Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Cerium-Catalyzed, Oxidative Synthesis of Annulated, Tetrasubstituted Dihydrofuran-Derivatives

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Supplementary Information

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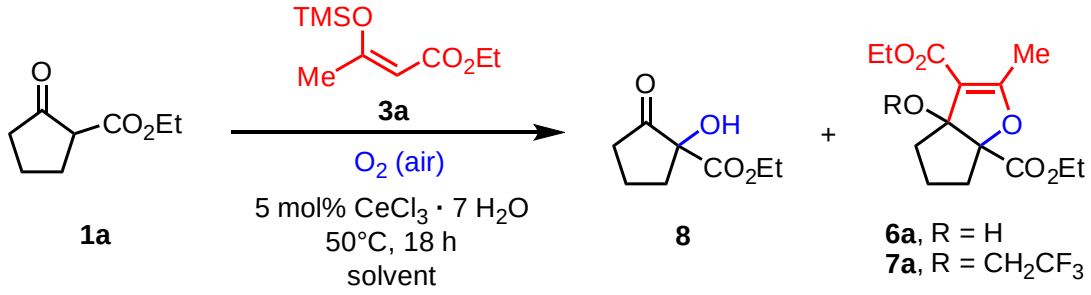
Screening of other solvents in the title reaction

Some other, especially, aprotic solvents were examined in the title reaction given in Table S1. All reactions were performed on a GC-scale with mesitylene as internal standard according to following procedure: $CeCl_3 \cdot 7\ H_2O$ (5 mol%, 19 mg, 50 µmol) was added to a mixture of β-oxoester **1a** (156 mg, 1.0 mmol, 1 equiv.), mesitylene (72 mg, 0.60 mmol, 0.6 equiv.) and enol ether **3a** (405 mg, 2.0 mmol, 2 equiv.) in solvent (1 L mol^{-1} β-oxoester), and the reaction mixture was stirred at 50°C for 18 h under an atmosphere of air. Table S1 gives relative GC integrals of the product mixtures after 18 h.

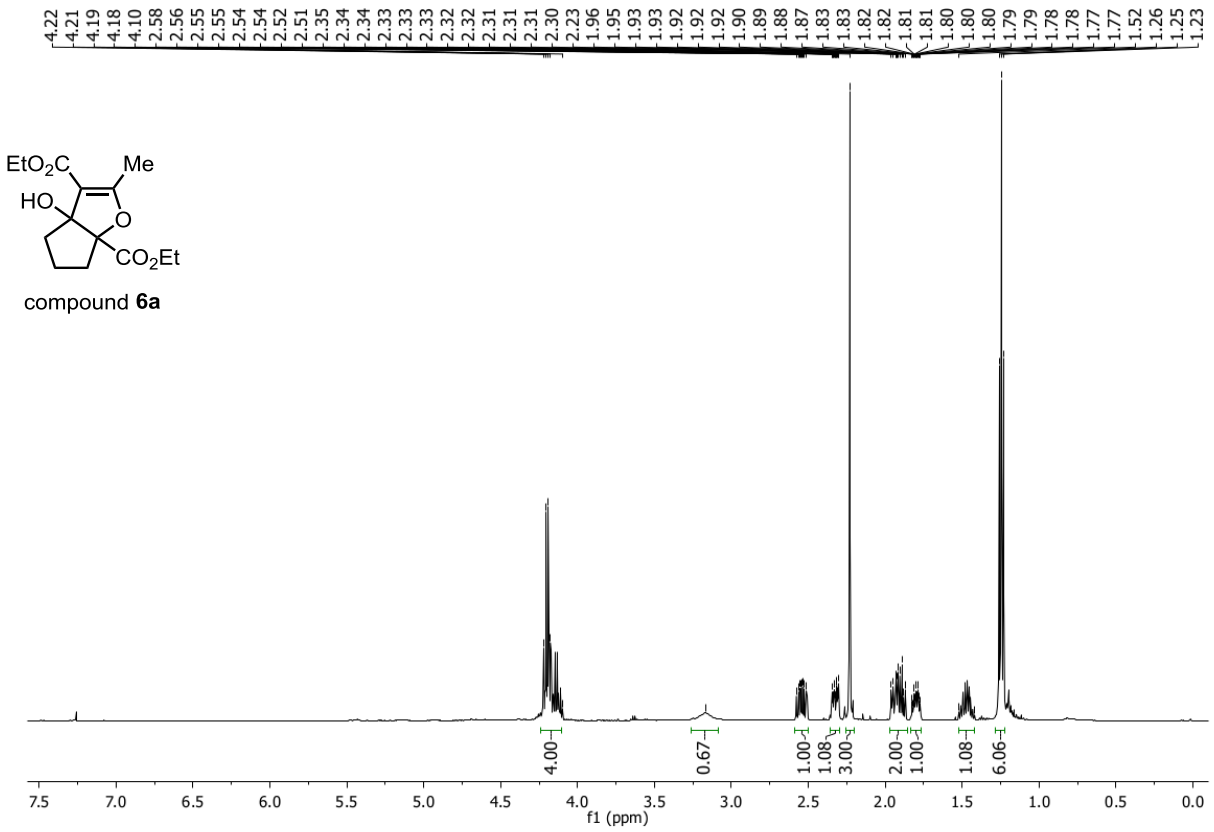
Table S1. Results of solvent screening; given are relative GC-integrals of the reaction depicted in Scheme S1 after 18 h relative to mesitylene as internal standard.



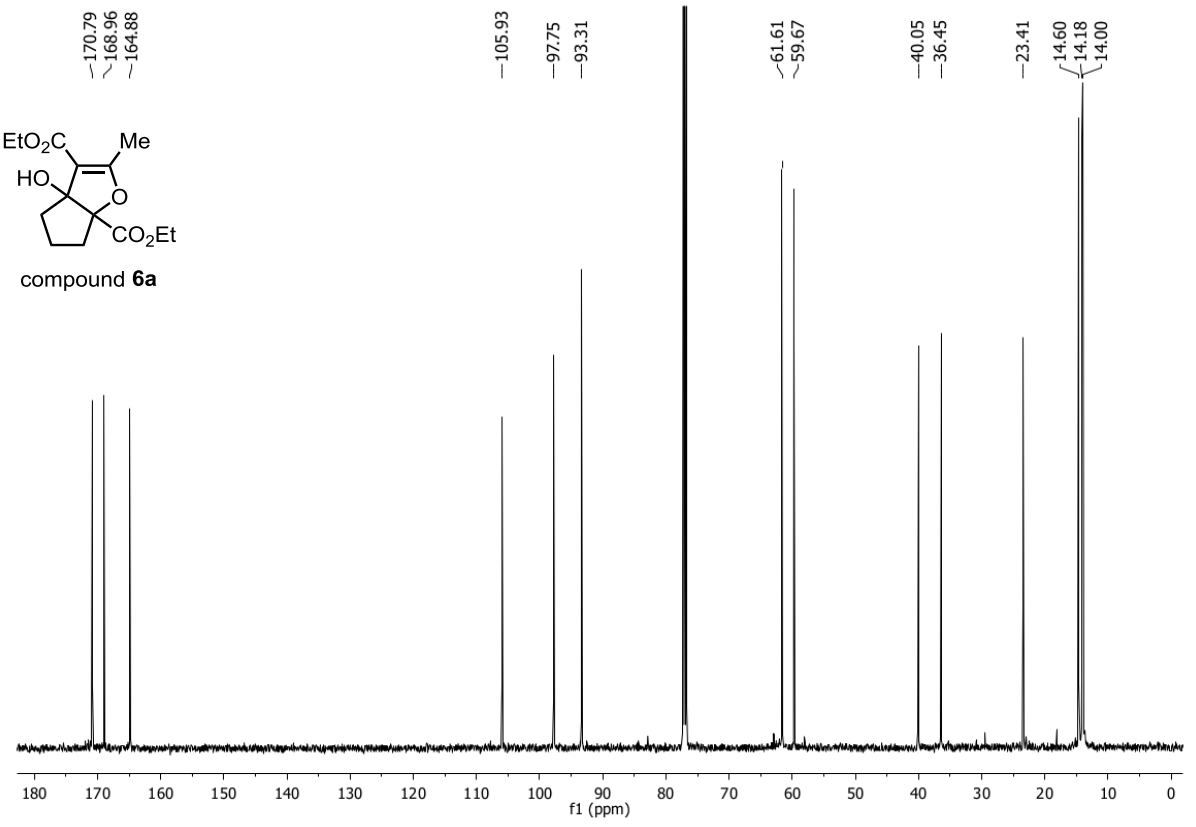
Solvent	8	7a	6a
THF	0.18	0.04	0.19
CH_2Cl_2	0.15	0.00	0.01
toluene	0.49	0.00	0.00
EtOH	0.06	0.00	0.19
TFE	0.00	0.13	0.87
TFE[a]	0.09	0.14	0.11

[a]Instead of ether **3a**, ethyl 3-oxobutanoate was applied.

