

## Electronic Supplementary Information:

### Synthesis of the Four Stereoisomers of 2,3-Epoxy-4-hydroxynonanal, Potential Genotoxic Products of Lipid Peroxidation, and Their Reactivity with Deoxyguanosine

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### Procedures for the synthesis of (4*S*)- and (4*R*)-4-hydroxy-2*E*-nonenal

**(2*S*,3*S*)-2,3-Epoxy-1-octanol.** Prepared in 79% yield by Sharpless epoxidation of 2*E*-octen-1-ol as previously described.<sup>1,2</sup>  $[\alpha]_{\text{D}}^{25}$  -40.7° (*c* 0.43,  $\text{CHCl}_3$ ). lit.<sup>2</sup>  $[\alpha]_{\text{D}}^{20}$  -40.4° (*c* 1.08,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ );  $\delta$  0.91 (t, 3H,  $J=7.0$  Hz,  $\text{CH}_3$ ), 1.31-1.36 (m, 4H, 2 $\text{CH}_2$ ), 1.42-1.49 (m, 2H,  $\text{CH}_2$ ), 1.55-1.64 (m, 2H,  $\text{CH}_2$ ), 1.73 (br. t, 1H, OH), 2.92-3.0 (m, 2H,  $\text{CH}_2$ ), 3.62-3.65 (m, 1H), 3.88-3.90 (m, 1H).

**(2*R*,3*R*)-2,3-Epoxy-1-octanol.** Prepared in 87 % yield.<sup>2</sup>  $[\alpha]_{\text{D}}^{24.5}$  +40.0° (*c* 1.11,  $\text{CHCl}_3$ ). lit.<sup>3</sup>  $[\alpha]_{\text{D}}^{27}$  +38.9° (*c* 1.11,  $\text{CHCl}_3$  99 % ee); lit.<sup>2</sup>  $[\alpha]_{\text{D}}^{20}$  +40.0° (*c* 0.56,  $\text{CHCl}_3$ )  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ );  $\delta$  0.91 (t, 3H,  $J=6.9$  Hz,  $\text{CH}_3$ ), 1.31-1.35 (m, 4H, 2 $\text{CH}_2$ ), 1.44-1.46 (m, 2H,  $\text{CH}_2$ ), 1.55-1.59 (m, 2H,  $\text{CH}_2$ ), 1.73 (br. d, 1H, OH), 2.91-2.99 (m, 2H,  $\text{CH}_2$ ), 3.68 (ddd, 1H,  $J=4.2, 7.2, 12.4$  Hz), 3.93 (ddd, 1H,  $J=2.5, 5.3, 12.5$  Hz).

**(2*R*,3*S*)- Epoxyoctanal.** (Diacetoxyiodo)benzene (4.61 g, 14.3 mmol) was added to a solution of (2*S*,3*S*)-epoxy-1-octanol (1.90 g, 13.0 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.20 g 1.3 mmol) in 25 mL dry methylene chloride. The reaction mixture was stirred at ambient temperature until the starting material was no longer detectable by GC/MS. The reaction mixture was diluted with methylene chloride (50 mL), then washed with a saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (25 mL) and the aqueous layer was extracted with methylene chloride (5 x 25 mL). The combined organic layers were washed with 5 %  $\text{NaHCO}_3$  (25 mL) and brine, dried over  $\text{MgSO}_4$ , filtrated and evaporated. Purification by flash chromatography on silica, eluting with 10 % ethyl acetate in hexanes afforded (2*R*,3*S*)-epoxyoctanal (1.51 g, 82 %).  $[\alpha]_{\text{D}}^{24.7}$  +98.3° (*c* 0.48,  $\text{CHCl}_3$ )  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ );  $\delta$  0.91 (t, 3H,  $J=7.1$  Hz,  $\text{CH}_3$ ), 1.31-1.37 (m, 4H, 2 $\text{CH}_2$ ), 1.46-1.52 (m, 2H,  $\text{CH}_2$ ), 1.63-1.71 (m, 2H,  $\text{CH}_2$ ), 3.14 (dd, 1H,  $J=2.0, 6.3$  Hz, H-2), 3.24 (ddd, 1H,  $J=2.0, 5.6, 11.0$  Hz, H-3), 9.01 (d, 1H,  $J=6.3$  Hz, CHO); *m/z* (GC-EI) 143 (0.5,  $\text{M}^+ + 1$ ), 71 (100), 55 (20), 41 (25).

**(2*S*,3*R*)-Epoxyoctanal.** Prepared from (2*R*,3*R*)-epoxy-1-octanol in 84 % yield following the procedure described above for (2*R*,3*S*)-epoxyoctanal.  $[\alpha]_{\text{D}}^{25.7}$  -98.6° (*c* 0.35,  $\text{CHCl}_3$ ).

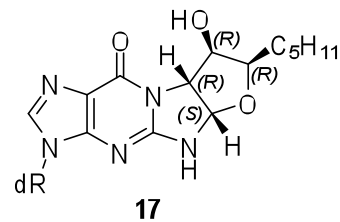
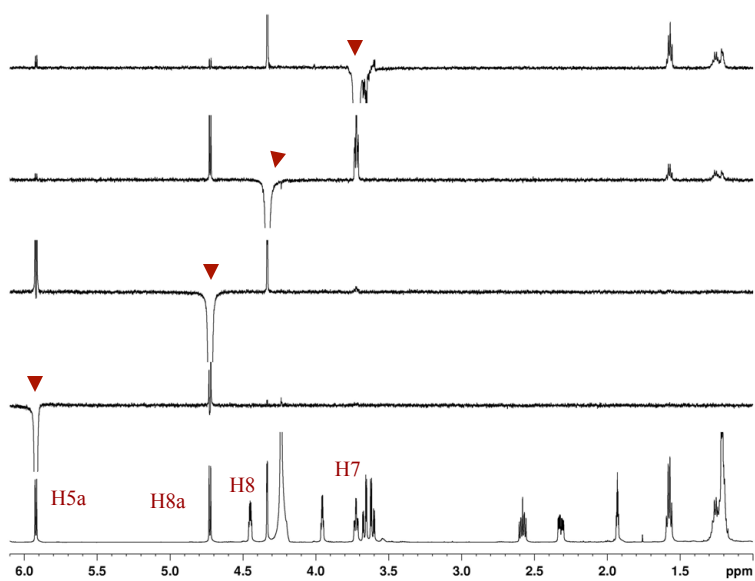
**(4*S*)-4-Hydroxy-2*E*-nonenal (1).** (Methoxymethyl)triphenylphosphonium chloride (2.74 g, 7.98 mmol), which was dried before use, was placed in a flame-dried flask and dry THF (10 mL) was added. The suspension was cooled to -40 °C and potassium *tert*-butoxide (1.12 g, 9.98 mmol) dissolved in dry THF (10 mL) was added dropwise resulting in an orange solution. The mixture was stirred 15 min at -40 °C, then cooled to -78 °C. A solution of (2*R*,3*S*)-epoxyoctanal (0.85 g, 6.0 mmol) in dry THF (5 mL) was stirred over activated 4Å molecular sieves for 15 min, then added dropwise to the Wittig reagent at -78 °C. The mixture was stirred for 15 min at -78 °C, then

allowed to warm to room temperature over 1h. The reaction was quenched by the addition of saturated aqueous NH<sub>4</sub>Cl (15 mL) to the reaction, and the mixture was stirred for 30 min. The mixture was extracted with methylene chloride (3 x 50 mL); the combined organics were washed with water, dried over MgSO<sub>4</sub>, filtrated and concentrated. Purification by flash chromatography on silica, eluting at the beginning with 3:1 methylene chloride:hexanes (v/v) to remove trace of impurities, then followed by 65:35 hexanes:ether (v/v) to afford (4*S*)-HNE (**1**, 0.53 g, 56 %).  $[\alpha]_D^{24.5} +44.7^\circ$  (*c* 0.36, CHCl<sub>3</sub>) (lit.<sup>4</sup>  $[\alpha]_D^{20} = +48^\circ$  (*c* 0.69, CHCl<sub>3</sub>)); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>);  $\delta$  0.91 (t, 3H, *J*=6.9 Hz, CH<sub>3</sub>), 1.29-1.51 (m, 6H, 3CH<sub>2</sub>), 1.54-1.69 (m, 2H, CH<sub>2</sub>), 1.86 (br.s., 1H, OH), 4.43 (m, 1H, *J*=5.2 Hz, H-4), 6.27 (ddd, 1H, *J*=1.6, 7.9, *J*=15.7 Hz, H-2), 6.84 (dd, 1H, *J*=4.4, 15.6 Hz, H-3), 9.56 (d 1H, *J*=8.0 Hz, CHO); *m/z* (GC-EI) 157 (100, M<sup>+</sup>+1), 139 (25), 109 (40), 81 (30).

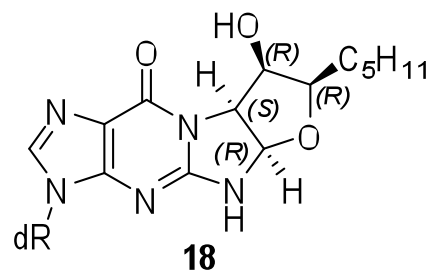
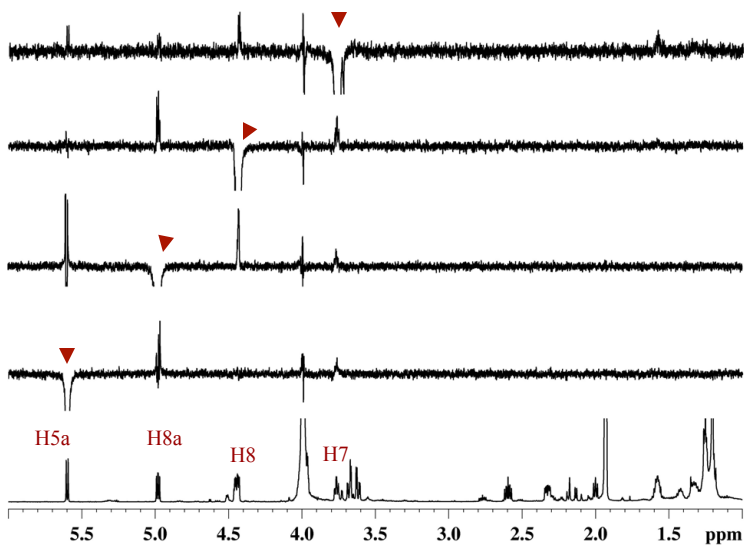
**(4*R*)-Hydroxy-2*E*-nonenal (2).** (4*R*)-HNE was prepared from (2*S*,3*R*)-epoxyoctanal in 68 % yield following the procedure described above for synthesis of **1**.  $[\alpha]_D^{25} -46.7^\circ$  (*c* 0.73, CHCl<sub>3</sub>) (lit.<sup>4</sup>  $[\alpha]_D^{25} -46^\circ$  (*c* 0.45, CHCl<sub>3</sub>));

- (1) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; B., S. K. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
- (2) Wang, H.; Kozekov, I. D.; Harris, T. M.; Rizzo, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 5687-700.
- (3) Richardson, T. I.; Rychnovsky, S. D. *Tetrahedron* **1999**, *55*, 8977-8996.
- (4) de Montarby, L.; Mosset, P.; Gree, R. *Tetrahedron Lett.* **1988**, *29*, 3937-3940.

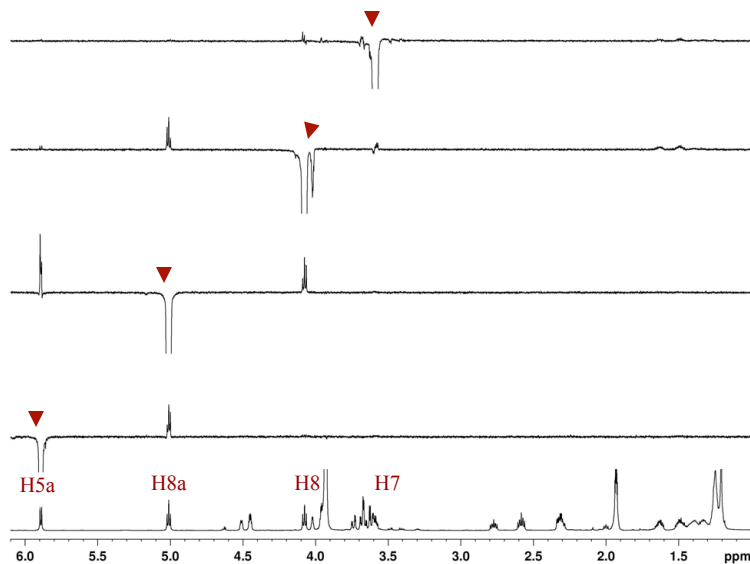
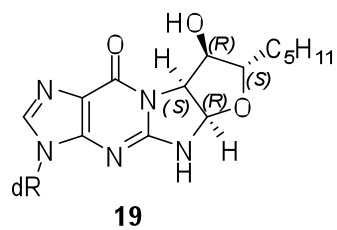
**Figure S1.** Selective NOE spectra of tetracyclic adduct **17**



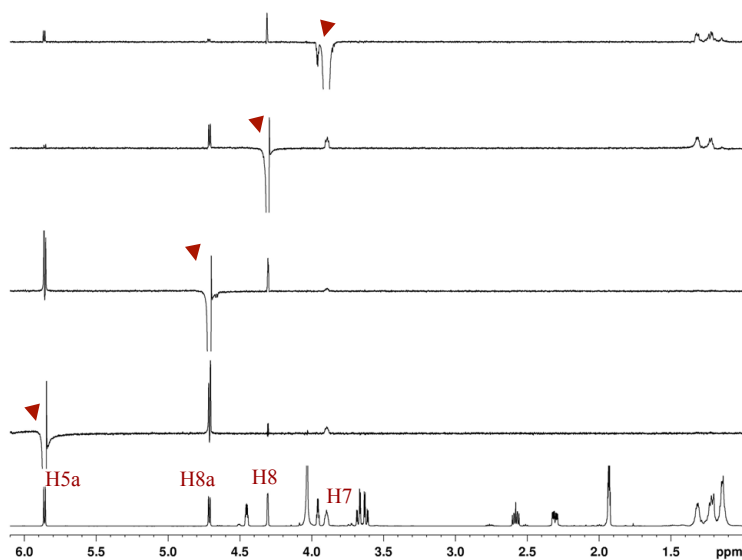
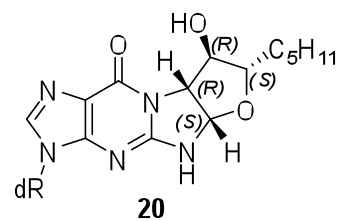
**Figure S2.** Selective NOE spectra of tetracyclic adduct **18**



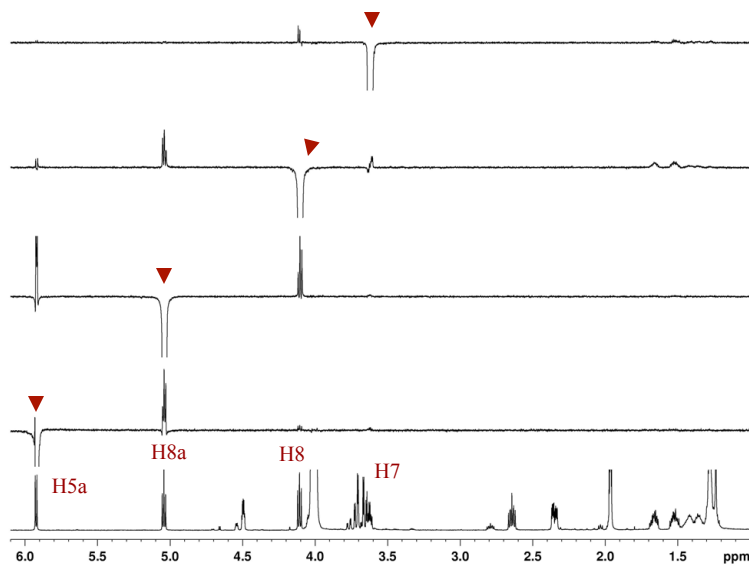
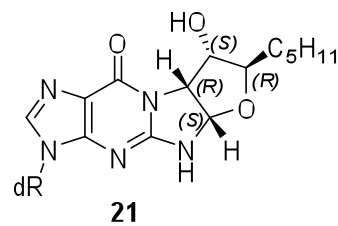
**Figure S3.** Selective NOE spectra of tetracyclic adduct **19**



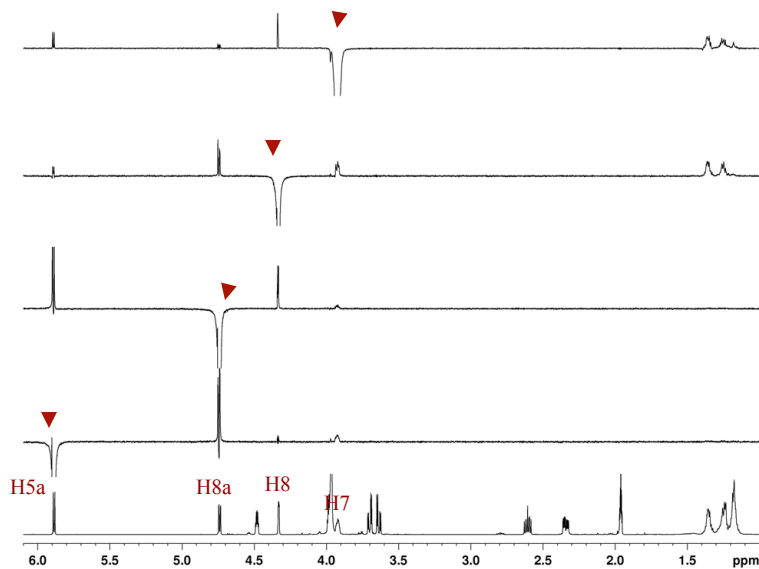
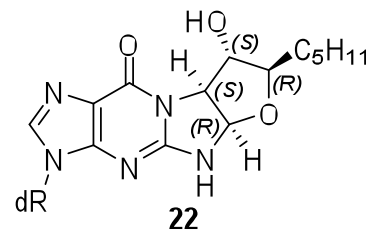
**Figure S4.** Selective NOE spectra of tetracyclic adduct **20**



