Supplementary Information

Synthesis and Expansion of Bicyclic Enol Ether: A Probable Precursor for the Synthesis of Macrolide (±)-Pyrenophorin

Maísa B. Costa,*[a] Marcos P. Martins,[a] Hugo C. de Araújo[b] and Inês S. Resck[b]

[a]Laboratório de Síntese, Isolamento e Modificações de Compostos Orgânicos, Universidade Estadual de Goiás, Campus Henrique Santillo, BR 153, No. 3105, Fazenda Barreiro do Meio, Setor Arco Verde, CP 459, 75132-400 Anápolis-GO, Brazil

[b]Instituto de Química, Universidade de Brasília, Campus Darcy Ribeiro, CP 4478, 70910-970 Brasília-DF, Brazil

The compounds (**2**-**9**) were characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) and elementary analysis.

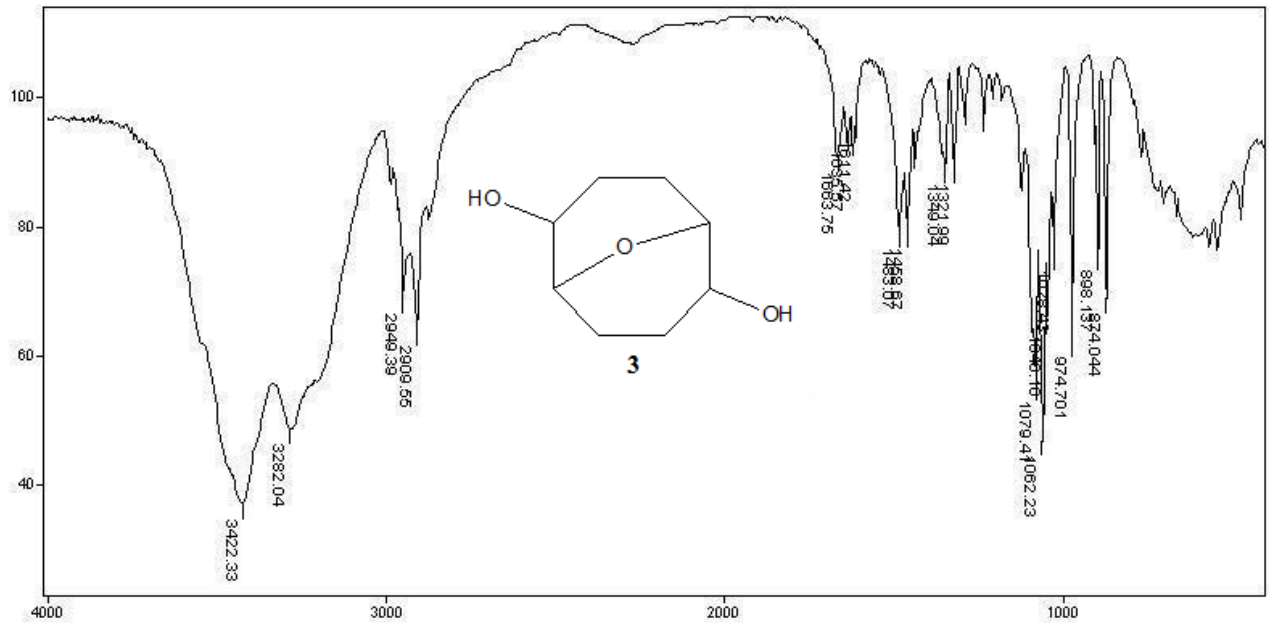
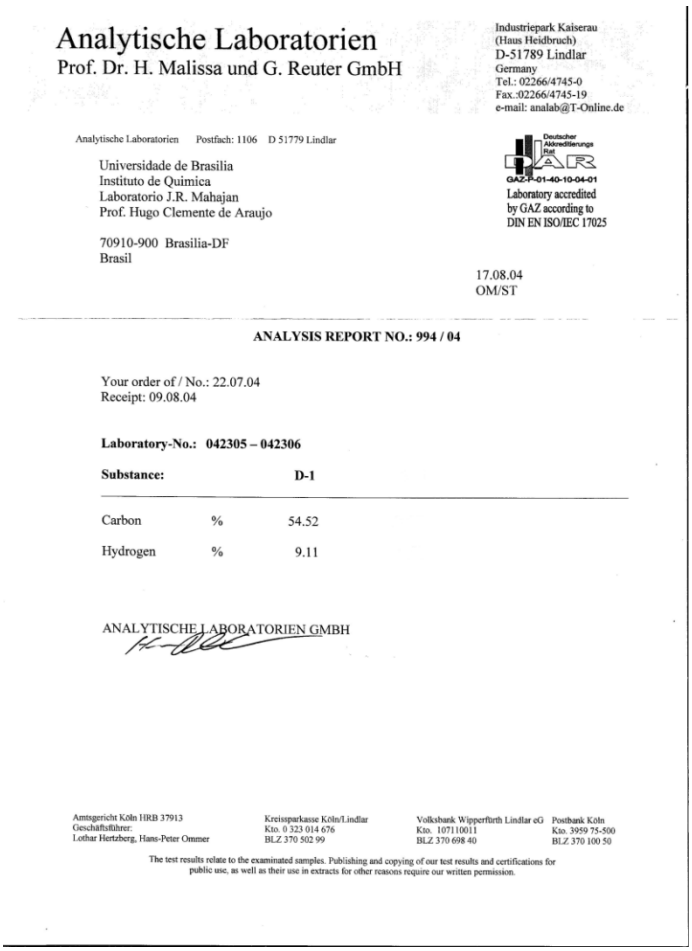


Figure S1. FTIR (KBr) spectrum of compound **3**.

*e-mail: maisabc@gmail.com, maisa.costa@ueg.br



Analytische Laboratorien
Prof. Dr. H. Malissa und G. Reuter GmbH

Industriepark Kaiserau
(Haus Heidbruch)
D-51789 Lindlar
Germany
Tel.: 02266/4745-0
Fax.:02266/4745-19
e-mail: analab@T-Online.de

Analytische Laboratorien Postfach: 1106 D 51779 Lindlar

Universidade de Brasilia
Instituto de Quimica
Laboratorio J.R. Mahajan
Prof. Hugo Clemente de Araujo

70910-900 Brasilia-DF
Brasil

Deutscher Akkreditierungs Rat
GAZ-P-01-40-10-04-01
Laboratory accredited by GAZ according to DIN EN ISO/IEC 17025

17.08.04
OM/ST

ANALYSIS REPORT NO.: 994 / 04

Your order of / No.: 22.07.04
Receipt: 09.08.04

Laboratory-No.: 042305 – 042306

Substance: D-1

Carbon	%	54.52
Hydrogen	%	9.11

ANALYTISCHE LABORATORIEN GMBH

Amtsgericht Köln HRB 37913
Geschäftsführer:
Lothar Hertzberg, Hans-Peter Ommer

Kreissparkasse Köln/Lindlar
Kto. 0 323 014 676
BLZ 370 502 99

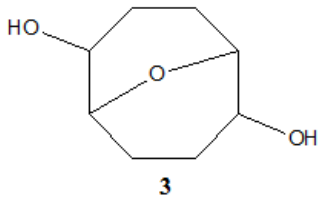
Volksbank Wipperfürth Lindlar eG
Kto. 107110011
BLZ 370 698 40

Postbank Köln
Kto. 3959 75-500
BLZ 370 100 50

The test results relate to the examinated samples. Publishing and copying of our test results and certifications for public use, as well as their use in extracts for other reasons require our written permission.

Figure S2. Elementary analysis of compound **3**.

Comment	44hmb17
Frequency (MHz)	300.07
Nucleus	1H
Acquisition Time (sec)	3.6422
Number of Transients	8
Original Points	16384
Points Count	16384
Solvent	DMSO-d6
Sweep Width (Hz)	4498.43
Temperature (grad C)	27.000



3

Figure S3. ^{1}H NMR (300 MHz, DMSO-d_6) of compound **3**.

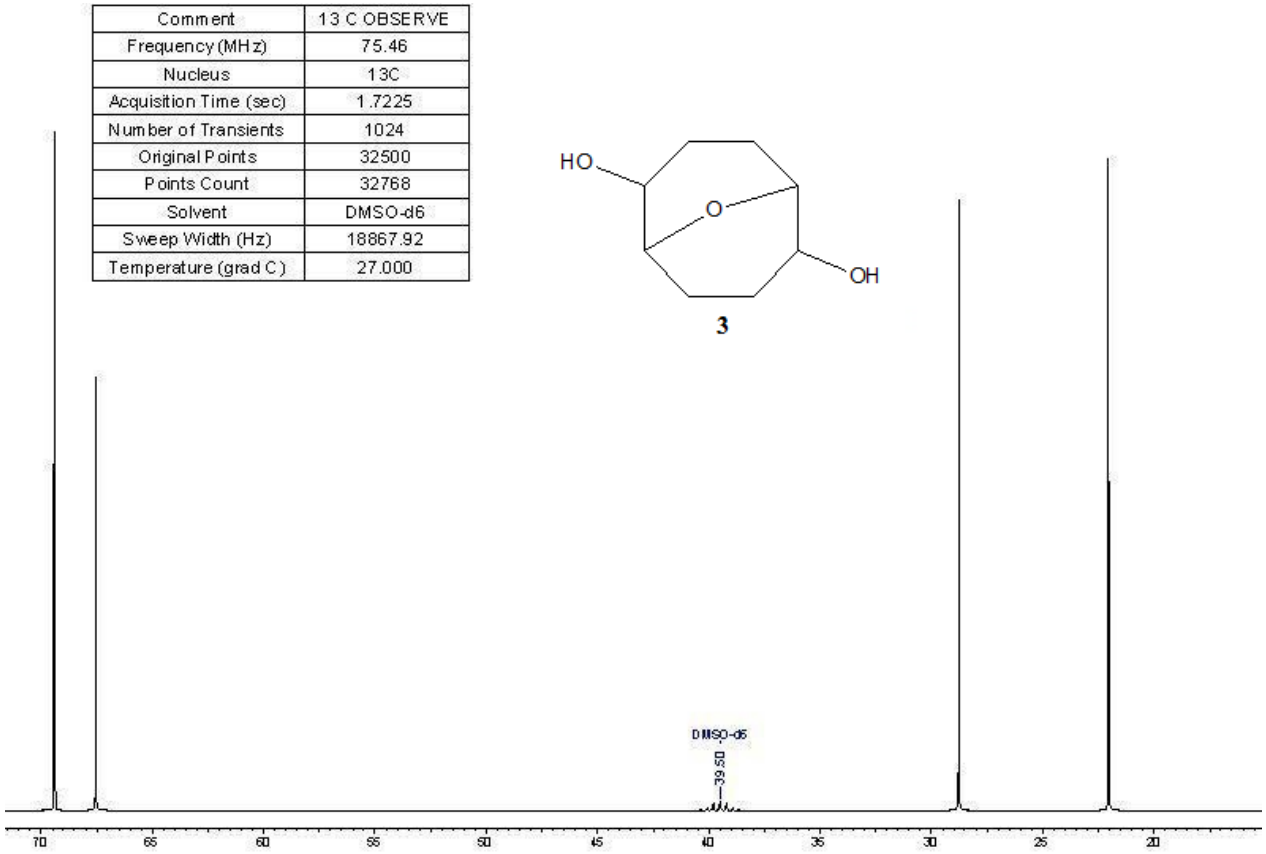


Figure S4. ^{13}C NMR (75 MHz, DMSO-d_6) of compound **3**.

