Supplementary Materials

Novel Stemphol Derivatives from a Marine Fungus *Pleospora* sp.

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Four novel stemphol derivatives, pleosporols A-D (**1**, **2** and mixture of **3** and **4**) together with known compounds stemfolones (mixture of **5** and **6**), stemphol (**7**) were isolated from a marine fungus *Pleospora* sp. (PO4) derived from the gut of marine isopod *Ligia oceanica*. The planar structures of novel compounds were elucidated on the basis of mass and NMR spectral analysis and their stereochemistry was determined by CD spectra, NOESY data, coupling constants analysis and modified Mosher's method. Novel compounds contained α,β-unsaturated cyclohexanone ring and possibly derived from the oxidation of stemphol. All novel ones showed strong antimicrobial activity against *S. epidermidis* CMCC26069 with MIC values less than 10 μg/mL.

Keywords: Pleosporols; *Pleospora* sp.; Dialkylresorcinols; Antibacterial

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1.General experimental procedures

Optical rotation was measured on a Jasco P-1010 polarimeter. ECD spectra were obtained on an Applied Photophysics Chirascan spectrometer. The ultraviolet (UV) absorption spectra were measured in MeOH on a METASH UV-8000 spectrophotometer. IR spectra were recorded on a Bruker VECTOR 22 FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ (ALDRICH, St. Louis, MO, USA) or MeOH-d_4 (ALDRICH, St. Louis, MO, USA) with tetramethylsilane (TMS) as an internal standard, using a Bruker AVANCE-Ⅲ 600 MHz NMR spectrometer. HR-ESIMS data were obtained on an Agilent 6224 TOF LC/MS, MS/MS data was collected by a TripleTOF® 5600+ LC/MS/MS system (AB SCIEX). Column chromatography (CC) was performed with silica (100-200 and 200-300 mesh, Qingdao Haiyang Chemical Co., Ltd., Qingdao, China).

2.Fungal material and fermentation

The fungal colony (PO4) was isolated from the gut of marine isopod *Ligia oceanica* which was collected at Dongsha of Dinghai in Zhoushan, Zhejiang Province of China in May 2013. The fungal PO4 was determined as *Pleospora* sp. by 26S rDNA analysis.

26s rDNAD1/D2 sequence of PO4

CTCAAATTTGAAATCTGGCTCTTTTAGGGTCCGAGTTGTAATTTGCAGA
GGGCGCTTTGGCTTTGGCAGCGGTCCAAGTTCCTTGGAACAGGACGTCAC
AGAGGGTGAGAATCCCGTACGTGGTCGCTAGCTATTGCCGTGTAAAGCCC
CTTCGACGAGTCGAGTTGTTTGGGAATGCAGCTCTAAATGGGAGGTAAAT
TTCTTCTAAAGCTAAATATTGGCCAGAGACCGATAGCGCACAAGTAGAGT
GATCGAAAGATGAAAAGCACTTTGGAAAGAGAGTCAAACAGCACGTGAA
ATTGTTGAAAGGGAAGCGCTTGCAGCCAGACTTGCTTGCAGTTGCTCATC
CGGGCTTTTGCCCGGTGCACTCTTCTGTAGGCAGGCCAGCATCAGTTTGGG
CGGTGGGATAAAGGTCTCTGTCACGTACCTCTCTTCGGGGAGGCCTTATA
GGGGAGACGACATACCACCAGCCTAGACTGAGGTCCGCGCATCTGCTAGG

ATGCTGGCGTAATGGCTGTAAGCGGC

The strain (PO4) was static cultured in rice cultural medium (rice 40g, artificial sea water 40 mL) at 28℃ for 30 days in 500-mL Erlenmeyer-flasks (100 flasks).

3.Extraction and isolation

The cultured medium was extracted with EtOAc and evaporated under vacuum to recycle EtOAc. The extract was dissolved in MeOH and partitioned with petroleum ether to remove the lipidic substance. Finally 12.95g of secondary metabolites (SM) extract was obtained from EtOAc layer. All of SM extract was fractionated by silica gel column chromatography (CC) eluted in gradient from petroleum ether - EtOAc (10:1-2:1) to CH_2Cl_2-MeOH (50:1-1:1) to yield 19 fractions (Frs. 1-19) based on TLC analysis. Frs. 10 and 11 were subjected to ODS MPLC (Medium Pressure Liquid Chromatography) and eluted by MeOH/H_2O (50%~100%) and the subfractions further purified by semi-preparative HPLC (COSMOSIL PACKED COLUMN, 5C18-MS-II column, 10ID×250mm, 3 mL/min). Compounds **1** (50% MeOH/H_2O, t_R = 14 min, 19.7 mg) and **2** (80% MeOH/H_2O, t_R=8 min, 11.0 mg) were isolated from different subfractions of Fr.10 while Compounds **3/4** (t_R=10 min, 10.8 mg) and **5/6** (t_R=11 min, 8.9 mg) were successively obtained from Fr.11-4 eluted by 55% MeOH/H_2O. Compound **7** (t_R = 10 min 13.0 mg) was isolated from Fr.18 through semi-preparative ODS-HPLC eluted by 20% MeOH/H_2O.

Physicochemical and spectral data

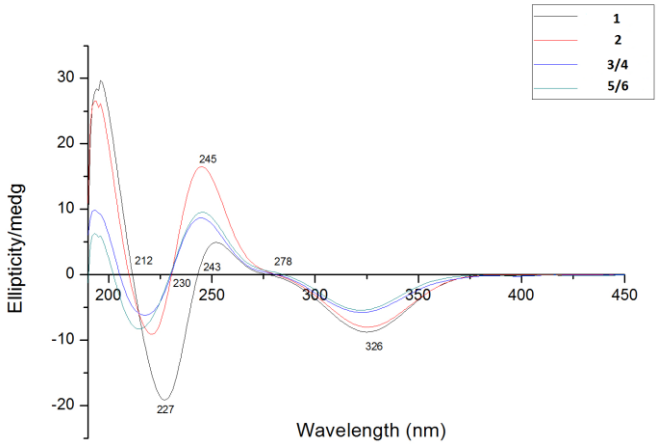
Pleosporol A (**1**): colorless oil; $[\alpha]^{25}_D$ +11.15 (c=2.75, MeOH); UV (MeOH) λ_{max}(logε) 205 (3.28), 234 (3.75) nm; CD (c 1.03×10^{-4}mol/L, MeOH), λ_{max} (Δε) 325 (-8.76), 252 (4.93), 227 (-19.17); IR (KBr) ν_{max} (cm^{-1}): 3421, 2956, 2931, 2867, 1668, 1378, 1211, 1138, 1073, 1030, 985; HRESIMS *m/z* 269.1779 $[M-H]^-$ (Calcd. for $C_{15}H_{25}O_4$, 269.1753); NMR data in the Tables 1 and 2.

Pleosporol B (**2**): colorless oil; $[\alpha]^{25}_D$ +3.27 (c=3.40, MeOH); UV (MeOH) λ_{max}(logε) 204 (3.43), 233 (3.98) nm; CD (c 1.46×10^{-4}mol/L, MeOH), λ_{max} (Δε) 325 (-8.00), 245 (16.49), 221 (-9.10); IR (KBr) ν_{max} (cm^{-1}): 3421, 2956, 2932, 2867, 1670, 1378, 1210, 1138, 1072, 1032; HRESIMS *m/z* 269.1782 $[M-H]^-$ (Calcd. for $C_{15}H_{25}O_4$,

269.1753); NMR data in the Tables 1 and 2.

Pleosporols C/D (**3**/**4**): colorless oil; $[\alpha]^{25}_{D}$ +2.96 (c=2.96, MeOH); UV (MeOH) λ_{max}(logε) 205 (3.16), 234 (3.79) nm; CD (c 2.68×10^{-4}mol/L, MeOH), λ_{max} (Δε) 323 (-5.78), 245 (8.80), 218 (-6.10); IR (KBr) ν_{max} (cm^{-1}): 3419, 2957, 2931, 2869, 1666, 1374, 1210, 1116, 1072, 1032; HRESIMS *m/z* 269.1781 $[M-H]^-$ (Calcd. for $C_{15}H_{25}O_4$, 269.1753); NMR data in the Tables 1 and 2.

Stemfolone B and 14-*epi*-stemfolone B(**5**/**6**): colorless oil; $[\alpha]^{25}_{D}$ +4.32 (c=1.20, MeOH); UV (MeOH) λ_{max}(logε) 205 (3.29), 234 (3.79) nm; CD (c 5.44×10^{-4}mol/L, MeOH), λ_{max} (Δε) 322 (-5.44), 245 (9.56), 215 (-8.30); IR (KBr) ν_{max} (cm^{-1}): 3421, 2957, 2930, 2871, 1666, 1374, 1210, 1116, 1072, 1032; HRESIMS *m/z* 269.1781 $[M-H]^-$ (Calcd. for $C_{15}H_{25}O_4$, 269.1753); NMR data in the Tables 1 and 2.

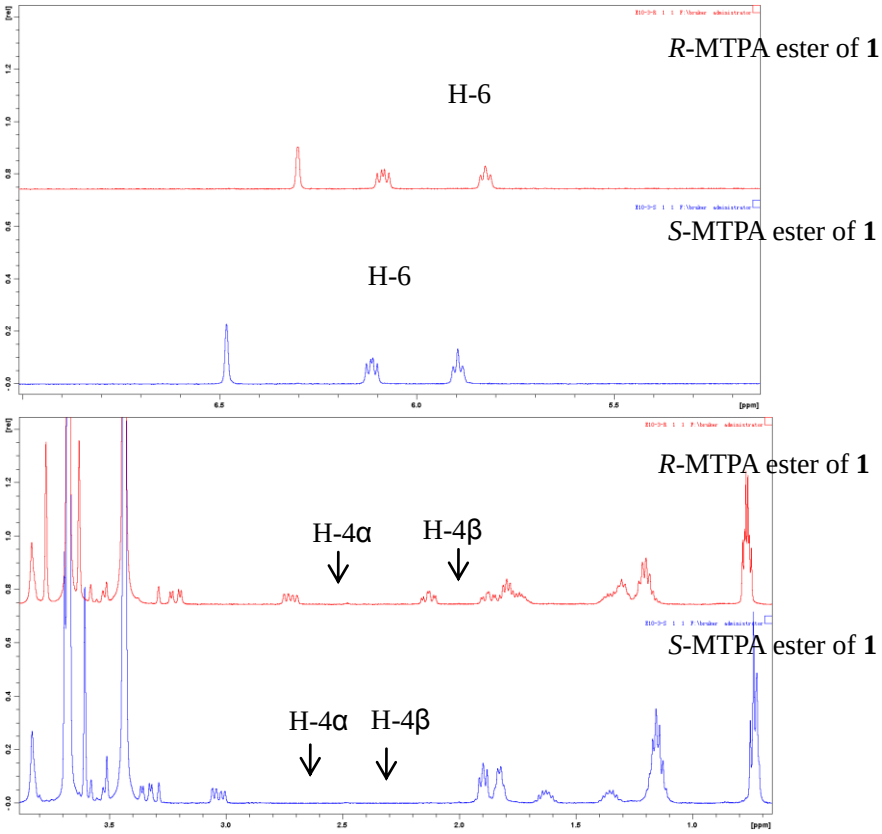


Measured CD spectra for **1**-**6**

4. MTPA Esterification of 1

Compound **1** was transferred into two clean NMR tubes (0.5mg in each tube) and dried completely under vacuum. Deuterated pyridine (400μL) was added to dissolve the sample and (*R*)-MTPA-Cl/(*S*)-MTPA-Cl (8μL) were quickly added into the tubes, respectively. All contents were mixed thoroughly by shaking the tubes carefully. The

reaction was performed at room temperature for 2.5h to obtained the *S*-MTPA and the *R*-MTPA ester (**1a** and **1b**), respectively[1]. The chemical shift differences ($\Delta\delta = \delta_S - \delta_R$) calculated from the ^{1}H NMR spectra of the two diastereomeric esters **1a** and **1b** enabled us to determine the absolute configuration of C-3 as *R*.



^{1}H NMR spectrum of esters of **1**

5. Biological assay

Antibacterial activities of novel compounds were tested against Methicillin-resistant *S. aureus* ATCC43300, *P. Aeruginosa* ATCC27853, *E. coli* ATCC35218 and *S. epidermidis* CMCC26069 using broth dilution methods to determine the minimal inhibitory concentration. These bacteria were inoculated into nutrient broth medium in 96-well microtiter plate in the presence of serial dilution concentrations of compounds. After incubation for 24h, the MIC value was read.Vancomycin hydrochloride (0.5μg/ml) and aerosporin (0.5μg/ml) were used as positive controls against gram-positive and gram-negative bacteria, respectively.

