Electronic Supplementary Material (ESI) for ChemComm.

Palladium-Catalyzed *ortho*-Halogen-Induced Deoxygenative Approach of Alkyl Aryl Ketones to 2-Vinylbenzoic Acids

Shankar Ram,[a,b] Ajay Kumar Sharma,[a,b] Arvind Singh Chauhan[a,b] and Dr. Pralay Das[a,b*]

[a] Natural Product Chemistry & Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur 176061, HP, India.
[b] Academy of Scientific & Innovative Research, CSIR-IHBT, Palampur, H. P. , India.

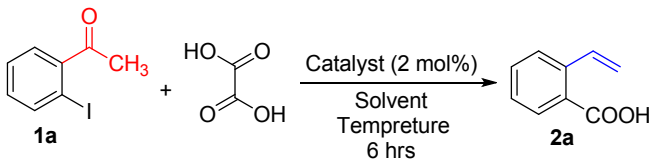
Supporting Information

Contents

1. General information

All the reactions were set up under atmospheric air utilizing glassware and 25 mL Pyrex reaction tube. Commercial reagents were purchased from Sigma Aldrich, Tokyo ChemicalIndustry (TCI, India) pvt. Ltd., Alfa Aesar, Sd Fine-chem. Ltd. and used without further purification.Amberlite® IRA 900 Cl^- resin (PS) used as support (Chloride form) was purchased from Across Organics.The catalyst palladium on carbon (Pd/C) 5 wt% purchased from Sd Fine-chem. Ltd. All solvents were purchased from CDH-Central Drug House (P) Ltd., Sd Fine-chem. Ltd. and Across Organics. Reactions were monitored using thin-layer chromatography (TLC) on silica gel 60 F_{254} (Merck)plates. Visualization of developed plates was performed under UV light (254 nm). Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Column chromatography was performed on 60-120 or 230-400 mesh silica. NMR characterization data were recorded at 298 K ona Bruker Advance 600 spectrometer operating at 600 MHz (^{1}H) and 150 MHz (^{13}C) and Bruker Advance 300 spectrometer operating at 300 MHz (^{1}H) and 75 MHz (^{13}C).^{1}H NMR spectra were internally referenced to residual solvent signal (δ_H 7.28 ppm) or TMS. ^{13}C NMR spectra were internally referenced to residual solvent signal (δ_C 77.00 ppm). Chemical shifts were recorded in δ (ppm) relative to the TMS, coupling constants (*J*) are given in Hz and multiplicities of signals are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublets, td = triplets of doublets. High resolution mass spectra (HRMS) were obtained on a micro mass Q-TOF ultima spectrometer andBruker Daltonik GmbH Impact HD model instrument. LC-MS spectra were obtainedon a Waters micro mass Q-TOF Ultima Spectrometer, Germany.

Table 1S. Optimization of reaction parameters.[a]



Entry	Catalyst	Solvent	Tempreture	Yield (%)[b]
1	–	DMF	130 °C	nr
2[c]	Pd/C	DMF	130 °C	nr
3	Pd/C	DMF	130 °C	76
4	Pd/C	DMA	130 °C	70
5	Pd/C	PEG-400	130 °C	nd
6	Pd/C	DMSO	130 °C	nd
7	Pd/C	Xylene	130 °C	nr
8	**Pd/C**	**DMF:Xylene(3:1)**	**130 °C**	**90**
9	Pd@PS	DMF	130 °C	60
10	$Pd(OAc)_2$	DMF	130 °C	56
11	$PdCl_2$	DMF	130 °C	50
12	$PdCl_2(PPh_3)_2$	DMF	130 °C	67
13[d]	Pd/C	DMF:Xylene(3:1)	130 °C	73
14	Pd/C	DMF:Xylene(3:1)	110 °C	27
15[e]	Pd/C	DMF:Xylene(3:1)	130 °C	40
16[f]	Pd/C	DMF:Xylene(3:1)	130 °C	53
17[g]	Pd/C	DMF:Xylene(3:1)	130 °C	70
18[h]	Pd/C	DMF:Xylene(3:1)	130 °C	traces

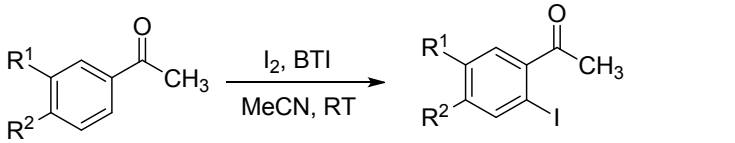
[a] Standard conditions: 2-iodoacetophenone (0.20 mmol), oxalic acid (1.22 mmol) catalyst (2 mol%), DMF:xylene (1.5:0.5) mL, 130 °C, 6 h; nd = not detectable, nr = no reaction; [b] Isolated yield of **2a**; [c] Without oxalic acid; [d] 1 mol% of Pd/C; [e] 3 equiv. of oxalic acid; [f] Reaction time 3h; [g] N-formylsachharin instead of oxalic acid; [h] Formic acid instead of oxalic acid.

2. Preparation of starting materials and characterization data

2.1 Synthesis of1-(2-iodo-4-methoxyphenyl)ethanone (1c).[1]

To an oven dried round bottom flask equipped with magnetic bar were added anhydrous aluminum chloride (200 mg, 1.5 mmol), DCE (5 mL) under nitrogen at 0^{o}C and stirred for 5 min. Then the acetyl chloride (94.2 mg, 1.2 mmol) was added drop-wise under N_2 and stirred for another 10 min. To the stirred solution, 3-iodoanisole (218 mg,1.0 mmol) was added and the reaction mixture allows warm to room temperature and stirred at that temperature for overnight under nitrogen. The progress of reaction was monitored by TLC. After completion of reaction 5 mL of 4N HCl was added and the reaction mixture was extracted with ethyl acetate (4X5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The organic phase was concentrated over rotary evaporator and the crude mixture further purified by column chromatography using hexane:ethyl acetate (98:2) as eluent; gave **1c** as light yellow oil (80 mg, 29%); ^{1}H NMR (600 MHz, $CDCl_3$)δ 7.60 (d, *J* = 8.64 Hz, 1H), 7.51 (s, 1H), 6.93 (d, *J* = 8.64 Hz, 1H), 3.83 (s, 3H), 2.59 (s, 3H);^{13}CNMR (600 MHz, $CDCl_3$) δ198.76, 161.55, 134.25, 130.98, 127.15, 113.51, 92.96, 55.68, 28.78.

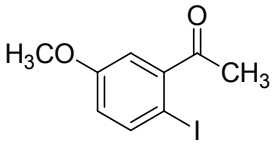
2.2 Synthesis of 1f and 1g



1f: R^1 = -OCH_3 , R^2 = H
1g: R^1 = -OCH_3 , R^2 = -OCH_3

Methoxy substituted acetophenone(1 mmol) andI_2 (0.6 equiv.), anhydrous CH_3CN (3 mL) was added to an oven dried 25 mL round bottom flask at room temperature and stirred for 5 min. To the stirred solutionbis-[(trifluoroacetoxy)iodo]benzene (BTI) (1.2 equiv.) was added at once. After a few minutes, the red-brown color of solutiondisappeared and the reactions were complete within 2 hours. After completion of the reaction,5 mL of 0.1 M NaOH solution was added to the reaction mixture to quench the residual BTI and the organic part was extracted with ethyl acetate (5 x 5 mL).The combined organic layer was washed with water, brine and then dried over

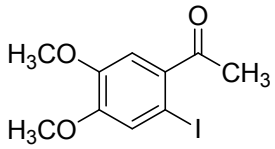
Na_2SO_4. The organic phase was concentrated over rotary evaporator and the crude mixture further purified by column chromatography using hexane and ethyl acetate as eluent.



1-(2-Iodo-5-methoxyphenyl)ethanone (1f)[2]**:** Prepared as described in general procedure **2.2**.

^{1}H NMR (600 MHz, $CDCl_3$)δ2.61 (s, 3H), 3.97 (s, 3H), 7.28 (dd, *J*= 8.0 Hz, 2.0 Hz, 1H), 7.41 (s, 1H),7.91 (d, *J*= 8.0 Hz, 1H).

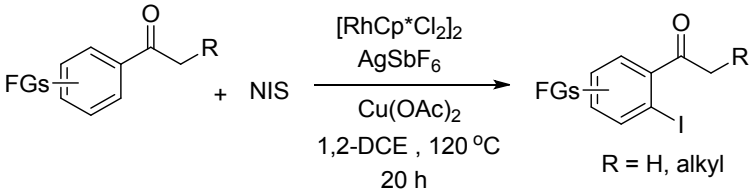
ESI-MS(M+H$^+$)calculated for $C_9H_{10}IO_2^+$is 277.07842 observed 277.4490.



1-(2-Iodo-4,5-dimethoxyphenyl)ethanone (1g)[2]**:**Prepared as described in general procedure **2.2**.

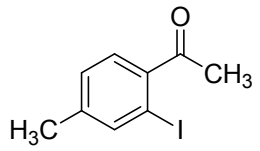
^{1}H NMR (600 MHz, $CDCl_3$)δ2.67 (s, 3H),3.93 (s, 3H), 3.94 (s,3H),7.12 (s, 1H), 7.37(s, 1H);^{13}CNMR (600 MHz, $CDCl_3$) δ 199.72, 151.38, 148.81, 135.39, 123.44, 112.41, 81.59, 56.32, 56.09, 29.19.

2.3 General procedure for the synthesis of 1b-1e and 1i-1n



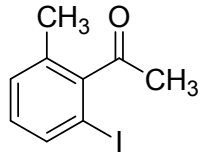
To anovendried screw-capped 25 mL reaction tube equipped with a magnetic stir bar were added aryl ketones (100 mg, 1.0 equiv.),$[RhCp^*Cl_2]_2$ (3 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (2.2 equiv.), NIS (1.4 equiv.) and1,2-DCE (3 mL). The closed reaction tube is added to a preheated (120 ^{o}C) oil bath and stirred for 20h. The progress of reaction was monitored by TLC. After

completion of reaction, the mixture was then allowed to cool down to room temperature. 5 mL of saturated aqueous solution of sodium thiosulphate was added to remove iodine color and the organic mixture was extractedethyl acetate.The organic layer was washed with water, brine and then dried over Na_2SO_4. The organic phase was concentrated over rotary evaporator and the crude mixture further purified by column chromatography using hexane and ethyl acetate as eluent.



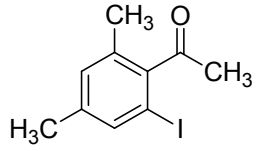
1-(2-Iodo-4-methylphenyl)ethanone (1b)[3]: Prepared as described in general procedure **2.3**.

^{1}H NMR (600 MHz, $CDCl_3$) δ2.36 (s, 3H),2.63 (s, 3H),7.24 (d, *J*= 7.8Hz, 1H),7.46 (d, *J*= 7.9Hz, 1H), 7.83(s, 1H);^{13}C NMR (600 MHz, $CDCl_3$) δ200.90, 142.83,141.81, 140.39, 128.83, 128.78, 91.50, 29.27, 20.78.



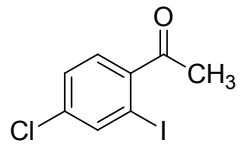
1-(2-Iodo-6-methylphenyl)ethanone(1d)[3]: Prepared as described in general procedure **2.3**.

^{1}H NMR (600 MHz, $CDCl_3$)δ2.30(s,3H), 2.58 (s,3H),6.99(t, *J*=7.8Hz,1H), 7.20(d, *J*= 7.8Hz,1H), 7.67(d, *J*= 7.9Hz,1H);^{13}C NMR (600 MHz, $CDCl_3$) δ206.34, 147.05, 136.43, 134.50, 130.11, 130.07, 89.30, 30.91, 19.68.



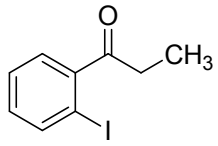
1-(2-Iodo-4,6-dimethylphenyl)ethanone (1e)[3]: Prepared as described in general procedure **2.3**.

^{1}H NMR (300 MHz, $CDCl_3$) δ2.16 (s, 3H),2.20 (s, 3H), 2.47 (s, 3H), 6.91 (s,1H), 7.41 (s, 1H); ^{13}CNMR (300 MHz, $CDCl_3$) δ206.47, 144.34, 140.20, 136.83, 134.20, 130.95, 89.33, 31.04, 20.56, 19.58.



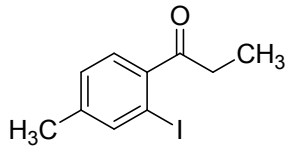
1-(4-Chloro-2-iodophenyl)ethanone (1i)[3]**:** Prepared as described in general procedure **2.3**.

^{1}H NMR (300 MHz, $CDCl_3$)δ2.63 (m, 3H), 7.40-7.47 (m, 2H), 7.98(d, *J*= 1.7Hz, 1H);^{13}C NMR (300 MHz, $CDCl_3$) δ200.28, 141.86, 140.51, 137.20, 129.27, 128.31, 91.47, 29.27.



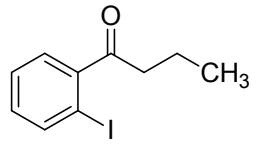
1-(2-Iodophenyl)propan-1-one (1j)[3]**:** Prepared as described in general procedure **2.3**.

^{1}H NMR (600 MHz, $CDCl_3$)δ1.25 (t, *J* = 7.3Hz, 3H),2.93 (q, *J* = 14.5, 7.2 Hz, 2H), 7.14 (t, *J*= 16.9 Hz, 1H),7.38 (d, *J*= 9.1 Hz, 1H),7.43(t, *J*= 15.9 Hz, 1H), 7.92 (d, *J*= 8.5 Hz, 1H);^{13}CNMR (600 MHz, $CDCl_3$) δ205.64, 145.01, 140.39, 131.34, 128.0, 127.47, 90.83, 35.37, 8.12.



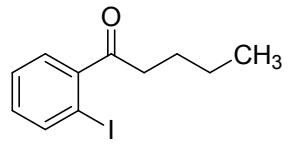
1-(2-Iodo-4-methylphenyl)propan-1-one (1k)[3]**:** Prepared as described in general procedure **2.3**.

^{1}H NMR (600 MHz, $CDCl_3$)δ1.23(t, *J*=7.2Hz, 3H), 2.35(s, 3H), 2.92(q, *J*= 14.5, 7.2Hz,2H),7.22(d, *J*= 8.2Hz, 1H), 7.34(d, *J*=7.8Hz, 1H), 7.79(s,1H);^{13}C NMR (600 MHz, $CDCl_3$) δ204.84, 142.24, 141.31, 128.74, 127.86, 91.33, 35.03, 20.77, 8.28.



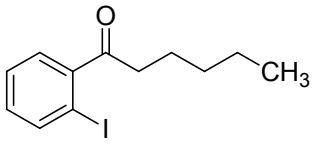
1-(2-Iodophenyl)butan-1-one (1i)[3] **:**Prepared as described in general procedure **2.3**.

^{1}H NMR (300 MHz, $CDCl_3$)δ1.03 (t, 3H, *J* = 7.40), 1.72-1.84 (m, 2H), 2.89 (t, 2H, *J* = 7.23), 7.10-7.16 (m, 1H), 7.36-7.44 (m, 2H), 7.93 (d, 1H, *J* = 7.89); ^{13}CNMR (300 MHz, $CDCl_3$) δ205.06, 145.00,140.48, 131.35, 127.98, 127.58, 90.88, 43.99, 17.56, 13.76.



1-(2-Iodophenyl)pentan-1-one (1m)[3]**:** Prepared as described in general procedure **2.3**.

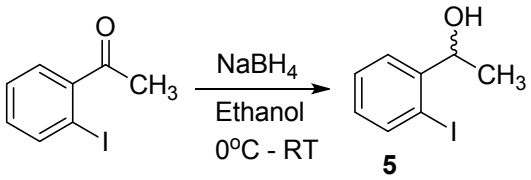
^{1}H NMR (300 MHz, $CDCl_3$)δ0.96 (t, *J*= 7.3 Hz, 3H), 1.37-1.47 (m, 2H), 1.60-1.75 (m, 2H), 2.90 (t, *J*= 7.4 Hz, 2H),7.10 – 7.16 (m, 1H), 7.35-7.41 (m, 2H), 7.92 (d, *J*= 7.8 Hz, 1H); ^{13}CNMR (300 MHz, $CDCl_3$) δ205.22,145.07, 140.46, 131.34, 127.98, 127.57, 90.89, 41.85, 26.15, 22.33, 13.86.



1-(2-Iodophenyl)hexan-1-one (1n)[3]**:** Prepared as described in general procedure **2.3**.

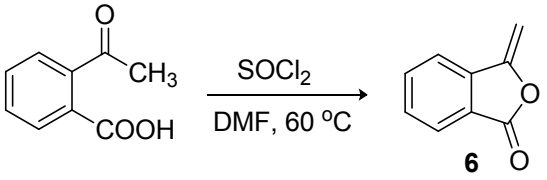
^{1}H NMR (300 MHz, $CDCl_3$)δ0.83 (t, *J*= 6.9 Hz, 3H), 1.27-1.34 (m, 4H), 1.60-1.67 (m, 2H), 2.81 (t, *J*= 7.4Hz, 2H), 7.01-7.06 (m, 1H),7.26 -7.35 (m, 2H), 7.82 (d, *J*= 7.9 Hz, 1H);^{13}CNMR (300 MHz, $CDCl_3$) δ205.24,145.02, 140.44, 131.33, 127.97, 127.56, 90.89, 42.0831.32,23.7322.44,13.91.

2.4 Synthesis of 1-(2-iodophenyl)ethanol (5).[4]



The 2-iodoacetophenone (0.81 mmol) was dissolved in ethanol and cooled to 0°C. $NaBH_4$(3.24 mmol) was added in one portion to this solution. The suspension was stirred for 10 min at 0 °C, then allowed to warm to room temperature and stirred at that temperature for 12 h. After completion of reaction, saturatedaqueous NH_4Cl was added and the organic mixture was extracted with ethyl acetate. The combined organic layer was washed with saturated aqueous NH_4Cl, brine and dried over anhydrous Na_2SO_4.The organic phase was concentrated over rotary evaporatorand finally yielded the desired alcohol **5** as light yellow oil (95 mg, 47%) after purification by silica gel column chromatography (using ethyl acetate and hexane as eluent);^{1}H NMR (600 MHz, Chloroform-d) δ7.80-7.82 (m, 1H), 7.55-7.58 (m, 1H), 7.38-7.41 (m, 1H), 6.97-7.00 (m, 1H), 5.06-5.08 (m, 1H), 1.45-1.48 (m, 3H); ^{13}C NMR (600 MHz, Chloroform-d) δ 147.42, 139.25, 129.10, 128.69, 126.28, 97.17, 73.66, 23.71.

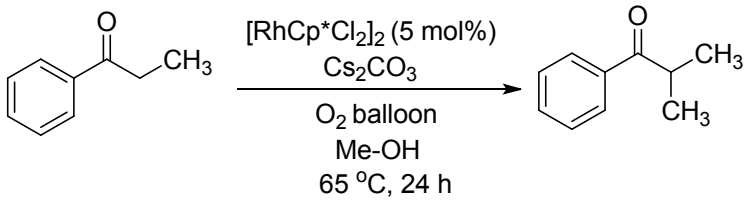
2.5 Synthesis of3-methyleneisobenzofuran-1(3H)-one (6).[5]



A solution of o-acetylbenzoic acid (1 mmol) in anhydrous DMF (5 mL) was placed into a roundbottomed flask equipped with a stirrer and was heated to 60°C. Thionyl chloride (1.2 equiv.) was added slowlyto the stirred solution and after addition the reaction mixture was heated at 60°C for 2 hrs. The progress of reaction was monitored by TLC.After completion of reaction, the mixture allows cool down to room temperature. Then, to the reaction mixture ice cold water was added and the organic mixture was extracted with ethyl acetate. The combined organic layer was washed with brine and dried over Na_2SO_4. The organic phase was concentrated over rotary evaporator and the crude mixture further purified by column chromatography using hexane and

ethyl acetate as eluent, gave **6** as white solid (90 mg, 61%); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 4.4 Hz, 2H), 7.57-7.60 (m, 1H); ^{13}C NMR (600 MHz, Chloroform-d) δ 166.9, 151.8, 146.5, 139.0, 134.5, 130.5, 125.3, 125.1, 120.6, 91.3.

Synthesis of 2-methyl-1-phenylpropan-1-one[6]



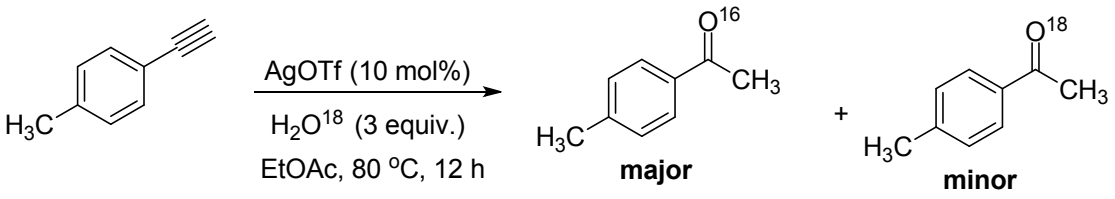
An oven dried 25ml vialcharged with [RhCp*$Cl_{2]2}$(5 mol%, 30.9mg),Cs_2CO_3(5.0 mmol, 1629.1mg) were added to a with a stir bar, followed by "wet" methanol and starting propiophenone (1.0 mmol, 132.9 microlitre). The vial was sealed with a microwave vial cap and a balloon of O_2 was inserted via a needle through the septum. The reaction was heated to 65 °C for 24 hours. The reaction was quenched by diluting with water and extracted with CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography on silica gel mess size 60-120 to give yellowish liquid product (102 mg, 69%).

3. General procedure for the preparation of 2-vinylbenzoic acids

2-Halophenylketones (1 equiv.), Pd/C (2 mol %), anhydrous oxalic acid (6 equiv.) and DMF:xylene (3:1) (1.5 mL) were added to an oven dried 25 mL screw capped reaction tube. The reaction mixture was heated at 130 °C for 6 hrs. The progress of the reaction was monitored by TLC. After completion of the reaction it allows to cool down to room temperature. Water was added to the reaction mixture and the organic mixture was extracted with ethyl acetate (4 X 5 mL).The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4,and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography using hexane and ethyl acetate as eluent to give the desired product.

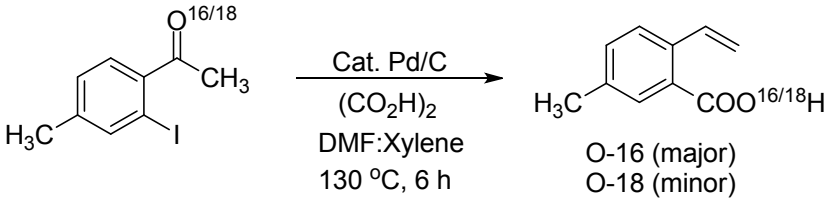
4. Mechanistic investigations

Synthesis of O-18 labeled 4-methylacetophenone[7]



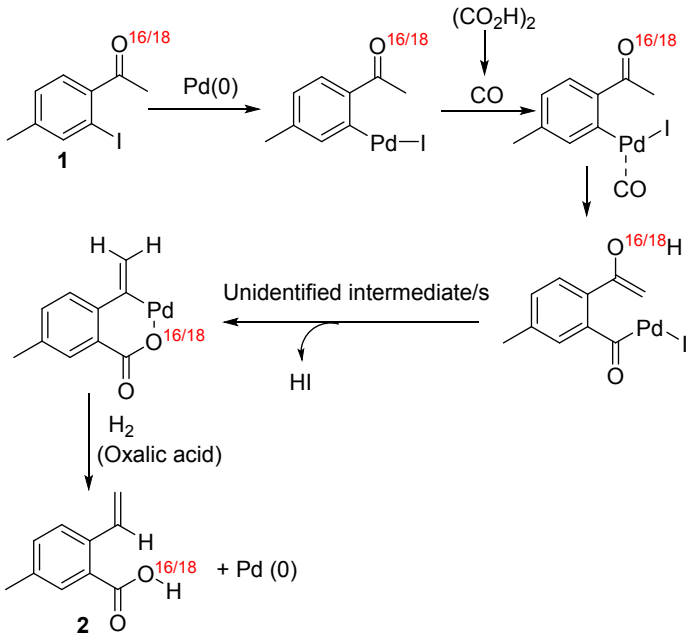
To an oven dried 5ml screw caped reaction vial equipped with stirring bar charged with EtOAc (2 ml) followed by addition of alkyne (0.5mmol, 63.4 microlitre), AgOTf (13.0mg, 10 mol %) and water (3 mmol, 27 microlitre). The reaction mixture was heated up to 80 °C for 12 hours and progress of the reaction was monitored by TLC. After completion of the reaction, the crude mixture was allowed to cool at room temperature and the solvent was removed under vacuum. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography on silica gel mess size 60-120 to give yellowish liquid product (45.0 mg, 67%). (SI, pages S70-71)

O-18 labeled experiment for mechanistic investigation



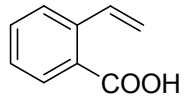
With the mixtures of O-16 and O-18 4-methyl-2-iodoactophenone, we set up a reaction as described in GP-3. After completion of the reaction it allows to cool down to room temperature. Water was added to the reaction mixture and the organic mixture was extracted with ethyl acetate (4 X 5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4,and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography using hexane and ethyl acetate as eluent and given for UPLC/ESI-MS analysis.

On the basis of these analyses, we got both product O-16 (4-methyl-2-iodoactophenones) in major and O-18 (4-methyl-2-iodoactophenones) in minor. (SI, page S68-69)



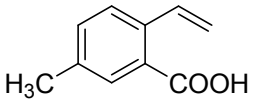
Scheme S1: Plausible mechanism

5. Characterization data of synthesized compounds



2-Vinylbenzoic acid (Table 1, entry 2a)

Following the general procedure, 2-iodoacetophenone (50 mg, 0.20 mmol) afforded **2a** (27 mg, 90%, mp: 91-93 ^{o}C) after purification by silica gel column chromatographyusing ethyl acetate:hexane (20:80). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80-7.81 (m, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.53-7.56 (m, 1H), 7.37-7.45 (m, 2H), 5.77 (dd, *J* = 17.5, 1.1 Hz, 1H), 5.35 (dd, *J* =



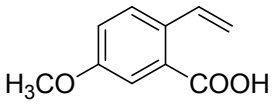
11.0, 1.1 Hz, 1H);^{13}C NMR (150 MHz, Chloroform-d) δ 169.02, 138.40, 135.73, 132.27, 130.40, 130,19, 128.15, 126.98, 116.89.

HRMS (ESI) $(M-H)^+$ calcd. for$C_9H_7O_2^+$ is 147.0451 obsd. 147.0440.

5-Methyl-2-vinylbenzoic acid (Table 1, entry 2b)

Following the general procedure, 4-methyl-2-iodoacetophenone (50 mg, 0.19 mmol) afforded **2b** (29 mg, 93%) after purification by silica gel column chromatographyusing ethyl acetate:hexane (20:80).^{1}H NMR (600 MHz, Chloroform-d) δ 1H NMR (600 MHz, Chloroform-d) δ 7.90 (s, 3H), 7.53-7.60 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 5.68 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.37 (dd, *J* = 10.9, 1.1 Hz, 1H), 2.42 (s, 3H);^{13}C NMR (150 MHz, Chloroform-d) δ 172.90, 137.77, 137.43, 135.82, 133.92, 131.64, 127.44, 126.95, 115.97, 20.94.

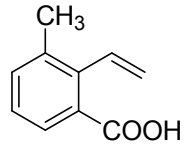
HRMS (ESI) $(M-H)^+$ calcd. for $C_{10}H_9O_2^+$ is 161.0608 obsd. 161.0597.



5-Methoxy-2-vinylbenzoic acid (Table 1, entry 2c)

Following the general procedure, 4-methoxy-2-iodoacetophenone (50 mg, 0.18 mmol) afforded **2c** (27 mg, 84%) after purification by silica gel column chromatographyusing ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ 1H NMR (300 MHz, Chloroform-d) δ 7.39-7.49 (m, 3H), 7.01-7.05 (m, 1H), 5.54 (d, *J* = 17.4 Hz, 1H), 5.24 (d, *J*= 11 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 172.61, 158.78, 135.38, 133.30, 128.81, 128.02, 119.86, 115.21, 115.15, 55.52.

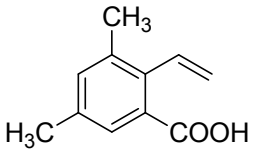
HRMS (ESI) $(M+Na)^+$ calcd. for $C_{10}H_{10}NaO_3^+$ is 201.0522 obsd. 201.0529.



3-Methyl-2-vinylbenzoic acid (Table 1, entry 2d)

Following the general procedure, 6-methyl-2-iodoacetophenone (50 mg, 0.19 mmol) afforded**2d** (24 mg, 77%) after purification by silica gel column chromatographyusing ethyl acetate:hexane (20:80).^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.20 Hz, 1H), 7.25-7.28 (m, 1H), 7.05-7.10 (m,1H), 5.55 (d, *J* = 11.4 Hz, 1H), 5.28 (d,*J* = 17.8 Hz,1H), 2.40 (s, 3H);^{13}C NMR (150 MHz, Chloroform-d) δ 173.47, 139.81, 136.92, 135.19, 134.38, 129.41, 128.12, 126.67, 119.07, 20.88.

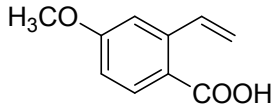
HRMS (ESI) $(M-H)^{+}$calcd. for $C_{10}H_9O_2^{+}$ is 161.0608 obsd. 161.0597.



3,5-Dimethyl-2-vinylbenzoic acid (Table 1, entry 2e)

Following the general procedure, 4,6-dimethyl-2-iodoacetophenone (50 mg, 0.18 mmol) afforded**2e** (23 mg, 71%, mp: 102-104 ^{o}C) after purification by silica gel column chromatographyusing ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ 7.61 (s, 1H), 7.24 (s, 1H), 7.01-7.06 (m, 1H), 5.51 (dd, *J*=11.4, 1.6 Hz, 1H) 5.26 (dd, *J*=17.8, 1.6 Hz, 1H), 2.37 (s, 1H), 2.36 (s, 3H);^{13}C NMR (150 MHz, Chloroform-d) δ 173.17, 136.82, 136.75, 136.38, 135.22, 135.06, 129.16, 128.56, 118.88, 20.83, 20.82.

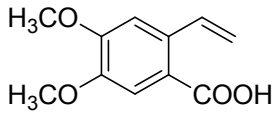
HRMS (ESI) $(M-H)^{+}$ calcd. for $C_{11}H_{11}O_2^{+}$ is 175.0764 obsd. 175.0753



4-Methoxy-2-vinylbenzoic acid (Table 1, entry 2f)

Following the general procedure, 5-methoxy-2-iodoacetophenone (50 mg, 0.18 mmol) afforded **2f** (21 mg, 65%) after purification by silica gel column chromatographyusing ethyl acetate:hexane (20:80).^{1}H NMR (300 MHz, Chloroform-d) δ 8.0 (d, *J*=8.8 Hz, 1H), 7,51-7.60 (m, 1H), 6.99 (s, 1H), 6.776.81 (m, 1H), 5.59 (d, *J*=17.4 Hz, 1H), 5.32 (d, *J*=10.9 Hz, 1H), 3.82 (s, 3H);^{13}C NMR (75 MHz, Chloroform-d) δ 171.97, 163.25, 143.37, 136.58, 133.84, 119.57, 116.61, 112.85, 112.81, 55.44.

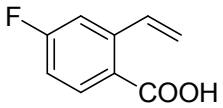
HRMS (ESI) $(M-H)^+$ calcd. for $C_{10}H_9O_3^+$ is 177.0557 obsd. 177.0546.



4,5-Dimethoxy-2-vinylbenzoic acid (Table 1, entry 2g)

Following the general procedure, 4,5-dimethoxy-2-iodoacetophenone (50 mg, 0.16 mmol) afforded **2g** (19 mg, 56%, mp: 167-169 ^oC) after purification by silica gel column chromatographyusing ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ 7.64-7.69 (m, 1H), 7.60 (s, 1H), 7.07 (s, 1H), 5.63 (dd, *J*=17.4, 1.1 Hz, 1H), 5.37 (dd, *J*=11.0, 1.1 Hz, 1H), 4.01 (s, 3H), 3.96 (s, 3H);^{13}C NMR (150 MHz, Chloroform-d) δ 172.07, 152.87, 148.09, 136.18, 135.71, 119.00, 115.50, 113.51, 109.67, 56.06, 56.02.

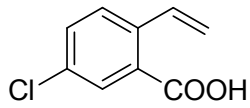
HRMS (ESI) $(M-H)^+$ calcd. for $C_{11}H_{11}O_4^+$ is 207.0663 obsd. 207.0651.



4-Fluoro-2-vinylbenzoic acid (Table 1, entry 2h)

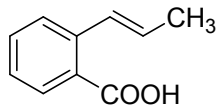
Following the general procedure, 5-fluoro-2-iodoacetophenone (50 mg, 0.19 mmol) afforded **2h** (25 mg, 79%) after purification by silica gel column chromatography using ethyl acetate:hexane (30:70). ^{1}H NMR (600 MHz, Chloroform-d) δ7.897.91 (m, 1H), 7.44-7.51 (m, 2H), 7.22 (td, *J*=8.46, 2.64 Hz, 1H), 5.86 (d, *J*=17.46 Hz, 1H), 5.41 (d, *J*=11.7 Hz, 1H);^{13}C NMR (150 MHz, Chloroform-d) δ 168.02, 164.47 (*J* = 247.5 Hz), 141.84, 134.72, 133.57 (*J* = 9 Hz), 126.43, 118.40, 115.07 (*J* = 21 Hz), 113.46.

HRMS (ESI) $(M-H)^+$ calcd. for $C_9H_6FO_2^+$ is 165.0357 obsd. 165.0346.



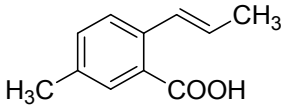
5-Chloro-2-vinylbenzoic acid (Table 1, entry 2i)

Following the general procedure, 4-chloro-2-iodoacetophenone (50 mg, 0.18 mmol) afforded**2i**(22 mg, 67%, mp: 93-95 ^{o}C) after purification by silica gel column chromatography using ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ 8.05 (d, *J*=2.0 Hz, 1H), 7.52-7.61 (m, 3H), 5.71 (d, *J*=17.4, 1.1 Hz, 1H), 5.45 (d, *J*=11.04, 1.1 Hz, 1H);^{13}C NMR (150 MHz, Chloroform-d) δ 170.88, 139.06, 134.89, 133.41, 133.16, 131.10, 128.98, 128.28, 117.55.
HRMS (ESI) $(M-H)^{+}$ calcd. for $C_9H_6ClO_2^{+}$ is 181.0061 obsd. 181.0050.



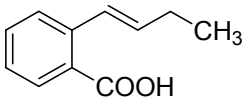
2-(Prop-1-en-1-yl)benzoic acid (Table 1, entry 2j) *E:Z = 10.8:1*

Following the general procedure, 2-iodopropiophenone (50 mg, 0.19 mmol) afforded **2j** (26 mg, 83%) after purification by silica gel column chromatography using ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ8.02 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.51 (m, 1H), 7.26 – 7.31 (m, 2H), 6.19 (dq, *J* = 15.6, 6.6 Hz, 1H), 1.95 (dd, *J* = 6.6, 1.8 Hz, 4H); ^{13}C NMR (150 MHz, Chloroform-d) δ173.16, 140.68, 132.89, 131.27, 129.83, 129.05, 127.50, 126.73, 126.57, 18.81.
HRMS (ESI) $(M-H)^{+}$ calcd. for $C_{10}H_9O_2^{+}$ is 161.0608 obsd. 161.0597.



5-Methyl-2-(prop-1-en-1-yl)benzoic acid (Table 1, entry 2k) *E:Z = 23.2:1*

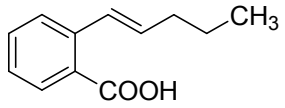
Following the general procedure, 4-methyl-2-iodopropiophenone (50 mg, 0.18 mmol) afforded **2k** (28 mg, 87%, mp: 109-111 ^{o}C) after purification by silica gel column chromatography using ethyl acetate:hexane (20:80).^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.23 (dd, *J* = 15.6, 1.8 Hz, 1H), 6.15 (dq, *J* = 15.6, 6.6 Hz, 1H), 2.37 (s, 3H), 1.93 (dd, *J* = 6.6, 1.8 Hz, 3H);^{13}C NMR (150 MHz, Chloroform-d) δ 173.27, 137.85, 136.40, 133.82, 131.61, 129.60, 128.21, 127.45, 126.44, 20.91, 18.85.
HRMS (ESI) $(M-H)^{+}$ calcd. for $C_{11}H_{11}O_2^{+}$ is 175.0764 obsd. 175.0752.



2-(But-1-en-1-yl)benzoic acid(Table 1, entry 2l) *E:Z = 8.7:1*

Following the general procedure, 2-iodobutyrophenoene (50 mg, 0.18 mmol) afforded **2l** (26 mg, 81%) after purification by silica gel column chromatography using ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ8.02 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.24 (m, 1H), 2.28 – 2.33 (m, 2H), 1.12 – 1.14 (m, 3H); ^{13}C NMR (150 MHz, Chloroform-d) δ 172.97, 140.72, 135.96, 132.90, 131.28, 127.64, 127.50, 126.77, 126.58, 26.32, 13.56.

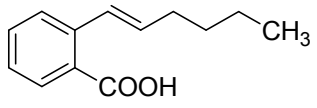
HRMS (ESI) $(M-H)^+$ calcd. for $C_{11}H_{11}O_2^+$ is 175.0764 obsd. 175.0753.



