

STUDIES OF 2,3'-BIQUINOLYL.

6.* REGIOSELECTIVITY OF NUCLEOPHILIC

ADDITION OF ORGANOMETALLIC COMPOUNDS TO

1-ALKYL-3-(2-QUINOLYL)QUINOLINIUM HALIDES

A. V. Aksenov, O. N. Nadein, D. V. Moiseev, and Yu. I. Smushkevich

Nucleophilic addition of organometallic lithium and magnesium compounds to 1-alkyl-3-(2-quinolyl)quinolinium cations produces a mixture of the corresponding 1'-alkyl-2'-R-1',2'-dihydro-2,3'-biquinolyls and 1'-alkyl-4'-R-1',4'-dihydro-2,3'-biquinolyls. The portion of the latter decreases with increasing "hardness" of the organometallic compound.

In previous work [1] we studied the regioselectivity of nucleophilic addition of soft nucleophiles (enolates, sodium indolate, cyanide) to 1-alkyl-3-(2-quinolyl)quinolinium halides I and demonstrated that the reaction results in addition to the 4'-position to give 4'-substituted 1',4'-dihydro-2,3'-biquinolyls. In the present work we report the reaction of I with "harder" nucleophiles, organolithium and -magnesium compounds.

Pyridinium and quinolinium salts are known [2] to react with these reagents to give the addition products at the position of maximum positive charge. This is the 2-position in I according to quantum-chemical calculations (Fig. 1).

In contrast with quinolinium salts, I is highly capable of delocalizing the unpaired electron and complexing to the metal ion. Therefore, the SET mechanism is expected to be more probable.

In fact, addition of organolithium and -magnesium compounds to I produces a mixture of addition products to the 2- and 4-positions, respectively. These are 1'-alkyl-2'-R-1',2'-dihydro-2,3'-biquinolyls II and 1'-alkyl-4'-R-1',4'-dihydro-2,3'-biquinolyls III. The ratio of these compounds depends on the nature of the organometallic compound (Table 1). Thus, compounds III predominate for the relatively "soft" isopropylmagnesium iodide and benzylmagnesium chloride whereas addition products III are in general not isolated for the rather hard phenylethynyllithium and allylmagnesium chloride.

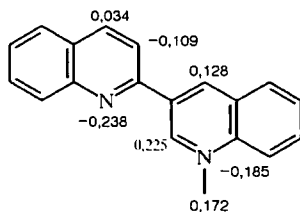
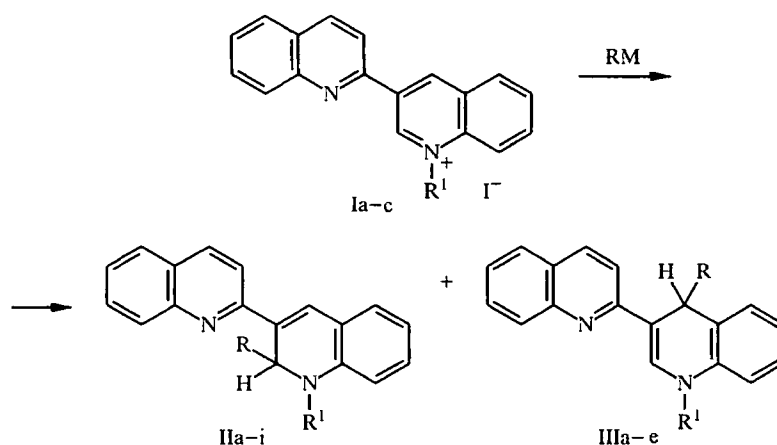


Fig. 1. Charge distribution in Ia from MNDO calculations.

* For No. 5, see [1].

