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Oxidative Coupling of Substituted 1,2,3,4,4a,5-Hexahydro-13*H*-benzimidazo[2,1-*j*]quinolines with Methylene-Active Derivatives of Carboxylic Acids

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Abstract—The oxidative coupling of substituted 1,2,3,4,4a,5-hexahydro-13*H*-benzimidazo[2,1-*j*]quinolines with methylene-active derivatives of carboxylic acids led to the formation of *p*-methylenequinone imines of the mentioned series; in some events the reaction was accompanied with a hydrolytic cleavage of the exocyclic fragment.

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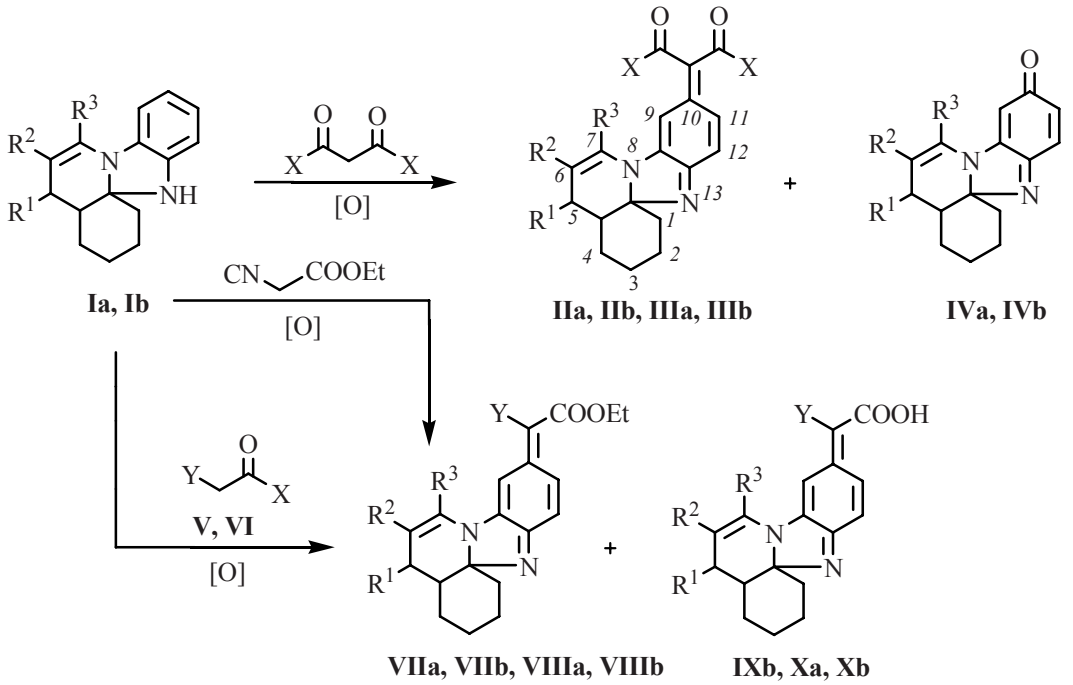
Heterocyclic *p*-methylenequinone imines belong to one among the least investigated types of quinoid compounds presumably because they are difficultly available due to the lack of general and convenient preparation methods. Methylenequinone imines are known based on phen(oxa, thia)-azines obtained either by oxidative condensation with CH-acids where the first stage consists in the formation of *ortho*-quinoid cations of phen(oxa, thia)-azinium [1], or as a result of molecular rearrangements of products of the nucleophilic substitution in the aromatic ring of phenoxazinones [2] or ion-radical betaines based on phenazine [3]. Also methylenequinone imines were obtained by oxidation of the products of nucleophilic addition of C-nucleophiles to the *ortho*-quinoid ring of 2*H*-benzimidazoles [4] and by oxidative condensation of 1-naphthylmalononitrile with aromatic amines [5]. All the mentioned preparation procedures provided the target compounds in poor yields.

