Advanced Synthesis & Catalysis

Supporting Information

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Supporting Information

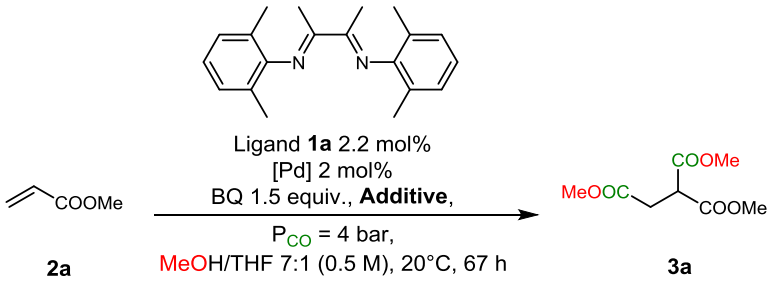
Contents:

1. Abbreviations

The abbreviations used in the main text and in the SI are reported here: BQ = *p*-benzoquinone; H_2Q = 1,4-hydroquinone; HTFA = trifluoroacetic acid; TFA = trifluoroacetate; *p*-TSA = *p*-toluenesulfonic acid; HFIP = hexafluoroisopropanol; THF = tetrahydrofuran; Me = methyl; ^{i}Pr = isopropyl; Bn = benzyl; ^{t}Bu = *tert*-butyl; Ph = phenyl; BIAN= bis(aryl)acenaphthenequinonediimine; EWG = electron-withdrawing group.

2. Further parameters affecting the bis-alkoxycarbonylation reaction of methyl acrylate 2a

Table S1. Experiments performed for parameter optimization affecting the bis-alkoxycarbonylation reaction of methyl acrylate **2a**



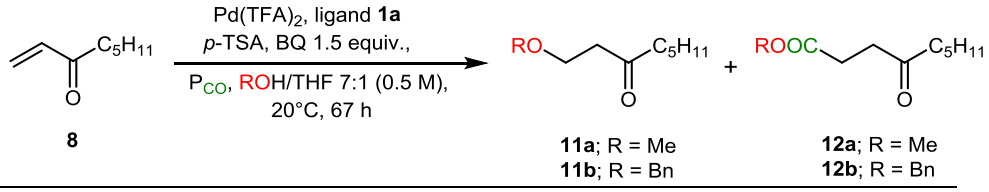
Entry[a]	[Pd]	Additive/Reagent	Conversion (%)[b]
1[c]	$PdCl_2(PhCN)_2$	AgOTf	60
2	$Pd(TFA)_2$	--	71
3	$Pd(TFA)_2$	HFIP	73
4	$Pd(TFA)_2$	NEt_3	< 5
5[d]	$Pd(TFA)_2$	*p*-TSA	43
6[e]	$Pd(TFA)_2$	*p*-TSA	70
7[f]	$Pd(TFA)_2$	*p*-TSA	96
8[g]	$Pd(TFA)_2$	*p*-TSA	30

[a] Reactions performed in autoclave at P_{CO} = 4 bar, with olefin **2a** (2 mmol), palladium salts [Pd] 2 mol%, ligands **1a** 2.2 mol%, additive (2 mol%) and BQ (1.5 equiv), in 7:1 MeOH/THF (4 mL), for 67 h. [b] Determined by ^{1}H NMR analysis of the reaction crude. [c] Reaction performed using 4.4 mol% of AgOTf (the AgOTf has been added to the catalyst solution after the addition of the ligand and the solution was left stirring for 30 min). [d] Reaction performed using 5 mol% of *p*-TSA. [e] Reaction performed using 1.1 equiv. of BQ. [f] Reaction performed at 50 °C. [g] Reaction performed at 1 bar of CO.

Procedure for the bis-alkoxycarbonylation optimization reactions: In a nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, the olefin **2a** in 2 mmol-scale and the methanol (3.5 mL) were added. The mixture was left under stirring for 10 min. In another nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, the Pd salt and THF (0.5 mL) were added in sequence. After the mixture turned in a red/brown color (25 min), the ligand **1a** was added. The mixture was left under stirring for 20 min. The olefin solution and the formed catalyst were injected in sequence in a nitrogen flushed autoclave, equipped with a magnetic stirring bar, containing *p*-benzoquinone (325 mg, 3 mmol) and *p*-TSA·H_2O (other possible additives were directly added with a syringe in the autoclave). After 10 min, the autoclave was flushed three times with CO and pressurized with 4 bar of carbon monoxide. The reaction was vigorously stirred at 20 °C for 67 h. The autoclave was vented off, flushed with nitrogen and the reaction mixture was directly analyzed by ^{1}H NMR to determine the conversion of the olefin.

3. Study of the reactivity of the vinyl ketone 8

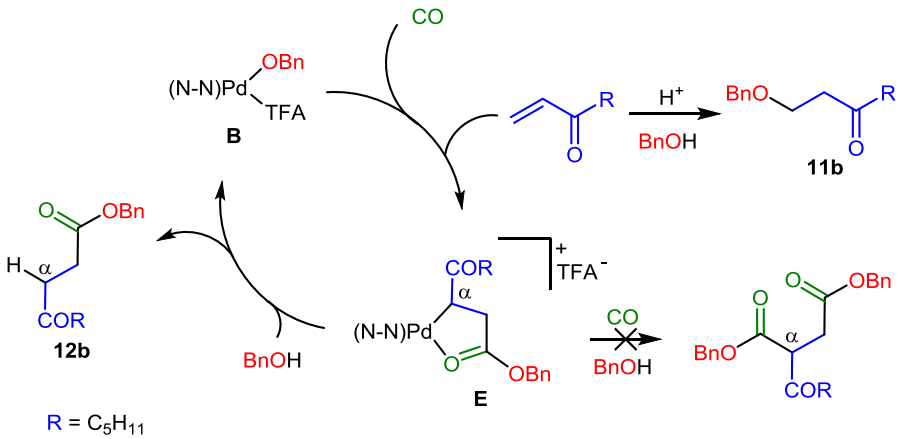
Table S2. Reactivity of the ketone **8c**



Entry[a]	Catalyst Loading (mol%)	*p*-TSA (mol%)	R	Conversion (%)[b]	Ratio **11**/**12**
1	2	2	Me	> 98	1 / 0
2	--	2	Me	> 98	1 / 0
3	2	--	Me	> 98	6 / 1
4	2	2	Bn	> 98	1 / 1

[a] Reaction performed in autoclave at P_{CO} = 4 bar, with olefin **8** (2 mmol), using BQ (1.5 equiv.) and the indicated amount of catalyst loading and of *p*-TSA, in 7:1 ROH/THF (4 mL) as the reaction medium, for 67 h. [b] Determined by direct ^{1}H NMR analysis on a sample of the reaction mixture.

Comment on the data shown in Table S2: in our bis-alkoxycarbonylation reaction conditions, the vinyl ketone **8** was mainly converted into the 1-methoxyoctan-3-one product **11a** (entry 1). This product comes from a preferential competitive methoxylation reaction that does not involve palladium catalysis (entry 2). However, performing the reaction without *p*-TSA, a small quantity of the mono-carbonylated methyl 4-oxononanoate product **12a** was also obtained (entry 3). Using benzyl alcohol as nucleophile, the mono-carbonylated benzyl 4-oxononanoate product **12b** was formed in 1:1 ratio with the alkoxylated 1-(benzyloxy)octan-3-one product **11b** (entry 4 and Scheme S1). In all cases, no trace of the expected bis-alkoxycarbonylated product has been detected and a small amount of unidentified by-products were found.



Scheme S1. Proposed pathways for the formation of the products **11b** and **12b**

Although it was not possible to isolate compounds **11a**,[1] **11b**,[2] **12a**[3] and **12b**[4] separately, spectral data were identical to those previously reported in the literature.

Purification of compounds 11b and 12b

The mixture obtained from the reaction reported in Table S2 entry 4 was dried under reduced pressure and filtered off a plug of silica gel eluting with CH_2Cl_2/Et_2O 1:1, the resulting solution was dried up in vacuum. After chromatography column (petroleum ether/ethyl acetate 80:20), a mixture of **11b** and **12b** (1 : 1 ratio) has been isolated as an orange oil (0.4852 g, overall yield = 98 %).