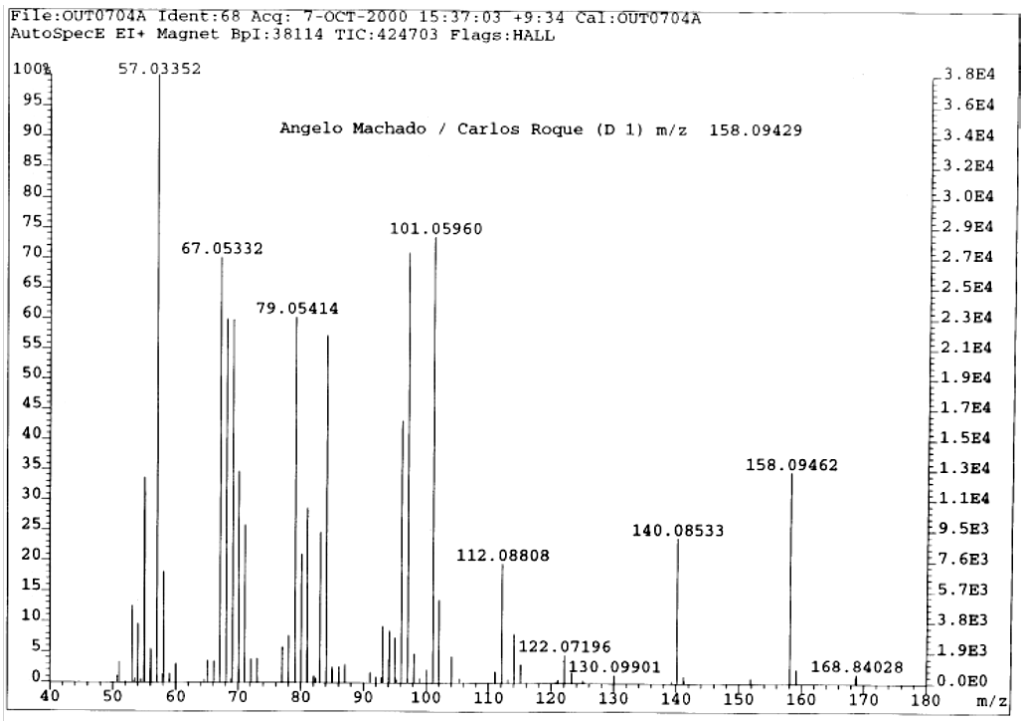


Figure S5. Mass spectrum of compound **3**.

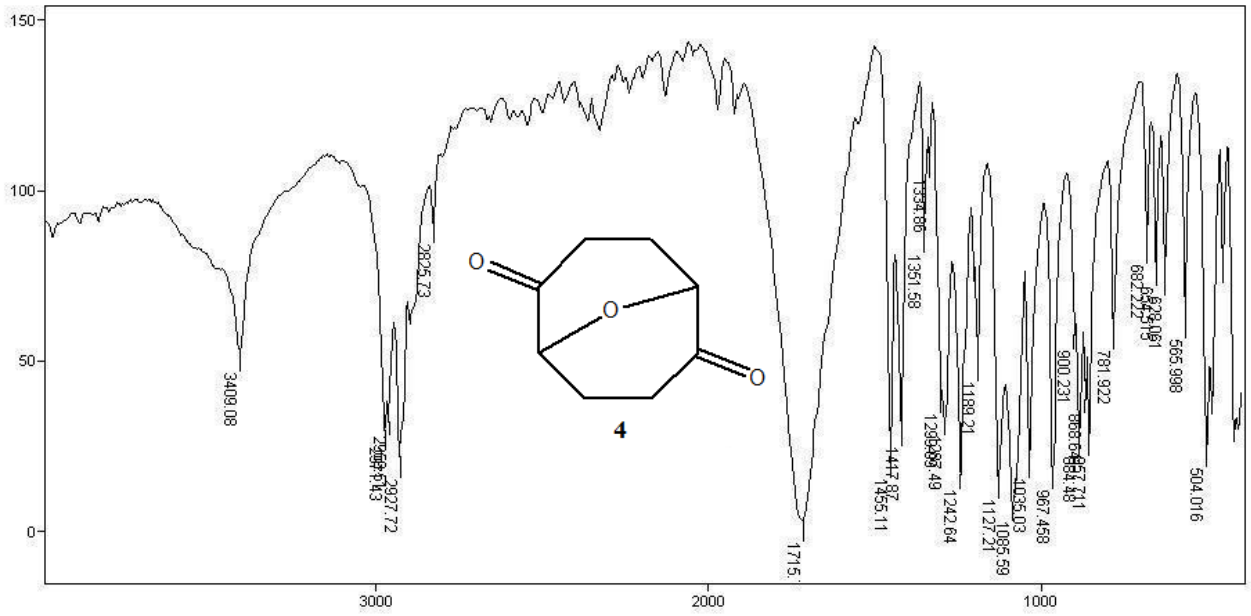
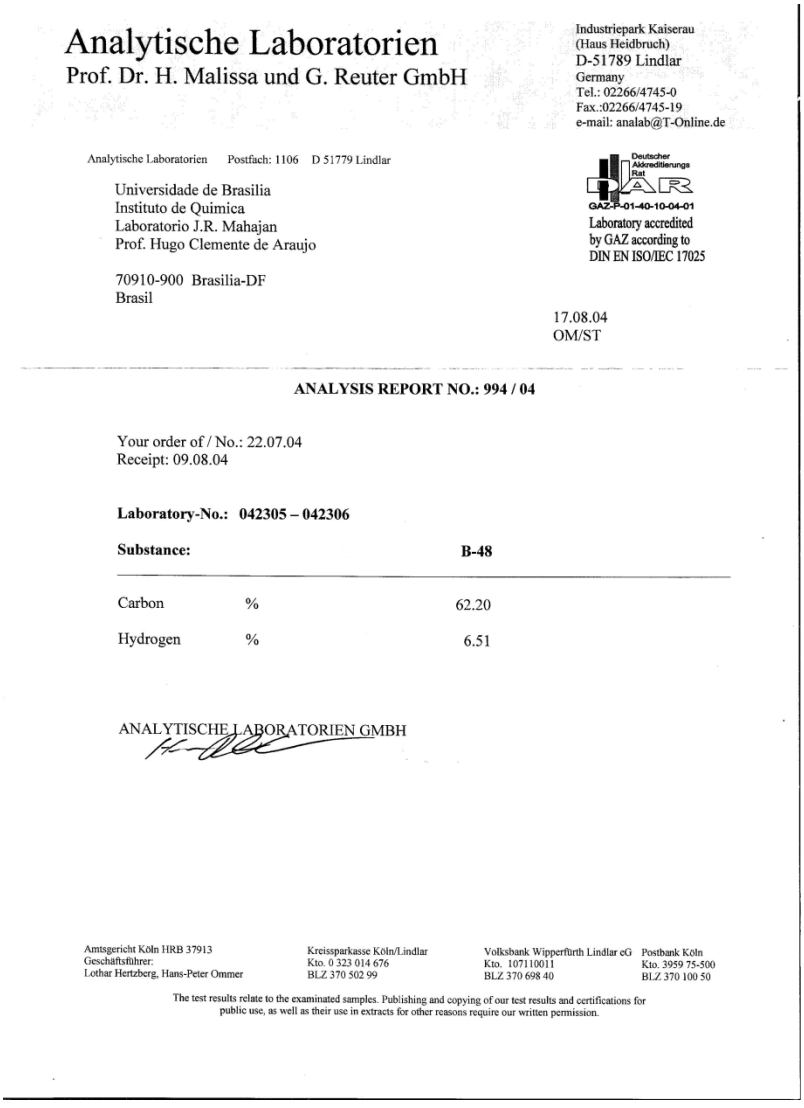


Figure S6. FTIR (KBr) spectrum of compound **4**.



Analytische Laboratorien
Prof. Dr. H. Malissa und G. Reuter GmbH

Industriepark Kaiserau
(Haus Heidbruch)
D-51789 Lindlar
Germany
Tel.: 02266/4745-0
Fax.:02266/4745-19
e-mail: analab@T-Online.de

Analytische Laboratorien Postfach: 1106 D 51779 Lindlar

Universidade de Brasilia
Instituto de Quimica
Laboratorio J.R. Mahajan
Prof. Hugo Clemente de Araujo

70910-900 Brasilia-DF
Brasil

Deutscher Akkreditierungs Rat
GAZ-P-01-40-10-04-01
Laboratory accredited by GAZ according to DIN EN ISO/IEC 17025

17.08.04
OM/ST

ANALYSIS REPORT NO.: 994 / 04

Your order of / No.: 22.07.04
Receipt: 09.08.04

Laboratory-No.: 042305 – 042306

Substance:		**B-48**
Carbon	%	62.20
Hydrogen	%	6.51

ANALYTISCHE LABORATORIEN GMBH

Amtsgericht Köln HRB 37913
Geschäftsführer:
Lothar Hertzberg, Hans-Peter Ommer

Kreissparkasse Köln/Lindlar
Kto. 0 323 014 676
BLZ 370 502 99

Volksbank Wipperfürth Lindlar eG
Kto. 107110011
BLZ 370 698 40

Postbank Köln
Kto. 3959 75-500
BLZ 370 100 50

The test results relate to the examinated samples. Publishing and copying of our test results and certifications for public use, as well as their use in extracts for other reasons require our written permission.

