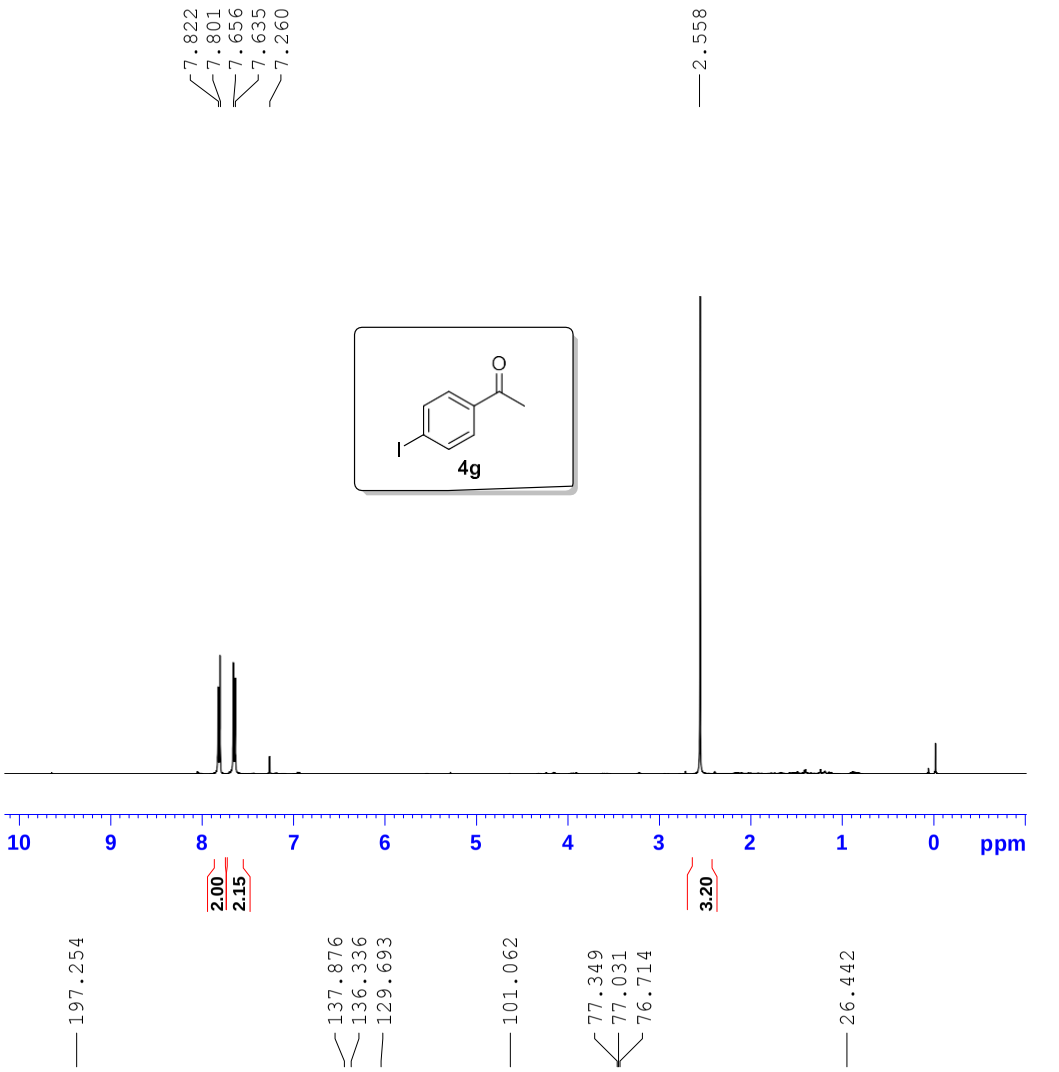

196.362
166.934
164.404
133.532
133.503
130.894
130.803
115.649
115.432
77.318
77.000
76.682
26.402
200
180
160
140
120
100
80
60
40
20
0
ppm

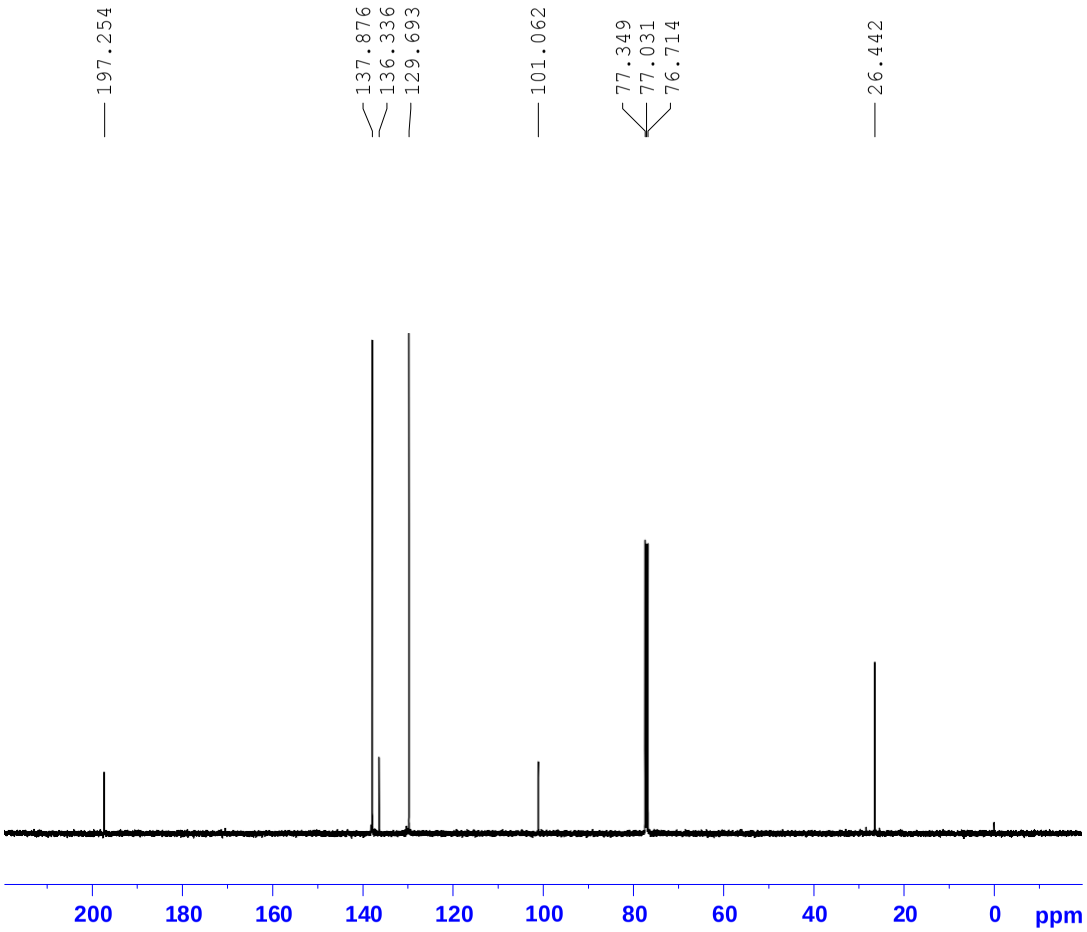

7.880
7.858
7.418
7.397
7.260
2.565
O
Cl
4e
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.98
3.06

