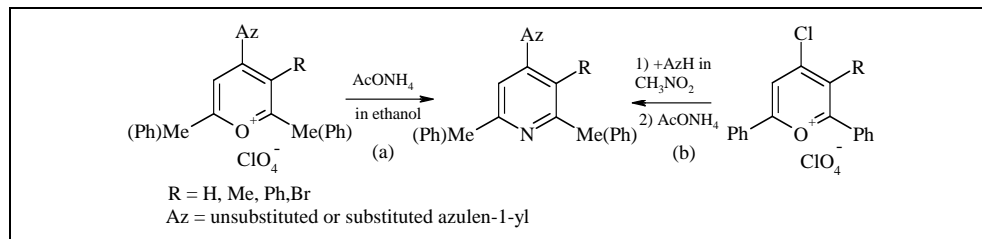


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4-Azulen-1-yl substituted 2,6-dimethyl- and 2,6-diphenyl-pyridines are obtained in good yields from the reaction of corresponding 4-azulen-1-yl-pyranylium salts and ammonium acetate in ethanol or starting from 4-chloro-2,6-diphenyl-pyranylium salts in two steps: reaction with azulenes followed by *in situ* treatment with ammonium acetate. The effect of substitution at the 3-position of the heterocycle was taken into account. The structure assignment was accomplished with NMR and uv-vis spectra.

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## INTRODUCTION

As the need for new technical valuable materials grows, highly conjugated scaffold featuring polarization over the entire molecule framework was a continuous target of our studies. We have recently focused our attention on the synthesis and the properties of azulene-substituted pyranium salts [1]. The compounds obtained present interest as efficient push-pull systems in which azulene plays the electron donor role and the heterocyclic ring is the withdrawing group. This property could be valuable in technical purposes, such as for optical applications (*e.g.* materials with non-linear optical properties) [2,3]. The possibility to obtain the new heterocyclic systems, namely pyridines and pyridinium salts, starting from these synthons [4] motivated us to undertake a systematic study regarding the generation of such compounds. This first paper describes our results on scope and limitations of azulenyl-pyridine synthesis. Some peculiarities regarding the structure and the properties of obtained pyridines will be reported and compared with those for the corresponding pyridinium salts explored in the next paper of this series [5].

## RESULTS AND DISCUSSION

Two main procedures are available for the generation of pyridines from pyranium salts. The first route, the classic one, consists in the replacement of heterocyclic oxygen atom by nitrogen using ammonium acetate as the nitrogen source (route (a) in Scheme 1) in ethanol. This procedure requires the opening of pyranium ring, the substitution of O by N and cyclization of the intermediate.

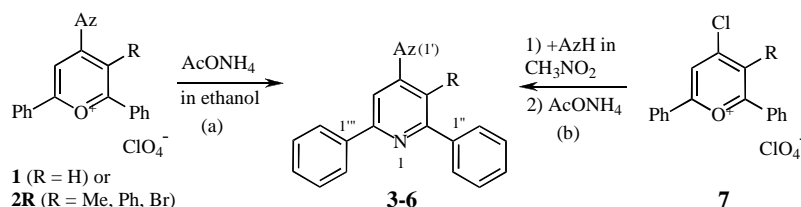
As an alternative procedure (route (b) in Scheme 1), the nucleophilic substitution of chlorine in pyranium salt **7** by azulenes is followed by *in situ* replacement of oxygen by nitrogen, as shown for the previous procedure. The last sequence of reactions occurs in nitromethane as solvent.

Whereas route (a) can be used both for 2,6-diphenyl or 2,6-dimethyl-pyridines, only the 2,6-diphenyl derivatives were obtained by route (b) because the 4-chloro-2,6-dimethyl-pyranium salts can not be separated from the reaction mixture after halogenation of the corresponding pyranone [2]. The last route is, however, preferable for the preparation of 2,6-diphenyl derivatives, especially with a substituent at the 3-position (the compounds **4–6**) because, here, the azulenyl-pyranium salts, used as reactant, resulted from the synthesis contaminated with starting material making separation difficult [2]. Whereas the yields of pyridines 3-substituted with Me were very good, those with Ph or Br resulted in somewhat lower yields.

## EXPERIMENTAL

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. <sup>1</sup>H- and <sup>13</sup>C-NMR: Bruker ARX 500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125.75 MHz) and Bruker Avance DRX4 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100.62 MHz) spectrometers; chemical shifts (δ) are expressed in ppm, and J values are given in Hz; TMS was used as internal standard in CDCl<sub>3</sub> as solvent; the signals were assigned on the basis of COSY, HETCOR and HMBC experiments. Mass spectra: JEOL JMS-DX303 spectrometer coupled to analytical gas-chromatograph Shimadzu GC-14B with a DB-1 capillary column and C-R6A integrator and Finnigan MAT 311-A/100

Scheme 1



Az = unsubstituted or substituted azulene-1-yl

**Table 1.** Synthesis of 4-(azulen-1-yl)-2,6-diphenylpyridines **3**, yield in % (without recovering starting azulene-pyranilium salt)\*

Compound <b>3</b> (R = H)	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>e</b>	<b>f</b>	<b>g</b>
Az substituents	-	3-Me	3- <i>t</i> Bu	4,8-Me <sub>2</sub>	4,6,8-Me <sub>3</sub>	Gu**	2- <i>t</i> Bu,6-Me
Yield	98	85	89	85	95	78	75

\*The compounds **3a-f** are obtained by route (a) starting from the corresponding pyranilium salts, **1a-f**; compound **3g** was obtained by the route (b) starting from **7**. \*\*Gu = 3,8-Me<sub>2</sub>,5-*i*Pr.

**Table 2.** Synthesis of 3-R substituted 4-(azulen-1-yl)-2,6-diphenylpyridines, **4** (R = Me), **5** (R = Ph) and **6** (R = Br), yield in %

Compound	Az substituent	<b>4</b> R = Me	<b>5</b> R = Ph	<b>6</b> R = Br
<b>a</b>	-	92*	60**	63**
<b>e</b>	4,6,8-Me <sub>3</sub>	88*	78**	64**
<b>f</b>	Gu	91*	63**	83**
<b>g</b> **	2- <i>t</i> Bu,6-Me	71**	48**	40**

\*The compounds were obtained by the route (a) starting from **2R**. \*\*The compounds are obtained by the route (b).

MS; for the spectra recording in solid state Carlo Erba QMD 1000 (EI+, 70 eV). Column chromatography: silica gel [70-230 mesh (ASTM)] and alumina [act. II-III, 70-230 mesh ASTM]. Dichloromethane (DCM) was distilled over CaH<sub>2</sub>, ethyl acetate was distilled over Na<sub>2</sub>CO<sub>3</sub>. UV spectra in methanol: Specord UV-Vis spectrometer (C. Zeiss Jena). The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06).

