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N-Heterocyclic Carbenes. IV.[1] Synthesis of Symmetrical and Unsymmetrical Imidazolium Salts with Abietane Moiety

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ABSTRACT: *Methyl 12-chloromethyl-dehydroabietate reacts with 1-benzyl- and 1-arylimidazoles to give unsymmetrically substituted imidazolium chlorides (***1a–i***), with abietane moiety. Starting from methyl 12-aminodehydroabietate, symmetrically substituted diterpene-based salts of imidazolinium (***4***) and imidazolium (***5***) were synthesized. Anion exchange afforded corresponding (***1e**BF_4*) and (***1e**PF_6*). The new compounds were tested as ligands for a Pd-catalyzed Suzuki-Miyaura reaction. The molecular structure of (***1e***) is reported.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:5–15, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20745

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[1]For III see ref. [1].

INTRODUCTION

Substituted imidazolylidenes and imidazolinylidenes represent the largest group among other *N*-heterocyclic carbenes (NHCs) [2]. *N*-Heterocyclic carbenes are widely used as reagents in modern organic chemistry [3]; the NHC-transition metal complexes have found wide applications in organometallic chemistry [4], as well as in other fields of chemistry [5]. Outstanding results were obtained with NHCs as ligands for the 2nd generation of Grubb's catalysts [6] and Pd-mediated cross-coupling reactions [7]. In the latter case, to obtain reasonable yields, sterically demanding NHCs need to be used, of which their high activity may be rationalized by the acceleration of the reductive elimination stage in the catalytic cycle [7b,8]. Despite the availability of a wide variety of versatile NHC-based ligands, the intensive development of new imidazolium salts continues today due to the fact that varying the steric bulk of the substituents surrounding the metal center offers promising opportunities for tuning the NHC ligands. Currently, a great deal of imidazolium salts exhibiting diverse structural

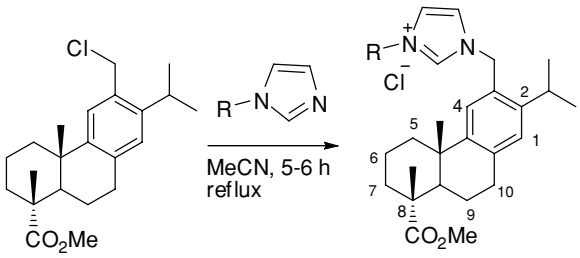
motifs with high steric demands has been synthesized. Among them are derivatives of substituted naphthalene [9], terphenyl [10], phenanthrene and anthracene [11], phenanthroline [12], diamantane (dimer of adamantane) [13], and highly hindered aromatics [14]. Imidazolium salts containing monoterpenes have been described [15], but derivatives of di- and triterpenes are still unknown. In our preliminary communication [16], we disclosed unsymmetrical diterpene imidazolium salts from methyl 12-chloromethyl-dehydroabietate and alkylimidazoles. In this work, we report the synthesis of imidazolinium and imidazolium salts from diterpenes, methyl 12-aminodehydroabietate and methyl 12-chloromethyldehydroabietate, and the study of their catalytic activity in the Suzuki-Miyaura reaction. Compounds **1** and **5** represent the class of chiral imidazolium salts; some representative examples are documented [17].

We suppose that diterpene moiety with an *ortho-iso*-propyl group provides the necessary steric bulk of new ligands **1,4,5**.

RESULTS AND DISCUSSION

Our initial efforts were focused on the unsymmetrical ligands **1a–i**. Asymmetrical imidazolium salts were obtained by the reaction of methyl 12-chloromethyl-dehydroabietate [18] with corresponding 1-alkyl-, 1-benzyl-, or 1-aryl-1*H*-imidazoles (Scheme 1) in MeCN under reflux for 5 h. We had supposed that changing the R substituent allows for variation of the electronic and steric character of NHCs over a wide range.

The structure of compound **1e** was confirmed by the single-crystal X-ray diffraction analysis as shown in Fig. 1. It crystallizes in chiral space group $P2_1$ in the hydrate form with **1e**: water ratio = 1:4.



1: R = (**a**) Me (62%), (**b**) *i*-Pr (57%), (**c**) *t*-Bu (44%), (**d**) Bn (75%), (**e**) Ph (44%), (**f**) 2-MeC_6H_4 (52%), (**g**) 4-MeC_6H_4 (45%), (**h**) 2,6-$Me_2C_6H_3$ (33%), (**i**) 2,4,6-$Me_3C_6H_2$ (73%)

SCHEME 1

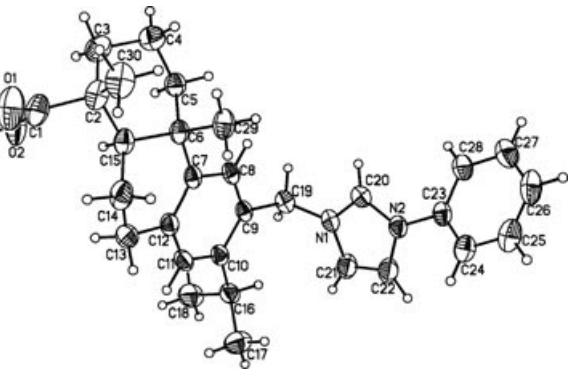


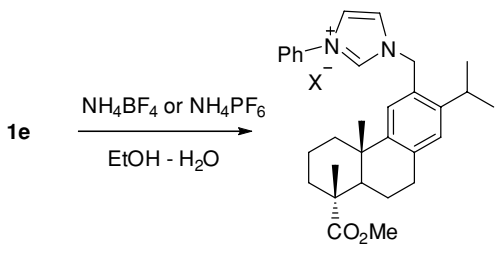
FIGURE 1 ORTEP view of compound **1e**; displacement ellipsoids drawn at 30% probability level. Only the first independent cation structure is shown.