NMR Spectra

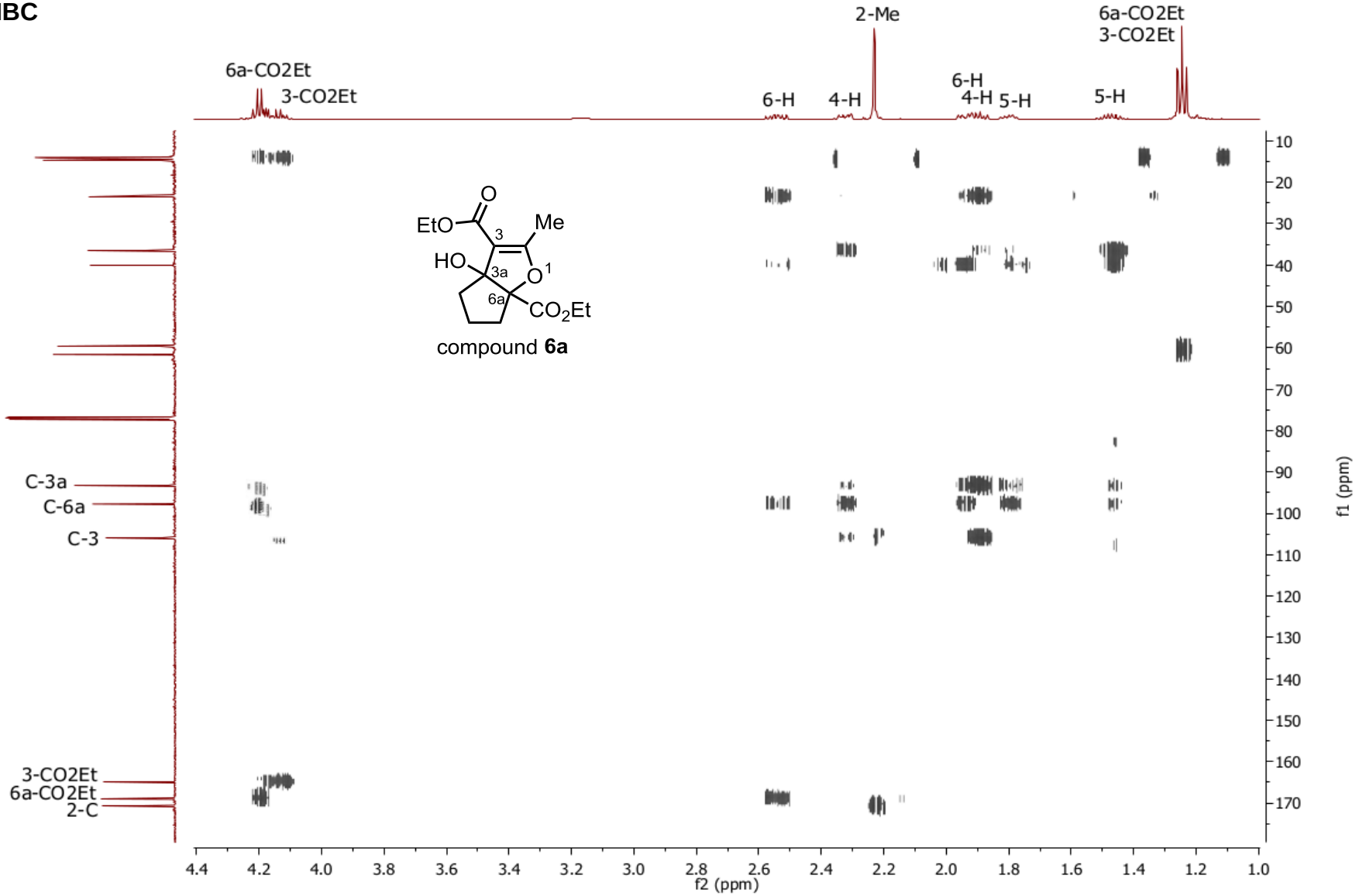


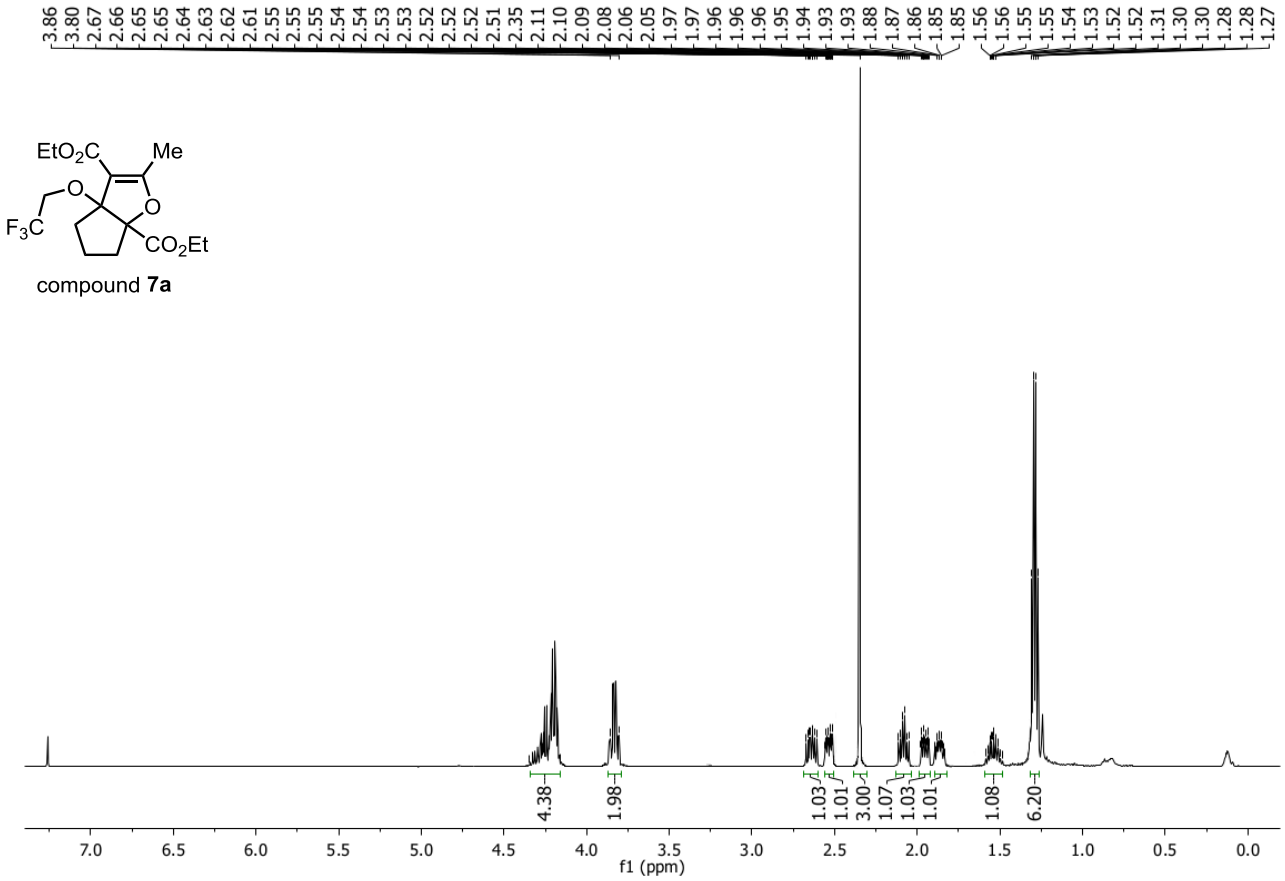
compound **6a**

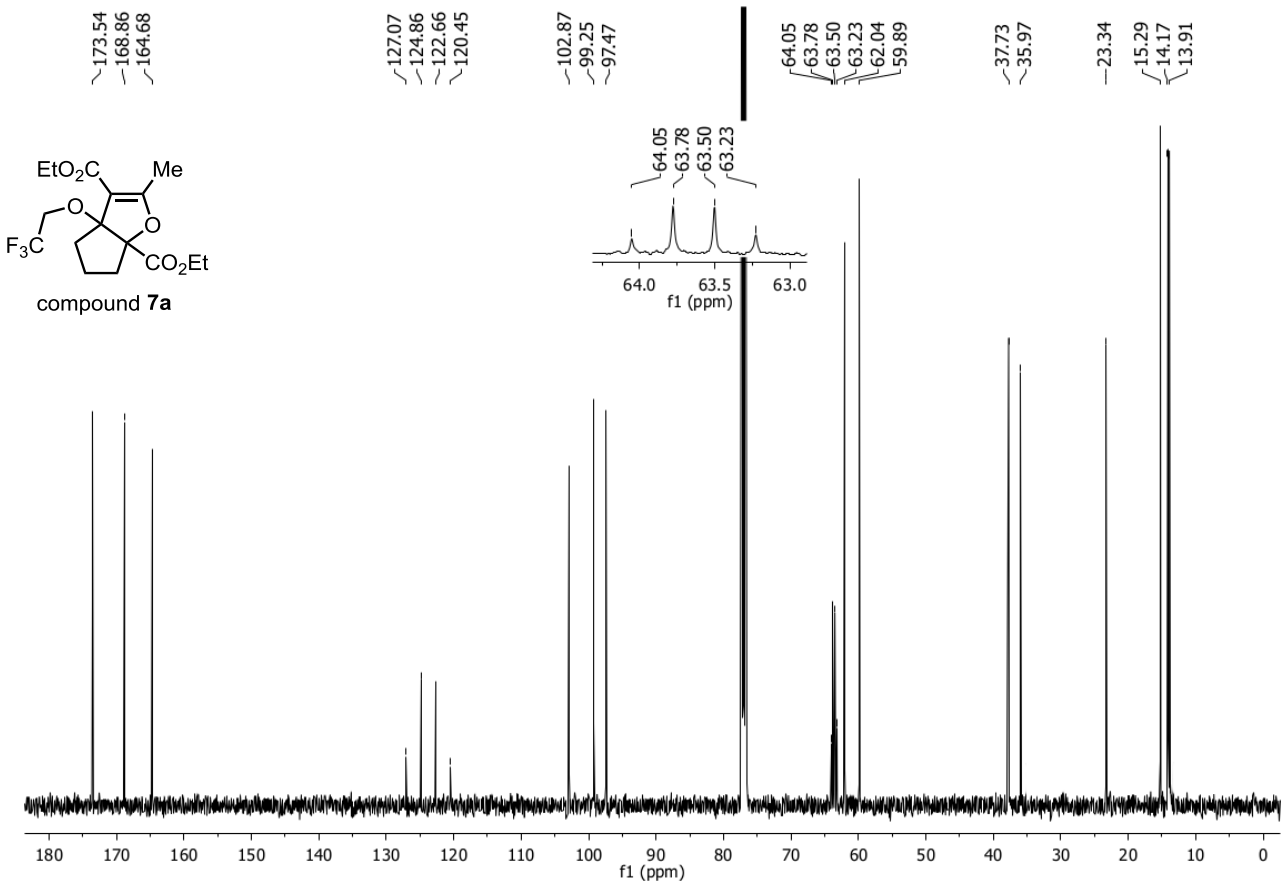


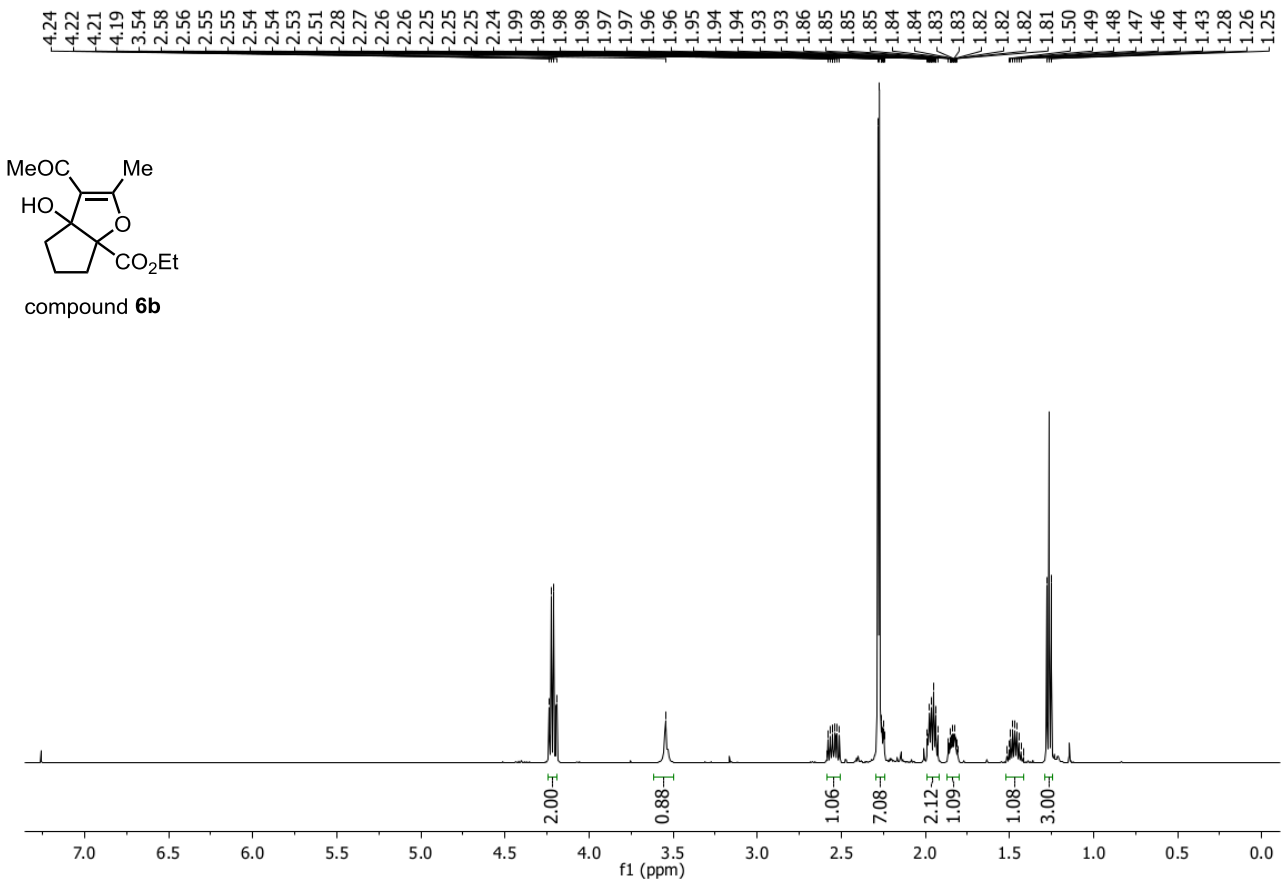
compound **6a**

HMBC

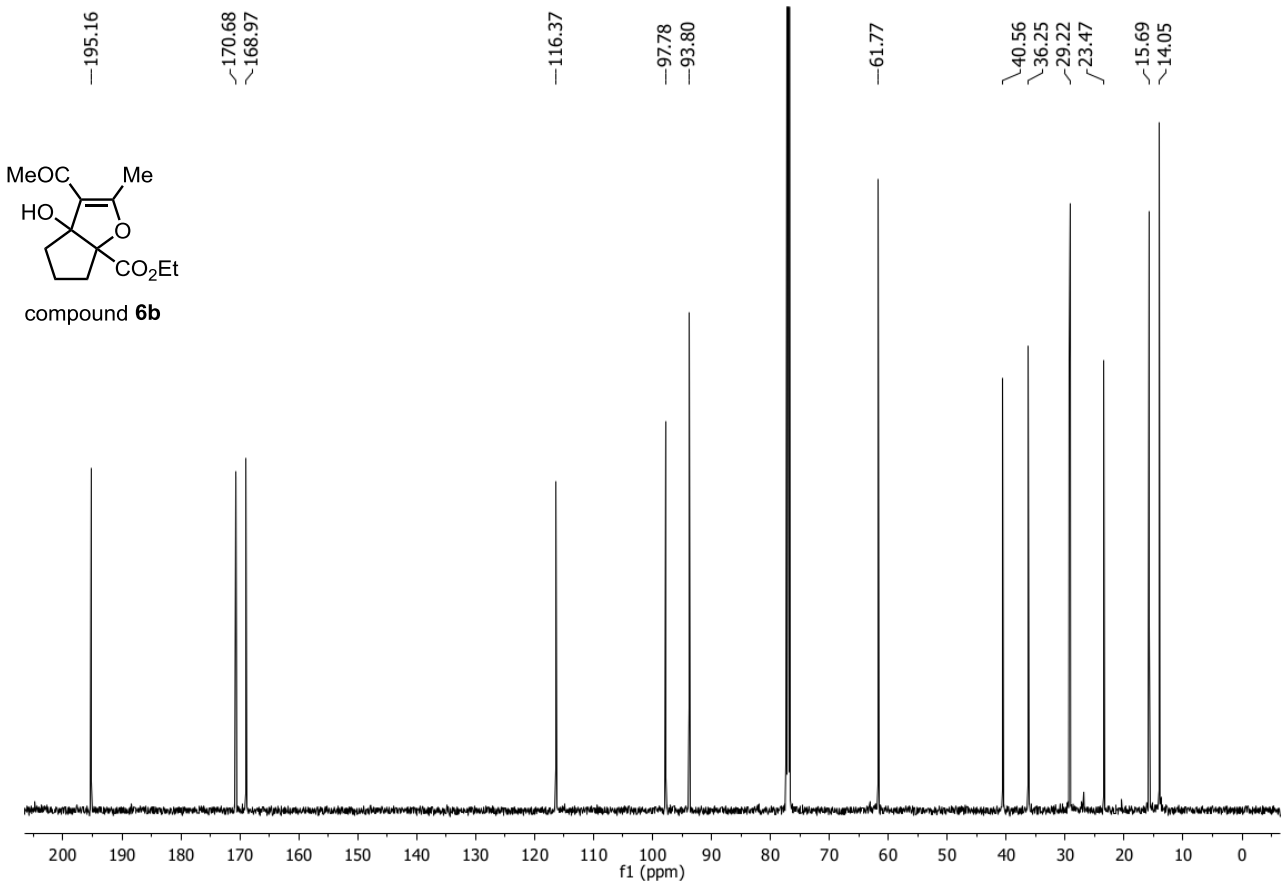

6a-CO2Et
3-CO2Et
2-Me
6a-CO2Et
3-CO2Et
6-H
4-H
6-H
4-H
5-H
5-H
EtO
O
Me
3
HO
3a
O
1
6a
CO2Et
compound 6a
C-3a
C-6a
C-3
3-CO2Et
6a-CO2Et
2-C
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
f1 (ppm)


EtO2C
Me
O
O
F3C
CO2Et
compound 7a
f1 (ppm)