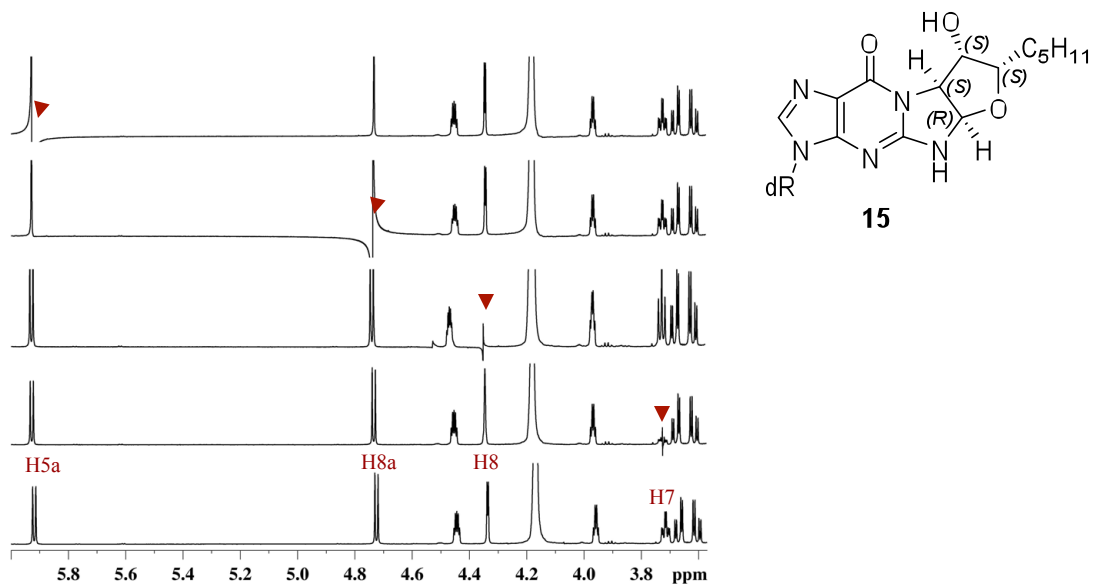
**Figure S5.** Selective NOE spectra of tetracyclic adduct **21**



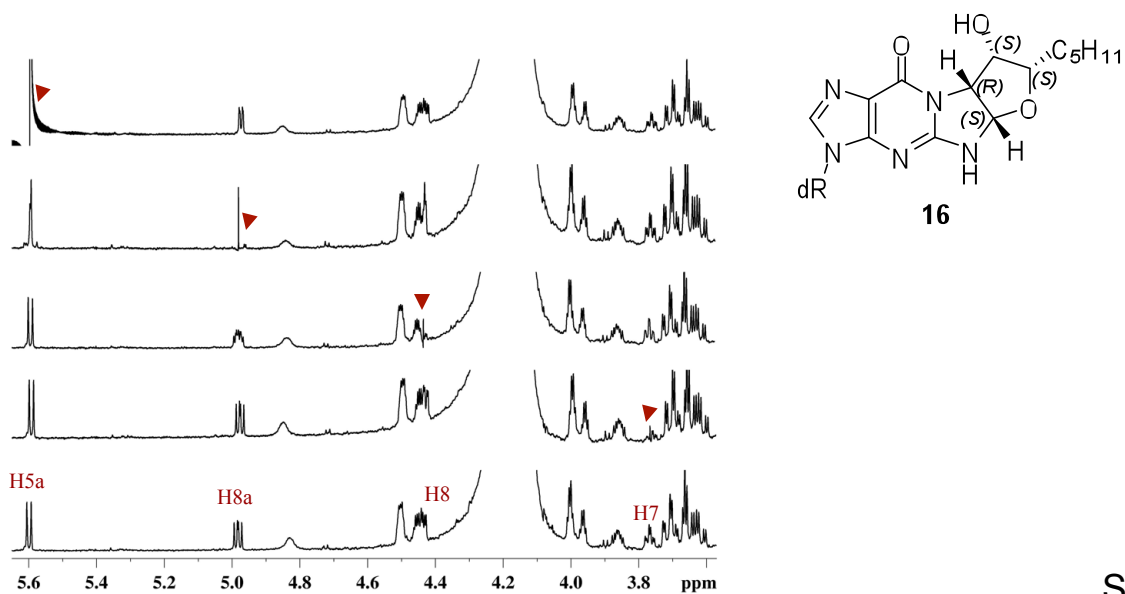
**Figure S6.** Selective NOE spectra of tetracyclic adduct **22**



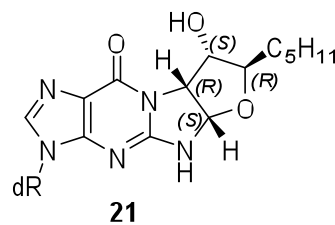
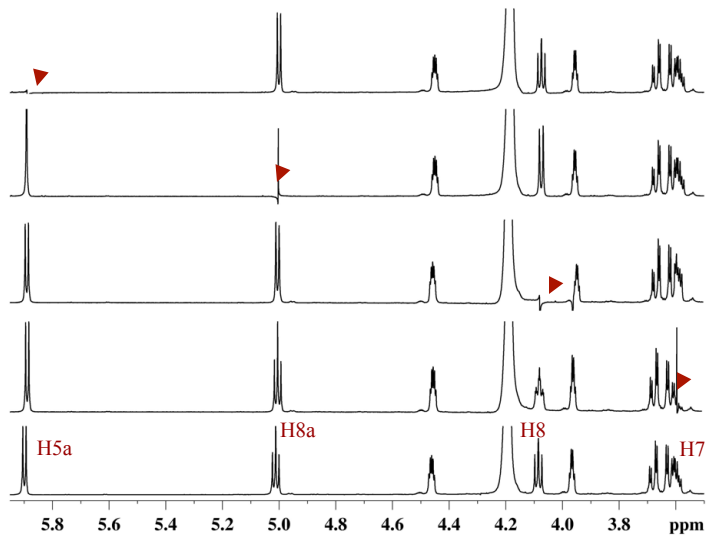
**Figure S7.** 1D  $^1\text{H}$  homonuclear decoupling experiments for tetracyclic adduct **15**



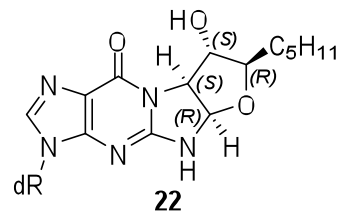
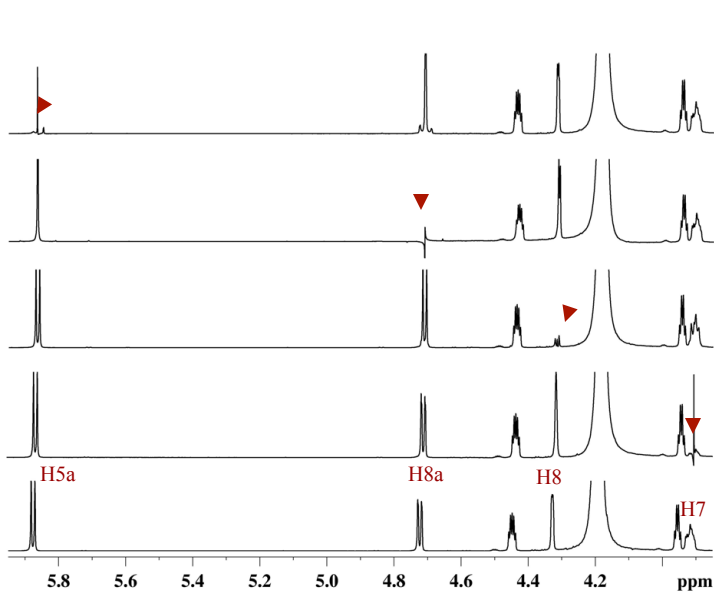
**Figure S8.** 1D  $^1\text{H}$  homonuclear decoupling experiments for tetracyclic adduct **16**



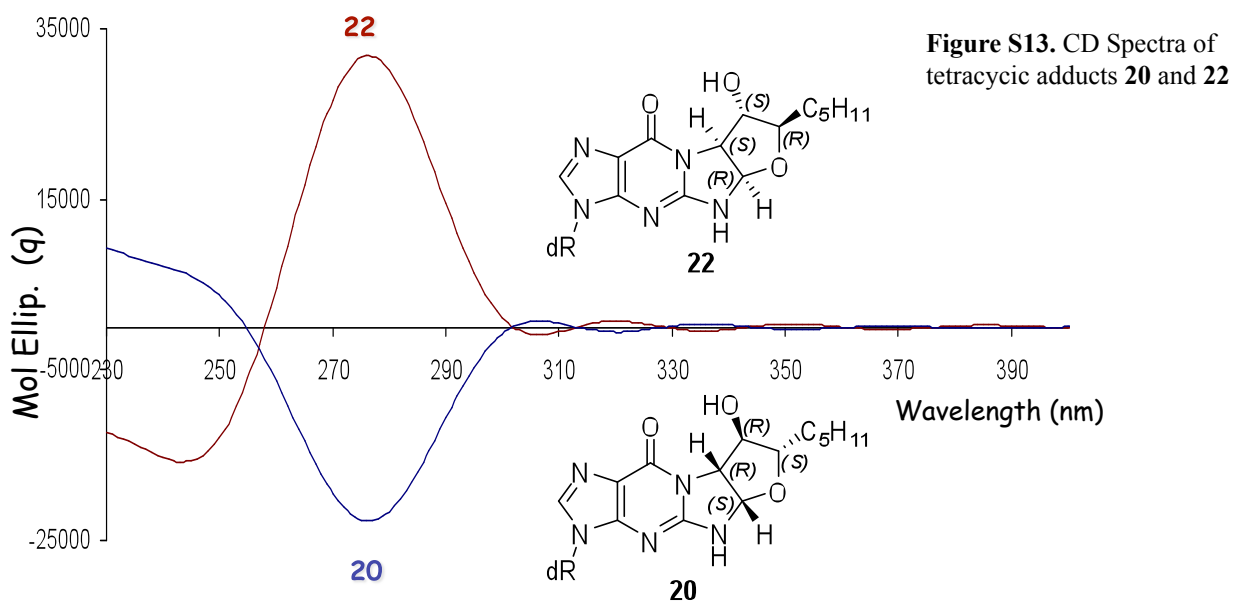
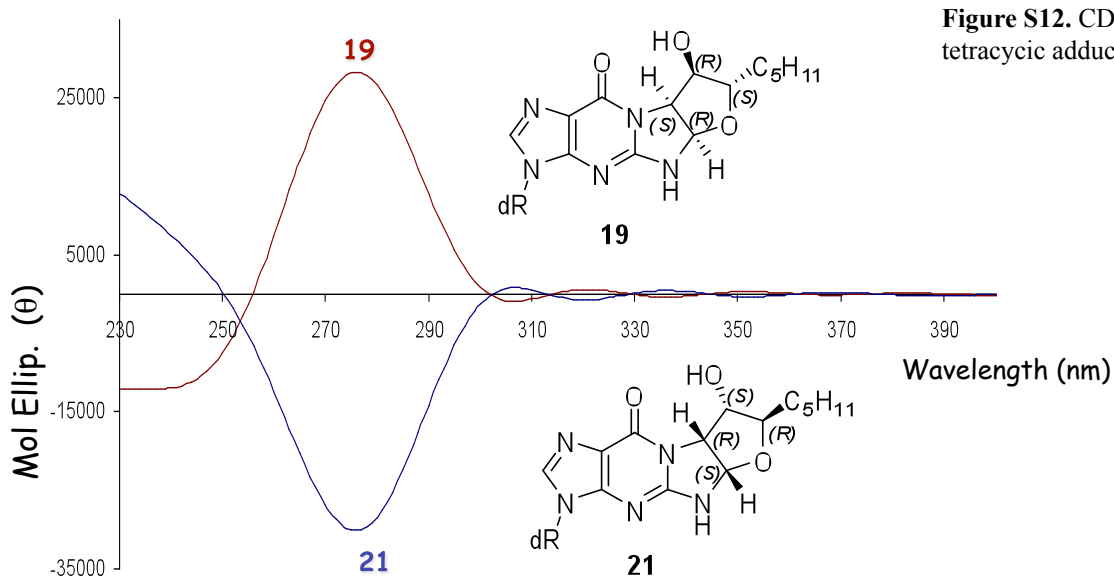
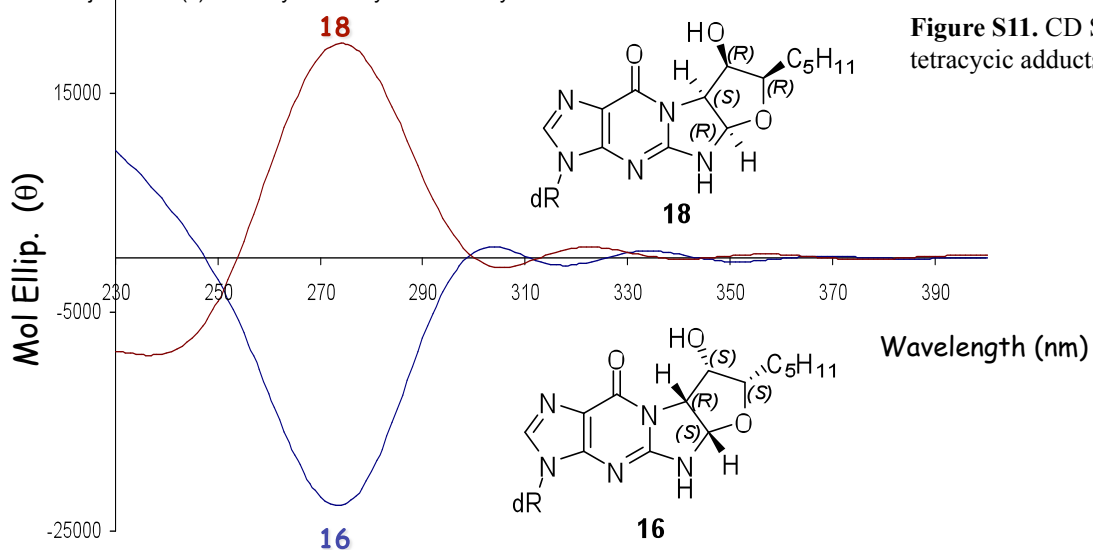
**Figure S9.** 1D  $^1\text{H}$  homonuclear decoupling experiments for tetracyclic adduct **21**



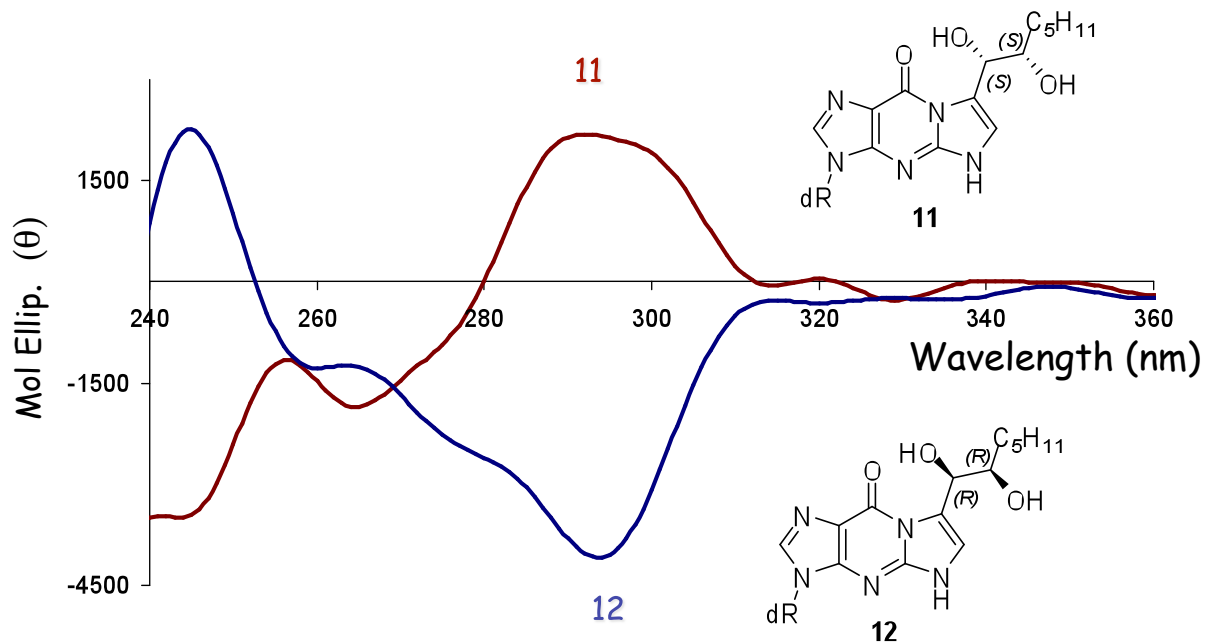
**Figure S10.** 1D  $^1\text{H}$  homonuclear decoupling experiments for tetracyclic adduct **22**



