Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Gold(I)-Catalyzed Access to Neomerane Skeletons

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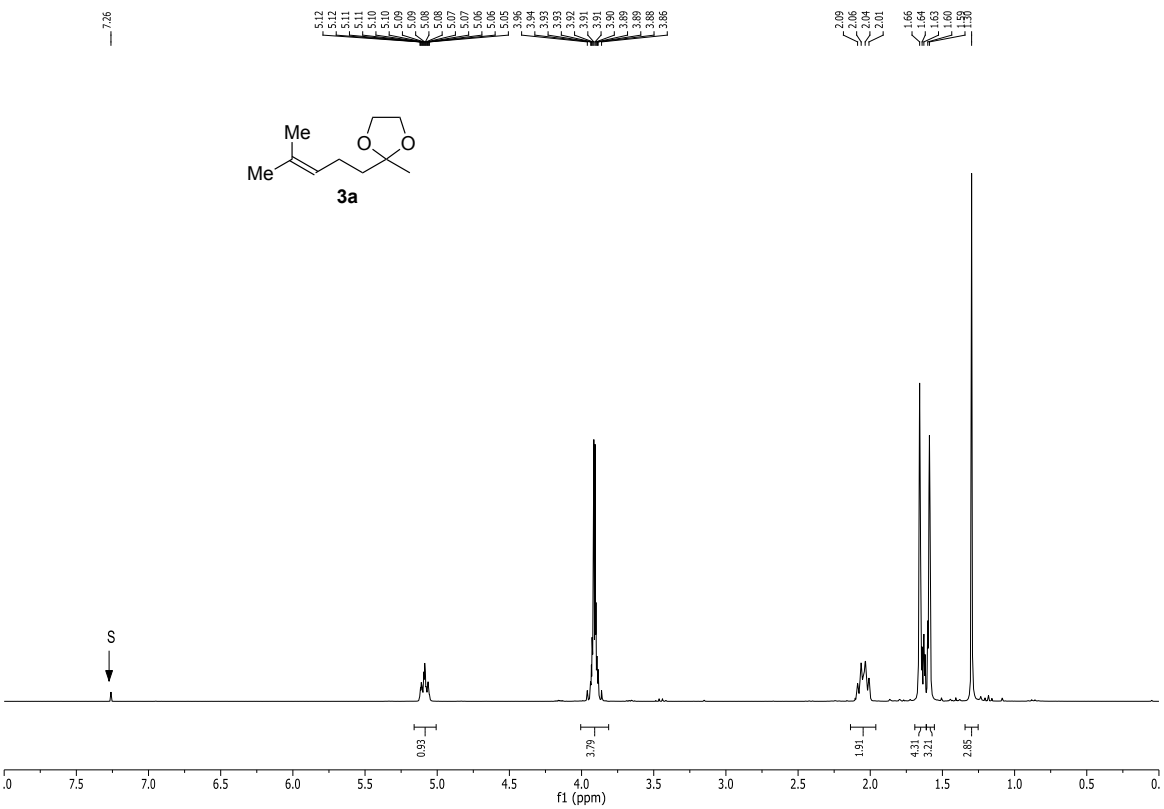
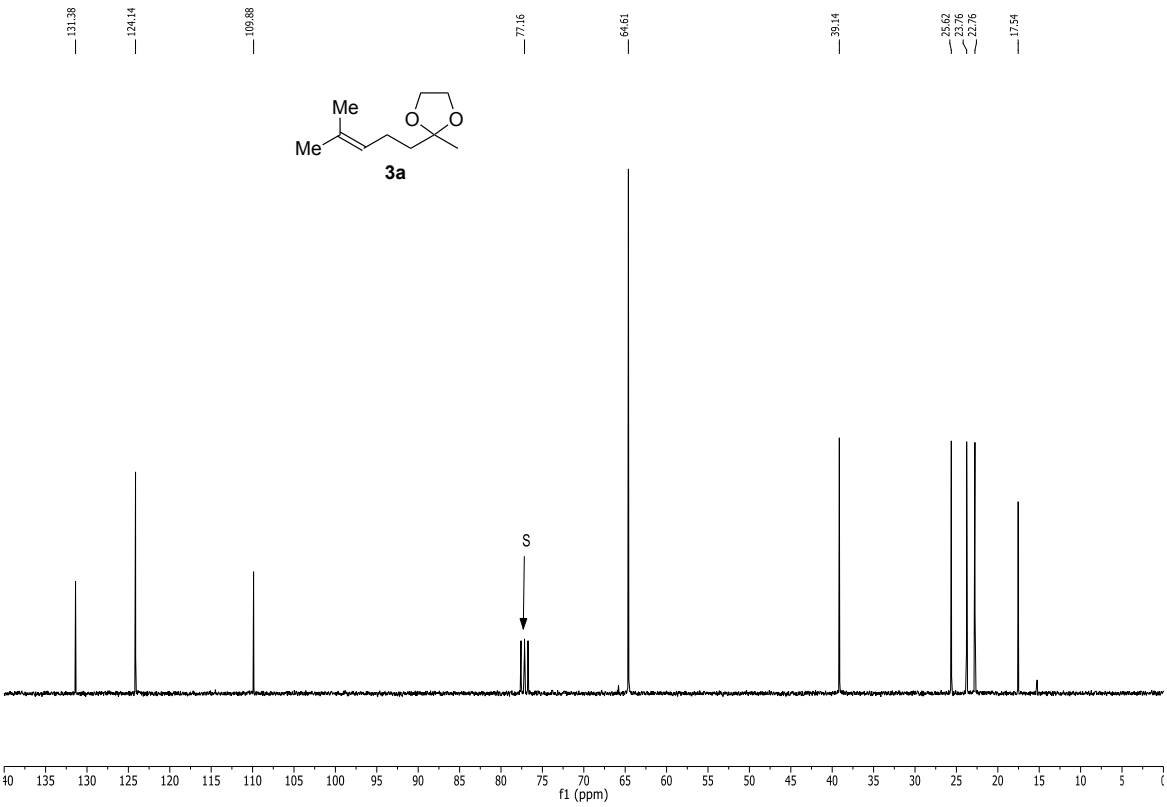
Table of contents

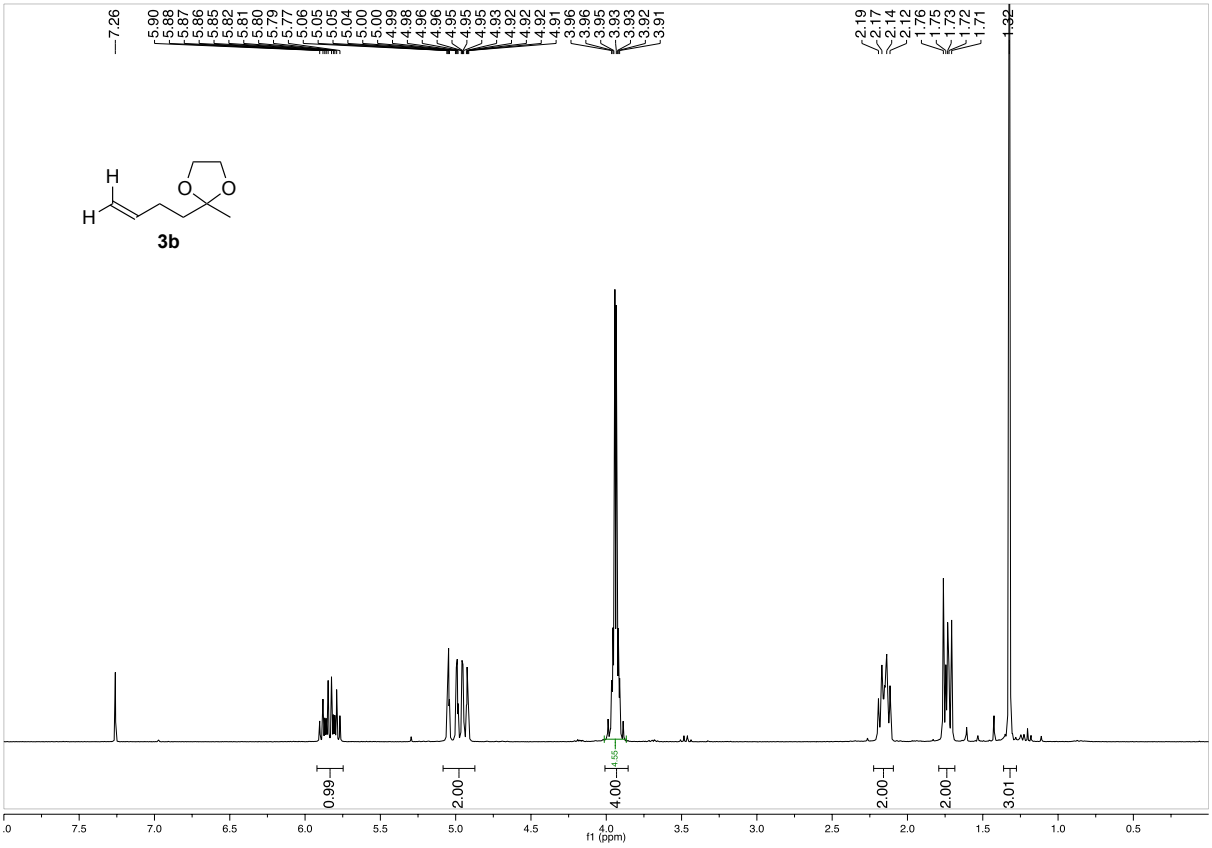
1. Spectral data

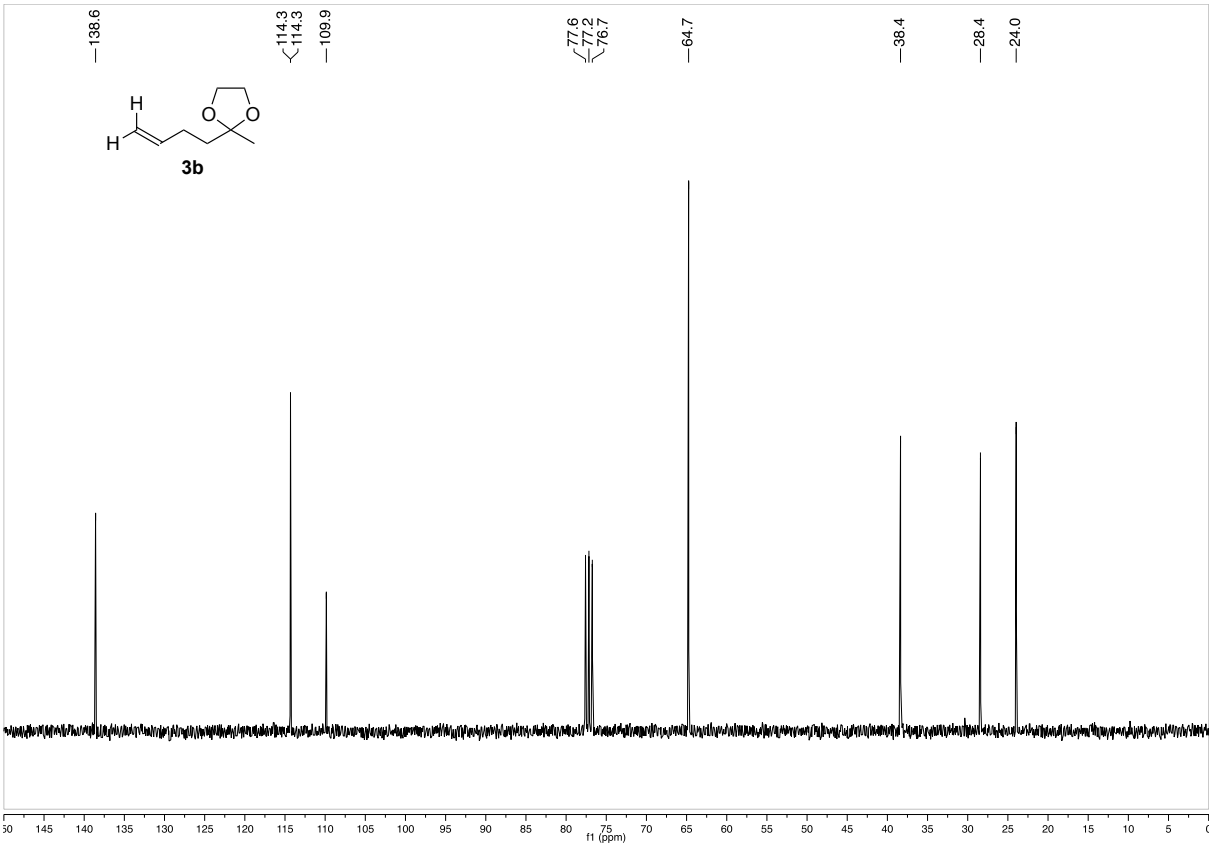
*2-Methyl-2-(4-methylpent-3-en-1-yl)-1,3-dioxolane (**3a**)*



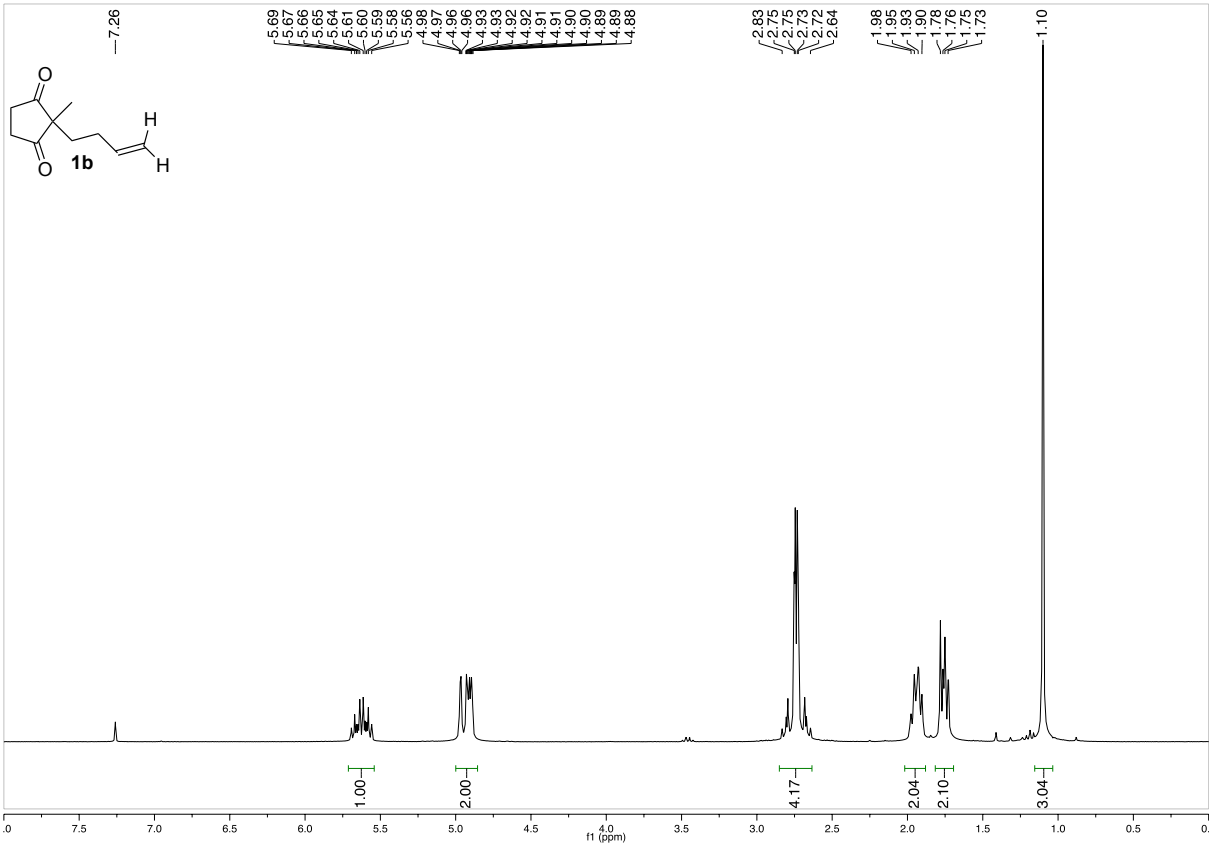


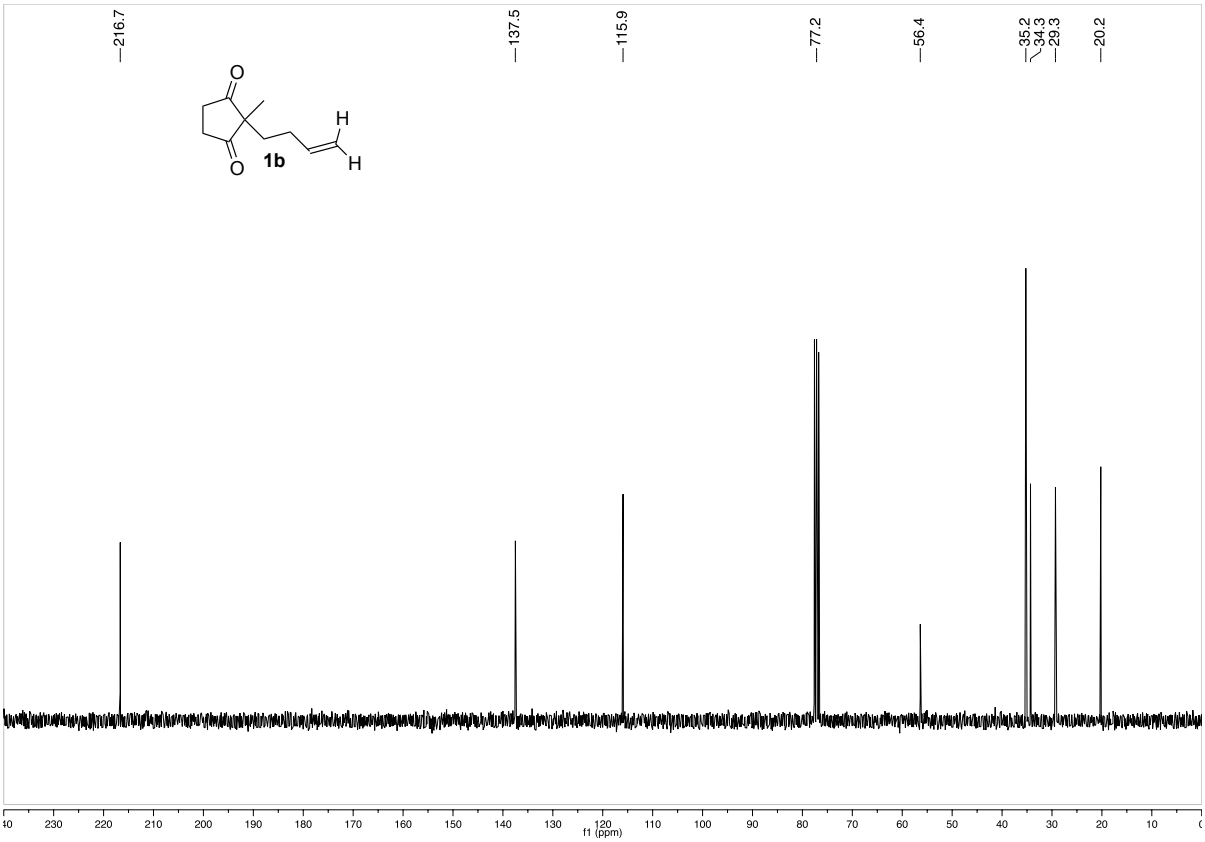
*2-(But-3-en-1-yl)-2-methyl-1,3-dioxolane (***3b)**



