Supporting Information-Part I

The Repertoire of Steric Effects in the Tuning of the Diastereoselectivity of the Intramolecular Free-radical Cyclization to an Olefin as Exemplified Through the Synthesis of Carba-Pentofuranose Scaffold

Mansoureh Karimiahmadabadi, Sayeh Erfan, Andras Földesi and Jyoti Chattopadhyaya*

Program of Chemical Biology, Department of Cell and Molecular Biology, Biomedical Centre,
Uppsala University, SE-75123 Uppsala, Sweden.
Phone: +46-18-4714577, Fax: +46-18-554495, E-mail: jyoti@boc.uu.se

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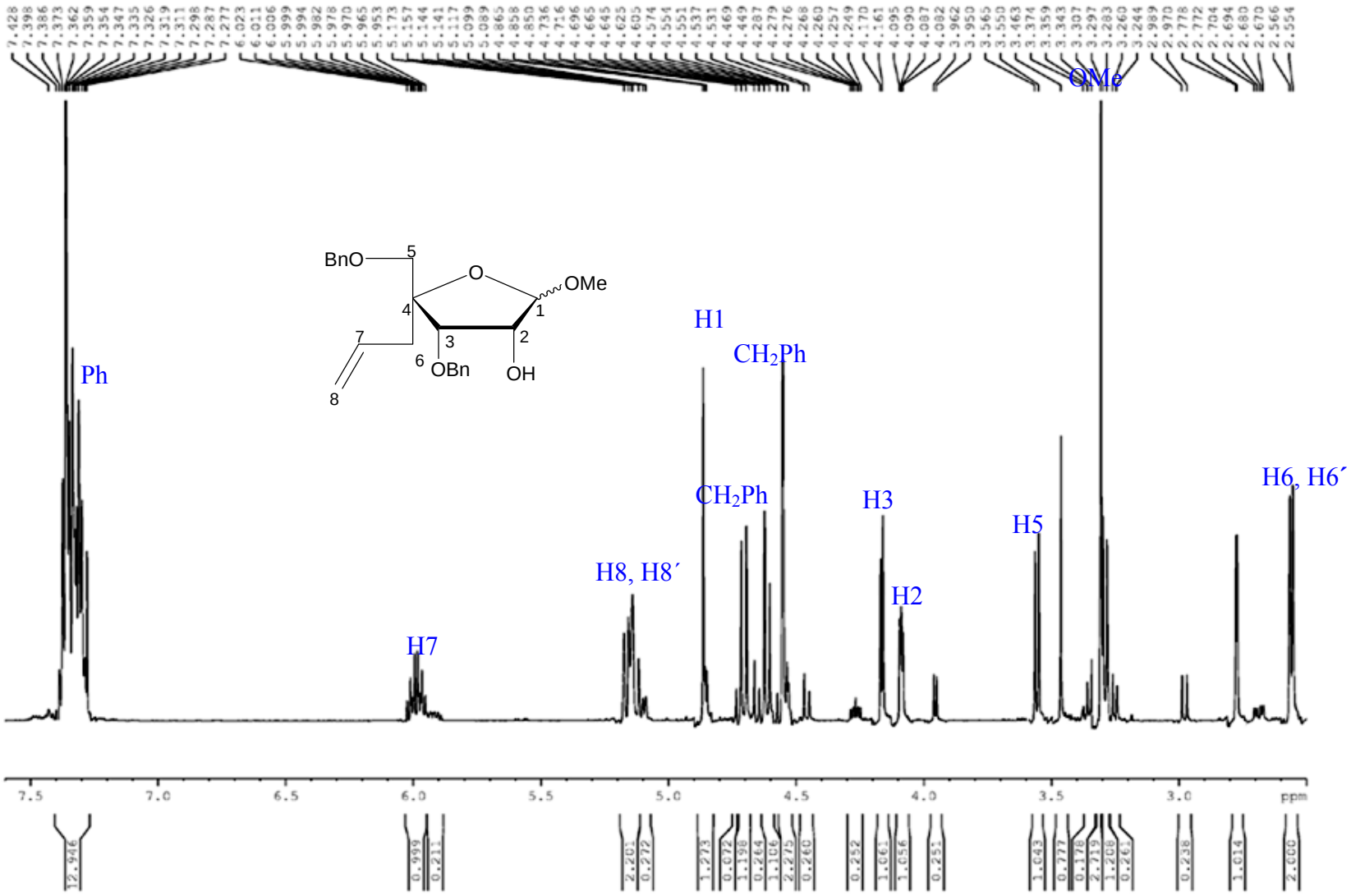


Figure S1: ^{1}H NMR spectrum of compound **2** (anomeric mixture)

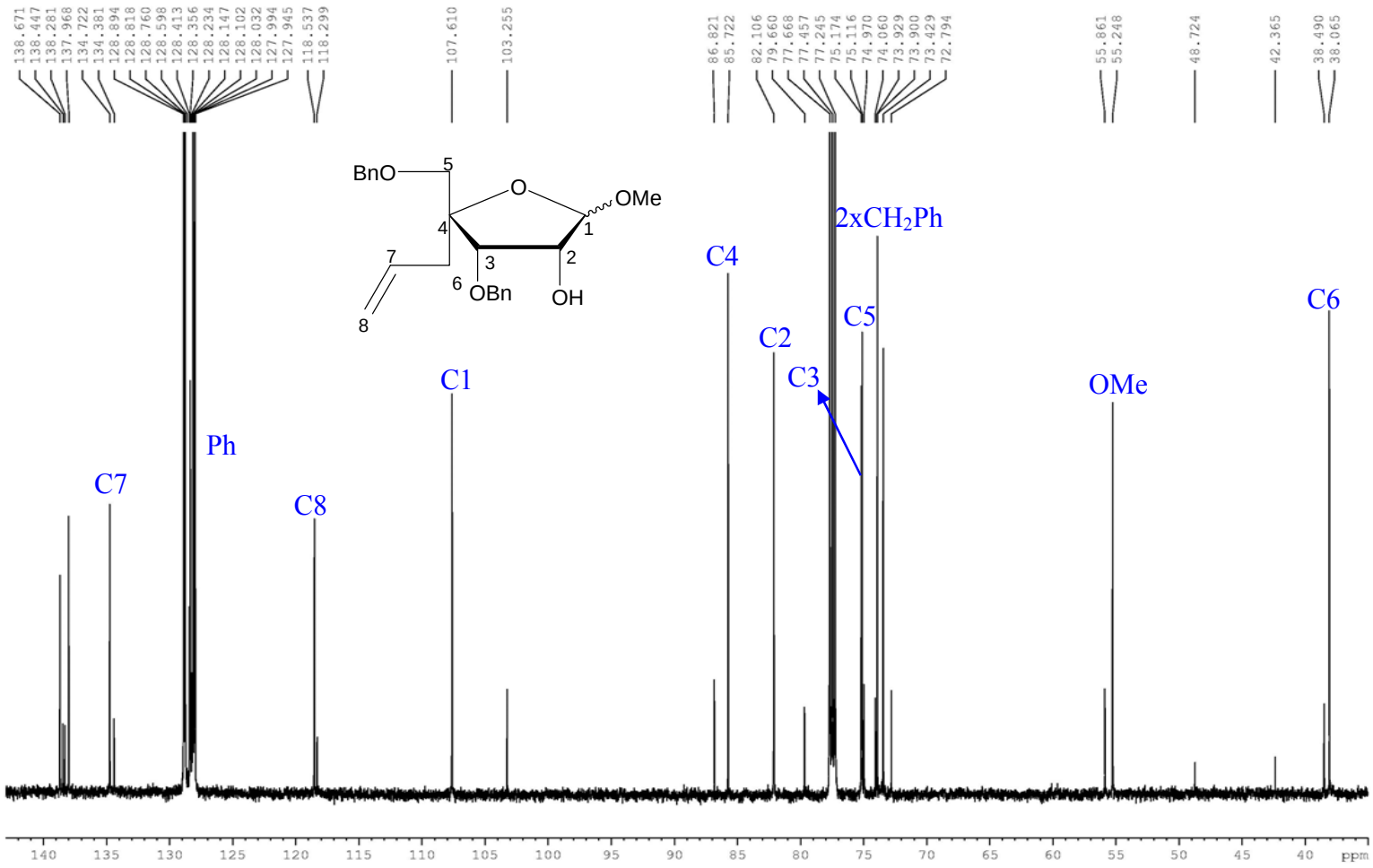


Figure S2: ^{1}C NMR spectrum of compound **2**(anomeric mixture)

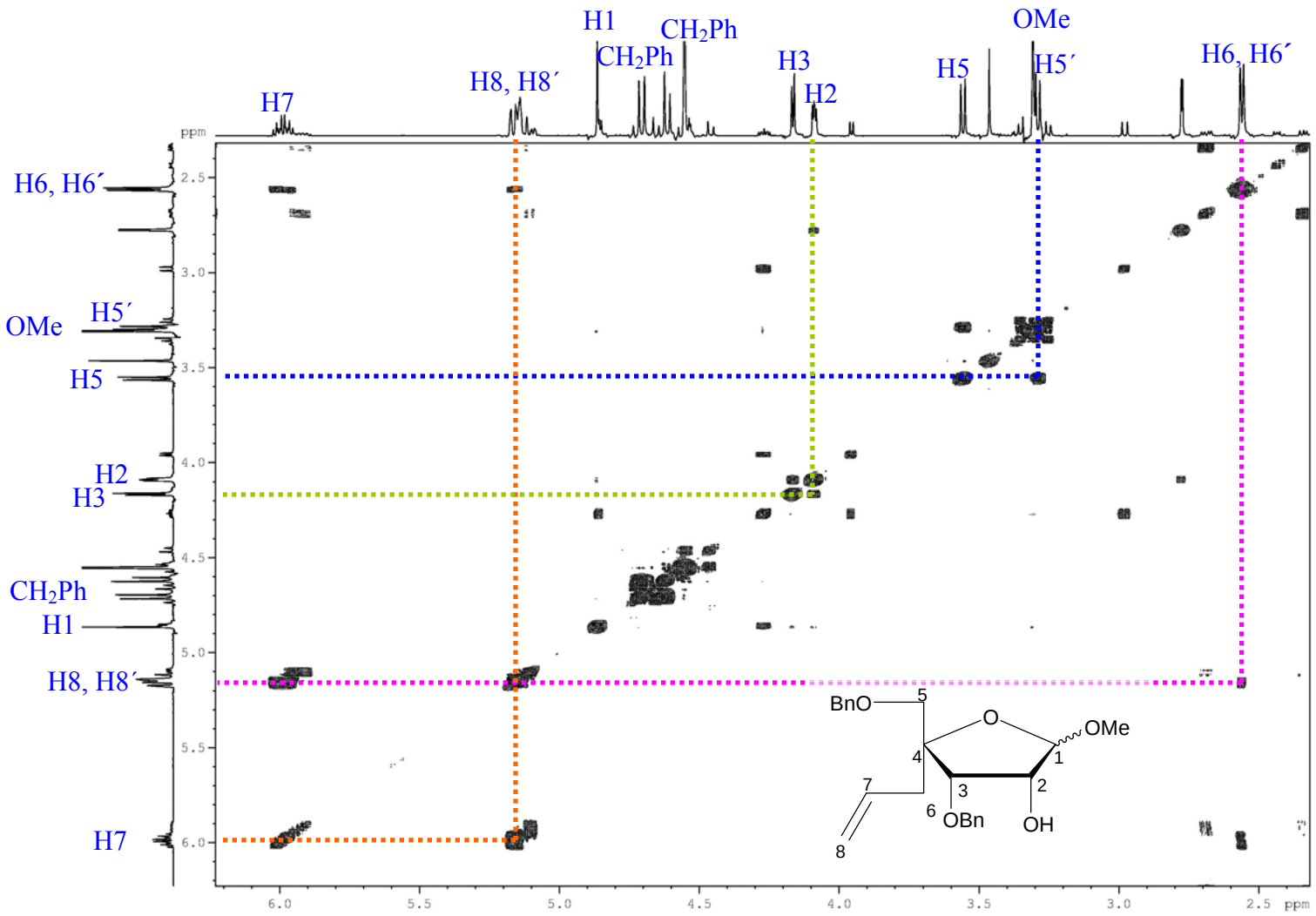


Figure S3: COSY spectrum of compound **2** (anomeric mixture)

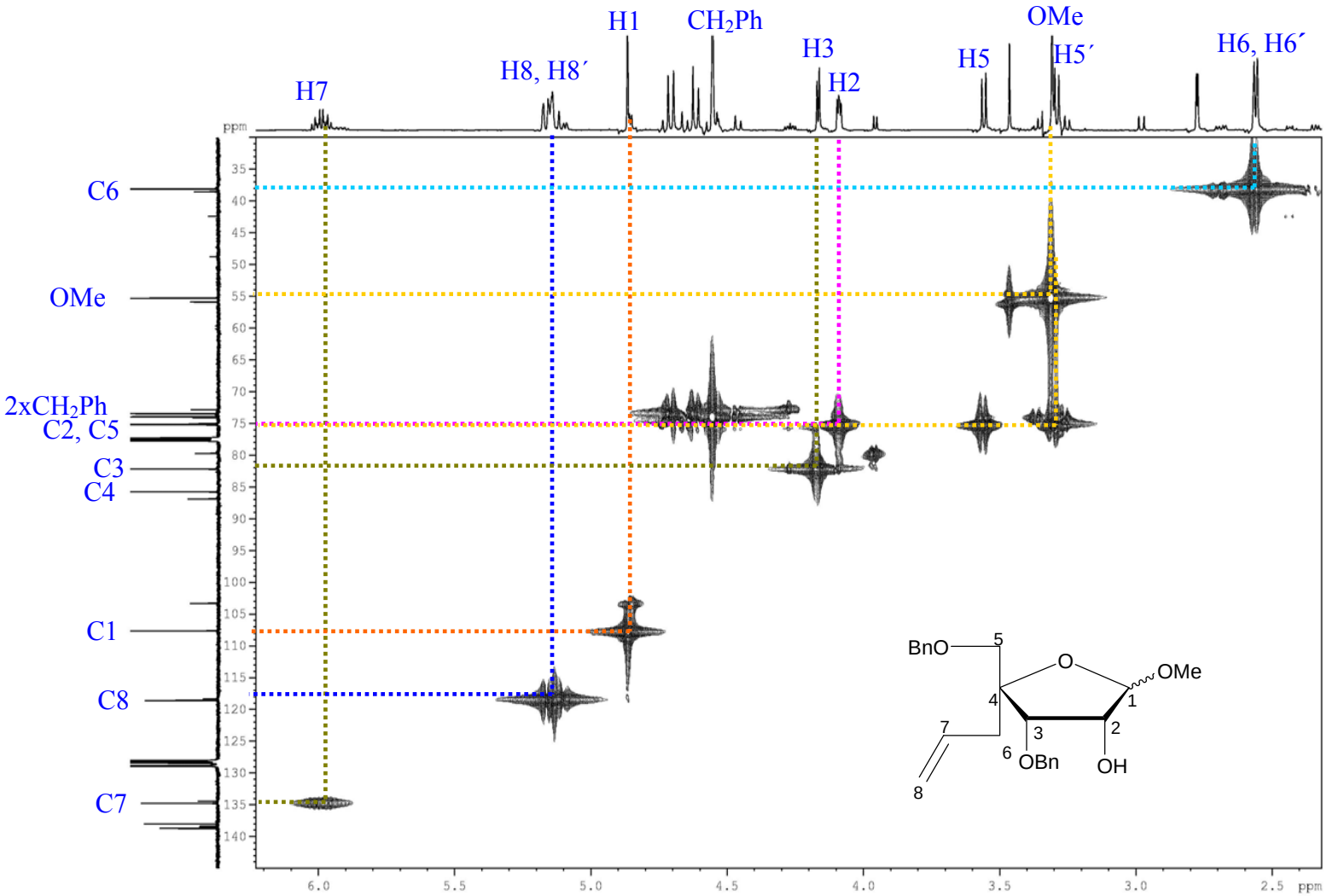


Figure S4: HMQC spectrum of compound **2** (anomeric mixture)

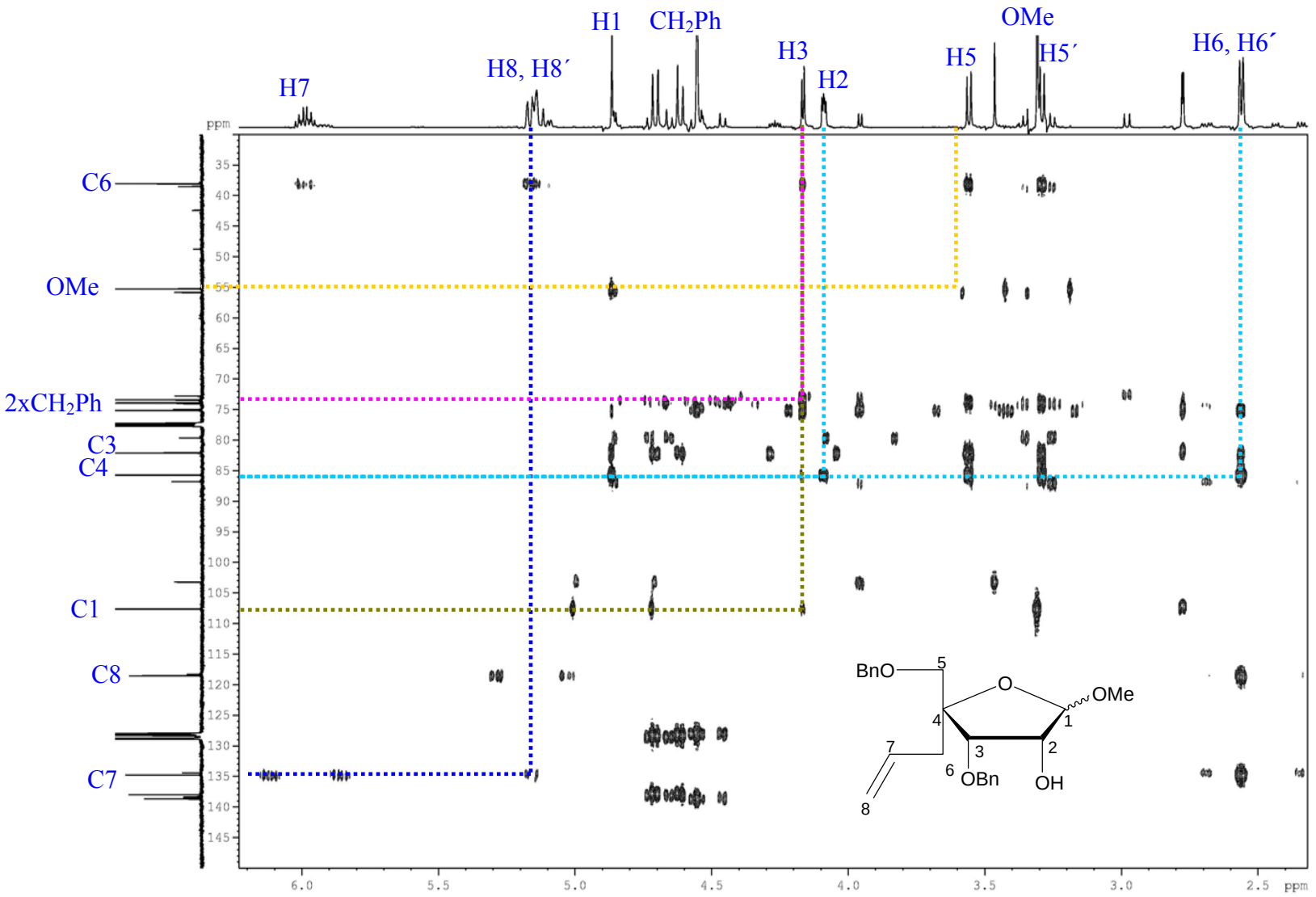


Figure S5: HMBC spectrum of compound **2** (anomeric mixture)