6. The spectra for compounds 1-7

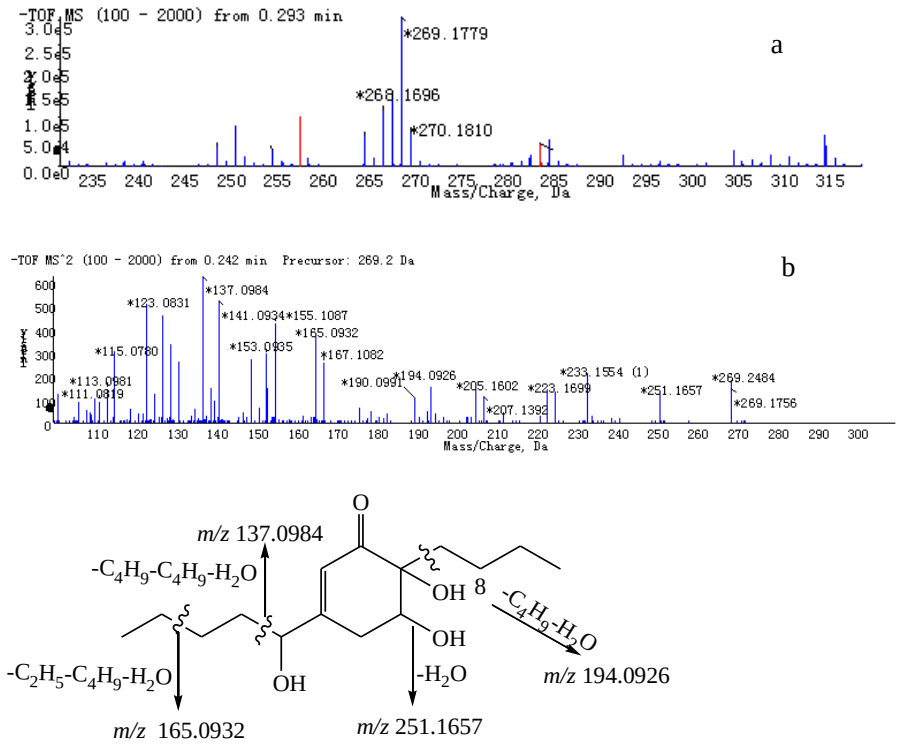


Figure S1 MS/MS fragment ion peaks of **1** (a: MS^1, b: MS^2)

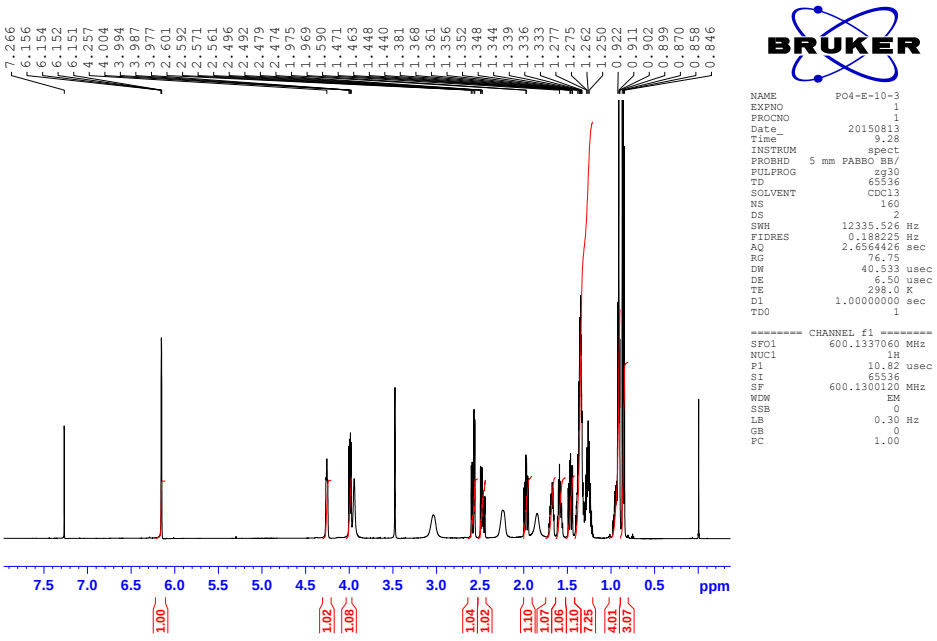
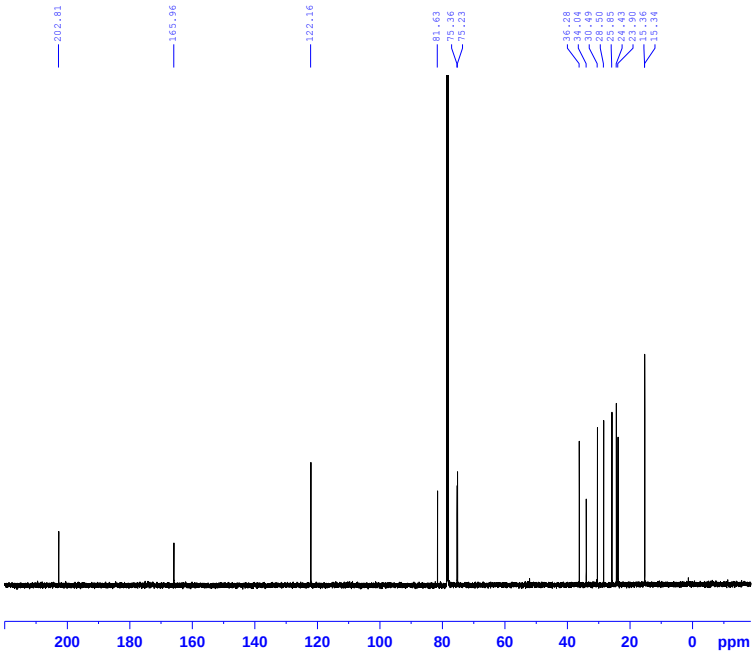


Figure S2 ^{1}H NMR spectrum of **1** in $CDCl_3$




```
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EXPNO                        2
PROCNO                       1
Date_                 20150814
Time                     22.27
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                 zppg30
TD                       65536
SOLVENT                  CDCl3
NS                         324
DS                           4
SWH                  36231.883 Hz
FIDRES                0.552855 Hz
AQ                   0.9044468 sec
RG                      183.37
DW                      13.800 usec
DE                       6.50 usec
TE                      298.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                150.9178981 MHz
NUC1                        13C
P1                       12.31 usec
SI                       32768
SF                  150.9025969 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
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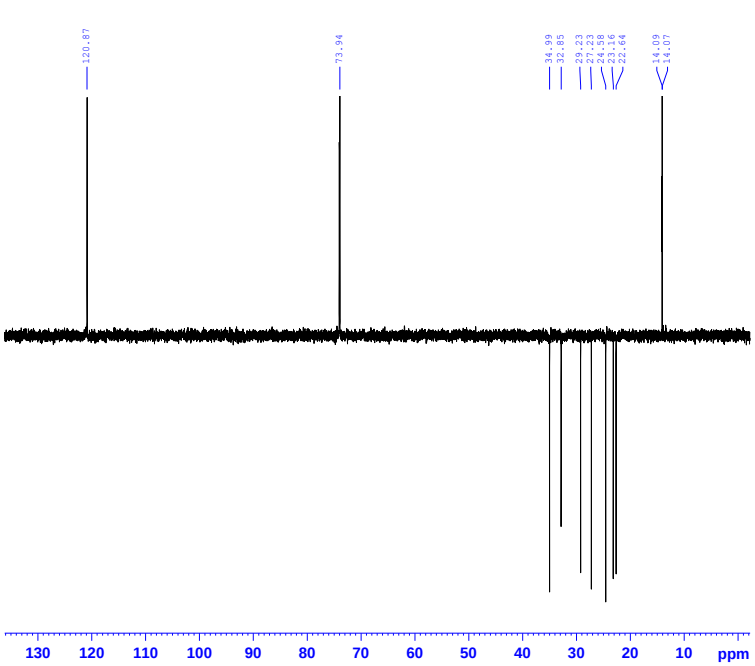
Figure S3 ^{13}C NMR spectrum of **1** in $CDCl_3$

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EXPNO                        6
PROCNO                       1
Date_                 20150824
Time                     15.55
INSTRUM                  spect
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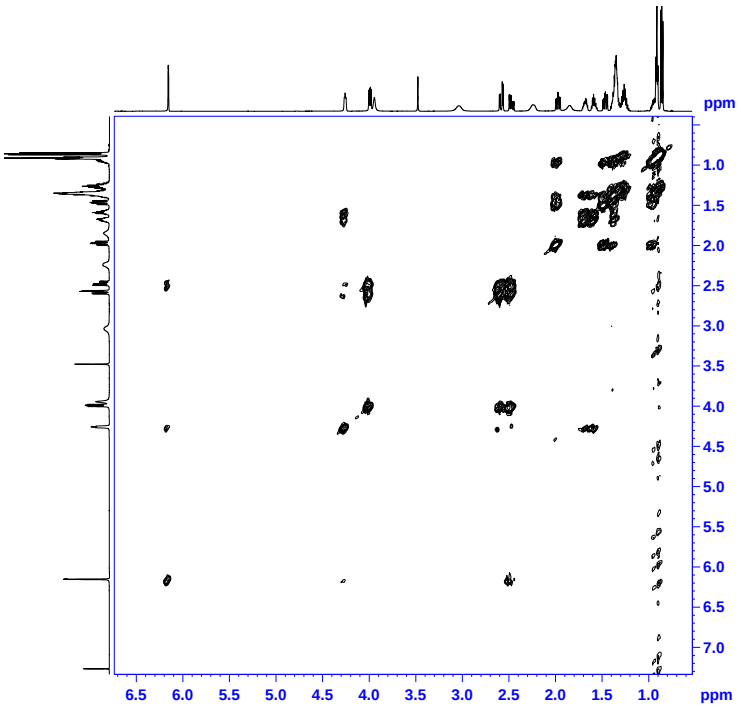
PULPROG              deptsp135
TD                       65536
SOLVENT                  CDCl3
NS                          35
DS                           4
SWH                  37878.789 Hz
FIDRES                0.577984 Hz
AQ                   0.8651252 sec
RG                      183.37
DW                      13.200 usec
DE                       6.50 usec
TE                      298.1 K
CNST2               145.0000000
D1                   2.00000000 sec
D2                   0.00344828 sec
D12                  0.00002000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                150.9148800 MHz
NUC1                        13C
P1                       12.31 usec
P13                    2000.00 usec
SI                       32768
SF                  150.9027878 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

Figure S4 DEPT spectrum of **1** in $CDCl_3$



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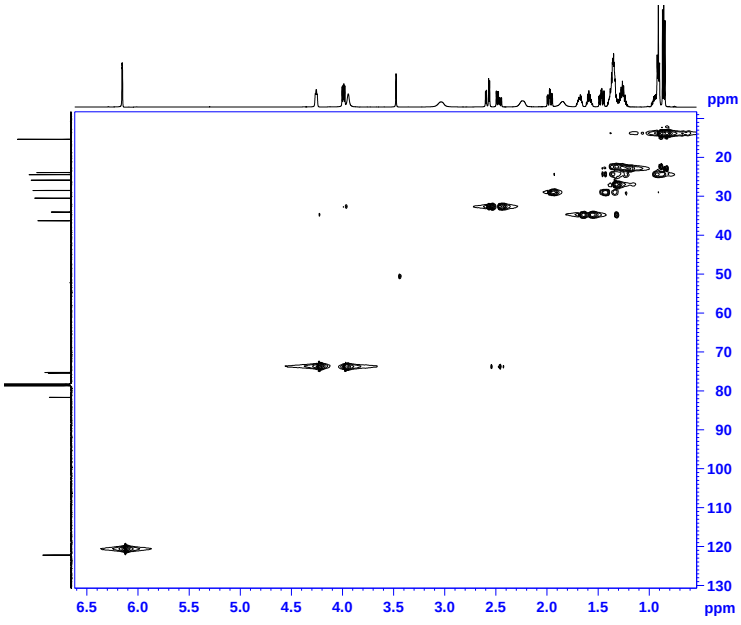
NAME                PO4-E-10-3
EXPNO                        3
PROCNO                       1
Date_                20150820
Time                    14.38
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG          cosygpmfqf
TD                        2048
SOLVENT                 CDCl3
NS                           4
DS                          16
SWH                  6009.615 Hz
FIDRES               2.934382 Hz
AQ                   0.1704436 sec
RG                       183.37
DW                       83.200 usec
DE                         6.50 usec
TE                       298.0 K
D0                   0.00000300 sec
D1                   2.00000000 sec
D13                  0.00000400 sec
D16                  0.00020000 sec
IN0                  0.00016660 sec

======== CHANNEL f1 ========
SFO1                600.1324005 MHz
NUC1                        1H
P1                       10.82 usec
ND0                          1
TD                         256
SFO1                 600.1324 MHz
FIDRES              23.446878 Hz
SW                      10.002 ppm
FnMODE                      QF
SI                        1024
SF                  600.1300061 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.40
SI                        1024
MC2                         QF
SF                  600.1300015 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
```

