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SUPPORTING INFORMATIONS

$In(OTf)_3$-Catalysed Easy Access to Dihydropyranocoumarin and Dihydropyranochromone Derivatives

Naouel BOUFROUA,[a,b] Elisabet DUNACH,[b] Fabien FONTAINE-VIVE,[b]
Samia ACHOUCHE-BOUZROURA*[a] and Sophie POULAIN-MARTINI*[b]

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[a] Laboratoire de Chimie Organique Appliquée,
Faculté de Chimie,
Université des Sciences et de la Technologie Houari Boumediene,
BP 31, El-Alia, Bab-Ezzouar, 16111, Alger, Algérie.
[b] Université Côte d'Azur, Institut de Chimie de Nice, CNRS,
Parc Valrose, 06108 Nice cedex 2, France.
E-mail: sophie.martini@univ-cotedazur.fr; http://icn.unice.fr,
Supporting information for this article is available on the web.

I. General informations

In this work, the reactions are air and moisture sensitive. They are performed under inert conditions, under nitrogen atmosphere, using dried glassware, round bottom flask fitted with rubber septa and anhydrous solvents.

The commercial starting reagents were used without further purification. The solvents used are pure to more than 99.5% or are pure solvent for synthesis. The anhydrous solvents for reaction were dried and distilled according to the protocols described in the literature.[1] The distillation head, representing 10% in volume, is removed and the distillation core is collected under nitrogen stream in schlenk-type flask. The solvents are stored under nitrogen on molecular sieve of 4Å and away from light. 1,2-Dichloroethane ($C_2H_4Cl_2$) was dried by distillation over P_2O_5 (10 g/l).

The reactions were followed by thin layer chromatography (TLC), using 0.20 mm pre-coated silica plates (Silica gel 60, F254, Macherey-Nagel). UV-active substances were detected with UV-light at wavelengths of 254 nm and 366 nm, respectively. Detection of non UV-active substances was carried out by staining with $KMnO_4$ (this fuchsia stain is prepared by dissolving 3 g of $KMnO_4$ and 20 g of K_2CO_3, in 5 ml of 5% NaOH and 300 ml of water) and subsequent heating. The purification of crude reaction was realized by column chromatography on a CombiFlash® RF^+ (Teledyne Isco, USA), using CHROMABOND® Flash columns (Macherey-Nagel GmbH & Co. KG, Germany). The solvents for flash and thin layer chromatography (TLC) [petroleum ether (PE), diethyl ether (Et_2O), ethyl acetate (EtOAc)] were used without further purification.

NMR spectra (^1H, ^{13}C, COSY, DEPT135, HSQC, HMBC, NOESY) were recorded on a Bruker AV-200 or AV-400 or AV-500 spectrometer (Bruker, Rheinstetten, Germany) at a temperature of 300 K. Chemical shifts (δ) are given in parts per million (ppm) and refer to the residual proton signal of the used solvent. In ^1H spectra, the $CDCl_3$ residual peak was applied as an internal standard with a chemical shift of 7.26 ppm. Coupling constants J are given in Hertz (Hz). Spectral splitting patterns are designated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ^{13}C-spectra were calibrated according to the deuterium-coupled signals of the used solvent ($CDCl_3$ = 77.16 ppm). COSY, HSQC, HMBC, correlations were established to identify the structures of some cyclic molecules. Infrared spectra were recorded on a Jasco FT/IR-4600 spectrometer (ATR

[1] A. F. Burchat, J. M. Chong, N. Nielsen, *J. Organomet. Chem.* **1997**, *542*, 281-283.

diamond). Absorption maxima are reported in wave numbers (cm^{-1}). GC analyses were performed on a Shimadzu GC-2025 capillary gas chromatograph. GC/MS analyses were performed on a Shimadzu QP2010S-MS chromatograph (EI, 70 eV) equipped with a SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm). High resolution mass spectrometry (HRMS) was performed on a mass spectrometer LTQ-Orbitrap hybrid.

The crystal structures data have been deposited *via* the joint CCDC/FIZ Karlsruhe deposition service. They have been assigned the following deposition numbers: 1954293-1954296.

Abbreviations used:

EtOAc = ethyl acetate

DCE = 1,2-dichloroethane

DCM = dichloromethane

CH_3NO_2 = nitromethane

K_2CO_3 = potassium carbonate

$MgSO_4$ = magnesium sulfate

$NaHCO_3$ = sodium bicarbonate

TLC = thin layer chromatography

MP = melting point

RF = retention factor

$In(OTf)_3$ = indium (III) triflate

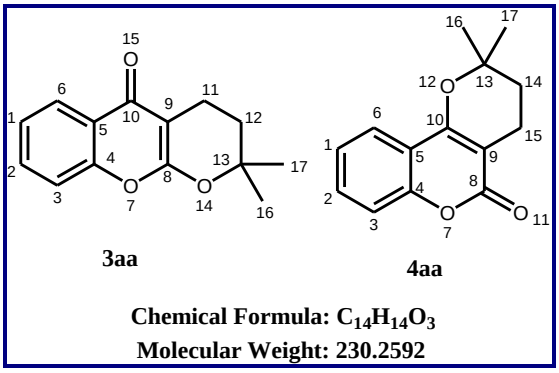
II- Reaction of allyl derivatives 2 with β-ketolactones and β-diketones 1

1. General protocol A

In a schlenk-type bicol, pre-purged three times with nitrogen (vacuum/nitrogen), equipped of a refreshing and undergoing nitrogen flow out, the β-ketolactones and β-diketones **1** (1 eq, 2 mmol) and the indium (III) triflate catalyst (2 mol%, 5 mol% or 10 mol%) are introduced and solubilized in 10 ml of dry dichloroethane or nitromethane. The allyl acetate **2** (5 eq, 10 mmol) is then added. The reaction mixture is brought to reflux of the solvent used, with the aid of a bath of silicone oil until complete conversion of the starting β-ketolactones and β-diketones **1**. The reaction is monitored by GC, TLC and GC/MS. The reaction crude is hydrolyzed with a saturated solution of $NaHCO_3$ and extracted twice with dichloromethane. The organic phases are dried over $MgSO_4$ and evaporated on a rotary evaporator. The obtained products are purified by flash column chromatography of silica gel.

2. Reaction of β-ketolactones and β-diketones 1 with prenyl acetate 2a.

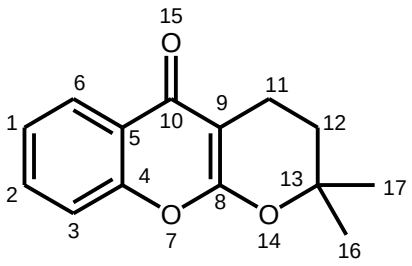
---------- 2,2-Dimethyl-3,4-dihydro-2*H*-pyrano[2,3-*b*]chromen-5-one **3aa** ---------
---------- 2,2-Dimethyl-3,4-dihydro-2*H*-pyrano[3,2-*c*]chromen-5-one **4aa** --------



3aa **4aa**

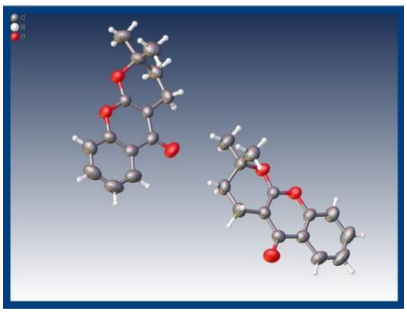
Chemical Formula: $C_{14}H_{14}O_3$
Molecular Weight: 230.2592

According to the general protocol **A**, products **3aa** and **4aa** are obtained with a total yield of 99% (**3aa**/**4aa**=72/28), starting from 4-hydroxycoumarin **1a** (1 eq, 324 mg, 2 mmol), prenyl acetate **2a** (5 eq, 1281.7 mg, 10 mmol) and $In(OTf)_3$ (5 mol%, 56.1 mg), after 2 hours under reflux of dichloroethane (10 ml). Compounds **3aa** and **4aa** are purified by flash column chromatography, using a mixture of PE/Et_2O:90/10. Compounds **3aa** and **4aa** are isolated with 71% and 28%, respectively.



3aa

Yield : 71%
Cas Number: 31490-71-8
3aa : yellow solid
TLC: Rf = 0.32 (PE/Et_2O:9/1)
Mp = 70 °C



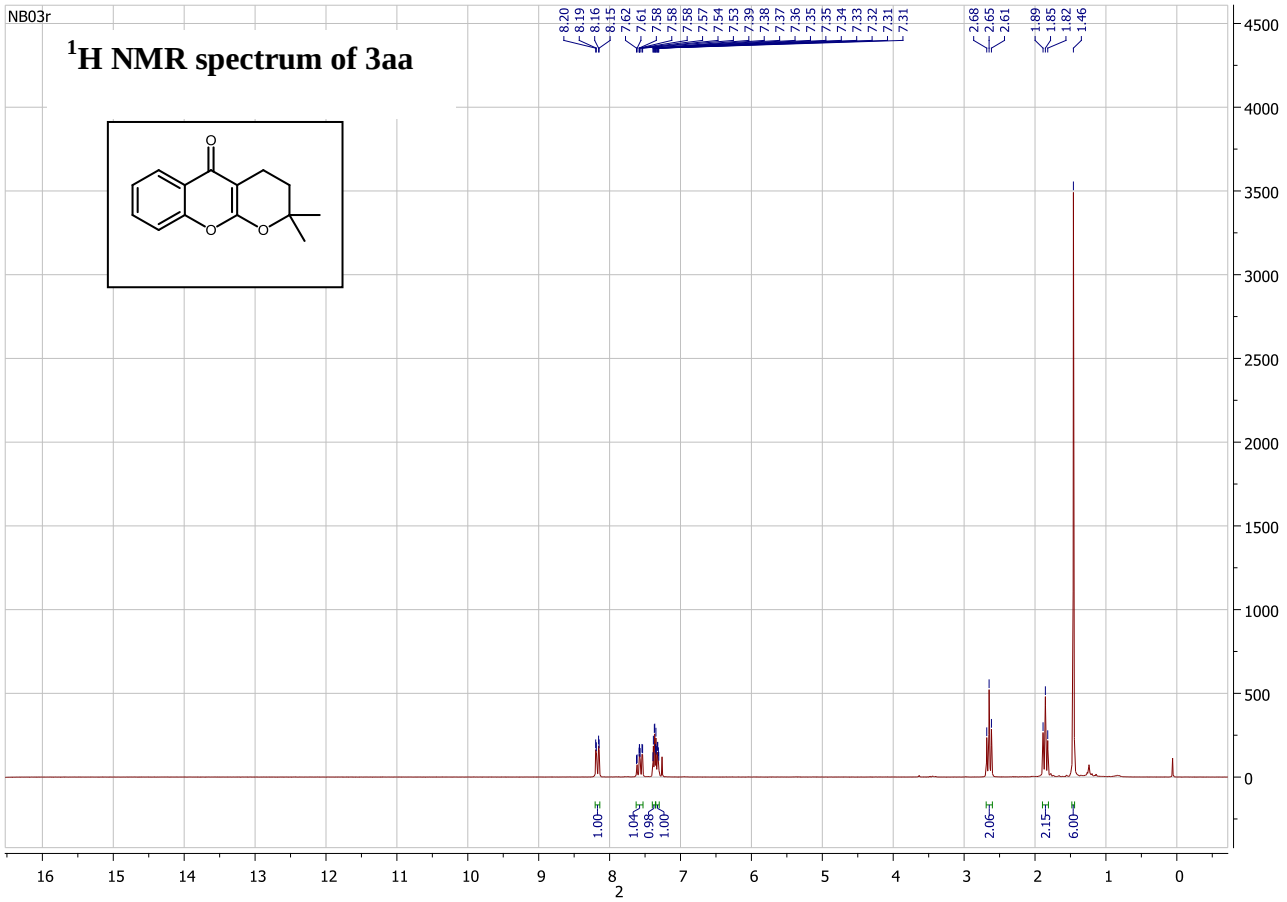
X-ray crystal structure of **3aa**

^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 8.20 – 8.15 (dd, *J* = 8.2 Hz, *J* = 2 Hz, $1H_6$), 7.62 – 7.53 (td, *J* = 7.4 Hz, *J* = 1.8 Hz, $1H_2$), 7.39 – 7.36 (dd, *J* = 7.4 Hz, *J* = 1.8 Hz, $2H_3$), 7.35 – 7.31 (td, *J* = 8.2 Hz, *J* = 1.8 Hz, $2H_1$), 2.65 (t, *J* = 6.6 Hz, $2H_{11}$), 1.85 (t, *J* = 6.6 Hz, $2H_{12}$), 1.46 (s, $6H_{16, 17}$).

^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 177.89 (C10), 163.07 (C8), 153.34 (C4), 132.73 (C2), 125.77 (C1), 124.87 (C6), 122.68 (C5), 117.14 (C3), 95.44 (C9), 82.23 (C13), 32.21 (C12), 26.56 (C16, 17), 15.77 (C11).

IR (neat): ν_{max} (cm^{-1}) : 2974, 2934, 1717, 1609, 1559, 1465, 1415, 1303, 1234, 1181, 1159, 1114, 943, 890, 818, 761, 754, 713, 693, 680, 611, 584, 529, 499, 466, 414.

MS (EI, 70 eV): 231 (0.78) [$M^{+\cdot}$+1] : 230 (59), 215 (2), 187 (45), 175 (79), 162 (2), 145 (3), 136 (13), 128 (8), 121 (65), 93 (18), 92 (75), 77 (23), 56 (20), 41 (100).


NB03r
^{1}H NMR spectrum of 3aa
8.20
8.19
8.16
8.15
7.62
7.61
7.58
7.58
7.58
7.57
7.54
7.53
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
2.68
2.65
2.61
1.89
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1.82
1.46
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1.04
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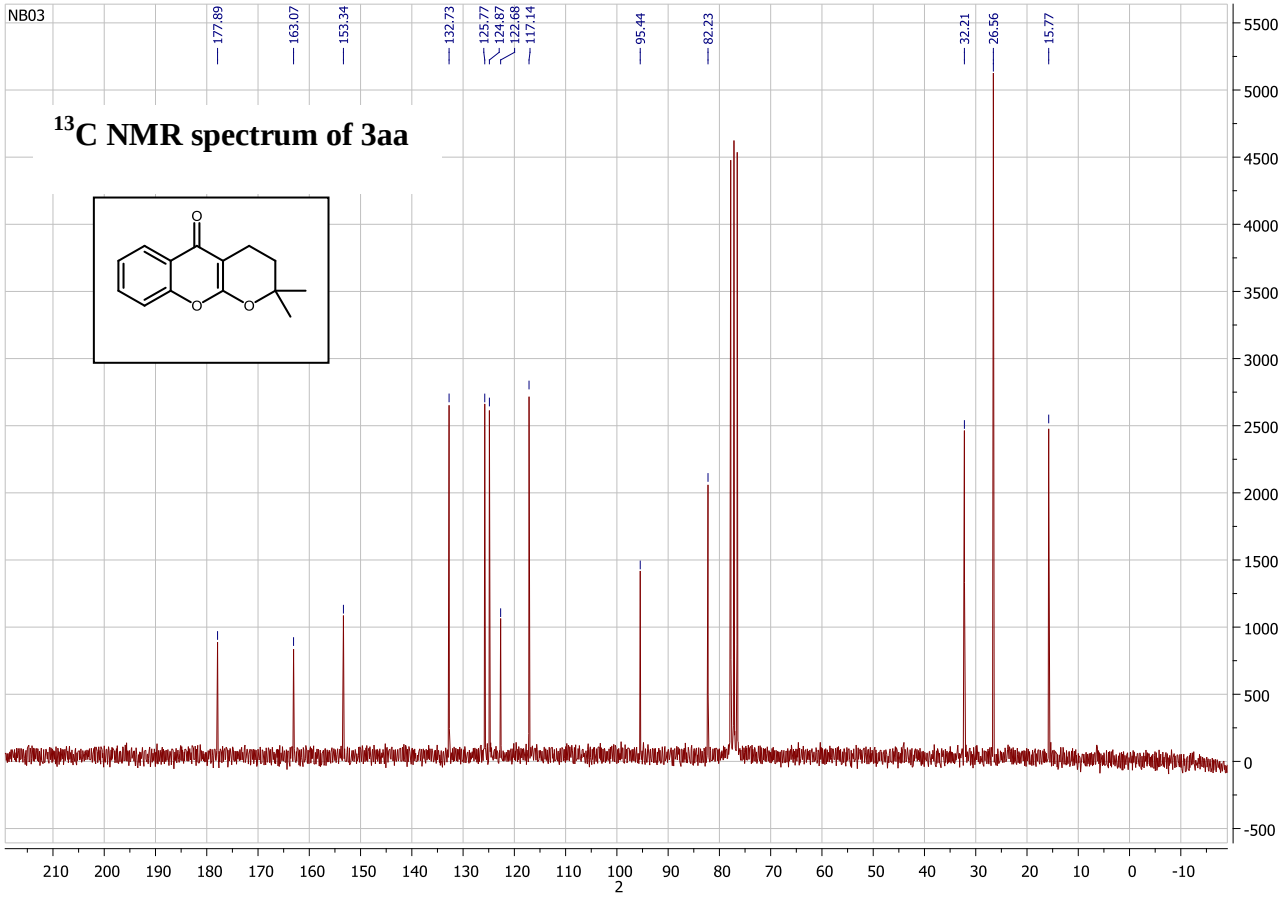
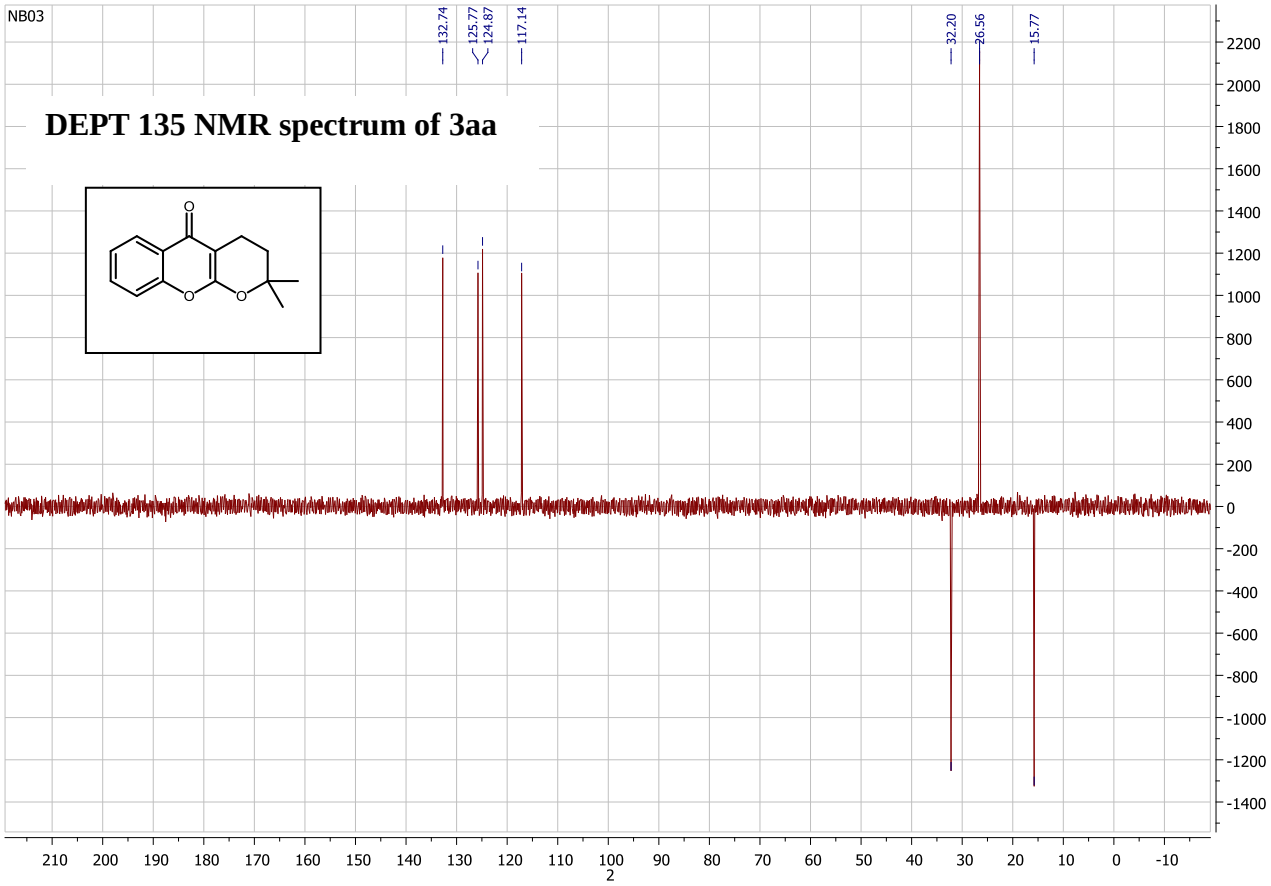
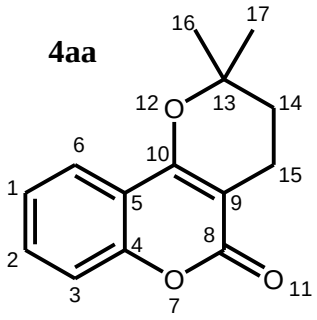
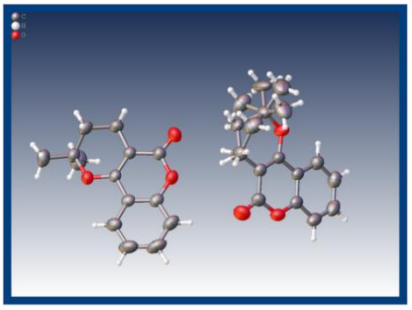
1.00
2.06
2.15
6.00
f2


NB03
^{13}C NMR spectrum of 3aa
177.89
163.07
153.34
132.73
125.77
124.87
122.68
117.14
95.44
82.23
32.21
26.56
15.77
f2





Yield : 28%
Cas Number: 31490-68-3
4aa : brown solid
TLC: Rf = 0.62 (PE/Et_2O:9/1)
Mp = 124 °C



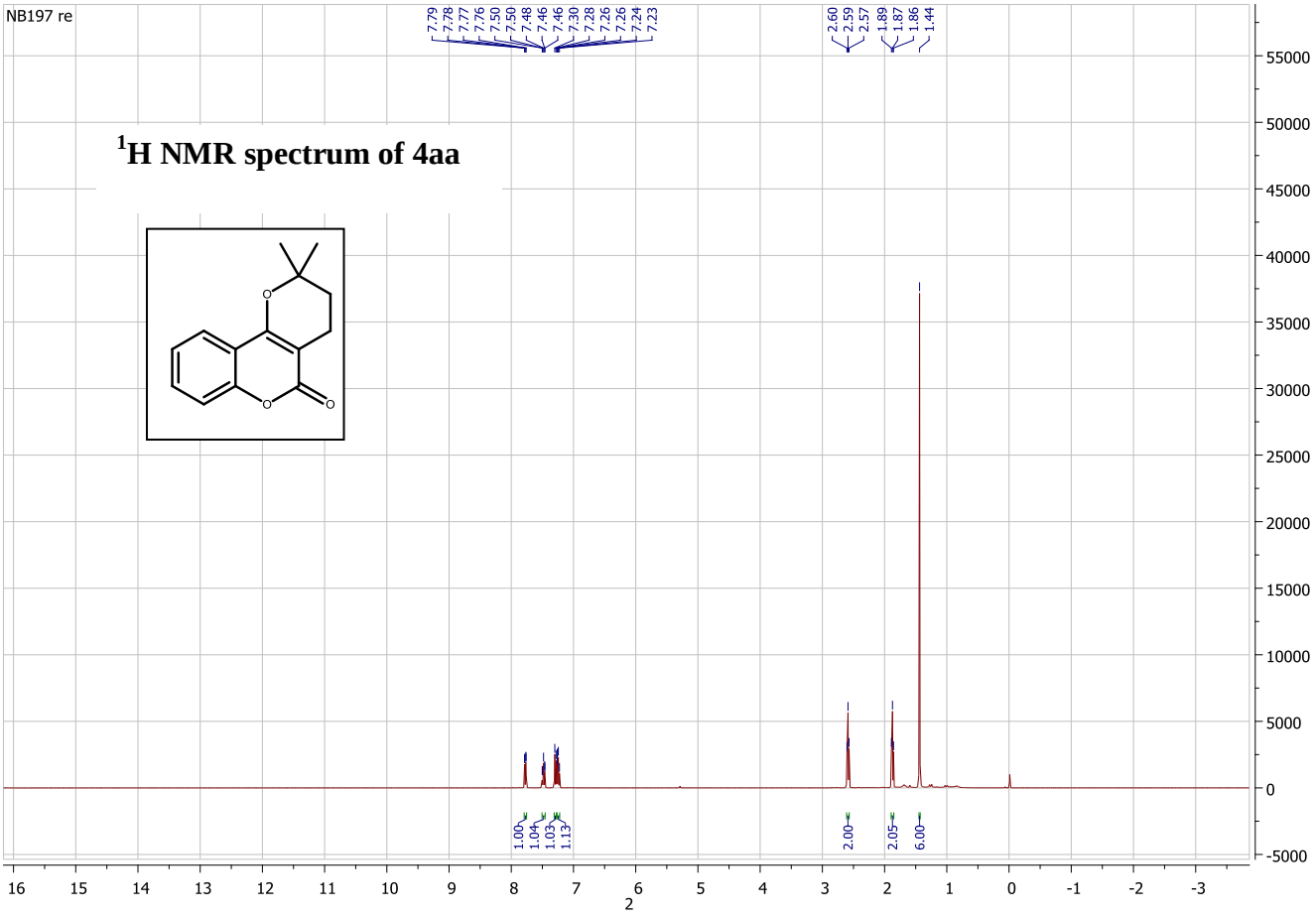
X-ray crystal structure of **4aa**

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.79 – 7.76 (dd, *J* = 8 Hz, *J* = 1.6 Hz, $1H_6$), 7.50 – 7.46 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, $1H_2$), 7.30 – 7.28 (d, *J* = 8 Hz, $1H_3$), 7.26 – 7.23 (t, *J* = 7.6 Hz, $1H_1$), 2.59 (t, *J* = 6.8 Hz, $2H_{15}$), 1.87 (t, *J* = 6.8 Hz, $2H_{14}$), 1.44 (s, $6H_{16, 17}$).

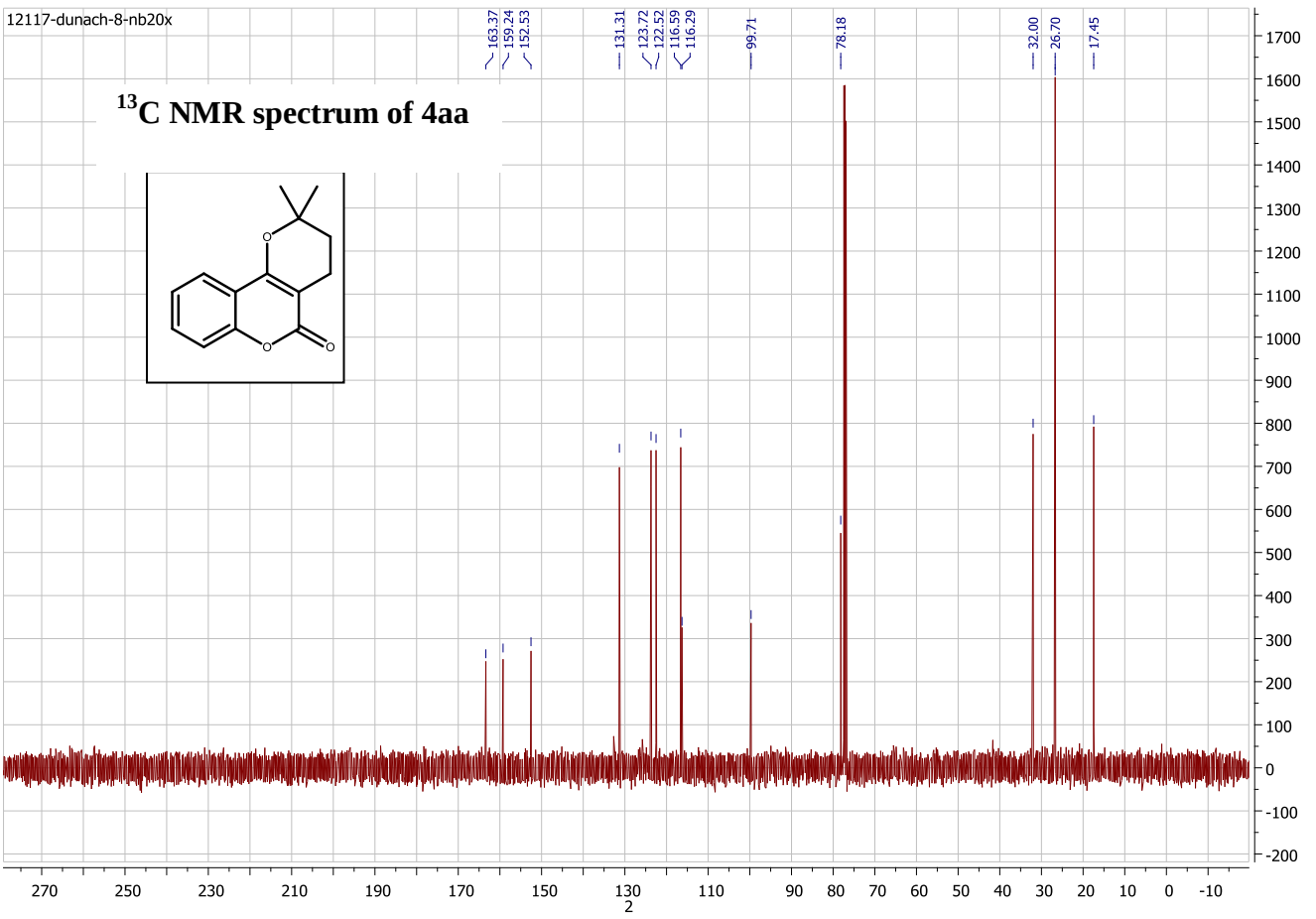
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm]: 163.37 (C8), 159.24 (C10), 152.53 (C4), 131.31 (C2), 123.72 (C1), 122.52 (C6), 116.59 (C3), 116.29 (C5), 99.71 (C9), 78.18 (C13), 32.00 (C14), 26.70 (C16, 17), 17.45 (C15).

IR (neat): ν_{max} (cm^{-1}) : 2977, 2944, 1698, 1625, 1608, 1575, 1491, 1396, 1327, 1172, 1159, 1152, 1114, 1108, 1054, 998, 983, 919, 900, 827, 778, 756, 729, 690, 658, 599.

MS (EI, 70 eV): 231 (12) [$M^{+\cdot}$ + 1]: 230 (70), 215 (14), 187 (52), 175 (100), 162 (3), 129 (3), 121 (69), 120 (41), 92 (68), 89 (11), 43 (21), 41 (56).

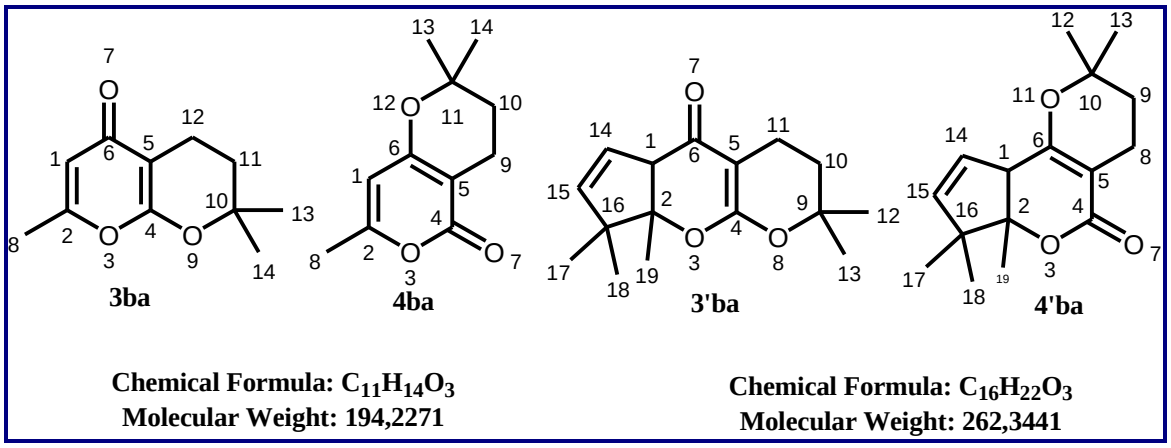


^{1}H NMR spectrum of 4aa

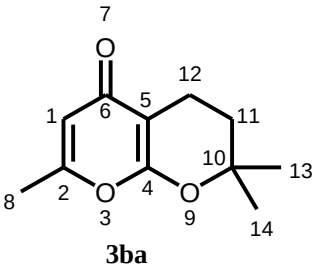


^{13}C NMR spectrum of 4aa

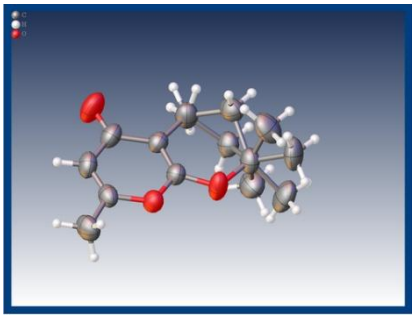
---------- 2,7,7-Trimethyl-6,7-dihydro-5*H*-pyrano[2,3-*b*]pyran-4-one **3ba** ----------
---------- 2,2,7-Trimethyl-3,4-dihydro-2*H*-pyrano[4,3-*b*]pyran-5-one **4ba** ----------
-- 3,3,3a,6,6-Pentamethyl-3a,7,8,9a-tetrahydro-3*H*,6*H*-4,5-dioxa-cyclopenta[*b*]naphthalen-9-one **3'ba** --
-- 3,3,3a,8,8-Pentamethyl-3,3a,6,7,8,9b-hexahydro-4,9-dioxa-cyclopenta[*a*]naphthalen-5-one **4'ba** --



According to the general protocol **A**, 4-hydroxy-6-methyl-2*H*-pyran-2-one **1b** (1 eq, 252 mg, 2 mmol) and prenyl acetate **2a** (5 eq, 1281.7 mg, 10 mmol) are reacted with 2 mol% of $In(OTf)_3$. After 9 h of reaction and complete conversion of **1b**, the crude of reaction is extracted and purified by column chromatography, by eluting with PE/EtOAc:80/20. Compounds **3ba**, **4ba**, **3'ba** and **4'ba** are isolated with a yield of 49%, 13%, 10% and 8% respectively.



Yield : 49%
3ba : yellow solid
TLC: Rf = 0.19 (PE/EtOAc:1/1)
Mp = 97 °C



X-ray crystal structure of **3ba**

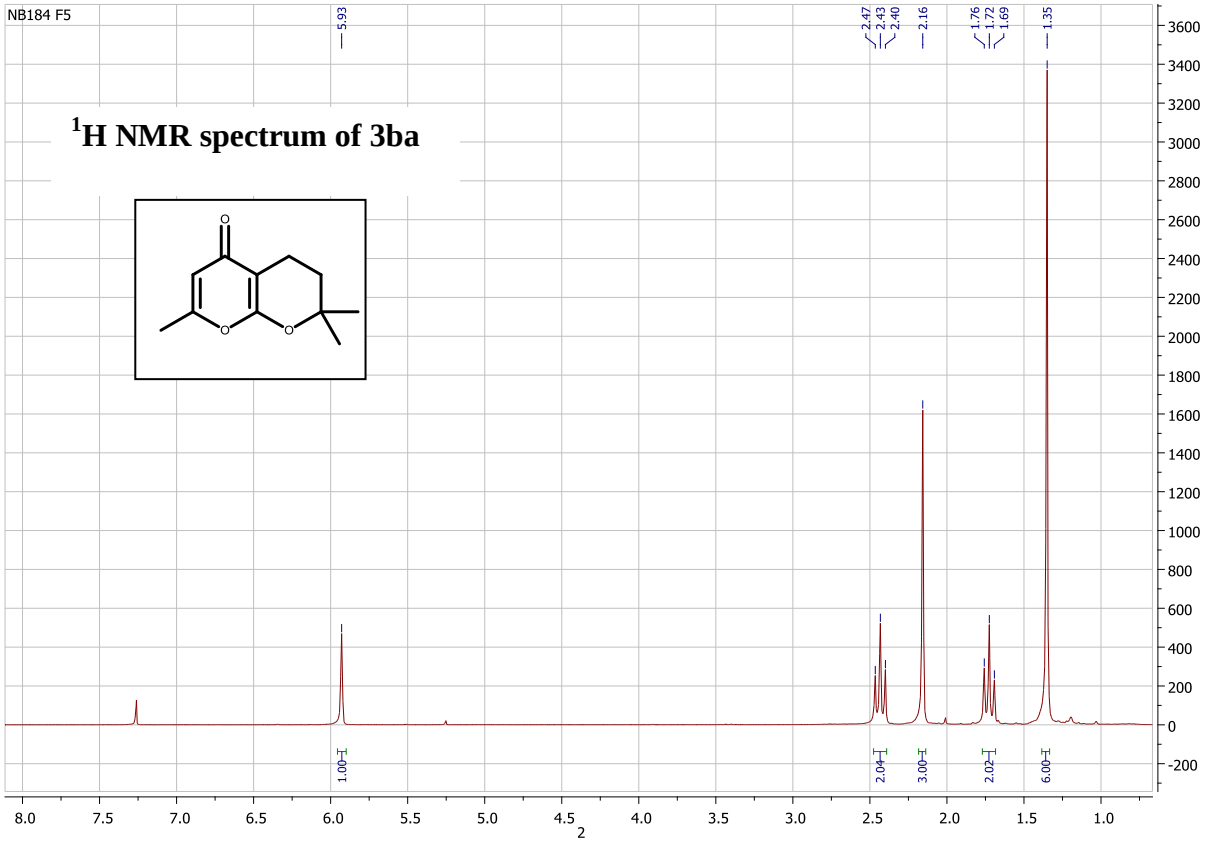
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 5.93 (s, $1H_1$), 2.43 (t, J = 6.6 Hz, $2H_{12}$), 2.16 (s, $3H_8$), 1.72 (t, J = 6.6 Hz, $2H_{11}$), 1.35 (s, $6H_{13, 14}$).

^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 180.25 (C6), 163.07 (C2), 160.53 (C4), 111.87 (C1), 97.50 (C5), 81.57 (C10), 32.01 (C11), 26.32 (C13, 14), 19.19 (C_8), 15.18 (C12).

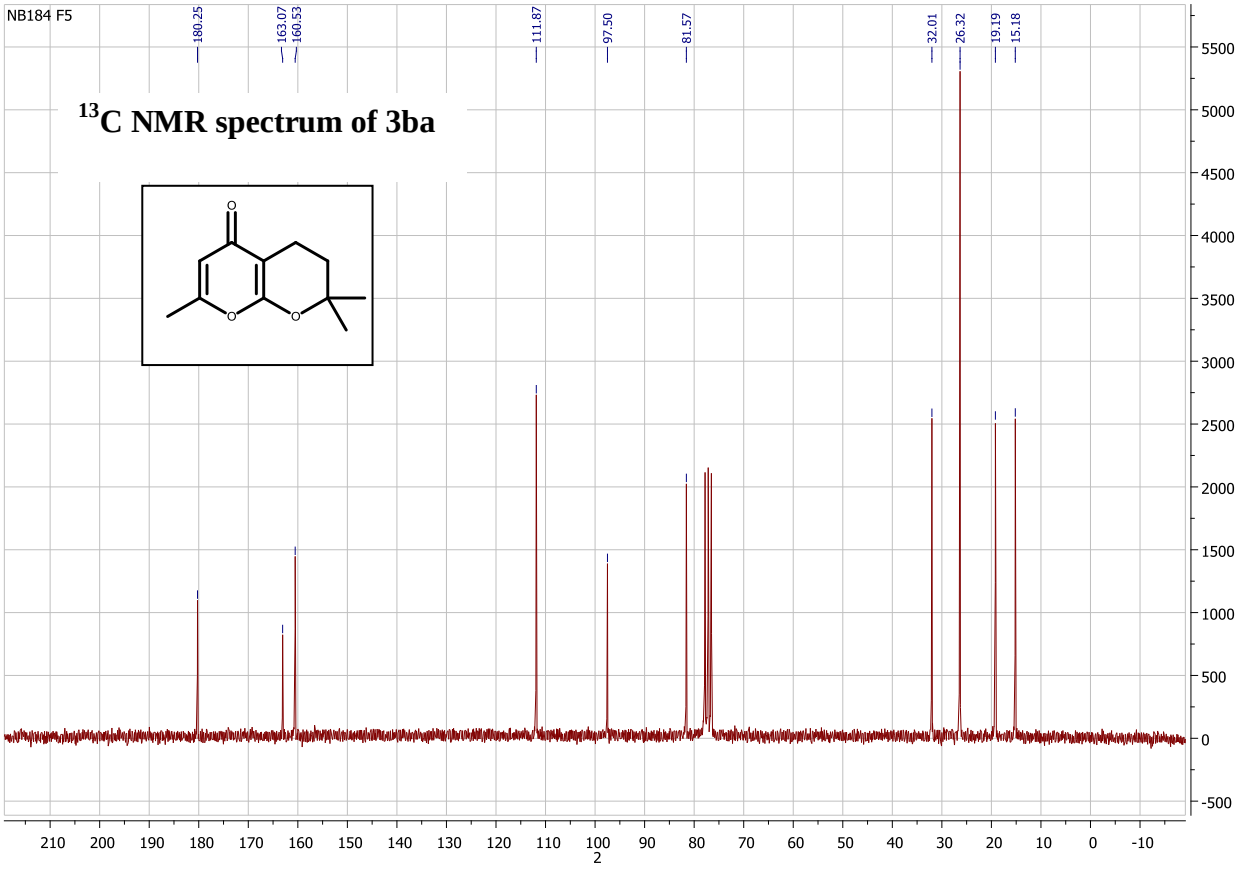
IR (neat): ν_{max} (cm^{-1}) : 3056, 1661, 1619, 1579, 1425, 1385, 1373, 1311, 1274, 1261, 1221, 1179, 1158, 1136, 1113, 996, 887, 834, 760, 737, 666.

MS (EI, 70 eV): 194 (10) [$M^{+\cdot}$]: 139 (28), 44 (92), 40 (100).

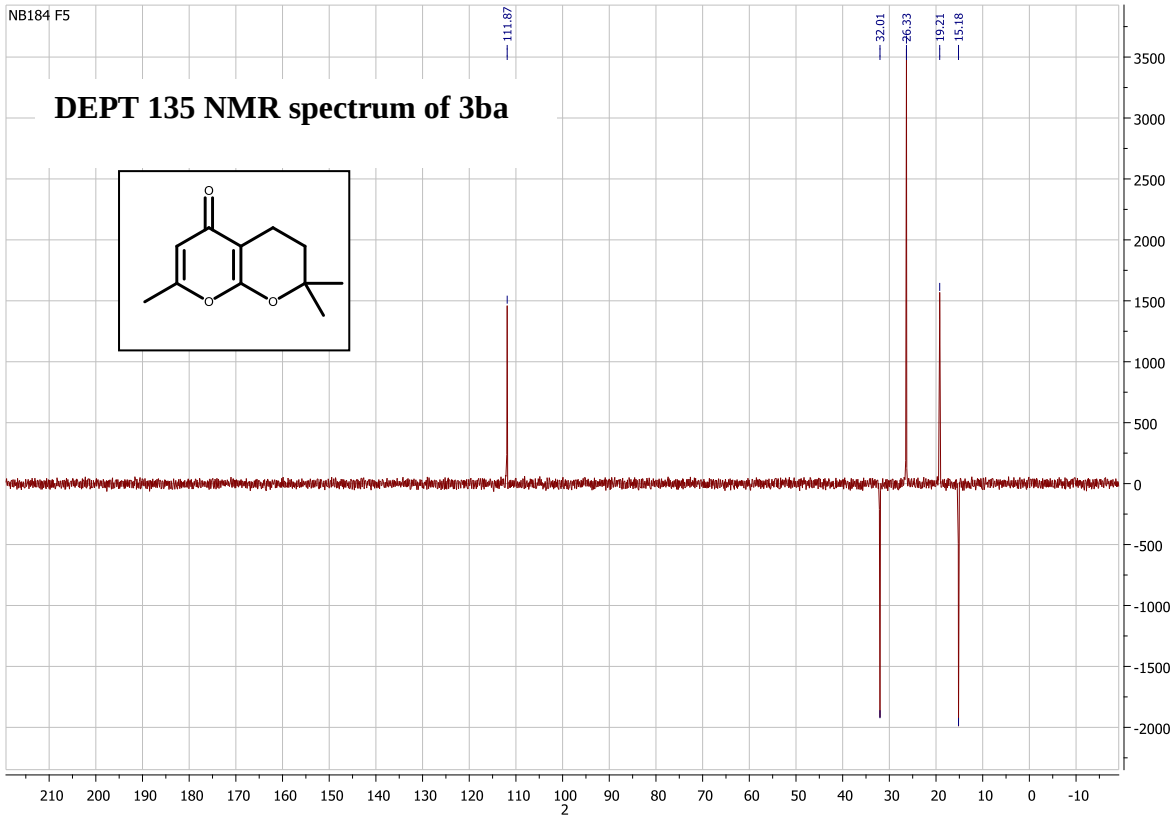
HRMS m/z calcd. For $C_{11}H_{14}O_3$ [$M^{+\cdot}$]: 194.0943, found 194.1000.



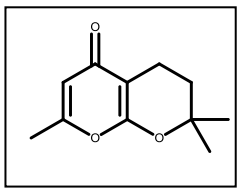
^{1}H NMR spectrum of 3ba



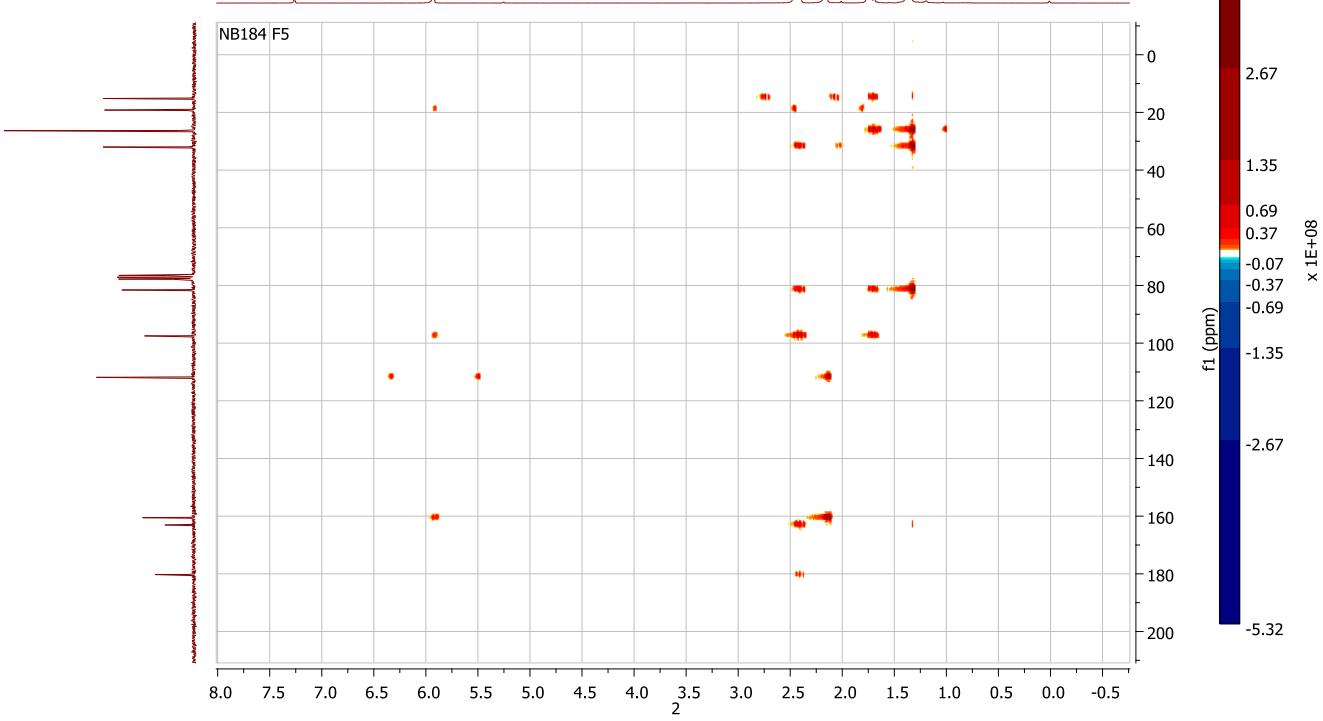
^{13}C NMR spectrum of 3ba



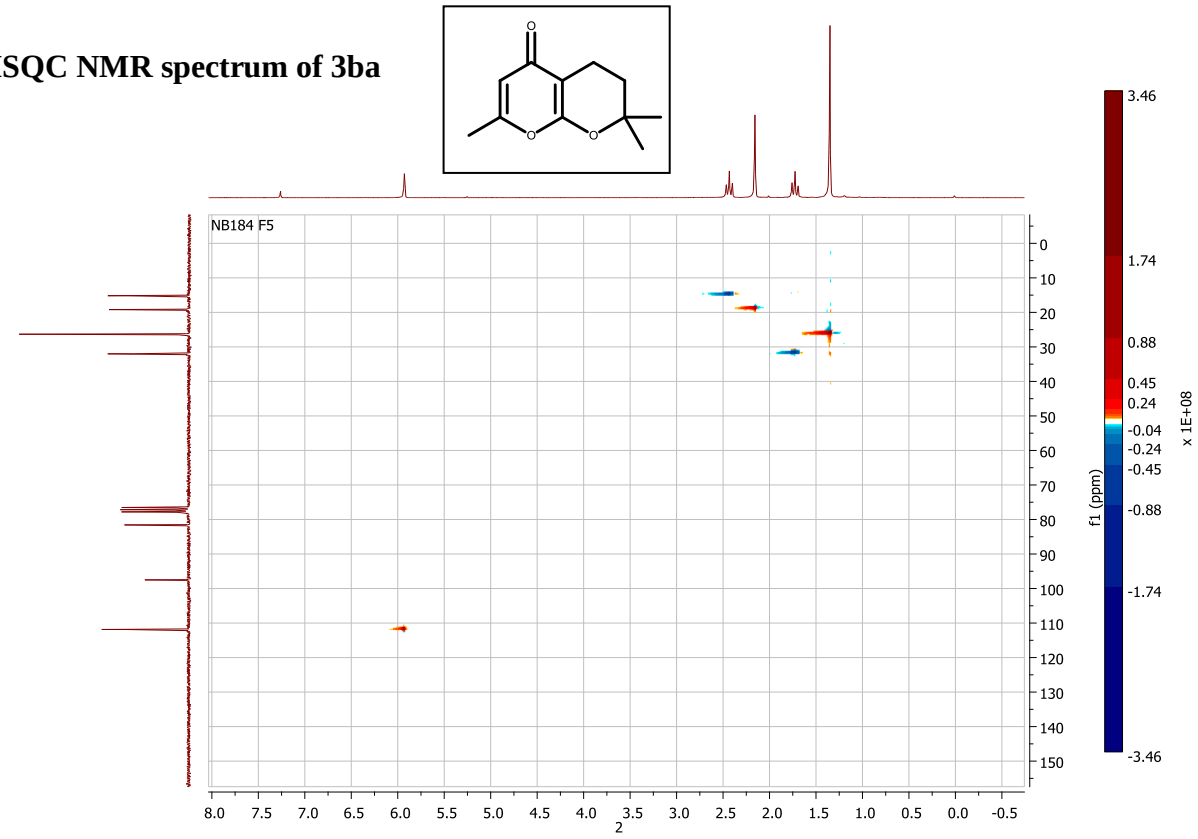
DEPT 135 NMR spectrum of 3ba



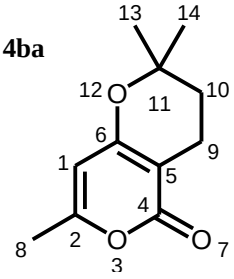
HMBC NMR spectrum of 3ba



HSQC NMR spectrum of 3ba



4ba



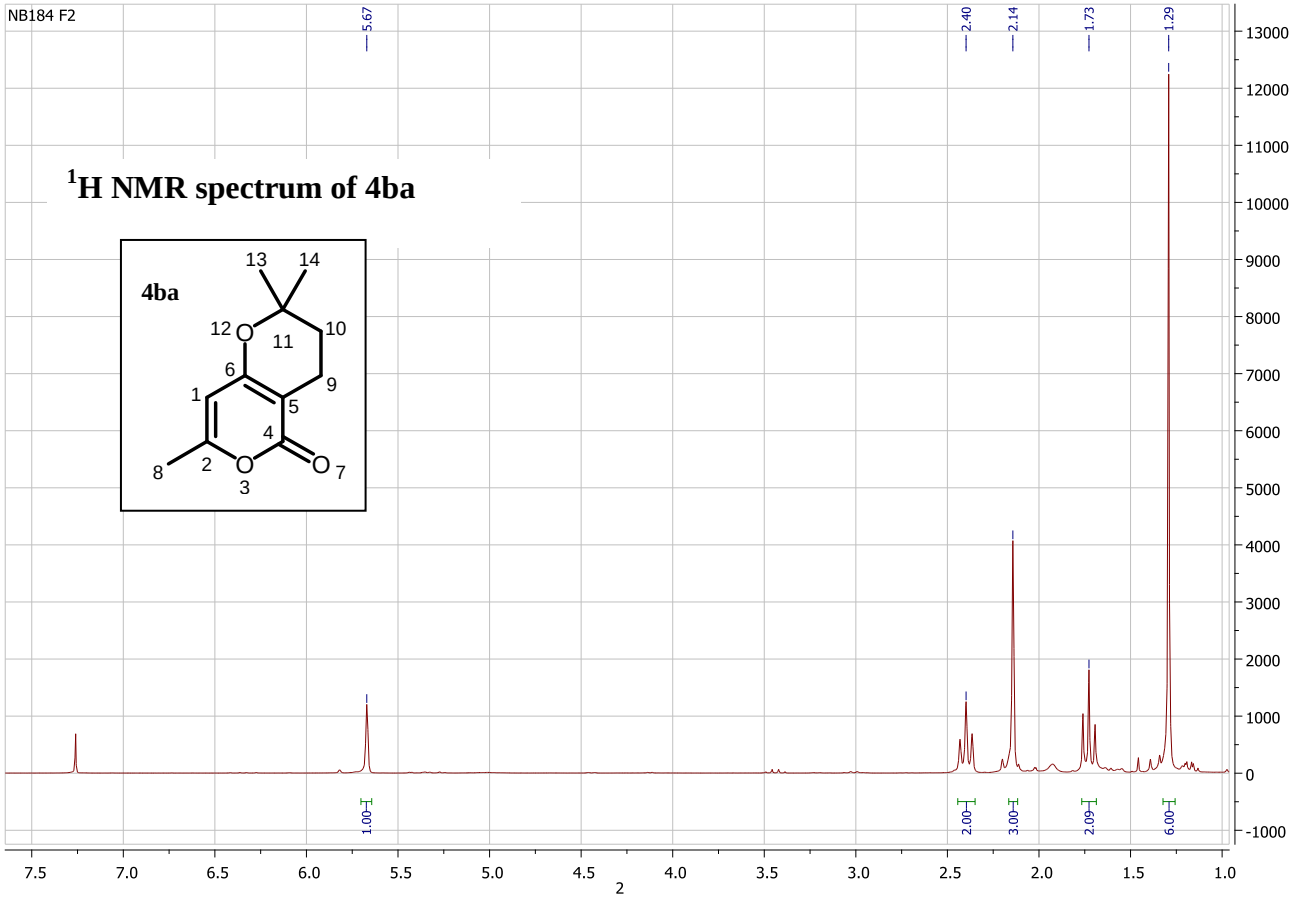
Yield : 13%
Cas number: 77901-42-9
4ba : beige solid
TLC: Rf = 0.4 (PE/EtOAc:9/1)
Mp = 128 °C

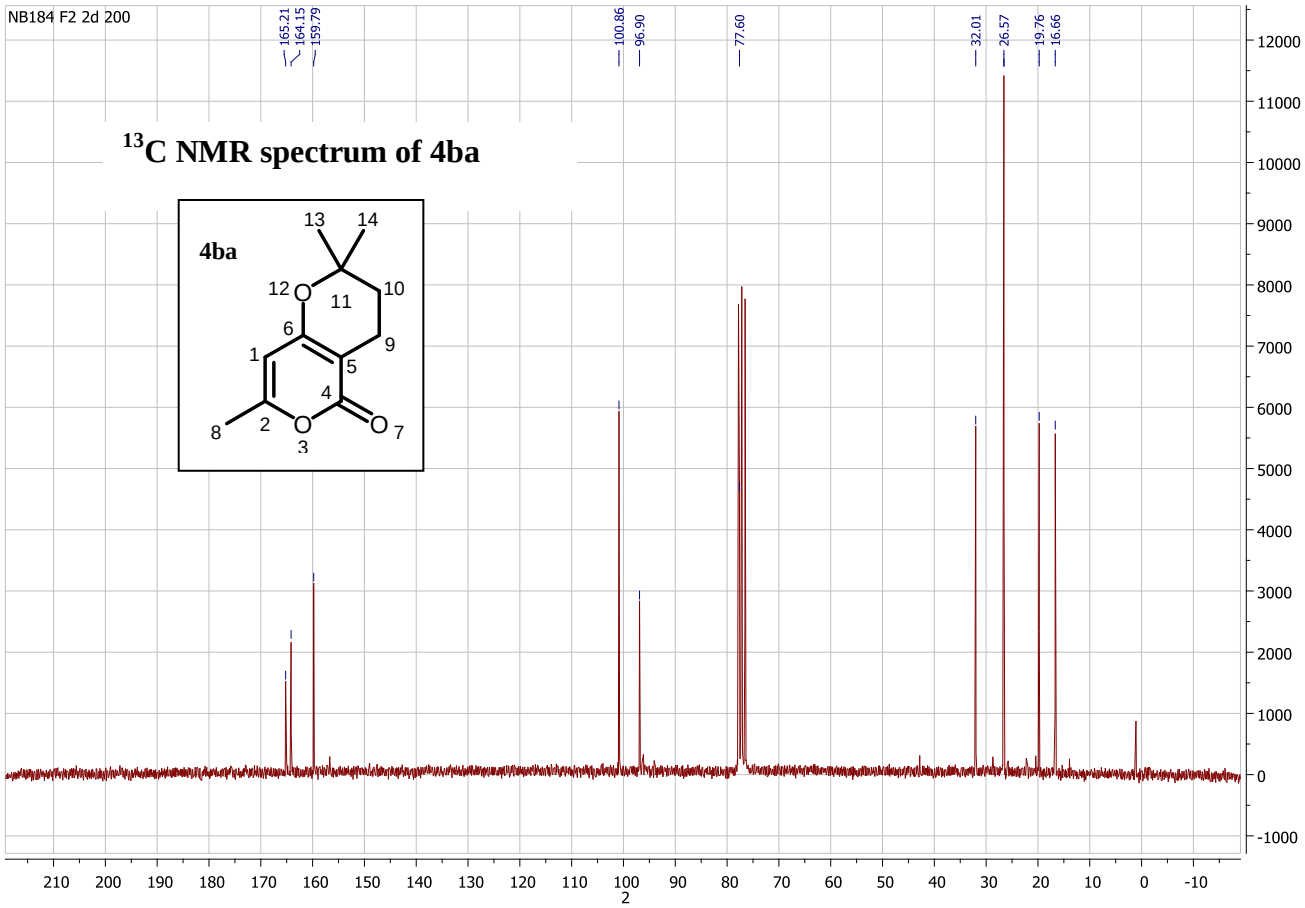
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 5.67 (s, $1H_1$), 2.40 (t, *J* = 6.6 Hz, $2H_9$), 2.14 (s, $3H_8$), 1.73 (t, *J* = 6.6 Hz, $2H_{10}$), 1.29 (s, $6H_{13, 14}$).

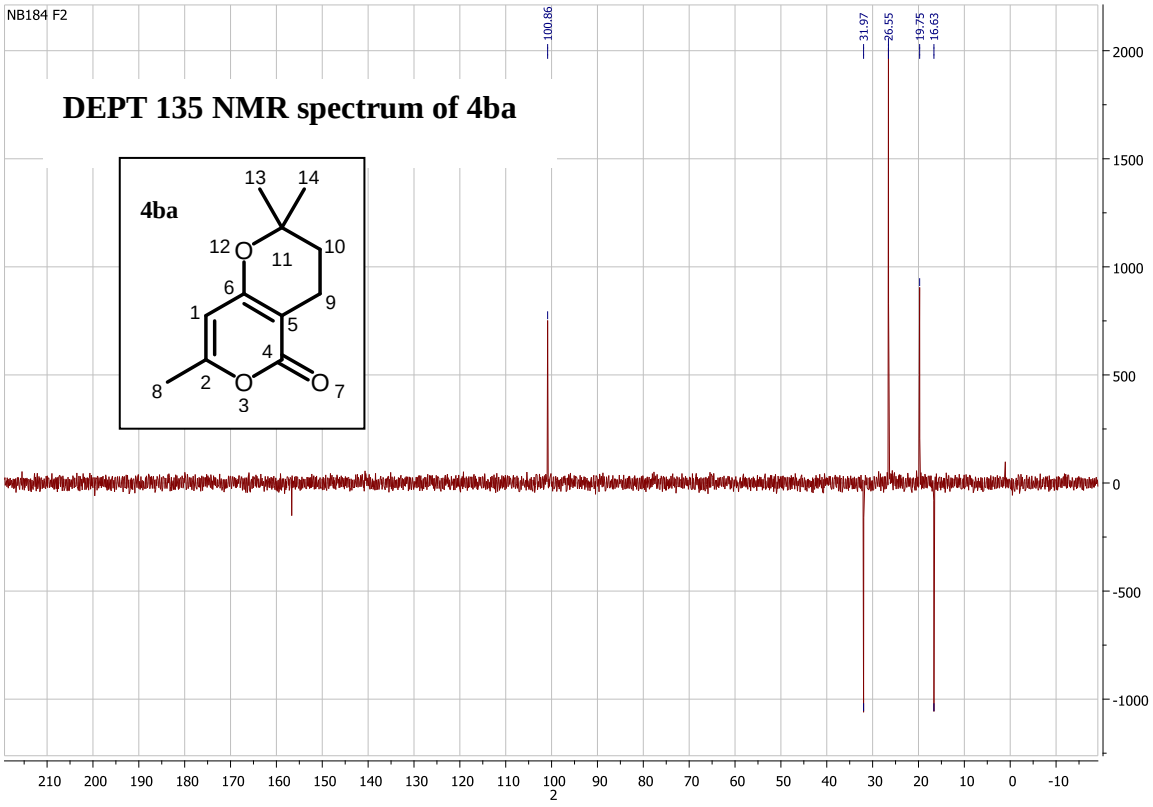
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 165.21 (C6), 164.15 (C4), 159.79 (C2), 100.86 (C1), 96.90 (C5), 77.60 (C11), 32.01 (C10), 26.57 (C13, 14), 19.76 (C8), 16.66 (C9).

IR (neat): ν_{max} (cm^{-1}) = 2976, 1701, 1652, 1578, 1446, 1406, 1385, 1372, 1308, 1246, 1206, 1180, 1143, 1113, 1040, 996, 954, 855, 811, 766, 734.

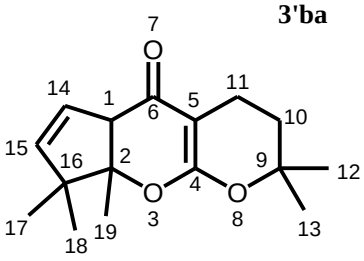
MS (EI, 70 eV): 194 (39) [M+.], 179 (10), 151 (18), 139 (100), 85 (21), 55 (13), 43 (48).


NB184 F2
5.67
2.40
2.14
1.73
1.29
1H NMR spectrum of 4ba
4ba
1.00
2.00
3.00
2.09
6.00
f2


NB184 F2 2d 200
165.21
164.15
159.79
100.86
96.90
77.60
32.01
26.57
19.76
16.66
13C NMR spectrum of 4ba
4ba
f2



3'ba



Yield : 10%
3'ba : yellow liquid
TLC: Rf = 0.36 (PE/EtOAc:1/1)

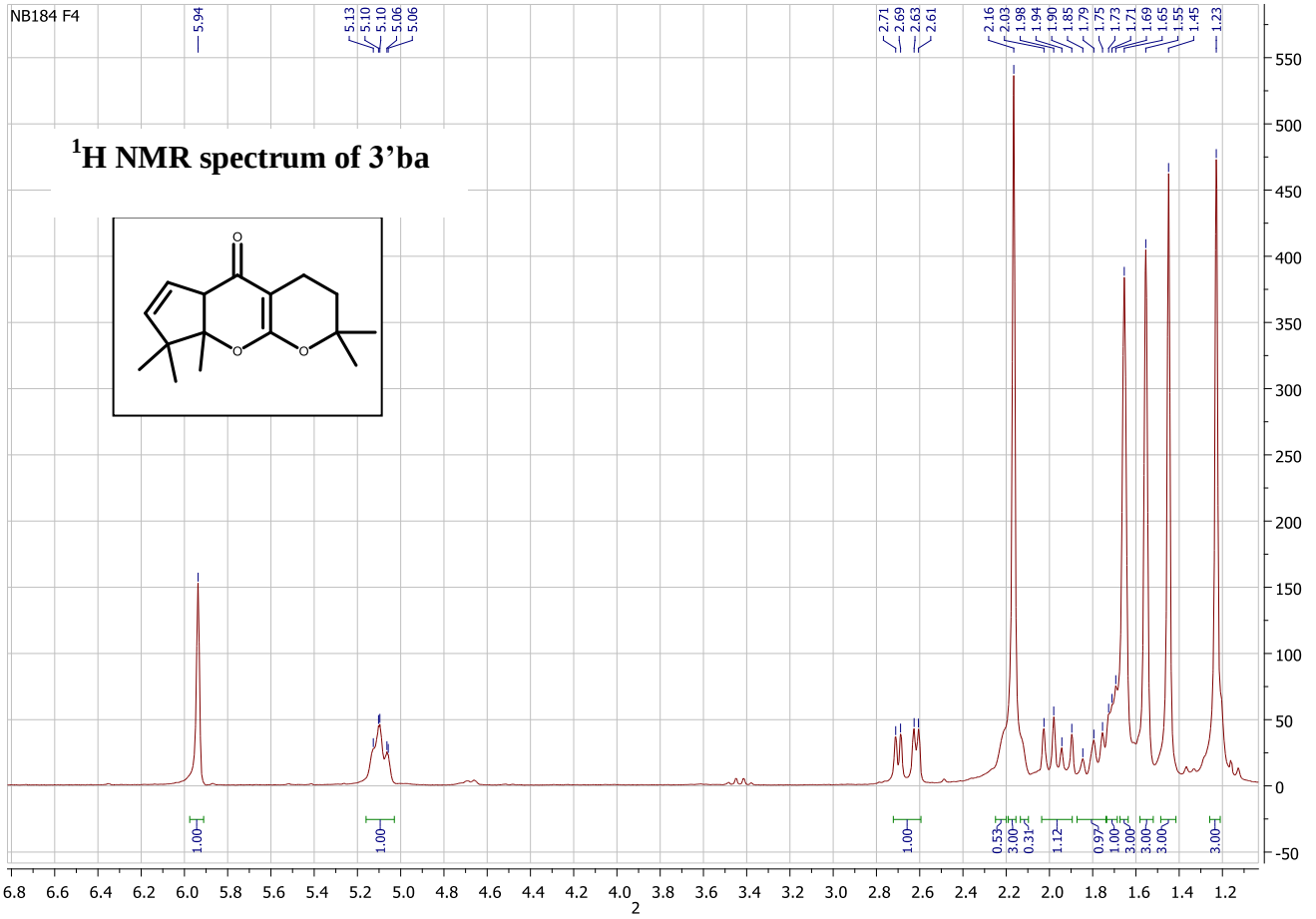
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 5.94 (d, *J* = 1.4 Hz, $1H_{15}$), 5.10 (t, *J* = 7.6 Hz, $1H_{14}$), 2.71 – 1.90 (m, $2H_{11}$), 2.17 – 1.75 (m, $2H_{10}$), 2.16 (s, $3H_{19}$), 1.73–1.69 (m, $1H_1$), 1.65 (s, $3H_{13}$), 1.55 (s, $3H_{12}$), 1.45 (s, $3H_{17}$), 1.23 (s, $3H_{18}$).

