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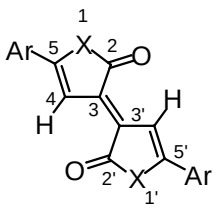
PREPARATION AND SPECTRAL PROPERTIES OF THE NITROGEN ANALOGS OF (*E*)- 5,5'-DIARYL-3,3'-BIFURANYLIDENE-2,2'-DIONES AND THEIR DERIVATIVES

Hajime Irikawa* and Norihide Adachi

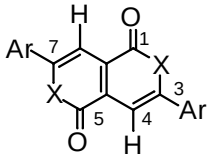
Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422-8529, Japan

Abstract- (*E*)-5,5'-bis(2-methylphenyl)- and (*E*)-5,5'-bis(2,4,6-trimethylphenyl)-3,3'-bifuranylidene-2,2'-diones and their isomeric pyrano[4,3-*c*]pyran-1,5-diones were converted into the nitrogen analogs, in which the aryl groups were twisted relative to the parent skeletons, and had small conjugation effect. Another nitrogen analogs bearing coplanar aryl rings were prepared, and their UV-VIS and NMR spectral data were compared with those of the analogs having twisted aryl groups. Conjugation effect of the 2-alkylphenyl group is bathochromic shift by 24 nm. Steric compression due to coplanarity of the aryl rings causes a deshielding of a ^{1}H NMR signal by ~ 0.6 ppm, and a shielding of a ^{13}C NMR signal by ~ 5 ppm.

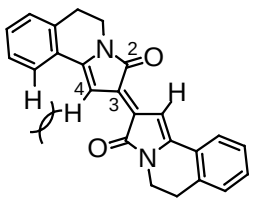
It is well known that two aromatic rings in biphenyls are twisted as the *o,o*- and *o',o'*-substituents become bulky, and that in ultraviolet spectrum λmax of such biphenyl derivatives comes close to that of monophenyl analogs.[1a-c] In a previous paper, we have reported the absorption spectrum of the nitrogen analog (**1a**) derived from a Pechmann dye, 5,5'-diphenyl-3,3'-bifuranylidene-2,2'-dione (**2a**), and of the analog (**3a**) obtained from an isomeric pyrano[4,3-*c*]pyran-1,5-dione (**4a**).[2a] Calculation using MOPAC AM1 suggested that the phenyl groups in **1a** were twisted by 38° relative to the parent skeleton. The X-Ray analysis of **3a** showed that the phenyl groups were twisted by 51.8° and 61.5°.[2b] Presence of methyl groups in the *o, o*-positions of the phenyl groups in **1a** and **3a** seemed to make the aryl groups more



1a-c X=NMe
2a-c X=O



3a-c X=NMe
4a-c X=O



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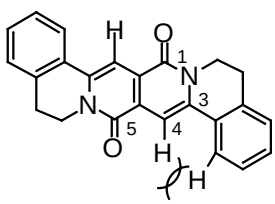

