

Electronic Supplementary Information 2

A Facile and Versatile Preparation of Bilindiones and Biladienones from Tetraarylporphyrins

Takae Yamauchi,^a Tadashi Mizutani,^{a,b} Kenji Wada,^a Shoji Horii,^b Hiroataka Furukawa,^a
Shigeyuki Masaoka,^a Ho-Chol Chang,^a and Susumu Kitagawa^a

^a Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510 Japan

^b Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321 Japan.

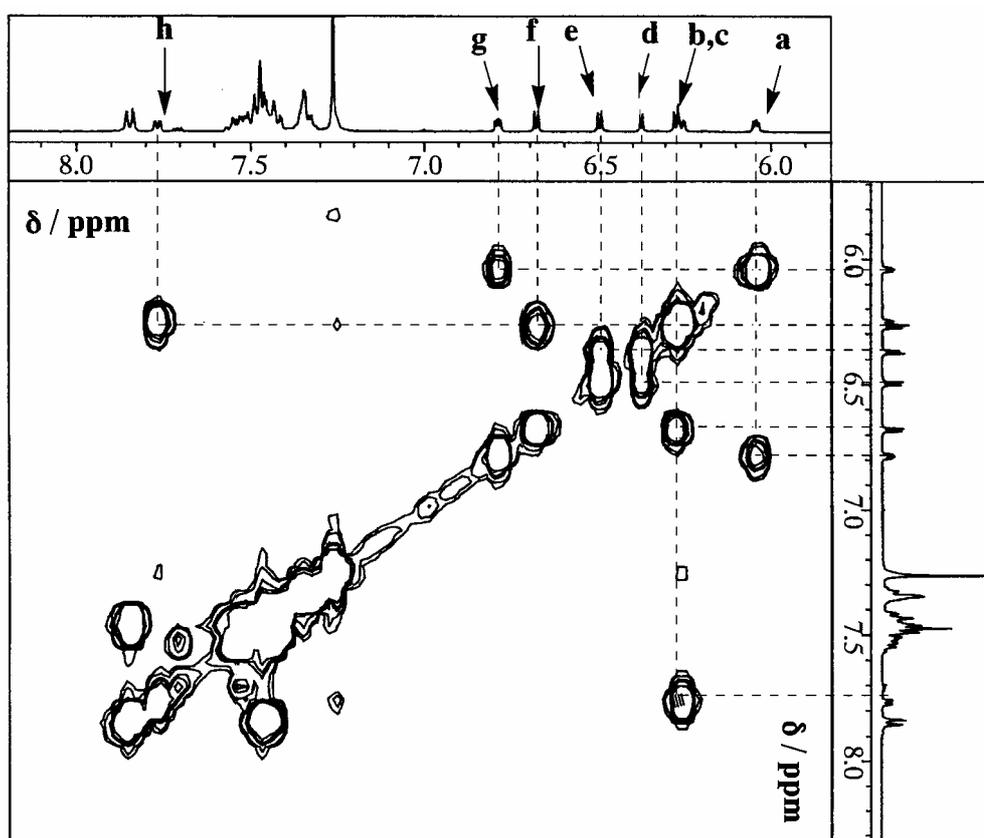


Figure S5. ¹H-¹H COSY of **2** (CDCl₃)

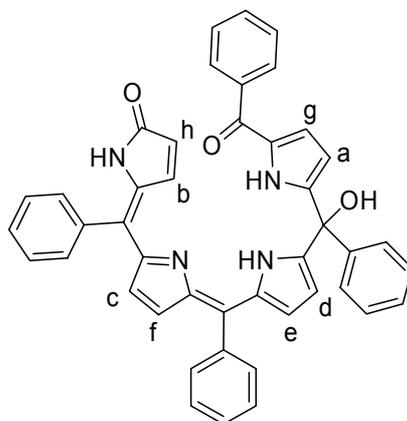


Table S1. β -protons and NH protons in the ^1H NMR spectra of **1** and **2** (CDCl_3)

