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A New Entry to the Preparation of Pyrrolo[2,3-*b*]quinolines by an aza Wittig/electrocyclic ring-closure/nitrene insertion Process.

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Abstract: A new method for the preparation of the pyrrolo[2,3-*b*]quinoline ring system involving the sequential formation of the pyridine ring (electrocyclic ring-closure) and the pyrrole (nitrene insertion reaction) rings. This approach is based on the regioselective formation of the iminophosphorane **2** from the bis(azide) **1**, followed by aza Wittig reaction with isocyanates and further thermal treatment.
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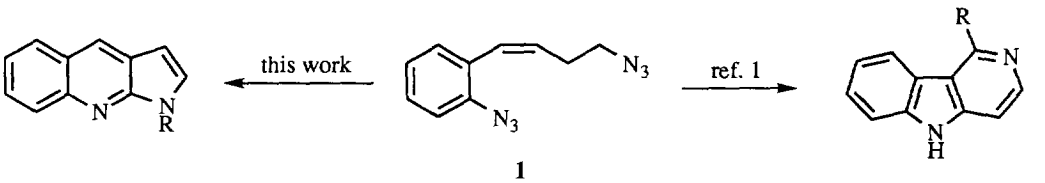
We have previously reported[1] that bis(azide) **1** is a valuable building block for the preparation of γ-carboline derivatives through a reaction sequence which involves thermolysis and further aza Wittig/electrocyclic ring-closure. Herein, we wish to report that bis(azide)[1]**1** is also valuable as a starting material for the preparation of the isomeric pyrrolo[2,3-*b*]quinoline ring system, simply by changing the reaction sequence. Interest in the pyrrolo[2,3-*b*]quinoline ring system stems from the fact that it constitutes the "aza" analogue of furo[2,3-*b*]quinoline, the parent ring feature of the dictamine group of alkaloids which occurr widely in the Rutaceae[2] and from its antiinflammatory, antibacterial, antihypertensive, antipyretic, and anticonvulsant properties, and interferon including activity.[3]

Methods reported for the construction of the title heterocyclic system involve photolyses of 3-(2-aminobenzylidene)pyrrolidin-2(1H)-ones,[4] cyclization of 3-substituted quinolin-2(1H)-ones,[5] pyrolysis of azepine derivatives,[6] cyclization of *N*-phenacyl-3-aminopropiolamides,[7] and reaction of 3-lithiomethylquinolines with nitriles.[8]

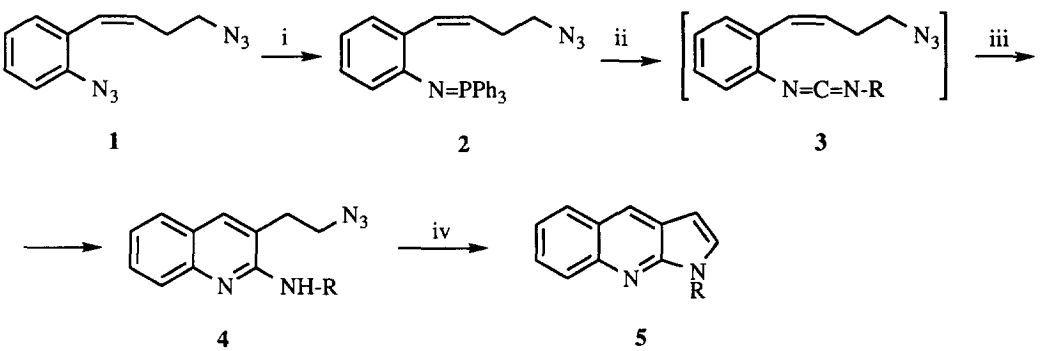


1

The bis(azide) **1** reacted with triphenylphosphine in diethyl ether at room temperature to give a mixture of iminophosphorane **2** and the corresponding iminophosphorane derived from the alkyl substituted azido group in 9:1 ratio as evidenced from the ^{1}H-NMR spectrum of the reaction crude. Attemps to isolate the

iminophosphorane **2** by column chromatograpy resulted in a considerable loss of material due to the hydrolysis of the iminophosphorane **2** during the work-up and the corresponding amine was found to be the major isolated product. For this reason, the iminophosphorane **2** was used without further purification for the next step. Compound **2** reacted with isocyanates at room temperature to give the intermediates carbodiimides **3**, which were cyclised by heating in toluene at 160 °C to give the quinoline derivatives **4**, no products derived from the decomposition of the alkyl substituted azido group were observed. The one-flask conversion of the bis(azide) **1** into the quinoline derivative **4** was achieved in yields ranging from 68% to 49% (Scheme 1).

