

STERICALLY CROWDED HETEROCYCLES. IV. DIASTEREoisOMERIC PRODUCTS BY FERRICYANIDE OXIDATION OF QUATERNARY PYRIDINIUM SALTS

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While ferricyanide oxidation of achiral 4-(4-dimethylaminophenyl)-2,6-diphenyl-1-(pyridin-2-yl)pyridinium perchlorate (**2**) gave racemic 3-(4-dimethylaminophenyl)-1-phenyl-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-one (**7**), the same oxidative procedure applied to racemic 1-[5-(1-methylpyrrolidin-2-yl)pyridin-2-yl]-2,4,6-triphenylpyridinium perchlorate (**5**) or its dimethylamino derivative **6** led to mixtures of diastereoisomeric 3-[6-(1-methylpyrrolidin-2-yl)-2-phenylimidazo[1,2-*a*]pyridin-3-yl]-1,3-diphenyl-2-en-1-ones (**8**) or their dimethylamino derivatives **9**, respectively.

Key words: Ferricyanide oxidation; Sterically crowded heterocycles; Atropisomerism.

It has been found that chirality of variously substituted (2-arylimidazo[1,2-*a*]heteroaren-3-yl)-1,3-diarylprop-2-en-1-ones is caused by restricted rotations of single bonds in the sterically crowded molecules¹. This stereochemical phenomenon, known in carbocyclic chemistry for a considerable long time², has recently been recognized also in various heterocyclic molecules³. Introduction of one additional chirality element into the sterically crowded molecules can present one of possible experimental methods enabling to prove the chirality type in racemic compounds, for example, by transformation of a prochiral side-chain carbonyl C-atom to asymmetric carbon centre³. Another possibility is to start from a compound possessing one asymmetric centre while corresponding sterically crowded molecular fragment is formed during a reaction.

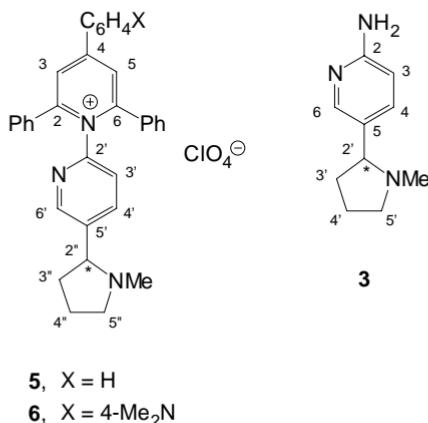
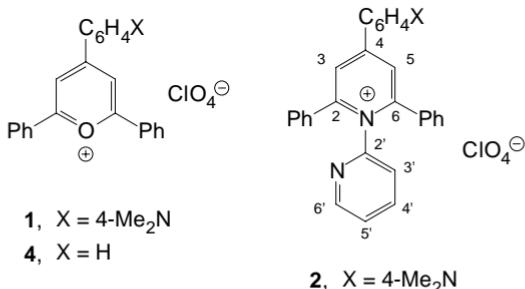
Recent studies on ferricyanide oxidation of quaternary 2,4,6-triarylpyridinium salts possessing a pyridin-2-yl-like *N*-substituents have shown^{1,4} that chiral sterically crowded imidazo[1,2-*a*]pyridines are easily accessible in this way. Structural variations in the starting substrates made possible to obtain different alkyl and aryl substituted products⁴. To make resolution of the racemic compounds easier, introduction of hetero-substituents enhancing basicity of the chiral heterocycles should be considered. On the

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other hand, another chiral substituent in the starting pyridinium salts might offer a direct axial chirality proof in the arising imidazo[1,2-*a*]pyridinoic skeletons by establishment of the above mentioned diastereoisomerism.

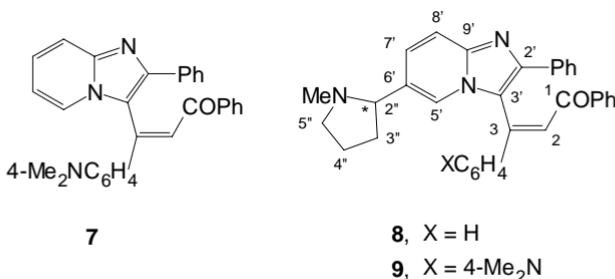
A combination of the two structural variations has been preparatively investigated and the results are reported in this communication. In connection with this aim, the first example of the extended Decker oxidation⁵ of racemic quaternary pyridinium salts to diastereoisomeric imidazo[1,2-*a*]pyridines is reported here.