We formerly reported [6] on a simple and convenient procedure for the synthesis of heterocyclic methylenequinone imines by an oxidative coupling of substituted pyrido[1,2-*a*]-benzimidazoles with CH-acid nucleophiles; the main attention was drawn to the 1,3-dicarbonyl reagents. In this study we carried out a purposeful investigation of an oxidative coupling of substituted 1,2,3,4,4a,5-hexahydro-13*H*-benzimidazo[2,1-*j*]-quinolines **Ia** and **Ib** with certain methylene-active functional derivatives of carboxylic acids aiming at preparation of water-soluble methylenequinone imines arising further by hydrolytic transformations. We selected as reagents diethyl malonate and malonodiamide, ethyl nitroacetate, and cyanoacetic acid hydrazide; at the use of the latter compound a problem of the regioselectivity existed for the reagent possessed both C- and N-nucleophilic sites.

We established that the main result of the oxidative coupling of compounds **Ia** and **Ib** with diethyl malonate, malonodiamide, and ethyl nitroacetate (**V**) in the presence of MnO_2 was the formation in good yield of *p*-methylenequinone imines, derivatives of 1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinoline (compounds **IIa, IIb, IIIa, IIIb, VIIa**, and **VIIb**); in reaction with the latter compound formed also in a minor amount the product of its hydrolytic cleavage (compound **IXb**). Compounds **VIIa, VIIb**, and **IXb** are first examples of methylenequinone imine having as an exocyclic fragment derivatives of nitroacetic acid. In the reaction of compounds **Ia** and **Ib** with malonodiamide alongside the main products we observed the formation in substantial amounts of products of a competing oxidation reaction, quinone monoimines **IVa** and **IVb**, which had been described before [7]. The formation of the latter products was caused presumably by the low solubility of the reagents preventing the presence of its excess in the reaction mixture. In neither



R^1 = H, R^2,R^3 = $(CH_2)_4$ (a); R^1 = R^3 = Ph, R^2 = H (b); X = OEt (**II, V**), NH_2 (**III**), $NHNH_2$ (**VI**); Y = NO_2 (**V, VII, IX**), CN (**VI**, **VIII, X**).

of the other reactions the quinone monoimines formation was observed.

The oxidative coupling of substrates **Ia** and **Ib** with cyanoacetic acid hydrazide (**VI**) in ethanol occurred exclusively at the CH-acid site of the reagent: mixtures were obtained that after chromatographic separation afforded *p*-methylenequinone imines lacking the hydrazine fragment and consisting of comparable quantities of alcoholysis (compounds **VIIIa** and **VIIIb**) and hydrolysis (compounds **Xa** and **Xb**) products. These results are in agreement with the data of review [8] on the oxidative transformations of phenylhydrazides into the corresponding carboxylic acids in the presence of MnO_2; no methylenequinones with a hydrazide groups in an exocyclic fragment have been described indirectly confirming that their preparation in oxidative conditions is impossible. Methylenequinone imines **VIIIa** and **VIIIb** were also prepared by an independent synthesis: by the coupling of substrates **Ia** and **Ib** with ethyl cyanoacetate in the presence of MnO_2 (the reaction products were identified by TLC, melting points, and IR spectra).

All compounds obtained are colored and relatively stable (compounds **VIIa** and **VIIb** are an exception for they are labile under the conditions of the preparative chromatography). Compounds **IXb, Xa**, and **Xb** are well soluble in a water-alkaline medium.

