Electronic Supplementary Information

Pd(II)-Catalyzed Cycloisomerisation of γ-Alkynoic Acids and One-Pot Tandem Cycloisomerisation/CuAAC Reactions in Water.

Joaquín García-Álvarez,[a]* Josefina Díez[a] and Cristian Vidal[a]

Laboratorio de Química Organometálica y Catálisis (Unidad Asociada al CSIC). Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles", Facultad de Química, Universidad de Oviedo, E-33071, Oviedo, Spain

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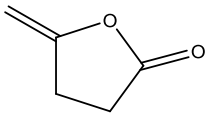
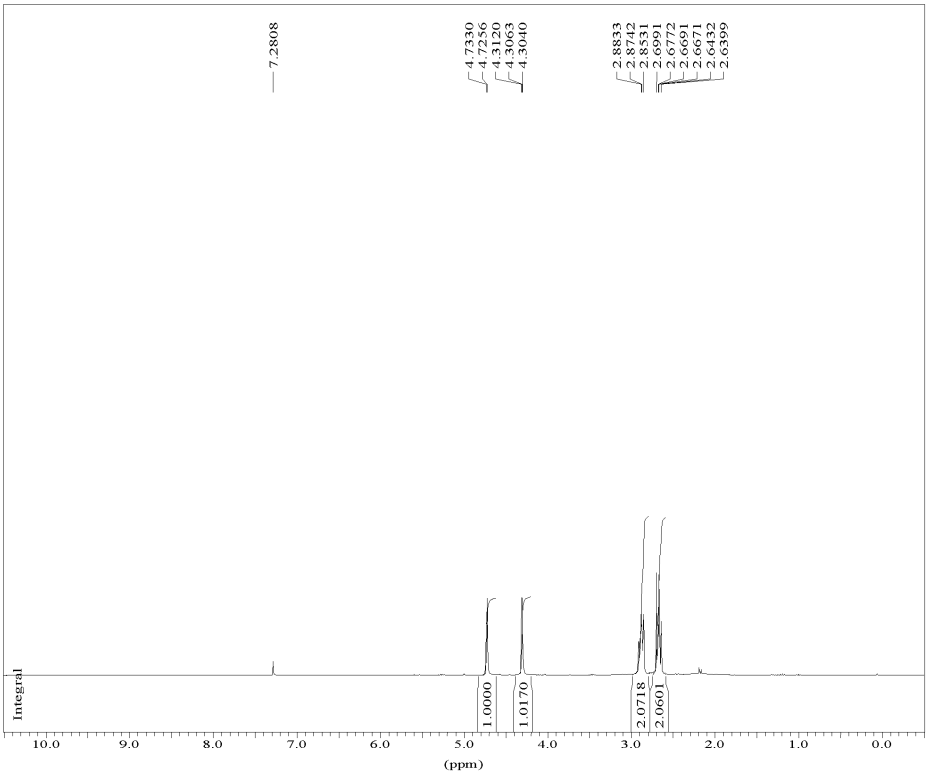
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of enol-lactones 5a-h and 7a-e

5-methylenedihydrofuran-2(*3H*)-one (5a)





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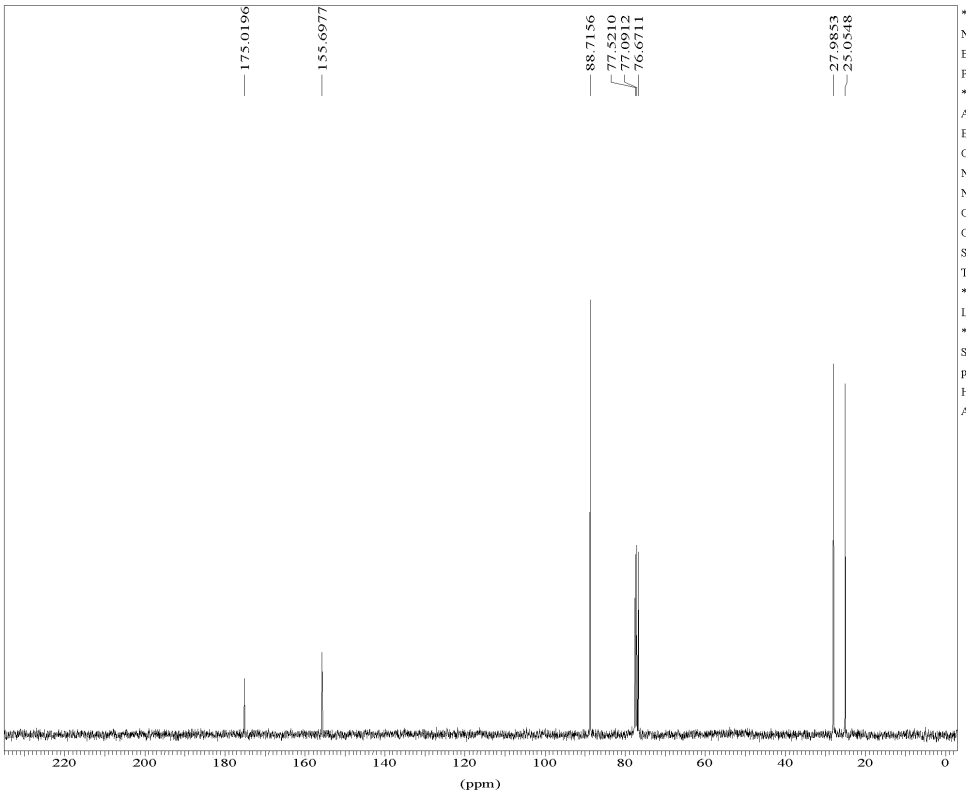

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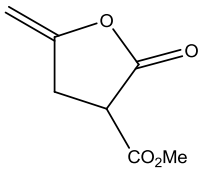
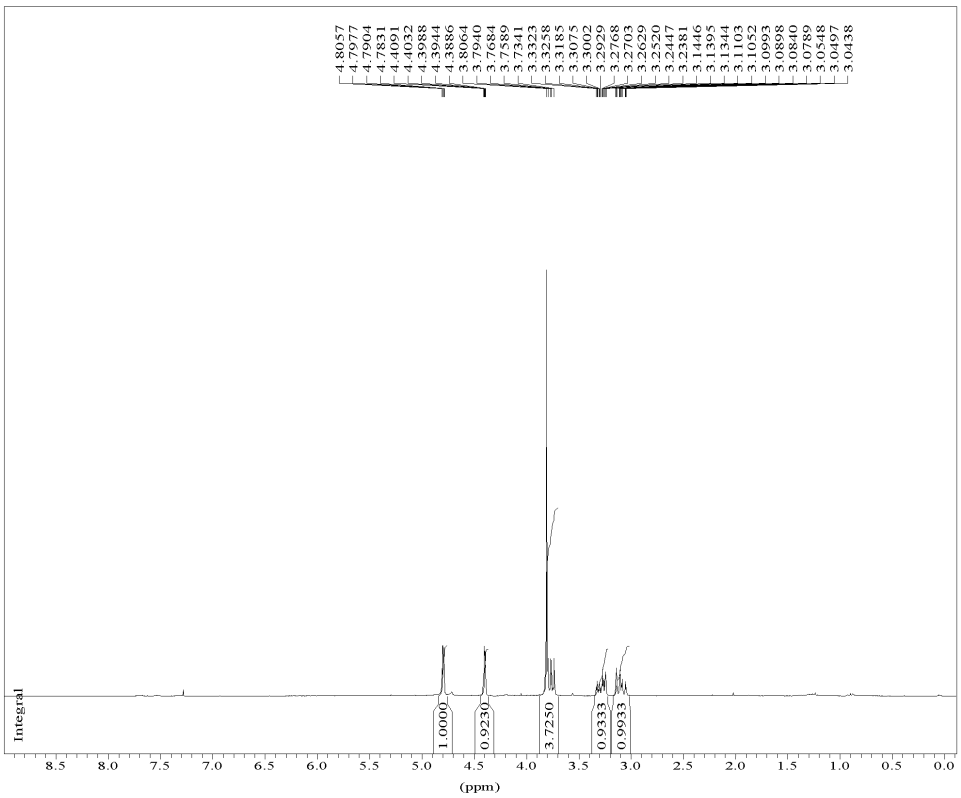
methyl 5-methylene-2-oxotetrahydrofuran-3-carboxylate (5b)



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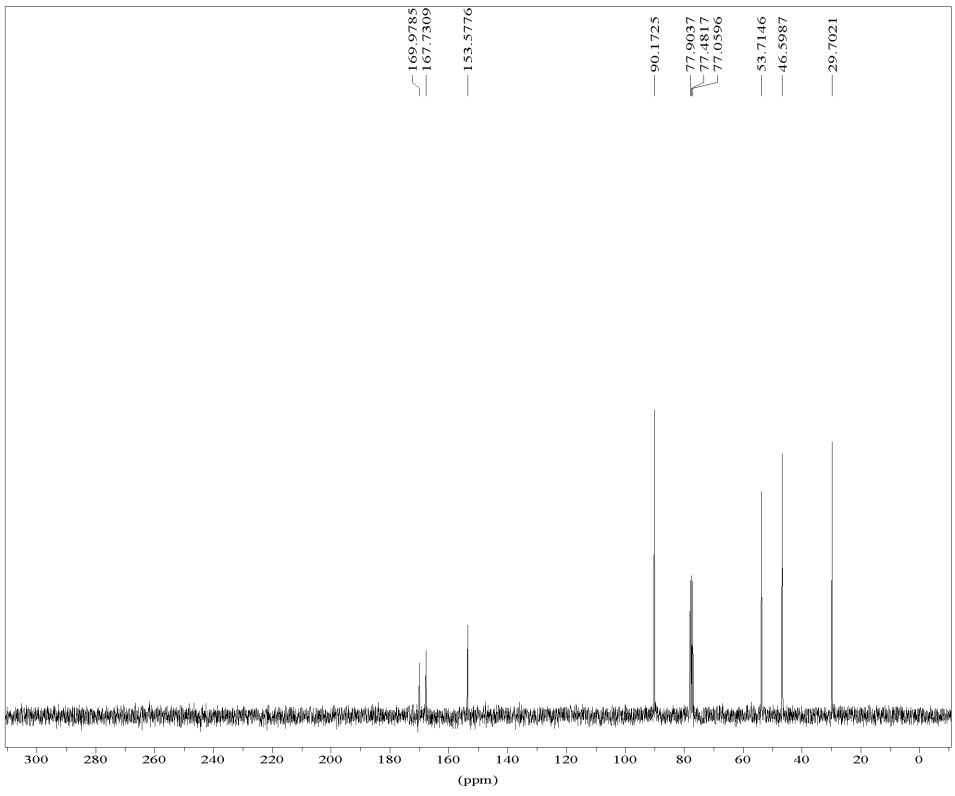


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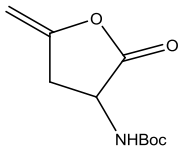

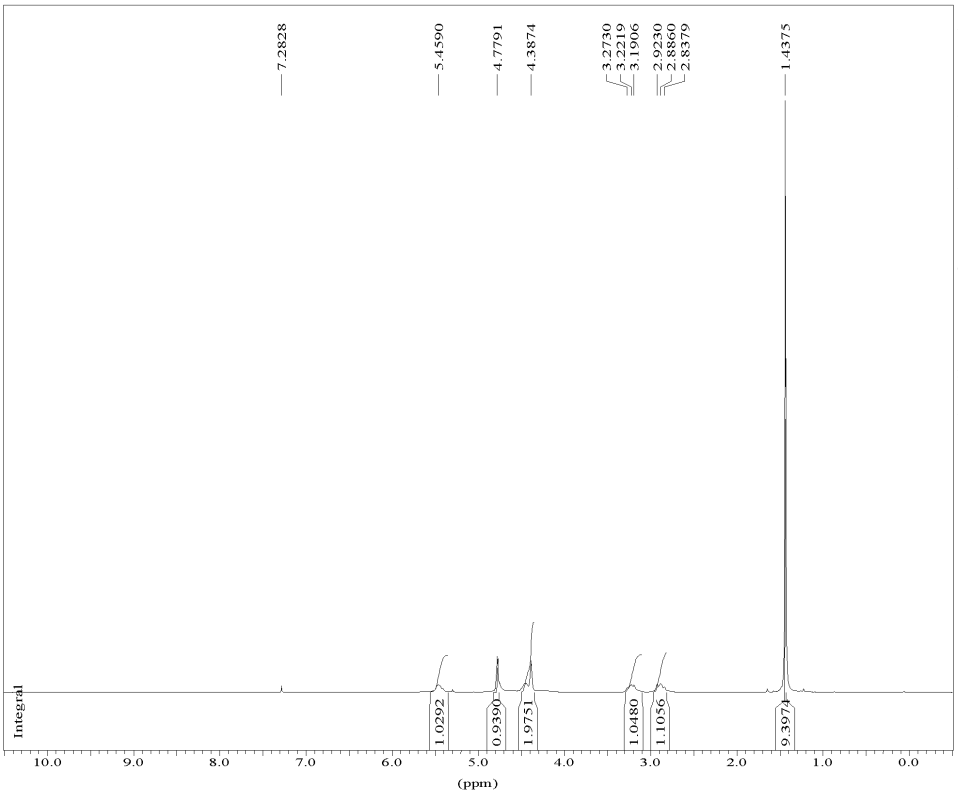

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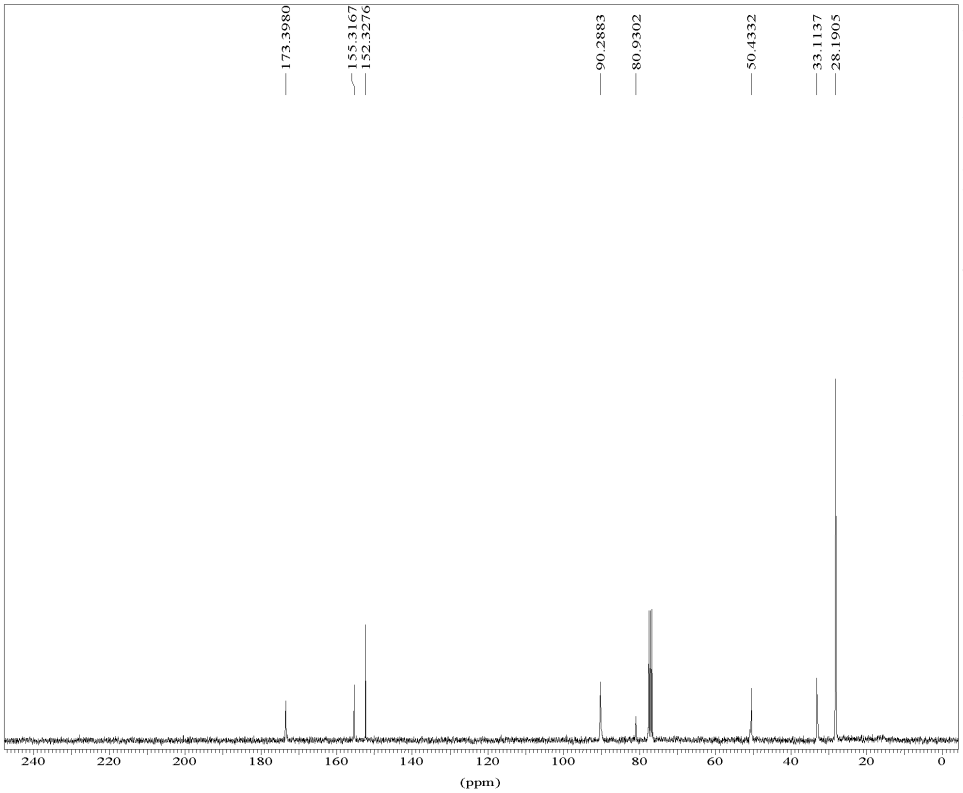

