PREPARATION AND SPECTROSCOPIC PROPERTIES OF TRICHTOMINE DERIVATIVES BEARING STERICALLY HINDERED ACYL GROUPS ON C-1 AND -1'

Hajime Irikawa* and Yasuhiro Kobayashi

Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422

Abstract- The absorption and $^{13}$C NMR spectra of 1,1'-diacyltrichotomine derivatives showed that the central C(2)=C(2') double bond was twisted, and coplanarity of the 1,1'-diacyl groups and the trichotomine chromophore was hindered by steric interactions between the 1,1'-diacyl groups and the 3,3' dicarbonyl groups.

It is well known that steric interaction between bulky substituents on ethylenic double bond causes the C=C bond twisted, and coplanarity of two aromatic rings in biphenyls is hindered by the $o,o'$- and $o':o'$-substituents. A blue pigment, trichotomine dimethyl ester (1a), has an H-type chromophore similar to that of indigo (2a).1 We planned to compare the properties of 1,1'-disubstituted trichotomine derivatives with those of $N,N'$-disubstituted indigos. In a previous paper, we reported the preparation and spectroscopic properties of 1,1'-dialkyltrichotomine derivatives (1b).2 As the 1,1'-dialkyl groups became bulkier, the absorption spectra of 1b showed bathochromism, which was attributed to twisting of the central C(2)=C(2') double bond, and was similar to that observed in $N,N'$-dialkylindigos (2b).3 It is also reported that $N,N'$-diacylindigos (2c) show bathochromism as the substituents on the nitrogen atoms become bulkier.4 In this paper, we wish to report the preparation and spectroscopic properties of 1,1'-diacyltrichotomine derivatives (1c), in which the central C(2)=C(2') double bond seems to be twisted, and coplanarity of the 1,1'-diacyl groups and the trichotomine chromophore is supposed to be sterically hindered.

\[ \text{1a - 1d} \]

\[ \text{2a - 2c} \]

\begin{itemize}
  \item a \hspace{1em} R = H
  \item b \hspace{1em} R = Alkyl
  \item c \hspace{1em} R = Acyl
  \item d \hspace{1em} R = COOEt
\end{itemize}
RESULTS AND DISCUSSION

Preparation. L-Tryptophan methyl ester reacted with 2-oxoglutaric acid to give a condensation product, which was dehydrogenated with N-bromosuccinimide to give a compound (3). The \( \text{C(1)=C(11b)} \) double bond of 3 showed enamine-type reactivity, and 1-acylated compounds (4a, 5a, 6a, and 7a) were obtained from 3 by treatment with acetic anhydride / acetic acid, with propionic anhydride / propionic acid, with isobutyric anhydride / isobutyric acid, and trifluoroacetic acid / acetic anhydride, respectively. In the \(^{13}\text{C} \) NMR spectrum of 7a, the signals of the \( \text{CF,CO} \) group were observed at \( \delta =117.5 \) and 173.6.

1-Aroyl derivatives (8a, 9a, and 10a) were obtained by treatment of 3 with the corresponding acid chlorides in the presence of pyridine. Dimerization of 4a - 10a was examined under similar conditions to those used in the preparation of 1d. Upon stirring in \( \text{CH}_2\text{Cl}_2 \) containing \( \text{i-Pr,NH} \), 1-acylated compounds (4a - 9a) underwent autoxidative dimerization to give the corresponding bluish green 1,1'-diacyltrichotomine derivatives (4b - 9b), respectively. The compound (10a) did not give a desired dimeric product.