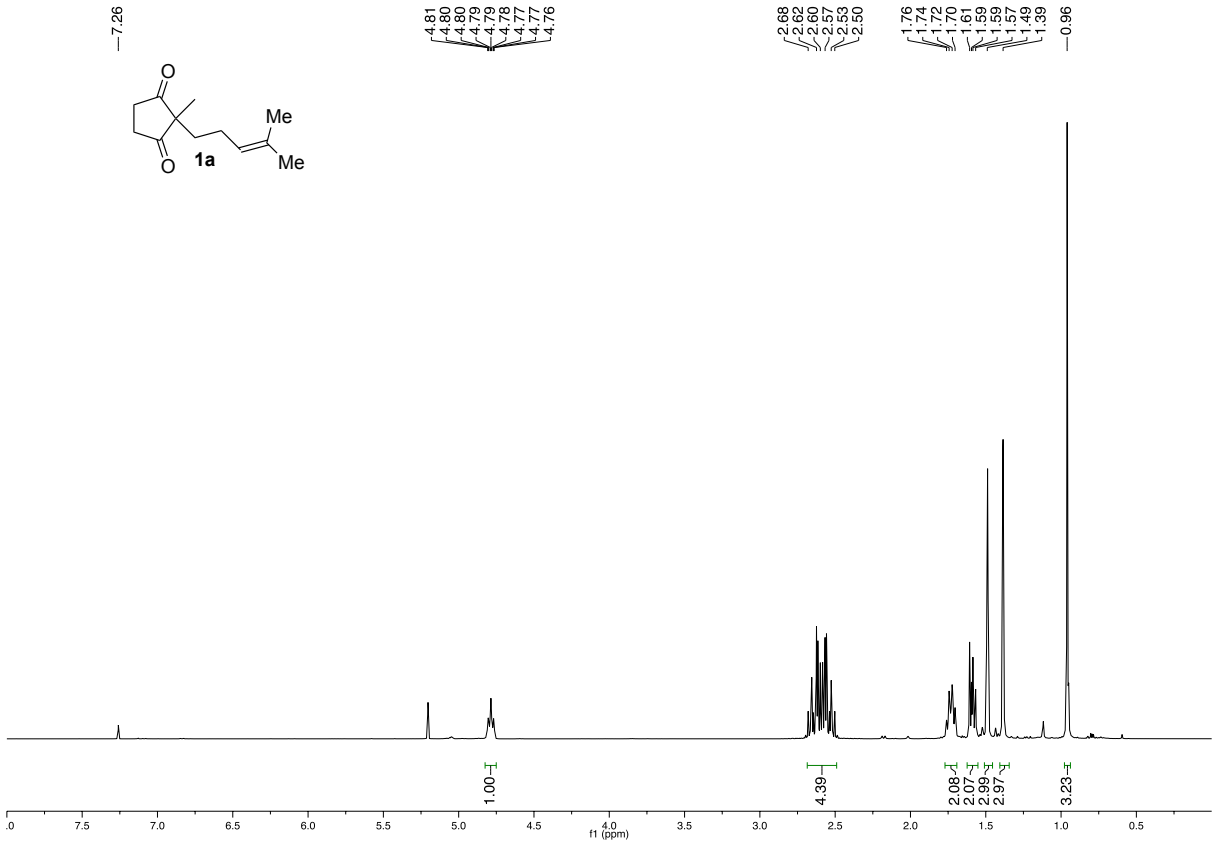


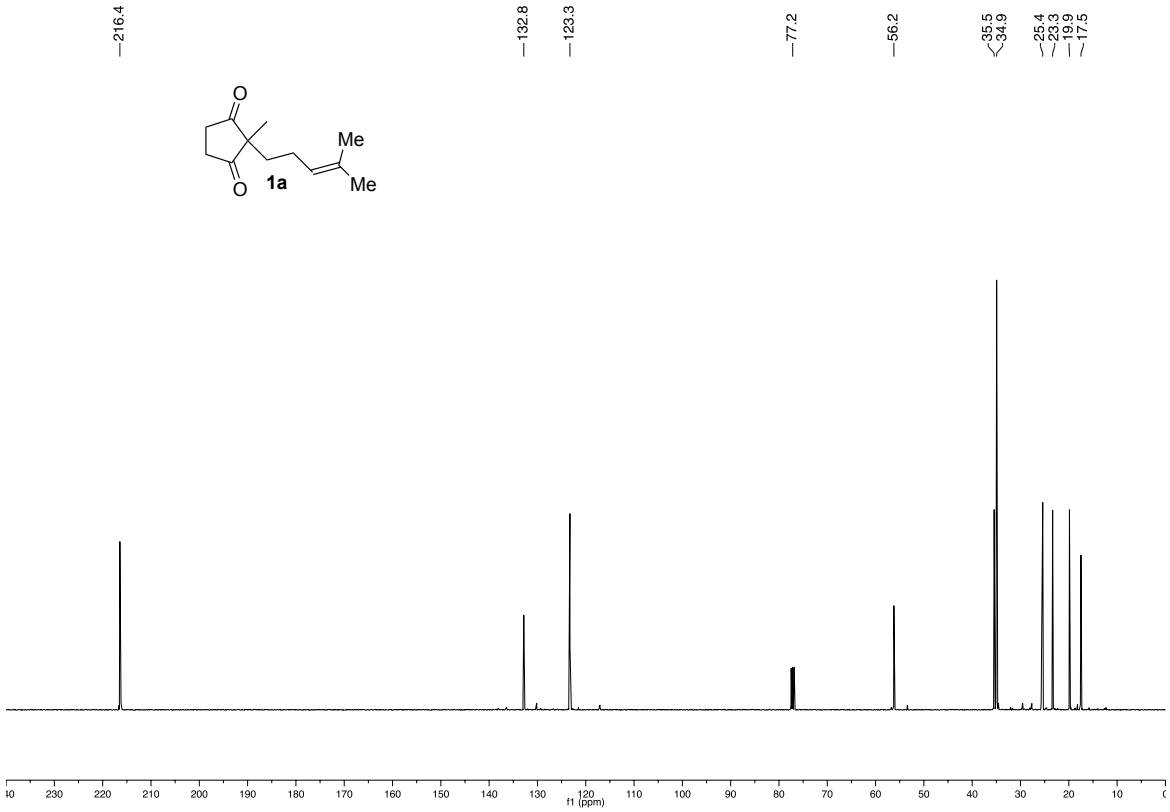
*2-(but-3-en-1-yl)-2-methylcyclopentane-1,3-dione (**1b**)*



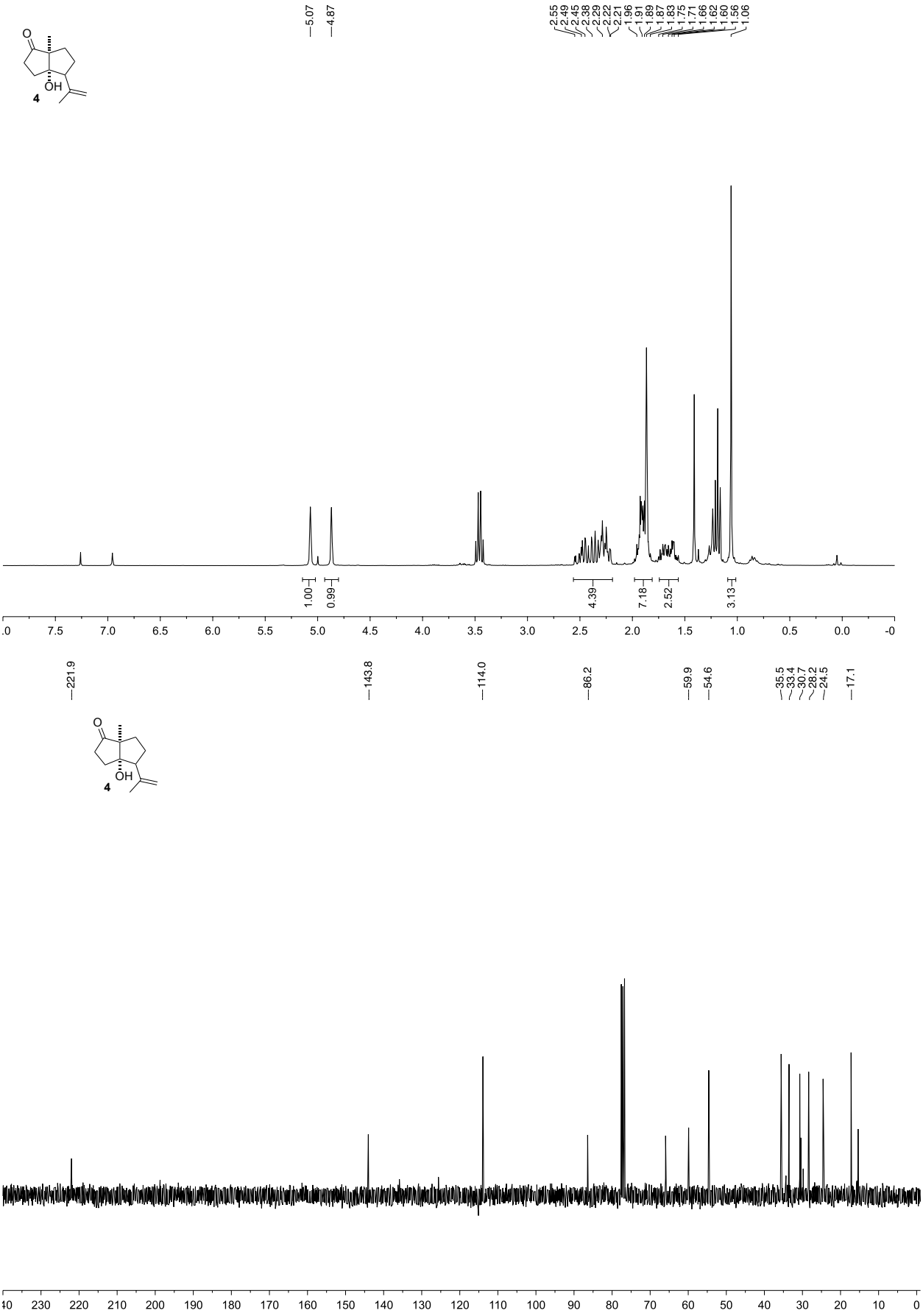


*2-methyl-2-(4-methylpent-3-en-1-yl)cyclopentane-1,3-dione (**1a**)*

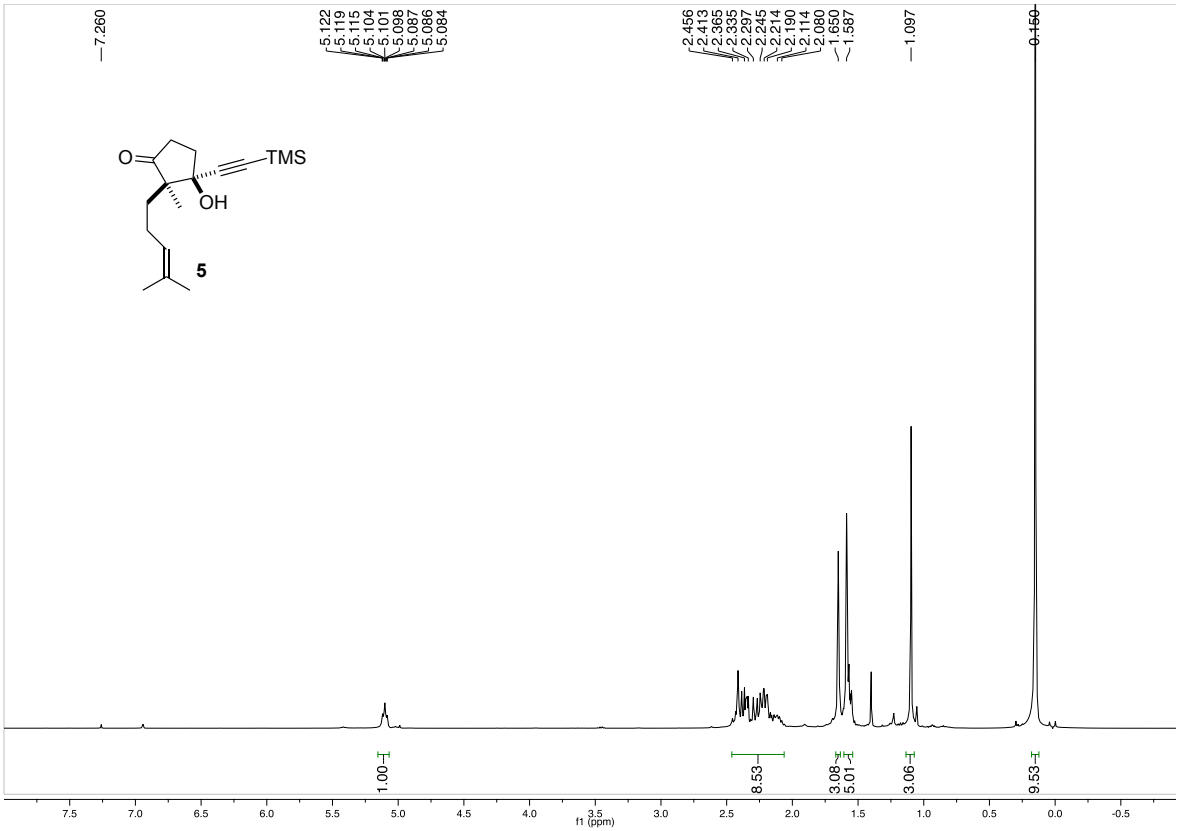


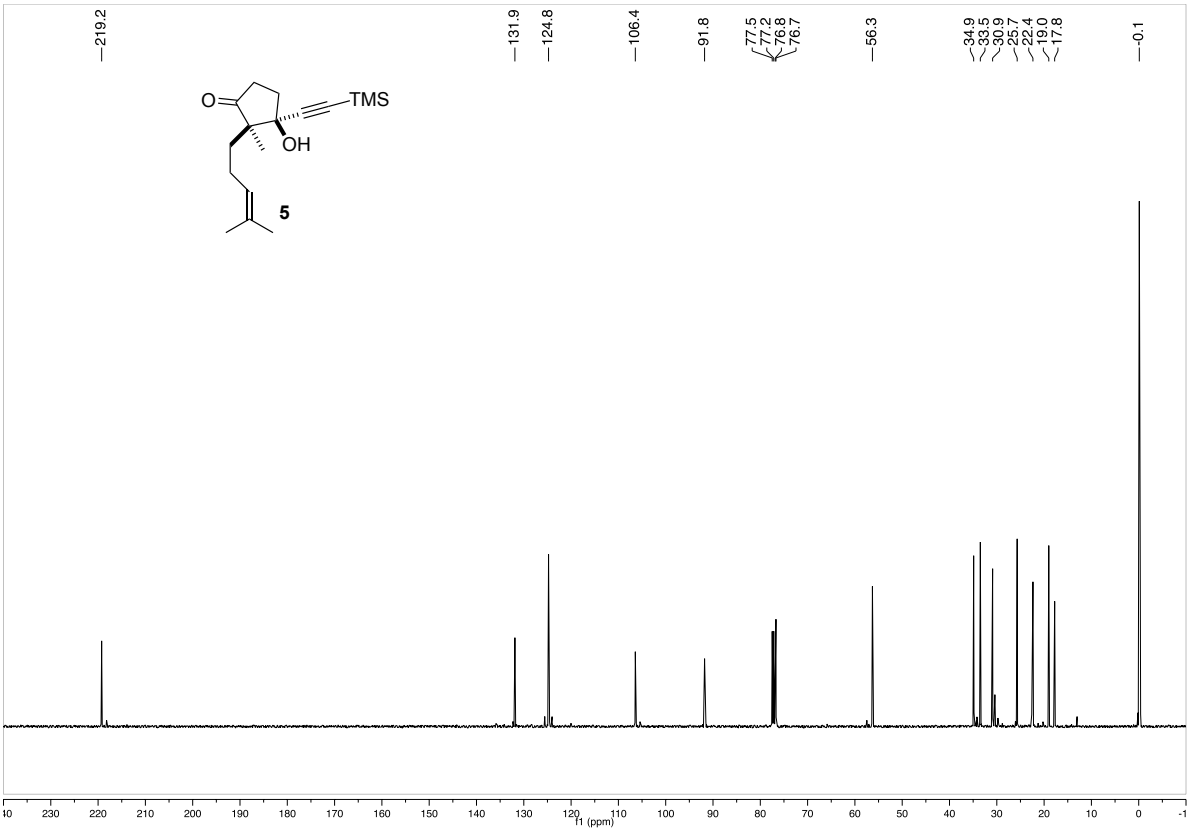


*3α-hydroxy-6α-methyl-4-(prop-1-en-2-yl)hexahydropentalen-1(2H)-one (**4**)*



*3-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-3-((trimethylsilyl)ethynyl)cyclopentanone (**5**)*





