Pd/C-Catalyzed Regiodivergent Hydrocarboxylation and Esterification of Alkynes

Pushkar Mehara,[a,b] Poonam Sharma,[a,b] Rohit Bains, [a,b] Ajay Kumar Sharma,[a,b] Pralay Das*[a,b]

[a] Chemical Technology Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur-176061, H.P, India.

[b] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

*Corresponding Author

E-mail: pdas@ihbt.res.in, pralaydas1976@gmail.com.

Table of Contents

A. General Information

High quality reagents and analytical grade solvents were purchased from Sigma Aldrich, TCI Chemicals, Merck and Sd Fine Chem. Ltd. Pd/C, Pd/Al_2O_3, $Pd(OAc)_2$ $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, and $Pd_2(dba)_3$ were purchased from TCI chemicals and Sigma Aldrich respectively. Reactions were monitored using TLC which was performed on pre-coated silica gel plates 60 F254 (purchased from Merck) in UV light detector. Silica gel (60-120 mesh size) for column chromatography purchased from Merck was used for the purification of compounds. ^1H and ^{13}C NMR spectra were recorded using a Bruker Advance 600 spectrometer operating at Bruker Advance 600 spectrometer (600 MHz, ^1H at 600 MHz, ^{13}C at 151 MHz) and JEOL ECX500 MHz (^1H at 500 MHz, ^{13}C at 126 MHz) Spectra were recorded at 25 °C in DMSO-d_6 [residual DMSO (δ_H 2.50 and 3.33 ppm), DMSO (δ_C 39.52 ppm), $CDCl_3$ (δ_H 7.26 ppm and δ_C 77.00 ppm)] with TMS as an internal standard. Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal, coupling constants (J) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet. Mass spectra were recorded on electrospray ionization (ESI) quadrupole time of flight (Q-TOF) mass spectrometer.

B. Optimization studies of terminal alkynes to cinnamic acid (2a)

Table S1: Effect of Pd/C loading on 2a:

Sr. No.	Pd/C (mol%)	Isolated Yield (%)
1	2	65
2	3	75
3	4	76
4	5	76

Reaction conditions: Phenyl acetylene (1 equiv), xantphos (0.06 equiv), TBAI (0.5 equiv), Oxalic acid (5 equiv), DMF (2 mL) at 125 ^oC for 24 hrs.

Table S2: Effect of Temperature in Reaction Progress

Sr. No.	Temperature (ºC)	Isolated Yield (%)
1	115	n.r.
2	125	75
3	135	72

Reaction conditions: Phenyl acetylene (1 equiv), Pd/C (0.03 equiv), xantphos (0.06 equiv), TBAI (0.5 equiv), Oxalic acid (5 equiv), DMF (2 mL) for 24 hrs.

Table S3: Effect of Time in Reaction Progress

Sr. No.	Time (hours)	Isolated Yield (%)
1	9	48
2	12	60
3	15	68
4	18	75
5	24	75

Reaction conditions: Phenyl acetylene (1 equiv), Pd/C (0.03 equiv) ligand (0.06 equiv), TBAI (0.5 equiv), Oxalic acid (5 equiv), DMF (2 mL) at 125 ºC.

Table S4: Effect of Oxalic acid:

Sr. No.	Oxalic acid (equiv)	Isolated yield (%)
1	2	72
2	3	85

3	4	80
4	5	75

Reaction conditions: Phenyl acetylene (1 equiv), Pd/C (0.03 equiv), xantphos (0.06 equiv), TBAI (0.5 equiv), DMF (2 mL) for 18 hrs.

Table S5: Screening of other CO sources:

Sr. No.	**CO Source (3 equiv)**	**Isolated Yield (%)[a]**
1	Oxalyl Chloride	Traces
2[b]	Formic acid	46
3	Formic acid	28
4	*N*-Formylsaccharin	34
5	$(HCHO)_n$	Traces
6	DMF	nr
7[c]	DMF	nr

[a] **Reaction conditions**: Phenyl acetylene (1 equiv), Pd/C (3 mol%), xantphos (0.06 equiv), TBAI (0.5 equiv), DMF (2 mL) at 125 ^{o}C for 18 hrs. [b] Acetic anhydride (3 equiv). [c] Acetic acid (3 equiv).

Table S6: Screening of ligands:

Sr. No.	**Ligand**	**Isolated Yield (%)**

1	Dppb	46
2	Dppp	38
3	Dppf	n.r.
4	1,10-Phenanthroline	Traces
5	Tri(*p*-tolyl)phosphine	48

Reaction conditions: Phenyl acetylene (1 equiv), Pd/C (0.03 equiv) ligand (0.06 equiv), TBAI (0.5 equiv), Oxalic acid (3 equiv), DMF (2 mL) at 125 ^{o}C for 18 hrs.

Table S7: Screening of solvent:

Sr. No.	**Solvent**	**Isolated Yield (%)**
1	DMA	80
2	Toluene	n.r
3	Propylene carbonate	n.r
4	PEG-400	35
5	Xylene	n.r
6	1,4-dioxane	n.r
7	DMSO	44

Reaction conditions: Phenyl acetylene (1 equiv), Pd/C (0.03 equiv) Xantphos (0.06 equiv), TBAI (0.5 equiv), Oxalic acid (3 equiv), Solvent (2 mL) at 125 ^{o}C for 18 hrs.

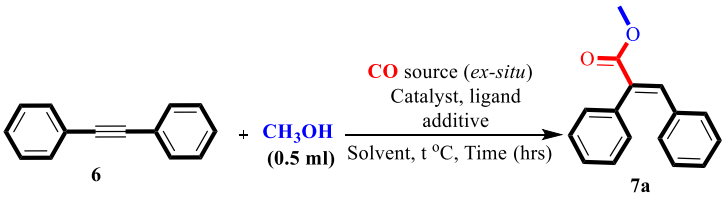
C. Optimization study of internal alkynes to *α,β*-unsaturated acid

4 5

S.No.	Catalyst (mol%)	Ligand (mol%)	Additive (equiv.)	Solvent	Yield(%)[b]
1	Pd/C	Xantphos	TBAI	DMF	42
2[c]	Pd/C	Xantphos	TBAI	DMF	52
3[d]	Pd/C	Xantphos	TBAI	DMF	58
4[d,e]	Pd/C	Xantphos	TBAI	DMF	65
5[d,f]	Pd/C	Xantphos	TBAI	DMF	66
6[d,g]	Pd/C	Xantphos	TBAI	DMF	71
7[d,h]	Pd/C	Xantphos	TBAI	DMF	79
8[d,i]	Pd/C	Xantphos	TBAI	DMF	88

[a]Reaction conditions: **4** (1.0 equiv), Pd/C (3 mol%), xantphos (6 mol%), TBAI (0.5 equiv), oxalic acid (3.0 equiv), 2.0 mL of DMF; heated for 18 hrs at 125 °C; [b] Isolated yields; [c] 24 h; [d] 30 h; [e] 4 equiv oxalic acid; [f] 5 equiv oxalic acid; [g] temperature 135 °C; [h] Pd/C:xantphos (mol%) 4:8; [i] Pd/C:xantphos (mol%) 5:10

D. Optimization study of internal alkynes to *α,β*-unsaturated esters



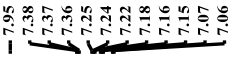
6 7a

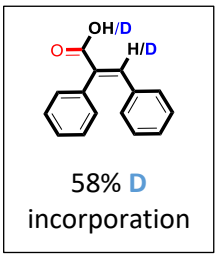
S.No.	Catalyst (mol%)	Ligand (mol%)	Additive (equiv)	Solvent	Yield(%)[b]
1	Pd/C (5)	Xantphos (10)	TBAI (0.5)	DMF	48
2[c]	Pd/C (5)	Xantphos (10)	TBAI (0.5)	DMF	28
3	Pd/C (5)	Xantphos (10)	CF_3CO_2H (0.5)	DMF	58
4	Pd/C (5)	Xantphos (10)	$(CH_3)_3CCO_2H$ (0.5)	DMF	25
5	Pd/C (5)	Xantphos (10)	CH_3COOH (0.5)	DMF	42
6	**Pd/C (5)**	**Xantphos (10)**	**PTSA (0.5)**	**DMF**	**80**
7	Pd/C (5)	Xantphos (10)	PTSA (1.0)	DMF	80
8	Pd/C (5)	Xantphos (10)	PTSA (0.25)	DMF	50
9	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMSO	53
10	Pd/C (5)	Xantphos (10)	PTSA (0.5)	PEG	45
11	Pd/C (5)	Xantphos (10)	PTSA (0.5)	Xylene	trace
12	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMA	76
13[d]	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMF	69
14[e]	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMF	65
15[f]	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMF	80
16[g]	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMF	76
17[h]	Pd/C (5)	Xantphos (10)	PTSA (0.5)	DMF	74
18[i]	Pd/Al_2O_3 (5)	Xantphos (10)	PTSA (0.5)	DMF	72

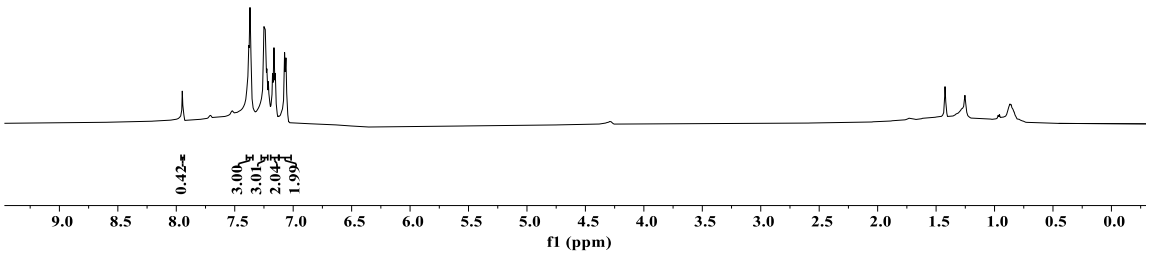
[a]Reaction conditions: Inner vial: **6** (0.28 mmol, 1 equiv.), 0.5 mL of methanol, Pd/C (5 mol%), Xantphos (10 mol%), Additive (equiv), 1.5 mL of DMF; Outer vial: oxalic acid (4 equiv) in 0.5 mL of DMF heated for 24 h at 125 °C; [b] Isolated yields; [c] one-pot reaction; [d] 1 mL of methanol; [e] 3 equiv oxalic acid; [f] 5 equiv oxalic acid; [g] temperature 135 °C; [h] 18 h [i] 5 wt%.

E. Control experiments data

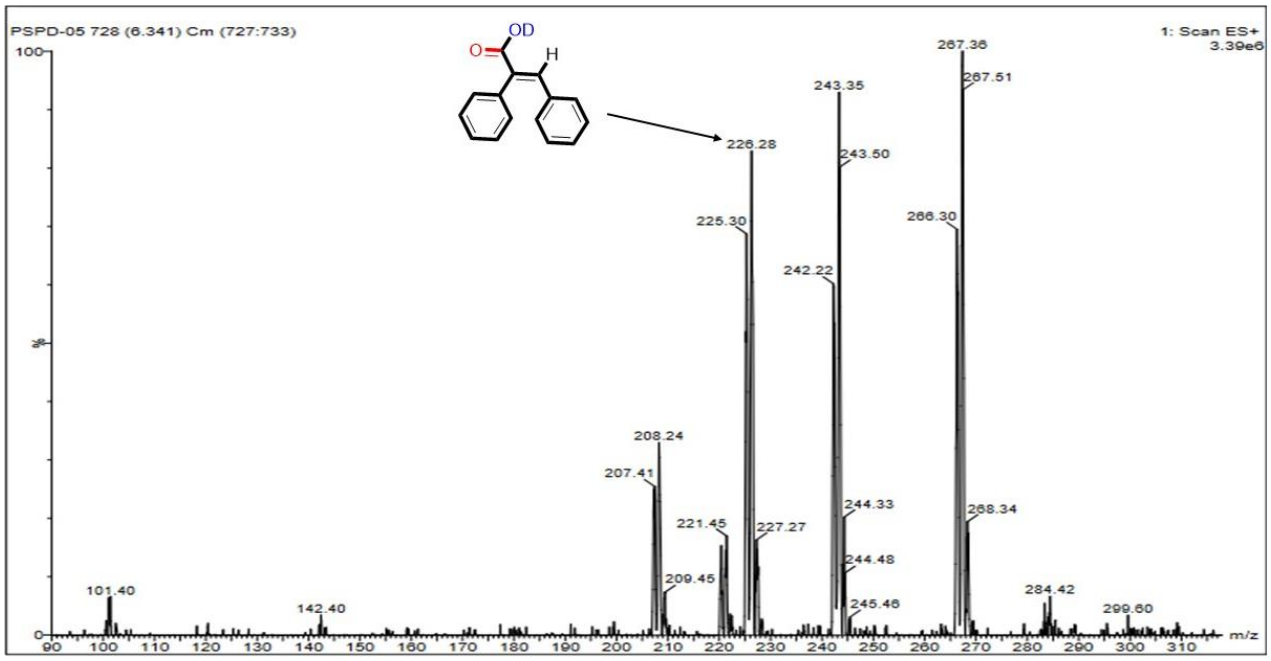
i) ^{1}H NMR spectra of 5aD (600 MHz, CHLOROFORM-*D*) δ (*ppm*) 7.37 (d, *J* = 6.9 Hz, 3H), 7.25 – 7.22 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 2H).



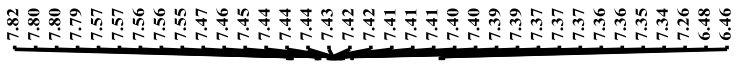


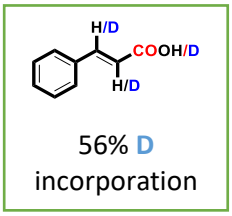


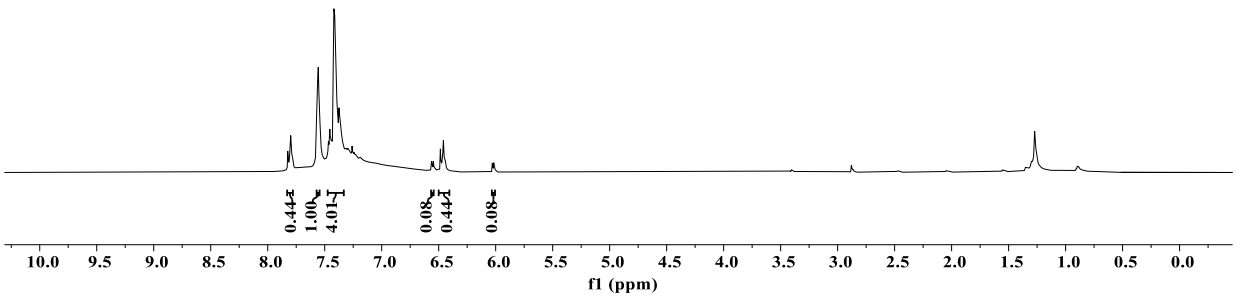
ii) LC-MS spectra of compound 5aD



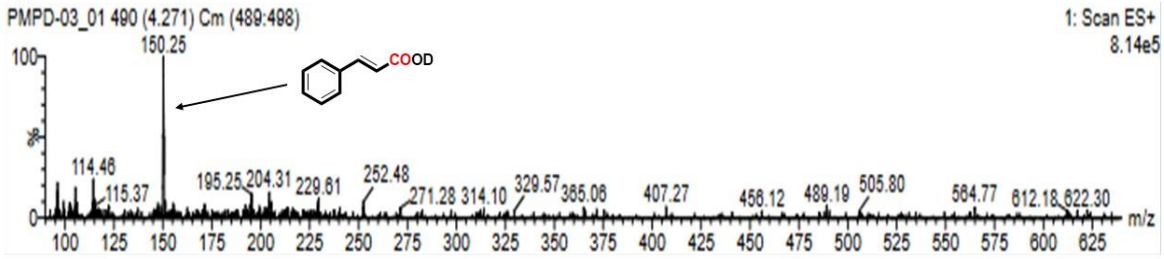
iii) ^{1}H NMR of 2aD (600 MHz, CHLOROFORM-*D*) δ 7.57 – 7.55 (m, 1H), 7.47 – 7.34 (m, 4H)

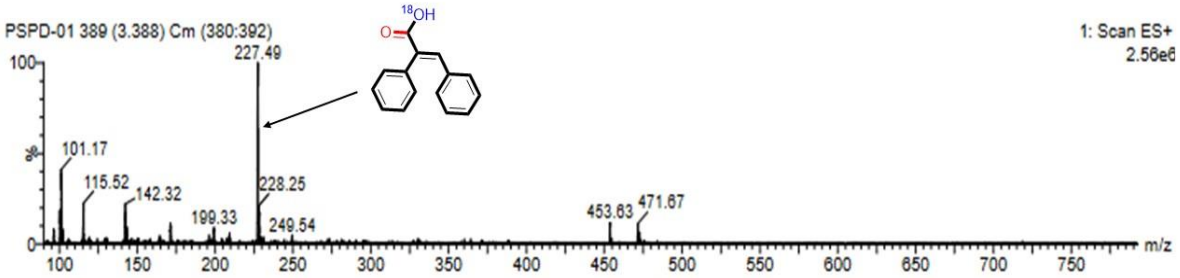




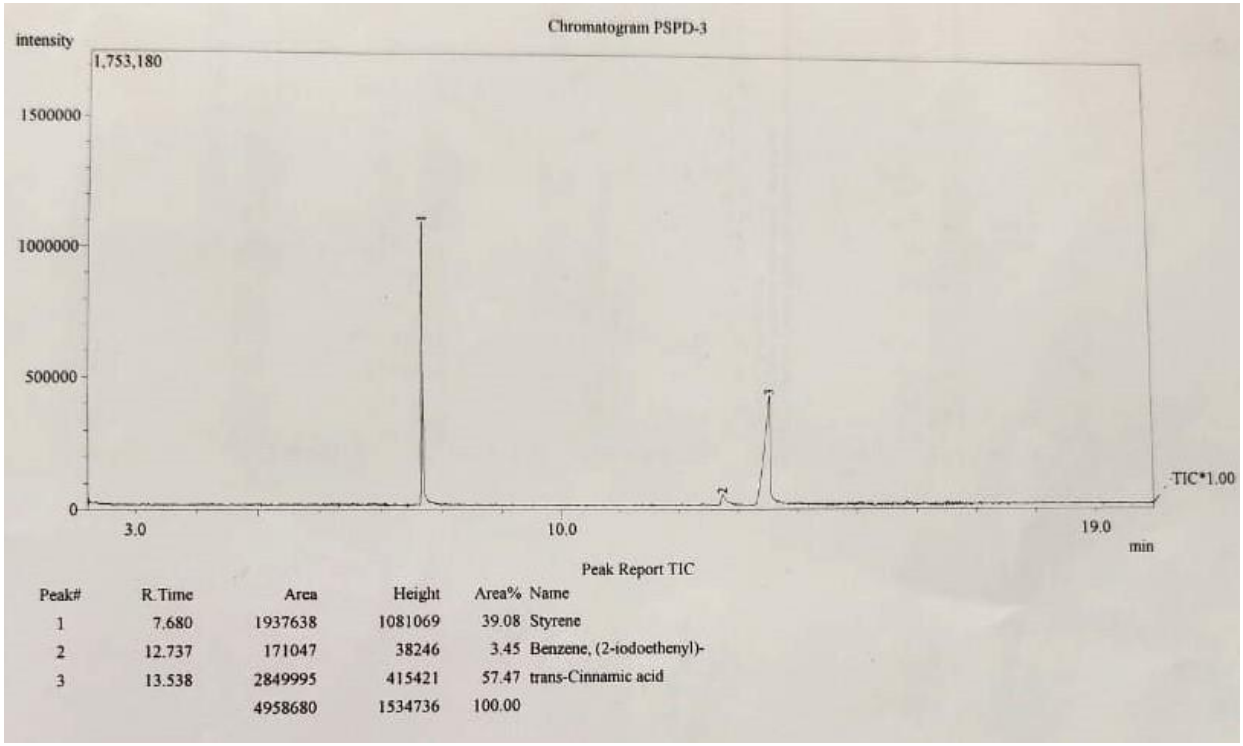


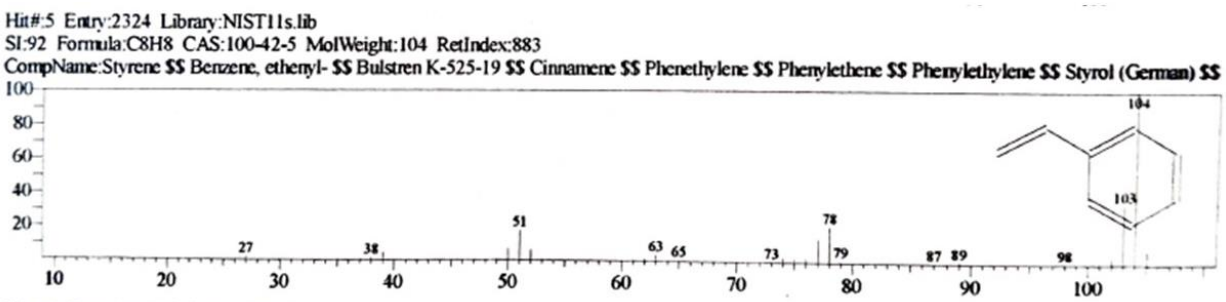
iv) LC-MS spectra of compounds 2aD and 9

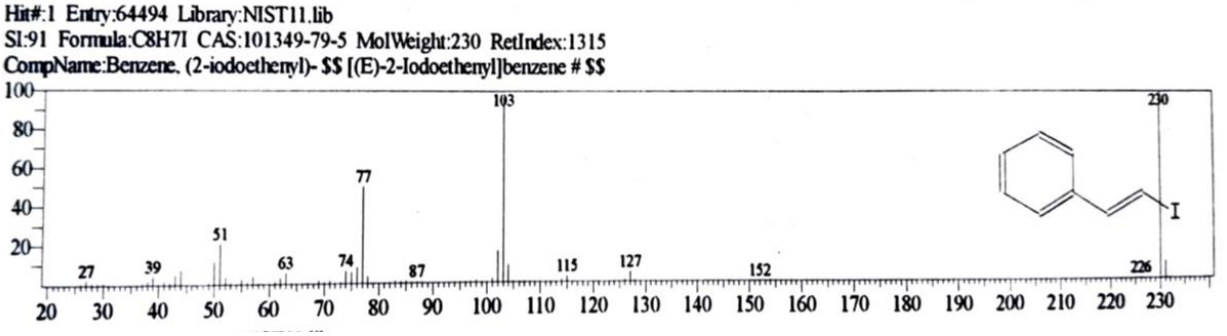


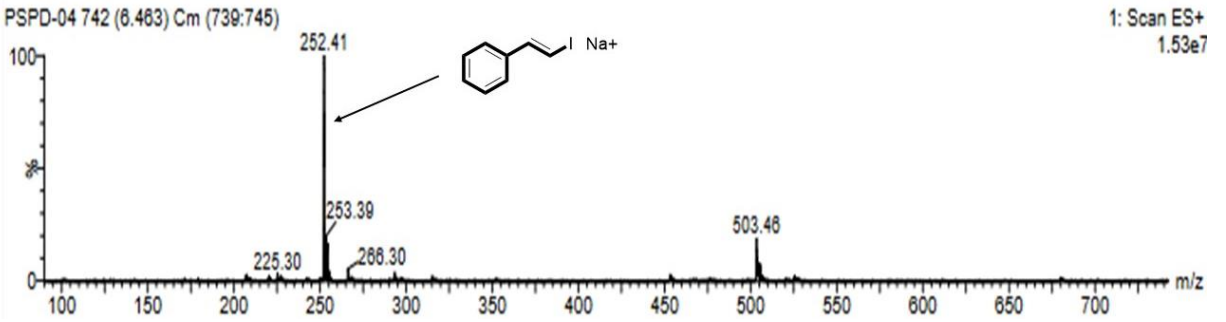


v) GC-MS and LC-MS spectra of styrene (10) and E-(*β*-iodo styrene) (11)



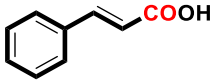






F. General procedure for the synthesis and characterization of compounds 2a-t, 3a-n and 5a-u

Cinnamic acid (2a)

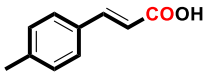


We executed the reaction using WHEATON® NextGen™ V Vial® (5 mL) and the entire system was fitted with PTFE faced black solid cap. Initially, the system was charged with phenylacetylene 1 (0.49 mmol, 53.7 µL), 5 wt% Pd/C (0.0147 mmol, 31 mg), Xantphos (0.0294 mmol, 17 mg), TBAI (0.245 mmol, 90 mg), oxalic acid (1.47 mmol, 132 mg) and DMF (2 mL). Further, the entire system was capped with the solid PTFE-faced cap and further tightened with Teflon tape to prevent the leakage of gas. The whole system was allowed to heat in preheated heating blocks at 125 ^{o}C for 18 hrs. The reaction progress was observed with the help of TLC. After the accomplishment of the reaction, the reaction mixture was placed in a separatory funnel. Further, 3 mL of water was added to the reaction mixture

and organic contents were extracted with ethyl acetate. The combined organic layer was passed over anhydrous Na_2SO_4 and concentrated under reduced pressure. The concentrated crude mixture was further purified by silica gel (mesh 100:200) column chromatography (15% EtOAc in *n*-hexane) afforded **2a** as white solid (61 mg, 85% yield, *α:β* = 16:84).

^{1}H NMR (500 MHz, DMSO-D_6) *δ* (*ppm*) 12.41 (s, 1H), 7.65-7.63 (m, 2H), 7.57 (d, *J* = 16.1 Hz, 1H), 7.37 – 7.36 (m, 3H), 6.51 (d, *J* = 15.6 Hz, 1H).^{13}C NMR (126 MHz, DMSO-D_6) *δ* (*ppm*) 167.73, 144.06, 134.33, 130.31, 129.00, 128.30, 119.32. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_7O_2^-$ is 147.0446, obsd. 147.0453.

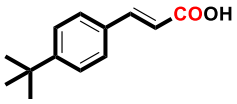
4-Methylcinnamic acid (2b)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-methylbenzene (0.43 mmol, 50 mg), 5 wt% Pd/C (0.0129 mmol, 27 mg), Xantphos (0.025 mmol, 17 mg), TBAI (0.215 mmol, 79 mg), oxalic acid (1.29 mmol, 116 mg) and DMF (2 mL) gave **2b** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (60 mg, 87% yield, *α:β* = 5:95).

^{1}H NMR (600 MHz, $CDCl_3$) *δ* (*ppm*) 7.77 (d, *J* = 15.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* (*ppm*) 172.50, 147.09, 141.27, 131.33, 129.68, 128.37, 116.14, 21.49. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{10}H_{11}O_2^+$ is 163.0754, obsd. 163.0766

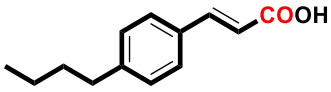
4-(*tert*-butyl)cinnamic acid (2c)



Prepared as described for **2a**; the reaction of 1-(*tert*-butyl)-4-ethynylbenzene (0.316 mmol, 50 mg), 5 wt% Pd/C (0.0094 mmol, 20 mg), Xantphos (0.0189 mmol, 11 mg), TBAI (0.158 mmol, 58 mg), oxalic acid (0.949 mmol, 86 mg) and DMF (2 mL) gave **2c** after purification silica gel (mesh 60:120) column chromatography (12% EtOAc in *n*-hexane) as white solid (50 mg, 78% yield, *α:β* = 50:50).

^{1}H NMR (600 MHz, $CDCl_3$) *δ* (*ppm*) 7.91 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.18 (m, 4H), 7.03 (d, *J* = 8.5 Hz, 2H), 1.37 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* (*ppm*) 173.10, 153.01, 150.90, 142.11, 132.53, 131.60, 130.87, 129.28, 125.68, 125.28, 34.78, 34.67, 31.40, 31.09. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{13}H_{15}O_2^-$ is 203.1072, obsd. 203.1082

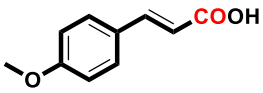
4-(*n*-butyl)cinnamic acid (2d)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-butylbenzene (0.316 mmol, 50 mg), 5 wt% Pd/C (0.0094 mmol, 20 mg), Xantphos (0.0189 mmol, 11 mg), TBAI (0.158 mmol, 58 mg), oxalic acid (0.949 mmol, 86 mg) and DMF (2 mL) gave **2d** after purification silica gel (mesh 60:120) column chromatography (12% EtOAc in *n*-hexane) as white solid (52 mg, 80% yield, *α:β* = 7:93).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.79 (d, *J* = 15.9 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 2.66 – 2.63 (m, 2H), 1.65 – 1.58 (m, 2H), 1.41-1.33 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 172.87, 147.14, 146.28, 131.47, 129.03, 128.40, 116.16, 35.56, 33.32, 22.29, 13.89. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{13}H_{15}O_2^-$ is 203.1072, obsd. 203.1082.

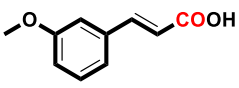
4-Methoxycinnamic acid (2e)



Prepared as described for **2a**, the reaction of 1-ethynyl-4-methoxybenzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), TBAI (0.189 mmol, 70 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **2e** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (59 mg, 88% yield).

^{1}H NMR (600 MHz, $CDCl_3$) *δ* (*ppm*) 7.74 (d, *J* = 15.9 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) *δ* (*ppm*) 172.25, 161.76, 146.72, 130.10, 126.82, 114.61, 114.41, 55.40. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_9O_3^-$ is 177.0552, obsd. 177.0556.

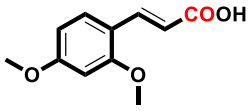
3-Methoxycinnamic acid (2f)



Prepared as described for **2a**; the reaction of 1-ethynyl-3-methoxybenzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), TBAI (0.189 mmol, 70 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **2f** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in n-hexane) as white solid (49 mg, 74% yield, *α:β* = 14:86).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 7.58 (d, *J* = 16.0 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.23 (m, 2H), 6.96.97 (m, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.74, 159.66, 143.93, 135.72, 129.96, 120.79, 119.62, 116.27, 112.98, 55.24. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_9O_3^-$ is 177.0552, obsd. 177.0556.

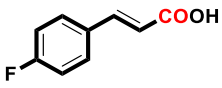
2,4-Dimethoxycinnamic acid (2g)



Prepared as described for 2a; the reaction of 1-ethynyl-2,4-dimethoxybenzene (0.308 mmol, 50mg), 5 wt% Pd/C (0.009 mmol, 20 mg), Xantphos (0.0226 mmol, 11 mg), TBAI (0.154 mmol, 57 mg), oxalic acid (0.925 mmol, 84 mg) and DMF (2 mL) gave **2g** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (42 mg, 66% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 12.07 (s, 1H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.53 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 168.24, 162.56, 159.33, 138.81, 129.94, 116.33, 115.44, 106.13, 98.36, 55.72, 55.46. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{11}H_{11}O_4^-$ is 207.0658, obsd. 207.0673

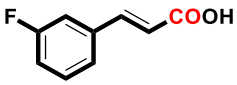
4-Fluorocinnamic acid (2h)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-fluorobenzene (0.4166 mmol, 50 mg), 5 wt% Pd/C (0.0125 mmol, 26 mg), Xantphos (0.025 mmol, 14 mg), TBAI (0.208 mmol, 77 mg), oxalic acid (1.25 mmol, 113 mg) and DMF (2 mL) gave **2h** after purification silica gel (mesh 60:120) column chromatography (12% EtOAc in *n*-hexane) as white solid (53 mg, 77% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.44 – 7.42 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 6.01 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.07, 162.81 (d, *J* = 247.8 Hz), 139.54, 132.06 (d, *J* = 3.4 Hz), 130.26 (d, *J* = 8.2 Hz), 129.58, 115.09 (d, *J* = 21.6 Hz). ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6FO_2^-$ is 165.0352, obsd. 165.0364

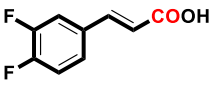
3-Fluorocinnamic acid (2i)



Prepared as described for **2a**; the reaction of 1-ethynyl-3-fluorobenzene (0.4166 mmol, 50 mg), 5 wt% Pd/C (0.0125 mmol, 26 mg), Xantphos (0.025 mmol, 14 mg), TBAI (0.208 mmol, 77 mg), oxalic acid (1.25 mmol, 113 mg) and DMF (2 mL) gave **2i** after purification silica gel (mesh 60:120) column chromatography (12 % EtOAc in n-hexane) as white solid (47 mg, 68% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 12.42 (s, 1H), 7.77 – 7.74 (m, 2H), 7.59 (d, J = 16.0 Hz, 1H), 7.23 (t, J = 8.8 Hz, 2H), 6.49 (d, J = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.57, 163.19 (d, J = 248.4 Hz), 142.74, 130.94 (d, J = 3.0 Hz), 130.54 (d, J = 8.4 Hz), 119.16, 119.14, 115.98, 115.84. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6FO_2^-$ is 165.0352, obsd. 165.0360.

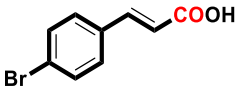
3,4-Difluorocinnamic acid (2j)



Prepared as described for **2a**; the reaction of 4-ethynyl-1,2-difluorobenzene (0.362 mmol, 50 mg), 5 wt% Pd/C (0.010 mmol, 23 mg), Xantphos (0.020 mmol, 13 mg), TBAI (0.181 mmol, 67 mg), oxalic acid (1.08 mmol, 98 mg) and DMF (2 mL) gave **2j** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (43 mg, 65% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 12.60 (s, 1H), 7.55 (d, J = 16.0 Hz, 1H), 7.48-7.45 (m, 2H), 7.25-7.20 (m, 1H), 6.66 (d, J = 16.0 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 167.27, 163.65 (d, J = 13.6 Hz), 161.70 (d, J = 13.2 Hz), 141.45, 138.16 (t, J = 9.9 Hz), 122.38, 111.32 (d, J = 6.0 Hz), 111.17 (d, J = 5.8 Hz), 105.21 (t, J = 26.1 Hz). ^{19}F NMR (471 MHz, DMSO-d_6) δ (*ppm*) -136.95 (d, J = 20.6 Hz), -139.00 (d, J = 22.9 Hz). ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_5F_2O_2^-$ is 183.0258, obsd. 183.0269.

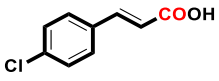
4-Bromocinnamic acid (2k)



Prepared as described for **2a**; the reaction of 1-bromo-4-ethynylbenzene (0.274 mmol, 50 mg), 5 wt% Pd/C (0.008 mmol, 18 mg), Xantphos (0.0165 mmol, 10 mg), TBAI (0.137 mmol, 51 mg), oxalic acid (0.824 mmol, 74 mg) and DMF (2 mL) gave **2k** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as pale yellow solid (42 mg, 67% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 7.61 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 16.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.48, 142.53, 133.60, 131.88, 130.17, 123.52, 120.29. ESI-MS [M-H]$^-$ & [M+2-H]$^-$ *(m/z)* calcd. for $C_9H_6BrO_2^-$ is 224.9551, obsd. 224.9562.

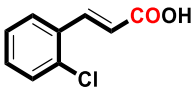
4-Chlorocinnamic acid (2l)



Prepared as described for **2a**; the reaction of 1-chloro-4-ethynylbenzene (0.366 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0219 mmol, 13 mg), TBAI (0.183 mmol, 68 mg), oxalic acid (1.09 mmol, 98 mg) and DMF (2 mL) gave **2l** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as pale yellow solid (43 mg, 64% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 12.49 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.42, 142.51, 134.71, 133.22, 129.93, 128.93, 120.09. ESI-MS [M-H]$^-$ *(m/z)* calcd. for $C_9H_6ClO_2^-$ is 181.0057, obsd. 181.0061.

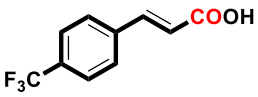
2-Chlorocinnamic acid (2m)



Prepared as described for **2a**; the reaction of 1-chloro-2-ethynylbenzene (0.366 mmol, 50mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0219 mmol, 13 mg), TBAI (0.183 mmol, 68 mg), oxalic acid (1.09 mmol, 98 mg) and DMF (2 mL) gave **2m** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as pale yellow solid (37 mg, 56% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 12.64 (s, 1H), 7.92- 7.90 (m, 1H), 7.87 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40-7.37 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 167.18, 138.72, 133.59, 131.88, 131.68, 129.96, 128.25, 127.78, 122.32. ESI-MS [M-H]$^-$ *(m/z)* calcd. for $C_9H_6ClO_2^-$ is 181.0057, obsd. 181.0061.

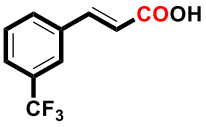
4-(Trifluoromethyl)cinnamic acid (2n)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-(trifluoromethyl)benzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), TBAI (0.189 mmol, 70 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **2n** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (47 mg, 73% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 12.61 (s, 1H), 7.92 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 16.1 Hz, 1H), 6.68 (d, J = 16.1 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.67, 142.52, 138.78, 130.39 (d, J = 32.1 Hz), 129.31, δ 126.16 (d, J = 3.7 Hz),125.41 122.68. ^{19}F NMR (565 MHz, DMSO-d_6) δ (*ppm*) -61.26. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_6F_3O_2^-$ is 215.032, obsd. 215.0334.

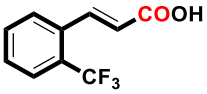
3-(Trifluoromethyl)cinnamic acid (2o)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-(trifluoromethyl)benzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), TBAI (0.189 mmol, 70 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **2o** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (42 mg, 66% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 12.58 (s, 1H), 8.06 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.68 (d, J = 16.1 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 6.71 (d, J = 16.1 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 167.43, 142.25, 135.52, 131.85, 129.98, 129.60 (d, J = 32.4 Hz), 126.46, 125.01 (d, J = 4.2 Hz), 122.98, 121.52. ^{19}F NMR (471 MHz, DMSO-d_6) δ (*ppm*) -62.21. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_6F_3O_2^-$ is 215.032, obsd. 215.0334.

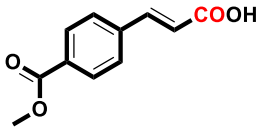
2-(Trifluoromethyl)cinnamic acid (2p)



Prepared as described for **2a**, reaction of 1-ethynyl-2-(trifluoromethyl)benzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), TBAI (0.189 mmol, 70 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **2p** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (37 mg, 58% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 12.78 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.83 (m, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 6.62 (dd, *J* = 15.7, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 138.24 (d, *J* = 2.3 Hz), 133.09, 132.51 (d, *J* = 1.6 Hz), 130.27, 128.50, 127.71 – 126.54 (m), 126.14 (q, *J* = 5.6 Hz), 125.28, 123.93, 123.10. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_6F_3O_2^-$ is 215.032, obsd. 215.0334.

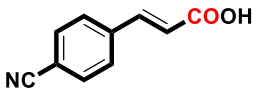
4-(2-Carboxy-vinyl)-benzoic acid methyl ester (2q)



Prepared as described for **2a**; the reaction of methyl 4-ethynylbenzoate (0.287 mmol, 50 mg), 5 wt% Pd/C (0.0087 mmol, 18 mg), Xantphos (0.017 mmol, 10 mg), TBAI (0.143 mmol, 53 mg), oxalic acid (0.862 mmol, 78 mg) and DMF (2 mL) gave **2q** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (47 mg, 79% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 7.97 – 7.95 (m, 2H), 7.83 – 7.82 (m, 2H), 7.63 (d, *J* = 16.0 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.28, 165.80, 142.47, 138.79, 130.60, 129.62, 128.45, 121.95, 52.31. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{11}H_9O_4^-$ is 205.0501, obsd. 205.0503

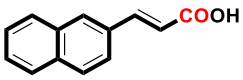
4-Cyanocinnamic acid (2r)



Prepared as described for **2a**; the reaction of 4-ethynyl benzonitrile (0.397 mmol, 50 mg), 5 wt% Pd/C (0.0118 mmol, 25 mg), Xantphos (0.0236 mmol, 14 mg), TBAI (0.196 mmol, 73 mg), oxalic acid (1.18 mmol, 106 mg) and DMF (2 mL) gave **2r** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (47 mg, 69% yield, α:β = 14:86).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 12.62 (s, 1H), 7.90 – 7.86 (m, 4H), 7.64 (d, *J* = 16.1 Hz, 1H), 6.71 (d, *J* = 16.1 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.14, 141.90, 138.84, 132.72, 128.88, 122.85, 118.60, 112.11. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_6NO_2^-$ is 172.0399, obsd. 172.0413

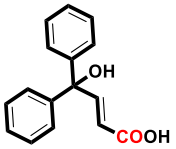
(*E*)-3-(naphthalen-2-yl)acrylic acid (2s)



Prepared as described for **2a**; the reaction of 2-ethynyl naphthalene (0.328 mmol, 50 mg), 5 wt% Pd/C (0.009 mmol, 21 mg), Xantphos (0.019 mmol, 12 mg), TBAI (0.164 mmol, 61 mg), oxalic acid (.98 mmol, 89 mg) and DMF (2 mL) gave **2s** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (48 mg, 74% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ (*ppm*) 8.39 (d, J = 15.7 Hz, 1H), 8.19 (t, J = 7.6 Hz, 2H), 8.02 – 7.92 (m, 2H), 7.63 – 7.55 (m, 3H), 6.60 (d, J = 15.7 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (*ppm*) 167.45, 140.08, 133.30, 131.04, 130.76, 130.33, 128.72, 127.13, 126.29, 125.72, 125.21, 122.98, 122.07. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{13}H_9O_2^-$ is 197.0603, obsd. 197.0611.

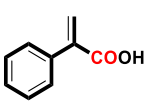
(*E*)-4-hydroxy-4,4-diphenylbut-2-enoic acid (2t)



Prepared as described for **2a**; the reaction of 1,1-diphenylprop-2-yn-1-ol (0.240 mmol, 50 mg), 5 wt% Pd/C (0.007 mmol, 15 mg), Xantphos (0.014 mmol, 8 mg), TBAI (0.120 mmol, 44 mg), oxalic acid (0.72 mmol, 89 mg) and DMF (2 mL) gave **2t** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (37 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.43 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 3.7 Hz, 6H), 7.23 (d, J = 7.6 Hz, 2H), 6.29 (t, J = 7.4 Hz, 1H), 3.26 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 178.55, 145.22, 141.71, 138.99, 129.67, 128.40, 128.13, 127.77, 127.48, 127.40, 119.40, 35.16. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{16}H_{14}O_3^-$ is 253.0865, obsd. 253.0877

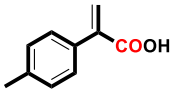
2-phenylacrylic acid (3a)



Prepared as described for **2a**; the reaction of phenylacetylene (0.49 mmol, 53.7 µL), 5 wt% Pd/C (0.0147 mmol, 31 mg), Xantphos (0.0294 mmol, 17 mg), oxalic acid (1.47 mmol, 132 mg) and DMF (2 mL) gave **3a** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (56 mg, 78% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.49-7.47 (m, 2H), 7.41 – 7.39 (m, 3H), 6.59-6.58 (m, 1H), 6.06-6.05 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.34, 140.63, 136.06, 129.43, 128.43, 128.32, 128.11. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_7O_2^-$ is 147.0446, obsd. 147.0453.

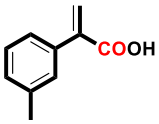
2-(*p*-tolyl)acrylic acid (3b)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-methylbenzene (0.43 mmol, 50 mg), 5 wt% Pd/C (0.0129 mmol, 27 mg), Xantphos (0.025mmol, 17 mg), oxalic acid (1.29 mmol, 116 mg) and DMF (2 mL) gave **3b** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (56 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.35 – 7.34 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.50 (d, *J* = 1.2 Hz, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 172.19, 140.43, 138.27, 133.20, 128.84, 128.69, 128.31, 21.19. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_9O_2^-$ is 161.0603, obsd. 161.0616

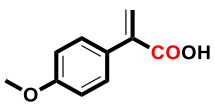
2-(*m*-tolyl)acrylic acid (3c)



Prepared as described for **2a**; the reaction of 1-ethynyl-3-methylbenzene (0.43 mmol, 50 mg), 5 wt% Pd/C (0.0129 mmol, 27 mg), Xantphos (0.025mmol, 16.9 mg), oxalic acid (1.29 mmol, 116 mg) and DMF (2 mL) gave **3c** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (51 mg, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.28 – 7.18 (m, 3H), 7.17 – 7.16 (m, 1H), 6.52 (d, *J* = 1.2 Hz, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 172.13, 140.70, 137.75, 136.03, 129.21, 129.12, 129.11, 128.04, 125.52, 21.41. ESI-MS $[M+H]^+$ *(m/z)* calcd. for $C_{10}H_{11}O_2^+$ is 163.0754, obsd. 163.0766.

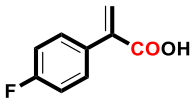
2-(4-methoxyphenyl)acrylic acid (3d)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-methoxybenzene (0.378 mmol, 50 mg), 5 wt% Pd/C (0.0113 mmol, 24 mg), Xantphos (0.0226 mmol, 13 mg), oxalic acid (1.13 mmol, 102 mg) and DMF (2 mL) gave **3d** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (53 mg, 82% yield).

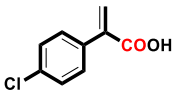
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.41 – 7.26 (m, 2H), 6.91-6.89 (m, 2H), 6.46 (d, *J* = 1.2 Hz, 1H), 5.97 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 172.18, 159.72, 139.88, 129.67, 128.52, 127.99, 113.57, 55.30. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_9O_3^-$ is 177.0552, obsd. 177.0556.

2-(4-fluorophenyl)acrylic acid (3e)



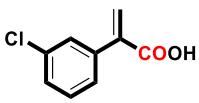
Prepared as described for **2a**; the reaction of 1-ethynyl-3-fluorobenzene (0.4166 mmol, 50 mg), 5 wt% Pd/C (0.0125 mmol, 26 mg), Xantphos (0.025 mmol, 14 mg), oxalic acid (1.25 mmol, 113 mg) and DMF (2 mL) gave **3e** after purification silica gel (mesh 60:120) column chromatography (12% EtOAc in *n*-hexane) as white solid (54 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.44 – 7.42 (m, 2H), 7.08 – 7.05 (m, 2H), 6.56 (s, 1H), 6.01 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.07, 162.81 (d, *J* = 247.8 Hz), 139.54, 132.06 (d, *J* = 3.3 Hz), 130.26 (d, *J* = 8.2 Hz), 129.57, 115.09 (d, *J* = 21.6 Hz). ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6FO_2^-$ is 165.0352, obsd. 165.0364.

2-(4-chlorophenyl)acrylic acid (3f)



Prepared as described for **2a**; the reaction of 1-chloro-4-ethynylbenzene (0.366 mmol, 50 mg), 5 wt% Pd/C (0.0109 mmol, 23 mg), Xantphos (0.0219 mmol, 13 mg), oxalic acid (1.09 mmol, 98 mg) and DMF (2 mL) gave **3f** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in n-hexane) as white solid (48 mg, 72% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 2H), 6.58 (d, *J* = 0.9 Hz, 1H), 6.04 (d, *J* = 0.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.70, 139.43, 134.48, 134.40, 130.02, 129.80, 128.35. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6ClO_2^-$ is 181.0057, obsd. 181.0061.

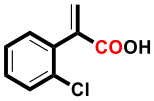
2-(3-chlorophenyl)acrylic acid (3g)



Prepared as described for **2a**; the reaction of 1-chloro-3-ethynylbenzene (0.366 mmol, 50 mg), 5 wt% Pd/C (0.0109 mmol, 23 mg), Xantphos (0.0219 mmol, 13 mg), oxalic

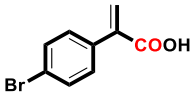
acid (1.09 mmol, 98 mg) and DMF (2 mL) gave **3g** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (43 mg, 65% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.45 (t, *J* = 1.8 Hz, 1H), 7.37 – 7.28 (m, 3H), 6.60 (s, 1H), 6.06 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.36, 139.34, 137.70, 134.03, 130.56, 129.38, 128.60, 128.47, 126.68. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6ClO_2^-$ is 181.0057, obsd. 181.0061

2-(2-chlorophenyl)acrylic acid (3h)



Prepared as described for **2a**; the reaction of 1-chloro-2-ethynylbenzene (0.366 mmol, 50 mg), 5 wt% Pd/C (0.0109 mmol, 23 mg), Xantphos (0.0219 mmol, 13 mg), oxalic acid (1.09 mmol, 98 mg) and DMF (2 mL) gave **3h** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (35 mg, 52% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.55 – 7.36 (m, 1H), 7.33 – 7.19 (m, 3H), 6.67 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 170.98, 139.46, 135.81, 133.40, 131.47, 130.95, 129.69, 129.36, 126.71. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_6ClO_2^-$ is 181.0057, obsd. 181.0061.

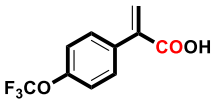
2-(4-bromophenyl)acrylic acid (3i)



Prepared as described for **2a**; the reaction of 1-bromo-4-ethynylbenzene (0.274 mmol, 50 mg), 5 wt% Pd/C (0.008 mmol, 18 mg), Xantphos (0.0165 mmol, 10 mg), oxalic acid (0.824 mmol, 74 mg) and DMF (2 mL) gave **3i** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (36 mg, 58% yield).

1H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.50 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 1.0 Hz, 1H), 6.04 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.33, 139.46, 134.89, 131.32, 130.10, 130.02, 122.71. ESI-MS $[M-H]^-$ & $[M+2,-H]^-$ *(m/z)* calcd. for $C_9H_6BrO_2^-$ is 224.9551, 226.9531, obsd. 224.9562.

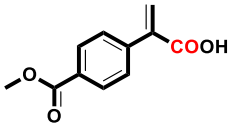
2-(4-(trifluoromethoxy)phenyl)acrylic acid (3j)



Prepared as described for **2a**; the reaction of 1-ethynyl-4-(trifluoromethoxy)benzene (0.268 mmol, 50 mg), 5 wt% Pd/C (0.008 mmol, 18 mg), Xantphos (0.0161 mmol, 9 mg), oxalic acid (0.806 mmol, 73 mg) and DMF (2 mL) gave **3j** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (43 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.32 – 7.28 (m, 1H), 7.18 – 7.13 (m, 3H), 6.60 (s, 1H), 6.05 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.63, 151.47 – 148.74 (m), 138.53, 132.75 (t, J = 5.4 Hz), 130.65, 124.72 (t, J = 4.8 Hz), 117.77 (d, J = 17.5 Hz), 116.98 (d, J = 16.8 Hz). ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{10}H_8F_3O_3^+$ is 233.0420, obsd. 233.0420.

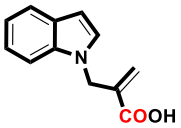
2-(4-(methoxycarbonyl)phenyl)acrylic acid (3k)



Prepared as described for **2a**; the reaction of 1 methyl 4-ethynylbenzoate (0.287 mmol, 50 mg), 5 wt% Pd/C (0.0087 mmol, 18 mg), Xantphos (0.017 mmol, 10 mg), oxalic acid (0.862 mmol, 78 mg) and DMF (2 mL) gave **3k** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (44 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 8.05 – 8.03 (m, 2H), 7.53 – 7.51 (m, 2H), 6.64 (d, J = 0.9 Hz, 1H), 6.11 (d, J = 0.9 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.09, 166.74, 140.48, 139.77, 130.83, 129.93, 129.42, 128.50,52.21. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{11}H_9O_4^-$ is 205.0501, obsd. 205.0503.

2-((1*H*-indol-1-yl)methyl)acrylic acid (3l)

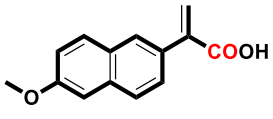


Prepared as described for **2a**; the reaction of 1-(prop-2-yn-1-yl)-1*H*-indole (0.3225 mmol, 50 mg), 5 wt% Pd/C (0.0096 mmol, 20 mg), Xantphos (0.0193 mmol, 11 mg), oxalic acid (0.967 mmol, 87 mg) and DMF (2 mL) gave **3l** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as pale yellow solid (47 mg, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 9.66 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.14 – 7.11 (m, 2H), 6.55 (d, J = 3.3 Hz, 1H), 6.39 (s, 1H), 5.28 (s, 1H), 4.99 (s, 2H); ^{13}C

NMR (126 MHz, $CDCl_3$) δ (*ppm*) 170.99, 135.90, 135.76, 128.72, 128.61, 128.33, 121.84, 121.05, 119.67, 109.44, 102.02, 46.30. ESI-MS $[M-H]^-$ (m/z) calcd. for $C_{12}H_{10}NO_2^-$ is 200.0712, obsd. 200.0717.

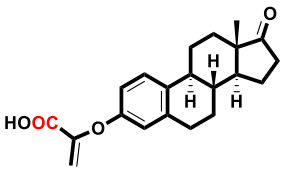
2-(6-methoxynaphthalen-2-yl)acrylic acid (3m)



Prepared as described for **2a**, reaction of 2-ethynyl-6-methoxynaphthalene (0.274 mmol, 50 mg), 5 wt% Pd/C (0.008 mmol, 17 mg), Xantphos (0.0164 mmol, 10 mg), oxalic acid (0.824 mmol, 74 mg) and DMF (2 mL) gave **3m** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (34 mg, 55% yield, α:β = 58:42).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 8.09 (s, 1H), 7.91-7.90 (m, 1H), 7.86-7.78 (m, 4H), 7.76-7.69 (m, 2H), 7.55- 7.52 (m, 1H), 7.35 (m, 1H), 7.32-7.31 (m, 1H), 7.21 – 7.16 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.26 (s, 1H), 6.05 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 168.04, 167.76, 158.38, 157.62, 144.19, 141.52, 135.32, 133.84, 131.83, 130.08, 129.73, 129.59, 129.53, 128.24, 128.00, 127.41, 126.85, 126.56, 126.27, 125.40, 124.54, 119.21, 118.84, 118.26, 106.23, 105.71, 55.32, 55.21. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{14}H_{11}O_3^-$ is 227.0708, obsd. 227.0721

2-(((9S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)acrylic acid (3n)

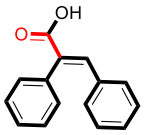


Prepared as described for **2a**; the reaction of (9S,14S)-3-(ethynyloxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (0.179 mmol, 50 mg), 5 wt% Pd/C (0.0053 mmol, 11 mg), Xantphos (0.0107 mmol, 6 mg), oxalic acid (0.537 mmol, 49 mg) and DMF (2 mL) gave **3n** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (37 mg, 65% yield, α:β = 57:43).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.34 (s, 1H), 7.29 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 6.49 (s, 1H), 5.99 (s, 1H), 2.97-2.89 (m, 6H), 2.69 (t, *J* = 7.9 Hz, 5H), 2.42 – 2.55 (m, 5H), 2.35 – 2.30 (m, 2H), 2.19 – 2.13 (m, 2H), 2.10 – 1.96 (m, 8H), 1.66 – 1.59 (m,

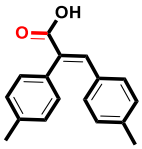
5H), 1.58-1.46 (m, 11H), 0.92-0.90 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 221.21, 221.00, 172.53, 172.11, 147.19, 143.20, 140.58, 140.22, 137.34, 136.46, 133.82, 131.69, 129.24, 129.12, 129.03, 128.83, 126.15, 125.98, 125.87, 125.79, 125.69, 125.36, 116.48, 50.57, 48.11, 48.05, 44.72, 44.49, 38.26, 38.13, 38.02, 35.98, 35.66, 31.65, 30.15, 29.50, 29.37, 26.56, 26.41, 25.73, 21.69, 18.22, 13.93.

(E)-2,3-diphenylacrylic acid (5a)



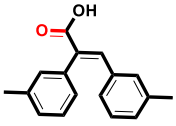
Prepared as described for **2a**; the reaction of diphenylacetylene (0.28 mmol), 5 wt% Pd/C (0.014 mmol, 29 mg), Xantphos (0.028 mmol, 16 mg), TBAI (0.14 mmol, 52 mg), oxalic acid (1.13 mmol, 101 mg) and DMF (2 mL) gave **5a** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (55 mg, 88% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 8.01 (s, 1H), 7.43 – 7.42 (m, 3H), 7.31 – 7.26 (m, 3H), 7.23- 7.20 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.18, 142.35, 135.30, 134.29, 131.71, 130.81, 129.75, 129.43, 128.66, 128.22, 127.99. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{15}H_{11}O_2^-$ is 223.0759, obsd. 223.0765

(E)-2,3-di-*p*-tolylacrylic acid (5b)



Prepared as described for **2a**; the reaction of 1,2-di-*p*-tolylethyne (0.24 mmol, 50 mg), 5 wt% Pd/C (0.012 mmol, 26 mg), Xantphos (0.024 mmol, 14 mg), TBAI (0.12 mmol, 45 mg), oxalic acid (0.968 mmol, 87 mg) and DMF (2 mL) gave **5b** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (55 mg, 90% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.92 (d, *J* = 1.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.01 (s, 4H), 2.41 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.49, 142.20, 139.78, 137.64, 132.50, 131.65, 130.86, 130.63, 129.60, 129.44, 128.99, 21.34, 21.33. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_2^-$ is 251.1072, obsd. 251.1087

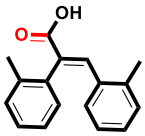
(E)-2,3-di-*m*-tolylacrylic acid (5c)



Prepared as described for **2a**; the reaction of 1,2-di-*m*-tolylethyne (0.24 mmol, 50 mg), 5 wt% Pd/C (0.012 mmol, 26 mg), Xantphos (0.024 mmol, 14 mg), TBAI (0.12 mmol, 45 mg), oxalic acid (0.968 mmol, 87 mg) and DMF (2 mL) gave **5c** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (49 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.91 (s, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.18 (m, 1H), 7.08 – 67.03 (m, 4H), 6.93 (d, *J* = 2.1 Hz, 1H), 6.86 – 6.84 (m, 1H), 2.35 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.14, 142.39, 138.29, 137.78, 135.35, 134.26, 131.93, 131.52, 130.27, 130.20, 128.75, 128.57, 128.07, 127.79, 126.70, 21.41, 21.22. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_2^-$ is 251.1072, obsd. 251.1087

(E)-2,3-di-*o*-tolylacrylic acid (5d)

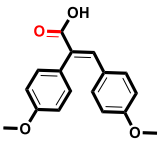


Prepared as described for 2a; the reaction of 1,2-di-*o*-tolylethyne (0.24 mmol, 50 mg), 5 wt% Pd/C (0.012 mmol, 26 mg), Xantphos (0.024 mmol, 14 mg), TBAI (0.12 mmol, 45 mg), oxalic acid (0.968 mmol, 87 mg) and DMF (2 mL) gave 5d after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (38 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 8.25 (s, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.10 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 2.46 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 173.40, 140.80, 138.08, 136.68, 134.71, 133.38, 131.60, 130.19, 130.13, 129.99, 129.16, 128.93, 128.09, 125.95, 125.52, 20.03, 19.59.

ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_2^-$ is 251.1072, obsd. 251.1087

(E)-2,3-bis(4-methoxyphenyl)acrylic acid (5e)

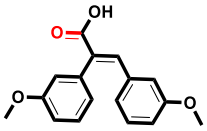


Prepared as described for **2a**; the reaction of 1,2-bis(4-methoxyphenyl)ethyne**,** 1 (0.21 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 22 mg), Xantphos (0.021 mmol, 12 mg), TBAI (0.10 mmol, 39 mg), oxalic acid (1.05 mmol, 95 mg) and DMF (2 mL) gave **5e** after purification

silica gel (mesh 60:120) column chromatography (25% EtOAc in *n*-hexane) as white solid (56 mg, 93% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.88 (s, 1H), 7.18 – 7.16 (m, 2H), 7.07 – 7.05 (m, 2H), 6.94 – 6.92 (m, 2H), 6.72 – 6.70 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.30, 160.53, 159.22, 141.96, 132.64, 131.04, 128.70, 127.83, 127.14, 114.29, 113.76, 55.21, 55.21. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_4^-$ is 283.0971, obsd. 283.0964.

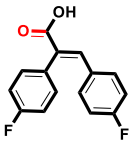
(E)-2,3-bis(4-methoxyphenyl)acrylic acid (5f)



Prepared as described for **2a**; the reaction of 1,2-bis(3-methoxyphenyl)ethyne**,** (0.21 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 22 mg), Xantphos (0.021 mmol, 12 mg), TBAI (0.10 mmol, 39 mg), oxalic acid (1.05 mmol, 95 mg) and DMF (2 mL) gave **5f** after purification silica gel (mesh 60:120) column chromatography (25% EtOAc in *n*-hexane) as white solid (49 mg, 82% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.91 (s, 1H), 7.32 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.93-6.91 (m, 1H), 6.87-6.85 (m, 1H), 6.81-6.77 (m, 3H), 6.59 (t, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.80, 159.90, 159.11, 142.34, 136.73, 135.36, 131.51, 129.85, 129.24, 124.06, 122.06, 116.60, 114.99, 114.53, 113.93, 55.25, 54.82. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_4^-$ is 283.0971, obsd. 283.0964.

(E)-2,3-bis(4-fluorophenyl)acrylic acid (5g)

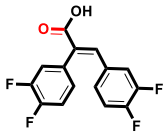


Prepared as described for **2a**; the reaction of 1,2-bis(4-fluorophenyl)ethyne**,** (0.23 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 25 mg), Xantphos (0.023 mmol, 13 mg), TBAI (0.11 mmol, 44 mg), oxalic acid (0.93 mmol, 84 mg) and DMF (2 mL) gave **5g** after purification silica gel (mesh 60:120) column chromatography (20% EtOAc in *n*-hexane) as white solid (54 mg, 89% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.93 (s, 1H), 7.22 – 7.20 (m, 2H), 7.11 – 7.05 (m, 4H), 6.89 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.98, 163.71 (d, *J* = 93.0 Hz), 162.05 (d, *J* = 88.6 Hz), 141.66, 132.75 (d, *J* = 8.4 Hz), 131.62 (d, *J* = 8.1 Hz), 130.81 (d, *J* =

3.5 Hz), 130.25,130.27, 115.95 (d, *J* = 21.5 Hz), 115.57 (d, *J* = 21.8 Hz). ^{19}F NMR (471 MHz, DMSO-d_6) δ (*ppm*) -112.24, -115.36. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{15}H_{12}F_2O_2^+$ is 261.0722, obsd. 261.0724.

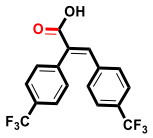
(E)-2,3-bis(3,4-difluorophenyl)acrylic acid (5h)



Prepared as described for **2a**; the reaction of 1,2-bis(3,4-difluorophenyl)ethyne (0.20 mmol, 50 mg), 5 wt% Pd/C (0.01 mmol, 21 mg), Xantphos (0.020 mmol, 12 mg), TBAI (0.10 mmol, 37 mg), oxalic acid (0.80 mmol, 72 mg) and DMF (2 mL) gave **5h** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as white solid (43 mg, 74% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.87 (s, 1H), 7.20 (dt, *J* = 10.1, 8.2 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.96 – 6.94 (m, 1H), 6.88 – 6.83 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 172.22, 151.93 (d, *J* = 12.9 Hz), 151.35 (dd, *J* = 21.7, 12.5 Hz), 150.90 (d, *J* = 13.1 Hz), 150.25 (d, *J* = 12.9 Hz), 149.69 (dd, *J* = 22.7, 12.5 Hz), 149.24 (d, *J* = 12.8 Hz), 141.15, 130.89 (dt, *J* = 52.5, 5.3 Hz), 130.43, 127.57 (dd, *J* = 6.6, 3.4 Hz), 126.18 (dd, *J* = 6.2, 3.6 Hz), 119.12 (t, *J* = 17.5 Hz), 118.03 (d, *J* = 17.5 Hz), 117.58 (d, *J* = 17.5 Hz). ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{15}H_7F_4O_2^-$ is 295.0382, obsd. 295.0394.

(E)-2,3-bis(4-(trifluoromethyl)phenyl)acrylic acid (5i)



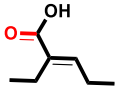
Prepared as described for **2a**; the reaction of 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (0.16 mmol, 50mg), 5 wt% Pd/C (0.008 mmol, 17 mg), Xantphos (0.016 mmol, 9 mg), TBAI (0.079 mmol, 29 mg), oxalic acid (0.64 mmol, 57 mg) and DMF (2 mL) gave **5i** after purification silica gel (mesh 60:120) column chromatography (20 % EtOAc in n-hexane) as white solid (50 mg, 87% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 8.03 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 171.59, 141.66, 138.24, 137.12, 132.57, (130.71-130.29), (125.80- 125.47), 125.42, 125.39, 124.82, 124.51, 123.01, 122.71. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_9F_6O_2^-$ is 359.0520, obsd. 359.0528

(E)-2-methylbut-2-enoic acid (5j)

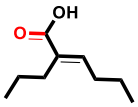
Prepared as described for **2a**; the reaction of but-2-yne (0.92 mmol, 50 mg), 10 wt% Pd/C (0.046 mmol, 24 mg), Xantphos (0.046 mmol, 27 mg), TBAI (0.46 mmol, 169 mg), oxalic acid (1.84 mmol, 166 mg) and DMF (2 mL) gave **5j** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as semi-solid (78 mg, 85% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.00 (q, *J* = 6.6 Hz, 1H), 1.89 – 1.71 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 173.95, 139.96, 128.02, 14.50, 11.51.

(E)-2-ethylpent-2-enoic acid (5k)



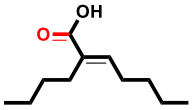
Prepared as described for **2a**; the reaction of hex-3-yne (0.609 mmol, 50 mg), 5 wt% Pd/C (0.030 mmol, 32 mg), Xantphos (0.0609 mmol, 35 mg), TBAI (0.30 mmol, 110 mg), oxalic acid (1.83 mmol, 164 mg) and DMF (2 mL) gave **5k** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as semi-solid (64 mg, 82% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 6.87 (s, 1H), 2.30 (q, *J* = 7.5 Hz, 2H), 2.22 (p, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.6 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.81, 146.32, 132.84, 21.82, 19.60, 13.85, 13.19. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_7H_{11}O_2^-$ is 127.0759, obsd. 127.0766.

(E)-2-propylhex-2-enoic acid (5l)



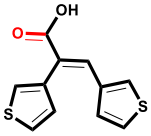
Prepared as described for **2a**; the reaction of oct-4-yne (0.453 mmol, 50 mg), 5 wt% Pd/C (0.0226 mmol, 24 mg), Xantphos (0.045 mmol, 26 mg), TBAI (0.226 mmol, 83 mg), oxalic acid (1.81 mmol, 163 mg) and DMF (2 mL) gave **5l** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as semi-solid (55 mg, 78% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 6.91 (t, *J* = 7.5 Hz, 1H), 2.28 – 2.17 (m, 4H), 1.51 – 1.41 (m, 4H), 0.96-0.90 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.72, 145.49, 131.74, 30.76, 28.37, 22.42, 21.98, 13.95, 13.90.

(E)-2-butylhept-2-enoic acid (5m)



Prepared as described for **2a**, reaction of dec-5-yne (0.362 mmol, 50 mg), 5 wt% Pd/C (0.018 mmol, 19 mg), Xantphos (0.036 mmol, 21 mg), TBAI (0.181 mmol, 67 mg), oxalic acid (1.44 mmol, 130 mg) and DMF (2 mL) gave **5m** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as semi-solid (50 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 6.90 (t, *J* = 7.5 Hz, 1H), 2.30 – 2.27 (m, 2H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.46 – 1.31 (m, 8H), 0.93-0.90 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.85, 145.44, 131.87, 31.47, 30.85, 28.43, 26.18, 22.67, 22.46, 13.91, 13.85. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{11}H_{19}O_2^-$ is 183.0258, obsd. 183.0265.

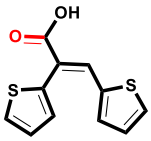
(E)-2,3-di(thiophen-3-yl)acrylic acid (5n)



Prepared as described for **2a**; the reaction of 1,2-di(thiophen-3-yl)ethyne (0.263 mmol, 50 mg), 5wt% Pd/C (0.0131 mmol, 28 mg), Xantphos (0.026 mmol, 15 mg), TBAI (0.131 mmol, 48 mg), oxalic acid (1.31 mmol, 118 mg) and DMF (2 mL) gave **5n** after purification silica gel (mesh 60:120) column chromatography (25% EtOAc in *n*-hexane) as pale yellow solid (48 mg, 78% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 7.81 (d, *J* = 0.7 Hz, 1H), 7.59-7.58 (m, 1H), 7.57-7.56 (m, 1H), 7.38-7.37 (m, 1H), 7.35-7.34 (m, 1H), 6.96-6.95 (m, 1H), 6.44-6.43 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 168.35, 136.79, 136.22, 134.25, 130.43, 129.03, 127.16, 126.66, 126.20, 126.18, 124.58. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{11}H_7S_2O_2^-$ is 234.9888, obsd. 234.9888.

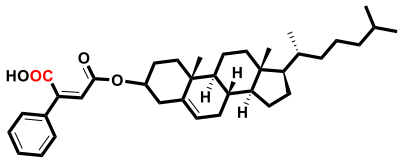
(E)-2,3-di(thiophen-2-yl)acrylic acid (5o)



Prepared as described for **2a**; the reaction of 1,2-di(thiophen-3-yl)ethyne (0.263 mmol, 50 mg), 5 wt% Pd/C (0.0131 mmol, 28 mg), Xantphos (0.026 mmol, 15 mg), TBAI (0.131 mmol, 48 mg), oxalic acid (1.31 mmol, 118 mg) and DMF (2 mL) gave **5o** after purification silica gel (mesh 60:120) column chromatography (25% EtOAc in *n*-hexane) as pale yellow solid (43 mg, 69% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ (*ppm*) 8.12 (s, 1H), 7.72 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.15 (m, 1H), 7.06 – 7.04 (m, 1H), 7.00 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ (*ppm*) 167.57, 137.70, 136.33, 135.33, 135.21, 132.53, 128.79, 128.43, 127.67, 126.96, 122.04. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{11}H_7S_2O_2^-$ is 234.9888, obsd. 234.9882.

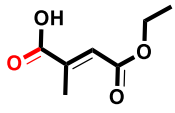
(Z)-4-(((3S,9S,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-4-oxo-2-phenylbut-2-enoic acid (5p)



Prepared as described for **2a**; reaction of (3S,9S,14S,17R)-10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl-3-phenylpropiolate (0.0967 mmol, 50 mg), 5 wt% Pd/C (0.0029 mmol, 7 mg), Xantphos (0.0058 mmol, 4 mg), TBAI (0.049 mmol, 18 mg), oxalic acid (0.77 mmol, 70 mg) and DMF (2 mL) gave **5p** after purification silica gel (mesh 60:120) column chromatography (25% EtOAc in n-hexane) as pale yellow solid (32 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.37 (d, *J* = 4.1 Hz, 3H), 7.25 – 7.24 (m, 2H), 7.12 (s, 1H), 5.30 – 5.29 (m, 1H), 4.55-4.48 (m, 1H), 2.12 – 1.90 (m, 3H), 1.86 – 1.75 (m, 2H), 1.23-1.56 (m, 13H), 1.17 – 0.96 (m, 10H), 0.92-0.89 (m, 6H), 0.87 – 0.85 (m, 6H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 171.58, 164.56, 142.07, 139.20, 133.44, 131.86, 128.91, 128.64, 127.82, 122.81, 74.97, 56.58, 56.06, 49.87, 42.23, 39.63, 39.47, 37.46, 36.74, 36.45, 36.13, 35.75, 31.80, 31.74, 28.18, 27.97, 27.18, 24.23, 23.79, 22.80, 22.54, 20.94, 19.15, 18.67, 11.80. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{37}H_{51}O_4^-$ is 559.3788, obsd. 559.3805.

(E)-4-ethoxy-2-methyl-4-oxobut-2-enoic acid (5q)

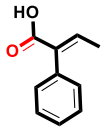


Prepared as described for **2a**; the reaction of ethyl but-2-ynoate (0.446 mmol, 50 mg), 5 wt% Pd/C (0.0223 mmol, 47 mg), Xantphos (0.045 mmol, 26 mg), TBAI (0.223 mmol, 82 mg), oxalic acid (1.78 mmol, 160 mg) and DMF (2 mL) gave **5q** after purification silica gel

(mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (56 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 11.91 (s, 1H), 6.87 (d, *J* = 1.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.26 (d, *J* = 1.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 172.65, 165.65, 142.40, 128.73, 60.84, 14.05, 13.79. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_7H_9O_4^-$ is 157.0501, obsd. 157.0511.