IR spectra of all compounds obtained contain the absorption bands of vibrations of C=C and C=N bonds in the quinoid structure, and also of the functional groups of the exocyclic fragment; ^{1}H NMR spectra contain the signals of protons H^9, H^{11}, H^{12} proving the *para*-quinoid structure of the products. In the spectra of compounds **IIa, IIb, VIIa, VIIb, VIIIa**, and **VIIIb** ethoxy group signals are present, and in the spectra of compounds **IXb, Xa**, and **Xb**, those of the OH from the carboxy group. In the spectrum of compound **IIIb** four one-proton broadened singlets were observed disappearing at the addition of deuteromethanol and belonging to non-equivalent protons of the primary amino groups, whereas in the spectrum of compound **IIIa** the proton signals of both amino groups coalesce into one four-proton broadened singlet. This difference in the spectra of related methylenequinone imines may be caused by the higher inversion barrier with respect the exocyclic C^{10}=C^2 bond due to the intramolecular charge transfer in the system N^8–C^{8a}=C^9–C^{10}=C^2 of compound **IIIb** as compared to compound **IIIa**. The double sets of signals in different integral ratios of the protons of the quinoid system, ethoxy fragments and some other protons observed in the ^{1}H NMR spectra of compounds **VIIIa, VIIIb, Xa**, and **Xb** we attribute to the presumable *p*-diastereoisomerism with

respect to the double C^{10}=C^{2} bond with the prevalence of the *Z*-isomer [the ratio *Z/E* 3:1 (**VIIIa**), 3:2 (**VIIIb**), 4:1 (**Xa**), 3:2 (**Xb**)]; a similar effect has been observed formerly in the obtained methylenequinone imines [6]. In the spectrum of the oxidative coupling product with ethyl nitroacetate **VIIb** on the contrary prevailed the *E*-isomer (the ratio *Z/E* 1:2), and compounds **VIIa** and **IXb** were completely in the thermodynamically more stable *E*-form; the signals assignment was carried out by the comparison with the spectral data for the *Z/E*-isomers of the previously obtained product of the oxidative coupling with nitromethane [6]. In the ^{1}H NMR spectrum of compound **IIb** four quartets were observed from the methylene groups of the ethoxy fragment in the ratio 1:1, whereas the methyl groups gave rise to only two triplets; this was apparently due to the existence of sufficiently stable conformers with respect to the CH_2–OCO bond. In the spectra of compounds **IIa, VIIa, VIIIa**, and **Xa** from the multiplet of aliphatic protons a one-proton multiplet separated located downfield and belonging to the allyl equatorial proton $H^{1'}$ of the fused cyclohexene ring that suffered deshielding spatial influence of the electron-acceptor substituents in the exocyclic fragment (as suggested by models). The mass values of pseudo-molecular ions in the mass spectra of all compounds synthesized obtained by the chemical ionization were in agreement with the calculated figures.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers Specord 75IR and Spectrum BX-II from solutions in CH_2Cl_2 and pellets with KBr. ^{1}H NMR spectra were registered on a spectrometer Bruker AC-250 at operating frequency 250 MHz, internal reference TMS, solvent $CDCl_3$. Elemental analysis was carried out on a CHN-analyzer Flash EA 1112 CHN/MAS200.

The analysis by the method HPLC-MS was performed on an instrument HP 1100 LC/MSD, column Hypersil ODS (4×125 mm), mobile phase 2-propanol–water, 60 : 40, flow rate 0.3 ml/min, temperature 55°C; (a) diode matrix, (b) direct admission into the ion source. The conditions of recording mass spectrum: source APCI, positive polarity (negative for compound **IXb**), voltage on the fragmentor 70V.

The melting points of compounds btained were measured in a capillary and on a Boëtius heating block. The reaction course was monitored and the homogeneity of compounds obtained was checked by TLC on Silufol UV-254 and Sorbfil plates, eluents petroleum ether–ethyl acetate, ethyl acetate–acetone. The products mixtures were separated and the products were purified by preparative TLC on 25 × 30 cm plates with aluminum oxide of the II Brockmann grade or with silica gel, the layer thickness 1.5 mm, single charge 0.25 g.

All compounds were synthesized by the general procedure, only the separation and purification differed. Commercially available reagents (Aldrich, Fluka) were used without additional purification.

