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N-Heterocyclic Carbenes: V.* Synthesis of Imidazolium Salts from Lupane Series

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Abstract—By the reaction of *N*-alkyl- and *N*-arylimidazoles with 30-bromo-3,28-diacetoxylup-20(29)-ene a series was synthesized of unsymmetrically substituted chiral imidazolium bromides with a lupane fragment.

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The use of N-heterocyclic carbenes as ligands in Pd-catalyzed cross-coupling reactions after the pioneering research of Herrmann [2] became an everyday practice of the organic synthesis [3]. The development of this field of chemistry occurs along the following main directions: the application of preliminary prepared stable N-heterocyclic palladium(II) complexes ("well-defined catalysts") as precursors of active catalysts [4], synthesis of chiral imidazolium salts for enantioselective conversions [5], employing mixed phosphano-carbene catalysts [6], the use of so-called "abnormal" carbenes [7], the involvement into the reaction of inactive chloroarenes [8], application of sterically hindered ligands to raise the yield of cross-coupled products [9]. In the latter case the interest was not yet directed to the possibility to use imidazolium salts underlain by di- and triterpene matrices. However we recently demonstrated the possibility to synthesize imidazolium salts from methyl dehydroabietate and successfully used them as N-heterocyclic carbene ligands in Suzuki–Miyaura reaction [10]. The aim of this study was the preparation of imidazolium salts from triterpenes, namely, from betulin 3,28-diacetate and testing their possible application as N-heterocyclic carbene ligands in cross-coupling reactions.

Some 30-dialkylamino [11] and 30-hydroxylamino lupane derivatives [12] have been described synthesized for the study of their biological action, whereas imidazole-substituted triterpenes are yet poorly understood; as one example 1-[3,12-dioxo-2-cyanooleana-1,9(11)-dien-28-oyl]-4-ethynylimidazole may be cited, a new antiphlogistic and cytoprotective agent −[13].

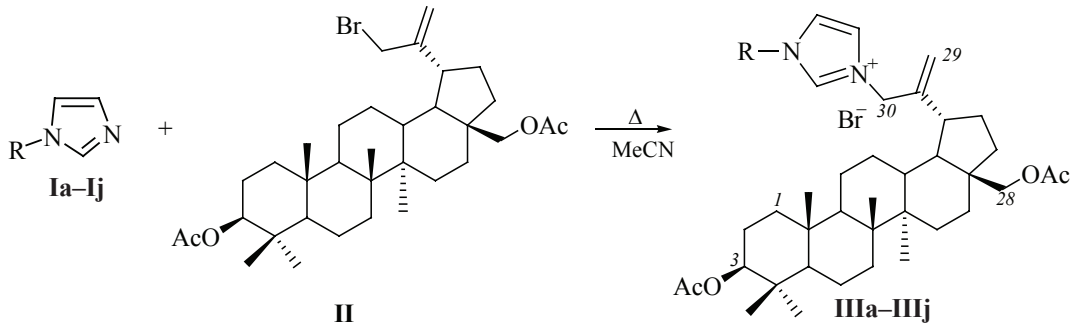
Compounds **IIIa–IIIj** were obtained from 1-alkyl(aryl)-1*H*-imidazoles and 30-bromo-3,28-diacetoxylup-20(29)-ene (**II**) in boiling acetonitrile (see the scheme).

Synthesized salts **IIIa–IIIj** were purified by column chromatography on silica gel and were isolated as hydrates or solvates with ethanol of diverse composition in 27–98% yields (previously the inclusion of water into the crystal lattice was observed in a number of imidazolium salts based on diterpenes [1]). Compounds **IIIa–IIIj** are light-yellow crystalline or glassy substances soluble in acetone, toluene, chloroform, ethyl acetate, poorly soluble in hexane. Their structure was confirmed by IR, ^{1}H and ^{13}C NMR spectra (see EXPERIMENTAL). The IR spectra of compounds **IIIa–IIIj** contain the bands of two acetoxy groups at 1727–1734 cm^{-1} showing the stability of the ester function under the reaction conditions. All samples contain a broadened band at 3340 cm^{-1} corresponding to OH groups of water and (or) of ethanol solvate, whose presence is also confirmed by the date of ^{1}H NMR spectra (a triplet at δ 1.17–1.25 and a quartet at δ 3.65–3.73 ppm, *J* 6.9–7.2 Hz).