2-(Pent-1-en-1-yl)benzoic acid (Table 1, entry 2m) *E:Z = 8.4:1*

Following the general procedure, 2-iodovalerophenone (50 mg, 0.17 mmol) afforded **2m** (26 mg, 79%) after purification by silica gel column chromatography using ethyl acetate:hexane (30:70).^{1}H NMR (600 MHz, Chloroform-d) δ8.02 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 (td, *J* = 7.8, 1.2 Hz, 1H), 7.29 – 7.31 (m, 1H), 7.26 (d, *J* = 16.2, Hz, 1H), 6.15 – 6.20 (m, 1H), 2.26 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.51 – 1.57 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-d) δ 173.06, 140.73, 134.32, 132.90, 131.27, 128.73, 127.54, 126.78, 126.59, 35.29, 22.45, 13.77.

HRMS (ESI) $(M-H)^+$ calcd. for $C_{12}H_{13}O_2^+$ is 189.0921 obsd. 189.0910.



2-(Hex-1-en-1-yl)benzoic acid (Table 1, entry 2n) *E:Z = 7.1:1*

Following the general procedure, 2-iodohexanophenone (50 mg, 0.17 mmol) afforded **2n** (25 mg, 74%) after purification by silica gel column chromatography using ethyl acetate:hexane

(30:70).^{1}H NMR (600 MHz, Chloroform-d) δ 8.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 – 7.28 (td, *J* = 7.8, 1.2 Hz, 1H), 7.26 (d, *J* = 15.6 Hz, 1H), 6.14 – 6.19 (m, 1H), 2.26 – 2.30 (m, 2H), 1.47 – 1.52 (m, 2H), 1.37 – 1.43 (m, 2H), 0.93 – 0.95 (m, 3H); ^{13}C NMR (150 MHz, Chloroform-d) δ 172.93, 140.74, 134.52, 132.88, 131.27, 128.57, 127.53, 126.76, 126.57, 32.90, 31.38, 22.27, 13.98.

HRMS (ESI) $(M-H)^+$ calcd. for $C_{13}H_{15}O_2^+$ is 203.1077 obsd. 203.1066.

6. References

1. Friedel craft acylation reaction
2. B. Panunzi, L. Rotiroti and M. Tingoli, *Tetrahedron Lett.,* 2003, **44**, 8753.
3*. N. Schroeder, J. W. Delord and F. Glorius, *J. Am. Chem. Soc.,* 2012, **134**, 8298-8301.
4. B. Schulte, R. Frohlich, A. Studer, *Tetrahedron,* 2008, **64**, 11852–11859.
5. S. N. Salazkina, G. S. Chelidze, *Polymer Science***,** 2009, **51**, 126–132.
6. L. K. M. Chan, D. L. Poole, D. Shen, M. P. Healy, T. J. Donohoe, *Angew. Chem. Int. Ed.,* 2014, **53**, 761 –765.
7. R. Das, D. Chakraborty, *Appl. Organometal. Chem.,* 2012, **26**, 722–726.

Note (*): In the reference 3, Glorius et al reported [Rh(III)Cp*]-catalyzed ortho-iodination of acetophenone molecule and got 62% yield of 2-iodoacetophenone. We follow the same procedure and reagent system for other acetophenones derivatives to prepare ortho iodinated acetophenones which are new and not reported in this paper.

7. Recyclability experiments:

In order to investigate the stability and recyclability of the Pd/C catalyst, we conducted a reaction of 2-iodoacetophenone (1a) under standard conditions. After the reaction was completed, the Pd/C catalyst was recovered from the reaction mixture using centrifugation. It was washed with methanol and acetone and a subsequent reaction cycle was performed with the dried catalyst. To our delight, the catalyst showed excellent recyclability and could be reused up to six cycles (Figure S1).

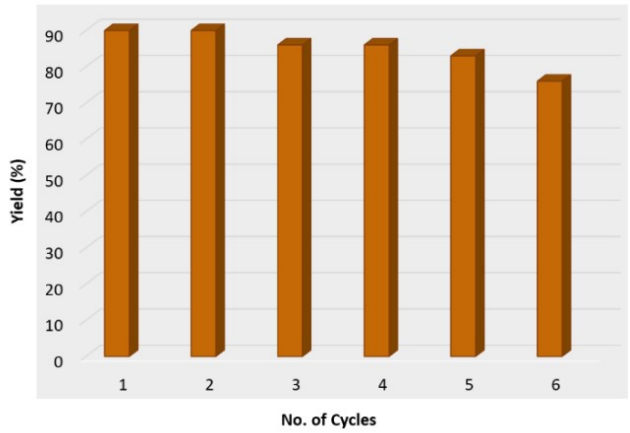
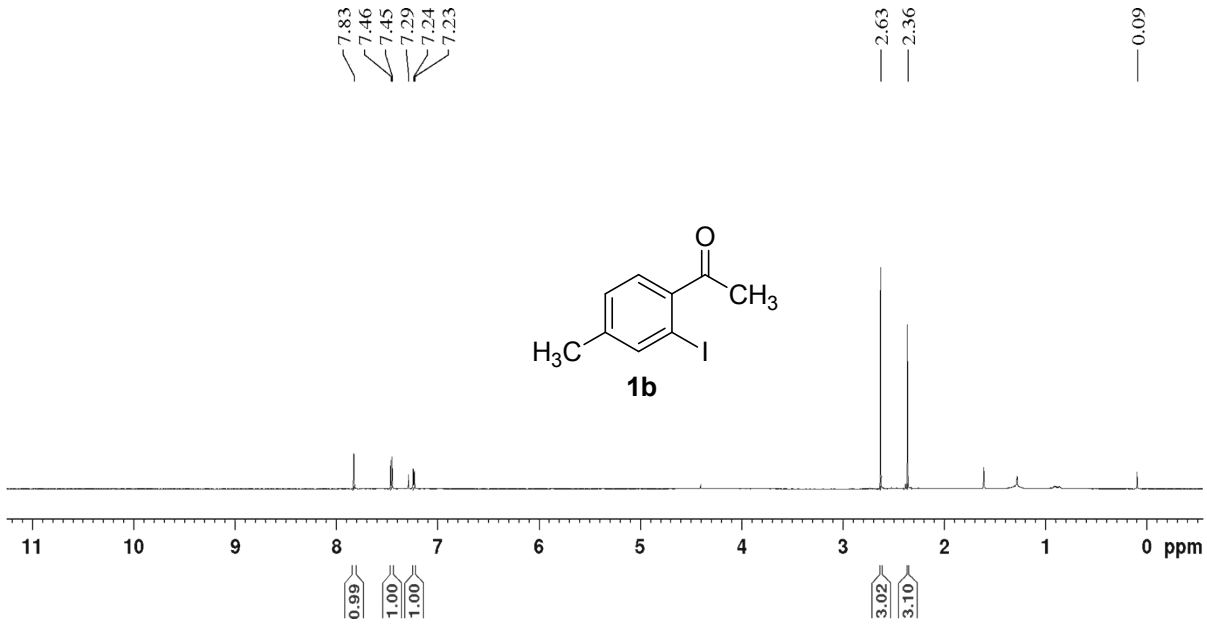
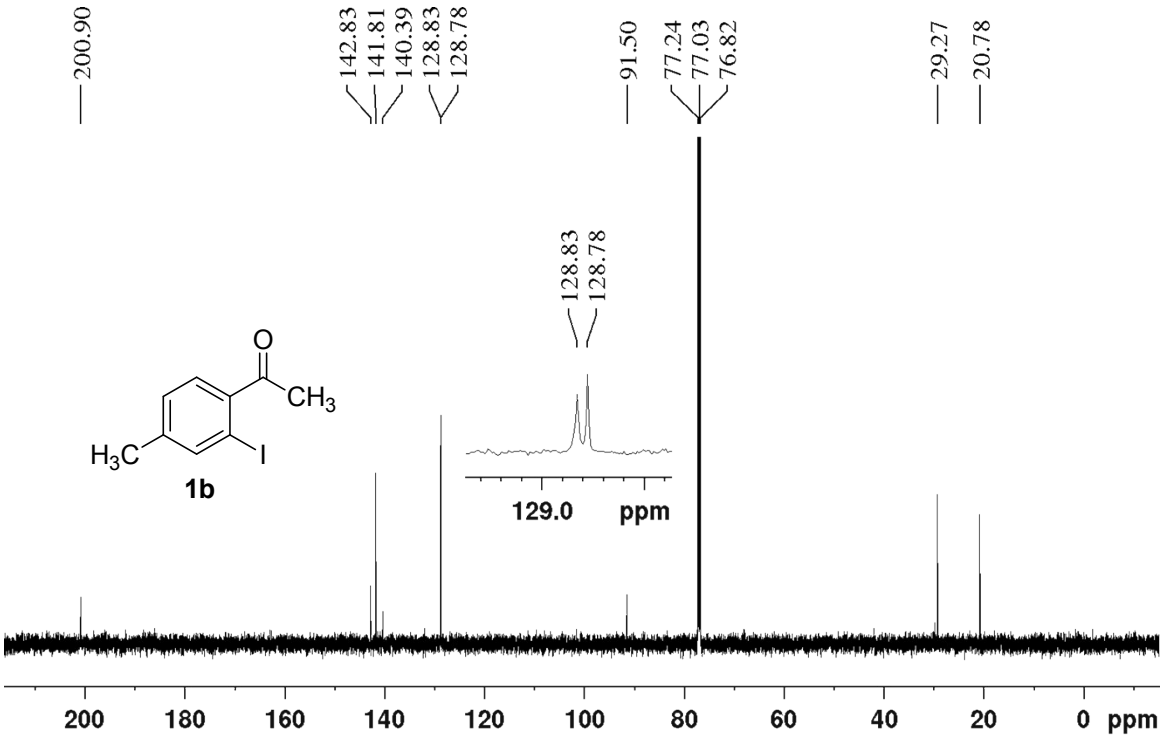
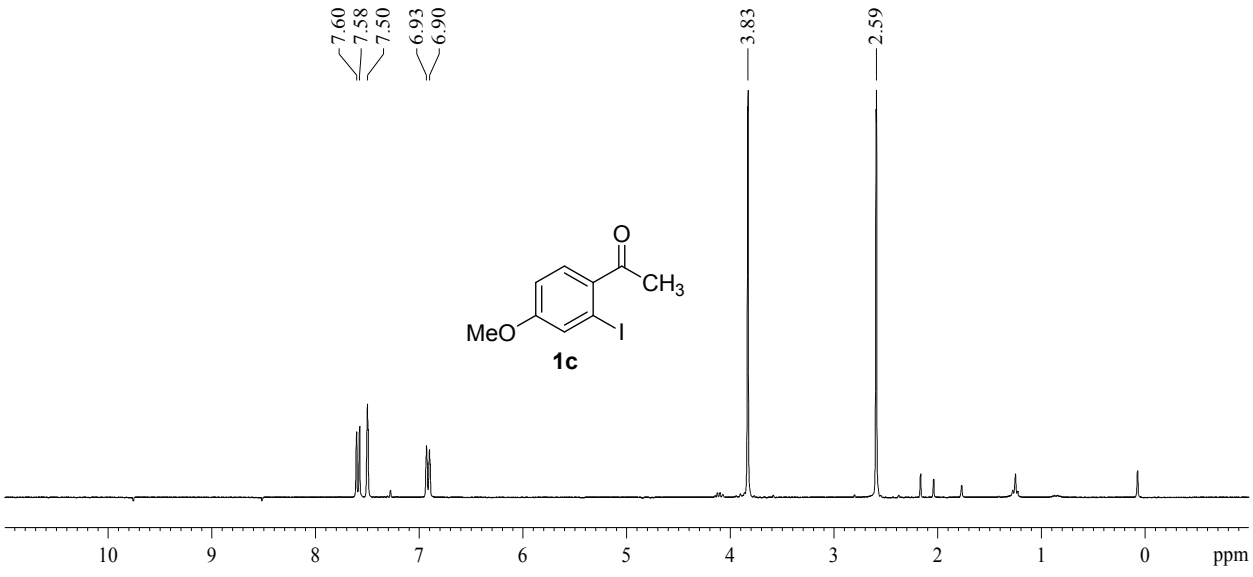


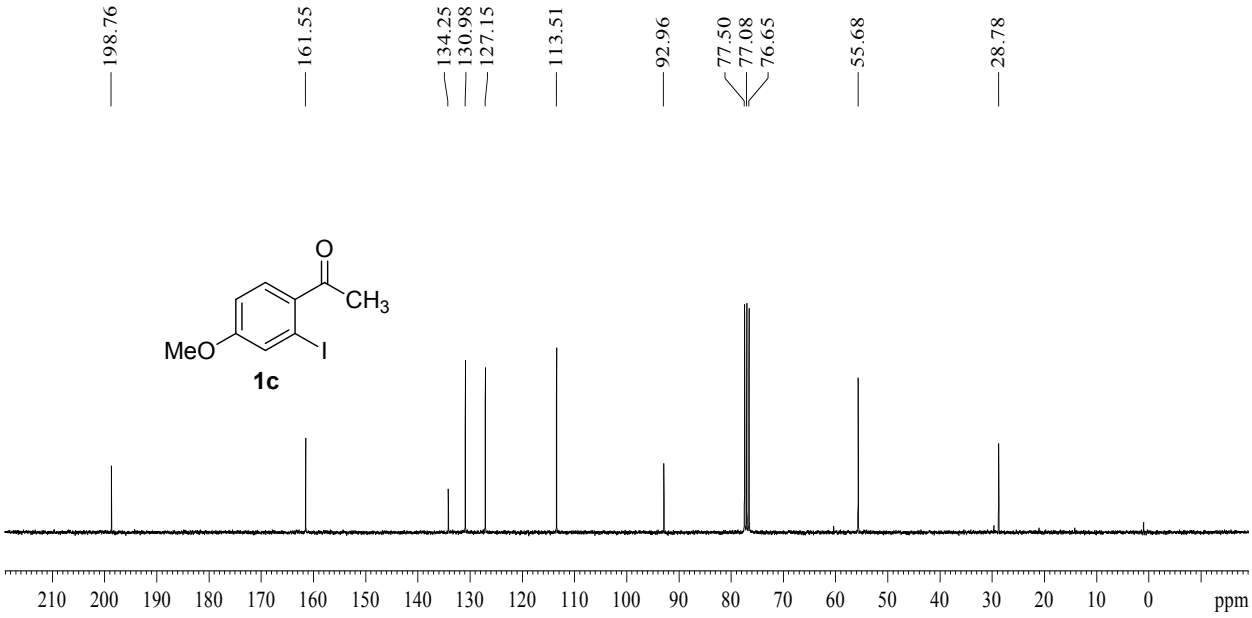
Figure S1. Recyclability of Pd/C catalyst

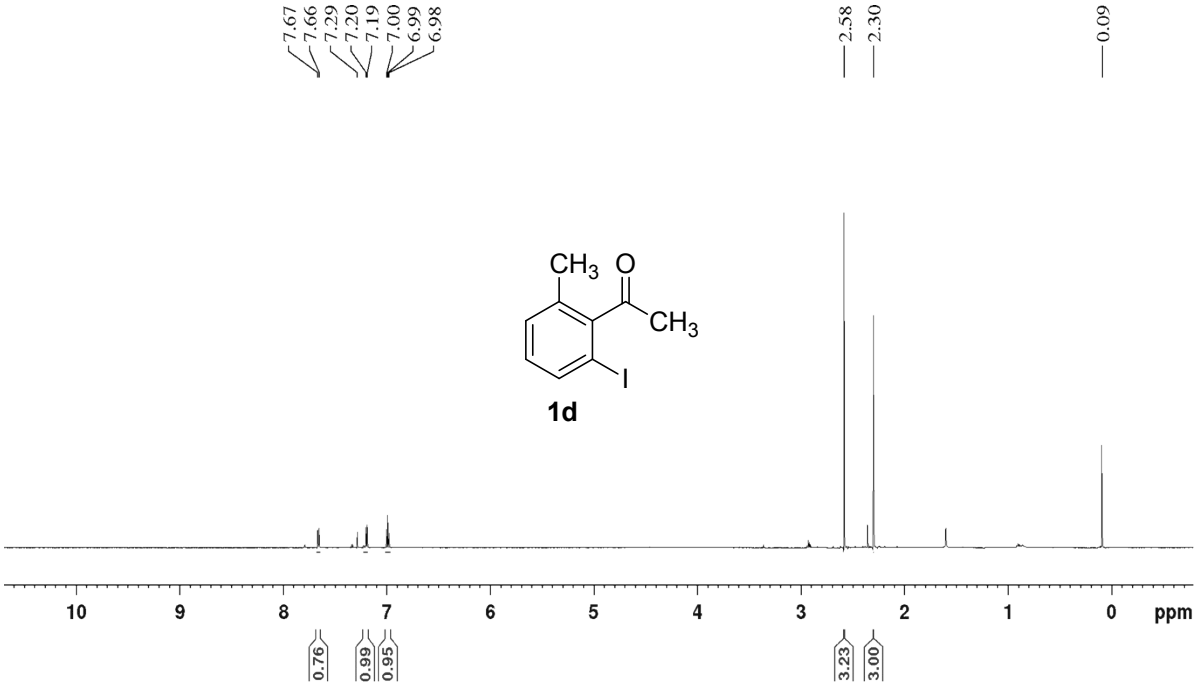
8. NMR spectra of starting materials

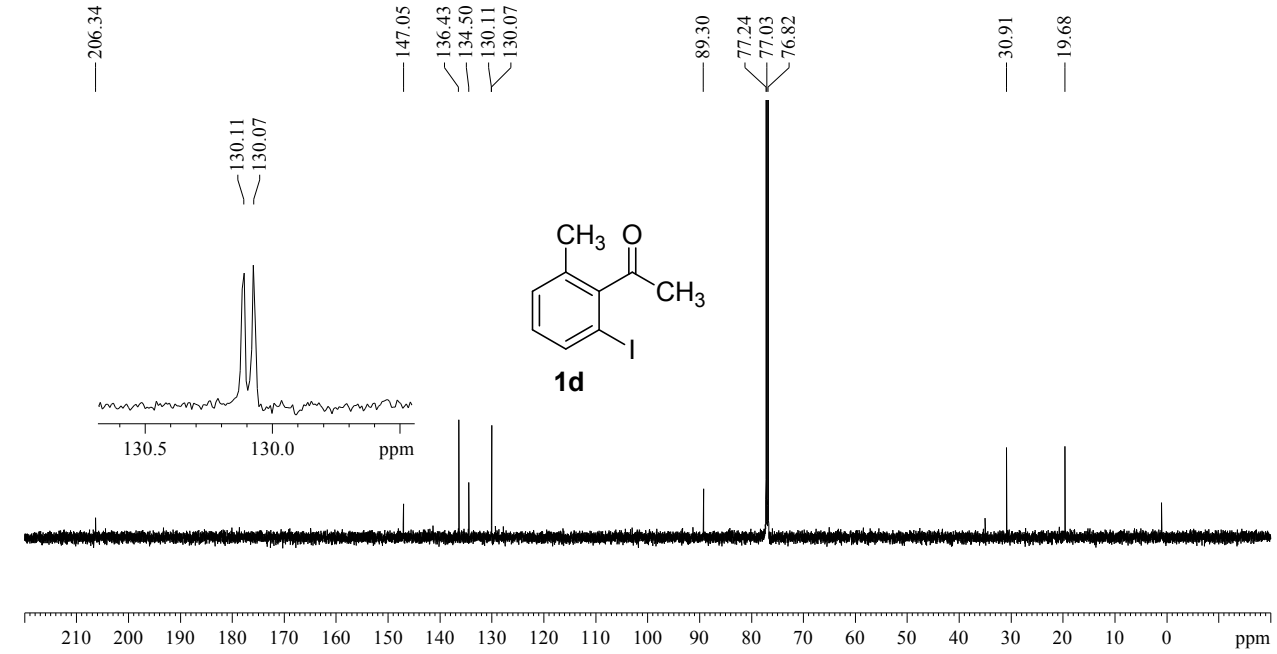


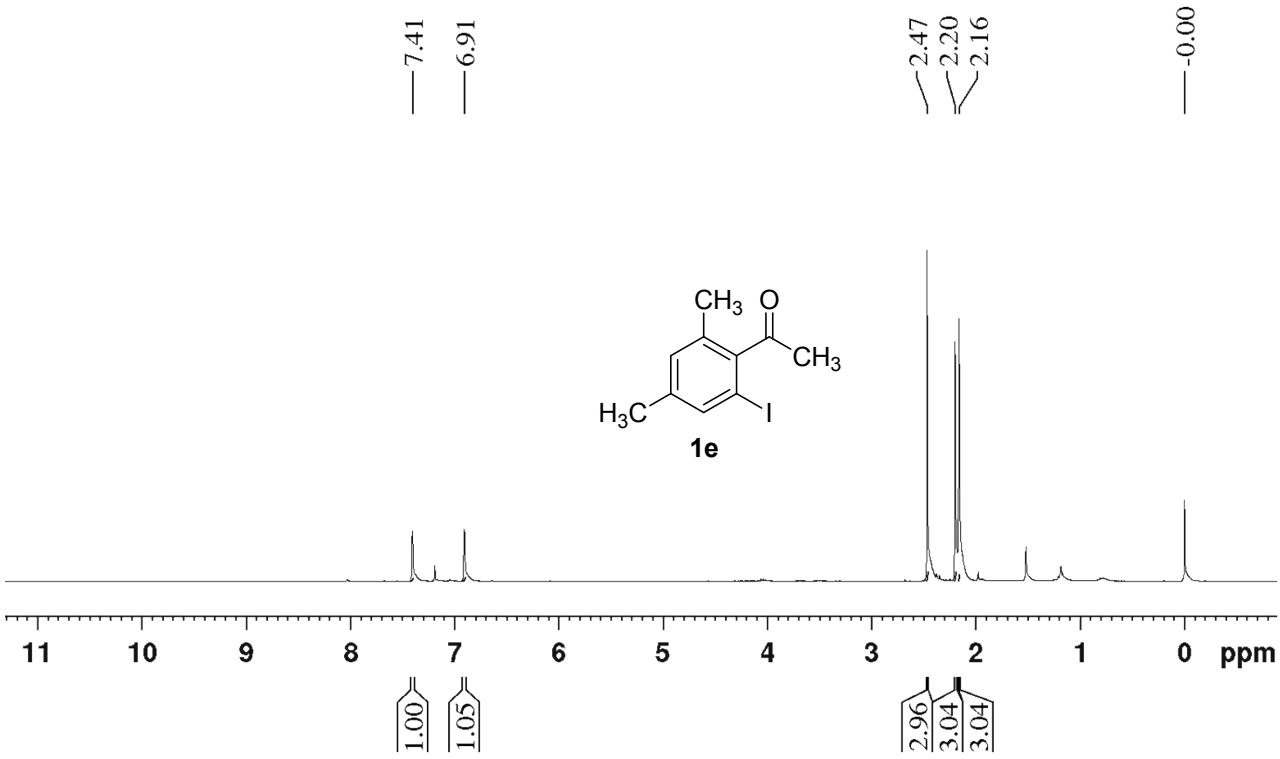

200.90
142.83
141.81
140.39
128.83
128.78
91.50
77.24
77.03
76.82
29.27
20.78
128.83
128.78
O
CH3
H3C
I
1b
129.0
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

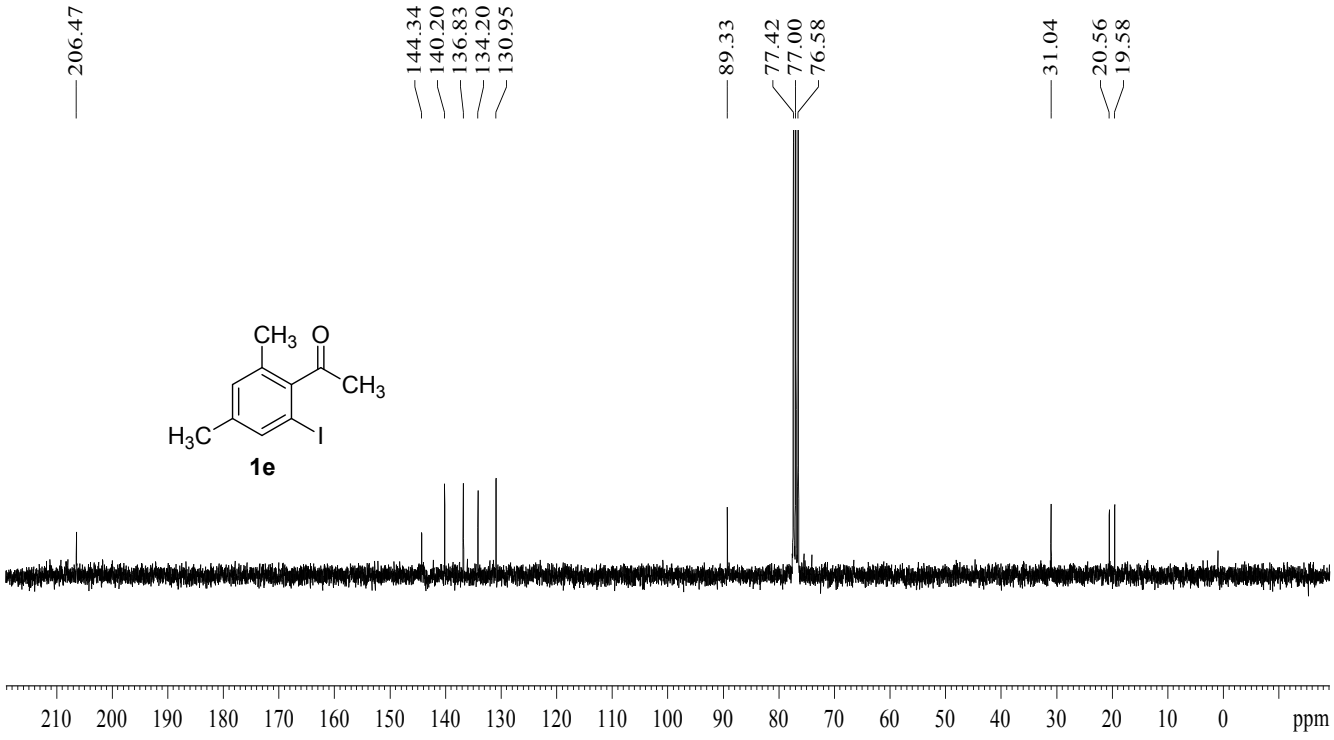

7.60
7.58
7.50
6.93
6.90
3.83
2.59
O
CH3
MeO
I
1c
10
9
8
7
6
5
4
3
2
1
0
ppm

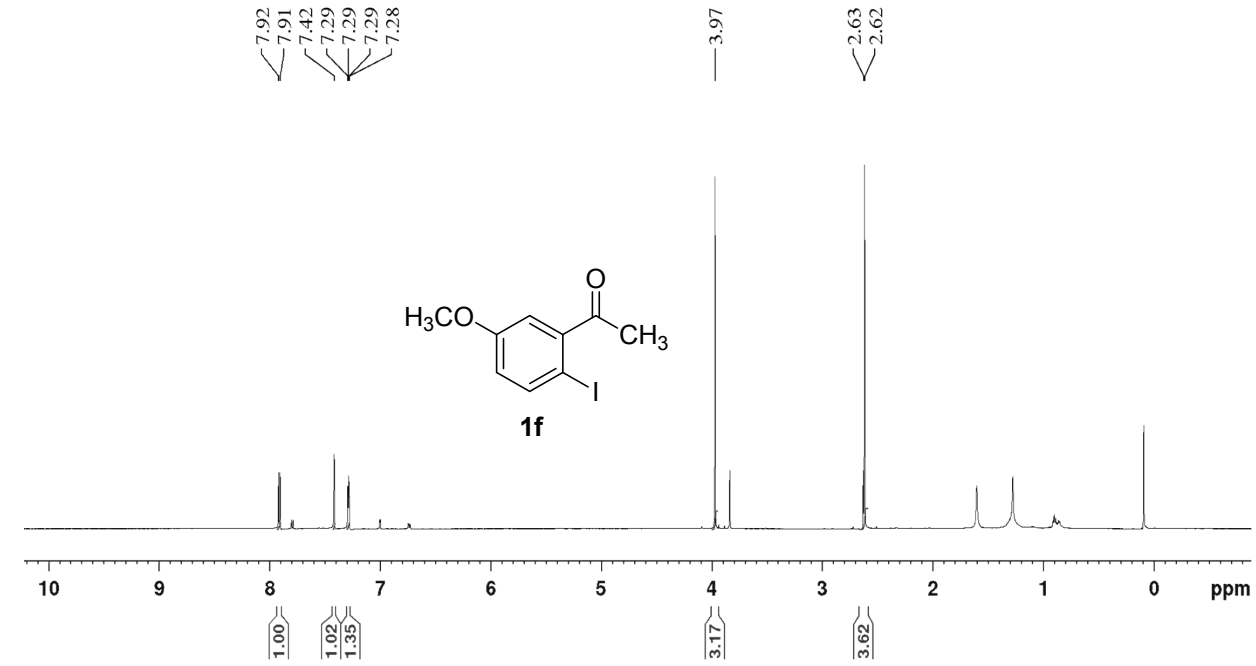

198.76
161.55
134.25
130.98
127.15
113.51
92.96
77.50
77.08
76.65
55.68
28.78
O
CH3
MeO
I
1c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

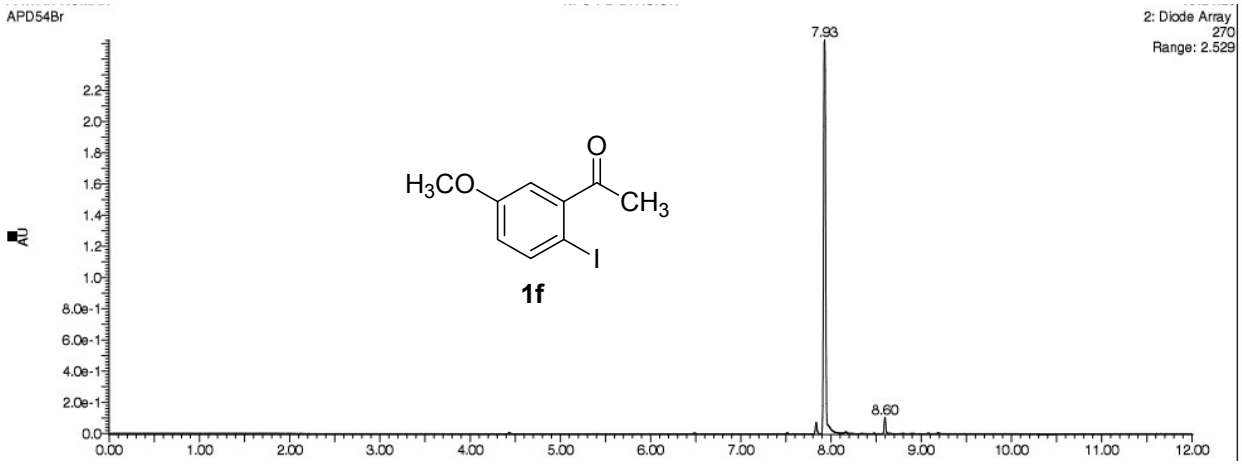

7.67
7.66
7.29
7.20
7.19
7.00
6.99
6.98
2.58
2.30
0.09
CH3
O
CH3
I
1d
10 9 8 7 6 5 4 3 2 1 0 ppm
0.76
0.99
0.95
3.23
3.00


206.34
147.05
136.43
134.50
130.11
130.07
89.30
77.24
77.03
76.82
30.91
19.68
130.11
130.07
130.5
130.0
ppm
CH3 O
CH3
I
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

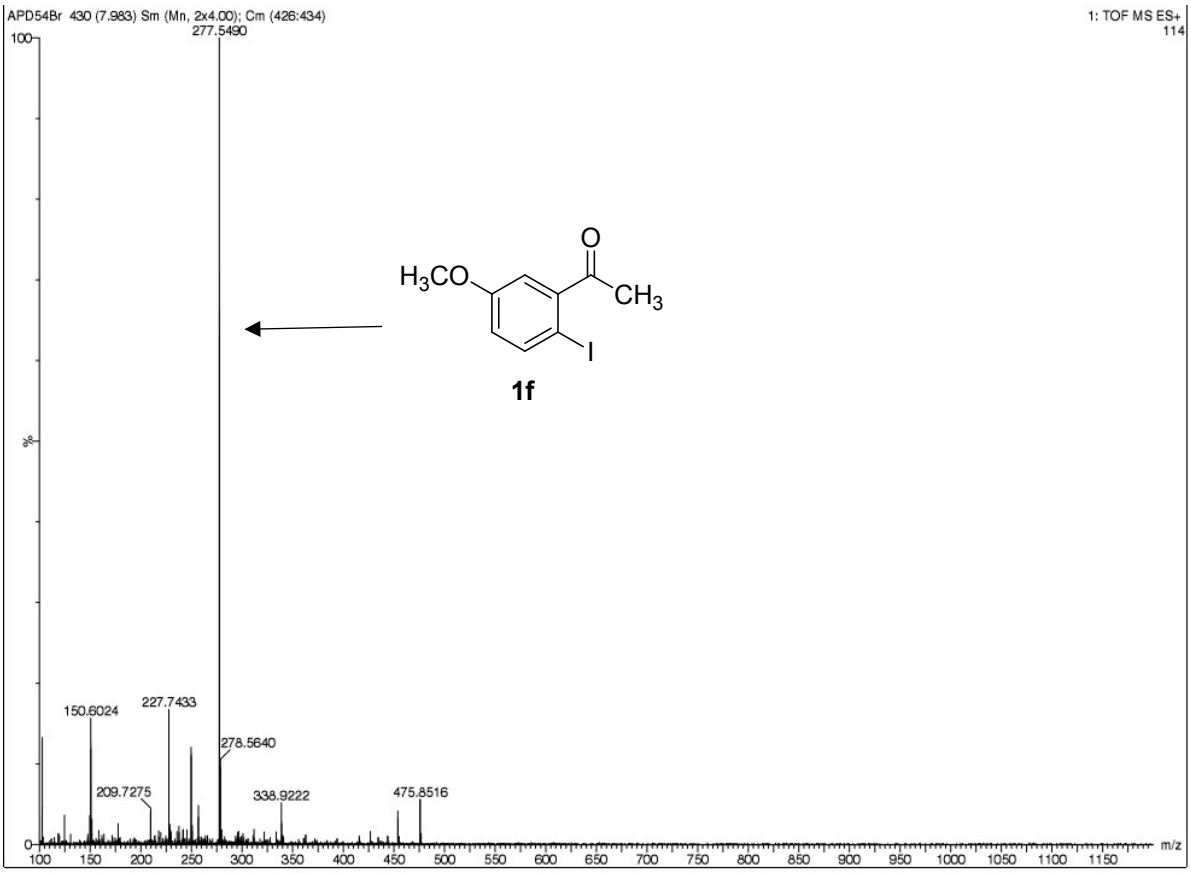

7.41
6.91
2.47
2.20
2.16
-0.00
CH3 O
CH3
H3C
I
1e
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.05
2.96
3.04
3.04


206.47
144.34
140.20
136.83
134.20
130.95
89.33
77.42
77.00
76.58
31.04
20.56
19.58
CH3 O
CH3
H3C
I
1e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

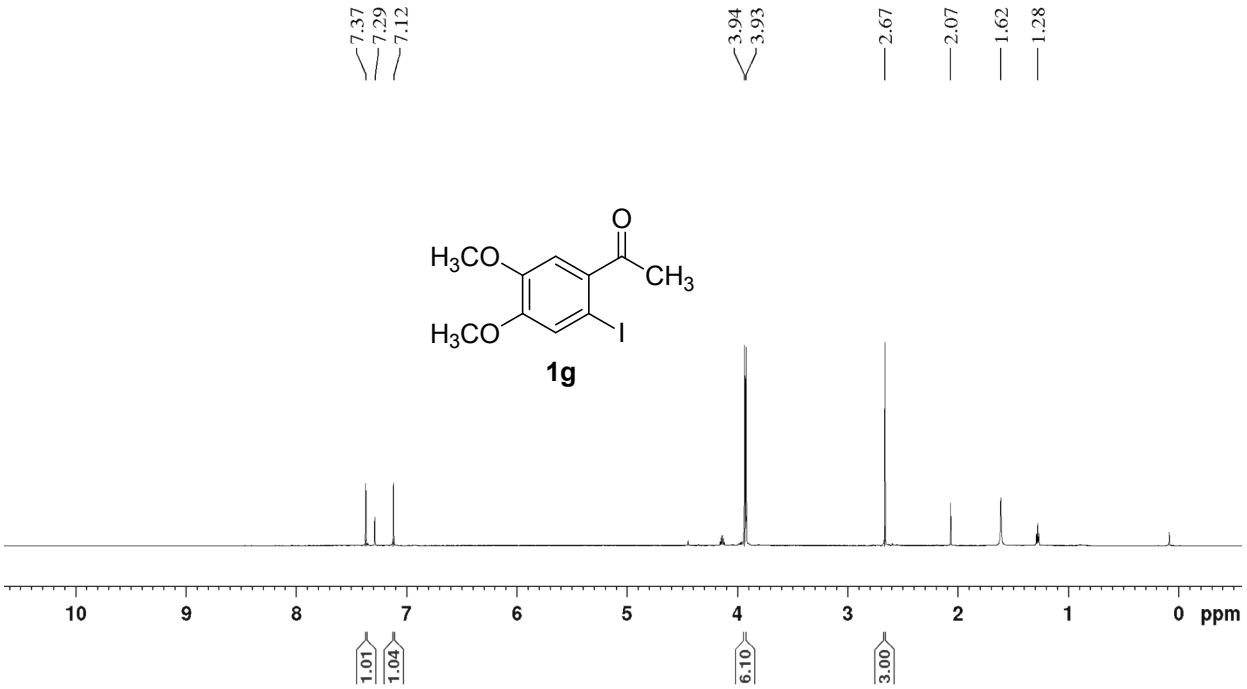

7.92
7.91
7.42
7.29
7.29
7.29
7.28
3.97
2.63
2.62
O
H3CO
CH3
I
1f
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
1.35
3.17
3.62