Figure S5 ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$



BRUKER

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NAME                PO4-E-10-3
EXPNO                        5
PROCNO                       1
Date_                20150822
Time                    10.33
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG          hsqcetgpsisp2.2
TD                        2048
SOLVENT                 CDCl3
NS                           8
DS                          32
SWH                  6009.615 Hz
FIDRES               2.934382 Hz
AQ                   0.1704436 sec
RG                       183.37
DW                       83.200 usec
DE                         6.50 usec
TE                       298.0 K
CNST2               145.0000000
CNST17               -0.5000000
D0                   0.00000300 sec
D1                   2.00000000 sec
D4                   0.00172414 sec
D11                  0.03000000 sec
D16                  0.00020000 sec
D24                  0.00089000 sec
IN0                  0.00001330 sec

======== CHANNEL f1 ========
SFO1                600.1324005 MHz
NUC1                        1H
P1                       10.82 usec
P2                       21.64 usec
P28                    1000.00 usec
ND0                          2
TD                         256
SFO1                 150.9179 MHz
FIDRES              146.851501 Hz
SW                      249.102 ppm
FnMODE          Echo-Antiecho
SI                        1024
SF                  600.1300205 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
PC                        1.40
SI                        1024
MC2               echo-antiecho
SF                  150.9028085 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
```

Figure S6 HMQC spectrum of **1** in $CDCl_3$

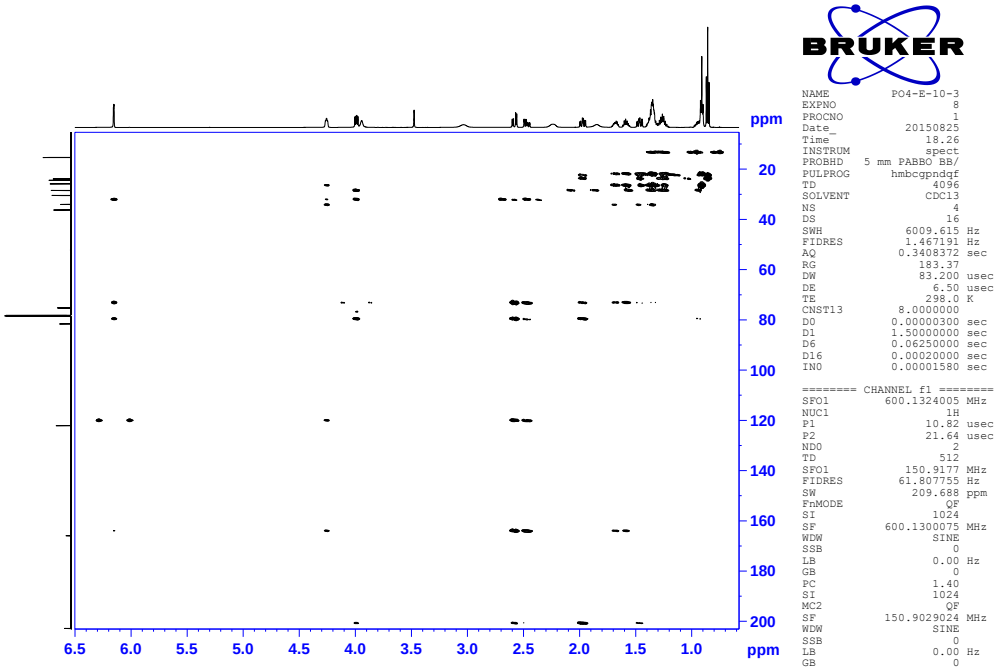


Figure S7 HMBC spectrum of **1** in $CDCl_3$

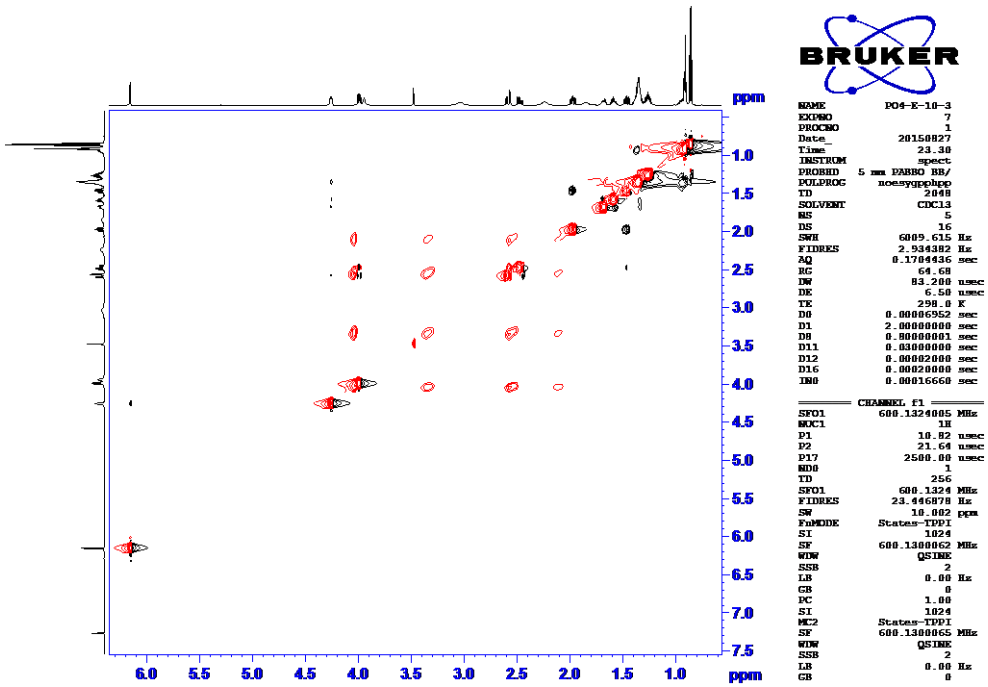


Figure S8 NOESY spectrum of **1** in $CDCl_3$

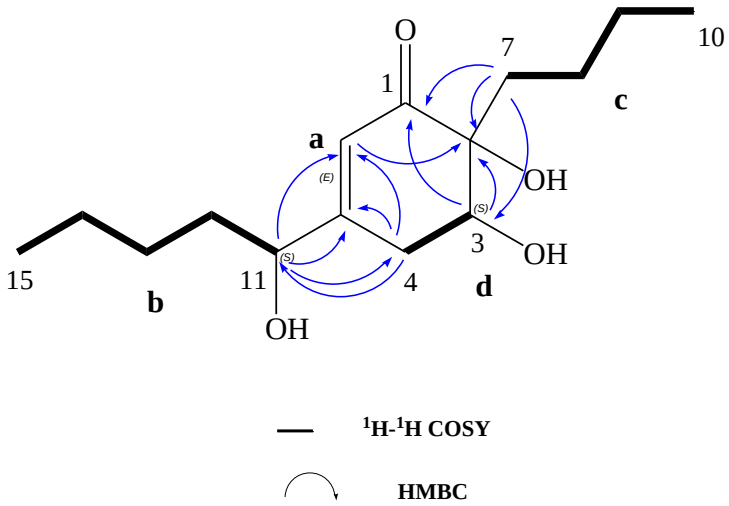


Figure S9 ^{1}H-^{1}H COSY and key HMBC correlations for **1**

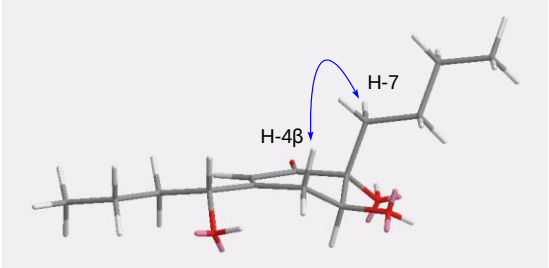


Figure S10 key NOESY correlations for **1-6**

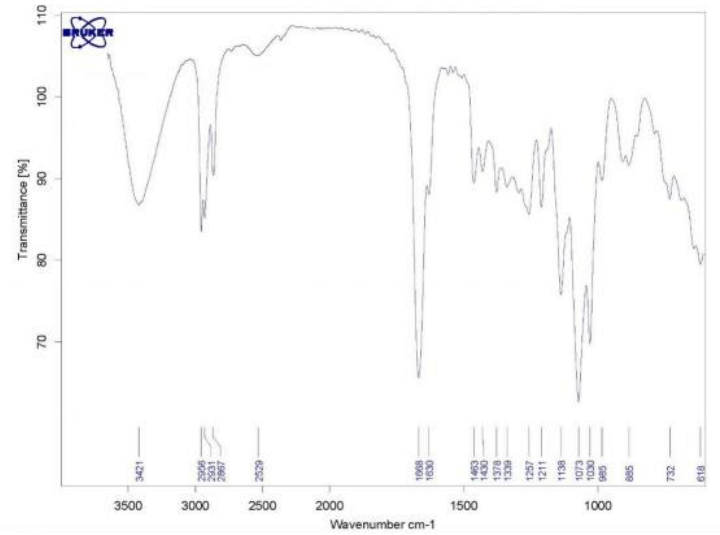


Figure S11 IR spectrum of **1**

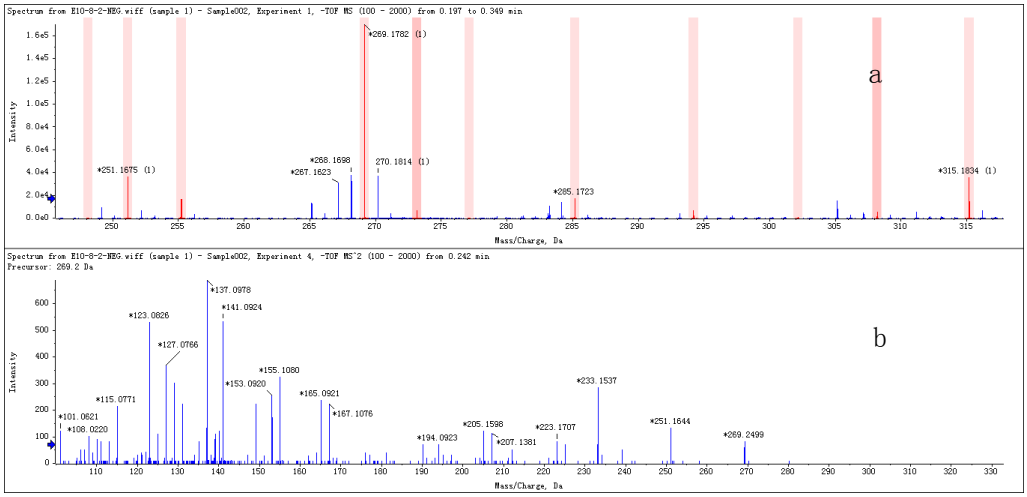
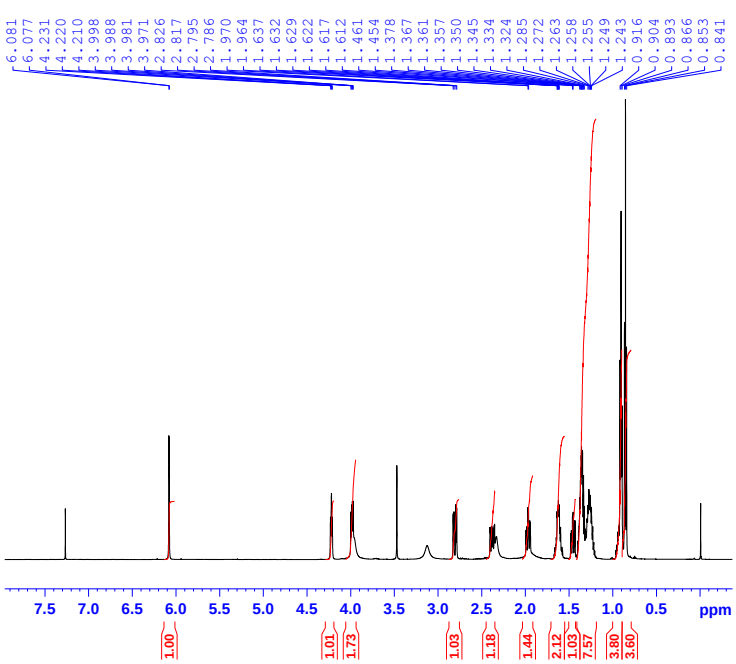


Figure S12 MS/MS of **2** (a: MS^1, b: MS^2)