For the estimation of the possibility to use new ligands

*For Communication IV, see [1].

Scheme.



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**).

in cross-coupling reaction we chose Heck model reaction [14] between iodobenzene and butyl acrylate in the presence of 2 mol% Pd(II) acetate, 3 mol% of NHC-ligand, 3 equiv of triethylamine as a base and pentadecane as an internal reference. The application of complexes NHC–Pd(II) in Heck reaction is described in numerous papers [15]. It is generally agreed now that the catalytically active are mono-coordinated Pd(0) species generated in the reaction mixture at the thermal decay of the first formed bicoordinated complexes [16], therefore we have taken the ratio Pd–ligand equal to 1:1.5. The reaction was carried out for 1.5 h in DMF at 90°C (the formation of palladium black was observed to the end of experiments). The composition of the mixture was analyzed by GC-MS method. The quantitative evaluation of the mixtures composition was performed by comparison with calibration curves measured on arbitrary prepared mixtures of pure iodobenzene and butyl cinnamate. The conversion was estimated by the amount of the remaining iodobenzene, the yield, by the quantity of the formed butyl cinnamate. The experiments showed that in the above conditions for NHC-ligands **IIIa, IIIb, IIId–IIIj** in the model reaction the conversion attained 95–97%, the yields of butyl cinnamate 54–88%. Ligand **IIIc** containing a vinyl group in the imidazole ring inhibited Heck reaction: conversion was 6%, no product of cross-coupling was detected.

EXPERIMENTAL

Imidazole, *N*-methylimidazole, *N*-benzylimidazole, N-vinylimidazole, and N-phenylimidazole were purchased from Alfa Aesar (Lancaster); 1-(2-methylphenyl)-1*H*-imidazole, 1-(2,6-dimethylphenyl)-1*H*-imidazole, and 1-mesityl-1*H*-imidazole were synthesized by method [17]. Melting points were measured on an instrument OptiMelt Automated Melting Point System (Stanford Research Systems). As the melting point was considered the threshold melting temperature at a heating rate 1 deg/min. TLC was performed on Sorbfil plates, eluent chloroform–ethanol, 5:1 v/v, development under UV irradiation or by treatment with 5% H_2SO_4 followed by heating to 120–150°C. The column chromatography was carried out on Silica gel 60 (0.035–0.070 mm, 220–440 mesh, Alfa Aesar, eluent chloroform–ethyl acetate, 10 : 1, adding 2% of ethanol to the end of chromatographing. IR spectra were registered on a spectrophotometer Bruker IFS 66ps from mulls in mineral oil or a thin film prepared from a chloroform solution. ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a spectrometer Varian Mercury+300 at 300 and 75 MHz respectively, internal reference for ^1H NMR spectra HMDS (δ_H 0.055 ppm), for ^{13}C NMR spectra the solvent signal served as internal reference ($CHCl_3$, δ_C 77.0 ppm). The optical rotation was measured on a polarimeter Perkin Elmer 341 in chloroform stabilized with 0.5% of ethanol, and it is reported in the units 10^{-1} deg g^{-1} cm^2. The elemental analysis was carried out in the Institute of Technical Chemistry, Ural Division, Russian Academy of Sciences on an analyzer Leco CHNS 9321P.