Absorption Spectra. The absorption spectral data of 4a - 10a and 1,1'-diacyltrichotomine derivatives (4b - 9b) were summarized in Table 1. The \( \lambda_{\text{max}} \) of 4a - 6a were observed at 402 - 403 nm, and those of 7a - 10a were found at 418 - 428 nm. The substituent effects observed for 4a - 10a were similar to those reported for benzene derivatives: \( \text{C(=O)Ph} > \text{C(=O)Alk} \). Accordingly, the 1-acyl groups in 4a - 10a seem to be little sterically hindered, and conjugate with the indolizinoindole chromophore. It is reported that the \( \lambda_{\text{max}} \) of \( \text{N,N'-diacylindigos (2c)} \) are shifted to longer wavelengths as the acyl groups become bulkier (R=MeCO 561, R=EtCO 568, and R=i-PrCO 577 nm). But, the \( \lambda_{\text{max}} \) of the trichotomine derivatives (4b, 5b, and 6b) were observed at 715, 714, and 712 nm, respectively, although the bulkiness of the 1,1'-diacyl groups changed. The characteristic difference between 4b - 6b and diacylindigos (2c) might be explained as follows. Twisting of the \( \text{C(2)=C(2')} \) double bond in 1b and 1d is shown by the bathochromism and the X-Ray analysis, respectively, and suggested to result from steric interactions between the 1,1'-disubstituents and the 3,3'-dicarbonyl groups. Therefore, the \( \text{C(2)=C(2')} \) double bond of 4b - 6b seems similarly to be twisted as the 1,1'-diacyl groups become bulkier. Twisting of the \( \text{C(2)=C(2')} \) double bond is expected to cause bathochromic shifts. On the other hand, the steric interactions mentioned above in 4b - 6b seem to hinder coplanarity of the 1,1'-diacyl groups and the trichotomine chromophore. Such loss of coplanarity is expected to cause hypsochromic...
Table 1. Absorption and $^{13}$C NMR Spectral Data of 1-RCO-Compounds (4a - 10a) and 1,1'-Di(RCO)trichotomine Derivatives (4b - 9b)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\delta$ c (ppm)</th>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\delta$ c (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>4a</td>
<td>402</td>
<td>193.1</td>
<td>4b</td>
<td>715</td>
<td>197.2</td>
</tr>
<tr>
<td>R = Et</td>
<td>5a</td>
<td>402</td>
<td>196.1</td>
<td>5b</td>
<td>714</td>
<td>201.1</td>
</tr>
<tr>
<td>R = i-Pr</td>
<td>6a</td>
<td>403</td>
<td>200.0</td>
<td>6b</td>
<td>712</td>
<td>204.7</td>
</tr>
<tr>
<td>R = CF$_3$</td>
<td>7a</td>
<td>428</td>
<td>173.6</td>
<td>7b</td>
<td>691</td>
<td>180.0</td>
</tr>
<tr>
<td>R = C$_6$H$_5$</td>
<td>8a</td>
<td>418</td>
<td>190.4</td>
<td>8b</td>
<td>712</td>
<td>192.6</td>
</tr>
<tr>
<td>R = p-MeOC$_6$H$_5$</td>
<td>9a</td>
<td>421</td>
<td>189.2</td>
<td>9b</td>
<td>713</td>
<td>191.6</td>
</tr>
<tr>
<td>R = p-NO$_2$C$_6$H$_4$</td>
<td>10a</td>
<td>427</td>
<td>187.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