An asymmetric unit of **1e** contains two cations ($C_{31}H_{39}N_2O_2^+$), two Cl^-, and two quarters of disordered water molecules. It is interesting to note that the formation of hydrates is a distinguishing characteristic for all chlorides **1a–i** (but not for tetrafluoroborate **Ie·BF**$_4$ and hexafluorophosphate **Ie·PF**$_6$) as evidenced by elemental analysis data and IR spectra (broad absorption band OH at 3329–3468 cm^{-1}). The ester group displays strong bands at 1715–1727 cm^{-1}.

Anion exchange in chloride **1e** gave rise to corresponding tetrafluoroborate **Ie·BF**$_4$ and hexafluorophosphate **Ie·PF**$_6$ (Scheme 2).

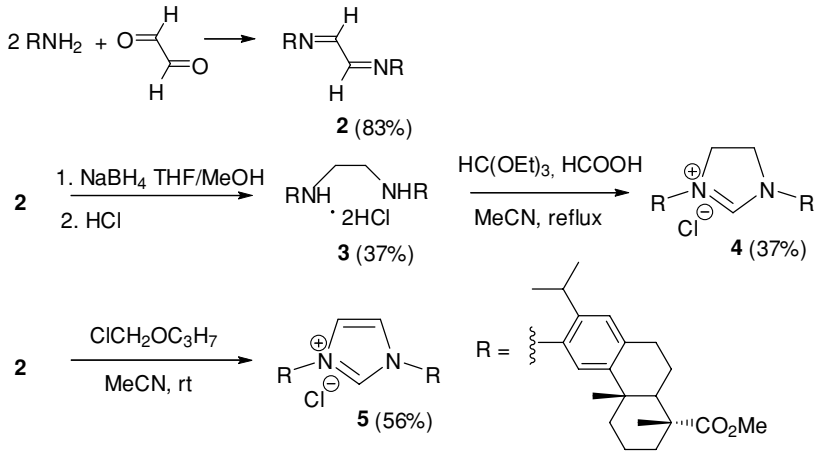
Compound **2** was synthesized from methyl 12-aminodehydroabietate [19]. The structure of **2** is confirmed by the single-crystal X-ray diffraction analysis (Fig. 2). The central diimine moiety is nearly planar. The structure of tricyclic fragments is similar to that described earlier [20].

Compounds **4** and **5** were synthesized from diimine **2** by the Arduengo method [21] (Scheme 3). Reduction of compound **2** resulted in bis-amine **3** dihydrochloride. Heating the compound **3** with ethyl orthoformate afforded imidazolinium salt **4**.



X = BF_4 **1e·BF$_4$** 62%
X = PF_6 **1e·PF$_6$** 63%

SCHEME 2



SCHEME 3

Compound **5** was synthesized by the reaction of diimine **2** with chloromethyl-propyl ether [10].

The screening of salts **1a-i, 4**, and **5** as possible ligands for the Suzuki-Miyaura reaction of 4-bromotoluene and 4-tolylboronic acid was carried out (Scheme 4).

Solvent/base optimization was fulfilled using compounds **1a–c**, synthesized earlier [16]. A summary of the more relevant results obtained is listed in Table 1. We had initially conducted the reaction using 5 mol% of $Pd(OAc)_2$ as a catalyst precursor and K_3PO_4 as a base in dioxane (Table 1, entries 2–4), dimethoxyethane (entry 6), and toluene (entry 7); after 5 h, heating at 90°C under aerobic conditions produced only modest conversion (60%–67%) and low yield (47%–57%). At the end of the reaction, palladium black was formed. In the presence of PPh_3 (1 equiv. to $Pd(OAc)_2$) as a coligand (entry 5) in dioxane, the yield was still moderate (56%), though conversion was high (96%). It is worth noting that $Pd(OAc)_2$ alone led to 8% yield (entry 1).

The reaction yields were significantly improved when DMF was introduced as a solvent and K_2CO_3 as a base (entry 8). Loading of 1 mol% instead of 5 mol% of catalyst slightly reduces yields (compare entries 8 and 9, 12 and 13); nevertheless, we had conducted the following experiments using 1 mol% of $Pd(OAc)_2$. In the initial runs, we had taken two equivalents of ligand to palladium [7a,22]. Now it is considered reasonable that monoligated palladium(0) complexes, generated by thermal decomposition of the initially formed diligated species [7g,8], are involved in the reaction [23]; so, starting from entry 11, we had taken the ratio [Pd]/L 1:1, although the yield in dioxane was reduced from 72% to 50% (entry 11 versus entry 10).