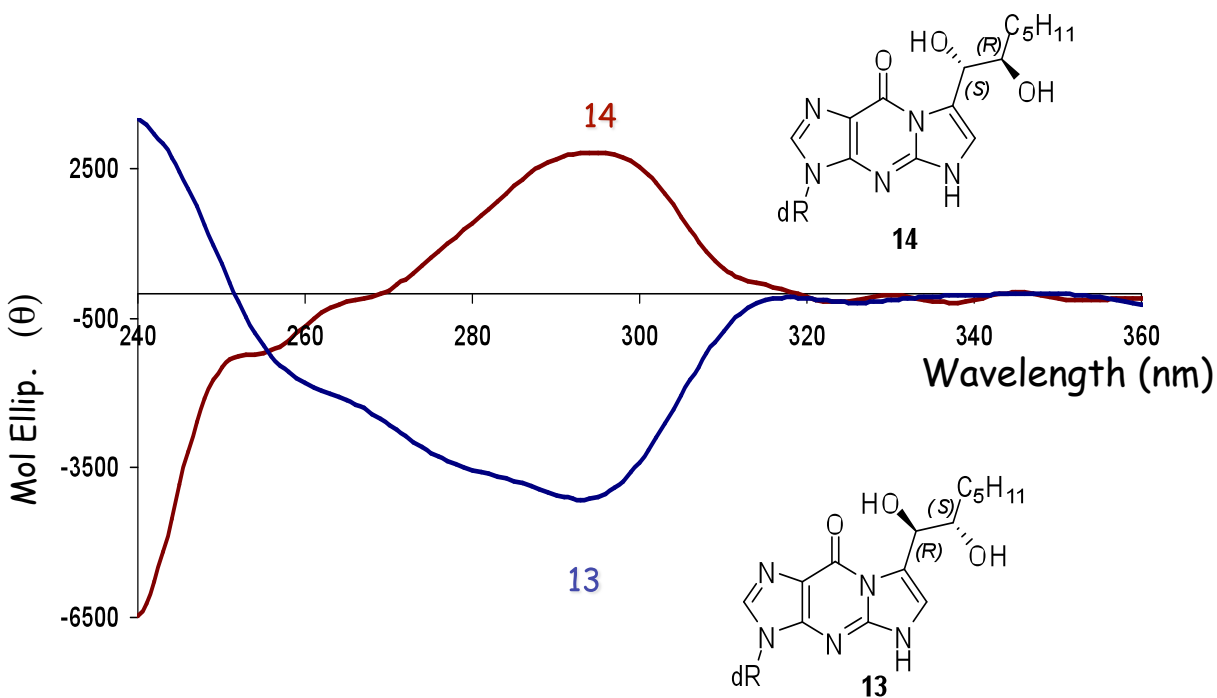




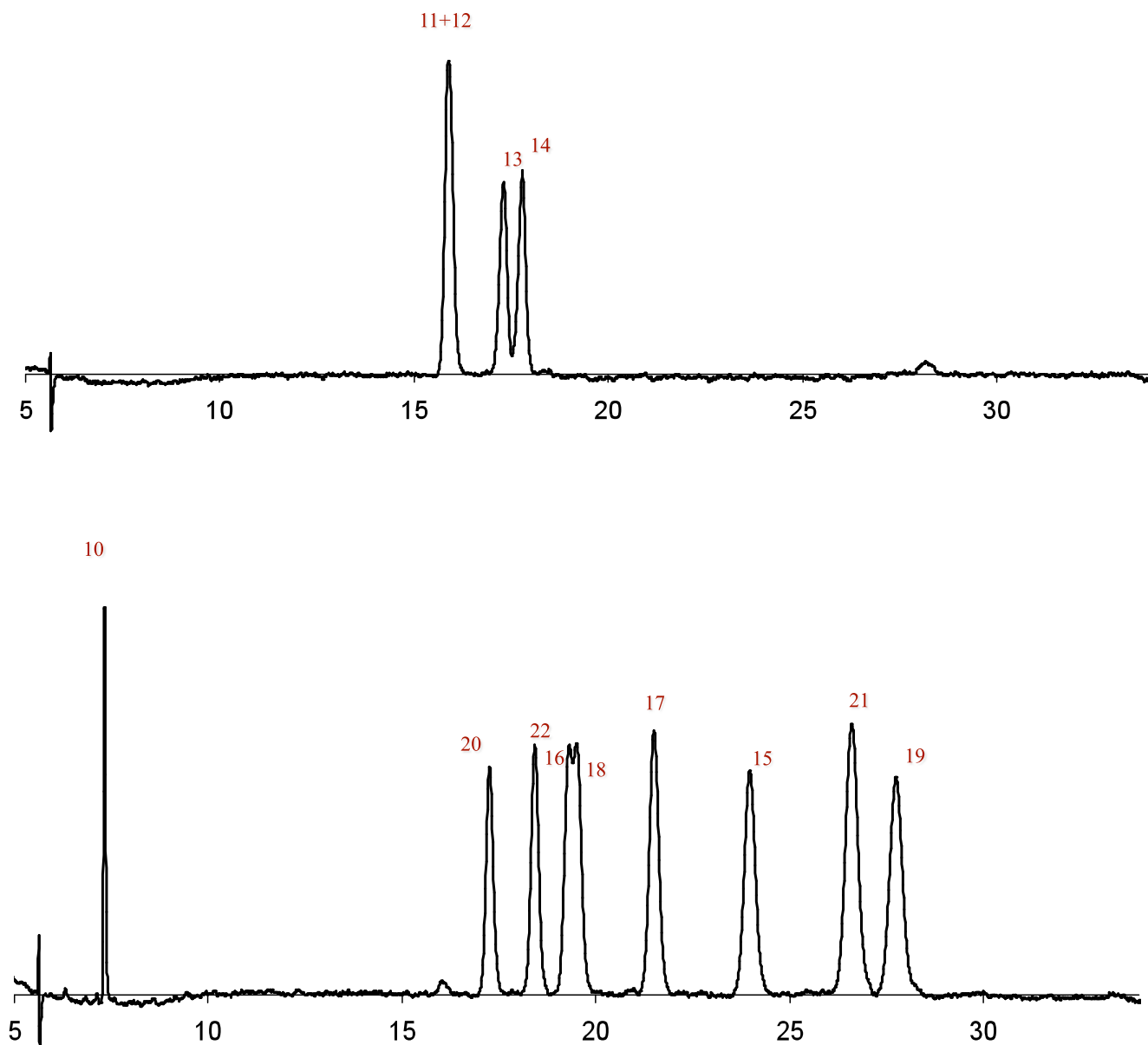
**Figure 14.** Spectra of C7-(1,2-dihydroxyheptyl)- $\epsilon$ dGuo adducts **11** and **12**



**Figure 15.** Spectra of C7-(1,2-dihydroxyheptyl)- $\epsilon$ dGuo adducts **13** and **14**

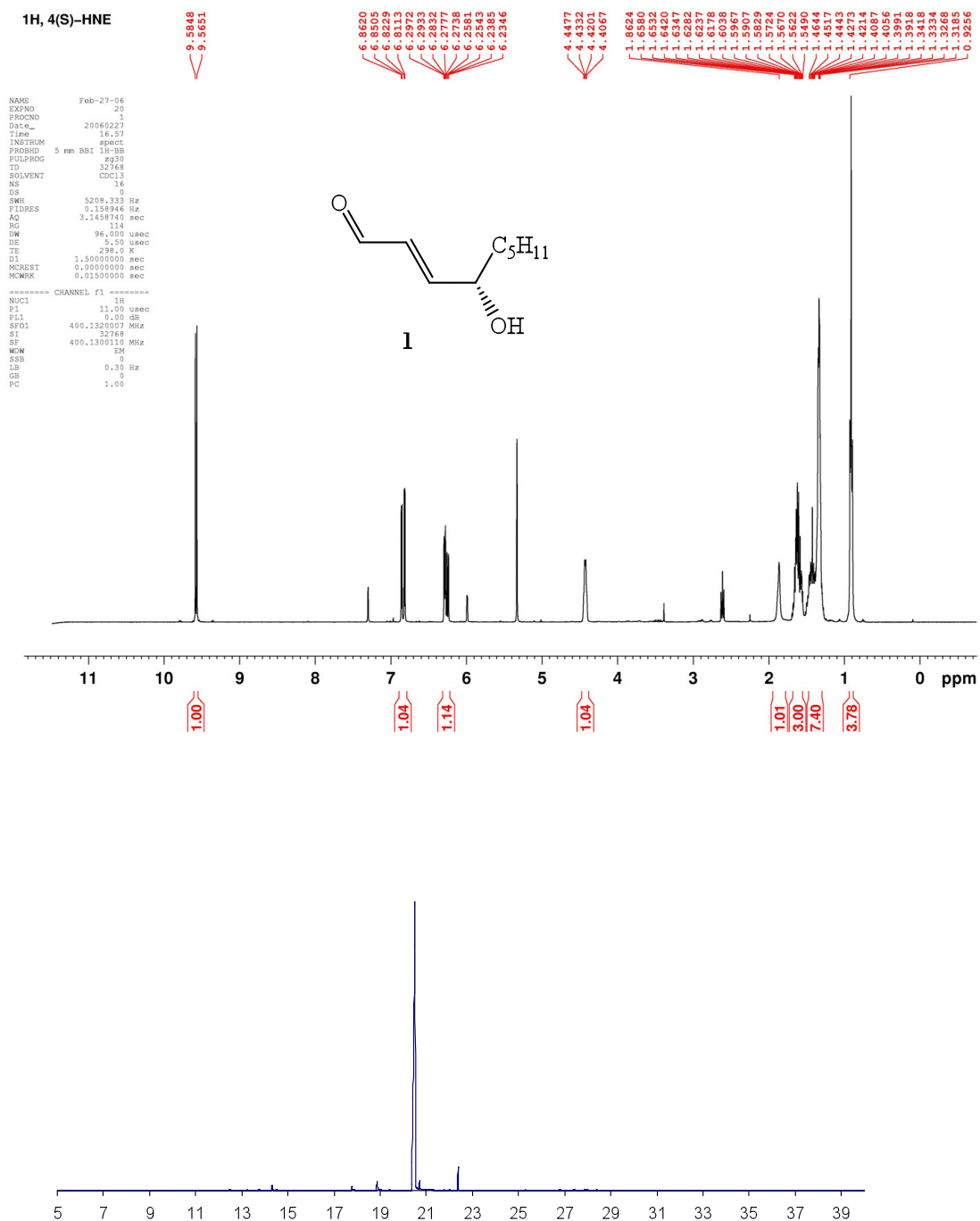


**Figure S16.** HPLC chromatograms of four C7-(1,2-dihydroxyheptyl)-  
εdGuo adducts **11-14** and eight tetracyclic adducts **15-22**

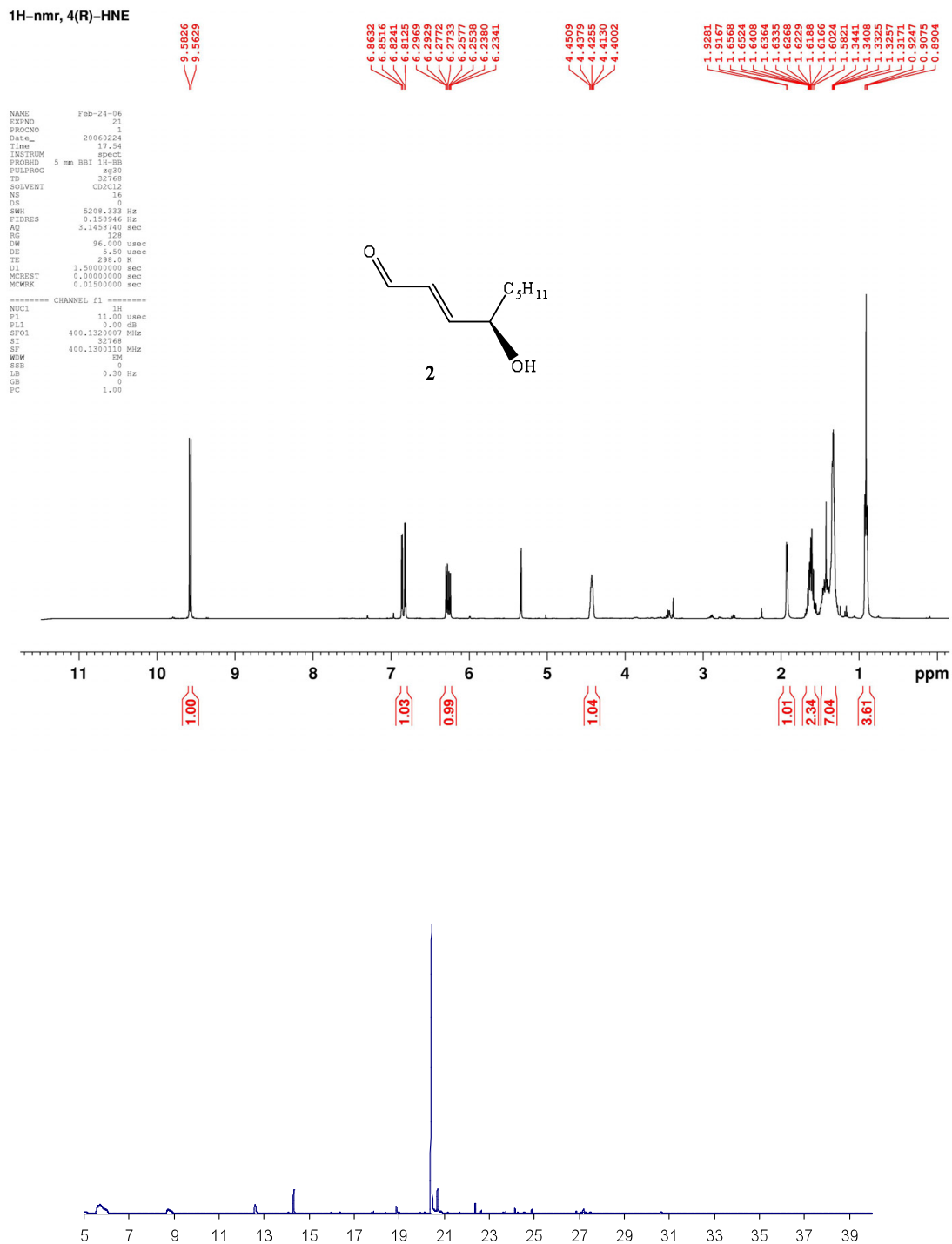


HPLC separation of EHN-dGuo adducts was conducted on a Beckman gradient HPLC system with a diode array UV detector monitoring at 260 nm using a Waters YMC ODS-AQ column (250 mm × 4.6 mm) at flow rate 1.0 mL/min. The mobile phase consisted of H<sub>2</sub>O and CH<sub>3</sub>CN using the following gradients: initially 90 % H<sub>2</sub>O; a 3 min linear gradient to 78 % H<sub>2</sub>O; isocratic at 78 % H<sub>2</sub>O for 25 min, 4 min linear gradient to 20 % H<sub>2</sub>O, followed by a 4 min linear gradient to 90 % H<sub>2</sub>O and remained for 1 min at the initial conditions.