	1	2	$\Delta\delta(\mathbf{1} - \mathbf{2})$
H-2	6.11 (m)	6.24 (dd)	-0.13
H-3	6.83 (d)	7.74 (dd)	-0.91
H-7	6.14 (d)	6.32 (d)	-0.18
H-8	6.72 (d)	6.68 (d)	0.04
H-12	6.44 (d)	6.50 (d)	-0.06
H-13	6.11 (m)	6.40 (d)	-0.29
H-17	6.11 (m)	6.07 (dd)	0.04
H-18	6.78 (dd)	6.80 (dd)	-0.02
NH ring A	10.75	7.2	3.55
NH ring D	9.87	9.78	0.09
NH ring B + C	12.46	10.86	1.6

$\Delta\delta(\mathbf{1-2})$ is smaller than 0.25 except for H-3, H-13, NH_A , and NH_{B+C} . A similar trend was observed for ^1H NMR spectra of *ZZ*- and *ZE*-*meso*-butylbiladienone.

Table S2. C-13 signals assigned by HMQC and HMBC of **1** and **2** (CDCl₃)

Protons	δ , ppm (multiplicity)		
	1 ^a	2	$\Delta\delta(\mathbf{1} - \mathbf{2})$
C-1	173.2		
C-2	124.4	125.7	-1.3
C-3	137.7	127.2	+10.5
C-4	139.4		
C-5	121.3 ^a		
C-6	164.6		
C-7	125.9	120.7	+5.2
C-8	134.6	134.5	+0.1
C-9	149.6		
C-10	142.7 ^a		
C-11	132.1		
C-12	125.3	126.3	-1.0
C-13	111.3	117.9	-6.6
C-14	149.7		
C-15	76.7		
C-16	142.5		
C-17	109.9	110.5	-0.6
C-18	119.8	119.5	+0.3
C-19	130.4		
C-20	184.6		

^a Taken from the literature (ref 10).