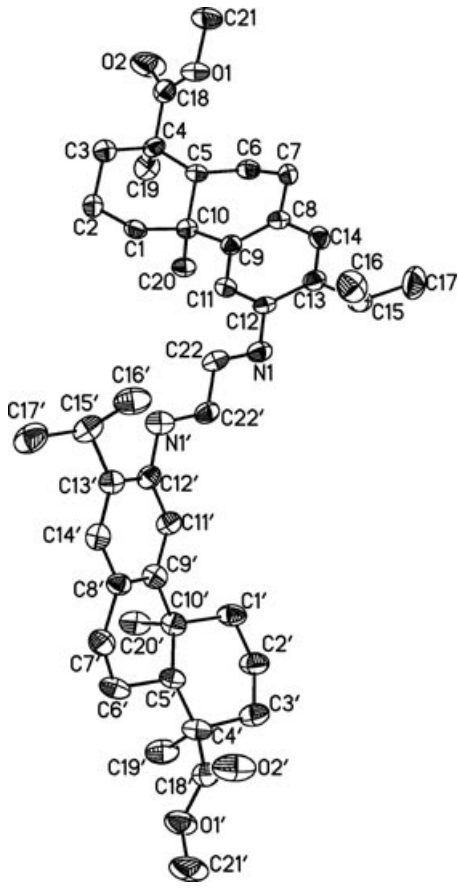
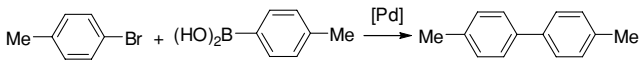


FIGURE 2 ORTEP view of compound **2**; displacement ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.



SCHEME 4

TABLE 1 Catalytic Activities of Salts **1a–e,g,i; 4,5**

Entry[a]	*Compound (R)*	*L/[Pd]*	*[Pd] (mol%)*	*Base*	*Solvent*	*Conversion, (%)*	*Yield (%)*[c]
1	none	–	5	K_3PO_4	dioxane	56	8
2	**1a** (Me)	2/1	5	K_3PO_4	dioxane	60	57
3	**1b** (i-Pr)	2/1	5	K_3PO_4	dioxane	63	55
4	**1c** (t-Bu)	2/1	5	K_3PO_4	dioxane	67	47
5	**1c** (t-Bu)	1/1[b]	5	K_3PO_4	dioxane	96	56
6	**1c** (t-Bu)	2/1	5	K_3PO_4	DME	38	24
7	**1c** (t-Bu)	2/1	5	K_3PO_4	toluene	45	41
8	**1c** (t-Bu)	1/1	5	K_2CO_3	DMF	99	92
9	**1c** (t-Bu)	1/1	1	K_2CO_3	DMF	94	88
10	**1d** (Bn)	2/1	5	K_3PO_4	dioxane	72	72
11	**1d** (Bn)	1/1	5	K_3PO_4	dioxane	58	50
12	**1d** (Bn)	1/1	5	K_2CO_3	DMF	88	88
13	**1d** (Bn)	1/1	1	K_2CO_3	DMF	84	84
14	**1e** (Ph)	1/1	1	K_2CO_3	DMF	82	82
15	**1g** (p-Tolyl)	1/1	1	K_2CO_3	DMF	94	89
16	**1i** (Mesityl)	1/1	1	K_2CO_3	DMF	78	69
17	**4**	1/1	1	K_2CO_3	DMF	83	39
18	**5**	1/1	1	K_2CO_3	DMF	94	77

[a]Conditions: 2.8 mmol of 4-bromotoluene, 2.8 mmol of 4-tolylboronic acid, and 5.6 mmol of base in 50 mL of solvent at 90°C, 5 h under aerobic conditions.
[b]Eq. (1) of Ph_3P to Pd was added.
[c]GC yield with pentadecane as the internal standard.

It appears that the steric hindrance has little influence on catalytic activities of ligands (compare entries 9,13-16). The most active ligands are compounds **1c,d,g**, bearing *tert*-Bu, benzyl-, or *p*-tolyl-groups (entries 8,12,15). Ligands **4** and **5** show a modest level of activity (entries 17,18).

To exclude homo-coupling, the reaction of *para*-tolylboronic acid with bromobenzene in optimized conditions ($Pd(OAc)_2$ (1 mol%), **1c** (1 mol%), DMF, K_2CO_3, 90°C, 5 h) was studied; it was shown that the yield of homo-coupling product did not exceed 9%–10%. To our regret, our catalytic system is not appropriate for cross-coupling of aryl chlorides: 4-chloroanisole as a deactivated challenging substrate does not enter into coupling reactions in our conditions.

CONCLUSION

Starting from the derivatives of dehydroabietic acid, we had prepared the family of sterically demanding ligands for the Suzuki–Miyaura reaction: six new asymmetrically (**1d–i)** and two symmetrically substituted (**4,5**) chiral imidazolium salts bearing the diterpene moiety. Some of them showed activity as ligands for the Pd-mediated coupling reaction of 4-bromotoluene and 4-tolylboronic acid, although coupling of 4-chloroanisole was inefficient. We had found that DMF as a solvent and K_2CO_3 as a base appeared to be quite suitable for the coupling reactions of new ligands.