Synthesis of imidazolium salts of lupane series. General procedure. A solution of 599 mg (1 mmol) of 30-bromo-3,28-diacetoxylup-20(29)-ene [18] and 1 mmol of an appropriate imidazole in 30 ml of acetonitrile was boiled for 6–8 h, evaporated, the residue was subjected to column chromatography.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1*H*-imid-

azol-3-olium bromide·C_2H_5OH (IIIa). Yield 27%. Light-yellow crystals, mp 144.3°C, R_f 0.73, $[\alpha]_D^{25}$ +1.0 (*c* 0.5, $CHCl_3$). ANDQ IR spectrum, cm^{-1} (from thin film): 3427 br.w (OH), 2941, 2871, 1730, 1651 w, 1560 w, 1456, 1372, 1246, 1155 w, 1031, 979, 907, 755. ^1H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.84 s (6H, 2Me), 0.97 s (3H, Me), 1.02 s (3H, Me), 1.23 t (3H, $C\underline{H}_3CH_2O$, *J* 7.2 Hz), 1.39 s (3H, Me), 2.03 s (3H, MeC=O), 2.06 s (3H, MeC=O), 2.27 m (1H, H^{19}), 3.69 q (2H, $CH_3C\underline{H}_2O$, *J* 7.2 Hz), 3.75 d (1H, H^{28}, *J* 10.8 Hz), 4.23 d (1H, H^{28}, *J* 10.8 Hz), 4.46 m (1H, H^3), 4.71 s (1H, H^{29}), 4.94 d (1H, H^{30}, *J* 15.0 Hz), 5.04 d (1H, H^{30}, *J* 15.0 Hz), 5.14 s (1H, H^{29}), 6.87 s ($1H_{Ht}$), 7.13 s (1H, NH), 7.49 s ($1H_{Ht}$), 10.46 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.60, 15.87, 16.01, 16.34, 17.98, 20.74, 20.88, 21.18, 23.51, 26.75, 27.16, 27.79, 29.49, 31.35, 33.95, 34.08, 36.89, 37.15, 37.63, 38.26, 40.74, 42.53, 43.47, 46.28, 50.03, 51.31, 54.17, 55.19, 57.98, 62.02, 80.72, 112.39, 122.25, 128.81, 148.18, 170.89 (C=O), 171.34 (C=O). Found, %: C 65.33; H 8.65; N 3.72. $C_{37}H_{57}BrN_2O_4·C_2H_5OH$. Calculated, %: C 65.07; H 8.82; N 3.89.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1-methyl-1*H*-imidazol-3-olium bromide·$^1/_2C_2H_5OH$ (IIIb). Yield 79%. Light-yellow crystals, mp 141.3°C, R_f 0.24, $[\alpha]_D^{21}$ +2.6 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (mull in mineral oil): 3405 br (OH), 1729, 1563, 1244, 1029, 896, 723. ^1H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.83 s (3H, Me), 0.84 s (3H, Me), 0.96 s (3H, Me), 1.01 s (3H, Me), 1.23 t (1.5H, $^1/_2C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.38 s (3H, Me), 2.03 s (3H, MeC=O), 2.06 s (3H, MeC=O), 2.26 m (1H, H^{19}), 3.71 q (1H, $^1/_2CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.79 d (1H, H^{28}, *J* 11.1 Hz), 4.13 s (3H, NMe), 4.23 d (1H, H^{28}, *J* 11.1 Hz), 4.45 m (1H, H^3), 4.77 s (1H, H^{29}), 4.92 d (1H, H^{30}, *J* 15.6 Hz), 5.02 d (1H, H^{30}, *J* 15.6 Hz), 5.15 s (1H, H^{29}), 7.15 s ($1H_{Ht}$), 7.27 s (1H, NH), 7.49 s ($1H_{Ht}$), 10.66 s (1H, NCH=N). Found, %: C 67.22; H 8.27; N 4.50. $C_{38}H_{59}BrN_2O_4·^1/_2C_2H_5OH$. Calculated, %: C 65.90; H 8.79; N 3.94.