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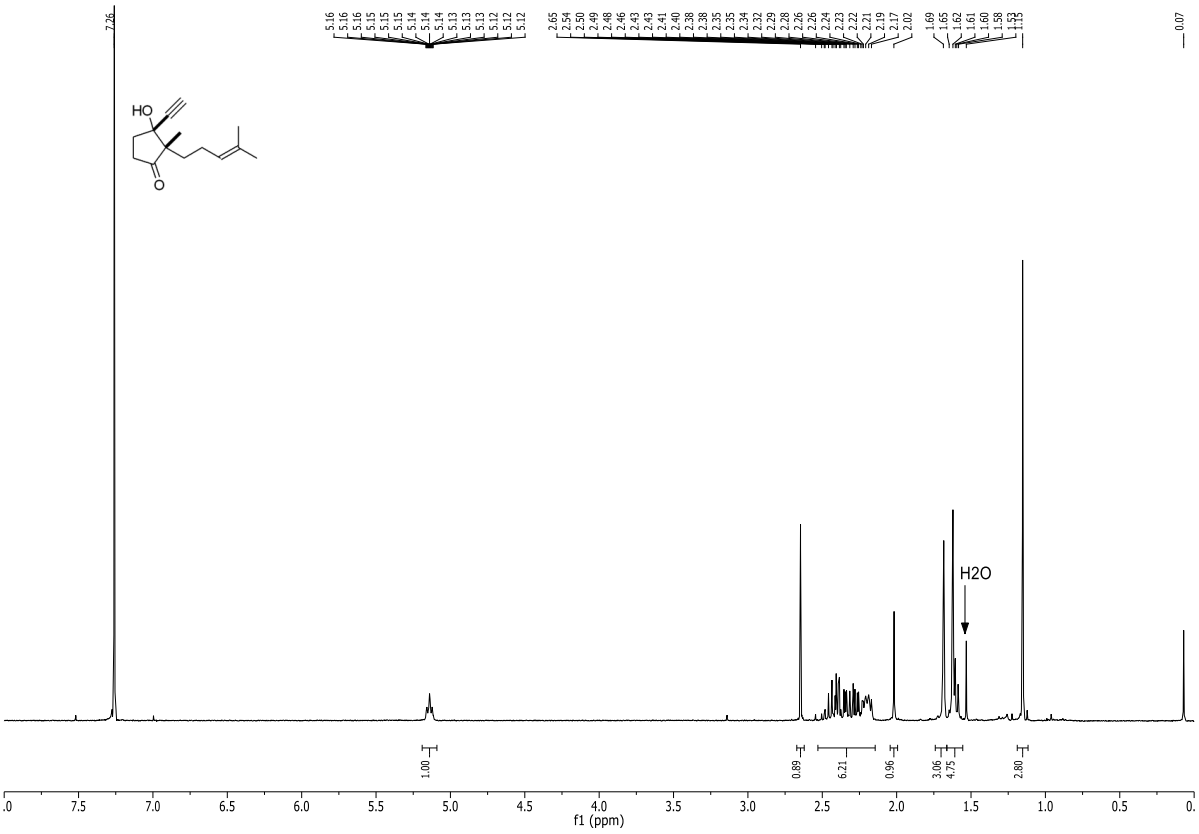
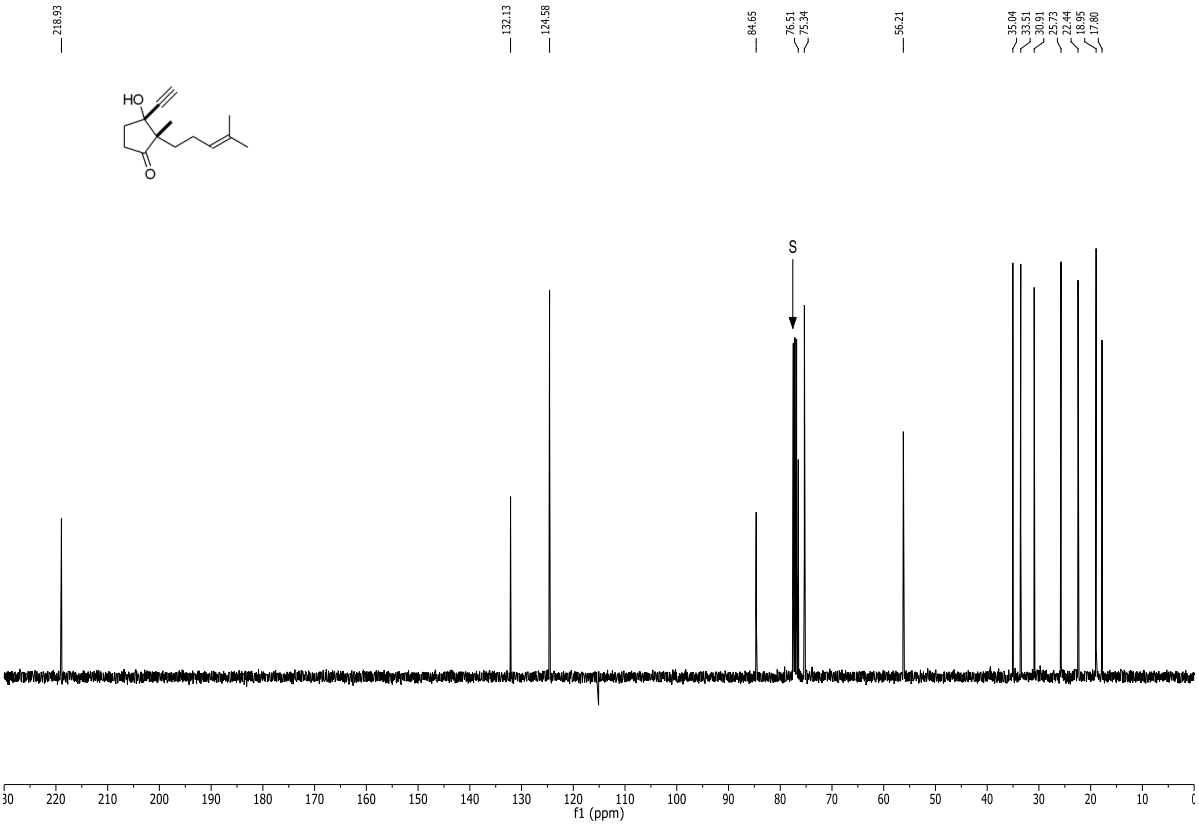
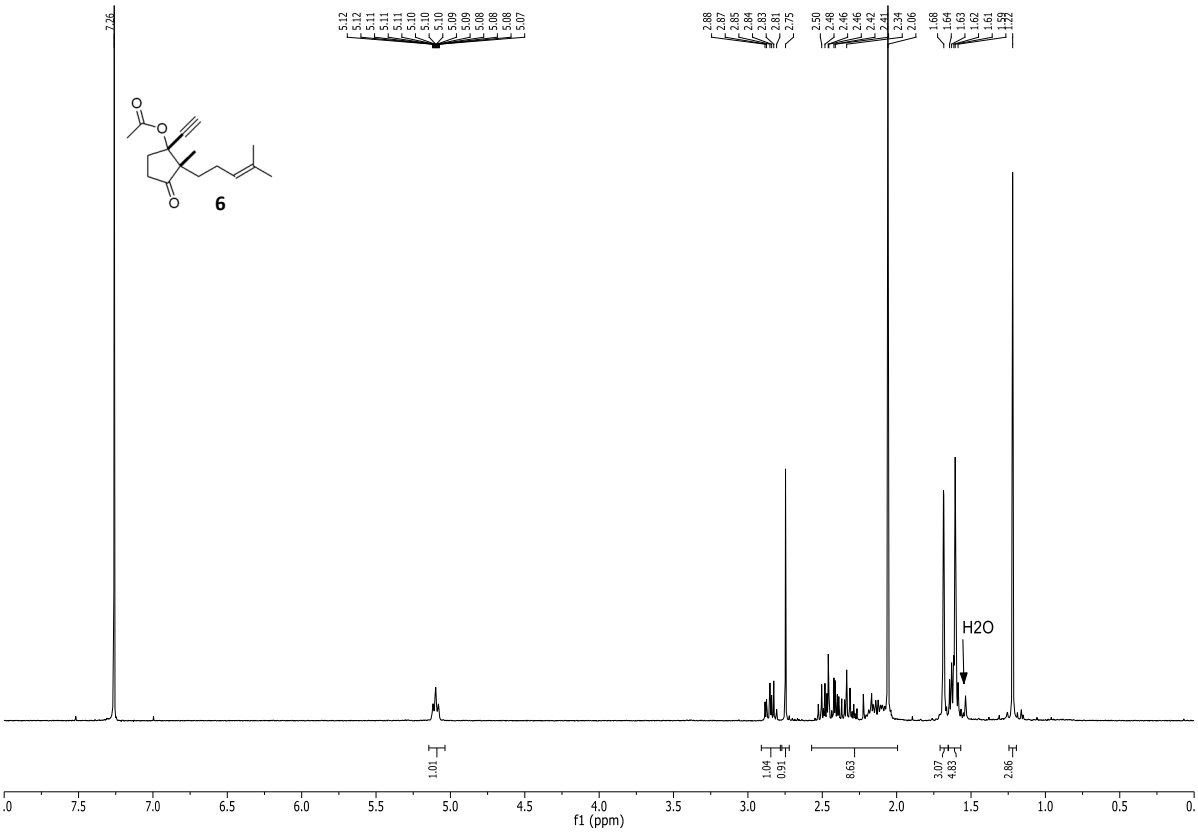
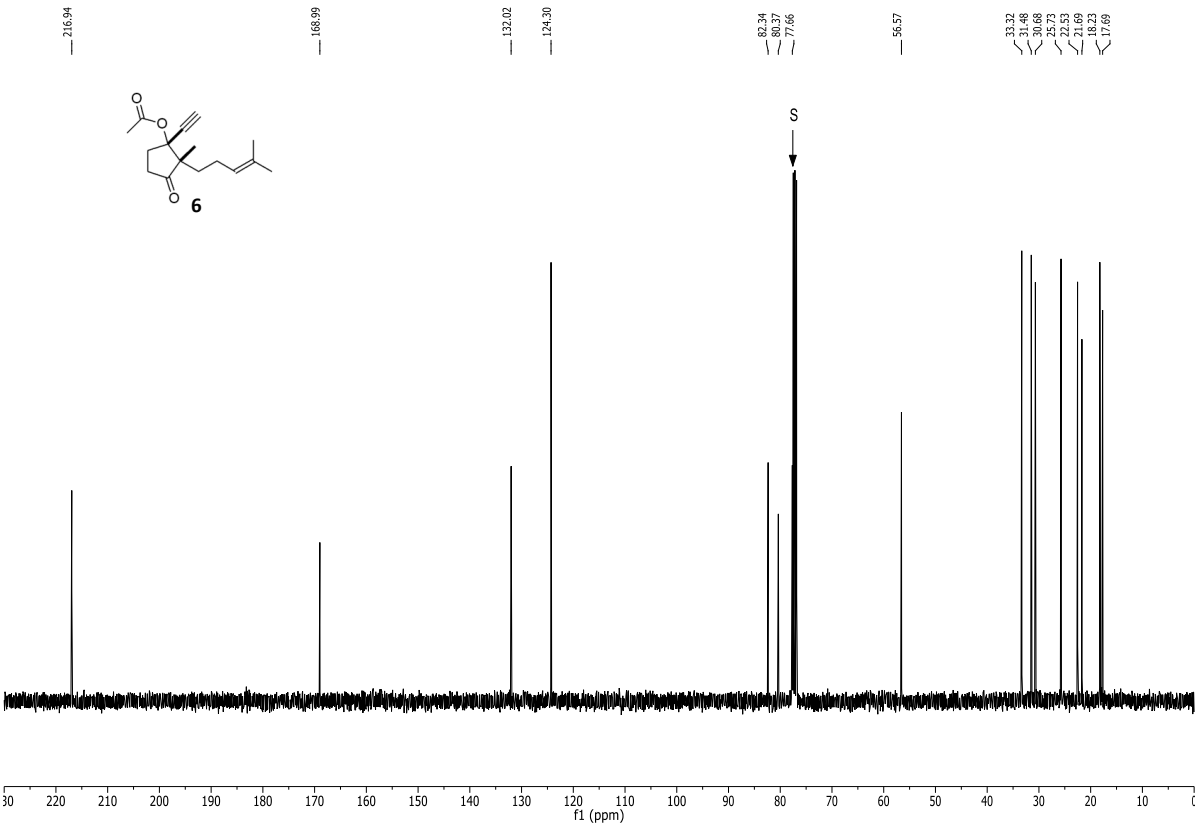


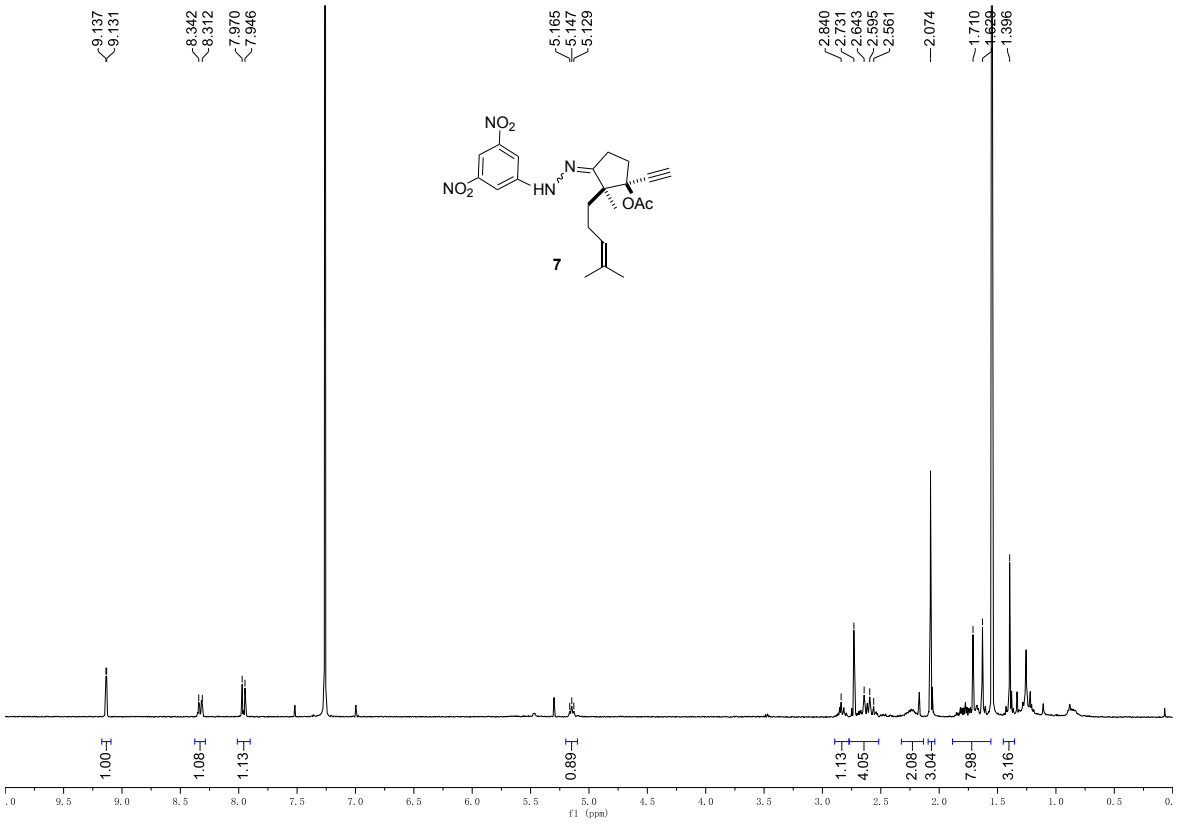


*1-ethynyl-2-methyl-2-(4-methylpent-3-en-1-yl)-3-oxocyclopentyl acetate (**6**)*

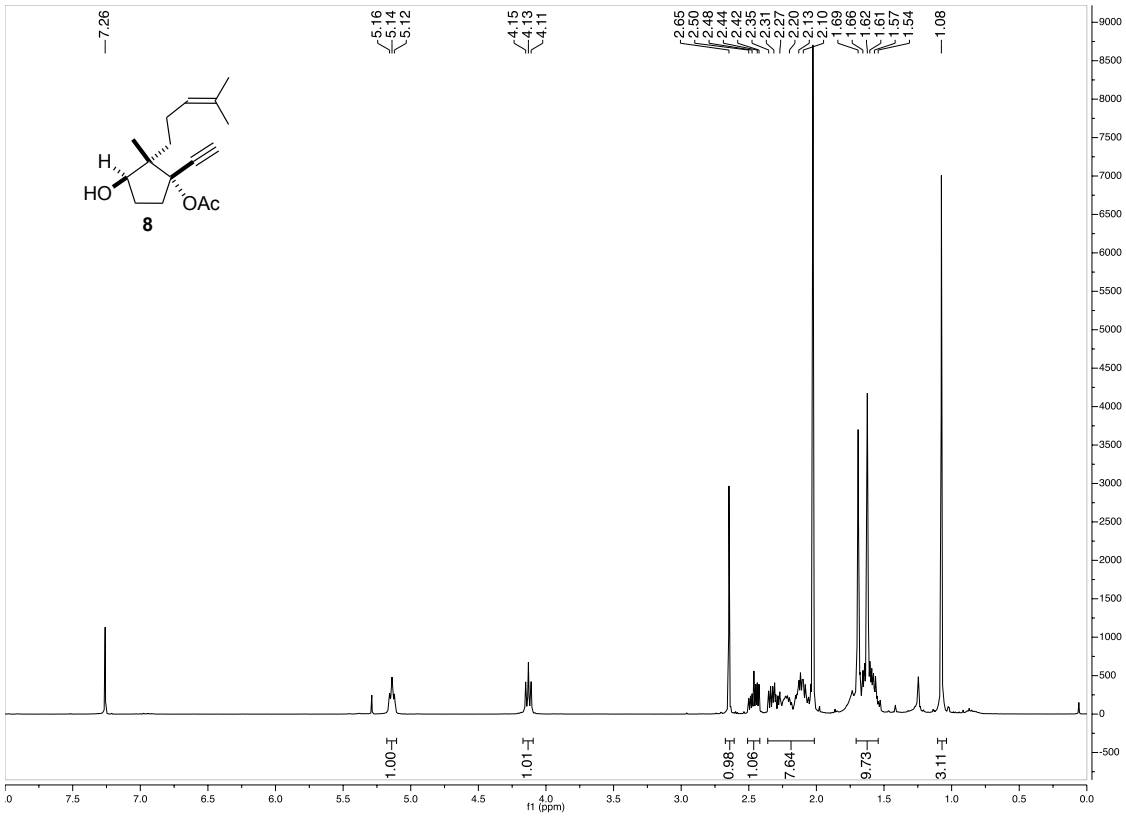


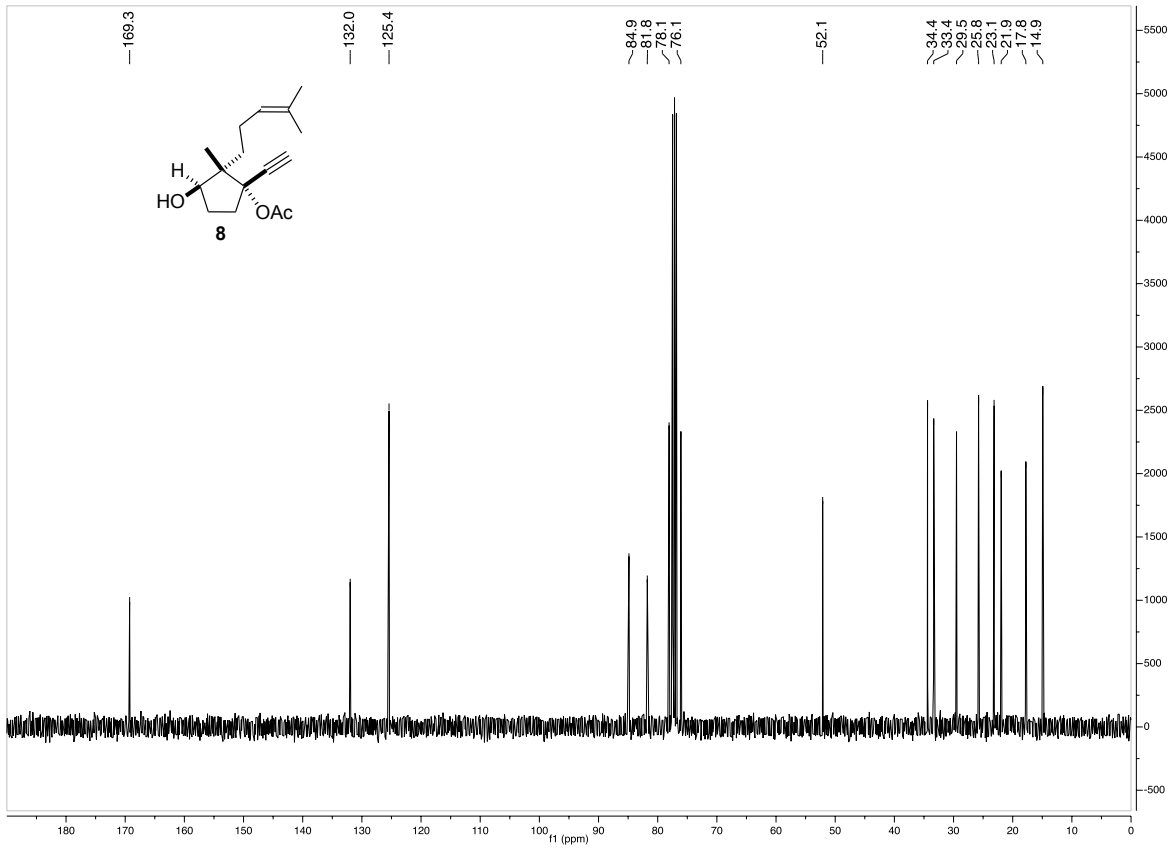


*3-((2,4-dinitrophenyl)imino)-1-ethynyl-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopentyl acetate (**7**)*

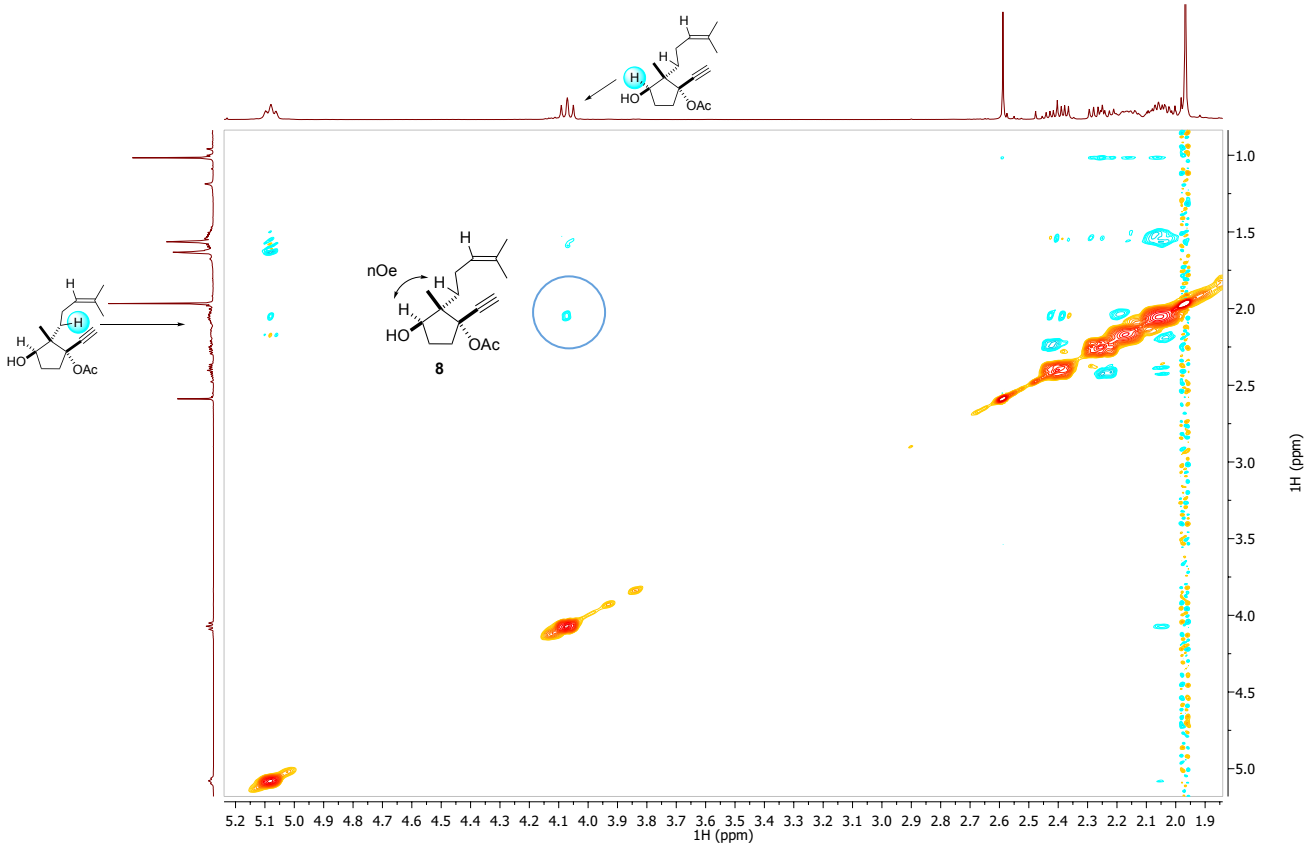


*1-ethynyl-3-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopentyl acetate (**8**)*

