Supporting Information

Copper on charcoal: Cu^0 nanoparticles catalysed aerobic oxidation of α-diazo esters

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Table

1. General Information

Materials. Commercial reagents were acquired from Macklin, Adamas-beta, Aladdin, Bidepharm or, and used as received. All solvents were distilled from CaH_2 unless otherwise stated. Flash column chromatography was performed over silica gel 300-400 mesh.

Instruments. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV400 spectrometer at room temperature. Proton chemical shifts are reported in ppm downfield from tetramethylsilane or from the residual solvent as internal standard in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.16 ppm). High Resolution Mass Spectrometer (HRMS) was obtained by a GCT Premier instrument. High Resolution Transmission Electron Microscopy (HRTEM) investigations were carried out on a JEM-2100 instrument. Inductively Coupled Plasma (ICP) was obtained on an Agilent 725 instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a ESCALAB 250Xi instrument. X-ray Powder Diffractometer (XRD) was obtained by D/max2550VB/PC instrument. Gas chromatography - mass spectrometry (GC-MS) was carried out on an Agilent 7890A-5975C instrument. Gas chromatography (GC) was obtained on a Shimadzu GC-2010 Plus instrument.

General GC conditions. FID detector; carrier gas: nitrogen.
Compounds were detected under a condition as: column temperature: 50 ℃ for 5 minutes, raising to 250 ℃ in a rate of 20 ℃/min, holding at 250 ℃ for 5 min.

2. Preparation of Cu/C Catalyst

To a solution of $CuCl_2 \cdot 2H_2O$ (1 g) in ethanol (80 mL), naphthalene (2 g) and activated carbon (4 g) were added subsequently. This suspension was heated to reflux with stirring. At this point, hydrazine hydrate (80%, 20 mL) was added drop wisely in half an hour. After addition, the resulting mixture was refluxed for 8h. Finally, reaction mixture was cooled to room temperature, and the solid was collected by filtration through a Buchner funnel, and washed twice with anhydrous ethanol (2×10 mL). Thus obtained solid was dried and then heated at 300 ^{o}C under nitrogen atmosphere for an hour, which was stored in a bottle and used as catalyst.

3. Characterization of Cu/C Catalyst

3.1 High Resolution Transmission Electron Microscopy (**HRTEM**)

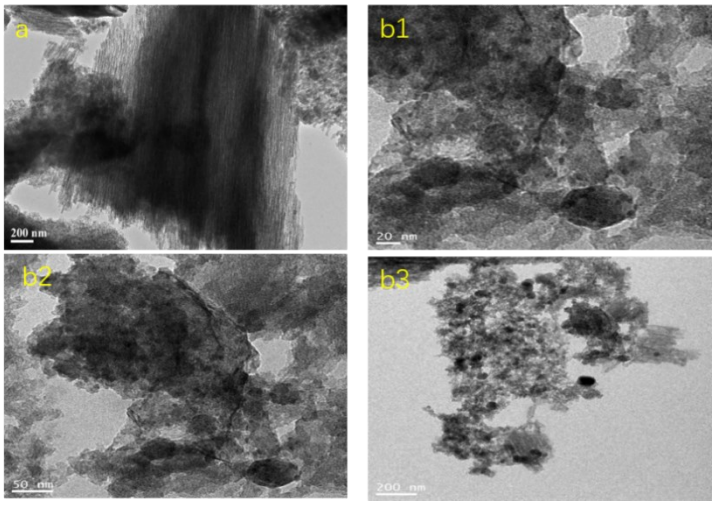


Fig. 1 a, HRTEM of Charcoal; b, Cu/C catalyst

3.2 X-ray Photoelectron Spectroscopy (**XPS**)

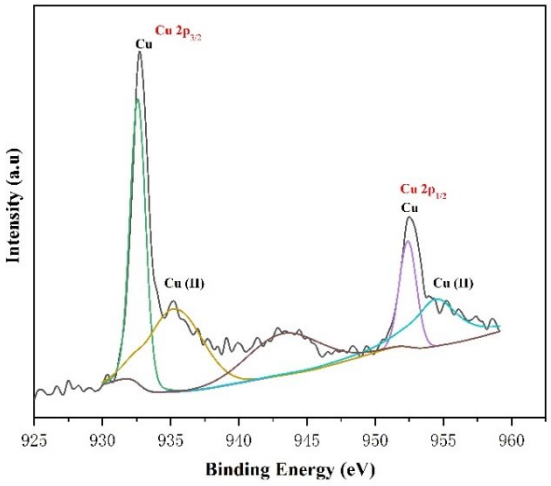


Fig. 2 XPS of Cu/C catalyst

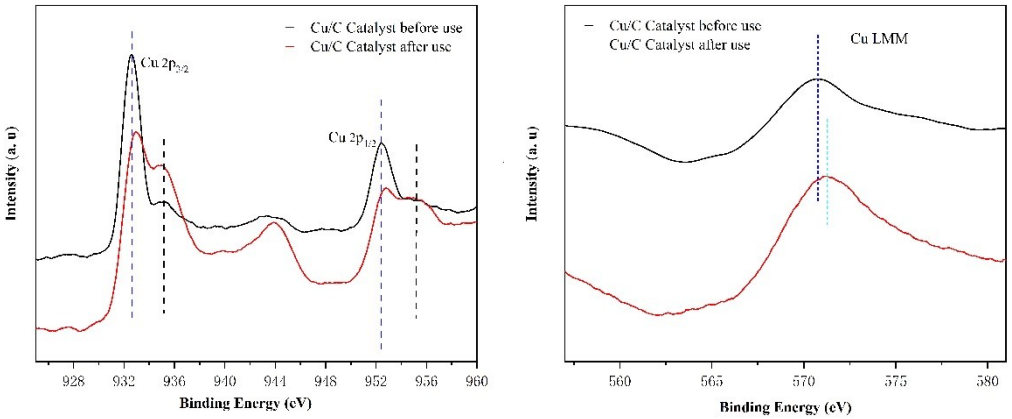


Fig. 3 XPS of the Cu/C catalyst before and after the reaction

3.3 X-ray Powder Diffraction (**XRD**)

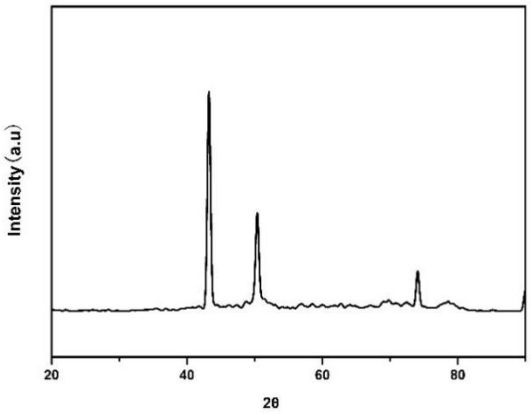
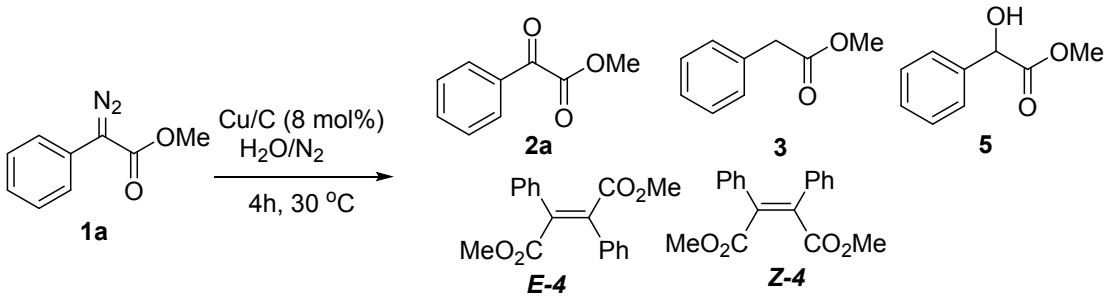
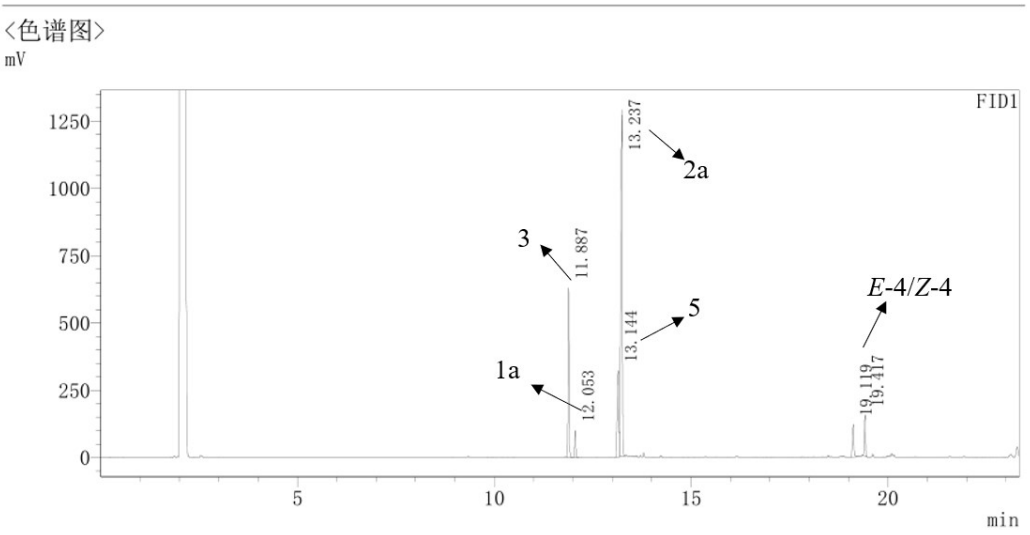


Fig. 4 XRD of Cu/C catalyst

4. Experimental Section

4.1 Reaction of **1a** with H_2O under nitrogen atmosphere (GC spectrum)



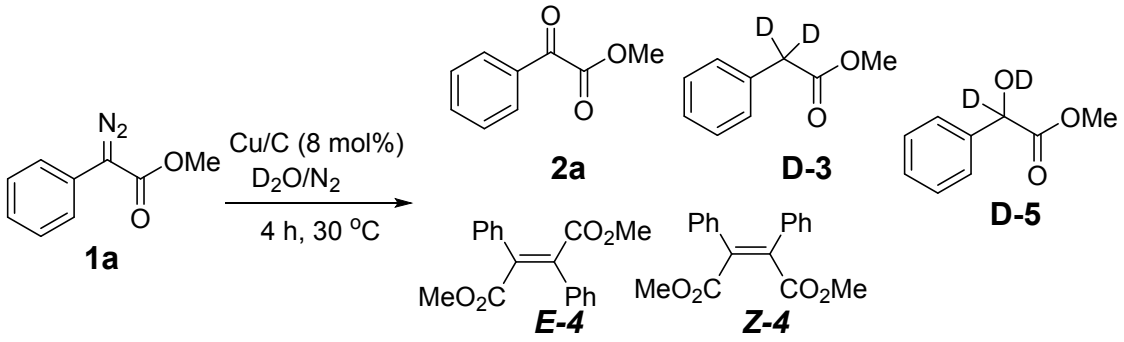


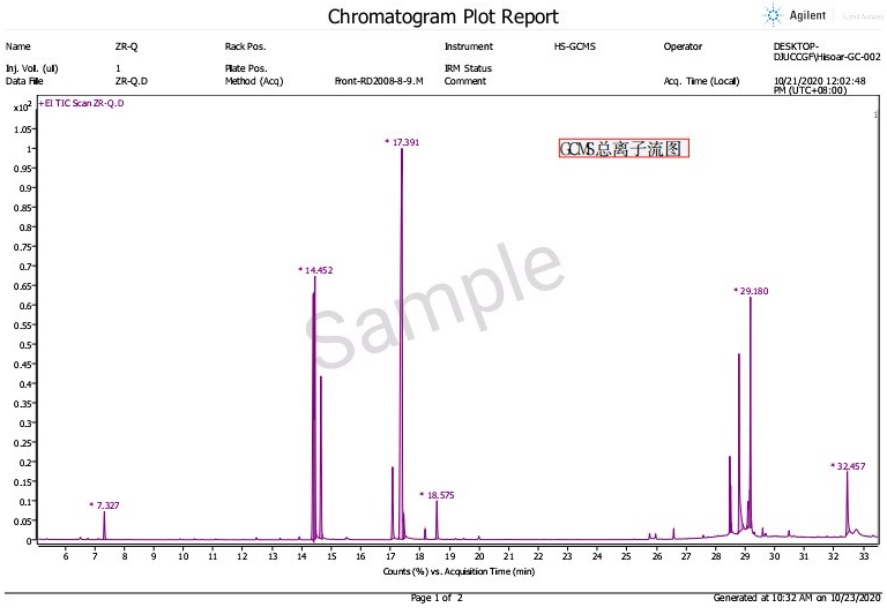
Peak Table

Peak	Ret. Time(min)	Area	Height	Conc.	Units	Mark	Area%
1	11.887	1142924	617141	0.000			18.292
2	12.053	173733	99016	0.000			2.780
3	13.144	877450	319016	0.000			14.043
4	13.237	3458365	1280705	0.000		V	55.347
5	19.119	296223	119625	0.000			4.741
6	19.417	299763	150838	0.000			4.797
Total		6248359	2586341				100

Figure 5 GC diagram Cu/C (8 mol%) catalyzed reaction of **1a** with H_2O under nitrogen atmosphere for 4 h, all of peaks were confirmed by authority sample.

4.2 Reaction of **1a** with D_2O (GC-MS spectrum)

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Instrument HS-GCMS
Operator DESKTOP-DJUCCGF\Hisoar-GC-002
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Plate Pos.
IRM Status
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Method (Acq) front-RD2008-8-9.M
Comment
Acq. Time (Local) 10/21/2020 12:02:48 PM (UTC+08:00)
+EI TIC Scan ZR-Q.D
GCMS总离子流图
* 17.391
* 14.452
* 29.180
* 32.457
* 18.575
* 7.327
Sample
Counts (%) vs. Acquisition Time (min)
Page 1 of 2
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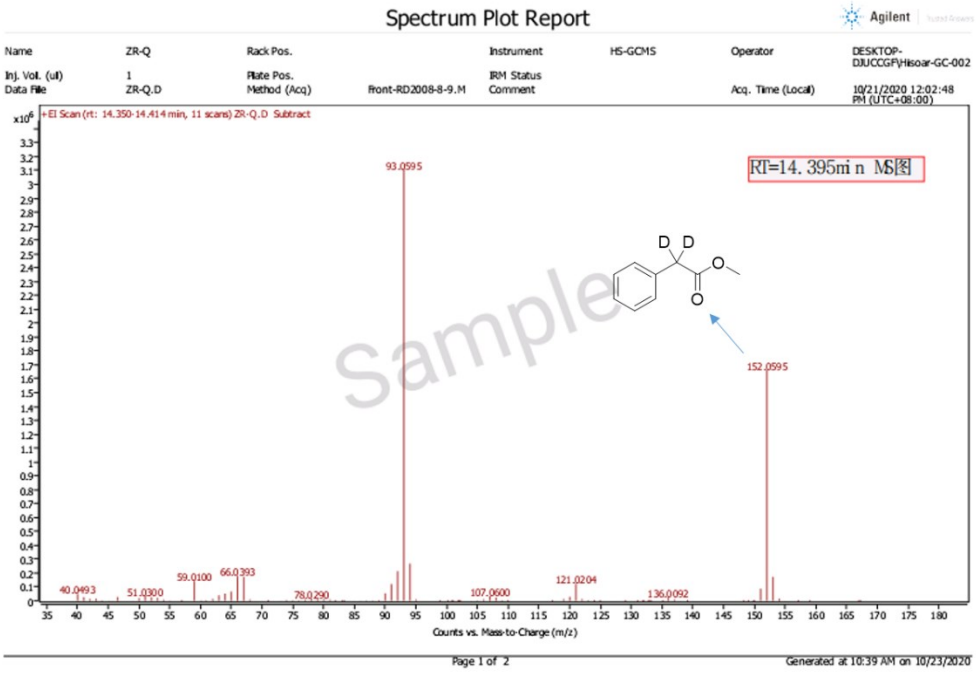
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Agilent
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Rack Pos.
Instrument HS-GCMS
Operator DESKTOP-DJUCCGF\Hisoar-GC-002
Inj. Vol. (ul) 1
Plate Pos.
IRM Status
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Method (Acq) front-RD2008-8-9.M
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152.0595
D D
O
O
Sample
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51.0300
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Counts vs. Mass-to-Charge (m/z)
Page 1 of 2
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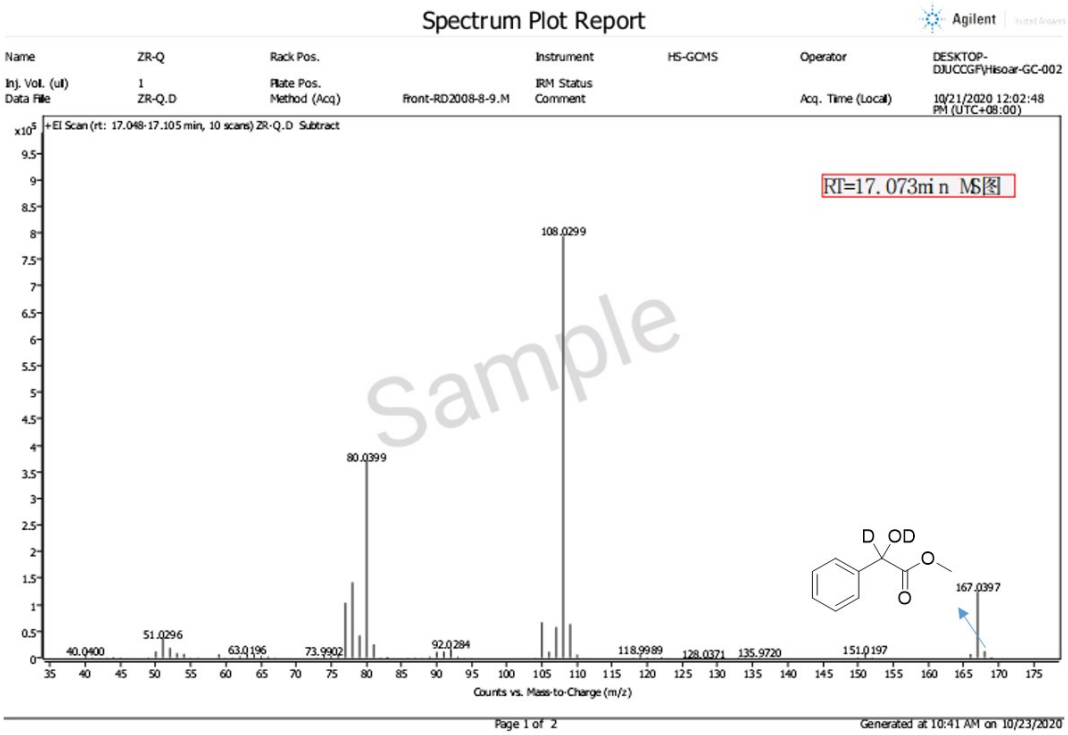
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Plate Pos.
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118.9989
128.0371
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D OD
O
O
Sample
Counts vs. Mass-to-Charge (m/z)
Page 1 of 2
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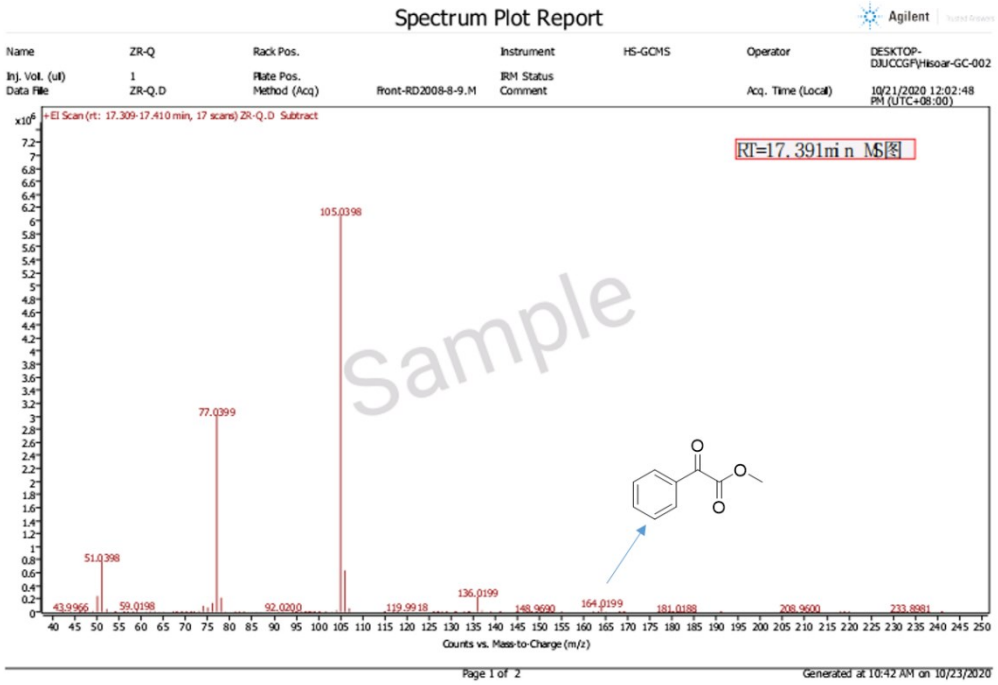
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Operator DESKTOP-DJUCCGF\Hisoar-GC-002
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Plate Pos.
IRM Status
Data File ZR-Q.D
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59.0198
92.0200
119.9918
136.0199
148.9690
164.0199
181.0188
208.9600
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O
O
O
Sample
Counts vs. Mass-to-Charge (m/z)
Page 1 of 2
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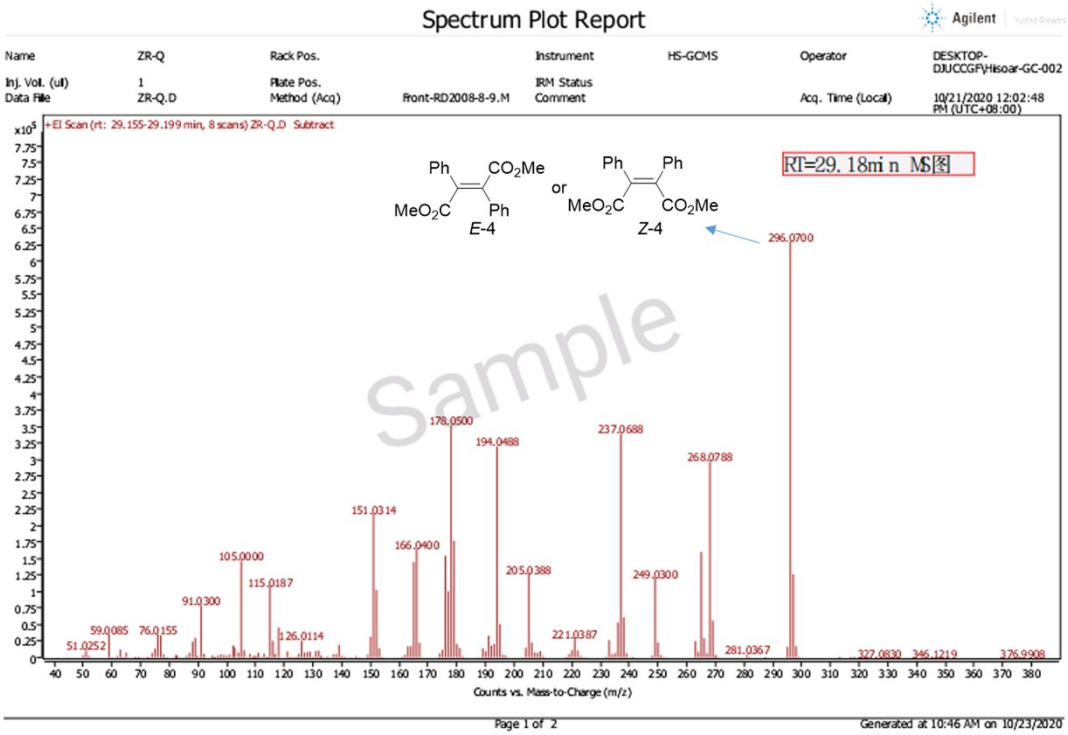