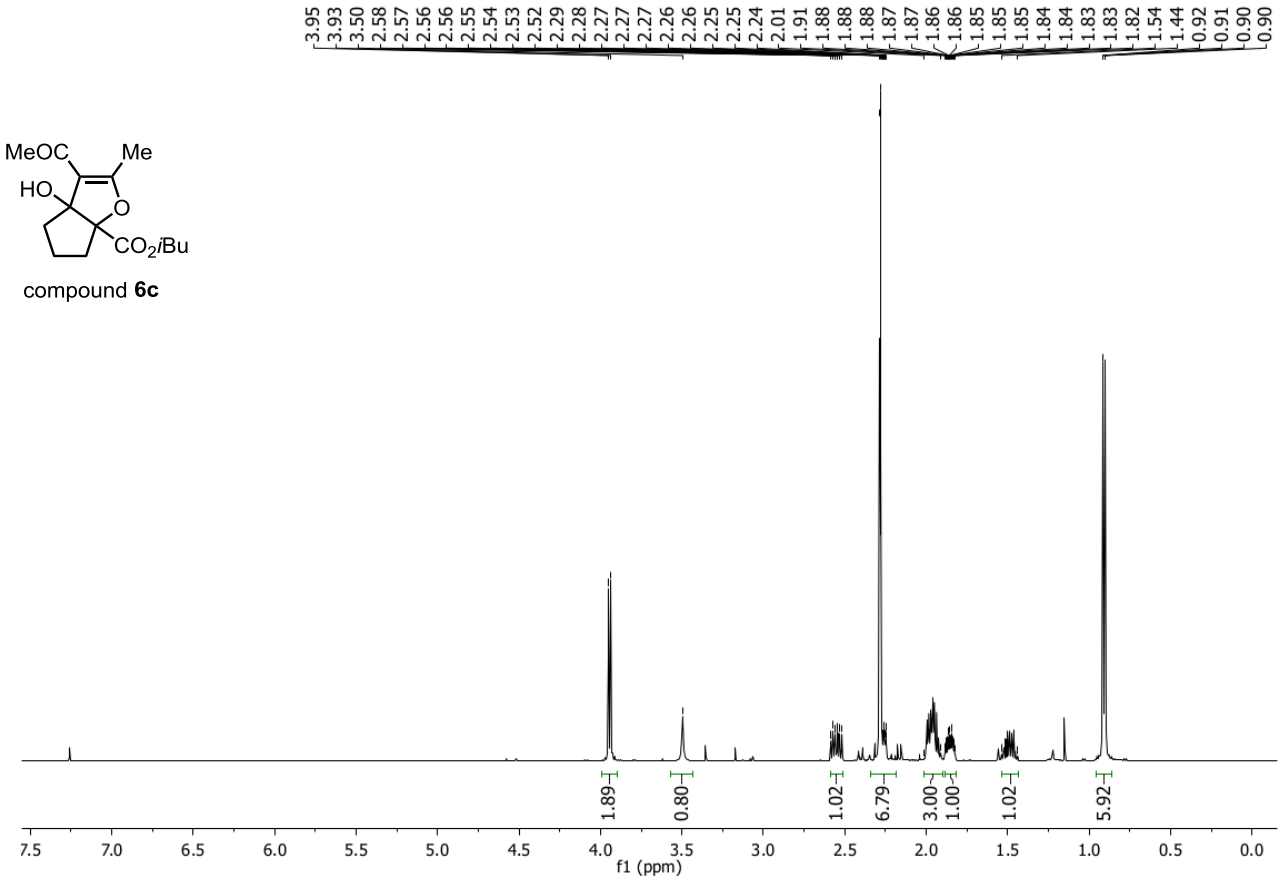

EtO2C
Me
O
O
F3C
CO2Et
compound 7a
f1 (ppm)