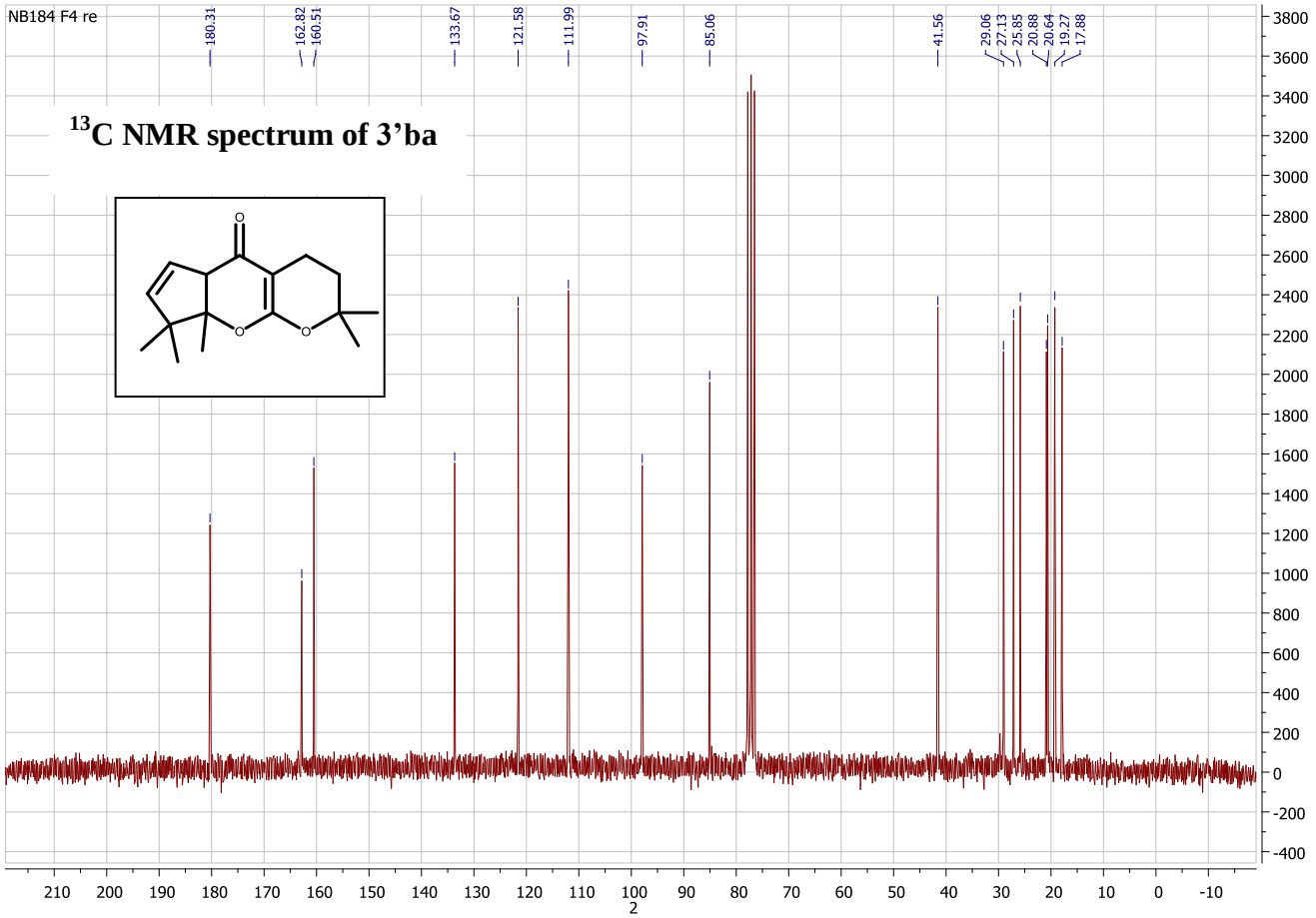
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 180.31 (C6), 162.82 (C4), 160.51 (C2), 133.67 (C5), 121.58 (C14), 111.99 (C15), 97.91 (C16), 85.06 (C9), 41.56 (C1), 29.06 (C10), 27.13 (C17), 25.85 (C13), 20.88 (C11), 20.64 (C18), 19.27 (19), 17.88 (C12).

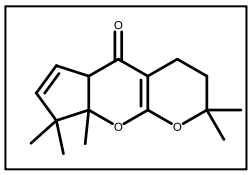
IR (neat): ν_{max} (cm^{-1}) = 2974, 2925, 2871, 1701, 1663, 1631, 1580, 1434, 1386, 1375, 1286, 1260, 1243, 1186, 1120, 1105, 1027, 991, 849, 833, 788, 678, 510, 499, 404.

MS (EI, 70 eV): 262 (62) [M+.], 247 (70), 193 (25), 177 (25), 151 (29), 139 (100), 121 (42), 109 (48), 81 (32), 69 (82), 41 (94).

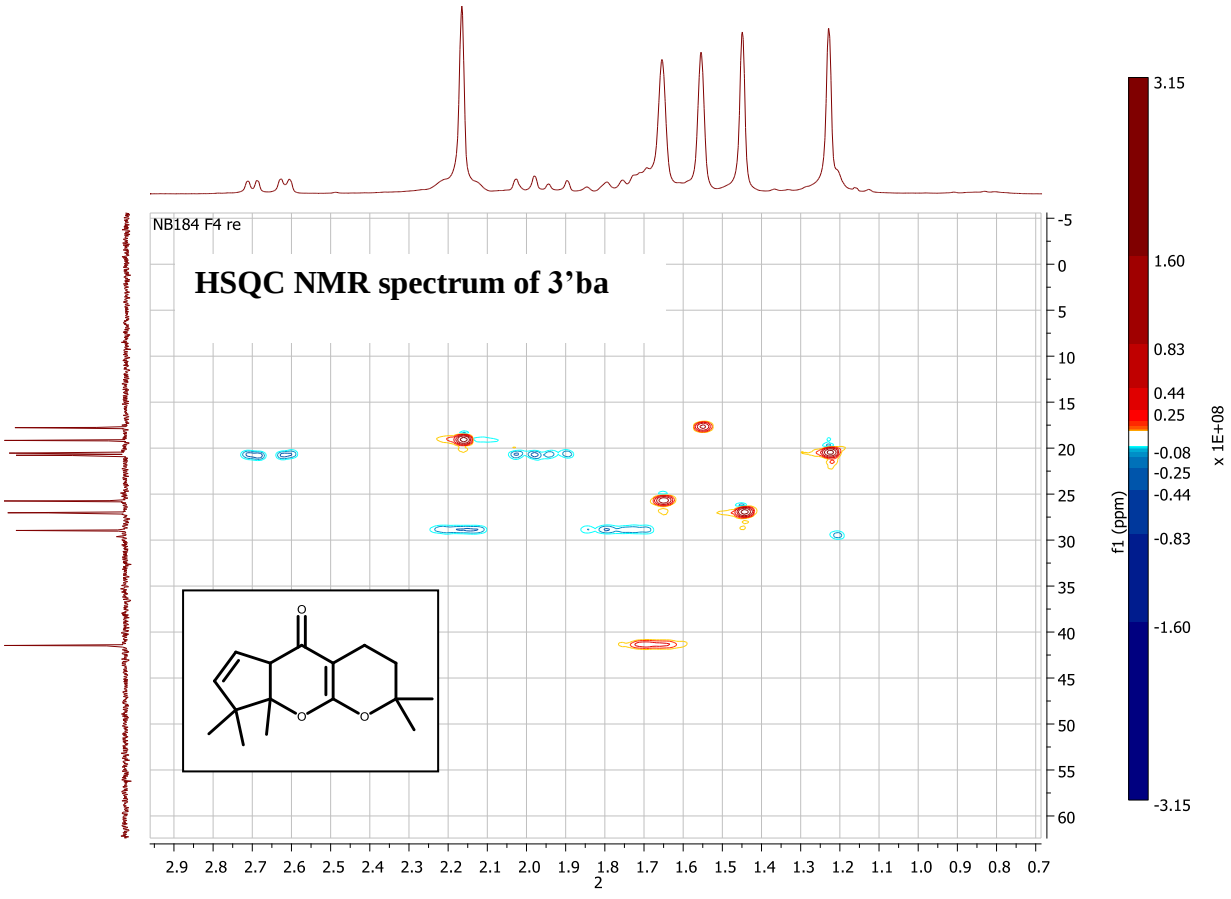
HRMS m/z calcd. For $C_{16}H_{22}O_3$ [$M^{+\cdot}$]: 262.1569, found 262.1581.


NB184 F4
5.94
5.13
5.10
5.10
5.06
5.06
2.71
2.69
2.63
2.61
2.16
2.03
1.98
1.94
1.90
1.85
1.79
1.75
1.73
1.71
1.69
1.65
1.55
1.45
1.23
1H NMR spectrum of 3'ba
O
O
O
1.00
1.00
1.00
0.53
3.00
0.31
1.12
0.97
1.00
3.00
3.00
3.00
6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 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
2

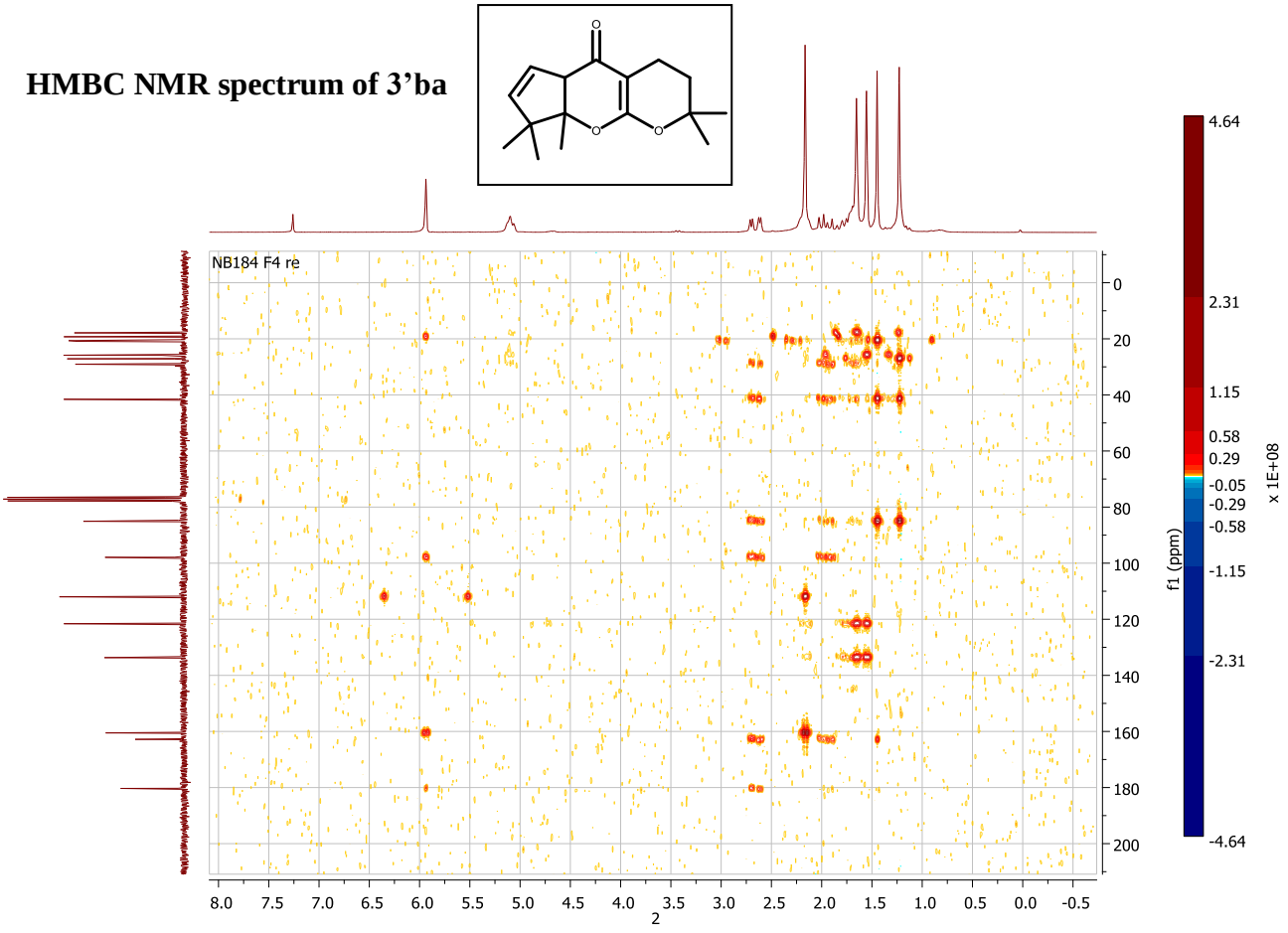

NB184 F4 re
180.31
162.82
160.51
133.67
121.58
111.99
97.91
85.06
41.56
29.06
27.13
25.85
20.88
20.64
19.27
17.88
13C NMR spectrum of 3'ba
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
2



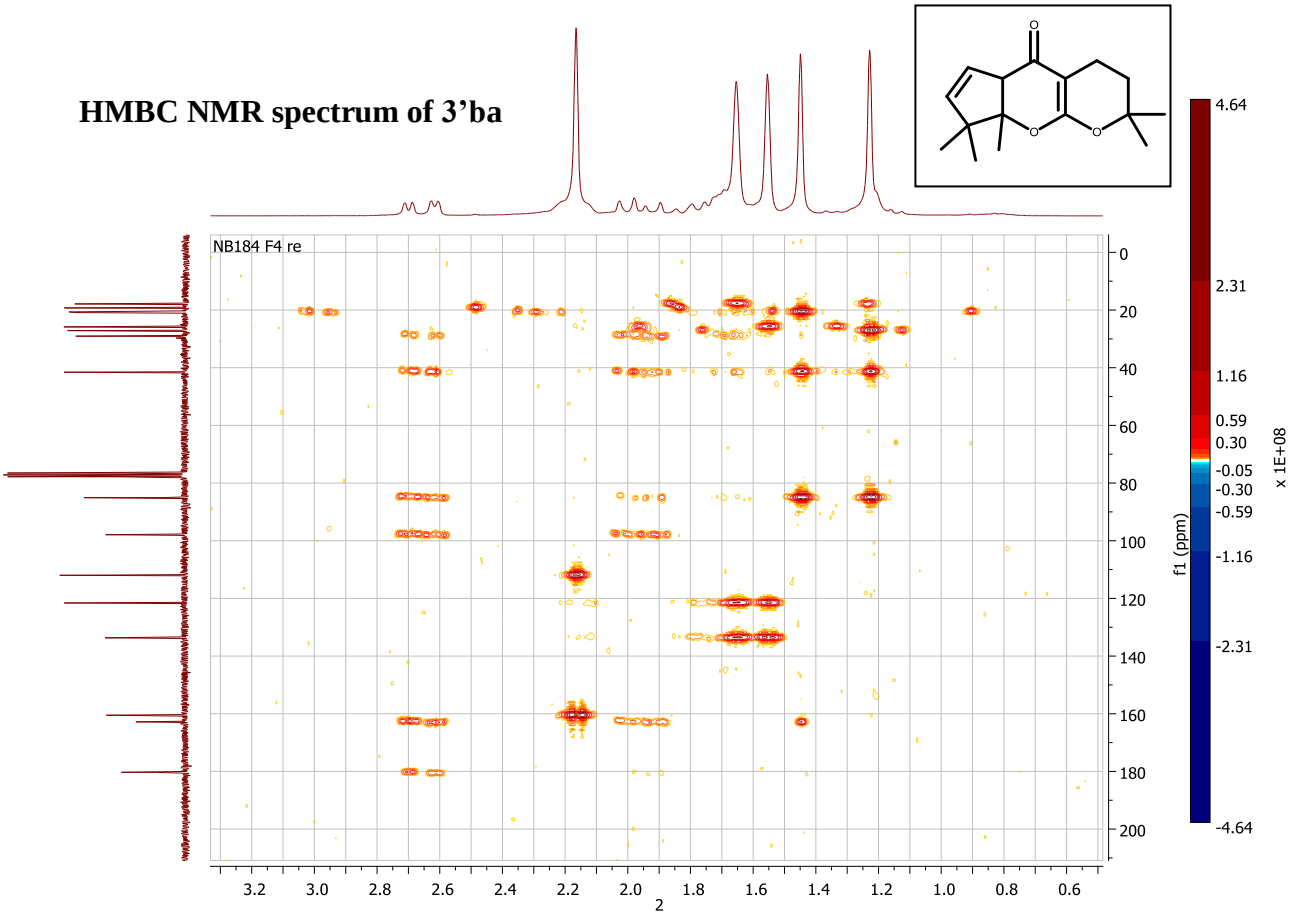
HSQC NMR spectrum of 3’ba



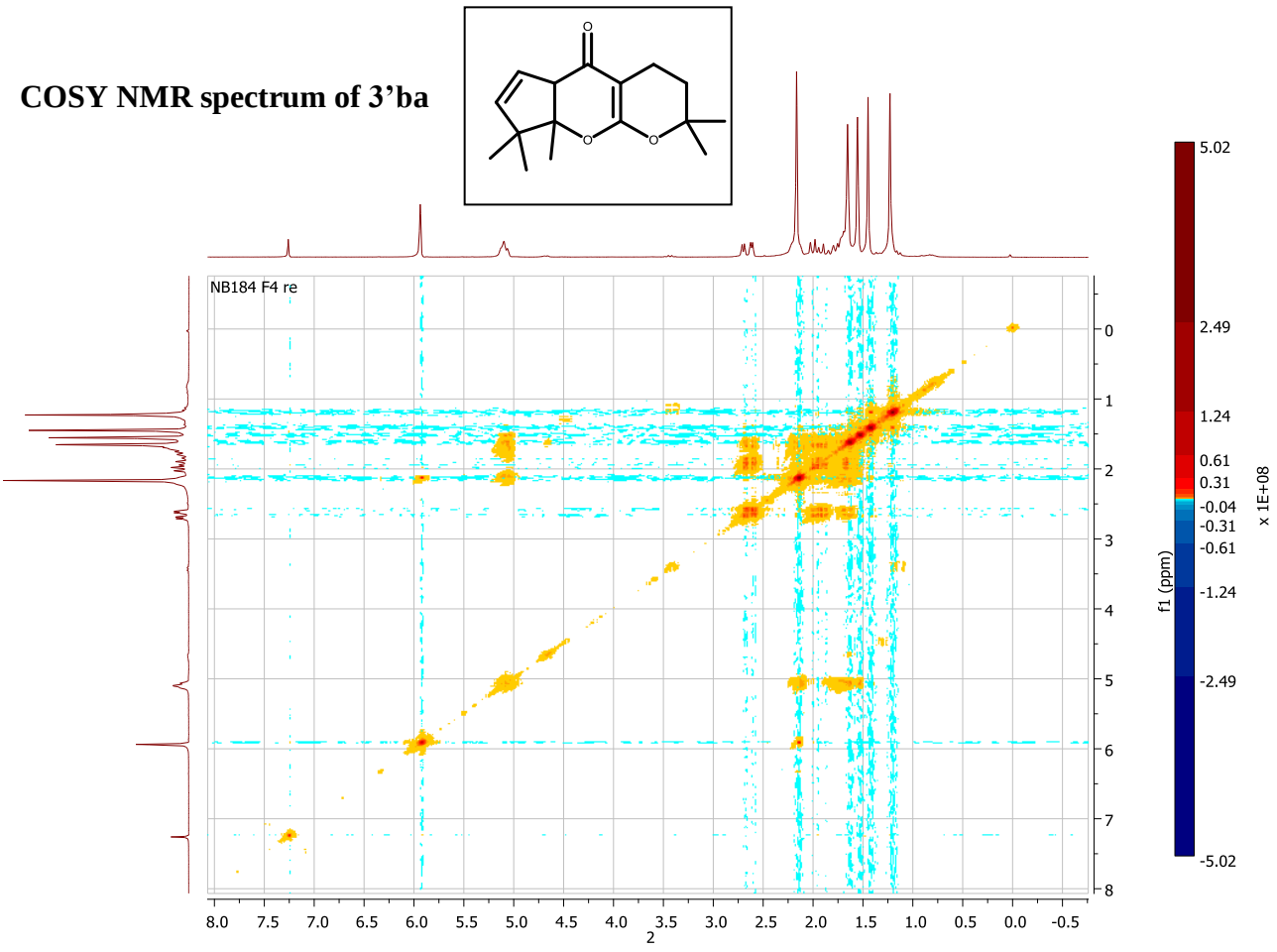
HMBC NMR spectrum of 3’ba



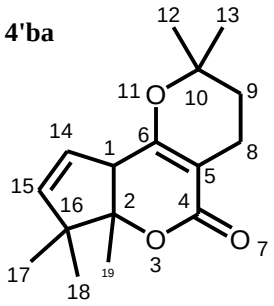
HMBC NMR spectrum of 3’ba



COSY NMR spectrum of 3'ba



4'ba



Yield : 8%
4'ba : colorless liquid
TLC: Rf = 0.7 (PE/EtOAc:9/1)

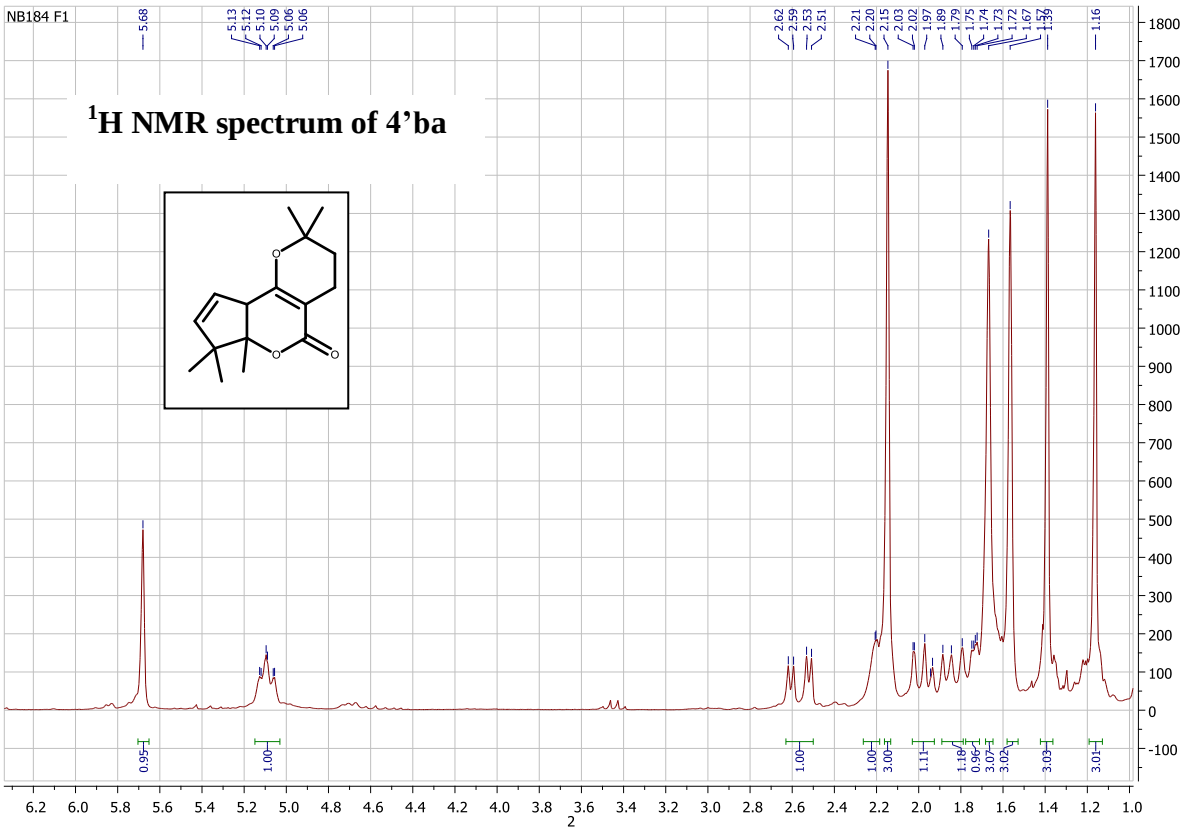
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 5.68 (d, *J* = 1 Hz, $1H_{15}$), 5.10 (t, *J* = 6.2 Hz, $1H_{14}$), 2.62 – 1.93 (m, $2H_8$), 2.21 – 1.79 (m, $2H_9$), 2.15 (s, $3H_{19}$), 1.75 – 1.72 (m, H_1), 1.67 (s, $3H_{12}$), 1.57 (s, $3H_{13}$), 1.39 (s, $3H_{17}$), 1.16 (s, $3H_{18}$).

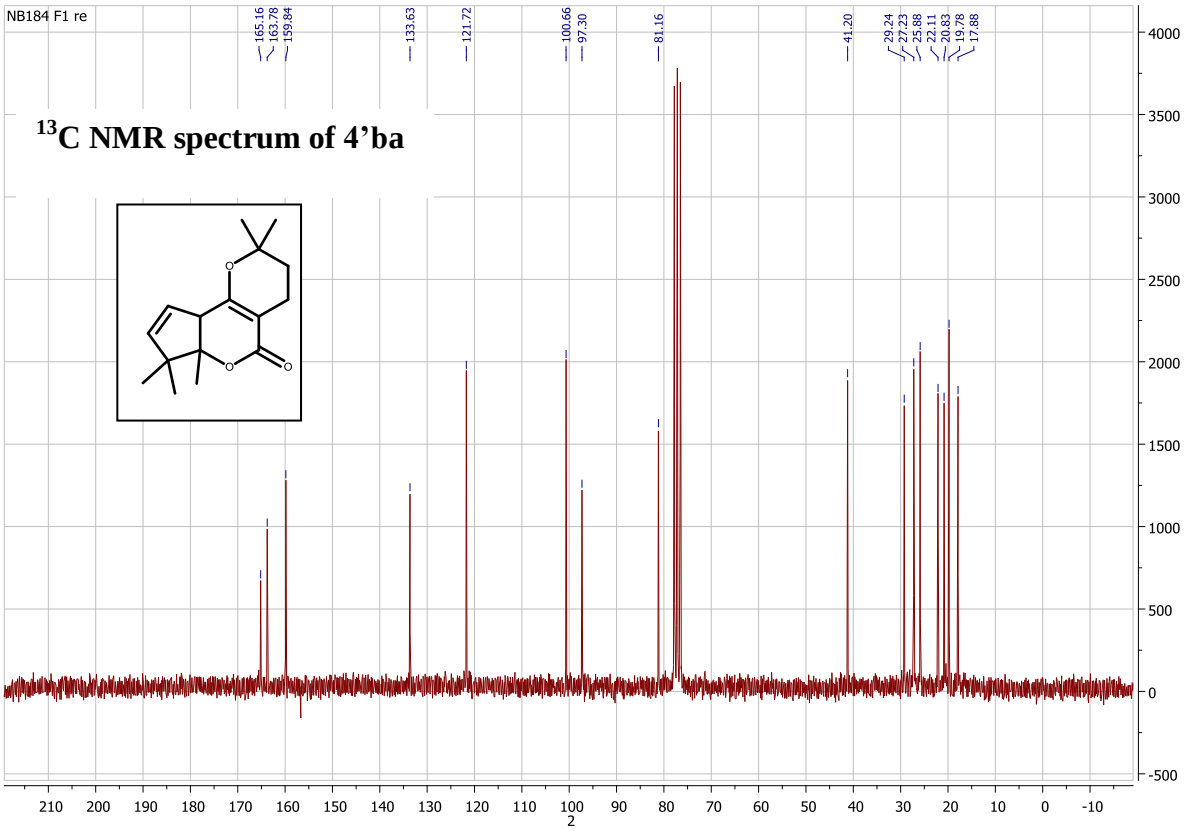
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 165.16 (C6), 163.78 (C4), 159.84 (C5), 133.63 (C2), 121.72 (C15), 100.66 (C14), 97.30 (C10), 81.16 (C16), 41.20 (C1), 29.24 (C9), 27.23 (C12), 25.88 (C13), 22.11 (C8), 20.83 (17), 19.78 (18), 17.88 (C19).

IR (neat): ν_{max} (cm^{-1}) = 2978, 2928, 2854, 1718, 1664, 1626, 1573, 1428, 1388, 1375, 1294, 1259, 1242, 1186, 1142, 1119, 1006, 835, 680, 566, 507, 497,473, 450, 403.

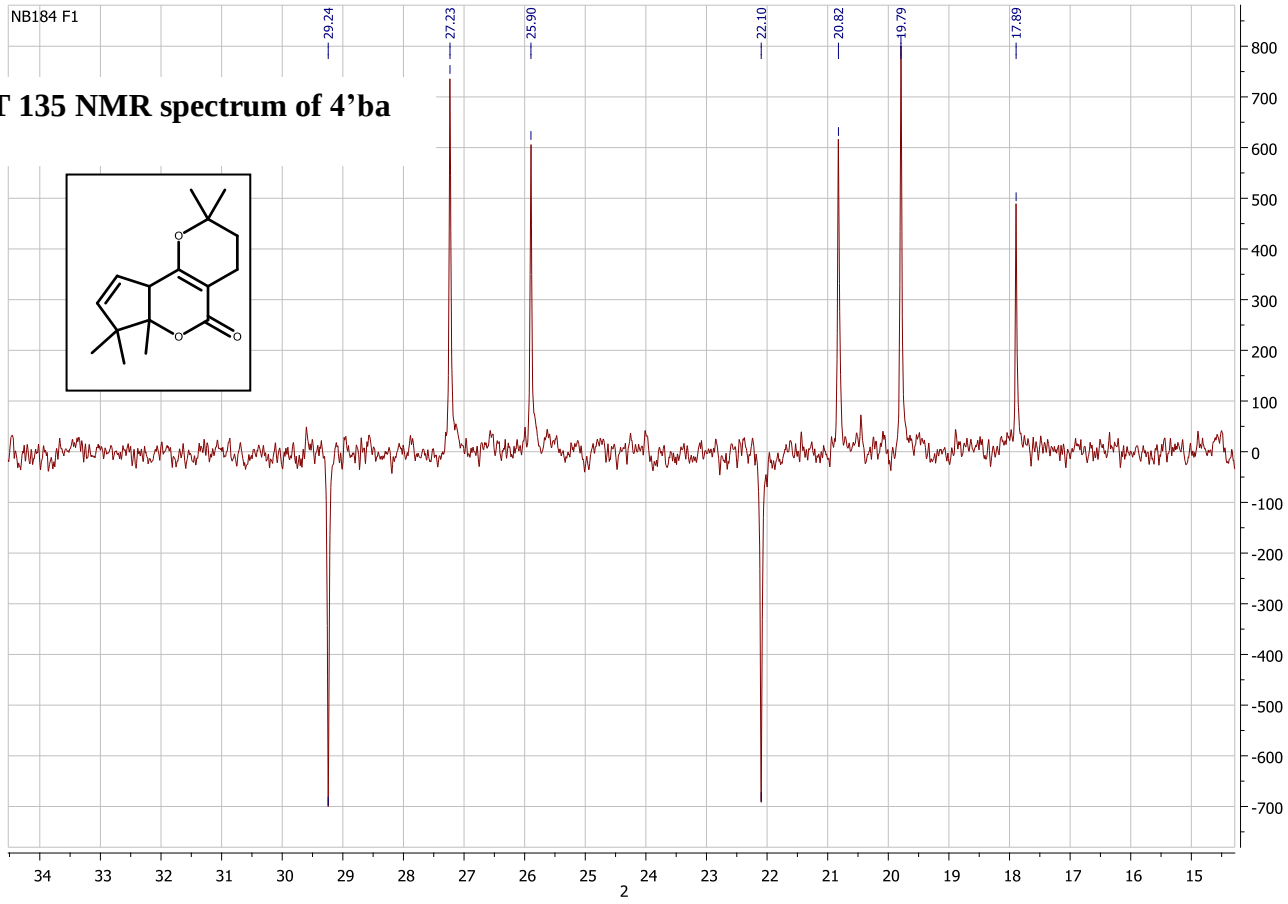
MS (EI, 70 eV): 262 (62) [M+.], 247 (70), 193 (25), 177 (25), 151 (29), 139 (100), 121 (42), 109 (48), 81 (32), 69 (82), 41 (94).

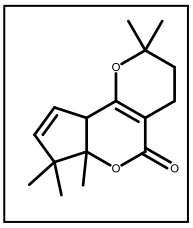
HRMS m/z calcd. For $C_{16}H_{22}O_3$ [$M^{+\cdot}$]: 262.1569, found 262.1611.



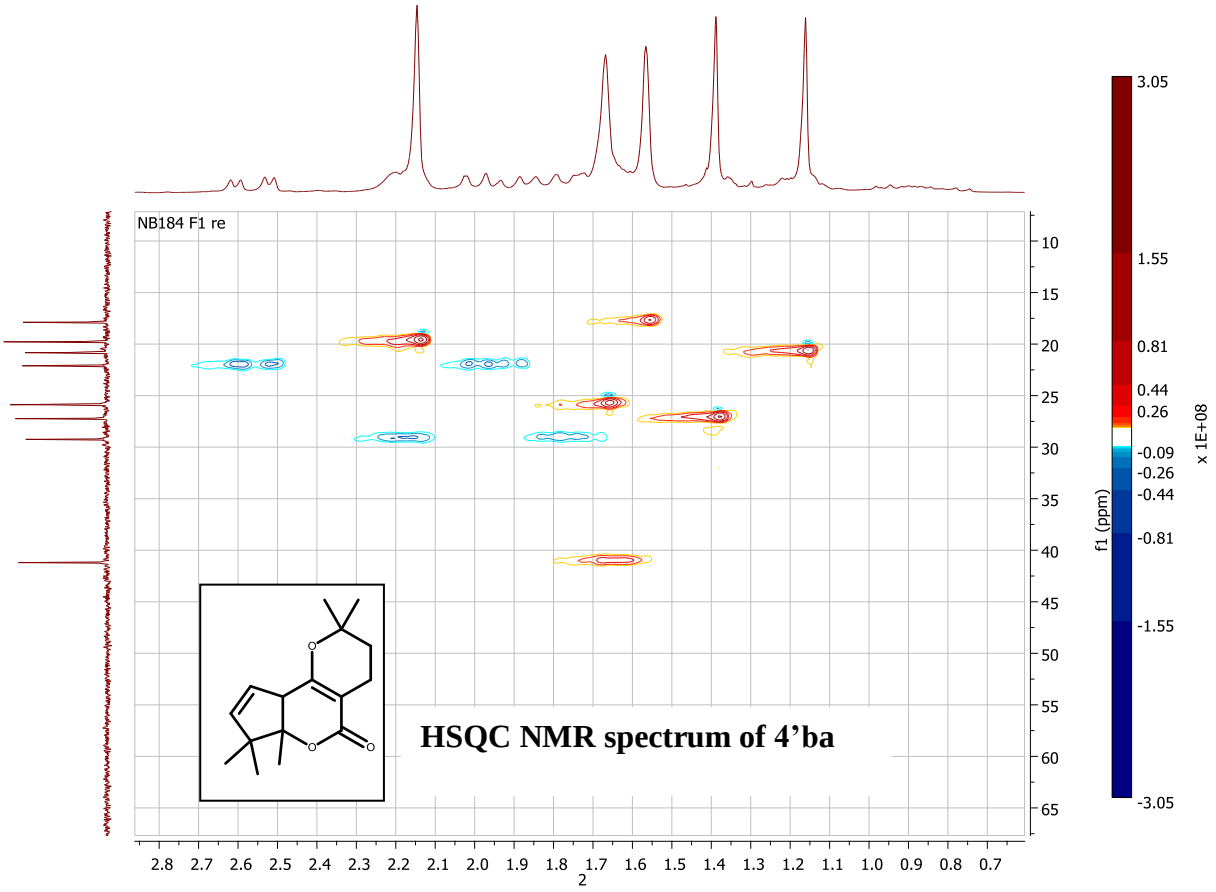


DEPT 135 NMR spectrum of 4’ba

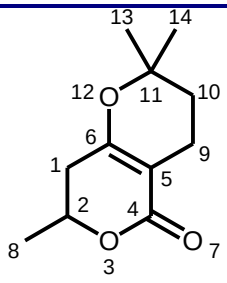




HSQC NMR spectrum of 4’ba



------- 2,2,7-Trimethyl-3,4,7,8-tetrahydro-2*H*-pyrano[4,3-*b*]pyran-5-one 4ca ------

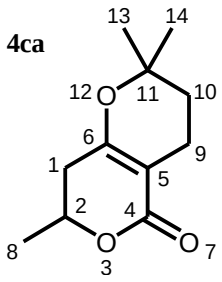


4ca

Chemical Formula: $C_{11}H_{16}O_3$
Molecular Weight: 196,2429

Product **4ca** (199.72 mg, 61%) is obtained as a brown liquid, following the general protocol **A**, from 4-hydroxy-6-methyl-5,6-dihydro-2*H*-pyran-2-one **1c** (1 eq, 256 mg, 2 mmol) and **2a** (5 eq, 1281.7 mg, 10 mmol), using 2 mol% of $In(OTf)_3$, after 12 hours. The crude of the reaction is purified by column chromatography, by eluting with PE/EtOAc:4/1.

4ca



Yield : 61%
4ca : brown liquid
TLC: Rf = 0.4 (PE/EtOAc:1/1)

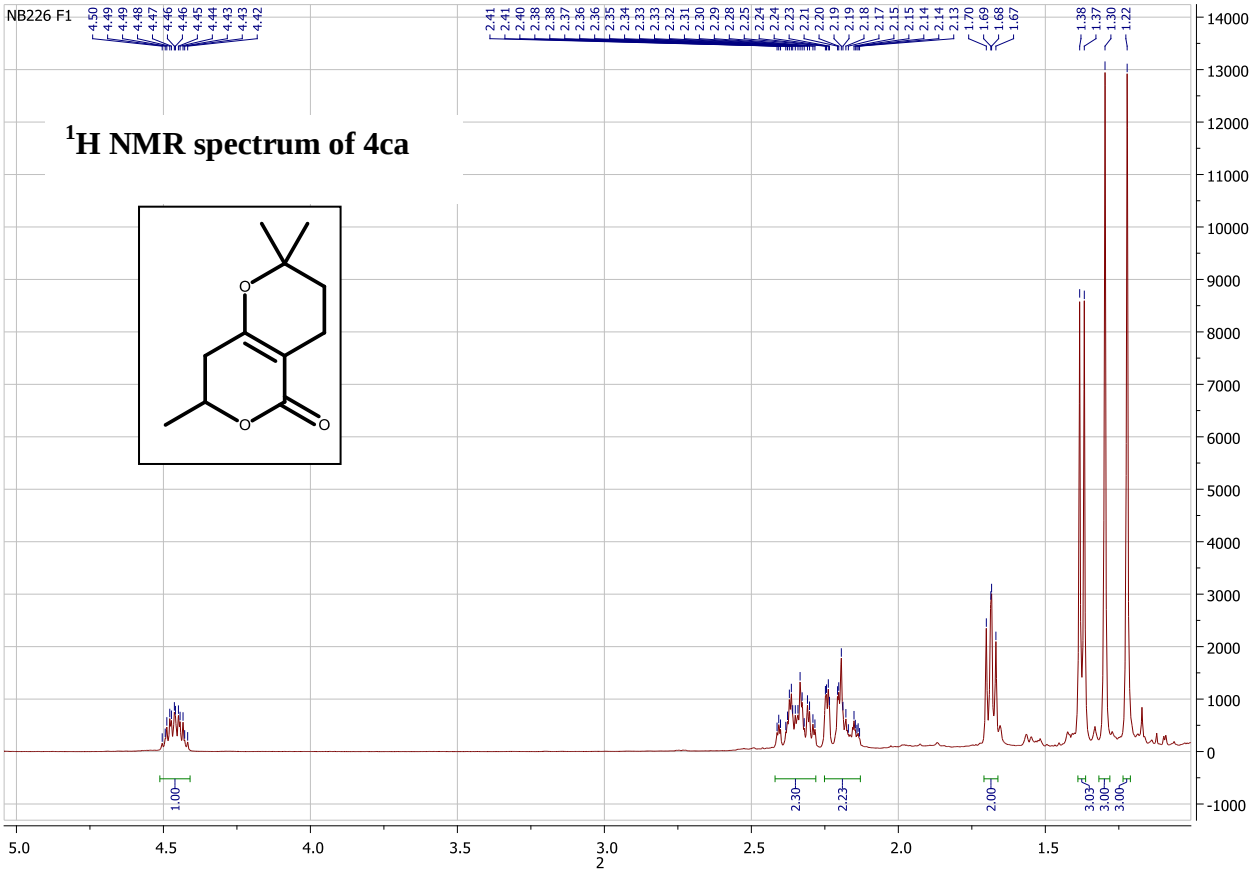
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 4.50 – 4.42 (m, $1H_2$), 2.41 – 2.28 (m, $2H_1$), 2.25 – 2.13 (m, $2H_9$), 1.70 – 1.67 (m, $2H_{10}$), 1.38 – 1.37 (d, J = 6.4 Hz, $3H_8$), 1.30 (s, $3H_{13}$), 1.22 (s, $3H_{14}$).

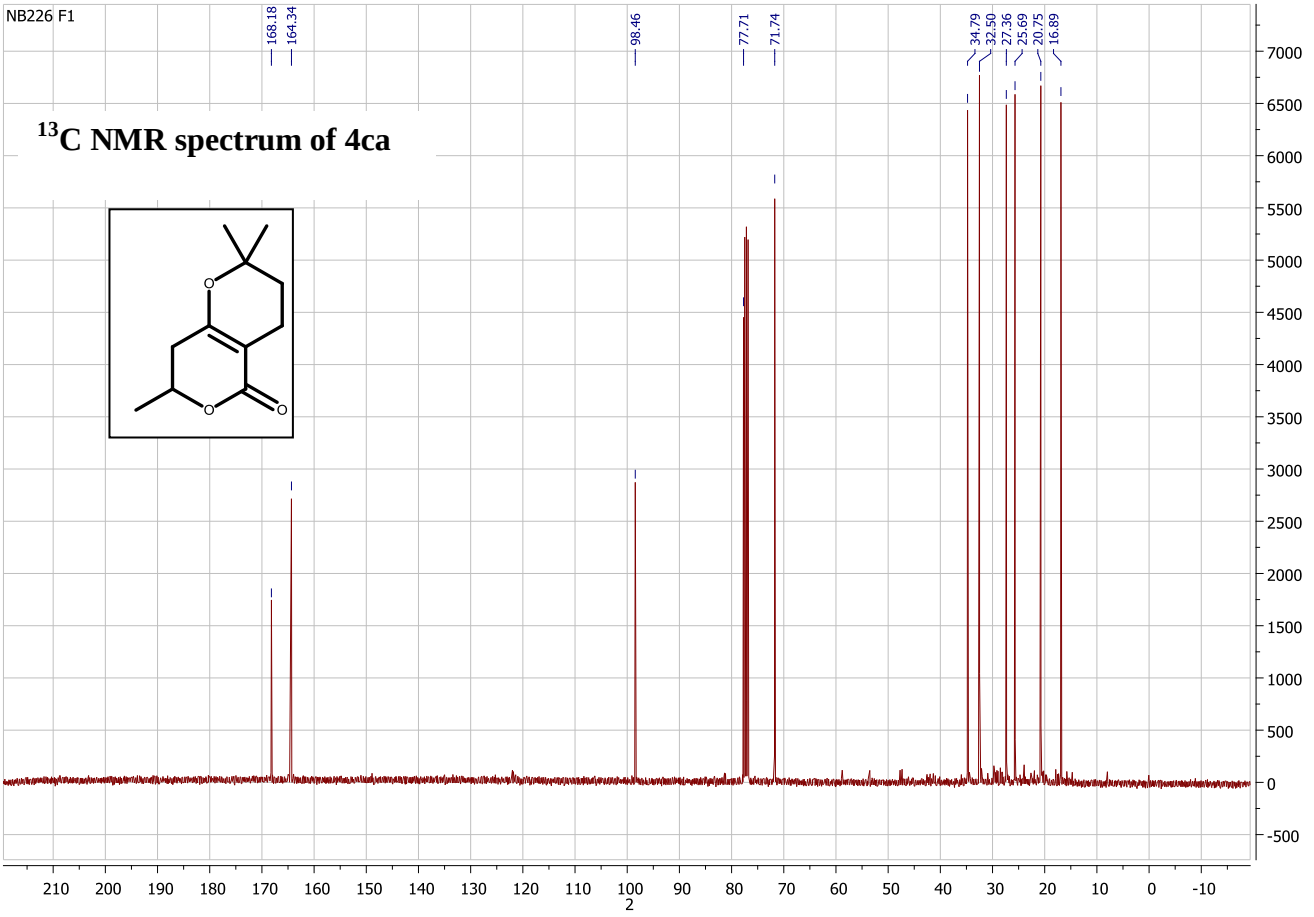
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 168.18 (C6), 164.34 (C4), 98.46 (C5), 77.71 (C11), 71.47 (C2), 34.79 (C10), 32.50 (C1), 27.36 (C13), 25.69 (C14), 20.75 (C8), 16.89 (C9).

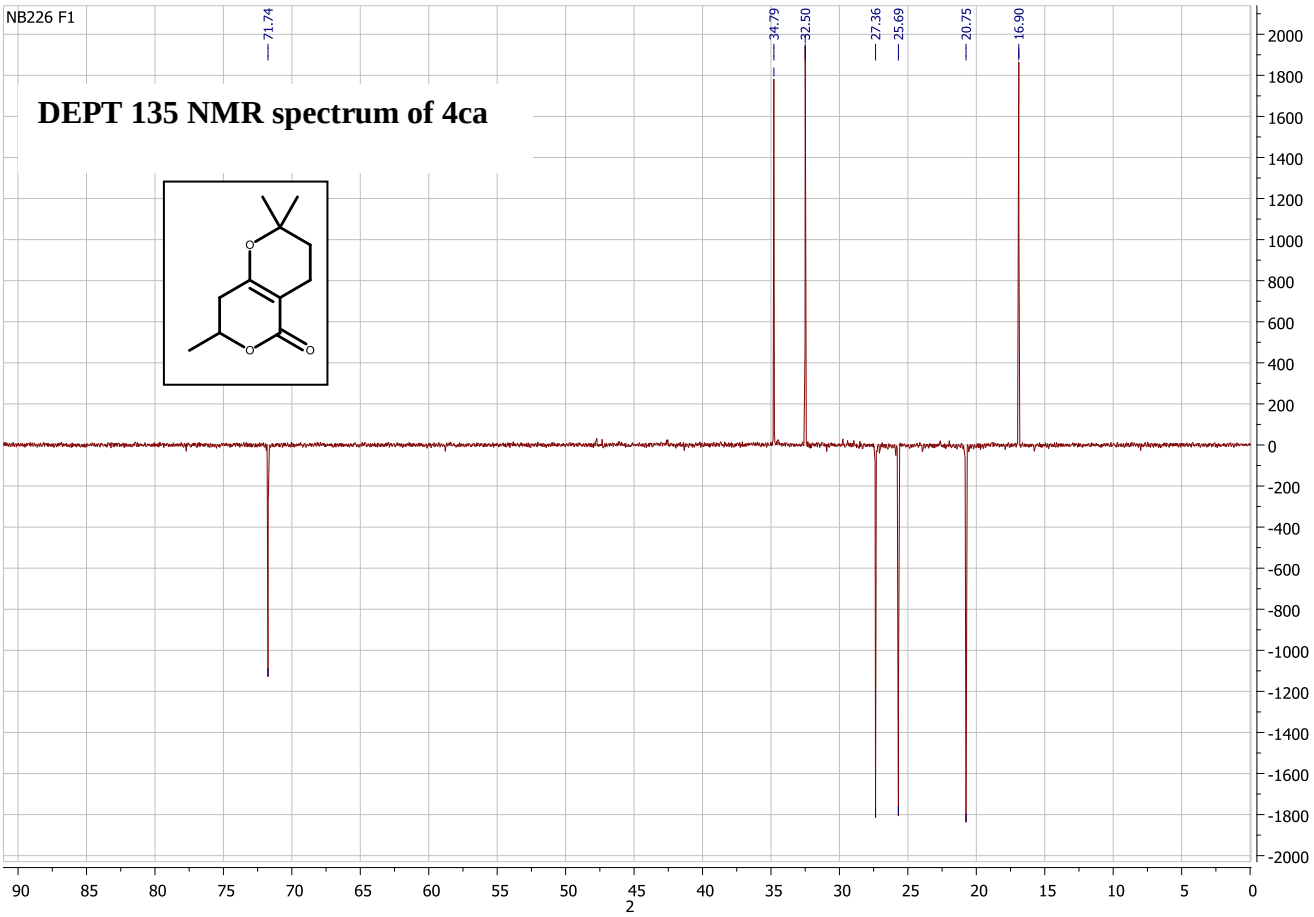
IR (neat): ν_{max} (cm^{-1}) = 2976, 2935, 1696, 1644, 1397, 1371, 1315, 1288, 1246, 1226, 1159, 1134, 1115, 1059, 1044, 1001, 952, 926, 900, 841, 767, 734.

MS (EI, 70 eV): 196 (71) [$M^{+\cdot}$], 178 (39), 163 (97), 153 (24), 135 (51), 123 (86), 99 (100), 69 (54), 56 (60), 41 (86).

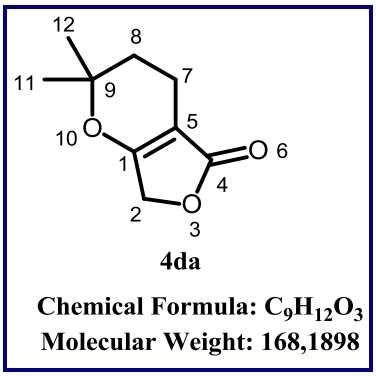
HRMS m/z calcd. For $C_{11}H_{16}O_3$ [$M^{+\cdot}$]: 196.1099, found 196.1169.




NB226 F1
168.18
164.34
98.46
77.71
71.74
34.79
32.50
27.36
25.69
20.75
16.89
13C NMR spectrum of 4ca
f2


NB226 F1
71.74
34.79
32.50
27.36
25.69
20.75
16.90
DEPT 135 NMR spectrum of 4ca
f2

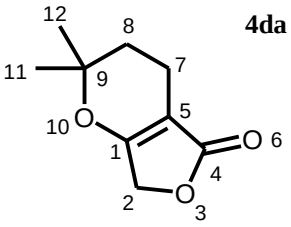
---------- 2,2-Dimethyl-2,3,4,7-tetrahydro-furo[3,4-*b*]pyran-5-one 4da ----------



4da

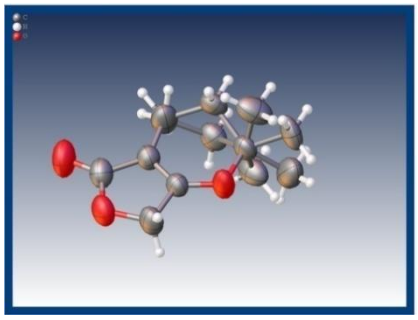
Chemical Formula: $C_9H_{12}O_3$
Molecular Weight: 168,1898

According to the general protocol **A**, **4da** is isolated as a beige solid, starting from tetronic acid **1d** (1 eq, 250 mg, 2.5 mmol) and allylic acetate **2a** (5 eq, 1602.1 mg, 12.5 mmol), using 2 mol% of $In(OTf)_3$, after 9 hours of reaction. The crude of the reaction is purified by column chromatography, by eluting with PE/EtOAc:4/1.



4da

Yield : 55%
4da : beige solid
TLC: Rf = 0.27 (PE/EtOAc:1/1)
Mp = 80 °C



X-ray crystal structure of **4da**

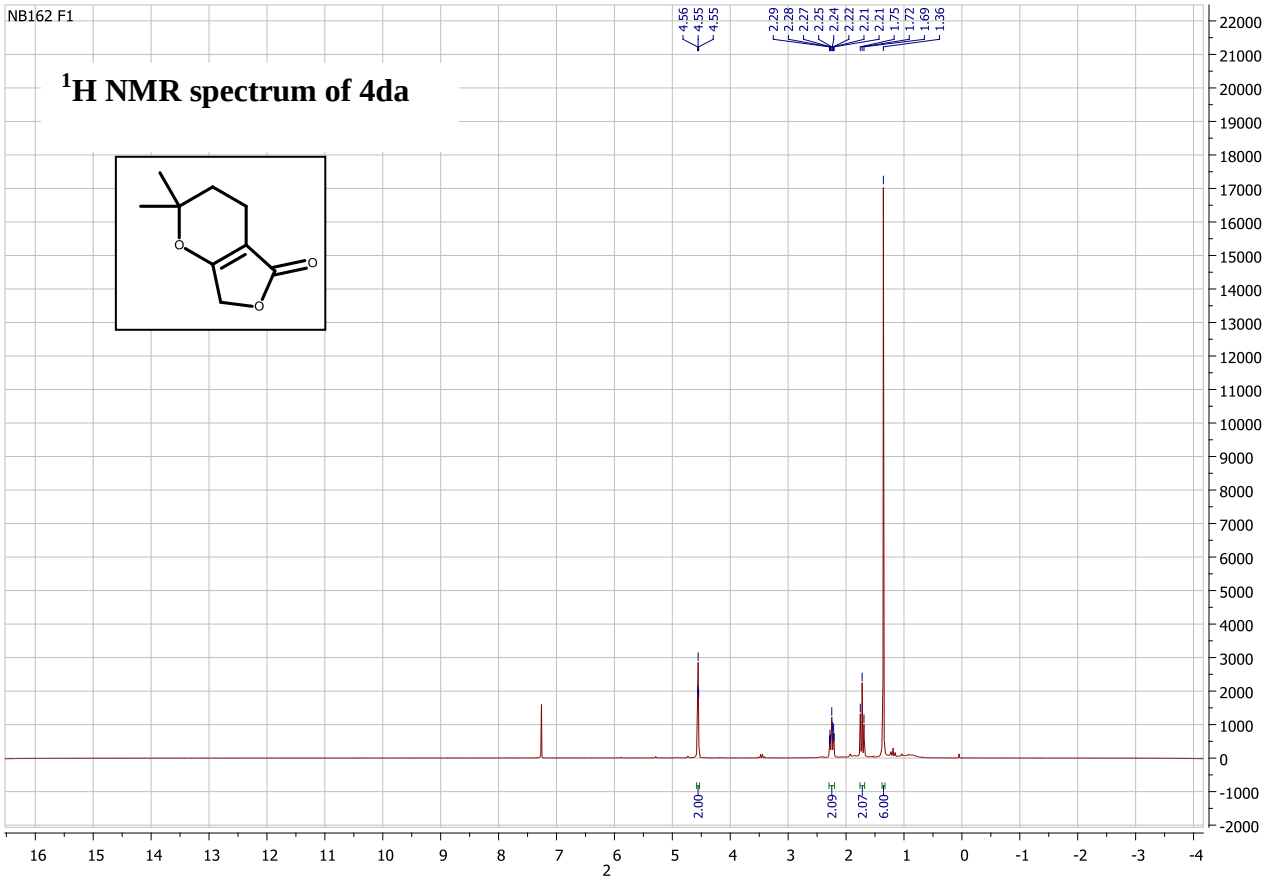
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 4.55 (t, *J* = 1.8 Hz, $2H_2$), 2.29 – 2.21 (dd, *J* = 6.3, 1.7 Hz, $2H_8$), 1.72 (t, *J* = 6.2 Hz, $2H_7$), 1.36 (s, $3H_{11, 12}$).

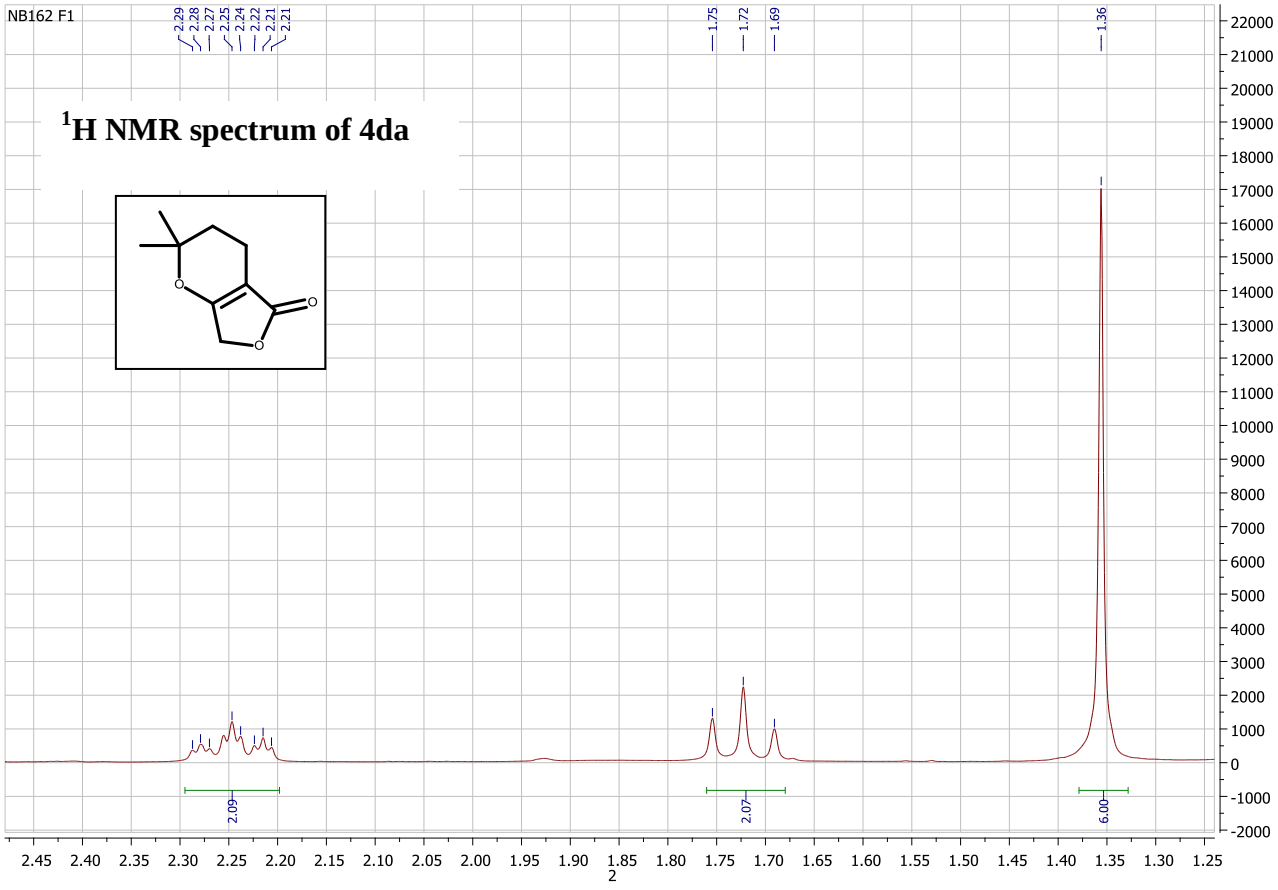
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 173.76 (C1), 173.51 (C4), 98.10 (C5), 81.58 (C9), 66.80 (C2), 32.20 (C8), 26.26 (C11, 12), 14.60 (C7).

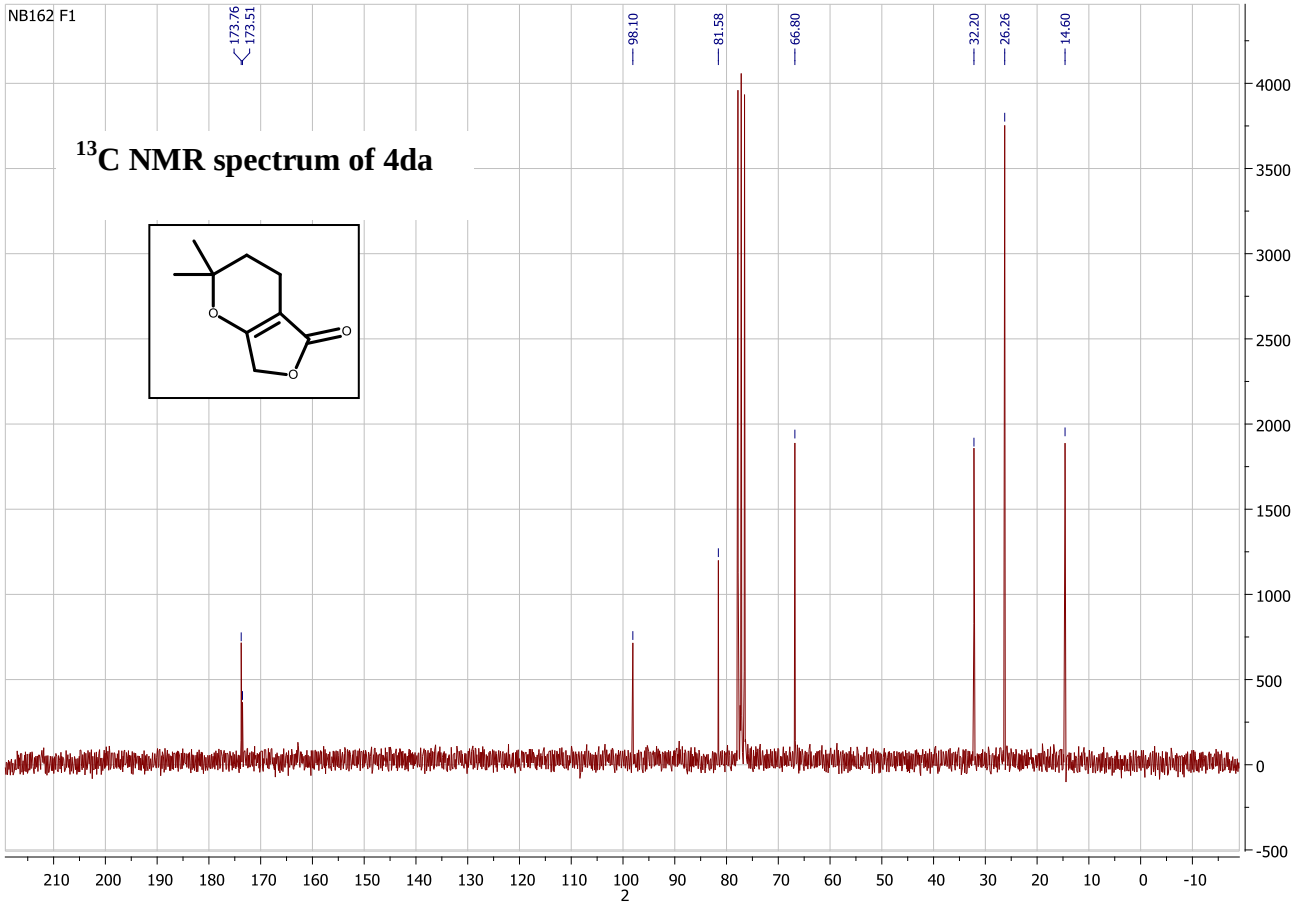
IR (neat): ν_{max} (cm^{-1}) = 2934, 1745, 1661, 1456, 1400, 1372, 1355, 1306, 1269, 1237, 1223, 1156, 1112, 1013, 993, 975, 827.

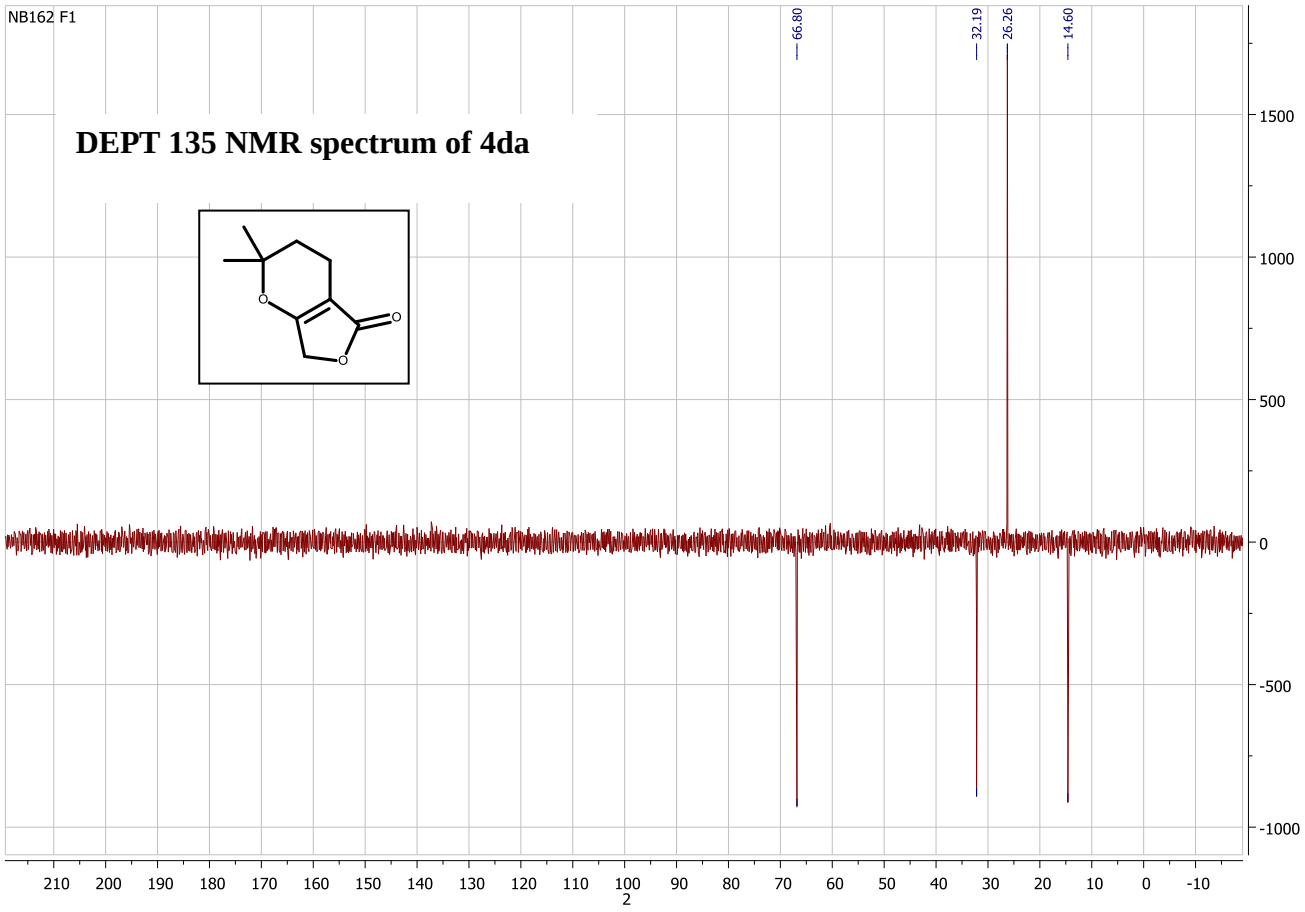
MS (EI, 70 eV): 168 (23) [$M^{+\cdot}$], 150 (42), 135 (100), 113 (63), 79 (23), 56 (74), 41 (59).

HRMS m/z calcd. For $C_9H_{12}O_3$ [$M^{+\cdot}$]: 168.0786, found 168.1012.

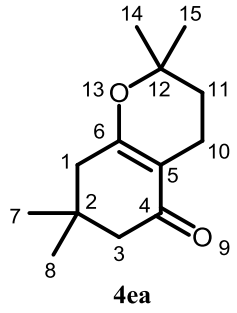

NB162 F1
^{1}H NMR spectrum of 4da
4.56
4.55
4.55
2.29
2.28
2.27
2.25
2.24
2.22
2.21
2.21
1.75
1.72
1.69
1.36
2.00
2.09
2.07
6.00
f2


NB162 F1
^{1}H NMR spectrum of 4da
2.29
2.28
2.27
2.25
2.24
2.22
2.21
2.21
1.75
1.72
1.69
1.36
2.09
2.07
6.00
f2


NB162 F1
173.76
173.51
98.10
81.58
66.80
32.20
26.26
14.60
^{13}C NMR spectrum of 4da
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f2


NB162 F1
66.80
32.19
26.26
14.60
DEPT 135 NMR spectrum of 4da
1500
1000
500
0
-500
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f2

---------- 2,2,7,7-Tetramethyl-2,3,4,6,7,8-hexahydro-chromen-5-one 4ea ----------

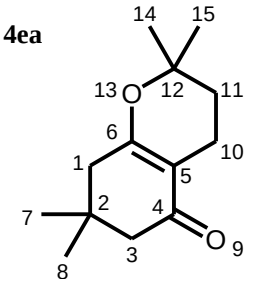


4ea

Chemical Formula: $C_{13}H_{20}O_2$
Molecular Weight: 208,2967

According to the general protocol **A**, product **4ea** is obtained as a white solid, starting from 5,5-dimethylcyclohexane-1,3-dione **1e** (1 eq, 280.3 mg, 2 mmol) and **2a** (5 eq, 1281.7 mg, 10 mmol), using 2 mol% of $In(OTf)_3$, after 9.5 hours of reaction. The crude of the reaction is purified by column chromatography, by eluting with PE/Et_2O:4/1.