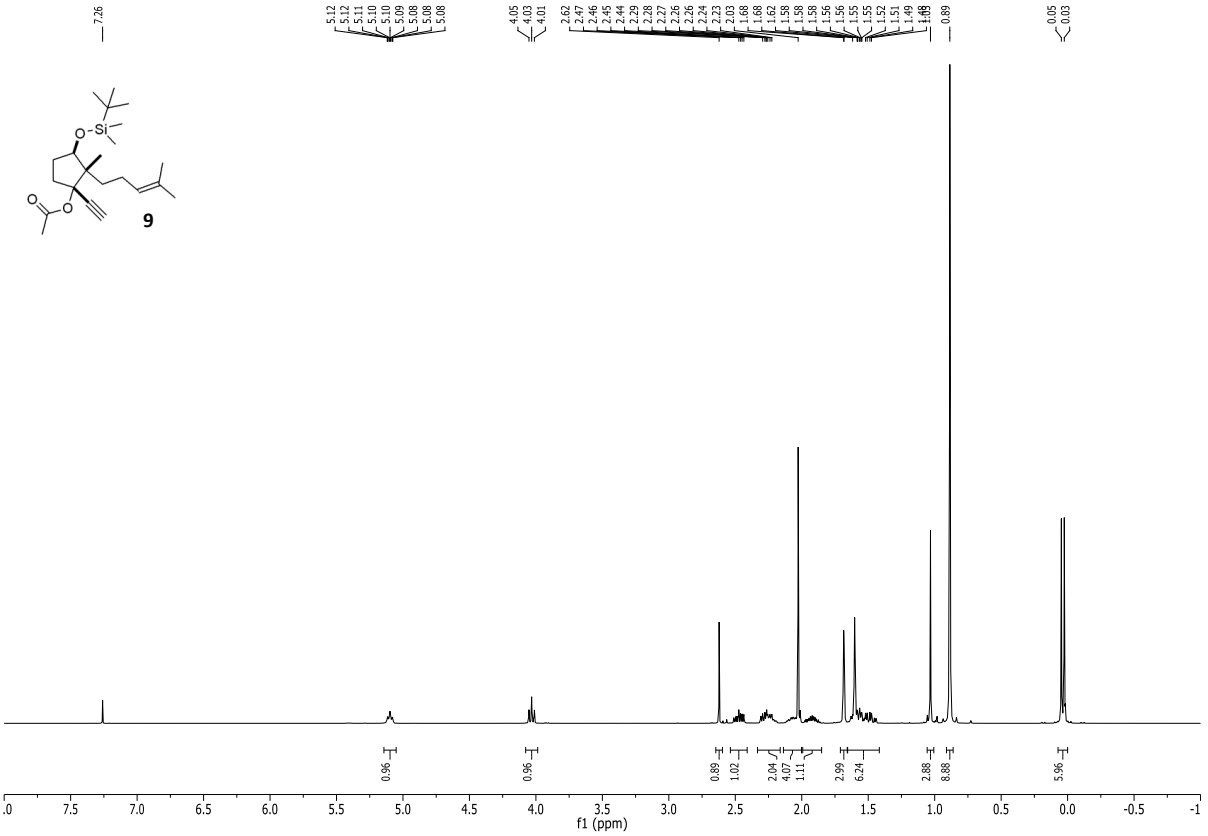


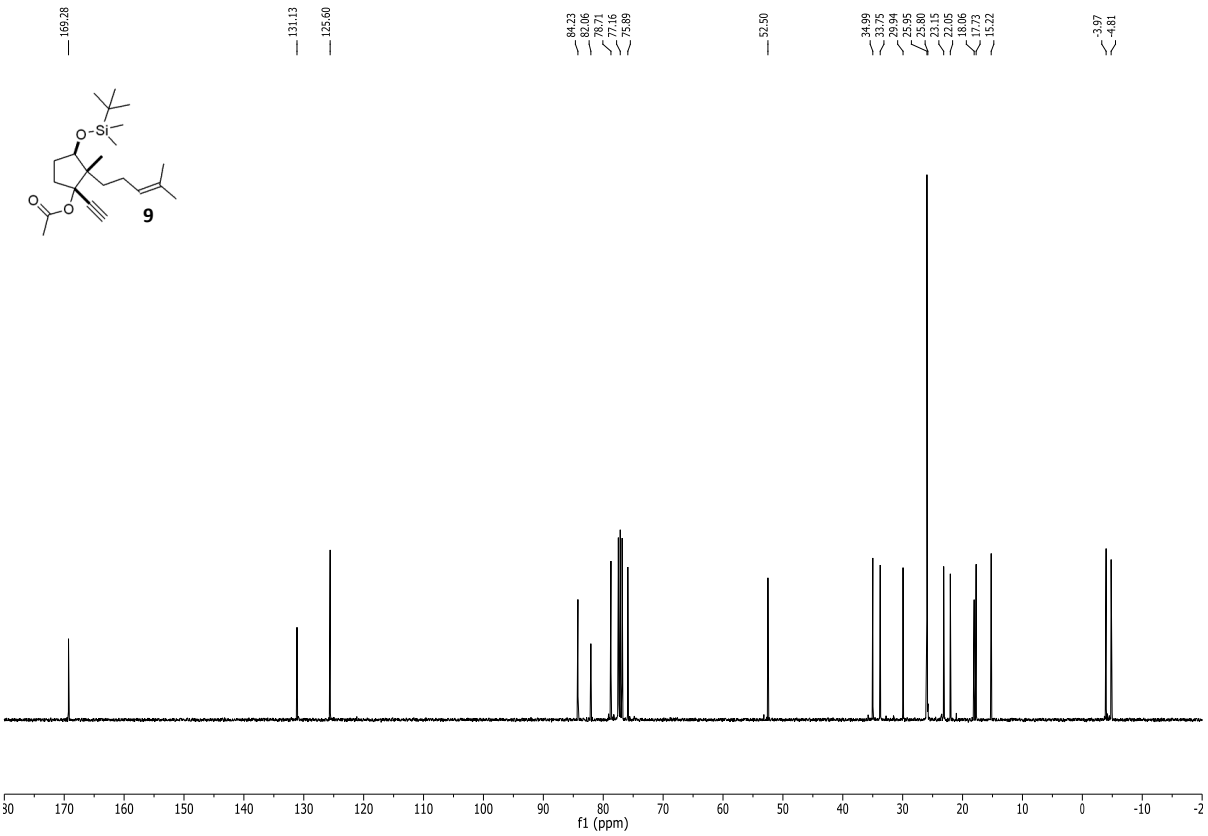


nOe effect compound **8**

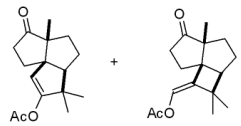


*3-(tert-butyldimethylsilyl)oxy)-1-ethynyl-2-methyl-2-(4-methylpent-3-en-1-yl)cyclopentyl acetate (**9**)*





*(E)-(2,2,4a-trimethyl-5-oxooctahydro-1H-cyclobuta[c]pentalen-1-ylidene)methyl acetate (**10**) and 3,3,5a-trimethyl-6-oxo-3,3a,4,5,5a,6,7,8-octahydrocyclopenta[c] pentalen-2-yl acetate (**11**)*



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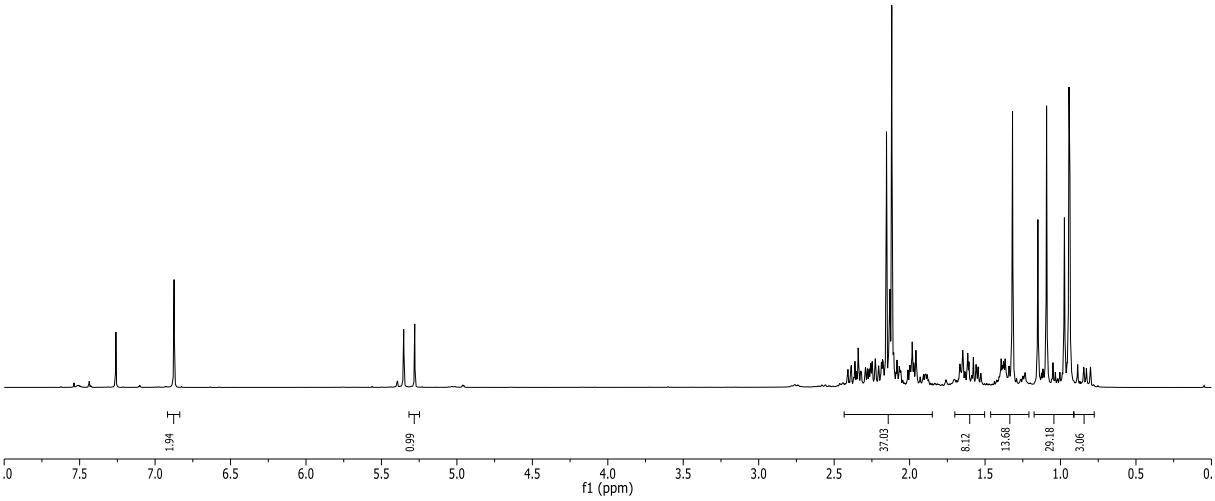

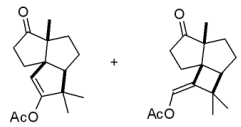

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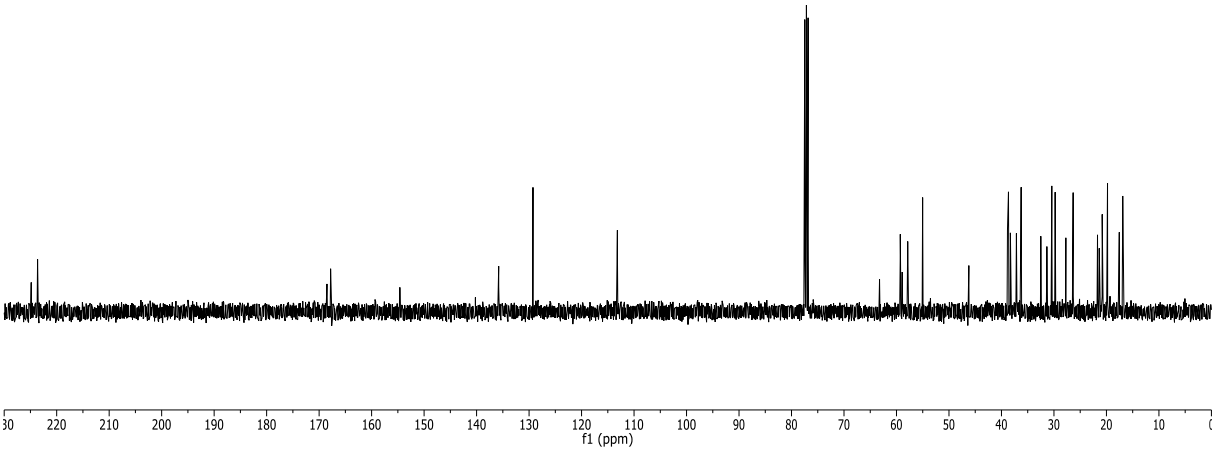
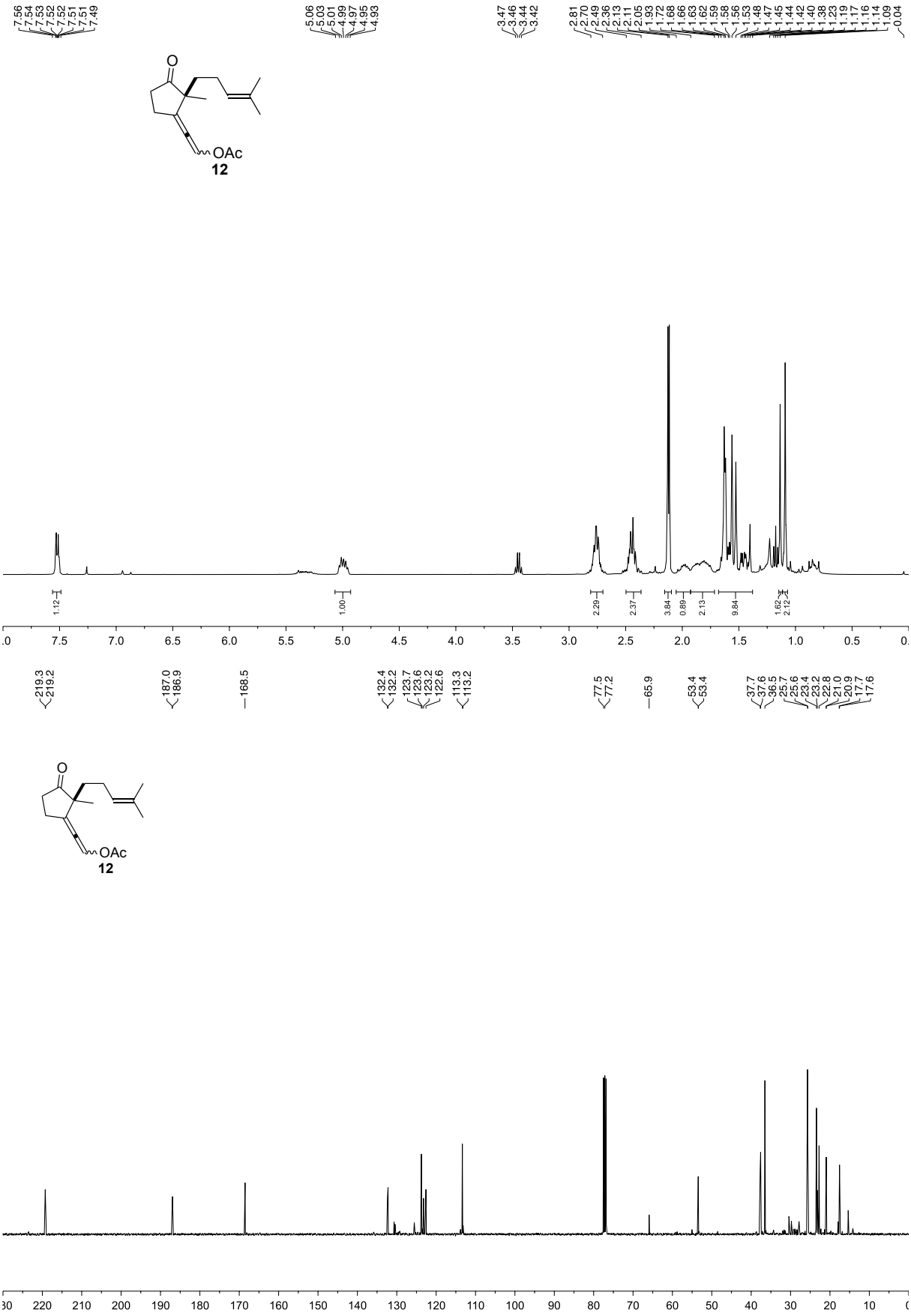
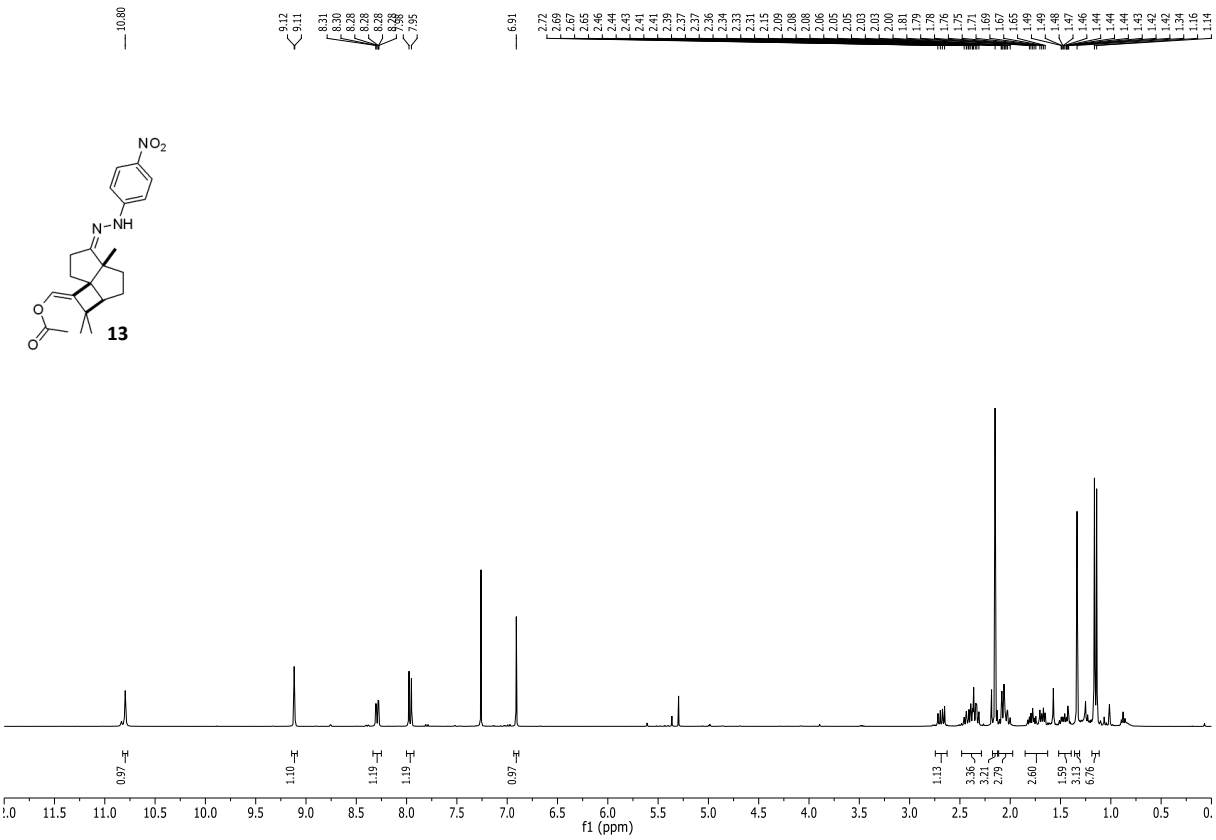
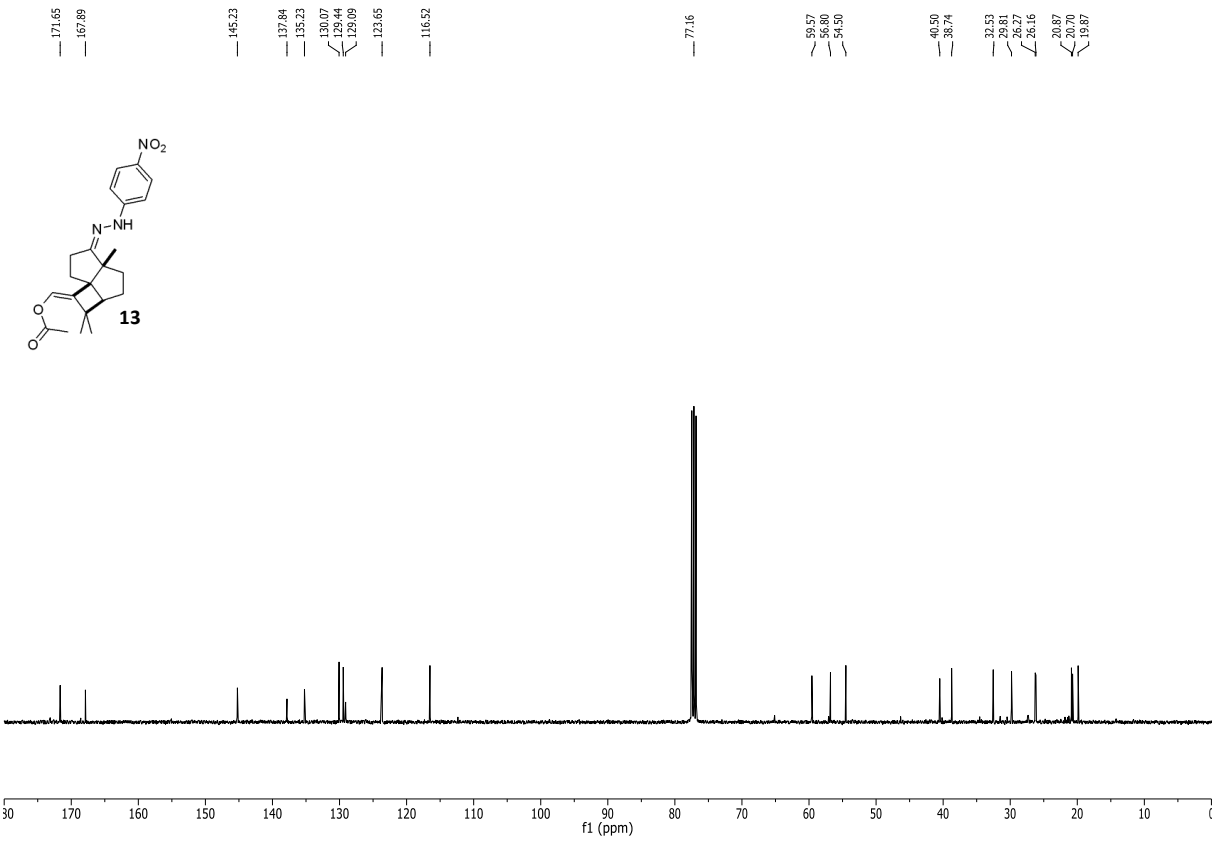


*2-(2-methyl-2-(4-methylpent-3-en-1-yl)-3-oxocyclopentylidene)vinyl acetate (**12**)*

