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N-Heterocyclic Carbenes: III.* N-Heterocyclic Carbene Ligands Based on Abietane in Suzuki–Miyaura Reaction

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Abstract—By reactions of *N*-alkyl- and *N*-arylimidazoles with methyl 12-bromoacetyldehydroabietate a series of unsymmetrically substituted chiral imidazolium bromides with the abietane fragment was synthesized. The salts obtained were suggested as new N-heterocyclic carbene ligands in the Suzuki–Miyaura reaction.

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Nowadays the ligands underlain by the N-heterocyclic carbenes (NHC) firmly occupied an important place in the homogeneous metallocomplex catalysis [2–4] partially replacing the traditional tertiary phosphanes. The ligands based on NHC are more advantageous due to their thermal and hydrolytic stability, and also due to the resistance to oxidation [3]. The most frequently used NHC are generated from the imidazolium salts at the treatment with strong bases; therewith the complexing of the metal with the NHC-ligand is conveniently carried out directly in the reaction mixture (in situ), although an approach is now under development where the preparation and storage of the NHC–Pd complexes is performed in the form of the precatalysts of a definite stereochemistry ("well-defined precatalysts") [5]. Notwithstanding the versatility of NHC types known by now [6] the research on the synthesis of new imidazolium salts is going on with high intensity all over the world since the efficient catalytic centers as a rule are characterized by certain topology of the reaction site [4, 7] and their discovery requires experimental testing of various versions of the electronic and spatial structure of ligands.

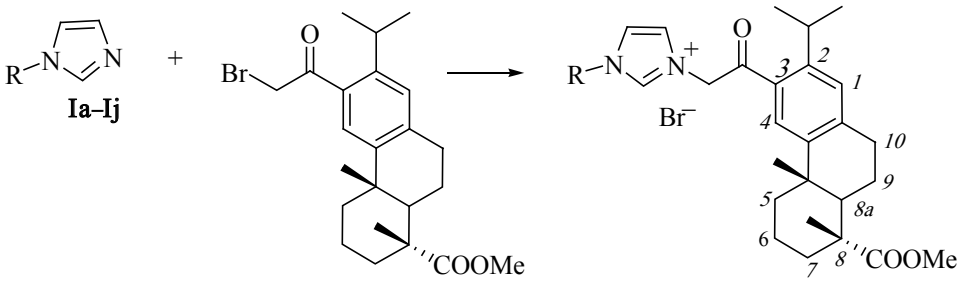
The sterically loaded ligands are known to accelerate the stage of the reductive elimination in the catalytic cycle [4, 7, 8], and therefore one of the directions of the search for efficient catalytic systems consists in the application of spatially hindered imidazolium salts. Among the multitude of such compounds recently synthesized the salts can be mentioned based on substituted naphthalene [9], terphenyl [10], phenanthrene [11], phenanthroline [12], and diamantane (adamantane dimer) [13].

Imidazolium salts have been synthesized from monoterpenes [14], whereas di- and triterpenes yet do not attract the attention. We formerly prepared chiral asymmetric imidazolium salts proceeding from the methyl 12-chloromethyldehydroabietate [1, 15]. The presumed high efficiency of this series of salts was provided by the sterical loading of the isopropyl group of abietane. The goal of this study was the synthesis of imidazolium salts from the methyl 12-bromoacetyldehydroabietate and the investigation of their catalytic activity as NHC-ligands in the model Suzuki–Miyaura reaction.

We established that the reaction of *N*-alkyl- and *N*-aryl-1*H*-imidazoles **Ia–Ij** with methyl 12-bromoacetyldehydroabietate (**II**) [16] in toluene afforded unsymmetrical imidazolium salts **IIIa–IIIj**.

N-Alkylimidazoles reacted with bromoketone **II** in toluene already at room temperature, while the reaction of *N*-arylimidazoles required a short heating of the reaction mixture. All obtained bromides **IIIa–IIIj** except for compound **IIIg** separated from toluene in 50–89% yield in the form of analytically pure colorless crystals. Compound **IIIg** is well soluble in toluene but precipitated under the

* For Communication II, see [1].