Figure S7. Elementary analysis of compound **4**.

Comment	10hwa08/RPA
Frequency (MHz)	300.07
Nucleus	1H
Acquisition Time (sec)	7.3053
Number of Transients	8
Original Points	29221
Points Count	32768
Solvent	CDCl3
Sweep Width (Hz)	4000.00
Temperature (grad C)	15.000

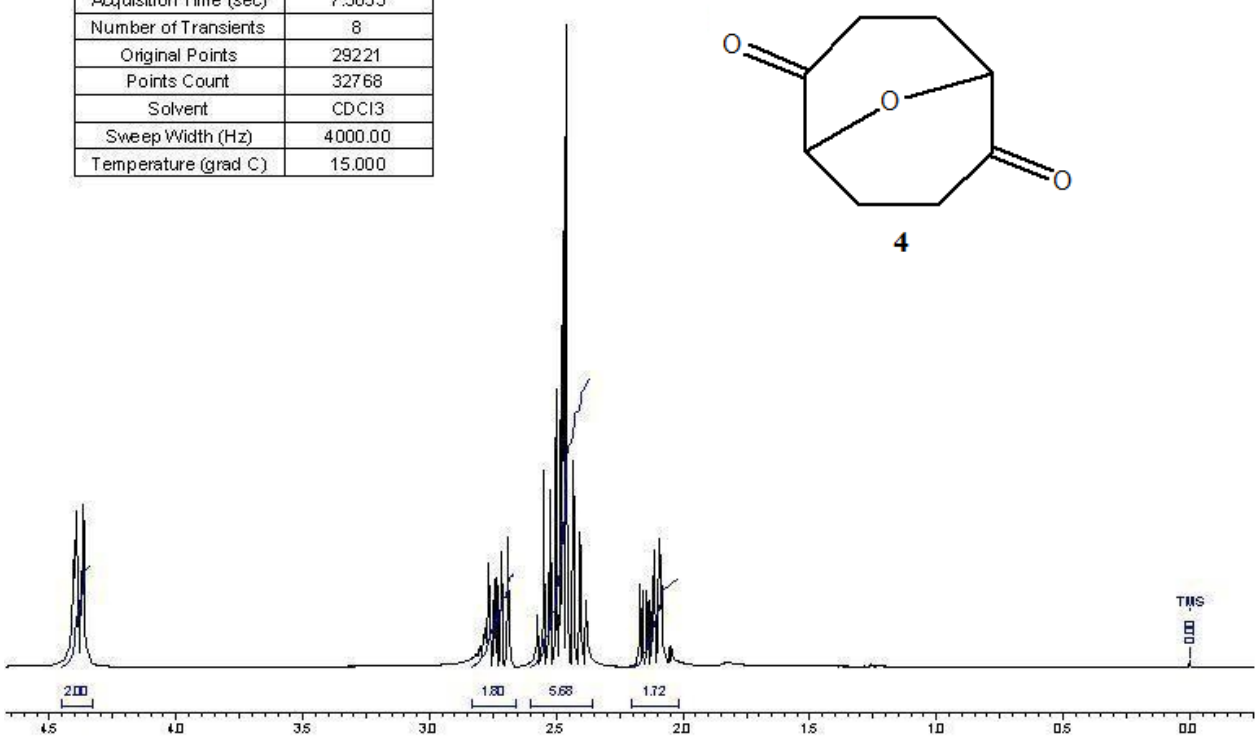


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **4**.

Comment	10cmb28
Frequency (MHz)	75.46
Nucleus	13C
Acquisition Time (sec)	1.7225
Number of Transients	1000
Original Points	32747
Points Count	32768
Solvent	CDCl3
Sweep Width (Hz)	19011.41
Temperature (grad C)	15.000

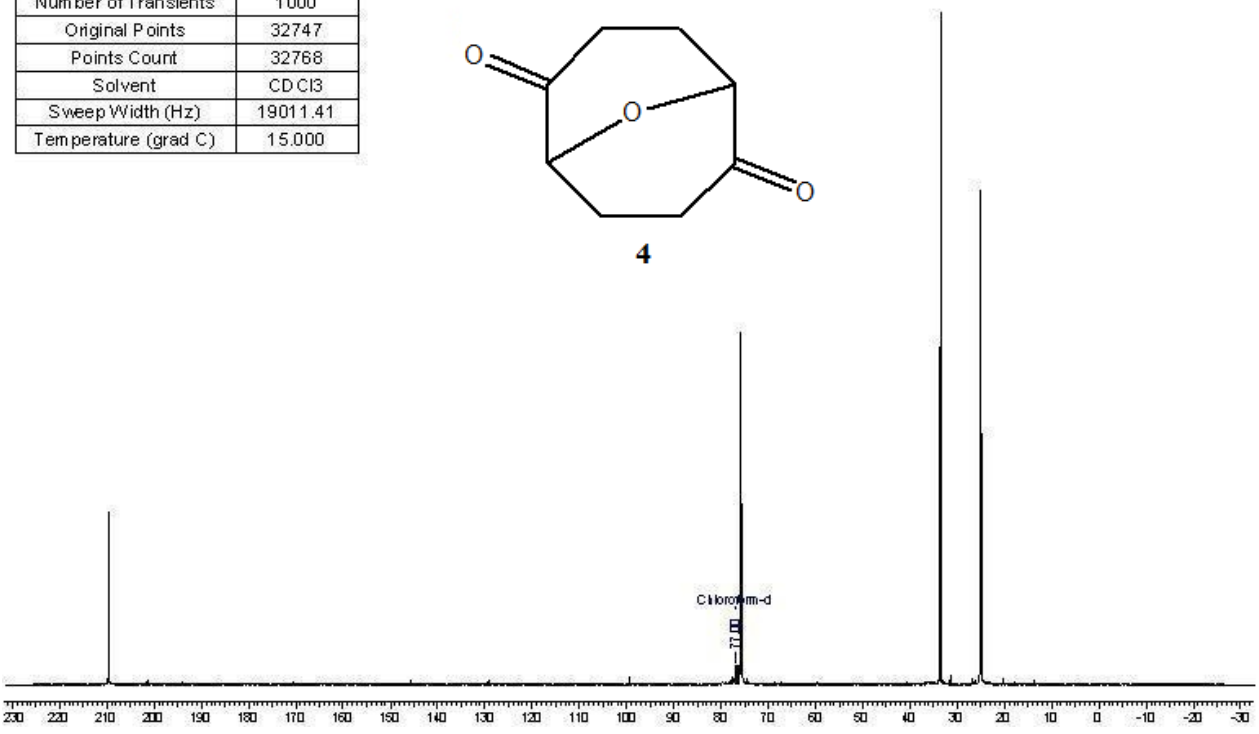


Figure S9. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **4**.

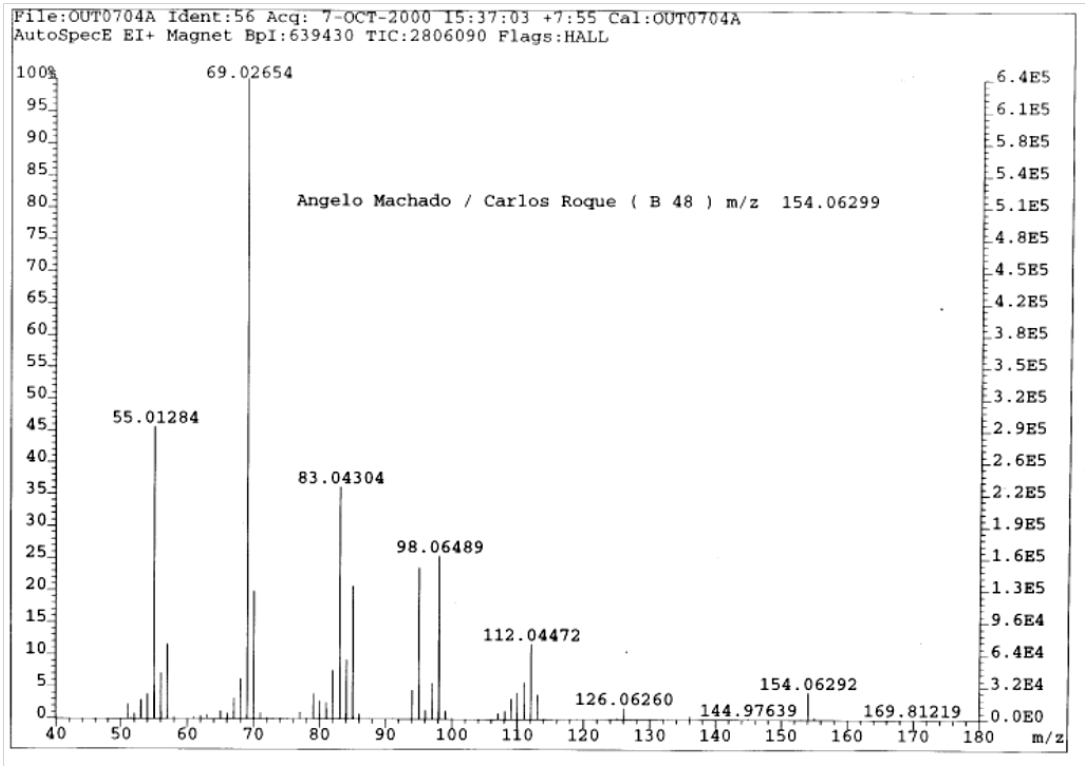


Figure S10. Mass spectrum of compound **4**.

