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One-pot Stereoselective Synthesis of Dimethanodibenzo[e,i][1,4]diazecines by a Zinc-Acetic Acid Promoted Cascade Reaction

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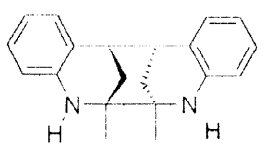
Abstract: The title compounds are interesting C_2 symmetrical diamines. They were prepared in a one-pot process by reacting quinaldines with a zinc-acetic acid mixture in THF solution. During this simple and stereoselective process, two C-C bonds and 4 stereogenic centres are created under mild conditions. Influence of the concentration of reagents upon yields and intramolecular cyclization regiochemistry is demonstrated. Experiments using deuteriated acetic acid allowed a good understanding of these results.

Keywords : zinc-acetic acid , dimerization, intramolecular cyclization, dibenzodiazecines.

The zinc-acetic acid couple is a well known reducing reagent, capable of a wide range of reactions[1] of which the reduction of carbonyl or activated alkenes is the most common. In contrast, it has been rarely used in the heteroaromatic series, except for the reduction of potentially labile functionalities like halogen-carbon bonds at the 2-position[2]. We have recently shown that it reacts with quinaldine **1a** to yield 5,6,7,8,13,14-hexahydro-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i] [1,4]-diazecine, **2a,** *via* a reductive dimerization of the heterocycle followed by a spontaneous intramolecular cyclization[3]. As this pentacyclic diamine exhibits interesting features which could lead to pharmacological properties[4] as well as applications in enantioselective catalysis due to the C_2 symmetry[5], it appeared important to study the versatility of this reaction. Indeed, obtention of complex targets from commercially available starting materials in one simple and efficient operation is of increasing importance in synthetic organic chemistry. In this paper, we describe the development of this reaction as a source of a variety of dibenzo[e,i][1,4]diazecines starting from a series of substituted quinaldines.



2a

RESULTS AND DISCUSSION

We focused on the commercially available quinaldines **1b-1i,** whose reactivity was compared to that of quinaldine itself (**1a**). The reactions were conducted at reflux of THF, using the best conditions defined for **1a**[3] i.e. 15 ml of THF, 41 mmol of zinc and 70 mmol of acid for 28 mmol of substrate. Our

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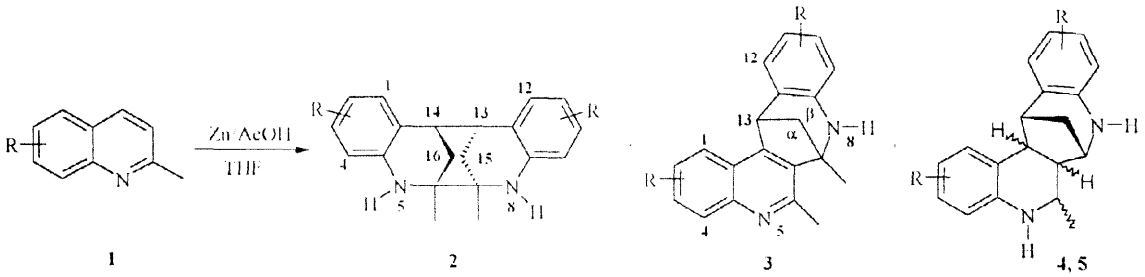
results (scheme 1 ; Table 1, entries 1-9) show that like quinaldine itself, the 8-hydroxy derivative **1i** led to the dibenzodiazecine **2i** as the only product, but in lower yield (66% instead of 96). In all the other cases, introduction of substituents in position 6-, 7- or 8- results in a loss of selectivity in the cyclization process, and the dibenzodiazecines **2** are isolated in mixture with quinobenzazepines **3** along with small amounts of the corresponding tetrahydro-derivatives **4**, **5** in the case of the haloquinaldines **1d-1f**. However, the diazecine **2** remains the major product as shown by the **2/3-5** ratio, which varies from 75/25 to 95/5. The global yield in pentacyclic products varies in the range 62-96%, except with the 8-acetoxyquinaldine **1h**, for which it is only 30%. With this substrate, 8-hydroxyquinaldine was systematically found in the reaction mixture (5-10%). The poor reactivity of **1h** could be related to steric crowding around the nitrogen as well as electronic deactivation due to interaction between the substituent and the nitrogen. Migration of the acetoxy group from oxygen to nitrogen has been recently reported when reducing **1h** with sodium cyanoborohydride in THF solution[6]. About 10-13% of starting material is systematically recovered in the case of **1c** and **1f**, along with the corresponding tetrahydroquinaldines (respectively 8 and 6%). Increasing the reaction time did not improve these results, but led to formation of tars



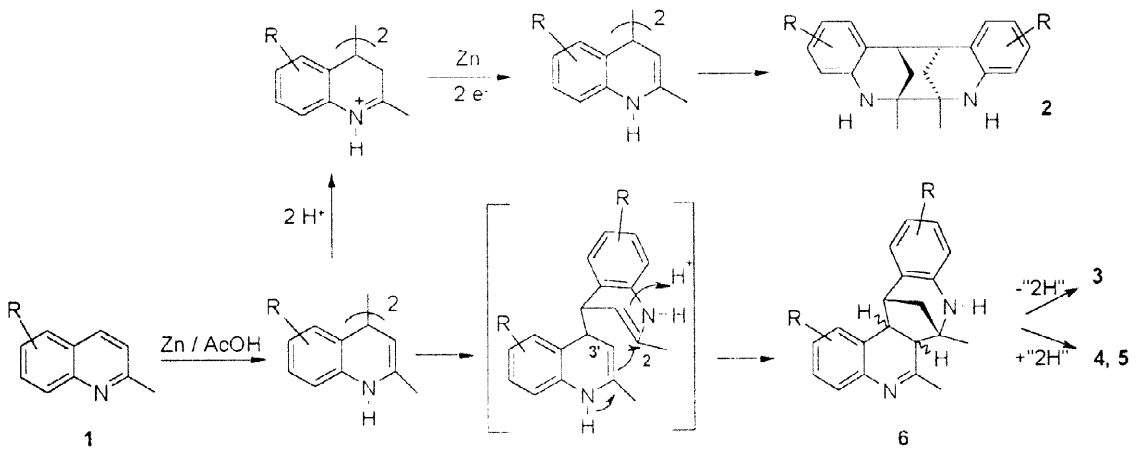
Scheme 1.