TABLE 1. Regioselectivity of Addition of Organolithium and -magnesium Compounds to 1-Alkyl-3-(2-quinolyl)quinolinium Halides (Ia-c)

Organometallic compound	Compounds II and III	Total yield, %	Ratio of II:III isomers
MeLi	a	98	51:49
MeMgI	a	99	87:13
<i>i</i> -PrMgI	b	90	29:71
PhCH ₂ MgCl	c	75	26:74
PhLi	d	64	61:39
PhMgBr	d	71	68:32
α -Naphthyllithium	e	68	65:35
α -Naphthylmagnesium bromide	e	98	51:49
CH ₂ =CHCH ₂ MgCl	f	65	100:0
PhC \equiv CLi	g	84	100:0
PhC \equiv CLi	h	89	100:0
PhC \equiv CLi	i	76	100:0



Ia R¹ = Me, b R¹ = Et, c R¹ = Bu; II, III a R = Me, R¹ = Me; b R = *i*-Pr, R¹ = Me; c R = PhCH₂, R¹ = Me; d R = Ph, R¹ = Me; e R = 1-naphthyl, R¹ = Me; f R = CH₂=CHCH₂, R¹ = Me; g R = PhC \equiv C, R¹ = Me; h R = PhC \equiv C, R¹ = Et; i R = PhC \equiv C, R¹ = Bu;

EXPERIMENTAL

NMR spectra were recorded on a Bruker WP-200 instrument using TMS as an internal standard. The course of the reactions and the purity of the synthesized compounds were monitored using Silufol UV-254 plates and ethyl acetate–hexane (11:2) eluent. Column chromatography was performed on silica gel (L 40/100). Diethyl ether was purified by distillation over benzophenoneketal. The 1-alkyl-3-(2-quinolyl)quinolinium iodides were synthesized by the literature method [3]. Organometallic compounds were prepared by the usual methods [4, 5].

General Method for Synthesis of 2'-Substituted 1'-Methyl-1',2'-dihydro-2,3'-biquinolyls IIa-f and 4'-Substituted 1'-Methyl-1',4'-dihydro-2,3'-biquinolyls IIIa-e. A solution of the organometallic compound (3 mmol) in ether (10 ml) is treated with finely ground 1-methyl-3-(2-quinolyl)quinolinium iodide (1 g, 2.5 mmol) and an additional portion of ether (5 ml), stirred under an Ar atmosphere at room temperature for 1 h, boiled for 1 h, treated with alcohol (2 ml) and water (50 ml), and extracted with benzene (3 \times 30 ml). The organic layer is separated, dried over Na₂SO₄, and evaporated under vacuum. The solid is dissolved in benzene (10 ml) and chromatographed on a column using benzene. The first colored fraction is collected. The solution is evaporated to give a yellow oil (2'-substituted 1'-methyl-1',2'-dihydro-2,3'-biquinolyls), which for IIa,b,d,e is crystallized from

various solvents. The next colored fraction* is eluted with ethyl acetate. The solution is evaporated to give a reddish oil (4'-substituted 1'-alkyl-1',4'-dihydro-2,3'-biquinolyls), which for IIIb-d is crystallized from alcohol; for IIIa,e, from benzene with hexane.

For II(III)a,d,e, two yields are given for preparations starting with the lithium and magnesium organometallic compounds, respectively.

1',2'-Dimethyl-1',2'-dihydro-2,3'-biquinolyl (IIa). Yield 0.358 g (50%) and 0.616 g (86%); mp 168-169°C (benzene-hexane mixture). R_f 0.88. PMR spectrum (CDCl_3): 1.22 (3H, d, $J = 6.41$ Hz, 2'-CH₃); 3.06 (3H, s, 1'-CH₃); 5.27 (1H, q, $J = 6.41$ Hz, 2'-H); 6.59 (1H, d, $J_{78} = 8.10$ Hz, 8'-H); 6.70 (1H, dd, $J_{56} = 7.52$, $J_{67} = 7.37$ Hz, 6'-H); 7.13 (1H, d, $J_{56} = 7.61$ Hz, 5'-H); 7.19 (1H, dd, $J_{67} = 7.37$, $J_{78} = 8.16$ Hz, 7'-H); 7.29 (1H, s, 4'-H); 7.48 (1H, dd, $J_{56} = 8.09$ Hz, $J_{67} = 7.14$ Hz, 6-H); 7.68 (1H, dd, $J_{67} = 7.14$, $J_{78} = 8.41$ Hz, 7-H); 7.77 (1H, d, $J_{56} = 8.09$ Hz, 5-H); 7.83 (1H, d, $J_{34} = 9.05$ Hz, 3-H); 8.05 (1H, d, $J_{78} = 8.41$ Hz, 8-H); 8.09 ppm (1H, d, $J_{34} = 9.04$ Hz, 4-H). Found, %: C 83.98; H 6.17; N 9.85. $\text{C}_{20}\text{H}_{18}\text{N}_2$. Calculated, %: C 83.88; H 6.34; N 9.78.

