1-R-2-[(1*E*,3*E*)-4-Aminobuta-1,3-dien-1-yl]-1*H*-benzimidazoles. Synthesis and some transformations

*A. V. Varlamov,[a] A. I. Komarova,[a] A. N. Levov,[a] E. V. Savitkina,[a] A. P. Krapivko,[a†] V. N. Khrustalev,[b] E. A. Sorokina,[a] L. N. Kulikova,[a] E. V. Nikitina,[a] V. P. Zaytsev,[a] and F. I. Zubkov[a]**

[a]*Peoples' Friendship University of Russia, 6 ul. Miklukho-Maklaya, 117198 Moscow, Russian Federation. Fax: +7 (495) 955 0779. E-mail: fzubkov@sci.pfu.edu.ru*

[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. E-mail: vkh@xray.ineos.ac.ru*

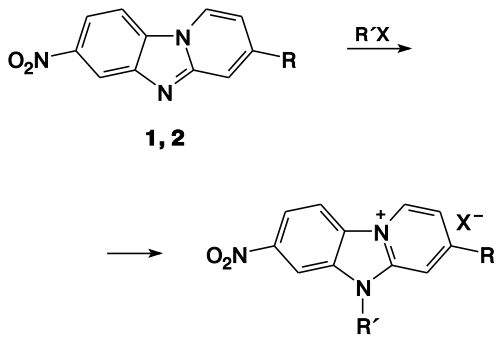
7-Nitropyridobenzimidazolium salts are cleaved with secondary amines to form 2-[(*E*,*E*)-4-aminobuta-1,3-dienyl]-1*H*-benzimidazoles. The latter react with dimethyl acetylenedicarboxylate to yield 4a-[(*E*,*Z*,*E*)-6-amino-4,5-dimethoxycarbonylhexa-1,3,5-trien-1-yl]-1,2,3,4-tetra(methoxycarbonyl)-4a,5-dihydropyrido[1,2-*a*]benzimidazoles.

Key words: 4-aminobuta-1,3-diene, cleavage of pyridobenzimidazolium salts, 1*H*-benzimidazole, pyrido[1,2-*a*]benzimidazole.

Reactions of 2-aryloxazolo[3,2-*a*]pyridinium salts with nucleophilic reagents are studied and described in the literature in detail.[1—3] It was found that these salts upon the action of secondary amines undergo cleavage of the pyridine ring to give (1*E*,3*E*)-1-amino-4-(oxazolyl-2)buta-1,3-dienes. 1-Methyl-2-*p*-nitrophenylimidazo-[3,2-*a*]pyridinium perchlorate undergoes analogous transformation to 1*E*,3*E*-aminobutadienes in the reaction with piperidine in boiling acetonitrile. Its 5-methyl-substituted analog under these conditions undergoes demethylation to imidazo[3,2-*a*]pyridine.[4] Earlier,[5] we have shown that 7-nitropyrido[1,2-*a*]benzimidazoles with substituted and unsubstituted pyridine ring upon the action of dimethyl acetylenedicarboxylate (DMAD) in excess amount recyclize to 1,2,3,4-tetra(methoxycarbonyl)-8-nitropyrido[1,2-*a*]benzimidazoles. There is no literature information on the reactions of imidazopyridinium salts fused by the imidazole ring with an electron-withdrawing aromatic fragment.

In the present work, we have studied reactions of 7-nitropyrido[1,2-*a*]benzimidazolium **1** and 3-methyldiphenylsilyl-7-nitropyrido[1,2-*a*]benzimidazolium salts **2** with secondary amines. Tertiary salts **3—7** were obtained by the reaction of pyridobenzimidazole **1** (see Ref. 6) with methyl iodide, benzyl chloride in the presence of KI, dibromoethane, allyl bromide, and ethyl 4-bromobutyrate in acetonitrile or DMF, whereas salts **8** and **9**, upon the action of methyl iodide or phenacyl bromide on the silyl substituted pyridobenzimidazole **2** (see Ref. 7) in boiling toluene and ethyl acetate (Scheme 1).

Scheme 1



Compound	R	R´	X
1	H	—	—
2	$SiMePh_2$	—	—
3	H	Me	I
4	H	Bn	I
5	H	CH_2CH_2Br	Br
6	H	Allyl	Br
7	H	$(CH_2)_3CO_2Et$	Br
8	$SiMePh_2$	Me	I
9	$SiMePh_2$	CH_2COPh	Br

The IR spectrum of salt **9** with phenacyl substituent on the nitrogen atom, in addition to the band for CO at 1696 cm^{-1}, exhibits a broad band for the bound hydroxyl

† Deceased.

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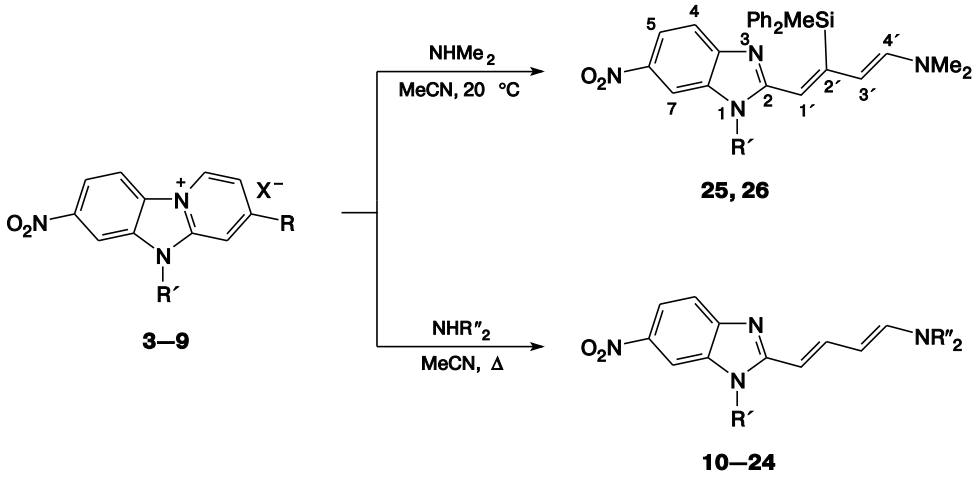
Scheme 2