Table 1. Cyclization of Quinaldine with Zn/AcOH/THF Reagent

entry	1 : R	AcOH (equiv)	Product yields 2	3	4,5	2/3+4,5	Time (h)
1	**a**: H	2.5	96	-	-	100/0	10
2	**b** : 6-CH_3	2.5	48	14	-	77/23	24
3	**c** : 7-CH_3	2.5	51	16	-	76/24	22
4	**d** : 6-F	2.5	52	10	5	75/25	21
5	**e** : 6-Cl	2.5	71	19	5	75/25	20
6	**f** : 7-Cl	2.5	62	traces	3	95/5	16
7	**g** : 6-OCH_3	2.5	70	16	-	81/19	15
8	**h** : 8-OAc	2.5	25	5	-	83/17	24
9	**i** : 8-OH	2.5	66	-	-	100/0	5
10	**b** : 6-CH_3	5	56	11	-	84/16	24
11	**d** : 6-F	5	67	traces	4	94/6	22
12	**g** : 6-OCH_3	5	85	-	-	100/0	20

Despite the weaker selectivity resulting from the introduction of substituents, the process remained very efficient due to the easiness of the purification step. Indeed, the dibenzodiazecine is in all cases eluted first as a pure product even after a rapid filtration through silica gel. The structure assignments are based on satisfactory elemental analysis and physicochemical data (IR, mass and NMR). In particular, the ^{1}H and ^{13}C NMR spectra of **2a-2i** exhibit signals for a half molecule, which is in agreement with the C_2 symmetry. The same is true for the mass spectra, which are dominated by initial fragmentation to give monomeric species (M/2). In contrast, the molecular peak in compounds **3-5** is systematically observed, and no equivalence appeared in NMR, as expected for dissymmetrical structures.

The formation of **3** is not due to an isomerization of **2** in the reaction mixture. Indeed, the stability of both **2a** and **2d** towards acetic acid/THF or acetic acid/zinc acetate/THF was checked, and they were recovered unchanged even after 3 days at reflux. From a mechanistic point of view, the cascade is initiated by the protonation of the nitrogen and an electron transfer leading to a radical. Its coupling is followed by an intramolecular cyclization (Scheme 2). The easiness of this step is demonstrated by the absence of dimers in the reaction mixture. Compounds **2-5** contain the same 4,4'-linkage, demonstrating that all of them come from a 1,4-dihydro-4,4'-biquinaldine derivative or its dianion.

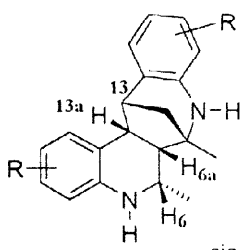


Scheme 2

Globally, **2** results from an intramolecular reductive cyclization leading to addition of a hydrogen atom on both the 3- and 3'-positions and a new C-C bond between the 2- and 2'- positions. This could proceed through protonation of the enamine followed by transfer of two electrons and cyclization of the resulting diradical. In contrast, the cyclisation step leading to **3** can be summarized as an intramolecular electronic transfer initiated by the protonation of one of the enamine moieties. This

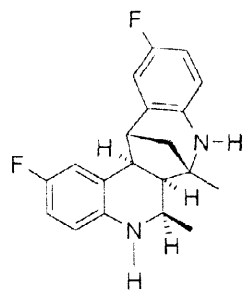
leads to a new C-C bond between the 2- and 3'-positions with « an apparent » proton migration from N-1 to C-3'. The resulting imine **6** has never been isolated, except in the case of the 6-fluoroquinaldine **1d**. With R = Me, OMe or OAc, its oxidation spontaneously occurred in the reaction mixture leading to **3**. This fact agrees well with the great oxidability of **6a** (R = H), which was very difficult to prevent even under an inert atmosphere, as previously reported by both Russell *et al.*[7] and by us[8].

With haloquinaldines **1d-1f**, oxidation of the imine competes with its reduction leading to **4d-4f** and **5d**, whose stereochemistries were unambiguously assigned on the basis of the ^{1}H NMR spectra. The 6a, 13a coupling constant values (**4d** : 11.9, **4f** : 11.9 and **5d** : 8.3 Hz) clearly show that these protons are in a *cis* position. The four remaining possible stereoisomers were rebuilt with PCModel and the ^{3}J (^{1}H, ^{1}H) coupling constants were calculated according to the work of Altona *et al.* as implemented in the program[9]. The decisive two pairs of proton are respectively 13, 13a for the cyclic junction and 6a, 6 for the position of the methyl group. Comparison of the measured and calculated values allow assignment of the *cis-trans* stereochemistry for **4d-4f** and *trans-cis* for **5d**, demonstrating that these products are respectively issued from a *meso* (**4**) and *threo* dimer (**5**). In the same way, a *cis* stereochemistry was assigned to the fluoroimine **6d**. The *trans* stereochemistry of the dibenzodiazecine has been previously established by X-ray[10]. It implies that the dimer precursor has the *threo* stereochemistry. Our results show that dimerization of quinaldines in Zn/AcOH/THF medium is stereoselective. It is worth noting that silylation of quinaldine itself using Me_3SiCl/Mg/THF reagent also led to the *threo* N-silyl dimer as the only product[8].