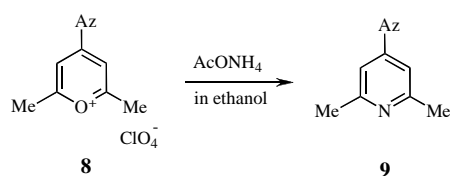
**Pyridine preparations from pyranilium salts; general procedure.** The mixture of pyranilium perchlorates and an excess (ten times) of ammonium acetate in ethanol (50 ml for one mmol pyranilium salt) was refluxed for one hour. The solvent was vaporized in vacuum and the residue was treated with a mixture of dichloromethane (DCM) and water. The separated organic layer was washed twice with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The DCM was removed in vacuum and the product was obtained by column chromatography. For the 2,6-diphenyl series, silica gel was used as support. The eluent was *n*-pentane for unreacted azulenes and, usually, DCM for pyridines (sometimes, a mixture of DCM and ethyl acetate 10% was necessary). During chromatogram the pyridine fraction are brown colored, however, they turned blue, green or violet in the eluted solutions. For the 2,6-dimethyl series alumina was used as support and as eluent a mixture of *n*-pentane:DCM = 1:2. On the column as well as in eluted solutions the color of 2,6-dimethyl-

pyridines are: blue for **9a**, violet for **9e** and **9g** and green for **9f**. The obtained pyridines are viscose liquid or they crystallized over a very long time (weeks).

**Pyridine preparations from 4-chloro-2,6-diphenylpyranilium perchlorate; general procedure.** The azulenic compound (1 mmol) and 4-chloro-2,6-diphenylpyranilium perchlorate (1 mmol) are dissolved in nitromethane (10 ml). The reaction mixture was heated under stirring at 100 °C for 1 hour and then cooled at room temperature. Ammonium acetate (10 mmols) was added and the reaction mixture was heated with stirring at 100 °C for one hour. The solvent was evaporated in vacuum and the residue was worked-up as above (for column chromatography the eluent was chloroform).

The numbering of atom positions, used for the pyridines characterization, is described in Scheme 1 and 2.

Scheme 2



Az = unsubstituted or substituted azulene-1-yl

**Table 3.** Synthesis of 4-(azulen-1-yl)-2,6-dimethyl-pyridines **9** on route (a), yield in % (without recovering starting azulene-pyranilium salt)

Compounds <b>9</b>	<b>a</b>	<b>e</b>	<b>f</b>	<b>g</b>
Az substituents	-	4,6,8-Me <sub>3</sub>	Gu**	2- <i>t</i> Bu,6-Me
Yield	66	61	68	57

**4-(Azulen-1-yl)-2,6-diphenyl-pyridine, (3a).** This compound was obtained as blue crystals; mp 175 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 217 (4.46), 243 (4.53), 279 (4.46), 300 (4.40), 313 sh (4.32), 370 (3.93) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  7.28 (t, J = 9.9 Hz, 1H, 5'-H), 7.29 (t, J = 9.9 Hz, 1H, 7'-H), 7.45 (t, J = 7.0 Hz, 2H, 4''-H), 7.53 (d, J = 4.0 Hz, 1H, 3'-H), 7.54 (t, J = 7.0 Hz, 4H, 3''-H, 5''-H), 7.72 (t, J = 9.9 Hz, 1H, 6'-H), 7.95 (s, 2H, 3-H, 5-H), 8.18 (d, J = 4.4 Hz, 1H, 2'-H), 8.25 (d, J = 8.2 Hz, 4H, 2''-H, 6''-H), 8.39 (d, J = 9.2 Hz, 1H, 4'-H), 8.66 (d, J = 9.7 Hz, 1H, 8'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  118.0 (C3'), 119.6 (C3, C5), 124.1 (C5''), 124.5 (C7'), 127.2 (C2'', C6''), 128.6 (C1'), 128.7 (C3'', C5''), 128.9 (C4''), 135.3 (C8'), 135.9 (C3a'), 137.1 (C2'), 137.8 (C4'), 138.7 (C6'), 139.8 (C1''), 142.5 (C8a'), 146.6 (C4), 157.2 (C2, C6) ppm; ms (70 eV): m/z 357 [M<sup>+</sup>, 25], 102 (24), 77 (100). *Anal.* Calcd. for C<sub>27</sub>H<sub>19</sub>N: C, 90.72; H, 5.36; N 3.92. Found: C, 90.64; H, 5.42; N 3.94.

**4-(3-Methyl-azulen-1-yl)-2,6-diphenyl-pyridine (3b).** This compound was obtained as green oil; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 217 (4.42), 241 (4.51), 282 (4.43), 301 (4.33), 380 (3.82) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$ : 2.75 (s, 3H, Me), 7.17 (t, J = 9.4 Hz, 1H, 5'-H), 7.19 (t, J = 9.6 Hz, 1H, 7'-H), 7.47 (t, J = 7.0 Hz, 2H, 4''-H), 7.55 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.62 (t, J = 9.8 Hz, 1H, 6'-H), 7.93 (s, 2H, 3-H, 5-H), 8.03 (s, 1H, 2'-H), 8.25 (d, J = 7.6 Hz, 4H, 2''-H, 6''-H), 8.32 (d, J = 9.2 Hz, 1H, 4'-H), 8.60 (d, J = 9.6 Hz, 1H, 8'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$ : 12.7 (Me), 119.5 (C3, C5), 122.6 (C7'), 123.7 (C5''), 126.1 (C3'), 126.9 (C1'), 127.1 (C2'', C6''), 128.7 (C3'', C5''), 128.9 (C4''), 134.7 (C4'), 134.8 (C8'), 136.0 (C3a'), 138.0 (C2'), 138.6 (C6'), 138.9 (C8a'), 139.8 (C1''), 146.5 (C4), 157.1 (C2, C6) ppm; ms (70 eV): m/z 372 (25), 371 [M<sup>+</sup>, 100], 141 (38). *Anal.* Calcd. for C<sub>28</sub>H<sub>21</sub>N: C, 90.53; H, 5.70; N 3.77. Found C, 90.54; H, 5.62; N 3.84.

**4-(3-*tert*-Butyl-azulen-1-yl)-2,6-diphenyl-pyridine (3c).** This compound was obtained as green oil; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 217 (4.39), 244 (4.47), 283 (4.40), 304 (4.33), 380 (3.92) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  1.69 (s, 9 H, Me), 7.17 (t, J = 9.6 Hz, 1H, 5'-H), 7.20 (t, J = 10.0 Hz, 1H, 7'-H), 7.46 (t, J = 7.2 Hz, 2H, 4''-H), 7.54 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.64 (t, J = 9.6 Hz, 1H, 6'-H), 7.93 (s, 2H, 3-H, 5-H), 8.09 (s, 1H, 2'-H), 8.24 (d, J = 7.2 Hz, 4H, 2''-H, 6''-H), 8.63 (d, J = 9.6 Hz, 1H, 8'-H), 8.78 (d, J = 9.6 Hz, 1H, 4'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  32.1 (Me<sub>3</sub>C), 33.4 (Me<sub>3</sub>C), 119.7 (C3, C5), 122.2 (C7'), 123.8 (C5''), 126.5 (C1'), 127.2 (C2'', C6''), 128.7 (C3'', C5''), 128.9 (C4''), 135.0 (C8'), 135.8 (C2'), 136.6 (C4'), 137.0 (C3a'), 137.2 (C8a'), 138.5 (C6'), 139.3 (C3'), 139.9 (C1''), 146.8 (C4), 157.1 (C2, C6) ppm; ms (70 eV): m/z 414 (13), 413 [M<sup>+</sup>, 51], 398 (100). *Anal.* Calcd. for C<sub>31</sub>H<sub>27</sub>N: C, 90.03; H, 6.58; N 3.39. Found: C, 90.12; H, 6.62; N 3.26.