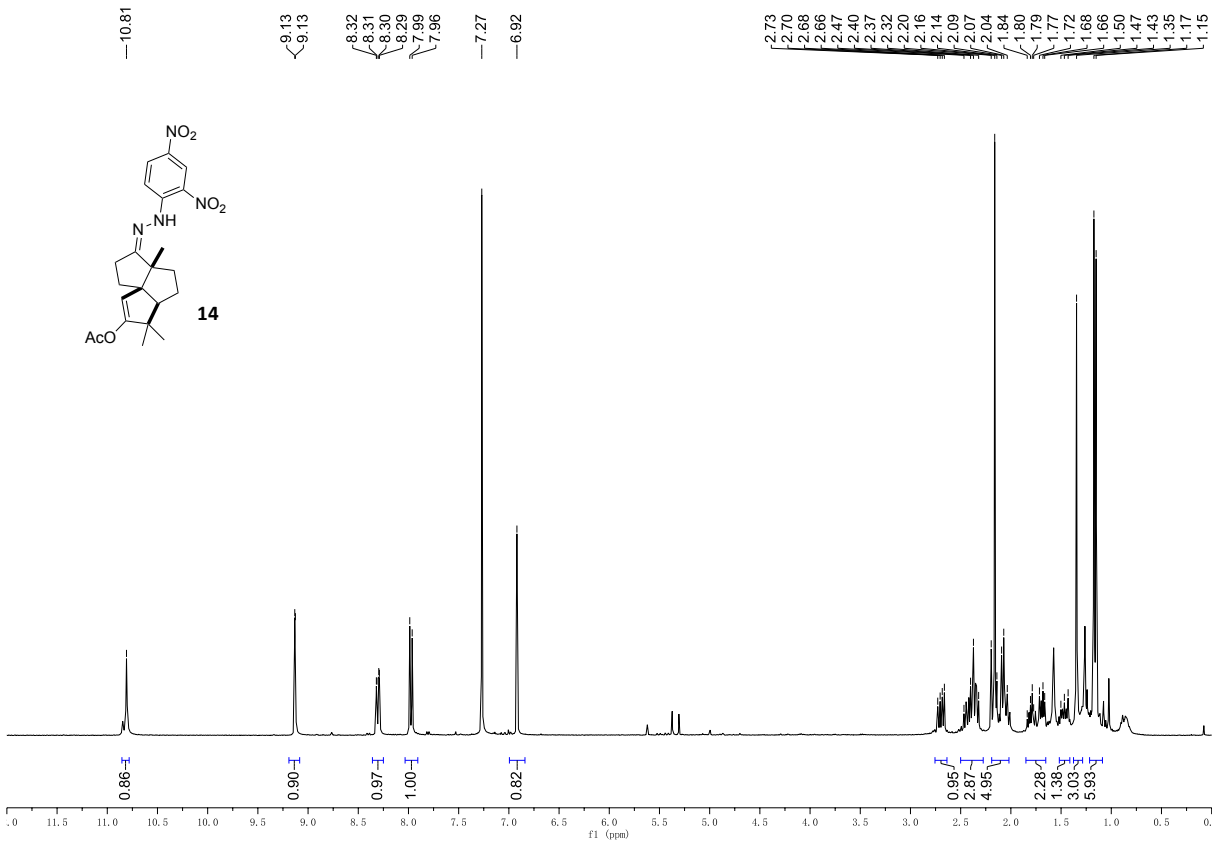


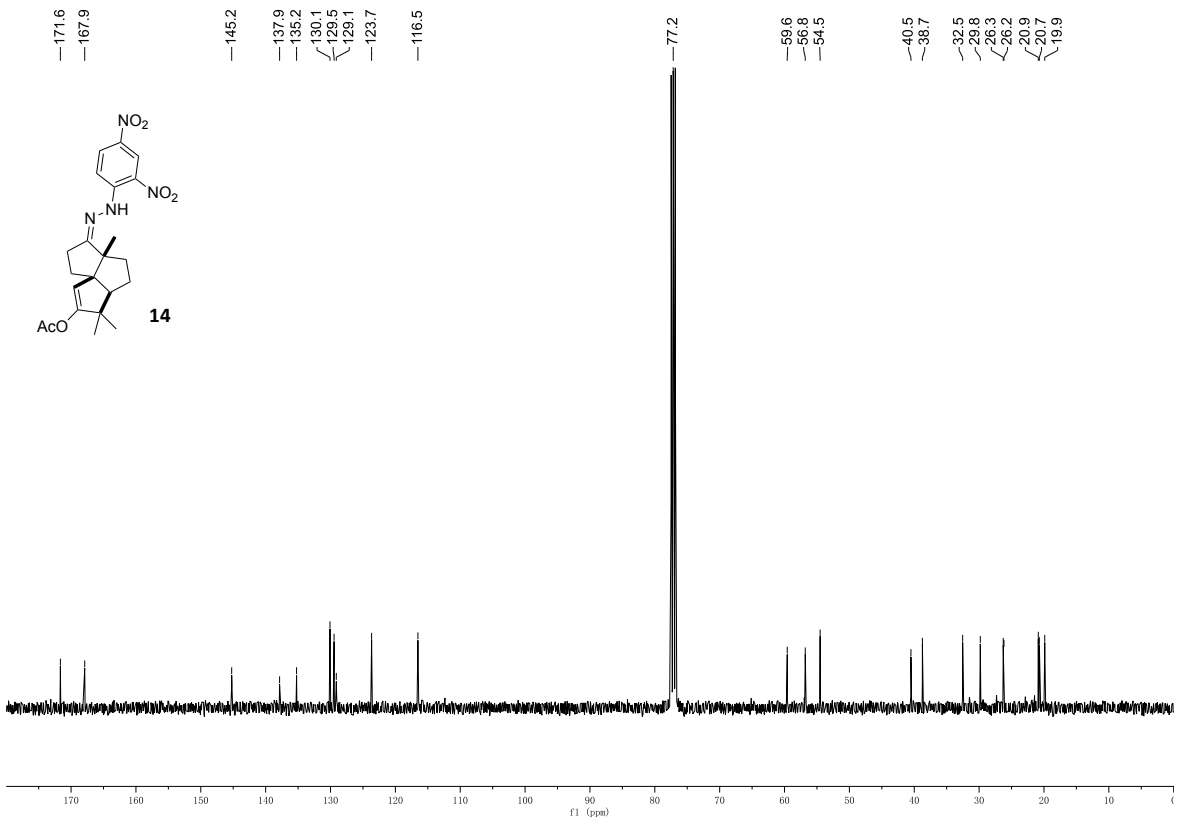
*(E)-(2,2,4a-trimethyl-5-(2-(4-nitrophenyl)hydrazono)octahydro-1H-cyclobuta[c]pentalen-1-ylidene)methyl acetate (**13**)*



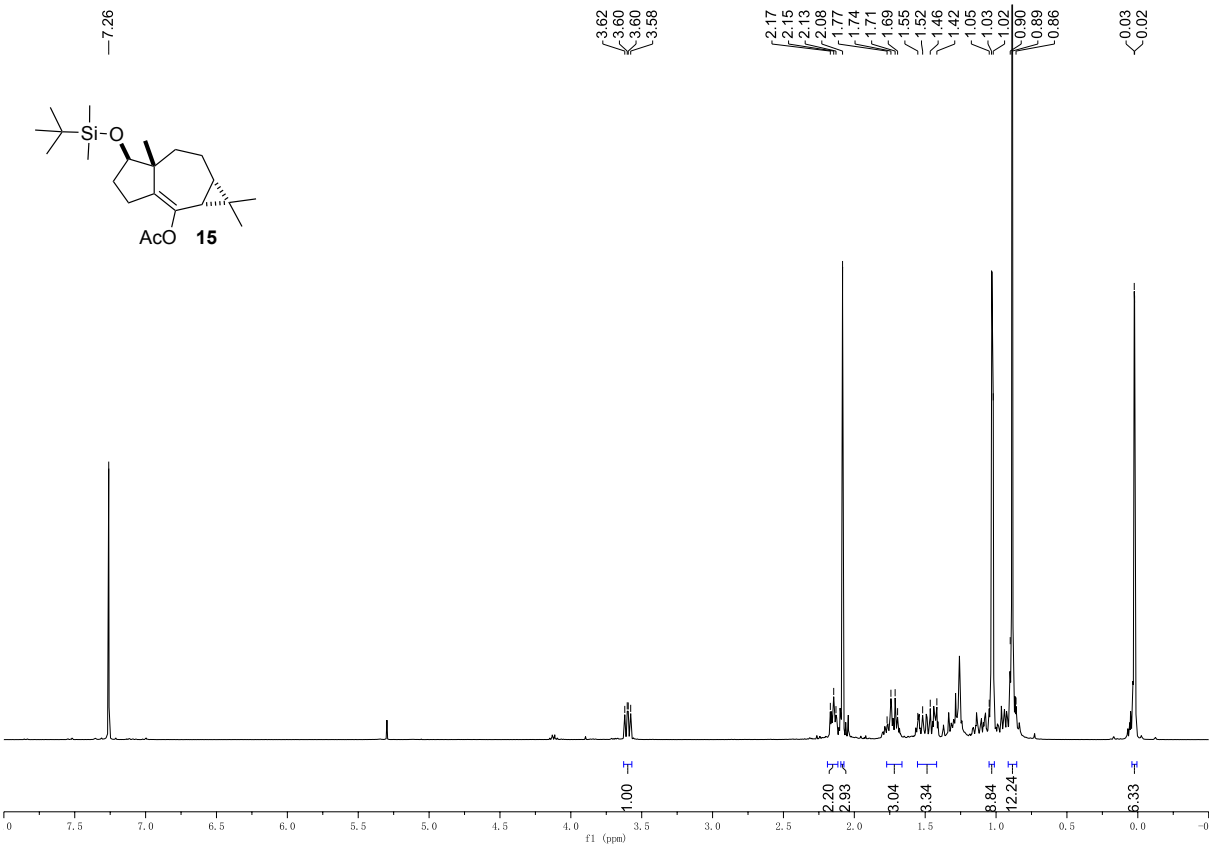


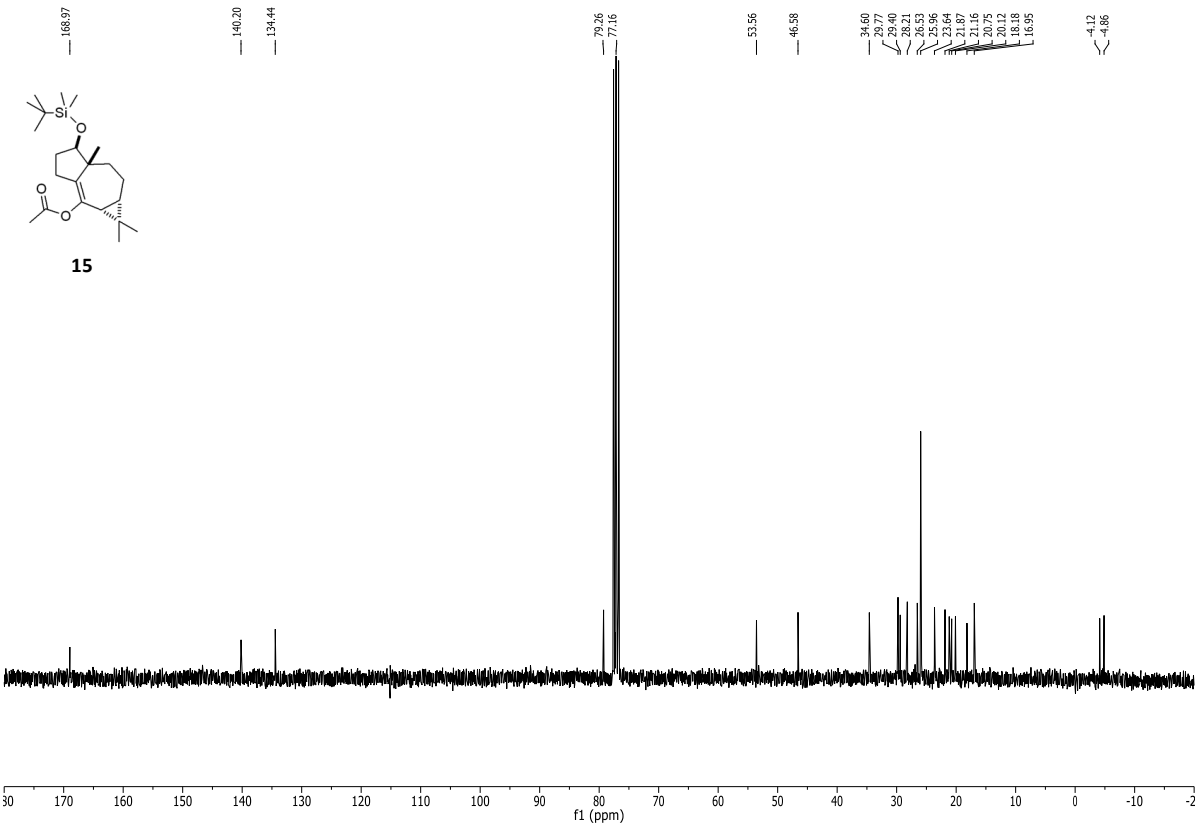
*3,3,5a-trimethyl-6-(2-(4-nitrophenyl)hydrazono)-3,3a,4,5,5a,6,7,8-octahydrocyclopenta[c]pentalen-2-yl acetate (**14**)*



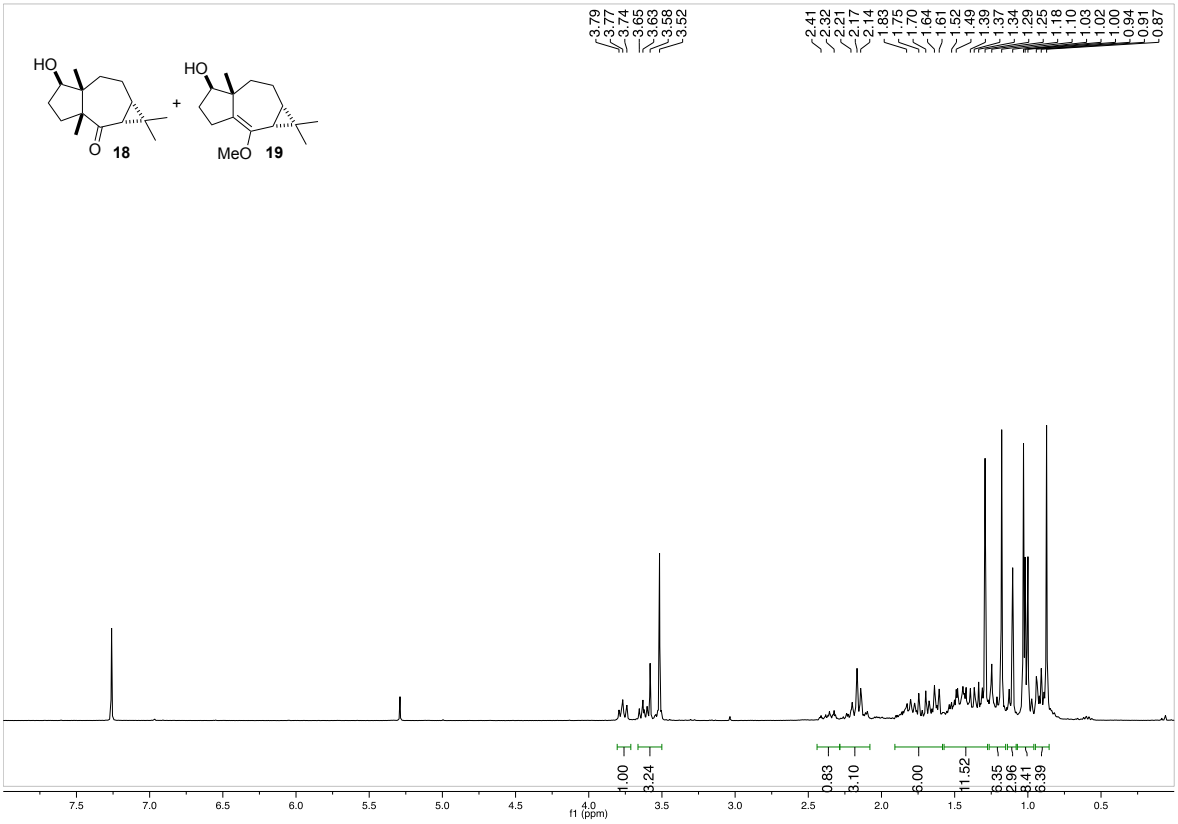


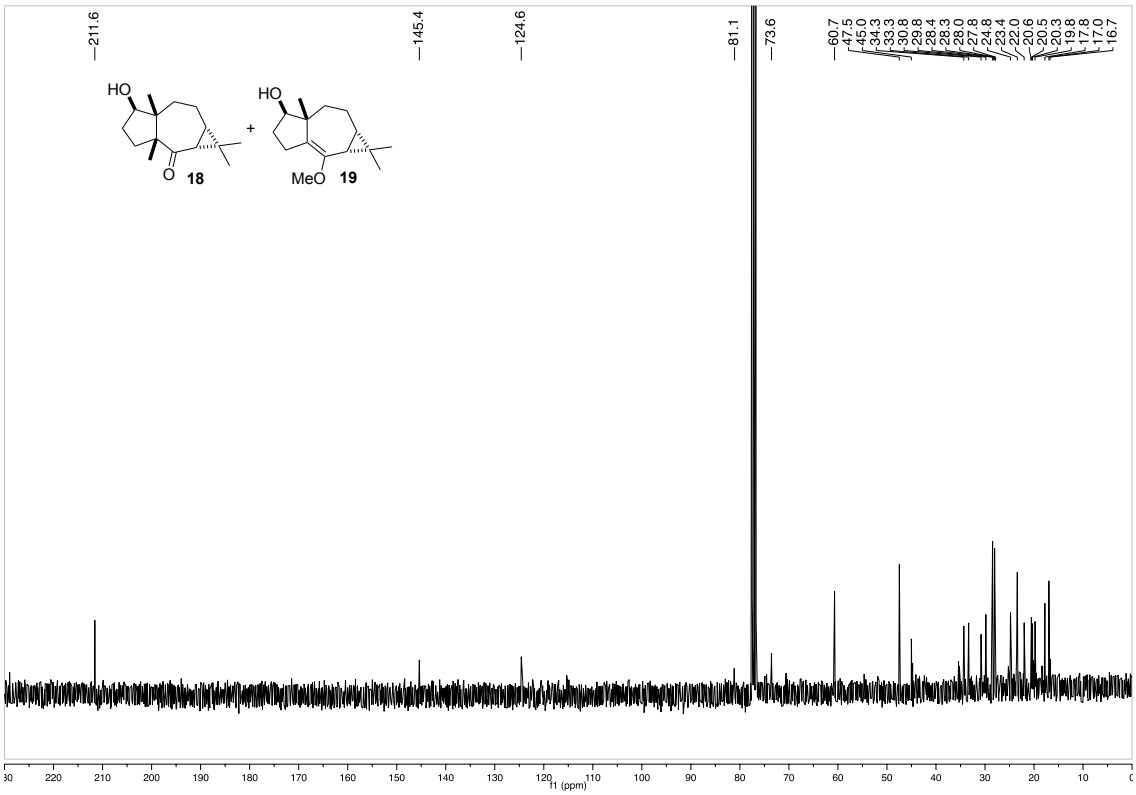
*5-((tert-butyldimethylsilyl)oxy)-1,1,5a-trimethyl-1a,3,4,5,5a,6,7,7a-octahydro-1H-cyclopropa[f]azulen-2-yl acetate (**15**)*



