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

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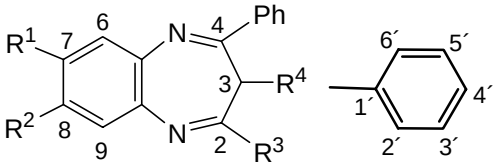

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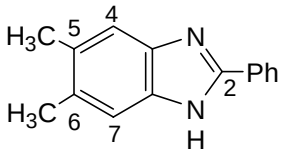
a $R^1=R^2=R^4=H$, $R^3=CH_3$
b $R^1=R^2=R^4=H$, $R^3=Ph$
c $R^1=R^2=R^3=CH_3$, $R^4=H$
d $R^1=R^2=CH_3$, $R^3=Ph$, $R^4=H$
e $R^1=R^2=R^4=CH_3$, $R^3=Ph$



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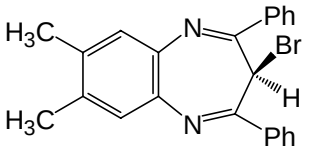

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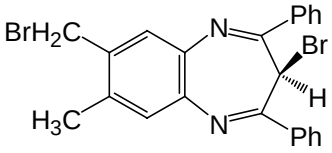

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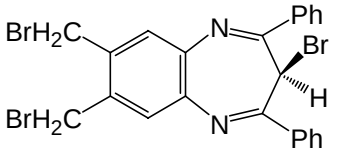

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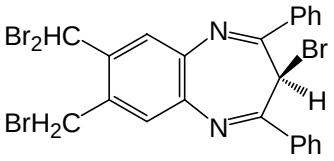

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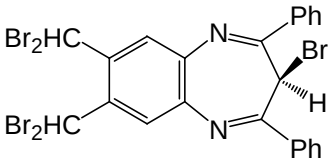

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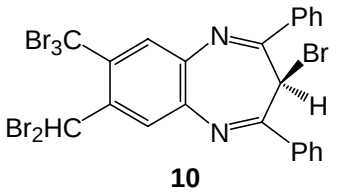

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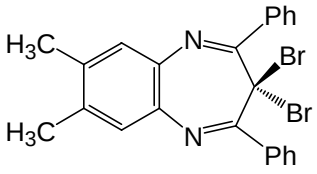

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Scheme S1. The Benzodiazepines **3a**–**e**, the benzimidazole **4** and the brominated derivatives **5**–**11** synthesized and studied in this work.

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] CH_3, CH_2Br, $CHBr_2$ or CBr_3 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.