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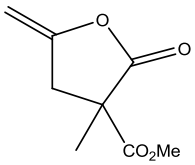
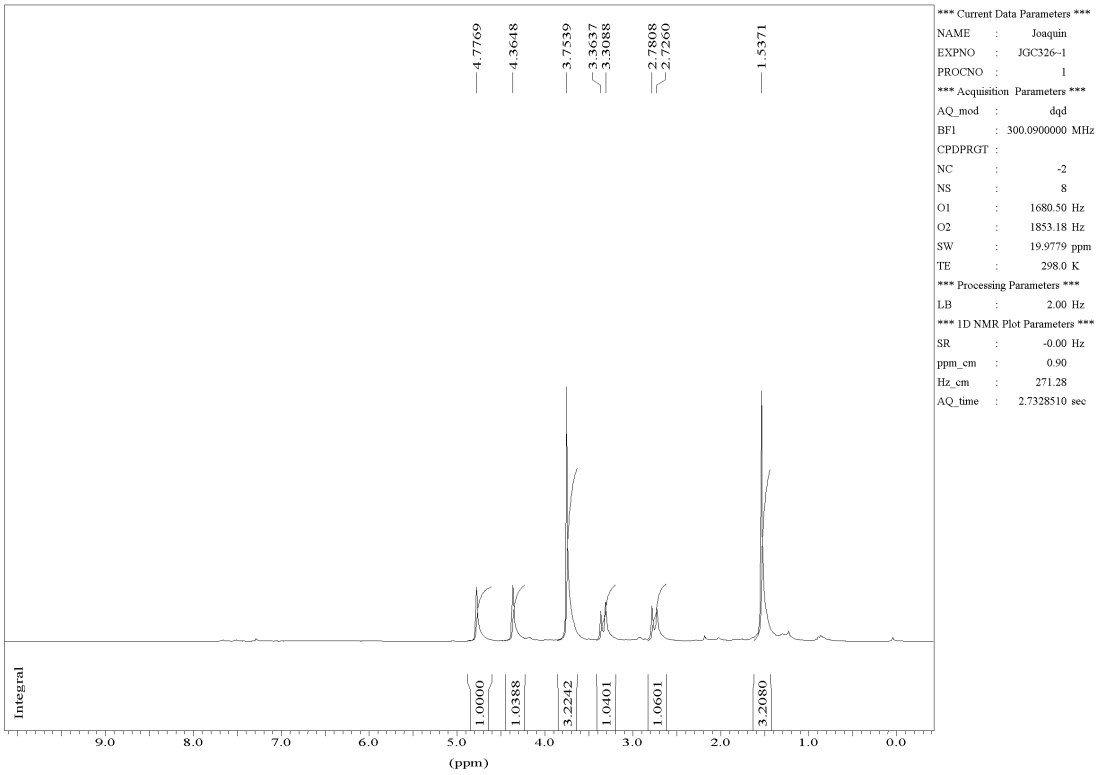
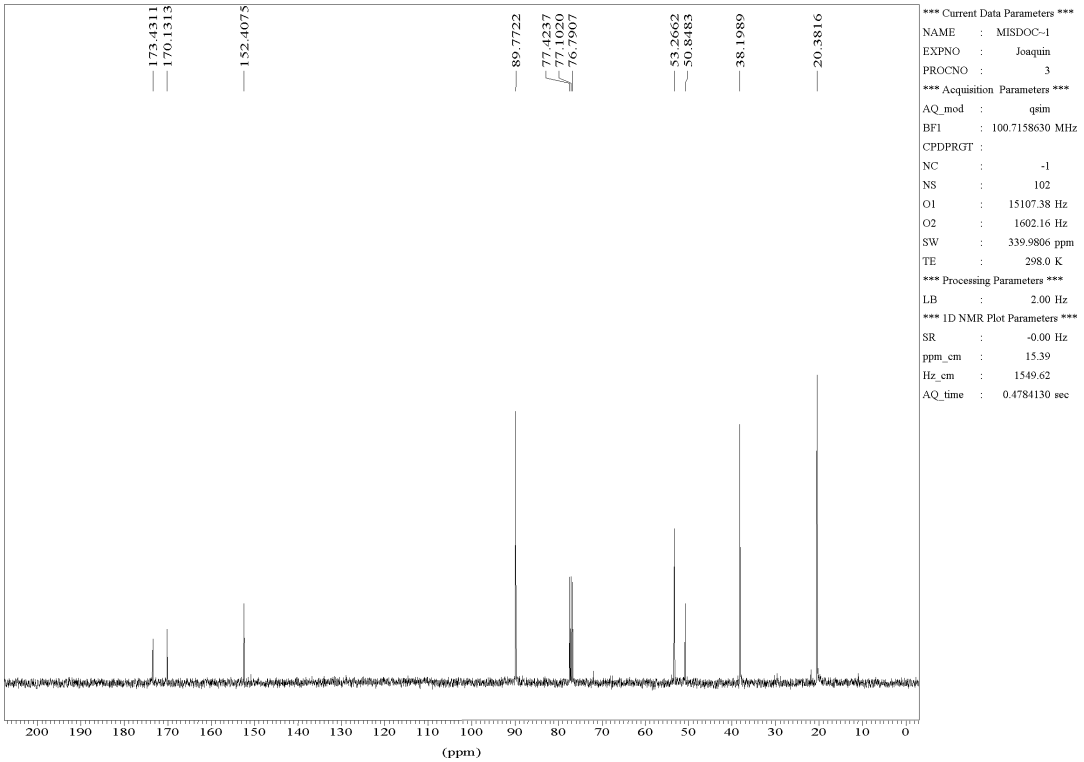
methyl 3-methyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate (5d)







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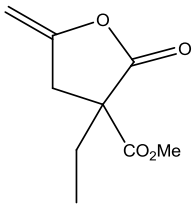
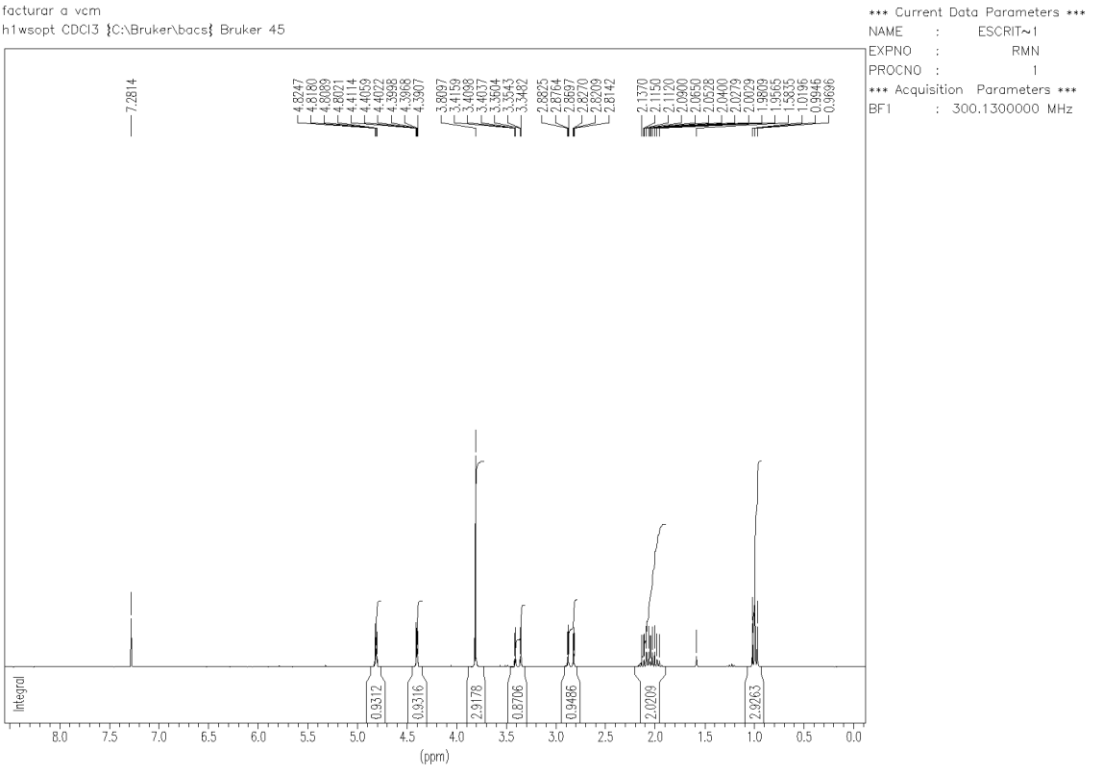
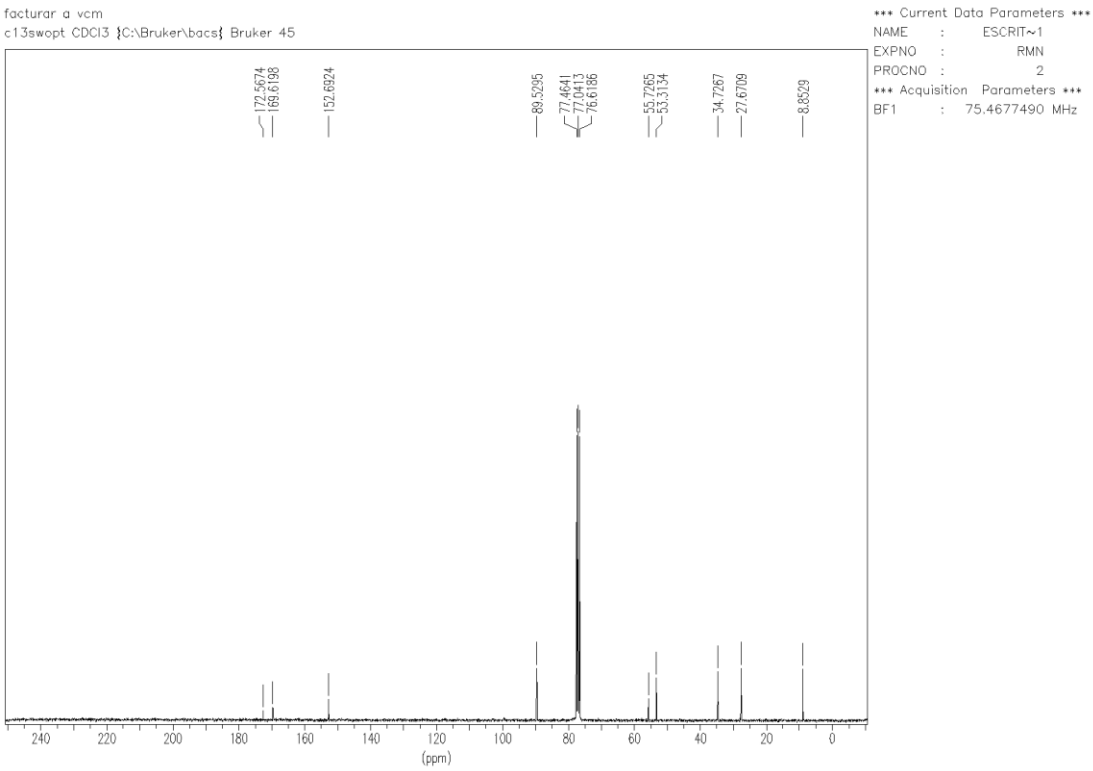
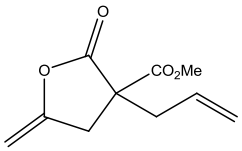
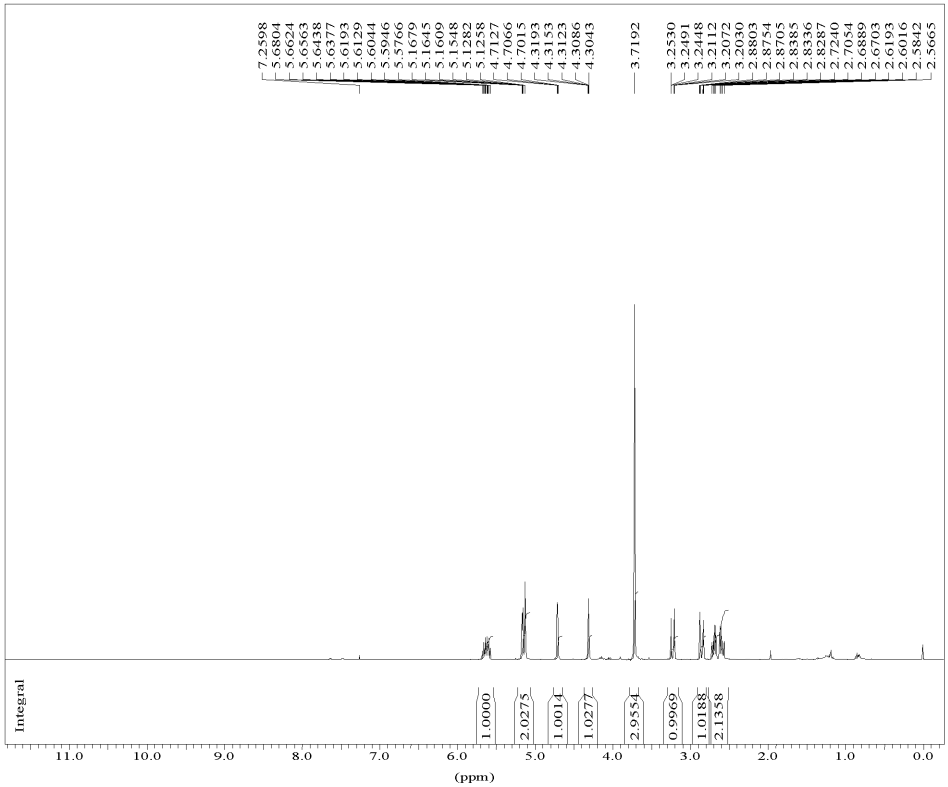






methyl 3-allyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate (5f)





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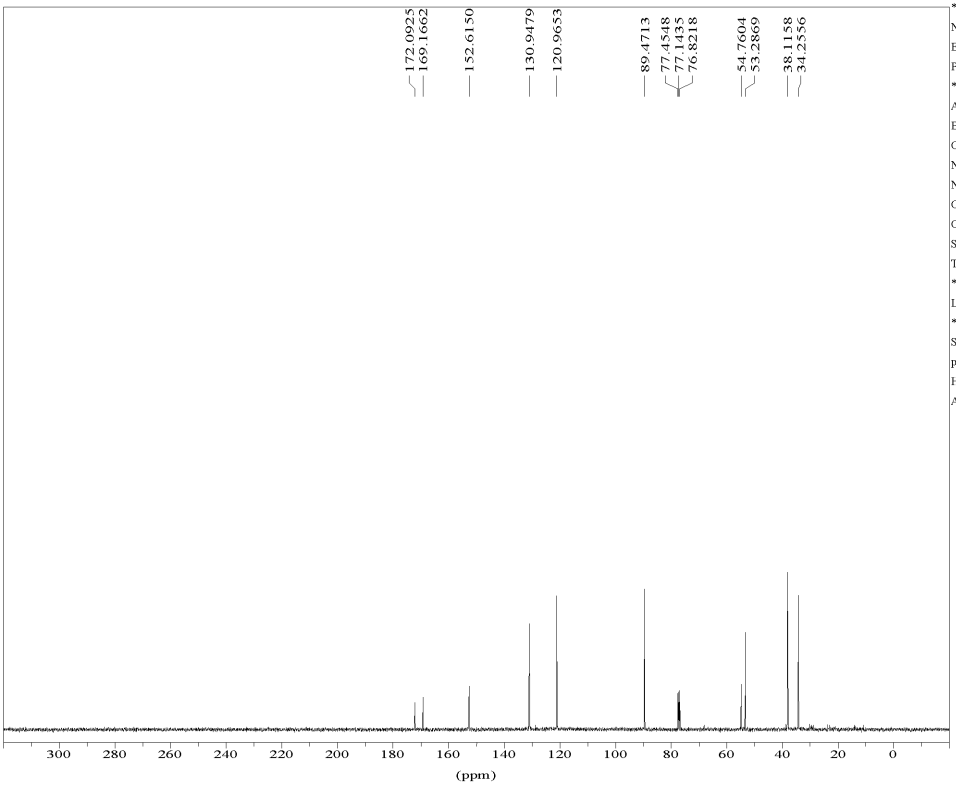