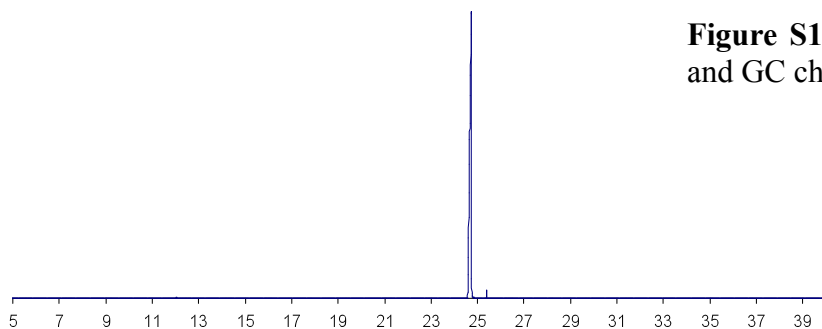
**Figure S17.**  $^1\text{H}$  NMR spectrum and GC chromatogram of (4*S*)-4-hydroxy-2*E*-nonenal **1**



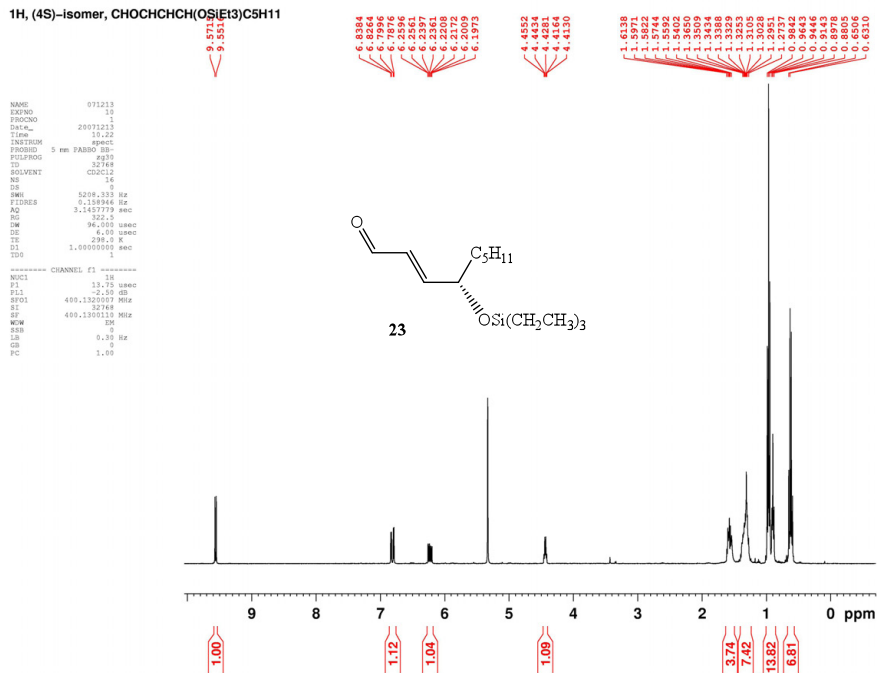
**Figure S18.**  $^1\text{H}$  NMR spectrum and GC chromatogram of (*4R*)-4-hydroxy-2*E*-nonenal **2**



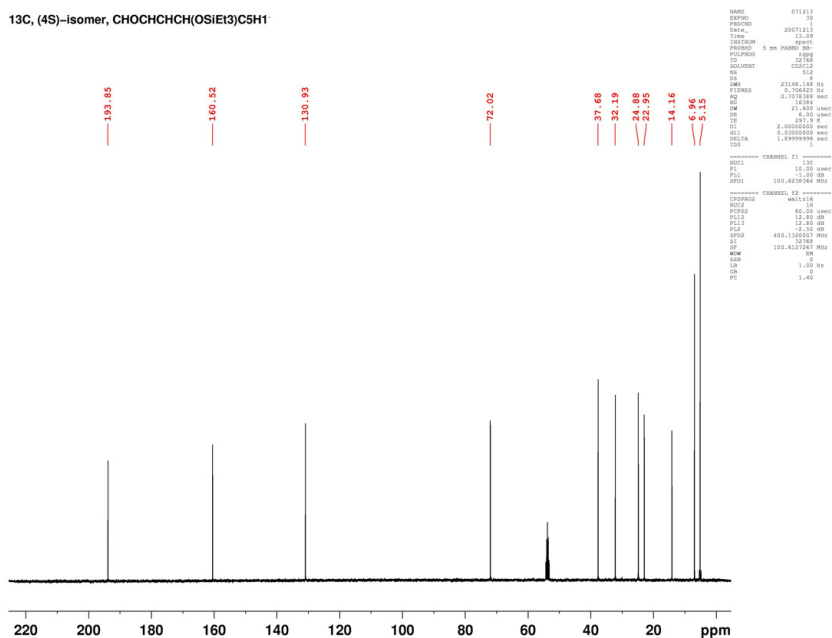
**Figure S19.** <sup>1</sup>H and <sup>13</sup>C NMR spectra and GC chromatogram of **23**



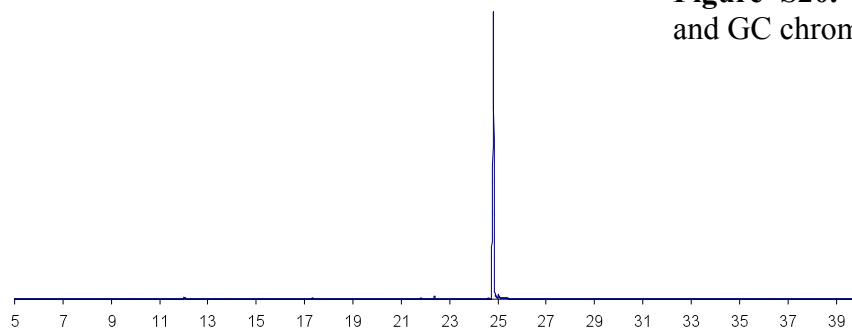
**<sup>1</sup>H, (4S)-isomer, CHOCHCHCH(OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>**



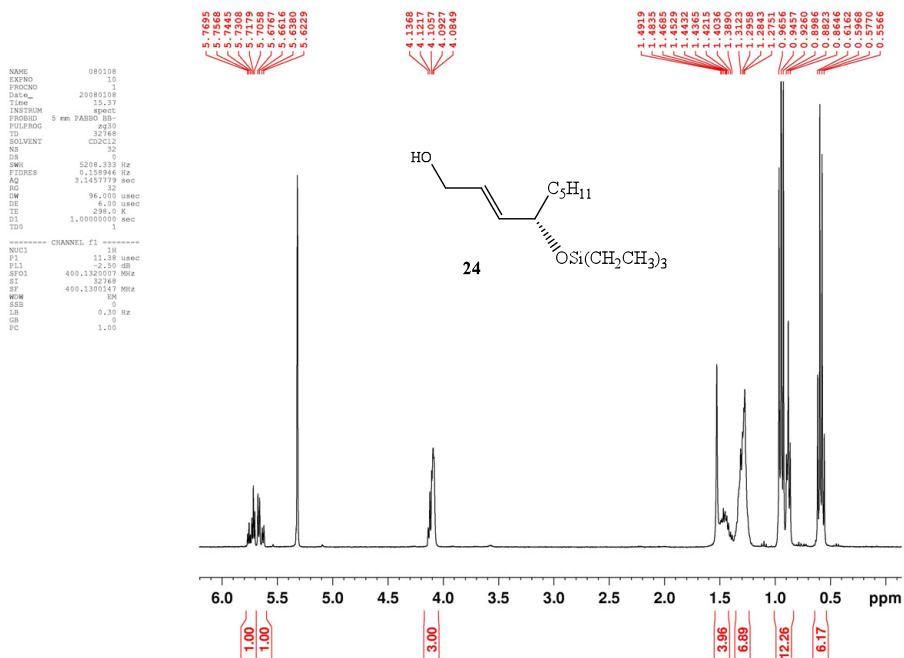
**<sup>13</sup>C, (4S)-isomer, CHOCHCHCH(OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>**



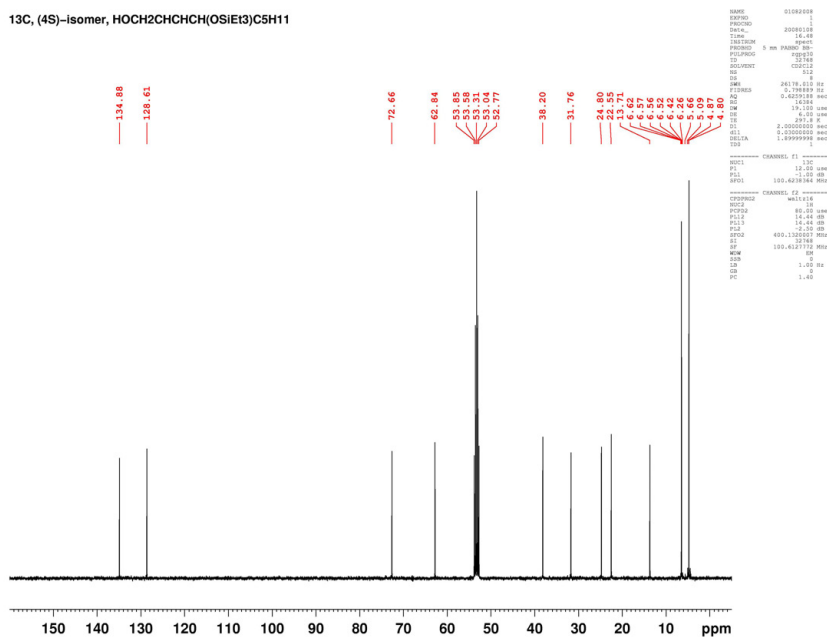
**Figure S20.** <sup>1</sup>H and <sup>13</sup>C NMR spectra and GC chromatogram of **24**



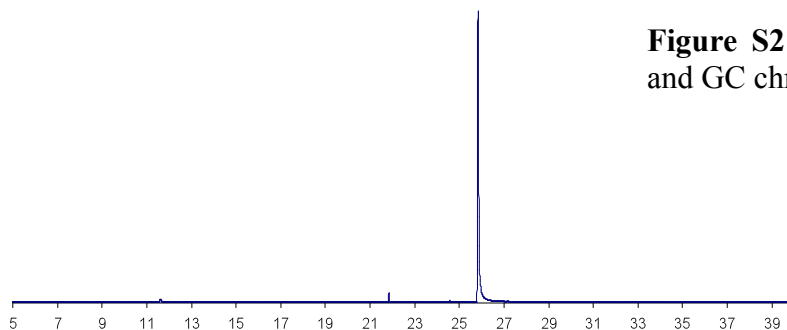
**<sup>1</sup>H, (4S)-isomer, CH<sub>2</sub>OHCHCH(CH<sub>2</sub>OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>**



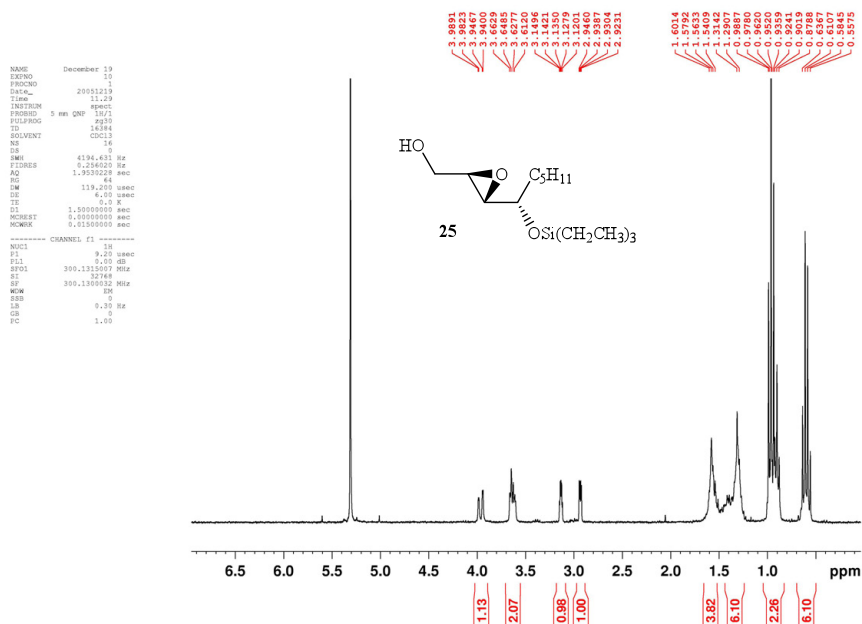
**<sup>13</sup>C, (4S)-isomer, HOCH<sub>2</sub>CHCH(CH<sub>2</sub>OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>**



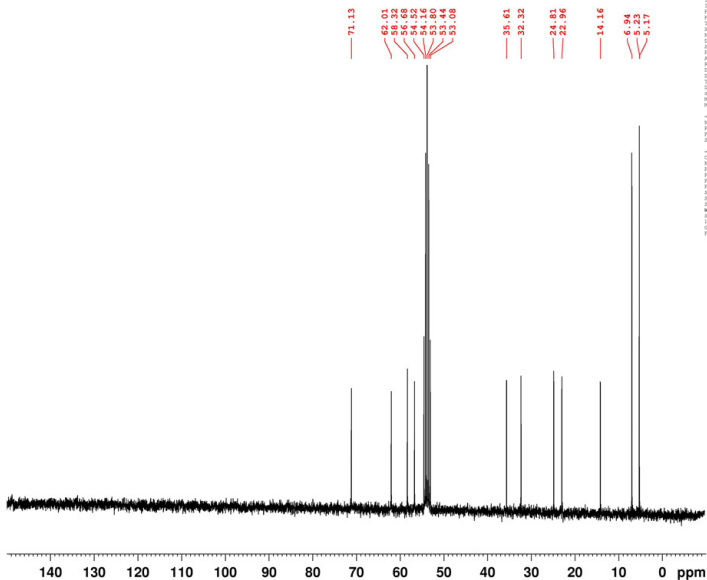
**Figure S21.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC chromatogram of **25**



$^1\text{H}$ , HOCH<sub>2</sub>CHOCH-CH(OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>, (2R,3S,4S-isomer)

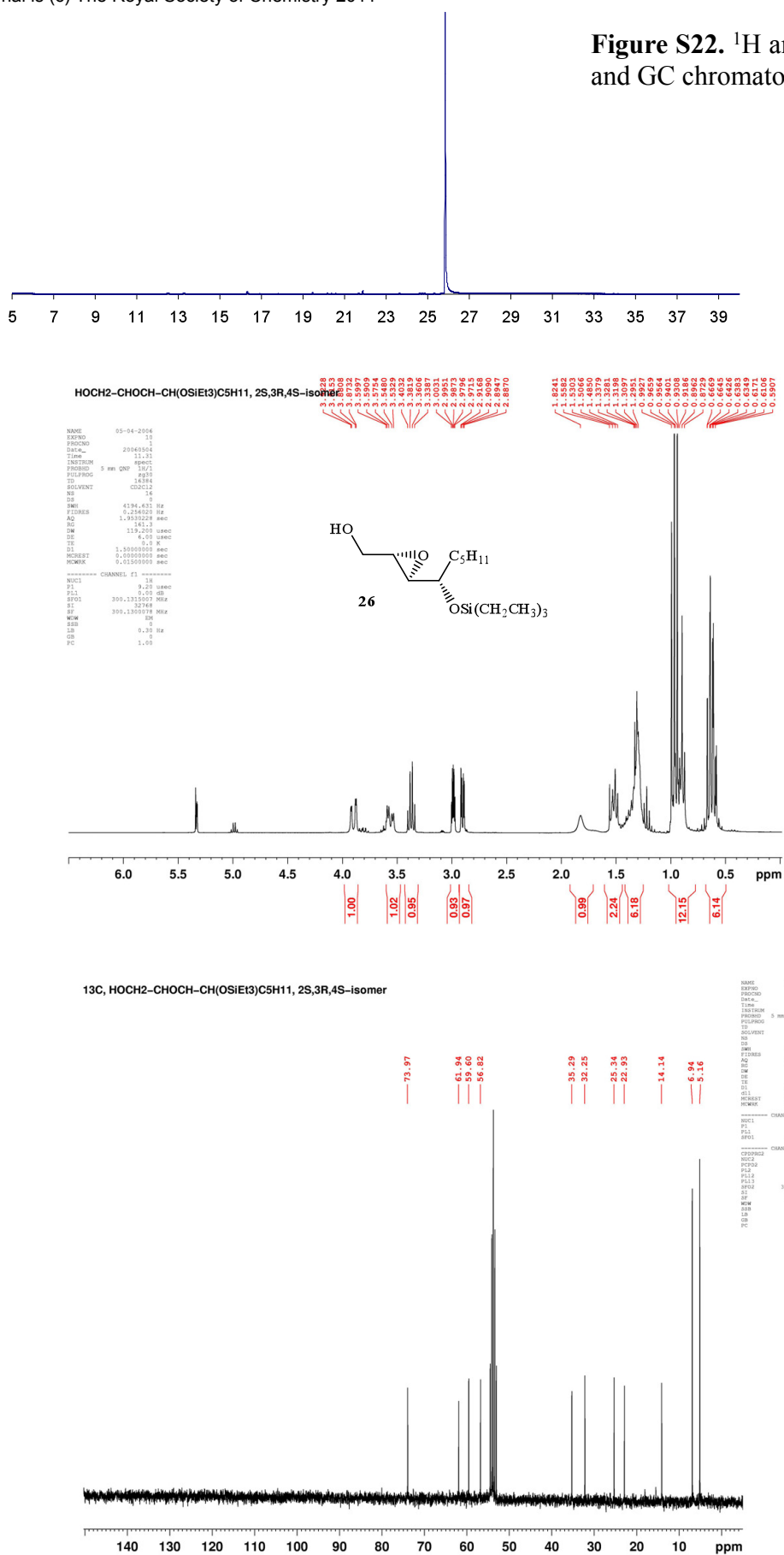


$^{13}\text{C}$ , HOCH<sub>2</sub>CHOCH-CH(OSiEt<sub>3</sub>)C<sub>5</sub>H<sub>11</sub>, 2R,3S,4S-isomer