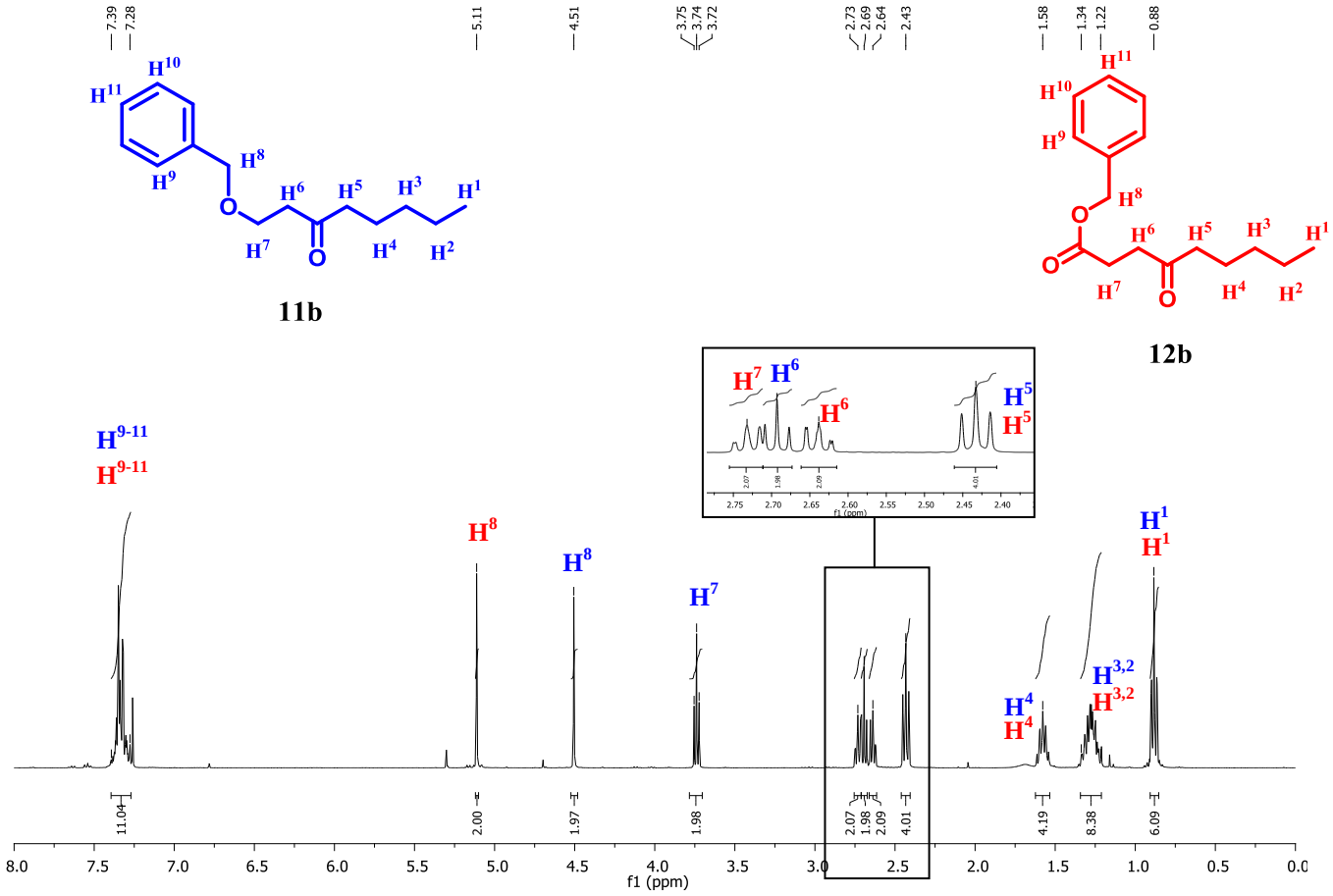


Figure S1 – ^{1}H NMR of the isolated mixture of **11b** and **12b**

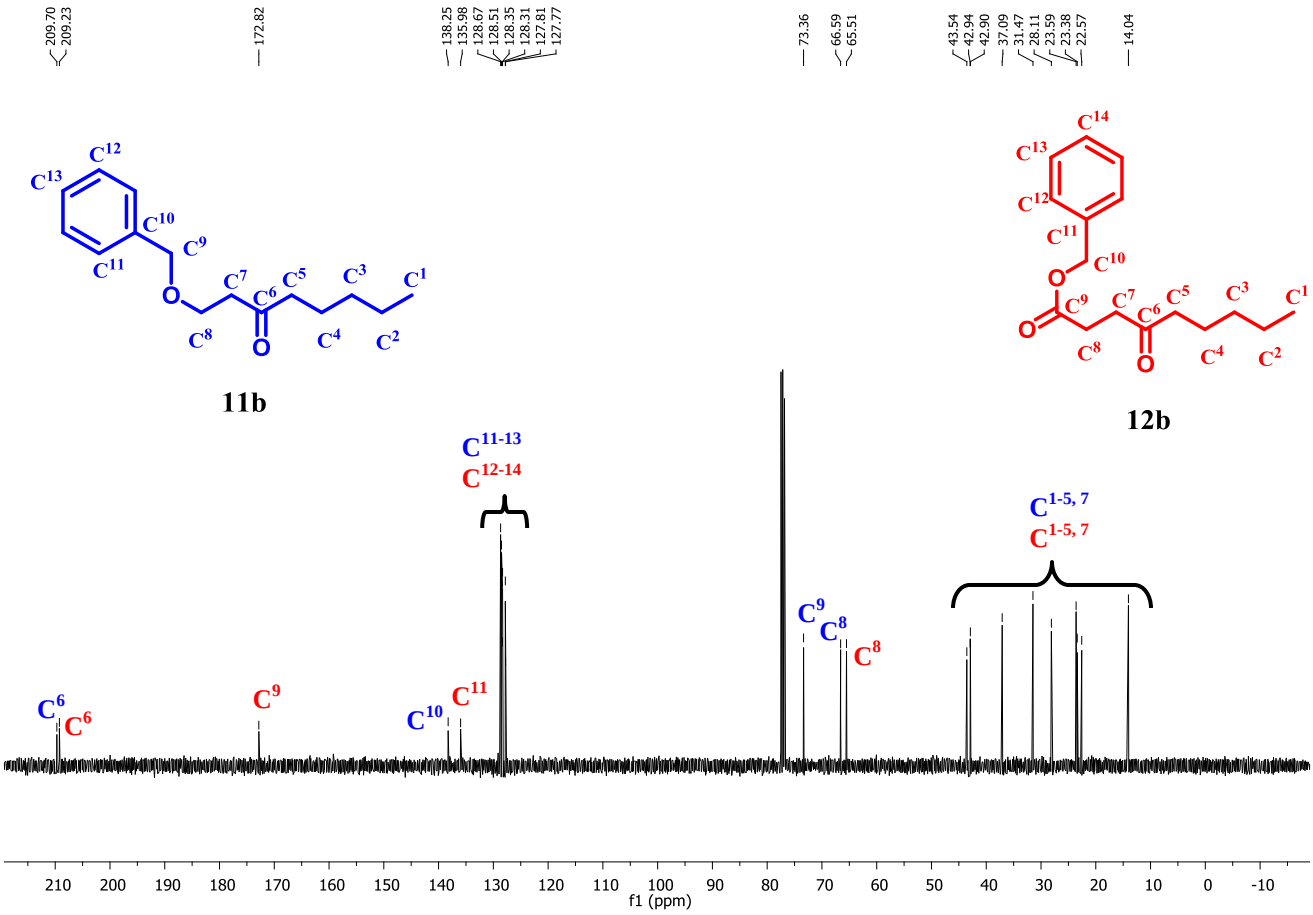


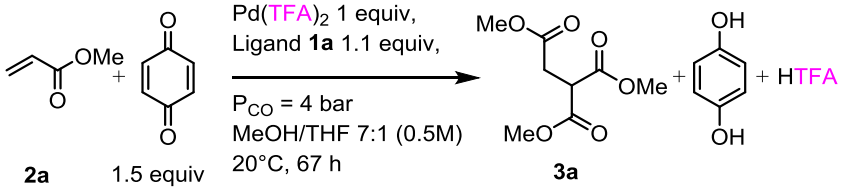
Figure S2 – ^{13}C NMR of the isolated mixture of **11b** and **12b**

4. Experiments to study the proposed catalytic cycle

The complex **A**, utilized in the following experiments, has been synthesized as previously reported by us.[5]

- In a nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, containing 25 mg (0.04 mmol) of **A**, 0.5 mL of MeOH and 43.3 mg (0.4 mmol) of BQ were added. The suspension was stirred at 20 °C for 12 h. After removal of the solvent, the ^{1}H NMR, registered in $CDCl_3$ (+ 75μL of HFIP), showed the presence of the initial complex **A**.
- In a nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, containing 25 mg (0.04 mmol) of **A**, 0.5 mL of THF and 1.6 μL of MeOH (1 equiv) were added. The suspension was stirred at 20 °C for 6 h. After removal of the solvent, the ^{1}H NMR, registered in $CDCl_3$ (+ 75 μL of HFIP), showed the presence of the initial complex **A**. The same result has been obtained also when the experiment was performed utilizing 0.5 mL of MeOH.
- In a nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, 25 mg (0.04 mmol) of **A**, were dissolved in 70 μL of HFIP and then 0.5 mL of MeOD were added. The suspension was stirred at 20 °C for 3 h. The ^{1}H NMR confirmed the presence of the starting complex **A**.

Unfortunately, in all cases the subsequent addition of CO produced decomposition of the complex to palladium black.
From these experiments it is evident that in this case, mainly due to the insolubility of **A**, is not possible to identify the first intermediates of the proposed catalytic cycle. However, various examples of methoxycarbonylation reactions with similar substrates have been widely reported in the literature.[6]
It is important to note that, despite the low solubility of complex **A**, the reaction mixture obtained at the end of the bis-methoxycarbonylation reactions (reported in Table 3 and 4 of the main text), appears as an homogeneous solution. Probably the presence of a great excess of olefin and benzoquinone allows the dissolution of the complex as the reaction proceeds.
Therefore, to get some information on the proposed catalytic cycle, a stoichiometric bis-alkoxycarbonylation reaction with **2a** was performed, without using *p*-TSA (Scheme S2).

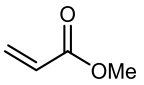
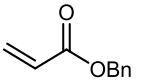
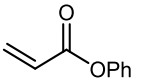
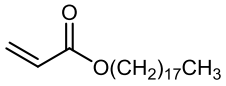
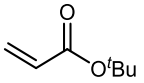
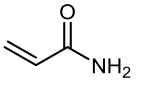
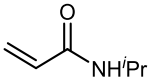
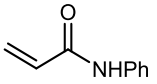
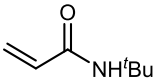
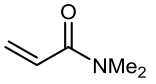
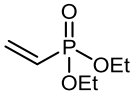
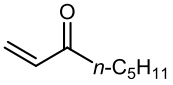
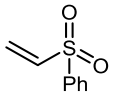


Scheme S2 – Stoichiometric bis-methoxycarbonylation reaction of **2a**

In a nitrogen flushed Schlenk tube, equipped with a magnetic stirring bar, the olefin **2a** (1 mmol) and methanol MeOH (1.75 mL) were added. The mixture was left under stirring for 10 min. Whereupon, THF (0.25 mL) and the olefin solution were injected in sequence in a nitrogen flushed autoclave, equipped with a magnetic stirring bar, containing *p*-benzoquinone (162.3 mg, 1.5 mmol), $Pd(TFA)_2$ (332.4 mg, 1 mmol) and the ligand **1a** (321.2 mg, 1.1 mmol). After 20 min, the autoclave was flushed three times with CO and pressurized with 4 bar of carbon monoxide. The reaction was vigorously stirred at 20 °C for 67 h. The autoclave was vented off, flushed with nitrogen. At the end of the reaction palladium black was present. From the ^{1}H NMR spectrum in $CDCl_3$ of the reaction mixture, resulted that 95% of **2a** was converted in **3a** and a complete conversion of *p*-benzoquinone to hydroquinone was observed. The ^{19}F NMR spectrum of the crude reveled the presence of HTFA, in agreement with our proposed catalytic cycle. ^{19}F NMR (376 MHz, $CDCl_3$) δ –76.3 ppm.

5. Natural Population Analysis (NPA)

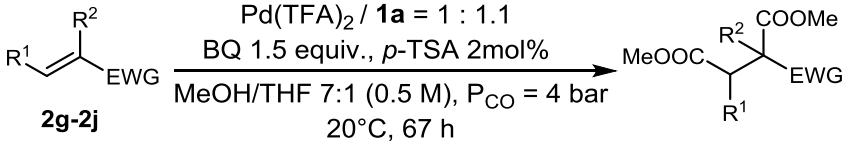
Table S3. Natural Population Analysis (NPA) charges for the oxygen of the X=O group (X=C, P, S)

Entry		Olefin	NPA
1	**2a**		-0.566
2	**2b**		-0.579
3	**2c**		-0.569
4	**2d**		-0.568
5	**2e**		-0.593
6	**4a**		-0.581
7	**4b**		-0.619
8	**4c**		-0.595
9	**4d**		-0.620
10	**4g**		-0.591
11	**6**		-0.995
12	**8**		-0.521
13	**9**		-0.301[a]
14	**10**		-0.880[b]

[a]Partial charge on the nitrogen. [b]Average value for the two oxygens

6. Study of the reactivity of α- or β- substituted acrylic esters and amides

Table S4. Study of the bis-alkoxycarbonylation reaction with olefins **2g**-**2j**.

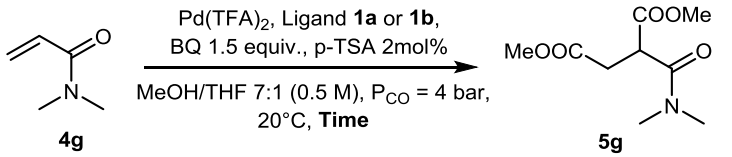


Entry[a]	Olefin	EWG	R^1	R^2	Catalyst Loading (mol%)	Conversion (%)[b]
1	**2g**	COOMe	Me	H	2	< 5
2	**2g**	COOMe	Me	H	5	< 5
3	**2h**	COOMe	H	Me	2	< 5
4	**2i**	COOEt	Ph	H	3	< 5
5	**2j**	$CONH_2$	Ph	H	3	< 5

[a] Reaction performed in autoclave at P_{CO} = 4 bar, with olefins **2g** – **2j** (2 mmol-scale), catalyst loading ($Pd(TFA)_2$ / ligand **1a** = 1 : 1.1) in the indicated amount, *p*-TSA (2 mol%) and BQ (1.5 equiv.), in 7:1 MeOH/THF (4 mL) as the reaction medium, for 67 h. [b] Determined by ^1H NMR analysis of the reaction crude.

7. Optimization study for the bis-methoxycarbonylation reaction of acrylic amides

Table S5. Bis-methoxycarbonylation reaction of **4g**. Influence of the ligand and of the reaction time.



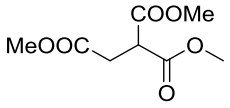
4g **5g**

Entry[a]	$Pd(TFA)_2$ (mol%)	Ligand (mol%)	Time (h)	Conversion (%)[b]
1	0.5	**1a** 0.55	67	35
2	0.5	**1b** 0.55	67	27
3	2	**1a** 2.2	24	39
4	2	**1a** 2.2	46	72
5	2	**1a** 2.2	67	> 98
6[c]	2	**1a** 2.2	67	30

[a] Reaction performed in autoclave at P_{CO} = 4 bar, with olefin **4g** (2 mmol), $Pd(TFA)_2$ (0.55 - 2 mol%), ligand **1a** or **1b (**0.55 - 2.2 mol%), *p*-TSA (2 mol%) and BQ (1.5 equiv.), in 7:1 MeOH/THF (4 mL) as the reaction medium, for the indicated time. [b] Determined by ^1H NMR analysis of the reaction crude. [c] Reaction performed at 1 bar of CO.

8. Experimental Section of Compounds 3a, 5c and 7

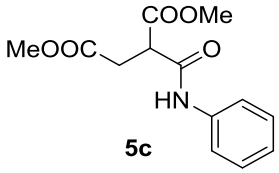
Trimethyl ethane-1,1,2-tricarboxylate (3a):



3a

Synthesized following the general procedure. The compound **3a** has been purified by column chromatography (petroleum ether/CH_2Cl_2 30:70), obtaining a colorless oil; isolated yield: 89% (0.363 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (t, J = 7.4 Hz, 1H), 3.77 (s, 6H), 3.70 (s, 3H), 2.95 (d, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 168.9, 53.0, 52.3, 47.6, 33.1. ESI-MS: m/z = 205 $[M+H]^+$. Spectral data were identical to the previously reported literature data.[7]

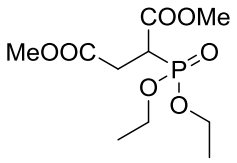
Dimethyl 2-(phenylcarbamoyl)succinate (5c):



5c

Synthesized following the general procedure. The compound **5c** has been purified by column chromatography (petroleum ether/ethyl acetate 20:80), obtaining a white powder; isolated yield: 90% (0.477 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (bs, 1H), 7.55 – 7.49 (m, 2H), 7.32 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 3.85 (t, J = 6.6 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.09 (d, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 170.4, 164.7, 137.6, 129.1, 124.8, 120.1, 53.2, 52.3, 48.9, 32.5. ESI-MS: m/z = 266 $[M+H]^+$. Spectral data were identical to the previously reported literature data.[8]

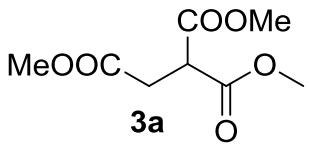
Dimethyl 2-(diethoxyphosphoryl)succinate (7)