```
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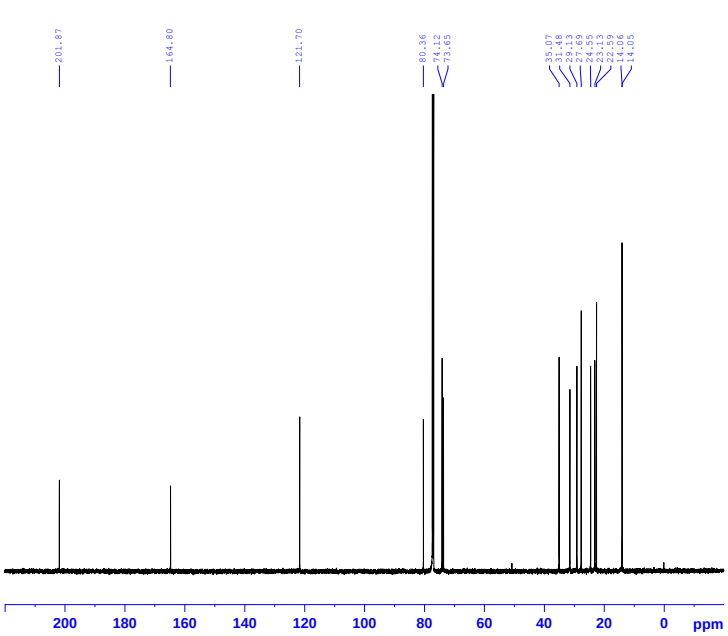
EXPNO                       1
PROCNO                      1
Date_                20150813
Time                     8.59
INSTRUM                 spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                       160
DS                         2
SWH                12335.526 Hz
FIDRES              0.188225 Hz
AQ                  2.6564426 sec
RG                      64.68
DW                     40.533 usec
DE                       6.50 usec
TE                      298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            600.1337060 MHz
NUC1                      1H
P1                     10.82 usec
SI                     65536
SF              600.1300120 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

Figure S13 ^{1}H NMR spectrum of **2** in $CDCl_3$




```
NAME                PO4-E10-8
EXPNO                       2
PROCNO                      1
Date_                20150819
Time                    14.39
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         591
DS                           4
SWH                 36231.883 Hz
FIDRES              0.552855 Hz
AQ                  0.9044468 sec
RG                     183.37
DW                  13.800 usec
DE                   6.50 usec
TE                     298.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             150.9178981 MHz
NUC1                     13C
P1                   12.31 usec
SI                      32768
SF                150.9027914 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                       1.40
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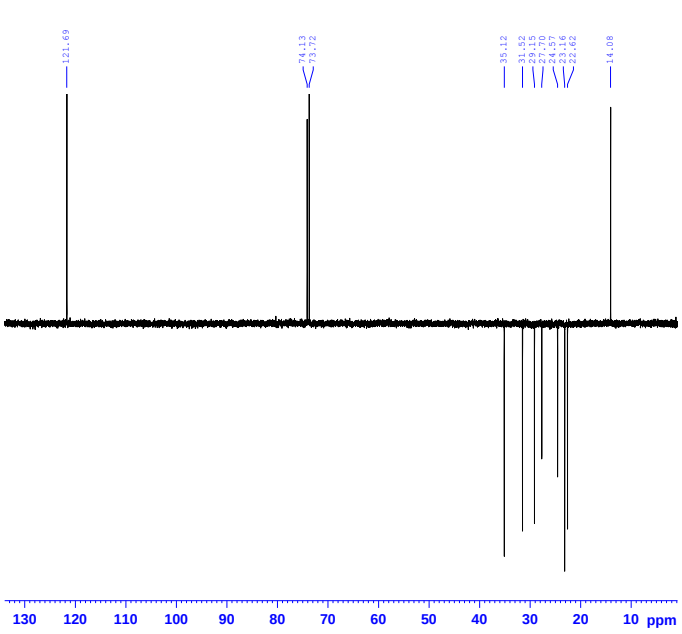
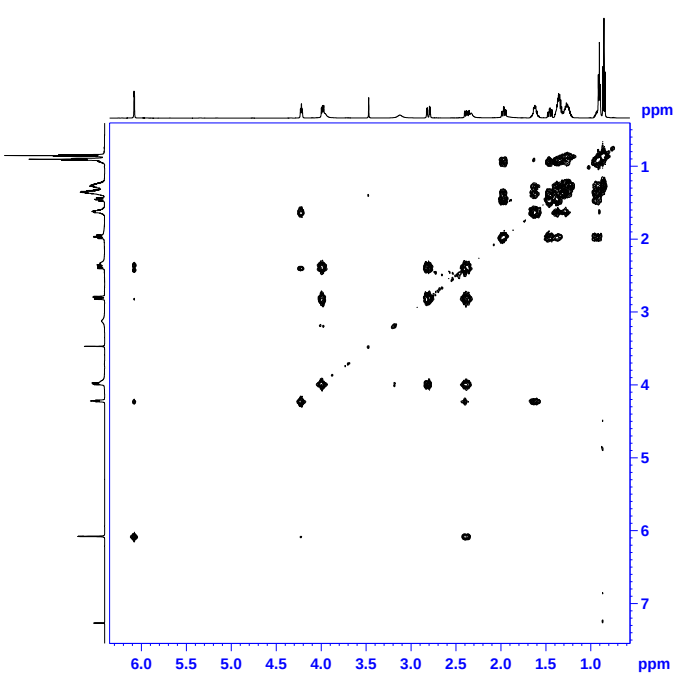
Figure S14 ^{13}C NMR spectrum of **2** in $CDCl_3$




```
NAME                PO4-E10-8
EXPNO                       4
PROCNO                      1
Date_                20150827
Time                    16.26
INSTRUM                 spect
PROBHD     5 mm PABBO BB/
PULPROG             deptsp135
TD                       65536
SOLVENT                  CDCl3
NS                          66
DS                           4
SWH                 36231.883 Hz
FIDRES              0.552855 Hz
AQ                  0.9044468 sec
RG                     183.37
DW                  13.800 usec
DE                   6.50 usec
TE                     298.1 K
CNST2              145.0000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1             150.9163903 MHz
NUC1                     13C
P1                   12.31 usec
P13                2000.00 usec
SI                      32768
SF                150.9027878 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                       1.40
```

Figure S15 DEPT spectrum of **2** in $CDCl_3$




```
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EXPNO                        5
PROCNO                       1
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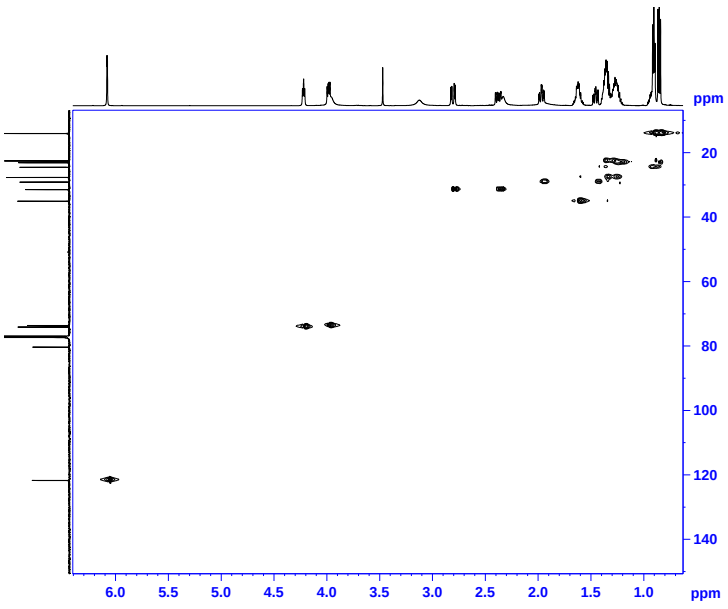
Time_                    13.19
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG          cosygpmfqf
TD                        2048
SOLVENT                 CDCl3
NS                           4
DS                          16
SWH                  6009.615 Hz
FIDRES               2.934382 Hz
AQ                  0.1704436 sec
RG                      183.37
DW                     83.200 usec
DE                      6.50 usec
TE                     298.0 K
D0                  0.00000300 sec
D1                  2.00000000 sec
D13                 0.00000400 sec
D16                 0.00020000 sec
IN0                 0.00016660 sec

======== CHANNEL f1 ========
SFO1               600.1324005 MHz
NUC1                       1H
P1                       10.82 usec
ND0                          1
TD                         256
SFO1                600.1324 MHz
FIDRES               23.446878 Hz
SW                      10.002 ppm
FnMODE                      QF
SI                        1024
SF                 600.1300061 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                        1024
MC2                         QF
SF                 600.1300015 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
```

Figure S16 ^{1}H-^{1}H COSY spectrum of **2** in $CDCl_3$




```
NAME                 PO4-E10-8
EXPNO                        6
PROCNO                       1
Date_                 20150827
Time_                    14.01
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG          hsqcetgpsisp2.2
TD                        2048
SOLVENT                 CDCl3
NS                           8
DS                          32
SWH                  6009.615 Hz
FIDRES               2.934382 Hz
AQ                  0.1704436 sec
RG                      183.37
DW                     83.200 usec
DE                      6.50 usec
TE                     298.0 K
CNST2               145.0000000
CNST17               -0.5000000
D0                  0.00000300 sec
D1                  2.00000000 sec
D4                  0.00172414 sec
D11                 0.03000000 sec
D16                 0.00020000 sec
D24                 0.00089000 sec
IN0                 0.00001330 sec