4ea



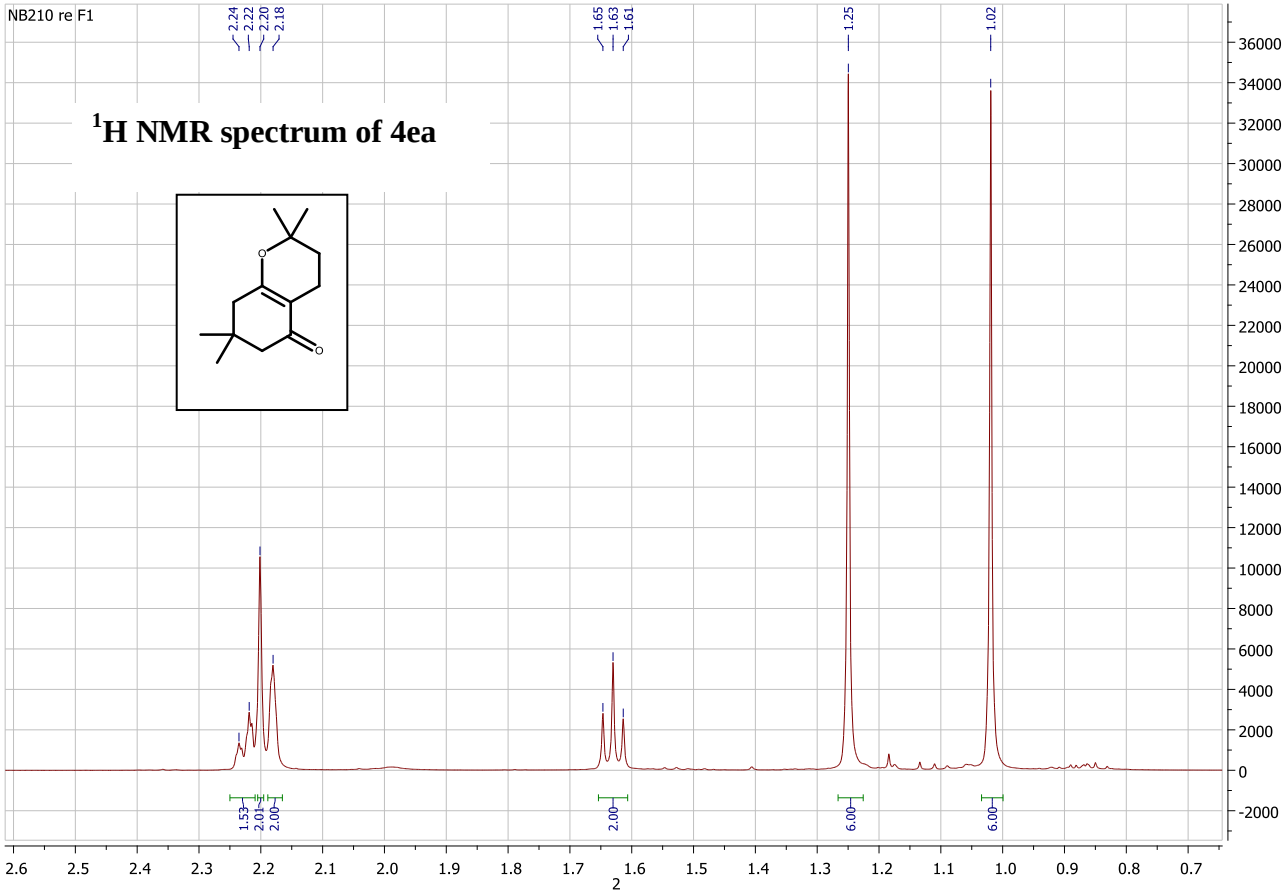
Cas number: 111094-89-4
Yield : 88%
4ea : white solid
TLC: Rf = 0.4 (PE/Et_2O:1/1)
Mp = 68 °Cv

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 2.22 (t, *J* = 6.4 Hz, $2H_{10}$), 2.20 (s, $2H_3$), 2.18 (s, $2H_1$), 1.63 (t, *J* = 6.8 Hz, $2H_{11}$), 1.25 (s, $6H_{14,\,15}$), 1.02 (s, $6H_{7,\,8}$).

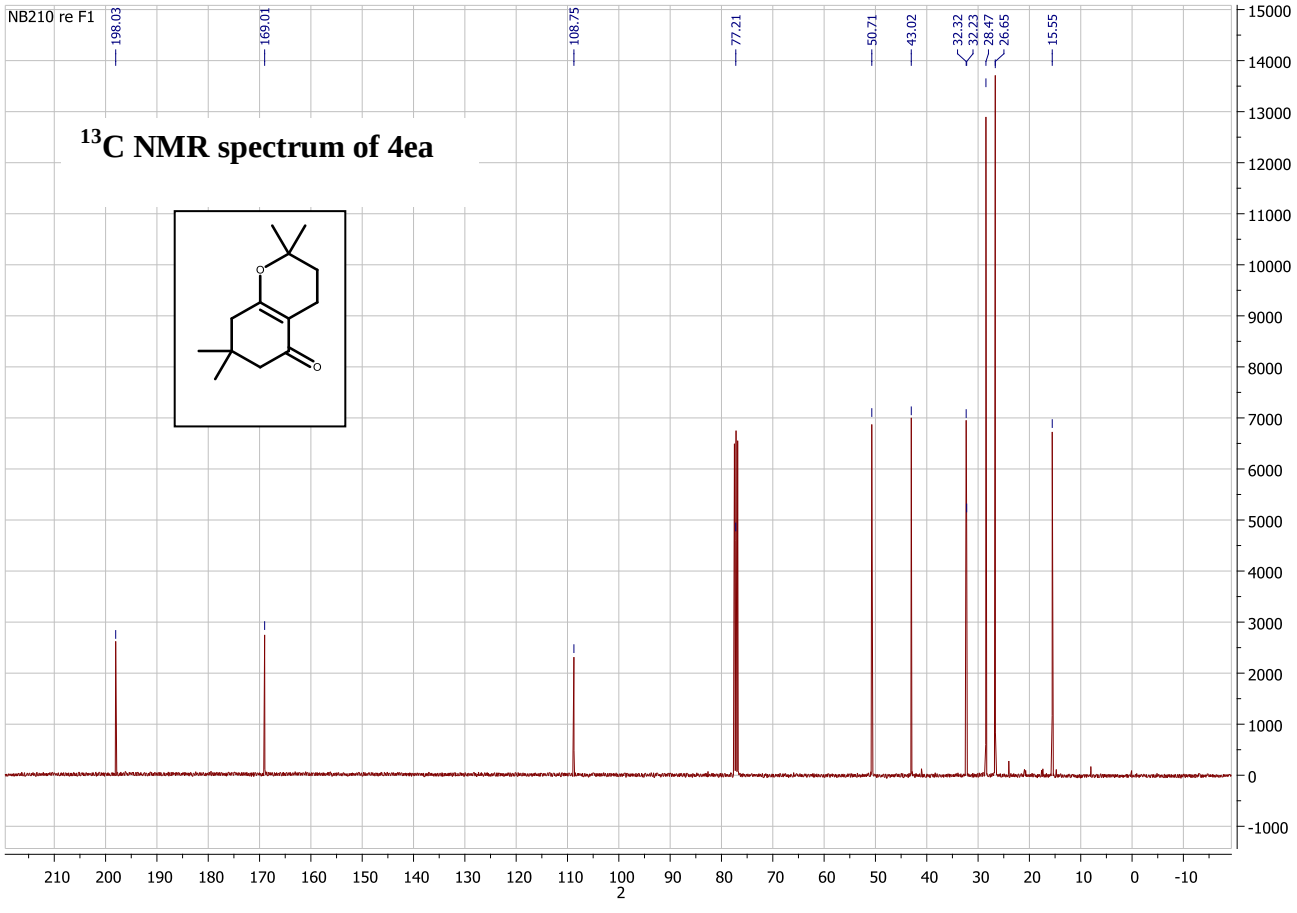
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 198.03 (C4), 169.01 (C6), 108.75 (C5), 77.21 (C12), 50.71 (C3), 43.02 (C1), 32.32 (C11), 32.23 (C2), 28.47 (C7, 8), 26.65 (C14, 15), 15.55 (C10).

IR (neat): ν_{max} (cm^{-1}) = 2958, 2921, 2886, 2869, 1638, 1603, 1465, 1453, 1390, 1382, 1365, 1344, 1311, 1294, 1264, 1250, 1225, 1157, 1144, 1111, 1047, 967, 855, 738.

MS (EI, 70 eV): 208 (43) [$M^{+\cdot}$], 193 (19), 165 (100), 153 (24), 109 (22), 97 (60), 69 (24), 55 (26), 41 (37).

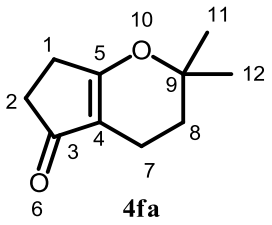


^{1}H NMR spectrum of 4ea



^{13}C NMR spectrum of 4ea

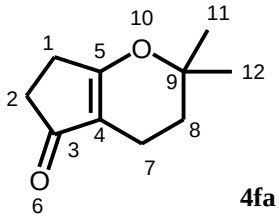
------ 2,2-Dimethyl-3,4,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyran-5-one 4fa -------



4fa

Chemical Formula: $C_{10}H_{14}O_2$
Molecular Weight: 166,2170

According to the general protocol **A**, the product **4fa** is obtained as an orange solid, starting from cyclopentane-1,3-dione **1f** (1 eq, 196.2 mg, 2 mmol) and **2a** (5 eq, 1281.7 mg, 10 mmol), using 2 mol% of $In(OTf)_3$, after 9.5 hours of reaction. The crude of the reaction is purified by column chromatography, by eluting with PE/EtOAc:4/1.



4fa

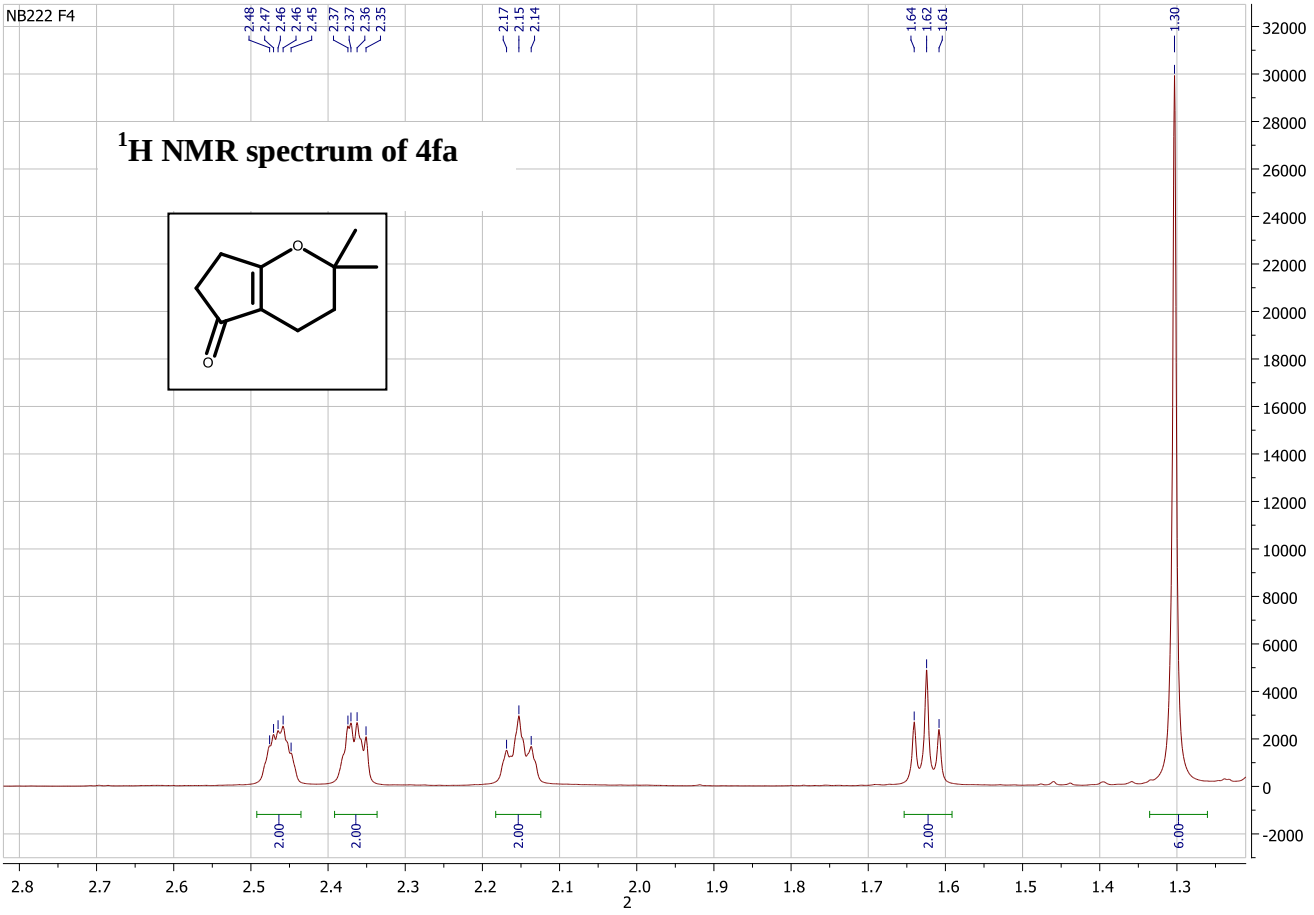
Cas number: 1260424-80-3
Yield : 59%
4fa : orange solid
TLC: Rf = 0.16 (PE/EtOAc:1/1)
Mp = 40 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 2.48 – 2.45 (m, $2H_2$), 2.37 – 2.35 (m, $2H_1$), 2.15 (t, *J* = 6.4 Hz, $2H_8$), 1.62 (t, *J* = 6.4 Hz, $2H_7$), 1.30 (s, $6H_{11, 12}$).

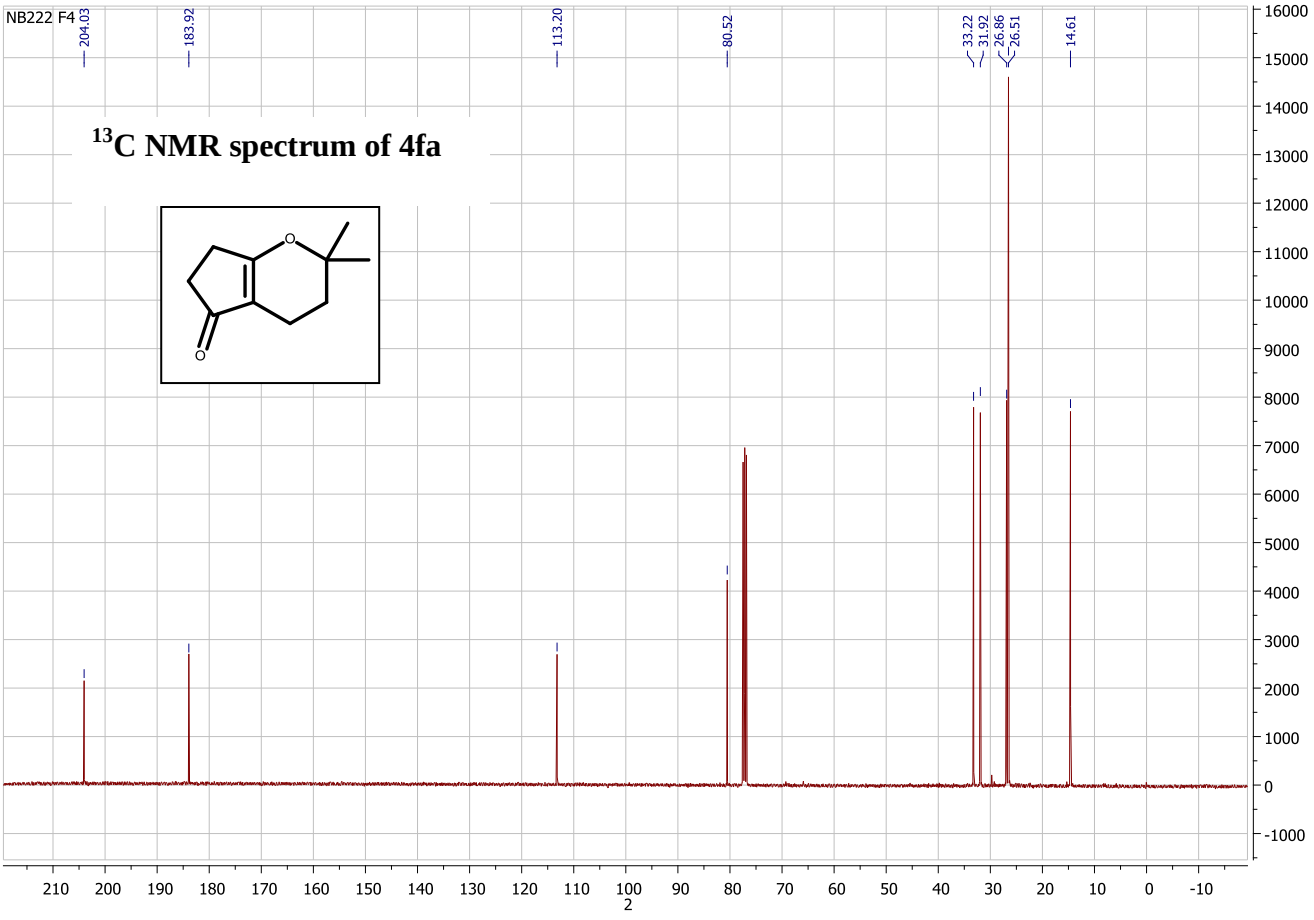
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 204.03 (C3), 183.92 (C5), 113.20 (C4), 80.52 (C9), 33.22 (C8), 31.92 (C2), 26.86 (C1), 26.51 (C11, 12), 14.61 (C7).

IR (neat): ν_{max} (cm^{-1}) = 1682, 1617, 1443, 1397, 1371, 1332, 1295, 1222, 1155, 1111, 1101, 1024, 988, 975, 912, 880, 839, 825, 739.

MS (EI, 70 eV): 166 (94) [$M^{+\cdot}$], 151 (73), 133 (50), 123 (37), 111 (100), 83 (26), 56 (72), 55 (57), 43 (32), 41 (55).

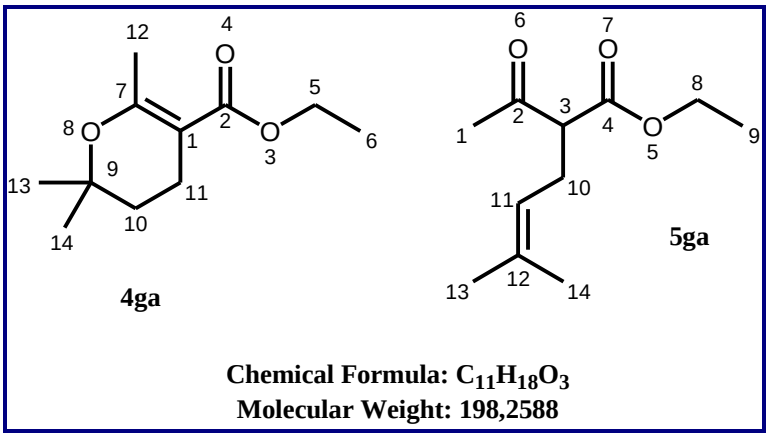


^{1}H NMR spectrum of 4fa



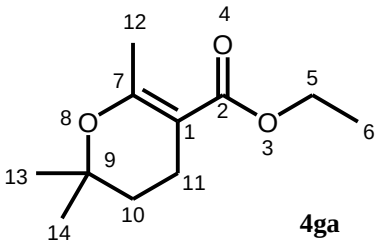
^{13}C NMR spectrum of 4fa

------ 2,6,6-Trimethyl-5,6-dihydro-4*H*-pyran-3-carboxylic acid ethyl ester 4ga ------
---------- 2-Acetyl-5-methyl-hex-4-enoic acid ethyl ester 5ga ----------



Chemical Formula: $C_{11}H_{18}O_3$
Molecular Weight: 198,2588

According to the general protocol **A**, the reaction of ethyl acetoacetate **1g** (1 eq, 325.25 mg, 2.5 mmol), with prenyl acetate **2a** (5 eq, 1602.1 mg, 12.5 mmol), leads to the formation of a mixture of compounds **4ga** and **5ga**. The crude product is purified by flash chromatography (PE/Et_2O:96/4).



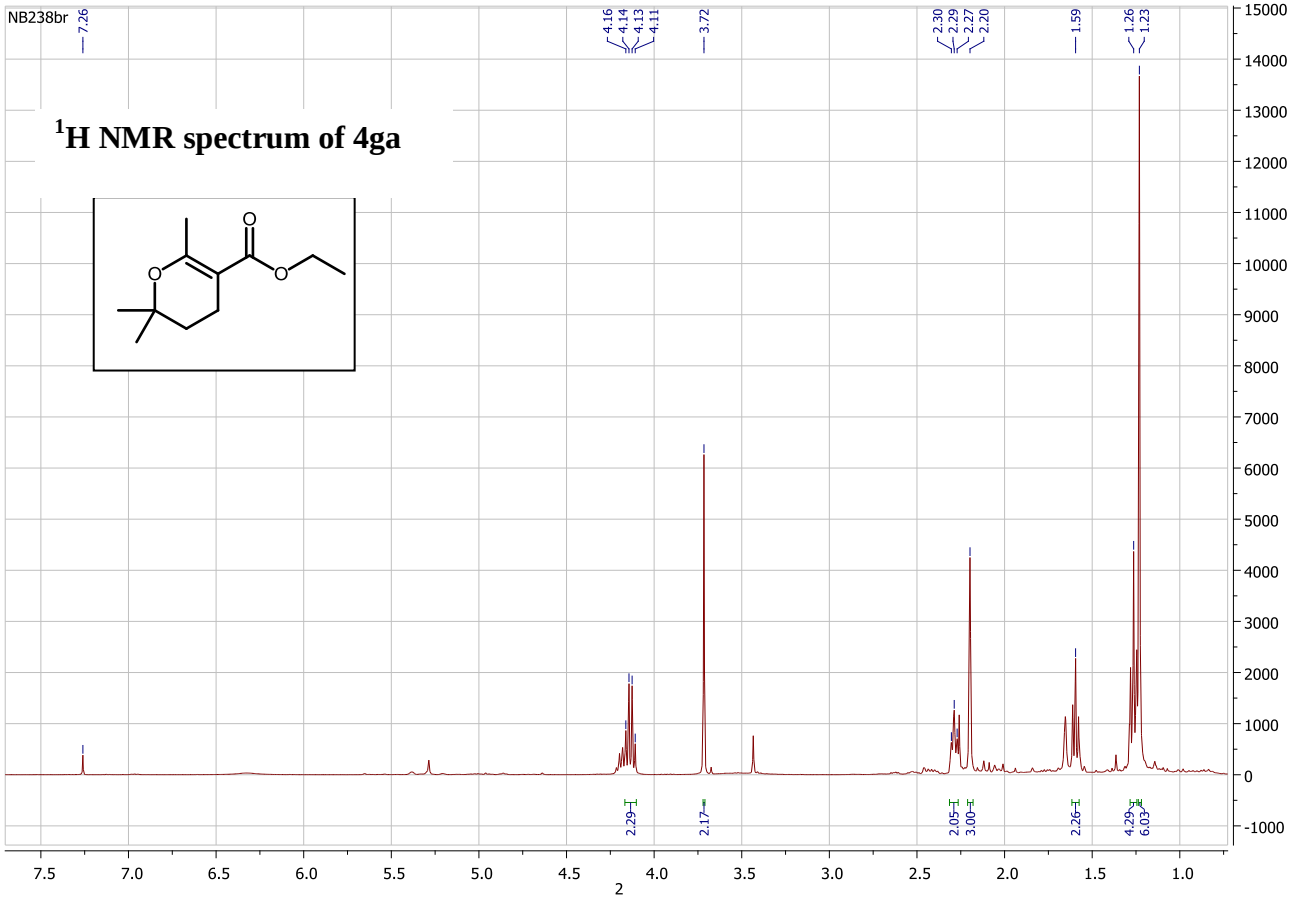
Cas number: 51079-17-5
Yield : 9%
4ga : yellow oil
TLC: Rf = 0.25 (PE/ Et_2O:1/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 4.16 – 4.11 (q, *J* = 7.1 Hz, $2H_5$), 2.30 – 2.27 (t, *J* = 6.6 Hz, $2H_{11}$), 2.20 (s, $3H_{12}$), 1.59 (t, *J* = 6.7 Hz, $2H_{10}$), 1.26 (t, *J* = 3.6 Hz, $3H_6$), 1.23 (s, $6H_{13,\,14}$).

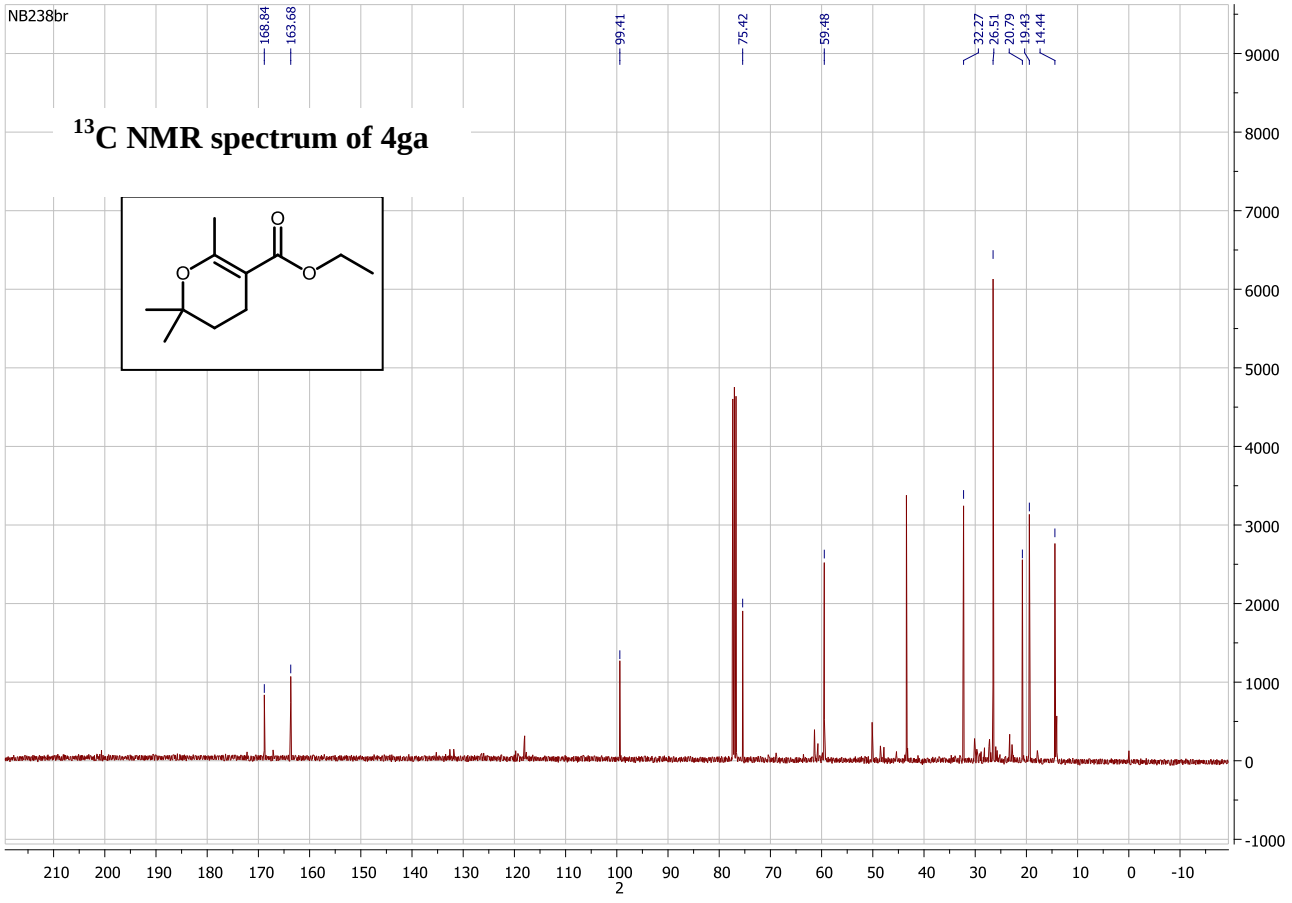
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 168.97 (C2), 163.81 (C7), 99.54 (C1), 75.55 (C9), 59.60 (C5), 32.40 (C10), 26.64 ($C_{13,\,14}$), 20.91 (C12), 19.55 (C11), 14.56 (C6).

The experimental data are in accordance with those reported in the literature.[2]

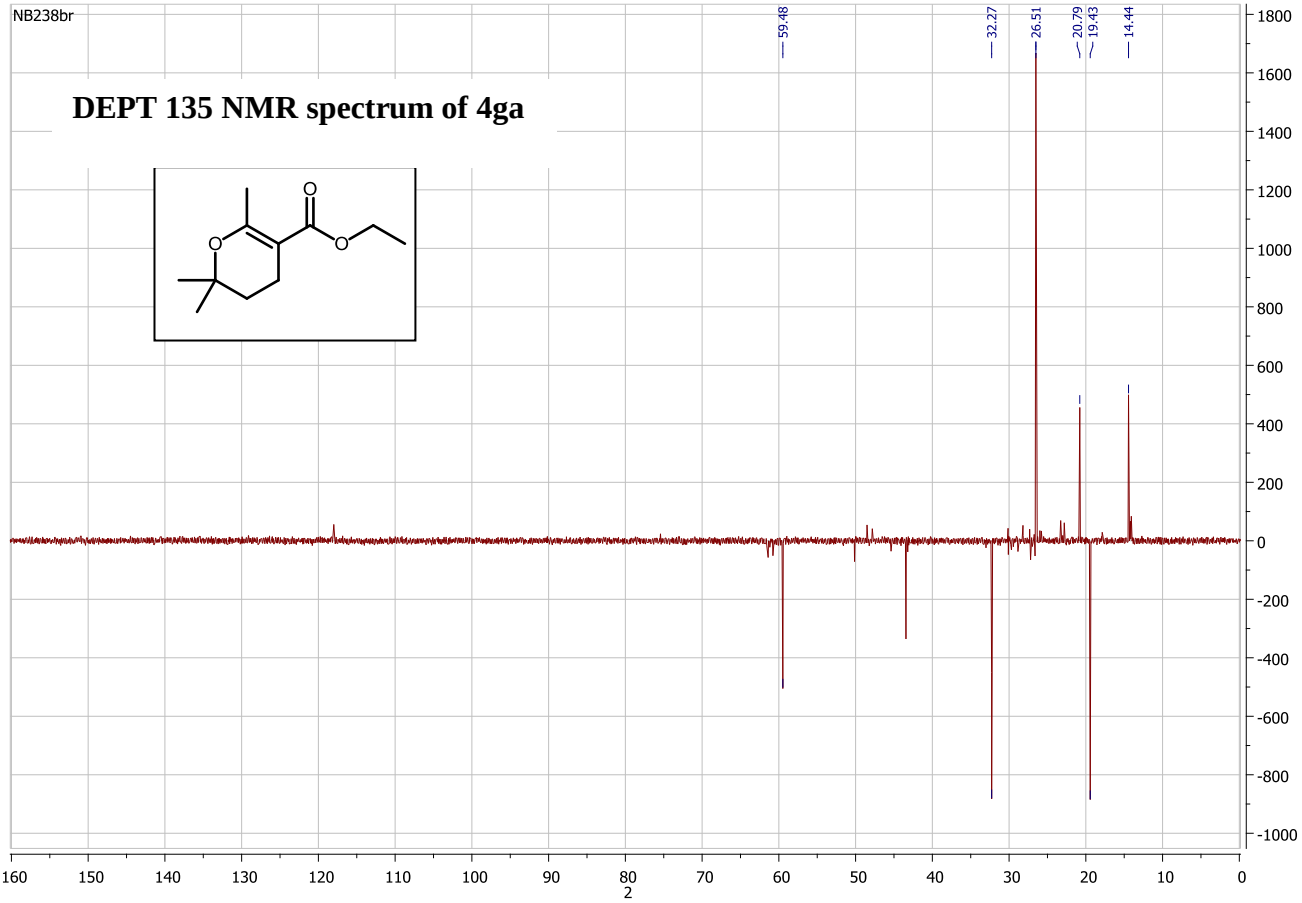
[2] R. B. Watson et al. « Iron (III) chloride catalyzed formation of 3,4-dihydro-2H-pyrans from α-alkylated 1,3-dicarbonyls. Selective synthesis of α- and β-lapachone ». *Org-Lett*. **2016**, *18*, 1310-1313.

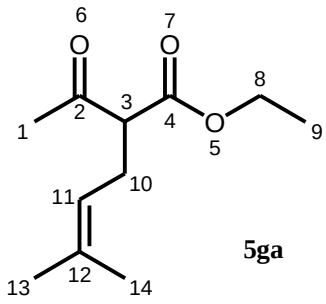


^{1}H NMR spectrum of 4ga



^{13}C NMR spectrum of 4ga





5ga

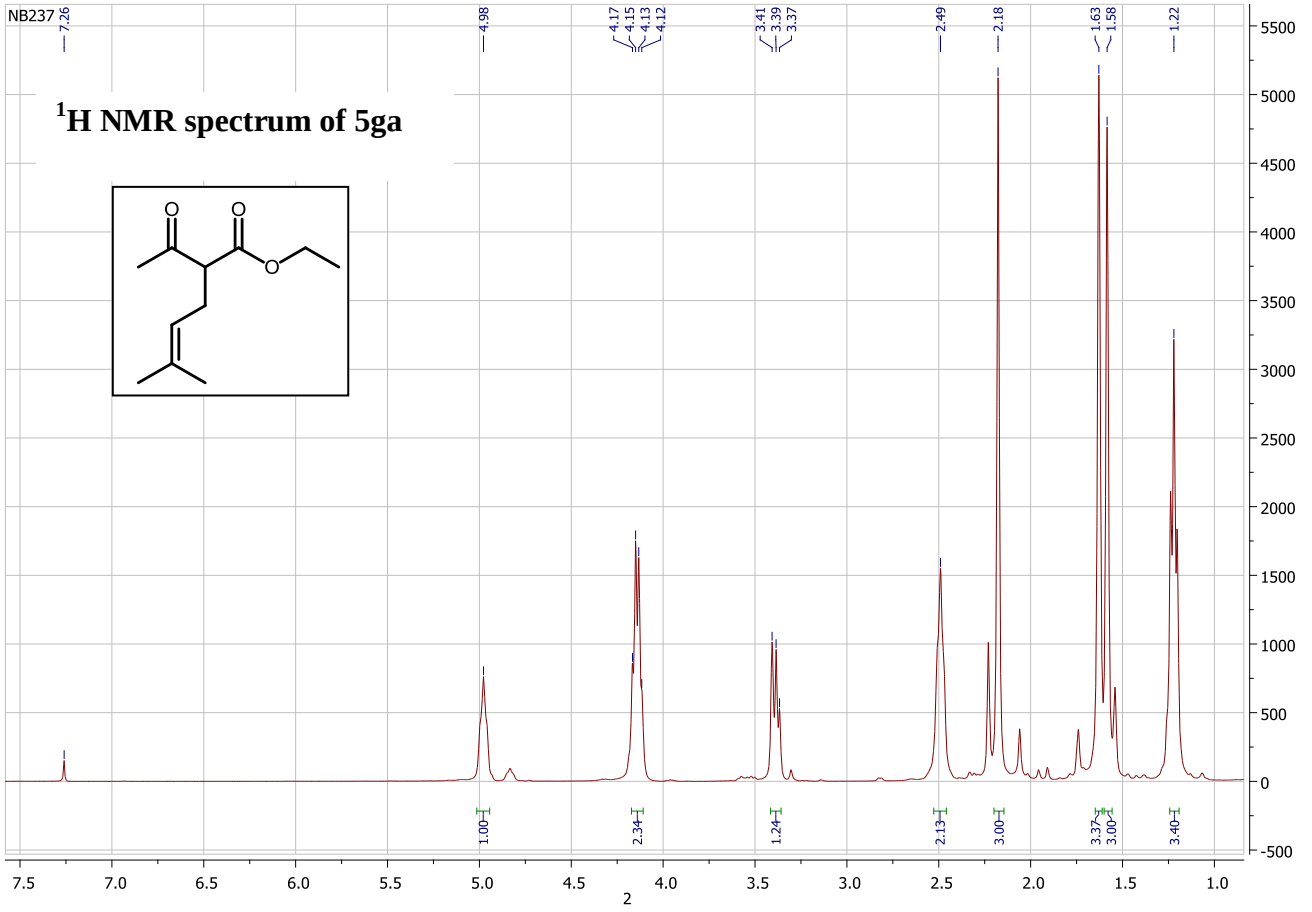
Cas number: 1845-52-9
Yield : 4%
5ga : yellow oil
TLC: Rf = 0.3 (PE/ Et_2O:1/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 4.98 (t, *J* = 7.2 $1H_{11}$), 4.17 – 4.12 (q, *J* = 7.2 Hz, $2H_8$), 3.41 – 3.37 (m, $1H_3$), 2.49 (t, *J* = 7.2 Hz, $2H_{10}$), 2.18 (s, $3H_1$), 1.63 (s, $3H_{13}$), 1.58 (s, $3H_{14}$), 1.22 (t, $3H_9$).

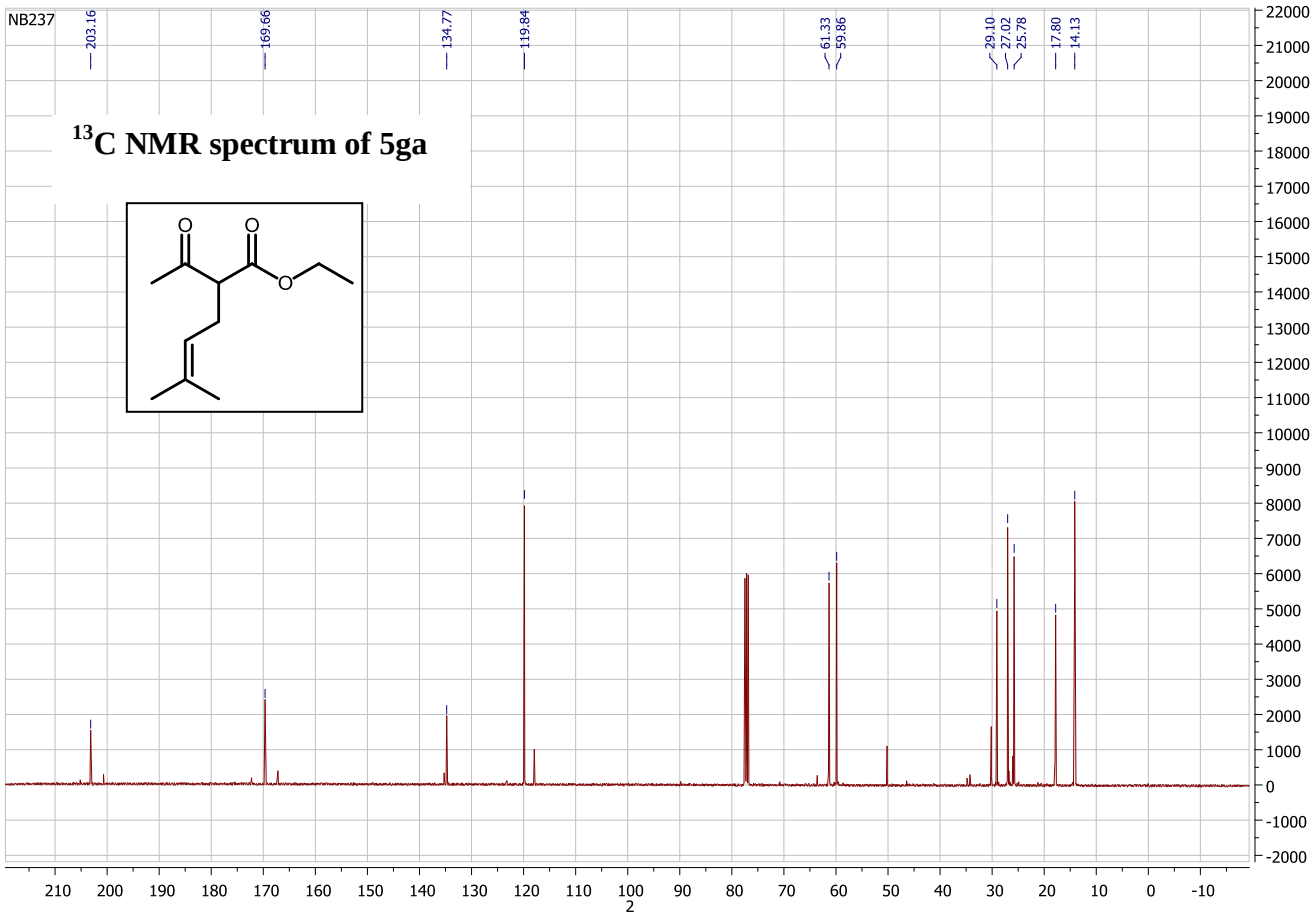
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 203.16 (C2), 169.66 (C4), 134.77 (C12), 119.84 (C11), 61.33 (C8), 59.86 (C3), 29.09 (C1), 27.02 (C10), 25.77 (C13), 17.80 (C14), 14.13 (C9).

The experimental data are in accordance with those reported in the literature.[3]

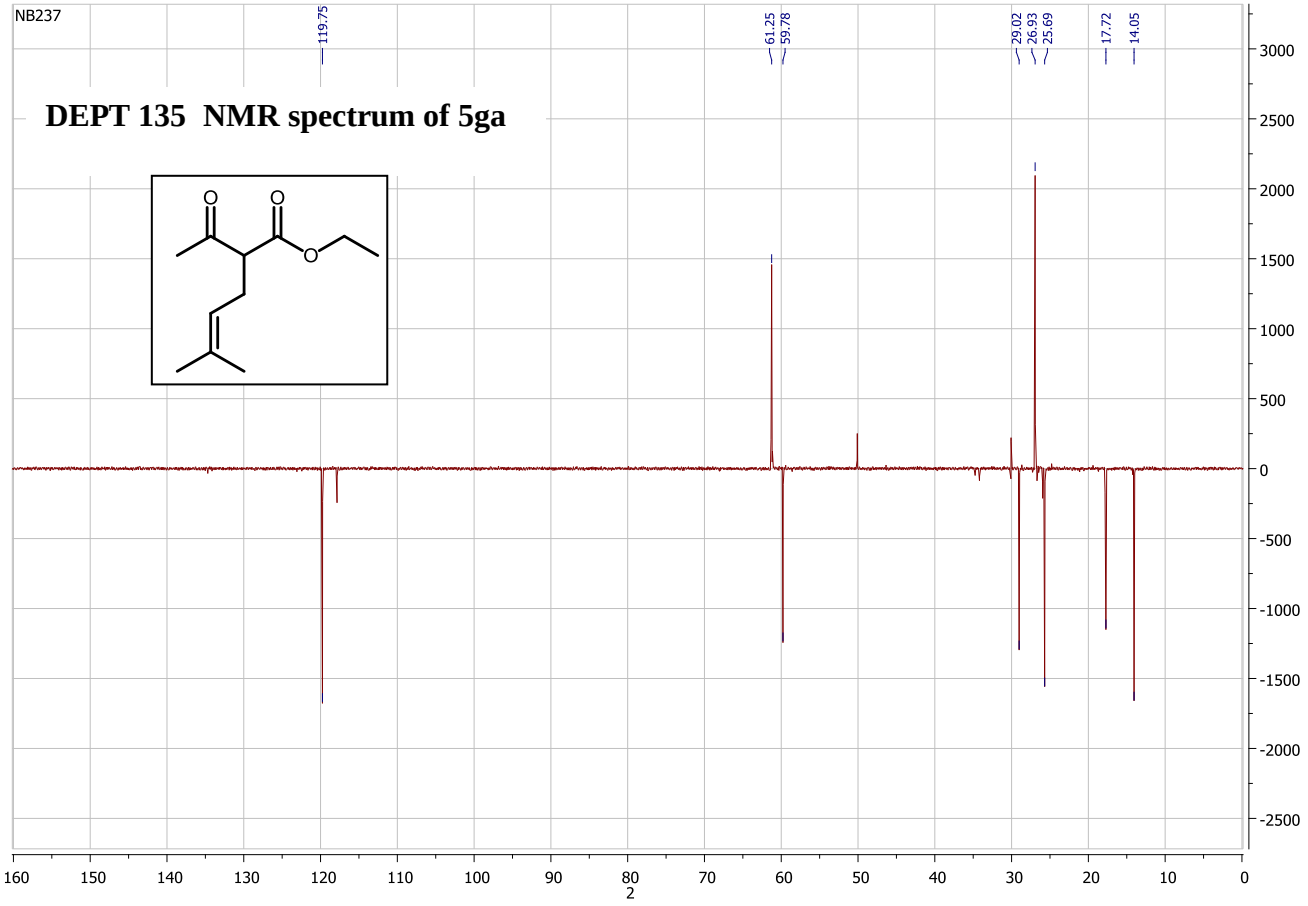
[3] Ju Yeming et al. « Catalytic oxidation of β-keto esters by manganese (III) / cobalt (II) and consecutive cyclization to heterocycles ». *Adv.Synth.Catal.* **2014**, *356 (14-15)*, 3059-3066.



^{1}H NMR spectrum of 5ga

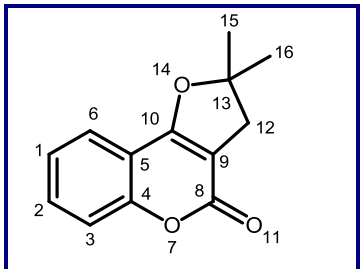


^{13}C NMR spectrum of 5ga



3. Reaction of β-ketolactones and β-diketones 1 with methallyl acetate 2b

---------- 2,2-Dimethyl-2,3-dihydro-furo[3,2-*c*]chromen-4-one 4ab ----------

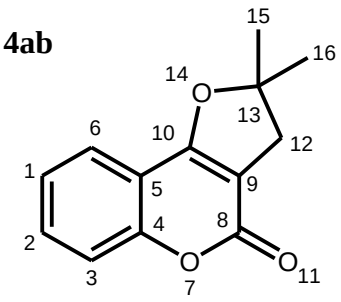


4ab

Chemical Formula: $C_{13}H_{12}O_3$
Molecular Weight: 216,2326

According to the general protocol **A**, the compound **4ab** is obtained after 17 hours under reflux of nitromethane, from 4-hydroxycoumarin **1a** (1 eq, 324 mg, 2 mmol), methallyl acetate **2b** (5 eq, 1141.4 mg, 10 mmol) and $In(OTf)_3$ (5 mol%, 0.1 mmol). The crude product is purified by flash chromatography (PE/EtOAc:95/5).

4ab



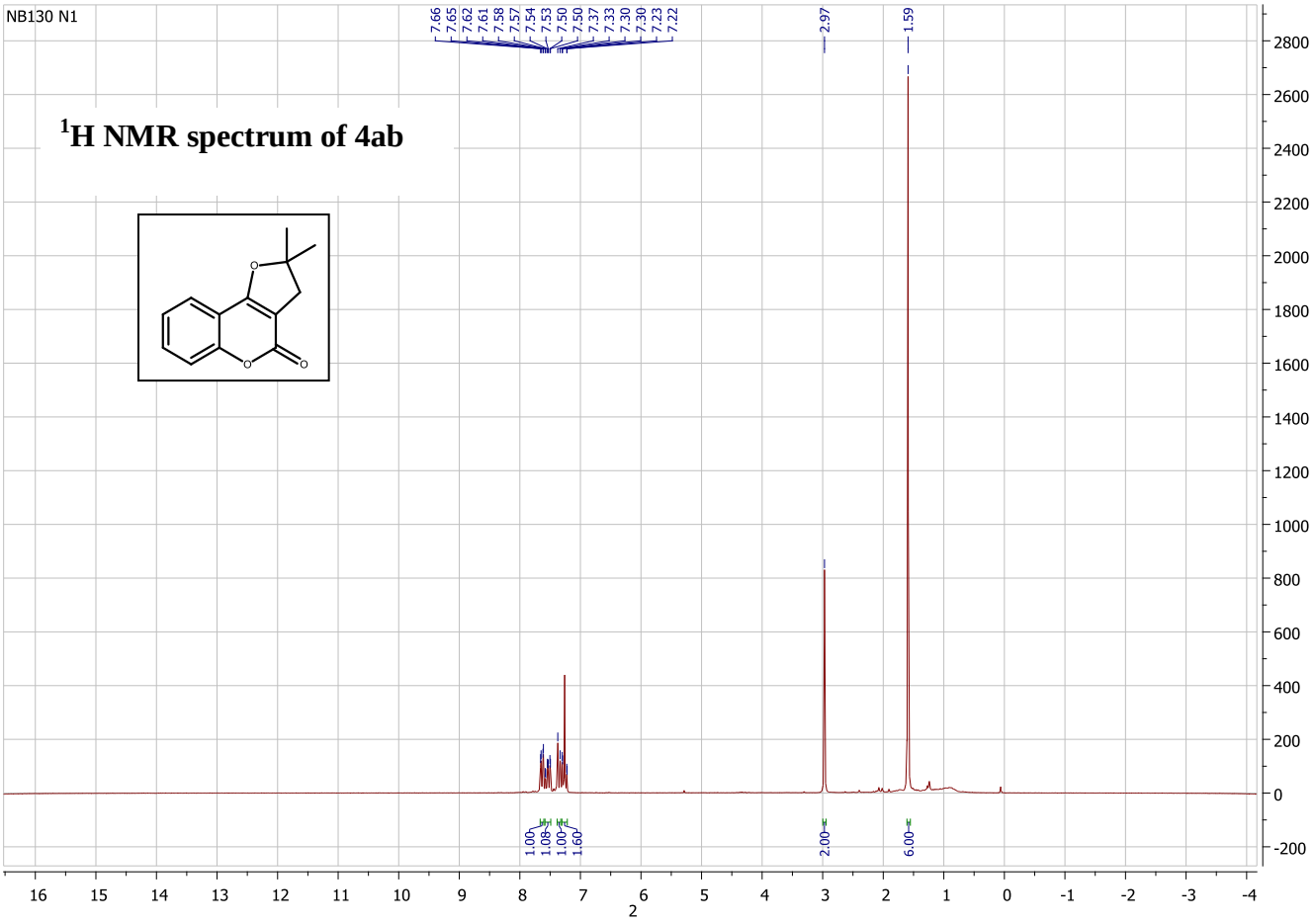
Cas number: 109797-44-6
Yield : 94%
4ab : beige solid
TLC: Rf = 0.5 (PE/EtOAc:7/3)
Mp = 110 °C

^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 7.66 – 7.61 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, $1H_6$), 7.58 – 7.50 (td, *J* = 7.4 Hz, *J* = 1.6 Hz, $1H_2$), 7.37 – 7.33 (d, *J* = 7.8 Hz, $1H_3$), 7.30 – 7.22 (dd, *J* = 15.0 Hz, *J* = 1.0 Hz, $1H_1$), 2.97 (s, $2H_{12}$), 1.59 (s, $6H_{15, 16}$).

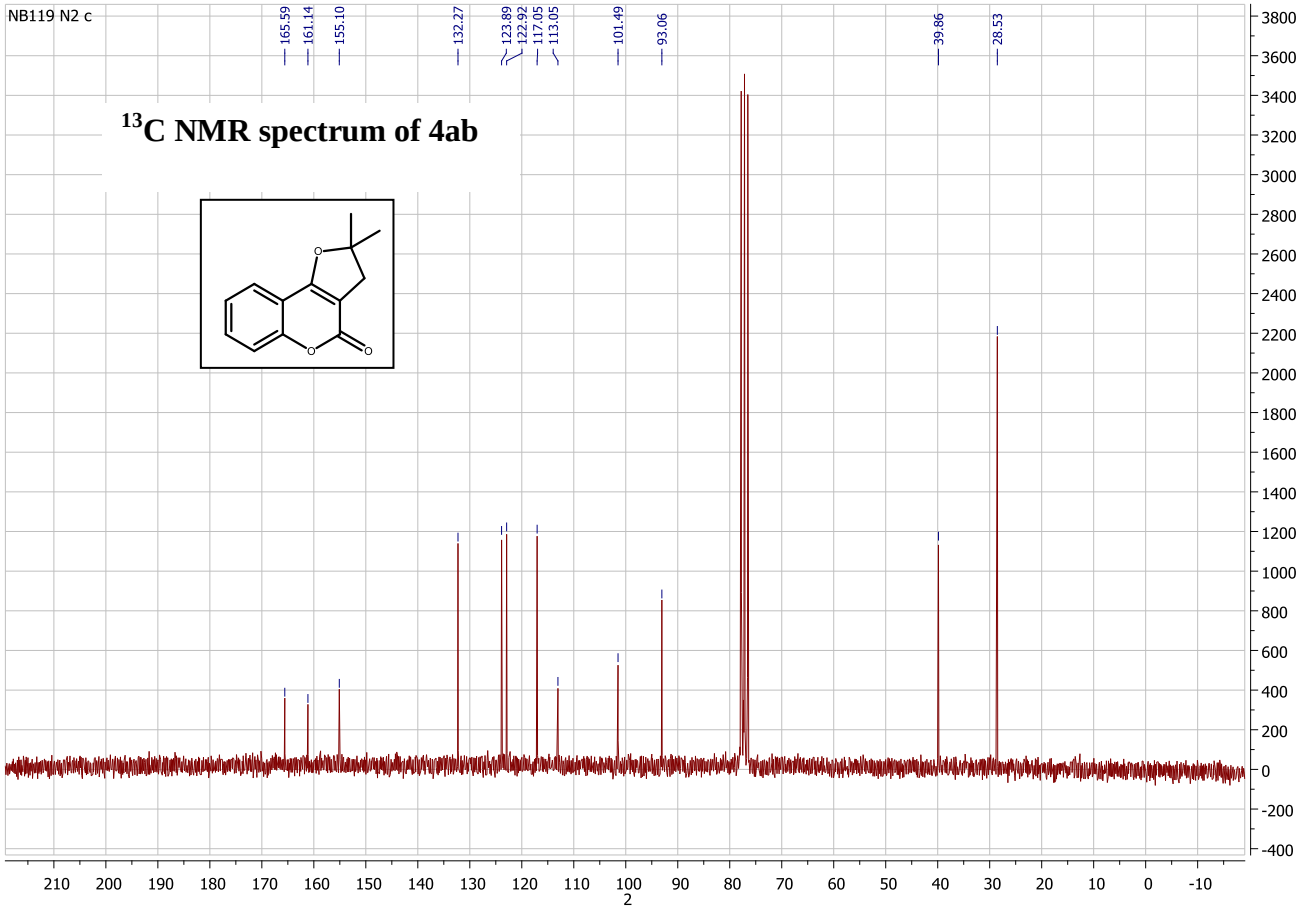
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 165.59 (C10), 161.14 (C8), 155.10 (C4), 132.27 (C2), 123.89 (C1), 122.92 (C6), 117.05 (C3), 113.05 (C5), 101.49 (C9), 93.06 (C13), 39.86 (C12), 28.53 (C15, 16).

IR (neat): ν_{max} (cm^{-1}) = 1706, 1637, 1608, 1566, 1497, 1445, 1405, 1371, 1342, 1321, 1280, 1267, 1205, 1184, 1121, 1084, 1024, 971, 952, 892, 838, 759, 741, 724.

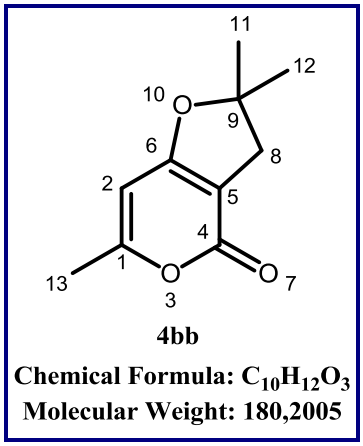
MS (EI, 70 eV): 216 (64) [$M^{+\cdot}$], 201 (61), 121 (100), 96 (37), 92 (20), 65 (25), 41 (19).



^{1}H NMR spectrum of 4ab



---------- 2,2,6-Trimethyl-2,3-dihydro-furo[3,2-*c*]pyran-4-one 4bb ----------



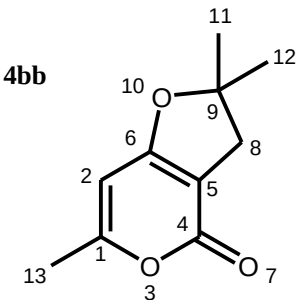
4bb

Chemical Formula: $C_{10}H_{12}O_3$

Molecular Weight: 180,2005

According to the general protocol **A**, compound **4bb** is synthesized, starting from **1b** (1 eq, 252 mg, 2 mmol) and **2b** (5 eq, 1141.4 mg, 10 mmol), using 5 mol% of $In(OTf)_3$ under reflux of CH_3NO_2 for 9 hours. The purification of the crude product is performed by flash chromatography (PE/EtOAc:90/10).

4bb



Yield : 65%
4bb : yellow solid
TLC: Rf = 0.66 (PE/EtOAc:4/1)
Mp = 74 °C

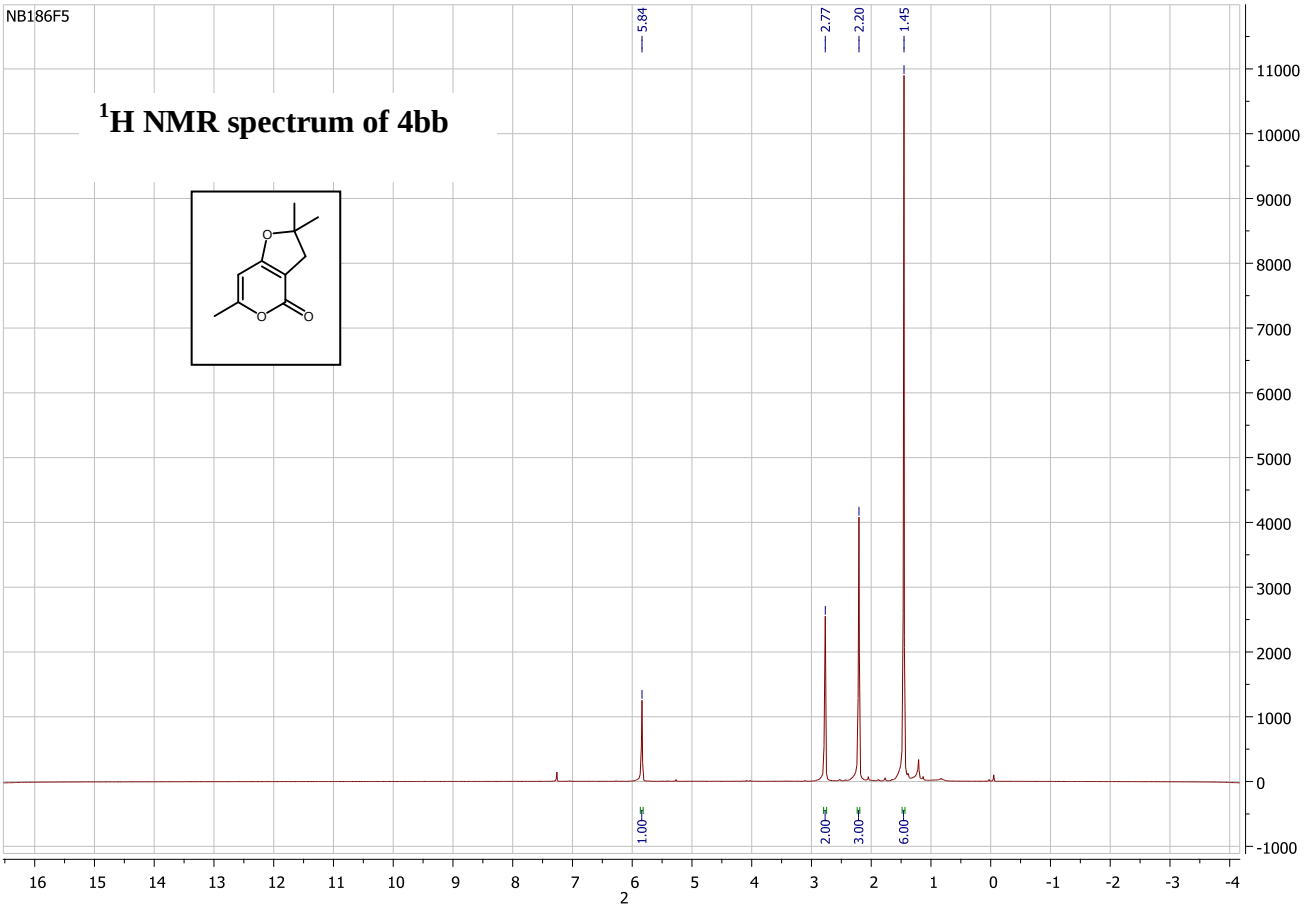
^{1}H NMR (200 MHz, $CDCl_3$) δ [ppm]: 5.84 (s, $1H_2$), 2.77 (s, $2H_8$), 2.20 (s, $3H_{13}$), 1.45 (s, $6H_{11, 12}$).

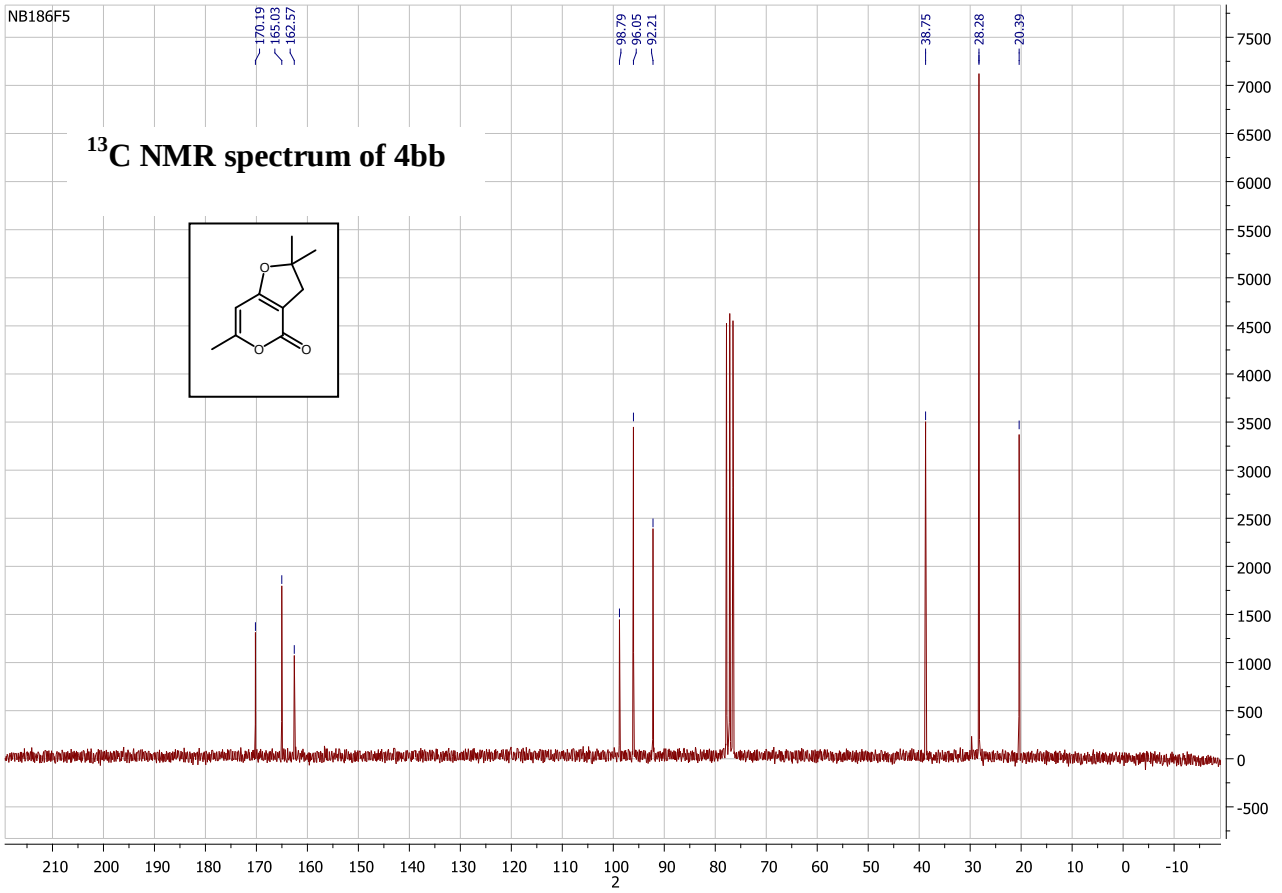
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 170.19 (C6), 165.03 (4), 162.57 (C1), 98.79 (C5), 96.05 (C2), 92.21 (C9), 38.75 (C8), 28.28 (C11, 12), 20.39 (C13).

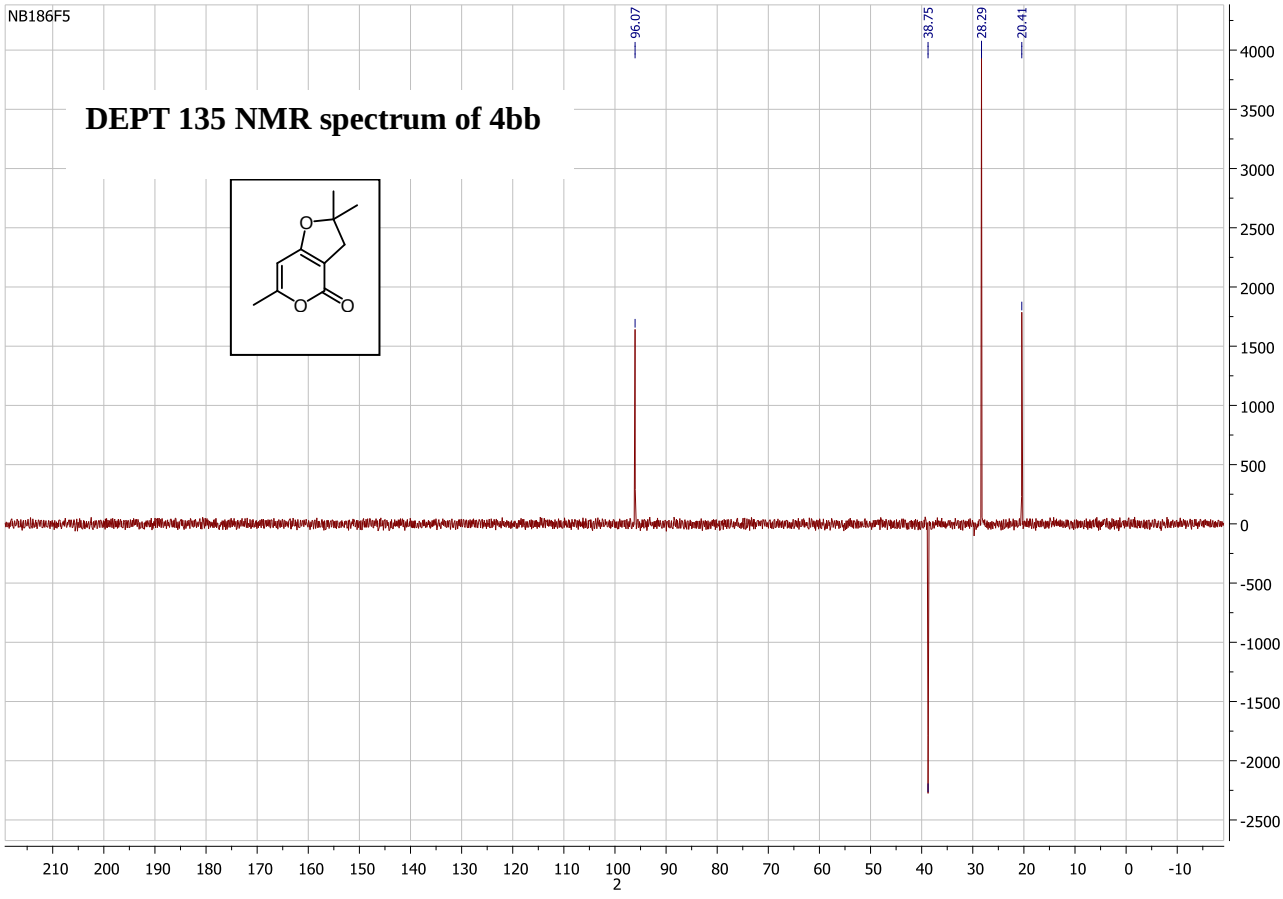
IR (neat): ν_{max} (cm^{-1}) = 2974, 2870, 1710, 1637, 1580, 1449, 1369, 1282, 1177, 1086, 978, 921, 856, 833, 775, 754, 734, 682, 610.