Compound	R′	R″	Compound	R′	R″	Compound	R′	R″
10	Me	Me	**15**	Me	—$(CH_2)_2$NBn$(CH_2)_2$—	**20**	Allyl	—$(CH_2)_2$NBn$(CH_2)_2$—
11	Me	Et	**16**	Bn	Me	**21**	Allyl	Furfuryl
12	Me	—$(CH_2)_2$O$(CH_2)_2$—	**17**	Allyl	Me	**22**	CH_2CH_2Br	Me
13	Me	Furfuryl	**18**	Allyl	—$(CH_2)_2$O$(CH_2)_2$—	**23**	CH_2CH_2Br	—$(CH_2)_2$O$(CH_2)_2$—
14	Me	—$(CH_2)_5$—	**19**	Allyl	—$(CH_2)_5$—	**24**	$(CH_2)_3CO_2Et$	—$(CH_2)_2$O$(CH_2)_2$—

R′ = Me (**25**), CH_2COPh (**26**)

at 3430 cm^{-1}, which can indicate the presence of an enol form >N—CH_2COPh ⇌ >N—CH=C(OH)Ph. Tertiary salts **3—9** are cleaved with secondary amines, *viz.*, dimethyl-, diethyl-, and difurfurylamines, morpholine, piperidine, and *N*-benzylpiperazine, in boiling acetonitrile to the corresponding 1-R′-2-[(*E*,*E*)-4-aminobuta-1,3-dien-1-yl]-6-nitro-1*H*-benzimidazoles **10—26**, the yields of which were 10—75% (Scheme 2).

Cleavage of 3-methyldiphenylsilyl-7-nitropyrido-[1,2-*a*]benzimidazolium iodide (**8**) with dimethylamine in boiling acetonitrile is accompanied by elimination of the silicon-containing substituent and leads to diene **10** (R′ = R″ = Me). The reaction of dimethylamine with salts **8** and **9** at room temperature allows one to obtain the target 2′-methyldiphenylsilyl-substituted butadienes **25** and **26**. Compounds **10—26** are red crystals of various intensities.

It is interesting that other nucleophiles used in this work (sodium cyanide, azide, and phenylacetylide) do not cleave salts **3—9**.

The *E*,*E*-configuration of the diene fragment in compounds **10—24** is inferred from the spin-spin coupling constant values $J_{H(1'),H(2')}$ = 14.3—14.7, $J_{H(2'),H(3')}$ = 11.3—12.1, and $J_{H(3'),H(4')}$ = 12.5—12.8 Hz in their ^{1}H NMR spectra. These data are in good agreement with those described for 1-amino-4-(oxazol-2-yl)dienes.[8,9] The mass spectra of butadienylamines synthesized exhibit peaks of molecular ions of low intensities corresponding to their molecular formulas. A principal direction for the fragmentation of molecular ions $[M]^{+\bullet}$ of compounds **10—24** consists in the elimination of dialkylamine radical NR''_2. The intensities of ions $[M - NR''_2]^+$ are 80—100%. These ions further eliminate radicals $NO_2^\bullet$ and $R'^\bullet$ forming fragment ions $[M - NR''_2 - NO_2]^+$ and $[M - NR''_2 - R']^+$. The latter cation apparently has the structure of 8-nitropyrido[1,2-*a*]benzimidazole with *m/z* 213 (Table 1).

The spatial structure of compound **17** was studied by X-ray diffraction (Fig. 1).

The X-ray diffraction study confirms unambiguous *E*,*E*-configuration of the diene fragment and reveals virtually planar structure of molecule **17** (except carbon atoms C(9) and C(10) of the allyl substituent on the nitrogen atom N(1)), the deviation of atoms from the mean-square plane of the molecule, excluding carbon atoms

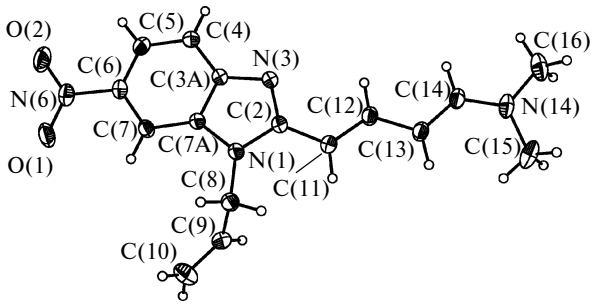


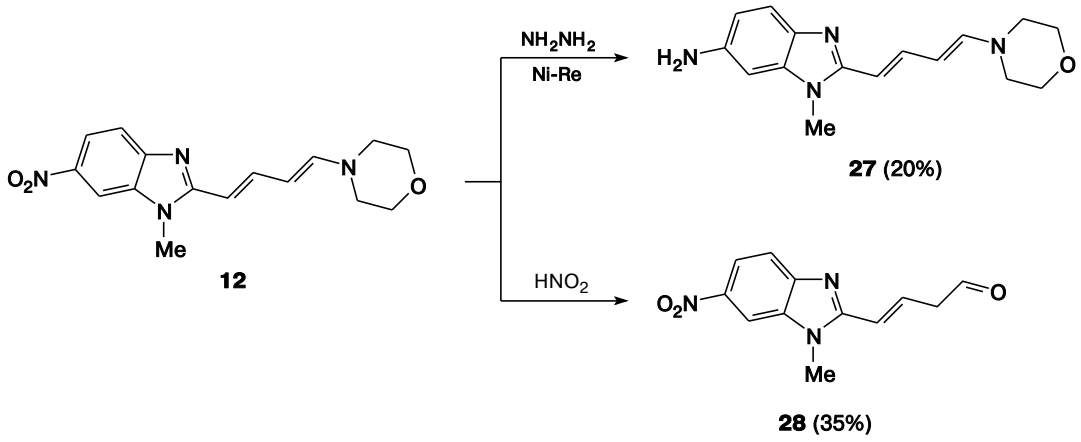
Fig. 1. Molecular structure of compound **17** in representation of atoms by 40% probability ellipsoids of anisotropic displacments.