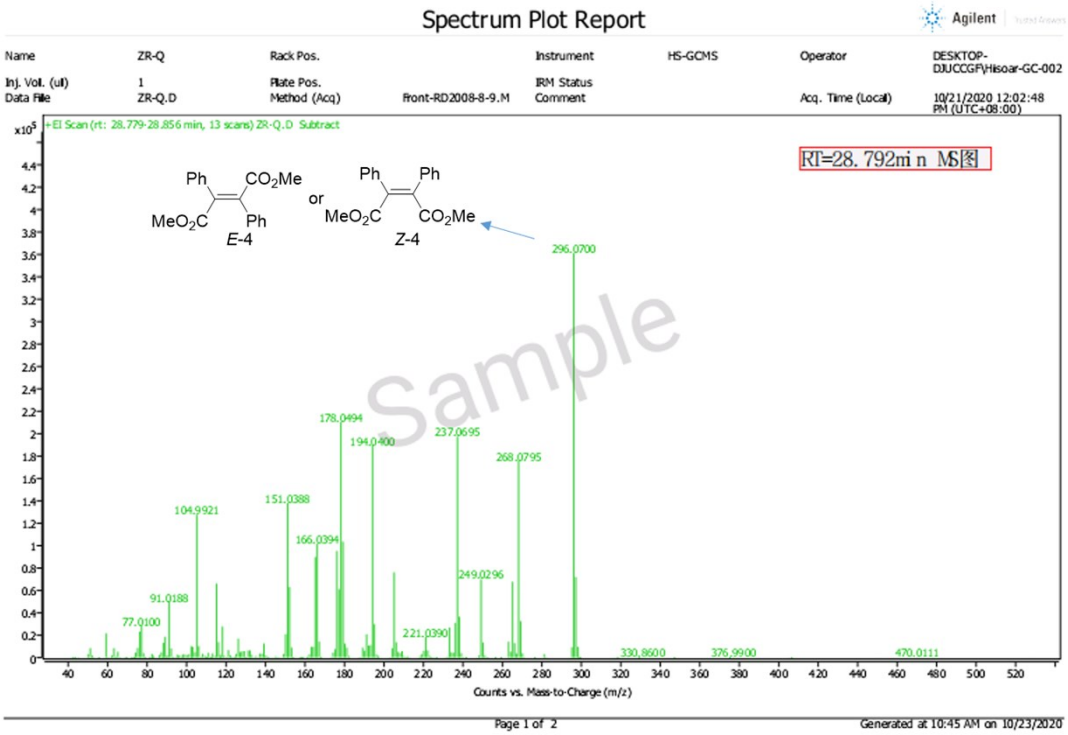
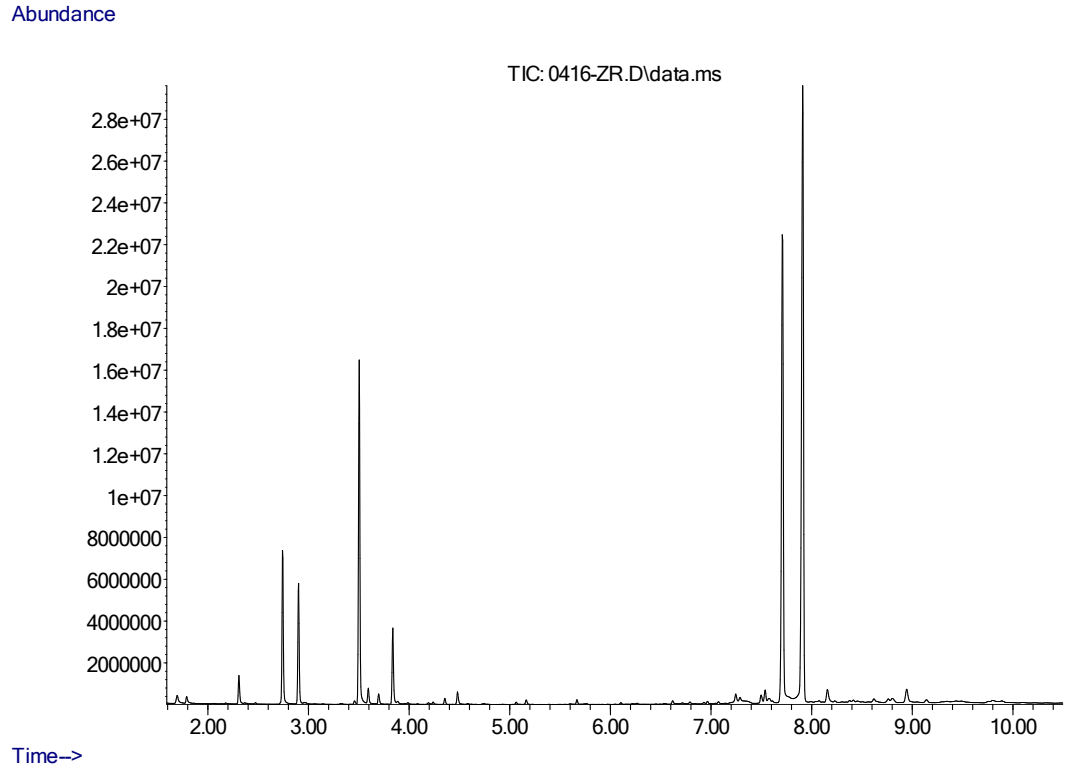
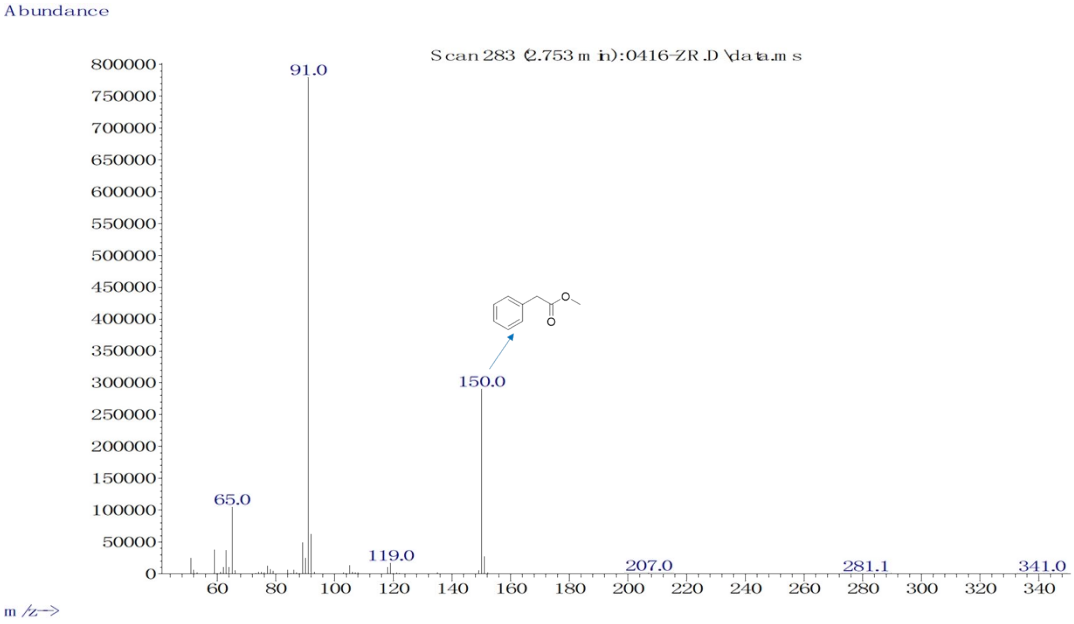
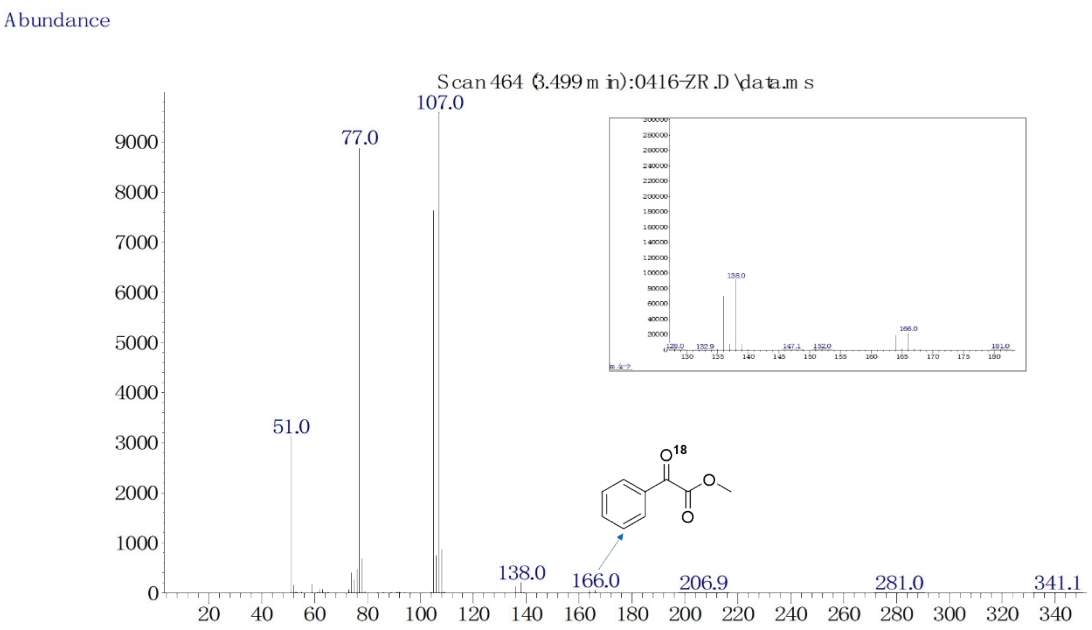


Figure 6 GC-MS diagram of 1a reacts with D_2O

4.3 Reaction of **1a** with H_2O^{18} (GC-MS spectrum)



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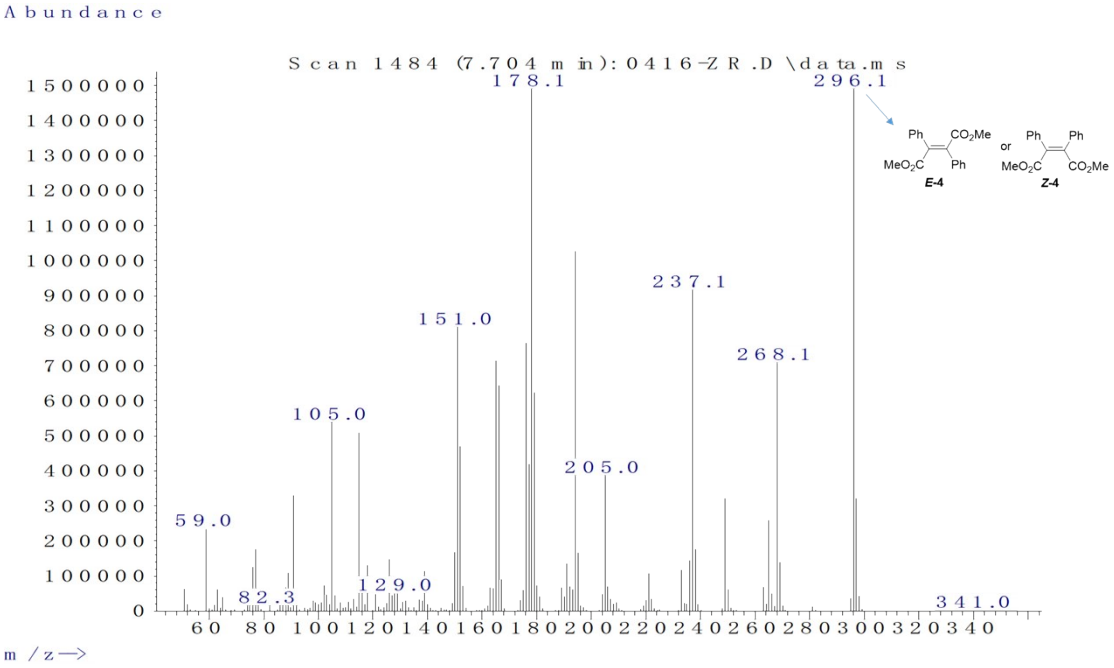
O18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m/z
E-4
Z-4

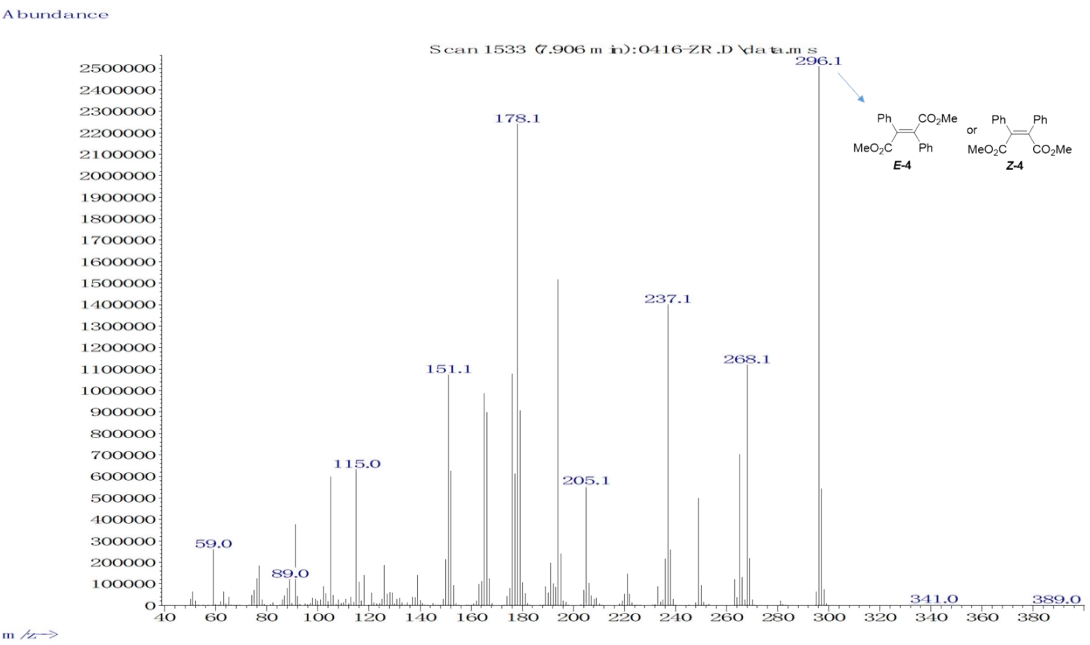
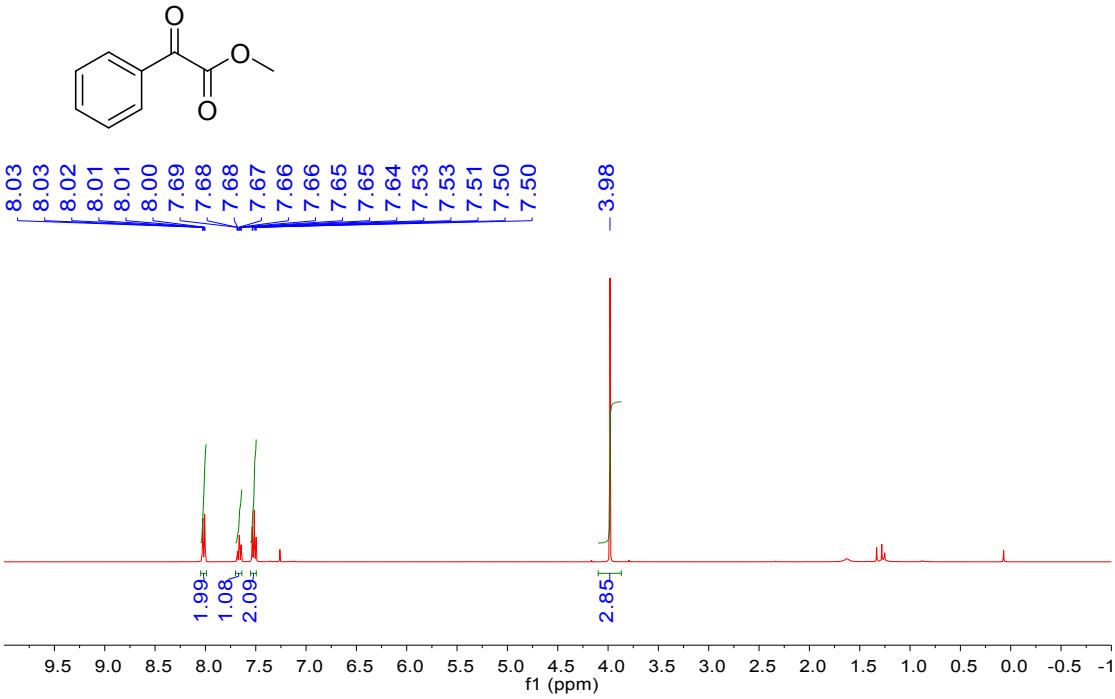
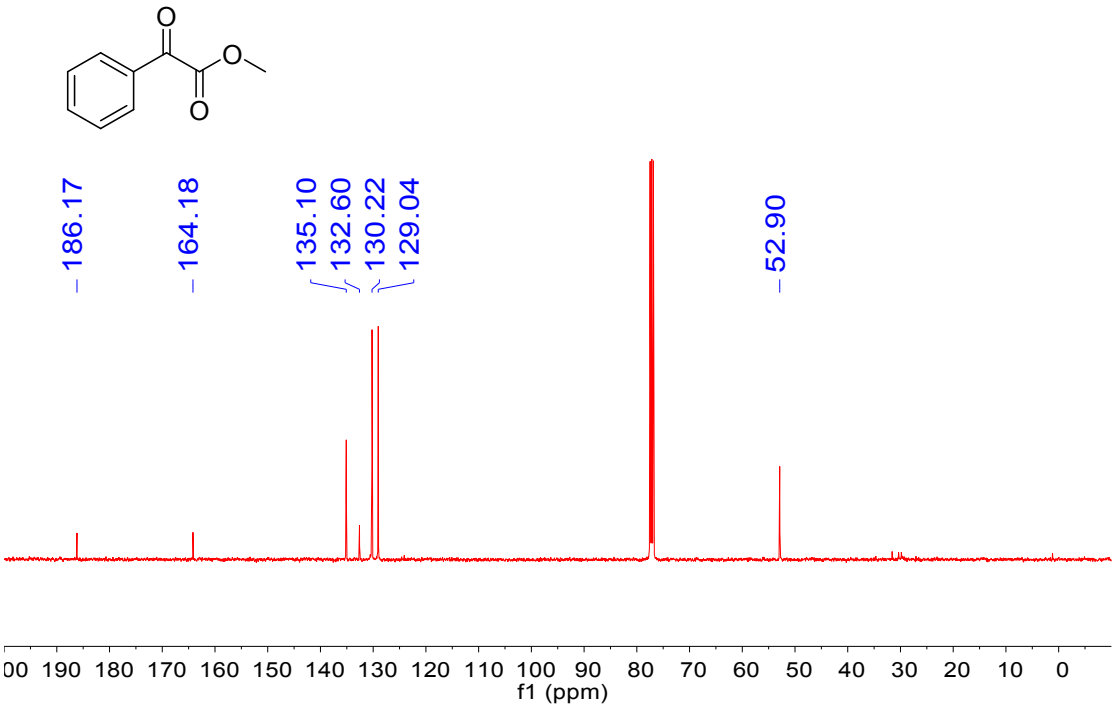