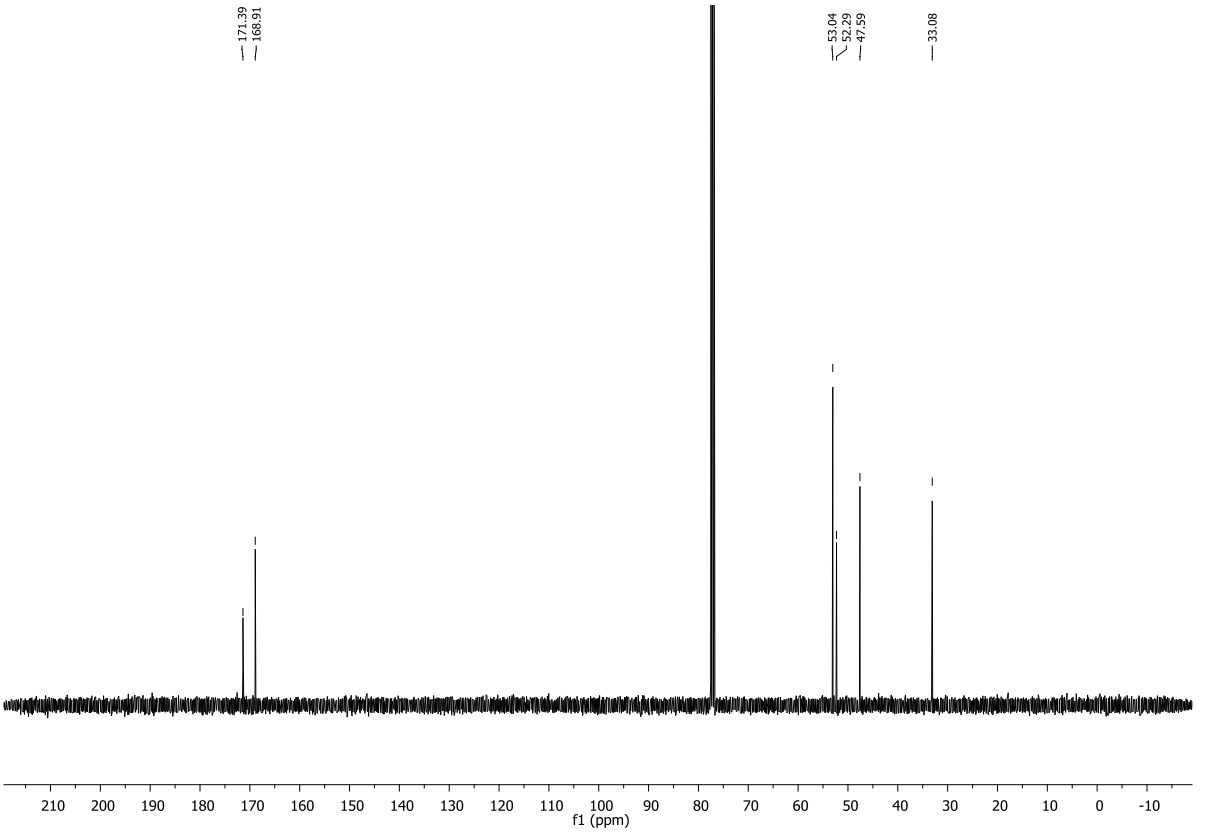
7

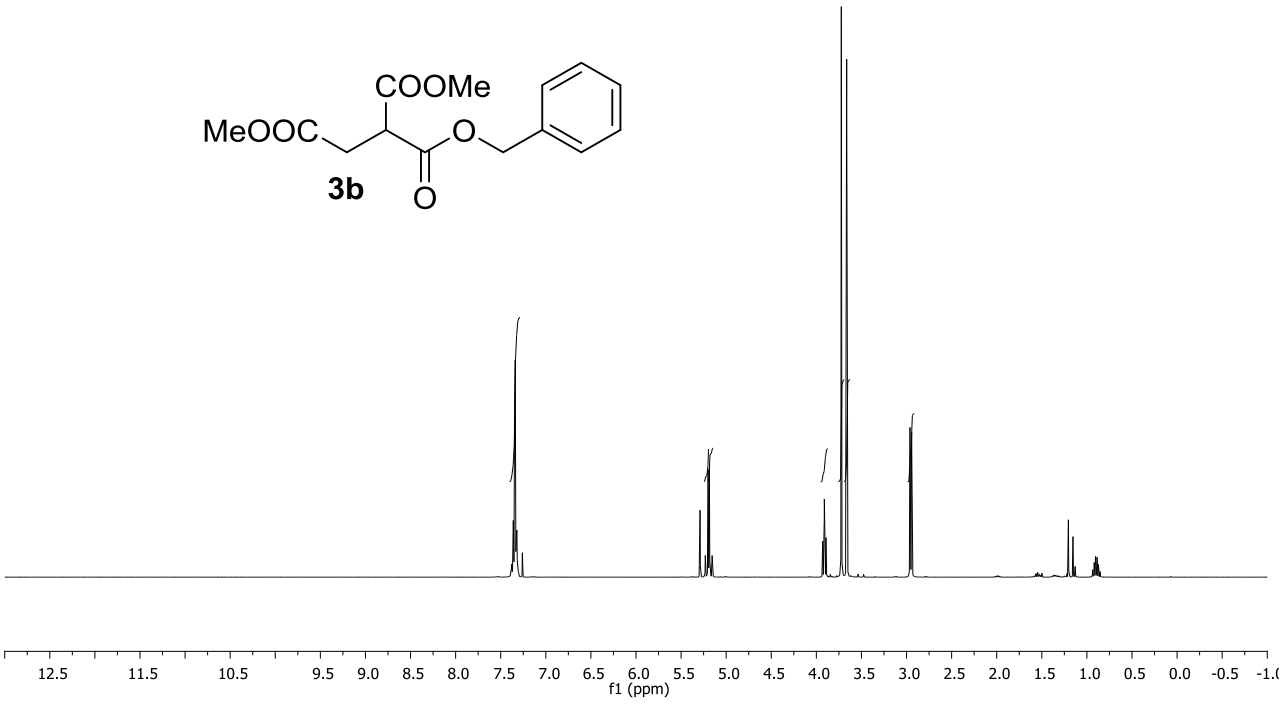
Synthesized following the general procedure. Olefin **6** was converted for 32%. The compound **7** has been purified by column chromatography (petroleum ether/ethyl acetate 70:30 then 50:50), obtaining a colorless oil; isolated yield: 25% (0.141 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 – 4.06 (m, 4H), 3.77 (s, 3H), 3.68 (s, 3H), 3.47 (ddd, J = 24.1, 11.3, 3.5 Hz, 1H), 3.07 (ddd, J = 17.7, 11.3, 7.5 Hz, 1H), 2.81 (ddd, J = 17.6, 9.3, 3.5 Hz, 1H), 1.37 – 1.28 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7 (d), 168.9 (d), 63.2 (dd), 52.95 (s), 52.34 (s), 41.3 (d, J = 132.0 Hz), 31.4 (d), 16.4 (dd). ESI-MS: m/z = 283 $[M+H]^+$; m/z = 305 $[M+Na]^+$; m/z = 321 $[M+K]^+$. Spectral data were identical to the previously reported literature data.[9]

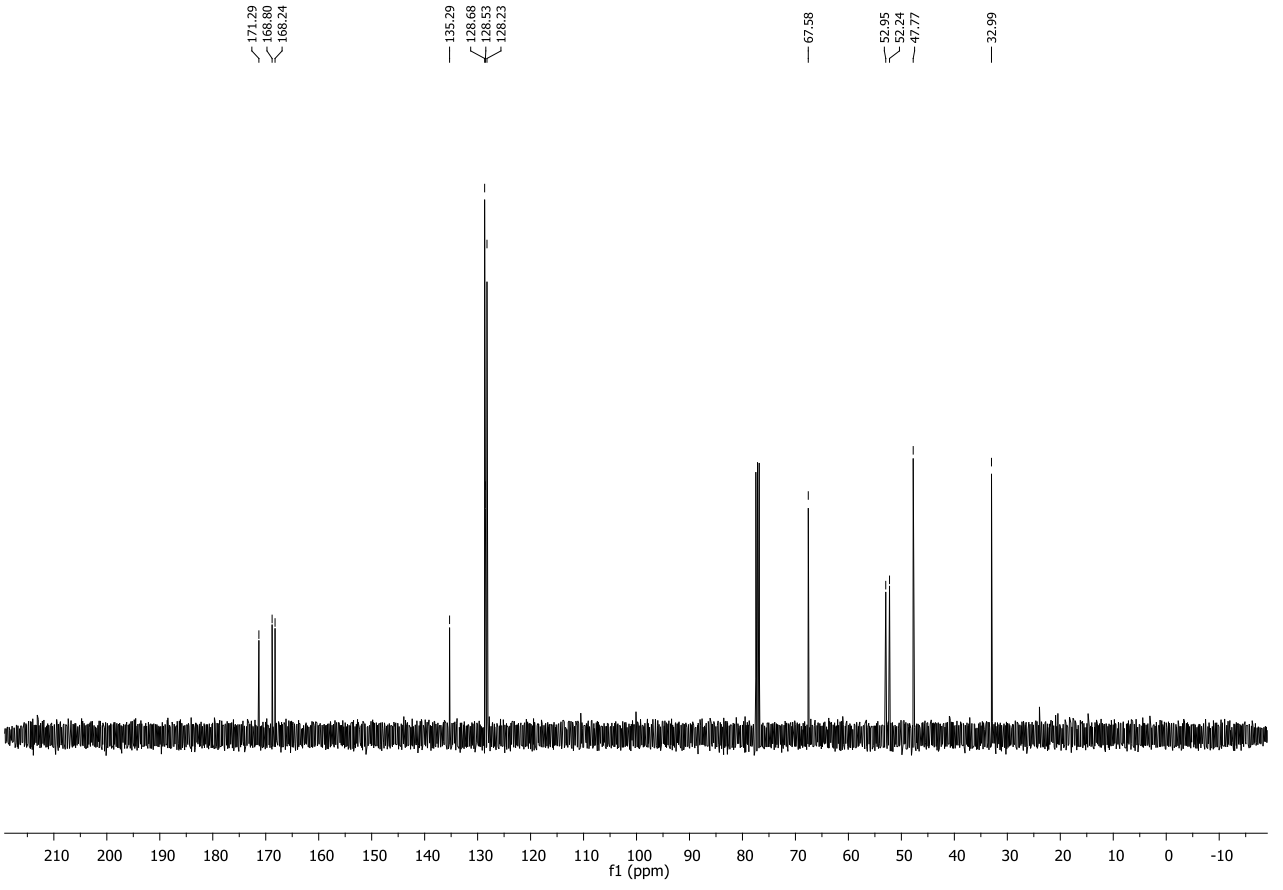
9. NMR Spectra

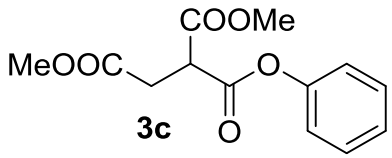


3a



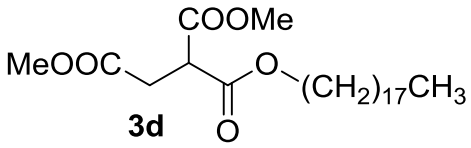

COOMe
MeOOC
O
O
3b
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.29
168.80
168.24
135.29
128.68
128.53
128.23
67.58
52.95
52.24
47.77
32.99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
O

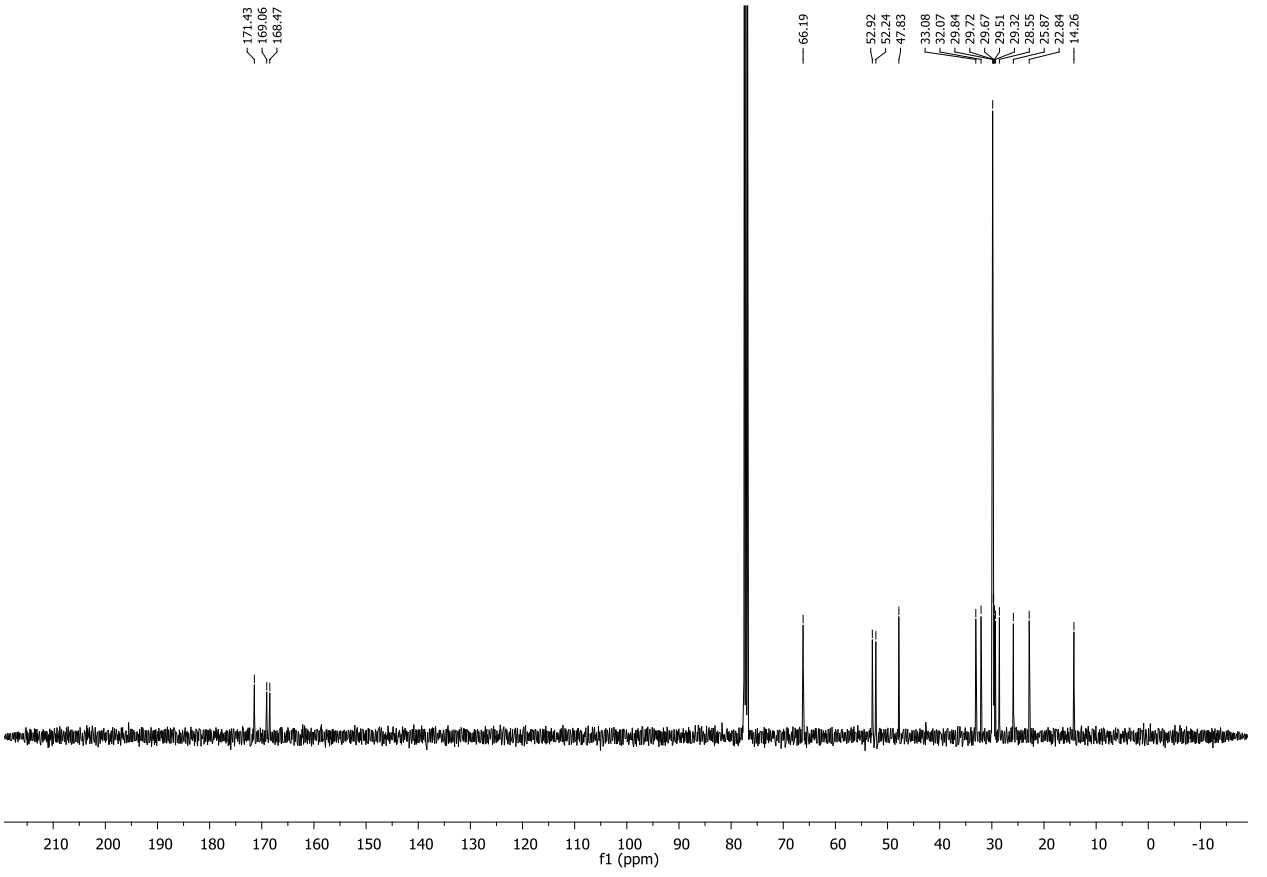
3c

12.5 11.5 10.5 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 -0.5
f1 (ppm)
171.27
168.61
167.22
150.59
129.63
126.39
121.38
53.22
52.39
47.86
33.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
(CH2)17CH3
O