R = H (**a**), Me (**b**), Vin (**c**), *i*-Pr (**d**), *t*-Bu (**e**), Bn (f), Ph (**g**), 2-MeC_6H_4 (**h**), 2,6-$Me_2C_6H_3$ (**i**), 2,4,6-$Me_3C_6H_2$ (**j**).

action of ethyl ether on its acetonitrile solution. The low yield (25%) of the imidazolium salt with vinyl substituent is apparently due to the competing oligomerization reactions of the initial imidazole.

IR spectra of compounds **IIIa–IIIj** contain two absorption bands of carbonyl groups: a strong band at 1711–1728 (carboxy group) and a medium band at 1581–1655 cm^{-1} (keto group). A characteristic feature of the crystals of salts **IIIa–IIIj** is the presence of crystallization water as indicated by the elemental analysis and by the IR spectra. The latter contain a broad band of OH groups at 3376–3414 cm^{-1}. The crystallization water is not removed by drying in a vacuum (55°C, 2 mm Hg, 3 h). ^1H and ^{13}C NMR spectra confirm the structure of compounds **IIIa–IIIj** (see EXPERIMENTAL).

The synthesized salts **IIIa–IIIj** were tested as N-heterocyclic carbene ligands in the palladium-catalyzed Suzuki–Miyaura reaction. The model reaction was the interaction between *p*-tolylboric acid and *p*-bromotoluene. The scheme of the homogeneous catalytic process with the use of NHC-ligands is in general similar to the traditional scheme of the cross-coupling with the complexes of zero-valence palladium with phosphanes. The conditions of the cross-coupling we optimized before [1]: amount of the catalyst 1 mol%, solvent DMF. The reaction was carried out in aerobic conditions at 90°C over 4–5 h (to the end of the run palladium black formed). It is now a common concept that the catalytic activity is inherent to monocoordinated Pd(0) species generated in the reaction mixture by the thermal decomposition of the initially formed bicoordinated complexes [17], therefore we take the ratio Pd/ligand equal 1 : 1.

After the completion of the reaction and the workup of the reaction mixture its composition was analyzed by GC-MS method with dodecane as internal reference (see the table).

As seen from the table, both alkyl- and aryl-containing salts show approximately equal catalytic activity (conversion 81–96%, yields in the range 60–88%). Note the activity of the unsubstituted imidazole **IIIa**. The reaction practically does not proceed without addition of salts **IIIa–IIIj**. For instance, in the blank run without a ligand [dioxane, 110°C, 5 mol% $Pd(OAc)_2$] the yield of the cross-coupling products was only 8%. To exclude the possibility of the homo-coupling a control experiment was performed with bromobenzene. The reaction of *p*-tolylboric acid with bromobenzene in the presence of 1 mol% of palladium(II) acetate and ligand **IIIe** (DMF, K_2CO_3, 90°C, 4 h) gave the product of the homo-coupling (di-*p*-tolyl) in the yield not exceeding 10% showing that the formation of the di-*p*-tolyl in the model reaction was due prevailingly to the normal Suzuki–Miyaura reaction.

The experimental results permit a conclusion that the imidazolium salts **IIIa–IIIj** we synthesized possess a high catalytic activity in the Suzuki–Miyaura reaction of *p*-bromotoluene with *p*-tolylboric acid.

EXPERIMENTAL

Imidazole, *N*-methylimidazole, *N*-benzylimidazole,

Catalytic activity of 1-R-imidazolium salts **IIIa–IIIj** in the model Suzuki–Miyaura reaction

Compound no.	Conversion %	Yield, %
IIIa	84	68
IIIb	94	75
IIIc	88	78
IIId	96	88
IIIe	93	60
IIIf	89	79
IIIg	95	87
IIIh	81	62
IIIi	96	81
IIIj	90	78

N-vinylimidazole, and *N*-phenylimidazole were purchased from Alfa Aesar (Lancaster); 1-isopropyl-1*H*-imidazole and 1-*tert*-butyl-1*H*-imidazole were prepared by procedure [18], 1-(2-methylphenyl)-1*H*-imidazole, 1-(2,6-dimethylphenyl)-1*H*-imidazole, and 1-mesityl-1*H*-imidazole, by procedure [19]. The melting points were measured on a device PTP. TLC was performed on plates with silica gel Sorbfil; spots were visualized by UV irradiation or by treating with 5% H_2SO_4 followed by heating at 100–120°C. IR spectra were recorded on a Fourier spectrophotometer Bruker IFS 66ps from mulls in mineral oil or from thin films obtained by evaporation of the compound solution in chloroform. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Varian Mercury+300 (300 and 75 MHz), solvent $CDCl_3$, internal reference HMDS and the residual solvent signal ($CHCl_3$, ^{13}C NMR spectra, δ 77.0 ppm). The specific rotation was measured on an instrument Perkin-Elmer 341 in chloroform stabilized with 0.5% of ethanol; the results are reported in the units 10^{-1} deg g^{-1} cm^2. Mass spectra were obtained on an instrument Agilent 6890N with the mass-detector MSD 5975B (ionizing energy 70 eV). Elemental analyses were carried out on an analyzer Leco CHNS 9321P.