The achiral basic functionality is represented by the dimethylamino group at the *para*-position of one of the phenyl substituents. It was introduced into cations of the starting salts via 4-(4-dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate (**1**) which was almost quantitatively converted to corresponding 1-(pyridin-2-yl)pyridinium salt (**2**) by heating with 2-aminopyridine in dimethylformamide. The (*R,S*)-1-methylpyrrolidin-2-yl moiety is considered as the chiral basic functionality. To introduce it to the starting salts, the reaction of easily accessible⁶ (*R,S*)-2-amino-5-(1-methylpyrrolidin-2-yl)pyridine (**3**) with 2,4,6-triphenylpyrylium perchlorate (**4**) in boiling ethanol was applied. Expected (*R,S*)-1-[5-(1-methylpyrrolidin-2-yl)pyridin-2-yl]-2,4,6-triphenylpyridinium perchlorate (**5**) was obtained in 76% yield. Combination of the both func-



tionalities was finally realized by the conversion of racemic 2-amino derivative **3** with dimethylamino substituted pyrylium salt **1** to yield 74% of quaternary perchlorate **6**.

Oxidative retro-heterocyclization of achiral perchlorate **2** by heating with aqueous potassium ferricyanide–potassium hydroxide reagent gave racemic 3-(4-dimethylamino-phenyl)-1-phenyl-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-one (**7**) in 76% yield. On the other hand, the same procedure applied to racemic perchlorates **5** and **6** let to comparable yields of diastereoisomeric mixtures of 3-[6-(1-methylpyrrolidin-2-yl)-2-phenylimidazo[1,2-*a*]pyridin-3-yl-1,3-diphenylprop-2-en-1-ones **8** and **9**, respectively.



The assigned formulae of investigated compounds **2**, **3**, **5–9** are supported by the mutual comparison of their ¹H NMR and ¹³C NMR spectra. Thus, almost the same subspectral patterns of the 1-methylpyrrolidin-2-yl group in the regions of δ 1.3 to 3.2 have been observed in the proton spectra of compounds **3**, **5**, **6**, **8** and **9**. The wavenumber of C=C–C=O stretching vibration mode in the IR spectra of ketone **8** (1 653 cm⁻¹) indicates the (Z)-configuration^{4,7} of the fragment. On the other hand, the π -electron releasing 4-dimethylamino group evidently enhances π -conjugation between the 3-aryl group and the π -electron withdrawing C=C–C=O moiety. This charge transfer effect causes a shift in the IR spectra of compounds **7** and **9** to lower wavenumbers (1 607 cm⁻¹). Hence, the (Z)-configuration of ketones **7** and **9** may be only expected to be the same as in the above mentioned case **8** in agreement with similarities of other spectral patterns.

Diastereoisomerism of ketones **8** and **9** was proved by two independent measurements, namely by interpretation of ¹H NMR and ¹³C NMR spectra. In addition to a number of overlapping or not assigned signals, typical temperature independent counterpart signals of individual diastereoisomers can be observed in the NMR spectra. Thus, the diastereoisomeric mixture of ketones **8** exhibits the following couples: proton *N*-methyl signals (δ 2.00 and 2.02), carbon signals of the C=O group (δ 191.37 and 191.76) and carbon signals at the positions 2'', 3'' and 4'' (68.88, 68.98; 34.99, 35.04; 23.04, 23.08). Similarly, the NMR spectra of diastereoisomeric mixture of ketones **9** show couples of proton *meta*-position signals of the Me₂NC₆H₄ group (δ 6.60 and 6.62), proton dimethylamino signals (δ 2.97 and 2.98), proton methylamino signals (δ 2.02 and 2.07), carbon carbonyl signals (δ 191.35 and 191.73), carbon *meta*-position signals

of the 3-aryl group (δ 112.69 and 112.76) and carbon signals of the position 3" (δ 34.84 and 35.01). In general, the spectral patterns resemble those found in other similar sterically crowded imidazo-[1,2-*a*]pyridinoic ketones^{4,7}.

The mentioned NMR data can be explained only by occurrence of couples of diastereoisomers represented by the same molecular topology (formula **8** or **9**). The oxidation of perchlorates **5** and **6** exhibit no diastereoselectivity according to equal integral intensities of the proton counterpart signals. In contrast to similar diastereoisomeric alcoholes³, our attempts to preparatively separate a couple of racemic diastereoisomers **8** or **9** have been unsuccessful. This is probably associated with their very similar molecular shapes as follows from appropriate computer models.