3d

12.5 11.5 10.5 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 -0.5
f1 (ppm)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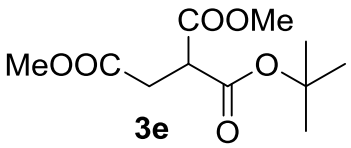
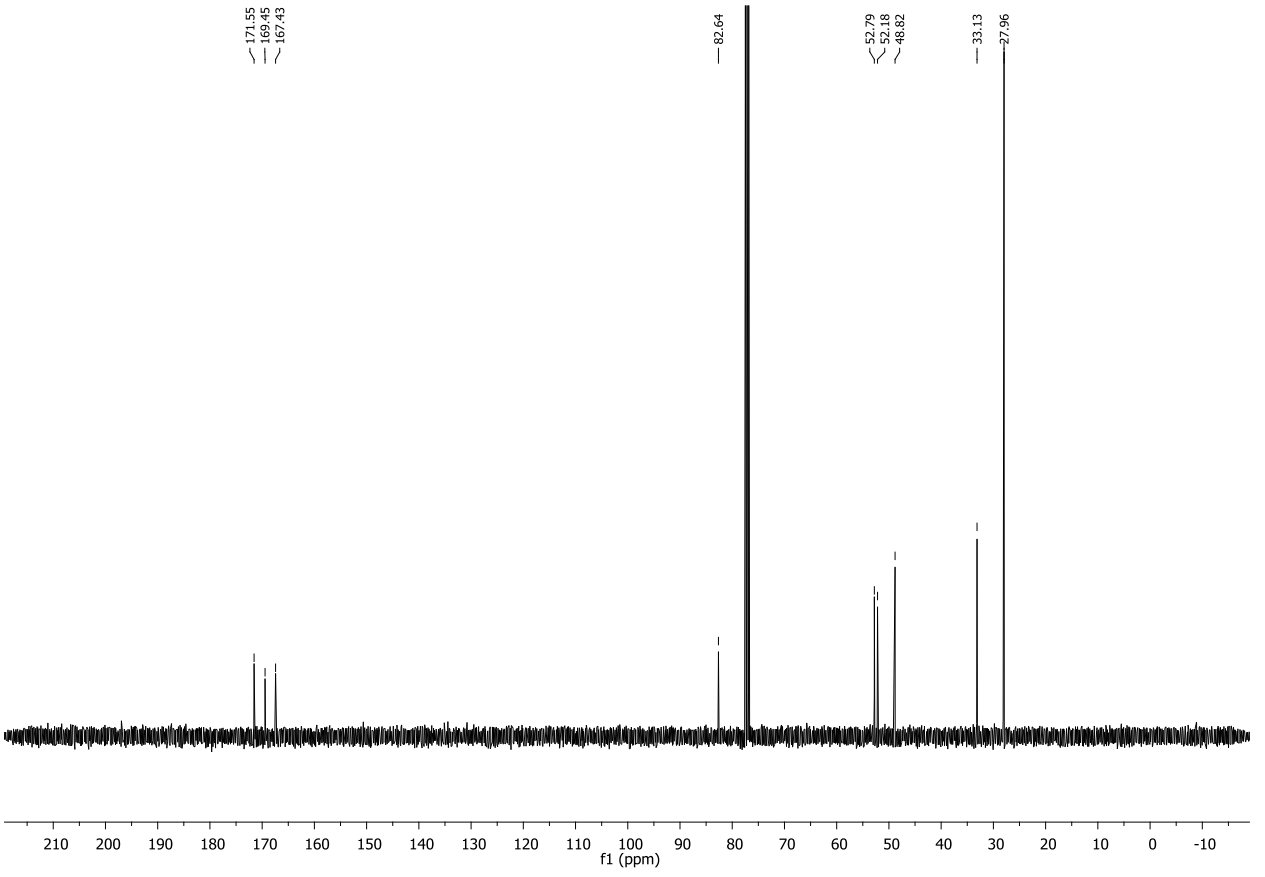
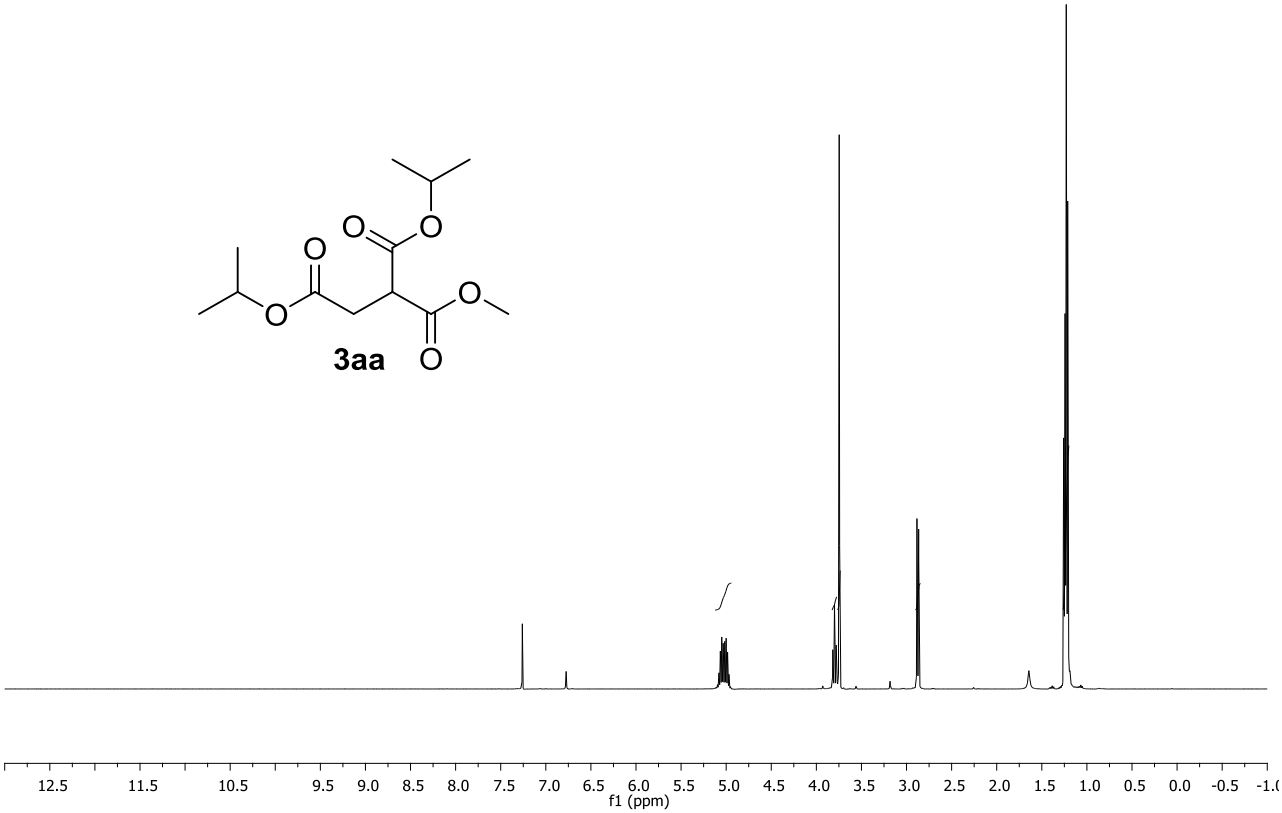
169.06
168.47
66.19
52.92
52.24
47.83
33.08
32.07
29.84
29.72
29.67
29.51
29.32
28.55
25.87
22.84
14.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

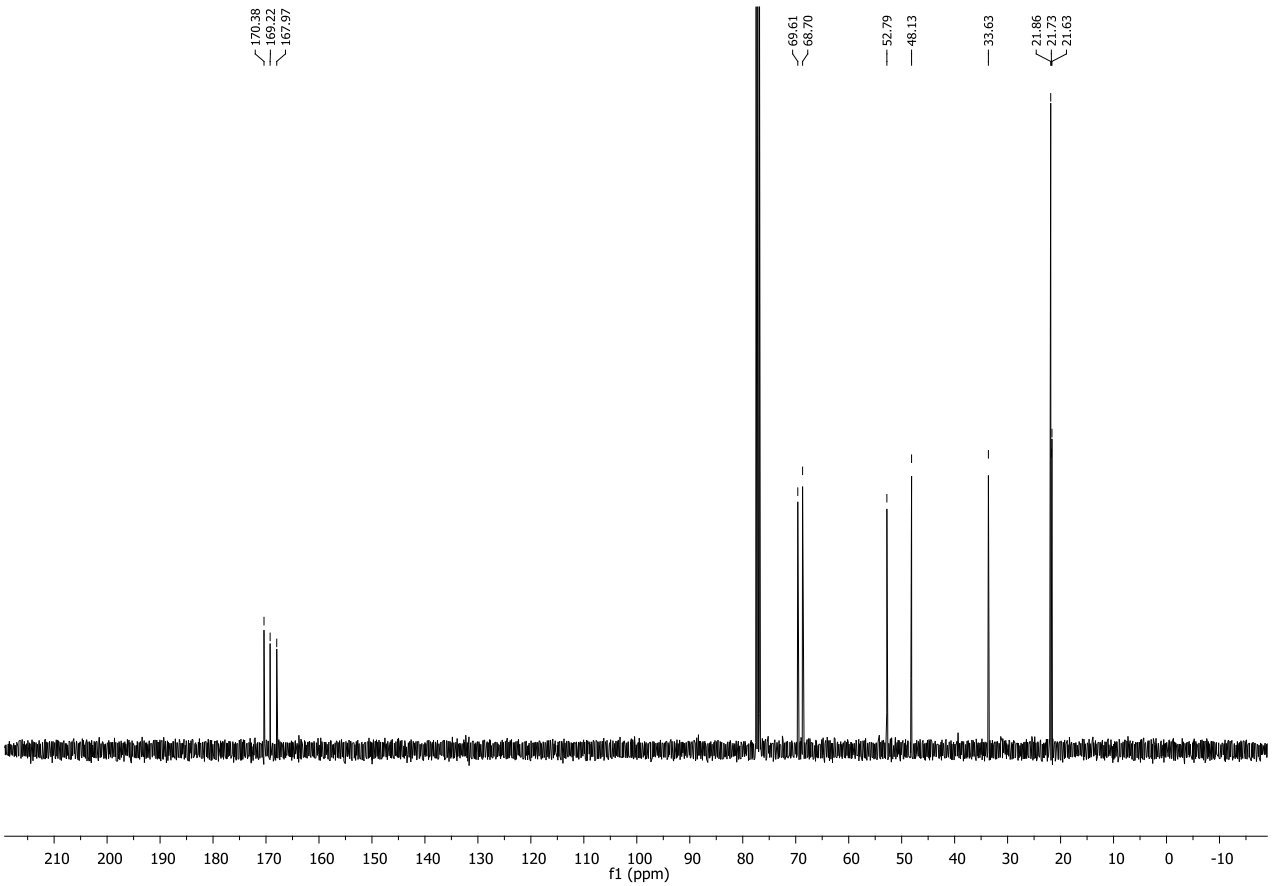

COOMe
MeOOC
O
O

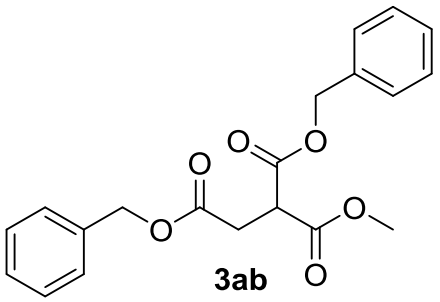
3e

12.5 11.5 10.5 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 -0.5
f1 (ppm)


