

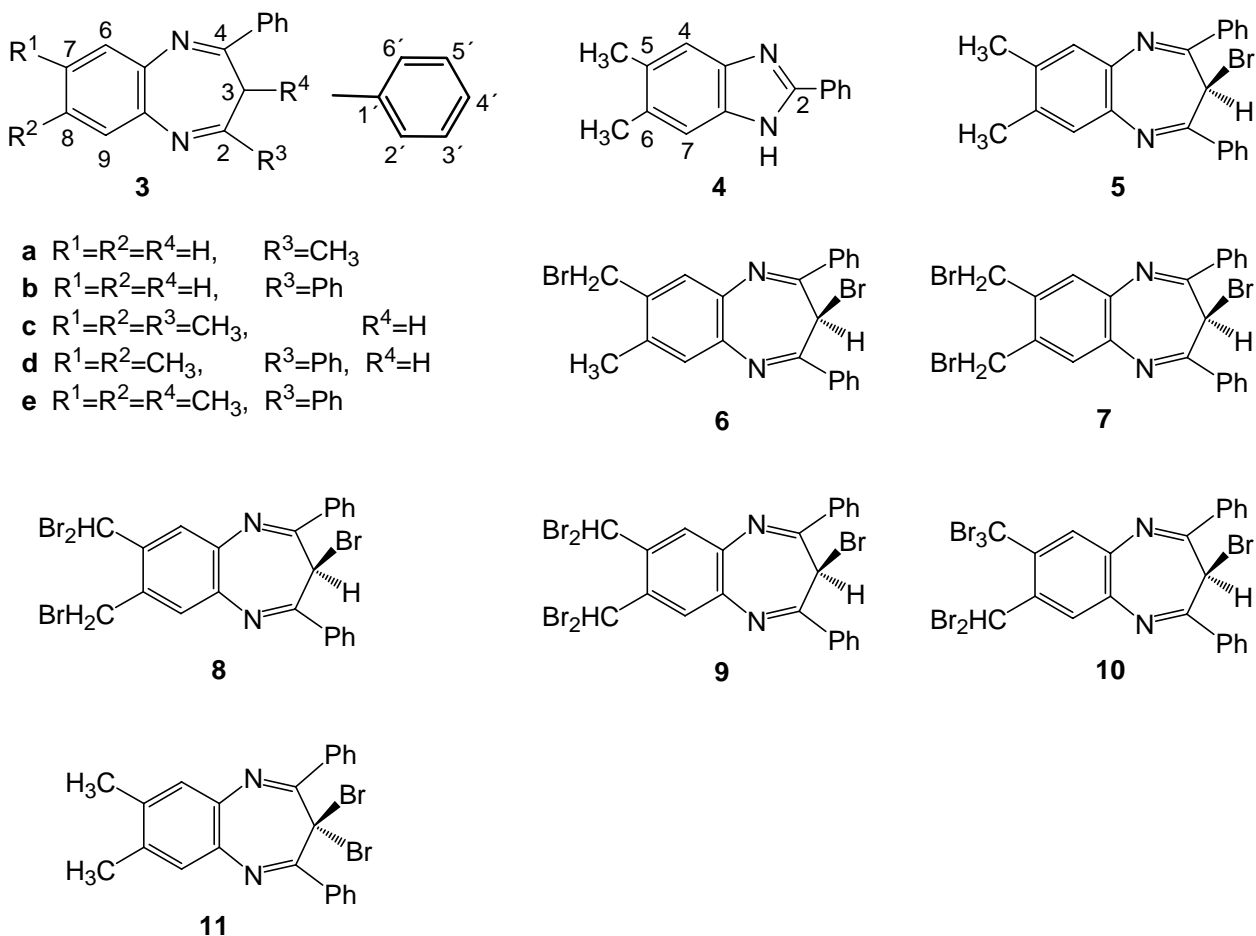
SUPPLEMENTARY INFORMATION

An experimental and theoretical study on the regioselectivity of successive bromination sites of 7,8-dimethyl-2,4-diphenyl-3*H*-1,5-benzodiazepine. Efficient microwave assisted solventless synthesis of 4-phenyl-3*H*-1,5-benzodiazepines