General procedure. To a solution of 1.0 mmol of compounds **Ia** or **Ib** and 2.0 mmol of a reagent (1.1 mmol of reagent **VI**) in 30–40 ml of acetone (DMF for compounds **IIIa** and **IIIb**, ethanol for **VIIIa, VIIIb**, **Xa**, and **Xb**) was added at stirring 10–12 mmol of MnO_2, the reaction mixture was stirred for 1 h at room temperature (compounds **IIa**, **IIIa**, and **IIIb**), 2 h (compounds **IIb, VIIa, VIIb**, and **IXb**), 5 h (compounds **VIIIb** and **Xb**), 8 h (compounds **VIIIa** and **Xa**) till complete consumption of the initial compound (TLC monitoring), MnO_2 was filtered off and washed with the solvent used in the reaction. The filtrates of all compounds obtained were diluted with water to 2–3 fold volume, saturated with NaCl (compounds **IIIa** and **IIIb**) or Na_2CO_3 (compounds **IIa** and **IIb**) till a precipitate formed. The latter was subjected to preparative TLC on aluminum oxide using as eluent petroleum ether–ethyl acetate, 5:1, for compounds **IIa, IIb, VIIb**, **IXb**, 3:1, for compound **IIIa**, 2:1, for compounds **VIIIa, VIIIb, Xa, Xb**; or on silica gel using as eluent petroleum ether–ethyl acetate, 3:1, for compound **VIIa**, ethyl acetate–acetone, 5:1, for compound **IIIb**.

Diethyl (6,7-tetramethylene-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)-malonate (IIa). Yield 78%, mp. 96–98°C. IR spectrum, ν, cm^{-1}: 1698, 1675 (C=O), 1636 (C^6=C^7), 1615, 1580, 1498 (C=N, C=C_{quin}). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3, *J* 7.2 Hz), 1.33 t (3H, CH_3, *J* 7.2 Hz), 1.45–2.40 m (18H), 2.73 m (1H, $H^{1}_{eqiov.}$), 4.23 q (2H, OCH_2, *J* 7.2 Hz), 4.26 q (2H, OCH_2, *J* 7.2 Hz), 6.78 d (1H, H^9, *J* 2.0 Hz), 6.90 d (1H, H^{12}, *J* 10.0 Hz), 7.55 d.d (1H, H^{11}, *J* 10.0, 2.0 Hz). Found, %: C 71.32; H 7.06; N 6.68. $[M + H]^+$ 437. $C_{26}H_{32}N_2O_4$. Calculated, %: C 71.53; H 7.39; N 6.42. *M* 436.54.

Diethyl (5,7-diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)-malonate (IIb). Yield 85%, mp. 124–126°C. IR spectrum, ν, cm^{-1}: 1709, 1684 (C=O), 1642 (C^6=C^7), 1619, 1582, 1504 (C=N, C=C_{quin}). ^{1}H NMR spectrum, δ, ppm:

1.15 t (3H, CH_3, *J* 7.2 Hz), 1.25 t (3H, CH_3, *J* 7.2 Hz), 1.45–2.25 m (9H), 3.83 d.d (1H, H*5*, *J* 10.0, 3.2 Hz), 3.87 q (2H, OCH_2, *J* 7.1 Hz), 3.94 q (2H, OCH_2, *J* 7.1 Hz), 4.19 q (2H, OCH_2, *J* 7.1 Hz), 4.21 q (2H, OCH_2, *J* 7.1 Hz), 5.06 d (1H, H*9*, *J* 1.7 Hz), 5.42 d (1H, H*6*, *J* 3.2 Hz), 6.92 d (1H, H*12*, *J* 10.0 Hz), 7.15–7.53 m (8H, ArH), 7.90 m (1H, ArH), 7.92 m (1H, ArH), 8.03 d.d (1H, H*11*, *J* 10.0, 1.7 Hz). Found, %: C 76.69; H 6.22; N 5.38. $[M + H]^+$ 535. $C_{34}H_{34}N_2O_4$. Calculated, %: C 76.38; H 6.41; N 5.24. *M* 534.65.