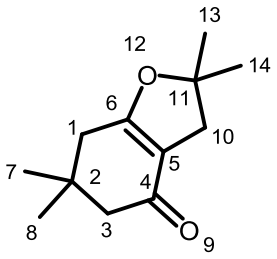
MS (EI, 70 eV): 180 (95) [$M^{+\cdot}$], 165 (54), 138 (33), 123 (32), 96 (67), 85 (61), 67 (23), 55 (27), 43 (100).

HRMS m/z calcd. For $C_{10}H_{12}O_3$ [$M^{+\cdot}$]: 180.0786, found 180.1026.




NB186F5
170.19
165.03
162.57
98.79
96.05
92.21
38.75
28.28
20.39
^{13}C NMR spectrum of 4bb
O
O
O
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f2

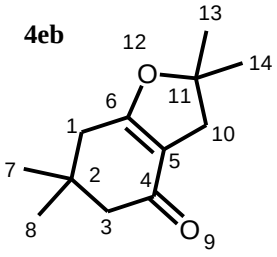

NB186F5
96.07
38.75
28.29
20.41
DEPT 135 NMR spectrum of 4bb
O
O
O
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f2



4eb

Chemical Formula: $C_{12}H_{18}O_2$
Molecular Weight: 194,2701

According to the general protocol **A**, compound **4eb** is obtained starting from **1e** (1 eq, 280 mg, 2 mmol) and **2b** (5 eq, 1141.4 mg, 10 mmol), using 5 mol% of $In(OTf)_3$ under reflux of CH_3NO_2 for 12 hours. The crude of the product is purified by flash chromatography (PE/EtOAc:9/1).



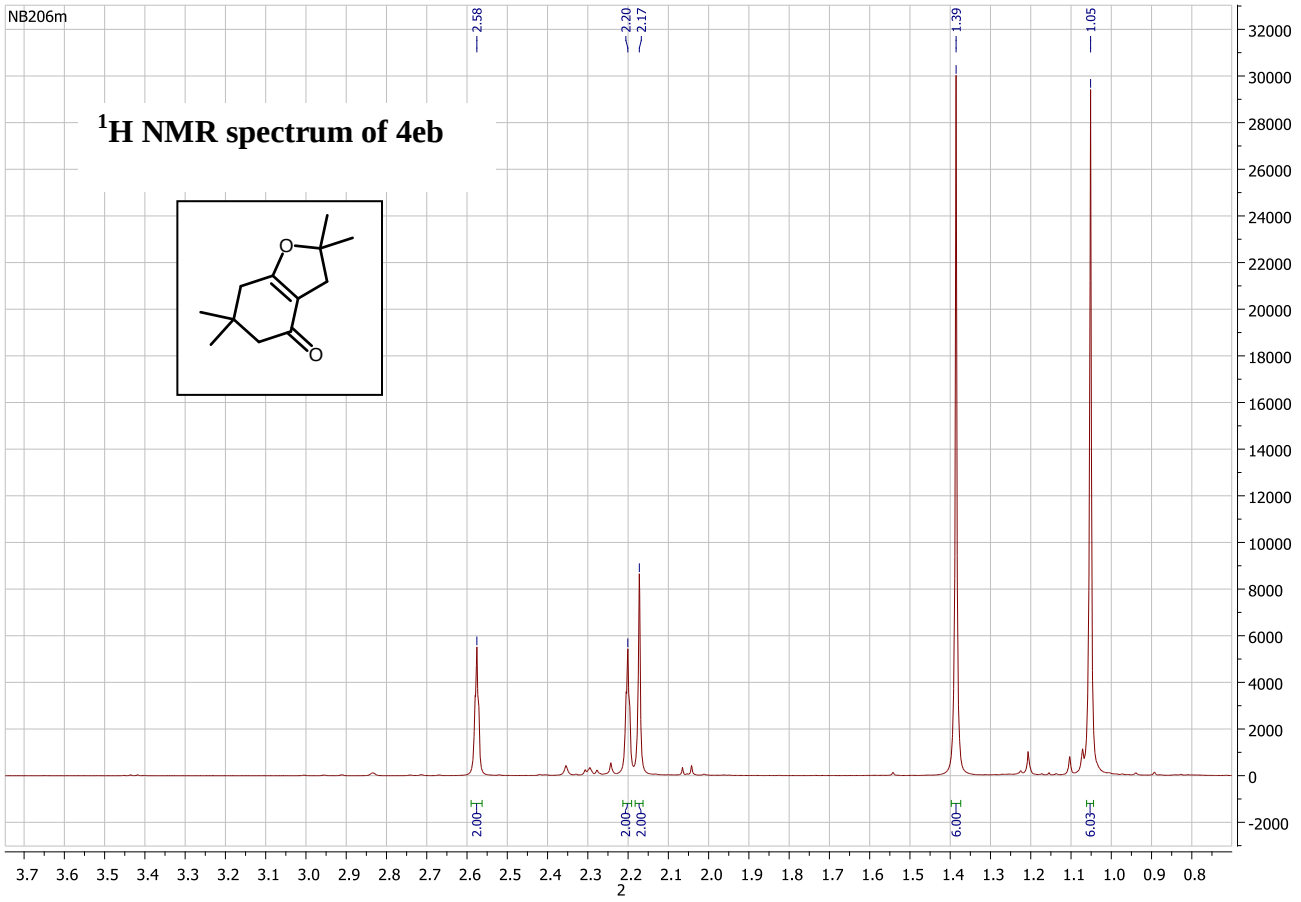
Cas number: 83814-10-2
Yield : 60%
4eb : orange solid
TLC: Rf = 0.54 (PE/EtOAc:1/1)
Mp = 35 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 2.58 (s, $2H_{10}$), 2.20 (s, $2H_3$), 2.17 (s, $2H_1$), 1.39 (s, $6H_{13, 14}$), 1.05 (s, $6H_{7, 8}$).

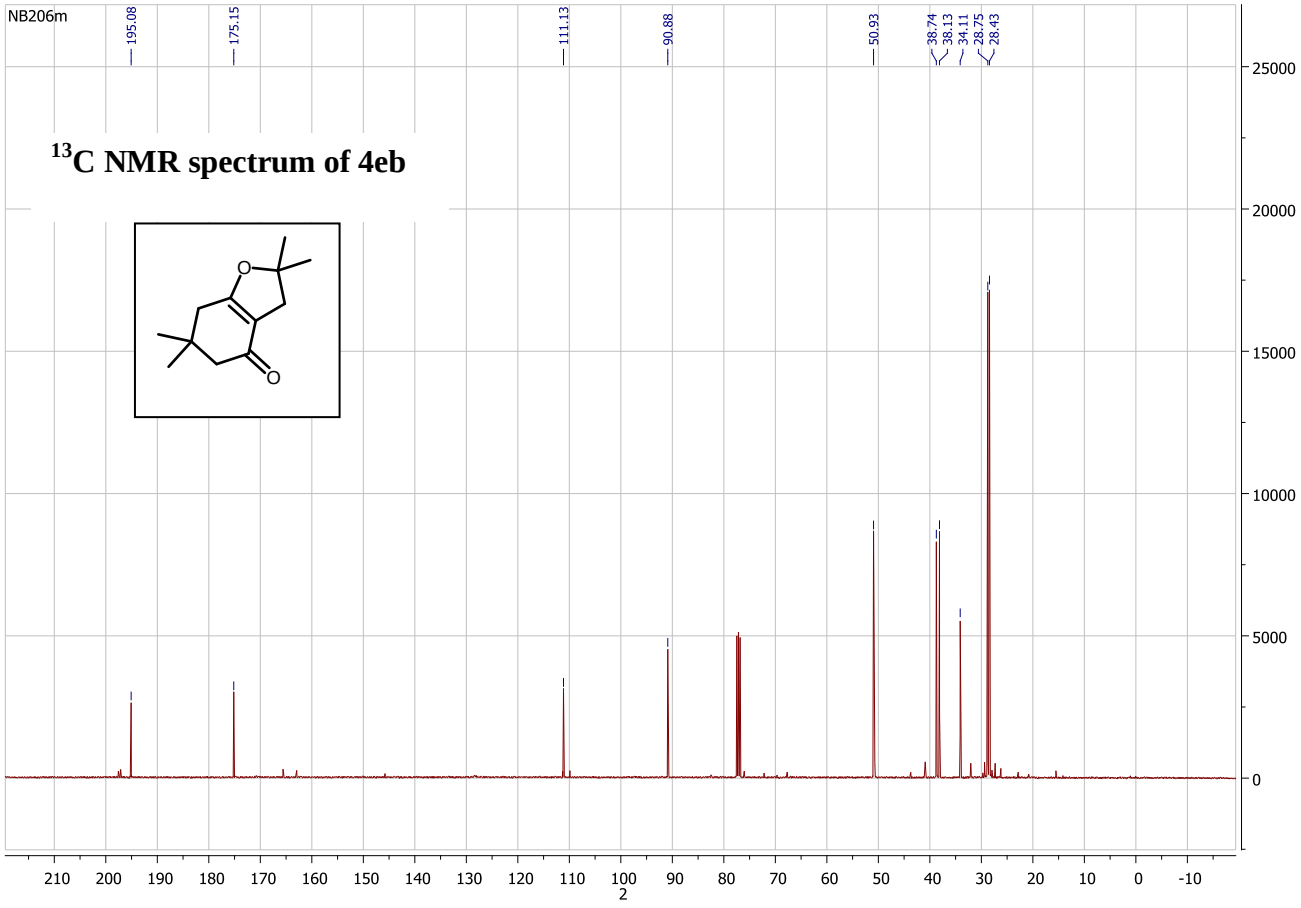
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 195.08 (C4), 175.15 (C6), 111.13 (C5), 90.88 (C11), 50.93 (C3), 38.74 (C10), 38.13 (C1), 34.11 (C2), 28.75 (C7, 8), 28.43 (C13, 14).

IR (neat): ν_{max} (cm^{-1}) = 1653, 1618, 1401, 1370, 1332, 1294, 1279, 1253, 1217, 1166, 1149, 1111, 1101, 1089, 1030, 1014, 974, 912, 879, 850, 840, 826.

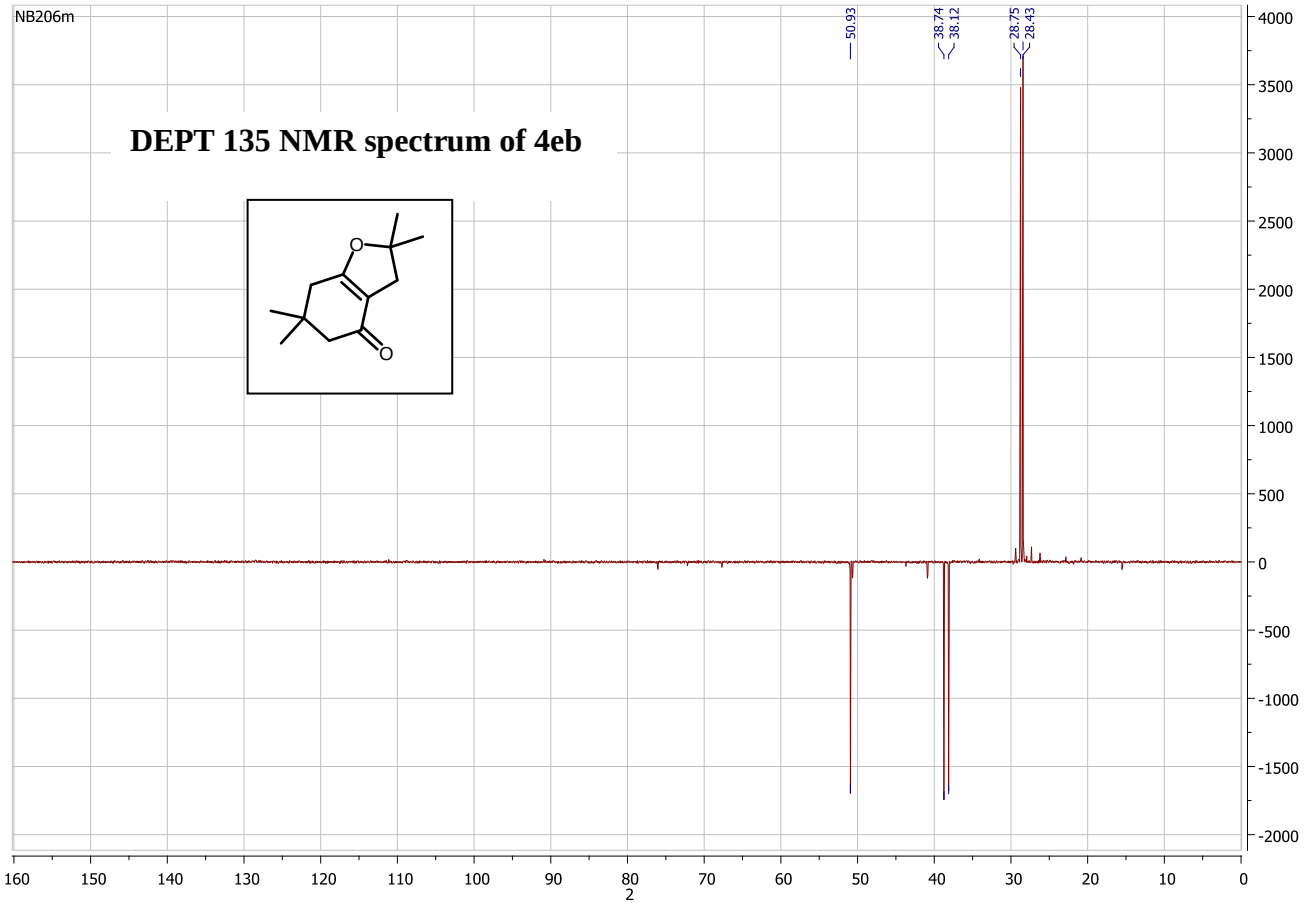
MS (EI, 70 eV): 194 (69) [$M^{+\cdot}$], 179 (100), 161 (50), 138 (60), 123 (38), 110 (41), 95 (58), 67 (33), 55 (36), 44 (35), 43 (61).



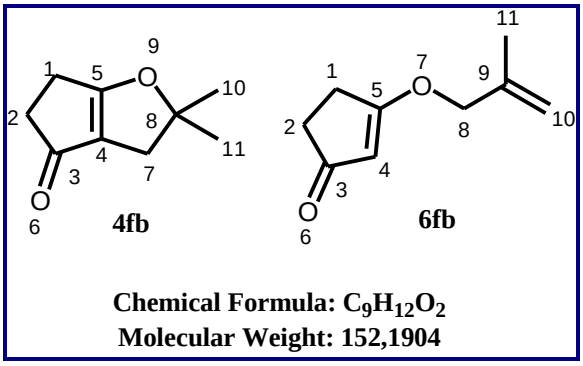
^{1}H NMR spectrum of 4eb



^{13}C NMR spectrum of 4eb

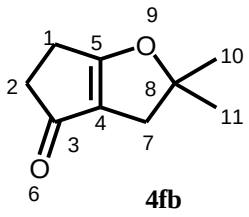


---------- 2,2-Dimethyl-2,3,5,6-tetrahydro-cyclopenta[*b*]furan-4-one 4fb ----------
---------- 3-(2-Methyl-allyloxy)-cyclopent-2-enone 6fb ----------

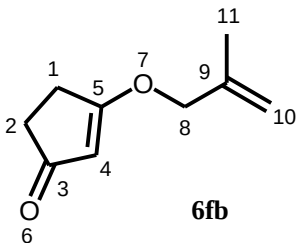


Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152,1904

According to the general protocol **A**, **4fb** and **6fb** (ratio **4fb**/**6fb** = 5/95) are obtained starting from **1f** (1 eq, 196.06 mg, 2 mmol) and **2b** (5 eq, 1141.4 mg, 10 mmol), using 5 mol% of $In(OTf)_3$ under reflux of CH_3NO_2 for 9 hours. The crude of the reaction is purified by column chromatography (PE/EtOAc:4/1).



4fb



6fb

Yield : 55%
Ratio **4fb**/**6fb** = 5/95
4fb/6fb : yellow oil
TLC: Rf = 0.31 (PE/EtOAc :1/1)

^{1}H NMR (400 MHz, $CDCl_3$) :

4fb δ [ppm]: 2.65 – 2.63 (m, $2H_2$), 2.51– 2.49 (m, $2H_1$), 2.10 (s, $2H_7$), 1.51 (s, $3H_{10}$), 1.25 (s, $3H_{11}$).

6fb δ [ppm]: 5.31 (s, $1H_4$), 5.06 – 5.03 (d, J = 11.2 Hz, $2H_{10}$), 4.41 (s, $2H_8$), 2.65 – 2.63 (m, $2H_2$), 2.46 – 2.43 (m, $2H_1$), 1.80 (s, $3H_{11}$).

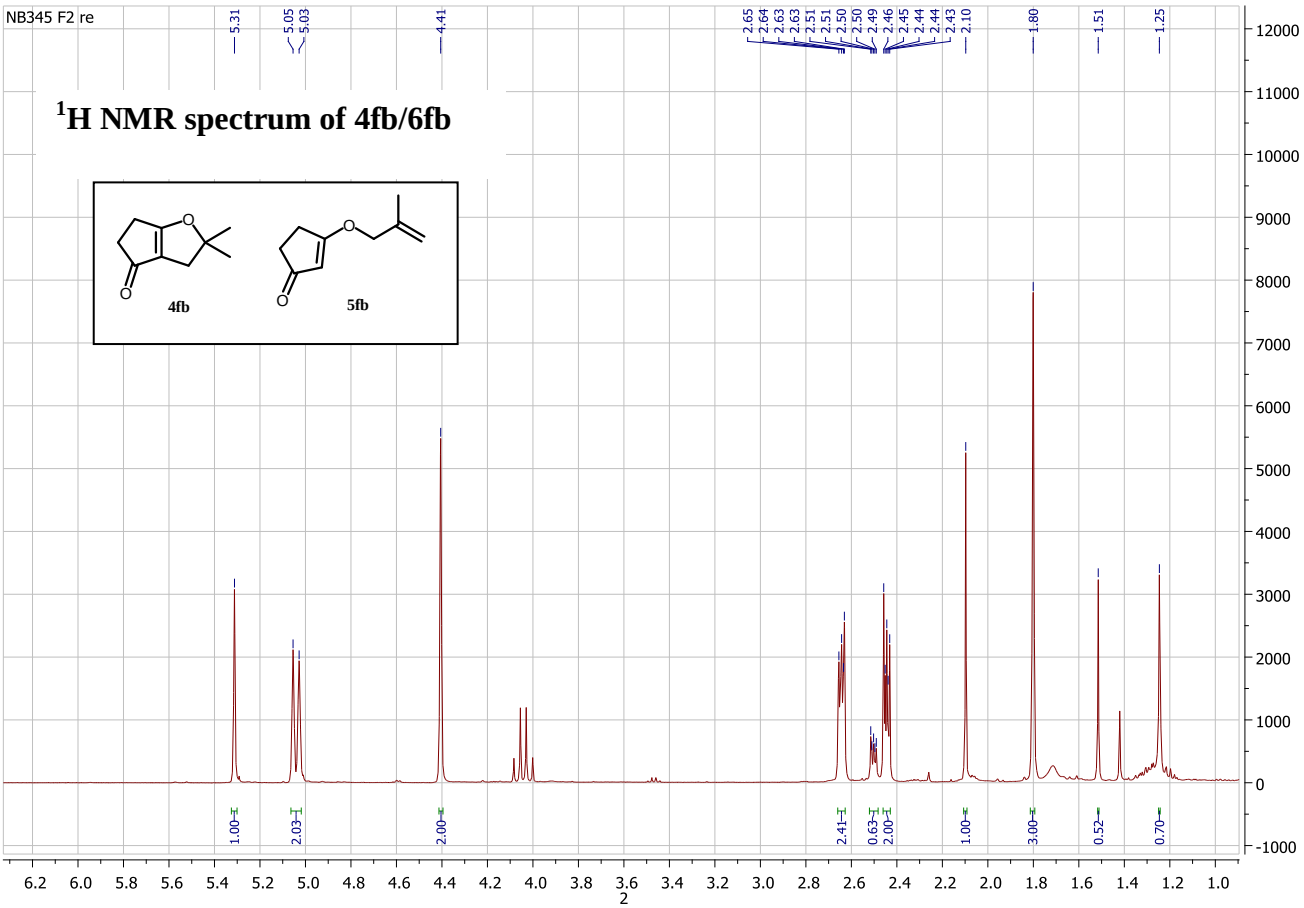
^{13}C NMR (101 MHz, $CDCl_3$) :

4fb δ [ppm]: 202.62 (C6), 176.67 (C5), 125.49 (C4), 70.91 (C8), 68.26 (C7), 34.56 (C2), 25.24 (C10), 24.58 (C1), 20.95 (C11).

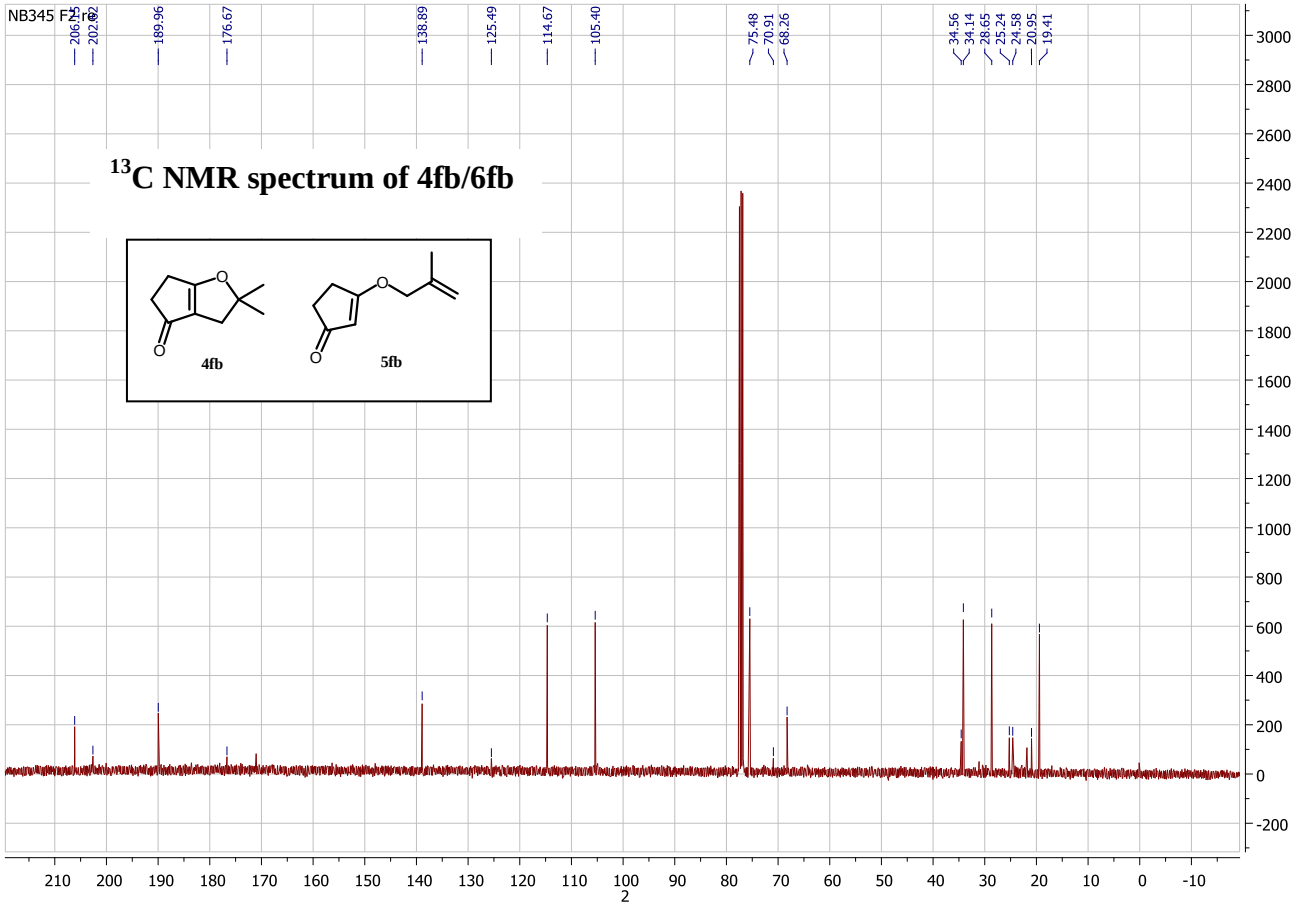
6fb δ [ppm]: 206.15 (C3), 189.96 (C5), 138.89 (C9), 114.67 (C10), 105.40 (C4), 75.48 (C7), 34.14 (C2), 28.64 (C1), 19.41 (C11).

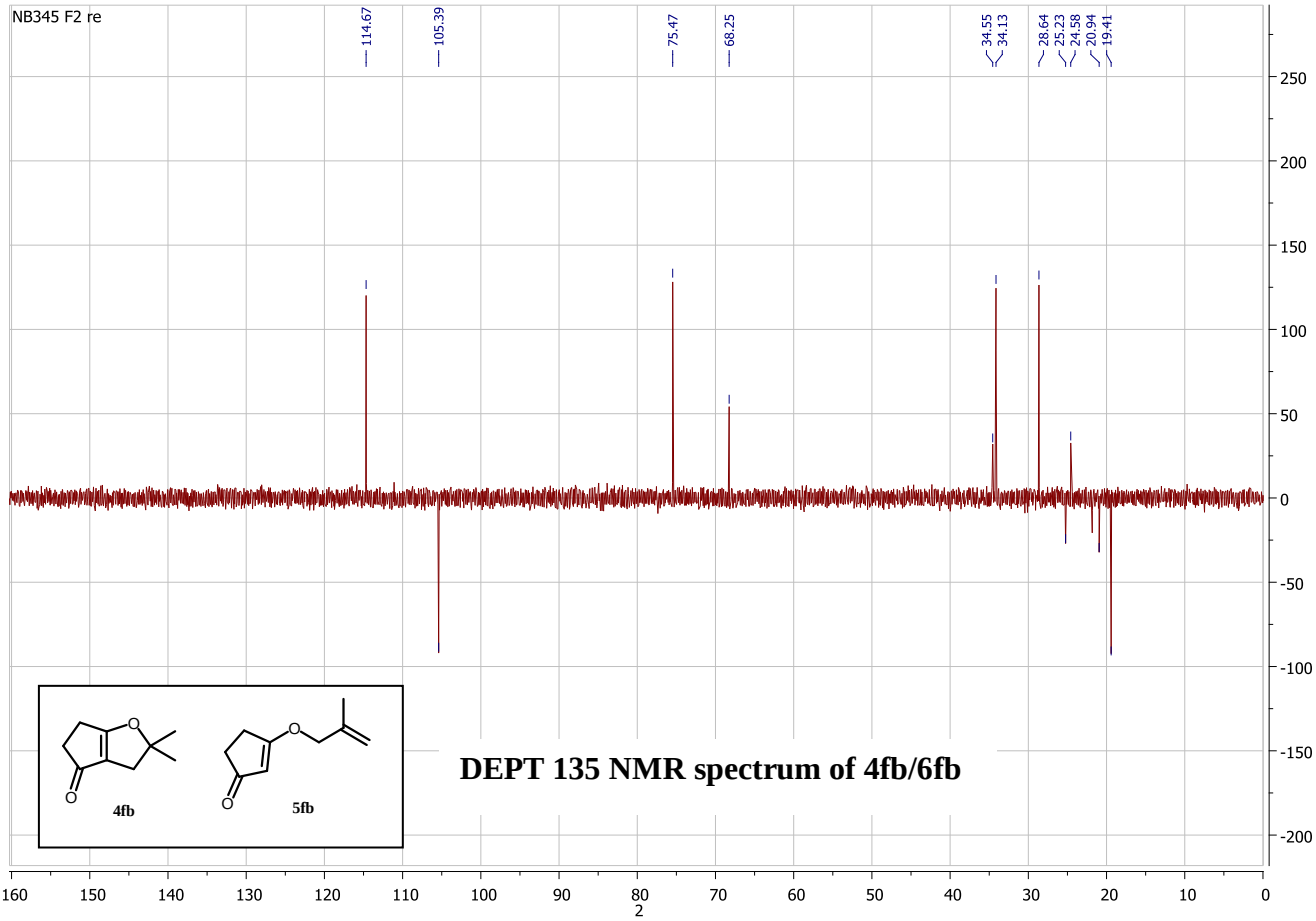
MS (EI, 70 eV): 152 (3) [$M^{+\cdot}$], 110 (17), 109 (28), 95 (10), 69 (31), 55 (100), 44 (31), 40 (55).

HRMS m/z calcd. For $C_9H_{12}O_2$ [$M^{+\cdot}$]: 152.0837, found 152.0832.

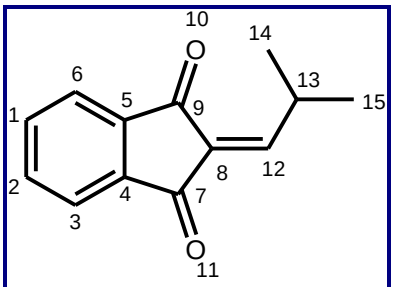


^{1}H NMR spectrum of 4fb/6fb


NB345 F2 re
206.45
202.92
189.96
176.67
138.89
125.49
114.67
105.40
75.48
70.91
68.26
34.56
34.14
28.65
25.24
24.58
20.95
19.41
13C NMR spectrum of 4fb/6fb
4fb
5fb
f2


NB345 F2 re
114.67
105.39
75.47
68.25
34.55
34.13
28.64
25.23
24.58
20.94
19.41
4fb
5fb
DEPT 135 NMR spectrum of 4fb/6fb
f2

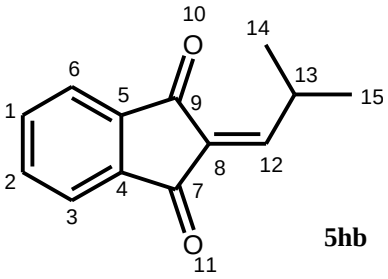
---------- 2-Isobutylidene-indan-1,3-dione 5hb ----------



5hb

Chemical Formula: $C_{13}H_{12}O_2$
Molecular Weight: 200,2332

According to the general protocol **A**, **5hb** is obtained starting from indan-1,3-dione **1h** (1 eq, 292.06 mg, 2 mmol) and **2b** (5 eq, 1141.4 mg, 10 mmol), using 5 mol% of $In(OTf)_3$ under reflux of CH_3NO_2 for 2 hours. The crude of the reaction is purified by column chromatography (PE/Et_2O:95/5).



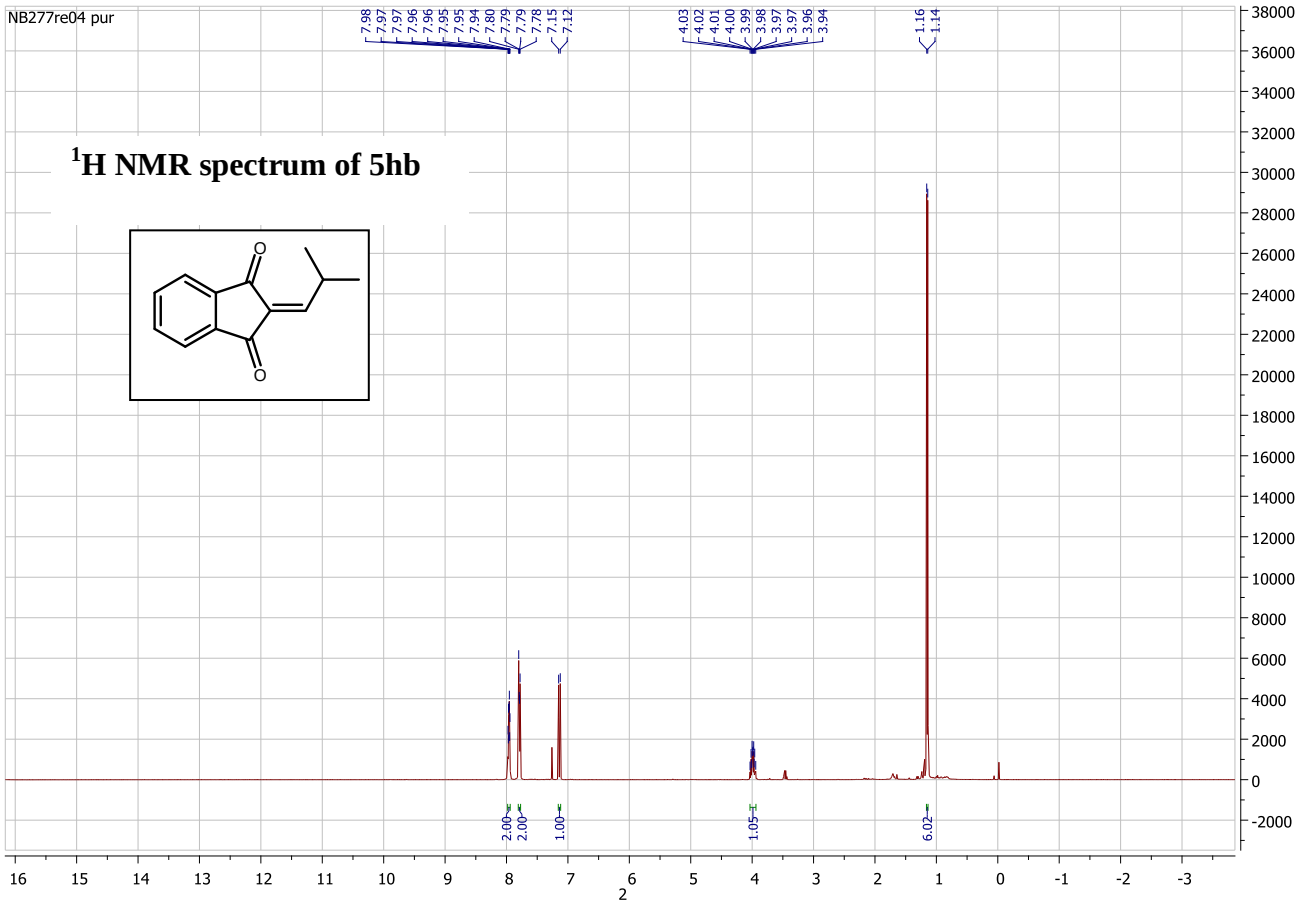
5hb

Cas number: 22123-54-2
Yield : 52%
5hb : brown oil
TLC: Rf = 0.42 (PE/Et_2O:9/1)

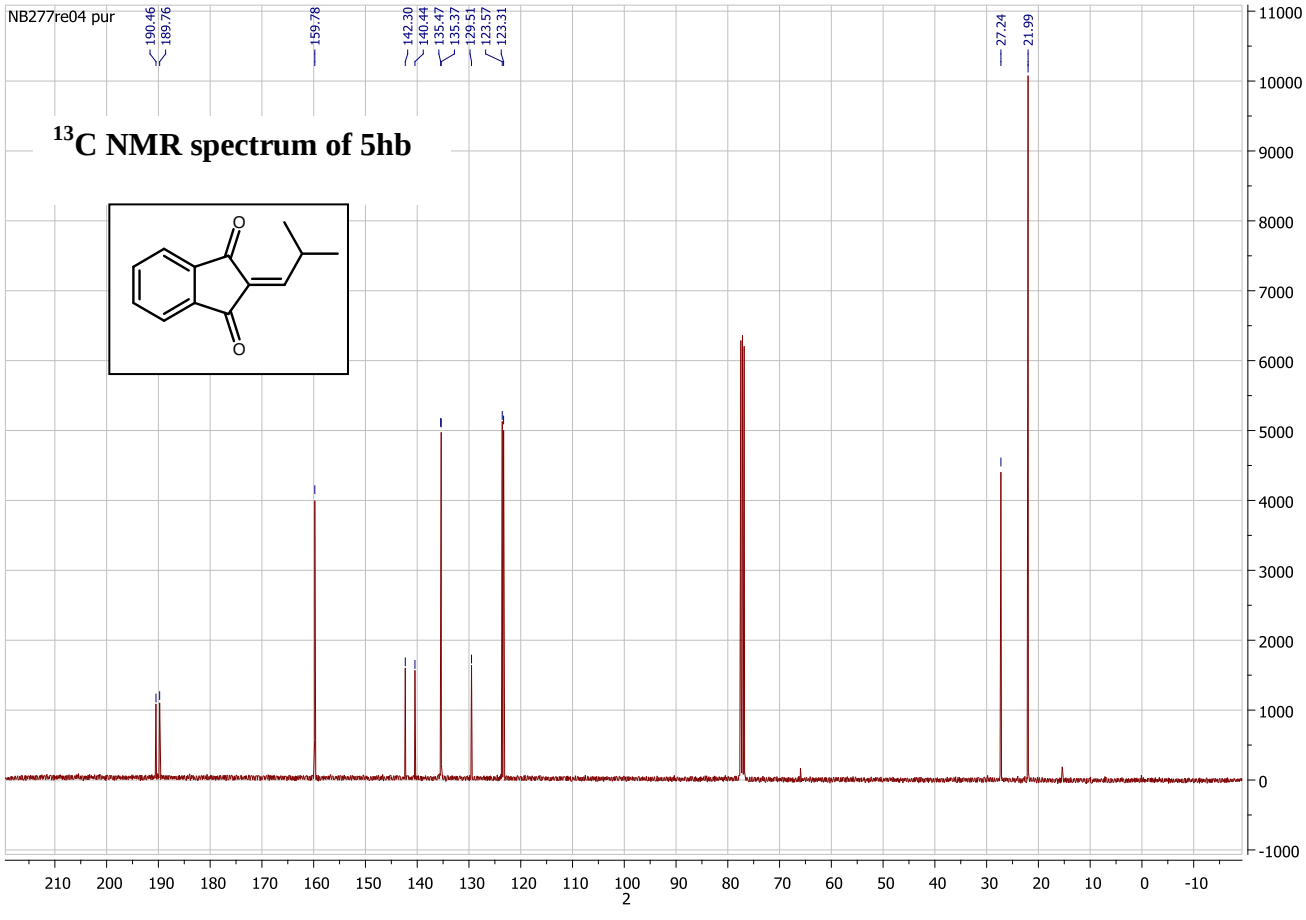
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.98 – 7.94 (m, $2H_{3,6}$), 7.80 – 7.78 (m, $2H_{1,2}$), 7.15 – 7.12 (d, J = 12 Hz, $1H_{12}$), 4.03 – 3.94 (m, $1H_{13}$), 1.16 – 1.14 (d, J = 6.6 Hz, $6H_{14,15}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 190.46 (C7), 189.76 (C9), 159.78 (C12), 142.30 (C4), 140.44 (C5), 135.47 (C1), 135.37 (C2), 129.51 (C8), 123.57 (C3), 123.31 (C6), 27.24 (C13), 21.99 (C14, 15).

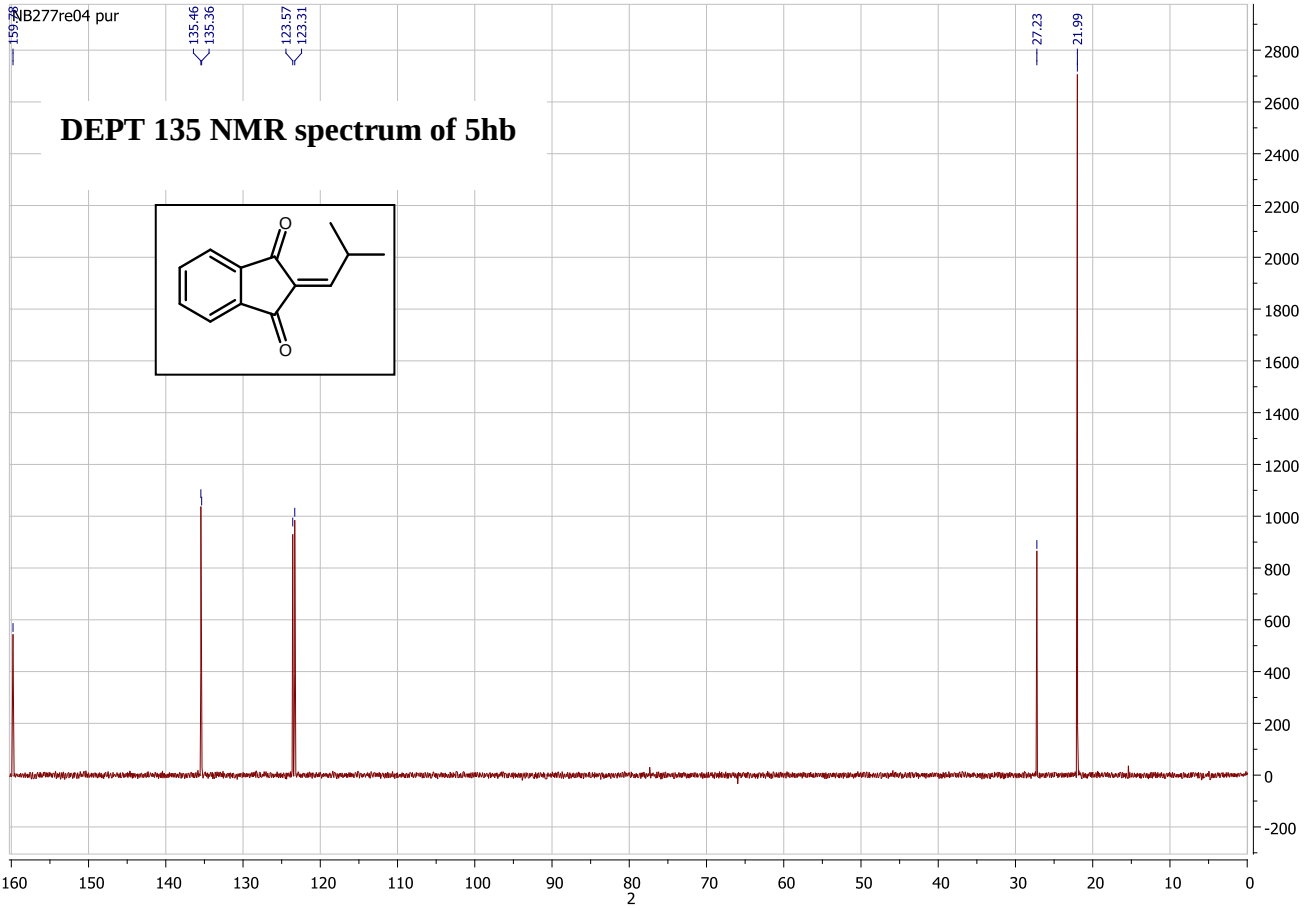
MS (EI, 70 eV): 200 (100) [$M^{+\cdot}$], 185 (30), 157 (19), 128 (37), 105 (23), 76 (45), 53 (25), 50 (31), 40 (49).



^{1}H NMR spectrum of 5hb

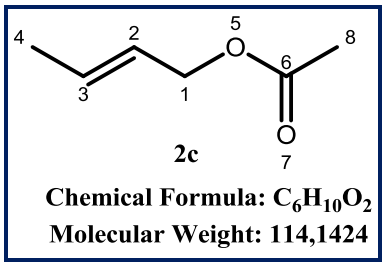


^{13}C NMR spectrum of 5hb

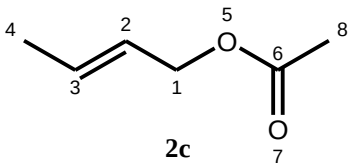


4. Reaction of β-ketolactones 1 with disubstituted allylic acetates 2c-2e

---------- But-2(*E*)-enyl acetate 2c ----------



(*E*)-2-Buten-1-ol (58 mmol) is introduced into a round bottom flask, equipped with a magnetic stir bar and pre-purged three times with nitrogen (vacuum/nitrogen). DMAP (1 mmol) and acetic anhydride (63 mmol) are added successively. The mixture is cooled to 0 °C, and the reaction is followed by GC and TLC. The crude of reaction is hydrolyzed with HCl 1M and extracted twice with Et_2O. The organic phases are washed with water and saturated NaCl, dried over $MgSO_4$ and evaporated under pressure. The product obtained is purified on a flash column chromatography of silica gel (PE/Et_2O:9/1).

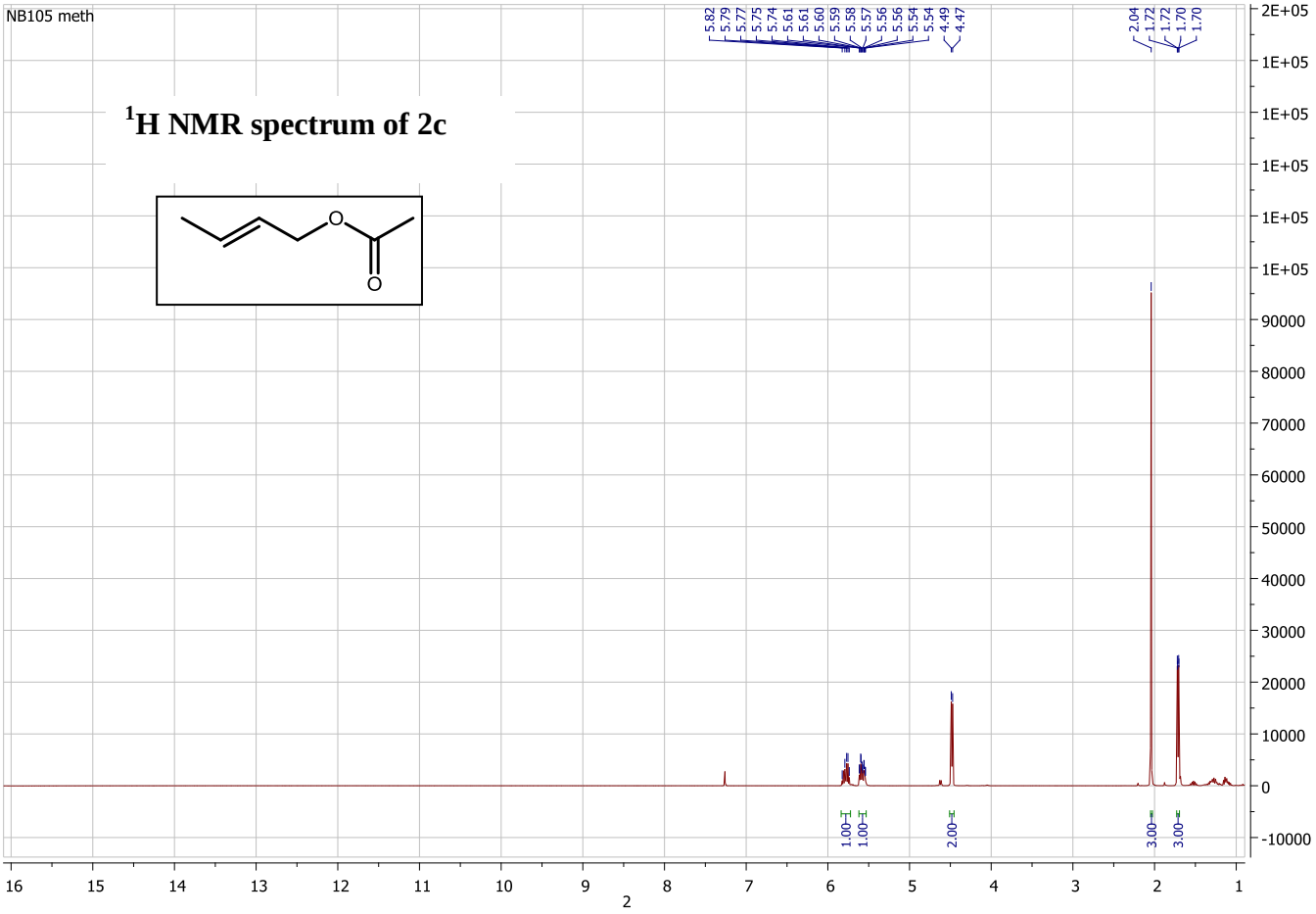


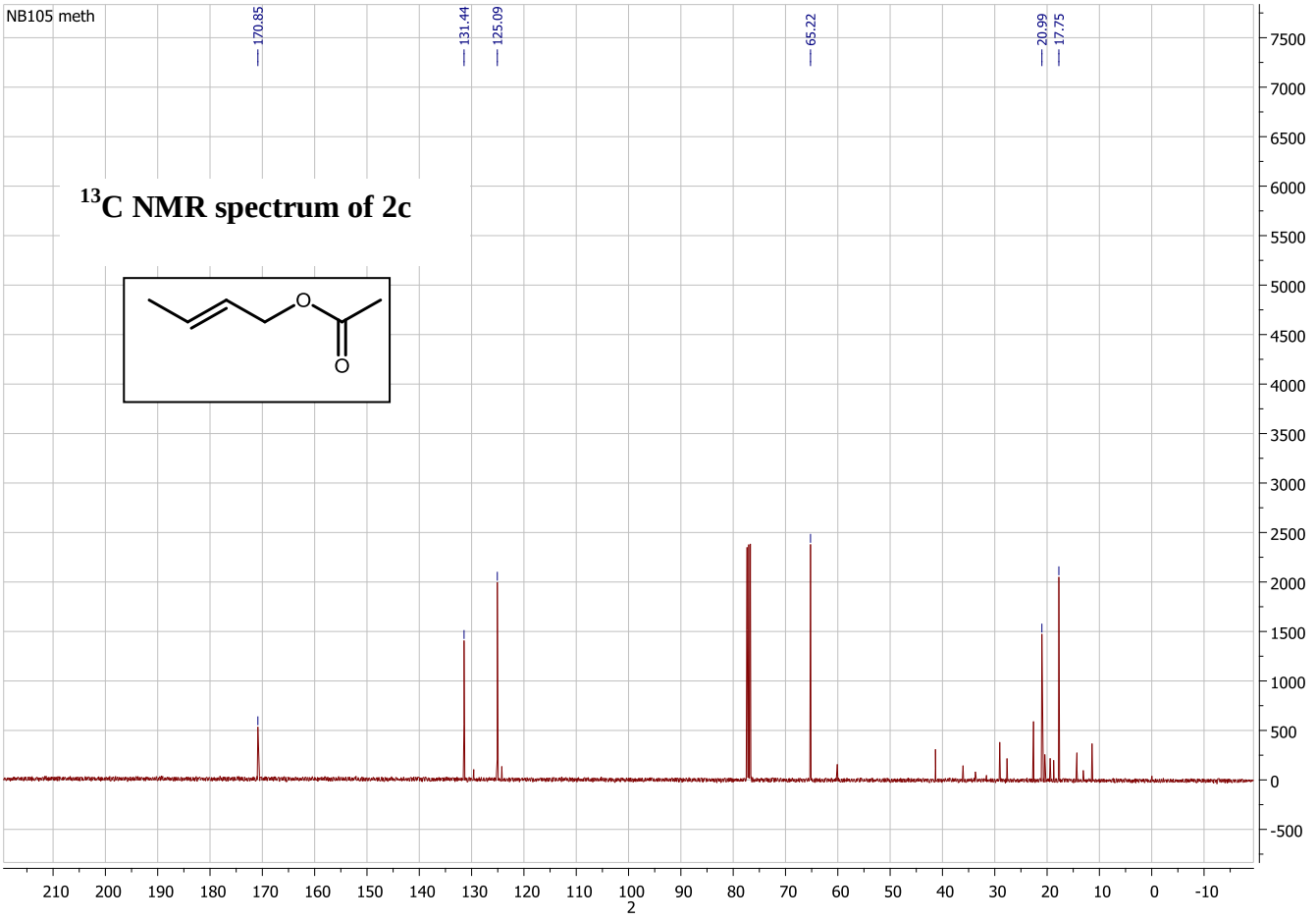
2c

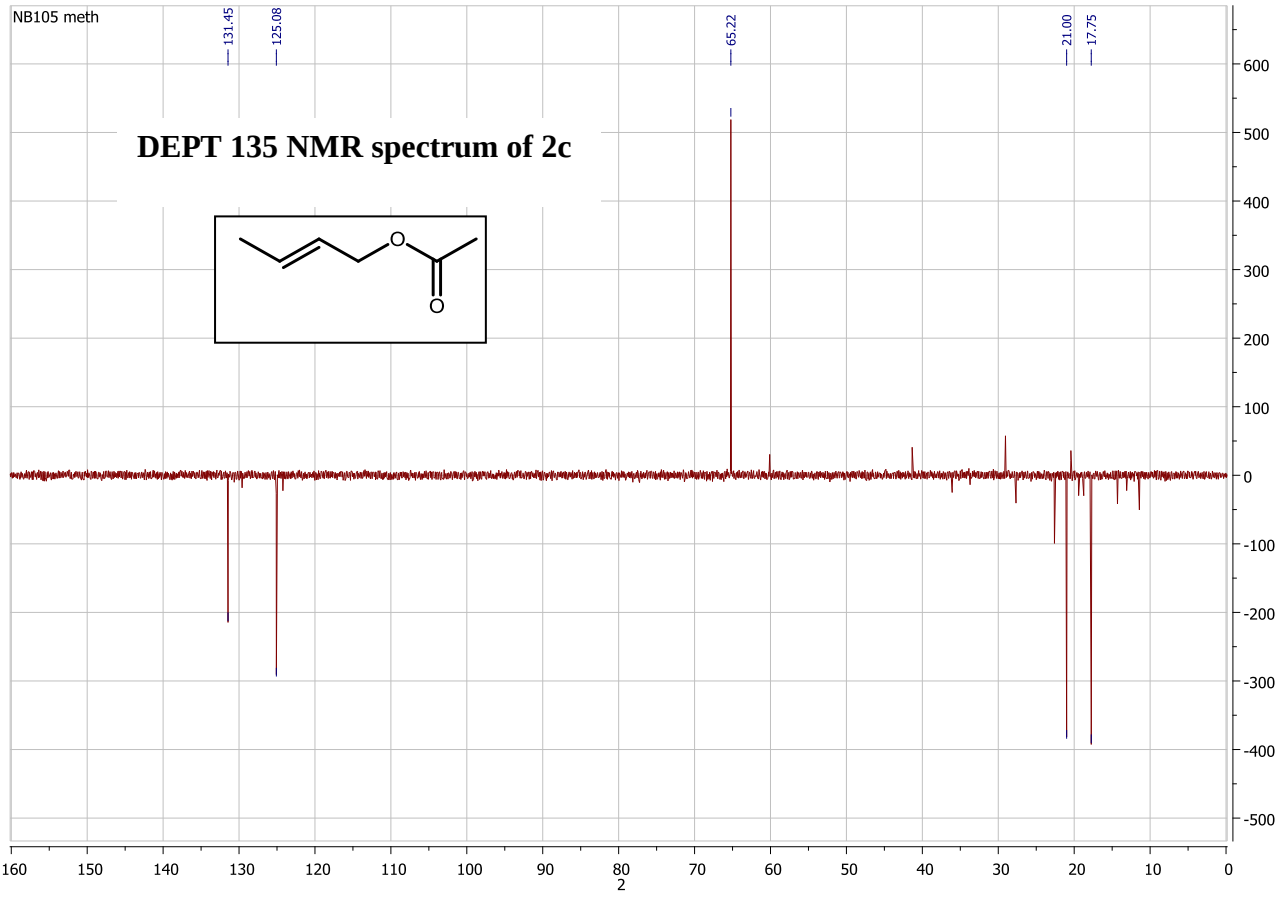
Cas number: 628-08-0
Yield : 75%
2c : colorless oil
TLC: Rf = 0.78 (PE/Et_2O:9/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 5.82 – 5.74 (m, $1H_3$), 5.61 – 5.54 (m, $1H_2$), 4.49 – 4.47 (d, *J* = 6.8 Hz, $2H_1$), 2.04 (s, $3H_8$), 1.72 – 1.70 (dd, *J* = 6.4, 1.2 Hz, $3H_4$).

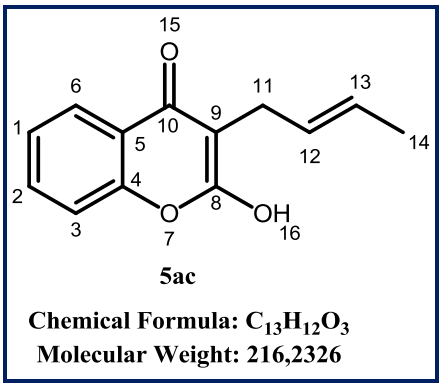
^{13}C NMR (50 MHz, $CDCl_3$) δ [ppm]: 170.85 (C5), 131.44 (C2), 125.09 (C1), 65.22 (C3), 20.99 (C7), 17.75 (C8).




NB105 meth
170.85
131.44
125.09
65.22
20.99
17.75
^{13}C NMR spectrum of 2c
O
O
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
2


NB105 meth
131.45
125.08
65.22
21.00
17.75
DEPT 135 NMR spectrum of 2c
O
O
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
2

---------- *(E)*-3-But-2-enyl-2-hydroxy-chromen-4-one 5ac ----------

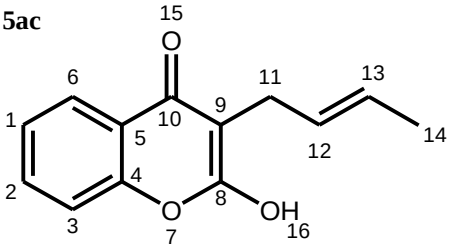


5ac

Chemical Formula: $C_{13}H_{12}O_3$
Molecular Weight: 216,2326

According to the general protocol **A**, (*E*)-but-2-enyl-acetate **2c** (5 eq, 1141.4 mg, 10 mmol) reacts with the 4-hydroxycoumarine **1a** (1 eq, 324 mg, 2 mmol), with 5 mol% of $In(OTf)_3$, under reflux of dichloroethane during 14 hours. The purification of the crude of the reaction is performed by flash chromatography (PE/Et_2O:95/5).

5ac



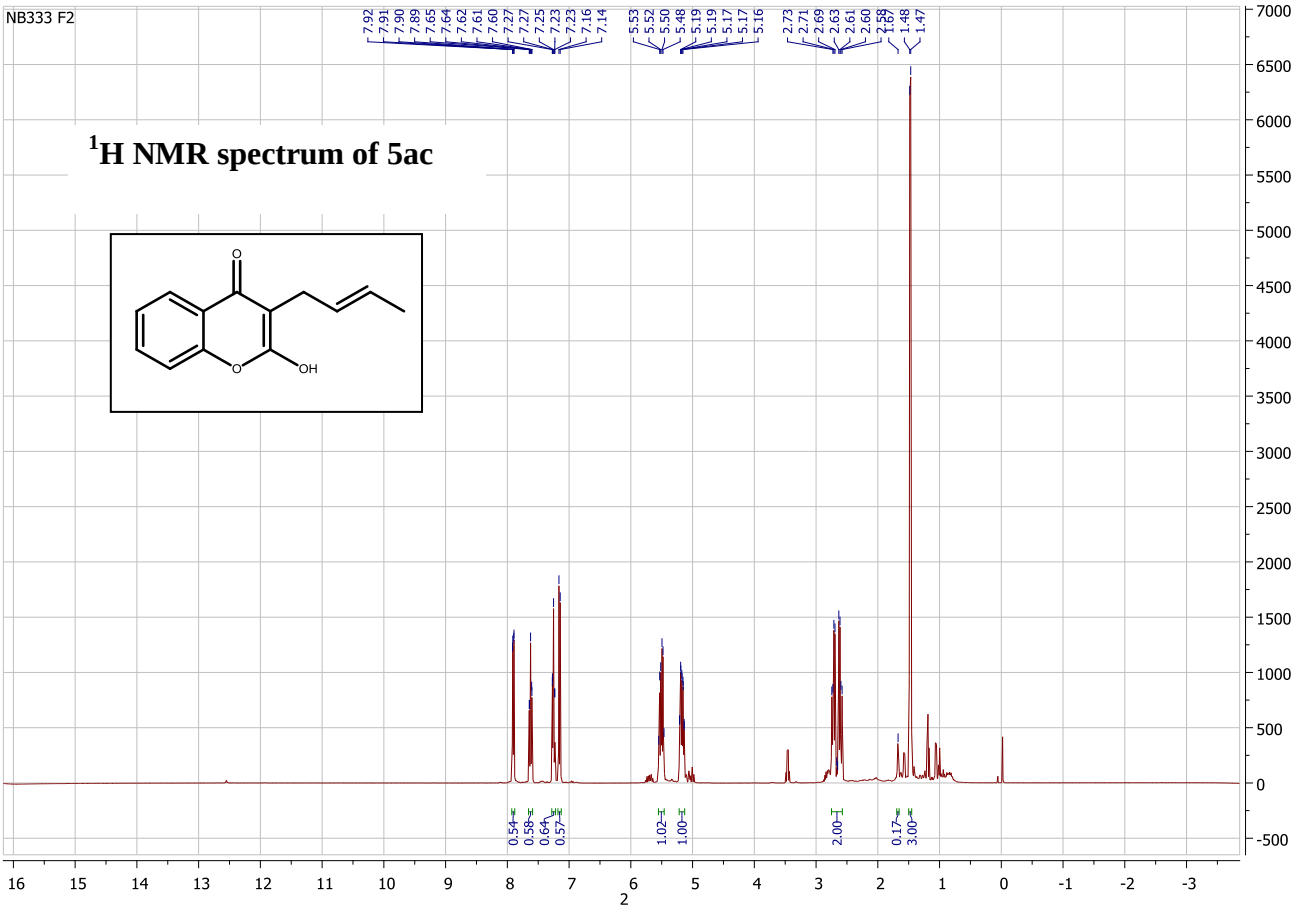
Yield : 13%
5ac : colorless oil
TLC: Rf = 055 (PE/Et_2O:9/1)

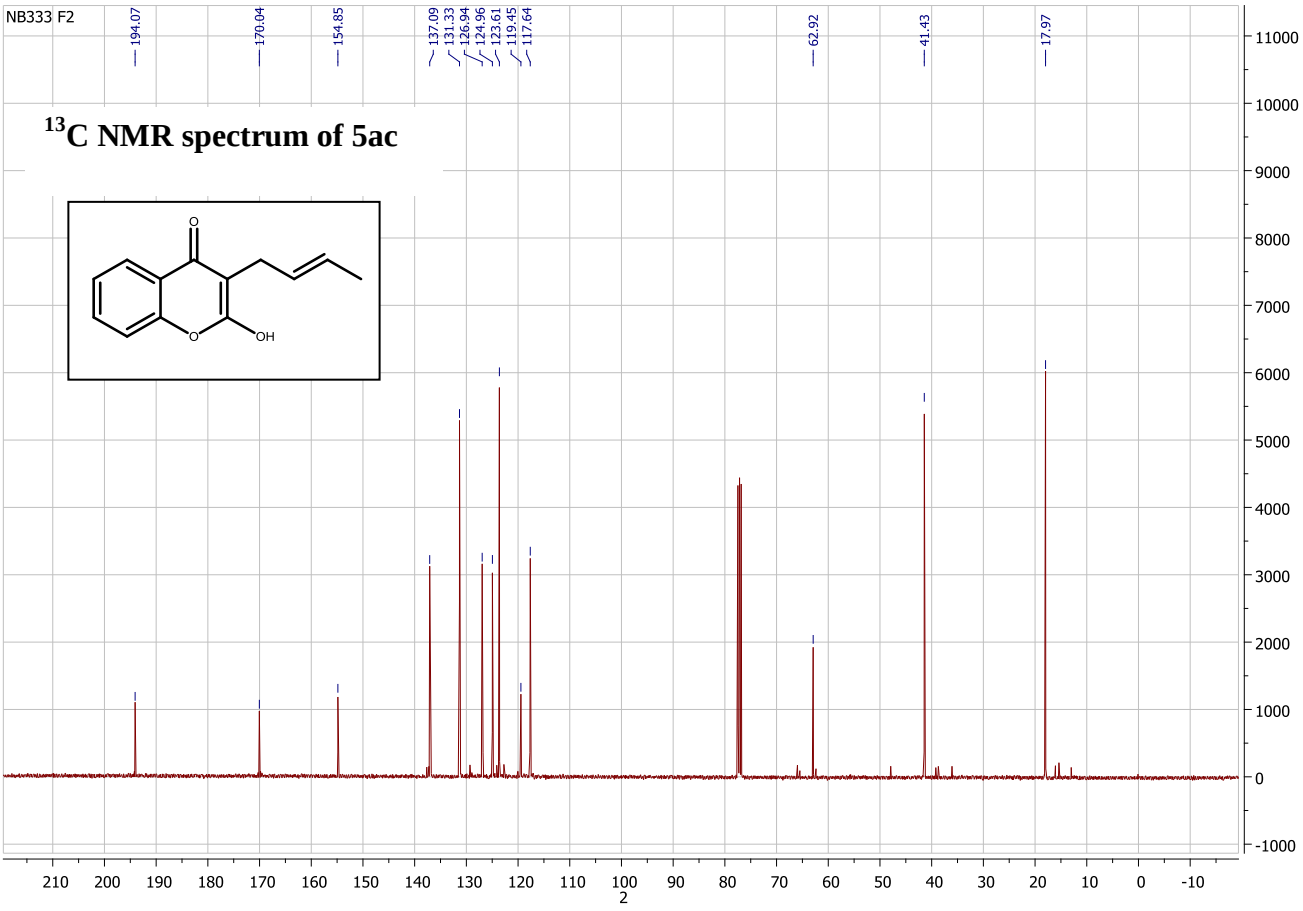
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.92 – 7.89 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, $1H_6$), 7.65 – 7.60 (td, *J* = 8.4 Hz, *J* = 1.6 Hz, $1H_2$), 7.27 – 7.23 (td, *J* = 8 Hz, *J* = 0.4 Hz, $1H_1$), 7.16 – 7.14 (d, *J* = 8.3 Hz, $1H_3$), 5.55 – 5.46 (m, $1H_{12}$), 5.21 – 5.13 (m, $1H_{13}$), 2.74 – 2.58 (m, $2H_{11}$), 1.67 (s, $1H_{16}$), 1.48 – 1.47 (d, *J* = 6.4 Hz, $3H_{14}$).