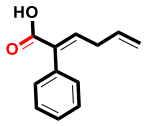
(E)-2-phenylbut-2-enoic acid (5r)



Prepared as described for **2a**; the reaction of ethyl prop-1-yn-1-ylbenzene (0.431 mmol, 50 mg), 5 wt% Pd/C (0.0215 mmol, 44 mg), Xantphos (0.0431 mmol, 25 mg), TBAI (0.215 mmol, 79 mg), oxalic acid (1.72 mmol, 155 mg) and DMF (2 mL) gave **5r** after purification silica gel (mesh 60:120) column chromatography (10% EtOAc in *n*-hexane) as white solid (59 mg, 85% yield, α:β = 68:32).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.87 (t, *J* = 1.7 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.38 – 7.36 (m, 2H), 7.26 – 7.23 (m, 1H), 2.17 (d, *J* = 1.5 Hz, 3H), 1.81 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 174.50, 172.74, 142.81, 141.10, 135.54, 134.39, 134.20, 129.81, 129.79, 128.67, 128.40, 128.04, 127.60, 127.54, 15.73, 13.65.

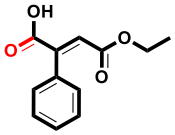
(E)-2-phenylhexa-2,5-dienoic acid (5s)



Prepared as described for **2a**; the reaction of pent-4-en-1-yn-1-ylbenzene (0.352 mmol, 50 mg), 5 wt% Pd/C (0.0176 mmol, 37 mg), Xantphos (0.0352 mmol, 20 mg), TBAI (0.176 mmol, 65 mg), oxalic acid (1.4 mmol, 126 mg) and DMF (2 mL) gave **5s** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (52 mg, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.62 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.19 (m, 5H), 6.40 – 6.35 (m, 1H), 1.87 (d, *J* = 6.2 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 173.66, 139.26, 135.31, 133.54, 130.17, 128.98, 128.78, 128.33, 123.40, 19.26. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{10}H_9O_2^-$ is 161.0603, obsd. 161.0616.

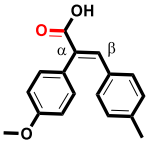
(E)-4-ethoxy-4-oxo-2-phenylbut-2-enoic acid (5t)



Prepared as described for **2a**; the reaction of pent-4-en-1-yn-1-ylbenzene (0.287 mmol, 50 mg), 5 wt% Pd/C (0.0143 mmol, 30 mg), Xantphos (0.0287 mmol, 16 mg), TBAI (0.143 mmol, 52 mg), oxalic acid (1.149 mmol, 103 mg) and DMF (2 mL) gave **5t** after purification silica gel (mesh 60:120) column chromatography (15% EtOAc in *n*-hexane) as white solid (51 mg, 76% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.38-7.37 (m, 3H), 7.26 – 7.24 (m, 2H), 7.12 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 171.04, 165.12, 142.68, 133.37, 131.08, 128.86, 128.69, 127.82, 61.03, 14.09. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{12}H_{11}O_4^-$ is 219.0658, obsd. 219.0673

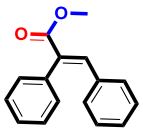
(E)-2-(4-methoxyphenyl)-3-(*p*-tolyl)acrylic acid (5u)



Prepared as described for **2a**; the reaction of 1-methoxy-4-(*p*-tolylethynyl)benzene (0.223 mmol, 50mg), 5wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), TBAI (0.115 mmol, 42 mg), oxalic acid (0.892 mmol, 80 mg) and DMF (2 mL) gave **5u** after purification silica gel (mesh 60:120) column chromatography (15 % EtOAc in n-hexane) as white solid (50 mg, 84% yield, α:β = 67:33).

^{1}H NMR (600 MHz, $CDCl_3$) δ (*ppm*) 7.21 (d, J = 7.7 Hz, 1H), 7.17 – 7.14 (m, 3H), 7.06– 7.05 (m, 1H), 7.00 (s, 4H), 6.71 – 6.70 (m, 1H), 3.84 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (*ppm*) 173.64, 160.49, 159.19, 142.02, 141.77, 139.64, 137.53, 132.74, 132.65, 131.78, 131.03, 130.80, 130.47, 129.63, 129.51, 129.26, 128.98, 127.75, 127.13, 114.12, 113.70, 55.18, 55.16, 21.35, 21.33. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_{17}H_{15}O_3^-$ is 269.1172, obsd. 269.1177.

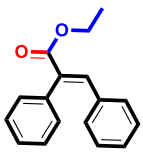
G. General procedure for the synthesis and characterization of compounds 7a-m methyl (E)-2,3-diphenylacrylate (7a)



We executed the reaction using Double-Vial (DV) system comprised of an inner vial of 2 mL and an outer vial of 5 mL and the entire system was fitted with PTFE faced black solid cap. Initially, the inner vial of the DV system was charged with diphenylacetylene (0.223 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), PTSA (0.14 mmol, 27 mg), methanol (0.5 mL) and DMF (1.5 mL), while the outer vial contained oxalic acid (0.892 mmol, 80 mg) in 0.5 mL of DMF. Thereafter, the inner vial having contents was positioned carefully inside the outer vial (5 mL) containing oxalic acid/DMF (0.5 mL). Further, the entire system was capped with the solid PTFE faced cap and further tightened with Teflon tape to prevent the leakage of gas. The whole system was allowed to subjected in pre-heated blocks at 125 ^{o}C for 24 hrs. The reaction progress was observed with the help of TLC. After the accomplishment of the reaction, the inner vial containing contents was removed and the contents of the inner vial were transferred to a separatory funnel. Further, 3 mL of water was added in the reaction mixture and organic contents were extracted with ethyl acetate. The combined organic layer was passed over anhydrous Na_2SO_4 and concentrated under reduced pressure. The concentrated crude mixture was further purified by silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) afforded **7a** as white solid (54 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*) 7.98 – 7.90 (m, 1H), 7.42-7.40 (m, 3H), 7.33 – 7.21 (m, 5H), 7.19 – 7.07 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (*ppm*) 168.26, 140.47, 135.83, 134.63, 132.43, 130.58 (d, J = 5.5 Hz), 129.74 (d, J = 6.6 Hz), 129.03 (d, J = 6.2 Hz), 128.62 (d, J = 5.7 Hz), 128.25 – 128.04 (m), 127.82 (d, J = 4.8 Hz), 52.31. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{16}H_{15}O_2^+$ is 239.1067, obsd. 239.1074

ethyl (E)-2,3-diphenylacrylate (7b)

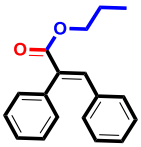


Prepared as described for **7a**; the reaction of diphenylacetylene (0.223 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), PTSA (0.14 mmol, 27 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.892 mmol, 80 mg), in 0.5 mL of

DMF gave **7b** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (58 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.84 (s, 1H), 7.38 – 7.34 (m, 3H), 7.24 – 7.14 (m, 5H), 7.06 – 7.03 (m, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 167.81, 140.09, 135.87, 134.65, 132.77, 130.54, 129.76, 128.92, 128.53, 128.14, 127.72, 61.17, 14.25. ESI-MS $[M-H]^-$ *(m/z)* calcd. for $C_9H_7O_2^-$ is 147.0446, obsd. 147.0453. ESI-MS $[M-H]^+$ (m/z) calcd. for C17H17O2+ is 253.1223, obsd. 253.1226.

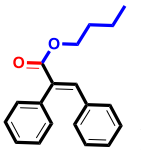
propyl (E)-2,3-diphenylacrylate (7c)



Prepared as described for **7a**; the reaction of diphenylacetylene (0.223 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), PTSA (0.14 mmol, 27 mg), propanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.892 mmol, 80 mg), in 0.5 mL of DMF gave **7c** after purification silica gel (mesh 60:120) column chromatography (3-5% EtOAc in *n*-hexane) as white solid (59 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*) 7.84 (s, 1H), 7.39 – 7.33 (m, 3H), 7.23 – 7.13 (m, 5H), 7.06 – 7.04 (m, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.72-1.63 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (*ppm*) 167.87, 140.03, 135.97, 134.70, 132.88, 130.56, 129.74, 128.92, 128.50, 128.15, 127.68, 66.72, 22.01, 10.40. ESI-MS $[M-H]^+$ (m/z) calcd. for C18H19O2+ is 267.1380, obsd. 267.1387.

butyl (E)-2,3-diphenylacrylate (7d)

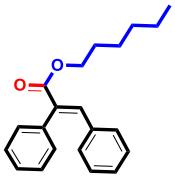


Prepared as described for **7a**; the reaction of diphenylacetylene (0.223 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), PTSA (0.14 mmol, 27 mg), butanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.892 mmol, 80 mg), in 0.5 mL of DMF gave **7d** after purification silica gel (mesh 60:120) column chromatography (3-5% EtOAc in *n*-hexane) as semi-solid (60 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.86 (s, 1H), 7.40 – 7.35 (m, 3H), 7.25 – 7.15 (m, 5H), 7.08 – 7.06 (m, 2H), 4.24-4.22 (m, 2H), 1.69-1-63 (m, 2H), 1.41 – 1.34 (m, 2H), 0.94 (t, *J* =

7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 167.80, 139.98, 135.87, 134.60, 132.76, 130.50, 129.66, 128.87, 128.45, 128.09, 127.63, 64.96, 30.57, 19.08, 13.64. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{19}H_{21}O_2^+$ is 281.1536, obsd. 281.1541.

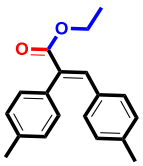
hexyl(E)-2,3-diphenylacrylate (7e)



Prepared as described for **7a**; the reaction of diphenylacetylene (0.223 mmol, 50 mg), 5 wt% Pd/C (0.011 mmol, 23 mg), Xantphos (0.0223 mmol, 13 mg), PTSA (0.14 mmol, 27 mg), butanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.892 mmol, 80 mg) in 0.5 mL of DMF gave **7e** after purification silica gel (mesh 60:120) column chromatography (3-5% EtOAc in *n*-hexane) as semi-solid (58 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*) 7.85 (s, 1H), 7.39 – 7.34 (m, 3H), 7.24 – 7.14 (m, 5H), 7.07-7.05 (m, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.67 – 1.62 (m, 2H), 1.35 – 1.27 (m, 6H), 0.91 – 0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (*ppm*) 167.84, 139.98, 135.96, 134.68, 132.88, 130.53, 129.72, 128.89, 128.47, 128.12, 127.65, 65.29, 31.30, 28.50, 25.51, 22.41, 13.92. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{21}H_{25}O_2^+$ is 309.1849, obsd. 309.1861.

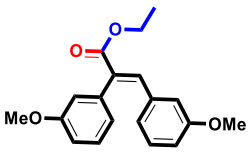
ethyl (E)-2,3-di-*p*-tolylacrylate (7f)



Prepared as described for **7a**; the reaction of 1,2-di-*p*-tolylethyne (0.242 mmol, 50 mg), 5 wt% Pd/C (0.0121 mmol, 13 mg), Xantphos (0.0242 mmol, 14 mg), PTSA (0.121 mmol, 23 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.968 mmol, 87 mg), in 0.5 mL of DMF gave **7f** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (56 mg, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.82 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 2.29 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 168.03, 139.83, 139.05, 137.24, 133.00, 131.93, 131.69, 130.51, 129.55, 129.25, 128.84, 60.97, 21.29, 21.24, 14.24. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{19}H_{20}O_2^+$ is 281.1536, obsd. 281.1542.

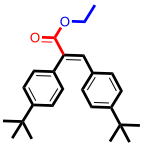
ethyl (E)-2,3-bis(3-methoxyphenyl)acrylate (7g)



Prepared as described for **7a**; the reaction of 1,2-bis(3-methoxyphenyl)ethyne (0.21 mmol, 50 mg), 5 wt% Pd/C (0.0105 mmol, 11 mg), Xantphos (0.021 mmol, 12 mg), PTSA (0.105 mmol, 20 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.84 mmol, 76 mg), in 0.5 mL of DMF gave **7g** after purification silica gel (mesh 60:120) column chromatography (8% EtOAc in *n*-hexane) as white solid (47 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*) 7.79 (s, 1H), 7.32 – 7.26 (m, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.91-6.88 (m, 1H), 6.85-6.82 (m, 1H), 6.79 – 6.74 (m, 3H), 6.56 (t, *J* = 2.1 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.50 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (*ppm*) 167.58, 159.77, 159.05, 139.93, 137.33, 135.76, 132.72, 129.61, 129.09, 123.66, 122.11, 115.94, 115.02, 114.34, 113.57, 61.14, 55.23, 54.76, 14.23. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{19}H_{21}O_4^+$ is 313.1434, obsd. 313.1443

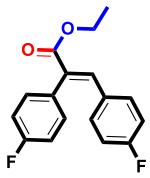
ethyl (E)-2,3-bis(4-(*tert*-butyl)phenyl)acrylate (7h)



Prepared as described for **7a**; the reaction of 1,2-bis(4-(*tert*-butyl)phenyl)ethyne (0.172 mmol, 50 mg), 5 wt% Pd/C (0.0086 mmol, 18 mg), Xantphos (0.0172 mmol, 10 mg), PTSA (0.086 mmol, 16 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.69 mmol, 63 mg), in 0.5 mL of DMF gave **7h** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (47 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (*ppm*) 7.80 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.17 (m, 4H), 7.08 – 6.96 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.38 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (*ppm*) 168.15, 152.25, 150.51, 139.64, 133.07, 131.92, 131.74, 130.48, 129.26, 125.44, 125.09, 60.97, 34.64, 34.58, 31.37, 31.07, 14.28. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{25}H_{33}O_2^+$ is 365.2475, obsd. 365.2487.

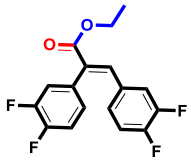
ethyl (E)-2,3-bis(4-fluorophenyl)acrylate (7i)



Prepared as described for **7a**; the reaction of 1,2-bis(4-fluorophenyl)ethyne (0.21 mmol, 50 mg), 5 wt% Pd/C (0.0117 mmol, 25 mg), Xantphos (0.0234 mmol, 14 mg), PTSA (0.117 mmol, 22 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.934 mmol, 84 mg), in 0.5 mL of DMF gave **7i** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (55 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.80 (s, 1H), 7.19 – 7.17 (m, 2H), 7.08 – 7.01 (m, 4H), 6.88 – 6.85 (m, 2H), 4.29 – 4.26 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 167.46, 163.56 (d, J = 52.8 Hz), 161.58 (d, J = 48.5 Hz), 139.22, 132.36 (d, J = 8.1 Hz), 131.55 (d, J = 7.6 Hz), 131.43 (d, J = 5.9 Hz), 130.62, 115.74 (d, J = 21.3 Hz), 115.37 (d, J = 21.6 Hz), 61.29, 14.20. ESI-MS $[M\text{-}H]^+$ *(m/z)* calcd. for $C_{17}H_{15}F_2O_2^+$ is 289.1035, obsd. 289.1035.

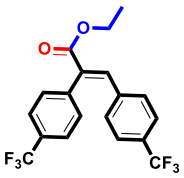
ethyl (E)-2,3-bis(3,4-difluorophenyl)acrylate (7j)



Prepared as described for **7a**; the reaction of 1,2-bis(3,4-difluorophenyl)ethyne (0.20 mmol, 50 mg), 5 wt% Pd/C (0.01 mmol, 21 mg), Xantphos (0.020 mmol, 12 mg), PTSA (0.10 mmol, 19 mg), ethanol (0.5 mL), DMF (1.5 mL) and oxalic acid (0.80 mmol, 72 mg), in 0.5 mL of DMF gave **7j** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as white solid (47 mg, 72% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.74 (s, 1H), 7.20-7.14 (m, 1H), 7.06 – 6.98 (m, 2H), 6.93-6.90 (m, 1H), 6.84 – 6.79 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 166.63, 152.27 – 150.54 (m), 149.96 – 148.60 (m), 138.63, 131.80 (dd, J = 6.0, 4.2 Hz), 131.61, 131.15, 127.11 (dd, J = 6.6, 3.6 Hz), 126.10 (dd, J = 6.0, 3.6 Hz), 118.95 (d, J = 11.6 Hz), 118.80 (d, J = 12.1 Hz), 117.83, 117.70, 117.41, 117.27, 61.61, 14.14. ESI-MS $[M\text{-}H]^+$ *(m/z)* calcd. for $C_{17}H_{13}F_4O_2^+$ is 325.0846, obsd. 325.0850.

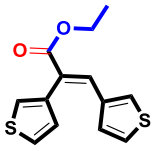
ethyl (E)-2,3-bis(4-(trifluoromethyl)phenyl)acrylate (7k)



Prepared as described for **7a**; the reaction of 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (0.159 mmol, 50 mg), 5wt% Pd/C (0.0079 mmol, 17 mg), Xantphos (0.0159 mmol, 9 mg), PTSA (0.079 mmol, 15 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (0.636 mmol, 57 mg), in 0.5 mL of DMF gave **7k** after purification silica gel (mesh 60:120) column chromatography (5% EtOAc in *n*-hexane) as pale yellow solid (50 mg, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.91 (s, 1H), 7.64-7.62 (m, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.14-7.12 (m, 2H), 4.32 – 4.28 (m, 2H), 1.33 – 1.30 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 166.61, 139.29, 138.95, 137.63, 133.76, 130.86, 130.60, 130.45, 130.36, 130.26, 130.10, 125.61 (q, J = 3.7 Hz), 125.28 (q, J = 3.7 Hz), 61.71, 14.15. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{19}H_{15}F_6O_2^+$ is 389.0971, obsd. 389.0981.

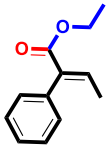
ethyl (E)-2,3-di(thiophen-3-yl)acrylate (7l)



Prepared as described for **7a**; the reaction of 1,2-di(thiophen-3-yl)ethyne (0.263 mmol, 50 mg), 5 wt% Pd/C (0.0131 mmol, 27 mg), Xantphos (0.0263 mmol, 15 mg), PTSA (0.131 mmol, 25 mg), ethanol (0.5 mL), DMF (1.5 mL) and oxalic acid (1.05 mmol, 118 mg), in 0.5 mL of DMF gave **7l** after purification silica gel (mesh 60:120) column chromatography (8% EtOAc in *n*-hexane) as pale yellow solid (47 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.85 (d, J = 0.7 Hz, 1H), 7.38-7.36 (m, 1H), 7.20 – 7.19 (m, 2H), 7.11-7.09 (m, 1H), 6.99-6.98 (m, 1H), 6.58-6.57 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 167.36, 136.64, 135.56, 134.60, 129.17, 128.80, 127.87, 125.74, 125.41, 125.35, 124.45, 60.96, 14.18. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{13}H_{13}S_2O_2^+$ is 265.0351, obsd. 265.0353.

ethyl (E)-2-phenylbut-2-enoate (7m)

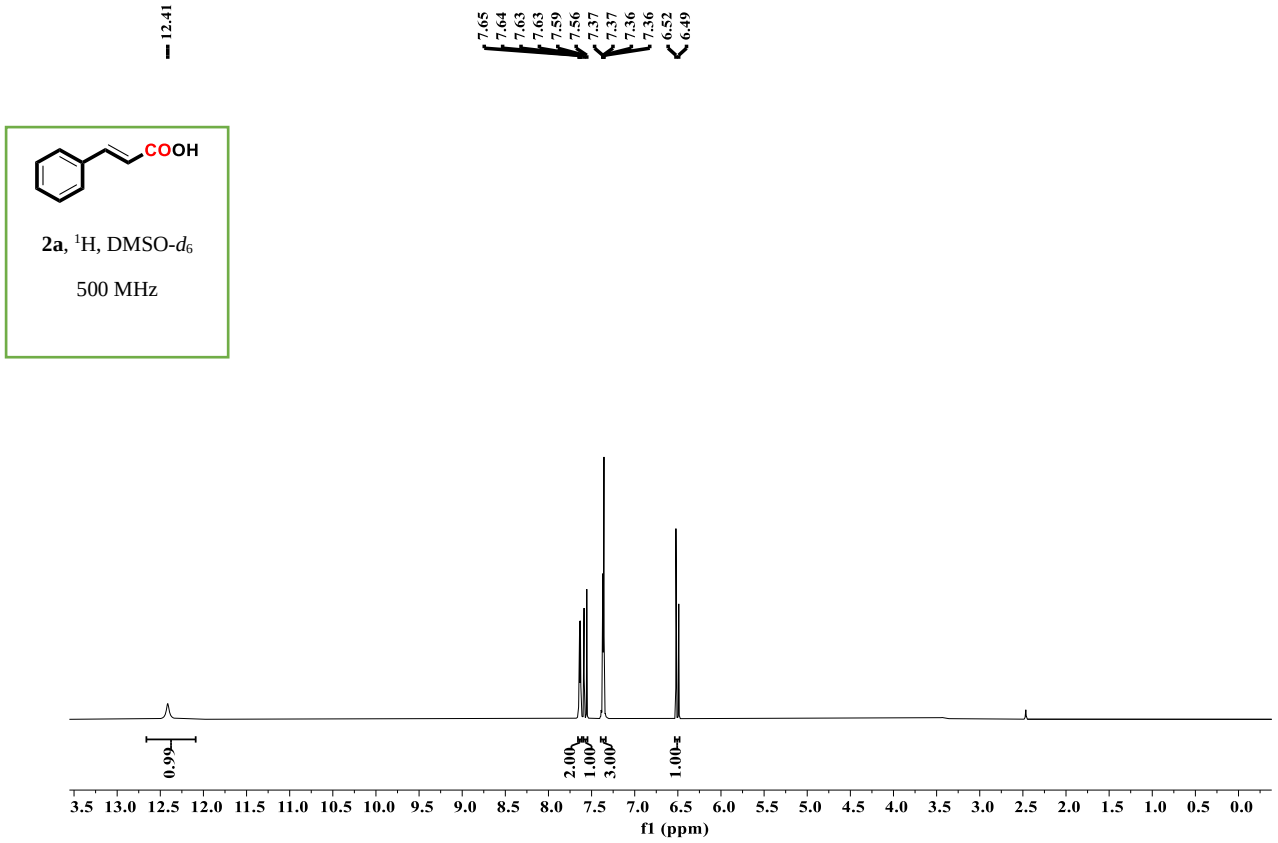


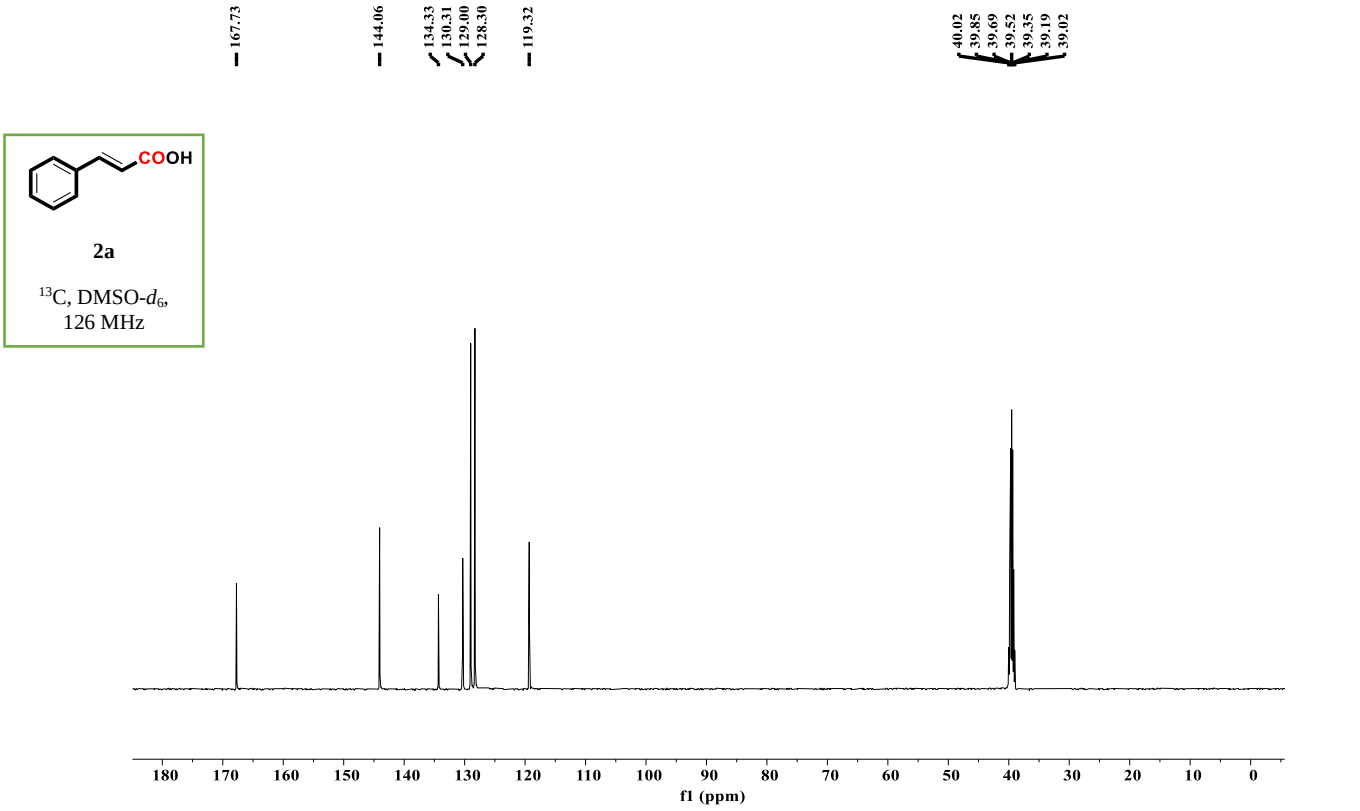
Prepared as described for **7a**; the reaction of ethyl prop-1-yn-1-ylbenzene (0.431 mmol, 50 mg), 5 wt% Pd/C (0.0215 mmol, 44 mg), Xantphos (0.0431 mmol, 25 mg), PTSA (0.215 mmol, 41 mg), ethanol (0.5 ml), DMF (1.5 mL) and oxalic acid (1.72 mmol, 118 mg),

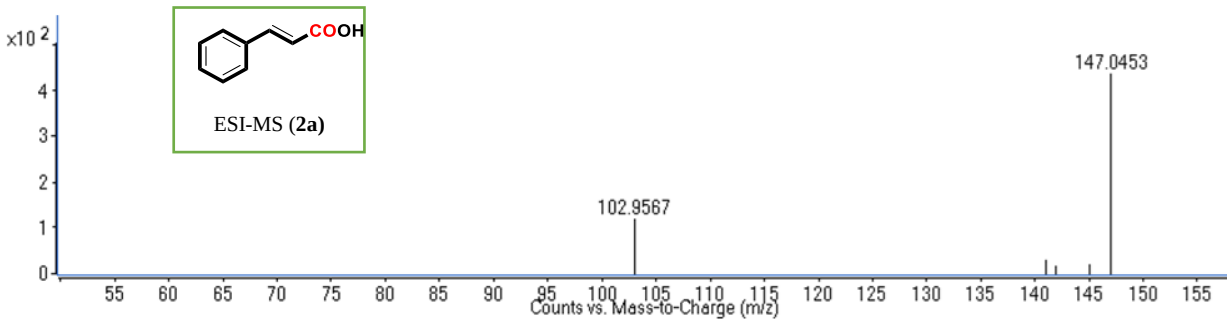
in 0.5 mL of DMF gave **7m** after purification silica gel (mesh 60:120) column chromatography (3-5% EtOAc in *n*-hexane) as colourless liquid (60 mg, 74% yield).

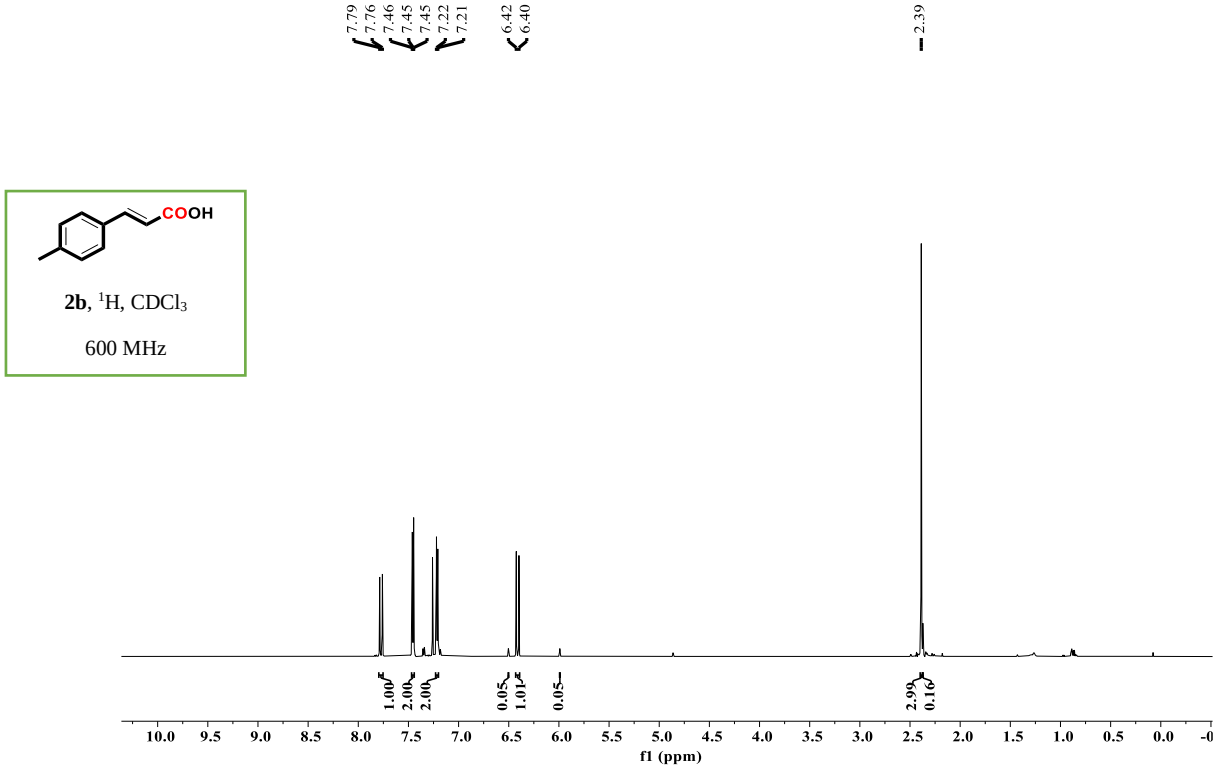
^{1}H NMR (500 MHz, $CDCl_3$) δ (*ppm*) 7.70 (m, 1H), 7.41 – 7.39 (m, 4H), 7.33 – 7.31 (m, 1H), 4.28 (q, J = 6.9 Hz, 2H), 2.13 (d, J = 1.9 Hz, 3H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (*ppm*) 168.64, 138.59, 135.88, 129.57, 128.54, 128.28, 128.18, 60.82, 14.26, 13.99. ESI-MS $[M-H]^+$ *(m/z)* calcd. for $C_{12}H_{15}O_2^+$ is 191.1067, obsd. 191.1067.

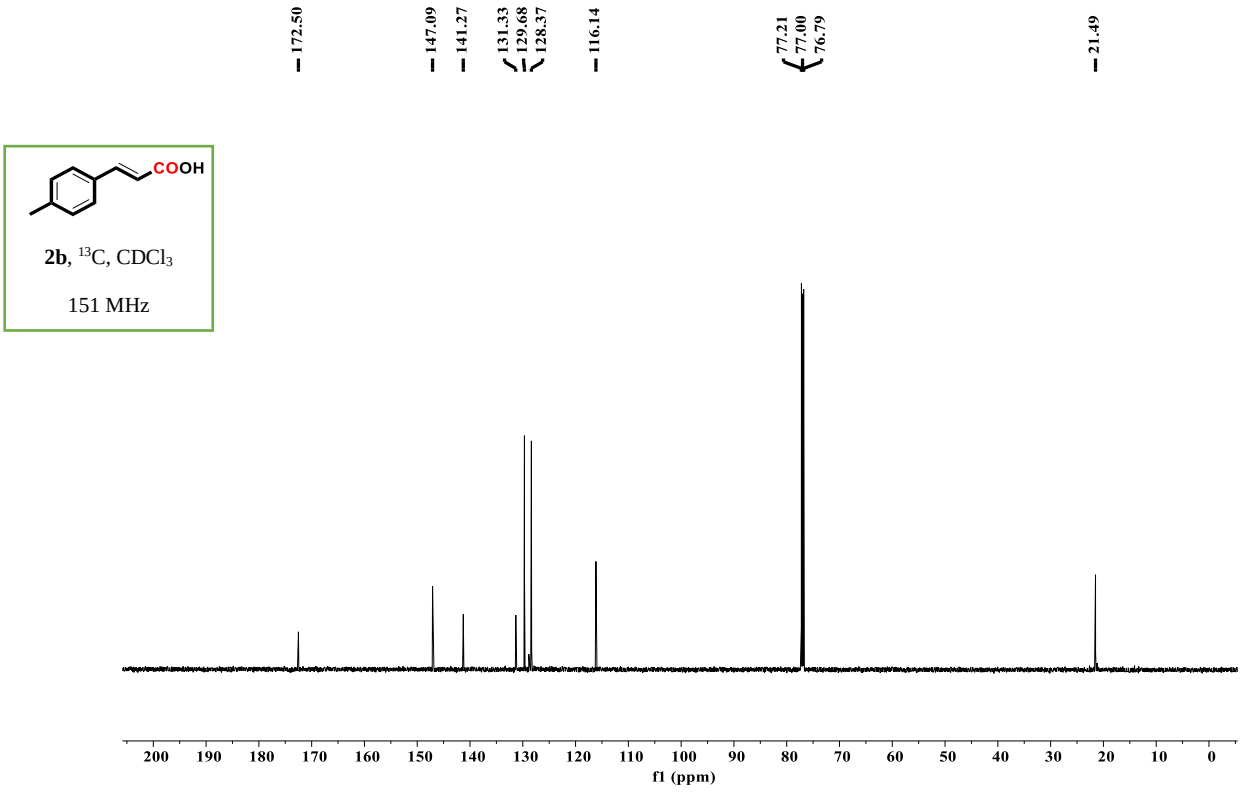
H. ^{1}H, ^{13}C NMR and ESI-MS Spectra of compounds 2a-t, 3a-n, 5a-u and 7a-m

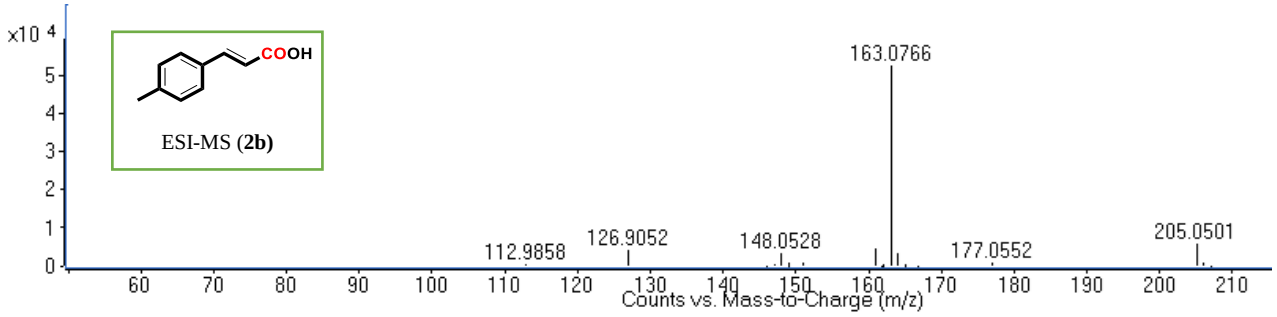


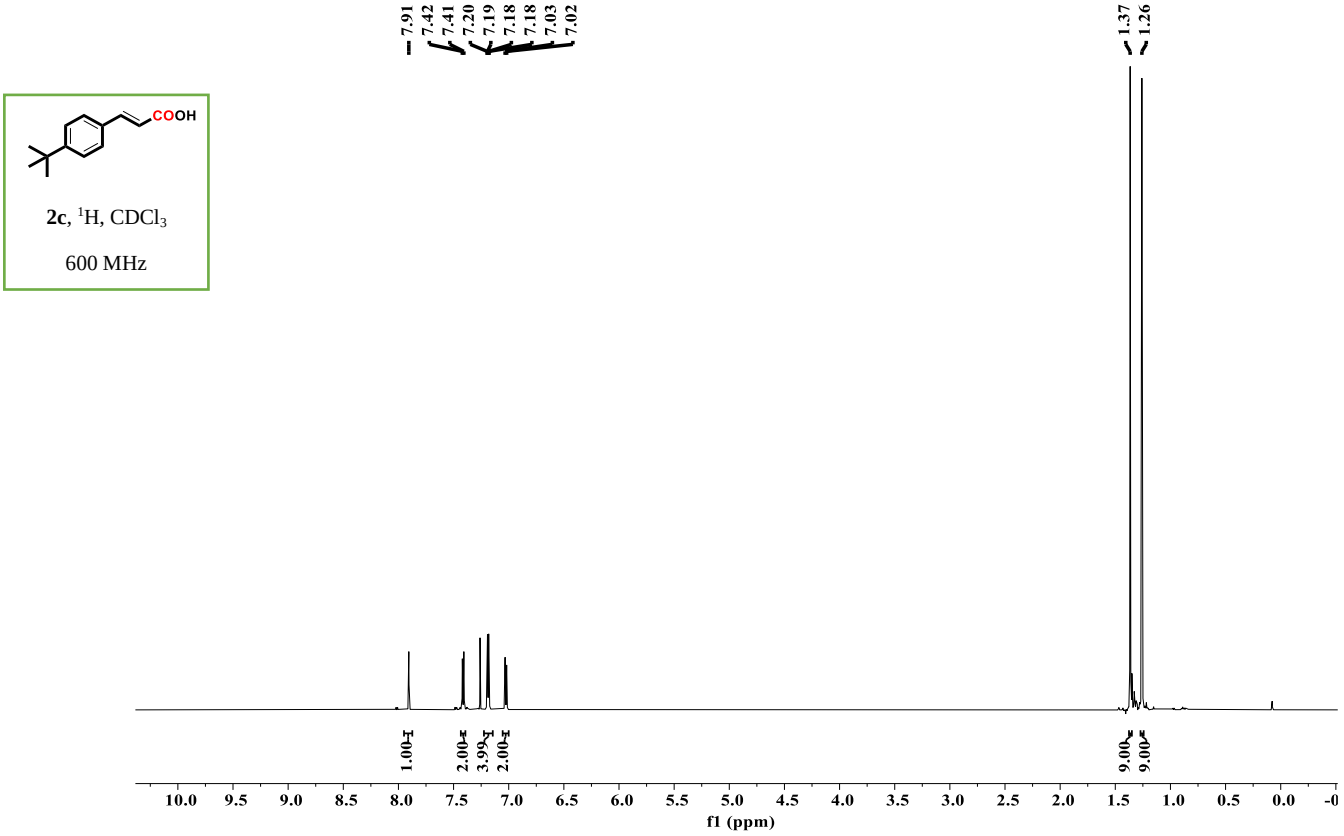

167.73
144.06
134.33
130.31
129.00
128.30
119.32
40.02
39.85
39.69
39.52
39.35
39.19
39.02
COOH
2a
^{13}C, DMSO-d_6,
126 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

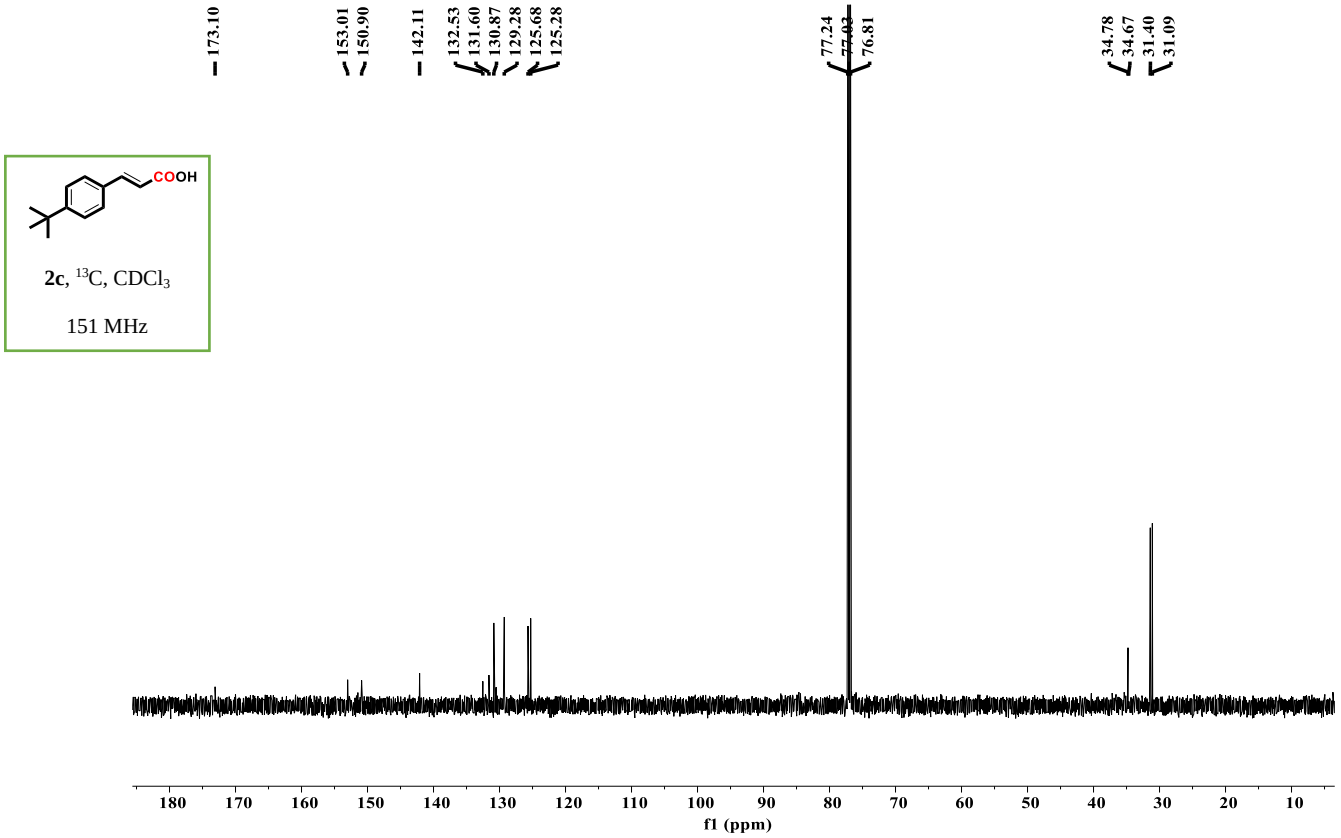

COOH
ESI-MS (2a)
x10 2
4
3
2
1
0
147.0453
102.9567
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155
Counts vs. Mass-to-Charge (m/z)

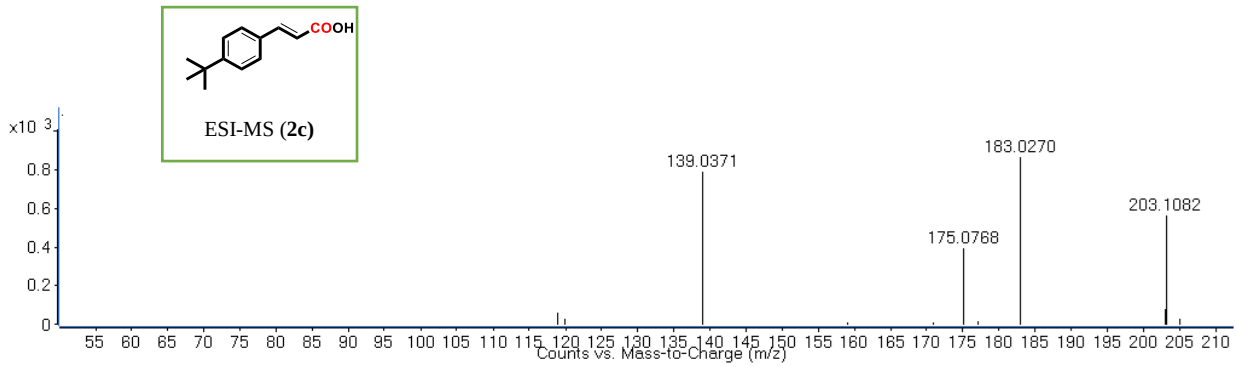

7.79
7.76
7.46
7.45
7.45
7.22
7.21
6.42
6.40
2.39
COOH
2b, 1H, CDCl3
600 MHz
1.00
2.00
2.00
0.05
1.01
0.05
2.99
0.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

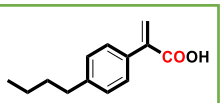

172.50
147.09
141.27
131.33
129.68
128.37
116.14
77.21
77.00
76.79
21.49
COOH
2b, 13C, CDCl3
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


COOH
ESI-MS (2b)
x10 4
163.0766
112.9858
126.9052
148.0528
177.0552
205.0501
Counts vs. Mass-to-Charge (m/z)


COOH
2c, 1H, CDCl3
600 MHz
7.91
7.42
7.41
7.20
7.19
7.18
7.03
7.02
1.37
1.26
1.00
2.00
3.99
2.00
9.00
9.00
f1 (ppm)

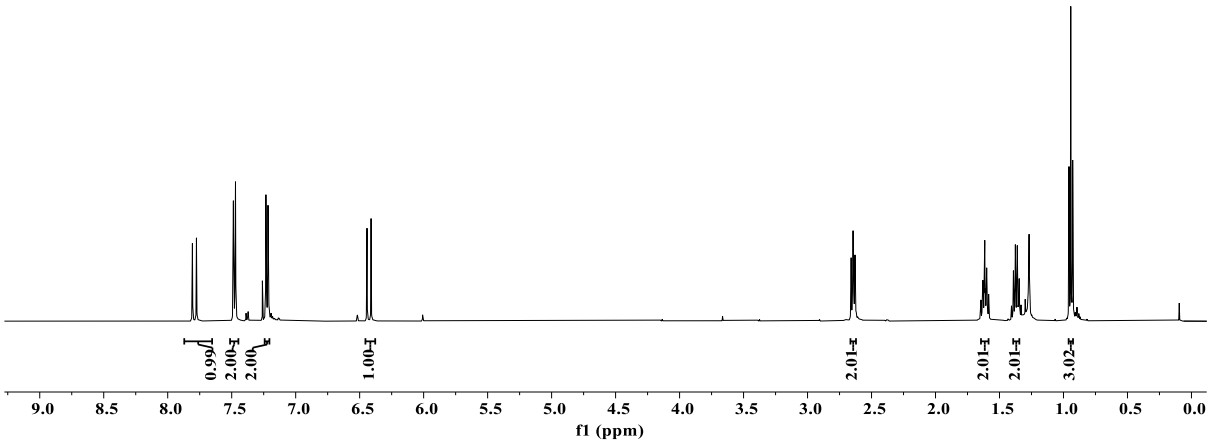

173.10
153.01
150.90
142.11
132.53
131.60
130.87
129.28
125.68
125.28
77.24
77.02
76.81
34.78
34.67
31.40
31.09
COOH
2c, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

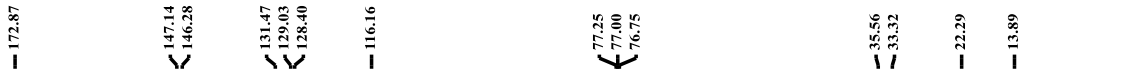

COOH
ESI-MS (2c)
x10 3
0.8
0.6
0.4
0.2
0
139.0371
183.0270
203.1082
175.0768
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210
Counts vs. Mass-to-Charge (m/z)

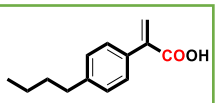


2d, ^{1}H, $CDCl_3$

500 MHz

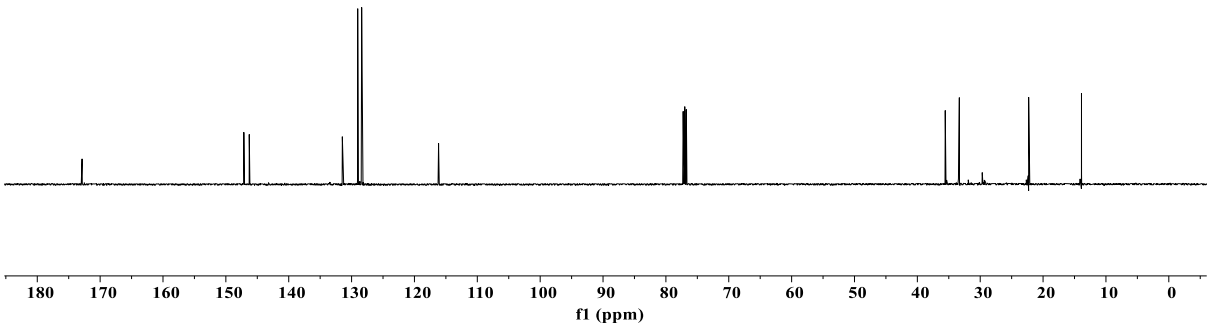


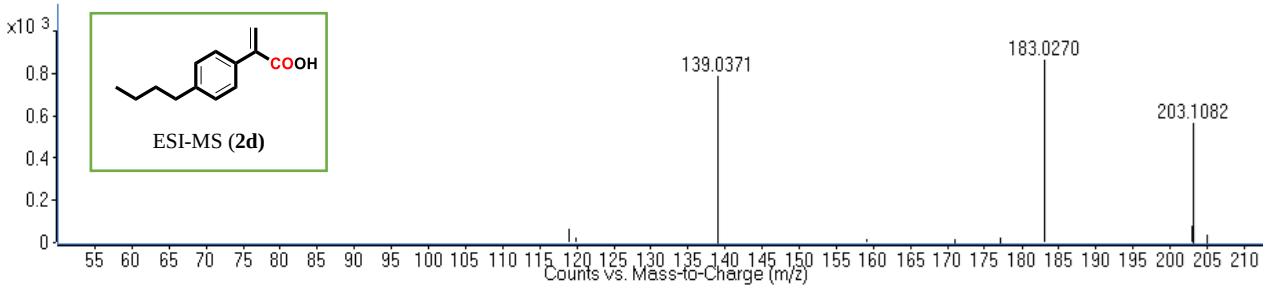


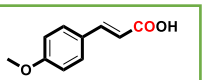


2d, ^{13}C, $CDCl_3$

126 MHz



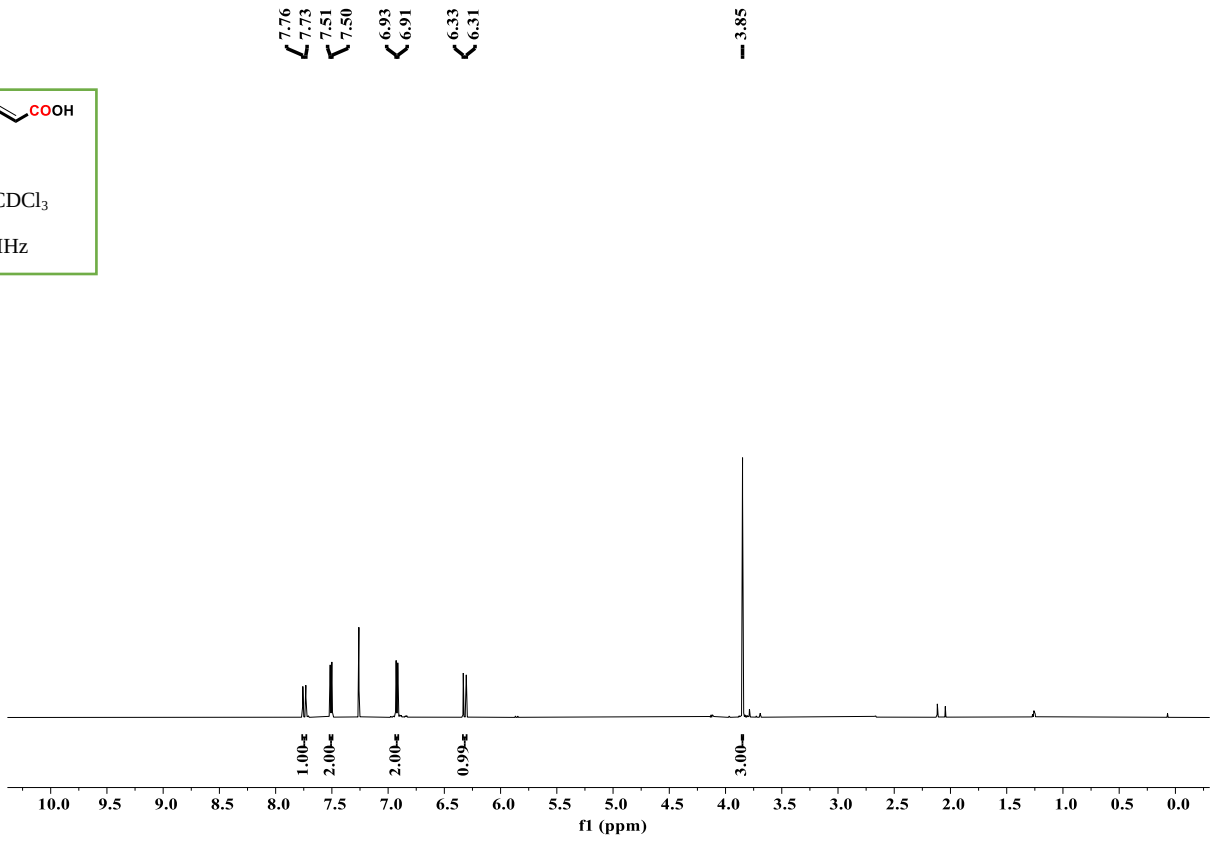


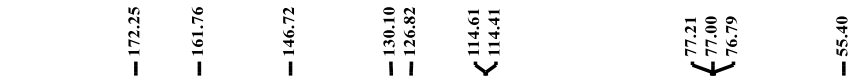


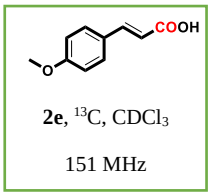
ESI-MS (**2d**)

2e, ^{1}H, $CDCl_3$

600 MHz

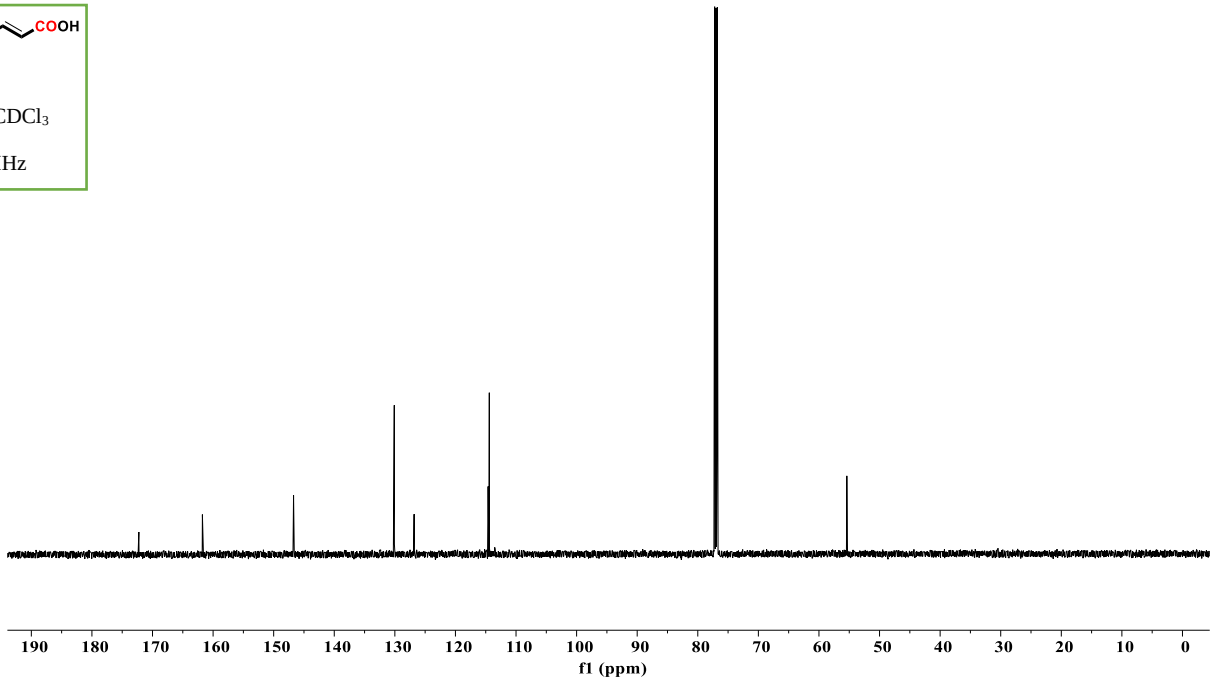


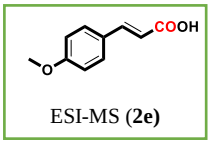




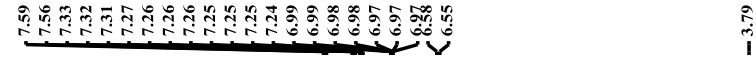
2e, ^{13}C, $CDCl_3$

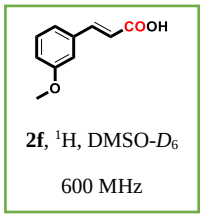
151 MHz





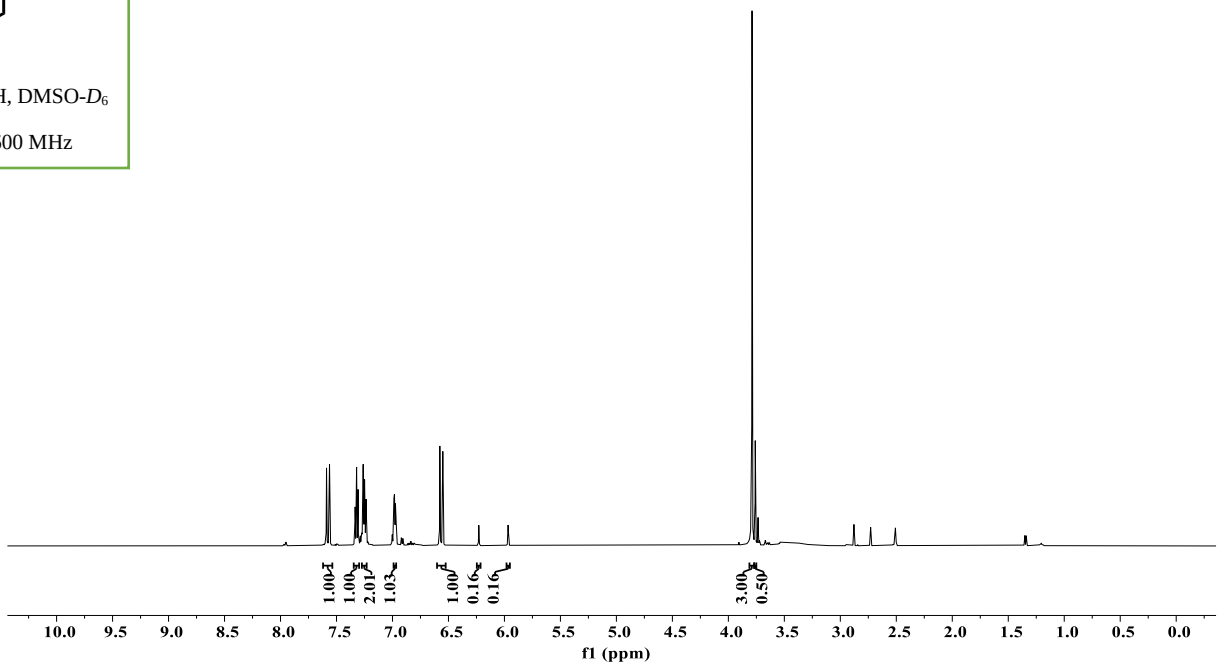
ESI-MS (**2e**)

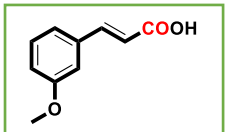




2f, ^{1}H, DMSO-D_6

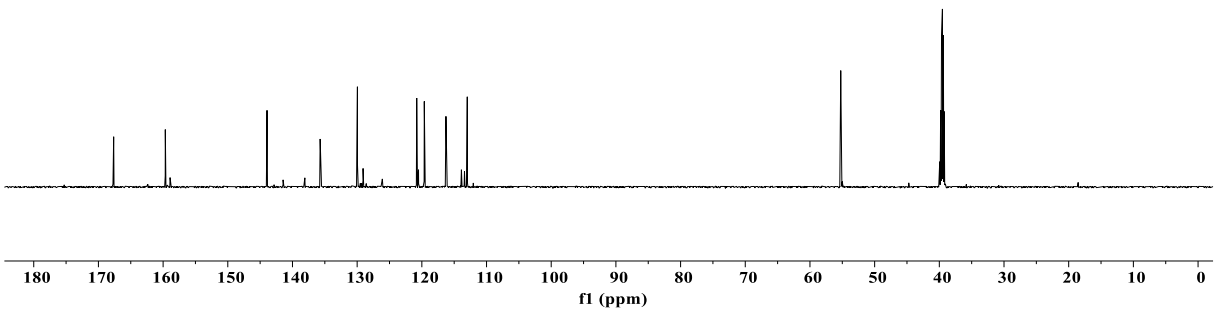
600 MHz

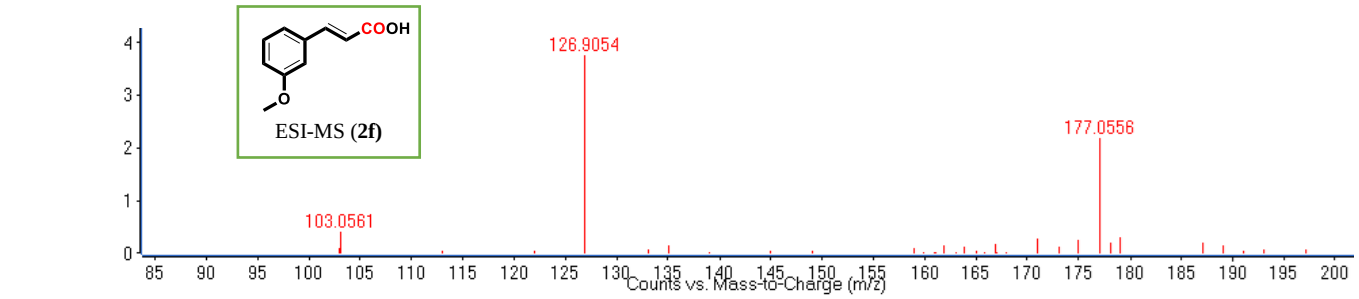


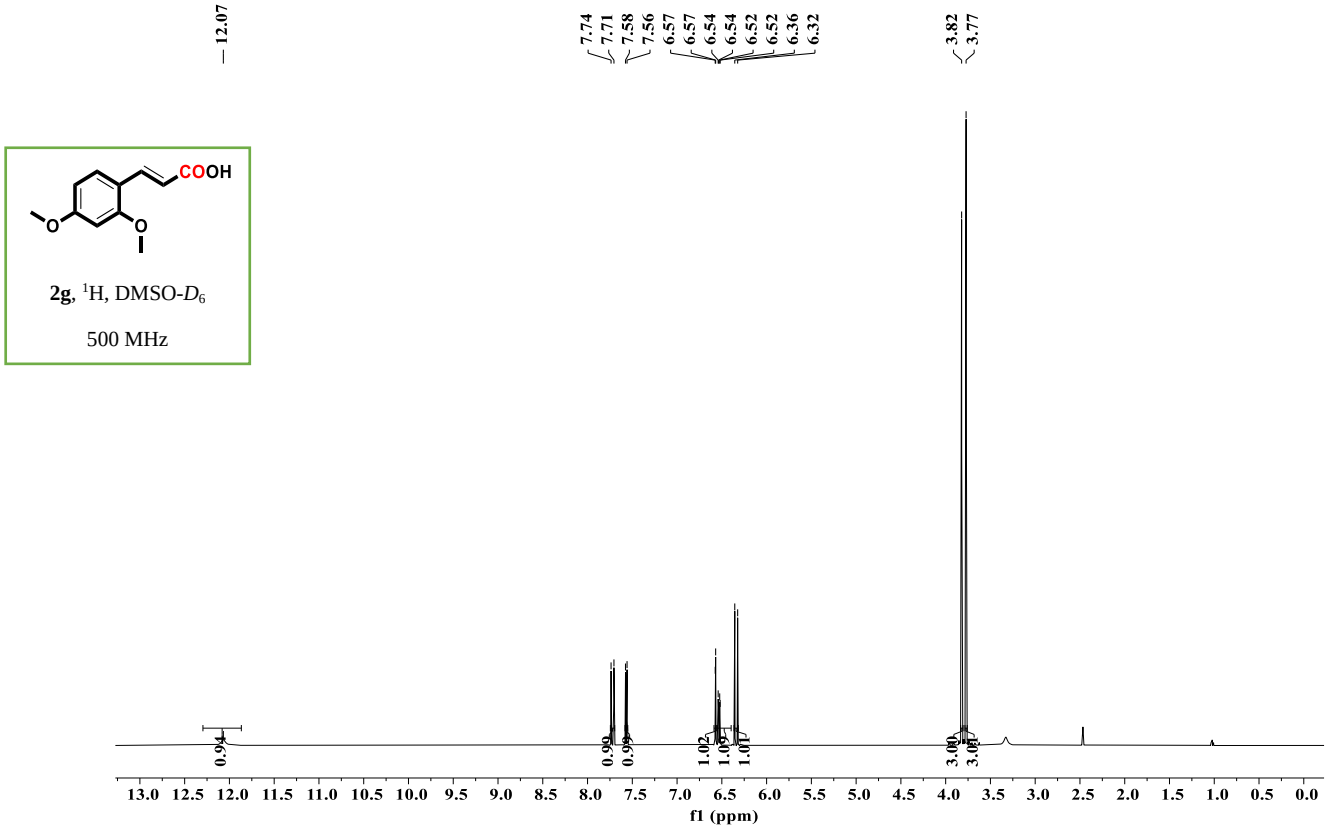


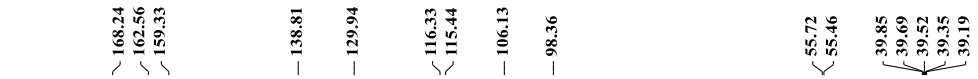
2f, ^{13}C, DMSO-D_6

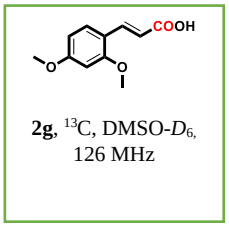
151 MHz



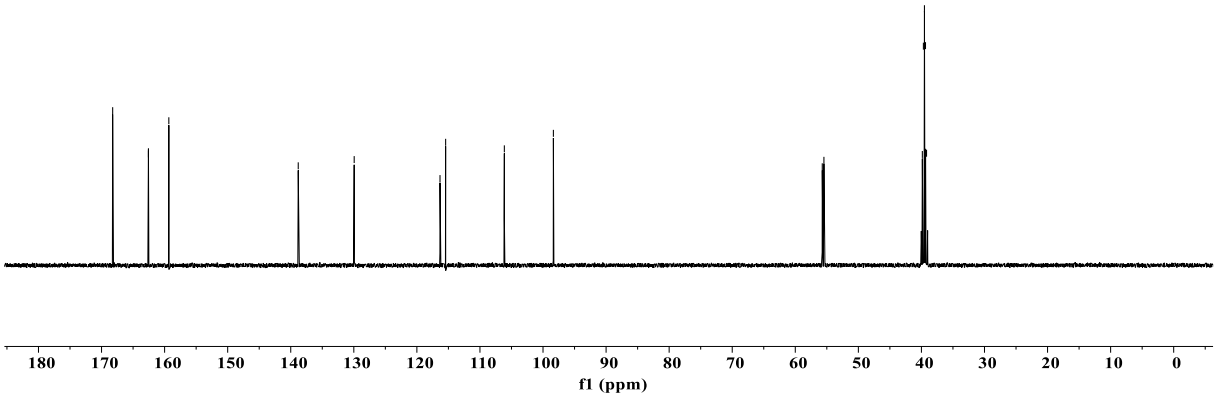

COOH
ESI-MS (2f)
126.9054
177.0556
103.0561
Counts vs. Mass-to-Charge (m/z)

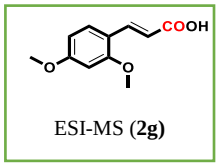

COOH
2g, 1H, DMSO-D6
500 MHz
f1 (ppm)



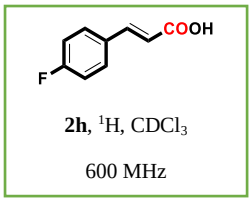


2g, ^{13}C, DMSO-D_6, 126 MHz



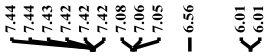


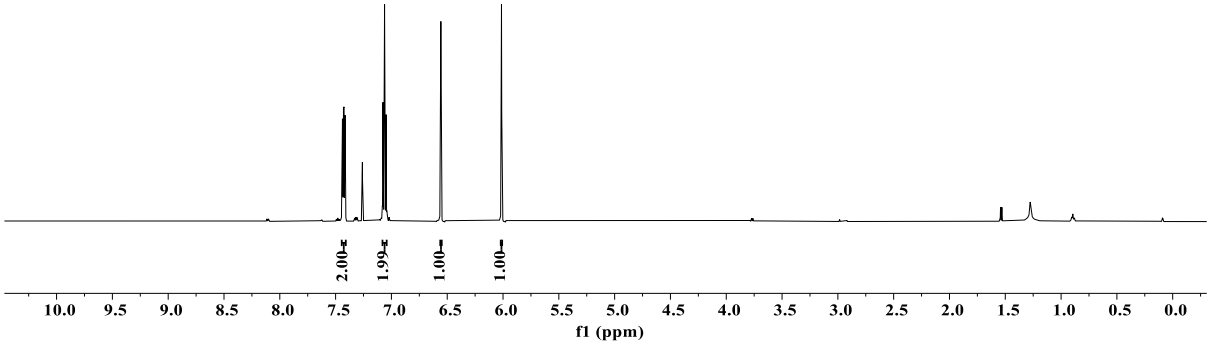
ESI-MS (**2g**)