Table 1. The yields, physico-chemical and spectral characteristics of 7-nitropyrido[1,2-*a*]benzimidazolium salts **3—9** and 1-*R*′-2-[(*E*,*E*)-4-aminobuta-1,3-dien-1-yl]-1*H*-benzimidazoles **10—26**

Compound	Yield (%)	M.p./°C (AcOEt)	Found / Calculated (%)			Molecular formula	MS, *m*/*z* (I_{rel} (%))			
			C	H	N		$[M]^+$	$[M - NR''_2]^+$	$[M - NR''_2 - NO_2]^+$	$[M - NR''_2 - NR'_2]^+$
3	66	232—234	40.00 40.58	2.75 2.84	11.50 11.83	$C_{12}H_{10}IN_3O_2$	—	—	—	—
4	59	218—220	50.05 50.13	3.10 3.27	9.51 9.74	$C_{18}H_{14}IN_3O_2$	—	—	—	—
5	62	224—225	39.10 38.93	2.56 2.76	10.60 10.48	$C_{13}H_{11}Br_2N_3O_2$	—	—	—	—
6	83	234—236	50.00 50.32	3.67 3.62	12.51 12.57	$C_{14}H_{12}BrN_3O_2$	—	—	—	—
7	60	209—211	49.76 50.01	4.37 4.44	10.11 10.29	$C_{17}H_{18}BrN_3O_4$	—	—	—	—
8	75	233—234	54.20 54.45	4.40 4.02	7.55 7.62	$C_{25}H_{22}IN_3O_2Si$	—	—	—	—
9	75	230—231	63.20 63.16	4.40 4.31	7.00 6.90	$C_{32}H_{26}BrN_3O_3Si$	—	—	—	—
10	79	212—214	61.52 61.75	5.63 5.92	20.11 20.58	$C_{14}H_{16}N_4O_2$	272 (10)	228 (99)	182 (67)	213 (25)
11	60	173—175	63.52 63.98	6.33 6.71	18.52 18.65	$C_{16}H_{20}N_4O_2$	300 (90)	228 (100)	182 (70)	213 (2)
12	57	214—216	61.12 61.13	5.33 5.77	17.52 17.82	$C_{16}H_{18}N_4O_3$	314 (5)	228 (100)	182 (52)	213 (15)
13	5	110—112	64.89 65.34	4.35 4.98	13.61 13.85	$C_{22}H_{20}N_4O_4$	404 (1)	228 (40)	182 (5)	213 (48)
14	47	202—204	65.12 65.37	6.35 6.45	17.63 17.94	$C_{17}H_{20}N_4O_2$	312 (4)	228 (100)	182 (51)	—
15	60	212—214	68.45 68.47	6.02 6.25	17.12 17.36	$C_{23}H_{25}N_5O_2$	403 (1)	228 (20)	182 (38)	213 (3)
16	75	197—198	68.45 68.95	5.63 5.75	15.69 16.08	$C_{20}H_{20}N_4O_2$	248 (15)	304 (20)	258 (20)	213 (5)
17	51	129—131	64.35 64.41	6.01 6.08	18.69 18.78	$C_{16}H_{18}N_4O_2$	298 (15)	254 (100)	208 (24)	213 (15)
18	60	179—181	63.35 63.52	5.41 5.92	16.09 16.46	$C_{18}H_{20}N_4O_3$	340 (3)	254 (94)	208 (24)	213 (8)
19	65	132—133	67.34 67.44	6.21 6.55	16.09 16.56	$C_{19}H_{22}N_4O_2$	338 (8)	254 (98)	208 (26)	213 (7)
20	10	107—109	69.24 69.91	6.98 6.34	16.00 16.31	$C_{25}H_{27}N_5O_2$	429 (1)	254 (100)	208 (21)	213 (2)
21	66	140—142	66.03 66.97	5.13 5.15	12.50 13.02	$C_{24}H_{22}N_4O_4$	430 (2)	254 (89)	208 (0)	213 (22)
22	10	183 (decomp.)	48.95 49.45	4.23 4.69	15.12 15.38	$C_{15}H_{17}BrN_4O_2$	364 (4)*	320 (87)	274 (26)	213 (9)
23	55	172—173	50.51 50.25	4.23 4.70	13.12 13.76	$C_{17}H_{19}BrN_4O_3$	406 (5)*	320 (98)	274 (28)	213 (89)
24	57	151—153	60.90 60.86	6.23 6.30	14.20 13.52	$C_{21}H_{26}N_4O_5$	414 (30)	328 (99)	252 (30)	213 (73)
25	59	140 (decomp.)	69.30 69.20	6.00 6.02	12.02 11.96	$C_{27}H_{28}N_4O_2Si$	468	—	—	—
26	53	152 (decomp.)	71.20 71.30	5.69 5.63	9.72 9.78	$C_{34}H_{32}N_4O_3Si$	572	—	—	—

* For ^{79}Br.

Scheme 3



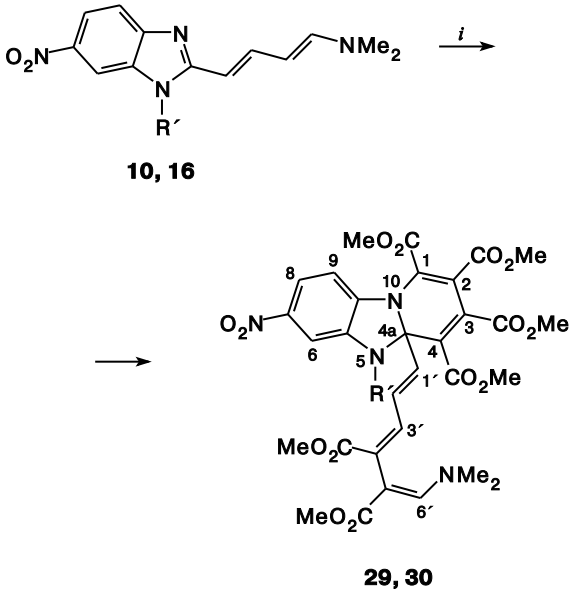
C(9) and C(10), does not exceed 0.06 Å. The planar structure of the molecule is determined by the elongated system of conjugate bonds. The *S-cis*-conformation of the fragment N(3)=C(2)—C(11)=C(12), as well as the torsional angle N(1)—C(8)—C(9)—C(10) (131.5(2)°) value are determined by steric effects of substituents. Based on this, the general structure of compounds **10—26** can be represented as a planar conjugated system with partial redistribution of the charge $A^{(\delta-)}$-π-$D^{(\delta+)}$ (A is an acceptor (NO_2), D is a donor (NMe_2)), which is the one to determine their bright color.

6-Nitrobenzimidazole **12** was reduced to amino derivative **27** with hydrazine in the presence of Raney Ni (Scheme 3).

Morpholino-substituted butadiene **12** upon the action of nitrous acid is transformed to aldehyde **28** in moderate yield. The structure of the latter is in good agreement with the IR and ^{1}H NMR spectroscopic and mass spectrometric data. The mass spectrum of compound **28** exhibits peak of the molecular ion maximum in intensity with *m/z* 245 (100%) corresponding to its molecular formula. The IR spectrum contains a band of stretching vibrations of the carbonyl group at 1680 cm^{-1}. The signal for the aldehyde proton is found at δ 9.80 in the ^{1}H NMR spectrum.