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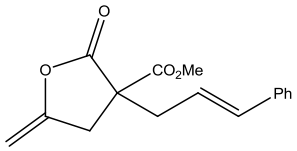
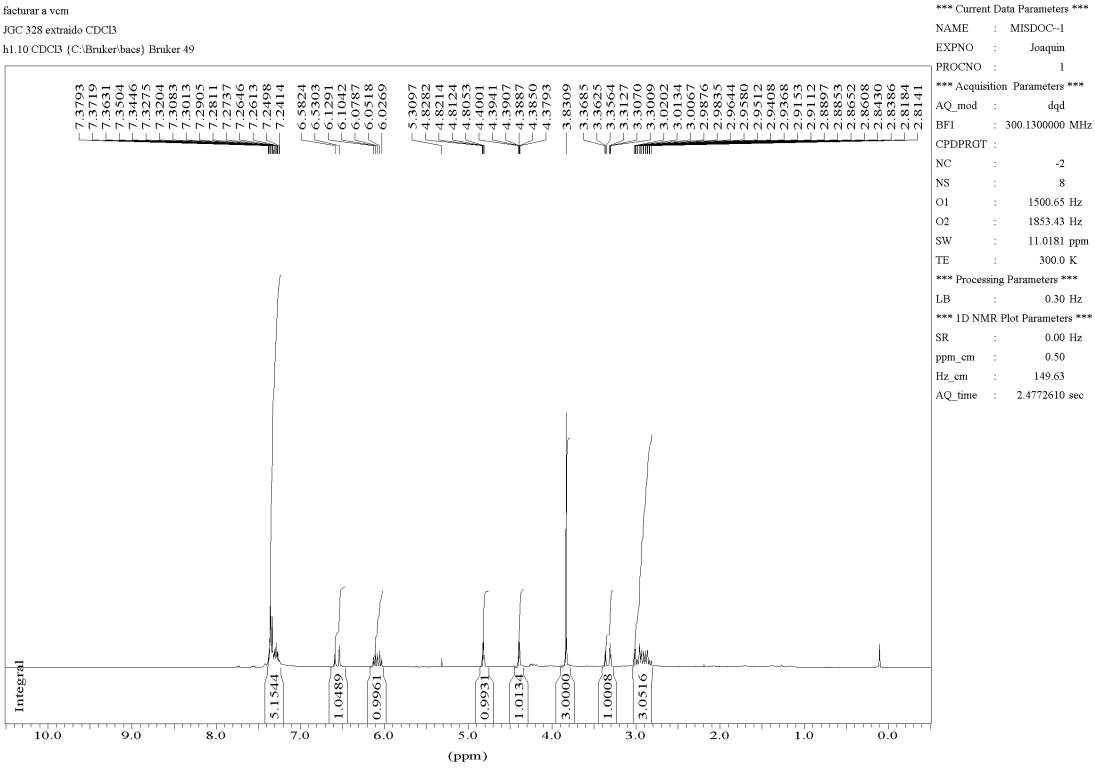
methyl 3-cinnamyl-5-methylene-2-oxotetrahydrofuran-3-carboxylate (5g)





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O1 : 1500.65 Hz
O2 : 1853.43 Hz
SW : 11.0181 ppm
TE : 300.0 K
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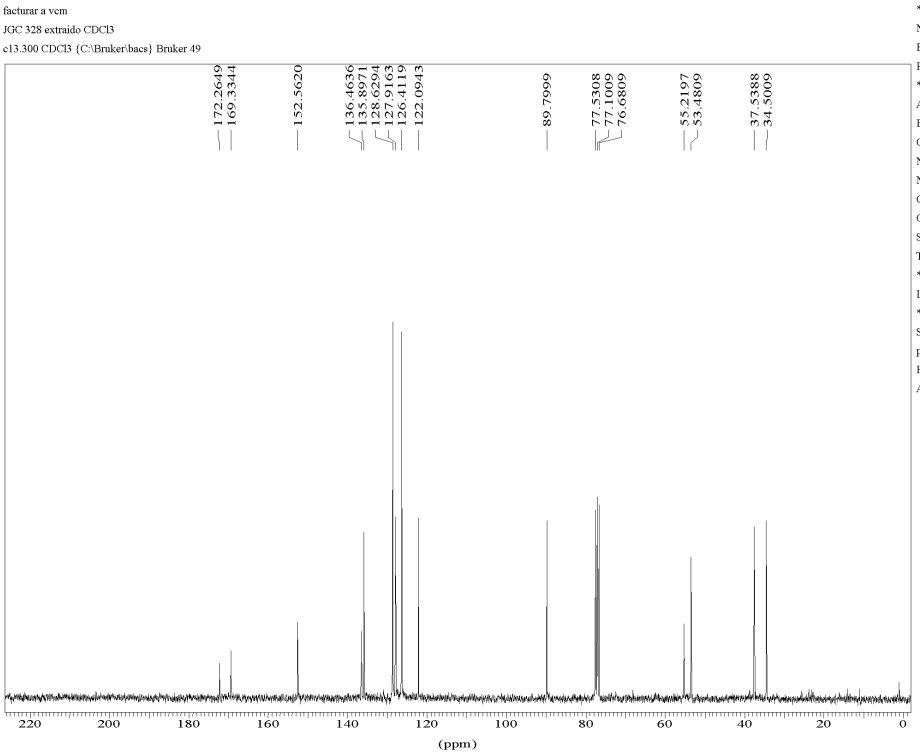

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O2 : 2011.55 Hz
SW : 320.0171 ppm
TE : 300.0 K
*** Processing Parameters ***
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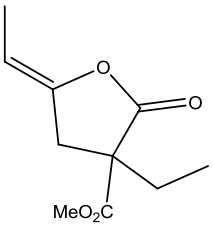
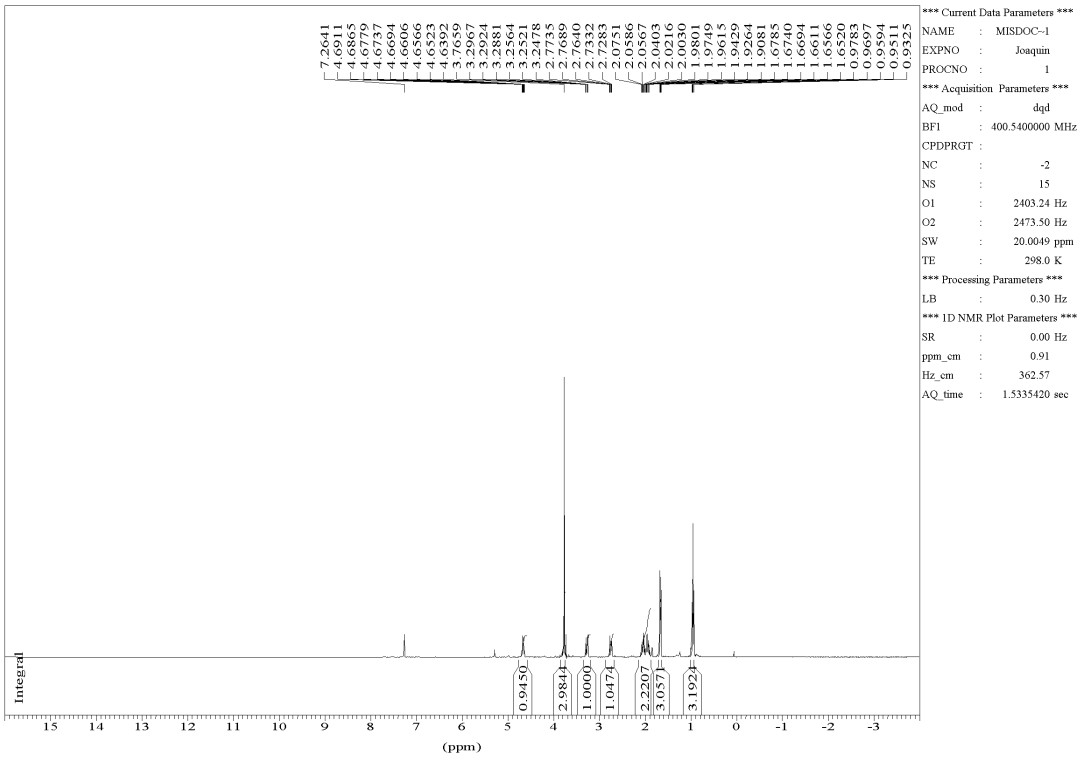
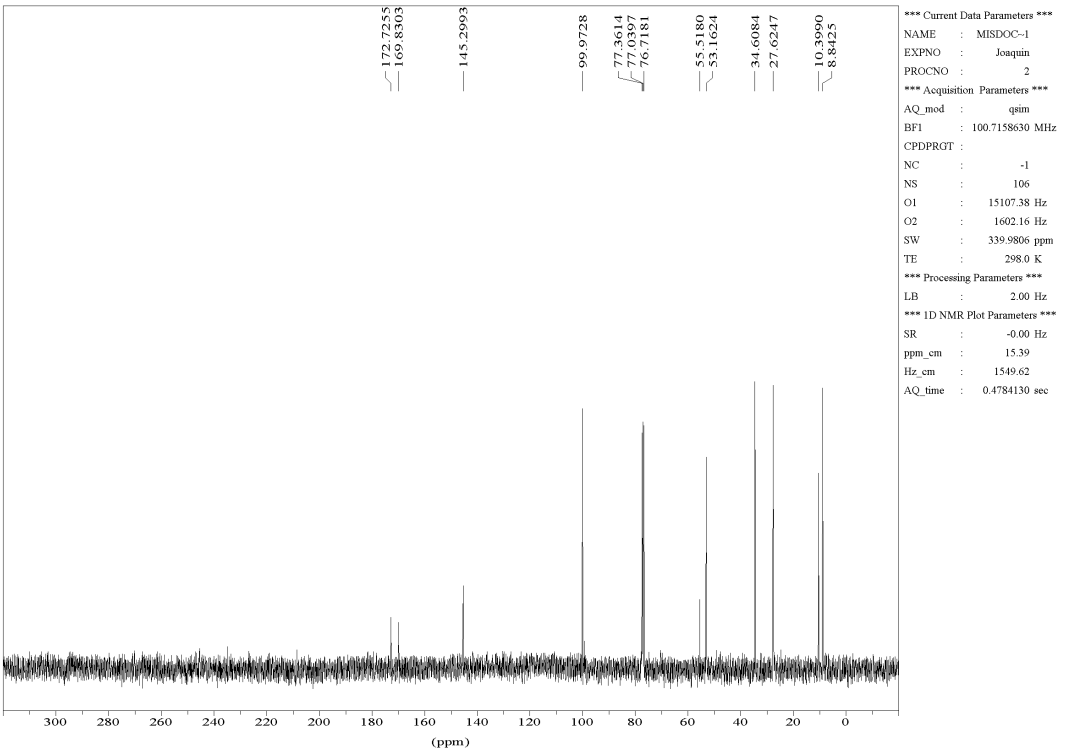
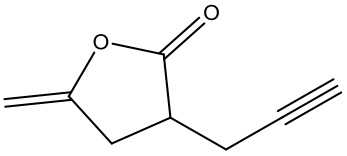
(*Z*)-methyl 3-ethyl-5-ethylidene-2-oxotetrahydrofuran-3-carboxylate (5h)

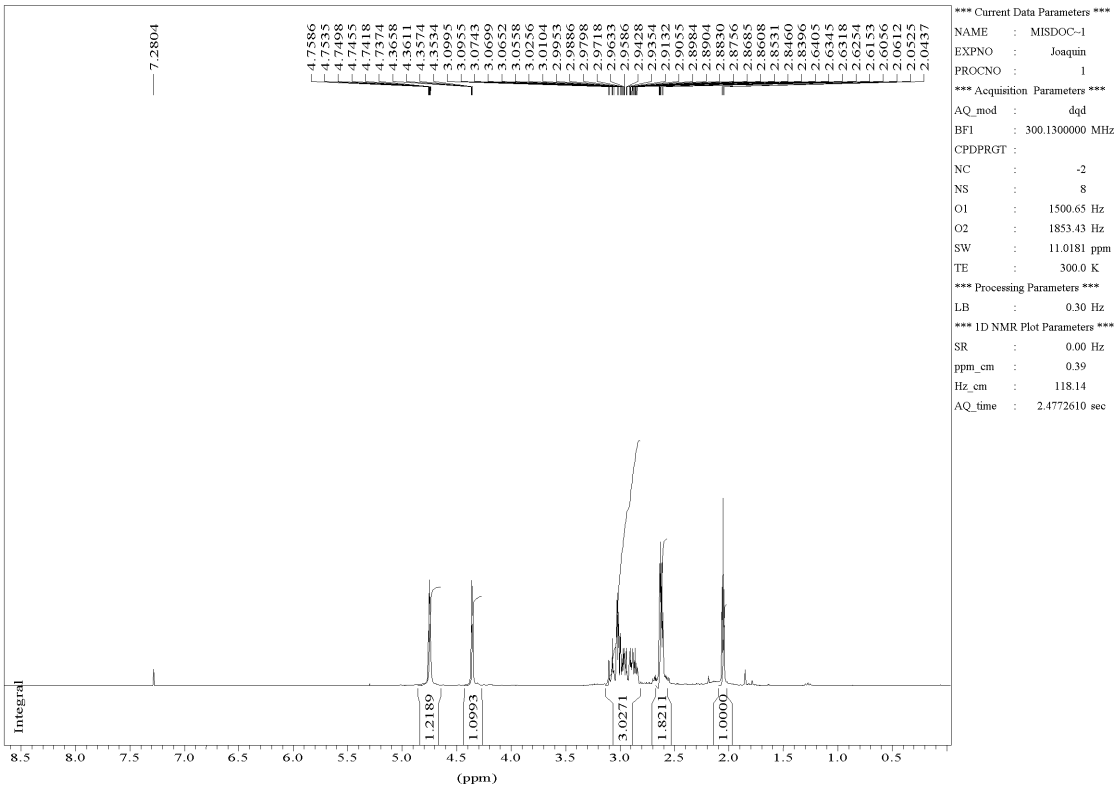






5-methylene-3-(prop-2-ynyl)dihydrofuran-2(*3H*)-one (7a)