shifts. Similar trend is described on the absorption spectra of substituted acetophenone derivatives (acetophenone 243, 4-methyl 256, and 2,4,6-trimethyl 242 nm). According to these speculations, MO calculation using MOPAC AM1 was performed for 4a, b - 6a, b. The X-Ray analysis data of 1d were used for the molecular modeling, and geometries were fully optimized by use of EF routine in the MOPAC package with the key word PRECISE. The calculation indicated that the 1-acyl groups in 4a - 6a existed in the $s$-cis conformations as shown in the described structure for 4a - 10a, since the dihedral angles of C(11b)=C(1)-C=O were 2.6, 3.3, and 8.4°, respectively. The $s$-cis forms might be more favorable in energy than the corresponding $s$-trans forms which have steric interaction between the hydrogen atom on the indole nitrogen and the alkyl moiety of the 1-acyl group. In 4b - 6b, the dihedral angles of C(11b)=C(1)-C=O were 50.8, 50.0, and 52.7°, respectively, and indicated the loss of coplanarity between the 1,1'-diacyl groups and the trichotomine chromophore. Furthermore, twisting of the central C(2)=C(2') double bond of 4b - 6b is shown by the dihedral angles of C(1)-C(2)=C(2')-C(3') (11.8, 12.8, and 14.5°, respectively). These dihedral angles are similar to those of 1d clarified by the X-Ray analysis (C(11b)=C(1)-C=O 42.4° and C(1)-C(2)=C(2')-C(3') 17.1°). The trifluoroacetyl compound (7a, 428 nm) indicated a bathochromic shift relative to 4a (402 nm), whereas 7b (691 nm) showed a hypsochromic shift by 24 nm compared with 4b (715 nm). It is described that the bathochromic and hypsochromic shifts observed for indigo derivatives bearing substituents on the benzene rings are explained by the donor character of the substituents and the $\pi$-electron density changes accompanying the first excitation. For 4a, b and 7a, b, the LCAO (linear combination of atomic orbitals) coefficients of the HOMO and LUMO were calculated by MOPAC AM1 with the key word VECTORS. At the 1-acyl carbonyl carbons of 4a and 7a, the coefficients of the HOMO (4a pz: 0.044, 7a 0.060) are smaller than those of the LUMO (4a 0.270, 7a 0.335). The bathochromic shift of 7a, caused by replacement of the CH$_3$ in 4a with an electron withdrawing CF$_3$, might be in line with the increase of the $\pi$-electron density accompanying the first excitation at the carbonyl carbon of 4a. At the 1,1'-diacyl carbonyl carbons of 4b and 7b, the coefficients of the HOMO (4b 0.007, 7b 0.007) are similar to those
of the LUMO (4b 0.021, 7b 0.023), while at the adjacent C(1) and C(1'), the coefficients of the HOMO (4b 0.330, 7b 0.333) are larger than those of the LUMO (4b 0.154, 7b 0.155). Therefore, the hypsochromic shift of 7b might be due to the decrease of the \( \pi \)-electron densities accompanying the first excitation at the C(1) and C(1') of 4b, since the \( \pi \)-electron density changes at the 1,1'-diacetyl carbonyl carbons of 4b are small. The compounds (8a) and (9a) showed bathochromism relative to 4a, while 8b and 9b did not show bathochromism compared with 4b. The MO calculation for 8a showed that the 1-benzoyl carbonyl group and the indolizinoindole chromophore is almost coplanar, since the dihedral angle of C(11b)-C(1)-C=O was 10.3°. Furthermore, the dihedral angle between the phenyl and the carbonyl groups (C(Ph)=C(Ph)-C=O) was 61.2°. Twisting of the phenyl ring of 8a might be due to steric repulsion by the hydrogen atoms on C(2). It is reported that the benzoyl groups in 4,4'-dibenzoyl Pechmann dye are located perpendicularly to the bis-furanone system. The 1,1'-diaryl carbonyl groups of 8b and 9b might similarly be twisted out of the trichotomine chromophore, and out of the aryl rings, which might conjugate slightly with the trichotomine chromophore.

\[ ^{13}C \text{ NMR Spectra.} \] The \(^{13}C\) NMR chemical shifts of the 1-acyl carbonyl carbons in 4a - 10a, and those of the 1,1'-diacyl carbonyl carbons in 4b - 9b are summarized in Table 1. The carbonyl signals of 5a,b and 6a,b are observed at a lower field relative to that of 4a,b because of \( \beta \)-effect of the methyl group in the 1-substituents of 5a,b and 6a,b. The carbonyl signals of 7a,b and 10a are shifted to a higher field relative to those of 4a,b and 8a due to the electron-withdrawing properties of the CF\(_3\) and p-nitrophenyl groups, respectively. The carbonyl carbon signals of 4b - 9b are observed at a lower field relative to those of the corresponding compounds (4a - 9a) by 2.2 - 6.4 ppm. It is reported that the carbonyl signals of ortho-substituted acetophenones appear at a lower field (acetophenone 195.7, 2-methyl 199.0, 2,6-dimethyl 205.4 ppm), and the deshielding is attributed to the steric hindrance to coplanarity of the carbonyl groups and the aromatic rings. Accordingly, the observed deshielding of the acyl carbonyl carbons of 4b - 9b might reflect the loss of coplanarity of the 1,1'-diacyl groups and the trichotomine chromophore.