Pyrolysis of quinoline derivatives **4** at 230 °C under nitrogen for a short period of time provided the corresponding pyrrolo[2,3-*b*]quinolines **5** in 39-75% yields (Scheme 1).



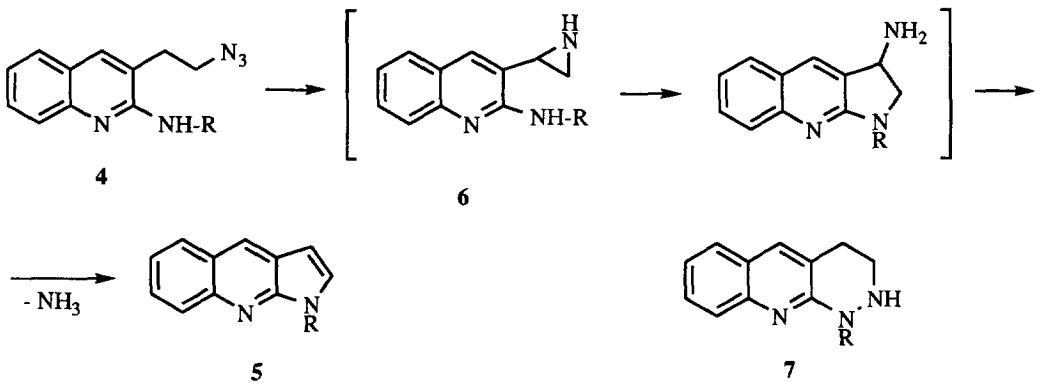
Regents and Conditions: i) Ph_3P, ether, rt; ii) R-NCO, ether, r.t; iii) toluene, sealed tube, 160 °C, 8h; iv) pyrolysis at 240 °C, 4 min.

Scheme 1

The conversion **4** → **5** could be rationalised by loss of nitrogen from the azide **4** and formal insertion of the nitrene into the methylene group at position 3 of the pyridine nucleus. Ring-opening of the resulting aziridine **6** by nucleophilic attack of the amino group at position 2 of the pyridine, followed by elimination of ammonia, which was detected, provided the final product **5** (Scheme 2). The formation of **5** establishes the fact that nitrenes can attack primary aliphatic hydrogen and is another example of an insertion reaction at a saturated carbon.[9] Although, no identifiable products were obtained from the interaction of the nitrene with the amino group presents in the position 2, it is not possible to rule out such a reaction and it may be that the difficulty arises from the fact that the temperature necessary for the decomposition was too high for any product such as **7** to survive.

Experimental.

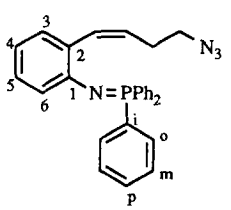
All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC-200 and Varian UNITY-300 spectrometers. Chemical shifts refer to



Scheme 2

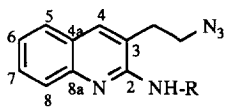
signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P spectra. The mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