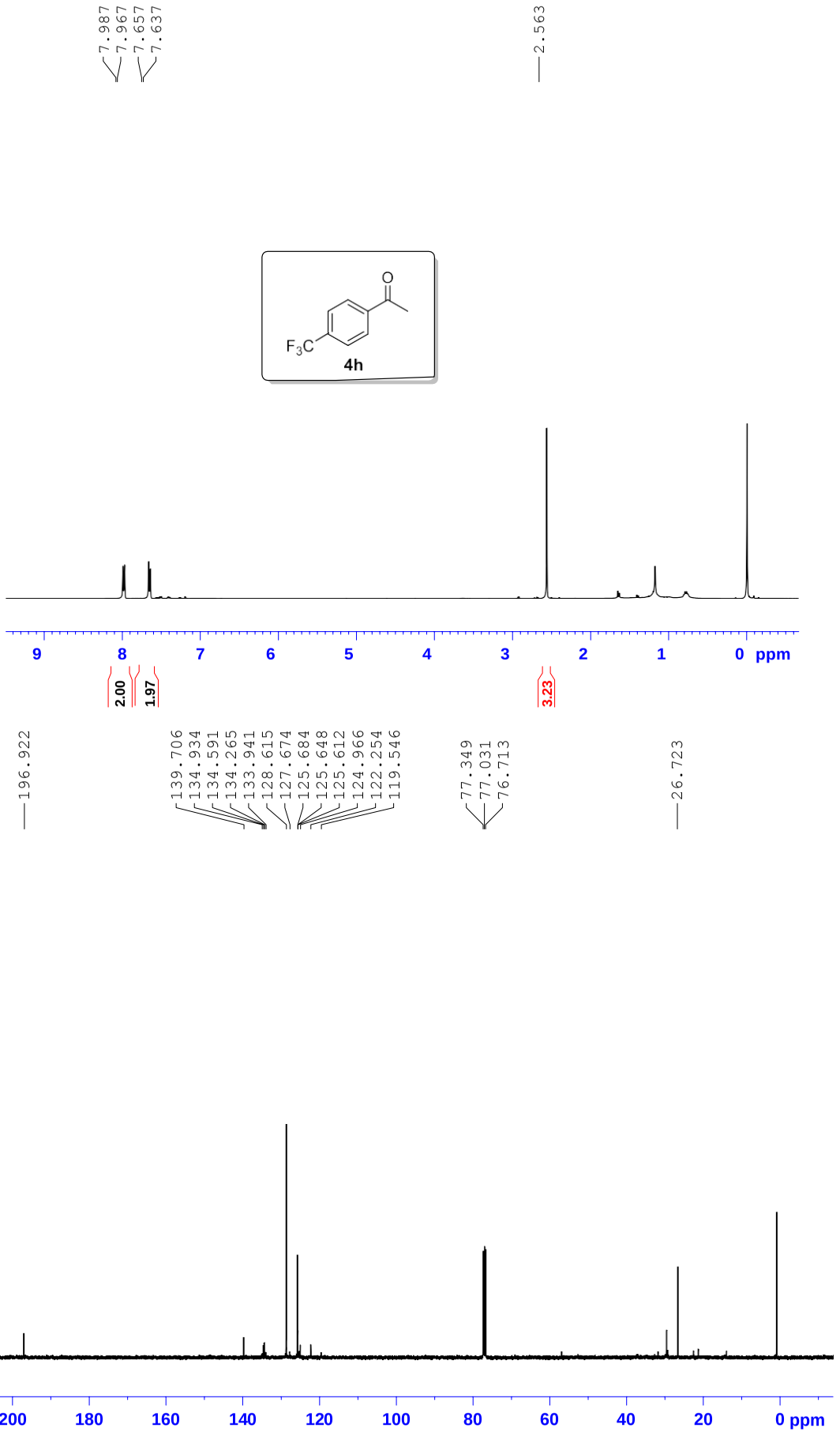

196.700
139.459
135.357
129.640
128.794
77.319
77.002
76.684
26.452
200
180
160
140
120
100
80
60
40
20
0
ppm

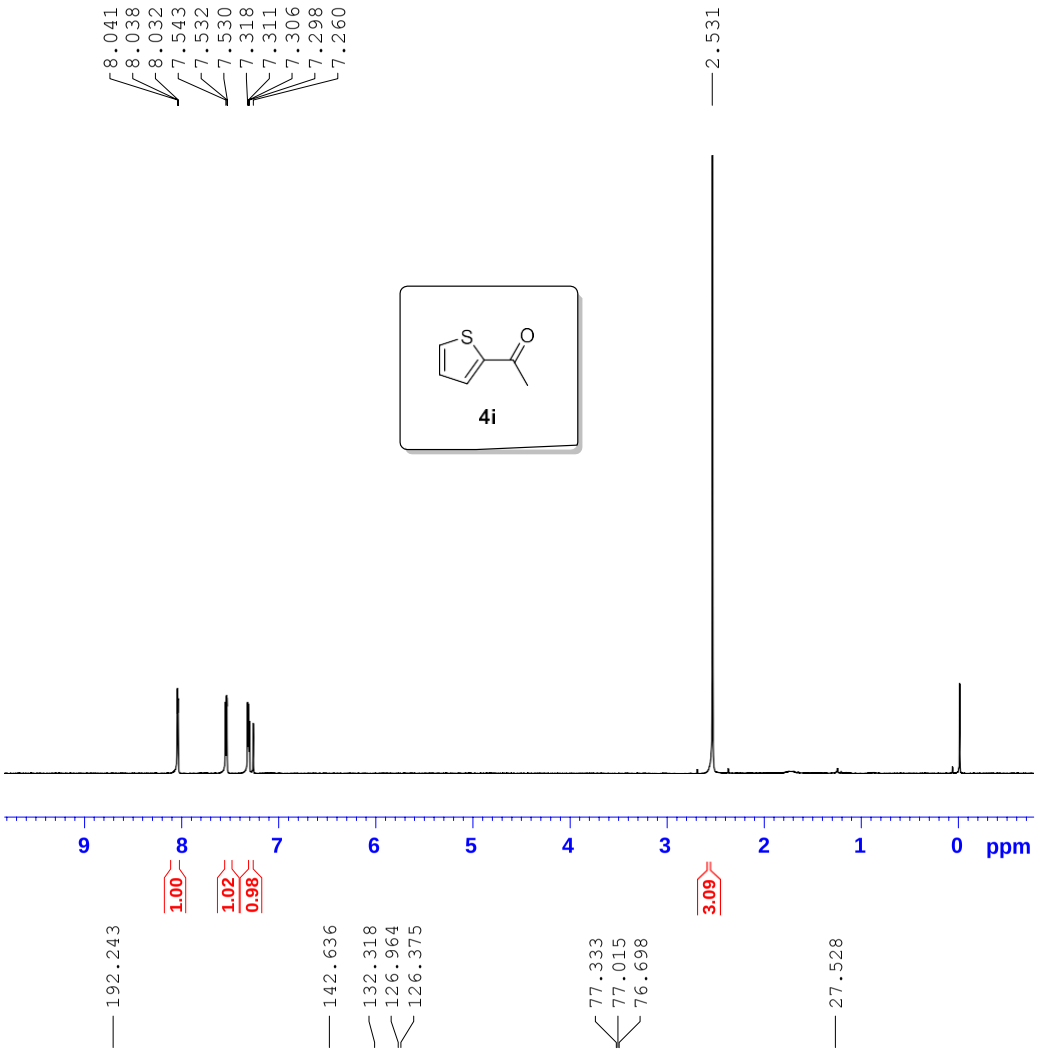

7.824
7.802
7.610
7.588
7.260
2.579
O
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.96
3.04