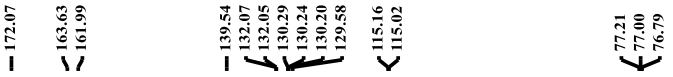


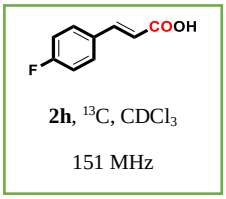
2h, ^{1}H, $CDCl_3$

600 MHz



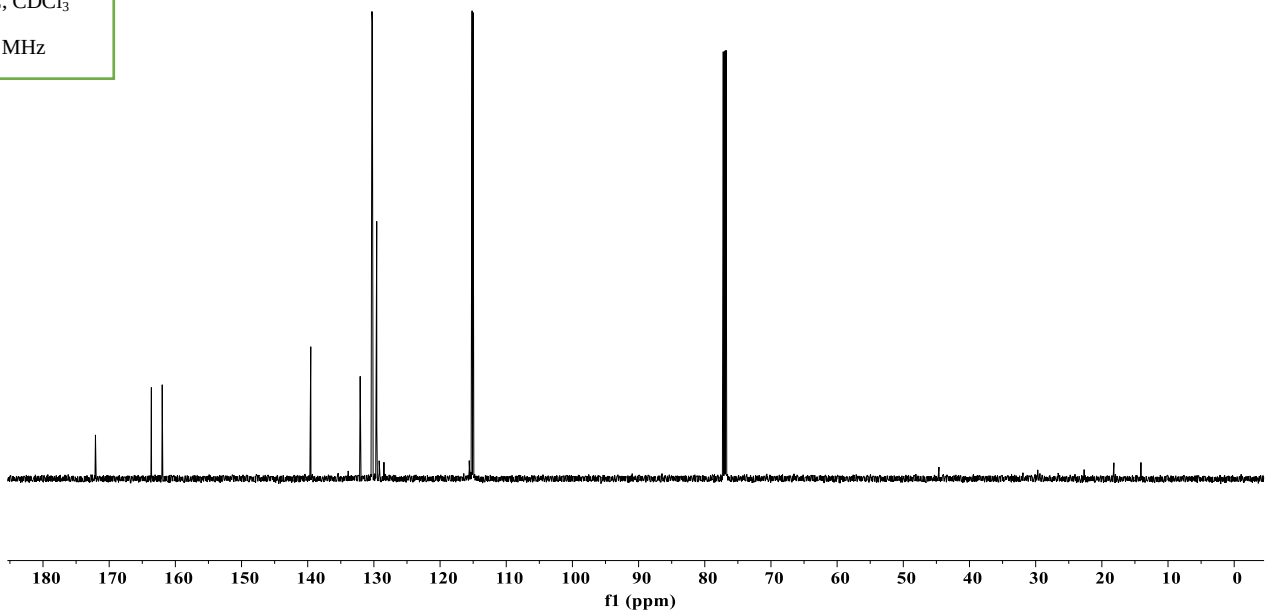


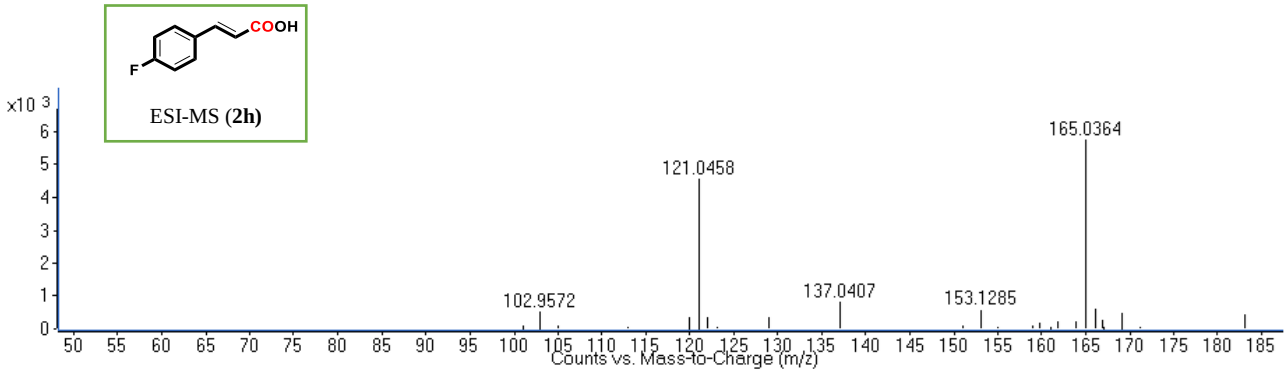


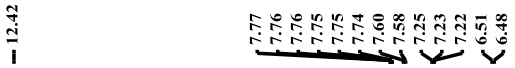


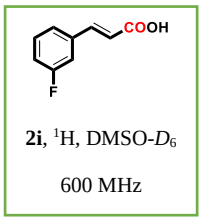
2h, ^{13}C, $CDCl_3$

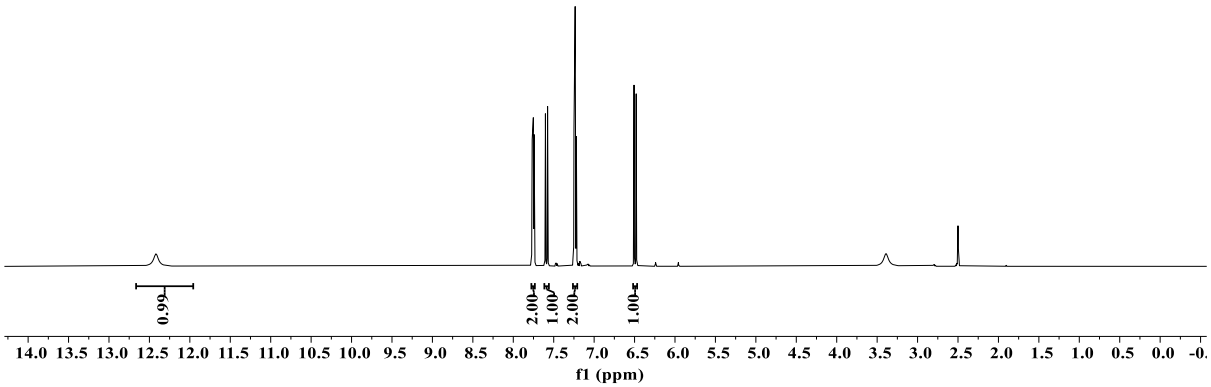
151 MHz

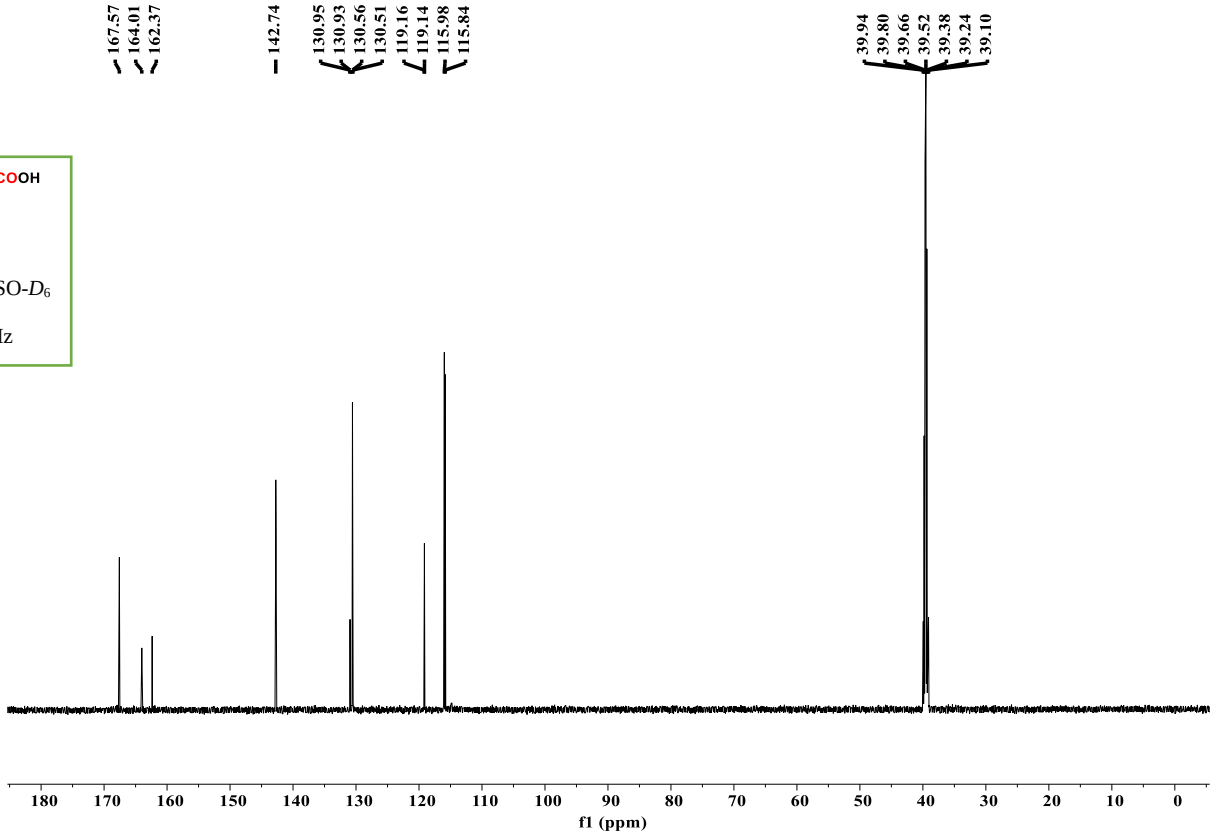



COOH
F
ESI-MS (2h)
x10 3
6
5
4
3
2
1
0
165.0364
121.0458
137.0407
153.1285
102.9572
50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185
Counts vs. Mass-to-Charge (m/z)


12.42
7.77
7.76
7.76
7.75
7.75
7.74
7.60
7.58
7.25
7.23
7.22
6.51
6.48

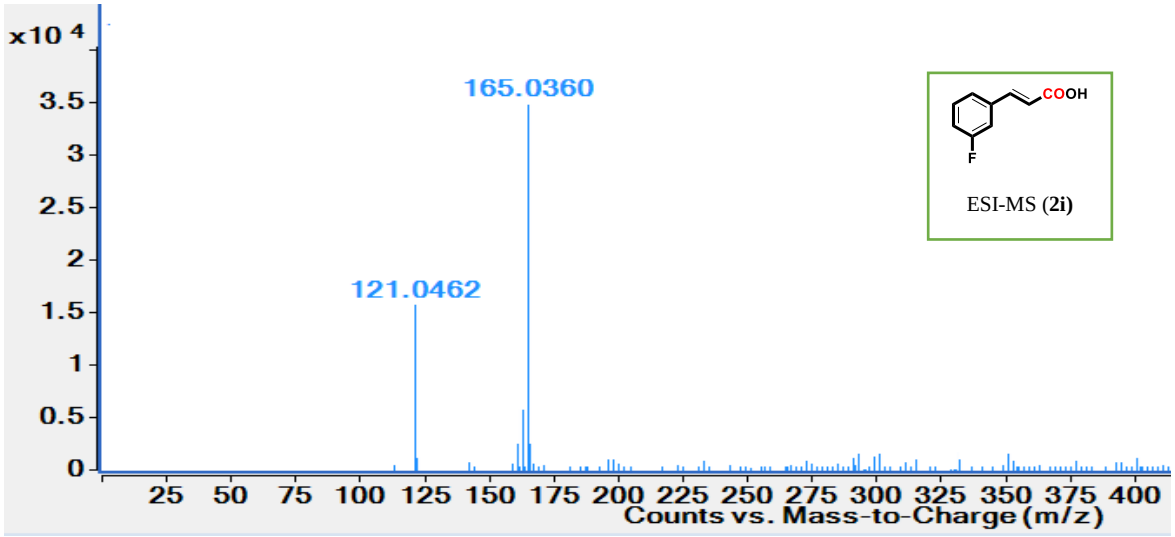

COOH
F
2i, 1H, DMSO-D6
600 MHz


0.99
2.00
1.00
2.00
1.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 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 0.0 -0.
f1 (ppm)

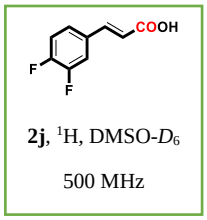


2i, ^{13}C, DMSO-D_6

151 MHz

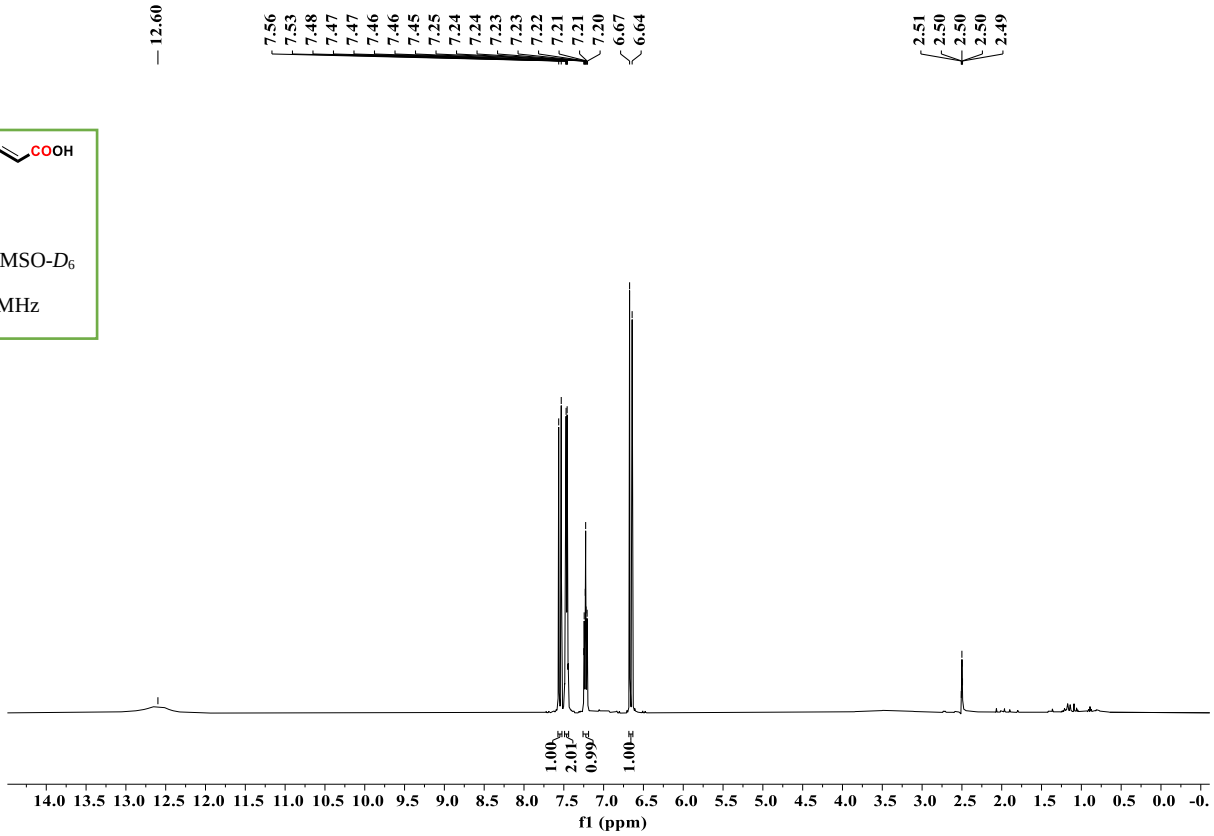


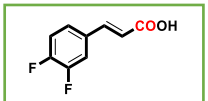
ESI-MS (**2i**)



2j, ^{1}H, DMSO-D_6

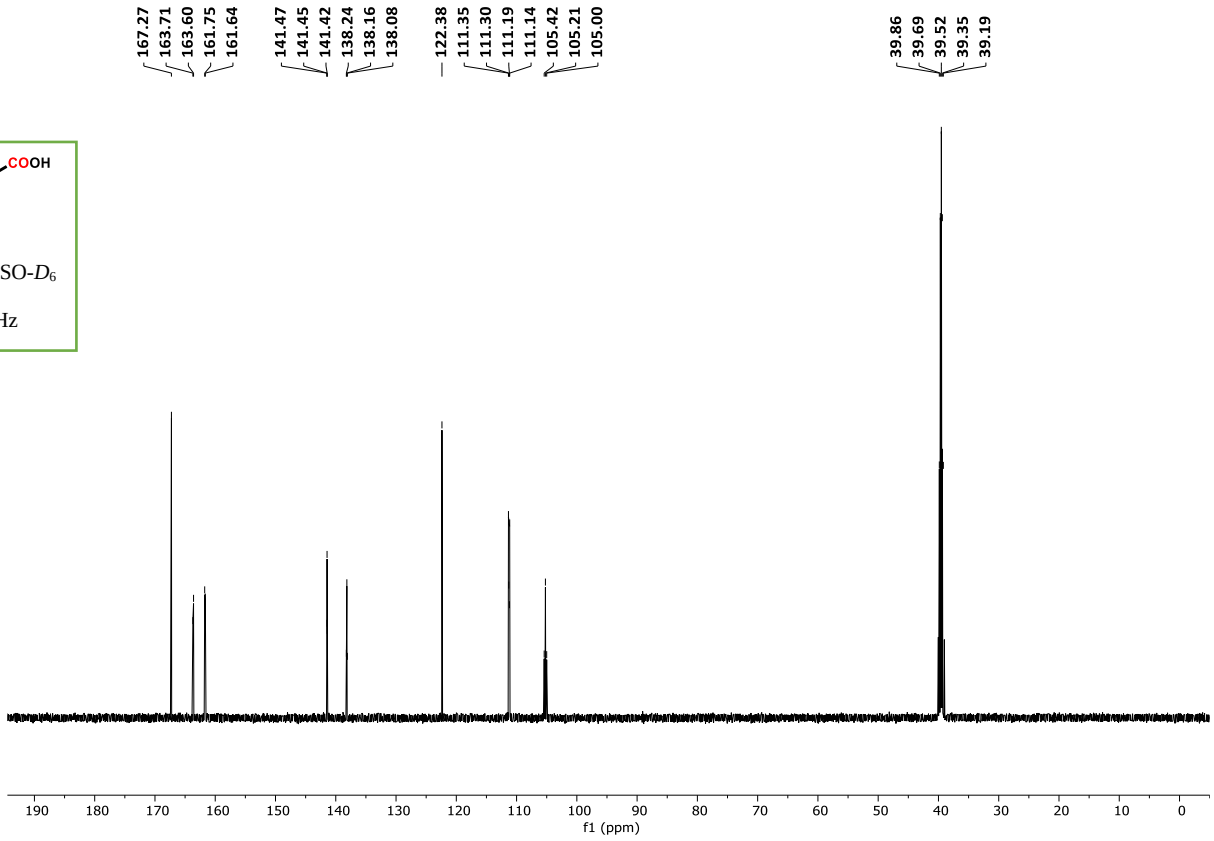
500 MHz

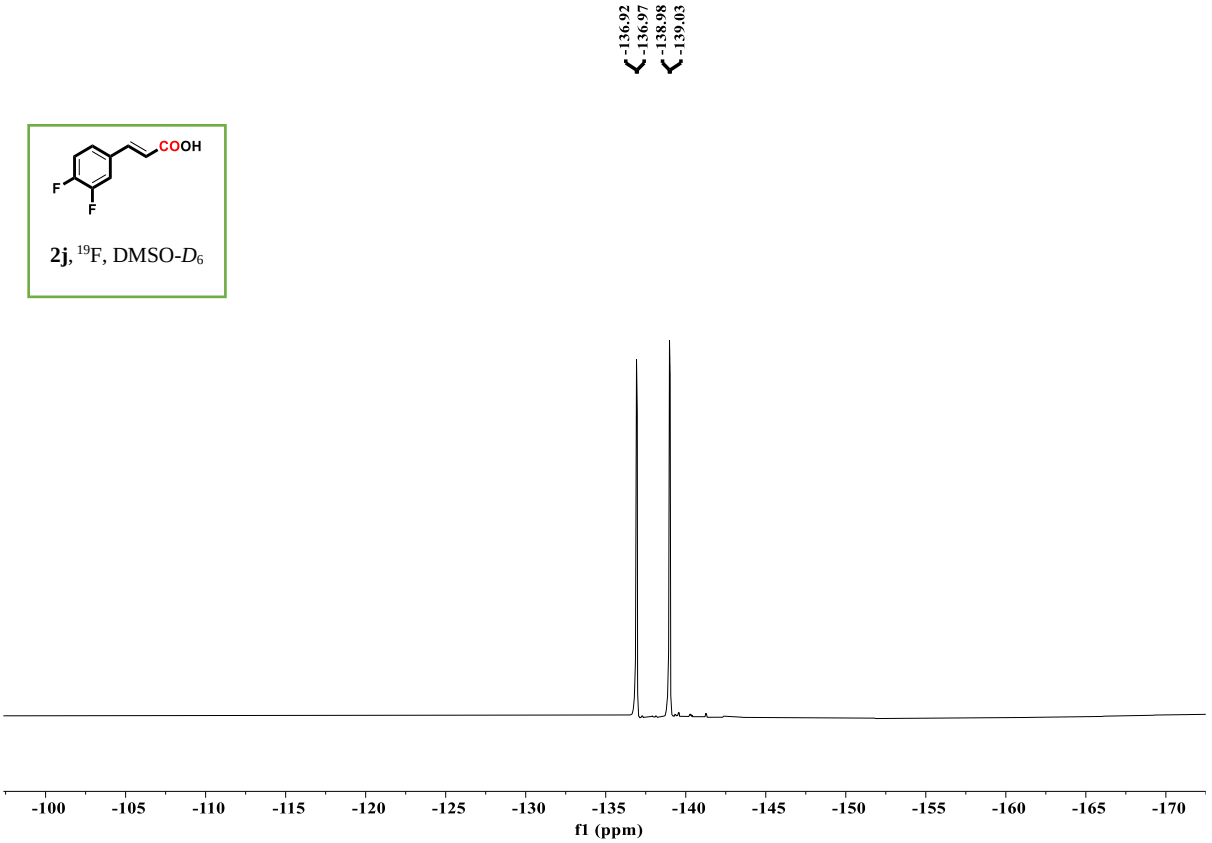


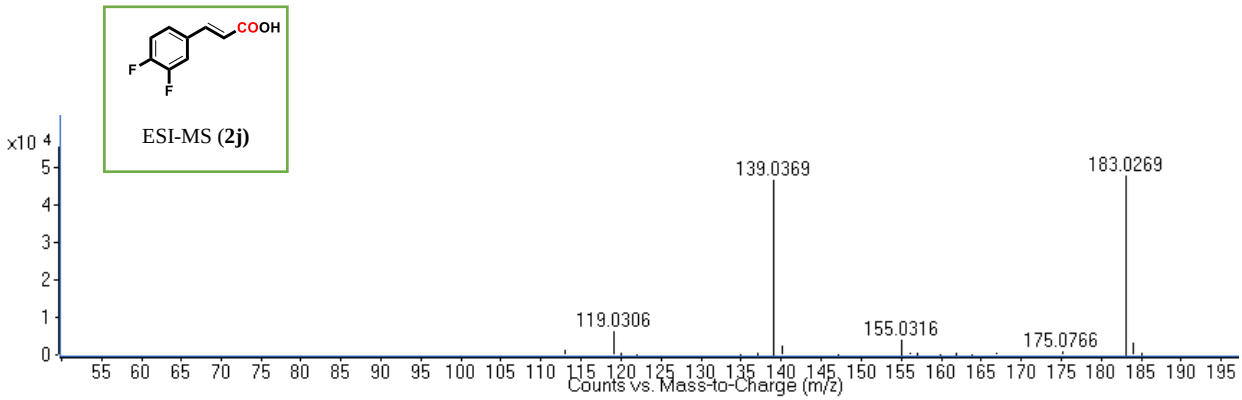


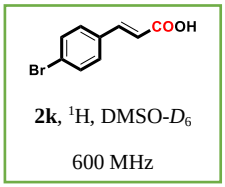
2j, ^{13}C, DMSO-D_6

126 MHz



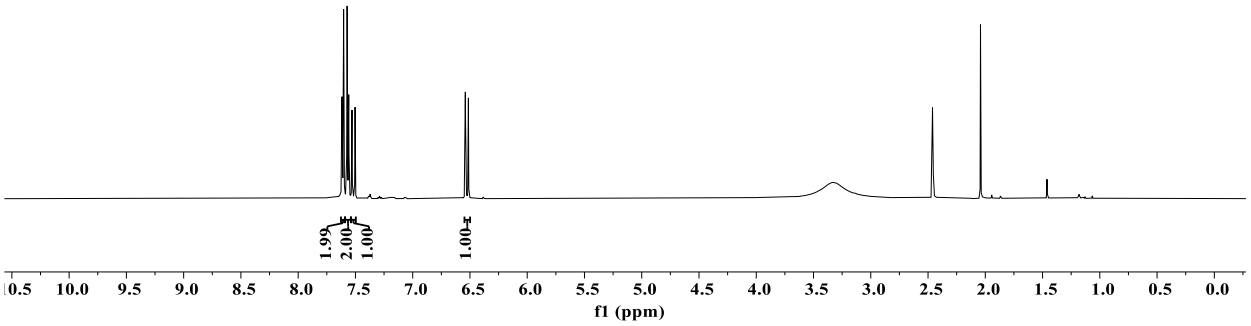

-136.92
-136.97
-138.98
-139.03
COOH
F
F
2j, 19F, DMSO-D6
-100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
f1 (ppm)

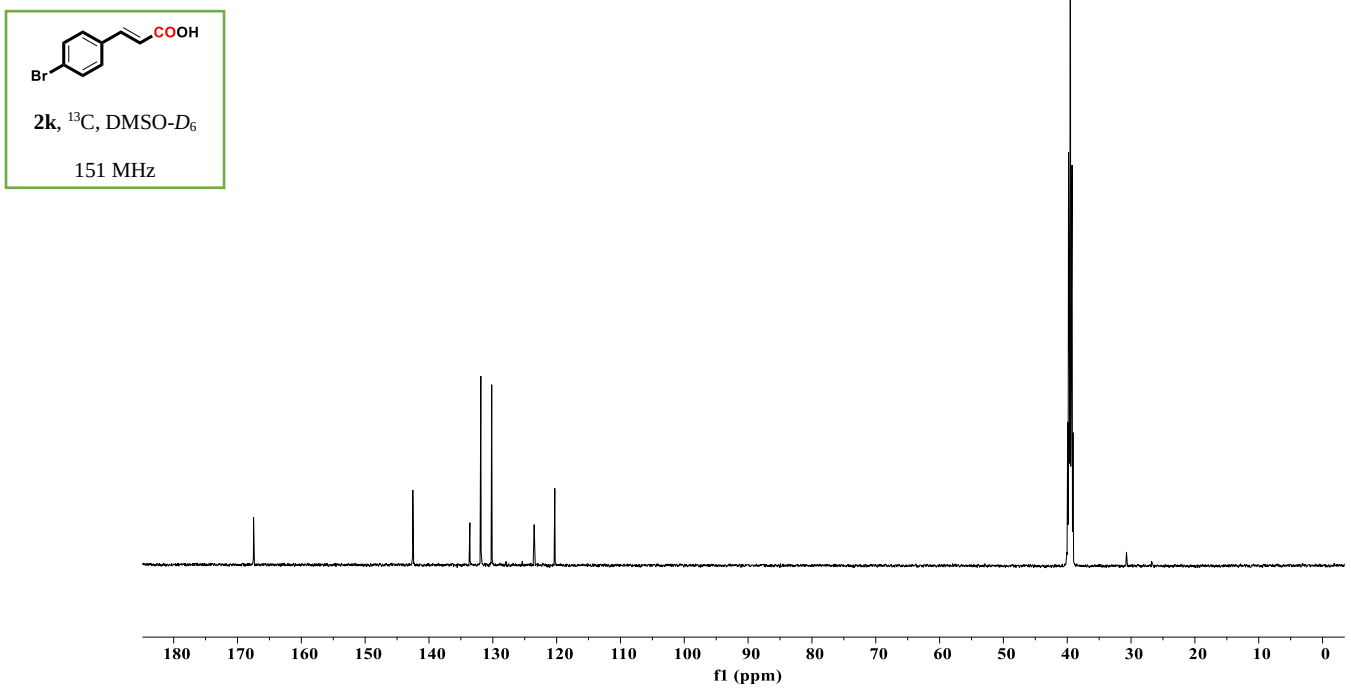

COOH
F
F
ESI-MS (2j)
x10 4
5
4
3
2
1
0
139.0369
183.0269
119.0306
155.0316
175.0766
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195
Counts vs. Mass-to-Charge (m/z)



2k, ^{1}H, DMSO-D_6

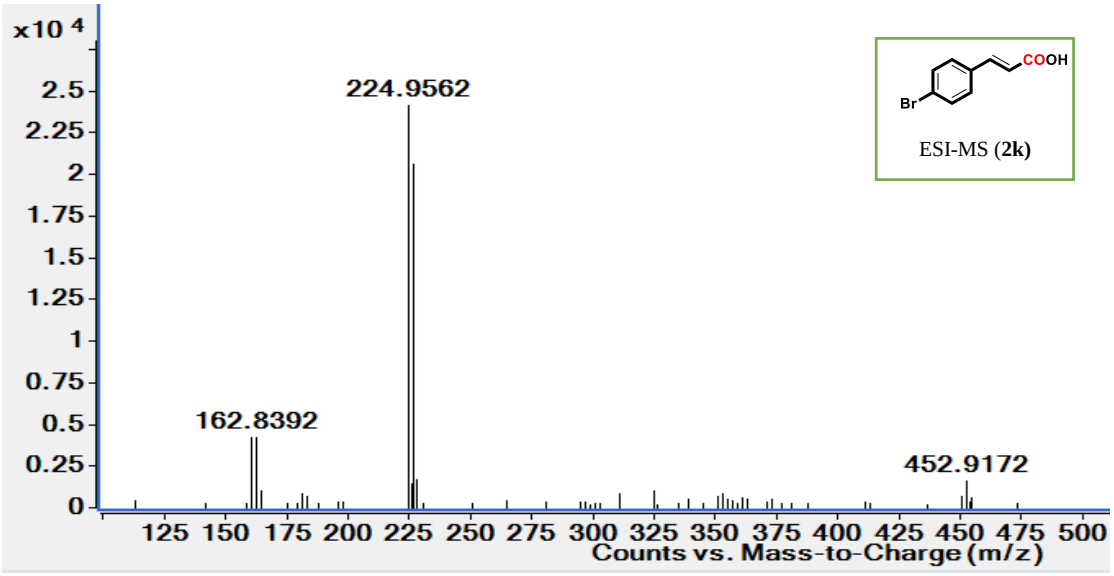
600 MHz



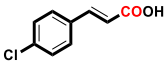


2k, ^{13}C, DMSO-D_6

151 MHz

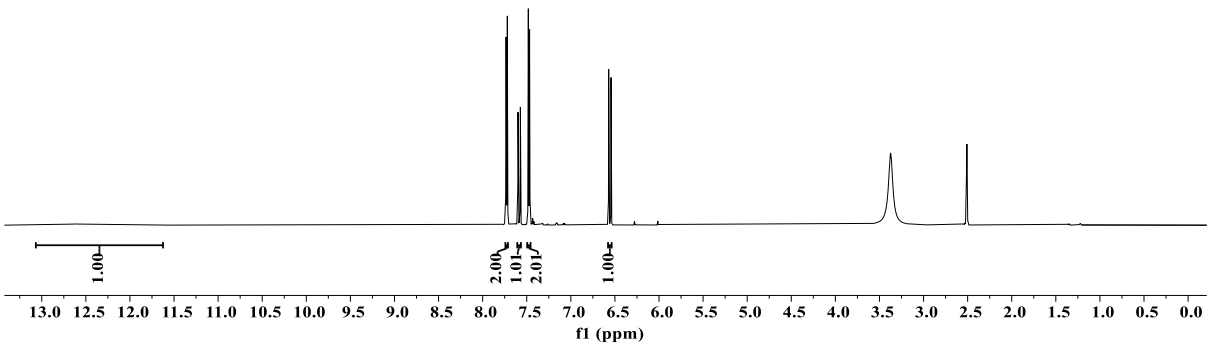


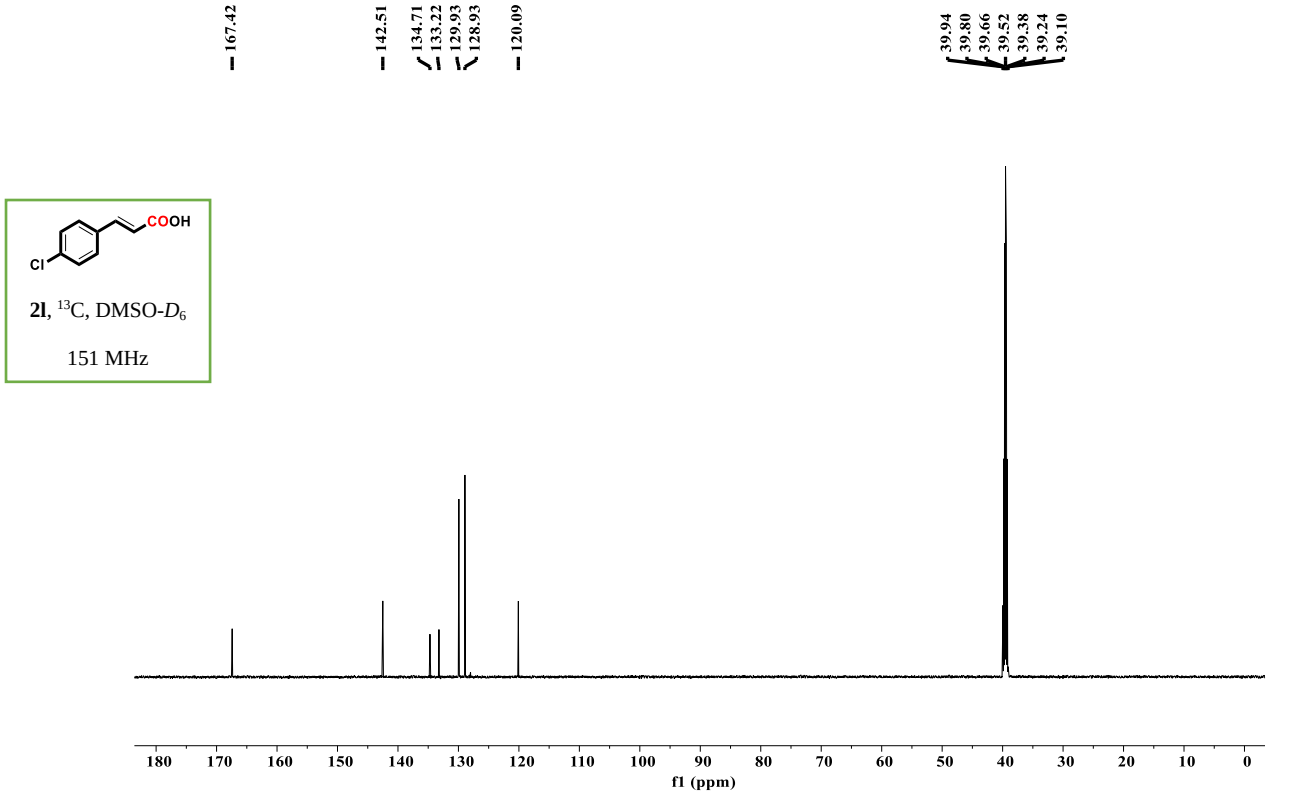
ESI-MS (**2k**)

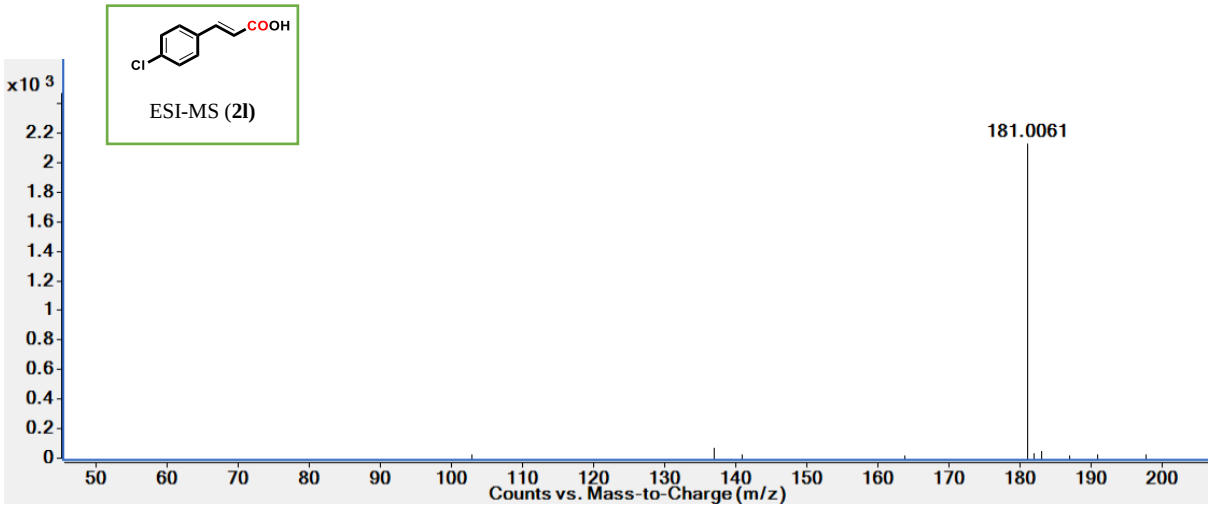


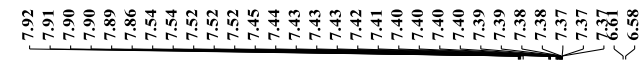
2l, ^{1}H, DMSO-D_6

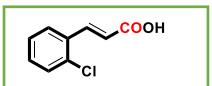
600 MHz




167.42
142.51
134.71
133.22
129.93
128.93
120.09
39.94
39.80
39.66
39.52
39.38
39.24
39.10
COOH
Cl
2l, 13C, DMSO-D6
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

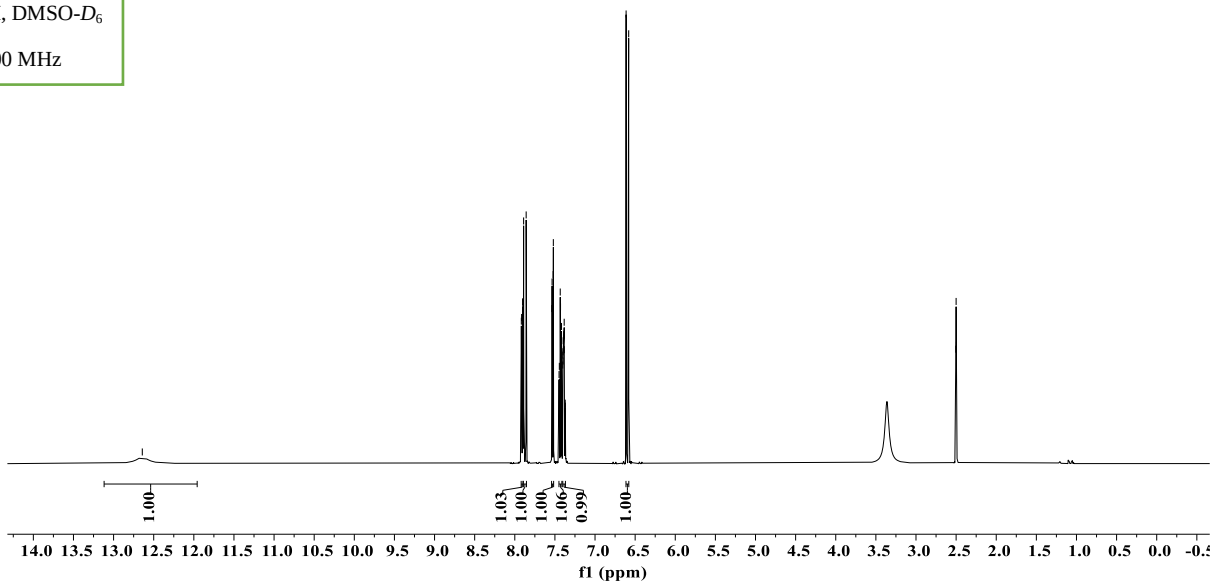

COOH
Cl
ESI-MS (2l)
x10 3
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
181.0061
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Counts vs. Mass-to-Charge (m/z)

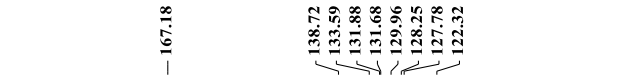


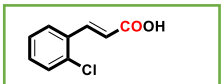


2m, ^{1}H, DMSO-D_6

600 MHz

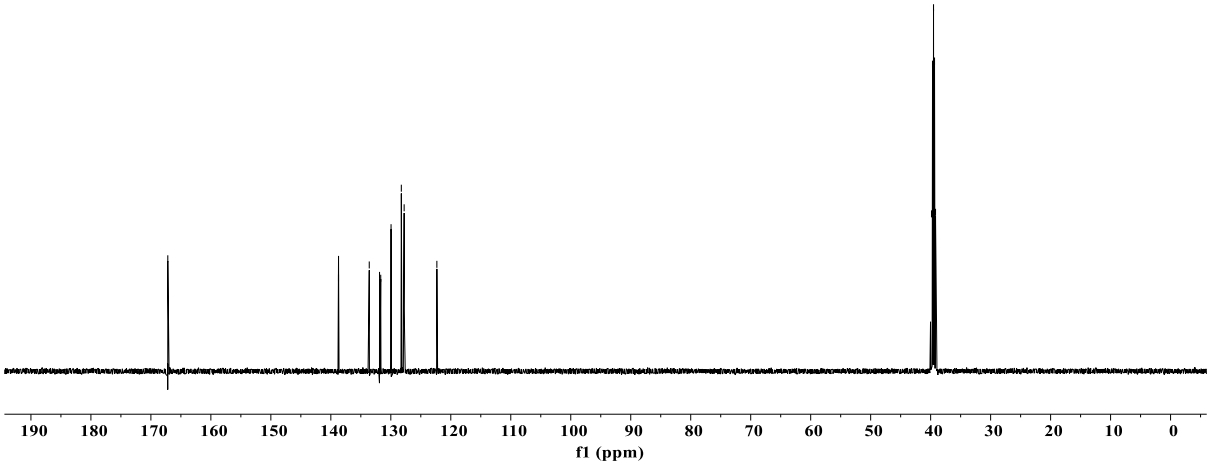


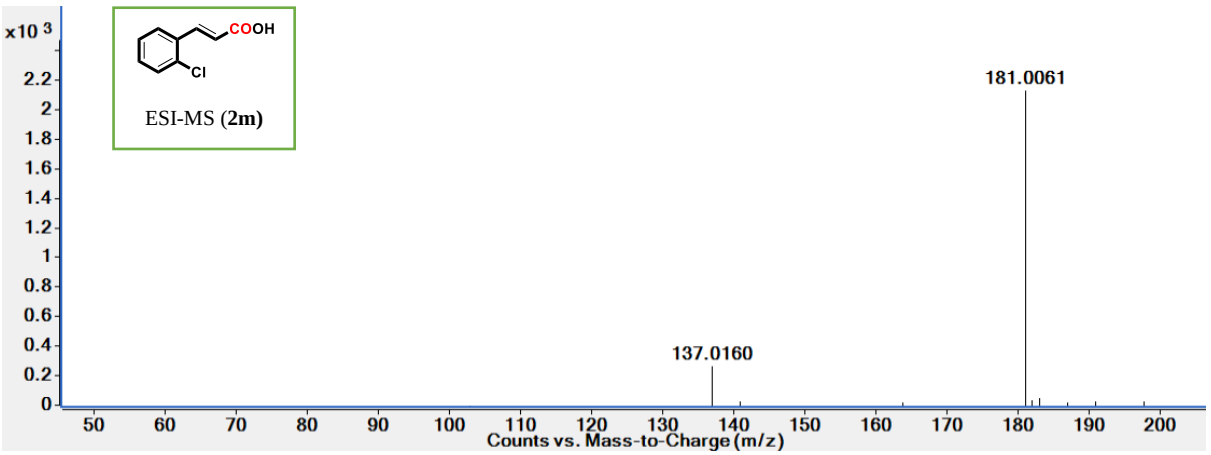


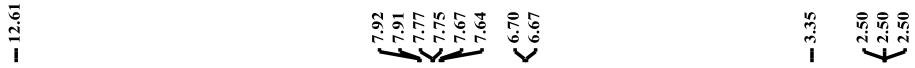


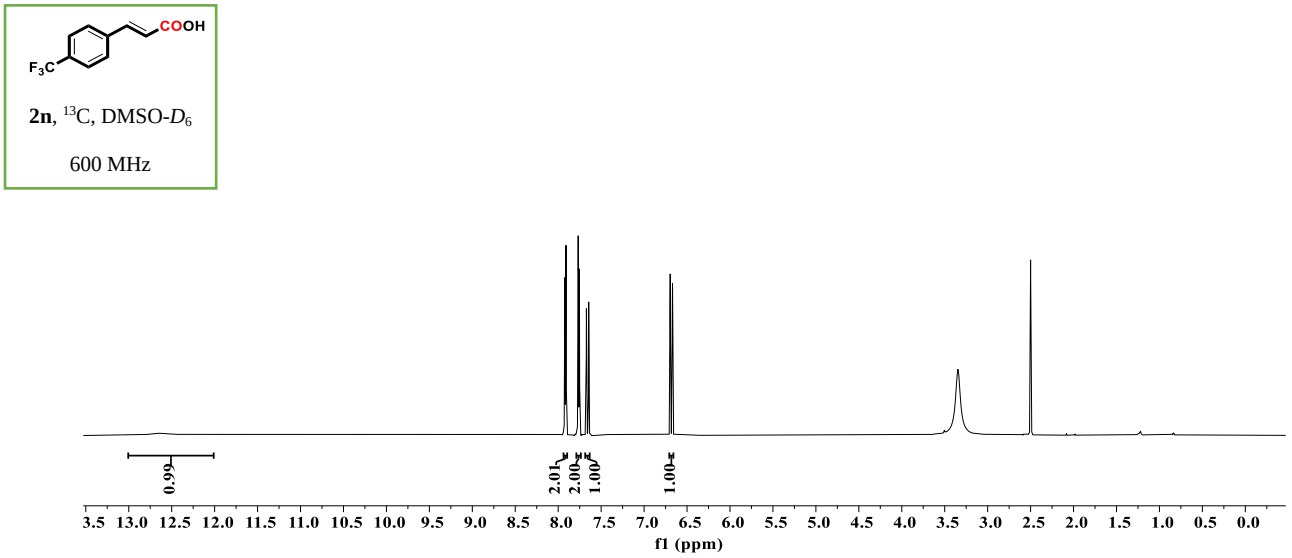
2m, ^{13}C, DMSO-D_6

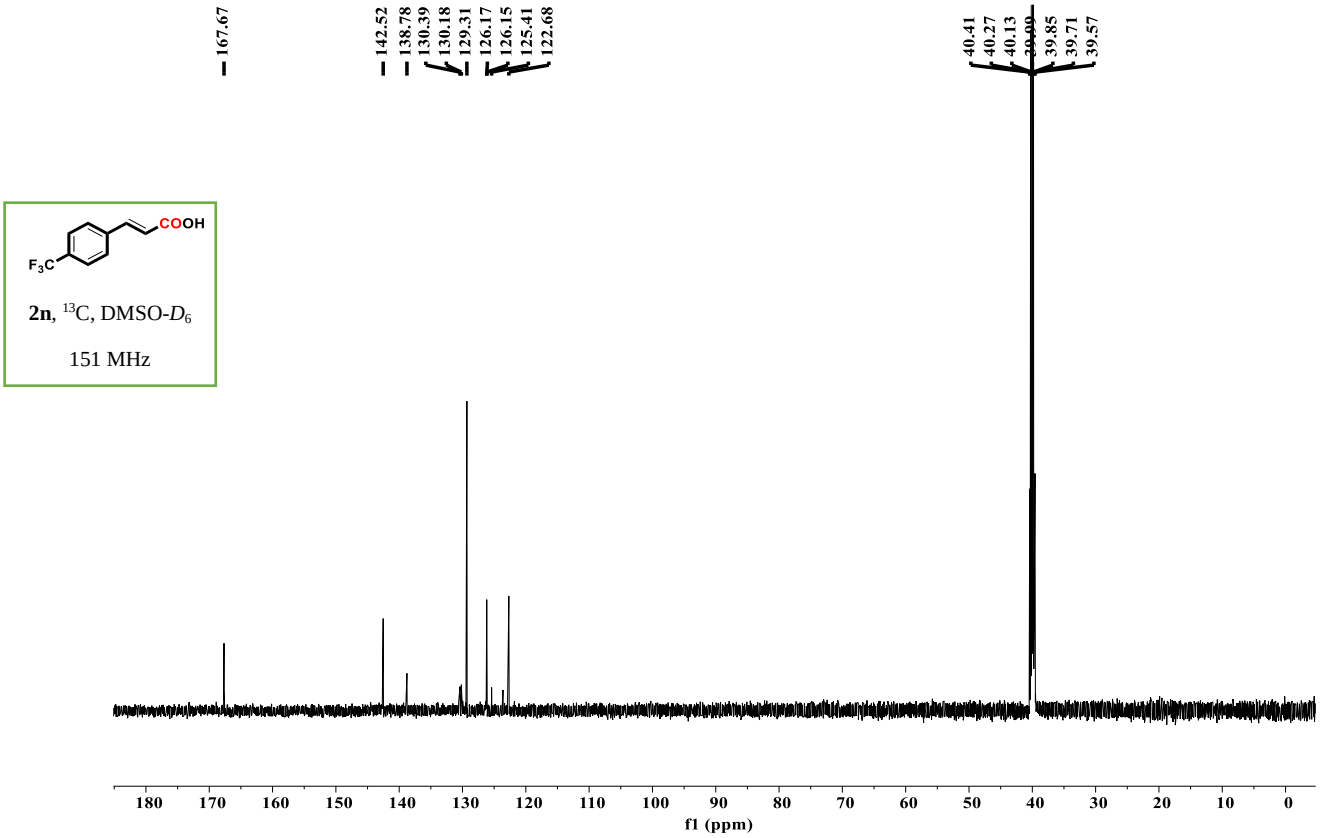
151 MHz

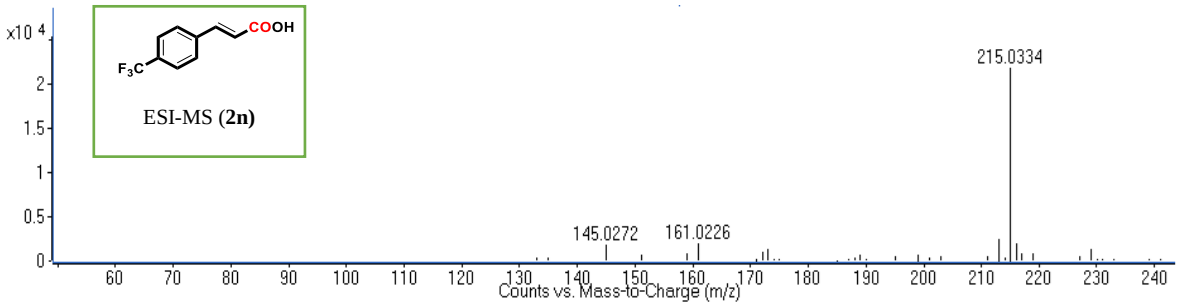


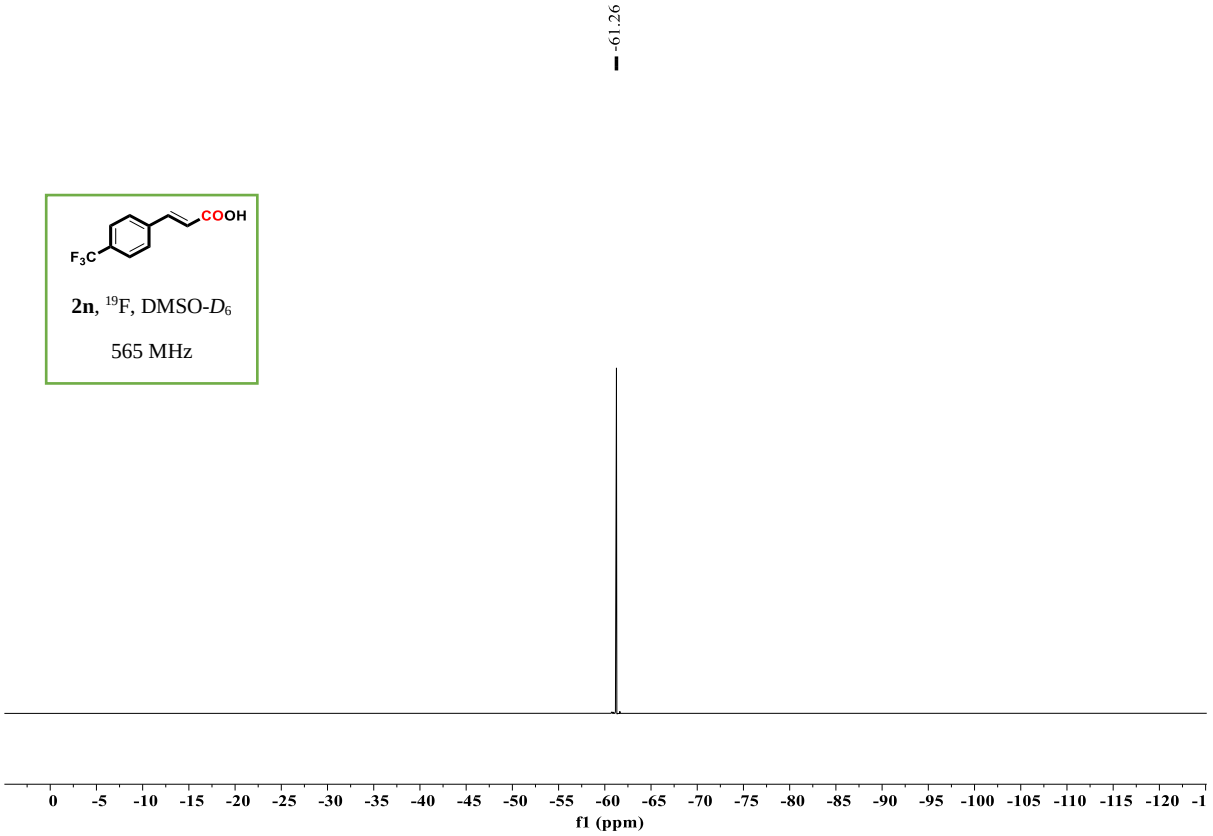

COOH
Cl
ESI-MS (2m)
x10 3
181.0061
137.0160
Counts vs. Mass-to-Charge (m/z)

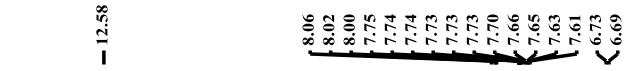

12.61
7.92
7.91
7.77
7.75
7.67
7.64
6.70
6.67
3.35
2.50
2.50
2.50

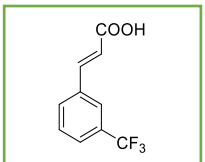

COOH
F3C
2n, 13C, DMSO-D6
600 MHz
0.99
2.01
2.00
1.00
1.00
f1 (ppm)


167.67
142.52
138.78
130.39
130.18
129.31
126.17
126.15
125.41
122.68
40.41
40.27
40.13
39.99
39.85
39.71
39.57
COOH
F3C
2n, 13C, DMSO-D6
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 4
2
1.5
1
0.5
0
COOH
F3C
ESI-MS (2n)
215.0334
145.0272
161.0226
60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
Counts vs. Mass-to-Charge (m/z)

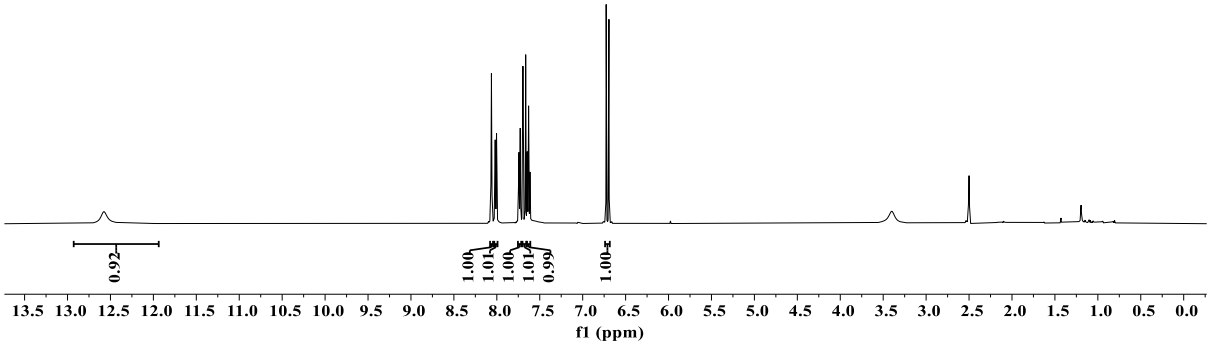

-61.26
COOH
F3C
2n, 19F, DMSO-D6
565 MHz
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -1
f1 (ppm)

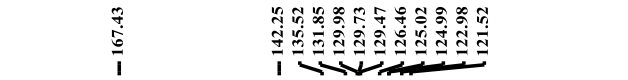


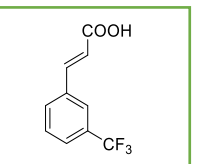


2o, ^{1}H, DMSO-D_6

500 MHz

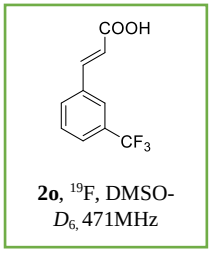




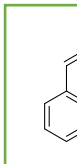


2o, ^{13}C, DMSO-D_6

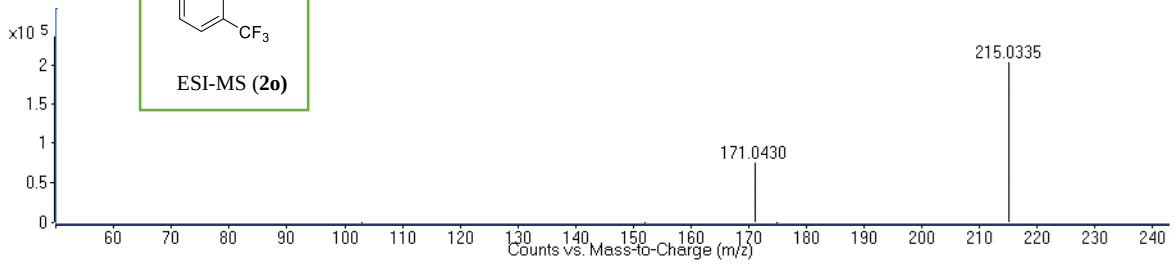
126 MHz

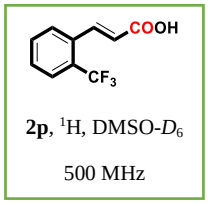


2o, ^{19}F, DMSO-D_6, 471MHz



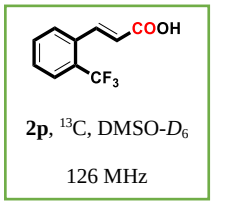
ESI-MS (**2o**)





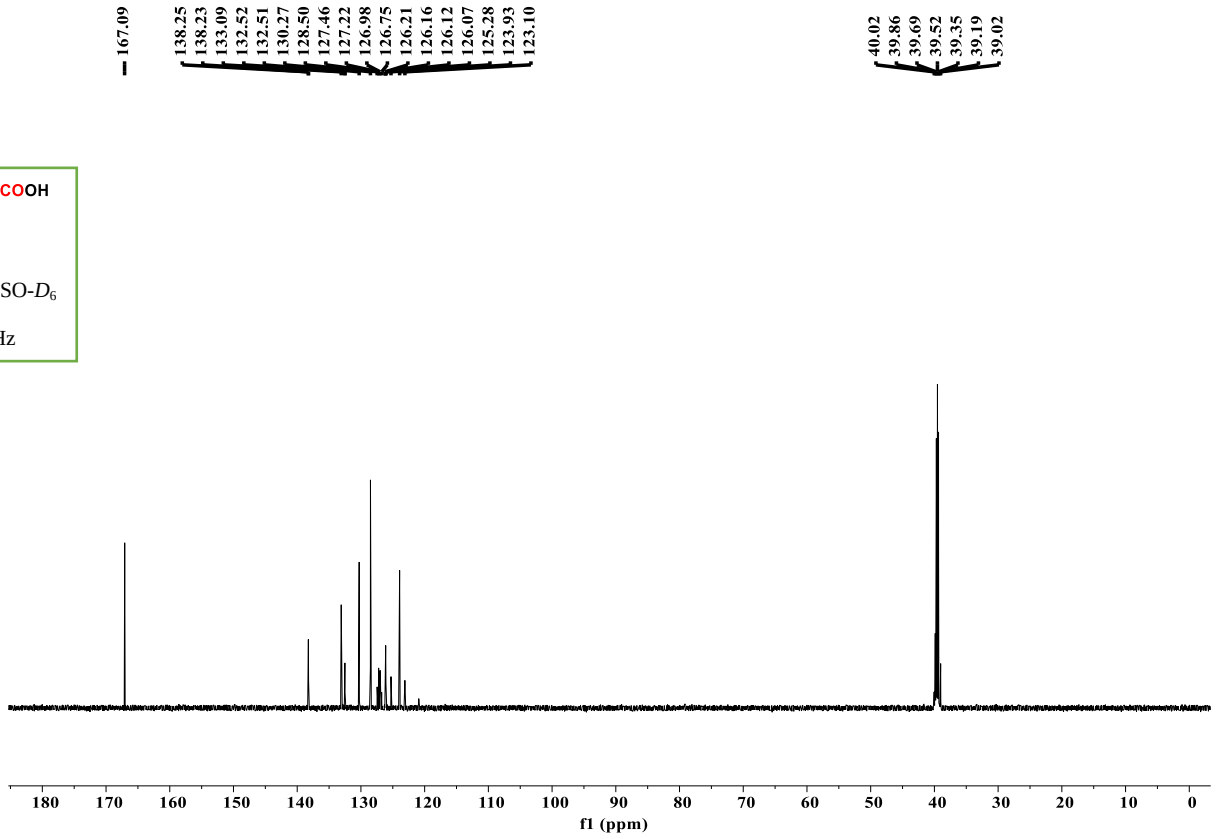
2p, ^{1}H, DMSO-D_6

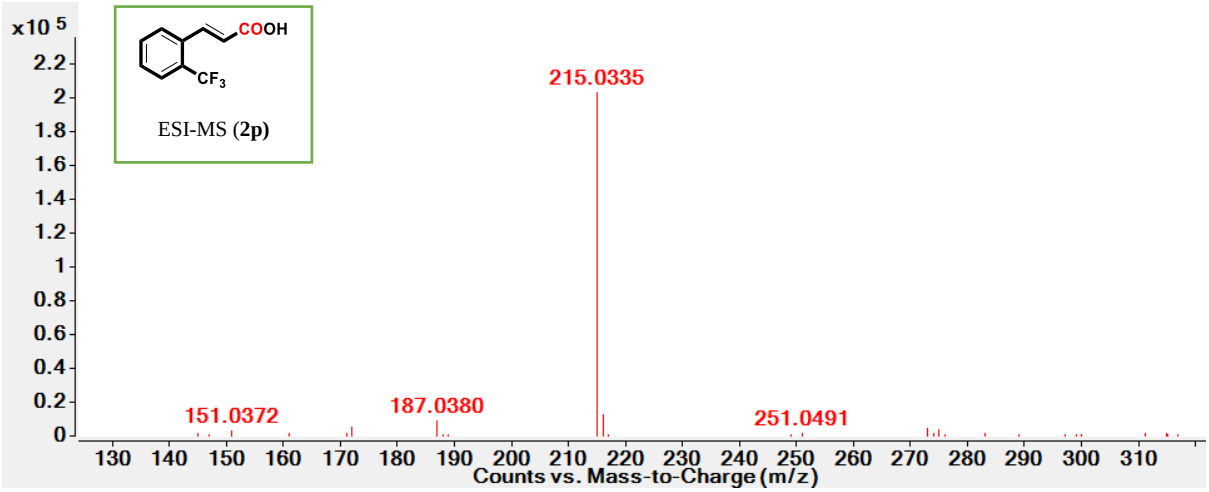
500 MHz

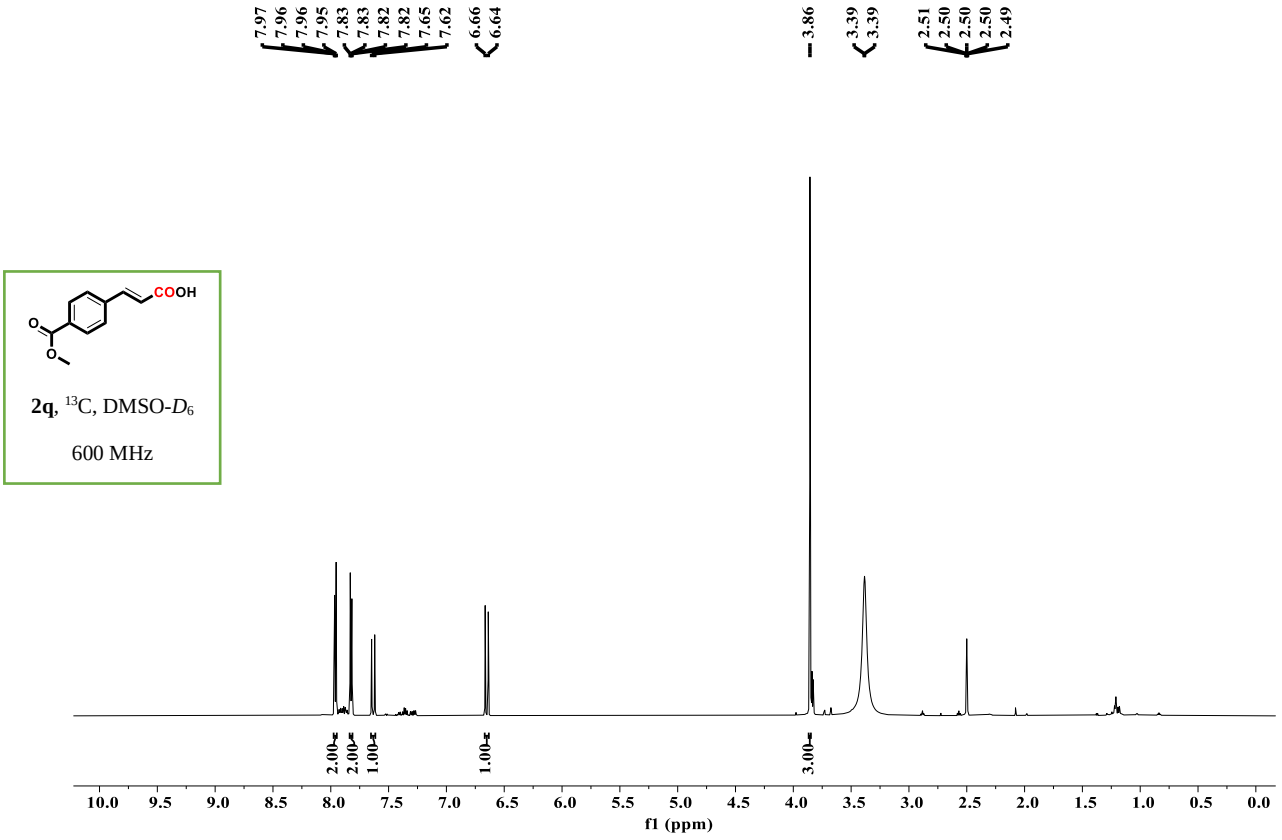


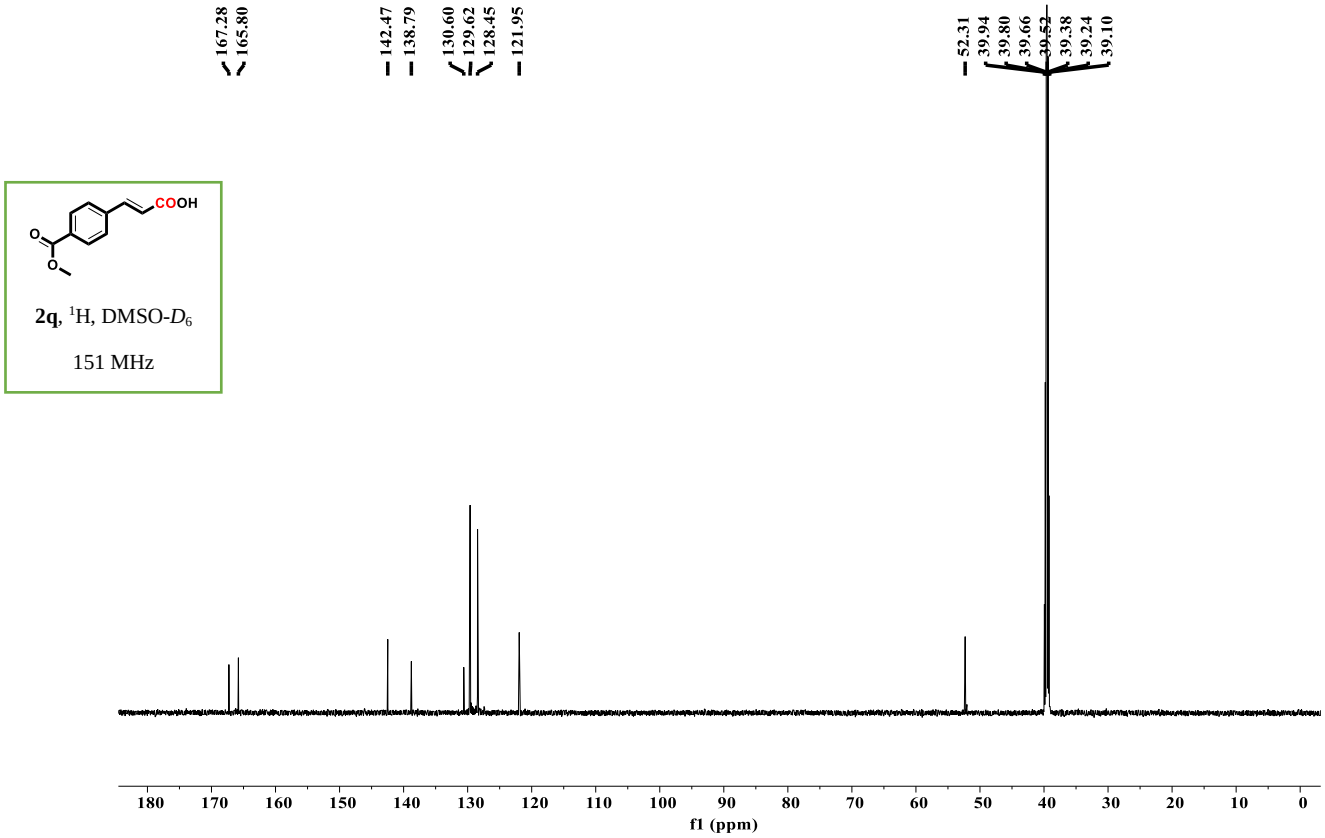
2p, ^{13}C, DMSO-D_6

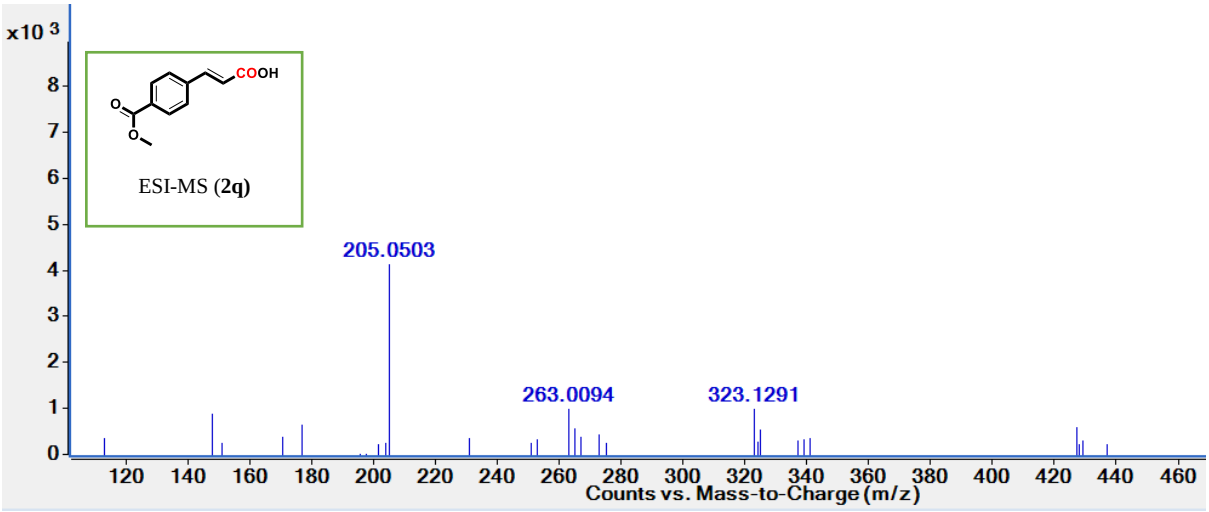
126 MHz

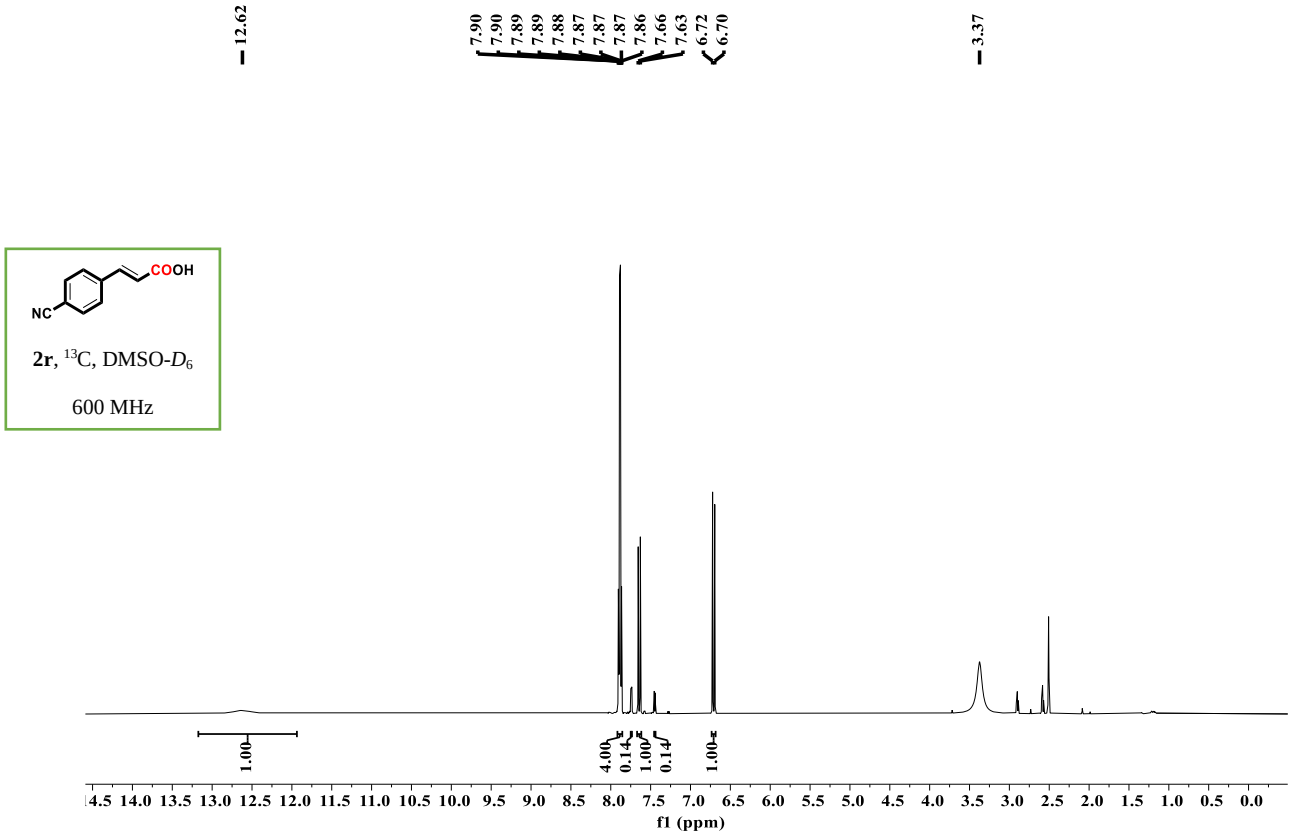


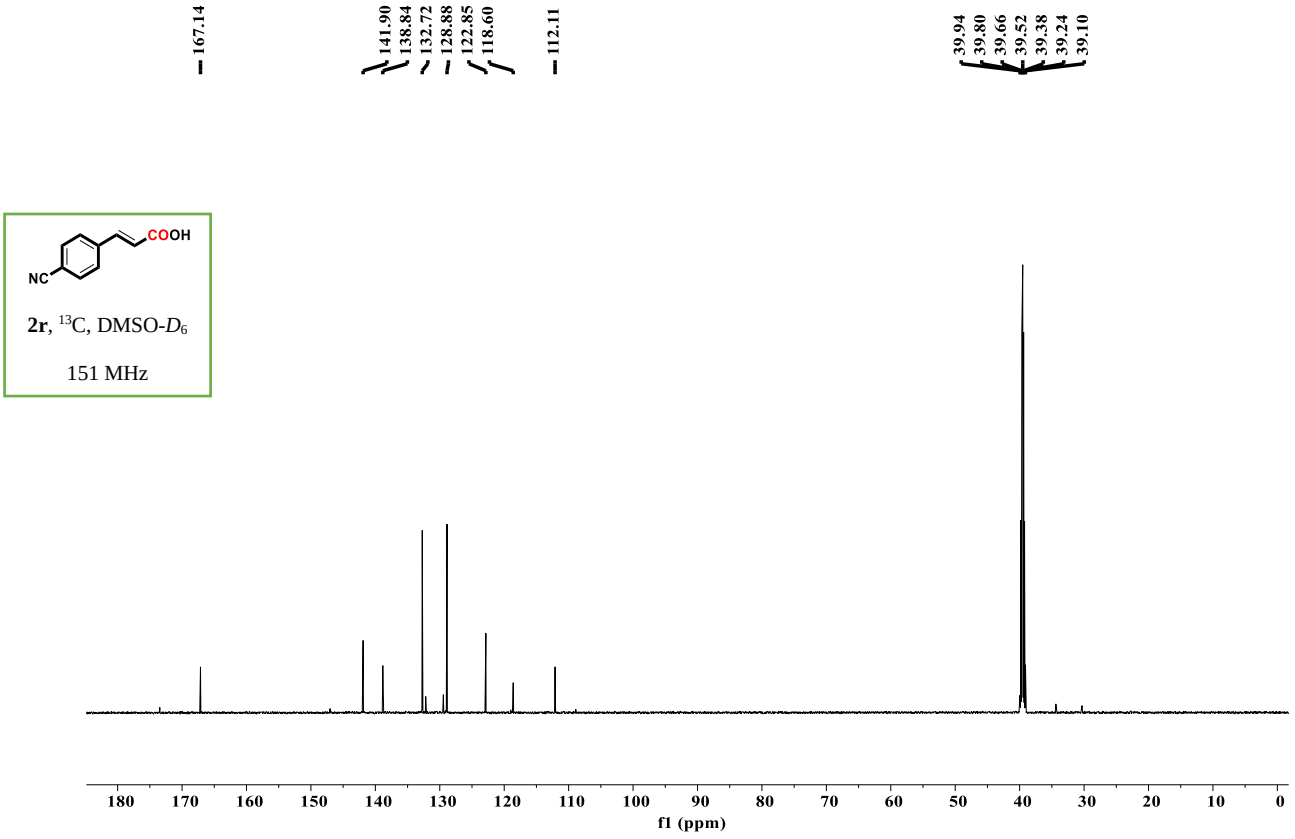

x10 5
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
COOH
CF3
ESI-MS (2p)
215.0335
151.0372
187.0380
251.0491
130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310
Counts vs. Mass-to-Charge (m/z)