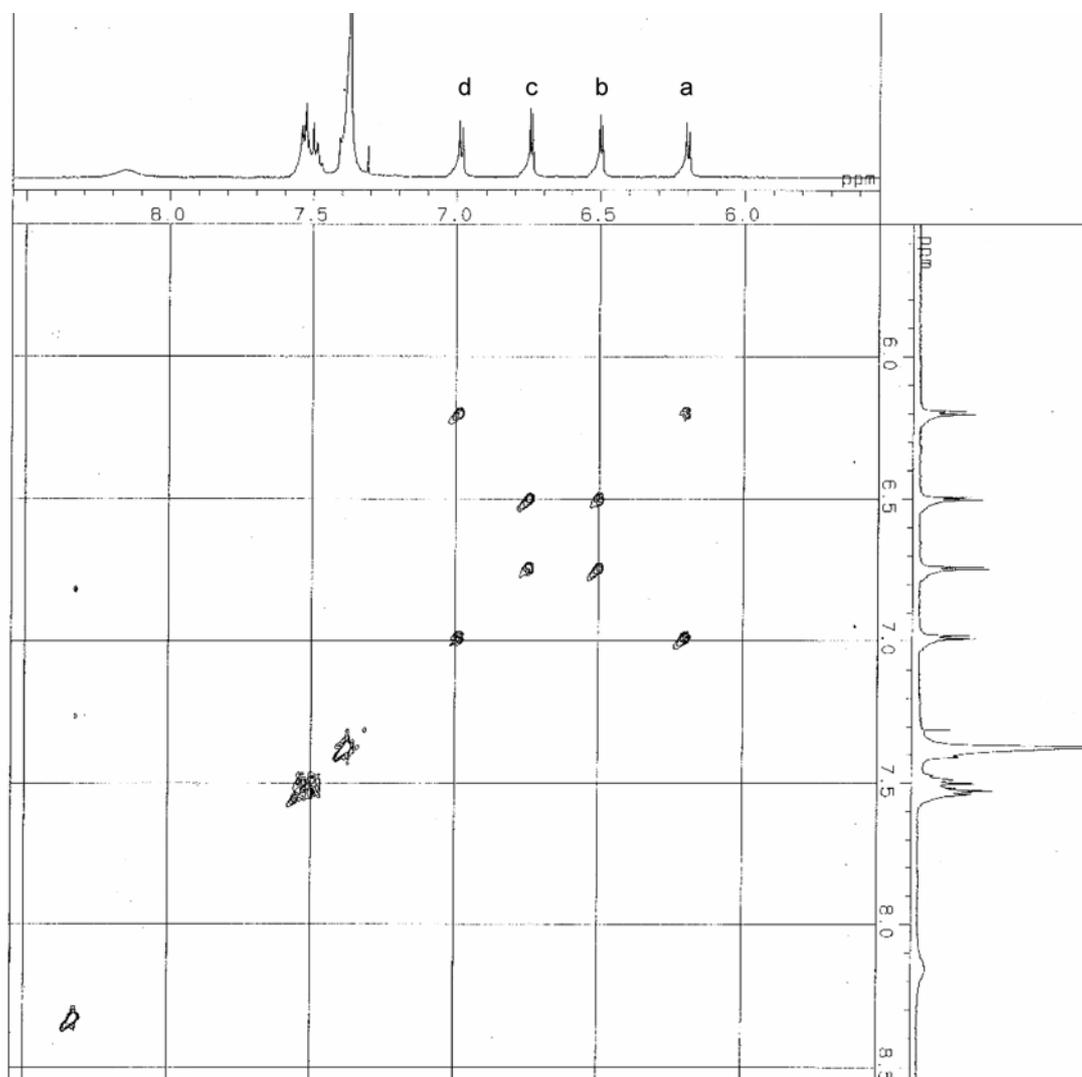


Figure S6. ^1H - ^1H COSY of **3** (CD_2Cl_2)

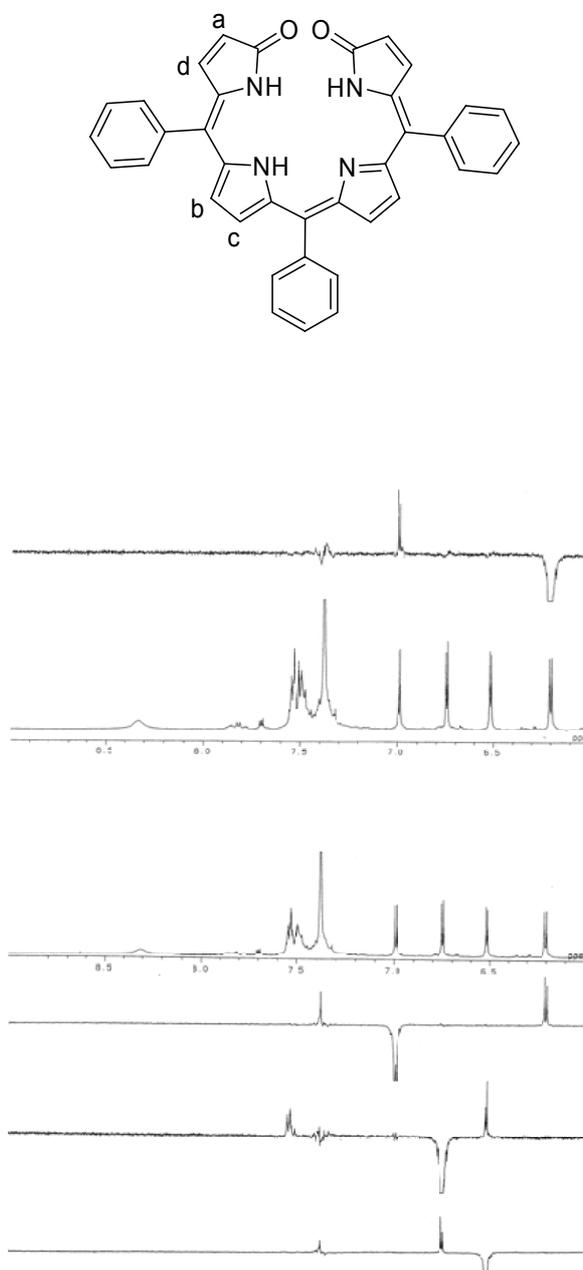


Figure S7. NOE of **3** (CD₂Cl₂)