2-(6,7-Tetramethylene-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)-malonamide (IIIa). Yield 74%, mp. 202–204°C. IR spectrum, ν, cm^{-1}: 3481, 3401, 3358 (NH_2), 1653 (C=O), 1637 (C^6=C^7), 1600, 1538 (C=N, C=C_{quin}). ^1H NMR spectrum, δ, ppm: 1.40–2.50 m (19H), 6.38 d (1H, H*9*, *J* 1.7 Hz), 6.83 d (1H, H*12*, *J* 10.0 Hz), 7.45 br.s (4H, NH_2), 7.54 d.d (1H, H*11*, *J* 10.0, 1.7 Hz). Found, %: C 70.10; H 7.14; N 14.73. $[M + H]^+$ 379. $C_{22}H_{26}N_4O_2$. Calculated, %: C 69.82; H 6.92; N 14.80. *M* 378.47.

2-(5,7-Diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)malonamide (IIIb). Yield 62%, mp. 242–244°C. IR spectrum, ν, cm^{-1}: 3497, 3413, 3366 (NH_2), 1656 (C=O), 1642 (C^6=C^7), 1598, 1570, 1501 (C=N, C=C_{quin}). ^1H NMR spectrum, δ, ppm: 1.50–2.20 m (9H), 3.83 d.d (1H, H*5*, *J* 10.1, 3.0 Hz), 5.20 br.s (1H, NH), 5.22 d (1H, H*9*, *J* 1.5 Hz), 5.42 d (1H, H*6*, *J* 3.0 Hz), 5.51 br.s (1H, NH), 5.68 br.s (1H, NH), 6.82 br.s (1H, NH), 6.91 d (1H, H*12*, *J* 10.1 Hz), 7.20–7.45 m (10H, C_6H_5), 7.93 d.d (1H, H*11*, *J* 10.1, 1.5 Hz). Found, %: C 75.44; H 6.09; N 11.56. $[M + H]^+$ 477. $C_{30}H_{28}N_4O_2$. Calculated, %: C 75.61; H 5.92; N 11.76. *M* 476.57.

Ethyl (2*E*)-(6,7-tetramethylene-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)(nitro)acetate (VIIa). Yield 54%, mp. 129–131°C. IR spectrum, ν, cm^{-1}: 1691 (C=O), 1666 (C^6=C^7), 1627, 1573, 1520 (C=N, C=C_{quin}), 1498, 1352 (NO_2). ^1H NMR spectrum, δ, ppm: 1.34 t (3H, CH_3, *J* 7.2 Hz), 1.55–2.40 m (18H), 2.70 m (1H, H^1_e), 4.29 q (2H, OCH_2, *J* 7.2 Hz), 6.56 br.s (1H, H*9*), 7.12 d (1H, H*12*, *J* 9.5 Hz), 7.75 d (1H, H*11*, *J* 9.5 Hz). Found, %: C 67.69; H 6.73; N 10.18. $[M + H]^+$ 410. $C_{23}H_{27}N_3O_4$. Calculated, %: C 67.46; H 6.65; N 10.26. *M* 409.48.