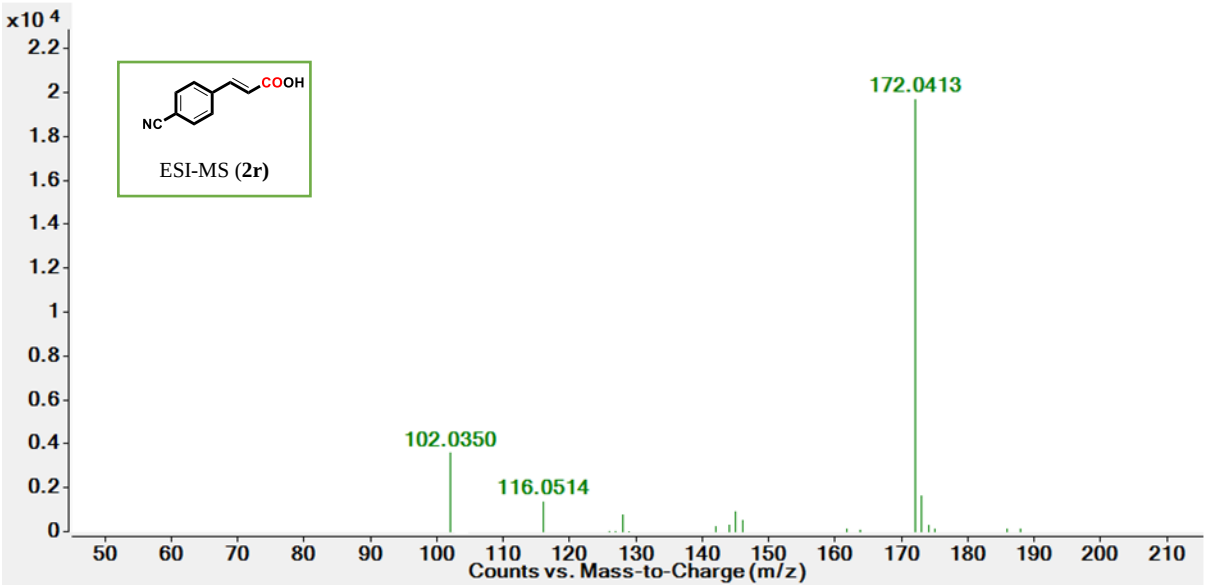

7.97
7.96
7.96
7.95
7.83
7.83
7.82
7.82
7.65
7.62
6.66
6.64
3.86
3.39
3.39
2.51
2.50
2.50
2.50
2.49
COOH
O
O
2q, 13C, DMSO-D6
600 MHz
2.00
2.00
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

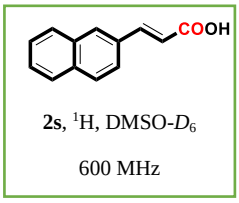

167.28
165.80
142.47
138.79
130.60
129.62
128.45
121.95
52.31
39.94
39.80
39.66
39.52
39.38
39.24
39.10
COOH
O
O
2q, 1H, DMSO-D6
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 3
8
7
6
5
4
3
2
1
0
COOH
O
O
ESI-MS (2q)
205.0503
263.0094
323.1291
120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460
Counts vs. Mass-to-Charge (m/z)


12.62
7.90
7.90
7.89
7.89
7.88
7.87
7.87
7.87
7.86
7.66
7.63
6.72
6.70
3.37
COOH
NC
2r, 13C, DMSO-D6
600 MHz
1.00
4.00
0.14
1.00
0.14
1.00
f1 (ppm)

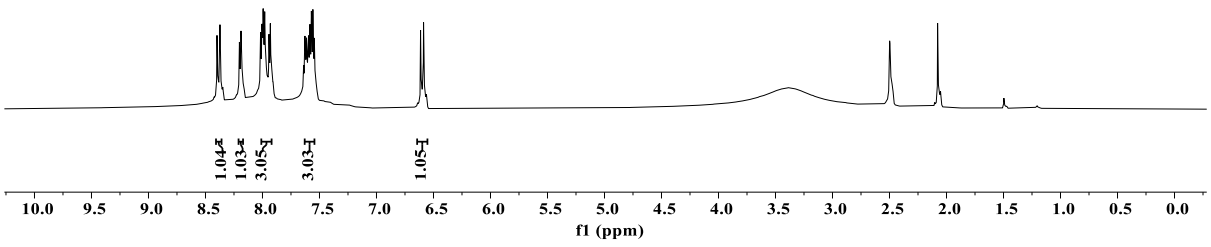

167.14
141.90
138.84
132.72
128.88
122.85
118.60
112.11
39.94
39.80
39.66
39.52
39.38
39.24
39.10
COOH
NC
2r, 13C, DMSO-D6
151 MHz
f1 (ppm)

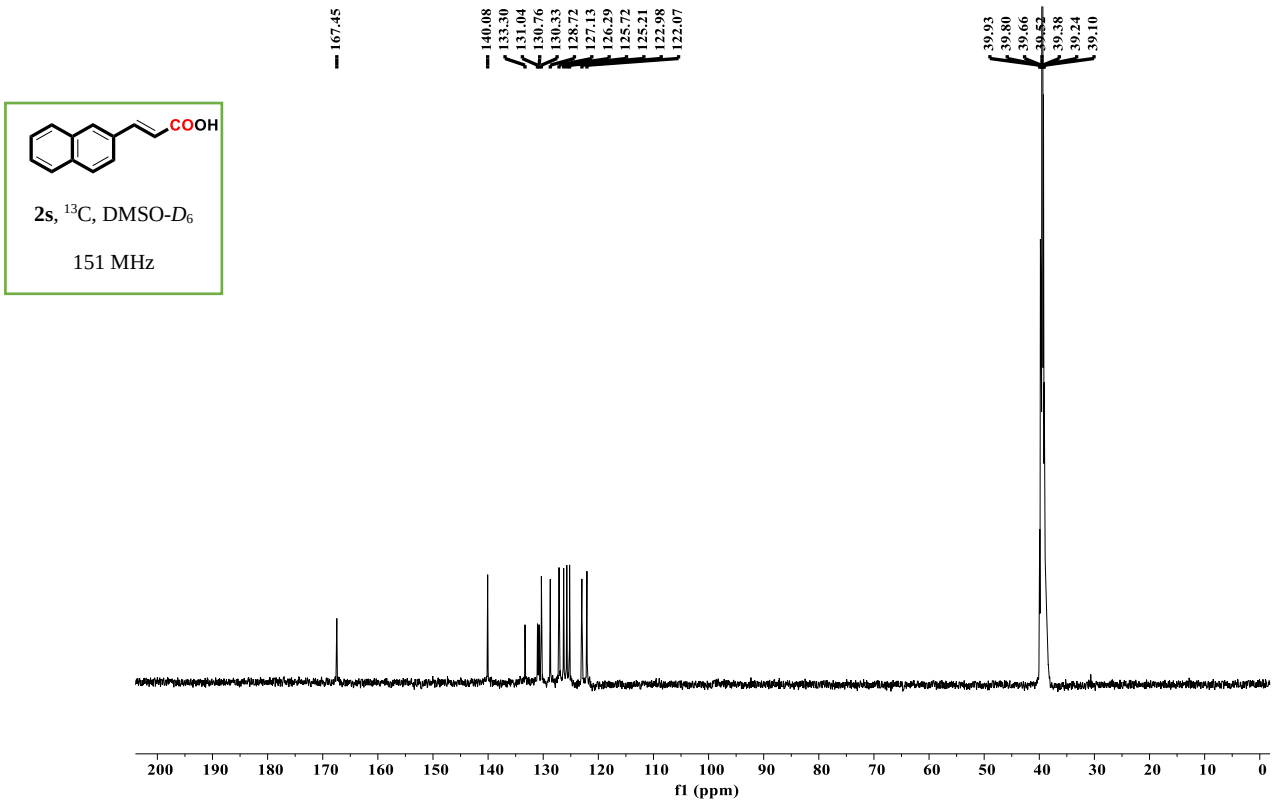


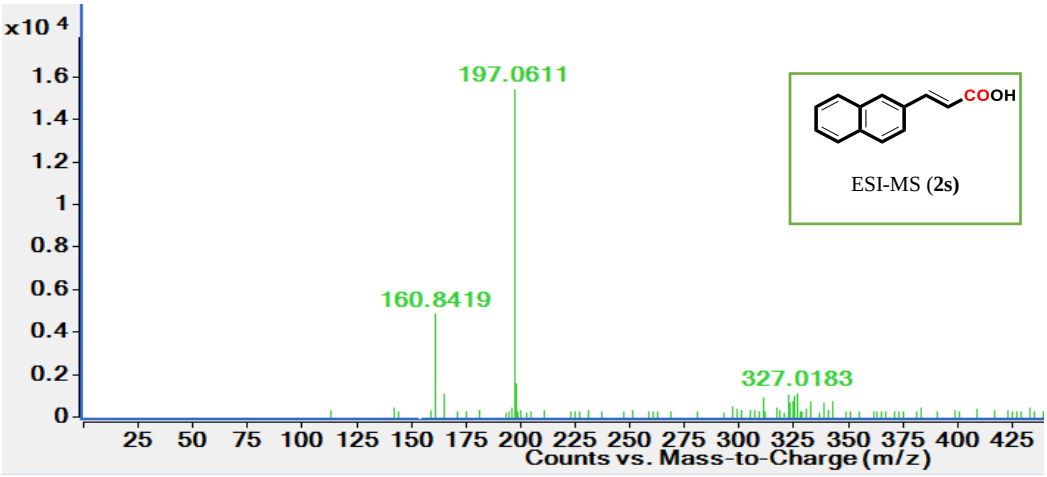


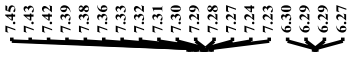
2s, ^{1}H, DMSO-D_6

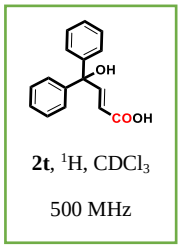
600 MHz




167.45
140.08
133.30
131.04
130.76
130.33
128.72
127.13
126.29
125.72
125.21
122.98
122.07
39.93
39.80
39.66
39.52
39.38
39.24
39.10
COOH
2s, 13C, DMSO-D6
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

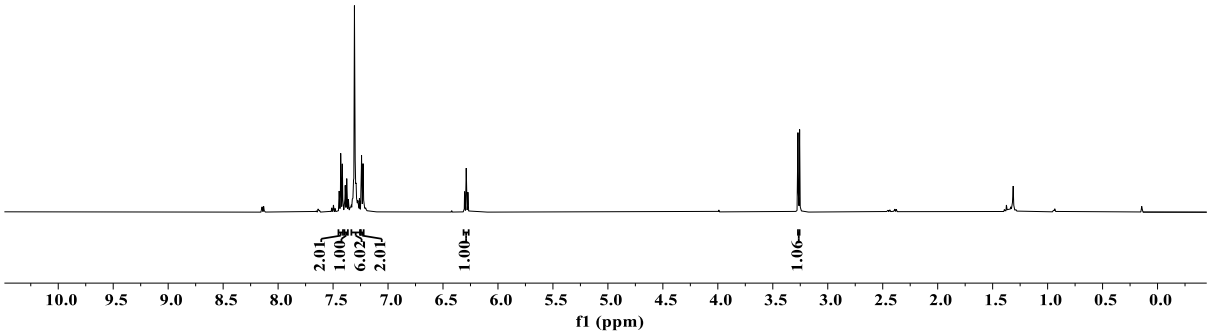

x10 4
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
197.0611
160.8419
327.0183
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425
Counts vs. Mass-to-Charge (m/z)
COOH
ESI-MS (2s)

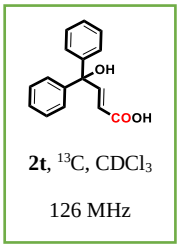




2t, ^{1}H, $CDCl_3$

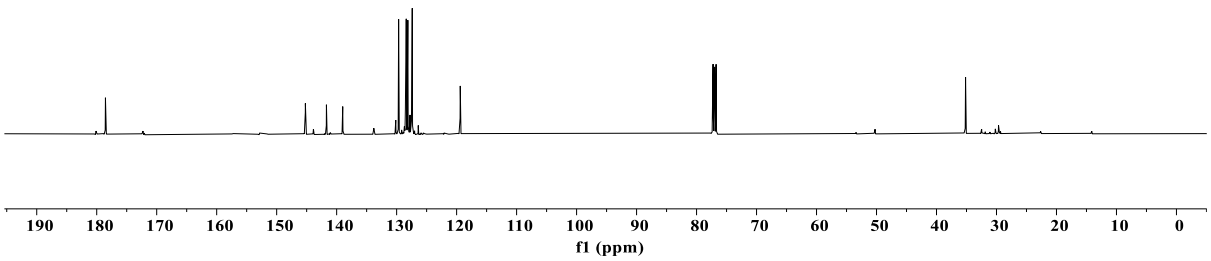
500 MHz

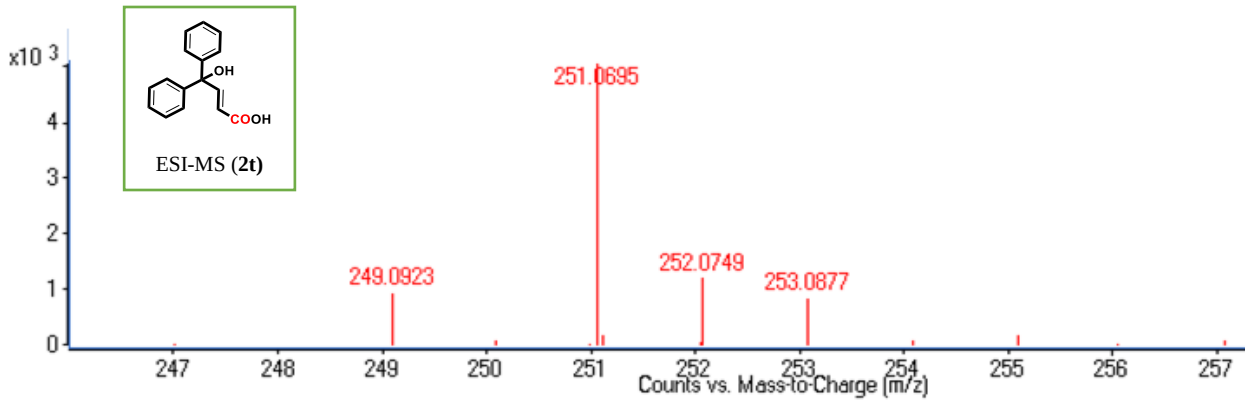


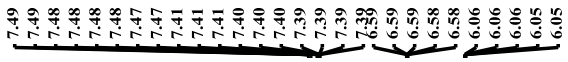


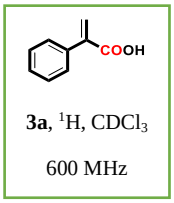
2t, ^{13}C, $CDCl_3$

126 MHz



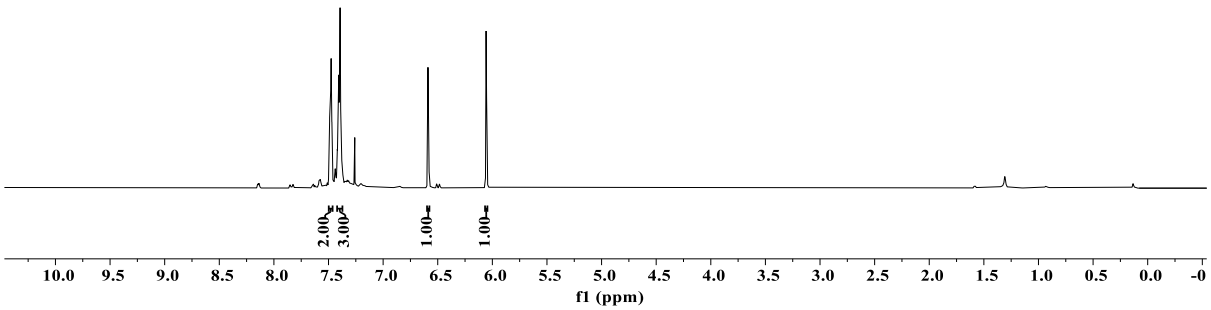


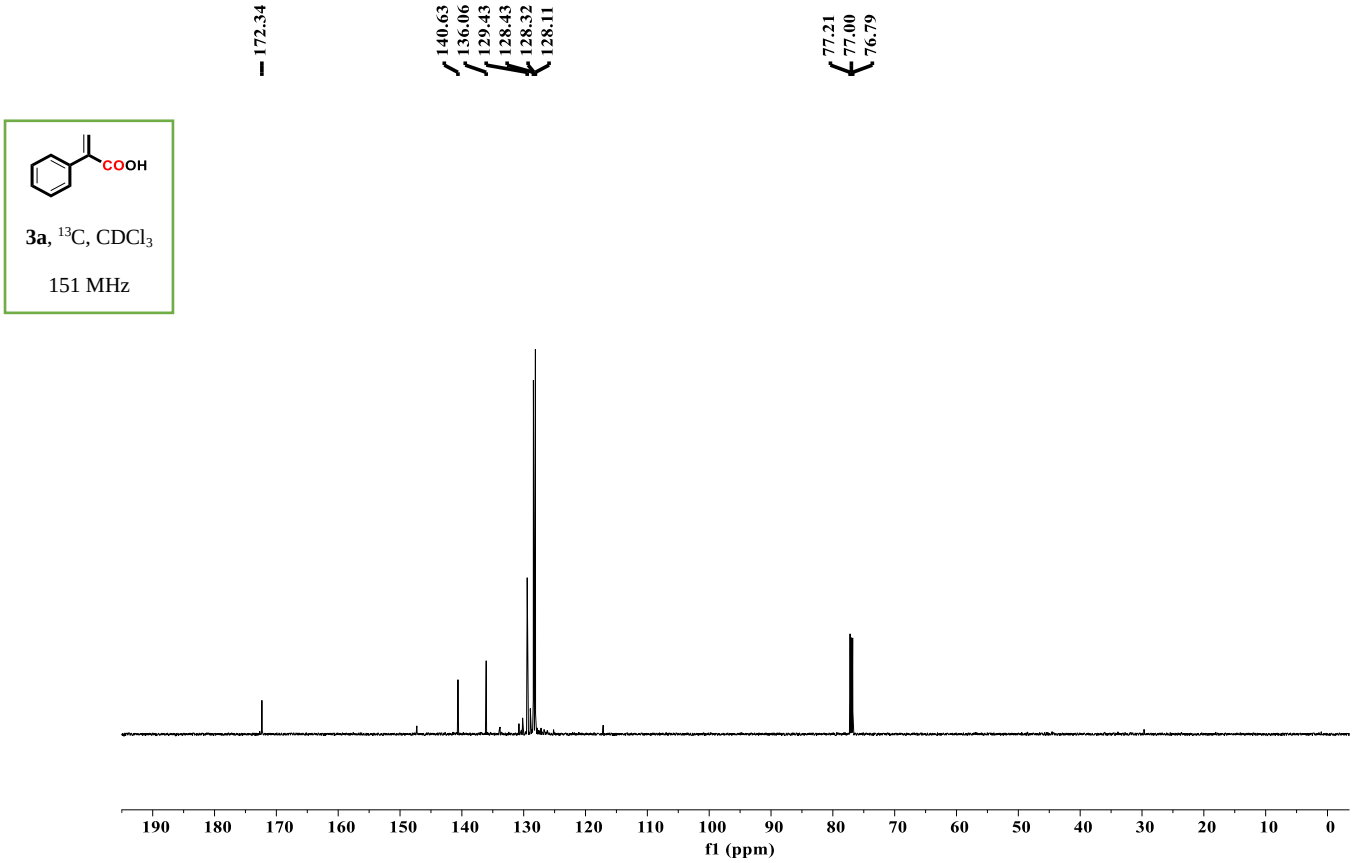


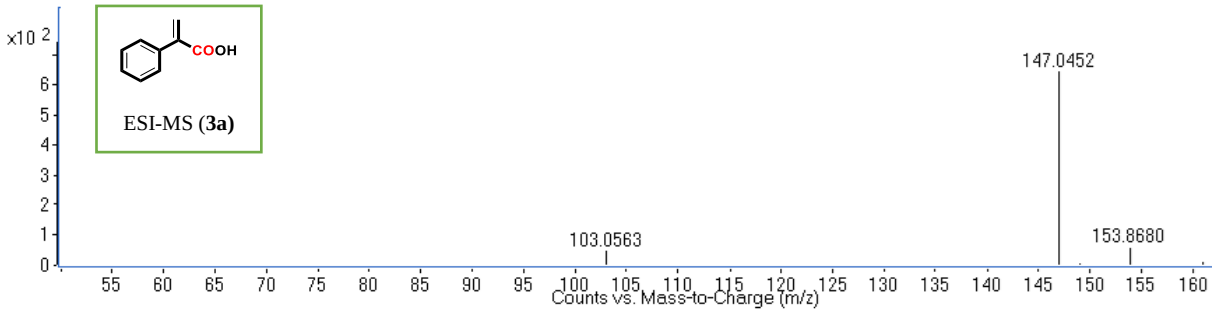


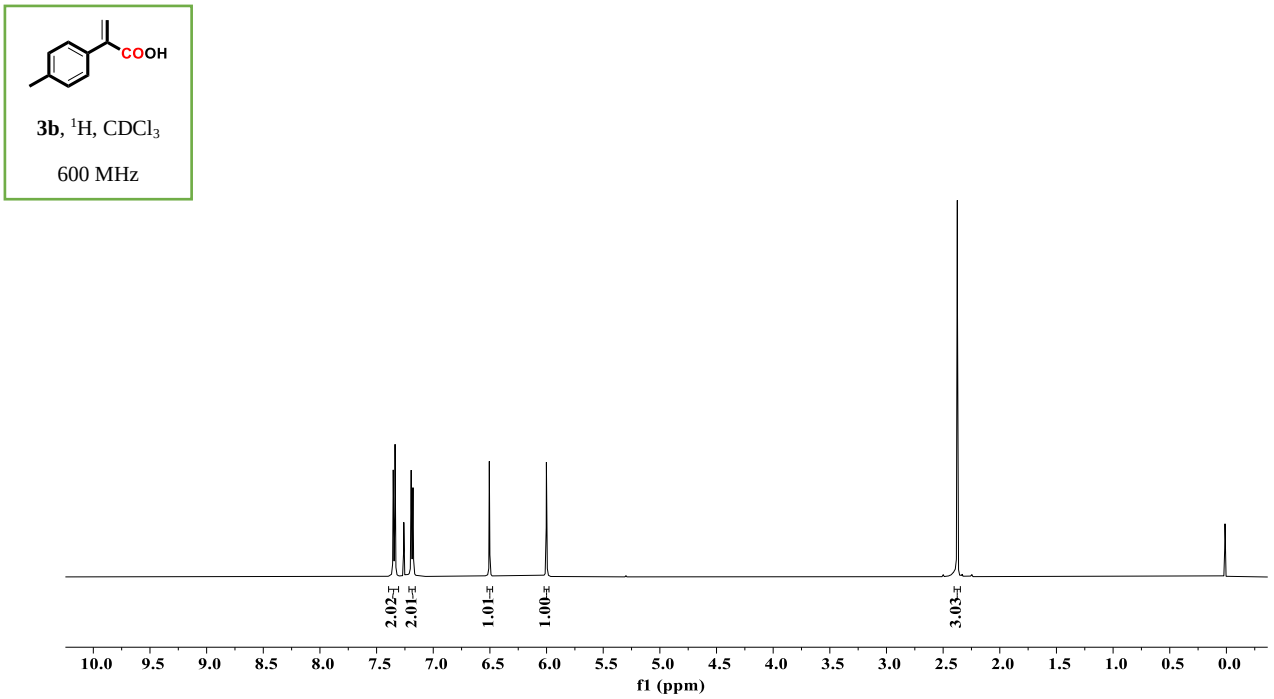
3a, ^{1}H, $CDCl_3$

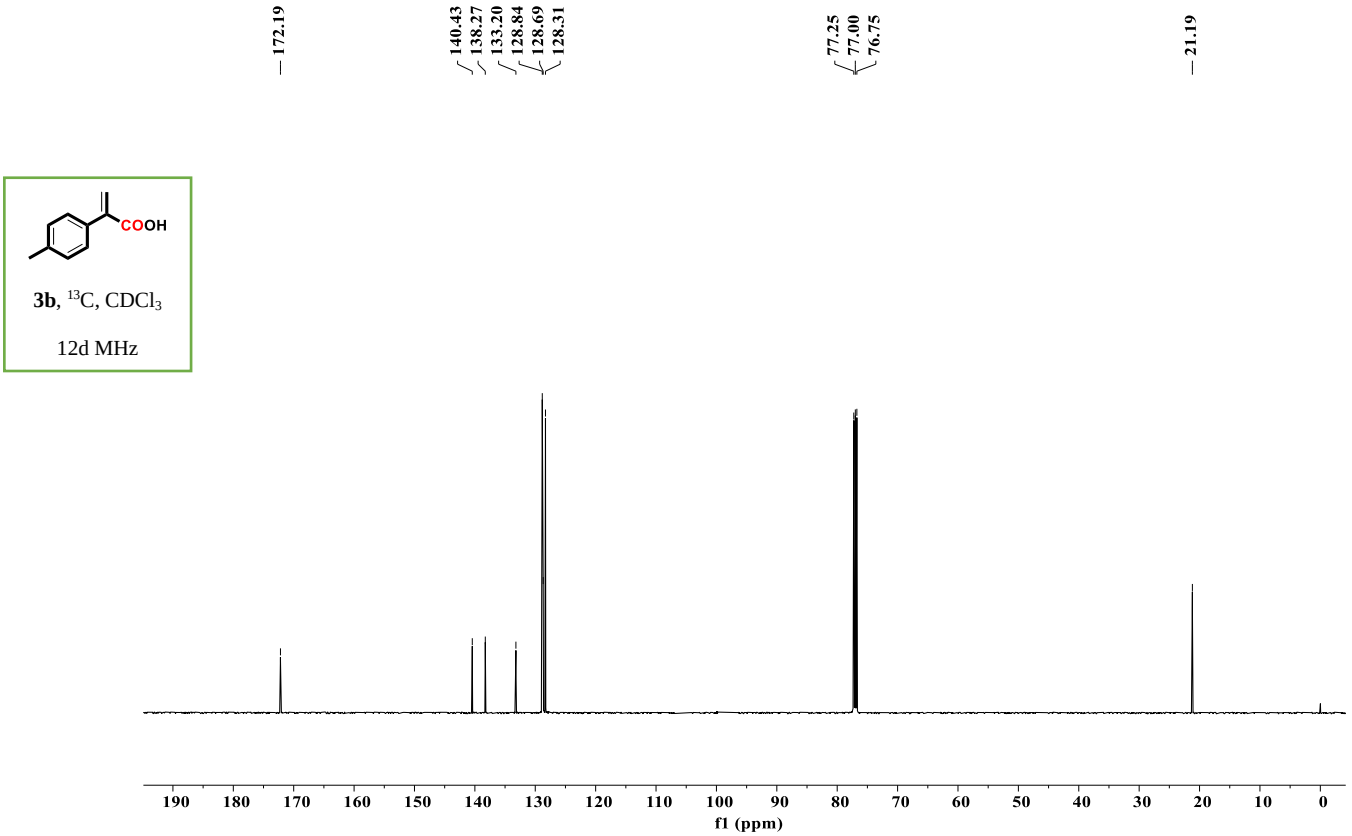
600 MHz

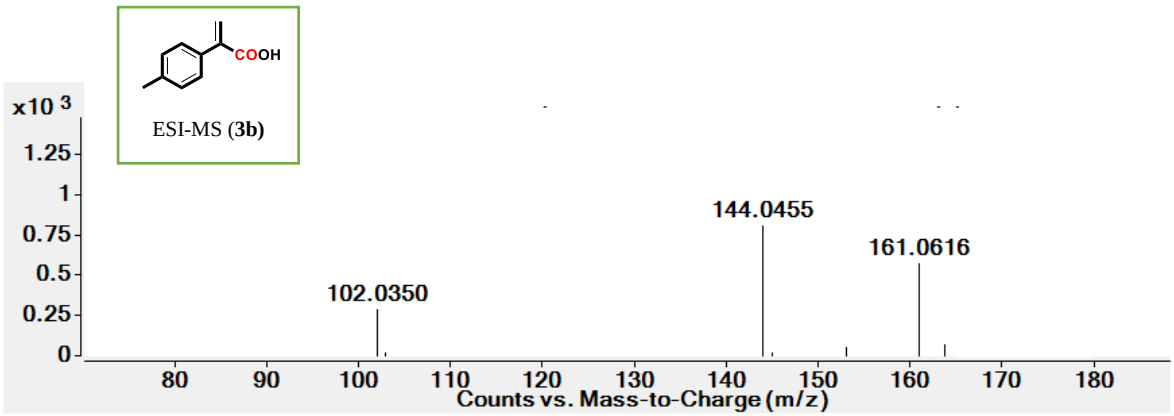


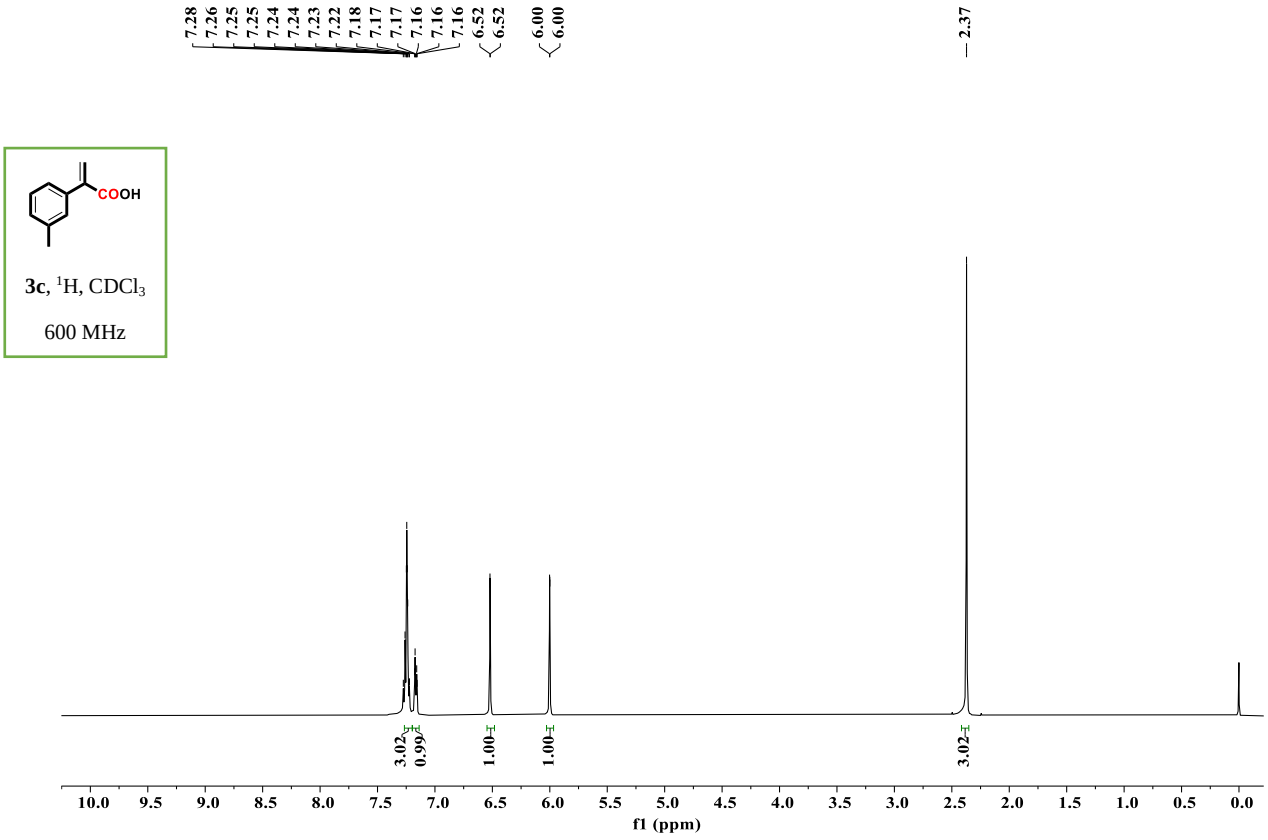

172.34
140.63
136.06
129.43
128.43
128.32
128.11
77.21
77.00
76.79
COOH
3a, 13C, CDCl3
151 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

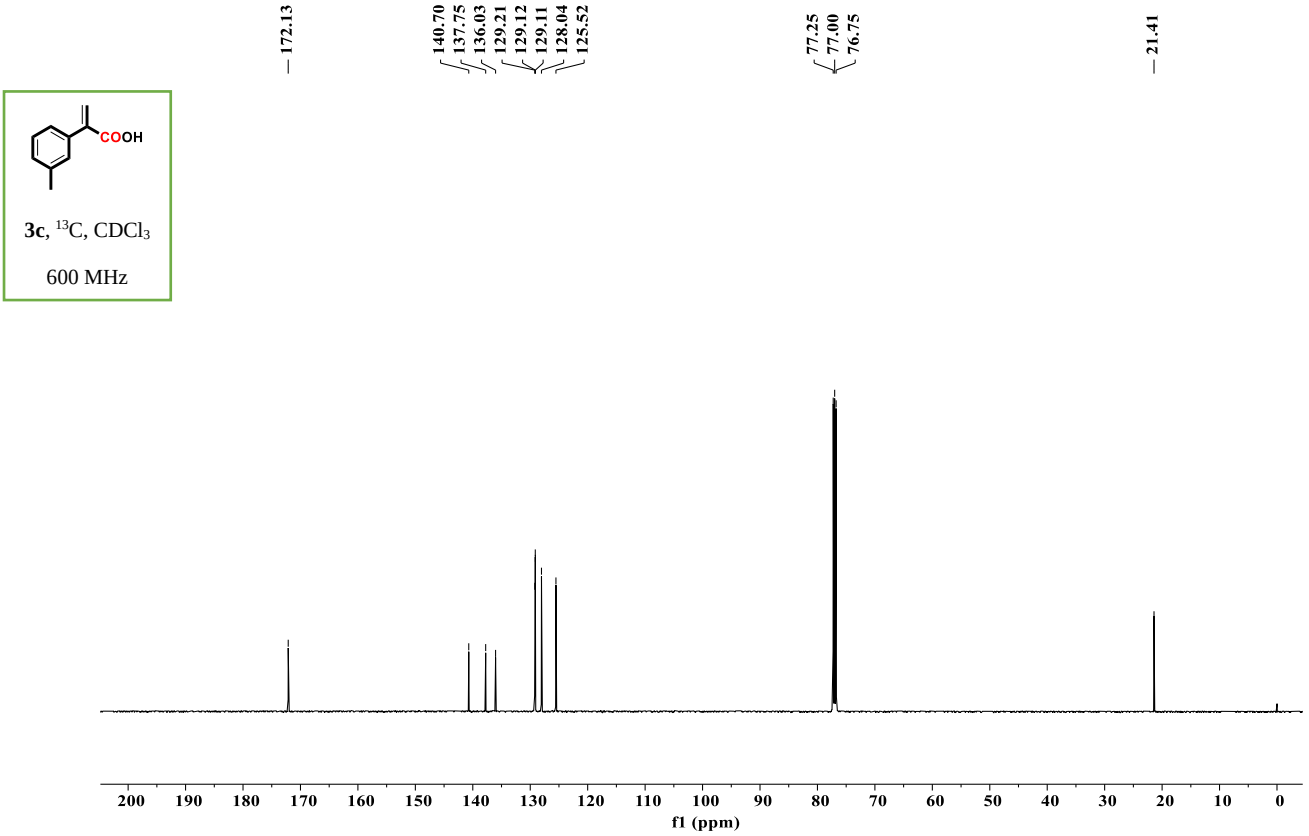

x10 2
6
5
4
3
2
1
0
COOH
ESI-MS (3a)
147.0452
103.0563
153.8680
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160
Counts vs. Mass-to-Charge (m/z)

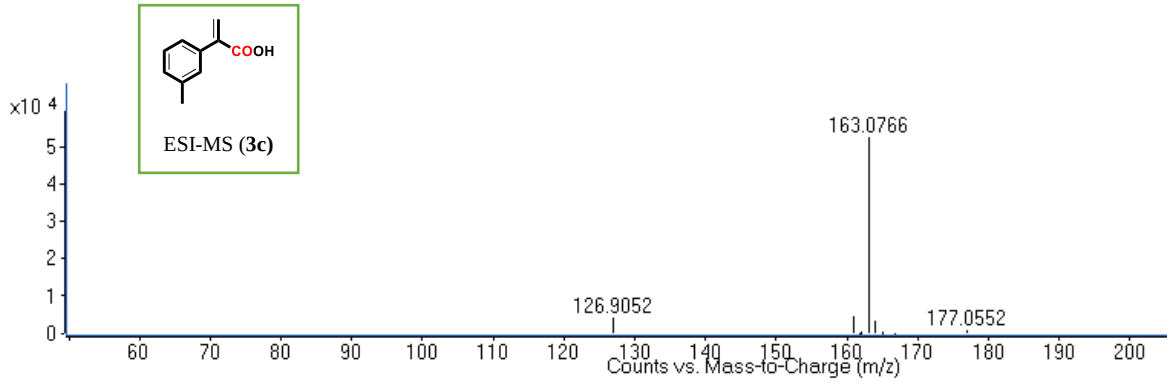

7.35
7.35
7.34
7.34
7.19
7.18
6.51
6.50
6.00
6.00
2.37
COOH
3b, 1H, CDCl3
600 MHz
2.02
2.01
1.01
1.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

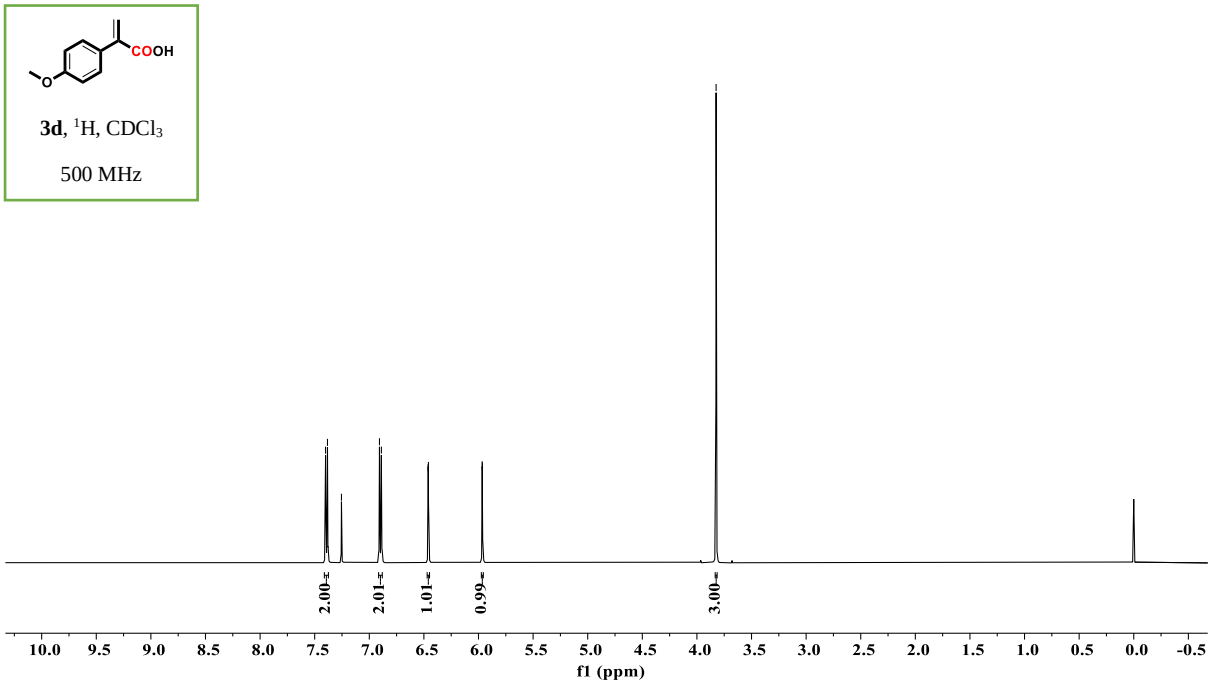

172.19
140.43
138.27
133.20
128.84
128.69
128.31
77.25
77.00
76.75
21.19
COOH
3b, 13C, CDCl3
12d MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


COOH
ESI-MS (3b)
x10 3
1.25
1
0.75
0.5
0.25
0
144.0455
161.0616
102.0350
80
90
100
110
120
130
140
150
160
170
180
Counts vs. Mass-to-Charge (m/z)


7.28
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.18
7.17
7.17
7.16
7.16
7.16
6.52
6.52
6.00
6.00
2.37
COOH
3c, 1H, CDCl3
600 MHz
3.02
0.99
1.00
1.00
3.02
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
f1 (ppm)

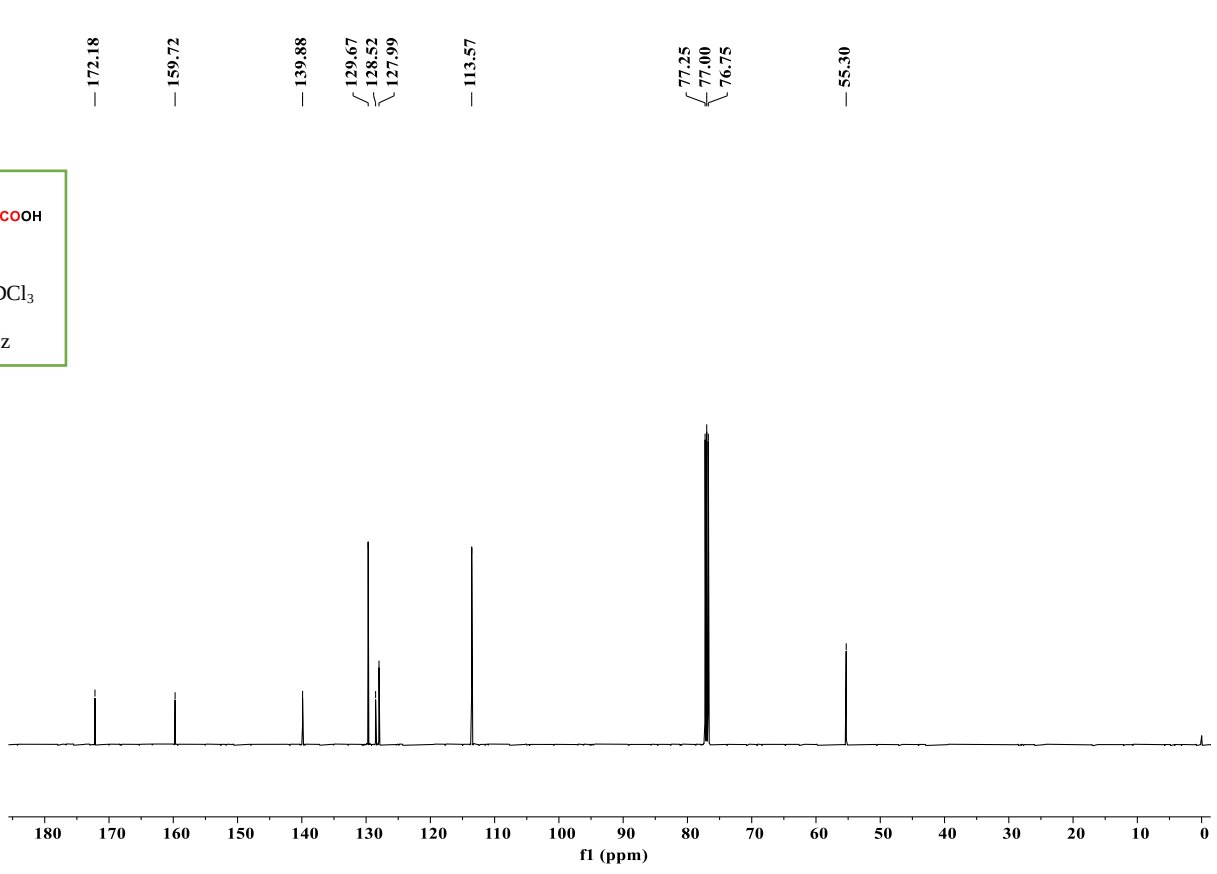

172.13
140.70
137.75
136.03
129.21
129.12
129.11
128.04
125.52
77.25
77.00
76.75
21.41
COOH
3c, 13C, CDCl3
600 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


COOH
ESI-MS (3c)
x10 4
5
4
3
2
1
0
163.0766
126.9052
177.0552
60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Counts vs. Mass-to-Charge (m/z)



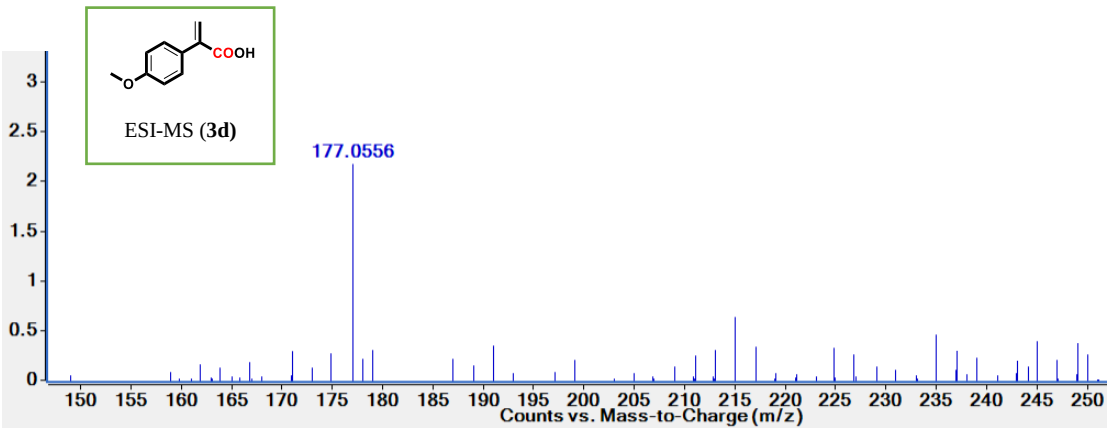
3d, ^{1}H, $CDCl_3$

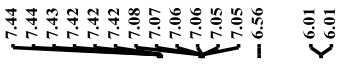
500 MHz

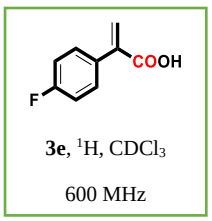


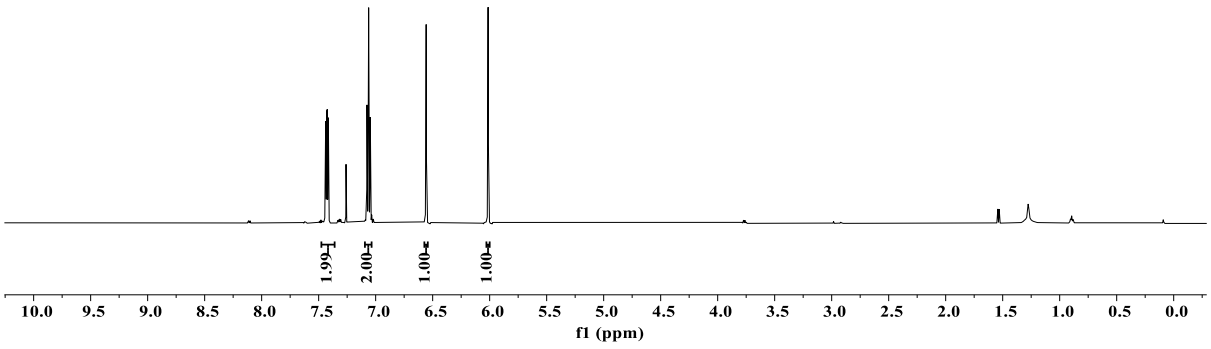
3d, ^{13}C, $CDCl_3$

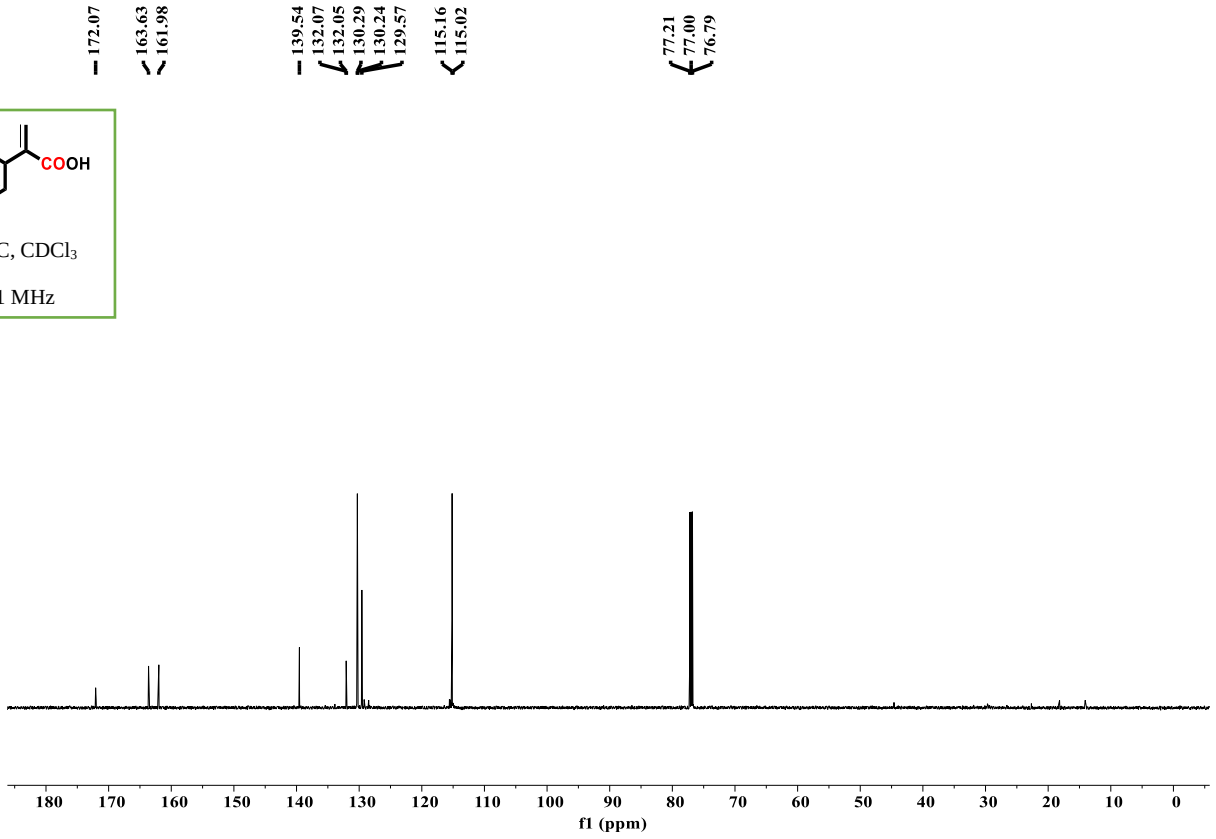
126 MHz


COOH
O
ESI-MS (3d)
177.0556
3
2.5
2
1.5
1
0.5
0
150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250
Counts vs. Mass-to-Charge (m/z)


7.44
7.44
7.43
7.42
7.42
7.42
7.08
7.07
7.06
7.06
7.05
7.05
6.56
6.01
6.01

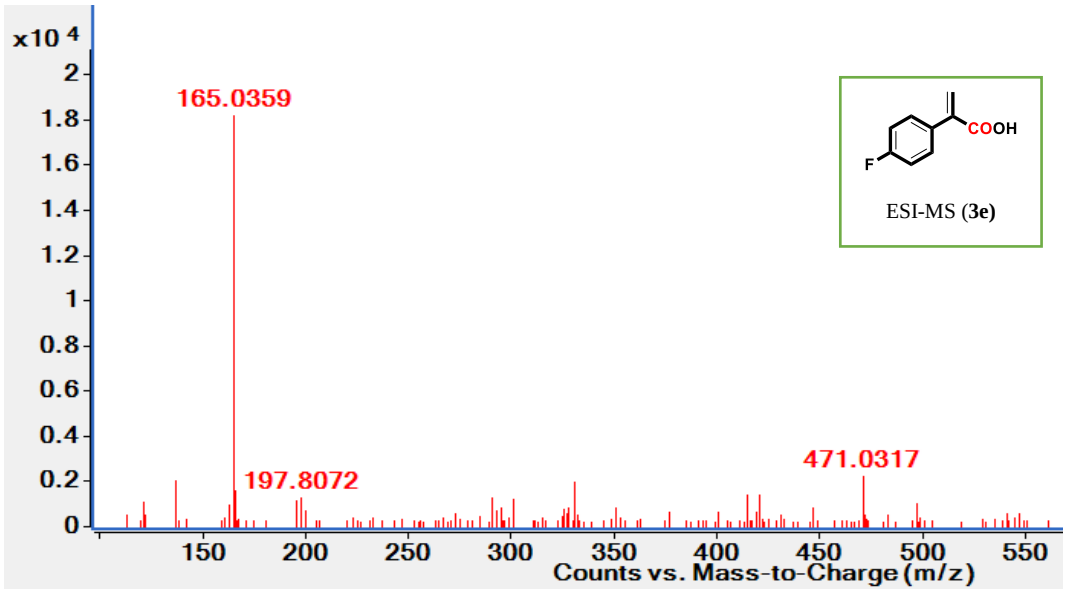

COOH
F
3e, 1H, CDCl3
600 MHz


1.99
2.00
1.00
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 0.5 0.0
f1 (ppm)

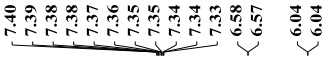


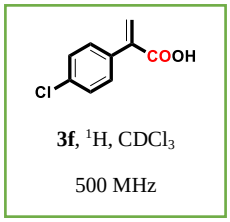
3e, ^{13}C, $CDCl_3$

151 MHz



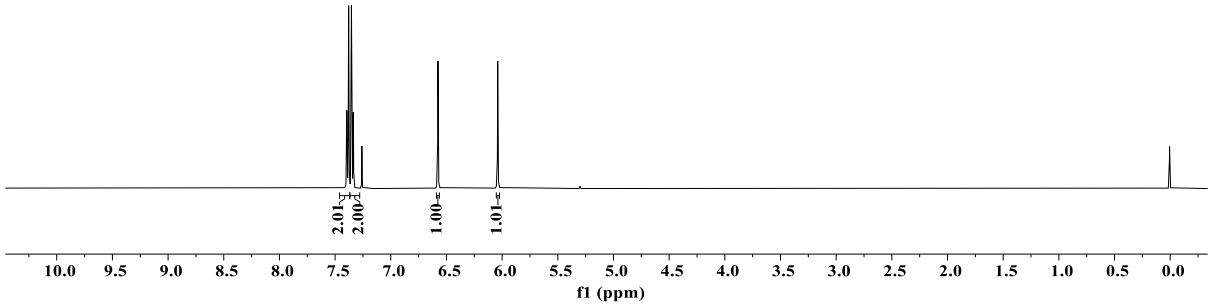
ESI-MS (**3e**)

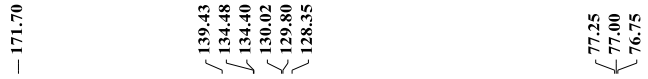


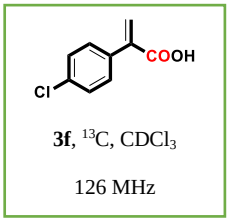


3f, ^{1}H, $CDCl_3$

500 MHz

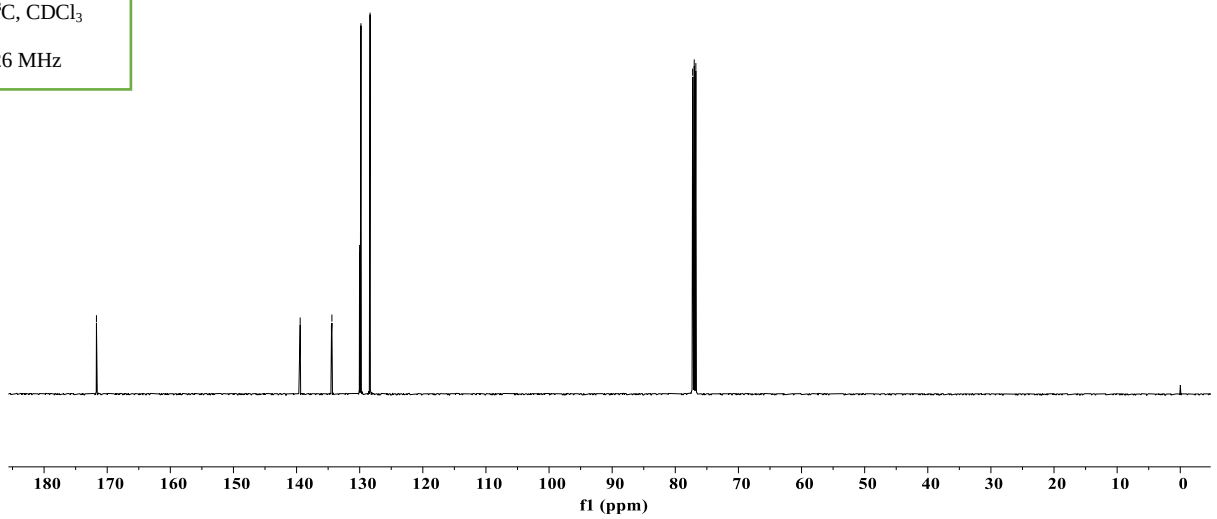


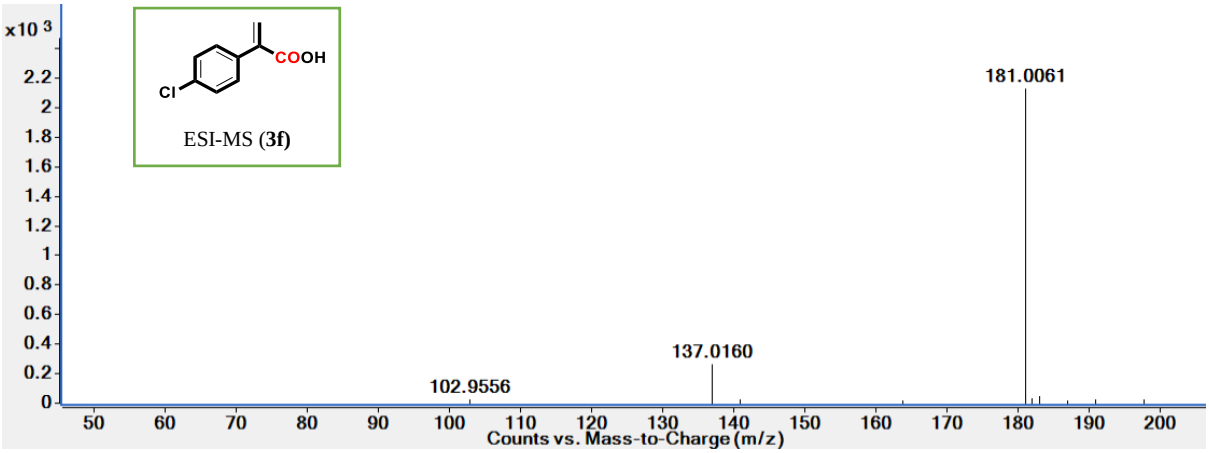




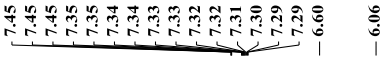
3f, ^{13}C, $CDCl_3$

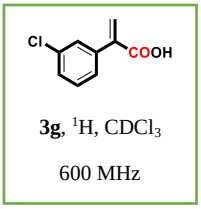
126 MHz





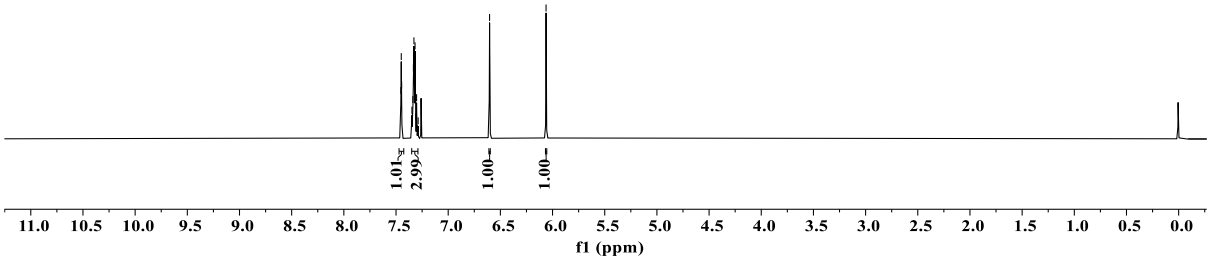
ESI-MS (**3f**)

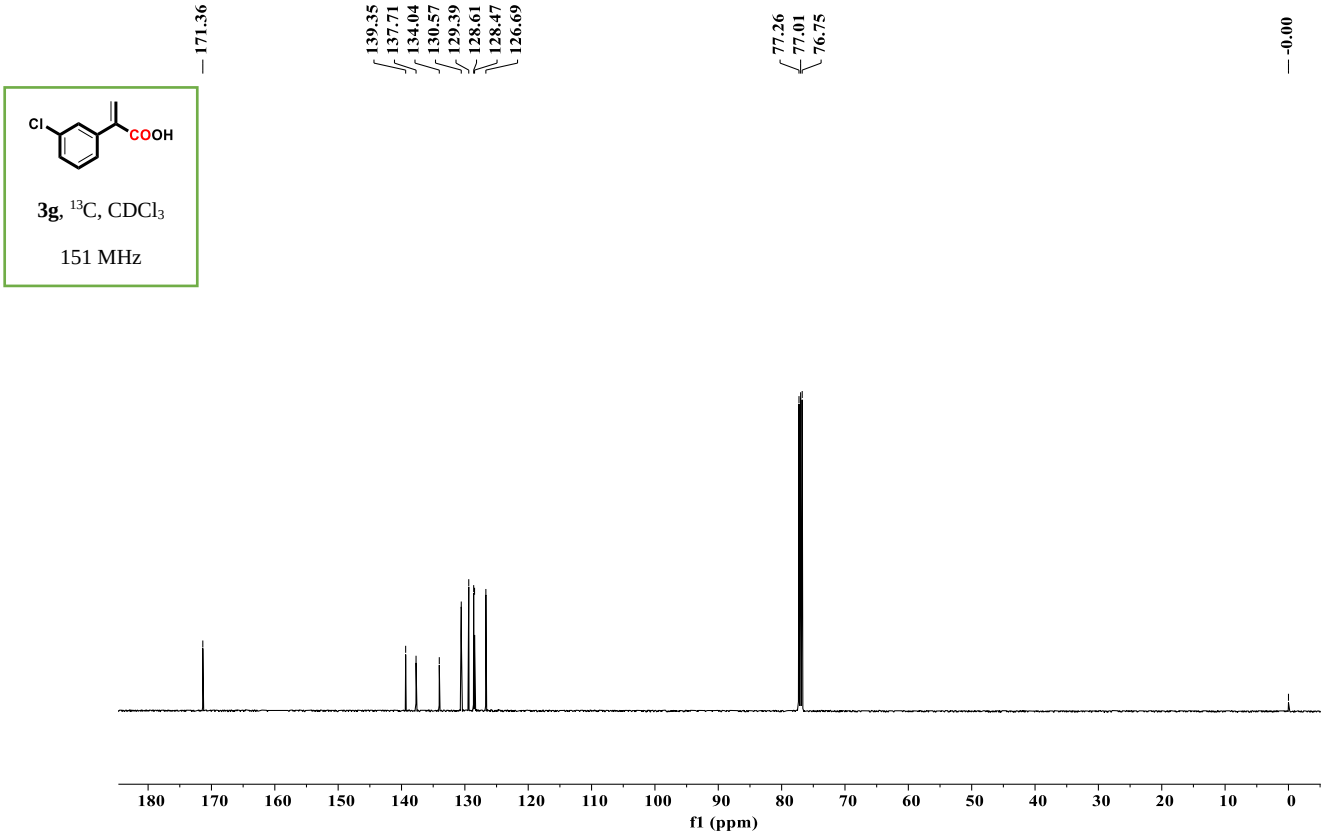


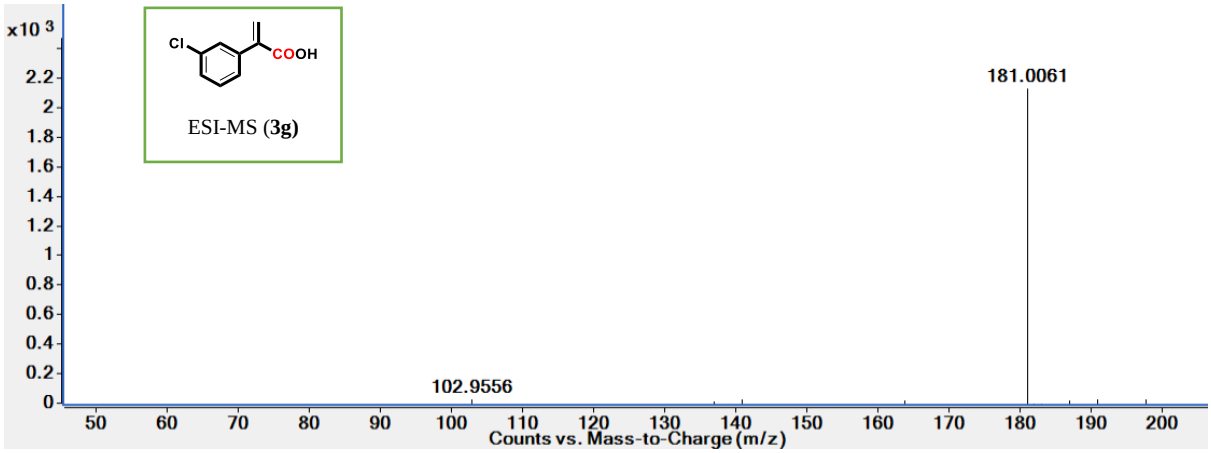


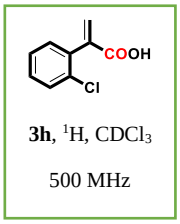
3g, ^{1}H, $CDCl_3$

600 MHz



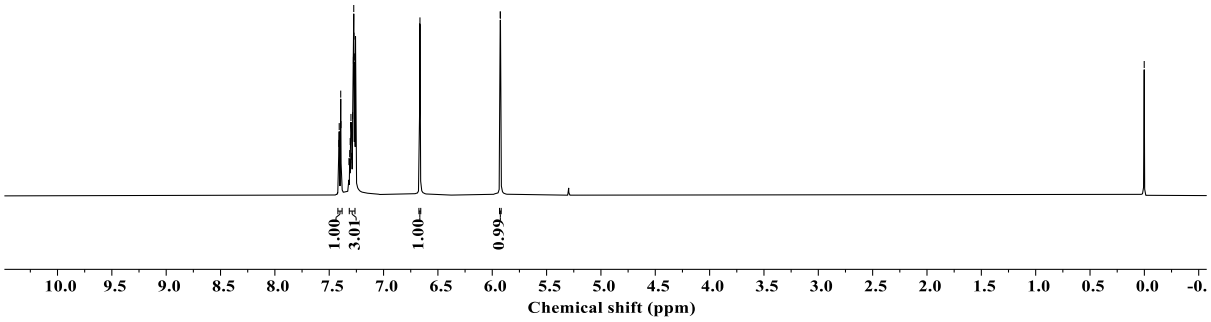

171.36
139.35
137.71
134.04
130.57
129.39
128.61
128.47
126.69
77.26
77.01
76.75
-0.00
Cl
COOH
3g, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