Benzimidazoles **10—26** contain two nucleophilic centers for the reactions with activated alkynes: the pyridine-type nitrogen atom of the imidazole ring and the enamine fragment. We studied reactions of azadienes **10** and **16** with DMAD in excess amount in dichloromethane. It turned out that both nucleophilic fragments are involved into the reaction to form 5-R-1,2,3,4-tetra(methoxycarbonyl)-4a-[(1*E*,3*Z*,5*E*)-4,5-di(methoxycarbonyl)-6-dimethylaminohexa-1,3,5-trien-1-yl]-7-nitro-4a,5-dihydropyrido[1,2-*a*]benzimidazoles **29** and **30** in low yield (Scheme 4). No other individual products were isolated from the reaction mixture.

Scheme 4

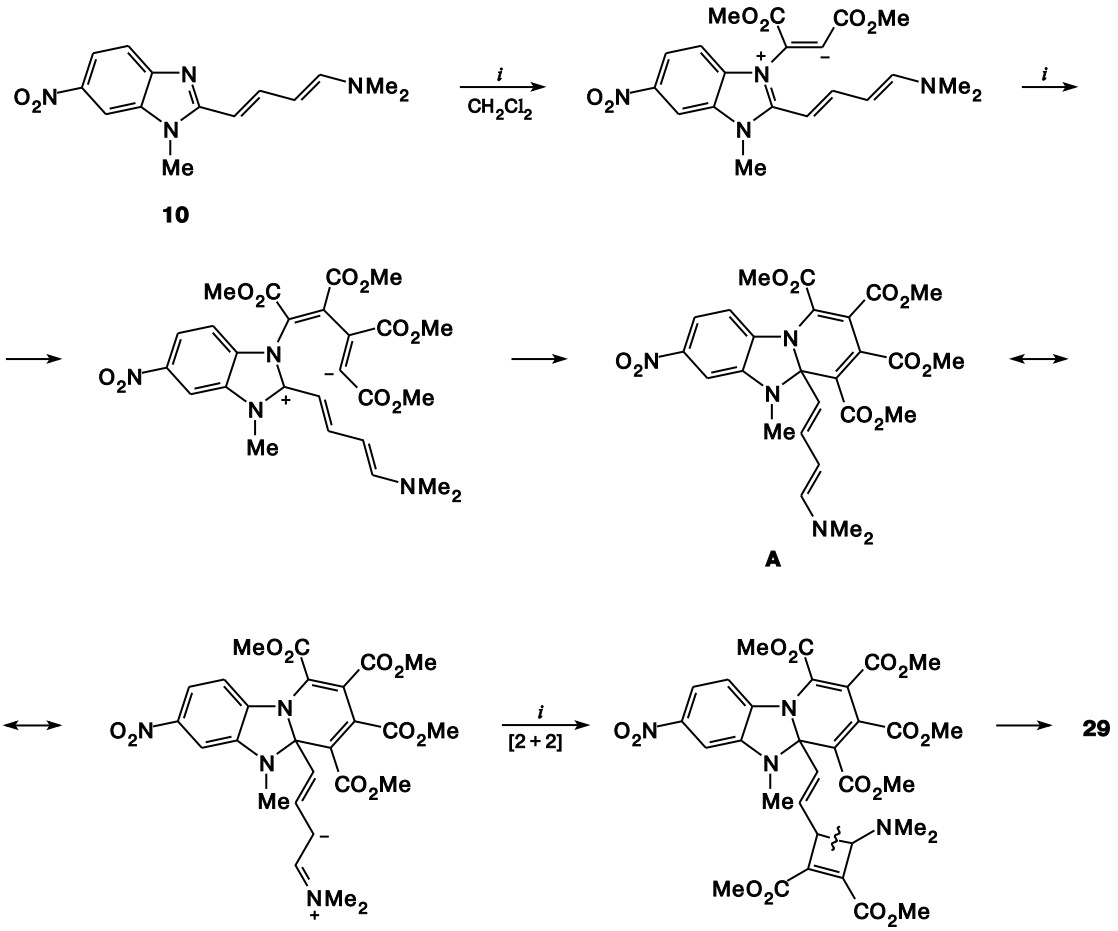


i. DMAD, CH_2Cl_2

R´ = Me (**29**, 17%), Bn (**30**, 18%)

General outline of the process is given in Scheme 5 using the transformation of diene **10** to polycycle **29** as an example. Successive nucleophilic addition of two DMAD molecules to the pyridine nitrogen atom of the imidazole ring and then to dimethyl maleate fragment formed leads to the tetra(methoxycarbonyl)-substituted dihydropyridine ring closure to yield intermediate **A**.[10] The aminodiene fragment is transformed to the aminotriene one, apparently, through the intermediate step of [2+2] cycloaddition. Formation of [2+2] cycloaddition products of alkynes with 1-aminobuta-1,3-dienes is reported in works.[11,12]

Scheme 5



The structure of dihydrobenzimidazoles **29** and **30** could not be determined based only on the NMR data. Their ^{1}H NMR spectra exhibit six signals for the methoxycarbonyl groups in the region δ 3.28—4.07, a singlet signal at δ ~7.49 for the terminal proton of the hexatrienyl fragment, and singlets for the protons of the dimethylamino group at δ 2.87 or δ 2.86, respectively.

The structure of compound **30** (R´ = Bn) was unambiguously determined by X-ray diffraction (Fig. 2).

The molecule **30** consists of three substituted fused rings, *viz.*, benzene, dihydroimidazole, and dihydropyridine, and has an asymmetric carbon atom C(4a). The presence of bulky substituents on the carbon atom C(4a) lead to distortion of the planar structure of the nitrobenzimidazole fragment: the atom C(4a) deviates by 0.27(2) Å from the mean-square plane drawn through the rest atoms of this fragment. The dihydropyridine ring adopts the slightly distorted sofa conformation with deviation of the atom C(4a) from the mean-square plane drawn through the rest atoms of this fragment by 0.58(2) Å.

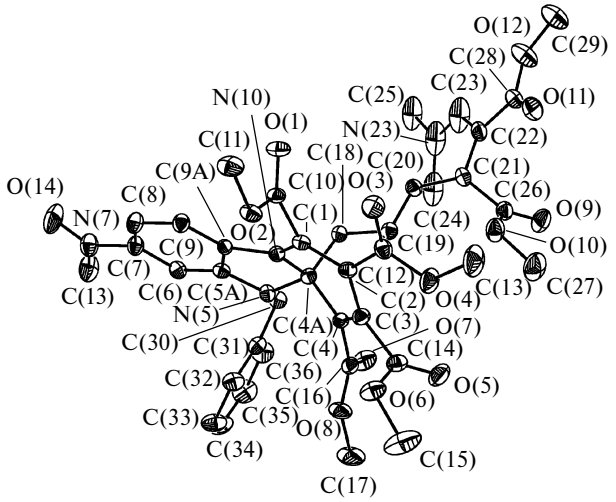


Fig. 2. Molecular structure of compound **30** in representation of atoms by 40% probability ellipsoids anisotropic displacments (H atoms are not shown).