**EXPERIMENTAL**

All melting points are uncorrected. Absorption spectra were measured on a Shimadzu-UV-3100 or Hitachi U-3000 in CHCl\(_3\). \(^1H\) and \(^{13}C\) NMR spectra were recorded on a Bruker AC300 (300 MHz, 75 MHz) in CDCl\(_3\), using TMS as an internal standard. MS spectra were obtained on a JEOL-DX303. Column chromatography was performed with silica gel 60 (70 - 230 mesh).

**Preparation of 4a - 6a.** A typical procedure is described for the preparation of 4a. A solution of 3 (41 mg, 0.15 mmol) in a mixture of acetic anhydride (1.5 mL, 16 mmol) and acetic acid (1.5 mL) was refluxed for 2 h under argon atmosphere, and concentrated under reduced pressure. The residue was purified with column chromatography (SiO\(_2\), MeOH-CHCl\(_3\)) to give 4a (crystallized from CHCl\(_3\)-hexane, 26 mg, 54%): mp 210 - 215 °C (decomp); UV-VIS 314 (\( \varepsilon \) 11500), 386 (21700), and 402 nm (18900);

\(^1H\) NMR \( \delta = 2.32\) (3H, s), 3.36 (1H, dd, J=16.8 and 7.5 Hz), 3.65 (2H, AB-q, J=23.9 Hz), 3.65 (3H,

3.78 (1H, d, J=16.8 Hz), 5.24 (1H, d, J=7.5 Hz), 7.10 - 7.65 (4H, m), and 11.93 (1H, br s); H NMR δ =23.1, 29.3, 38.0, 50.8, 53.2, 107.1, 112.8, 114.4, 119.8, 120.6, 123.8, 125.3, 126.0, 137.1, 142.4, 169.9, 174.7, and 193.1. High resolution MS Calcd for C_{18}H_{16}N_{2}O_{4}: 324.1108. Found: 324.1091.

5a (yield 55%): mp 195 - 197 °C (decomp); UV-VIS 313 (ε = 10500), 384 (20500), and 402 nm (17600); H NMR δ =1.21 (3H, t, J=7.2 Hz), 2.62 (2H, m), 3.37 (1H, dd, J=16.9 and 7.5 Hz), 3.65 (2H, AB-q, J=23.6 Hz), 3.65 (3H, s), 3.79 (1H, d, J=16.9 Hz), 5.25 (1H, d, J=7.5 Hz), 7.11 - 7.65 (4H, m), and 11.99 (1H, br s); C NMR δ =23.1, 29.3, 38.0, 50.8, 53.2, 107.1, 112.8, 114.4, 119.8, 120.6, 123.8, 125.3, 126.0, 137.1, 142.4, 169.9, 174.7, and 193.1. High resolution MS Calcd for C_{18}H_{16}N_{2}O_{4}: 324.1108. Found: 324.1091.

6a (as an oil, yield 30%): UV-VIS 315 (ε = 10600), 386 (19600), and 403 nm (17600); H NMR δ =1.18 (3H, d, J=6.7 Hz), 1.22 (3H, d, J=6.7 Hz), 2.90 (1H, m), 3.36 (1H, dd, J=16.8 and 7.4 Hz), 3.64 (3H, s), 3.71 (2H, AB-q, J=23.6 Hz), 3.79 (1H, d, J=16.8 Hz), 5.26 (1H, d, J=7.4 Hz), 7.10 - 7.65 (4H, m), and 12.08 (1H, br s); C NMR δ =18.8, 19.1, 23.1, 37.4, 38.0, 50.8, 53.1, 106.4, 112.8, 114.3, 119.8, 120.5, 123.9, 125.4, 126.0, 137.1, 143.2, 169.9, 174.7, and 200.0. High resolution MS Calcd for C_{20}H_{20}N_{2}O_{4}: 352.1423. Found: 352.1398.