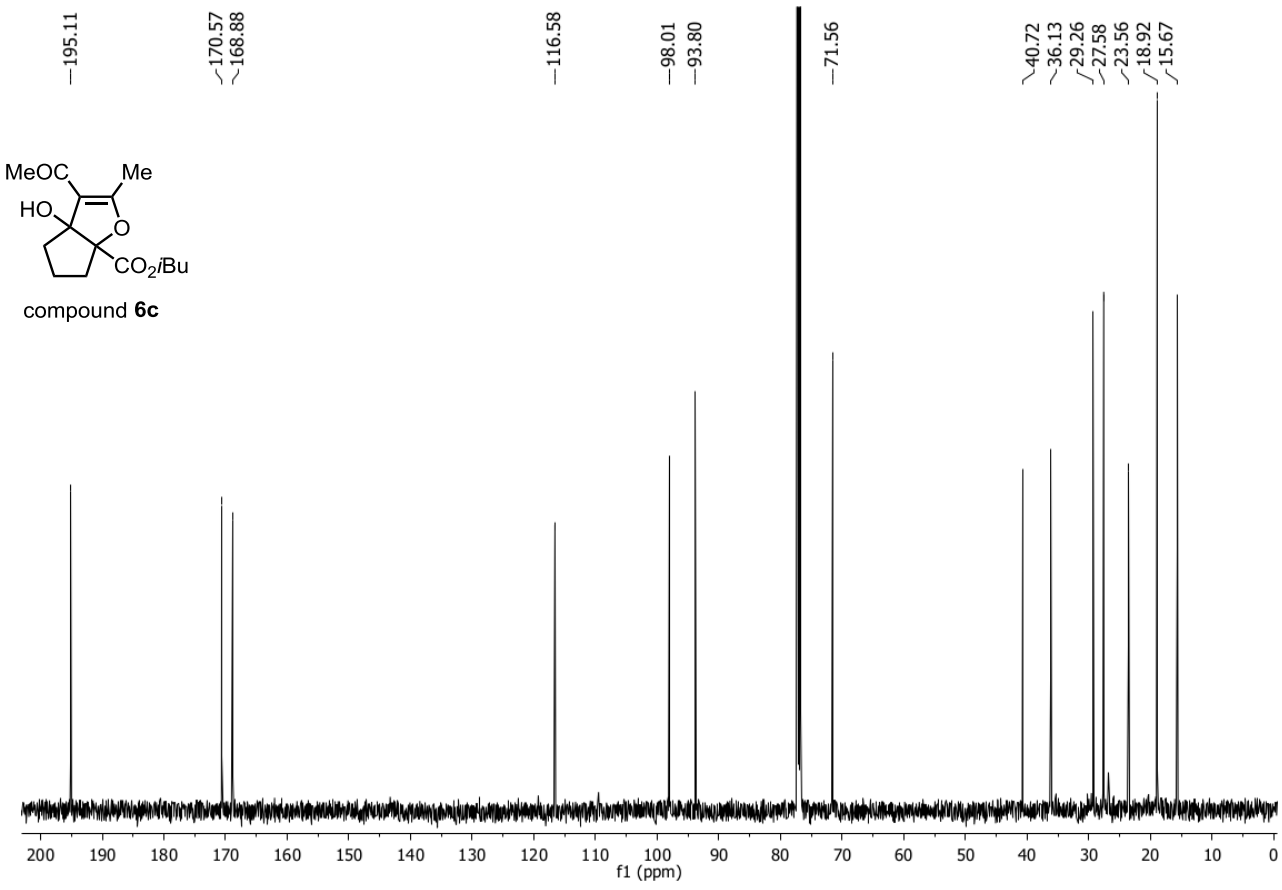


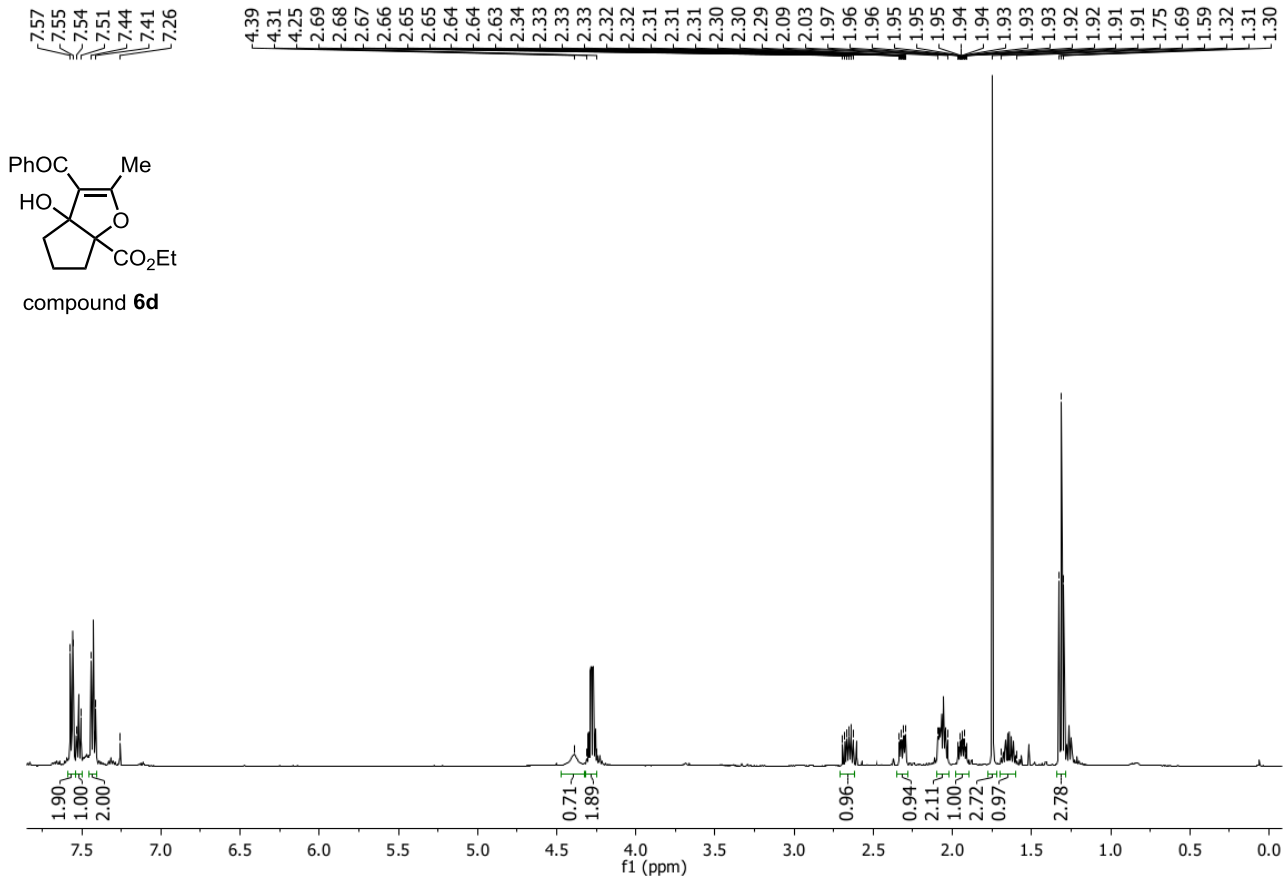
compound **6b**



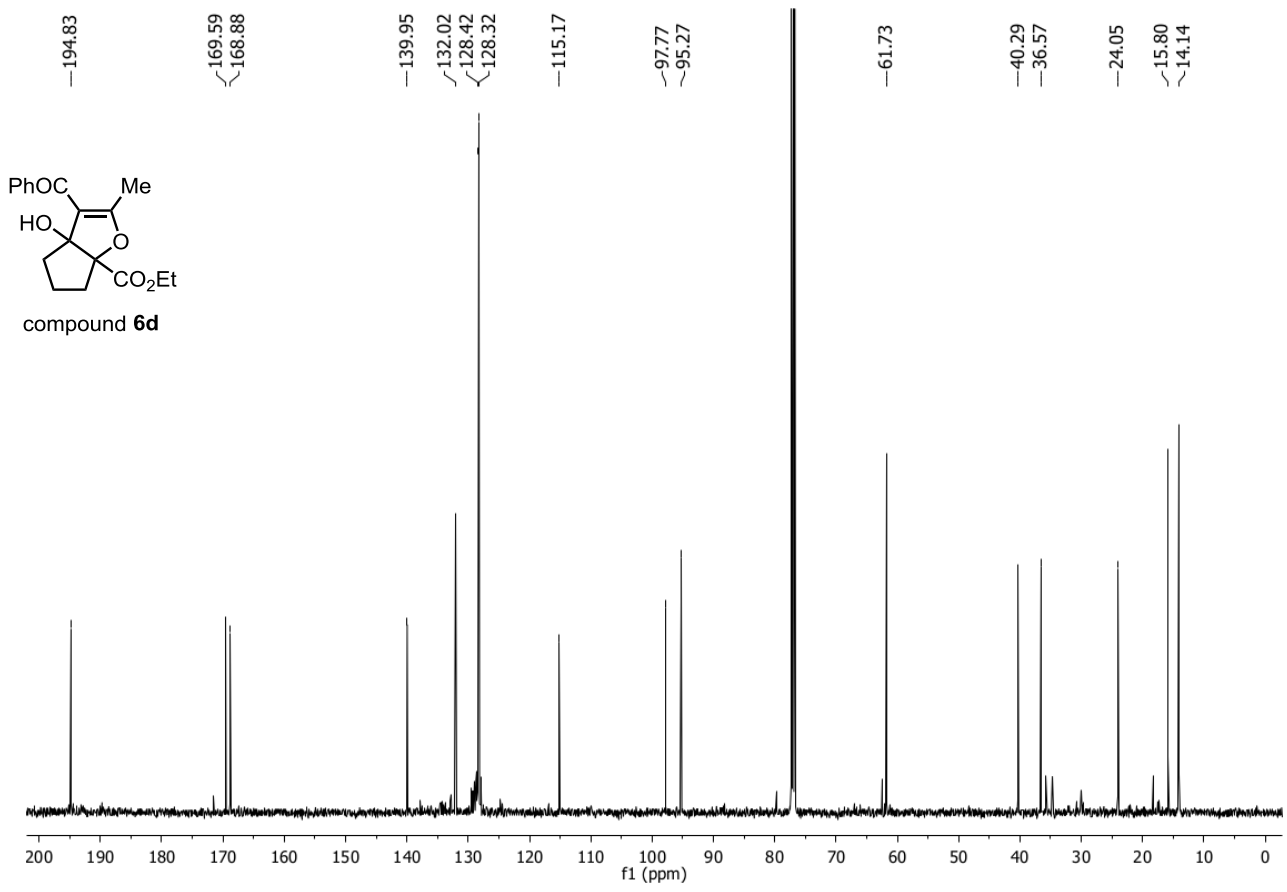
compound **6b**


MeOC
Me
HO
O
CO2iBu
compound 6c
3.95 3.93 3.50 2.58 2.57 2.56 2.56 2.55 2.54 2.53 2.52 2.29 2.28 2.27 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.01 1.91 1.88 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.54 1.44 0.92 0.91 0.90 0.90
1.89 0.80 1.02 6.79 3.00 1.00 1.02 5.92
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)


195.11
170.57
168.88
116.58
98.01
93.80
71.56
40.72
36.13
29.26
27.58
23.56
18.92
15.67
MeOC
Me
HO
O
CO2iBu
compound 6c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