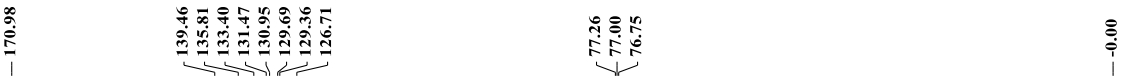

x10 3
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Cl
COOH
ESI-MS (3g)
181.0061
102.9556
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Counts vs. Mass-to-Charge (m/z)

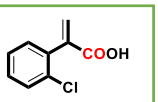


3h, ^{1}H, $CDCl_3$

500 MHz

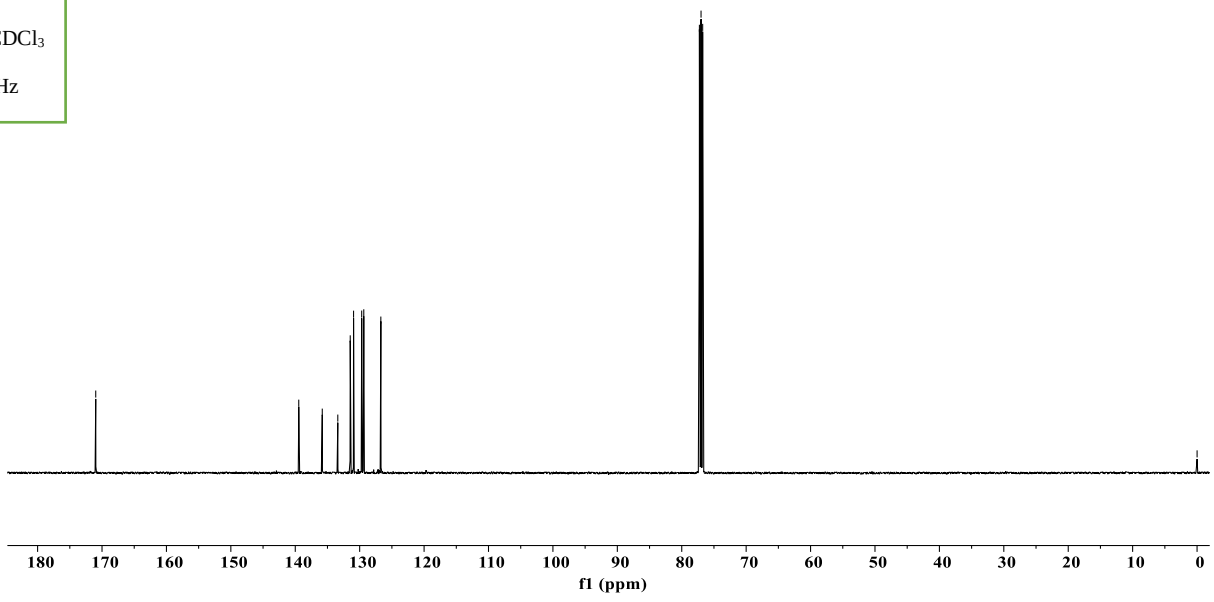


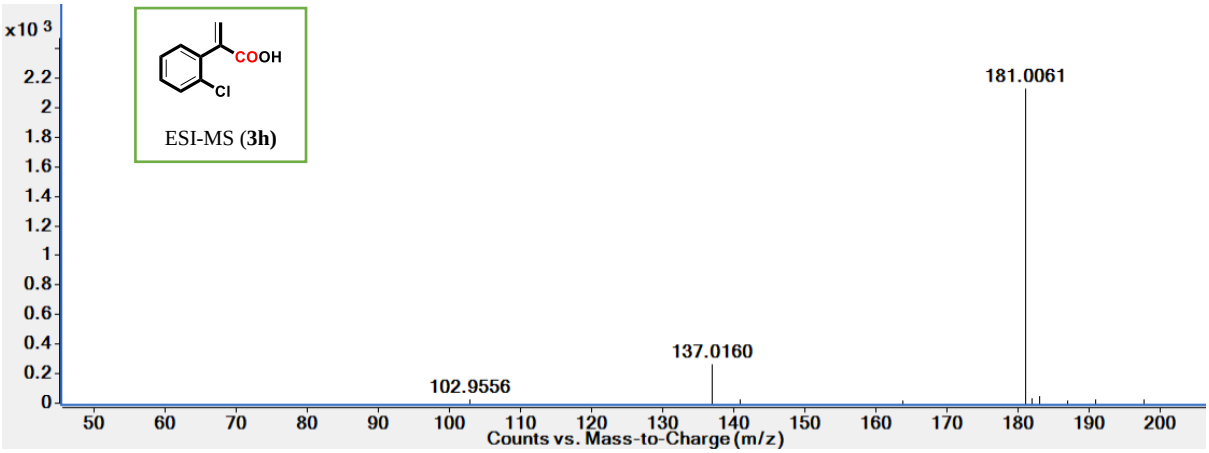


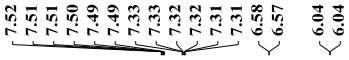


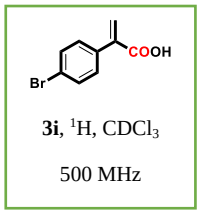
3h, ^{13}C, $CDCl_3$

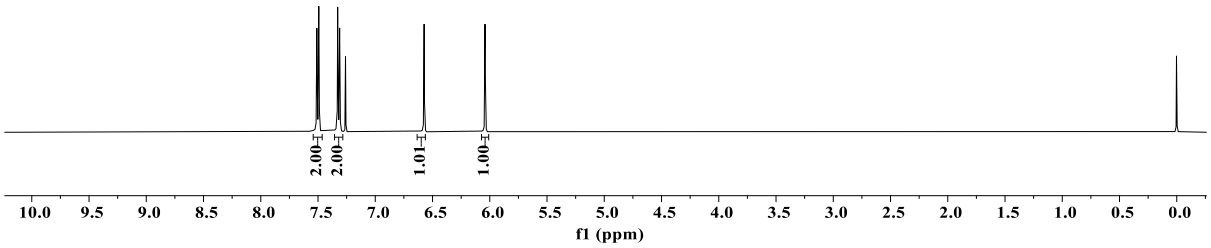
126MHz

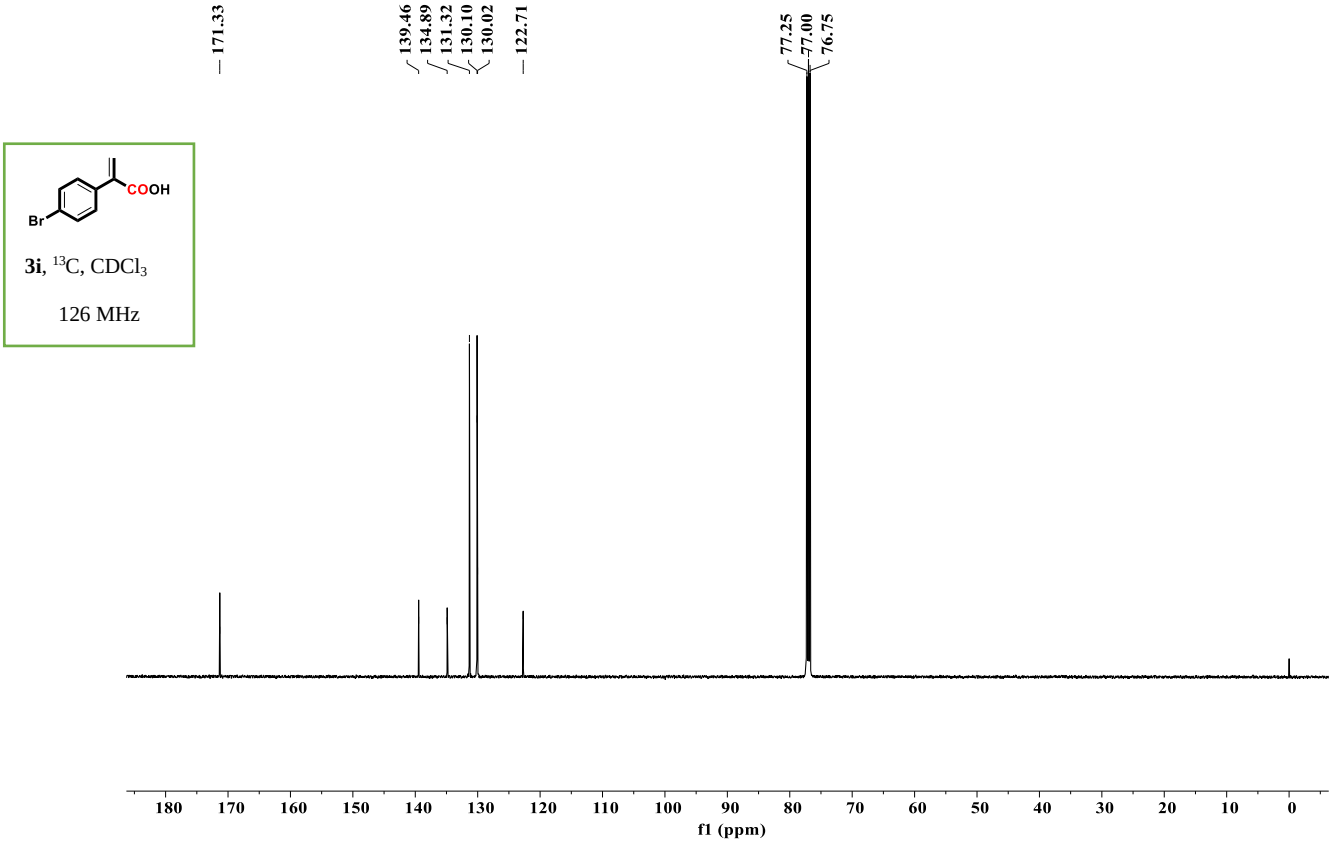


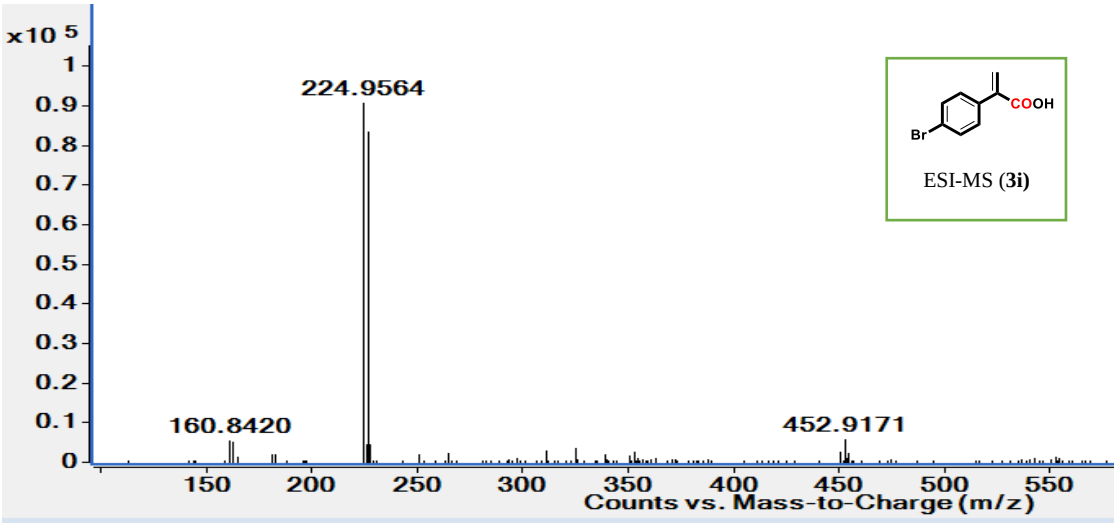

x10 3
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
COOH
Cl
ESI-MS (3h)
181.0061
137.0160
102.9556
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Counts vs. Mass-to-Charge (m/z)

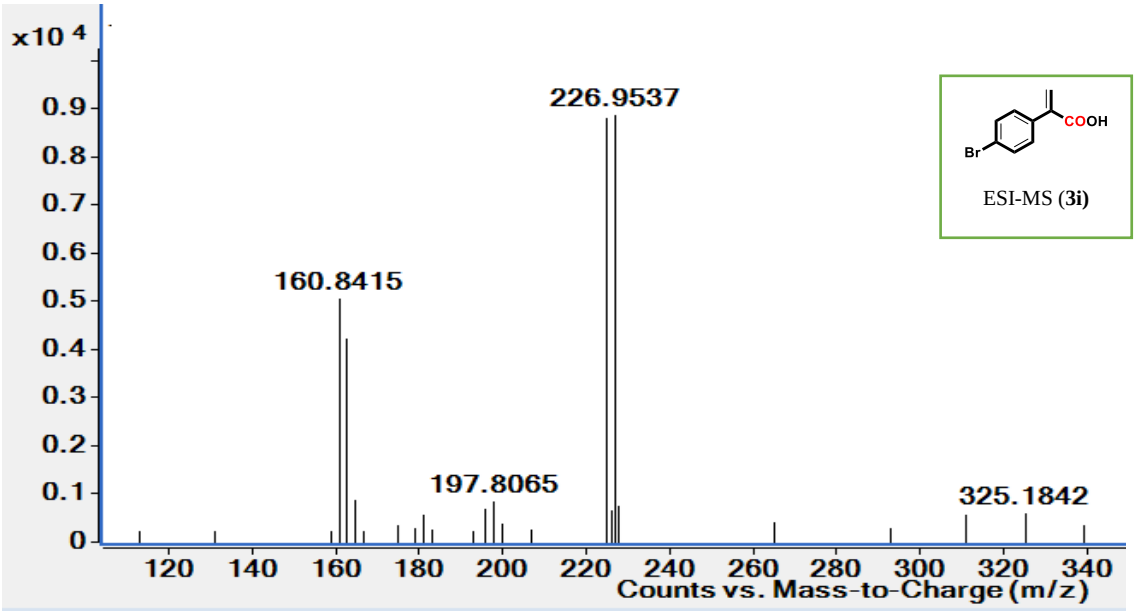

7.52
7.51
7.51
7.50
7.49
7.49
7.33
7.33
7.32
7.32
7.31
7.31
6.58
6.57
6.04
6.04


COOH
Br
3i, 1H, CDCl3
500 MHz

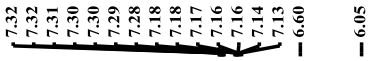

2.00
2.00
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

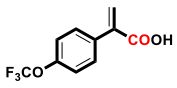

171.33
139.46
134.89
131.32
130.10
130.02
122.71
77.25
77.00
76.75
COOH
Br
3i, 13C, CDCl3
126 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 5
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
224.9564
160.8420
452.9171
150 200 250 300 350 400 450 500 550
Counts vs. Mass-to-Charge (m/z)
COOH
Br
ESI-MS (3i)



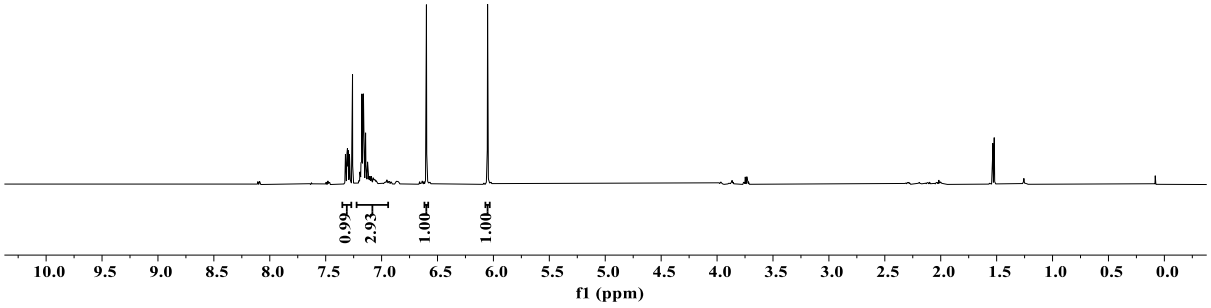
ESI-MS (**3i**)

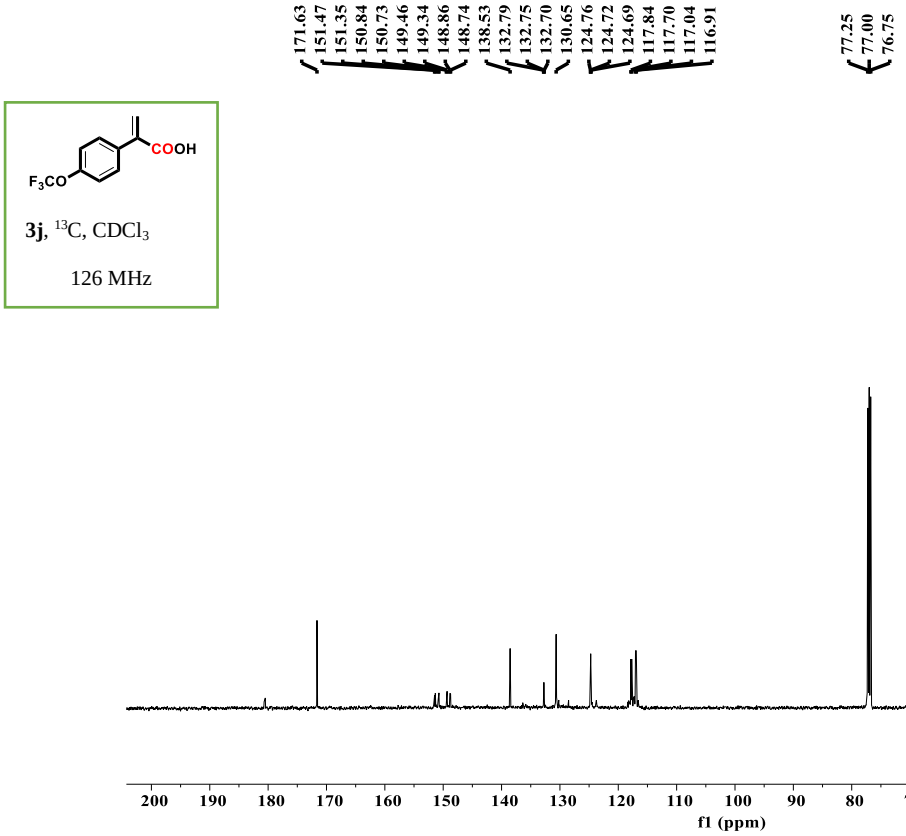


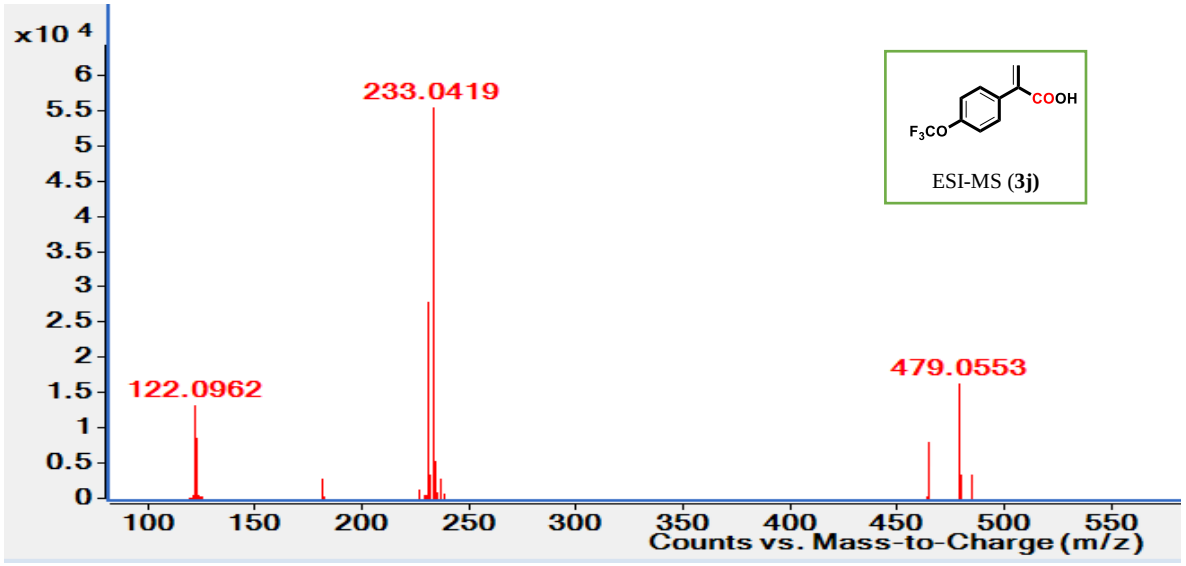


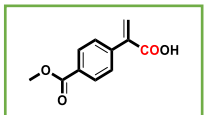
3j, ^{1}H, $CDCl_3$

600 MHz



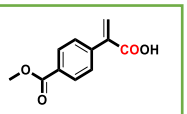

171.63
151.47
151.35
150.84
150.73
149.46
149.34
148.86
148.74
138.53
132.79
132.75
132.70
130.65
124.76
124.72
124.69
117.84
117.70
117.04
116.91
77.25
77.00
76.75
COOH
F3CO
3j, 13C, CDCl3
126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 4
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
233.0419
122.0962
479.0553
100 150 200 250 300 350 400 450 500 550
Counts vs. Mass-to-Charge (m/z)
COOH
F3CO
ESI-MS (3j)



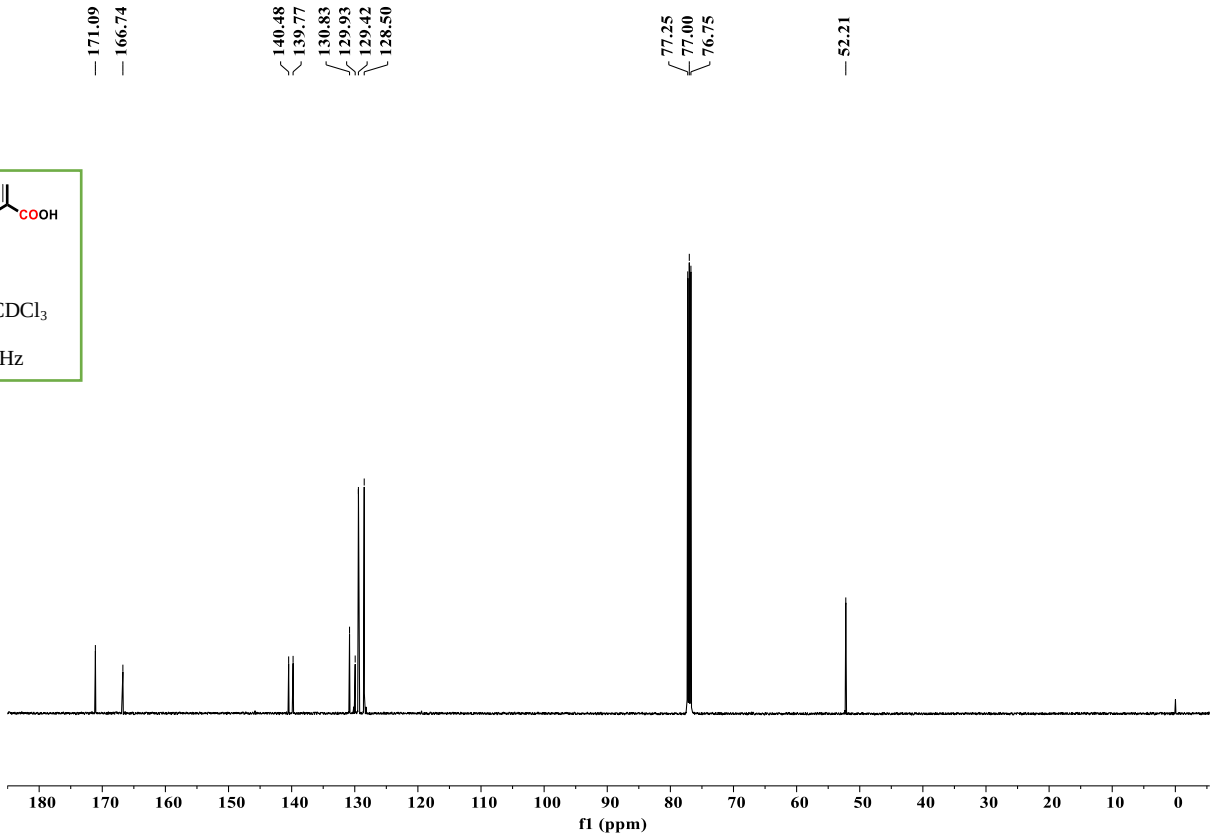
3k, ^{1}H, $CDCl_3$

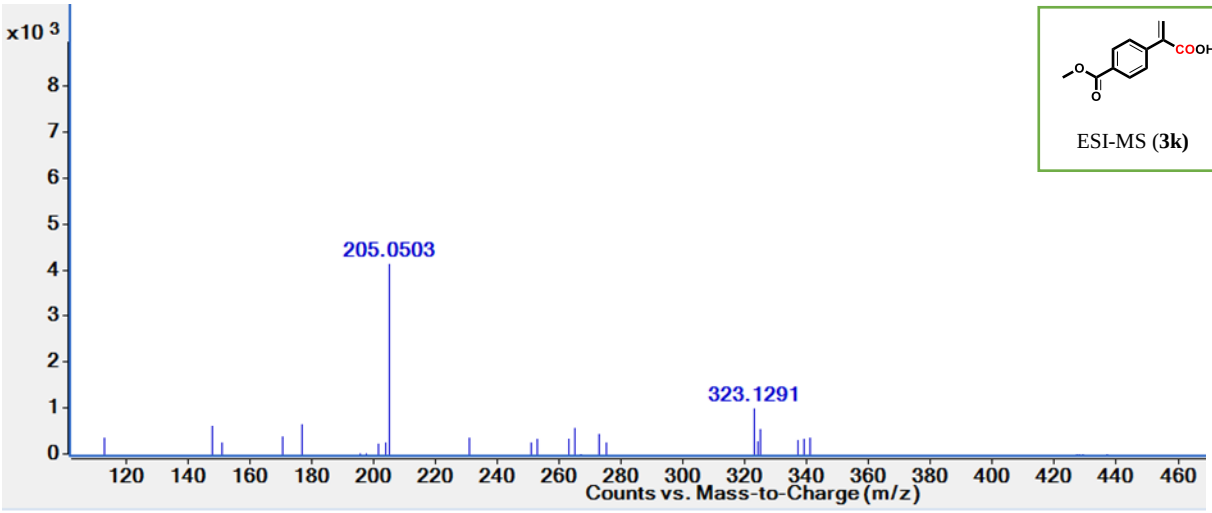
600 MHz



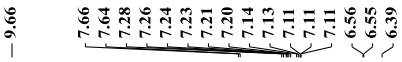
3k, ^{13}C, $CDCl_3$

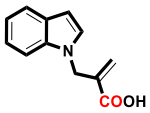
151 MHz





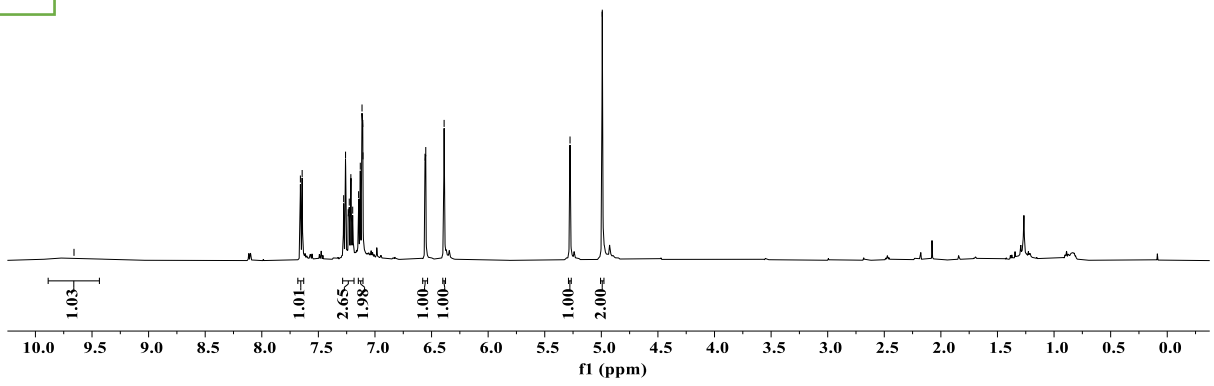
ESI-MS (**3k**)

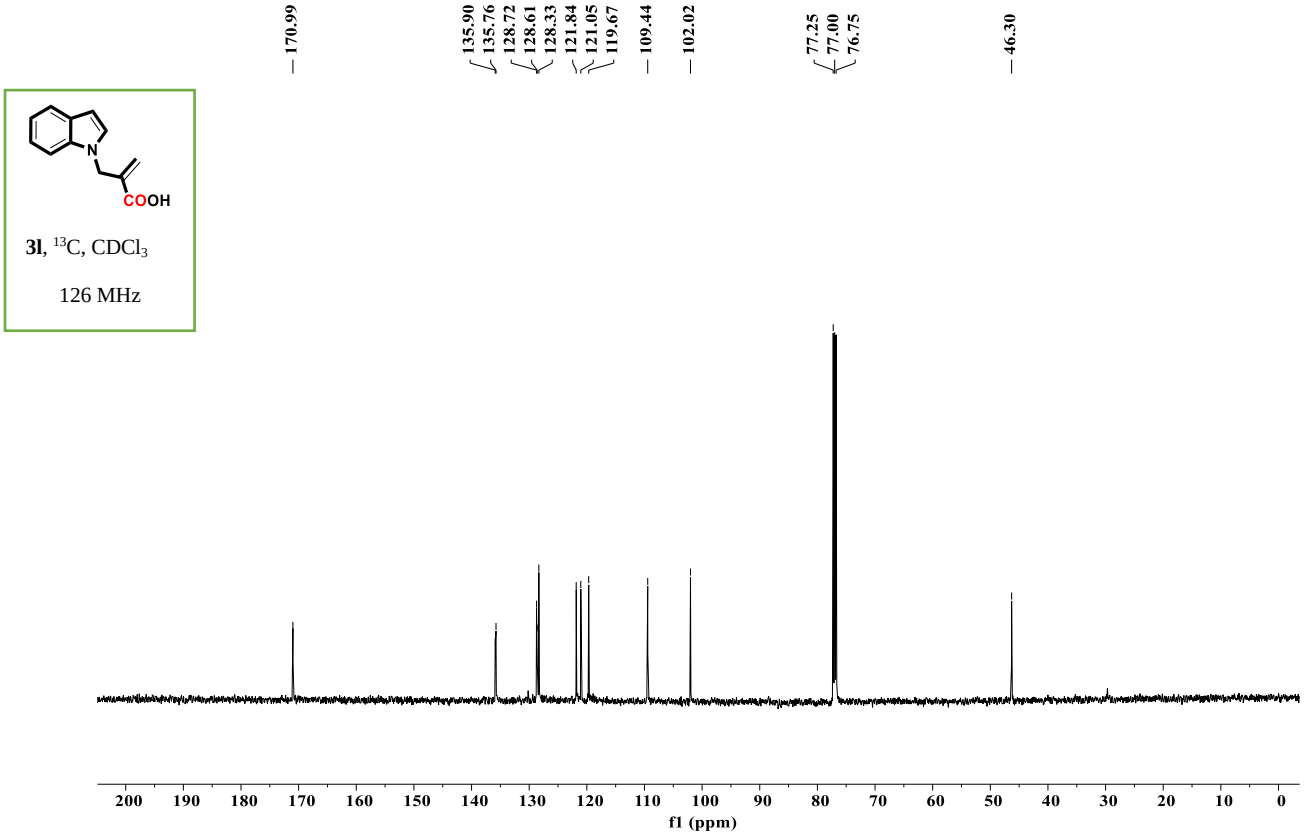


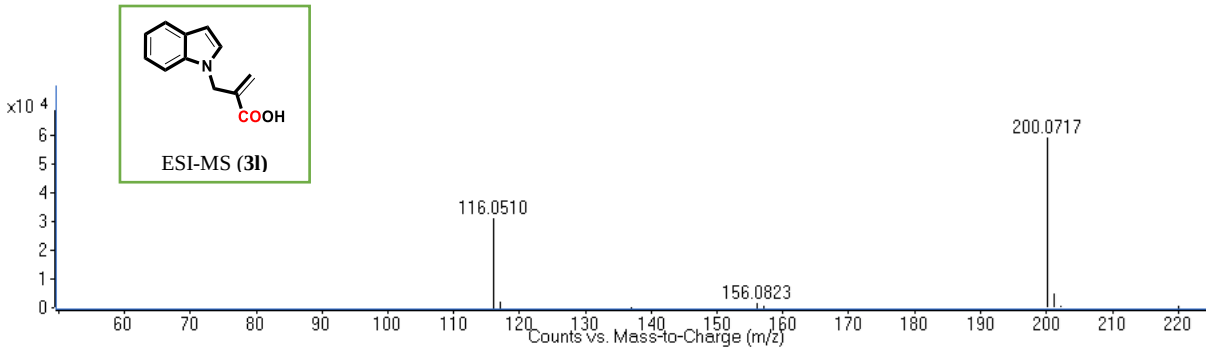


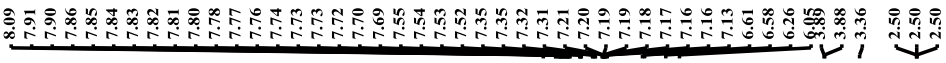
3l, ^{1}H, $CDCl_3$

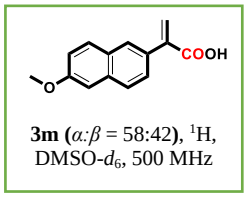
500 MHz



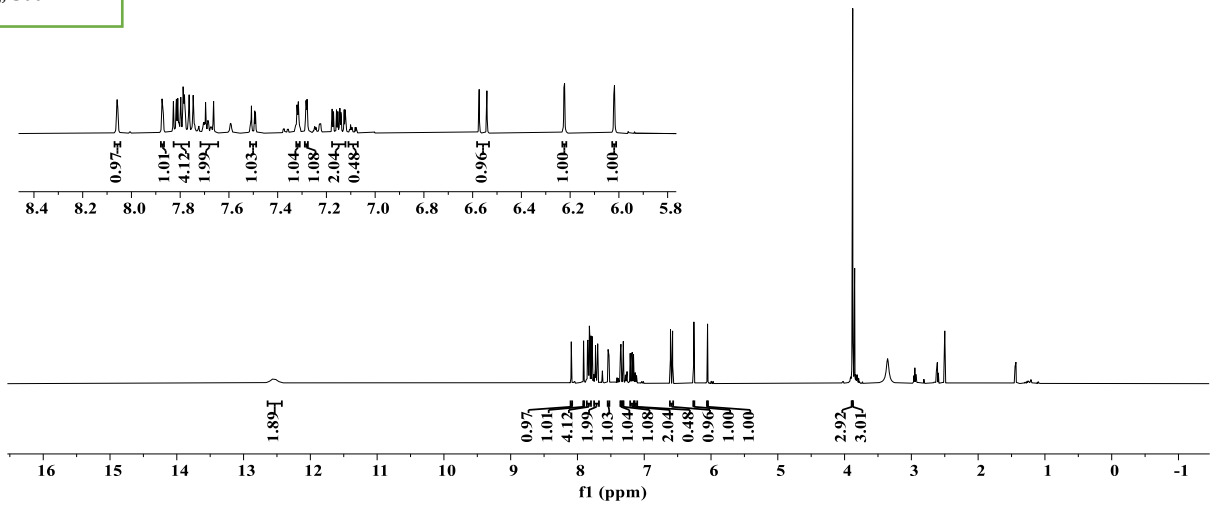

170.99
135.90
135.76
128.72
128.61
128.33
121.84
121.05
119.67
109.44
102.02
77.25
77.00
76.75
46.30
COOH
3l, 13C, CDCl3
126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

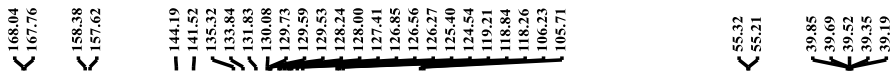

COOH
ESI-MS (3l)
x10 4
200.0717
116.0510
156.0823
Counts vs. Mass-to-Charge (m/z)

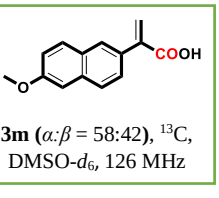




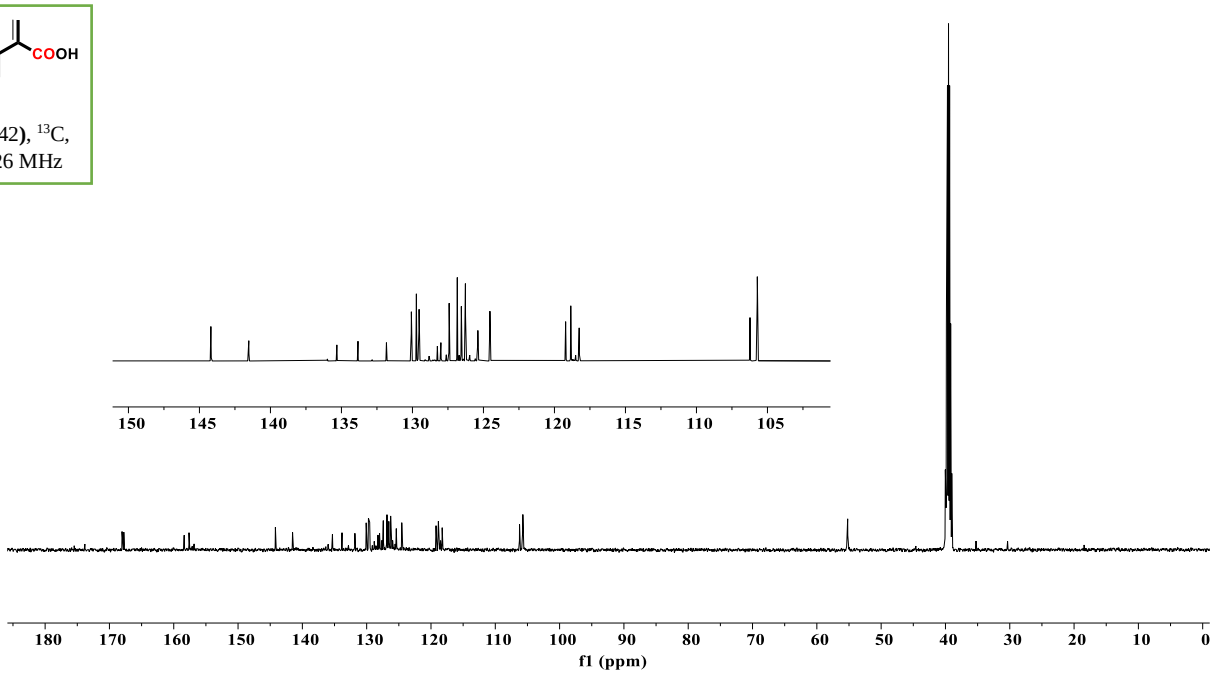
3m (*α*:*β* = 58:42), ^{1}H, DMSO-d_6, 500 MHz

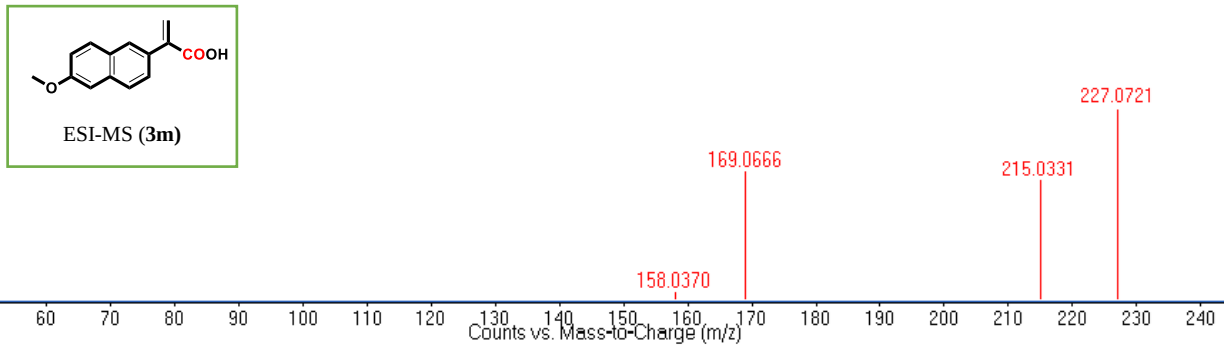


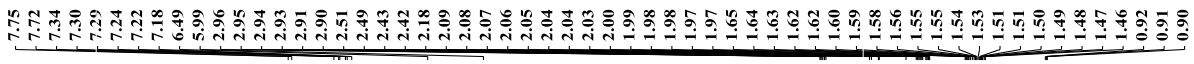


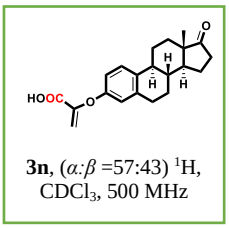


3m (*α*:*β* = 58:42), ^{13}C, DMSO-d_6, 126 MHz

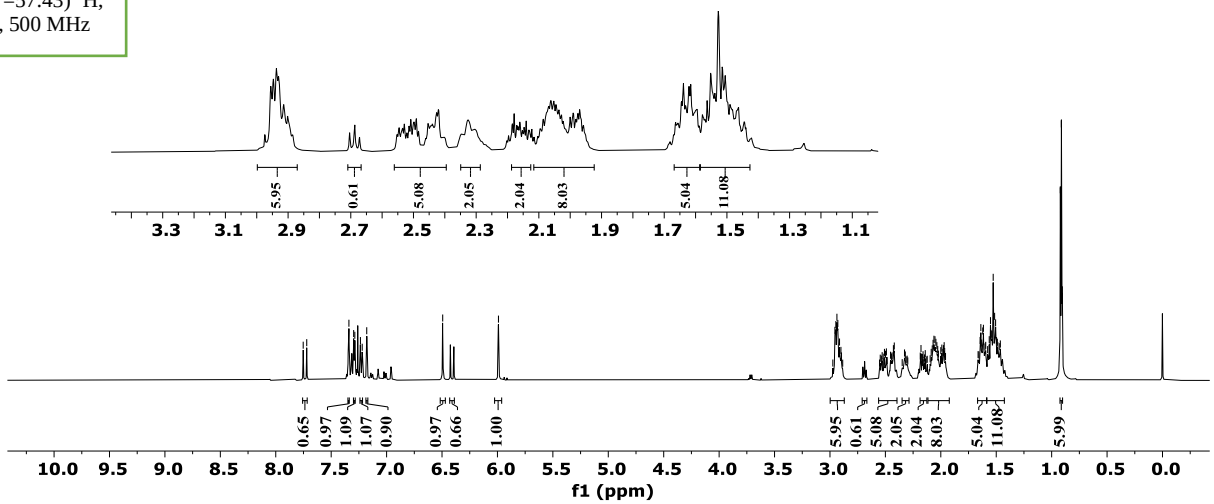


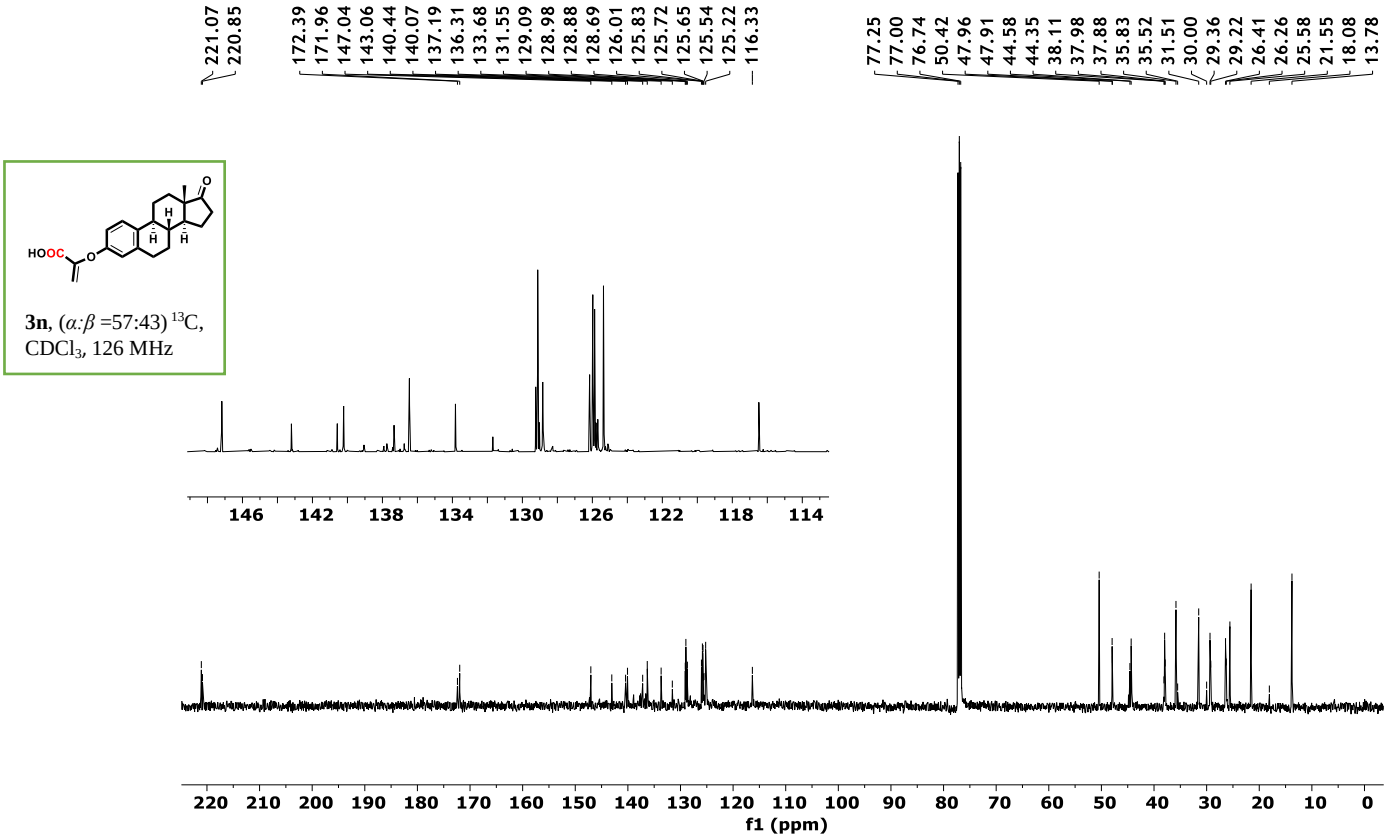


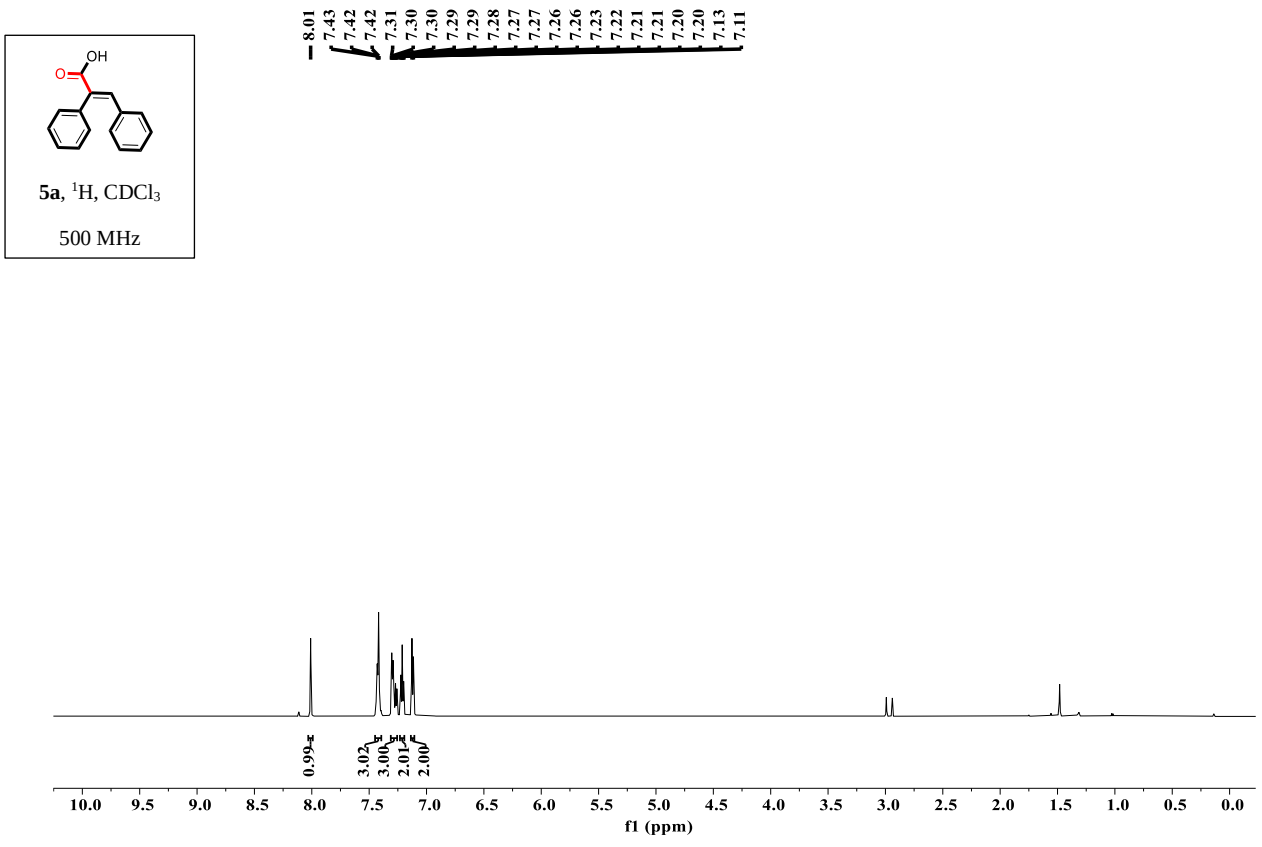


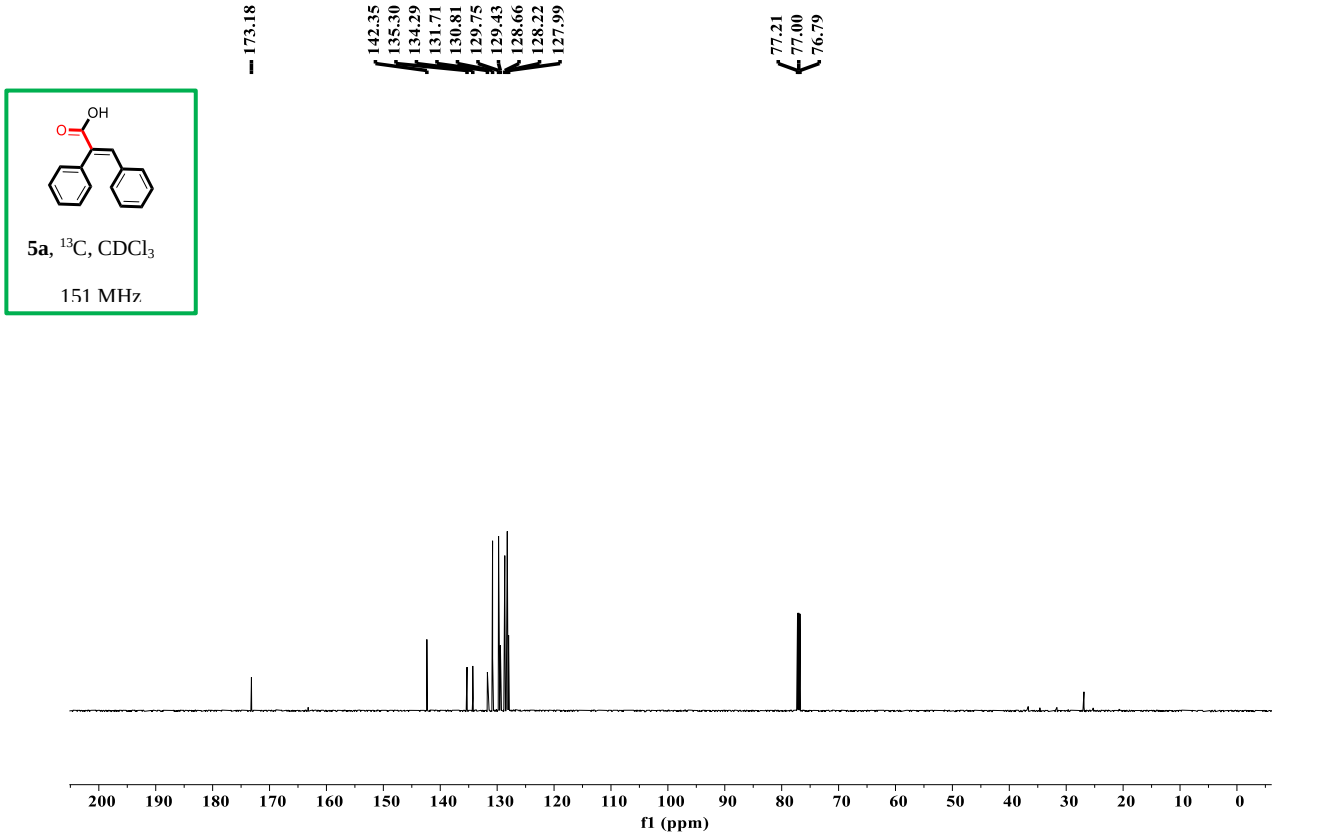


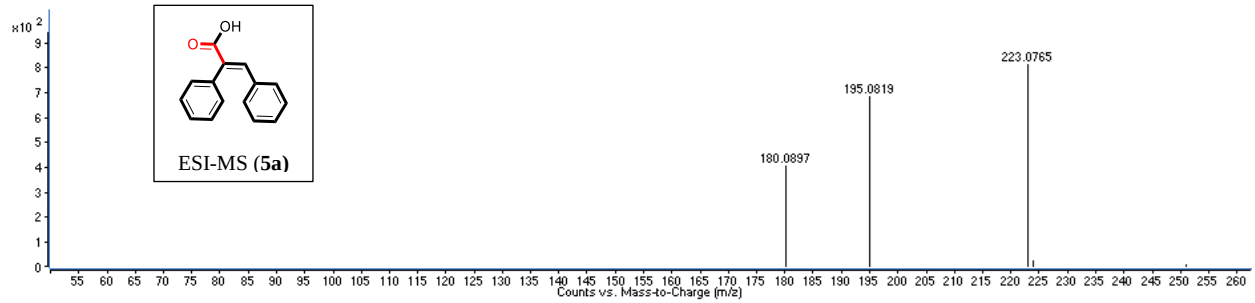
3n, (α:β =57:43) ^{1}H, $CDCl_3$, 500 MHz

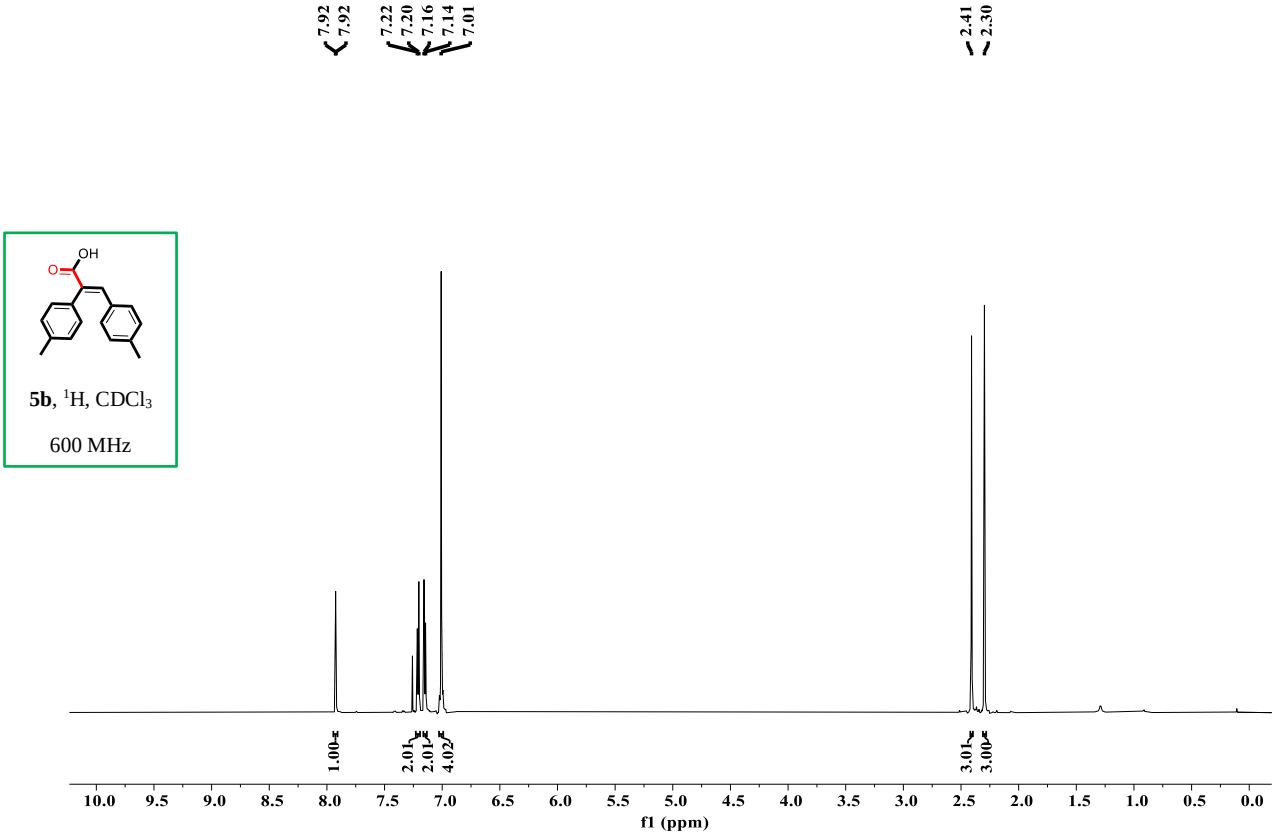


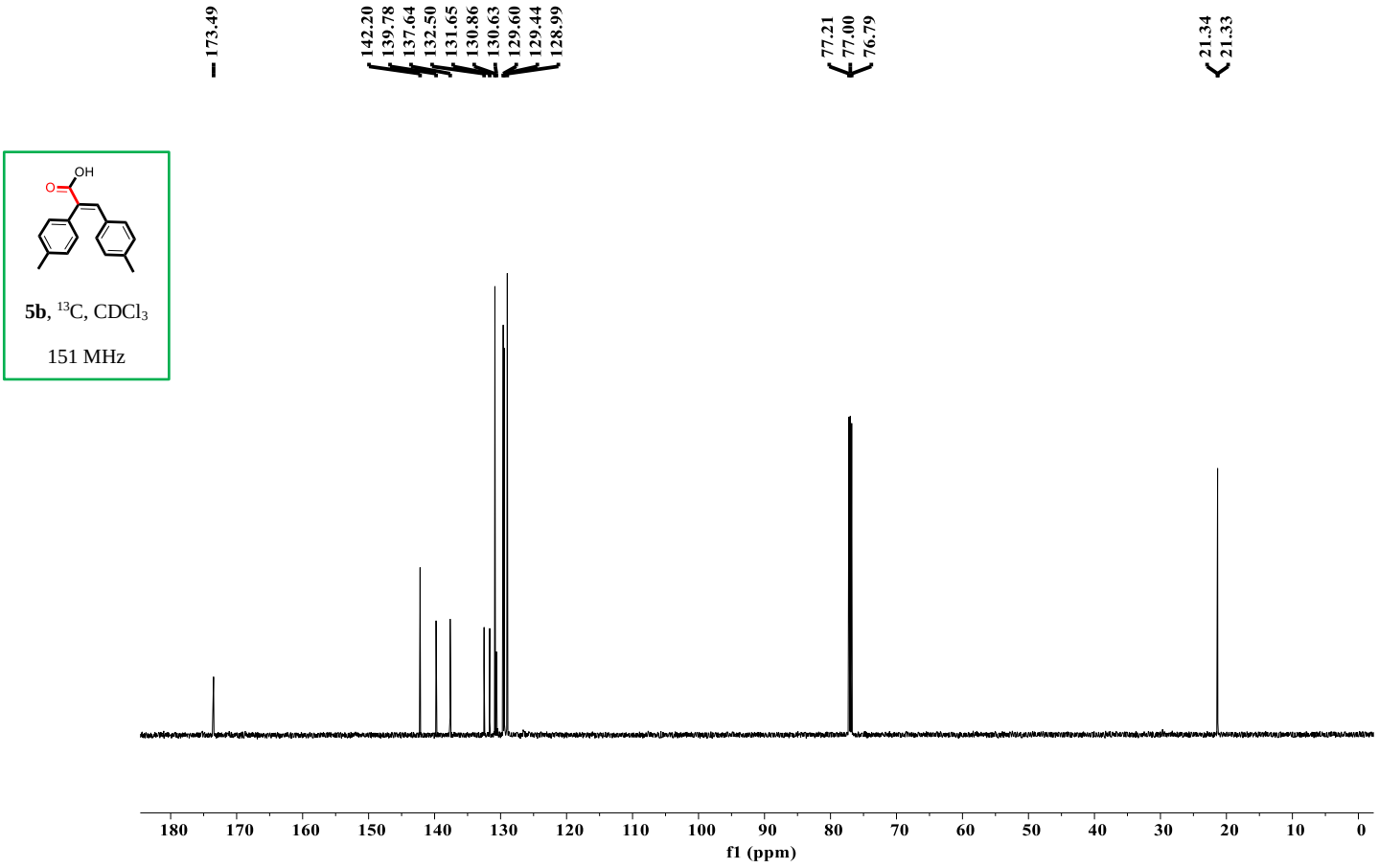

221.07
220.85
172.39
171.96
147.04
143.06
140.44
140.07
137.19
136.31
133.68
131.55
129.09
128.98
128.88
128.69
126.01
125.83
125.72
125.65
125.54
125.22
116.33
77.25
77.00
76.74
50.42
47.96
47.91
44.58
44.35
38.11
37.98
37.88
35.83
35.52
31.51
30.00
29.36
29.22
26.41
26.26
25.58
21.55
18.08
13.78
HOOC
O
H
H
H
O
3n, (α:β =57:43) 13C, CDCl3, 126 MHz
146
142
138
134
130
126
122
118
114
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

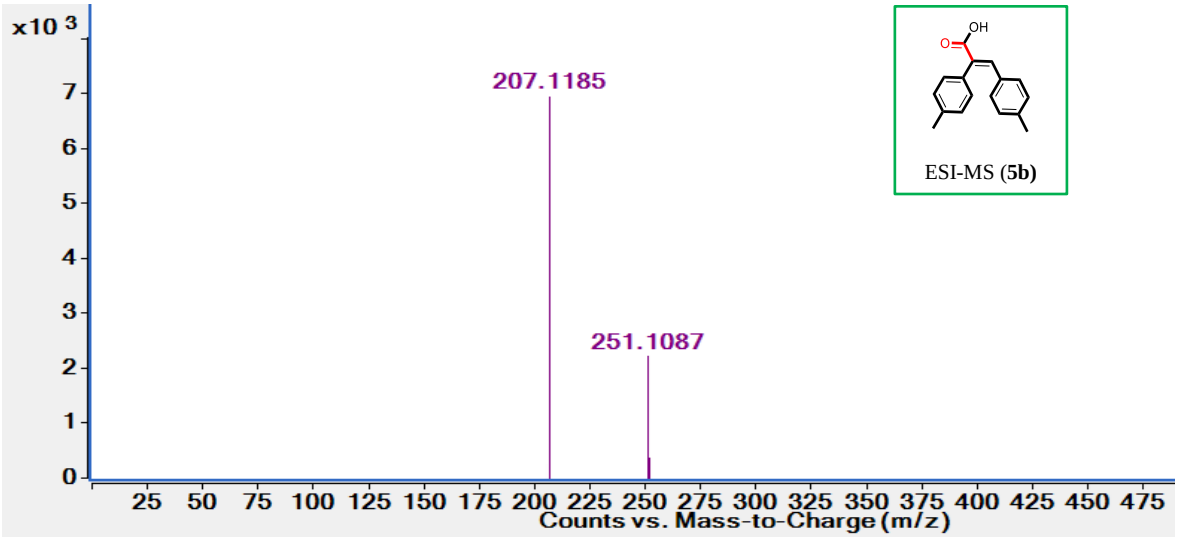

8.01
7.43
7.42
7.42
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.23
7.22
7.21
7.21
7.20
7.20
7.13
7.11
OH
O
5a, 1H, CDCl3
500 MHz
0.99
3.02
3.00
2.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.18
142.35
135.30
134.29
131.71
130.81
129.75
129.43
128.66
128.22
127.99
77.21
77.00
76.79
OH
O
5a, 13C, CDCl3
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

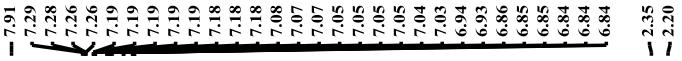

x10 2
OH
O
ESI-MS (5a)
180.0897
195.0819
223.0765
Counts vs. Mass-to-Charge (m/z)

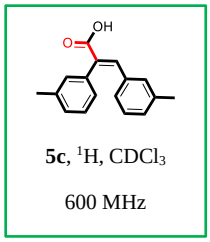

7.92
7.92
7.22
7.20
7.16
7.14
7.01
2.41
2.30
OH
O
5b, 1H, CDCl3
600 MHz
1.00
2.01
2.01
4.02
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.49
142.20
139.78
137.64
132.50
131.65
130.86
130.63
129.60
129.44
128.99
77.21
77.00
76.79
21.34
21.33
OH
O
5b, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



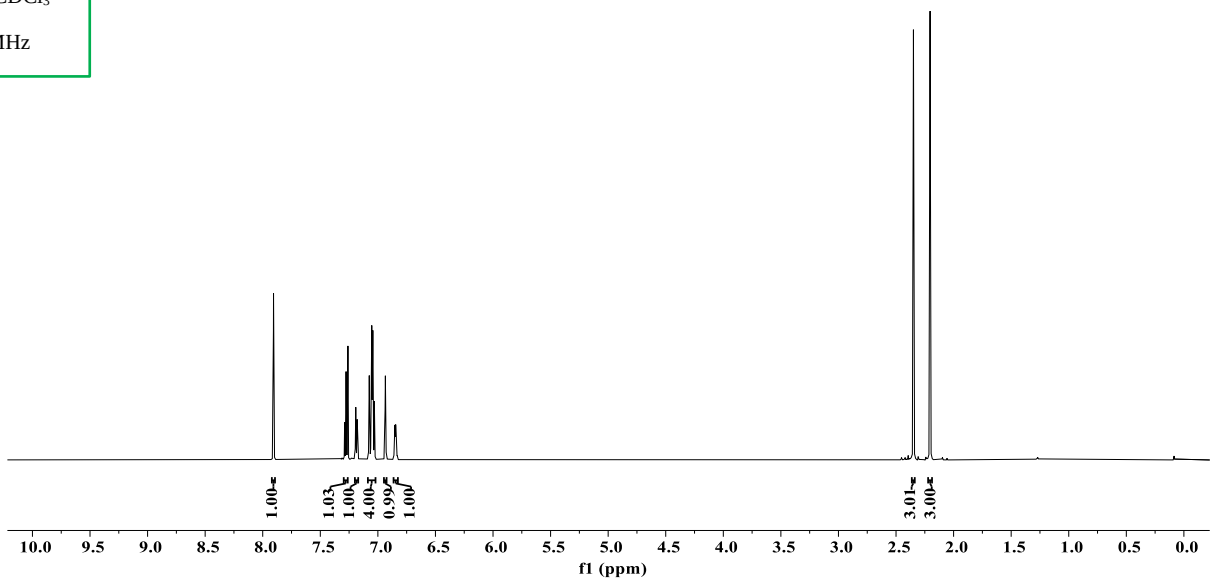
ESI-MS (**5b**)

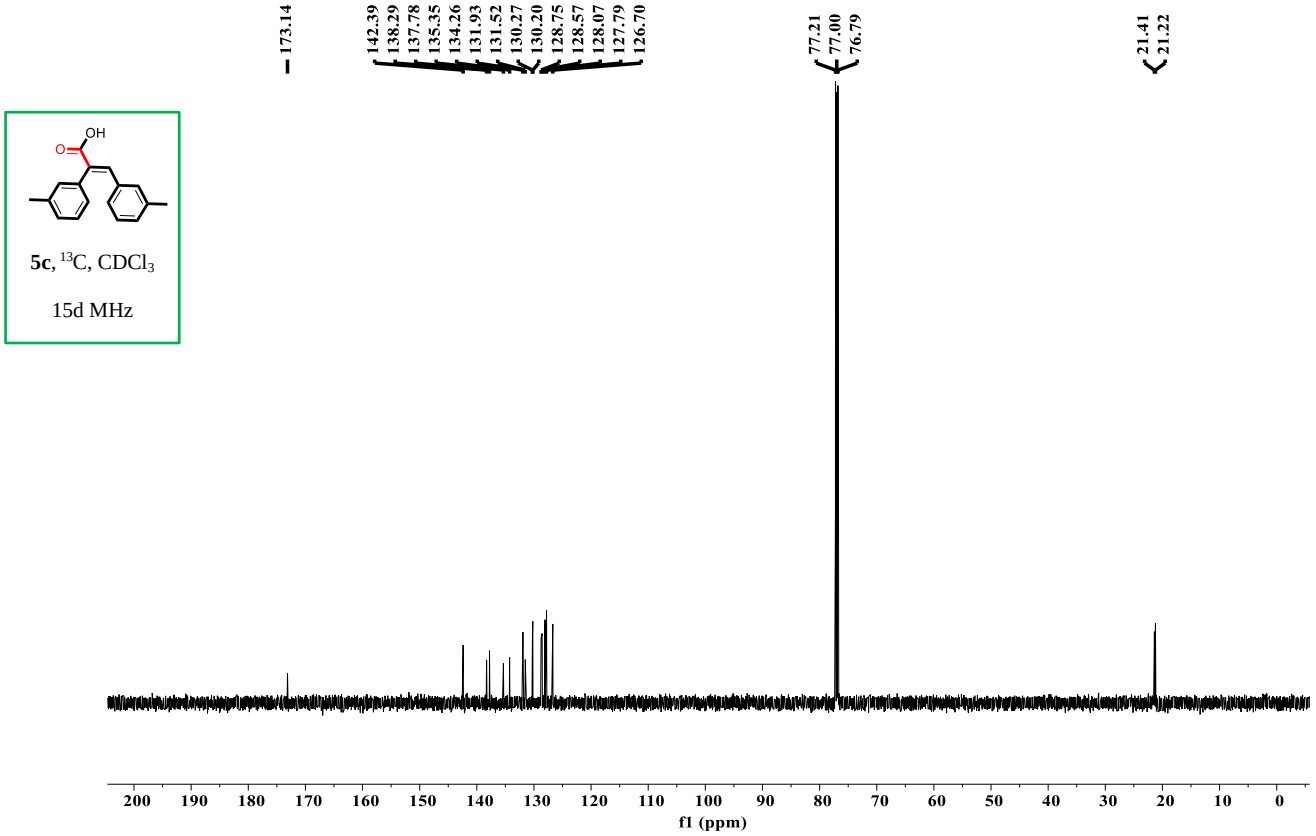


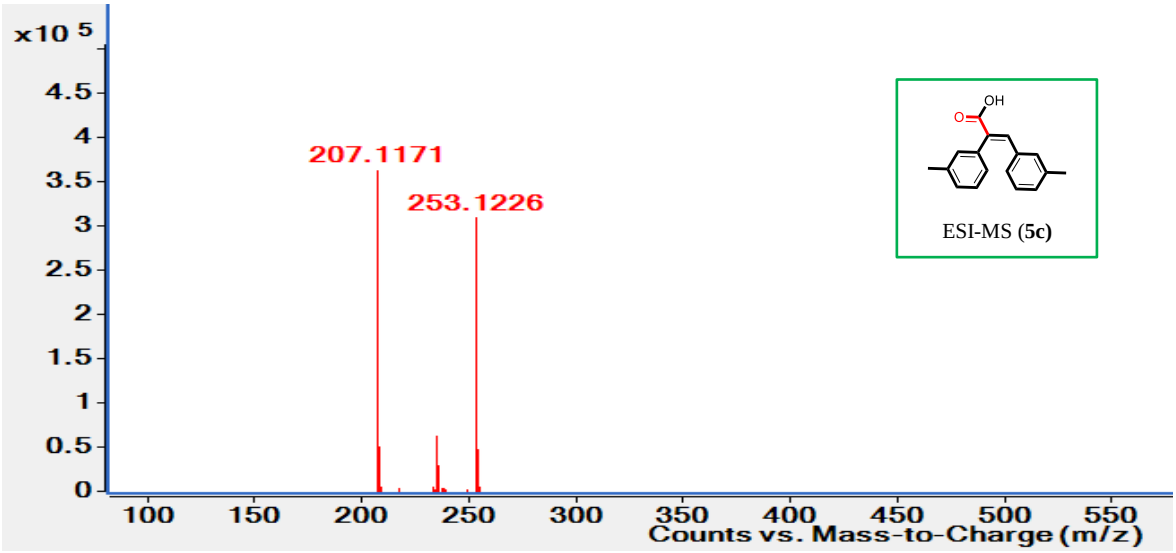


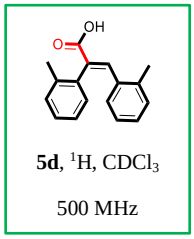
5c, ^{1}H, $CDCl_3$

600 MHz



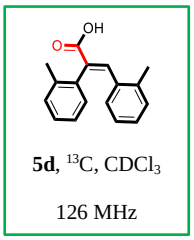

173.14
142.39
138.29
137.78
135.35
134.26
131.93
131.52
130.27
130.20
128.75
128.57
128.07
127.79
126.70
77.21
77.00
76.79
21.41
21.22
OH
O
5c, 13C, CDCl3
15d MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
207.1171
253.1226
100 150 200 250 300 350 400 450 500 550
Counts vs. Mass-to-Charge (m/z)
OH
O
ESI-MS (5c)