1-(2-Methylphenyl)-1*H*-imidazole (**Ih**). Yield 63%. Yellow thick oily or light-yellow crystalline substance, bp 200–205°C (15 mm Hg), mp 65–68°C. ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, Me), 7.04 m (1H$_{Ht}$), 7.18–7.35 m (4H$_{arom}$), 7.61 m (1H$_{Ht}$), 8.99 br.s. (1H, H$^2_{Ht}$). ^{1}H NMR spectrum is consistent with that published in [20].

1-(2,6-Dimethylphenyl)-1*H*-imidazole (**Ii**). Yield 35%. Light-yellow crystals, bp 215–220°C (15 mm Hg), mp 76–78°C. ^{1}H NMR spectrum, δ, ppm: 2.02 s (6H, 2Me), 6.90 d (1H, H$_{Ht}$, *J* 1.2 Hz), 7.13 d (2H, H$^{3'}$, H$^{5'}$, *J* 7.2 Hz), 7.22–7.27 m (1H, H$^{4'}$), 7.24 m (1H, H$_{Ht}$, *J* 1.2 Hz), 7.44 s (1H, NCH=N).

1-Mesityl-1*H*-imidazole (**Ij**). Yield 51%. Light-brown crystals, mp 106–108°C (mp 112–114°C [19]). ^{1}H NMR spectrum, δ, ppm: 1.98 s (6H, 2Me), 2.33 s (3H, Me), 6.88 m (1H$_{Ht}$), 6.96 s (2H, H$^{3',5'}$), 7.22 m (1H$_{Ht}$), 7.42 s (1H, NCH=N). The substance is sufficiently pure to be used in the amination of bromoketone **II**.

Methyl 12-bromoacetyldehydroabietate (**II**) was obtained by procedure [16] by the bromination of the methyl 12-acetyldehydroabietate with molecular bromine in acetic acid. Yield 93%, mp 114–116°C (mp 115–117°C [16]). IR spectrum, cm^{-1} (from thin film): 1722, 1683, 1607, 1549, 1495, 1459, 1388, 1249, 1194, 1134, 1107, 1051, 976, 900. ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, Me, *J* 7.2 Hz), 1.21 s (3H, Me), 1.22 d (3H, Me, *J* 7.2 Hz), 1.27 s (3H, Me), 1.47 m (2H, H^{1a,6a}), 1.65–1.88 m (5H, C^{2}H$_2$, C^{3}H$_2$, H^{6e}), 2.10 d.d (1H, H^5, *J* 12.3, 2.1 Hz), 2.29 m (1H, H^{1e}), 2.91 m (2H, C^{7}H$_2$), 3.35 m (1H, H^{15}, *J* 7.2 Hz), 3.66 s (3H, OMe), 4.37 c (2H, BrCH$_2$), 7.08 s (1H, H^{14}), 7.38 s (1H, H^{11}). Found, %: C 64.62; H 6.74. $C_{24}H_{33}BrO_3$. Calculated, %: C 64.14; H 7.40.