Ethyl (5,7-diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)(nitro)-acetate (VIIb). Yield 75%, mp. 194–196°C. IR spectrum, ν, cm^{-1}: 1700 (C=O), 1645 (C^6=C^7), 1624, 1580, 1518 (C=N, C=C_{quin}), 1508, 1363 (NO_2). ^1H NMR spectrum, δ, ppm (*Z*/*E* 1:2): 1.15 t (3H, CH_3, *J* 7.2 Hz, *Z*-isomer), 1.28 t (3H, CH_3, *J* 7.2 Hz, *E*-isomer), 1.45–2.30 m (9H), 3.87 d.d (1H, H*5*, *J* 10.5, 3.0 Hz), 4.05 q (2H, OCH_2, *J* 7.2 Hz, *Z*-isomer), 4.28 q (2H, OCH_2, *J* 7.2 Hz, *E*-isomer), 4.98 d (1H, H*9*, *J* 1.8 Hz, *E*-isomer), 5.52 d (1H, H*6*, *J* 3.0 Hz), 5.65 d (1H, H*9*, *J* 1.5 Hz, *Z*-isomer), 7.04 d (1H, H*12*, *J* 10.0 Hz), 7.20–7.50 m (10H, C_6H_5), 8.00 d. d (1H, H*11*, *J* 10.0, 1.8 Hz, *E*-isomer). Found, %: C 73.39; H 5.88; N 8.11. $[M + H]^+$ 508. $C_{31}H_{29}N_3O_4$. Calculated, %: C 73.35; H 5.76; N 8.28. *M* 507.58.

Ethyl 2-(6,7-tetramethylene-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)-(cyano)acetate (VIIIa). Yield 43%, mp. 168–170°C. IR spectrum, ν, cm^{-1}: 2197 (CN), 1684 (C=O), 1654 (C^6=C^7), 1621, 1564, 1482 (C=N, C=C_{quin}). ^1H NMR spectrum, δ, ppm (*Z*/*E* 3:1): 1.35 t (3H, CH_3, *J* 7.2 Hz), 1.55–2.40 m (18H), 2.80 m (1H, H^1_{equiv}), 4.26 q (2H, OCH_2, *J* 7.2 Hz), 6.42 d (1H, H*9*, *J* 1.7 Hz, *E*-isomer), 7.01 d (1H, H*12*, *J* 10.0 Hz, *E*-isomer), 7.07 d (1H, H*12*, *J* 10.0 Hz, *Z*-isomer), 7.58 d.d (1H, H*11*, *J* 10.0, 1.7 Hz, *Z*-isomer), 7.73 d (1H, H*9*, *J* 1.7 Hz, *Z*-isomer), 8.77 d.d (1H, H*11*, *J* 10.0, 1.7 Hz, *E*-isomer). Found, %: C 74.22; H 7.17; N 10.75. $[M + H]^+$ 390. $C_{24}H_{27}N_3O_2$. Calculated, %: C 74.01; H 6.99; N 10.79. *M* 389.49.

Ethyl 2-(5,7-diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)(cyano)-acetate (VIIIb). Yield 41%, mp. 177–179°C. IR spectrum, ν, cm^{-1}: 2195 (CN), 1699 (C=O), 1643 (C^6=C^7), 1619, 1569, 1498 (C=N, C=$C_{quin.}$). ^1H NMR spectrum, δ, ppm (*Z*/*E* 3:2): 1.25 t (3H, CH_3, *J* 7.1 Hz), 1.50–2.40 m (9H), 3.47 q (2H, OCH_2, *J* 7.1 Hz), 3.89 m (1H, H*5*), 5.56 d (1H, H*6*, *J* 3.0 Hz, *E*-isomer), 5.58 d (1H, H*6*, *J* 3.0 Hz, *Z*-isomer), 6.84 d (1H, H*9*, *J* 1.6 Hz, *E*-isomer), 6.91 d (1H, H*9*, *J* 1.6 Hz, *Z*-isomer), 7.16 d (1H, H*12*, *J* 10.0 Hz, *Z*-isomer), 7.19–7.55 m (10H, C_6H_5), 7.57 d.d (1H, H*11*, *J* 10.0, 1.6 Hz, *Z*-isomer), 8.85 d.d (1H, H*11*, *J* 10.0, 1.6 Hz, *E*-isomer). Found, %: C 79.08; H 6.28; N 8.53. $[M + H]^+$ 488. $C_{32}H_{29}N_3O_2$. Calculated, %: C 78.82; H 5.99; N 8.62. *M* 487.59.