**4-(4,8-Dimethyl-azulen-1-yl)-2,6-diphenyl-pyridine (3d).** This compound was obtained as blue oil; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 214 (4.40), 245 (4.54), 287 (4.49), 305 (4.30), 342 sh (4.77), 370 (3.74) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  2.68 (s, 3H, 4'-Me), 3.03 (s, 3H, 8'-Me), 7.15 (d, J = 10.4 Hz, 1H, 5'-H), 7.23 (d, J = 10.4 Hz, 1H, 7'-H), 7.48 (t, J = 7.1 Hz, 2H, 4''-H), 7.50 (t, J = 10.0 Hz, 1H, 6'-H), 7.55 (d, J = 4.8 Hz, 1H, 3'-H), 7.55 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.83 (s, 2H, 3-H, 5-H), 7.84 (d, J = 4.4 Hz, 1H, 2'-

H), 8.28 (d, J = 7.0 Hz, 4H, 2''-H, 6''-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  25.3 (8'-Me), 28.8 (4'-Me), 115.4 (C3'), 120.7 (C3, C5), 125.4 (C7'), 127.1 (C2'', C6''), 127.9 (C5''), 128.7 (C3'', C5''), 128.9 (C4''), 129.9 (C1'), 133.0 (C3a'), 135.6 (C6'), 137.4 (C2'), 139.4 (C8a'), 139.6 (C1''), 147.4 (C8'), 148.4 (C4'), 151.4 (C4), 155.7 (C2, C6) ppm; ms (70 eV): m/z 385 [M<sup>+</sup>, 26], 103 (42), 102 (40), 77 (100). *Anal.* Calcd. for C<sub>29</sub>H<sub>23</sub>N: C, 90.35; H, 6.01; N 3.63. Found: C, 90.28; H, 6.08; N 3.64.

**2,6-Diphenyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (3e).** This compound was obtained as violet crystals; mp 97-8 °C (lit 97-8 °C); [6] uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 217 (4.40), 244 (4.54), 291 (4.46), 309 (4.30), 345 sh (3.78), 374 (3.70) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  2.66 (s, 3H, 6'-Me), 2.69 (s, 3H, 4'-Me), 3.00 (s, 3H, 8'-Me), 7.12 (s, 1H, 5'-H), 7.19 (s, 1H, 7'-H), 7.47 (d, J = 4.8 Hz, 1H, 3'-H), 7.48 (t, J = 7.1 Hz, 2H, 4''-H), 7.56 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.75 (d, J = 4.4 Hz, 1H, 2'-H), 7.84 (s, 2H, 3-H, 5-H), 8.29 (d, J = 7.0 Hz, 4H, 2''-H, 6''-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  25.6 (8'-Me), 28.5 (6'-Me), 29.2 (4'-Me), 115.4 (C3'), 120.6 (C3, C5), 127.1 (C2'', C6''), 127.8 (C7'), 128.6 (C3'', C5''), 128.9 (C4''), 129.5 (C5'), 130.0 (C1'), 132.3 (C3a'), 136.1 (C2'), 139.7 (C1''), 139.7 (C8a'), 146.3 (C8'), 146.8 (C4'), 147.3 (C6'), 151.5 (C4), 155.7 (C2, C6); ms (70 eV): m/z 400 (29), 399 [M<sup>+</sup>, 100], 193 (28), 77 (26). *Anal.* Calcd. for C<sub>30</sub>H<sub>25</sub>N: C, 90.19; H, 6.31; N 3.51. Found: C, 90.14; H, 6.36; N 3.51.

**2,6-Diphenyl 4-(5-*iso*-propyl-3,8-dimethyl-azulen-1-yl)-pyridine (3f).** This compound was obtained as blue-violet oil; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 219 (4.47), 245 (4.55), 288 (4.48), 304 (4.32), 337 sh (3.90), 385 (3.88) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  1.47 (d, J = 6.8 Hz, 6H, Me<sub>2</sub>CH), 2.64 (s, 3H, 3'-Me), 2.78 (sept, J = 6.8 Hz, 1H, Me<sub>2</sub>CH), 3.18 (s, 3H, 8'-Me), 7.08 (d, J = 10.8 Hz, 1H, 7'-H), 7.49 (t, J = 7.0 Hz, 2H, 4''-H), 7.53 (d, J = 10.8 Hz, 1H, 6'-H), 7.56 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.74 (s, 1H, 2'-H), 7.83 (bs, 2H, 3-H, 5-H), 8.30 (d, J = 6.8 Hz, 4H, 2''-H, 6''-H), 8.36 (s, 1H, 4'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  12.9 (8'-Me), 24.7 (Me<sub>2</sub>CH), 28.1 (3'-Me), 37.9 (Me<sub>2</sub>CH), 120.8 (C3, C5), 124.7 (C3'), 125.6 (C1'), 127.0 (C2'', C6''), 127.7 (C7'), 128.6 (C3'', C5''), 128.9 (C4''), 132.2 (C3a'), 134.1 (C4'), 135.3 (C6'), 138.5 (C8a'), 139.7 (C2', C1''), 140.9 (C5'), 145.9 (C8'), 150.8 (C4), 155.6 (C2, C6) ppm; ms (70 eV): m/z 428 (32), 427 [M<sup>+</sup>, 100], 412 (36), 77 (18). *Anal.* Calcd. for C<sub>32</sub>H<sub>29</sub>N: C, 89.89; H, 6.84; N 3.28. Found: C, 89.85; H, 6.86; N 3.29.