2'-Isopropyl-1'-methyl-1',2'-dihydro-2,3'-biquinolyl (IIb). Yield 0.205 g (26%); mp 86-87°C (hexane). R_f 0.82. PMR spectrum (CDCl_3): 0.74 (3H, d, $J = 6.95$ Hz, A-CH₃); 0.89 (3H, d, $J = 6.95$ Hz, B-CH₃); 2.03 [1H, m, 2'-CH(CH₃)₂], 3.24 (3H, s, 1'-CH₃); 5.29 (1H, d, $J = 4.39$ Hz, 2'-H); 6.56 (1H, d, $J_{78} = 8.10$ Hz, 8'-H); 6.63 (1H, dd, $J_{56} = 7.41$, $J_{67} = 7.41$ Hz, 6'-H); 7.11 (1H, d, $J_{56} = 7.41$ Hz, 5'-H); 7.16 (1H, dd, $J_{67} = 7.41$, $J_{78} = 8.10$ Hz, 7'-H); 7.32 (1H, s, 4'-H); 7.47 (1H, dd, $J_{56} = 7.97$, $J_{67} = 7.07$ Hz, 6-H); 7.68 (1H, dd, $J_{67} = 7.07$, $J_{78} = 8.47$ Hz, 7-H); 7.77 (1H, d, $J_{56} = 7.97$ Hz, 5-H); 7.82 (1H, d, $J_{34} = 8.77$ Hz, 3-H); 8.09 (1H, d, $J_{78} = 8.47$ Hz, 8-H); 8.09 ppm (1H, d, $J_{34} = 8.77$ Hz, 4-H). Found, %: C 84.15; H 6.87; N 8.98. $\text{C}_{22}\text{H}_{22}\text{N}_2$. Calculated, %: C 84.04; H 7.05; N 8.91.

2'-Benzyl-1'-methyl-1',2'-dihydro-2,3'-biquinolyl (IIc). Yield 0.176 g (19%). Yellow oil. R_f 0.94. PMR spectrum (CDCl_3): 2.83 (1H, dd, $J_{\text{gem}} = 12.82$, $J_{\text{trans}} = 7.63$ Hz, 2'-CH^AH^BPh); 3.00 (1H, dd, $J_{\text{gem}} = 12.82$, $J_{\text{cis}} = 4.28$ Hz, 2'-CH^AH^BPh); 3.16 (3H, s, 1'-CH₃); 4.79 (1H, dd, $J_{\text{trans}} = 7.63$, $J_{\text{cis}} = 4.28$ Hz, 2'-H); 6.56 (1H, d, $J_{78} = 7.93$ Hz, 8'-H); 6.70 (1H, dd, $J_{56} = 7.43$, $J_{67} = 7.35$ Hz, 6'-H); 6.86 (3H, m, 3"-H, 4"-H, 5"-H); 7.10 (2H, d, $J = 7.11$ Hz, 2"-H, 6"-H); 7.16 (1H, d, $J_{56} = 7.43$ Hz, 5'-H); 7.23 (1H, dd, $J_{67} = 7.35$, $J_{78} = 7.93$ Hz, 7'-H); 7.43 (1H, s, 4'-H); 7.52 (1H, dd, $J_{56} = 7.94$, $J_{67} = 7.20$ Hz, 6-H); 7.70 (1H, dd, $J_{67} = 7.20$, $J_{78} = 8.52$ Hz, 7-H); 7.89 (1H, d, $J_{56} = 7.94$ Hz, 5-H); 7.77 (1H, d, $J_{34} = 8.72$ Hz, 3-H); 8.03 (1H, d, $J_{78} = 8.52$ Hz, 8-H); 8.10 ppm (1H, d, $J_{34} = 8.72$ Hz, 4-H). Found, %: C 86.26; H 5.95; N 7.79. $\text{C}_{26}\text{H}_{22}\text{N}_2$. Calculated, %: C 86.15; H 6.12; N 7.73.