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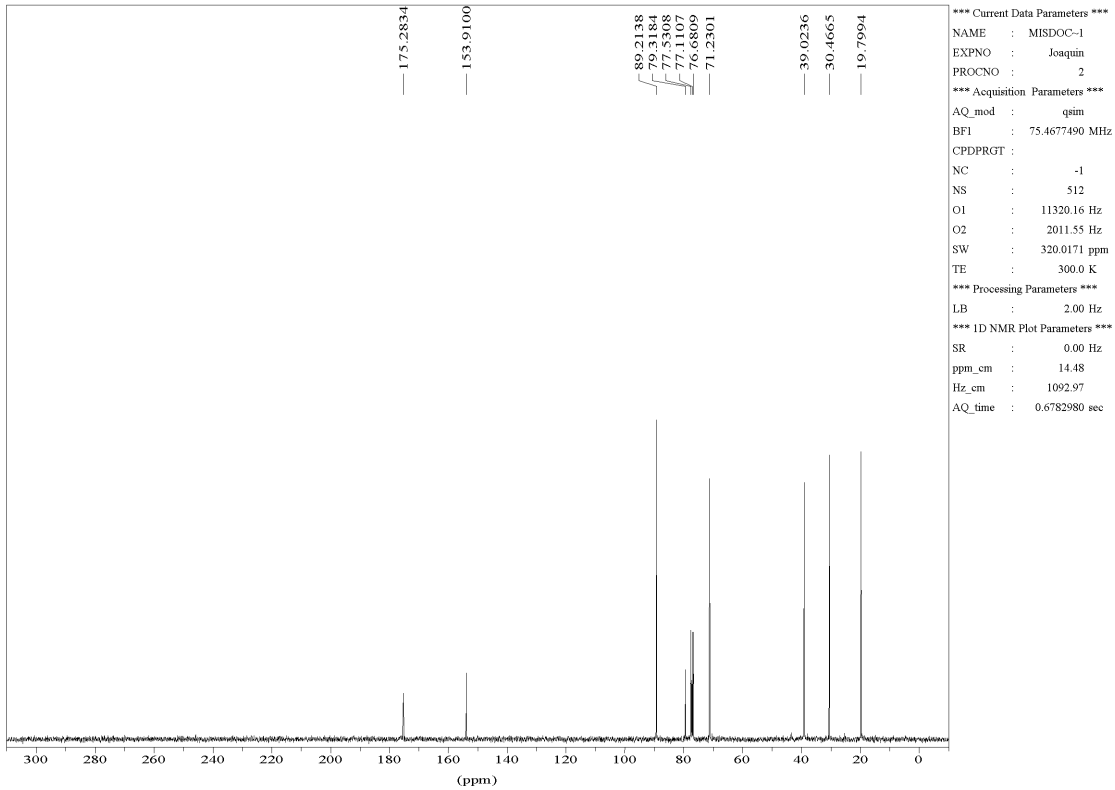

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O2 : 2011.55 Hz
SW : 320.0171 ppm
TE : 300.0 K
*** Processing Parameters ***
LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
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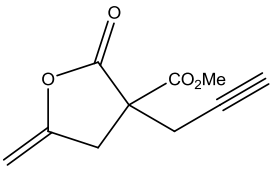
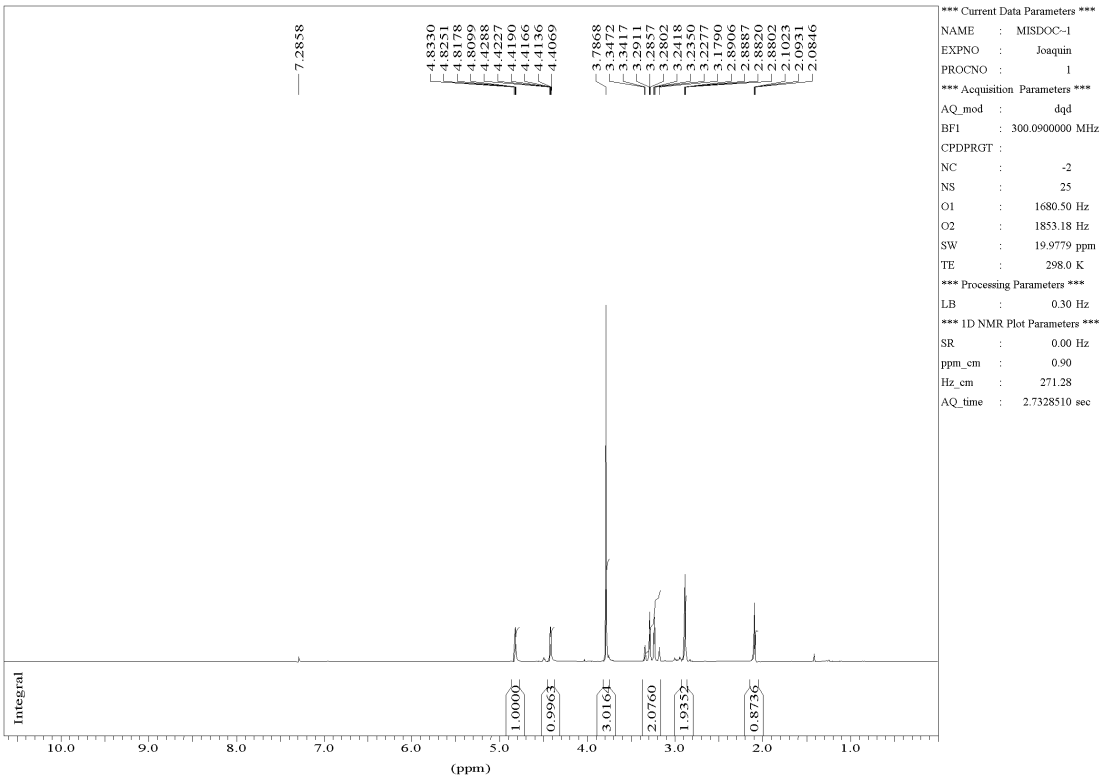
methyl 5-methylene-2-oxo-3-(prop-2-ynyl)tetrahydrofuran-3-carboxylate (7b)





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NS : 25
O1 : 1680.50 Hz
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SW : 19.9779 ppm
TE : 298.0 K
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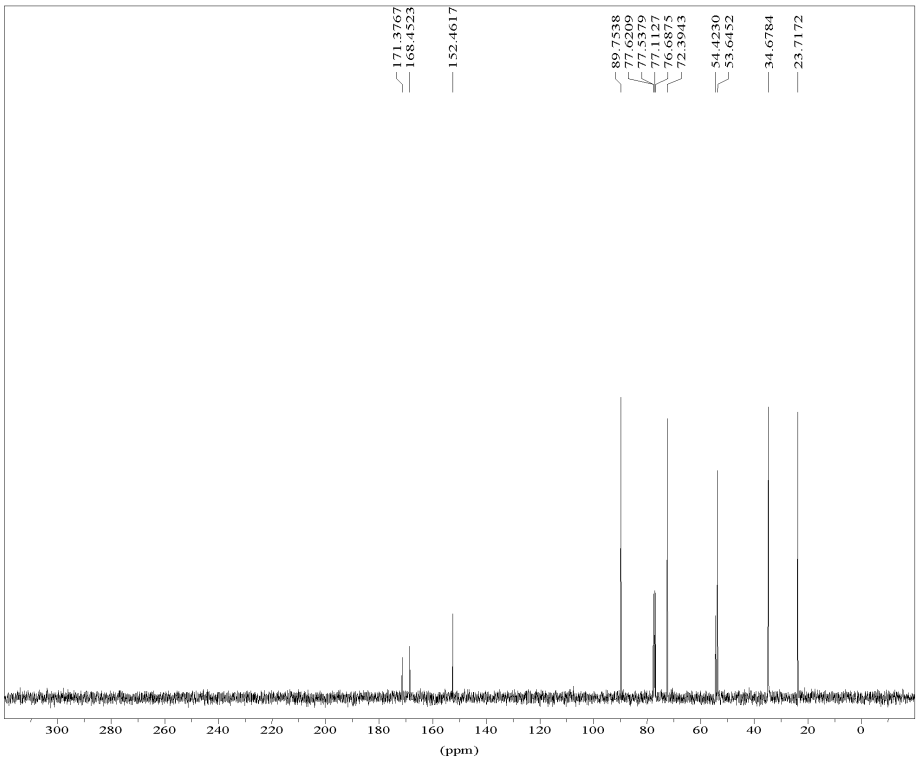

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SW : 339.7557 ppm
TE : 298.0 K
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*** 1D NMR Plot Parameters ***
SR : -0.00 Hz
ppm_cm : 15.38
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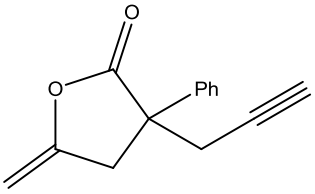
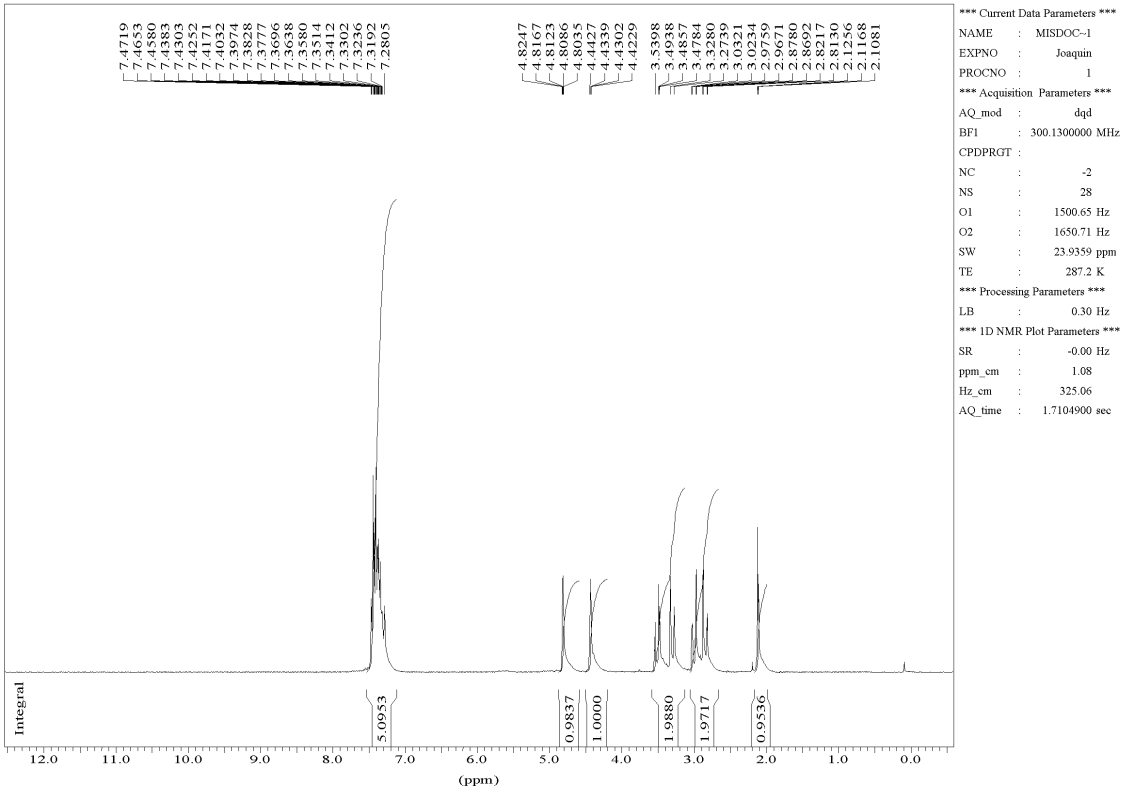
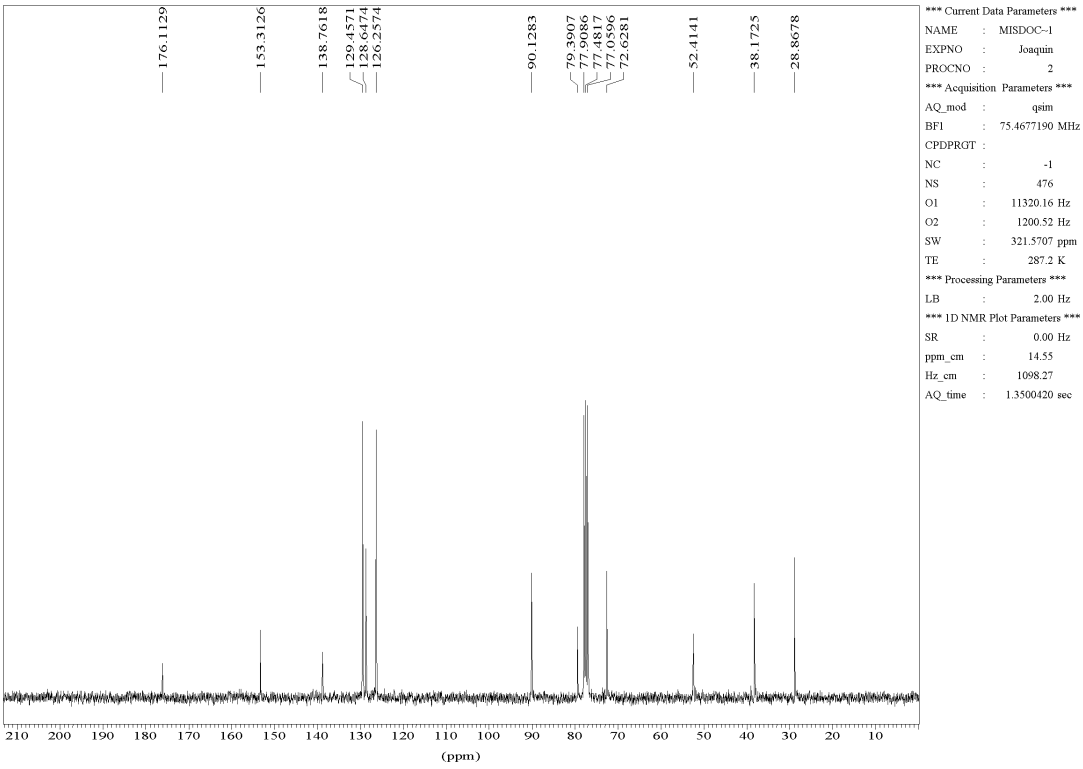
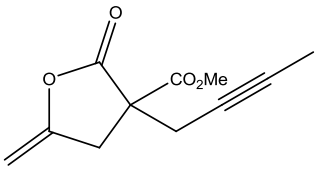
5-methylene-3-phenyl-3-(prop-2-ynyl)dihydrofuran-2(3H)-one (7c)

