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

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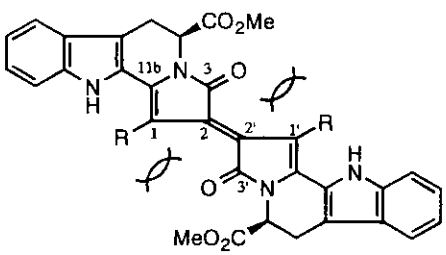
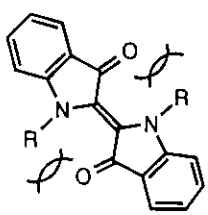
Abstract- The absorption and ^{13}C NMR spectra of 1,1'-diacyltrichotomine derivatives showed that the central C(2)=C(2') double bond was twisted, and coplanarity of the 1,1'-diacyl groups and the trichotomine chromophore was hindered by steric interactions between the 1,1'-diacyl groups and the 3,3'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



1a - 1d

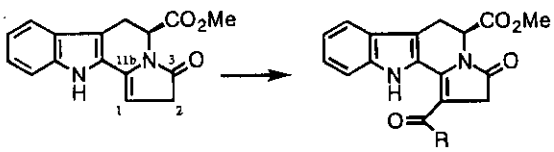


2a - 2c

a R = H
b R = Alkyl
c R = Acyl
d R = COOEt

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**).[2b] The 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}C NMR spectrum of **7a**, the signals of the CF_3CO group were observed at δ =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**.[2c] Upon stirring in CH_2Cl_2 containing *i*-Pr_2NH, 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.



3 **4a - 10a** **4b - 9b**

4a,b R = Me
5a,b R = Et
6a,b R = *i*-Pr
7a,b R = CF_3
8a,b R = C_6H_5
9a,b R = *p*-$MeOC_6H_4$
10a R = *p*-$NO_2C_6H_5$

Absorption Spectra. The absorption spectral data of **4a** - **10a** and 1,1'-diacyltrichotomine derivatives (**4b** - **9b**) were summarized in Table 1. The λ 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: C(=O)Ph > C(=O)Alk.[5] 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 λ max of *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).[4b] But, the λ 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 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.[2a,2c] Therefore, the 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 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**)

Substituent	Compound	λ max (nm)	δ c (ppm)	Compound	λ max (nm)	δ c (ppm)
R = Me	**4a**	402	193.1	**4b**	715	197.2
R = Et	**5a**	402	196.1	**5b**	714	201.1
R = *i*-Pr	**6a**	403	200.0	**6b**	712	204.7
R = CF_3	**7a**	428	173.6	**7b**	691	180.0
R = C_6H_5	**8a**	418	190.4	**8b**	712	192.6
R = *p*-$MeOC_6H_5$	**9a**	421	189.2	**9b**	713	191.6
R = *p*-$NO_2C_6H_4$	**10a**	427	187.9			

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).[6] Accordingly, in **4b - 6b** the bathochromic and hypsochromic shifts might be compensated each other. In order to confirm 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 donar character of the substituents and the π-electron density changes accompanying the first excitation.[7] 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 π-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 π-electron densities accompanying the first excitation at the C(1) and C(1') of **4b**, since the π-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.[8] The 1,1'-diaroyl 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 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 β-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.[9] 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 $CHCl_3$. ^{1}H 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 ℃ (decomp); UV-VIS 314 (ε 11500), 386 (21700), and 402 nm (18900); ^{1}H NMR δ =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,

s), 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); ^{13}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 $C_{18}H_{16}N_2O_4$: 324.1108. Found: 324.1091.

5a (yield 55%): mp 195 - 197 ℃ (decomp); UV-VIS 313 (ε 10500), 384 (20500), and 402 nm (17600); ^{1}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); ^{13}C NMR δ =8.0, 23.2, 34.5, 37.5, 50.8, 53.2, 107.0, 112.8, 114.2, 119.8, 120.6, 123.9, 125.4, 126.0, 137.1, 142.1, 170.0, 174.8, and 196.1. High resolution MS Calcd for $C_{19}H_{18}N_2O_4$: 338.1265. Found: 338.1284.