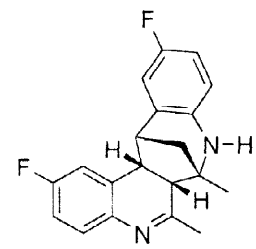


cis-trans

R = 2,11-difluoro : **4d**
2,11-dichloro : **4e**
3,10-dichloro : **4f**



5d (trans-cis)

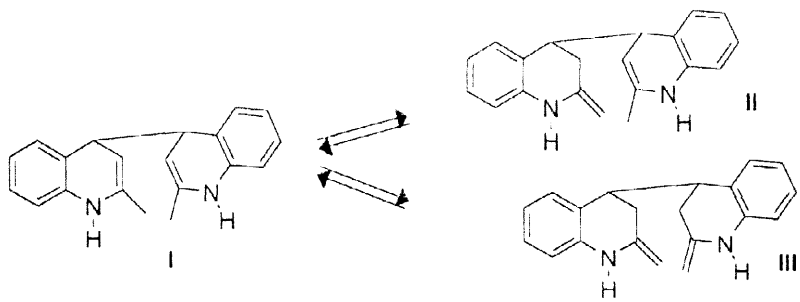


6d (cis)

In the case of **1a**, we have shown that increasing the volume of THF to 50 ml led to a mixture of **2a**, **3a** (2/1; 46% yield) and unreacted quinaldine (51%)[3]. The decrease of both reactivity and regioselectivity when increasing the THF volume agrees well with the first bimolecular step and the proposed mechanism for the cyclization. Indeed, it leads to a decrease in the acetic acid concentration, which is involved in the formation rate of **2** while the formation of **3** is not acetic acid consuming. These

facts suggest the possibility of improving the yields either in dibenzodiazecine by increasing the concentration in acetic acid or in quinobenzazepine **3** by using catalytic amount of acid. Experiments with 5 equiv. of acetic acid instead of 2.5 were conducted with **1b**, **1d** and **1g** (Table 1, entries 10-12). As expected, we obtained better yield in dibenzodiazecine, which became the only product with **1g**. In addition, trying to favor the quinobenzazepine **3**, the reaction was also conducted with only 0.5 equiv. of acid in the case of **1g**. Under these conditions, the reaction became very slow and the transformation rate was only 20% after 40 h at reflux, the dibenzodiazecine remaining the main product (**2g/3g** = 93:3). In the case of quinaldine, we also performed the reaction in acetic acid as the solvent (10 equiv. per mol of quinaldine), and obtained the diazecine as the only product (85% yield). This result shows that THF is not necessary to the electron transfer and/or the cyclization step. However, work-up is easier when the reaction is conducted in THF.

To better understand the regioselection of the cyclization step, the reaction with **1a** was also conducted with d-acetic acid in THF solution. Deuteriated dibenzodiazecine was isolated as the only product (70% yield). ^{1}H and ^{2}H NMR spectra were recorded, showing as expected the incorporation of a deuterium atom in 15- and 16-position (methylene groups), but also on the methyl groups. These results were confirmed by the non-decoupled carbon spectrum, which clearly show the presence of both CHD_2 and CH_2D moieties. This implies that an imine-enamine equilibrium takes place in the dimer before the cyclization step. This would led to exomethylene intermediate like **II** or **III** (Scheme 3). This last one should be more reactive than **I** and can only lead to the dibenzodiazecine through a 2,2' cyclization. This fact agrees well with the observed regioselectivity of the cyclization step.



Scheme 3.

This very simple and stereoselective process constitutes a synthetically attractive and versatile approach for the rapid construction of C_2 symmetrical pentacyclic diamines. Indeed, two C-C bonds and 4 stereogenic centres are created under mild conditions in a one-pot process. This procedure offers the following advantages : (i) the reactions are easy to set-up, to perform and to work up, (ii) only inexpensive reagents are required (iii) the diazecines are easy to isolate and yields are good. Synthetic exploitation of these results is now in progress.

EXPERIMENTAL

Quinaldine, zinc dust (20,998-8) and acetic acid were bought from Aldrich and were used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Melting points were determined on a Metler capillary apparatus and are uncorrected. IR spectra were obtained on a Perkin Elmer Paragon spectrophotometer. The NMR spectra were recorded on a Bruker AC 250 spectrometer ($CDCl_3$ solutions, δ values in ppm, J values in Hz, TMS as internal standard). Mass spectra were measured on a VG AUTOSPEC-Q spectrometer. All reactions were monitored by thin layer chromatography (SiO_2 , CH_2Cl_2 , UV light detection). In addition, reaction mixtures as well as pure products were analyzed by gas chromatography (capillary column HP Ultra -1.25 m x 0.32 mm x 0.52 μm). The GC oven temperature programming was 5 °C.min^{-1} starting from 140 °C until 300 °C, followed by an isothermal period of 10 min at 300 °C. Retention time (R_T) are given in minute.

Typical procedure for the reduction of quinaldines by Zn-AcOH-THF reagent.

Acetic acid (4.0 ml, 70 mmol) was added to a mixture of **1a** (4 g, 28 mmol) and zinc dust (2.7 g, 41 mmol) in dry THF (15 ml). The reaction mixture was then heated at reflux for 7 h and vigorously stirred until total conversion of the starting material, as monitored by TLC (SiO_2, CH_2Cl_2). The THF was then removed under reduced pressure and dichloromethane (30 ml) was added. The mixture was filtered through celite to remove zinc acetate and water (20 ml) was added. The organic layer was washed until neutrality, dried over anhydrous $MgSO_4$ then concentrated. The crude product was chromatographed on silica gel. Eluting first with C_6H_{12}/CH_2Cl_2 (50 : 50 v/v) led to the dibenzodiazecine **2a**, then the hexahydro-methanoquino[3,4-c][1]benzazepines, **4-5**, if present. Elution with CH_2Cl_2/acetone (8 : 2 v/v) led to the dihydro-methanoquino[3,4-c][1]benzazepine, **3**. Yields are reported in Table 1. The atomic numbering for compounds **2-6** is shown in Scheme 1.

5,6,7,8,13,14-hexahydro-2,6,7,11-tetramethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2b). White solid, mp : 152°C (C_6H_{12}). R_T = 8.9 min. IR (cm^{-1}) : 3400, 3040, 2900, 1650, 1500. MS (EI) : m/z : 318 (6.77), 158 (100), 144 (7.78). Elemental analysis : calcd for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80; found : C, 83.10; H, 8.21; N, 8.68. ^{1}H NMR (250 MHz, $CDCl_3$) δ : 1.20 and 2.06 (AB, ^2J = 12.7, 2 H, H_{15}), 1.30 (s, CH_3-6), 2.36 (s, CH_3-2), 2.97 (bs, 1 H, H_{14}), 3.80 (N-H), 6.52 (d, $^3J_{4,3}$ = 7.9, 1 H, H_4), 6.95 (d, $^3J_{3,4}$ = 7.9, 1 H, H_3), 7.01 (m, 1 H, H_1) . ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 20.59 (CH_3-6), 22.96 (CH_3-2), 30.29 (C_{15}), 43.14 (C_{14}), 57.69 (C_6), 112.31 (C_1), 127.83 (C_3), 129.07 (C_4), 124.86, 125.27, 143.20 (Cq).