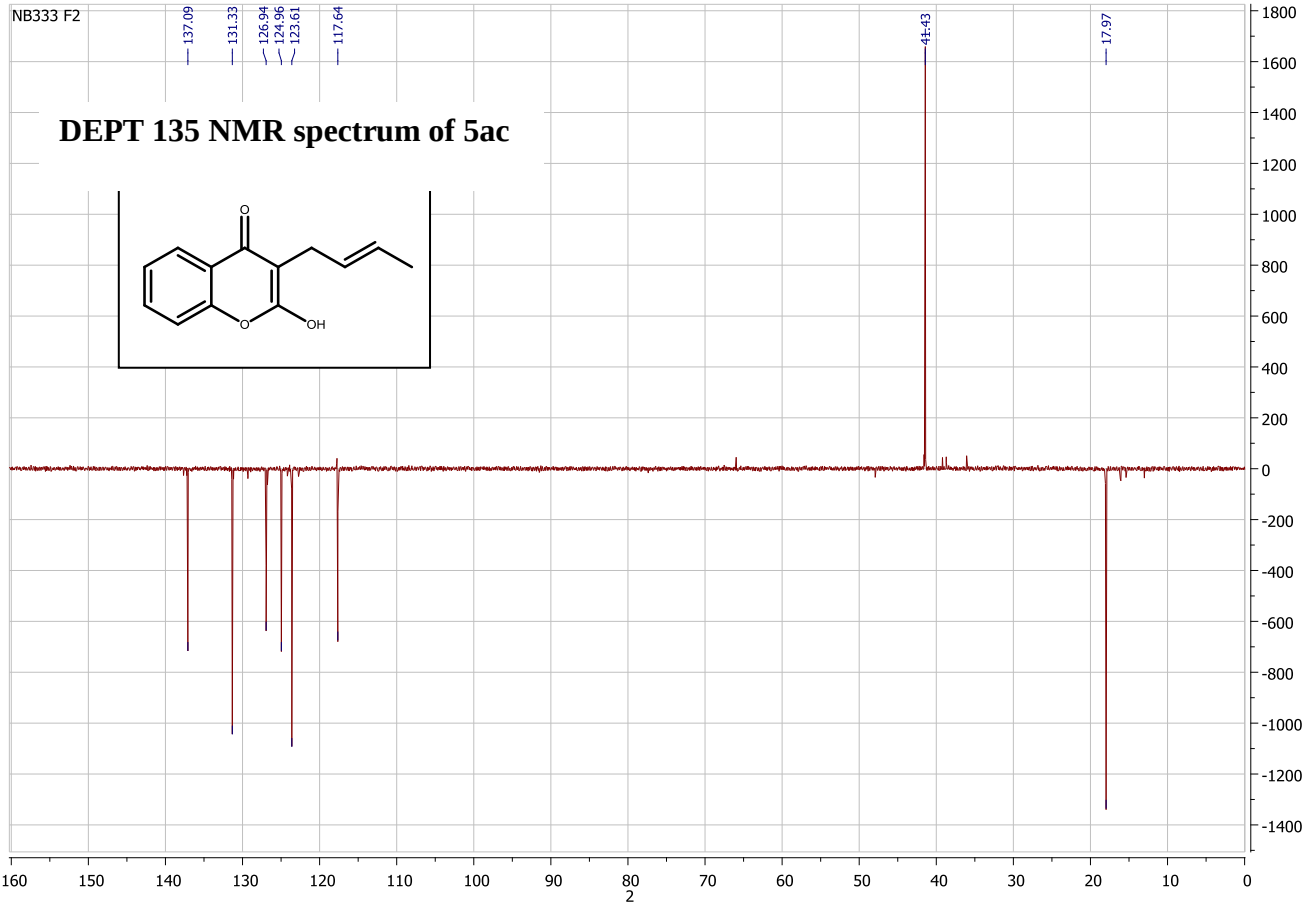
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 194.07 (C10), 170.04 (C4), 154.85 (C8), 137.09 (C2), 131.33 (C12), 126.94 (C1), 124.96 (C13), 123.61 (C6), 119.45 (C5), 117.64 (C3), 62.92 (C9), 41.43 (C11), 17.97 (C14).

MS (EI, 70 eV): 216 (71) [$M^{+\cdot}$], 201 (68), 121 (100), 96 (37), 65 (23), 53 (12), 41 (13).

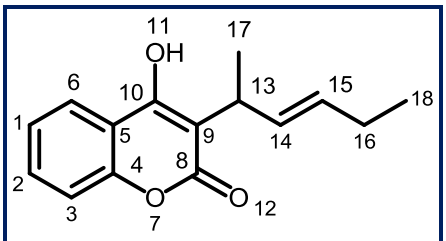
HRMS m/z calcd. For $C_{13}H_{12}O_3$ [$M^{+\cdot}$]: 216.0786, found 216.0854.


NB333 F2
7.92 7.91 7.90 7.89 7.65 7.64 7.62 7.61 7.60 7.27 7.27 7.25 7.23 7.23 7.16 7.14
5.53 5.52 5.50 5.48 5.19 5.19 5.17 5.17 5.16
2.73 2.71 2.69 2.63 2.61 2.60 1.58 1.48 1.47
0.54 0.58 0.64 0.57 1.02 1.00 2.00 0.17 3.00
^{1}H NMR spectrum of 5ac
O
O
OH
2


NB333 F2
194.07 170.04 154.85 137.09 131.33 126.94 124.96 123.61 119.45 117.64 62.92 41.43 17.97
^{13}C NMR spectrum of 5ac
O
O
OH
2



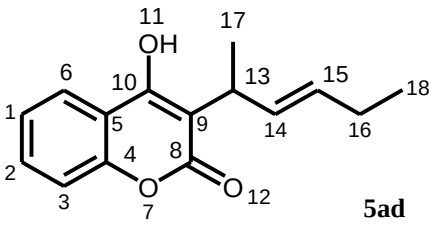
---------- (*E*)-4-Hydroxy-3-(1-methyl-pent-2-enyl)-chromen-2-one 5ad ----------



5ad

Chemical Formula: $C_{15}H_{16}O_3$
Molecular Weight: 244,2857

The compound **5ad** (92.74 mg) is isolated as a yellow solid, starting from **1a** (1 eq, 324 mg, 2 mmol) and **2d** (1422 mg, 10 mmol), in the presence of $In(OTf)_3$ (5 mol%, 56.1 mg, 0.0049 mmol), under reflux of DCE during 5 hours, according to the general protocol **A**. The crude of the reaction is purified by column chromatography (PE/Et_2O:4/1).



5ad

Yield : 19%
5ad : yellow solid
TLC: Rf = 0.45 (PE/Et_2O:1/1)
Mp = 85 °C

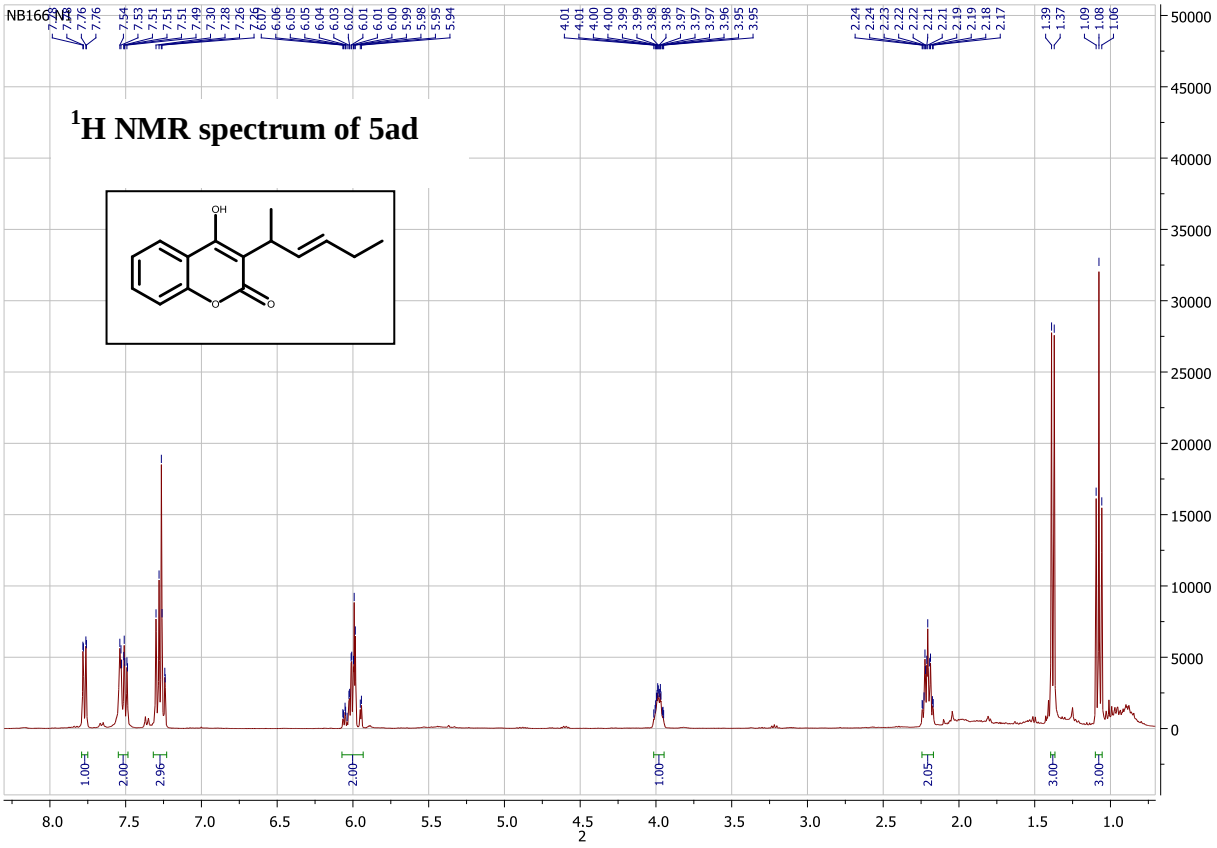
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.78 – 7.76 (dd, *J* = 7.9 Hz, *J* = 1.4 Hz, $1H_6$), 7.54 – 7.49 (m, $2H_{2,3}$), 7.30 – 7.24 (m, H_1) 7.26 (s, $1H_{11}$), 6.07 – 5.94 (m, $2H_{15,14}$), 4.01 – 3.95 (m, $1H_{13}$), 2.24 – 2.17 (m, $2H_{16}$), 1.39 – 1.37 (d, *J* = 7.1 Hz, $3H_{17}$), 1.08 (t, *J* = 7.5 Hz, $3H_{18}$).

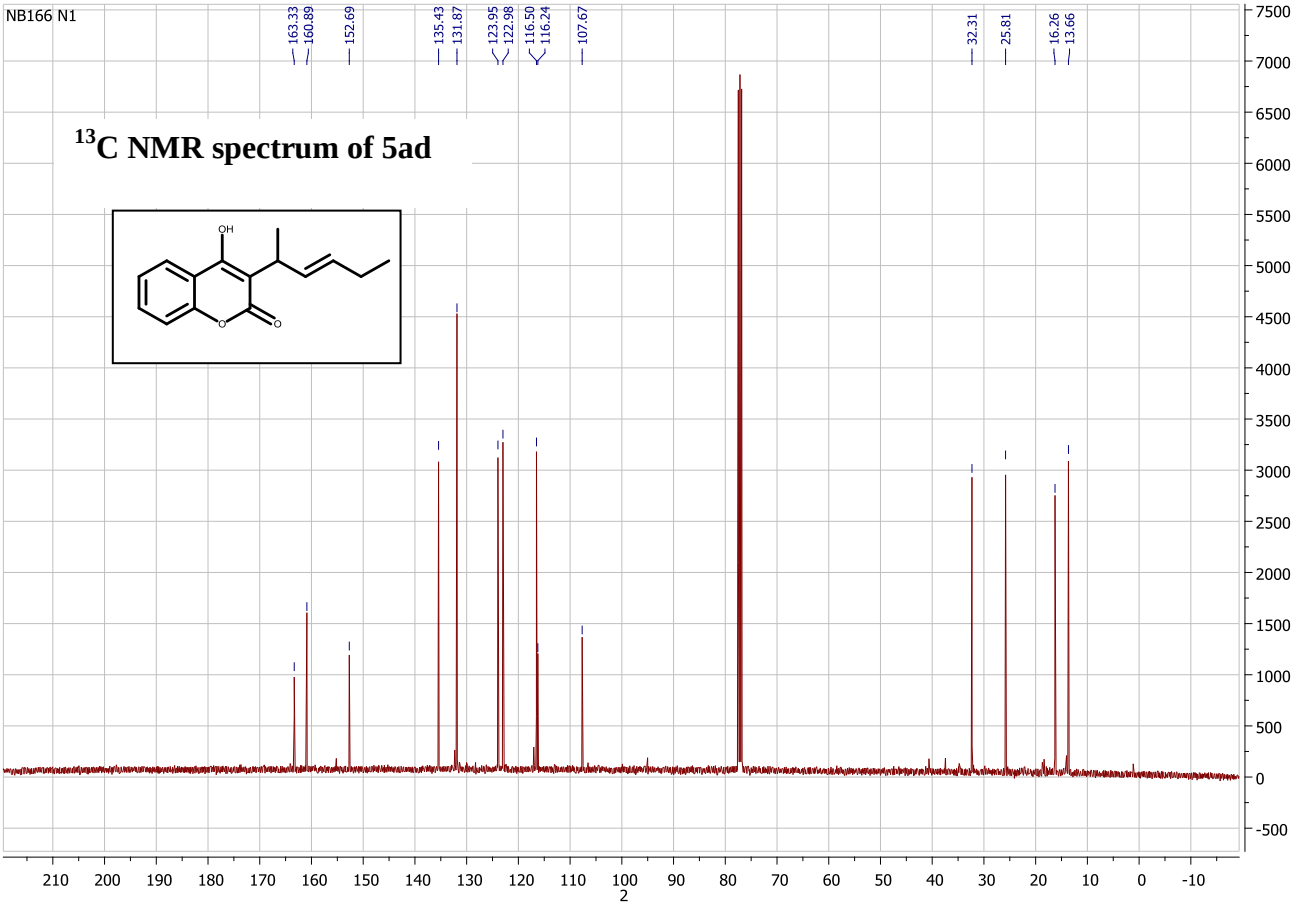
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 163.33 (C8), 160.89 (C10), 152.69 (C4), 135.43 (C14), 131.87 (C2, C15), 123.95 (C1), 122.98 (C6), 116.50 (C3), 116.24 (C5), 107.67 (C9), 32.31 (C13), 25.81 (C16), 16.26 (C17), 13.66 (C18).

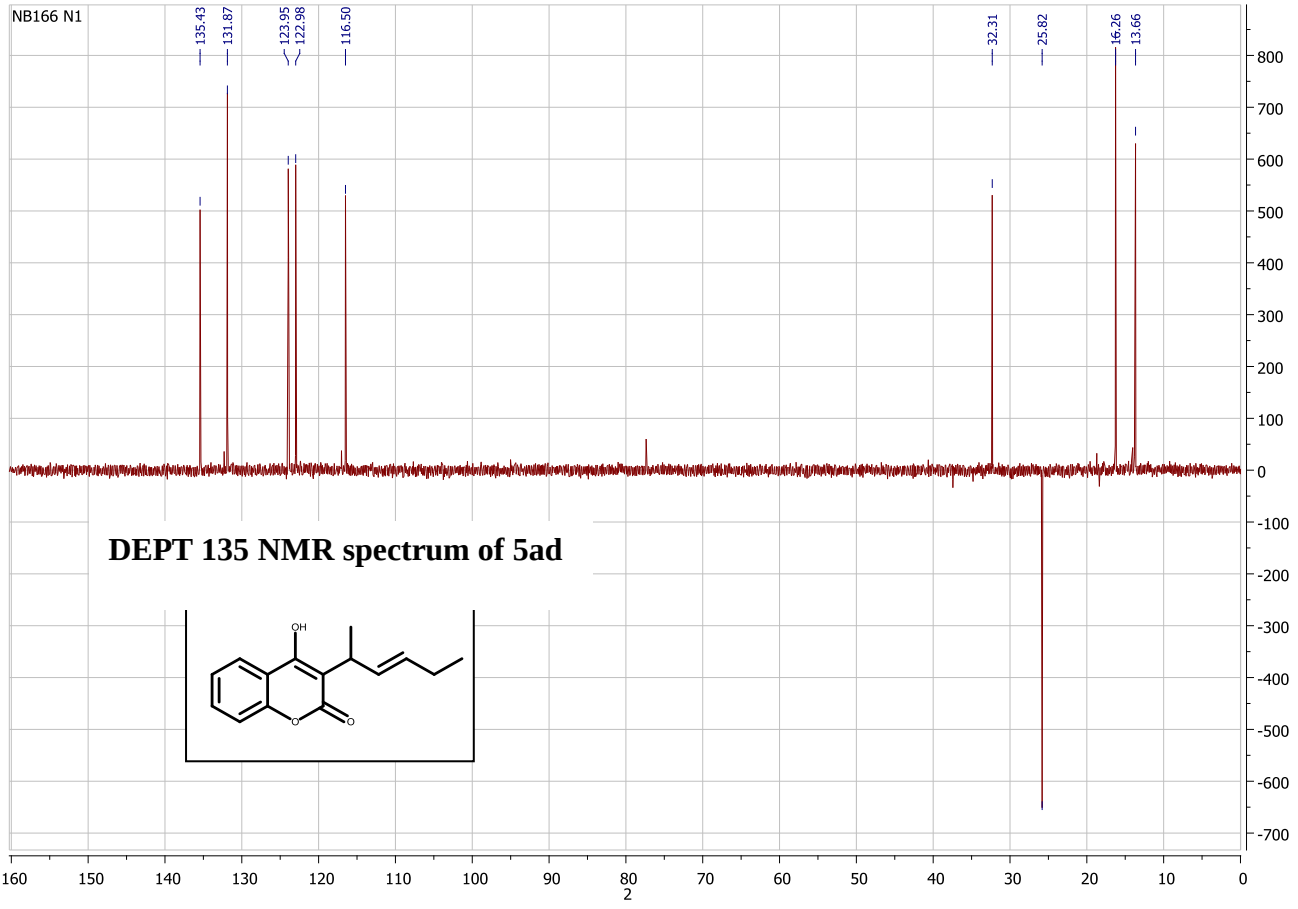
IR (neat): ν_{max} (cm^{-1}) = 3262, 2961, 2931, 2873, 1668, 1608, 1566, 1495, 1454, 1388, 1204, 1152, 1103, 1033, 971, 894, 855, 754, 652, 533, 507, 451, 413, 402.

MS (EI, 70 eV): 244 (36) [$M^{+\cdot}$], 216 (50), 215 (100), 187 (31), 175 (31), 128 (28), 121 (72), 95 (28), 65 (31).

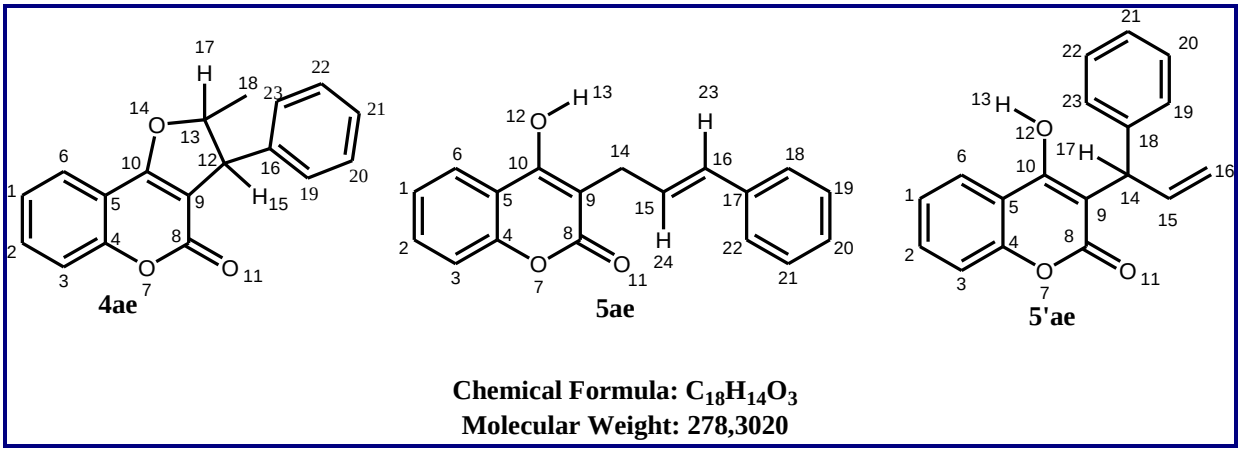
HRMS m/z calcd. For $C_{15}H_{16}O_3$ [$M^{+\cdot}$]: 244.1099, found 244.1152.




NB166 N1
163.33
160.89
152.69
135.43
131.87
123.95
122.98
116.50
116.24
107.67
32.31
25.81
16.26
13.66
^{13}C NMR spectrum of 5ad
OH
O
O

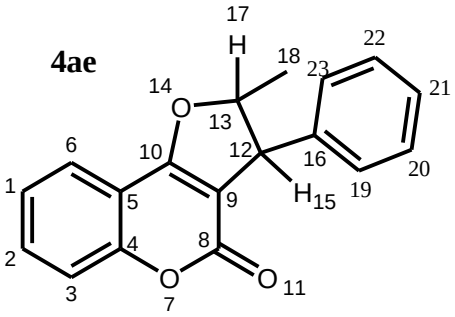

NB166 N1
135.43
131.87
123.95
122.98
116.50
32.31
25.82
16.26
13.66
DEPT 135 NMR spectrum of 5ad
OH
O
O

---------- 2-Methyl-3-phenyl-2,3-dihydro-furo[3,2-*c*]chromen-4-one 4ae ----------
---------- (*E*)-4-Hydroxy-3-(3-phenyl-allyl)-chromen-2-one 5ae ----------
---------- 4-Hydroxy-3-(1-phenyl-allyl)-chromen-2-one 5'ae ----------



Chemical Formula: $C_{18}H_{14}O_3$
Molecular Weight: 278,3020

According to the general protocol **A,** mixture of compounds **4ae**, **5ae** and **5'ae** is obtained after 5 hours of reaction, under reflux of DCE, starting from 4-hydroxycoumarin **1a** (1 eq, 324 mg, 2 mmol), cinnamyl acetate **2e** (1.5 eq, 352 mg, 3 mmol) and $In(OTf)_3$ (5%, 56.1 mg, 0.0049 mmol). The crude of the reaction is purified by column chromatography by eluting with PE/EtOAc:4/1.

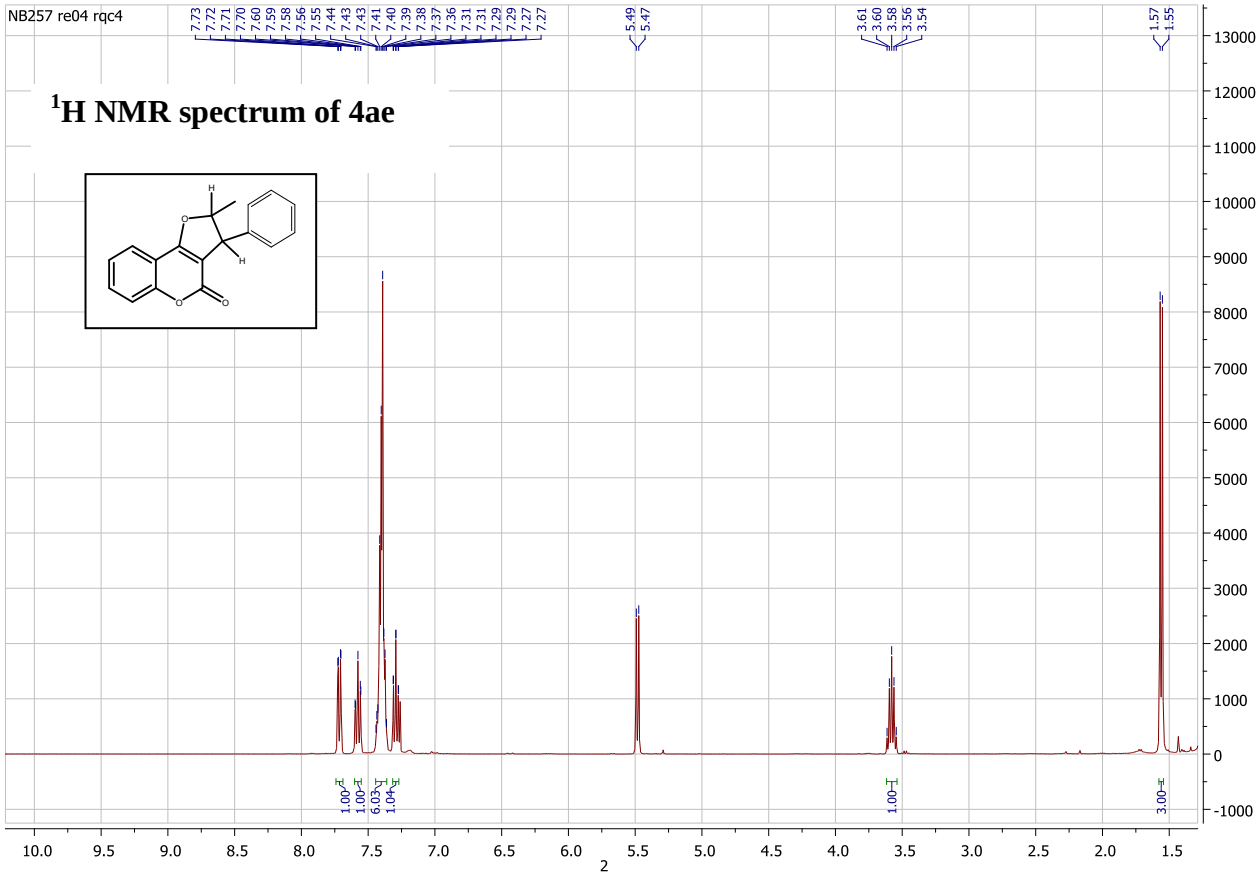


Cas number: 109797-51-5
Yield : 35%
4ae : golden solid
TLC: Rf = 0.62 (PE/EtOAc:1/1)
Mp = 74 °C

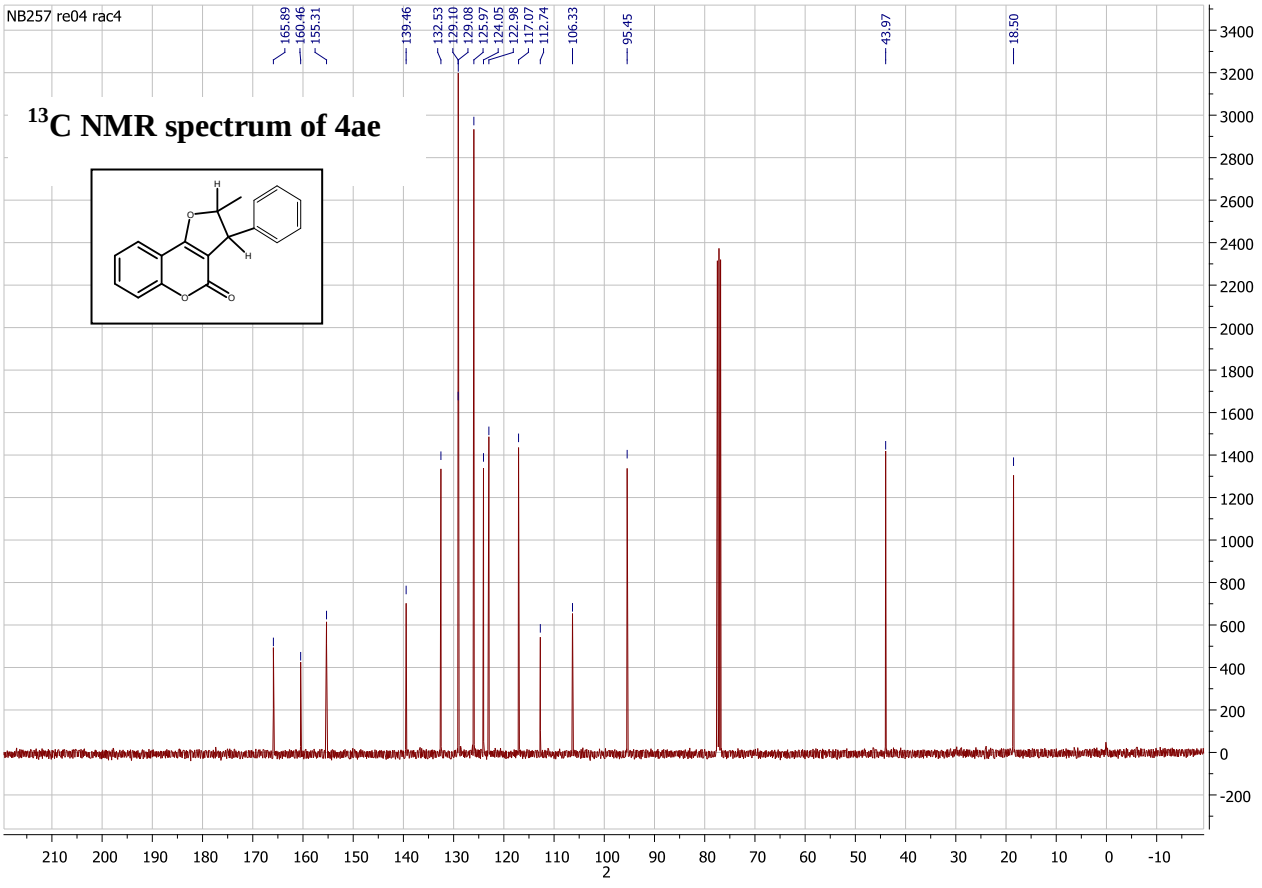
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] : 7.73 – 7.70 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, $1H_6$), 7.60 – 7.55 (ddd, *J* = 8 Hz, *J* = 1.6 Hz, $1H_2$), 7.44 – 7.36 (m, $6H_{22, 23, 21, 3}$), 7.31 – 7.27 (td, *J* = 8 Hz, *J* = 1.2 Hz, $1H_1$), 5.49 – 7.47 (d, *J* = 7.3 Hz, $1H_{17}$), 3.61 – 3.54 (m, $1H_{15}$), 1.57 – 1.55 (d, *J* = 6.8 Hz, $3H_{18}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] : 166.89 (C8), 160.46 (C10), 155.31 (C4), 139.46 (C16), 132.53 (C2), 129.10 (C23), 129.08 (C22), 125.97 (C21), 124.05 (C1), 122.98 (C6), 117.07 (C3), 112.74 (C5), 106.33 (C9), 95.45 (C13), 43.97 (C12), 18.50 (C18).

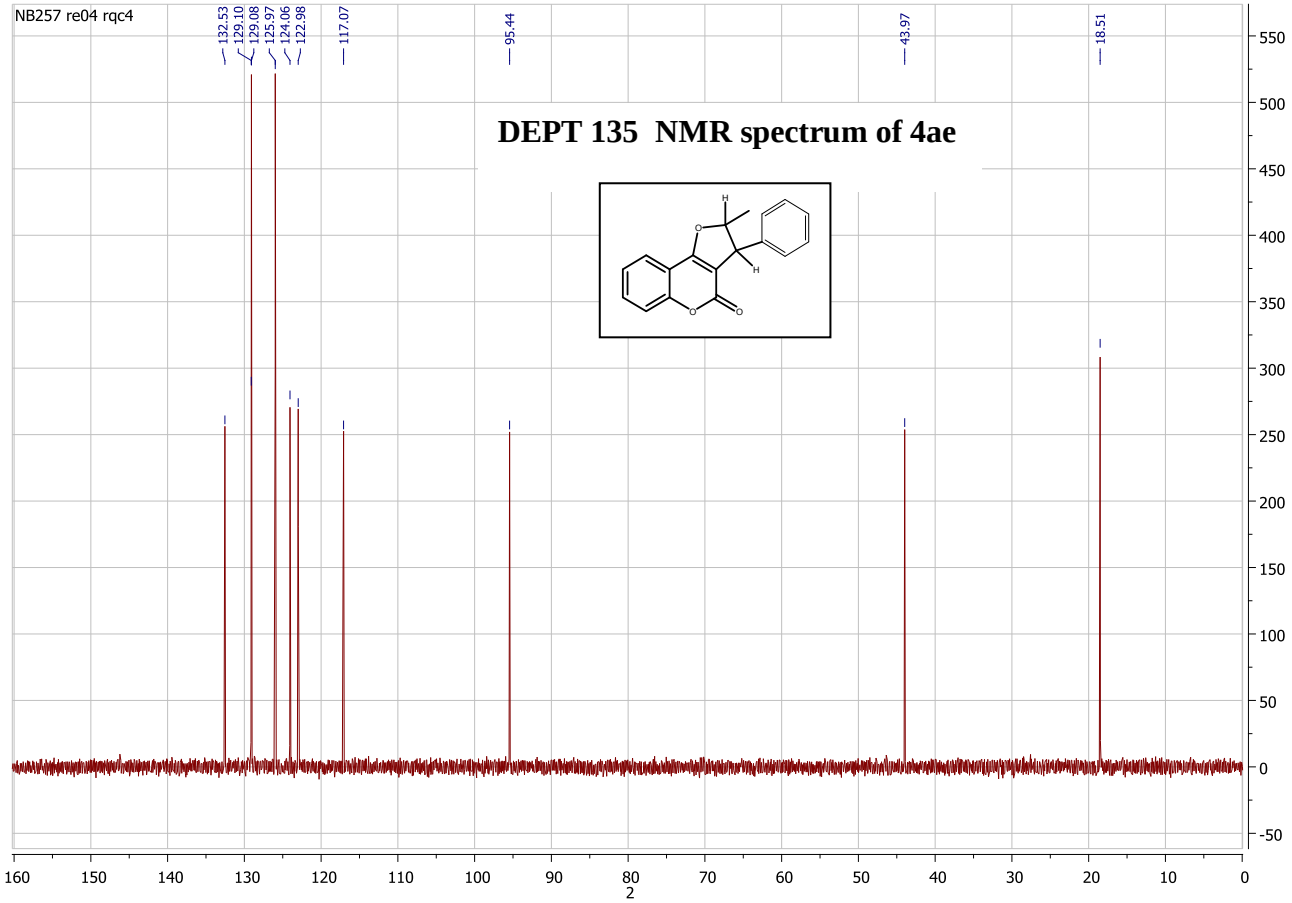
MS (EI, 70 eV): 278 (98) [$M^{+\cdot}$], 263 (49), 187 (31), 158 (82), 129 (31), 121 (100), 92 (27), 77 (28).



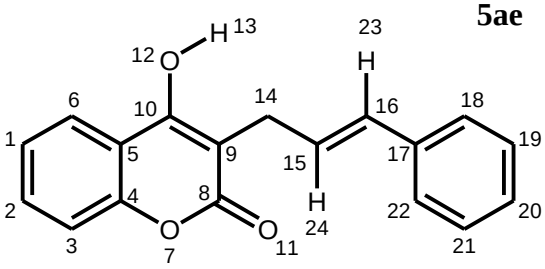
^{1}H NMR spectrum of 4ae



^{13}C NMR spectrum of 4ae



5ae

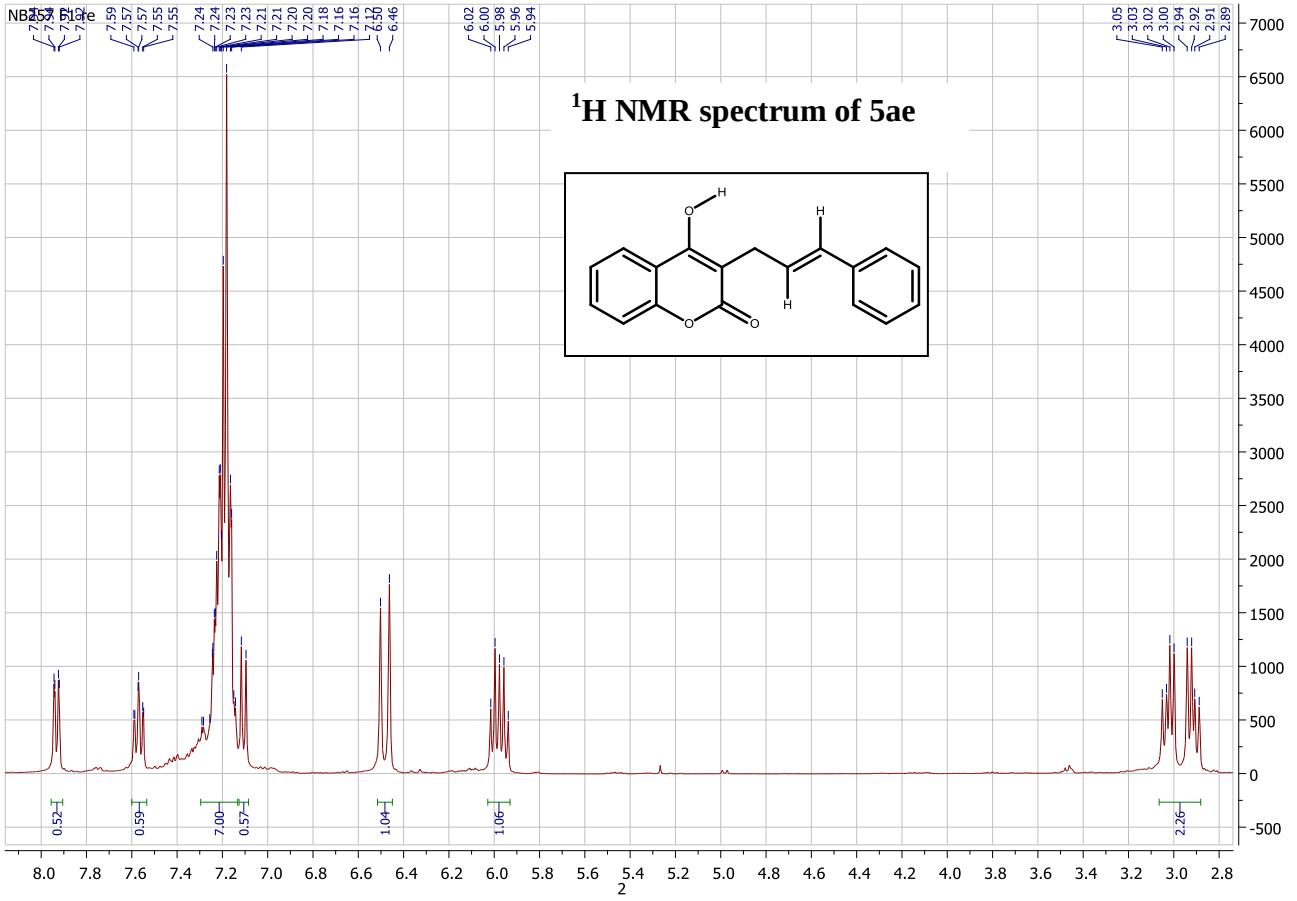


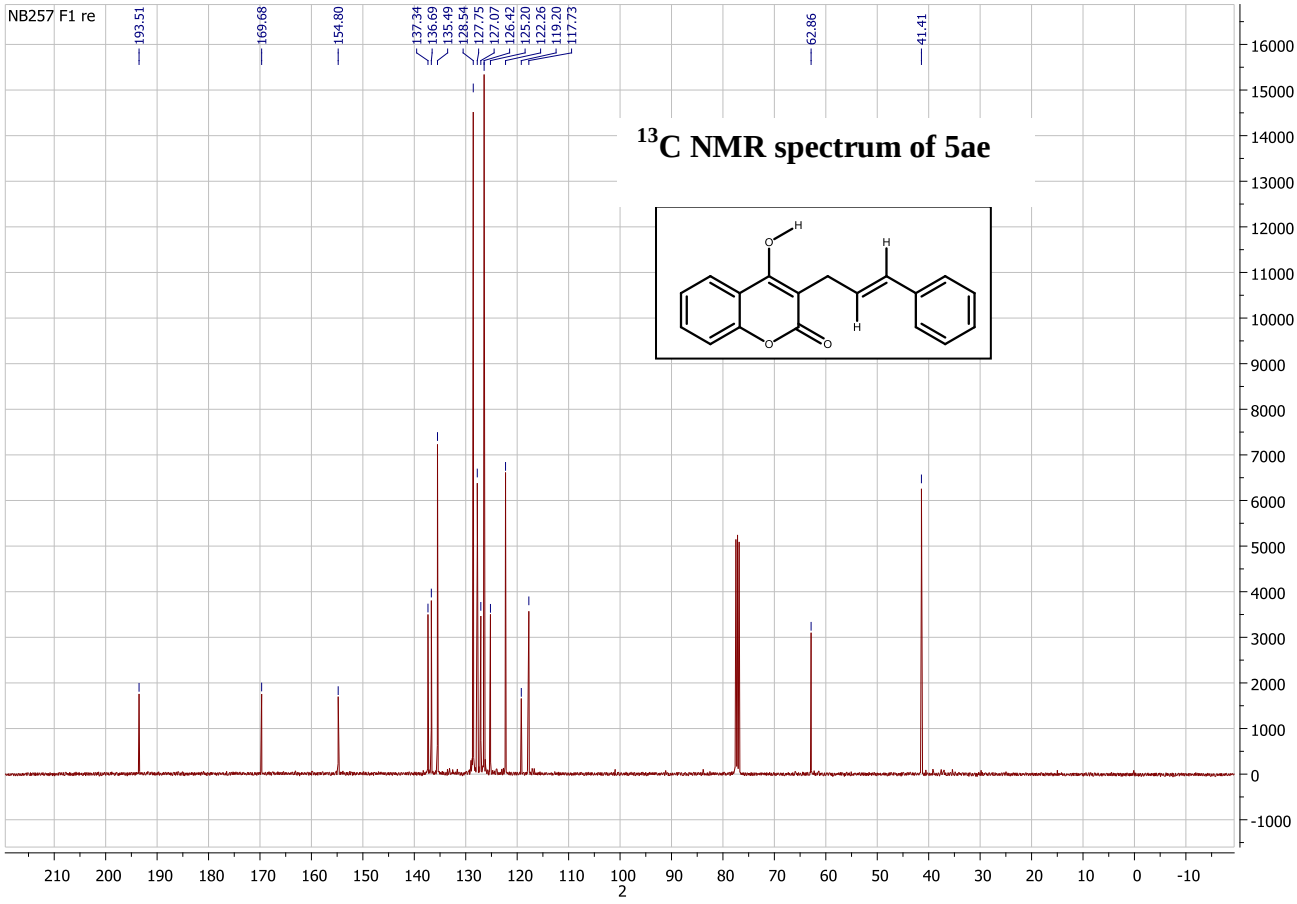
Cas number: 132356-66-2
Yield : 5%
5ae : yellow oil
TLC: Rf = 0.75 (PE/EtOAc:1/1)

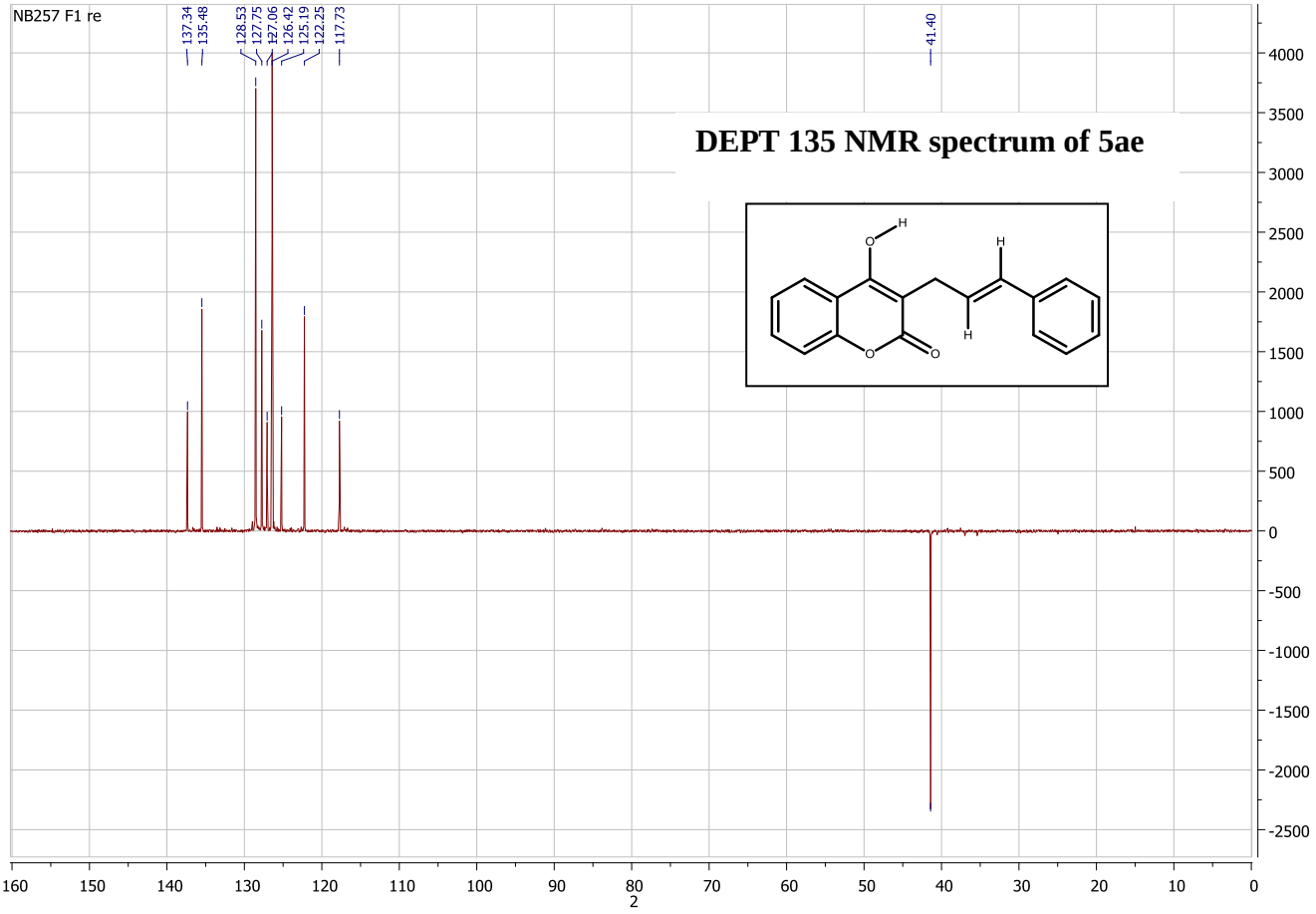
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] : 7.98 – 7.95 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, $1H_2$), 7.63 – 7.58 (m, $1H_6$), 7.29 – 7.18 (m, $7H_{22,\ 21,\ 3,\ 18,\ 19,\ 1,\ 13}$), 7.15 – 7.13 (d, *J* = 8.3 Hz, $1H_{20}$), 6.54 – 6.50 (d, J_E= 15.7 Hz, $1H_{23}$), 6.05 – 5.97 (m, $1H_{24}$), 3.09 – 2.92 (dd, *J* = 13.2 Hz, *J* = 7.6 Hz, $2H_{14}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 193.51 (C8), 169.68 (C10), 154.80 (C4), 137.34 (C16), 136.69 (C17), 135.49 (C2), 128.54 (C18, C22), 127.75 (C20), 127.07 (C15), 126.42 (C19, 21), 125.20 (C1), 122.26 (C6), 119.20 (C5), 117.73 (C3), 62.86 (C9), 41.41 (C14).

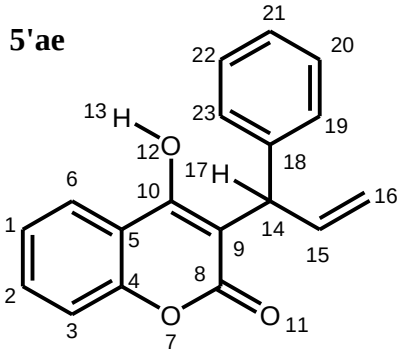
MS (EI, 70 eV): 278 (29) [$M^{+\cdot}$], 219 (33), 176 (53), 157 (16), 117 (100), 91 (81).


NB257 F1re
^{1}H NMR spectrum of 5ae


NB257 F1 re
^{13}C NMR spectrum of 5ae



5'ae

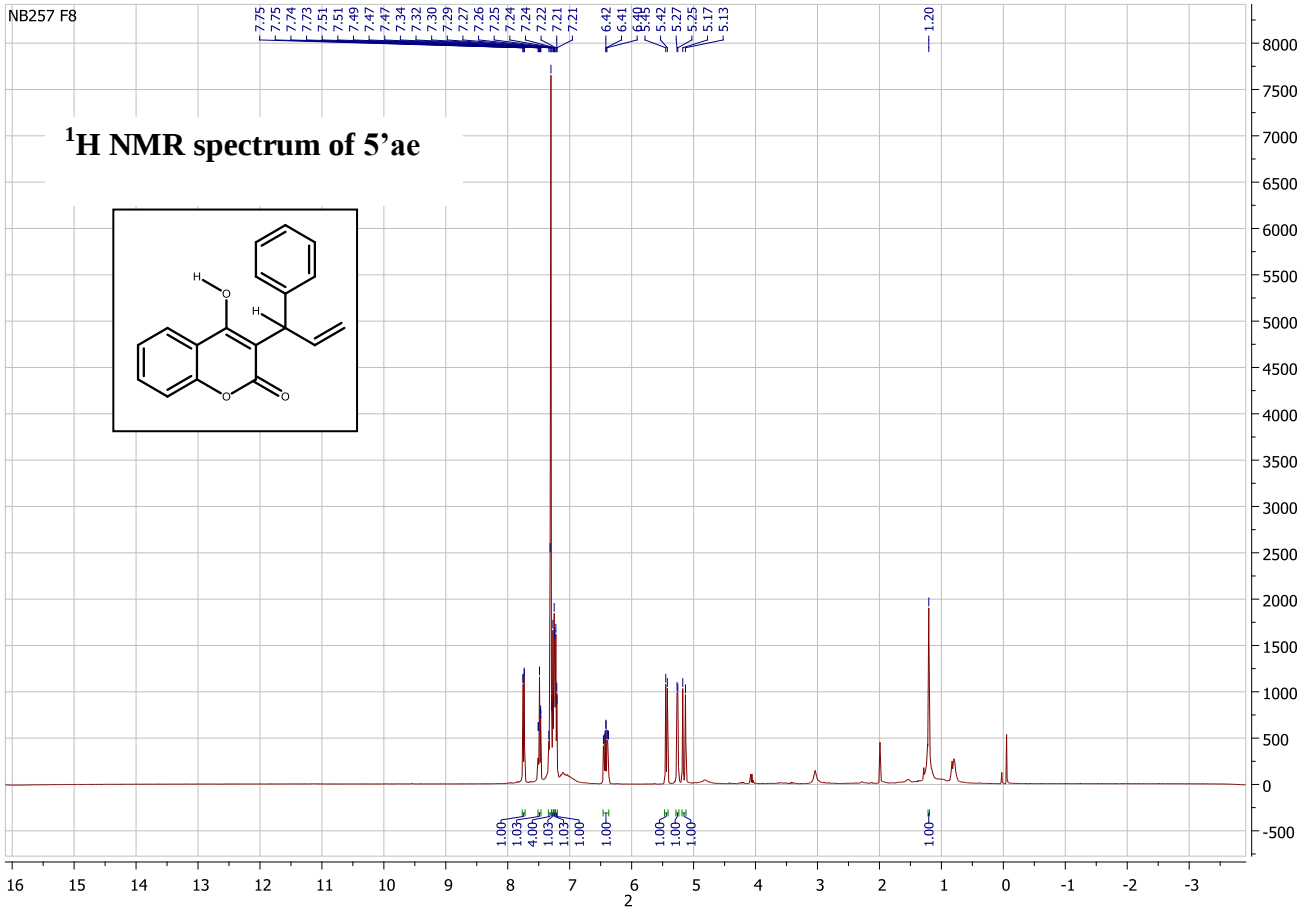


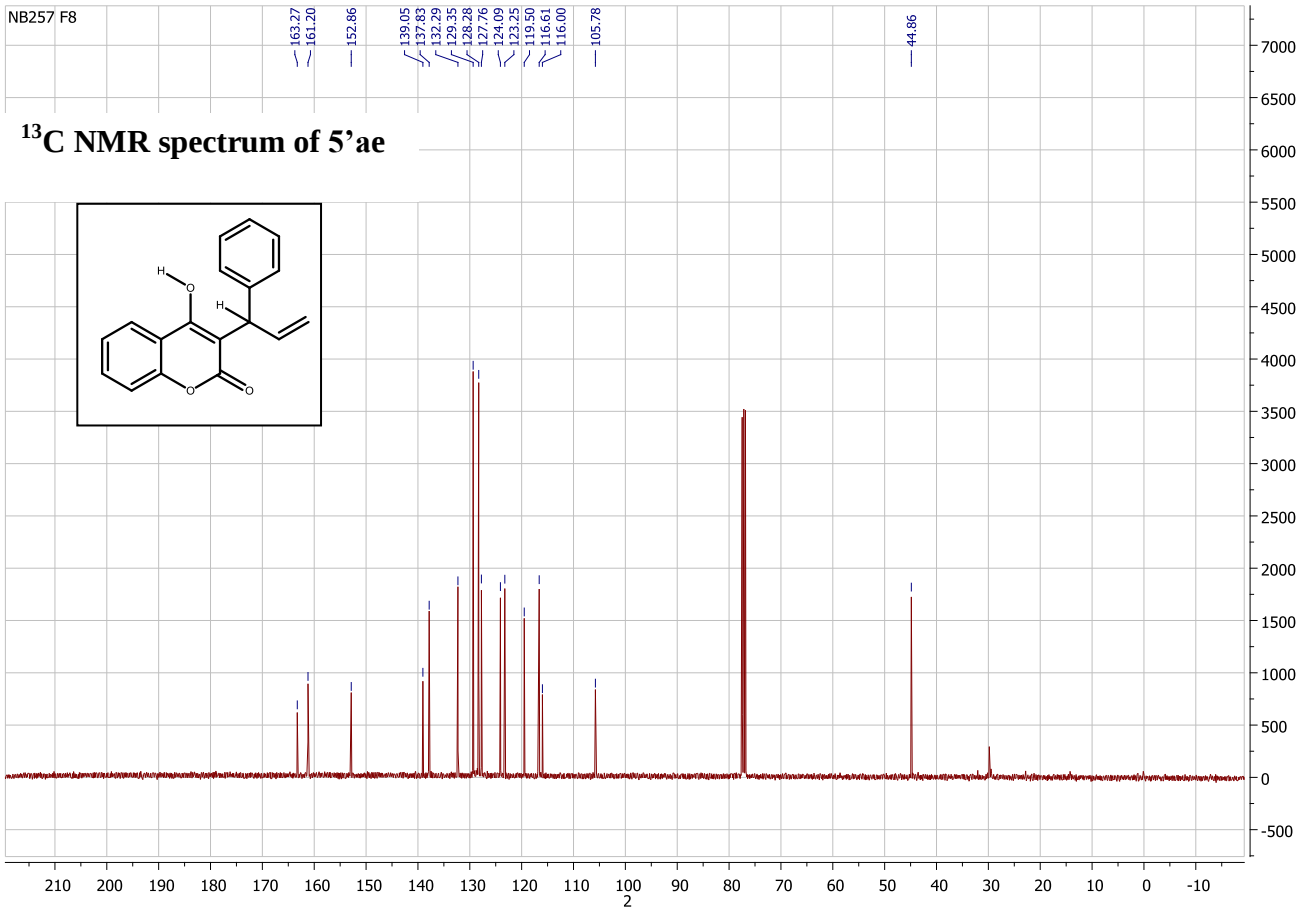
Cas number: 75572-80-4
Yield : 9%
5'ae : yellow oil
TLC: Rf = 0.18 (PE/EtOAc:1/1)

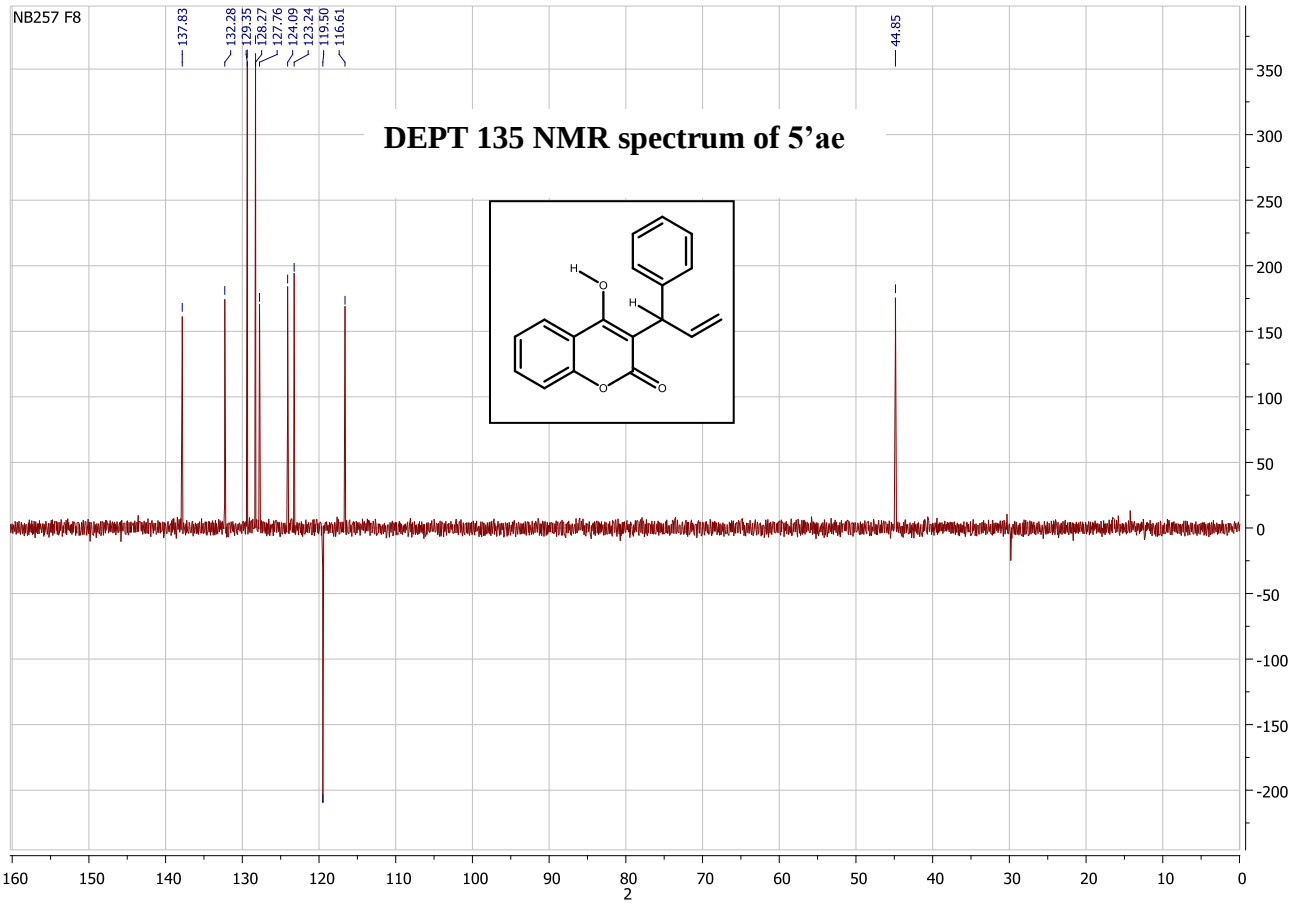
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] : 7.75 – 7.73 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, $1H_2$), 7.51 – 7.47 (td, *J* = 8.4 Hz, *J* = 1.6 Hz, $1H_6$), 7.34 – 7.30 (m, $4H_{23,\ 19,\ 22,\ 20}$), 7.29 – 7.26 (t, *J* = 7.2 Hz, $2H_{21}$), 7.25 – 7.22 (d, *J* = 10.8 Hz, $2H_3$), 7.24 – 7.21 (dd, *J* = 14 Hz, *J* = 1.2 Hz, $1H_1$), 6.46 – 6.37 (ddd, *J* = 10.4 Hz, *J* = 5.6 Hz, *J* = 7.2 Hz, $1H_{15}$), 5.45 – 5.13 (dd, *J* = 10.2 Hz, *J* = 5.3 Hz, $2H_{16}$), 5.27 – 5.25 (d, *J* = 17.5 Hz, $1H_{17}$), 1.20 (s, $1H_{13}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 163.27 (C8), 161.20 (C10), 152.86 (C4), 139.05 (C18), 137.83 (C15), 132.29 (C2), 129.35 (C19, 23), 128.28 (C20, 22), 127.76 (C21), 124.09 (C1), 123.25 (C6), 119.50 (C16), 116.61 (C3), 116.00 (C5), 105.78 (C9), 44.86 (C14).

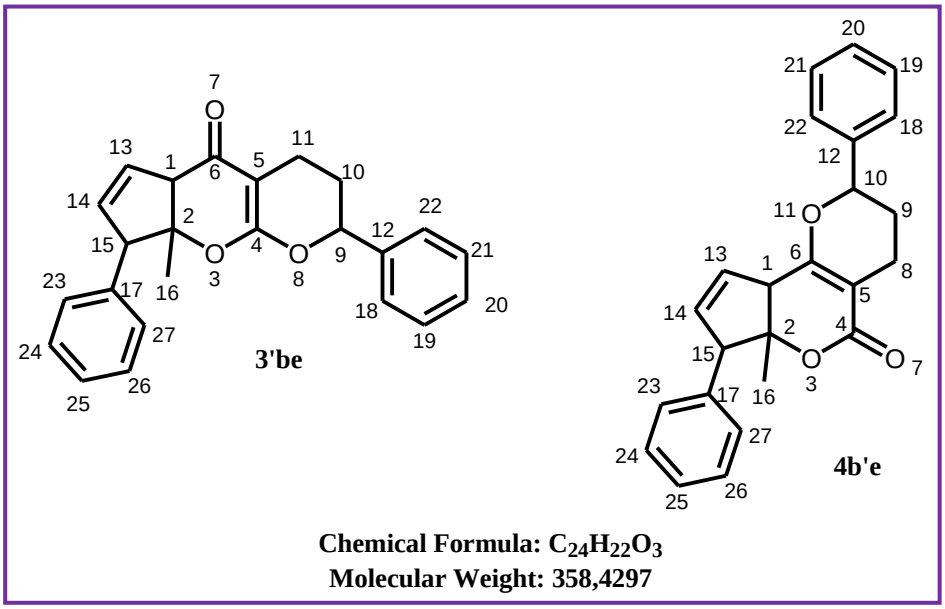
MS (EI, 70 eV): 278 (27) [$M^{+\cdot}$], 187 (56), 104 (100), 92 (26), 78 (32).

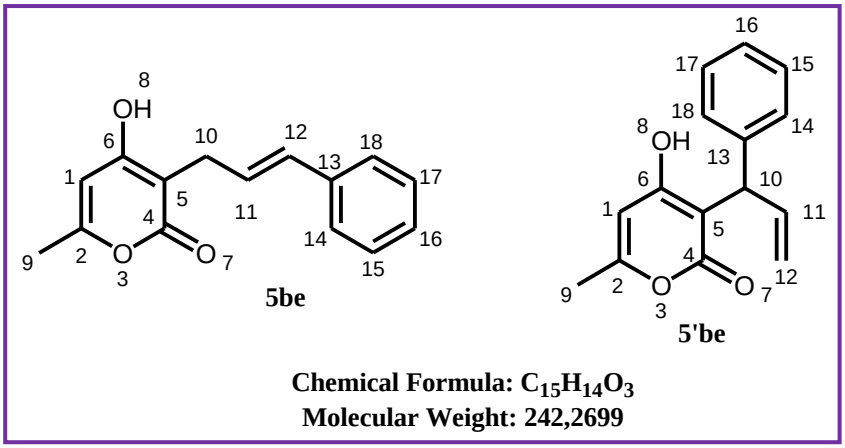

NB257 F8
7.75 7.75 7.74 7.73 7.51 7.51 7.49 7.47 7.47 7.34 7.32 7.30 7.29 7.27 7.26 7.25 7.24 7.24 7.22 7.21 7.21
6.42 6.41 6.40 6.40 5.42 5.27 5.25 5.17 5.13
1.20
1H NMR spectrum of 5’ae
1.00 1.03 4.00 1.03 1.03 1.00 1.00 1.00 1.00 1.00 1.00 1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f2
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


NB257 F8
163.27 161.20 152.86 139.05 137.83 132.29 129.35 128.28 127.76 124.09 123.25 119.50 116.61 116.00 105.78
44.86
13C NMR spectrum of 5’ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f2
7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500



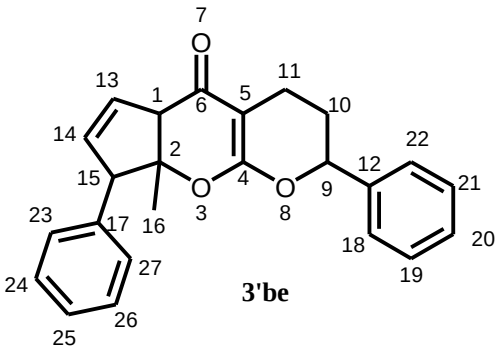
--- 3a-Methyl-3,6-diphenyl-3a,7,8,9a-tetrahydro-3*H*,6*H*-4,5-dioxa-cyclopenta[*b*]naphthalen-9-one 3'be ---
---- 3a-Methyl-3,8-diphenyl-3,3a,6,7,8,9b-hexahydro-4,9-dioxa-cyclopenta[*a*]naphthalen-5-one 4'be ----
---------- (*E*)-4-Hydroxy-6-methyl-3-(3-phenyl-allyl)-pyran-2-one 5be ----------
---------- 4-Hydroxy-6-methyl-3-(1-phenyl-allyl)-pyran-2-one 5'be ----------





Chemical Formula: $C_{15}H_{14}O_3$
Molecular Weight: 242,2699

According to the general protocol **A,** β-ketolactone **1b** (1 eq, 252 mg, 2 mmol) reacts with allyl acetate **2e** (5 eq, 1762.2 mg, 10 mmol), in the presence of $In(OTf)_3$ (5 mol%, 56.1 mg, 0.1 mmol), under reflux of DCE for 7 hours. A mixture of compounds **3'be**, **4b'e**, **5be** and **5'be** is isolated. The purification is performed by flash chromatography (PE/EtOAc:4/1).