**4-(2-*tert*-Butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-pyridine (3g).** This compound was obtained as blue powder; mp 86-7 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 215 (4.55), 243 (4.54), 291 (4.71), 306 sh (4.33), 351 (3.97) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  1.50 (s, 9 H, Me<sub>3</sub>C), 2.64 (s, 3H, 6'-Me), 7.44 (s, 1H, 3'-H), 7.58 (t, J = 7.6 Hz, 4H, 3''-H, 5''-H), 7.50 (t, J = 7.6 Hz, 2H, 4''-H), 7.00 (d, J = 10.0 Hz, 1H, 5'-H), 7.16 (d, J = 10.0 Hz, 1H, 7'-H), 8.31 (d, J = 8.0 Hz, 4H, 2''-H, 6''-H), 7.86 (s, 2H, 3-H, 5-H), 7.72 (d, J = 10.0 Hz, 1H, 4'-H), 8.24 (d, J = 10.0 Hz, 1H, 8'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>):  $\delta$  27.9 (6'-Me), 32.1 (Me<sub>3</sub>C), 34.1 (Me<sub>3</sub>C), 115.1 (C3'), 122.2 (C3, C5), 124.9 (C5''), 124.9 (C7'), 126.8 (C1'), 127.0 (C2'', C6''), 128.7 (C3'', C5''), 129.0 (C4''), 133.4 (C8'), 134.9 (C4'), 137.8 (C3a'), 137.8 (C8a'), 139.5 (C1''), 148.2 (C6'), 150.0 (C4), 156.0 (C2, C6), 159.4 (C2') ppm; ms (ESI): m/z 428 (32), 427 [M<sup>+</sup>, 100]. *Anal.* Calcd. for C<sub>33</sub>H<sub>29</sub>N: C, 89.89; H, 6.84; N 3.28. Found: C, 89.84; H, 6.89; N 3.27.

**4-(Azulen-1-yl)-2,6-diphenyl-3-methyl-pyridine (4a).** This compound was obtained as blue crystals; mp 193 °C; uv (MeOH,  $\lambda_{\max}$ ,  $\epsilon$ ): 221 (4.44), 234 (4.45), 278 (4.48), 343 (3.51), 363 (3.54) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>):  $\delta$  2.20 (s, 3H, 3-Me), 7.19 (t, J

= 9.8 Hz, 1H, 7'-H), 7.24 (t, J = 10.0 Hz, 1H, 5'-H), 7.37 (t, J = 7.2 Hz, 1H, 4''-H), 7.39-7.49 (m, 5 H, 3''-H, 4''-H, 5''-H, 3'''-H, 5'''-H), 7.50 (d, J = 4.0 Hz, 1H, 3'-H), 7.65 (t, J = 9.8 Hz, 1H, 6'-H), 7.73 (d, J = 7.6, 0.8 Hz, 2H, 2''-H, 6''-H), 7.74 (s, 1H, 5-H), 7.99 (d, J = 4.0 Hz, 1H, 2'-H), 8.08 (d, J = 7.6, 0.8 Hz, 2H, 2'''-H, 6'''-H), 8.21 (d, J = 9.2 Hz, 1H, 8'-H), 8.42 (d, J = 10.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  18.2 (Me), 117.3 (C3'), 121.6 (C5), 123.6 (C7'), 123.7 (C5'), 126.9 (C2''', C6'''), 127.8 (CH), 128.0 (CH), 128.5 (C4'''), 128.6 (C3''', C5'''), 128.7 (C1'), 128.7 (C3), 129.5 (C2'', C6''), 135.6 (C8'), 136.2 (C3a'), 137.4 (C4'), 137.8 (C2'), 138.2 (C6'), 139.5 (C<sub>q</sub>), 141.3 (C8a'), 141.6 (C<sub>q</sub>), 147.1 (C4), 153.7 (C<sub>q</sub>), 159.4 (C<sub>q</sub>) ppm; ms (ESI): m/z 373 (25), 372 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{28}\text{H}_{21}\text{N}$ : C, 90.53; H, 5.70; N 3.77. Found: C, 90.46; H, 5.76; N 3.78.

**2,6-Diphenyl-4-(4,6,8-trimethyl-azulen-1-yl)-3-methylpyridine (4e).** This compound was obtained as violet crystals; mp 94 °C; uv (MeOH,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 217 (4.48), 238 (4.48), 289 (4.48), 347 (3.60), 564 sh (3.41) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  2.08 (s, 3H, 3-Me), 2.48 (s, 3H, 6'-Me), 2.61 (s, 3H, 4'-Me), 2.93 (s, 3H, 8'-Me), 7.00 (s, 1H, 5'-H), 7.10 (s, 1H, 7'-H), 7.35 (t, J = 7.6 Hz, 1H, 4''-H), 7.38-7.50 (m, 5 H, 3''-H, 4''-H, 5''-H, 3'''-H, 5'''-H), 7.45 (d, J = 4.0 Hz, 1H, 3'-H), 7.53 (d, J = 4.0 Hz, 1H, 2'-H), 7.69 (d, J = 7.2 Hz, 2H, 2''-H, 6''-H), 7.70 (s, 1H, 5-H), 8.09 (d, J = 7.2 Hz, 2H, 2'''-H, 6'''-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  18.1 (3-Me), 25.6 (8'-Me), 27.8 (6'-Me), 28.54 (4'-Me), 115.5 (C3'), 121.2 (C5), 126.8 (C2''', C6'''), 127.4 (CH), 127.7 (C5'), 128.0 (CH), 128.3 (C1'), 128.5 (C7'), 128.6 (CH), 129.0 (C4'''), 129.2 (C3), 129.5 (C2'', C6''), 131.6 (C3a'), 135.0 (C2'), 137.2 (C8a'), 139.4 (C<sub>q</sub>), 141.6 (C<sub>q</sub>), 146.2 (C8'), 146.7 (C4'), 147.0 (C6'), 152.7 (C4), 152.8 (C<sub>q</sub>), 158.4 (C<sub>q</sub>) ppm; ms (ESI): m/z 415 (25), 414 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{31}\text{H}_{27}\text{N}$ : C, 90.03; H, 6.58; N 3.39. Found: C, 90.01; H, 6.59; N 3.40.

**2,6-Diphenyl-4-(5-iso-propyl-3,8-dimethyl-azulen-1-yl)-3-methylpyridine (4f).** This compound was obtained as blue powder; mp 113 °C; uv (MeOH,  $\lambda_{\text{max}}$ ,  $\epsilon$ ): 221 (4.40), 248 (4.45), 288 (4.50), 351 (3.52), 568 (3.56) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.39 (d, J = 6.8 Hz, 6H,  $\text{Me}_2\text{CH}$ ), 2.10 (s, 3H, 3-Me), 2.44 (s, 3H, 3'-Me), 2.70 (s, 3H, 8'-Me), 3.09 (sept, J = 6.8 Hz, 1H,  $\text{Me}_2\text{CH}$ ), 6.93 (d, J = 10.8 Hz, 1H, 7'-H), 7.38-7.50 (m, 5 H, 3''-H, 5''-H, 3'''-H, 4''-H, 5'''-H), 7.51 (s, 1H, 2'-H), 7.67 (s, 1H, 5-H), 7.70 (d, J = 8.0 Hz, 2H, 2''-H, 6''-H), 8.09 (d, J = 8.0 Hz, 2H, 2'''-H, 6'''-H), 8.25 (d, J = 2.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ ):  $\delta$  12.9 (3'-Me), 18.3 (3-Me), 24.7 ( $\text{Me}_2\text{CH}$ ), 26.7 (8'-Me), 37.9 ( $\text{Me}_2\text{CH}$ ), 121.4 (C5), 124.7 (C3'), 126.0 (C1'), 126.8 (C2''', C6'''), 127.0 (C7'), 127.7 (C4''), 128.0 (CH), 128.5 (CH), 128.6 (CH), 129.1 (C3), 129.5 (C2'', C6''), 134.1 (C4), 134.1 (C2'), 135.3 (C6'), 137.8 (C8a'), 138.6 (C3a'), 139.4 (C<sub>q</sub>), 140.3 (C<sub>q</sub>), 141.6 (C<sub>q</sub>), 145.7 (C8'), 152.6 (C<sub>q</sub>), 152.1 (C4), 158.3 (C<sub>q</sub>) ppm; ms (ESI): m/z 443 (38), 442 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{33}\text{H}_{31}\text{N}$ : C, 89.75; H, 7.08; N 3.17. Found: C, 89.72; H, 7.12; N 3.16.

