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ELECTRONIC SUPPORTING INFORMATION

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# PHOTOCHEMICAL REACTIONS OF PROP-2-ENYL AND PROP-2-YNYL SUBSTITUTED 4-AMINOMETHYL- AND 4-OXYMETHYL-2(5*H*)-FURANONES

**Diego A. Fort,[a,b] Thomas J. Woltering,[b] André M. Alker,[c] and Thorsten Bach[a]***

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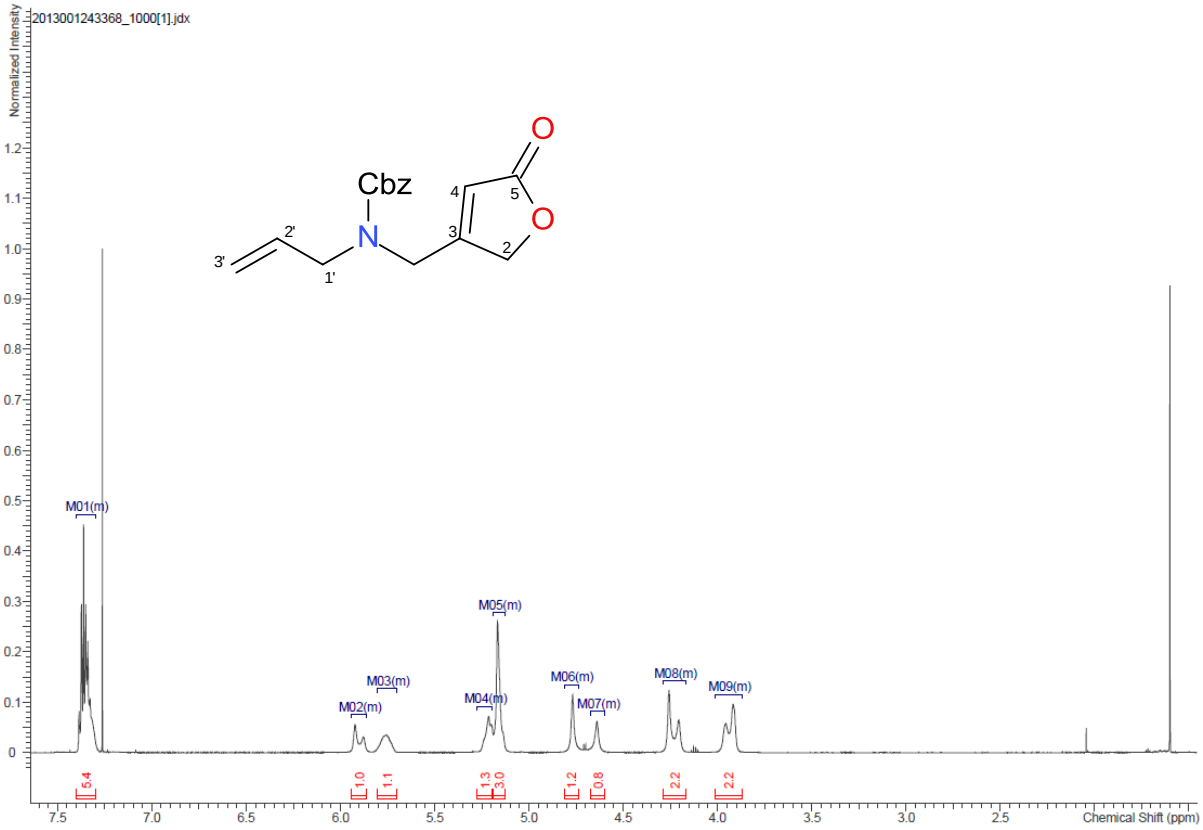
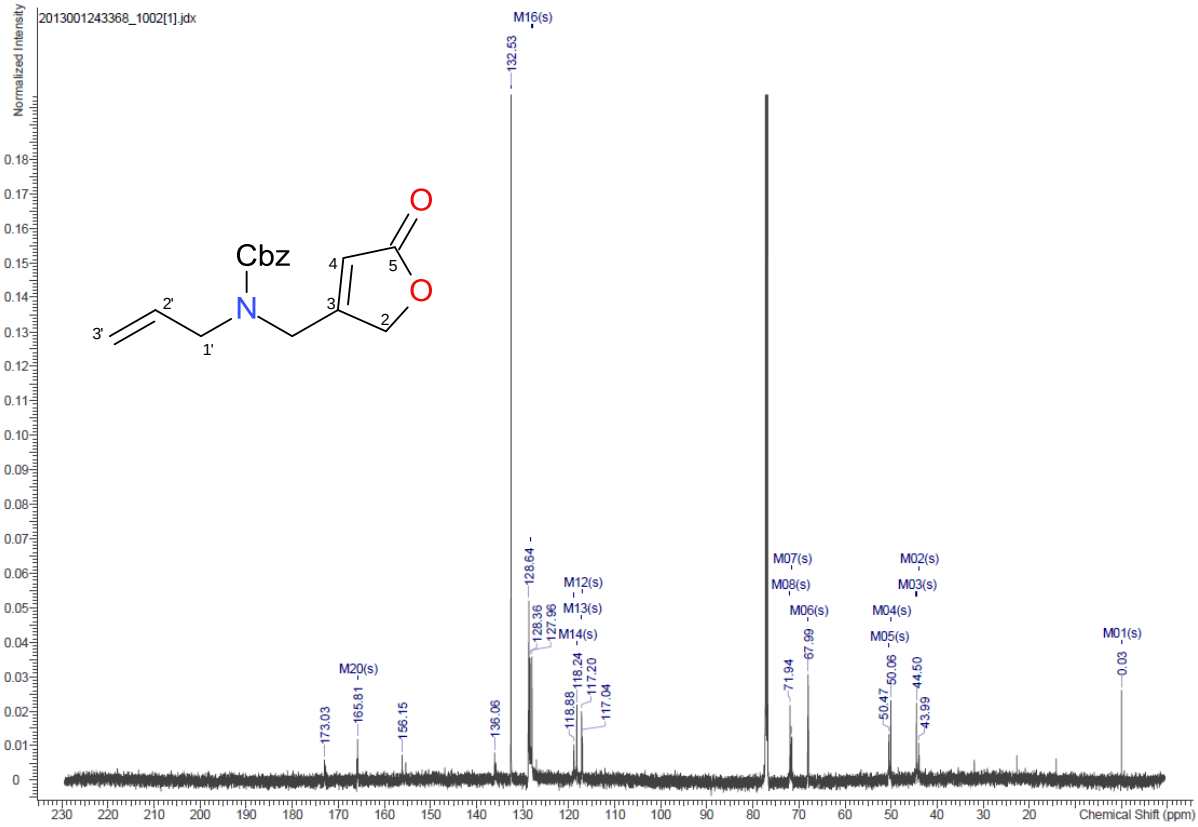
[b] Discovery Chemistry, PCMM, F. Hoffmann-La Roche Ltd., Grenzacherstrasse, CH-4070 Basel, Switzerland

[c] Biostructure Section, Molecular Design & Chemical Biology, Pharmaceuticals Division, F. Hoffmann-La Roche Ltd., Grenzacherstrasse, CH-4070 Basel, Switzerland

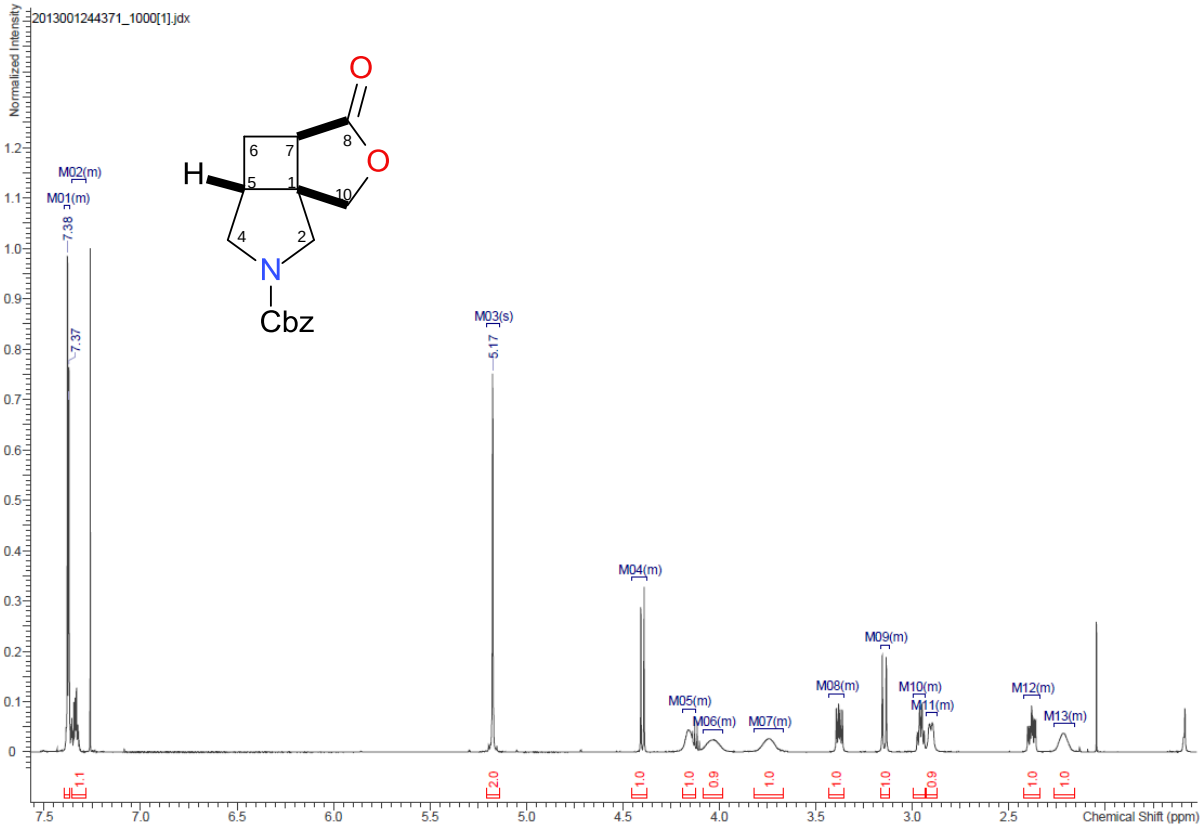
Table of Contents:

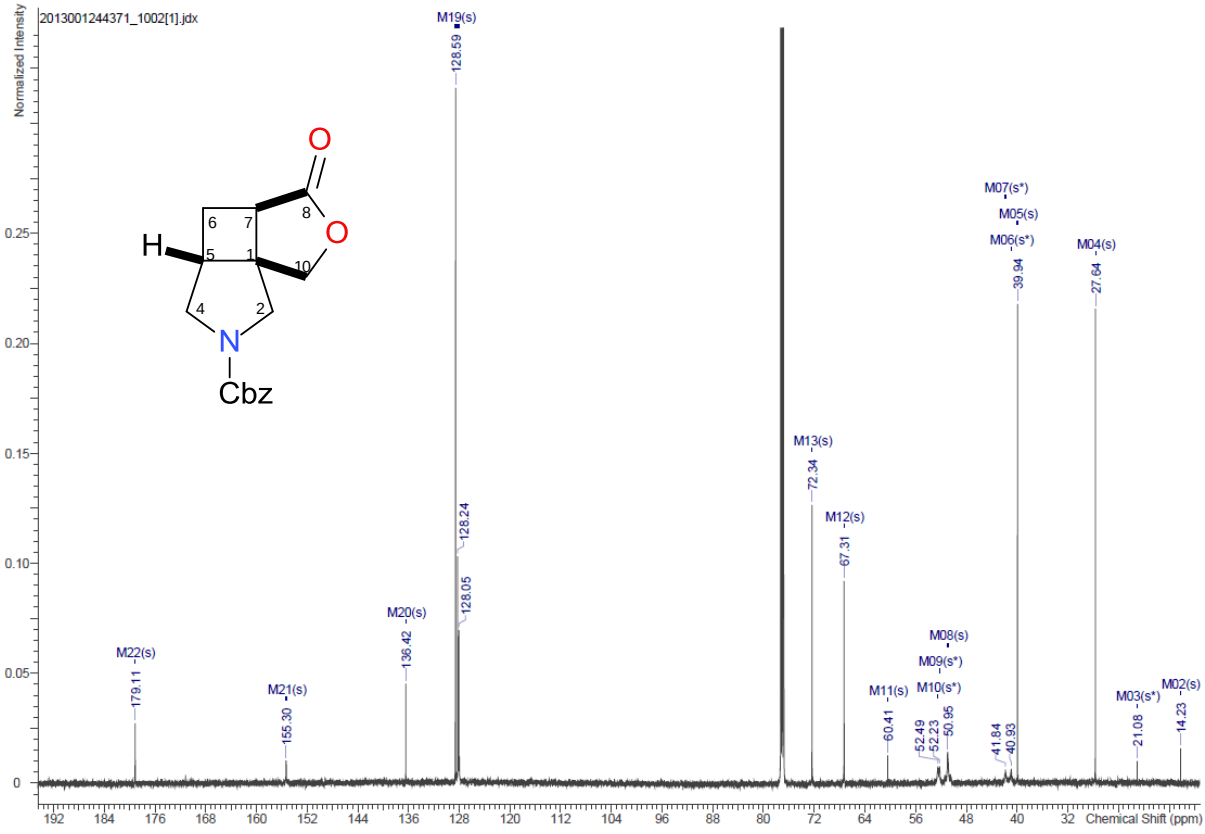
**Benzyl allyl[(5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate (7)**



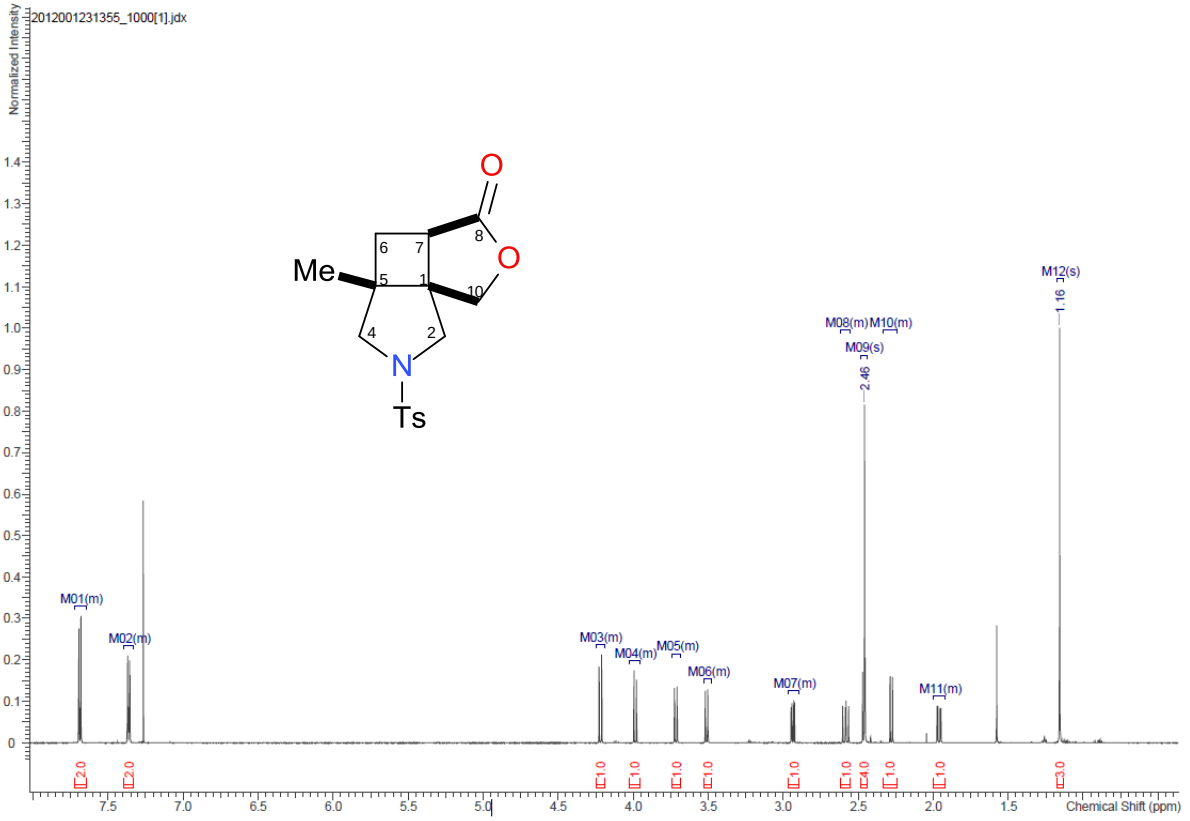



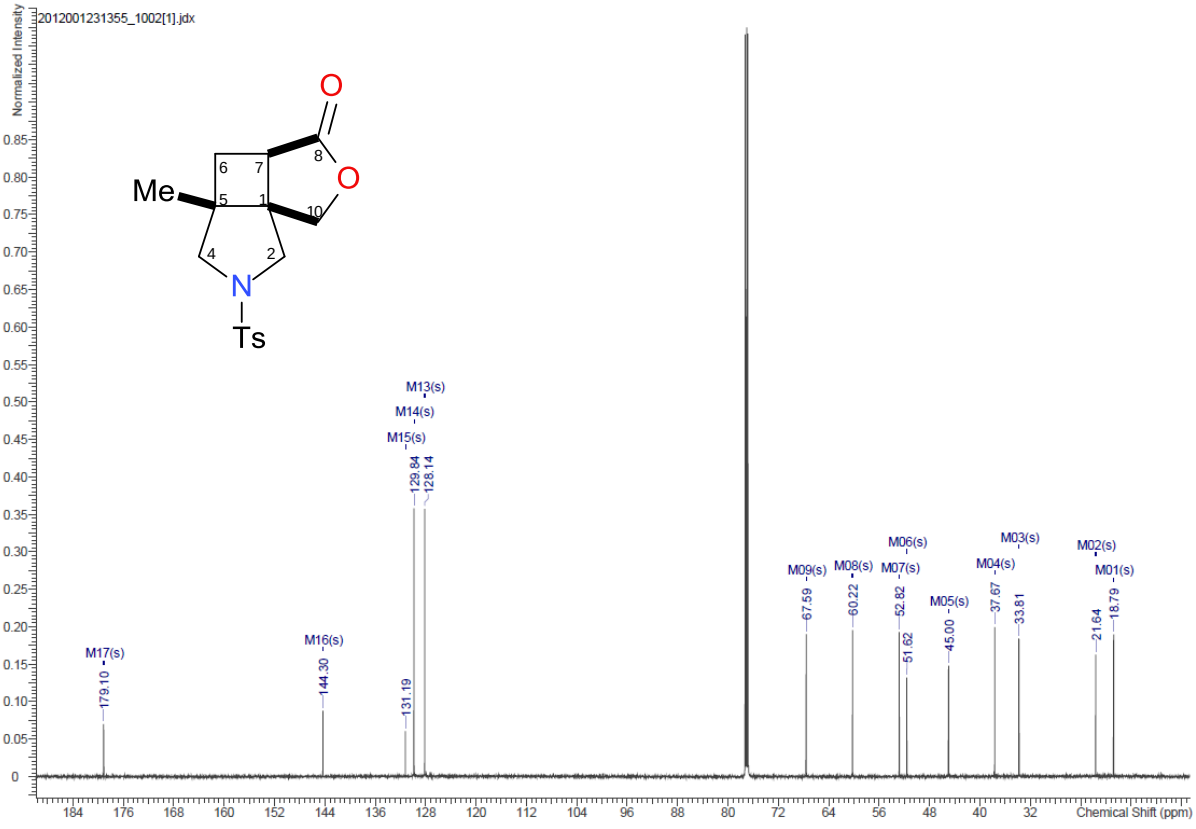
**Benzyl (3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one)carbamate (8)**