171.55
169.45
167.43
82.64
52.79
52.18
48.82
33.13
27.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

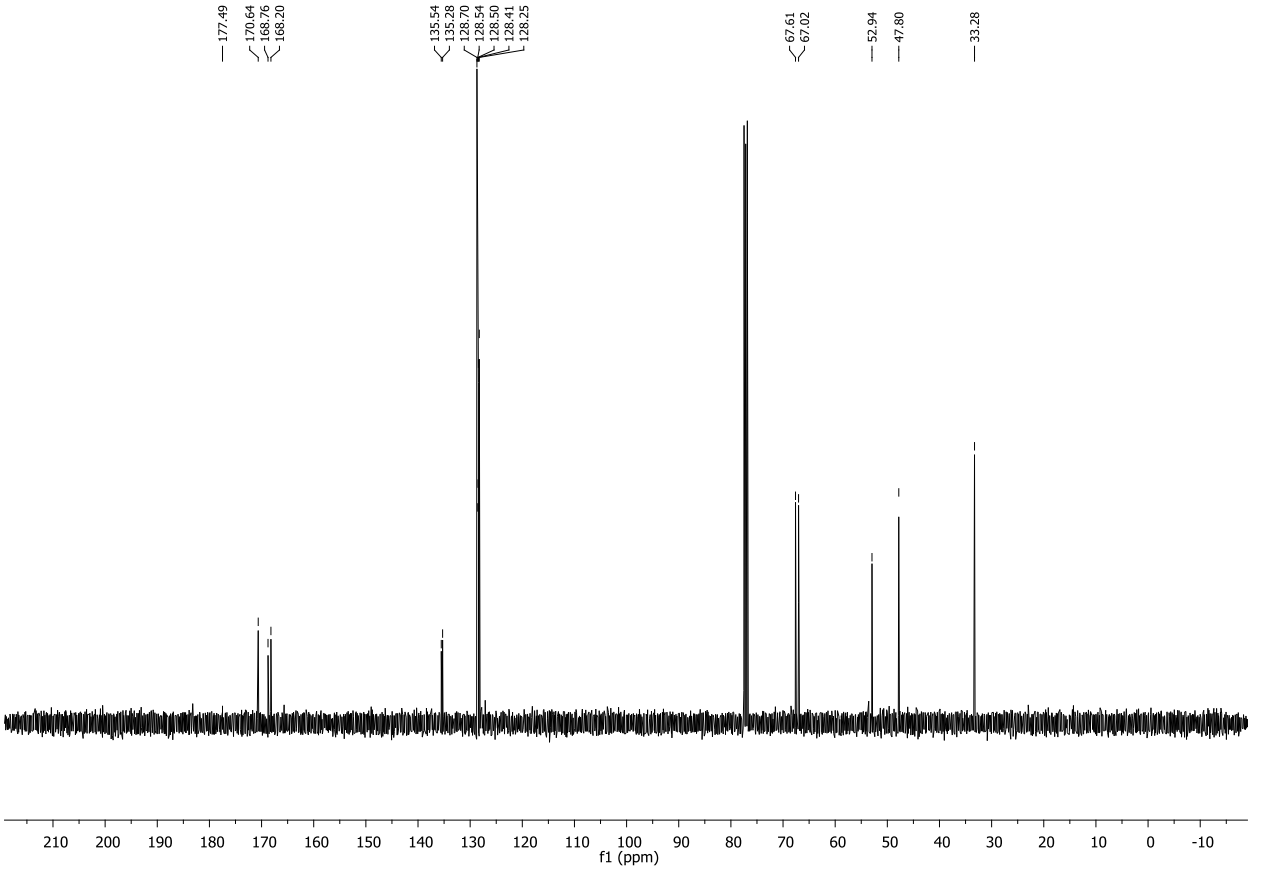

3aa
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


170.38
169.22
167.97
69.61
68.70
52.79
48.13
33.63
21.86
21.73
21.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3ab

12.5
11.5
10.5
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
-0.5
f1 (ppm)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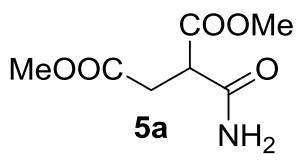
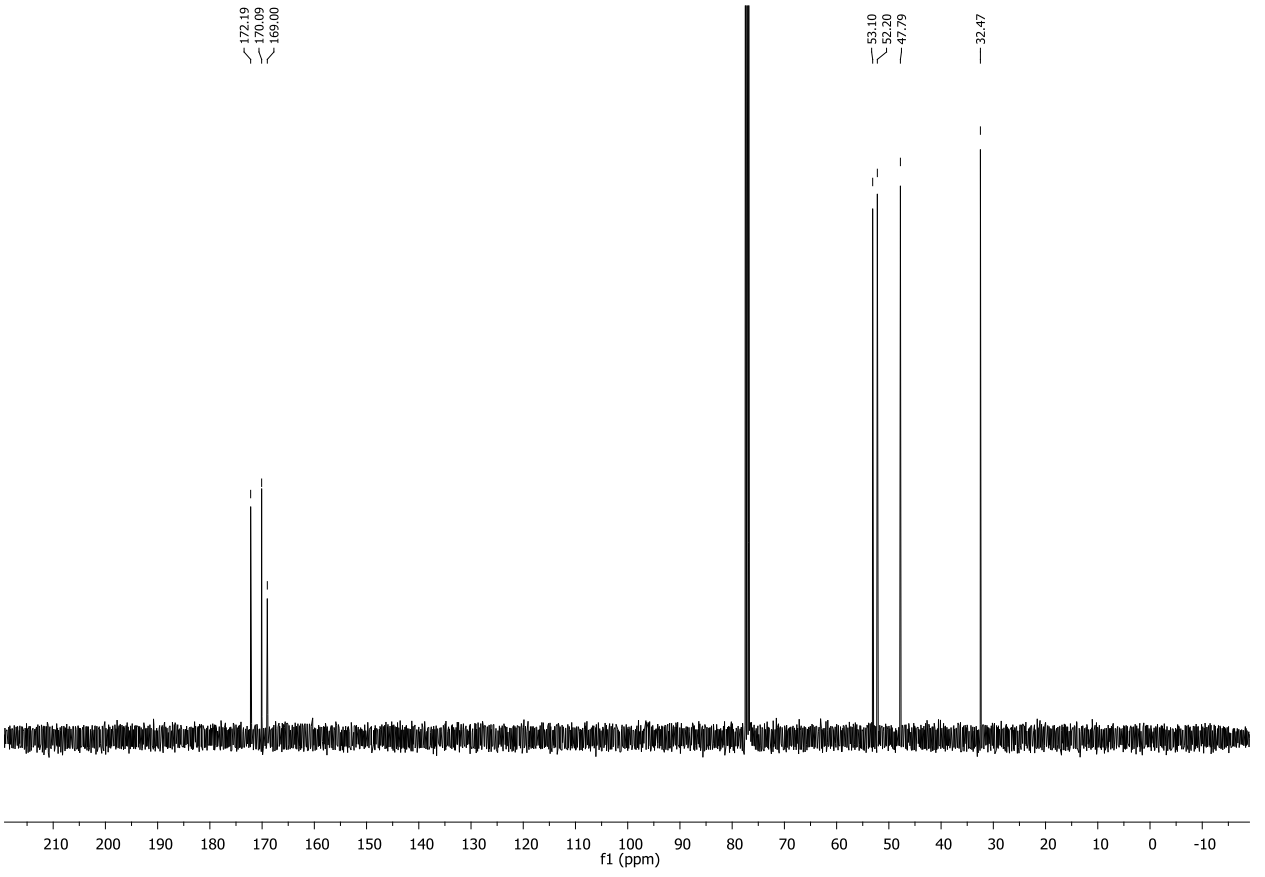
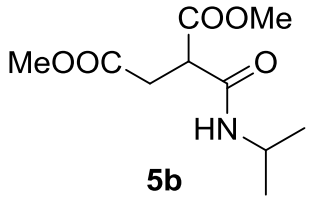
170.64
168.76
168.20
135.54
135.28
128.70
128.54
128.50
128.41
128.25
67.61
67.02
52.94
47.80
33.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


COOMe
MeOOC
O
NH2

5a

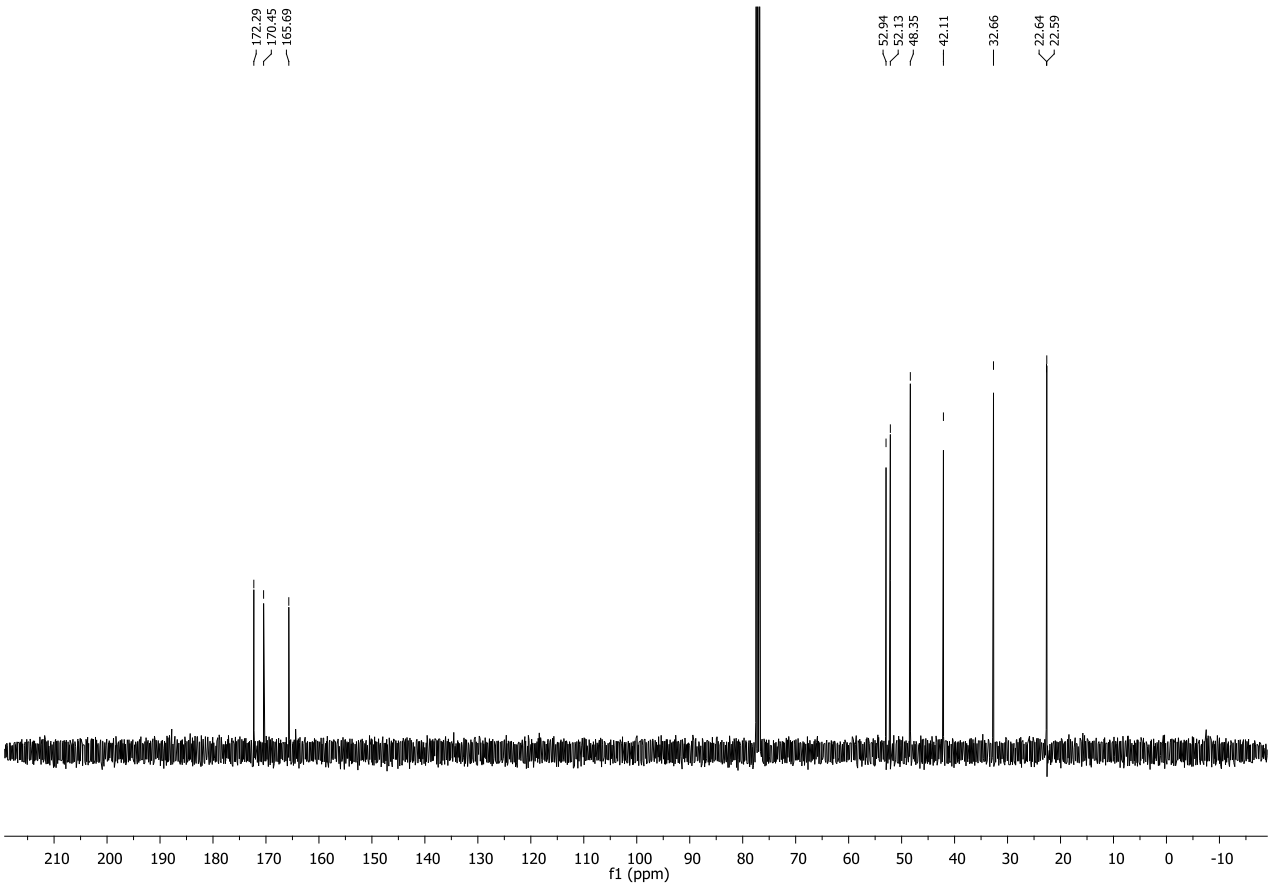
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

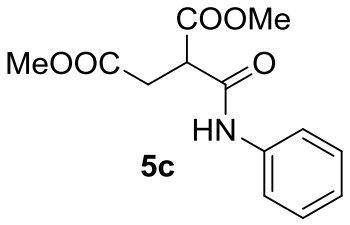

172.19
170.09
169.00
53.10
52.20
47.79
32.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
HN