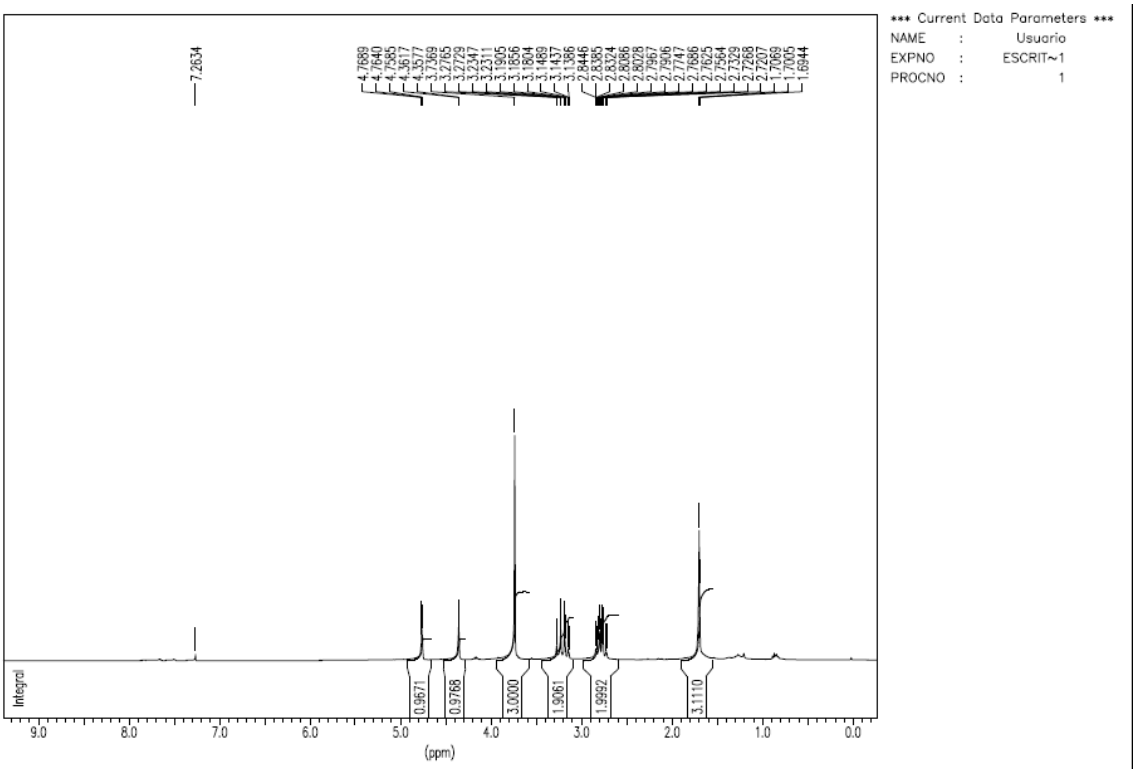


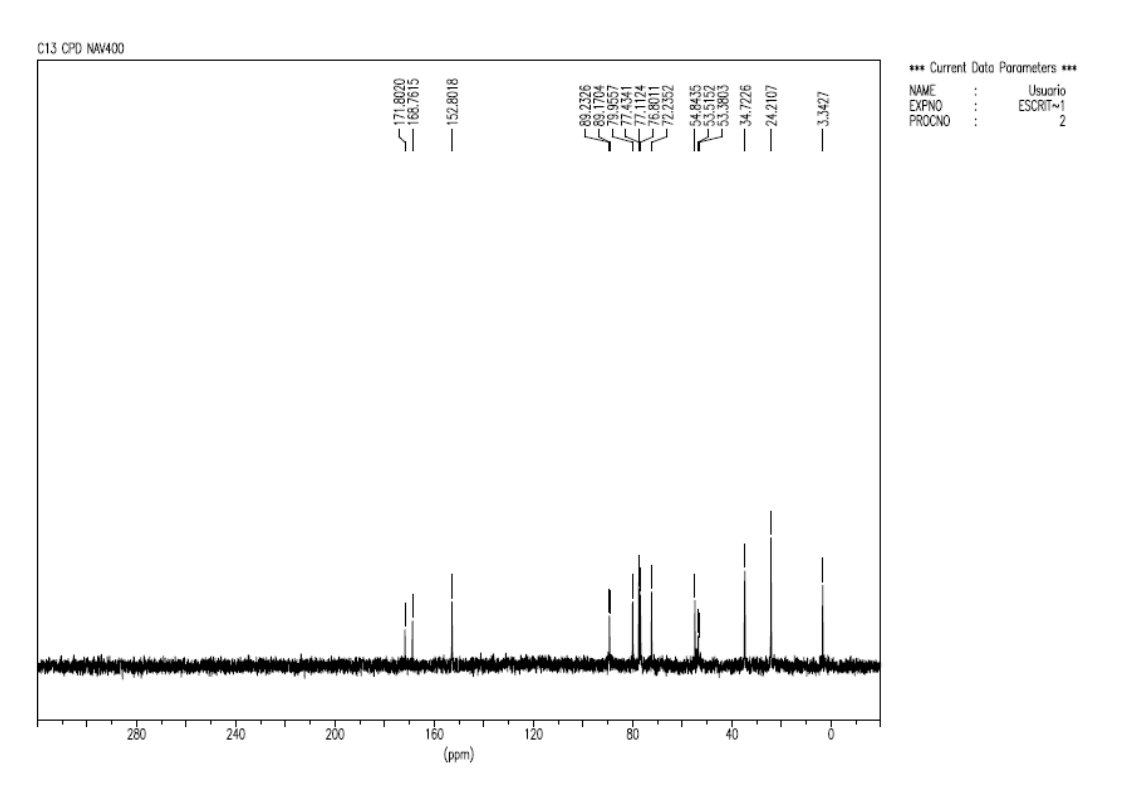




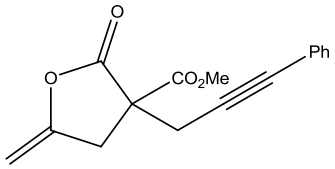
methyl 3-(but-2-ynyl)-5-methylene-2-oxotetrahydrofuran-3-carboxylate (7d)

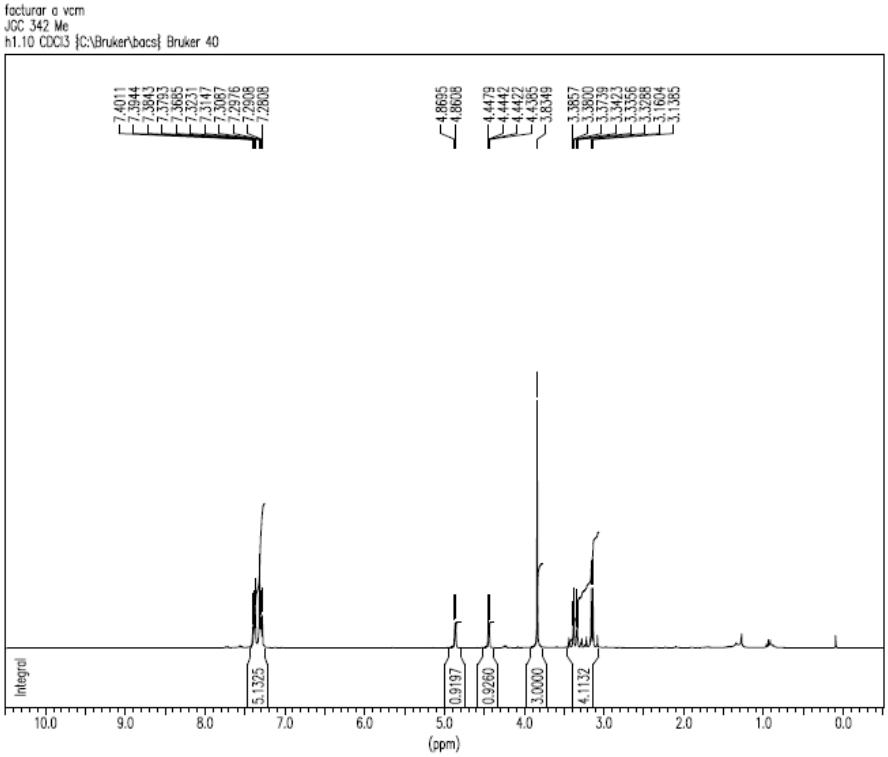


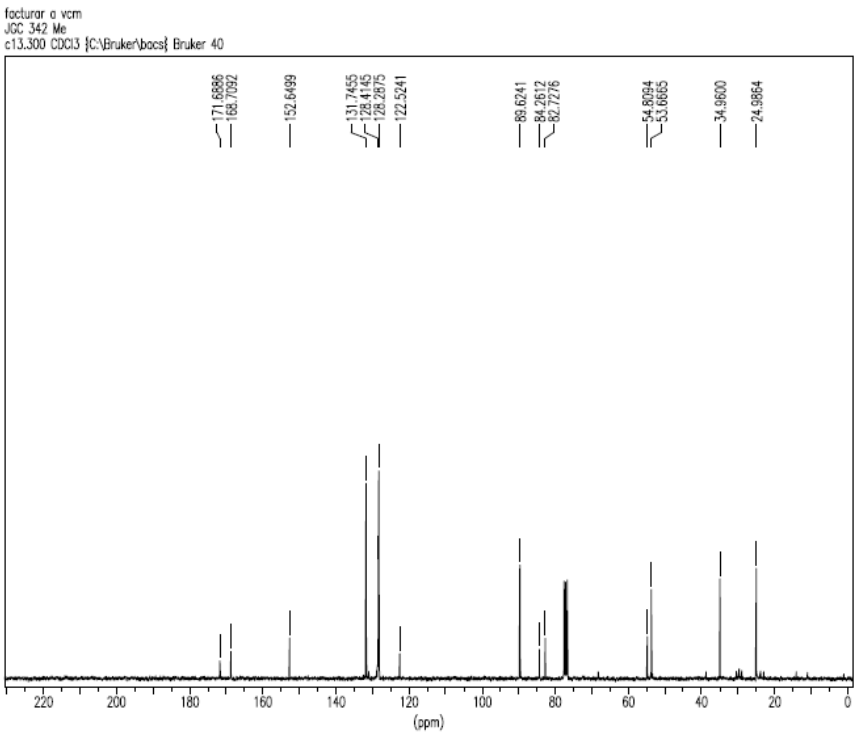




methyl 5-methylene-2-oxo-3-(3-phenylprop-2-ynyl)tetrahydrofuran-3-carboxylate (7e)

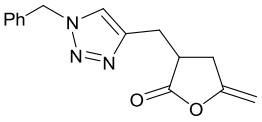


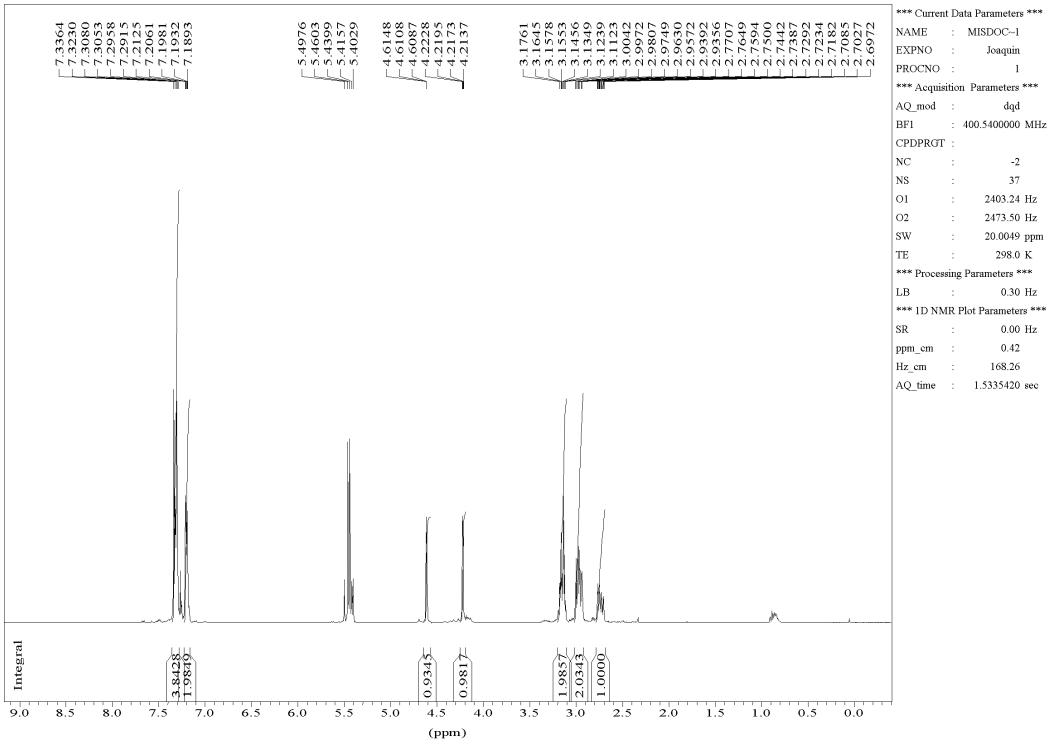


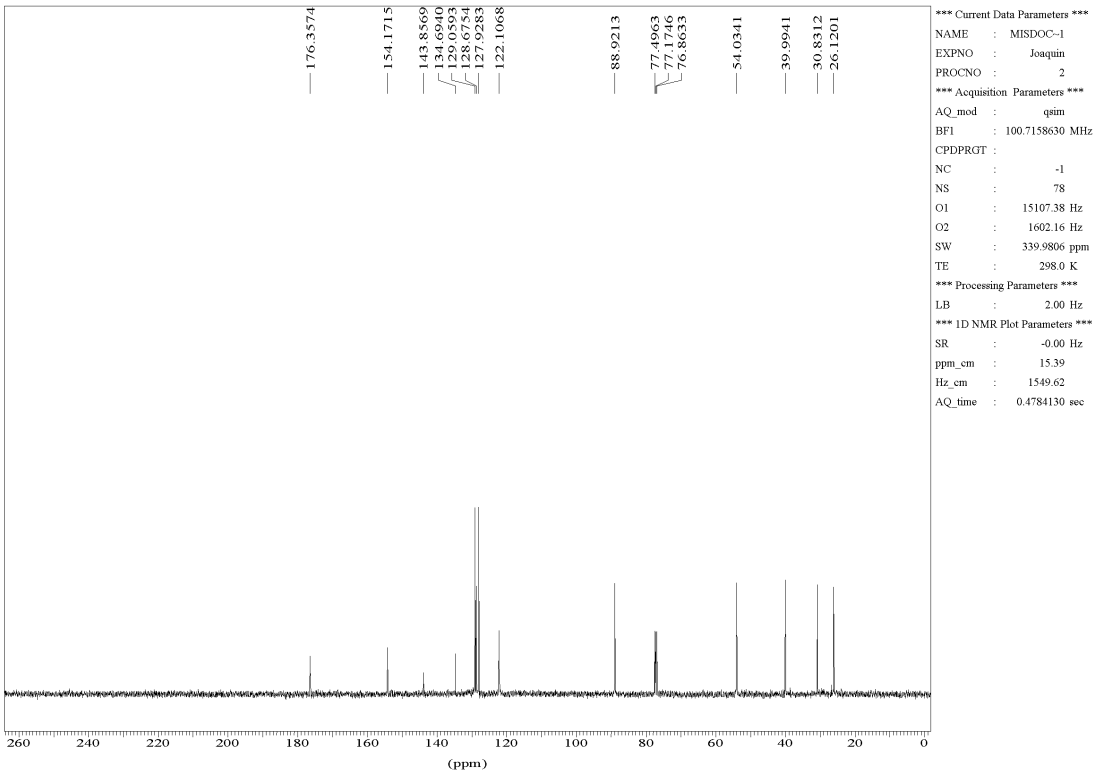


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of enol-lactones 5a-h and 7a-e

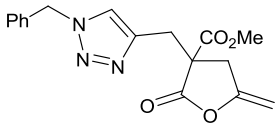
3-((1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylenedihydrofuran-2(*3H*)-one (9a)

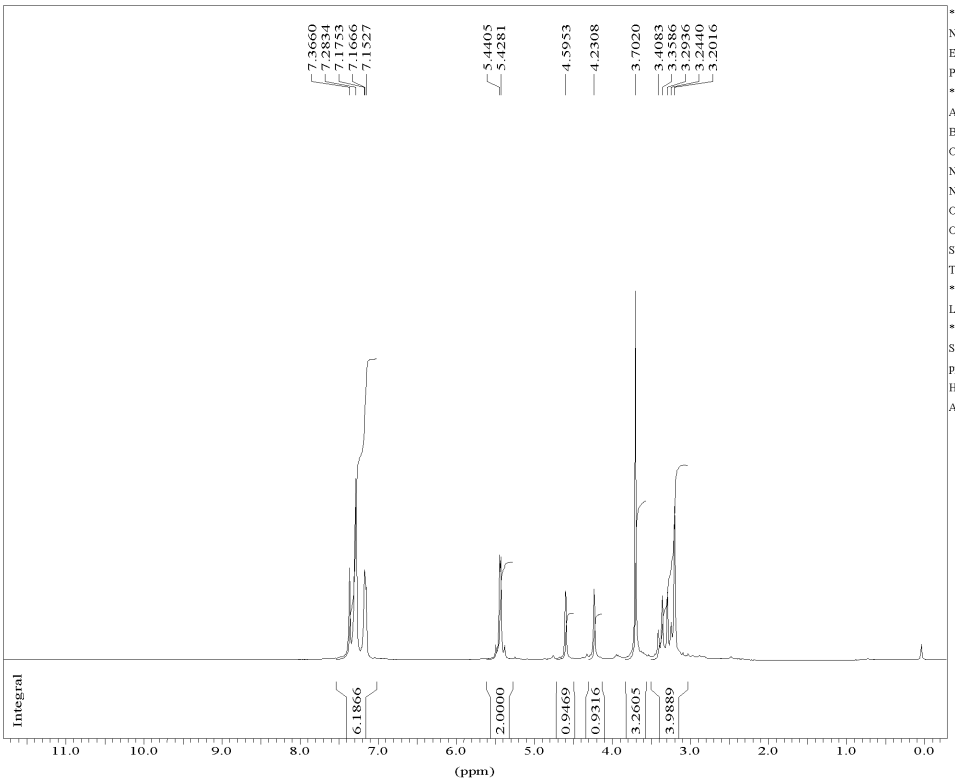






methyl 3-((1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylene-2-oxotetrahydrofuran-3-carboxylate (9b)