Figure 7 GC-MS diagram of 1a reacts with H_2O^{18}

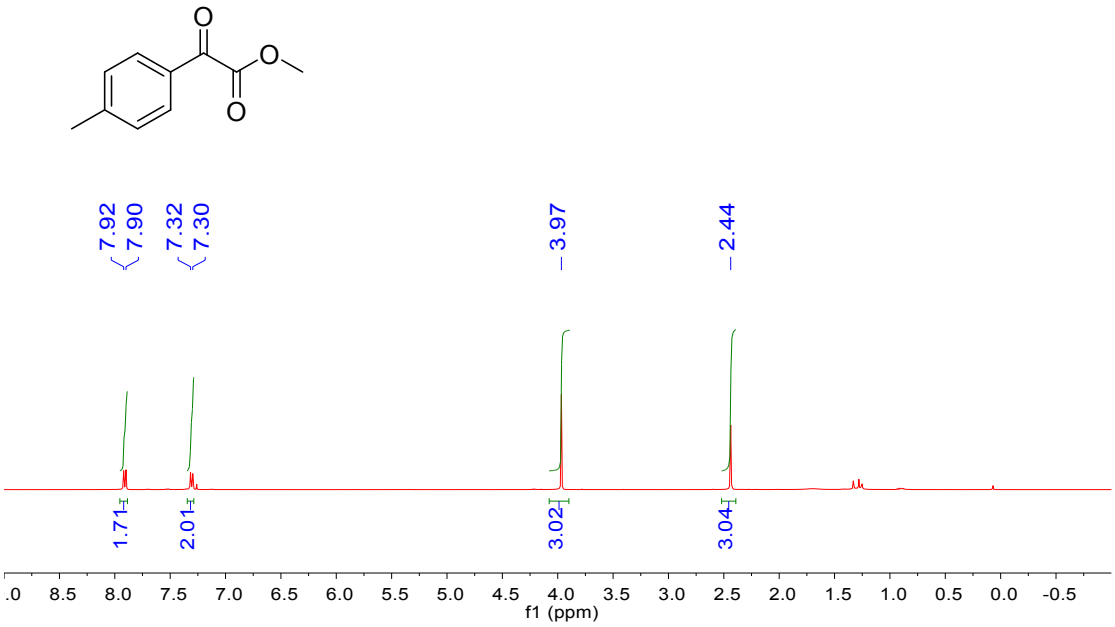
5. NMR spectrums



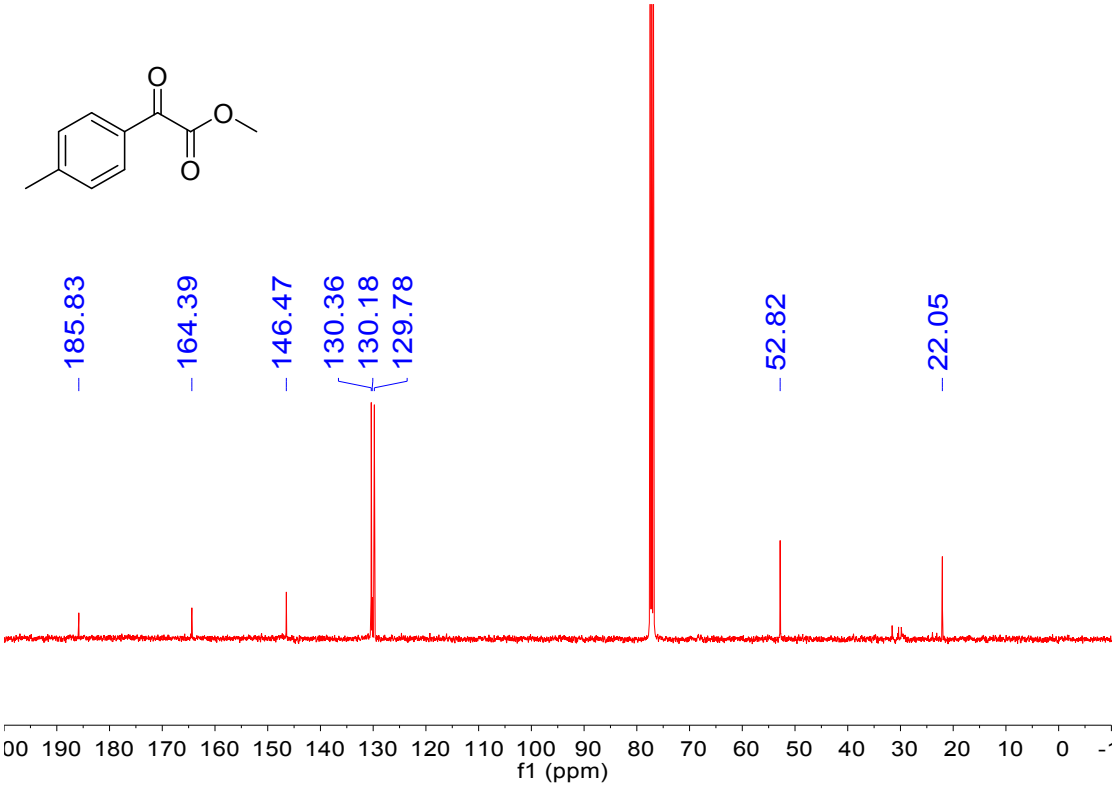
^{1}H NMR spectrum of compound 2a



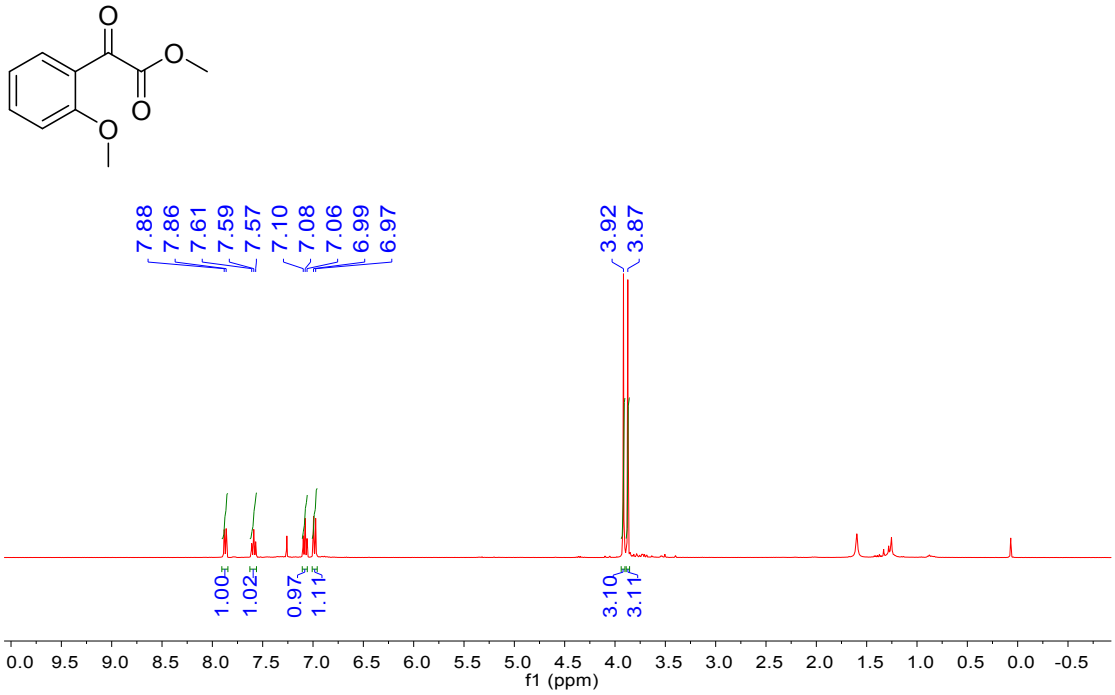
^{13}C NMR spectrum of compound 2a



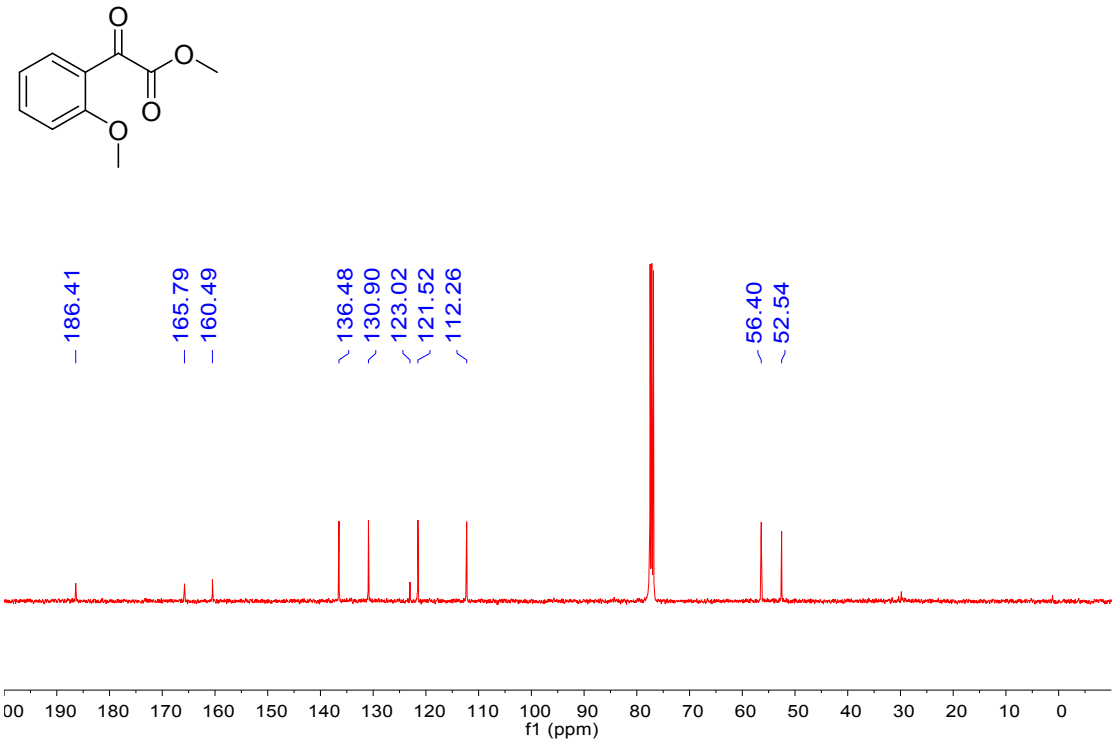
^{1}H NMR spectrum of compound 2b



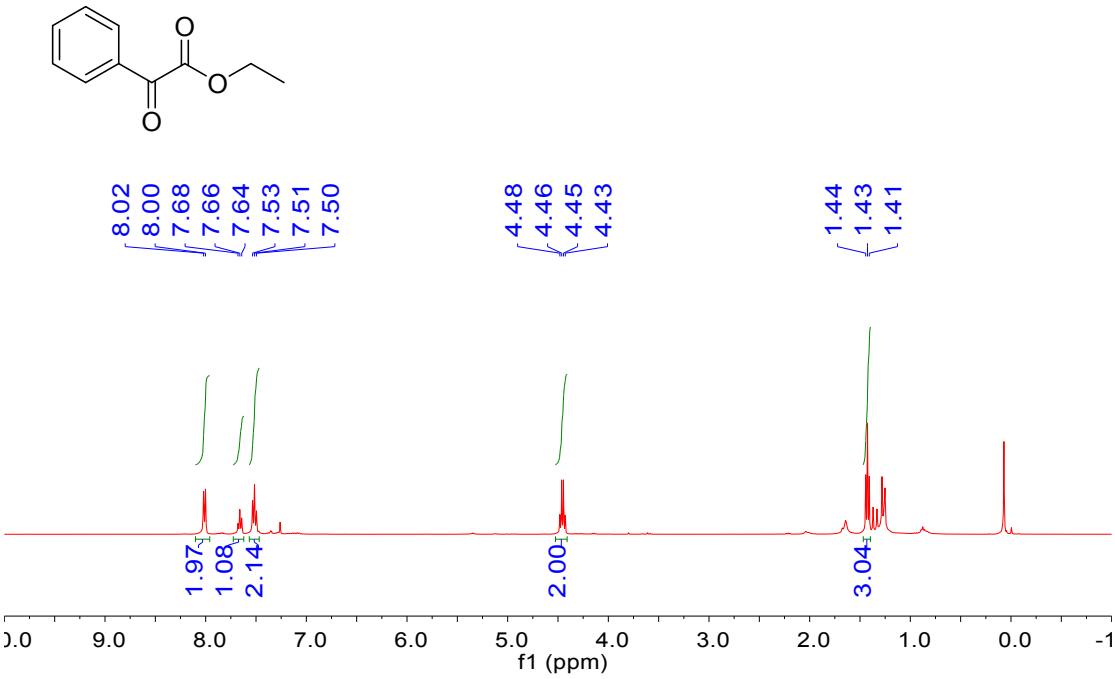
^{13}C NMR spectrum of compound 2b



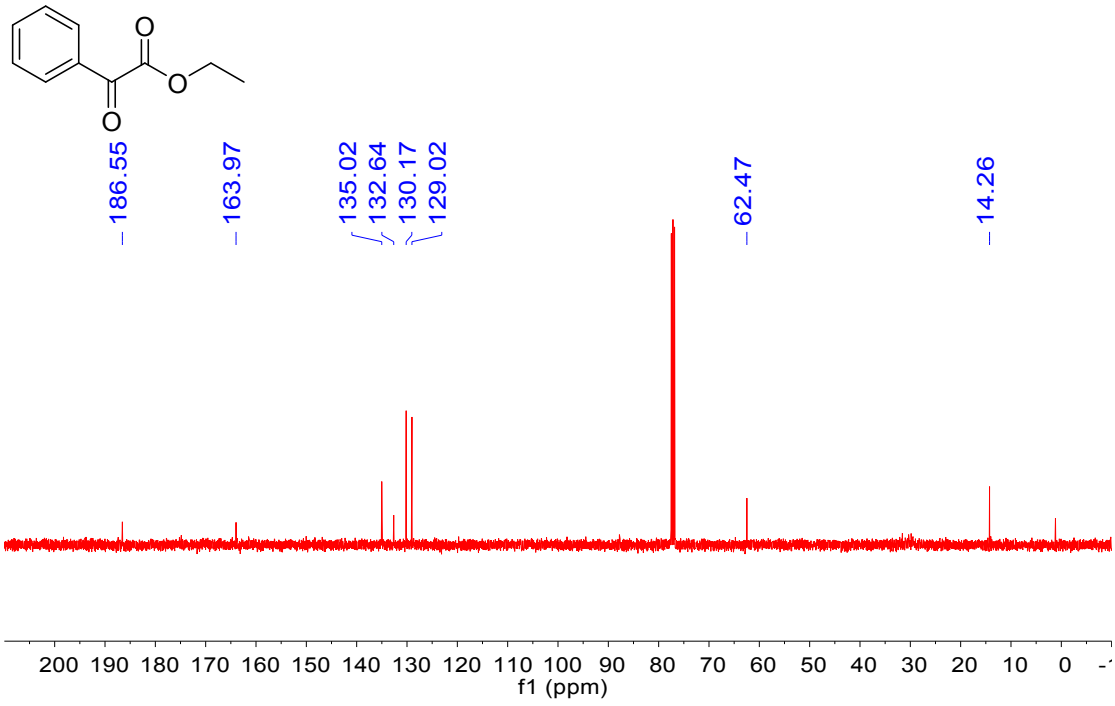
^{1}H NMR spectrum of compound 2c



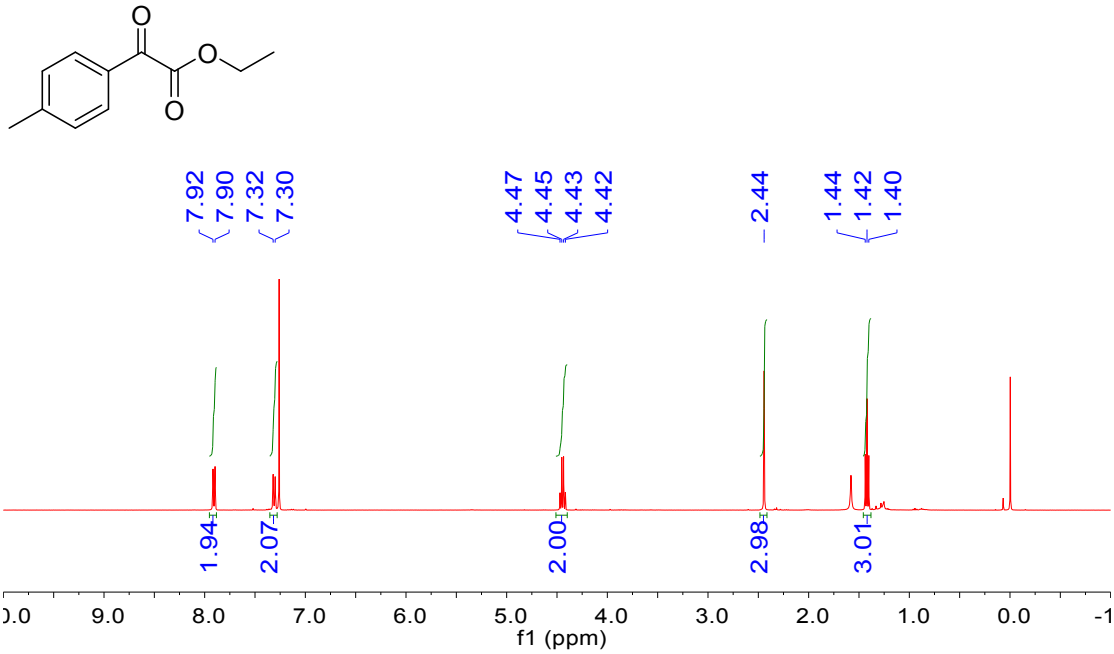
^{13}C NMR spectrum of compound 2c