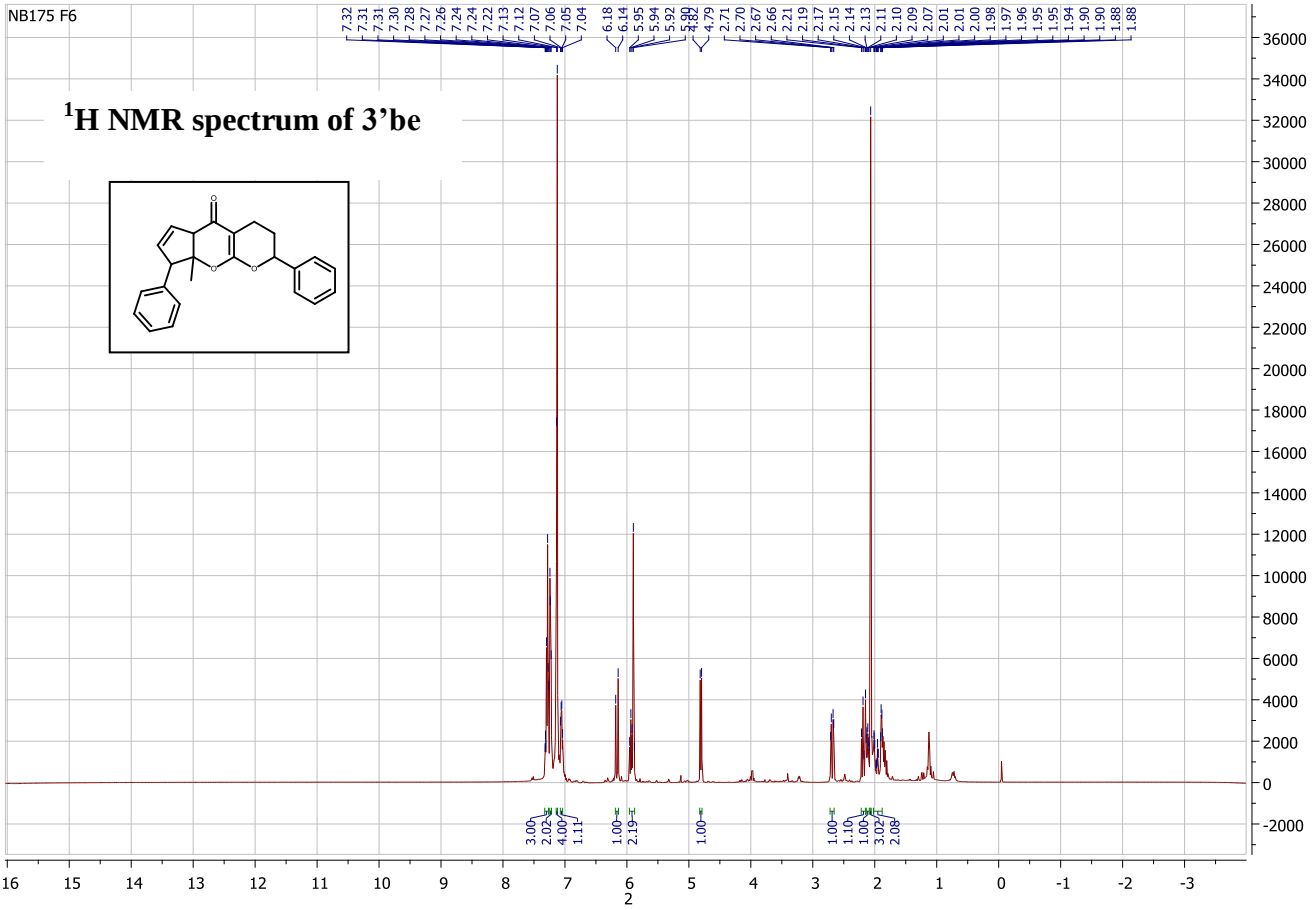
Yield : 8%
3'be : yellow solid
TLC: Rf = 0.4 (PE/EtOAc:2/3)
Mp = 68 °C

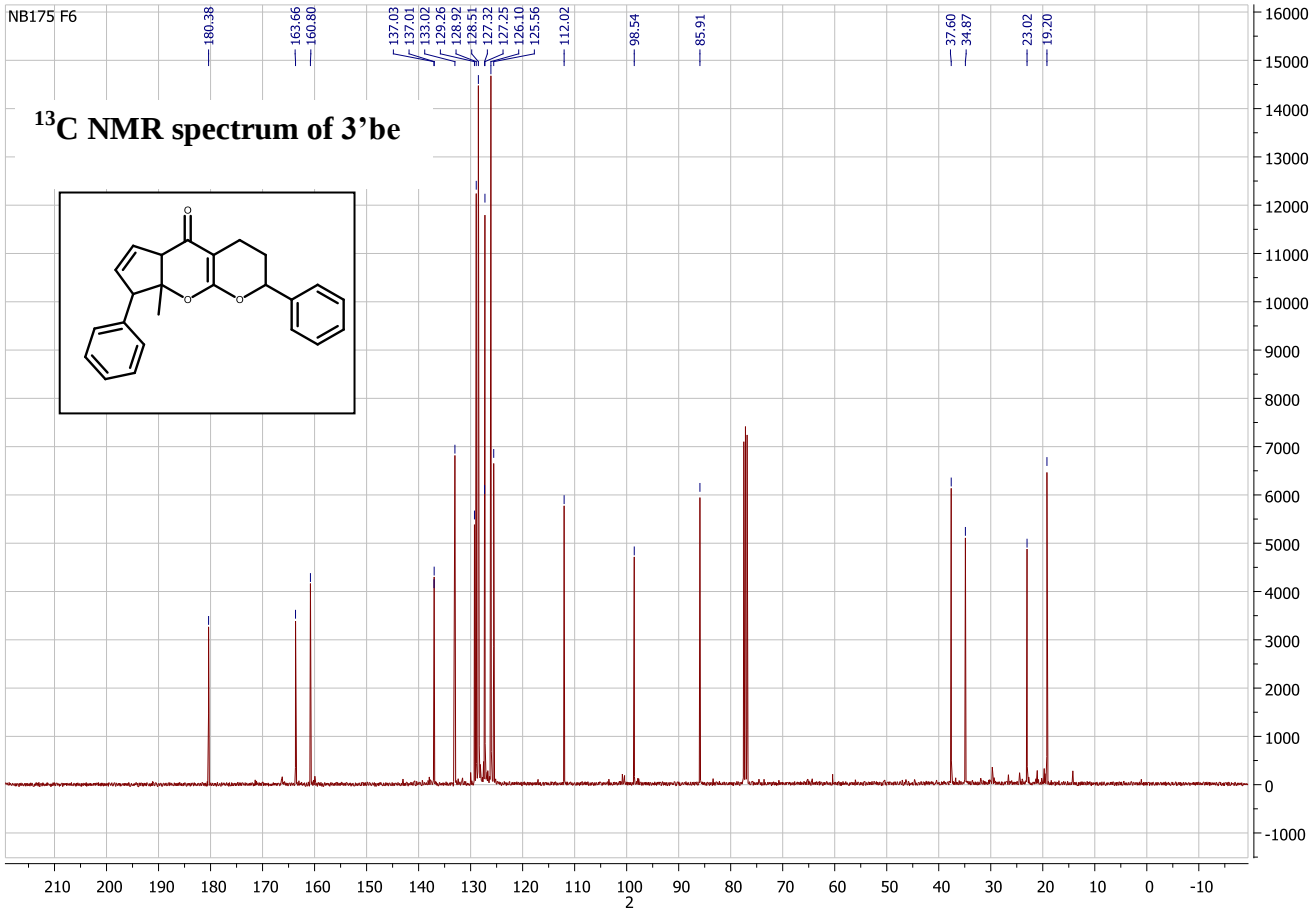
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.32 – 7.27 (m, $3H_{23, 27, 25}$), 7.24 – 7.22 (m, $2H_{19, 21}$), 7.13 – 7.12 (m, $4H_{18, 22, 24, 26}$), 7.08 – 7.04 (m, $1H_{20}$), 6.18 – 6.14 (d, *J* = 16 Hz, $1H_{14}$), 5.95 – 5.88 (m, $2H_{9, 13}$), 4.82 – 4.79 (d, *J* = 8.9 Hz, $1H_{15}$), 2.71 – 2.15 (m, $1H_{11}$), 2.14 – 2.09 (m, $1H_1$), 2.07 (s, $3H_{16}$), 2.01 – 1.88 (m, $2H_{10}$).

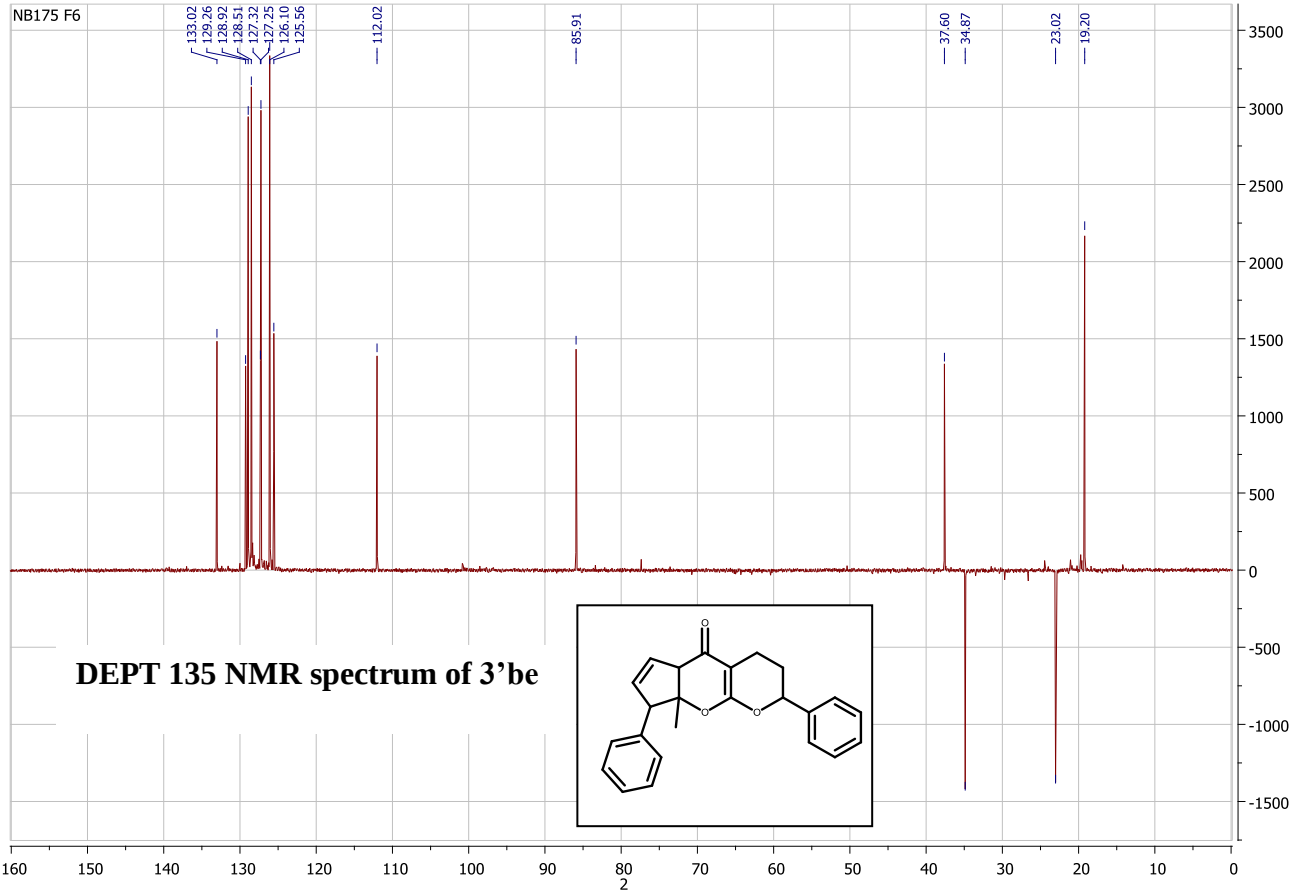
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 180.38 (C6), 163.66 (C4), 160.80 (C12), 137.03 (C17), 137.01 (C5), 133.02 (C14), 129.26 (C20), 128.92 (C24, 26), 128.51 (C19, 21), 127.32 (C25), 127.25 (C18, 22), 126.10 (C23, 27), 125.56 (C13), 112.02 (C9), 98.54 (C2), 85.91 (C15), 37.60 (C1), 34.87 (C10), 23.02 (C11), 19.20 (C16).

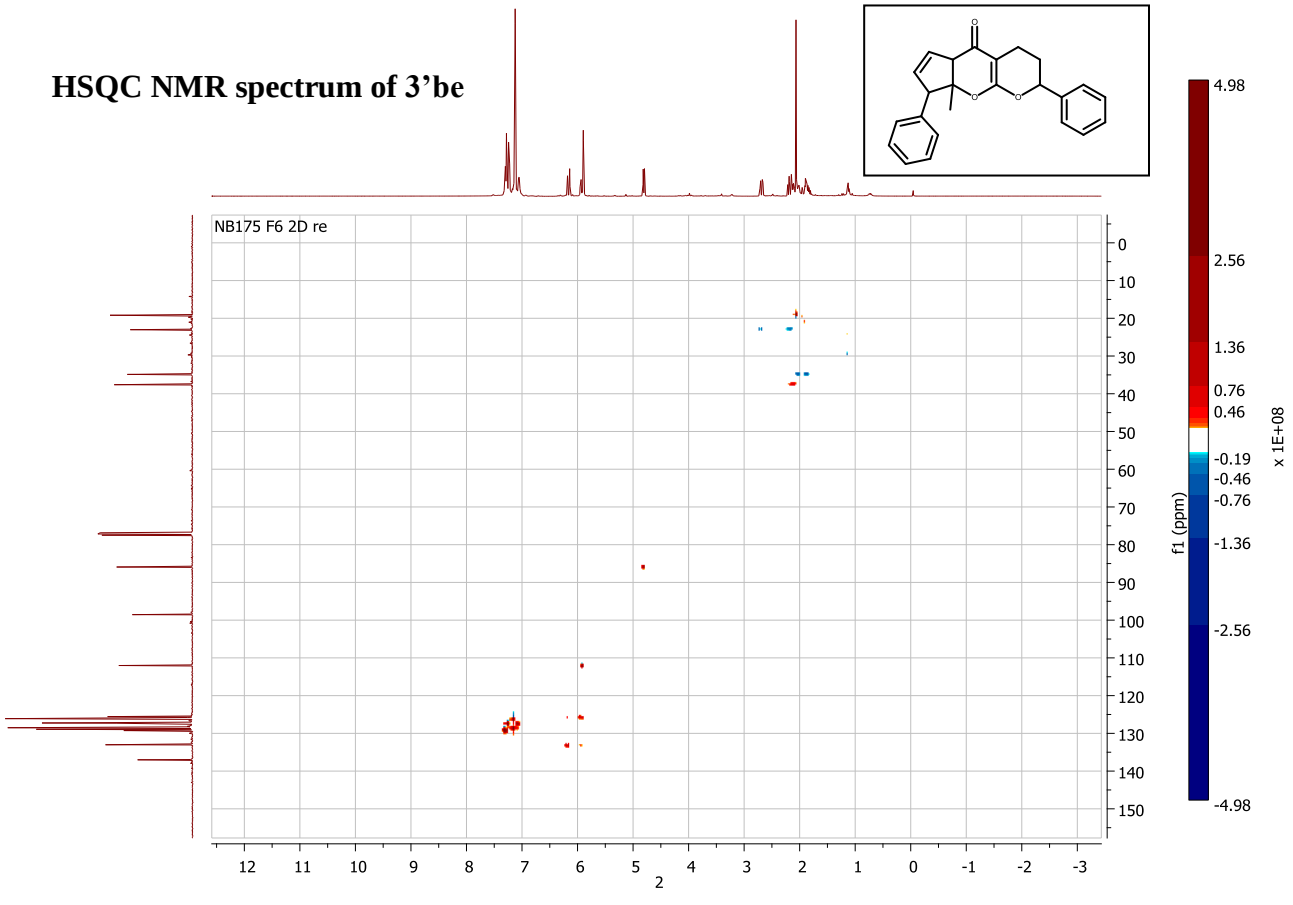
MS (EI, 70 eV): 358 (1) [$M^{+\cdot}$], 241 (27), 219 (22), 157 (59), 140 (72), 129 (21), 117 (100), 91 (64), 44 (39).

HRMS m/z calcd. For $C_{24}H_{22}O_3$ [$M^{+\cdot}$]: 358.1569, found 358.1615.

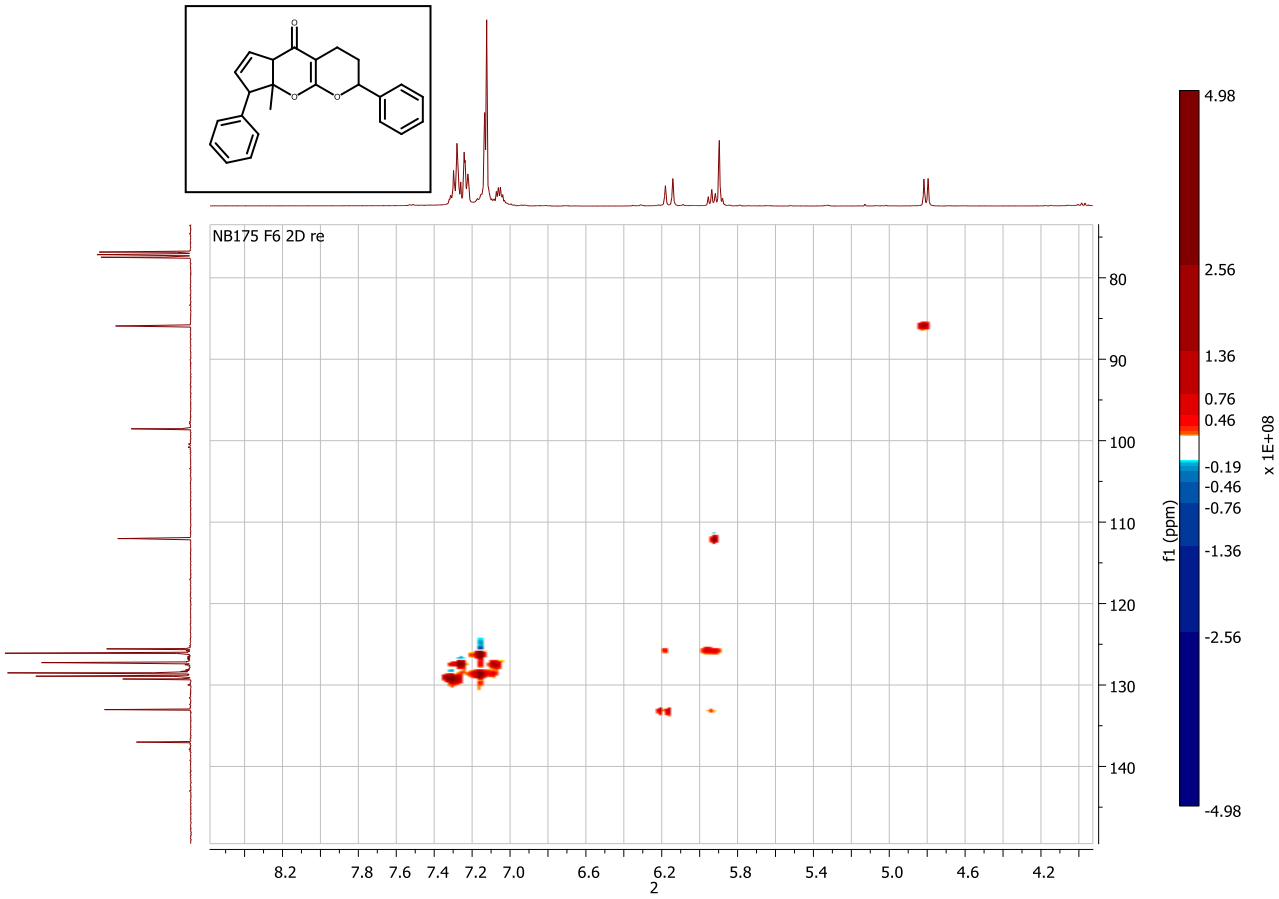

NB175 F6
^{1}H NMR spectrum of 3'be

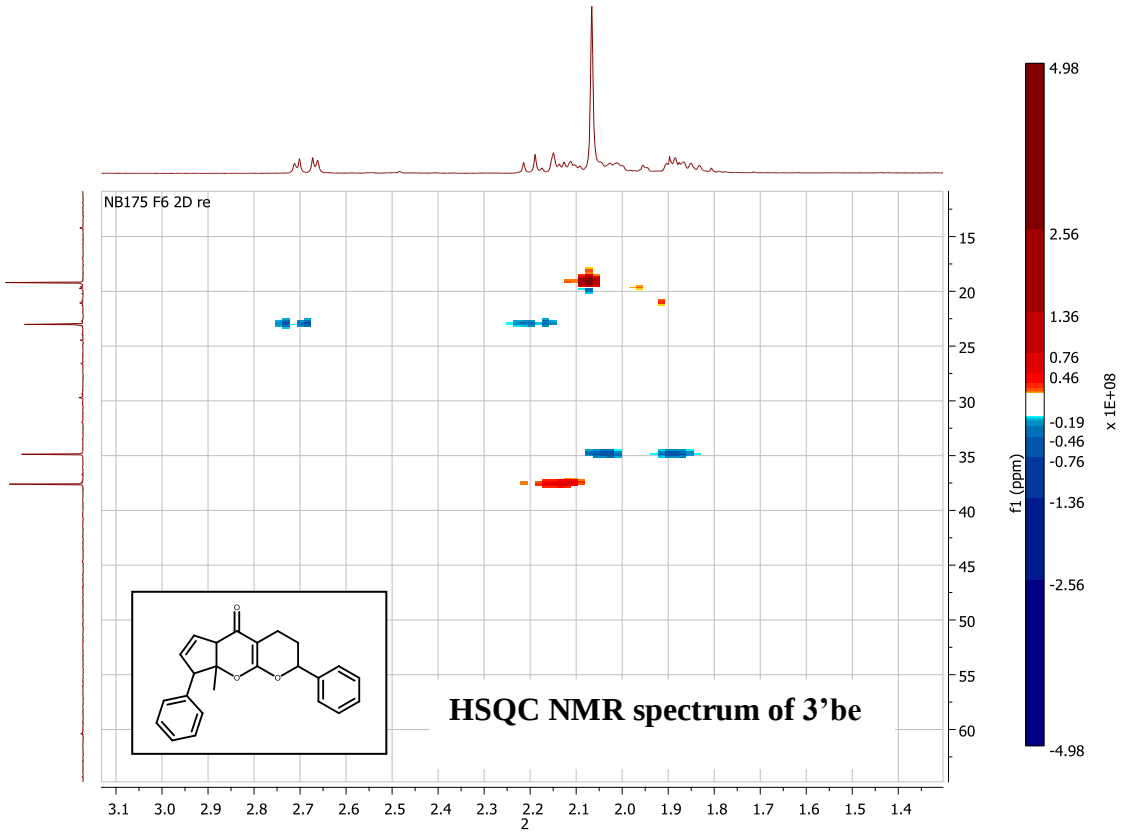

NB175 F6
^{13}C NMR spectrum of 3'be


NB175 F6
133.02
129.26
128.92
128.51
127.32
127.25
126.10
125.56
112.02
85.91
37.60
34.87
23.02
19.20
DEPT 135 NMR spectrum of 3’be

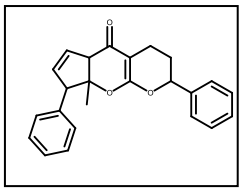

HSQC NMR spectrum of 3’be
NB175 F6 2D re
f1 (ppm)
x 1E+08

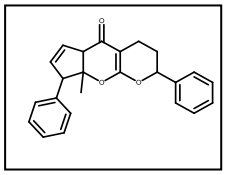
HSQC NMR spectrum of 3’be



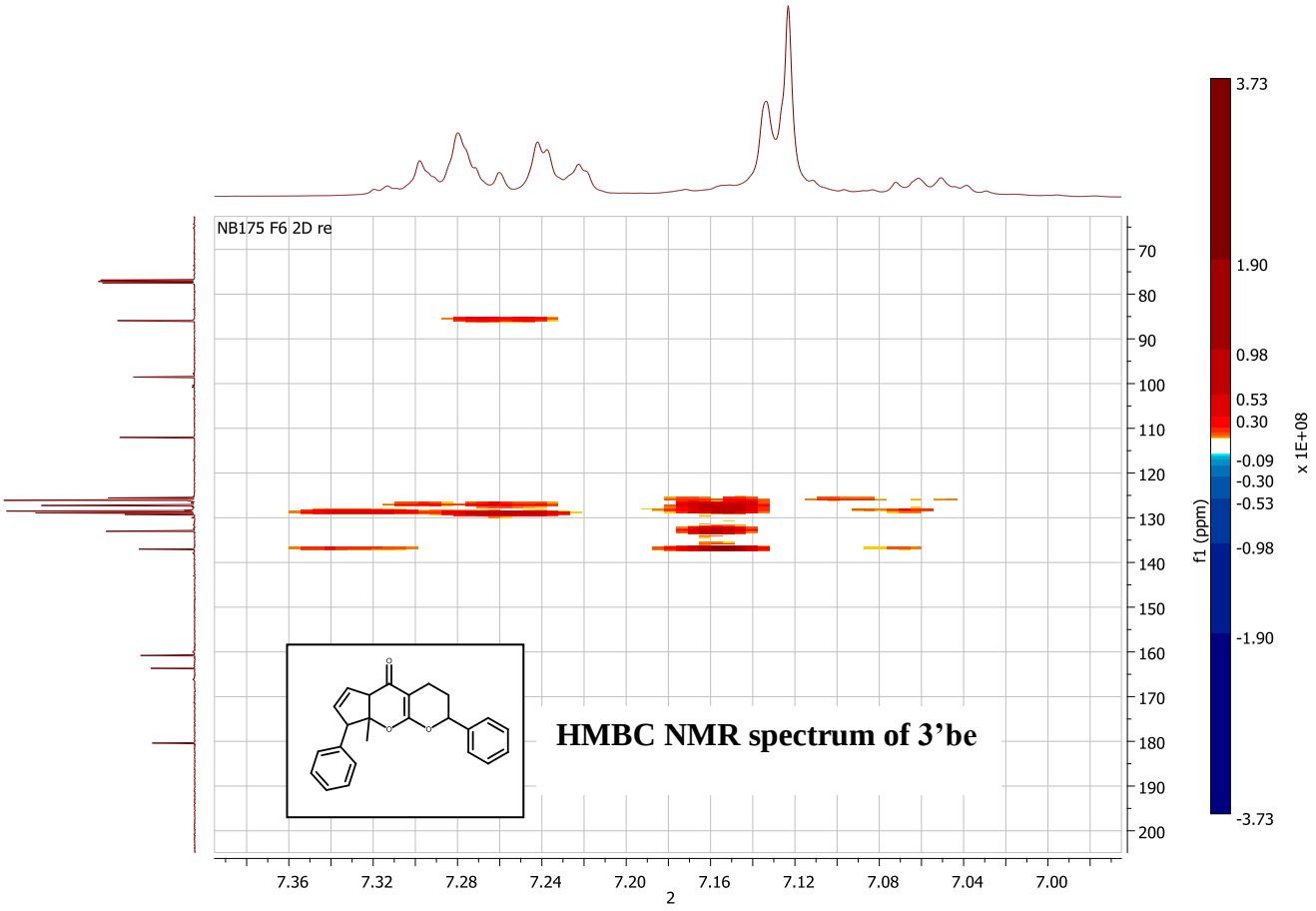


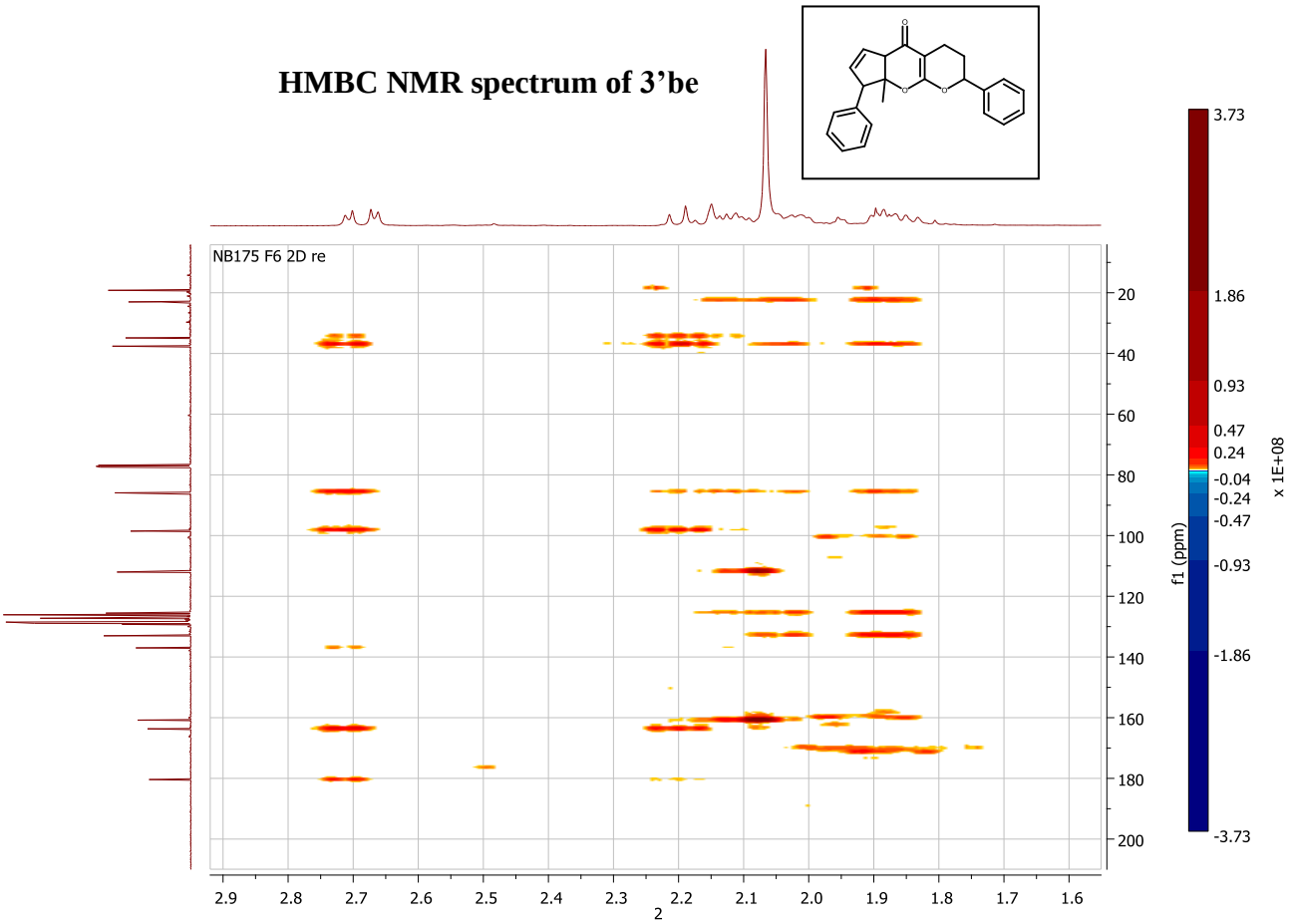
HMBC NMR spectrum of 3’be

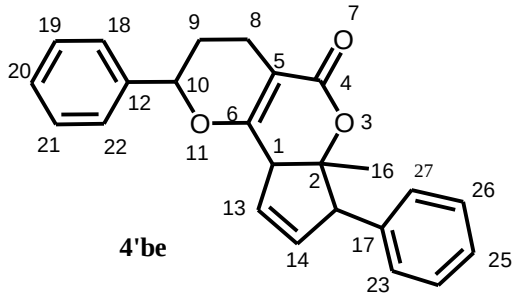




HMBC NMR spectrum of 3’be


NB175 F6 2D re
HMBC NMR spectrum of 3’be
f1 (ppm)
x 1E+08
3.73
1.90
0.98
0.53
0.30
-0.09
-0.30
-0.53
-0.98
-1.90
-3.73
7.36
7.32
7.28
7.24
7.20
7.16
7.12
7.08
7.04
7.00
2


HMBC NMR spectrum of 3’be
NB175 F6 2D re
f1 (ppm)
x 1E+08
3.73
1.86
0.93
0.47
0.24
-0.04
-0.24
-0.47
-0.93
-1.86
-3.73
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
2



4'be

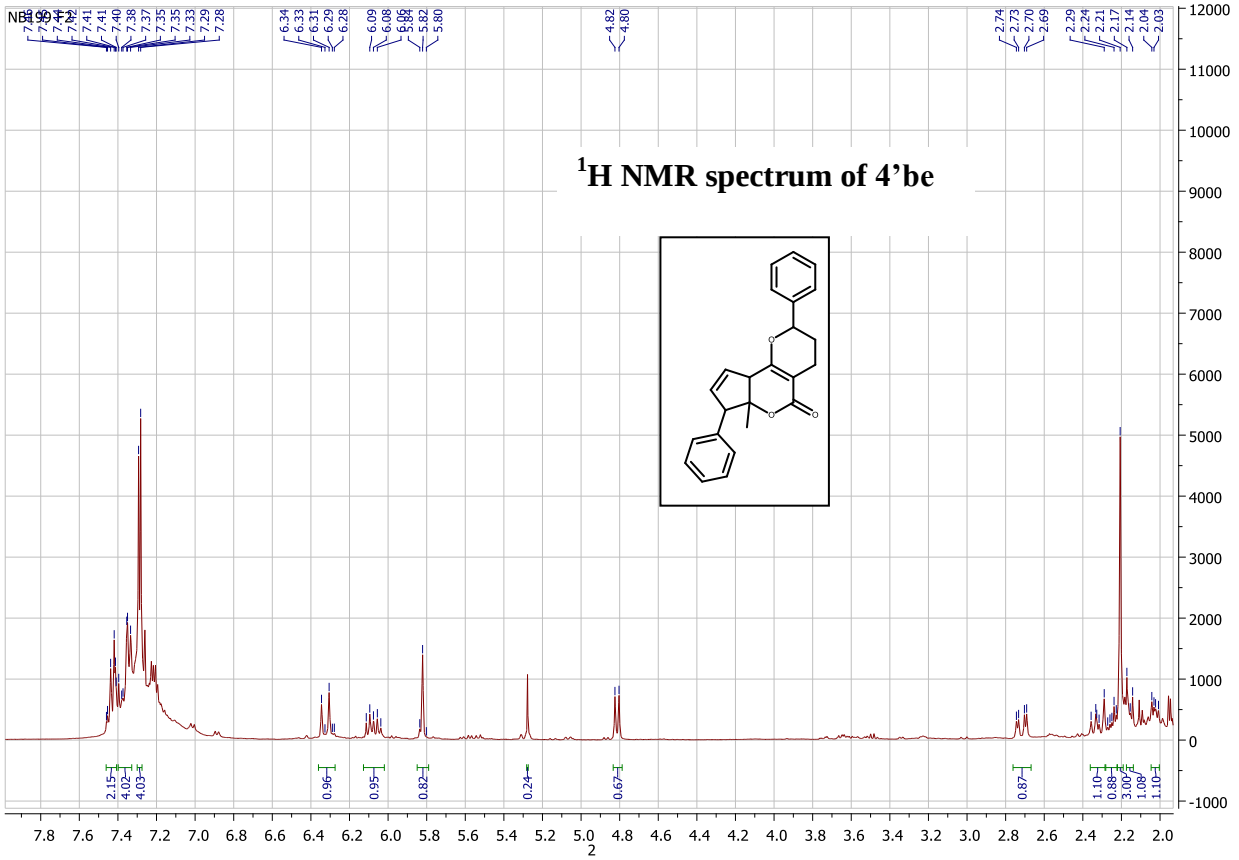
Yield : 18%
4'be : yellow solid
TLC: Rf = 0.31 (PE/EtOAc:2/3)
Mp = 80 °C

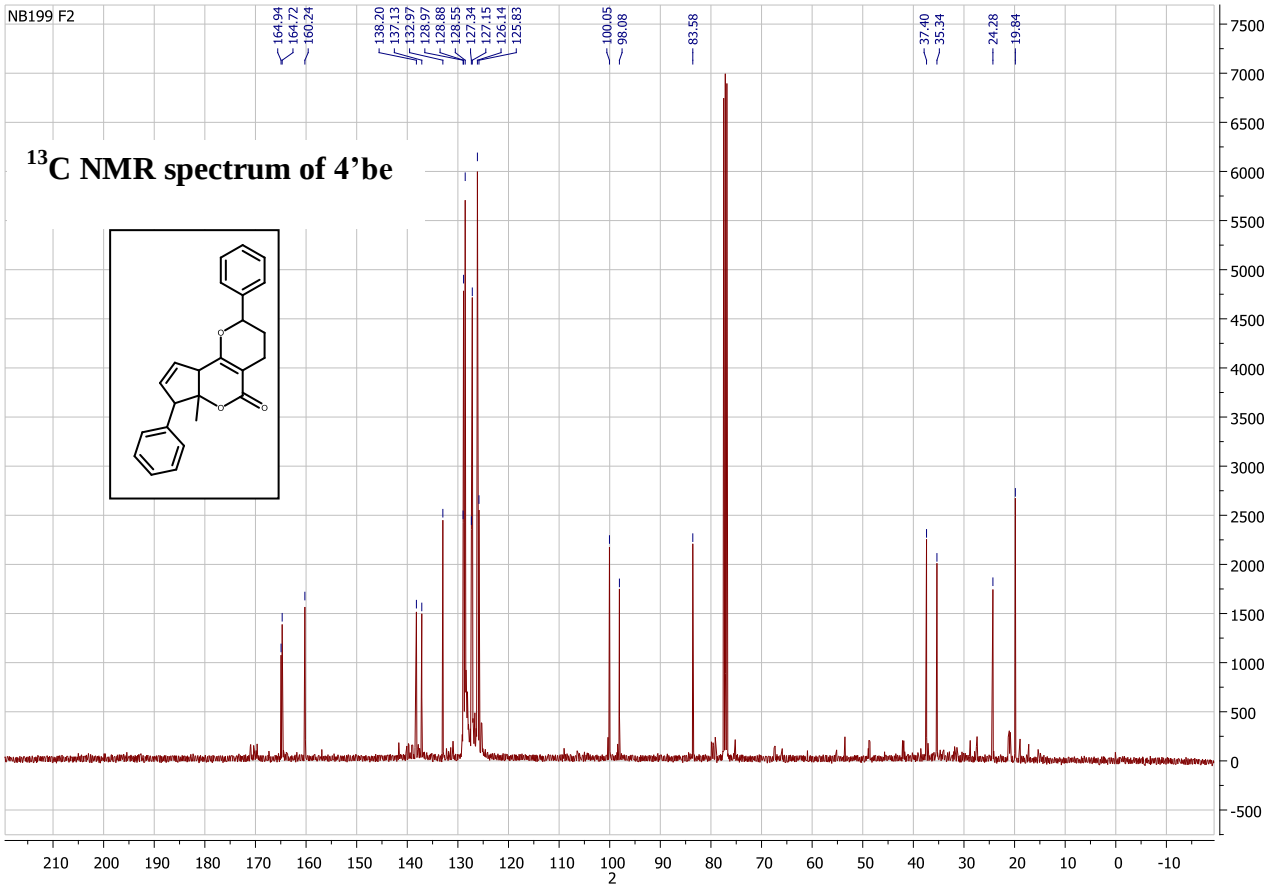
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.46 – 7.41 (m, $2H_{23, 27}$), 7.40 – 7.33 (m, $4H_{19, 21, 24, 26}$), 7.29 – 7.28 (m, $2H_{18, 22, 20, 25}$), 6.34 – 6.28 (m, $1H_{13}$), 6.11 – 6.04 (m, $1H_{14}$), 5.82 (t, *J* = 8 Hz, $1H_{10}$), 4.82-4.80 (d, *J* = 8.4 Hz, $1H_{15}$), 2.74 – 2.29 (m, $2H_8$), 2.27 – 2.23 (m, $1H_1$), 2.21 (s, $3H_{16}$), 2.17 – 2.01 (m, $2H_9$).

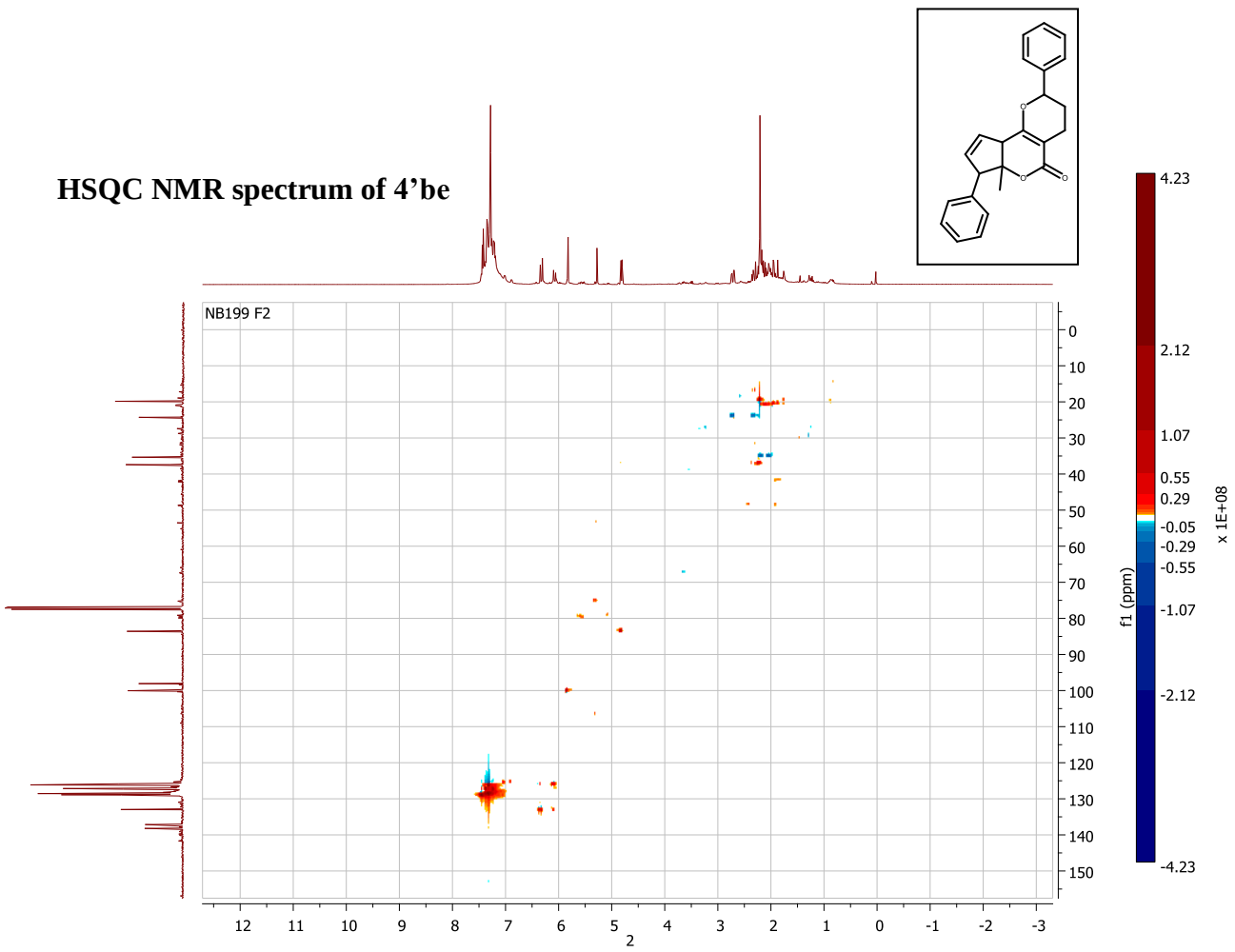
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 164.94 (C6), 164.72 (C4), 160.24 (C12), 138.20 (C17), 137.13 (C5), 132.97 (C14), 128.97 (C20), 128.88 (C24, 26), 128.55 (C19, 21), 127.34 (C25), 127.15 (C18, 22), 126.14 (C23, 27), 125.83 (C13), 100.05 (C10), 98.08 (C2), 83.58 (C15), 37.40 (C1), 35.34 (C9), 24.28 (C8), 19.84 (C16).

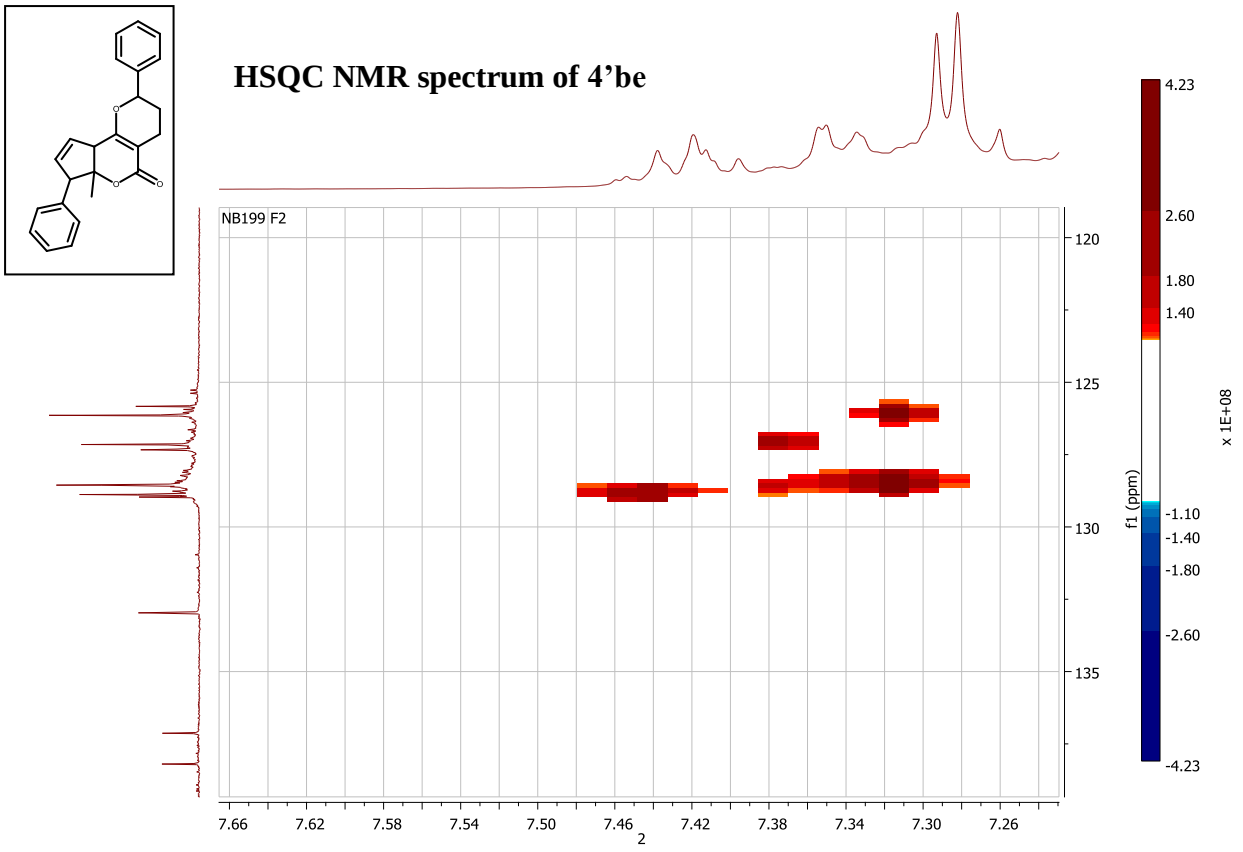
MS (EI, 70 eV): 358 (3) [$M^{+\cdot}$], 281 (3), 267 (5), 219 (6), 207 (12), 129 (16), 117 (14), 91 (16), 44 (100).

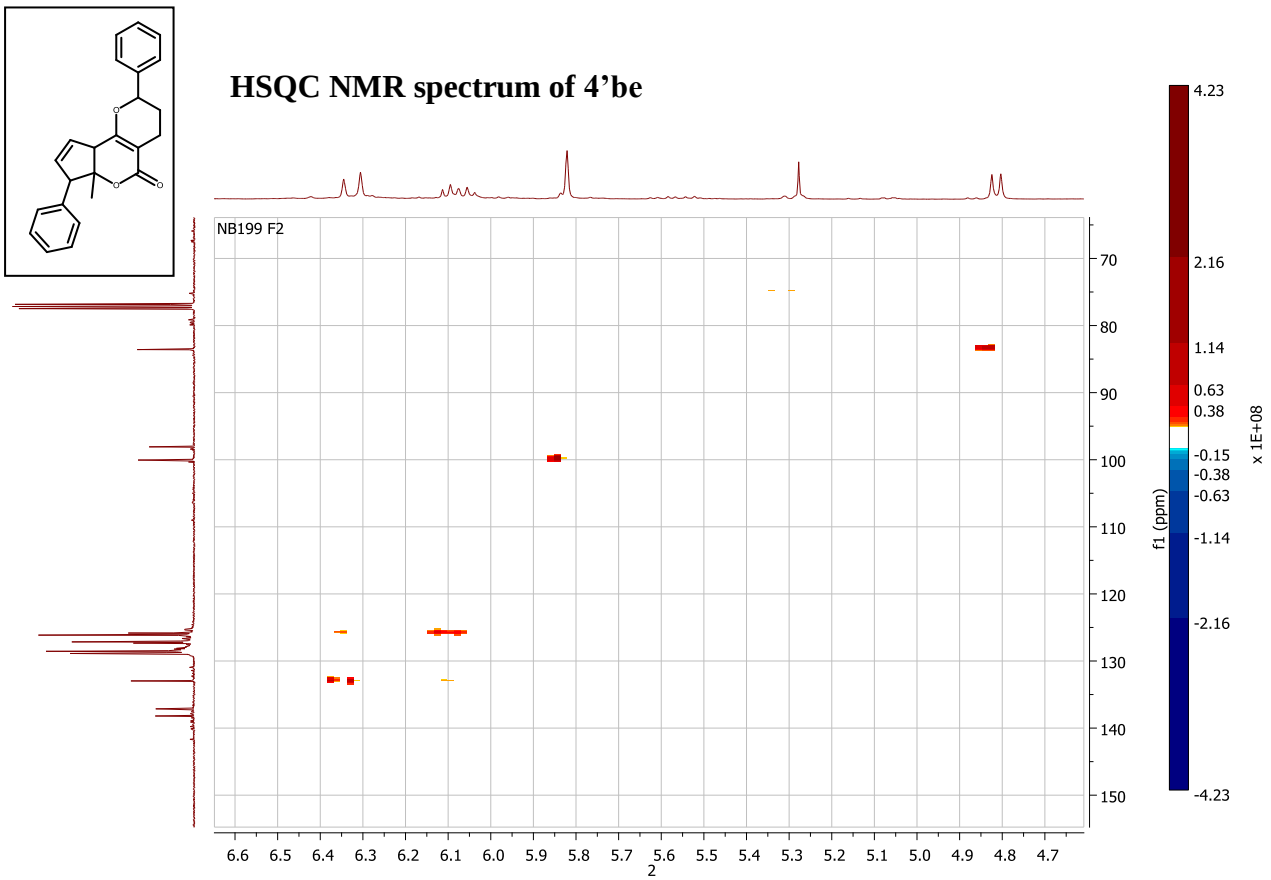
HRMS m/z calcd. For $C_{24}H_{22}O_3$ [$M^{+\cdot}$]: 358.1569, found 358.1537.

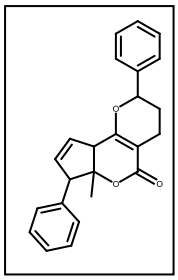



NB199 F2
164.94
164.72
160.24
138.20
137.13
132.97
128.97
128.88
128.55
127.34
127.15
126.14
125.83
100.05
98.08
83.58
37.40
35.34
24.28
19.84
13C NMR spectrum of 4’be
f2

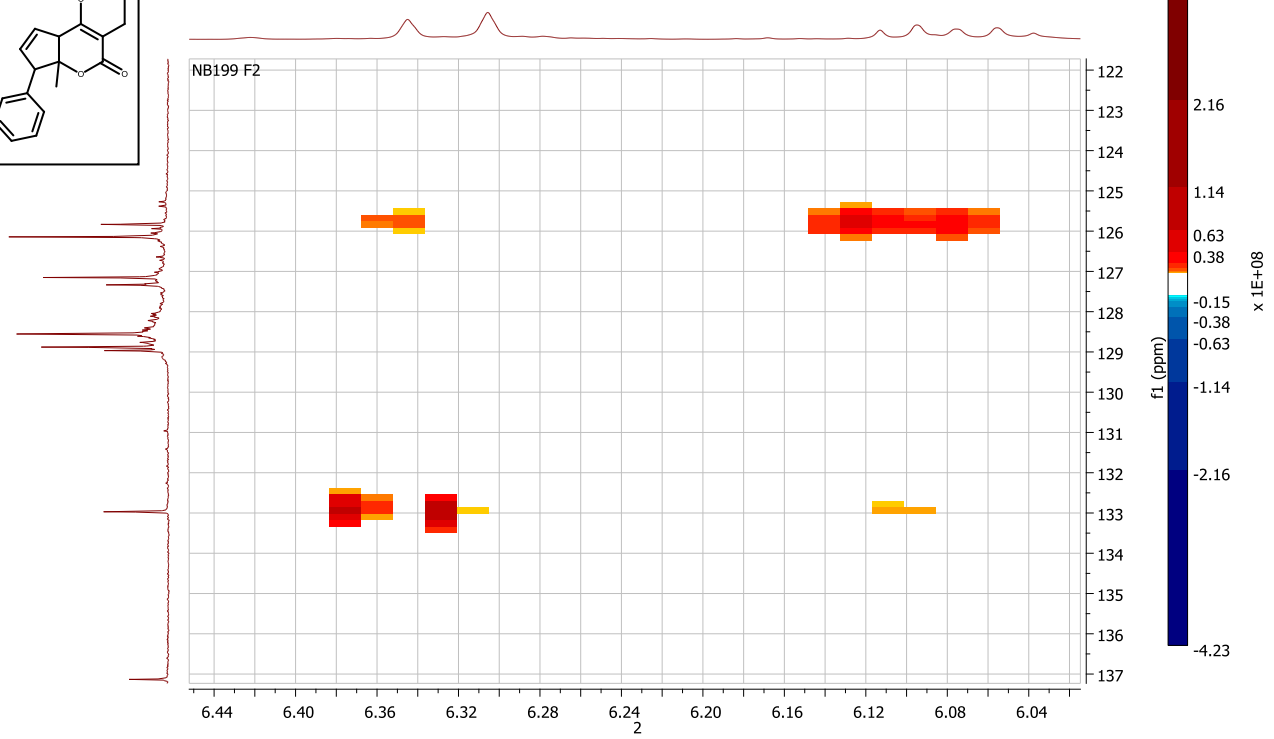

HSQC NMR spectrum of 4’be
NB199 F2
f2
f1 (ppm)
x 1E+08
4.23
2.12
1.07
0.55
0.29
-0.05
-0.29
-0.55
-1.07
-2.12
-4.23

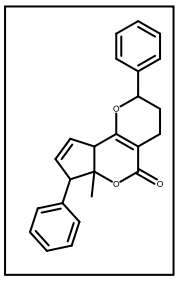

HSQC NMR spectrum of 4’be
NB199 F2
7.66
7.62
7.58
7.54
7.50
7.46
7.42
7.38
7.34
7.30
7.26
2
120
125
130
135
4.23
2.60
1.80
1.40
-1.10
-1.40
-1.80
-2.60
-4.23
f1 (ppm)
x 1E+08


HSQC NMR spectrum of 4’be
NB199 F2
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
2
70
80
90
100
110
120
130
140
150
4.23
2.16
1.14
0.63
0.38
-0.15
-0.38
-0.63
-1.14
-2.16
-4.23
f1 (ppm)
x 1E+08

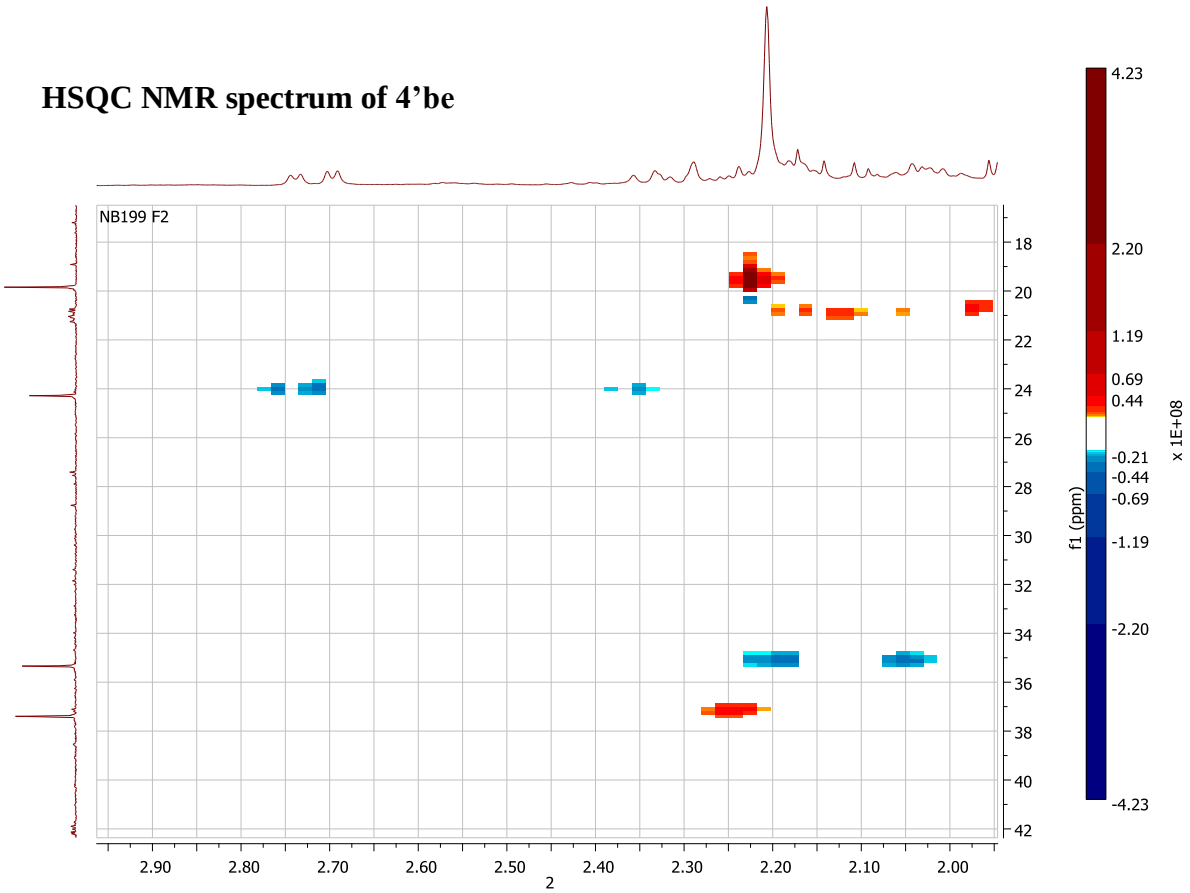


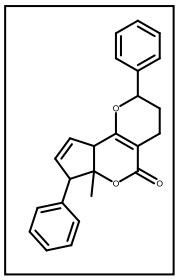
HSQC NMR spectrum of 4’be



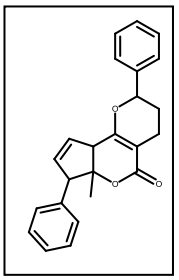


HSQC NMR spectrum of 4’be

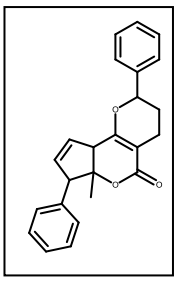




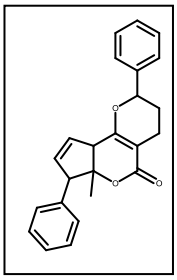
HMBC NMR spectrum of 4’be



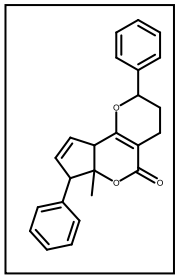
HMBC NMR spectrum of 4’be



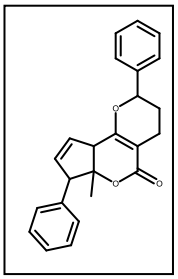
HMBC NMR spectrum of 4’be



HMBC NMR spectrum of 4’be

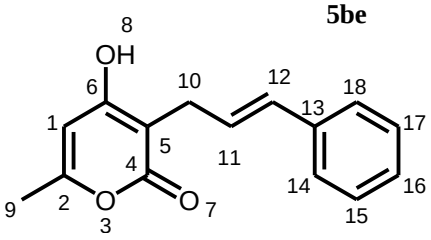


HMBC NMR spectrum of 4’be



HMBC NMR spectrum of 4’be

5be

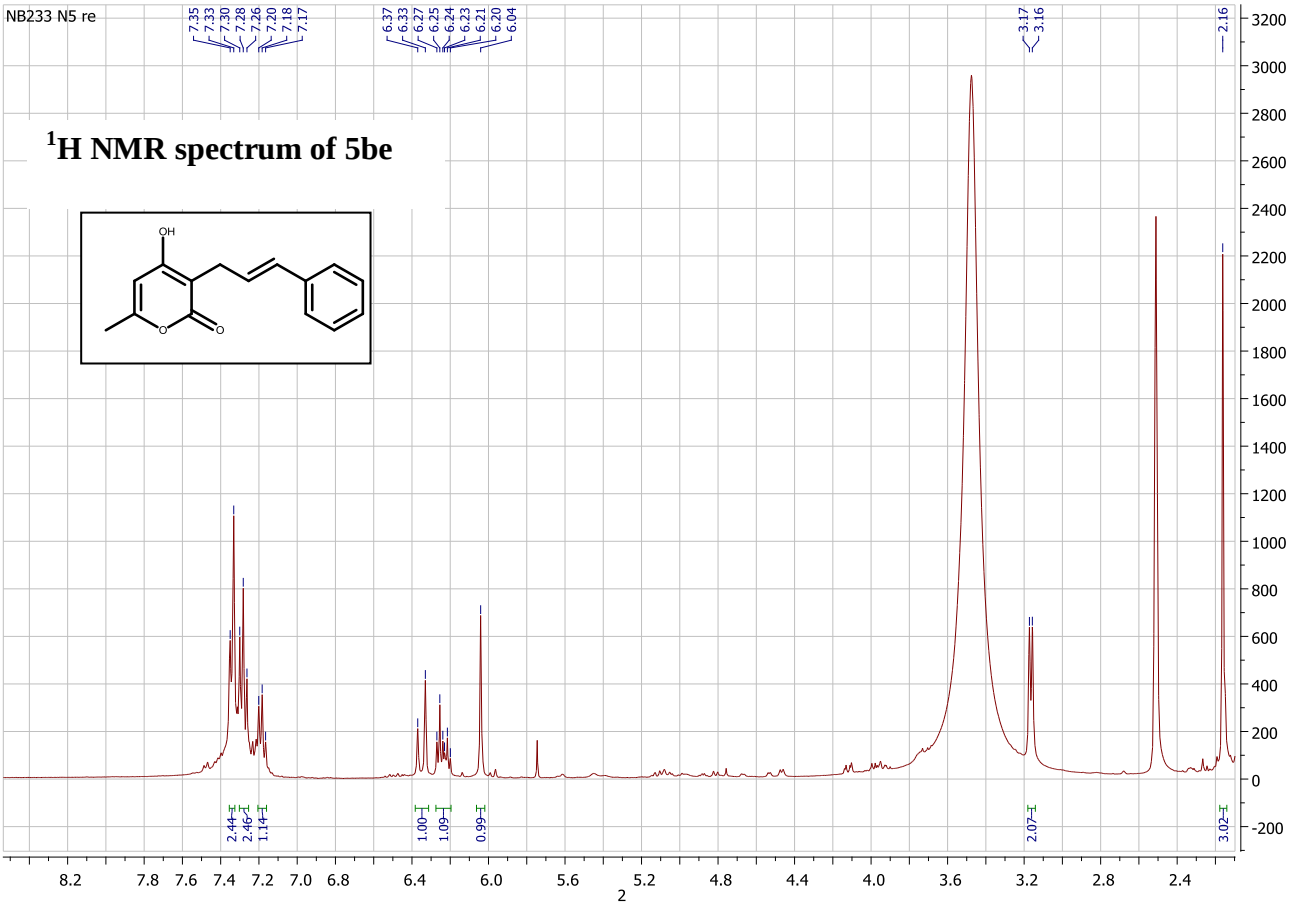


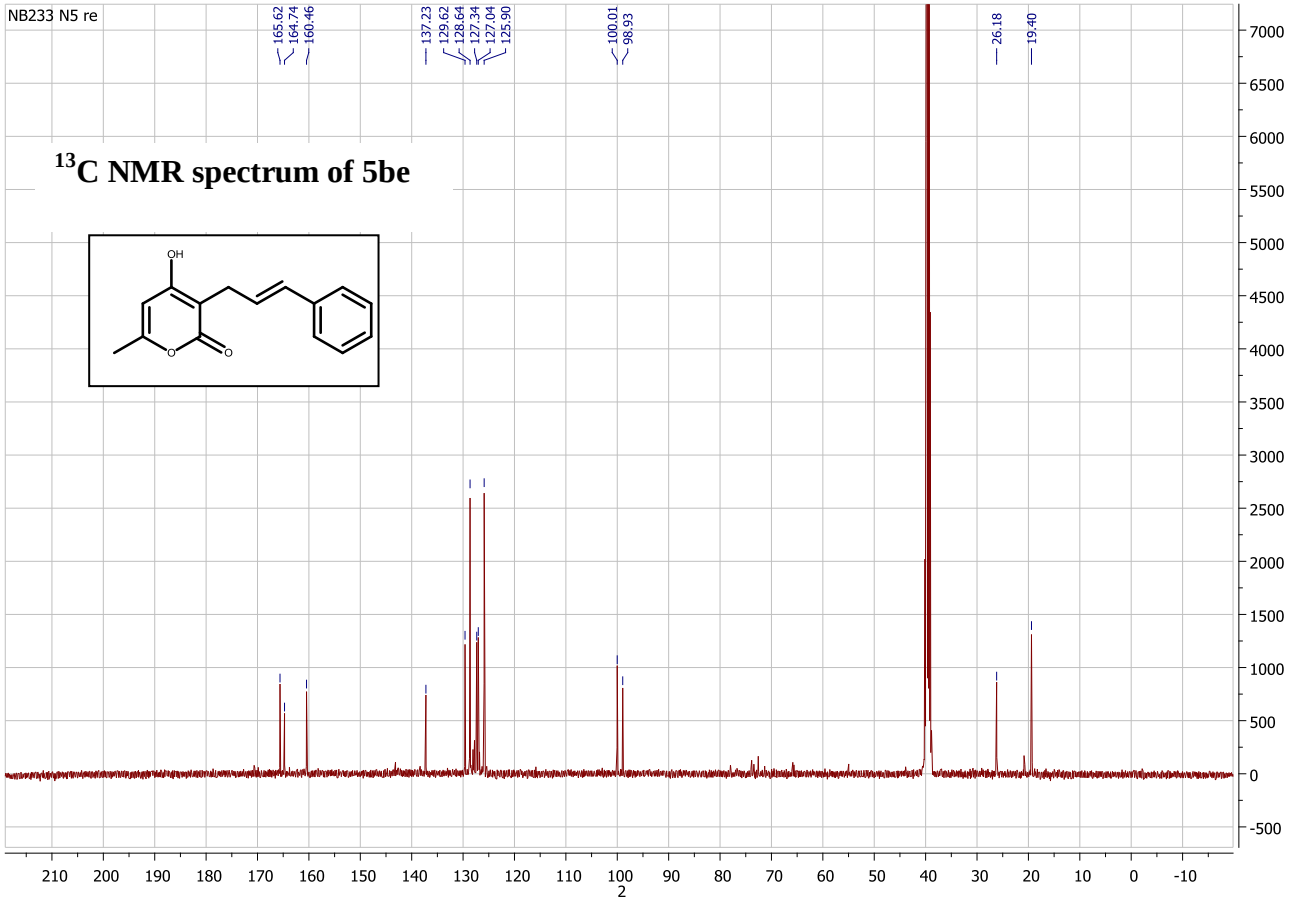
Cas number: 115580-35-3
Yield : 14%
5be : yellow solid
TLC: Rf = 0.28 (PE/EtOAc:2/3)
Mp = 172 °C

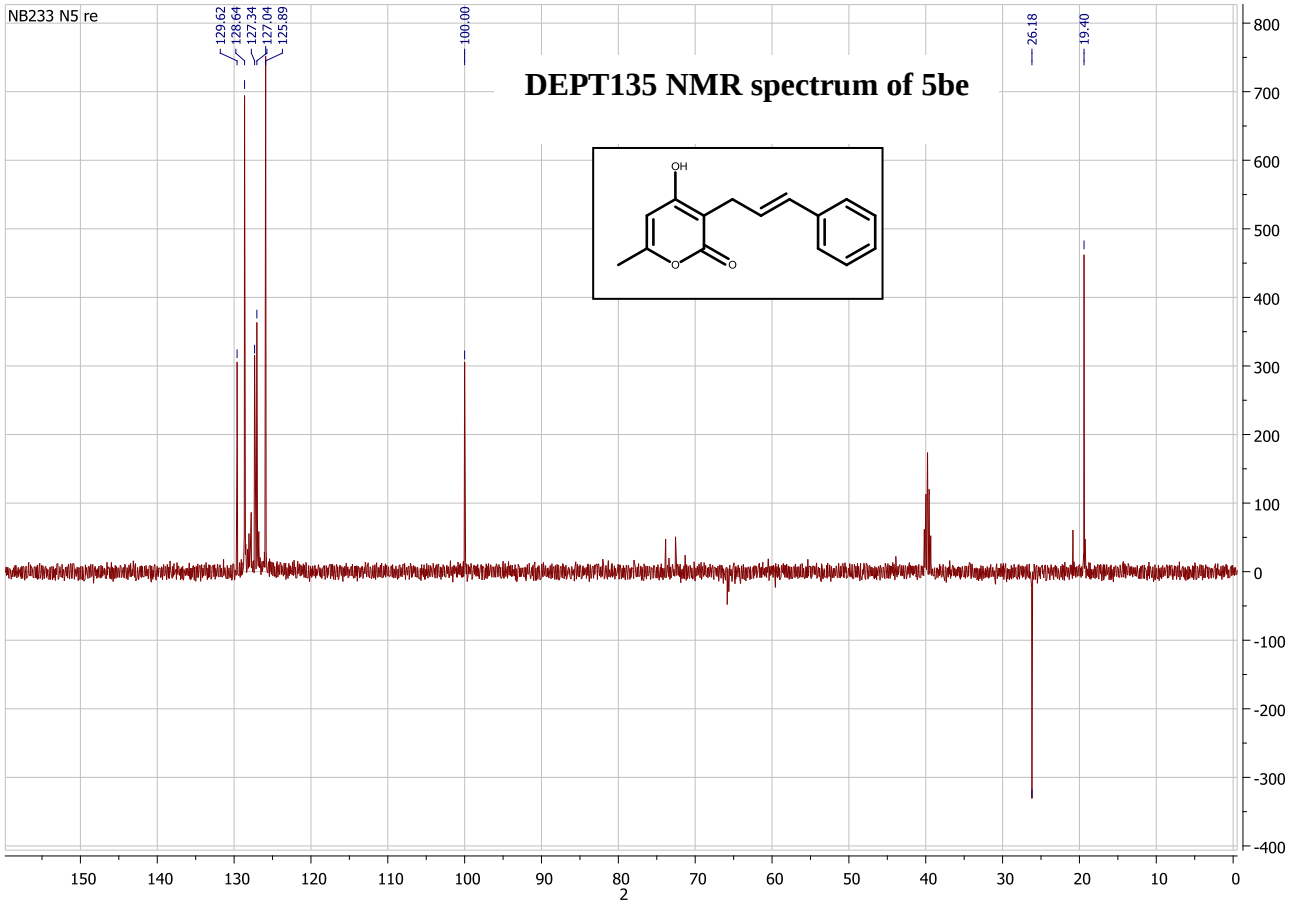
^{1}H NMR (400 MHz, DMSO) δ [ppm]: 7.34 – 7.32 (d, *J* = 7.5 Hz, $2H_{14, 18}$), 7.29 – 7.25 (t, *J* = 7.6 Hz, $2H_{15, 17}$), 7.19 – 7.15 (t, *J* = 7.2 Hz, $1H_{16}$), 6.36 – 6.32 (d, J_E = 15.9 Hz, $1H_{12}$), 6.26 – 6.19 (m, $1H_{11}$), 6.03 (s, $1H_1$), 3.16 – 3.15 (d, *J* = 6.1 Hz, $2H_{10}$), 2.15 (s, $3H_9$).