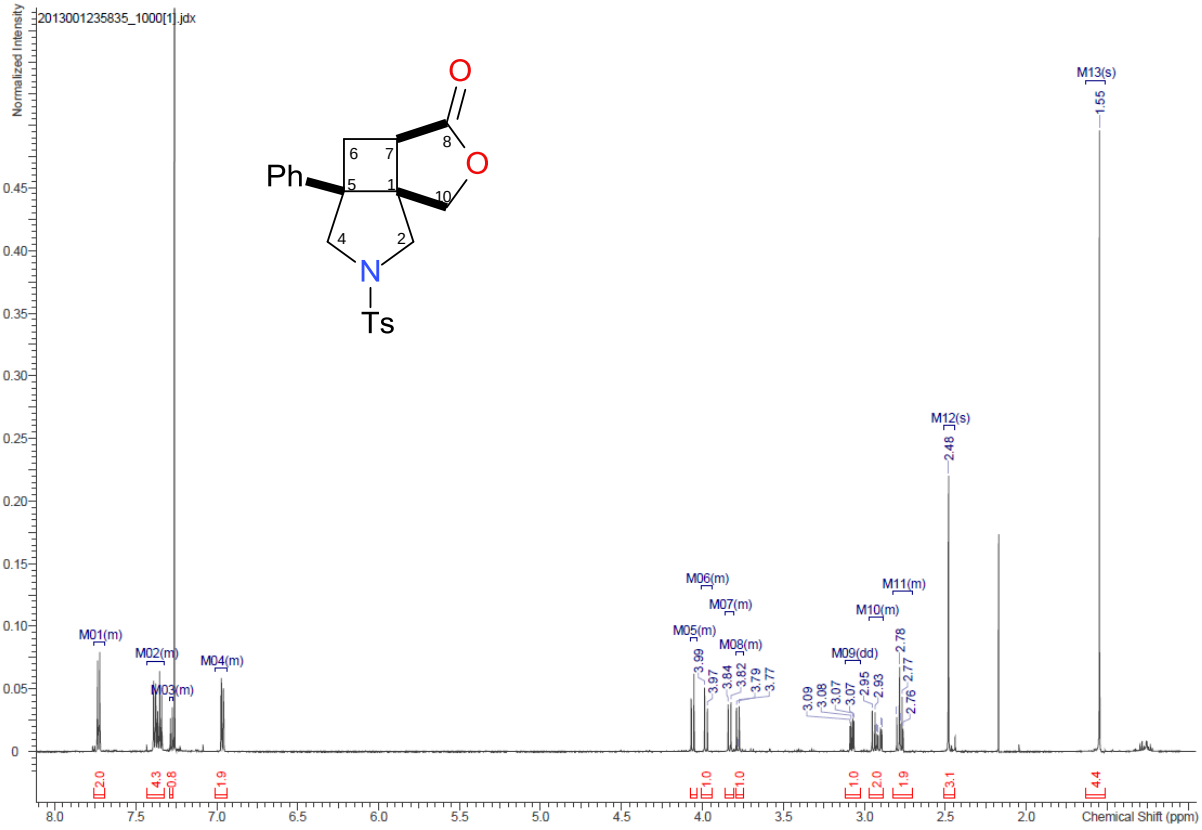



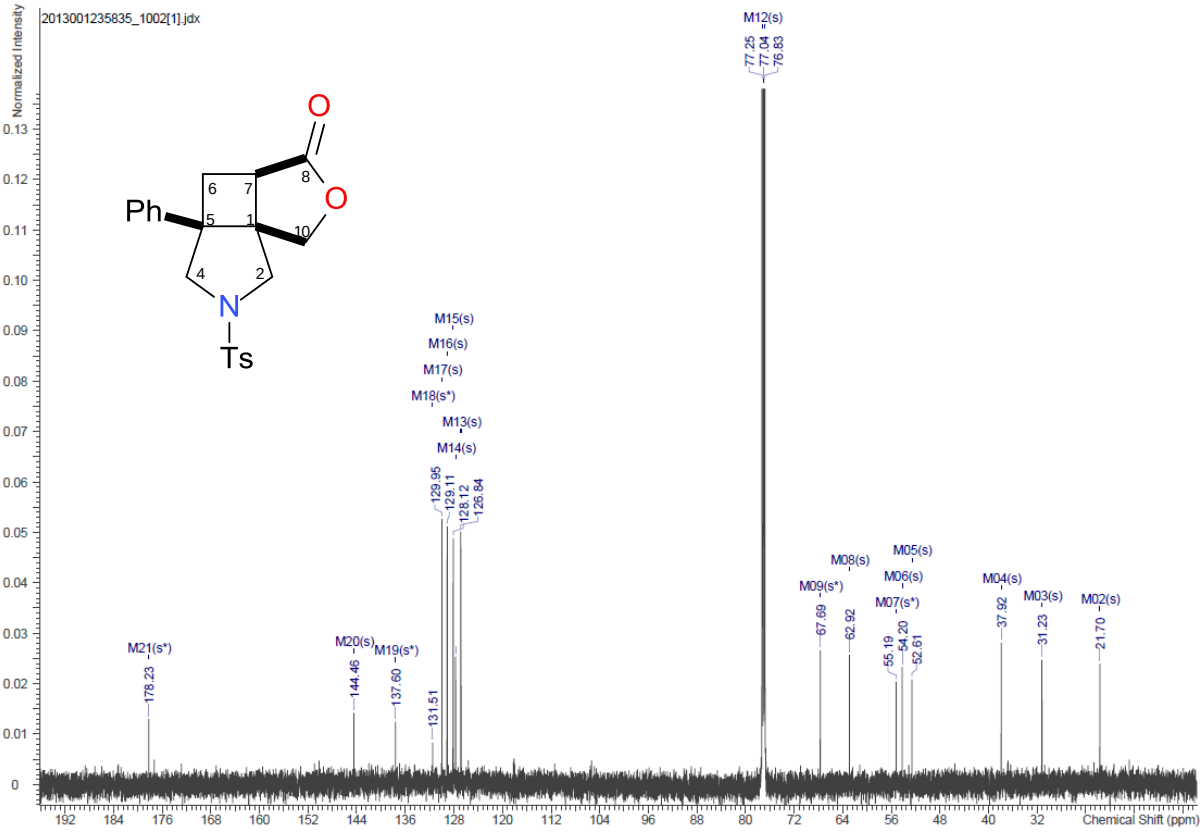
**N-(*p*-methylbenzenesulfonamide)-5-methyl-3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (9b)**



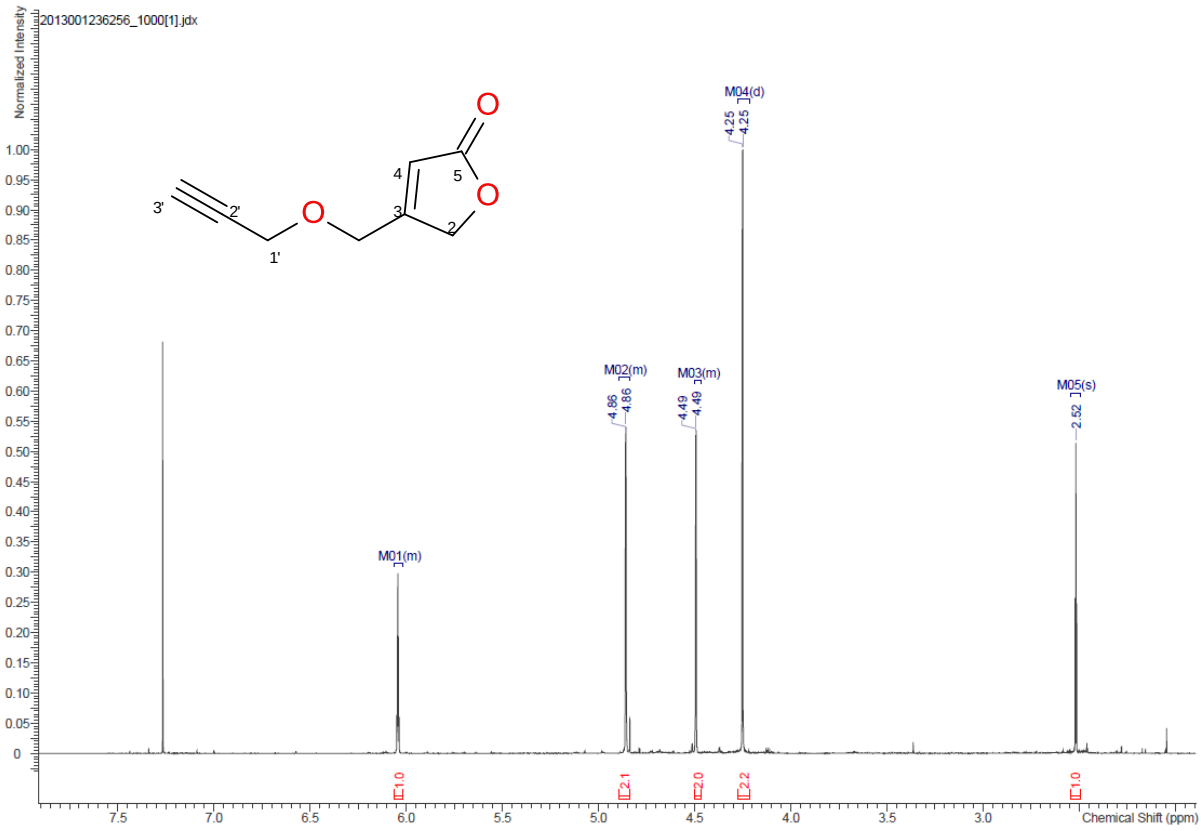



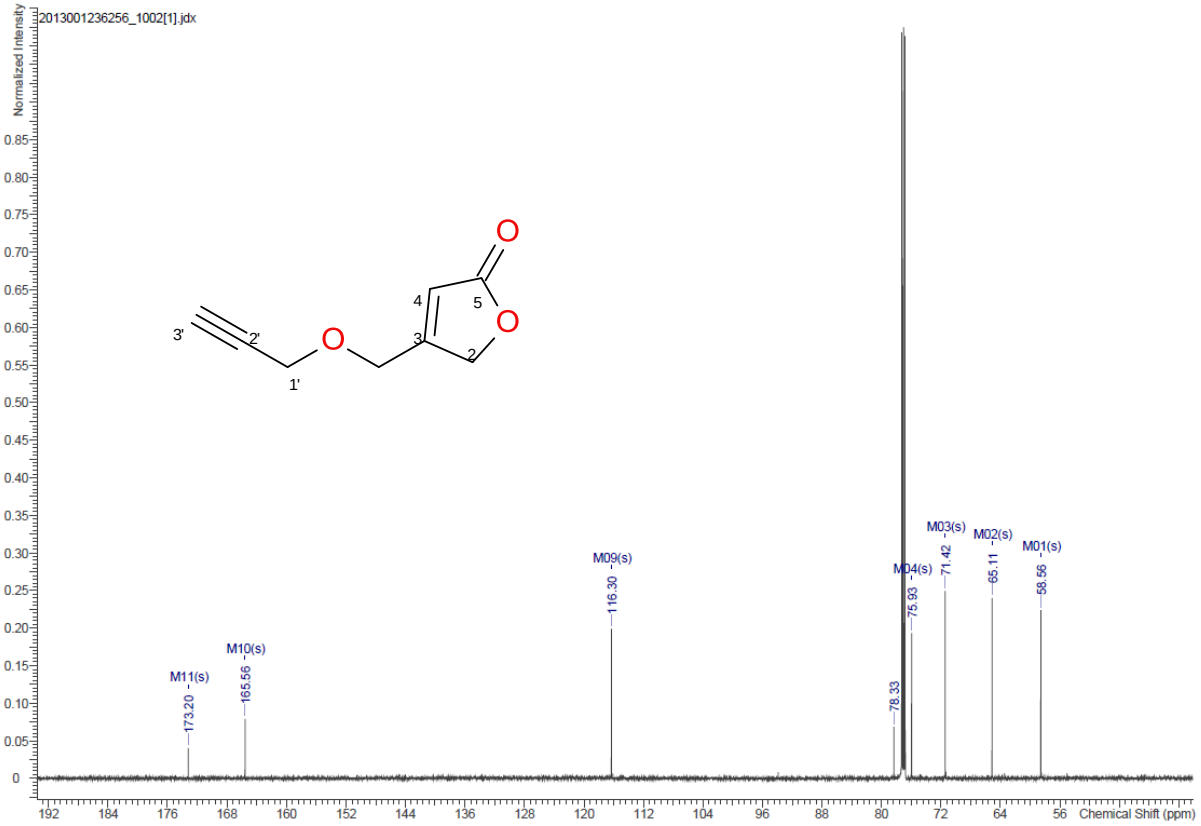
**N-(*p*-Methylbenzenesulfonamide)-5-phenyl-3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (9c)**