EXPERIMENTAL

1-Benzyl-1*H*-imidazole, 1-phenyl-1*H*-imidazole, *para*-tolylboronic acid, and DME were supplied from Alfa Aesar (Lancaster). DMF (analytical grade) and dichloromethane were products of Russia and were used without special purification. 1-(4-Tolyl)-1*H*-imidazole was synthesized by arylation of imidazole by 1-(4-tolyl)-boronic acid [24]; 1-(2-tolyl)-1*H*-imidazole, 1-(2,6-dimethylphenyl)-1*H*-imidazole, and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole were synthesized according to the recently published protocol [25]. Analytical thin-layer chromatography was performed using silica gel plates *Sorbfil* in a chloroform-acetone mixture (10:1, v/v); compound spots were visualized by UV light (254 nm). IR spectra, obtained by dissolving compounds in $CHCl_3$ with consequent evaporation of chloroform were recorded on a Fourier spectrometer Bruker IFS 66ps in nujol or in thin film; ^1H and ^{13}C NMR spectra were obtained on a Varian Mercury+300 instrument at 300 and 75 MHz respectively, in $CDCl_3$ or DMSO-d_6, and were referenced to HMDS (^1H NMR $\delta = 0.055$ ppm), residual $CHCl_3$ (^{13}C NMR $\delta = 77.0$ ppm), or residual DMSO (^{13}C NMR $\delta =$ 39,6 ppm). Mass-spectra were recorded on a GC-MS system Agilent 6890N series with a mass-selective detector MSD 5975B (EI, 70 eV). Optical rotation was measured on a Perkin-Elmer 341 polarimeter in $CHCl_3$ containing 0.5% of EtOH as a stabilizer. Elemental analyses (C,H,N) were obtained using a Leco

CHNS 9321P elemental analyzer at the Institute of Technical Chemistry, Perm.

General Procedure for the Synthesis of Compounds **1d–i**

Methyl 12-chloromethyl-dehydroabietate [18] (1.81 g, 5 mmol) and 5 mmol of corresponding 1-R-1*H*-imidazole were refluxed in dry acetonitrile (50 mL) for 6 h. The residue, after evaporation of MeCN, was treated with 30 mL of hot ethylacetate, resulting in the formation of compounds **1a–i** as white solids, which were dried at 55°C in vacuo. Analytical samples were obtained after recrystallization from EtOAc-MeCN mixture. Compounds **1a–c** were synthesized earlier [16].

*1-Benzyl-3-[((4bS,8R,8aR)-2-isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1H-imidazol-3-ium chloride, semihydrate (***1d***)*

Synthesized according to general procedure from 1.32 g (3.6 mmol) of methyl 12-chloromethyl-dehydroabietate and 576 mg (3.6 mmol) of 1-benzyl-1*H*-imidazole in 40 mL MeCN. Yield 1.43 g (75%), colorless prisms, mp 208-210°C, $[\alpha]_D^{25}$ + 45.4 (*c* 1, $CHCl_3$). IR, ν (thin film): 3398 (OH), 2943 (C-H), 1715 (O—C = O), 1607 (C=C), 1557, 1498 (C=C), 1455 (C—H), 1387 (C—H), 1360 (C—H), 1248, 1192, 1161, 1135, 1109, 1045, 971 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.04 (d, 3H, J = 6.9 Hz, Me), 1.08 (d, 3H, J = 6.9 Hz, Me), 1.25 (s, 3H, Me), 1.16 (s, 3H, Me), 1.40 (m, 2H, C(5)H_{ax}, C(6)H_{ax}), 1.63–1.87 (m, 5H, C(6)H_{eq}, C(7)H_2, C(9)H_2), 2.15 (m, 1H, C(5)H_{eq}), 2.22 (m, 1H, HC(8a)), 2.42 (br.s, 1H, OH), 2.87 (m, 2H, H_2C(10)H_2), 3.65 (s, 3H, OMe), 2.96 (m, 1H, ArCH), 5.46 (d, 1H, J = 14.7 Hz, NCH_2Ar), 5.53 (d, 1H, J = 14.7 Hz, NCH_2Ar), 5.64 (s, 2H, PhC$\underline{H}_2$), 6.85 (m, 1H, $CH_{imidazole}$), 6.97 (s, 1H, C(1)H), 7.08 (s, 1H, C(4)H), 7.27 (m, 2H, H_{arom}), 7.37 (m, 3H, $H_{imidazole}$+2H_{arom}), 7.48 (m, 2H, H_{arom}), 11.11 (s, 1H, NCH = N). ^{13}C NMR ($CDCl_3$) δ: 16.0, 18.0, 21.0, 23.4, 23.5, 24.7, 28.2, 29.3, 36.1, 36.5, 37.4, 44.2, 47.0, 50.8, 51.5, 52.8, 120.8, 122.1, 125.9, 126.1, 126.7, 128.5, 128.77, 128.82, 133.3, 136.7, 136.9, 144.1, 147.7, 178.4 (C = O). Found: C, 72.57; H, 7.78; N, 5.30%. Calcd for $C_{32}H_{41}ClN_2O_2 \cdot {}^1/_2H_2O$: C, 72.50; H, 7.99; N, 5.28%.