1'-Methyl-2'-phenyl-1',2'-dihydro-2,3'-biquinolyl (IId). Yield 0.339 g (39%) and 0.420 g (48%); mp 138-139°C (alcohol). R_f 0.77. PMR spectrum (CDCl_3): 2.93 (3H, s, 1'-CH₃); 6.34 (1H, s, 2'-H); 6.50 (1H, d, $J_{78} = 8.13$ Hz, 8'-H); 6.70 (1H, dd, $J_{56} = 7.53$, $J_{67} = 7.33$ Hz, 6'-H); 7.12 (1H, d, $J_{56} = 7.53$ Hz, 5'-H); 7.15 (1H, dd, $J_{67} = 7.33$, $J_{78} = 8.13$ Hz, 7'-H); 7.17 (3H, m, 3"-H, 4"-H, 5"-H); 7.42 (1H, s, 4'-H); 7.44 (2H, d, $J = 7.14$ Hz, 2"-H, 6"-H); 7.45 (1H, dd, $J_{56} = 8.22$, $J_{67} = 7.04$ Hz, 6-H); 7.65 (1H, dd, $J_{67} = 7.04$, $J_{78} = 8.51$ Hz, 7-H); 7.71 (1H, d, $J_{56} = 8.22$ Hz, 5-H); 7.76 (1H, d, $J_{34} = 8.85$ Hz, 3-H); 8.00 (1H, d, $J_{34} = 8.85$ Hz, 4-H); 8.04 ppm (1H, d, $J_{78} = 8.51$ Hz, 8-H). Found, %: C 86.28; H 5.63; N 8.09. $\text{C}_{25}\text{H}_{20}\text{N}_2$. Calculated, %: C 86.18; H 5.78; N 8.04.

1'-Methyl-2'-(1-naphthyl)-1',2'-dihydro-2,3'-biquinolyl (IIe). Yield 0.440 g (44%) and 0.498 g (50%); mp 225-226°C (alcohol). R_f 0.86. PMR spectrum (CDCl_3): 2.80 (3H, s, 1'-CH₃); 6.43 (1H, d, $J_{78} = 7.95$ Hz, 8'-H); 6.72 (1H, dd, $J_{56} = 7.55$, $J_{67} = 7.34$ Hz, 6'-H); 7.16 (1H, dd, $J_{67} = 7.34$, $J_{78} = 7.95$ Hz, 7'-H); 7.22 (1H, d, $J_{56} = 7.55$ Hz, 5'-H); 7.24 (2H, d, 2"-H, 4"-H); 7.33 (1H, s, 2'-H); 7.36 (1H, t, 3"-H); 7.50 (2H, m, 6-H, 6"-H); 7.56 (1H, s, 4'-H); 7.61 (2H, d, 7-H, 5"-H); 7.74 (2H, m, 5-H, 7"-H); 7.79 (2H, d, 3-H, 8-H); 7.94 (1H, d, $J_{34} = 8.54$ Hz, 4-H); 9.10 ppm (1H, d, $J_{78} = 8.54$ Hz, 8"-H). Found, %: C 87.52; H 5.41; N 7.07. $\text{C}_{29}\text{H}_{22}\text{N}_2$. Calculated, %: C 87.41; H 5.56; N 7.03.