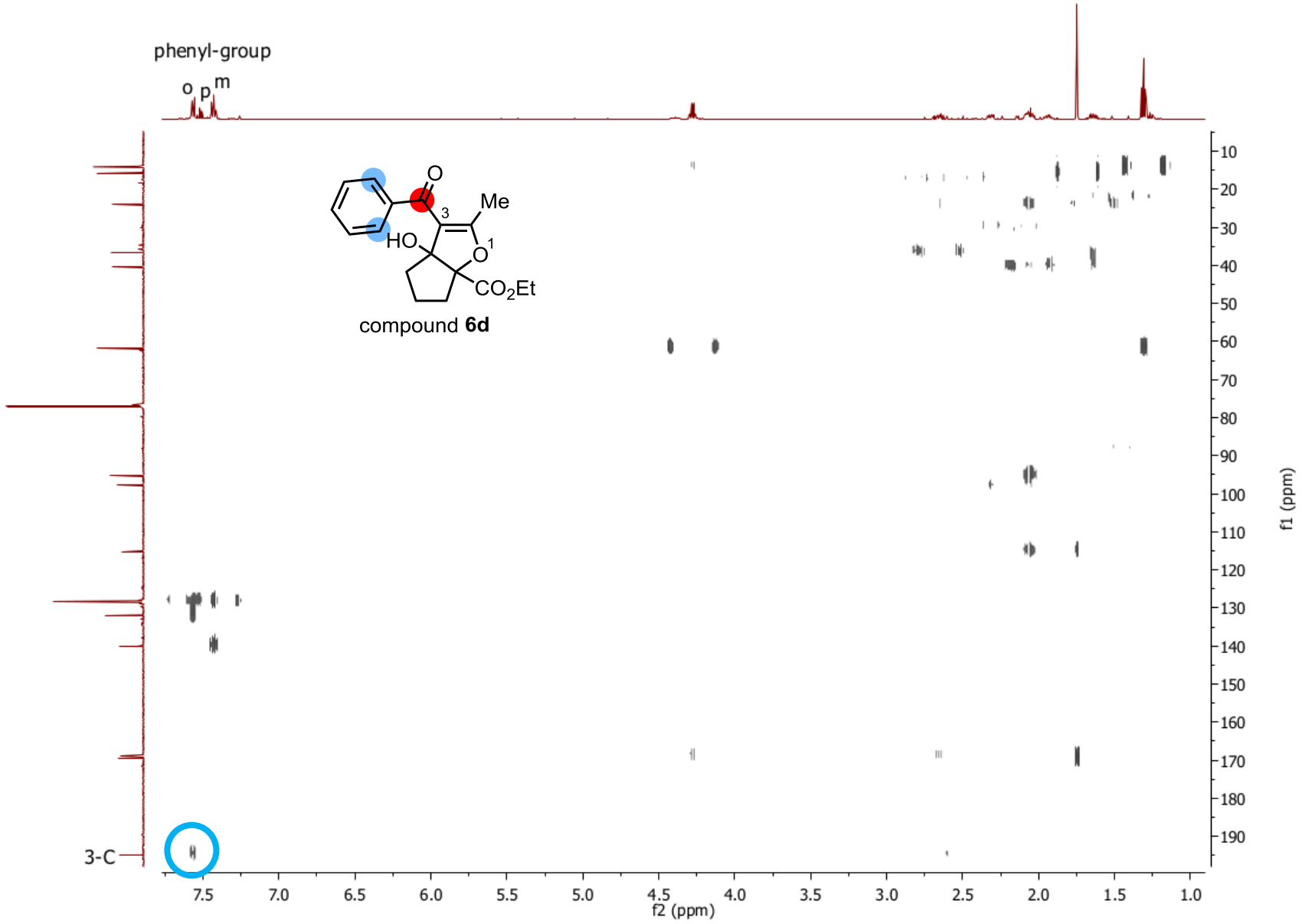


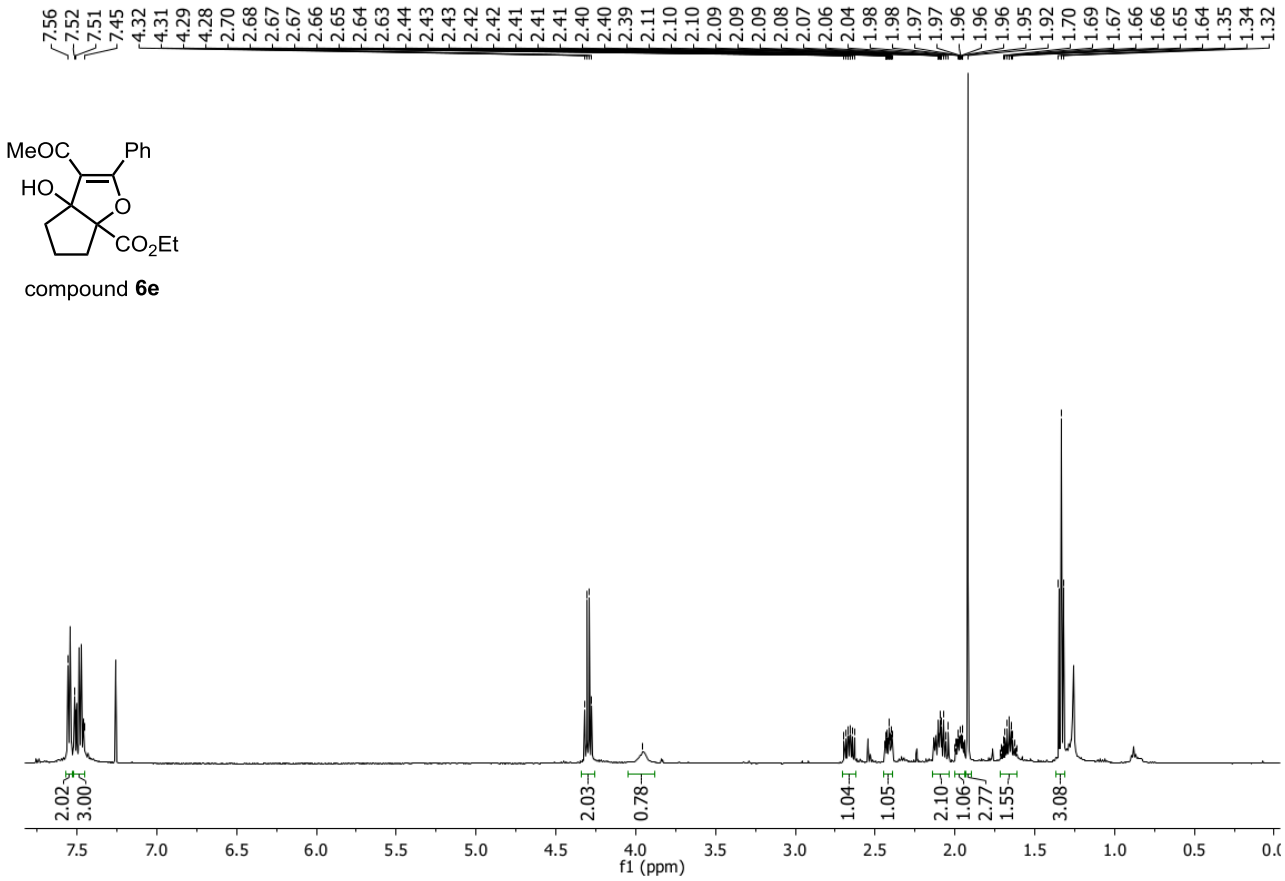
compound **6d**



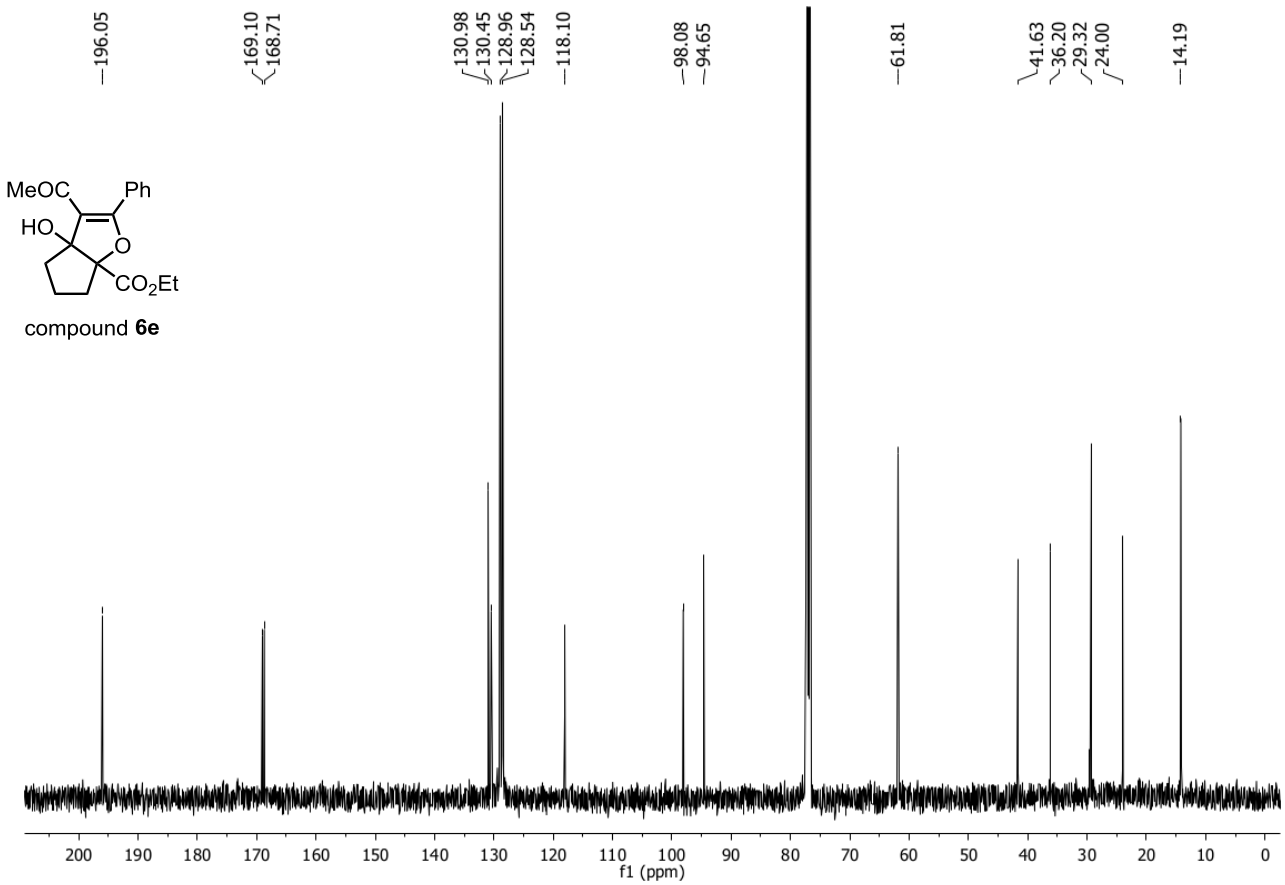
compound **6d**

HMBC


phenyl-group
o p m
O
Me
3
HO
1
O
CO2Et
compound 6d
3-C
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
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