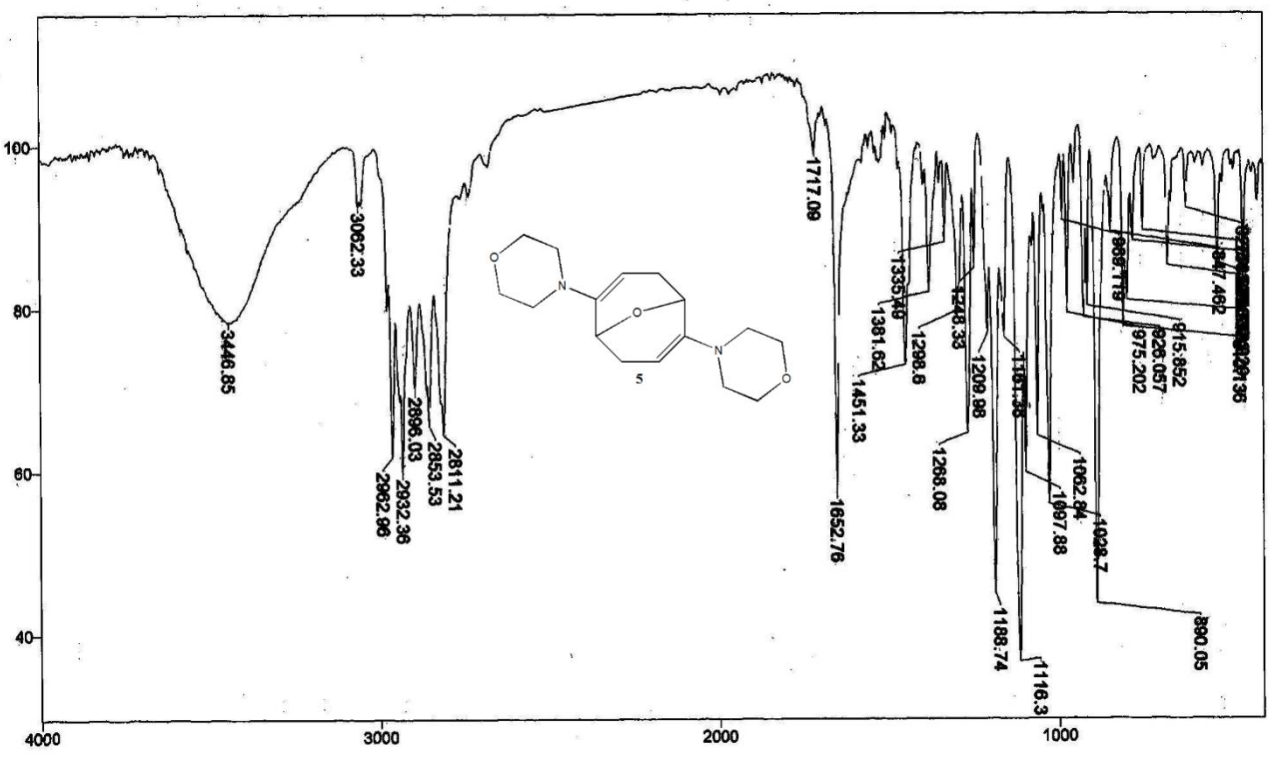


Figure S11. FTIR (film) spectrum of compound **5**.

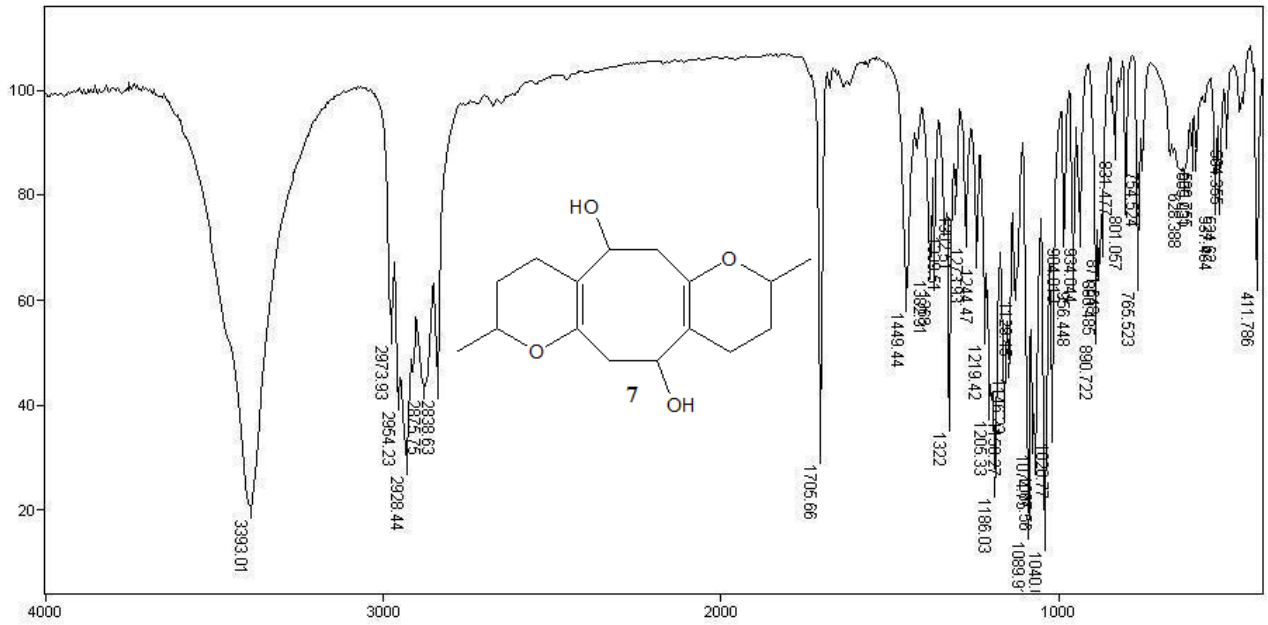


Figure S12. FTIR (KBr) spectrum of compound **7**.

Analytische Laboratorien
Prof. Dr. H. Malissa und G. Reuter GmbH

Industriepark Kaiserau
(Haus Heidbruch)
D-51789 Lindlar
Germany
Tel.: 02266/4745-0
Fax.:02266/4745-19
e-mail: analab@T-Online.de

Analytische Laboratorien Postfach: 1106 D 51779 Lindlar

Universidade de Brasilia
Instituto de Quimica
Laboratorio J.R. Mahajan
Prof. Hugo Clemente de Araujo

70910-900 Brasilia-DF
Brasil

Deutscher Akkreditierungs Rat
GAZ-P-01-40-10-04-01
Laboratory accredited by GAZ according to DIN EN ISO/IEC 17025

14.03.05
OM/ST

ANALYSIS REPORT NO.: 279 / 05

Your order of / No.:
Receipt: 28.02.05

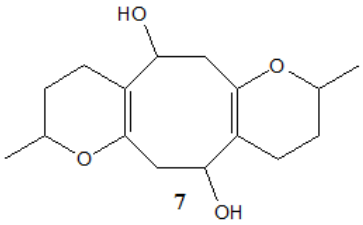
Laboratory-No.: 050655 – 050657

Substance	% C	% H	% N
F9 (Enol Ether)	68.42	8.88	

ANALYTISCHE LABORATORIEN GMBH

Figure S13. Elementary analysis of compound **7**.

Comment	38hmb61
Frequency (MHz)	300.07
Nucleus	1H
Acquisition Time (sec)	8.1250
Number of Transients	16
Original Points	32500
Points Count	32768
Solvent	CDCl3
Sweep Width (Hz)	4000.00
Temperature (grad C)	29.000



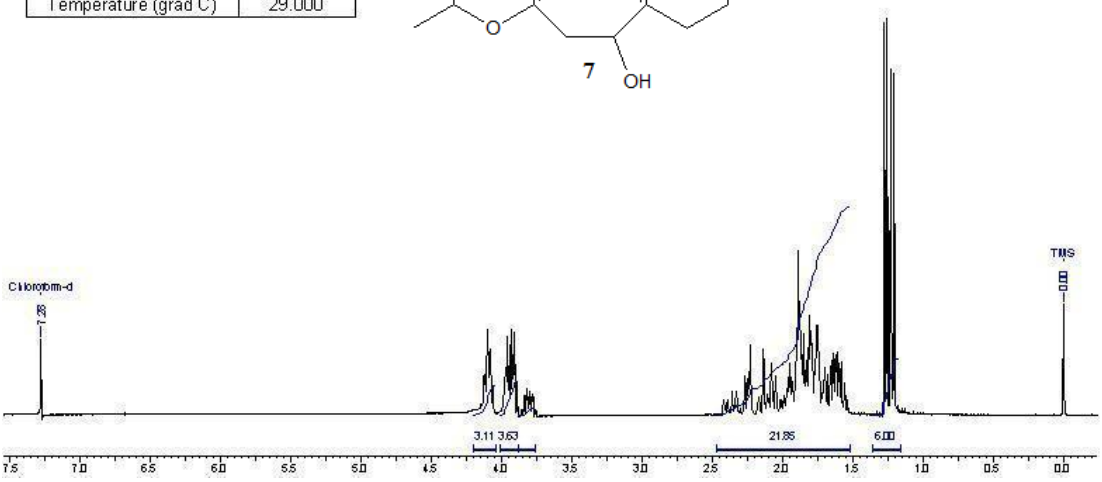


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **7**.

Comment	38cmb61
Frequency (MHz)	75.46
Nucleus	13C
Acquisition Time (sec)	1.7225
Number of Transients	1024
Original Points	32500
Points Count	32768
Solvent	CDCl3
Sweep Width (Hz)	18867.92
Temperature (grad C)	27.000

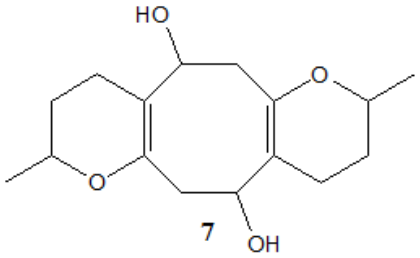


Figure S15. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **7**.