*3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1-phenyl-1H-imidazol-3-ium chloride × 0.25 H_2O (***1e***)*

Synthesized from 1.81 g (5 mmol) of methyl 12-chloromethyl-dehydroabietate and 721 mg (5 mmol, 0.63 mL) of 1-phenyl-1H-imidazole in 50 mL MeCN. Yield 1.74 g (67%), colorless prisms, mp 195–196°C (from AcOEt-MeCN); $[\alpha]_D^{20}$ + 47.6 (C 0.5, $CHCl_3$). IR, ν (Nujol) 3468, 3376 (OH), 1724 (O—C=O), 1597 (C=C), 1565 (C=C), 1549 (C=N), 1498 (C=C), 1435, 1247, 1212, 1176, 1132, 1111, 1081, 763 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.09 (d, 3H, J = 6.9 Hz, Me), 1.14 (d, 3H, J = 6.9 Hz, Me), 1.19 (s, 3H, Me), 1.26 (s, 3H, Me), 1.42 (m, 2H, C(5)H_{ax}, C(6)H_{ax}), 1.63–1.90 (m, 5H, C(6)H_{eq}, H_2C(7), H_2C(9)), 2.18 (m, 1H, C(5)H_{eq}), 2.35 (m, 1H, HC(8a)), 2.90 (m, 2H, H_2C(10)), 3.10 (m, 1H, J = 6.9 Hz, ArCH), 3.66 (s, 3H, OMe), 5.73 (d, 1H, J = 14.4 Hz, NCH_2Ar), 5.81 (d, 1H, J = 14.4 Hz, NCH_2Ar), 7.01 (s, 1H, HC(1)), 7.10 (m, 1H, $CH_{imidazole}$), 7.28 (m, 1H, $CH_{imidazole}$), 7.45-7.56 (m, 3H, HC(4)+2H_{arom}), 7.82 (m, 3H, H_{arom}), 11.55 (s, 1H, NCH=N). ^{13}C NMR ($CDCl_3$) δ: 16.22, 18.15, 21.18, 23.72, 23.81, 24.89, 28.49, 29.52, 36.34, 36.72, 37.69, 44.38, 47.28, 51.43, 51.73, 120.62, 121.45, 121.69, 125.97, 126.90, 127.05, 129.77, 130.25, 134.32, 135.75, 135.74, 137.34, 144.72, 148.04, 178.70. Found: C, 72.34; H, 7.39; N, 5.87%. Calcd for $C_{31}H_{39}ClN_2O_2 \times 0.25\ H_2O$: C, 72.78; H, 7.78; N, 5.47%.

*3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1-phenyl-1H-imidazol-3-ium tetrafluoroborate (***1e**·BF_4*)*

To a solution of compound **1e (**570 mg, 1.12 mmol) in ethanol (40 mL) NH_4BF_4 (151 mg, 1.43 mmol) in H_2O (40 mL) was added. Ethanol was evaporated in vacuo; the residue was filtered, washed with water, dried in air, and crystallized from a AcOEt-MeCN mixture. Yield 390 mg (62%), colorless plates, mp 168–170°C; $[\alpha]_D^{20}$ + 39.2 (*c* 0.5, $CHCl_3$). IR, ν (thin film): 3164, 3075, 2946, 2869, 1723, 1597, 1551, 1496, 1463, 1431, 1384, 1248, 1190, 1133, 1058, 760 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.10 (d, 3H, J = 7.2 Hz, Me), 1.14 (d, 3H, J = 7.2 Hz, Me), 1.20 (s, 3H, Me), 1.27 (s, 3H, Me), 1.44 (m, 2H, C(5)H_{ax}, C(6)H_{ax}), 1.55–1.90 (m, 5H, C(6)H_{eq}, C(7)H_2, C(9)H_2), 2.18 (m, 1H, C(5)H_{eq}), 2.34 (m, 1H, HC(8a)), 2.89 (m, 2H, C(10)H_2), 2.96 (m, 1H, ArCH), 3.66 (s, 3H, OMe), 5.57 (d, 1H, J = 14.7 Hz, NCH_2Ar), 5.62 (d, 1H, J = 14.7 Hz, NCH_2Ar), 7.02 (s, 1H, HC(1)), 7.14 (m, 1H, $CH_{imidazole}$), 7.29 (s, 1H, HC(4)), 7.46 (m, 1H, $CH_{imidazole}$), 7.55–7.63 (m, 5H, Ph), 9.30 (s, 1H, NCH=N). ^{13}C NMR ($CDCl_3$) δ: 16.4, 18.3, 21.3, 23.7, 24.9, 28.5, 29.7, 36.5, 36.8, 37.6, 44.5, 47.4, 51.5, 51.8, 121.3, 121.9, 122.6, 126.0, 127.0, 127.4, 130.2, 130.4, 133.9, 134.4, 137.6, 144.8, 148.3, 178.8 (C=O). Found: C, 66.37; H, 6.99; N,

5.02%. Calcd for $C_{31}H_{39}BF_4N_2O_2$: C, 66.67; H, 7.04; N, 5.02%.