2'-Allyl-1'-methyl-1',2'-dihydro-2,3'-biquinolyl (IIIf). Yield 0.509 g (65%). Yellow oil. R_f 0.89. PMR spectrum (acetone- d_6): 2.47 (2H, dd, $J = 7.31$, $J_2 = 5.11$ Hz, 2'-CH₂CH=CH₂); 3.15 (3H, s, 1'-CH₃); 4.77 (1H, dd, $J_{\text{trans}} = 17.08$, $J_{\text{gem}} = 5.48$ Hz, 2'-CH₂CH=CH^AH^B); 4.89 (1H, dd, $J_{\text{cis}} = 9.96$, $J_{\text{gem}} = 5.48$ Hz, 2'-CH₂CH=CH^AH^B); 5.46 (1H, t, $J = 5.11$ Hz, 2'-H); 5.86 (1H, m, 2'-CH₂CH=CH₂); 6.60 (1H, d, $J_{78} = 8.40$ Hz, 8'-H); 6.65 (1H, dd, $J_{56} = 7.50$, $J_{67} = 7.35$ Hz, 6'-H); 7.12 (1H, d, $J_{56} = 7.50$ Hz, 5'-H); 7.16 (1H, dd, $J_{67} = 7.35$, $J_{78} = 8.40$ Hz, 7'-H); 7.54 (1H, dd, $J_{56} = 8.12$, $J_{67} = 7.26$ Hz, 6-H); 7.55 (1H, s, 4'-H); 7.74 (1H, dd, $J_{67} = 7.26$, $J_{78} = 8.45$ Hz, 7-H); 7.91 (1H, d, $J_{56} = 8.12$ Hz, 5-H); 8.04 (1H, d, $J_{78} = 8.45$ Hz, 8-H); 8.05 (1H, d, $J_{34} = 8.77$ Hz, 3-H); 8.27 ppm (1H, d, $J_{34} = 8.77$ Hz, 4-H). Found, %: C 84.68; H 6.27; N 9.03. $\text{C}_{22}\text{H}_{20}\text{N}_2$. Calculated, %: C 84.58; H 6.45; N 8.97.

*For IId, only the first colored fraction is isolated.

1',4'-Dimethyl-1',4'-dihydro-2,3'-biquinolyl (IIIa). Yield 0.343 g (48%) and 0.092 g (12%); mp 126-127°C (benzene-hexane mixture). R_f 0.55. PMR spectrum (acetone- d_6): 1.27 (3H, d, $J = 6.83$ Hz, 4'-CH₃); 3.42 (3H, s, 1'-CH₃); 4.68 (1H, q, $J = 6.83$ Hz, 4'-H); 6.94 (1H, d, $J_{78} = 7.75$ Hz, 8'-H); 6.98 (1H, dd, $J_{5'6'} = 7.64$, $J_{6'7'} = 7.56$ Hz, 6'-H); 7.18 (1H, dd, $J_{6'7'} = 7.56$, $J_{78} = 7.75$ Hz, 7'-H); 7.28 (1H, d, $J_{5'6'} = 7.64$ Hz, 5'-H); 7.39 (1H, dd, $J_{56} = 7.67$, $J_{67} = 7.45$ Hz, 6-H); 7.57 (1H, s, 2'-H); 7.63 (1H, dd, $J_{67} = 7.45$, $J_{78} = 8.49$ Hz, 7-H); 7.78 (1H, d, $J_{56} = 7.67$ Hz, 5-H); 7.79 (1H, d, $J_{34} = 8.11$ Hz, 3-H); 7.89 (1H, d, $J_{78} = 8.49$ Hz, 8-H); 8.06 ppm (1H, d, $J_{34} = 8.11$ Hz, 4-H). Found, %: C 83.95; H 6.16; N 9.89. C₂₀H₁₈N₂. Calculated, %: C 83.88; H 6.34; N 9.78.

4'-Isopropyl-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (IIIb). Yield 0.502 g (64%); mp 128-129°C (alcohol). R_f 0.62. PMR spectrum (acetone- d_6): 0.63 (3H, d, $J = 6.58$ Hz, A-CH₃); 0.93 (3H, d, $J = 6.58$ Hz, B-CH₃); 1.99 [1H, m, 4'-CH(CH₃)₂], 3.41 (3H, s, 1'-CH₃); 4.61 (1H, d, $J = 3.96$ Hz, 4'-H); 6.95 (1H, d, $J_{78} = 7.92$ Hz, 8'-H); 7.00 (1H, dd, $J_{5'6'} = 7.63$, $J_{6'7'} = 7.38$ Hz, 6'-H); 7.19 (1H, dd, $J_{6'7'} = 7.38$, $J_{78} = 7.92$ Hz, 7'-H); 7.23 (1H, d, $J_{5'6'} = 7.63$ Hz, 5'-H); 7.39 (1H, dd, $J_{56} = 7.71$, $J_{67} = 7.39$ Hz, 6-H); 7.63 (1H, dd, $J_{67} = 7.39$, $J_{78} = 7.56$ Hz, 7-H); 7.70 (1H, s, 2'-H); 7.78 (1H, d, $J_{56} = 7.71$ Hz, 5-H); 7.81 (1H, d, $J_{34} = 8.12$ Hz, 3-H); 7.89 (1H, d, $J_{78} = 7.56$ Hz, 8-H); 8.07 ppm (1H, d, $J_{34} = 8.12$ Hz, 4-H). Found, %: C 84.11; H 6.90; N 8.99. C₂₂H₂₂N₂. Calculated, %: C 84.04; H 7.05; N 8.91.