2-(4-Azido-1-*Z*-butenyl)-N-(triphenylphosphoranylidene)aniline 2. To a solution of bis(azide) **1** (0.2 g, 0.93 mmol) in dry diethyl ether (10 ml) was added dropwise a solution of triphenylphosphine (0.24 g, 0.93 mmol) in the same solvent (10 ml) at room temperature under nitrogen. The resultant mixture was stirred for 15 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using dichloromethane/ethyl acetate (9:1) as eluent to give **2** (45%) (Rf= 0.7) which was recrystallised from n-hexane/diethyl ether, m.p. 71-73 °C as yellow prisms. (Found: C, 74.80; H, 5.50; N, 12.60. $C_{28}H_{25}N_4P$ requires: C, 74.98; H, 5.62; N, 12.49; IR (Nujol): 3057 (m), 3023 (m), 2129 (s), 2094 (s), 1589 (s), 1473 (vs), 1451 (m), 1432 (m), 1410 (m), 1118 (s), 1021 (m), 996 (m), 757 (s), 719 (s), 701 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 2.61 (q, 2H, J= 7.1 Hz, $C\underline{H}_2CH_2N_3$), 3.30 (t, 2H, J= 7.1 Hz, $CH_2C\underline{H}_2N_3$), 5.60 (dt, 1H, J= 7.1, 11.5 Hz, CH=C<u>H</u>-CH_2), 6.50 (d, 1H, J= 7.0 Hz, H_{arom}), 6.64 (t, 1H, J= 7.0 Hz, H_{arom}), 6.81 (t, 1H, J= 7.0 Hz, H_{arom}), 7.13-7.19 (m, 2H, C<u>H</u>=CH-CH_2 + H_{arom}), 7.40-7.47 (m, 9H, H_{arom}), 7.69-7.78 (m, 6H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 28.47 ($\underline{C}H_2CH_2N_3$), 51.39 ($CH_2\underline{C}H_2N_3$), 116.67 (C-5), 121.65 (d, J= 9.5 Hz, C-6), 123.91 (CH=<u>C</u>H-CH_2), 127.33 (C-4), 128.42 (d, J= 11.9 Hz, C_m), 129.20 (d, J= 1.3 Hz, C-3), 131.47 (q, d, J= 106.9 Hz, C_i), 131.51 (d, J= 2.6 Hz, C_p), 131.68 (q, d, J= 15.9 Hz, C-2), 131.88 (<u>C</u>H=CH-CH_2), 132.45 (d, J= 9.4 Hz, C_o), 149.51 (q, C-1) ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 0.34; m/z (%): 448 (M^+, 6), 406 (29), 378 (52), 262 (51), 183 (100), 130 (57), 108 (85), 77 (39).



General Procedure for the Preparation of 2-Alkyl(aryl)amino-3-(2-azidoethyl)quinoleines 4. To a solution of bis(azide) **1** (0.2 g, 0.93 mmol) in dry diethyl ether (10 ml) was added dropwise a solution of triphenylphosphine (0.24 g, 0.93 mmol) in the same solvent (10 ml) at room temperature under nitrogen. The mixture was stirred for 15 h. and then cooled at 0 °C. A solution of the appropriate isocyanate (0.93 mmol) in dry diethyl ether (5 ml) was added and the resultant solution was allowed to warm to room temperature and stirred for additional 2h. The solvent was removed under reduced pressure and the crude solid was dissolved

in dry toluene (30 ml) and treated in a sealed tube at 160 °C for 8 h. After cooling, the solvent was removed and the residue was chromatographed on a silica gel column using ethyl acetate/n-hexane (1:4) as eluent to give **4**. Compounds **4d** and **4c** were recrystallized from the appropriate solvent.



4a (R= C_6H_5-CH_2): (49%), orange oil; (Found: C, 71.14; H, 5.72; N, 23.19. $C_{18}H_{17}N_5$ requires: C, 71.27; H, 5.65; N, 23.09; IR (film): 3428 (m), 2100 (vs), 1633 (m), 1518 (s), 1487 (m), 1457 (m), 1415 (m), 1354 (m), 1257 (m), 754 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 2.72 (t, 2H, J= 6.8 Hz, $C\underline{H}_2CH_2N_3$), 3.56 (t, 2H, J= 6.8 Hz, $CH_2C\underline{H}_2N_3$), 4.76 (d, 2H, J= 5.1 Hz, $C\underline{H}_2Ph$), 4.78 (d, 1H, J= 5.1 Hz, NH), 7.11-7.71 (m, 10H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 30.42 ($\underline{C}H_2CH_2N_3$), 45.77 ($\underline{C}H_2Ph$), 50.08 ($CH_2\underline{C}H_2N_3$), 121.40 (q, C-3), 122.30, 123.49 (q, C-4a), 126.12, 126.86, 127.21 (C-4'), 128.03 (C-2'), 128.55 (C-3'), 129.03, 135.54 (C-4), 139.58 (q, C-1'), 146.98 (q, C-8a), 154.78 (q, C-2); m/z (%): 303 (M^+, 8), 261 (14), 258 (12), 169 (49), 143 (100), 91 (96), 77 (18).