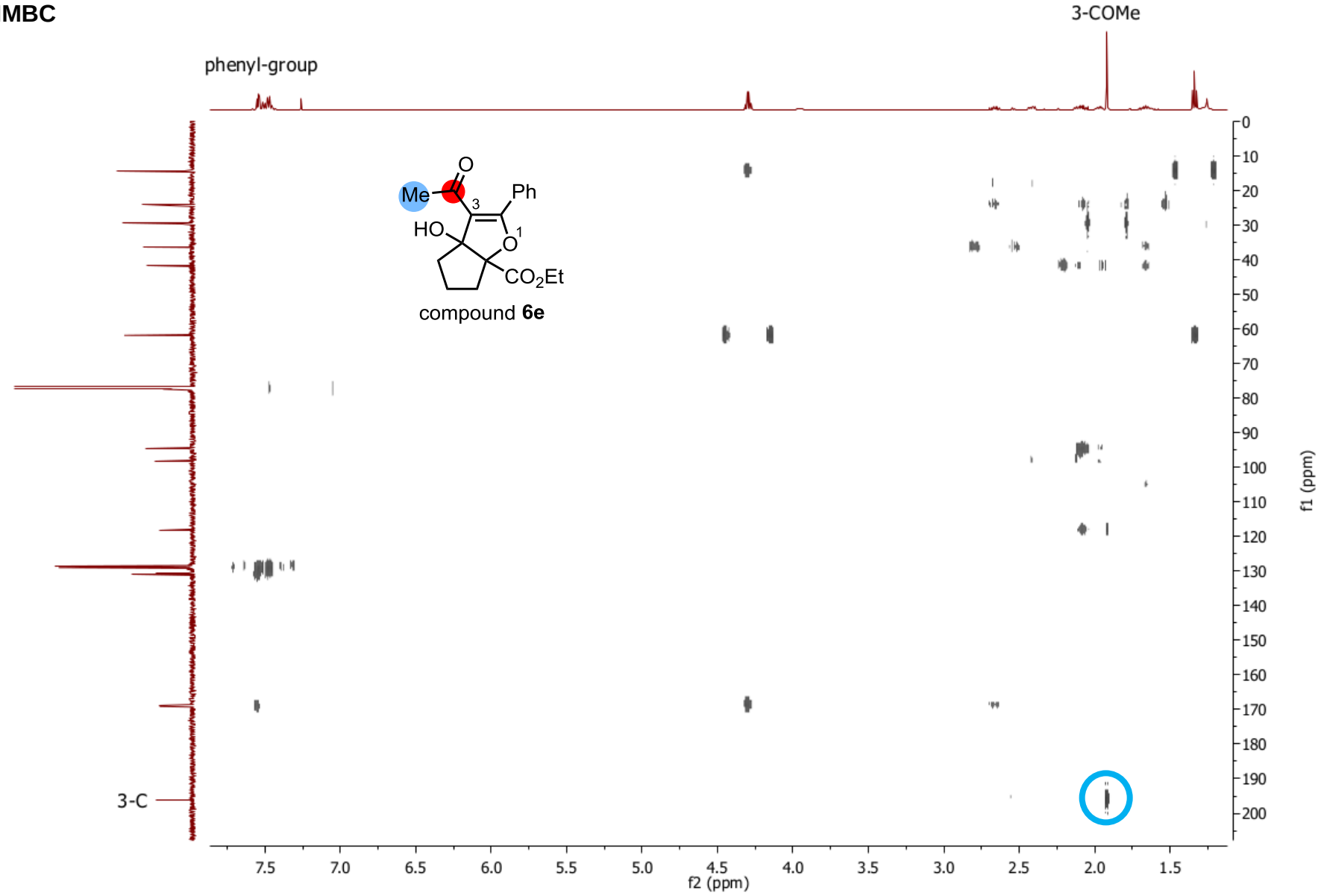


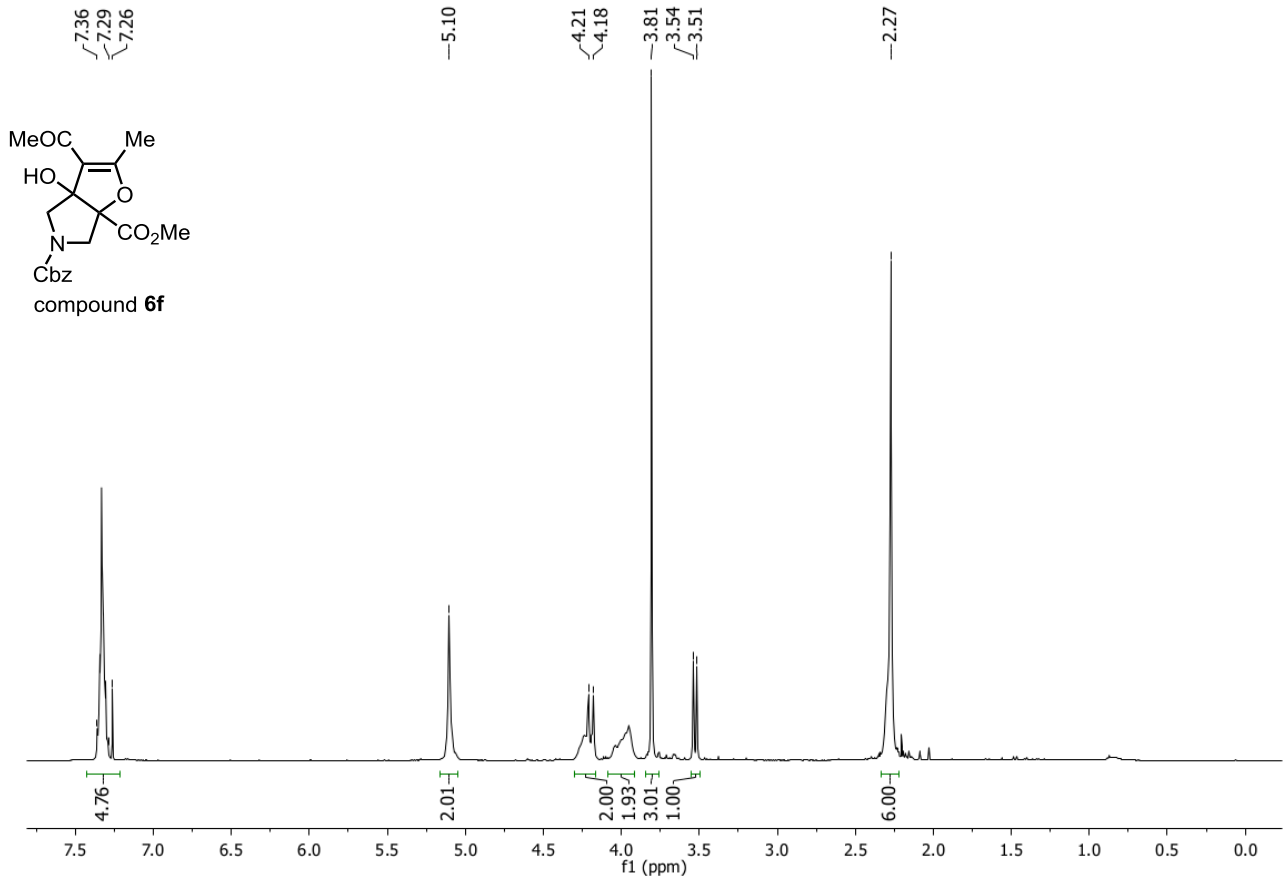
compound **6e**



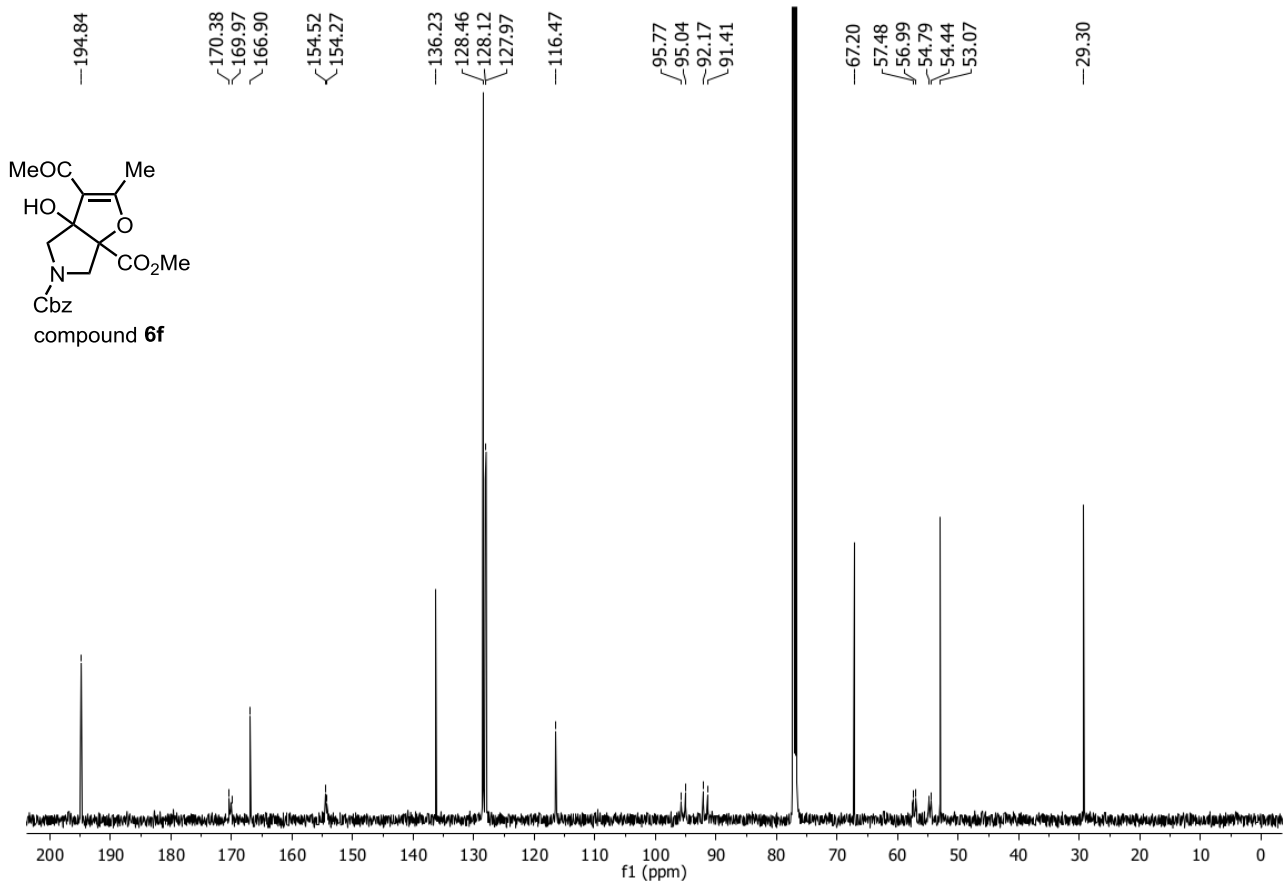
compound **6e**

HMBC

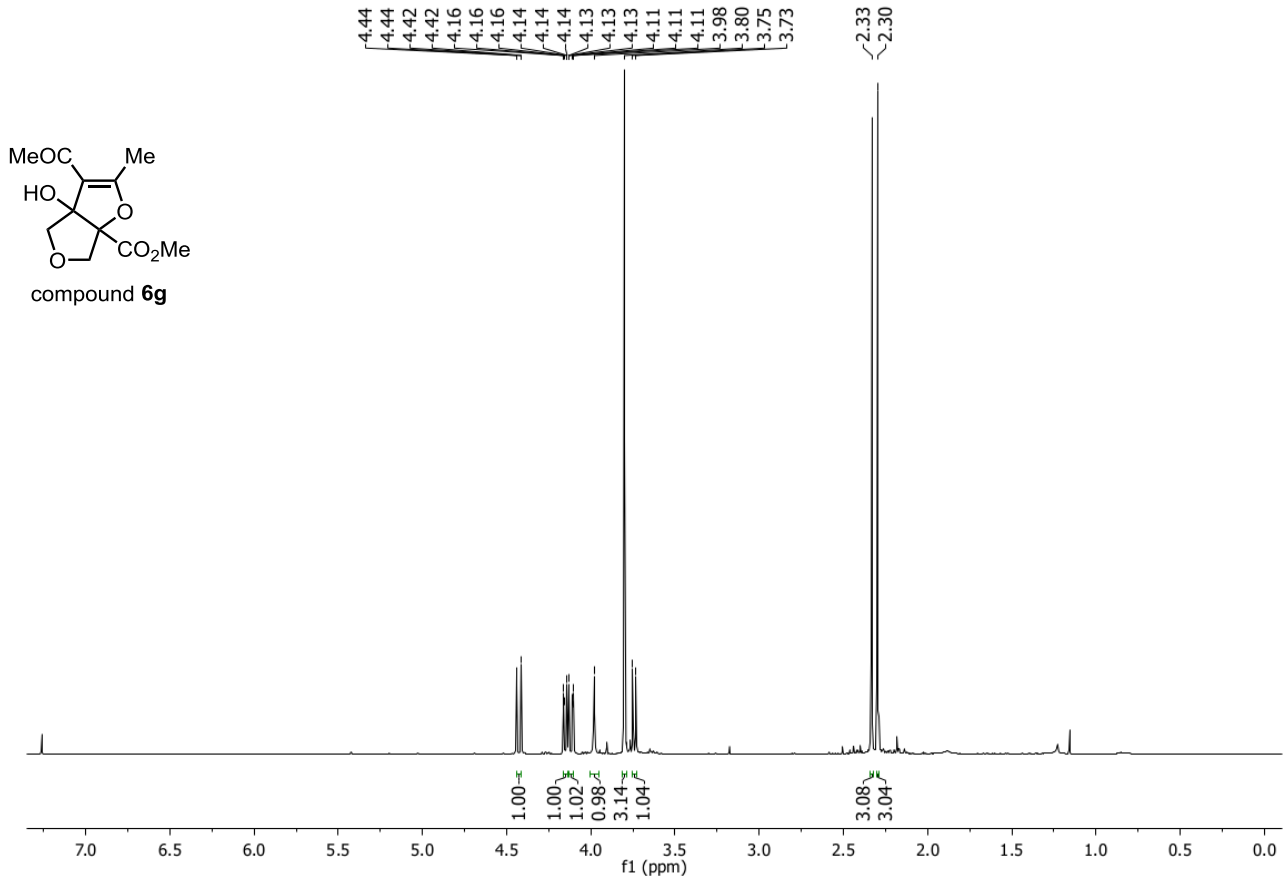

3-COMe
phenyl-group
Me
O
3
Ph
HO
1
O
CO2Et
compound 6e
3-C
f2 (ppm)
f1 (ppm)



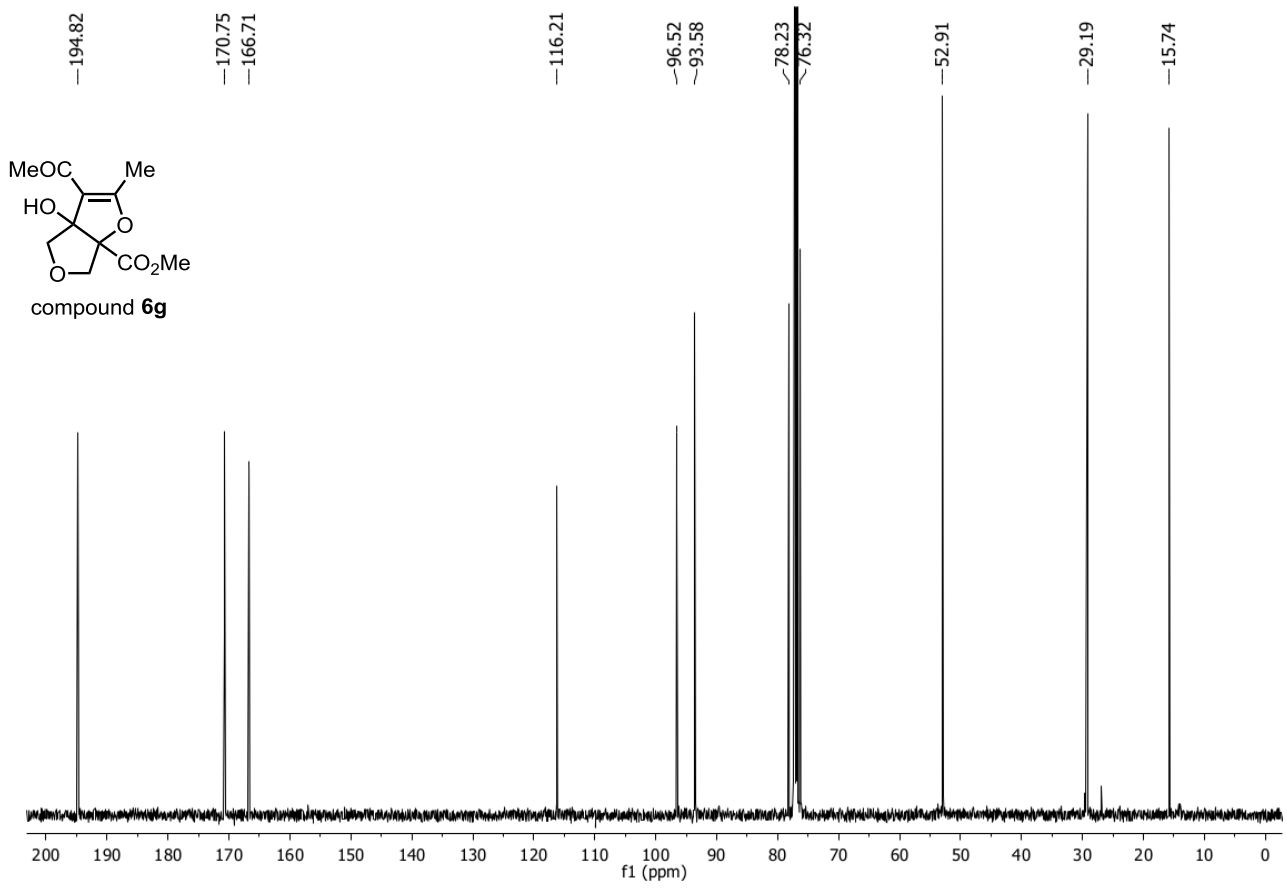
compound **6f**



compound **6f**



compound **6g**



compound **6g**

Brief text description of the crystal structure determination: Single crystal X-ray data of **6g** were measured at 100 K on a Bruker AXS Apex II diffractometer (Mo-Kα radiation, λ = 0.71073 Å, Kappa 4 circle goniometer, Bruker Apex II detector). A semi-empirical absorption correction was performed based on symmetry-related measurements with the program SADABS (L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3–10). The structure was solved with the program SHELXS and refined with SHELXL (G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8). Non H atoms were refined anisotropically, H atoms were located from the difference Fourier maps, but subsequently fixed to geometric positions using appropriate riding models with the exception of the hydroxyl H which was refined freely. CCDC 1559311 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