^{13}C NMR (101 MHz, DMSO) δ [ppm]: 165.62 (C6), 164.74 (C4), 160.46 (C2), 137.23 (C13), 129.62 (C12), 128.64 (C15, 17), 127.34 (C16), 127.04 (C11), 125.90 (C14, 18), 100.01 (C1), 98.93 (C5), 26.18 (C10), 19.40 (C9).

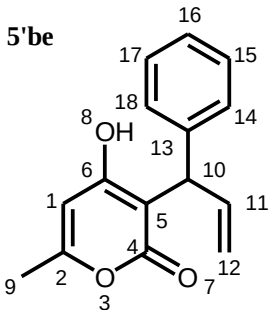
MS (EI, 70 eV): 242 (7) [M+.], 151 (20), 128 (13), 115 (14), 104 (8), 85 (9), 77 (13), 40 (100).




NB233 N5 re
165.62
164.74
160.46
137.23
129.62
128.64
127.34
127.04
125.90
100.01
98.93
26.18
19.40
^{13}C NMR spectrum of 5be
OH
O
O


NB233 N5 re
129.62
128.64
127.34
127.04
125.89
100.00
26.18
19.40
DEPT135 NMR spectrum of 5be
OH
O
O

5'be



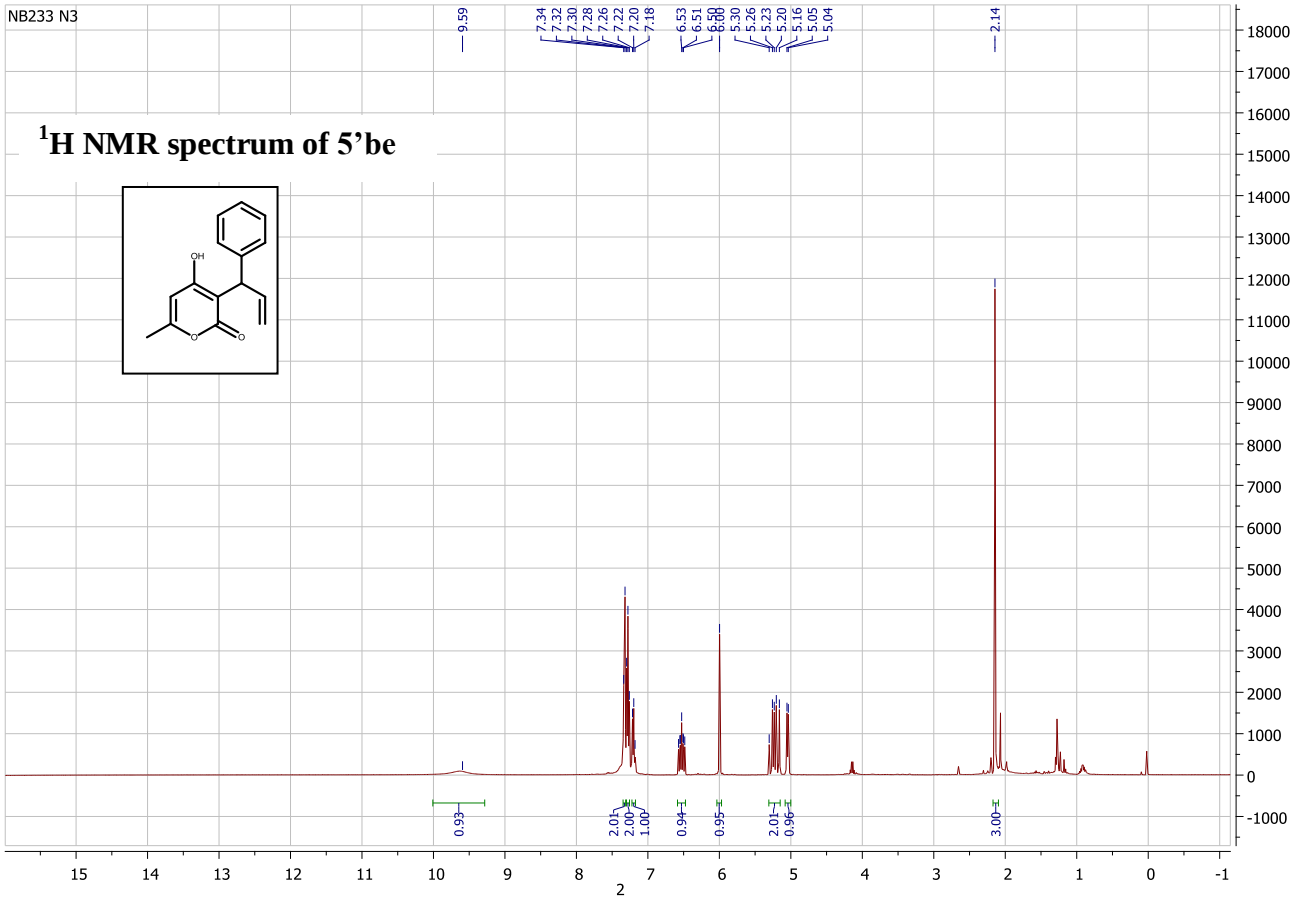
Yield : 9%
5'be : yellow solid
TLC: Rf = 0.14 (PE/EtOAc:2/3)
Mp = 112 °C

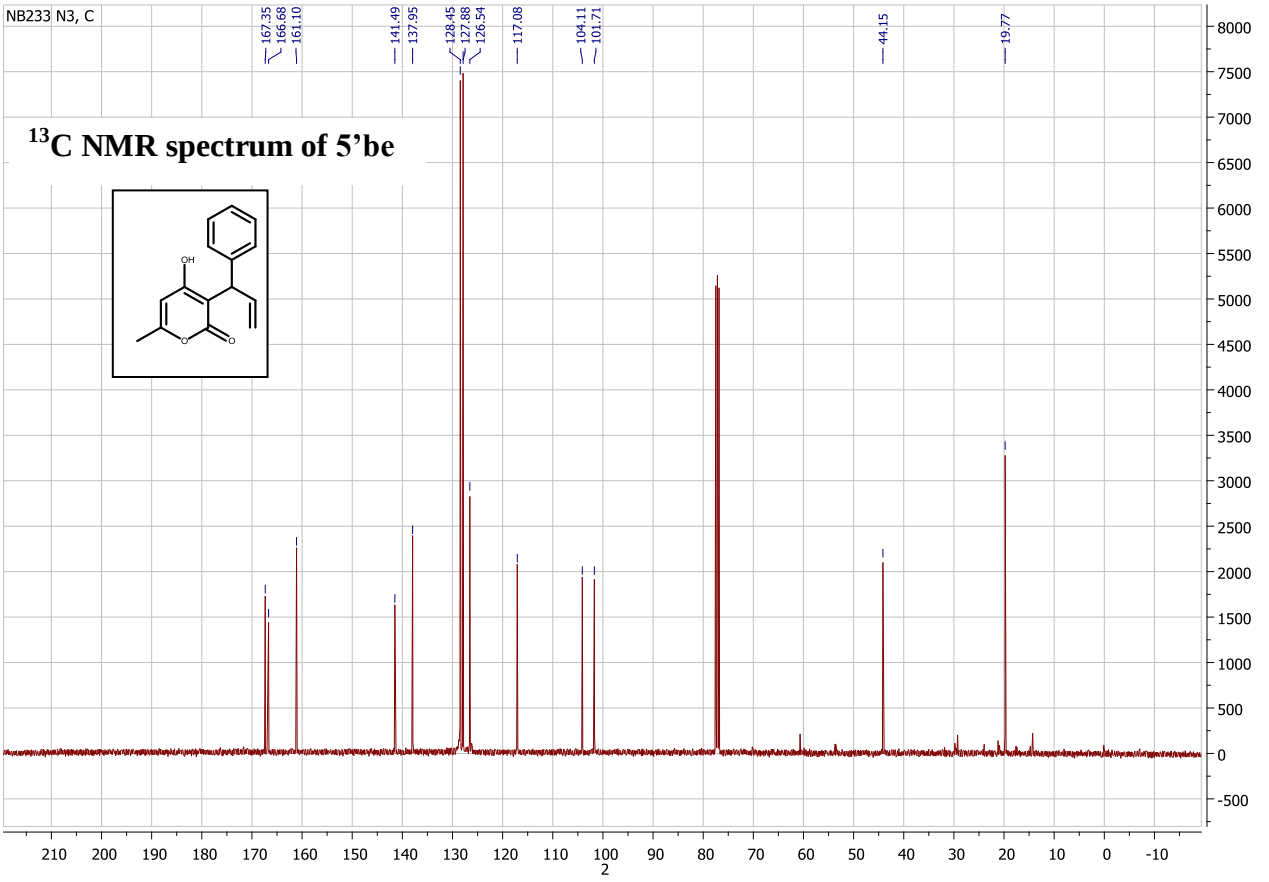
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 9.59 (s, $1H_8$), 7.34 – 7.32 (d, *J* = 7.3 Hz, $2H_{14, 18}$), 7.30 – 7.26 (t, *J* = 7.5 Hz, $2H_{15, 17}$), 7.22 – 7.18 (t, *J* = 7.1 Hz, $1H_{16}$), 6.57 – 6.48 (m, $1H_{11}$), 6.00 (s, $1H_1$), 5.30 – 5.16 (m, $2H_{12}$), 5.05 – 5.04 (d, *J* = 7.4 Hz, $1H_{10}$), 2.14 (s, $3H_9$).

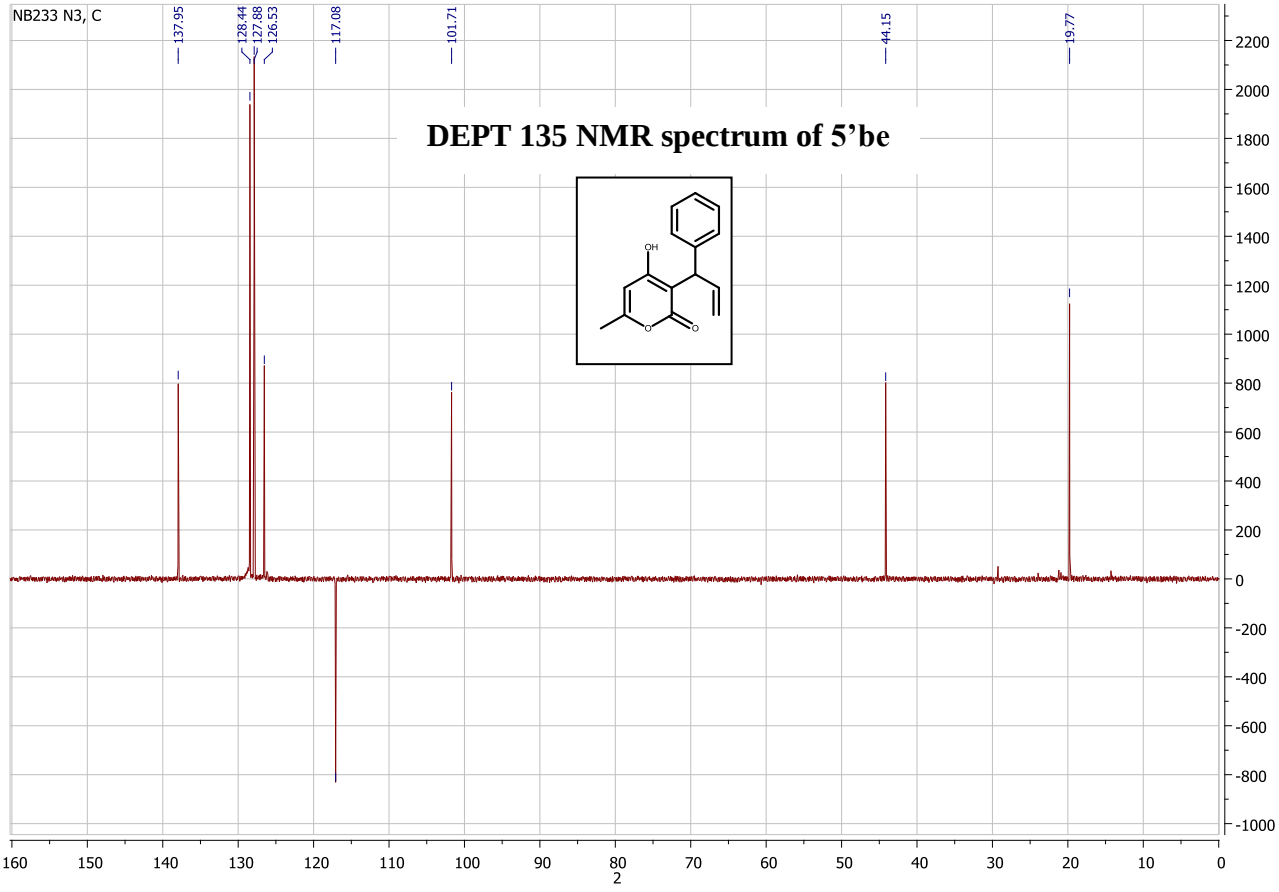
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 167.35 (C6), 166.68 (C4), 161.10 (C2), 141.49 (C13), 137.95 (C11), 128.45 (C15, 17), 127.88 (C14, 18), 126.54 (C16), 117.08 (C12), 104.11 (C5), 101.71 (C1), 44.15 (C10), 19.77 (C9).

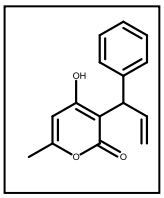
MS (EI, 70 eV): 242 (46) [$M^{+\cdot}$], 227 (40), 199 (33), 158 (41), 129 (31), 115 (42), 91 (20), 85 (25), 77 (26), 43 (100).

HRMS m/z calcd. For $C_{15}H_{14}O_3$ [$M^{+\cdot}$]: 242.2699, found 242.2641.

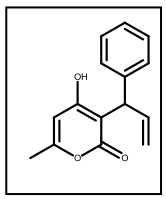



NB233 N3, C
167.35
166.68
161.10
141.49
137.95
128.45
127.88
126.54
117.08
104.11
101.71
44.15
19.77
^{13}C NMR spectrum of 5'be
OH
O
O
2

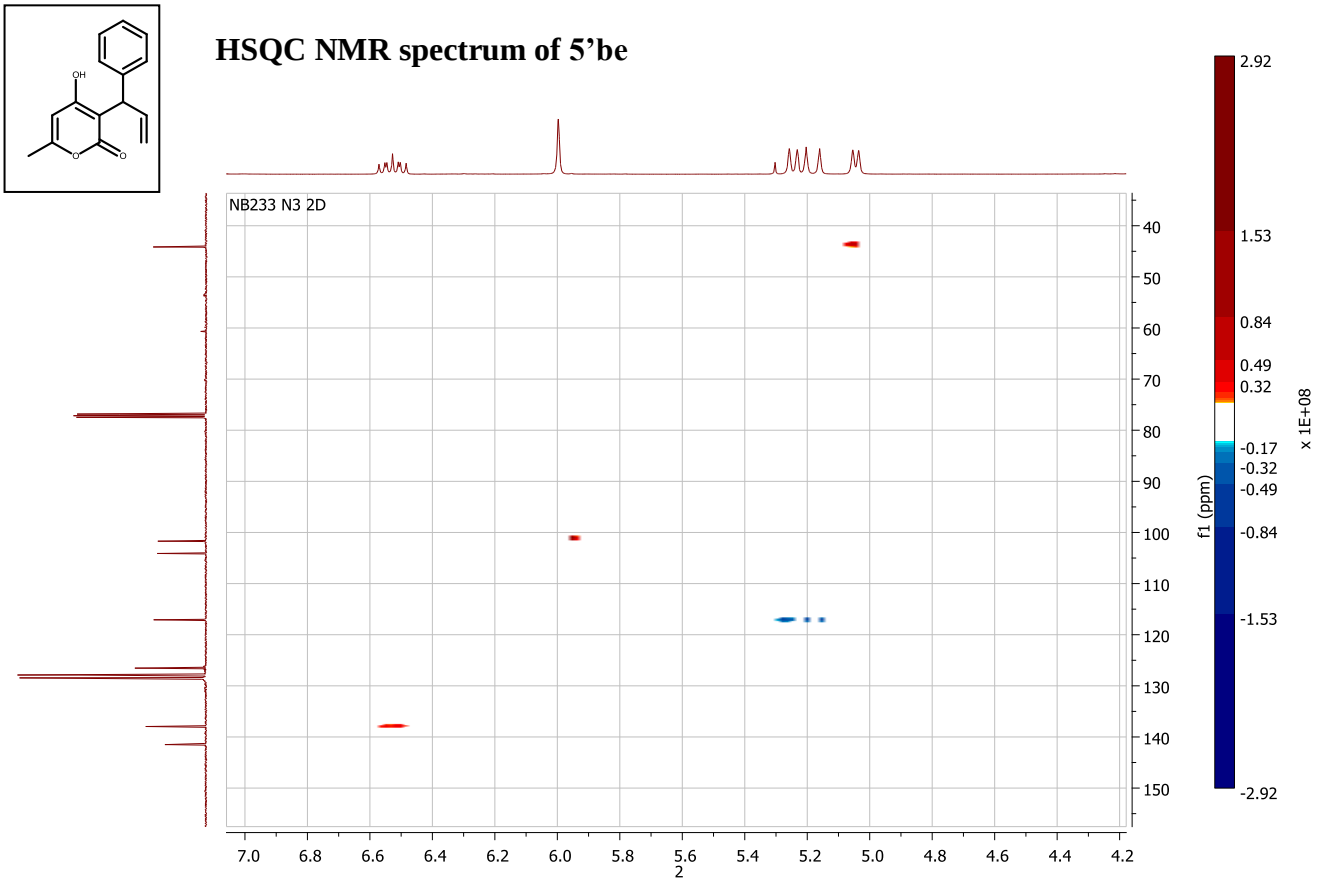

NB233 N3, C
137.95
128.44
127.88
126.53
117.08
101.71
44.15
19.77
DEPT 135 NMR spectrum of 5'be
OH
O
O
2



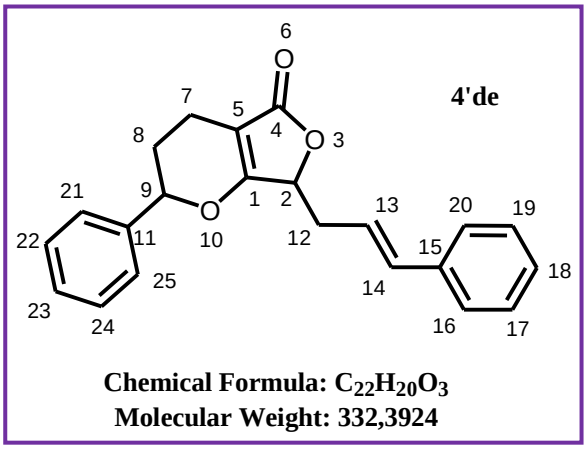
HSQC NMR spectrum of 5’be



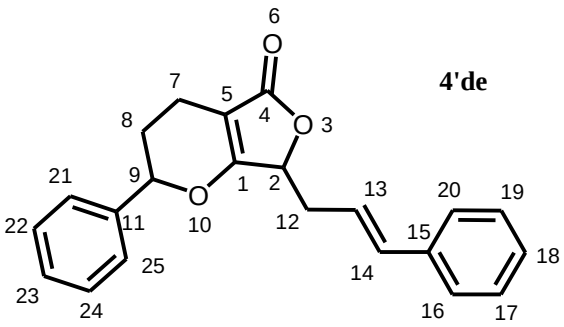
HSQC NMR spectrum of 5’be



-- (*E*)-2-Phenyl-7-(3-phenyl-allyl)-2,3,4,7-tetrahydro-furo[3,4-*b*]pyran-5-one 4'de --



According to the general protocol **A,** compound **4'de** (166.17 mg) is synthesized starting from tetronic acid **1d** (1 eq, 250 mg, 2.5 mmol) and cinnamyl acetate **2e** (5 eq, 2202.7 mg, 12 mmol), using $In(OTf)_3$ (5 mol%, 70.2 mg, 0.125 mmol), under reflux of dry DCE (12.5 ml), during 3 hours. The crude of the reaction is purified by flash chromatography (PE/EtOAc:90/10).



4'de

Yield : 20%
4'de : yellow solid
TLC: Rf = 0.39 (PE/EtOAc:4/1)
Mp = 80 °C

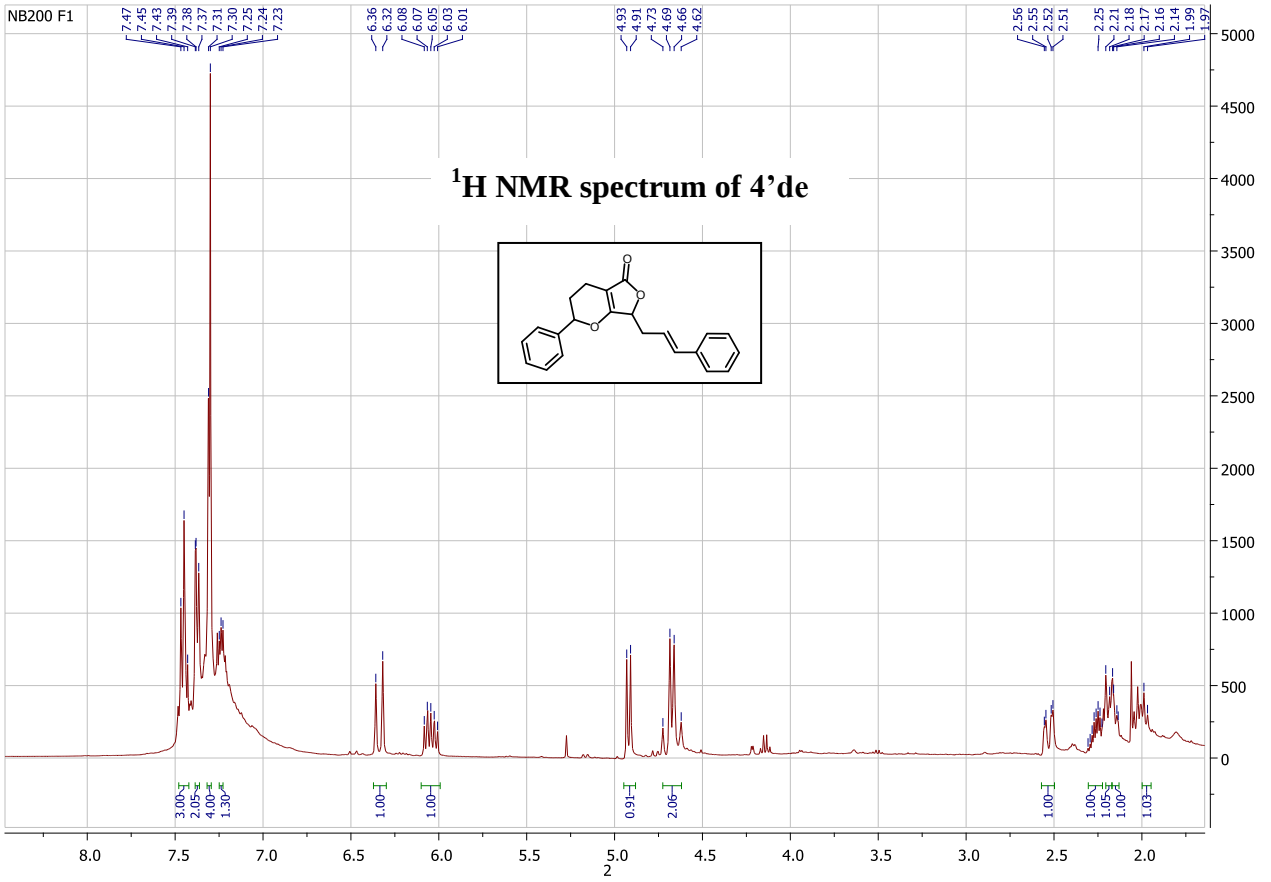
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.47 – 7.43 (m, $3H_{23, 17, 19}$), 7.39 – 7.37 (m, $2H_{21, 25}$), 7.31 – 7.30 (m, $4H_{22, 24, 16, 20}$), 7.25 – 7.23 (t, J = 4 Hz, $1H_{18}$), 6.36 – 6.32 (d, J_E = 15.7 Hz, $1H_{14}$), 6.08 – 6.01 (m, $1H_{13}$), 4.93 – 4.91 (d, J = 8.7 Hz, $1H_9$), 4.73 – 4.62 (m, $2H_{12}$), 2.56 – 2.13 (m, $2H_7$), 2.31 – 2.23 (m, $1H_2$), 2.21 – 1.97 (m, $2H_8$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 173.88 (C4), 172.88 (C1), 137.40 (C11), 136.95 (C15), 133.14 (C14), 129.26 (C23), 128.96 (C17, 19), 128.56 (C22, 24), 127.41 (C18), 127.22 (C21, 25), 126.07 (C16, 20), 125.42 (C13), 100.18 (C5), 86.28 (C9), 66.40 (C12), 37.25 (C2), 35.10 (C8), 22.18 (C7).

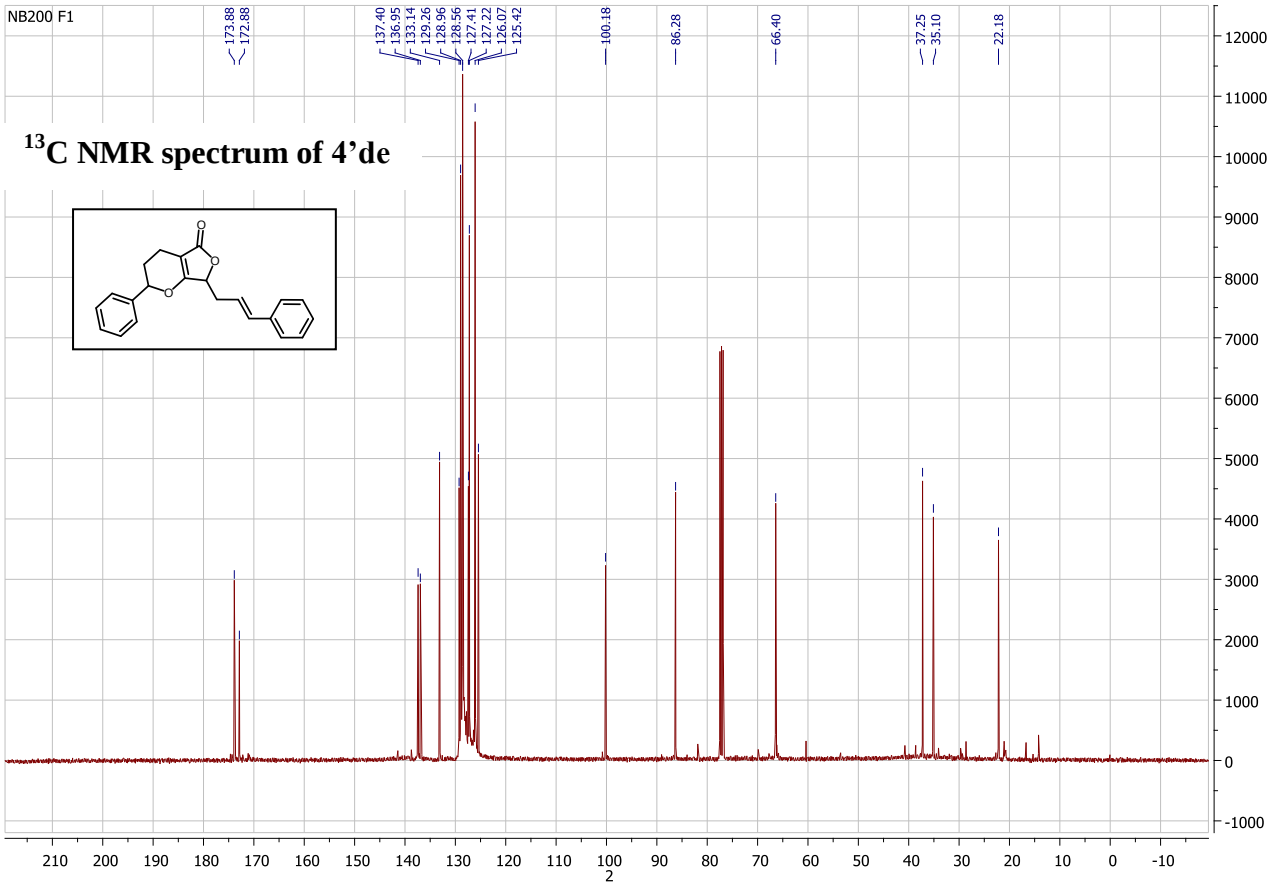
IR (neat): ν_{max} (cm^{-1}) = 3085, 3059, 3027, 2971, 2929, 2851, 1752, 1675, 1494, 1448, 1417, 1364, 1348, 1257, 1234, 1136, 1114, 1027, 1006, 967, 935, 909, 747, 697, 499, 492, 484, 422, 413.

MS (EI, 70 eV): 332 (55) [$M^{+\cdot}$], 241 (9), 220 (15), 213 (20), 168 (21), 143 (31), 129 (100), 91 (86), 77 (20), 65 (17), 44 (19).

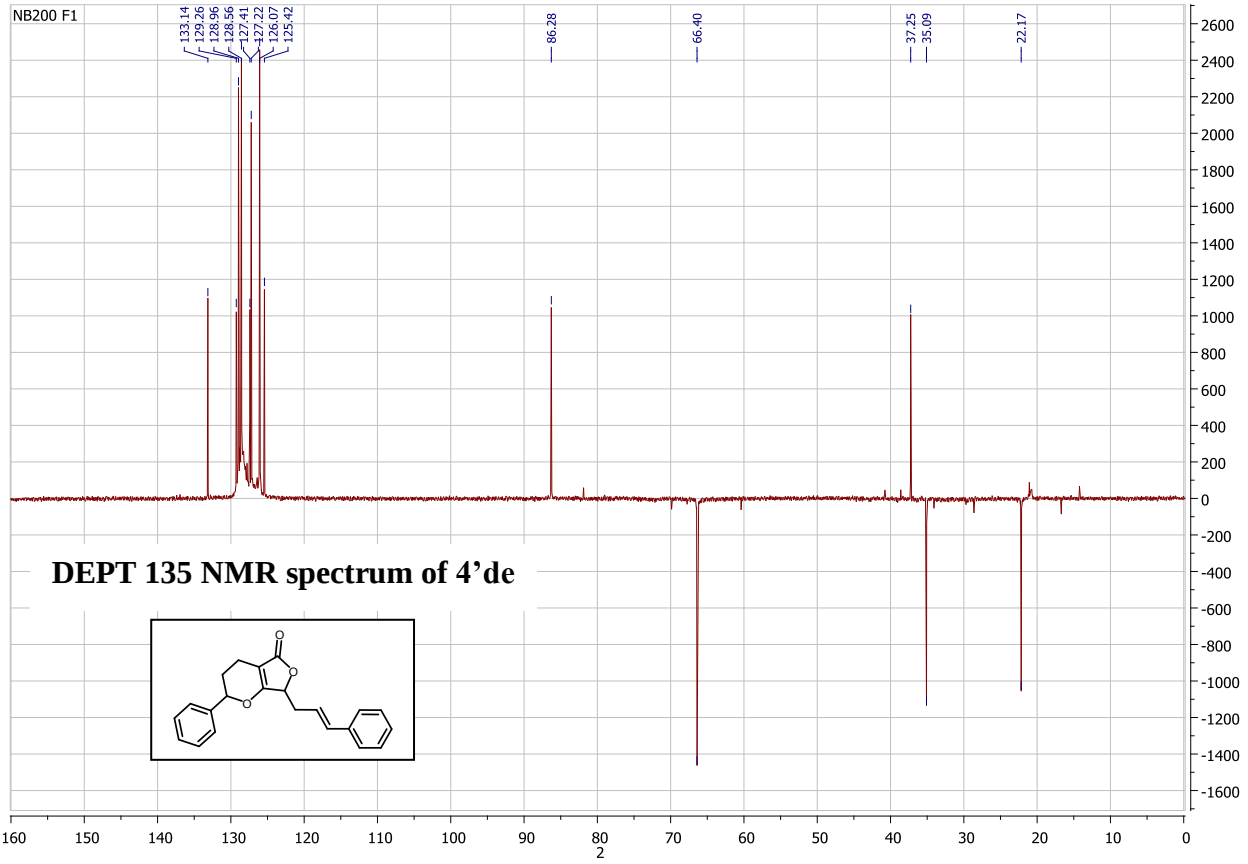
HRMS m/z calcd. For $C_{22}H_{20}O_3$ [$M^{+\cdot}$]: 332.1412, found 332.1367.

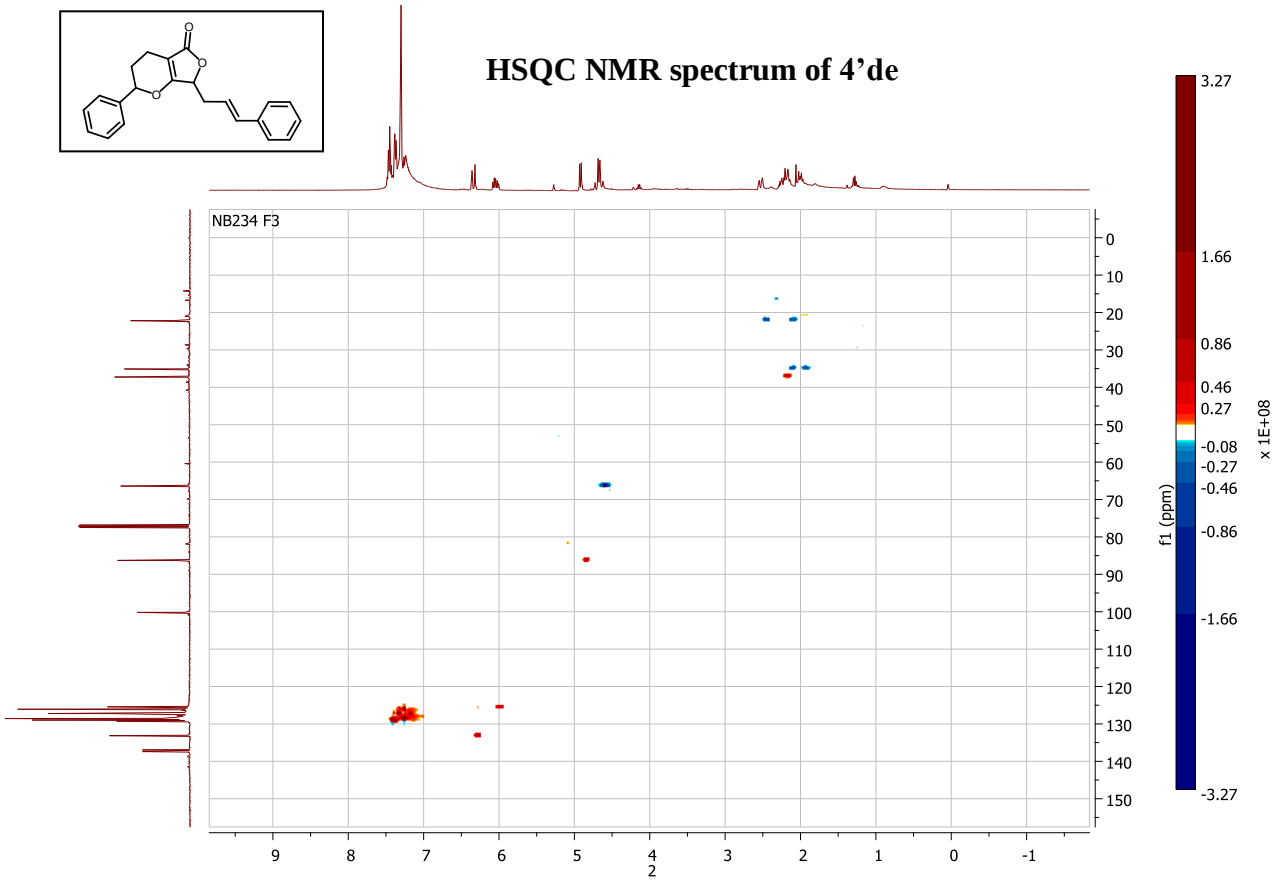


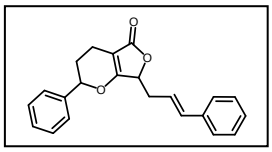
^{1}H NMR spectrum of 4'de



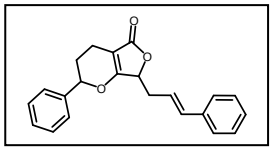
^{13}C NMR spectrum of 4'de


NB200 F1
133.14
129.26
128.96
128.56
127.41
127.22
126.07
125.42
86.28
66.40
37.25
35.09
22.17
DEPT 135 NMR spectrum of 4’de

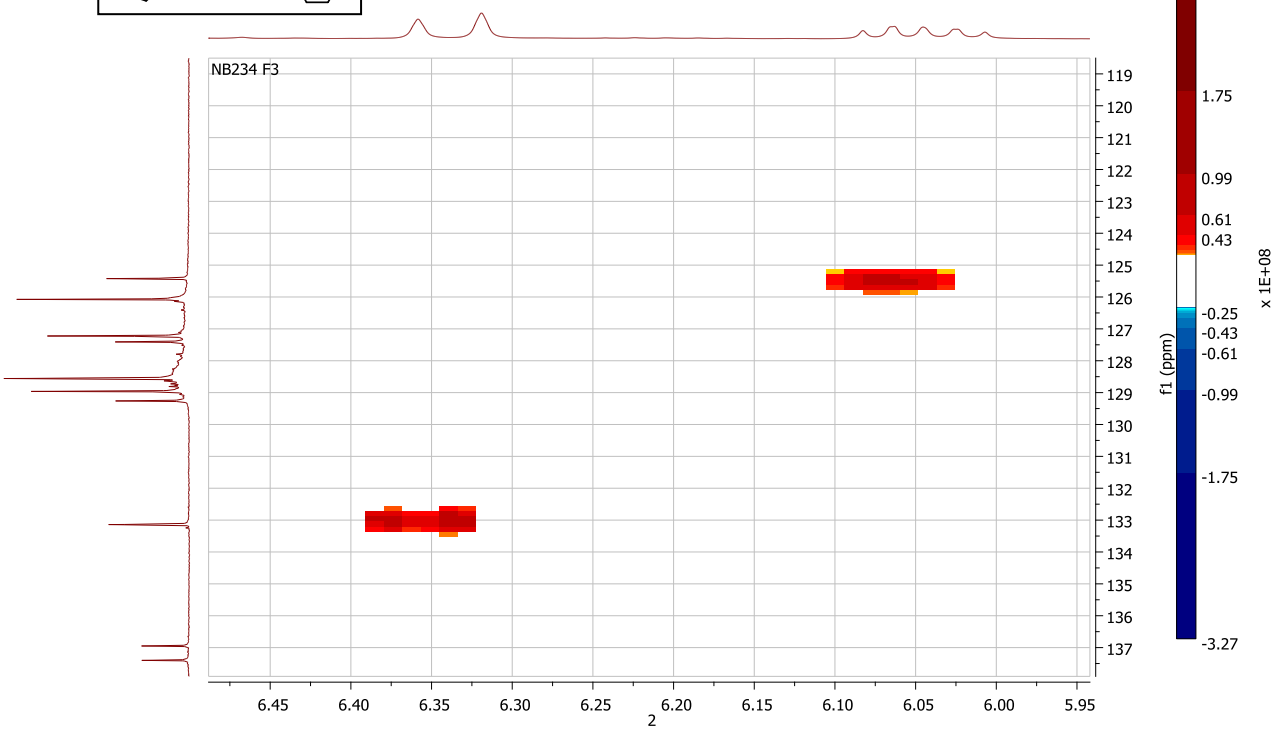

HSQC NMR spectrum of 4’de
NB234 F3
f1 (ppm)
x 1E+08

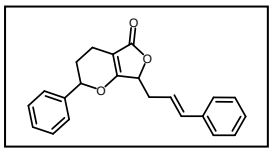


HSQC NMR spectrum of 4’de

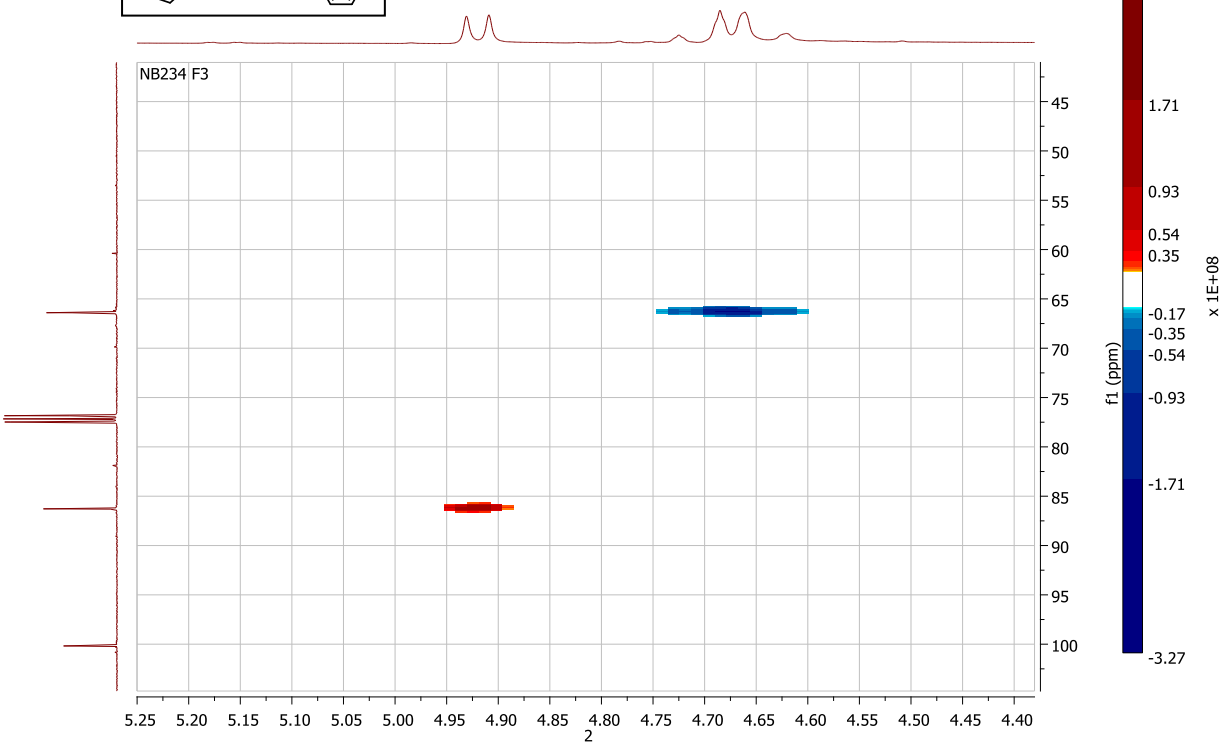


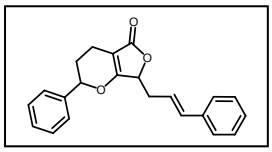
HSQC NMR spectrum of 4’de



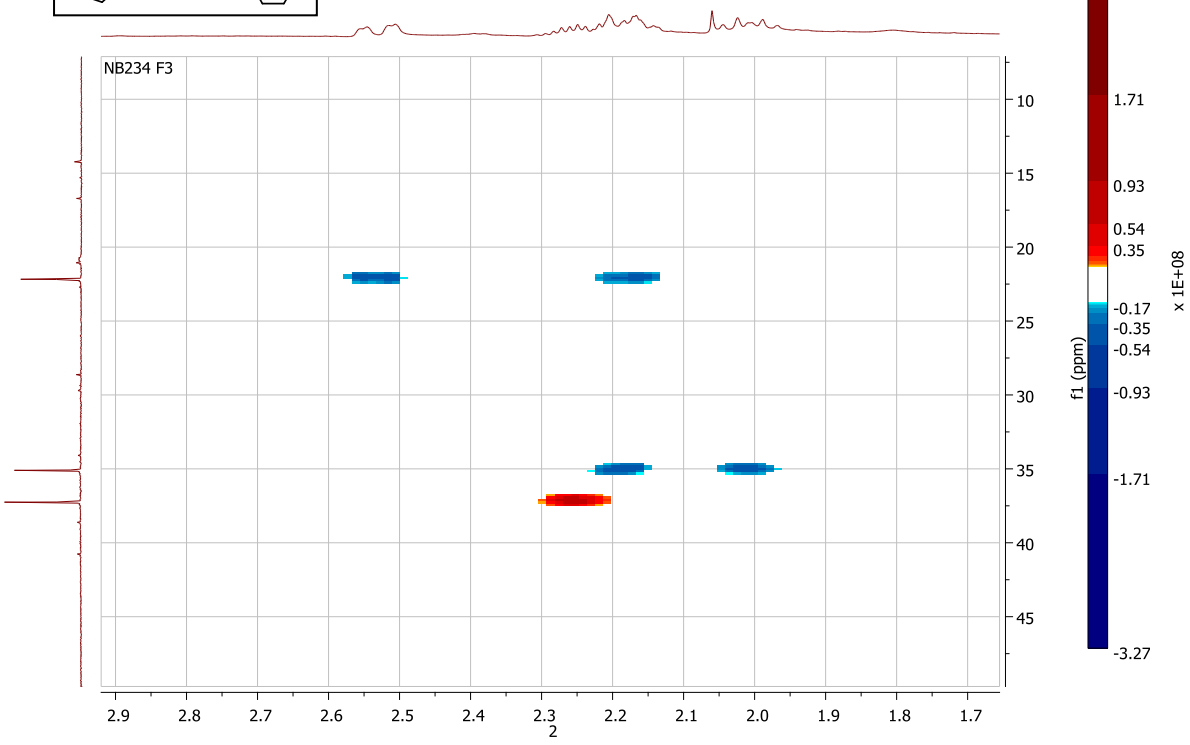


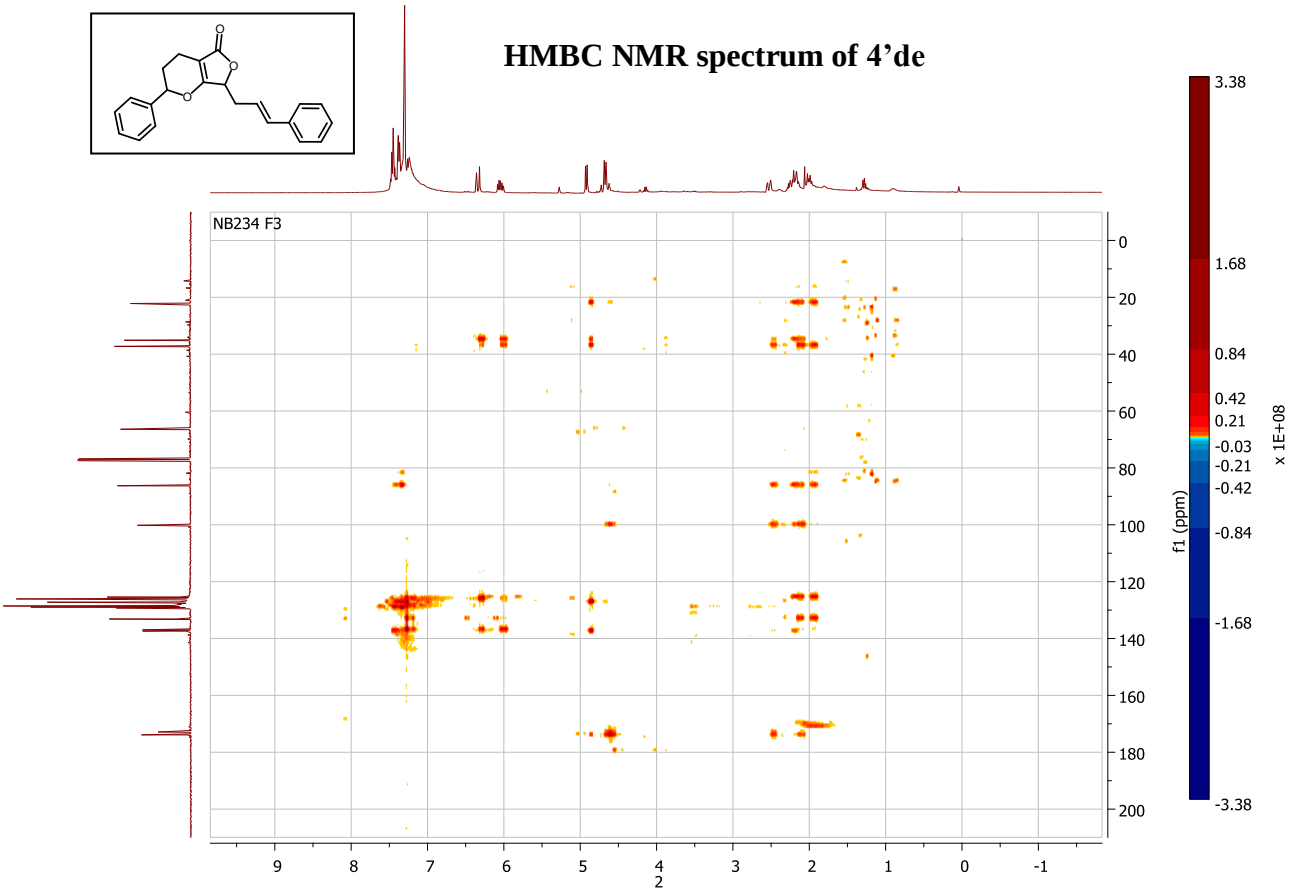
HSQC NMR spectrum of 4’de

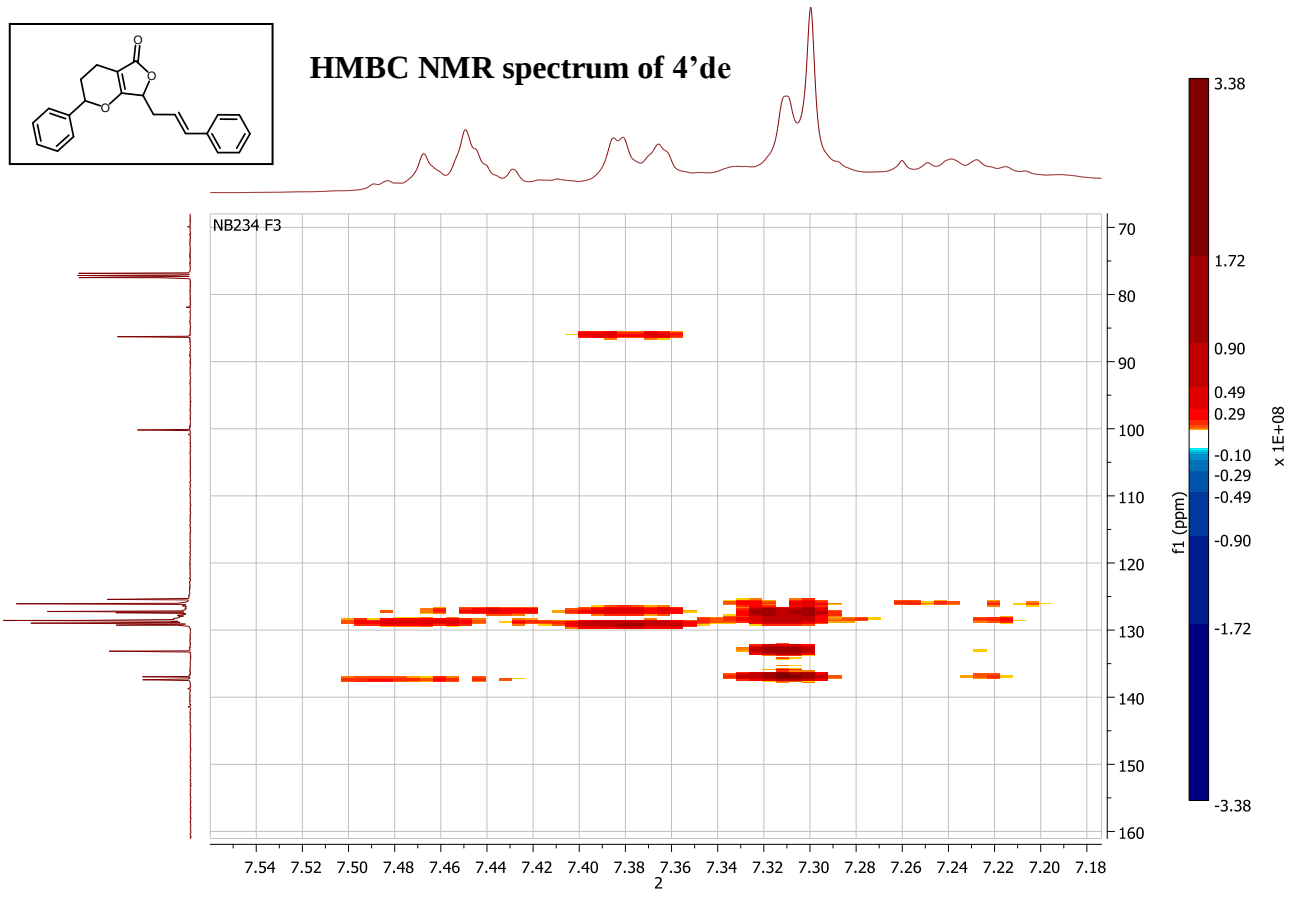


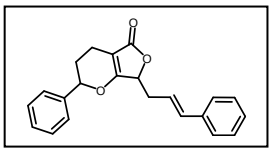


HSQC NMR spectrum of 4’de

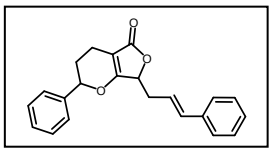



HMBC NMR spectrum of 4’de
NB234 F3
f1 (ppm)
x 1E+08
2

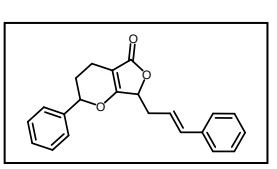

HMBC NMR spectrum of 4’de
NB234 F3
f1 (ppm)
x 1E+08
2



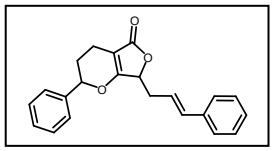
HMBC NMR spectrum of 4’de



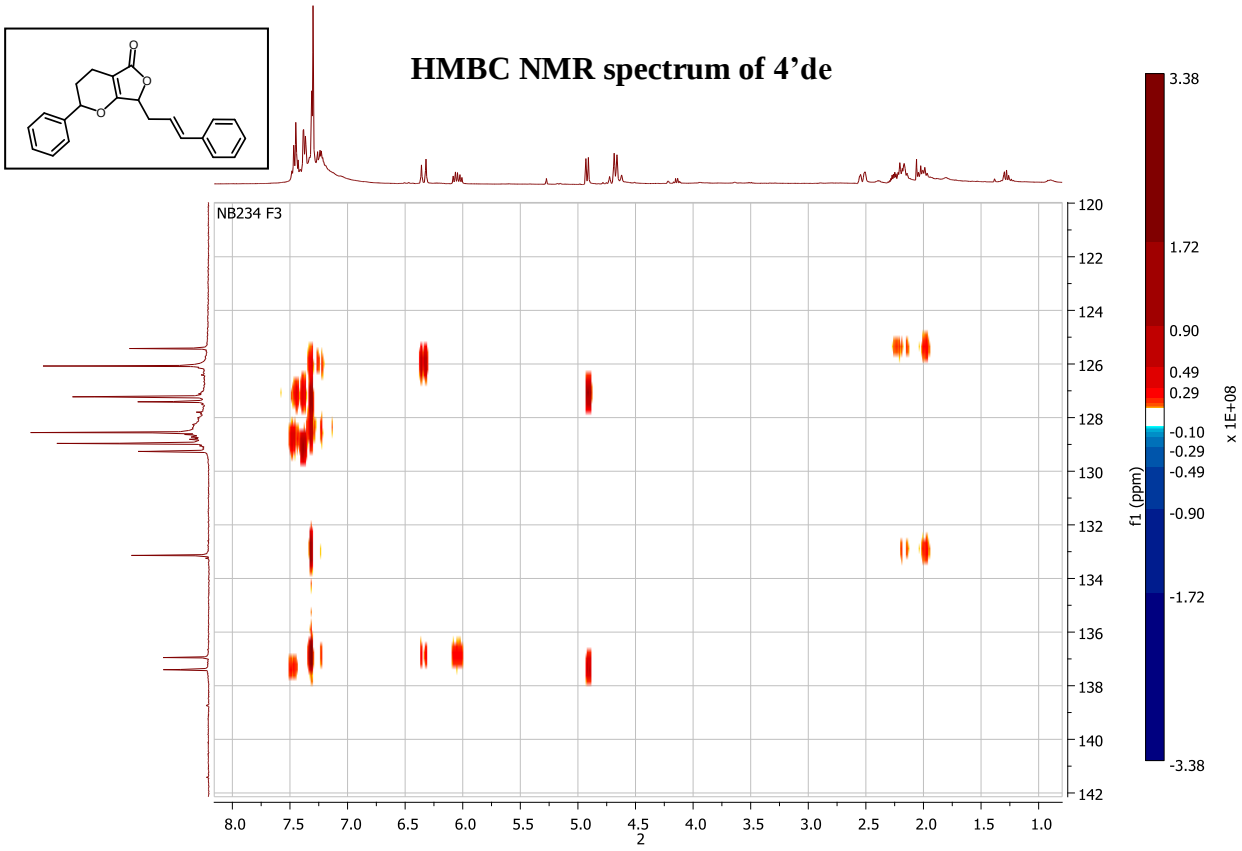
HMBC NMR spectrum of 4’de

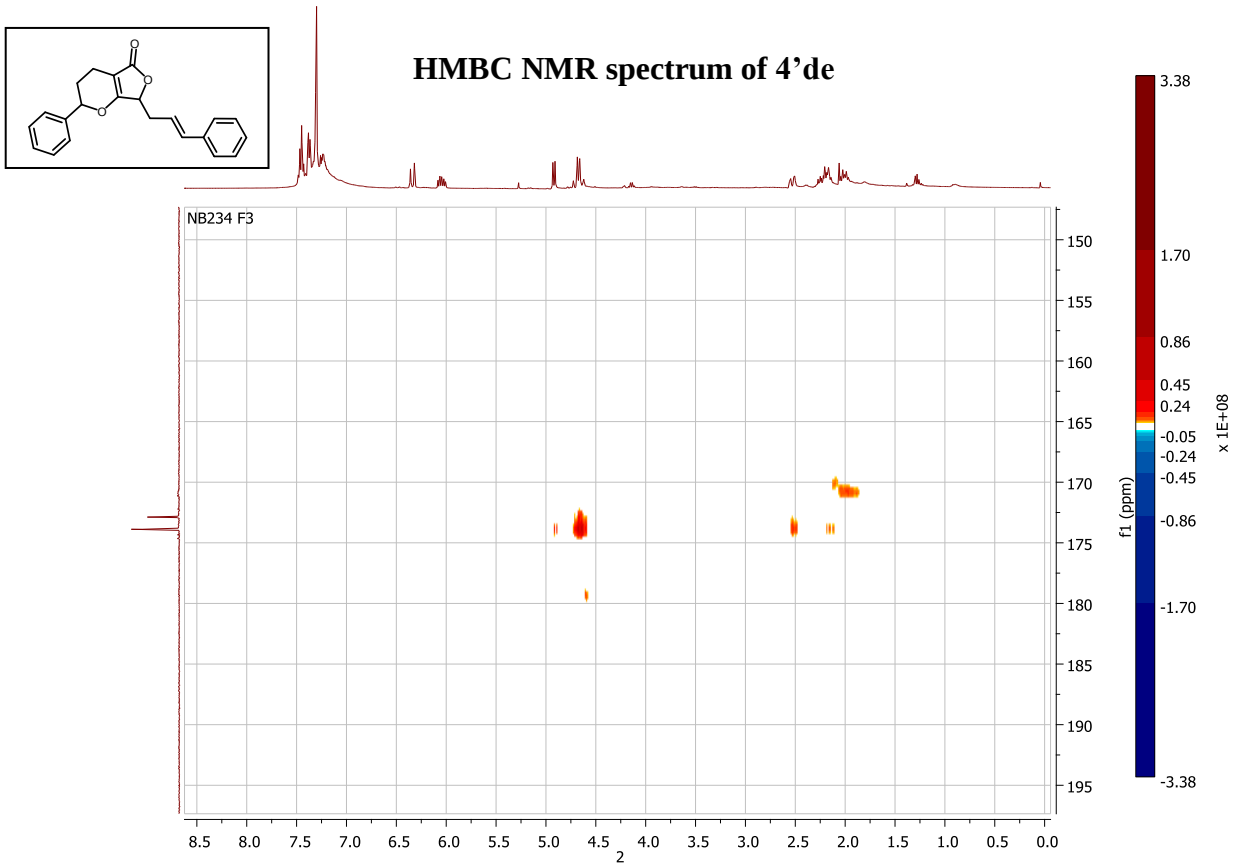


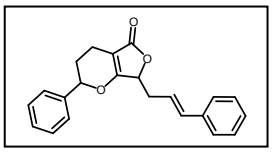
HMBC NMR spectrum of 4’de



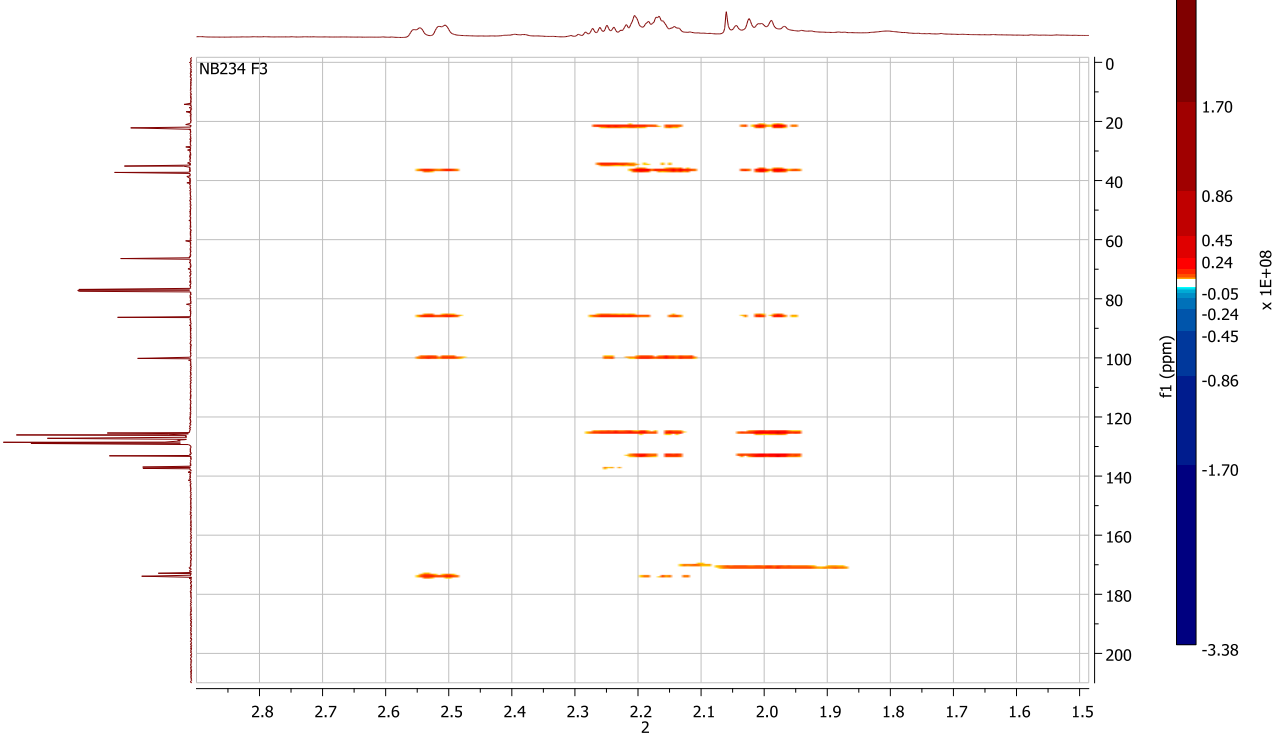
HMBC NMR spectrum of 4’de


HMBC NMR spectrum of 4’de
NB234 F3
f1 (ppm)
x 1E+08
3.38
1.72
0.90
0.49
0.29
-0.10
-0.29
-0.49
-0.90
-1.72
-3.38
2


HMBC NMR spectrum of 4’de
NB234 F3
f1 (ppm)
x 1E+08
3.38
1.70
0.86
0.45
0.24
-0.05
-0.24
-0.45
-0.86
-1.70
-3.38
2

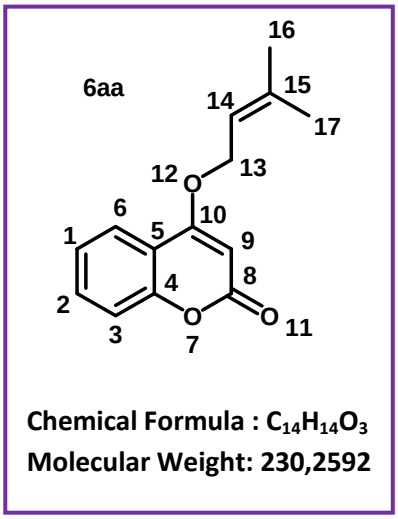


HMBC NMR spectrum of 4'de



III. Mechanism study: preparation of compound 4aa* and 6aa.

1. Synthesis of 4-(3-methyl-but-2-enyloxy)-chromen-2-one 6aa.

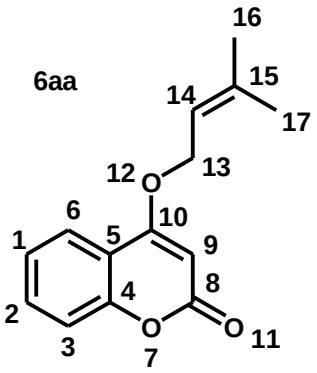


Chemical Formula : $C_{14}H_{14}O_3$

Molecular Weight: 230,2592

In a dry round bottom flask equipped with a magnetic stir bar, K_2CO_3 (3 eq, 4975.5 mg, 38.21 mmol) is introduced, and solvated with dry acetone (20 ml, 0.2 M). 4-Hydroxycoumarin **1a** (1 eq, 648.5 mg, 4 mmol) is then added, followed by prenyl bromide (1.5 eq, 894.1 mg, 6 mmol). The resulting mixture is stirred at room temperature for 24 hours. The reaction is monitored by GC/MS, GC and TLC. The crude of the reaction is hydrolyzed with HCl 1 M, extracted twice with EtOAc, dried over $MgSO_4$ and concentrated in a vacuum rotary evaporator. The crude product is purified using a flash column chromatography of silica gel (PE/Et_2O:95/5). Compound **6aa** is isolated with 30% yield.