3-{2-[(4b*S*,8*R*)-2-Isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide, hydrate (**IIIa**). Yield 50%, mp 217–218°C, $[\alpha]_D^{22}$ +75.9 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3373 (OH), 3090, 2929, 2869, 1711, 1581, 1555, 1440, 1389, 1249, 1181, 1134, 1105, 1052, 972, 755. ^{1}H NMR spectrum, δ, ppm: 1.17 d (3H, Me, *J* 6.6 Hz), 1.19 d (3H, Me, *J* 6.6 Hz), 1.25 s (3H, Me), 1.28 s (3H, Me), 1.49 m (2H, H^{9a}, H^{5a}), 1.68-1.88 m (5H, C^{6}H$_2$, C^{7}H$_2$, H^{9e}), 2.17 d.d (1H, H^{8a}, *J* 12.6, 2.4 Hz), 2.58 m (1H, H^{5e}), 2.93 m (2H, C^{10}H$_2$), 3.45 m (1H, C<u>H</u>Me$_2$, *J* 7.2 Hz), 3.67 s (3H, OMe), 4.80 br.s (2H, HN+OH), 5.92 d (1H, NCH$_2$, *J* 18.0 Hz), 6.16 d (1H, NCH$_2$, *J* 18.0 Hz), 7.13 s (1H, H^1), 7.17 m (1H$_{Ht}$), 7.51 m (1H$_{Ht}$), 7.76 s (1H, H^4), 8.28 s (1/3H, NCH=N), 10.26 s (2/3H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.35, 18.25, 21.12, 23.88, 23.95, 24.85, 28.62, 30.08, 36.49, 37.07, 37.79, 44.58, 47.39, 51.85, 57.23, 119.07, 123.23, 125.35, 127.69, 130.46, 132.94, 138.68, 141.50, 146.76, 147.48, 178.79, 192.54. Found, %: C 60.12; H 7.30; N 5.90. $C_{26}H_{35}BrN_2O_3\cdot H_2O$. Calculated, %: C 59.88; H 7.15; N 5.37.

1-Methyl-3-{2-[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide (IIIb). Yield 78%, mp 221–223°C, $[\alpha]_D^{22}$ +66.6 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3414 (OH), 2940 (C–H), 1715 (O–C=O), 1607 (C=O), 1561, 1499 (C=C), 1459 (C–H), 1388 (C–H), 1353, 1249, 1176, 1107, 1052, 973. ^{1}H NMR spectrum, δ, ppm: 1.16 d (3H, Me, *J* 7.2 Hz), 1.18 d (3H, Me, *J* 7.2 Hz), 1.24 s (3H, Me), 1.26 s (3H, Me), 1.46 m (2H, H^{5a,9a}), 1.65-1.87 m (5H, C^{6}H$_2$, C^{7}H$_2$, H^{9e}), 2.17 d.d (1H, H^{8a}, *J* 12.6, 1.8 Hz), 2.66 m (1H, H^{5e}), 2.91 m (2H, C^{10}H$_2$), 3.40 m (1H, C<u>H</u>Me$_2$, *J* 7.2 Hz), 3.66 s (3H, OMe), 4.05 s (3H, NMe), 6.06 d (1H, NCH$_2$, *J* 18.3 Hz), 6.28 d (1H, NCH$_2$, *J* 18.3 Hz), 7.01 s (1H, H^1), 7.46 m (1H$_{Ht}$), 7.53 m (1H$_{Ht}$), 7.83 s (1H, H^4), 10.09 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.30, 18.20,

21.07, 23.85, 23.90, 24.76, 28.56, 30.03, 36.44, 36.60, 37.04, 37.69, 44.57, 47.34, 51.77, 57.22, 122.61, 123.90, 125.38, 127.49, 130.60, 138.04, 141.17, 146.49, 147.39, 178.77, 193.15. Found, %: C 62.17; H 6.62; N 5.30. $C_{27}H_{37}BrN_2O_3$. Calculated, %: C 62.66; H 7.21; N 5.41.