In addition to this, steric effects in the molecule result in the pyramidal configuration of the nitrogen atom N(5) (the sum of bond angles at the atom N(5) is 348.2°), the rest of the nitrogen atoms have planar configuration. Due to the presence of adjacent methoxycarbonyl groups, the triene substituent at position 4a is nonplanar with the *trans*,*gauche*-arrangement of the double bonds (the torsional angle C(20)—C(21)—C(22)—C(23) is −42.8(8)°), the C=C bonds have *E*,*Z*,*E*-configuration, respectively. Due to the steric reasons, only one of four methoxycarbonyl groups on the carbon atom C(2) is placed in the plane of the dihydropyridine ring (the torsional angle C(1)—C(2)—C(12)—O(3) is −0.1(7)°). The rest of the MeO_2C substituents are significantly turned with respect to this plane (the torsional angles C(2)—C(1)—C(10)—O(1), C(2)—C(3)—C(14)—O(5) and C(3)—C(4)—C(16)—O(7) are 109.1(5), −120.3(5) and −129.3(5)°, respectively). The angle between the planes of nitrobenzimidazole and phenyl fragments is 74.9(2)°.

In conclusion, we found that 7-nitropyrido[1,2-*a*]-benzimidazolium salts upon the action of secondary amines undergo cleavage of the pyridine fragment to be transformed to (*E*,*E*)-4-amino-1-(6-nitrobenzimidazol-2-yl)buta-1,3-dienes. The latter by the reaction with excess of DMAD are transformed to hexa-1,3,5-trienyl-substituted pyrido[1,2-*a*]benzimidazoles through the dipolar 1,3- and [2+2] cycloadditions.

Experimental

Reagents from Acros Organics were used as purchased. IR spectra of compounds **9** and **28** were recorded on a Infralum FT-801 Fourier-spectrometer in KBr pellets. ^{1}H NMR spectra (δ, *J*/Hz) were recorded on a Bruker WH-400 spectrometer (400.13 MHz for ^{1}H and 100.6 MHz for ^{13}C) in $CDCl_3$ at 27 °C. Residual signals of the solvent were used as a reference: δ 7.26 (in the ^{1}H NMR spectra) and δ 77.4 (in the ^{13}C NMR spectra). Mass spectra (EI, 70 eV) were recorded on a HP MS 5988 mass spectrometer or Finnigan MAT-95-XL GLC-MS spectrometer with direct injection of the sample in the source of ions. Silufol UV-254 plates were used for thin-layer chromatography (visualization with iodine vapors), neutral activated Al_2O_3 (Brockmann II) or Merck silica gel (230S400 mesh) were used for column chromatography.

Melting points, yields, parameters of mass spectra, and elemental analysis data for all the compounds synthesized are given in Table 1.

X-ray diffraction study. Compound **17**. Dark red crystals ($C_{16}H_{18}N_4O_2$, *M* = 298.34), triclinic, space group $P\bar{1}$, at *T* = 293 K *a* = 8.4565(17) Å, *b* = 9.3177(19) Å, *c* = 11.531(2) Å, α = 68.83(3)°, β = 85.42(3)°, γ = 65.58(3)°, *V* = 769.0(3) Å^3, *Z* = 2, d_{calc} = 1.289 g cm^{-3}, *F*(000) = 316, μ = 0.088 mm^{-1}.

Compound **30**. Orange crystals ($C_{38}H_{38}N_4O_{14}$, M = 774.72), triclinic, space group $P1^-$; at *T* = 293 K *a* = 8.9655(18) Å, *b* = 13.950(3) Å, *c* = 16.451(3) Å, α = 83.41(3)°, β = 79.87(3)°, γ = 84.06(3)°, *V* = 2004.7(7) Å^3, *Z* = 2, d_{calc} = 1.283 g cm^{-3}, *F*(000) = 812, μ = 0.099 mm^{-1}.

Parameters of unit cells and intensities of 3973 (**17**) and 7474 (**30**) reflections were measured on a Siemens P3/PC automatic four-circle diffractometer (Mo-Kα irradiation, a graphite monochromator, θ/2θ-scanning, θ_{max} = 28° (**17**) and 25° (**30**)). Structures were solved by the direct method and refined by the least-squares full-matrix method in anisotropic approximation for nonhydrogen atoms. Hydrogen atoms, whose positions were calculated geometrically, were included into the refinement in isotropic approximation with the fixed positional ("riding" model) and thermal parameters. The final divergence factors R_1 = 0.0543 for 2344 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.1585 for all the 3724 independent reflections (**17**) and R_1 = 0.0827 for 3095 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.1934 for all the 6980 independent reflections (**30**). All the calculations were performed using the *SHELXTL* program package.[13] Tables of atom coordinates, bond distances, bond and torsional angles, and parameters of anisotropic displacements for compounds **17** and **30** were deposited with the Cambridge Structural Database (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

5-R-7-Nitropyrido[2,1-*a*]benzimidazolium halides (3—9) (general procedure). Pyridobenzimidazole **1** (1 g, 4.7 mmol) was refluxed with methyl iodide, benzyl chloride (in the presence of equimolar amount of anhydrous KI), dibromoethane, allyl bromide, ethyl 4-bromobutyrate (10—20 mmol) in acetonitrile (50 mL) or heated in DMF (30 mL) at 100 °C; silyl-substituted pyridobenzimidazole **2** (1 g, 2.44 mmol) was refluxed with equimolar amount of methyl iodide or phenacyl bromide in toluene and ethyl acetate, respectively. The reaction course was monitored by TLC (~6—7 h is required for the reaction to reach completion). Then the reaction mixture was cooled, a precipitate formed was filtered off and recrystallized from ethanol. When DMF was used as the solvent, water (20 mL) was added to the reaction mixture, a precipitate was filtered off, dried in air, and recrystallized from ethyl acetate. Yellow crystals of the following compounds were obtained: 5-methyl- (**3**), 5-benzyl-7-nitropyrido[1,2-*a*]benzimidazolium (**4**) iodides, 5-bromoethyl- (**5**), 5-allyl- (**6**), and 5-(3-ethoxycarbonylpropyl)-7-nitropyrido-[1,2-*a*]benzimidazolium (**7**) bromides, 5-methyl-3-methyldiphenylsilyl-7-nitropyrido[1,2-*a*]benzimidazolium iodide (**8**), 3-methyldiphenylsilyl-5-phenacylpyrido[1,2-*a*]benzimidazolium bromide (**9**). The yields, elemental analysis data, and physicochemical constants for quaternary salts **3—9** are given in Table 1.