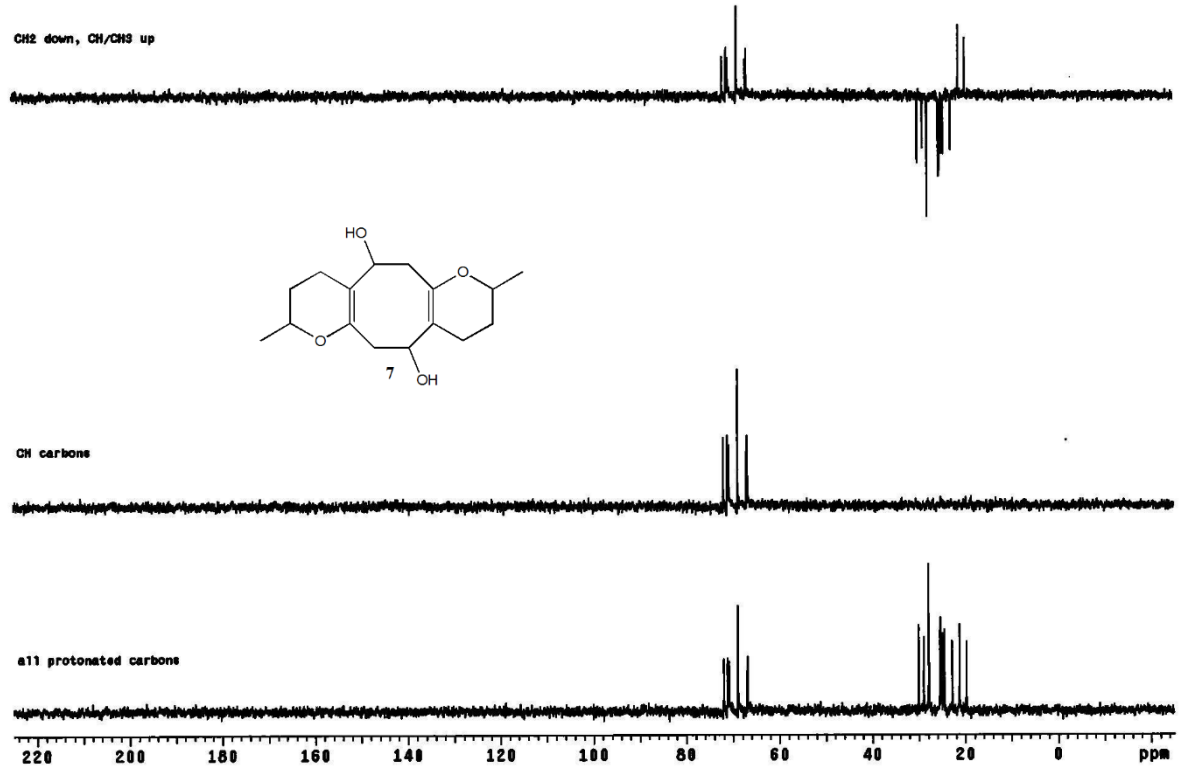


Figure S16. DEPT NMR (75 MHz, $CDCl_3$) of compound **7**.

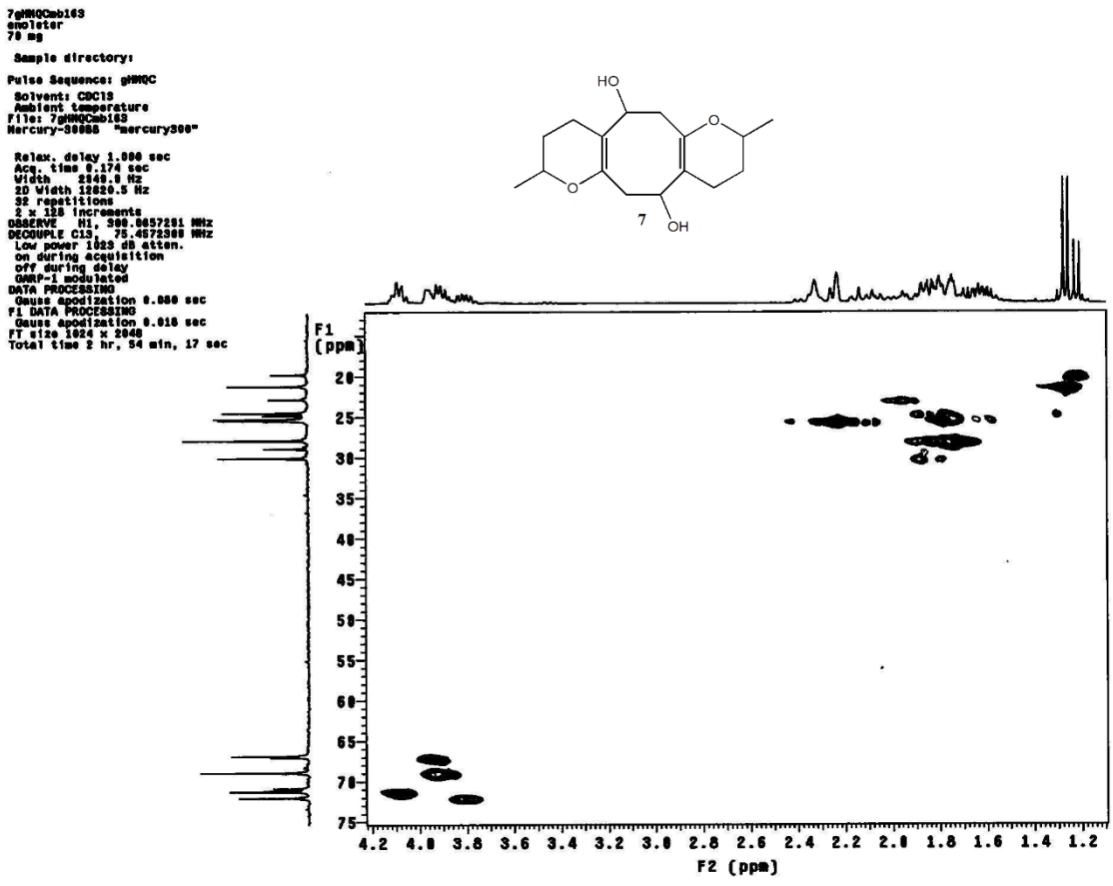


Figure S17. gHSQC of compound **7**.

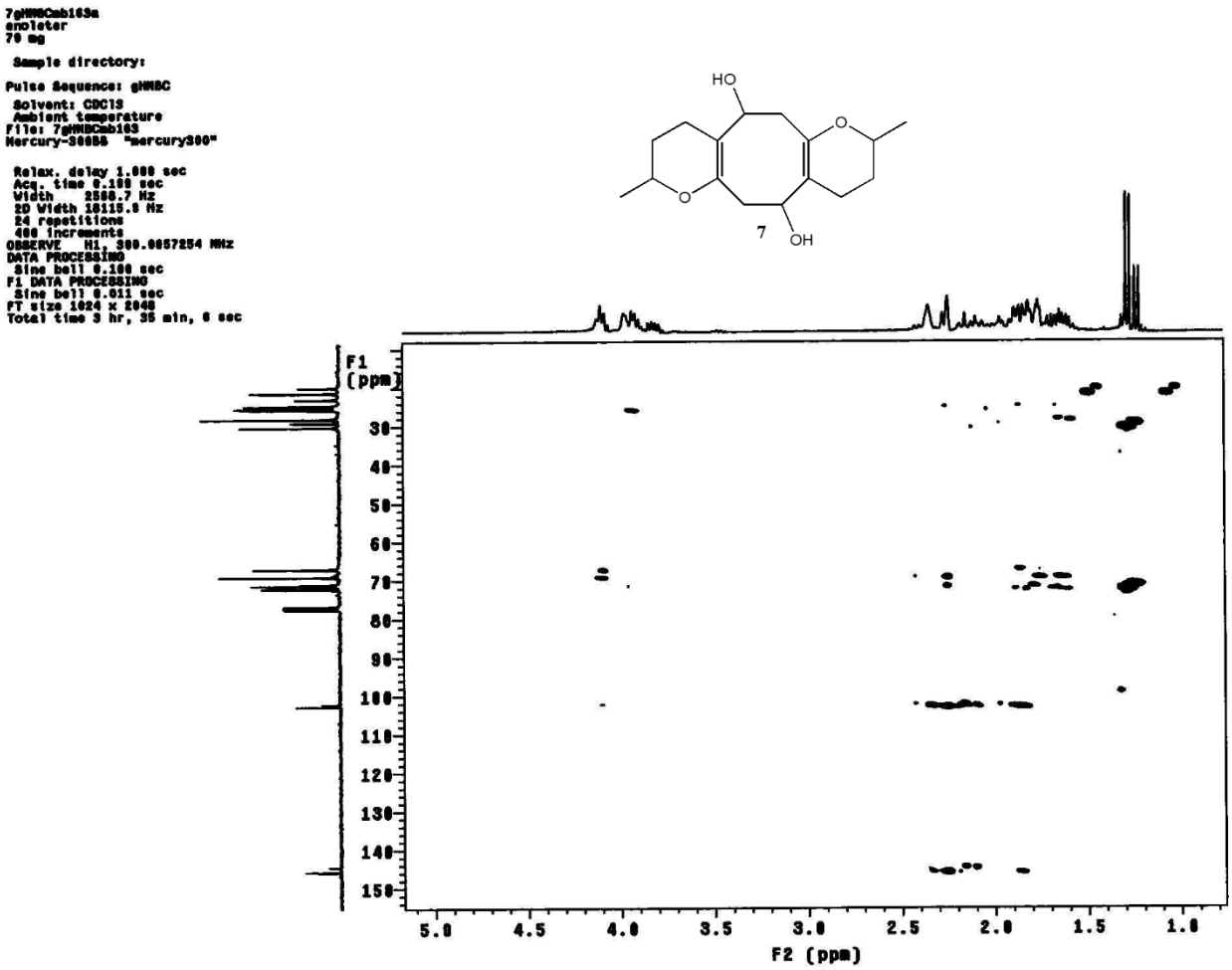


Figure S18. gHMBC of compound **7**.