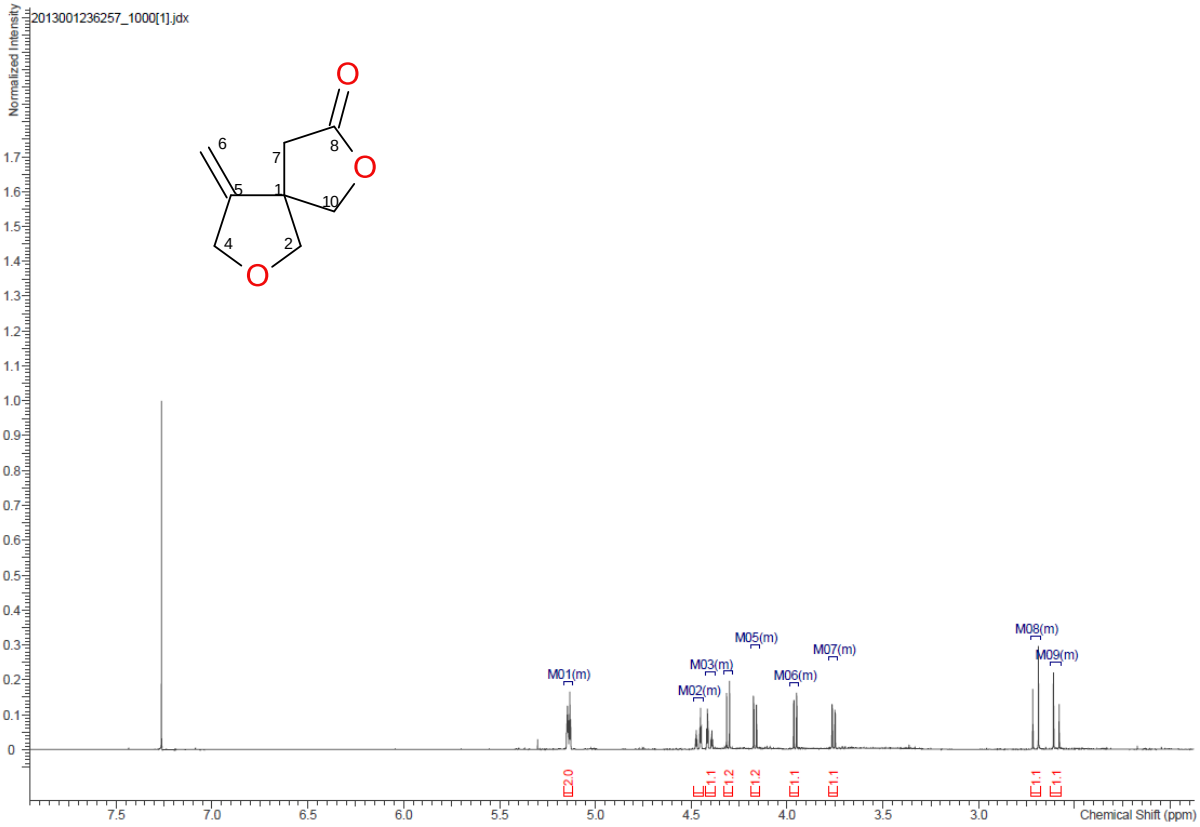



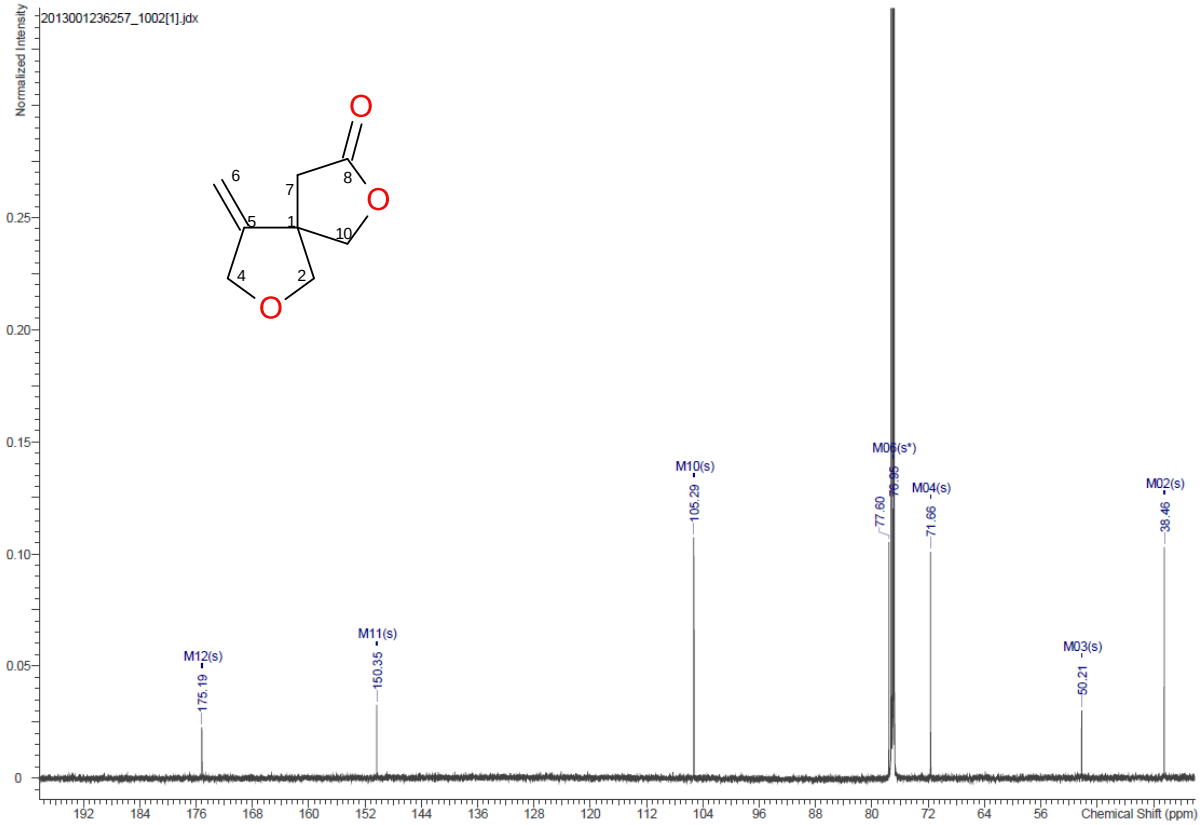
**4-(Prop-2-ynoxymethyl)-2(5H)-furanone (10b) (10b)**



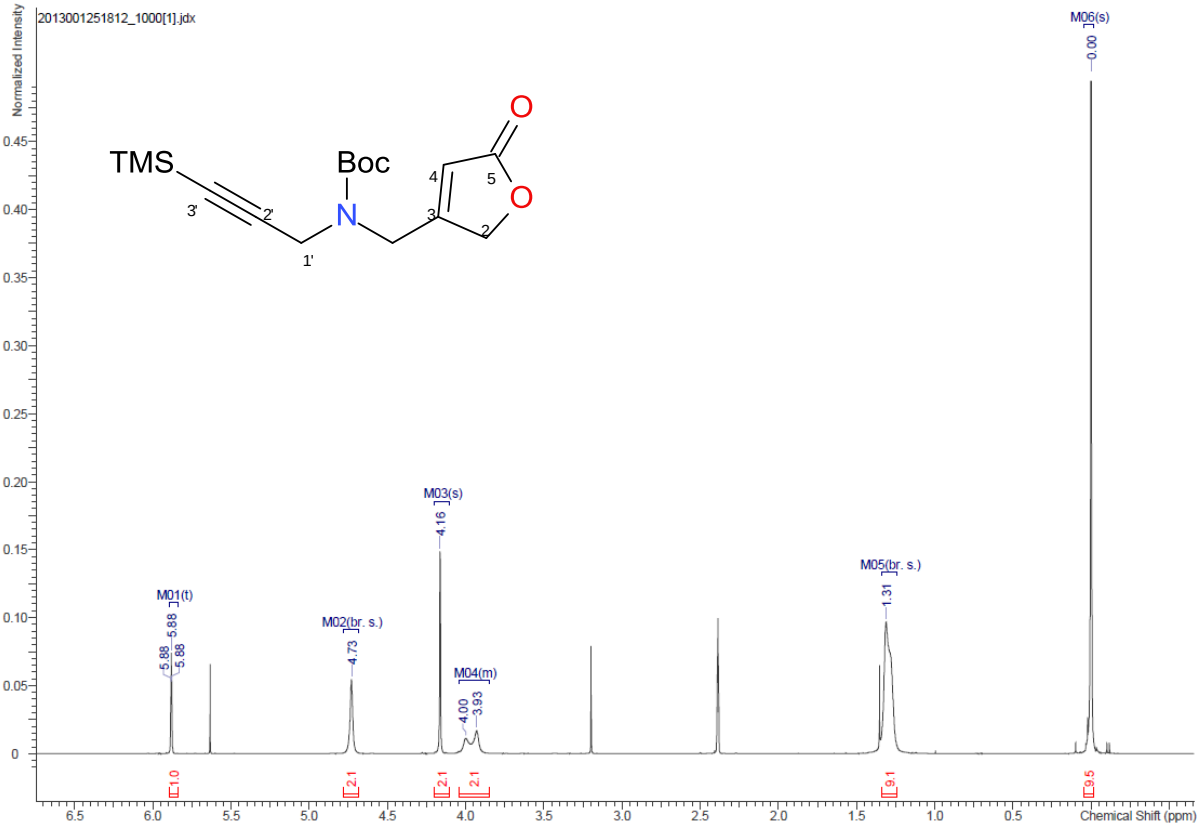



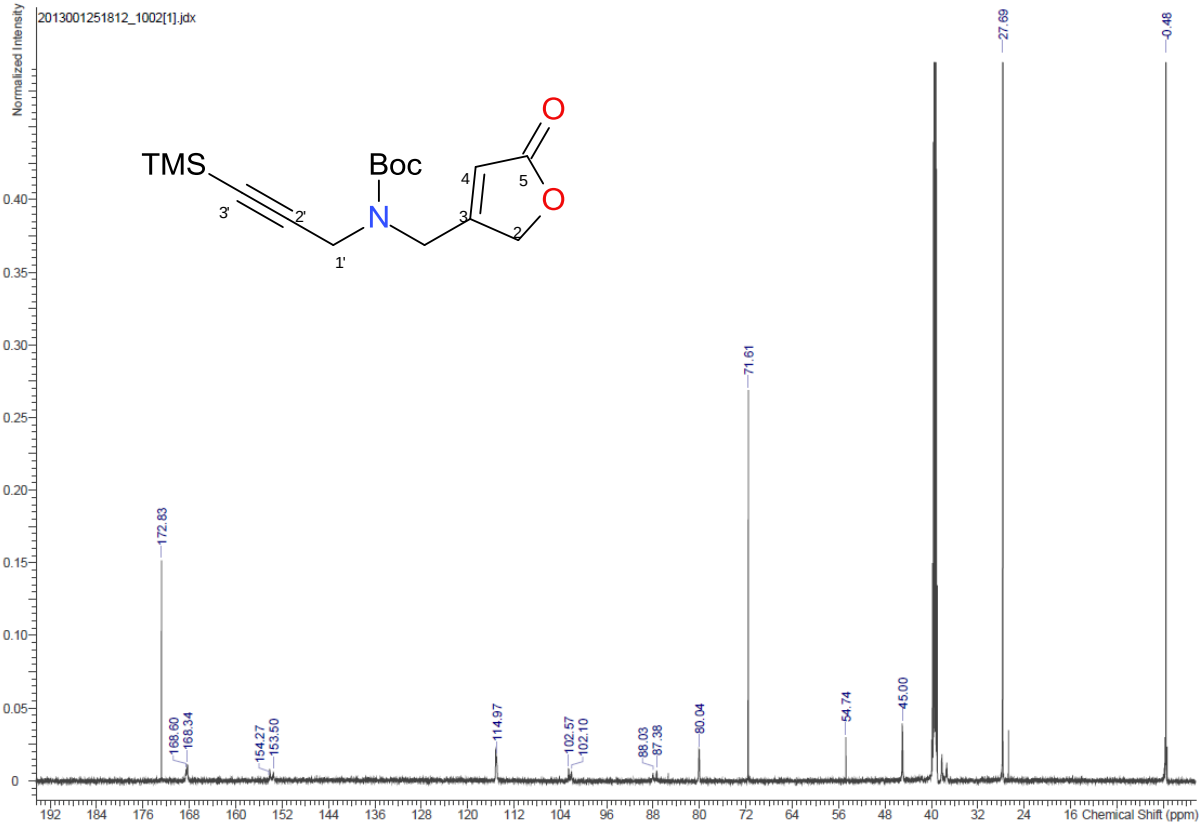
**9-Methylene-2,7-dioxaspiro[4.4]nonan-3-one (11b)**



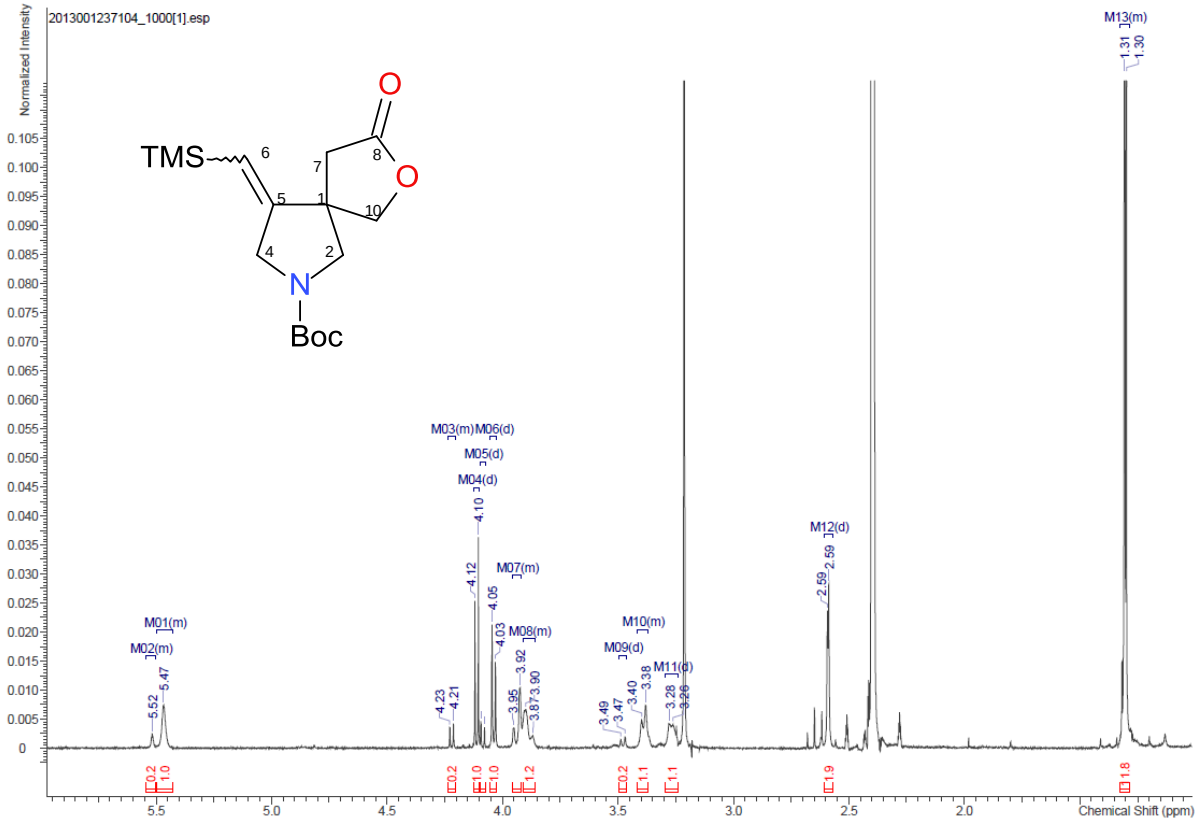



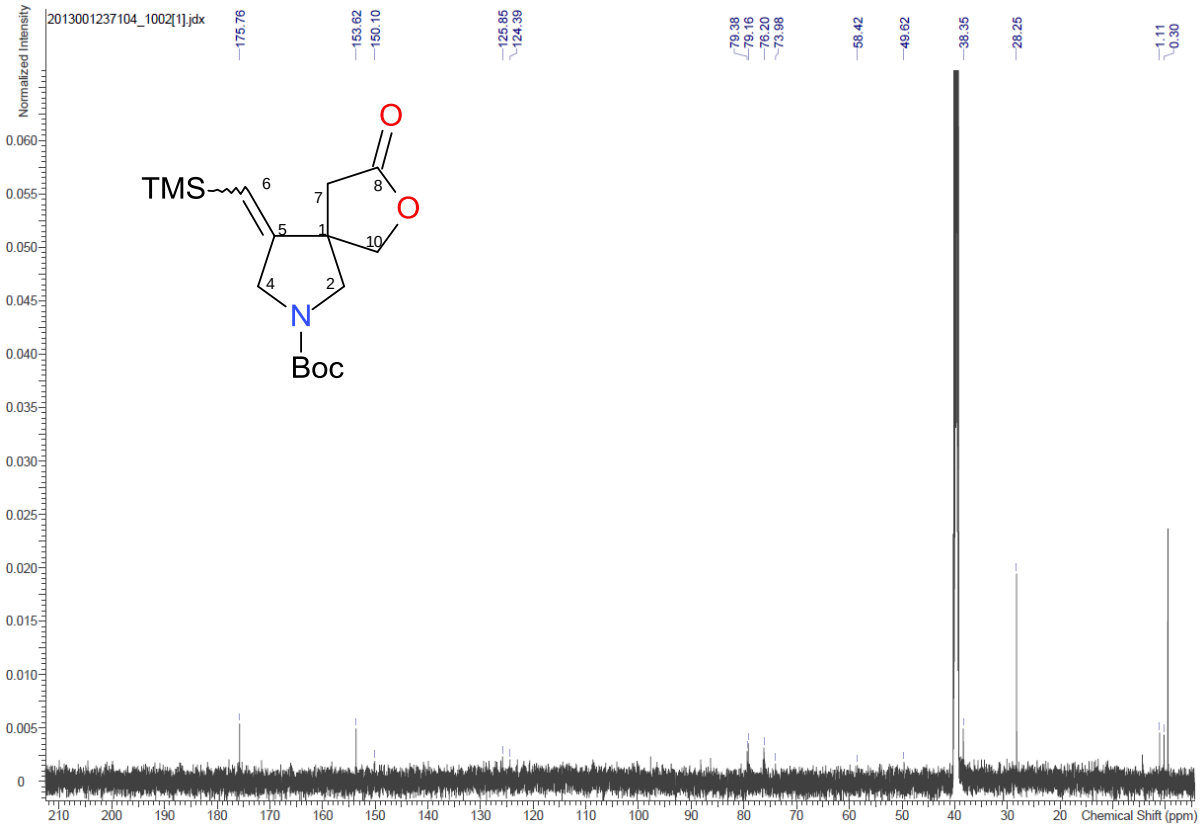
**tert-Butyl N-[(5-oxo-2H-furan-3-yl)methyl]-N-(3-trimethylsilylprop-2-ynyl)carbamate (12)**