*3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1-phenyl-1H-imidazol-3-ium hexafluorophosphate (**Ie**·PF_6)*

To a solution of compound **1e** (540 mg, 1.06 mmol) in ethanol (10 mL), NH_4PF_6 (240 mg, 1.5 mmol) in H_2O (10 mL) was added. The resulting crystals were filtered, washed with water, and dried in air. Yield 410 mg (63%), colorless powder, mp 209–211°C (from AcOEt-MeCN); $[\alpha]_D^{20}$ + 38.0 (*c* 0.5, $CHCl_3$). IR, ν (Nujol): 1724 (O—C = O), 1599 (C = C), 1567 (C = C), 1554 (C = N), 1498 (C = C), 1413, 1247, 1204, 1186, 1135, 1111, 1076, 847, 821 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.07 (d, 3H, J = 6 Hz, Me), 1.12 (d, 3H, J = 6 Hz, Me), 1.19 (s, 3H, Me), 1.26 (s, 3H, Me), 1.41 (m, 2H, C(5)H_{ax}, C(6)H_{ax}), 1.58-1.90 (m, 5H, C(6)H_{eq}, C(7)H_2, C(9)H_2), 2.17 (m, 1H, C(5)H_{eq}), 2.35 (m, 1H, C(8a)H), 2.90 (m, 2H, C(10)H_2), 2.94 (m, 1H, ArCH), 3.66 (s, 3H, OMe), 5.42 (d, 1H, J = 14.4 Hz, NCH_2Ar), 5.49 (d, 1H, J = 14.4 Hz, NCH_2Ar), 7.01 (s, 1H, C(1)H), 7.21 (m, 1H, $CH_{imidazole}$), 7.25 (m, 1H, $CH_{imidazole}$), 7.28 (s, 1H, C(4)H), 7.52 (m, 5H, Ph), 8.80 (s, 1H, NCH = N). ^{13}C NMR ($CDCl_3$) δ: 16.3, 16.4, 18.3, 21.4, 23.7, 23.8, 24.9, 28.6, 29.7, 36.6, 36.9, 37.6, 44.6, 47.5, 51.9, 121.4, 122.1, 122.2, 122.7, 125.6, 127.2, 127.5, 130.4, 133.5, 134.4, 137.8, 144.9, 148.4, 178.9 (C = O). Found: C, 60.25; H, 6.09; N, 4.78%. Calcd for $C_{31}H_{39}F_6N_2O_2P$: C, 60.38; H, 6.38; N, 4.54%.

*1-(2-Methylphenyl)-3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1H-imidazol-3-ium chloride, hydrate (**1f**)*

Prepared from 726 mg (2 mmol) of methyl 12-chloromethyl-dehydroabietate and 314 mg (2 mmol) of 1-(2-methylphenyl)-1*H*-imidazole in 30 mL MeCN. Yield 541 mg (52%), off-white powder, mp 201–203°C; $[\alpha]_D^{21}$ + 45.2 (*c* 1, $CHCl_3$). IR, ν (Nujol): 3380 (OH), 1727 (O-C = O), 1553, 1500, 1302, 1246, 1187, 1130, 1046, 984, 916, 761 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.10 (d, 3H, J = 6.6 Hz, Me), 1.15 (d, 3H, J = 6.6 Hz, CH), 1.20 (s, 3H, Me), 1.27 (s, 3H, Me), 1.43 (m, 2H, C(9)H_{ax}, C(5)H_{ax}), 1.64–1.90 (m, 5H, C(6)H_2, C(7)H_2, C(9)H_{eq}), 2.18 (dd, 1H, J = 12.3, 2.1 Hz, C(8a)H), 2.29 (s, 3H, MeAr), 2.32 (m, 1H, C(5)H_{eq}), 2.89 (m, 2H, C(10)H_2), 3.12 (m, 1H, J = 6.6 Hz, C*H*$(Me)_2$), 3.67 (s, 3H, OMe), 5.84 (d, 1H, J = 14.7 Hz, NCH_2), 5.93 (d, 1H, J = 14.7 Hz, NCH_2), 7.01 (s, 1H, C(1)H), 7.21 (s, 1H, $H_{imidazole}$), 7.27–7.48 (m, 6H, 4H_{arom}+C(4)H+$H_{imidazole}$), 10.95 (s, 1H, NCH=N). ^{13}C NMR ($CDCl_3$) δ: 16.2, 17.6, 18.2, 21.2, 23.7, 23.8, 28.4, 29.5, 36.3, 36.7, 37.7, 44.4, 47.3, 51.6, 51.7, 121.5, 123.0, 126.0, 126.3, 126.9, 127.0, 127.5, 130.7, 131.8, 132.9, 133.7, 137.2, 137.5, 144.7, 148.0, 178.7 (C=O). Found: C, 67.37; H, 7.10; N, 4.52%. Calcd for $C_{32}H_{41}ClN_2O_2$·2.5 H_2O: C, 67.91; H, 8.19; N, 4.95%.