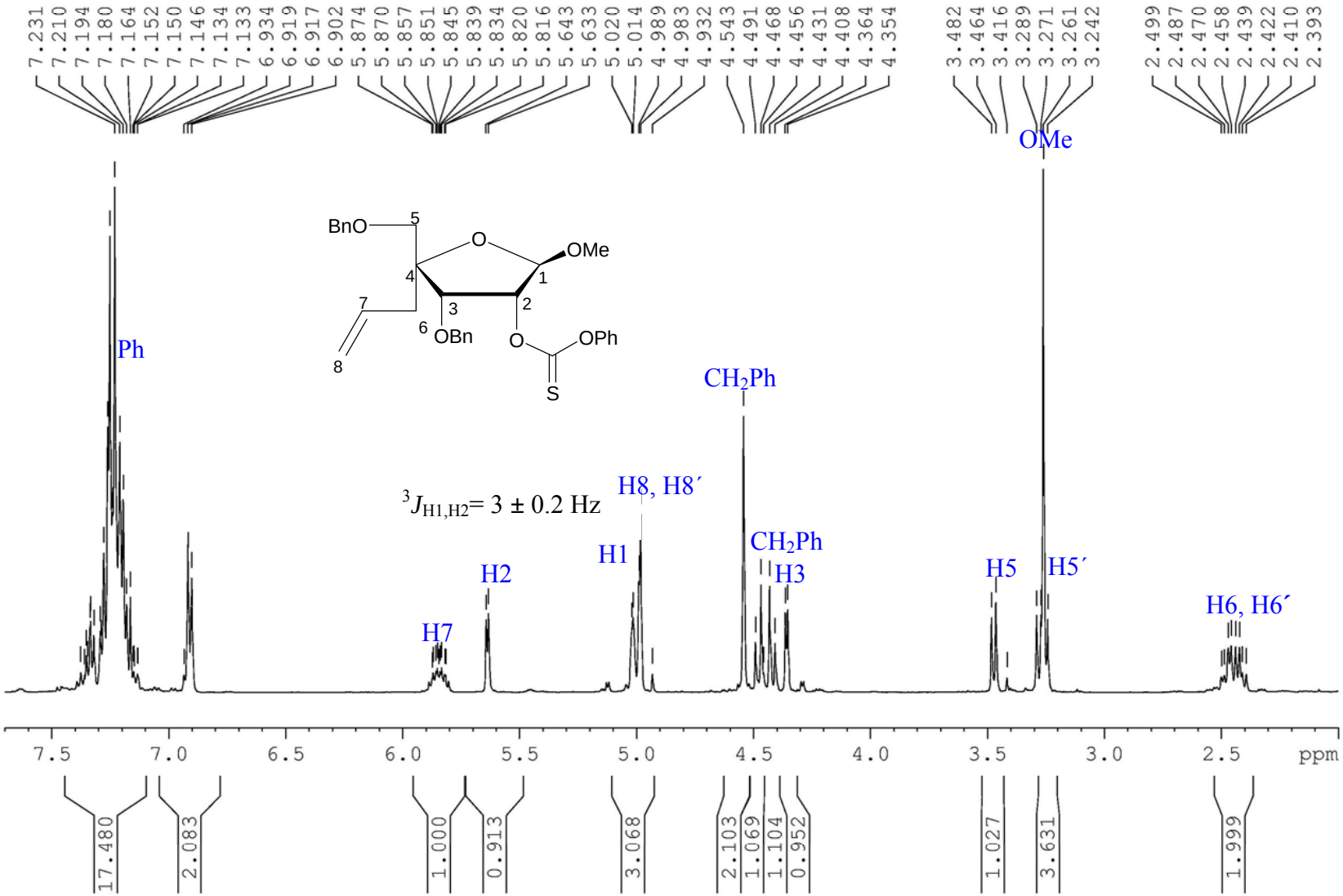


Figure S6: ^{1}H NMR spectrum of compound **3a**

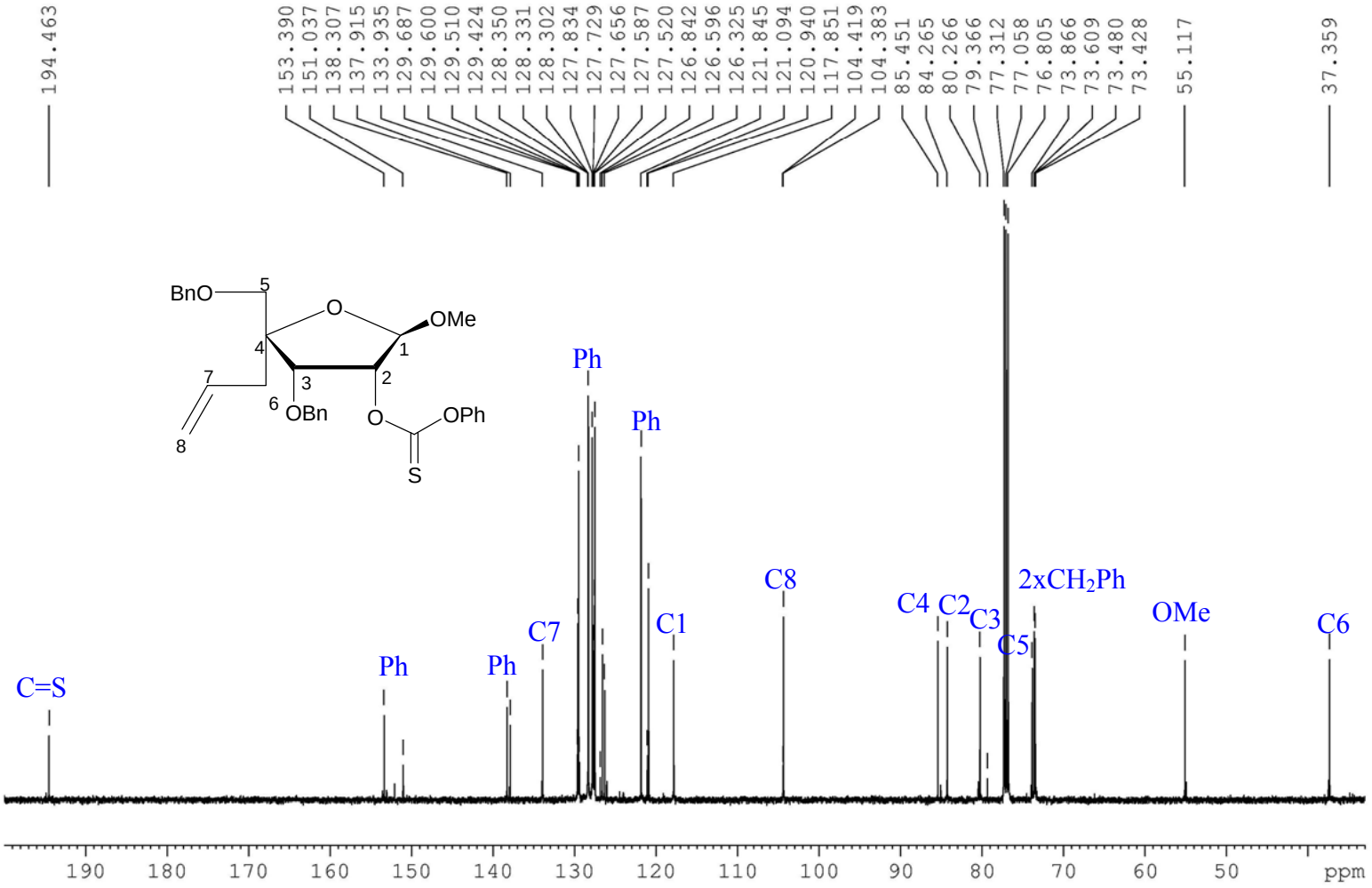


Figure S7: ^{13}C NMR spectrum of compound **3a**

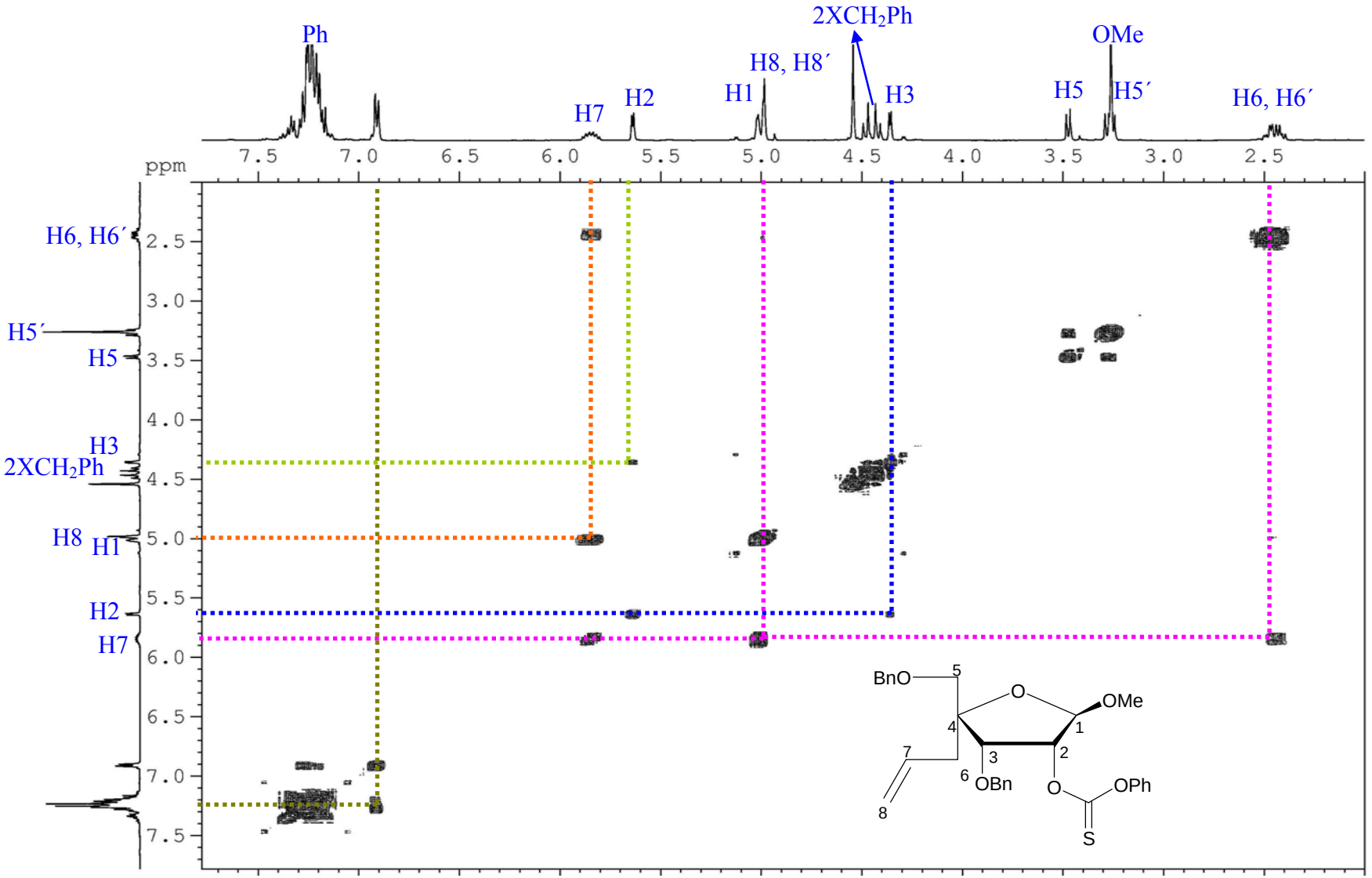


Figure S8: COSY spectrum of compound **3a**

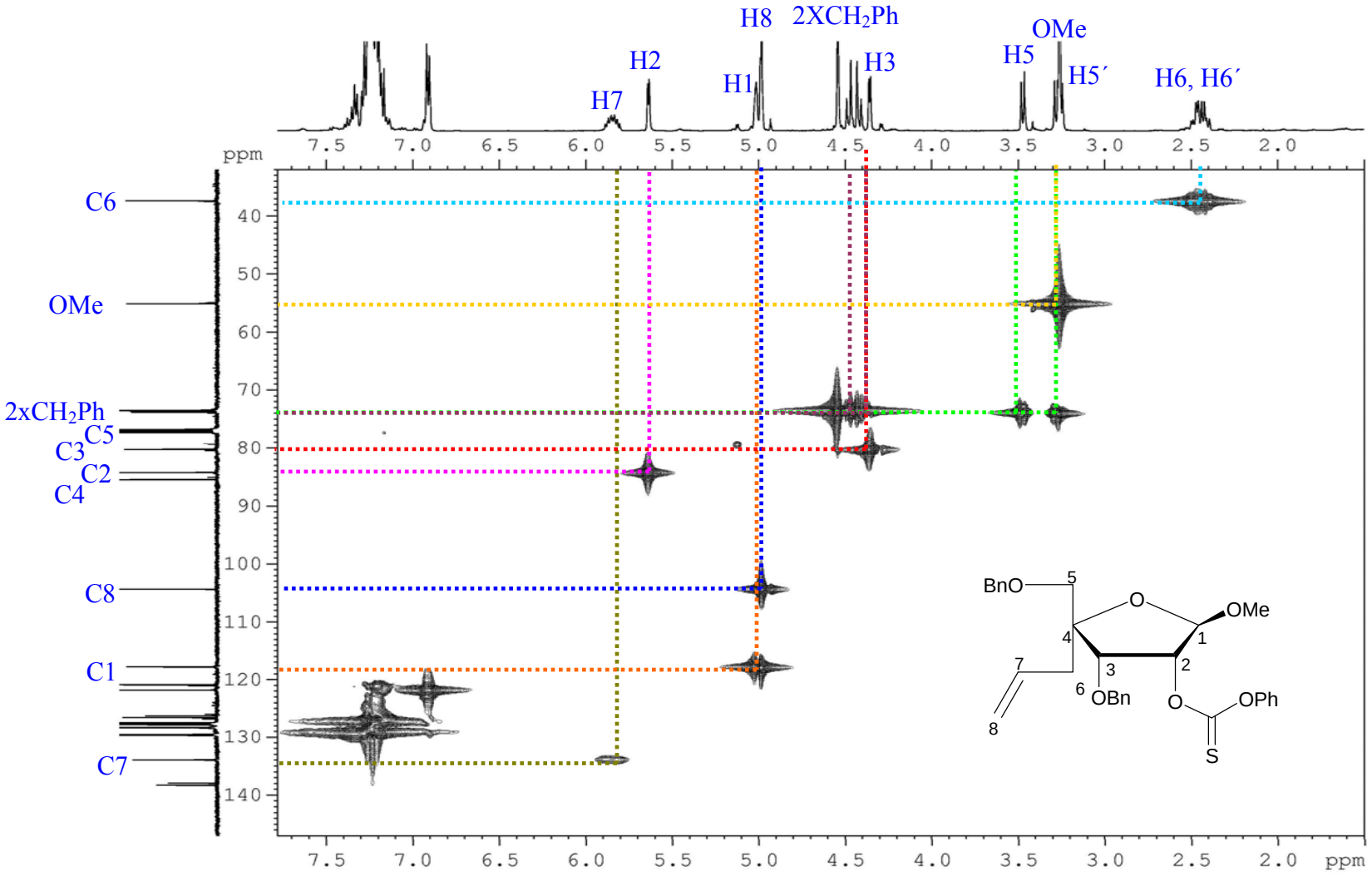


Figure S9: HMQC spectrum of compound **3a**

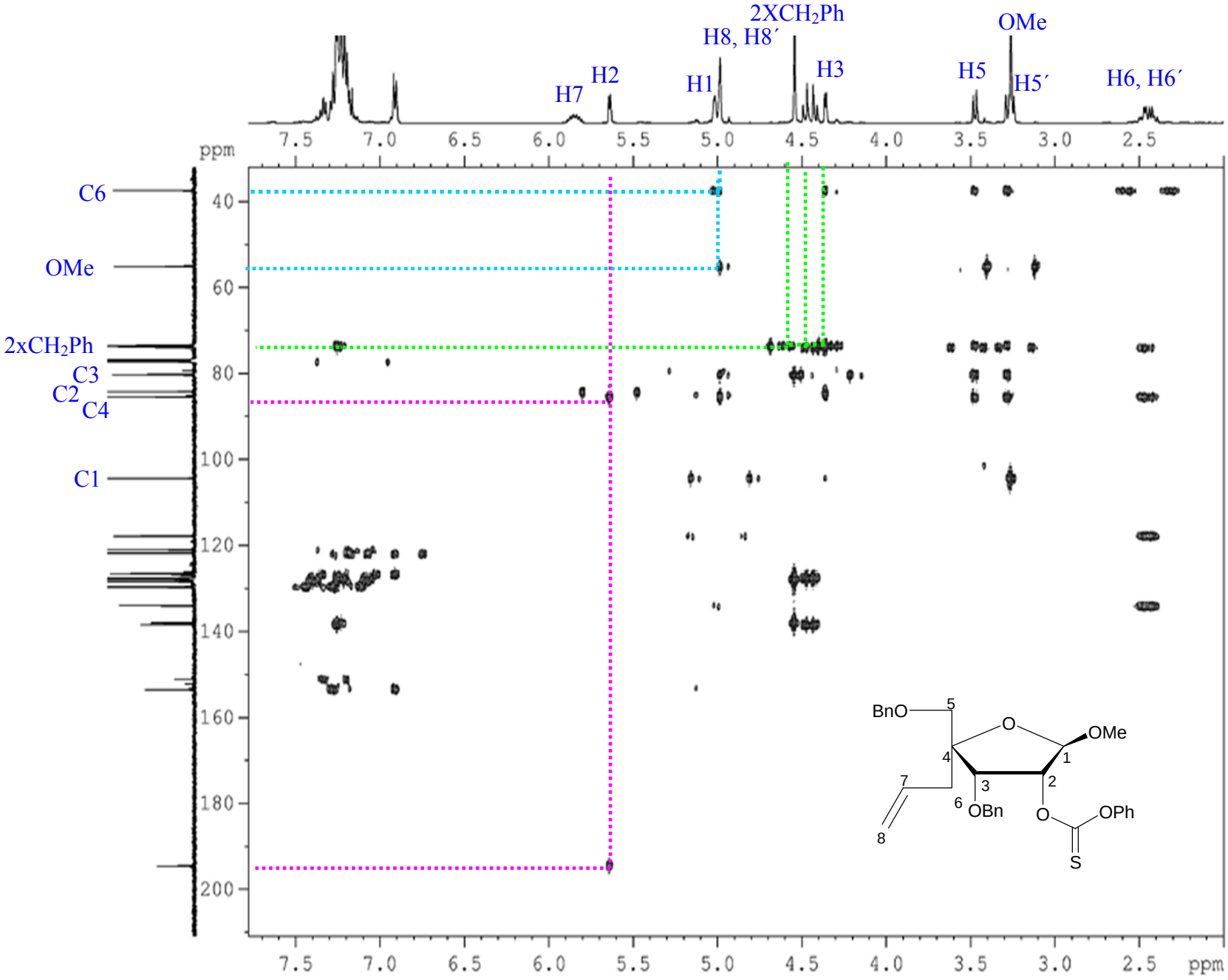


Figure S10: HMBC spectrum of compound **3a**

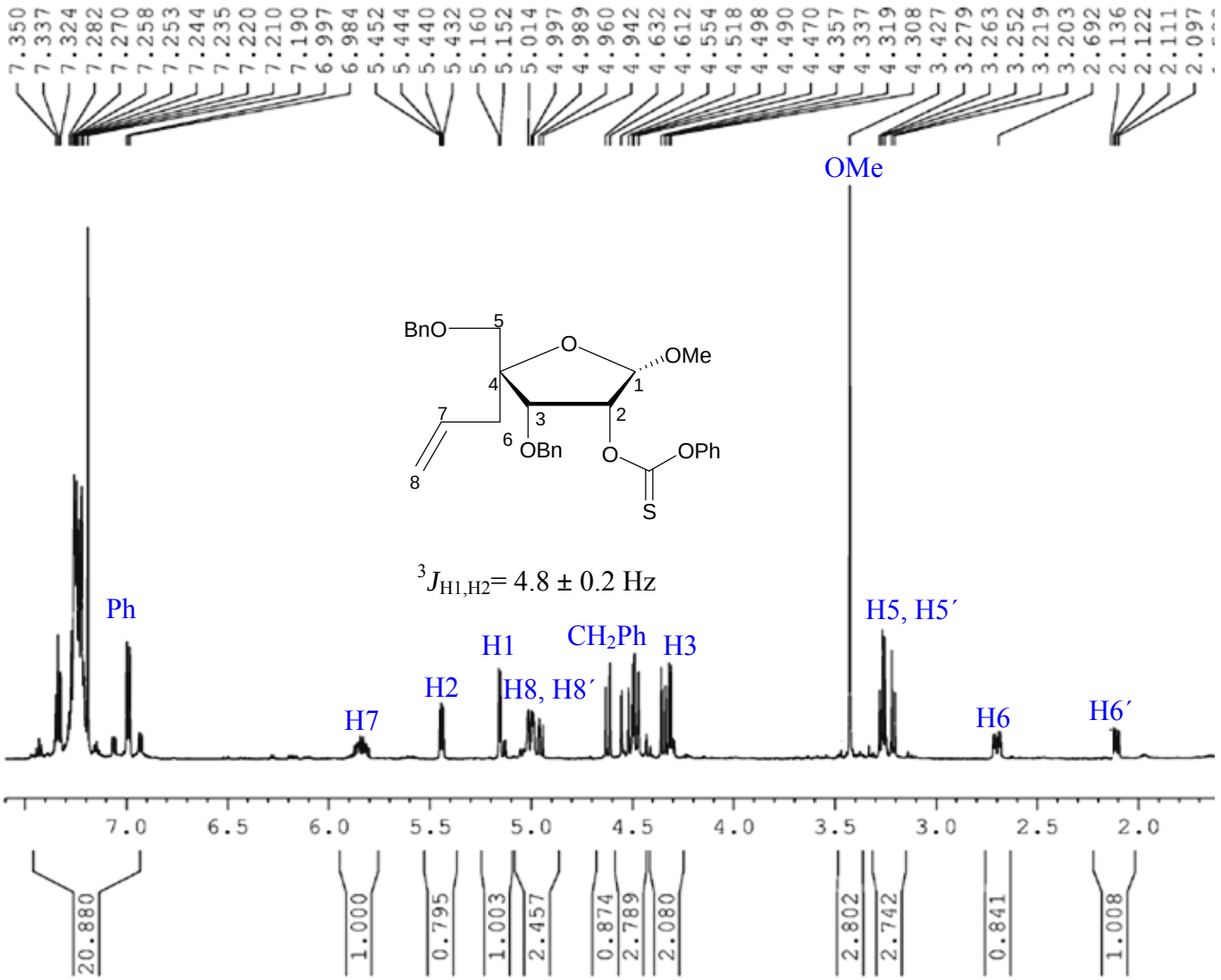


Figure S11: ^{1}H NMR spectrum of compound **3b**

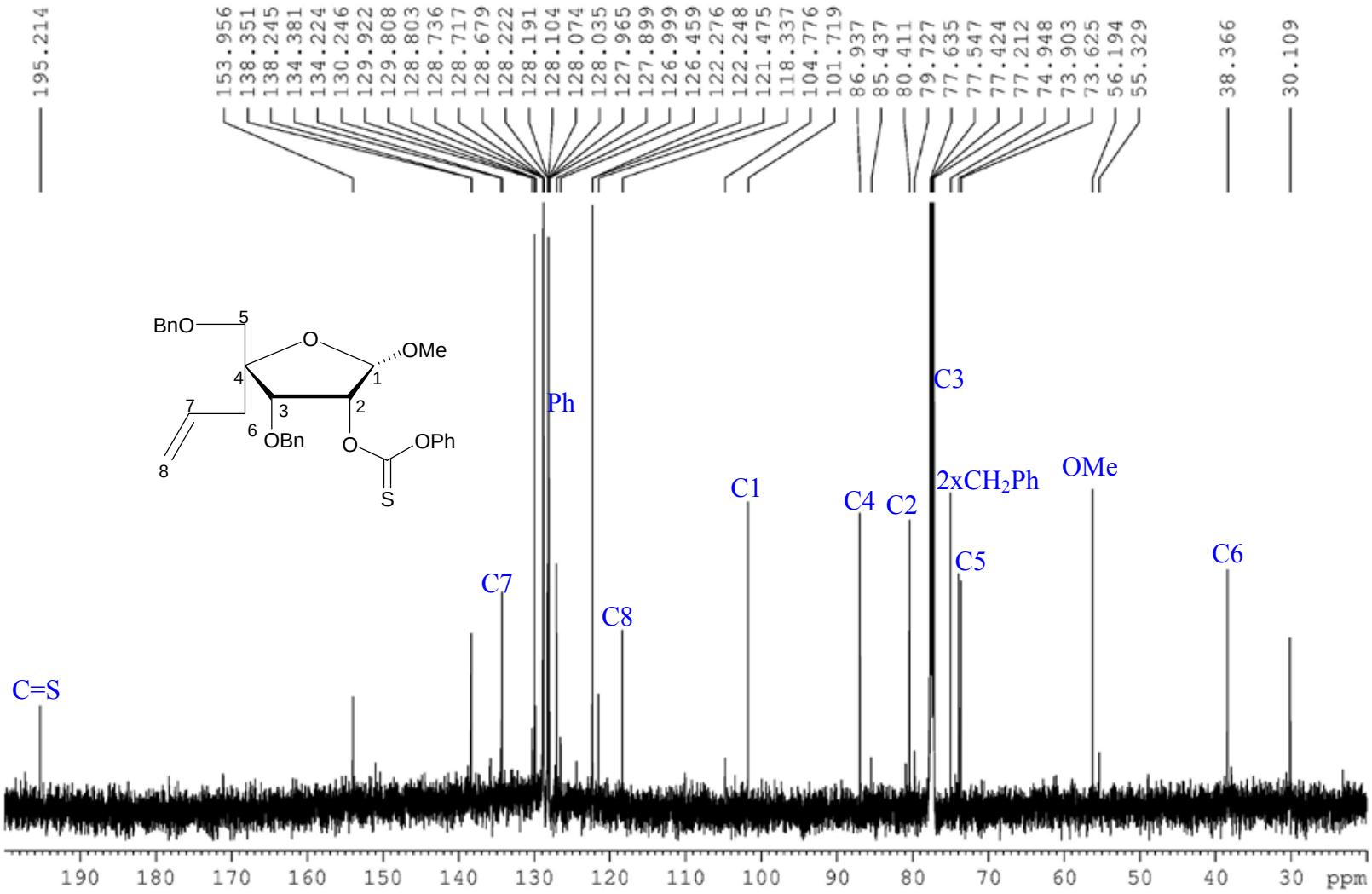


Figure S12: ^{13}C NMR spectrum of compound **3b**

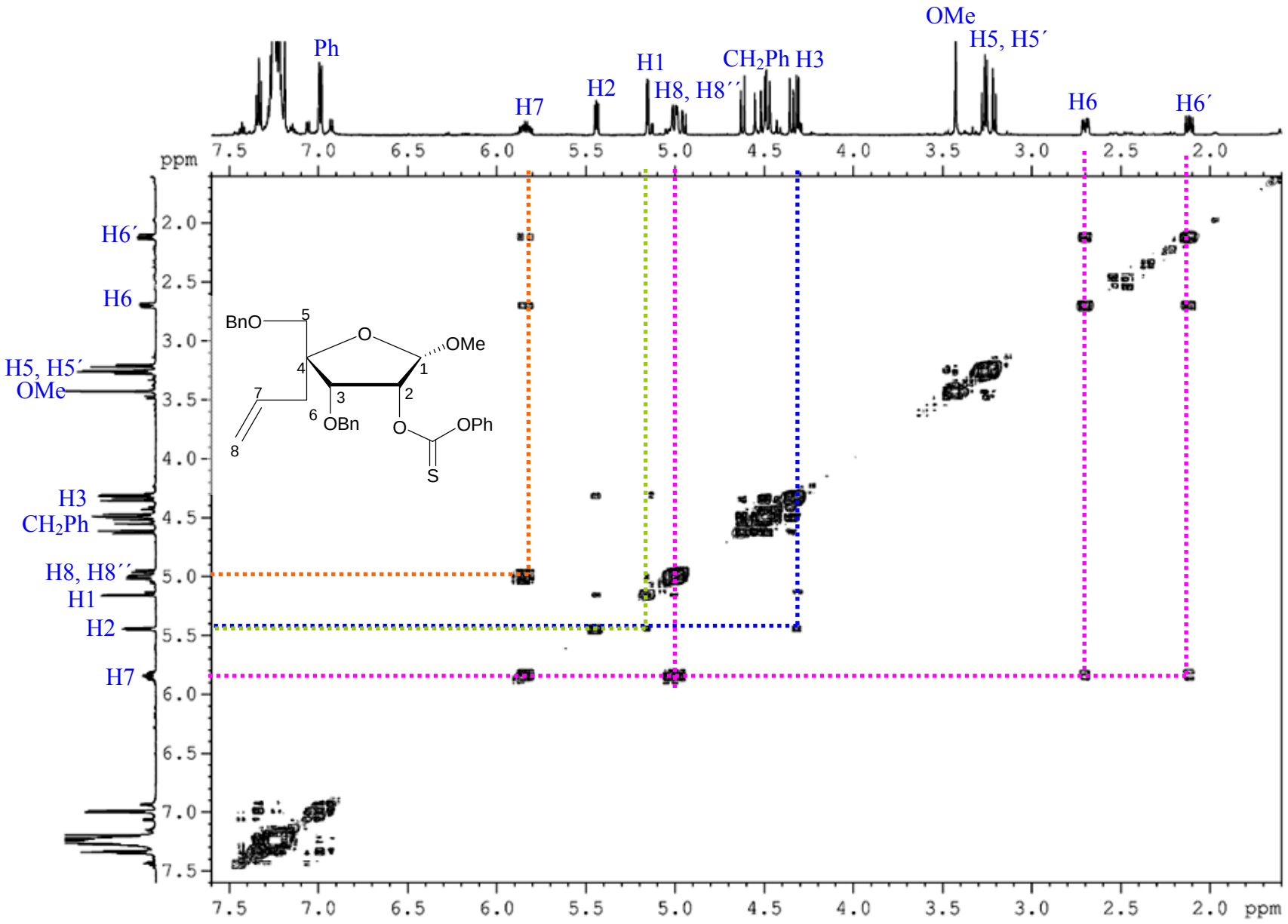


Figure S13: COSY spectrum of compound **3b**

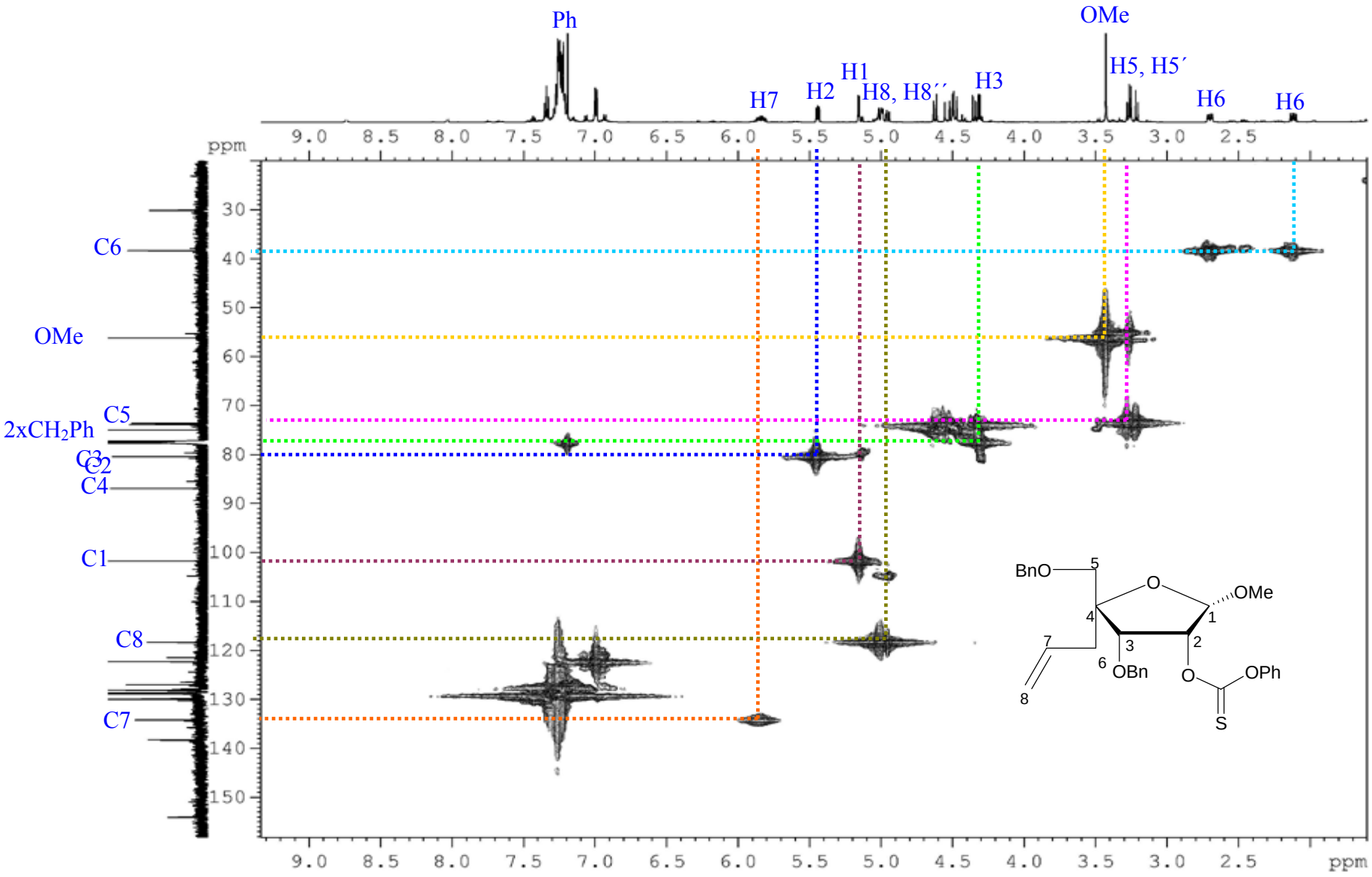


Figure S14: HMQC spectrum of compound **3b**

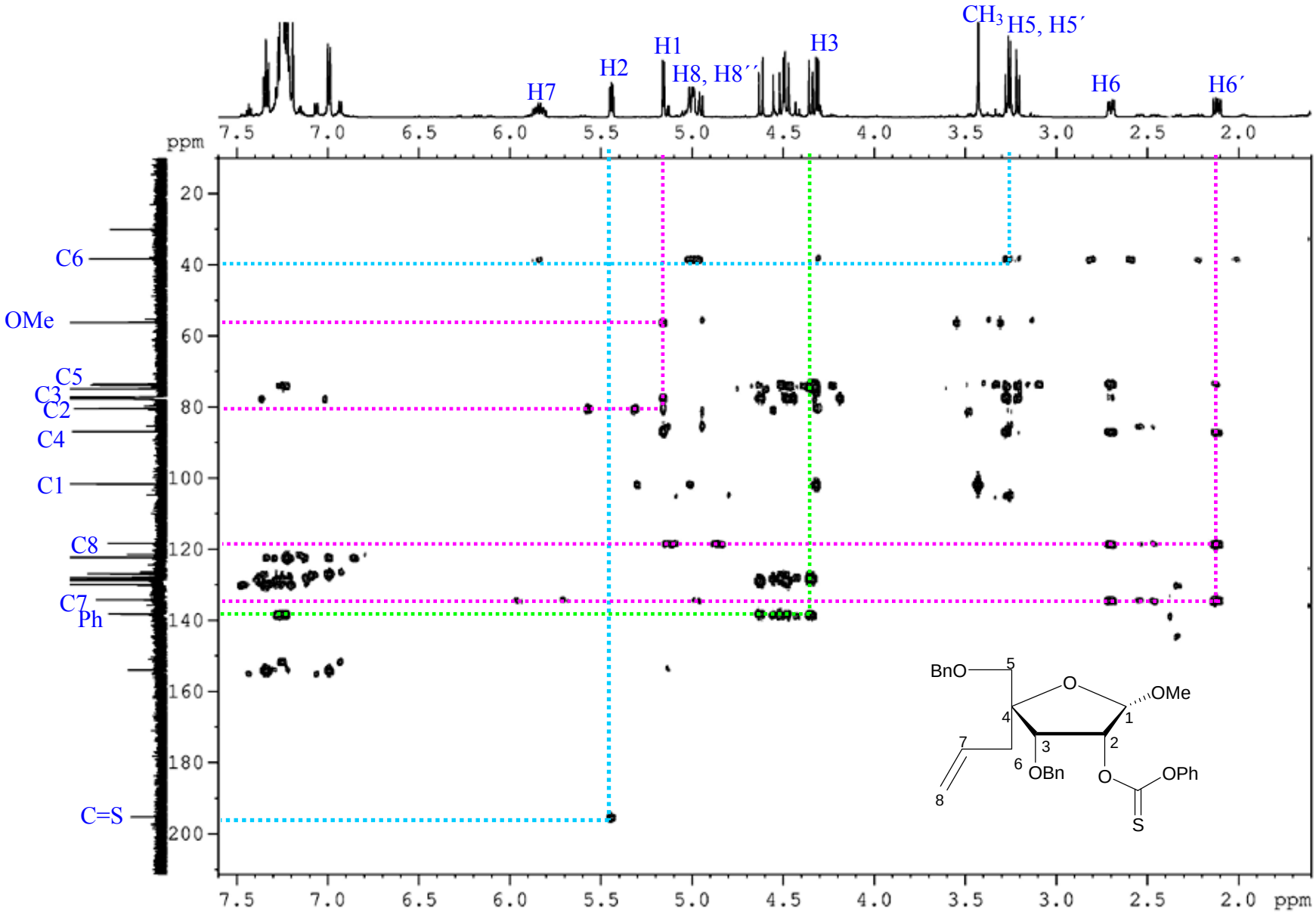


Figure S15: HMBC spectrum of compound **3b**

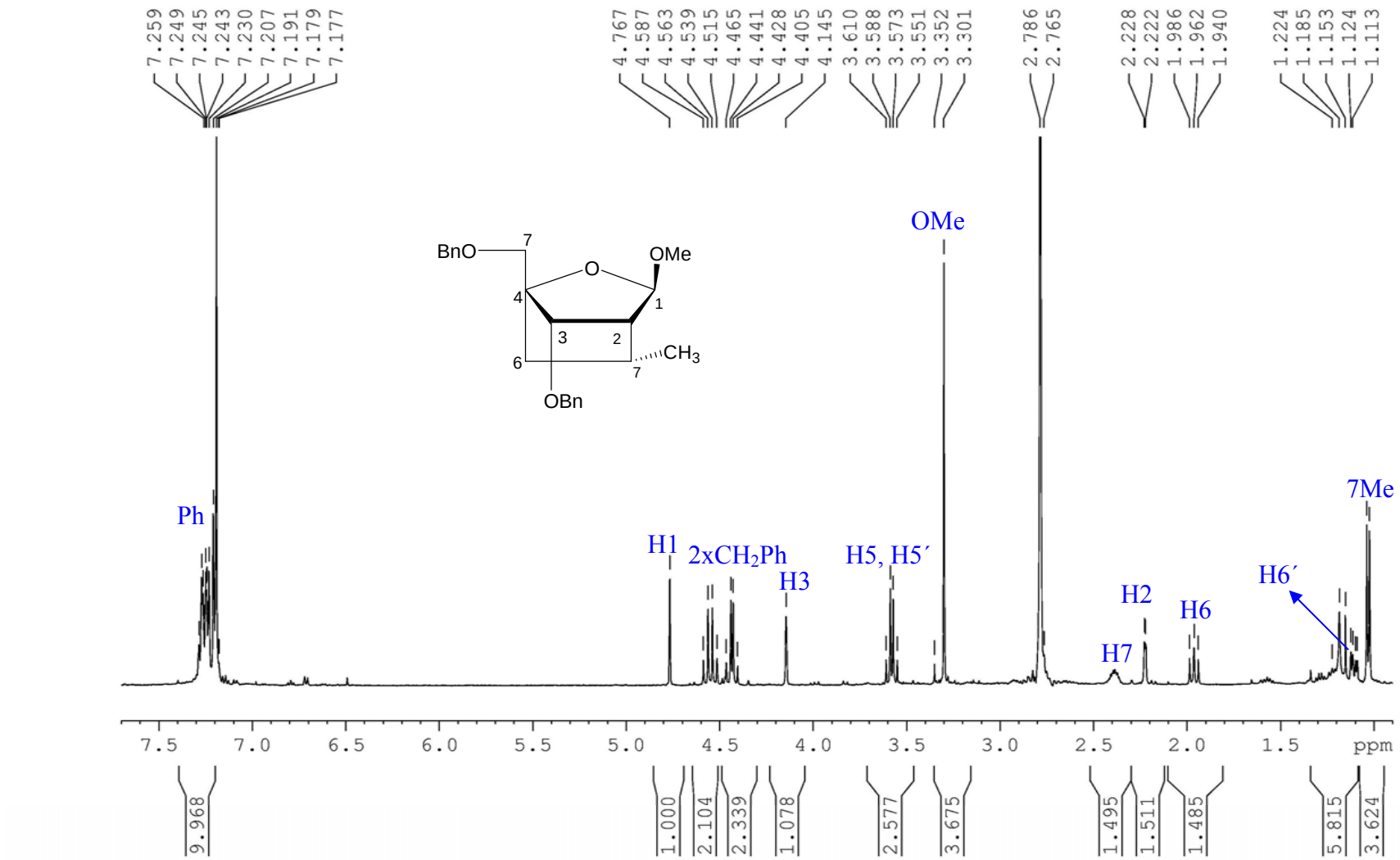


Figure S16: ^{1}H NMR spectrum of compound **4a**

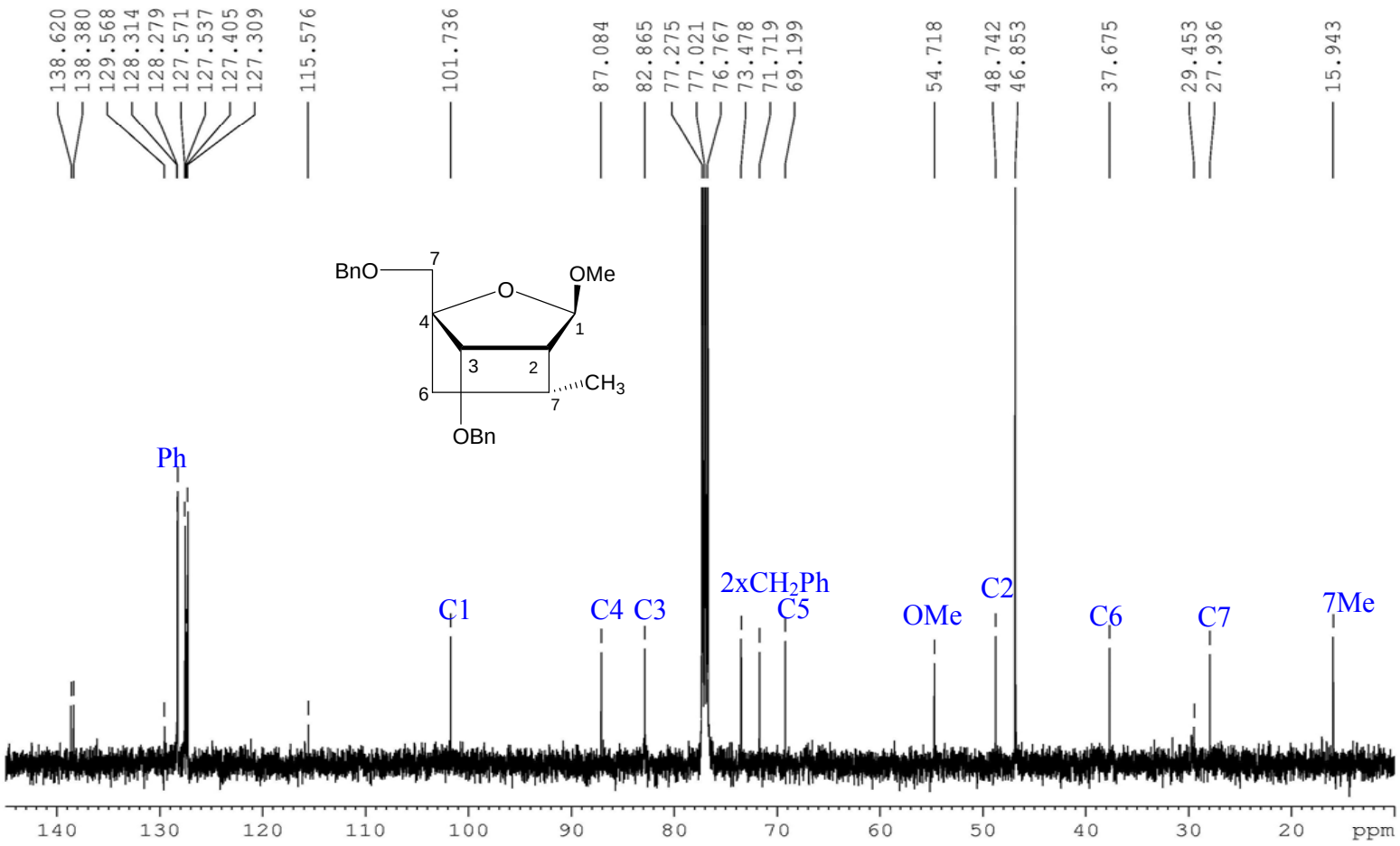


Figure S17: ^{13}C NMR spectrum of compound **4a**

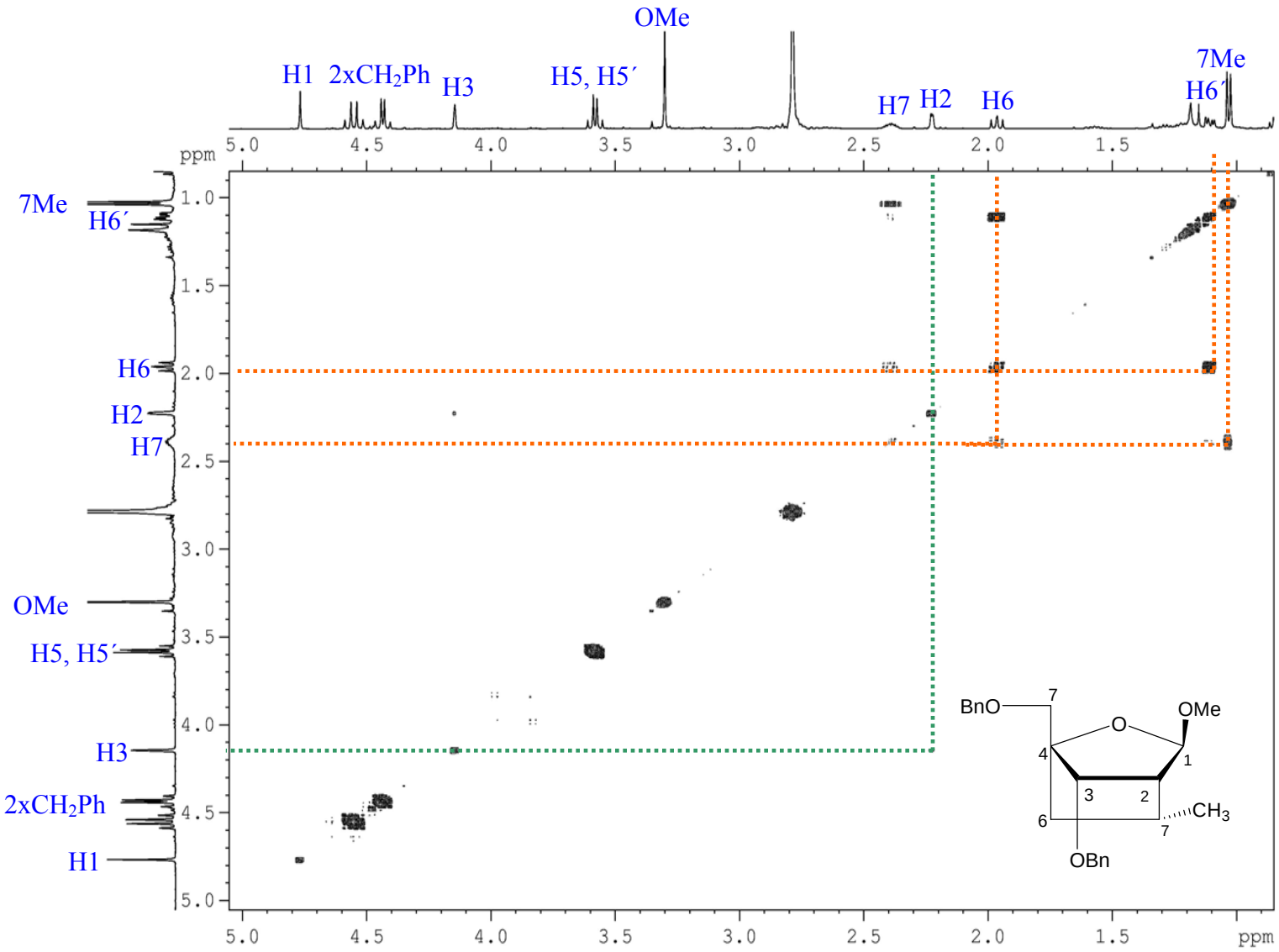


Figure S18: COSY spectrum of compound **4a**

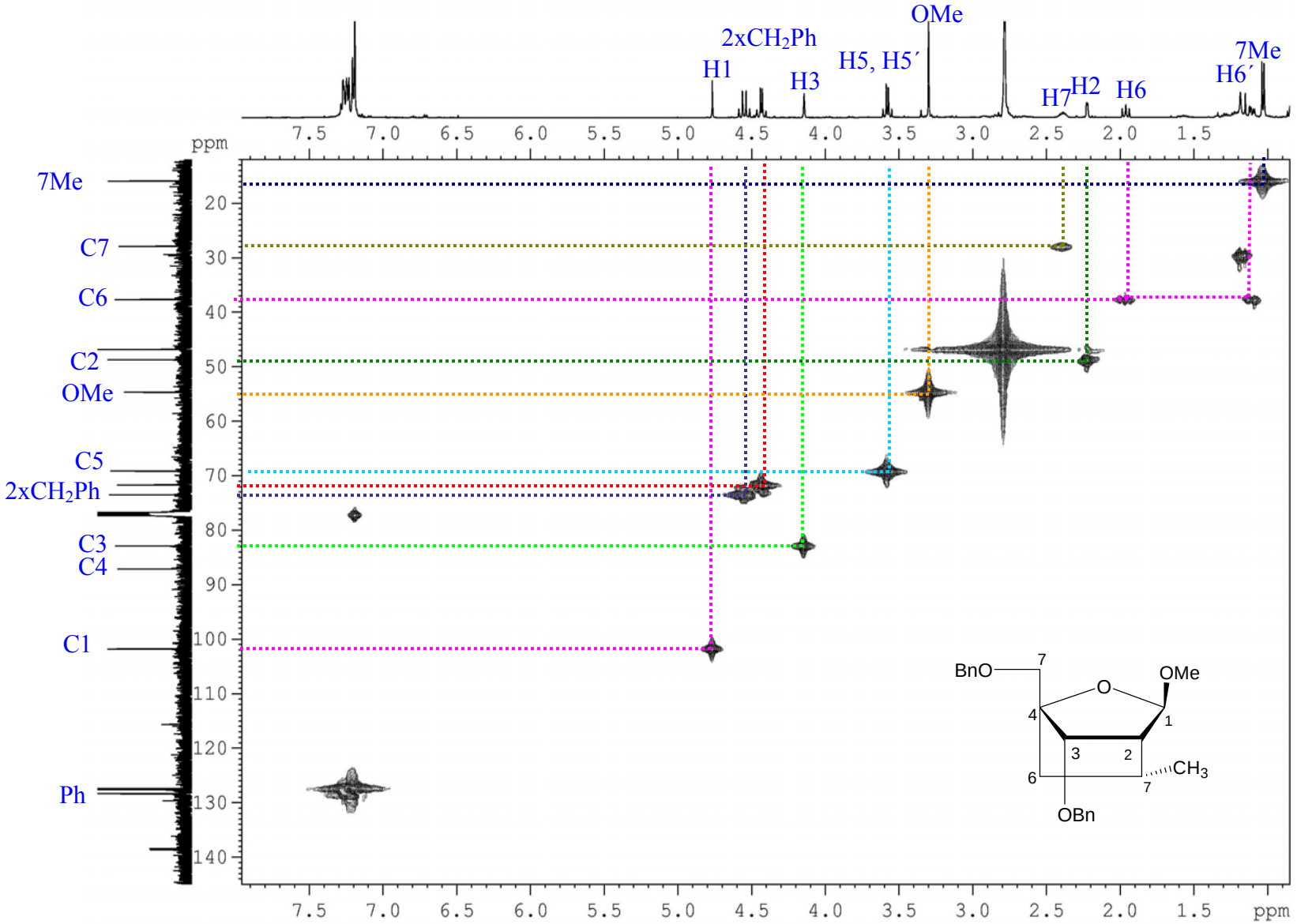


Figure S19: HMQC spectrum of compound **4a**

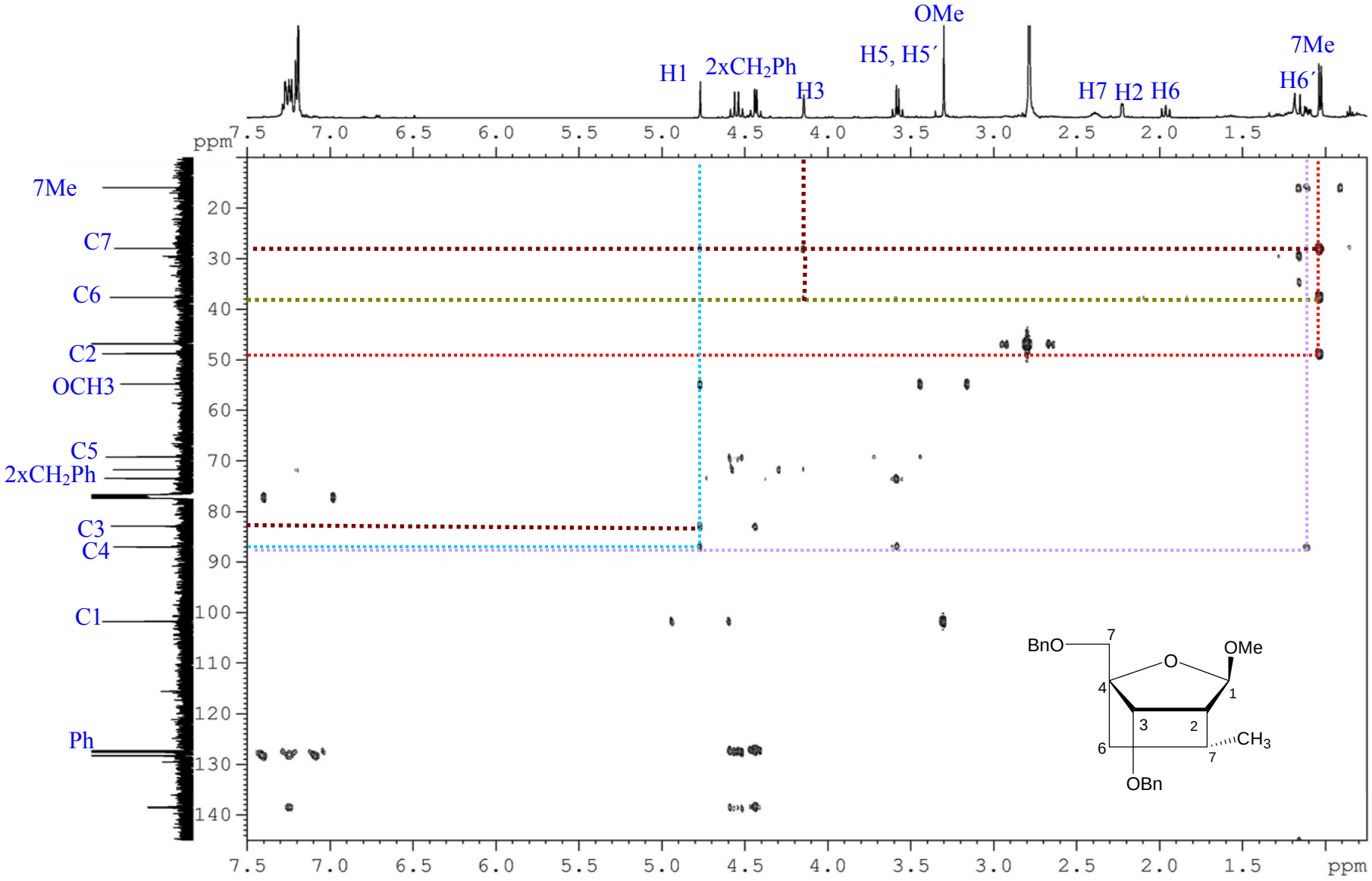


Figure S20: HMQC spectrum of compound **4a**

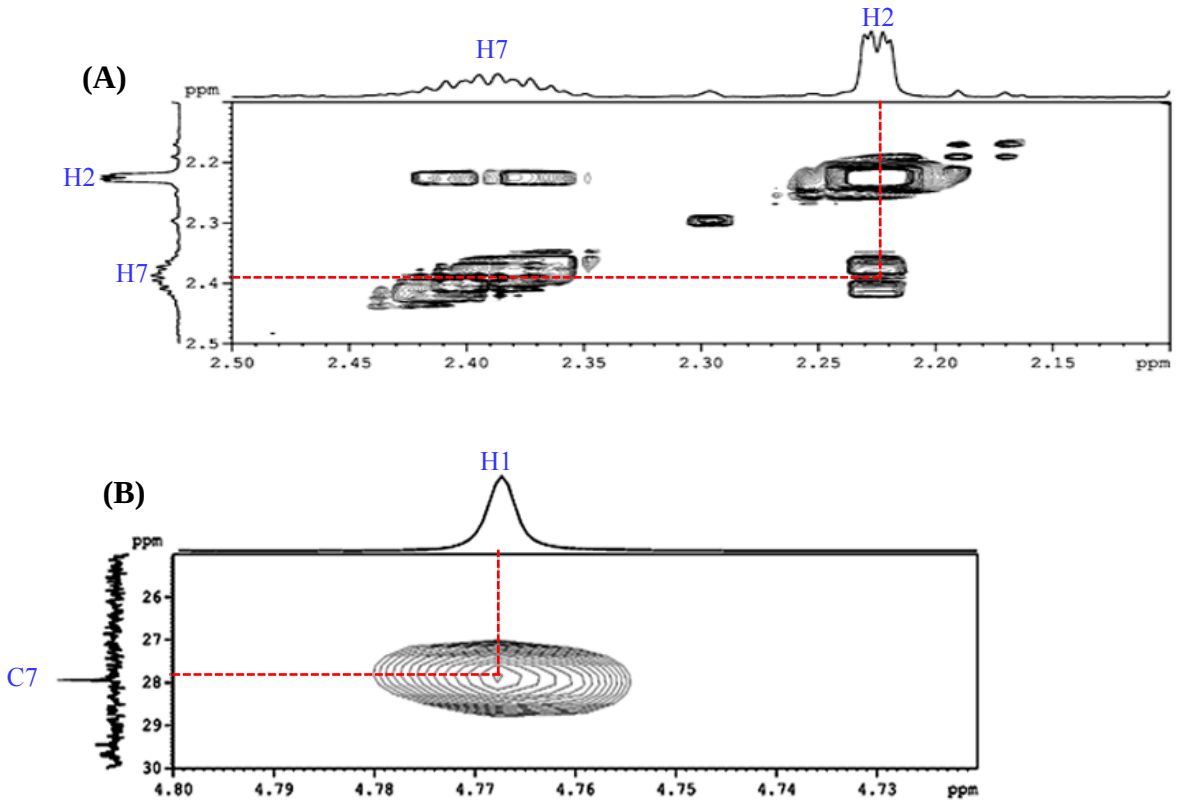


Figure S21: Panel A shows the COSY spectrum of compound **4a** which confirms the correlation between H2 and H7; Panel B shows the HMBC spectrum of compound **4a** which confirms the correlation between H1 and C7, thereby proving that the new covalent bond between C2 and C7 is indeed formed.