5,6,7,8,13,14-hexahydro-3,6,7,10-tetramethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2c). White solid, mp : 160°C (C_6H_{12}). R_T = 9.1 min. IR (cm^{-1}) : 3400, 3040, 2900, 1650, 1500. MS (EI) : m/z : 318 (12.65), 158 (100), 144 (13.37). Elemental analysis : calcd for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80; found : C, 82.69; H, 8.03; N, 8.73. ^{1}H NMR (250 MHz, $CDCl_3$) δ : 1.21 and 2.08 (AB part of ABX, ^2J = 12.7, $^3J_{15,14}$ = 2.0, 2 H, H_{15}), 1.32 (s, CH_3-3), 2.38 (s, CH_3-6), 2.99 (bs, 1 H, H_{14}), 3.88 (N-H), 6.45 (d, $^4J_{4,2}$ = 0.9, 1 H, H_4), 6.57 (dd, $^3J_{2,1}$ = 7.4 ; $^4J_{2,4}$ = 0.9, 1 H, H_2), 7.09 (d, $^3J_{1,2}$ = 7.4, 1 H, H_1) . ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 21.51 (CH_3-6), 22.95 (CH_3-3), 30.38 (C_{15}) ; 42.77 (C_{14}), 57.62 (C_6), 112.92 (C_4), 116.92 (C_2), 128.41 (C_1), 122.56, 136.91, 145.39 (Cq).

5,6,7,8,13,14-hexahydro-2,11-difluoro-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2d). White solid, mp : 191°C (C_6H_{12}). R_T = 7.6 min. IR (cm^{-1}) : 3430, 3030, 2900, 1500, 1230. MS (EI) : m/z : 326 (12.50), 162 (100), 83 (7.32). Elemental analysis : calcd for $C_{20}H_{20}N_2F_2$: C, 73.60; H, 6.18; N, 8.58; F, 11.64; found : C, 73.68; H, 6.45; N, 8.60; F, 11.11. ^{1}H NMR (250 MHz, $CDCl_3$) δ : 1.12 and 1.97 (AB part of ABX, ^2J = 12.8, $^3J_{15,14}$ = 1.9, 2 H, H_{15}), 1.24 (s, CH_3), 2.88 (d, $^3J_{14,15}$ = 1.9, 1 H, H_{14}), 3.74 (N-H), 6.43 (dd, ^3J = 8.6; ^4J = 4.6, 2 H); 6.80 (m, 4 H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 22.74 (CH_3), 29.70 (C_{15}), 42.91 (C_{14}), 57.62 (C_6), 112.69 (d, $^3J_{C,F}$ = 7.5, C_4), 113.75 (d, $^2J_{C,F}$ = 22,6, C_3), 114.68 (d, $^2J_{C,F}$ = 21.6, C_1), 125.74 (d, $^3J_{C,F}$ = 6,2, C_{13a}), 141.60 (C_{4a}), 154.78 (d, $^1J_{C,F}$ = 233.0, C_2) ; ^{19}F (200 MHz, $CDCl_3$) δ : -130.15 (td, $^3J_{F,H}$ = 8.5, $^4J_{F,H}$ = 5.0).

5,6,7,8,13,14-hexahydro-2,11-dichloro-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2e). White solid, mp : 232°C (C_6H_{12}). R_T = 13.5 min. IR (cm^{-1}) : 3400, 3040, 2900, 1610, 1500. MS (EI) : m/z : 359 (2.7), 178 (100). Elemental analysis : calcd for $C_{20}H_{20}Cl_2N_2$: C, 66.86; H, 5.61; Cl, 19.73; N, 7.80 ; found : C, 66.58; H, 5.55; Cl, 19.61; N, 7.62. ^{1}H NMR (250 MHz, $CDCl_3$) δ : 1.09 and 1.92 (AB, ^2J = 13.0, 2 H, H_{15}), 1.23 (s, CH_3), 2.86 (bs, 1 H, H_{14}), 3.97 (N-H), 6.43 (d, $^3J_{3,4}$ = 8.4, 1 H, H_4), 6.99 (dd, $^3J_{3,4}$ = 8.4 ; $^4J_{3,1}$ = 2.4, 1 H, H_3); 7.05 (d, $^4J_{1,3}$ = 2.4, 1 H, H_1). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 22.66 (CH_3), 29.60 (C_{15}), 42.69 (C_{14}), 57.65 (C_6), 113.40 (C_4), 127.11 (C_3), 128.0 (C_1), 120.30, 126.22, 143.89 (Cq).

5,6,7,8,13,14-hexahydro-3,10-dichloro-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4] diazeci-ne (2f). White solid, mp : 230°C (C_6H_{12}). IR (cm^{-1}) : 3400, 3200, 1610, 796. MS (EI) : m/z : 358 (1), 178 (100). Elemental analysis : calcd for $C_{20}H_{20}Cl_2N_2$: C, 66.86; H, 5.61; Cl, 19.73; N, 7.80 ; found : C, 66.78; H, 5.78; N, 7.60; Cl, 19.74. ^{1}H NMR (250 MHz, $CDCl_3$) δ : 1.09 and 1.93 (AB, ^2J =

13.0, 2 H, H_{15}), 1.22 (s, CH_3), 2.85 (bs, 1 H, H_{14}), 3.92 (N-H), 6.50 (d, $^4J_{4,2}$ = 2.0, 1 H, H_4), 6.59 (dd, $^3J_{2,1}$ = 7.9, $^4J_{2,4}$ = 2.0, 1 H, H_2), 6.98 (d, $^3J_{1,2}$ = 7.9, 1 H, H_1). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 22.62 (CH_3), 29.75 (C_{15}), 42.34 (C_{14}), 57.48 (C_6), 111.95 (C_4), 115.92 (C_2), 129.39 (C_1), 123.33, 132.60, 146.24 (Cq).