4b (R= C_6H_5): (68%), bronw oil; (Found: C, 70.42; H, 5.33; N, 24.08. $C_{17}H_{15}N_5$ requires: C, 70.57; H, 5.23; N, 24.20; IR (film): 3449 (m), 2099 (vs), 1629 (m), 1598 (m), 1538 (s), 1528 (s), 1499 (m), 1444 (m), 1413 (m), 1355 (m), 1307 (m), 1251 (m), 760 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 2.81 (t, 2H, J= 6.6 Hz, $C\underline{H}_2CH_2N_3$), 3.63 (t, 2H, J= 6.6 Hz, $CH_2C\underline{H}_2N_3$), 6.86 (d, 1H, NH), 7.0-7.8 (m, 10H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 30.91 ($\underline{C}H_2CH_2N_3$), 50.58 ($CH_2\underline{C}H_2N_3$), 119.51 (C-2'), 121.15 (q, C-3), 122.24 (C-4'), 123.31, 124.15 (q, C-4a), 126.72, 126.74, 128.78 (C-3'), 129.18, 136.87 (C-4), 140.40 (q, C-1'), 146.33 (q, C-8a), 152.14 (q, C-2); m/z (%): 290 (M^++1, 10), 289 (M^+, 56), 260 (48), 245 (46), 244 (22), 233 (100), 140 (25), 116 (33), 77 (51).

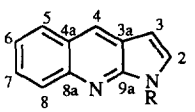
4c (R= 4-H_3C-C_6H_4): (64%), brown oil; (Found: C, 71.35; H, 5.75; N, 22.96. $C_{18}H_{17}N_5$ requires: C, 71.27; H, 5.65; N, 23.09; IR (film): 3444 (m), 2100 (vs), 1627 (m), 1605 (m), 1518 (s), 1471 (m), 1451 (m), 1415 (s), 1355 (m), 1308 (m), 1250 (m), 816 (m), 758 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 2.34 (s, 3H, CH_3), 2.91 (t, 2H, J= 6.6 Hz, $C\underline{H}_2CH_2N_3$), 3.72 (t, 2H, J= 6.6 Hz, $CH_2C\underline{H}_2N_3$), 6.79 (d, 1H, NH), 7.17 (d, 2H, J= 8.3 Hz, H_{arom}), 7.28 (t, 1H, J= 7.3 Hz, H_{arom}), 7.58-7.81 (m, 6H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 22.60 (CH_3), 31.14 ($\underline{C}H_2CH_2N_3$), 50.98 ($CH_2\underline{C}H_2N_3$), 119.92 (C-2'), 121.01 (q, C-3), 123.22, 124.17 (q, C-4a), 126.74, 126.86, 129.19, 129.35 (C-3'), 131.93 (q, C-4'), 136.91 (C-4), 137.86 (q, C-1'), 146.59 (q, C-8a), 152.41 (q, C-2); m/z (%): 304 (M^++1, 22), 303 (M^+, 100), 275 (32), 258 (52), 247 (93), 231 (66), 115 (30), 91 (19).