4'-Benzyl-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (IIIc). Yield 0.502 g (55%); mp 136-137°C (alcohol); lit. mp 136-137°C [4]. R_f 0.68. The melting point is not depressed by mixing with an authentic sample. The PMR spectra are identical.

1'-Methyl-4'-phenyl-1',4'-dihydro-2,3'-biquinolyl (IIId). Yield 0.218 g (25%) and 0.197 g (23%); mp 173-174°C (alcohol); lit. mp 173-174°C [5]. $R_f = 0.37$. The melting point is not depressed by mixing with an authentic sample. PMR spectra are identical.

1'-Methyl-4'-(1-naphthyl)-1',4'-dihydro-2,3'-biquinolyl (IIIe). Yield 0.237 g (24%) and 0.478 g (48%); mp 151-153°C (benzene-hexane mixture); lit. mp 151-153°C [5]. R_f 0.51. The temperature is not depressed by mixing with an authentic sample. PMR spectra are identical.

General Method for Synthesis of 1'-Alkyl-2'-phenylethynyl-1',2'-dihydro-2,3'-biquinolyls IIg-i. A solution of methyllithium (0.066 g, 3 mmol) in ether (10 ml) is cautiously treated with phenylacetylene (0.337 g, 3.3 mmol) in ether (5 ml) and stirred for 5 min. The reaction mixture is treated with finely ground 1-alkyl-3-(2-quinolyl)quinolinium iodide (2.5 mmol) and additional ether (5 ml); stirred under an Ar atmosphere at room temperature for 1 h, boiled for 1 h, treated with alcohol (2 ml); poured into water (50 ml); and extracted with benzene (3 × 30 ml). The organic layer is separated, dried over Na₂SO₄, and evaporated under vacuum. The solid is dissolved in benzene (10 ml) and chromatographed on a column using benzene. The first colored fraction is collected. The solution is evaporated to give a yellow oil that is crystallized from benzene or from benzene with alcohol.

1'-Methyl-2'-phenylethynyl-1',2'-dihydro-2,3'-biquinolyl (IIg). Yield 0.778 g (84%); mp 194-195°C (benzene). R_f 0.82. PMR spectrum (CDCl₃): 3.17 (3H, s, 1'-CH₃); 6.28 (1H, s, 2'-H); 6.74 (1H, d, $J_{78} = 8.11$ Hz, 8'-H); 6.81 (1H, dd, $J_{5'6'} = 7.45$, $J_{6'7'} = 7.36$ Hz, 6'-H); 7.15 (1H, d, $J_{5'6'} = 7.45$ Hz, 5'-H); 7.16 (1H, dd, $J_{6'7'} = 7.36$, $J_{78} = 8.11$ Hz, 7'-H); 7.17 (3H, m, 3"-H, 4"-H, 5"-H); 7.48 (1H, s, 4'-H); 7.44 (2H, d, $J = 7.12$ Hz, 2"-H, 6"-H); 7.52 (1H, dd, $J_{56} = 8.05$, $J_{67} = 7.11$ Hz, 6-H); 7.73 (1H, dd, $J_{67} = 7.11$, $J_{78} = 8.41$ Hz, 7-H); 7.80 (1H, d, $J_{56} = 8.05$ Hz, 5-H); 7.90 (1H, d, $J_{34} = 8.77$ Hz, 3-H); 8.19 (1H, d, $J_{78} = 8.41$ Hz, 8-H); 8.19 ppm (1H, d, $J_{34} = 8.77$ Hz, 4-H). Found, %: C 87.18; H 5.25; N 7.57. C₂₇H₂₀N₂. Calculated, %: C 87.07; H 5.41; N 7.52.