Preparation of 7a. A mixture of 3 (112 mg, 0.40 mmol), trifluoroacetic acid (0.3 g, 2.6 mmol), acetic anhydride (0.2 ml 2.1 mmol), and CHCl_3 (8 mL) was left at rt for 5 days, and worked up as described above to give 7a (21 mg, 14%): mp 169 - 170 °C (decomp); UV-VIS 333 (ε = 15100) and 428 nm (23700); H NMR δ =3.43 (1H, dd, J=17.2 and 7.7 Hz), 3.68 (3H, s), 3.81 (2H, AB-q, J=23.5 Hz), 3.88 (1H, d, J=17.2 Hz), 5.31 (1H, d, J=7.7 Hz), 7.16 - 7.69 (4H, m), and 11.71 (1H, br s); C NMR δ =23.1, 35.4, 50.9, 53.5, 100.1, 113.1, 117.5, 118.0, 120.5, 121.5, 122.9, 125.1, 127.8, 138.2, 150.5, 169.3, 173.6, and 174.3. High resolution MS Calcd for C_{18}H_{16}N_{2}F_3O_3: 378.0826. Found: m/z 378.0836.

Preparation of 8a - 10a. A typical procedure is described for the preparation of 8a. A mixture of 3 (50 mg, 0.18 mmol), benzoyl chloride (95 mg, 0.68 mmol), pyridine (0.1 mL), and CHCl_3 (5 mL) was heated under reflux for 3 h under nitrogen atmosphere. The solution was washed successively with 1% HCl, water, saturated aq. NaHCO_3, brine, and dried over Na_2SO_4, and then concentrated under reduced pressure. The residue was purified with column chromatography (SiO_2, CHCl_3) to give 8a (crystallized from MeOH, 50 mg, 73%): mp 186 - 189 °C (decomp); UV-VIS 321 (ε = 10400), 405 (21000), and 418 nm (20800); H NMR δ =3.40 (1H, dd, J=16.9 and 7.5 Hz), 3.66 (3H, s), 3.72 (2H, s), 3.84 (1H, d, J=16.9 Hz), 5.29 (1H, d, J=7.5 Hz), 7.14 - 7.68 (9H, m), and 12.10 (1H, br s); C NMR δ =23.1, 39.2, 50.8, 53.2, 106.6, 112.8, 115.1, 119.9, 120.7, 124.0, 125.4, 126.3, 127.3, 128.5, 131.1, 137.3, 141.1, 145.0, 169.8, 174.9, and 190.4. High resolution MS Calcd for C_{23}H_{18}N_{2}O_4: 386.1266. Found: 386.1267.
9a (yield 69%): mp 218 - 223 °C (decomp); UV-VIS 318 (ε 14800), 404 (29000), and 421 nm (27700); \(^1\)H NMR δ = 3.39 (1H, dd, J = 16.8 and 7.5 Hz), 3.65 (3H, s), 3.78 (2H, s), 3.82 (1H, d, J = 16.8 Hz), 3.88 (3H, s), 5.29 (1H, d, J = 7.5 Hz), 6.97 (2H, d, J = 8.8 Hz), 7.14 - 7.66 (4H, m), 7.69 (2H, d, J = 8.8 Hz), and 12.07 (1H, br s); \(^1\)C NMR δ = 23.1, 39.5, 50.8, 53.2, 55.5, 107.0, 112.8, 113.7, 114.8, 119.9, 120.6, 124.1, 125.5, 126.1, 129.8, 133.5, 137.2, 144.7, 162.2, 169.9, 175.0, and 189.2. High resolution MS Calcd for C\(_{24}\)H\(_{23}\)N\(_2\)O\(_5\): M + H, 417.1451. Found: 417.1478.