Similar examples of diastereoisomeric molecules possessing a simultaneous combination of axial and central elements of chirality are comparatively rare³. Preparative separation of corresponding diastereoisomers has been successful only in some cases³.

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block, the NMR spectra (δ , ppm; J , Hz; CDCl_3) were taken on a Gemini 300 HC instrument. The working frequency was 300 MHz for ^1H and 75 MHz for ^{13}C nuclei. The IR spectra ($\tilde{\nu}$, cm^{-1} , CHCl_3) were measured on a FTIR spectrometer NICOLET 704.

(*R,S*)-2-Amino-5-(1-methylpyrrolidin-2-yl)pyridine (**3**)

The reaction of (*S*)-nicotine with sodium amide was carried out according to ref.⁶. The obtained sirupy product was left to stand for several days affording colourless crystals of racemic compound **3**, m.p. 62–64 °C. Reference⁸ gives m.p. 66 °C. ^1H NMR spectrum: 1.51–1.73 m, 2 H (H-3' and H-4'); 1.74–1.89 m, 1 H (H-4'); 1.91–2.05 m, 4 H (H-3'); 2.01 s, 3 H (H_3C); 2.11 ddd, 1 H, J = 8.9, 8.9 and 8.9 (H-5'); 2.78 dd, 2 H, J = 8.2 and 8.2 (H-2'); 3.08 ddd, 1 H, J = 8.5, 8.5 and 1.8 (H-5'); 4.73 brs, 2 H (H_2N); 8.36 d, 1 H, J = 8.5 (H-3); 7.33 dd, 1 H, J = 8.5 and 2.2 (H-4); 7.83 d, 1 H, J = 2.2 (H-6); in satisfactory agreement with reported⁹ spectral data. ^{13}C NMR spectrum: 22.68 CH_2 (C-4'), 34.92 CH_2 (C-3'), 40.59 CH_3 (MeN), 57.25 CH_2 (C-5'), 68.96 CH (C-2'), 109.29 CH (C-3), 128.12 C (C-5), 137.30 CH (C-4), 147.75 CH (C-6), 158. 63 C (C-2).

4-(4-Dimethylaminophenyl)-2,6-diphenyl-1-(pyridin-2-yl)pyridinium Perchlorate (**2**)

A mixture obtained after 1 h refluxing of 4-(4-dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate (**1**) (ref.¹⁰; 2 g, 4.4 mmol) and 2-aminopyridine (0.6 g, 6.3 mmol) in 10 ml DMF was poured into cold water (100 ml). The precipitate was sucked off and crystallized from ethanol. Yield 2.1 g (90%) of orange crystals of perchlorate **2**, m.p. 231–233 °C. For $\text{C}_{30}\text{H}_{26}\text{ClN}_3\text{O}_4$ (528.0) calculated: 68.24% C, 4.96% H, 7.96% N; found: 67.98% C, 5.20% H, 7.87% N. ^1H NMR spectrum: 3.12 s, 6 H (Me_2N); 6.77 d, 2 H, J = 9.1 (*m*-Ph4); 7.09 dd, 1 H, J = 7.7 and 4.9 (H-5'); 7.23–7.34 m, 6 H (*m,p*-Ph2 and *m,p*-Ph6); 7.45 dd, 4 H, J = 7.9 and \approx 1.8 (*o*-Ph2 and *o*-Ph6); 7.53 ddd, 1 H, J = 7.8, 7.8 and 1.8 (H-4'); 7.66 d, 1 H, J = 7.9 (H-3'); 7.84 d, 2 H, J = 9.1 (*o*-Ph4); 7.93 s, 2 H (H-3 and H-5); 8.20 dd, 1 H, J = 6.3 and \approx 1.5 (H-6'). ^{13}C NMR spectrum: 40.76 CH_3 (Me_2N), 113.11 CH (*m*-Ph4), 120.34 C (*p*-Ph4), 122.91 CH (C-3 and C-5), 125.62 CH and 126.03 CH (C-3', C-5'), 129.05 CH (*m*-Ph2 and *m*-Ph6), 130.40 CH (*o*-Ph2 and *o*-Ph6), 130.64 CH (*o*-Ph4), 130.88 CH (*p*-Ph2 and *p*-Ph6),

133.70 C (*i*-Ph2 and *i*-Ph6), 139.60 CH (C-4'), 148.87 CH (C-6'), 152.24 C (C-2'), 154.30 C (*i*-Ph4), 155.45 C (C-2 and C-6), 157.06 C (C-4).