5,6,7,8,13,14-hexahydro-2,11-dimethoxy-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2g). White solid, mp : 198°C (C_6H_{12}). R_f = 12.26 min. IR (cm^{-1}) : 3400, 3200, 1620, 1500, 1235, 1035. MS (EI) : m/z : 350 (7.57), 174 (100), 131 (7.38). Elemental analysis : calcd for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99; O, 9.13; found : C, 75.08; H, 7.79; N, 8.03; O, 8.98. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.14 and 2.01 (AB, ^2J = 12.7, 2 H, H_{15}), 1.24 (s, CH_3-6), 2.92 (bs, 1 H, H_{14}), 3.64 (N-H), 3.82 (s, CH_3-O), 6.48 (d, $^3J_{4,3}$ = 8.5, 1 H, H_4), 6.70 (dd, $^3J_{3,4}$ = 8.5, $^4J_{3,1}$ = 2.8, 1 H, H_3), 6.75 (d, $^4J_{1,3}$ = 2.8, 1 H, H_1). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 22.9 (CH_3-7), 30.1 (C_{15}), 55.9 (C_{14}), 43.3 (CH_3-O), 57.6 (C_6), 113.02 (C_4), 113.37 (C_3), 114.05 (C_1), 126.0, 139.8, 150.8 (Cq).

5,6,7,8,13,14-hexahydro-4,9-diacetoxy-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2h). White solid, mp : 278°C (C_6H_{12}). IR (cm^{-1}) : 3440, 3050, 2950, 1764, 1610, 1580, 1490, 1265. MS (EI) : m/z : 406 (10.57), 202 (100), 160 (84.35), 43 (20.36). HRMS (EI) exact mass calcd for $C_{24}H_{26}N_2O_4$, 406.1892 ; found, 406.1893. Elemental analysis : calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89; O, 15.74; found : C, 71.32, H, 6.58; N, 6.73; O, 14.99. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.15 and 1.95 (AB, ^2J = 13.0, 2 H, H_{15}), 1.25 (s, CH_3-6), 2.36 (s, CH_3-CO), 2.96 (bs, 1 H, H_{14}), 3.77 (N-H), 6.63 (m, 1 H, H_2), 6.88 (dd, $^3J_{1,2}$ = 8.0, $^4J_{1,3}$ = 1.2, 1 H, H_1), 6.99 (d, $^3J_{3,2}$ = 6.5, 1 H, H_3). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 20.98 (CH_3-CO), 22.69 (CH_3-6), 29.51 (C_{15}), 42.58 (C_{14}), 57.14 (C_6), 115.37 (C_2), 120.03 (C_1), 125.71 (C_3), 127.06, 135.63, 136.97 (Cq), 169.08 (C=O).

5,6,7,8,13,14-hexahydro-4,9-dihydroxy-6,7-dimethyl-6,14:7,13-dimethanodibenzo[e,i][1,4]diazecine (2i). White solid, mp : 194°C (EtOH). IR (cm^{-1}) : 3490, 3460, 3200, 2900, 1610, 1500. MS (EI) : m/z : 324 (0.2), 161 (15.5), 160 (100). Elemental analysis : calcd for $C_{24}H_{26}N_2O_4$: C, 74.51, H, 6.88, N, 8.69, O, 9.92 ; found : C, 74.38, H, 6.90, N, 8.80, O, 9.87. ^1H NMR (250 MHz, DMSO-d_6) δ : 0.94 and 1.71 (AB, ^2J = 12.4, 2 H, H_{15}), 1.22 (s, CH_3-6), 2.75 (bs, 1 H, H_{14}), 4.58 (N-H), 6.31 (dd, $^3J_{1,2}$ = 7.6, $^3J_{2,3}$ = 7.3, 1 H, H_2), 6.54 (dd, $^3J_{1,2}$ = 7.6, $^4J_{1,3}$ = 1.4, 1 H, H_1), 6.56 (dd, $^3J_{3,2}$ = 7.3, $^4J_{1,3}$ = 1.4, 1 H, H_3), 9.02 (OH). ^{13}C NMR (62.88 MHz, DMSO-d_6) δ : 2.15 (CH_3-6), 30.1 (C_{15}), 42.6 (C_{14}), 57.1 (C_6), 112.1, 114.1, 124.7 (CH), 124.8, 134.2, 141.6 (Cq).

7,13-dihydro-2,6,7,11-tetramethyl-7,13-methanoquino[3,4-c][1]benzazepine (3b). White solid, mp : 242°C ($CHCl_3$). R_T = 9.7 min. IR (cm^{-1}) : 3400, 3200, 2900, 1630, 1500. MS : m/z : 314 (100), 299 (48.22), 284 (9.45),158 (9.26). Elemental analysis : calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91; found : C, 84.05; H, 6.97; N, 8.85. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.91 (s, CH_3-7), 2.06 (d, $^2J_{14\beta,14\alpha}$ = 10.5, 1 H, $H_{14\beta}$), 2.22 (s, CH_3-11), 2.36 (dd, $^2J_{14\alpha,14\beta}$ = 10.5, $^3J_{14\alpha,13}$ = 4.3, 1 H, $H_{14\alpha}$), 2.57(s, CH_3-2), 2.76 (s, CH_3-6), 4.13 (N-H), 4.39 (d, $^3J_{13,14\alpha}$ = 4.3, 1 H, H_{13}), 6.39 (d, $^3J_{9,10}$ = 8.0, 1 H, H_9), 6.78 (dd, $^3J_{9,10}$ = 8.0, $^4J_{10,12}$ = 1.5, 1 H, H_{10}), 7.06 (d, $^4J_{10,12}$ = 1.5, 1 H, H_{12}), 7.42 (dd, $^3J_{4,3}$ = 8.6, $^4J_{3,1}$ = 1.8, 1 H, H_3), 7.80 (d, $^4J_{1,3}$ = 1.8, 1 H, H_1), 7.86 (d, $^3J_{4,3}$ = 8.6, 1 H, H_4). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 20.62, 21.93, 24.32, 24.93 (CH_3), 41.65 (C_{13}), 44.60 (C_{14}), 61.95 (C_7), 115.83 (C_9), 123.09 (C_1), 126.96 (C_{12}), 128.59 (C_4), 128.65 (C_{10}), 131.03 (C_3), 122.24, 123.83, 127.22, 130.83, 135.67, 139.47, 146.28, 149.23, 152.50 (Cq).