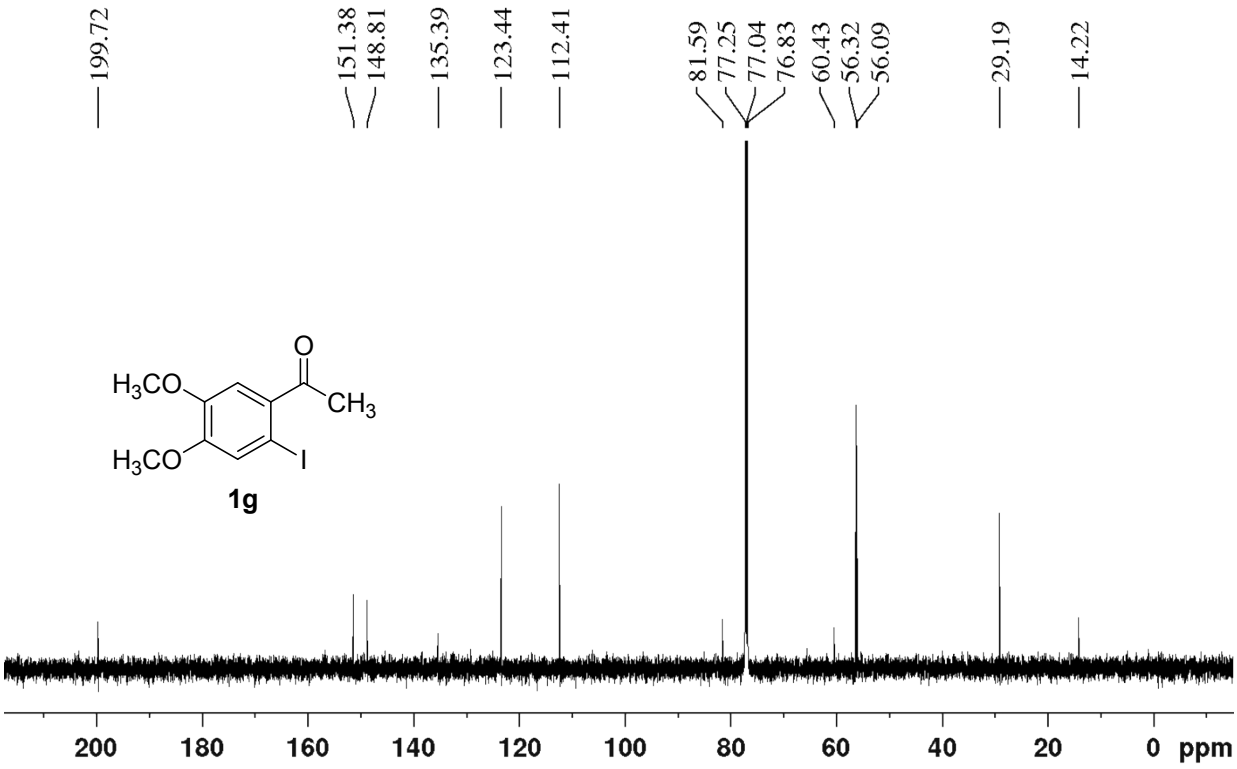

APD54Br
2: Diode Array
270
Range: 2.529
7.93
8.60
AU
2.2
2.0
1.8
1.6
1.4
1.2
1.0
8.0e-1
6.0e-1
4.0e-1
2.0e-1
0.0
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
O
H3CO
CH3
I

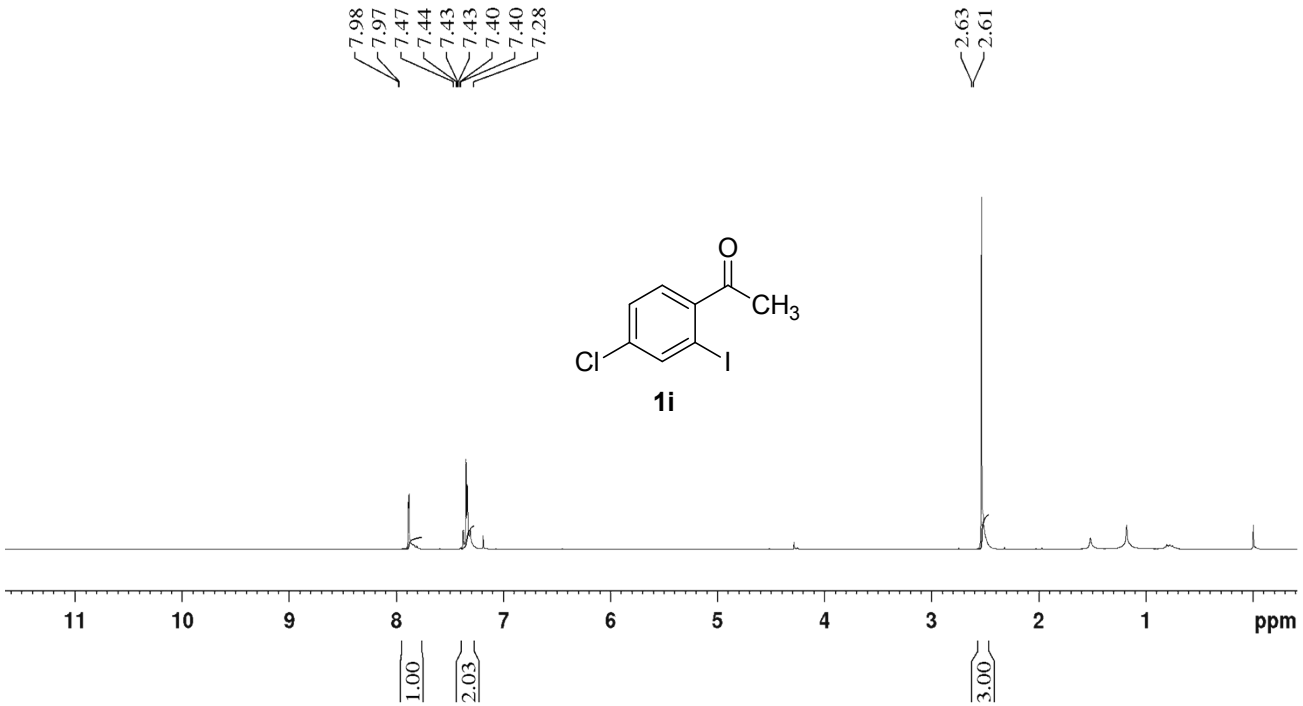
1f

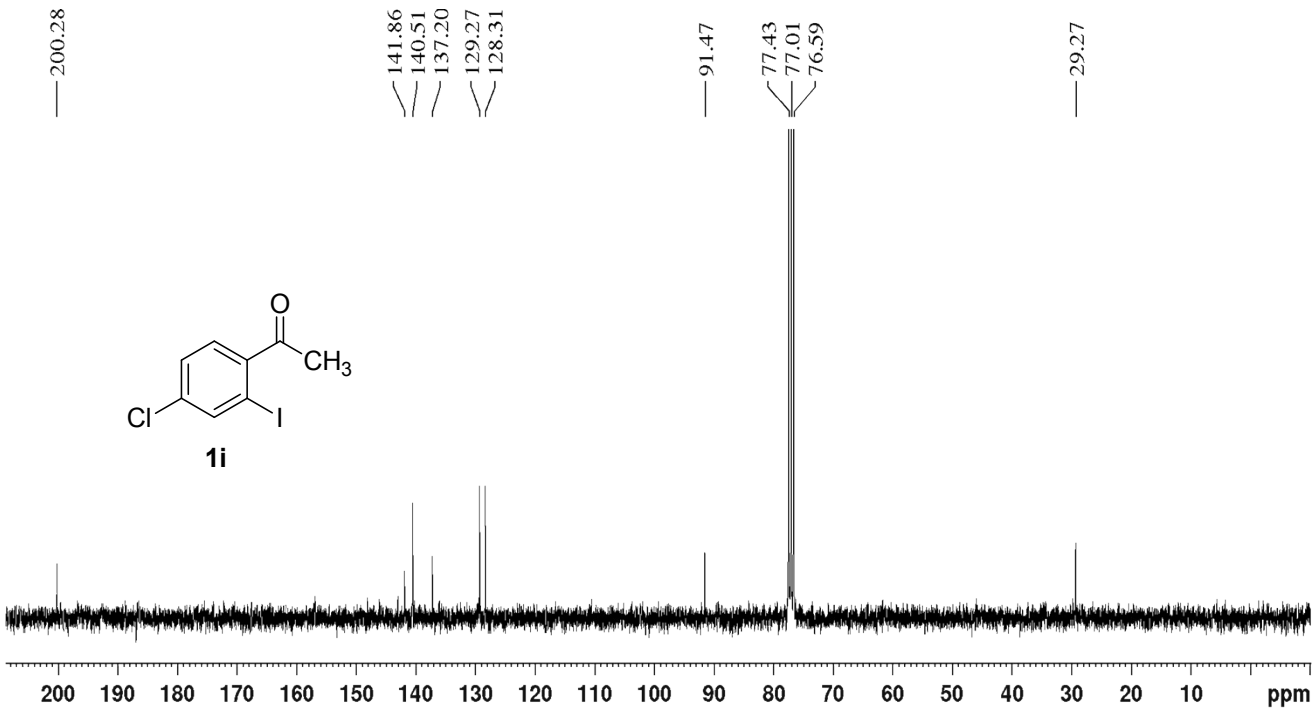

APD54Br 430 (7.983) Sm (Mn, 2x4.00); Cm (426:434)
1: TOF MS ES+
114
277.5490
100
%
0
150.6024
227.7433
278.5640
209.7275
338.9222
475.8516
m/z
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
O
H3CO
CH3
I

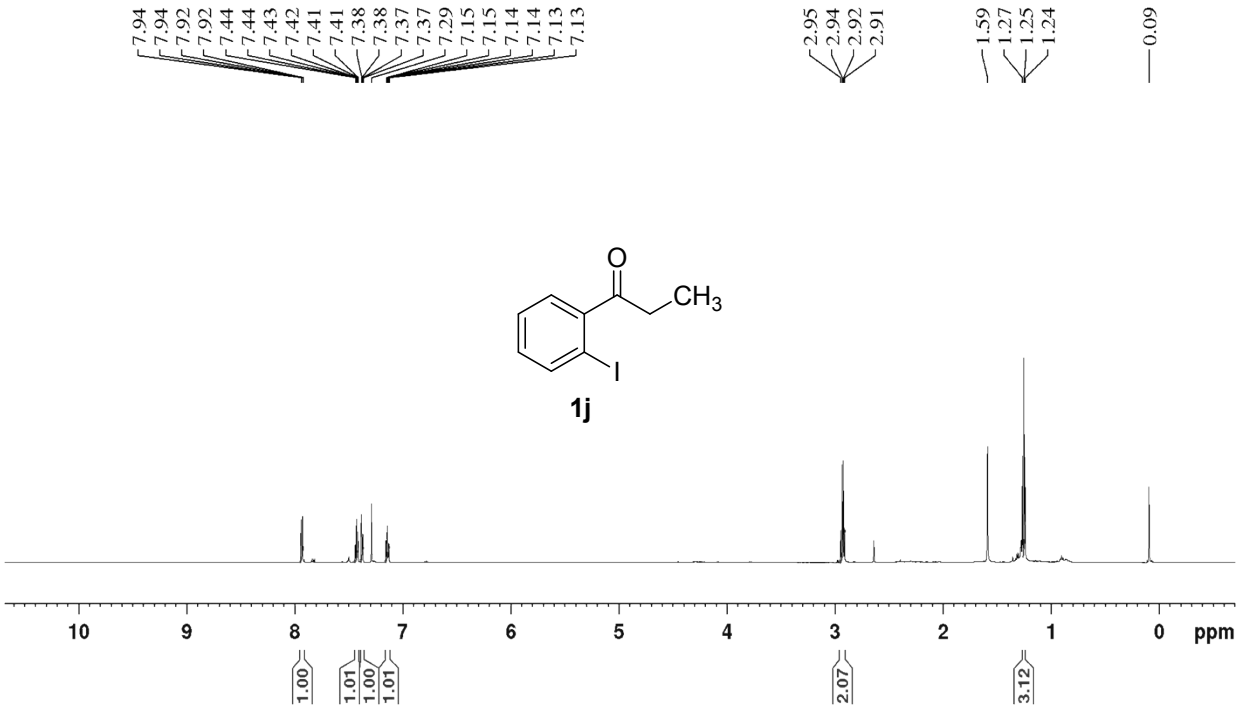
1f

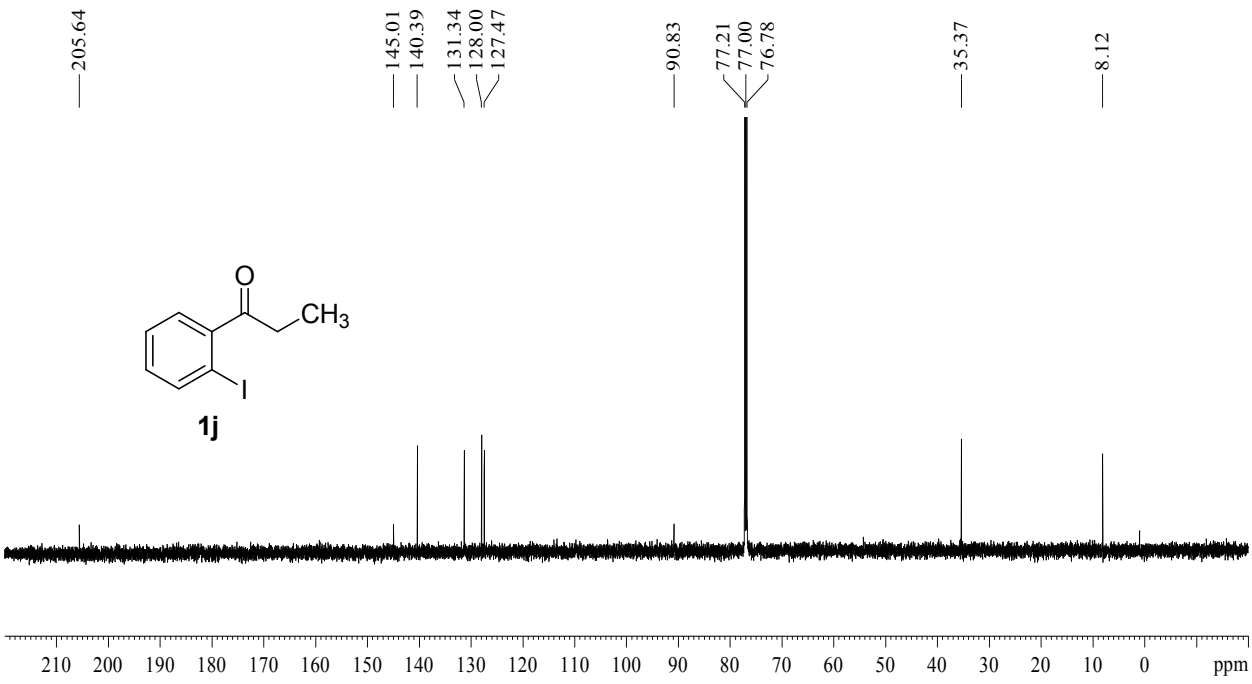

7.37
7.29
7.12
3.94
3.93
2.67
2.07
1.62
1.28
O
H3CO
CH3
H3CO
I
1g
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.04
6.10
3.00

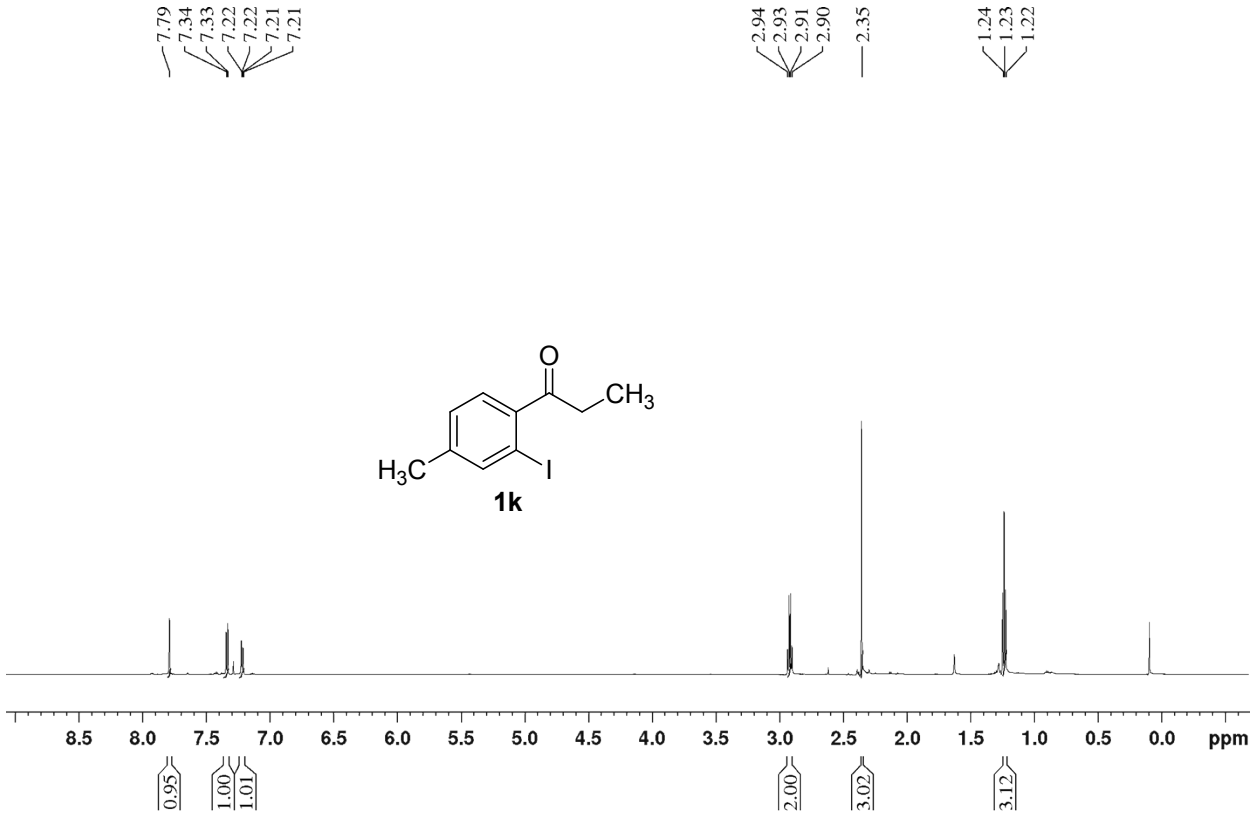

199.72
151.38
148.81
135.39
123.44
112.41
81.59
77.25
77.04
76.83
60.43
56.32
56.09
29.19
14.22
O
H3CO
CH3
H3CO
I
1g
200
180
160
140
120
100
80
60
40
20
0 ppm

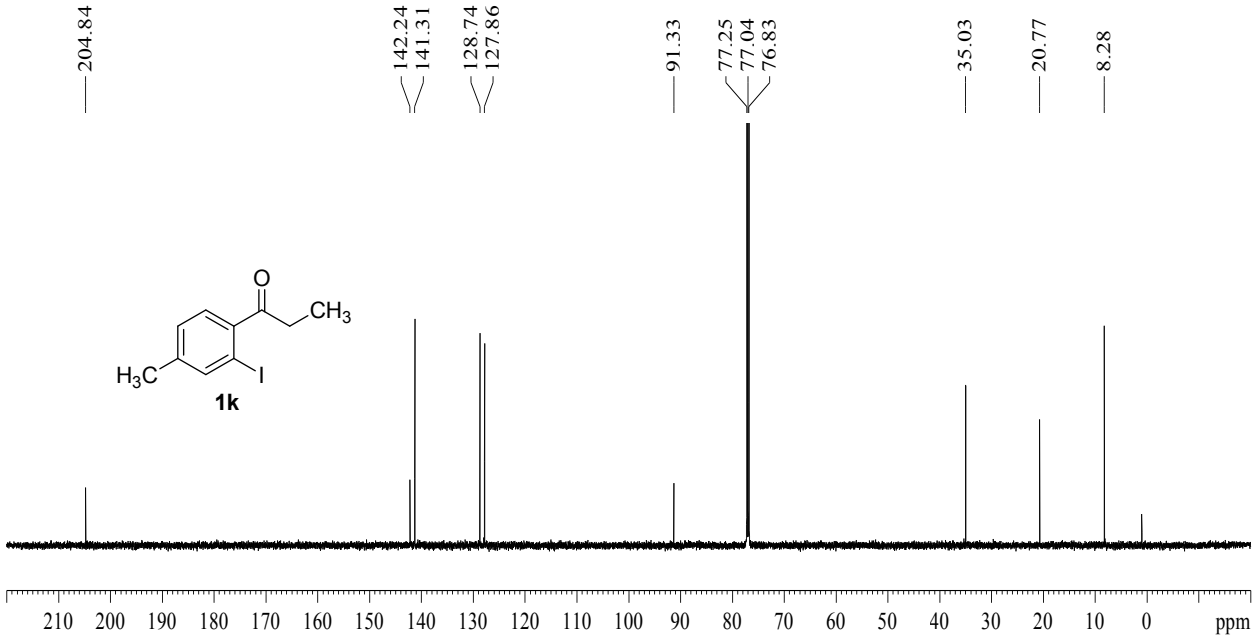

7.98
7.97
7.47
7.44
7.43
7.43
7.40
7.40
7.28
2.63
2.61
O
CH3
Cl
I
1i
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
3.00

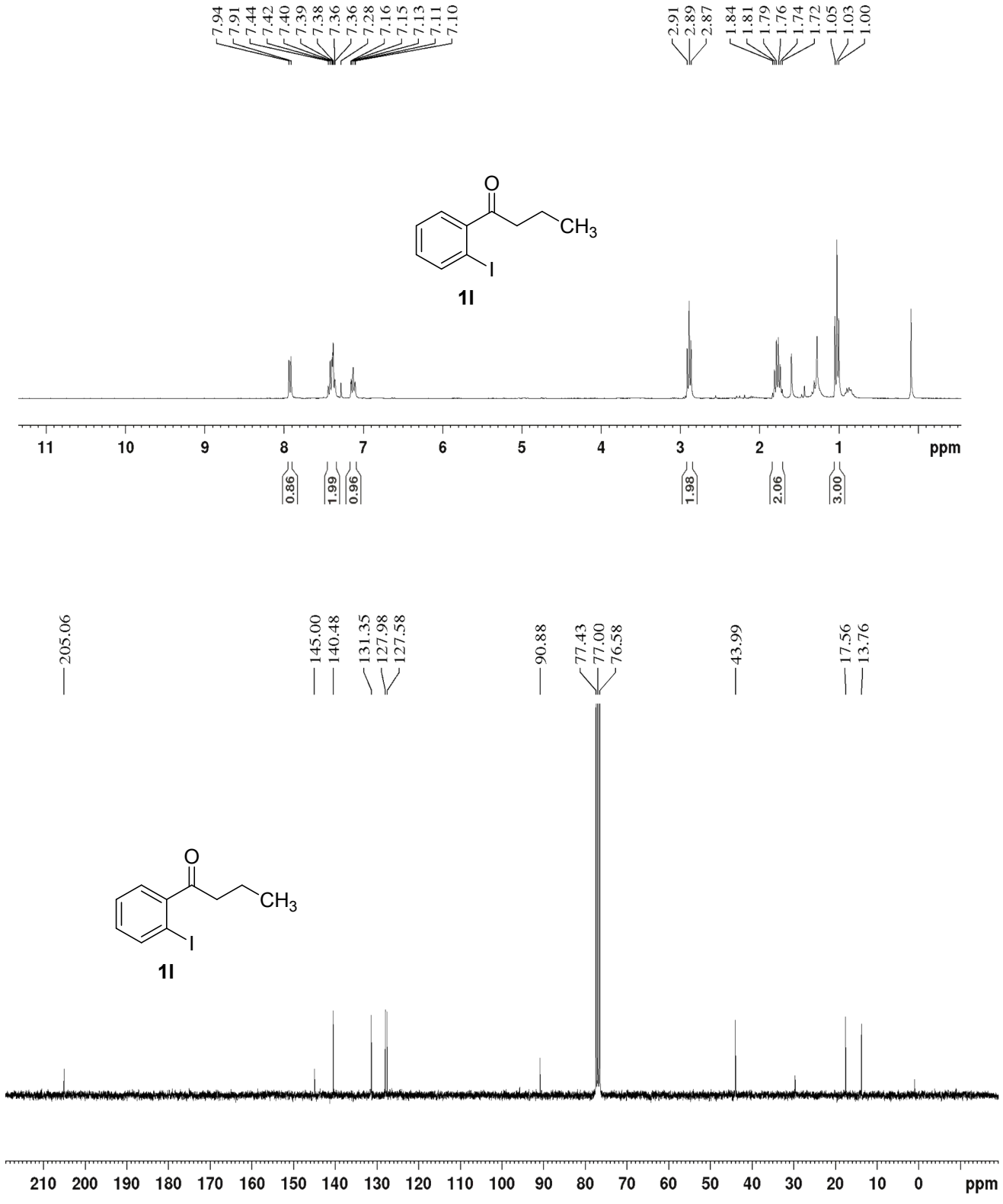

200.28
141.86
140.51
137.20
129.27
128.31
91.47
77.43
77.01
76.59
29.27
O
CH3
Cl
I
1i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

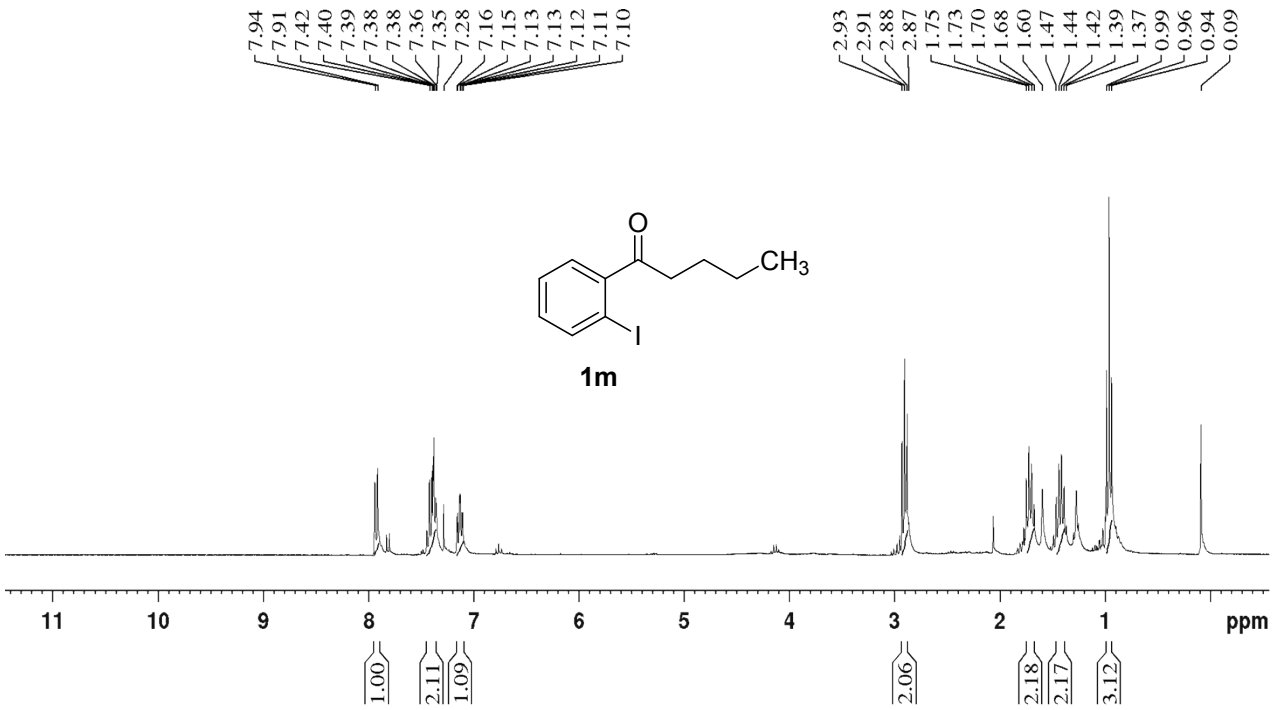

7.94
7.94
7.92
7.92
7.44
7.44
7.43
7.42
7.41
7.41
7.38
7.38
7.37
7.37
7.29
7.15
7.15
7.14
7.14
7.13
7.13
2.95
2.94
2.92
2.91
1.59
1.27
1.25
1.24
0.09
O
CH3
I
1j
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
1.01
2.07
3.12

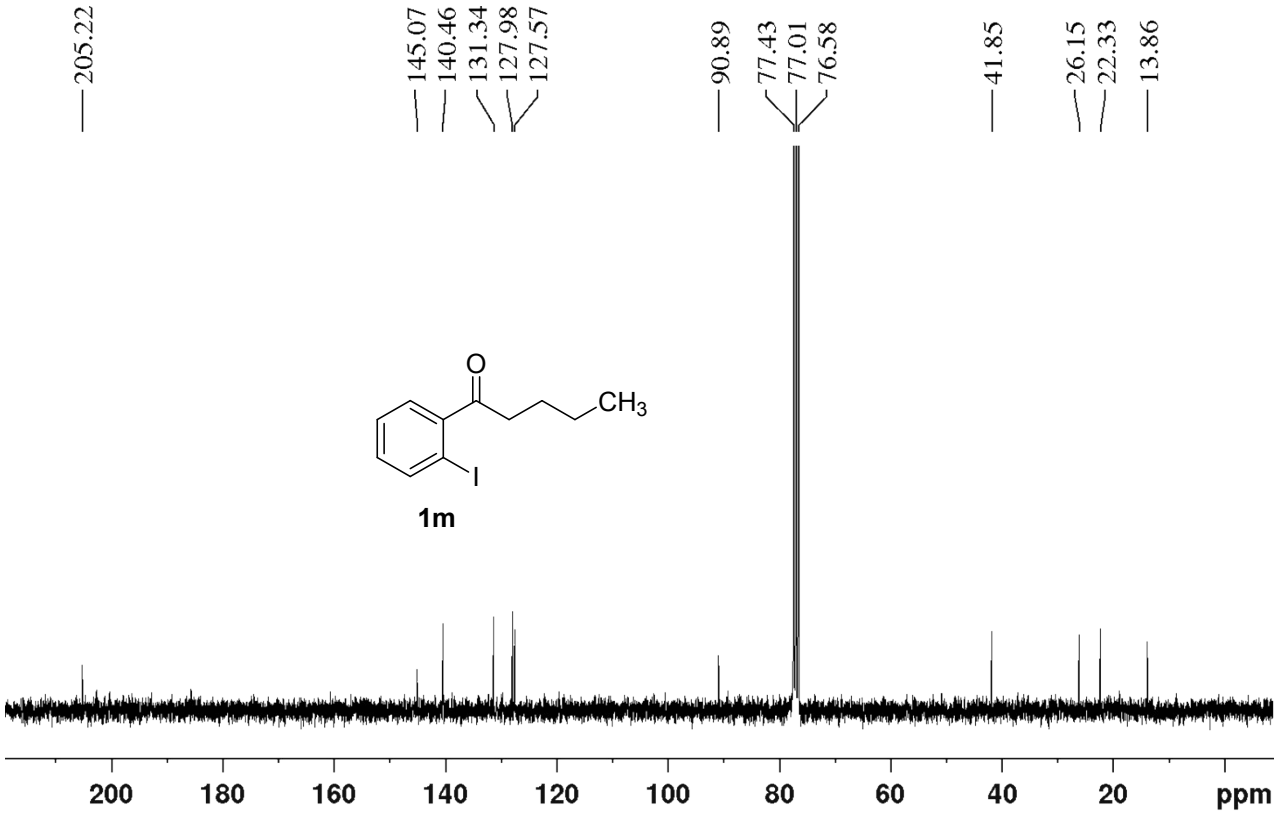

205.64
145.01
140.39
131.34
128.00
127.47
90.83
77.21
77.00
76.78
35.37
8.12
O
CH3
I
1j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

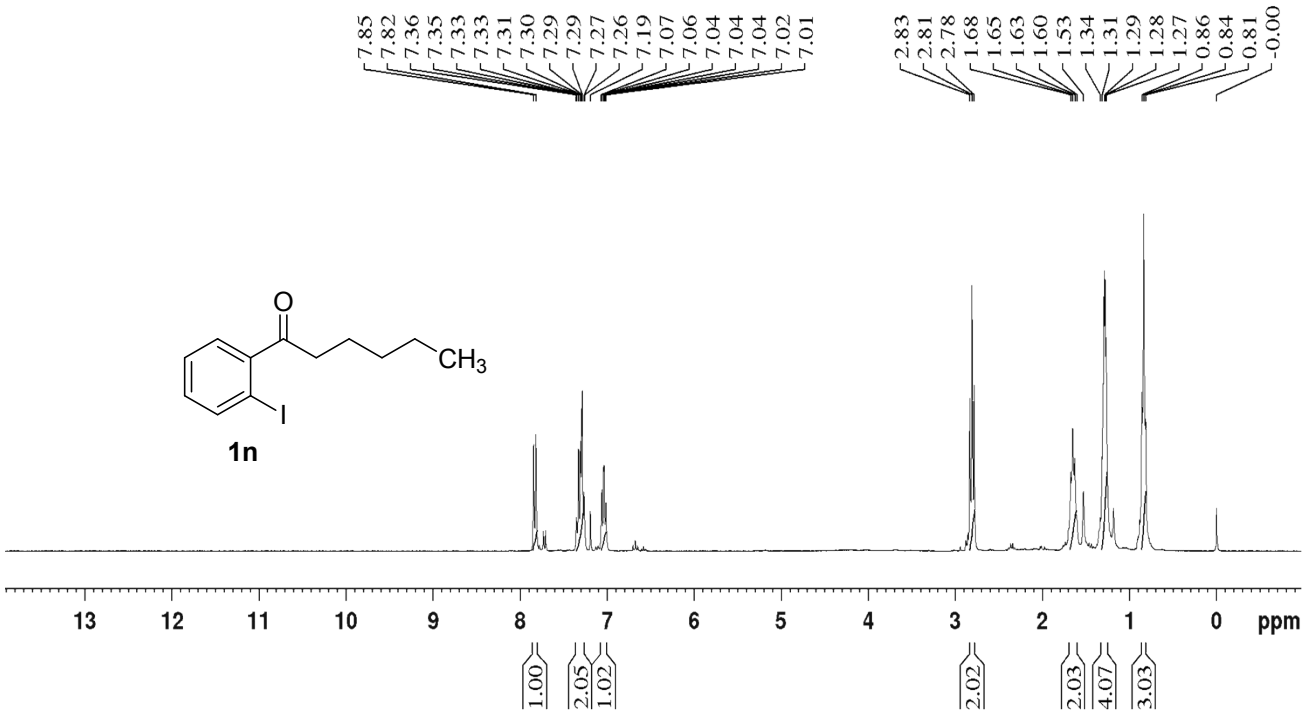

7.79
7.34
7.33
7.22
7.22
7.21
7.21
2.94
2.93
2.91
2.90
2.35
1.24
1.23
1.22
O
CH3
H3C
I
1k
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
1.00
1.01
2.00
3.02
3.12

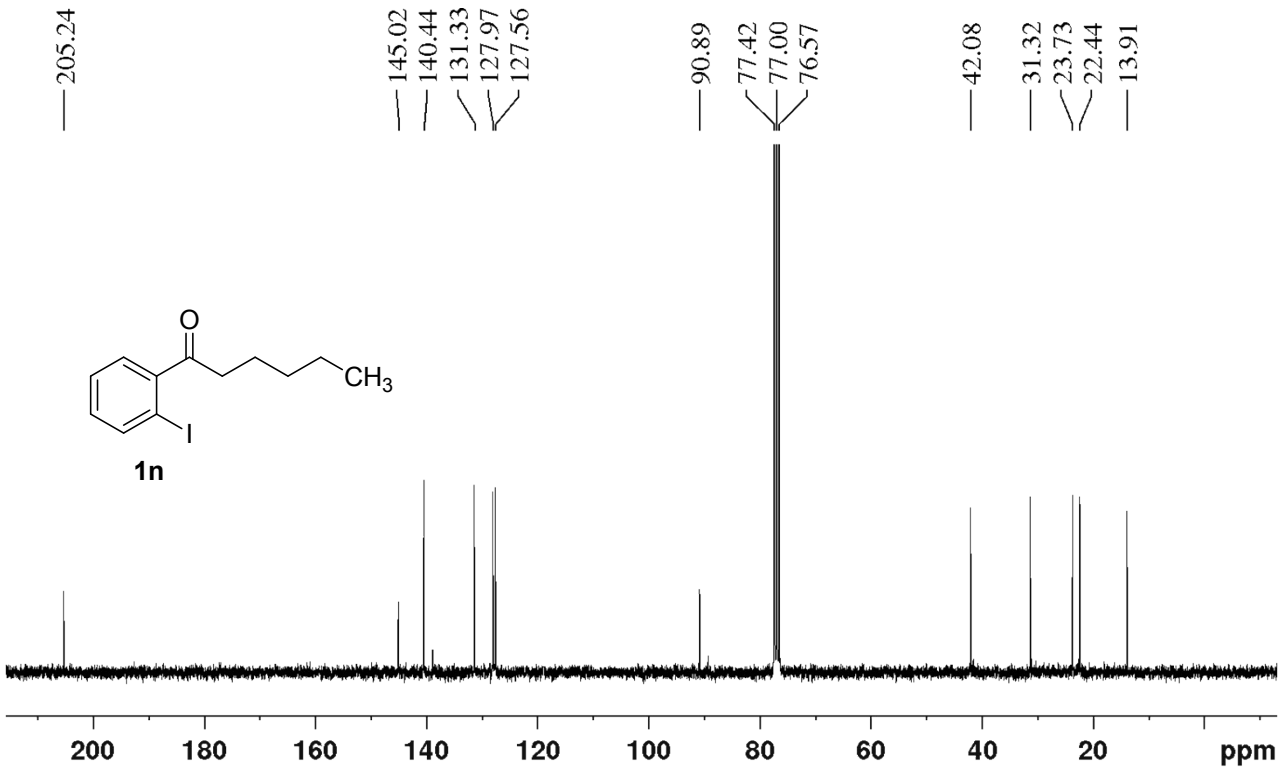

204.84
142.24
141.31
128.74
127.86
91.33
77.25
77.04
76.83
35.03
20.77
8.28
O
CH3
H3C
I
1k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