Constantinos A. Tsoleridis,^{1*} Minodora Pozarentzi,¹ Sophia Mitkidou,² and Julia Stephanidou-Stephanatou¹

¹ *Laboratory of Organic Chemistry, Aristotle University of Thessaloniki, Thessaloniki, 54124, Macedonia, Greece*

² *Department of Science, School of Technological Applications, Technological Institute of Kavala, Kavala, Greece*



Scheme S1. The Benzodiazepines **3a–e**, the benzimidazole **4** and the brominated derivatives **5–11** synthesized and studied in this work.

Table S1. ^{13}C -NMR chemical shifts of the studied compounds **3a–11**.

Position	3a	3b	3c	3d	3e	4^e	5	6	7	8	9	10	11
2 ^a	157.9	154.1	156.4	153.0	156.5	151.2	149.4	151.2	151.9	152.9	153.4	153.7	157.3
3	38.5	34.8	38.3	34.9	41.8		35.5	34.9	34.5	34.4	34.3	34.3	29.7
4	153.3	154.1	151.9	153.0	156.5		149.4	150.6	151.9	152.5	153.4	153.5	157.3
5a	140.2	140.7	138.5	138.8	139.3	137.9	139.1	139.1	141.1	141.5	141.6	139.7	138.5
6	127.6	128.7	128.7	129.1	129.1	115.3	129.5	130.5	131.5	131.3	130.2 br	127.7	131.5
7	125.2	125.4	133.8	134.6	134.6	131.5	136.6	135.1	135.1	138.5	135.9 br	137.0	133.2
8	125.0	125.4	134.1	134.6	134.6	131.5	136.6	136.4	135.1	131.1	135.9 br	138.5	133.2
9	128.4	128.7	128.0	129.1	129.1	115.3	129.5	130.7	131.5	130.7	130.2 br	136.0	131.5
9a	140.6	140.7	138.2	138.8	139.3	137.9	139.1	141.2	141.1	141.6	141.5	142.6	138.5
1' ^b	137.0	137.2	137.1	137.5	137.5	130.3	137.4	137.2 ^f	136.7	136.5 ^f	136.5	136.5 ^f	137.4
2',6'	128.1	128.1	127.9	128.1	127.9	126.7	127.8	127.8	127.9	128.0	128.1	128.2	128.2
3',5'	128.7	128.6	128.6	128.7	128.6	128.8	129.0	129.0	129.0	129.1	129.2	129.2	129.0
4'	130.7	130.5	130.3	130.4	130.1	129.6	130.8	131.0	131.6	131.4 ^g	131.7	131.8	131.2
R ¹ =Me ^c			19.25	19.5	19.4	20.4	19.7	31.7	29.7	36.2	35.8	30.0	19.5
R ² =Me ^c			19.33	19.5	19.4	20.4	19.7	18.7	29.7	28.9	35.8	37.2	19.5
R ³ =Me	27.0		26.8										
R ⁴ =Me					9.4								
1'' ^d		137.2		137.5	137.5		137.4	137.1 ^f	136.7	136.6 ^f	136.5	136.4 ^f	137.4
2'',6''		128.1		128.1	127.9		127.8	127.9	127.9	128.0	128.1	128.2	128.2
3'',5''		128.6		128.7	128.6		129.0	129.0	129.0	129.1	129.2	129.2	129.0
4''		130.5		130.4	130.1		130.8	131.2	131.6	131.5 ^g	131.7	131.8	131.2

^a For atom numbering see Scheme S1. ^b For 4-Ph. ^c CH₃, CH₂Br, CHBr₂ or CBr₃ carbons. ^d For 2-Ph. ^e For corresponding carbon atoms.

^{f,g} In most cases the differences in chemical shifts are less than 0.1 ppm and may be interchanged.