New Synthetic Route to 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imines through Photoamination of 5-Alkoxy- and 5-Hydroxy-5*H*-dibenzo[*a*,*d*]cycloheptenes Followed by a Transannular Reaction with Acetic Acid

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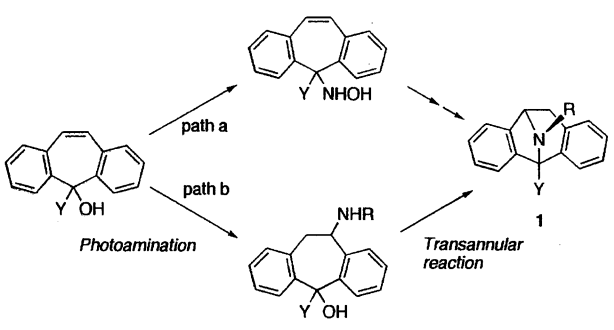
The photoadditions of ammonia and alkylamines (RNH_2) to 5-hydroxy- and 5-alkoxy-5*H*-dibenzo[*a*,*d*]-cycloheptene derivatives (**2**) occurred at the C10–C11 double bond upon the irradiation of **2** with RNH_2 in the presence of *p*-dicyanobenzene. The resulting 5-substituted 10-alkylamino-10,11-dihydro-5*H*-dibenzo-[*a*,*d*]cycloheptenes were converted to 5-substituted *N*-alkyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imines by a treatment with AcOH.

A number of heterocyclic compounds involving dibenzo[*a*,*d*]cycloalkenes have been of interest because of their useful medicinal activity.[1] Especially, the tetracyclic analogs, such as 10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclohepten-5,10-imines (**1**), e.g. MK 801,[2] have attracted considerable attention as anticonvulsant and neuroprotective agents.[3] Lamanec and co-workers of Merck Co., Inc. have reported on a synthetic method of **1** by a Ritter reaction of 5-hydroxyamino-5*H*-dibenzo-[*a*,*d*]cycloheptenes, which were derived from an amination of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ols (path a in Scheme 1).[3] During the course of our studies on photoamination via an electron transfer,[4] we have found that an amino group was added into the olefinic group of stilbenes under mild conditions by photoamination.[5] Therefore, our attention has been aimed at the synthesis of **1** via the photoamination of 5-alkoxy- and 5-hydroxy-5*H*-dibenzo[*a*,*d*]cycloheptenes (**2**), followed by transannular cyclization, as shown in path b of Scheme 1.



Scheme 1.

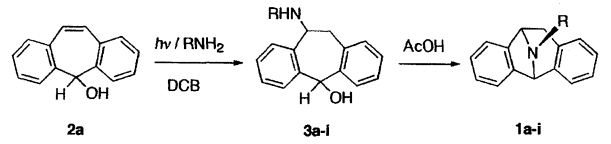
Results and Discussion

The photoaminations of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**2a**) with NH_3 and alkylamine (RNH_2) were performed by irradiating a deaerated MeCN–H_2O solution containing **2a**, *p*-dicyanobenzene (DCB), and RNH_2 for 8 h by a high-pressure mercury lamp through a Pyrex filter under cooling with water. After evaporation of the solvents, the aminated compounds were isolated by extraction from a benzene solution of photolysate with a dilute aqueous HCl solution. DCB and unreacted **2a** were recovered from the benzene solution by column chromatography on silica gel. The photoamination of **2a** with RNH_2 gave 10-alkylamino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ols (**3a**—**i**) in relatively good yields. It was confirmed that no photoamination of **2a** occurred in the absence of DCB. Although the **3a**—**i** were formed as a mixture of cis and trans isomers, resulting in a complex NMR spectra, their structures were deduced by a comparison of their ^1H and ^{13}C NMR spectra with those of 10-amino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, which was obtained in 79% yield by a photoamination of the parent 5*H*-dibenzo[*a*,*d*]cycloheptene with NH_3.