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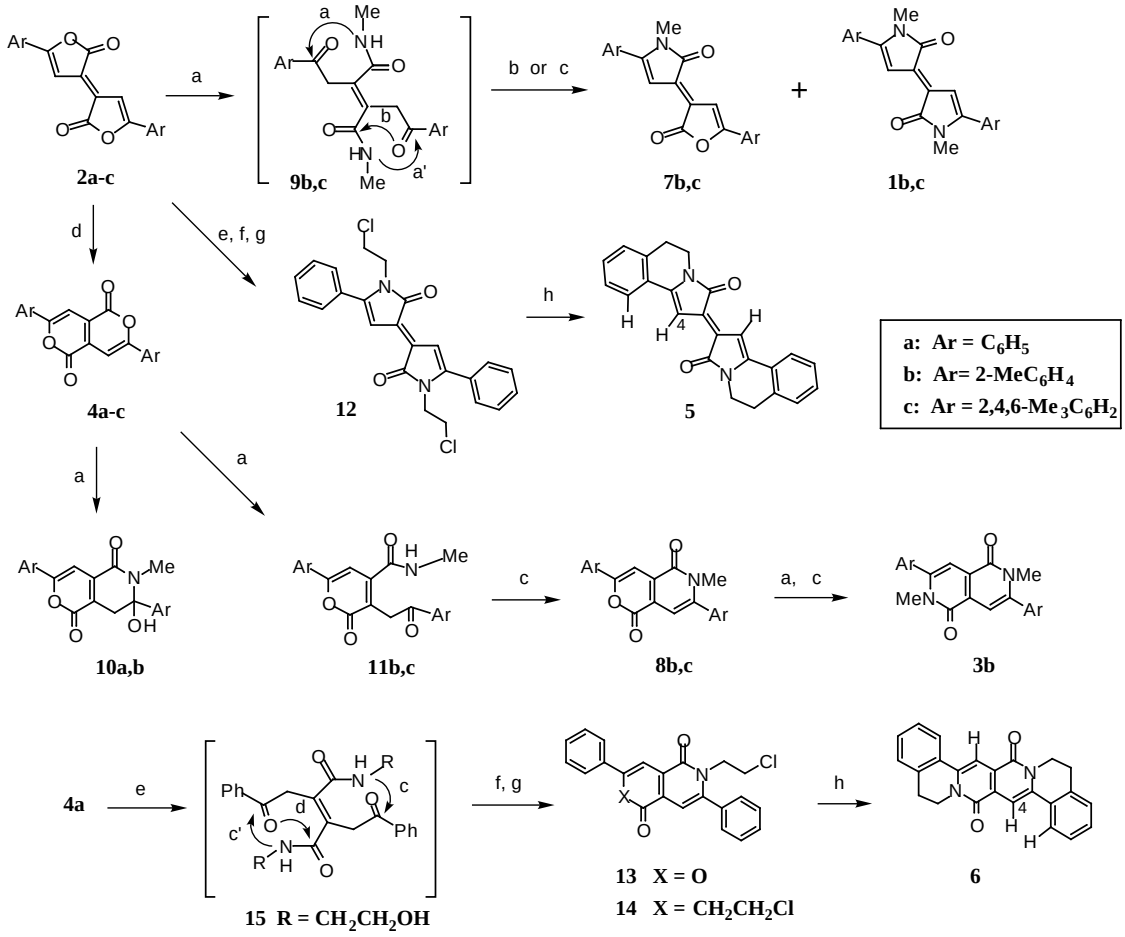
a : Ar = C_6H_5 b : Ar = 2-MeC_6H_4 c : Ar = 2,4,6-$Me_3C_6H_2$

twisted, and the λmax of such analogs (**1b, c** and **3b, c**) seemed to come close to that of the parent chromophores, respectively, because of small conjugation effect of the aryl groups. Comparison of the λmax of these analogs (**1b, c** and **3b, c**) with that of another nitrogen analogs (**5** and **6**) bearing coplanar aryl rings seemed to indicate conjugation effect of the aryl rings. Coplanarity of the aryl rings and the parent skeletons in **5** and **6** seemed to affect chemical shifts of the H-4 and C-4 in the ^{1}H and ^{13}C NMR spectra. This paper deals with comparisons of the spectral data (UV-VIS, ^{1}H and ^{13}C NMR) of the nitrogen analogs (**1b**,**c** and **3b**), derived from (*E*)-5,5'-bis(2-methylphenyl)- and (*E*)-5,5'-bis(2,4,6-trimethylphenyl)-3,3'-bifuranylidene-2,2'-diones (**2b** and **2c**), with those of another analogs (**5** and **6**) derived from **2a** and **4a**.

Preparation

The compound (**2b**) was prepared from 4-(2-methylphenyl)-4-oxo-2-butenoic acid according to the literature procedure.[3] Reaction of **2b** with $MeNH_2$ in CH_2Cl_2 gave complicated products,



a) $MeNH_2$ / CH_2Cl_2 ; b) Ac_2O / AcOH ; c) $POCl_3$ / CH_2Cl_2 ; d) Δ / 1,3-propanediol ;
e) 2-aminoethanol / CH_2Cl_3 ; f) 5% HCl ; g) PPh_3 / CCl_4 / CH_2Cl_2 ; h) $AlCl_3$ / C_6H_5Cl

which were treated with a mixture of acetic anhydride and acetic acid to give **7b** (7%) and **1b** (13%). Calculation using MOPAC AM1 showed that the 2-methylphenyl groups in **1b** were twisted by 48° relative to the parent skeleton. In order to obtain an analog bearing more twisted aryl groups, the compound (**2c**) was used.[4] On aminolysis with $MeNH_2$, **2c** gave complicated products, which were treated with $POCl_3$ in CH_2Cl_2 to give **7c** (44%) and **1c** (1%), along with a fluorescent compound (**8c**, 1%). Under conditions used for the preparation of **1b**, **2c** did not yield **1c**. The formation of **7b,c** and **1b,c** is explained by cyclization *via* routes a - b and a - a' shown in the structure of **9b,c**, respectively. A low yield of **1c** reflects bulkiness of the 2,4,6-trimethylphenyl (common name, mesityl) groups.