1-R-2-[(1*E*,3*E*)-4-Aminobuta-1,3-dien-1-yl]-1*H*-benzimidazoles (10—24) (general procedure). A mixture of salts **3—8** (1.4 mmol) and the corresponding secondary amine (4.2 mmol) was refluxed in acetonitrile (20 mL) for 0.5—24 h (TLC monitoring). The mixture was cooled, acetonitrile was evaporated at reduced pressure. Water (40 mL) was added to the residue and organic products were extracted with chloroform (3×50 mL). The extract was dried with magnesium sulfate. Chloroform was evaporated and the residue was subjected to chromatography either on SiO_2 (eluent: AcOEt—hexane, 1 : 1), or on Al_2O_3 (eluent: AcOEt—hexane, 1 : 3—1 : 1). Aminodienes **22—24** were eluted with ethyl acetate. The dienes were recrystallized from AcOEt—hexane solvent mixture. The following products were obtained: 2-[(1*E*,3*E*)-4-*N*,*N*-dimethylaminobuta-1,3-dien-1-yl]-1-methyl- (**10**), 2-[(1*E*,3*E*)-4-*N*,*N*-diethylaminobuta-1,3-dien-1-yl]-1-methyl- (**11**), 1-methyl-2-[(1*E*,3*E*)-4-morpholino- (**12**), 2-[(1*E*,3*E*)-4-*N*,*N*-difurfurylaminobuta-1,3-dien-

Table 2. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of 1-*R*′-2-[(*E*,*E*)-4-aminobuta-1,3-dien-1-yl]-1*H*-benzimidazoles **10—27**

Compound	δ (*J*/Hz)							
	H(4) (d)	H(5) H(7) (m)	NR′	H(1′) (d)	H(2′) (dd)	H(3′) (dd)	H(4′) (d)	NR''_2
10	7.54 (*J* = 9.2)	8.00—8.19	3.71 (s, 2 Me)	5.98 (*J* = 14.3)	7.71 (*J* = 14.3, *J* = 11.6)	5.27 (*J* = 12.5, *J* = 11.6)	6.71 (*J* = 12.5)	2.90 (s, Me)
11	7.53 (*J* = 9.5)	8.08—8.13	3.72 (s, 2 Me)	5.95 (*J* = 14.4)	7.71 (*J* = 14.4, *J* = 11.4)	5.33 (*J* = 12.6, *J* = 11.4)	6.72 (*J* = 12.6)	1.18 (t, *J* = 7.2); 3.21 (q, *J* = 7.2)
12	7.56 (*J* = 8.5)	8.12—8.16	3.75 (s, 2 Me)	5.98 (*J* = 14.3)	7.72 (*J* = 14.3, *J* = 11.5)	5.47 (*J* = 12.5, *J* = 11.5)	6.60 (*J* = 12.5)	3.18 (CH_2O); 3.65 (CH_2N)
13	7.58 (*J* = 8.5)	8.10—8.15	3.73 (s, 2 Me)	5.97 (*J* = 14.4)	7.71 (*J* = 14.4, *J* = 11.6)	5.47 (*J* = 12.6, *J* = 11.6)	6.65 (*J* = 12.6)	4.35 (s, NCH_2); 6.22 (d, *J* = 2.7); 6.38 (dd, *J* = 2.7, *J* = 1.7); 7.35 (d, *J* = 1.7)
14	7.56 (*J* = 9.5)	8.10—8.15	3.73 (s, 2 Me)	5.96 (*J* = 14.4)	7.74 (*J* = 14.4, *J* = 11.6)	5.42 (*J* = 12.8, *J* = 11.6)	6.68 (*J* = 12.8)	1.63 (s, 6 H); 3.19 (m, 4 H)
15	7.56 (*J* = 9.4)	8.10—8.16	3.73 (s, 2 Me)	6.01 (*J* = 14.2)	7.69 (*J* = 14.2, *J* = 11.6)	5.40 (*J* = 12.8, *J* = 11.6)	6.62 (*J* = 12.8)	3.54 (s, CH_2Ph); 3.22, 2.49 (both t, *J* = 4.7); 7.28—7.32 (m, Ph)
16	7.59 (*J* = 8.9)	8.09—8.15	4.72 (br.s, $C\underline{H}_2Ph$); 7.10—7.30 (m, Ph)	5.97 (*J* = 14.3)	7.76 (*J* = 14.3, *J* = 11.3)	5.23 (*J* = 12.5, *J* = 11.3)	6.72 (*J* = 12.5)	2.89 (s, Me)
17	7.57 (*J* = 8.5)	8.09—8.20	4.74 (m, CH_2); 5.03 (m, $C\underline{H}_2$=CH); 5.93 (m, $C\underline{H}_2$=CH); 5.94 (m, CH_2=C<u>H</u>)	5.93 (*J* = 14.3)	7.74 (*J* = 14.3, *J* = 11.3)	5.25 (*J* = 12.5, *J* = 11.3)	6.71 (*J* = 12.5)	2.90 (s, Me)
18	7.58 (*J* = 8.8)	8.10—8.15	4.72 (m, CH_2); 4.99 (d, $C\underline{H}_2$=CH, *J* = 17.1); 5.24 (d, $C\underline{H}_2$=CH, *J* = 10.3); 5.94 (m, CH_2=C<u>H</u>)	5.98 (*J* = 14.6)	7.89 (*J* = 14.6, *J* = 11.2)	5.42 (*J* = 12.9, *J* = 11.2)	6.59 (*J* = 12.9)	3.18 (t, $(CH_2)_2O$, *J* = 4.9); 3.65 (t, $(CH_2)_2N$, *J* = 4.9)
19	7.55 (*J* = 8.8)	8.00—8.10	4.75 (m, CH_2); 4.99 (d, $\underline{CH}_2$=CH, *J* = 17.0); 5.20 (d, $\underline{CH}_2$=CH, *J* = 10.5); 5.90 (m, CH_2=<u>CH</u>)	5.85 (*J* = 14.6)	7.65 (*J* = 14.6, *J* = 11.3)	5.25 (*J* = 12.5, *J* = 11.3)	6.58 (*J* = 12.5)	1.60 (br.s, 6 H); 3.19 (br.s, 4 H, NCH_2)
20	7.55 (*J* = 8.4)	8.03—8.10	4.70 (m, CH_2); 4.97 (d, $\underline{CH}_2$=CH, *J* = 16.3); 5.22 (d, $\underline{CH}_2$=CH, *J* = 10.4); 5.86 (m, CH_2=<u>CH</u>)	5.85 (*J* = 14.6)	7.63 (*J* = 14.6, *J* = 11.6)	5.30 (*J* = 12.6, *J* = 11.6)	6.56 (*J* = 12.6)	3.51 (s, CH_2Ph); 3.15, 2.42 (both m, NCH_2); 7.26 (m, Ph)
21	7.58 (*J* = 8.5)	8.10—8.15	4.72 (m, CH_2); 5.05 (d, $\underline{CH}_2$=CH, *J* = 17.1); 5.25 (d, $\underline{CH}_2$=CH, *J* = 10.5); 5.93 (m, CH_2=<u>CH</u>)	6.01 (*J* = 14.4)	7.76 (*J* = 14.4, *J* = 11.7)	5.57 (*J* = 12.9, *J* = 11.7)	6.82 (*J* = 12.9)	4.32 (s, NCH_2); 6.21 (d, *J* = 2.7); 6.38 (dd, *J* = 2.7, *J* = 1.7); 7.38 (d, *J* = 1.7)
22	7.57 (*J* = 8.9)	8.15—8.20	3.71 (m, 2 H, CH_2N); 4.32 (m, 2 H, CH_2Br)	6.01 (*J* = 14.3)	7.71 (*J* = 14.3, *J* = 11.6)	5.27 (*J* = 12.1, *J* = 11.6)	6.73 (*J* = 12.1)	2.90 (s, Me)
23	7.56 (*J* = 8.5)	8.13—8.15	3.75 (m, 2 H, CH_2N) 4.52 (m, 2 H, CH_2Br)	5.91 (*J* = 14.3)	7.71 (*J* = 14.3, *J* = 11.6)	5.25 (*J* = 12.5, *J* = 11.6)	6.71 (*J* = 12.5)	3.20 (CH_2O) 3.63 (CH_2N)
24	7.57 (*J* = 8.8)	8.12—8.14	1.16—1.28 (m, 2 H); 1.34 (t, Me); 4.12—4.36 (m, 6 H)	6.07 (*J* = 14.3)	7.71 (*J* = 14.3, *J* = 11.6)	5.44 (*J* = 12.1, *J* = 11.6)	6.59 (*J* = 12.1)	3.18 (CH_2O) 3.72 (CH_2N)