Transannular cyclizations of **3a**—**i** were performed by heating with AcOH at 100 °C for 5 h to give *N*-alkyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imines

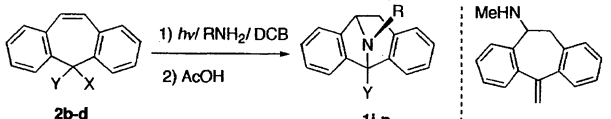
(**1a**—**i**). AcOH was most effective in the acids tested, e.g. *p*-toluenesulfonic acid and CF_3SO_3H. The transannular reaction with AcOH proceeded readily without any side reactions, except for the cases of **1a**, **1g** and **1h**, where acetylation occurred at the amino and hydroxy groups (Scheme 2). These results are summarized in Table 1.

Similarly, 5-substituted *N*-alkyl derivatives (**1j**—**n**) were synthesized from the 5,5-disubstituted 5*H*-dibenzo[*a*,*d*]cycloheptenes (**2b**—**d**) (Scheme 3). After the irradiation of **2b**—**d** with RNH_2 in the presence of DCB for 8 h, the solvent was evaporated; then, a sequential treatment of the photolysates with AcOH gave **1j**—**n**. Table 2 lists the yields of **1j**—**n** with the recovery of DCB. In the case of the photoamination of **2b**, the yield of **1j** was reduced by the formation of 5-methylene-10-methylamino-10,11-dihydro-5*H*-dibenzo-



a; R= H, **b**; R= Me, **c**; R= Et, **d**; R= i-Pr, **e**; CH(Me)Et, **f**; $CH_2CH{=}CH_2$
g; R= CH_2CH_2OH, **h**; R= $CH(Me)CH_2OH$, **i**; R= CH_2CO_2Et

Scheme 2.



2b; X= OH, Y= Me
2c; X,Y= $O(CH_2)_2O$
2d; X=Y= OMe

1j; R= Y= Me
1k; R= Me Y= $O(CH_2)_2OH$
1l; R= Me Y= OMe
1m; R= Et Y= OMe
1n; R= i-Pr Y= OMe

Scheme 3.

[*a*,*d*]cycloheptene (**4**; 23%).

As has been reported for the photoamination of stilbene derivatives,[5] the photoamination of **2** was initiated by a photoinduced electron transfer from **2** to DCB, since no photoamination of **2** occurred in the absence of DCB, and since the half peaks of the oxidation potentials of **2** were relatively low, i.e. 1.30 V (**2a**), 1.23 V (**2b**), 1.30 V (**2c**), and 1.27 V (**2d**). The resulting cation radicals of **2** ($2^{+\cdot}$) allow a nucleophilic addition of RNH_2 and a subsequent reduction by the anion radical of DCB to give the aminated products (**3**) after protonation (Scheme 4). Transannular cyclization with AcOH proceeded via an intramolecular nucleophilic addition of an amino group to the carbocation at C-5 generated by an elimination of the hydroxy and alkoxy groups under acidic condition.[3]

Thus, the present tranannular reaction according to path b in Scheme 1 can provide directly *N*-alkyl analogs of **1** from the precursors, although path a (Merck's method) was restricted to the transannular reaction of *N*-methoxy, *N*-hydroxy-, and *N*-amino precursors.[2a] Since **2** and the related compounds were easily pre-

Table 2. The Photoamination of **2b**—**d** Followed by the Transannular Reaction with AcOH