The compound (**2b**) was isomerized into **4b** by heating in 1,3-propanediol. On aminolysis with $MeNH_2$, followed by treatment with $POCl_3$, **4b** gave **8b** (71%), which was converted into **3b** (60%) by repeating the aminolysis and $POCl_3$ treatment. The compound (**3b**) might contain both atrop isomers, because the ^{1}H NMR spectrum of **3b** showed two singlet signals (assigned to the methyl groups on the aryl groups) at 2.19 and 2.20 ppm. In a previous paper, we reported that reaction of **4a** with $MeNH_2$ gave a ring tautomer (**10a**) of the ring-chain tautomerism.[2a,5] On the contrary, a chain tautomer (**11c)** was obtained almost quantitatively by aminolysis of **4c**[6] with $MeNH_2$. The aminolysis products of **4b** contained both ring-chain tautomers (**10b** and **11b**) in a ratio of 1.0 : 1.6 (determined by ^{1}H NMR). On heating above 300 °C, **11c** changed into **4c** almost quantitatively, while on treatment with $POCl_3$, **11c** yielded **8c** (19%), along with **4c** (60%). The compound (**3c)** was not obtained from **8c** by repeating the aminolysis and $POCl_3$ treatment.

The λmax of 9,10-dihydrophenanthrene, a two-atom-bridged biphenyl, is observed at considerably longer wavelength than that of biphenyl because of planarity of the structure (interplanar angle = 20°).[1b] In order to prevent twisting of the phenyl groups in **1a** and **3a**, another nitrogen analogs (**5** and **6**) were derived from **2a** and **4a**. On aminolysis with 2-aminoethanol, cyclization with 5% HCl, and chlorination with Ph_3P and CCl_4, **2a** gave a violet compound (**12**, 41%) as a main product. Under similar conditions, **4a** yielded fluorescent compounds (**13**, 25%; **14**, 9%), along and **12** (11%). Formation of **13** and **14** is explained by cyclization *via* c -d, and c - c' shown in the structure of **15,** respectively**,** and that of **12** by cyclization similar to that (a - a') shown in **9b,c**. Friedel-Crafts reaction of **12** and **14** with anhydrous $AlCl_3$ in chlorobenzene yielded **5** (36%) and **6** (72%), respectively.

Absorption Spectra

In a previous paper, we reported that replacement of the lactone-oxygen atoms in **2a** with *N*-methyl groups caused bathochromic shift.[2a] The λmax of **2b** was observed at 505 nm (shoulder at 530 nm), and that of **7b** and **1b** was found at 532 and 533 nm, respectively. In general, twisting of the benzene rings relative to the chromophore causes hypsochromic shift. In **7b** and **1b**, the bathochromic and hypsochromic shifts mentioned above might be compensated each other. Comparison of the λmax of **2c** (468 nm) with that of **7c** (510 nm) and **1c** (522 nm) showed bathochromic shifts as the lactone-oxygen atoms in **2c** were replaced with *N*-methyl groups. X-Ray analysis shows that **2c** exists in two forms and the mesityl groups are

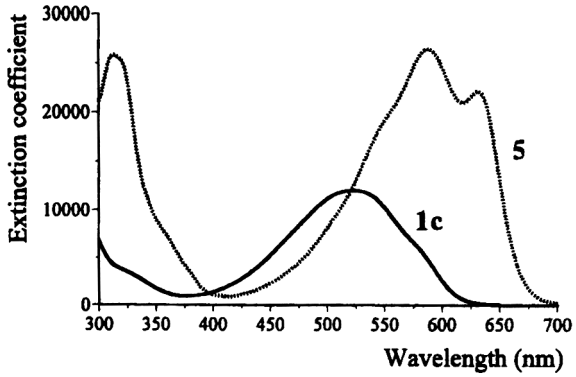


Figure 1. Absorption spectra of **1c** and **5**.