(to be continued)

Table 2. *(continued)*

Compound	δ (*J*/Hz)							
	H(4) (d)	H(5) H(7) (m)	NR´	H(1´) (d)	H(2´) (dd)	H(3´) (dd)	H(4´) (d)	NR''_2
25	7.66 (*J* = 9.5)	8.11—8.12	3.45 (s, Me)	6.68 (*J* = 13.7)	7.46 (d, *J* = 13.7)	0.88 (s, SiMe); 7.30—7.62 (m, Ph)	5.76 (c)	2.77 (s, Me)
26	7.72 (*J* = 8.9)	7.99—8.14	5.20 (s, CH_2CO) 7.10—7.84 (m, Ph)	6.65 (*J* = 13.7)	7.42 (d, *J* = 13.7)	0.81 (s, SiMe); 7.10—7.84 (m, Ph)	5.76 (c)	2.77 (s, Me)
27	7.41 (*J* = 8.1)	7.42—7.50	3.60 (s, Me)	6.10 (*J* = 13.5)	6.60 (*J* = 13.5, *J* = 11.6)	5.41 (*J* = 12.0, *J* = 11.6)	6.43 (*J* = 12.0)	3.18 (m, $(CH_2)_2O$); 3.72 (m, $(CH_2)_2N$)

1-yl]-1-methyl- (**13**), 1-methyl-2-[(1*E*,3*E*)-4-piperidino- (**14**), 2-[(1*E*,3*E*)-4-*N*-benzylpiperazinobuta-1,3-dien-1-yl]-1-methyl-6-nitro-1*H*-benzimidazoles (**15**); 1-benzyl-2-[(1*E*,3*E*)-4-(*N*,*N*-dimethylamino)buta-1,3-dien-1-yl]-6-nitro-1*H*-benzimidazole (**16**); 1-allyl-2-[(1*E*,3*E*)-4-*N*,*N*-dimethylamino- (**17**), 1-allyl-2-[(1*E*,3*E*)-4-morpholino- (**18**), 1-allyl-2-[(1*E*,3*E*)-4-piperidino- (**19**), 1-allyl-2-[(1*E*,3*E*)-4-*N*-benzylpiperazino- (**20**), 1-allyl-2-[(1*E*,3*E*)-4-*N*,*N*-difurfurylaminobuta-1,3-dien-1-yl]-6-nitro-1*H*-benzimidazoles (**21**); 1-bromoethyl-2-[(1*E*,3*E*)-4-*N*,*N*-dimethylamino- (**22**), 1-bromoethyl-2-[(1*E*,3*E*)-4-morpholino-1-bromoethyl-2-[(1*E*,3*E*)-4-buta-1,3-dien-1-yl]-6-nitro-1*H*-benzimidazoles (**23**); 1-(3-ethoxycarbonylpropyl-1)-2-[(1*E*,3*E*)-4-morpholinobuta-1,3-dien-1-yl]-6-nitro-1*H*-benzimidazole (**24**). The yields, elemental analysis results, and physico-chemical characteristics of aminodienes **10—24** are given in Table 1, the ^{1}H NMR spectral data, in Table 2.

2-[(1*E*,3*E*)-4-(*N*,*N*-Dimethylamino)-2-methyldiphenylsilyl-buta-1,3-dien-1-yl]-1-methyl-6-nitro-1*H*-benzimidazole (25) and 2-[(1*E*,3*E*)-4-(*N*,*N*-dimethylamino)-2-methyldiphenylsilylbuta-1,3-dien-1-yl]-6-nitro-1-phenacyl-1*H*-benzimidazole (26). A 30% aq. dimethylamine (0.5 mL) was added to a solution of salts **8** or **9** (0.36 mmol) in acetonitrile (10 mL) at 20 °C. After 1 h, a precipitate was filtered off, washed with water, dried in air, and recrystallized from AcOEt—hexane solvent mixture to obtain silyl-substituted azadienes **25** and **26**. The yields, elemental analysis results, and physico-chemical characteristics of organosilicon derivatives **25** and **26** are given in Table 1, ^{1}H NMR spectral data, in Table 2.