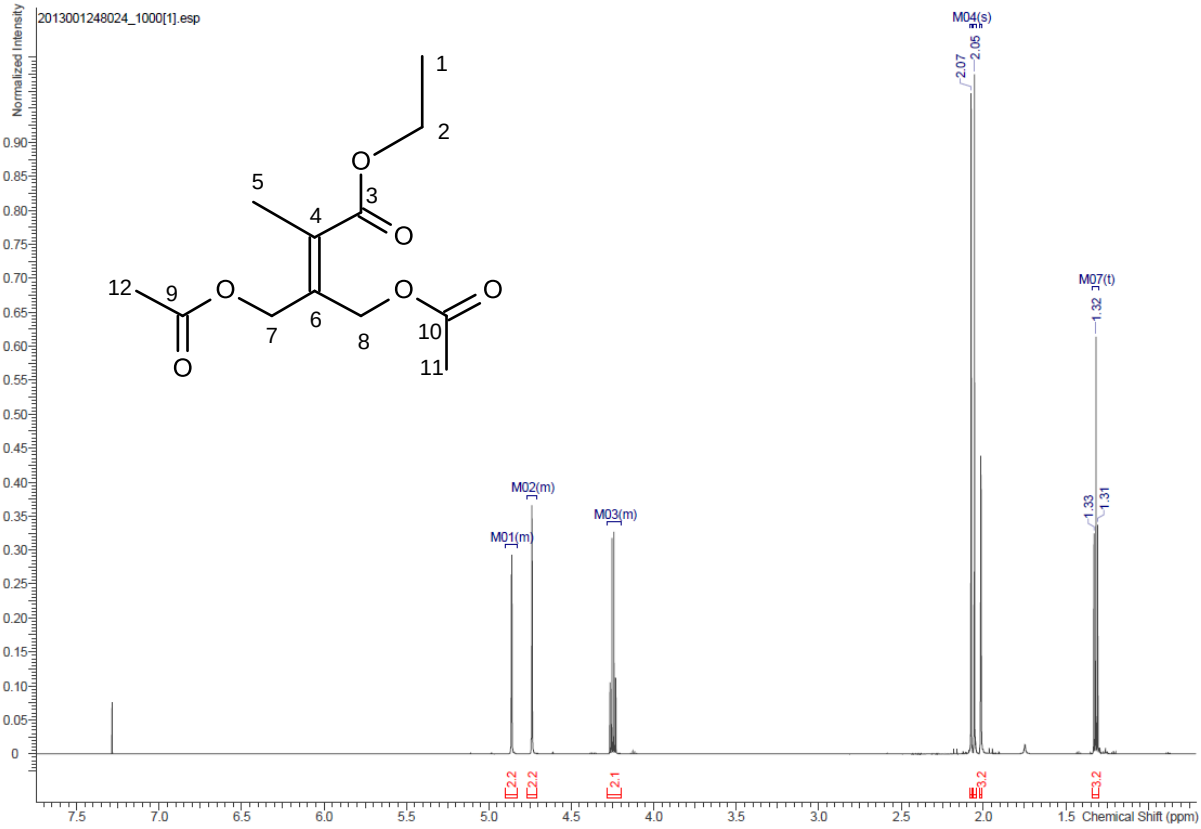



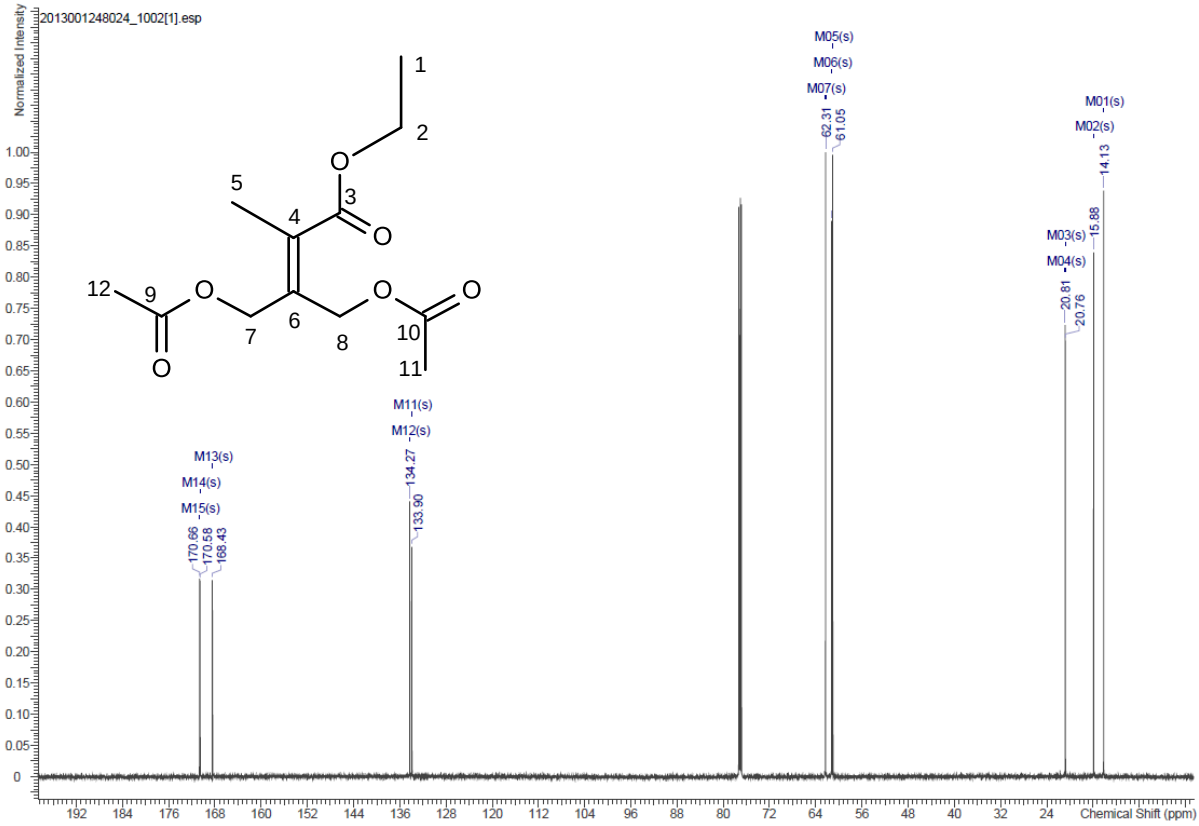
***tert*-Butyl-3-oxo-9-(silylmethylene)-2-oxa-7-azaspiro[4.4]nonane-7-carboxylate (13)**



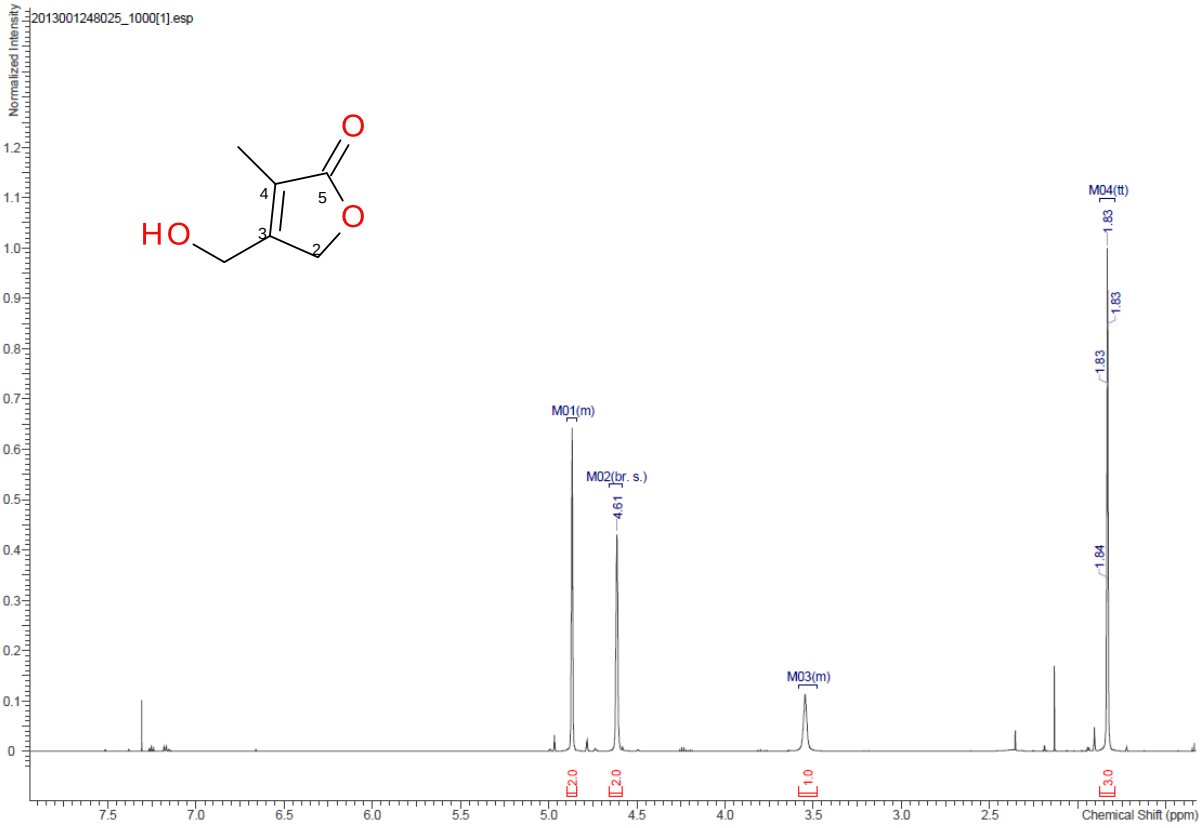



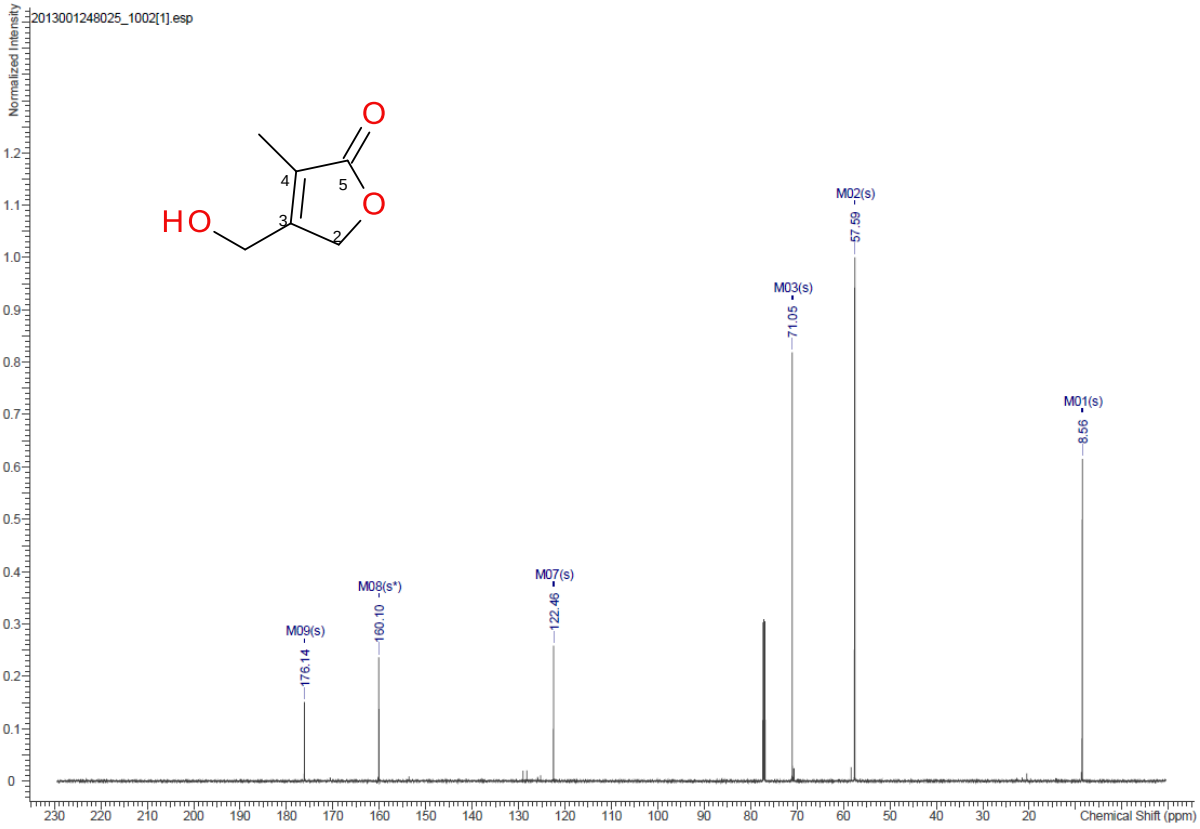
**Ethyl 4-acetoxy-3-(acetoxymethyl)-2-methyl-but-2-enoate (15a)**



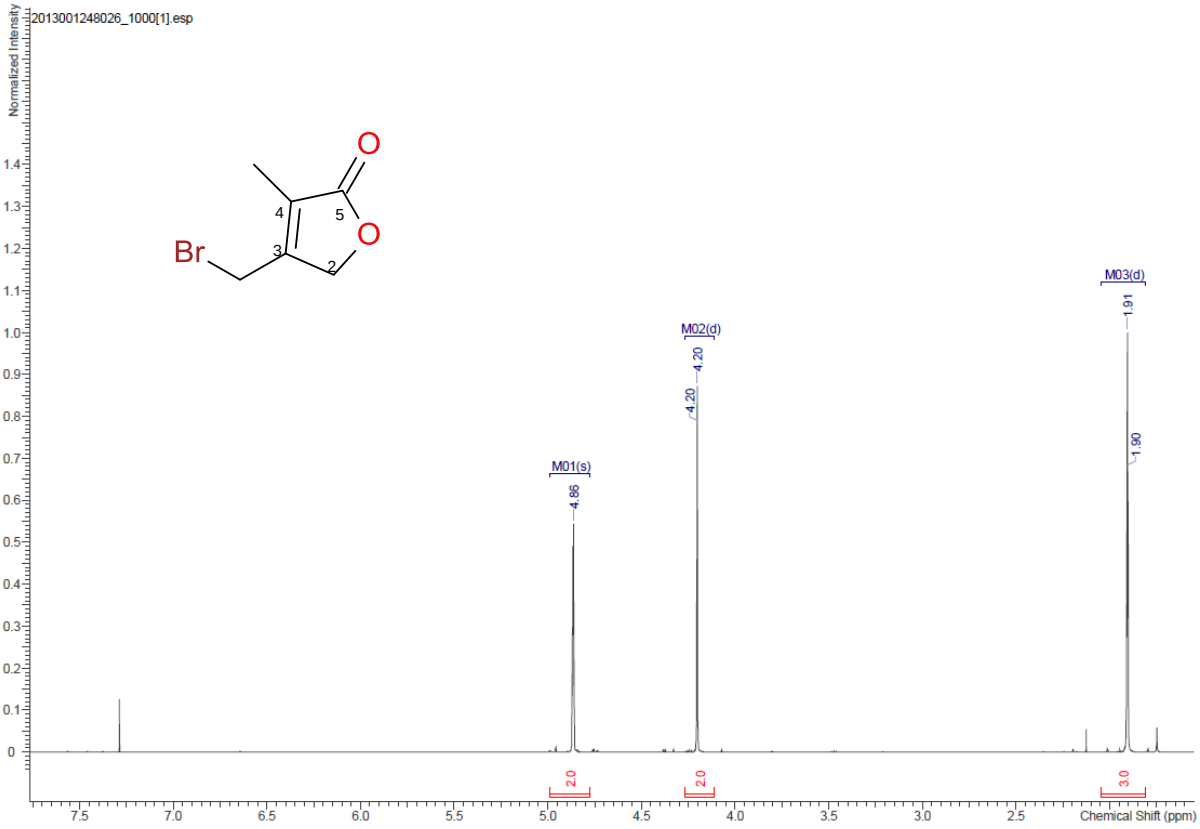



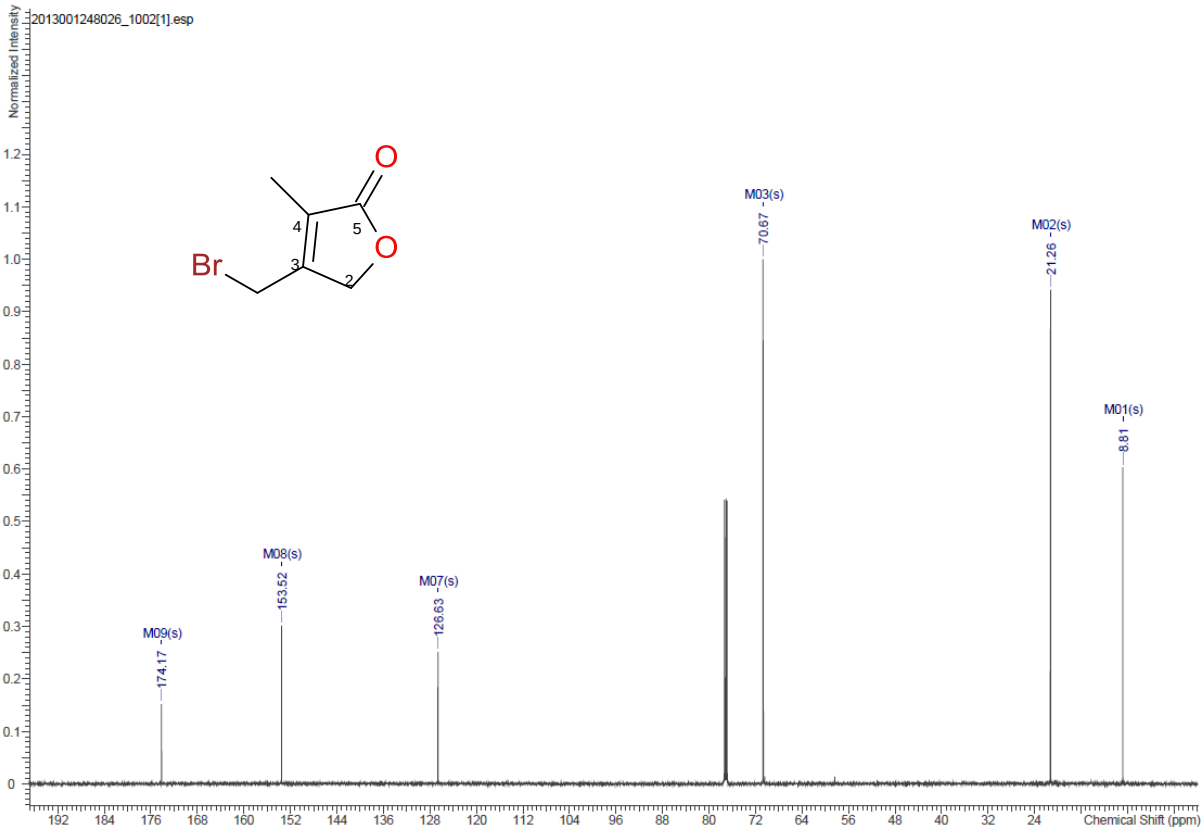
**4-(Hydroxymethyl)-3-methyl-2(5H)-furanone (16a)**