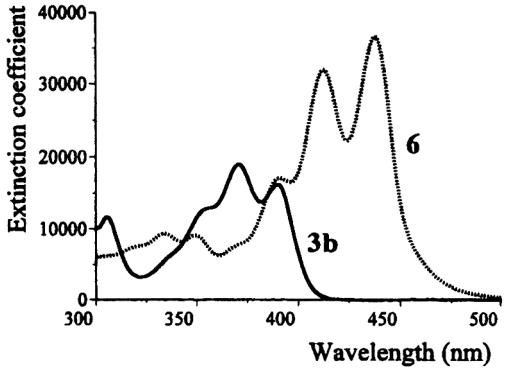


Figure 2. Absorption spectra of **3b** and **6**.

twisted by 39° and 56°.[4] Also in X-Ray analysis of **1c** the mesityl groups were shown to be twisted by 71°.[2c] In **7c** and **1c**, bathochromic shifts caused by introduction of the *N*-methyl groups might exceed hypsochromic shifts due to twisting of the mesityl groups, since the mesityl groups in **2c** are already twisted largely.

The λmax of biphenyls with four alkyl substituents in the *o*-, *o'*-positions is observed almost at the same wavelength as that of their corresponding monophenyl analogs.[1c] In *o,o'*-dimethylbiphenyl, two benzene rings are twisted by 70°, and the conjugation is hindered.[1a] So, in **3b** the 2-methylphenyl groups are suggested to be similarly twisted, and the conjugation effect of the 2-methylphenyl groups seems small. Twisting angle (71°) of the mesityl groups in **1c** is similar to that (70°) of *o,o'*-dimethylbiphenyl. Accordingly, the λmax of **1c** (522 nm) and **3b** (390 nm) is estimated to be close to that of the parent chromophores of compounds (**1a** and **3a**), respectively.

The absorption spectra of **1c** and **5**, and those of **3b** and **6** are shown in Figures 1 and 2, respectively. The λmax of **3b** is found at 390 nm, and that of **6** is observed at 438 nm, which is longer than that of **3b** by 48 nm. In **6**, two 2-alkylphenyl groups are conjugated with the parent chromophore. Therefore, the conjugation effect of the 2-alkylphenyl group in **6** is bathochromic shift by 24 nm. The planar derivative (**5**) shows two peaks at 632 and 587 nm, while **1c** indicates one peak at 522 nm. So, the conjugation effect of the 2-alkylphenyl group in **5** can not be calculated, but is bathochromic shift similar to that observed in **6**, as shown in Figure. 1.

^{1}H and ^{13}C NMR Spectra

Coplanarity of the aryl rings and the parent skeletons in **5** and **6** seemed to cause steric interactions around the hydrogen on C-4, as shown in the structures of **5** and **6**. Chemical shifts of the H-4 and C-4 in the analogs (**1b** and **3b**) and in the planar analogs (**5** and **6**) were summarized in Table 1. The H-4 signal of **5** and **6** was deshielded compared with that of **1c** and **3b** by 0.5 ~ 0.6 ppm. On the other hand, the C-4 signal of **5** and **6** was shielded compared with that of **1c** and **3b** by 4 ~ 5 ppm. The characteristics are rationalized by steric interactions around the hydrogen on C-4 in **5** and **6**, respectively, because it is well known that steric interactions arising from overlapping of van der Waals radii of closely spaced hydrogens cause a deshielding of the hydrogens and a shielding of the carbons attached to those hydrogens.[7] The *N* -

methyl signal in **1a-c** (**1a**, δ = 3.19 ppm; **1b**, δ = 2.91 ; **1c**, δ = 2.80) shows increase of the shielding, as methyl groups are introduced on the *o, o*-positions, and twisting of the 5,5'-aryl groups becomes larger. This trend might be in line with decrease of the deshielding due to anisotropic effect of the aryl rings.

Table 1. ^{1}H and ^{13}C NMR spectral data of the analogs (**1b**, **3b**, **5**, and **6**)

Compounds	δH-4	δC-4	Compounds	δH-4	δC-4
1b	6.78	102.5	**3b**	6.97	104.0
5	7.27	97.7	**6**	7.61	100.2

The results presented in this paper is an example of substituent effects of the twisted and coplanar aryl rings.

EXPERIMENTAL

All melting points are measured on a Yanaco MP-J3, and are uncorrected. Absorption spectra were measured on a Hitachi U3000 in $CHCl_3$. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC300 (300 MHz, 75 MHz) in $CDCl_3$, using a $CHCl_3$ signal (δ=7.26) and a $CDCl_3$ signal (δ=77.0) as an internal standard. MS spectra were obtained on a JEOL-DX303. Column chromatography was performed with silica gel 60 (70—230 mesh, Merck). TLC was carried out on Kieselgel $60F_{254}$ plates (Art. 5744, Merck).