*1-(4-Methylphenyl)-3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1H-imidazol-3-ium chloride, hydrate (**1g**)*

Prepared from 726 mg (2 mmol) of methyl 12-chloromethyl-dehydroabietate and 314 mg (2 mmol) of 1-(4-methylphenyl)-1*H*-imidazole in 30 mL MeCN. Yield 458 mg (44%), colorless prisms, mp 144-146°C (from ∋A-MeCN); $[\alpha]_D^{20}$ + 23.8 (*c* 0.5, $CHCl_3$). IR, ν (Nujol): 3456 (OH), 3067 (C–H_{arom}), 1728 (O—C = O), 1614 (C = C), 1556 (C = N), 1517 (C = C), 1306, 1244, 1186, 1173, 1132, 1076, 819 cm^{-1}.^1H NMR ($CDCl_3$) δ: 1.10 (d, 3H, J = 6.6 Hz, Me), 1.14 (d, 3H, J = 6.6 Hz, Me), 1.19 (s, 3H, Me), 1.26 (s, 3H, Me), 1.43 (m, 2H, C(5)H_{ax}, C(6)H_{ax}), 1.63–1.90 (m, 5H, C(6)H_{eq}, C(7)H_2, C(9)H_2), 2.16 (m, 1H, C(5)H_{eq}), 2.32 (m, 1H, C(8a)H), 2.39 (s, 3H, Ar-Me), 2.89 (m, 2H, C(10)H_2), 3.09 (m, 1H, ArCH), 3.66 (s, 3H, OMe), 5.73 (d, 1H, J = 14.7 Hz, NCH_2Ar), 5.82 (d, 1H, J = 14.7 Hz, NCH_2Ar), 7.01 (s, 1H, C(1)H), 7.07 (m, 1H, $CH_{imidazole}$), 7.28 (s, 1H, C(4)H), 7.33 (d, 2H, J = 8.1 Hz, C(2',6')H_{arom}), 7.58 (m, 1H, $CH_{imidazole}$), 7.65 (d, 2H, J = 8.1 Hz, C(3',5')H_{arom}), 11.43 (s, 1H, NCH = N). ^13C NMR ($CDCl_3$) δ: 16.2, 18.2, 20.8, 21.2, 23.7, 23.8, 24.8, 28.4, 29.5, 36.3, 36.7, 37.7, 44.4, 47.3, 51.3, 51.7, 120.6, 121.3, 121.6, 126.0, 126.8, 127.0, 130.7, 132.0, 135.5, 137.3, 140.1, 144.7, 148.0, 178.7 (C = O). Found: C, 70.70; H, 7.87; N, 5.17%. Calcd for $C_{32}H_{41}ClN_2O_2$·H_2O: C, 71.29; H, 8.04; N, 5.20%.

*1-(2,6-Dimethylphenyl)-3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1H-imidazol-3-ium chloride, trihydrate (**1h**)*

Prepared from 726 mg (2 mmol) of methyl 12-chloromethyl-dehydroabietate and 344 mg (2 mmol) of 1-(4-methylphenyl)-1*H*-imidazole in 30 mL MeCN. Yield 353 mg (33%), white powder, mp 241–243°C, $[\alpha]_D^{22}$ +47.7 (*c* 1, $CHCl_3$). IR, ν (thin film): 3376 (OH), 2937, 1720 (O-C = O), 1548, 1465, 1380, 1249,

1185, 1105, 1050, 959, 888 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.11 (d, 3H, $J = 6.6$ Hz, Me), 1.16 (d, 3H, $J = 6.6$ Hz, Me), 1.20 (s, 3H, Me), 1.27 (s, 3H, Me), 1.44 (m, 2H, $C(9)H_{ax}$, $C(5)H_{ax}$), 1.62-1.90 (m, 5H, $C(6)H_2$, $C(7)H_2$, $C(9)H_{eq}$), 2.12 (m, 6H, 2Me), 2.18 (dd, 1H, $J = 12.3$, 2.1 Hz, C(8a)H), 2.31 (m, 1H, $C(5)H_{eq}$), 2.90 (m, 2H, $C(10)H_2$), 3.12 (m, 1H, $J = 6.6$ Hz, $CH(Me)_2$), 3.67 (s, 3H, OMe), 5.90 (d, 1H, $J = 14.4$ Hz, NCH_2), 5.98 (d, 1H, $J = 14.4$ Hz, NCH_2), 7.01 (s, 1H, C(1)H), 7.14–7.32 (m, 6H, $3H_{arom}$+C(4)H+$2H_{imidazole}$), 10.93 (s, 1H, NCH=N). ^{13}C NMR ($CDCl_3$) δ: 16.3, 17.6, 18.28, 18.29, 21.3, 23.97, 24.04, 25.0, 28.6, 29.6, 36.4, 36.8, 37.9, 44.5, 47.4, 51.86, 51.94, 121.9, 122.8, 126.5, 126.9, 127.1, 129.1, 130.9, 133.1, 134.4, 137.3, 138.1, 144.8, 148.1, 178.8 (C=O). Found: C, 67.36; H, 7.10; N, 4.52%. Calcd for $C_{33}H_{43}ClN_2O_2 \cdot 3H_2O$: C, 67.28; H, 8.38; N, 4.75%.