7,13-dihydro-3,6,7,10-tetramethyl-7,13-methanoquino[3,4-c][1]benzazepine (3c). Pale yellow gum. R_T = 10.2 min. IR (cm^{-1}) : 3400, 3200, 2900, 1630, 1500. MS (EI) : m/z : 314 (100), 299 (59.97), 284 (13.32), 142 (11.56). HRMS (EI) exact mass calcd for $C_{22}H_{22}N_2$, 314.1782 ; found, 314.1780. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.94 (s, CH_3-7), 2.07 (d, $^2J_{14\alpha,14\beta}$ = 10.4, $H_{14\beta}$), 2.14 (s, CH_3), 2.39 (dd, $^2J_{14\alpha,14\beta}$ = 10.4, $^3J_{14\alpha,13}$ = 4.2, 1 H, $H_{14\alpha}$), 2.50 (s, CH_3), 2.79 (s, CH_3-6), 4.43 (d, $^3J_{14\alpha,13}$ = 4.2, 1 H, H_{13}), 6.29 (s, 1 H, H_9), 6.47 (d, $^3J_{11,12}$ = 7.6, 1 H, H_{11}), 7.11 (d, $^3J_{11,12}$ = 7.6, 1 H, H_{12}), 7.34 (dd, $^3J_{2,1}$ = 8.4, $^4J_{2,4}$ = 1.6, 1 H, H_2), 7.75 (d, $^4J_{2,4}$ = 1.6, 1 H, H_4), 7.94 (d, $^3J_{2,1}$ = 8.4, 1 H, H_1). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 21.26, 21.91, 24.35, 24.87 (CH_3), 41.41 (C_{14}), 44.54 (C_{13}), 61.89 (C_7), 116.22, 118.89, 123.89, 126.18, 127.90, 128.17 (CH), 119.90, 120.85, 129.88, 137.56, 138.66, 141.44, 147.78, 149.66, 153.13 (Cq).

7,13-dihydro-2,11-difluoro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (3d). White solid , mp : 160°C (C_6H_{12}, dec.). R_T = 7.5 min. IR (cm^{-1}) : 3200, 2900, 1500, 1226. MS (EI) : m/z : 322 (100), 307 (64.52), 161 (56.26). ^1H NMR (250 MHz, $CDCl_3$) δ : 1.96 (s, CH_3-7), 2.08 (d, $^2J_{14\alpha,14\beta}$ = 10.7, 1 H, $H_{14\beta}$), 2.41 (dd, $^2J_{14\alpha,14\beta}$ = 10.7, $^3J_{14\alpha,13}$ = 4.2, 1 H, $H_{14\alpha}$), 2.80 (s, CH_3-6), 4.32 (d, $^3J_{14\alpha,13}$ = 4.2, 1 H, H_{13}), 6.37 (dd, $^4J_{9,F}$ = 4.7, $^3J_{9,10}$ = 8.6, 1 H, H_9), 6.70 (ddd, $^4J_{10,12}$ = 2.9, $^3J_{10,9}$ = 8.6, $^3J_{10,F}$ = 8.7, 1 H, H_{10}), 6.95 (dd, $^4J_{12,10}$ = 2.9, $^3J_{12,F}$ = 8.5, 1 H, H_{12}), 7.36 (ddd, $^3J_{3,4}$ = 9.2, $^4J_{3,1}$ = 2.8, $^3J_{3,F}$ = 8.5, 1 H, H_3), 7.57 (dd, $^4J_{1,3}$ = 2.8, $^5J_{1,F}$ = 9.2, 1 H, H_1), 7.81 (dd, $^4J_{4,F}$ = 5.3, $^3J_{3,4}$ = 9.2, 1 H, H_4). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 24.20 (CH_3-7), 24.61 (CH_3-6), 41.65 (C_{13}), 43.72 (C_{14}), 61.97 (C_7), 107.21 (d, $^2J_{C,F}$ = 21.8), 112.90 (d, $^2J_{C,F}$ = 22.4), 114.56 (d, $^2J_{C,F}$ = 22.5), 116.40 ($^3J_{C9,F}$ = 7.6, C_9), 118.91 (d, $^2J_{C,F}$ = 25.6) (C_1, C_3, C_{10}, C_{12}), 122.62 (d, $^3J_{C,F}$ = 9.7), 124.15 (d, $^3J_{C,F}$ = 6.5), 131.07,

131.37 ($^3J_{C4,F}$ = 9.2, C_4), 137.64, 144,72, 148.38, 152.72, 155.69, 155.72 (d, $^1J_{C,F}$ = 203.0), 160.51 (d, $^1J_{C,F}$ = 213.0) (Cq). ^{19}F (200 MHz, $CDCl_3$) δ : -126.69 (td, F_2), -113.41 (td, F_{11}), $^5J_{H,F}$ = 8.5, $^4J_{H,F}$ = 3.8.

7,13-dihydro-2,11-dichloro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (3e). White solid, mp : 260°C (EtOH). IR (cm^{-1}) : 3400, 3040, 2900, 1610, 1500, 885. MS (EI) : m/z : 356 (51.37), 321 (11.15), 177 (100), 142 (16.30). Elemental analysis : calcd for $C_{20}H_{16}N_2Cl_2$: C, 67.61; H, 4.54; N, 7.89; Cl, 19.96 ; found : C, 67.32, H, 4.30, N, 7.63, Cl, 19.79. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.89 (s, CH_3-7), 1.99 (d, $^2J_{14\beta,14\alpha}$ = 10.7, 1 H, $H_{14\beta}$), 2.33 (dd, $^2J_{14\alpha,14\beta}$ = 10.7, $^3J_{14\alpha,13}$ = 4.2, 1 H, $H_{14\alpha}$), 2.74 (s, CH_3-6), 4.30 (d, $^3J_{13,14\alpha}$ = 4.2, 1 H, H_{13}), 4.45 (N-H), 6.33 (d, ^3J = 8.5, 1 H), 6.88 (dd, ^3J = 8.5 ; ^4J = 2.3, 1 H), 7.17 (d, ^4J = 2.3, 1 H), 7.49 (dd, ^3J = 9.0, ^4J = 2.3, 1 H), 7.85 (d, ^3J = 9.0, 1 H), 7.93 (d, ^4J = 2.2, 1 H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 24.27 (CH_3-7), 24.43 (CH_3-6), 41.51 (C_{14}), 43.61 (C_{13}), 61.9 (C_7), 116.62, 122.93, 126.20, 127.99, 129.84, 130.49 (CH), 122.92, 124.13, 130.15, 131.50, 131.85, 140.07, 145.95, 148.0, 153.79 (Cq).