**4-(2-tert-Butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-3-methylpyridine (4g).** This compound was obtained as blue powder; mp 93 °C; uv (MeOH,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 217 (4.39), 237 (4.40), 292 (4.69), 350 (3.77) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.41 (s, 9 H,  $\text{Me}_3\text{C}$ ), 2.01 (s, 3H, 3-Me), 2.62 (s, 3H, 6'-Me), 6.98 (t, J = 9.8 Hz, 1H, 7'-H), 7.11 (t, J = 10.0 Hz, 1H, 5'-H), 7.39 (s, 1H, 3'-H), 7.37-7.54 (m, 6 H, 3''-H, 4''-H, 5''-H, 3'''-H, 4'''-H, 5'''-H), 7.74 (d, J = 7.6 Hz, 2H, 2''-H, 6''-H), 7.75 (s, 1H, 5-H), 8.14 (d, J = 7.6 Hz, 2H, 2'''-H, 6'''-H), 7.52 (d, J = 9.2 Hz, 1H, 8'-H), 8.18 (d, J = 10.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  17.7 (3-Me), 27.9 (6'-Me), 31.5 ( $\text{Me}_3\text{C}$ ), 34.7 ( $\text{Me}_3\text{C}$ ), 115.4 (C3'), 122.7 (C5), 124.7 (C5'), 124.8 (C7'), 126.2 (C1'), 126.8 (C2''', C6'''), 127.8

(CH), 128.0 (CH), 128.5 (CH), 128.6 (CH), 129.4 (C2'', C6''), 130.4 (C3), 132.8 (C8'), 134.7 (C4'), 136.6 (C3a'), 137.9 (C8a'), 139.3 (C<sub>q</sub>), 141.5 (C<sub>q</sub>), 147.9 (C6'), 149.8 (C4), 152.9 (C<sub>q</sub>), 158.8 (C<sub>q</sub>), 159.0 (C2') ppm; ms (ESI): m/z 443 (38), 442 [ $\text{M}^+ + 1$ , 100]; *Anal.* Calcd. for  $\text{C}_{33}\text{H}_{31}\text{N}$ : C, 89.75; H, 7.08; N 3.17. Found: C, 89.78; H, 7.11; N 3.11.

**4-(Azulen-1-yl)-2,3,6-triphenylpyridine (5a).** This compound was obtained as blue powder; mp 184 °C; uv (MeOH,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 219 (4.55), 229 (4.54), 282 (4.52), 370 (3.57) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  6.86 (d, J = 7.2 Hz, 2H, 2''-H, 6''-H), 6.96 (t, J = 7.2 Hz, 2H, 3''-H, 5''-H), 7.01 (t, J = 7.2 Hz, 1H, 4''-H), 7.17 (t, J = 9.8 Hz, 1H, 5'-H), 7.18 (t, J = 9.8 Hz, 1H, 7'-H), 7.19-7.23 (m, 4 H, 3'-H, 3''-H, 4''-H, 5''-H), 7.31 (d, J = 4.4 Hz, 1H, 2'-H), 7.40-7.45 (m, 3 H, 2''-H, 6''-H, 4''-H), 7.48 (t, J = 7.6 Hz, 2H, 3''-H, 5''-H), 7.61 (t, J = 9.8 Hz, 1H, 6'-H), 7.90 (s, 1H, 5-H), 8.18 (d, J = 7.2 Hz, 2H, 2''-H, 6''-H), 8.28 (d, J = 9.6 Hz, 1H, 4'-H), 8.42 (d, J = 10.0 Hz, 1H, 8'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  117.2 (C3'), 121.9 (C5), 123.6 (C5'), 123.7 (C7'), 126.4 (C4'''), 127.1 (C2''', C6'''), 127.3 (CH), 127.5 (C3''', C5'''), 127.6 (CH), 128.2 (C1'), 128.7 (C3''', C5'''), 128.9 (CH), 130.2 (CH), 131.1 (C2''', C6'''), 134.3 (C3), 135.2 (C8'), 136.4 (C3a'), 137.0 (C4'), 137.9 (C6'), 138.5 (C<sub>q</sub>), 138.7 (C2'), 139.3 (C<sub>q</sub>), 141.2 (C8a'), 141.3 (C<sub>q</sub>), 146.3 (C4), 155.2 (C<sub>q</sub>), 158.2 (C<sub>q</sub>) ppm; ms (ESI): m/z 435 (38), 434 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{33}\text{H}_{23}\text{N}$ : C, 91.42; H, 5.35; N 3.23. Found: C, 91.38; H, 5.40; N 3.22.

**4-(4,6,8-Trimethyl-azulen-1-yl)-2,3,6-triphenylpyridine (5e).** This compound was obtained as violet crystals; mp 116 °C; uv (MeOH,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 217 (4.48), 243 (4.48), 293 (4.49), 345 sh (3.63), 370 (3.41) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  2.59 (s, 3H, 6'-Me), 2.66 (s, 3H, 4'-Me), 2.83 (s, 3H, 8'-Me), 6.94 (bs, 6H, 5'-H and Ph'''), 6.96 (s, 1H, 5'-H), 7.02 (s, 1H, 7'-H), 7.16-7.24 (m, 5 H, 2'-H, 3'-H, 3''-H, 4''-H, 5''-H), 7.34-7.48 (m, 5 H, 2''-H, 6''-H, 3''-H, 4''-H, 5''-H), 7.72 (s, 1H, 5-H), 8.15 (d, J = 7.6 Hz, 2H, 2''-H, 6''-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  25.5 (8'-Me), 28.4 (6'-Me), 28.7 (4'-Me), 115.2 (C3'), 122.4 (C5), 126.1 (C4'''), 127.0 (C2''', C6'''), 127.2 (C7'), 127.3 (CH), 127.4 (C3''', C5'''), 127.5 (CH), 128.6 (CH), 128.7 (C1'), 128.8 (C5'), 128.9 (CH), 130.3 (CH), 131.2 (C2''', C6'''), 132.3 (C3a'), 133.6 (C3), 136.6 (C2'), 137.2 (C8a'), 138.6 (C<sub>q</sub>), 139.1 (C<sub>q</sub>), 141.3 (C<sub>q</sub>), 145.6 (C8'), 146.2 (C6'), 146.4 (C4'), 151.3 (C<sub>q</sub>), 153.8 (C4), 157.5 (C<sub>q</sub>) ppm; ms (ESI): m/z 477 (33), 476 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{36}\text{H}_{29}\text{N}$ : C, 90.91; H, 6.15; N 2.94. Found: C, 90.88; H, 6.20; N 2.92.