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PROCNO : 1
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O2 : 1650.71 Hz
SW : 23.9359 ppm
TE : 290.2 K
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LB : 0.30 Hz
*** 1D NMR Plot Parameters ***
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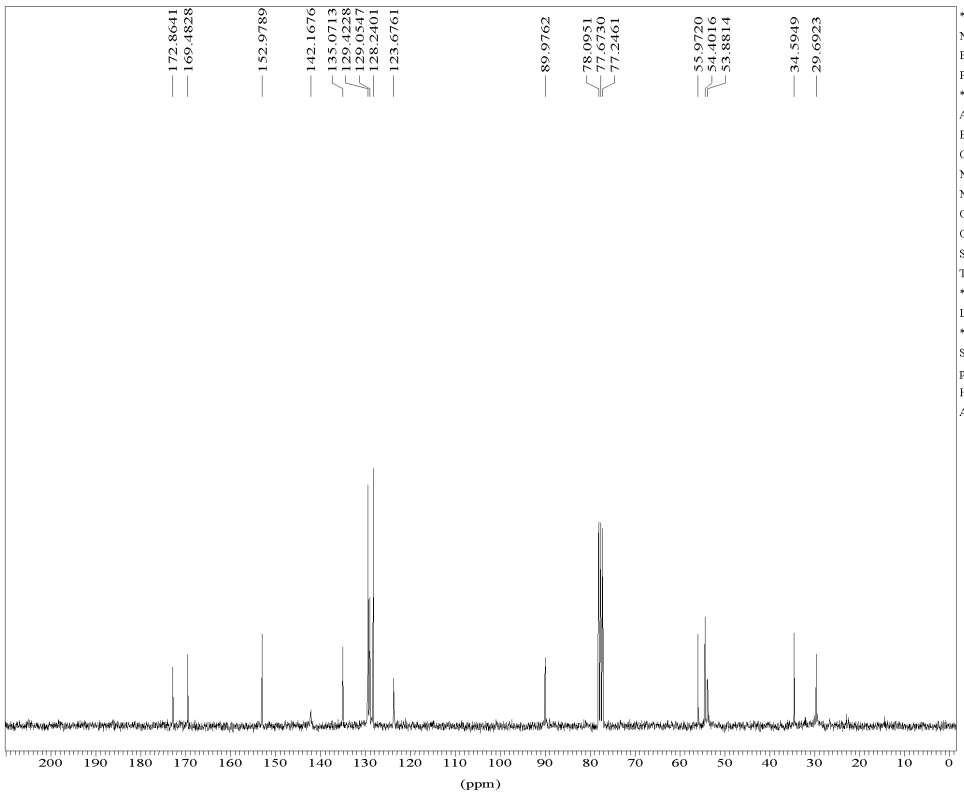

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LB : 2.00 Hz
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz
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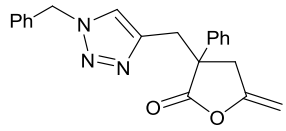
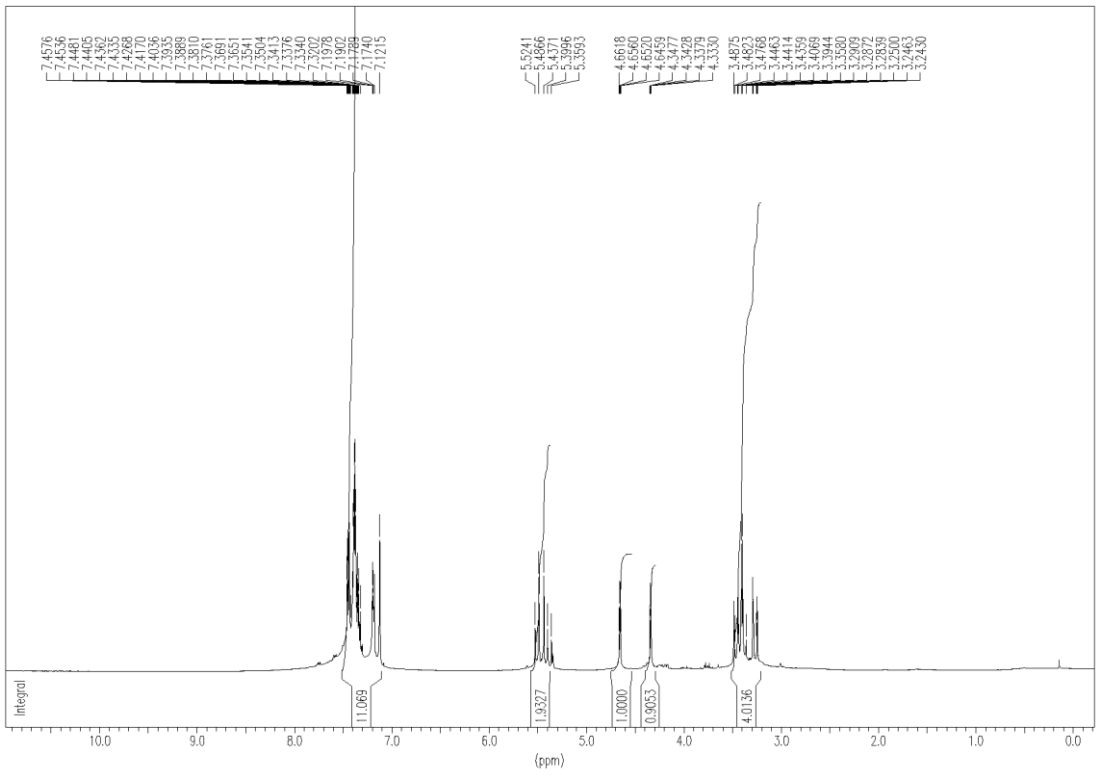
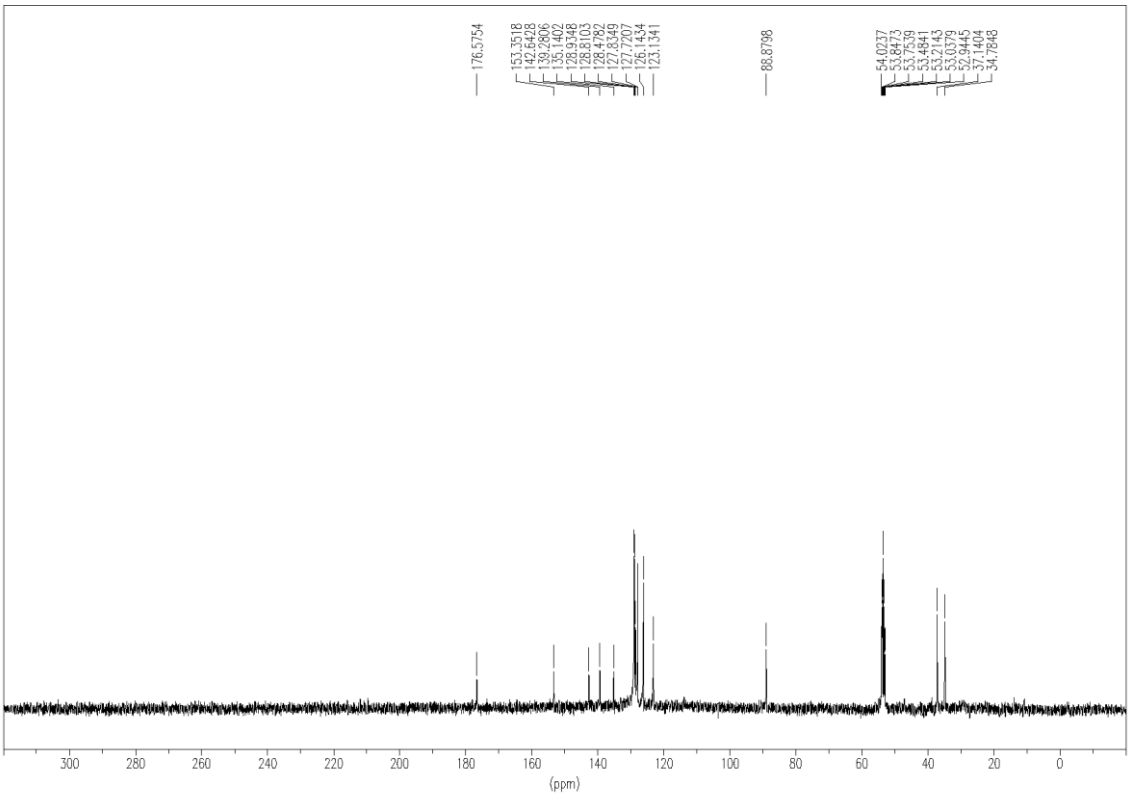
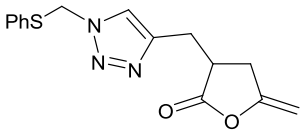
3-((1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylene-3-phenyldihydrofuran-2(*3H*)-one (9c)

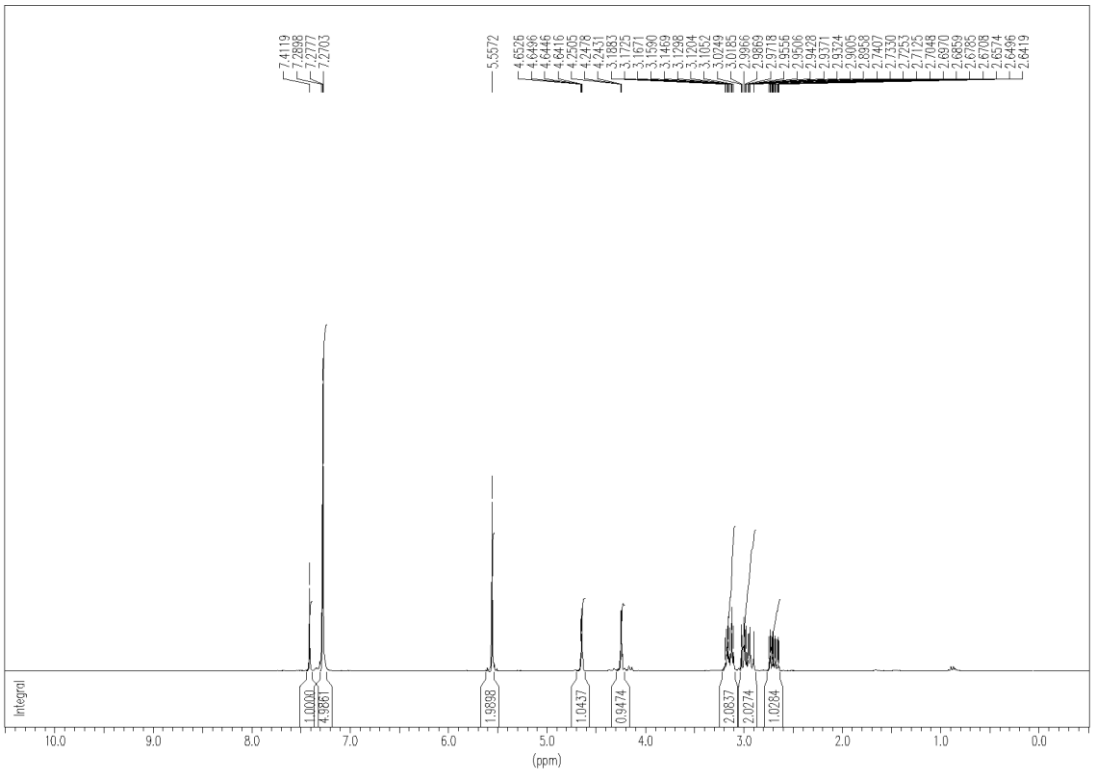


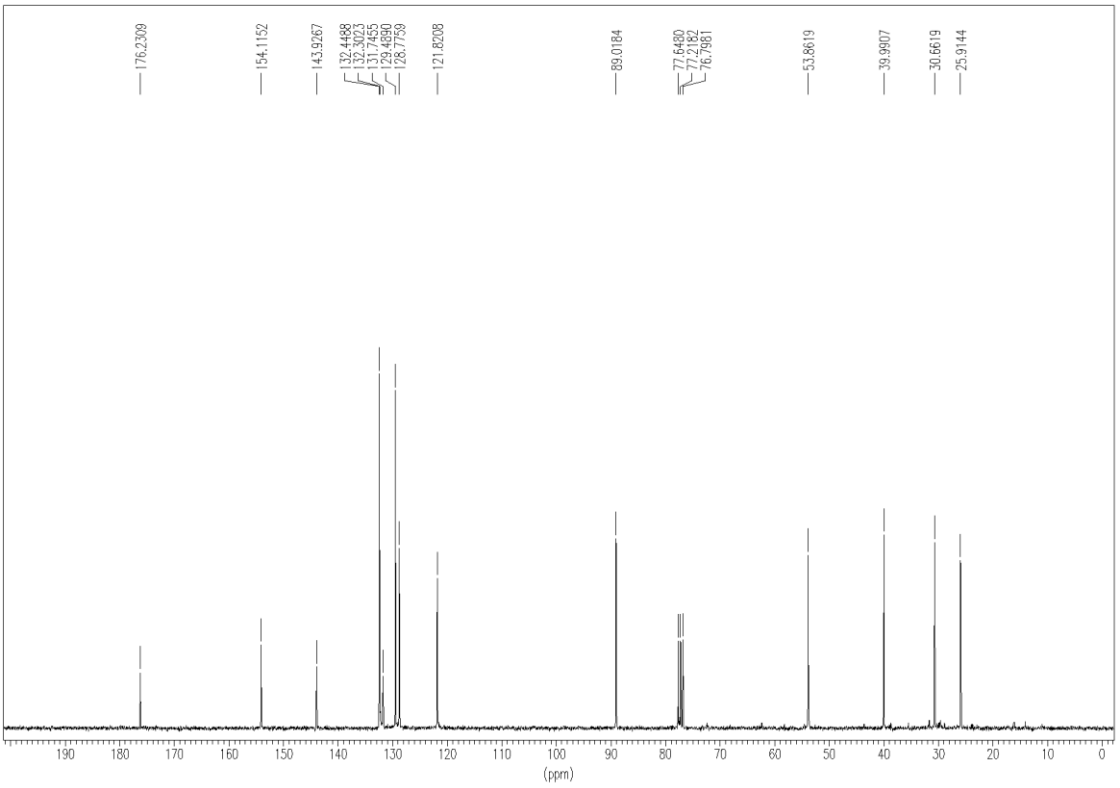




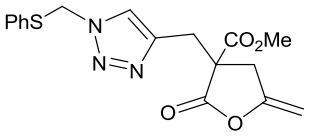
5-methylene-3-((1-(phenylthiomethyl)-*1H*-1,2,3-triazol-4-yl)methyl)dihydrofuran-2(*3H*)-one (9d)