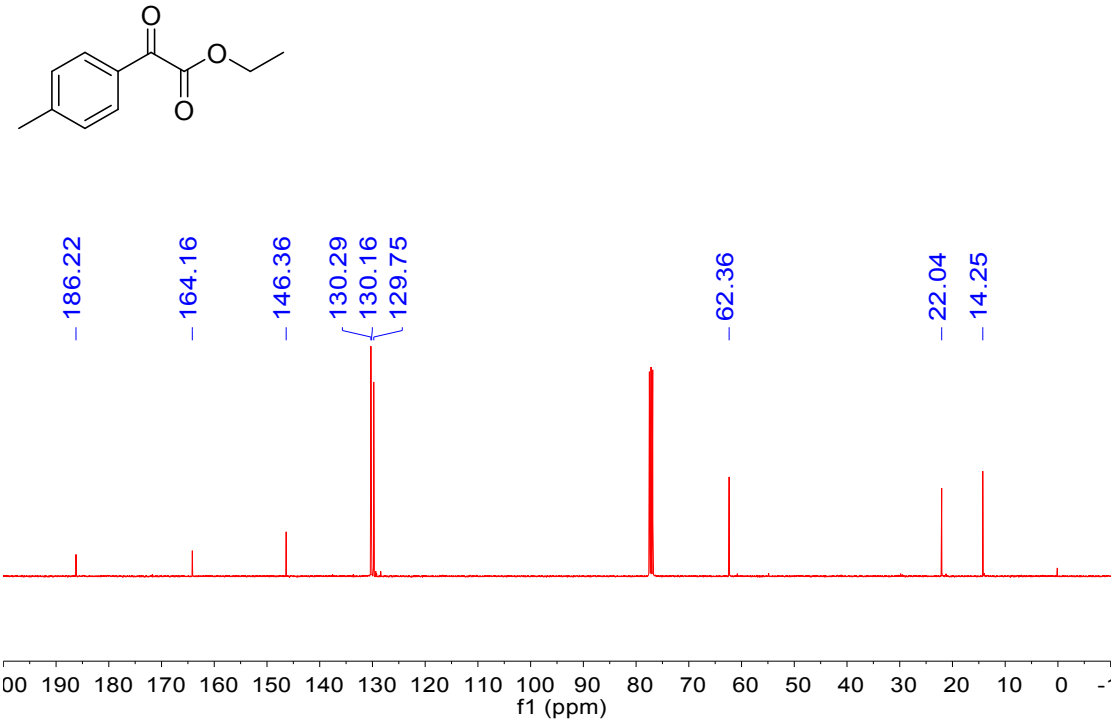
^{1}H NMR spectrum of compound 2d



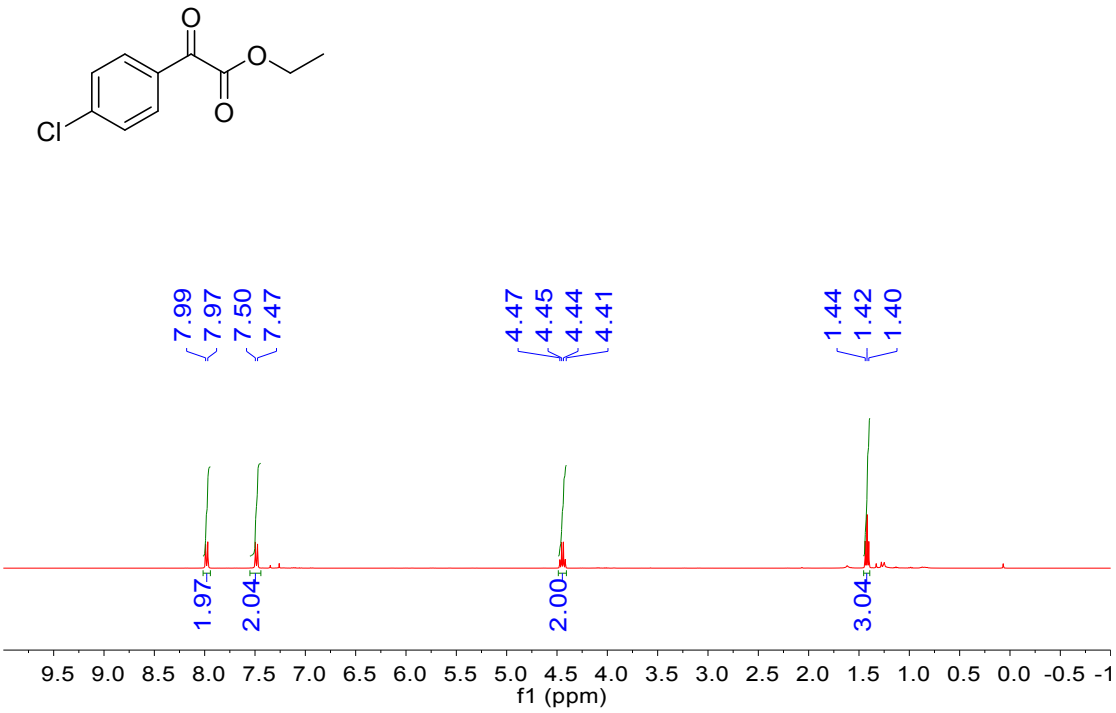
^{13}C NMR spectrum of compound 2d



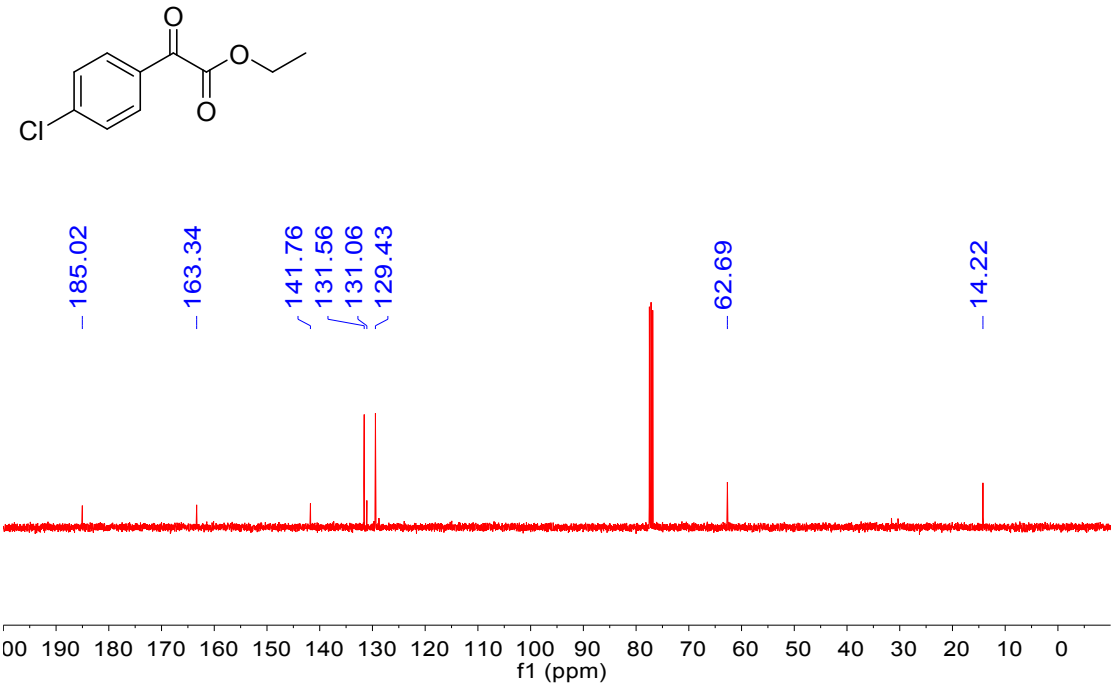
^{1}H NMR spectrum of compound 2e



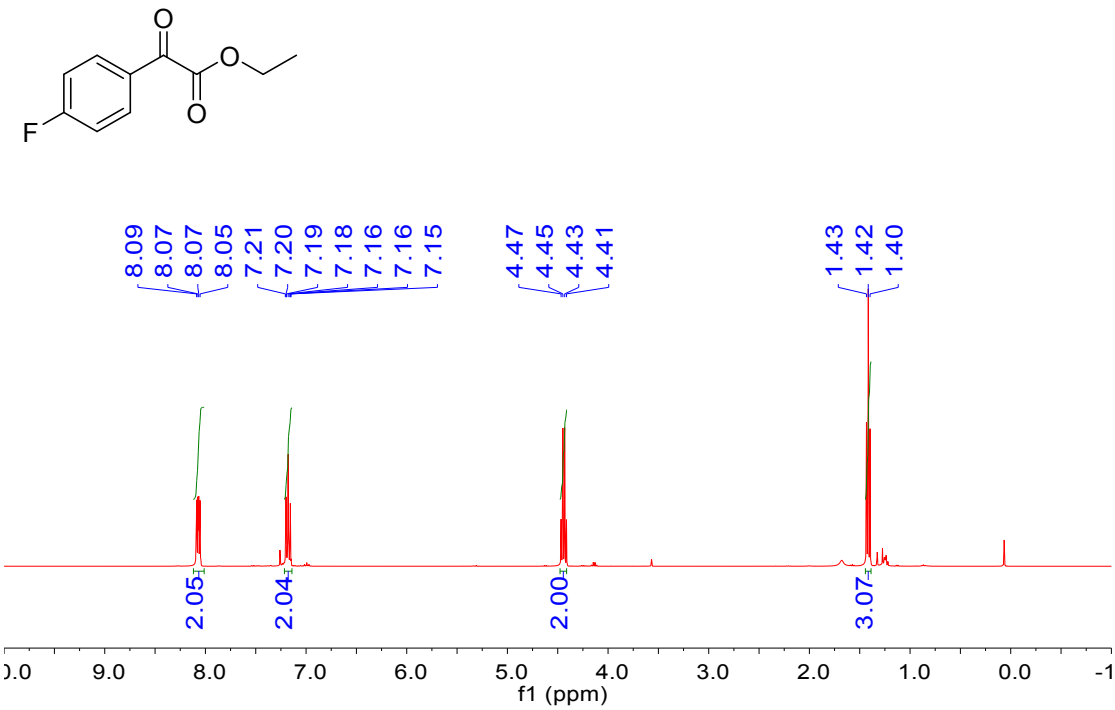
^{13}C NMR spectrum of compound 2e



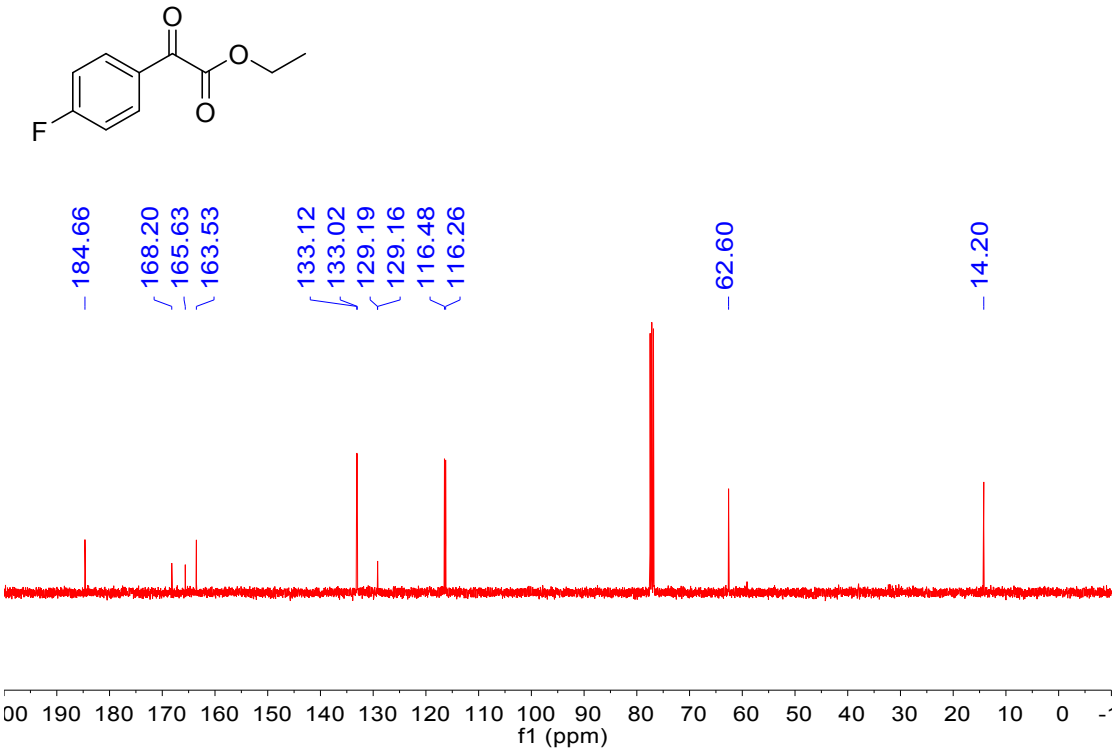
^{1}H NMR spectrum of compound 2f



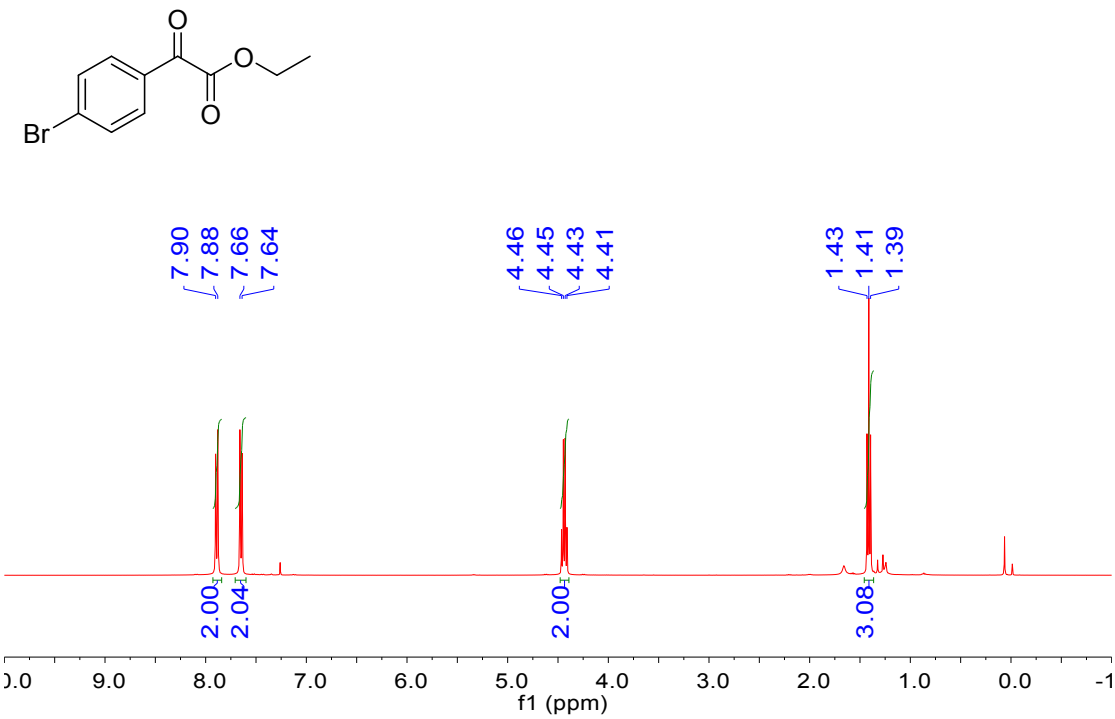
^{13}C NMR spectrum of compound 2f



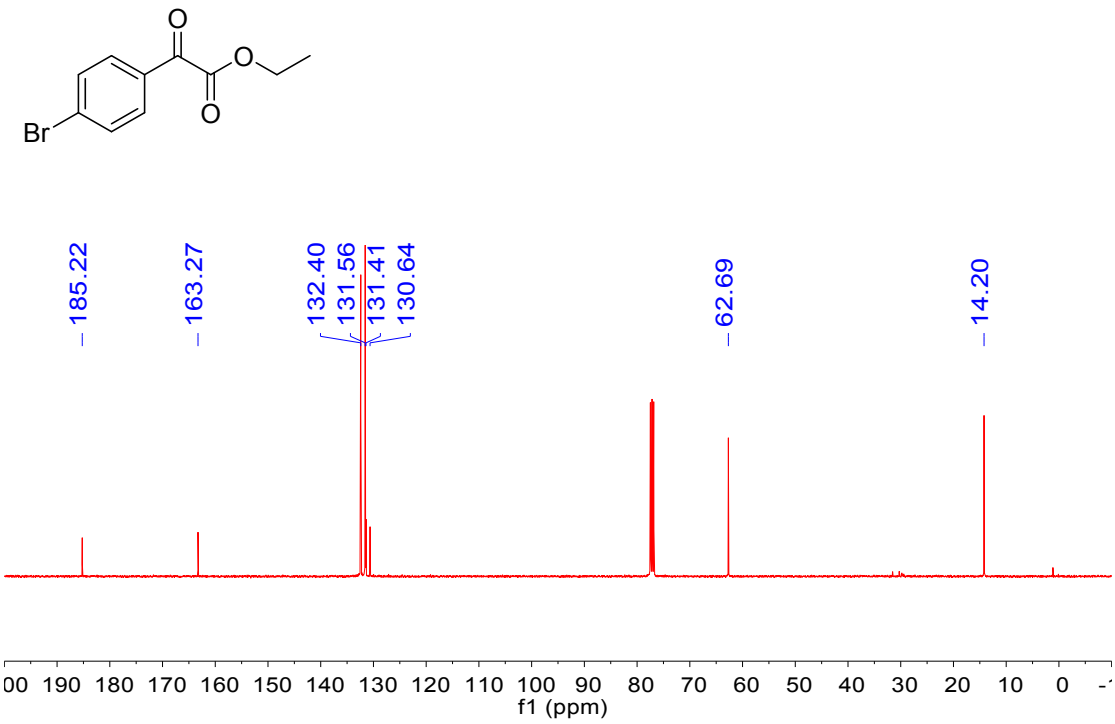
^{1}H NMR spectrum of compound 2g



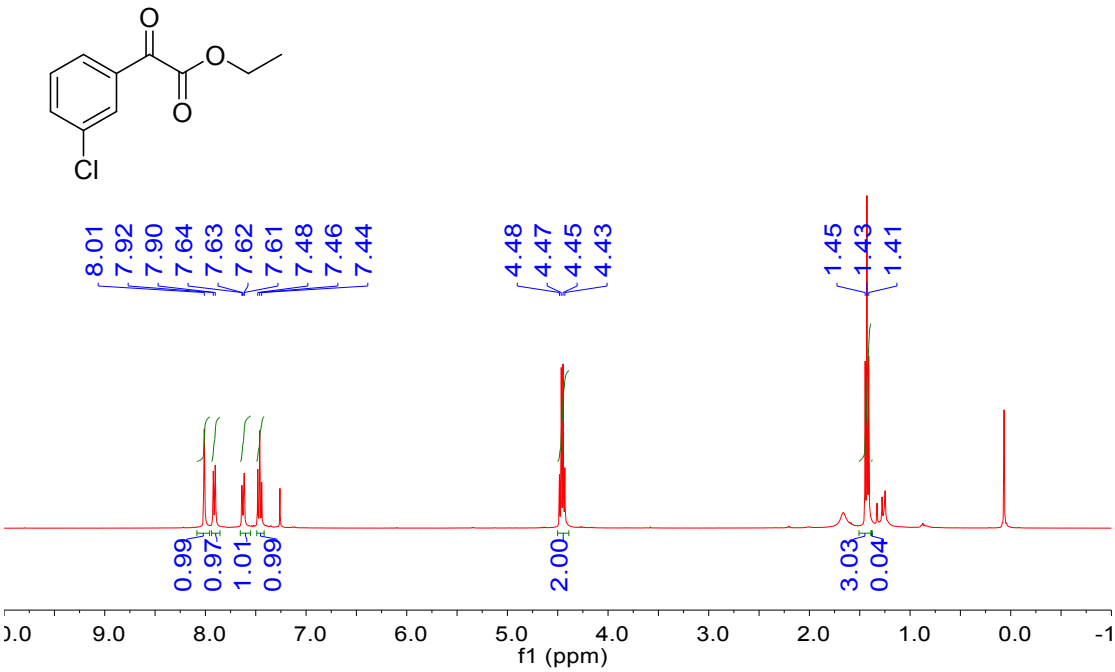