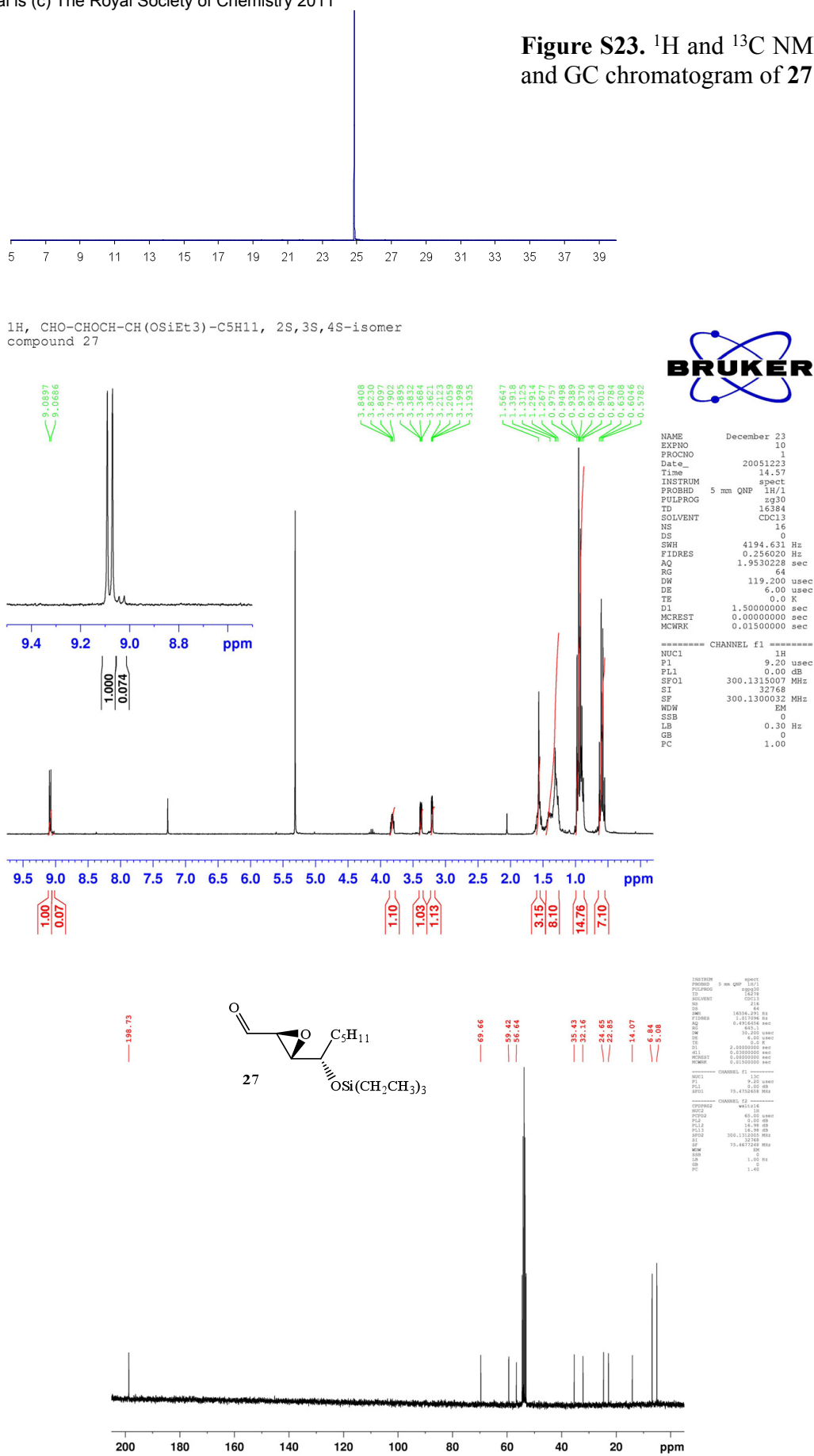




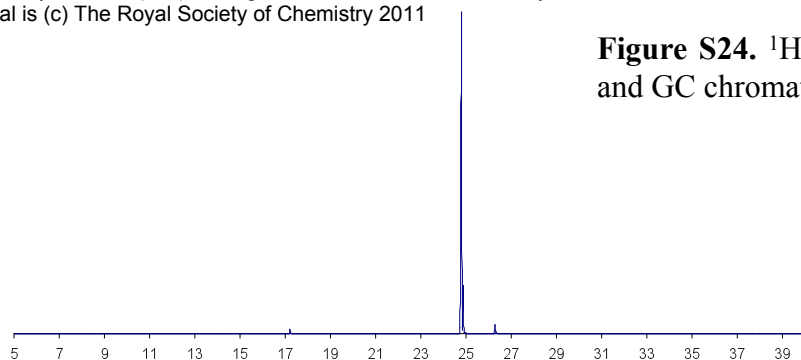
**Figure S22.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC chromatogram of **26**



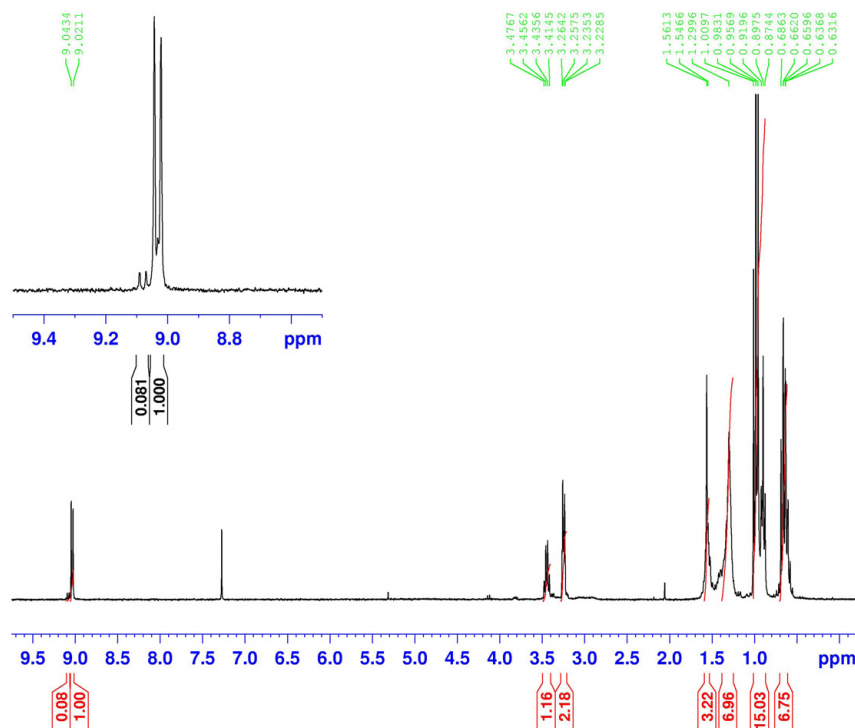
**Figure S23.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC chromatogram of **27**



**Figure S24.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC chromatogram of **28**



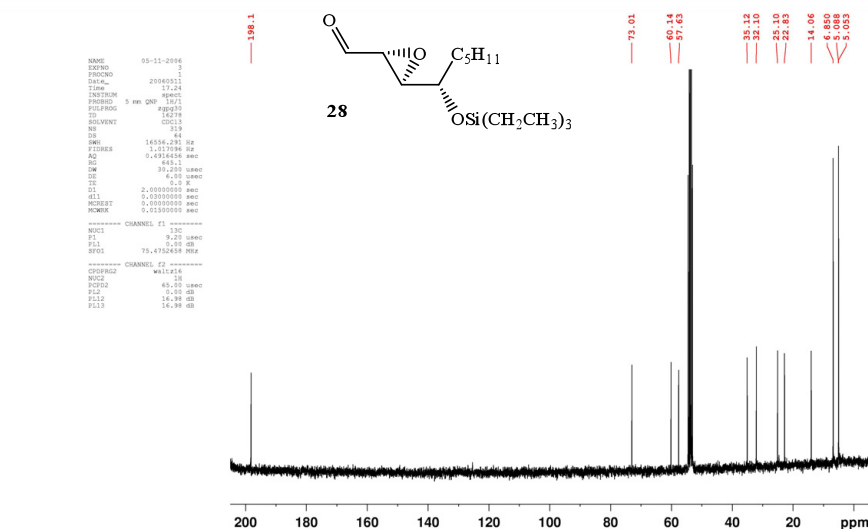
$^1\text{H}$ , CHO-CHOCH-CH(OSiEt<sub>3</sub>)-C<sub>5</sub>H<sub>11</sub>, (2R,3R,4S-isomer)  
 compound **28**



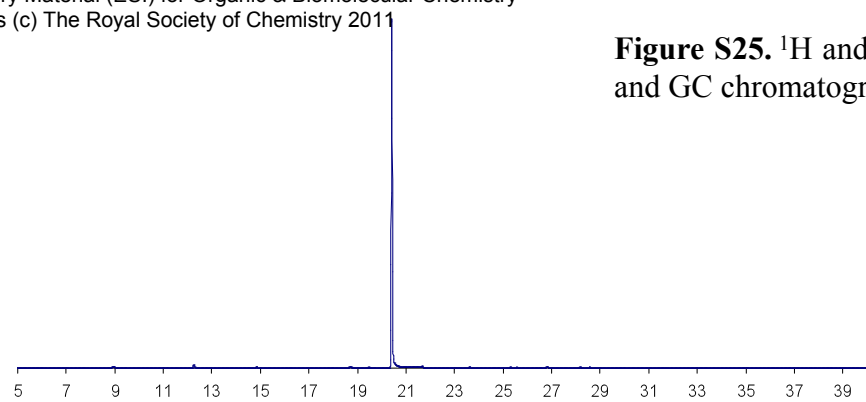
```

NAME      December 26
EXPNO     10
PROCNO    1
DATE_     20051226
Time      14.29
INSTRUM   spect
PROBHD    5 mm QNP 1H/1
PULPROG   zg30
TD         14384
SOLVENT   CDCl3
NS         16
DS         0
SWH        4194.631 Hz
FIDRES     0.256020 Hz
AQ         1.2530228 sec
RG         64
DM         119.200 use
DE         6.00 use
TE         0.0 K
D1         1.5000000 sec
MCREST     0.0000000 sec
MCWRK     0.0150000 sec

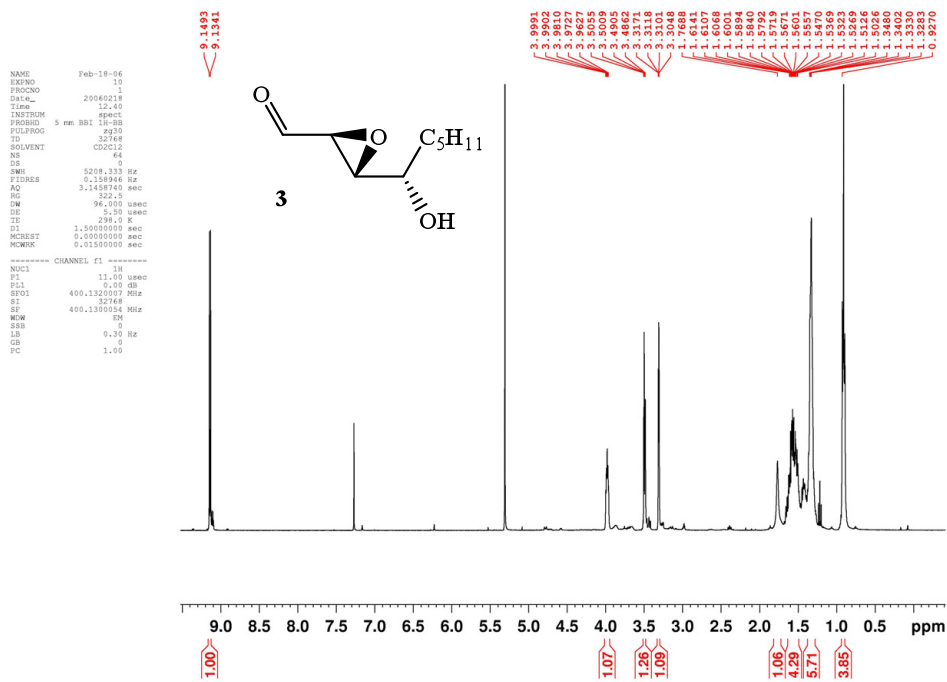
----- CHANNEL f1 -----
NUC1       1H
P1         9.20 use
PL1        0.00 dB
SFO1       300.1315007 MHz
SI         32768
SF         300.1300032 MHz
WDM        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
```



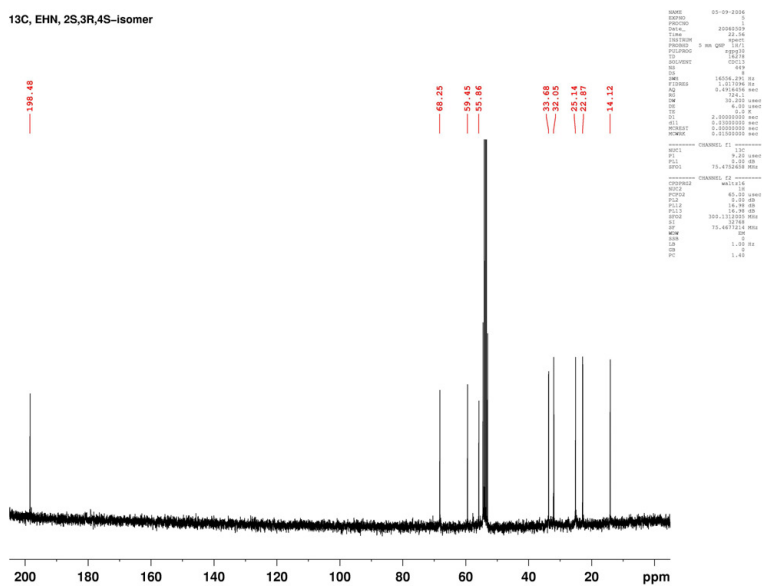
**Figure S25.** <sup>1</sup>H and <sup>13</sup>C NMR spectra and GC chromatogram of **3**



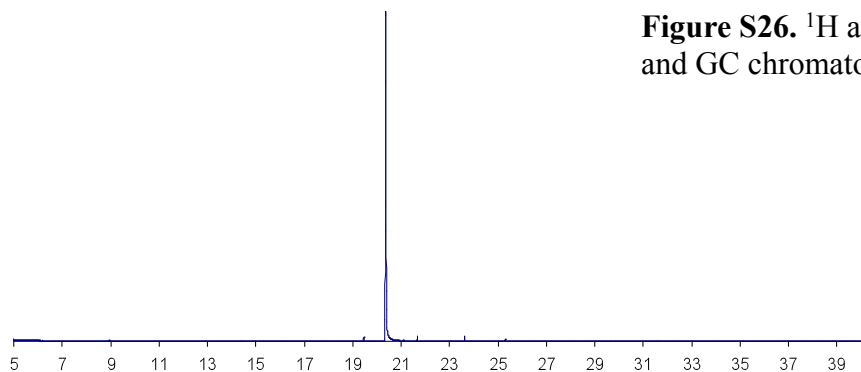
**<sup>1</sup>H, EHN 2S,3R,4S-isomer**



**<sup>13</sup>C, EHN, 2S,3R,4S-isomer**



**Figure S26.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and GC chromatogram of **5**

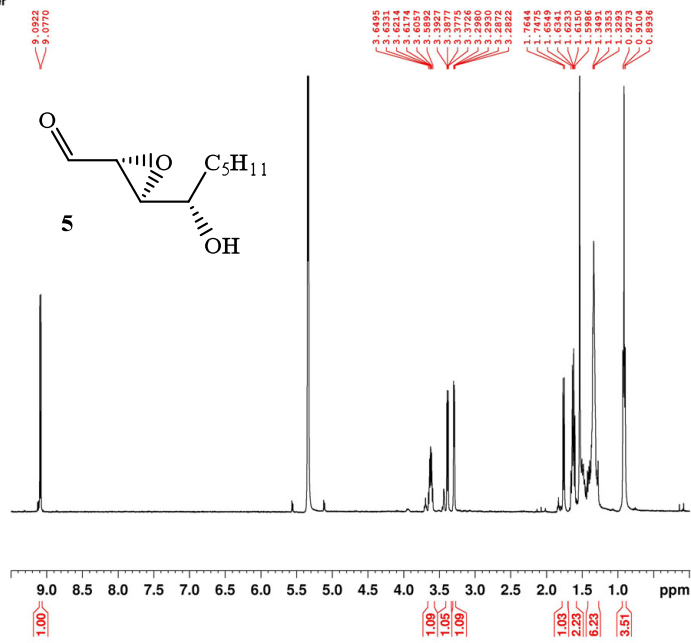
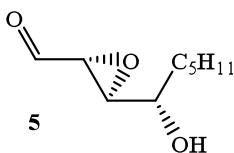


**$^1\text{H}$ , EHN, 2R,3S,4S-isomer**

```

NAME      Feb-21-06
EXPNO    10
PROCNO   1
Date_ac  20060221
Time     16.33
INSTRUM  spect
PROBHD   5 mm BBI IN-2D
PULPROG  zgpg30
TD        32768
SOLVENT  CDCl3
NS        64
DS        3208.333 Hz
F2       0.150946 MHz
F1       3.1450740 sec
AQ       11.874
RG       96.000 usec
DE       1.00
TE       300.2 K
SI        4
D1       1.30000000 sec
MICKDET  0.00000000 sec
MCMWRK  0.01500000 sec

----- CHANNEL f1 -----
NUC1      1H
P1        9.00 usec
PL1       -1.00 dB
SFO1     400.1320002 MHz
NUC2      13C
P2        9.00 usec
PL2       -1.00 dB
SFO2     101.3252013 MHz
SI        4
D1       1.30000000 sec
MICKDET  0.00000000 sec
MCMWRK  0.01500000 sec
    
```