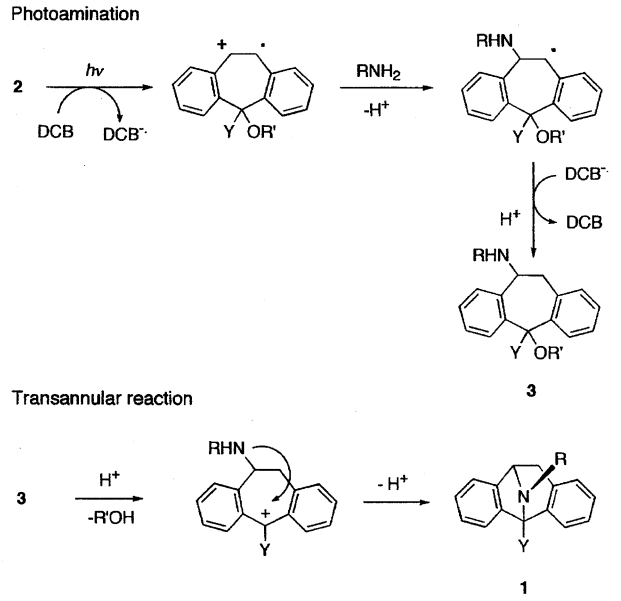
Entry	**2**	RNH_2	Product	Yield	Recovery/%	
				%	**2**	DCB
1	**2b**	$MeNH_2$	**1j**[a]	18	8[b]	90
2	**2c**	$MeNH_2$	**1k**	54	0	95
3	**2d**	$MeNH_2$	**1l**	59	7[c]	65
4	**2d**	$EtNH_2$	**1m**	89	0[c]	67
5	**2d**	*i*-$PrNH_2$	**1n**	74	5[c]	79

a) Accompanied by the formation of **4** in 23% yield.
b) Isolated as 5-methylene-5*H*-dibenzo[*a*,*d*]cycloheptene.
c) Isolated as 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one.

Table 1. Synthesis of *N*-Alkyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imines (**1**) from 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-ol (**2a**) by the Photoamination with RNH_2 and the Transannular Reaction with AcOH

		Photoamination[a]				Cyclization[b]	
		3		Recovery	Recovery	**1**	
Entry	RNH_2	(Yield/%)[c]		of **2a**/%	of DCB/%	(Yield/%)[d]	
1	NH_3	**3a**	(48)	29	88	**1a**	(82)[e]
2	$MeNH_2$	**3b**	(60)	8	95	**1b**	(82)
3	$EtNH_2$	**3c**	(85)	11	92	**1c**	(73)
4	*i*-$PrNH_2$	**3d**	(77)	8	87	**1d**	(90)
5	$EtCH(Me)NH_2$	**3e**	(76)	10	83	**1e**	(82)
6	$CH_2{=}CHCH_2NH_2$	**3f**	(41)	13	68	**1f**	(78)
7	$HOCH_2CH_2NH_2$	**3g**	(58)	21	90	**1g**	(70)[f]
8	$HOCH_2CH(Me)NH_2$	**3h**	(73)	6	72	**1h**	(72)[f]
9	$EtOCOCH_2NH_2$	**3i**	(60)	15	86	**1i**	(47)

a) The photoamination was performed by irradiating an MeCN–H_2O (9:1; 100 ml) solution containing **2a** (6 mmol), DCB (12 mmol), and RNH_2 (30 mmol) for 8 h. b) The transannular reaction was performed by heating of **3** with AcOH at 100 °C for 5 h. c) Isolated yields based on **2** used. d) Isolated yields based on **3** used. e) **1a** was isolated as the acetamide. f) **1g** and **1h** were isolated as the acetates.



Scheme 4.

pared from commercially available 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one, and since the photoamination and transannular reactions were performed under mild conditions, the present method will be developed as a new synthetic tool for the preparation of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine derivatives.

Experimental

General. The melting points were measured on a Shibata MEL 270 and were uncorrected. ^{1}H and ^{13}C NMR spectra were taken on a Bruker AC 250P in $CDCl_3$ using tetramethylsilane as an internal standard. MS spectra were measured on a Hitachi 2000A. The oxidation potentials were measured in an MeCN solution vs. an $Ag/AgNO_3$ reference electrode.