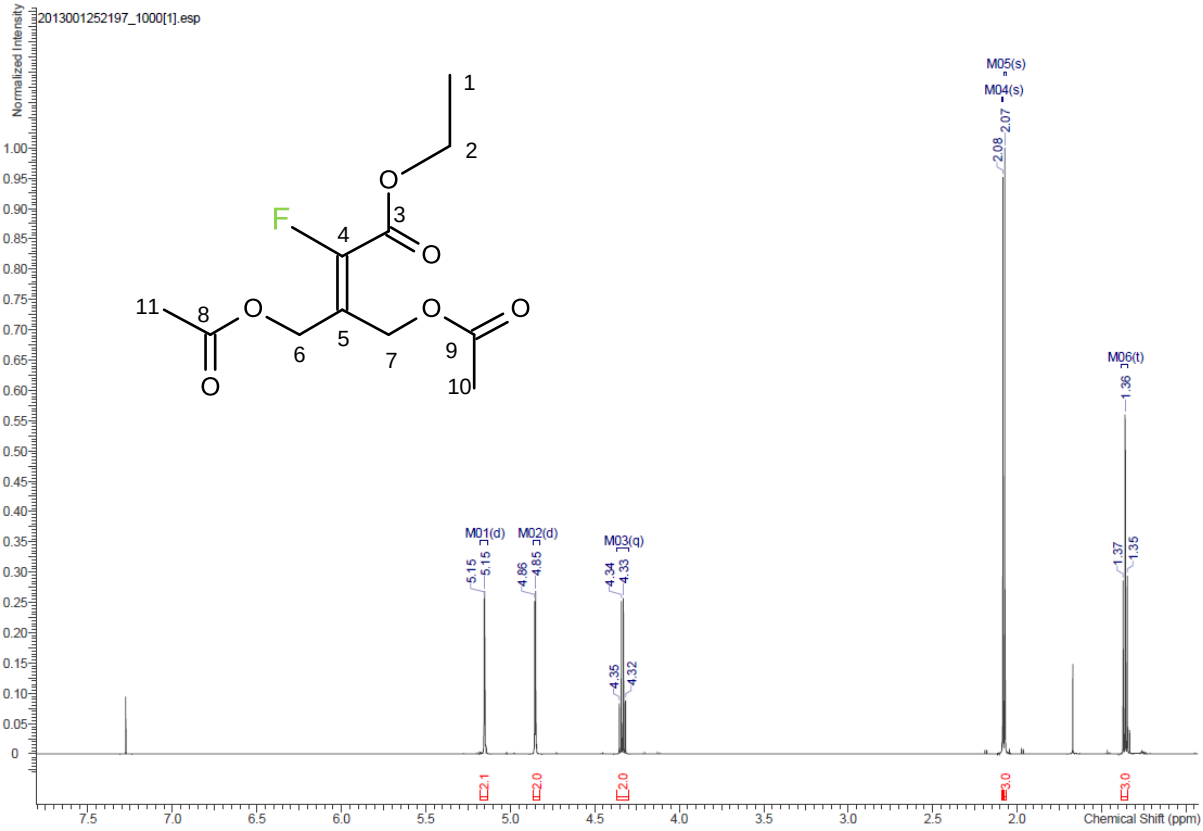



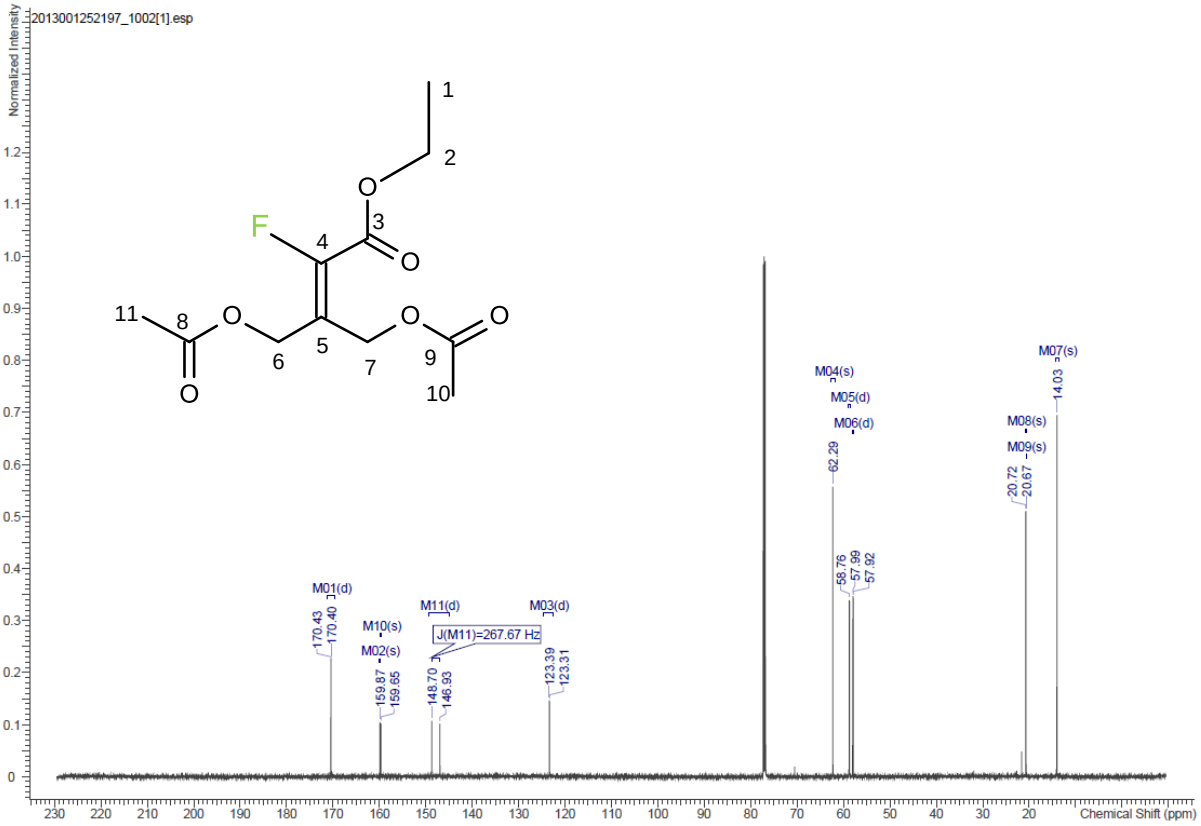
**4-(Bromomethyl)-3-methyl-2(5H)-furanone (17a)**



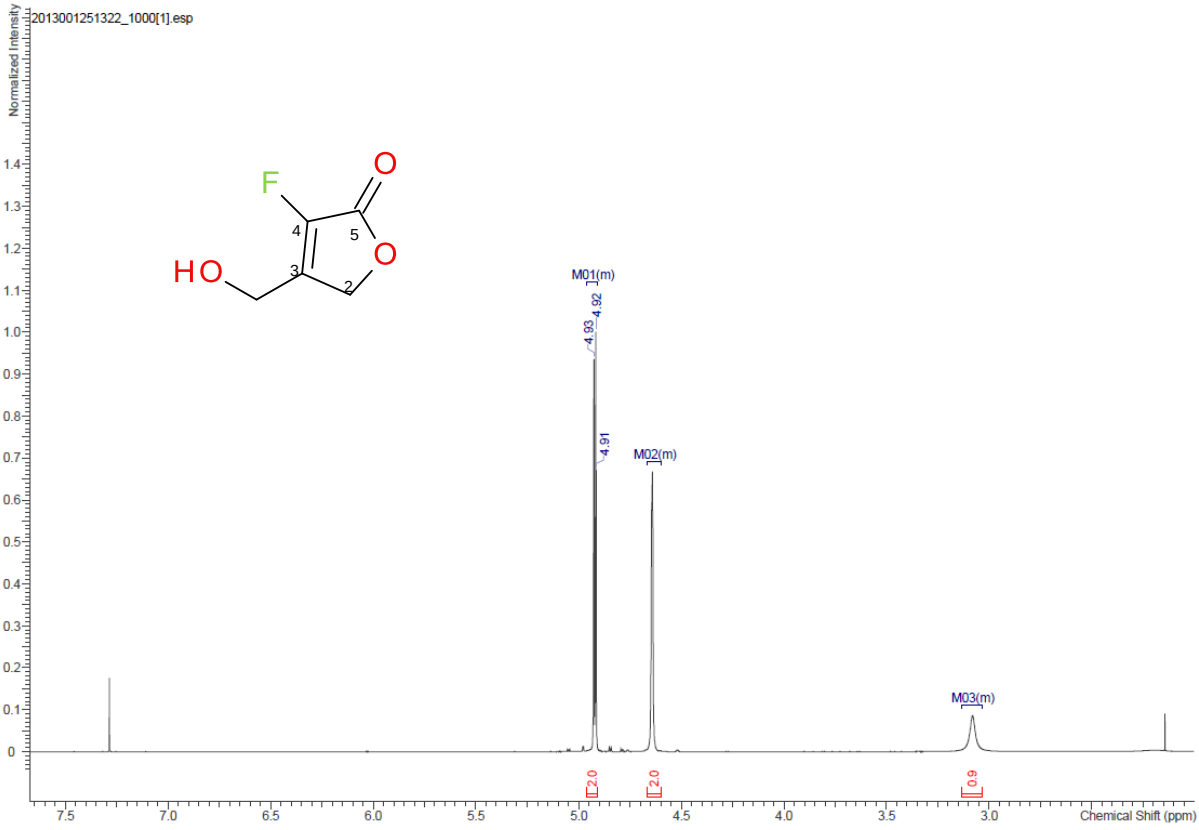



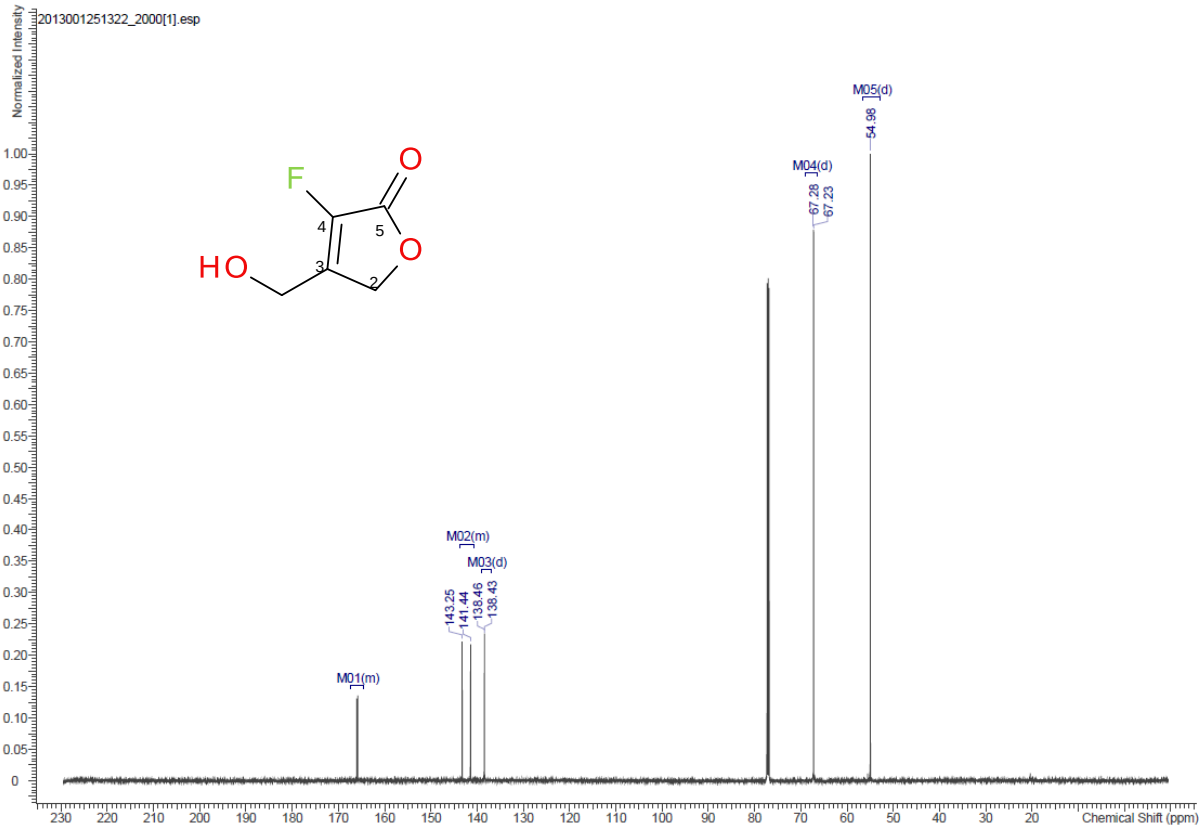
**Ethyl 4-acetoxy-3-(acetoxymethyl)-2-fluoro-but-2-enoate (15b)**



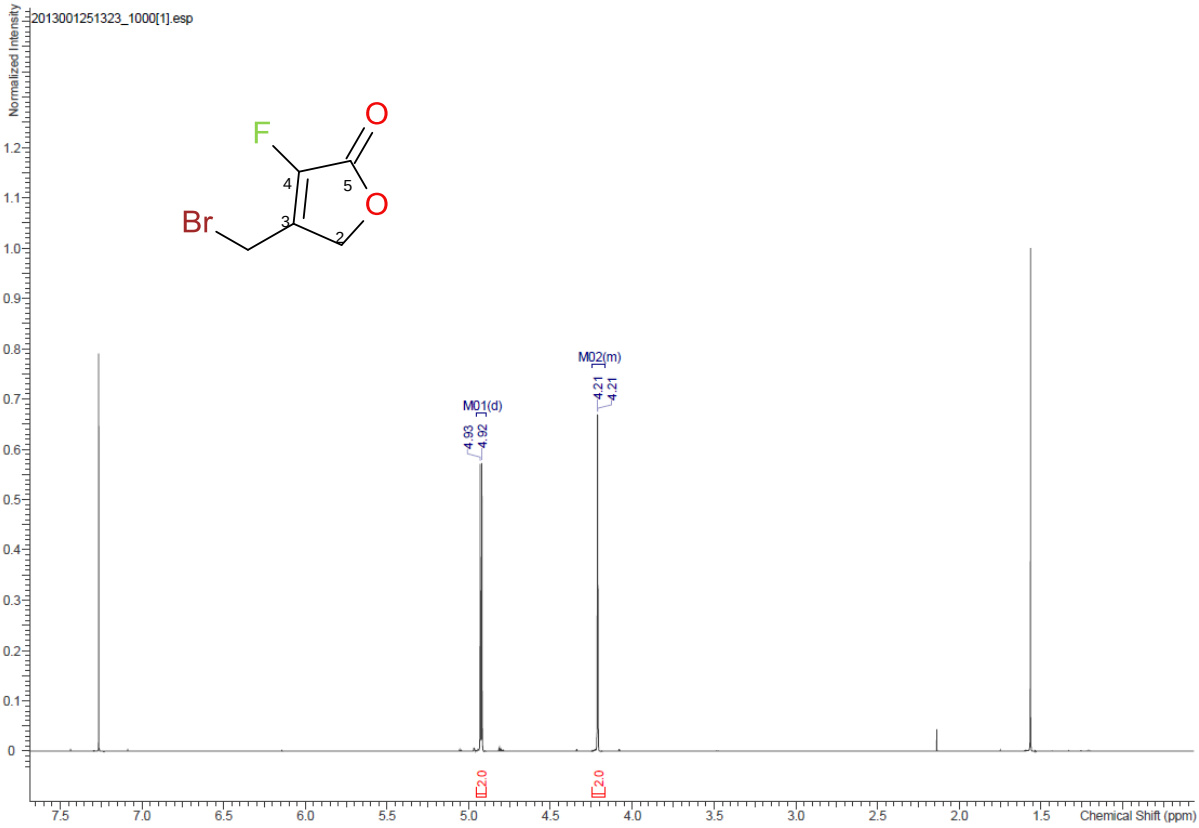



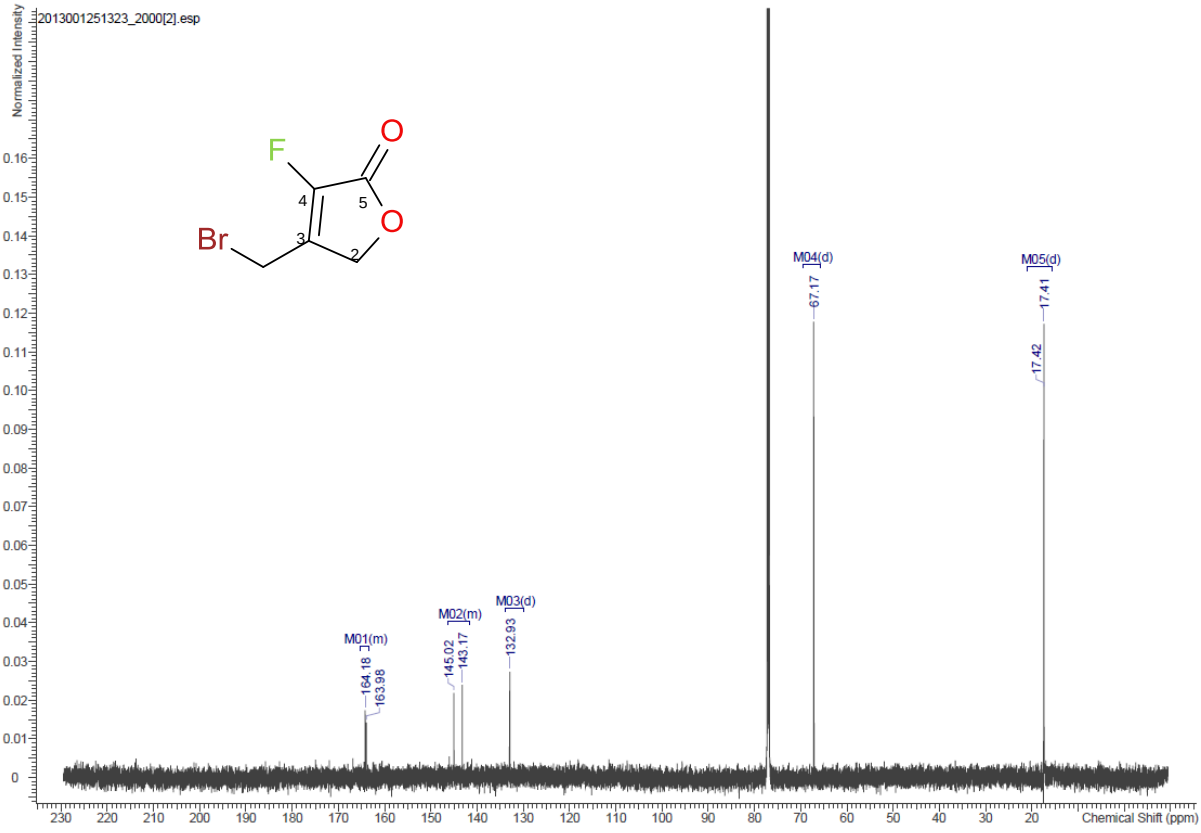
**3-Fluoro-4-(hydroxymethyl)-2(5H)-furanone (16b)**