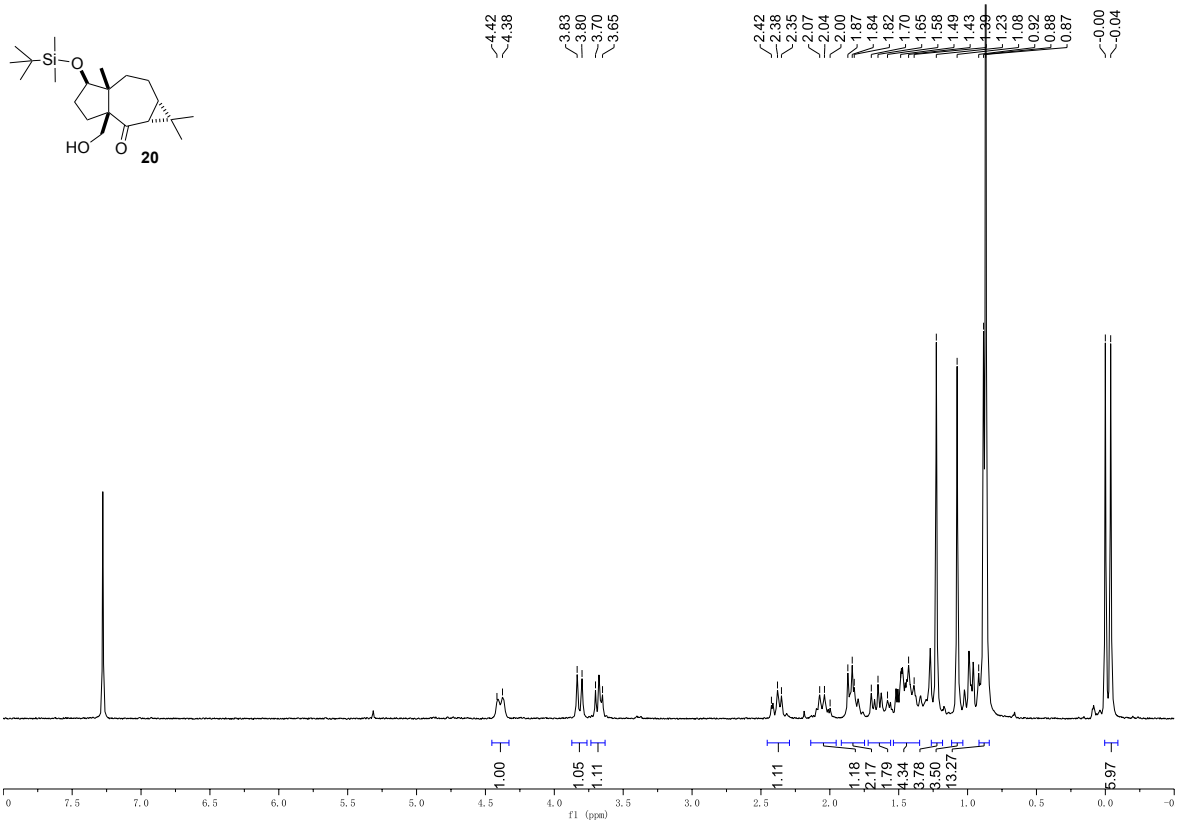


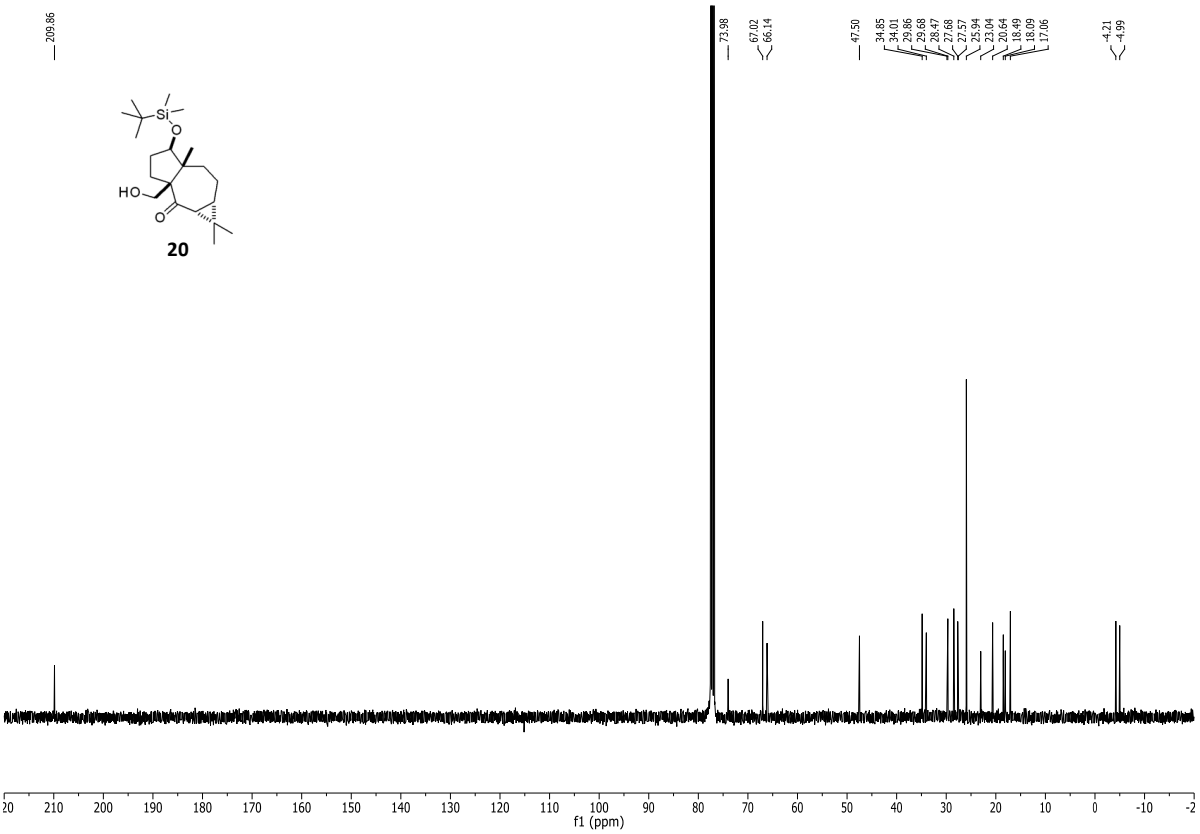
*5-hydroxy-1,1,5a-trimethyl-1a,3,4,5,5a,6,7,7a-octahydro-1H-cyclopropa[f]azulen-2-yl acetate (**18**) and 2-methoxy-1,1,5a-trimethyl-1a,3,4,5,5a,6,7,7a-octahydro-1H-cyclopropa[f]azulen-5-ol (**19**)*



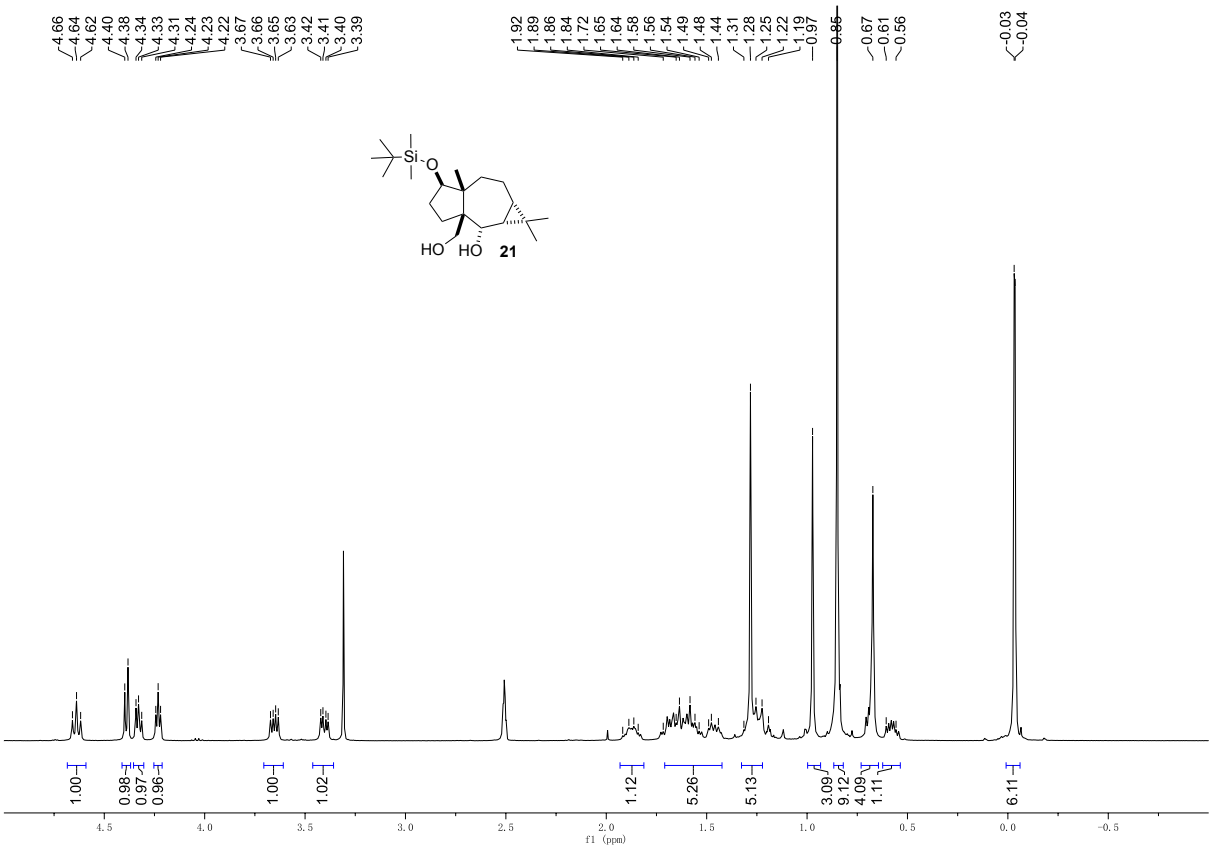


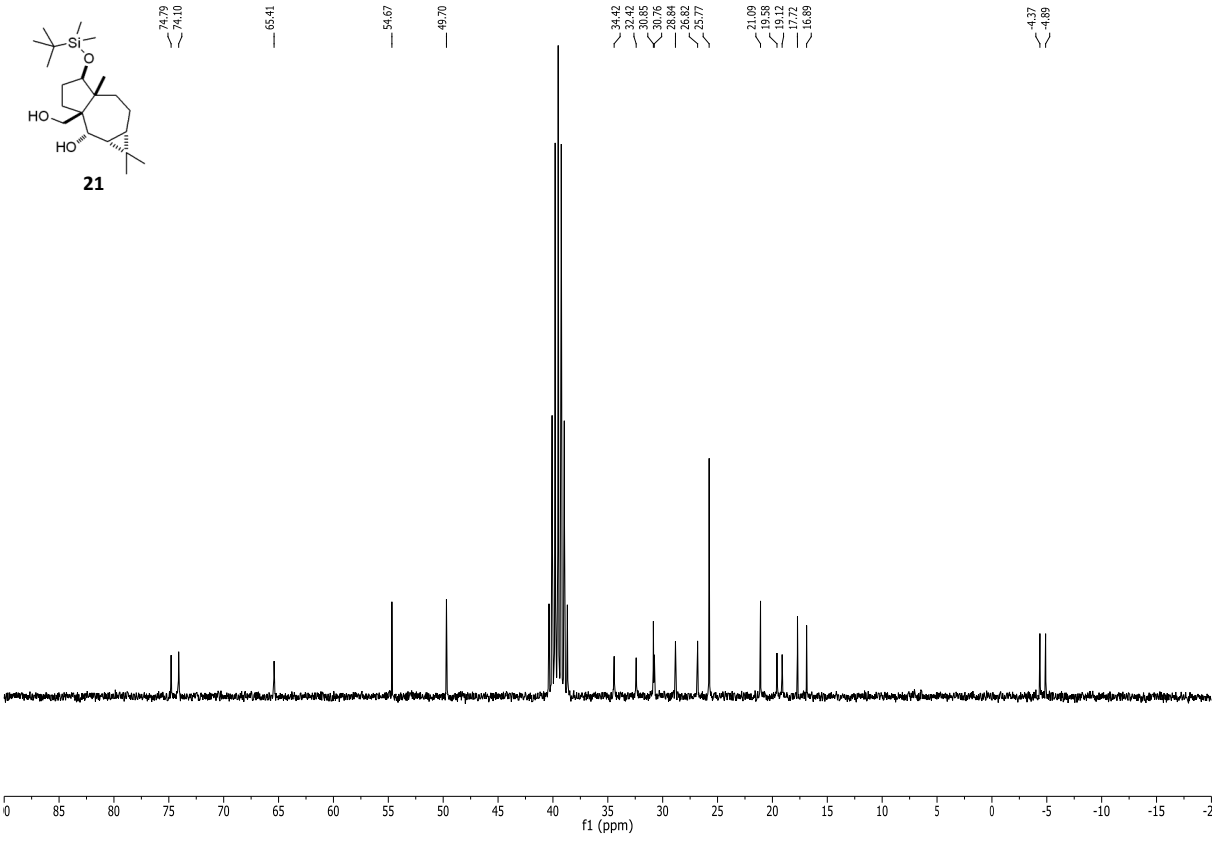
*5-((tert-butyldimethylsilyl)oxy)-2a-(hydroxymethyl)-1,1,5a-trimethyloctahydro-1H-cyclopropa[f]azulen-2(1aH)-one (**20**)*



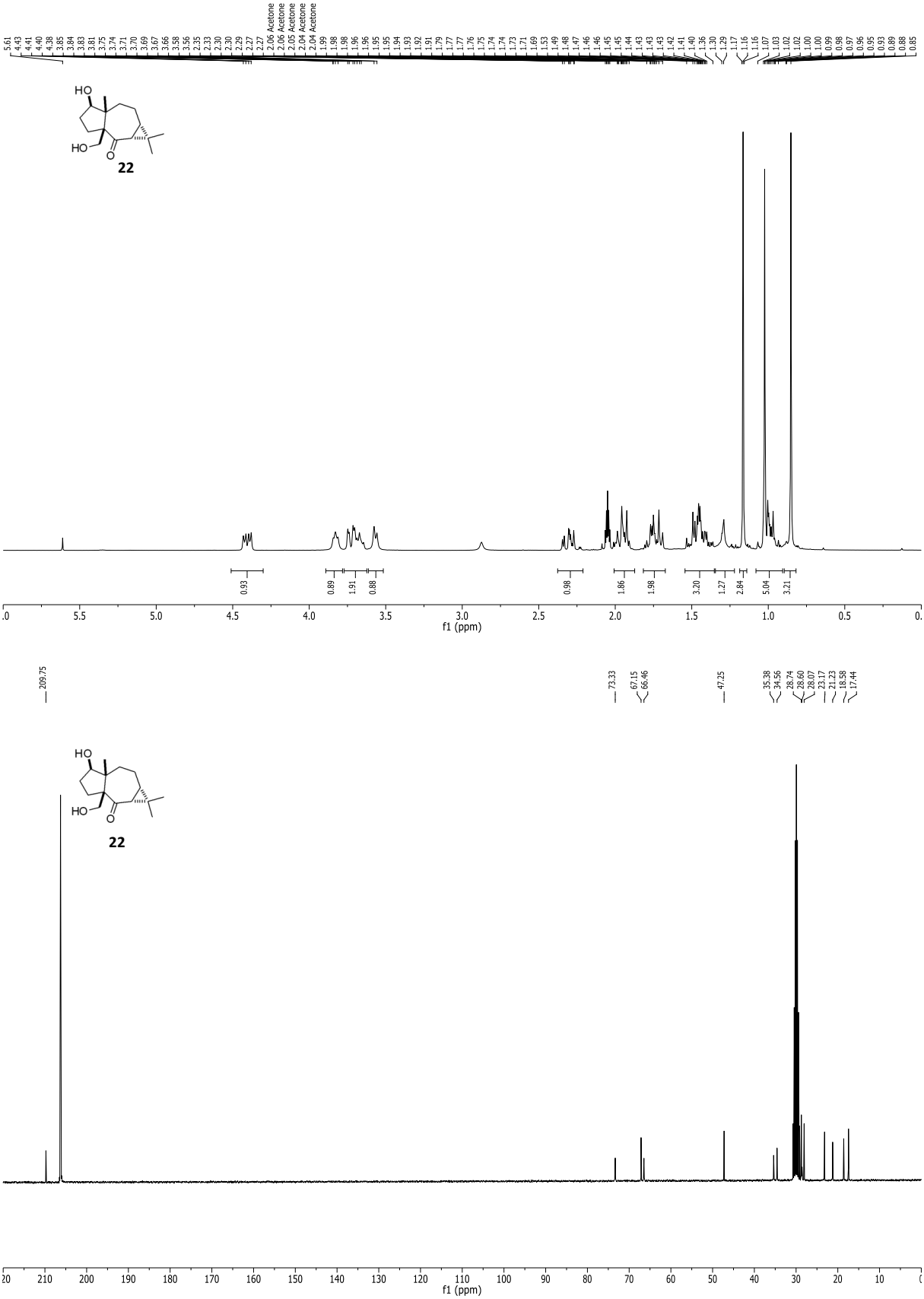


*5-((tert-butyldimethylsilyl)oxy)-2a-(hydroxymethyl)-1,1,5a-trimethyloctahydro-1H-cyclopropa[f]azulen-2(1aH)-one (**21**)*

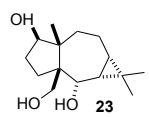


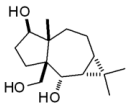


5-hydroxy-2a-(hydroxymethyl)-1,1,5a-trimethyloctahydro-1H-cyclopropa[f]azulen-2(1aH)-one (**22**)

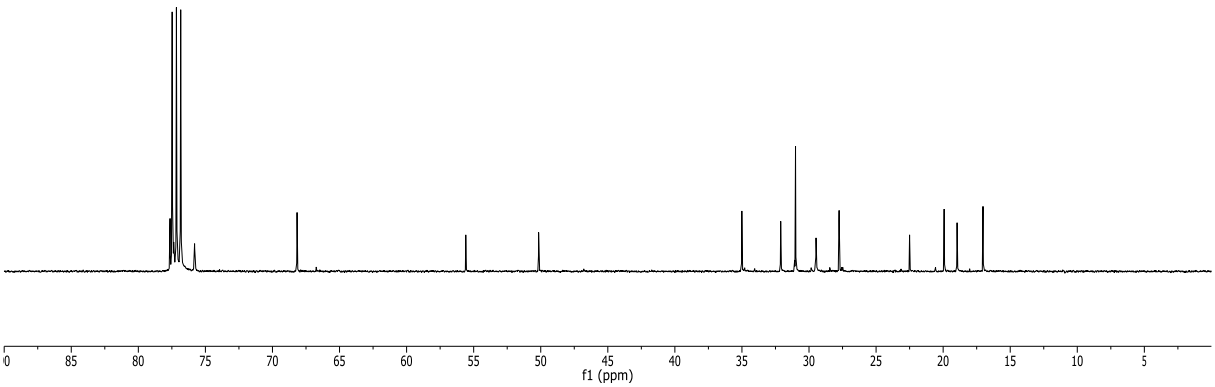


*2a-(hydroxymethyl)-1,1,5a-trimethyldecahydro-1H-cyclopropa [f]azulene-2,5-diol (**23**)*