4d (R= 4-H_3CO-C_6H_4): (65%), m.p. 107-108 °C (yellow prisms from dichoromethane/diethyl ether); (Found: C, 67.58; H, 5.50; N, 22.09. $C_{18}H_{17}N_5O$ requires: C, 67.70; H, 5.37; N, 21.93; IR (Nujol): 3404 (m), 2105 (vs), 1635 (m), 1612 (m), 1578 (m), 1516 (s), 1476 (m), 1452 (s), 1357 (m), 1295 (m), 1249 (s), 1051 (m), 841 (m), 758 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 2.74 (t, 2H, J= 6.6 Hz, $C\underline{H}_2CH_2N_3$), 3.57 (t, 2H, J= 6.6 Hz, $CH_2C\underline{H}_2N_3$), 3.75 (s, 3H, OCH_3), 6.67 (d, 1H, NH), 6.88 (d, 2H, J= 8.3 Hz, H_{arom}), 7.22 (t, 1H, J= 7.3 Hz, H_{arom}), 7.46-7.77 (m, 6H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 30.73 ($\underline{C}H_2CH_2N_3$), 50.59 ($CH_2\underline{C}H_2N_3$), 55.43 (OCH_3), 113.99 (C-2'), 120.83 (q, C-3), 121.72 (C-3'), 122.96, 124.02 (q, C-4a), 126.57, 126.75, 129.08, 133.61 (q, C-1'), 136.54 (C-4), 146.44 (q, C-8a), 152.51 (q, C-2), 155.19 (q, C-4'); m/z (%): 319 (M^++1, 33), 291 (16), 275 (31), 274 (32), 259 (22), 231 (42), 140 (41), 115 (100), 109 (40), 89 (38).

4e (R= 4-Br-C_6H_4): (62%), m.p. 102-103 °C (yellow prisms from diethyl ether); (Found: C, 55.32; H, 3.70; N, 18.89. $C_{17}H_{14}N_5Br$ requires: C, 55.45; H, 3.83; N, 19.02; IR (film): 3433 (m), 2099 (vs), 1630 (m), 1588 (m), 1522 (s), 1492 (s), 1465 (s), 1421 (s), 1353 (m), 1312 (m), 1293 (m), 1266 (m), 816 (m), 745 (m) cm^{-1}; ^{1}H-

NMR ($CDCl_3$, 300 MHz) δ: 2.84 (t, 2H, J= 6.2 Hz, $C\underline{H}_2CH_2N_3$), 3.68 (t, 2H, J= 6.2 Hz, $CH_2C\underline{H}_2N_3$), 6.93 (d, 1H, NH), 7.29 (t, 1H, J= 7.3 Hz, H_{arom}), 7.41 (d, 2H, J= 8.4 Hz , H_{arom}), 7.54 (t, 1H, J= 7.3 Hz, H_{arom}), 7.58 (d, 1H, J= 7.3 Hz, H_{arom}), 7.65 (d, 2H, J= 8.4 Hz, H_{arom}), 7.69 (s, 1H, H_{arom}), 7.78 (d, 1H, J= 7.3, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 30.98 ($\underline{C}H_2CH_2N_3$), 51.20 ($CH_2\underline{C}H_2N_3$), 114.22 (q, C-4'), 121.05 (C-2'), 121.28 (q, C-3), 123.60, 124.26 (q, C-4a), 126.76, 126.78, 129.36, 131.58 (C-3'), 137.11 (C-4), 139.57 (q, C-1'), 146.20 (q, C-8a), 151.86 (q, C-2); m/z (%): 369 (M^++2, 14), 367 (M^+, 14), 324 (15), 322 (15), 231 (100), 140 (27), 116 (31), 76 (32).

General Procedure for the Preparation of 1-Alkyl(aryl)pyrrolo[2,3-*b*]quinolines 5. The corresponding quinoline **4** (0.15 mmol) was treated at 230 °C in a molten salt bath ($NaNO_2/NaNO_3/KNO_3$ 40:7.53) under nitrogen for 4 min. The solid residue of the pyrolysis was chromatographed on a silica gel colunm using ethyl acetate/n-hexane as eluent to give **5** which were recrystallized from the appropriate solvent.