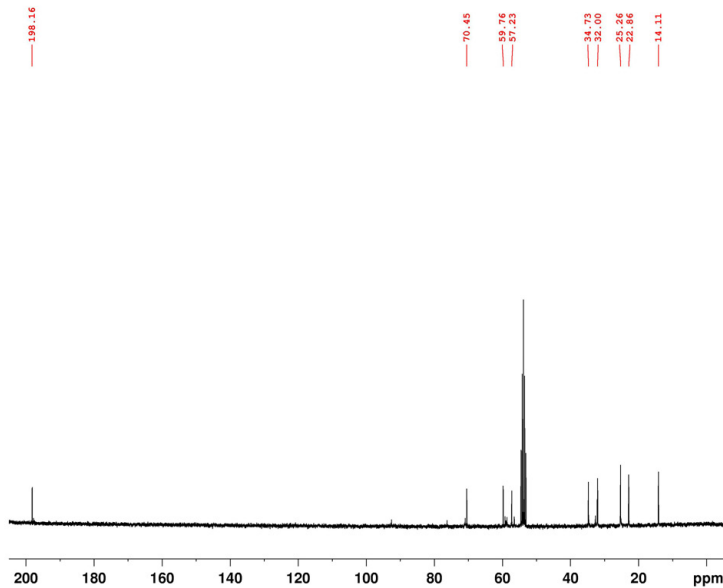


**$^{13}\text{C}$ , EHN, 2R,3S,4S-isomer**

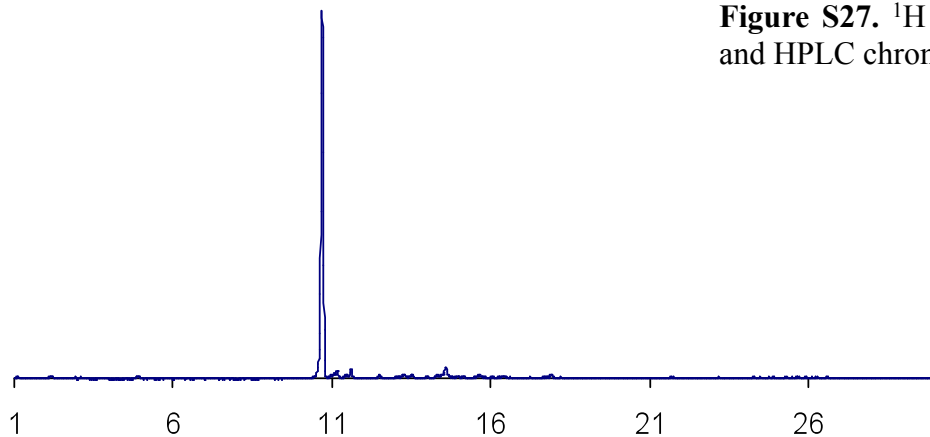
```

NAME      05-13-2006
EXPNO    5
PROCNO   1
Date_ac  20060513
Time     11.34
INSTRUM  spect
PROBHD   5 mm gpc 1H/13
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        64
DS        1636.291 Hz
F2       0.1013252 MHz
F1       125.7613600 MHz
AQ       12.211
RG       300.000 usec
DE       1.00
TE       300.2 K
SI        4
D1       1.30000000 sec
MICKDET  0.00000000 sec
MCMWRK  0.01500000 sec

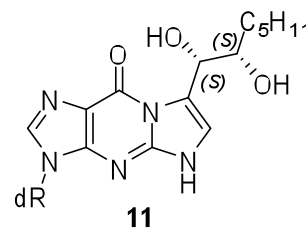
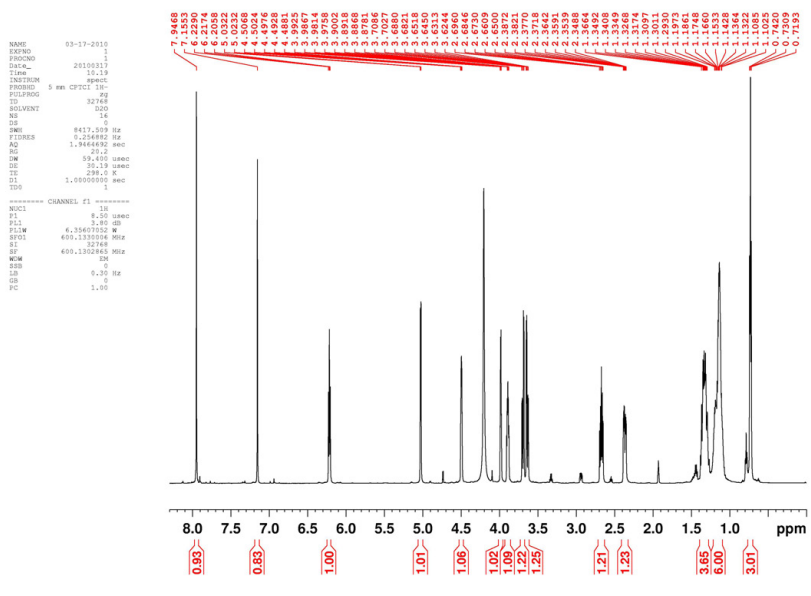
----- CHANNEL f1 -----
NUC1      13C
P1        9.00 usec
PL1       -1.00 dB
SFO1     101.3252013 MHz
NUC2      1H
P2        9.00 usec
PL2       -1.00 dB
SFO2     400.1320002 MHz
SI        4
D1       1.30000000 sec
MICKDET  0.00000000 sec
MCMWRK  0.01500000 sec
    
```



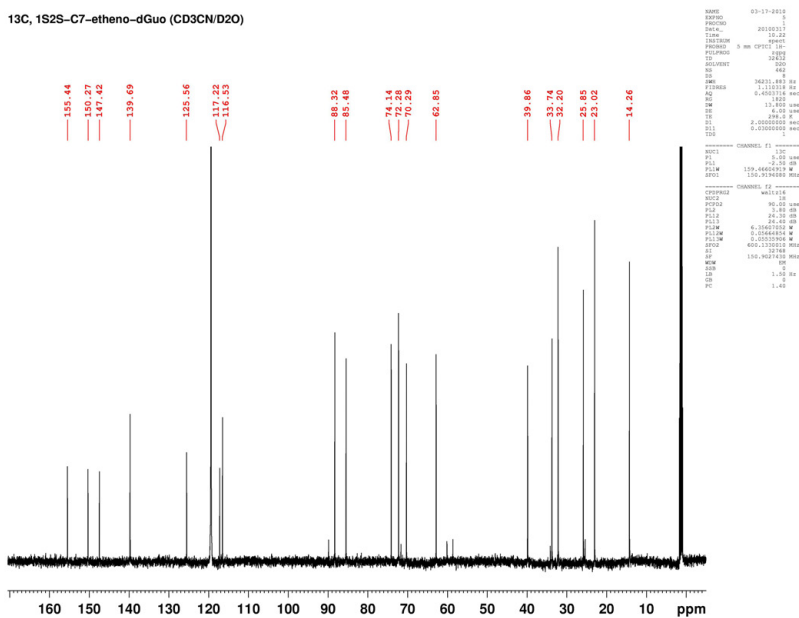
**Figure S27.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and HPLC chromatogram of **11**



$^1\text{H}$  NMR, 1S2S-C7-etheno-dGuo (CD $_3$ CN/D $_2$ O)



$^{13}\text{C}$  NMR, 1S2S-C7-etheno-dGuo (CD $_3$ CN/D $_2$ O)

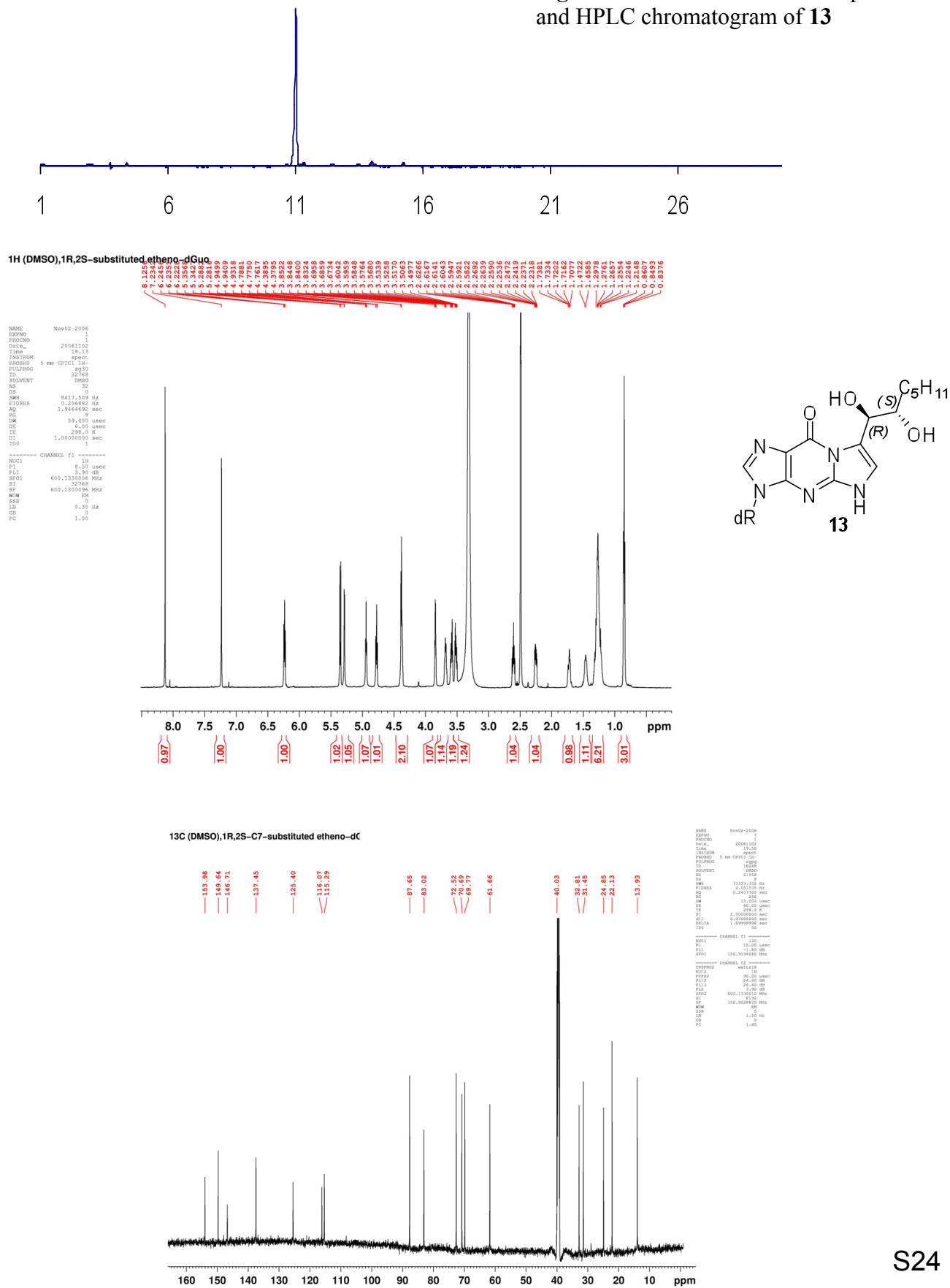


```

NAME 03-17-2010
EXPNO 1
PROCNO 1
PROBHD 5 mm CPYX130
PULPROG zgpg30
SOLVENT CD3
NS 402
DS 4
SWH 400.1302600 MHz
F2 130.2500000 MHz
AQ 0.4633333 sec
RG 320
SI 32768
SF 400.1302600 MHz
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40
    
```

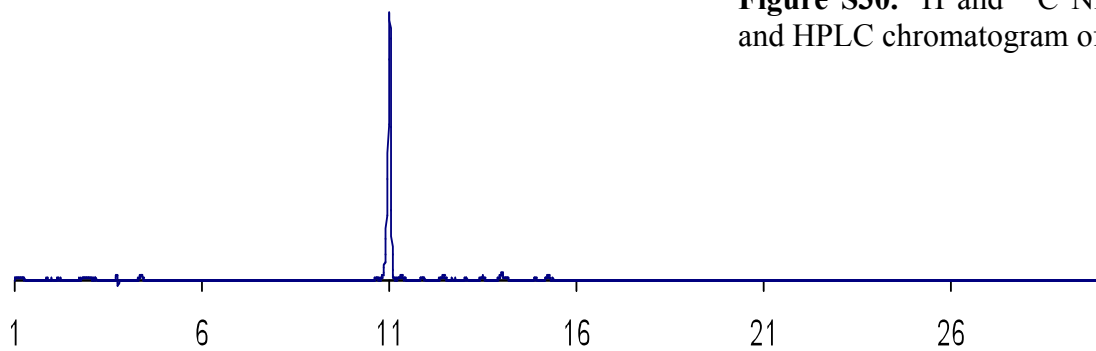


Figure S29.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and HPLC chromatogram of **13**

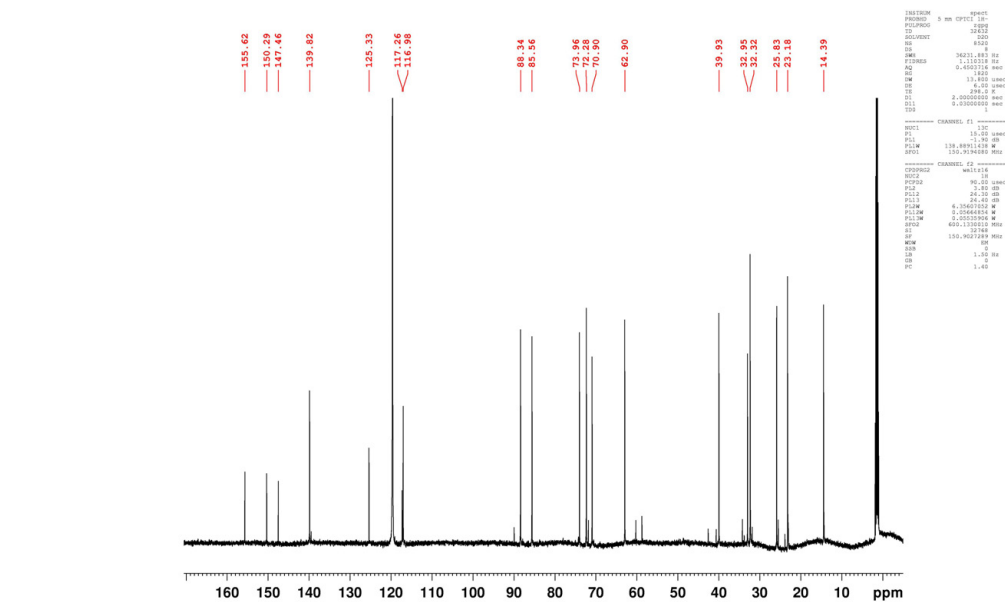
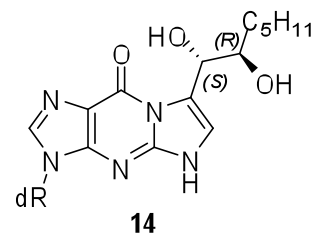
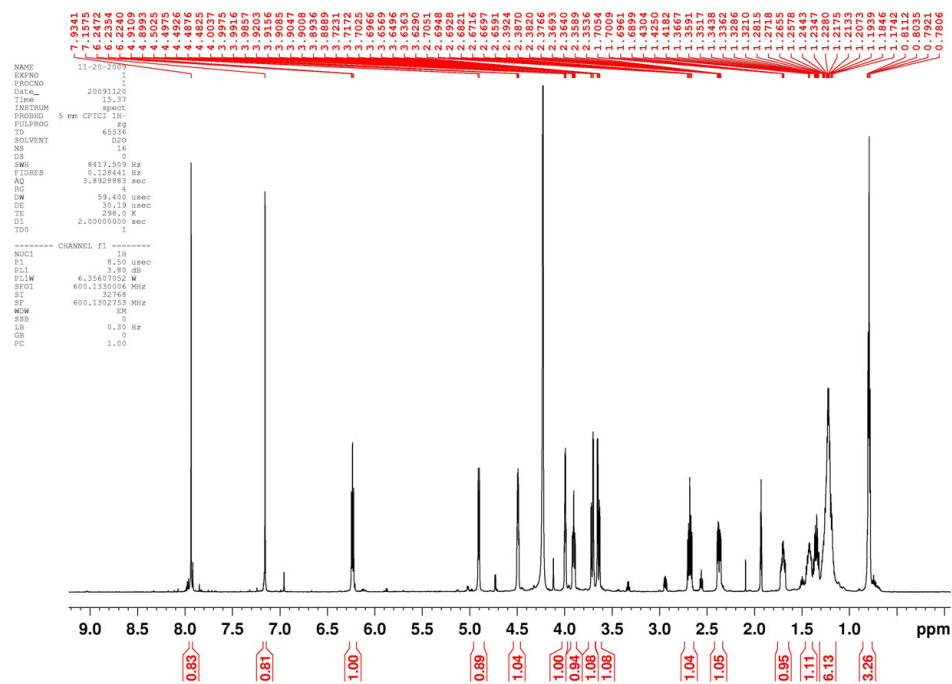