^{13}C NMR spectrum of compound 2g



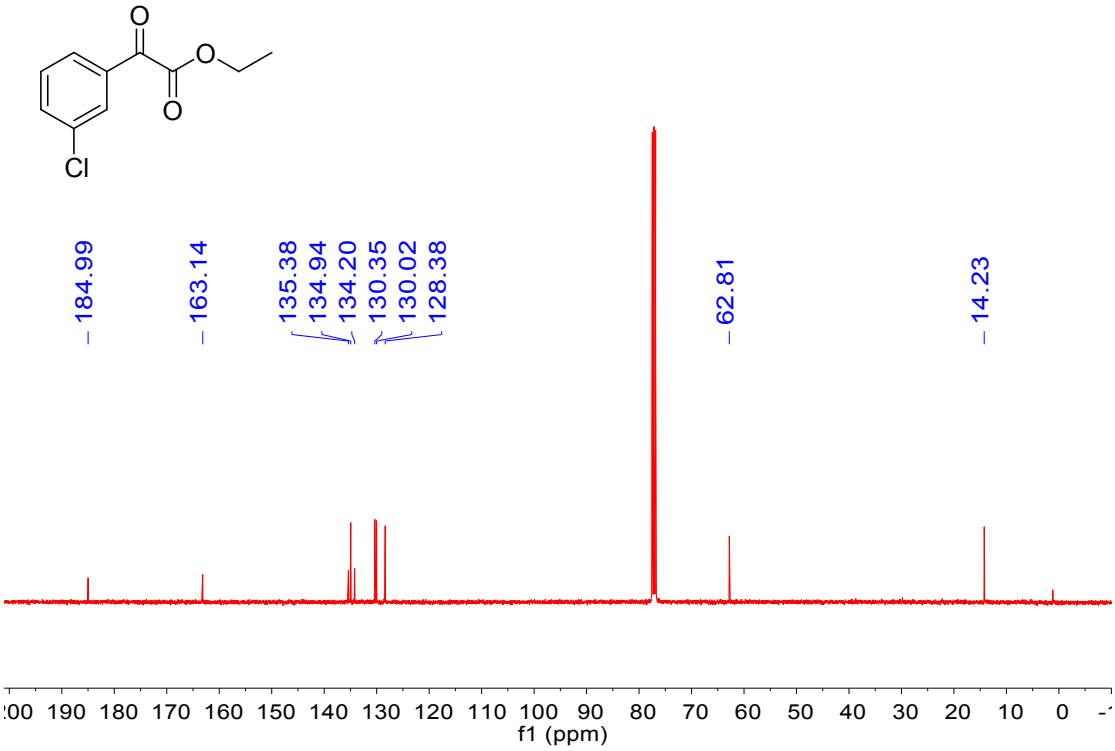
^{1}H NMR spectrum of compound 2h



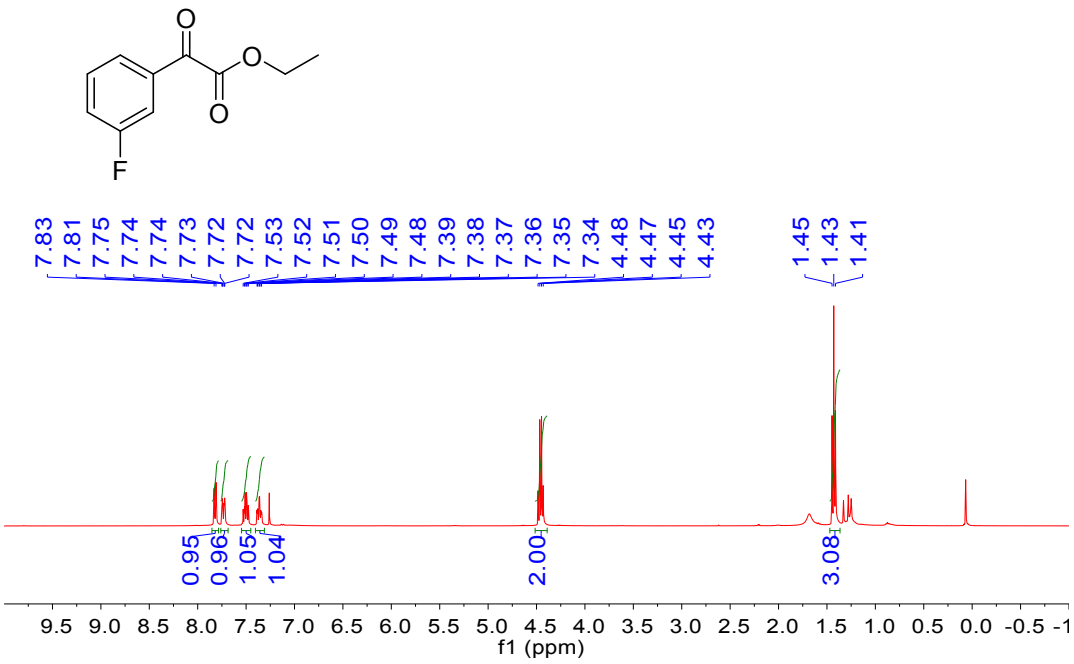
^{13}C NMR spectrum of compound 2h



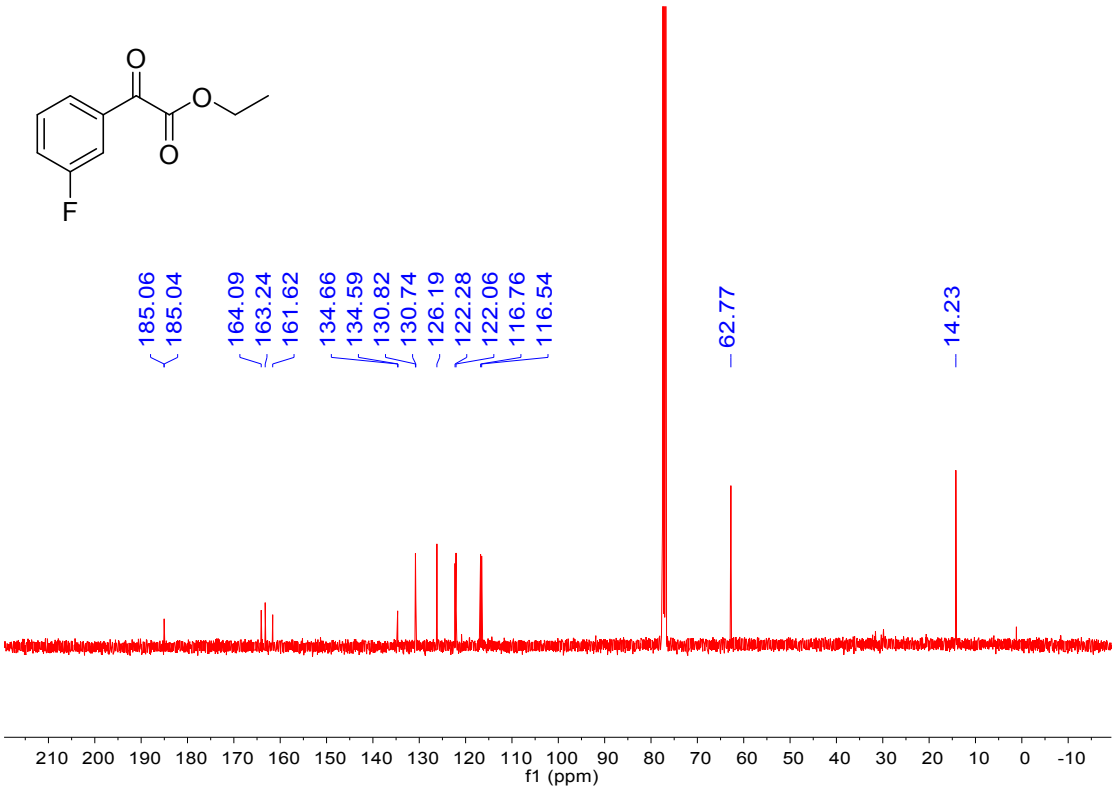
^{1}H NMR spectrum of compound 2i



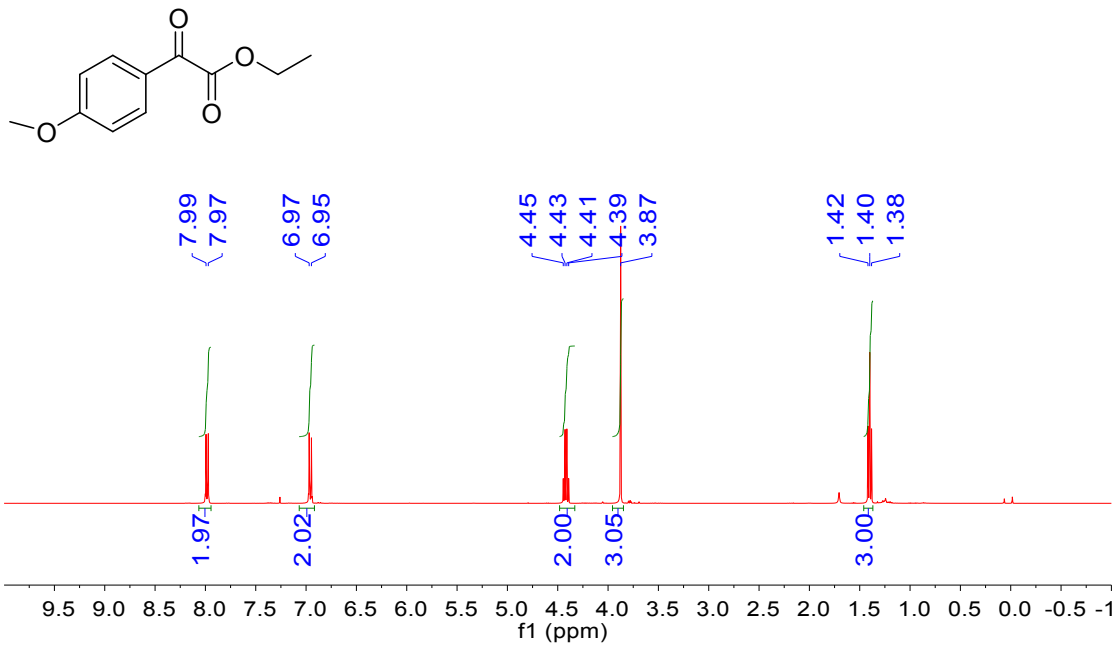
^{13}C NMR spectrum of compound 2i



^{1}H NMR spectrum of compound 2j



^{13}C NMR spectrum of compound 2j



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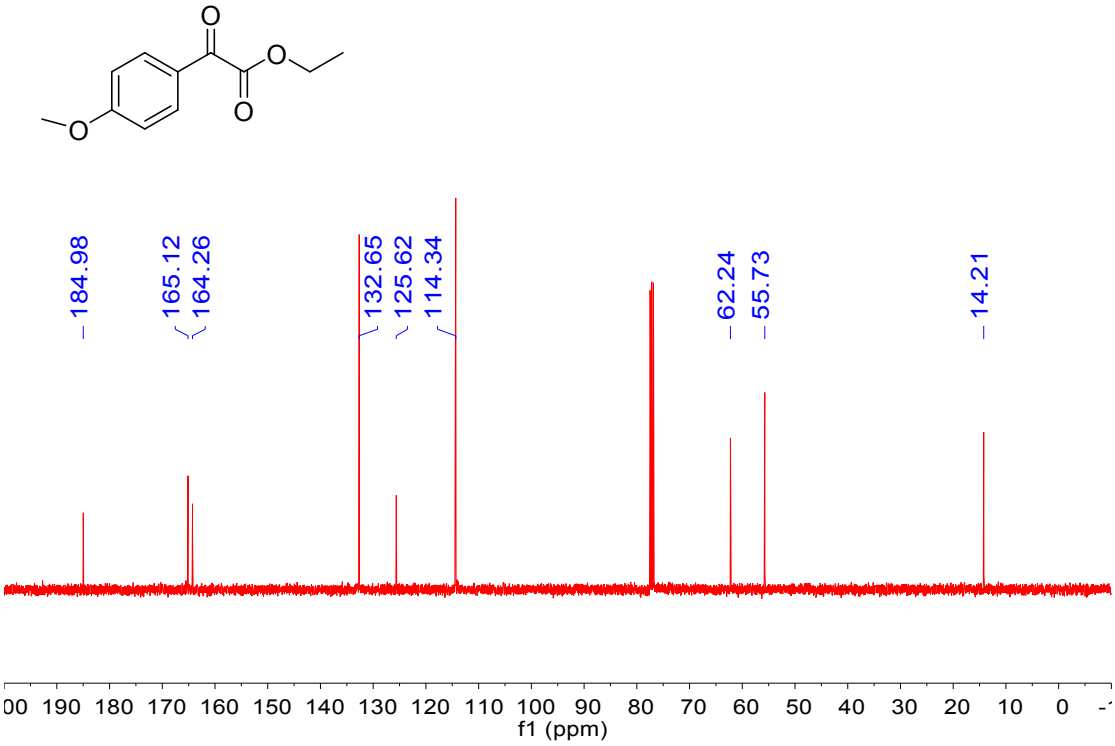
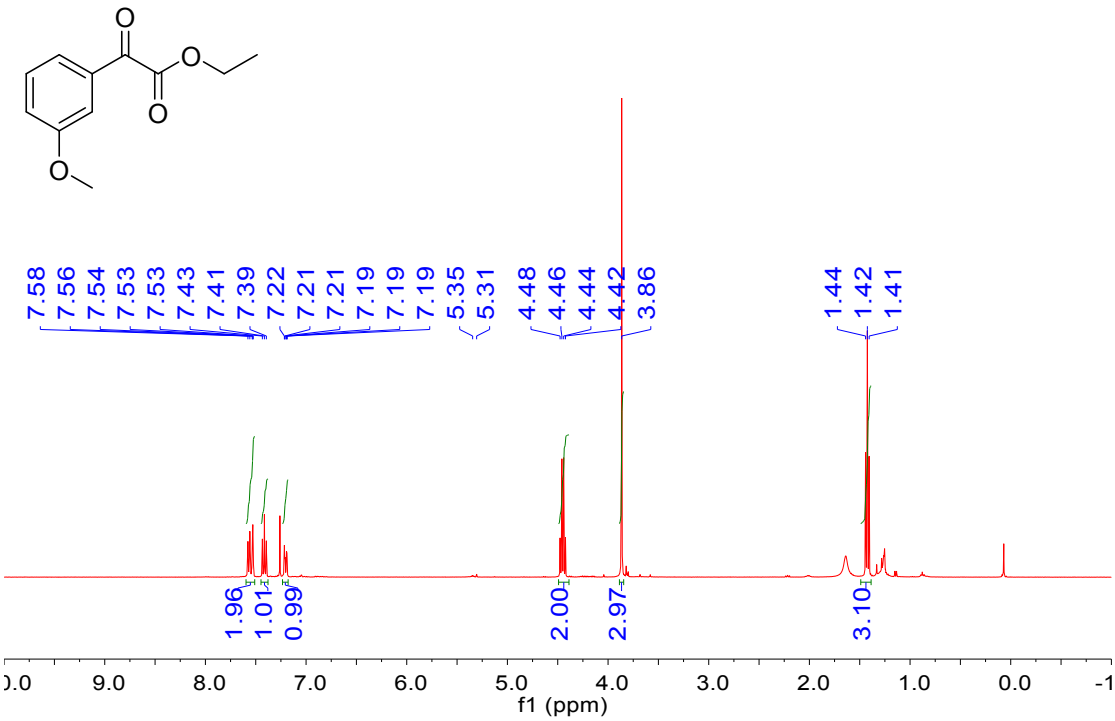
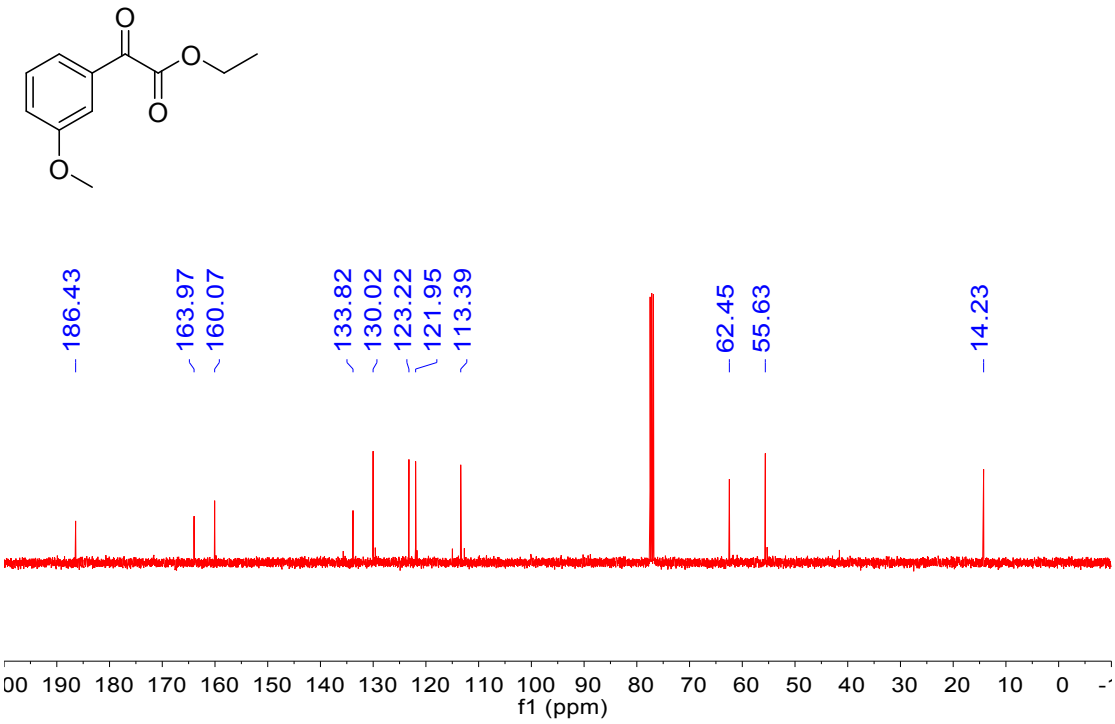