1-Vinyl-3-{2-[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide, hemihydrate (IIIc). Yield 25%, mp 200–202°C, $[\alpha]_D^{22}$ +71.9 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3401 (OH), 2940 (C–H), 1714 (O–C=O), 1655 (C=O), 1608 (C=C), 1551, 1499 (C=C), 1459 (C–H), 1386 (C–H), 1355 (C–H), 1249 (C–O–C), 1180, 1135, 1108, 1052, 1014, 967, 914. ^{1}H NMR spectrum, δ, ppm: 1.17 d (3H, Me, *J* 6.6 Hz), 1.19 d (3H, Me, *J* 6.6 Hz), 1.25 s (3H, Me), 1.27 s (3H, Me), 1.44 m (2H, $H^{5a,9a}$), 1.66–1.87 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.18 m (1H, H^{8a}), 2.68 m (1H, H^{5e}), 2.92 m (2H, $C^{10}H_2$), 3.42 m (1H, C<u>H</u>Me_2, *J* 6.6 Hz), 3.66 s (3H, OMe), 5.44 d.d (1H, CH=, *J* 9.0, 3.0 Hz), 5.90 d.d (1H, CH=, *J* 15.0, 3.0 Hz), 6.15 d (1H, NCH_2, *J* 18.0 Hz), 6.39 d (1H, NCH_2, *J* 18.0 Hz), 7.11 s (1H, H^1), 7.28 d.d (1H, CH, *J* 15.0, 9.0 Hz), 7.56 s ($1H_{Ht}$), 7.66 s ($1H_{Ht}$), 7.86 s (1H, H^4), 10.74 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.48, 18.39, 21.25, 24.04, 24.95, 28.81, 30.25, 36.67, 37.28, 37.90, 44.76, 47.55, 51.91, 57.55, 58.32, 110.47, 118.04, 124.57, 125.79, 127.75, 128.15, 137.17, 141.74, 146.86, 147.81, 153.65, 178.95, 192.76. Found, %: C 62.71; H 6.33; N 5.62. $C_{28}H_{37}BrN_2O_3 \cdot {}^1/_2H_2O$. Calculated, %: C 62.44; H 7.11; N 5.20.

1-Isopropyl-3-{2-{(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide (IIId). Yield 64%, mp 237–238°C, $[\alpha]_D^{22}$ +64.1 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3410 (OH), 2937 (C–H), 1716 (O–C=O), 1608 (C=O), 1553, 1499 (C=C), 1463 (C–H), 1386 (C–H), 1347, 1247, 1181, 1154, 1134, 1110, 1047, 971, 887. ^{1}H NMR spectrum, δ, ppm: 1.18 d (3H, Me, *J* 7.2 Hz), 1.20 d (3H, Me, *J* 7.2 Hz), 1.26 s (3H, Me), 1.27 s (3H, Me), 1.47 m (2H, H^{9a}, H^{5a}), 1.65 d [6H, NCH(<u>C</u>H_3]$_2$, *J* 6.6 Hz), 1.69–1.88 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.18 d.d (1H, H^{8a}, *J* 12.6, 2.1 Hz), 2.71 m (1H, H^{5e}), 2.92 m (2H, $C^{10}H_2$), 3.43 m (1H, CHAr, *J* 7.2 Hz), 3.66 s (3H, OMe), 4.76 m [1H, NC<u>H</u>$(CH_3]_2$, *J* 6.6 Hz), 6.11 d (1H, NCH_2, *J* 18.3 Hz), 6.34 d (1H, NCH_2, *J* 18.3 Hz), 7.10 s (1H, H^1), 7.33 m ($1H_{Ht}$), 7.39 m ($1H_{Ht}$), 7.87 s (1H, H^4), 10.60 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.23, 18.14, 21.01, 22.76, 23.83, 23.87, 24.67, 28.46, 29.95, 36.38, 37.00, 37.61, 44.50, 47.27, 51.68, 53.11, 57.04, 119.22, 123.99, 125.35, 127.34, 130.68, 136.42, 140.92, 146.31, 147.31, 178.70, 193.25. Found, %: C 63.28; H 6.95; N 5.10. $C_{29}H_{41}BrN_2O_3$. Calculated, %: C 63.85; H 7.58; N 5.13.

1-*tert*-Butyl-3-{2-[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazole-3-olium bromide (IIIe). Yield 75%, mp 244–246°C, $[\alpha]_D^{22}$ +62.6 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3404 br (OH), 2938 (C–H), 1715 (O=C–O), 1606 (C=O), 1551, 1466, 1388, 1355, 1248, 1200, 1134, 1054, 970, 882, 754. ^{1}H NMR spectrum, δ, ppm: 1.19 d (3H, Me, *J* 6.9 Hz), 1.21 d (3H, Me, *J* 6.9 Hz), 1.27 s (6H, 2Me), 1.47 m (2H, H^{9a}, H^{5a}), 1.68-1.84 m (14H, *tert*-C_4H_9, C^6H_2, C^7H_2, H^{9e}), 2.18 d.d (1H, H^{8a}, *J* 12.3, 1.8 Hz), 2.73 m (1H, H^{5e}), 2.92 m (2H, $C^{10}H_2$), 3.43 m (1H, CHAr, *J* 6.9 Hz), 3.66 s (3H, OMe), 6.16 d (1H, NCH_2, *J* 18.6 Hz), 6.40 d (1H, NCH_2, *J* 18.6 Hz), 7.10 s (1H, H^1), 7.34 m (2H, H_{Ht}), 7.90 s (1H, H^4), 10.77 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.21, 17.37, 18.09, 18.11, 21.03, 23.87, 24.59, 28.35, 30.02, 36.36, 37.01, 37.53, 44.53, 47.27, 51.63, 57.74, 121.89, 125.75, 127.16, 128.88, 130.73, 134.51, 138.45, 146.11, 147.31, 178.73, 193.20. Found, %: C 63.88, H 7.47; N 5.12. $C_{30}H_{43}BrN_2O_3$. Calculated, %: C 64.39; H 7.75; N 5.01.