Preparation of 2b. A mixture of 4-(2-methylphenyl)-4-oxo-2-butenoic acid (4.5 g, 24 mmol), cuprous chloride (0.84 g, 8.5 mmol), ammonium chloride (0.93 g, 17 mmol), and acetic anhydride (30 mL) was heated under reflux for 2 h. The mixture was cooled, and the solid was collected and washed with acetic acid and ethanol. The crude product was then extracted with boiling toluene to give **2b** (2.7 g, 66%): mp 215 - 217 °C ($CHCl_3$); UV-VIS λmax 283 (ε 20400), 505 (37600), and 530 nm (sh, 34300); ^{1}H NMR δ = 2.62 (6H, s, 2×Me), 7.29 - 7.39 (6H, m), 7.42 (2H, s), and 7.85 (2H, dd, J=7.7 and 2.2 Hz); ^{13}C NMR δ = 22.6, 107.0, 126.5, 126.8, 126.9, 128.6, 131.3, 132.1, 138.2, 160.4, and 167.0. *Anal.* Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C,76.57; H, 4.71.

Preparation of 7b and 1b. A mixture of **2b** (52 mg, 0.15 mmol), 40% methanolic $MeNH_2$ (0.1 mL, 1 mmol), and CH_2Cl_2 (5 mL) was allowed to stand at rt overnight. The mixture was concentrated under reduced pressure to give a residue, which was dissolved in a mixture of acetic anhydride (1 mL) and acetic acid (1 mL). The solution was heated under reflux for 5 min, and concentrated under reduced pressure. The residue was separated with column chromatography ($CHCl_3$) and with TLC (AcOEt:hexane 1:4) to give **7b** (4 mg, 7%) and **1b** (7 mg, 13%). **7b**: mp 162 - 164 °C ($CHCl_3$ - hexane); UV-VIS λmax 281 (ε 13200), 437 (8700), and 532 nm (13700); ^{1}H NMR δ = 2.35 (3H, s), 2.62 (3H, s), 2.95 (3H, s), 6.64 (1H, s), 7.25 - 7.41 (7H, m), 7.57 (1H, s), and 7.83 (1H, m); ^{13}C NMR δ = 20.0, 22.6, 27.4, 102.6, 107.1, 125.1, 126.1, 126.4, 127.3, 128.3, 129.2, 130.1, 130.2, 130.7, 131.0, 131.9, 136.9, 137.8, 154.0, 159.4, 167.9, and 169.8. High resolution MS Calcd for $C_{23}H_{19}NO_3$: M, 357.1365. Found: 357.1366. **1b**: mp 210 - 213 °C ($CHCl_3$ - MeOH); UV-VIS λmax 288 (ε 15200) and 533 nm (12900);

^{1}H NMR δ = 2.33 (6H, s, 2×Me), 2.91 (6H, s), 6.78 (2H, s), and 7.25 - 7.39 (8H, m); ^{13}C NMR δ = 19.9, 27.3, 102.5, 126.0, 129.3, 129.7, 130.6, 130.7, 137.0, 152.5, and 170.6; MS m/z 370 (M^+). *Anal.* Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.48; H, 6.01; N, 7.48.