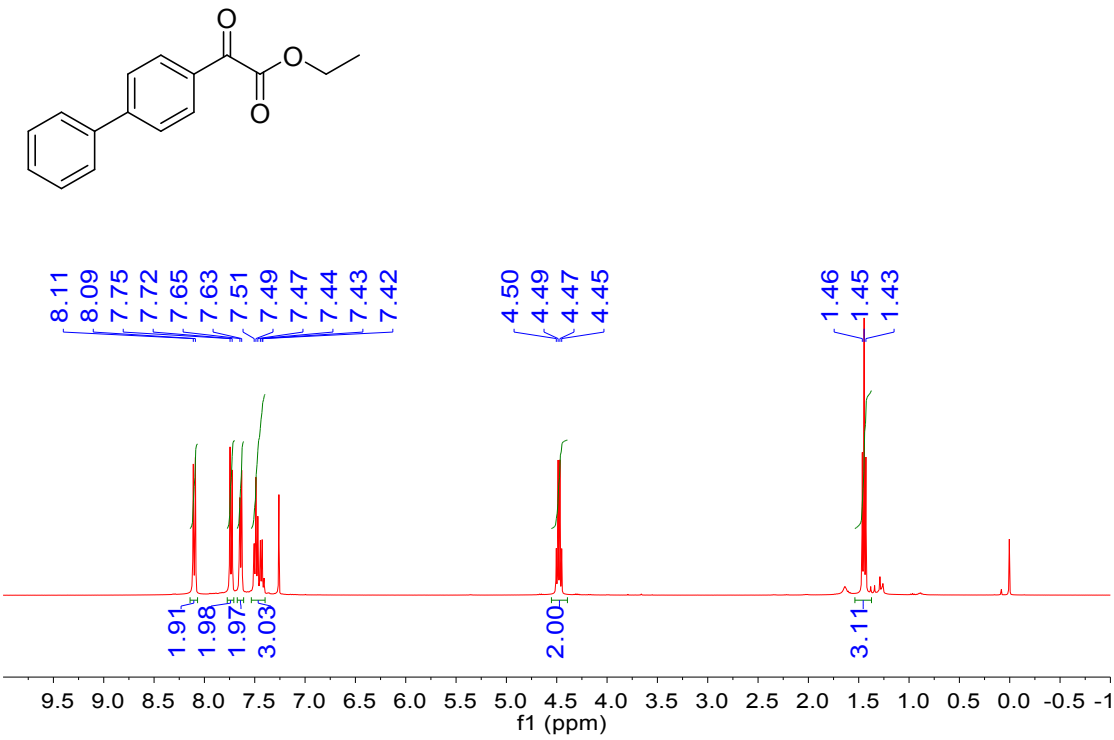
^{13}C NMR spectrum of compound 2k



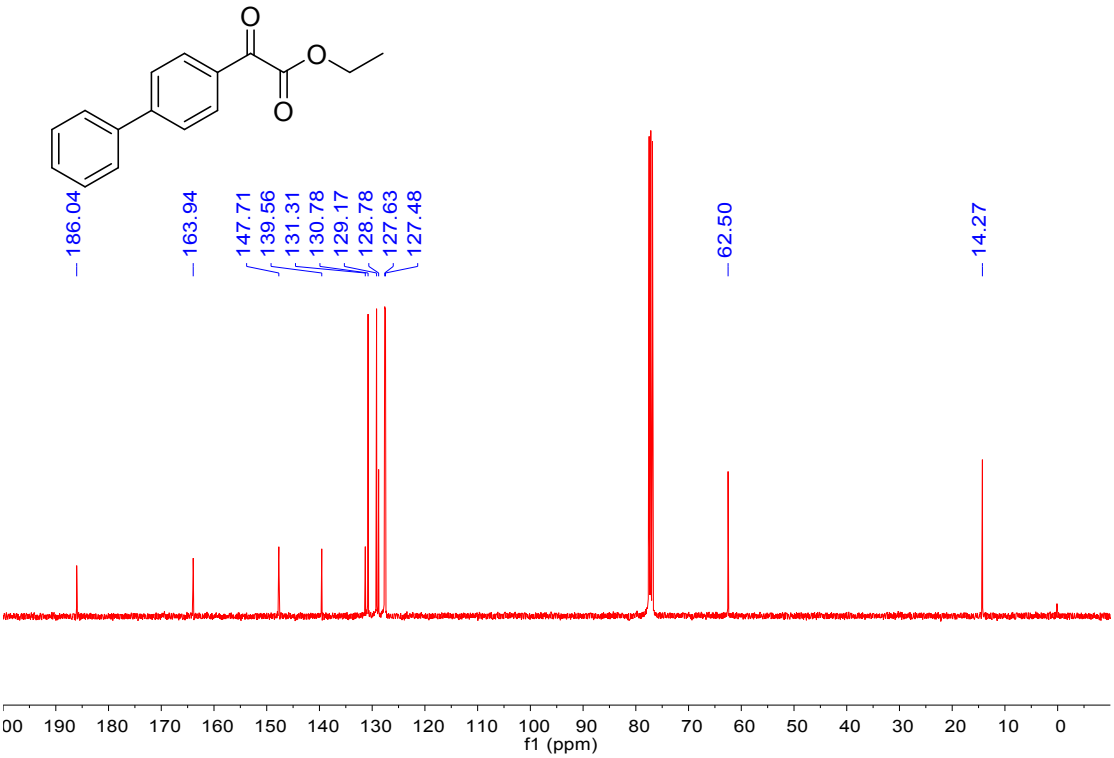
^{1}H NMR spectrum of compound 2l



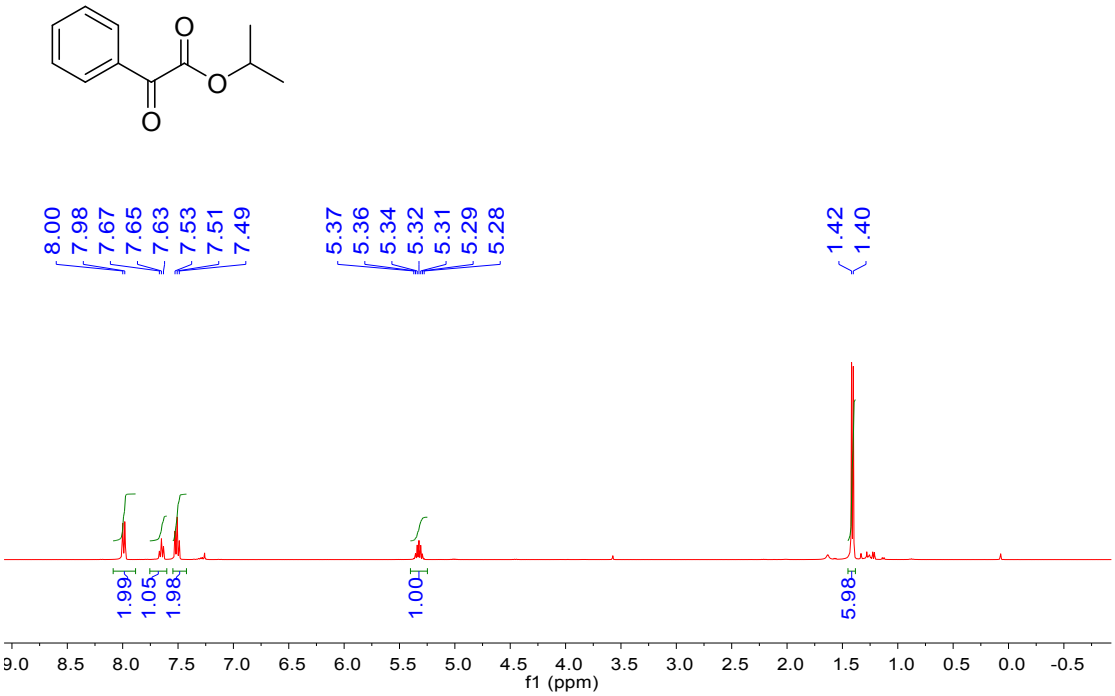
^{13}C NMR spectrum of compound 2l



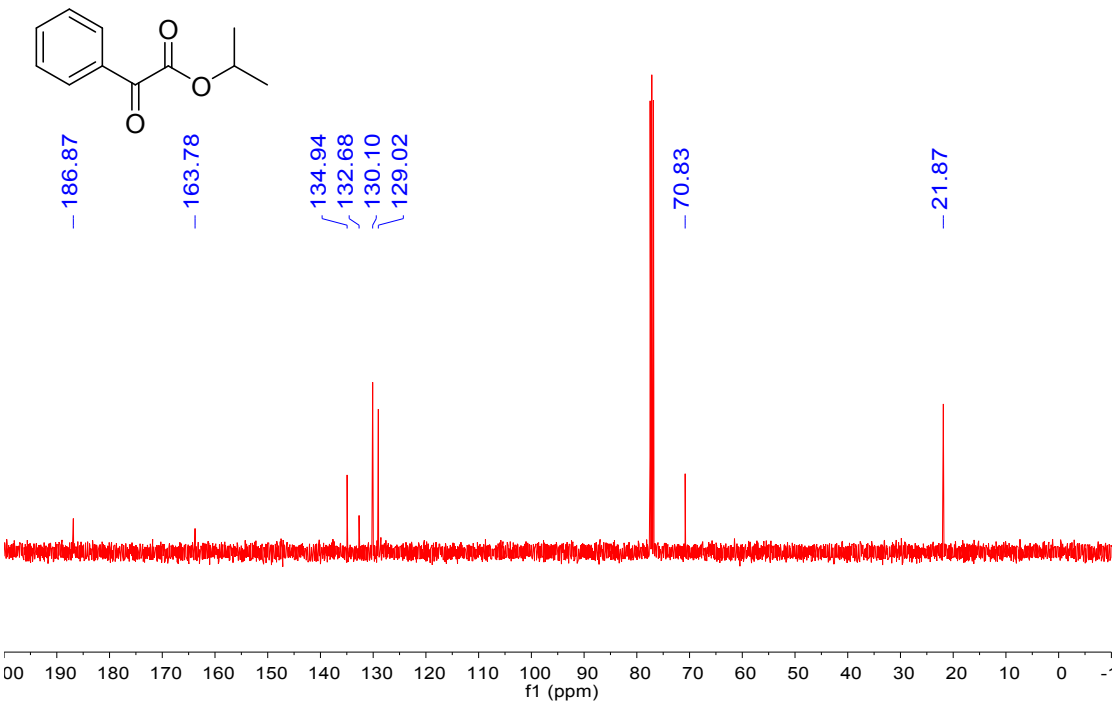
^{1}H NMR spectrum of compound 2m



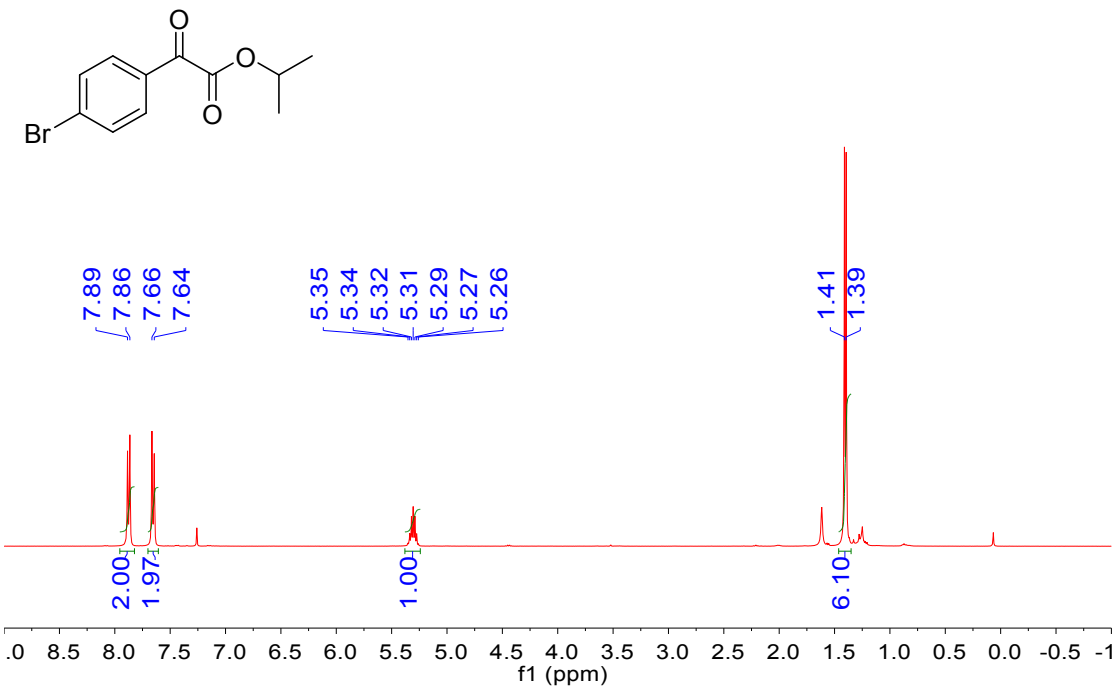
^{13}C NMR spectrum of compound 2m



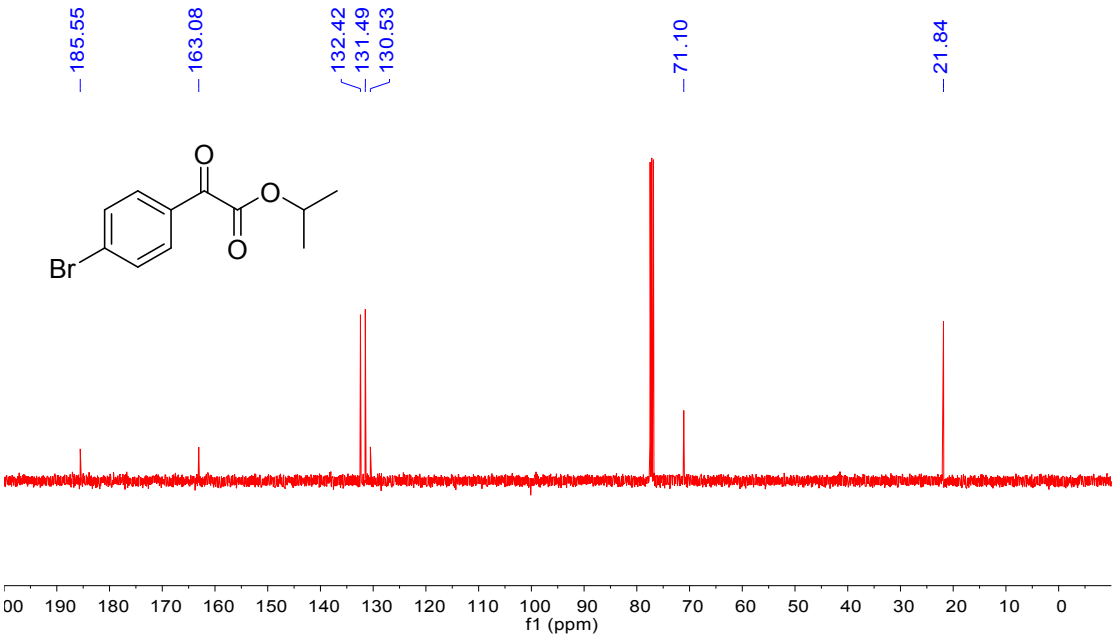
^{1}H NMR spectrum of compound 2n



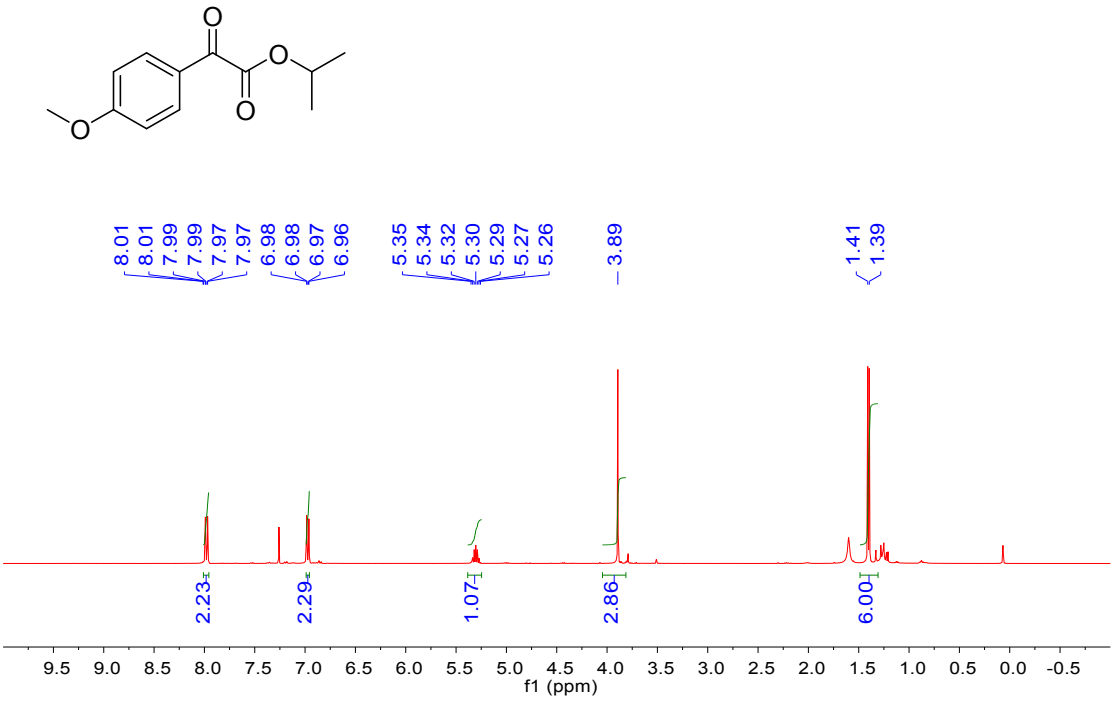
^{13}C NMR spectrum of compound 2n



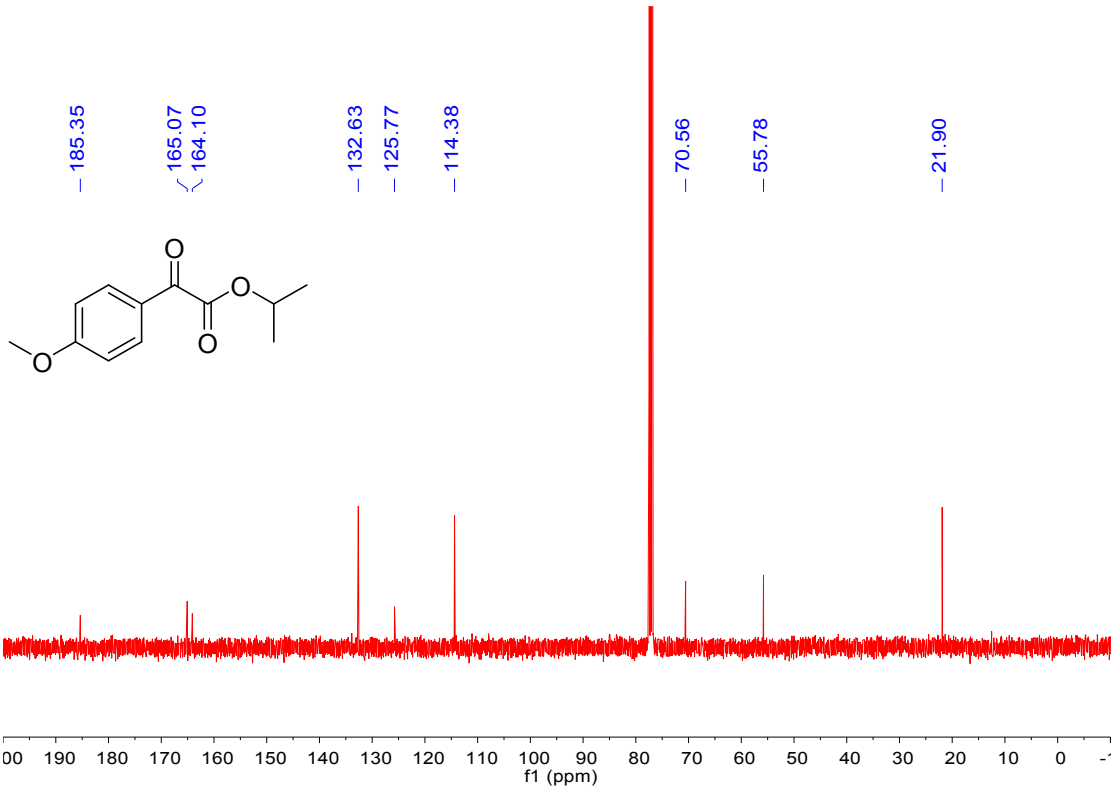
^{1}H NMR spectrum of compound 2o



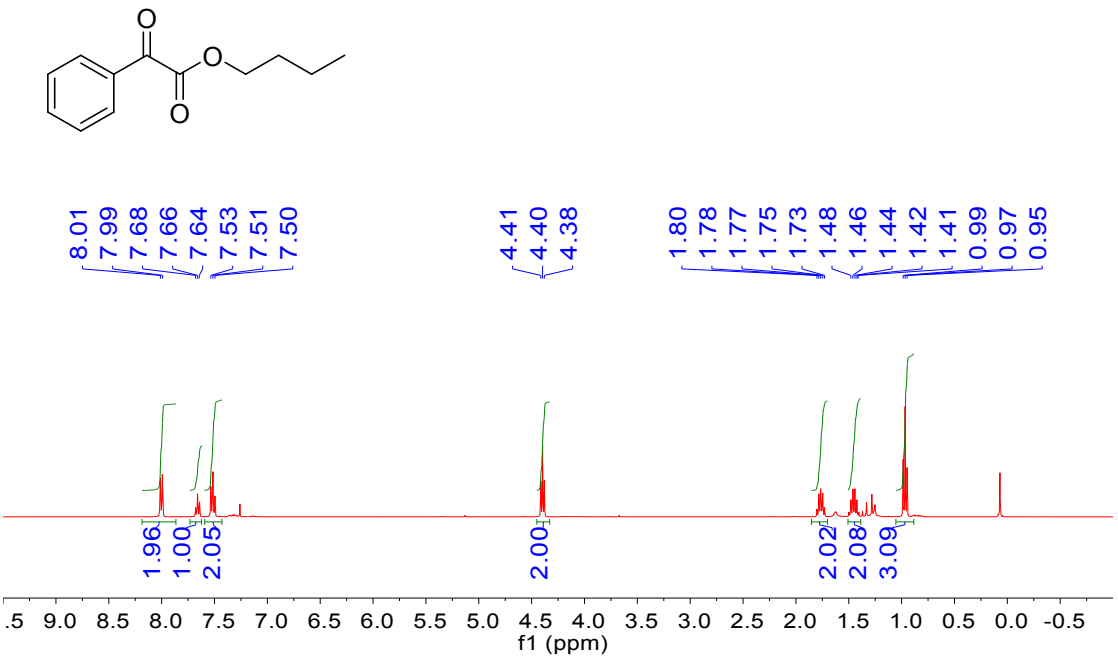
^{13}C NMR spectrum of compound 2o



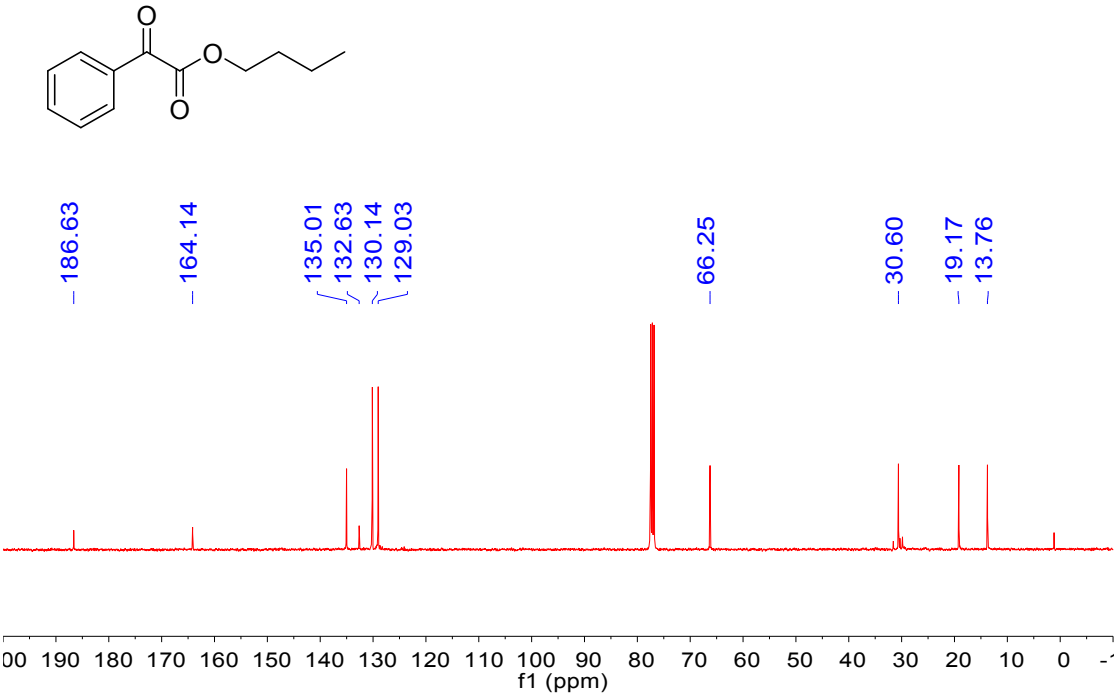
^{1}H NMR spectrum of compound 2p