**Figure S30.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and HPLC chromatogram of **14**



$^1\text{H}$  (CD $_3$ CN/D $_2$ O) for 1S2R-C7-substituted etheno-dGuo



```

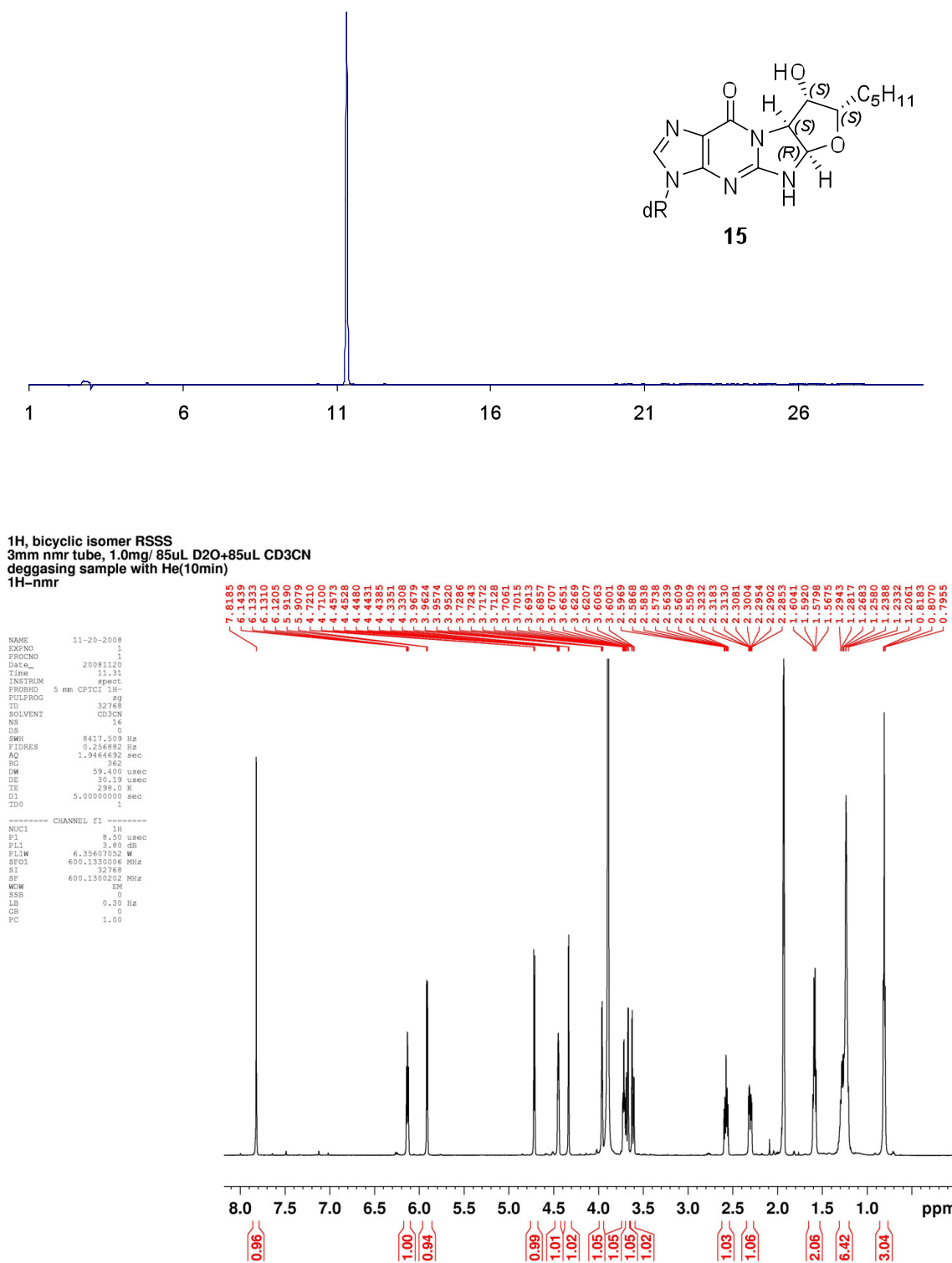
NAME          11-20-2009
EXPNO         1
PROCNO        1
DATE_         20091120
Time         10.37
INSTRUM       spect
PROBHD        5 mm CPYCI 1H-
PULPROG       zgpg30
SOLVENT       DMSO
NS            16
DS            4
SWH           8417.369 Hz
F2RES        0.128441 Hz
AQ           3.8928883 sec
RG           59.480 usec
DE           30.13 usec
TE           298.0 K
SI           2.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          13C
P1            8.50 usec
PL1          0.00 dB
PL12         6.35697052 W
SFO1         600.1330000 MHz
SF           32768
SF2          600.1330000 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00

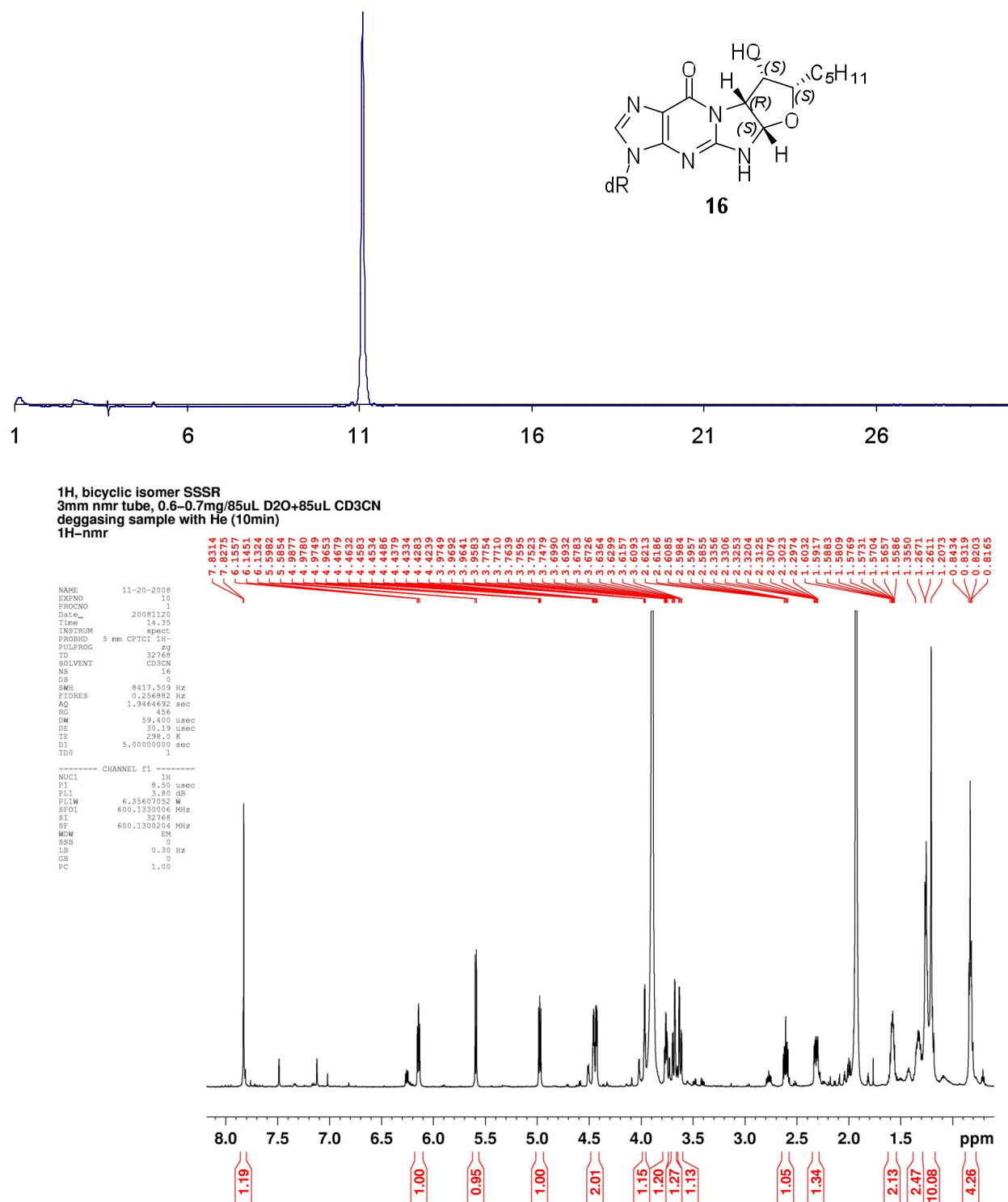
===== CHANNEL f2 =====
NAME          11-20-2009
EXPNO         1
PROCNO        1
DATE_         20091120
Time         10.37
INSTRUM       spect
PROBHD        5 mm CPYCI 1H-
PULPROG       zgpg30
SOLVENT       DMSO
NS            16
DS            4
SWH           8417.369 Hz
F2RES        0.128441 Hz
AQ           3.8928883 sec
RG           59.480 usec
DE           30.13 usec
TE           298.0 K
SI           2.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          13C
P1            8.50 usec
PL1          0.00 dB
PL12         6.35697052 W
SFO1         600.1330000 MHz
SF           32768
SF2          600.1330000 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
    
```

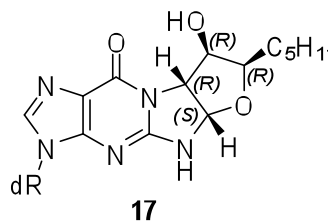
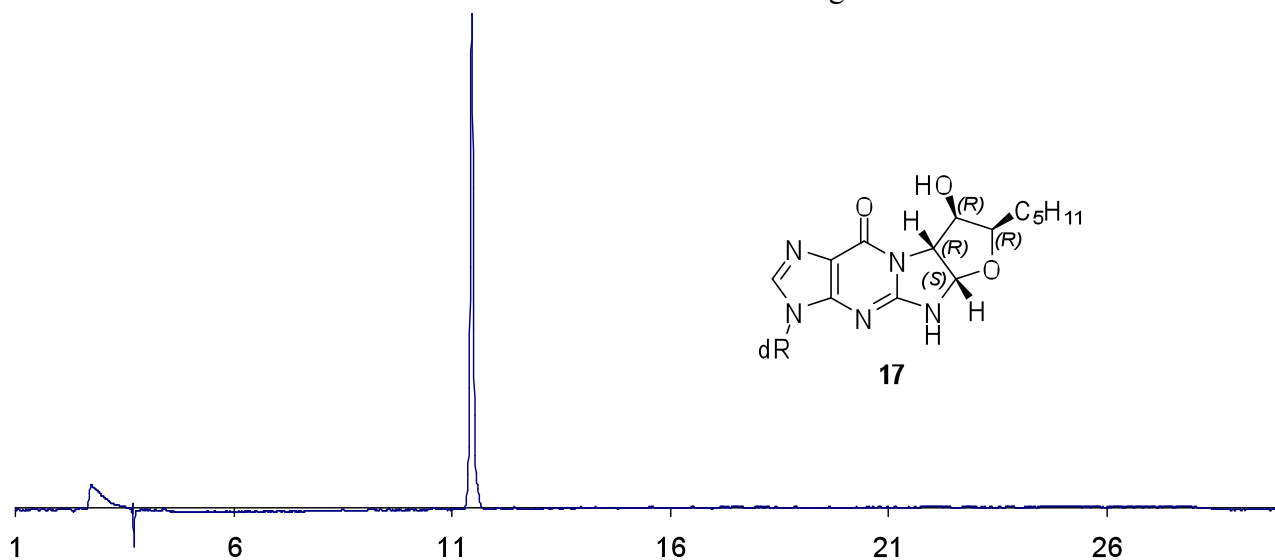
**Figure S31.**  $^1\text{H}$  spectrum and HPLC chromatogram of **15**



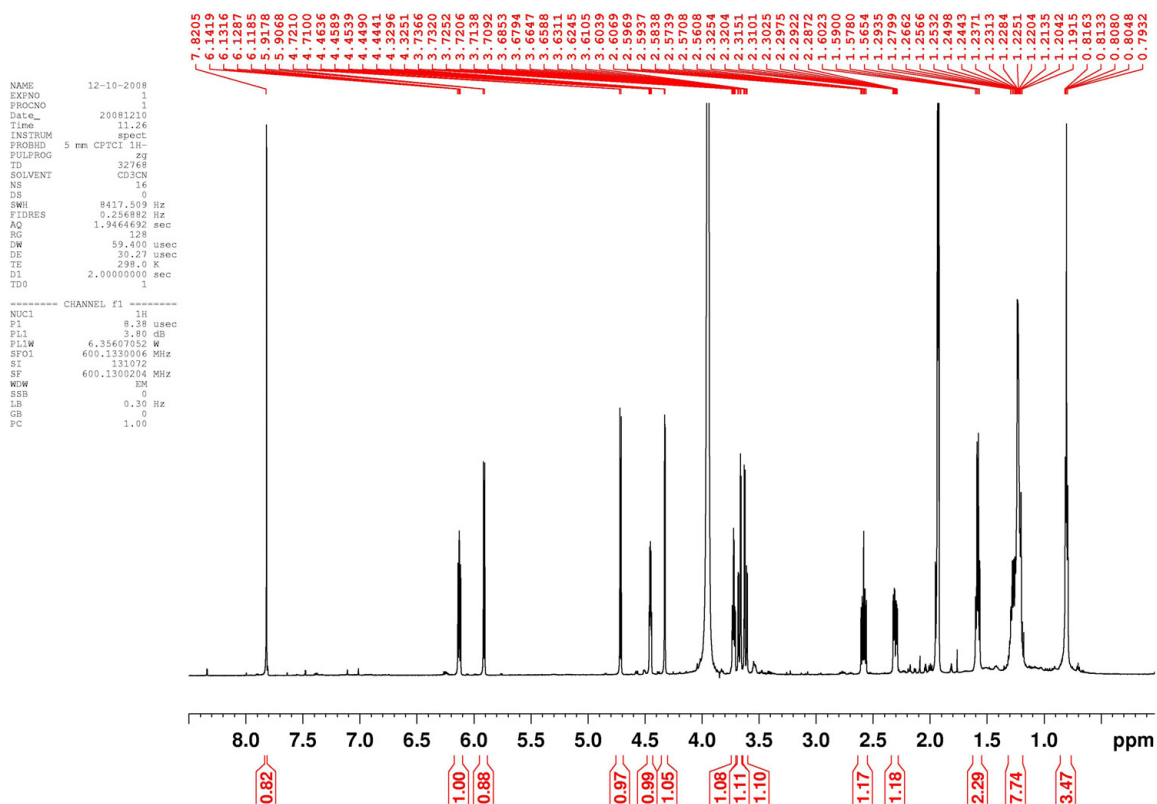
**Figure S32.**  $^1\text{H}$  spectrum and HPLC chromatogram of **16**



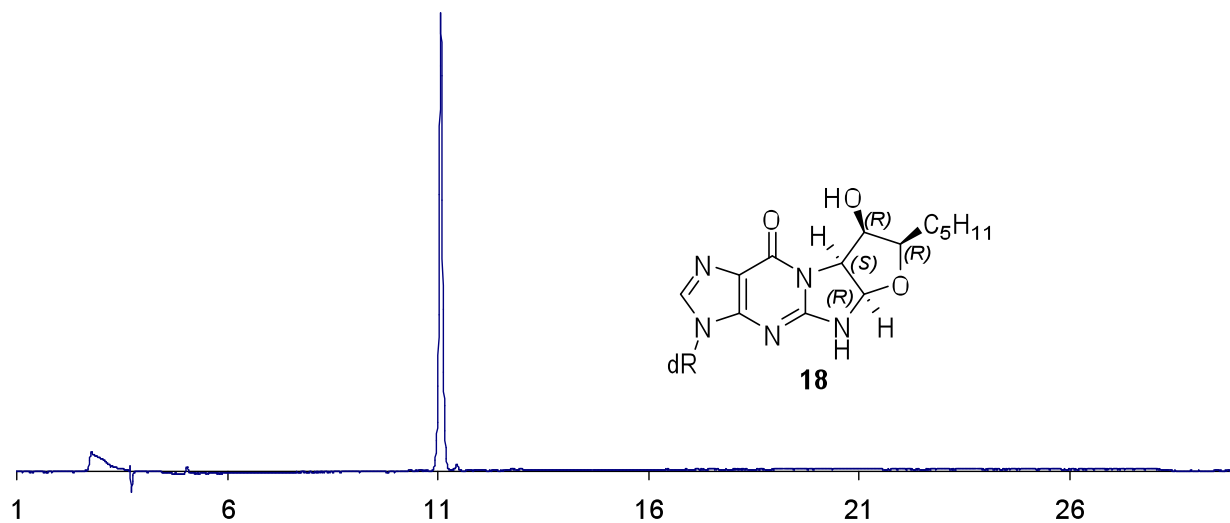
**Figure S33.**  $^1\text{H}$  spectrum and HPLC chromatogram of **17**



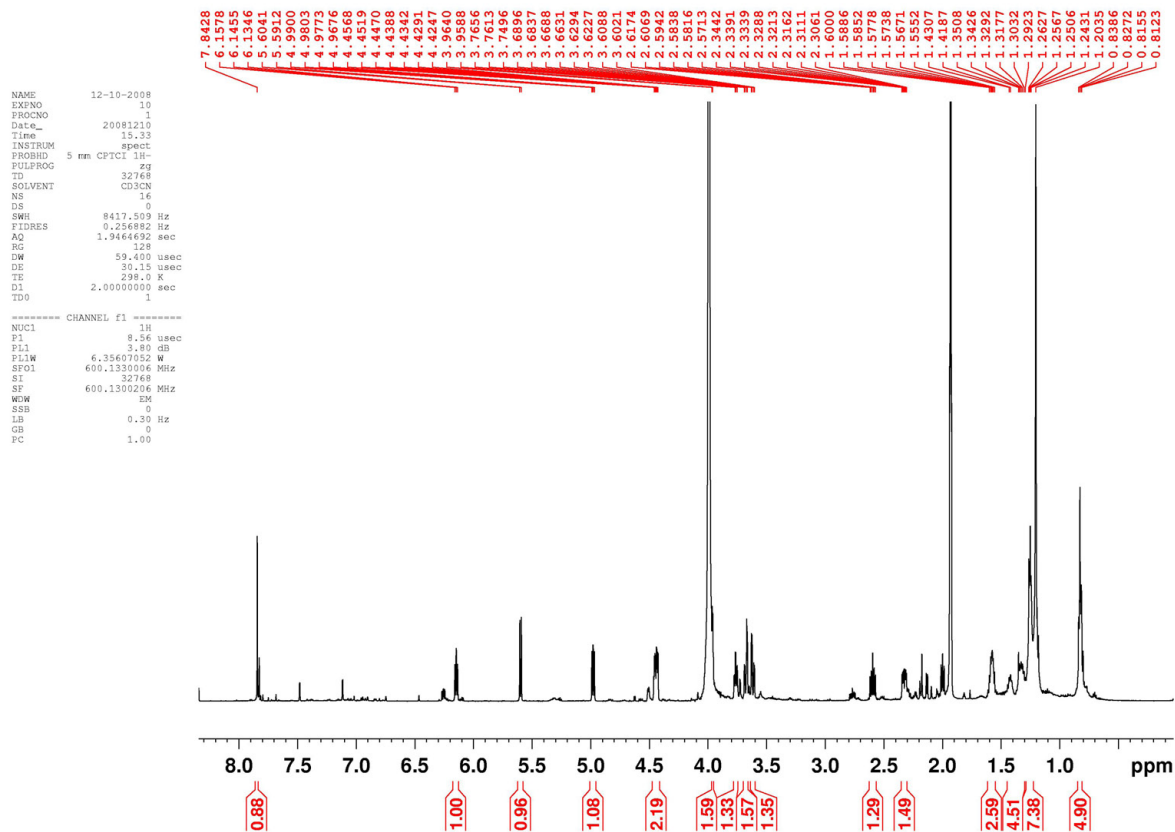
**$^1\text{H}$ , bicyclic isomer SRRR**  
 3mm nmr tube, 0.7 mg/ 85uL D2O+85uL CD3CN  
 degassing sample with He (11min)