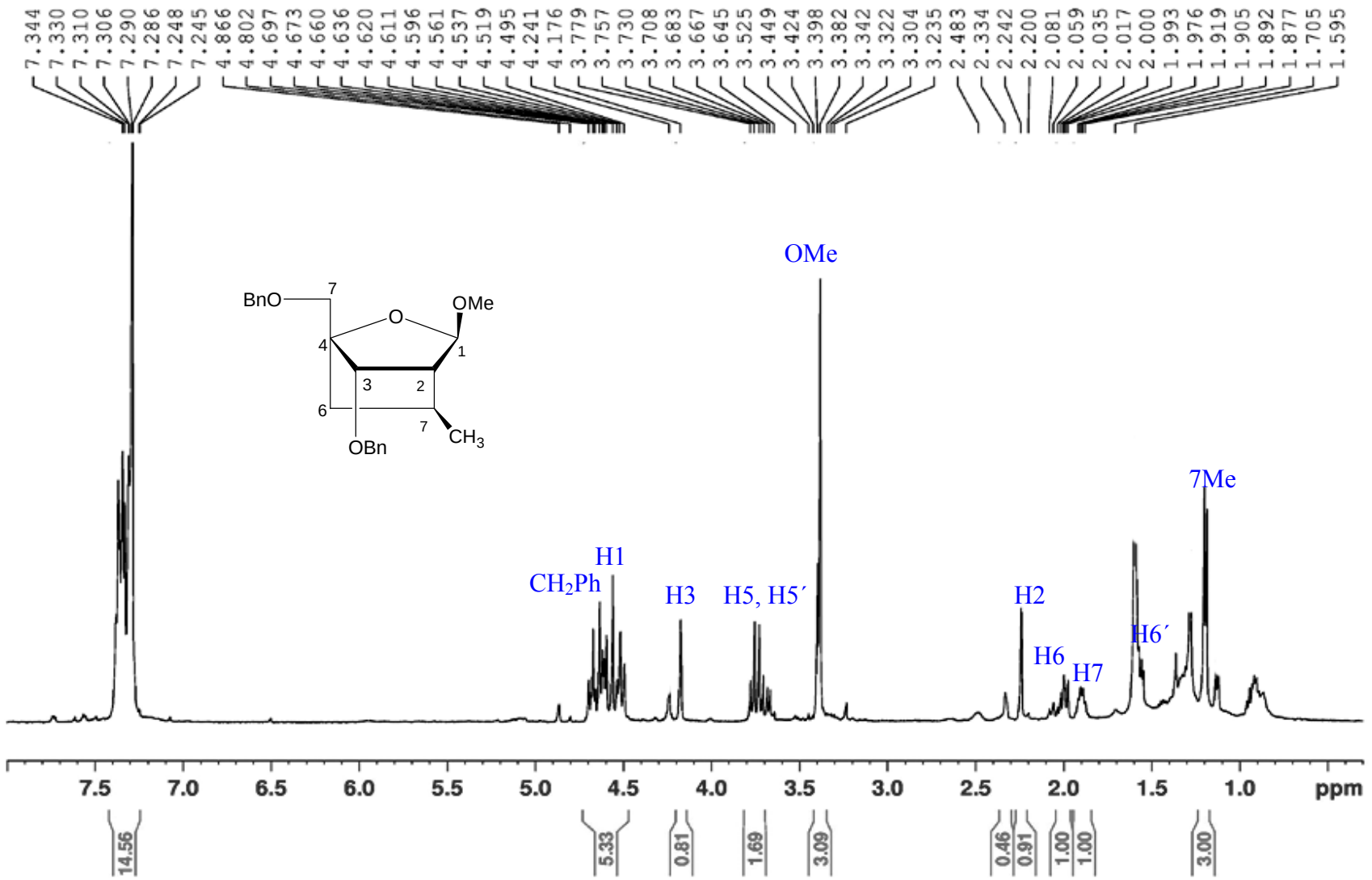


Figure S22: ^{1}H NMR spectrum of compound **4b**

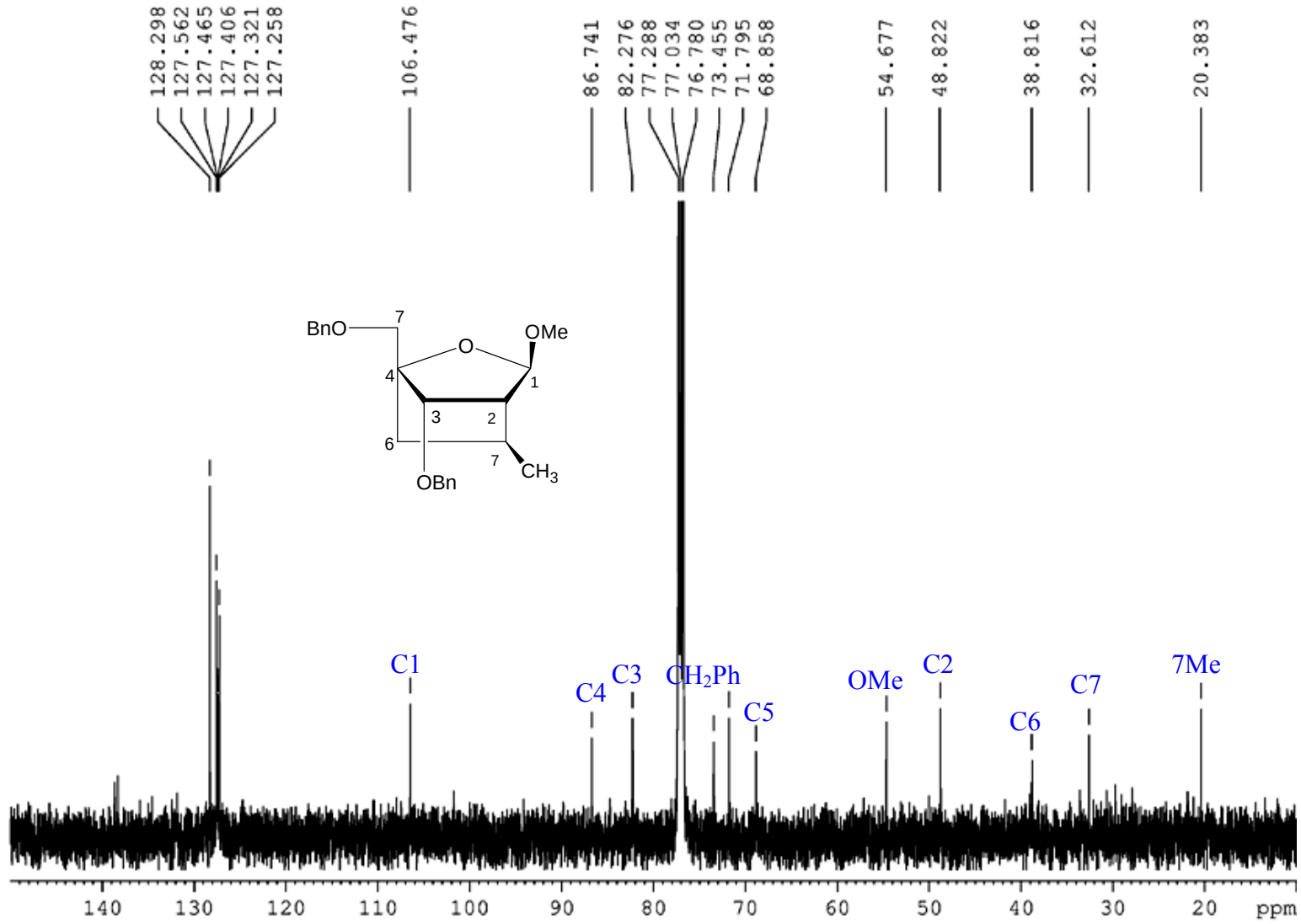


Figure S23: ^{13}C NMR spectrum of compound **4b**

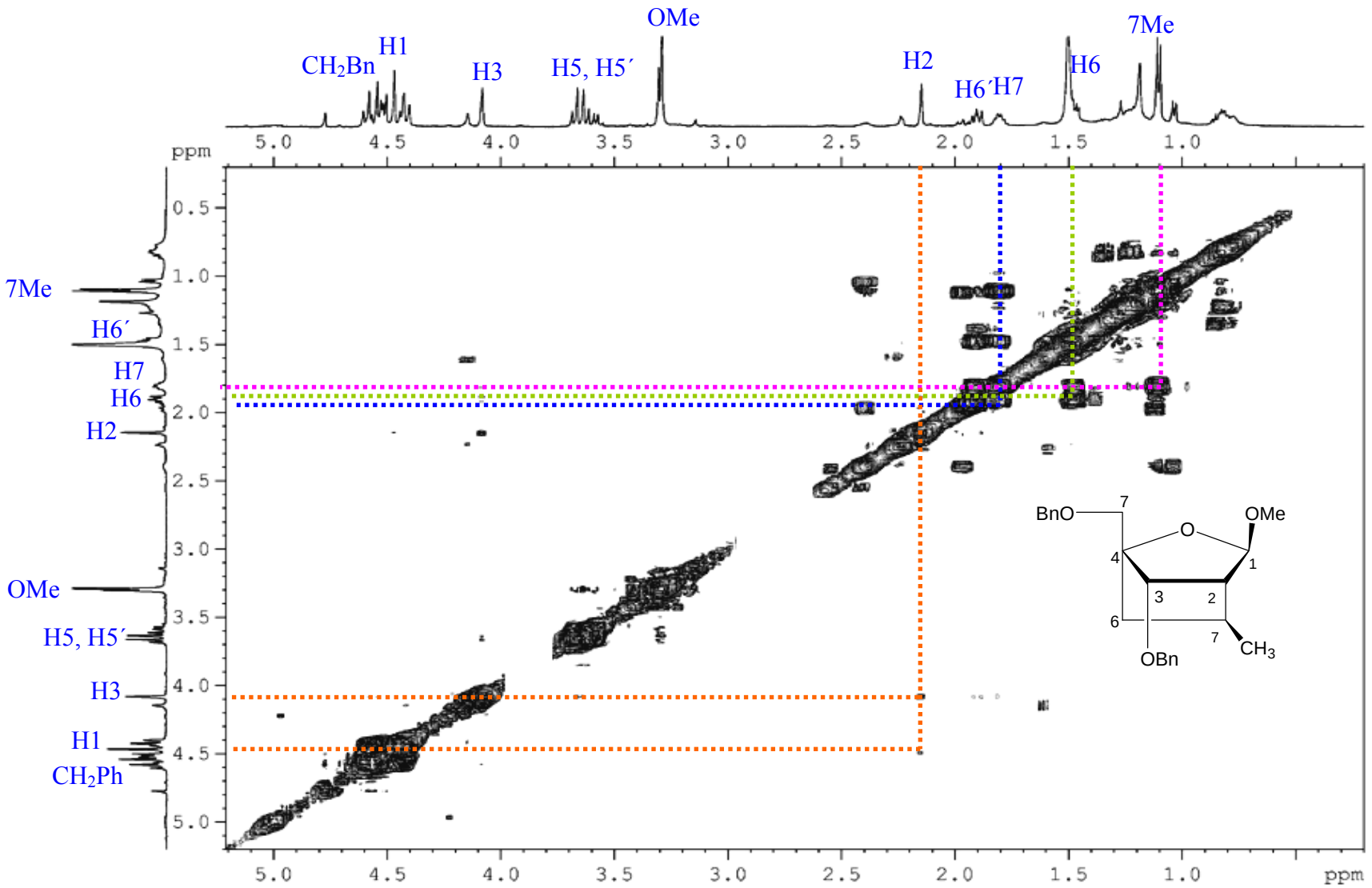


Figure S24: COSY spectrum of compound **4b**

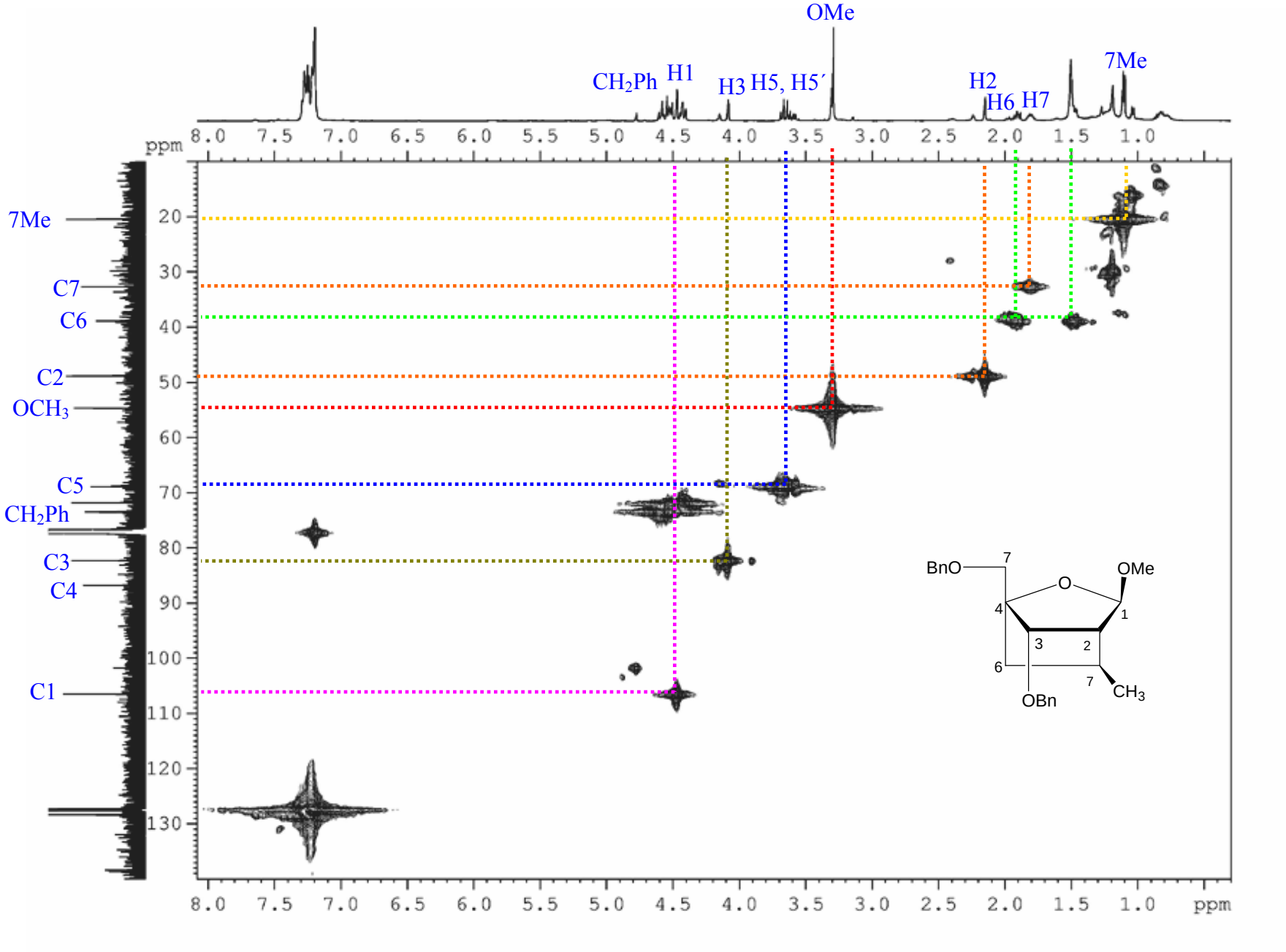


Figure S25: HMQC spectrum of compound **4b**

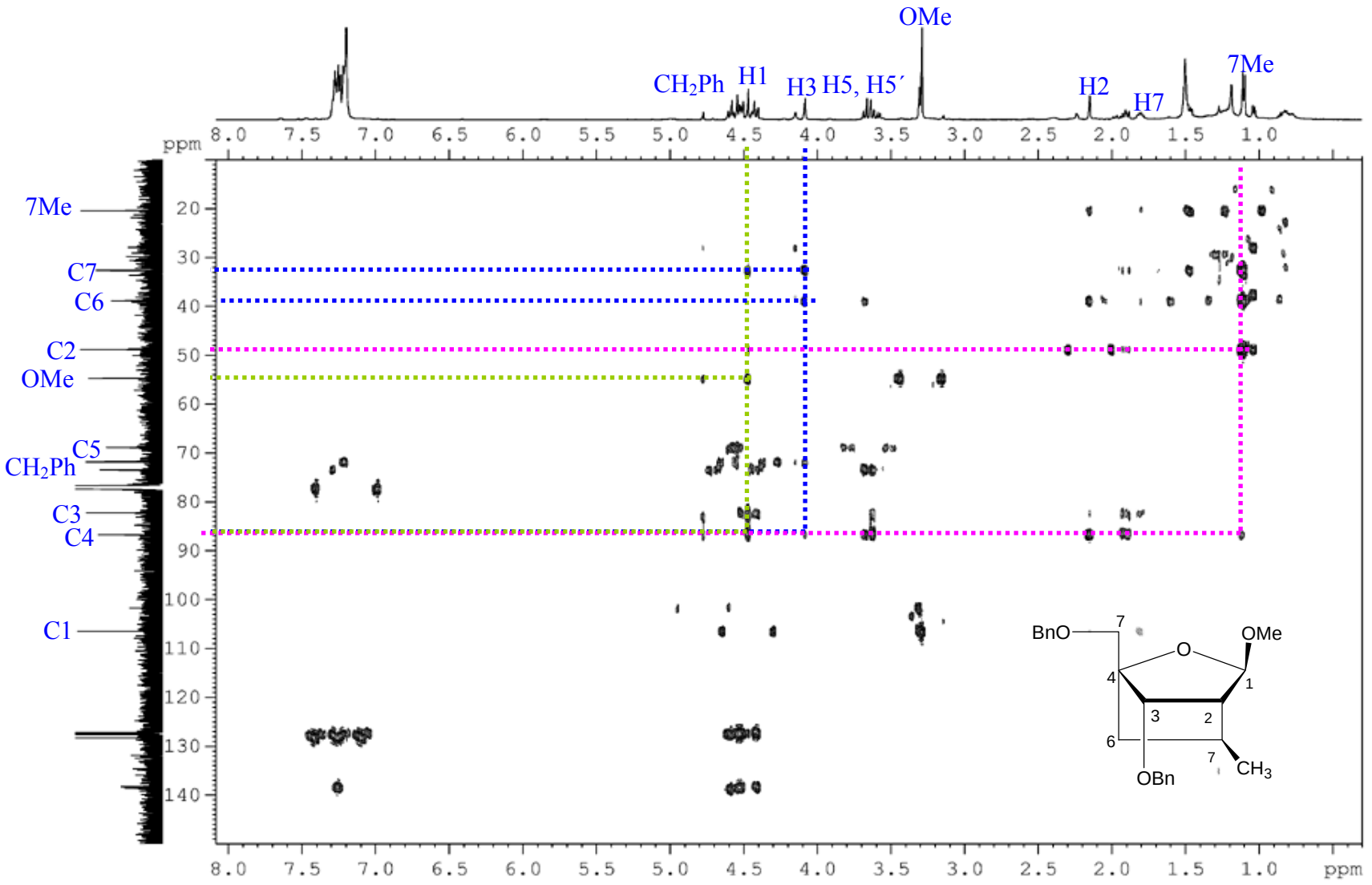
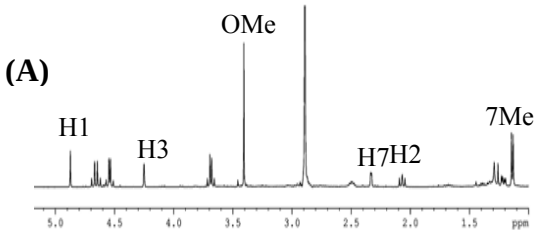
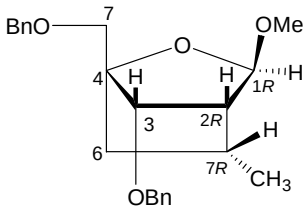
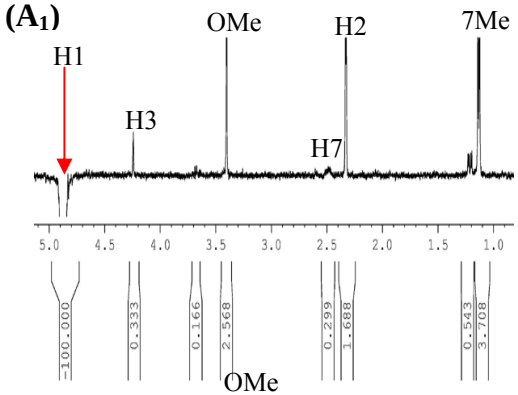
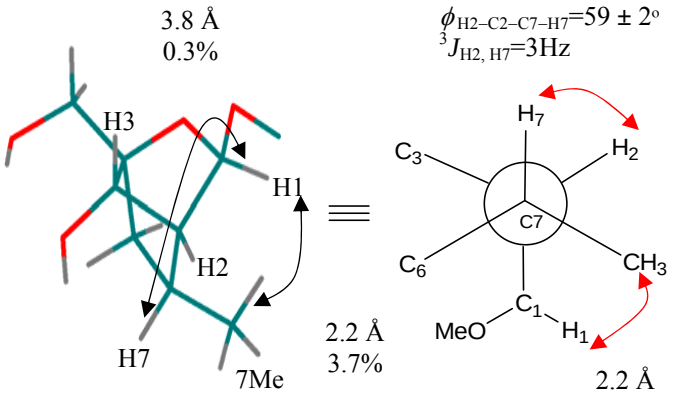


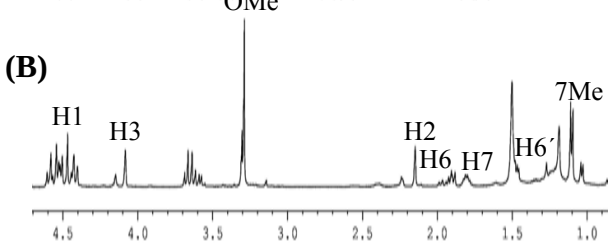
Figure S26: HMBC spectrum of compound **4b**

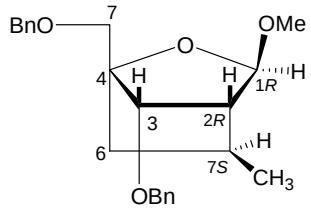

(A)
OMe
H1
H3
H7H2
7Me

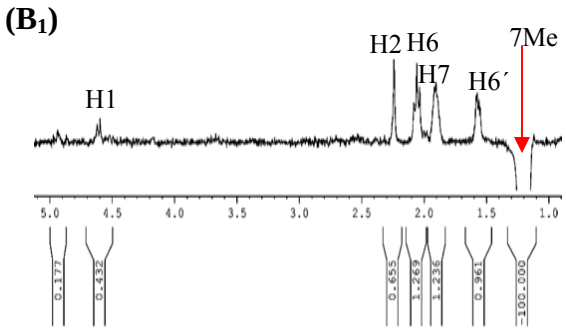

BnO
7
O
OMe
4
H
H
1R
H
3
2R
H
6
7R
CH3
OBn

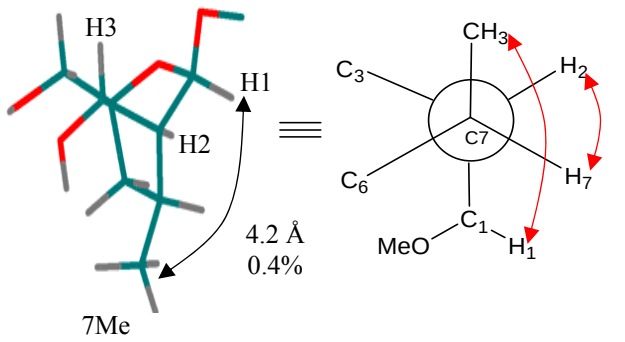

(A1)
OMe
H2
7Me
H1
H3
H7


3.8 Å
0.3%
H3
H1
H2
H7
7Me
2.2 Å
3.7%
ϕH2–C2–C7–H7=59 ± 2°
3JH2, H7=3Hz
H7
H2
C3
C7
C6
CH3
C1
MeO
H1
2.2 Å
3.7%


(B)
OMe
7Me
H1
H3
H2
H6
H7
H6´


BnO
7
O
OMe
4
H
H
1R
H
3
2R
H
6
7S
CH3
OBn


(B1)
H2 H6
7Me
H7
H6´
H1


H3
H1
H2
4.2 Å
0.4%
7Me
ϕH2–C2–C7–H7 = 81 ± 2°
3JH2, H7 = 0Hz
CH3
H2
C3
C7
C6
H7
C1
MeO
H1

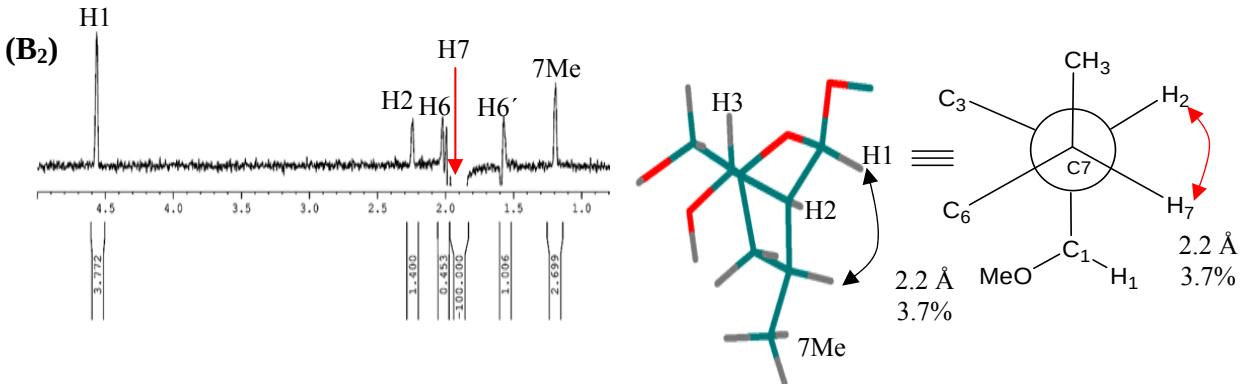


Figure S27: Panels A & B show ^{1}H-NMR spectrum (500 MHz) of compounds **4a** & **4b**, respectively, whereas their respective nOe enhancements are: Panel A_1 shows the irradiation at H1 of the major isomer **4a** with 3.7 % nOe enhancement for 7Me ($d_{H1,\ 7Me\ (calc)} \approx 2.2$ Å), which shows that H1 and 7Me are on the α–face of the carba-sugar, thereby proving the configuration of C7 to be (*R*). Panels B_1 & B_2 show the irradiation of 7(*S*)-Me where a weak nOe enhancement for H1 (0.4 %, $d_{H1,H7\ (calc)} \approx 4.2$ Å) is observed. Irradiation of H7 shows 3.7 % nOe enhancement for H1 ($d_{H7,H1\ (calc)} \approx 2.2$ Å), which shows that H1 and H7 are on the α–face of the carba-sugar, thereby proving the configuration of C7 to be (*S*) for **4b**.