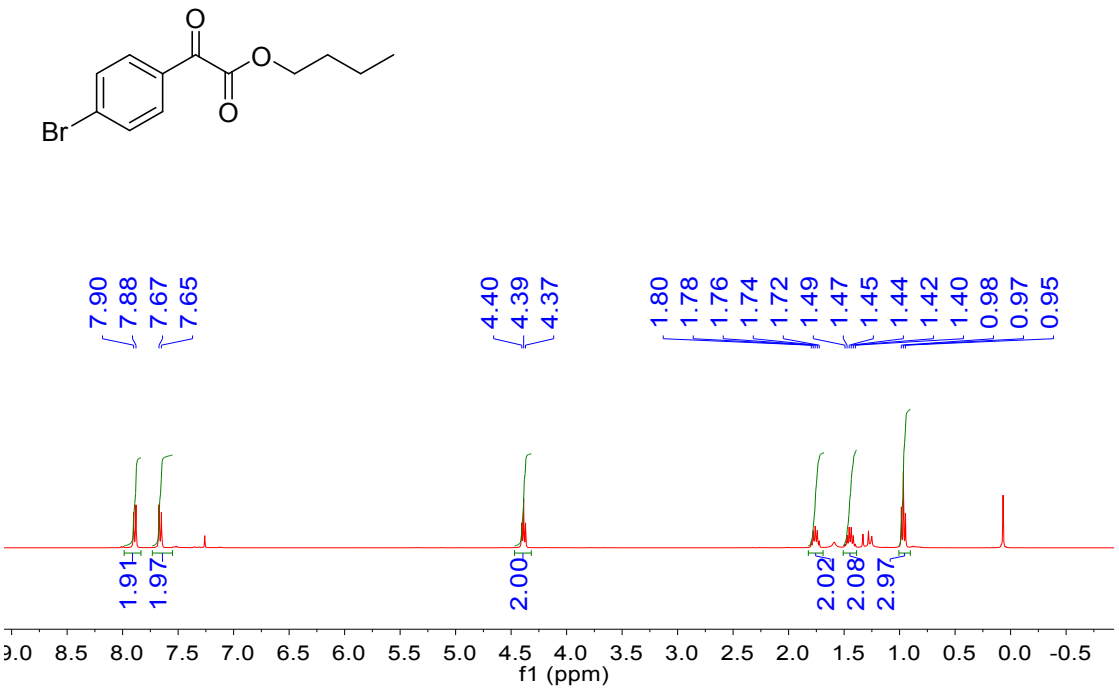
^{13}C NMR spectrum of compound 2p



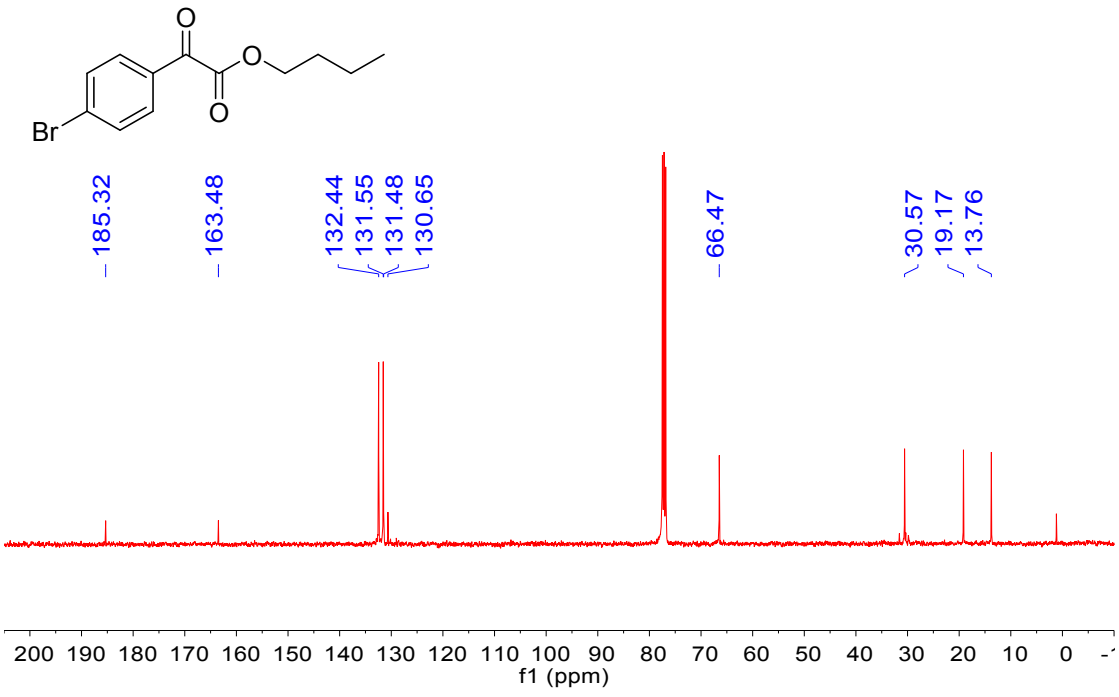
^{1}H NMR spectrum of compound 2q



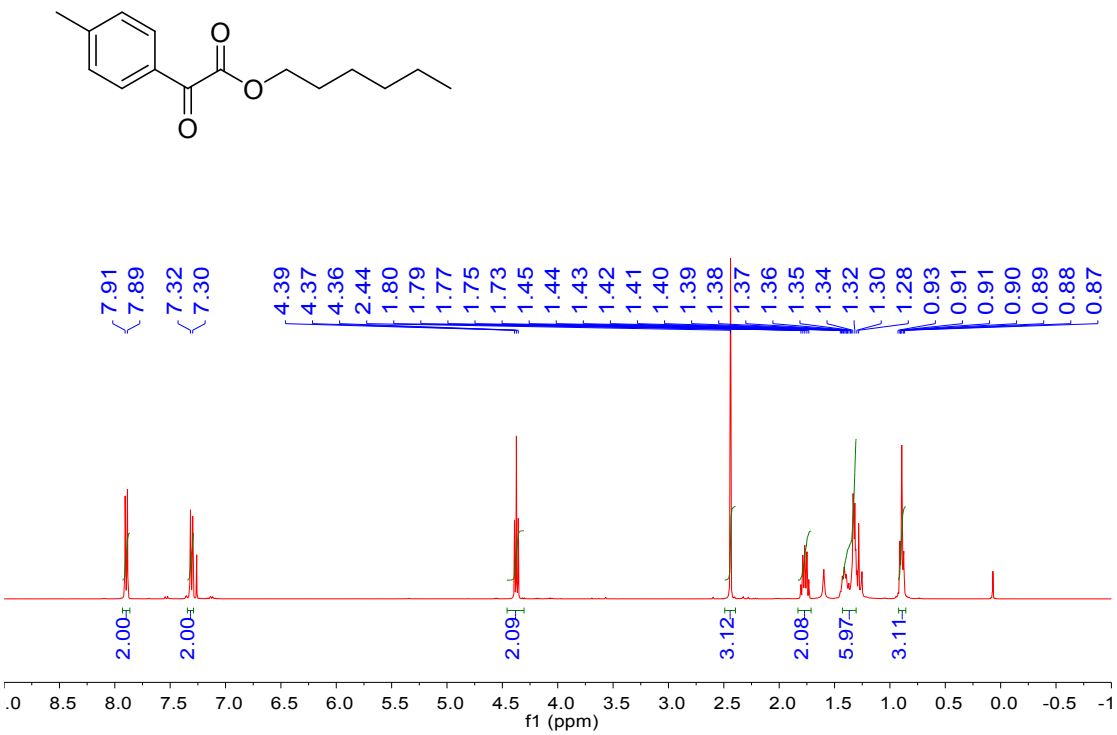
^{13}C NMR spectrum of compound 2q



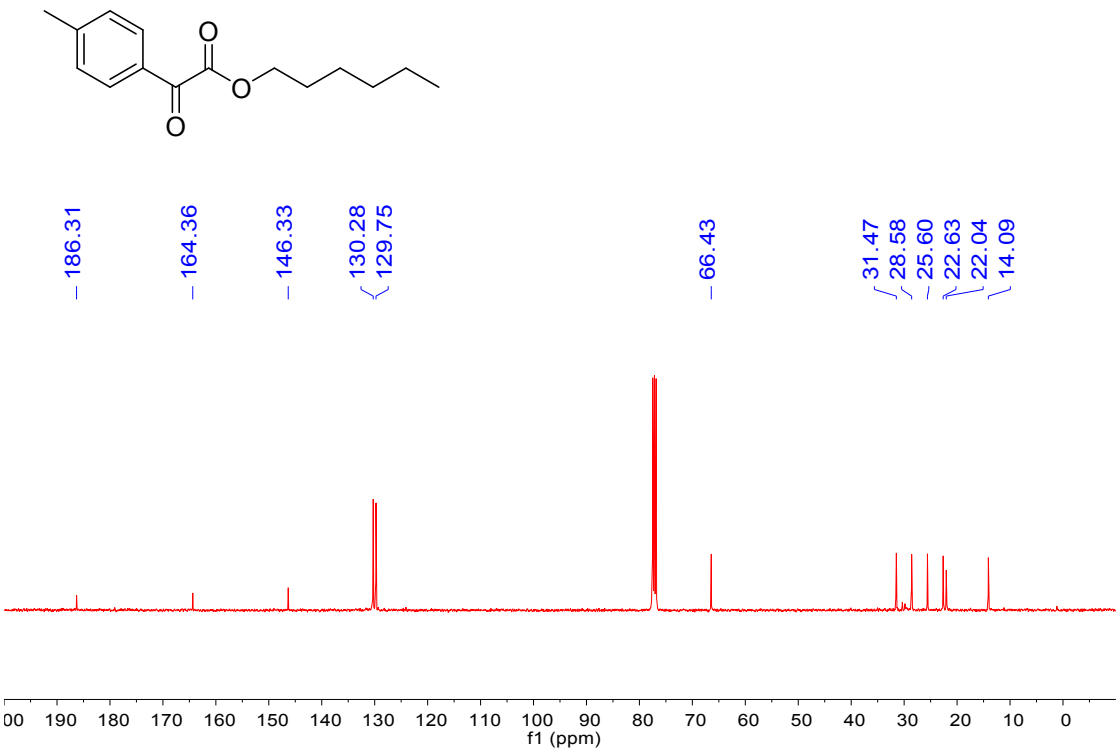
^{1}H NMR spectrum of compound 2r



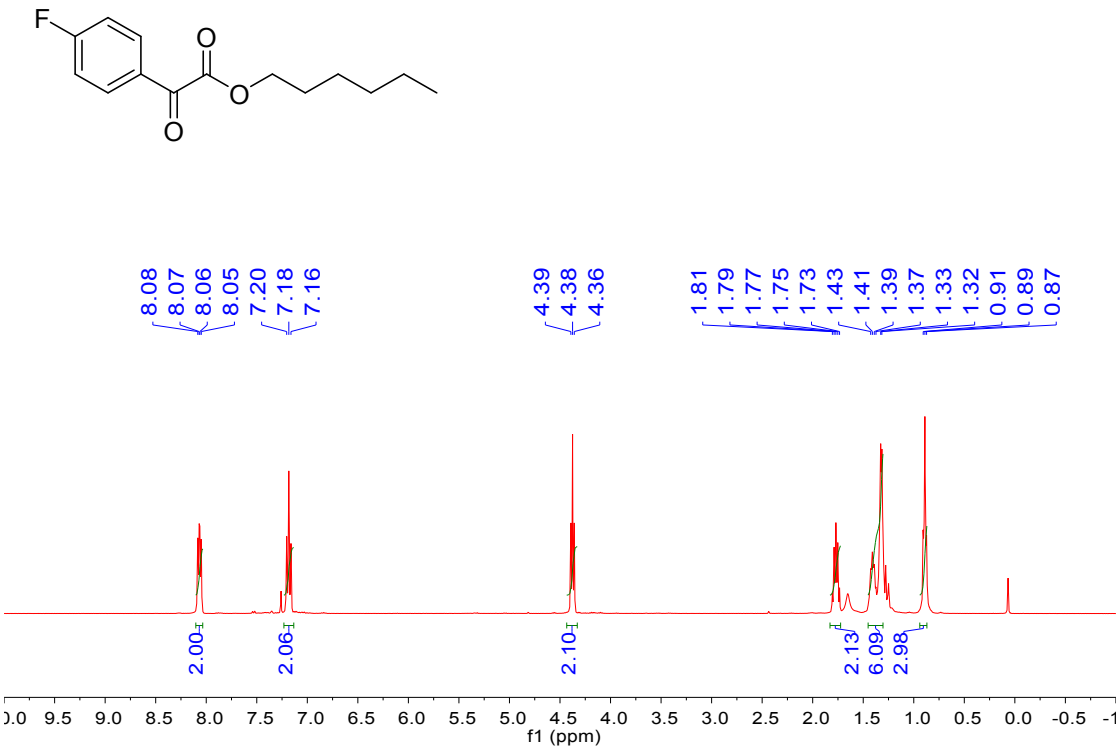
^{13}C NMR spectrum of compound 2r



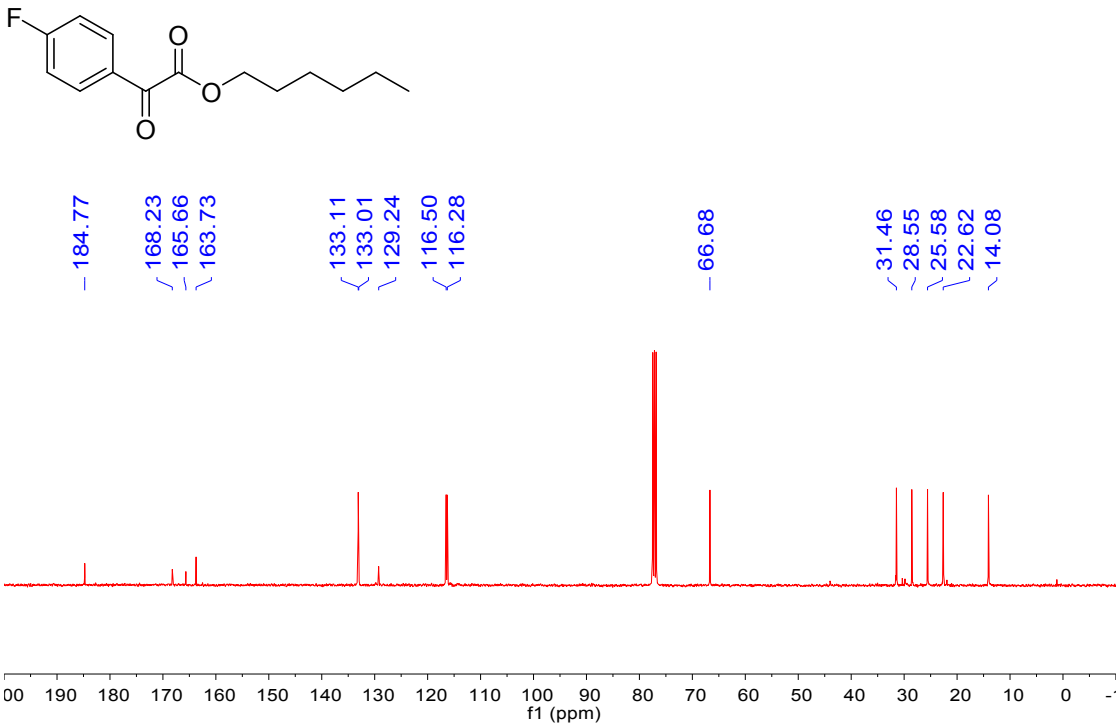
^{1}H NMR spectrum of compound 2s



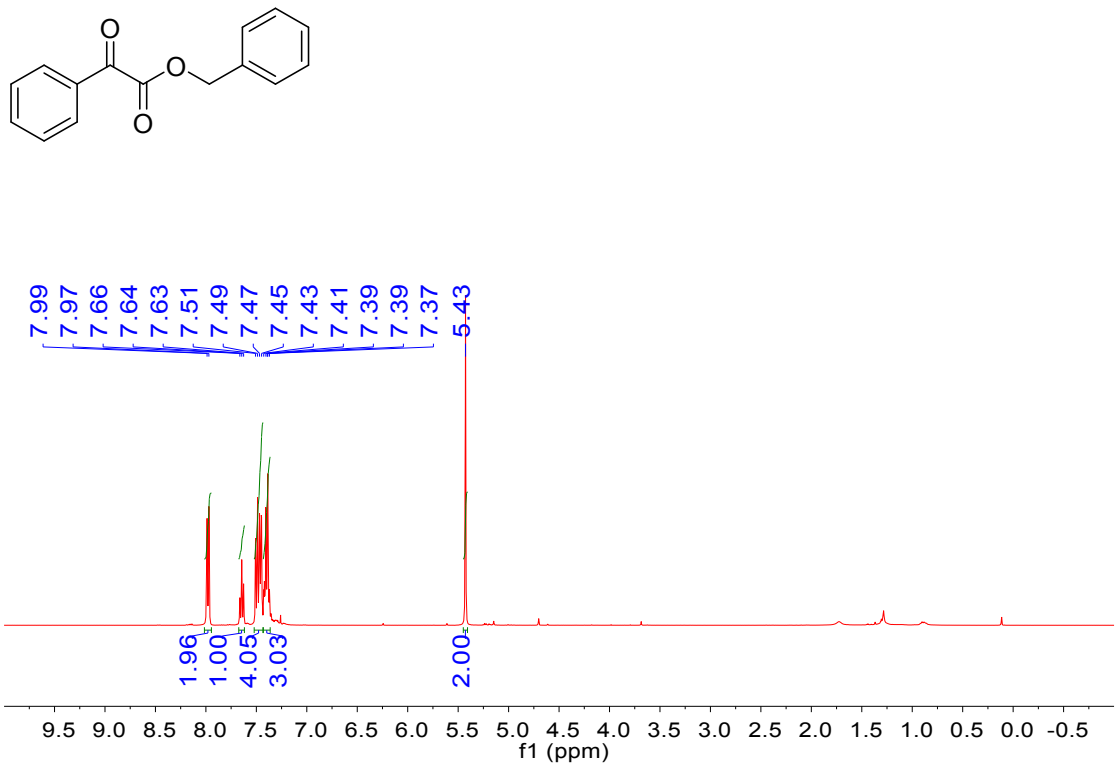
^{13}C NMR spectrum of compound 2s



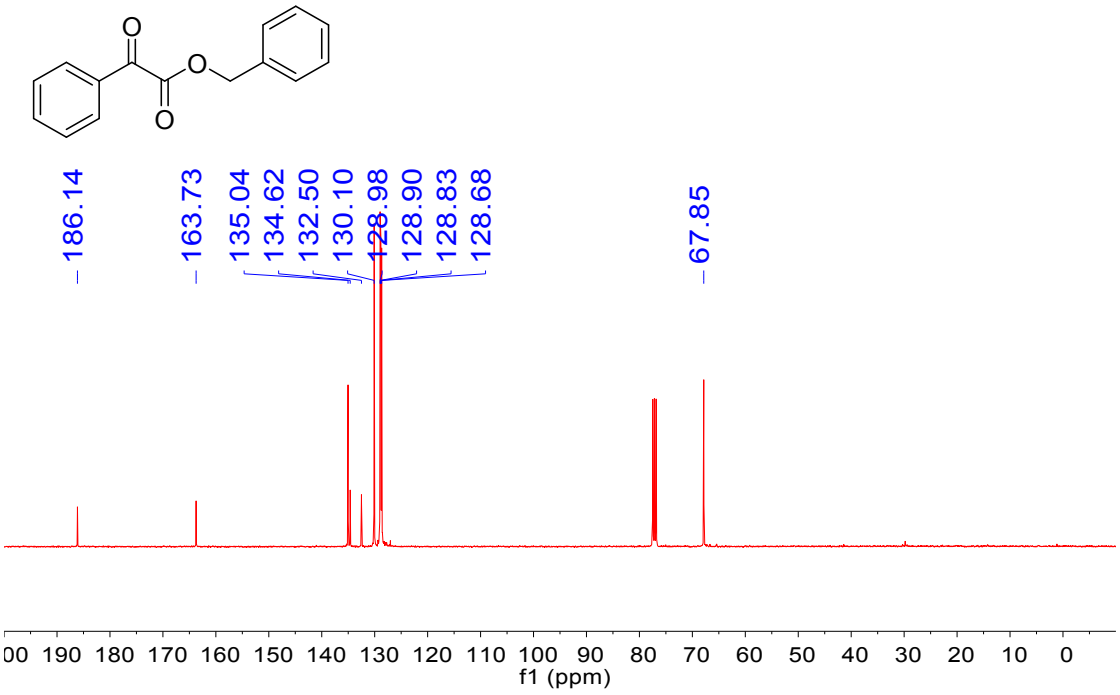
^{1}H NMR spectrum of compound 2t



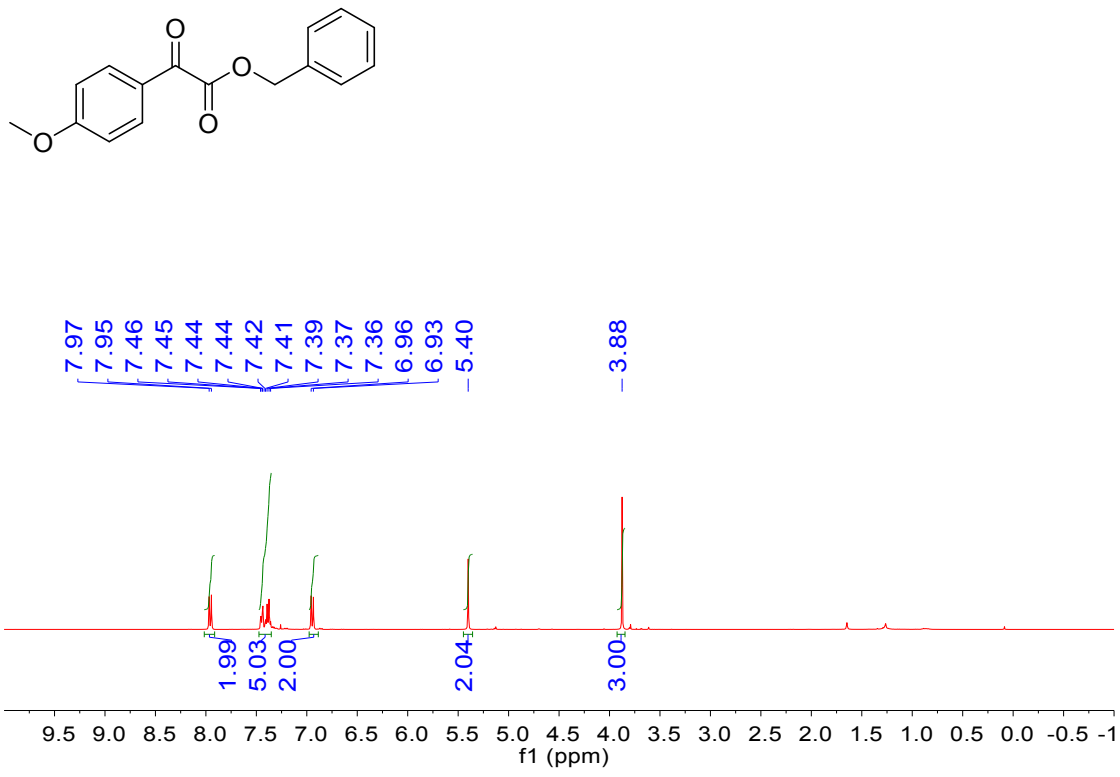
^{13}C NMR spectrum of compound 2t



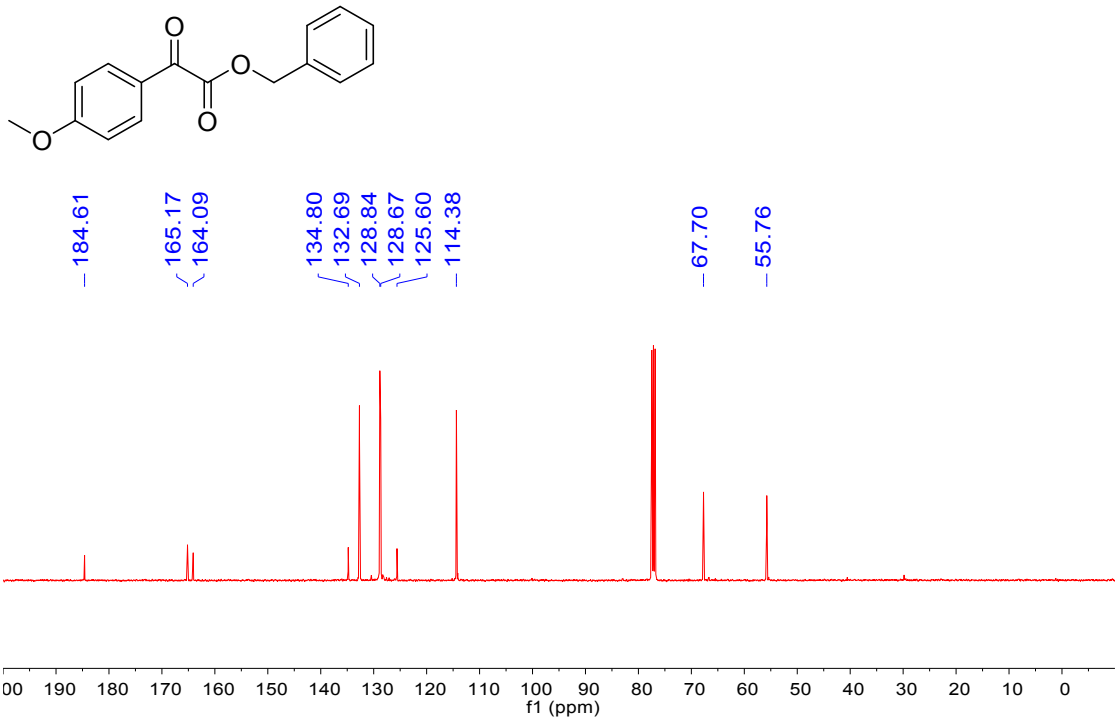