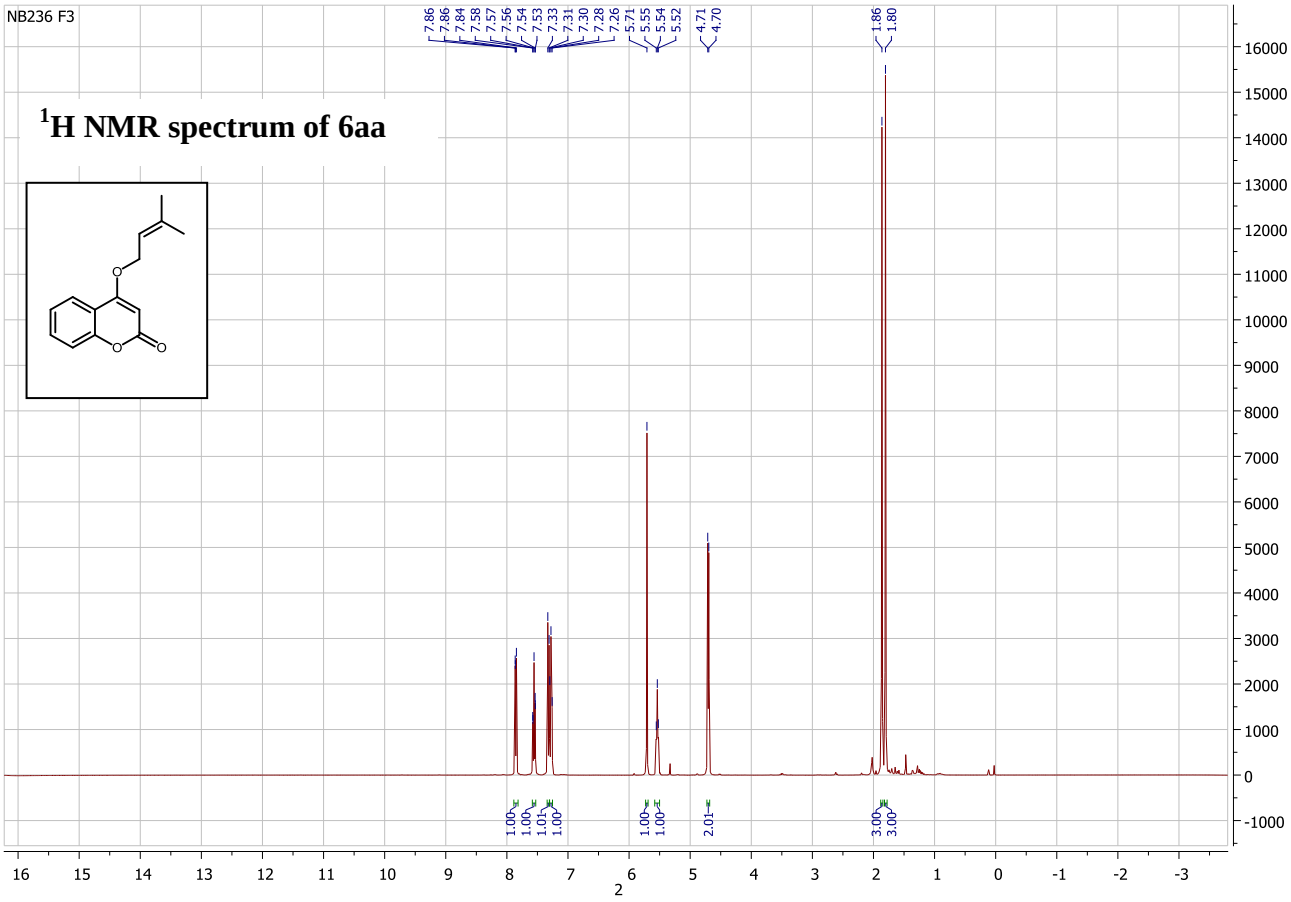
---------- 4-(3-Methyl-but-2-enyloxy)-chromen-2-one 6aa ----------

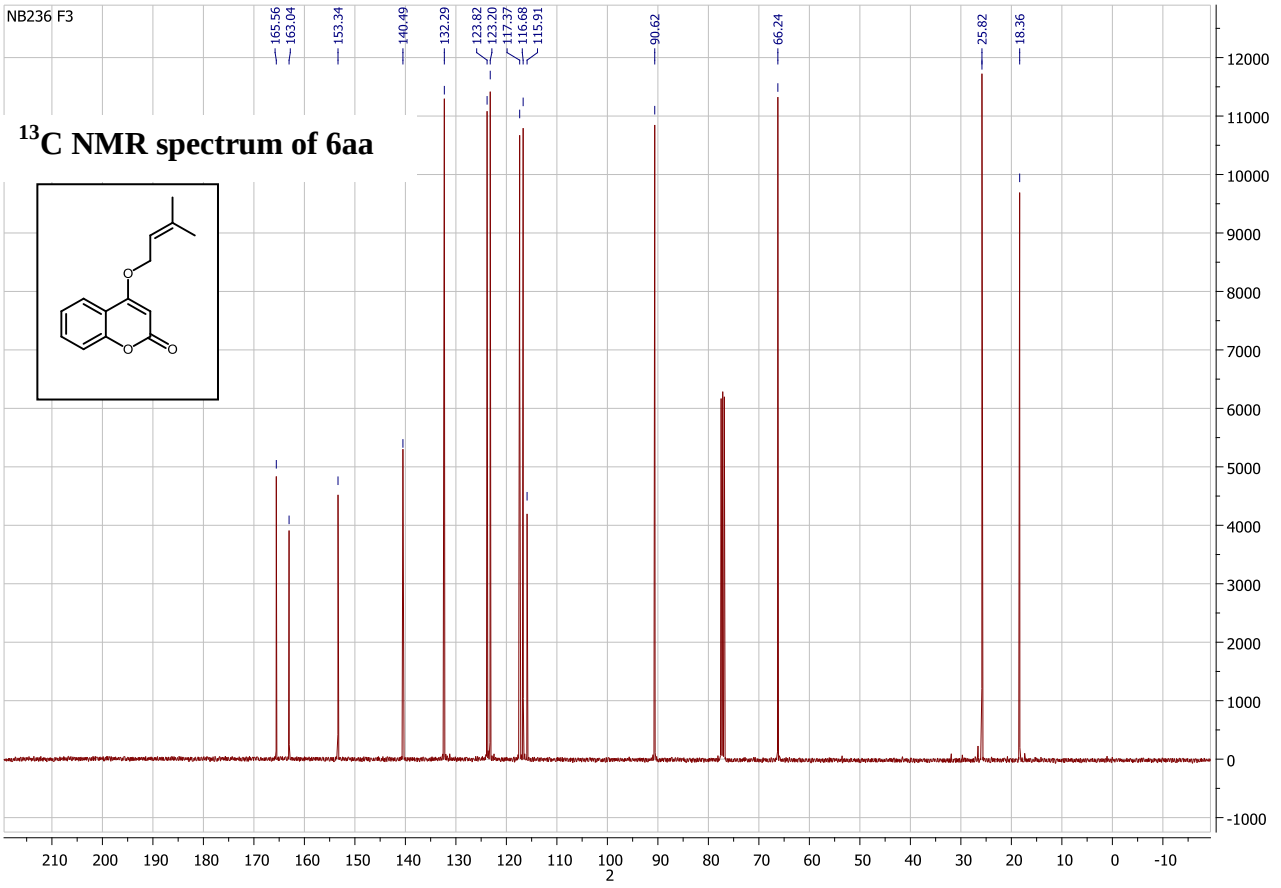


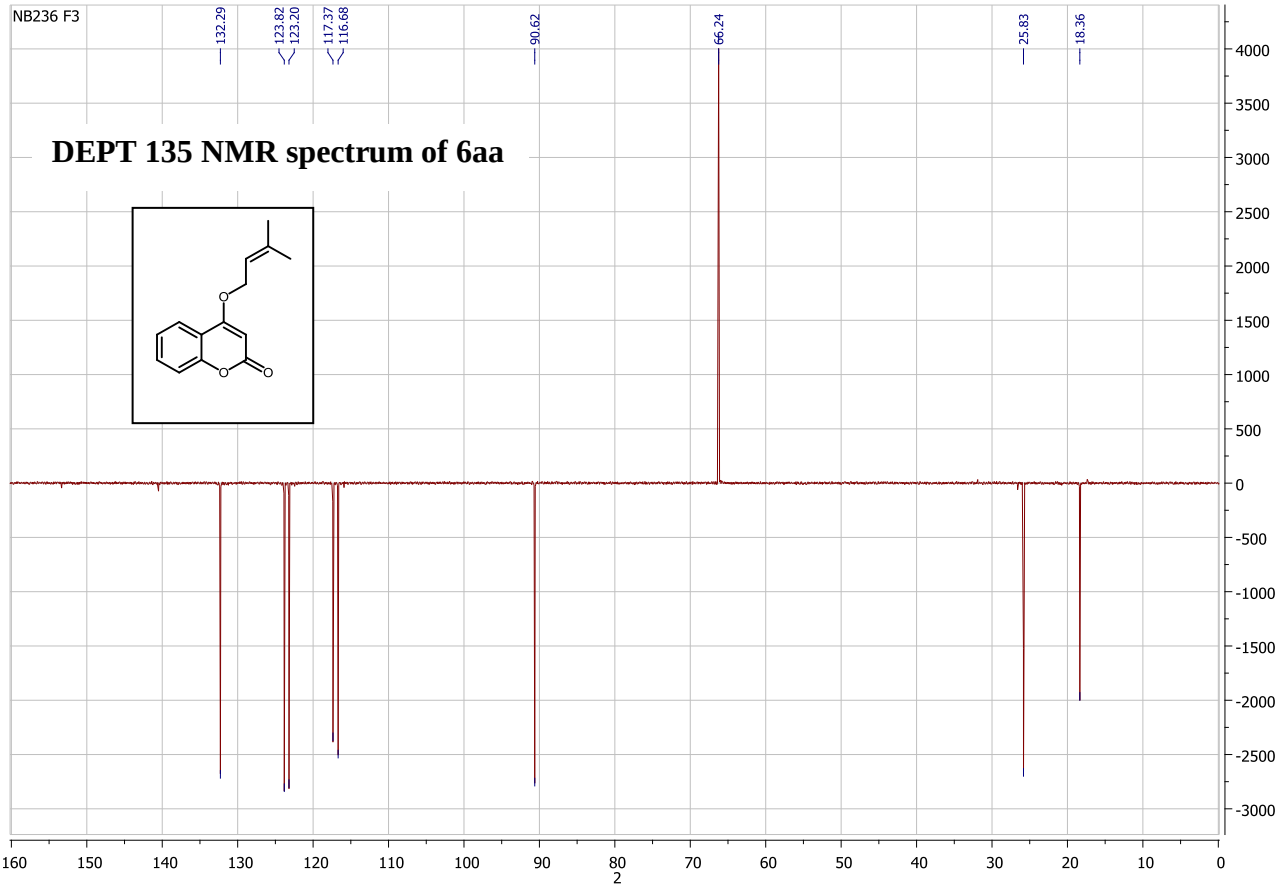
Cas number: 31490-69-4
Yield : 30%
6aa : white solid
TLC: Rf = 0.6 (PE/Et_2O:9/1)
Mp = 92 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.86 – 7.84 (d, *J* = 7.9, Hz, $1H_6$), 7.58 – 7.53 (t, *J* = 8.4 Hz, $1H_2$), 7.33 – 7.31 (d, *J* = 8.3 Hz, $1H_3$), 7.28 (t, *J* = 7.6 Hz, $1H_1$), 5.71 (s, $1H_9$), 5.54 (t, *J* = 6.8 Hz, $1H_{14}$), 4.71 – 4.70 (d, *J* = 6.8 Hz, $2H_{13}$), 1.86 (s, $3H_{16}$), 1.80 (s, $3H_{17}$).

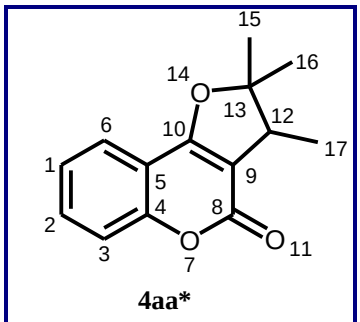
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 165.56 (C10), 163.04 (C8), 153.34 (C4), 140.49 (C15), 132.29 (C2), 123.82 (C6), 123.20 (C1), 117.37 (C14), 116.68 (C3), 115.91 (C5), 90.62 (C9), 66.24 (C13), 25.82 (C16), 18.36 (C17).


NB236 F3
^{1}H NMR spectrum of 6aa
7.86
7.86
7.84
7.58
7.57
7.56
7.54
7.53
7.33
7.31
7.30
7.28
7.26
5.71
5.55
5.54
5.52
4.71
4.70
1.86
1.80
1.00
1.00
1.01
1.00
1.00
1.00
2.01
3.00
3.00
f2


NB236 F3
^{13}C NMR spectrum of 6aa
165.56
163.04
153.34
140.49
132.29
123.82
123.20
117.37
116.68
115.91
90.62
66.24
25.82
18.36
f2



2. Synthesis of 2,2,3-trimethyl-2,3-dihydro-furo[3,2-*c*]chromen-4-one 4aa*.

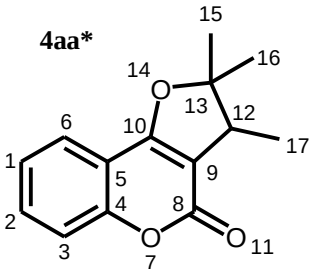


4aa*

Chemical Formula: $C_{14}H_{14}O_3$
Molecular Weight: 230,2592

The tricyclic compound **4aa*** (16.1 mg, 14 %) is obtained as a yellow solid, according to the general protocol **A**, starting from **6aa** (115 mg, 0.5 mmol), in the presence of $In(OTf)_3$, under reflux of $C_2H_4Cl_2$ for 24 hours. The crude of the reaction is purified by flash chromatography (PE/Et_2O:95/5).

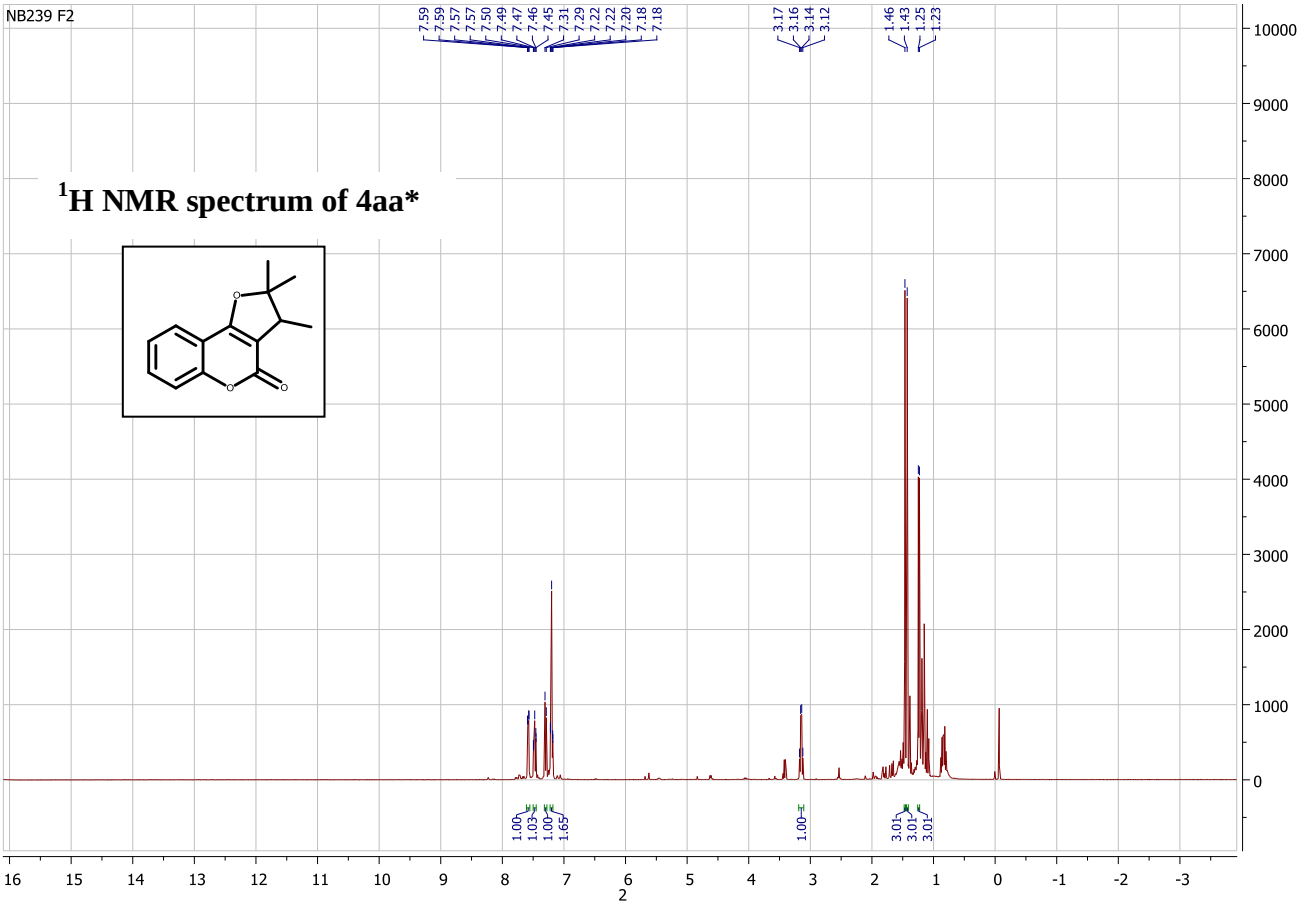
---------- 2,2,3-trimethyl-2,3-dihydro-furo[3,2-*c*]chromen-4-one 4aa* ----------

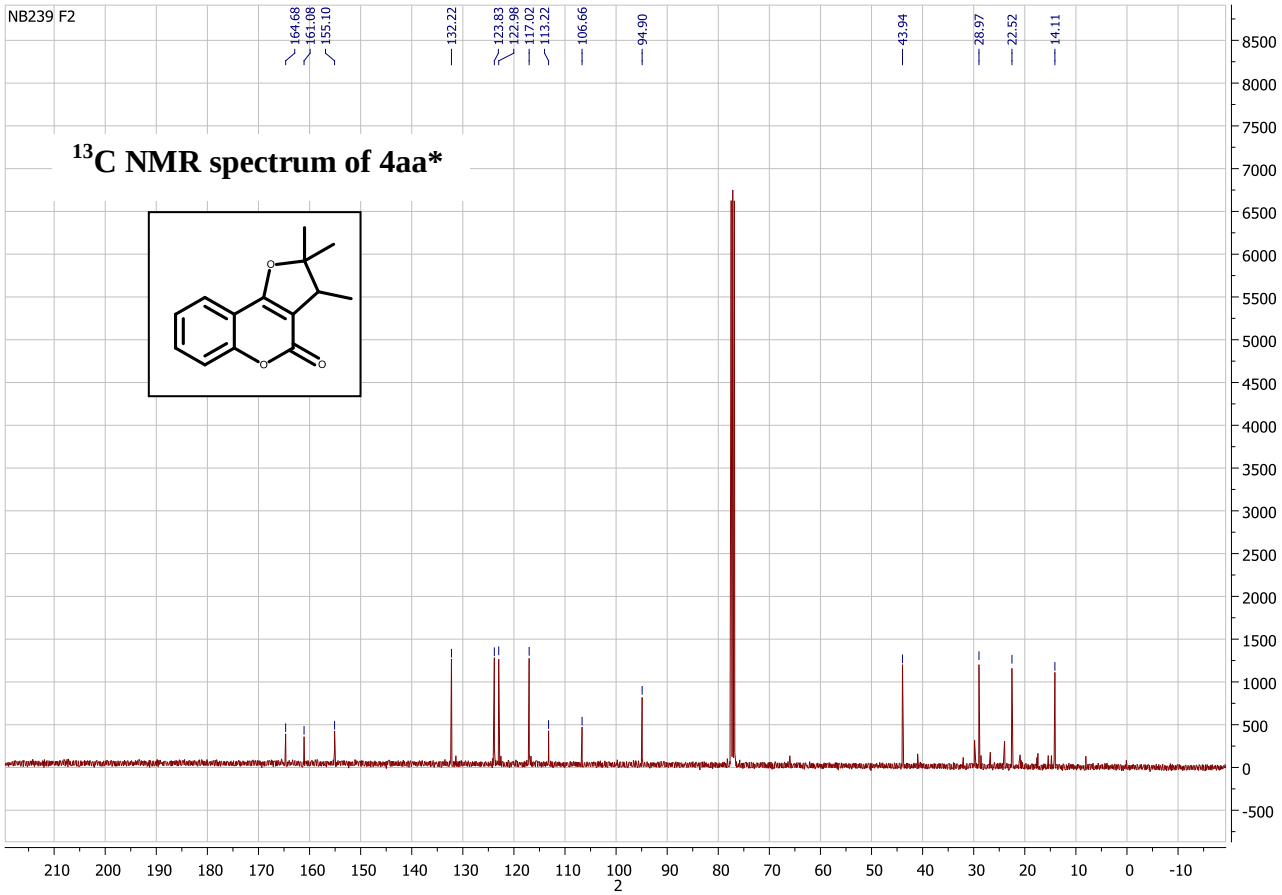


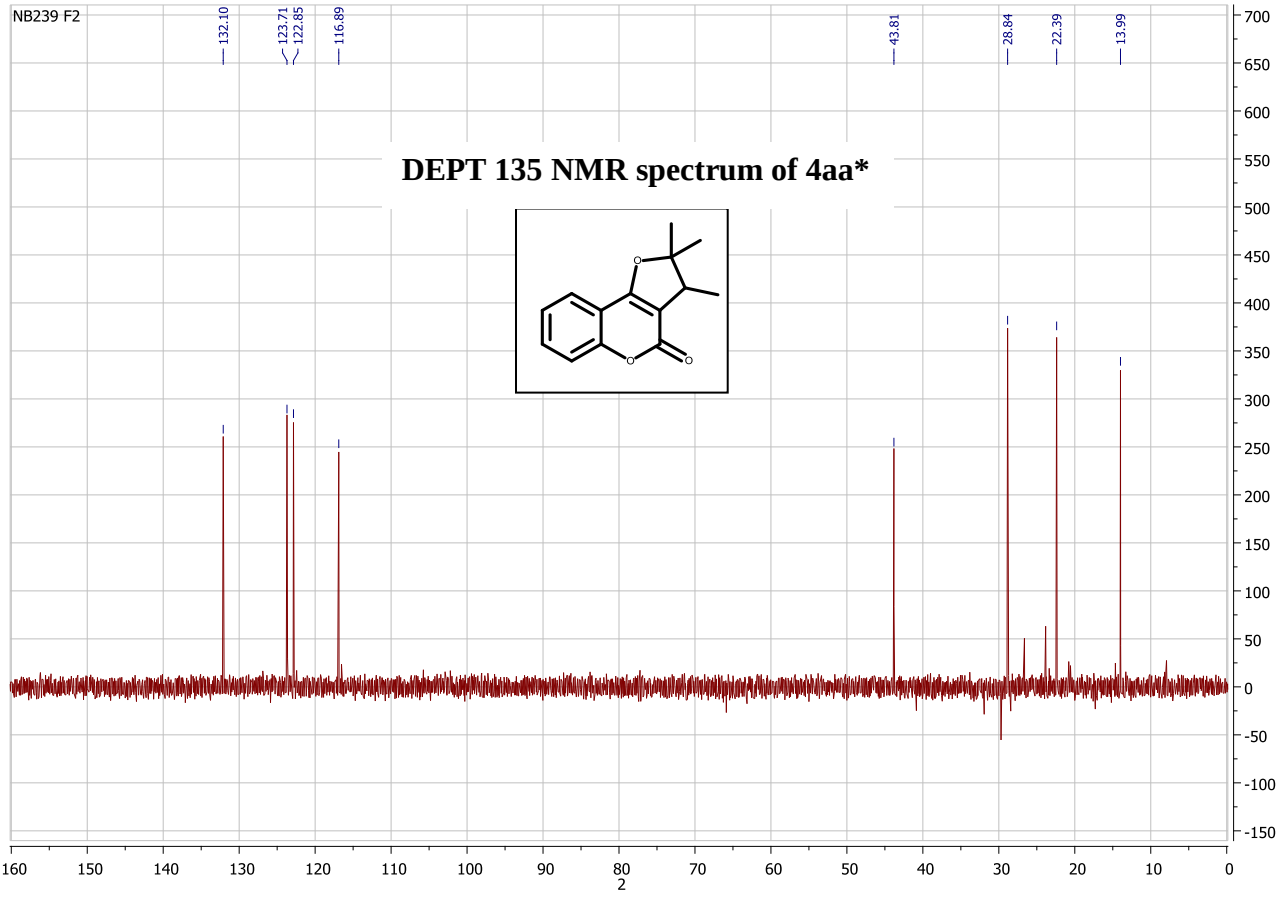
Cas number: 31581-57-4
Yield : 14%
4aa* : yellow solid
TLC: Rf = 0.75 (PE/Et_2O:9/1)
Mp = 85-86 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 7.59 – 7.57 (dd, *J* = 8 Hz, *J* = 1.6 Hz, $1H_6$), 7.50 – 7.45 (td, *J* = 8.8 Hz, *J* = 1.6 Hz, $1H_2$), 7.31 – 7.29 (d, *J* = 8 Hz, $1H_3$), 7.22 – 7.18 (td, *J* = 8 Hz, *J* = 1.6 Hz, $1H_1$), 3.17 – 3.12 (q, *J* = 7.2 Hz, $1H_{12}$), 1.46 (s, $3H_{15}$), 1.43 (s, $3H_{16}$), 1.25 – 1.23 (d, *J* = 6.8 Hz, $3H_{17}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm]: 164.68 (C10), 161.08 (C8), 155.10 (C4), 132.22 (C2), 123.83 (C1), 122.98 (C6), 117.02 (C3), 113.22 (C5), 106.66 (C9), 94.90 (C13), 43.94 (C12), 28.97 (C15), 22.52(C16), 14.11 (C17).




NB239 F2
164.68
161.08
155.10
132.22
123.83
122.98
117.02
113.22
106.66
94.90
43.94
28.97
22.52
14.11
^{13}C NMR spectrum of 4aa*
f2


NB239 F2
132.10
123.71
122.85
116.89
43.81
28.84
22.39
13.99
DEPT 135 NMR spectrum of 4aa*
f2

IV- Calculated total energies and geometrical coordinates of the structures.

#molecule	energies in Hartree	energies in kJ/mol
3#	-615.029746	-1614760.7211
4#	-615.040918	-1614790.0532
5#	-615.023734	-1614744.9366
6#	-615.014193	-1614719.8867
1#+2#	-615.413510	-1615768.2936
3+	-615.443316	-1615846.5492
4+	-615.446776	-1615855.6335
5+	-615.414339	-1615770.4701
6+	-615.396147	-1615722.7070
7+	-615.402322	-1615738.9195
TS3+	-615.407886	-1615753.5278
TS4+	-615.403137	-1615741.0593
TS5+	-615.366187	-1615644.0470
TS6+	-615.347997	-1615596.2892
TS7+	-615.392101	-1615712.0843
8#	-575.731350	-1511582.7746
9#	-575.720455	-1511554.1697
10#	-575.749219	-1511629.6896
11#	-575.737985	-1511600.1948
1#+7#	-576.101937	-1512555.7508
8+	-576.129833	-1512628.9918
9+	-576.107590	-1512570.5928
10+	-576.155722	-1512696.9633
11+	-576.156846	-1512699.9144
12+	-576.114778	-1512589.4649
TS8+	-576.082255	-1512504.0757
TS9+	-576.059101	-1512443.2849
TS10+	-576.115255	-1512590.7172
TS11+	-576.128526	-1512625.5602
TS12+	-576.086984	-1512516.4917

3#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.37014000	-1.62107800	-0.32740500
C	-0.20156400	-0.72454500	-0.07010400
C	-0.65985300	0.57127800	-0.14908600
C	-2.06261500	0.83241500	0.06880700
C	-2.93895200	-0.38441800	0.34413700
H	-2.41919400	-1.53578600	-1.41942200
H	-3.95207700	-0.19124200	-0.01941600
C	0.31811400	1.70404600	-0.35134500
C	1.68915800	1.16716300	-0.77752900
H	2.45467500	1.94459800	-0.68906100
C	2.12145200	-0.04715900	0.05521100
O	1.07575700	-1.09473900	-0.07867800
O	-0.97456200	-1.81474100	0.02840500
O	-2.54285000	1.97805300	0.08733700
H	1.65760700	0.86277900	-1.83050600
H	-0.06612400	2.38837400	-1.11529400
H	0.40290200	2.30028100	0.56678100
C	3.37599100	-0.70547900	-0.50962600
H	3.23832600	-0.96430100	-1.56348900
H	4.22178600	-0.01629200	-0.42878500
H	3.61848500	-1.61567600	0.04681200
C	2.27479900	0.26183300	1.54675700
H	2.56455800	-0.64060500	2.09260300
H	3.05500200	1.01639300	1.68754300
H	1.34774100	0.64496900	1.98076300
H	-3.00046400	-0.52773900	1.43126900
H	-2.86832100	-2.53867200	-0.01520400

.4#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.50249800	-1.50945400	-0.35109600
C	2.06424000	0.82317900	0.07528100
C	0.64245600	0.54038600	-0.11836100
C	0.19408800	-0.73907100	0.00246400
C	1.13900900	-1.88576600	0.20390400
H	2.47431000	-1.46308400	-1.44590400
H	3.27706400	-2.21278000	-0.04529400
H	1.19663700	-2.12904700	1.27316100
H	0.76058600	-2.77496600	-0.31046100
O	2.94252200	-0.22086600	0.14145500
O	2.51524900	1.95469600	0.22245700
O	-1.09762700	-1.10354200	-0.01640800
C	-0.31022400	1.68758100	-0.34004300
H	-0.42091700	2.27997400	0.57725600
H	0.09984000	2.37212000	-1.08986100
C	-1.66580400	1.14733300	-0.81231000
C	-2.13982300	-0.05117800	0.02289900
H	-2.43044500	1.92948800	-0.77059100
H	-1.58858500	0.82653600	-1.85802300
C	-2.37275900	0.30031700	1.49561100
H	-2.70004600	-0.58464400	2.04903500
H	-1.46588700	0.68580200	1.96890400
H	-3.15145900	1.06550200	1.57562000
C	-3.36914100	-0.71448200	-0.59099800
H	-4.21513800	-0.02082200	-0.57026300
H	-3.17917800	-0.99864600	-1.63029400
H	-3.64517900	-1.61080500	-0.02742200

5#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.90611500	0.07002200	1.16907900
C	1.53740500	-1.21457000	-0.34631800
C	0.67006100	-0.03714800	-0.49536500
C	1.16171300	1.18275400	-0.16020900
C	2.52685100	1.35005000	0.44252800
H	2.29595500	-0.05499300	2.07083700
H	3.96001100	0.05749500	1.44699500
H	3.25416100	1.59305100	-0.34380100
H	2.53316000	2.17885300	1.16034600
O	2.71712300	-1.09042400	0.33019500
O	1.28286800	-2.30897700	-0.83501700
O	0.42794600	2.29349400	-0.40895400
H	0.89607700	3.08942900	-0.11792800
C	-0.69873000	-0.23915300	-1.11787600
H	-1.02340200	0.69645700	-1.57502000
H	-0.59515300	-0.97616200	-1.92359300
C	-1.71886800	-0.74526200	-0.12085100
H	-1.45006800	-1.68712200	0.35845700
C	-2.89077500	-0.18448100	0.22790700
C	-3.43608500	1.10876100	-0.32994700
H	-3.64835700	1.81570500	0.48287200
H	-2.76084800	1.59867200	-1.03358500
H	-4.39029700	0.93181900	-0.84386700
C	-3.78942000	-0.84973300	1.24619300
H	-4.77433400	-1.07228200	0.81419300
H	-3.36163500	-1.78451600	1.62013000
H	-3.96835600	-0.18658600	2.10332500

6#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-3.06547300	-1.37682100	0.71543800
C	-3.03056300	0.89952700	-0.08184000
C	-1.57616300	0.79258800	-0.13409600
C	-0.96719200	-0.42260300	-0.15755700
C	-1.78182900	-1.67872700	-0.04224900
H	-2.85254600	-1.17514300	1.77145400
H	-3.77863100	-2.19832800	0.64790400
H	-1.04442500	1.72722200	-0.24697800
H	-1.99524400	-2.06558300	-1.04716200
H	-1.21065700	-2.44649000	0.48854000
O	-3.75808500	-0.22659200	0.17061600
O	-3.64288000	1.94202100	-0.28689900
O	0.34166700	-0.65292800	-0.30755600
C	1.24106300	0.48329100	-0.50745700
H	0.88172700	1.03542000	-1.38393100
H	1.17339400	1.13245100	0.36836200
C	2.61518200	-0.05432500	-0.73881600
H	2.73052100	-0.62305000	-1.66058200
C	3.69333400	0.10807800	0.05050900
C	3.71224300	0.86313100	1.35675400
H	2.73390900	1.23264400	1.66804400
H	4.10118900	0.21910800	2.15508100
H	4.39290900	1.72127800	1.28916400
C	5.02605900	-0.47801100	-0.34994100
H	4.96949900	-1.01489600	-1.30061600
H	5.78427000	0.31017800	-0.44255400
H	5.38850900	-1.17158300	0.41950500

1#+2#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	14.49468800	-0.65745900	-0.37942800
C	13.18194200	1.34098400	-0.05677000
C	12.17274400	0.49735400	0.57168700
C	12.15342400	-0.83960900	0.36456900
C	13.23107800	-1.50696900	-0.43962900
H	15.22977200	-0.97903100	-1.11691400
H	14.94291100	-0.71004700	0.61902900
H	11.38559400	0.99822100	1.12179100
H	13.45577300	-2.50309500	-0.04095200
H	12.88580100	-1.63856200	-1.47373200
O	14.23288900	0.73275000	-0.68240400
O	13.12330200	2.56415800	-0.09395200
O	11.13191600	-1.57709600	0.84572200
C	-20.12619500	2.03154600	0.32946300
H	-19.73983500	1.95795700	1.34010000
H	-20.40096500	3.02335300	-0.01578000
C	-20.27454600	0.95619100	-0.49034400
H	11.25586200	-2.51833700	0.65280900
C	-19.94622300	-0.37738200	-0.11228000
C	-19.43549800	-0.76229900	1.21735400
H	-18.60817200	-1.47257100	1.10306800
H	-19.13854000	0.06246500	1.86065500
H	-20.23552400	-1.33241400	1.71545300
C	-20.11246800	-1.44899500	-1.11397000
H	-20.88971000	-1.22722600	-1.84822800
H	-19.15702700	-1.49541500	-1.66779200
H	-20.25642800	-2.43006000	-0.65724500
H	-20.66804500	1.10609500	-1.49109800

3+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.34601200	-1.68919100	-0.31092600
C	-0.16473200	-0.78335600	-0.05615500
C	-0.65604500	0.54832000	-0.16028400
C	-2.00344900	0.72017100	0.06297900
C	-2.91204500	-0.43759000	0.33168800
H	-2.41366900	-1.65344100	-1.40175100
H	-3.90574000	-0.23172600	-0.07598400
C	0.31925700	1.68577000	-0.38013400
C	1.68945200	1.14768200	-0.81004200
H	2.43701900	1.94377900	-0.75875000
C	2.16180200	-0.01907100	0.05925100
O	1.09231300	-1.09220000	-0.00397600
O	-0.92702000	-1.84866500	0.01525000
O	-2.59972400	1.90070900	0.11645300
H	1.64519800	0.81066700	-1.85136800
H	-0.05397600	2.35391200	-1.16476300
H	0.41517400	2.28629800	0.53289300
C	3.38689300	-0.71128000	-0.52149900
H	3.21296300	-1.01209100	-1.55798000
H	4.23381600	-0.01982500	-0.49822400
H	3.64703800	-1.59500600	0.06679100
C	2.33966800	0.32352500	1.53641300
H	2.62285600	-0.56805800	2.10137500
H	3.13840800	1.06405200	1.63741900
H	1.43135400	0.73994900	1.97915000
H	-3.02285300	-0.55263900	1.41784300
H	-2.81520200	-2.59793400	0.05895800
H	-1.98567200	2.64343300	-0.01518400

4+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.44934900	1.60410200	-0.33925900
C	-2.01165800	-0.69487600	0.05000900
C	-0.62371900	-0.52846900	-0.09132500
C	-0.14687300	0.76848200	0.02612700
C	-1.08177300	1.92445800	0.23295600
H	-2.44299100	1.58351200	-1.43227100
H	-3.22355200	2.27964400	0.01646900
H	-1.13372300	2.13625500	1.30882100
H	-0.68168800	2.81796800	-0.25449900
O	-2.89671300	0.27059500	0.09213900
O	-2.50031500	-1.90552900	0.17463000
O	1.12138700	1.08488000	0.03016000
C	0.31249100	-1.69887900	-0.27183900
H	0.43534100	-2.24201500	0.67225200
H	-0.10996000	-2.41079700	-0.98655000
C	1.65980200	-1.18088700	-0.79145600
C	2.18569700	0.01561700	0.00896300
H	2.41046400	-1.97531100	-0.75427300
H	1.55700800	-0.88178900	-1.84068000
C	2.48559000	-0.30604800	1.47270900
H	2.80619600	0.59456400	2.00287000
H	1.61585800	-0.72064400	1.98896300
H	3.29443300	-1.04126800	1.52081300
C	3.36363300	0.69356600	-0.67876600
H	4.21042200	0.00206100	-0.71183100
H	3.10838800	0.97806800	-1.70328400
H	3.67027800	1.58726300	-0.12847300
H	-3.47439600	-1.88946700	0.21751800

5+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	3.18594900	-0.72038800	0.69802200
C	1.09277600	-1.18547000	-0.39344000
C	0.73036100	0.22532900	-0.22255000
C	1.71072700	1.13574600	0.01915300
C	3.13991000	0.71577600	0.20064500
H	2.83840000	-0.78165700	1.73501600
H	4.18924000	-1.13956700	0.63181800
H	3.67376700	0.82707000	-0.75263000
H	3.64083000	1.36039000	0.93204300
O	2.35354300	-1.59233300	-0.10372400
O	0.30118600	-2.02348000	-0.82042000
O	1.41357000	2.44988100	0.03816700
H	2.19524800	2.98389400	0.24382700
C	-0.70418500	0.61225000	-0.49552700
H	-0.82525600	1.68404700	-0.32301100
H	-0.93516400	0.41952100	-1.54892600
C	-1.68537100	-0.16600800	0.39503100
H	-1.57096300	-1.25303900	0.15939900
C	-3.11921800	0.00568800	0.21208400
C	-3.67183900	0.58061500	-1.02100900
H	-4.75636600	0.67697300	-1.00408600
H	-3.19369200	1.54661700	-1.23059800
H	-3.37488700	-0.06522600	-1.86299100
C	-4.03209400	-0.43149200	1.27358200
H	-4.92942800	-0.90483900	0.86242100
H	-3.55627500	-1.04368400	2.04004300
H	-4.38931600	0.50221000	1.74696100
H	-1.43462800	-0.11752900	1.46258100

6+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.74120400	1.67920800	0.07582100
C	3.07355900	-0.70631400	0.20648900
C	1.61530200	-0.84580800	0.18548400
C	0.83451700	0.16187000	-0.26981900
C	1.43336600	1.47500900	-0.67538900
H	2.55217000	1.87072000	1.13790300
H	3.31870000	2.50564100	-0.33727100
H	1.23966400	-1.82148100	0.46228400
H	1.59213200	1.48173600	-1.76140200
H	0.74421200	2.29223600	-0.44130500
O	3.60991600	0.52299500	-0.02196300
O	3.83480500	-1.64838000	0.38077600
O	-0.50298900	0.11106500	-0.44370400
C	-1.18890700	-1.12322900	-0.17207800
H	-0.75533900	-1.92717800	-0.77353100
H	-1.08247800	-1.38339400	0.88652000
C	-2.64350700	-0.93711400	-0.57404400
H	-3.17376500	-1.90539000	-0.51943900
C	-3.49524600	0.01143800	0.16424600
C	-3.00783600	0.73998900	1.33353800
H	-2.10035900	1.29224200	1.04691100
H	-3.74877500	1.40189000	1.77772000
H	-2.65077500	0.01052900	2.07819400
C	-4.86970300	0.21649400	-0.29358900
H	-5.15409100	-0.38941500	-1.15246200
H	-5.55033000	0.04842000	0.55460600
H	-4.99024700	1.28815600	-0.52121400
H	-2.73105700	-0.67941500	-1.64234700

7+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	3.08801300	0.81261900	0.76721700
C	1.97096900	-1.13455600	-0.09012500
C	0.66363700	-0.34755000	0.26399500
C	0.84159100	1.02653000	-0.24417900
C	2.10805000	1.73891400	0.04662000
H	2.83172000	0.68560100	1.82233500
H	4.10365600	1.19526300	0.69462300
H	2.52586700	2.11612500	-0.89663400
H	1.88598400	2.62178100	0.66358500
O	3.12652200	-0.49061800	0.13370100
O	1.94352300	-2.25342100	-0.53210500
O	-0.08649900	1.52335300	-0.96537600
H	0.09055600	2.42886300	-1.29443000
C	-0.63581000	-1.08042400	-0.10993400
H	-0.79041700	-1.01808100	-1.18894800
H	-0.46116400	-2.13727300	0.11685700
C	-1.82186900	-0.57923700	0.67675900
H	-1.69842700	-0.63405600	1.75938100
C	-2.99943500	-0.13097800	0.20713900
C	-3.36358700	-0.00900500	-1.25187400
H	-3.67644200	1.01768700	-1.48010400
H	-2.55339300	-0.27596300	-1.93237200
H	-4.22173100	-0.65327200	-1.48167700
C	-4.09509700	0.28294700	1.16162000
H	-4.38811300	1.32647300	0.98821500
H	-4.99601000	-0.32393800	1.00462300
H	-3.79026200	0.17912100	2.20667700
H	0.73104000	-0.23839100	1.36468100

TS3+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.95539300	-1.06037200	-0.69367100
C	-0.82600800	-1.13215000	0.42668800
C	-0.73449900	0.32911500	0.26851400
C	-1.86642700	1.03882600	0.00816200
C	-3.18431600	0.35396500	-0.19060400
H	-2.59005400	-1.05310500	-1.72646200
H	-3.78364700	0.91188300	-0.91651900
C	0.62920000	0.91602700	0.54501800
C	1.63284600	0.57854200	-0.58589300
H	1.84003900	1.48145700	-1.19874000
C	2.98706600	0.12648900	-0.26247700
O	0.10602700	-1.80234900	0.85960100
O	-1.98254600	-1.76646900	0.11654800
O	-1.95930900	2.37858700	-0.06169300
H	1.21246700	-0.10845100	-1.33302500
H	0.58792500	1.99972400	0.68337200
H	0.98139900	0.50828600	1.49499900
C	3.79610500	-0.49684100	-1.31543500
H	3.91131300	-1.55565400	-1.02090800
H	3.34572900	-0.45400300	-2.30680600
H	4.81506200	-0.09392300	-1.31223200
C	3.54669400	0.26744700	1.08406100
H	3.00045000	-0.45108800	1.72138400
H	4.61227000	0.04995700	1.13768200
H	3.31504300	1.25021700	1.51087800
H	-3.73668100	0.35704000	0.75808700
H	-3.86189600	-1.66223200	-0.64105800
H	-1.11440600	2.81545700	0.12751200

TS4+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	3.02176400	-0.81712100	-0.85010300
C	1.85837300	0.99196500	0.14573200
C	0.69705800	0.26787300	0.27944700
C	0.77016700	-1.17292300	0.18919700
C	2.14300200	-1.77603500	-0.06880400
H	2.65236100	-0.67437900	-1.87128000
H	4.06546300	-1.12595100	-0.87982600
H	2.59690800	-2.01759600	0.90122600
H	2.03060400	-2.71280600	-0.62125900
O	3.04175400	0.50054000	-0.22096400
O	1.90194500	2.29898700	0.40853100
O	-0.22415100	-1.89861000	0.36387200
C	-0.61575200	0.91512600	0.65748600
H	-0.96640100	0.46962200	1.59193400
H	-0.46477400	1.97706900	0.85761600
C	-1.69443500	0.78420800	-0.44095800
C	-2.98802600	0.15623600	-0.16632400
H	-1.85251500	1.71577800	-0.99894400
H	-1.34529800	0.09172200	-1.24144900
C	-3.19884200	-0.68009400	1.01363700
H	-4.16665300	-1.17811100	1.02915600
H	-2.36226300	-1.40113200	1.05027800
H	-3.06977600	-0.07073000	1.92007800
C	-4.07305400	0.31987700	-1.14234200
H	-4.81944200	0.96429800	-0.64361400
H	-3.76566700	0.79889800	-2.07193600
H	-4.59153100	-0.62822900	-1.32102400
H	2.78105600	2.64953100	0.18572200

TS5+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.54769300	0.18266100	1.37982000
C	1.53731900	-1.19629100	-0.31808000
C	0.54758700	-0.08148700	-0.51359000
C	1.00399600	1.21823500	-0.25155500
C	2.21600600	1.44113600	0.58823300
H	1.82179700	0.01762800	2.18176800
H	3.54578600	0.23897400	1.81029800
H	3.04111400	1.71235300	-0.08643700
H	2.06904100	2.28366100	1.27369600
O	2.56665500	-0.98839400	0.52769900
O	1.43991700	-2.25587100	-0.90370900
O	0.34183300	2.23104400	-0.76229000
H	0.69165300	3.09326600	-0.47776000
C	-0.66047700	-0.37057000	-1.41720900
H	-1.01124400	0.53016300	-1.91811800
H	-0.43405300	-1.13623600	-2.15906800
C	-1.60231200	-0.87947600	-0.32317100
H	-1.47003000	-1.93039400	-0.06520800
C	-2.66867100	-0.21937800	0.25586600
C	-3.13489600	1.14368400	-0.14437900
H	-3.18384000	1.80181200	0.73061200
H	-2.52330100	1.61428400	-0.91287600
H	-4.16255200	1.06080200	-0.52167200
C	-3.41660600	-0.86936400	1.37853700
H	-3.42115900	-0.22172400	2.26309200
H	-4.46635200	-0.99697900	1.08418700
H	-3.00700300	-1.84493800	1.64569700
H	-0.49491500	-0.33179700	0.45136800

TS6+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.73552100	-1.70837500	0.25183300
C	3.15348700	0.64882900	-0.06840700
C	1.72290100	0.87302700	0.22113000
C	0.85923900	-0.14545600	0.10801300
C	1.28732500	-1.54383200	-0.19697100
H	3.17910100	-2.61508400	-0.15674000
H	2.80019100	-1.73532300	1.34419400
H	1.43681000	1.89246500	0.44430000
H	0.65861300	-2.26177400	0.33899900
H	1.17113800	-1.73882800	-1.27092800
O	3.58121600	-0.62757800	-0.22011300
O	3.94278300	1.56464300	-0.22404500
O	-0.51261200	0.00303300	0.27131300
C	-1.26571200	1.32007200	0.14196900
H	-1.46534400	1.68378800	1.14698600
H	-0.66745300	2.01989800	-0.43674000
C	-2.40481200	0.72569800	-0.64776400
H	-1.49382200	-0.37702000	-0.44666900
C	-3.48315000	0.05675300	-0.09605000
C	-3.68423000	-0.13828100	1.37032000
H	-3.89025600	-1.19097800	1.58887200
H	-2.85370600	0.20206800	1.98708300
H	-4.58421900	0.41909100	1.66099600
C	-4.51477300	-0.53700100	-0.99813800
H	-4.28738900	-0.38789900	-2.05423700
H	-4.63240600	-1.60628200	-0.79212500
H	-5.48234000	-0.07061500	-0.77258900
H	-2.41478900	0.93710500	-1.71425200

TS7+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-3.04266900	-1.09023500	0.18045000
C	-0.73549800	-1.16274000	-0.54460200
C	-0.74030400	0.31620000	-0.62888200
C	-1.84026400	1.03407000	-0.17273200
C	-2.89696300	0.35994200	0.63905000
H	-3.52131100	-1.13997700	-0.80218100
H	-3.62860200	-1.66805600	0.89305700
H	-2.61401300	0.40772500	1.70003200
H	-3.85662800	0.87683300	0.53689400
O	-1.76724700	-1.77113300	0.09274900
O	0.18900300	-1.83288000	-0.96346400
O	-1.88161100	2.32850100	-0.41033600
H	-2.66246800	2.75622500	-0.01837600
C	0.66964900	0.92606300	0.96038200
H	0.76931700	1.90429200	0.50460700
H	-0.04299100	0.86597900	1.77485500
C	1.74327600	0.01305600	0.97071400
H	1.65969600	-0.84329900	1.63316800
C	2.89569600	0.13233600	0.21957300
C	3.13693300	1.20402500	-0.79272100
H	3.18306400	0.74280200	-1.78835100
H	2.37844200	1.98588700	-0.81309700
H	4.11649800	1.66560800	-0.62472600
C	3.99617500	-0.86197300	0.39779800
H	4.23884500	-1.32540800	-0.56699000
H	4.91007000	-0.35175800	0.72760900
H	3.74327200	-1.64305800	1.11612600
H	-0.11053800	0.74584000	-1.39840700

8#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.94592600	-0.15775300	-0.09587000
C	0.81541800	-1.29355400	-0.08970400
C	0.17109000	-0.00581800	-0.37539700
C	0.85678100	1.14045800	-0.12658300
C	2.27599200	1.12768800	0.36047700
H	3.89999900	-0.31854100	0.40575800
H	3.10770400	-0.14404600	-1.17952100
H	2.83189100	1.98153100	-0.04353300
H	2.28968000	1.21883600	1.45481000
O	2.14345100	-1.31712200	0.22500400
O	0.21885200	-2.36493900	-0.08485000
O	0.23512100	2.33079000	-0.27476400
H	0.84716100	3.06505400	-0.11732300
C	-1.25824900	-0.01661800	-0.85867400
H	-1.41464500	0.84066400	-1.52623200
H	-1.41127800	-0.91005700	-1.47602400
C	-2.35448900	0.01276800	0.19883500
C	-2.12185000	0.11494200	1.51408300
H	-1.11523000	0.17918400	1.91660300
H	-2.94037800	0.13628000	2.22864100
C	-3.75258900	-0.07744600	-0.36353100
H	-4.50913500	-0.03354400	0.42462600
H	-3.94381300	0.73972500	-1.07128200
H	-3.88954100	-1.01291700	-0.92146200

9#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.54035700	1.54007400	0.06714600
C	-2.54371600	-0.87199900	0.14207000
C	-1.08941300	-0.81021400	0.23376600
C	-0.41663100	0.30878400	-0.14382900
C	-1.16662400	1.53199400	-0.58493100
H	-3.19538300	2.28870400	-0.37791100
H	-2.45747100	1.73100900	1.14284000
H	-0.59992000	-1.73001300	0.52274800
H	-0.61636600	2.43251600	-0.29590100
H	-1.24597900	1.53350100	-1.67971100
O	-3.23157200	0.27705200	-0.10979100
O	-3.18740200	-1.91222900	0.24486000
O	0.91184800	0.45121400	-0.20627800
C	1.75893600	-0.68063600	0.13907400
H	1.52821200	-0.97112300	1.17178500
H	1.52589900	-1.51322100	-0.53105700
C	3.19607100	-0.25014800	0.00976800
C	4.01067300	-0.88768700	-0.84159300
H	5.06233100	-0.62639200	-0.92144400
H	3.65409800	-1.69392200	-1.47692000
C	3.64702800	0.87350500	0.90788300
H	4.70673800	1.09745600	0.76214000
H	3.07086200	1.78531800	0.71411100
H	3.48817700	0.61582900	1.96286200

10#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.47748500	-1.24615800	0.32240400
C	-1.70615200	1.03845100	-0.00802400
C	-0.36729900	0.50388800	0.06375700
C	-0.12865800	-0.81726000	-0.11823900
C	-1.20718600	-1.82644500	-0.30114800
H	-2.40504900	-1.26842500	1.41540000
H	-3.36519600	-1.79729000	0.01294300
H	-1.33922900	-2.03678600	-1.37042400
H	-0.95575600	-2.77153200	0.19045100
O	-2.73094800	0.12743200	-0.07650000
O	-1.99471000	2.23129400	-0.06209200
O	1.16101100	-1.15950700	-0.16518300
C	0.94261700	1.24374600	0.14321500
H	1.05831200	1.96748600	-0.67158900
H	1.06293900	1.79080300	1.08467800
C	1.98756500	0.08702500	0.02721300
C	2.87610100	0.20107300	-1.20456600
H	3.52350500	-0.67582400	-1.30025700
H	2.27137100	0.29455400	-2.11165600
H	3.50865100	1.09058300	-1.11992800
C	2.78179400	-0.12800700	1.31010100
H	2.11098500	-0.25584200	2.16521700
H	3.42104800	-1.01209400	1.22770100
H	3.41783300	0.74274500	1.49938900

11#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.37275600	-1.39581900	-0.25681900
C	-0.13699900	-0.80181300	0.00613100
C	-0.38266100	0.53992600	-0.14782300
C	-1.70866400	1.04973500	-0.02421400
C	-2.75869800	-0.02400100	0.28297000
H	-2.40088900	-1.41203300	-1.35131300
H	-3.71649600	0.27025700	-0.15618700
C	0.94520000	1.23945200	-0.28757900
C	1.97100800	0.09836000	0.00415400
O	1.13776100	-1.16236000	0.04389900
O	-1.01158600	-1.78662600	0.12869300
O	-2.01959300	2.25378400	-0.08249600
H	1.09551400	1.65610000	-1.29070200
H	1.06392300	2.06026000	0.42760600
C	2.99034600	-0.10583800	-1.10611700
H	2.49229900	-0.26242300	-2.06735700
H	3.62150600	0.78491800	-1.18669800
H	3.63268800	-0.96595000	-0.89498900
C	2.61040500	0.21870900	1.38239300
H	1.84570000	0.32569400	2.15795900
H	3.21972200	-0.66195000	1.60563700
H	3.25435600	1.10342100	1.41055900
H	-2.89643700	-0.05939100	1.37171600
H	-3.00763000	-2.18955200	0.13441700

1#+7#
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-12.29941100	-0.31366900	-0.99184300
C	-10.99288400	1.35417700	0.16352200
C	-9.97215100	0.33230000	0.34897900
C	-10.27402700	-0.98289800	0.23817800
C	-11.64889500	-1.42168900	-0.17363200
H	-13.36624700	-0.48840500	-1.12801400
H	-11.82092200	-0.23148000	-1.97384400
H	-8.99527500	0.66486600	0.67806600
H	-11.60276900	-2.33139400	-0.78323100
H	-12.23898900	-1.65807900	0.72171600
O	-12.20434900	0.97536300	-0.33748600
O	-10.84372400	2.53333800	0.46798100
O	-9.34590600	-1.90985400	0.54459600
C	21.16945300	-0.13412500	1.37639400
H	21.96300700	0.27972800	1.99387900
H	20.35903100	-0.64772700	1.88530000
C	21.18886700	-0.01552100	-0.00804100
C	22.29865800	0.69546300	-0.74007800
H	22.30288800	1.75721000	-0.47650900
H	22.17829900	0.60709400	-1.82048400
C	20.10638200	-0.60213700	-0.64919600
H	20.00594500	-0.58242100	-1.73125900
H	19.32369900	-1.10202500	-0.08613700
H	-9.68178900	-2.80623600	0.39418600
H	23.26899400	0.27669300	-0.46010600

8+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.72506900	-0.39477100	0.68382400
C	1.19057600	1.27942100	-0.11944100
C	0.20372400	0.20843800	-0.30553500
C	0.61369700	-1.08541200	-0.37766100
C	2.04975800	-1.45723100	-0.17169300
H	3.80905200	-0.49784000	0.67045600
H	2.36996500	-0.44632700	1.71805600
H	2.12899700	-2.42588800	0.33427200
H	2.53894200	-1.55608000	-1.14964100
O	2.46483600	0.94388400	0.18937300
O	0.91666600	2.46476700	-0.27261100
O	-0.28994000	-2.03256500	-0.67744300
H	0.10828700	-2.91638400	-0.70611200
C	-1.20182300	0.62991200	-0.63424400
H	-1.25770100	1.73634900	-0.51522800
H	-1.46277700	0.48318200	-1.69119400
C	-2.31039300	0.18228200	0.21387000
C	-2.08141300	-0.32482900	1.56695500
H	-1.18826700	0.10899200	2.02502600
H	-2.96067000	-0.25317900	2.20676800
C	-3.67192300	0.23216900	-0.32838900
H	-4.40683200	0.51276800	0.42998300
H	-3.75614800	0.83679300	-1.23233000
H	-3.90850800	-0.81250600	-0.60425500
H	-1.85048100	-1.39844400	1.43352700

9+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.64648000	1.44124200	0.38376400
C	-2.56872400	-0.93439000	-0.03612400
C	-1.11015000	-0.84472000	0.08947000
C	-0.48841600	0.34726100	-0.04420600
C	-1.26523200	1.61328200	-0.23124200
H	-3.32296000	2.24095200	0.08496000
H	-2.58397400	1.41267000	1.47671200
H	-0.59647100	-1.79022900	0.19946700
H	-0.74850400	2.44605300	0.25519000
H	-1.32869300	1.84630600	-1.30180900
O	-3.28892600	0.21629400	-0.05785000
O	-3.16425200	-1.99649500	-0.16229100
O	0.85307200	0.54832400	-0.05871300
C	1.71279600	-0.56445200	0.04859000
H	1.55266200	-1.12446900	0.98684500
H	1.55796600	-1.29211800	-0.76806000
C	3.12646700	-0.16186500	0.01274300
C	4.13935900	-1.20814700	0.11557100
H	4.77847400	-1.14417500	-0.77953700
H	3.74292000	-2.21558700	0.23375000
C	3.49256900	1.23985600	-0.11835600
H	4.56571400	1.40837200	-0.17390500
H	2.96308800	1.66825400	-0.98276900
H	3.05020600	1.78213600	0.73472200
H	4.81729400	-0.95155200	0.94400900

10+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.44099200	-1.33272700	0.31318500
C	-1.68192600	0.90750100	-0.00443600
C	-0.35130800	0.49079000	0.06444100
C	-0.08825700	-0.85329900	-0.11048600
C	-1.15623100	-1.86847400	-0.31155300
H	-2.39805300	-1.36459000	1.40490800
H	-3.32331500	-1.86125600	-0.03927400
H	-1.26707100	-2.04959500	-1.38841200
H	-0.89054700	-2.82019500	0.15651100
O	-2.69230900	0.07082500	-0.04396800
O	-2.09367000	2.15372300	-0.06528900
O	1.17740600	-1.15859800	-0.15154200
C	0.95212400	1.24866100	0.14276100
H	1.07187800	1.96428200	-0.67676900
H	1.06295000	1.79142700	1.08605400
C	2.01288100	0.10582000	0.03067400
C	2.88276500	0.20517600	-1.21216200
H	3.53250700	-0.66953300	-1.30132900
H	2.27083400	0.28942000	-2.11476200
H	3.51188300	1.09735800	-1.13747700
C	2.80778800	-0.10899700	1.30958700
H	2.14409700	-0.23379800	2.17003400
H	3.44866700	-0.99036900	1.22250800
H	3.44266400	0.76434700	1.48755600
H	-1.35896600	2.78819500	-0.11522300

11+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.33697400	-1.47382700	-0.23205700
C	-0.08956000	-0.86496600	0.00111000
C	-0.36751900	0.50869800	-0.17745500
C	-1.65874600	0.92672300	-0.03298100
C	-2.72796700	-0.08814400	0.26977900
H	-2.39238100	-1.53812500	-1.32089000
H	-3.66979100	0.18628500	-0.21647700
C	0.94499900	1.22580600	-0.34307500
C	1.99601400	0.12827900	0.00612200
O	1.16804300	-1.16406000	0.06862900
O	-0.94942700	-1.83148300	0.12413400
O	-1.94028600	2.22082000	-0.07641200
H	1.08002400	1.58495600	-1.36825500
H	1.03776700	2.08300600	0.32864900
C	3.03170000	-0.10569000	-1.07812500
H	2.55460900	-0.30530800	-2.04130900
H	3.64652200	0.79408500	-1.17755400
H	3.68491500	-0.94330300	-0.82002800
C	2.59447400	0.28771200	1.39528700
H	1.81414500	0.41297700	2.15167200
H	3.20711400	-0.57962000	1.65442800
H	3.23027100	1.17803300	1.40675300
H	-2.90826000	-0.08570000	1.35271500
H	-2.94298500	-2.25556000	0.21901000
H	-2.88712000	2.39851100	0.04883900

12+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.62350900	0.35716500	0.95129100
C	-1.30215700	-1.18110100	-0.34536600
C	-0.10665400	-0.24567100	0.02563200
C	-0.55297600	1.15468300	-0.14428200
C	-1.90177700	1.54578600	0.32386200
H	-3.69098600	0.55062400	1.02863600
H	-2.23352300	0.11698300	1.94385600
H	-1.81521100	2.37531400	1.03864100
H	-2.45612800	1.93788700	-0.54159800
O	-2.51076400	-0.81513300	0.10357500
O	-1.15182100	-2.18730300	-0.99188800
O	0.23664300	1.96300000	-0.73376300
H	-0.10247700	2.87870600	-0.81935800
C	1.22306500	-0.64623900	-0.64292900
H	1.21374800	-1.73915600	-0.69941200
H	1.23207700	-0.27660600	-1.67153900
C	2.47044600	-0.19643600	0.09886800
C	3.34564500	0.64179600	-0.47186200
H	-0.03457600	-0.36073300	1.12485100
H	4.26450400	0.92811100	0.03240000
C	2.70723300	-0.80463000	1.46106700
H	1.92124400	-0.53805600	2.17944000
H	2.71927900	-1.90015400	1.40118600
H	3.65958500	-0.47165400	1.88078900
H	3.17410700	1.06210800	-1.45896900

TS8+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.50682000	-0.47770100	0.91573000
C	-0.59380000	-1.34752200	-0.26282500
C	-0.07864900	0.06770200	-0.29625100
C	-1.05445300	1.07630500	-0.34202400
C	-2.45317600	0.80211000	0.09329400
H	-3.53129100	-0.82104200	1.04543000
H	-2.04849900	-0.33758800	1.89885600
H	-2.84865100	1.63932700	0.67881300
H	-3.07115700	0.71823600	-0.81221400
O	-1.82327000	-1.56428900	0.24259300
O	0.06054000	-2.28581800	-0.67431800
O	-0.69751900	2.27265800	-0.74260300
H	-1.41229900	2.92923500	-0.66485800
C	1.30662100	0.25706200	-0.92488200
H	1.53297700	-0.56961000	-1.59961000
H	1.35797900	1.18717300	-1.50120800
C	2.29324100	0.30138100	0.23112000
C	1.82354300	0.89751900	1.38005800
H	0.54265900	0.26263500	0.99660800
H	2.35874900	0.78454500	2.31759400
C	3.57800100	-0.43030800	0.12560600
H	4.17110300	0.04202200	-0.67104600
H	4.15296900	-0.40486800	1.05180300
H	3.41409000	-1.46562300	-0.19538400
H	1.17630700	1.77586200	1.33088600

TS9+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.39723500	1.46133200	0.66657300
C	-2.60312100	-0.84504500	-0.02019200
C	-1.13087800	-0.88272600	-0.10738500
C	-0.44604100	0.26587000	-0.19146700
C	-1.09807900	1.60760600	-0.11819700
H	-3.03049200	2.33950600	0.55183300
H	-2.19168000	1.30000800	1.72919900
H	-0.68822100	-1.86523700	-0.20085300
H	-0.45477000	2.33060200	0.39247400
H	-1.27630900	1.98323100	-1.13348100
O	-3.20259200	0.34908100	0.19432100
O	-3.29565600	-1.83685600	-0.18207400
O	0.92002500	0.31420500	-0.42857600
C	1.82061900	-0.85559400	-0.39740300
H	1.50087600	-1.55222900	0.37725400
H	1.80752200	-1.32338500	-1.38416800
C	3.12711200	-0.17366200	-0.04669700
C	4.05372500	-0.86491200	0.88467800
H	3.53508200	-1.17546000	1.79871600
H	4.91862300	-0.24893500	1.13035100
C	3.24769500	1.12544500	-0.46512500
H	4.03678500	1.75146700	-0.06505100
H	2.79173100	1.47835800	-1.39275200
H	1.83086300	1.12750200	-0.10045200
H	4.40299800	-1.78675700	0.39885300

TS10+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.70162800	-0.45608400	0.68958400
C	-1.14602000	1.16507400	-0.07392300
C	-0.19038600	0.20238900	-0.34111100
C	-0.60668000	-1.18486300	-0.44676200
C	-2.08616000	-1.46575700	-0.25976300
H	-2.31126200	-0.56700500	1.70652600
H	-3.78903000	-0.50227900	0.71005800
H	-2.57116000	-1.42041500	-1.24362200
H	-2.21834400	-2.47831000	0.12959200
O	-2.39928700	0.90712700	0.26726300
O	-0.98007800	2.48638800	-0.11347400
O	0.19911900	-2.08694900	-0.71768800
C	1.23316400	0.51625400	-0.70635100
H	1.48565200	0.05017300	-1.67613600
H	1.44217900	1.57723600	-0.91502700
C	2.32120500	0.07746700	0.19712400
C	3.70874900	0.31011100	-0.21384600
H	3.82067000	0.64781600	-1.24345000
H	4.09579400	1.08745600	0.46834100
H	4.32688600	-0.57163800	-0.00711700
C	2.04533000	-0.59232300	1.45960400
H	1.15278400	-0.18448700	1.94632300
H	1.75507000	-1.61895900	1.16110600
H	2.90758300	-0.65139600	2.12276500
H	-0.12029900	2.74566100	-0.47551400

TS11+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	-2.96470500	0.11556700	-0.11235100
C	-0.99652100	-1.27359800	-0.11655800
C	-0.20821100	-0.06308100	-0.36966800
C	-0.73453500	1.15997400	-0.09779300
C	-2.15015100	1.30721700	0.37120500
H	-3.11919200	0.16554100	-1.19494200
H	-2.59356600	2.22664600	-0.02708400
C	1.20011400	-0.23257200	-0.87247400
C	2.32320400	-0.12020700	0.07063600
O	-0.50500100	-2.39731100	-0.12756900
O	-2.30958300	-1.14368600	0.18703500
O	0.05487800	2.24119000	-0.20601500
H	1.32571600	-1.28244900	-1.21806800
H	1.41252700	0.36730300	-1.76603200
C	3.66907800	0.09881200	-0.45787900
H	4.41973300	-0.47498000	0.09354500
H	3.74893700	-0.03573500	-1.53672700
H	3.88899900	1.15900600	-0.22669600
C	2.11173200	-0.23794900	1.51425500
H	1.51357900	0.62925300	1.83590900
H	1.46715800	-1.10355300	1.72065700
H	3.03520900	-0.28465500	2.08829200
H	-2.16138900	1.38534400	1.46624200
H	-3.93117900	0.05992500	0.38646000
H	-0.42891200	3.06182600	-0.02538500

TS12+
Atom type // Cartesian coordinates in Ångström (X Y Z)

C	2.00802900	-1.41754200	0.71813200
C	0.13399200	-1.06696500	-0.76195600
C	0.66159500	0.26312400	-1.04360400
C	1.63218800	0.81984900	-0.24031000
C	2.11844900	0.08256200	0.96917800
H	2.14707400	-1.98409900	1.63743100
H	2.74529900	-1.74427900	-0.02173900
H	3.16047300	0.33754300	1.18646300
H	1.51945900	0.38749400	1.83752400
O	0.69245100	-1.79506000	0.23424500
O	-0.84750800	-1.52723600	-1.34151700
O	2.09901000	2.02246900	-0.53867600
H	2.77518600	2.32184000	0.09190500
C	-1.33755100	1.63855400	-0.05509400
H	-0.73757600	2.19361800	0.65954500
H	-1.36986200	2.02047600	-1.06856300
C	-2.20227000	0.62057500	0.35308100
C	-2.89496900	-0.02096300	-0.65543400
H	0.37143700	0.72856800	-1.97654800
H	-3.55304200	-0.85923100	-0.44908100
C	-2.27285200	0.16909400	1.79370800
H	-1.43827700	-0.50001700	2.02820400
H	-2.21983600	1.02302400	2.47330300
H	-3.20142300	-0.37210900	1.98661900
H	-2.83020300	0.31606800	-1.68368900