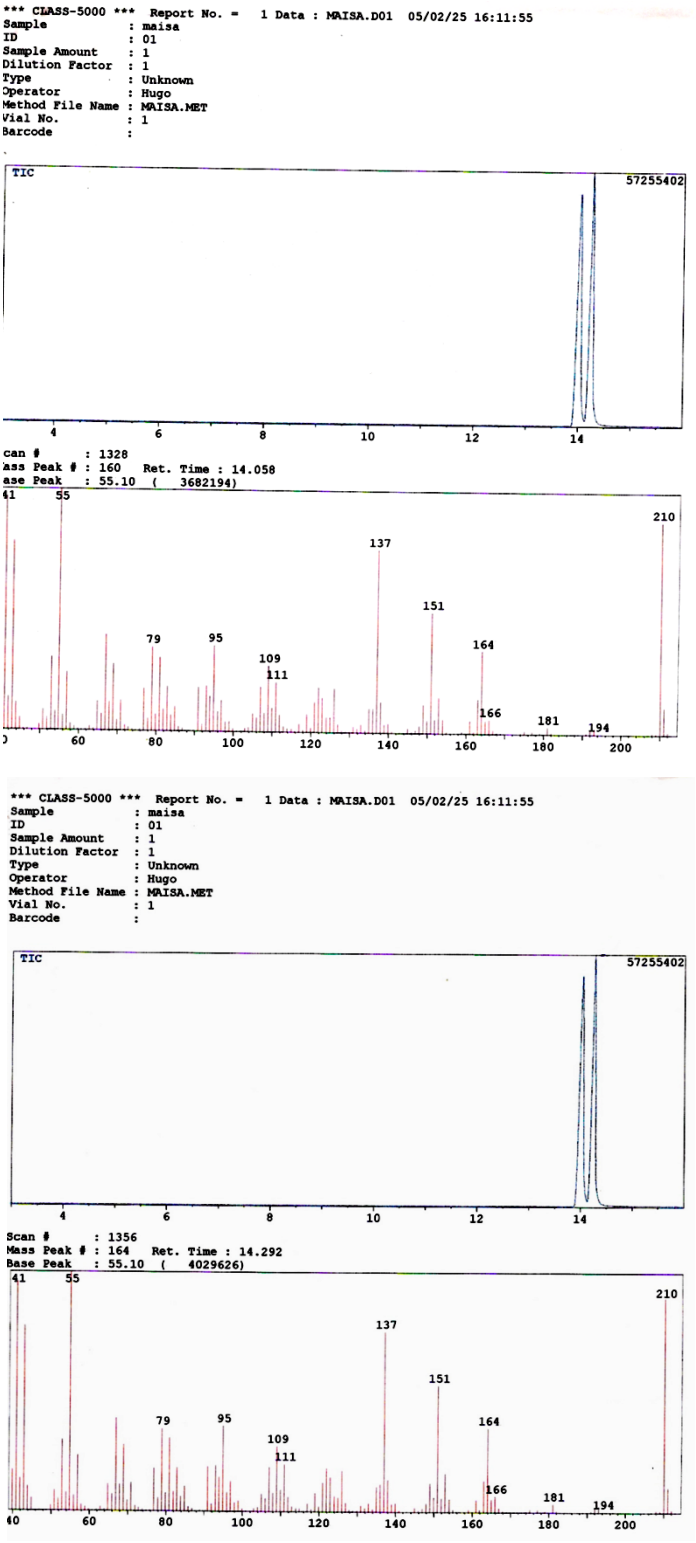


Figure S19. Mass spectrum of compound **7**.

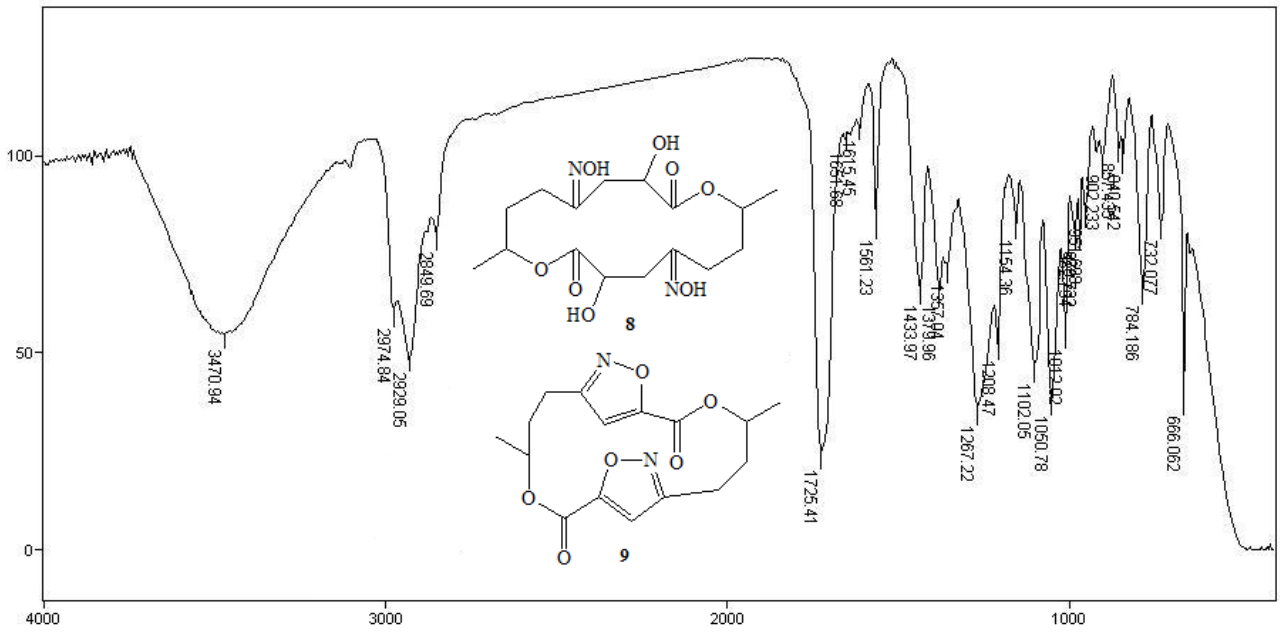


Figure S20. FTIR (KBr) spectrum of compounds **8** and **9**.

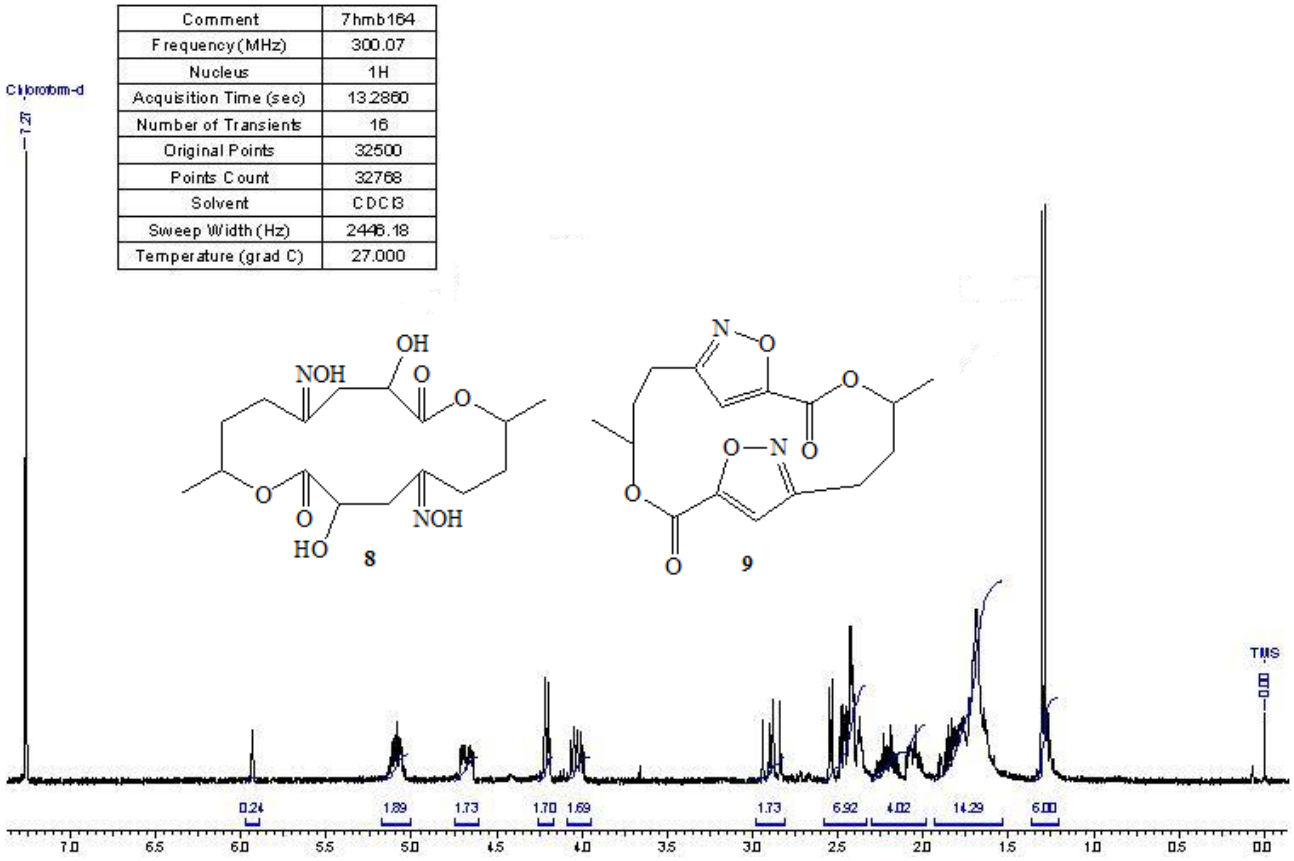


Figure S21. ^{1}H NMR (300 MHz, $CDCl_3$) of compounds **8** and **9**.

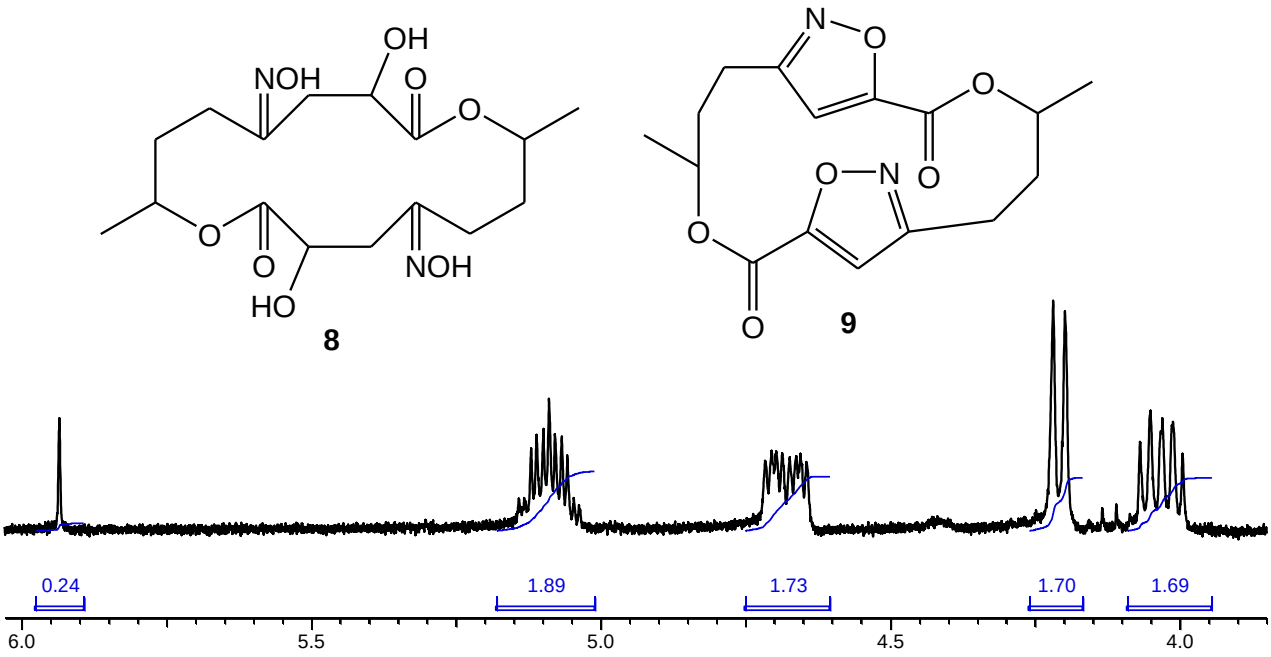


Figure S22. Expansions ^{1}H NMR (300 MHz, $CDCl_3$) of compounds **8** and **9**.