(*R,S*)-1-[5-(1-Methylpyrrolidin-2-yl)pyridin-2-yl]-2,4,6-triphenylpyridinium Perchlorate (**5**)

A mixture of 2,4,6-triphenylpyrrolidinium perchlorate (**4**) (ref.¹¹; 2 g, 4.9 mmol) and amino derivative **3** (1 g, 5.6 mmol) and ethanol (45 ml) was refluxed for 5 h. After cooling the reaction mixture was evaporated in *vacuo*, the residue was treated with ether and the precipitate was separated by suction, washed with ether and dried in *vacuo* to give slightly pink crystals of perchlorate **5** (2.1 g, 76%), m.p. 125–128 °C. For $C_{33}H_{30}ClN_3O_4$ (568.1) calculated: 69.77% C, 5.32% H, 7.40% N; found: 69.48% C, 5.49% H, 7.19% N. 1H NMR spectrum: 1.36–1.52 m, 1 H (H-4''); 1.68–1.96 m overlapping 1.91 s, 5 H (Me, H-3'' and H-4''); 2.02–2.18 m, 1 H (H-3''); 2.19–2.33 m, 1 H (H-5''); 2.95 dd, 1 H, J = 8.2 and 8.2 (H-2''); 3.13 ddd, 1 H, J = 8.5, 8.5 and \approx 1.8 (H-5''); 7.20–7.36 m, 6 H (*m,p*-Ph2 and *m,p*-Ph6); 7.43–7.62 m, 9 H (H-3', H-4' and *m,p*-Ph4); 7.47 d, 4 H, J = 7.6 (*o*-Ph2 and *o*-Ph6); 7.87 dd, 2 H, J = 7.9 and \approx 1.6 (*o*-Ph4); 8.07 s, 2 H (H-3 and H-5); 8.16 d, 1 H, J = \approx 1.8 (H-6). ^{13}C NMR spectrum: 23.24 CH_2 (C-4''), 35.80 CH_2 (C-3''), 40.45 CH_3 , 57.34 CH_2 (C-5''), 68.44 CH (C-2''), 125.18 CH (C-3''), 126.78 CH (C-3 and C-5), 128.95 CH (*m*-Ph2 and *m*-Ph6), 129.13 CH (*o*-Ph4), 130.34 CH (*m*-Ph4), 130.47 CH (*o*-Ph2 and *o*-Ph6), 130.88 CH (*p*-Ph2 and *p*-Ph6), 132.77 CH (*p*-Ph4), 133.13 C (*i*-Ph2 and *i*-Ph6), 135.29 C (*i*-Ph4), 138.63 CH (C-4''), 142.25 C (C-5''), 148.23 CH (C-6''), 150.94 C (C-2''), 156.78 C (C-2 and C-6), 158.87 C (C-4).

(*R,S*)-4-(4-Dimethylaminophenyl)-1-[5-(1-methylpyrrolidin-2-yl)pyridin-2-yl]-2,6-diphenylpyridinium Perchlorate (**6**)

Perchlorate **1** (ref.¹¹; 0.45 g, 1.0 mmol) and 6-amino derivative **3** (0.2 g, 1.1 mmol) in 4 ml DMF was refluxed for 30 min and then the mixture was poured into cold water (100 ml). The precipitate was sucked off, dried in *vacuo* and recrystallized from a methanol–ether mixture. Yield 0.45 g (74%) of pyridinium salt **6**, orange crystals, m.p. 155–157 °C. For $C_{35}H_{35}ClN_4O_4$ (611.1) calculated: 68.79% C, 5.77% H, 9.17% N; found: 68.61% C, 5.90% H, 9.01% N. 1H NMR spectrum: 1.37–1.53 m, 1 H (H-4''); 1.68–1.95 m overlapping 1.91 s, 5 H (Me, H-3'' and H-4''); 2.05–2.16 m, 1 H (H-3''); 2.17–2.29 m, 1 H (H-5''); 2.92 dd, 1 H, J = 8.5 and 8.5 (H-2''); 3.04–3.20 m, 7 H (H-5''); 3.11 s, 6 H (Me_2N); 6.77 d, 2 H, J = 9.0 (*m*-Ph4); 7.21–7.33 m, 6 H (*m,p*-Ph2 and *m,p*-Ph6); 7.43 d, 4 H, J = 7.7 (*o*-Ph2 and *o*-Ph6); 7.47 dd, 1 H, J = 8.2 and \approx 1.7 (H-4''); 7.54 d, 1 H, J = 8.2 (H-3''); 7.84 d, 2 H, J = 9.0 (*o*-Ph4); 7.94 s, 2 H (H-3 and H-5); 8.13 d, 1 H, J = \approx 1.7 (H-6'). ^{13}C NMR spectrum: 23.28 CH_2 (C-4''), 35.81 CH_2 (C-3''), 40.52 CH_3 (Me_2N), 40.75 CH_3 (Me_2N), 57.42 CH_2 (C-5''), 68.56 CH (C-2''), 113.10 CH (*m*-Ph4), 120.37 C (*p*-Ph4), 122.86 CH (C-3 and C-5), 125.53 CH (C-3''), 128.94 CH (*m*-Ph2 and *m*-Ph6), 130.42 CH (*o*-Ph2 and *o*-Ph6), 130.56 CH (*o*-Ph4), 130.85 CH (*p*-Ph2 and *p*-Ph6), 133.78 C (*i*-Ph2 and *i*-Ph6), 138.68 CH (C-4''), 141.81 C (C-5''), 148.20 CH (C-6''), 151.04 C (C-2''), 154.28 C (*i*-Ph4), 155.51 C (C-2 and C-6), 157.01 C (C-4).