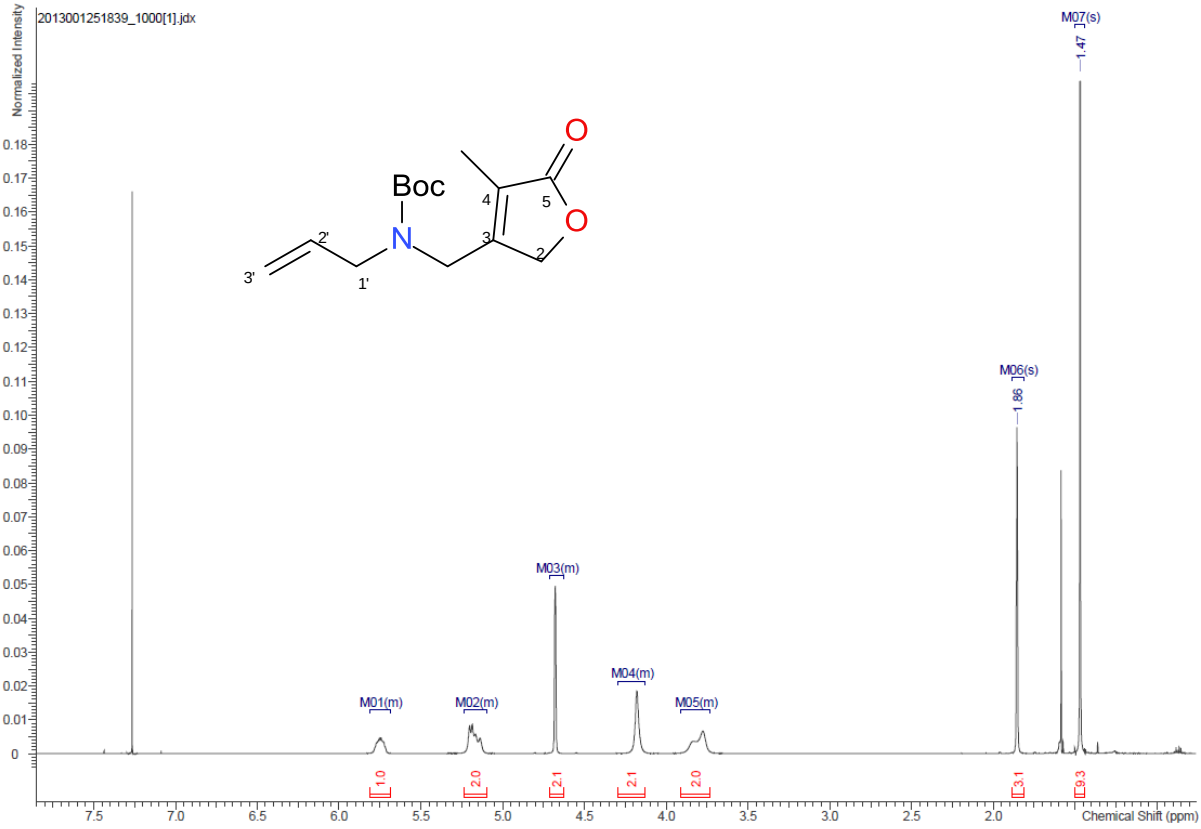



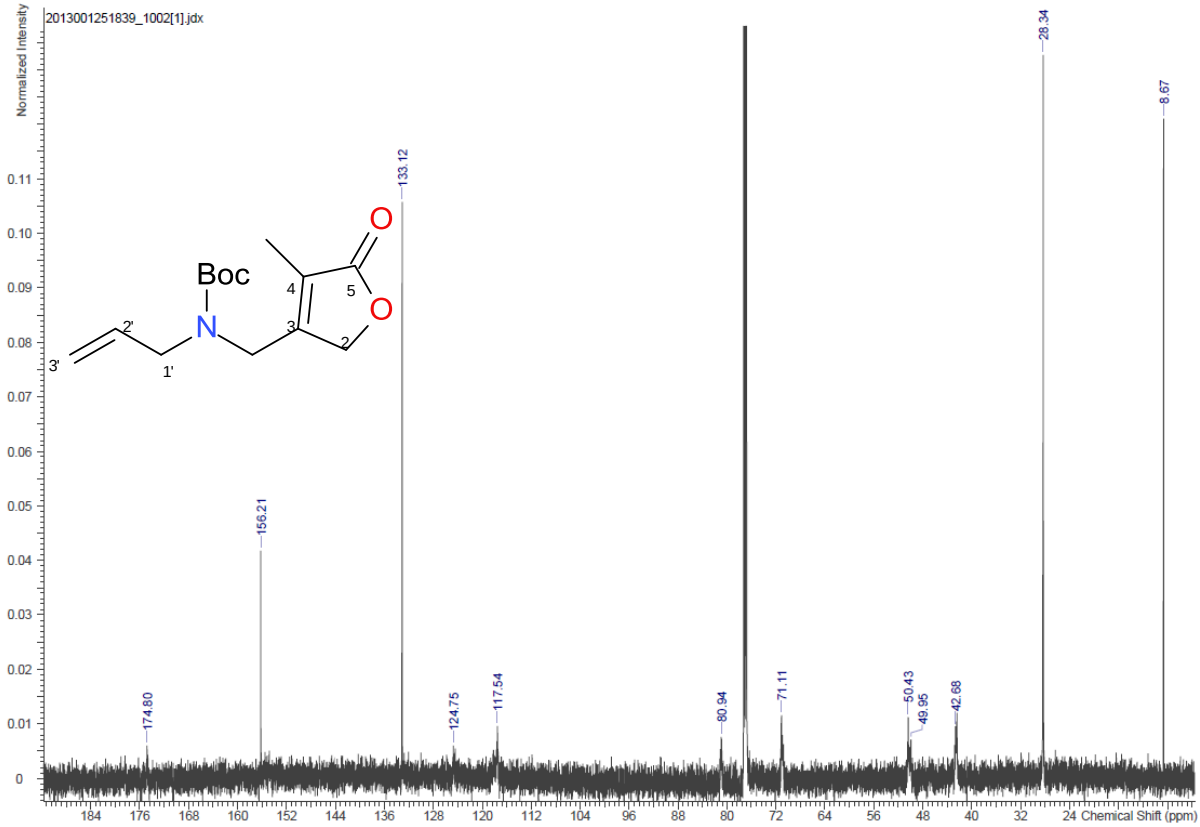
**4-(Bromomethyl)-3-fluoro-2(5H)-furanone (17b)**



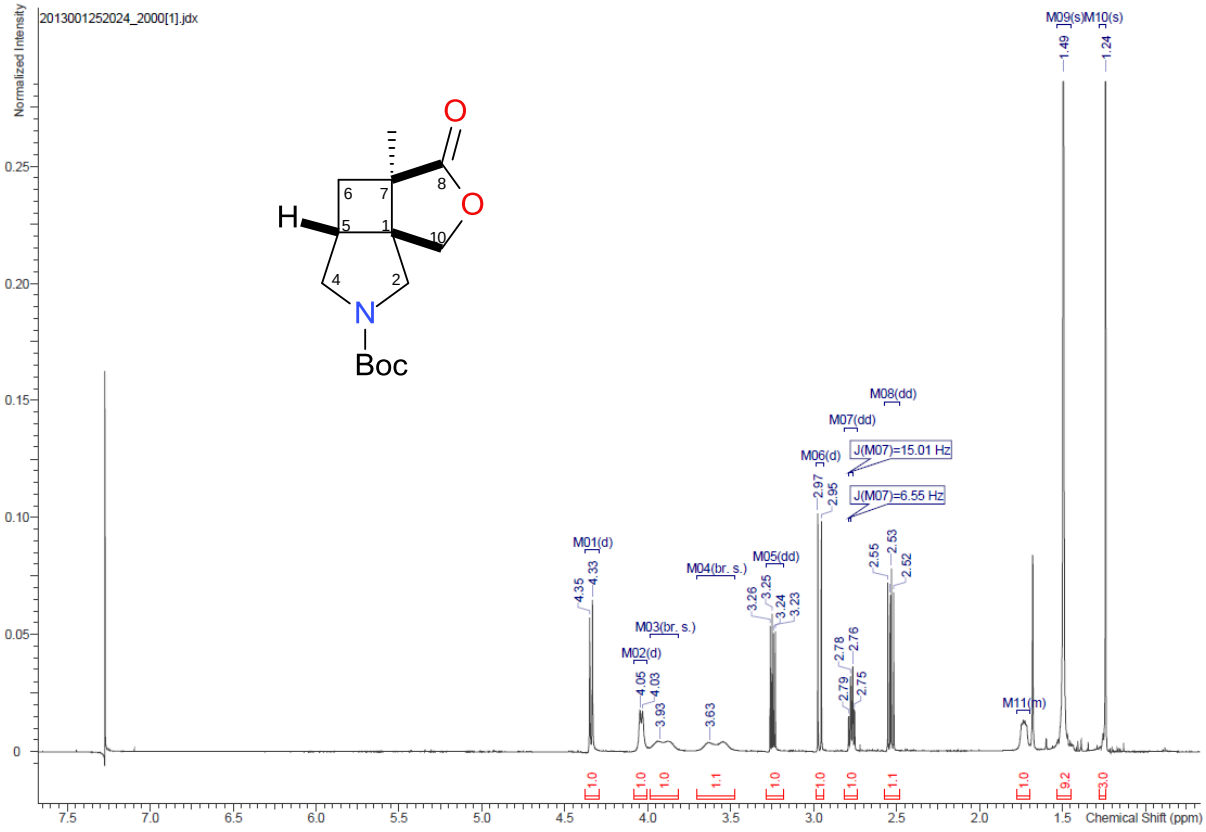



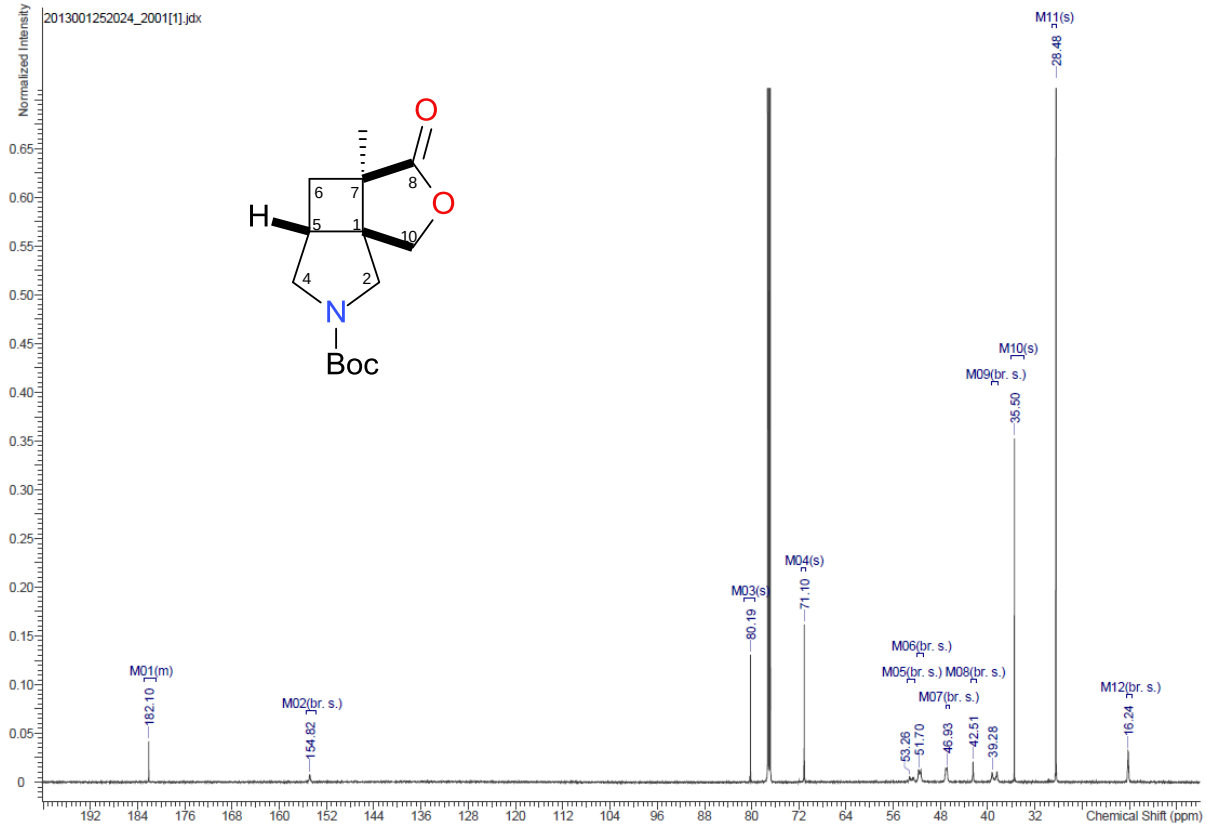
**_tert_-Butyl N-allyl-N-[(4-methyl-5-oxo-2H-furan-3-yl)methyl]carbamate (18a)**