[3,28-Diacetoxylup-20(29)-en-30-yl]-1-vinyl-3-1*H*-imidazol-3-olium bromide·$C_2H_5OH·H_2O$ (IIIc). Yield 45%. Light-yellow crystals, mp 148.9°C, R_f 0.38, $[\alpha]_D^{25}$ +4.8 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3421 br (OH), 2943, 2872, 1728, 1653 w, 1556, 1455, 1372, 1248, 1168, 1031, 977, 912, 755. ^1H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 0.96 s (3H, Me), 1.01 s (3H, Me), 1.23 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.38 s (3H, Me), 2.03 s (3H, MeC=O), 2.05 s (3H, MeC=O), 2.29 m (1H, H^{19}), 3.73 q (2H, $CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.75 d (1H, H^{28}, *J* 10.8 Hz), 4.38 d (1H, H^{28}, *J* 10.8 Hz), 4.45 m (1H, H^3), 4.82 s (1H, H^{29}), 5.02 d (1H, H^{30}, *J* 15.0 Hz), 5.10 d (1H, H^{30}, *J* 15.0 Hz), 5.16 s (1H, H^{29}), 5.45 d.d ($H_CC=$, J_{ca} 9.0, J_{cb} 3.3 Hz), 5.96 d.d ($H_bC=$, J_{ba} 15.6, J_{bc} 3.3 Hz), 7.29 s ($1H_{Ht}$), 7.47 ($H_aC=$, J_{ab} 15.6, J_{ac} 9.0 Hz), 7.70 s ($1H_{Ht}$), 11.14 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm : 14.52, 15.79, 15.95, 16.27, 17.90, 20.67, 20.86, 21.13, 23.43, 26.67, 27.11, 27.72, 29.41, 31.26, 33.85, 34.01, 36.81, 37.12, 37.54, 38.17, 40.65, 42.45, 43.16, 46.17, 49.88, 49.93, 54.24, 55.10, 62.04, 80.69, 109.95, 113.00, 119.57, 122.82, 128.11, 136.13, 147.67, 171.86 (C=O), 171.33 (C=O). Found, %: C 63.62; H 7.93; N 4.09. $C_{39}H_{59}BrN_2O_4·C_2H_5OH·H_2O$. Calculated, %: C 64.16; H 8.61; N 3.74.

3-[(3,28-Diacetoxylup-20(29)-en-30-yl]-1-isopropyl-1*H*-imidazol-3-olium bromide·$C_2H_5OH·2H_2O$ (IIId). Yield 84%. Light-yellow glassy substance, mp 164.9°C, R_f 0.38, $[\alpha]_D^{21}$ –1.2 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3409 br.w (OH), 2943, 2873, 1729, 1649 w, 1557, 1457, 1372, 1247, 1150, 1031, 978. ^1H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 0.96 s (3H, Me), 1.02 s (3H, Me), 1.23 t (6H, $2C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.38 s (3H, Me), 1.65 d (6H, $\underline{Me}_2CH$, *J* 6.6 Hz), 2.03 s (3H, MeC=O), 2.05 s (3H, MeC=O), 2.30 m (1H, H^{19}), 3.71 q (4H, $2CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.76 d (1H, H^{28}, *J* 11.1 Hz), 4.23 d (1H, H^{28}, *J* 11.1 Hz), 4.45 m (1H, H^3), 4.77 s (1H, H^{29}), 4.91 m (1H, $Me_2C\underline{H}$, *J* 6.6 Hz), 5.01 d (1H, H^{30}, *J* 15.9 Hz), 5.09 d (1H, H^{30}, *J* 15.9 Hz), 5.14 s (1H, H^{29}), 7.16 m ($1H_{Ht}$), 7.29 m ($1H_{Ht}$), 10.91 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.49, 15.74, 15.88, 16.22, 17.85, 20.63, 20.79, 21.07, 22.91, 22.94, 23.38, 26.62, 27.00, 27.67, 29.35, 31.16, 33.81, 33.95, 36.75, 36.99, 37.49, 38.12, 40.60, 42.39, 43.16, 46.12, 49.83, 53.21, 53.93, 55.05, 61.94, 80.61, 112.62, 120.22, 122.29, 136.22, 148.00, 170.77 (C=O), 171.24 (C=O). Found, %: C 62.40; H 8.20; N 3.48. $C_{40}H_{63}BrN_2O_4·C_2H_5OH·2H_2O$. Calculated, %: C 62.90; H 9.01; N 3.58.