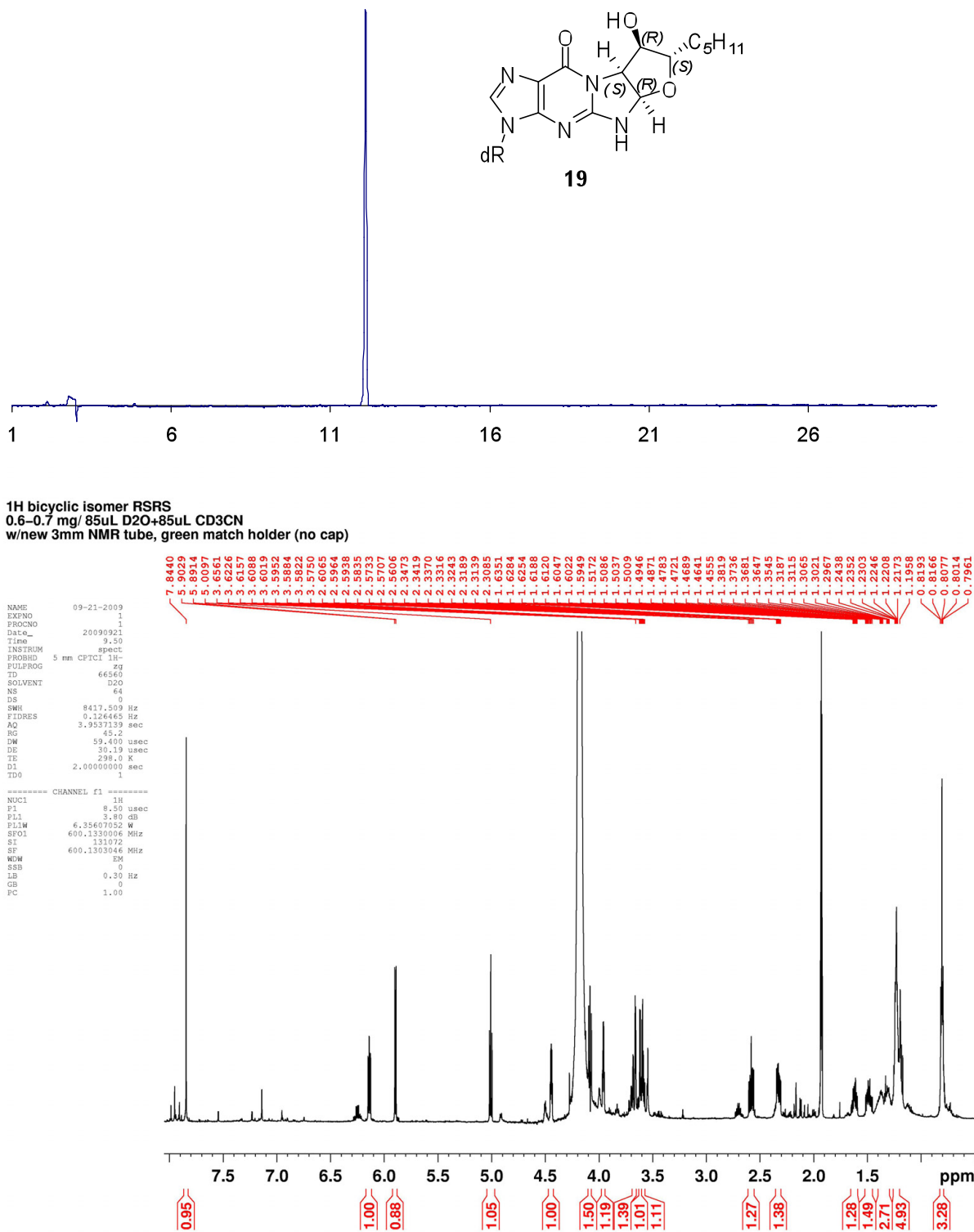
**Figure S34.**  $^1\text{H}$  spectrum and HPLC chromatogram of **18**



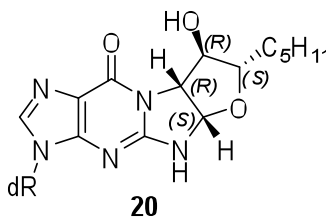
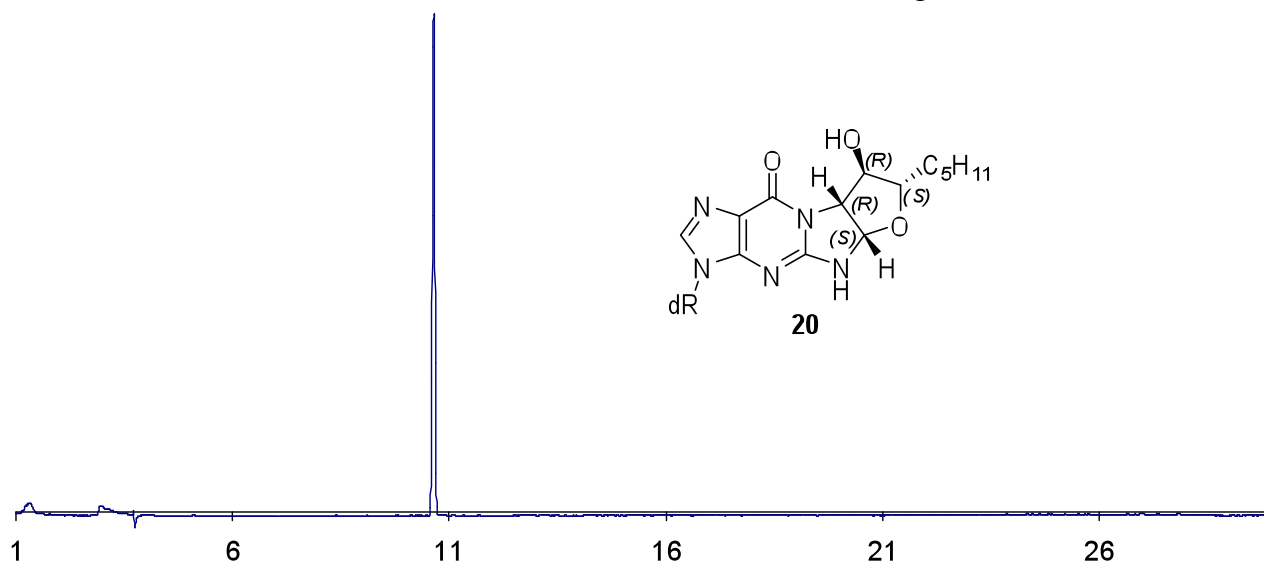
**$^1\text{H}$ , bicyclic isomer RRRS**  
3mm nmr tube, 0.7 mg/ 85uL D2O+85uL CD3CN  
deassinga sample with He (11min)



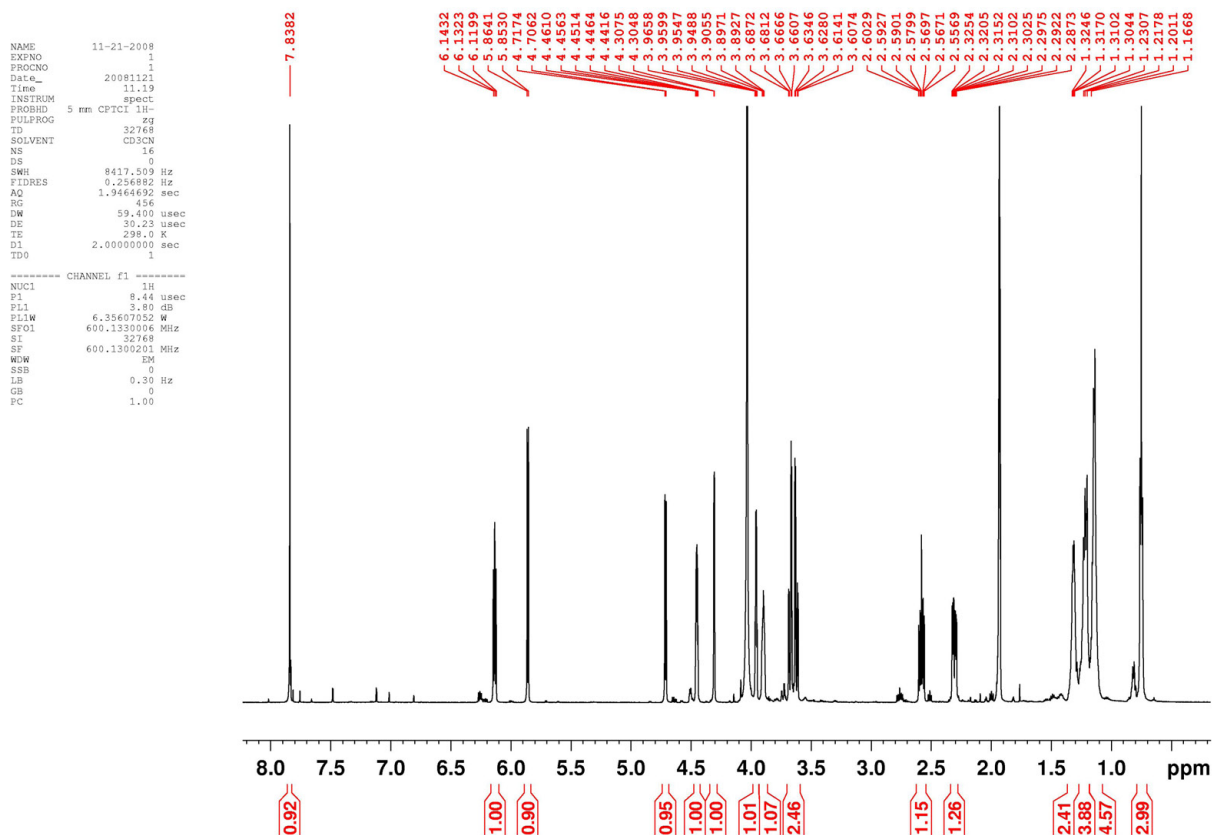
**Figure S35.**  $^1\text{H}$  spectrum and HPLC chromatogram of **19**



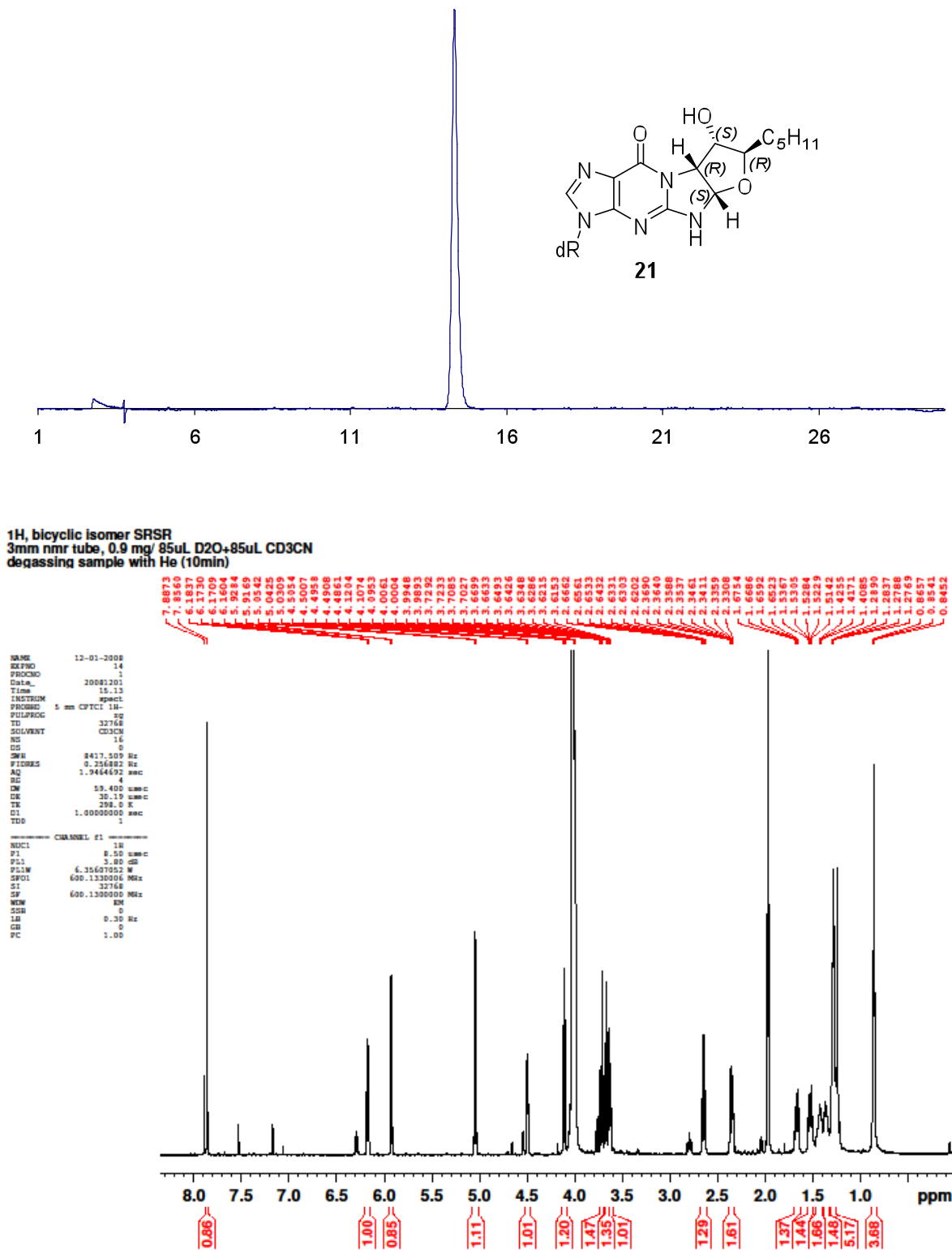
**Figure S36.**  $^1\text{H}$  spectrum and HPLC chromatogram of **20**



**$^1\text{H}$ , bicyclic isomer SSRR**  
**3mm nmr tube, 0.9 mg/85uL D2O+85uL CD3CN**  
**degassing sample with He (11 min)**  
 **$^1\text{H}$ -nmr**

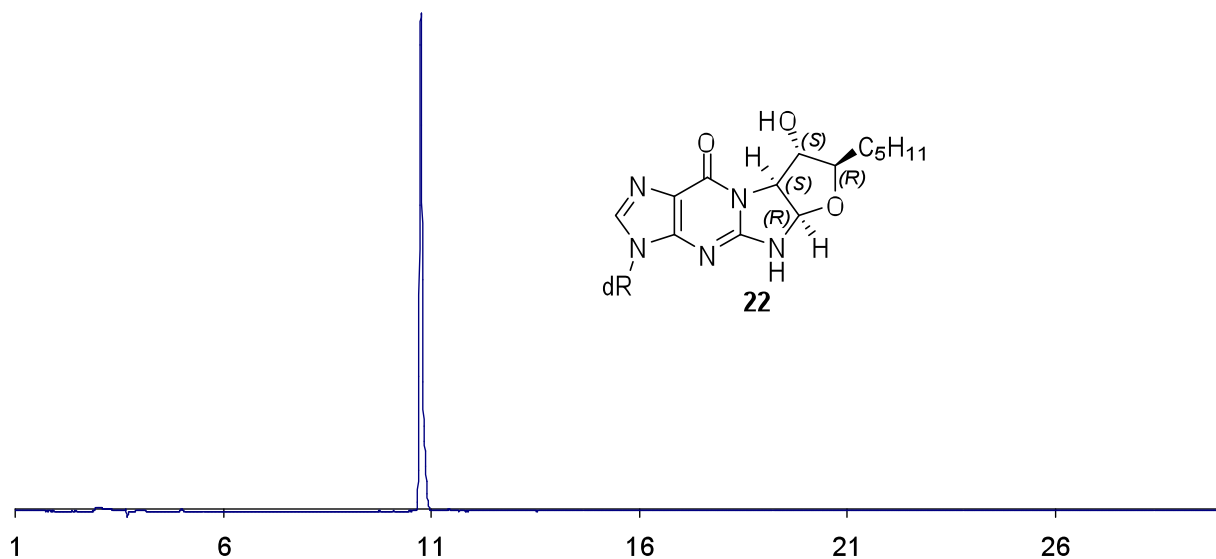


**Figure S37.**  $^1\text{H}$  spectrum and HPLC chromatogram of **21**





**Figure S38.**  $^1\text{H}$  spectrum and HPLC chromatogram of **22**



**$^1\text{H}$ , bicyclic isomer RRSS**  
3mm nmr tube, 1.4 mg/ 85uL D2O+85uL CD3CN  
deassing sample with He (10min)