Materials. 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-ol (**2a**)[3a] was prepared by the reduction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with $NaBH_4$. The preparation of 5-methyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**2b**) was performed by the reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with MeMgBr below 30 °C.[3a] 5,5-Ethylenedioxy-5*H*-dibenzo[*a*,*d*]cycloheptene (**2c**) and 5,5-dimethoxy-5*H*-dibenzo[*a*,*d*]cycloheptene (**2d**)[6] were prepared by the reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with ethylene glycol and HC(OMe)$_3$ in the presence of *p*-toluenesulfonic acid, respectively. 5*H*-Dibenzo[*a*,*d*]cycloheptene was prepared by the reduction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with $LiAlH_4$ in the presence of $AlCl_3$.[7]

2c: Mp 131—132 °C; ^{1}H NMR δ=3.87 (4H, brs), 7.06 (2H, s), 7.24—7.40 (6H, m), 7.88 (2H, d, J=7.3 Hz); ^{13}C NMR δ=64.50, 106.41, 123.96, 127.56, 127.83, 129.28, 131.02, 133.38, 138.17. HRMS Found: m/z 250.0954. Calcd for $C_{17}H_{14}O_2$: M, 250.0992.

General Procedure. Photoaminations of **2** were performed by irradiation of an MeCN–H_2O solution containing **2**, DCB, and the amine by an Eikosha high-pressure mercury lamp through a Pyrex filter under cooling with water. The aminated products (**3a**—**i**) were isolated as a mixture of cis and trans isomers.

The transannular cyclization was performed by heating an acetic acid solution of **3** at 100 °C in an oil bath. After the reaction, the solution was neutralized with an aqueous Na_2CO_3 solution, and extracted with Et_2O to give transannular products (**1**). The structures of **1a**—**n** were determined by the ^{1}H and ^{13}C NMR spectra: In their ^{1}H NMR spectra, one of the methylene protons (H-11) showed no coupling with the methine proton (H-10), whereas another H-11 proton showed J=ca. 5 Hz with the H-10 proton. The H-5 proton appeared as a singlet in the case of **1a**—**g**. The spectral data are as follows:

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1a):[3a] N-Acetyl Derivative; ^{1}H NMR δ=2.13 and 2.18 (3H, s), 2.66 and 2.83 (1H, dd, J=17.0 and 16.8 Hz), 3.46 and 3.61 (1H, dd, J=16.8, 5.4 and 17.0, 5.5 Hz), 5.34 and 5.75 (1H, d, J=5.4 and 5.5 Hz), 5.53 and 6.13 (1H, s), 6.94—7.63 (8H, m); ^{13}C NMR δ=20.28 and 21.20, 31.63 and 33.51, 56.72 and 59.66, 59.78 and 63.55, 119.61 and 120.11, 121.34 and 121.91, 123.31 and 124.49, 125.92 and 126.24, 126.81 and 127.12, 127.27 and 127.48, 128.05 and 128.34, 130.46 and 130.86, 132.21 and 132.30, 139.27 and 139.86, 140.28 and 140.38, 146.18 and 146.43, 165.96 and 167.35. HRMS Found: m/z 249.1186. Calcd for $C_{17}H_{15}NO$: M, 249.1153.

***N*-Methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1b):** Oil; ^{1}H NMR δ=2.71 (3H, s), 2.81 (1H, d, J=17.5 Hz), 3.67 (1H, dd, J=17.5, 5.5 Hz), 4.83 (1H, d, J=5.5 Hz), 5.19 (1H, s), 6.99—7.39 (8H, m); ^{13}C NMR δ=30.57, 37.01, 64.99, 68.77, 121.48, 123.17, 125.16, 126.76, 128.45, 128.55, 128.74, 129.81, 132.72, 135.11, 137.37, 143.55. HRMS Foudn: m/z 221.1200. Calcd for $C_{16}H_{15}N$: M, 221.1203.

***N*-Ethyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1c):** Oil; ^{1}H NMR δ=1.17 (3H, t, J=7.1 Hz), 2.45—2.71 (3H, m), 3.32 (1H, dd, J=17.1, 5.5 Hz), 4.39 (1H, d, J=5.5 Hz), 4.71 (1H, s), 6.89—7.30 (8H, m); ^{13}C NMR δ=13.34, 30.51, 44.61, 62.38, 67.15, 120.95, 122.62, 124.86, 125.94, 126.86, 126.86, 127.20, 129.93, 132.34, 139.28, 142.51, 148.10. HRMS Found: m/z 235.1340. Calcd for $C_{17}H_{17}N$: M, 235.1359.