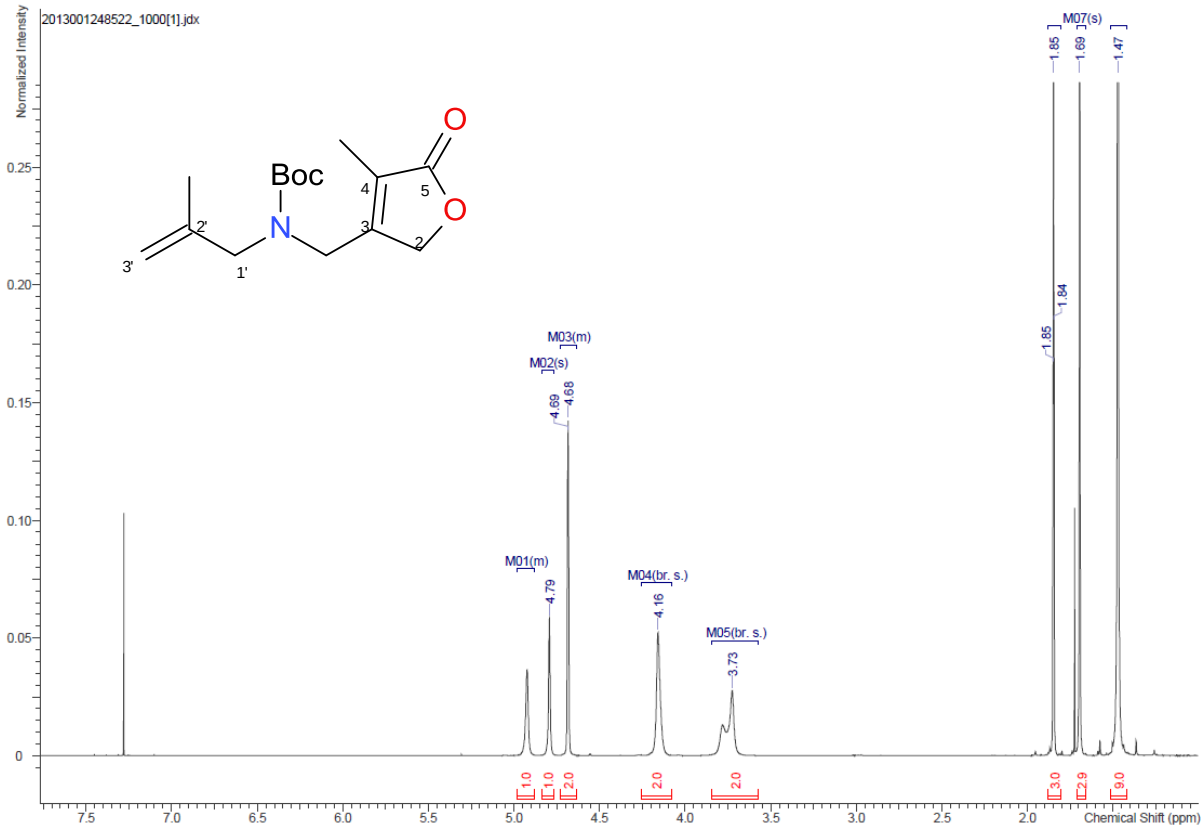



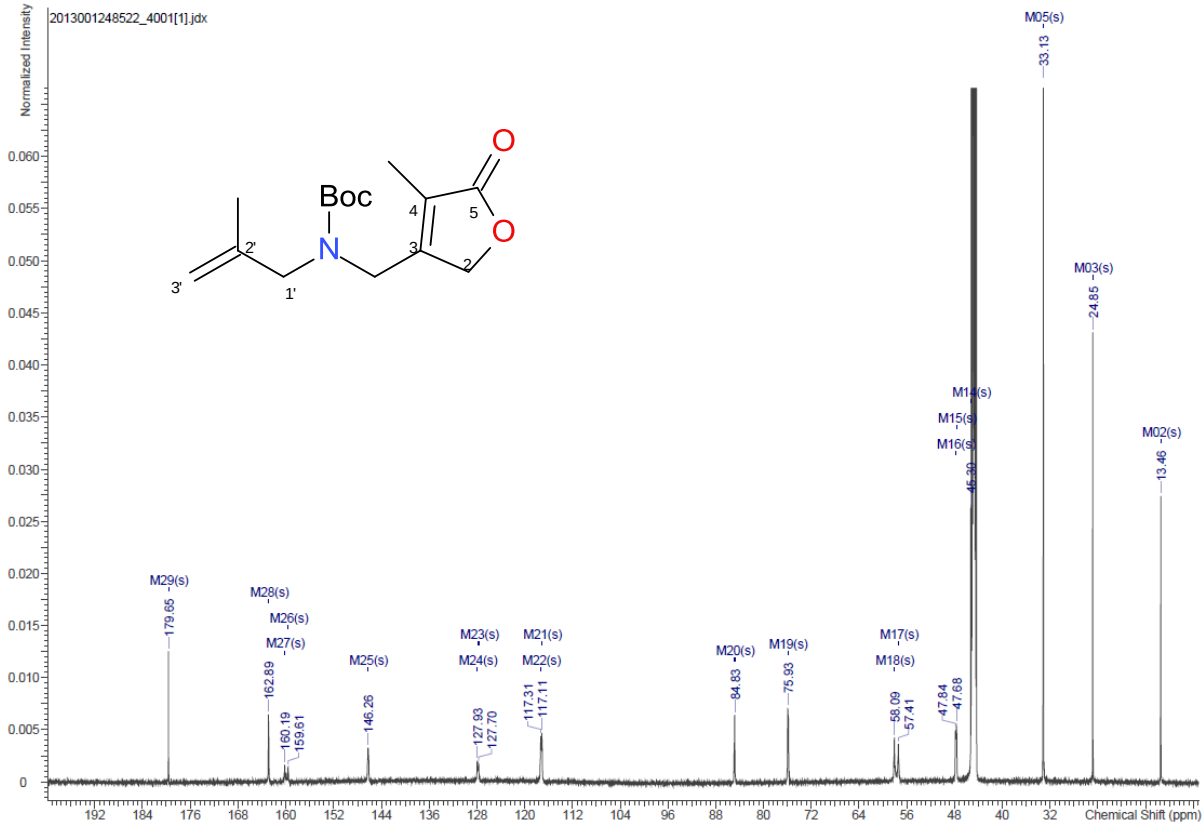
**N-*tert*-Butoxycarbonyl-7-methyl-3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (19a)**



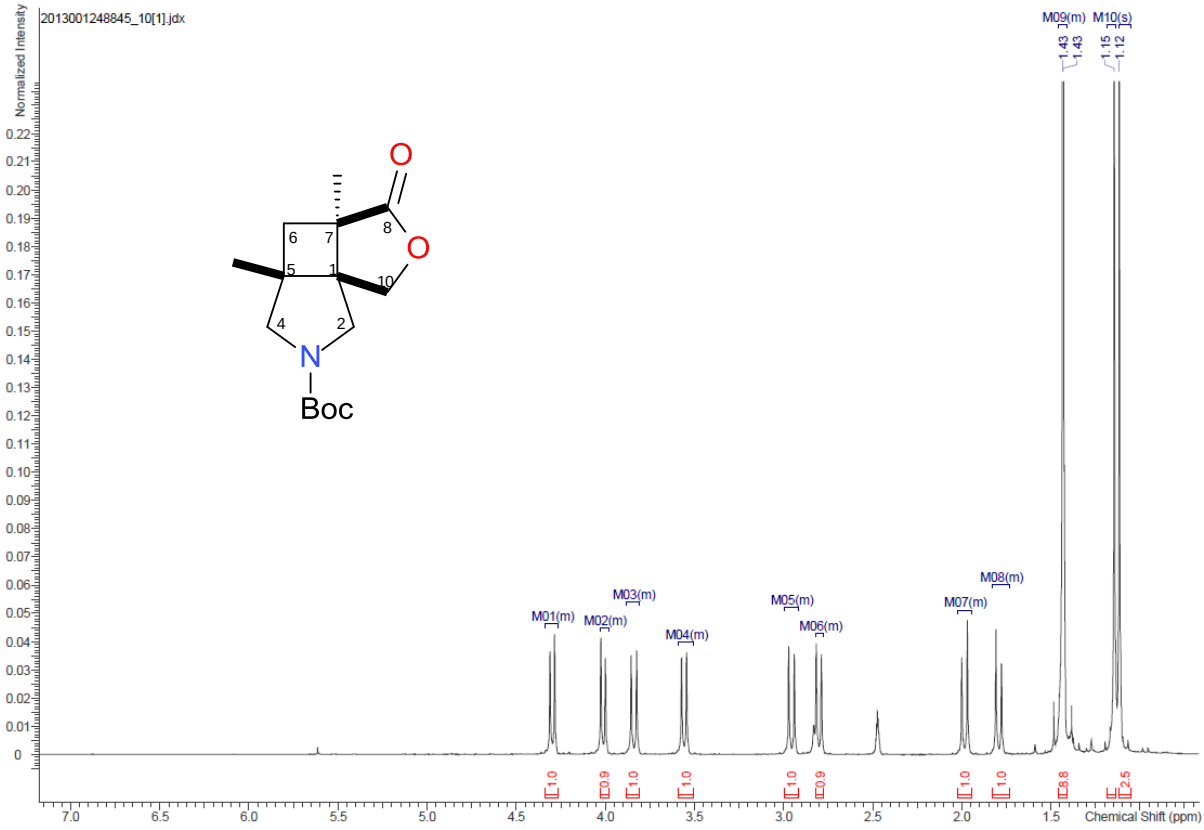



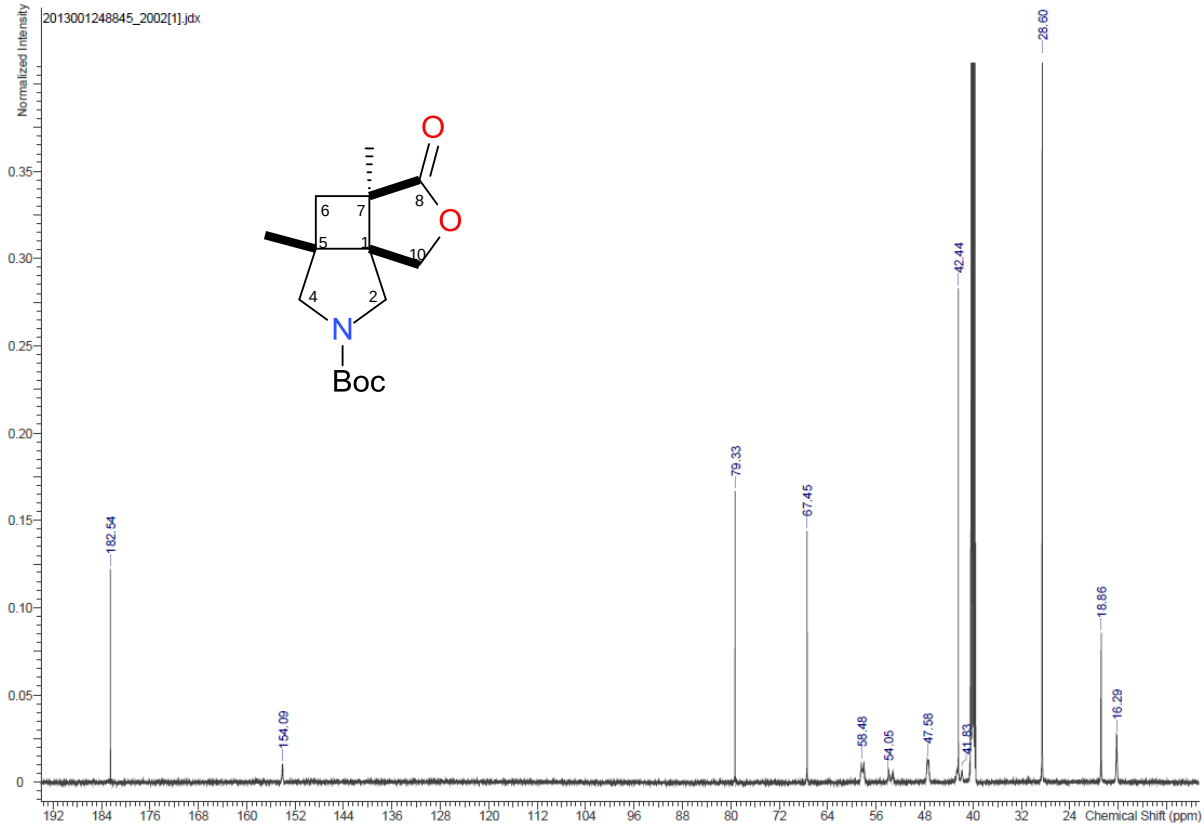
**_tert_-Butyl N-(2-methylallyl)-N-[(4-methyl-5-oxo-2H-furan-3-yl)methyl]carbamate (18b)**



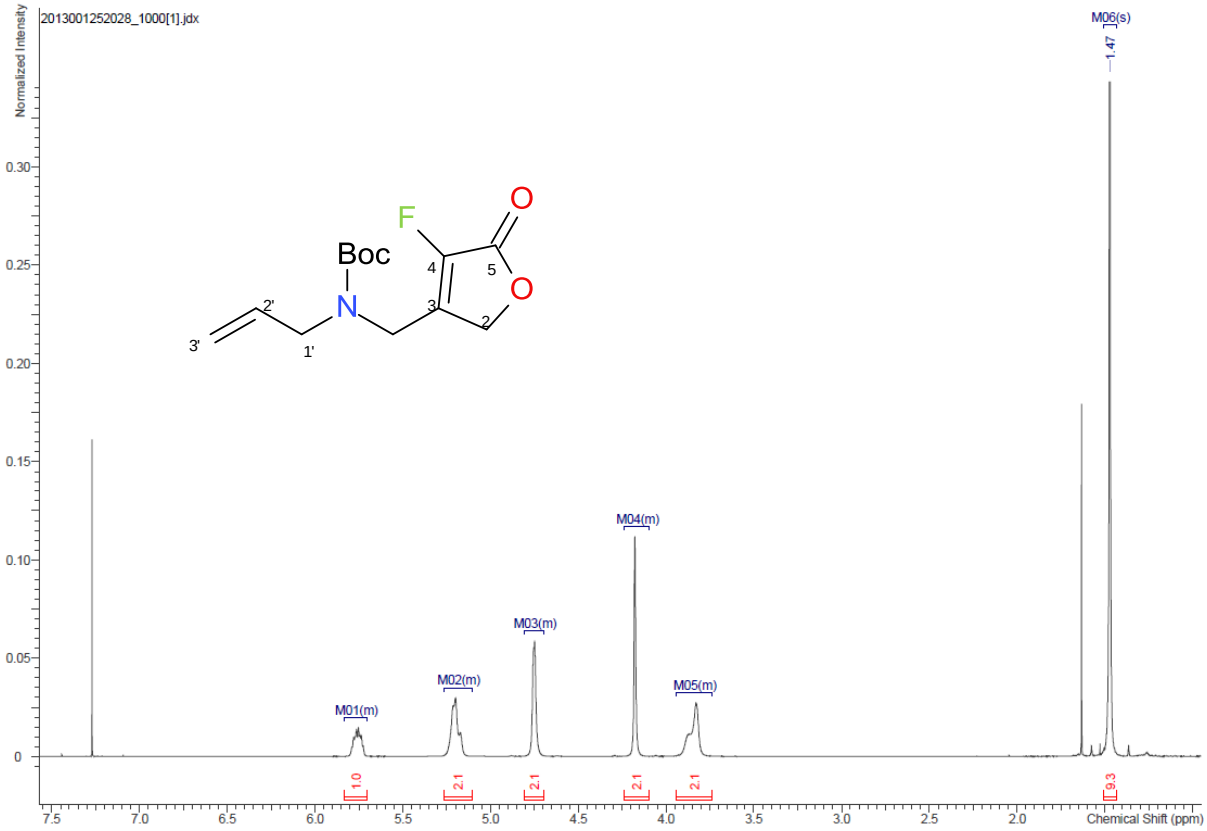



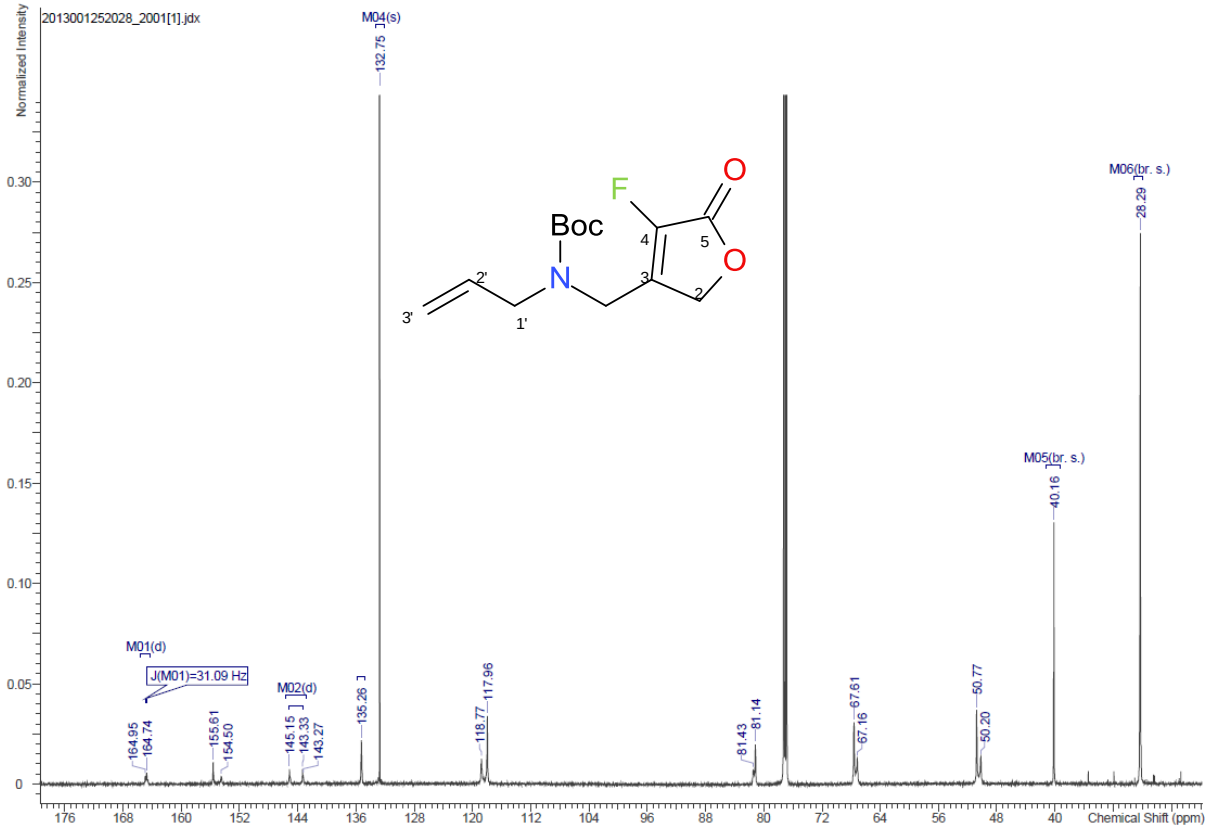
**N-*tert*-Butoxycarbonyl-5-methyl-7-methyl-3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (19b)**