1-Benzyl-3-{2-[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide (IIIf). Yield 78%, mp 232–234°C, $[\alpha]_D^{22}$ +60.5 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3398 (OH), 2943 (C–H), 1715 (O–C=O), 1607 (C=O), 1557, 1498 (C=C), 1455 (C–H), 1387 (C-H), 1360 (C-H), 1248, 1192, 1161, 1135, 1109, 1045, 971. ^{1}H NMR spectrum, δ, ppm: 1.17 d (3H, Me, *J* 7.2 Hz), 1.19 d (3H, Me, *J* 7.2 Hz), 1.26 s (3H, Me), 1.27 s (3H, Me), 1.46 m (2H, H^{9a}, H^{5a}), 1.64–1.88 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.18 d.d (1H, H^{8a}, *J* 12.3, 2.1 Hz), 2.67 m (1H, H^{5e}), 2.91 m (2H, $C^{10}H_2$), 3.42 m (1H, C<u>H</u>Me_2, *J* 7.2 Hz), 3.66 s (3H, OMe), 5.47 s (2H, PhC<u>H</u>$_2$), 6.06 d (1H, NCH_2, *J* 18.0 Hz), 6.31 d (1H, NCH_2, *J* 18.0 Hz), 7.11 s (1H, H^1), 7.16 m ($1H_{Ht}$), 7.37 m ($1H_{Ht}$), 7.42 m (5H, Ph), 7.84 s (1H, H^4), 10.63 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.32, 18.21, 21.09, 23.89, 23.93, 24.78, 28.56, 30.06, 36.45, 37.07, 37.71, 44.57, 47.36, 51.78, 53.22, 57.24, 120.96, 124.17, 125.48, 127.51, 128.64, 129.29, 129.34, 130.58, 132.51, 137.65, 141.21, 146.52, 147.46, 178.78, 192.97. Found, %: C 67.32; H 6.93; N 4.72. $C_{33}H_{41}BrN_2O_3$. Calculated, %: C 66.77; H 6.96; N 4.72.

3-{2-[(4b*S*,8*R*)-2-Isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octa-hydrophenanthren-3-yl]-2-oxoethyl}-1-phenyl-1*H*-imidazol-3-olium bromide, hydrate (IIIg). Yield 61%, mp 170–172°C (MeCN–ether), $[\alpha]_D^{22}$ +65.3 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3402 ш (OH), 2944 (C–H), 1715 (O–C=O), 1602 (C=O), 1553, 1497, 1460, 1355, 1248, 1134, 1108, 1071, 972, 910, 813. ^1H NMR spectrum, δ, ppm: 1.18 d (3H, Me, *J* 6.6 Hz), 1.20 d (3H, Me, *J* 6.6 Hz), 1.25 s (3H, Me), 1.26 s (3H, Me), 1.46 m (2H, H^{9a}, H^{5a}), 1.64–1.90 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.16 d.d (1H, H^{8a}, *J* 12.3, 2.1 Hz), 2.72 m (1H, H^{5e}), 2.92 m (2H, $C^{10}H_2$), 3.45 m (1H, C<u>H</u>Me_2, *J* 6.6 Hz), 3.66 s (3H, OMe), 6.30 d (1H, NCH_2, *J* 18.0 Hz), 6.54 d (1H, NCH_2, *J* 18.0 Hz), 7.11 s (1H, H^1), 7.51–7.57 m (3H, $2H_{arom} + H_{Ht}$), 7.64 m ($1H_{Ht}$), 7.69 m ($3H_{arom}$), 7.92 s (1H, H^4), 10.64 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.19, 18.08, 20.99, 23.84, 24.61, 28.48, 29.95, 36.34, 36.97, 37.53, 37.54, 44.51, 47.24, 51.63, 57.51, 119.78, 121.52, 124.96, 125.49, 127.30, 129.93, 130.21, 130.73, 134.15, 136.29, 140.88, 146.31, 147.29, 178.67, 193.24. Found, %: C 64.47; H 7.05; N 4.67. $C_{32}H_{39}BrN_2O_3 \cdot H_2O$. Calculated, %: C 64.30; H 6.91; N 4.69.