***N*-Isopropyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1d):** Oil; ^{1}H NMR δ=1.11 (3H, d, J=6.2 Hz), 1.23 (3H, d, J=6.2 Hz), 2.48 (1H, d, J=17.3 Hz), 2.65 (1H, sept, J=6.2 Hz), 3.26 (1H, dd, J=17.3, 5.3 Hz), 4.61 (1H, d, J=5.3 Hz), 4.91 (1H, s), 6.89—7.30 (8H, m); ^{13}C NMR δ=21.16, 27.67, 45.93, 59.13, 64.46, 120.32, 121.82, 125.22, 126.11, 126.72, 126.72, 127.13, 129.74, 132.75, 137.86, 143.18, 148.18. HRMS Found: m/z 249.1540. Calcd for $C_{18}H_{19}N$: M, 249.1516.

***N*-*s*-Butyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1e):** Diastereomeric mixture, oil; ^{1}H NMR δ=0.84 and 0.91 (3H, d, J=7.4 Hz), 1.07 and 1.20 (3H, d, J=6.2 Hz), 1.36—1.53 and 1.59—1.90 (2H, m), 2.48 (1H, d, J=17.1 Hz), 2.40—2.50 (1H, m), 3.25 and 3.27 (1H, dd, J=17.3, 3.3 Hz), 4.62 and 4.65 (1H, d, J=5.8 Hz), 4.94 (1H, s), 6.91—7.30 (8H, m); ^{13}C NMR δ=9.56 and 10.07, 16.93, 26.55 and 26.65, 27.61 and 27.74, 51.51 and 51.75, 58.44 and 59.24, 63.86 and 64.36, 120.16, 121.64 and 121.78, 125.11, 126.02, 126.62, 126.62, 127.03, 129.63, 132.59 and 132.65, 137.69 and 137.94, 142.89 and 142.99, 147.95 and 148.03. HRMS Found: m/z 263.1662. Calcd for $C_{19}H_{21}N$:

M, 263.1672.

***N*-Allyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine (1f):** Oil; ^{1}H NMR δ=2.62 (1H, d, J=17.0 Hz), 3.15 (2H, t, J=7.5 Hz), 3.35 (1H, dd, J=17.0, 5.6 Hz), 4.38 (1H, d, J=5.6 Hz), 4.69 (1H, s), 5.09—5.24 (2H, m), 5.92—6.08 (1H, m), 6.95—7.41 (8H, m); ^{13}C NMR δ=31.18, 54.54, 62.75, 67.48, 117.66, 121.07, 122.76, 124.66, 125.85, 126.86, 126.91, 127.19, 129.92, 132.23, 132.72, 135.62, 142.17, 147.86. HRMS Found: m/z 247.1408. Calcd for $C_{18}H_{17}N$: M, 247.1360.

***N*-(2-Hydroxyethyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine (1g):** *O*-Acetyl Derivative. Oil; ^{1}H NMR δ=2.05 (3H, s), 2.59 (1H, d, J=17.2 Hz), 2.71—2.94 (2H, m), 3.35 (1H, dd, J=17.2, 5.3 Hz), 4.19—4.34 (2H, m), 4.45 (1H, d, J=5.3 Hz), 4.77 (1H, s), 6.94—7.40 (8H, m); ^{13}C NMR δ=21.25, 30.14, 49.20, 63.30, 63.52, 68.01, 120.97, 122.63, 125.16, 126.27, 127.14, 127.21, 127.57, 130.14, 132.09, 138.84, 142.29, 147.92, 170.50. HRMS Found: m/z 293.1441. Calcd for $C_{19}H_{19}NO_2$: M, 293.1415.