Preparation of 7c and 1c. A mixture of **2c** (200 mg, 0.5 mmol), 40% methanolic $MeNH_2$ (0.2 mL, 2 mmol), and CH_2Cl_2 (15 mL) was stirred at rt for 1 h, and concentrated under reduced pressure. To a mixture of the residue and CH_2Cl_2 (15 mL) was added $POCl_3$ (0.3 mL, 3 mmol). The mixture was stirred at rt for 2d. After dilution with $CHCl_3$, the mixture was washed (saturated aq. $NaHCO_3$ and saturated aq. NaCl), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was separated with column chromatography ($CHCl_3$: hexane 3:2) and with TLC ($CHCl_3$: hexane 2:1) to give **7c** (85 mg, 41%), **1c** (2 mg, 1%), and **8c** as an oil (2 mg, 1%), along with **2c** (17 mg, 8%). **7c**: mp 217 - 219 °C (EtOH); UV-VIS λmax 419 (ε 9100) and 510 nm (13300); ^{1}H NMR δ = 2.21 (6H, s), 2.32 (3H, s), 2.33 (3H, s), 2.36 (6H, s), 2.82 (3H, s), 6.56 (1H, s), 6.94 (2H, s), 6.96 (2H, s), and 7.24 (1H, s); ^{13}C NMR δ = 19.9, 20.8, 21.2, 21.3, 26.5, 101.9, 108.6, 124.4, 125.8, 127.0, 128.5, 128.9, 131.4, 136.8, 138.0, 139.6, 140.2, 153.6, 160.3, 168.6, and 169.4; MS m/z 413 (M^+). *Anal.* Calcd for $C_{27}H_{27}NO_3$: C, 78.42; H, 6.58; N, 3.39. Found: C, 78.27; H, 6.64; N, 3.50. **1c**: mp > 300 °C ($CHCl_3$ - EtOH); UV-VIS λmax 274 (ε 12400) and 522 nm (12100); ^{1}H NMR δ = 2.21 (12H, s, 4×Me), 2.34 (6H, s), 2.80 (6H, s), 6.72 (2H, s), and 6.96 (4H, s); ^{13}C NMR δ = 19.9, 21.2, 26.3, 102.0, 127.5, 128.3, 129.3, 137.0, 139.2, 151.7, and 170.4 High resolution MS Calcd for $C_{28}H_{30}N_2O_2$: M, 426.2307. Found: 426.2300. **8c** was identical with that described below.

Isomerization of 2b into 4b. A mixture of **2b** (532 mg) and 1,3-propanediol (15 mL) was heated under reflux for 1.5 h. The solution was cooled, and diluted with MeOH. The solid was collected and washed with MeOH to give **4b** (345 mg, 65%): mp 201 - 203 °C ($CHCl_3$ - hexane); UV-VIS λmax 292 (ε 18400) and 409 nm (24000); ^{1}H NMR δ = 2.54 (6H, s, 2×Me), 7.02 (2H, s), 7.26 - 7.58 (8H, m); ^{13}C NMR δ = 21.0, 101.7, 126.4, 127.4, 129.2, 130.7, 131.5, 131.6, 136.9, 160.1, and 160.4. *Anal.* Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.54; H, 4.75.

Preparation of 8b. A mixture of **4b** (75 mg, 0.22 mmol), 40% methanolic $MeNH_2$ (0.4 mL, 4 mmol), and CH_2Cl_2 (10 mL) was stirred at rt for 1d, and concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed the presence of **10b** and **11b** in a ratio of 1.0 : 1.6. **10b**: ^{1}H NMR δ = 2.37 (3H, s), 2.45 (3H, s), 2.83 (3H, s), 3.29 (2H, AB-q, J=19.5 Hz), 7.03 (1H, s), 7.22 - 7.72 (8H, m). **11b**: ^{1}H NMR δ = 2.50 (3H, s), 2.51 (3H, s), 2.94 (3H, d, J=4.8 Hz), 4.22 (2H, s), 6.53 (1H, s), 7.22 - 8.06 (8H, m). To a mixture of the residue and CH_2Cl_2 (3 mL) was added $POCl_3$ (1.5 mL, 16 mmol). The mixture was stirred at rt for 1d, and worked up as described above to give **8b** as an oil (55 mg, 71%): ^{1}H NMR δ = 2.19 (3H, s), 2.54 (3H, s), 3.33 (3H, s), 6.80 (1H, s), 7.19 (1H, s), and 7.21 - 7.59 (8H, m); ^{13}C NMR δ = 19.4, 21.0, 33.8, 102.3, 103.9, 125.2, 126.2, 126.5, 128.9, 129.2, 129.9, 130.1, 130.4, 130.6, 131.3,132.3, 134.5, 136.2, 136.7, 147.7, 157.9, 160.8, and 161.5. High resolution MS Calcd for $C_{23}H_{19}NO_3$: M, 357.1365. Found: 357.1364.

Preparation of 3b. A mixture of **8**b (55 mg, 0.15 mmol), 40% methanolic $MeNH_2$ (0.3 mL, 3 mmol), and CH_2Cl_2 (5 mL) was stirred at rt for 3 d, and concentrated under reduced pressure. To a mixture of the residue and CH_2Cl_2 (2 mL) was added $POCl_3$ (1 mL, 11 mmol). The mixture was stirred at rt for 1 d, and

worked up as described above to give **3b** (34 mg, 60%): mp >300 °C ($CHCl_3$ - hexane); UV-VIS λmax 294 (ε 12400), 306 (11700), 371 (19100), and 390 nm (16300); ^{1}H NMR δ = 2.19 (3H, s), 2.20 (3H, s), 3.31 (6H, s), 6.97 (2H, s), and 7.21 - 7.43 (8H, m); ^{13}C NMR δ = 19.5, 33.5, 104.0, 126.3, 128.9, 129.2*, 129.3*, 129.6, 130.5, 135.3, 136.5, 145.2, and 161.9; MS m/z 370 (M^+). *Anal.* Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.90; H, 6.08; N, 7.60. * These signals might be assigned to the C-6 in the 2-methylphenyl groups of the atrop isomers.