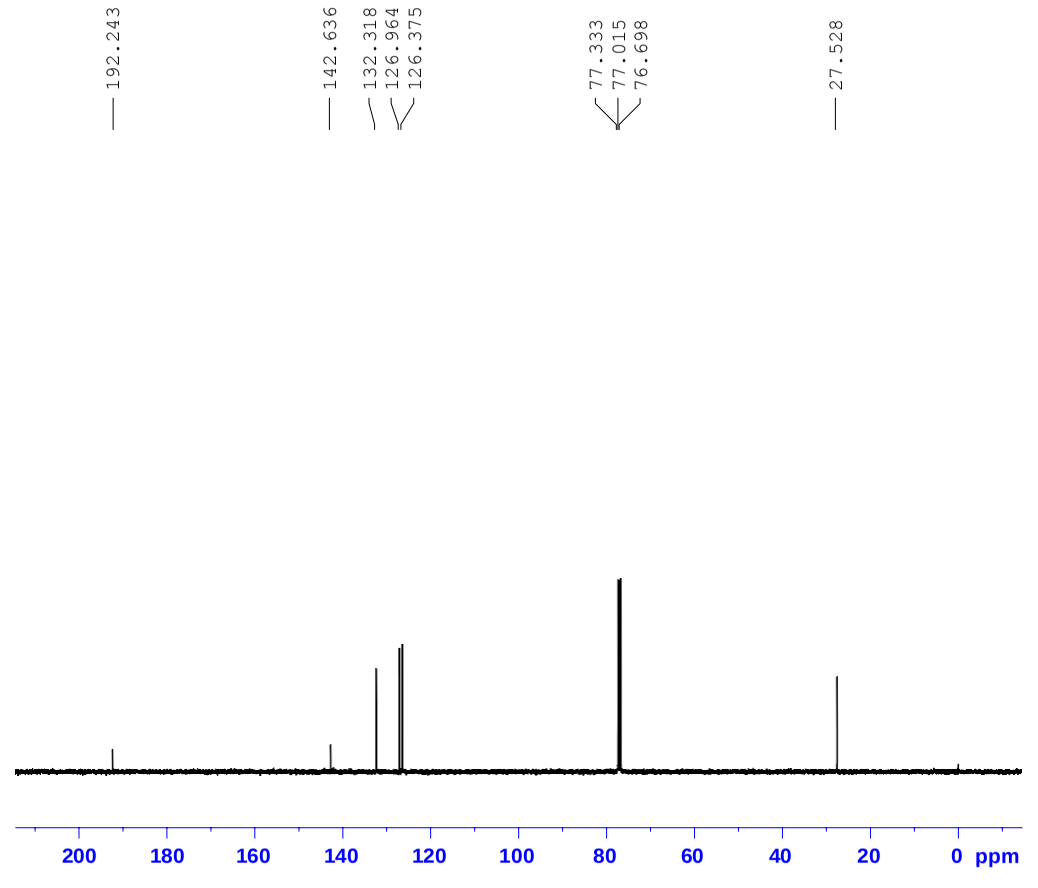

196.967
135.814
131.870
129.813
128.273
77.319
77.002
76.684
26.505
200
180
160
140
120
100
80
60
40
20
0
ppm

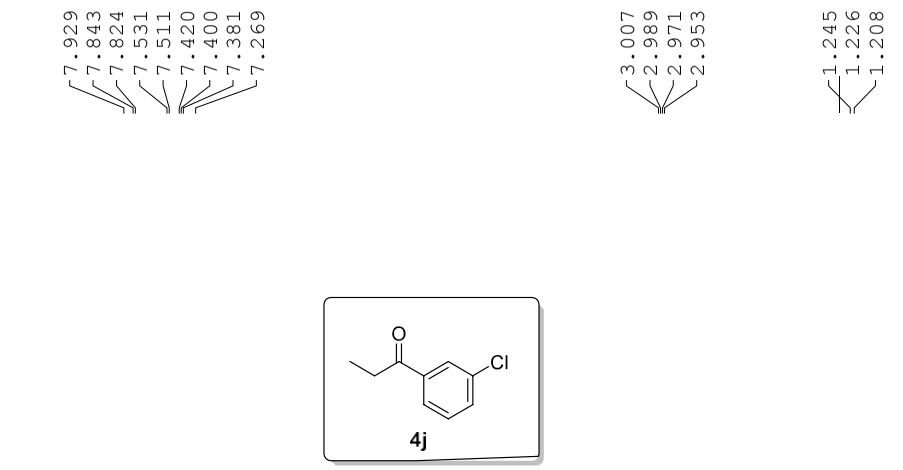

7.822
7.801
7.656
7.635
7.260
2.558
O
I
4g
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.15
3.20


197.254
137.876
136.336
129.693
101.062
77.349
77.031
76.714
26.442
200
180
160
140
120
100
80
60
40
20
0
ppm

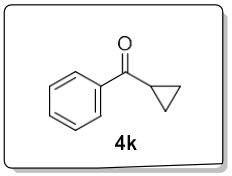

7.987
7.967
7.657
7.637
2.563
O
F3C
4h
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.97
3.23
196.922
139.706
134.934
134.591
134.265
133.941
128.615
127.674
125.684
125.648
125.612
124.966
122.254
119.546
77.349
77.031
76.713
26.723
200
180
160
140
120
100
80
60
40
20
0 ppm

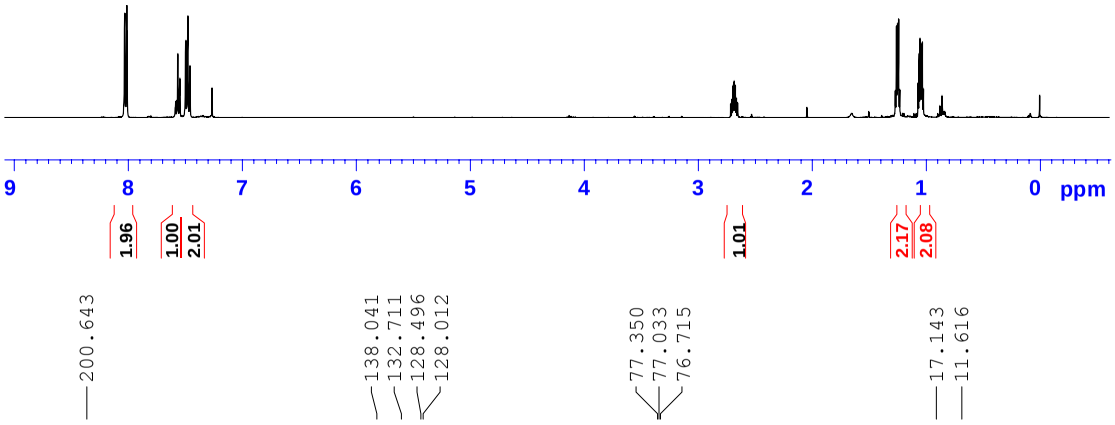

8.041
8.038
8.032
7.543
7.532
7.530
7.318
7.311
7.306
7.298
7.260
2.531
S
O
4i
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
0.98
3.09


192.243
142.636
132.318
126.964
126.375
77.333
77.015
76.698
27.528
200
180
160
140
120
100
80
60
40
20
0
ppm

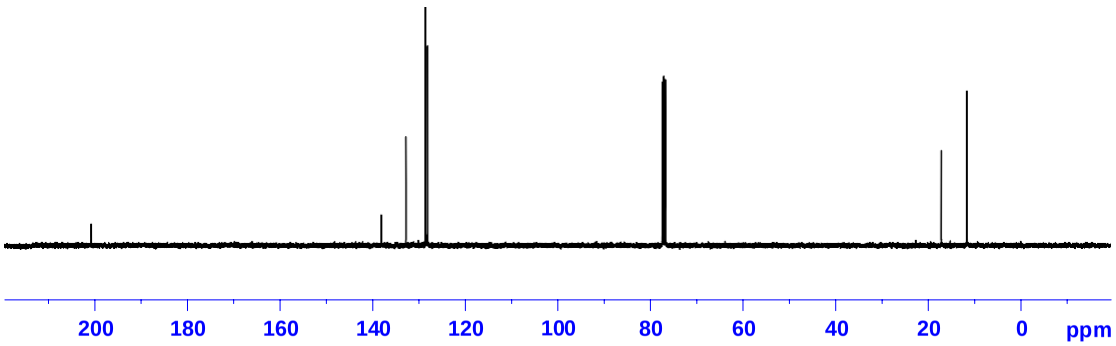

7.929
7.843
7.824
7.531
7.511
7.420
7.400
7.381
7.269
3.007
2.989
2.971
2.953
1.245
1.226
1.208
O
Cl
4j
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
0.98
1.02
2.01
3.09
199.400
138.448
134.879
132.772
129.879
128.102
126.023
77.330
77.012
76.695
31.912
8.062
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.028
8.010
8.006
7.580
7.567
7.563
7.547
7.543
7.493
7.473
7.455
7.260
2.711
2.699
2.691
2.680
2.670
2.660
2.650
1.266
1.256
1.246
1.237
1.228
1.065
1.056
1.048
1.038
1.029
1.019