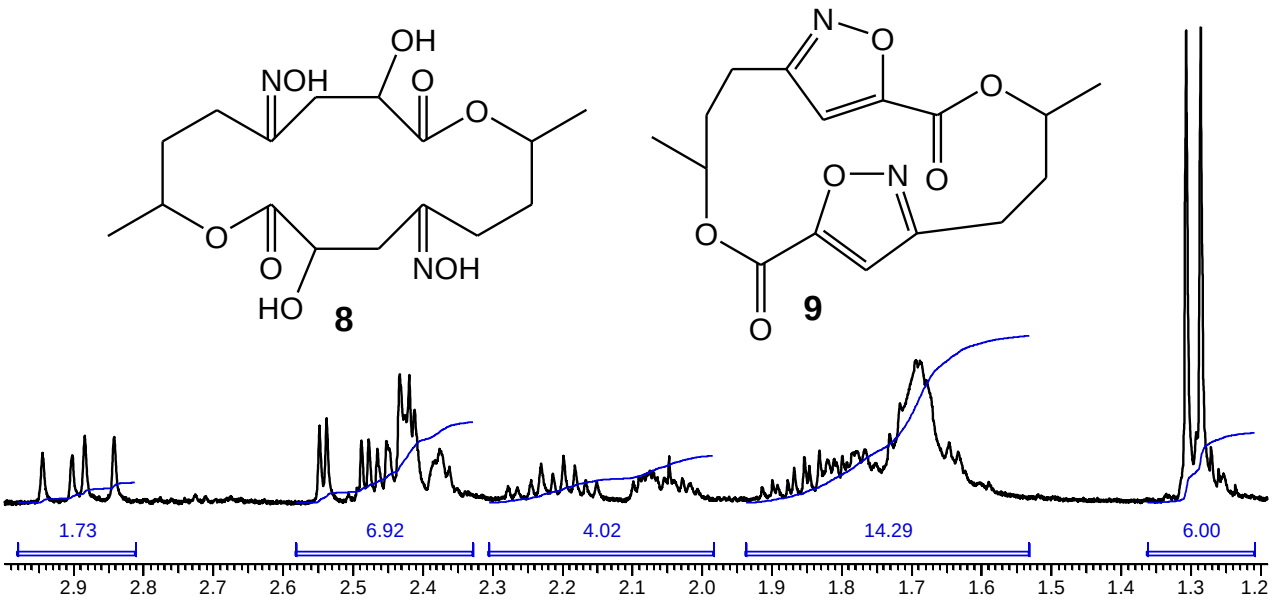


Figure S23. Expansions ^{1}H NMR (300 MHz, $CDCl_3$) of compounds **8** and **9**.

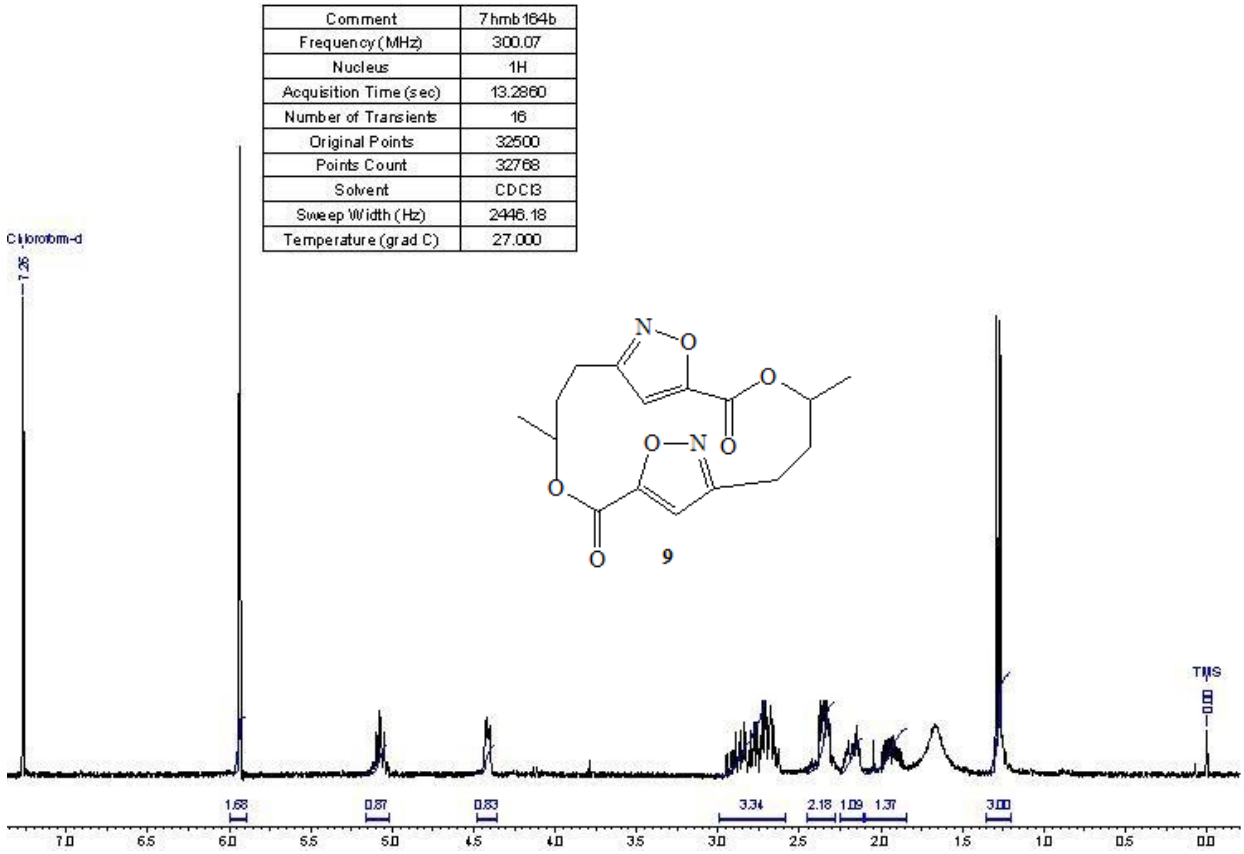


Figure S24. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **9**.

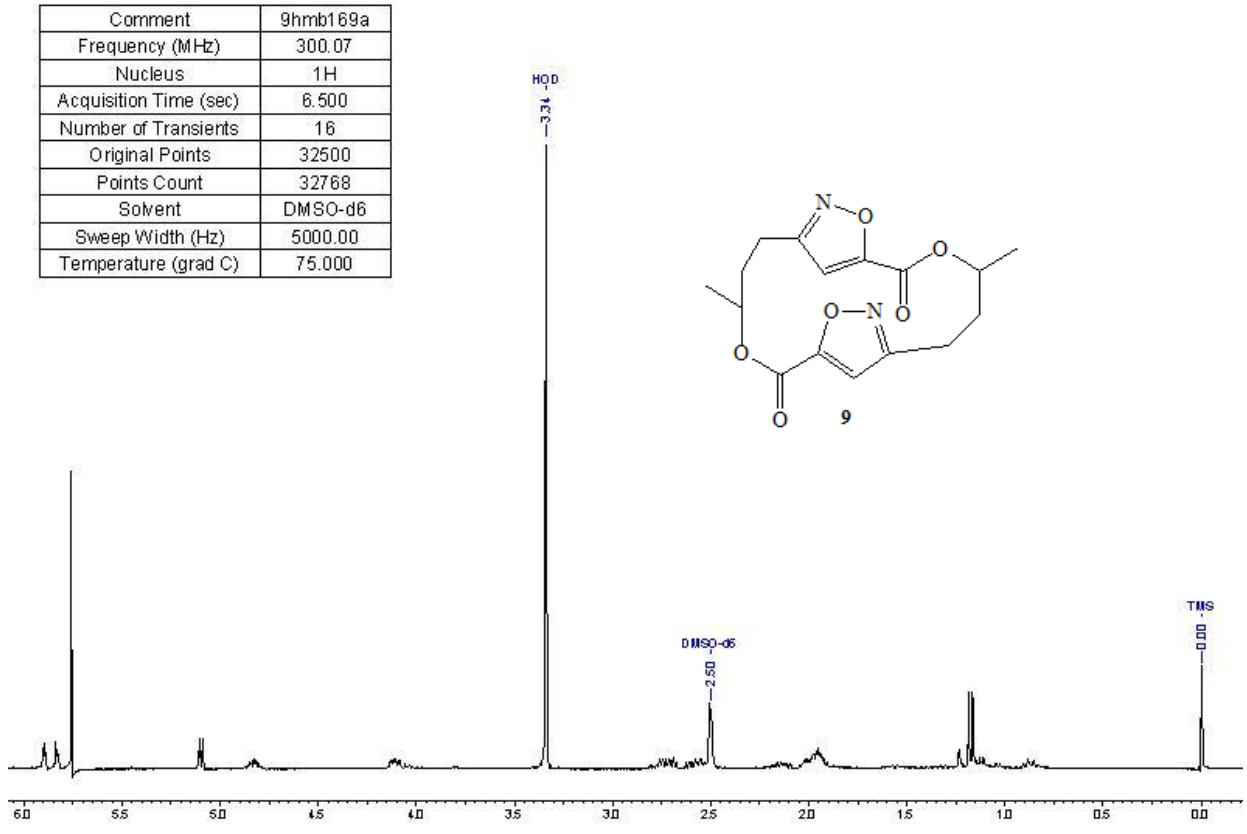


Figure S25. ^{1}H NMR (300 MHz, DMSO-d_6) of compound **9**.