6-Amino-1-methyl-2-[(1*E*,3*E*)-4-morpholino-1,3-dien-1-yl]-1*H*-benzimidazole (27). Raney nickel (50 mg) was added in portions over 15 min to a stirred solution of diene **12** (0.5 g, 1.8 mmol) and hydrazine hydrate (2 mL) in ethanol (10 mL). Then the reaction mixture was heated for 3 h at ~30 °C (TLC monitoring). The catalyst was filtered off. The alcohol was evaporated *in vacuo*, water (10 mL) was added to the residue, followed by extraction with chloroform (3×20 mL). The extract was dried with $MgSO_4$. After evaporation of chloroform, the residue was recrystallized from AcOEt to obtain diene **27** (90 mg, 20%), red crystals, m.p. 184—186 °C (with decomp.). Found (%): C, 67.50; H, 6.84; N, 19.91. $C_{16}H_{20}N_4O$. Calculated (%): C, 67.58; H, 7.09; N, 19.70. ^{1}H NMR data are given in Table 2. MS, *m/z*: 284 $[M]^+$.

(3*E*)-4-(1-Methyl-6-nitro-1*H*-benzimidazol-2-yl)but-3-enal (28). Sodium nitrite (0.25 g, 3.62 mmol) was added in five portions over 1.5 h to a stirred solution of diene **12** (0.5 g, 1.59 mmol) in ~15% aq. hydrochloric acid (6 mL) at 20 °C. After the addition was over, the mixture was stirred at room temperature for another 1 h. Then the reaction mixture was poured into water (10 mL) and neutralized with aq. ammonia to pH ~7. A precipitate formed was filtered off and recrystallized from AcOEt to obtain aldehyde **28** (0.15 g, 35%), pale yellow crystals with m.p. 214—216 °C. IR, ν/cm^{-1}: 1680 (C=O). Found (%): C, 58.65; H, 4.10; N, 17.03. $C_{12}H_{11}N_3O_3$. Calculated (%): C, 58.77; H, 4.52; N, 17.13. ^{1}H NMR ($CDCl_3$), δ: 3.73 (s, 3 H, NMe); 3.95 (m, 2 H, $C\underline{H}_2CHO$); 6.71 (d, 1 H, H(4), *J* = 14.5 Hz); 7.10 (m, 1 H, H(3)); 7.60 (d, 1 H, H(4´), *J* = 8.7 Hz); 8.10—8.15 (m, 2 H, H(5´), H(7´)); 9.80 (s, 1 H, CHO). MS, *m/z*: 245 $[M]^+$.

4a-[(1*E*,3*Z*,5*E*)-4,5-Di(methoxycarbonyl)-6-dimethylamino-hexa-1,3,5-trien-1-yl]-1,2,3,4-tetra(methoxycarbonyl)-5-methyl-7-nitro-4a,5-dihydropyrido[1,2-*a*]benzimidazole (29). A mixture of 1,3-diene (**10**) (0.6 g, 2.2 mmol) and DMAD (3 g, 21.1 mmol) was refluxed in dichloromethane (20 mL) for 3 h (TLC monitoring). After evaporation of the solvent, the residue was subjected to chromatography on a column with SiO_2 (eluent: AcOEt—hexane, 1 : 1) to obtain compound **29** (0.25 g). Recrystallization from ethyl acetate gave brown crystals, the yield was 17%, m.p. 116—118 °C. Found (%): C, 55.38; H, 4.67; N, 8.00. $C_{32}H_{34}N_4O_{14}$. Calculated (%): C, 55.01; H, 4.91; N, 8.02. ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 6 H, NMe_2); 3.06 (s, 3 H, N(5)Me); 3.62, 3.72, 3.79, 3.80, 3.83, 4.04 (all s, 3 H each, OMe); 5.65 (d, 1 H, H(1´), *J* = 15.2 Hz); 6.14 (d, 1 H, H(3´), *J* = 11.2 Hz); 6.63 (d, 1 H, H(9), *J* = 8.8 Hz); 7.26 (dd, 1 H, H(2´), *J* = 11.2 Hz, *J* = 15.2 Hz); 7.36 (d, 1 H, H(6), *J* = 2.0 Hz); 7.49 (s, 1 H, H(6´)); 7.68 (dd, 1 H, H(8), *J* = 8.8 Hz, *J* = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 33.5, 43.2 (2 C), 51.0, 51.8, 52.2, 52.5, 52.6, 53.6, 86.8, 96.3, 103.2, 108.2, 108.9, 116.4, 118.0, 127.0, 130.9, 131.9, 132.5, 134.8, 135.4, 137.0, 143.0, 145.0, 151.0, 162.6, 163.0, 163.4, 166.0, 167.7, 169.0. MS, *m/z*: 698 $[M]^+$.

5-Benzyl-4a-[(1*E*,3*Z*,5*E*)-4,5-di(methoxycarbonyl)-6-dimethylaminohexa-1,3,5-trien-1-yl]-1,2,3,4-tetra(methoxycarbonyl)-7-nitro-4a,5-dihydropyrido[1,2-*a*]benzimidazole (30). Compound **30** (60 mg) was obtained similarly to the synthesis

of polycycle **29** from butadiene **16** (0.15 g, 0.43 mmol) and DMAD (0.61 g, 4.3 mmol), the yield was 18%, orange crystals, m.p. 181—183 °C (from AcOEt). Found (%): C, 58.75; H, 4.62; N, 7.13. $C_{38}H_{38}N_4O_{14}$. Calculated (%): C, 58.91; H, 4.94; N, 7.23. ^{1}H NMR ($CDCl_3$), δ: 2.87 (s, 6 H, NMe_2); 3.28, 3.64, 3.74, 3.77, 3.82, 4.07 (all s, 3 H each, OMe); 4.29 (d, 1 H, NCH_2A, J = 16.8 Hz); 5.08 (d, 1 H, NCH_2B, J = 16.8 Hz); 5.74 (d, 1 H, H(1′), J = 15.3 Hz); 6.17 (d, 1 H, H(3′), J = 11.3 Hz); 6.68 (d, 1 H, H(9), J = 8.9 Hz); 7.01 (d, 1 H, H(6), J = 2.1 Hz); 7.11—7.40 (m, 6 H, H(2′), Ar); 7.49 (s, 1 H, H(6′)); 7.69 (dd, 1 H, H(8), J = 8.9 Hz, J = 2.1 Hz). MS, m/z: 774 $[M]^+$.

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