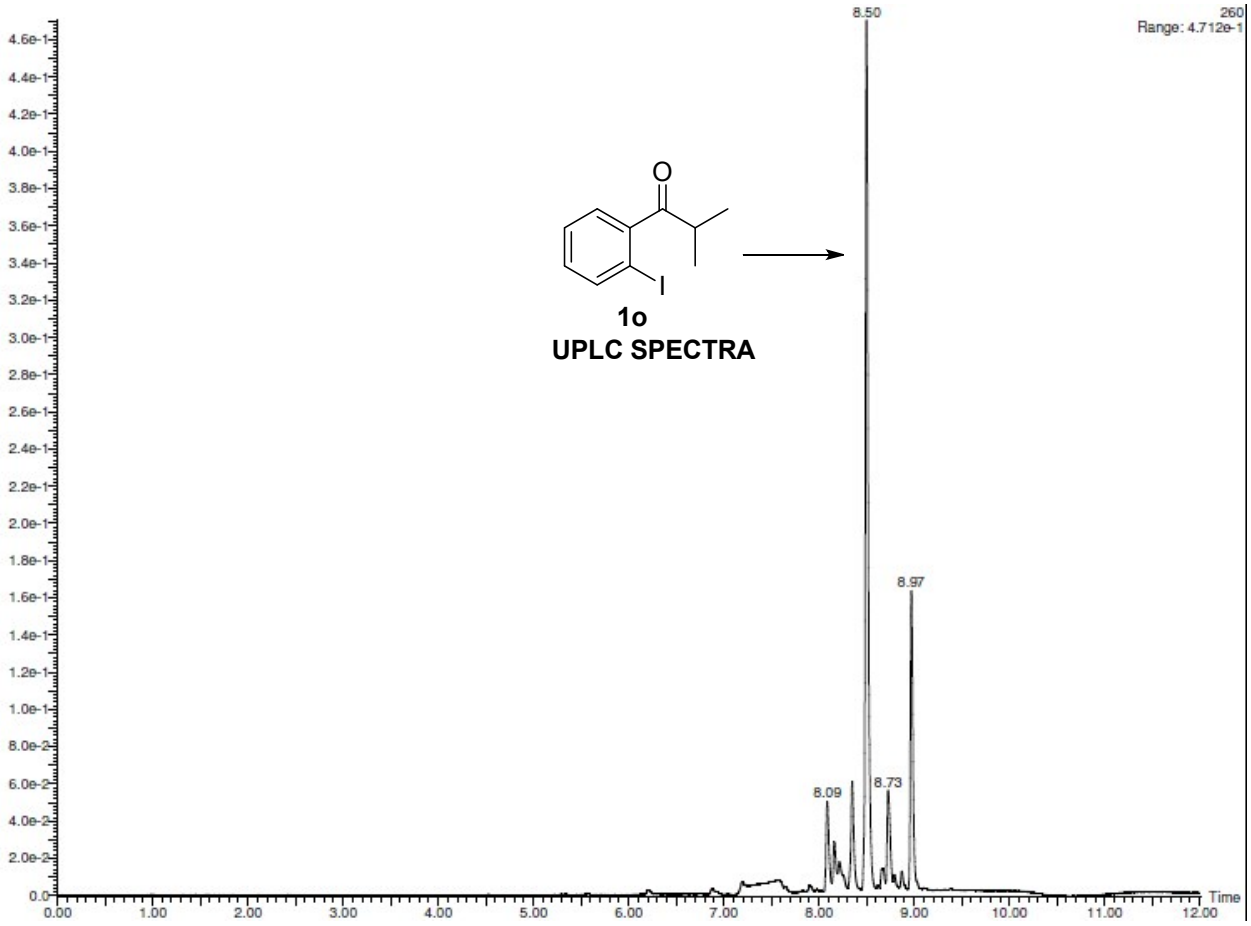

7.94
7.91
7.44
7.42
7.40
7.39
7.38
7.36
7.36
7.28
7.16
7.15
7.13
7.11
7.10
2.91
2.89
2.87
1.84
1.81
1.79
1.76
1.74
1.72
1.05
1.03
1.00
O
CH3
I
1l
11
10
9
8
7
6
5
4
3
2
1
ppm
0.86
1.99
0.96
1.98
2.06
3.00
205.06
145.00
140.48
131.35
127.98
127.58
90.88
77.43
77.00
76.58
43.99
17.56
13.76
O
CH3
I
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.94
7.91
7.42
7.40
7.39
7.38
7.38
7.36
7.35
7.28
7.16
7.15
7.13
7.13
7.12
7.11
7.10
2.93
2.91
2.88
2.87
1.75
1.73
1.70
1.68
1.60
1.47
1.44
1.42
1.39
1.37
0.99
0.96
0.94
0.09
O
CH3
I
1m
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.11
1.09
2.06
2.18
2.17
3.12


205.22
145.07
140.46
131.34
127.98
127.57
90.89
77.43
77.01
76.58
41.85
26.15
22.33
13.86
O
CH3
I
1m
200
180
160
140
120
100
80
60
40
20
ppm

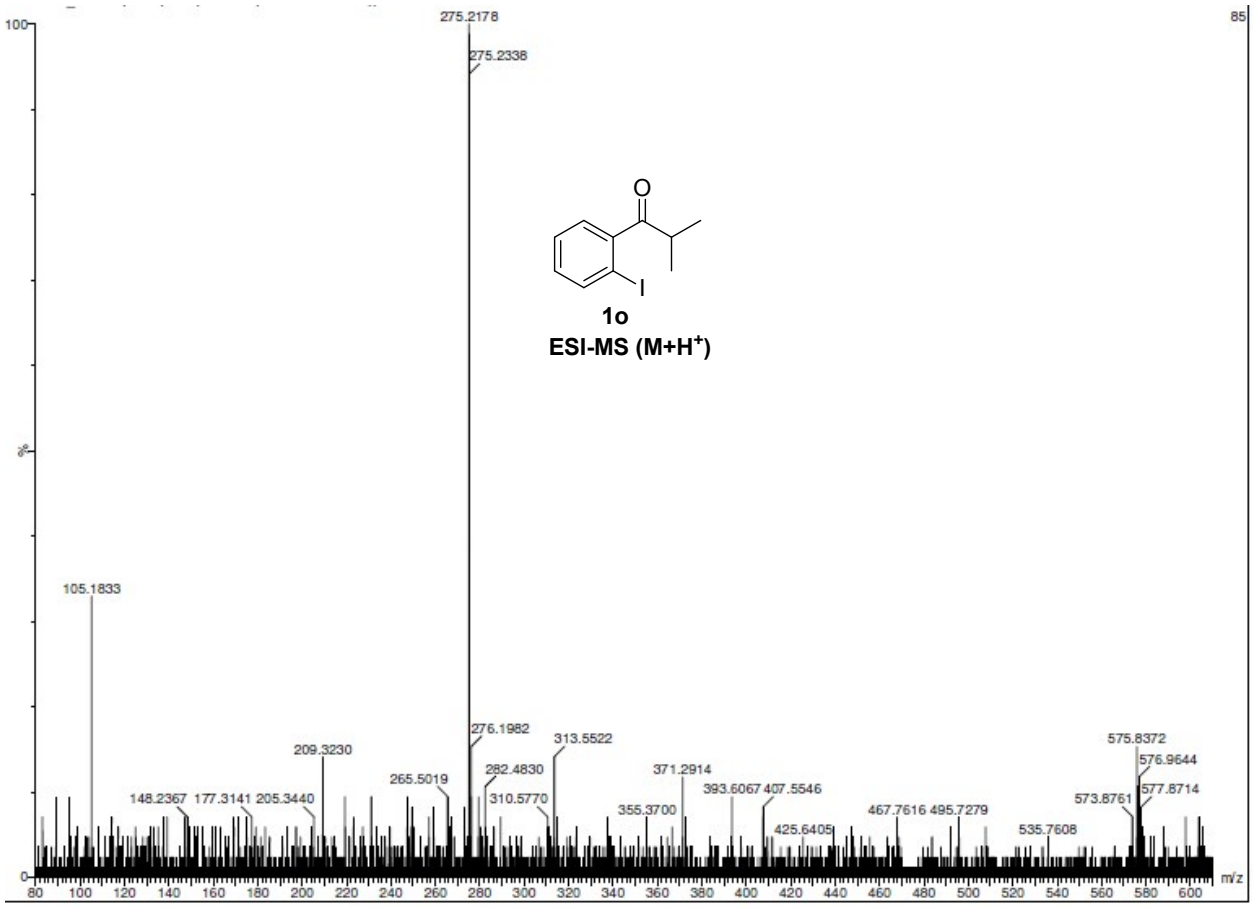

7.85
7.82
7.36
7.35
7.33
7.33
7.31
7.30
7.29
7.29
7.27
7.26
7.19
7.07
7.06
7.04
7.04
7.04
7.02
7.01
2.83
2.81
2.78
1.68
1.65
1.63
1.60
1.53
1.34
1.31
1.29
1.28
1.27
0.86
0.84
0.81
-0.00
O
CH3
I
1n
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.05
1.02
2.02
2.03
4.07
3.03


205.24
145.02
140.44
131.33
127.97
127.56
90.89
77.42
77.00
76.57
42.08
31.32
23.73
22.44
13.91
O
CH3
I
1n
200
180
160
140
120
100
80
60
40
20
ppm



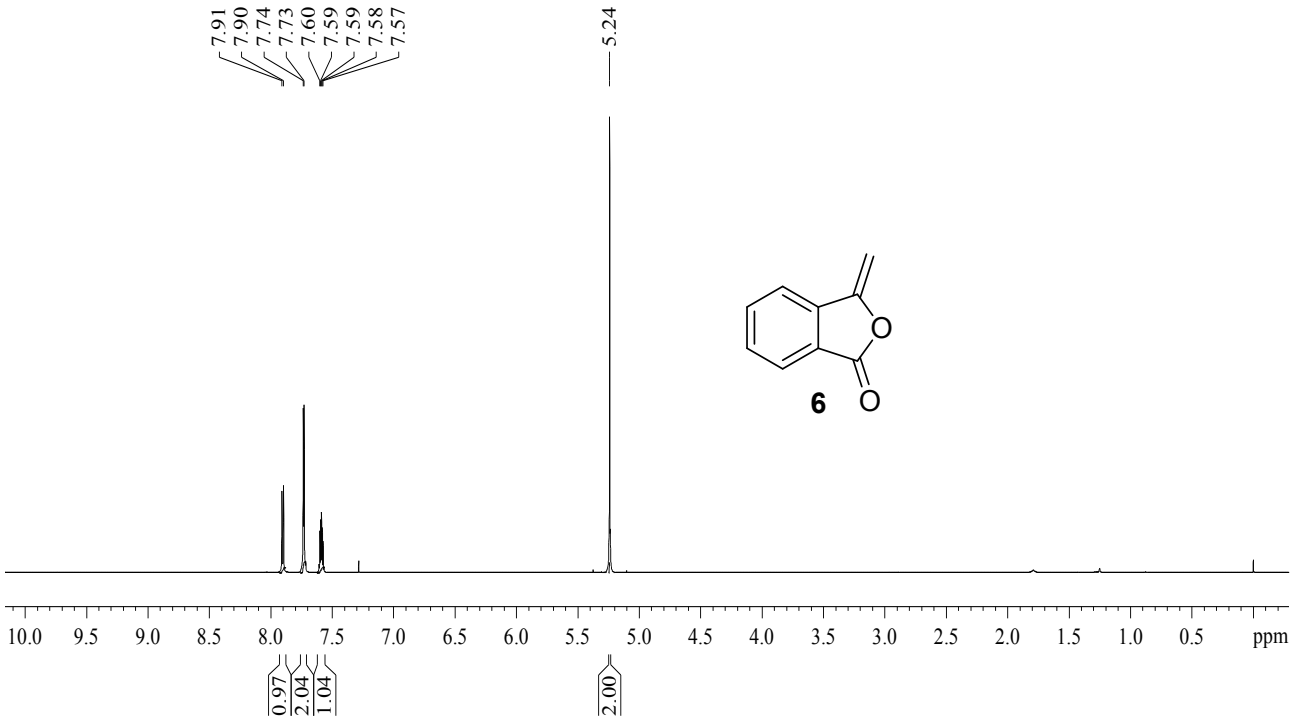
1o

UPLC SPECTRA

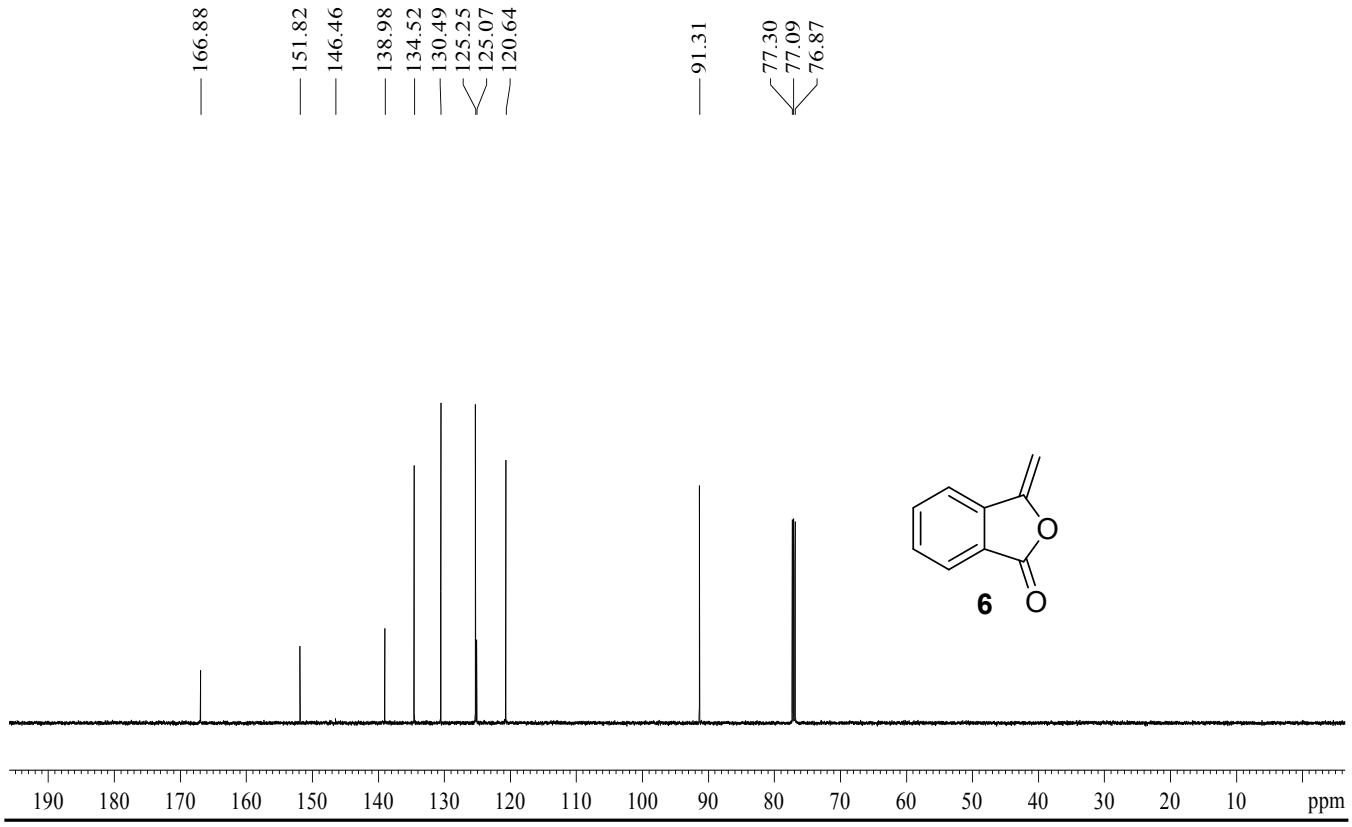

275.2178
275.2338
105.1833
209.3230
276.1982
313.5522
282.4830
265.5019
310.5770
371.2914
393.6067
407.5546
148.2367
177.3141
205.3440
355.3700
425.6405
467.7616
495.7279
535.7608
573.8761
575.8372
576.9644
577.8714
m/z

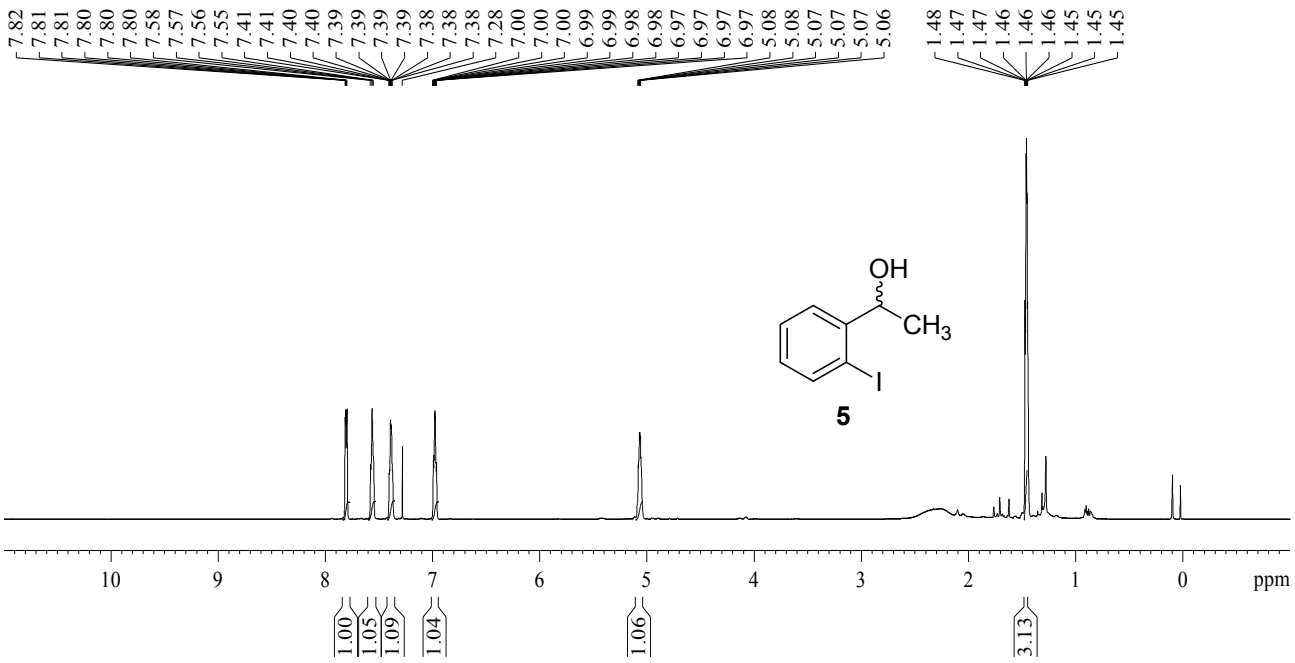
1o

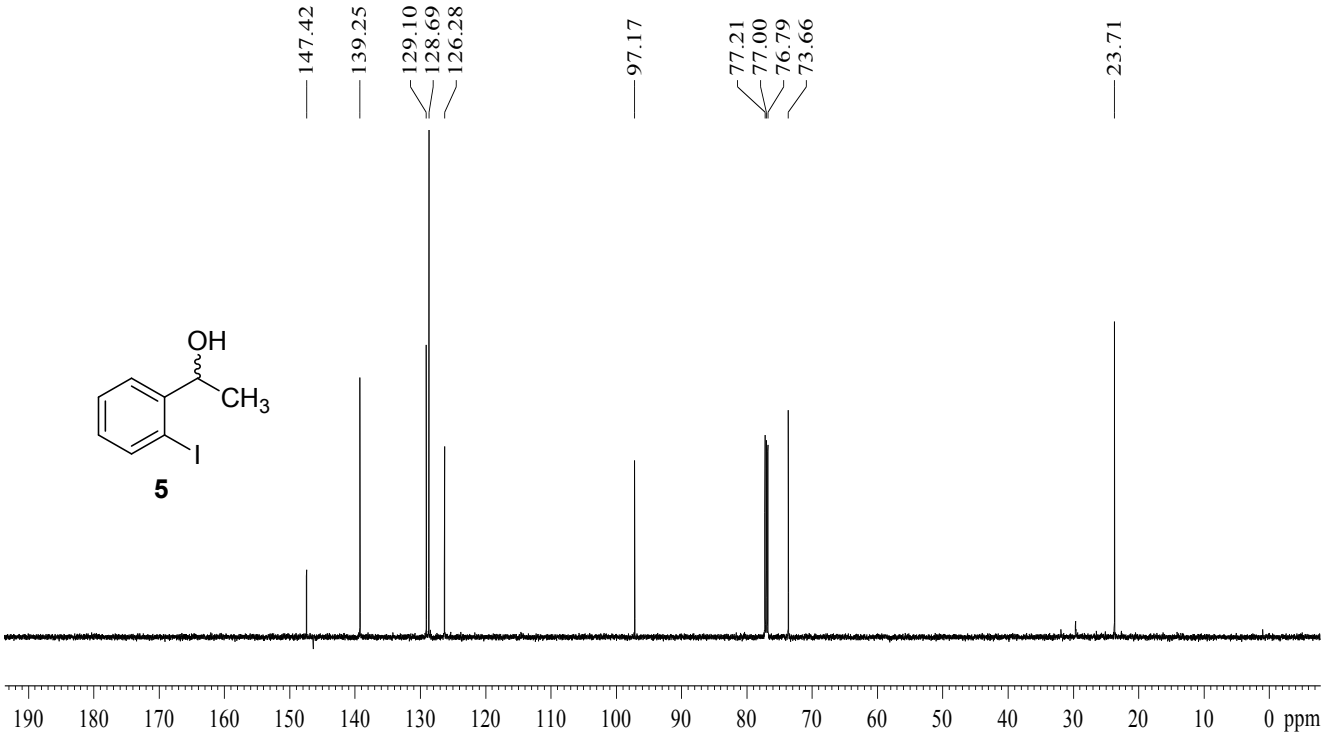
ESI-MS ($M+H^+$)


7.91
7.90
7.74
7.73
7.60
7.59
7.59
7.58
7.57
5.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
2.04
1.04
2.00

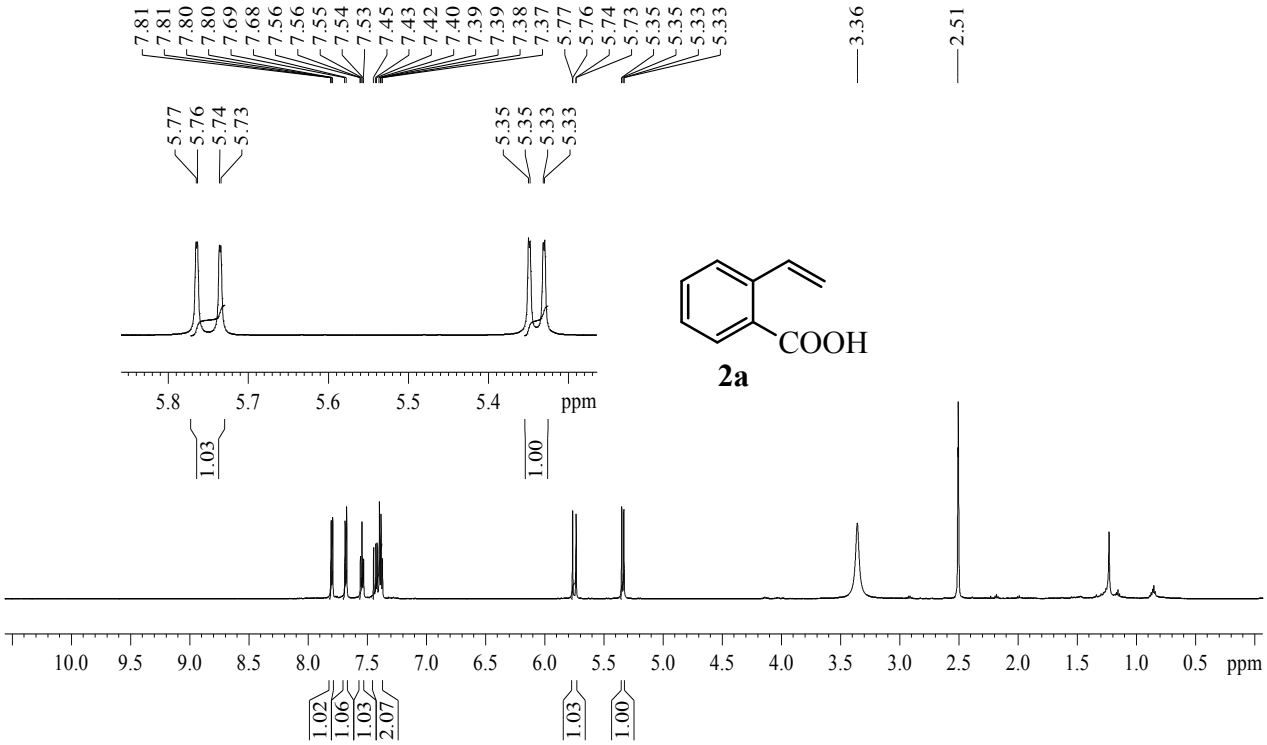
6

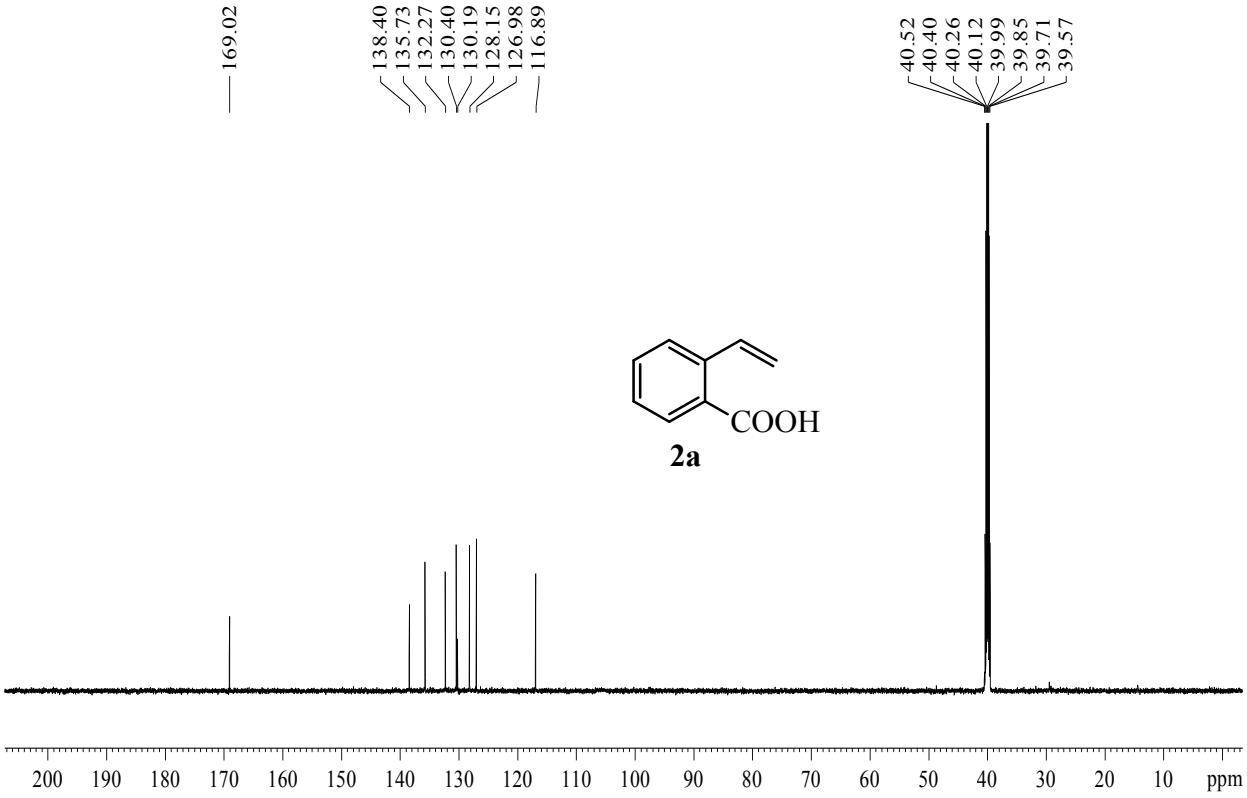

166.88
151.82
146.46
138.98
134.52
130.49
125.25
125.07
120.64
91.31
77.30
77.09
76.87
O
O
6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

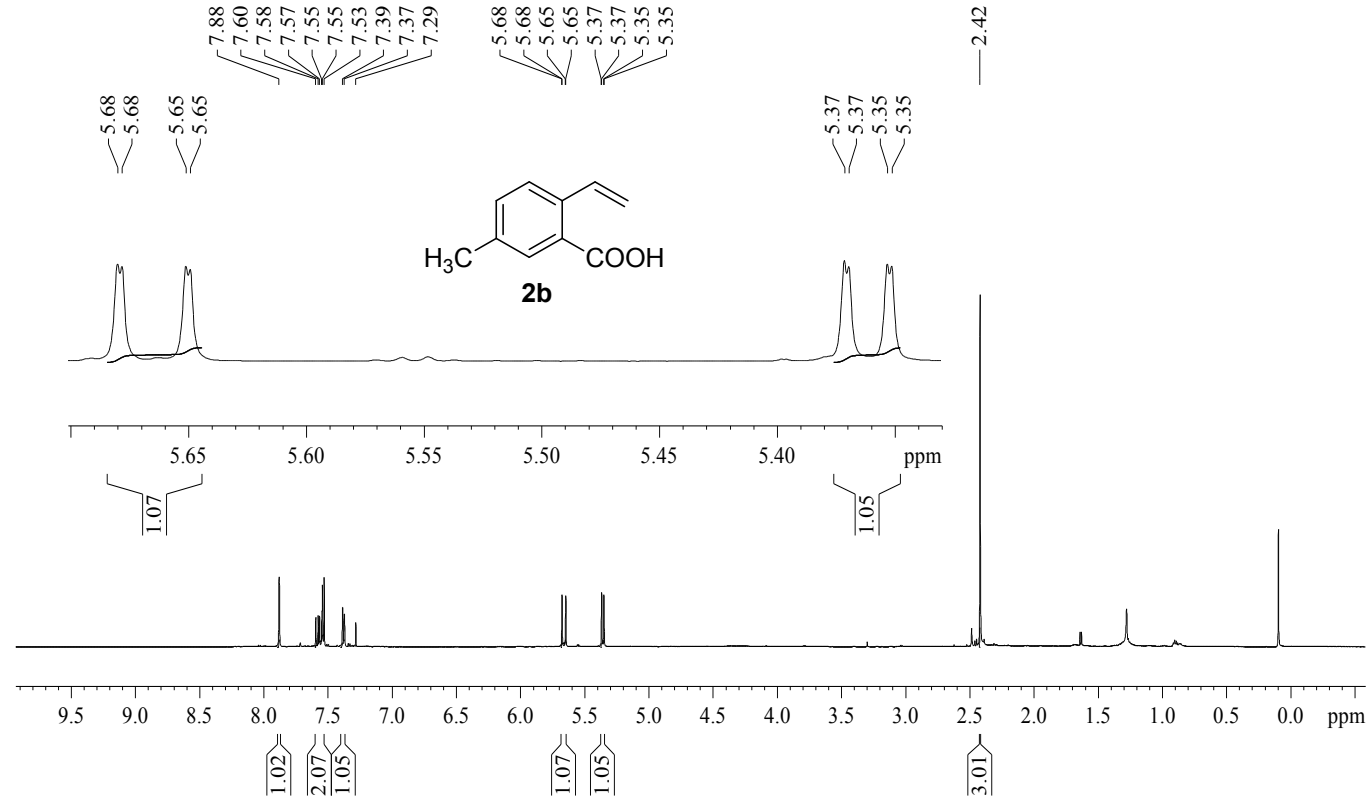

7.82 7.81 7.81 7.80 7.80 7.80 7.58 7.57 7.56 7.55 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.28 7.00 7.00 7.00 6.99 6.99 6.98 6.98 6.97 6.97 6.97 6.97 5.08 5.08 5.07 5.07 5.07 5.06
1.48 1.47 1.47 1.46 1.46 1.46 1.45 1.45 1.45
OH
CH3
I
5
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.05 1.09 1.04 1.06 3.13

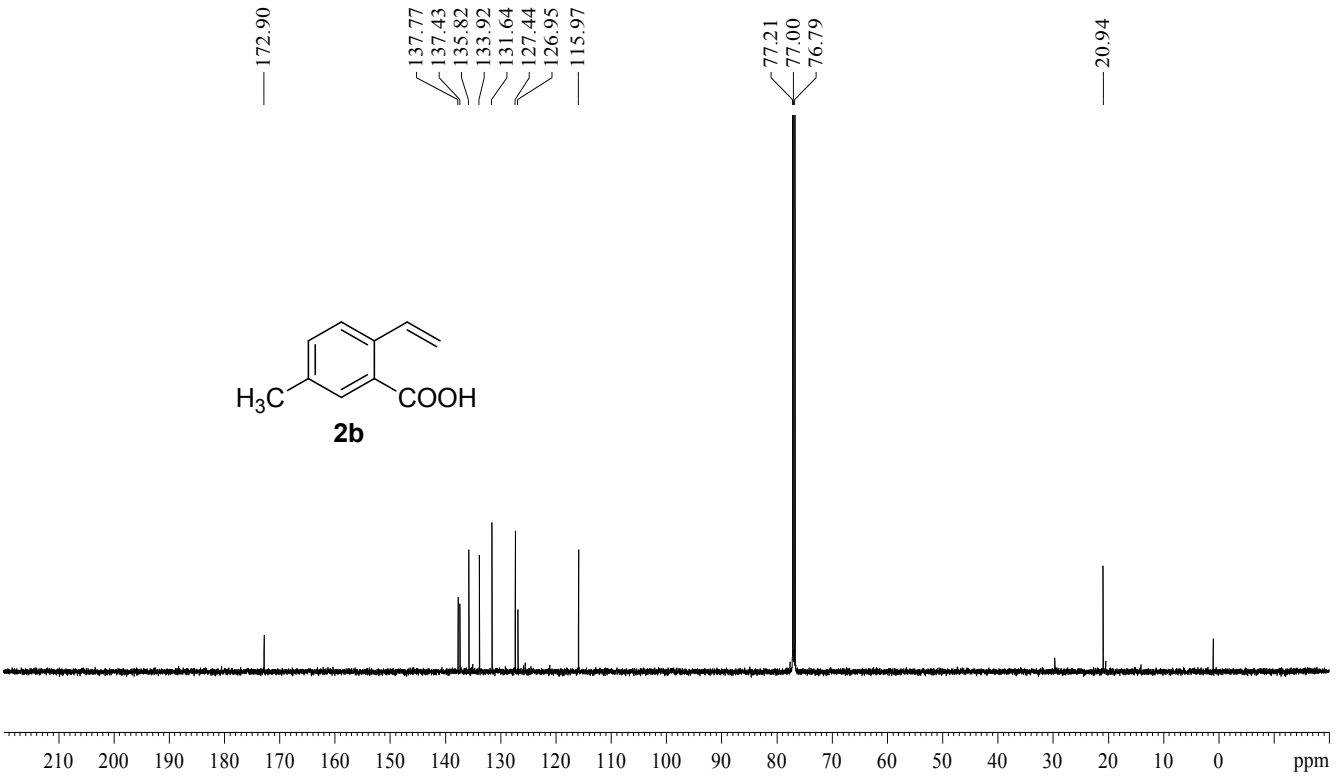

147.42
139.25
129.10
128.69
126.28
97.17
77.21
77.00
76.79
73.66
23.71
OH
CH3
I
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