5b

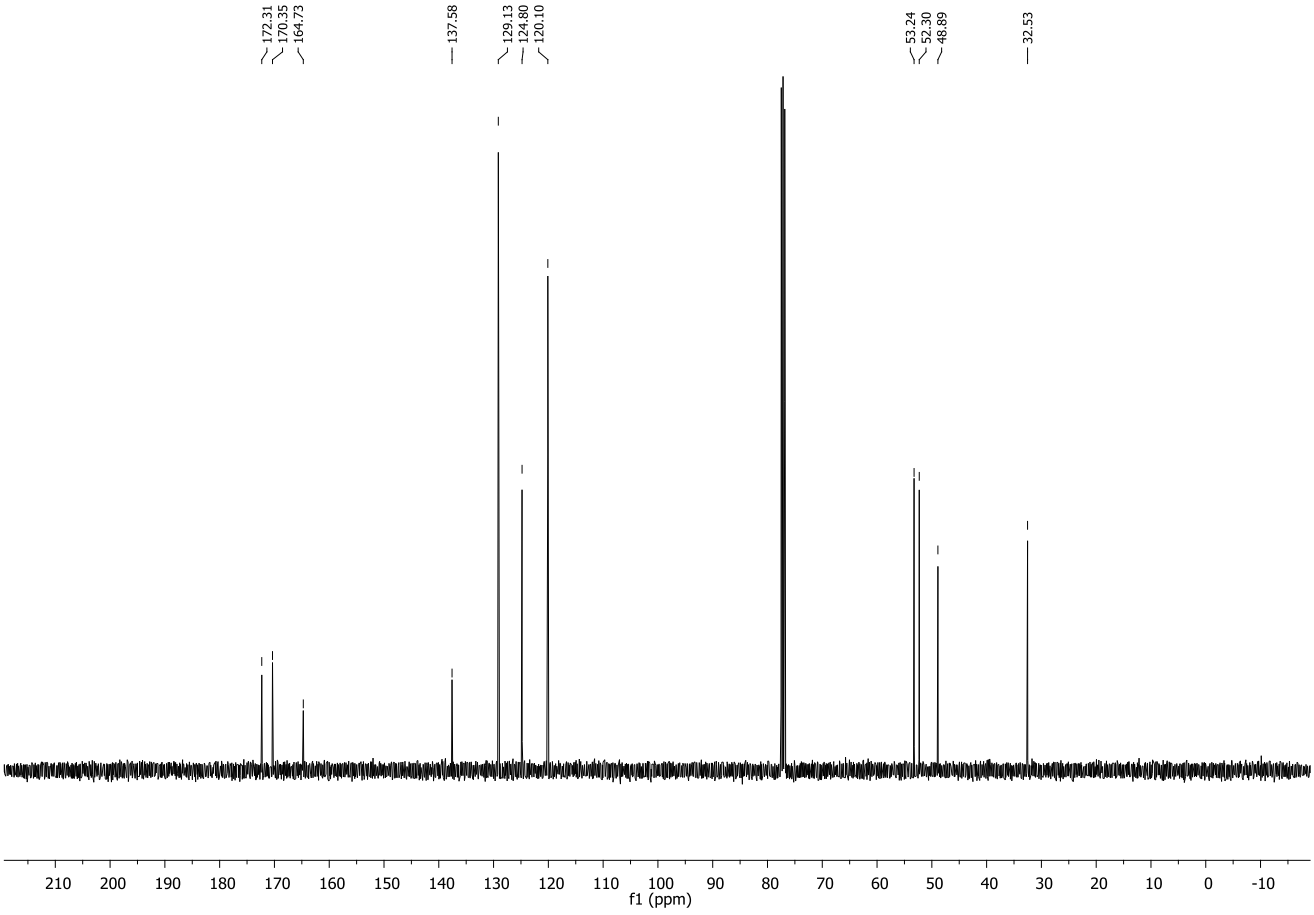
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

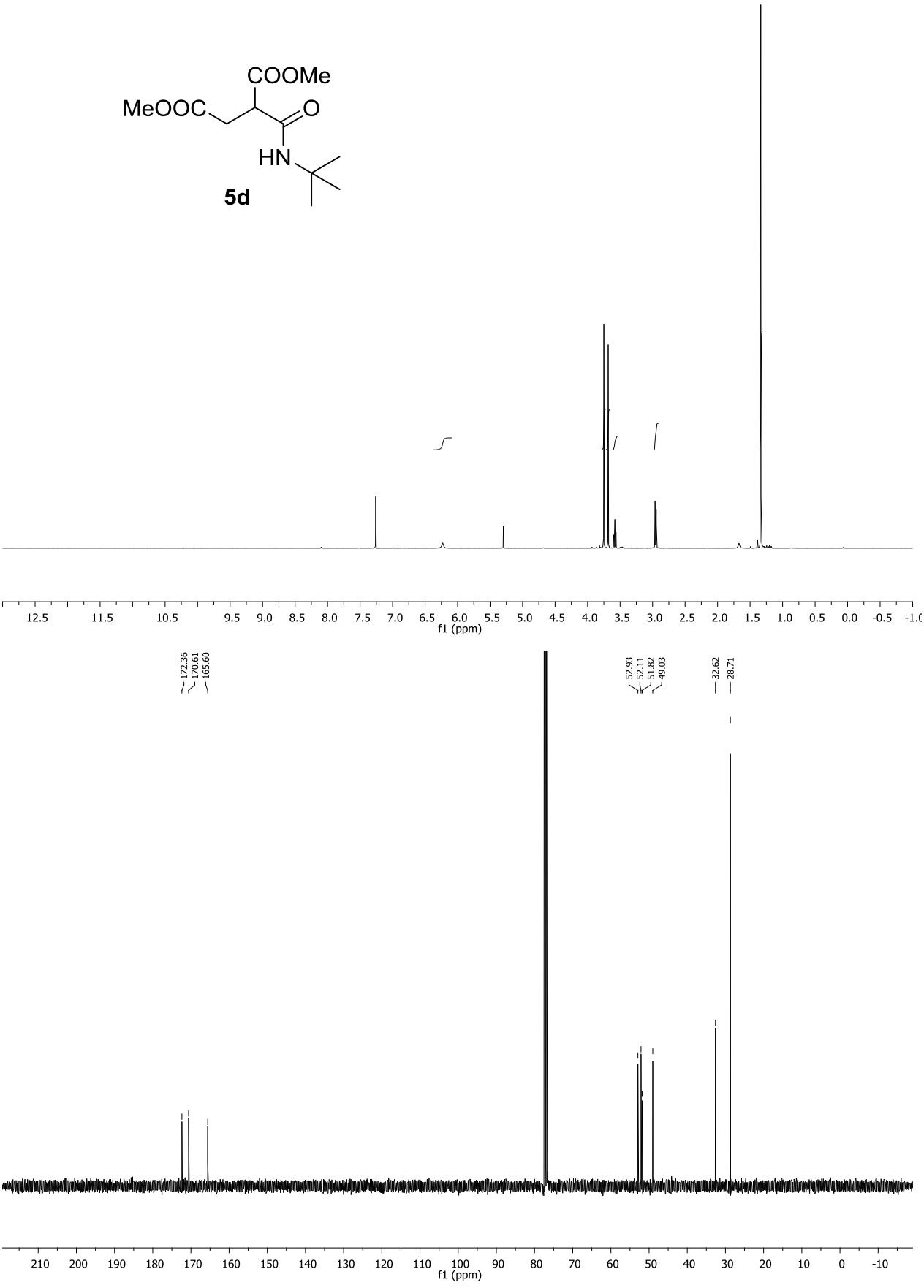

172.29
170.45
165.69
52.94
52.13
48.35
42.11
32.66
23.64
22.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

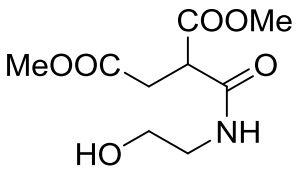

COOMe
MeOOC
O
HN

5c

12.5 11.5 10.5 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 -0.5
f1 (ppm)

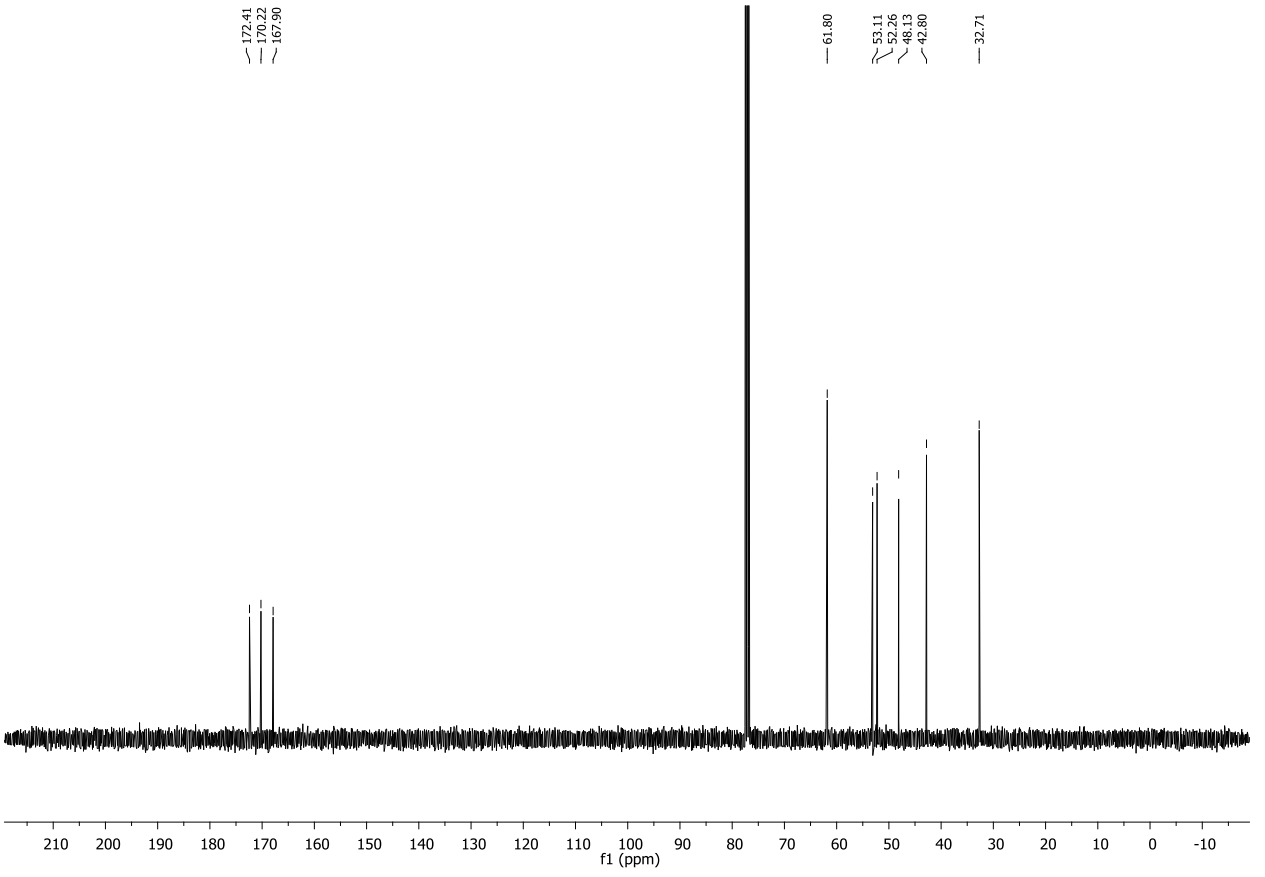

172.31
170.35
164.73
137.58
129.13
124.80
120.10
53.24
52.30
48.89
32.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
HN
5d
12.5 11.5 10.5 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 -0.5
f1 (ppm)
172.36
170.61
165.60
52.93
52.11
51.82
49.03
32.62
28.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
NH
HO

5e

12.5
11.5
10.5
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
-0.5
f1 (ppm)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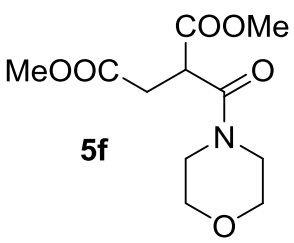
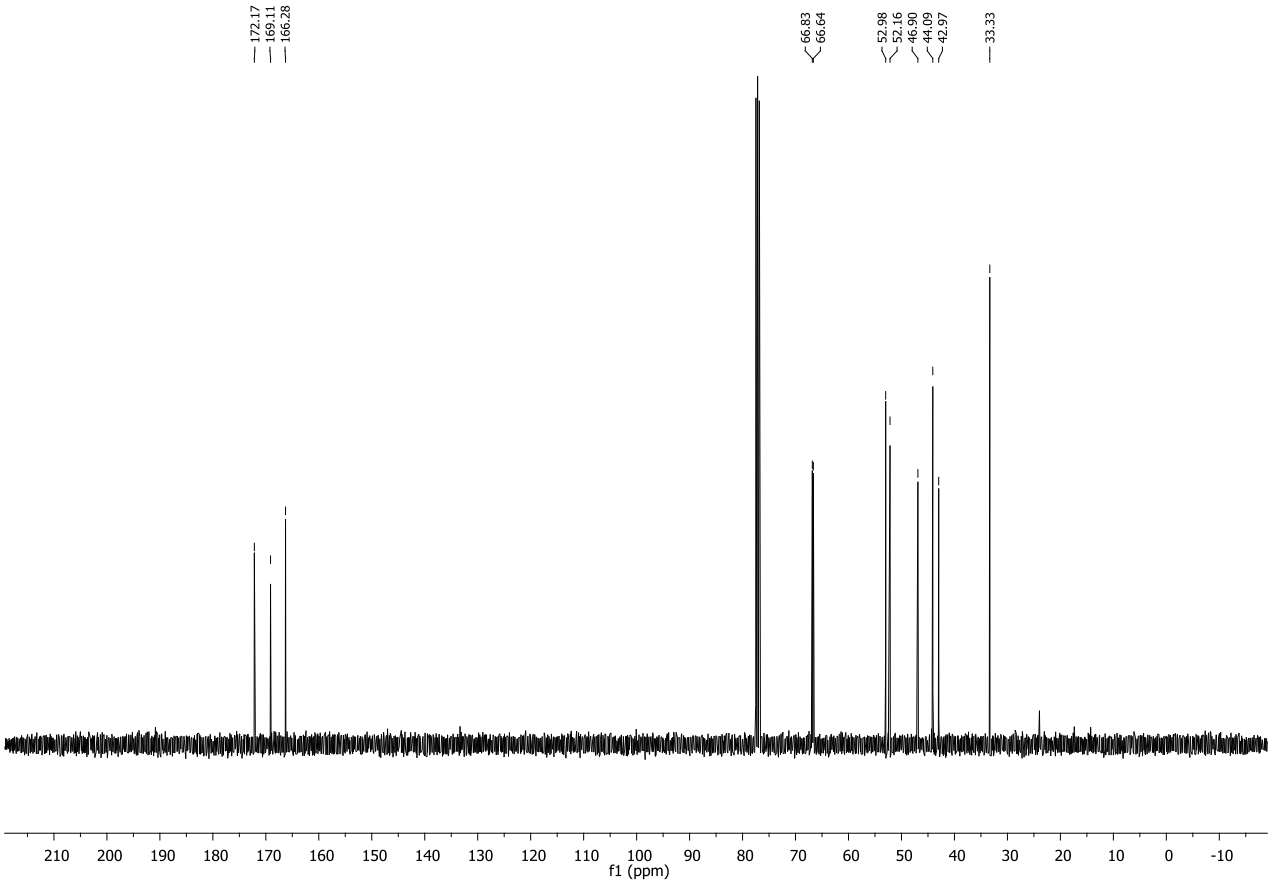
167.90
61.80
53.11
52.26
48.13
42.80
32.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