7,13-dihydro-2,11-dimethoxy-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (3g). White solid, mp : 250°C (EtOH). R_T = 13.02 min. IR (cm^{-1}) : 3400, 3200, 2900, 1630, 1500. MS (EI) : m/z : 346 (100), 331 (40), 173 (7.61). Elemental analysis : calcd for $C_{22}H_{22}N_2O_2$: C, 76.27; H, 6.40; N, 8.09; O, 9.24; found : C, 75.85; H, 6.47; N, 7.91; O, 9.17. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.93 (s, CH_3-7), 2.08 (d, $^2J_{14\beta,14\alpha}$ = 10.9, 1 H, $H_{14\beta}$), 2.37 (dd, $^2J_{14\alpha,14\beta}$ = 10.9, $^3J_{14\alpha,13}$=3.9, 1 H, $H_{14\alpha}$), 2.78 (s, CH_3-6), 3.71 (s, CH_3-O), 3.99 (s, CH_3-O), 4.33 (d, $^3J_{13,14\alpha}$ = 3.9, 1 H, H_{13}), 6.43 (d, $^3J_{9,10}$ = 8.6, 1 H, H_9), 6.58 (dd, $^4J_{10,12}$ = 2.8, $^3J_{9,10}$ = 8.6, 1 H, H_{10}), 6.84 (d, $^4J_{12,10}$ = 2.8, 1 H, H_{12}), 7.28 (m, 2 H, H_1, H_3), 7.88 (m, 1 H, H_4). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 24.47 (CH_3-7), 25.41 (CH_3-6), 56.08, 56.10 (CH_3-O), 42.29 (C_{13}), 44.84 (C_{14}), 62.51 (C_7), 102.49, 113.01, 113.47, 117.22, 121.39, 130.71 (CH), 123.34, 125.50, 131.32, 136.19, 144.09, 148.91, 151.15, 152.81, 157.75 (Cq).

7,13-dihydro-4,9-diacetoxy-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (3h). Pale yellow gummy solid. IR (cm^{-1}) : 3340, 3050, 2950, 1764, 1610, 1580, 1490, 1265. ^1H NMR (250 MHz, $CDCl_3$) δ : 2.09 (s, CH_3-7), 2.10 (d, $^2J_{14\alpha,14\beta}$ = 10.8, 1 H, $H_{14\beta}$), 2.45 (dd, $^2J_{14\alpha,14\beta}$ = 10.8, $^3J_{14\alpha,13}$ = 4.1, 1 H, $H_{14\alpha}$), 2.79 (s, CH_3-6), 4.46 (d, $^3J_{14\alpha,13}$ = 4.1, 1 H, H_{13}), 6.65 (m, 2 H), 6.83 (m, 2 H), 7.09 (m, 2H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 21.41 (x2), 24.12, 24.79 (CH_3), 41.86 (C_{13}), 43.32 (C_{14}), 61.14 (C_7), 110.31, 114.32, 117.69, 122.77, 126.76, 136.49 (CH), 122.33, 134.75, 137.46, 144.00, 150.70, 151.06, 151.56, 152.11, 156.95, 177.22 (2x C=O).

5,6,6a,7,13,13a-hexahydro-2,11-difluoro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (4d). Oil. R_T = 6.24 min. IR (cm^{-1}) : 3400, 3040, 2900, 1630, 1500, 1228. MS (EI) : m/z : 325 (55.36), 161 (100), 147 (94 88). ^1H NMR (250 MHz, $CDCl_3$) δ : 1.45 (d, $^3J_{CH3,6}$ = 7.1, CH_3-6), 1.53 (s, CH_3-7), 1.98 (d, $^2J_{14\alpha,14\beta}$ = 11.3, 1 H, $H_{14\beta}$), 2.18 (dd, $^2J_{14\alpha,14\beta}$ = 11.3, $^3J_{14\alpha,13}$ = 4.1, 1 H, $H_{14\alpha}$), 2.37 (dd, $^3J_{6a,13a}$ = 11.9, $^3J_{6a,6}$ = 4.8, 1 H, H_{6a}), 2.98 (dd, $^3J_{13,13a}$ = 6.7, $^3J_{14\alpha,13}$ = 4.1, 1 H, H_{13}), 3.35 (dq, $^3J_{6a,6}$ = 4.8, $^3J_{CH3,6}$ = 7.1, 1 H, H_6), 3.75 (dd, $^3J_{13,13a}$ = 6.7, $^3J_{6a,13a}$ = 11.9, 1 H, H_{13a}), 5.95 (dd, ^3J = 9.1, ^4J = 2.8, 1H), 6.20 (m, 2 H), 6.48 (m, 2 H), 6.67 (dd, ^3J = 9.1, ^4J = 2.8, 1 H) ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 19.97 (CH_3), 27.67 (CH_3), 43.40 (C_{14}), 46.94, 49.83, 51.93, 53.44 (CH), 61.66 (C_7), 112.39 (d, $^2J_{C,F}$ = 22.2), 112.92 (d, $^2J_{C,F}$ = 17.0), 114.03 (d, $^3J_{C,F}$ = 7.7), 114.63 (d, $^2J_{C,F}$ = 14.2), 114.98 (d, $^2J_{C,F}$ = 13.4), 115.91 (d, $^3J_{C,F}$ = 7.8) (CH), 127.39 (d, $^3J_{C,F}$ = 6.8), 127.66 (d, $^3J_{C,F}$ = 6.7), 140.71 , 144.35, 154.96 (d, $^1J_{C,F}$ = 233.7), 156.69 (d, $^1J_{C,F}$ = 236.0) (Cq). ^{19}F NMR (200 MHz, $CDCl_3$) δ : -129.50 (td), -125.98 (td), $^3J_{F,H}$ = 9.0, $^4J_{F,H}$ = 5.0.