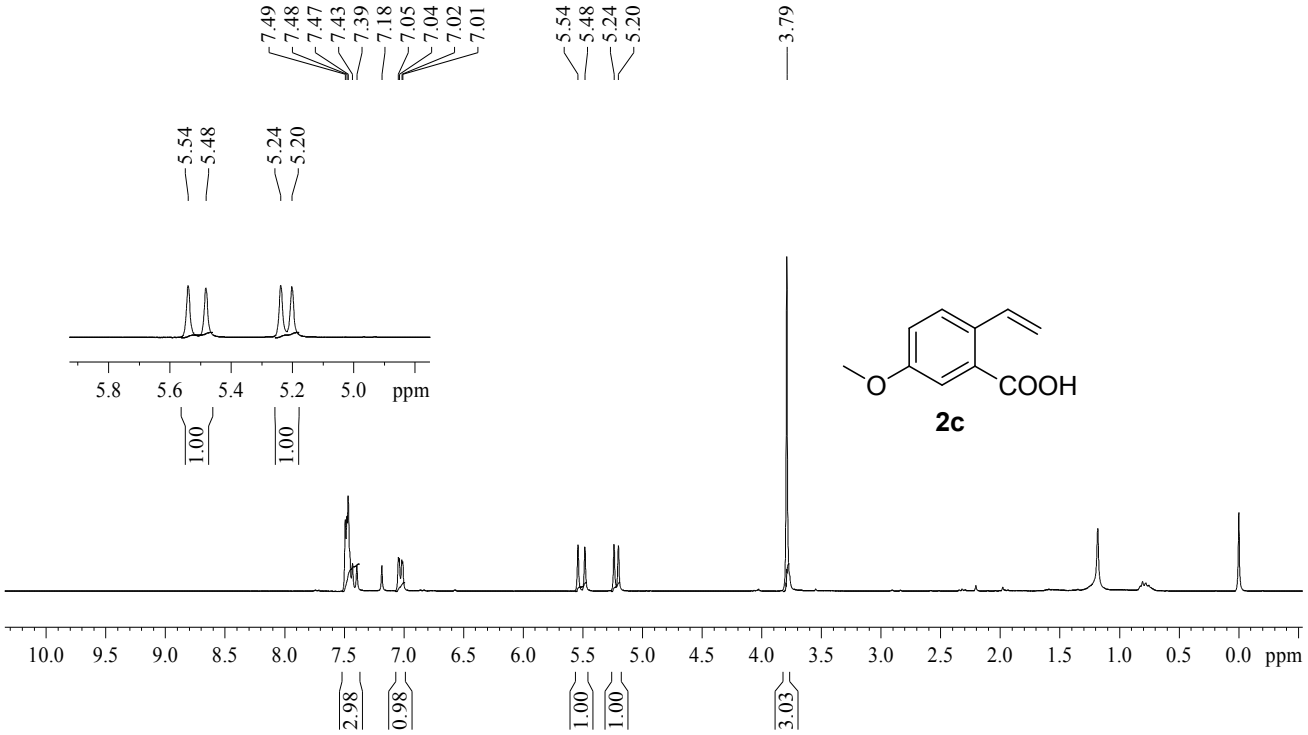
9. NMR spectra of final products

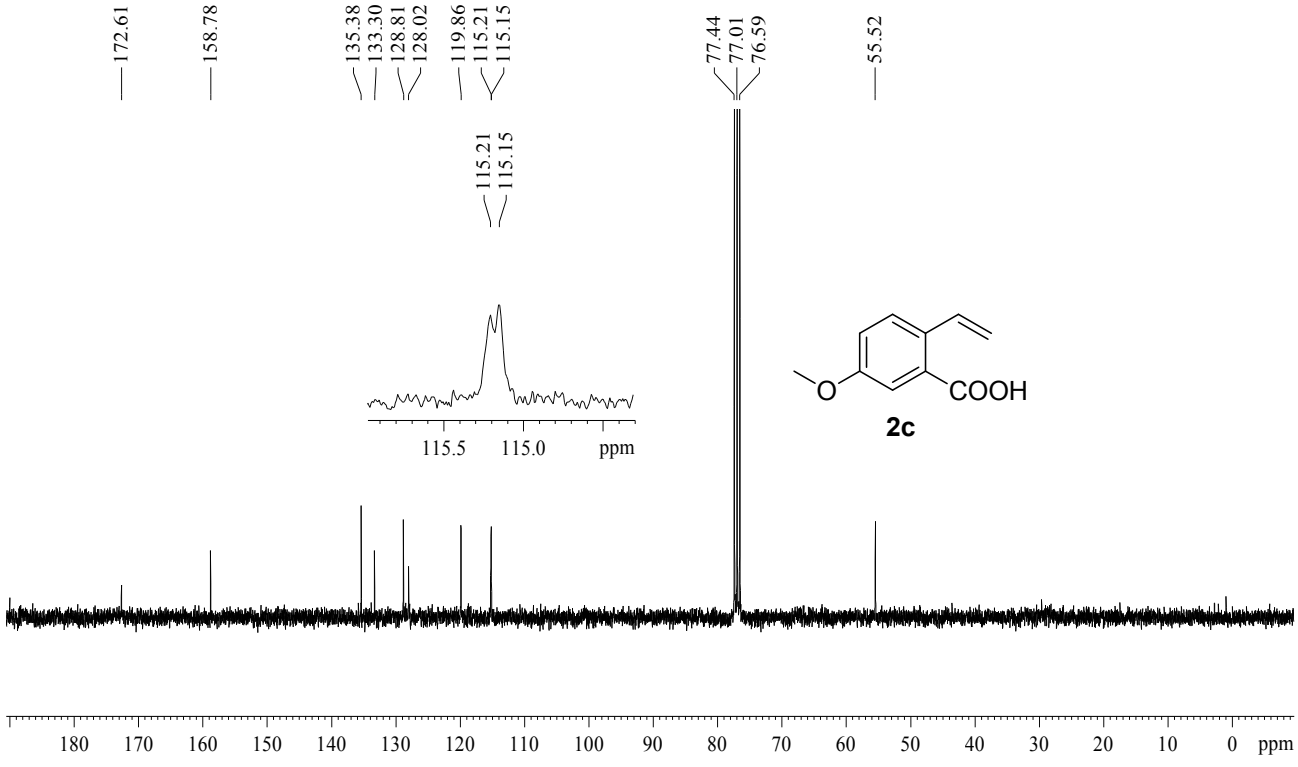


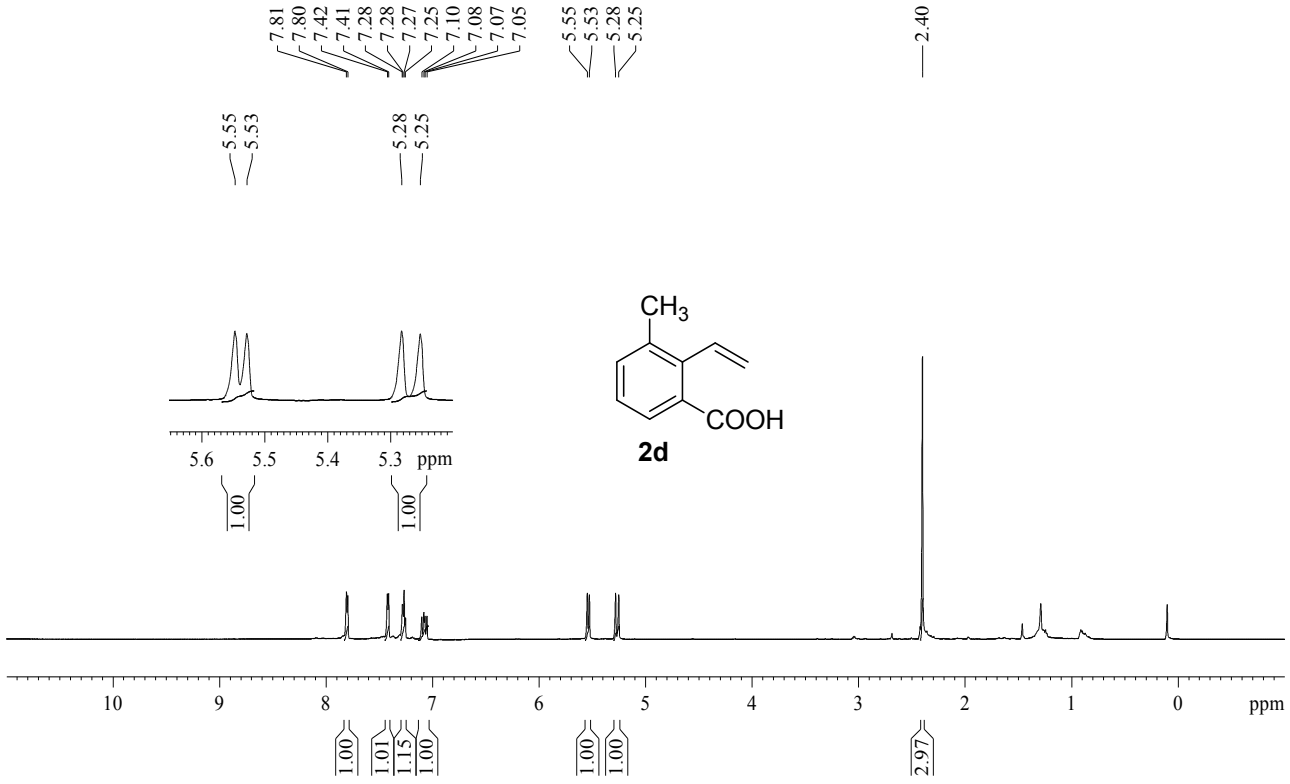


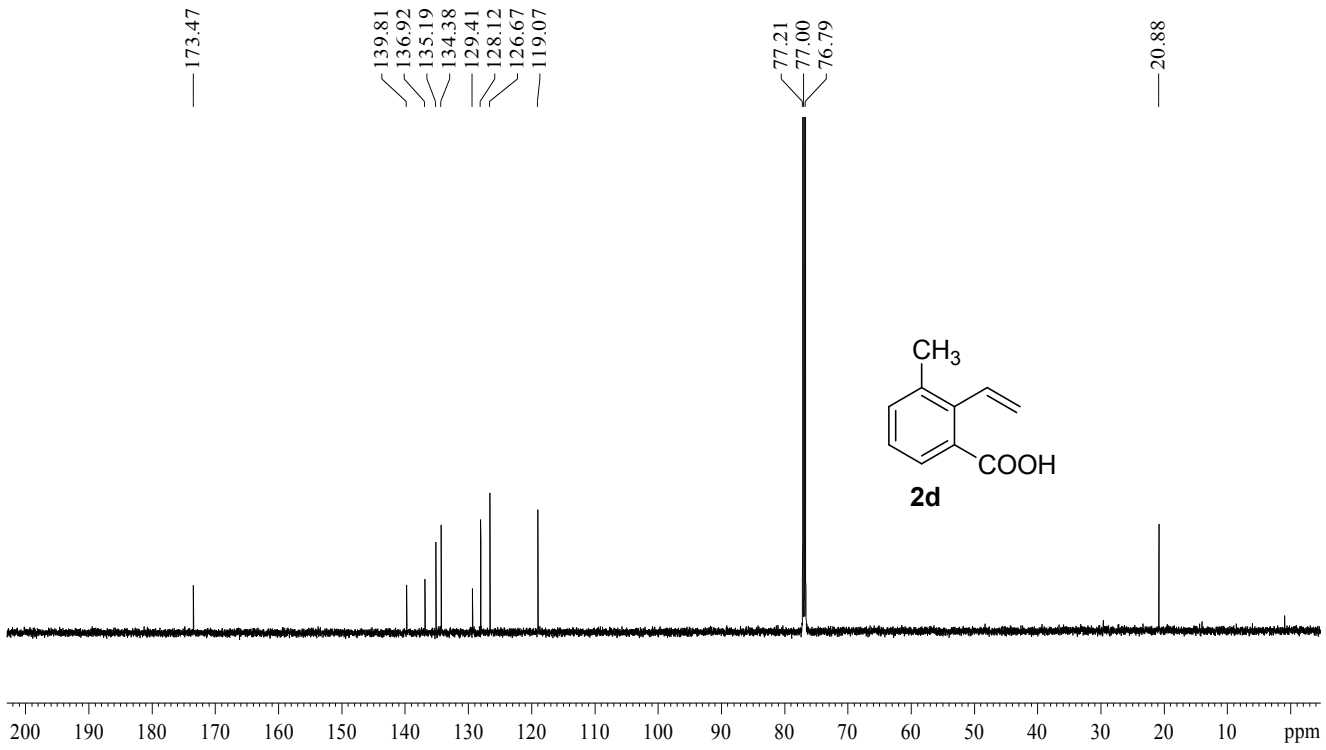

7.88
7.60
7.58
7.57
7.55
7.55
7.53
7.39
7.37
7.29
5.68
5.68
5.65
5.65
5.37
5.37
5.35
5.35
2.42
H3C
COOH
2b
5.65
5.60
5.55
5.50
5.45
5.40
ppm
1.07
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.02
2.07
1.05
1.07
1.05
3.01

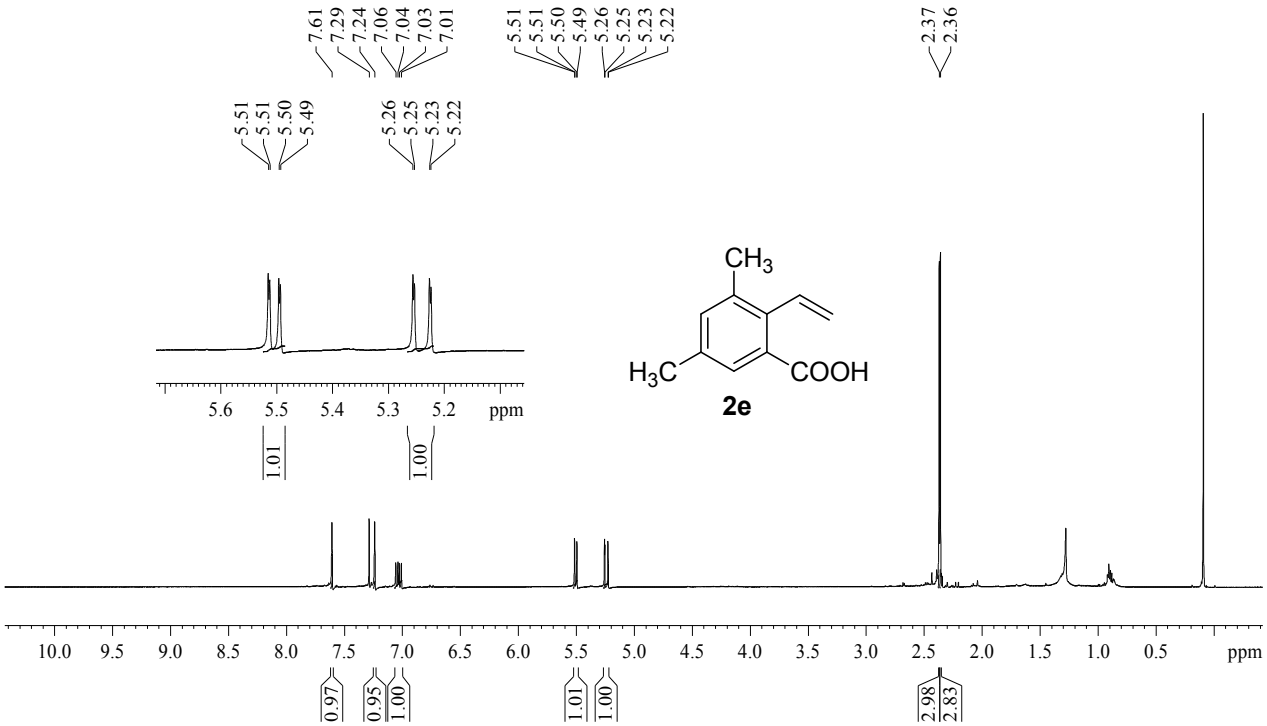

172.90
137.77
137.43
135.82
133.92
131.64
127.44
126.95
115.97
77.21
77.00
76.79
20.94
H3C
COOH
2b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

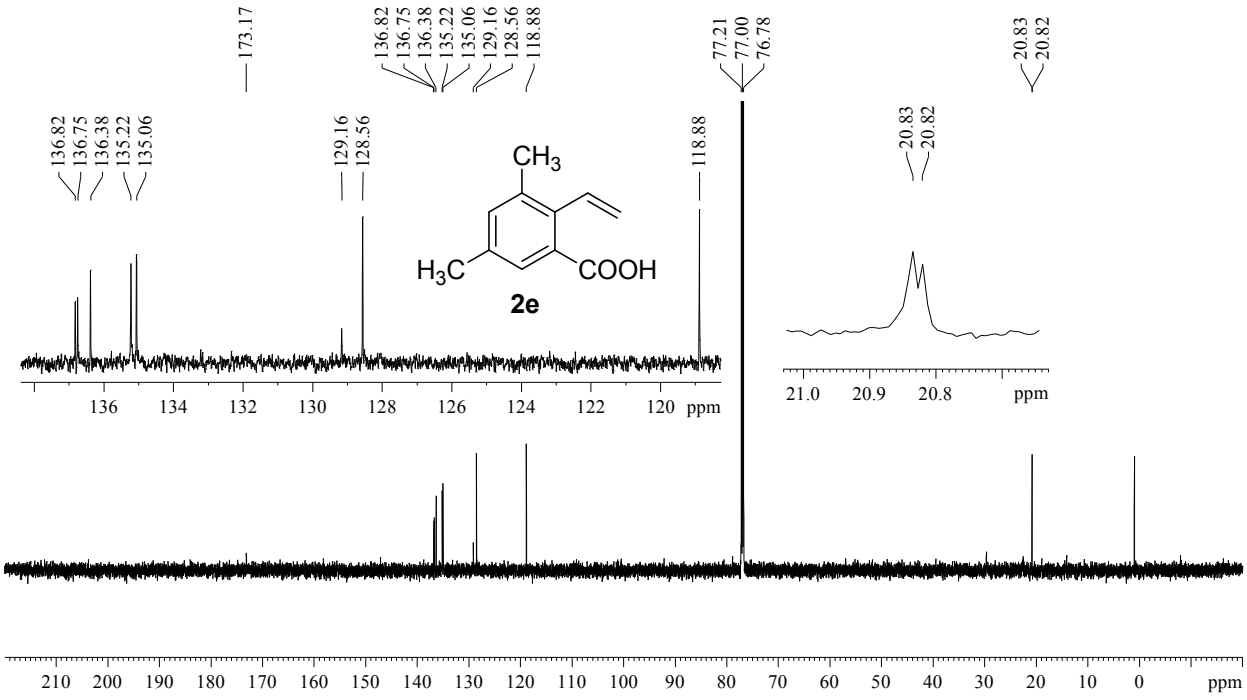

7.49
7.48
7.47
7.43
7.39
7.18
7.05
7.04
7.02
7.01
5.54
5.48
5.24
5.20
3.79
5.8
5.6
5.4
5.2
5.0
ppm
1.00
1.00
O
COOH
2c
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.98
0.98
1.00
1.00
3.03

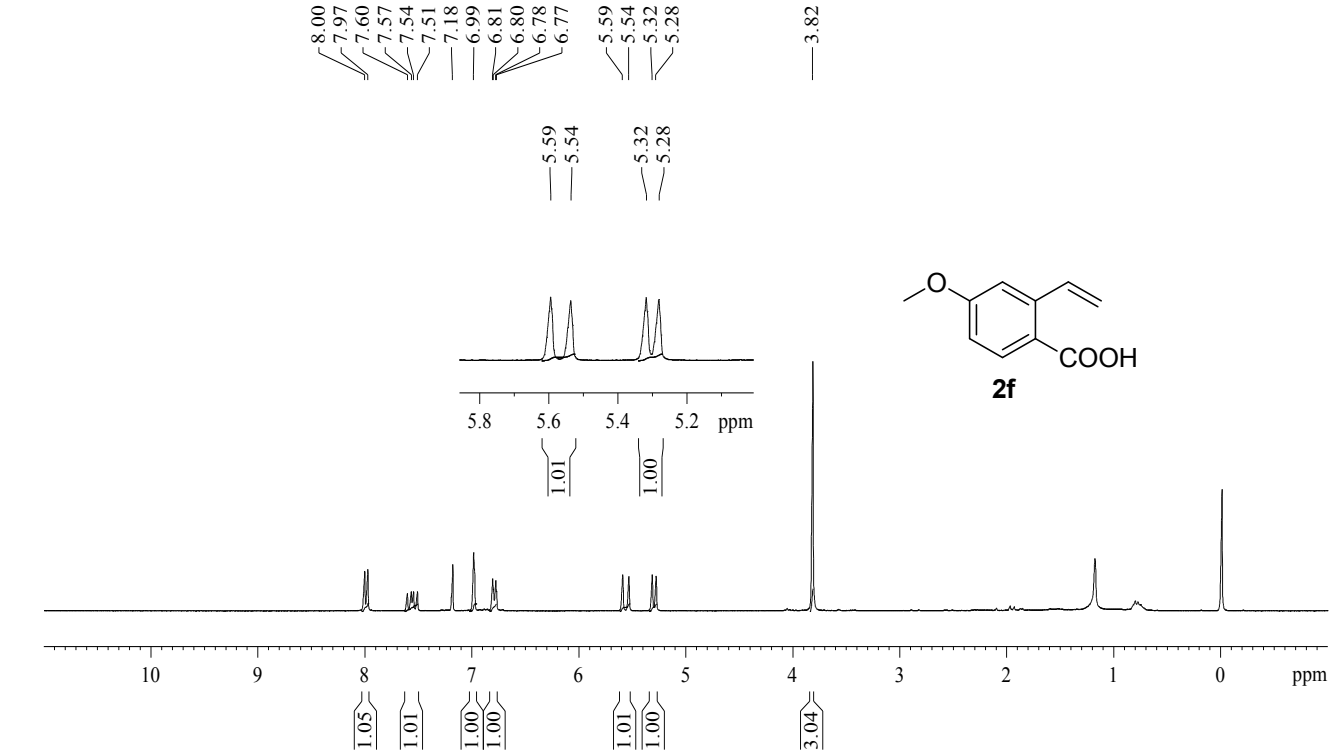

172.61
158.78
135.38
133.30
128.81
128.02
119.86
115.21
115.15
77.44
77.01
76.59
55.52
115.21
115.15
115.5
115.0
ppm
O
COOH
2c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

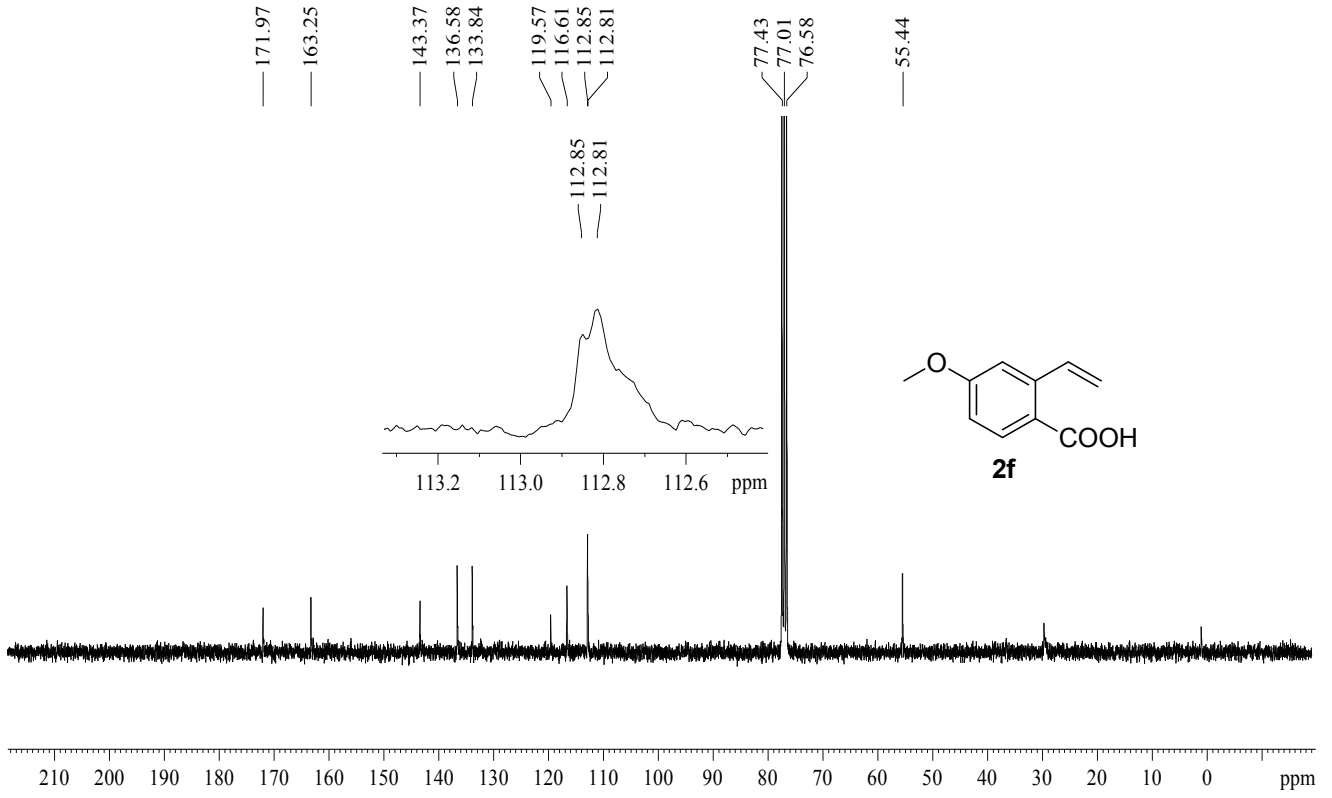

7.81
7.80
7.42
7.41
7.28
7.28
7.27
7.25
7.10
7.08
7.07
7.05
5.55
5.53
5.28
5.25
2.40
CH3
COOH
2d
5.6
5.5
5.4
5.3 ppm
1.00
1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.15
1.00
1.00
1.00
2.97

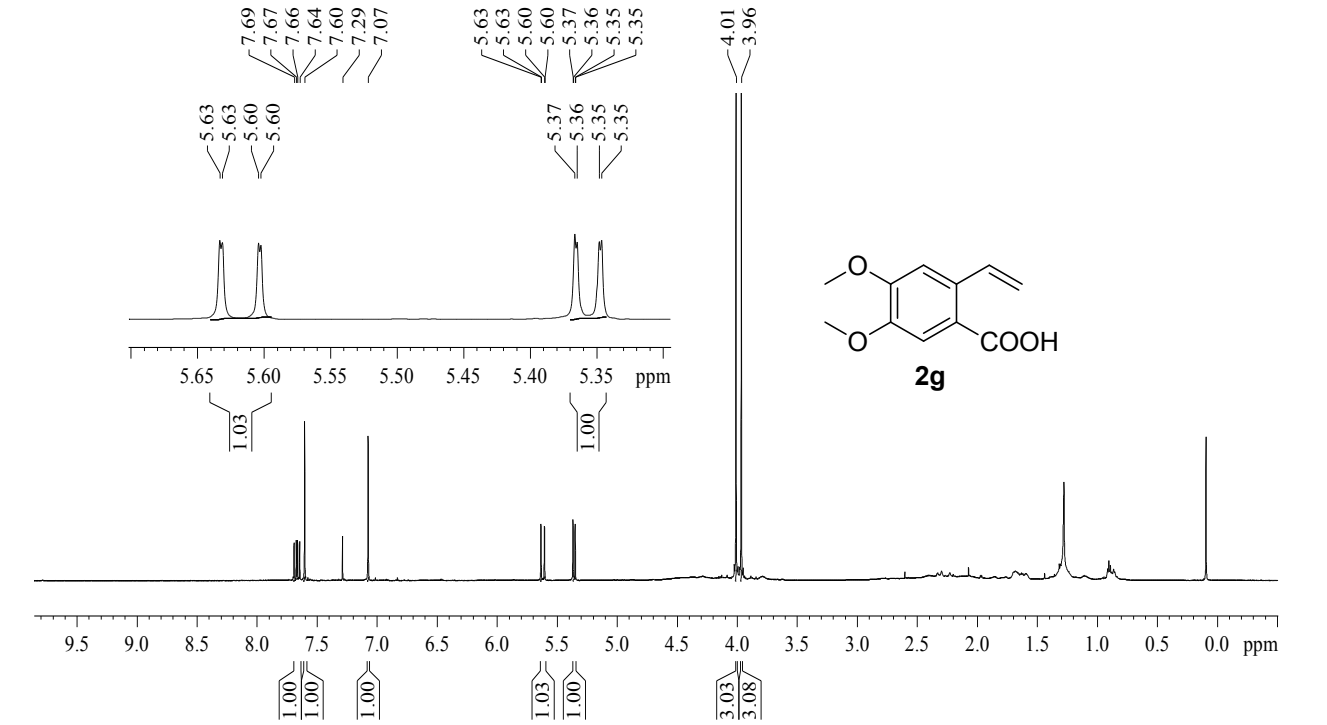

173.47
139.81
136.92
135.19
134.38
129.41
128.12
126.67
119.07
77.21
77.00
76.79
20.88
CH3
COOH
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

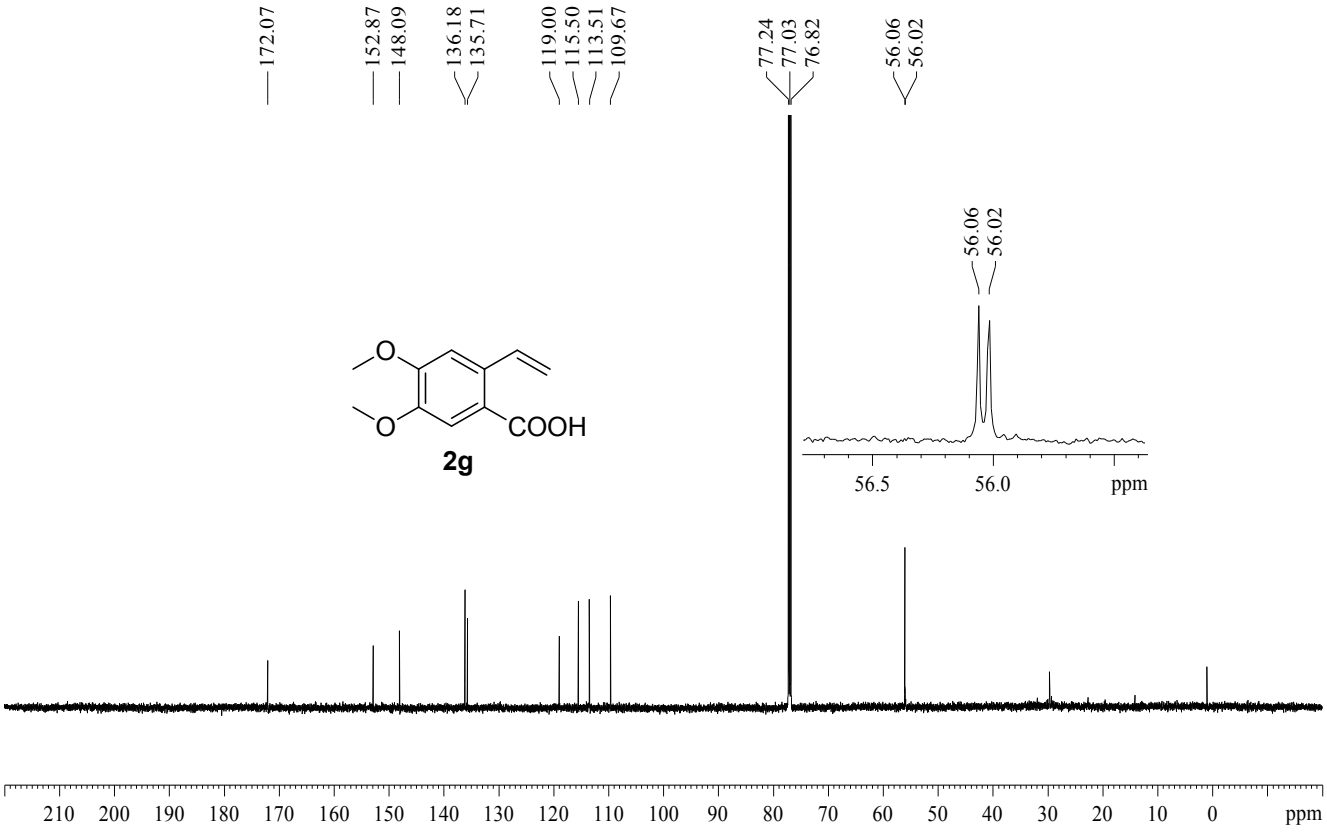

7.61
7.29
7.24
7.06
7.04
7.03
7.01
5.51
5.51
5.50
5.49
5.26
5.25
5.23
5.22
2.37
2.36
CH3
H3C
COOH
2e
ppm
0.97
0.95
1.00
1.01
1.00
2.98
2.83

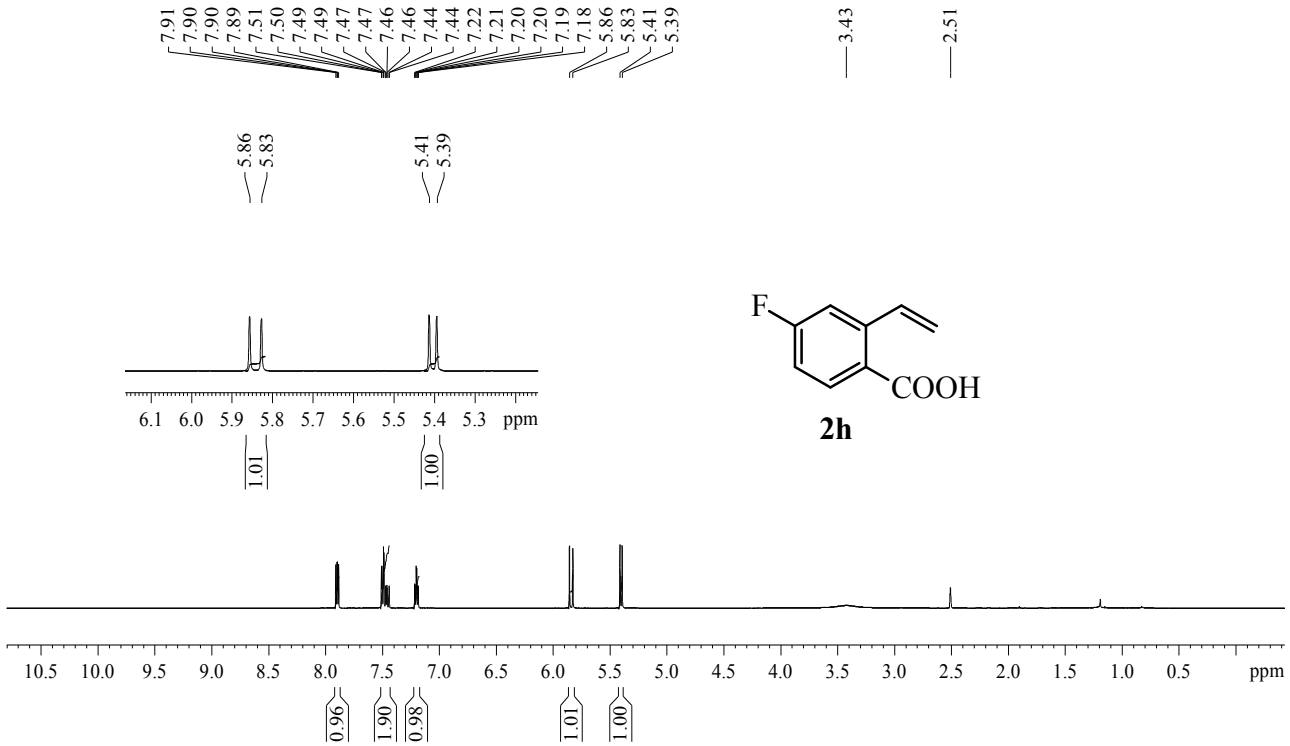

173.17
136.82
136.75
136.38
135.22
135.06
129.16
128.56
118.88
77.21
77.00
76.78
20.83
20.82
CH3
H3C
COOH
2e
ppm

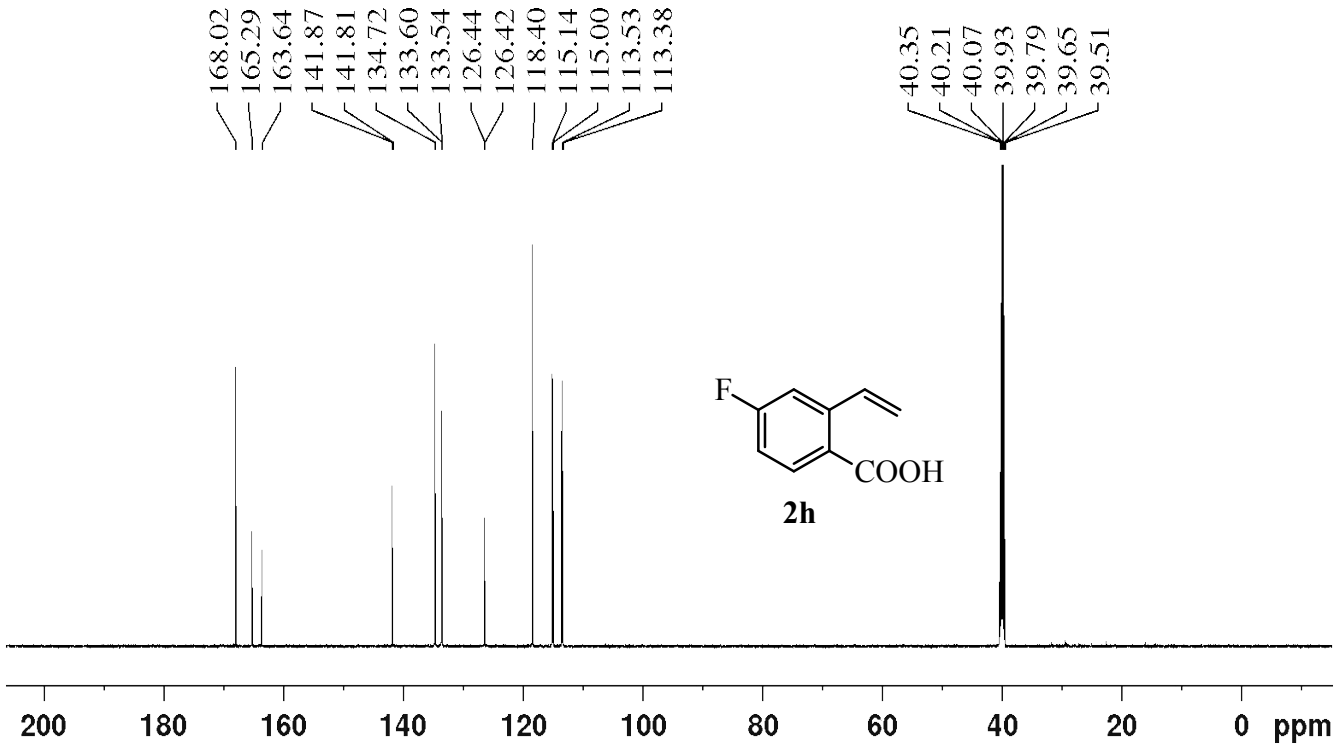

8.00
7.97
7.60
7.57
7.54
7.51
7.18
6.99
6.81
6.80
6.78
6.77
5.59
5.54
5.32
5.28
3.82
5.8
5.6
5.4
5.2
ppm
1.01
1.00
O
COOH
2f
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.01
1.00
1.00
1.01
1.00
3.04