**4-(5-iso-Propyl-3,8-dimethyl-azulene-1-yl)-2,3,6-triphenylpyridine (5f).** This compound was obtained as blue powder; mp 113 °C; uv (MeOH,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 221 (4.50), 242 (4.47), 290 (4.45), 379 (3.52) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.35 (d, J = 6.8 Hz, 6H,  $\text{Me}_2\text{CH}$ ), 2.48 (s, 3H, 3'-Me), 2.62 (s, 3H, 8'-Me), 3.05 (sept, J = 6.8 Hz, 1H,  $\text{Me}_2\text{CH}$ ), 6.92 (d, J = 10.4 Hz, 1H, 7'-H), 6.95 (bs, 5H, Ph'''), 7.12 (s, 1H, 2'-H), 7.20-7.25 (m, 3H, 3''-H, 4''-H, 5''-H), 7.35 (dd, 1H, J = 10.6, 2.0 Hz, 6'-H), 7.39 (tt, J = 7.6, 1.2 Hz, 1H, 4''-H), 7.43 (t, J = 7.5 Hz, 2H, 3''-H, 5''-H), 7.45 (d, J = 8.0 Hz, 2H, 2''-H, 6''-H), 7.68 (s, 1H, 5-H), 8.09 (d, J = 2.0 Hz, 1H, 4'-H), 8.15 (dd, J = 7.6, 2.0 Hz, 2H, 2''-H, 6''-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  12.7 (3'-Me), 24.6 ( $\text{Me}_2\text{CH}$ ), 27.7 (8'-Me), 37.8 ( $\text{Me}_2\text{CH}$ ), 122.7 (C5), 124.3 (C3'), 125.7 (C3), 126.2 (C1'), 126.2 (C4'''), 126.9 (C2''', C6'''), 127.0 (C7'), 127.3 (CH), 127.4 (C3''', C5'''), 127.5 (CH), 128.6 (C3''', C5'''), 128.8 (C4'''), 130.3 (C2'', C6''), 131.3 (C2''', C6'''), 132.9 (C3a'), 133.6 (C4'), 134.7 (C6'), 138.0 (C8a'), 138.6 (C1'''), 139.2 (C<sub>q</sub>), 140.0 (C2'), 140.3 (C5'), 141.3 (C<sub>q</sub>), 145.1 (C8'), 150.7 (C4), 153.6 (C<sub>q</sub>), 157.4 (C<sub>q</sub>); ms (ESI): m/z 504 [ $\text{M}^+ + 1$ , 100]. *Anal.* Calcd. for  $\text{C}_{38}\text{H}_{33}\text{N}$ : C, 90.62; H, 6.60; N 2.78; Found: C, 90.59; H, 6.59; N 2.86.

**4-(2-*tert*-Butyl-6-methyl-azulen-1-yl)-2,3,6-triphenylpyridine (5g).** This compound was obtained as blue powder, mp 105 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 219 (4.49), 241 (4.48), 293 (4.72), 354 (3.80) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.16 (s, 9 H,  $\text{Me}_3\text{C}$ ), 2.61 (s, 3H, 6'-Me), 6.78-6.86 (m, 4 H, 2'''-H, 6'''-H, 3'''-H, 5'''-H), 6.89 (t, J = 7.8 Hz, 1H, 4'''-H), 6.99 (d, J = 10.0 Hz, 1H, 7'-H), 7.04 (d, J = 10.0 Hz, 1H, 5'-H), 7.18-7.23 (m, 4 H, 3'-H, 3-H", 4"-H, 5"-H), 7.42 (t, J = 7.6 Hz, 1H, 4''-H), 7.45-7.52 (m, 4 H, 2"-H, 6"-H, 3-H", 5-H"), 7.66 (d, J = 9.6 Hz, 1H, 8'-H), 7.83 (s, 1H, 5-H), 8.06 (d, J = 9.2 Hz, 1H, 4'-H), 8.21 (d, J = 7.6 Hz, 2H, 2''-H, 6''-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  27.9 (6'-Me), 32.1 ( $\text{Me}_3\text{C}$ ), 34.8 ( $\text{Me}_3\text{C}$ ), 116.0 (C3'), 122.9 (C5), 124.6 (C3'), 124.7 (C7'), 125.1 (C1'), 126.2 (C4''), 127.0 (CH), 127.1 (CH), 127.3 (CH), 127.5 (CH), 128.7 (CH), 128.9 (C4'''), 130.4 (CH), 130.9 (C2''', C6'''), 133.5 (C8'), 134.4 (C4'), 135.3 (C3), 137.5 (C3a'), 138.4 (C8a'), 138.6 (C<sub>q</sub>), 139.0 (C<sub>q</sub>), 141.1 (C<sub>q</sub>), 147.5 (C6'), 149.5 (C4), 153.8 (C<sub>q</sub>), 157.8 (C<sub>q</sub>), 159.0 (C2') ppm; ms (ESI): m/z 504 [ $\text{M}^+$ +1, 100]. *Anal.* Calcd. for  $\text{C}_{38}\text{H}_{33}\text{N}$ : C, 90.62; H, 6.60; N 2.78. Found: C, 90.63; H, 6.61; N 2.76.

**4-(Azulen-1-yl)-2,6-diphenyl-3-bromo-pyridine (6a).** This compound was obtained as blue crystals; mp 167 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 218 (4.39), 236 (4.41), 281 (4.46), 367 (3.67) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  7.26 (t, J = 9.8 Hz, 1H, 5'-H), 7.30 (t, J = 9.6 Hz, 1H, 7'-H), 7.41-7.53 (m, 7 H, 3'-H, 3''-H, 4''-H, 5''-H, 3'''-H, 4'''-H, 5'''-H), 7.69 (t, J = 9.8 Hz, 1H, 6'-H), 7.78 (s, 1H, 5-H), 7.82 (d, J = 7.8 Hz, 2H, 2''-H, 6''-H), 8.08 (d, J = 8.0, 1.6Hz, 2H, 2'''-H, 6'''-H), 8.14 (d, J = 4.0 Hz, 1H, 2'-H), 8.30 (d, J = 10.0 Hz, 1H, 8'-H), 8.46 (d, J = 9.2 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  117.1 (C3'), 120.6 (C3), 122.7 (C5), 124.1 (C5'), 124.2 (C7'), 127.0 (CH), 127.2 (C<sub>q</sub>), 127.8 (CH), 128.2 (C1'), 128.3 (C<sub>q</sub>), 128.5 (C4'''), 128.8 (CH), 129.2 (C4''), 129.7 (CH), 135.5 (C8'), 136.2 (C3a'), 137.6 (C4'), 138.3 (C6'), 138.4 (C2'), 141.6 (C8a'), 148.3 (C4), 154.8 (C<sub>q</sub>), 159.4 (C<sub>q</sub>) ppm; ms (ESI): m/z 436/438 [ $\text{M}^+$ +1, 100/100]. *Anal.* Calcd. for  $\text{C}_{27}\text{H}_{18}\text{NBr}$ : C, 74.47; H, 4.17; N 3.22; Br 18.14. Found: C, 74.42; H, 4.23; N 3.25; Br 18.10.