***N*-(1-Methyl-2-hydroxyethyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine (1h):** *O*-Acetyl derivative. Diastereomeric mixture; oil; ^{1}H NMR δ=1.15 and 1.28 (3H, d, J=6.3 and 6.5 Hz), 1.99 and 2.03 (3H, s), 2.52 (1H, d, J=17.5 Hz), 2.74—2.83 (1H, m), 3.26 and 3.37 (1H, dd, J=17.5, 5.3 and 17.5, 5.4 Hz), 4.04 (1H, dd, J=11.1, 6.1 Hz), 4.39 (1H, dd, J=11.1, 4.4 Hz), 4.63 and 4.66 (1H, d, J=5.2 and 5.3 Hz), 4.93 and 4.97 (1H, s), 6.90—7.40 (8H, m); ^{13}C NMR δ=16.40, 20.99, 27.82 and 28.04, 50.14 and 50.33, 59.27 and 59.82, 64.55 and 64.73, 67.30 and 67.48, 120.23, 121.73 and 121.93, 125.07 and 125.34, 126.16, 126.87, 126.87, 127.31, 129.83, 132.20 and 132.30, 137.31 and 137.24, 142.30 and 142.84, 147.33 and 147.87, 170.97. HRMS Found: m/z 307.1585: Calcd for $C_{20}H_{21}NO_2$: M, 307.1571.

Ethyl 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine-*N*-acetate (1i): Oil; ^{1}H NMR δ=1.25 (3H, d, J=7.2 Hz), 2.63 (1H, d, J=17.1 Hz), 3.31 (1H, d, J=16.6 Hz), 3.40 (1H, dd, J=17.1, 5.4 Hz), 3.42 (1H, d, J=16.6 Hz), 4.18 (2H, q, J=7.2 Hz), 4.51 (1H, d, J=5.4 Hz), 4.84 (1H, s), 6.93—7.32 (8H, m); ^{13}C NMR δ=14.41, 30.97, 53.04, 60.94, 63.81, 68.23, 121.28, 123.00, 125.13, 126.26, 127.26, 127.34, 127.65, 130.20, 131.95, 139.02, 141.81, 147.62, 171.05. HRMS Found: m/z 293.1440. Calcd for $C_{19}H_{19}NO_2$. M, 193.1414.

5,*N*-Dimethyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-imine (1j): Oil; ^{1}H NMR δ=1.64 (3H, s), 2.37 (3H, s), 2.53 (1H, d, J=17.3 Hz), 3.35 (1H, dd, J=17.3, 5.4 Hz), 4.38 (1H, d, J=5.4 Hz), 7.04—7.34 (8H, m); ^{13}C NMR δ=16.13, 27.49, 31.22, 61.80, 64.87, 116.58, 120.56, 125.23, 125.58, 125.90, 126.66, 127.30, 128.57, 131.16, 138.35, 141.45, 149.85. HRMS Found: m/z 235.1413. Calcd for $C_{17}H_{17}N$: M, 235.1362.

5-(2-Hydroxyethoxy)-*N*-methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1k): Oil; ^{1}H NMR δ=2.32 (3H, s), 2.44 (1H, d, J=17.6 Hz), 3.33 (1H, dd, J=17.6 and 5.2 Hz), 3.67—3.73 (1H, m), 3.80—3.89 (1H, m), 3.95—4.10 (2H, m), 4.51 (1H, d, J=5.2 Hz), 6.92 (1H, d, J=6.8 Hz), 7.05—7.32 (6H, m), 7.59—7.63 (1H, m); ^{13}C NMR δ=27.82, 30.32, 60.36, 62.81, 66.87, 95.31, 120.34, 122.09, 123.21, 126.54, 126.92, 127.62, 127.69, 128.92, 131.50, 137.89, 141.02, 144.60; MS m/z 281 (M^+), 226 ($M-C_2H_5O$). HRMS Found: m/z 281.1414. Calcd for $C_{18}H_{19}NO_2$: M, 282.1414.