5a (R= C_6H_5-CH_2): (39%), m.p. 80-81 °C (yellow prisms from n-hexane); (Found: C, 83.57; H, 5.39; N, 10.95. $C_{18}H_{14}N_2$ requires: C, 83.69; H, 5.46; N, 10.84; IR (Nujol): 1612 (m), 1566 (m), 1524 (s), 1495 (m), 1457 (s), 1433 (m), 1423 (m), 1406 (vs), 1368 (m), 1356 (m), 1336 (m), 1282 (m), 1215 (m), 914 (m), 759 (s), 720 (vs) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 5.60 (s, 2H, $C\underline{H}_2Ph$), 6.58 (d, 1H, J= 3.9 Hz, H-3), 7.24-7.29 (m, 5H, H_{arom}), 7.32 (d, 1H, J= 3.9 Hz, H-2), 7.40 (ddd, 1H, J= 1.2, 6.8, 8.0 Hz, H-6), 7.63 (ddd, 1H, J= 1.5, 6.8, 8.7 Hz, H-7), 7.93 (dd, 1H, J= 1.5, 8.0 Hz, H-5), 8.11 (dd, 1H, J= 1.2, 8.7 Hz, H-8), 8.38 (s, 1H, H-4); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 47.71 ($\underline{C}H_2Ph$), 99.68 (C-3), 122.01 (q, C-3a), 122.75, 124.72 (q, C-4a), 127.54, 127.58, 127.68 (C-4'), 127.70 (C-2'), 127.94, 128.21, 128.67 (C-3'), 131.89 (C-2), 137.83 (C-1'), 145.14 (q, C-8a), 149.45 (q, C-9a); m/z (%): 259 (M^++1, 13), 258 (M^+, 75), 257 (77), 181 (32), 167 (15), 140 (22), 91 (100).

5b (R= C_6H_5): (62%), m.p. 63-64 °C (yellow prisms from n-hexane); (Found: C, 83.45; H, 5.07; N, 11.35. $C_{17}H_{12}N_2$ requires: C, 83.58; H, 4.95; N, 11.47; IR (Nujol): 1603 (s), 1537 (vs), 1499 (vs), 1422 (s), 1397 (s), 1342 (s), 1244 (m), 758 (s), 712 (m), 692 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 6.75 (d, 1H, J= 3.9 Hz, H-3), 7-3-7.68 (m, 5H, H_{arom}), 7.73 (d, 1H, J=3.9 Hz, H-2), 7.92-7.98 (m, 3H, H-5, H-6, H-7), 8.11 (d, 1H, J= 8.6 Hz, H-8), 8.42 (s, 1H, H-4); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 101.45 (C-3), 122.90 (q, C-3a), 123.34, 123.37 (C-2'), 124.94 (q, C-4a), 125.86 (C-4), 127.76, 127.84, 128.04, 128.49, 129.33 (C-3'), 131.62 (C-2), 138.66 (C-1'), 145.25 (q, C-8a), 148.80 (q, C-9a); m/z (%): 245 (M^++1, 18), 244 (M^+, 100), 243 (60), 140 (20), 122 (26), 77 (25).

5c (R= 4-H_3C-C_6H_4): (70%), m.p. 72-73 °C (yellow prisms from n-hexane); (Found: C, 83.71; H, 5.38; N, 10.72. $C_{18}H_{14}N_2$ requires: C, 83.69; H, 5.46; N, 10.84; IR (Nujol): 1612 (m), 1536 (vs), 1518 (s), 1424 (m), 1415 (m), 1393 (s), 1336 (s), 1242 (m), 820 (m), 760 (m), 708 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 2.43 (s, 3H, CH_3), 6.73 (d, 1H, J= 3.9 Hz, H-3), 7.35 (d, 2H, J= 7.8 Hz, H_{arom}), 7.42 (ddd, 1H, J= 1.8, 6.5, 8.4 Hz, H-6), 7.63 (ddd, 1H, J= 1.5, 6.5, 8.7 Hz, H-7), 7.71 (d, 1H, J= 3.9 Hz, H-2), 7.81 (d, 2H, J= 7.8 Hz, H_{arom}), 7.94 (dd, 1H, J= 1.5, 8.4 Hz, H-5), 8.10 (dd, 1H, J= 1.8, 8.7 Hz, H-8), 8.41 (s, 1H, H-4); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 21.14 (CH_3), 101.14 (C-3), 122.92 (q, C-3a), 123.35, 123.60 (C-2'), 124.98 (q, C-4a), 127.76, 127.84, 128.13, 128.59, 129.97 (C-3'), 131.95 (C-2), 135.84 (q), 136.24 (q), 145.36 (q, C-8a), 148.59 (q, C-9a); m/z (%): 259 (M^++1, 21), 258 (M^+, 100), 257 (44), 140 (38), 128 (53), 121 (11), 114 (28), 91 (34).