1-*tert*-Butyl-3-[3,28-diacetoxylup-20(29)-en-30-yl]-1*H*-imidazol-3-olium bromide·$C_2H_5OH·2H_2O$ (IIIe). Yield 88%. Light-yellow crystals, mp 147.7°C, R_f 0.46, $[\alpha]_D^{21}$ –0.6 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3402 br.w (OH), 2943, 1730, 1652 w, 1554, 1459,

1374, 1245, 1134, 1030, 979. ^{1}H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 0.96 s (3H, Me), 1.02 s (3H, Me), 1.25 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.38 s (3H, Me), 1.75 s (9H, $\underline{Me}_3C$), 2.03 s (3H, MeC=O), 2.05 s (3H, MeC=O), 2.32 m (1H, H*19*), 3.71 q (2H, $CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.77 d (1H, H*28*, *J* 11.1 Hz), 4.23 d (1H, H*28*, *J* 11.1 Hz), 4.45 m (1H, H*3*), 4.77 s (1H, H*29*), 5.12 s (1H, H*29*), 5.13 d (1H, H*30*, *J* 15.9 Hz), 5.20 d (1H, H*30*, *J* 15.9 Hz), 7.18 t (1H, H_{Ht}, *J* 1.8 Hz), 7.34 t (1H, H_{Ht}, *J* 1.8 Hz), 10.91 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.49, 15.72, 15.85, 16.19, 17.83, 20.63, 20.74, 21.03, 23.35, 26.60, 26.92, 27.65, 29.33, 29.88, 30.28, 31.09, 33.79, 33.91, 36.73, 36.99, 37.46, 38.11, 40.58, 42.37, 43.24, 46.11, 49.71, 49.82, 53.78, 55.03, 60.35, 61.91, 80.57, 112.42, 119.68, 122.31, 136.08, 148.11, 170.67 (C=O), 171.14 (C=O). Found, %: C 63.82; H 8.25; N 3.97. $C_{41}H_{65}BrN_2O_4 \cdot C_2H_5OH \cdot 2H_2O$. Calculated, %: C 63.61; H 9.31; N 3.45.