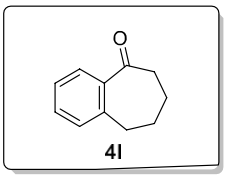

O
4k

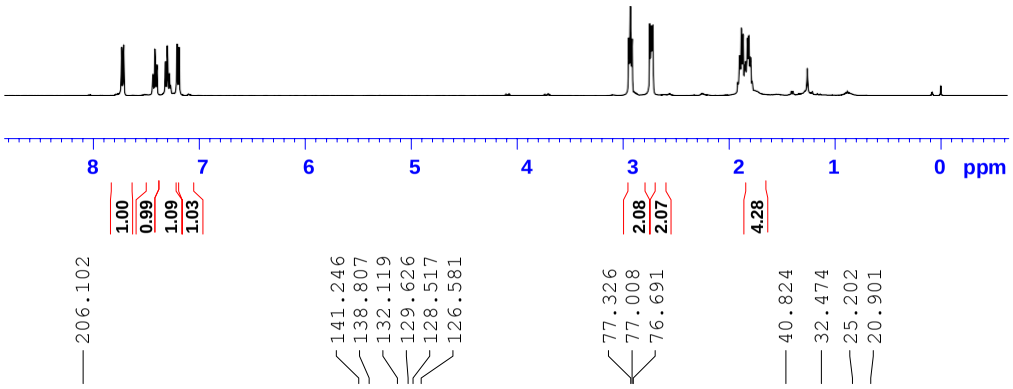

9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.00
2.01
1.01
2.17
2.08

200.643
138.041
132.711
128.496
128.012
77.350
77.033
76.715
17.143
11.616

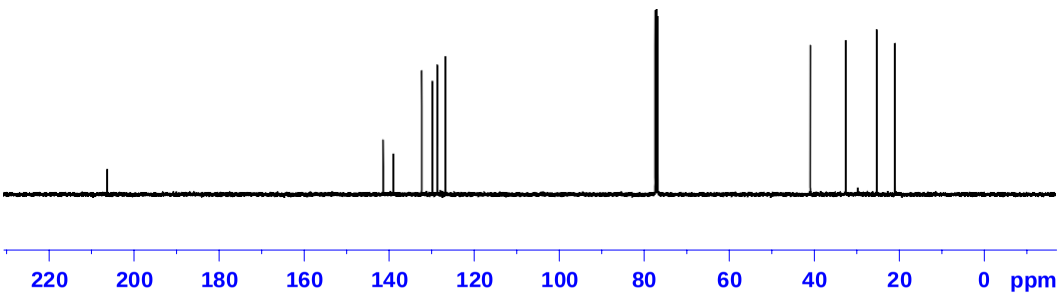

200
180
160
140
120
100
80
60
40
20
0
ppm

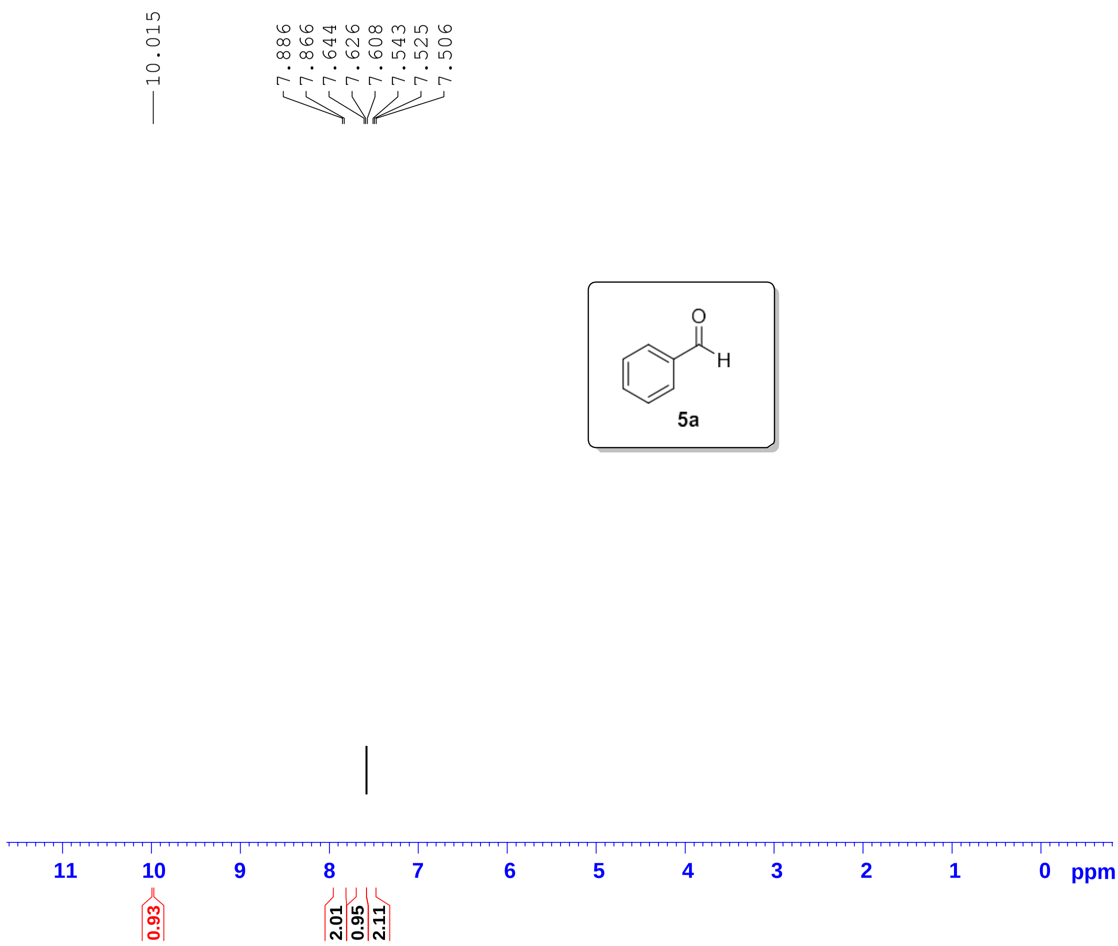

7.728
7.709
7.432
7.414
7.395
7.314
7.296
7.276
7.205
7.186
2.944
2.929
2.913
2.746
2.732
2.717
1.914
1.897
1.881
1.865
1.851
1.839
1.826
1.810
1.796
1.780