======== CHANNEL f1 ========
SFO1               600.1324005 MHz
NUC1                       1H
P1                       10.82 usec
P2                       21.64 usec
P28                    1000.00 usec
ND0                          2
TD                         256
SFO1                150.9179 MHz
FIDRES              146.851501 Hz
SW                      249.102 ppm
FnMODE         Echo-Antiecho
SI                        1024
SF                 600.1300205 MHz
WDW                      QSINE
SSB                          2
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                        1024
MC2              echo-antiecho
SF                 150.9028085 MHz
WDW                      QSINE
SSB                          2
LB                       0.00 Hz
GB                          0
```

Figure S17 HMQC spectrum of **2** in $CDCl_3$

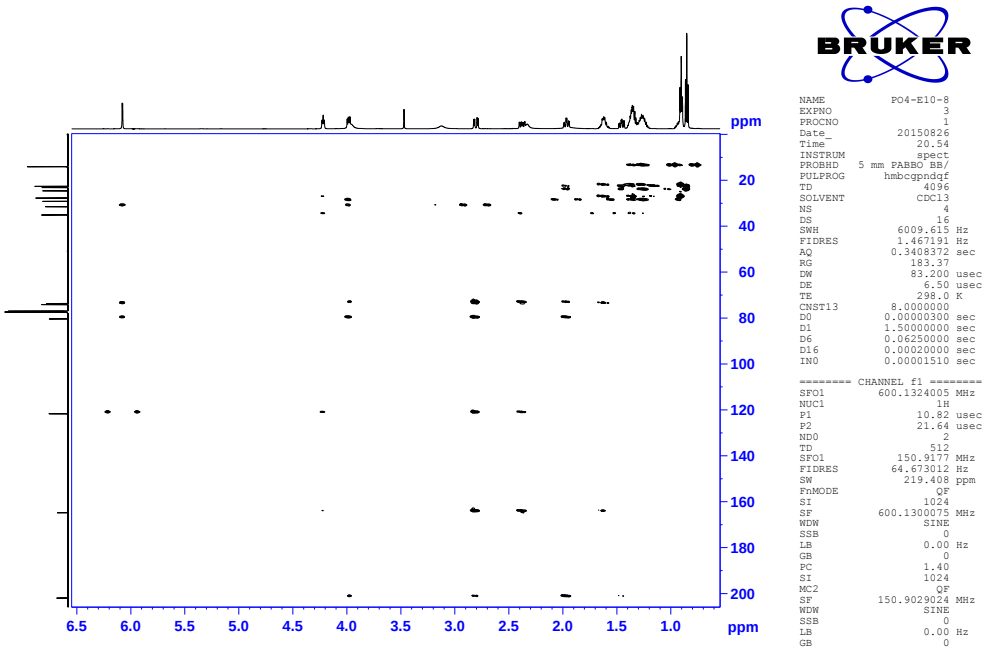


Figure S18 HMBC spectrum of **2** in $CDCl_3$

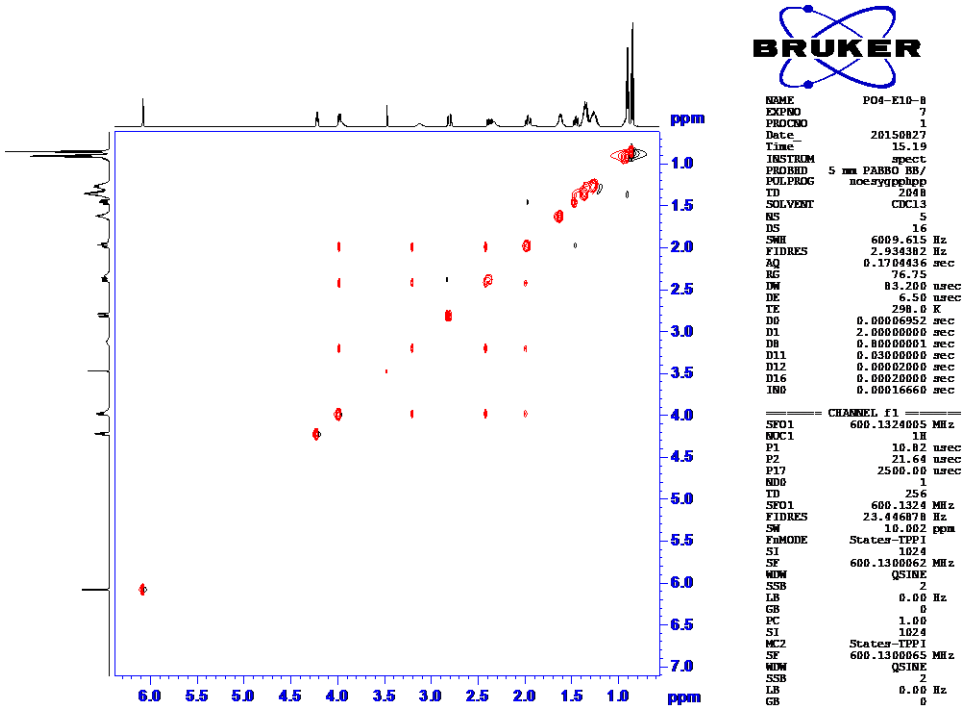


Figure S19 NOESY spectrum of **2** in $CDCl_3$

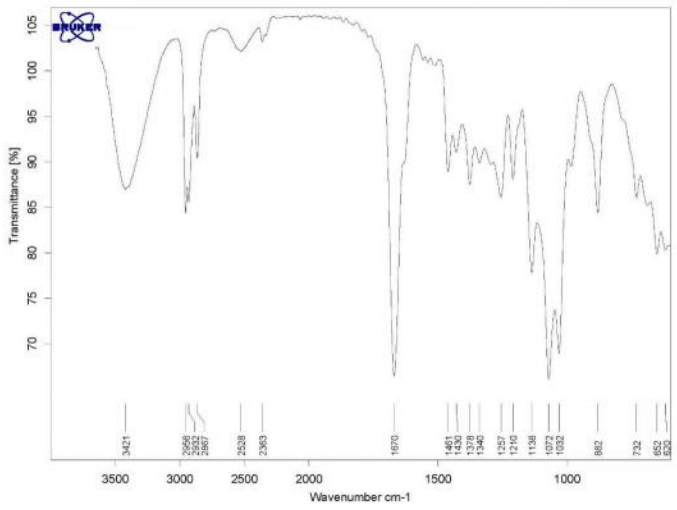


Figure S20 IR spectrum of **2**

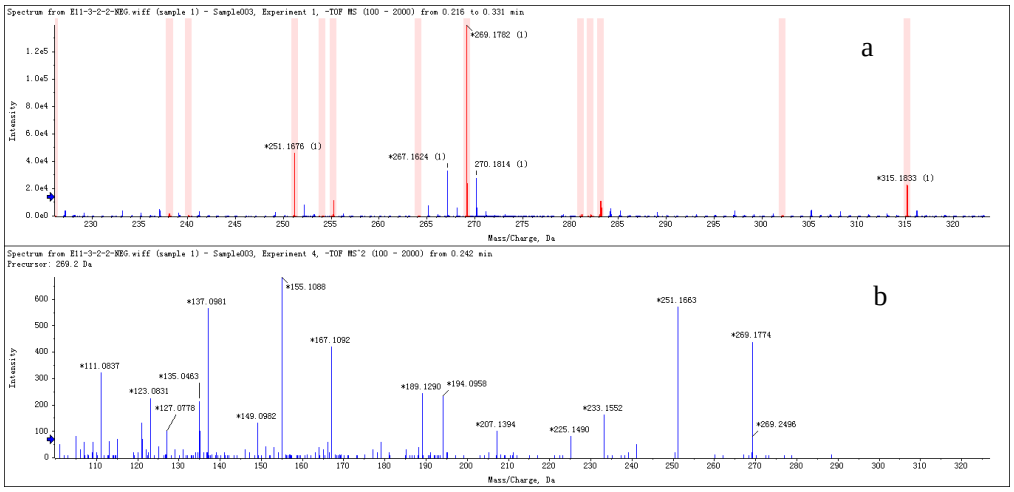


Figure S21 MS/MS of **3/4** (a: MS^1, b: MS^2)

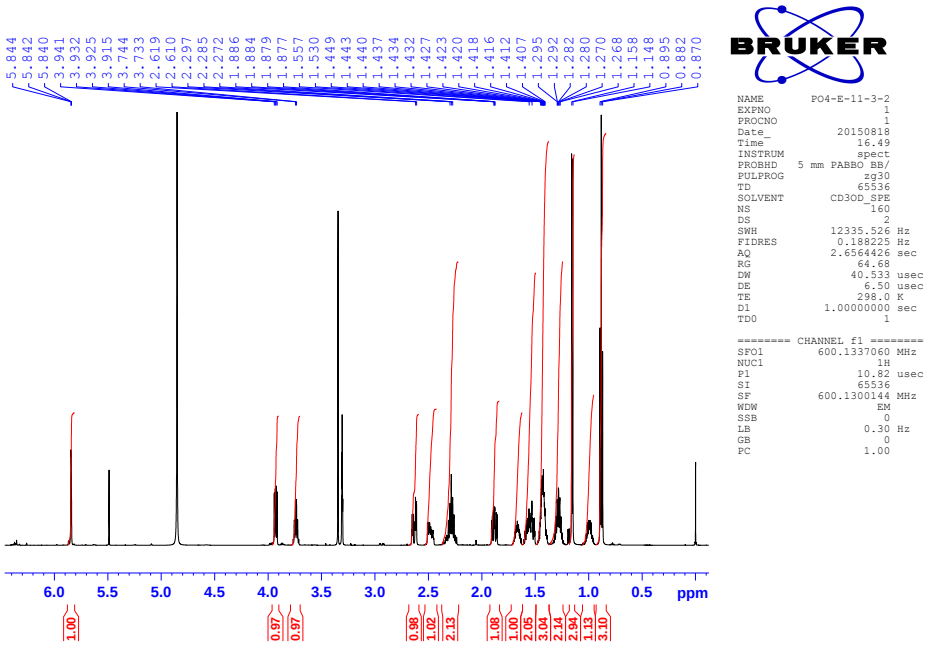
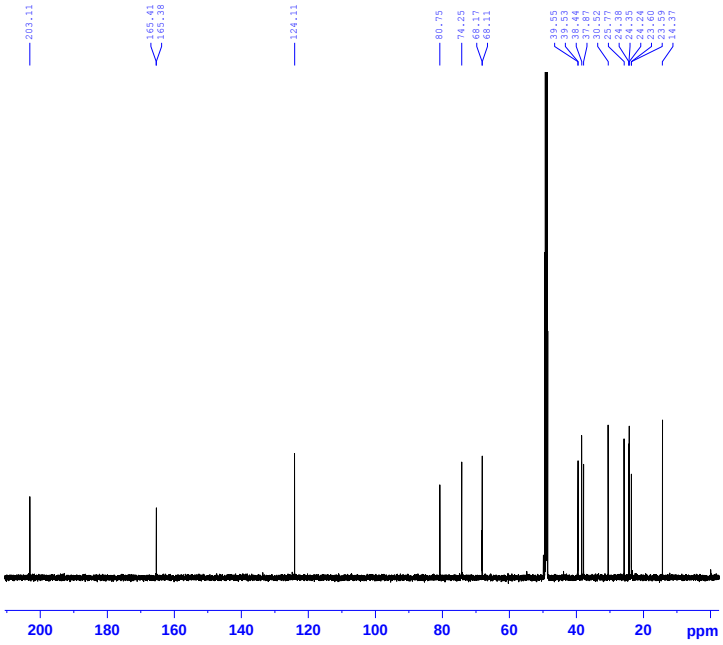


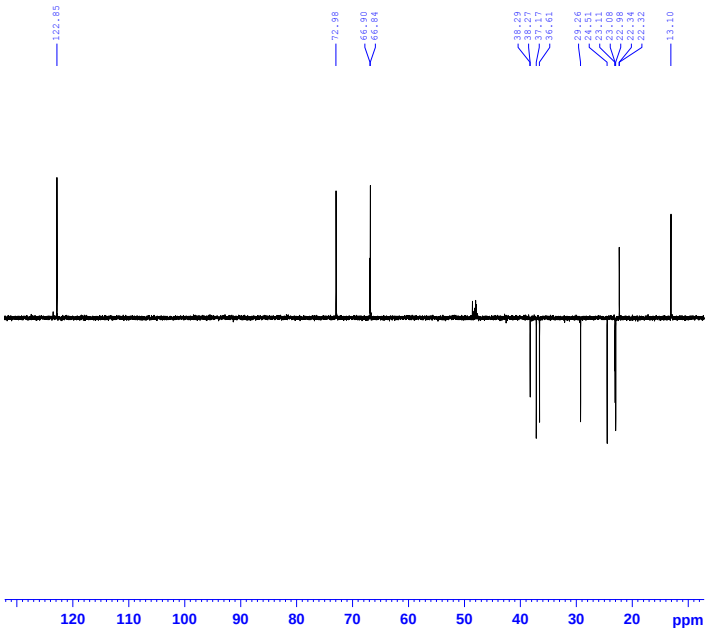
Figure S22 ^{1}H NMR spectrum of **3/4** in CD_3OD




```
NAME          PO4-E-11-3-2
EXPNO                    2
PROCNO                   1
Date_             20150818
Time_                18.01
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT         CD3OD_SPE
NS                   480
DS                     4
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ              0.9044468 sec
RG                 183.37
DW                 13.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1               13C
P1                12.31 usec
SI                32768
SF           150.9025969 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

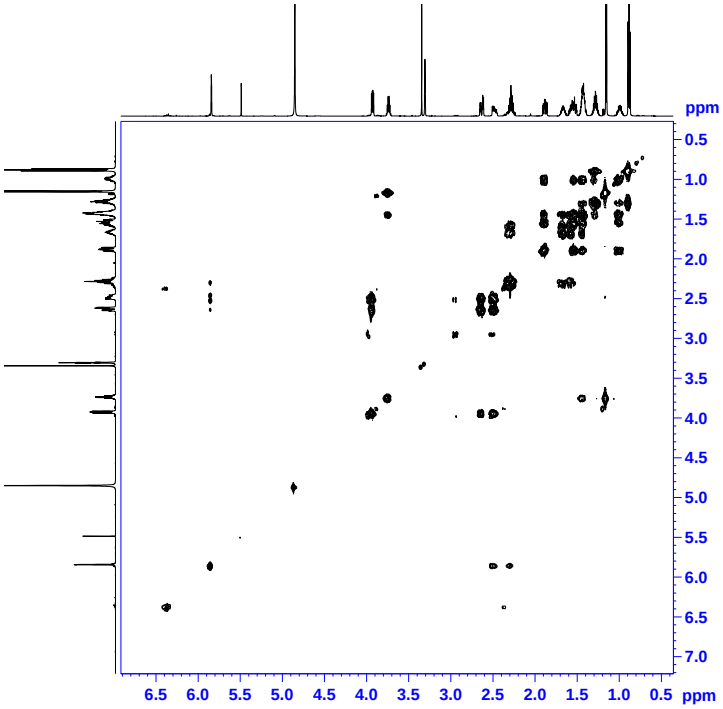
Figure S23 ^{13}C NMR spectrum of **3/4** in CD_3OD




```
NAME          PO4-E-11-3-2
EXPNO                    3
PROCNO                   1
Date_             20150827
Time_                19.51
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT         CD3OD_SPE
NS                   255
DS                     4
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ              0.9044468 sec
RG                 183.37
DW                 13.800 usec
DE                  6.50 usec
TE                 298.0 K
CNST2         145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9163903 MHz
NUC1               13C
P1                12.31 usec
P13             2000.00 usec
SI                32768
SF           150.9027878 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

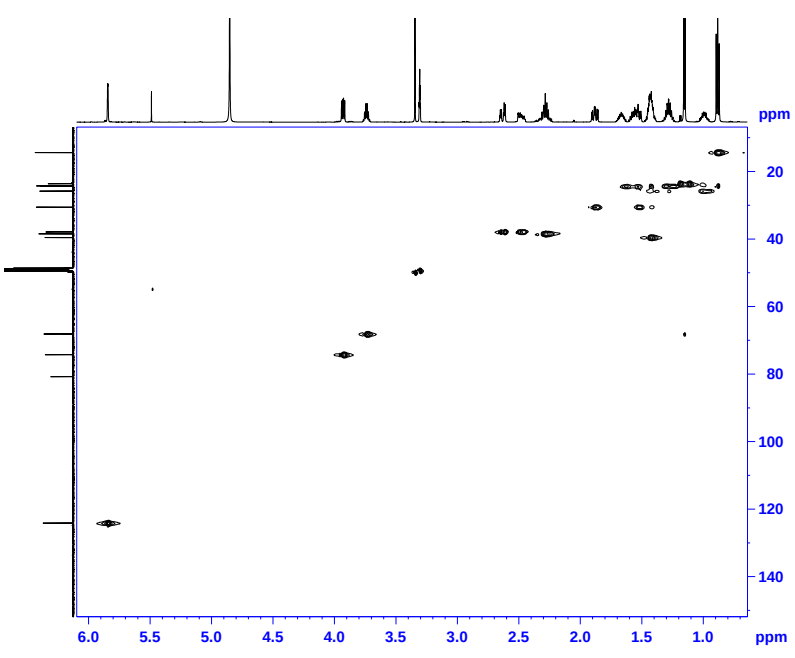
Figure S24 DEPT spectrum of **3/4** in CD_3OD