1-Benzyl-3-[3,28-diacetoxylup-20(29)-en-30-yl]-1*H*-imidazol-3-olium bromide·C_2H_5OH·H_2O (IIIf). Yield 98%. Light-yellow crystals, mp 171.1°C, R_f 0.42, $[\alpha]_D^{21}$ +1.1 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3401 br.w (OH), 2943, 2872, 1727, 1559, 1454, 1369, 1248, 1153, 1030, 978. ^{1}H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 0.94 s (3H, Me), 1.01 s (3H, Me), 1.23 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.38 s (3H, Me), 2.03 s (3H, MeC=O), 2.06 s (3H, MeC=O), 2.26 m (1H, H*19*), 3.71 q (2H, $CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.72 d (1H, H*28*, *J* 11.4 Hz), 4.24 d (1H, H*28*, *J* 11.4 Hz), 4.45 m (1H, H*3*), 4.77 s (1H, H*29*), 4.92 d (1H, H*30*, *J* 16.2 Hz), 4.99 d (1H, H*30*, *J* 16.2 Hz), 5.13 s (1H, H*29*), 5.61 s (2H, CH_2Ph), 7.12 m (1H_{Ht}), 7.20 t (1H_{Ht}), 7.40 m (3H, Ph), 7.47 m (2H, Ph), 10.81 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.70, 15.75, 15.88, 16.22, 17.85, 20.59, 20.78, 21.06, 23.39, 26.62, 27.05, 27.68, 29.39, 31.21, 33.83, 33.94, 36.75, 36.97, 37.49, 38.13, 40.59, 42.37, 43.03, 46.10, 49.85, 53.06, 54.18, 55.04, 61.95, 80.61, 112.80, 122.09, 122.31, 128.75, 129.14, 133.07, 137.10, 147.80, 170.76 (C=O), 170.21 (C=O). Found, %: C 64.49; H 7.60; N 3.77. $C_{44}H_{63}BrN_2O_4 \cdot C_2H_5OH \cdot 2H_2O$. Calculated, %: C 65.04; H 8.49; N 3.37.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1-phenyl-1*H*-imidazol-3-olium bromide·C_2H_5OH·1.5H_2O (IIIg). Yield 47%. Light-yellow crystals, mp 155.8°C, R_f 0.45, IR spectrum, cm^{-1} (from thin film): 3412 br.w (OH), 2944, 2872, 1729, 1598, 1555, 1499, 1456, 1370, 1247, 1030, 978. ^{1}H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 0.96 s (3H, Me), 1.01 s (3H, Me), 1.23 t (3H, $C\underline{H}_3CH_2O$, *J* 7.2 Hz), 1.38 s (3H, Me), 2.03 s (3H, MeC=O), 2.06 s (3H, MeC=O), 2.35 m (1H, H*19*), 3.70 q (2H, $CH_3C\underline{H}_2O$, *J* 7.2 Hz), 3.74 d (1H, H*28*, *J* 10.2 Hz), 4.25 d (1H, H*28*, *J* 10.2 Hz), 4.45 m (1H, H*3*), 4.86 s (1H, H*29*), 5.17 s (1H, H*29*), 5.20 d (1H, H*30*, *J* 14.7 Hz), 5.35 d (1H, H*30*, *J* 14.7 Hz), 6.79 m (1H_{Ht}), 7.20 m (1H_{Ht}), 7.56 m (3H, Ph), 7.82 m (2H, Ph), 10.50 s (1H, NCH=N). Found, %: C 65.58; H 7.66; N 3.87. $C_{43}H_{61}BrN_2O_4 \cdot C_2H_5OH \cdot 1.5H_2O$. Calculated, %: C 65.67; H 8.57; N 3.40.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1-(2-methylphenyl)-1*H*-imidazol-3-olium bromide, monohydrate (IIIh). Yield 97%. Light-yellow crystals, mp 148.2°C, R_f 0.47, $[\alpha]_D^{21}$ +3.7 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (from thin film): 3402, 2944, 2872, 1730, 1553 1494, 1455, 1370 1246, 1030, 978. ^{1}H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.83 s (9H, 3 Me), 0.98 s (3H, Me), 1.02 s (3H, Me), 2.03 s (3H, MeC=O), 2.05 s (3H, MeC=O), 2.32 s (3H, MeAr), 2.95 br.s (1H, OH), 3.78 d (1H, H*28*, *J* 10.8 Hz), 4.25 d (1H, H*28*, *J* 10.8 Hz), 4.45 m (1H, H*3*), 4.86 s (1H, H*29*), 5.16 s (1H, H*29*), 5.30 d (1H, H*30*, *J* 15.6 Hz), 5.42 d (1H, H*30*, *J* 15.6 Hz), 7.37–7.48 m (6H, 2H_{Ht} + 4H_{arom}), 10.60 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.63, 15.86, 15.99, 16.31, 17.75, 17.96, 20.75, 20.85, 21.13, 23.48, 26.76, 27.15, 27.77, 29.48, 31.44, 33.93, 34.05, 36.87, 37.16, 37.60, 38.24, 40.73, 42.52, 43.29, 46.27, 49.97, 54.51, 55.15, 62.05, 80.72, 112.55, 122.97, 126.32, 127.64, 130.95, 131.89, 133.05, 133.58, 137.94, 148.48, 170.85 (C=O), 171.25 (C=O). Found, %: C 67.15; H 8.00; N 4.03. $C_{44}H_{63}BrN_2O_4 \cdot H_2O$. Calculated, %: C 67.15; H 8.38; N 3.58.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1-(2,6-dimethylphenyl)-1*H*-imidazol-3-olium bromide·C_2H_5OH (IIIi). Yield 56%. Light-yellow crystals, mp 156.5°C, R_f 0.37, $[\alpha]_D^{25}$ +6.6 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (mull in mineral oil): 3381 br (OH), 1734, 1550 w, 1239, 1102 w, 1029, 977, 781, 747. ^{1}H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.77 s (3H, Me), 0.78 s (3H, Me), 0.94 s (3H, Me), 0.97 s (3H, Me), 1.17 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.33 s (3H, Me), 1.96 s (3H, MeC=O), 2.00 s (3H, MeC=O), 2.09 s (3H, MeAr), 2.11 s (3H, MeAr), 2.33 m (1H, H*19*), 3.65 q (2H, $CH_3C\underline{H}_2O$,