Preparation of 11c. A mixture of **4c**[6] (60 mg, 0.15 mmol), 40% methanolic $MeNH_2$ (0.1 mL, 1 mmol) and CH_2Cl_2 (2 mL) was allowed to stand at rt for 2 h, and concentrated under reduced pressure. Crystallization of the residue from $CHCl_3$ - hexane gave **11c** (59 mg, 91%): ^{1}H NMR δ = 2.27 (6H, s), 2.31 (3H, s), 2.32 (9H, s), 2.94 (3H, d, J=4.8 Hz), 4.10 (2H, s), 6.28 (1H, s), 6.82 (1H, br s), 6.89 (2H, s) and 6.92 (2H, s); ^{13}C NMR δ = 19.2, 20.1, 21.1, 21.2, 26.4, 43.7, 105.8, 116.2, 128.6, 128.8, 129.1, 133.1, 137.0, 138.5, 139.2, 140.0, 149.3, 161.2, 163.5, 166.5, and 208.4; MS m/z 431 (M^+). *Anal.* Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77; N, 3.25. Found: C, 74.97; H, 6.82; N, 3.21. The compound (**11c**) did not melted above 300 °C. After keeping above 300 °C for 10 min in a mp apparatus, the sample was examined by ^{1}H NMR, and the spectrum was in agreement with that of **4c** almost completely.

Preparation of 8c. Aminolysis of **4c** (120 mg, 0.3 mmol) as mentioned above gave **11c** almost quantitatively, which was used without further purification. A mixture of **11c** (129 mg), $POCl_3$ (0.5 mL, 5 mmol) and CH_2Cl_2 (5 mL) was stirred at rt for 3d, and worked up as described above. Separation of the products with column chromatography ($CHCl_3$:hexane 2:1) and with TLC ($CHCl_3$:hexane 2:1) gave **8c** (23 mg, 19%), along with **4c** (72 mg, 60%). **8c**: mp 239 - 242 °C ($CHCl_3$ - MeOH); UV-VIS λmax 283 (ε 15800), 383 (18000), and 400 nm (sh, 14400); ^{1}H NMR δ = 2.11 (6H, s), 2.29 (6H, s), 2.33 (3H, s), 2.36 (3H, s), 3.30 (3H, s), 6.78 (1H, s), 6.95 (2H, s), 6.99 (1H, s), and 7.00 (2H, s); ^{13}C NMR δ = 19.8, 20.1, 21.1, 21.2, 32.9, 103.7, 103.8, 125.5, 128.5, 128.7, 129.7, 130.0, 131.3, 136.1, 137.3, 139.5, 139.7, 147.1, 156.8, 161.1, and 162.2. High resolution MS Calcd for $C_{27}H_{27}NO_3$: M, 413.1990. Found: 413.1960.

Preparation of 12. A mixture of **2a** (147 mg, 0.47 mmol), 2-aminoethanol (0.2 mL, 3.3 mmol), and CH_2Cl_2 (10 mL) was allowed to stand at rt for 2 d, and then diluted with AcOEt. The mixture was shaken with 5% HCl for 10 min, washed (water and saturated aq. NaCl), dried (Na_2SO_4), and concentrated under reduced pressure. To the solution of the residue in CCl_4 (15 mL) and CH_2Cl_2 (15 mL) was added Ph_3P (508 mg, 1.96 mmol). The mixture was stirred at rt overnight, and concentrated under reduced pressure. The residue was separated with column chromatography ($CHCl_3$) to give **12** (84 mg, 41%): mp 206 - 207 °C ($CHCl_3$ - hexane); UV-VIS λmax 299 (ε 20900) and 548 nm (17500); ^{1}H NMR δ = 3.56 (4H, t, J=6.7 Hz, 2×CH_2), 4.02 (4H, t, J=6.7 Hz), 6.92 (2H, s), and 7.47 - 7.50 (10H, m); ^{13}C NMR δ = 41.0, 42.5, 103.8, 127.8, 128.8, 129.1, 130.2, 130.7, 152.3, and 171.3. High resolution MS Calcd for $C_{24}H_{20}N_2O_2Cl_2$: M, 438.0902. Found: 438.0896.