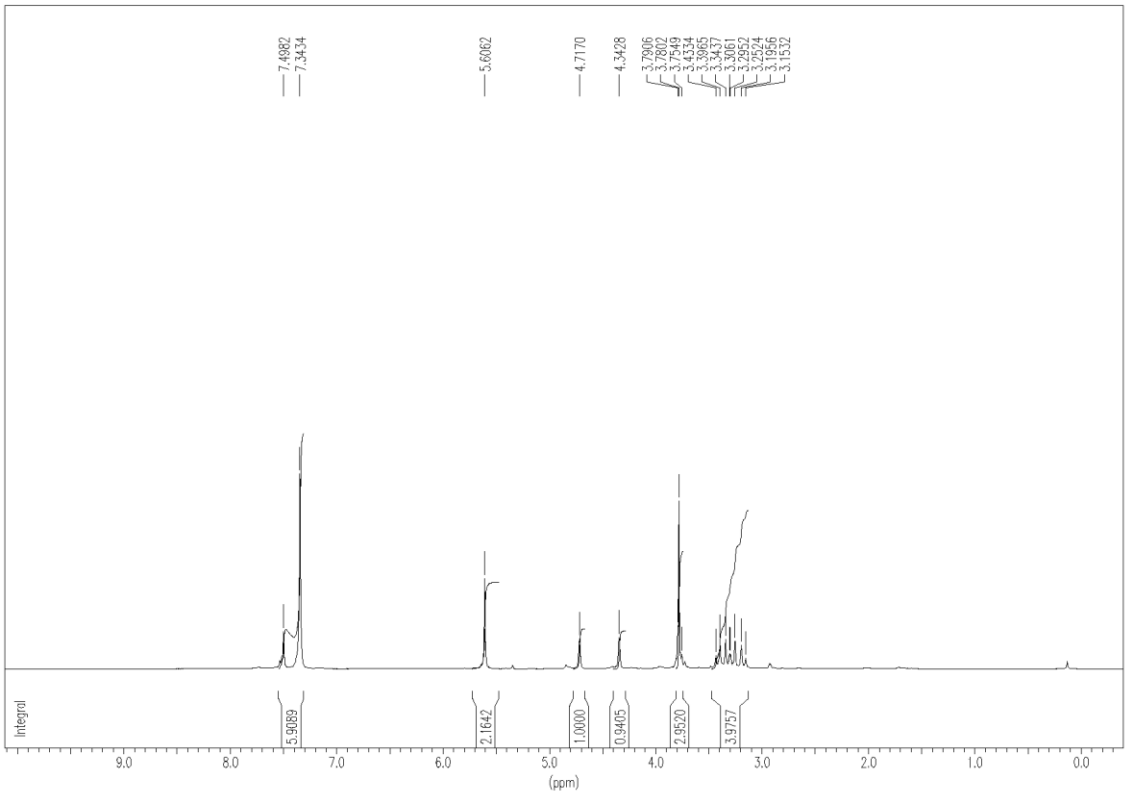


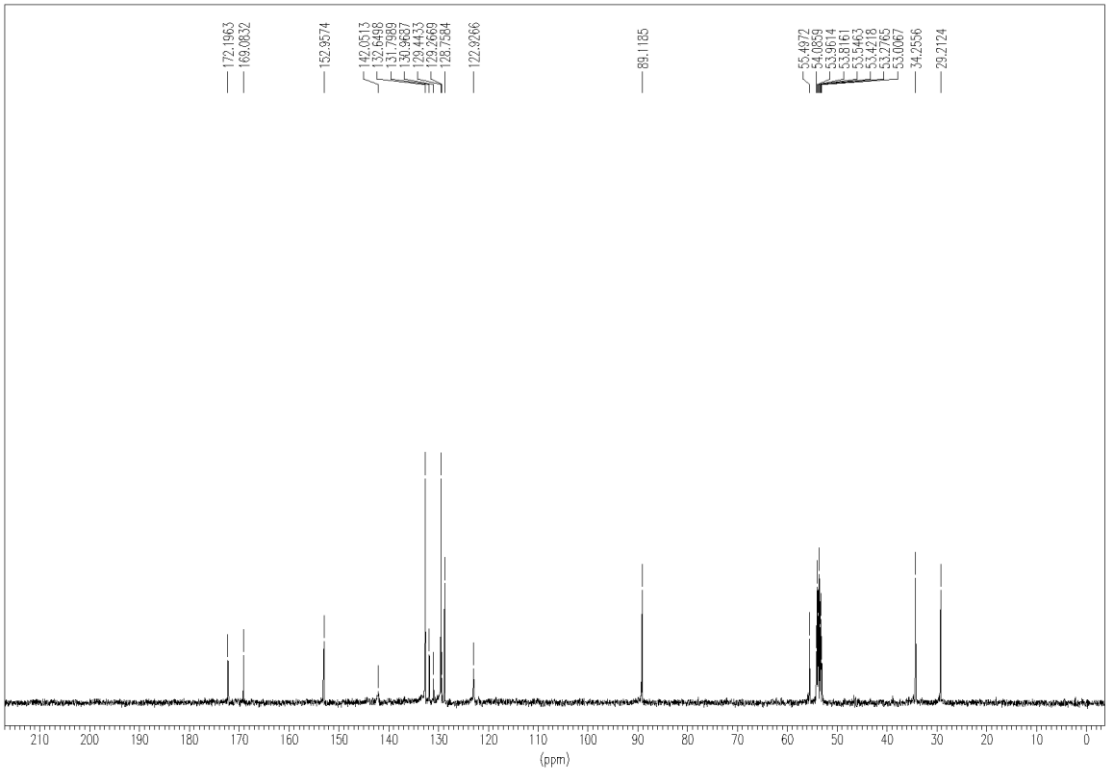




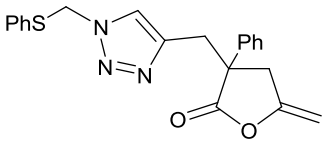
methyl 5-methylene-2-oxo-3-((1-(phenylthiomethyl)-*1H*-1,2,3-triazol-4-yl)methyl)tetrahydrofuran-3-carboxylate (9e)

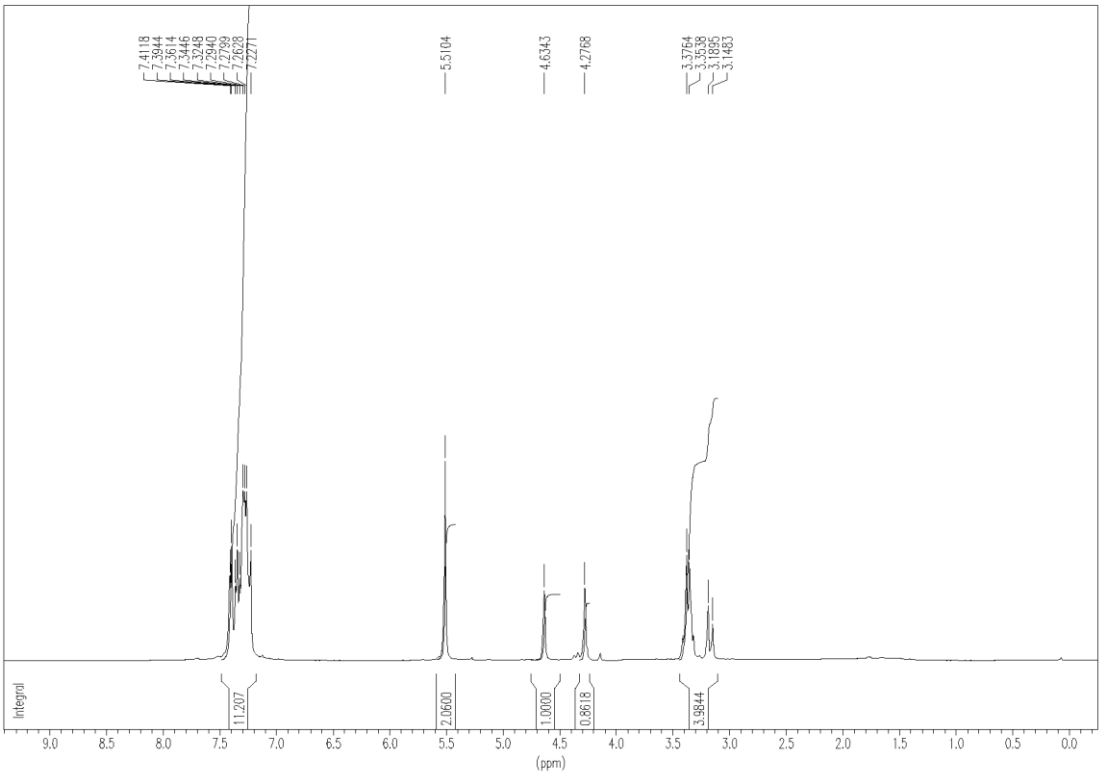


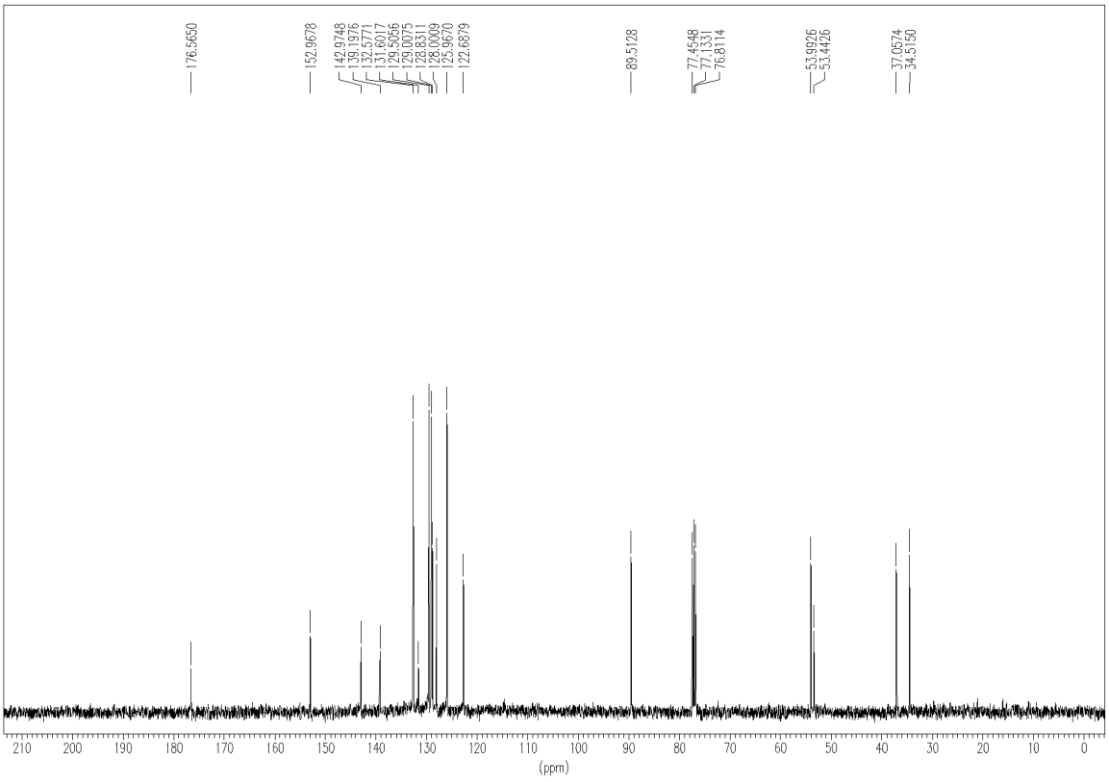




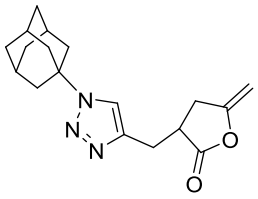
5-methylene-3-phenyl-3-((1-(phenylthiomethyl)-*1H*-1,2,3-triazol-4-yl)methyl) dihydrofuran-2(*3H*)-one (9f)

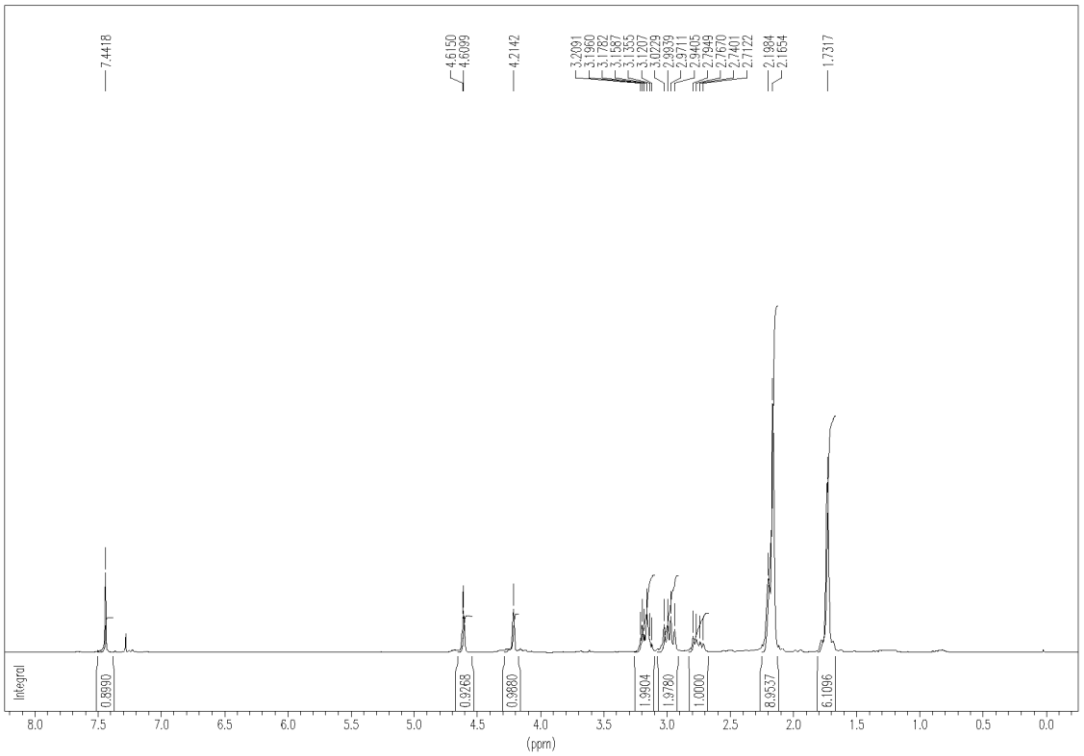


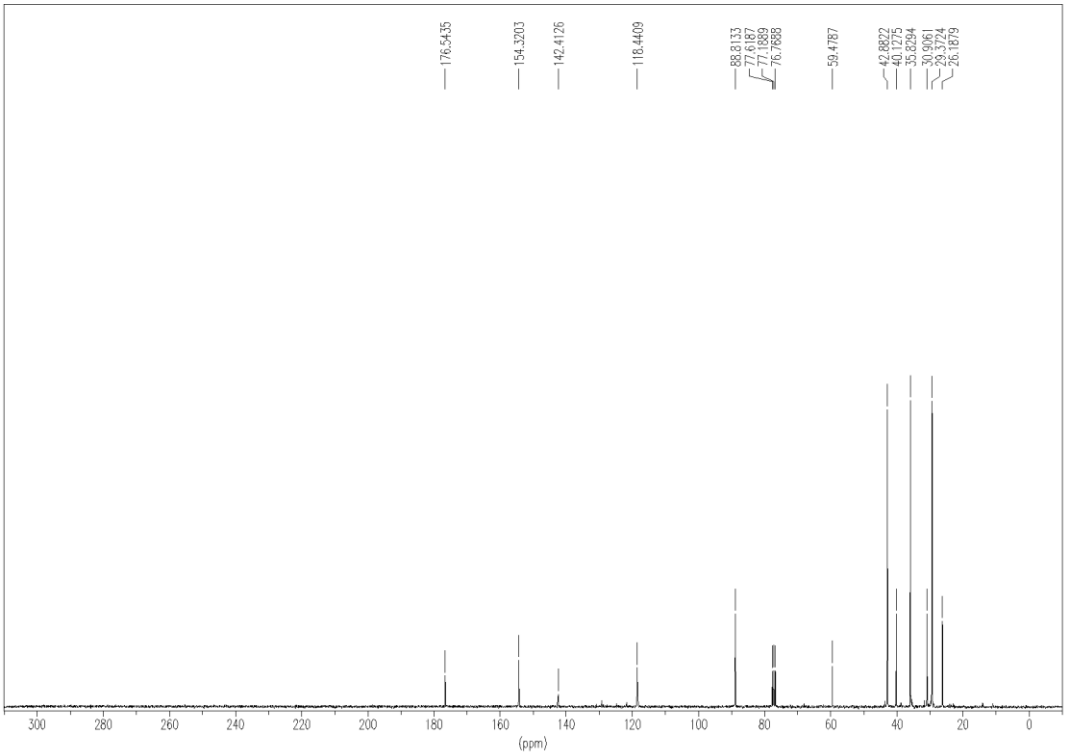




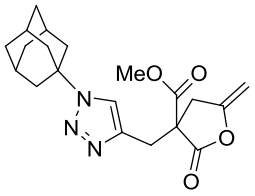
3-((1-adamantyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylenedihydrofuran-2(*3H*)-one (9g)