3-{2-[(4b*S*,8*R*)-2-Isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octa-hydrophenanthren-3-yl]-2-oxoethyl]-1-(2-methylphenyl)-1*H*-imidazol-3-olium bromide, hydrate (IIIh). Yield 88%, mp 241–243°C, $[\alpha]_D^{22}$ +59.4 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3407 (OH воды), 2939, 1715, 1606, 1551, 1464, 1388 w, 1355 w, 1248, 1200, 1133, 1107, 1055, 970, 754. ^1H NMR spectrum, δ, ppm: 1.19 d (3H, Me, *J* 6.9 Hz), 1.22 d (3H, Me, *J* 6.9 Hz), 1.26 s (3H, Me), 1.27 s (3H, Me), 1.47 m (2H, H^{9a}, H^{5a}), 1.62-1.88 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.17-2.21 m (4H, H^{8a} + <u>Me</u>Ar), 2.82 m (1H, H^{5e}), 2.92 m (2H, $C^{10}H_2$), 3.47 m (1H, C<u>H</u>Me_2, *J* 6.9 Hz), 3.66 s (3H, OMe), 6.38 d (1H, NCH_2, *J* 18.0 Hz), 6.83 d (1H, NCH_2, *J* 18.0 Hz), 7.11 s (1H, H^1), 7.21 t (1H, H_{Ht}, *J* 1.8 Hz), 7.23 s ($1H_{arom}$), 7.35-7.48 m ($3H_{arom}$), 7.68 t (1H, H_{Ht}, *J* 1.8 Hz), 8.04 s (1H, H^4), 10.30 t (1H, NCH=N, *J* 1.8 Hz). ^{13}C NMR spectrum, δ, ppm: 16.18, 17.48, 18.05, 20.99, 23.84, 24.55, 28.32, 28.40, 29.98, 36.33, 36.98, 37.50, 44.51, 47.24, 51.59, 57.72, 121.88, 124.89, 125.69, 125.77, 127.13, 128.84, 130.69, 130.74, 130.77, 132.87, 134.49, 138.42, 140.59, 146.07, 147.27, 178.68, 193.21. Found, %: C 64.59; H 6.62; N 4.15. $C_{33}H_{41}BrN_2O_3 \cdot H_2O$. Calculated, %: C 64.80; H 7.09; N 4.58.

1-(2,6-Dimethylphenyl)-3-{2-[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl]-2-oxoethyl}-1*H*-imidazol-3-olium bromide, hemihydrate (IIIi). Yield 58%, mp 243–245°C, $[\alpha]_D^{22}$ +65.0 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3376 (OH), 2937, 1720 (O-C=O), 1548, 1465, 1380 1249 1185 1105, 1050, 959, 888. ^1H NMR spectrum, δ, ppm: 1.19 d (3H, Me, *J* 6.9 Hz), 1.22 d (3H, Me, *J* 6.9 Hz), 1.27 s (6H, 2Me), 1.47 m (2H, H^{9a}, H^{5a}), 1.63–1.88 m (11H, C^6H_2, C^7H_2, H^{9e}, 2<u>Me</u>Ar), 2.19 m (1H, H^{8a}), 2.74 m (1H, H^{5e}), 2.91 m (2H, $C^{10}H_2$), 3.42 m (1H, C<u>H</u>Me_2, *J* 6.9 Hz), 3.66 s (3H, OMe), 6.16 d (1H, NCH_2, *J* 18.3 Hz), 6.39 d (1H, NCH_2, *J* 18.3 Hz), 7.10 s (1H, H^1), 7.25 s (2H, H_{Ht}), 7.36 m ($3H_{arom}$), 7.90 c (1H, H^4), 10.70 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.30, 18.22, 21.09, 23.92, 24.74, 28.55, 29.83, 30.03, 36.47, 37.07, 37.66, 44.59, 47.37, 51.73, 57.10, 60.23, 118.53, 124.01, 125.54, 127.37, 130.81, 136.48, 140.96, 146.30, 147.45, 178.80, 193.57. Found, %: C 63.95; H 7.79; N 4.90. $C_{34}H_{43}BrN_2O_3 \cdot {}^1/_2H_2O$. Calculated, %: C 64.29; H 6.87; N 4.54.