6a (as an oil, yield 30%): UV-VIS 315 (ε 10600), 386 (19600), and 403 nm (16900); ^{1}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); ^{13}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 $C_{20}H_{20}N_2O_4$: 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 CH_2Cl_2 (8 mL) was left at rt for 5 days, and worked up as described above to give **7a** (21 mg, 14%): mp 169 - 170 ℃ (decomp); UV-VIS 333 (ε 15100) and 428 nm (23700); ^{1}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); ^{13}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 $C_{18}H_{13}N_2O_4F_3$: 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 CH_2Cl_2 (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 ℃ (decomp); UV-VIS 321 (ε 10400), 405 (21000), and 418 nm (20800); ^{1}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); ^{13}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 $C_{23}H_{18}N_2O_4$: 386.1266. Found: 386.1267.

9a (yield 69%): mp 218 - 223 ℃ (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); ^{13}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 $C_{24}H_{21}N_2O_5$: M+H, 417.1451. Found: 417.1478.

10a (yield 68%): mp 227 - 231 ℃ (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); ^{13}C NMR δ =23.2, 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, 146.7, 148.9, 169.6, 174.4, and 187.9. High resolution MS Calcd for $C_{23}H_{17}N_3O_6$: 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_2NH (0.5 mL, 3.5 mmol), and CH_2Cl_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 ℃; UV-VIS 389 (ε 24900) and 715 nm (76300); ^{1}H NMR δ =2.49 (3H×2, s), 3.47 (1H×2, dd, J=17.1 and 7.4 Hz), 3.60 (3H×2, s), 3.88 (1H×2, d, J=17.1 Hz), 5.32 (1H×2, d, J=7.4 Hz), 7.11 - 7.65 (4H×2, m), and 10.92 (1H×2, br s); ^{13}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 $C_{36}H_{28}N_4O_8$: 644.1907. Found: 644.1908.

5b (yield 15%): mp 263 - 265 ℃; UV-VIS 388 (ε 25200) and 714 nm (70000); ^{1}H NMR δ =1.22 (3H×2, t, J=7.3 Hz), 2.50 - 3.10 (2H×2, m), 3.46 (1H×2, dd, J=17.1 and 7.7 Hz), 3.58 (3H×2, s), 3.86 (1H×2, d, J=17.1 Hz), 5.30 (1H×2, d, J=7.7 Hz), 7.11 - 7.66 (4H×2, m), and 10.74 (1H×2, br s); ^{13}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 $C_{38}H_{32}N_4O_8$: 672.2220. Found: 672.2215.

6b (yield 34%): mp 278 - 279 ℃; UV-VIS 388 (ε 26900) and 712 nm (71100); ^{1}H NMR δ =0.90 - 1.40 (6H×2, m), 3.36 (1H×2, m), 3.49 (1H×2, dd, J=16.8 and 7.3 Hz), 3.59 (3H×

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}C NMR δ =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 $C_{40}H_{36}N_4O_8$: 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 ℃; UV-VIS 286 (ε 14700), 398 (25500), 633 (57500), and 691 nm (92500); ^{1}H NMR δ =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, br s); ^{13}C NMR δ =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 $C_{36}H_{23}N_4O_8F_6$: M+H, 753.1421. Found: 753.1476.

8b (yield 51%): mp 281 - 282 ℃; UV-VIS 406 (ε 24800), 654 (46300), and 712 nm (69800); ^{1}H NMR δ =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, br s); ^{13}C NMR δ =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 $C_{46}H_{32}N_4O_8$: 768.2220. Found: 768.2286.

9b (yield 45%): mp 273 - 274 ℃; UV-VIS 297 (ε 30700), 400 (24400), 655 (49300), and 713 nm (73400); ^{1}H NMR δ =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, br s); ^{13}C NMR δ =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 $C_{48}H_{37}N_4O_{10}$: M+H, 829.2510. Found: 829.2402.

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