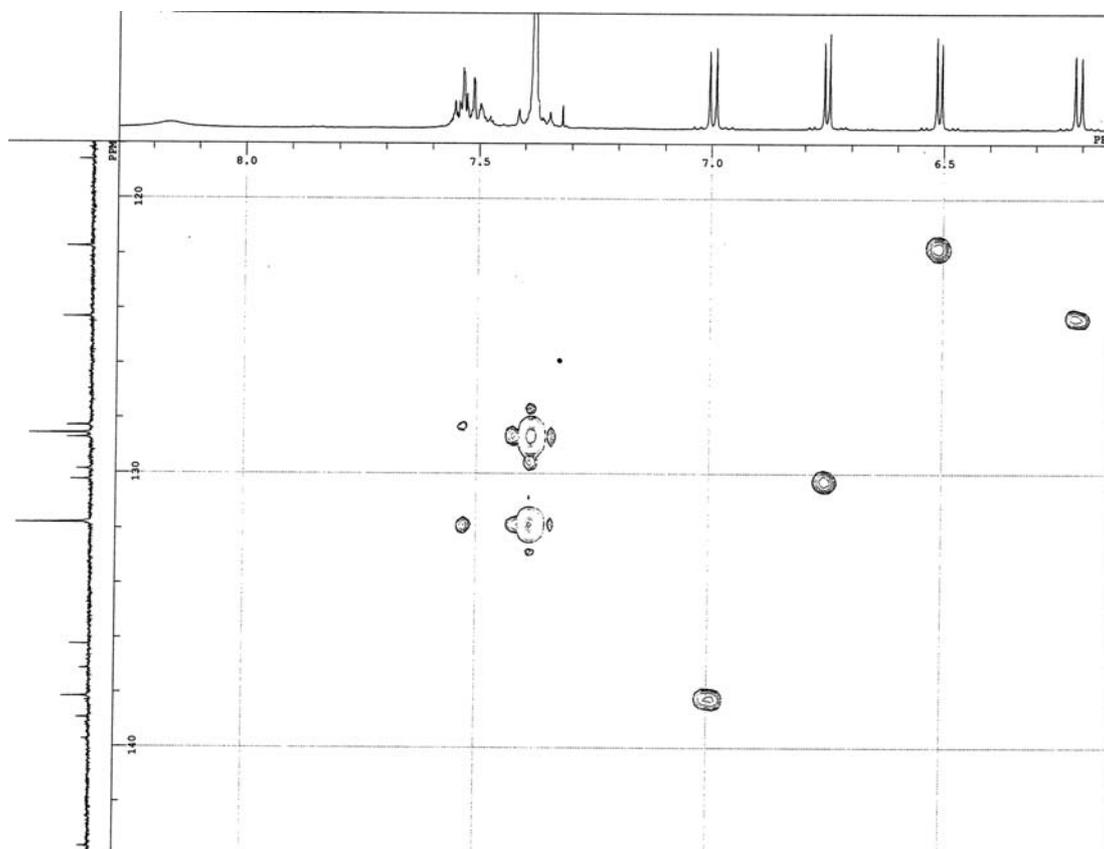


Figure S8. HMQC of **3** (CD_2Cl_2)