COOMe
MeOOC
O
N
O

5f

12.5
11.5
10.5
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
-0.5
f1 (ppm)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46.90
44.09
42.97
33.33
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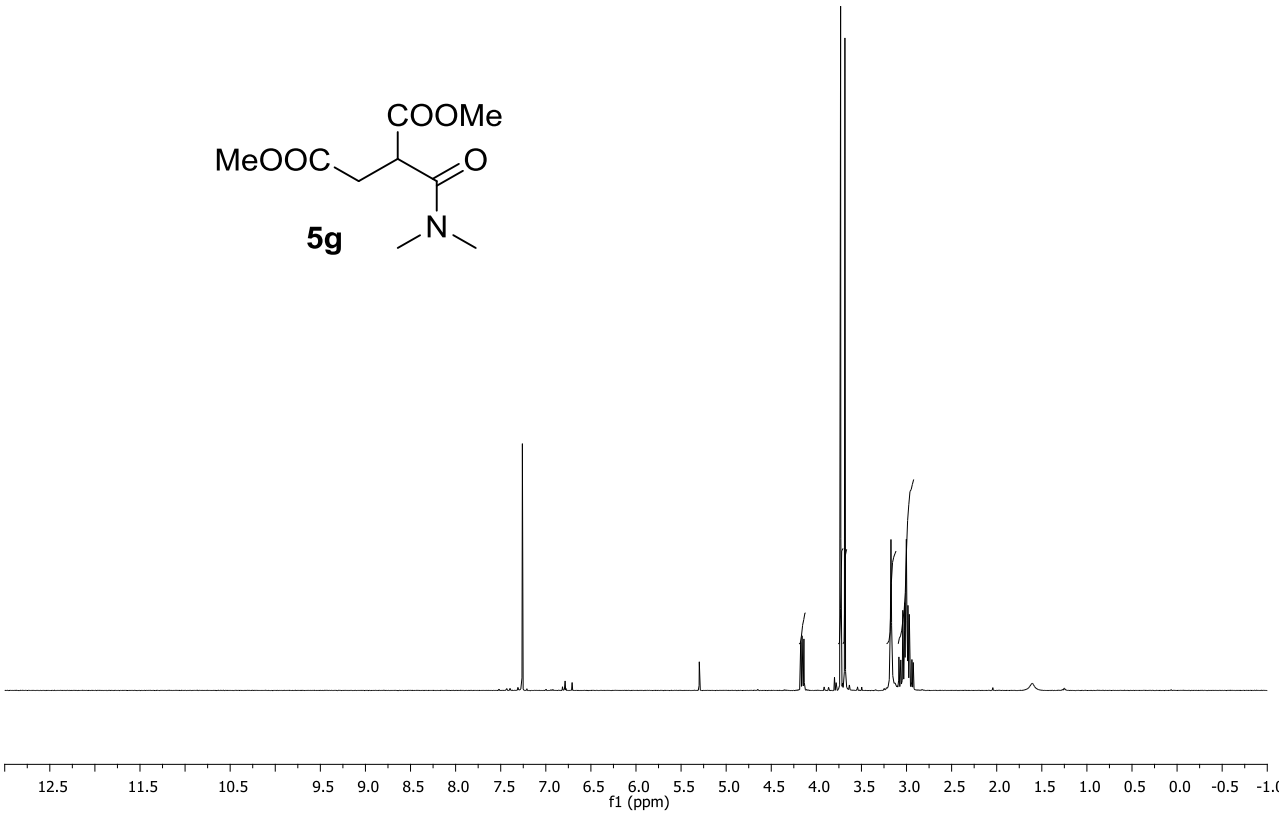
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


COOMe
MeOOC
O
N
5g
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11.5
10.5
9.5
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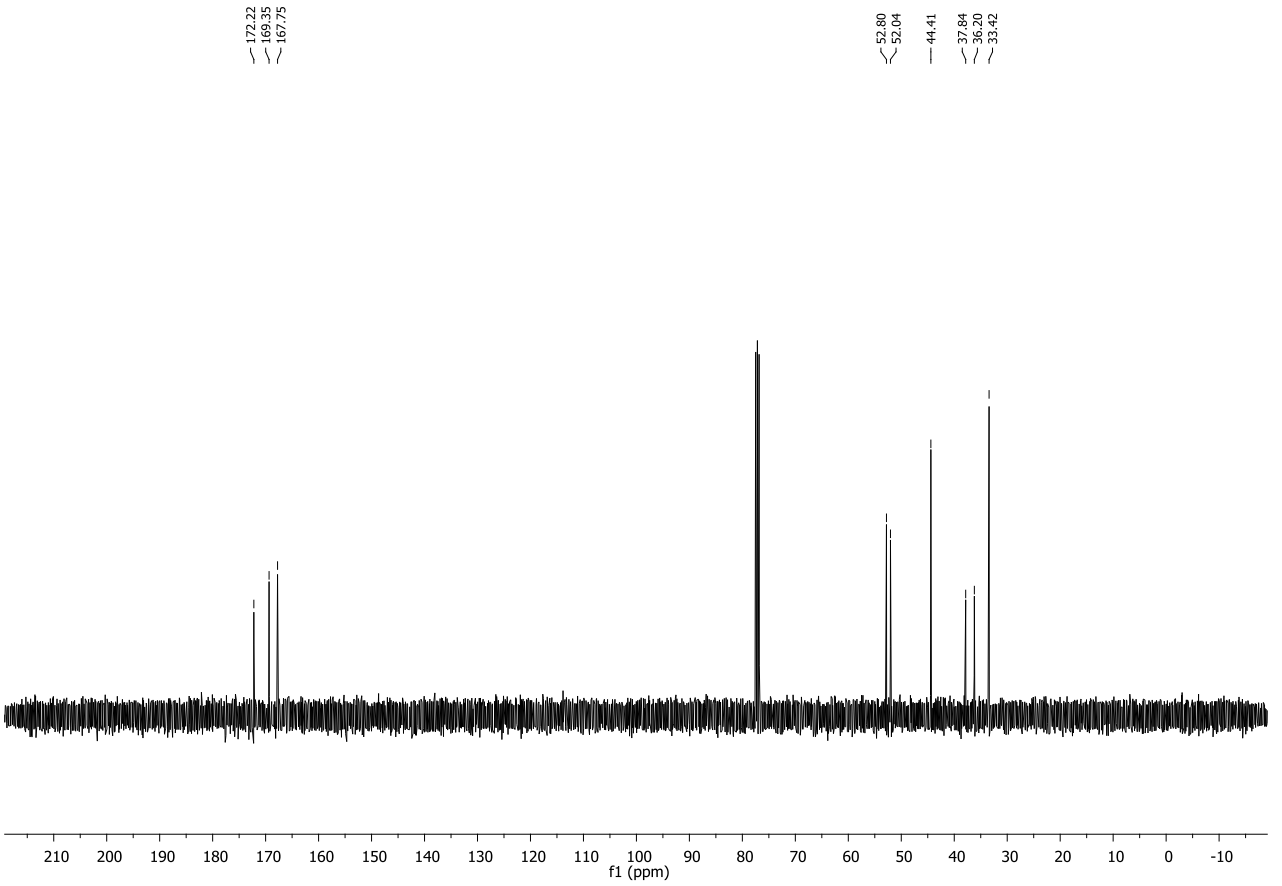
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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44.41
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36.20
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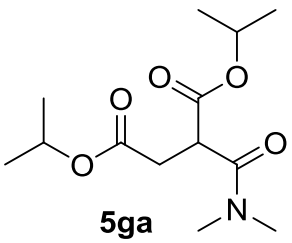
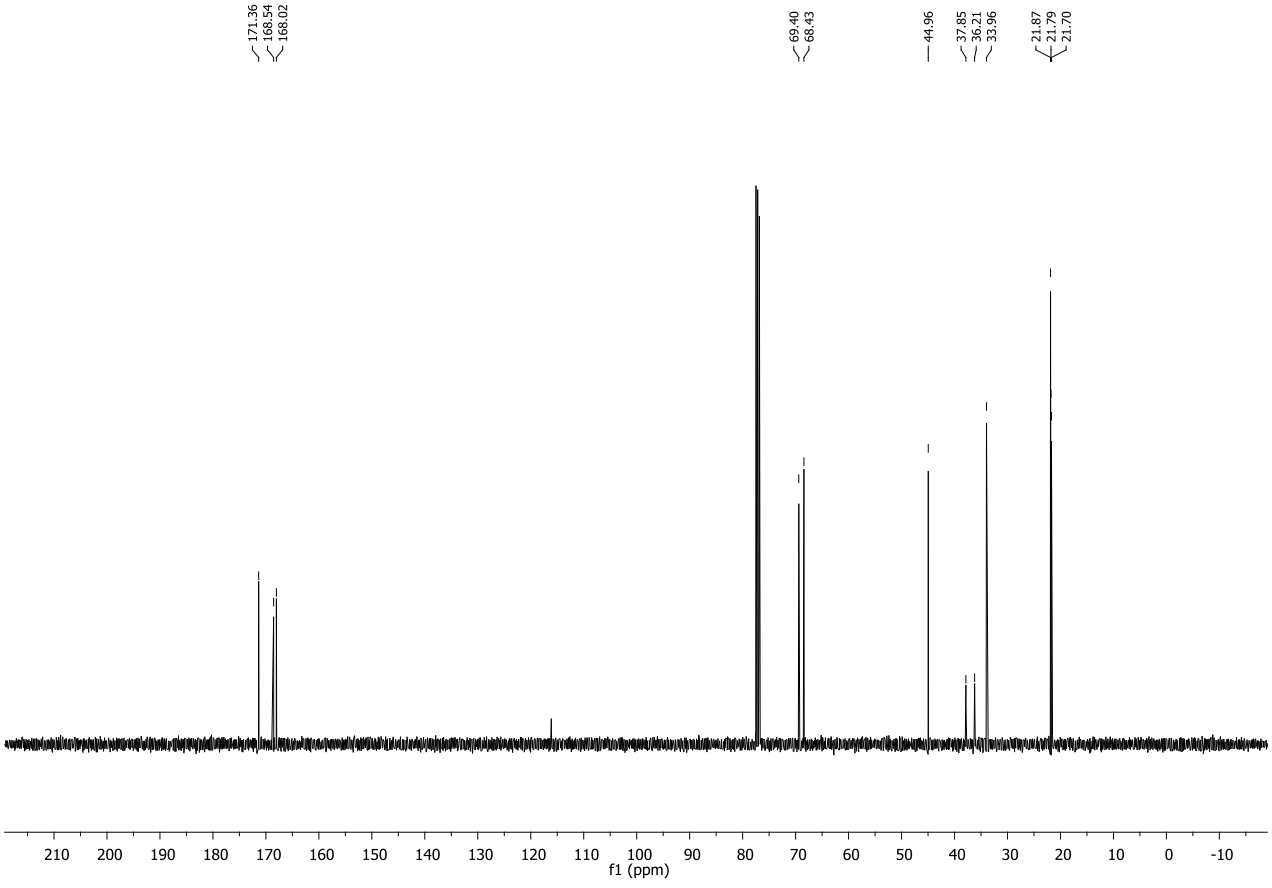
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
O
O
O
N