(2*E*)-(5,7-Diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)(nitro)-acetic acid (IXb). Yield 9%, mp. 232–234°C. IR spectrum, ν, cm^{-1}: 3298, 1723 (COOH), 1644 (C^6=C^7), 1621, 1592, 1516 (C=N, C=C_{quin}), 1502, 1327 (NO_2). ^1H NMR spectrum, δ, ppm: 1.15–2.20 m (9H), 3.78 d.d (1H, H*5*, *J* 10.5, 3.0 Hz), 5.32 d (1H, H*6*, *J* 3.0 Hz), 6.05 d (1H, H*9*, *J* 1.8 Hz), 6.34 d (1H, H*12*, *J* 10.0 Hz), 7.20–7.50 m (10H, C_6H_5), 7.58 d.d (1H, H*11*, *J* 10.0, 1.8 Hz), 8.51 s (1H,

COOH). Found, %: C 72.89; H 5.36; N 8.51. $[M - H]^-$ 478. $C_{29}H_{25}N_3O_4$. Calculated, %: C 72.64; H 5.25; N 8.76. *M* 479.53.

2-(6,7-Tetramethylene-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)-(cyano)acetic acid (Xa). Yield 54%, mp. >300°C (decomp.). IR spectrum, ν, cm^{-1}: 3452, 1724 (COOH), 2184 (CN), 1653 (C^6=C^7), 1618, 1583, 1561 (C=N, C=C_{quin}). ^{1}H NMR spectrum, δ, ppm (*Z*/*E* 4:1): 1.20–2.45 m (18H), 2.92 m (1H, H^1_{equiv}), 6.29 d (1H, H^9, *J* 1.5 Hz, *E*-isomer), 7.14 d (1H, H^{12}, *J* 10.0 Hz, *Z*-isomer), 7.15 d (1H, H^{12}, *J* 10.0 Hz, *E*-isomer), 7.44 d.d (1H, H^{11}, *J* 10.0, 1.5 Hz, *Z*-isomer), 7.65 br.s (1H, COOH, *Z*-isomer), 7.98 d (1H, H^9, *J* 1.5 Hz, *Z*-isomer), 8.79 br.s (1H, COOH, *E*-isomer), 8.98 d.d (1H, H^{11}, *J* 10.0, 1.5 Hz, *E*-isomer). Found, %: C 73.28; H 6.53; N 11.52. $[M + H]^+$ 362. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63. *M* 361.44.

2-(5,7-Diphenyl-1,2,3,4,4a,5-hexahydro-10*H*-benzimidazo[2,1-*j*]quinolin-10-ylidene)(cyano)-acetic acid (Xb). Yield 56%, mp. >300°C (decomp.). IR spectrum, ν, cm^{-1}: 3185, 1715 (COOH), 2189 (CN), 1645 (C^6=C^7), 1615, 1579, 1535 (C=N, C=C_{quin}). ^{1}H NMR spectrum, δ, ppm (*Z*/*E* 3:2): 1.45–2.30 m (9H), 3.87 m (1H, H^5), 5.32 d (1H, H^9, *J* 1.7 Hz, *E*-isomer), 5.55 d (1H, H^6, *J* 3.4 Hz, *E*-isomer), 5.57 d (1H, H^6, *J* 3.4 Hz, *Z*-isomer), 6.51 d (1H, H^9, *J* 1.7 Hz, *Z*-isomer), 7.03 d (1H, H^{12}, *J* 10.0 Hz, *E*-isomer), 7.09 d (1H, H^{12}, *J* 10.0 Hz, *Z*-isomer), 7.17–7.52 m (10H, C_6H_5), 7.55 d.d (1H, H^{11}, *J* 10.0, 1.7 Hz, *Z*-isomer), 8.67 d.d (1H, H^{11}, *J* 10.0, 1.7 Hz, *E*-isomer). Found, %: C 78.65; H 5.39; N 9.11. $[M + H]^+$ 460. $C_{30}H_{25}N_3O_2$. Calculated, %: C 78.41; H 5.48; N 9.14. *M* 459.54.

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