Racemic 3-(4-Dimethylaminophenyl)-1-phenyl-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-one (**7**)

A solution of potassium ferricyanide (2 g, 6.1 mmol) and potassium hydroxide (0.5 g, 8.9 mmol) in water (10 ml) was added under stirring to a boiling mixture of pyridinium salt **2** (1 g, 1.9 mmol) in ethanol (50 ml). After 10 min, the reaction mixture was poured into ice–water (150 ml) and extracted with chloroform (4 \times 50 ml). Collected organic extracts were washed with water (100 ml), dried over sodium sulfate and evaporated in *vacuo*. The residue was chromatographed on a column (60 g silica-gel, chloroform–ethyl acetate (7 : 1)). Fractions containing ketone **7** were collected, evaporated and

the yellow solid was dried in *vacuo*. Yield 0.65 g (77%), m.p. 90–95 °C. For $C_{30}H_{25}N_3O$ (443.6) calculated: 81.24% C, 5.68% H, 9.47% N; found: 81.00% C, 5.94% H, 9.23% N. 1H NMR spectrum: 2.98 s, 6 H (Me_2N); 6.62 d, 2 H, J = 9.0; 6.70 dd, 1 H, J = 6.9 and 6.9; 7.10–7.27 m, 6 H; 7.32 dd, 1 H, J = 7.6 and 7.6; 7.37 d, 2 H, J = 8.9; 7.43 s, 1 H; 7.58 d, 2 H, J = 6.7; 7.60 d, 1 H, J = 8.2; 7.66 d, 1 H, J = 7.1; 7.73 d, 2 H, J = 7.1. ^{13}C NMR spectrum: 40.65 CH_3 (Me_2N), 112.74 CH, 112.81 CH, 117.95 CH, 118.82 CH, 123.52 CH, 124.89 C, 125.23 CH, 125.30 CH, 128.07 CH, 128.14 CH, 128.46 CH, 128.59 CH, 128.75 CH, 129.69 CH, 132.37 CH, 134.38 C, 139.53 C, 143.09 C, 145.82 C, 146.07 C, 152.56 C, 191.59 C (C-1). IR spectrum: 1 607 (C=C–C=O).

Diastereoisomeric Mixture of 3-[6-(1-Methylpyrrolidin-2-yl)-2-phenylimidazo[1,2-*a*]pyridin-3-yl]-1,3-diphenylprop-2-en-1-ones (8)