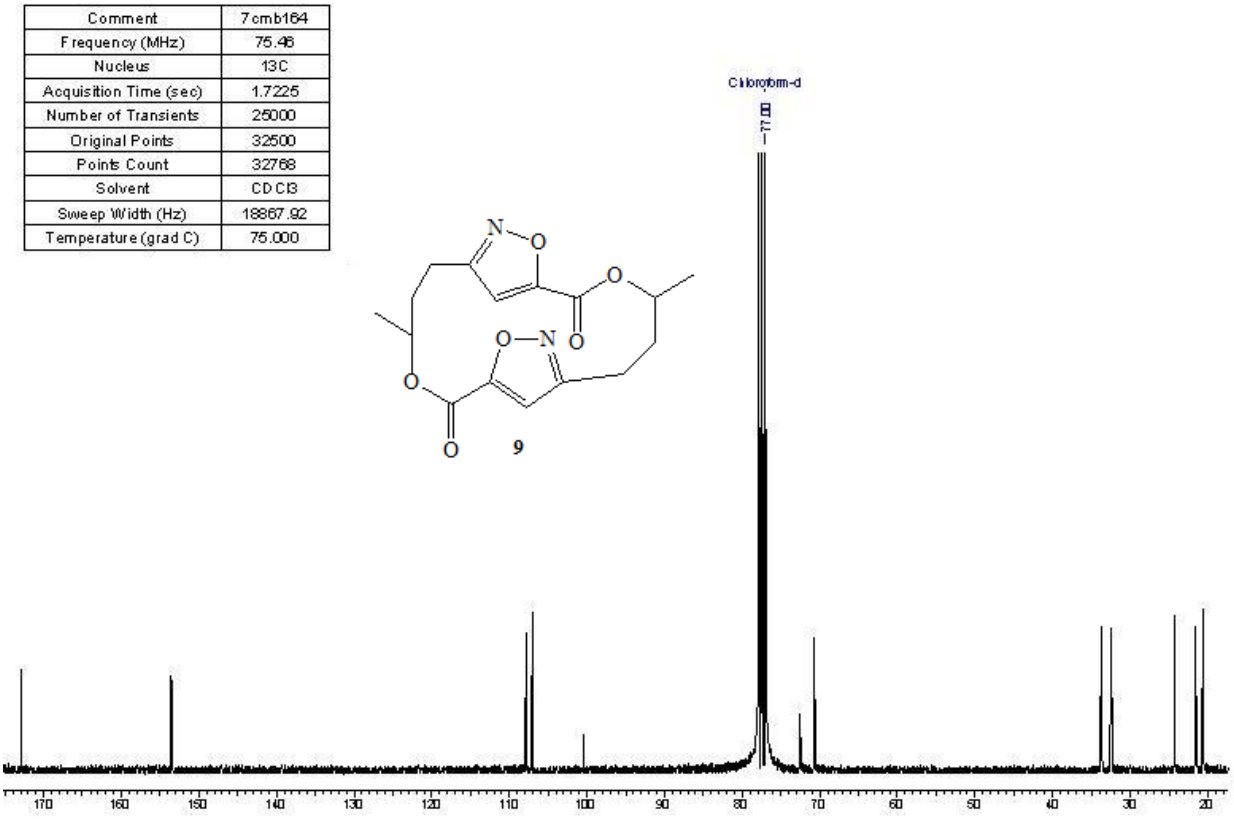


Figure S26. ^{13}C NMR (75 MHz, $CDCl_3$) of compound **9**.

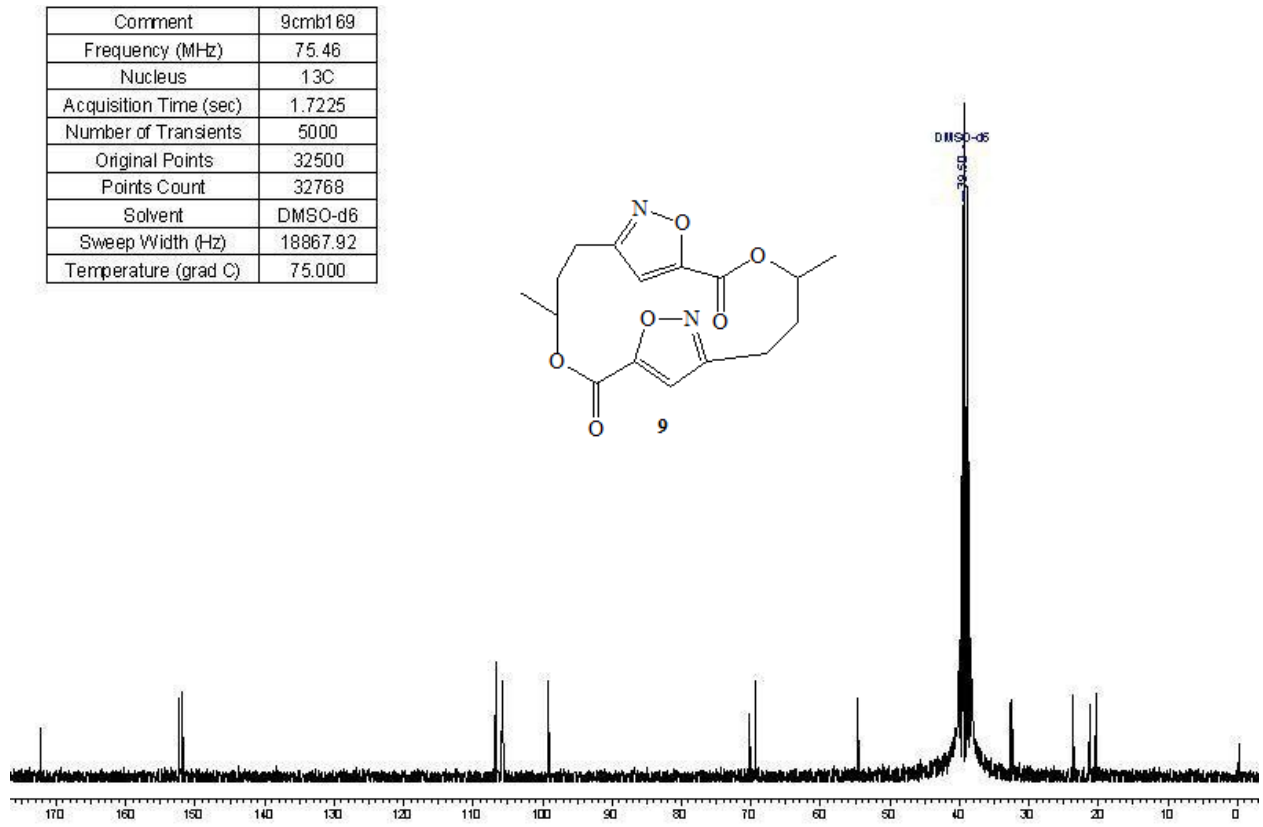
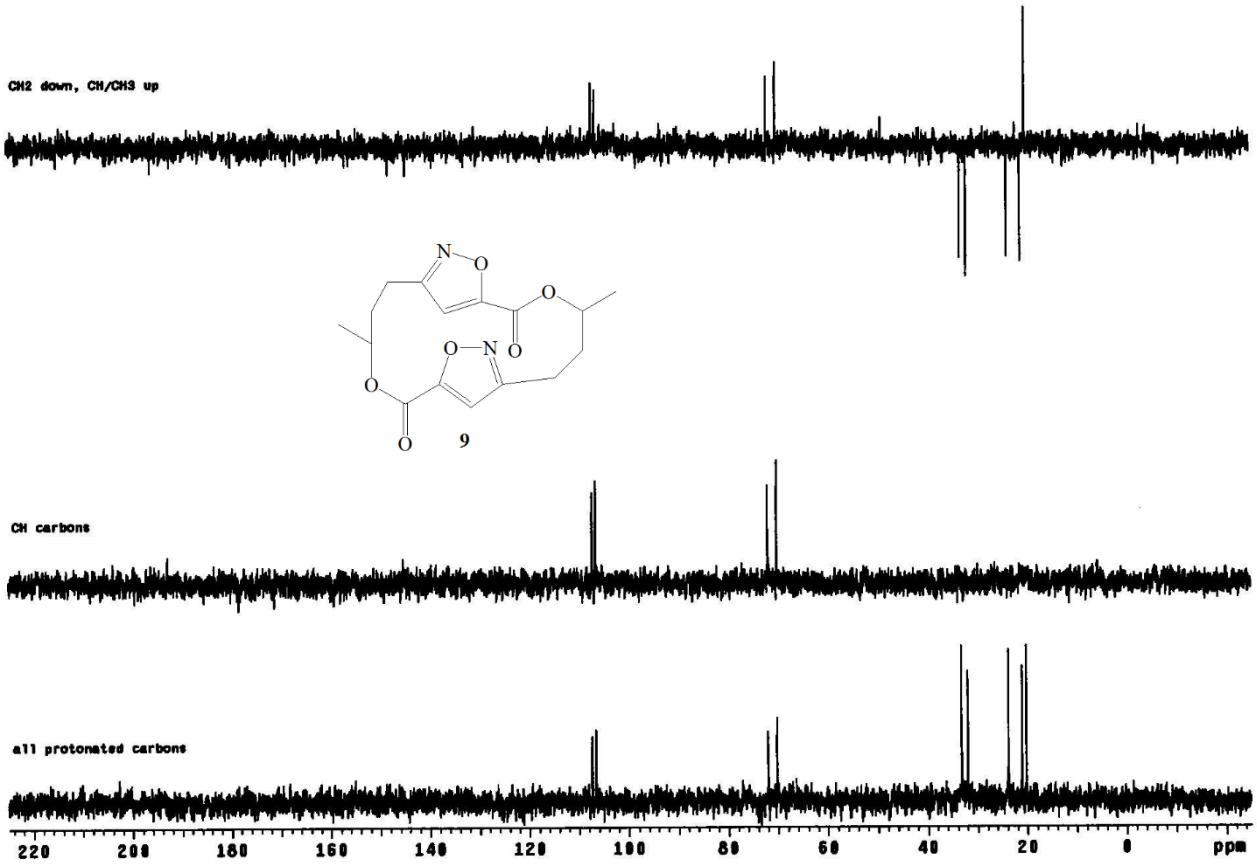


Figure S27. ^{13}C NMR (75 MHz, DMSO-d_6) of compound **9**.



9

Figure S28. DEPT NMR (75 MHz, DMSO-d_6) of compound **9**.