5ga

12.5
11.5
10.5
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
-0.5
f1 (ppm)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69.40
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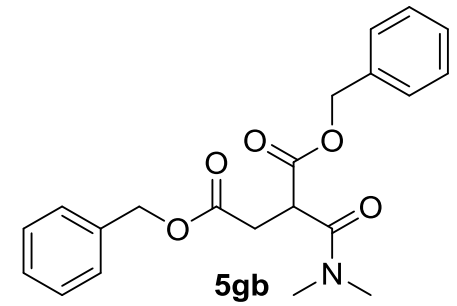
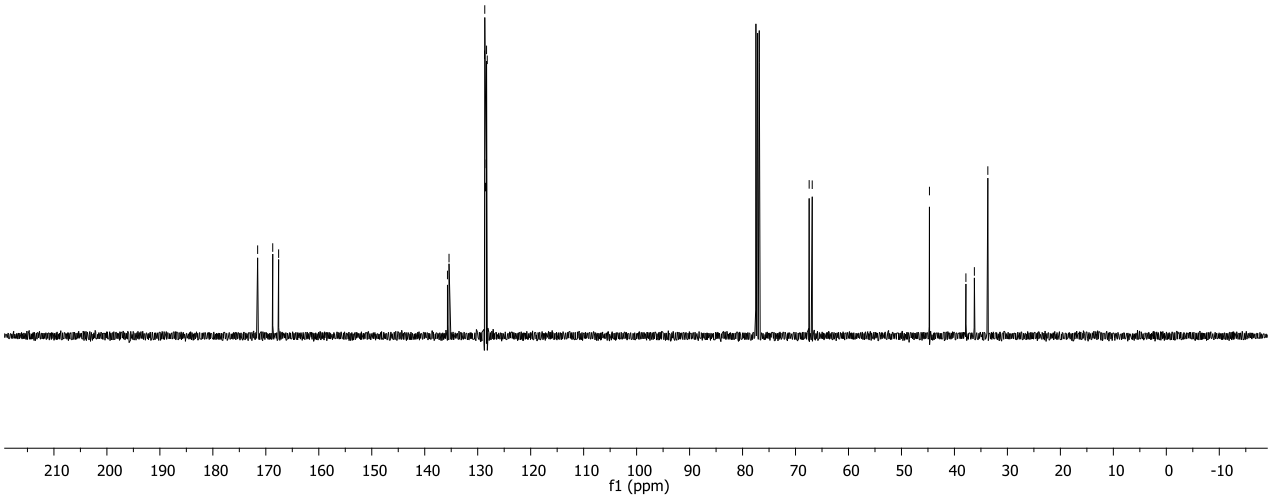
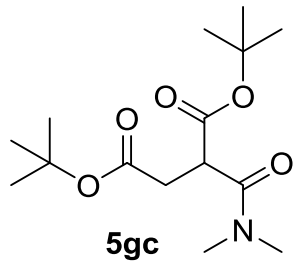
37.85
36.21
33.96
21.87
21.79
21.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



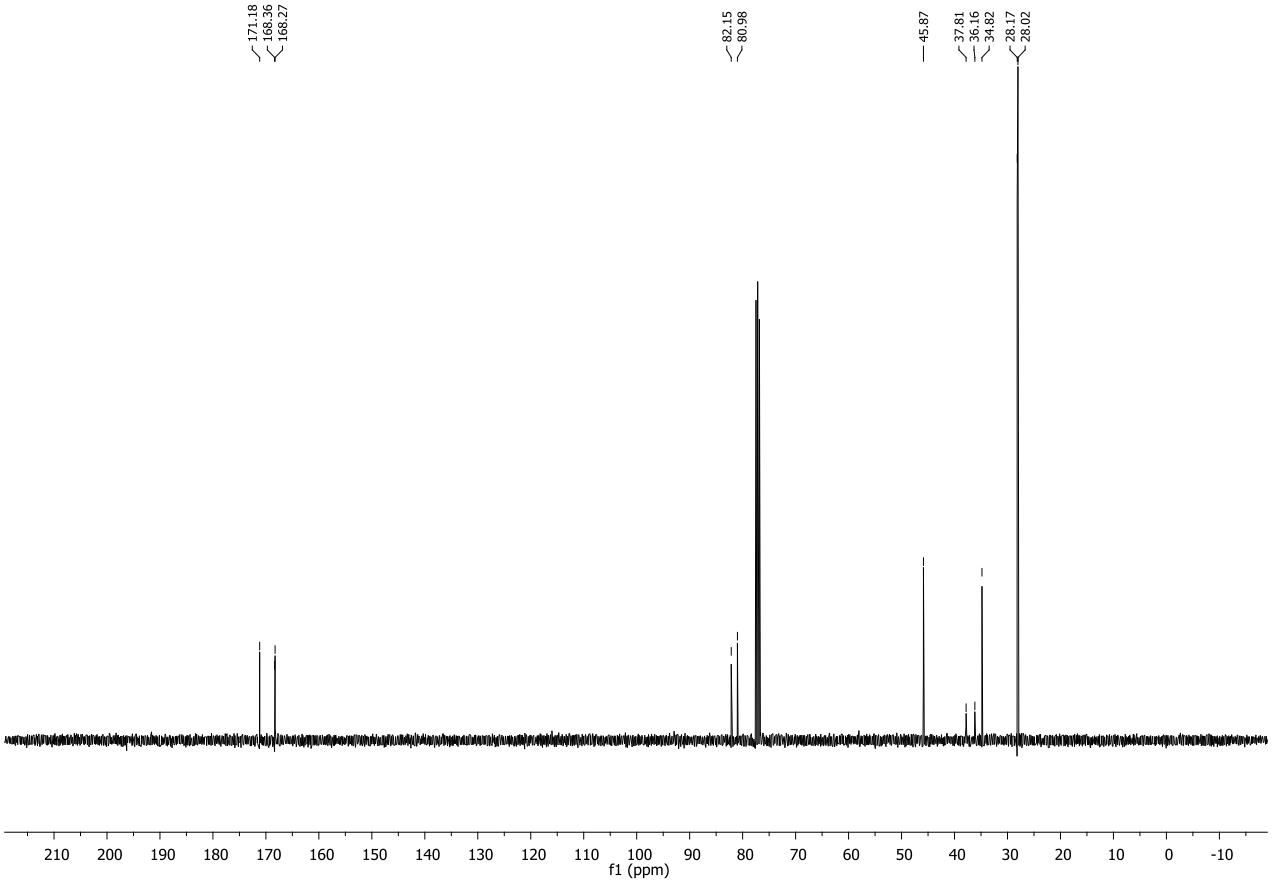
171.54
168.69
167.58
135.71
135.42
128.71
128.67
128.52
128.40
128.33
128.20
67.43
66.85
44.72
37.84
36.24
33.70

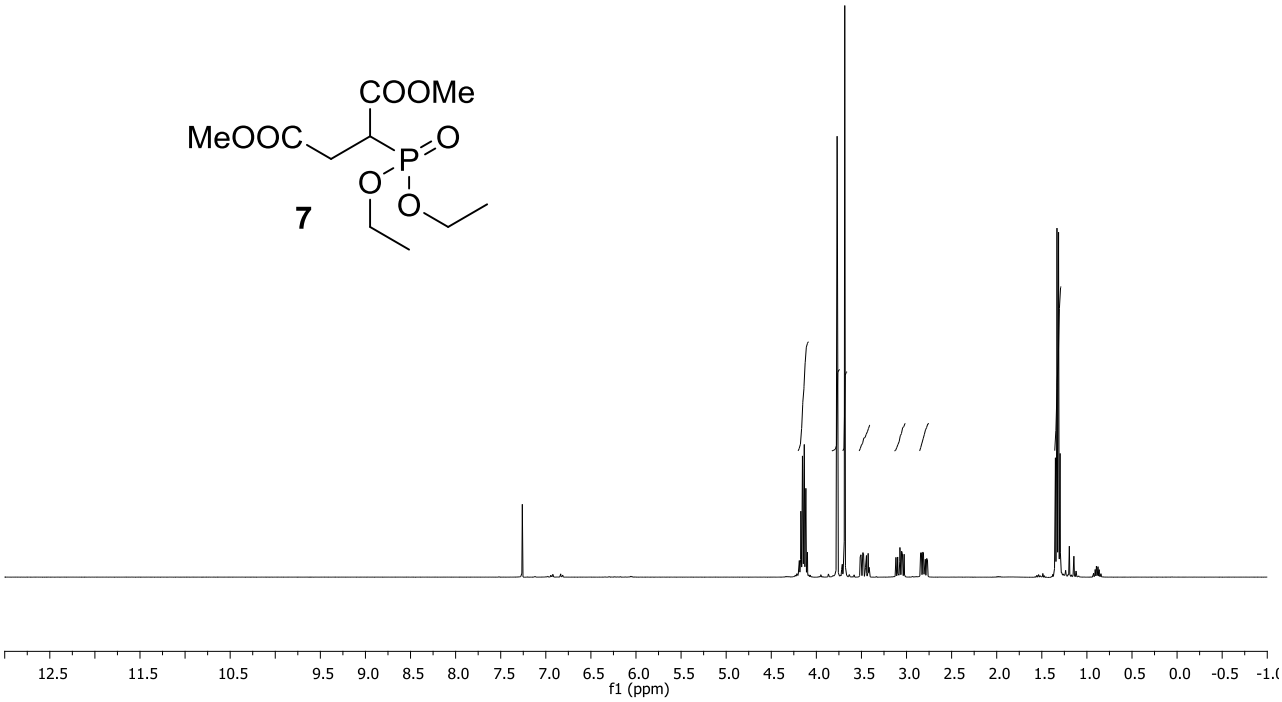


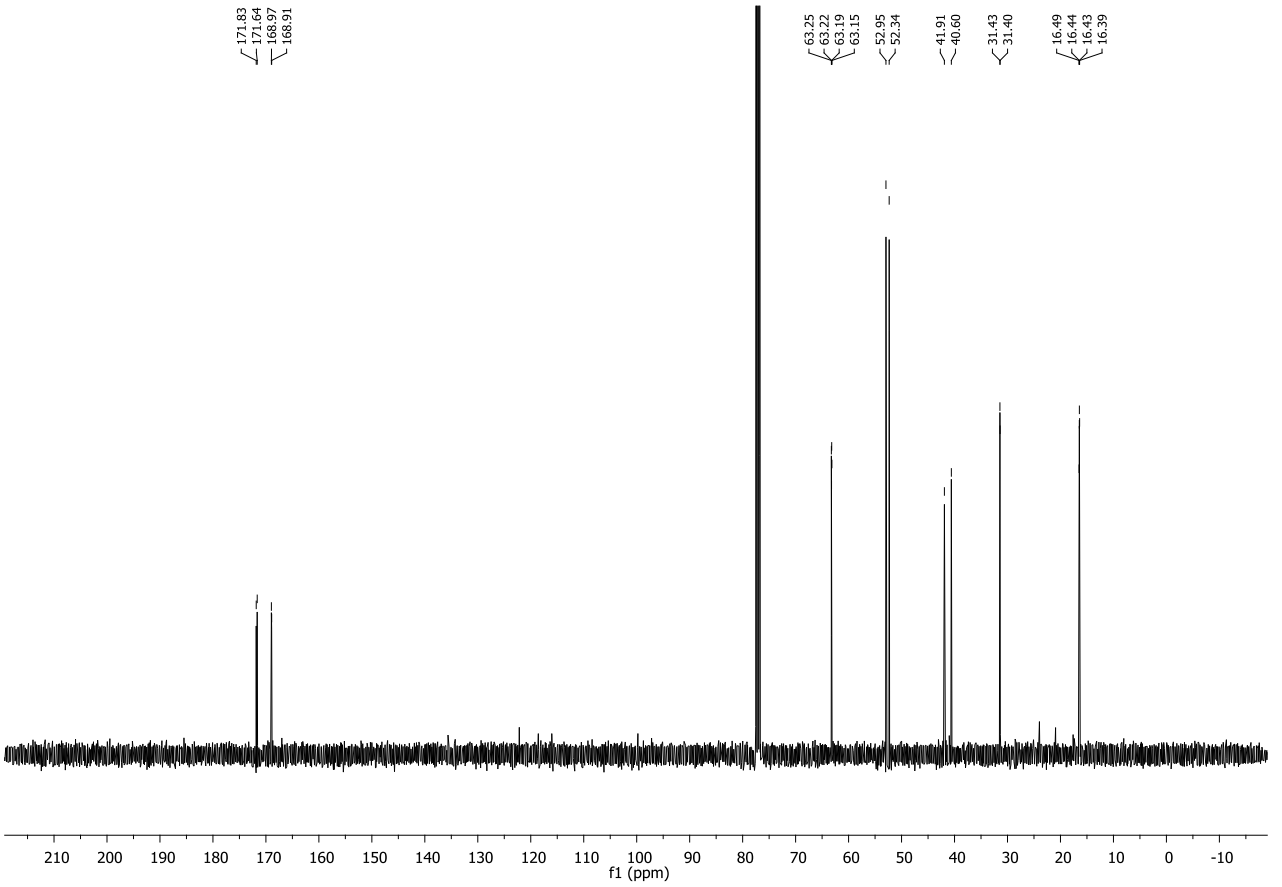

O
O
O
O
O
N

5gc

12.5 11.5 10.5 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 -0.5
f1 (ppm)


171.18
168.36
168.27
82.15
80.98
45.87
37.81
36.16
34.82
28.17
28.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
MeOOC
O
P
O
O
O
7
12.5
11.5
10.5
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
-0.5
f1 (ppm)


171.83
171.64
168.97
168.91
63.25
63.22
63.19
63.15
52.95
52.34
41.91
40.60
31.43
31.40
16.49
16.44
16.43
16.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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