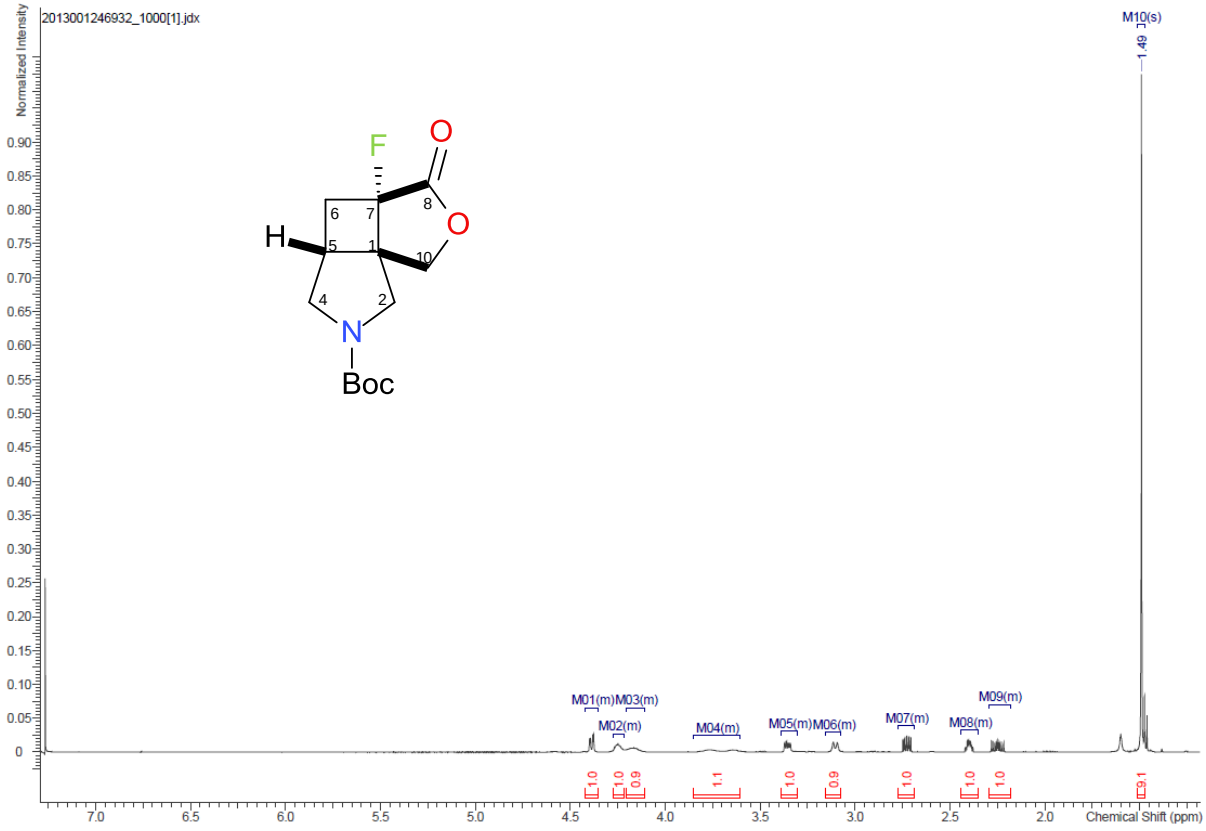



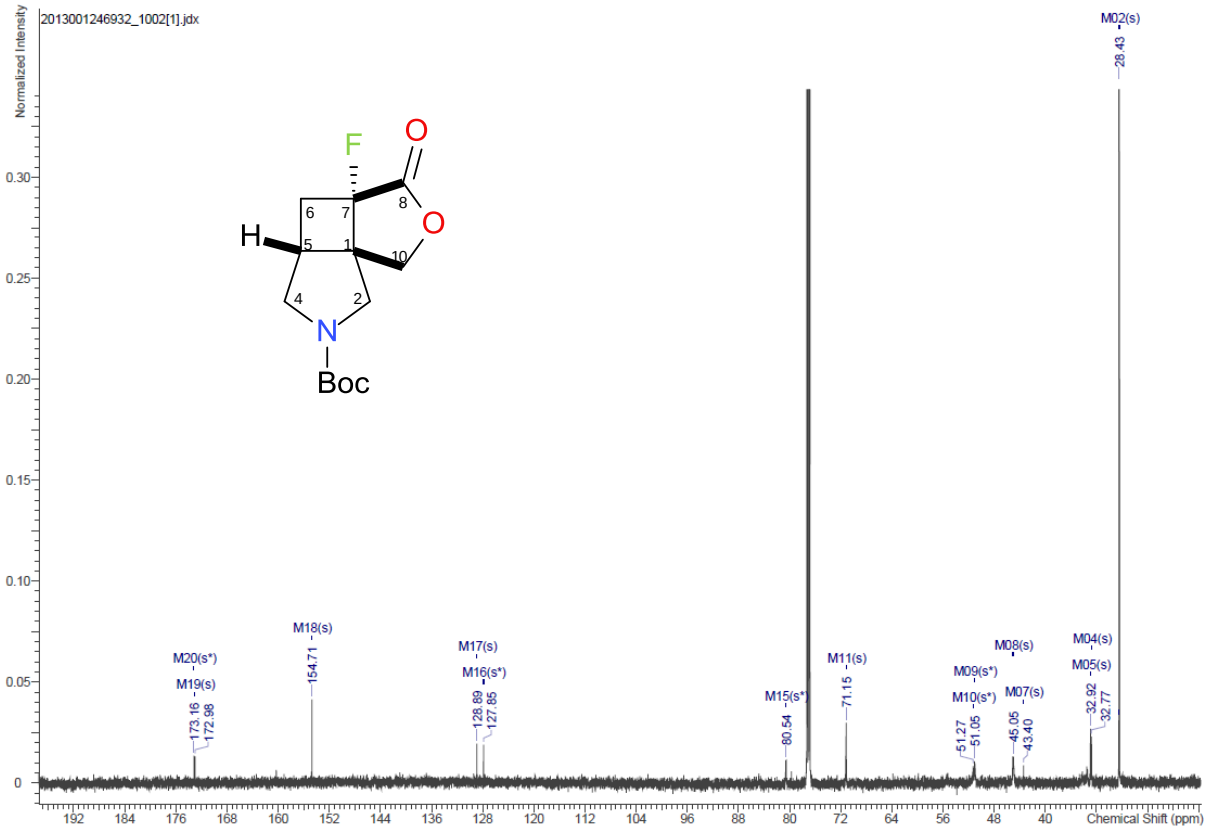
**_tert_-Butyl allyl((4-fluoro-5-oxo-2,5-dihydrofuran-3-yl)methyl)carbamate (20)**



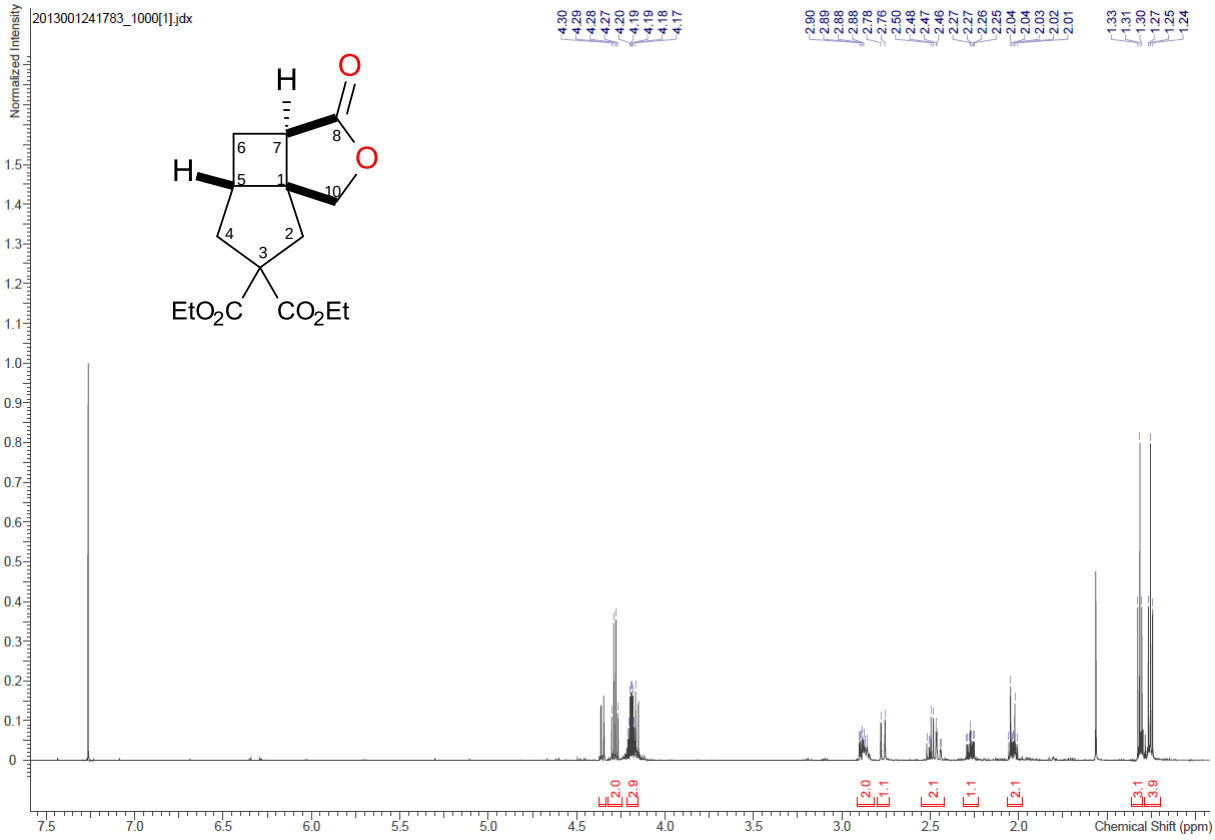



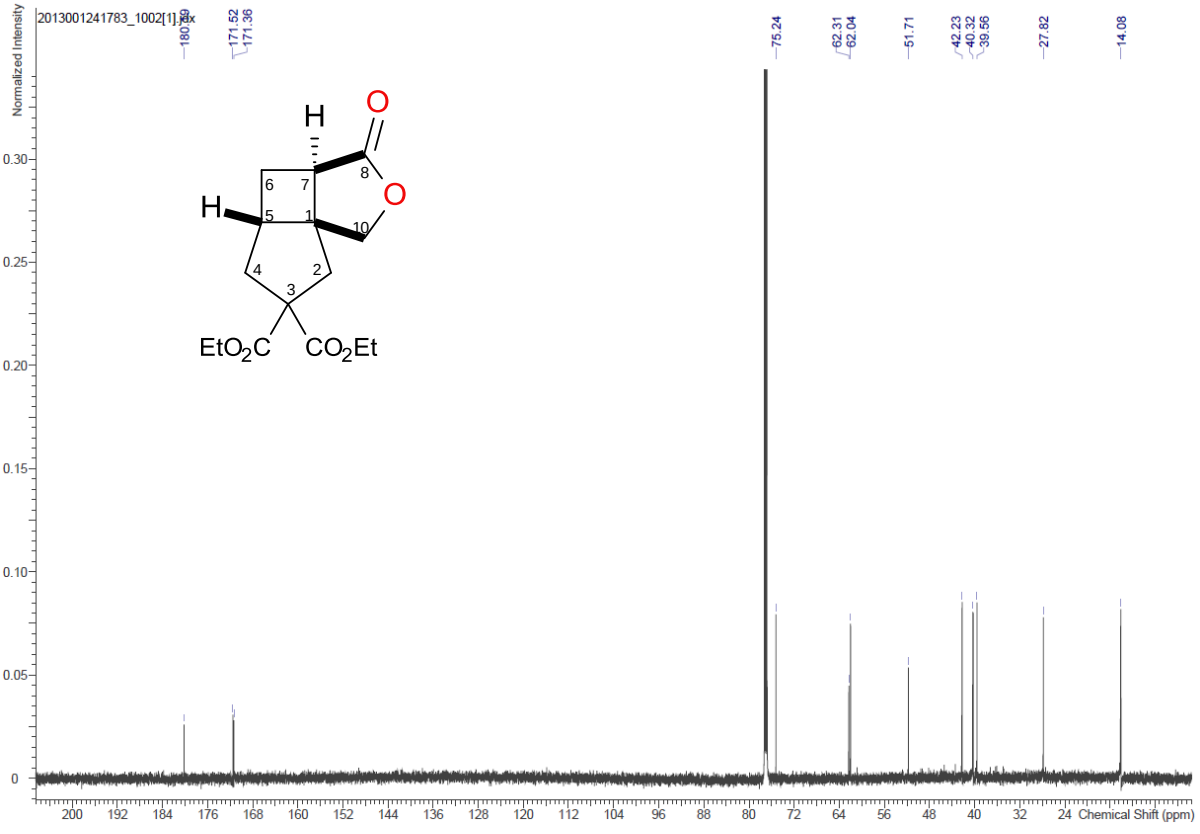
**N-*tert*-Butoxycarbonyl-7-fluor-3-aza-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (21)**



**3,3-Diethoxycarbonyl-9-oxatricyclo[5.3.0.0$^{1,5}$]decan-8-one (25)**



# *Structure Report*

# *No. x2685sls*

## Single crystal X-ray structural analysis of small molecules

Substance:

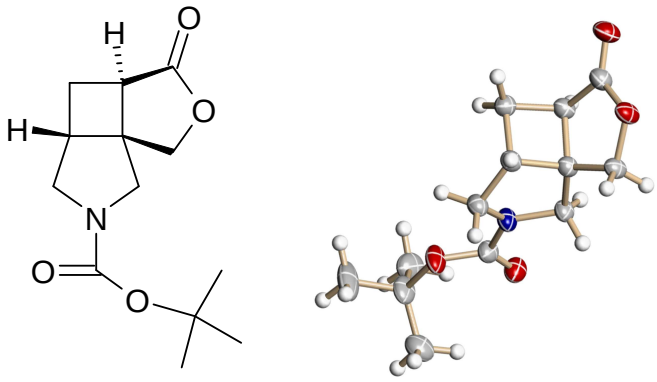
Sample: ELN018429-015-P1

Theme: 7626 Arcade: 2013001242905

Date: 25.03.2013

Analyst: André Alker (65/310) Visum:

Remarks: The structure corresponds to your suggestion (see below). The absolute configuration is **not** determined. It's a racemate.




Distribution: Dr.D.Fort (092/6.76A)

F. Hoffmann-La Roche AG

Crystal data and structure refinement for x2685sls,
Probe: ELN018429-015-P1,Dr.D.Fort

| | |
|---|---|
| Author | André Alker<br>Pharma Research Basel 65/310<br>Phone: 80935<br>Email: andre_m.alker@roche.com |
| Data deposition | Roche CSD structure No. 2685 |
| Empirical formula | C13 H19 N O4 |
| Formula weight | 253.29 |
| Temperature | 89(2) K |
| Wavelength | 0.70000 A |
| Crystal system, space group | Monoclinic, P2(1)/n |
| Unit cell dimensions | a = 10.633(2) A alpha = 90 deg.<br>b = 6.3900(13)A beta = 102.39(3)deg.<br>c = 20.622(4) A gamma = 90 deg. |
| Volume | 1368.5(5) A^3 |
| Z, Calculated density | 4, 1.229 Mg/m^3 |
| Absorption coefficient | 0.091 mm^-1 |
| F(000) | 544 |
| Crystal size | 0.2 x 0.1 x 0.07 mm |
| Theta range for data collection | 2.00 to 26.38 deg. |
| Limiting indices | -13<=h<=13, -7<=k<=7, -25<=l<=25 |
| Reflections collected / unique | 16357 / 2786 [R(int) = 0.0398] |
| Completeness to theta = 26.38 | 99.6 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2786 / 0 / 167 |
| Goodness-of-fit on F^2 | 1.072 |
| Final R indices [I>2sigma(I)] | R1 = 0.0447, wR2 = 0.1170 |
| R indices (all data) | R1 = 0.0455, wR2 = 0.1176 |
| Extinction coefficient | 0.042(4) |
| Largest diff. peak and hole | 0.334 and -0.287 e.A^-3 |

# *Structure Report*

# *No. x2639sls*

## Single crystal X-ray structural analysis of small molecules

Substance: RO6927612-000

Sample: AA0114KK002 (DAF140)

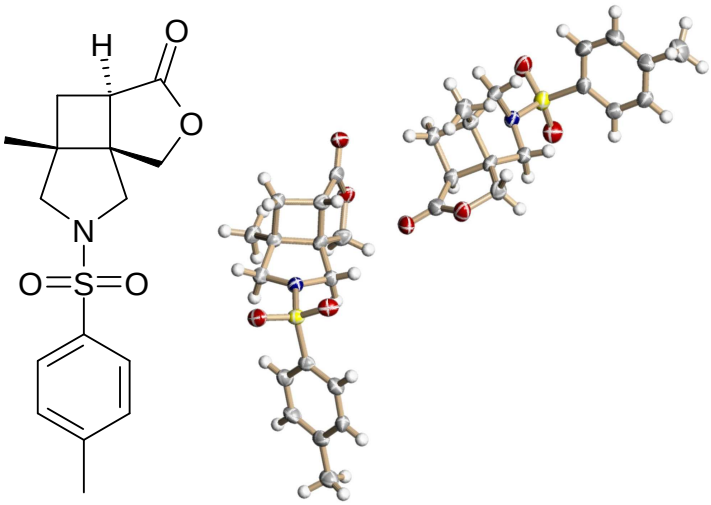
Theme: 7626 Arcade: 2012001233448

Date: 27.12.2012

Analyst: André Alker (65/310) Visum:

Approval: Dr.O.Grassmann Visum:

Remarks: Crystallized by A.Alker from EtOH (cooling crystallization). The relative configuration of the molecule is determined (see below). There are two molecules in the asymmetric unit.




Distribution: D.Fort (092/6.76A)

F. Hoffmann-La Roche AG

Crystal data and structure refinement for x2639sls,
Probe: RO6927612-000,AA0114KK002,DAF140,D.Fort,A.Alker

| | |
|---|---|
| Author | André Alker<br>Pharma Research Basel 65/310<br>Phone: 80935<br>Email: andre_m.alker@roche.com |
| Data deposition | Roche CSD structure No. 2639 |
| Empirical formula | C16 H19 N O4 S |
| Formula weight | 321.38 |
| Temperature | 89(2) K |
| Wavelength | 0.70000 A |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 39.216(8) A alpha = 90 deg.<br>b = 5.9050(12)A beta = 96.31(3)deg.<br>c = 13.085(3) A gamma = 90 deg. |
| Volume | 3011.7(10) A^3 |
| Z, Calculated density | 8, 1.418 Mg/m^3 |
| Absorption coefficient | 0.233 mm^-1 |
| F(000) | 1360 |
| Crystal size | 0.60 x 0.02 x 0.01 mm |
| Theta range for data collection | 0.52 to 23.25 deg. |
| Limiting indices | -43<=h<=43, -6<=k<=6, -14<=l<=14 |
| Reflections collected / unique | 26501 / 4314 [R(int) = 0.0197] |
| Completeness to theta = 23.25 | 99.3 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4314 / 0 / 402 |
| Goodness-of-fit on F^2 | 1.227 |
| Final R indices [I>2sigma(I)] | R1 = 0.0724, wR2 = 0.2069 |
| R indices (all data) | R1 = 0.0736, wR2 = 0.2073 |
| Extinction coefficient | 0.0027(4) |
| Largest diff. peak and hole | 0.524 and -0.399 e.A^-3 |