10a (yield 68%): mp 227 - 231 °C (decomp); UV-VIS 326 (ε 16900) and 427 nm (25400); \(^1\)H NMR δ = 3.43 (1H, dd, J = 17.3 and 7.9 Hz), 3.63 (2H, s), 3.68 (3H, s), 3.86 (1H, d, J = 17.3 Hz), 5.30 (1H, d, J = 7.9 Hz), 7.15 - 7.70 (4H, m), 7.76 (2H, d, J = 8.6 Hz), 8.32 (2H, d, J = 8.6 Hz), and 12.03 (1H, br s); \(^1\)C NMR δ = 23.1, 38.5, 50.9, 53.3, 105.2, 113.0, 116.3, 120.2, 121.1, 123.6, 123.8, 125.4, 126.9, 128.1, 137.6, 146.6, 148.9, 169.6, 174.4, and 187.9. High resolution MS Calcd for C\(_{24}\)H\(_{21}\)N\(_2\)O\(_6\): M, 431.1116. Found: 431.1144.

The compounds (4a - 9a) were subjected to following experiments without further purification for analysis, since they were sensitive to autoxidation.

Preparation of 4b - 9b. A typical procedure is described for the preparation of 4b. A mixture of 4a (50 mg, 0.15 mmol), i-Pr\(_2\)NH (0.5 mL, 3.5 mmol), and CH\(_2\)Cl\(_2\) (15 mL) was stirred at rt for 1 day, and concentrated under reduced pressure. The residue was purified with column chromatography (SiO\(_2\), CHCl\(_3\)) to give 4b (crystallized from AcOEt-hexane or MeOH, 13 mg, 26%): mp 248 - 251 °C; UV-VIS 389 (ε 24900) and 715 nm (76300); \(^1\)H NMR δ = 2.49 (3H x 2, s), 3.47 (1H x 2, dd, J = 17.1 and 7.4 Hz), 3.60 (3H x 2, s), 3.88 (1H x 2, d, J = 17.1 Hz), 5.32 (1H x 2, d, J = 7.4 Hz), 7.11 - 7.65 (4H x 2, m), and 10.92 (1H x 2, br s); \(^1\)C NMR δ = 23.6, 29.9, 50.9, 53.2, 112.8, 114.2, 118.5, 120.2, 121.0, 123.8, 125.6, 127.3, 128.0, 139.3, 140.5, 169.9, and 197.2. High resolution MS Calcd for C\(_{26}\)H\(_{28}\)N\(_2\)O\(_6\): 644.1907. Found: 644.1908.

5b (yield 15%): mp 263 - 265 °C; UV-VIS 388 (ε 25200) and 714 nm (70000); \(^1\)H NMR δ = 1.22 (3H x 2, t, J = 7.3 Hz), 2.50 - 3.10 (2H x 2, m), 3.46 (1H x 2, dd, J = 17.1 and 7.7 Hz), 3.58 (3H x 2, s), 3.86 (1H x 2, d, J = 17.1 Hz), 5.30 (1H x 2, d, J = 7.7 Hz), 7.11 - 7.66 (4H x 2, m), and 10.74 (1H x 2, br s); \(^1\)C NMR δ = 9.2, 23.7, 35.8, 51.1, 53.3, 112.8, 113.4, 117.8, 120.2, 121.1, 124.0, 125.8, 127.2, 127.9, 139.3, 139.8, 170.0, and 201.1. High resolution MS Calcd for C\(_{34}\)H\(_{32}\)N\(_2\)O\(_6\): 672.2220. Found: 672.2215.

6b (yield 34%): mp 278 - 279 °C; UV-VIS 388 (ε 26900) and 712 nm (71100); \(^1\)H NMR δ = 0.90 - 1.40 (6H x 2, m), 3.36 (1H x 2, m), 3.49 (1H x 2, dd, J = 16.8 and 7.3 Hz), 3.59 (3H x
2, s). 3.85 (1H × 2, d, J=16.8 Hz), 5.29 (1H × 2, d, J=7.3 Hz), 7.10 - 7.65 (4H × 2, m) and 10.61 (1H × 2, br; s); \(^{13}\text{C NMR}\) \(\delta =\)23.7, 39.7, 51.1, 53.2, 112.4, 112.8, 120.2, 121.0, 124.1, 125.8, 127.1, 127.7, 139.3, 140.0, 170.0, and 204.7. High resolution MS Calcd for C\(_{10}\)H\(_{16}\)N\(_2\)O\(_2\): 700.2533. Found: 700.2539.