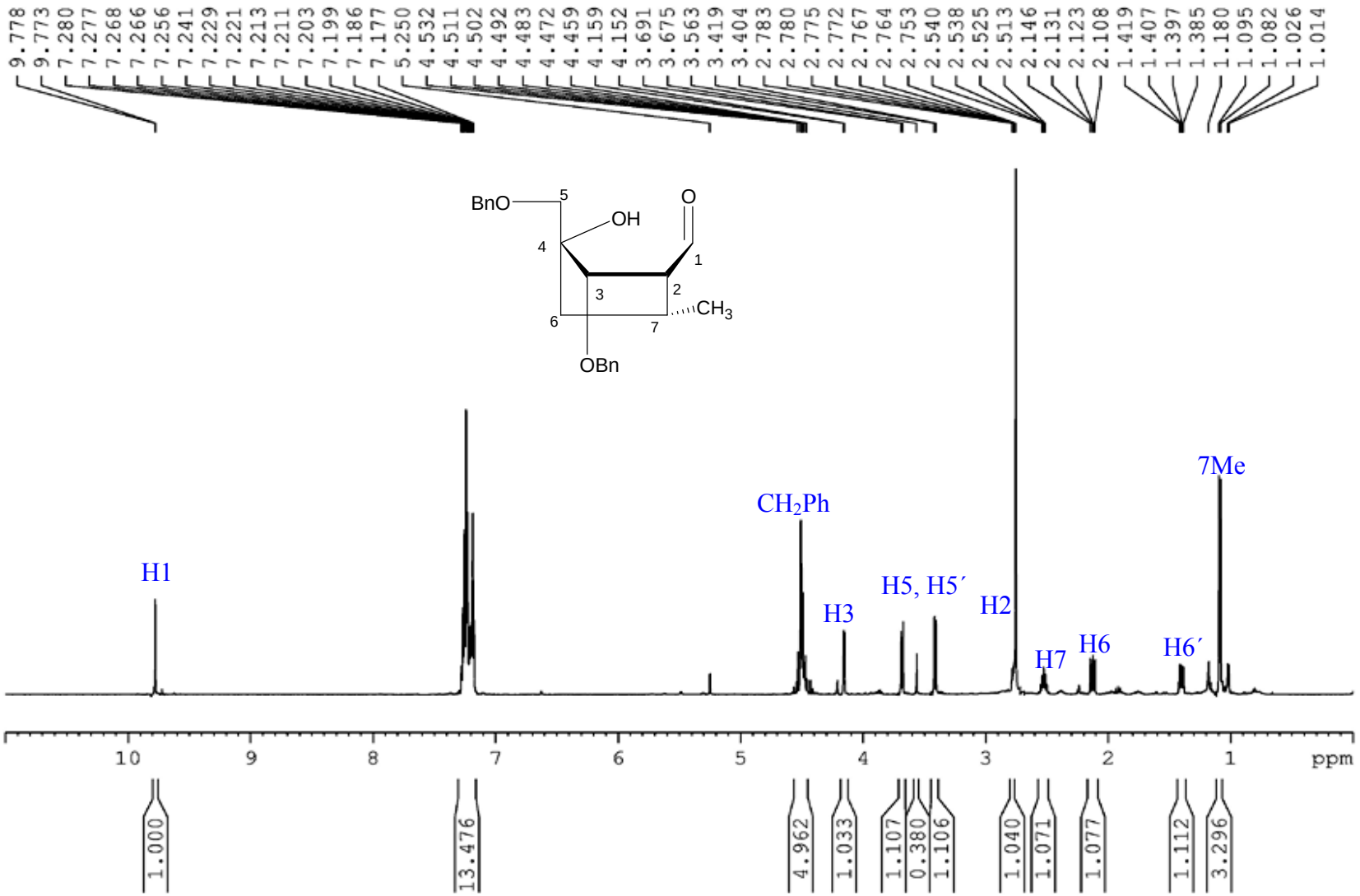


Figure S28: ^{1}H NMR spectrum of compound **5**

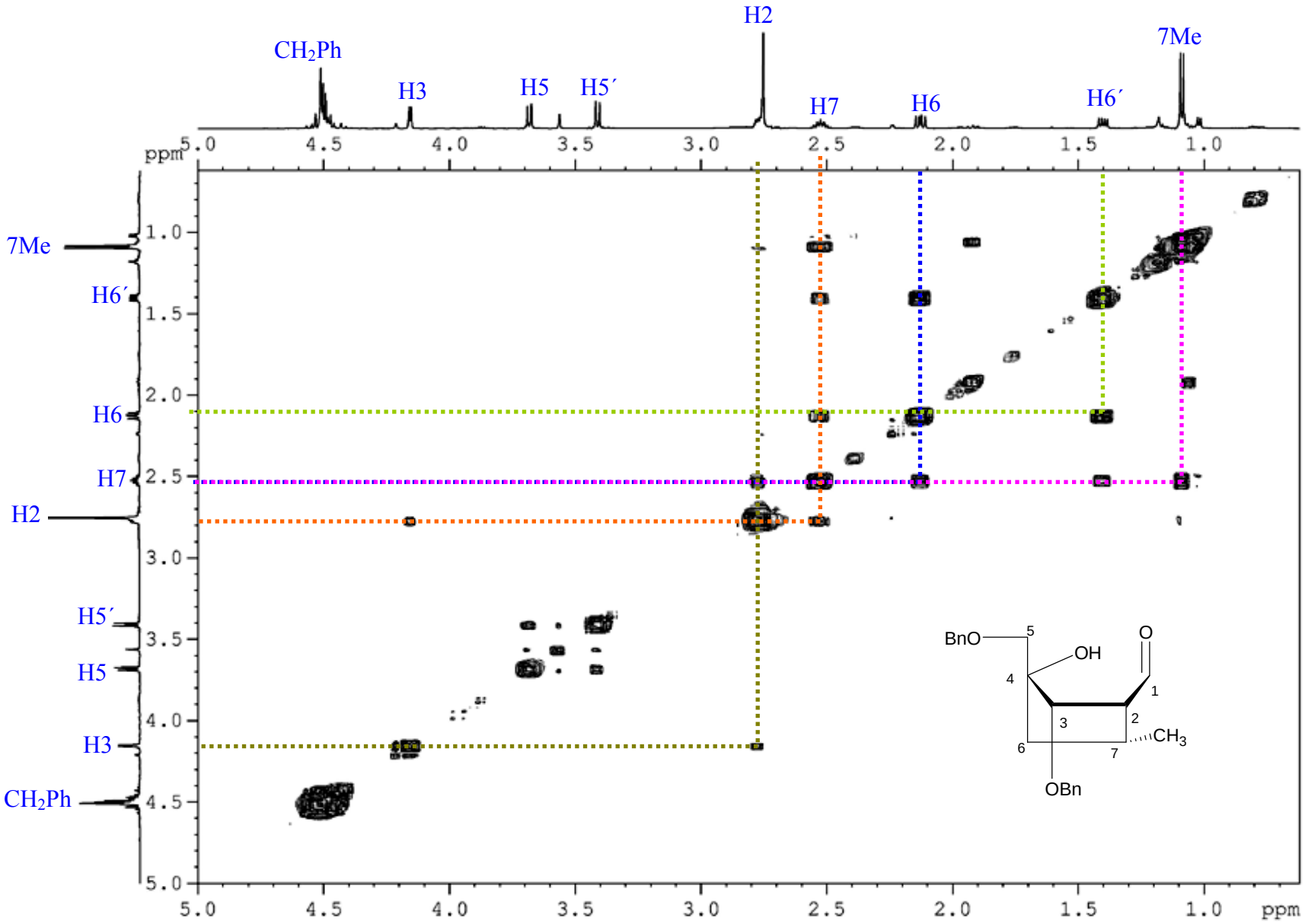


Figure S29: COSY spectrum of compound **5**

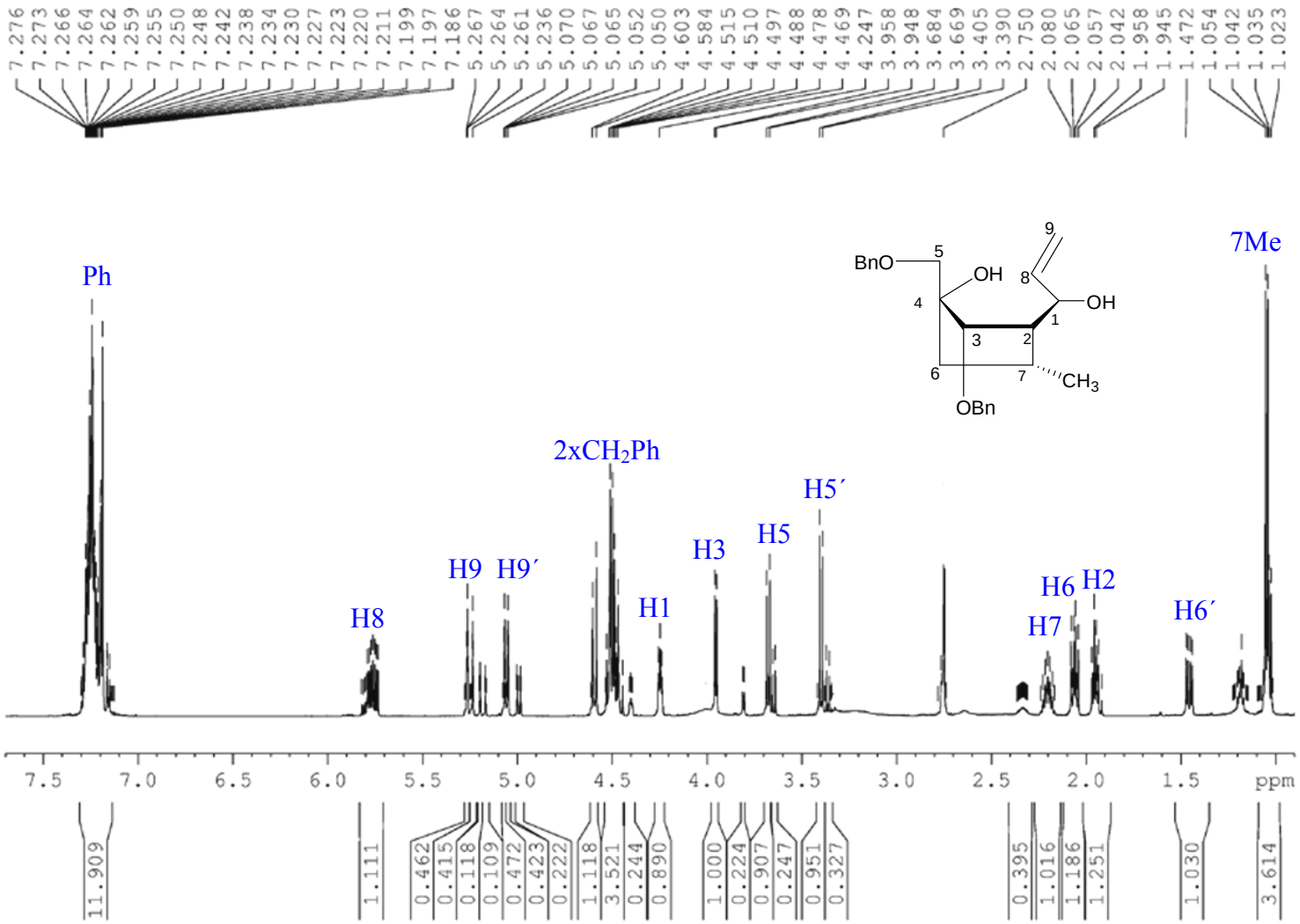


Figure S30: [1]HNMR spectrum of compound **6**

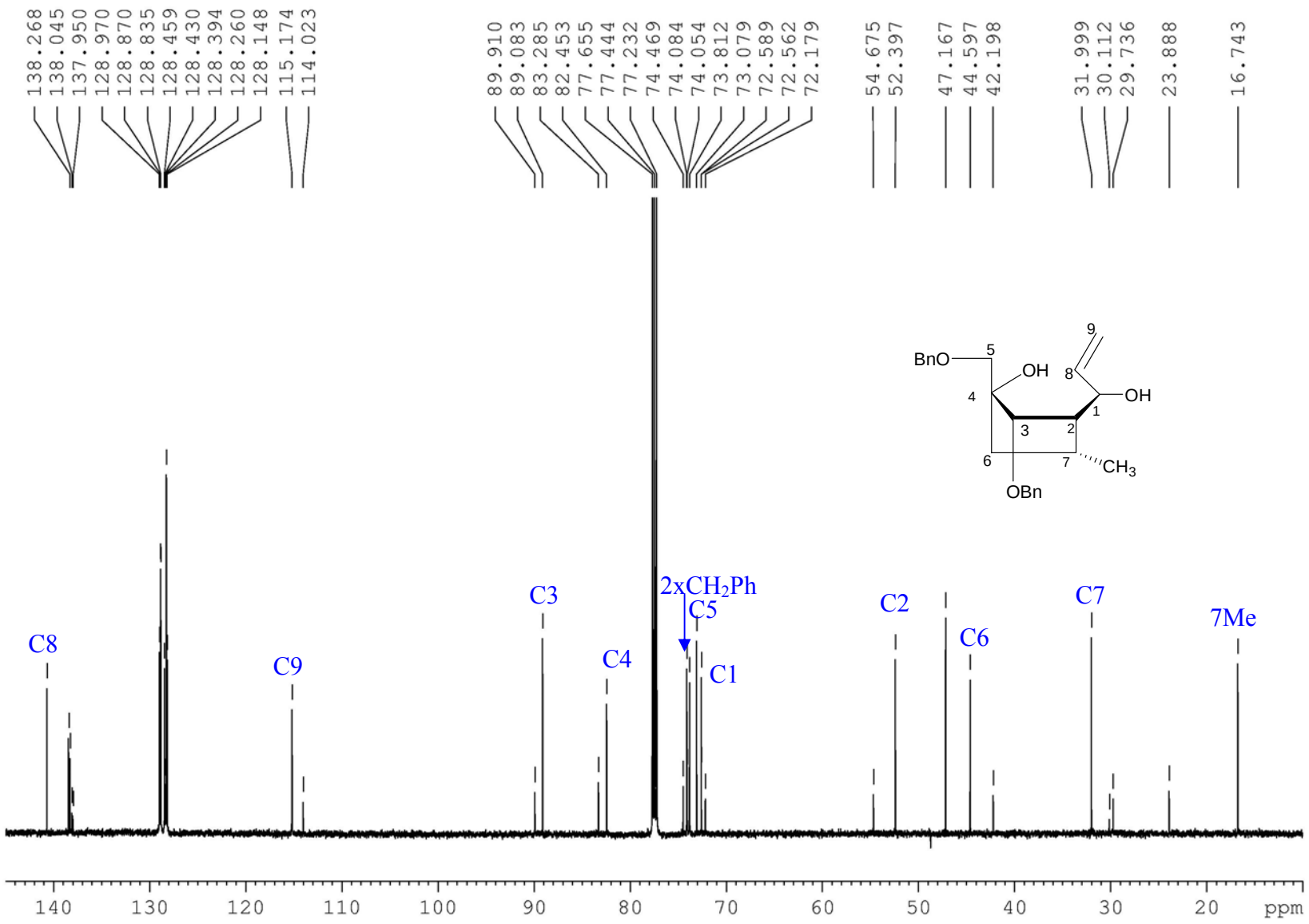


Figure S31: ^{13}C NMR spectrum of compound **6**

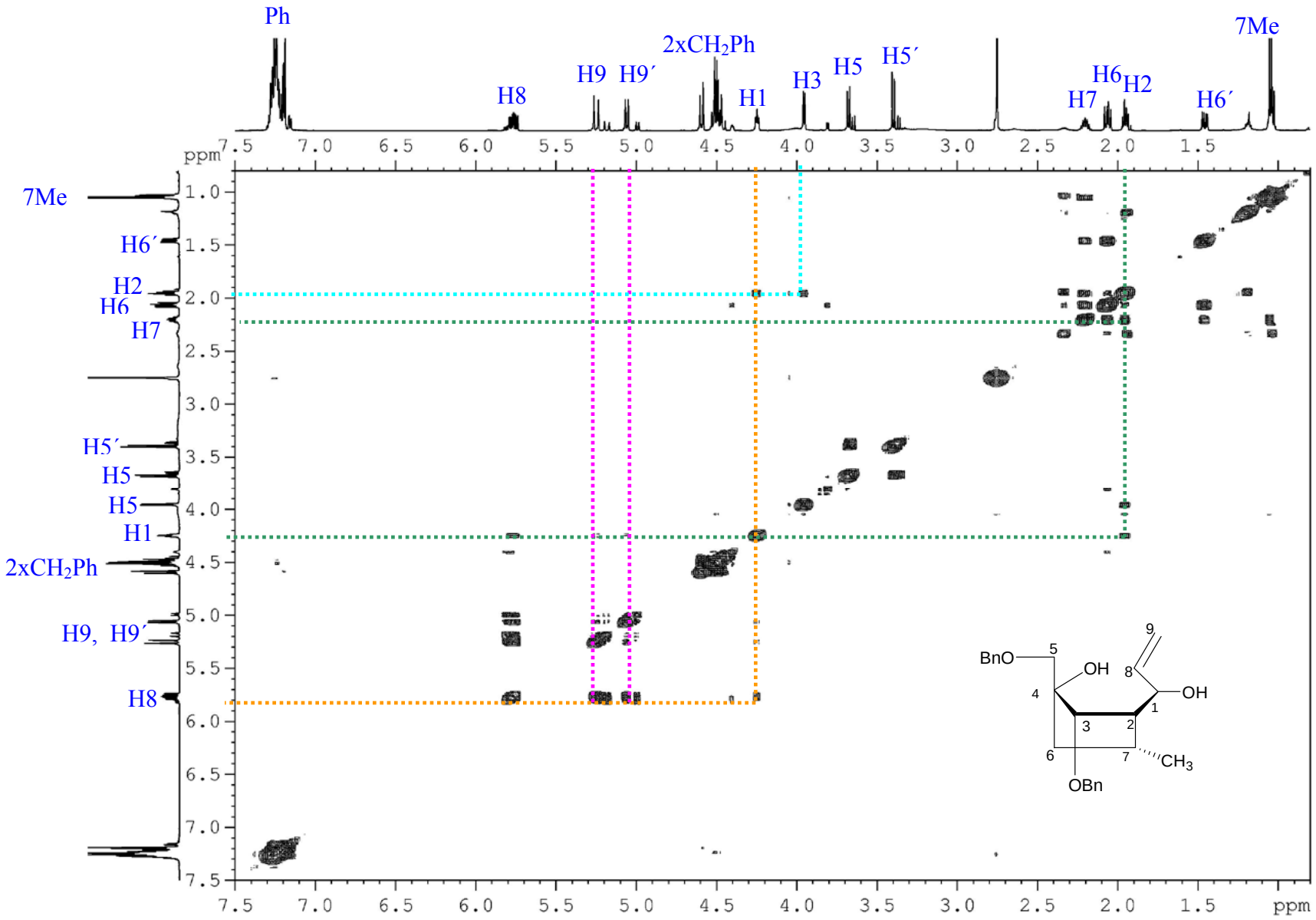


Figure S32: COSY spectrum of compound **6**

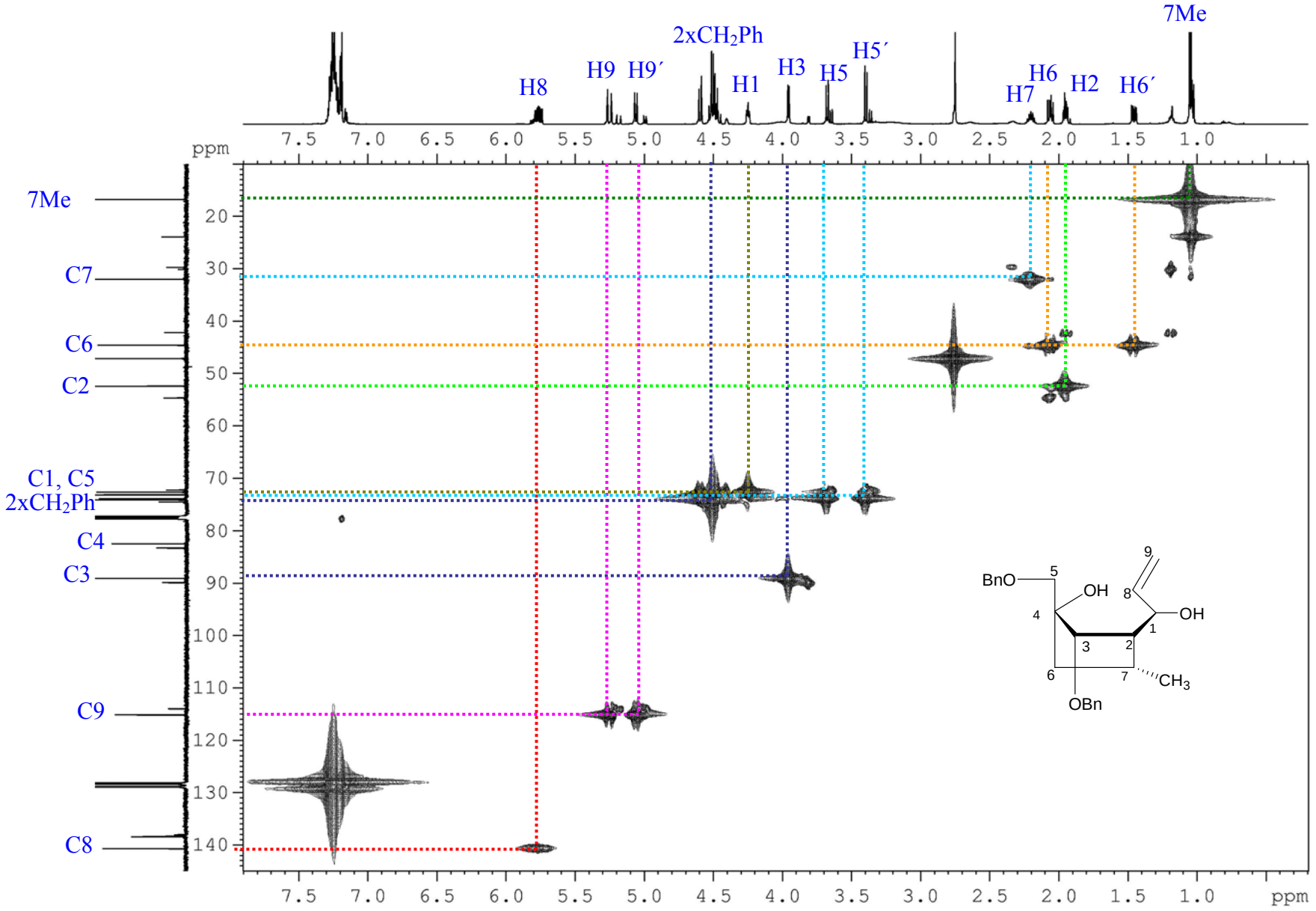


Figure S33: HMQC spectrum of compound **6**

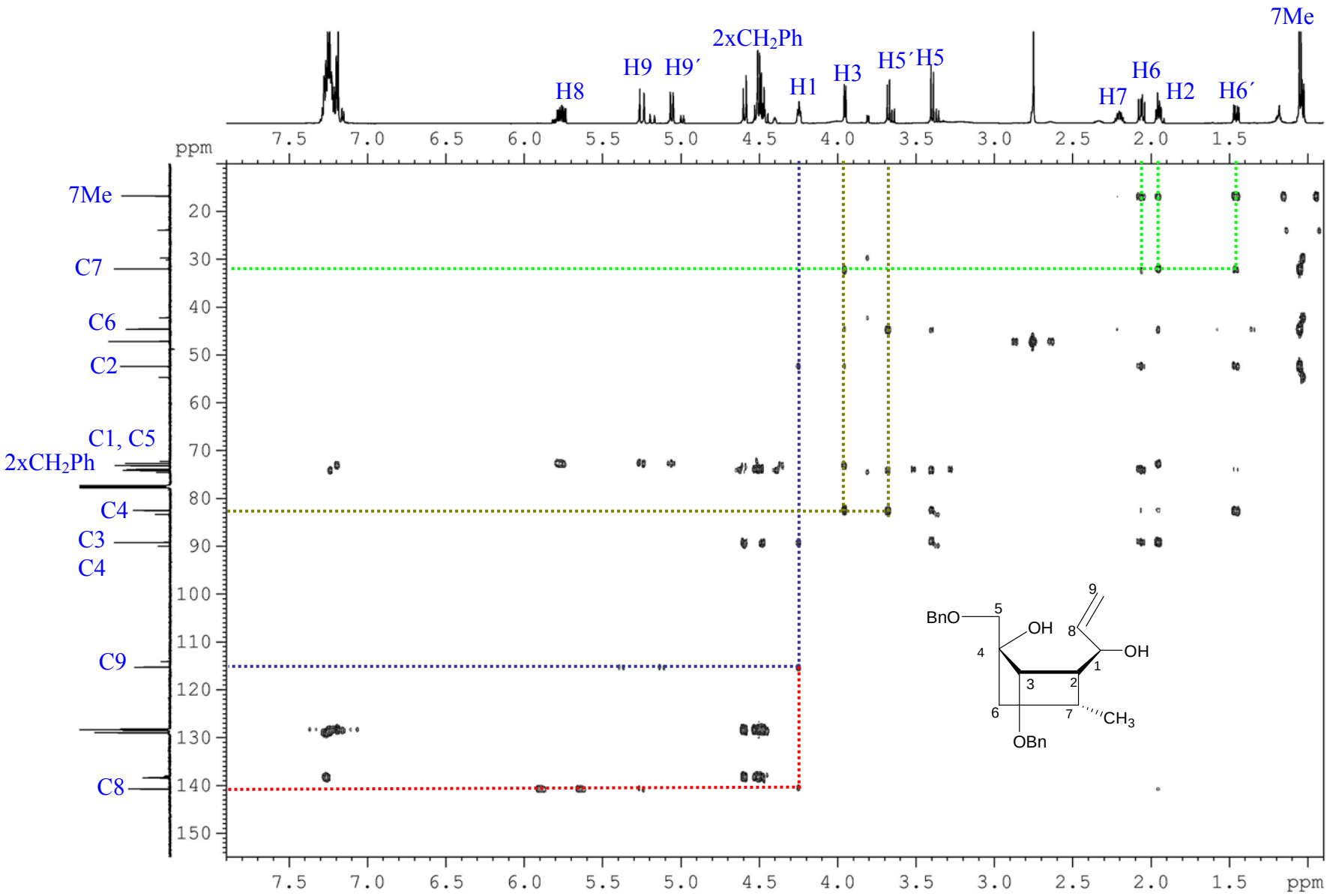


Figure S34: HMBC spectrum of compound **6**

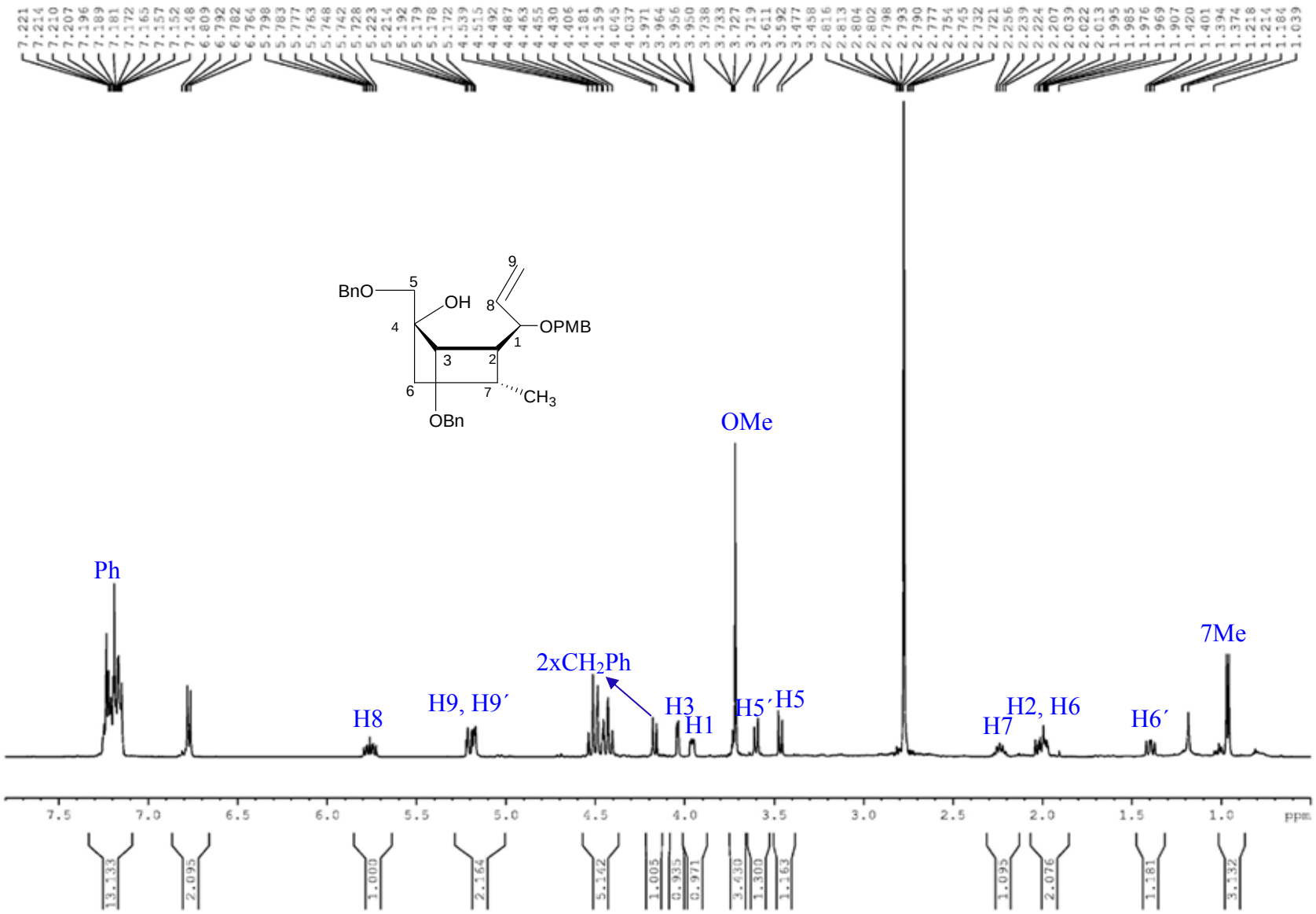


Figure S35: [1]HNMR spectrum of compound **7**

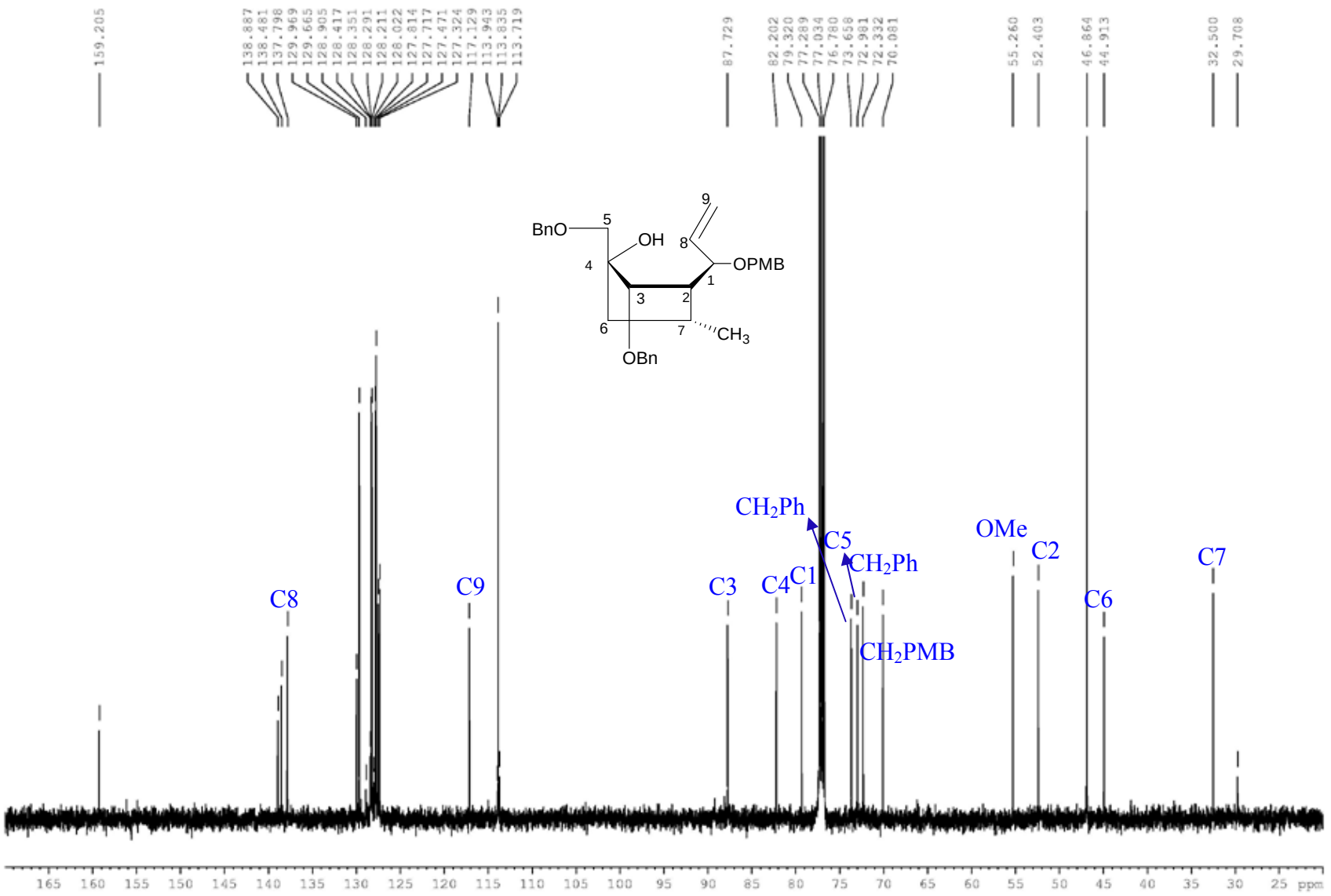


Figure S36: ^{13}C NMR spectrum of compound **7**

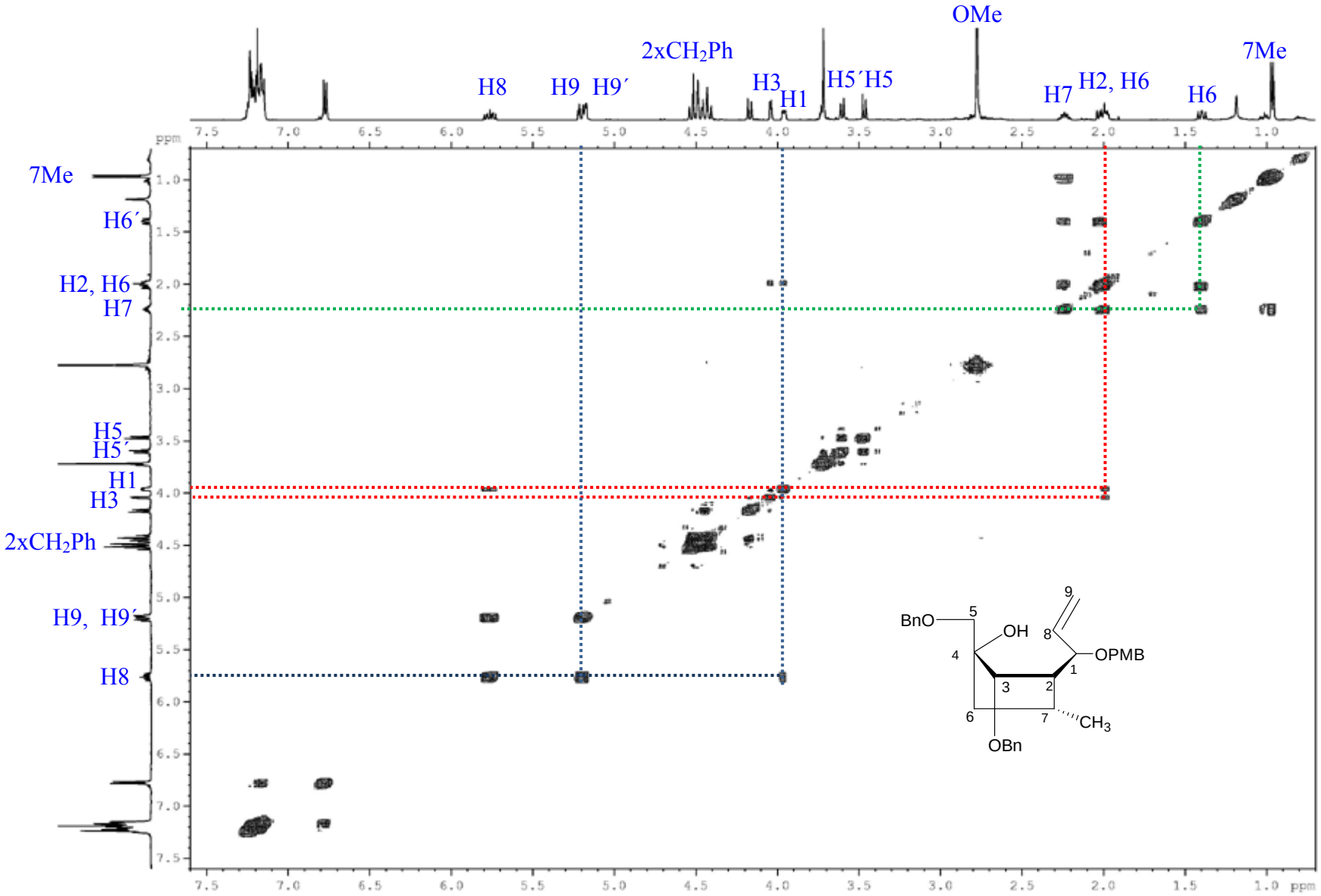


Figure S37: COSY spectrum of compound **7**

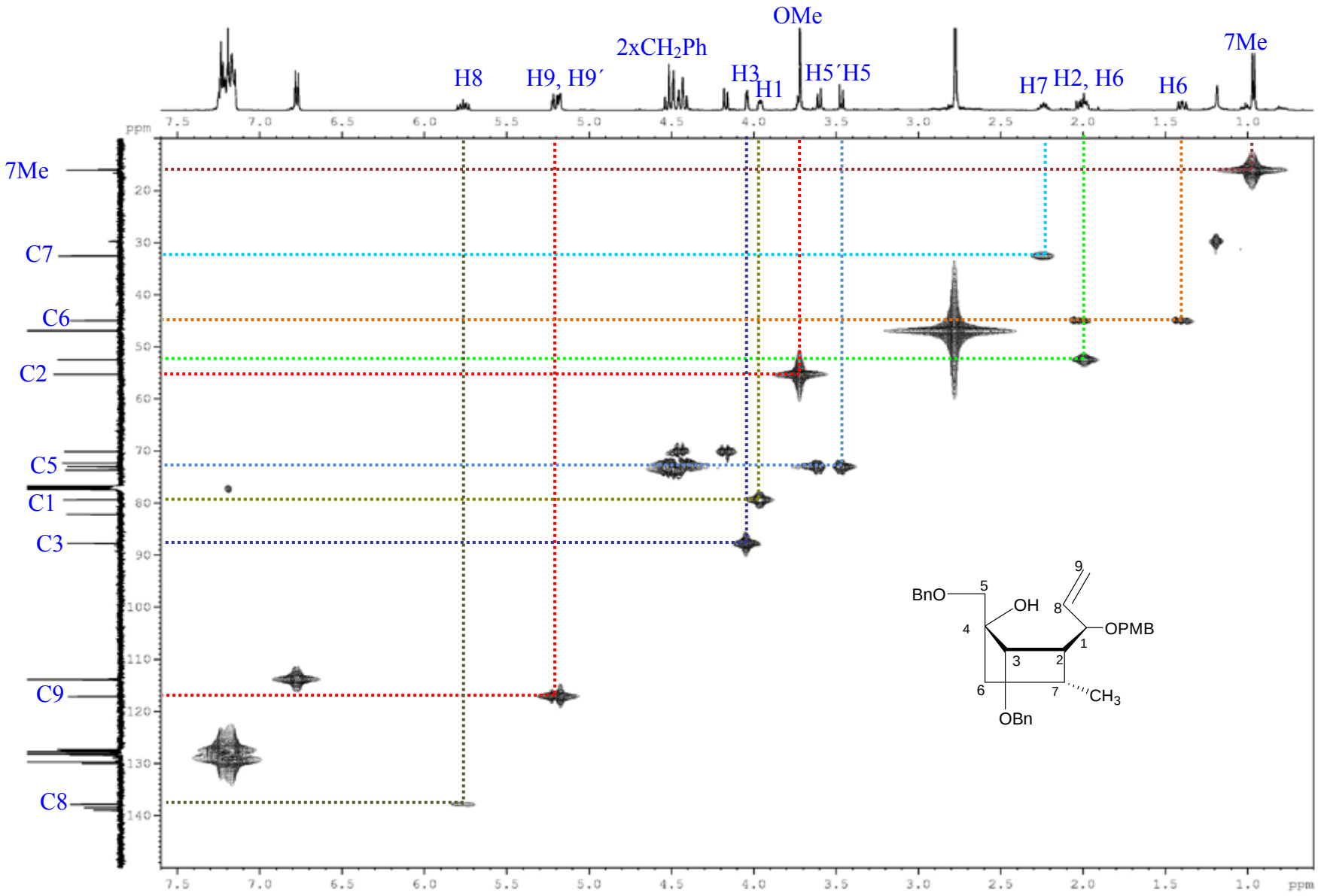


Figure S38: HMQC spectrum of compound **7**

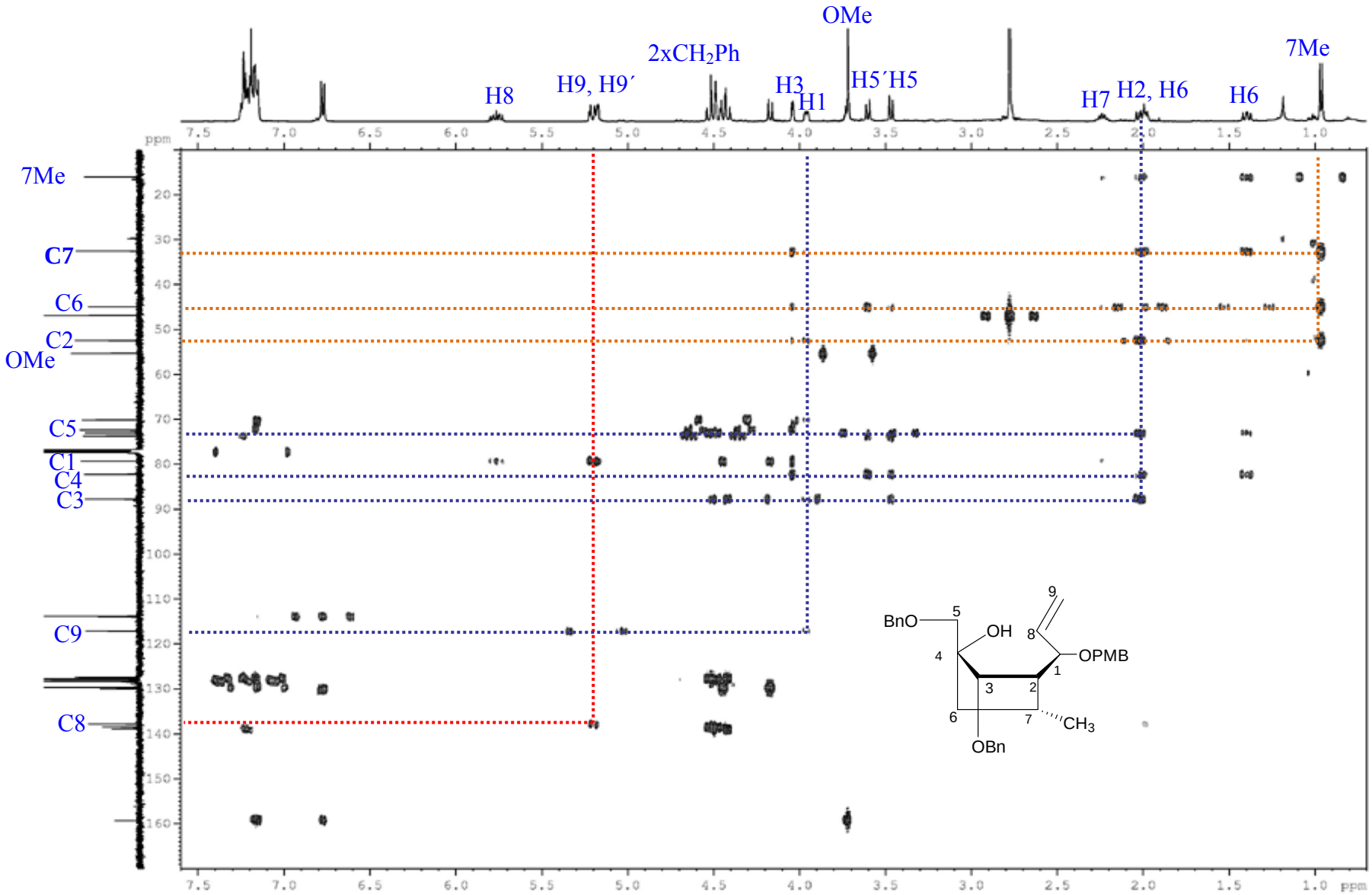