1'-Ethyl-2'-phenylethynyl-1',2'-dihydro-2,3'-biquinolyl (IIh). Yield 0.860 g (89%); mp 113-114°C (benzene-alcohol mixture). R_f 0.83. PMR spectrum (CDCl₃): 1.50 (3H, t, $J = 6.95$ Hz, 1'-CH₂CH₃); 3.64 (2H, q, $J = 6.95$ Hz, 1'-CH₂CH₃); 6.39 (1H, s, 2'-H); 6.78 (1H, d, $J_{78} = 7.90$ Hz, 8'-H); 6.80 (1H, dd, $J_{5'6'} = 7.50$, $J_{6'7'} = 7.31$ Hz, 6'-H); 7.14 (1H, d, $J_{5'6'} = 7.50$ Hz, 5'-H); 7.16 (1H, dd, $J_{6'7'} = 7.31$, $J_{78} = 7.90$ Hz, 7'-H); 7.17 (3H, m, 3"-H, 4"-H, 5"-H); 7.44 (1H, s, 4'-H); 7.44 (2H, d, $J = 7.13$ Hz, 2"-H, 6"-H); 7.51 (1H, dd, $J_{56} = 8.02$, $J_{67} = 7.20$ Hz, 6-H); 7.72 (1H, dd, $J_{67} = 7.20$, $J_{78} = 8.43$ Hz, 7-H); 7.79 (1H, d, $J_{56} = 8.02$ Hz, 5-H); 7.89 (1H, d, $J_{34} = 8.58$ Hz, 3-H); 8.16 (1H, d, $J_{78} = 8.43$ Hz, 8-H); 8.16 ppm (1H, d, $J_{34} = 8.58$ Hz, 4-H). Found, %: C 87.12; H 5.57; N 7.31. C₂₈H₂₂N₂. Calculated, %: C 87.01; H 5.74; N 7.25.

1'-Butyl-2'-phenylethynyl-1',2'-dihydro-2,3'-biquinolyl (III). Yield 0.787 g (76%); mp 111-112°C (benzene-alcohol mixture). R_f 0.87. PMR spectrum (CDCl_3): 1.01 (3H, t, $J = 6.77$ Hz, 1'- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); 1.50 (2H, m, 1'- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); 1.89 (2H, m, 1'- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); 3.54 (2H, t, $J = 6.79$ Hz, 1'- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); 6.34 (1H, s, 2'-H); 6.75 (1H, d, $J_{78'} = 8.08$ Hz, 8'-H); 6.77 (1H, dd, $J_{5'6'} = 7.48$, $J_{6'7'} = 7.37$ Hz, 6'-H); 7.12 (1H, d, $J_{5'6'} = 7.48$ Hz, 5'-H); 7.16 (1H, dd, $J_{6'7'} = 7.37$, $J_{78'} = 8.08$ Hz, 7'-H); 7.17 (3H, m, 3''-H, 4''-H, 5''-H); 7.38 (1H, s, 4'-H); 7.44 (2H, d, $J = 7.13$ Hz, 2''-H, 6''-H); 7.50 (1H, dd, $J_{56} = 8.14$, $J_{67} = 7.12$ Hz, 6-H); 7.71 (1H, dd, $J_{67} = 7.12$, $J_{78} = 8.41$ Hz, 7-H); 7.79 (1H, d, $J_{56} = 8.14$ Hz, 5-H); 7.88 (1H, d, $J_{34} = 8.77$ Hz, 3-H); 8.14 (1H, d, $J_{78} = 8.41$ Hz, 8-H); 8.14 ppm (1H, d, $J_{34} = 8.77$ Hz, 4-H). Found, %: C 87.03; H 6.15; N 6.82. $\text{C}_{30}\text{H}_{26}\text{N}_2$. Calculated, %: C 86.92; H 6.32; N 6.76.

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