Preparation of 13 and 14 As described above, **4a** (191 mg, 0.60 mmol) was reacted with 2-aminoethanol (0.3 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was shaken with 5% HCl, and then treated with Ph_3P (777 mg, 3.0 mmol) and CCl_4 (15 mL) in CH_2Cl_2 (15 mL). Separation of the products

with column chromatography ($CHCl_3$) and crystallization from $CHCl_3$ - hexane gave **13** (56 mg, 25%) and **14** (25 mg, 9%), along with **12** (30 mg, 11%). **13**: mp 236 - 239 °C; UV-VIS λmax 309 (ε 14700), 404 (24600), and 425 nm (20300); ^{1}H NMR δ = 3.74 (2H, t, J=6.6 Hz)), 4.35 (2H, t, J=6.6 Hz), 6.84 (1H, s), 7.37 - 7.52 (9H, m), and 7.91 - 7.94 (2H, m); ^{13}C NMR δ = 39.9, 47.7, 98.0, 105.2, 125.4, 128.9, 129.0, 129.1, 129.9, 130.6, 131.1, 131.5, 134.6, 147.9, 156.4, 160.5, and 161.0 High resolution MS Calcd for $C_{22}H_{16}NO_3Cl$: M, 377.0819. Found: 377.0826. **14**: mp 241 - 243 °C; UV-VIS λmax 305 (ε 11900), 378 (19700), and 395 nm (17200); ^{1}H NMR δ = 3.71 (4H, t, J=6.7 Hz, 2×CH_2), 4.32 (4H, t, J=6.7 Hz), 6.96 (2H, s), and 7.38 - 7.51 (10H, m); ^{13}C NMR δ = 40.1, 47.4, 105.1, 128.8, 129.2, 129.5, 135.1, 146.0, and 161.5. High resolution MS Calcd for $C_{24}H_{20}N_2O_2Cl_2$: M, 438.0902. Found: 438.0916.

Preparation of 5. A mixture of **12** (33 mg, 0.075 mmol), $AlCl_3$ (194 mg, 1.46 mmol), and chlorobenzene (5 mL) was heated under reflux for 1.5 h. To the reaction mixture was added water, and then $CHCl_3$. The mixture was washed (5% HCl, water, and saturated aq. NaCl), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was separated with column chromatography ($CHCl_3$) and with TLC ($CHCl_3$) to give **5** (10 mg, 36%): mp 296 - 300 °C ($CHCl_3$ - hexane); UV-VIS λmax 314 (ε 25800), 587 (26600), and 632 nm (22000); ^{1}H NMR δ = 3.06 (4H, t, J=6.3 Hz, 2×CH_2), 3.85 (4H, t, J=6.3 Hz), 7.24 - 7.37 (6H, m), 7.27 (2H, s), and 7.81 (2H, m); ^{13}C NMR δ = 28.7, 36.4, 97.7, 125.8, 126.5, 127.4, 128.7, 129.9, 130.3, 135.0, 145.1, and 169.4. High resolution MS Calcd for $C_{24}H_{18}N_2O_2$: M, 366.1368. Found: 366.1359.

Preparation of 6. A mixture of **14** (22 mg, 0.05 mmol), $AlCl_3$ (160 mg, 1.2 mmol), and chlorobenzene (5 mL) was heated under reflux for 1.5 h, and worked up as described above to give **6** (10 mg, 56%): mp >300 °C ($CHCl_3$ - MeOH); UV-VIS λmax 334 (ε 9400), 349 (9100), 391 (17200), 412 (32100), and 438 nm (36800); ^{1}H NMR δ = 3.05 (4H, t, J=6.3 Hz, 2×CH_2), 4.40 (4H, t, J=6.3 Hz), 7.28 - 7.40 (6H, m), 7.61 (2H, s), and 7.93 (2H, m); ^{13}C NMR δ = 28.2, 40.2, 100.2, 125.6, 127.8, 128.0, 129.0, 129.8, 129.9, 134.9, 139.2, and 161.0. High resolution MS Calcd for $C_{24}H_{18}N_2O_2$: M, 366.1368. Found: 366.1371.

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