O
4l

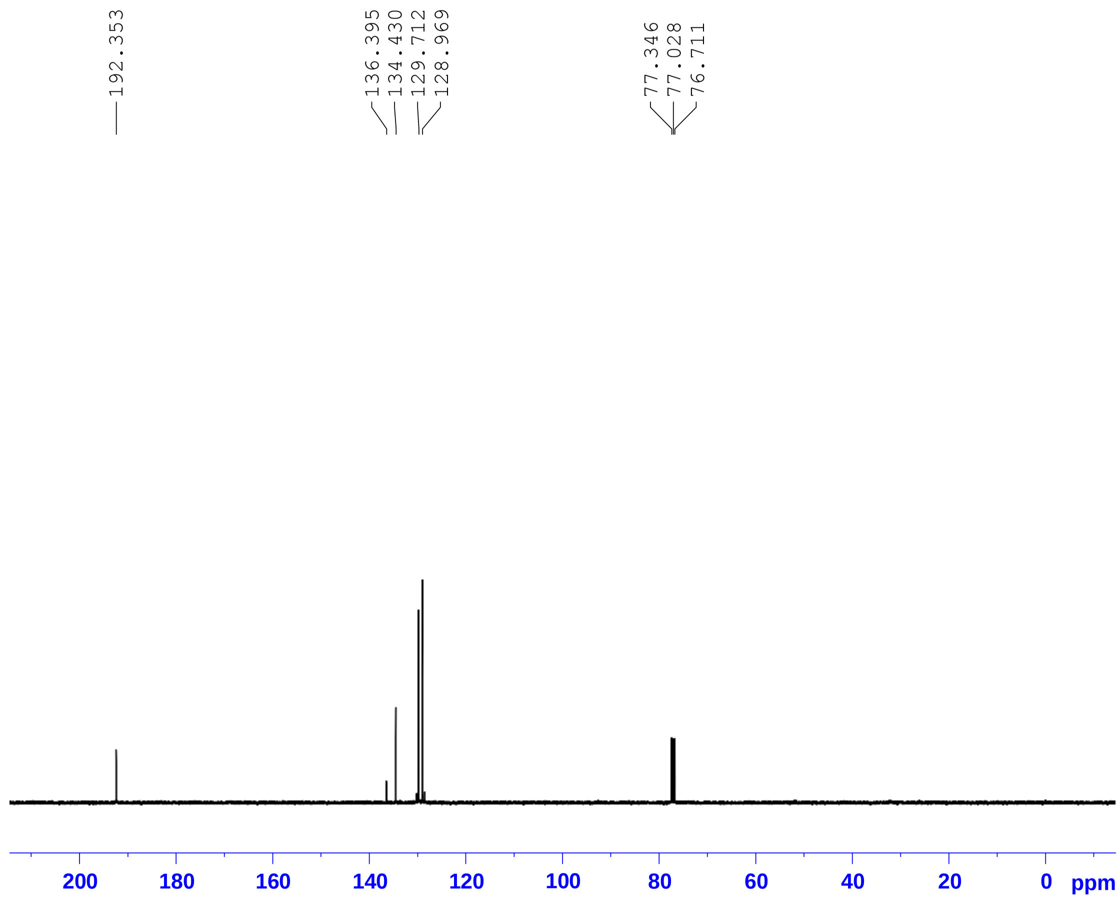

8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.09
1.03
2.08
2.07
4.28

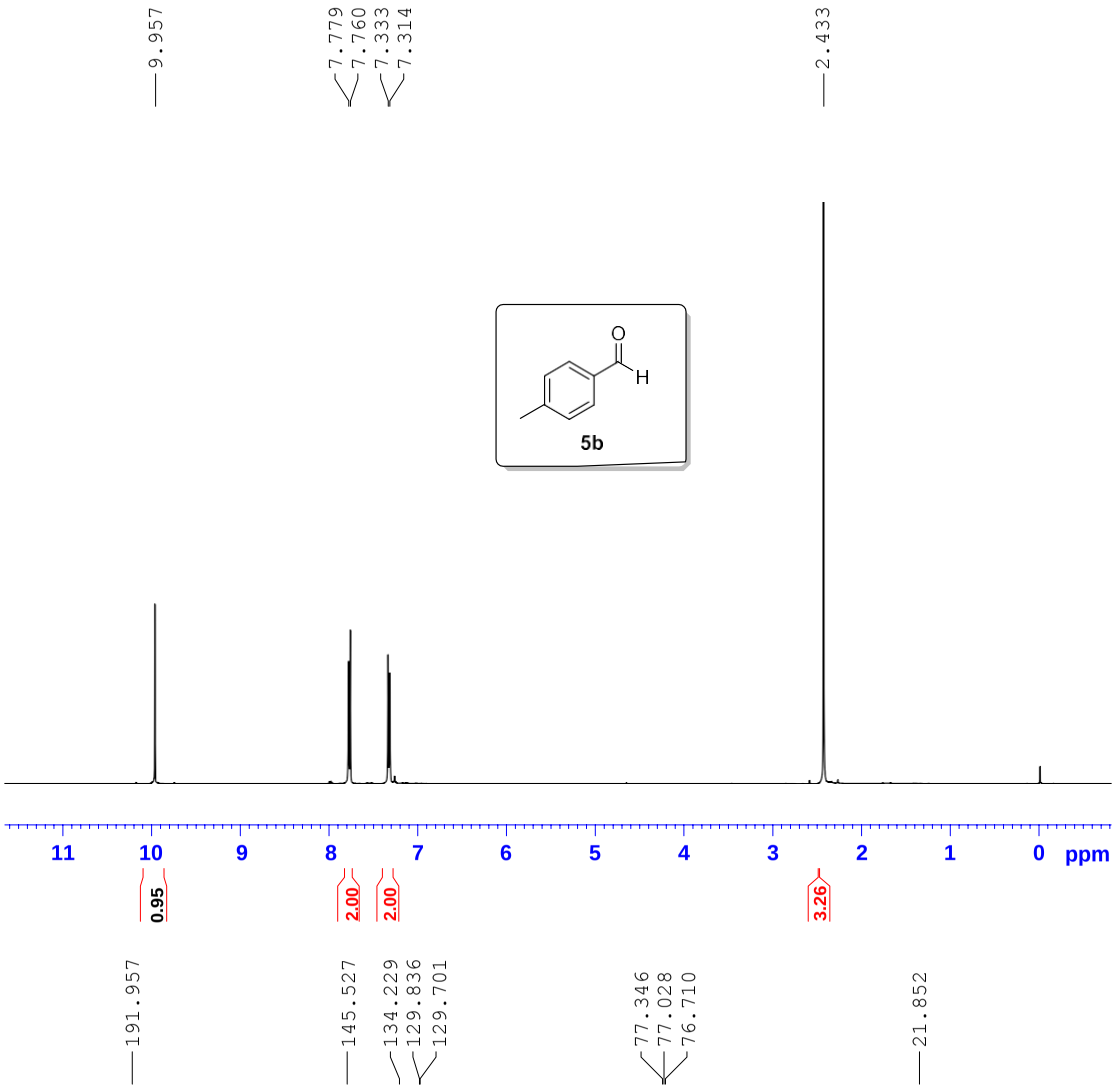
206.102
141.246
138.807
132.119
129.626
128.517
126.581
77.326
77.008
76.691
40.824
32.474
25.202
20.901