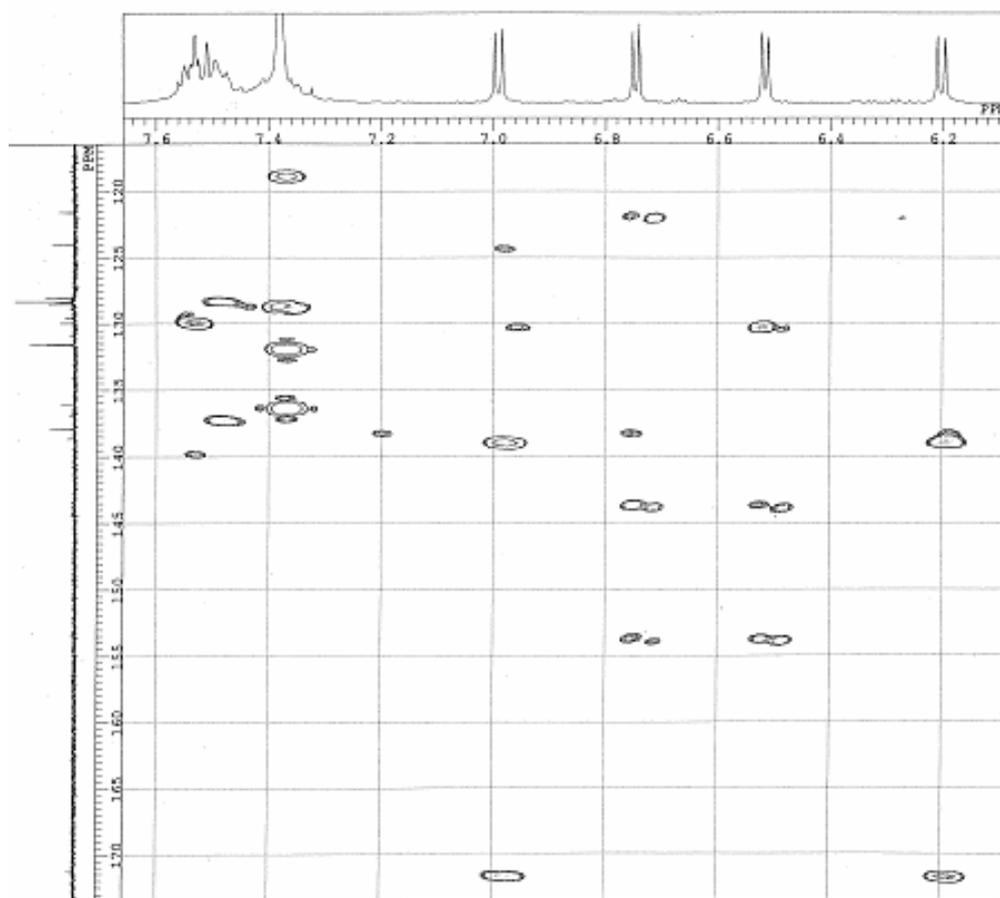


Figure S9. HMBC of **3** (CD_2Cl_2). Both of H-2 and H-3 (at 6.21 and 7.00 ppm) showed correlation with a resonance of the carbonyl C-1 at 171.4 ppm.

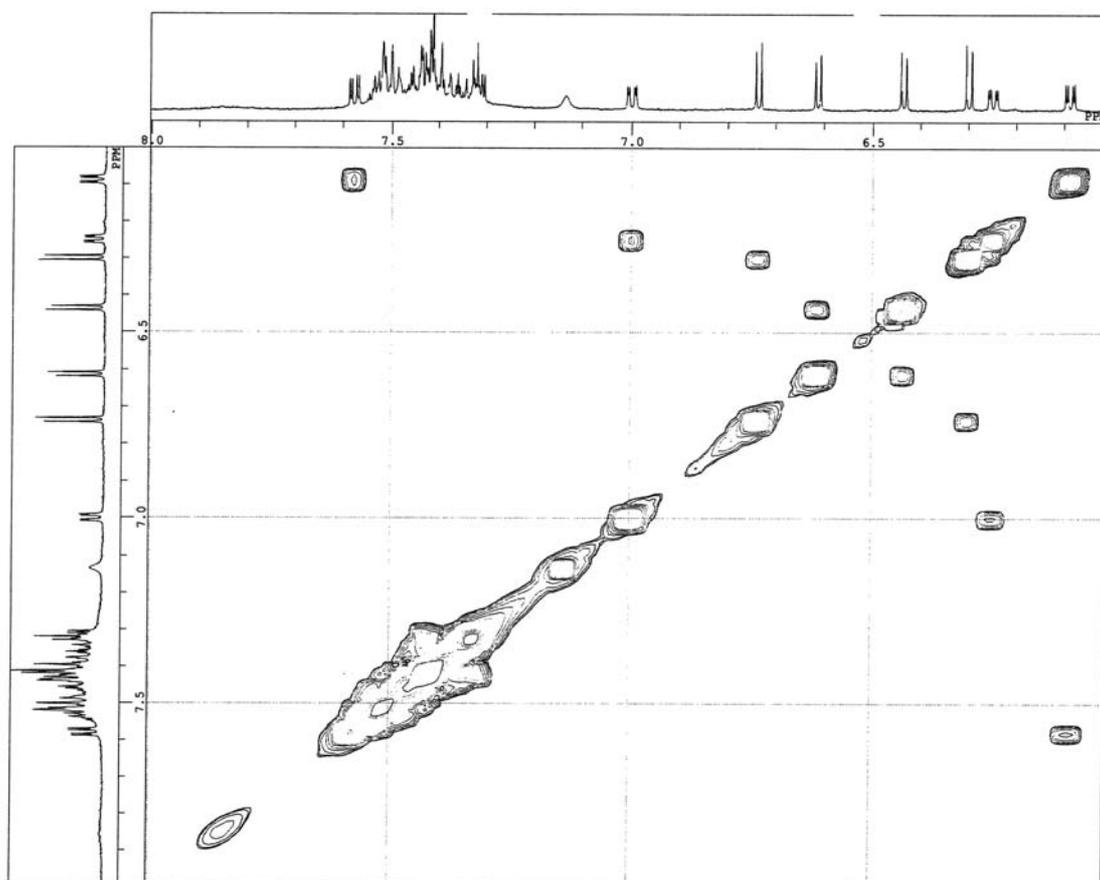


Figure S10. ^1H - ^1H COSY of **4** (CD_2Cl_2)