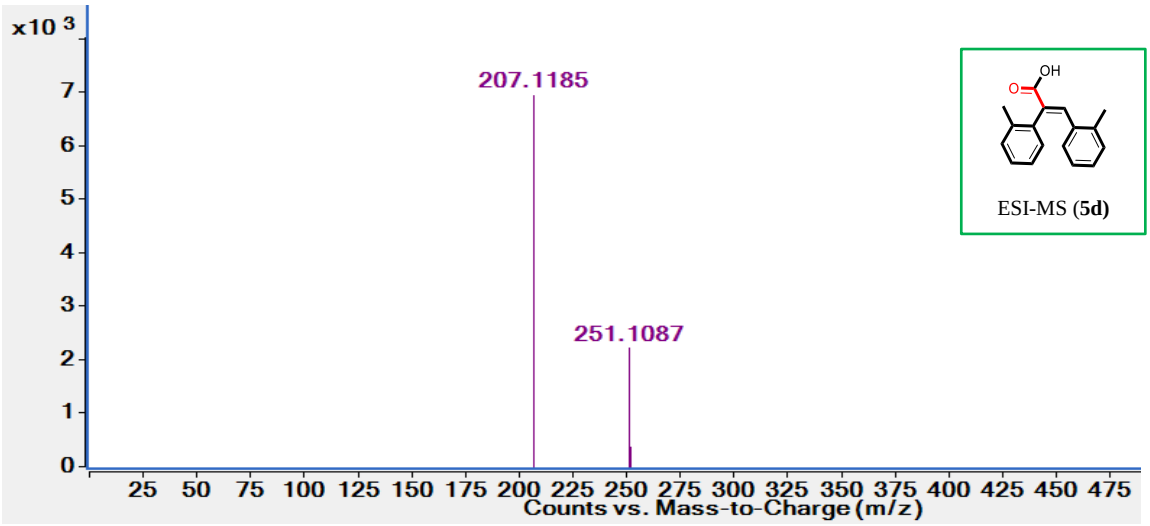
5d, ^{1}H, $CDCl_3$

500 MHz

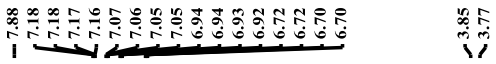


5d, ^{13}C, $CDCl_3$

126 MHz

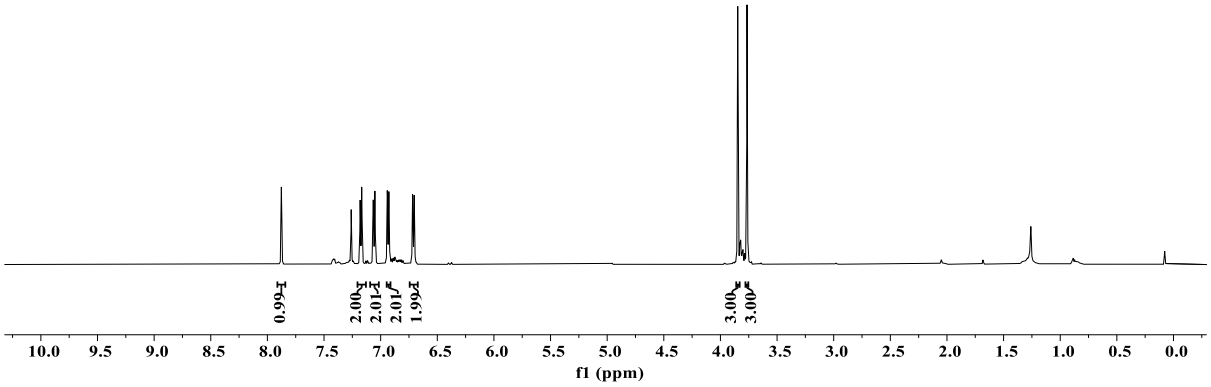


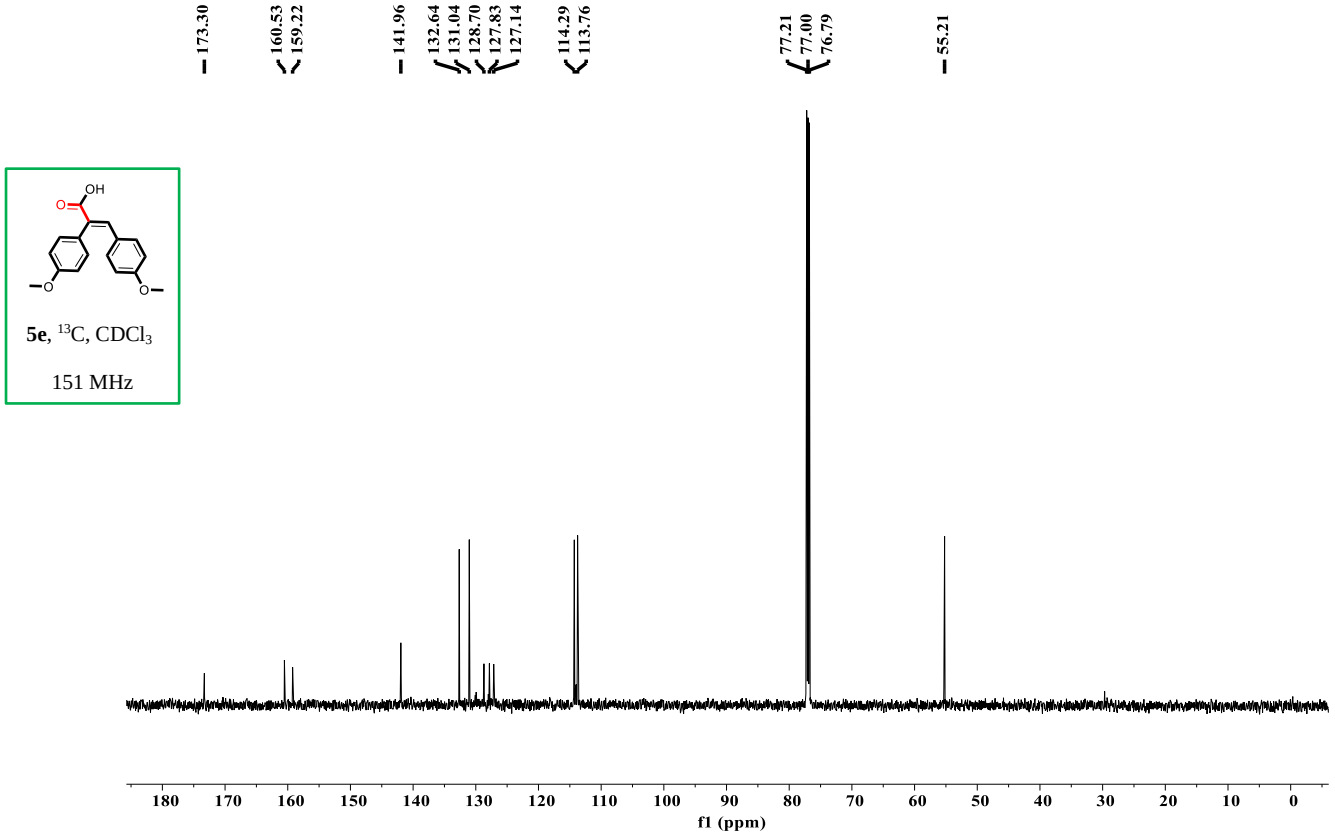
ESI-MS (**5d**)

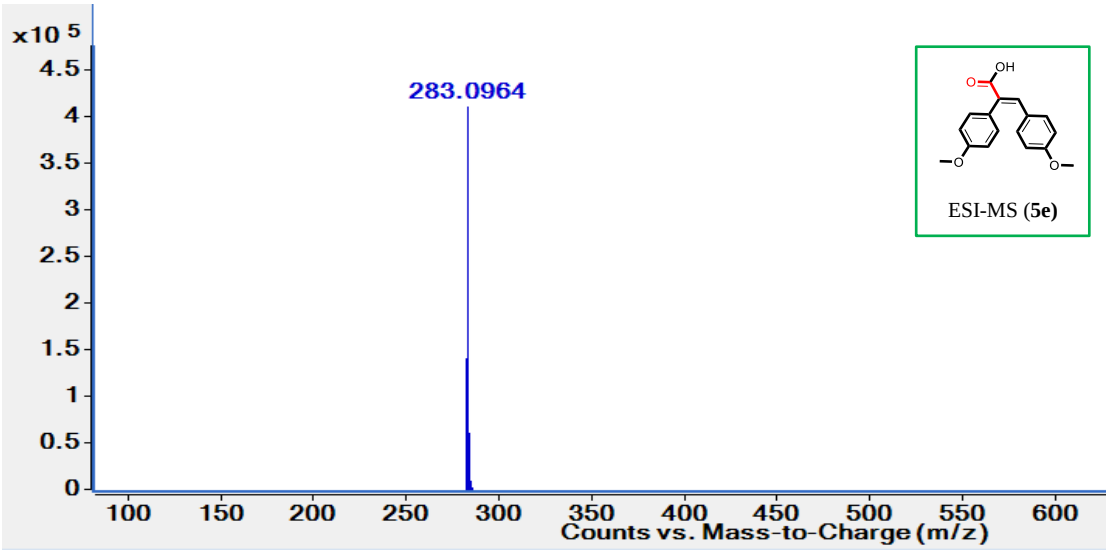


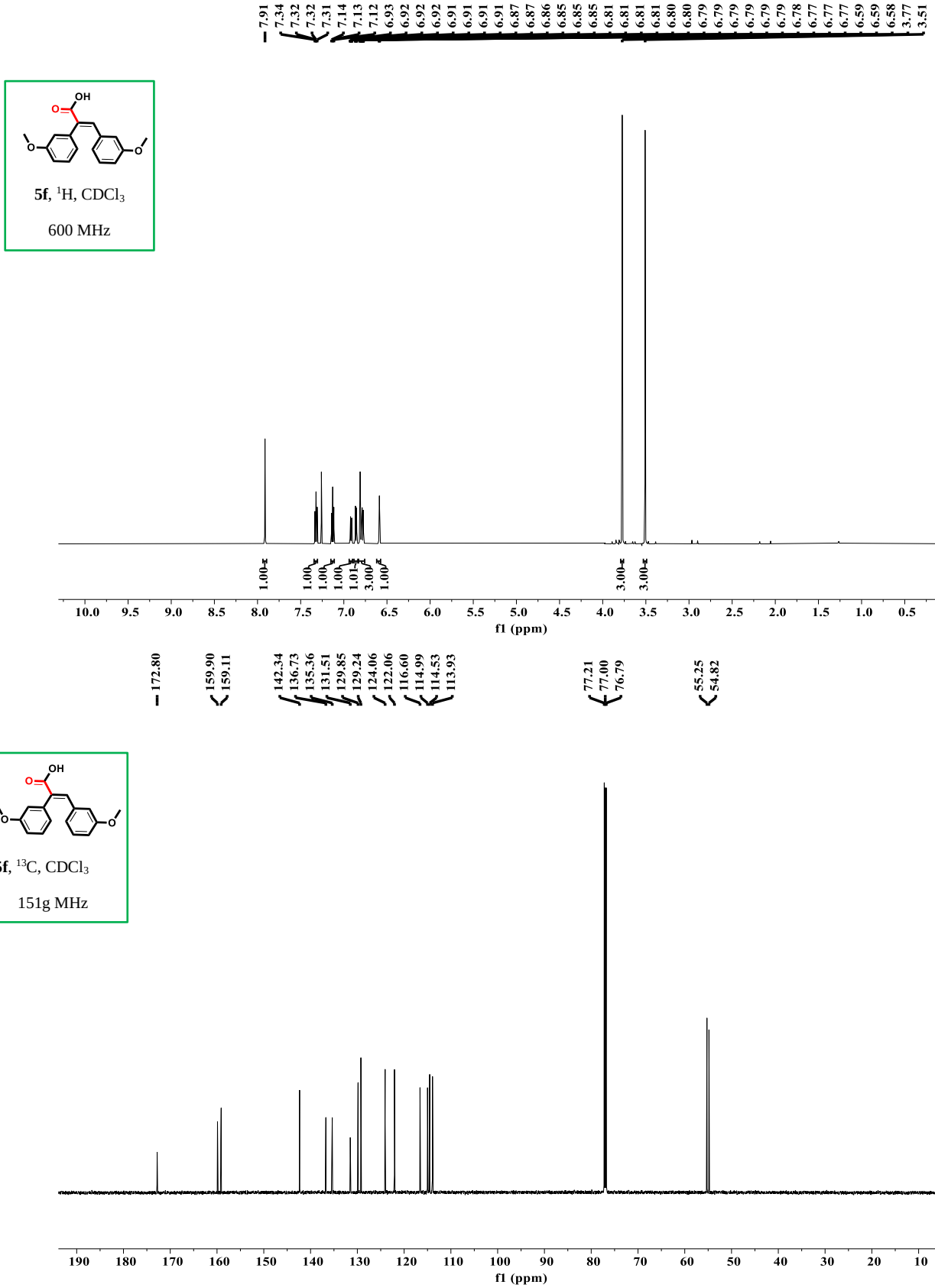
5e, ^{1}H, $CDCl_3$

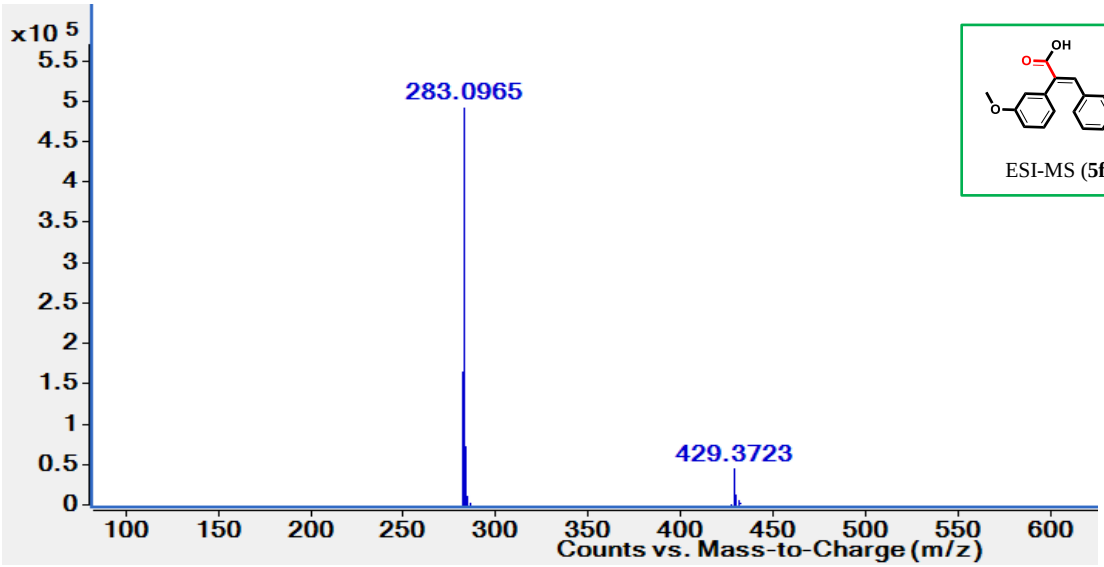
600 MHz



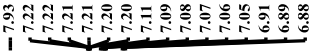

173.30
160.53
159.22
141.96
132.64
131.04
128.70
127.83
127.14
114.29
113.76
77.21
77.00
76.79
55.21
OH
O
O
O
5e, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

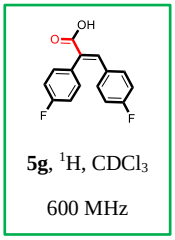

x10 5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
283.0964
100 150 200 250 300 350 400 450 500 550 600
Counts vs. Mass-to-Charge (m/z)
OH
O
O
O
ESI-MS (5e)


7.91
7.34
7.32
7.32
7.31
7.14
7.13
7.12
6.93
6.92
6.92
6.92
6.91
6.91
6.91
6.91
6.87
6.87
6.86
6.85
6.85
6.85
6.81
6.81
6.81
6.81
6.80
6.80
6.79
6.79
6.79
6.79
6.79
6.79
6.78
6.77
6.77
6.77
6.59
6.59
6.58
3.77
3.51
OH
O
O
O
5f, 1H, CDCl3
600 MHz
1.00
1.00
1.00
1.00
1.01
3.00
1.00
3.00
3.00
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
0.5
0.0
f1 (ppm)
172.80
159.90
159.11
142.34
136.73
135.36
131.51
129.85
129.24
124.06
122.06
116.60
114.99
114.53
113.93
77.21
77.00
76.79
55.25
54.82
OH
O
O
O
5f, 13C, CDCl3
151g MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



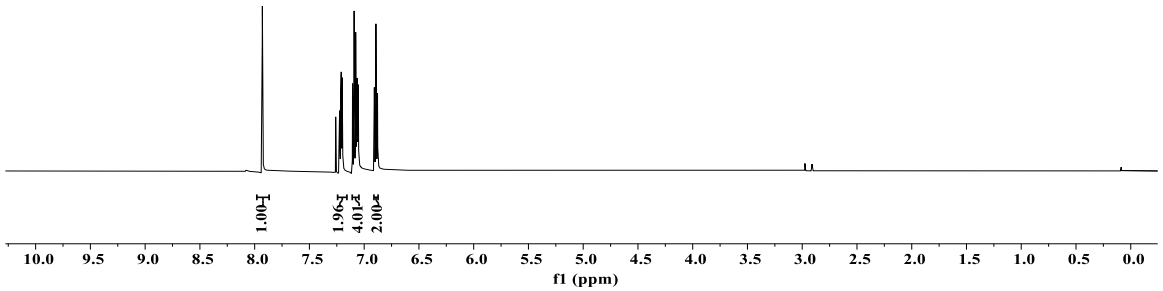
ESI-MS (**5f**)

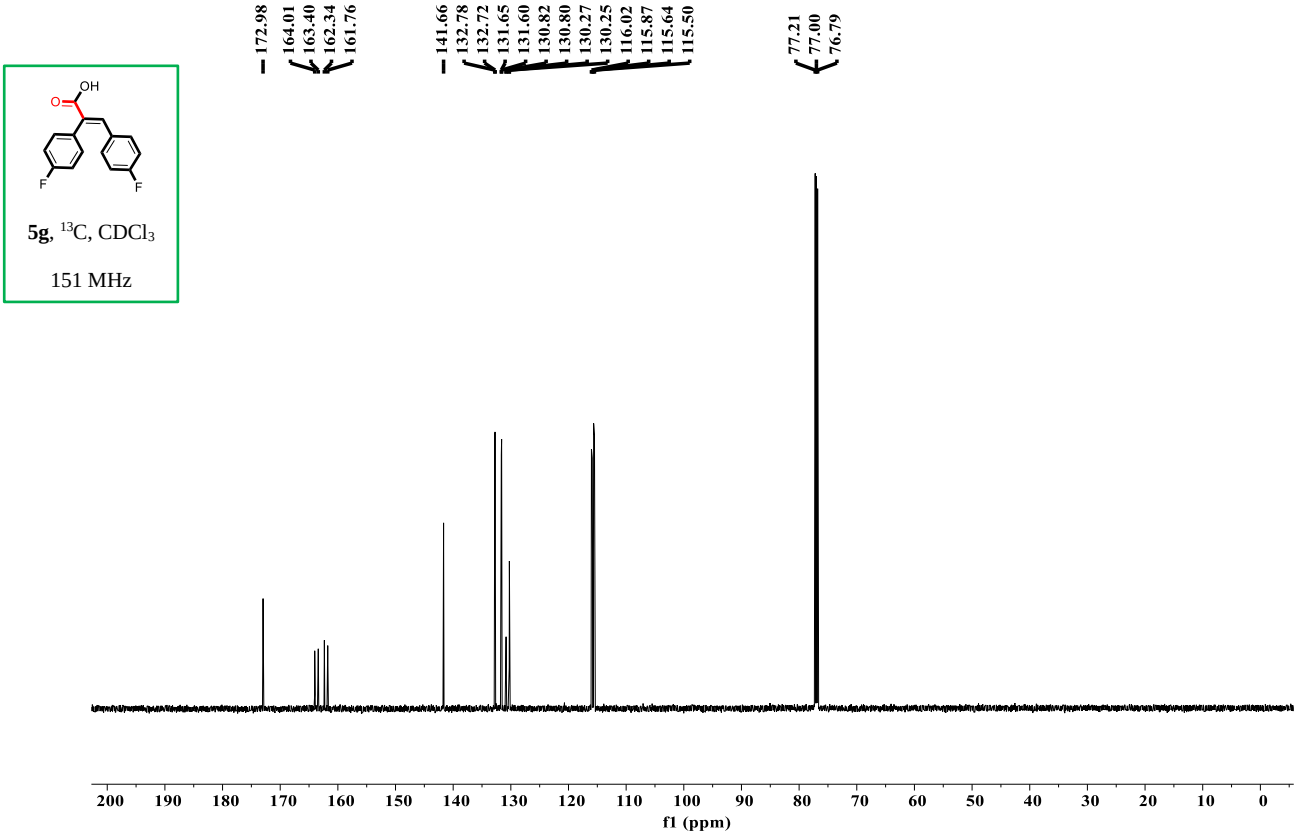


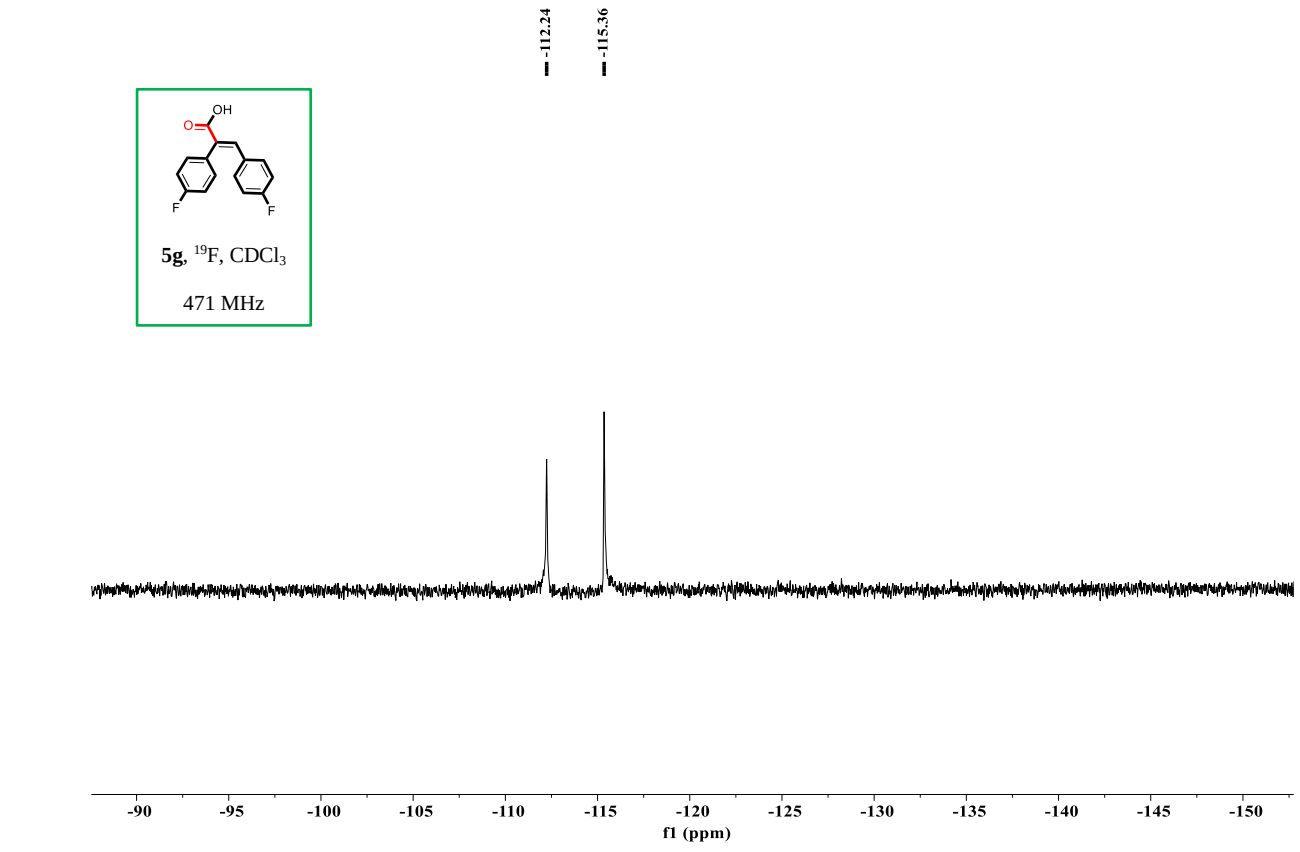


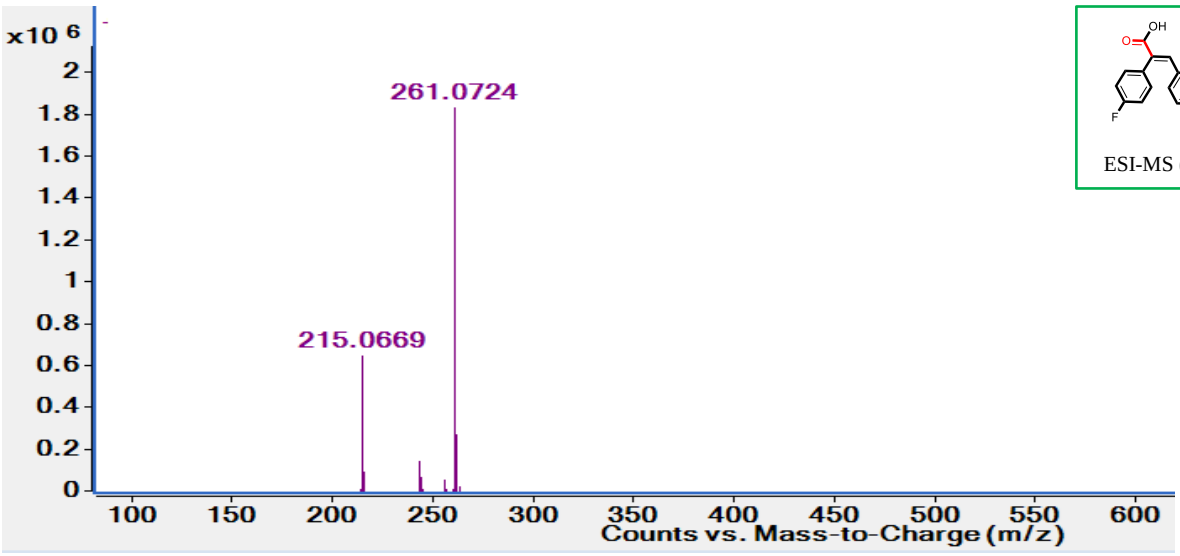
5g, ^{1}H, $CDCl_3$

600 MHz

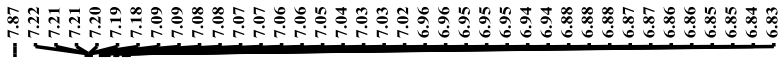


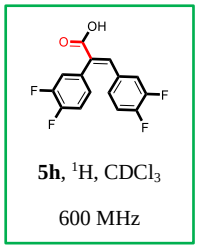

172.98
164.01
163.40
162.34
161.76
141.66
132.78
132.72
131.65
131.60
130.82
130.80
130.27
130.25
116.02
115.87
115.64
115.50
77.21
77.00
76.79
OH
O
F
F
5g, 13C, CDCl3
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.24
-115.36
OH
O
F
F
5g, 19F, CDCl3
471 MHz
-90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)



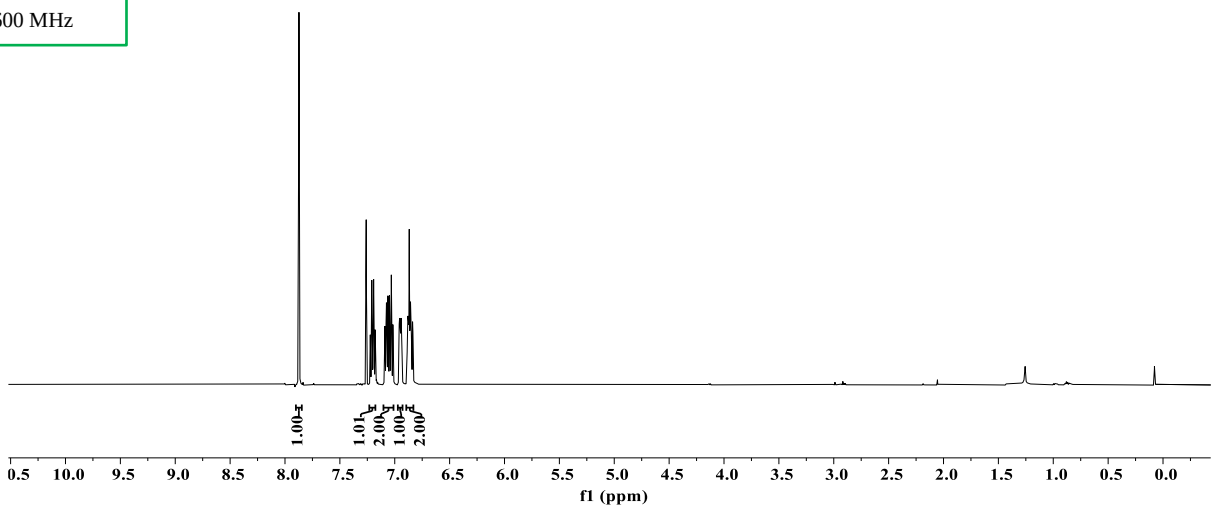
ESI-MS (**5g**)

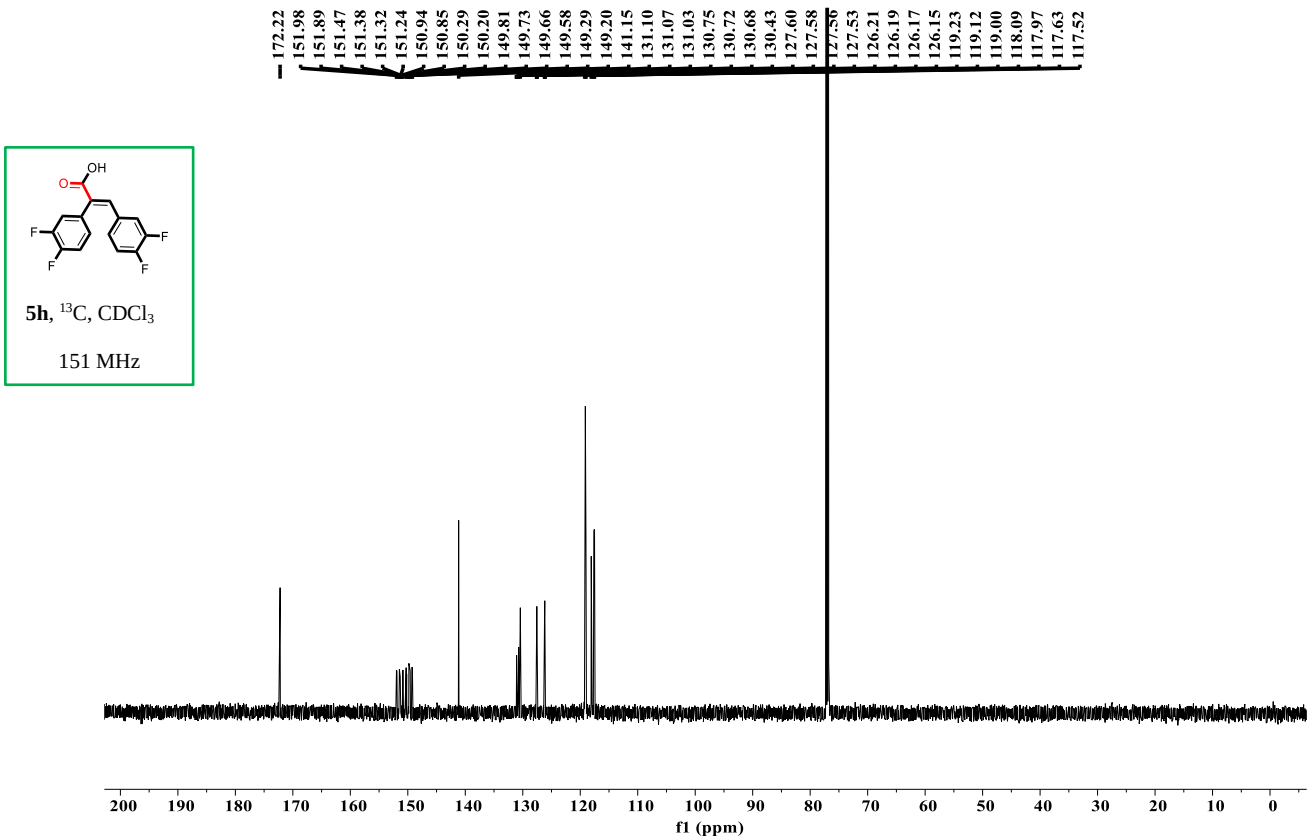


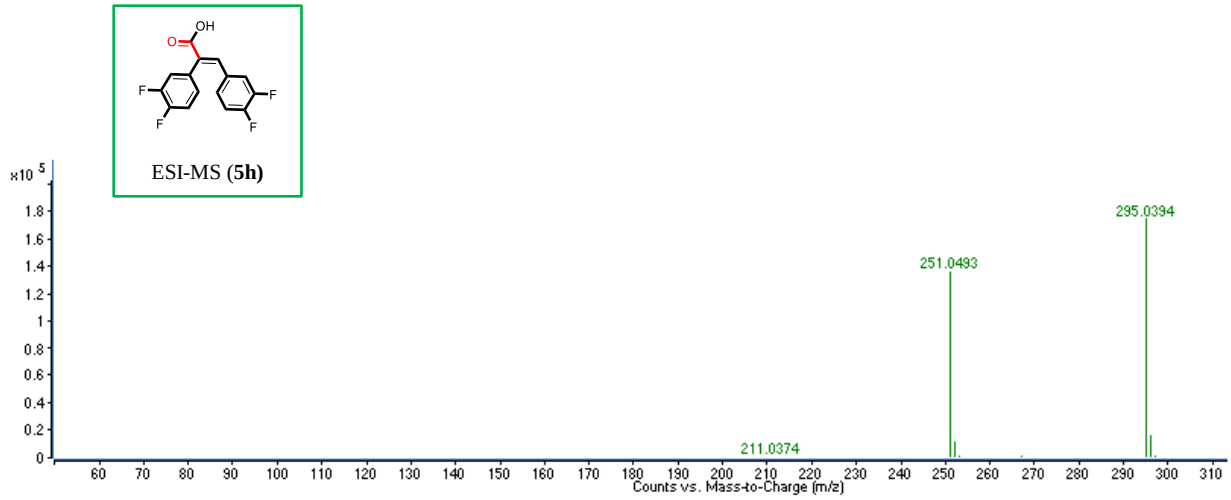


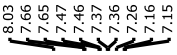
5h, ^{1}H, $CDCl_3$

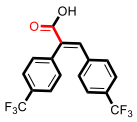
600 MHz




172.22
151.98
151.89
151.47
151.38
151.32
151.24
150.94
150.85
150.29
150.20
149.81
149.73
149.66
149.58
149.29
149.20
141.15
131.10
131.07
131.03
130.75
130.72
130.68
130.43
127.60
127.58
127.56
127.53
126.21
126.19
126.17
126.15
119.23
119.12
119.00
118.09
117.97
117.63
117.52
OH
O
F
F
F
F
5h, 13C, CDCl3
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

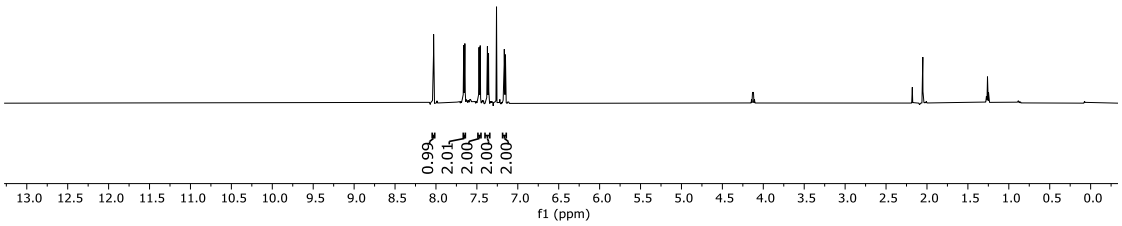

OH
O
F
F
F
F
ESI-MS (5h)
x10 5
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
295.0394
251.0493
211.0374
60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310
Counts vs. Mass-to-Charge (m/z)

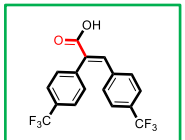




5i, ^{1}H, $CDCl_3$

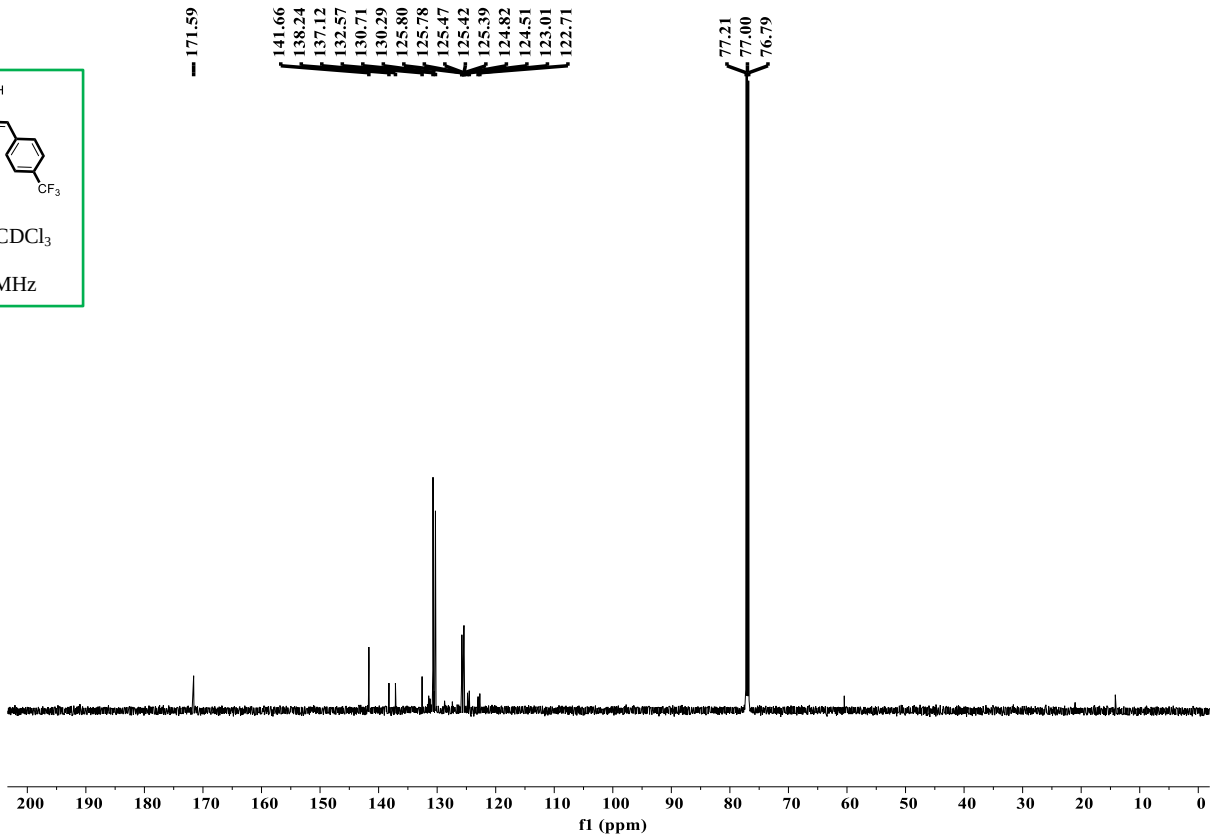
600 MHz

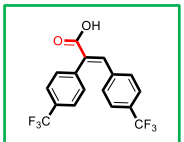




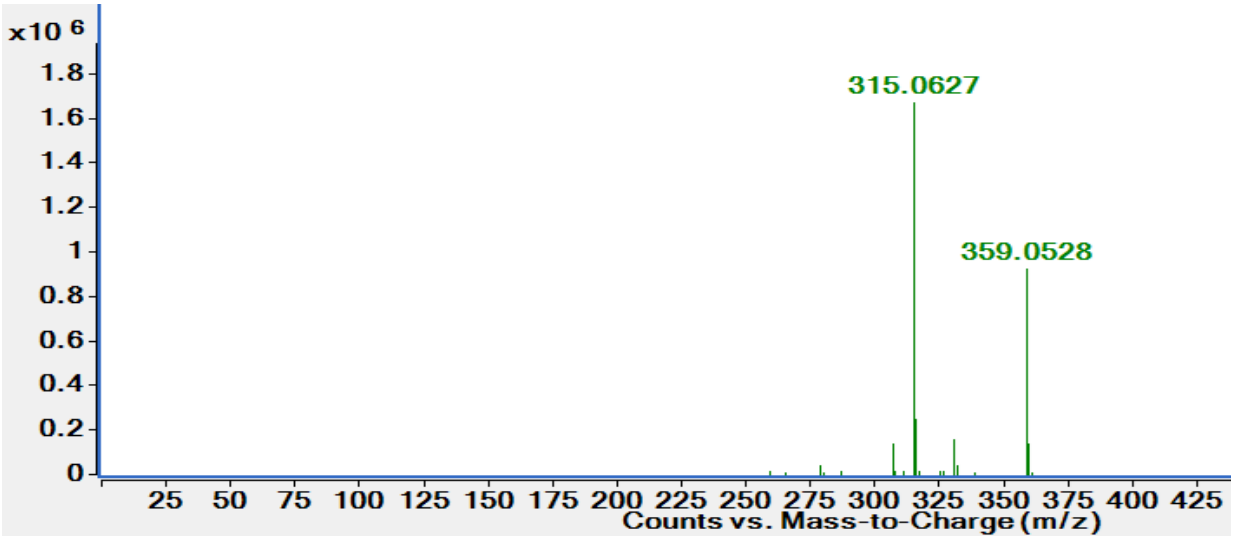
5i, ^{13}C, $CDCl_3$

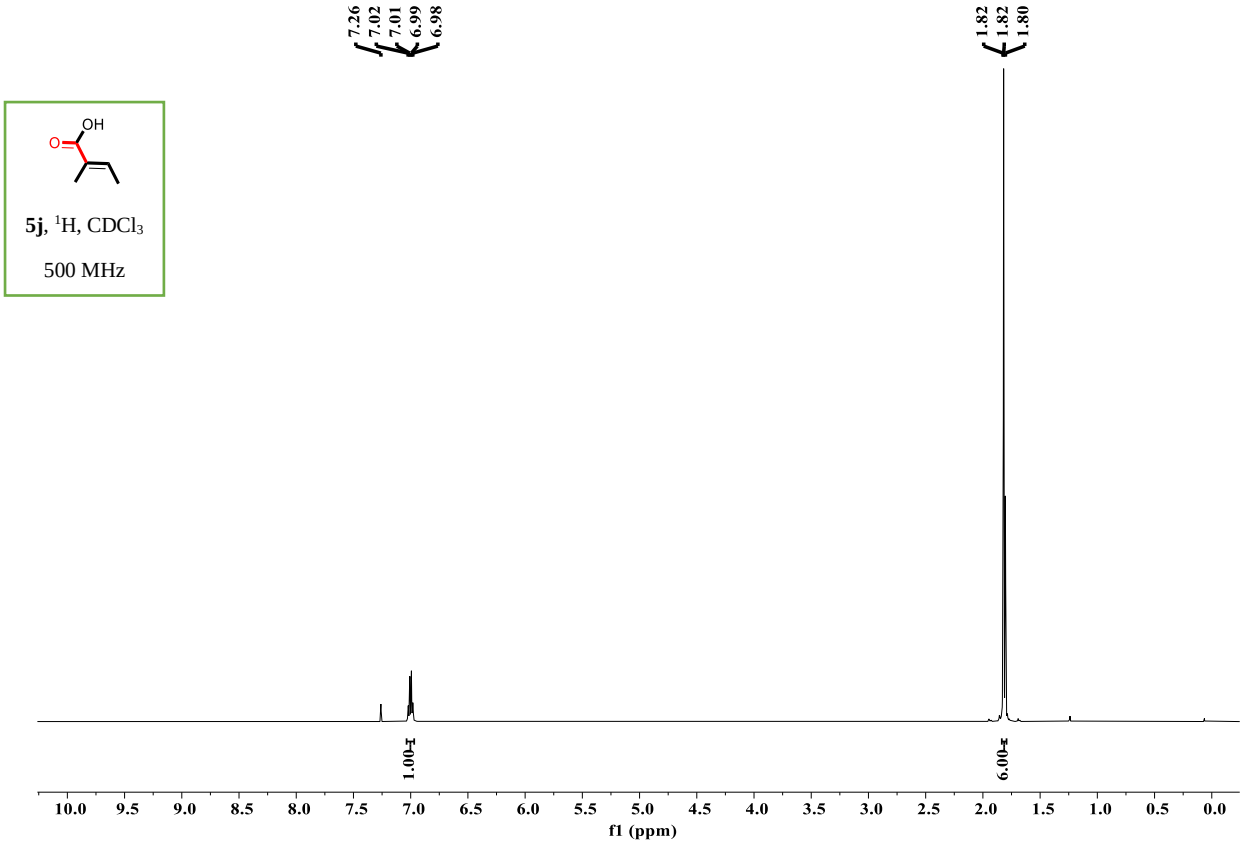
151 MHz

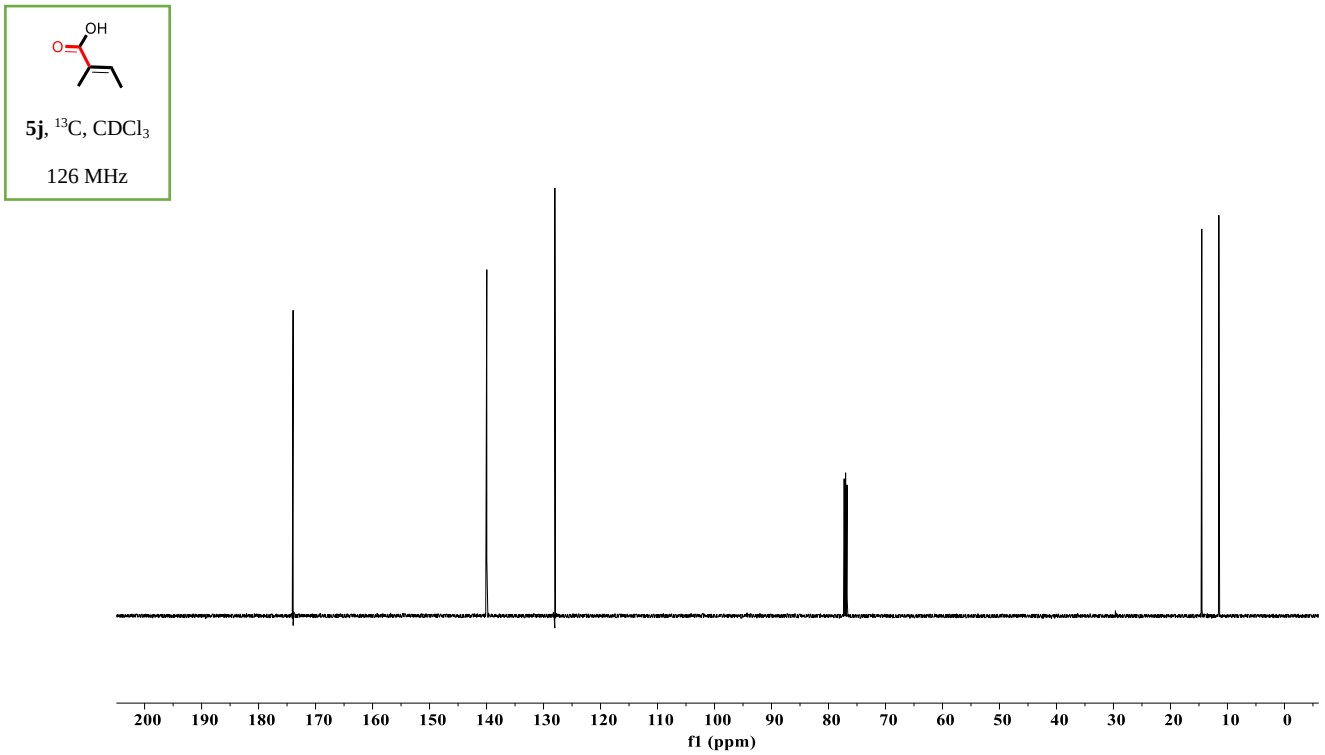


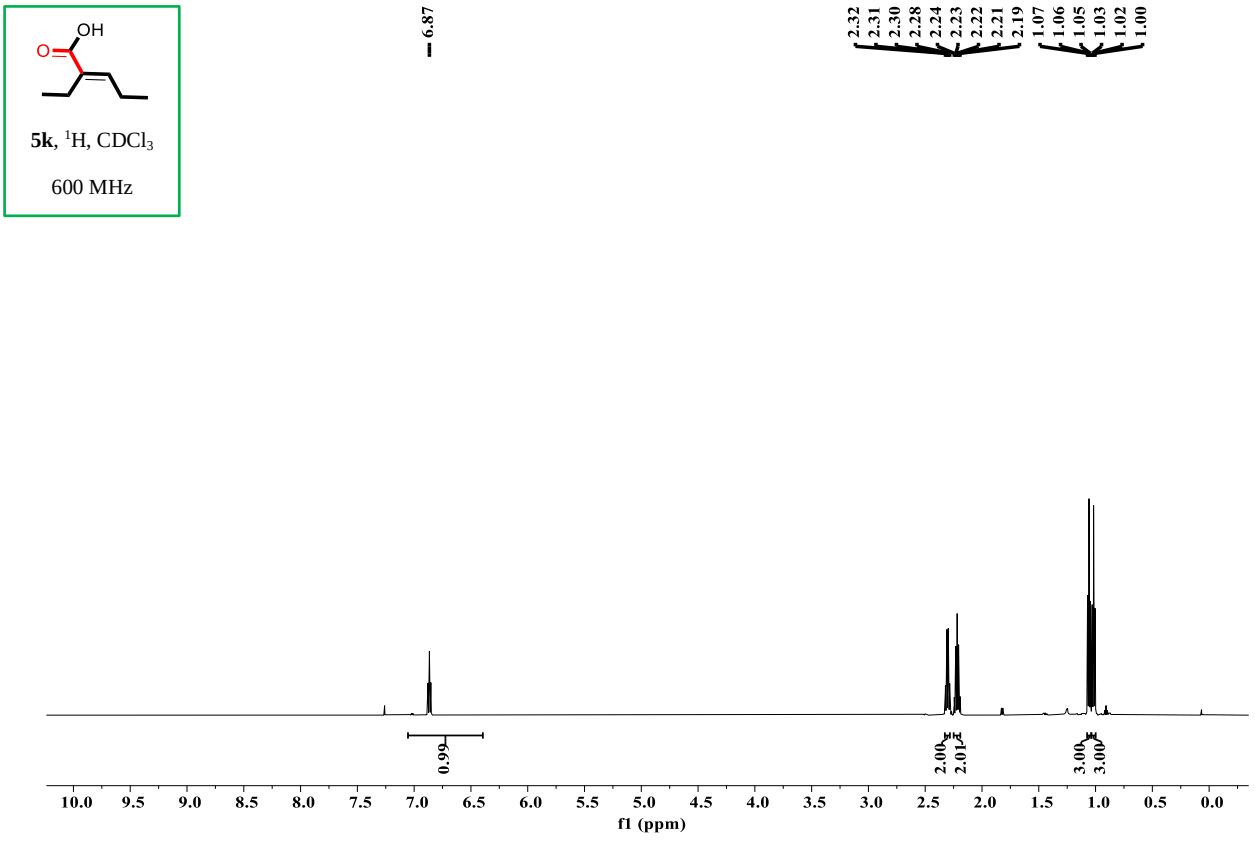


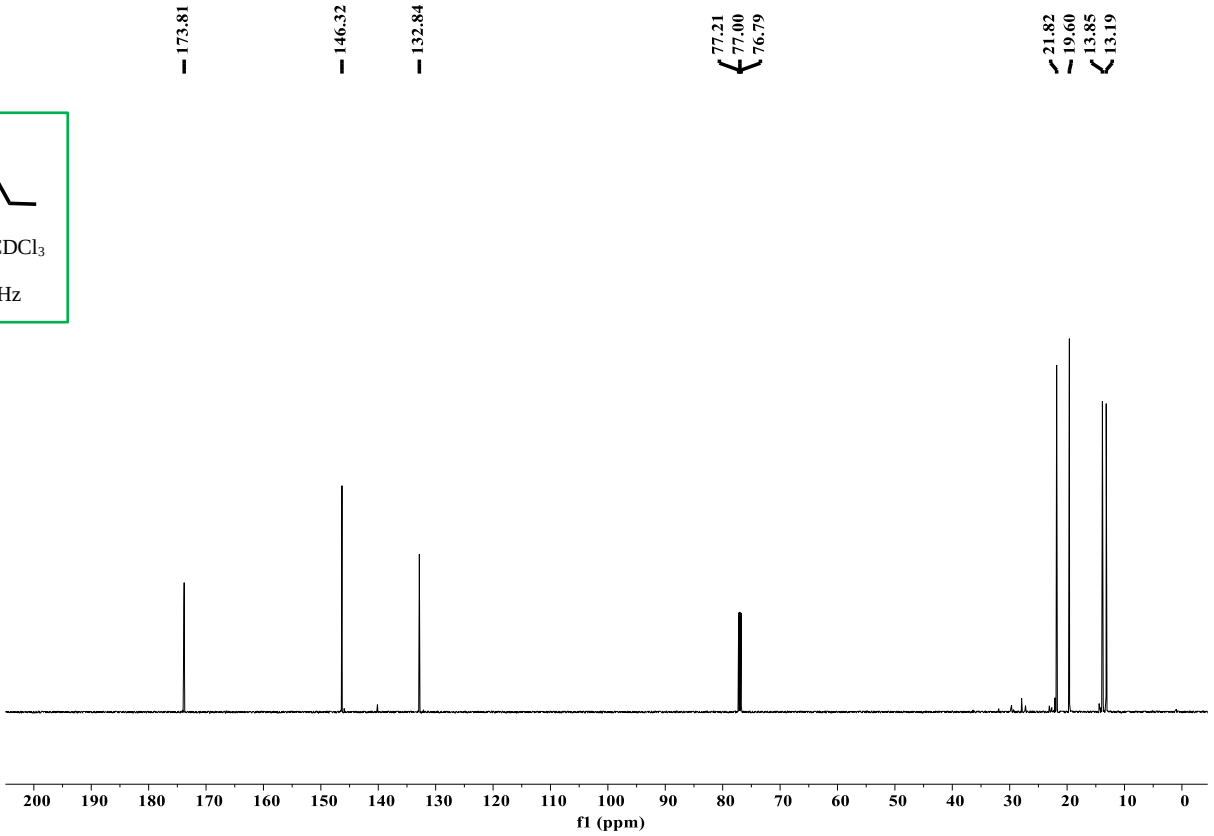
ESI-MS (**5i**)

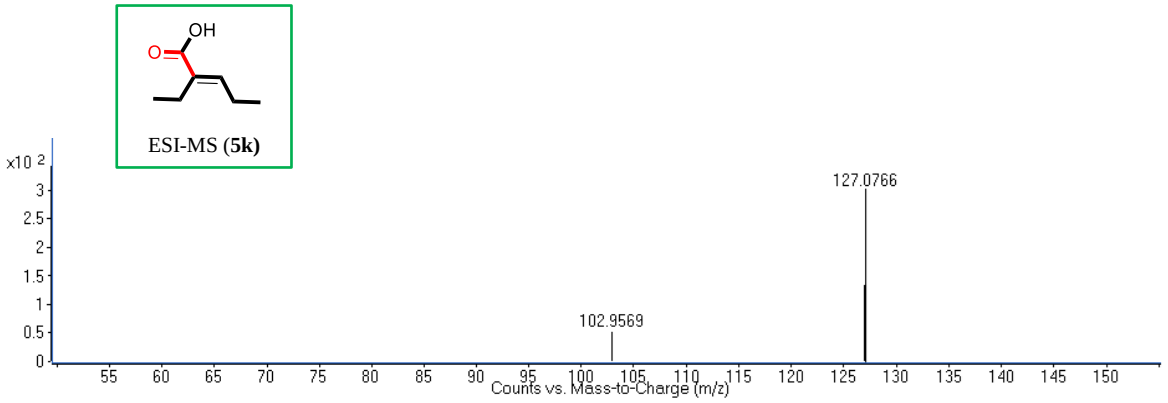

x10 6
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
315.0627
359.0528
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425
Counts vs. Mass-to-Charge (m/z)

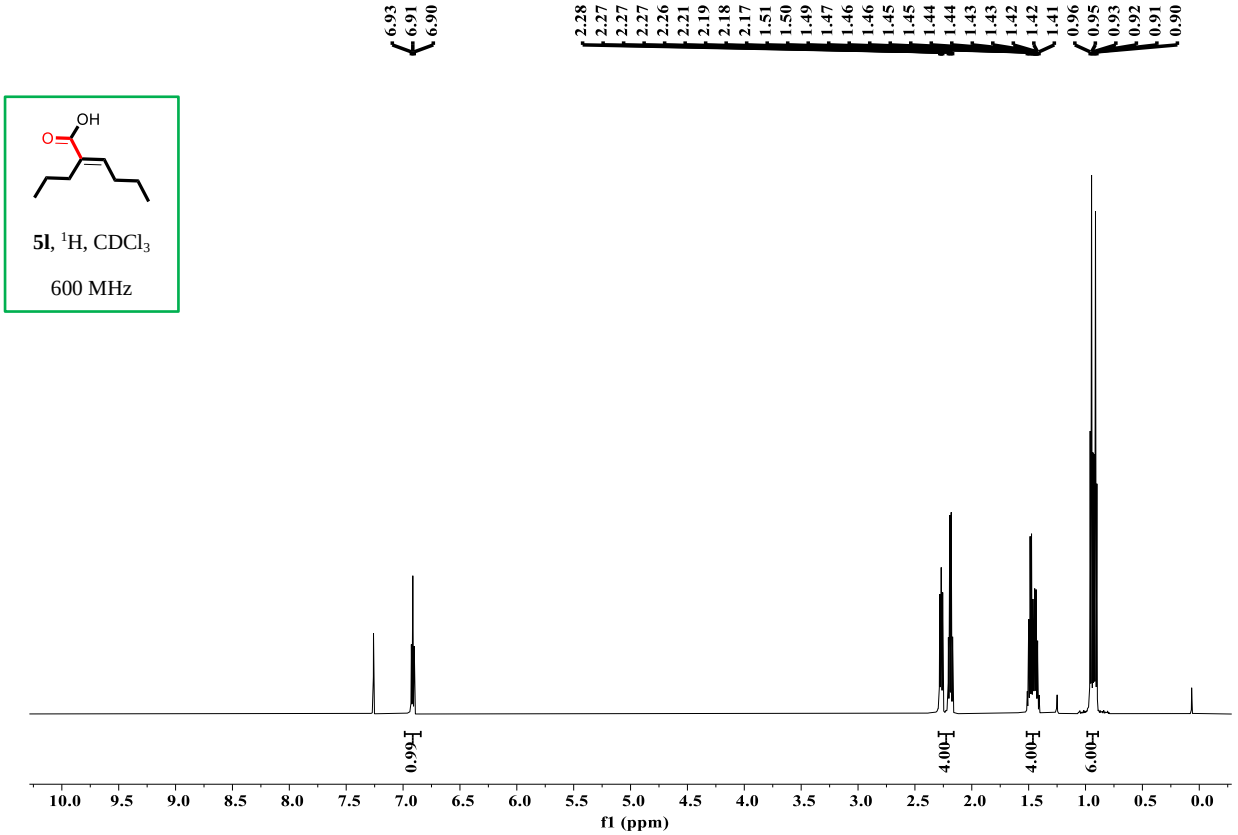

OH
O
5j, 1H, CDCl3
500 MHz
7.26
7.02
7.01
6.99
6.98
1.82
1.82
1.80
1.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

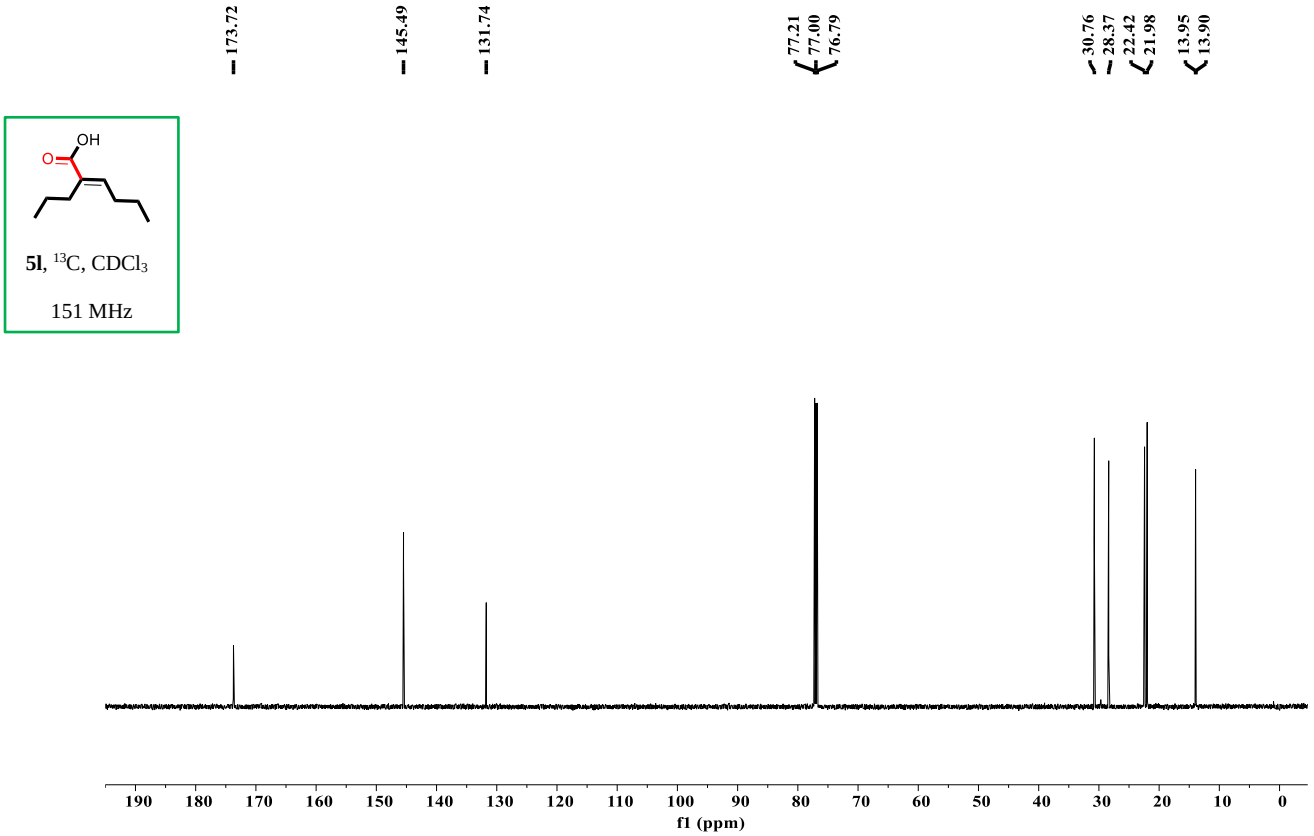

173.95
139.96
128.02
77.25
77.00
76.75
14.50
11.51
OH
O
5j, 13C, CDCl3
126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

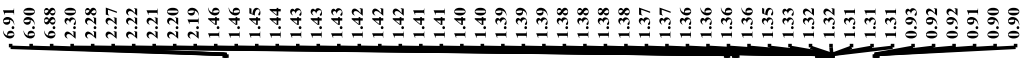

6.87
2.32
2.31
2.30
2.28
2.24
2.23
2.22
2.21
2.19
1.07
1.06
1.05
1.03
1.02
1.00
OH
O
5k, 1H, CDCl3
600 MHz
0.99
2.00
2.01
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

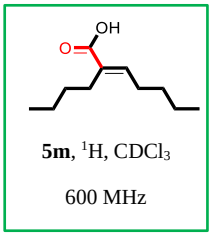

173.81
146.32
132.84
77.21
77.00
76.79
21.82
19.60
13.85
13.19
OH
O
5k, 13C, CDCl3
151 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
O
ESI-MS (5k)
x10 2
3
2.5
2
1.5
1
0.5
0
127.0766
102.9569
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150
Counts vs. Mass-to-Charge (m/z)


6.93
6.91
6.90
2.28
2.27
2.27
2.27
2.26
2.21
2.19
2.18
2.17
1.51
1.50
1.49
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
1.42
1.41
0.96
0.95
0.93
0.92
0.91
0.90
OH
O
5l, 1H, CDCl3
600 MHz
0.99
4.00
4.00
6.00
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 0.5 0.0
f1 (ppm)

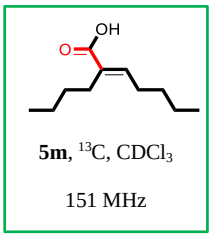

173.72
145.49
131.74
77.21
77.00
76.79
30.76
28.37
22.42
21.98
13.95
13.90
OH
O
5l, 13C, CDCl3
151 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)