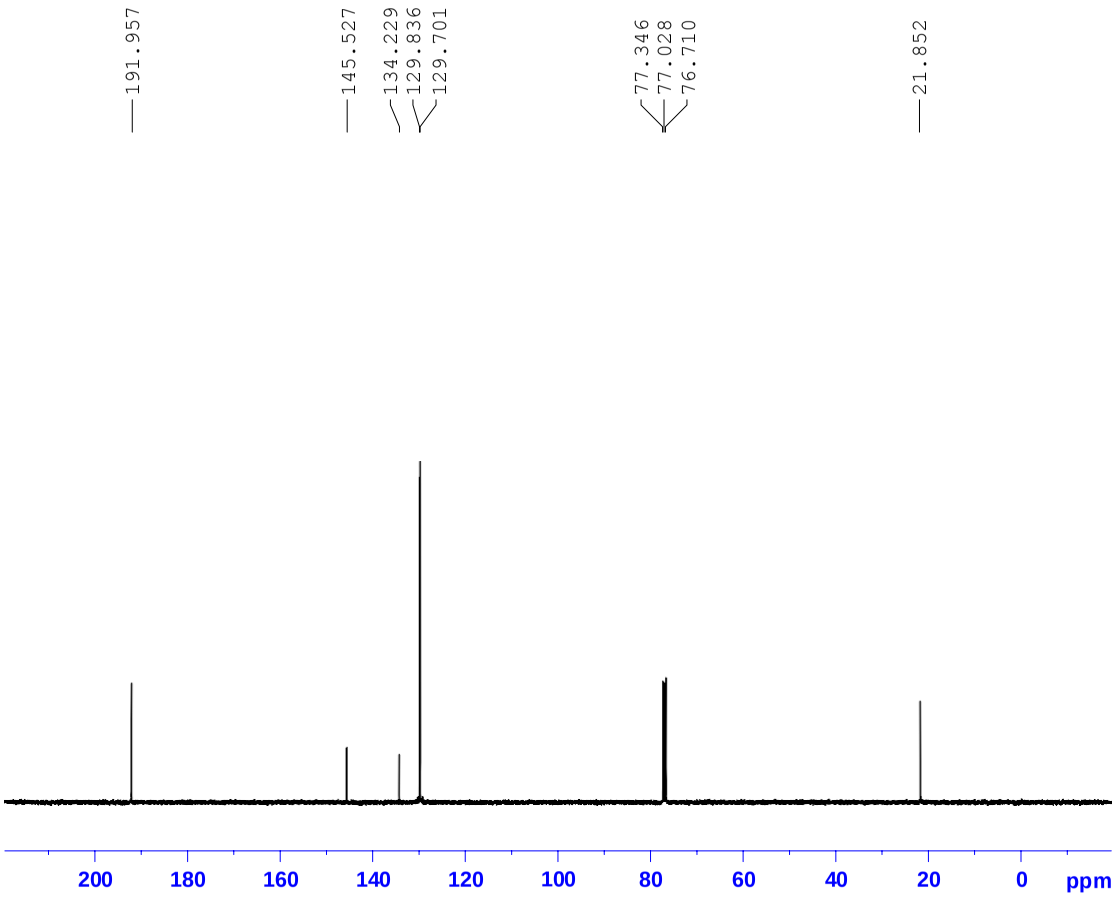

220
200
180
160
140
120
100
80
60
40
20
0
ppm

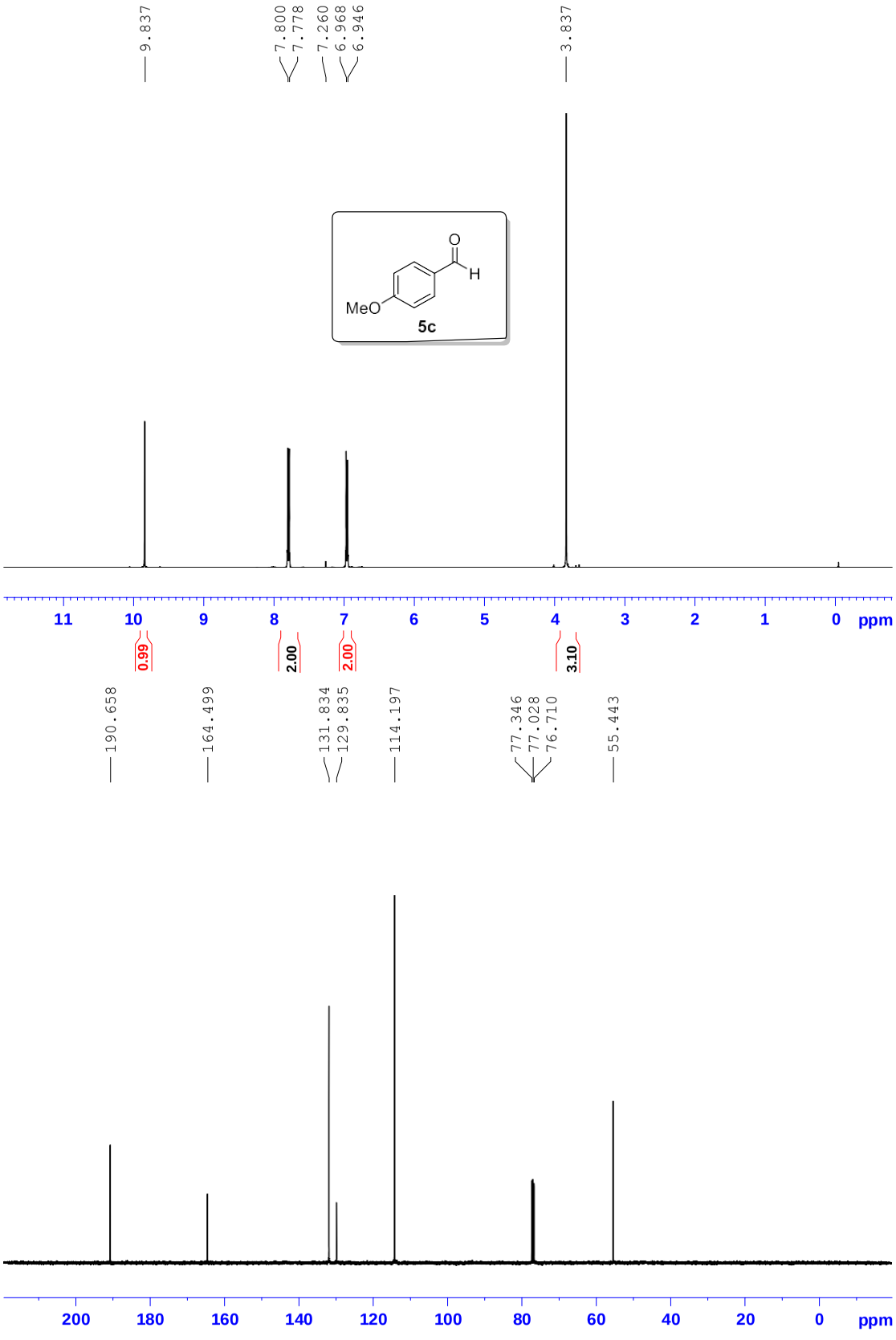

10.015
7.886
7.866
7.644
7.626
7.608
7.543
7.525
7.506
0.93
2.01
0.95
2.11
11
10
9
8
7
6
5
4
3
2
1
0
ppm

5a

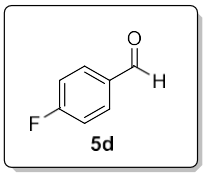

192.353
136.395
134.430
129.712
128.969
77.346
77.028
76.711
200
180
160
140
120
100
80
60
40
20
0
ppm

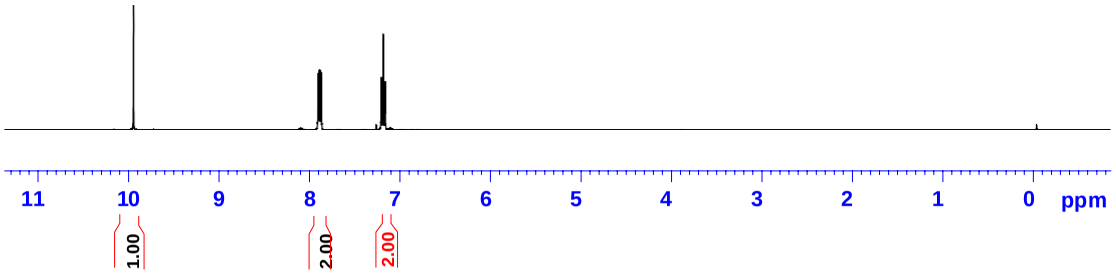

9.957
7.779
7.760
7.333
7.314
2.433
O
H
5b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.95
2.00
2.00
3.26

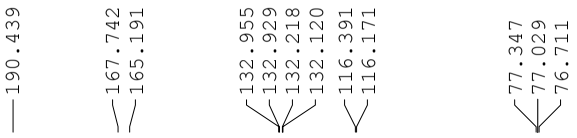

191.957
145.527
134.229
129.836
129.701
77.346
77.028
76.710
21.852
200
180
160
140
120
100
80
60
40
20
0
ppm

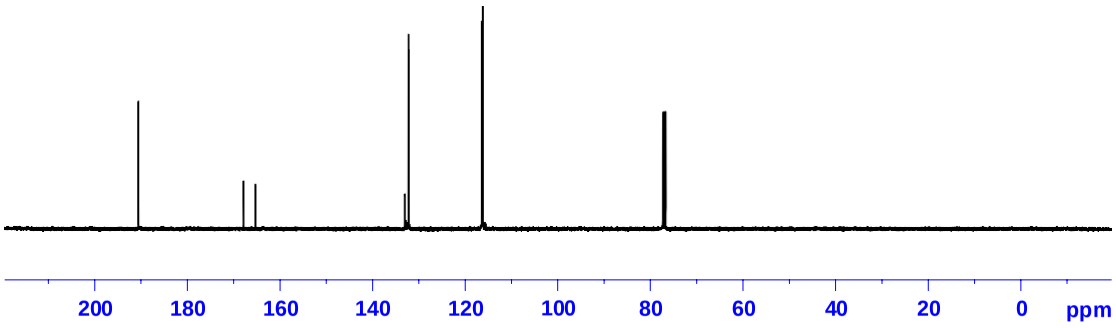

9.837
7.800
7.778
7.260
6.968
6.946
3.837
O
H
MeO
5c
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
2.00
2.00
3.10
190.658
164.499
131.834
129.835
114.197
77.346
77.028
76.710
55.443
200
180
160
140
120
100
80
60
40
20
0
ppm