5d (R= 4-H_3CO-C_6H_4): (75%), m.p. 137-138 °C (white needles from diethyl ether); (Found: C, 78.77; H, 5.06; N, 10.32. $C_{18}H_{14}N_2O$ requires: C, 78.81; H, 5.14; N, 10.21; IR (Nujol): 1616 (m), 1557 (m), 1533 (vs),

1464 (m), 1391 (s), 1331 (s), 1295 (m), 1248 (vs), 1143 (m), 1112 (m), 1031 (m), 847 (m), 825 (m), 764 (s), 715 (s), 607 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.87 (s, 3H, OCH_3), 6.70 (d, 1H, J= 3.7 Hz, H-3), 7.06 (d, 2H, J= 8.9 Hz, H_{arom}), 7.41 (ddd, 1H, J= 0.9, 7.4, 8.1 Hz, H-6), 7.62 (ddd, 1H, J= 1.5, 7.4, 8.2 Hz, H-7), 7.64 (d, 1H, J= 3.7 Hz, H-2), 7.78 (d, 2H, J= 8.9 Hz, H_{arom}), 7.93 (d, 1H, J= 8.1 Hz, H-5), 8.1 (d, 1H, J= 8.2 Hz, H-8), 8.39 (s, 1H, H-4); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 65.83 (OCH_3), 100.74 (C-3), 114.52 (C-2'), 122.62 (q, C-3a), 123.17, 124.82 (q, C-4a), 125.07 (C-3'), 127.68, 127.71, 128.04, 128.42, 131.75 (q, C-1'), 132.06 (C-2), 145.23 (q, C-8a), 148.86 (q, C-9a), 157.78 (q, C-4'); m/z (%): 275 (M^++1, 21), 274 (M^+, 100), 259 (75), 231 (58), 168 (34), 140 (48), 114 (27), 88 (16).

5e (R= 4-Br-C_6H_4): (56%), m.p. 120-121 °C (white needles from n-hexane); (Found: C, 63.27; H, 3.30; N, 8.77. $C_{17}H_{11}N_2Br$ requires: C, 63.18; H, 3.43; N, 8.67; IR (Nujol): 1591 (m), 1533 (s), 1527 (m), 1490 (vs), 1461 (m), 1427 (m), 1409 (m), 1388 (m), 1240 (m), 821 (m), 742 (m), 716 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 6.74 (d, 1H, J= 4.0 Hz, H-3), 7.44 (ddd, 1H, J= 0.9, 7.4, 8.1 Hz, H-6), 7.62-7.67 (m, 4H, H-2, H-7, H_{arom}), 7.87 (d, 2H, J= 8.7 Hz, H_{arom}), 7.93 (d, 1H, J= 8.1 Hz, H-5), 8.10 (dd, 1H, J= 0.9, 8.4 Hz, H-8), 8.40 (s, 1H, H-4); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 102.03 (C-3), 118.91 (q, C-4'), 122.81 (q, C-3a), 123.59, 124.63 (C-2'), 124.99 (q, C-4a), 127.95, 128.06, 128.08, 128.42, 130.90 (C-2), 132.33 (C-3'), 137.68 (q, C-1'), 145.23 (q, C-8a), 148.66 (q, C-9a); m/z (%): 325 (M^++3, 17), 324 (M^++2, 92), 323 (M^++1, 47), 322 (M^+, 100), 243 (29), 242 (39), 241 (20), 216 (23), 140 (44), 121 (76), 113 (20).

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