^{1}H NMR spectrum of compound 2u



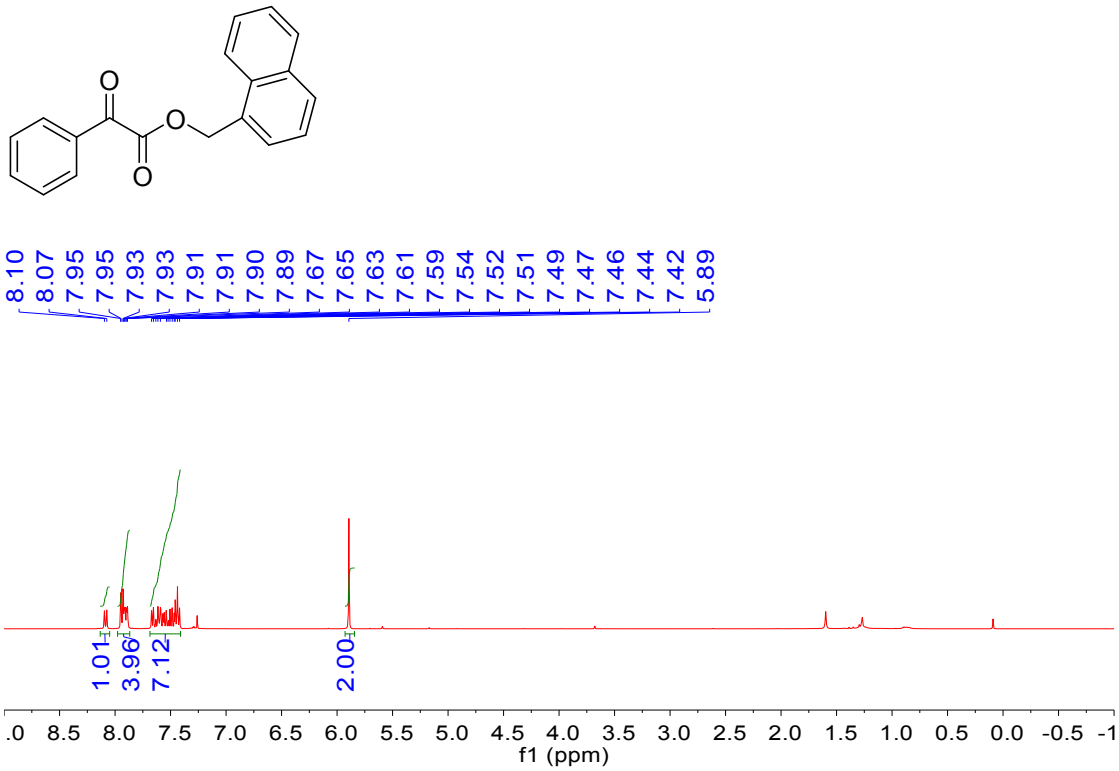
^{13}C NMR spectrum of compound 2u



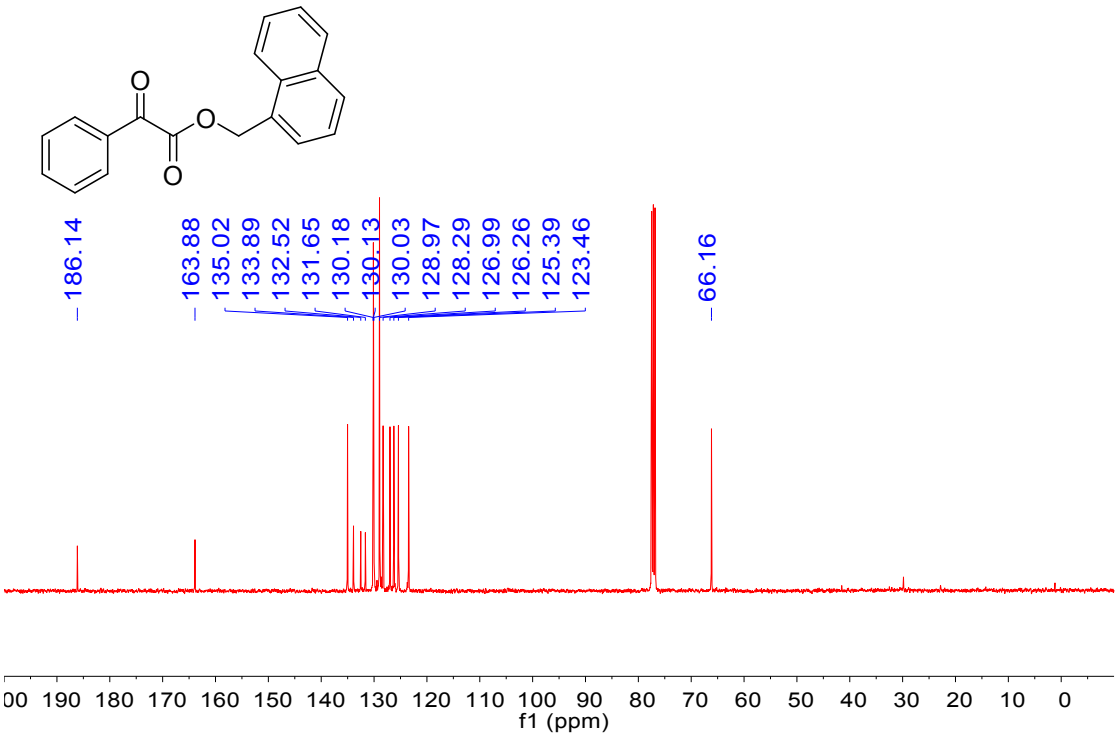
^{1}H NMR spectrum of compound 2v



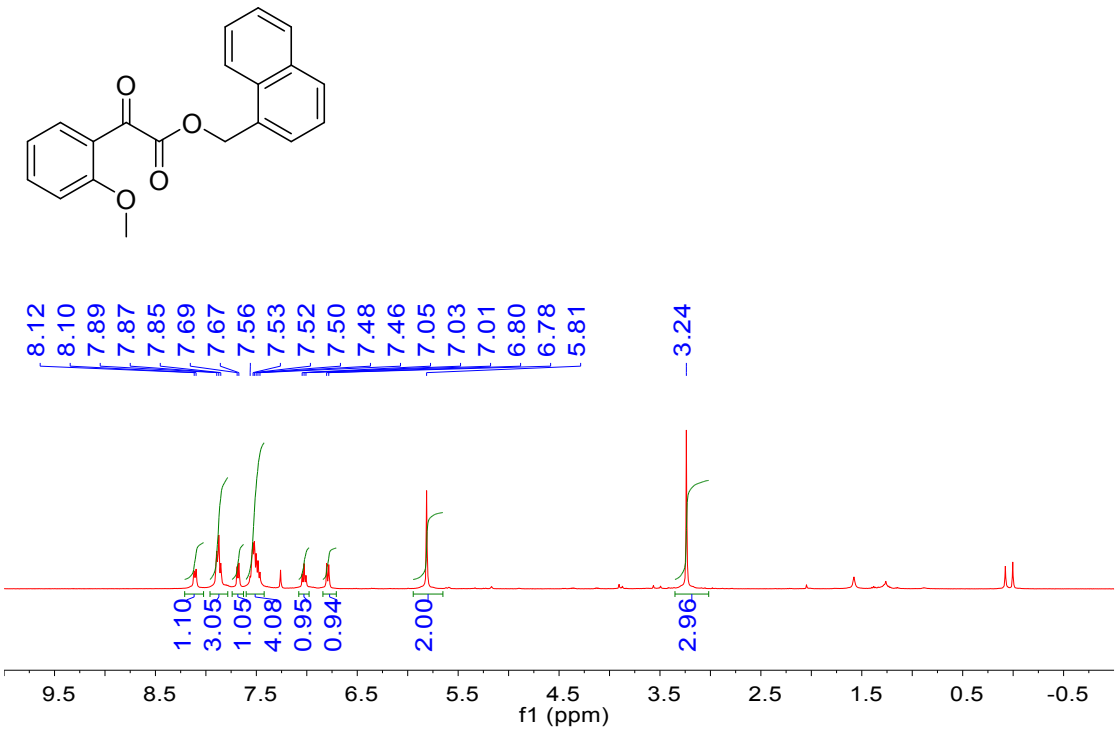
^{13}C NMR spectrum of compound 2v



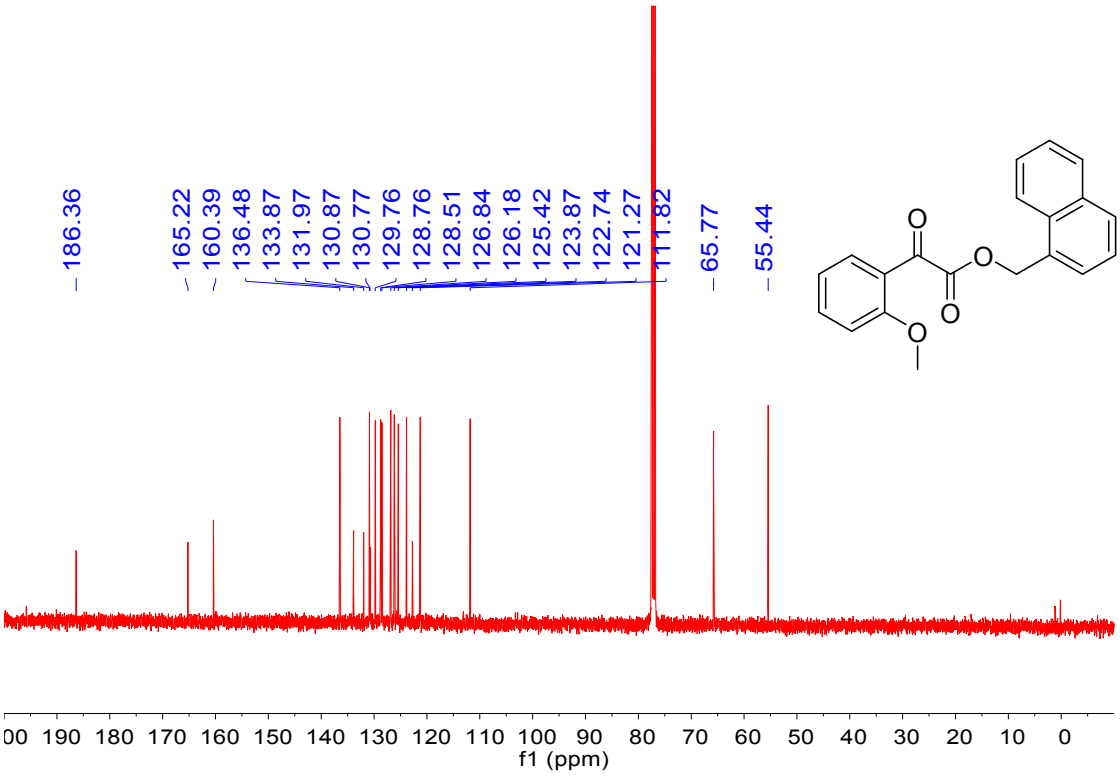
^{1}H NMR spectrum of compound 2w



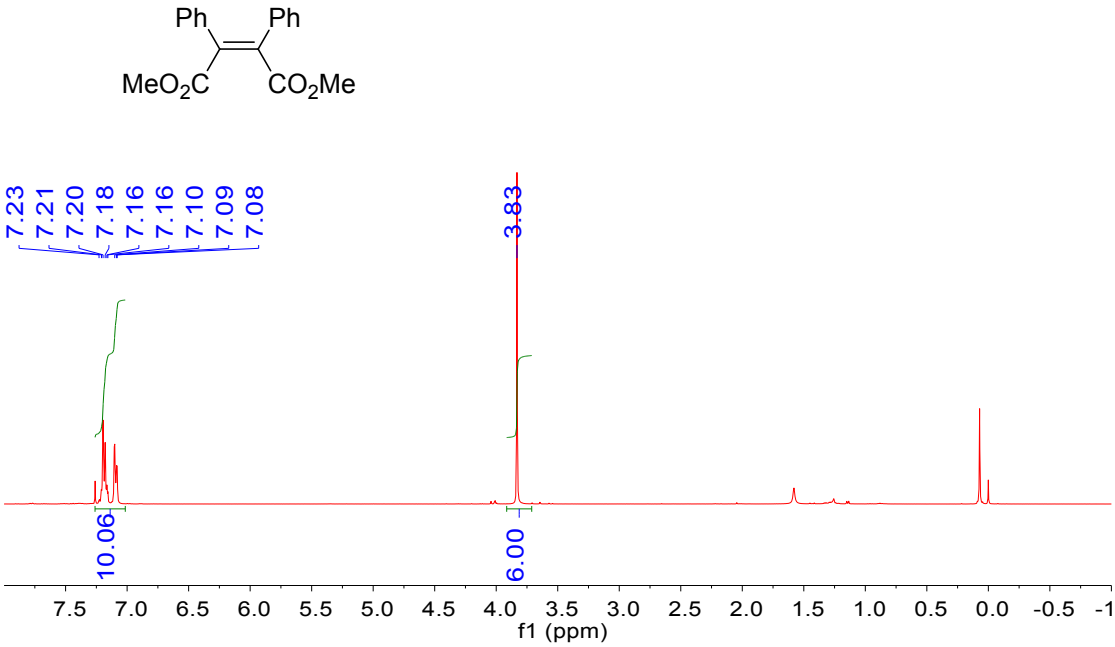
^{13}C NMR spectrum of compound 2w



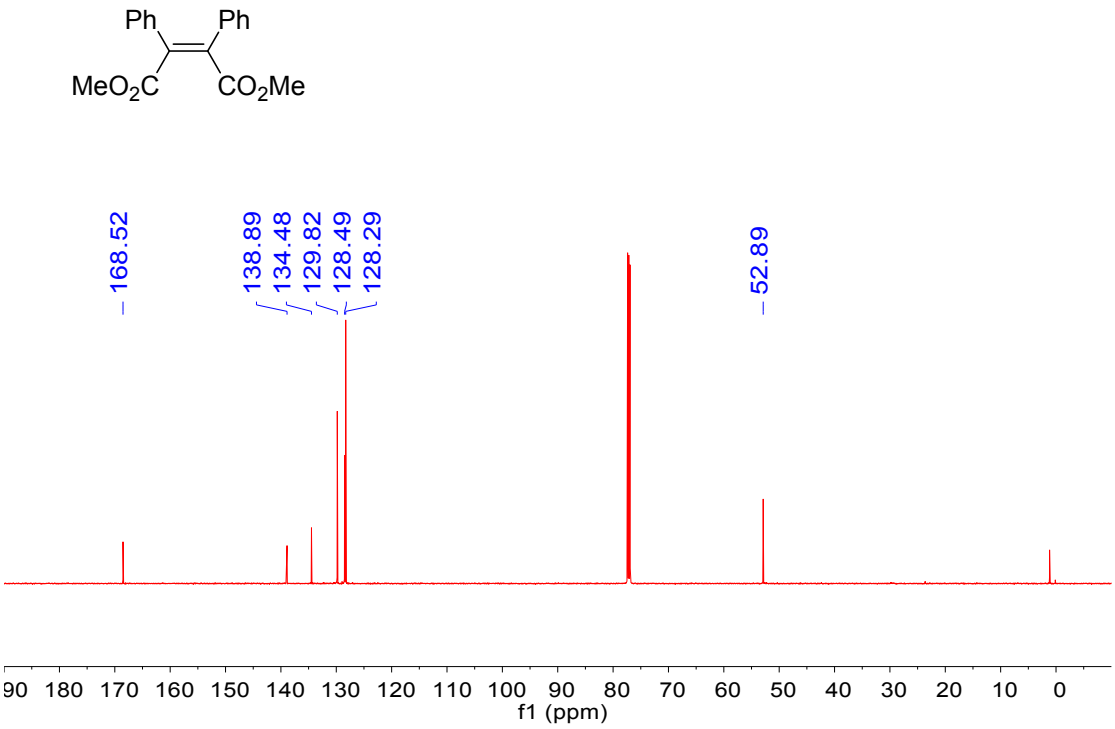
^{1}H NMR spectrum of compound 2x



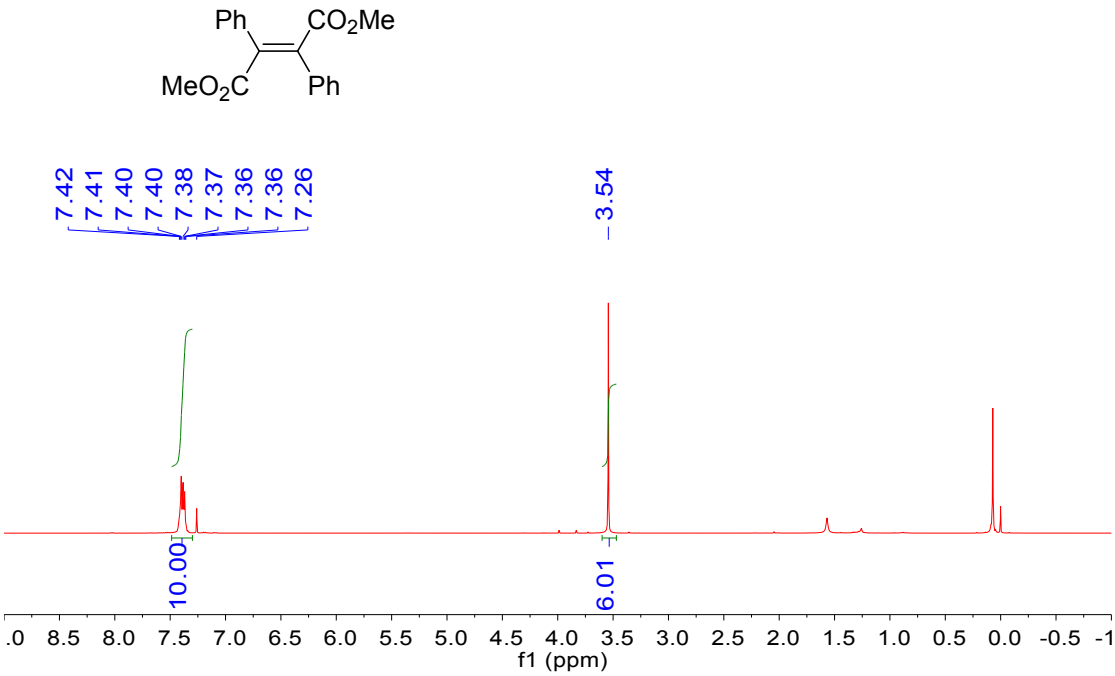
^{13}C NMR spectrum of compound 2x



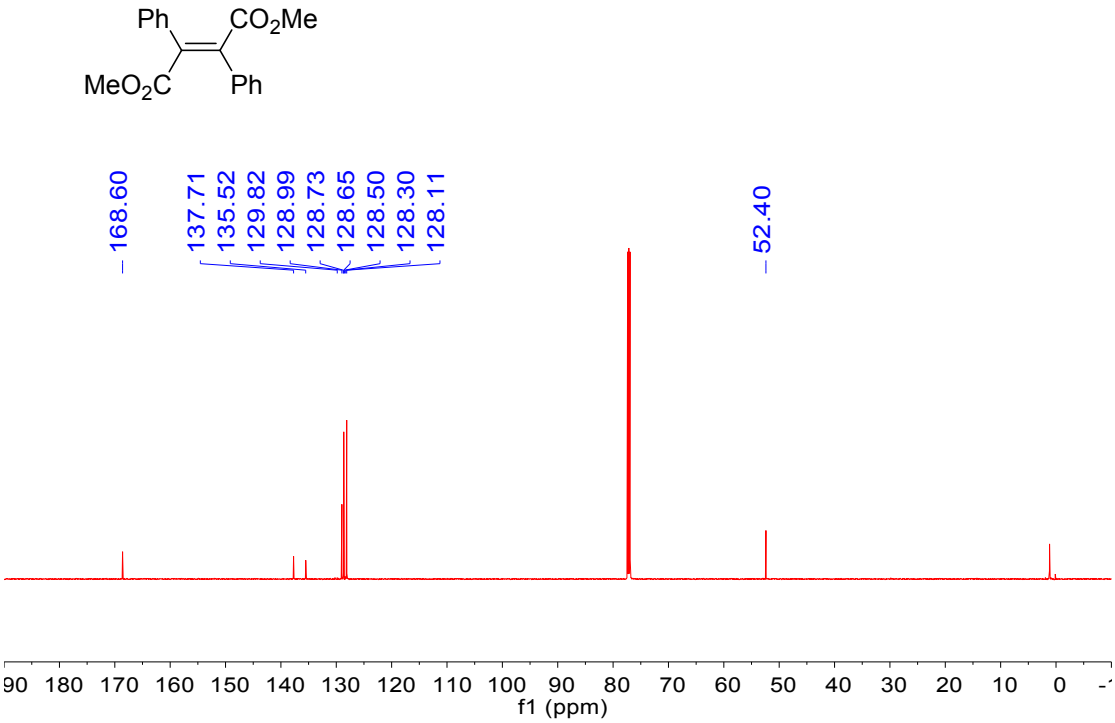
^{1}H NMR spectrum of compound *Z*-4



^{13}C NMR spectrum of compound *Z*-4



^{1}H NMR spectrum of compound *E*-4



^{13}C NMR spectrum of compound *E*-4