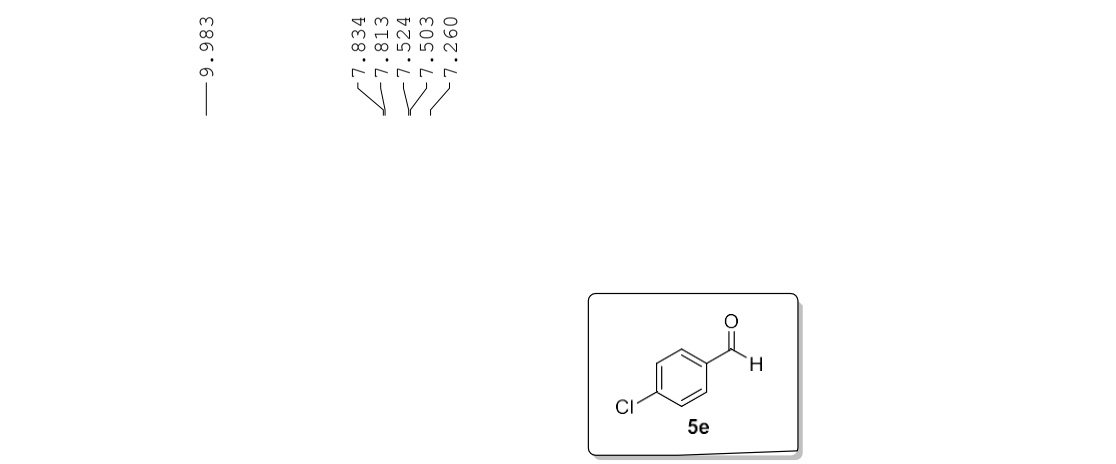

9.939
7.900
7.886
7.878
7.865
7.202
7.181
7.160

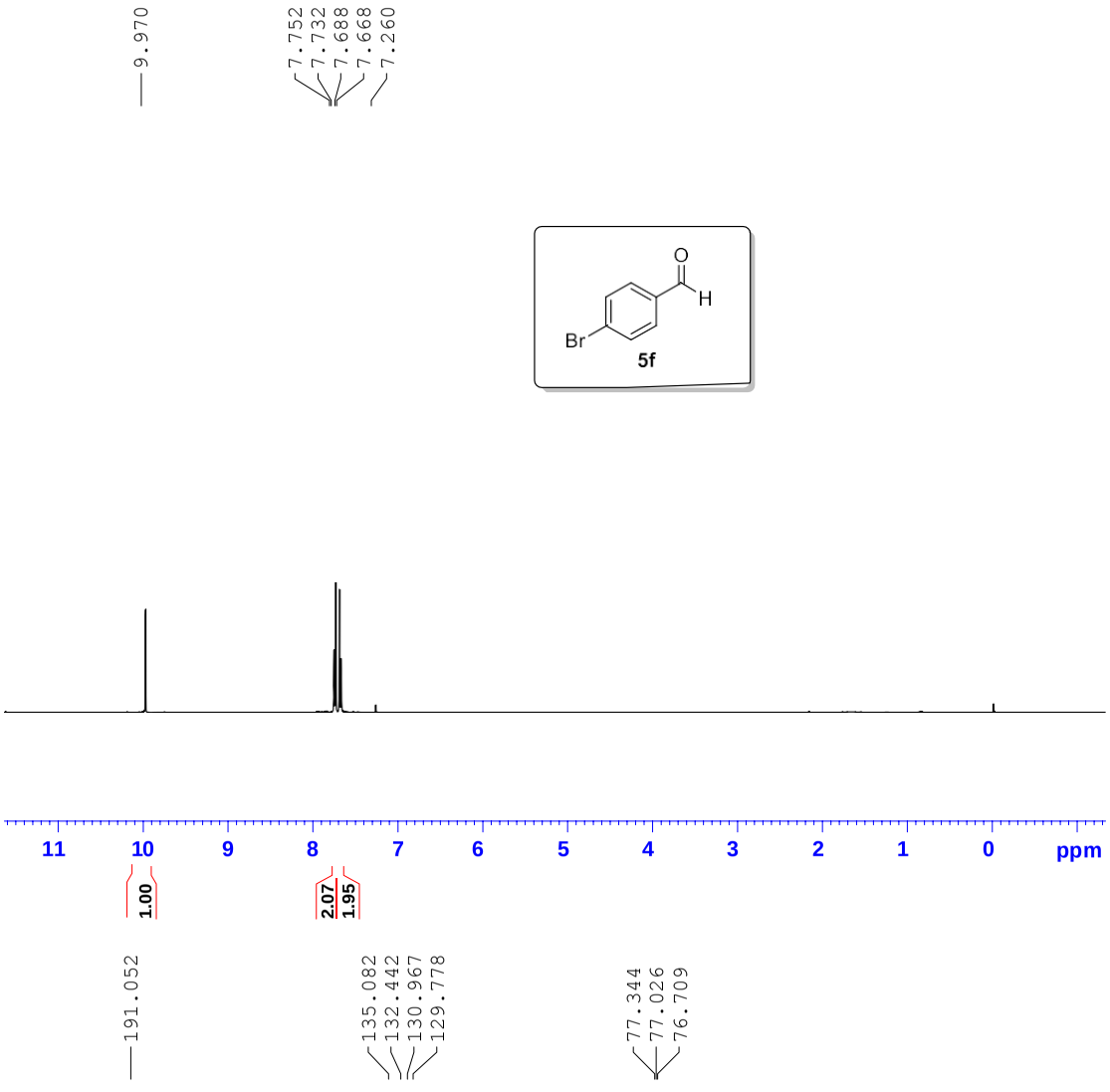

O
H
F
5d

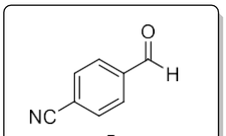

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.00
2.00


190.439
167.742
165.191
132.955
132.929
132.218
132.120
116.391
116.171
77.347
77.029
76.711

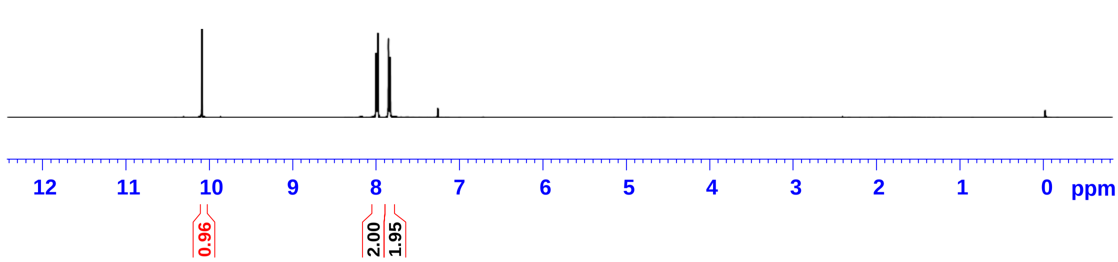

200
180
160
140
120
100
80
60
40
20
0
ppm

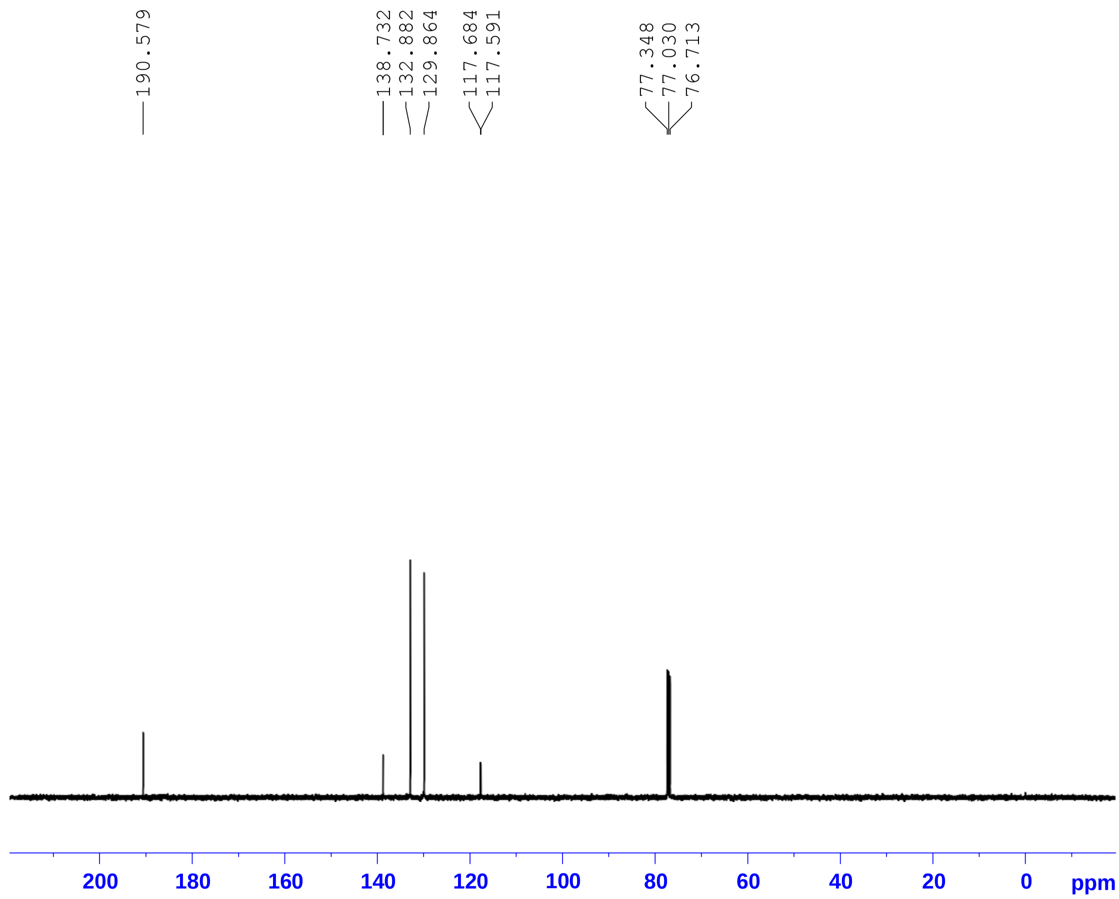

9.983
7.834
7.813
7.524
7.503
7.260
O
H
Cl
5e
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
2.00
190.827
140.960
134.730
130.898
129.459
77.334
77.016
76.699
200
180
160
140
120
100
80
60
40
20
0
ppm