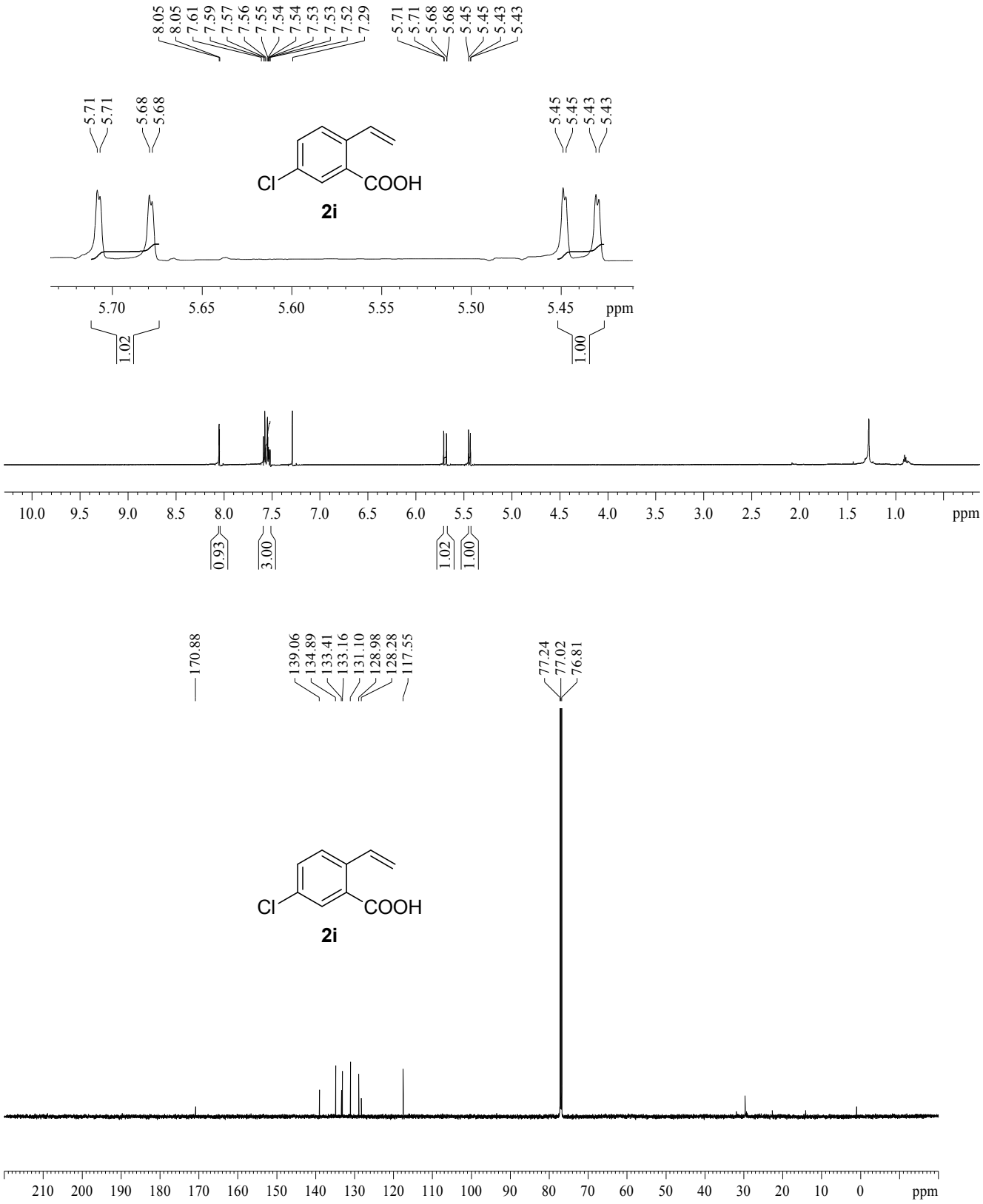

171.97
163.25
143.37
136.58
133.84
119.57
116.61
112.85
112.81
77.43
77.01
76.58
55.44
112.85
112.81
113.2
113.0
112.8
112.6
ppm
O
COOH
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

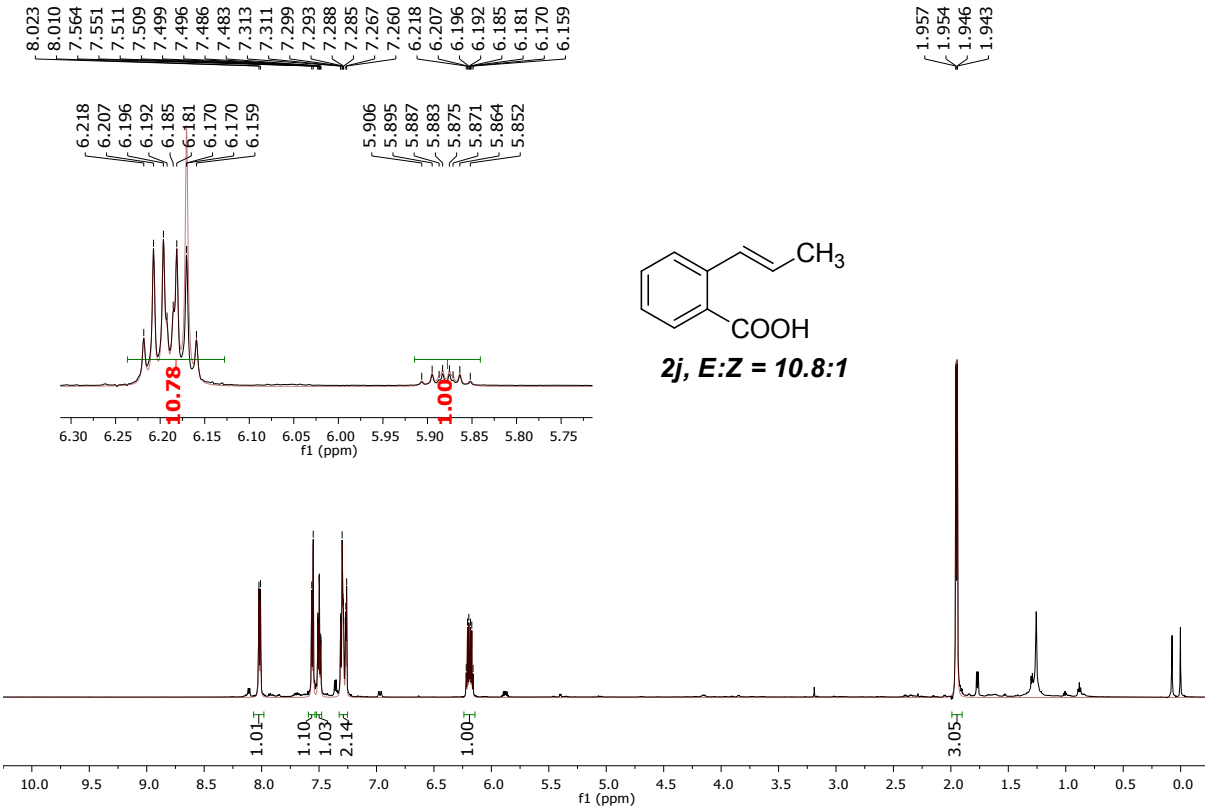

7.69
7.67
7.66
7.64
7.60
7.29
7.07
5.63
5.63
5.60
5.60
5.37
5.36
5.35
5.35
4.01
3.96
5.65
5.60
5.55
5.50
5.45
5.40
5.35
ppm
1.03
1.00
O
O
COOH
2g
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.00
1.00
1.03
1.00
3.03
3.08

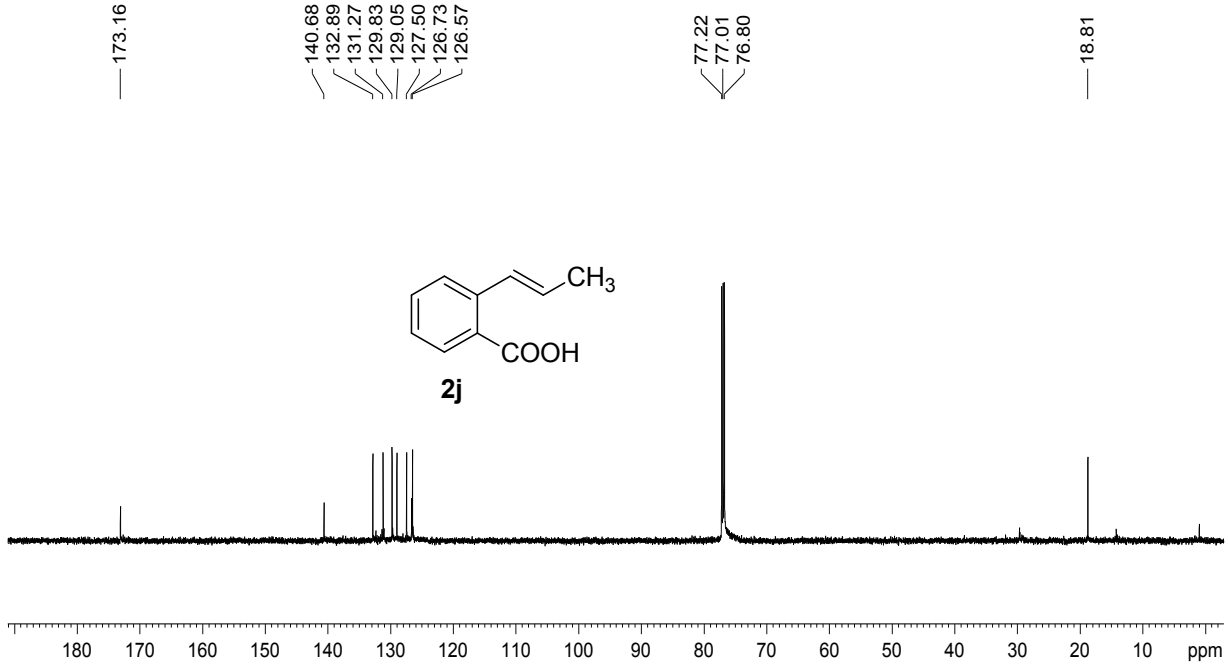

172.07
152.87
148.09
136.18
135.71
119.00
115.50
113.51
109.67
77.24
77.03
76.82
56.06
56.02
56.06
56.02
56.5
56.0
ppm
O
O
COOH
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

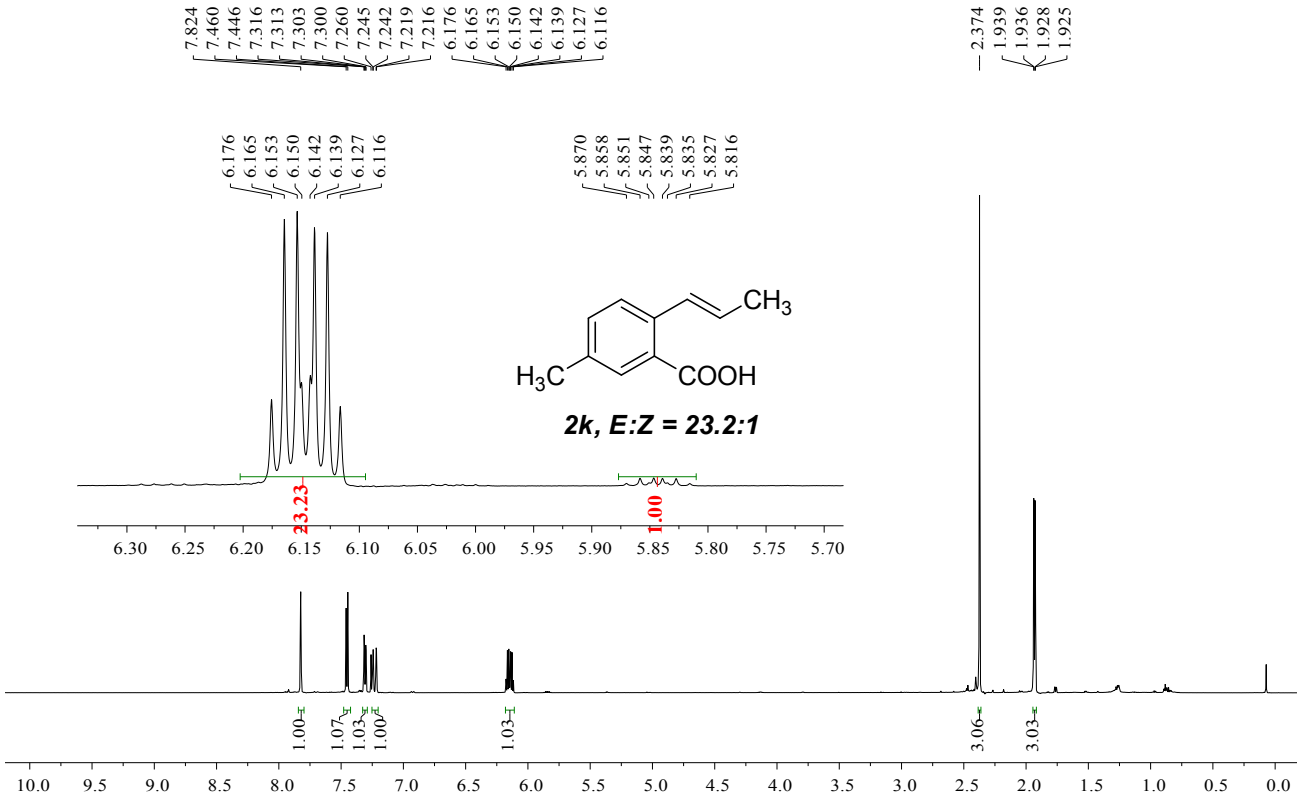

7.91
7.90
7.90
7.89
7.51
7.50
7.49
7.49
7.47
7.47
7.46
7.46
7.44
7.44
7.22
7.21
7.20
7.20
7.19
7.18
5.86
5.83
5.41
5.39
3.43
2.51
F
COOH
2h
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 ppm
1.01
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.96
1.90
0.98
1.01
1.00

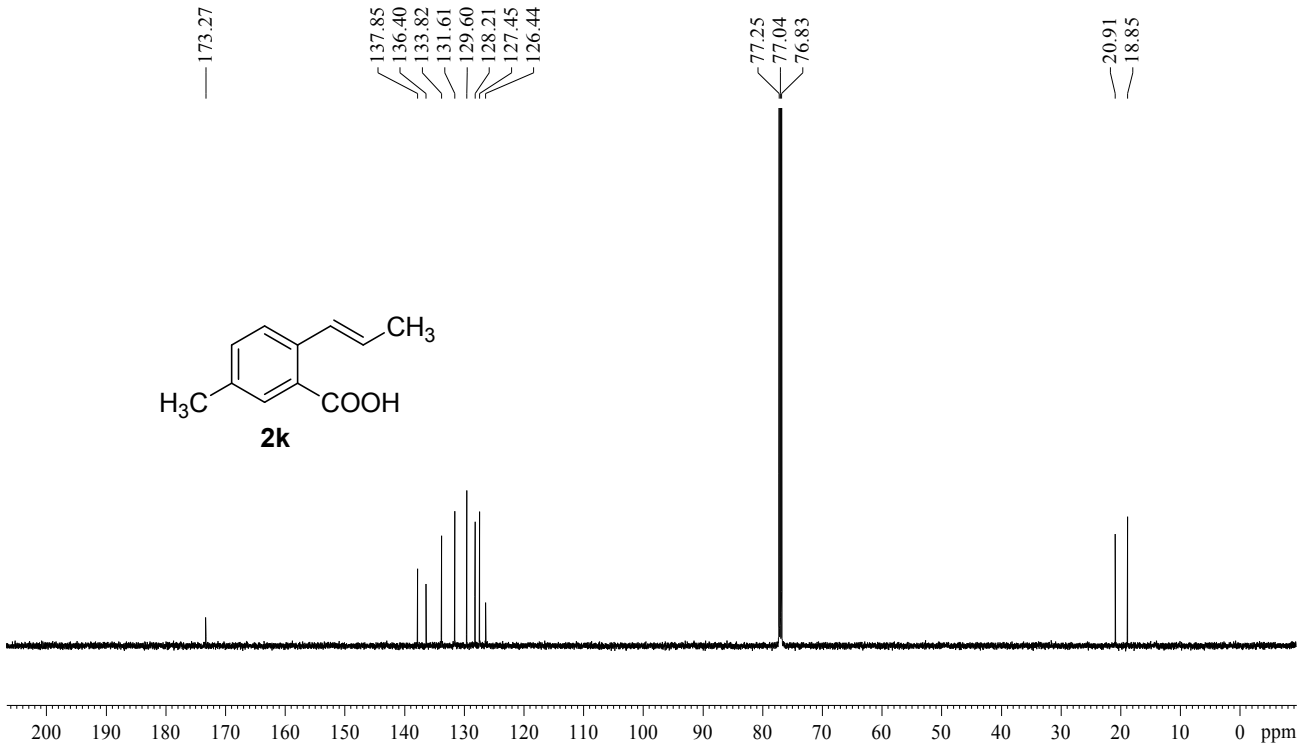

168.02
165.29
163.64
141.87
141.81
134.72
133.60
133.54
126.44
126.42
118.40
115.14
115.00
113.53
113.38
40.35
40.21
40.07
39.93
39.79
39.65
39.51
F
COOH
2h
200 180 160 140 120 100 80 60 40 20 0 ppm

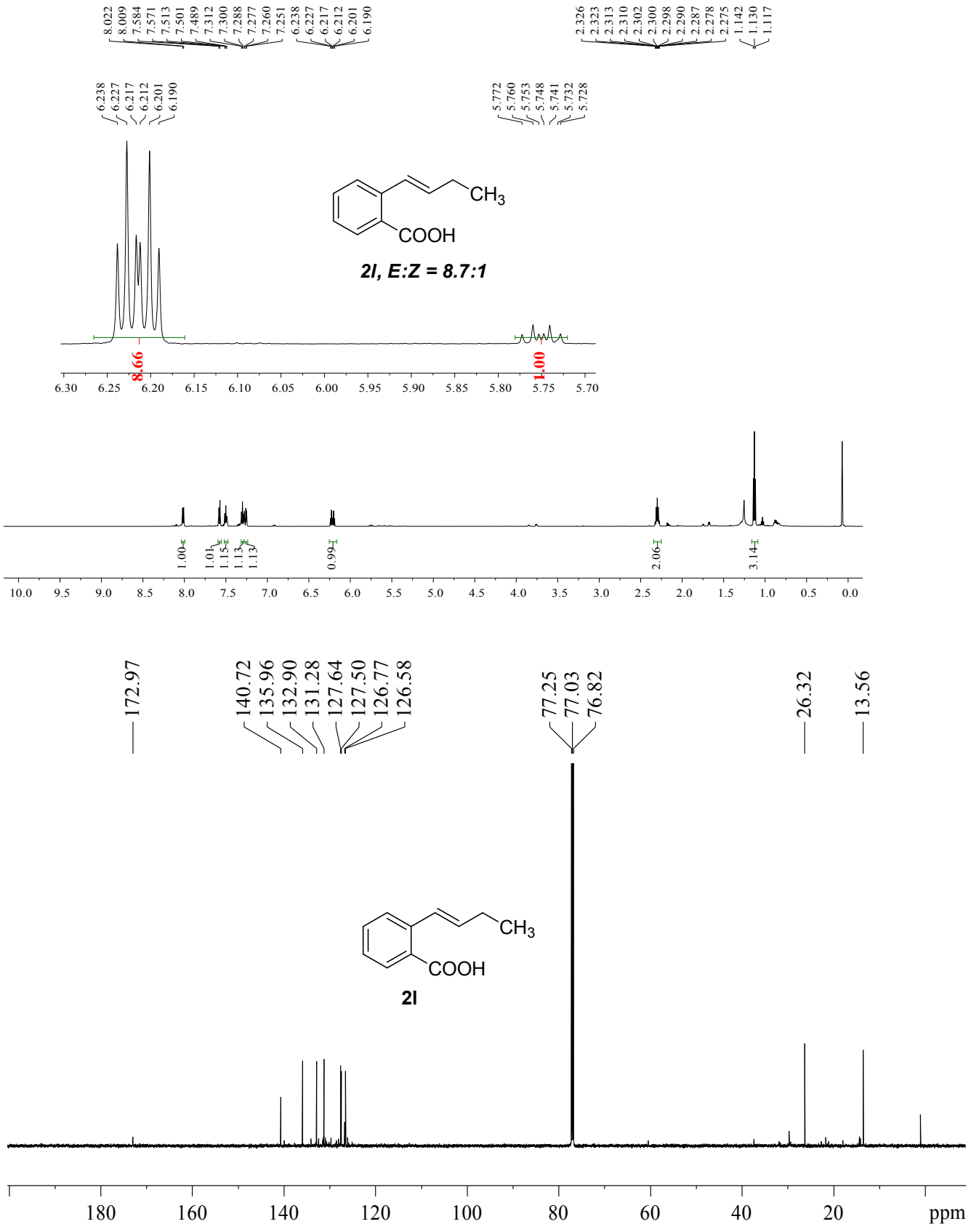

8.05
8.05
7.61
7.59
7.57
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.29
5.71
5.71
5.68
5.68
5.45
5.45
5.43
5.43
Cl
COOH
2i
5.70
5.65
5.60
5.55
5.50
5.45
ppm
1.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.93
3.00
1.02
1.00
170.88
139.06
134.89
133.41
133.16
131.10
128.98
128.28
117.55
77.24
77.02
76.81
Cl
COOH
2i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

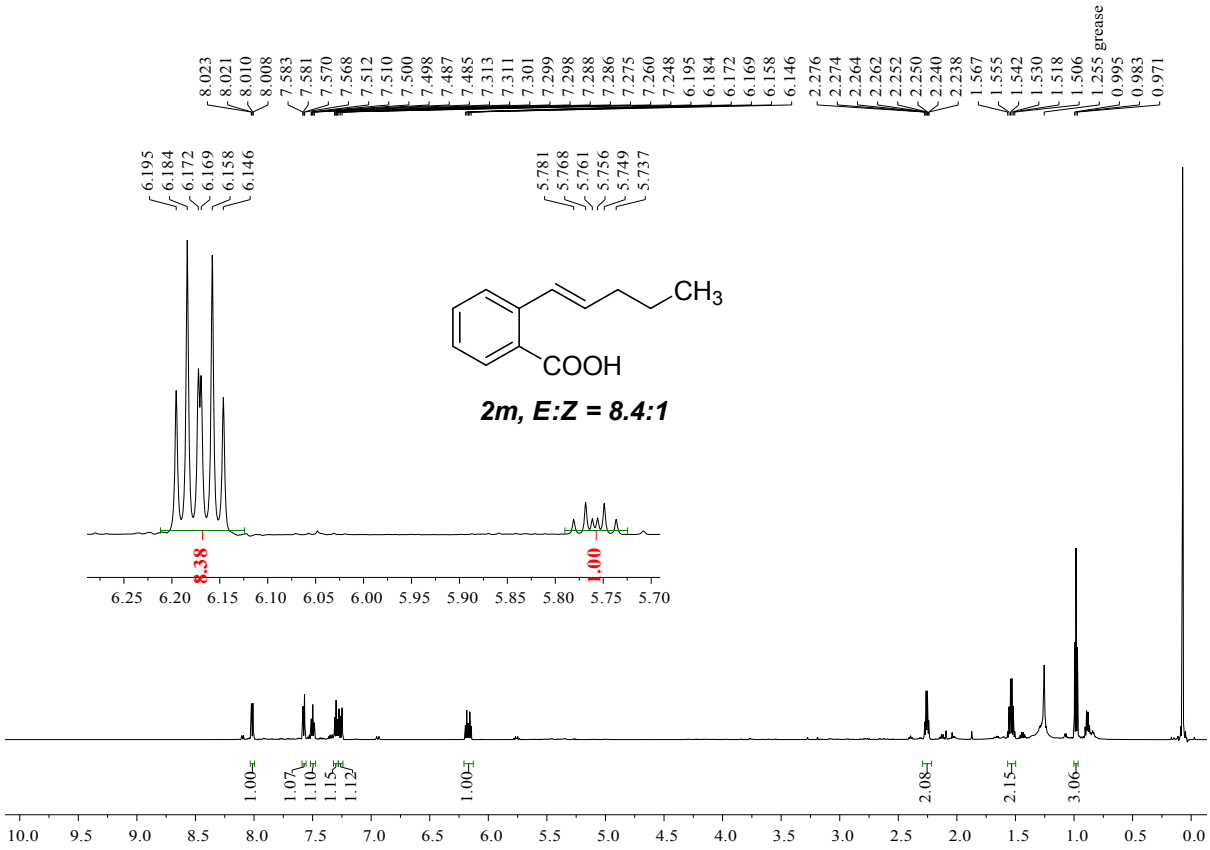

8.023
8.010
7.564
7.551
7.511
7.509
7.499
7.496
7.486
7.483
7.313
7.311
7.299
7.293
7.288
7.285
7.267
7.260
6.218
6.207
6.196
6.192
6.185
6.181
6.170
6.159
5.906
5.895
5.887
5.883
5.875
5.871
5.864
5.852
1.957
1.954
1.946
1.943
10.78
1.00
f1 (ppm)
CH3
COOH
2j, E:Z = 10.8:1
1.01
1.10
1.03
2.14
1.00
3.05
f1 (ppm)

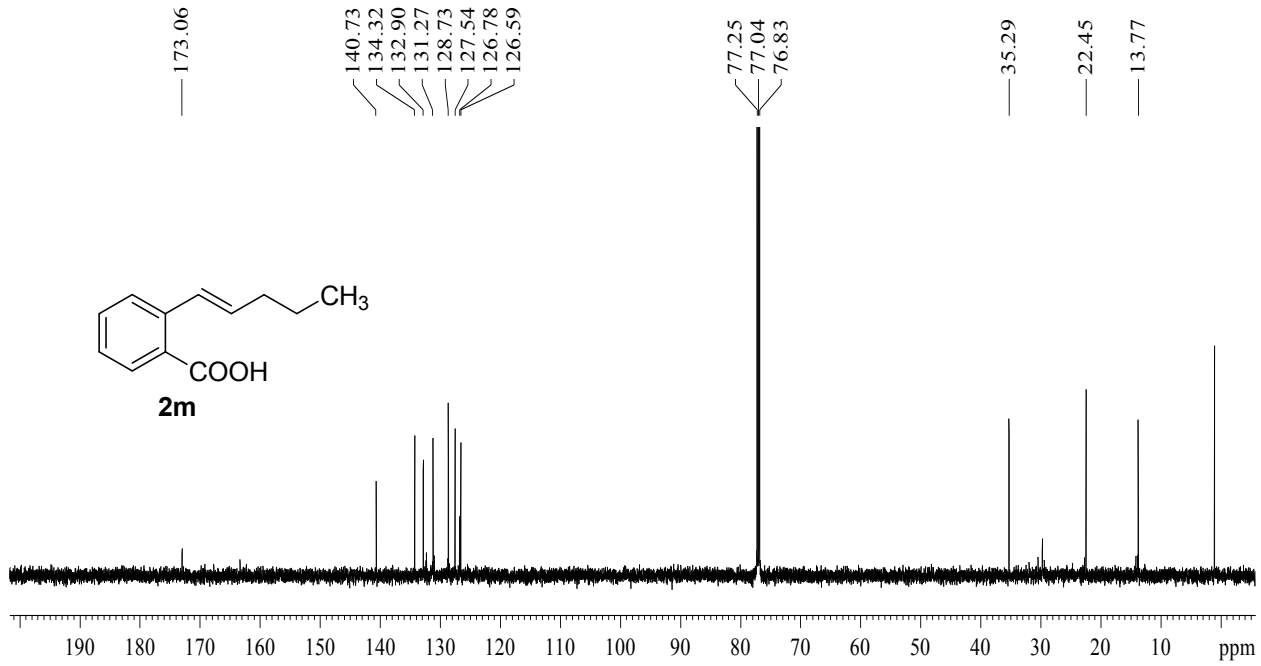

173.16
140.68
132.89
131.27
129.83
129.05
127.50
126.73
126.57
77.22
77.01
76.80
18.81
CH3
COOH
2j
ppm

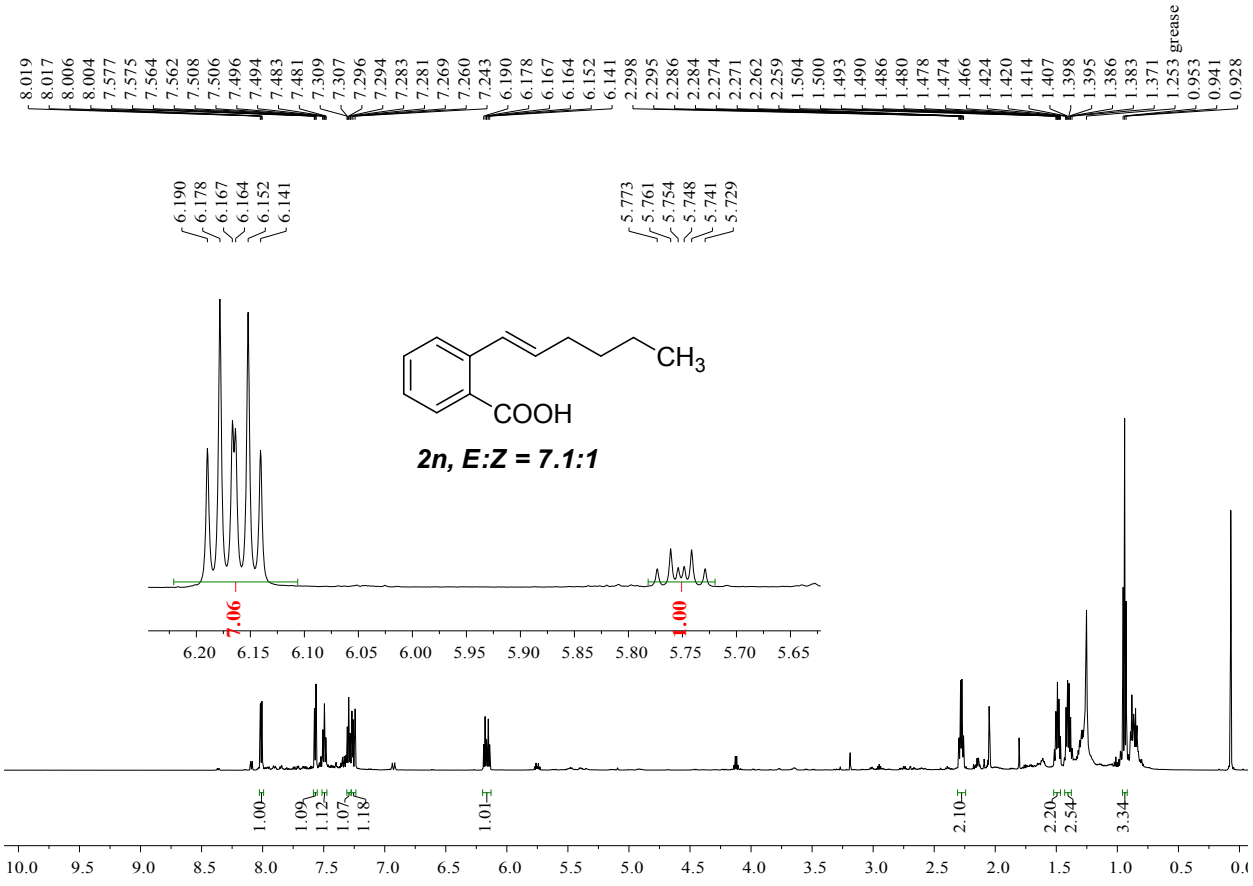

7.824
7.460
7.446
7.316
7.313
7.303
7.300
7.260
7.245
7.242
7.219
7.216
6.176
6.165
6.153
6.150
6.142
6.139
6.127
6.116
2.374
1.939
1.936
1.928
1.925
5.870
5.858
5.851
5.847
5.839
5.835
5.827
5.816
CH3
H3C
COOH
2k, E:Z = 23.2:1
23.23
1.00
1.00
1.07
1.03
1.00
1.03
3.06
3.03

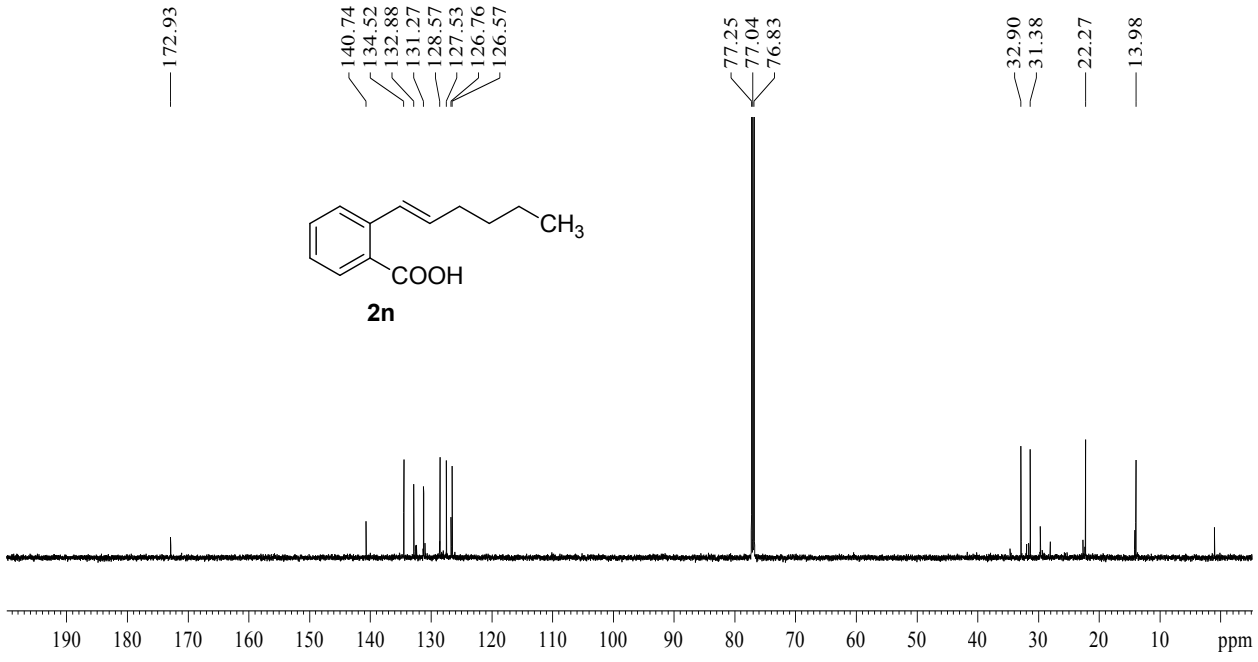

173.27
137.85
136.40
133.82
131.61
129.60
128.21
127.45
126.44
77.25
77.04
76.83
20.91
18.85
CH3
H3C
COOH
2k
ppm

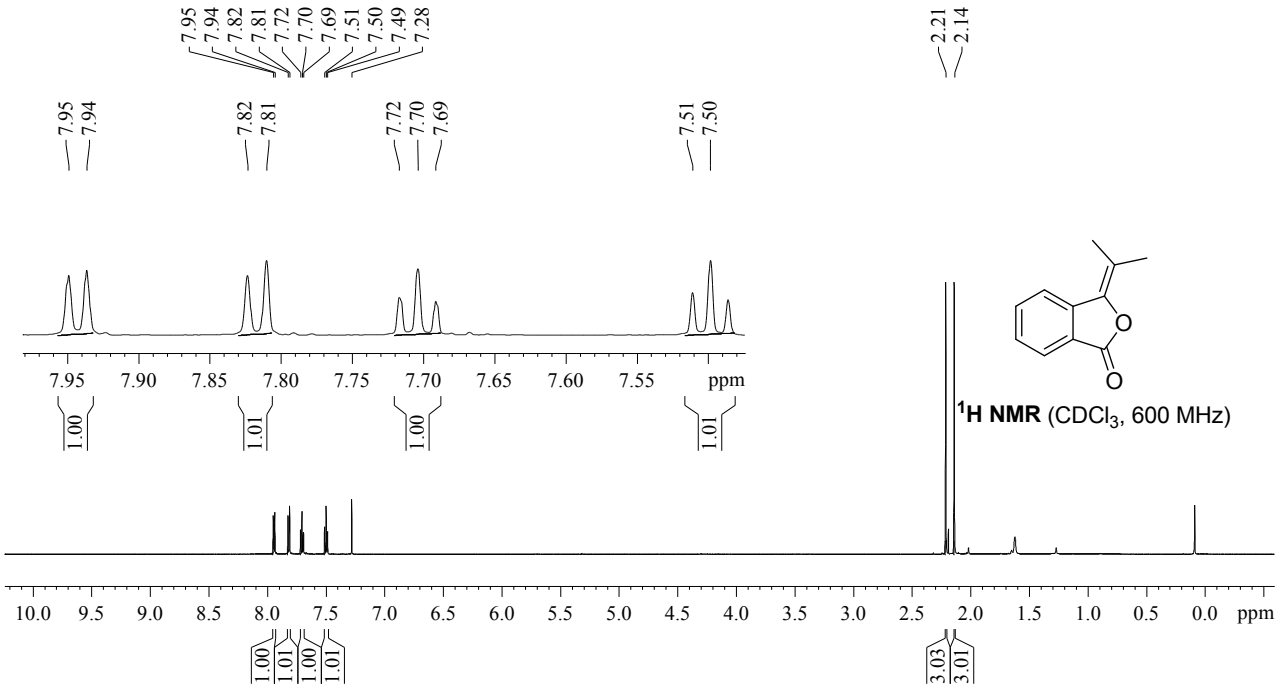

8.022
8.009
7.584
7.571
7.513
7.501
7.489
7.312
7.300
7.288
7.277
7.260
7.251
6.238
6.227
6.217
6.212
6.201
6.190
2.326
2.323
2.313
2.310
2.302
2.300
2.298
2.290
2.287
2.278
2.275
1.142
1.130
1.117
5.772
5.760
5.753
5.748
5.741
5.732
5.728
CH3
COOH
2l, E:Z = 8.7:1
8.66
1.00
1.00
1.01
1.15
1.13
1.13
0.99
2.06
3.14
172.97
140.72
135.96
132.90
131.28
127.64
127.50
126.77
126.58
77.25
77.03
76.82
26.32
13.56
CH3
COOH
2l
ppm