```
NAME            PO4-E-11-3-2
EXPNO                      4
PROCNO                     1
Date_               20150827
Time_                  16.38
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG         cosygpmfqf
TD                      2048
SOLVENT          CD3OD_SPE
NS                         4
DS                        16
SWH                 6009.615 Hz
FIDRES              2.934382 Hz
AQ                  0.1704436 sec
RG                     183.37
DW                     83.200 usec
DE                      6.50 usec
TE                     298.0 K
D0                  0.00000300 sec
D1                  2.00000000 sec
D13                 0.00000400 sec
D16                 0.00020000 sec
IN0                 0.00016660 sec

======== CHANNEL f1 ========
SFO1               600.1324005 MHz
NUC1                       1H
P1                      10.82 usec
ND0                        1
TD                       256
SFO1                600.1324 MHz
FIDRES             23.446878 Hz
SW                     10.002 ppm
FnMODE                     QF
SI                       1024
SF                 600.1300061 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                       1024
MC2                        QF
SF                 600.1300015 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
```

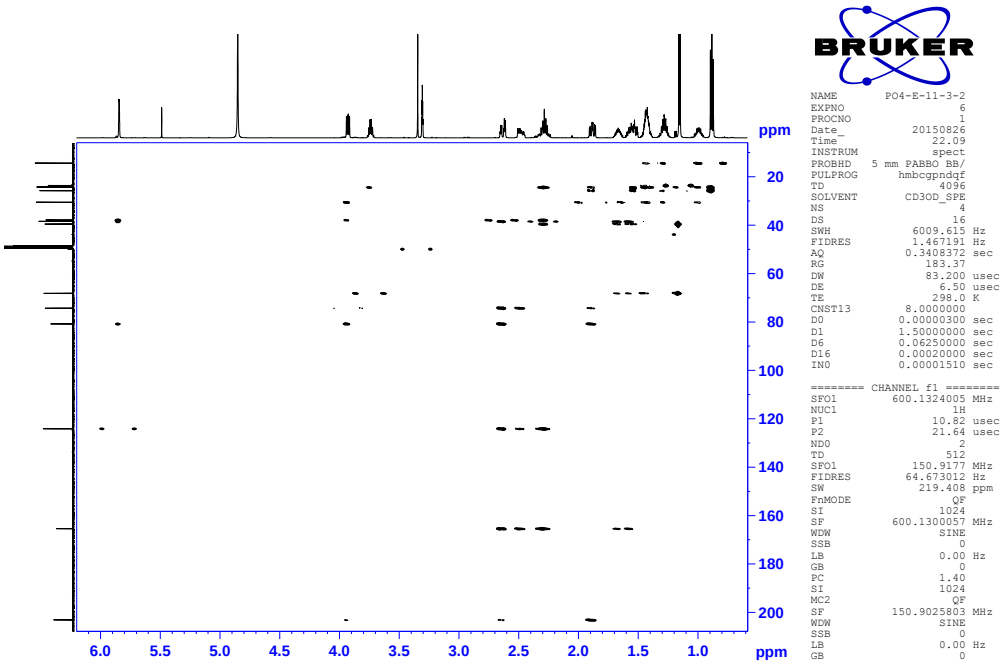
Figure S25 ^{1}H-^{1}H COSY spectrum of **3/4** in CD_3OD




```
NAME            PO4-E-11-3-2
EXPNO                      5
PROCNO                     1
Date_               20150827
Time_                  17.19
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG   hsqcetgpsisp2.2
TD                      2048
SOLVENT          CD3OD_SPE
NS                         8
DS                        32
SWH                 6009.615 Hz
FIDRES              2.934382 Hz
AQ                  0.1704436 sec
RG                     183.37
DW                     83.200 usec
DE                      6.50 usec
TE                     298.0 K
CNST2              145.0000000
CNST17              -0.5000000
D0                  0.00000300 sec
D1                  2.00000000 sec
D4                  0.00172414 sec
D11                 0.03000000 sec
D16                 0.00020000 sec
D24                 0.00089000 sec
IN0                 0.00001330 sec

======== CHANNEL f1 ========
SFO1               600.1324005 MHz
NUC1                       1H
P1                      10.82 usec
P2                      21.64 usec
P28                   1000.00 usec
ND0                        2
TD                       256
SFO1                150.9179 MHz
FIDRES             146.851501 Hz
SW                     249.102 ppm
FnMODE          Echo-Antiecho
SI                       1024
SF                 600.1300133 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                       1024
MC2             echo-antiecho
SF                 150.9025688 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

Figure S26 HMQC spectrum of **3/4** in CD_3OD

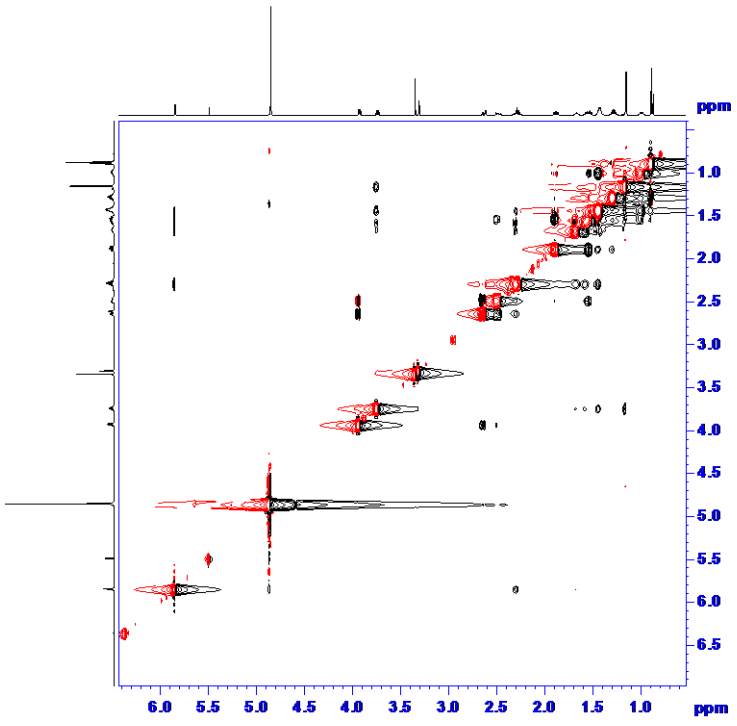


BRUKER

```
NAME            PO4-E-11-3-2
EXPNO                      6
PROCNO                     1
Date_            20150826
Time_              22.09
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG        hmbcgpndqf
TD                      4096
SOLVENT          CD3OD_SPE
NS                         4
DS                        16
SWH              6009.615 Hz
FIDRES           1.467191 Hz
AQ               0.3408372 sec
RG                   183.37
DW                 83.200 usec
DE                   6.50 usec
TE                 298.0 K
CNST13           8.0000000
D0               0.00000300 sec
D1               1.50000000 sec
D6               0.06250000 sec
D16              0.00020000 sec
IN0              0.00001510 sec

======== CHANNEL f1 ========
SFO1           600.1324005 MHz
NUC1                   1H
P1                   10.82 usec
P2                   21.64 usec
ND0                        2
TD                       512
SFO1             150.9177 MHz
FIDRES           64.673012 Hz
SW                 219.408 ppm
FnMODE                    QF
SI                      1024
SF             600.1300057 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.40
SI                      1024
MC2                       QF
SF             150.9025803 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0
```

Figure S27 HMBC spectrum of **3/4** in CD_3OD



BRUKER

```
NAME            PO4-E-11-3-2
EXPNO                      7
PROCNO                     1
Date_            20150827
Time_              18.36
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG        noesygpphpp
TD                      2048
SOLVENT          CD3OD_SPE
NS                         5
DS                        16
SWH              6009.615 Hz
FIDRES           2.934382 Hz
AQ               0.1704436 sec
RG                   76.75
DW                 83.200 usec
DE                   6.50 usec
TE                 298.0 K
D0               0.00006952 sec
D1               2.00000000 sec
D8               0.80000001 sec
D11              0.03000000 sec
D12              0.00002000 sec
D16              0.00020000 sec
IN0              0.00016660 sec

======= CHANNEL f1 =======
SFO1           600.1324005 MHz
NUC1                   1H
P1                   10.82 usec
P2                   21.64 usec
P17                2500.00 usec
ND0                        1
TD                       256
SFO1             600.1324 MHz
FIDRES           23.446878 Hz
SW                 10.002 ppm
FnMODE       States-TPPI
SI                      1024
SF             600.1300062 MHz
WDW                    QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
PC                      1.00
SI                      1024
MC2          States-TPPI
SF             600.1300065 MHz
WDW                    QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
```

Figure S28 NOESY spectrum of **3/4** in CD_3OD

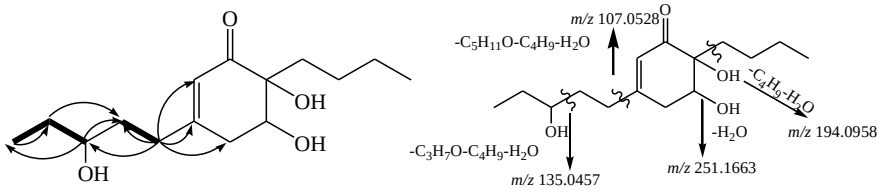


Figure S29 Key ^{1}H-^{1}H COSY and HMBC correlations and MS/MS fragment ion peaks for **3/4**

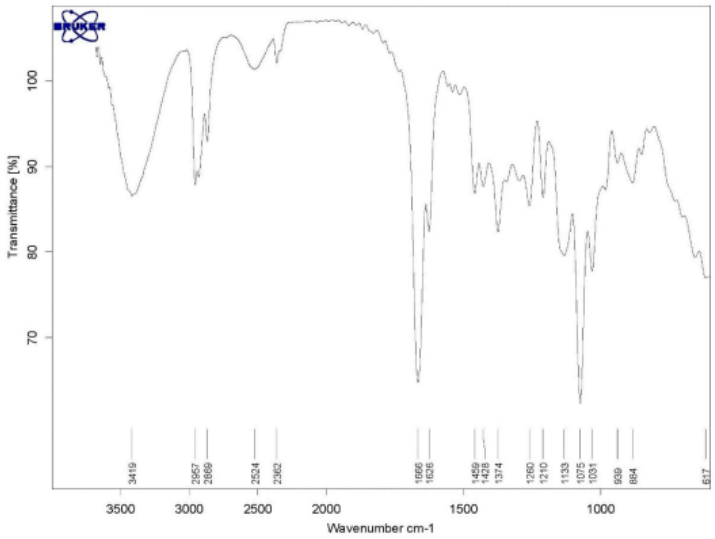


Figure S30 IR spectrum of **3/4**

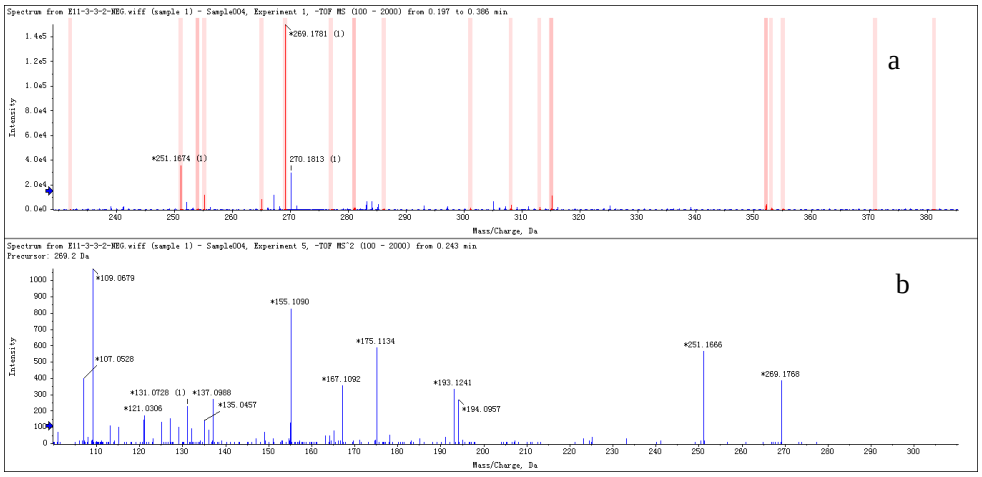


Figure S31MS/MS of **5/6** (a: MS^{1}, b: MS^{2})