5-Methoxy-*N*-methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1l): Oil; ^{1}H NMR δ=2.26 (3H, s), 2.41 (1H, d, J=17.4 Hz), 3.31 (1H, dd, J=17.4, 5.2 Hz), 3.47 (3H, s), 4.45 (1H, d, J=5.1 Hz), 6.87—7.59 (8H, m); ^{13}C NMR δ=27.74, 30.29, 50.48, 60.64, 95.38, 119.63, 122.07, 123.36, 126.49, 126.75, 127.32, 127.41, 128.91, 131.68, 138.39, 141.83, 145.78. HRMS Found: m/z 251.1273. Calcd for $C_{17}H_{17}NO$: M, 251.1308.

***N*-Ethyl-5-methoxy-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1m):** Oil; ^{1}H NMR δ=1.21 (3H, t, J=7.4 Hz), 2.24—2.34 (1H, m), 2.42 (1H, d, J=17.5 Hz), 2.53—2.73 (1H, m), 3.29 (1H, dd, J=17.5, 5.2 Hz), 3.38 (3H, s), 4.67 (1H, d, J=5.2 Hz), 6.88—7.84 (8H, m); ^{13}C NMR δ=13.07, 27.29, 36.65, 50.31, 56.72, 95.32, 119.62, 122.16, 123.06, 126.72, 127.33, 128.82, 128.82, 129.74, 132.18, 139.04, 141.67, 146.02. HRMS Found: m/z 265.1434. Calcd for $C_{18}H_{19}NO$: M, 265.1465.

***N*-Isopropyl-5-methoxy-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (1n):** Oil; ^{1}H NMR δ=1.19 (3H, d, J=6.0 Hz), 1.25 (3H, d, J=6.0 Hz), 2.36 (1H, d, J=17.5 Hz), 2.77 (1H, sept, J=6.0 Hz), 3.33 (1H, dd, J=17.5, 5.2 Hz), 3.48 (3H, s), 4.73 (1H, d, J=5.2 Hz), 6.88—7.30 (6H, m), 7.62—7.73 (2H, m); ^{13}C NMR δ=21.23, 22.63, 28.25, 46.05, 50.38, 58.47, 96.42, 120.20, 121.62, 122.91, 126.21, 126.73, 127.37, 128.70, 132.73, 139.00, 141.29, 146.19. HRMS Found: m/z 279.1584. Calcd for $C_{19}H_{21}NO$: M, 279.1621.

10-Methylamino-5-methylene-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (4): Oil; ^{1}H NMR δ=2.44 (3H, s), 2.97 (1H, br s), 3.20 (1H, dd, J=15.7, 7.9 Hz), 3.36 (1H, dd, J=15.7, 3.0 Hz), 4.07 (1H, dd, J=7.9, 3.0 Hz), 5.41 (1H, d, J=1.5 Hz), 5.45 (1H, d, J=1.5 Hz), 7.12—7.40 (8H, m); ^{13}C NMR δ=34.19, 38.62, 60.75, 117.54, 126.46, 127.03, 127.67, 127.73, 128.08, 128.24, 128.79, 130.31, 132.72, 135.01, 139.78, 140.23, 151.59. HRMS Found: m/z 235.1413. Calcd for $C_{17}H_{17}N$: M, 235.1362.

10-Amino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene: *N*-Acetyl derivative, mp 181—182 °C; ^{1}H NMR δ=1.85 (3H, s), 3.10 (1H, dd, J=14.1 and 6.5 Hz), 3.47 (1H, dd, J=14.1 and 3.3 Hz), 3.80 (1H, d, J=15.2 Hz), 4.33 (1H, d, J=15.2 Hz), 5.48—5.56 (1H, m), 5.75 (1H, br d, J=5.8 Hz), 7.06—7.25 (8H, m); ^{13}C NMR δ=23.06, 36.73, 40.96, 49.53, 126.71, 126.82, 126.95, 127.37, 128.00, 129.74, 129.96, 131.58, 136.03, 137.34, 138.09, 140.71, 168.60; MS m/z 251 (M^+), 192 (M−NHAc). Found: C, 80.96, H; 6.53, N; 5.72%. Calcd for $C_{17}H_{17}NO$: C; 81.24, H; 6.82, N; 5.57%.

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