**2,6-Diphenyl-4-(4,6,8-trimethyl-azulen-1-yl)-3-bromopyridine (6e).** This compound was obtained as violet crystals; mp 181 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 220 (4.39), 242 (4.43), 290 (4.47), 367 (3.55) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  2.57 (s, 3H, 6'-Me), 2.63 (s, 3H, 4'-Me), 2.94 (s, 3H, 8'-Me), 7.05 (s, 1H, 5'-H), 7.14 (s, 1H, 7'-H), 7.39-7.52 (m, 7 H, 3'-H, 3''-H, 4''-H, 5''-H, 3'''-H, 4'''-H, 5'''-H) 7.57 (d, J = 4.0 Hz, 1H, 2'-H), 7.75 (s, 1H, 5-H), 7.83 (d, J = 8.0, 1.4Hz, 2H, 2''-H, 6''-H), 8.08 (d, J = 7.2, 1.6Hz, 2H, 2'''-H, 6'''-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  25.7 (8'-Me), 27.9 (6'-Me), 28.6 (4'-Me), 115.3 (C3'), 121.7 (C3), 122.2 (C5), 127.0 (CH), 127.8 (CH), 127.9 (C7'), 128.5 (C4''), 128.7 (CH), 129.1 (C1'), 129.2 (C4'''), 129.4 (C5'), 129.7 (CH), 131.7 (C3a'), 135.1 (C2'), 137.3 (C8a'), 138.3 (C<sub>q</sub>), 140.9 (C<sub>q</sub>), 146.6 (C8'), 147.0 (C4', C6'), 154.0 (C4), 154.1 (C<sub>q</sub>), 158.1 (C<sub>q</sub>) ppm; ms (ESI): m/z 477/479 [ $\text{M}^+$ +1, 100/100]. *Anal.* Calcd. for  $\text{C}_{30}\text{H}_{24}\text{NBr}$ : C, 75.45; H, 5.07; N 2.93; Br 16.54. Found: C, 75.43; H, 5.11; N 2.98; Br 16.48.

**2,6-Diphenyl-4-(5-*iso*-propyl-3,8-dimethyl-azulene-1-yl)-3-bromopyridine (6f).** This compound was obtained as blue-green crystals; mp 195 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 221 (4.34), 243 (4.48), 286 (4.53), 342 (3.70), 372 (3.41) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.39 (d, J = 6.8 Hz, 6H,  $\text{Me}_2\text{CH}$ ), 2.53 (s, 3H, 3'-Me), 2.71 (s, 3H, 8'-Me), 3.10 (sept, J = 6.8 Hz, 1H,  $\text{Me}_2\text{CH}$ ), 7.00 (d, J = 10.8 Hz, 1H, 7'-H), 7.36 (s, 1H, 2'-H), 7.39-7.47 (m, 5 H, 6'-H, 3''-H, 4''-H, 5''-H, 4'''-H), 7.49 (t, J = 7.5 Hz, 2H, 3'''-H, 5'''-H), 7.71 (s, 1H, 5-H), 7.83 (d, J = 8.0 Hz, 2H, 2''-H, 6''-H), 8.07 (d, J = 8.0 Hz, 2H, 2'''-H, 6'''-H), 8.28 (d, J = 2.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  12.9 (3'-Me), 24.7 ( $\text{Me}_2\text{CH}$ ), 26.9 (8'-

Me), 38.0 ( $\text{Me}_2\text{CH}$ ), 121.6 (C3), 122.4 (C5), 124.6 (C3'), 125.9 (C1'), 126.9 (C2''', C6'''), 127.4 (C7'), 127.8 (CH), 128.5 (CH), 128.7 (C3''', C5'''), 129.2 (C4'''), 129.7 (C2'', C6''), 132.3 (C3a'), 134.4 (C4'), 135.5 (C6'), 137.9 (C8a'), 138.3 (C<sub>q</sub>), 138.6 (C2'), 140.9 (C<sub>q</sub>), 145.6 (C8'), 153.5 (C4), 153.7 (C6), 158.0 (C2) ppm; ms (ESI): 508/506 [ $\text{M}^+$ +1, 100/100]. *Anal.* Calcd. for  $\text{C}_{32}\text{H}_{28}\text{NBr}$ : C, 76.02; H, 5.59; N 2.77; Br 15.62. Found: C, 75.98; H, 5.65; N 2.75; Br 15.62.

**4-(2-*tert*-Butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-3-bromo-pyridine (6g).** This compound was obtained as blue powder; mp 93 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 217 (4.42), 238 (4.40), 294 (4.70), 352 (3.77) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.43 (s, 9 H,  $\text{Me}_3\text{C}$ ), 2.62 (s, 3H, 6'-Me), 7.02 (d, J = 9.8 Hz, 1H, 7'-H), 7.13 (d, J = 10.0 Hz, 1H, 5'-H), 7.37 (s, 1H, 3'-H), 7.40-7.57 (m, 6H, 3''-H, 4''-H, 5''-H, 3'''-H, 4'''-H, 5'''-H), 7.81 (s, 1H, 5-H), 7.87 (d, J = 7.6 Hz, 2H, 2''-H, 6''-H), 7.53 (d, J = 9.2Hz, 1H, 8'-H), 8.11 (d, J = 7.6Hz, 2H, 2'''-H, 6'''-H), 8.11 (d, J = 10.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  28.0 (6'-Me), 31.7 ( $\text{Me}_3\text{C}$ ), 34.8 ( $\text{Me}_3\text{C}$ ), 115.4 (C3'), 123.6 (C5), 123.1 (C3), 125.1 (C5'), 125.2 (C7'), 126.2 (C1'), 126.9 (C2''', C6'''), 127.7 (CH), 128.5 (C4''), 128.8 (CH), 129.3 (C4'''), 129.8 (C2''-C6''), 132.9 (C8'), 135.0 (C4'), 136.6 (C3a'), 137.8 (C8a'), 138.2 (C<sub>q</sub>), 140.8 (C<sub>q</sub>), 148.2 (C6'), 151.7 (C4), 154.1 (C<sub>q</sub>), 158.5 (C<sub>q</sub>), 158.5 (C2') ppm; ms (ESI): m/z 508/506 [ $\text{M}^+$ +1, 100/100]. *Anal.* Calcd. for  $\text{C}_{32}\text{H}_{28}\text{NBr}$ : C, 76.02; H, 5.59; N 2.77; Br 15.62. Found: C, 75.96; H, 5.63; N 2.78; Br 15.63.