Figure S39: HMBC spectrum of compound **7**

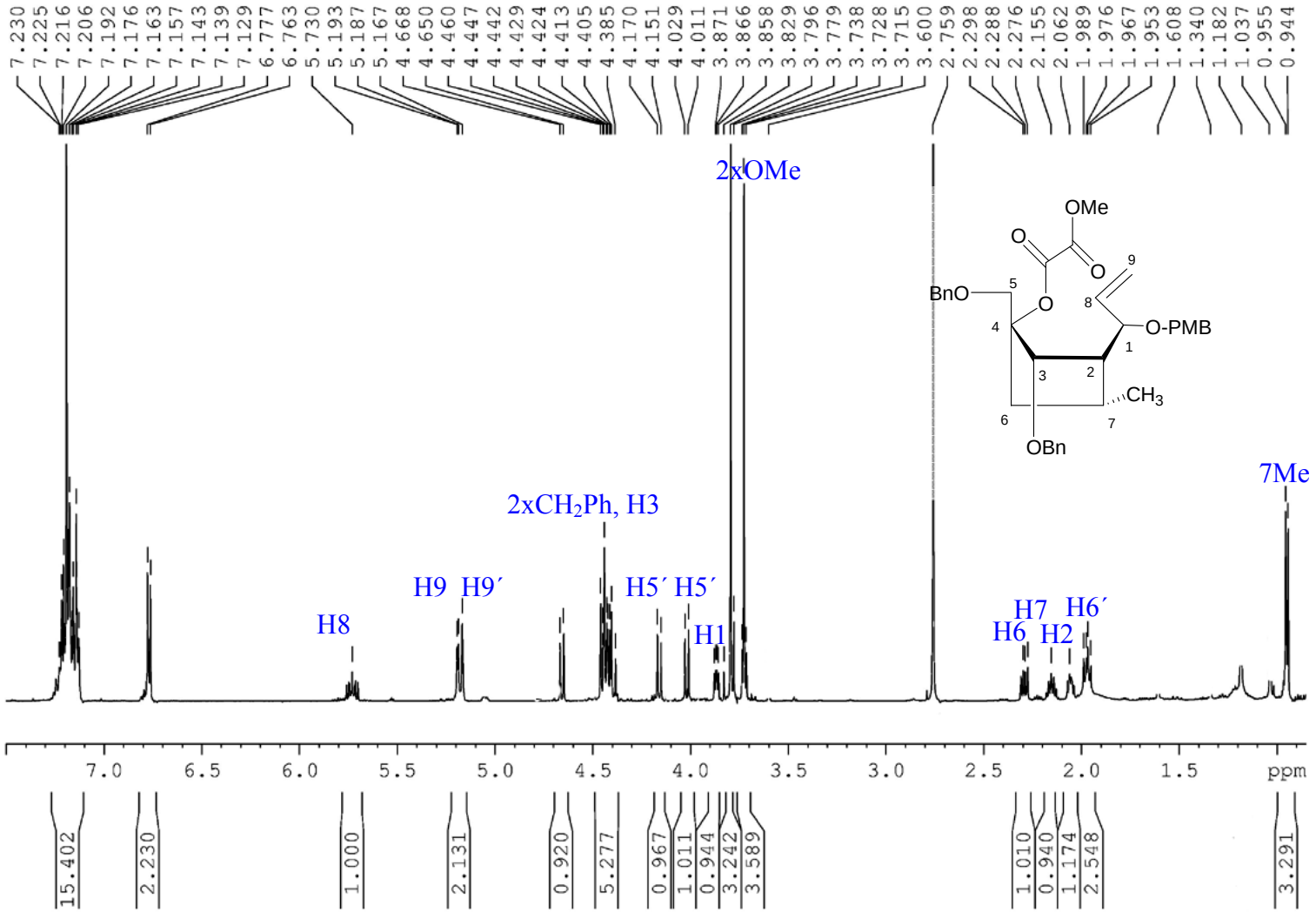


Figure S40: [1]HNMR spectrum of compound **8**

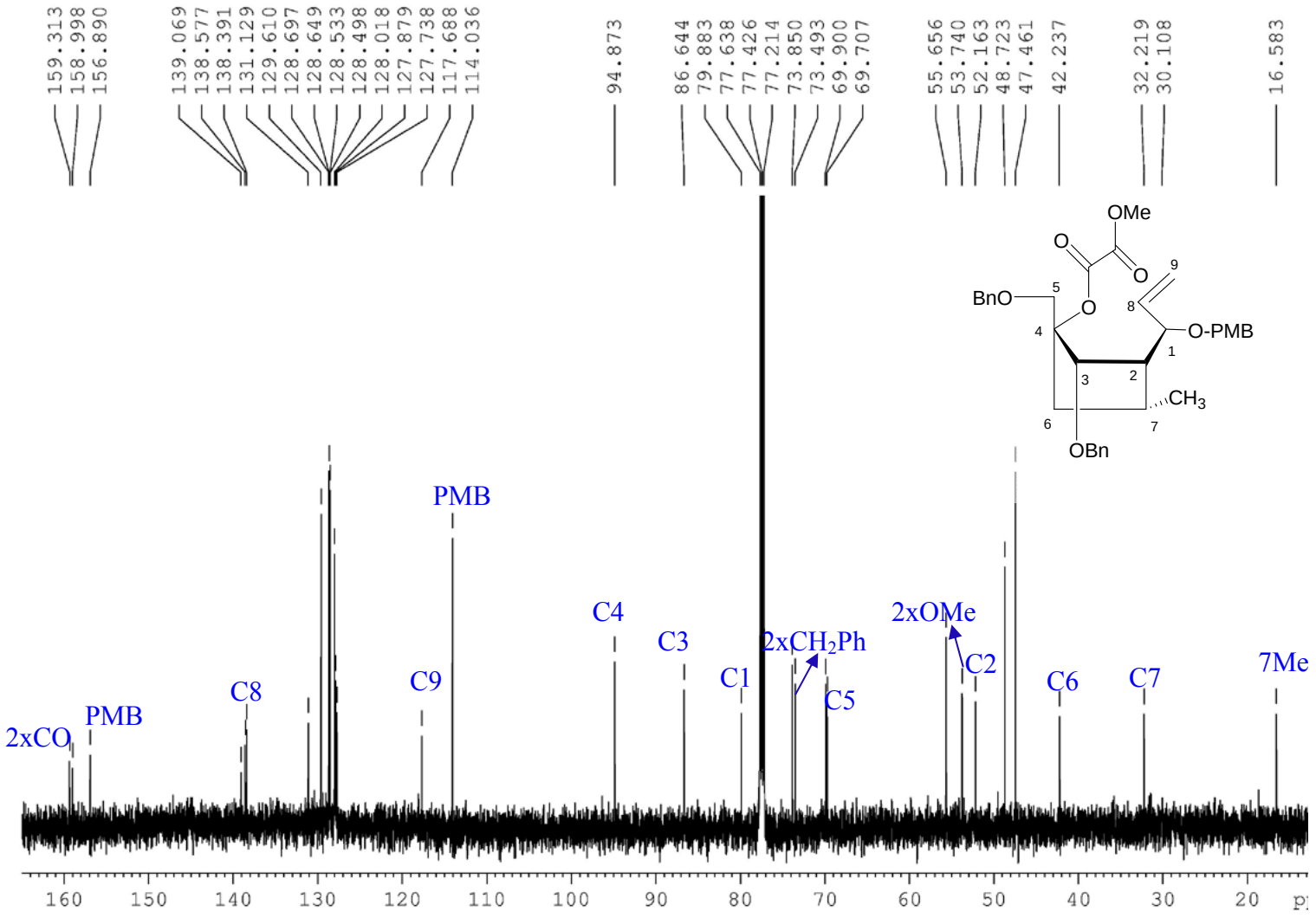


Figure S41: ^{13}CNMR spectrum of compound **8**

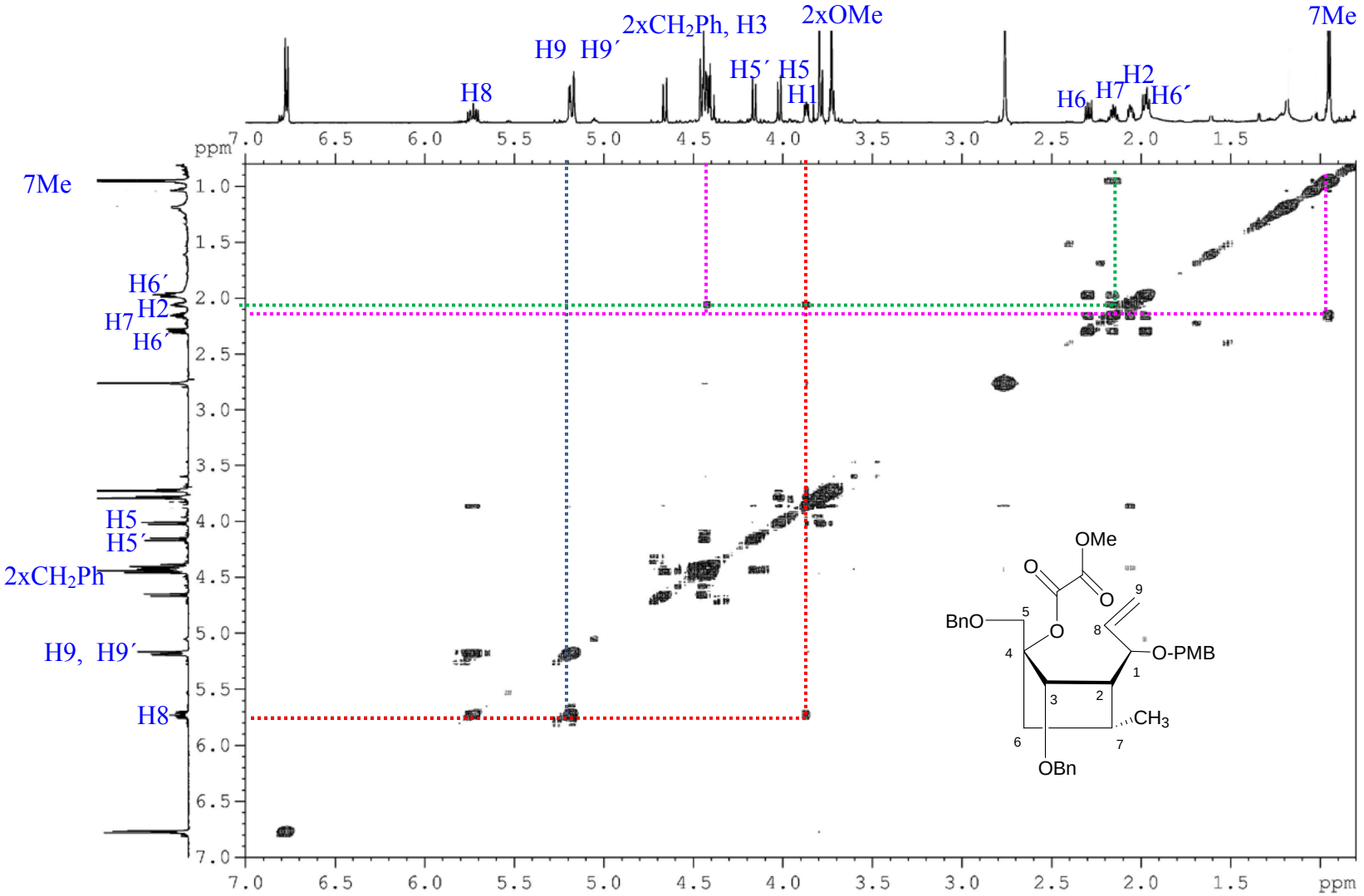


Figure S42: COSY spectrum of compound **8**

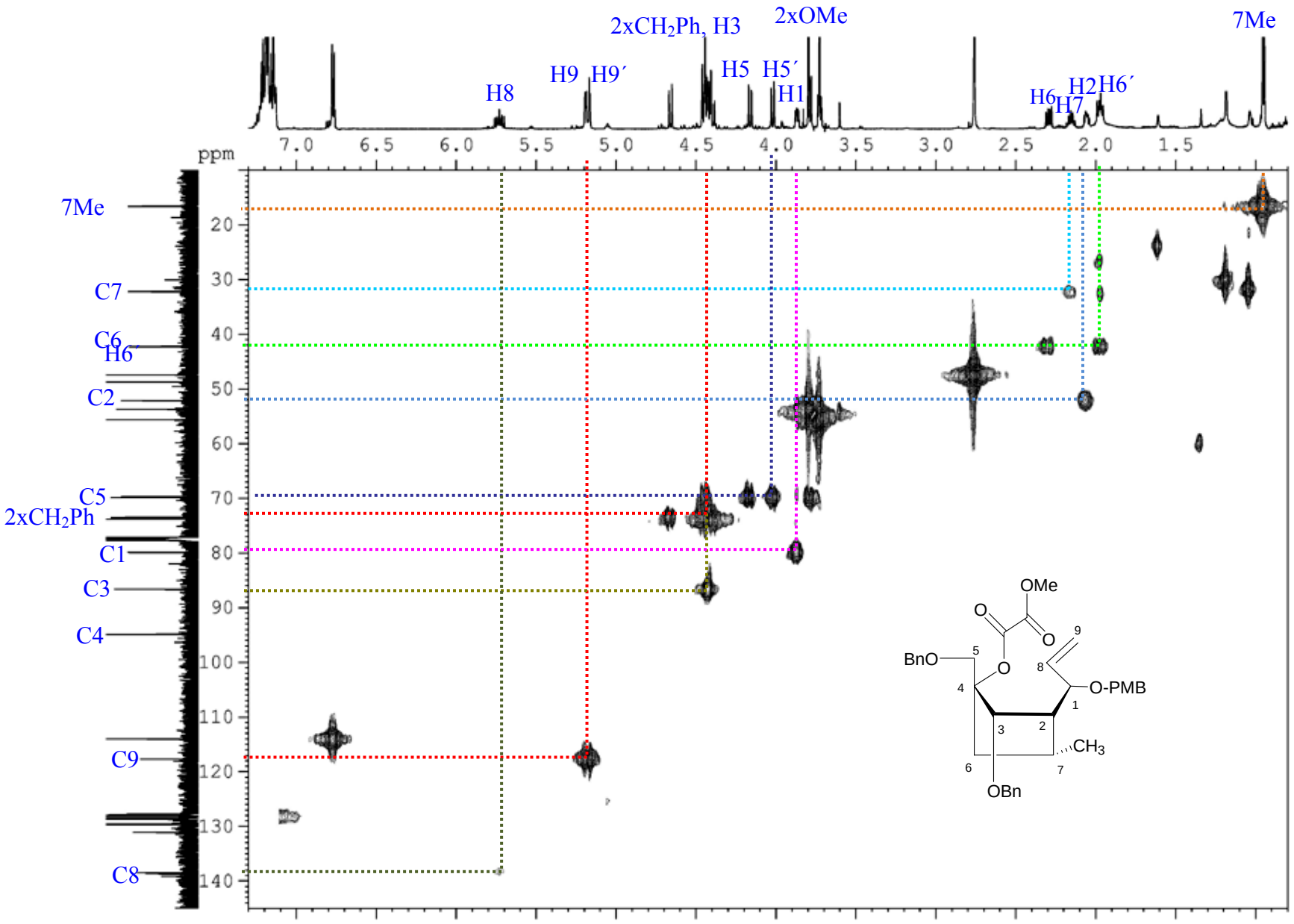


Figure S43: HMQC spectrum of compound **8**

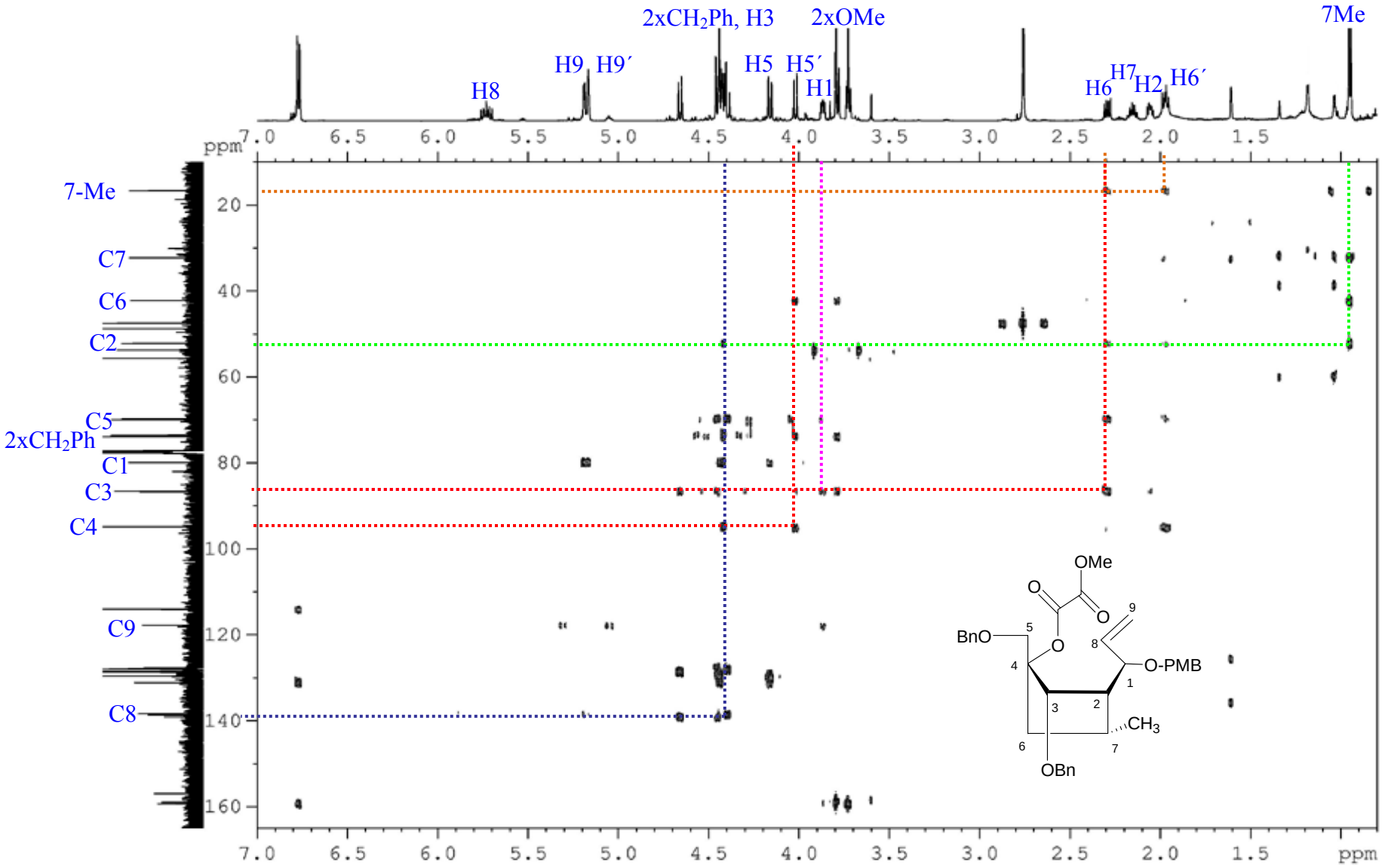


Figure S44: HMBC spectrum of compound **8**

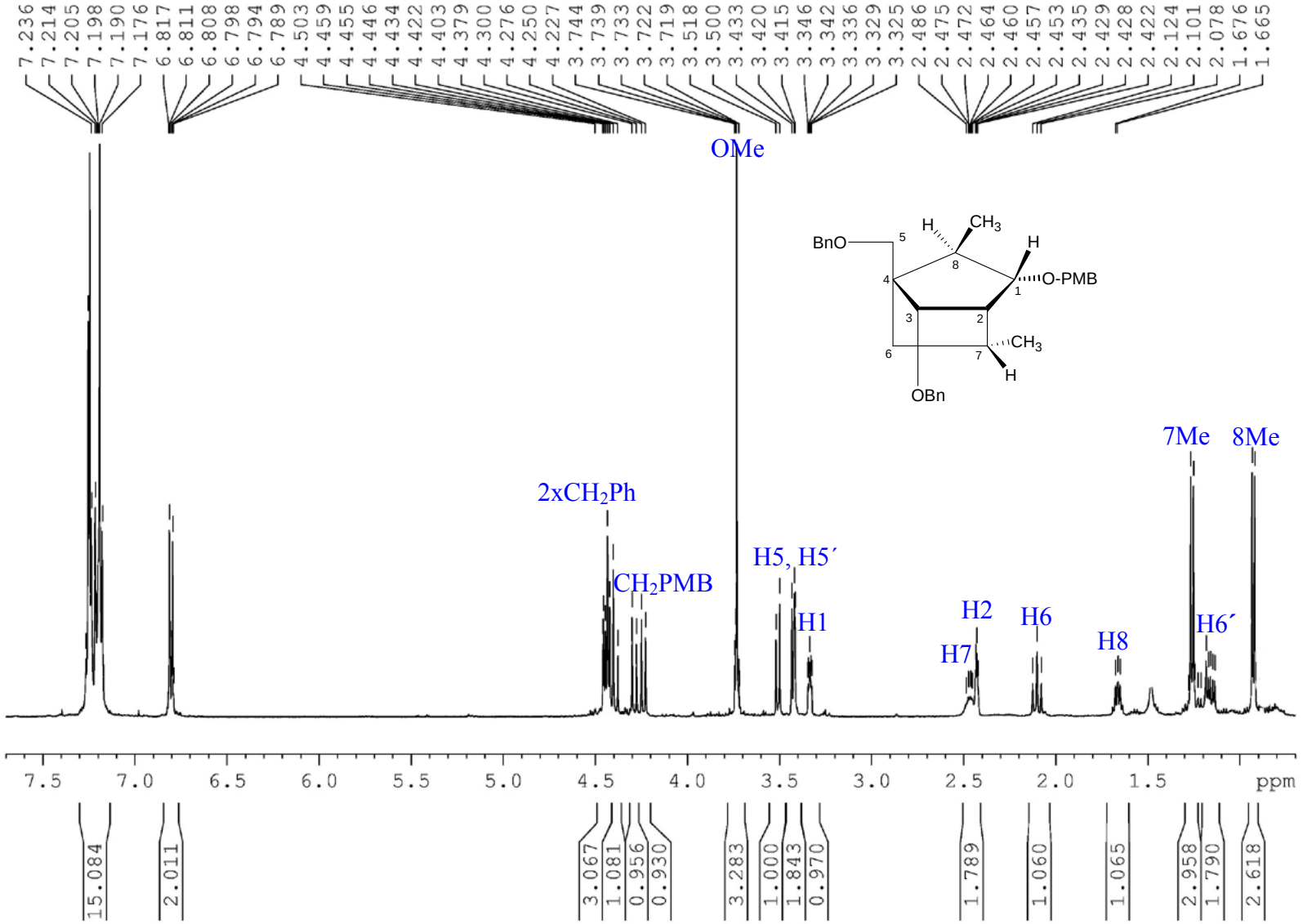


Figure S45: ^{1}H NMR spectrum of compound **9**

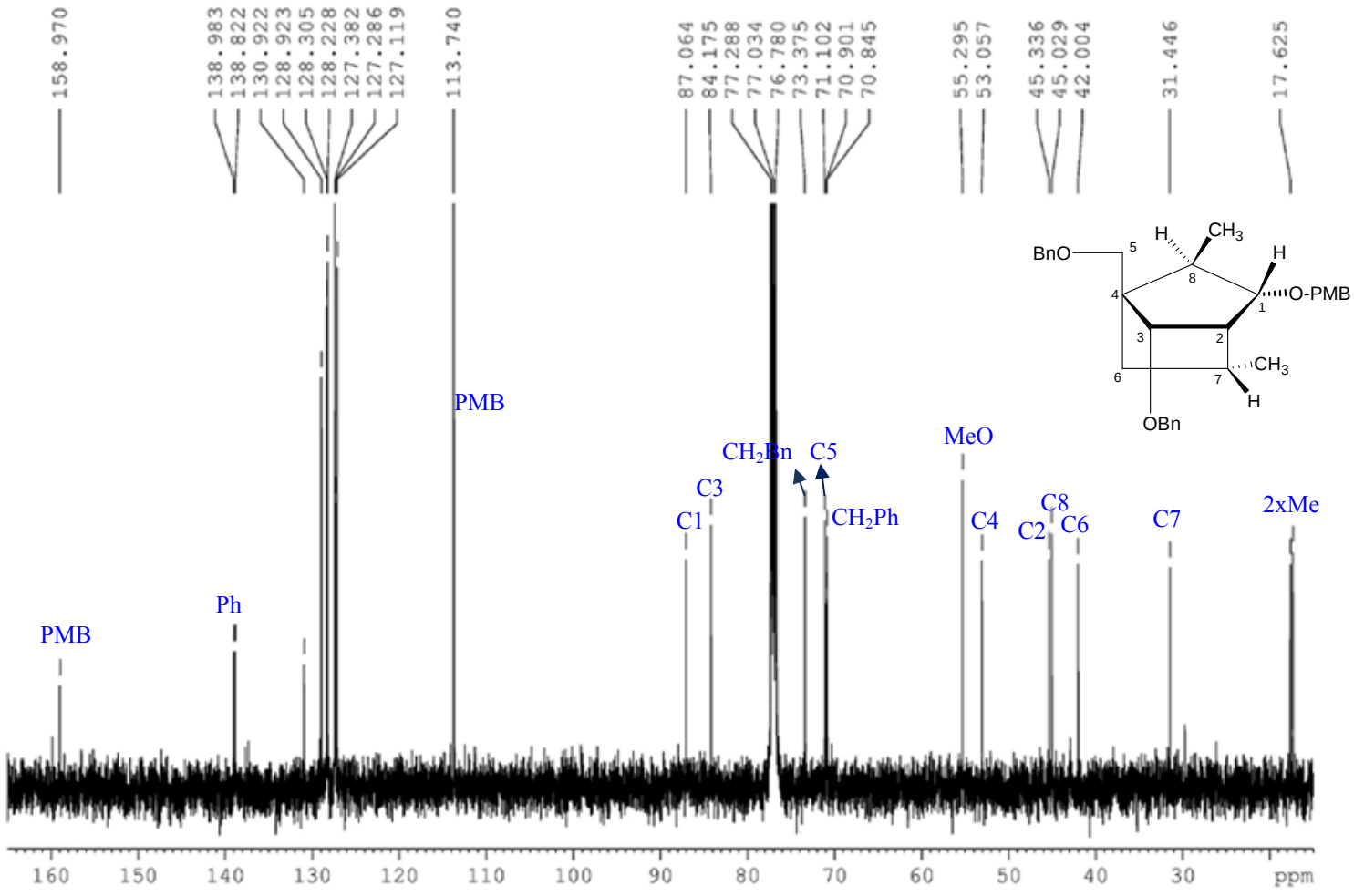


Figure S46: ^{13}C NMR spectrum of compound **9**

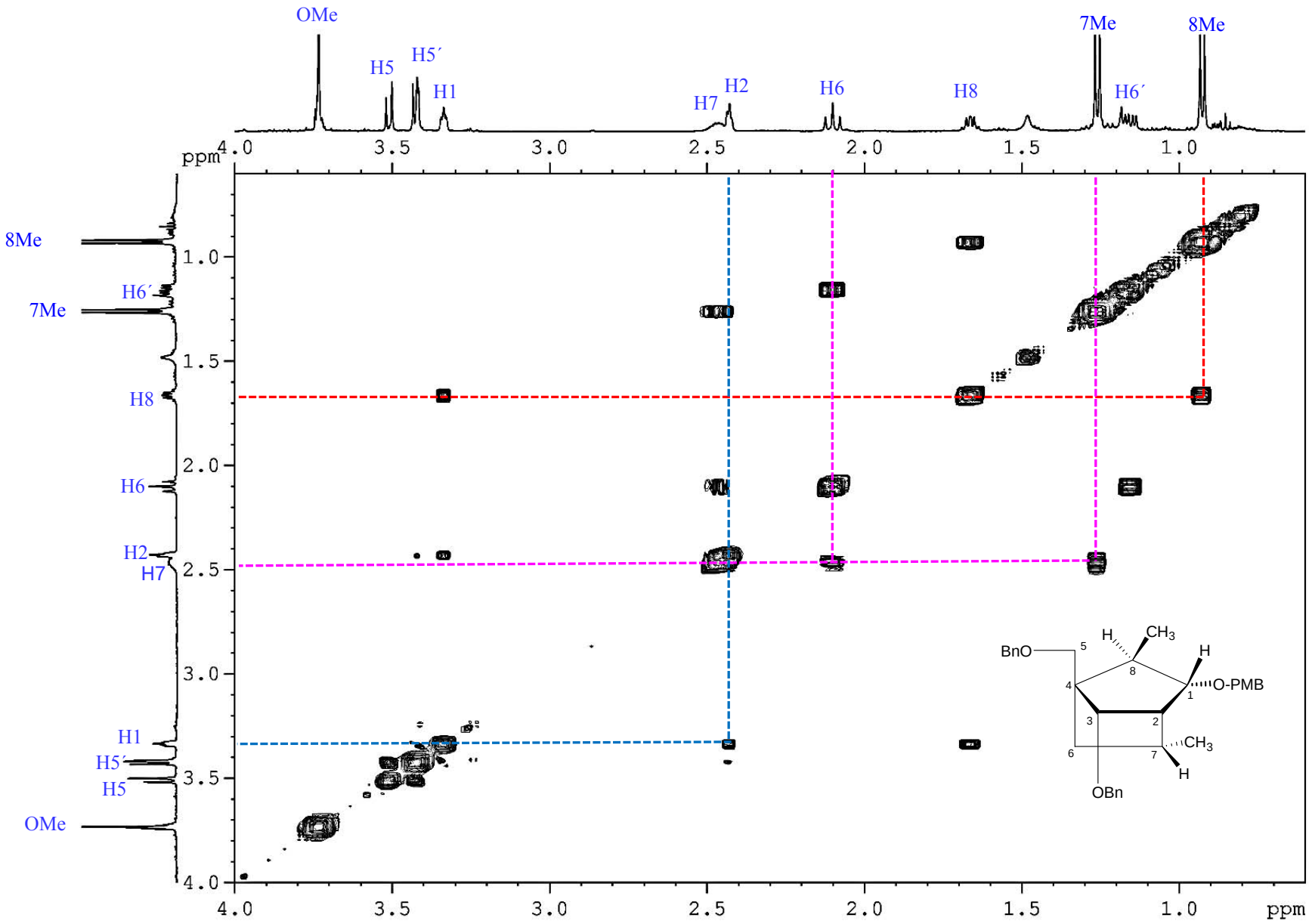


Figure S47: COSY spectrum of compound **9**

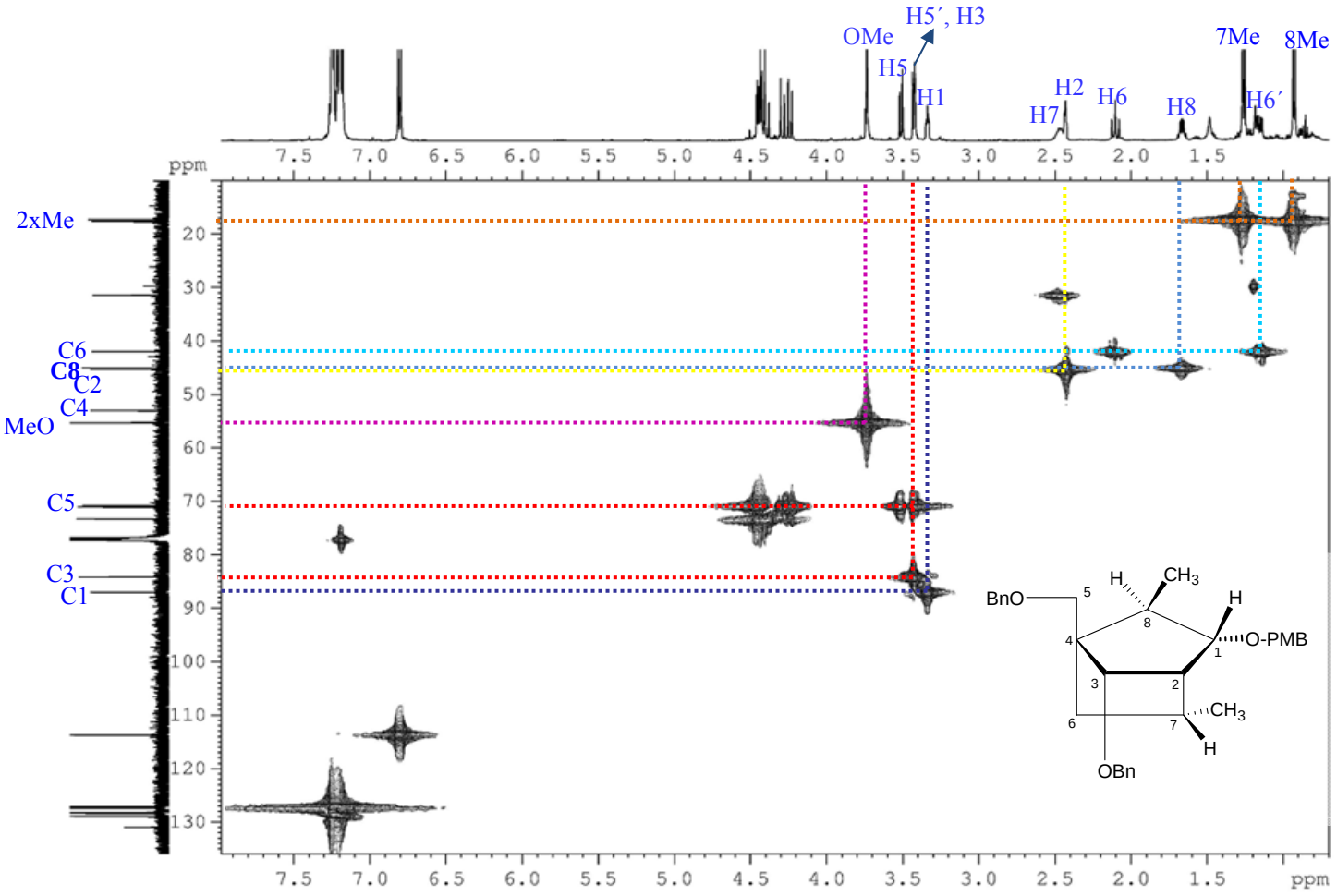


Figure S48: HMQC spectrum of compound **9**

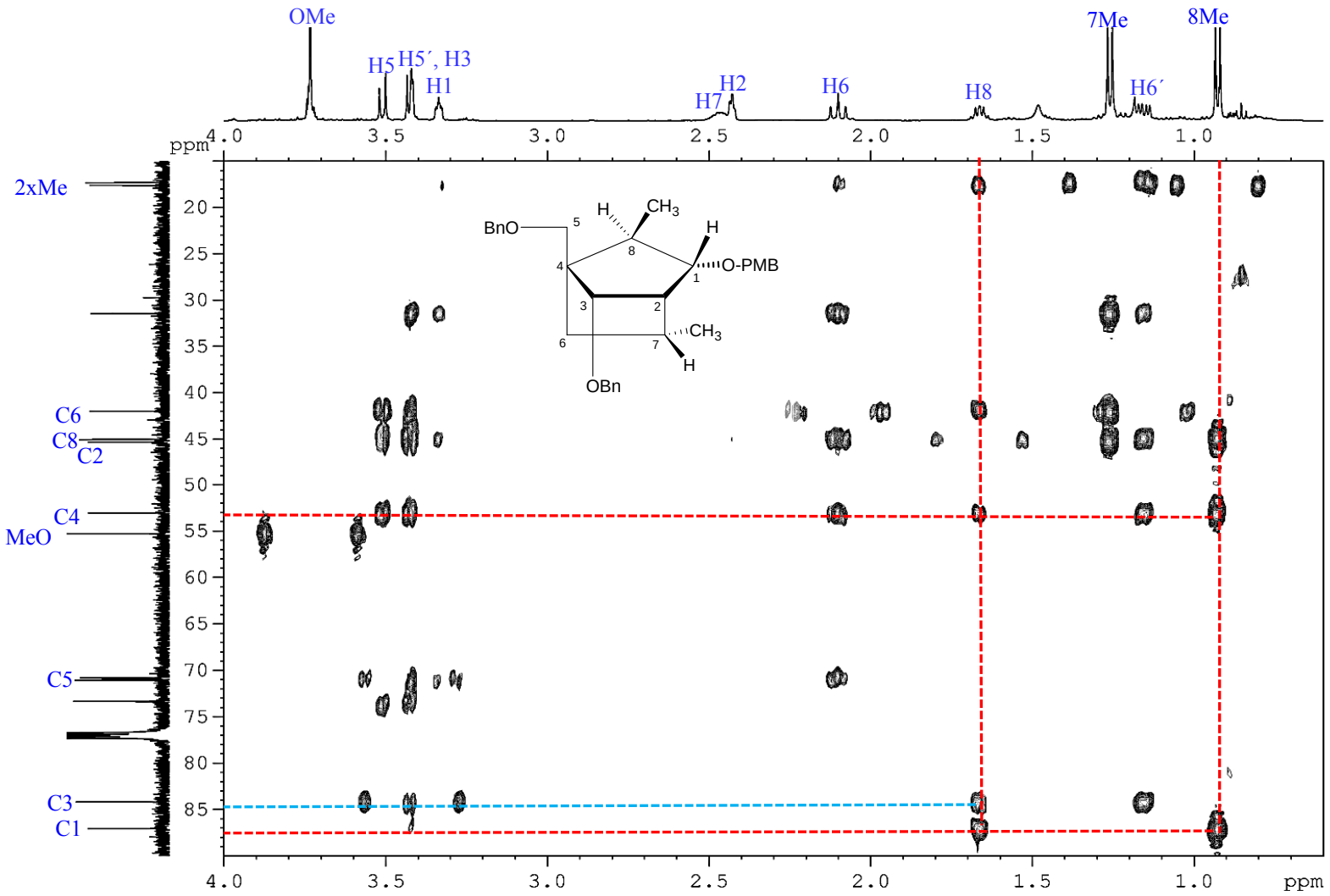
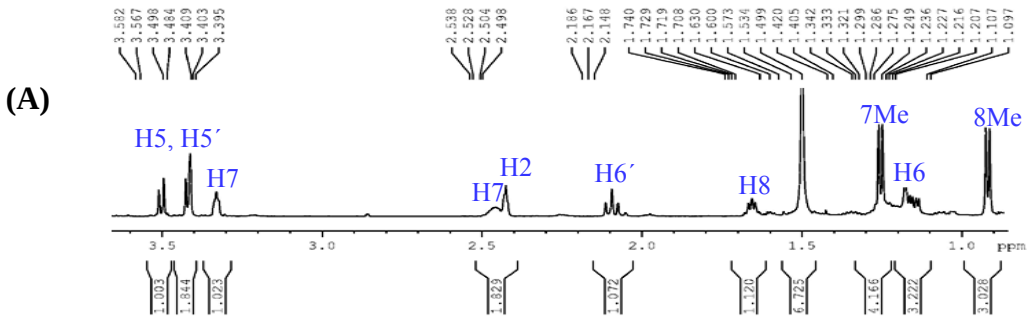
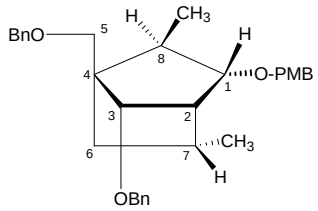
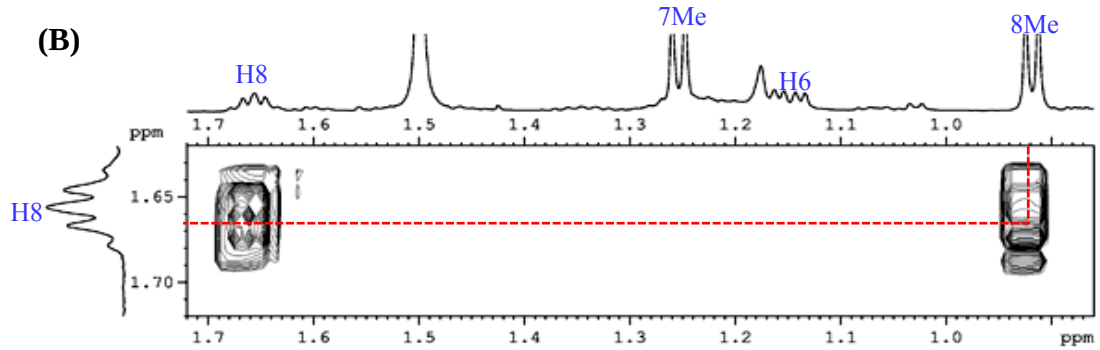
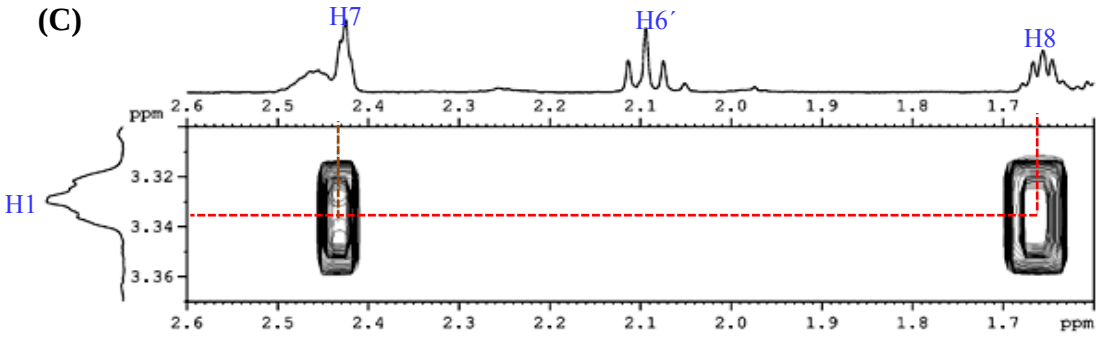