A solution of potassium ferricyanide (1.5 g, 11 mmol) and potassium hydroxide (0.8 g, 14 mmol) in water (30 ml) was added to a solution of perchlorate **5** (1.5 g, 2.6 mmol) in dioxane (40 ml). The reaction mixture was stirred for 2 h at ambient temperature, diluted with water (250 ml) and extracted with chloroform (7×60 ml). The collected organic portions were washed with water (100 ml), dried with sodium sulfate and evaporated to dryness. The residue was treated with chloroform, filtered (charcoal and alumina), evaporated and the residue was dried in *vacuo*. Yellowish solid mixture of diastereoisomers **8** (1.0 g, 78%) was obtained, m.p. 58–67 °C. For $C_{33}H_{29}N_3O$ (483.6) calculated: 81.96% C, 6.04% H, 8.69% N; found: 81.74% C, 6.23% H, 6.50% N. 1H NMR spectrum: 1.60–1.94 m, 4 H (H-3" and H-4"); 2.00 s, 1.5 H (Me); 2.02 s, 1.5 H (Me); 2.03–2.26 m and 2.85–2.94 m, 1 H (H-2"); 3.07–3.16 m, 2 H (H-5"); 7.05–7.72 m, overlapping 7.42 s (H-2 and remaining protons). ^{13}C NMR spectrum: 23.04 CH_2 (C-4"), 23.00 CH_2 (C-4"), 34.99 CH_2 (C-3"), 35.04 CH_2 (C-3"), 40.63 CH_3 (C-N1"), 57.31 CH_2 (C-5"), 68.88 CH (C-2"), 68.98 CH (C-2"), 117.81 CH, 118.22 C, 118.37 C, 123.09 CH, 123.15 CH, 126.20 CH, 127.84 CH, 128.17 CH, 128.25 CH, 128.34 CH, 128.38 CH, 128.49 CH, 128.53 CH, 128.58 C, 128.67 CH, 129.61 CH, 129.67 CH, 130.83 CH, 132.84 CH, 134.23 C, 134.27 C, 138.42 C, 138.54 C, 138.66 C, 142.29 C, 142.56 C, 146.19 C, 146.23 C, 146.93 C, 147.04 C, 191.37 C (C-1'), 191.76 C (C-1'). IR spectrum: 1 653 (C=C–C=O).

Diastereoisomeric Mixture of 3-(4-Dimethylaminophenyl)-3-[6-(1-methylpyrrolidin-2-yl)-2-phenylimidazo[1,2-*a*]pyridin-3-yl]-1-phenylprop-2-en-1-ones (9)

A solution of potassium ferricyanide (0.4 g, 1.2 mmol) and potassium hydroxide (0.1 g, 1.8 mmol) in water (4 ml) was added to a solution of perchlorate **6** in methanol (6 ml). The reaction mixture was stirred at 20 °C for 2 h, poured into water (100 ml) and extracted with chloroform (3×50 ml). Collected organic extracts were washed with water (50 ml), dried over sodium sulfate and evaporated at diminished pressure. The residue was dissolved in dichloromethane, filtered (alumina–charcoal layers), evaporated and chromatographed on a column (50 g silica gel, dichloromethane–acetone 5 : 1). Orange coloured fractions were collected, evaporated and dried in *vacuo*. Yield 0.1 g (58%) of aminoketones **9**, orange pulver, m.p. 52–63 °C. For $C_{35}H_{34}N_4O$ (526.7) calculated: 79.82% C, 6.51% H, 10.64% N; found 79.53% C, 6.69% H, 10.38% N. 1H NMR spectrum: 1.63–1.98 m, 3 H (H-3" and H-4"), 2.02 s, 1.5 H (NMe); 2.07 s, 1.5 H (NMe); 2.08–2.33 m, 3 H (H-3" and H-5"); 2.79–2.96 m, 1 H (H-2"); 2.97 s, 3 (NMe₂); 2.98 s, 3 H (NMe₂); 3.07–3.21 m, 2 H (H-5"); 6.60 d, 2 H, J = 8.9 (m-Ph3); 6.62 d, 2 H, J = 8.9 (m-Ph3); 7.06–7.80 m overlapping 7.46 s (H-2 and remaining protons). ^{13}C NMR spectrum: 23.13 CH_2 (C-4"), 34.84 CH_2 (C-3"), 35.01 CH_2 (C-3"), 40.72 CH_3 (C-N1"), 57.40 CH_2 (C-5"), 69.18 CH (C-2"), 112.69 CH (m-Ar3), 112.76 (m-Ar3), 117.85 CH, 117.88 CH, 118.86 C, 119.02 C, 122.77 CH, 123.29 CH, 123.42 CH, 125.17 C, 125.27 C, 125.74 CH, 125.80 CH, 127.99 CH, 128.05, 128.15 CH, 128.46 CH, 128.51 CH, 128.64 CH, 128.71 CH, 129.83 CH,

129.89 CH, 132.37 CH, 134.56 C, 134.63 C, 139.62 C, 139.75 C, 143.12 C, 143.41 C, 145.94 C, 146.05 C, 146.17 C, 152.58 C, 191.25 (C-1), 191.73 (C-1). IR spectrum: 1 607 (C=C-C=O).

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