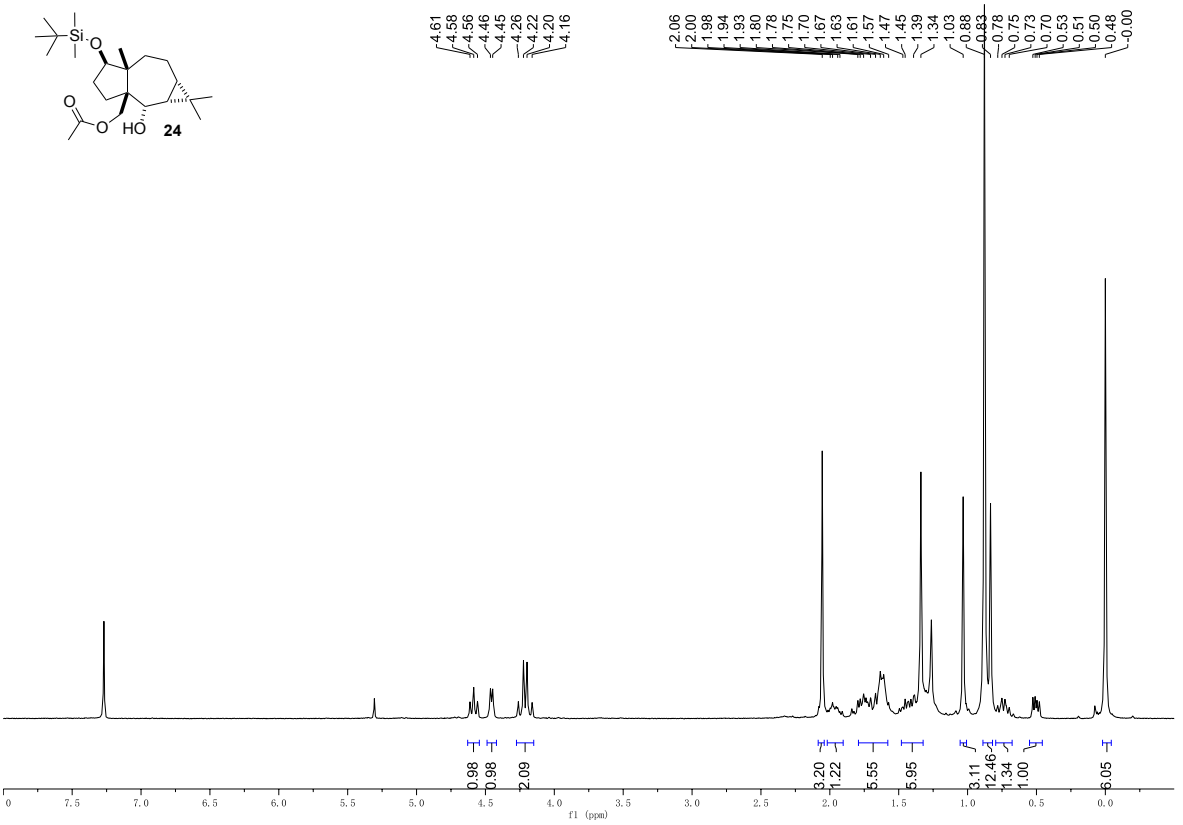


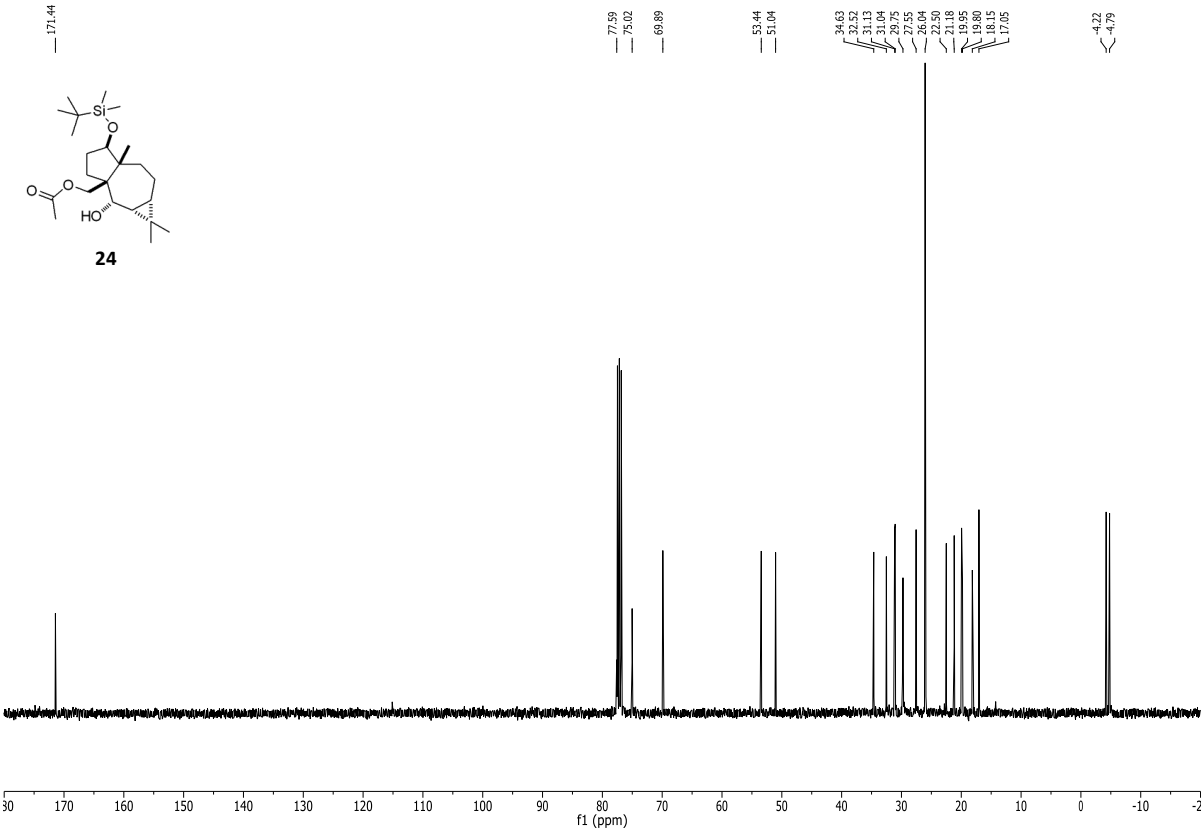


23

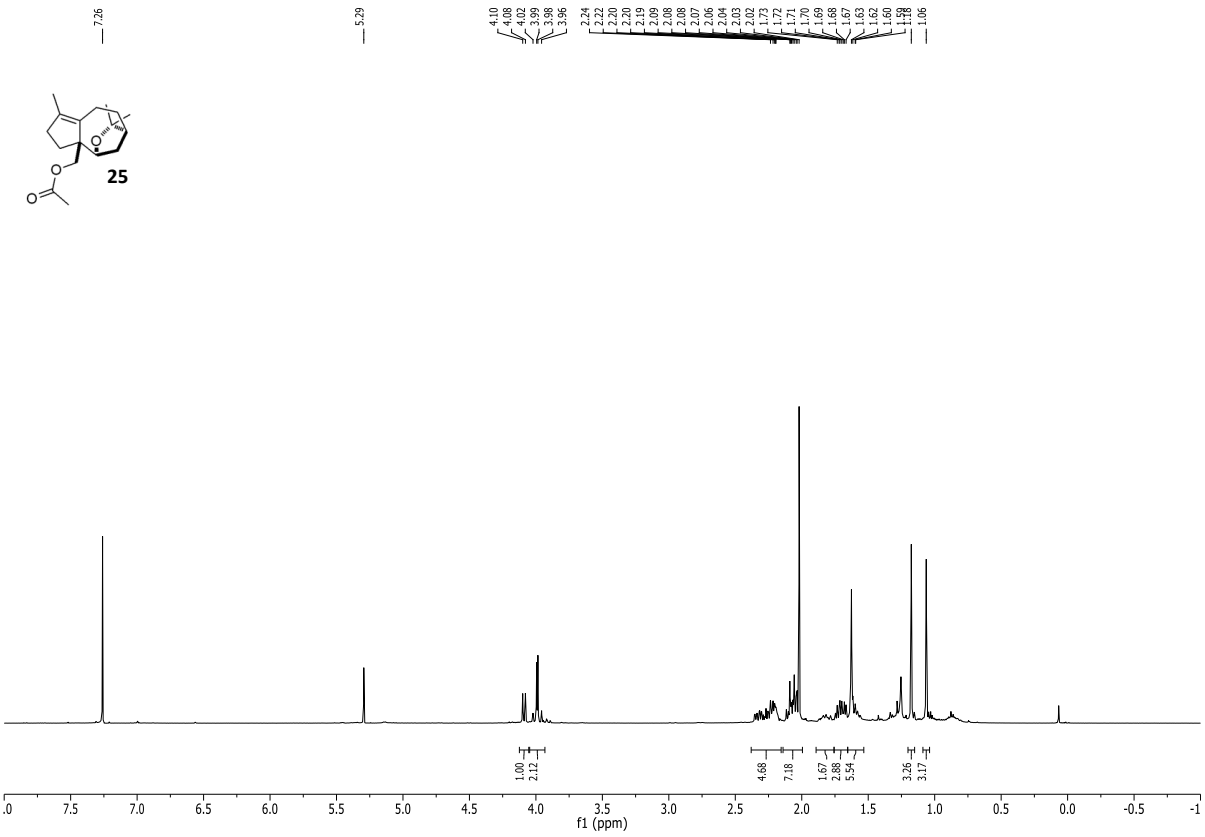


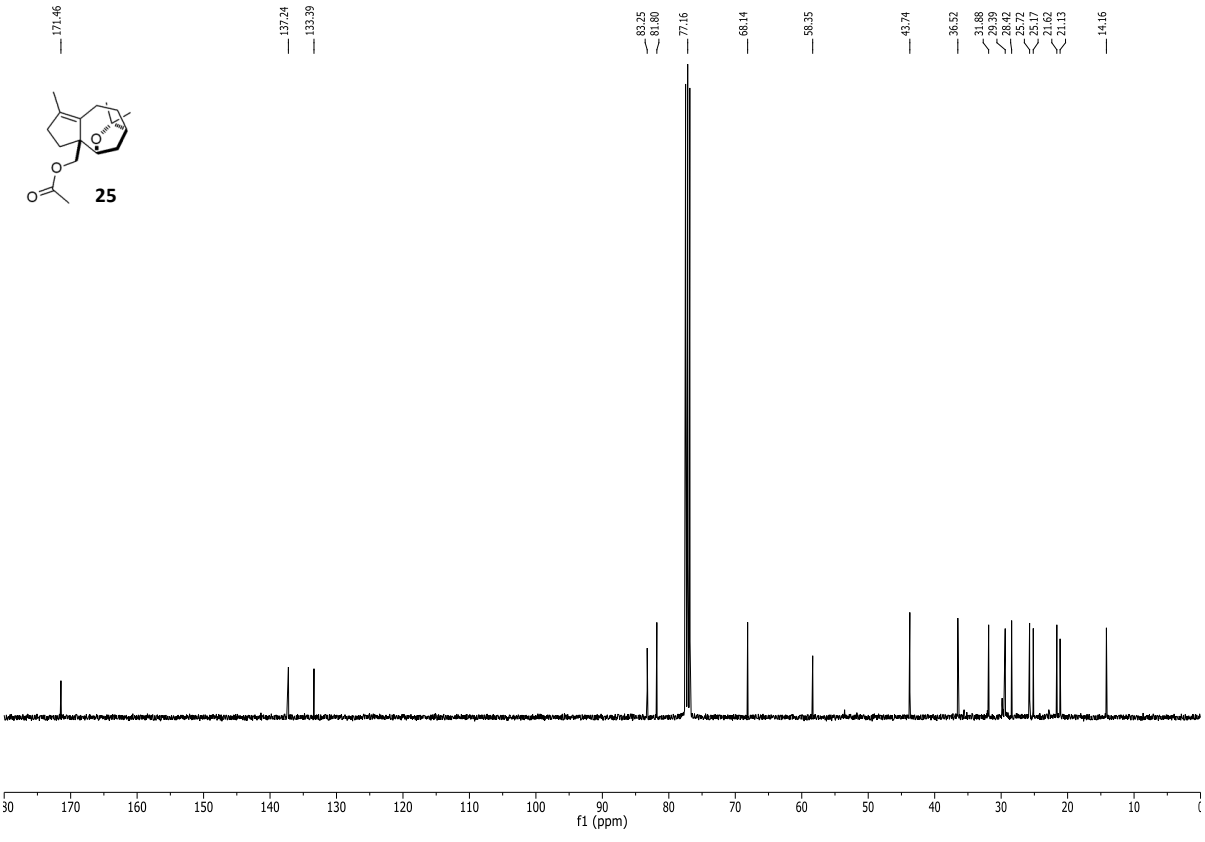
*5-((tert-butyldimethylsilyl)oxy)-2-hydroxy-1,1,5a-trimethyldeca hydro-1H-cyclopropa[f]azulen-2a-yl)methyl acetate (**24**)*



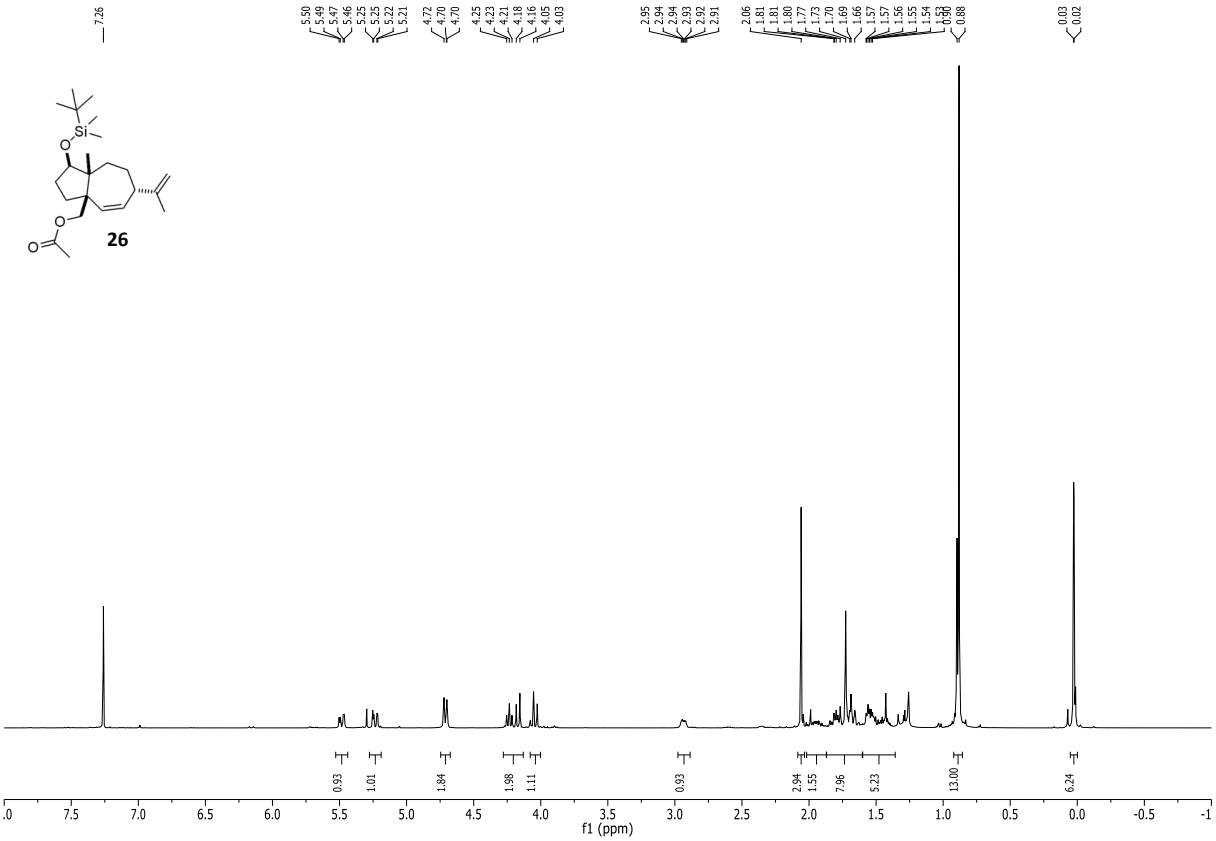


*(3,3,7-trimethyl-1,3,4,5,6,8,9,9a-octahydro-1,4-methanocyclopenta [c]oxocin-9a-yl)methyl acetate (**25**)*

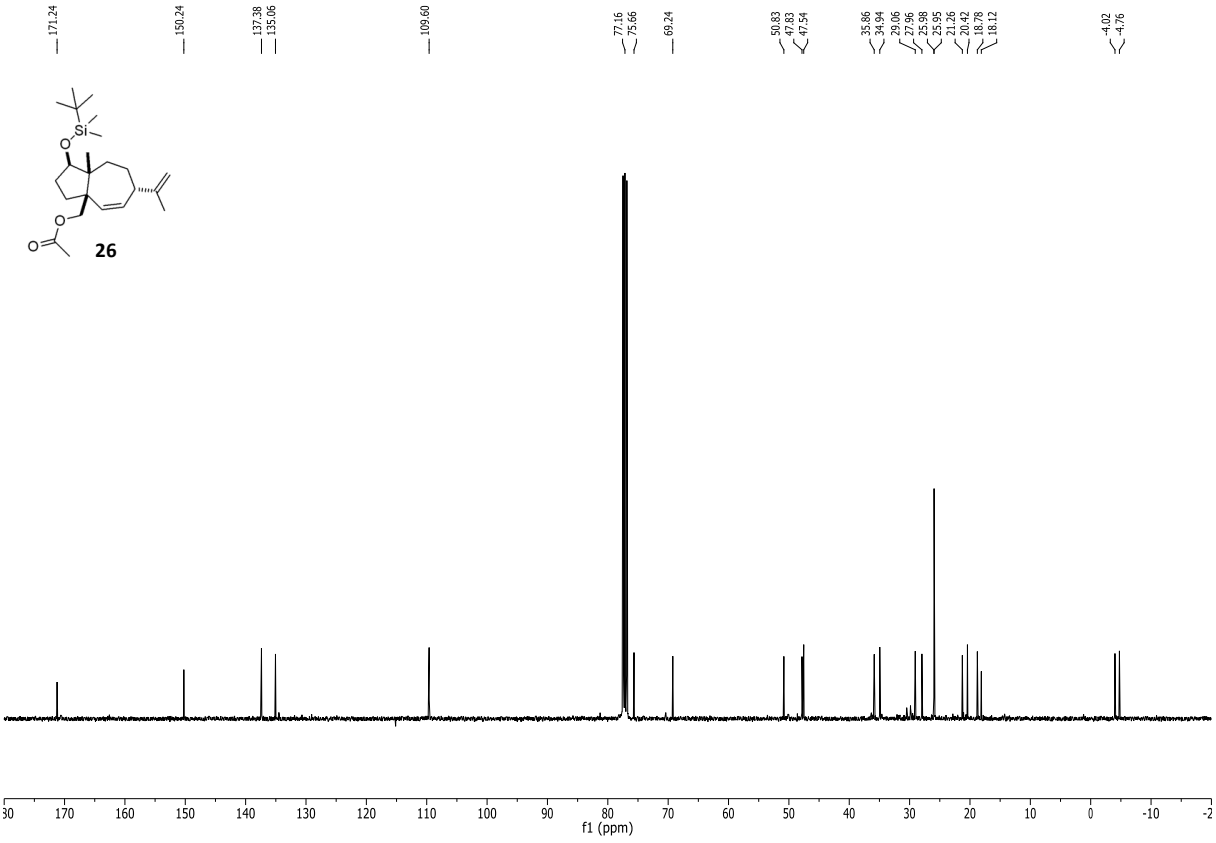




*1-((tert-butyldimethylsilyl)oxy)-8a-methyl-6-(prop-1-en-2-yl)-1,2,3,3a,6,7,8,8a-octahydroazulen-3a-yl)methyl acetate (**26**)*

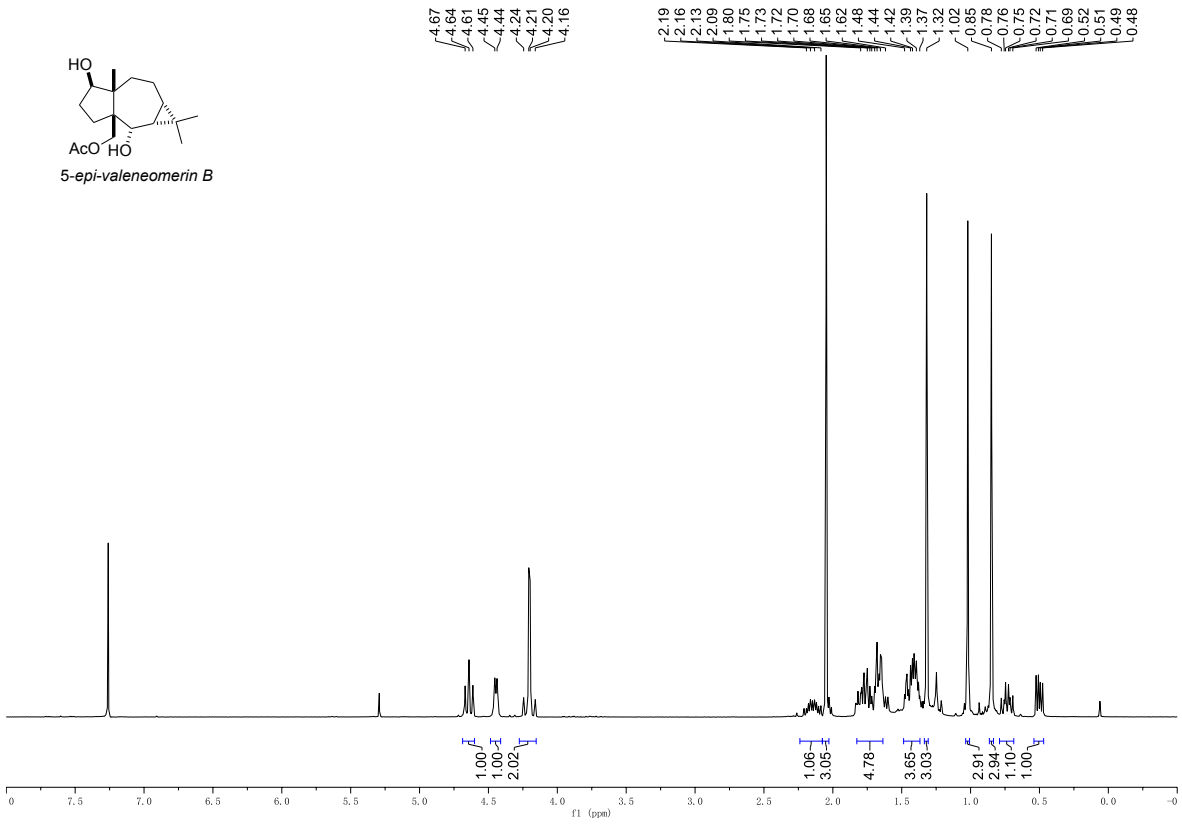


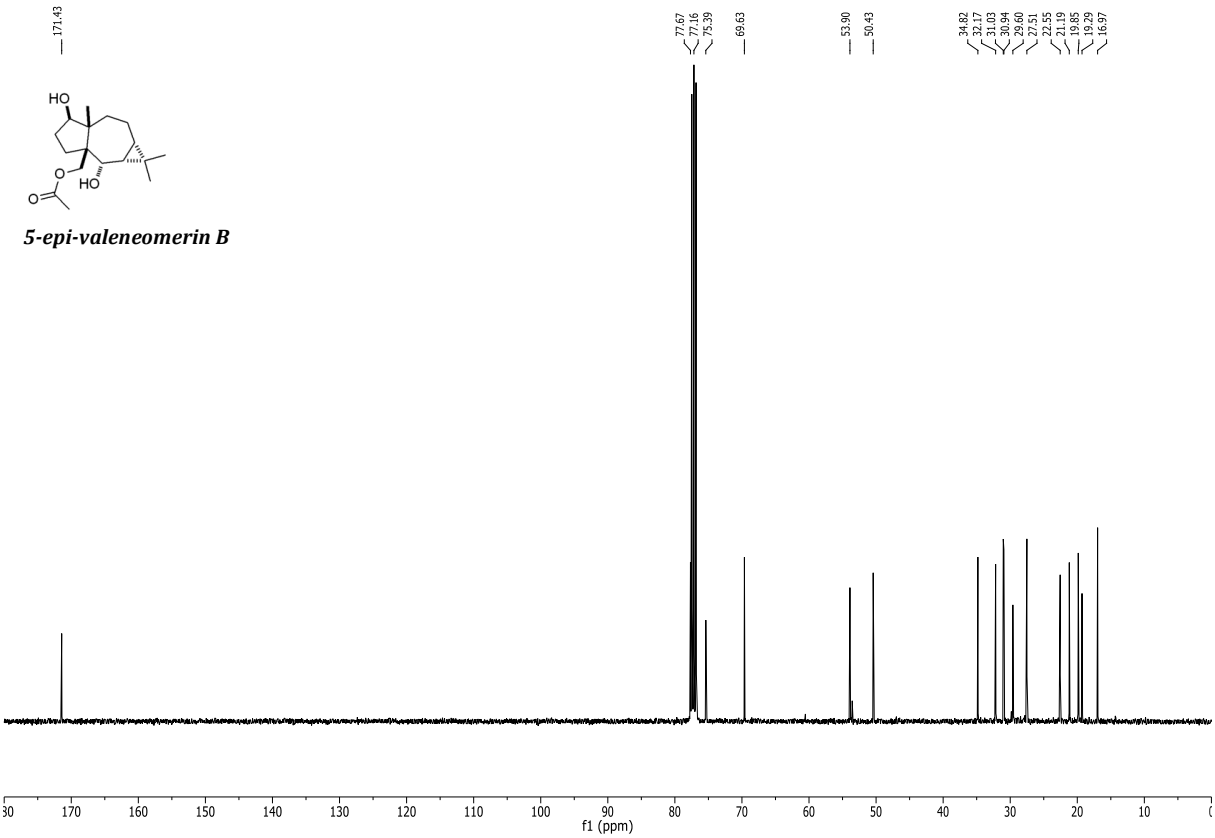
26



26

*2a-(hydroxymethyl)-1,1,5a-trimethyldecahydro-1H-cyclopropa [f]azulene-2,5-diol (**5-epi-valeneomerin B**)*





2. Computational data

Mechanistic proposal (left-side), based on NCI analysis (righ-side) showing interaction between CeCl3 and the alkene moiety.