Figure S49: HMBC spectrum of compound **9**


(A)
H5, H5´
H7
H2
H7
H6´
H8
7Me
H6
8Me
ppm


BnO
H
CH3
H
O-PMB
CH3
H
OBn


(B)
H8
7Me
H6
8Me
ppm


(C)
H7
H6´
H8
H1
ppm

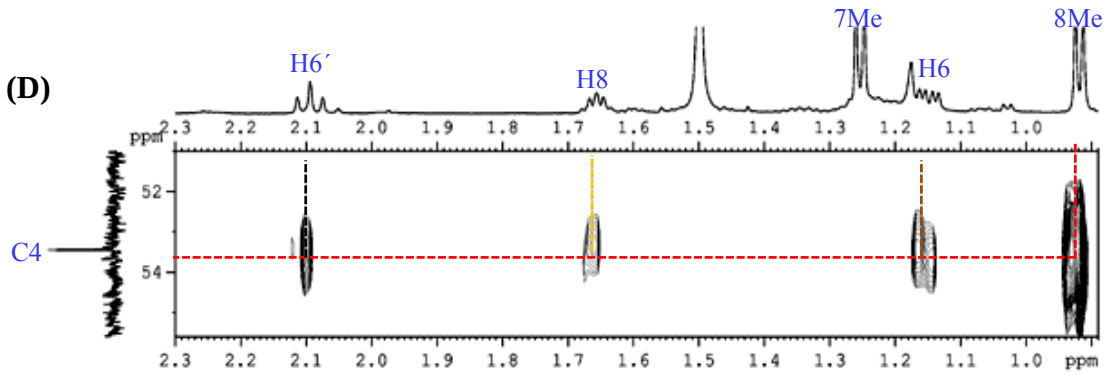
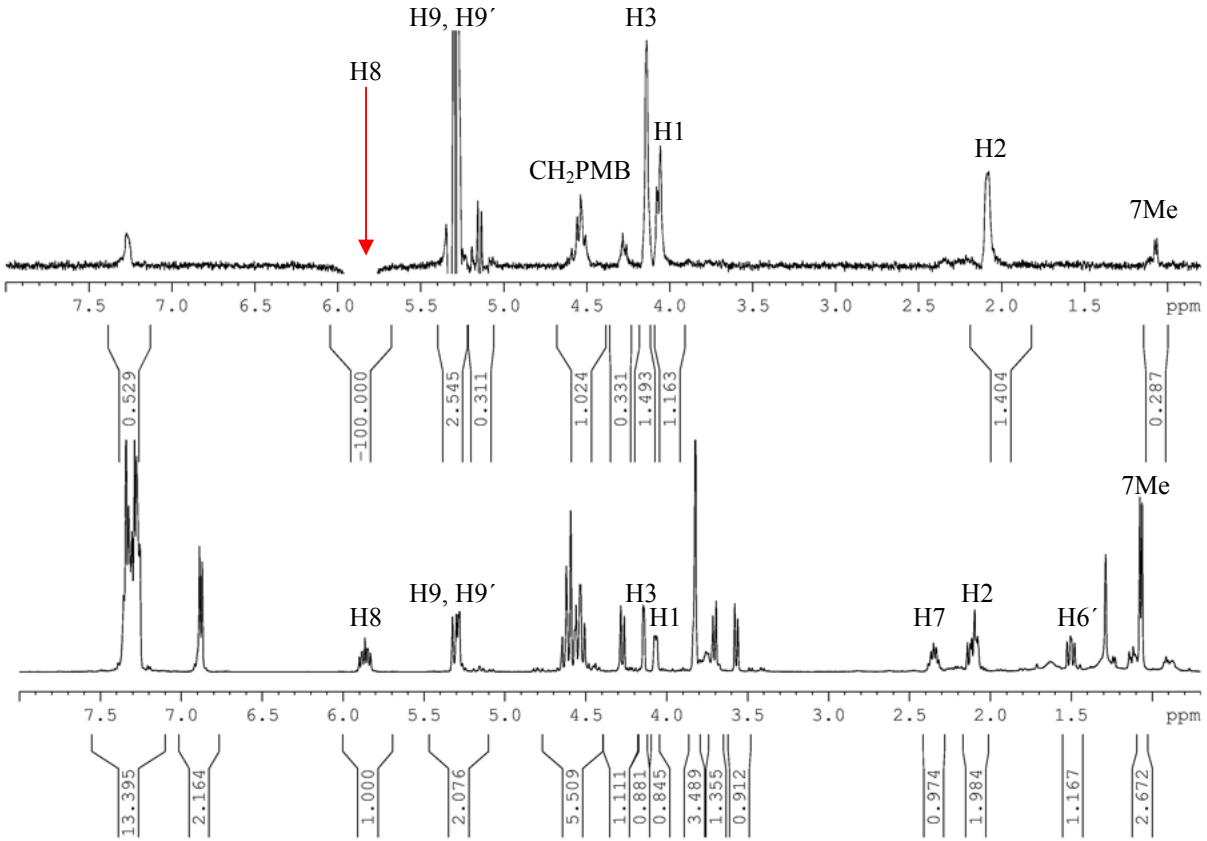
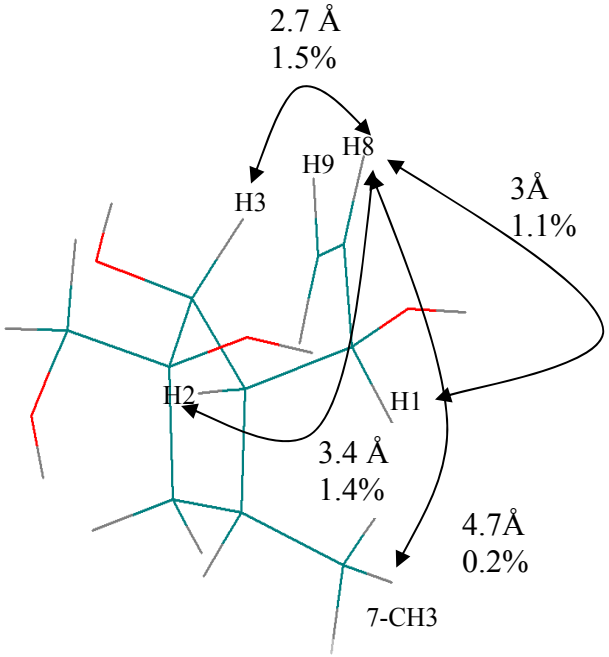


Figure S50: Panel A shows the ^{1}H-NMR spectrum (600 MHz) of compound **9**. Panel B shows the correlation of 8(*R*)-Me and H8 in the COSY spectra, and Panel C shows the correlation between the H8 and H1 in the COSY spectra, whereas Panel D shows the correlation of 8(*R*)-Me and C4 in the HMBC spectra of compound **9**.





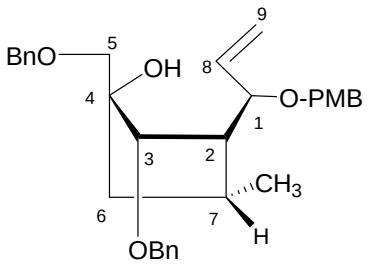
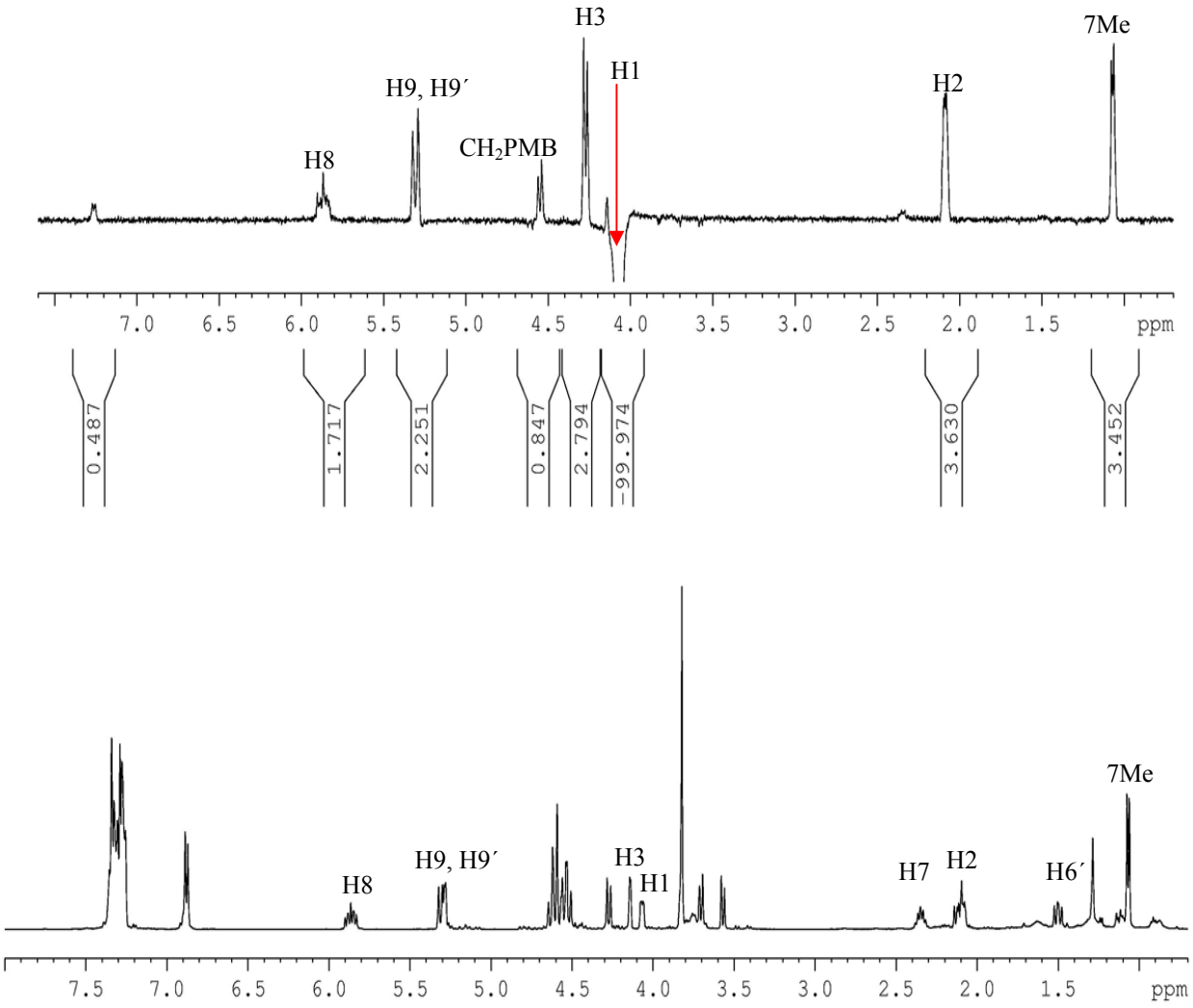
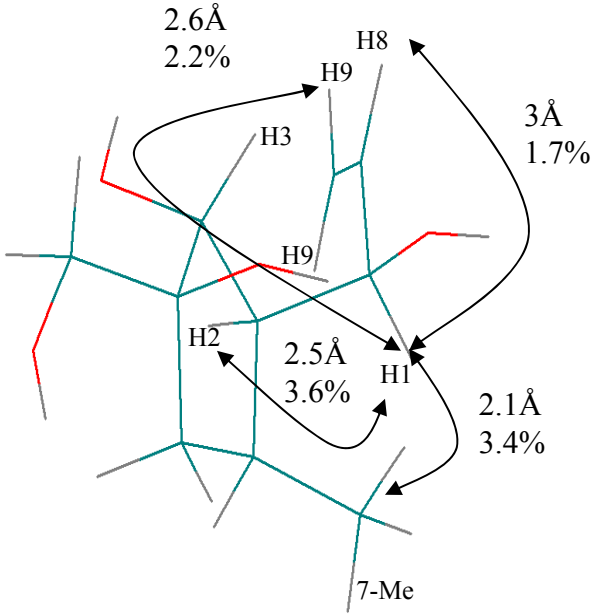


Figure S51: 1D nOe spectrum of compound **7** (H8 irradiated)





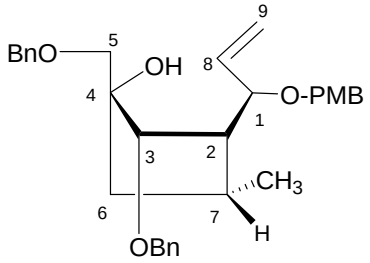
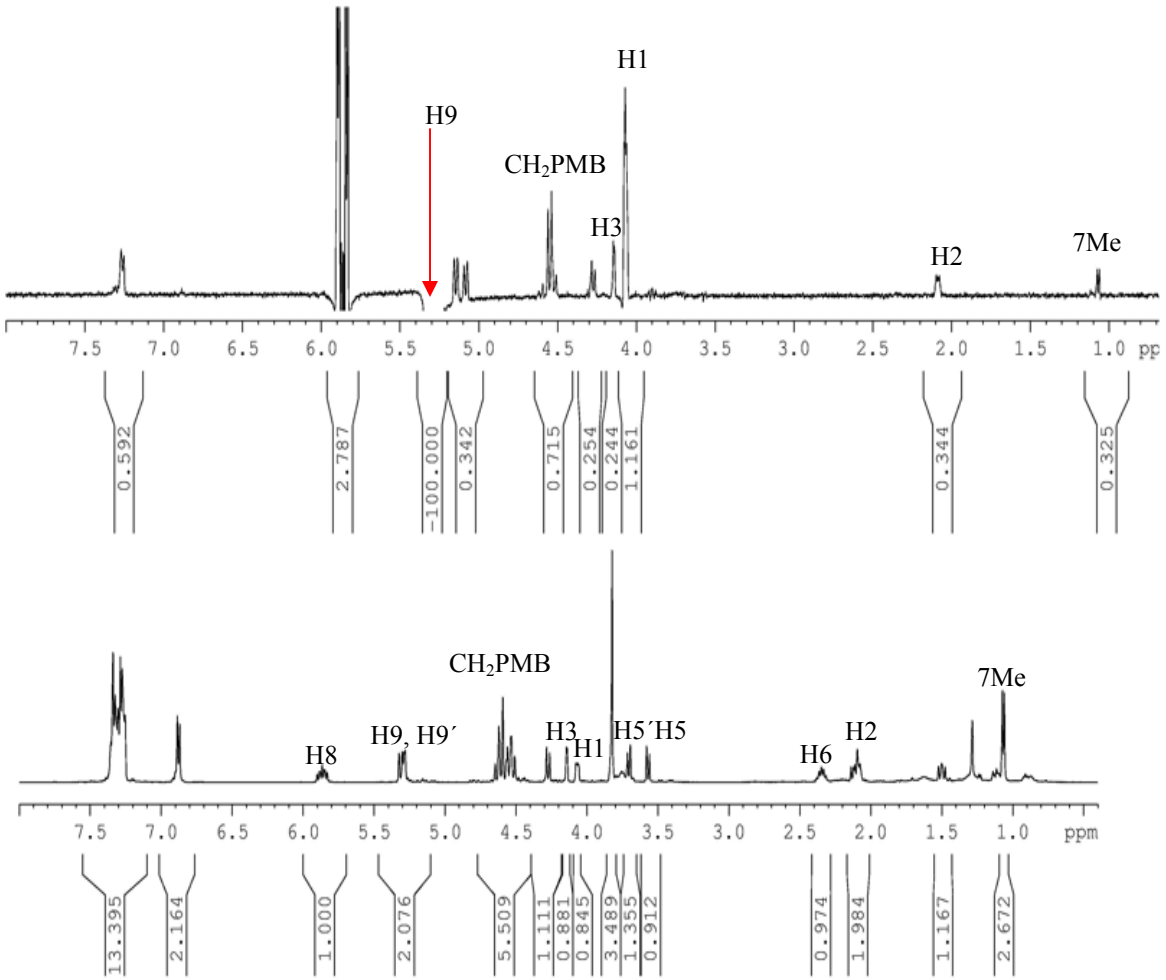
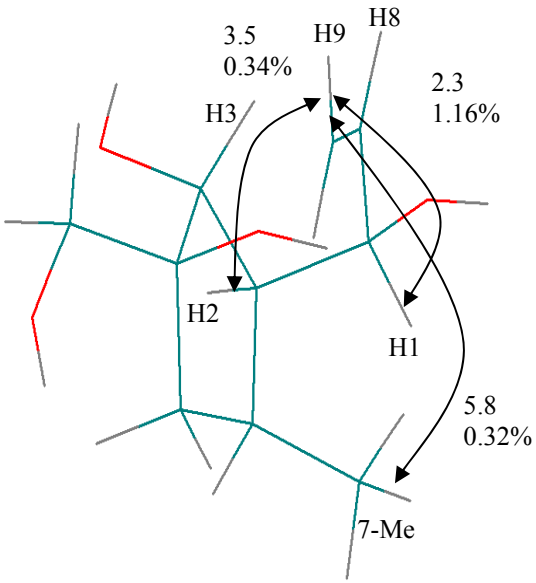


Figure S52: 1D nOe spectrum of compound **7** (H1 irradiated)





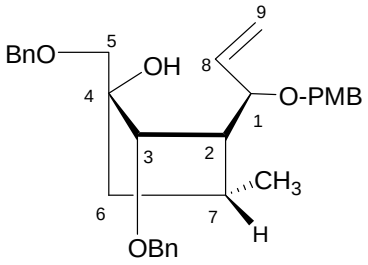
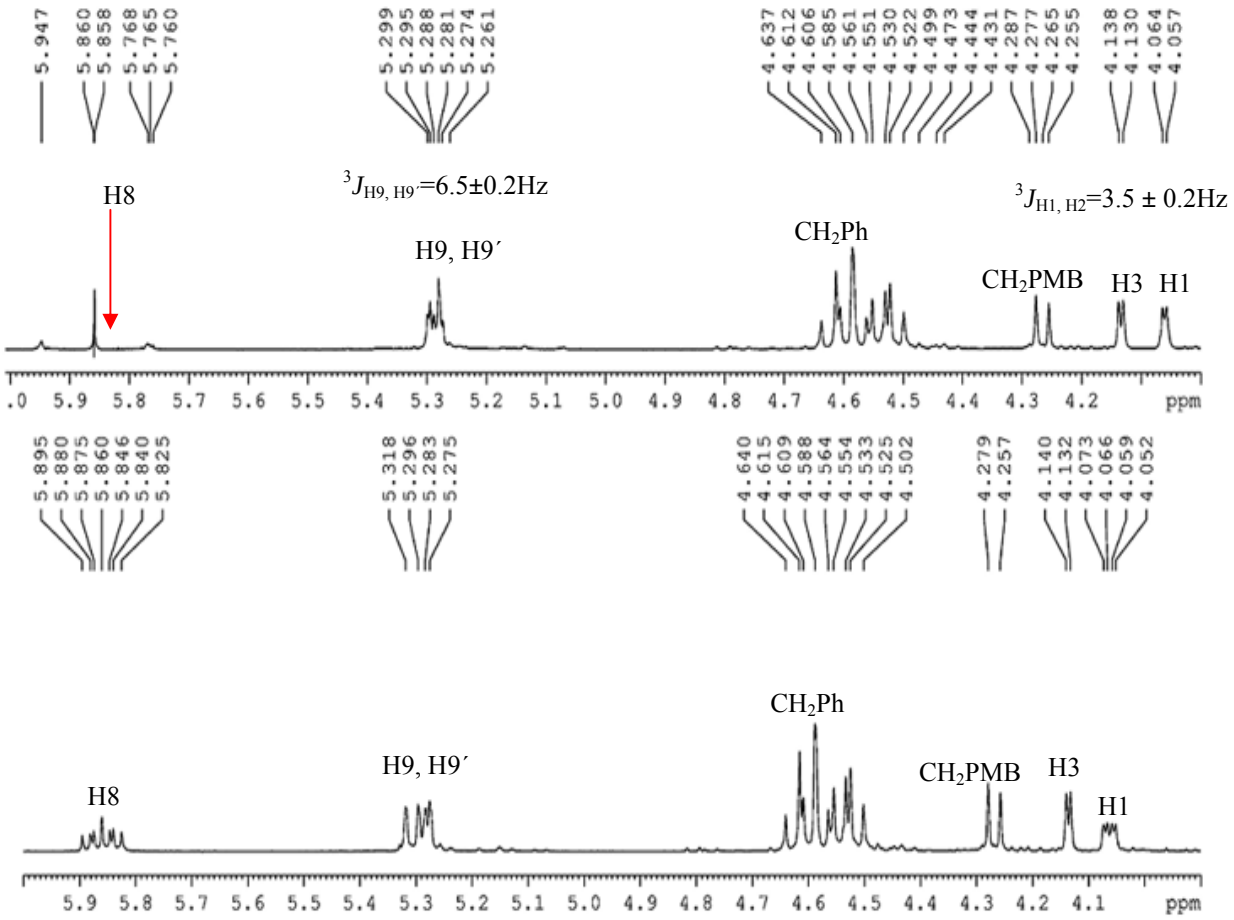


Figure S53: 1D nOe spectrum of compound **7** (H9 irradiated)



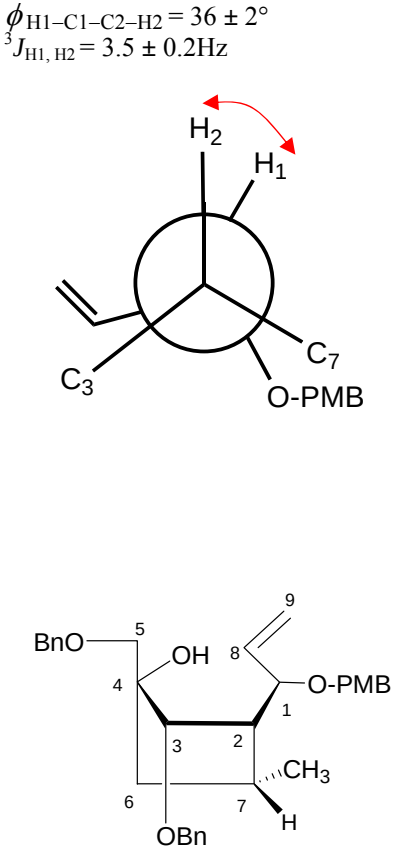


Figure S54: Homodecoupling spectrum of compound **7** (H8 decoupled)

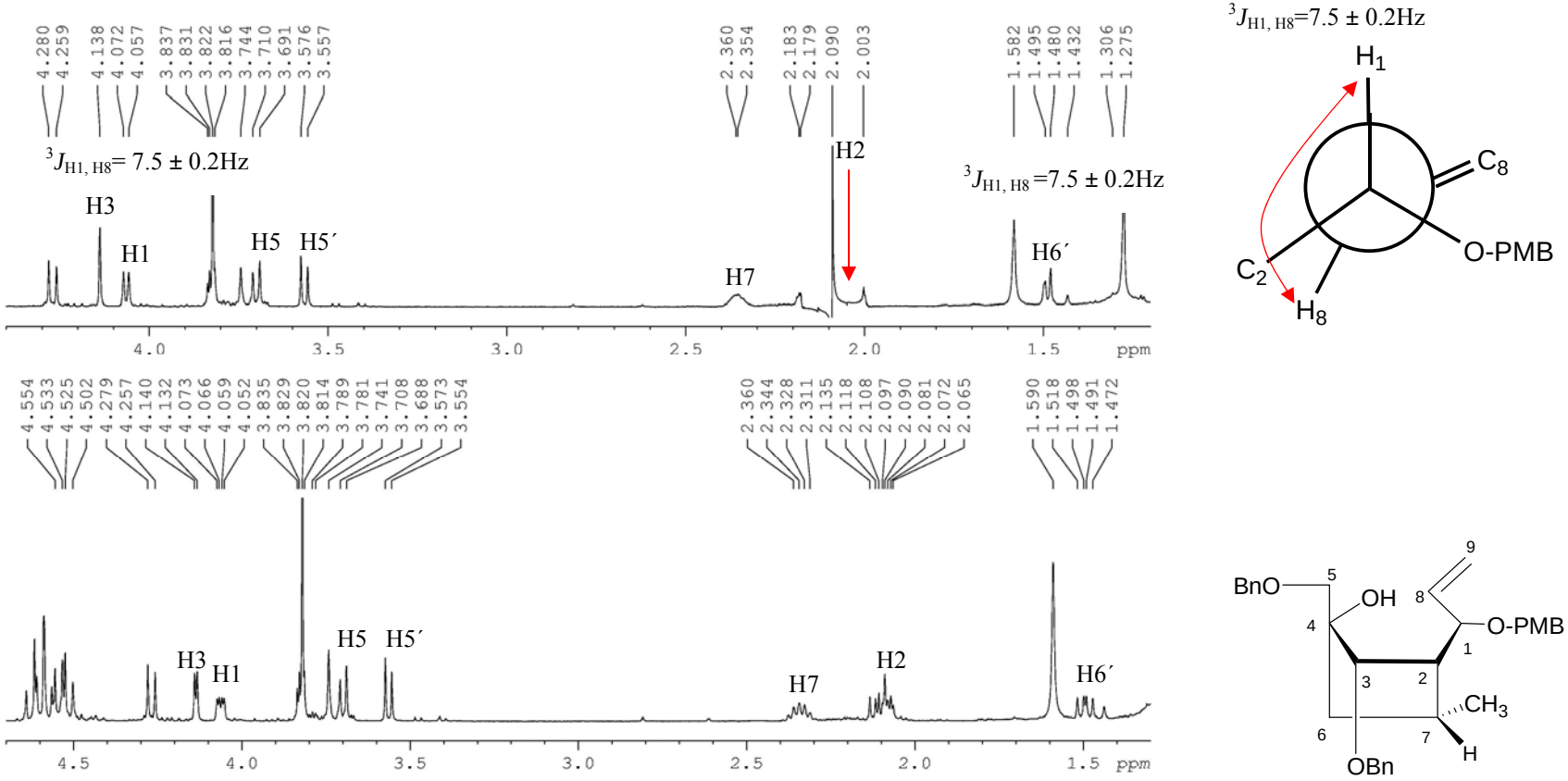


Figure S55: Homodecoupling spectrum of compound **7** (H2 decoupled)

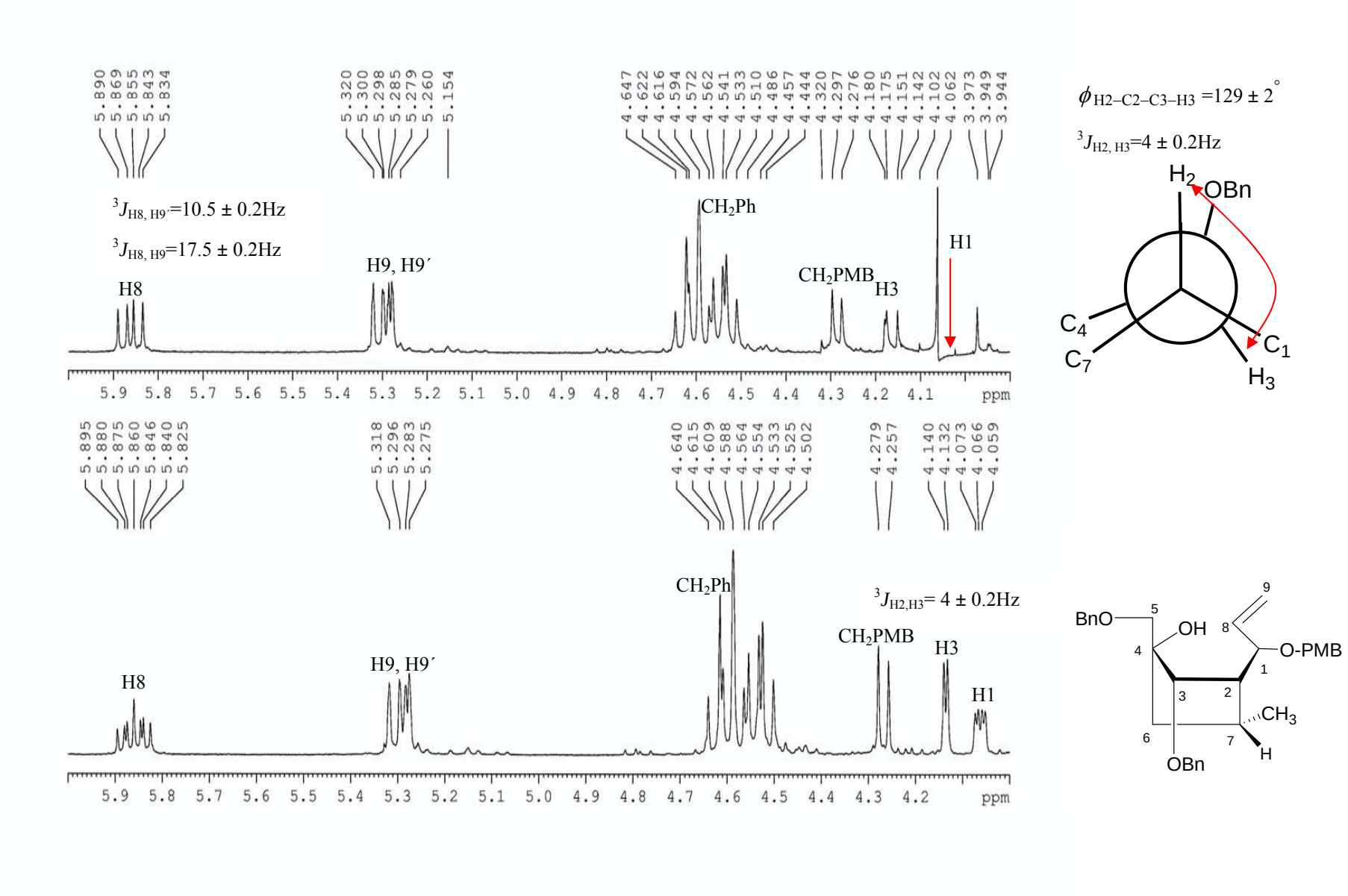


Figure S56: Homodecoupling spectrum of compound **7** (H1 decoupled)

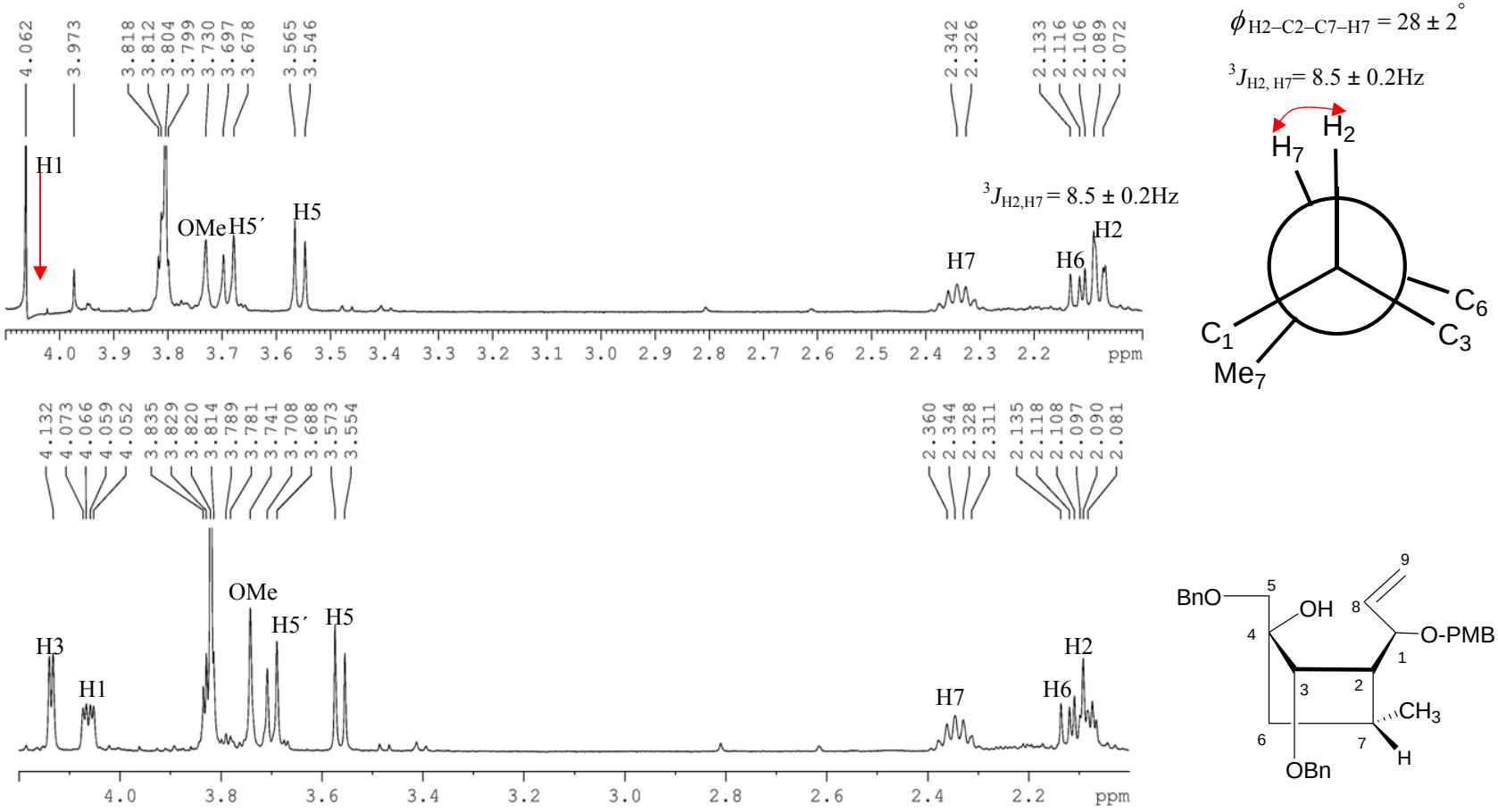
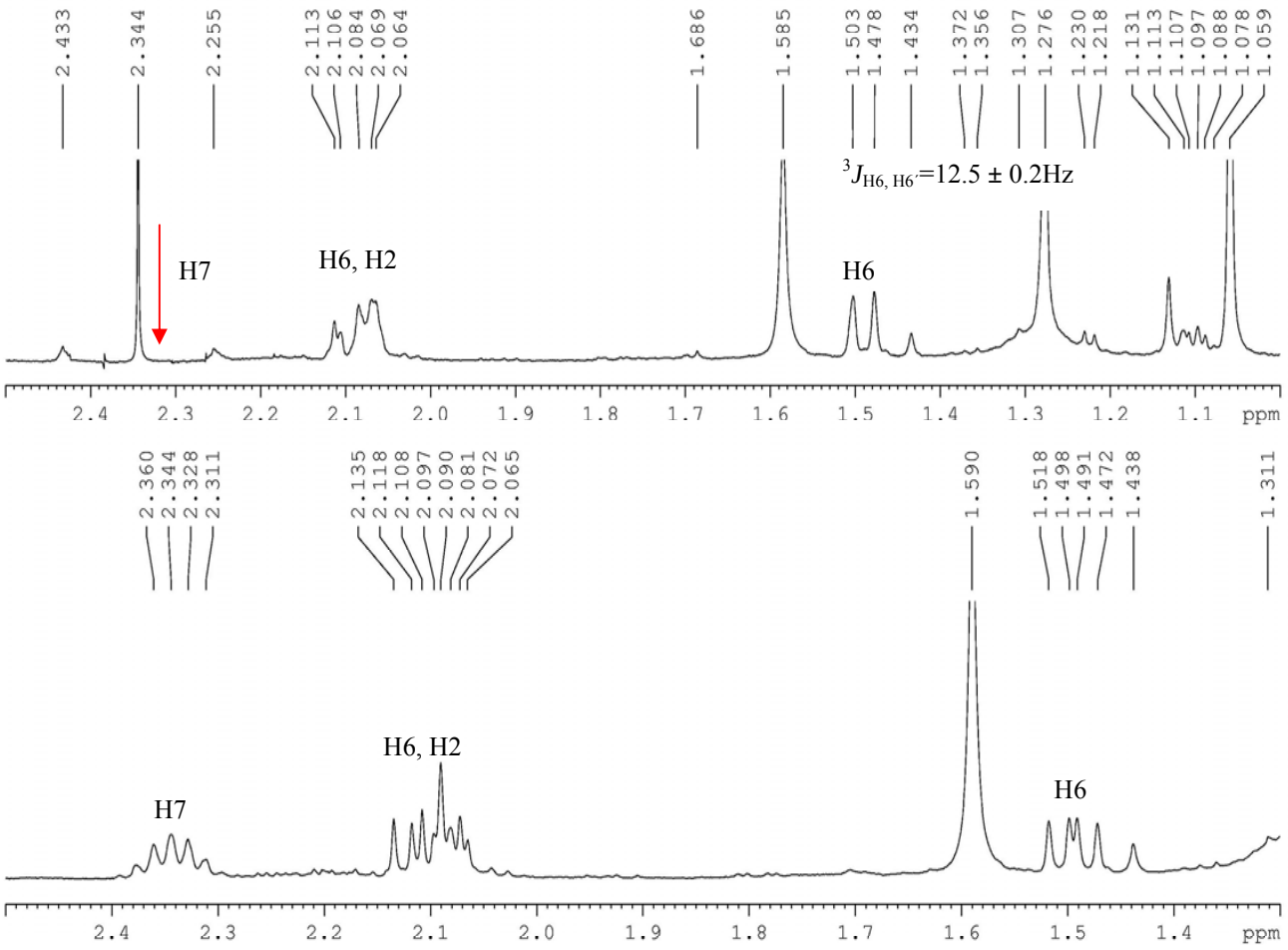