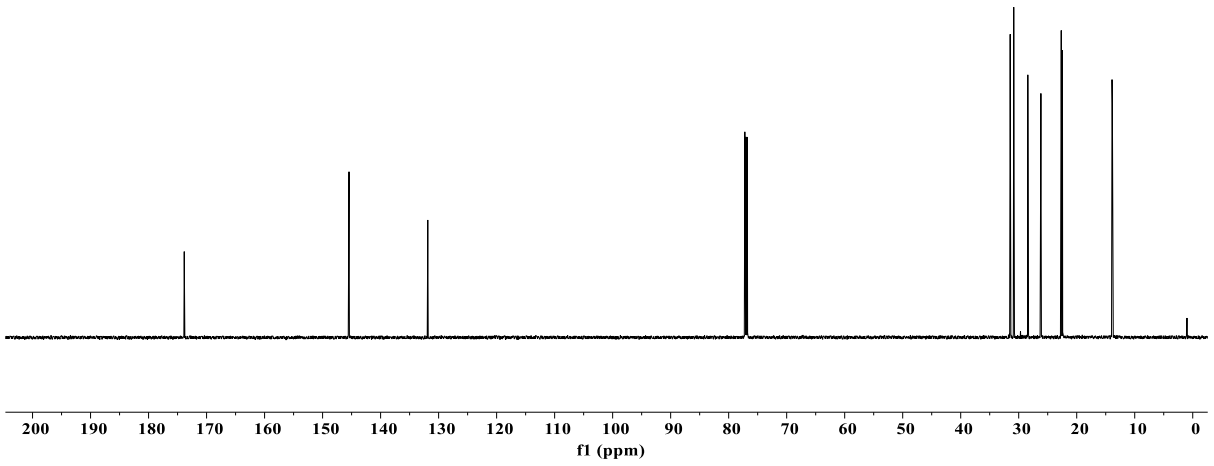
5m, ^{1}H, $CDCl_3$

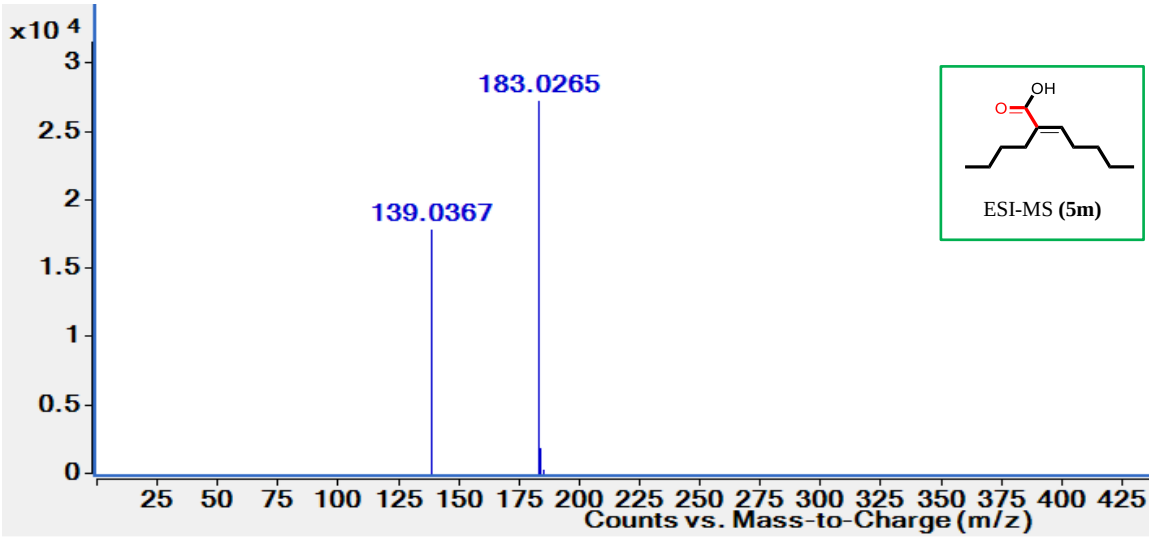
600 MHz



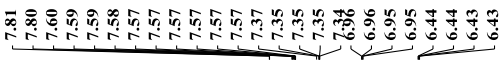
5m, ^{13}C, $CDCl_3$

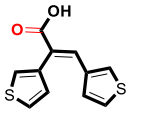
151 MHz





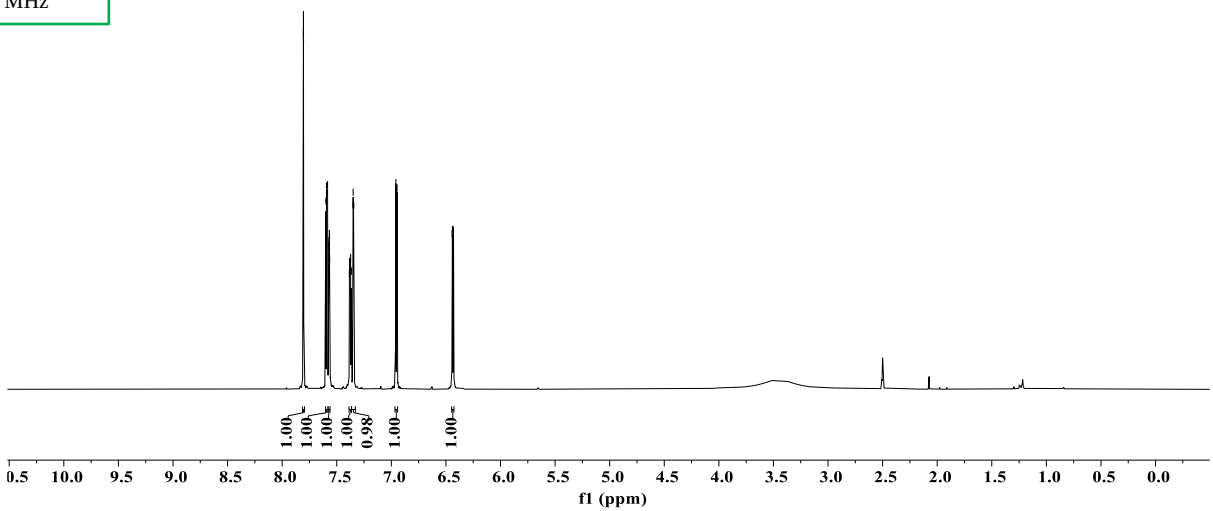
ESI-MS **(5m)**

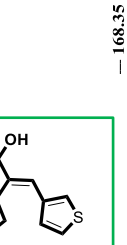




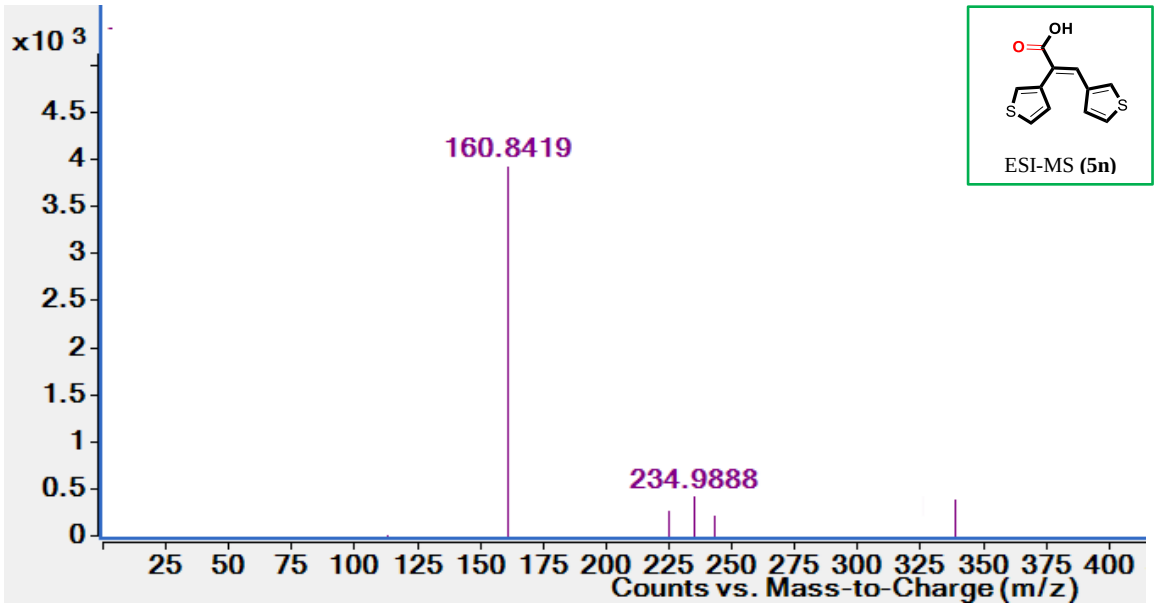
5n, ^{1}H, DMSO-D_6

500 MHz

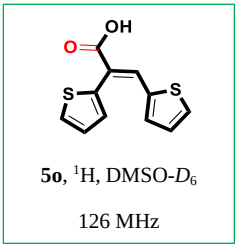




5n, ^{13}C, DMSO-D_6, 126 MHz

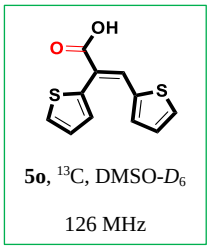


ESI-MS **(5n)**



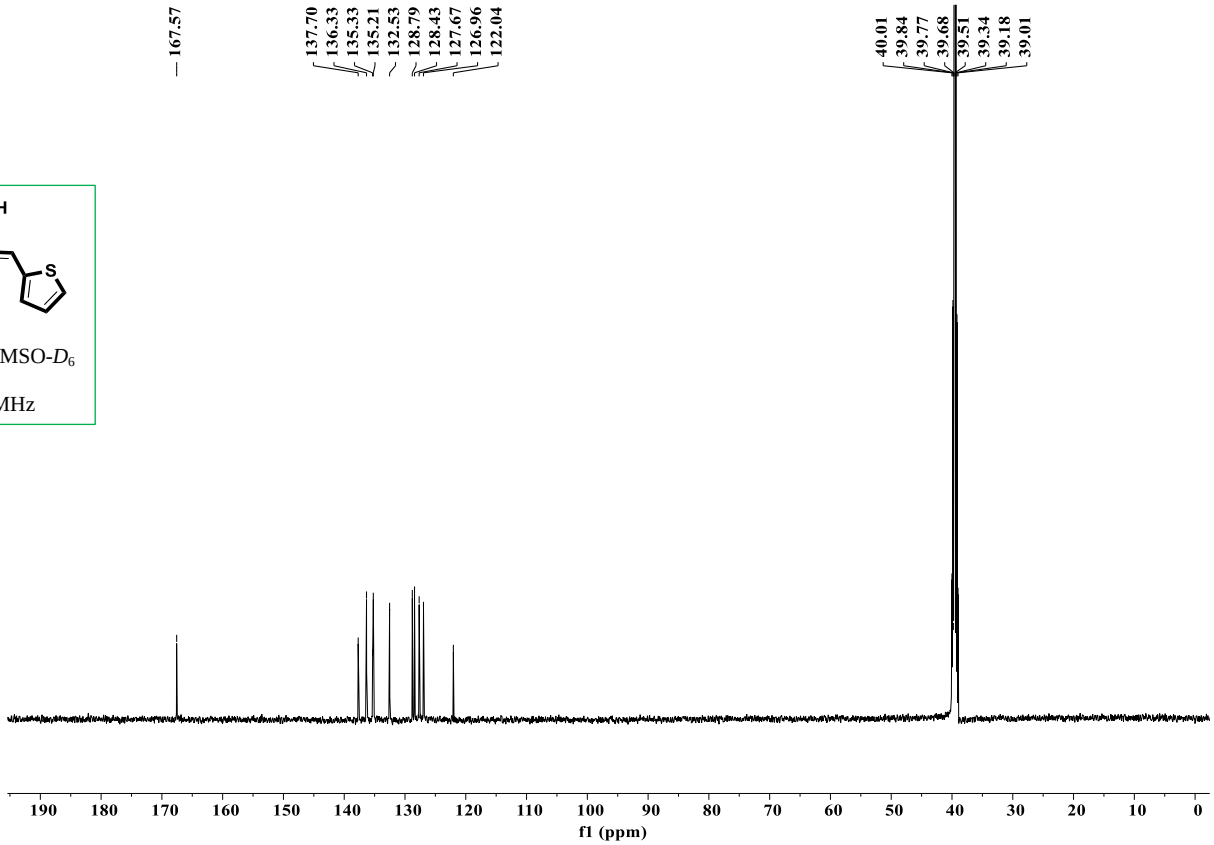
5o, ^{1}H, DMSO-D_6

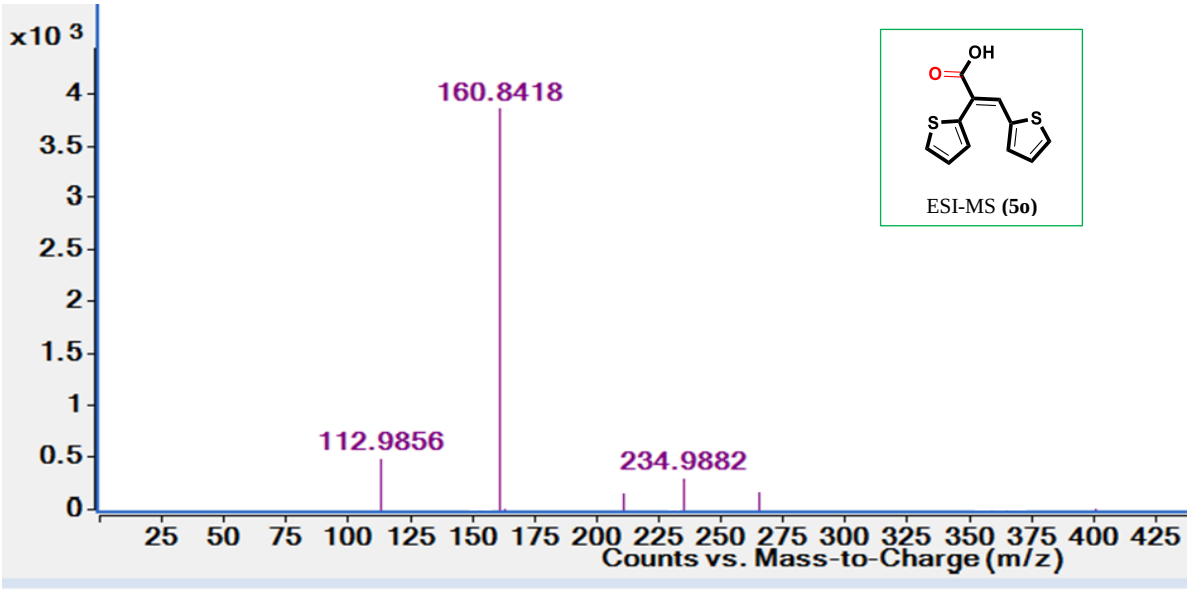
126 MHz



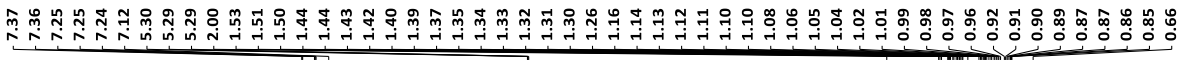
5o, ^{13}C, DMSO-D_6

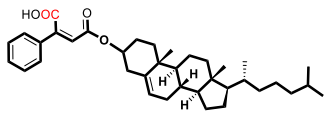
126 MHz



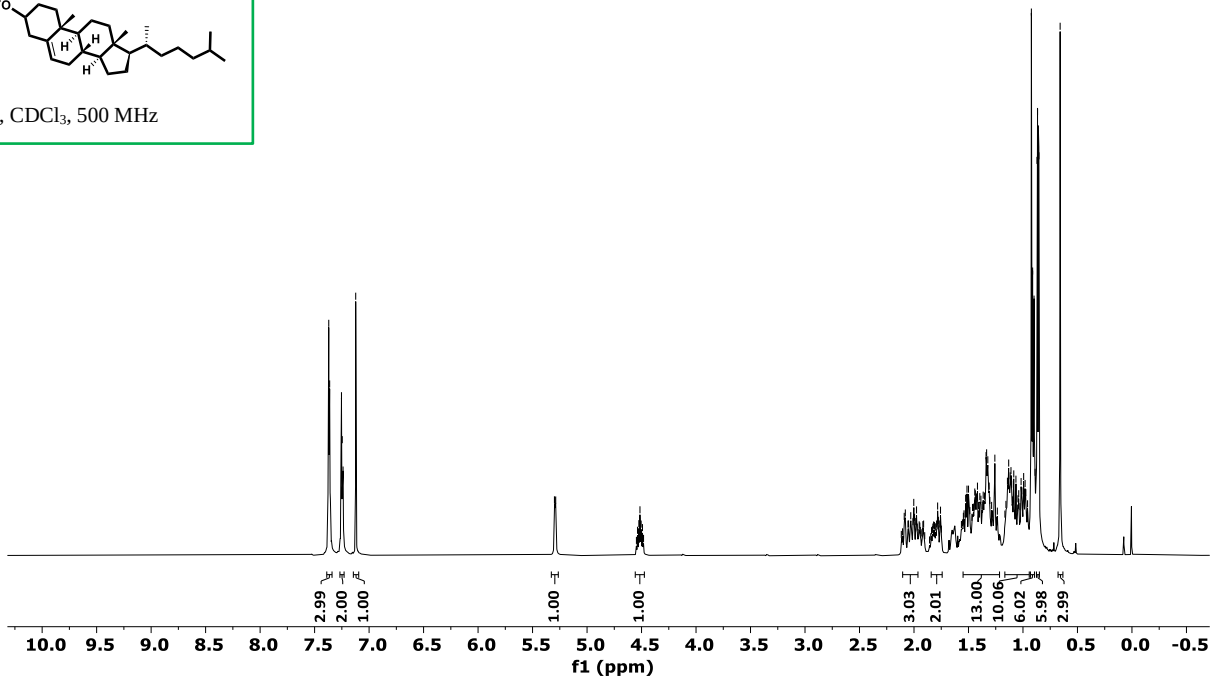

x10 3
4
3.5
3
2.5
2
1.5
1
0.5
0
160.8418
112.9856
234.9882
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425
Counts vs. Mass-to-Charge (m/z)
OH
O
S
S

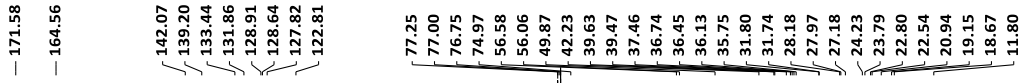
ESI-MS **(5o)**

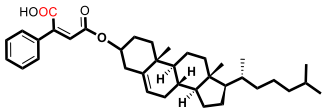




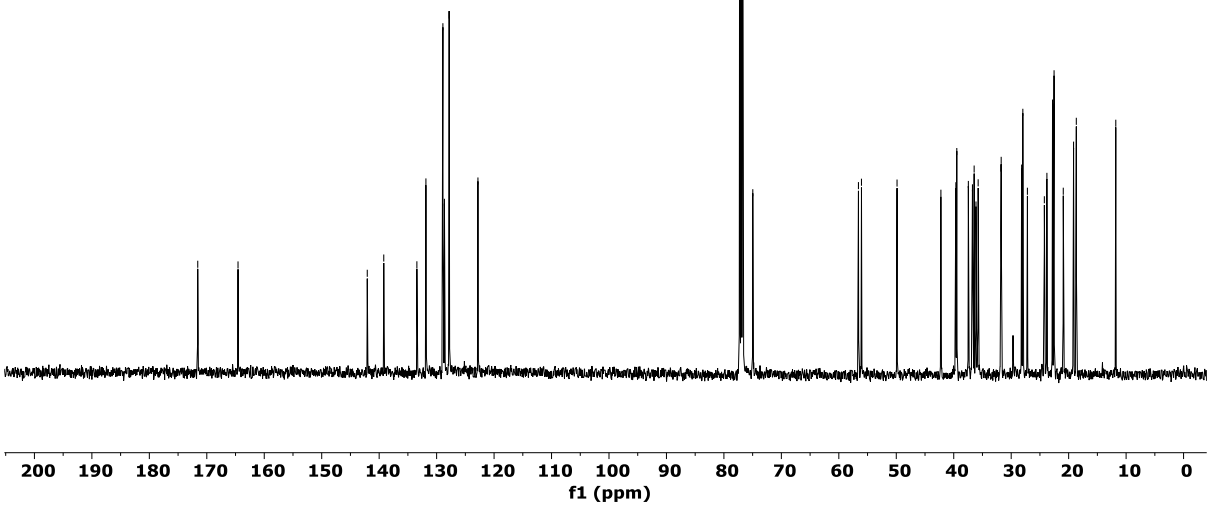
5p, ^{1}H, $CDCl_3$, 500 MHz

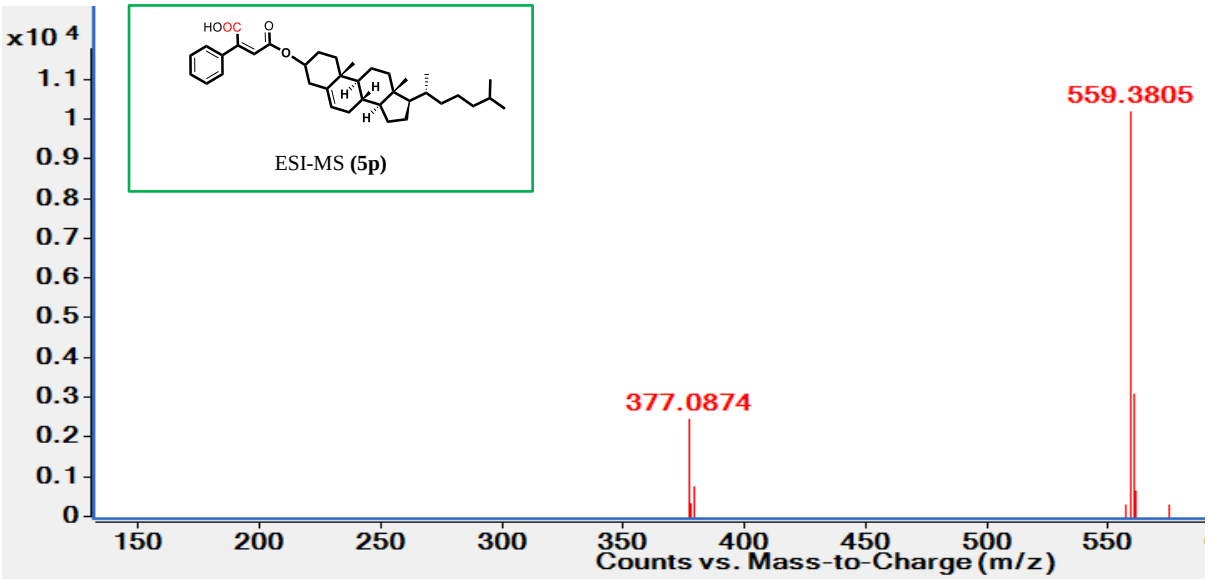




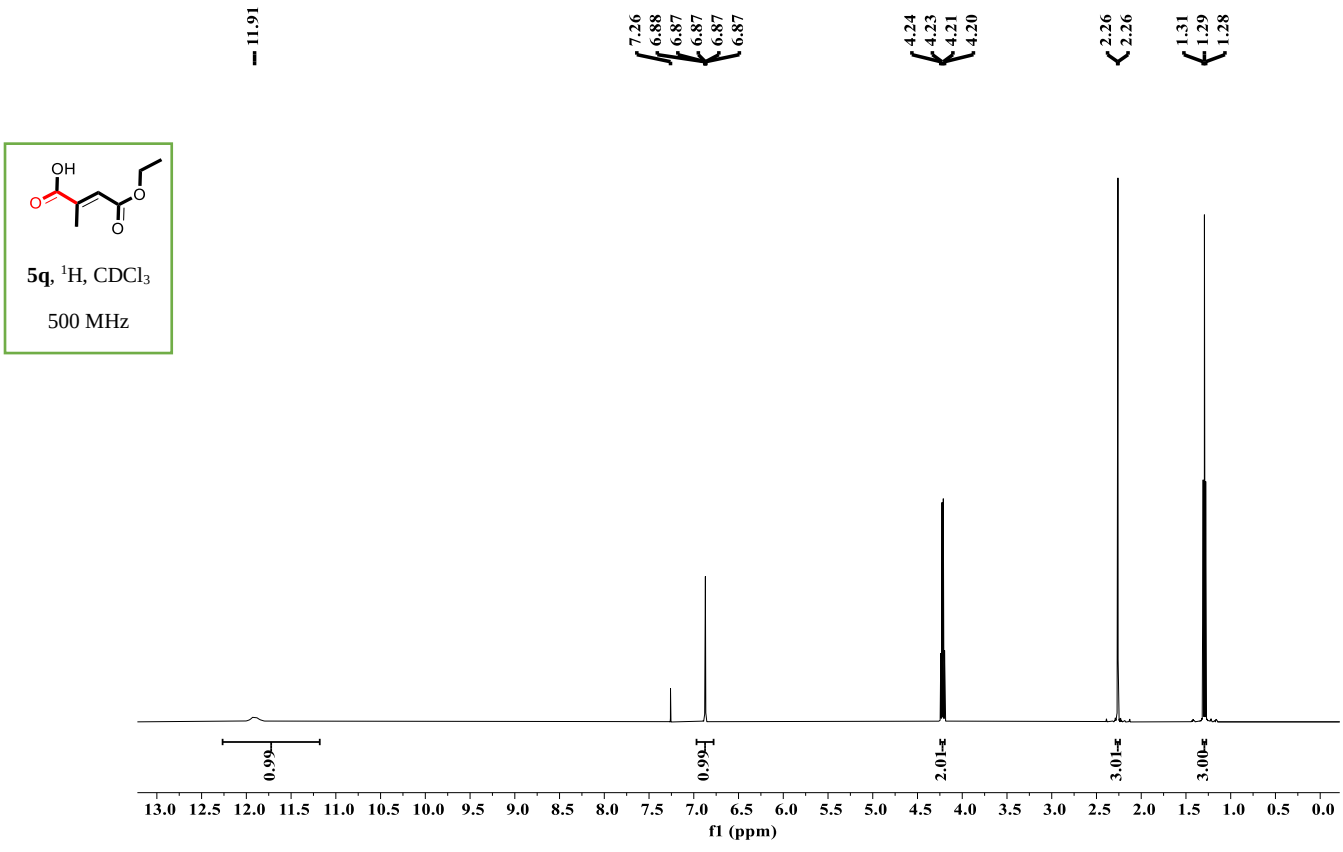


5p, ^{13}C, $CDCl_3$, 126 MHz



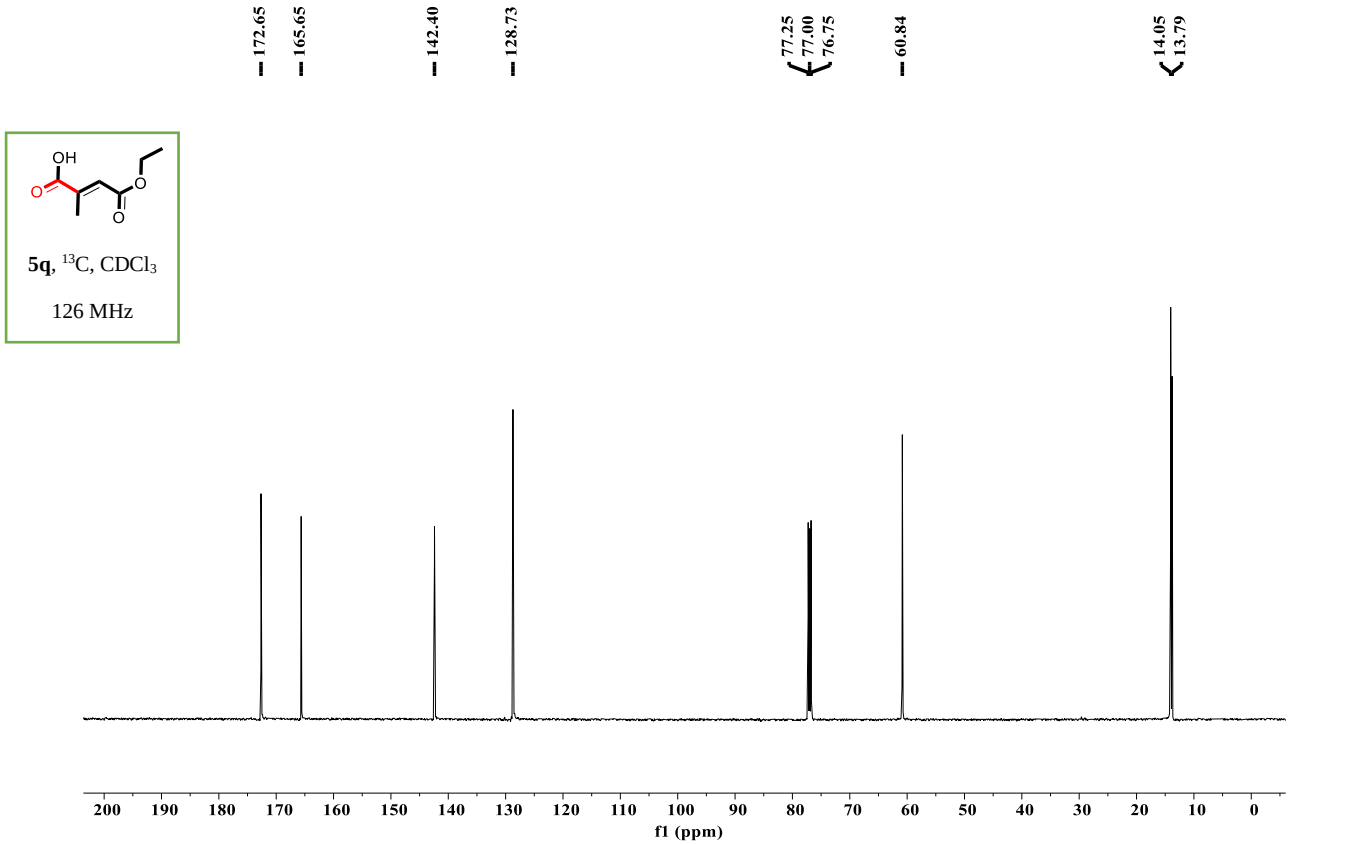


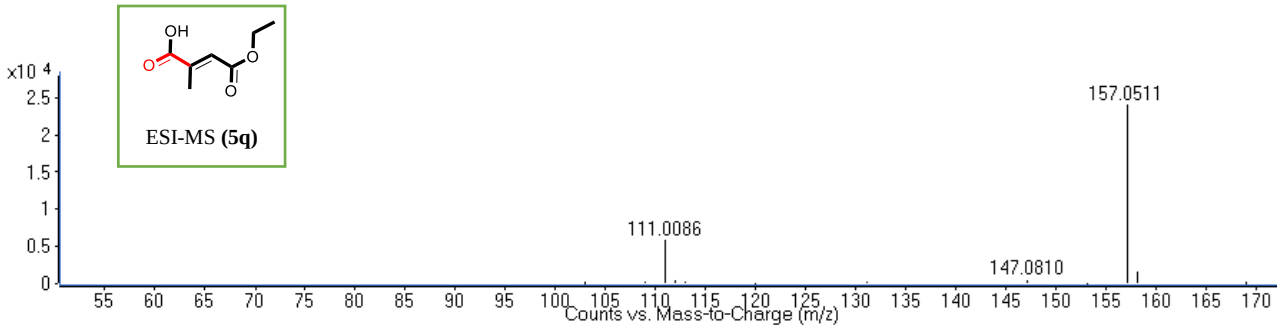
ESI-MS **(5p)**

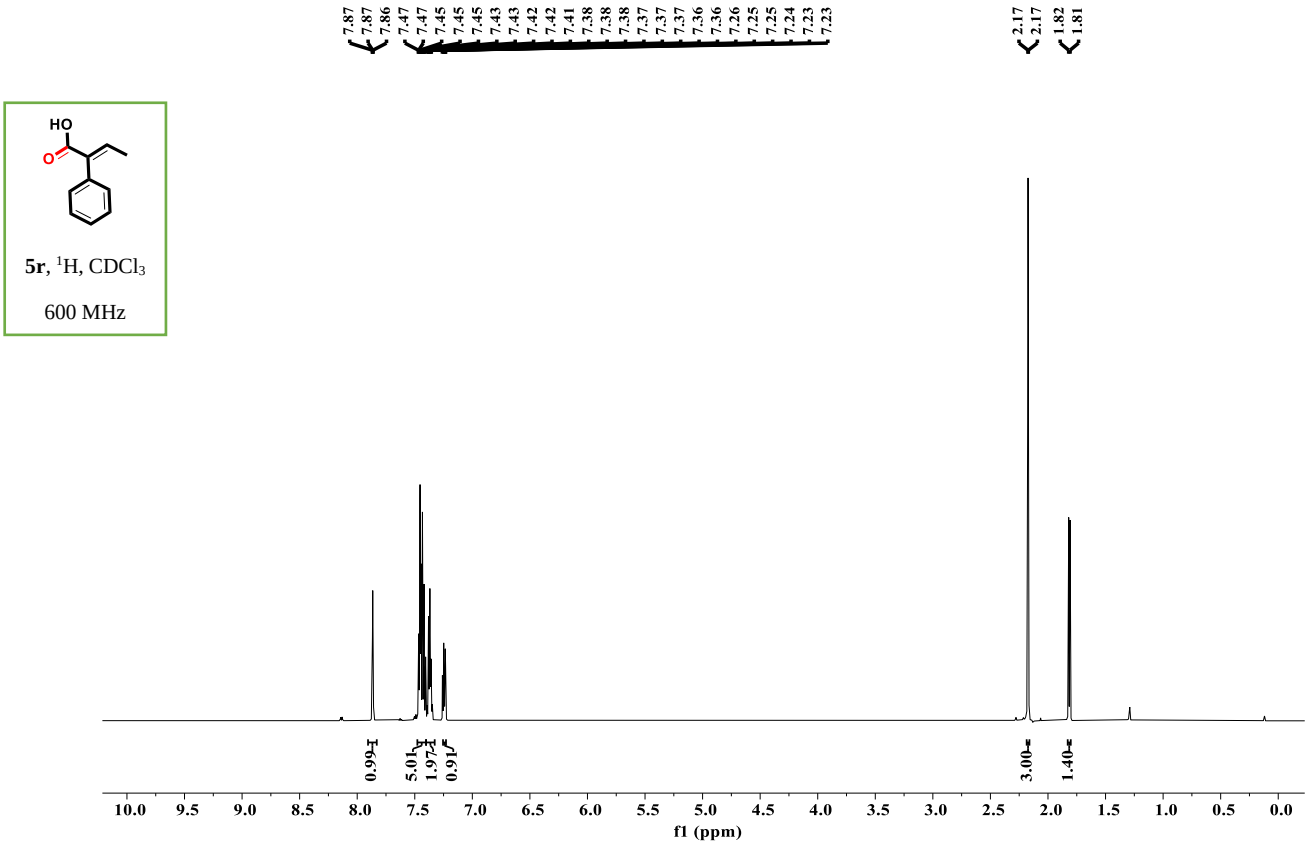


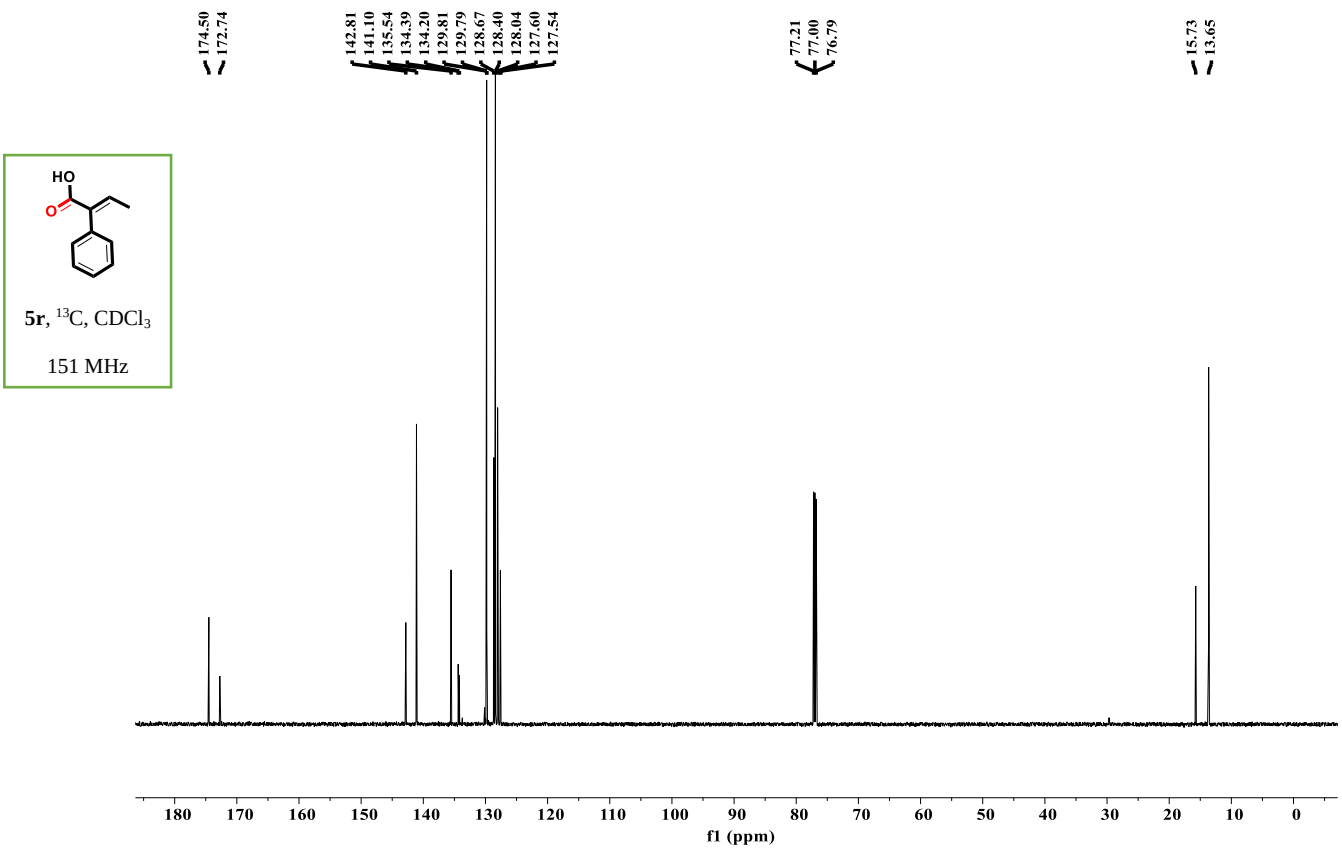
5q, ^{1}H, $CDCl_3$

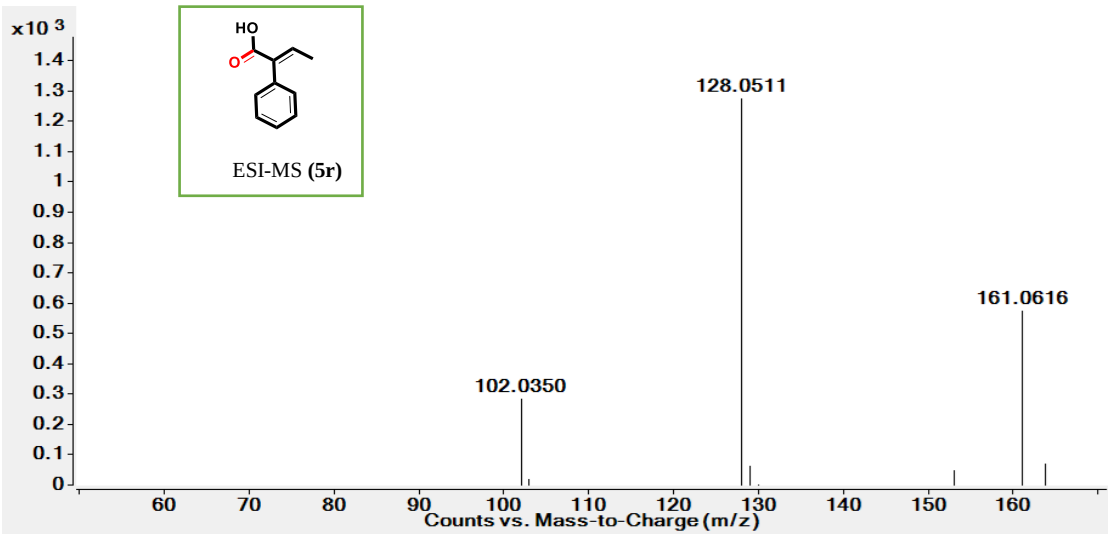
500 MHz


172.65
165.65
142.40
128.73
77.25
77.00
76.75
60.84
14.05
13.79
OH
O
O
O
5q, 13C, CDCl3
126 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

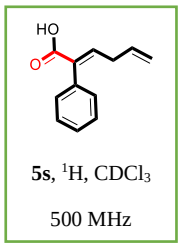

OH
O
O
O
ESI-MS (5q)
x10 4
2.5
2
1.5
1
0.5
0
157.0511
111.0086
147.0810
55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170
Counts vs. Mass-to-Charge (m/z)

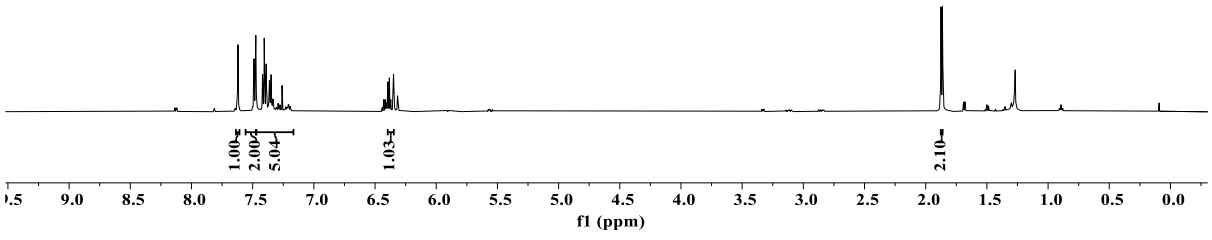

7.87
7.87
7.86
7.47
7.47
7.45
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.26
7.25
7.25
7.24
7.23
7.23
2.17
2.17
1.82
1.81
HO
O
5r, 1H, CDCl3
600 MHz
0.99
5.01
1.97
0.91
3.00
1.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

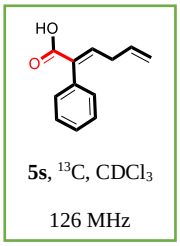

174.50
172.74
142.81
141.10
135.54
134.39
134.20
129.81
129.79
128.67
128.40
128.04
127.60
127.54
77.21
77.00
76.79
15.73
13.65
HO
O
5r, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


x10 3
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
HO
O
ESI-MS (5r)
128.0511
161.0616
102.0350
60
70
80
90
100
110
120
130
140
150
160
Counts vs. Mass-to-Charge (m/z)


7.62
7.49
7.47
7.42
7.40
7.39
7.37
7.36
7.35
7.33
7.33
7.29
7.28
7.26
7.22
7.21
7.19
6.40
6.38
6.35
1.88
1.86

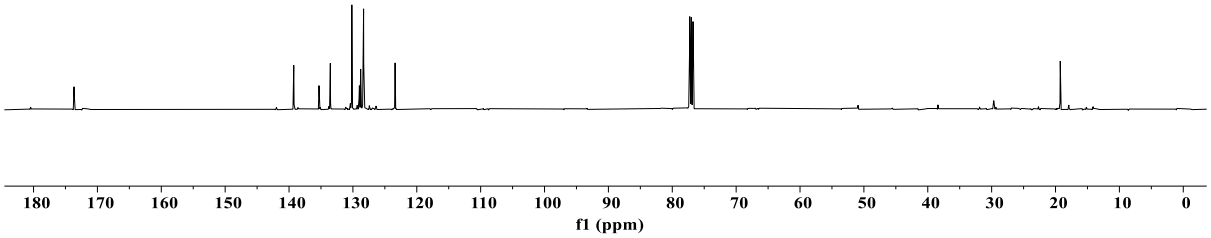

HO
O
5s, 1H, CDCl3
500 MHz

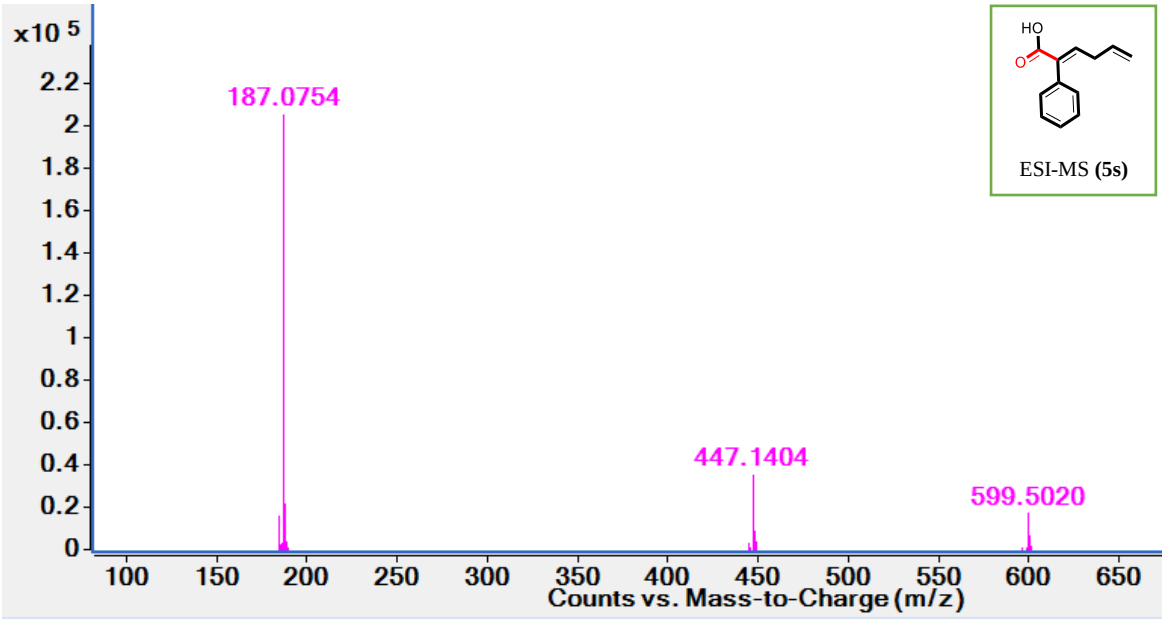

1.00
2.00
5.04
1.03
2.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



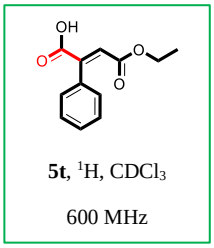
5s, ^{13}C, $CDCl_3$

126 MHz



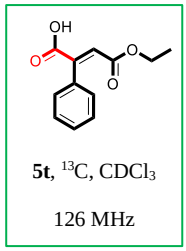


ESI-MS **(5s)**



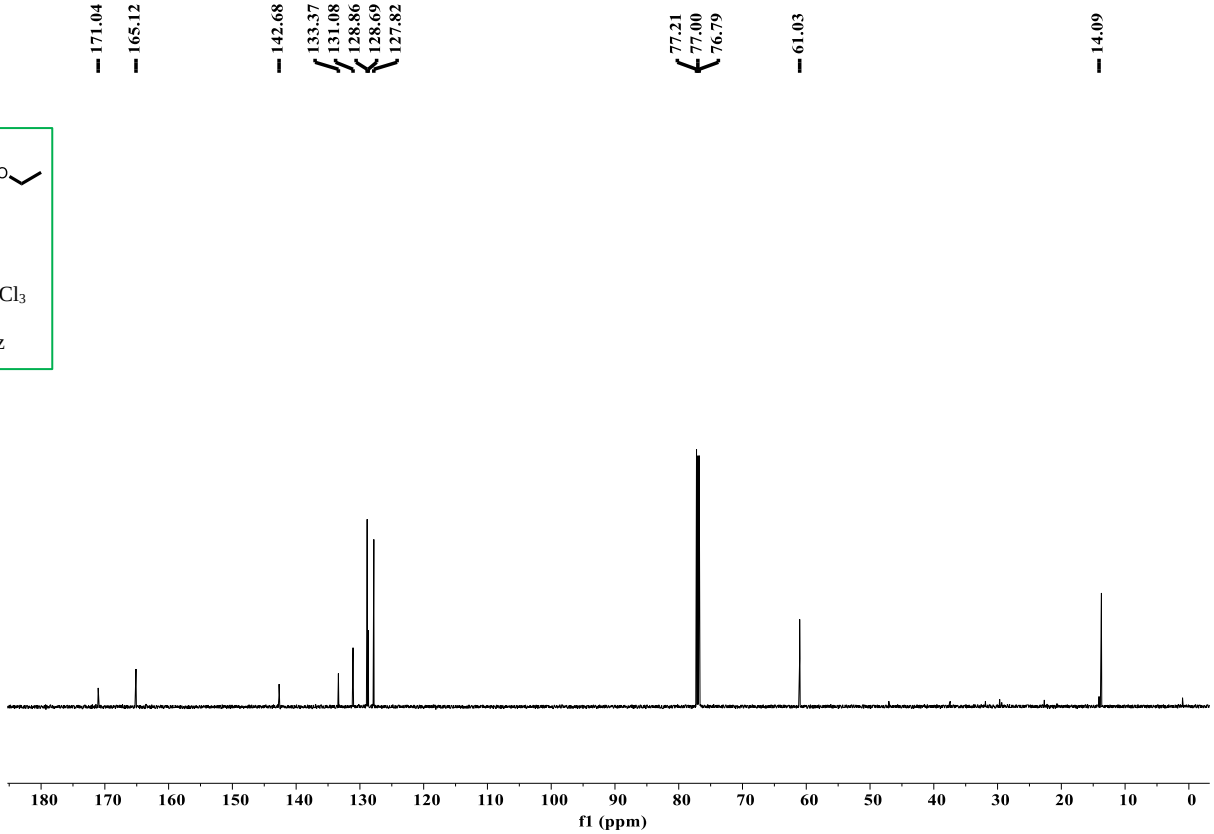
5t, ^{1}H, $CDCl_3$

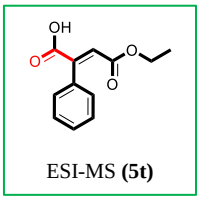
600 MHz



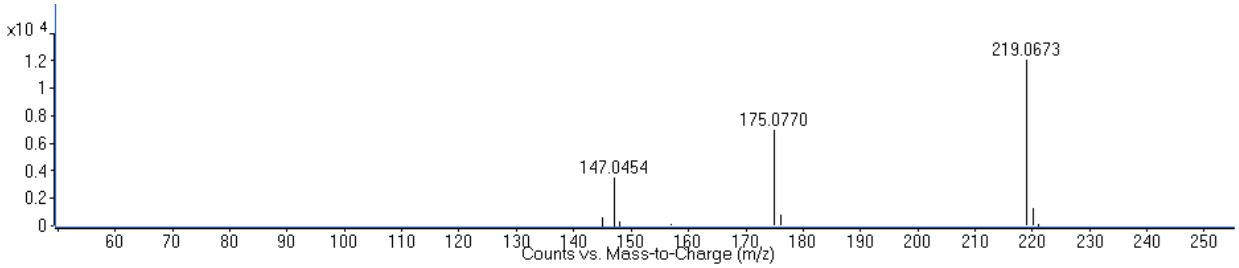
5t, ^{13}C, $CDCl_3$

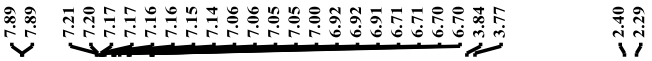
126 MHz

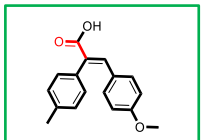




ESI-MS **(5t)**

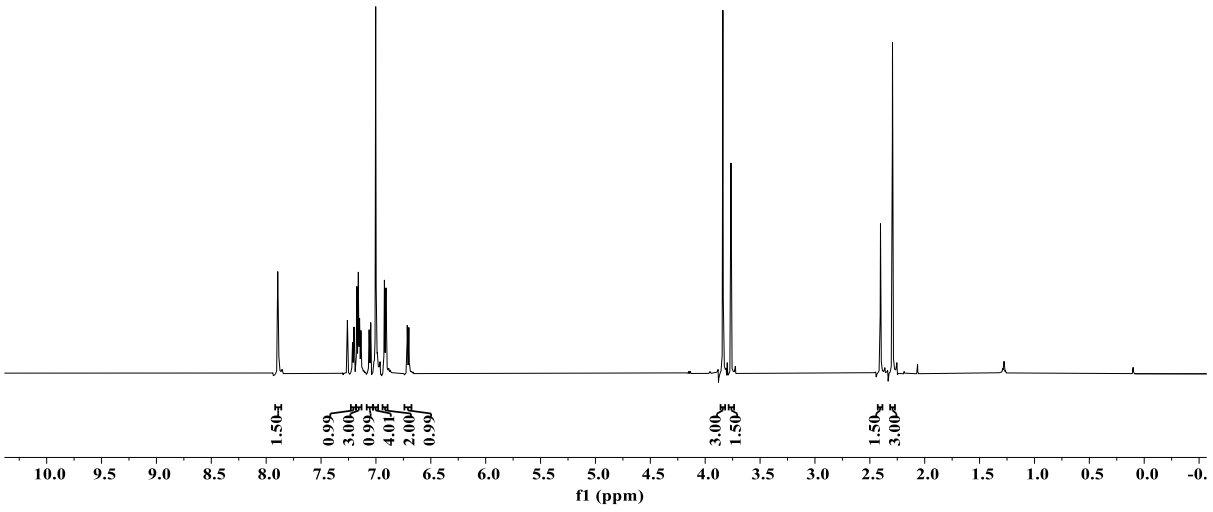


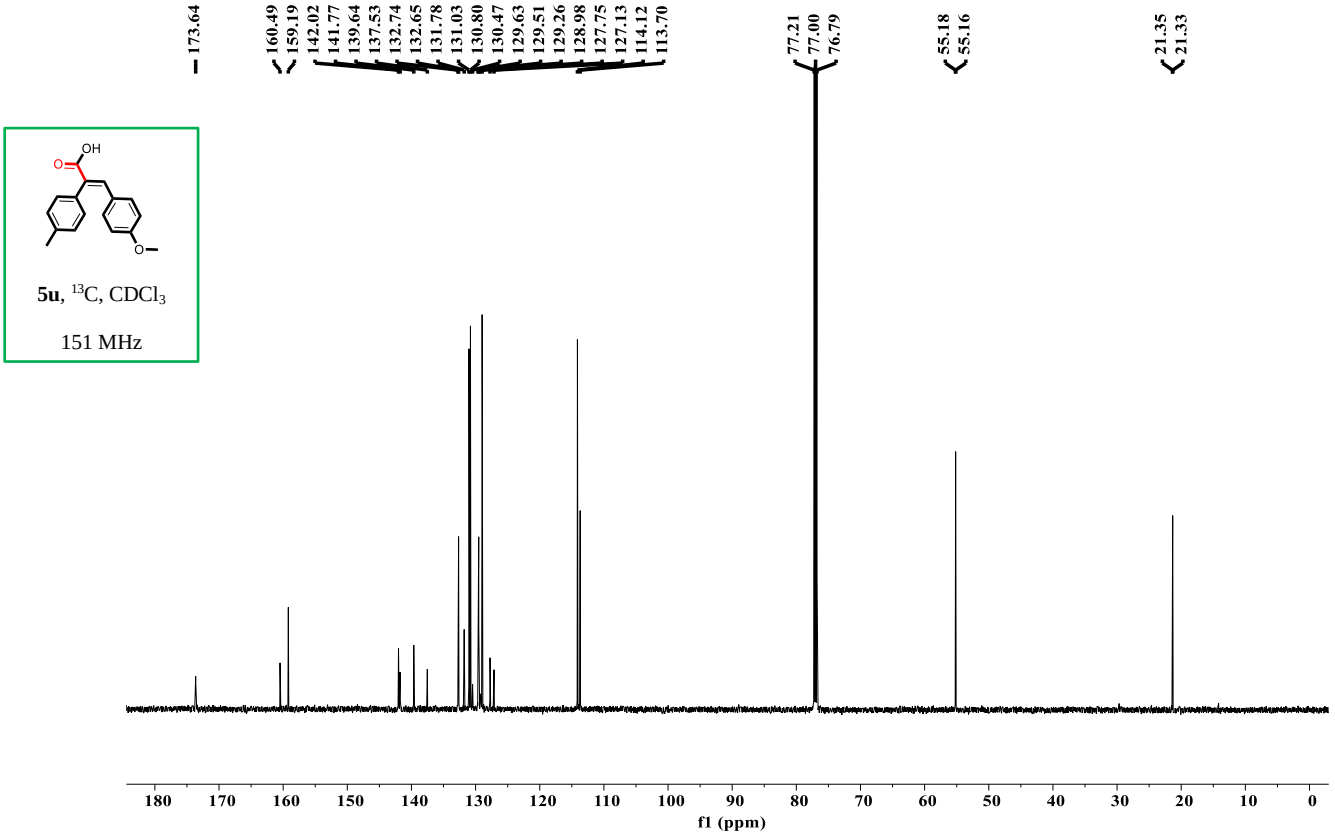


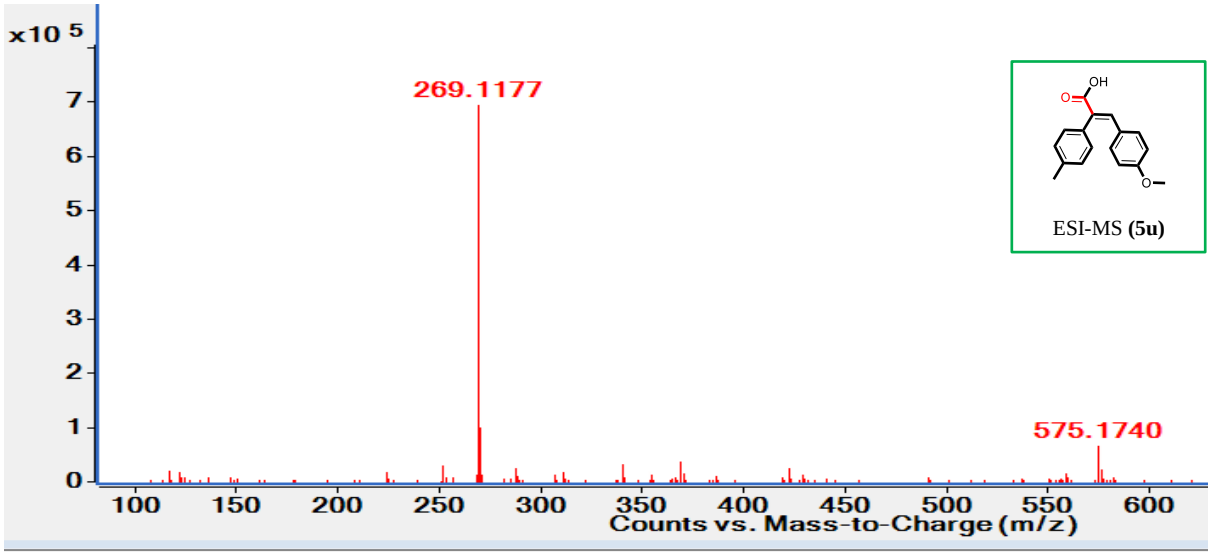


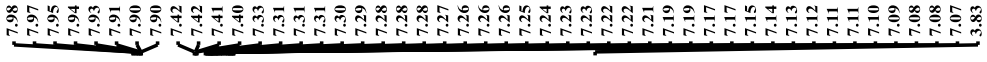
5u, ^{1}H, $CDCl_3$

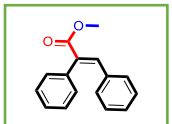
600 MHz




173.64
160.49
159.19
142.02
141.77
139.64
137.53
132.74
132.65
131.78
131.03
130.80
130.47
129.63
129.51
129.26
128.98
127.75
127.13
114.12
113.70
77.21
77.00
76.79
55.18
55.16
21.35
21.33
OH
O
O
5u, 13C, CDCl3
151 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

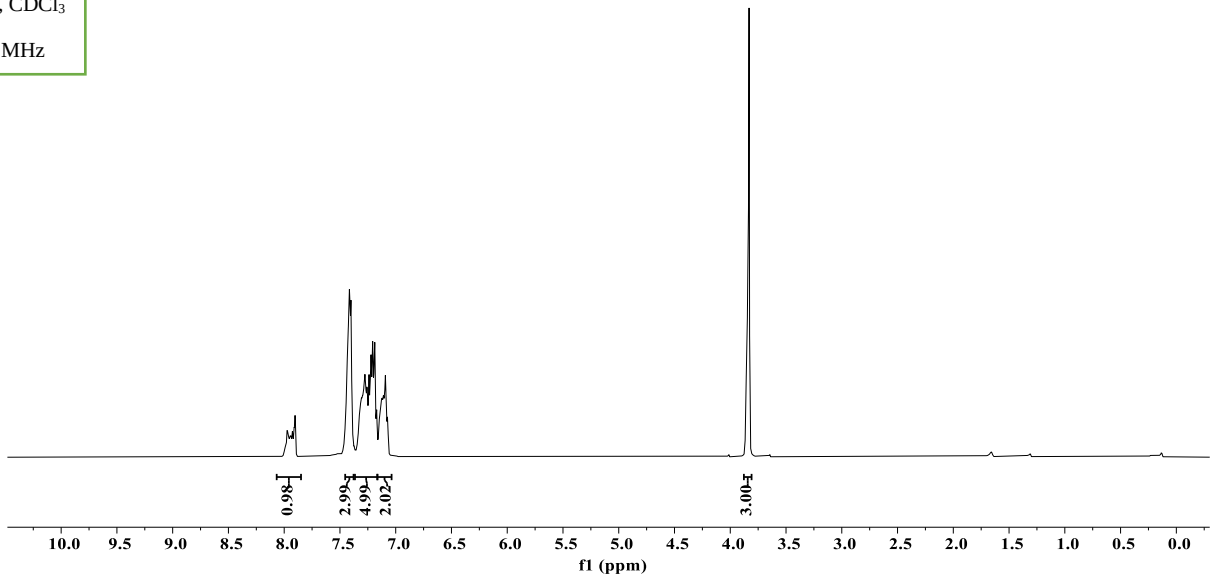

x10 5
7
6
5
4
3
2
1
0
269.1177
575.1740
100 150 200 250 300 350 400 450 500 550 600
Counts vs. Mass-to-Charge (m/z)
OH
O
O
ESI-MS (5u)

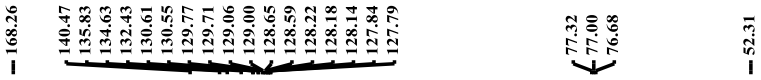


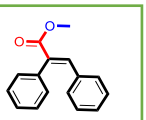


7a, ^{1}H, $CDCl_3$

400 MHz

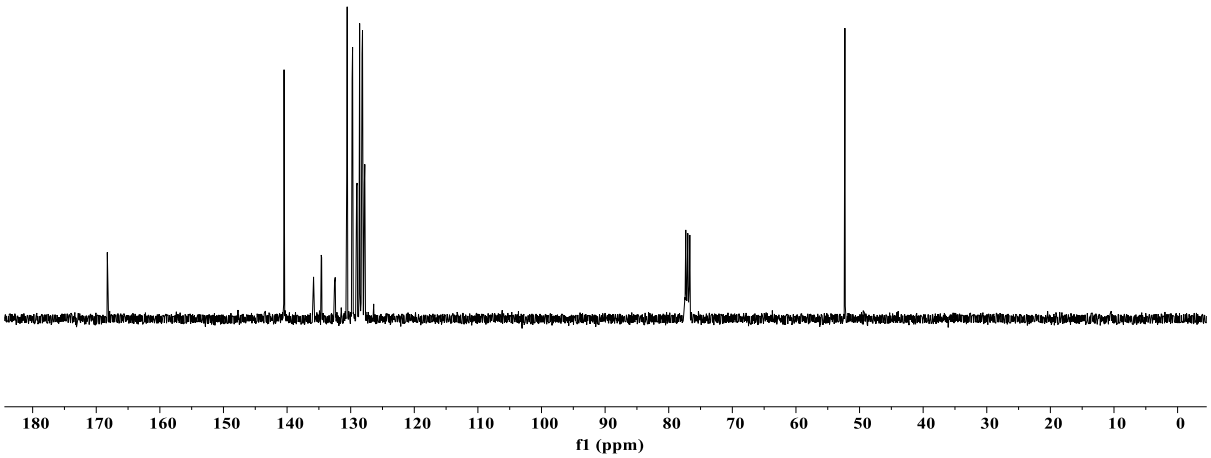


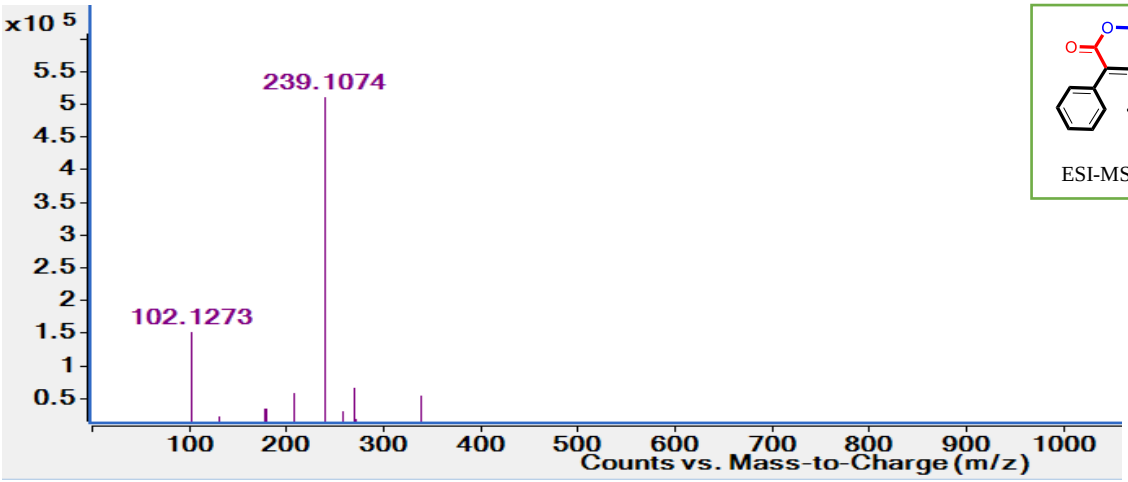




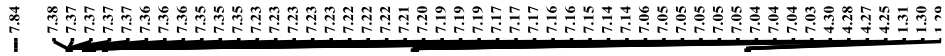
7a, ^{13}C, $CDCl_3$

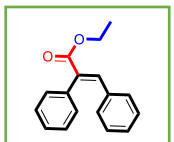
101 MHz





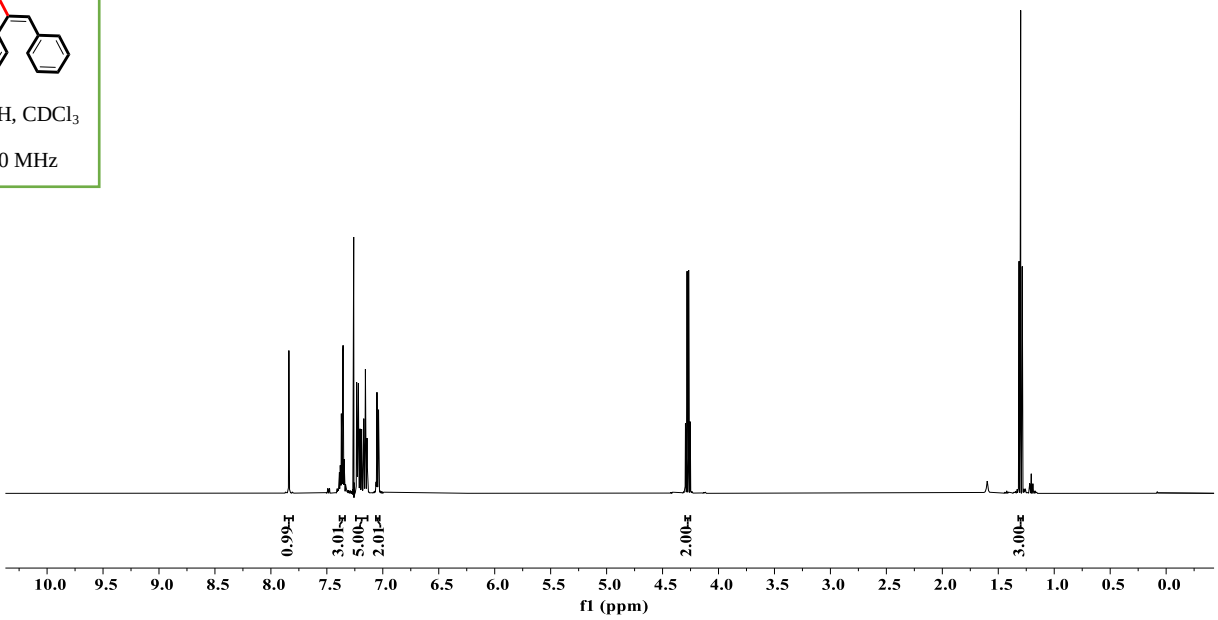
ESI-MS **(7a)**

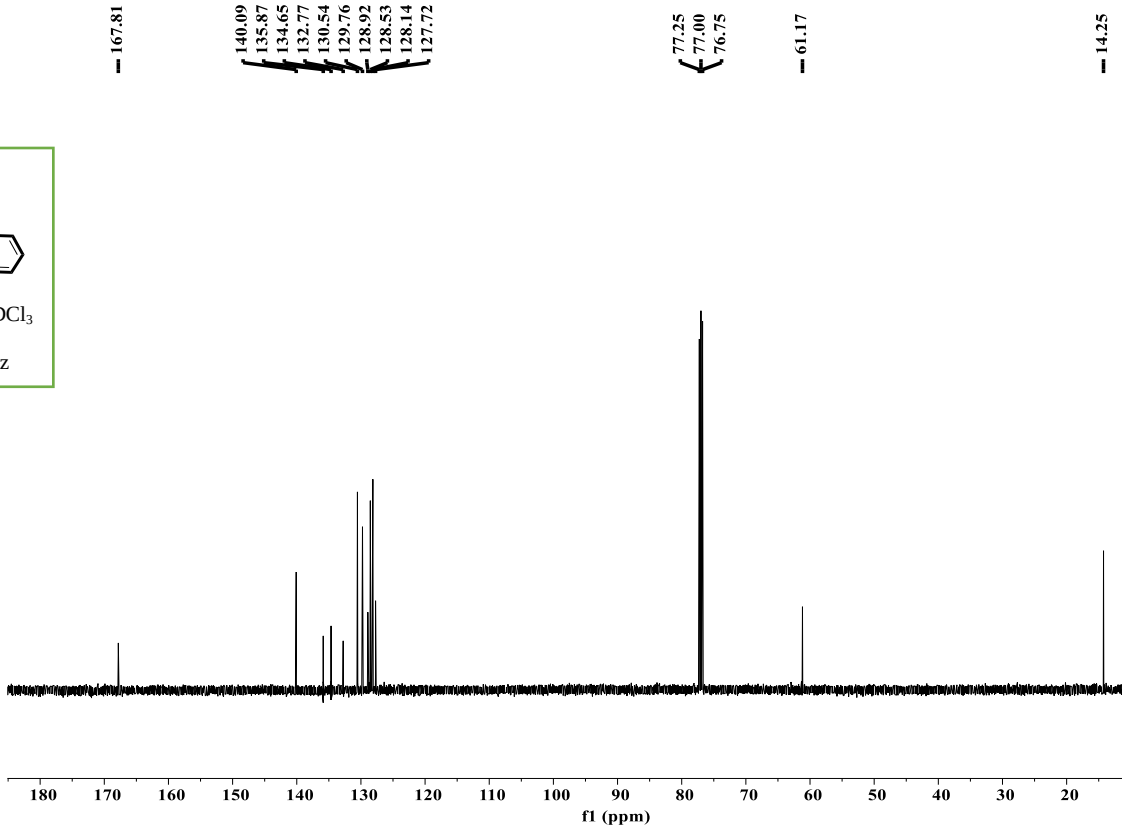


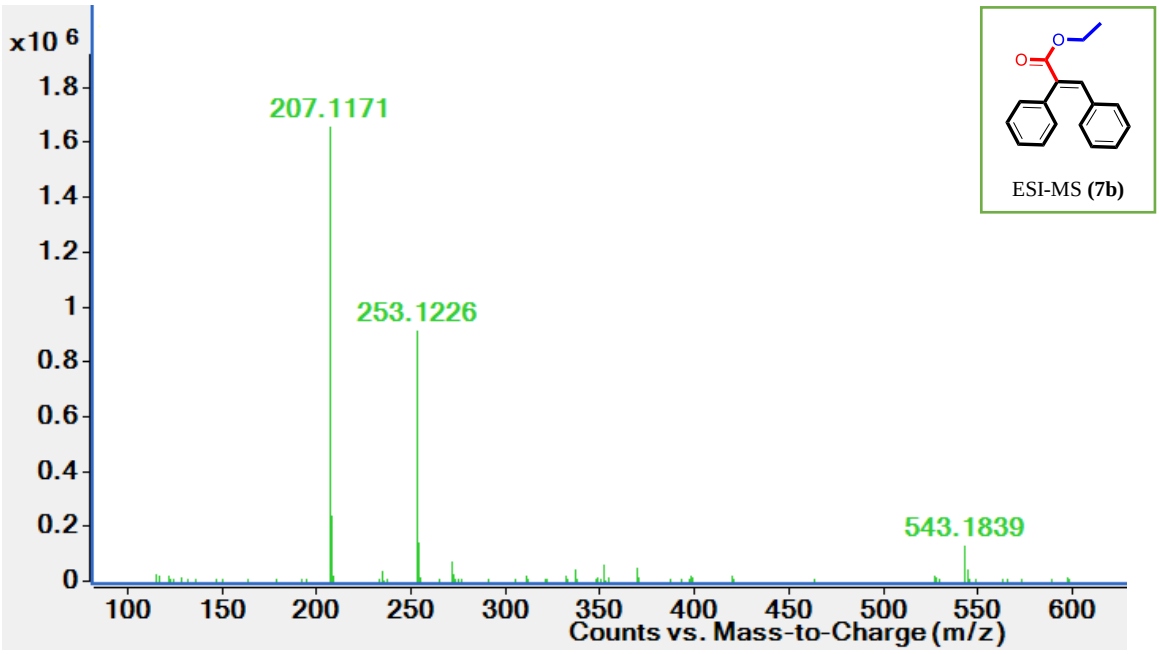


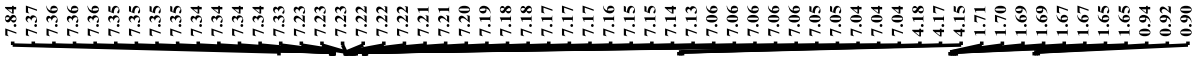
7b, ^{1}H, $CDCl_3$

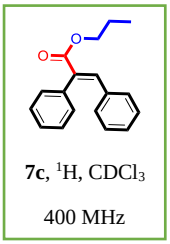
500 MHz




167.81
140.09
135.87
134.65
132.77
130.54
129.76
128.92
128.53
128.14
127.72
77.25
77.00
76.75
61.17
14.25
7b, 13C, CDCl3
126 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

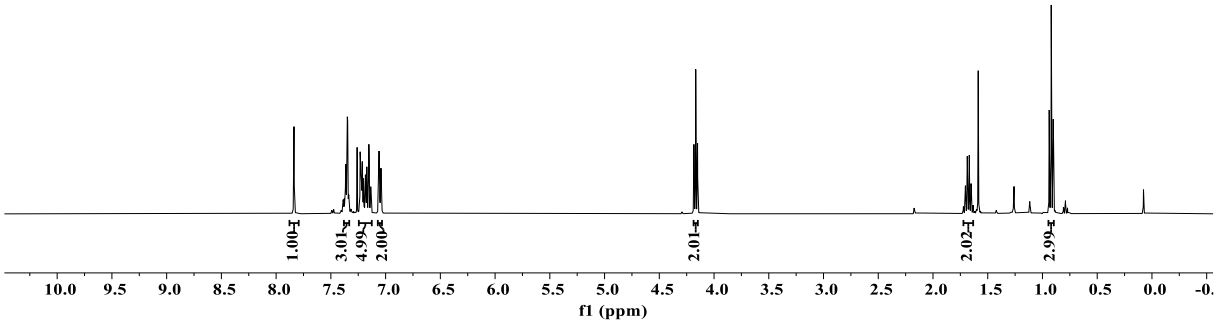

x10 6
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
207.1171
253.1226
543.1839
100 150 200 250 300 350 400 450 500 550 600
Counts vs. Mass-to-Charge (m/z)
ESI-MS (7b)