7b was prepared by stirring a solution of 7a (30 mg) in MeOH (20 mL) for 5 days. 7b (yield 50%): mp 261 - 263 °C; UV-VIS 286 (\(\epsilon = 14700\)), 398 (25500), 639 (57500), and 691 nm (92500); \(^{1}\text{H NMR}\) \(\delta =\)3.54 (1H × 2, dd, J=17.3 and 7.9 Hz), 3.62 (3H × 2, s), 3.93 (1H × 2, d, J=17.3 Hz), 5.38 (1H × 2, d, J=7.9 Hz), 7.18 - 7.70 (4H × 2, m), and 10.04 (1H × 2, brs); \(^{13}\text{C NMR}\) \(\delta =\)23.6, 51.4, 53.5, 104.0, 113.0, 117.1, 120.2, 120.7, 121.8, 122.8, 125.7, 126.9, 128.5, 139.9, 144.0, 166.9, 169.1, and 180.0. High resolution MS Calcd for C\(_{25}\)H\(_{38}\)N\(_4\)O\(_2\): M+H, 753.1421. Found: 753.1476.

8b (yield 51%): mp 281 - 282 °C; UV-VIS 406 (\(\epsilon = 24800\)), 654 (46300), and 712 nm (69800); \(^{1}\text{H NMR}\) \(\delta =\)3.30 (1H × 2, dd, J=16.4 and 7.1 Hz), 3.54 (3H × 2, s), 3.77 (1H × 2, d, J=16.4 Hz), 5.08 (1H × 2, d, J=7.1 Hz), 7.07 - 7.93 (9H × 2, m), and 10.34 (1H × 2, brs); \(^{13}\text{C NMR}\) \(\delta =\)23.7, 51.0, 53.2, 110.9, 112.7, 117.9, 120.2, 121.1, 123.9, 125.8, 127.1, 127.8, 128.0, 129.2, 132.3, 139.4, 140.6, 141.7, 165.8, 169.7, and 192.6. High resolution MS Calcd for C\(_{45}\)H\(_{37}\)N\(_4\)O\(_8\): M+H, 829.2220. Found: 829.2286.

9b (yield 45%): mp 273 - 274 °C; UV-VIS 297 (\(\epsilon = 30700\)), 400 (24400), 655 (49300), and 713 nm (73400); \(^{1}\text{H NMR}\) \(\delta =\)3.32 (1H × 2, dd, J=16.7 and 7.6 Hz), 3.54 (3H × 2, s), 3.77 (1H × 2, d, J=16.7 Hz), 3.89 (3H × 2, s), 5.08 (1H × 2, d, J=7.6 Hz), 6.98 (2H × 2, d, J=8.7 Hz), 7.06 - 7.59 (4H × 2, m), 7.89 (2H × 2, d, J=8.7 Hz), and 10.27 (1H × 2, brs); \(^{13}\text{C NMR}\) \(\delta =\)23.7, 50.9, 53.2, 55.5, 111.2, 112.6, 113.1, 117.5, 120.1, 121.0, 124.0, 125.8, 126.9, 128.3, 131.2, 133.4, 139.3, 141.2, 163.0, 169.8, and 191.6. High resolution MS Calcd for C\(_{48}\)H\(_{37}\)N\(_4\)O\(_{10}\): M+H, 829.2510. Found: 829.2402.

ACKNOWLEDGEMENT
The authors wish to thank Mr. Akihito Yagi of Shizuoka University for obtaining the MS spectra.

REFERENCES


Received, 30th October, 1997