Figure S57: Homodecoupling spectrum of compound **7** (H1 decoupled)



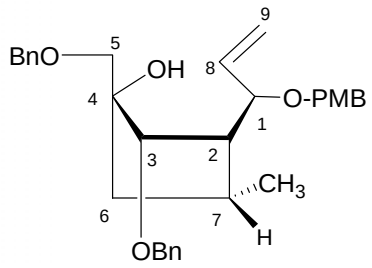
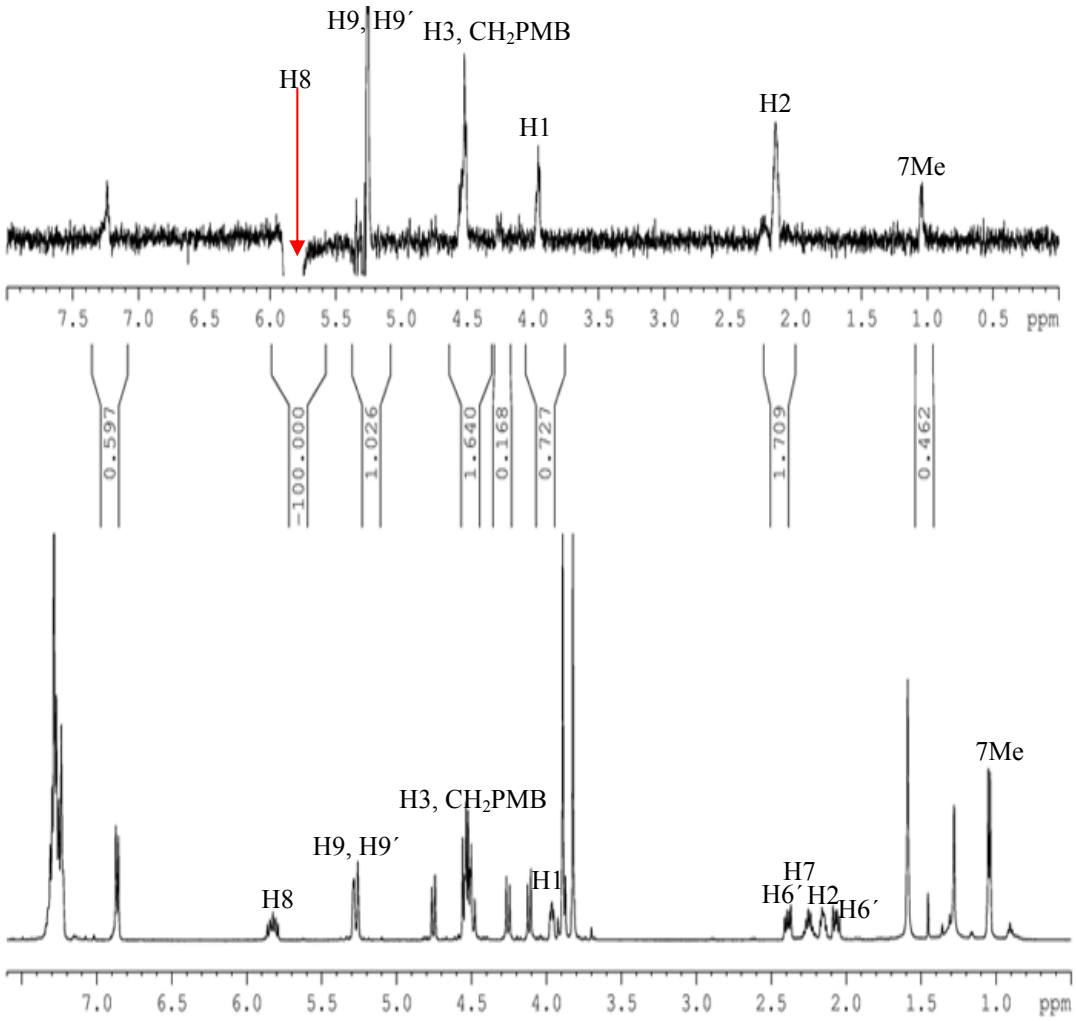
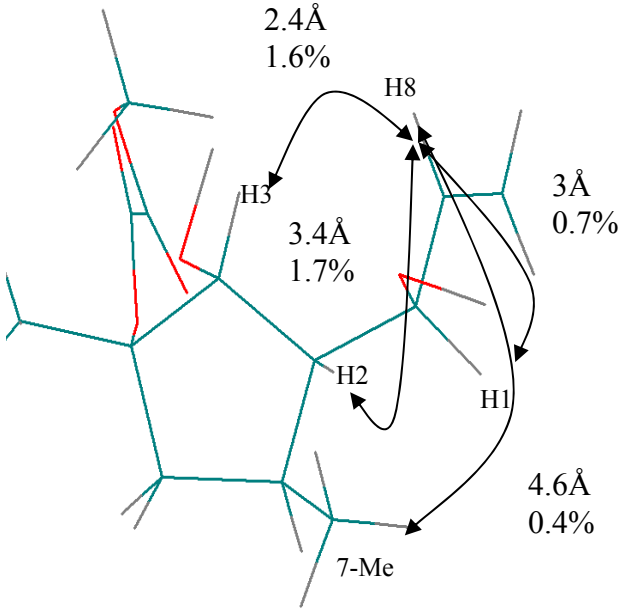


Figure S58: Homodecoupling spectrum of compound **7** (H7 decoupled)





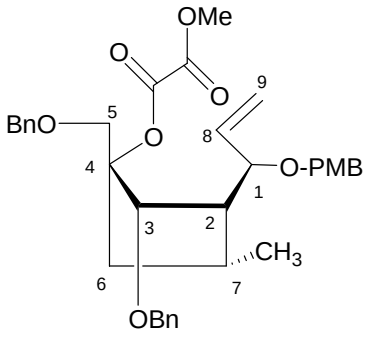
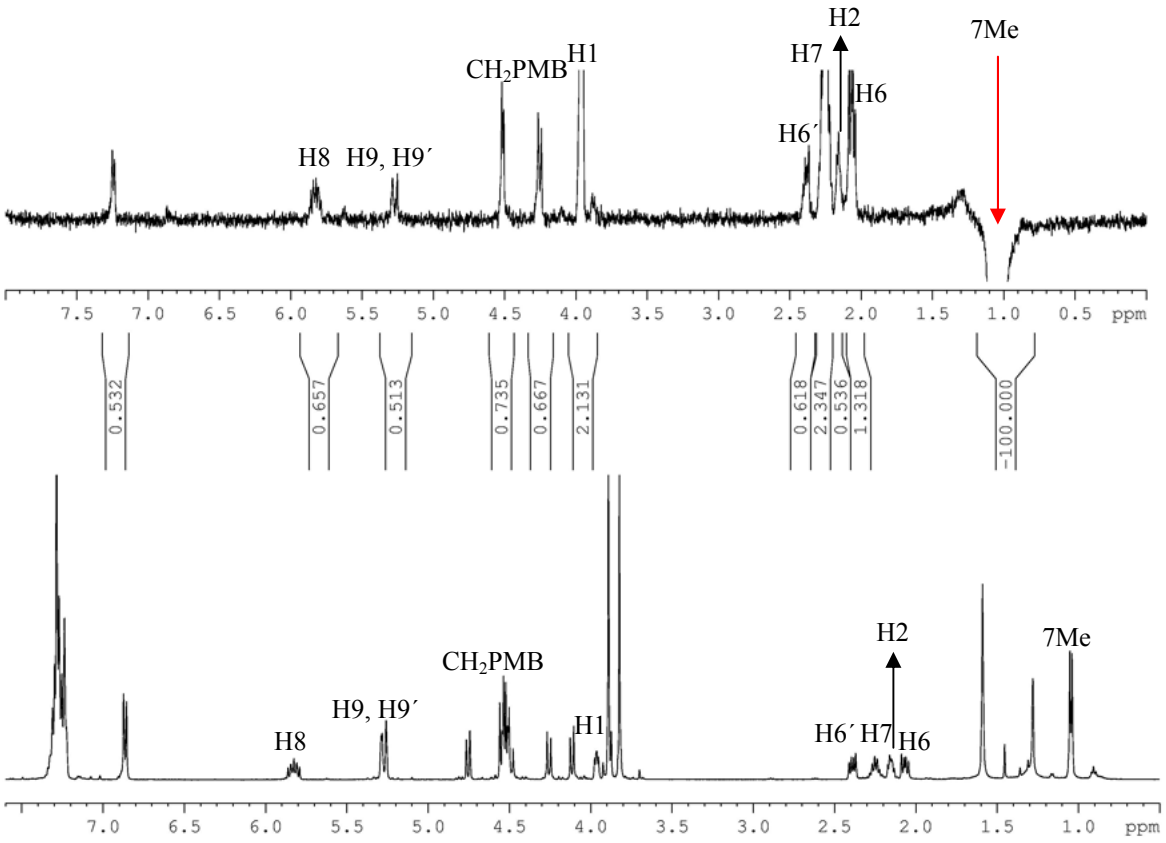
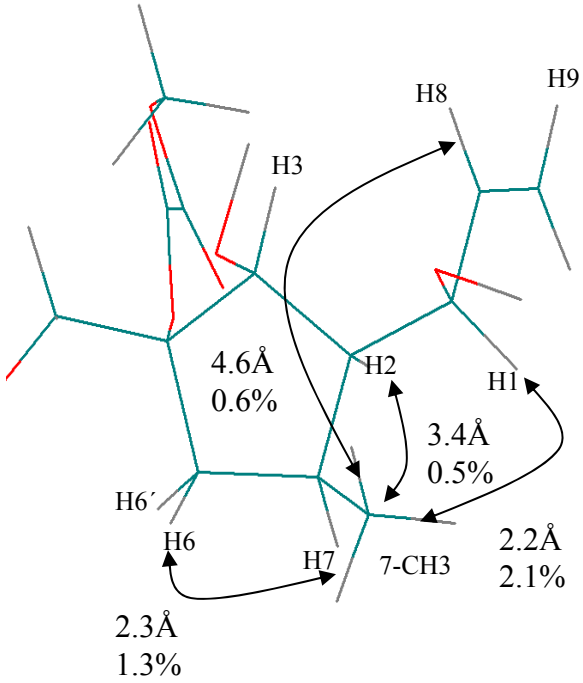


Figure S59: 1D nOe spectrum of compound **8** (H8 irradiated)





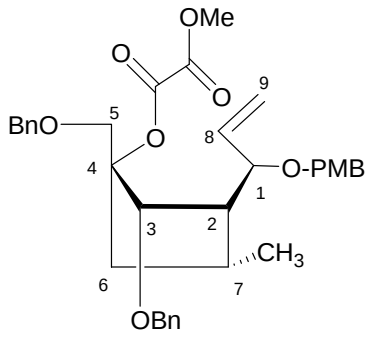
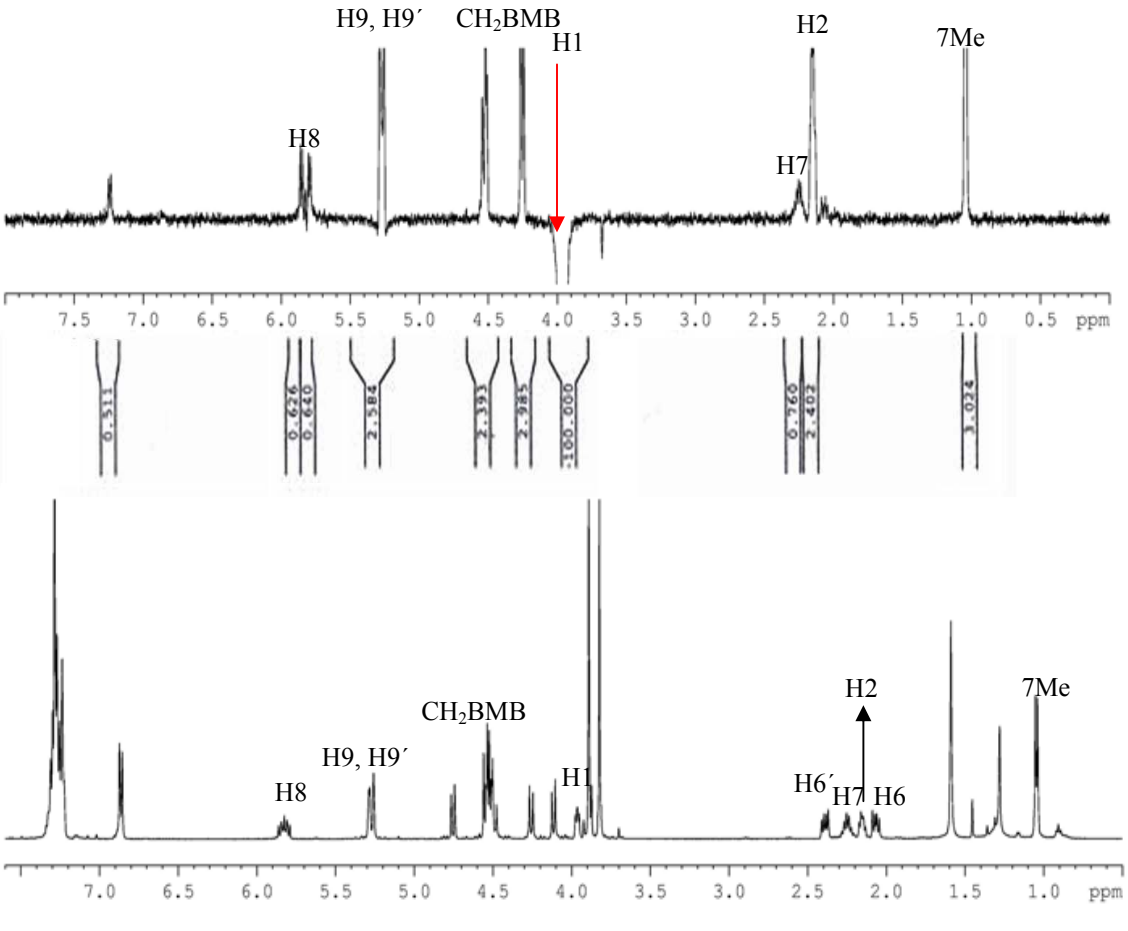
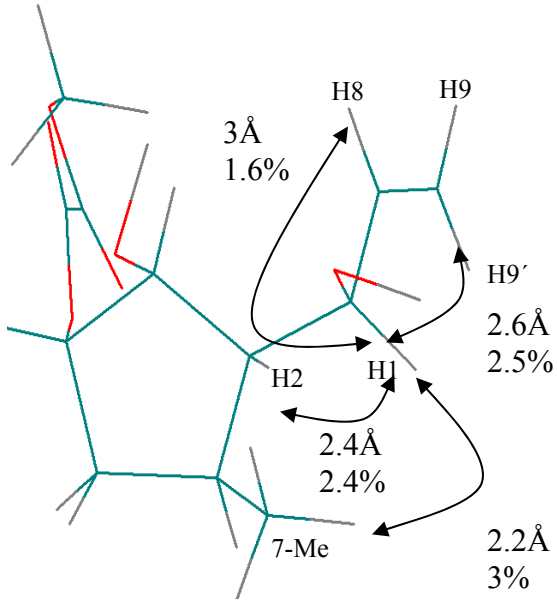


Figure S60: 1D nOe spectrum of compound **8** (7Me irradiated)





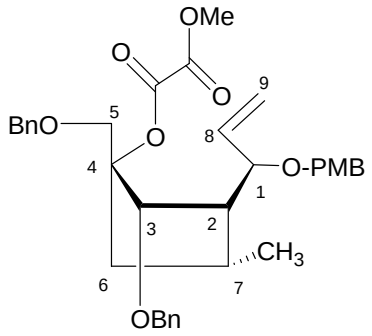
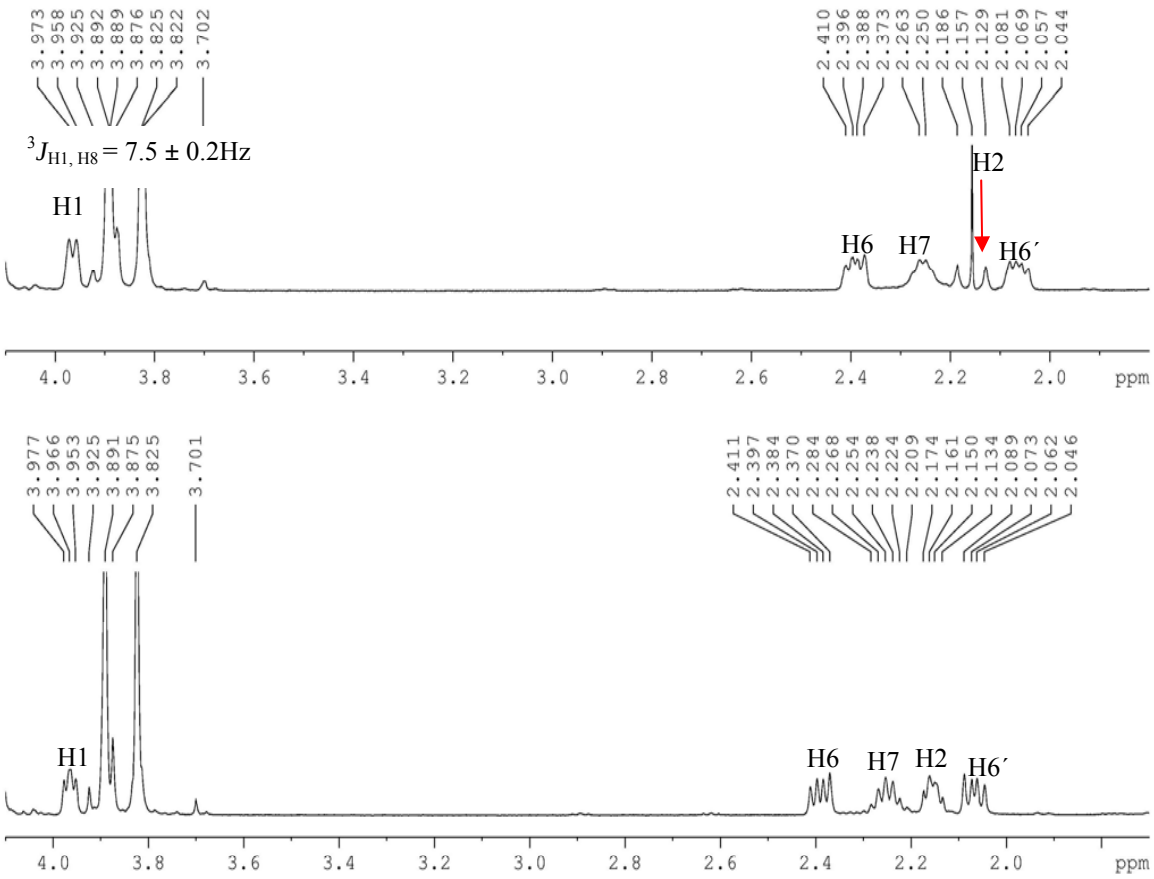
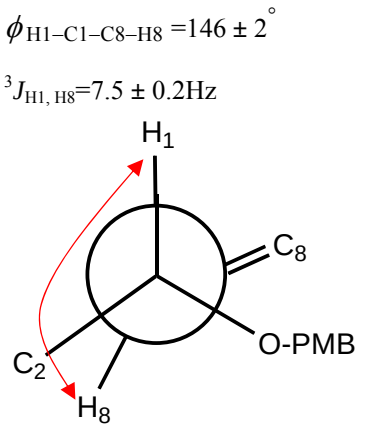


Figure S61: 1D nOe spectrum of compound **8** (H1 irradiated)





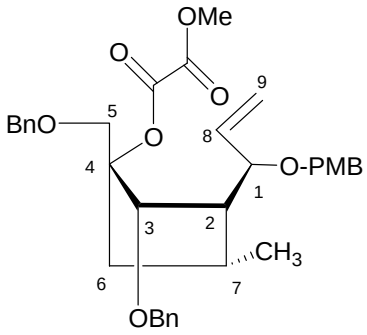


Figure S62: Homodecoupling spectrum of compound **8** (H2 decoupled)

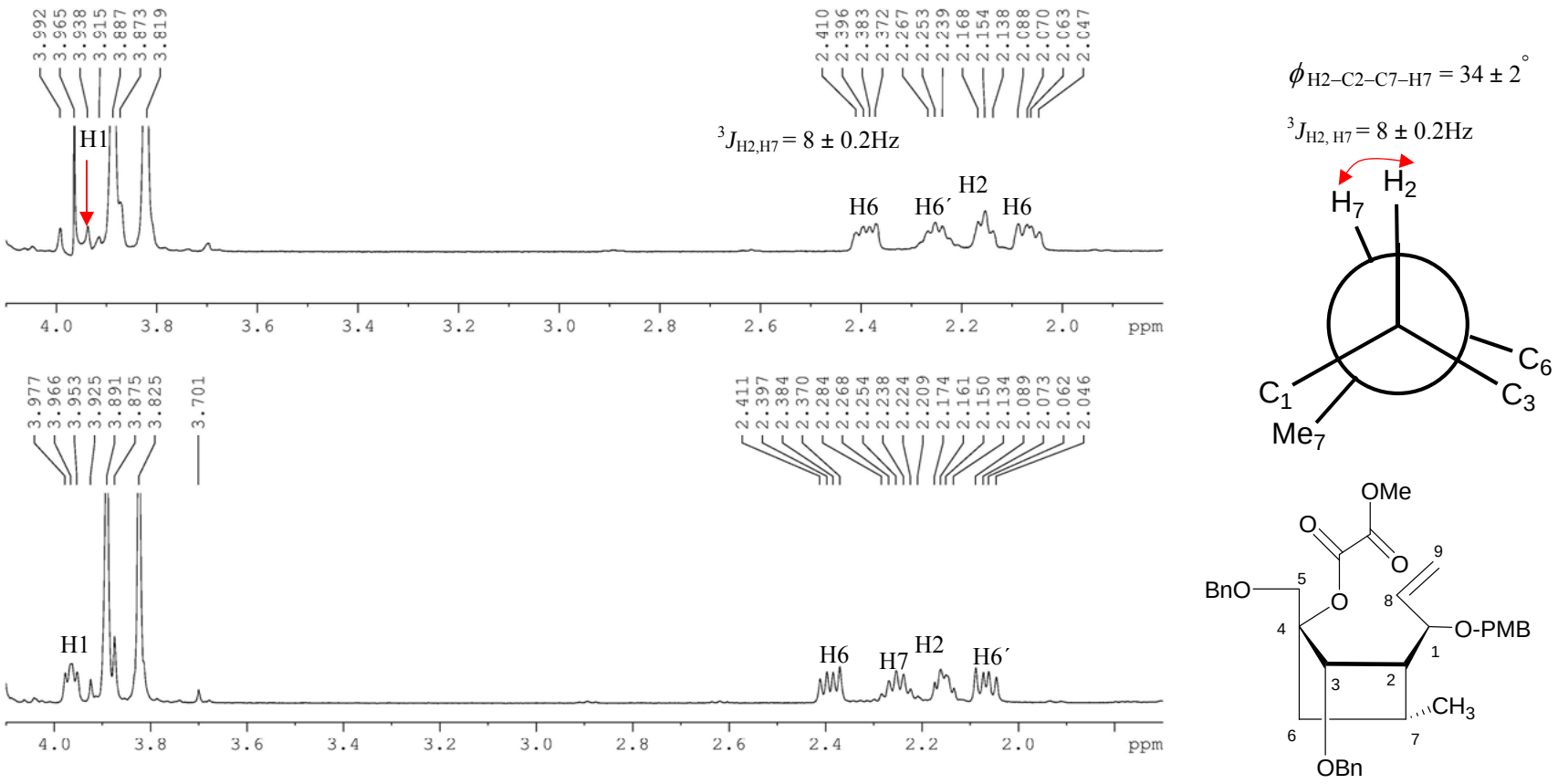
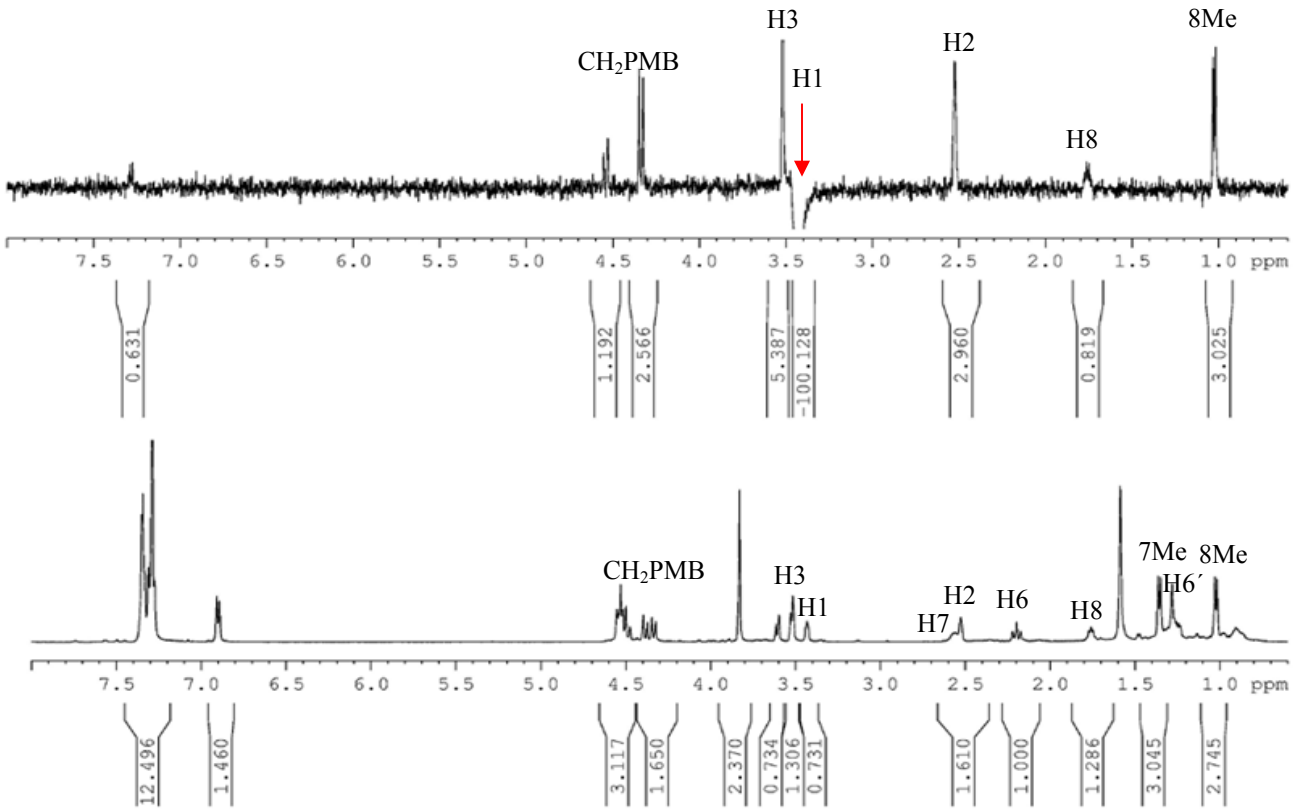
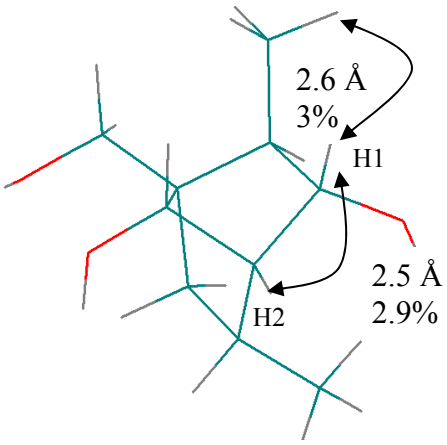


Figure S63: Homodecoupling spectrum of compound **8** (H1 decoupled)





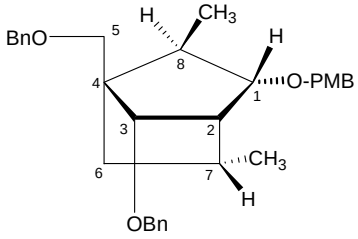
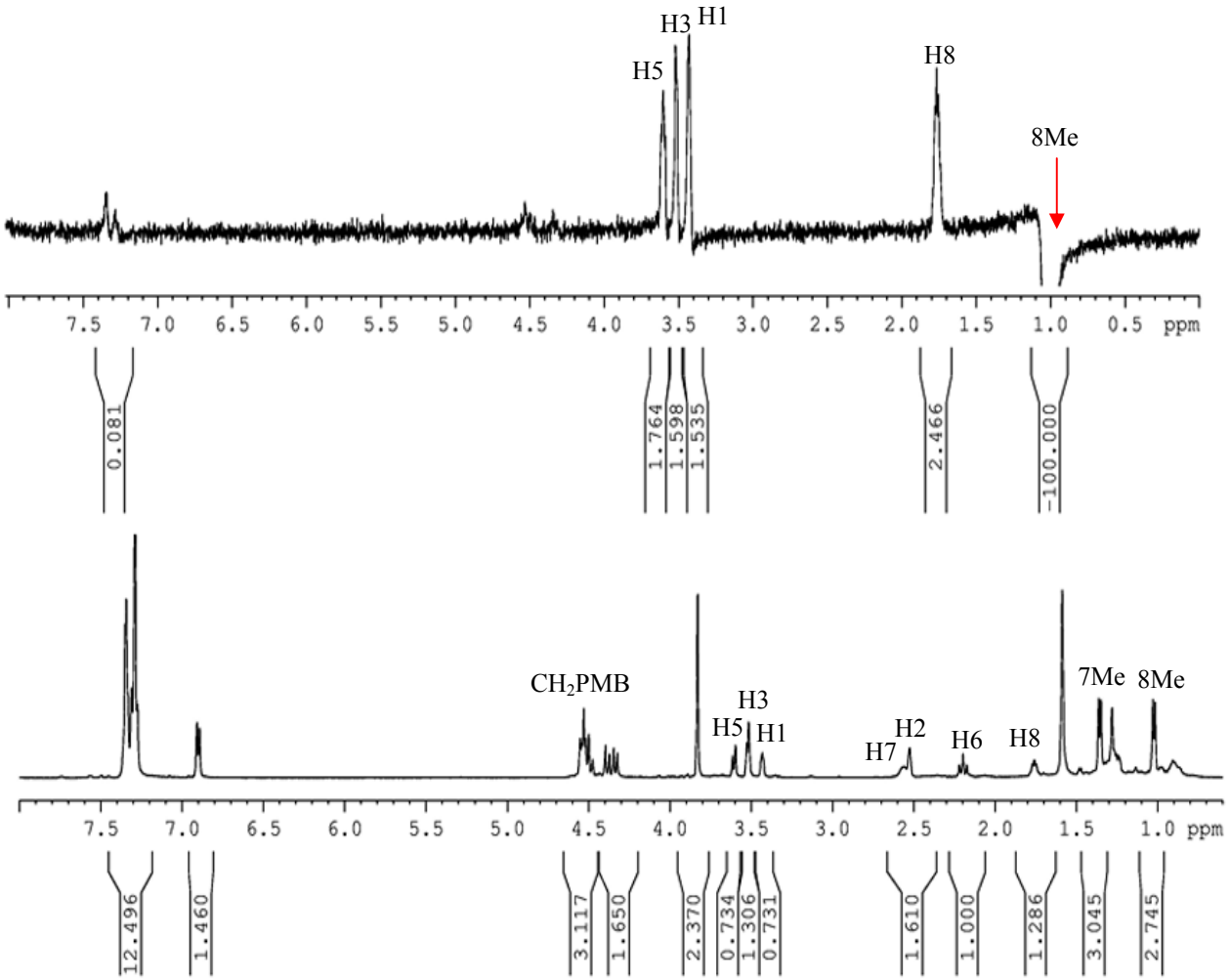


Figure S64: 1D nOe spectrum of compound **9** (H1 irradiated)



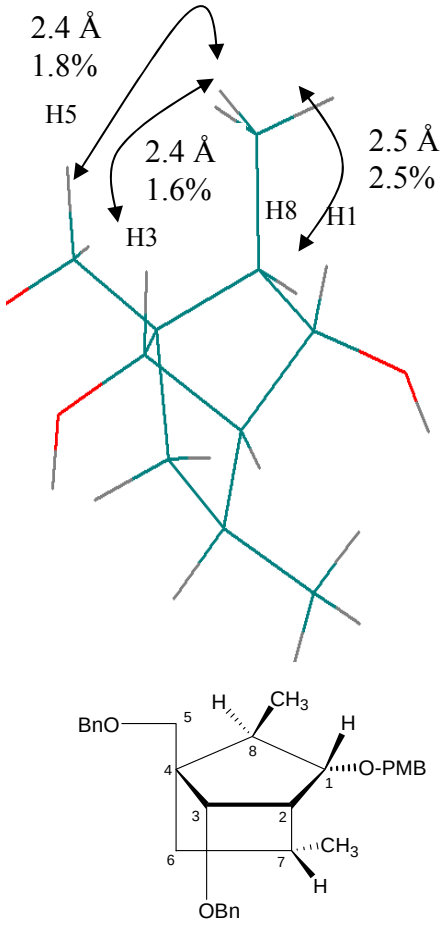
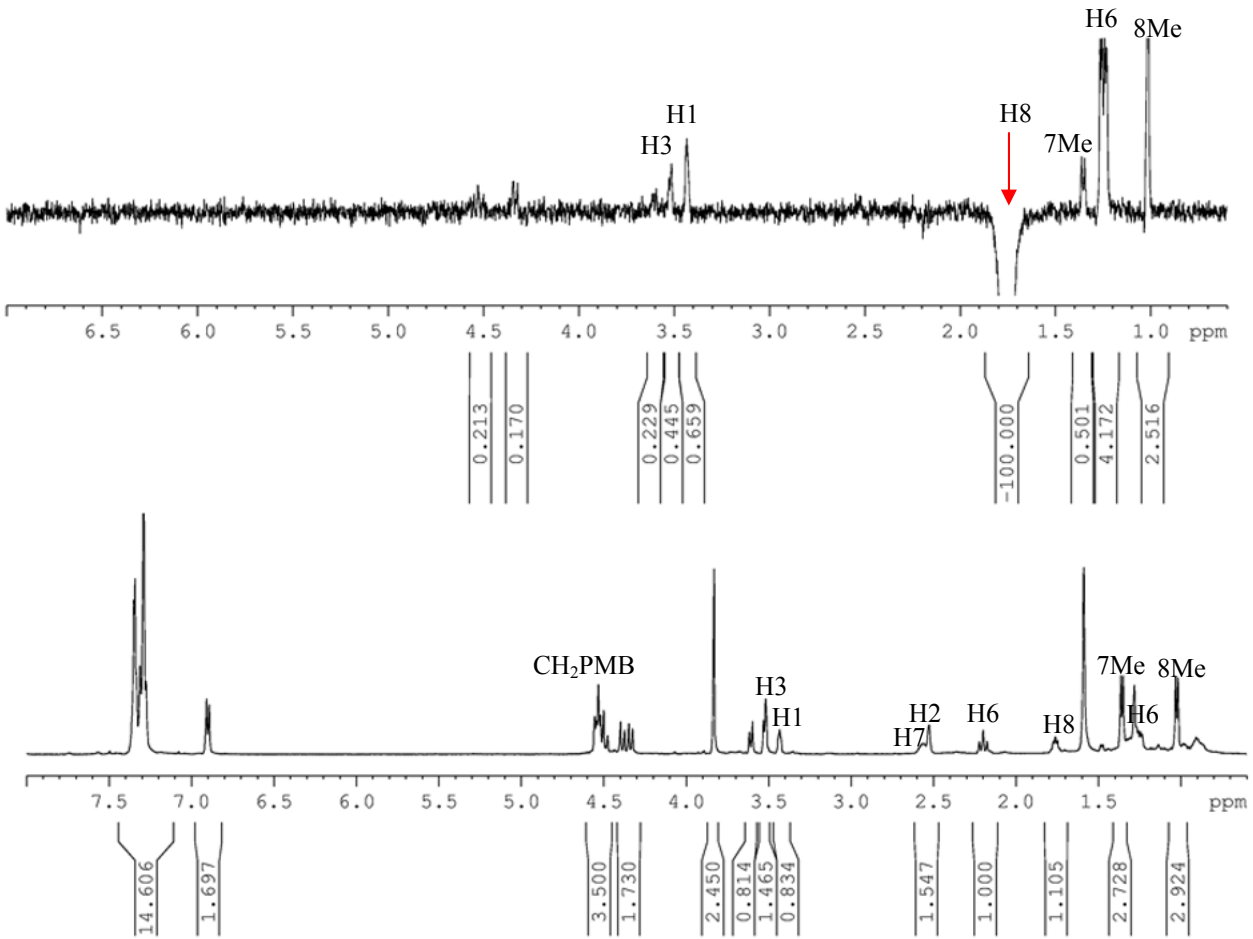
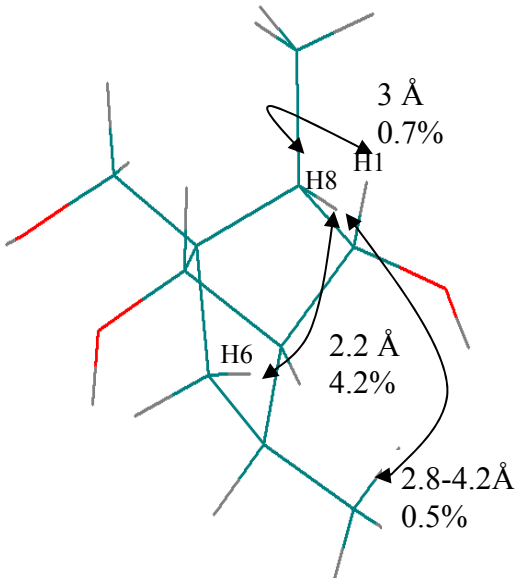