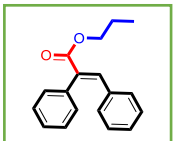




7c, ^{1}H, $CDCl_3$

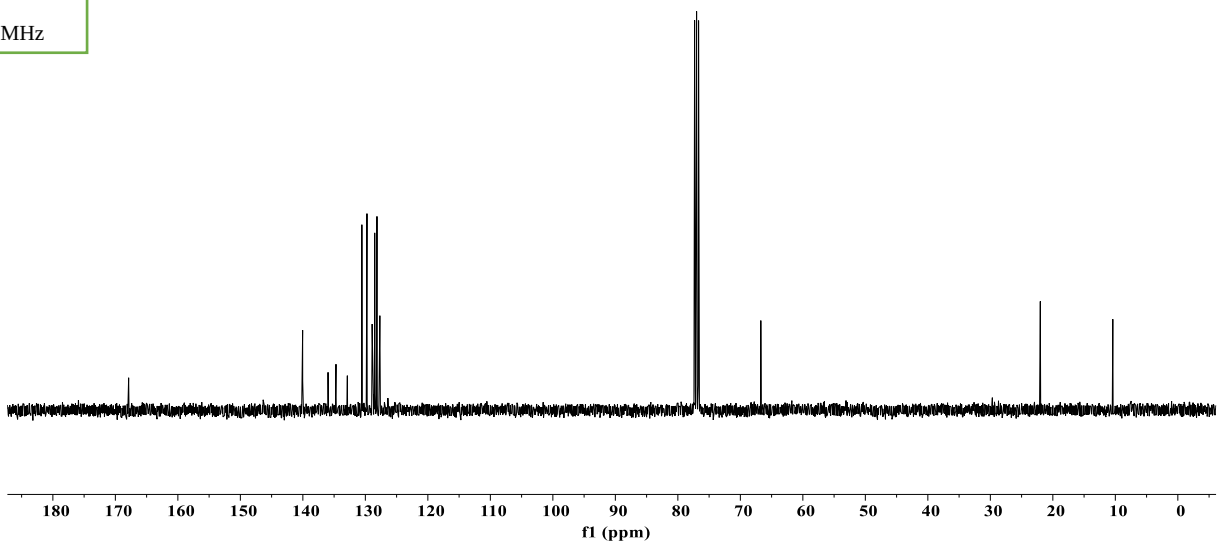
400 MHz

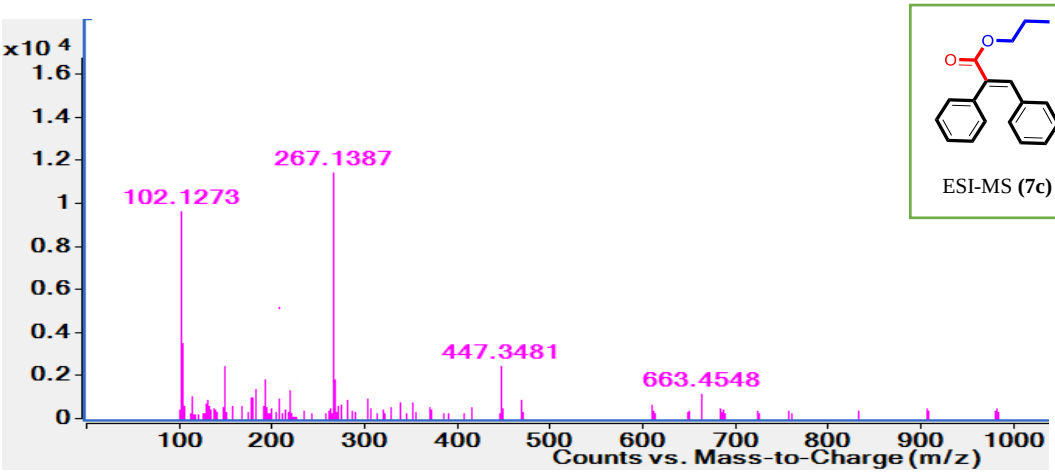




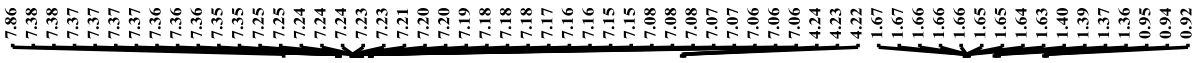
7c, ^{13}C, $CDCl_3$

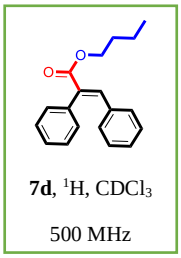
101 MHz





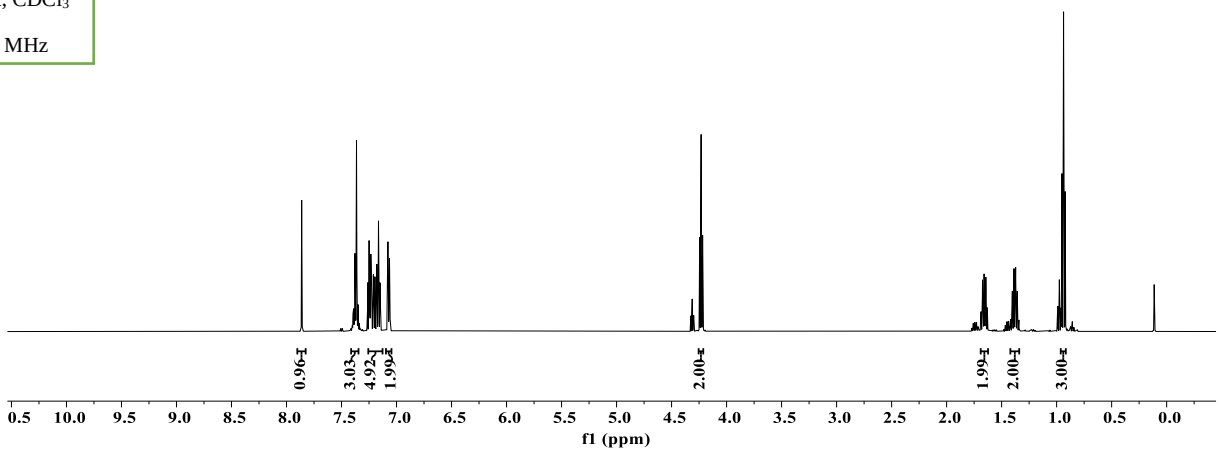
ESI-MS **(7c)**

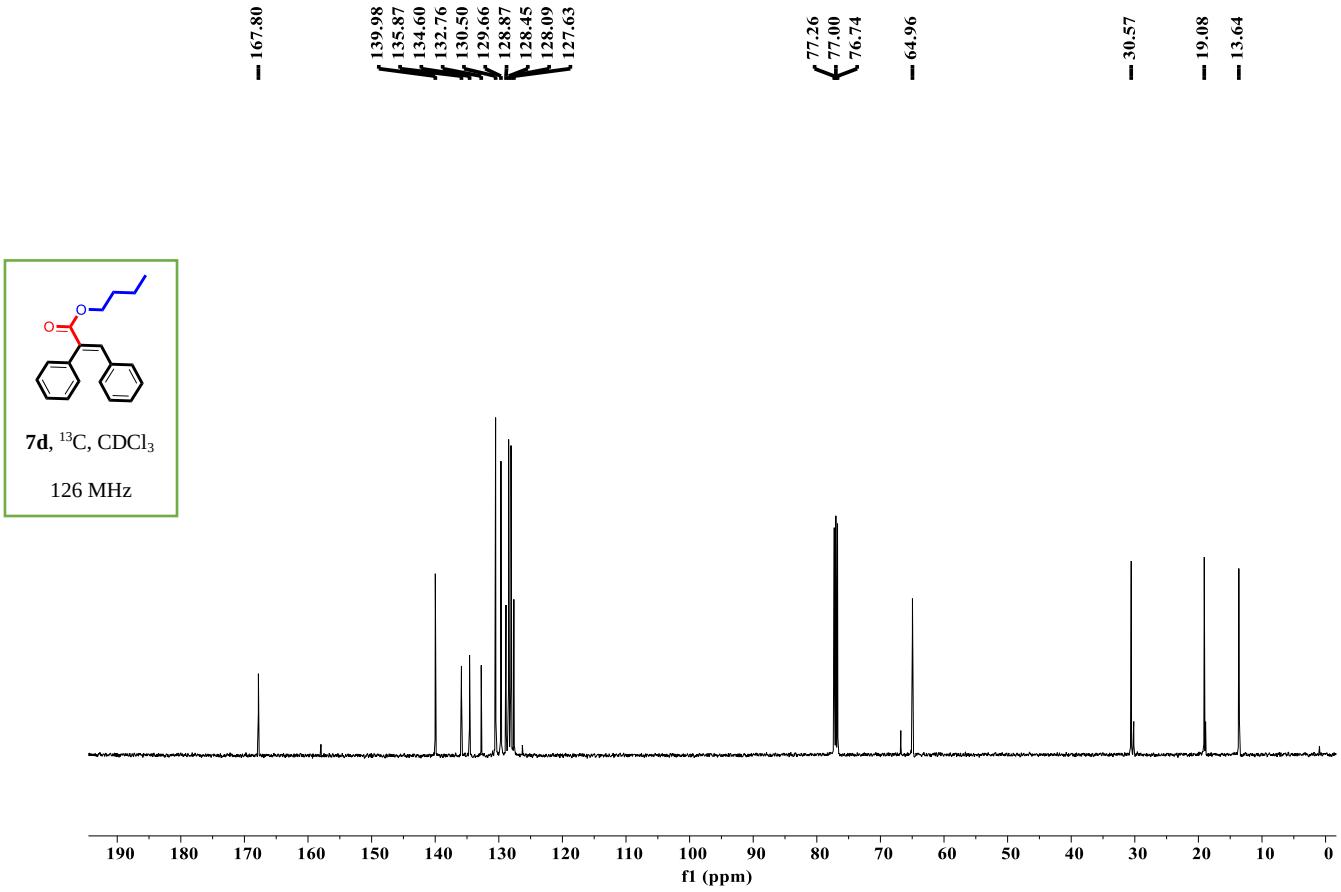


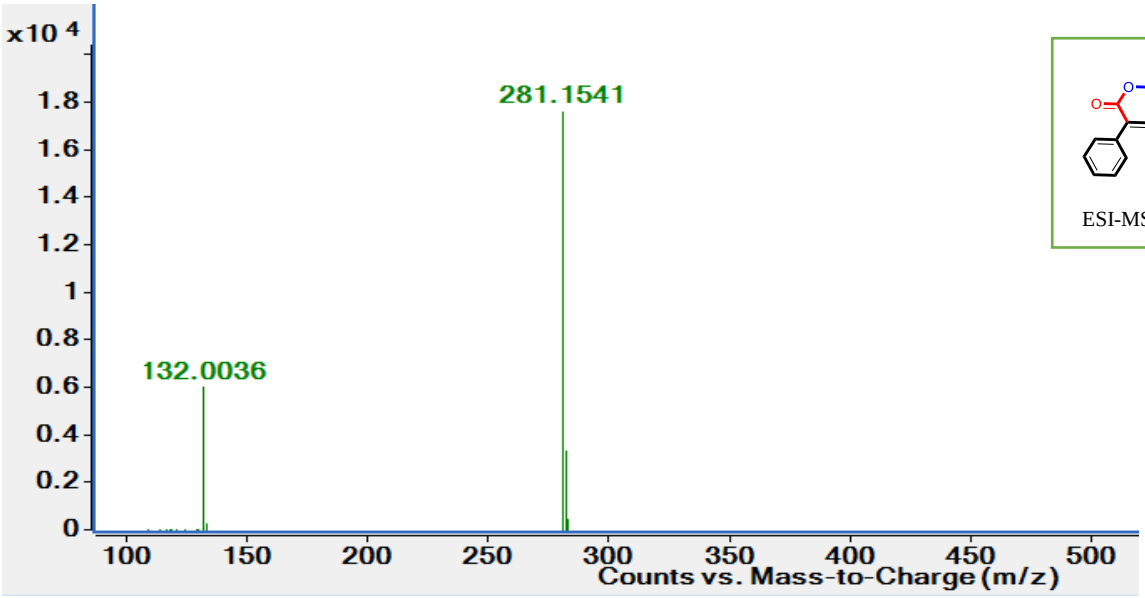


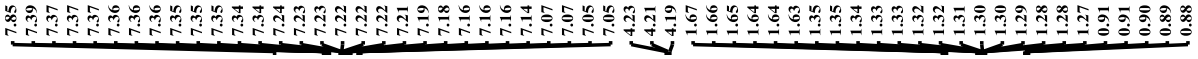
7d, ^{1}H, $CDCl_3$

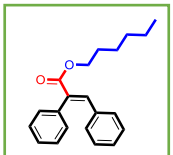
500 MHz




167.80
139.98
135.87
134.60
132.76
130.50
129.66
128.87
128.45
128.09
127.63
77.26
77.00
76.74
64.96
30.57
19.08
13.64
7d, 13C, CDCl3
126 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

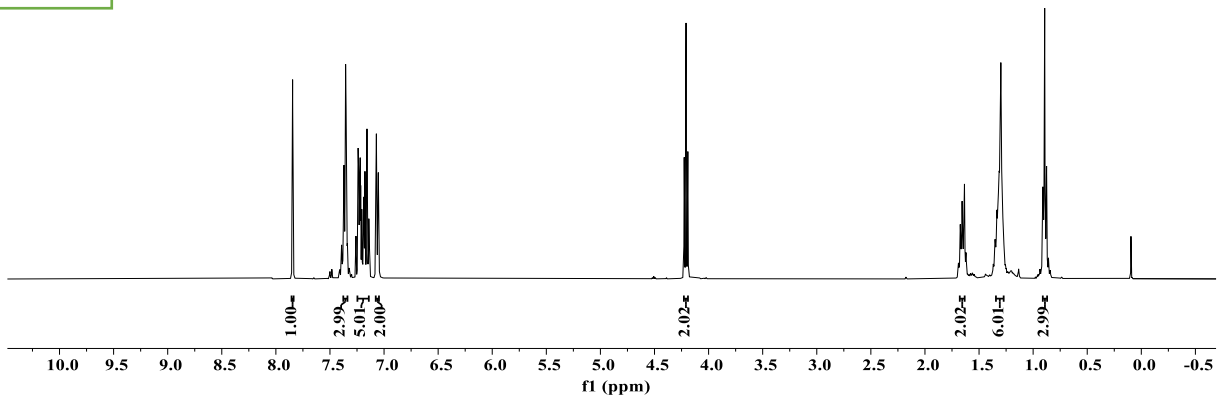

x10 4
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
281.1541
132.0036
100 150 200 250 300 350 400 450 500
Counts vs. Mass-to-Charge (m/z)
ESI-MS (7d)

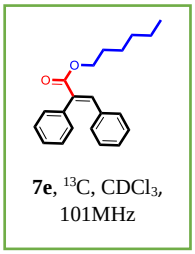




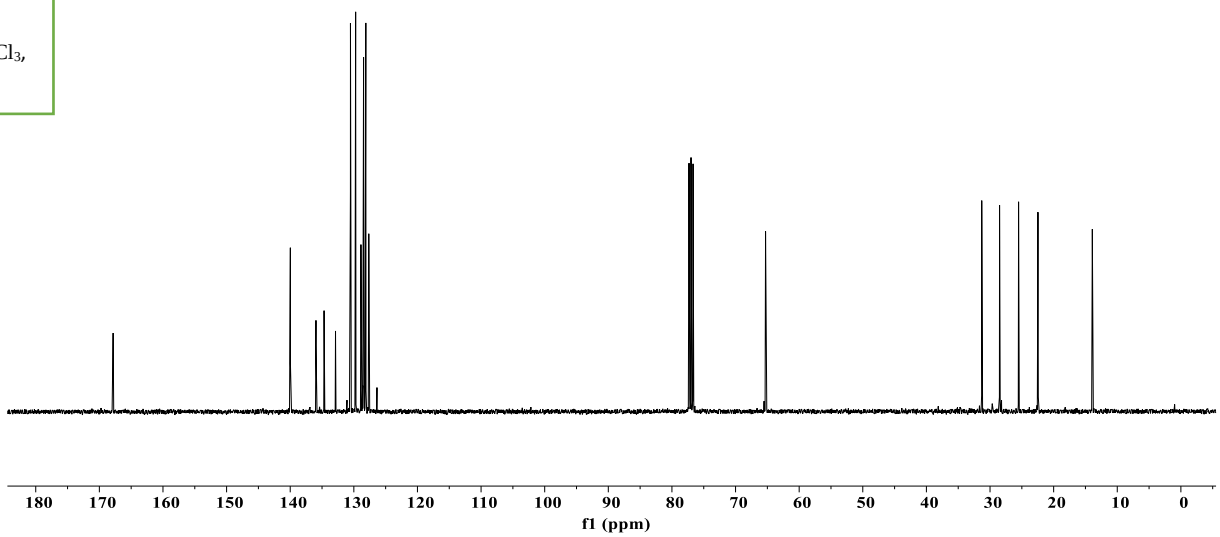
7e, ^{1}H, $CDCl_3$

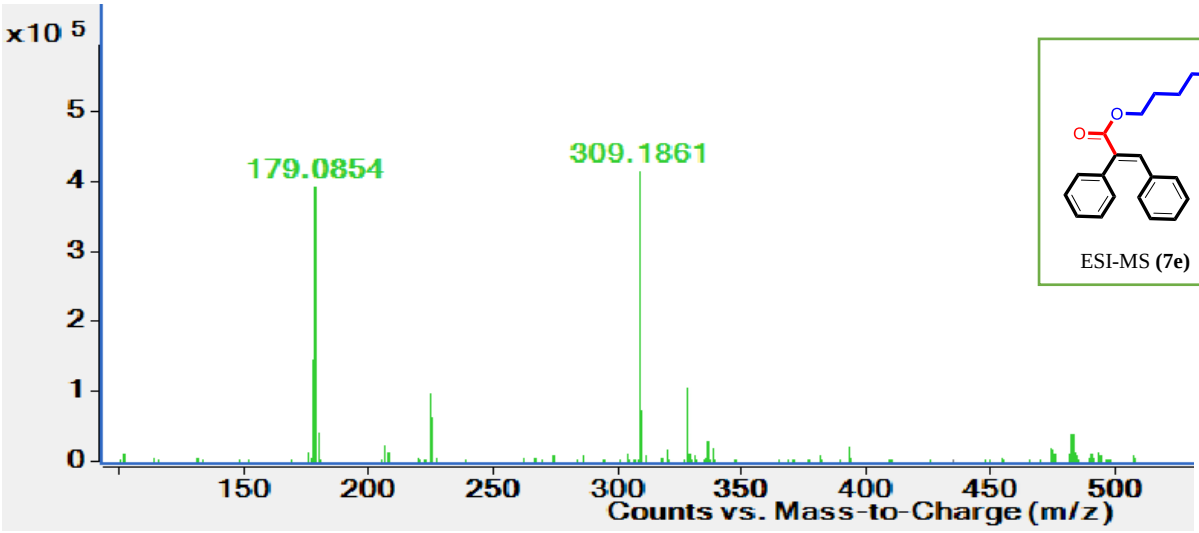
400 MHz



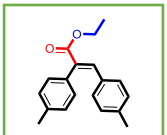


7e, ^{13}C, $CDCl_3$, 101MHz



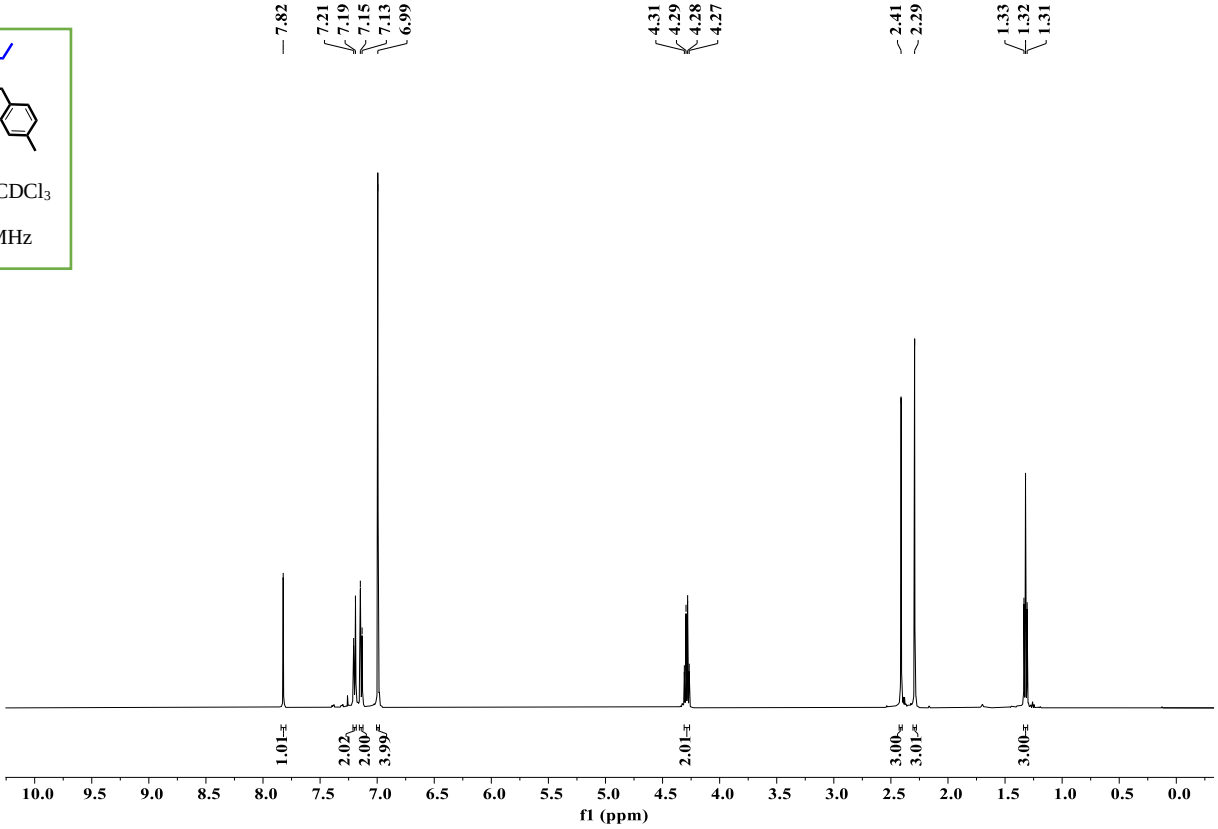


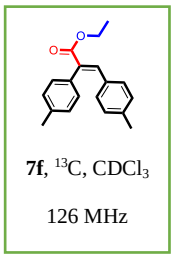
ESI-MS **(7e)**



7f, ^{1}H, $CDCl_3$

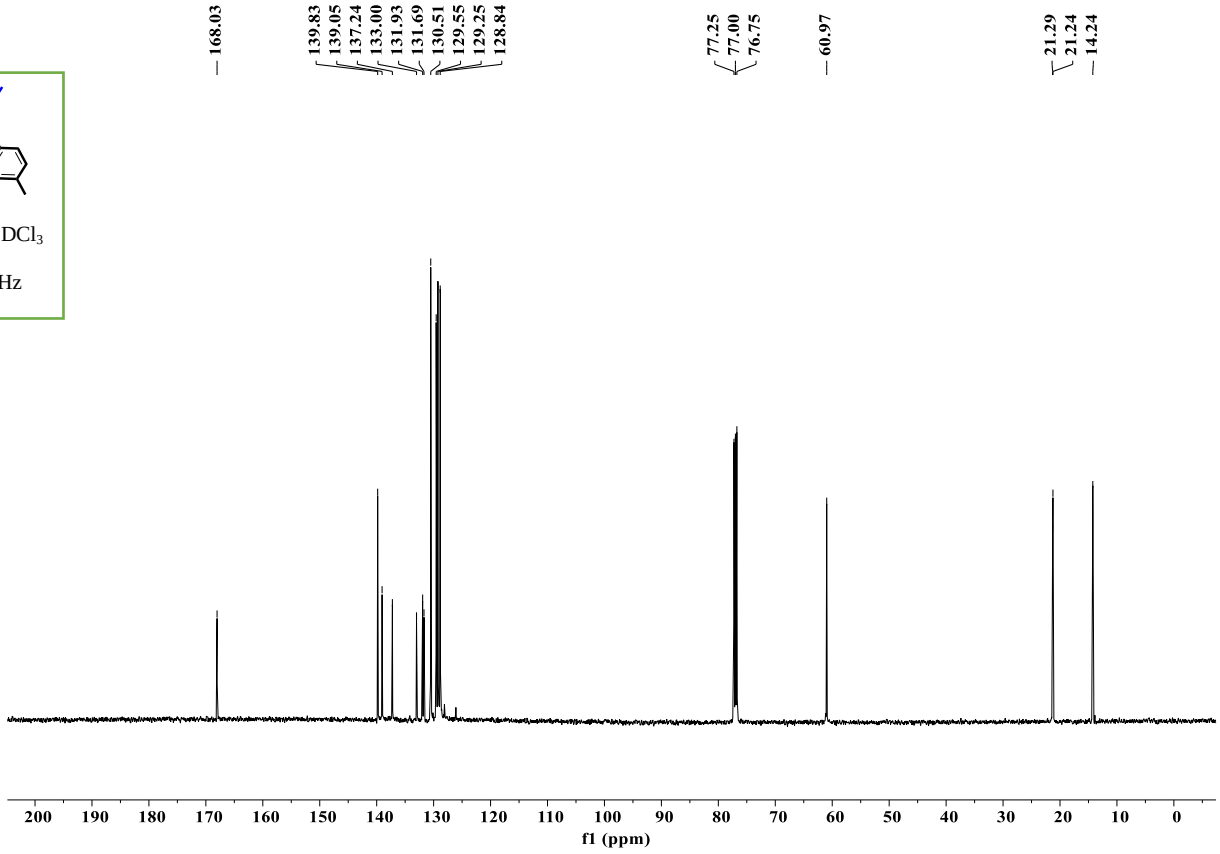
500 MHz

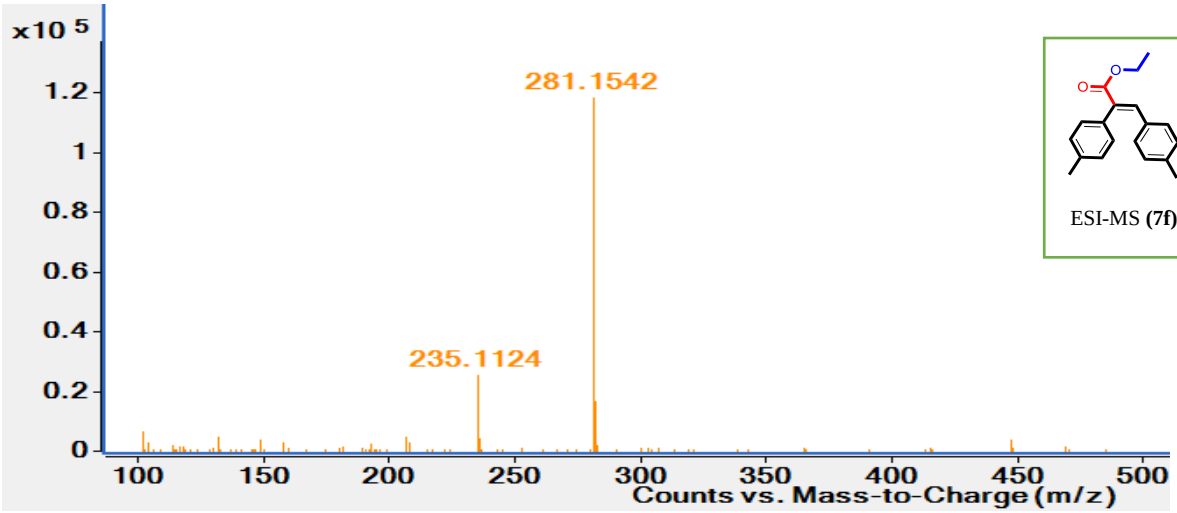




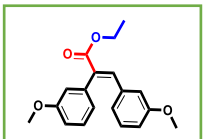
7f, ^{13}C, $CDCl_3$

126 MHz





ESI-MS (**7f**)

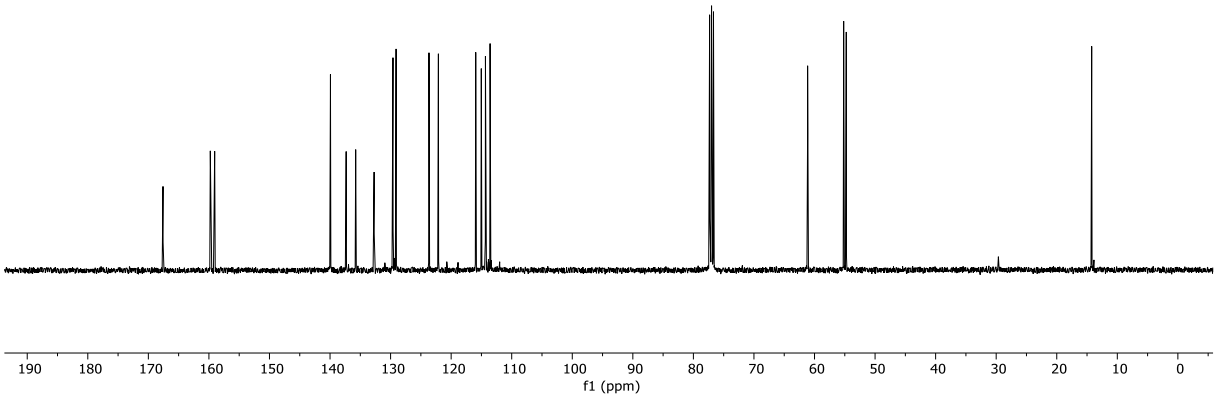


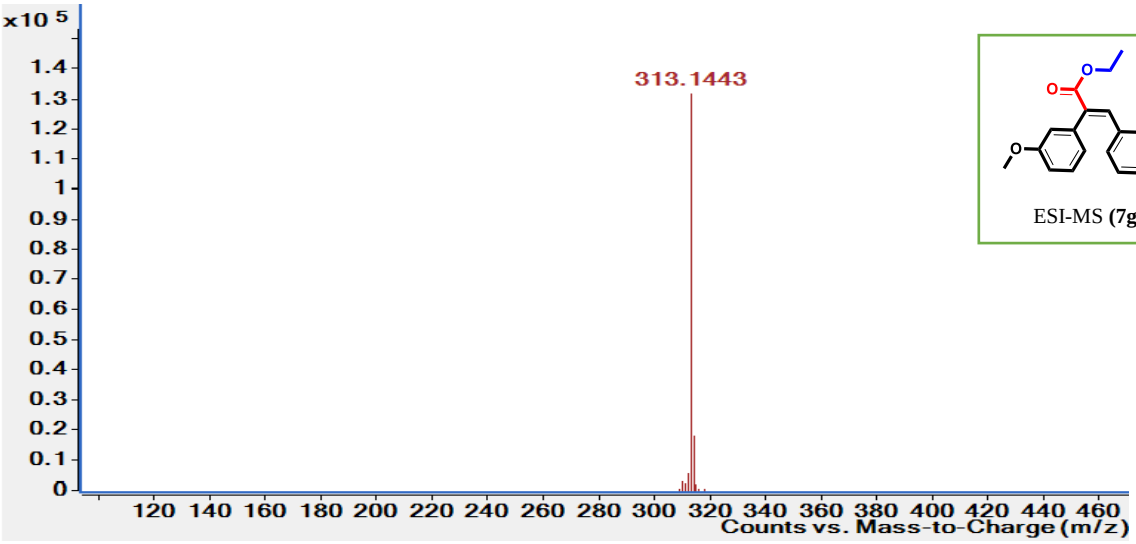
7g, ^{1}H, $CDCl_3$

400 MHz

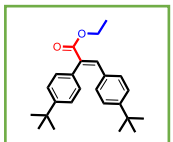
7g, ^{13}C, $CDCl_3$

101 MHz



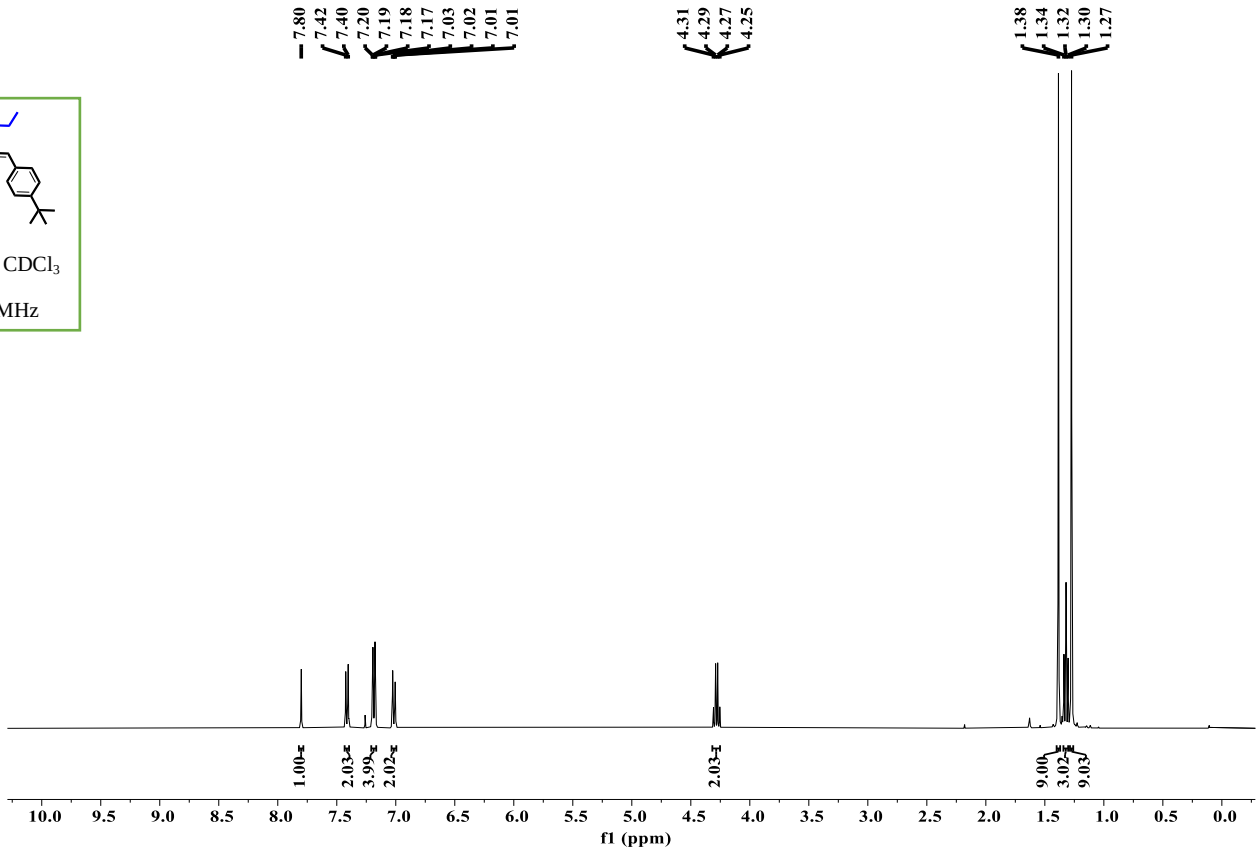


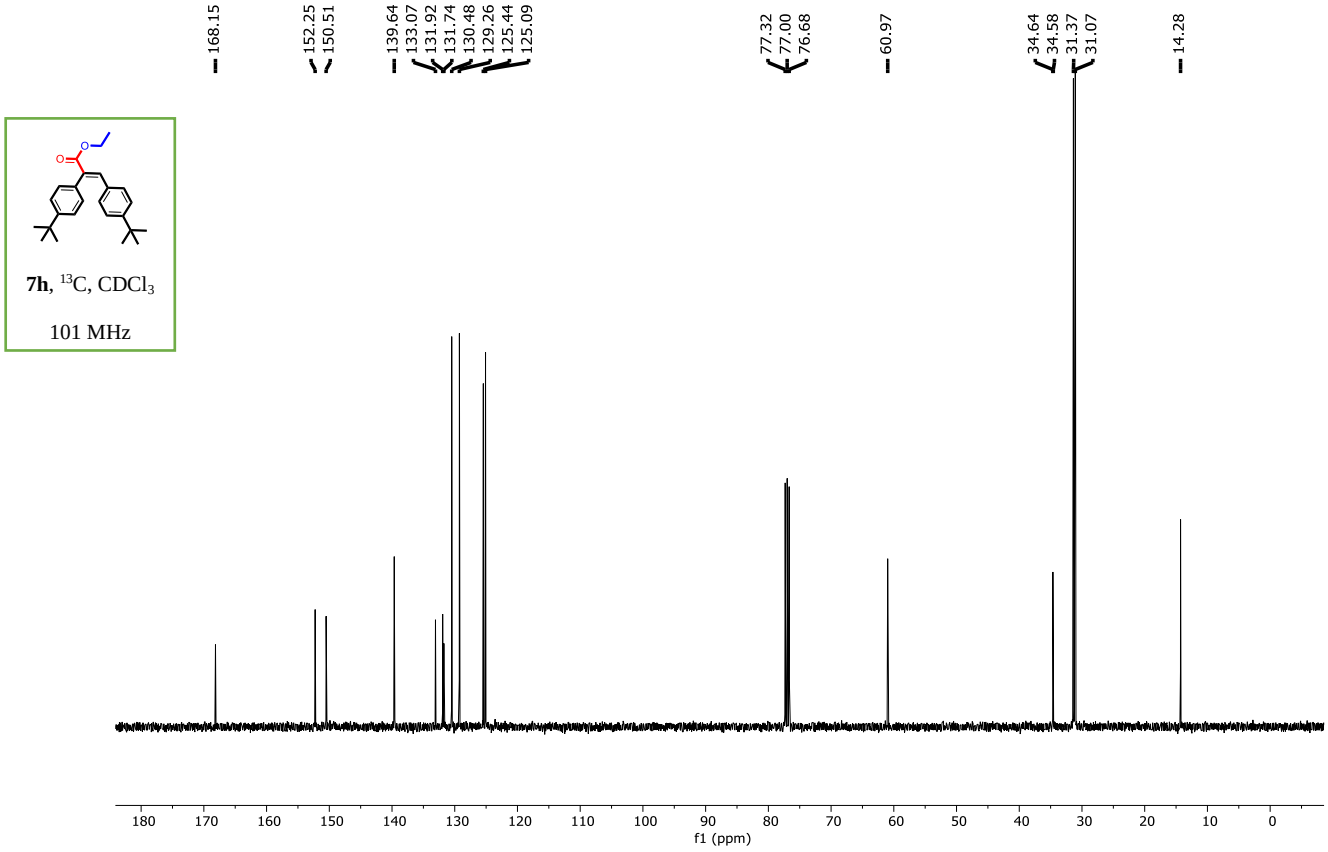
ESI-MS **(7g)**



7h, ^{1}H, $CDCl_3$

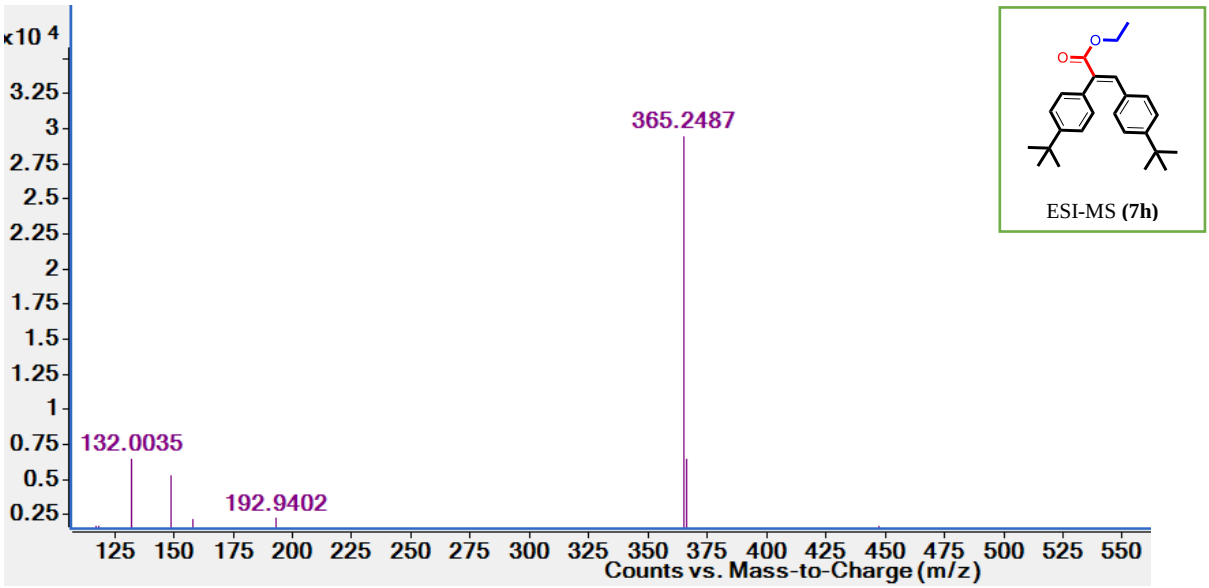
400 MHz



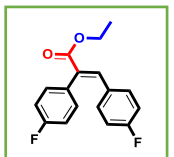


7h, ^{13}C, $CDCl_3$

101 MHz

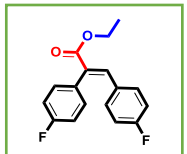


ESI-MS **(7h)**



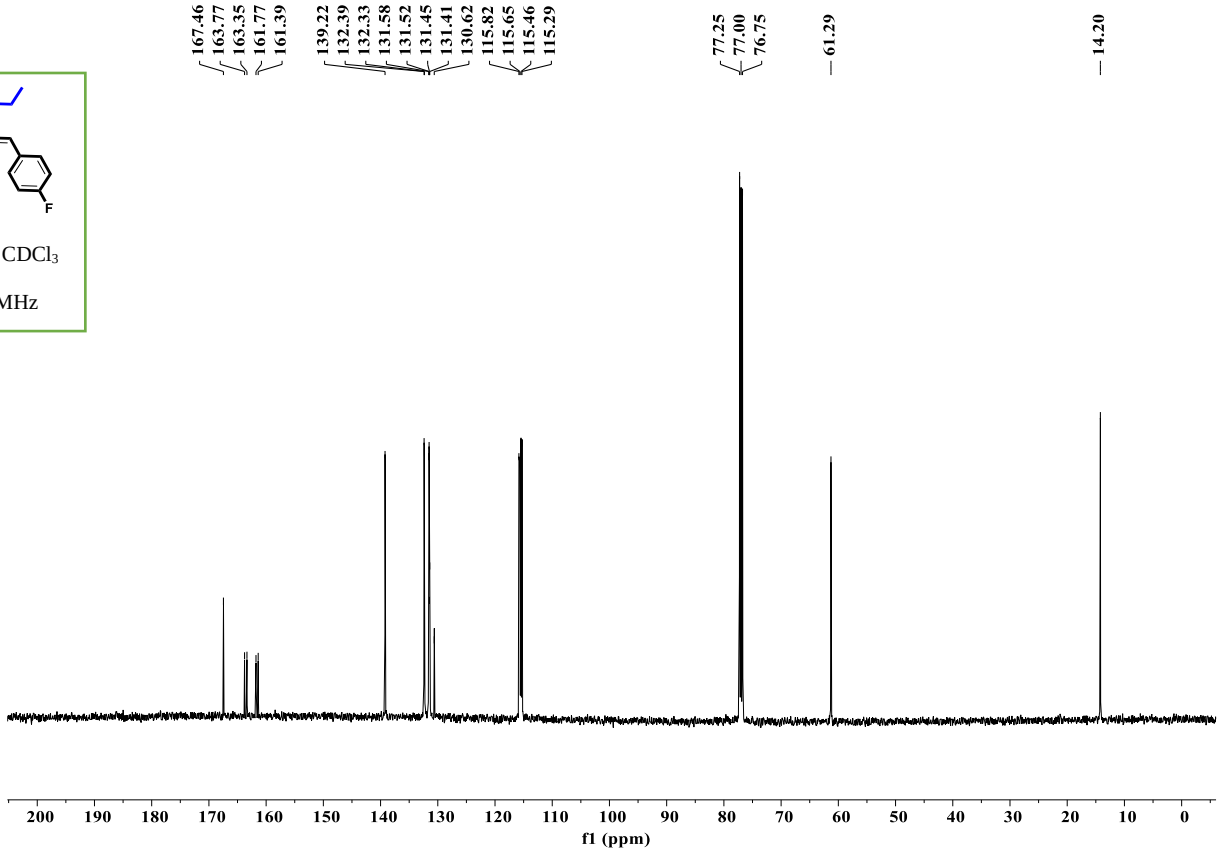
7i, ^{1}H, $CDCl_3$

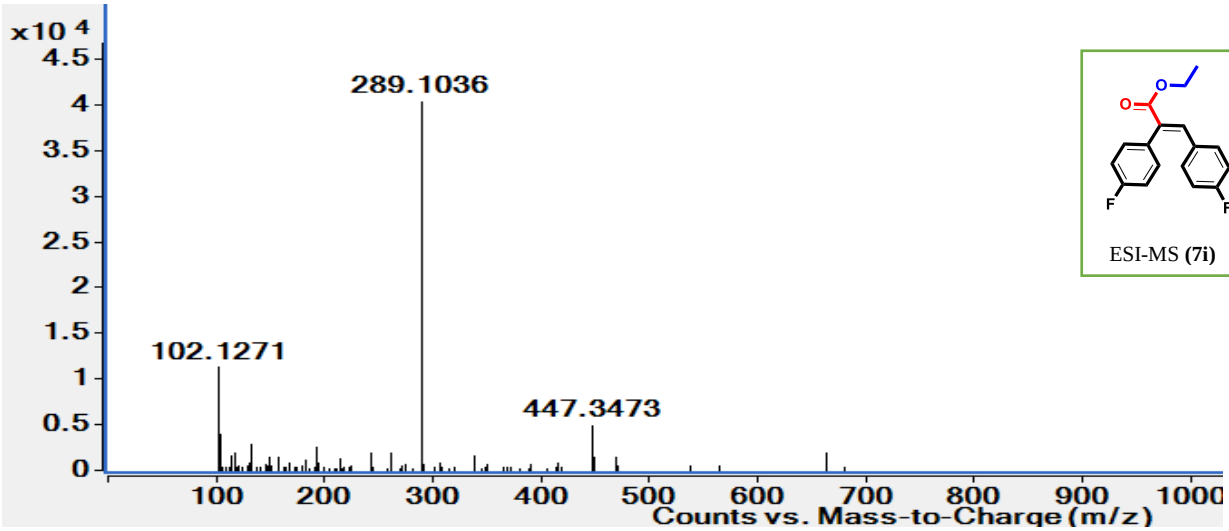
500 MHz



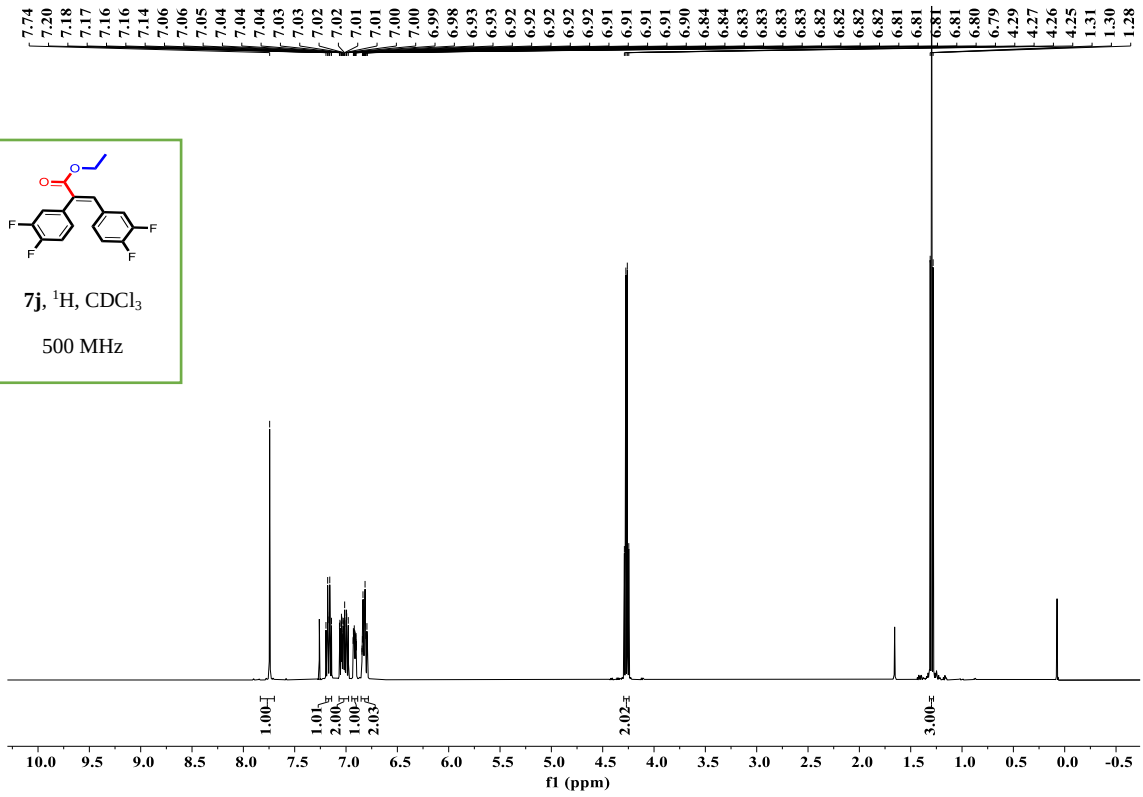
7i, ^{13}C, $CDCl_3$

101 MHz



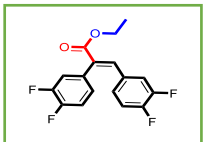


ESI-MS **(7i)**



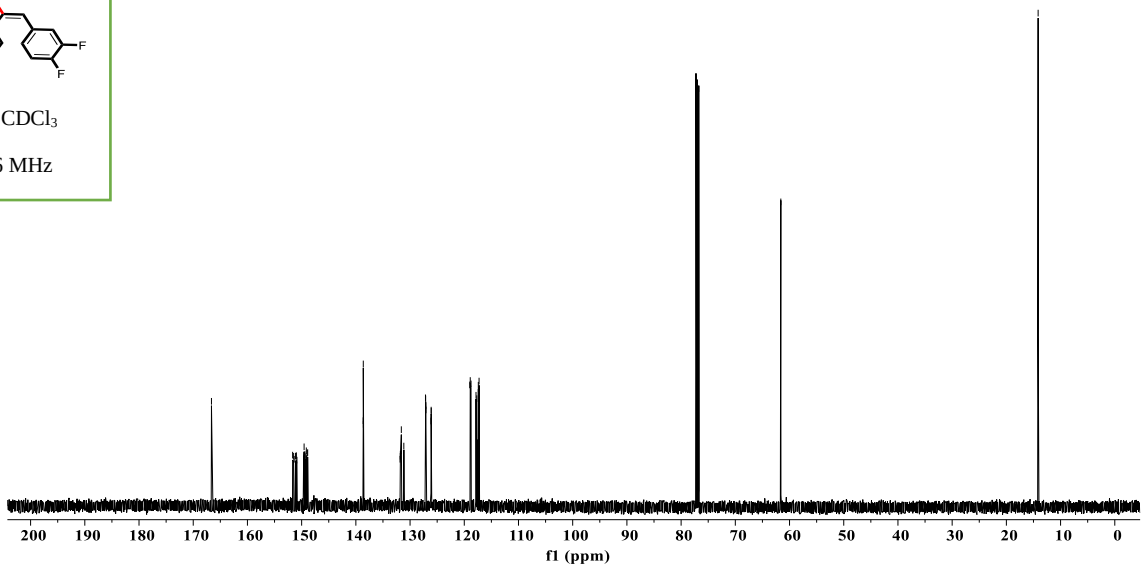
7j, ^{1}H, $CDCl_3$

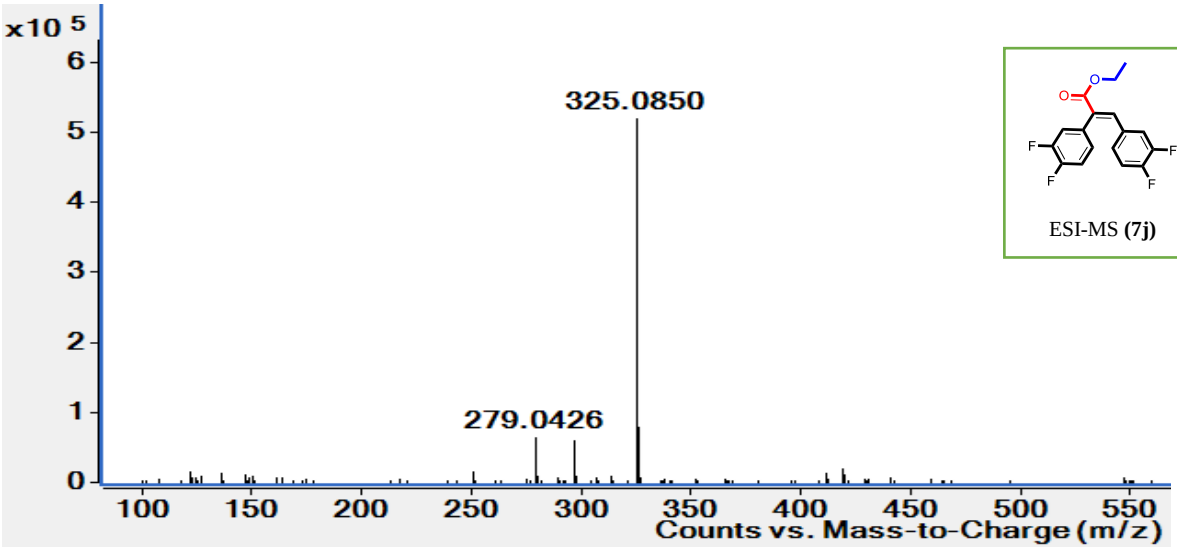
500 MHz



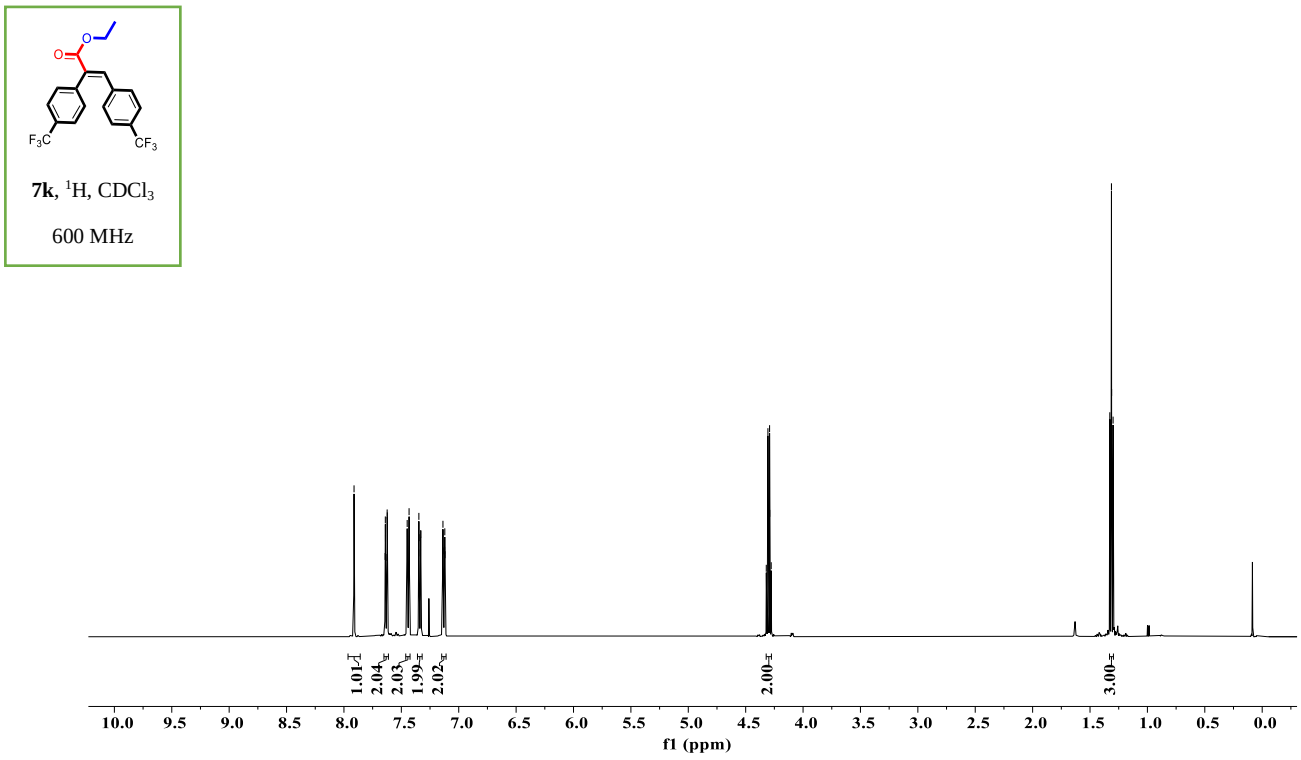
7j, ^{13}C, $CDCl_3$

126 MHz



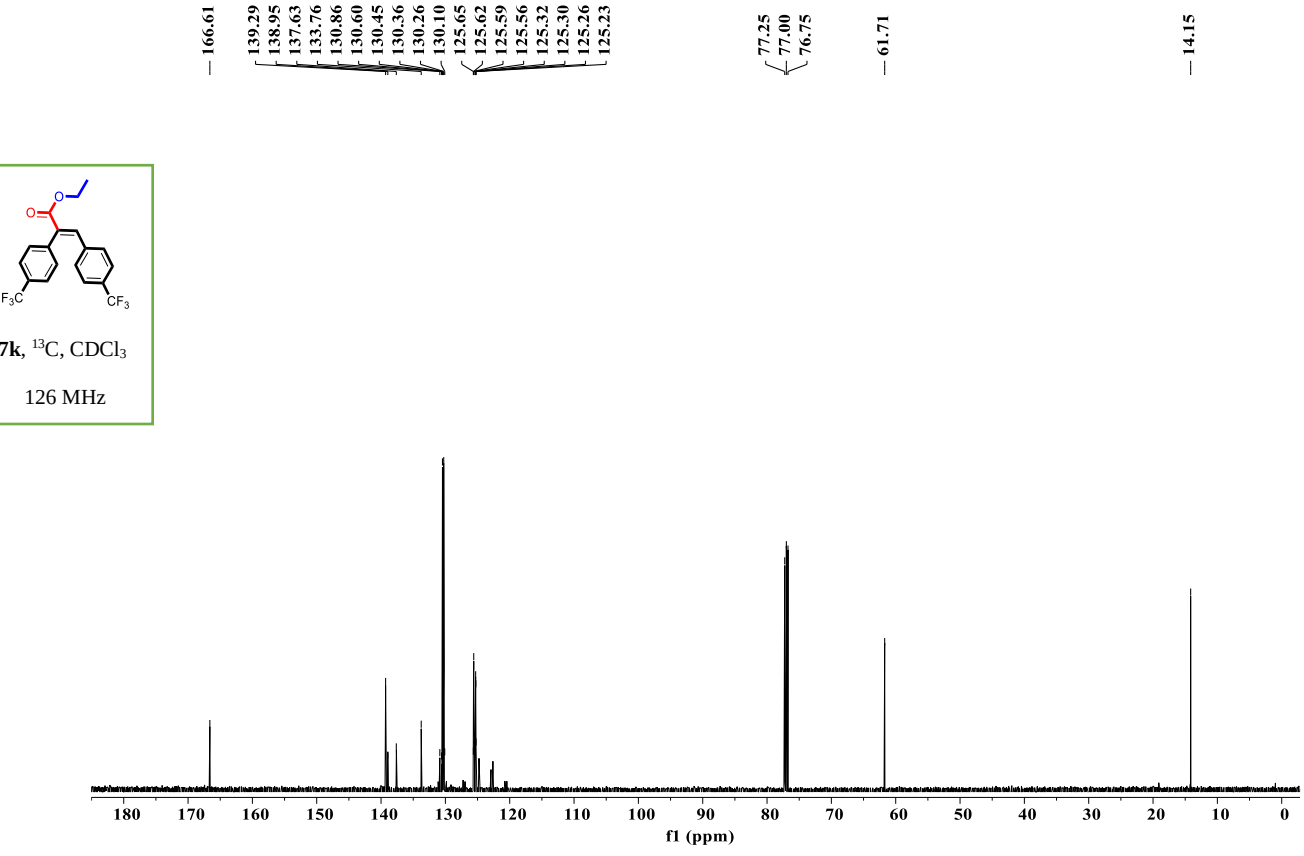


ESI-MS **(7j)**



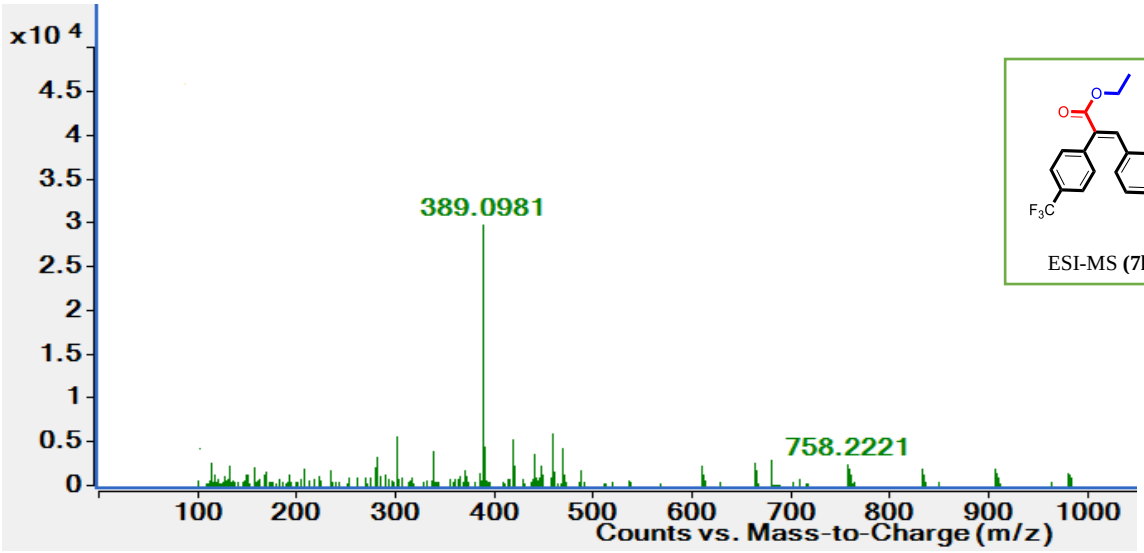
7k, ^{1}H, $CDCl_3$

600 MHz

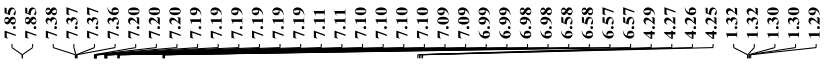


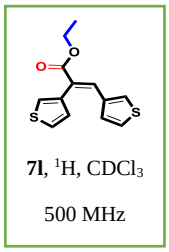
7k, ^{13}C, $CDCl_3$

126 MHz



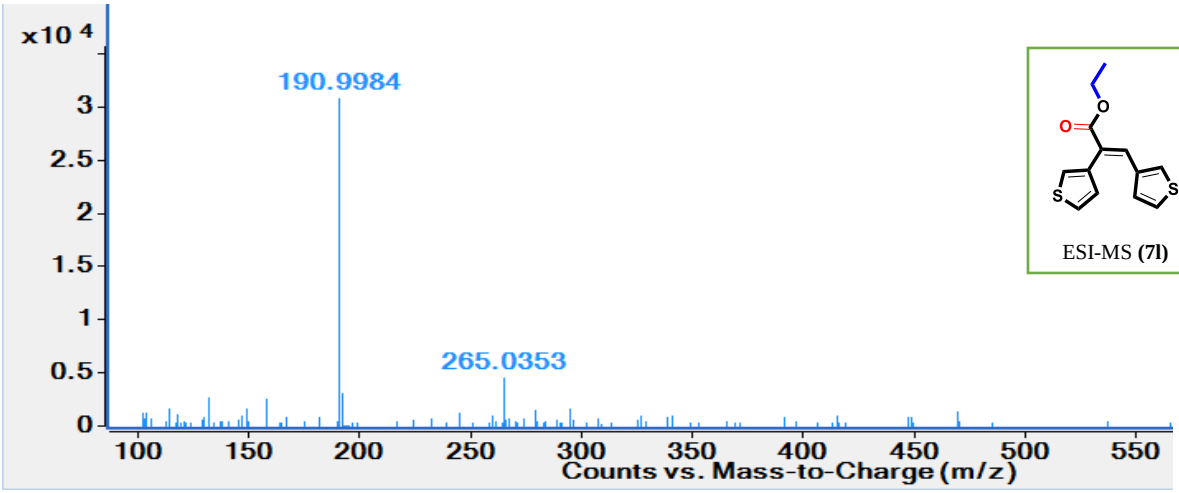
ESI-MS **(7k)**





7l, ^{1}H, $CDCl_3$

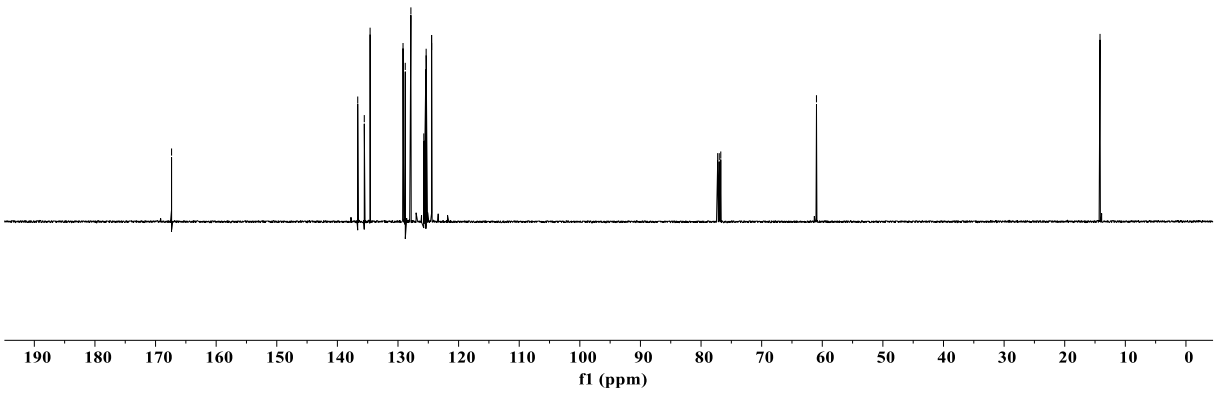
500 MHz

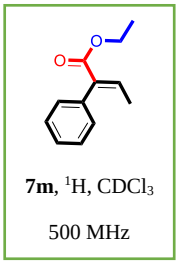


ESI-MS **(7l)**

7l, ^{13}C, $CDCl_3$

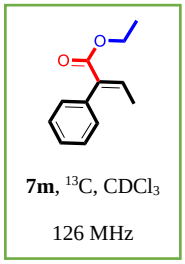
126 MHz





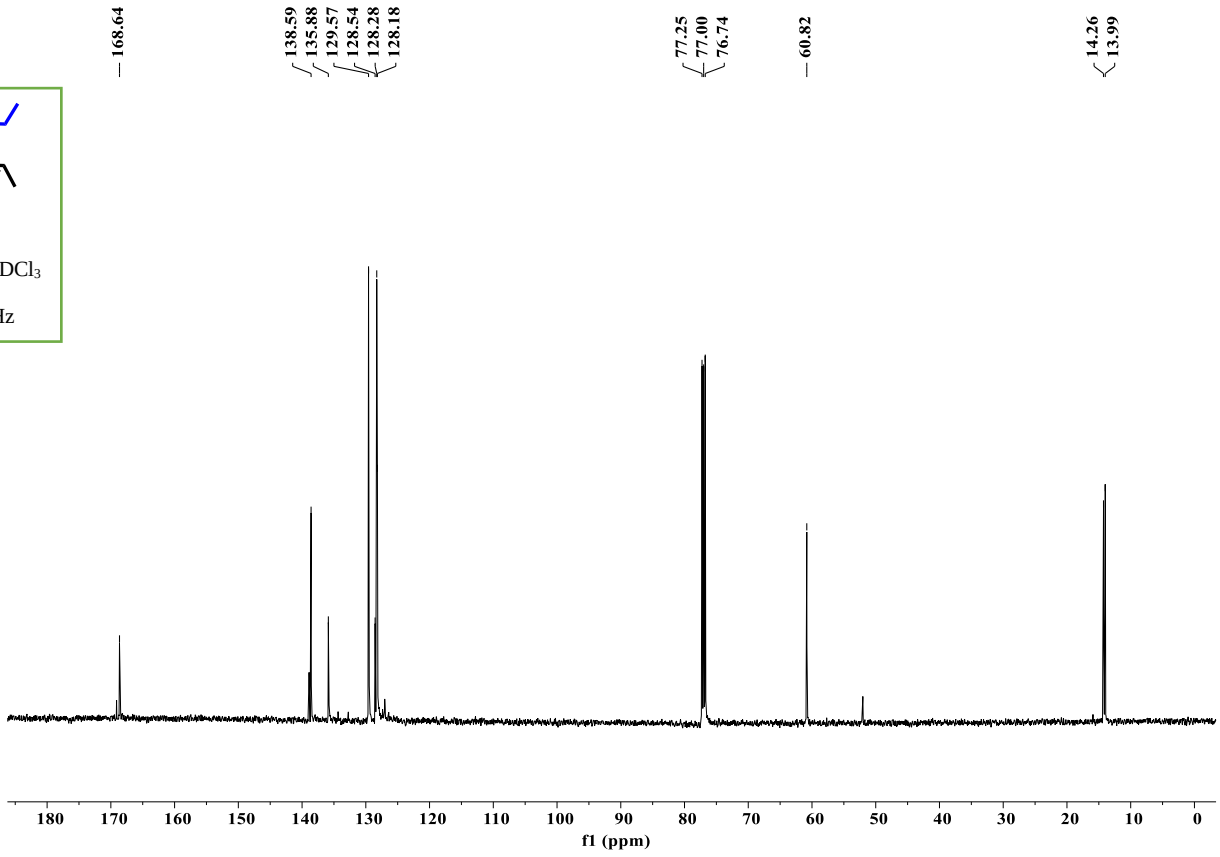
7m, ^{1}H, $CDCl_3$

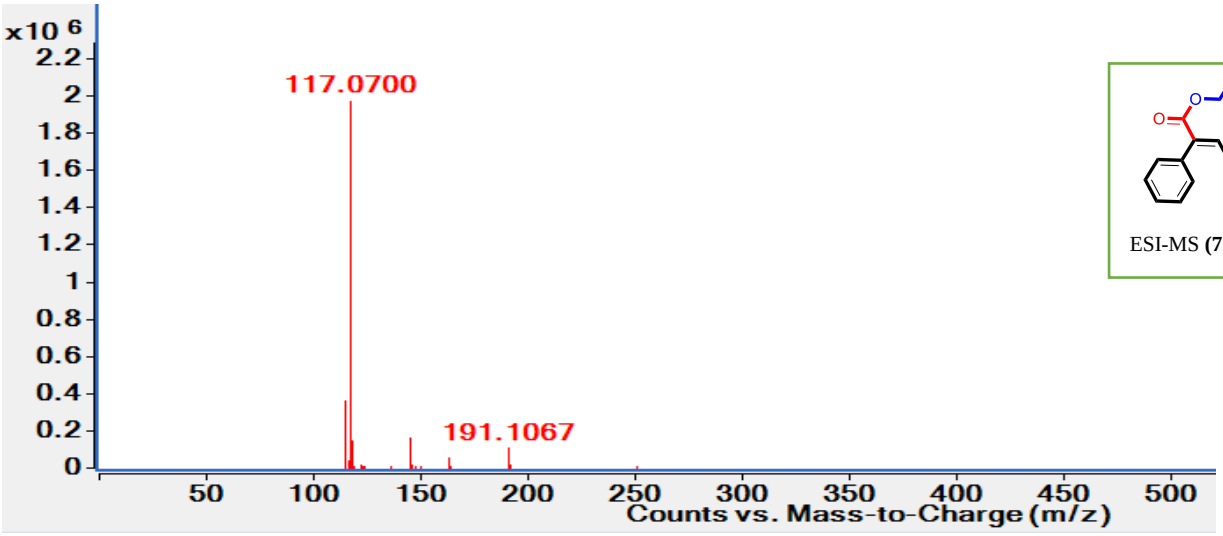
500 MHz



7m, ^{13}C, $CDCl_3$

126 MHz




x10 6
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
117.0700
191.1067
50
100
150
200
250
300
350
400
450
500
Counts vs. Mass-to-Charge (m/z)

ESI-MS **(7m)**