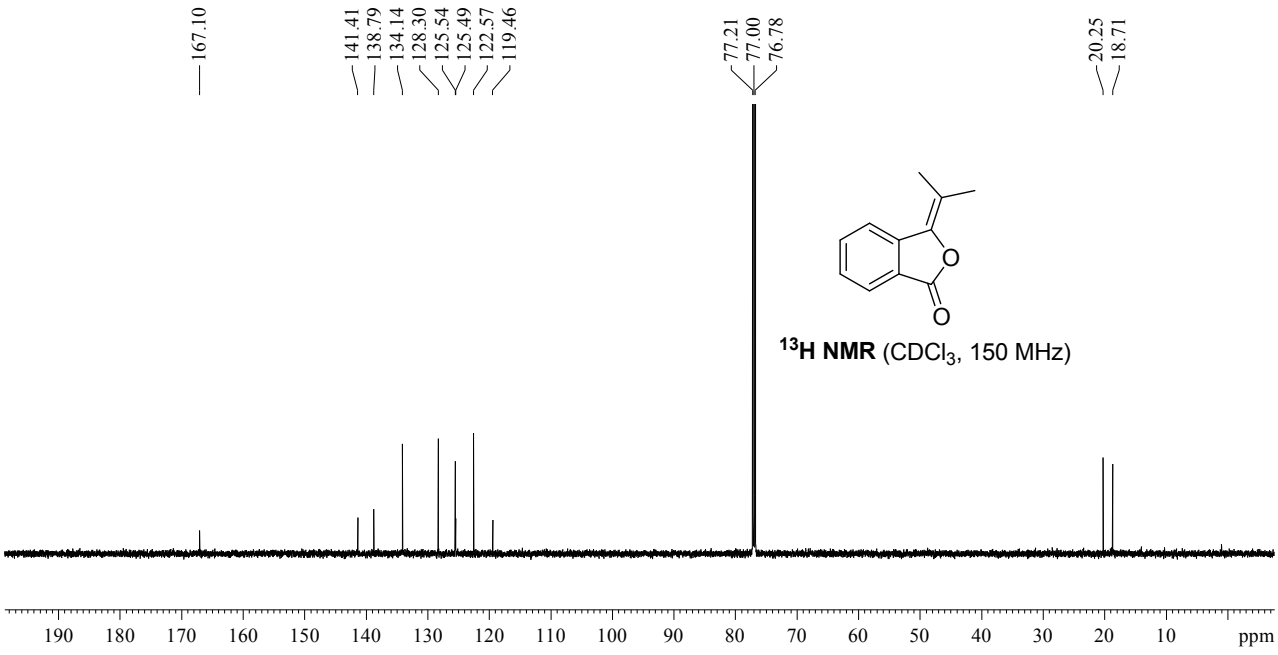

8.023
8.021
8.010
8.008
7.583
7.581
7.570
7.568
7.512
7.510
7.500
7.498
7.487
7.485
7.313
7.311
7.301
7.299
7.298
7.288
7.286
7.275
7.260
7.248
6.195
6.184
6.172
6.169
6.158
6.146
2.276
2.274
2.264
2.262
2.252
2.250
2.240
2.238
1.567
1.555
1.542
1.530
1.518
1.506
1.255 grease
0.995
0.983
0.971
6.195
6.184
6.172
6.169
6.158
6.146
5.781
5.768
5.761
5.756
5.749
5.737
CH3
COOH
2m, E:Z = 8.4:1
8.38
1.00
6.25 6.20 6.15 6.10 6.05 6.00 5.95 5.90 5.85 5.80 5.75 5.70
1.00
1.07
1.10
1.15
1.12
1.00
2.08
2.15
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


173.06
140.73
134.32
132.90
131.27
128.73
127.54
126.78
126.59
77.25
77.04
76.83
35.29
22.45
13.77
CH3
COOH
2m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

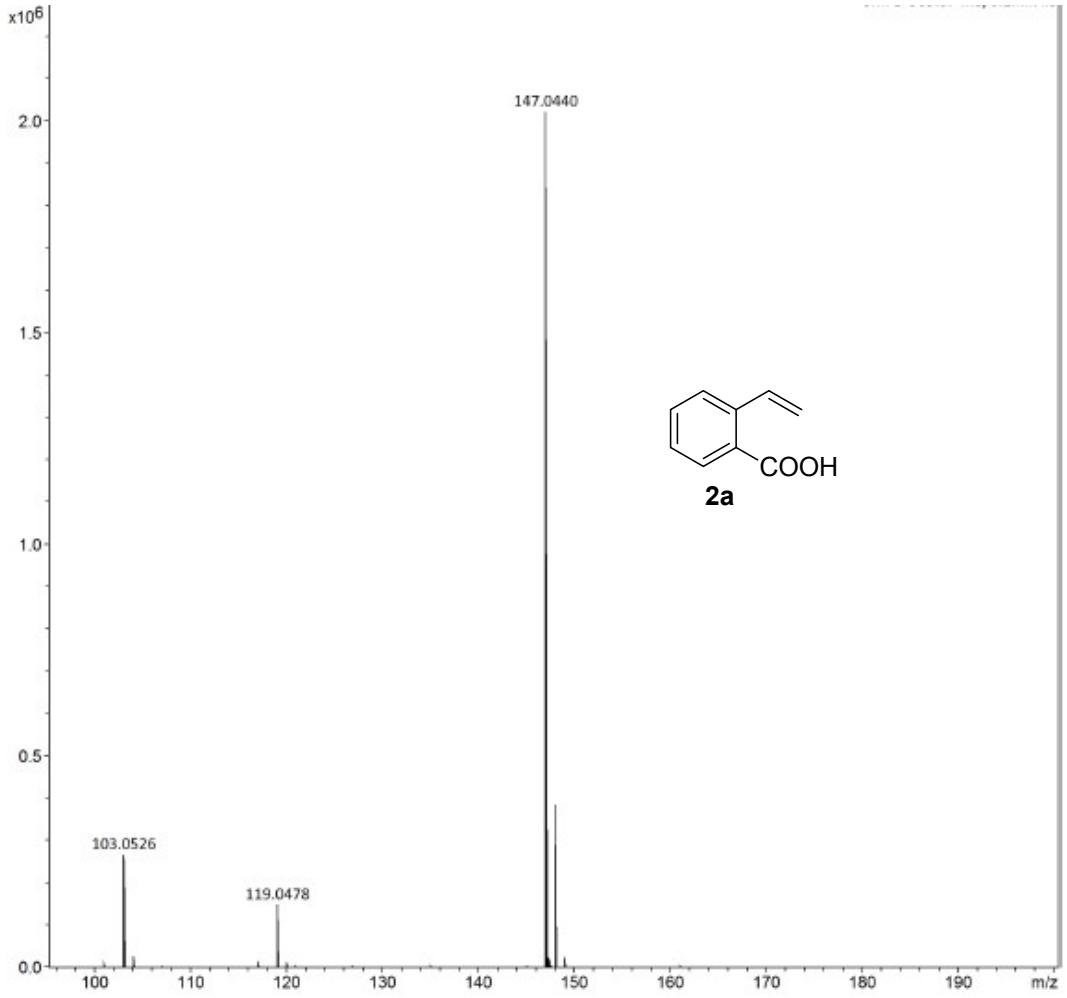

8.019
8.017
8.006
8.004
7.577
7.575
7.564
7.562
7.508
7.506
7.496
7.494
7.483
7.481
7.309
7.307
7.296
7.294
7.283
7.281
7.269
7.260
7.243
6.190
6.178
6.167
6.164
6.152
6.141
2.298
2.295
2.286
2.284
2.274
2.271
2.262
2.259
1.504
1.500
1.493
1.490
1.486
1.480
1.478
1.474
1.466
1.424
1.420
1.414
1.407
1.398
1.395
1.386
1.383
1.371
1.253 grease
0.953
0.941
0.928
6.190
6.178
6.167
6.164
6.152
6.141
5.773
5.761
5.754
5.748
5.741
5.729
CH3
COOH
2n, E:Z = 7.1:1
7.06
1.00
6.20
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
1.00
1.09
1.12
1.07
1.18
1.01
2.10
2.20
2.54
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

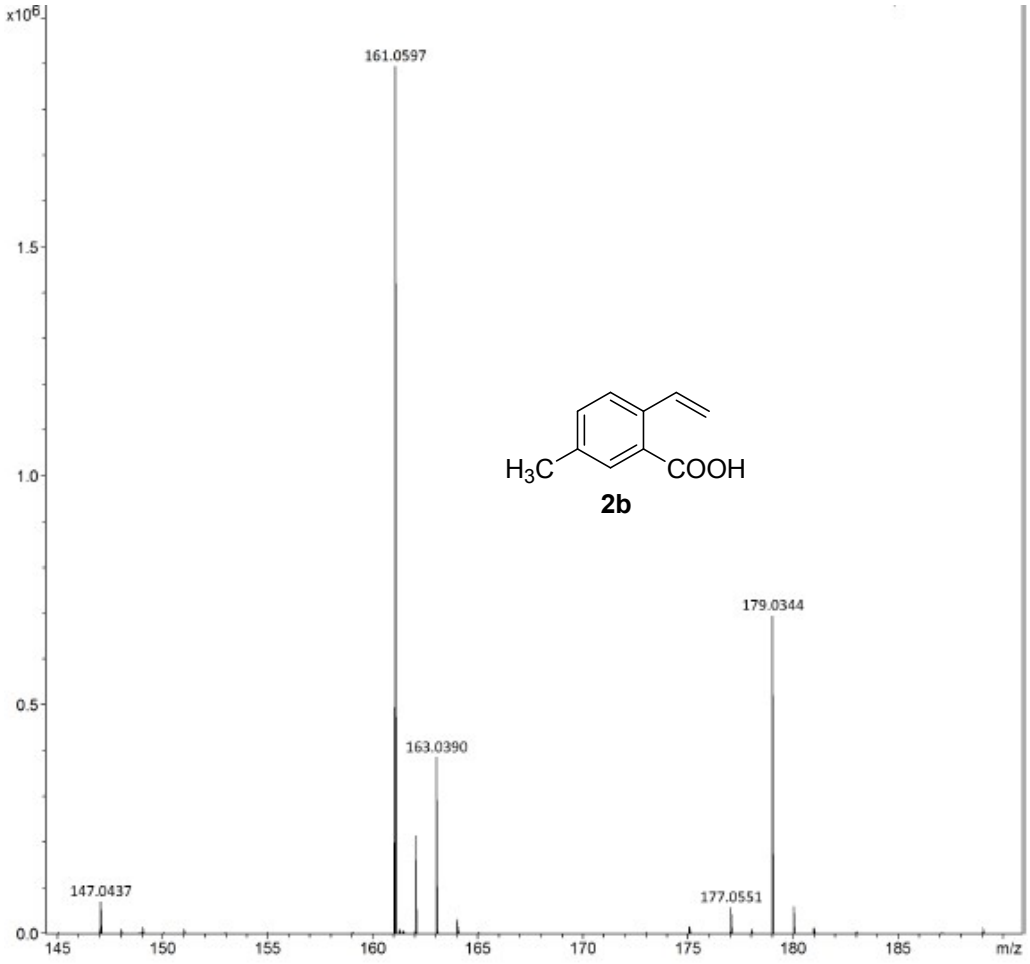

172.93
140.74
134.52
132.88
131.27
128.57
127.53
126.76
126.57
77.25
77.04
76.83
32.90
31.38
22.27
13.98
CH3
COOH
2n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.95
7.94
7.82
7.81
7.72
7.70
7.69
7.51
7.50
7.49
7.28
2.21
2.14
1.00
1.01
1.00
1.01
1.00
1.01
1.00
1.01
3.03
3.01
O
O
^{1}H NMR (CDCl$_3$, 600 MHz)
ppm

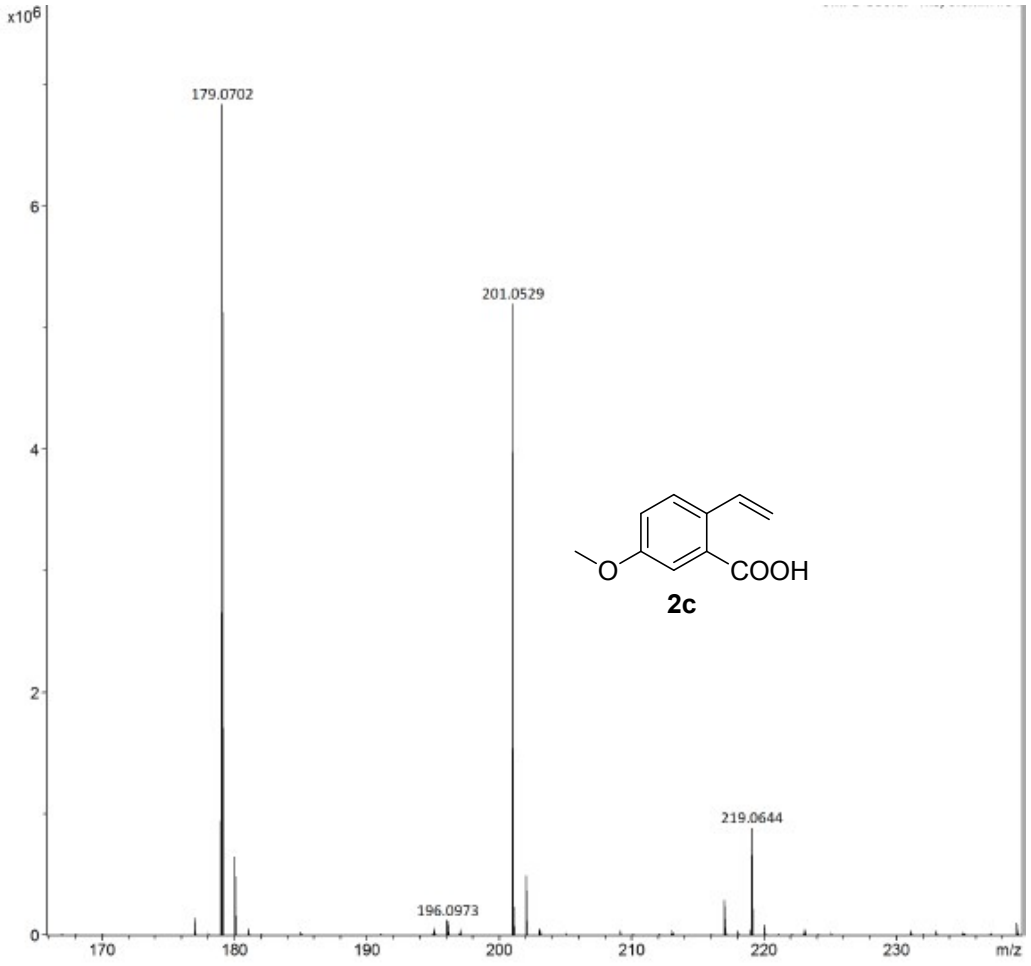

167.10
141.41
138.79
134.14
128.30
125.54
125.49
122.57
119.46
77.21
77.00
76.78
20.25
18.71
O
O
^{13}H NMR (CDCl$_3$, 150 MHz)
ppm

10. HR-MS of final products

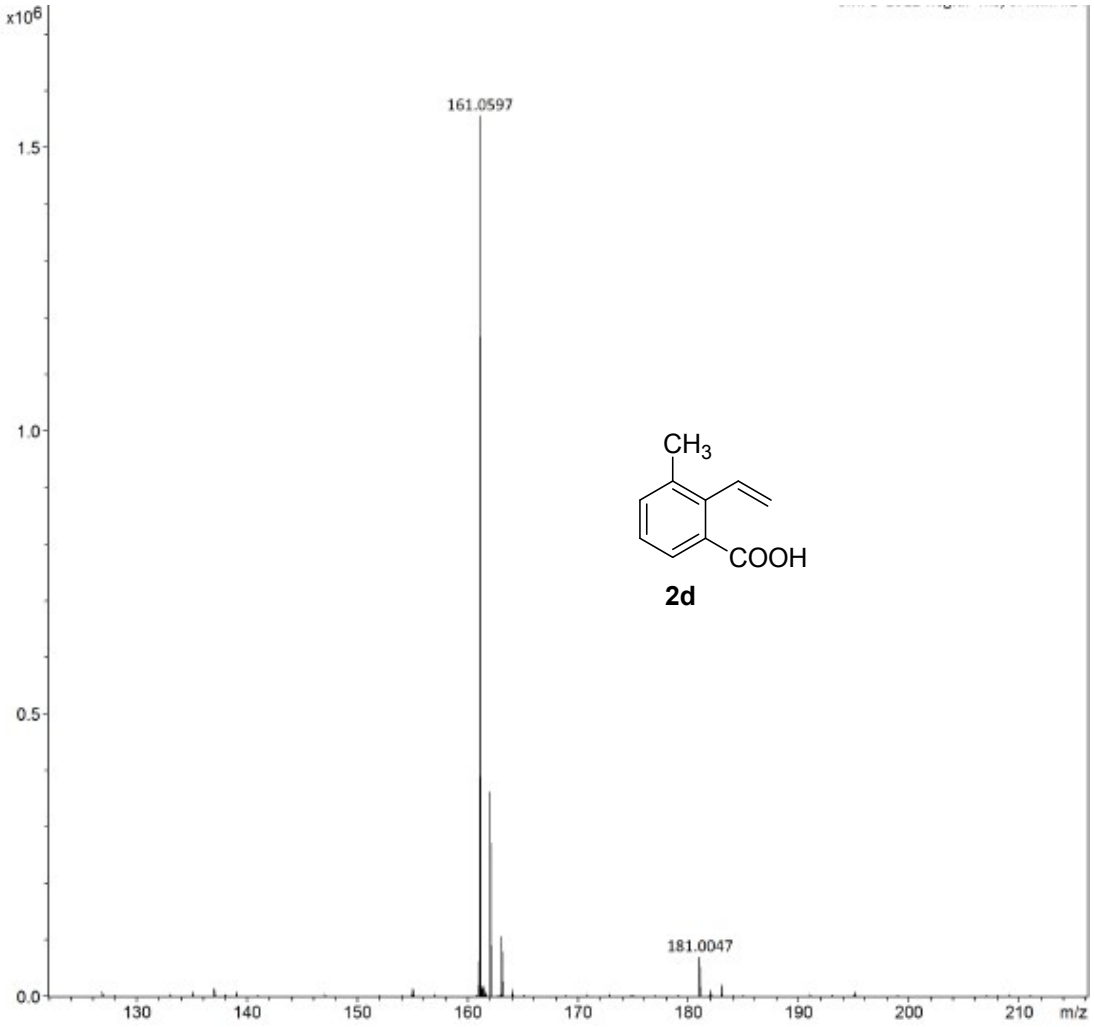



x10^6
161.0597
1.5
1.0
0.5
0.0
179.0344
163.0390
147.0437
177.0551
145
150
155
160
165
170
175
180
185
m/z
H3C
COOH

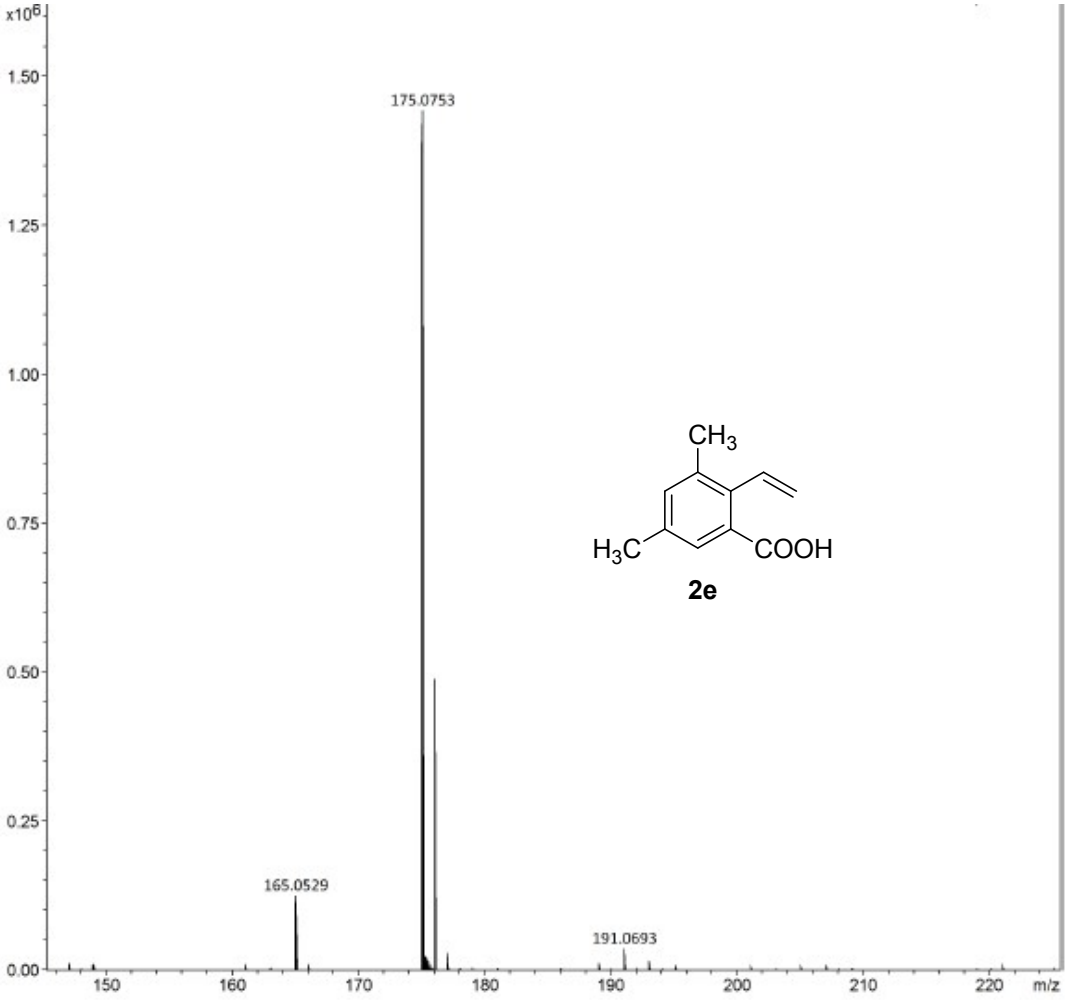
2b


x10^6
179.0702
201.0529
219.0644
196.0973
6
4
2
0
170
180
190
200
210
220
230
m/z
O
COOH

2c

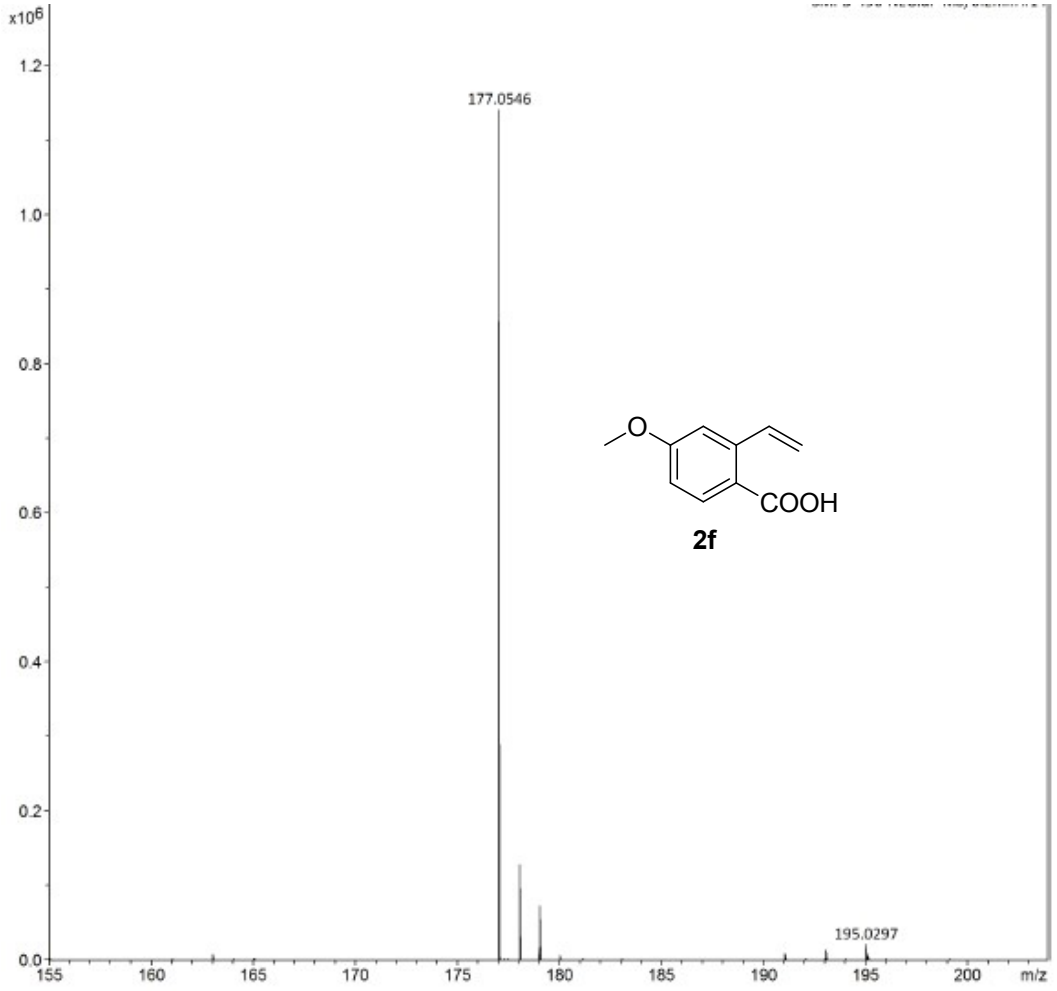

x10^6
161.0597
1.5
1.0
0.5
0.0
181.0047
130
140
150
160
170
180
190
200
210
m/z
CH3
COOH

2d

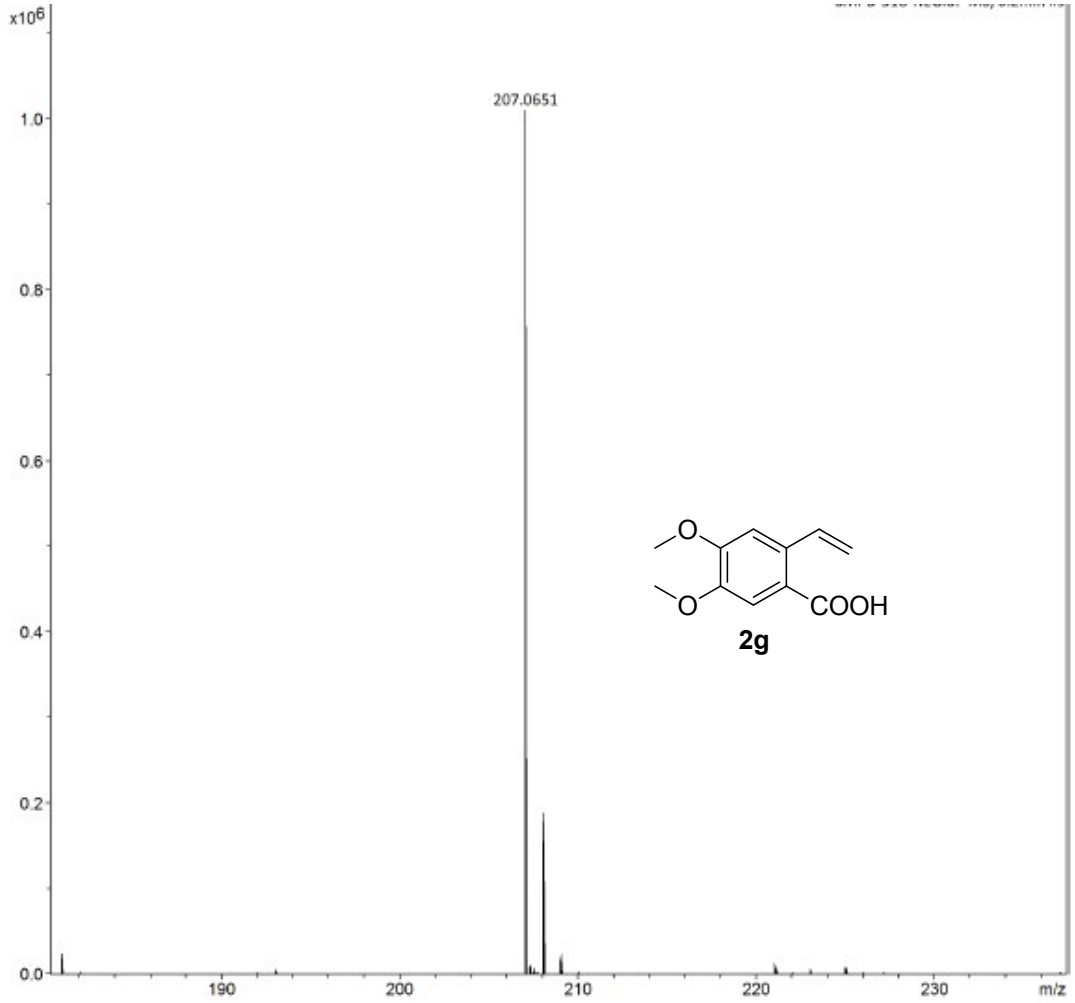

x10^6
1.50
1.25
1.00
0.75
0.50
0.25
0.00
175.0753
165.0529
191.0693
150
160
170
180
190
200
210
220
m/z

CH3
H3C
COOH

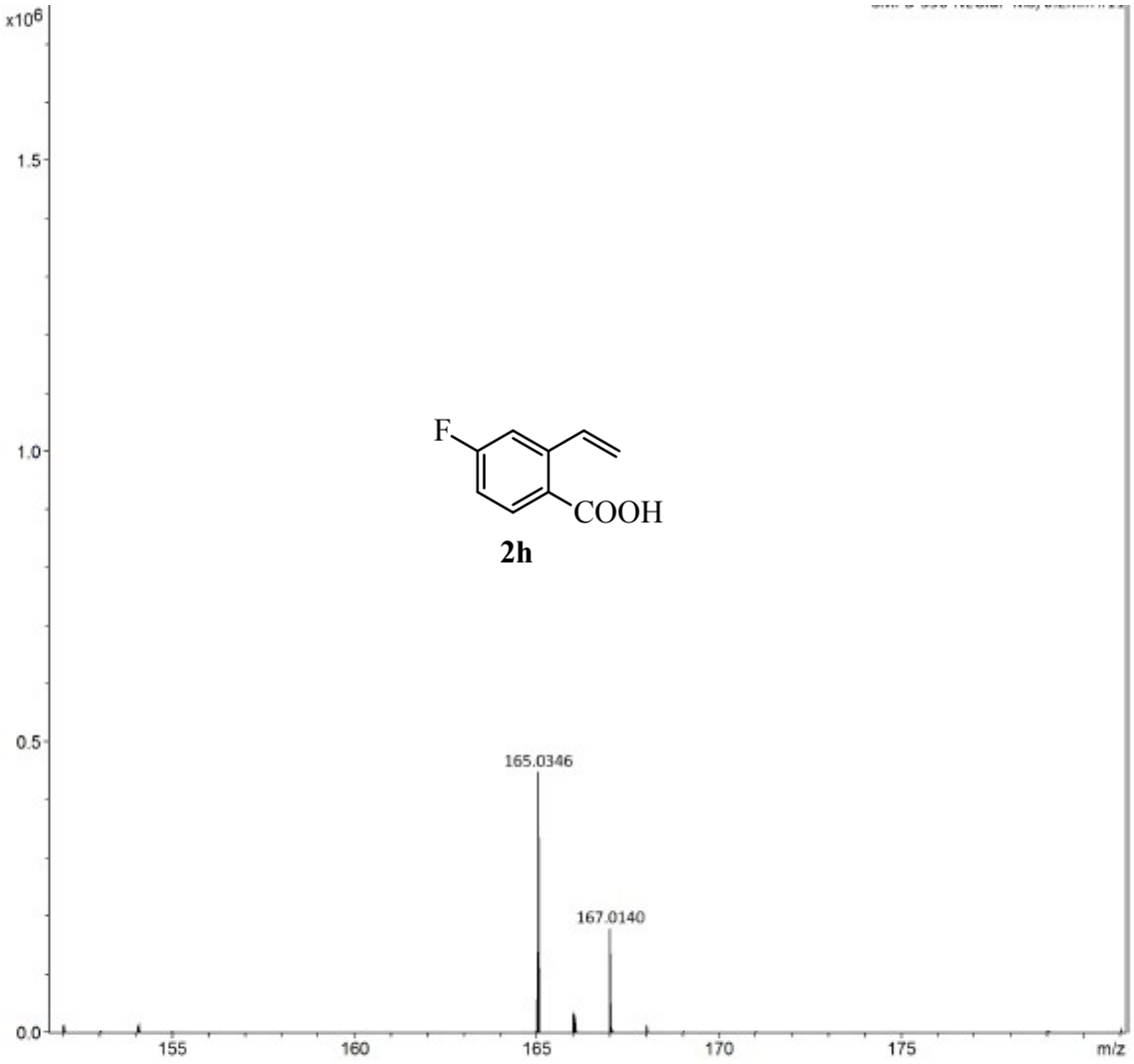
2e


x10^6
1.2
1.0
0.8
0.6
0.4
0.2
0.0
177.0546
195.0297
155
160
165
170
175
180
185
190
195
200
m/z
O
COOH

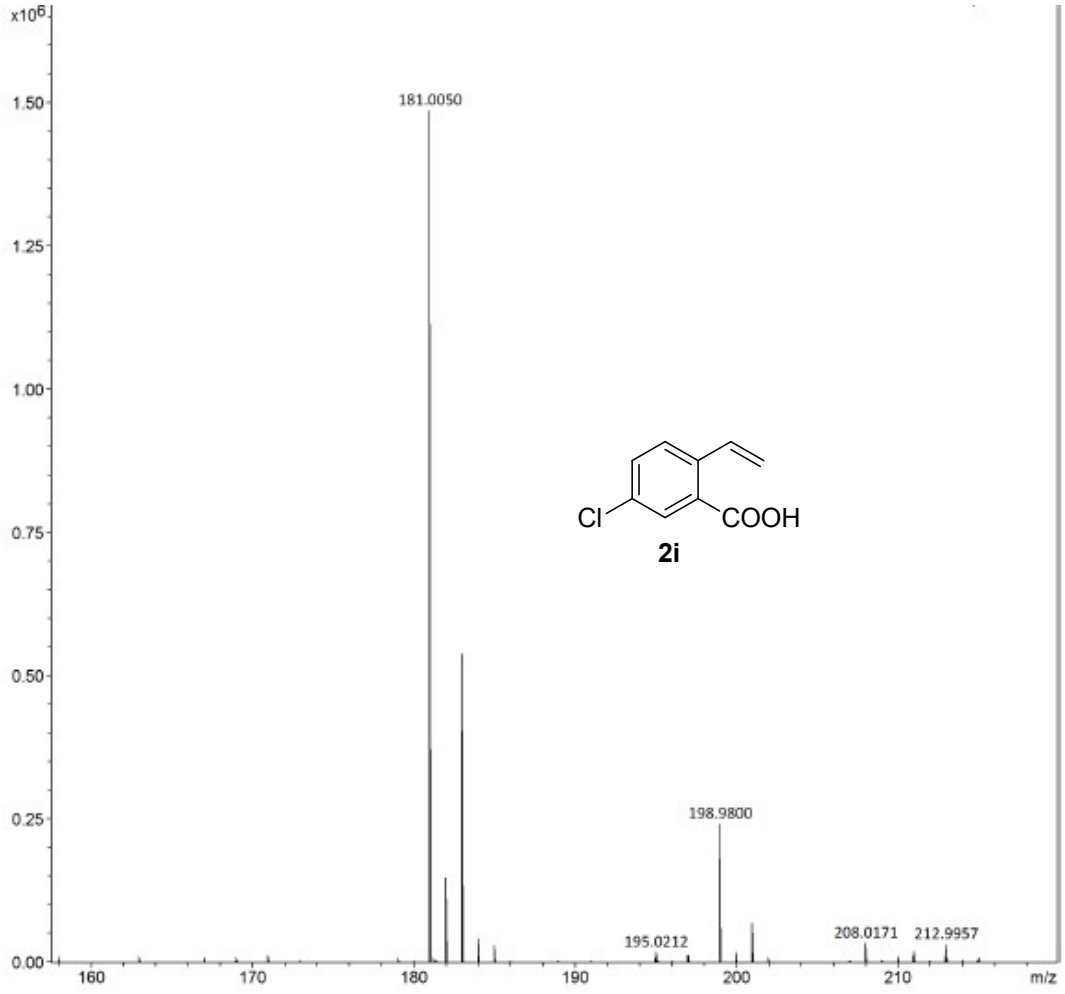
2f



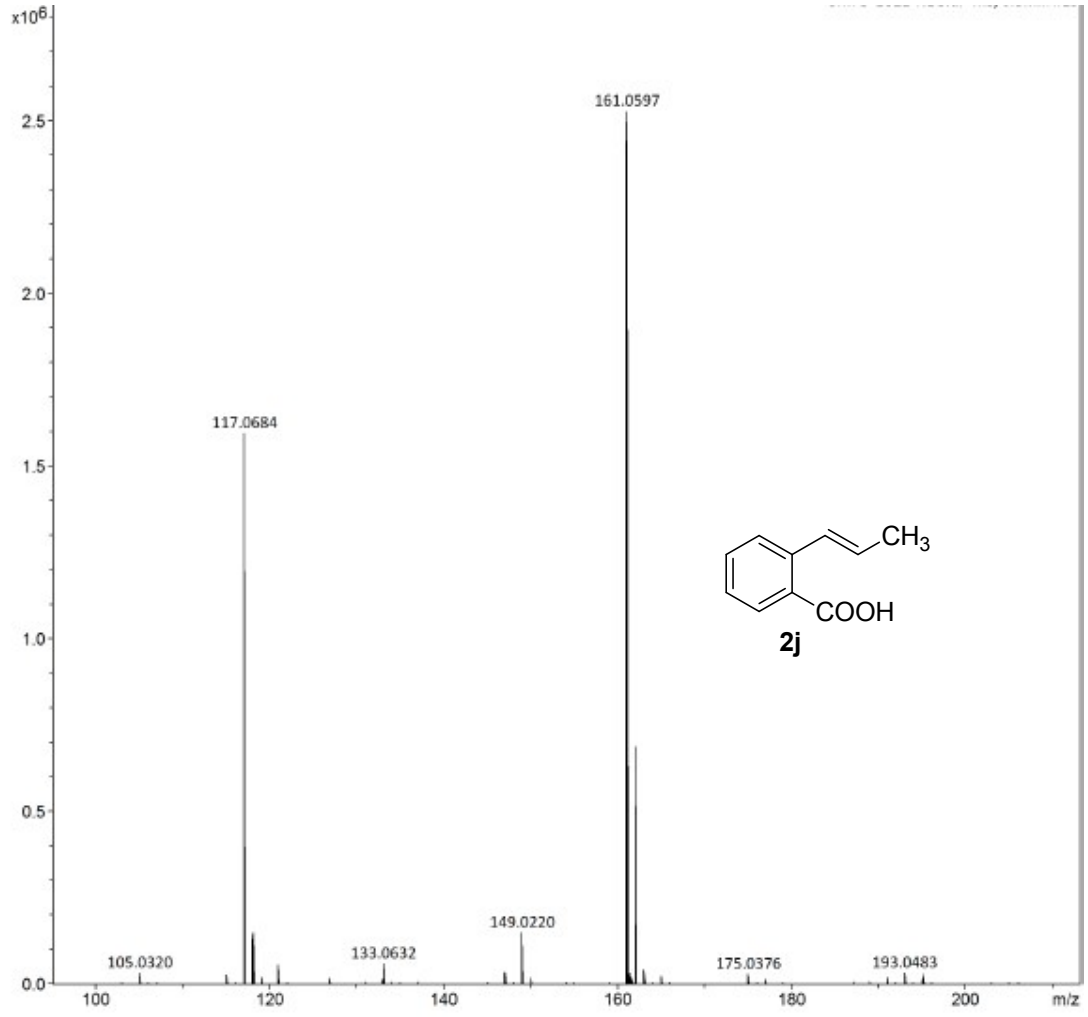
2g



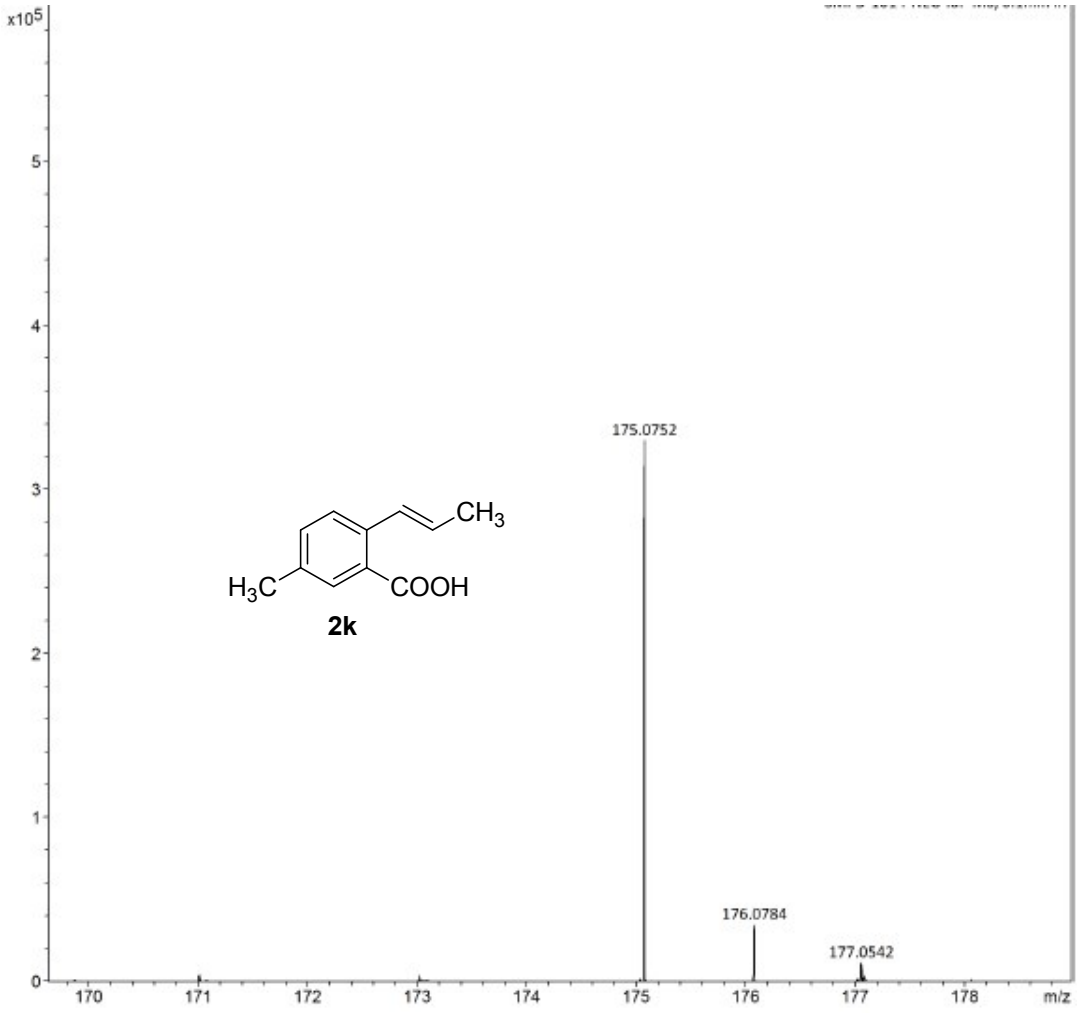
2h


x10^6
1.50
1.25
1.00
0.75
0.50
0.25
0.00
181.0050
198.9800
195.0212
208.0171
212.9957
160
170
180
190
200
210
m/z
Cl
COOH