Figure S65: 1D nOe spectrum of compound **9** (8Me irradiated)





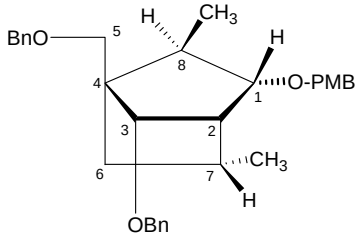
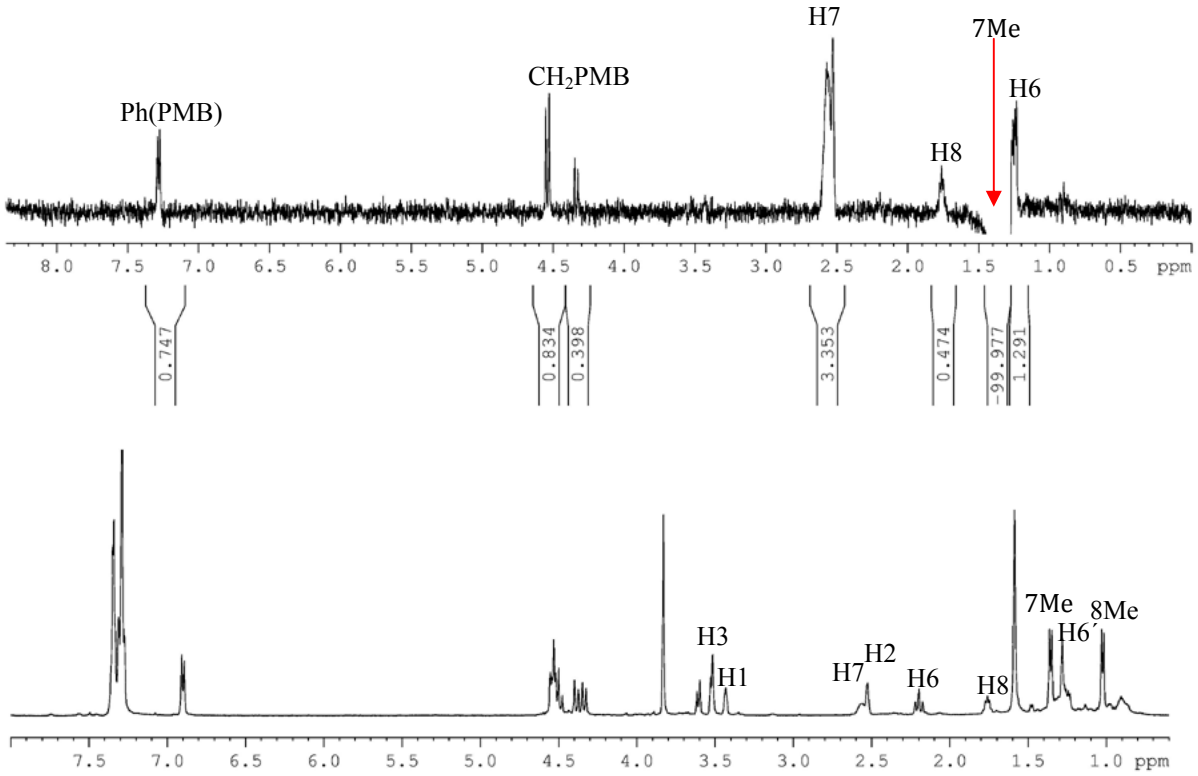


Figure S66:1D nOe spectrum of compound **9** (H8 irradiated)



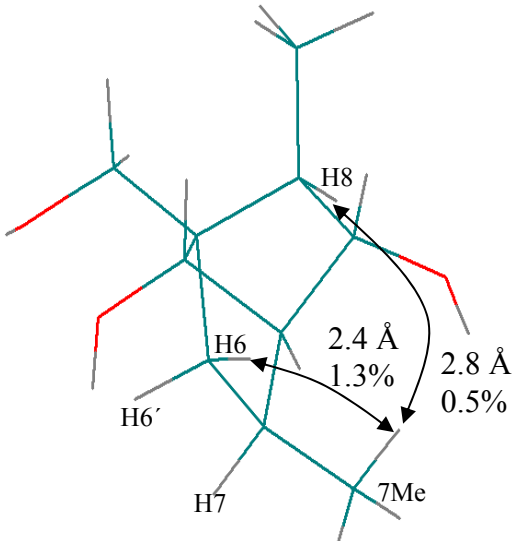
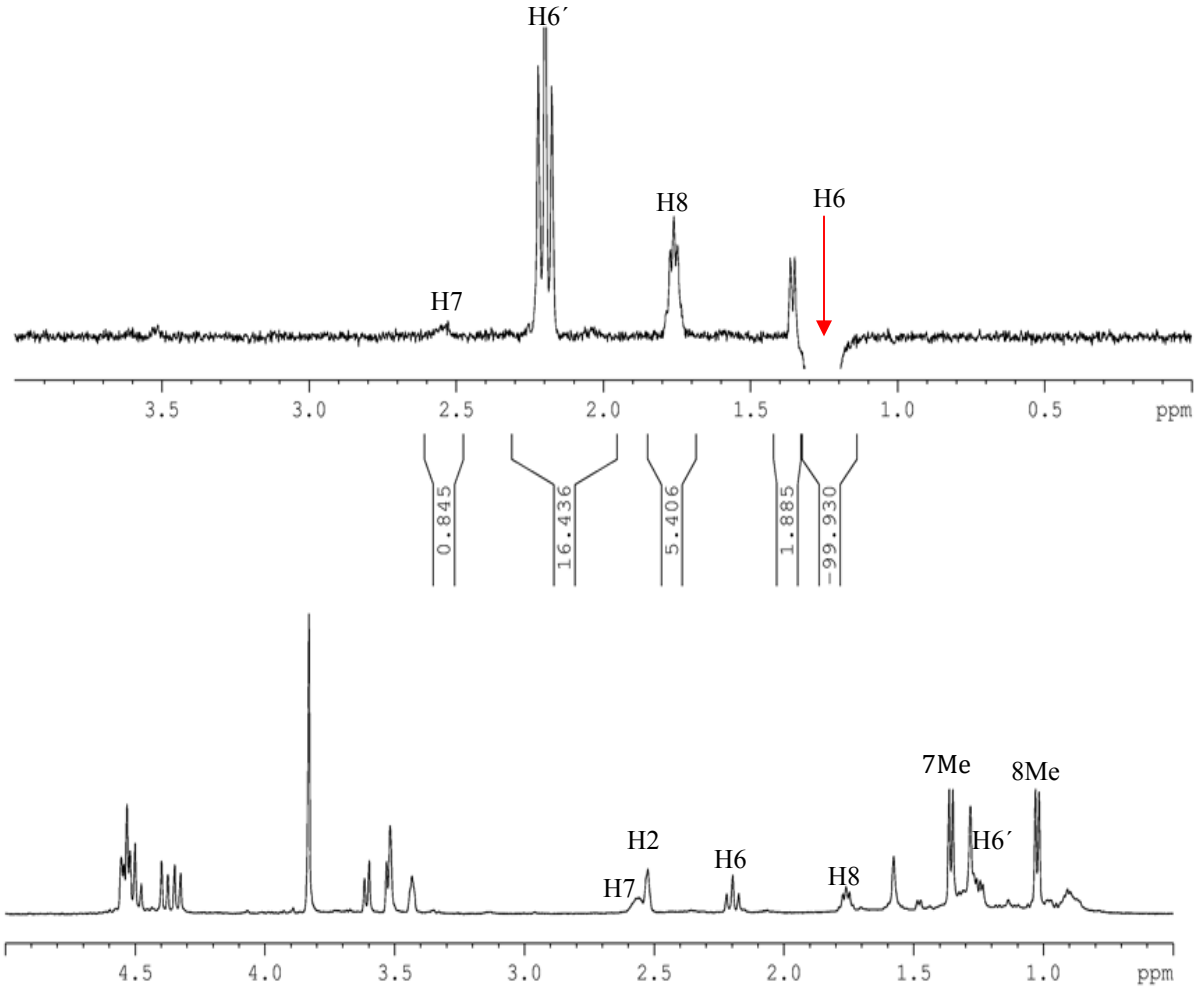
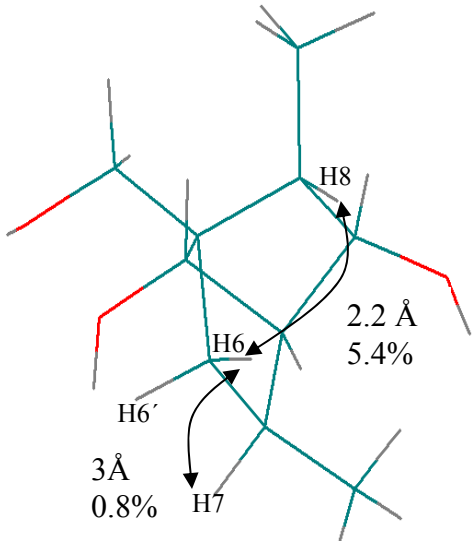


Figure S67:1D nOe spectrum of compound **9** (7-Me irradiated)





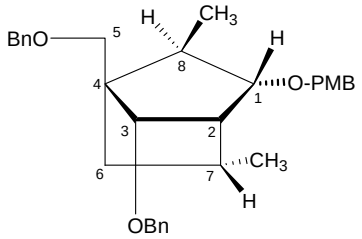
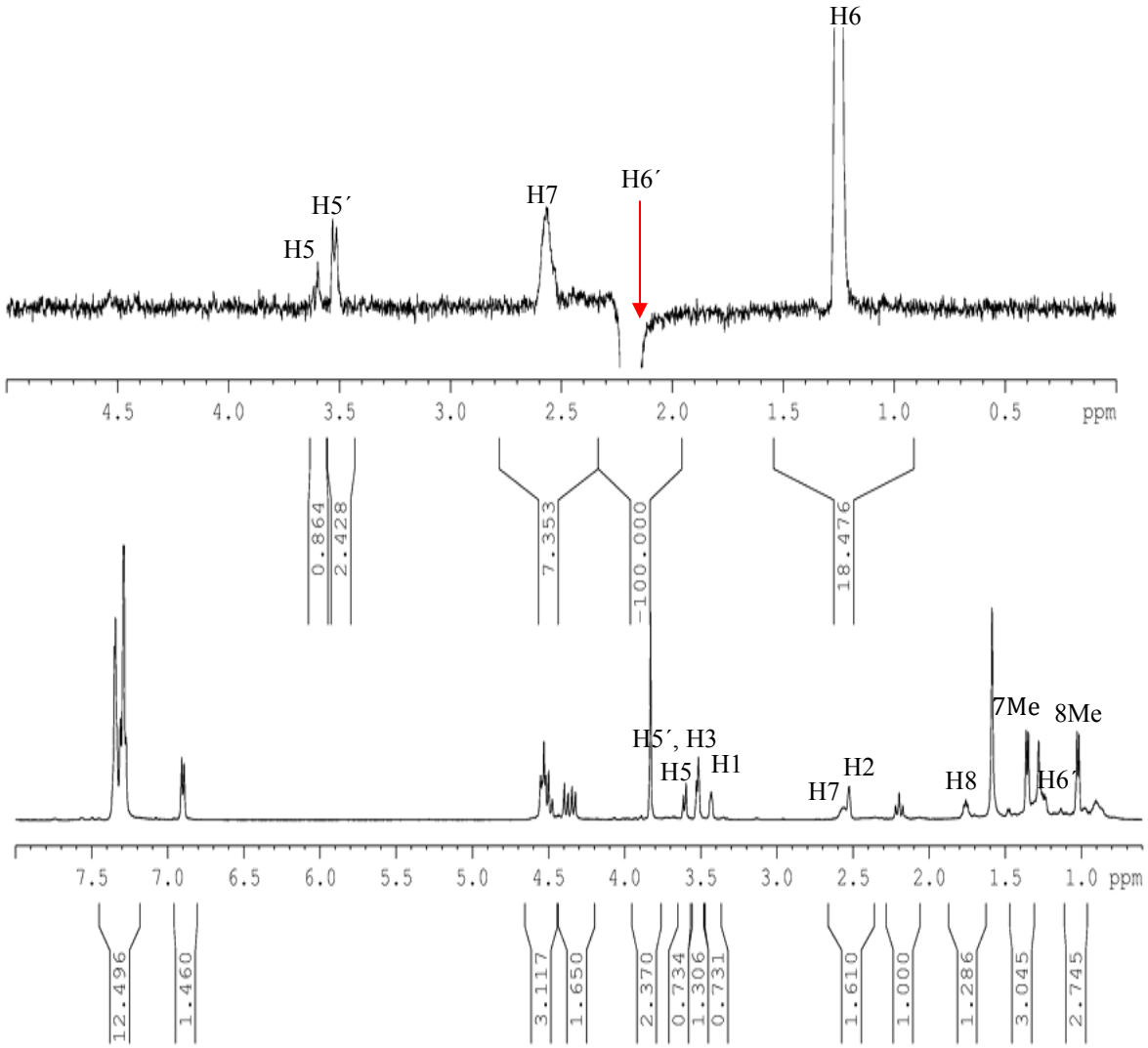
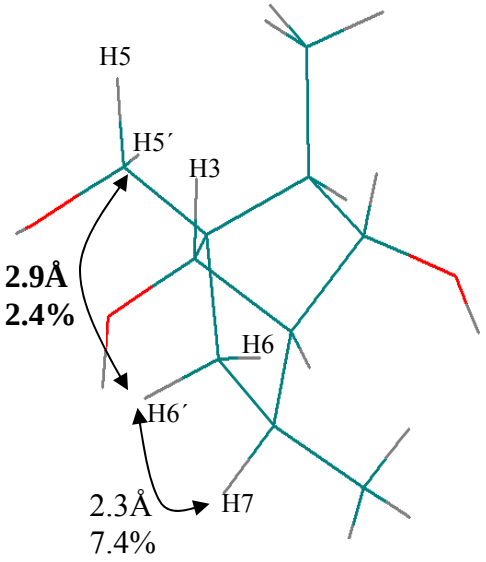


Figure S68:1D nOe spectrum of compound **9** (H6 irradiated)





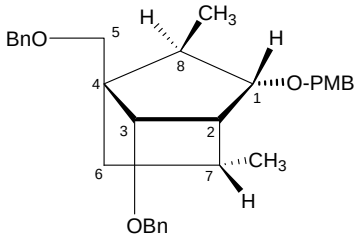
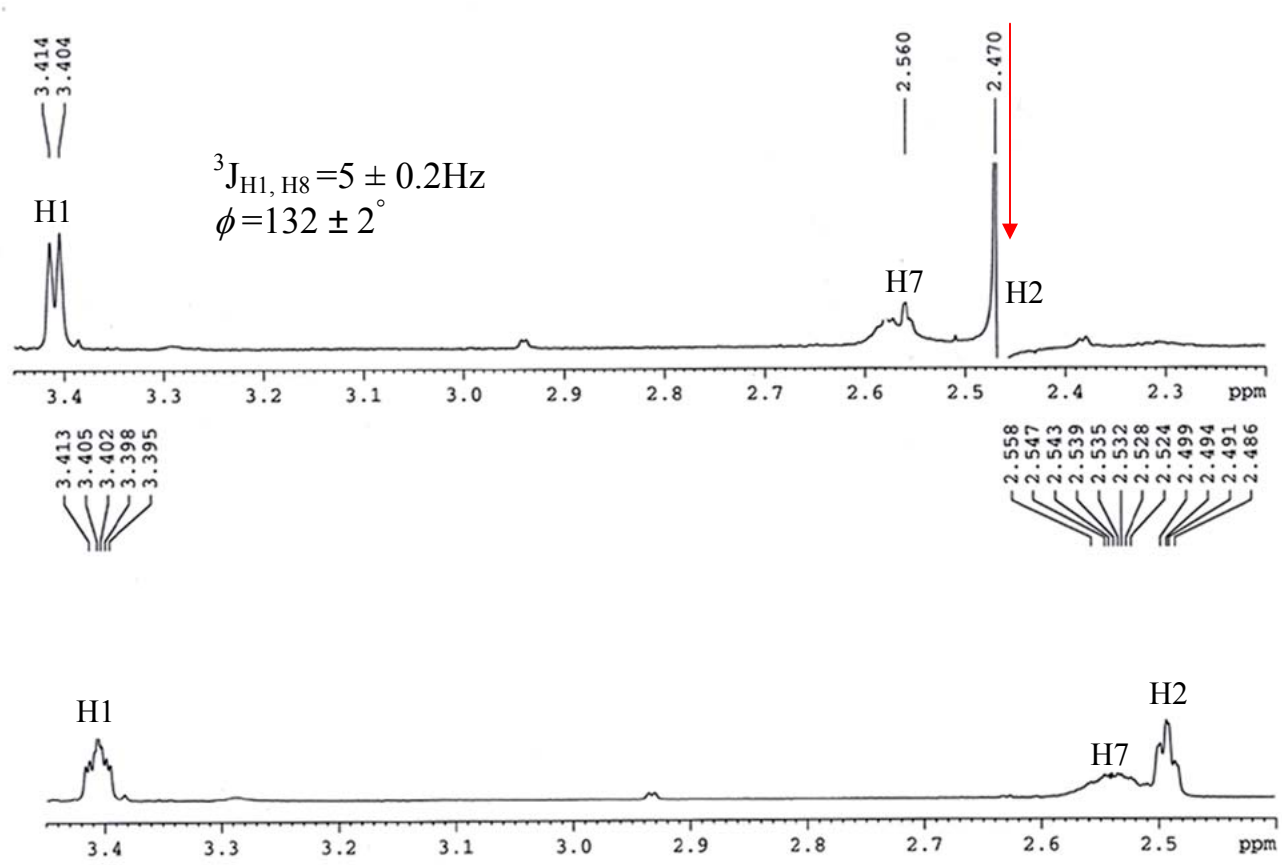
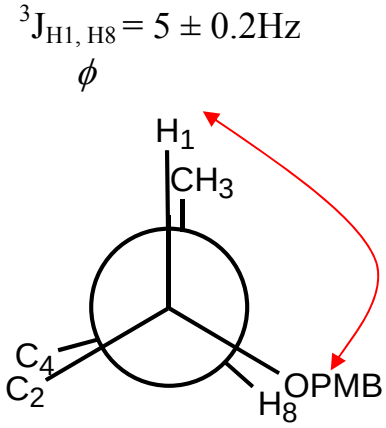


Figure S69:1D nOe spectrum of compound **9** (H6´ irradiated)





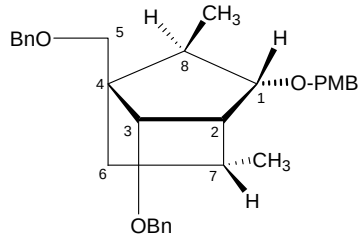


Figure S70: Homodecoupling spectrum of compound **9** (H2 decoupled)

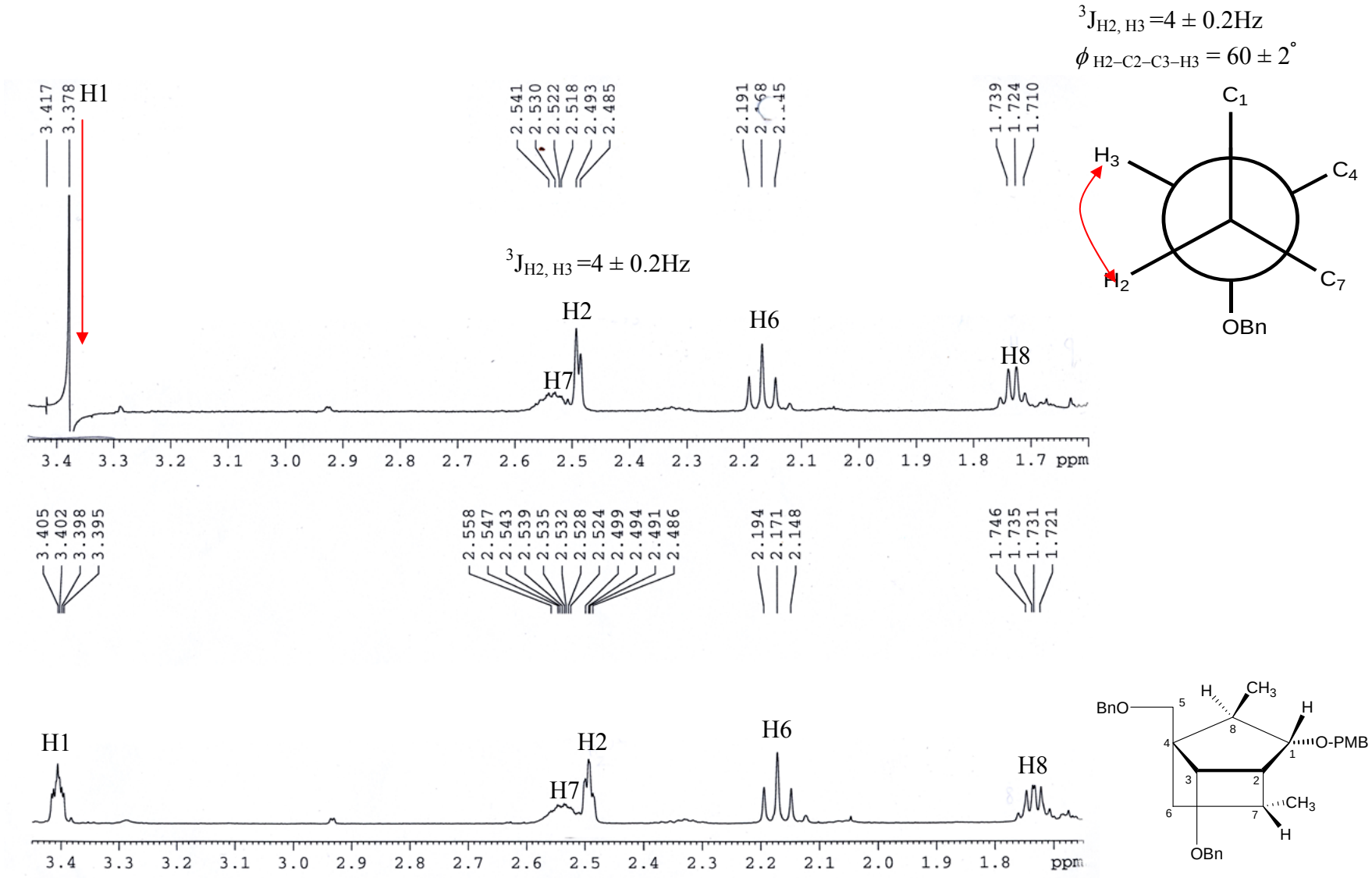
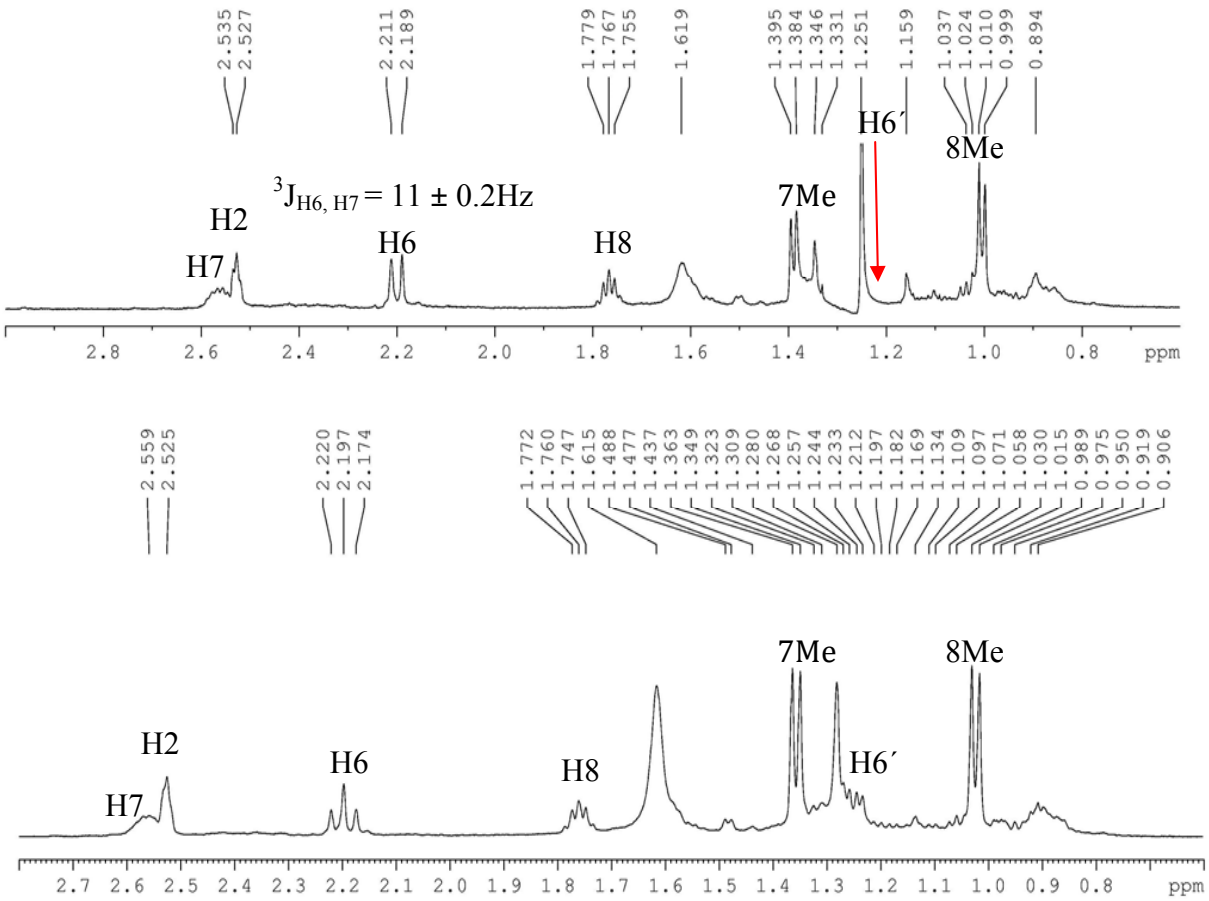
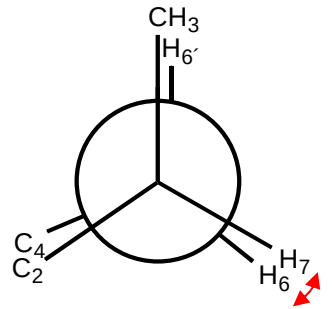


Figure S71: Homodecoupling spectrum of compound **9** (H1 decoupled)





$\phi_{H6–C6–C7–H7} = 7 \pm 2^{\circ}$

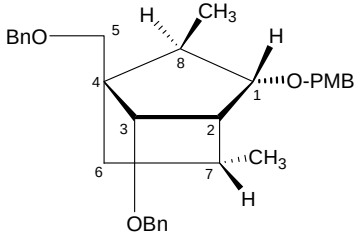


Figure S72: Homodecoupling spectrum of compound **9** (H6´ decoupled)

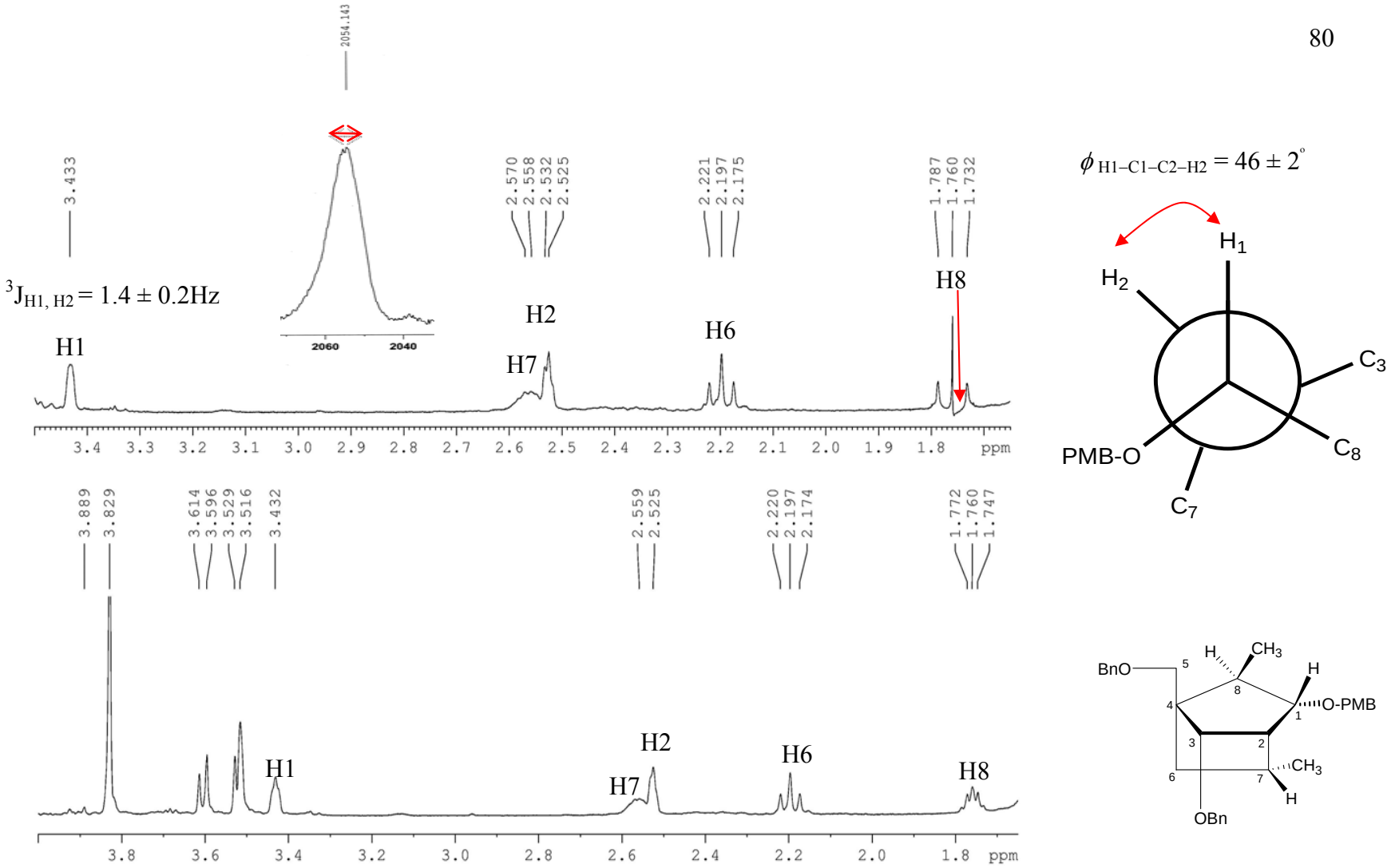
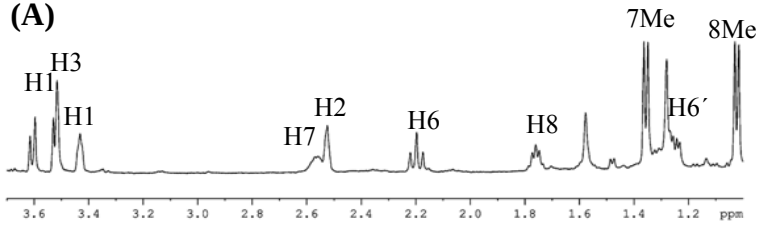
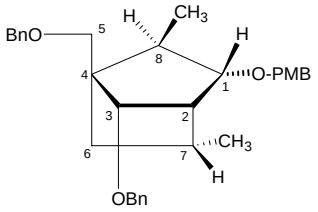


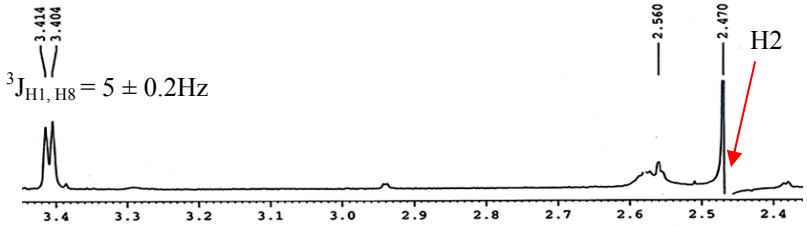
Figure S73: Homodecoupling spectrum of compound **9** (H8 decoupled)

(A)



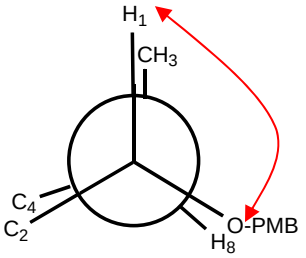


(A₁)

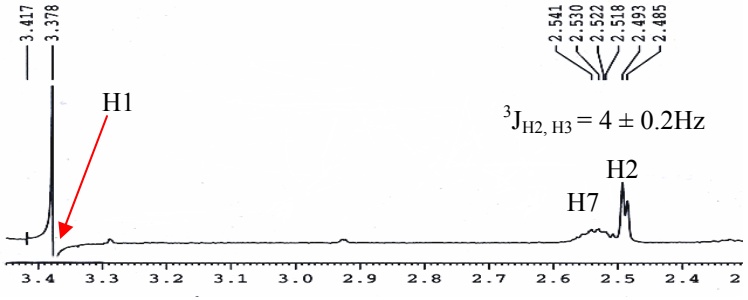


$^{3}J_{H1,\,H8} = 5 \pm 0.2\text{Hz}$

$\phi_{H1-C1-C8-H8} = 132 \pm 2^{\circ}$

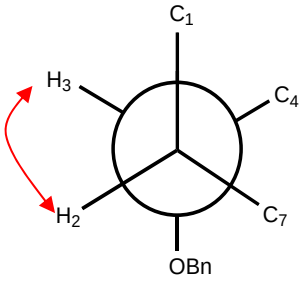


(A₂)

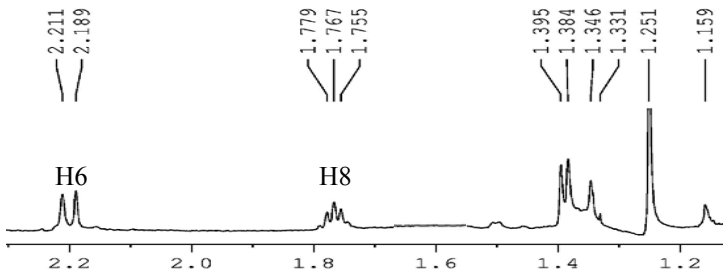


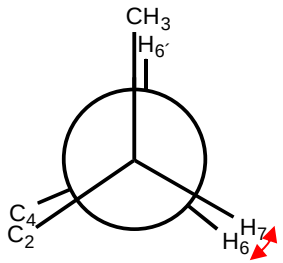
$^{3}J_{H2,\,H3} = 4 \pm 0.2\text{Hz}$

$\phi_{H2-C2-C3-H3} = 60 \pm 2^{\circ}$



(A_3)





$\phi_{H6–C6–C7–H7} = 7 \pm 2°$

Figure S74: Homonuclear ^{1}H-decoupling spectra and the Newman projections for compound **9**. Panel A_1 shows the Newman projection across the C1-C8 where decoupling of H2 shows $^3J_{H1,H8} = 5 \pm 0.2$Hz, Panel A_2: The Newman projection across the C2-C3 where decoupling of H1 shows $^3J_{H2,H3} = 4 \pm 0.2$Hz, Panels A_3 show the Newman projection across C7-C6 where H8 and H6´are decoupled. These derived $^3J_{H6,\ H7} = 11 \pm 0.2$Hz.

H8 irradiation in (**7**)	Distance (Å)	nOe obs (%)	**H7 irradiation** in (**15**)	Distance (Å)	nOe (%)	obs
$d_{H1,H8}$	3	1.2	$d_{H7,H1}$	3.1	0.9	
$d_{H2,H8}$	3.4	1.4	$d_{H7,H2}$	3.1	1.0	
$d_{H3,H8}$	2.7	1.4	$d_{H7,H3}$	3.7	0.4	
H1 irradiation in (**7**)	Distance (Å)	nOe obs (%)	**H1 irradiation** in (**15**)	Distance (Å)	nOe (%)	obs
$d_{H1,H2}$	2.5	3.6	$d_{H1,H2}$	2.6	1.8	
$d_{H1,H3}$	3.7	2.7	$d_{H1,H3}$	4.3	1.8	
$d_{H1,H8}$ *	3	1.7	$d_{H1,H7}$ *	3.1	1.1	
$d_{H1,H9}$	2.6	2.6	$d_{H1,H8}$	2.5	0.9	
$d_{H1,7Me}$	2.1	3.4	___	___	___	
H1 irradiation in (**9**)	Distance (Å)	nOe obs (%)	**H1 irradiation** in (**18a**)	Distance (Å)	nOe (%)	obs
$d_{H1,H2}$	2.5	2.9	$d_{H1,H2}$	2.7	1.9	
$d_{H1,H3}$	2.4	5.4	$d_{H1,H3}$	3.8	0.3	
$d_{H1,8Me}$	2.6	3	$d_{H1,H7}$	3.4	1.0	
$d_{H1,H8}$	3	0.8	$d_{H1,7Me}$	2.5	2.8	
H8 irradiation in (**9**)	Distance (Å)	nOe obs (%)	**H7 irradiation** in (**18a**)	Distance (Å)	nOe (%)	obs
$d_{H1,H8}$	3	0.7	$d_{H7,H1}$	3.4	1	
$d_{H2,H8}$	4.1	___	$d_{H7,H2}$	4.4	0.19	

$d_{H3,H8}$	3.7	0.4	$d_{H7,H3}$	2.5	3.7
$d_{H6,H8}$	2.2	4.2			
8Me irradiation in (**9**)	Distance (Å)	nOe obs (%)	**H7 irradiation** in (**18b**)	Distance (Å)	nOe obs (%)
$d_{H1,8Me}$	2.5	2.5	$d_{H7,H1}$	2.3	9.4
$d_{H2,8Me}$	4.8	___	$d_{H7,7Me}$	2.2	3.3
$d_{H3,8Me}$	2.4	1.6			
$d_{H8,8Me}$	2.5	2.5	**7Me irradiation** in (**18b**)	Distance (Å)	nOe obs (%)
$d_{H5,8Me}$	2.4	1.8			
			H1-7Me		1.6

* We have observed *J*-couplings in these systems, therefore the observed nOe intensity can not be fully trusted.

Table S1: Comparative nOes upon irradiation of different protons in **7**, **15**, **9** and **18a**/**18b**