**4-(Azulen-1-yl)-2,6-dimethyl-pyridine (9a).** This compound was obtained as blue crystals; mp 84-85 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 216 (4.11), 242 (4.16), 277 (4.15), 305 (4.31), 369 (3.93), 558 (2.36) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 6H, 2-Me, 6-Me), 7.13 (s, 2H, 3-H, 5-H), 7.15 (t, J = 9.0 Hz, 1H, 5'-H), 7.17 (t, J = 9.3 Hz, 1H, 7'-H), 7.36 (d, J = 3.9 Hz, 1H, 3'-H), 7.57 (t, J = 9.8 Hz, 1H, 6'-H), 7.95 (d, J = 4.0 Hz, 1H, 2'-H), 8.30 (d, J = 9.2 Hz, 1H, 4'-H), 8.52 (d, J = 9.8 Hz, 1H, 8'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  25.0 (2-Me, 6-Me), 118.3 (C3'), 121.2 (C3, C5), 124.4 (C5'), 124.6 (C7'), 128.8 (C1'), 135.7 (C8'), 136.1 (C3a'), 137.5 (C2'), 138.1 (C4'), 139.0 (C6'), 142.9 (C8a'), 146.0 (C4), 158.2 (C2, C6) ppm; ms (70 eV): m/z 233 [ $\text{M}^+$ , 100]. *Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}$ : C, 87.52; H, 6.48; N, 6.00. Found: C, 87.45; H, 6.56; N 5.99.

**2,6-Dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridine (9e).** This compound was obtained as violet crystals; mp 156-7 °C; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 214 (4.19), 250 (4.31), 287 (4.32), 312 (4.31), 350 (3.82), 526 (2.62) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  2.49 (s, 3H, 4'-Me), 2.57 (s, 6H, 2-Me, 6-Me), 2.62 (s, 3H, 6'-Me), 2.90 (s, 3H, 8'-Me), 7.00 (s, 2H, 3-H, 5-H), 7.02 (s, 1H, 5'-H), 7.09 (s, 1H, 7'-H), 7.35 (d, J = 4.0 Hz, 1H, 3'-H), 7.53 (d, J = 4.0 Hz, 1H, 2'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  24.5 (2-Me, 6-Me), 25.6 (8'-Me), 28.5 (6'-Me), 29.0 (4'-Me), 115.3 (C3'), 122.3 (C3, C5), 127.7 (C7'), 129.3 (C5'), 129.9 (C1'), 131.5 (C3a'), 136.0 (C2'), 137.8 (C8a'), 146.2 (C8'), 146.6 (C6'), 147.3 (C4'), 150.7 (C4), 156.4 (C2, C6) ppm; ms (70 eV): m/z 275 [ $\text{M}^+$ , 100]. *Anal.* Calcd. for  $\text{C}_{20}\text{H}_{21}\text{N}$ : C, 87.23; H, 7.69; N, 5.09. Found: C, 87.31; H, 7.63; N, 5.06.

**2,6-Dimethyl-4-(5-*iso*-propyl-3,8-dimethyl-azulen-1-yl)-pyridine (9f).** This compound was obtained as green oil; uv (MeOH,  $\lambda_{\max}$ , log  $\epsilon$ ): 216 (4.20), 251 (4.18), 285 (4.12), 308 (4.05), 377 (3.66) nm;  $^1\text{H}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  1.38 (d, J = 6.8 Hz, 6H,  $\text{Me}_2\text{CH}$ ), 2.47 (s, 3H, 8'-Me), 2.57 (s, 6H, 2-Me, 6-Me), 2.65 (s, 3H, 3'-Me), 3.10 (sept, J = 6.8 Hz, 1H,  $\text{Me}_2\text{CH}$ ), 6.99 (d, J = 10.0 Hz, 1H, 7'-H), 7.01 (s, 2H, 3-H, 5-H), 7.43 (dd, J = 10.0, 1.6 Hz, 1H, 6'-H), 7.52 (s, 1H, 2'-H), 8.22 (d, J = 2.0 Hz, 1H, 4'-H) ppm;  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ):  $\delta$  12.8 (3'-Me), 23.8 (2-Me, 6-Me), 24.6 ( $\text{Me}_2\text{CH}$ ), 27.9 (8'-Me), 37.9 ( $\text{Me}_2\text{CH}$ ), 126.1 (C1'),

122.6 (C3, C5), 124.6 (C3'), 127.6 (C7'), 132.2 (C8a'), 134.0 (C4'), 135.3 (C6'), 138.5 (C3a'), 139.6 (C2'), 141.0 (C5'), 145.8 (C8'), 150.6 (C4), 155.8 (C2, C6) ppm; ms (15 eV): m/z 304 [M<sup>+</sup>+1, 100]. *Anal.* Calcd. for C<sub>22</sub>H<sub>23</sub>N: C, 87.08; H, 8.30; N, 4.62. Found: C, 87.12; H, 8.45; N, 4.43.

**4-(2-*tert*-Butyl-6-methyl-azulen-1-yl)-2,6-dimethyl-pyridine (9g).** This compound was obtained as violet crystals; mp 152-153 °C; uv (MeOH, λ<sub>max</sub>, log ε): 214 (4.25), 235 (4.19), 288 (4.19), 338 (3.60), 353 (3.77), 536 (2.34) nm; <sup>1</sup>H nmr (CDCl<sub>3</sub>): δ 1.26 (s, 9H, Me<sub>3</sub>C), 2.51 (s, 3H, 6'-Me), 2.52 (s, 6H, 2-Me, 6-Me), 6.85 (d, J = 9.9 Hz, 1H, 7'-H), 6.92 (s, 2H, 3-H, 5-H), 6.98 (d, J = 9.9 Hz, 1H, 5'-H), 7.20 (s, 1H, 3'-H), 7.41 (d, J = 10.0 Hz, 1H, 8'-H), 8.05 (d, J = 9.6 Hz, 1H, 4'-H) ppm; <sup>13</sup>C nmr (CDCl<sub>3</sub>): δ 23.5 (2-Me, 6-Me), 26.9 (6'-Me), 30.9 (Me<sub>3</sub>C), 33.7 (Me<sub>3</sub>C), 114.0 (C3'), 122.9 (C3, C5), 123.6 (C7'), 123.7 (C5'), 125.9 (C1'), 132.2 (C8'), 133.7 (C4'), 136.7 (C3a', C8a'), 146.8 (C6'), 148.2 (C2'), 155.8 (C2, C6), 158.2 (C4) ppm; ms (70 eV): m/z 303 [M<sup>+</sup>, 100]. *Anal.* Calcd. for C<sub>22</sub>H<sub>25</sub>N: C, 87.08; H, 8.30; N, 4.68. Found: C, 86.92; H, 8.42; N, 4.66.

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