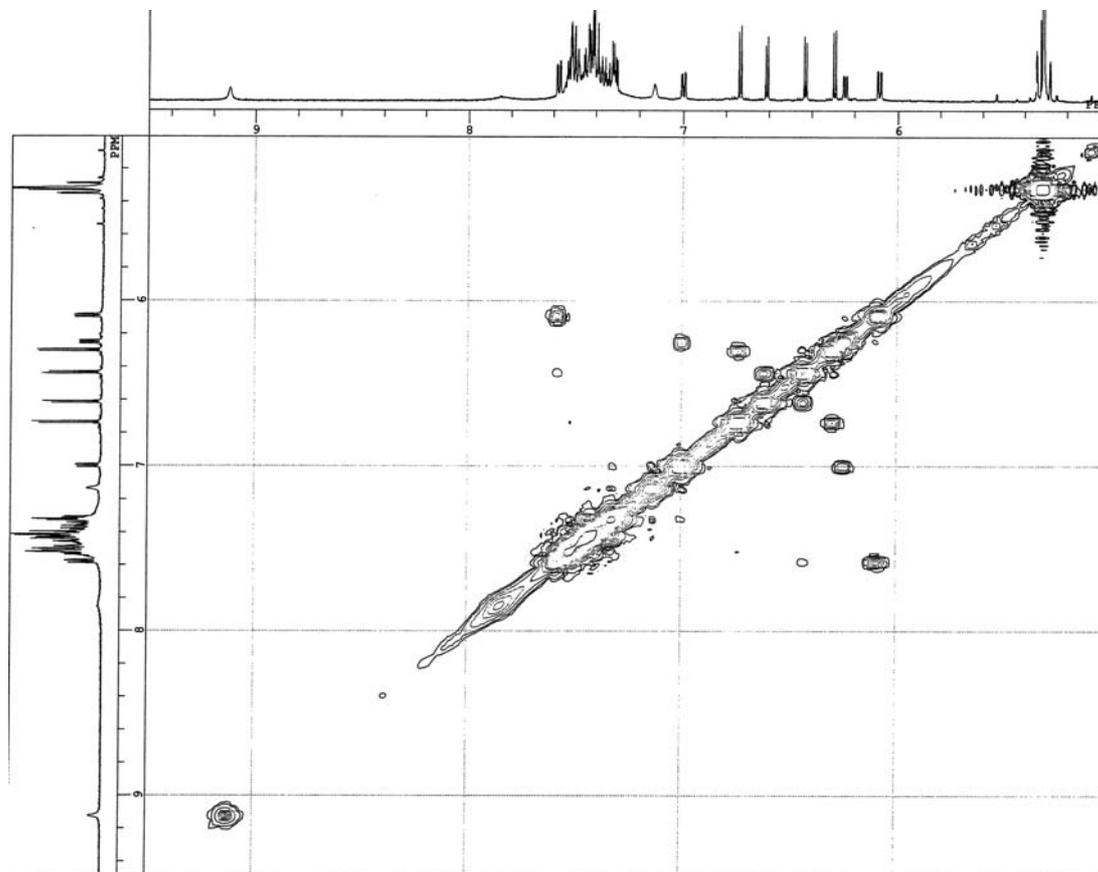


Figure S11. NOESY of **4** (CD_2Cl_2). H-17 at 7.0 ppm showed correlation with the phenyl proton at 7.3 ppm. N-H of the A-ring pyrrole showed correlation with the phenyl proton at 7.3 ppm. No NOE was observed between the phenyl protons and H-2 (6.09 ppm) and H-18 (6.25 ppm). Irradiation of other β -pyrrole protons caused NOE on the phenyl protons.