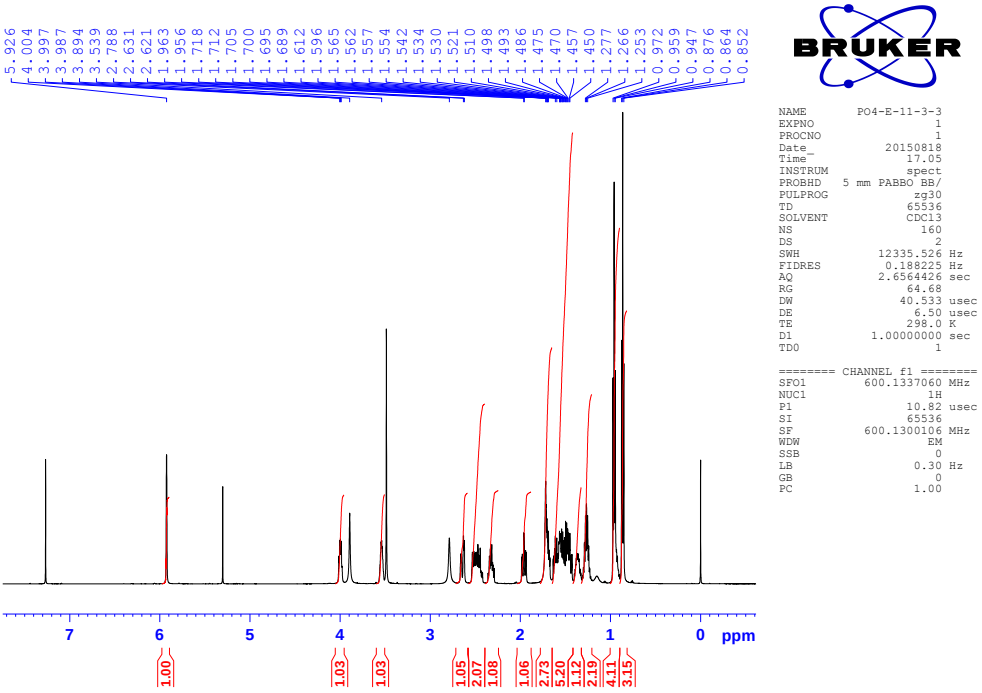


Figure S32 ^{1}H NMR spectrum of **5/6** in $CDCl_3$

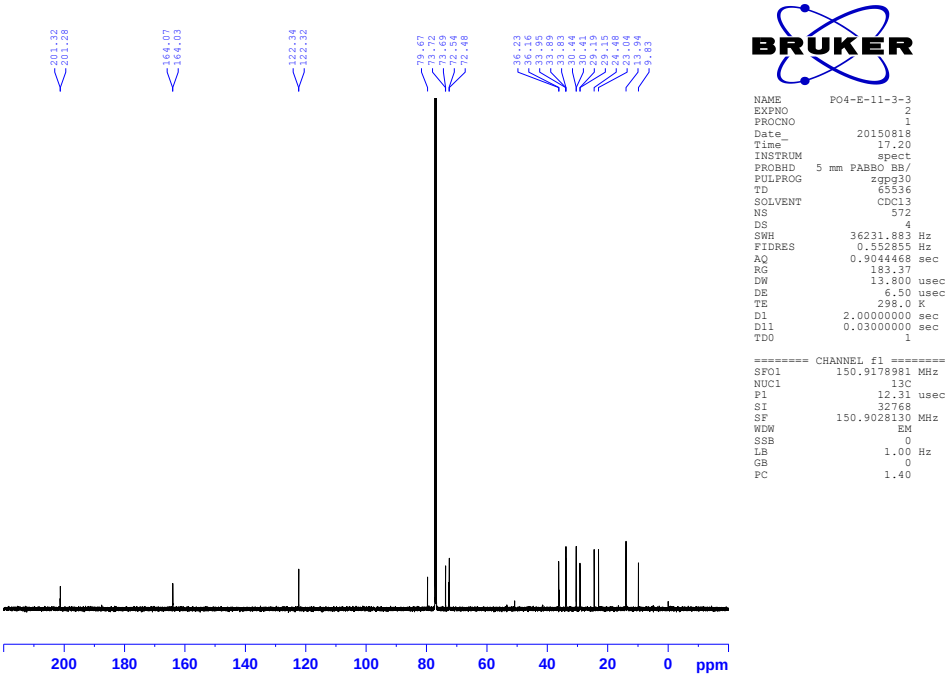
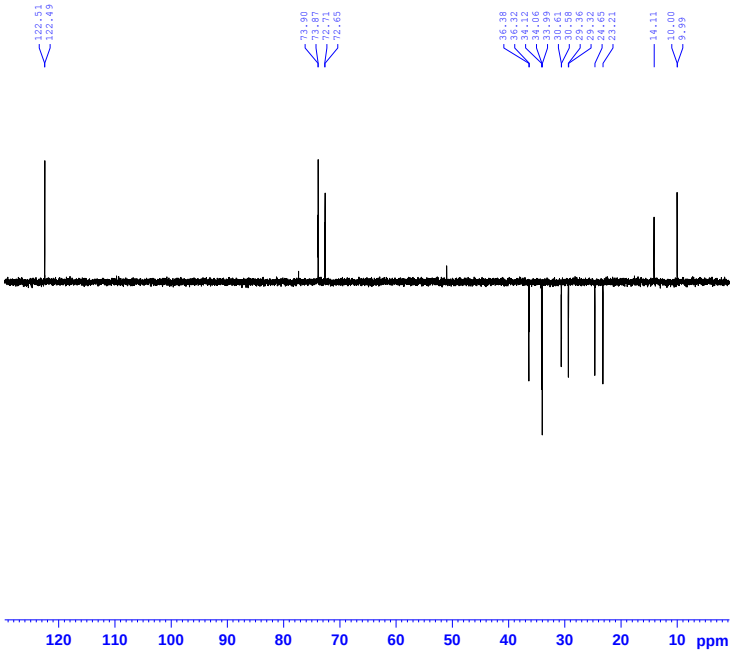


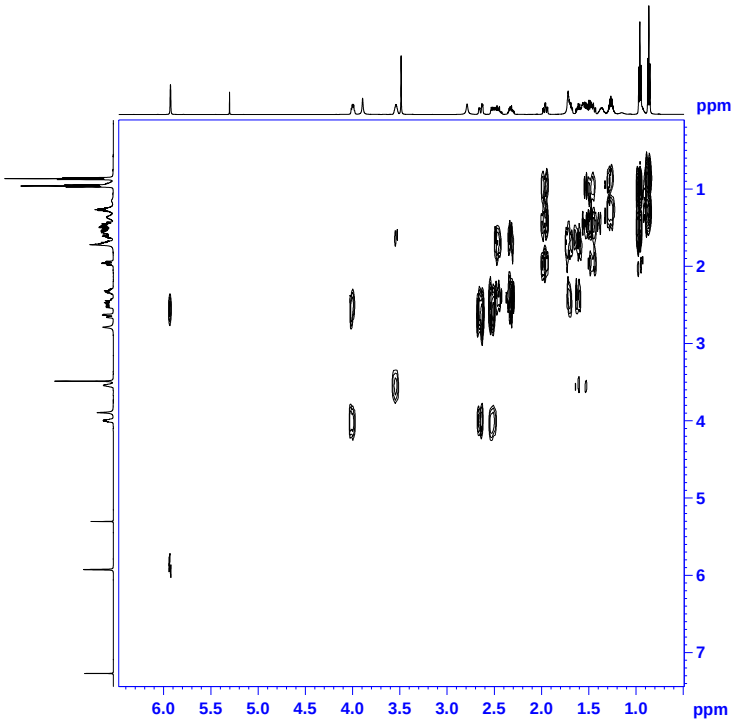
Figure S33 ^{13}C NMR spectrum of **5/6** in $CDCl_3$




```
NAME          PO4-E-11-3-3
EXPNO                    3
PROCNO                   1
Date_             20150827
Time                 19.51
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG         deptsp135
TD                  65536
SOLVENT         CD3OD_SPE
NS                    255
DS                      4
SWH             36231.883 Hz
FIDRES              0.552855 Hz
AQ                0.9044468 sec
RG                  183.37
DW                  13.800 usec
DE                   6.50 usec
TE                  298.0 K
CNST2          145.0000000
D1               2.00000000 sec
D2               0.00344828 sec
D12              0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           150.9163903 MHz
NUC1                   13C
P1                   12.31 usec
P13                2000.00 usec
SI                   32768
SF             150.9027878 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Figure S34 DEPT spectrum of **5/6** in $CDCl_3$




```
NAME          PO4-E-11-3-3
EXPNO                    4
PROCNO                   1
Date_             20150827
Time                 20.05
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG       cosygpmfqf
TD                    2048
SOLVENT              CDCl3
NS                       4
DS                      16
SWH              6009.615 Hz
FIDRES           2.934382 Hz
AQ               0.1704436 sec
RG                  183.37
DW                  83.200 usec
DE                   6.50 usec
TE                  298.0 K
D0               0.00000300 sec
D1               2.00000000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00016660 sec

======== CHANNEL f1 ========
SFO1           600.1324005 MHz
NUC1                   1H
P1                  10.82 usec
ND0                     1
TD                    256
SFO1             600.1324 MHz
FIDRES          23.446878 Hz
SW                 10.002 ppm
FnMODE                 QF
SI                   1024
SF             600.1300061 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2                    QF
SF             600.1300015 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
```

Figure S35 ^{1}H-^{1}H COSY spectrum of **5/6** in $CDCl_3$

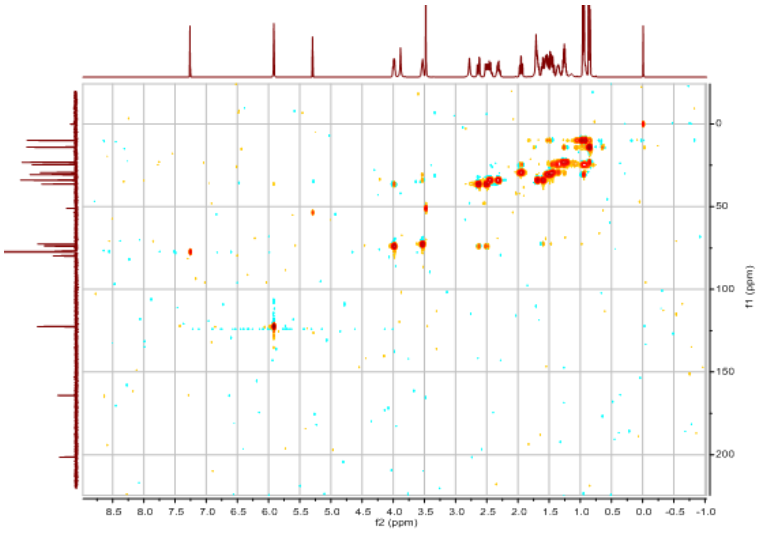
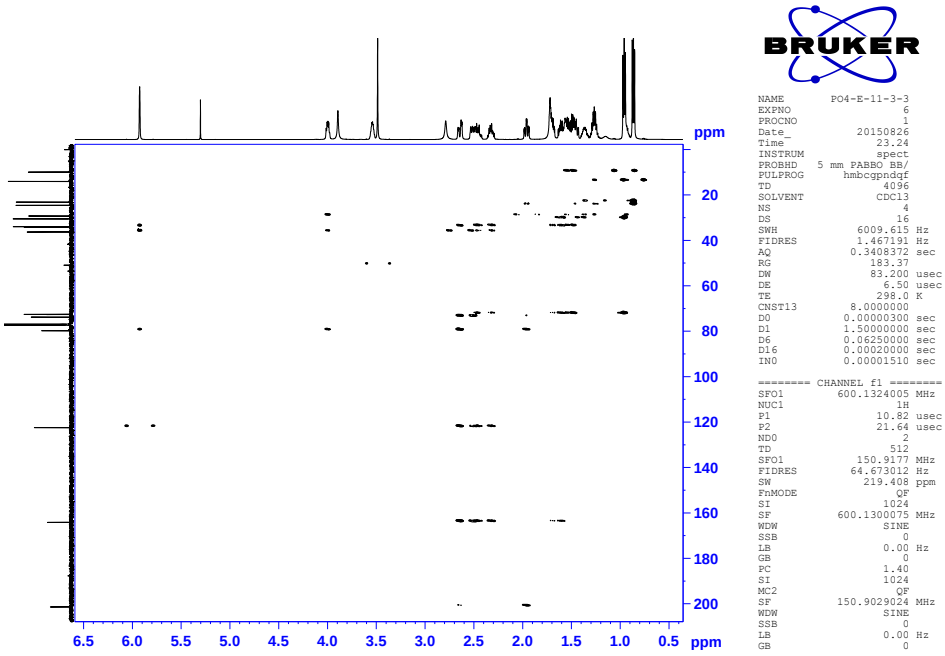


Figure S36 HMQC spectrum of **5/6** in $CDCl_3$




```
NAME          PO4-E-11-3-3
EXPNO                    6
PROCNO                   1
Date_             20150826
Time                 23.24
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG       hmbcgpndqf
TD                    4096
SOLVENT            CDCl3
NS                       4
DS                      16
SWH             6009.615 Hz
FIDRES          1.467191 Hz
AQ              0.3408372 sec
RG                  183.37
DW                83.200 usec
DE                 6.50 usec
TE                 298.0 K
CNST13          8.0000000
D0              0.00000300 sec
D1              1.50000000 sec
D6              0.06250000 sec
D16             0.00020000 sec
IN0             0.00001510 sec