J 6.9 Hz), 3.72 d (1H, H*28*, *J* 10.8 Hz), 4.19 d (1H, H*28*, *J* 10.8 Hz), 4.40 m (1H, H*3*), 4.73 s (1H, H*29*), 5.08 s (1H, H*29*), 5.29 d (1H, H*30*, *J* 15.0 Hz), 5.40 d (1H, H*30*, *J* 15.0 Hz), 7.08–7.47 m (5H, $2H_{Ht}$ + $3H_{arom}$), 10.48 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.65, 15.97, 16.30, 17.21, 17.59, 17.66, 17.95, 20.74, 20.84, 21.12, 23.47, 26.76, 27.16, 27.76, 29.48, 31.47, 33.90, 34.06, 36.86, 37.17, 37.58, 38.21, 40.71, 42.52, 43.31, 46.26, 49.93, 54.38, 55.14, 61.99, 80.71, 111.96, 122.92, 123.46, 128.28, 129.09, 130.91, 132.95, 134.54, 135.38, 138.34, 148.79, 170.82 (C=O), 171.22 (C=O). Found, %: C 67.93; H 7.92; N 3.95. $C_{45}H_{65}BrN_2O_4 \cdot C_2H_5OH$. Calculated, %: C 68.51; H 8.69; N 3.40.

3-[3,28-Diacetoxylup-20(29)-en-30-yl]-1-mesityl-1*H*-imidazol-3-olium bromide·$C_2H_5OH \cdot H_2O$ (IIIj). Yield 38%. Light-yellow crystals, mp 160.6°C, R_f 0.50, $[\alpha]_D^{25}$ +5.2 (*c* 0.5, $CHCl_3$). IR spectrum, cm^{-1} (mull in mineral oil): 3400 br (OH), 1731, 1550 w, 1244, 1157, 1030, 977, 751. ^1H NMR spectrum, δ, ppm (multiplets of groups CH and CH_2 of lupane framework are not shown): 0.82 s (3H, Me), 0.83 s (3H, Me), 1.00 s (3H, Me), 1.02 s (3H, Me), 1.23 t (3H, $C\underline{H}_3CH_2O$, *J* 6.9 Hz), 1.39 s (3H, Me), 2.03 s (3H, MeC=O), 2.05 s (3H, MeC=O), 2.10 s (3H, MeAr), 2.12 s (3H, MeAr), 2.33 m (4H, MeAr + H*19*), 3.71 q (2H, $CH_3C\underline{H}_2O$, *J* 6.9 Hz), 3.77 d (1H, H*28*, *J* 10.5 Hz), 4.25 d (1H, H*28*, *J* 10.5 Hz), 4.45 m (1H, H*3*), 4.77 s (1H, H*29*), 5.13 s (1H, H*29*), 5.33 d (1H, H*30*, *J* 15.9 Hz), 5.50 d (1H, H*30*, *J* 15.9 Hz), 7.10 s ($2H_{arom}$), 7.17 s ($1H_{Ht}$), 7.47 s ($1H_{Ht}$), 10.55 s (1H, NCH=N). ^{13}C NMR spectrum, δ, ppm: 14.67, 15.86, 16.00, 16.33, 17.15, 17.58, 17.98, 20.75, 20.88, 20.96, 21.16, 23.50, 26.78, 27.17, 27.79, 29.50, 31.48, 33.93, 34.08, 36.88, 37.20, 37.61, 38.23, 40.73, 42.54, 43.32, 46.29, 49.95, 54.38, 55.16, 62.02, 80.74, 111.93, 123.02, 123.27, 129.03, 129.72, 130.50, 134.12, 134.96, 138.57, 141.18, 148.85, 170.87 (C=O), 171.28 (C=O). Found, %: C 67.24; H 7.98; N 3.82. $C_{46}H_{67}BrN_2O_4 \cdot C_2H_5OH \cdot H_2O$. Calculated, %: C 67.12; H 8.63; N 3.33.

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