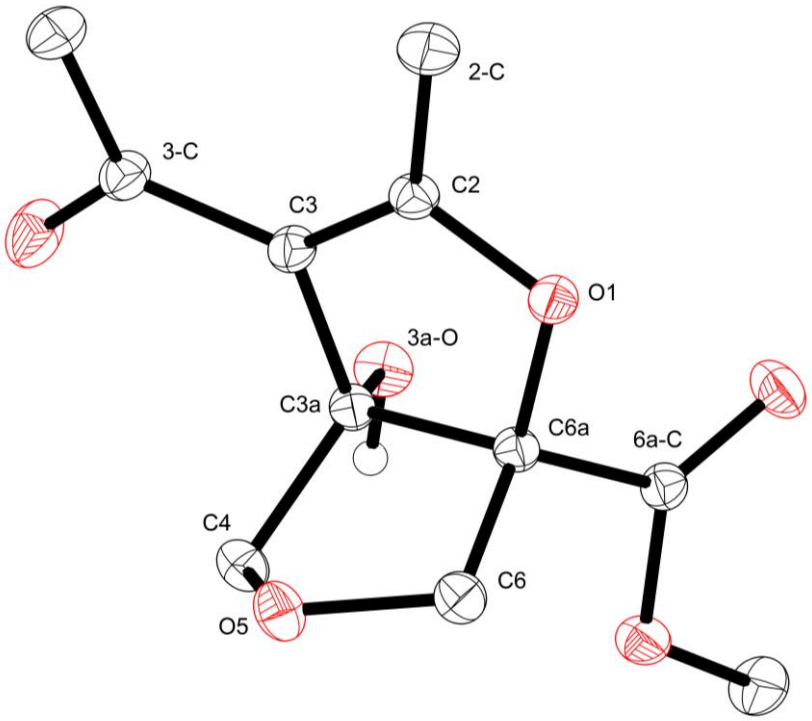


Figure S1. ORTEP-representation of the X-ray structure of dihydrofurane **6g**, ellipsoids at the 50% probability level, H atoms omitted for clarity; locants were used as atom labels.

Table S2. Crystal data and structure refinement for methyl 3-acetyl-3a-hydroxy-2-methyl-3a,4,6,6a-tetrahydrofuro[3,4-*b*]furan-6a-carboxylate (**6g**).

Empirical formula	$C_{11}H_{14}O_6$	
Formula weight	242.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7439(3) Å	α = 76.9720(13)°.
	b = 7.8264(3) Å	β = 81.6747(14)°.
	c = 9.1707(3) Å	γ = 83.9592(14)°.
Volume	534.27(3) $Å^3$	
Z	2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.124 mm^{-1}	
F(000)	256	
Crystal size	0.320 x 0.240 x 0.120 mm^3	
Theta range for data collection	2.297 to 36.317°	
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 15$	
Reflections collected	27838	
Independent reflections	5181 [R(int) = 0.0196]	
Observed reflections [I > 2(I)]	4819	
Completeness to theta = 36.317°	100.0%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9776	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	5181 / 0 / 161	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0863	
R indices (all data)	R1 = 0.0316, wR2 = 0.0879	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.581 and –0.231 e $Å^{-3}$	