======== CHANNEL f1 ========
SFO1          600.1324005 MHz
NUC1                     1H
P1                  10.82 usec
P2                  21.64 usec
ND0                      2
TD                     512
SFO1            150.9177 MHz
FIDRES          64.673012 Hz
SW                219.408 ppm
FnMODE                   QF
SI                     1024
SF            600.1300075 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
SI                     1024
MC2                      QF
SF            150.9029024 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
```

Figure S37 HMBC spectrum of **5/6** in $CDCl_3$

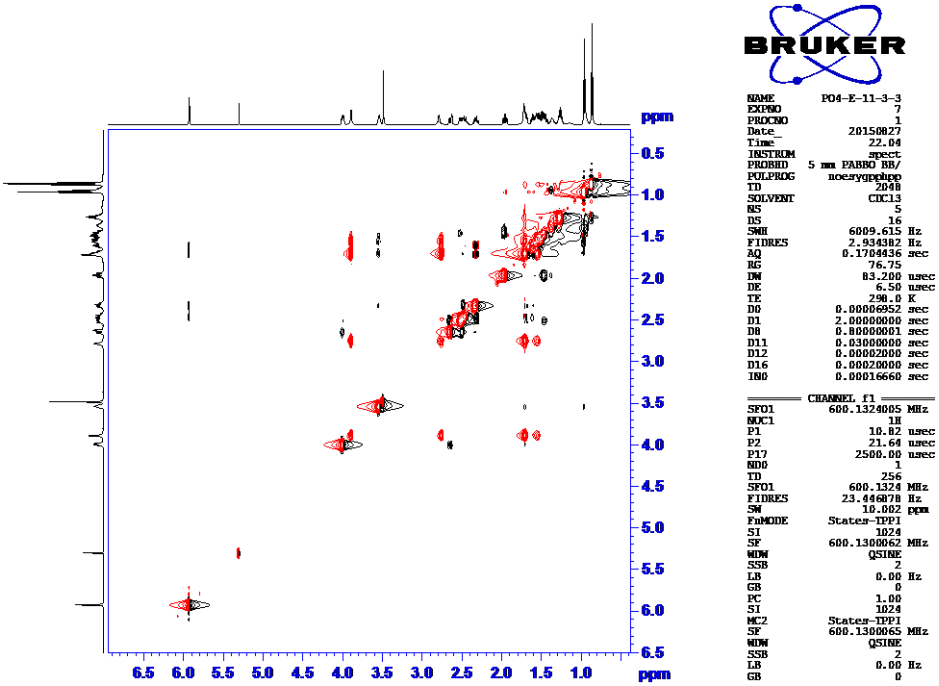


Figure S38 NOESY spectrum of **5/6** in $CDCl_3$

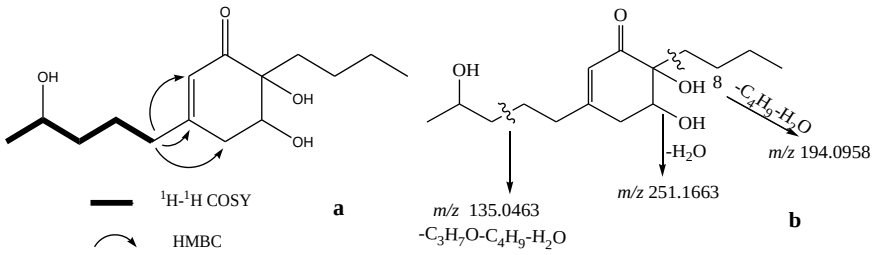


Figure S39 Key ^{1}H-^{1}H COSY and HMBC correlations and MS/MS fragment ion peaks for **5/6**

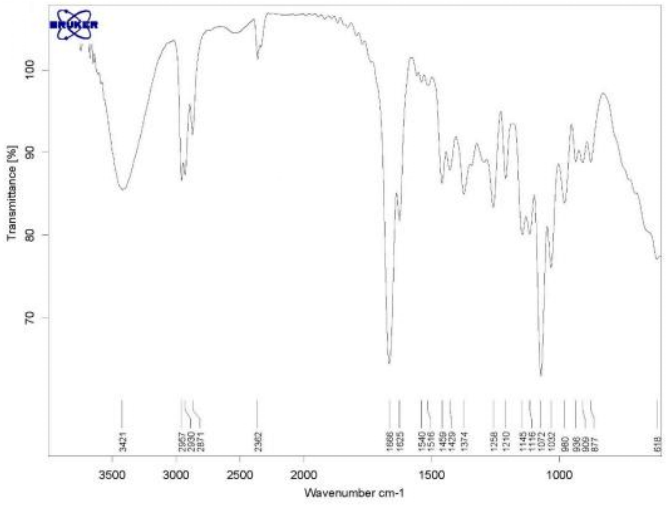


Figure S40 IR spectrum of **5/6**

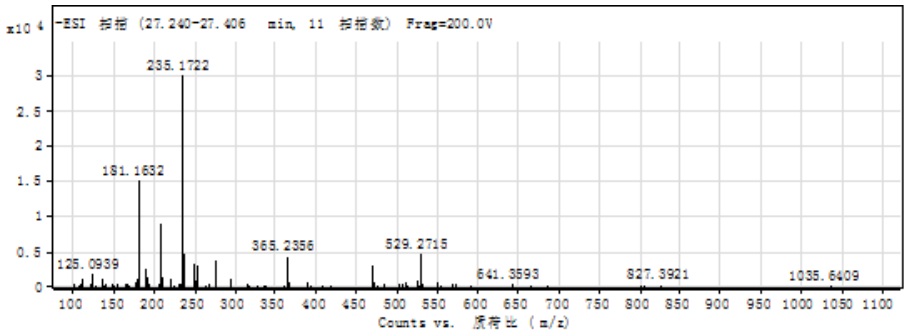


Figure S41 HRESI mass spectrum of **7**

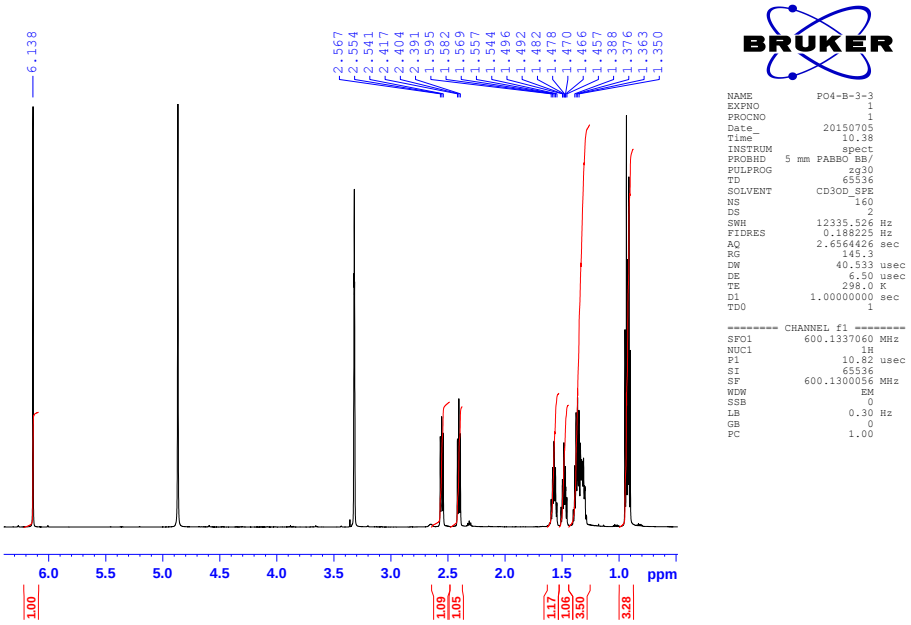


Figure S42 ^{1}H NMR spectrum of **7** in CD_3OD

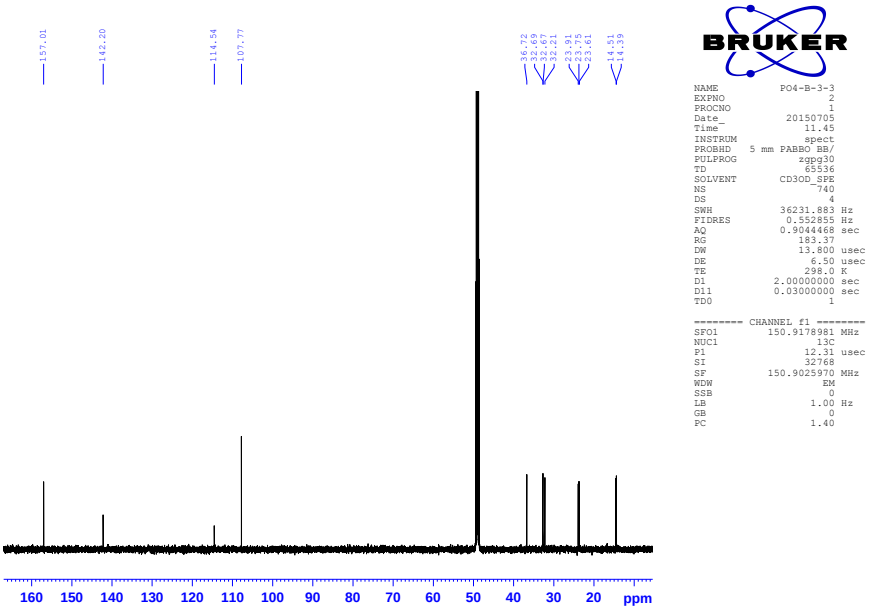


Figure S43 ^{13}C NMR spectrum of **7** in CD_3OD

Table S1^{1}H NMR data for **1-6**(600 MHz, in $CDCl_3$)

No.	1	2	3/4[a]	5/6
3	3.99 (dd, 10.2, 5.8)	3.99 (dd, 10.4, 5.8 Hz)	3.99 (dd, 10.5, 5.9 Hz)	3.92 (dd, 9.8, 5.7 Hz)
4	2.59 (dd, 18.5, 5.8 Hz) 2.47 (ddd, 18.5, 10.2, 2.6 Hz)	2.81 (dd, 18.7, 5.8 Hz) 2.38 (ddd, 18.7, 10.4, 2.6 Hz)	2.64 (ddd, 18.6, 5.9, 2.6 Hz) 2.51 (m)	2.48 (m), 2.63 (ddd, 18.6, 5.7, 3.0 Hz)
6	6.15 (dd, 2.6, 1.3 Hz)	6.08 (d, 2.4 Hz)	5.92 (bs)	5.84 (bs)
7	1.98 (dt, 13.2, 4.2 Hz) 1.47 (dt, 13.2, 4.2 Hz)	1.98 (dt, 13.2, 4.2 Hz) 1.47 (dt, 12.0, 4.2 Hz)	1.96 (dt, 13.2, 4.2 Hz) 1.47 (m)	1.88 (dt, 12.0, 4.2 Hz) 1.53 (m)
8	0.95 (m), 1.34 (m)	0.95 (m), 1.37 (m)	1.47 (m), 1.36 (m)	0.99 (m), 1.43 (m)
9	1.27 (m)	1.26 (m)	1.26 (m)	1.28 (m)
10	0.86 (t, 7.3 Hz)	0.86 (t, 7.3 Hz)	0.86 (t, 7.3 Hz)	0.88 (t, 7.3 Hz)
11	4.26 (bt, 5.4 Hz)	4.23 (t, 6.4 Hz)	2.44 (m), 2.31 (m)	2.28 (m)
12	1.68 (m), 1.59 (m)	1.61 (m)	1.69 (m), 1.60 (m)	1.67 (m), 1.57 (m)
13	1.34 (m)	1.36 (m), 1.25 (m)	3.54 (m)	1.43 (m)
14	1.34 (m)	1.36 (m)	1.54 (m)	3.73 (q, 6.0)
15	0.91 (t, 7.2 Hz)	0.91 (t, 7.1 Hz)	0.96 (t, 7.2 Hz)	1.15 (d, 6.0 Hz)

[a] Measured in CD_3OD

Table S2^{13}C NMR data for **1-6** (150 MHz, in $CDCl_3$)

No.	1	2	3/4[a]	5/6
1	201.5	201.9	201.46 (201.43)	203.1
2	80.4	80.4	79.84 (79.83)	80.7
3	74.1	73.7	73.88 (73.85)	74.2
4	32.8	31.5	36.39 (36.32)	37.9
5	164.7	164.8	164.22 (164.18)	165.39 (165.34)[b]
6	120.9	121.7	122.50 (122.48)	124.11 (124.09)
7	29.2	29.1	29.35 (29.32)	30.5
8	24.6	24.6	24.6	25.8
9	23.2	23.1	23.2	24.2
10	14.1	14.1	14.12 (14.11)	14.4
11	74.0	74.1	34.12 (34.06)	38.4
12	35.0	35.1	34.0	24.37 (24.34)
13	27.2	27.7	72.70 (72.63)	39.55 (39.52)
14	22.6	22.6	30.60 (30.57)	68.16 (68.10)
15	14.1	14.1	10.00 (9.99)	23.6

[a] Measured in CD_3OD; [b] data in () for stereoisomer with different orientation of hydroxyl group in amyl chain.