5,6,6a,7,13,13a-hexahydro-2,11-dichloro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]-benzazepine (*cis-trans*, 4e). Oil. IR (cm^{-1}) : 3417, 3040, 2900, 1630, 1500, 817. MS (EI) : m/z :358 (39.40), 195 (20.03), 180 (100), 164 (17.39), 149 (13.22). ^1H NMR (250 MHz, $CDCl_3$) δ : 1.44 (d, $^3J_{CH3,6}$ = 6.5, CH_3-6), 1.52 (s, CH_3-7), 1.97 (d, $^2J_{14\beta,14\alpha}$ = 11.3, 1 H, $H_{14\beta}$), 2.18 (dd, $^2J_{14\alpha,14\beta}$ = 11.3, $^3J_{14\alpha,13}$ = 4.2, 1 H, $H_{14\alpha}$), 2.37 (dd, $^3J_{6a,13a}$ = 11.9, $^3J_{6a,6}$ = 4.7, 1 H, H_{6a}), 2.96 (dd, $^3J_{13,14\alpha}$ = 4.2, $^3J_{13,13a}$ = 6.7, 1 H, H_{13}), 3.35 (dq, $^3J_{6,CH3}$ = 6.5, $^3J_{6,6a}$ = 4.7, 1 H, H_6), 3.72 (dd, $^3J_{13a,6a}$ = 11.9, $^3J_{13a,13}$ = 6.7, 1 H, H_{13a}), 6.16 (m, 3H), 6.72 (m, 2 H), 6.90 (d, J = 2.3, 1 H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 19.91 (CH_3-6), 27.40 (CH_3-7), 43.22 (C_{14}), 47.05 (C_{13}), 49.50 (C_{13a}), 51.49 (C_6), 53.84 (C_{6a}), 61.66 (C_7), 114.08, 115.86, 125.70, 126.31, 128.12, 128.44 (CH), 114.18, 120.54, 123.15, 127.33, 143.18, 146.62 (Cq).

5,6,6a,7,13,13a-hexahydro-2,11-dichloro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (*trans-cis*, 5e). Oil. IR (cm^{-1}) : 3417, 3040, 2900, 1630, 1500, 817. ^1H NMR (250 MHz, $CDCl_3$) δ : 1.46 (d, $^3J_{CH3,6}$ = 7.1, CH_3-6), 1.49 (d, $^2J_{14\alpha,14\beta}$ = 10.4, 1 H, $H_{14\beta}$), 1.61 (s, CH_3-7), 1.74 (dd, $^2J_{14\alpha,14\beta}$ = 10.4, $^3J_{14\alpha,13}$ = 3.3, 1 H, $H_{14\alpha}$), 2.45 (m, 1 H, H_{6a}), 2.78 (d, $^3J_{14\alpha,13}$ = 3.3, 1 H, H_{13}), 3.06 (dq, $^3J_{CH3,6}$ = 7.1, $^3J_{6,6a}$ = 2.7, 1 H, H_6), 3.57 (d, $^3J_{13a,6a}$ = 8.3, 1 H, H_{13a}), 6.38 (m, 2 H), 6.90 (m, 2 H), 7.01 (d, ^{4}J = 2.3, 1 H), 7.11 (d, ^{4}J = 2.3, 1 H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 20.19, 22.84 (CH_3), 38.61 (C_{14}), 49.88, 52.27, 54.82, 56.23 (CH), 61.20 (C_7), 115.88, 117.26, 126.62, 127.71, 127.92, 135.78 (x2) (CH), 115.96, 123.31, 122.10, 140.38, 142.34, 147.33 (Cq).

6a,7,13,13a-tetrahydro-2,11-difluoro-6,7-dimethyl-7,13-methanoquino[3,4-c][1]benzazepine (6d).

Oil. IR (cm^{-1}) : 3400, 3040, 2900, 1630, 1500, 1228. MS (EI) : m/z :324 (79.02), 164 (100). ^1H NMR (250 MHz, $CDCl_3$) δ : 1.62 (s, CH_3-7), 1.79 (m, 1 H, $H_{14\beta}$), 1.97 (m, 1 H, $H_{14\alpha}$), 2.09 (s, CH_3-6), 2.75 (d, $^3J_{6a,13a}$ = 13.5, 1 H, H_{6a}), 3.08 (dd, $^3J_{13,13a}$ = 5.7, $^3J_{13,14\alpha}$ = 3.7, 1 H, H_{13}), 3.58 (dd, $^3J_{13,13a}$ = 5.7, $^3J_{6a,13a}$ = 13.5, 1 H, H_{13a}), 5.99 (dd, ^3J = 9.0, ^4J = 2.9, 1 H), 6.10 (dd, ^3J = 8.6, ^4J = 4.7, 1 H), 6.35 (m, 1 H), 6.63 (m, 2 H), 6.92 (m, 1 H). ^{13}C NMR (62.88 MHz, $CDCl_3$) δ : 27.06 (CH_3), 27.68 (CH_3), 39.13 (C_{14}), 47.33, 48.38, 52.32 (CH), 64.42 (C_7), 113.50 (d, $^2J_{C,F}$ = 13.4), 113.78 (d, $^2J_{C,F}$ = 22.1), 113.85 (d, $^2J_{C,F}$ = 13.6), 114.37 (d, $^3J_{C,F}$ = 7.3), 115.48 (d, $^2J_{C,F}$ = 22.3), 125.42 (d, $^3J_{C,F}$ = 7.6), 128.25 (d, $^3J_{C,F}$ = 7.8), 128.92 (d, $^3J_{C,F}$ = 8.5) (CH), 137.79, 138.57, 155.12 (d, $^1J_{C,F}$ = 215.7), 160,00 (C_6), 164.84 (d, $^1J_{C,F}$ = 215.7) (Cq).

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REFERENCES AND NOTES

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