3-{2-[(4b*S*,8*R*)-2-Isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octa-hydrophenanthren-3-yl]-2-oxoethyl}-1-mesityl-1*H*-imidazol-3-olium bromide (IIIj). Yield 89%, mp 225–226°C, $[\alpha]_D^{22}$ +61.2 (*c* 1, $CHCl_3$). IR spectrum, cm^{-1} (mull in mineral oil): 3400 w (OH), 1728 (O–C=O), 1697, 1608 (C=O), 1549, 1245, 1209, 1132, 1109, 1063, 1045, 970, 871. ^1H NMR spectrum, δ, ppm: 1.18 d (3H, Me, *J* 7.2 Hz), 1.21 d (3H, Me, *J* 7.2 Hz), 1.26 s (6H, 2Me), 1.45 m (2H, H^{9a}, H^{5a}), 1.64–1.89 m (5H, C^6H_2, C^7H_2, H^{9e}), 2.10 m (7H, H^{8a} + 2<u>Me</u>Ar), 2.34 s (3H, <u>Me</u>Ar), 2.82 m (1H, H^{5e}), 2.91 m (2H, $C^{10}H_2$), 3.46 m (1H, C<u>H</u>Me_2, *J* 7.2 Hz), 3.66 s (3H, OMe), 6.37 d (1H, NCH_2, *J* 18.0 Hz), 6.79 d (1H, NCH_2, *J* 18.0 Hz), 7.00 s (2H, $H^{3'}$, $H^{5'}$), 7.10 s (1H, H^1), 7.19 m ($1H_{Ht}$), 7.76 m ($1H_{Ht}$), 8.03 s (1H, H^4), 10.19 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 16.11, 17.17, 18.00, 20.70, 20.94, 23.80, 24.46, 28.24, 29.92, 36.25, 36.91, 37.41, 44.45, 47.18, 51.54, 57.63, 122.04, 124.77, 125.65, 127.03, 129.36, 130.37, 130.76, 134.00, 138.39, 140.44, 140.79, 145.97, 147.17, 178.66, 193.24. Found, %: C 67.94; H 6.92; N 4.50. $C_{35}H_{45}BrN_2O_3$. Calculated, %: C 67.62; H 7.30; N 4.51.

General procedure of Suzuki–Miyaura cross-coupling. A mixture of 6 mg (0.028 mmol) of $Pd(OAc)_2$, 0.028 mmol of imidazolium salt, 60 mg (4.34 mmol) of K_2CO_3 in 70 ml of DMF was heated at 90°C for 15–20 min till the dissolution of the most part of $Pd(OAc)_2$ with the formation of a yellow solution of the complex Pd(0)–NHC, then was added 480 mg

(2.8 mmol) of *p*-bromotoluene (2 ml of a solution in DMF of the concentration 240 mg/ml), 380 mg (2.8 mmol) of *p*-tolylboric acid, 770 mg (5.6 mmol) of K_2CO_3, and 0.4 ml of dodecane as an internal reference. The mixture was heated at 90°C over 5 h (to the end of the experiment palladium black started to form), afterwards the reaction mixture was cooled, the inorganic salts were filtered off, washed with 20 ml of DMF, the solution was evaporated in a vacuum to the volume 4–5 ml, the residue was diluted with 100 ml of water, 30 ml of brine (to destroy the emulsion), and the mixture was extracted with dichloromethane (3–4 × 25 ml) till the transparent solution, the extract was dried with $MgSO_4$, and the composition of the mixture was analyzed by GC-MS method. The quantitative determination was performed using the calibration plots obtained with specially prepared mixtures from pure *p*-bromotoluene, dodecane, and di-*p*-tolyl. The conversion was estimated from the amount of the recovered *p*-bromotoluene, the yield, from the amount of the formed di-*p*-tolyl.

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