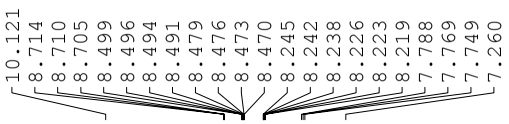

9.970
7.752
7.732
7.688
7.668
7.260
O
H
Br
5f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.07
1.95
191.052
135.082
132.442
130.967
129.778
77.344
77.026
76.709
200
180
160
140
120
100
80
60
40
20
0
ppm

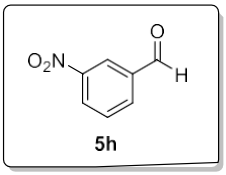

NC
O
H

5g

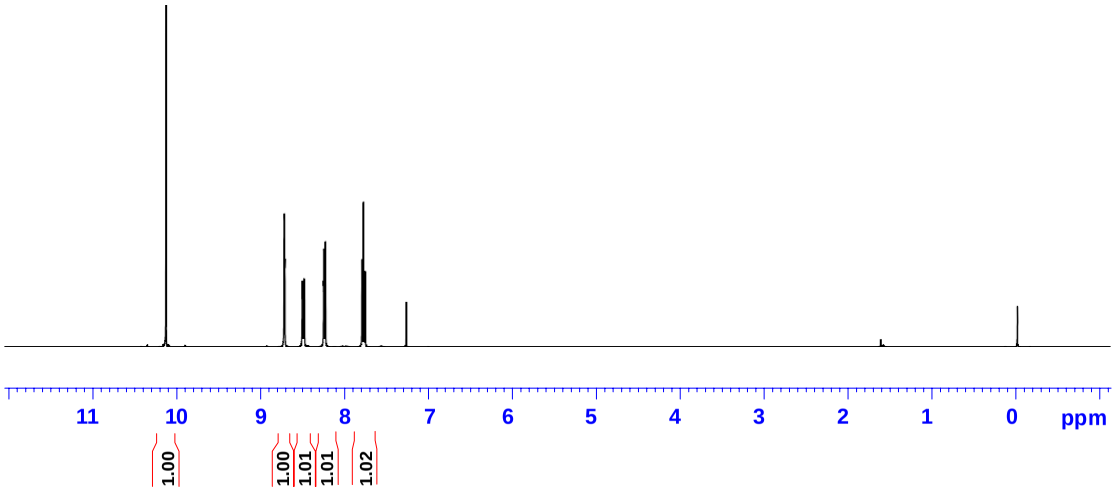

10.088
8.000
7.979
7.851
7.831
7.260
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
2.00
1.95

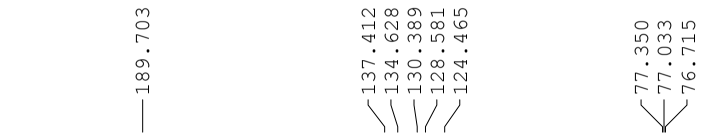

190.579
138.732
132.882
129.864
117.684
117.591
77.348
77.030
76.713
200
180
160
140
120
100
80
60
40
20
0
ppm

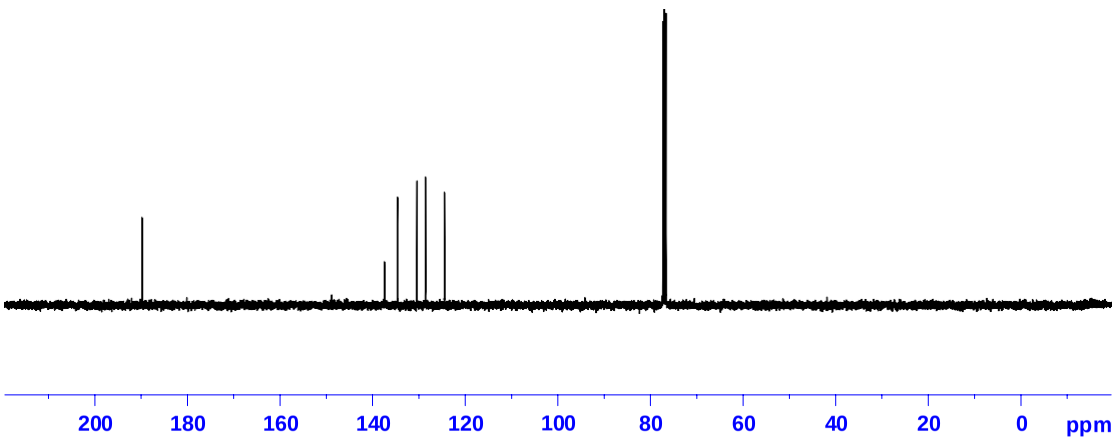

10.121
8.714
8.710
8.705
8.499
8.496
8.494
8.491
8.479
8.476
8.473
8.470
8.245
8.242
8.238
8.226
8.223
8.219
7.788
7.769
7.749
7.260

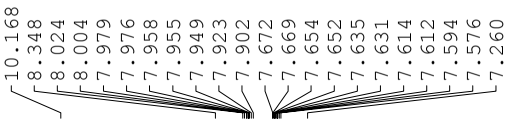

O2N
O
H

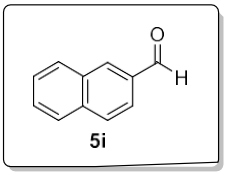
5h

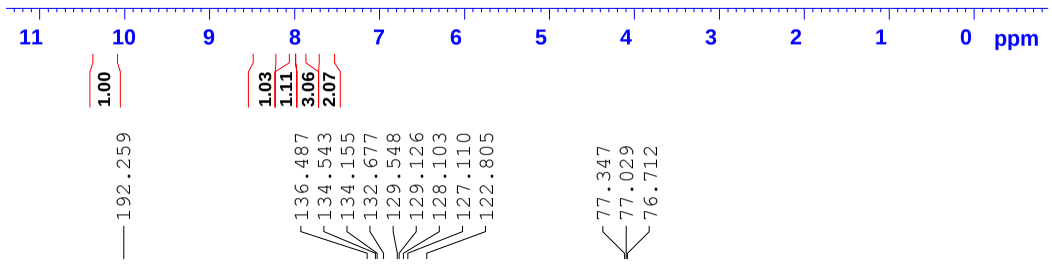

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
1.01
1.02

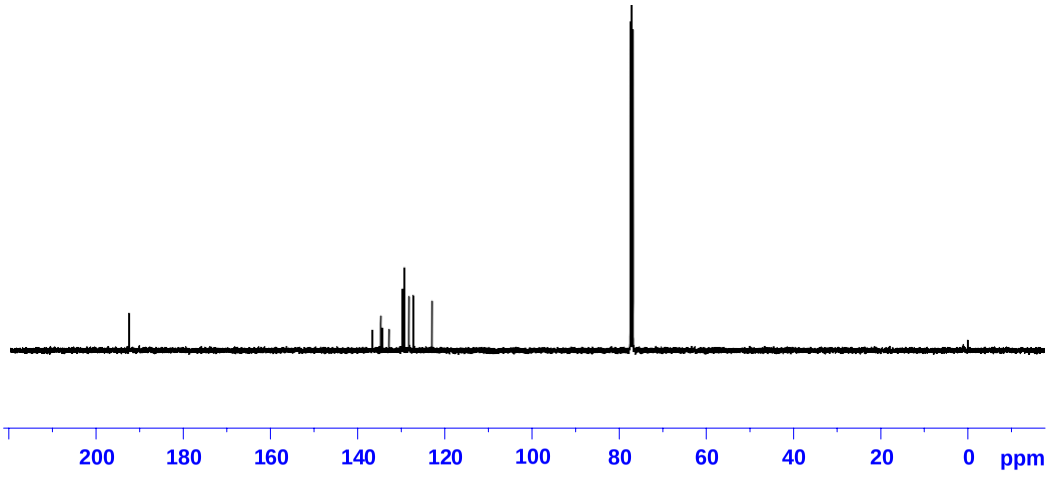

189.703
137.412
134.628
130.389
128.581
124.465
77.350
77.033
76.715


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


10.168
8.348
8.024
8.004
7.979
7.976
7.958
7.955
7.949
7.923
7.902
7.672
7.669
7.654
7.652
7.635
7.631
7.614
7.612
7.594
7.576
7.260


O
H
5i


11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.11
3.06
2.07
192.259
136.487
134.543
134.155
132.677
129.548
129.126
128.103
127.110
122.805
77.347
77.029
76.712


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