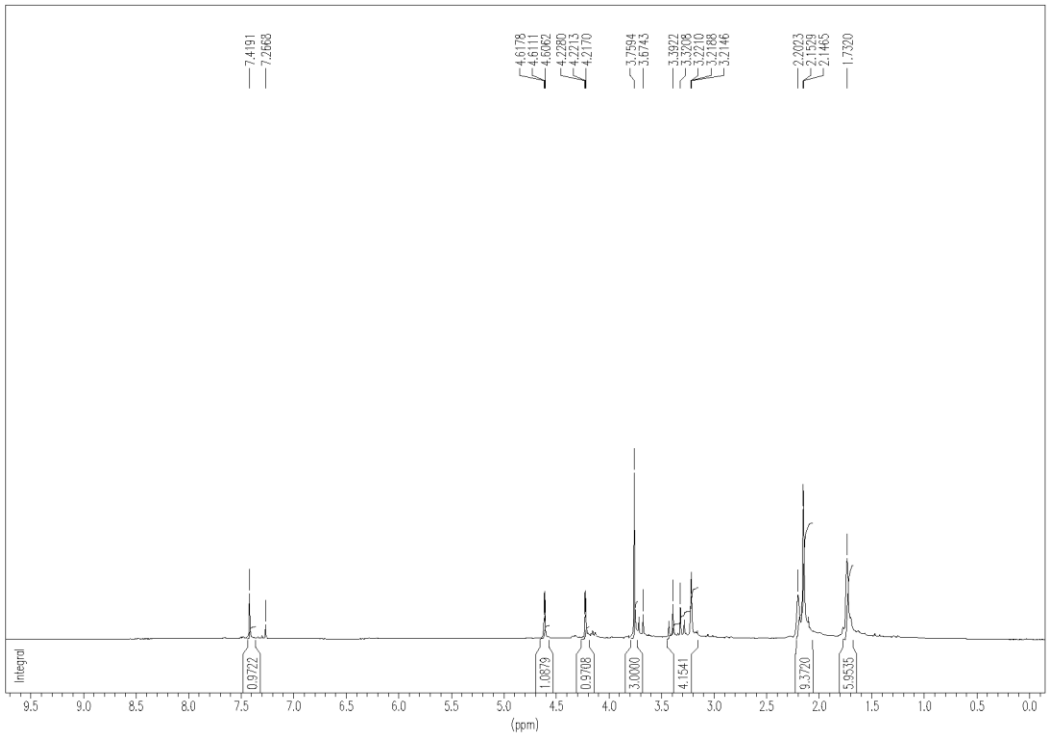


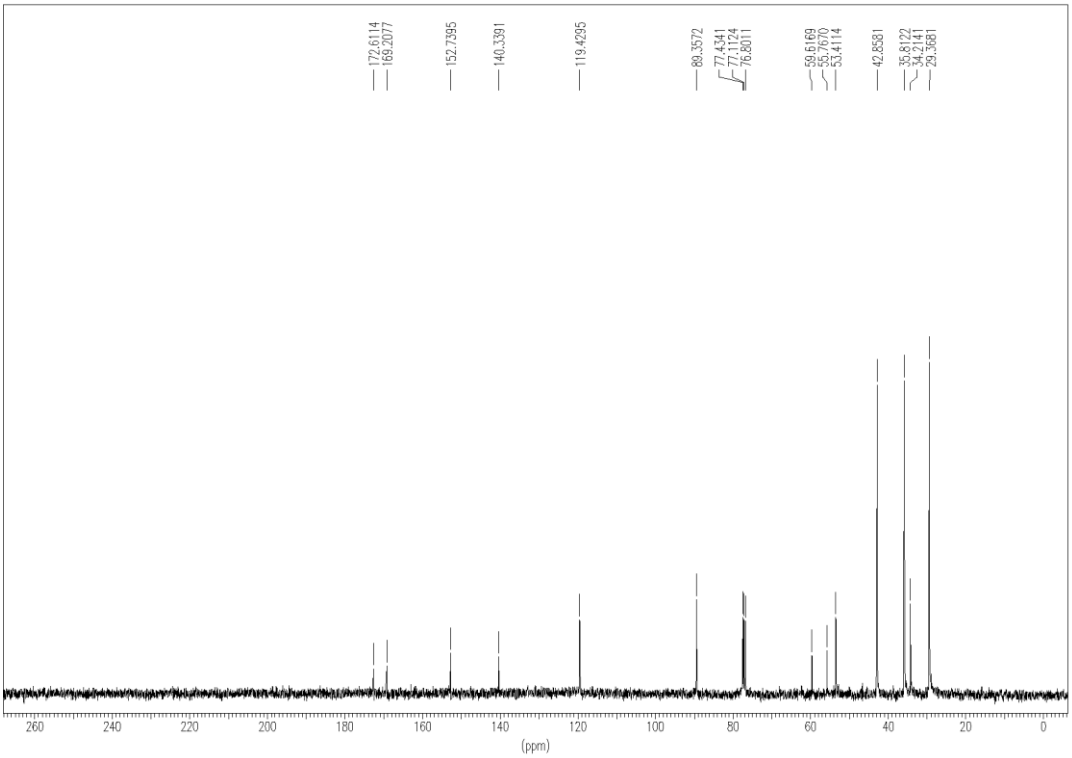




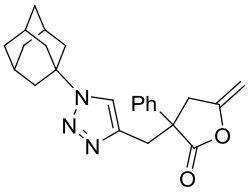
methyl 3-((1-adamantyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylene-2-oxotetrahydrofuran-3-carboxylate (9h)

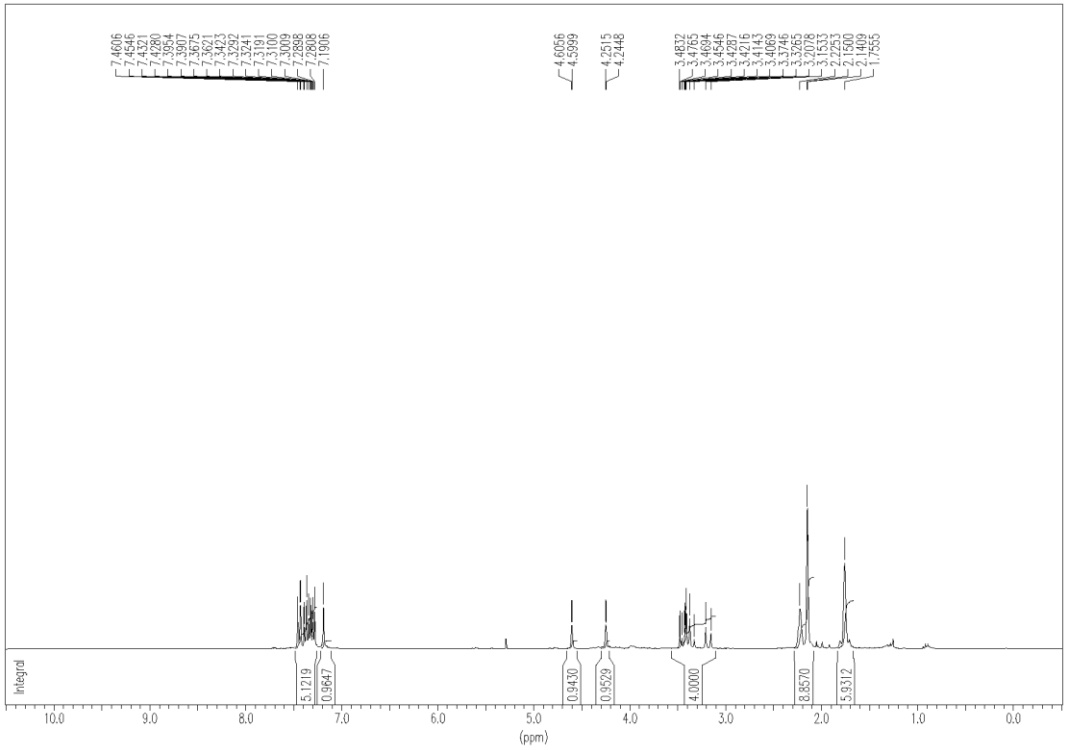


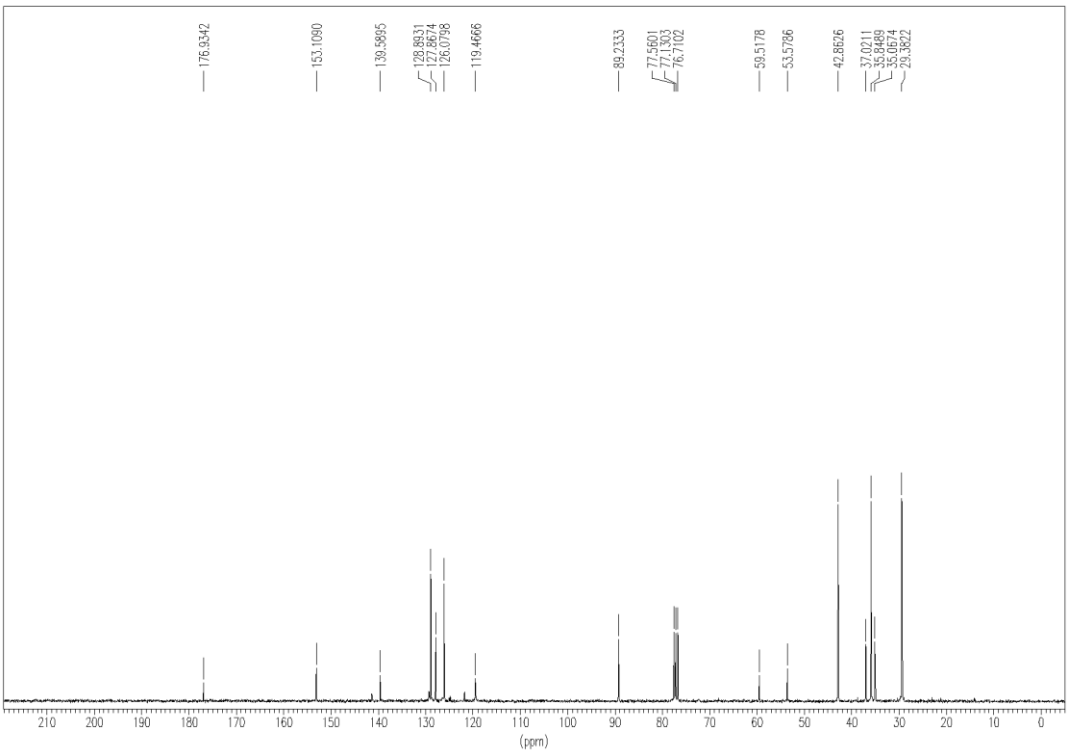




3-((1-adamantyl-*1H*-1,2,3-triazol-4-yl)methyl)-5-methylene-3-phenyldihydrofuran-2(*3H*)-one (9i)







Crystal data and structure refine for compounds 3 and 9b

Crystals suitable for X-ray diffraction analysis were obtained by: *i*) slow difusion of diethyl ether into a saturated solution of complex **3** in dichloromethane and, *ii*) slow evaporation of a saturated solution of the bicyclic derivative **9b** in toluene. The most relevant crystal and refinement data are collected in Table E.S.I.-1.

For **3** diffraction data were recorded on a Nonius KappaCCD single crystal diffractometer, using Mo-Kα radiation (λ= 0.71073 Å). Images were collected at a 40 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and 35 s exposure time per frame. Data collection strategy was calculated with the program Collect[1] (Bruker, **2004**). Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack[2] (Otwinowski & Minor, **1997**). A semi-empirical absorption correction was applied using the program SORTAV[3] (Blessing, **1995**).

For **9b** data collection was performed on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-Kα radiation (λ= 1.5418 Å). Images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and variable exposure time per image (2 - 8 s). Data collection strategy was calculated with the program CrysAlis Pro CCD.[4] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[4] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[4]

The software package WINGX[5] was used for space group determination, structure solution and refinement. The structure for the complexes were solved by Patterson interpretation and phase expansion using SIR92.[6]

Isotropic least-squares refinement on F^2 using SHELXL97[7] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined, (except the atoms of the molecule of ether, this disordered group was located from different Fourier maps and isotropically refined). The coordinates H atoms were geometrically located and their coordinates were refined riding on their parent atoms.

The function minimized was $([\Sigma wF_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are collected in Table 1) with $\sigma(F_o^2)$ from counting statistics and $P = (Max(F_o^2, 0) + 2F_c^2)/3$.

Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[8] Geometrical calculations were made with PARST (Nardelli, 1983).[9] The crystallographic plots were made with PLATON.[10]

Table ESI-1 Crystal data and structure refine for compound **3** and **9b**

	3	**9b**
Empirical formula	$C_{25}H_{56}Cl_6N_8O_5P_4Pd_2S_2$	$C_{17}H_{17}N_3O_4$
Formula weight	1162.28	327.34
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	1.54180
Crystal system	monoclinic	monoclinic
Space group	P $21/_c$	P $21/_n$
a/Å; α/°	12.8415(5); 90	11.6784(2); 90
b/Å; β/°	13.0797(5); 109.006(1)°	5.6853(1); 96.479(1)
c/Å; γ/	28.1381(12); 90	23.4754(3); 90
Z	4	4
Volume/$Å^3$	4468.5(3)	1548.70(4)
Calculated density/Mg m^{-3}	1.728	1.404
μ/mm^{-1}	1.444	0.846
F(000)	2352	688
Crystal size/mm	0.17 x 0.17 x 0.05	0.146 x 0.078 x 0.062
θ range/°	1.53 to 25.45	3.79 to 74.48
Index ranges	$-15 \le h \le 15$ $-15 \le k \le 0$ $-34 \le l \le 14$	-14<=h<=13 -6<=k<=6 -29<=l<=23
No. of reflns. collected	31922	10719
No. of unique reflns.	8114 [(R(int) = 0.051]	3079 [R(int) = 0.0487]
Completeness to θ_{max}	98.1	97.4
No. of parameters/restraints	414/5	218/0
Goodness-of-fit on F^2	0.946	1.045
Weight function (a, b)	0.0813, 0	0.0545, 0.3672
R_1 $[I > 2\sigma(I)]^a$	0.0459	0.0389
wR_2 $[I > 2\sigma(I)]^a$	0.1290	0.0984
Largest diff. peak and hole/e $Å^{-3}$	1.870 and -1.208	0.180 and -0.292

[a] $R_1 == \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

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(1) Bruker, **2004**. *Collect* data collection software. Bruker AXS, Delft, The Netherlands.

(2) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(3) SORTAV. Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33.

(4) *CrysAlis^{Pro} CCD*, *CrysAlis^{Pro} RED*. Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, **2008**.

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(7) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**.

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(9) PARST . Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

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