Methods B3LYP-D3/def2-SV(P)

C	6.0	-0.26364350	0.57606411	-0.49857330
C	6.0	1.00409186	-0.03000840	-1.12744105
C	6.0	1.36313713	-1.21410584	-0.26250181
C	6.0	0.25822321	-1.53873980	0.71182430
C	6.0	-0.50880629	-0.22689840	0.76240671
H	1.0	1.85767901	0.66554338	-1.14031589
H	1.0	-0.16476040	1.64379668	-0.25141111
H	1.0	-1.15469098	0.47523519	-1.14718354
H	1.0	0.88069761	-0.37508309	-2.16999245
O	8.0	2.43323421	-1.83194256	-0.32539150
O	8.0	-1.39525235	0.03399770	1.60504138
C	6.0	0.74431622	-2.11140943	2.04187274
C	6.0	-0.82201999	-2.48307776	0.02535380
C	6.0	-0.36797681	-3.88503623	-0.42340800
C	6.0	0.49733689	-3.96113491	-1.66433489
C	6.0	0.13892999	-3.62019801	-2.91929150
C	6.0	-1.21536624	-3.05664229	-3.28615952
C	6.0	1.08880103	-3.78134751	-4.08111811
H	1.0	1.49551010	-4.39400482	-1.52686465
H	1.0	0.13923740	-4.39477301	0.41220441
H	1.0	-1.30332983	-4.45581484	-0.58829510
H	1.0	-1.26377523	-1.96031678	-0.83781308
H	1.0	-1.62109637	-2.57557058	0.78161192
H	1.0	1.24114275	-3.08200002	1.88169444
H	1.0	-0.09799150	-2.25426102	2.73875284
H	1.0	1.47043514	-1.42701411	2.50827217
Ce	58.0	4.26717281	-2.45689821	-1.71006119
Cl	17.0	3.38932300	-0.95960790	-3.63028073
Cl	17.0	4.17643213	-5.00278282	-2.09026980
Cl	17.0	6.67405796	-1.78749084	-1.11840534
H	1.0	2.03936577	-4.25162363	-3.77846861
H	1.0	1.32355750	-2.80217576	-4.53975630
H	1.0	0.63197410	-4.40984058	-4.87032127
H	1.0	-1.98942780	-3.23231816	-2.52061129
H	1.0	-1.15247023	-1.96384621	-3.46511006
H	1.0	-1.57563281	-3.50210261	-4.23167515
Ce	58.0	-0.58764052	1.19153583	3.45796800
Cl	17.0	-0.34273440	-0.52691209	5.35362673
Cl	17.0	-1.69551384	3.47444320	3.80939531
C	6.0	1.45097744	1.26272321	2.13393998
C	6.0	2.63044858	1.17349458	1.75655067
Si	14.0	4.43655825	0.98706013	1.38260627
C	6.0	4.73639250	1.29518950	-0.45941189
C	6.0	4.90290546	-0.77124828	1.90590894
C	6.0	5.39973068	2.25588489	2.39504838
H	1.0	5.91762400	-1.04007995	1.56502247
H	1.0	4.85736609	-0.86305451	3.00680470
H	1.0	5.09580898	3.28538275	2.13127160
H	1.0	5.22540140	2.11526084	3.47737122
H	1.0	6.48543835	2.15899968	2.20514941
H	1.0	5.78261614	1.05609393	-0.72037560
H	1.0	4.54730988	2.35703802	-0.70301312
H	1.0	4.09305859	0.69462961	-1.12884533
H	1.0	4.19002151	-1.50916290	1.49176431

3. Crystal data

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) Compound_14, compound_21, compound_22, compound_7, compounds_13-14

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: compound_7

```
Bond precision:  C-C = 0.0086 A          Wavelength=1.54178

Cell:           a=19.2372(12)    b=19.7853(13)       c=12.5770(7)
                alpha=90         beta=107.983(3)     gamma=90
Temperature:    200 K

                Calculated                Reported
Volume          4553.1(5)                 4553.1(5)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C22 H26 N4 O6             C22 H26 N4 O6
Sum formula     C22 H26 N4 O6             C22 H26 N4 O6
Mr              442.47                    442.47
Dx,g cm-3       1.291                     1.291
Z               8                         8
Mu (mm-1)       0.793                     0.793
F000            1872.0                    1872.0
F000'           1878.19
h,k,lmax        19,19,12                  19,19,12
Nref            4846                      4753
Tmin,Tmax       0.867,0.961               0.719,0.863
Tmin'           0.788

Correction method= # Reported T Limits: Tmin=0.719 Tmax=0.863
AbsCorr = MULTI-SCAN

Data completeness= 0.981          Theta(max)= 50.785

R(reflections)= 0.0689( 3599)     wR2(reflections)= 0.2182( 4753)

S = 1.066                 Npar= 581
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

```
THETM01_ALERT_3_A  The value of sine(theta_max)/wavelength is less than 0.550
           Calculated sin(theta_max)/wavelength =    0.5025
```

Alert level B

```
PLAT220_ALERT_2_B Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        6.1 Ratio
PLAT220_ALERT_2_B Non-Solvent Resd 2   C   Ueq(max)/Ueq(min) Range        6.5 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for    C32    --  C33     ..        9.0 s.u.
PLAT242_ALERT_2_B Low    'MainMol' Ueq as Compared to Neighbors of       C10 Check
```

Alert level C

```
REFNR01_ALERT_3_C  Ratio of reflections to parameters is < 10 for a
           centrosymmetric structure
           sine(theta)/lambda               0.5025
           Proportion of unique data used   1.0000
           Ratio reflections to parameters  8.1807
PLAT088_ALERT_3_C Poor Data / Parameter Ratio .....................      8.18 Note
PLAT222_ALERT_3_C Non-Solvent Resd 1   H Uiso(max)/Uiso(min) Range        6.8 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 2   H Uiso(max)/Uiso(min) Range        7.4 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C30    --  C31     ..        6.0 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        N3 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C15 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C31 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C32 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ................   0.00862 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     2.925 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.503        92 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.        0 Note
```

Alert level G

```
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ...............        2 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large      0.13 Report
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C11 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C12 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C33 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....       C34 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #        2 Note
             C22 H26 N4 O6
PLAT793_ALERT_4_G The Model has Chirality at C4      (Centro SPGR)        S Verify
PLAT793_ALERT_4_G The Model has Chirality at C5      (Centro SPGR)        S Verify
PLAT793_ALERT_4_G The Model has Chirality at C26     (Centro SPGR)        R Verify
PLAT793_ALERT_4_G The Model has Chirality at C27     (Centro SPGR)        R Verify
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still        50 % Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)        2 Note
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   4 ALERT level B = A potentially serious problem, consider carefully
  13 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
```

```
  11 ALERT type 2 Indicator that the structure model may be wrong or deficient
  10 ALERT type 3 Indicator that the structure quality may be low
   9 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock: compounds_13-14

```
Bond precision:  C-C = 0.0018 A          Wavelength=0.71073

Cell:          a=8.7959(5)       b=10.4916(6)     c=13.2932(8)
               alpha=70.468(2)   beta=74.252(2)   gamma=71.371(2)
Temperature:   200 K
```

	Calculated	Reported
Volume	1076.80(11)	1076.80(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C22 H26 N4 O6	0.85(C22 H26 N4 O6), 0.15(C22 H26 N4 O6)
Sum formula	C22 H26 N4 O6	C22 H26 N4 O6
Mr	442.47	442.47
Dx,g cm-3	1.365	1.365
Z	2	2
Mu (mm-1)	0.101	0.101
F000	468.0	468.0
F000'	468.23	
h,k,lmax	12,15,19	12,15,19
Nref	6652	6584
Tmin,Tmax	0.994,0.995	0.990,0.990
Tmin'	0.990	

```
Correction method= # Reported T Limits: Tmin=0.990 Tmax=0.990
AbsCorr = MULTI-SCAN

Data completeness= 0.990          Theta(max)= 30.667

R(reflections)= 0.0453( 5516)     wR2(reflections)= 0.1323( 6584)

S = 1.036                 Npar= 343
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT430_ALERT_2_C Short Inter D...A Contact  O2A    ..  O3      ..       2.85 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.600         16 Report
```

```
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....          5 Note
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          6 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.002 Degree
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          1 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C15A   --  C16A    ..        7.1 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of O1A     is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O2A     is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O1B     is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O2B     is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C10A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C16A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C10B    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C14B    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C15B    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C16B    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16A    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16B    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16C    is Constrained at       0.85 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14B    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16D    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16E    is Constrained at       0.15 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H16F    is Constrained at       0.15 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1)..         19 % Note
PLAT432_ALERT_2_G Short Inter X...Y Contact  O6     ..  C15B    ..       2.94 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  O6     ..  C15A    ..       2.95 Ang.
PLAT793_ALERT_4_G The Model has Chirality at C5      (Centro SPGR)          R Verify
PLAT793_ALERT_4_G The Model has Chirality at C8      (Centro SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         30 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         52 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         17 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  37 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
  24 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock: Compound_14

Bond precision: C-C = 0.0031 A Wavelength=1.54178

```
Cell:            a=15.8792(5)     b=7.3830(3)        c=18.5839(7)
                 alpha=90         beta=94.011(2)     gamma=90
Temperature:     200 K

                 Calculated                Reported
Volume           2173.37(14)               2173.37(14)
Space group      P 21/n                    P 21/n
Hall group       -P 2yn                    -P 2yn
Moiety formula   C22 H26 N4 O6             C22 H26 N4 O6
Sum formula      C22 H26 N4 O6             C22 H26 N4 O6
Mr               442.47                    442.47
Dx,g cm-3        1.352                     1.352
Z                4                         4
Mu (mm-1)        0.830                     0.830
F000             936.0                     936.0
F000'            939.10
h,k,lmax         18,8,22                   18,8,21
Nref             3865                      3806
Tmin,Tmax        0.879,0.967               0.663,0.752
Tmin'            0.786

Correction method= # Reported T Limits: Tmin=0.663 Tmax=0.752
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 67.005

R(reflections)= 0.0500( 3056)     wR2(reflections)= 0.1289( 3806)

S = 1.034                 Npar= 303
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT230_ALERT_2_C Hirshfeld Test Diff for    O3     --  N3      ..        6.2 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    N4     --  C20     ..        5.3 s.u.
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ...........       O2B Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......     3.489 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L=  0.597        55 Report
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         2 Note
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records         1 Report
PLAT300_ALERT_4_G Atom Site Occupancy of O2A     is Constrained at       0.8 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O2B     is Constrained at       0.2 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1)..         3 % Note
PLAT793_ALERT_4_G The Model has Chirality at C1      (Centro SPGR)         R Verify
PLAT793_ALERT_4_G The Model has Chirality at C2      (Centro SPGR)         R Verify
PLAT793_ALERT_4_G The Model has Chirality at C5      (Centro SPGR)         R Verify
```

```
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still         56 % Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)          1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         3 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Datablock: compound_20

```
Bond precision:  C-C = 0.0016 A          Wavelength=0.71073

Cell:            a=15.0743(3)     b=6.8149(1)        c=21.2545(4)
                 alpha=90         beta=92.709(1)     gamma=90
Temperature:     200 K

                Calculated                Reported
Volume          2181.03(7)                2181.03(7)
Space group     P 21/n                    P 21/n
Hall group      -P 2yn                    -P 2yn
Moiety formula  C21 H38 O3 Si             C21 H38 O3 Si
Sum formula     C21 H38 O3 Si             C21 H38 O3 Si
Mr              366.60                    366.60
Dx,g cm-3       1.117                     1.116
Z               4                         4
Mu (mm-1)       0.123                     0.123
F000            808.0                     808.0
F000'           808.64
h,k,lmax        21,9,29                   21,9,29
Nref            6433                      6416
Tmin,Tmax       0.984,0.994               0.702,0.746
Tmin'           0.963

Correction method= # Reported T Limits: Tmin=0.702 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 30.101

R(reflections)= 0.0386( 5087)     wR2(reflections)= 0.1112( 6416)
```

S = 1.027 Npar= 235

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 2 Report

---

Alert level G

PLAT395_ALERT_2_G Deviating X-O-Y Angle from 120 Deg for O3 124.7 Degree
PLAT793_ALERT_4_G The Model has Chirality at C1 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at C4 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at C6 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at C9 (Centro SPGR) R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min) 3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 12 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 5 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 17 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
6 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Datablock: compound_21

Bond precision: C-C = 0.0021 A Wavelength=1.54178

Cell: a=15.7593(3) b=6.7689(2) c=21.0839(4)
alpha=90 beta=104.622(1) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	2176.24(9)	2176.24(9)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H40 O3 Si	C21 H40 O3 Si
Sum formula	C21 H40 O3 Si	C21 H40 O3 Si
Mr	368.62	368.62
Dx,g cm-3	1.125	1.125
Z	4	4
Mu (mm-1)	1.065	1.065
F000	816.0	816.0
F000'	819.04	
h,k,lmax	18,8,25	18,8,25
Nref	3925	3894
Tmin,Tmax	0.950,0.969	0.668,0.753
Tmin'	0.626	

Correction method= # Reported T Limits: Tmin=0.668 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 67.728

R(reflections)= 0.0372(3248) wR2(reflections)= 0.0995(3894)

S = 1.040 Npar= 235

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT420_ALERT_2_B D-H Without Acceptor O1 -- H1 ... Please Check

---

Alert level C

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.4 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 1 H Uiso(max)/Uiso(min) Range 4.2 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for Si1 -- C16 .. 5.9 s.u.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C18 Check
PLAT414_ALERT_2_C Short Intra D-H..H-X H1 .. H4 .. 1.94 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 29 Report

---

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT395_ALERT_2_G Deviating X-O-Y Angle from 120 Deg for O3 123.4 Degree
PLAT793_ALERT_4_G The Model has Chirality at C1 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at C3 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at C4 (Centro SPGR) S Verify
PLAT793_ALERT_4_G The Model has Chirality at C6 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at C9 (Centro SPGR) S Verify

```
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still          71 % Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)           1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          2 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         11 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  12 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   7 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

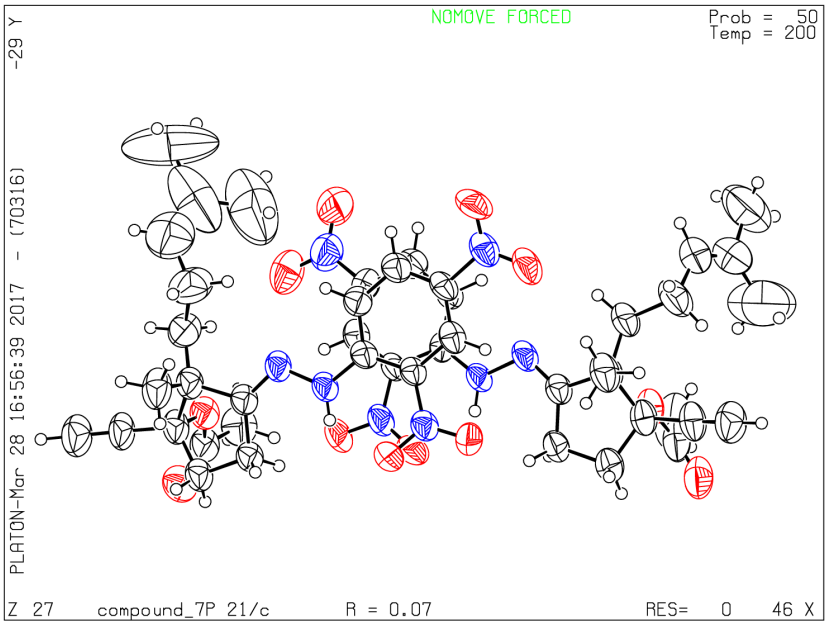
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

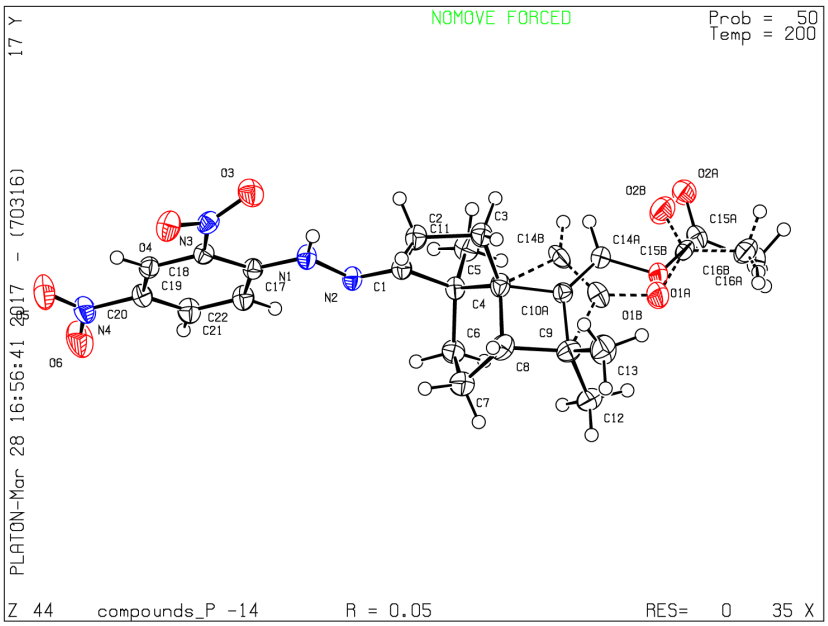
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

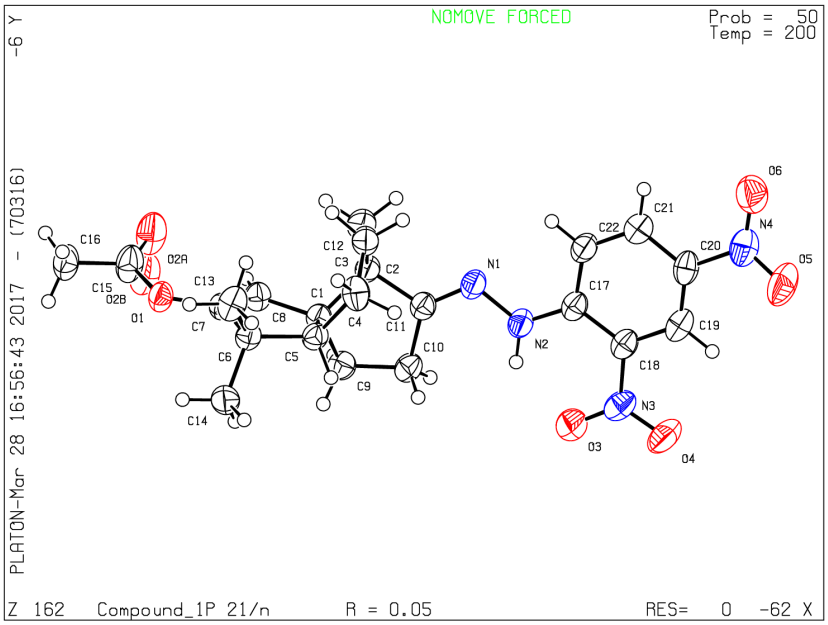
Datablock compound_7 - ellipsoid plot



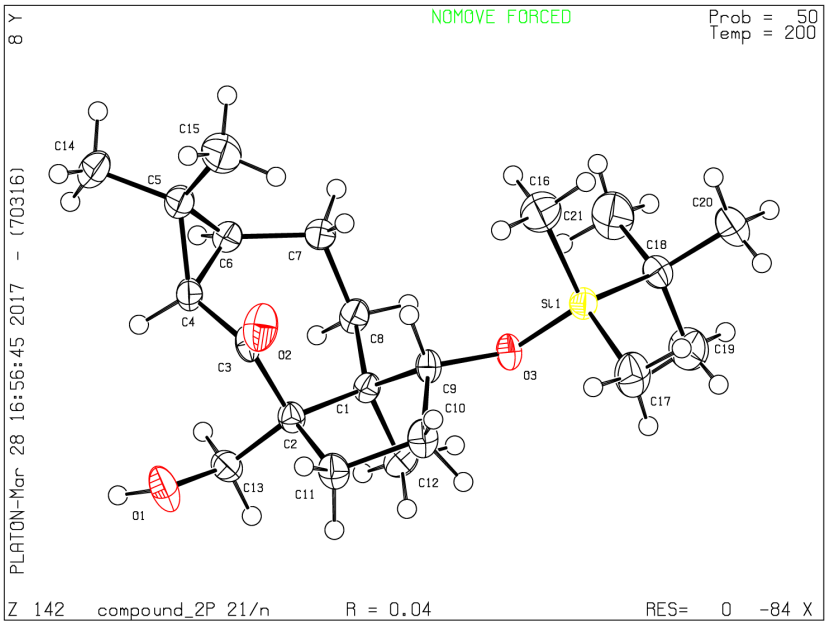
Datablock compounds_13-14 - ellipsoid plot



Datablock Compound_14 - ellipsoid plot



Datablock compound_20 ellipsoid plot



Datablock compound_21 ellipsoid plot