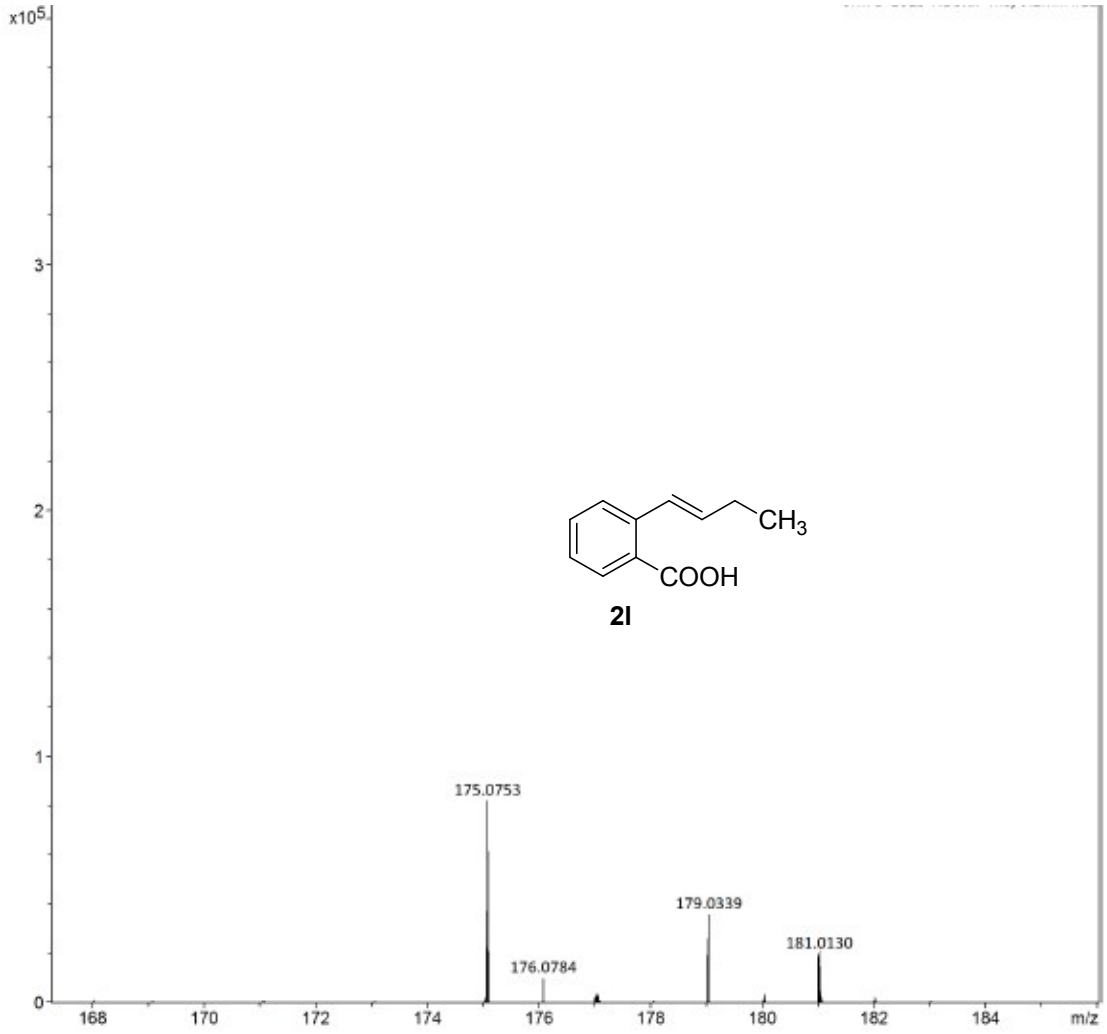
2i


x10^6
2.5
2.0
1.5
1.0
0.5
0.0
161.0597
117.0684
149.0220
133.0632
105.0320
175.0376
193.0483
100
120
140
160
180
200
m/z
CH3
COOH

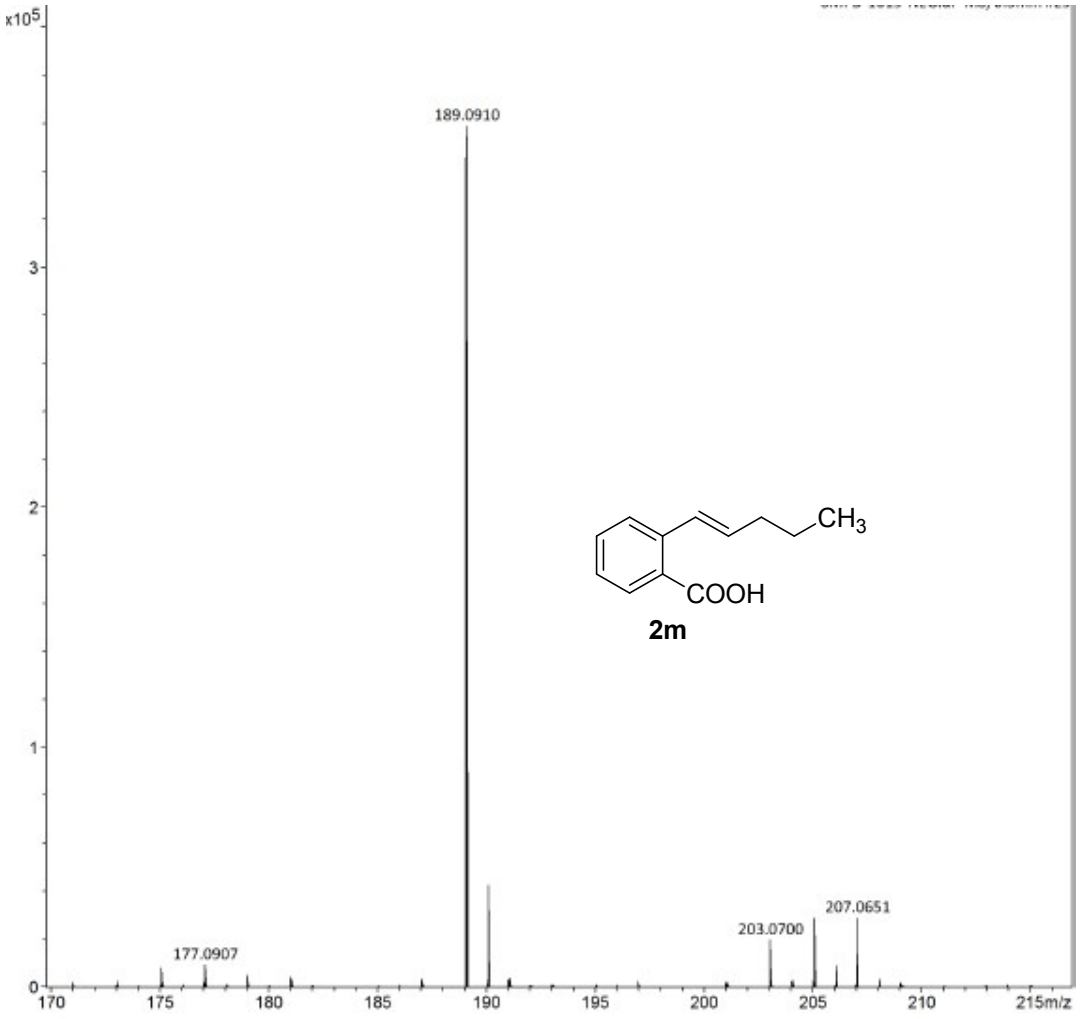
2j

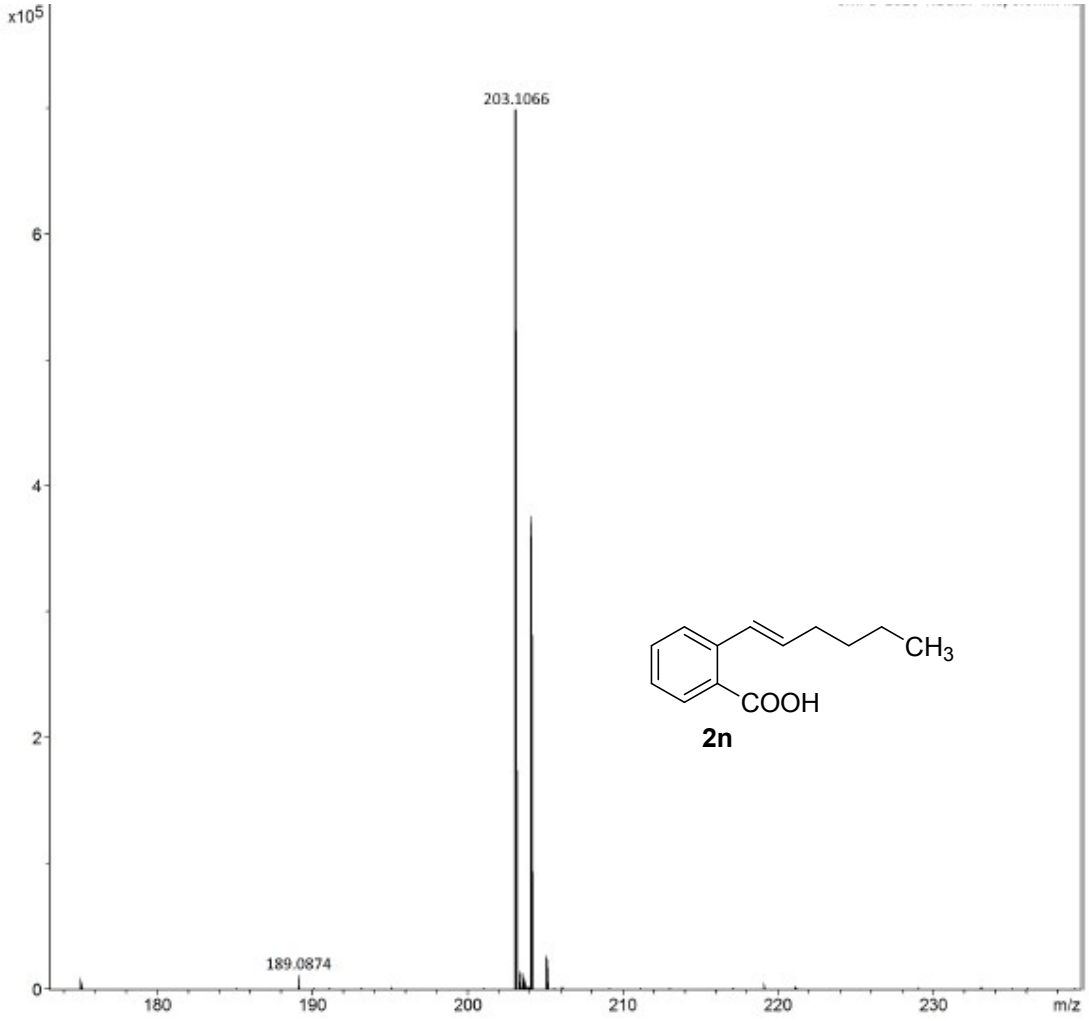

x10^5
5
4
3
2
1
0
175.0752
176.0784
177.0542
170
171
172
173
174
175
176
177
178
m/z
CH3
H3C
COOH

2k

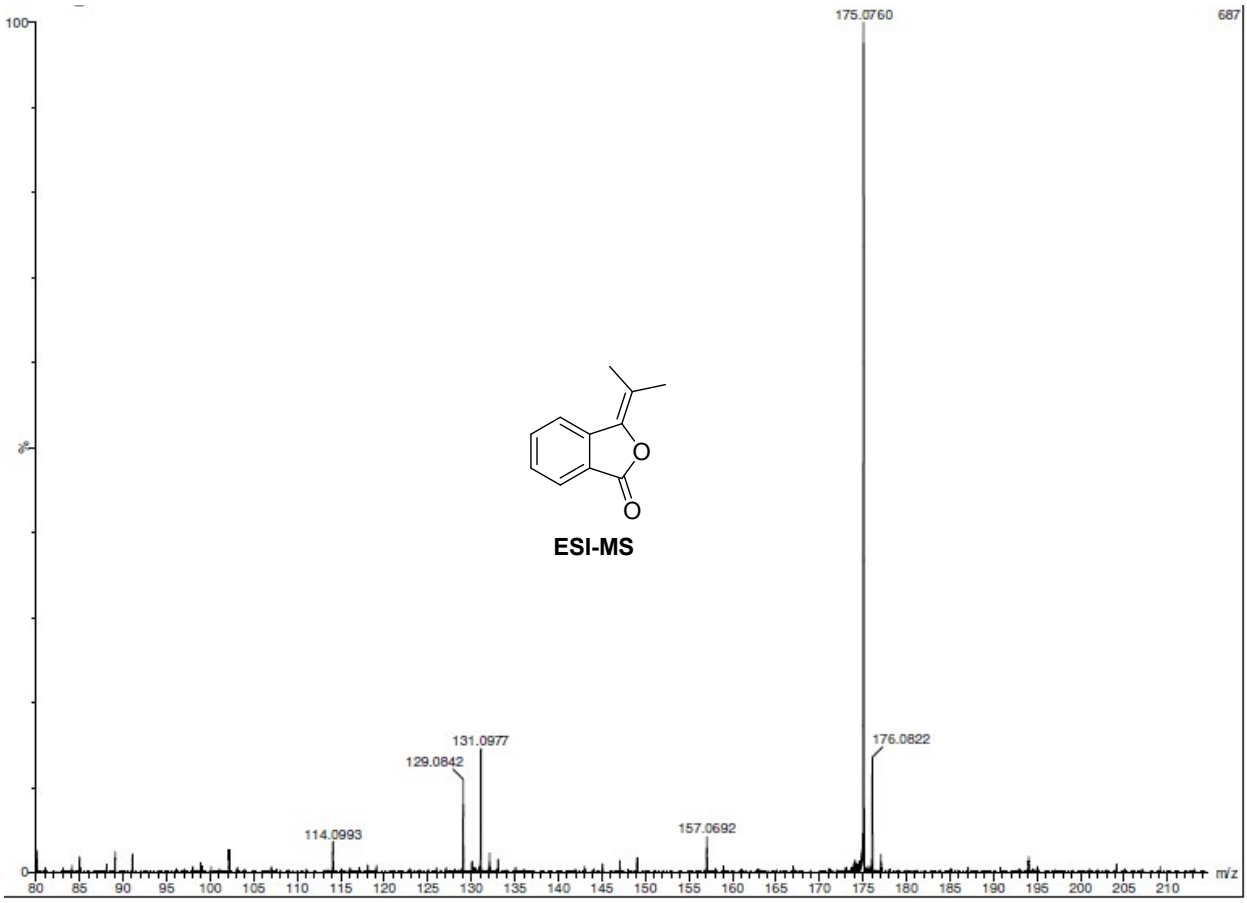

x10^5
3
2
1
0
CH3
COOH
175.0753
176.0784
179.0339
181.0130
168
170
172
174
176
178
180
182
184
m/z

2l

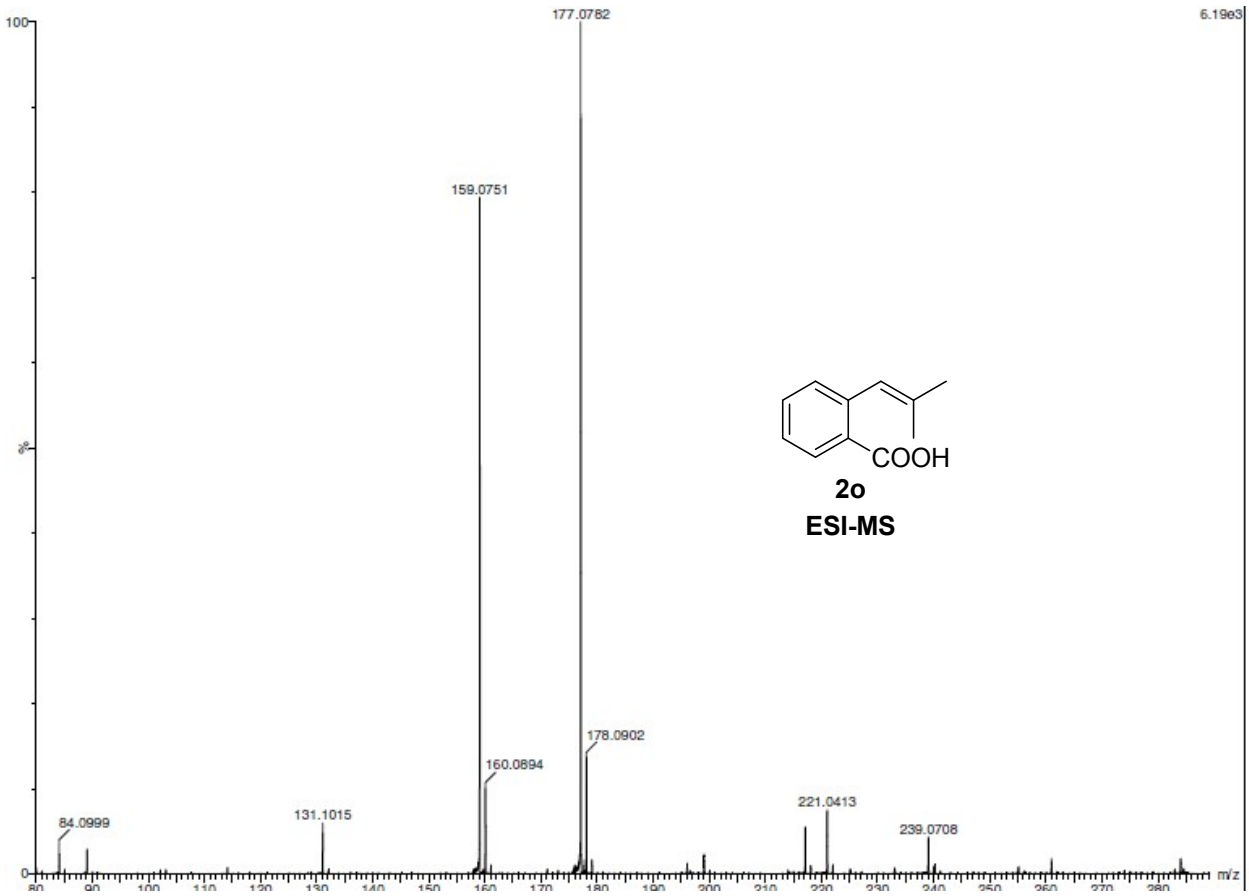

x10^5
189.0910
177.0907
203.0700
207.0651
CH3
COOH
2m
0
1
2
3
170
175
180
185
190
195
200
205
210
215m/z

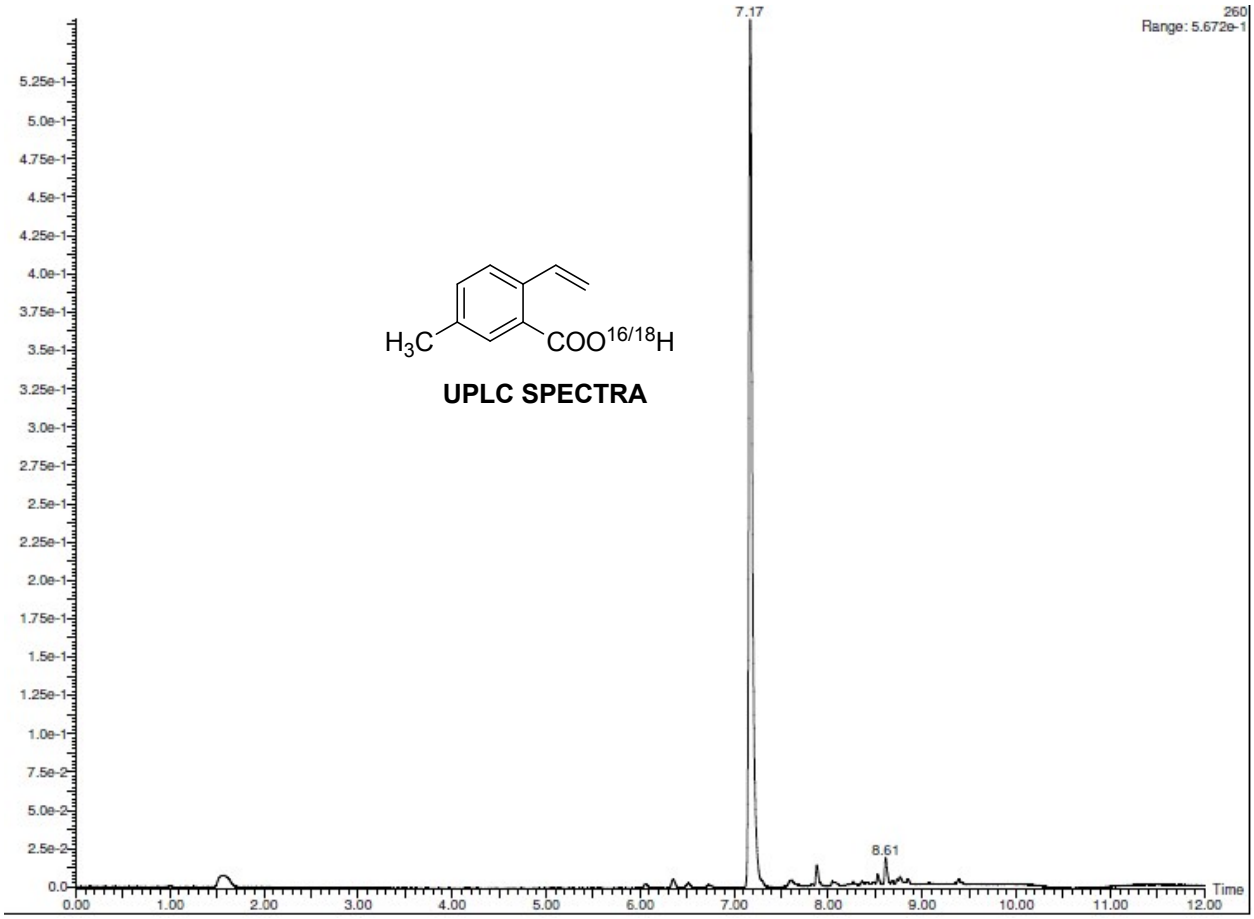


2n


100
%
0
175.0760
687
131.0977
129.0842
176.0822
114.0993
157.0692
80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210
m/z
O
O

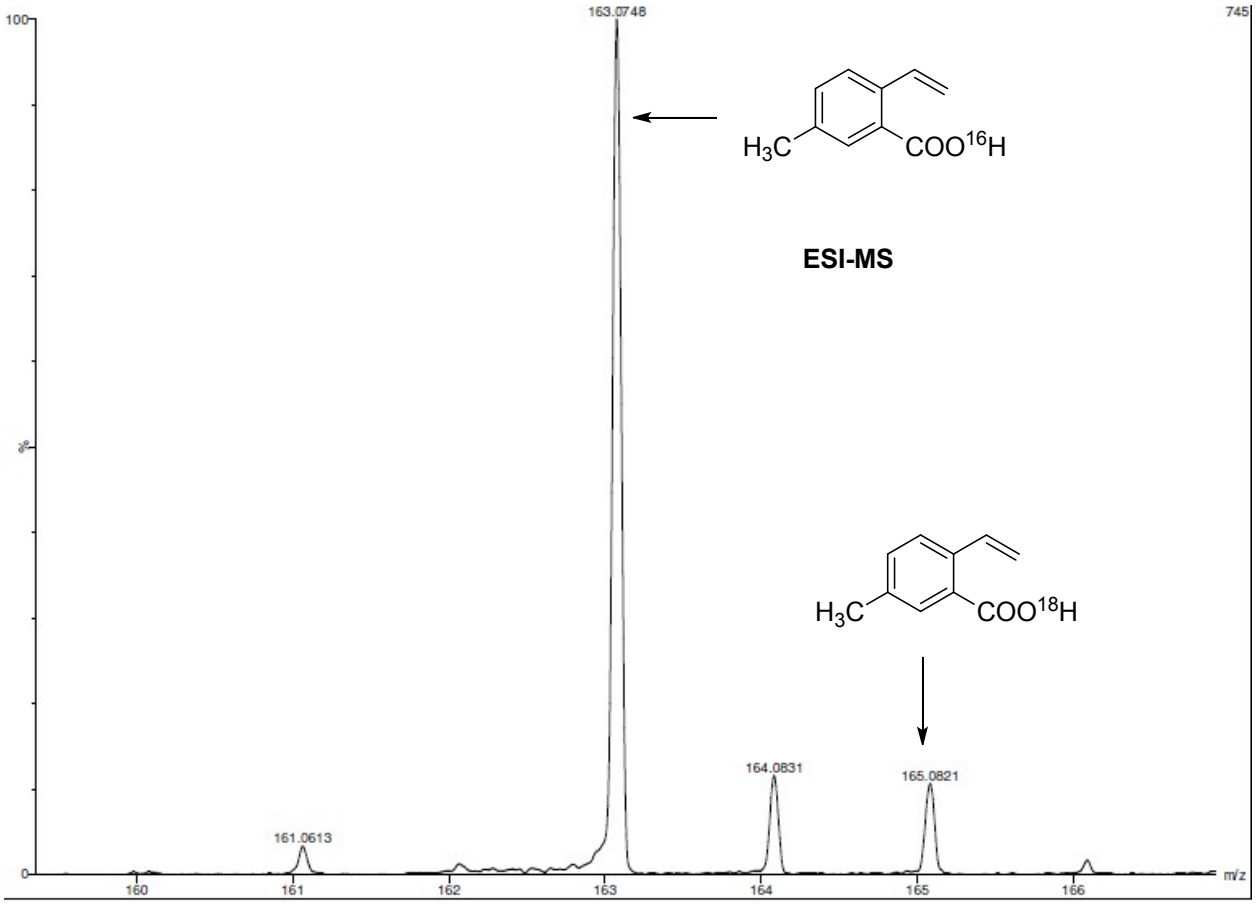
ESI-MS

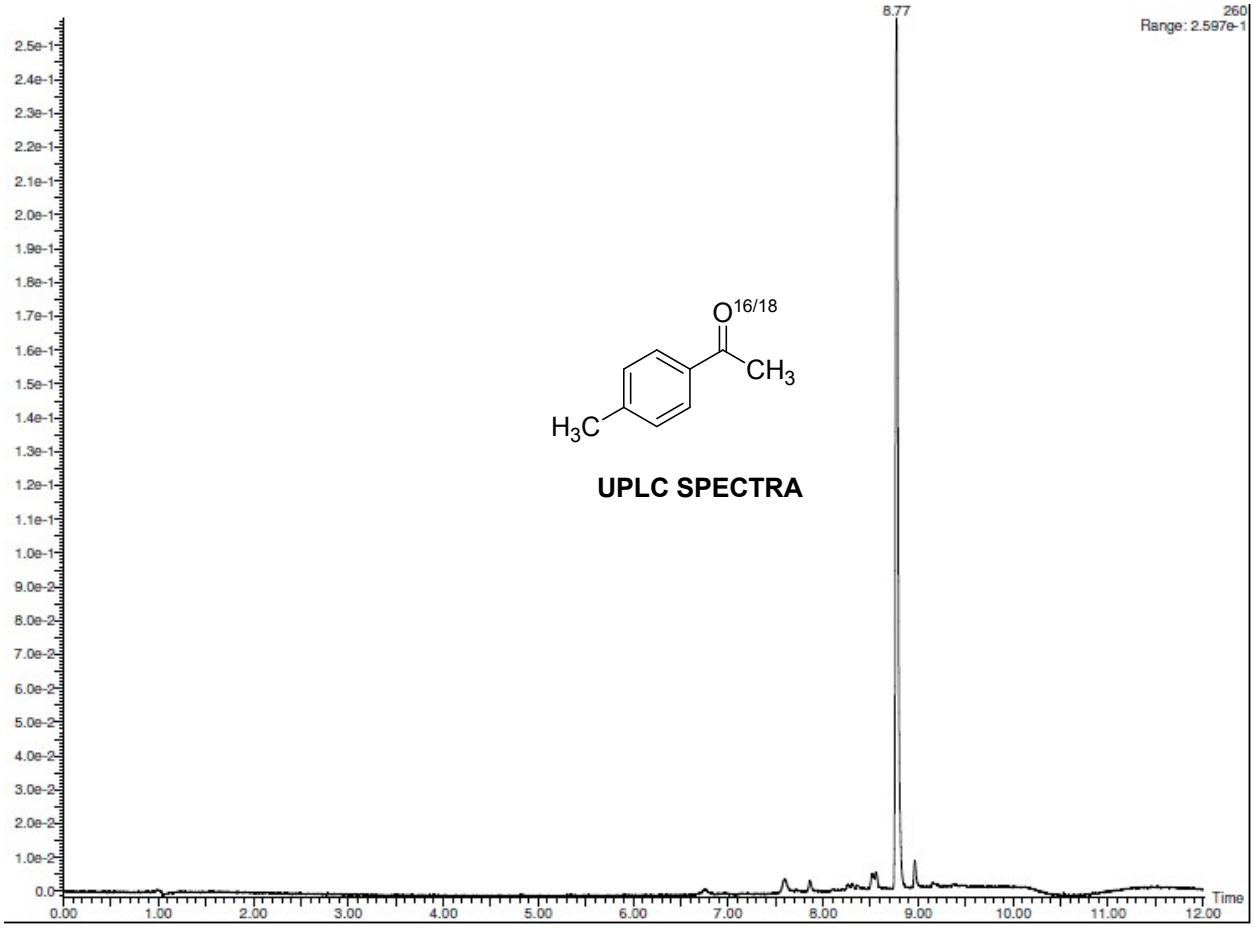

177.0782
6.19e3
159.0751
100
%
0
COOH
2o
ESI-MS
178.0902
160.0894
221.0413
131.1015
84.0999
239.0708
m/z

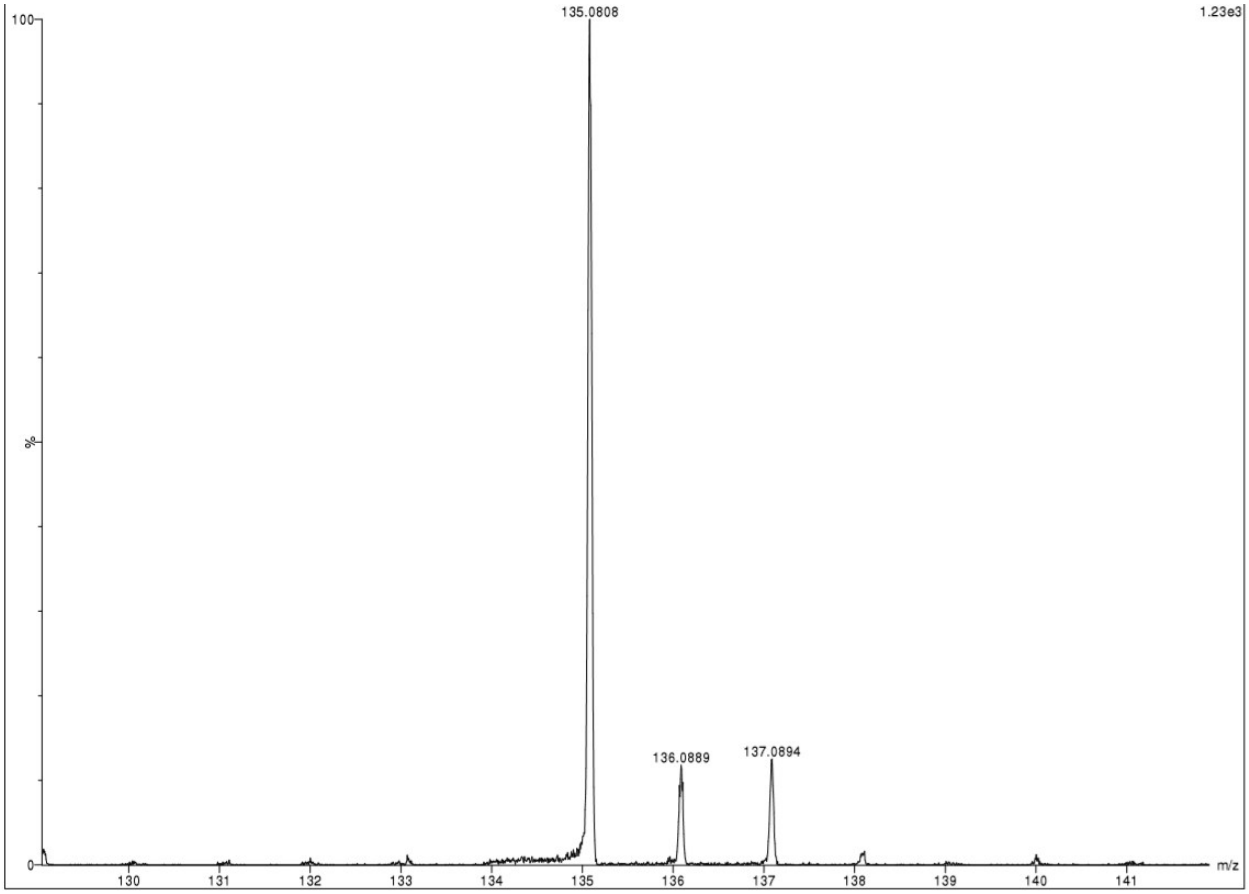


H_3C $COO^{16/18}H$

UPLC SPECTRA


100
%
0
163.0748
745
161.0613
164.0831
165.0821
160
161
162
163
164
165
166
m/z
H3C
COO16H
ESI-MS
H3C
COO18H


8.77
260
Range: 2.597e-1
O16/18
CH3
H3C
UPLC SPECTRA
Time


135.0808
1.23e3
100
%
0
136.0889
137.0894
130
131
132
133
134
135
136
137
138
139
140
141
m/z