*3-[((4bS,8R,8aR)-2-Isopropyl-8-(methoxycarbonyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-methyl]-1-mesityl-1H-imidazol-3-ium chloride (**1i**)*

Obtained from 726 mg (2 mmol) of methyl 12-chloromethyl-dehydroabietate and 372 mg (2 mmol) of 1-mesityl-1*H*-imidazole in 30 mL MeCN. Yield 802 mg (73%), white powder, mp 198–200°C, $[\alpha]_D^{25}$ + 44.4 (*c* 1, $CHCl_3$). IR, ν (Nujol) 3329 (br., OH), 1720 (C=O), 1609 (v.), 1543, 1245, 1198, 1133, 1112, 1061, 1044, 758, 722 cm^{-1}.^1H NMR ($CDCl_3$) δ: 1.09 (d, 3H, $J = 6.6$ Hz, Me), 1.14 (d, 3H, $J = 6.6$ Hz, Me), 1.19 (s, 3H, Me), 1.26 (s, 3H, Me), 1.43 (m, 2H, $C(5)H_{ax}$, $C(6)H_{ax}$), 1.72 (m, 5H, $C(6)H_{eq}$, $C(7)H_2$, $C(9)H_2$), 2.06 (s, 6H, 2Me), 2.18 (m, 1H, $C(5)H_{eq}$), 2.32 (s, 3H, Me), 2.45 (m, 1H, C(8a)H), 2.88 (m, 2H, $C(10)H_2$), 3.11 (m, 1H, ArCH), 3.66 (s, 3H, OMe), 5.84 (d, 1H, $J = 14.7$ Hz, NCH_2Ar), 5.92 (d, 1H, $J = 14.7$ Hz, NCH_2Ar), 6.97 (s, 2H, C(3',5')H), 7.00 (s, 1H, C(1)H), 7.23 (s, 2H, $H_{imidazole}$), 7.32 (s, 1H, C(4)H), 10.66 (s, 1H, NCH = N). ^{13}C NMR ($CDCl_3$) δ: 16.3, 17.4, 18.3, 20.9, 21.3, 23.9, 24.0, 25.0, 28.5, 29.6, 36.5, 36.8, 37.9, 44.5, 47.4, 51.8, 121.9, 123.0, 126.6, 126.9, 127.0, 129.7, 130.7, 134.0, 137.2, 138.2, 141.0, 144.8, 148.0, 178.8 (C=O). Found: C, 68.69; H, 7.68; N, 4.64%. Calcd for $C_{34}H_{45}ClN_2O_2 \cdot 2.5\ H_2O$: C, 68.71; H, 8.48; N, 4.71%.

*1,4-Bis-((4bR,8S,8aS)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-1,4-diazabutadiene (**2**)*

Methyl 12-aminodehydroabietate [19] (4.18 g, 12.7 mmol) was dissolved in propanol-2 (90 mL) and 0.93 mL (6.37 mmol) of glyoxal (40% aq. soln.) was added in one portion; after 4 h of stirring at room temperature, the bright yellow crystals were filtered, washed with propanol-2, and dried. Yield 3.60 g (83%). Compound 2 was used further without additional purification. An analytical sample was recrystallized from ethanol, bright yellow prisms, mp 225–228°C; $[\alpha]_D^{22}$ +300.0 (*c* 1, $CHCl_3$). IR, ν (Nujol): 1715 (O—C=O), 1600 (C=C), 1245, 1135, 1045, 990, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.13 (d, 6H, $J = 7$ Hz, Me), 1.14 (d, 6H, $J = 7$ Hz, Me), 1.18 (s, 6H, Me), 1.22 (s, 6H, Me), 1.35–1.86 (m, 14H, 2 $C(5)H_{ax}$, 2 $C(6)H_2$, 2 $C(7)H_2$, 2 $C(9)H_2$), 2.18 (m, 2H, $C(5)H_{eq}$), 2.27 (m, 2H, C(8a)H), 2.85 (m, 4H, $C(10)H_2$), 3.44 (m, 2H, ArC<u>H</u>), 3.61 (s, 6H, OMe), 6.80 (s, 2H, C(1)H), 6.92 (m, 2H, C(4)H), 8.23 (m, 2H, CH=N). ^{13}C NMR ($CDCl_3$) δ: 16.5, 18.5, 21.6, 23.2, 23.5, 25.0, 27.4, 29.8, 36.6, 37.2, 38.1, 44.8, 47.6, 51.9, 113.0, 126.2, 134.7, 140.4, 146.5, 147.7, 158.8, 178.9 (C=O). Found: C, 77.28; N, 8.63; H, 4.07%. Calcd for $C_{44}H_{60}N_2O_4$: C, 77.61; N, 8.88; H, 4.11%.

*1,4-Bis-((4bR,8S,8aS)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-1,4-diazabutane dihydrochloride, hydrate (**3**)*

To diimine **2** (0.9 g, 1.27 mmol), dissolved in a mixture of 40 mL THF and 10 mL MeOH, 150 mg (2.63 mmol) of $NaBH_4$ was added. Suspension was stirred for 12 h at room temperature; 50 mg of $NaBH_4$ was added and heated under reflux for 1 h; after cooling, 30 mL of cold water was added and stirred until gaseous products ceased to evaluate from the solution (~1 h); then 30 mL of 3N HCl was added. In 12 h, white crystals of dihydrochloride of **3** were filtered, washed with water, and dried in air for 12 h, then in a desiccator over P_2O_5 in vacuo for 12 h. Yield 365 mg (37%), white powder, mp 207–210°C, $[\alpha]_D^{24}$ +67.7 (*c* 1, $CHCl_3$). IR, ν (Nujol): 3400 (HN^+, br., OH), 1700 (O—C=O), 1200, 1170, 1130, 990 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.05 (s, 6H, Me), 1.06 (d, 6H, $J = 6$ Hz, Me), 1.07 (d, 6H, $J = 6$ Hz, Me), 1.13 (s, 6H, Me), 1.18–1.69 (m, 14H, 2 $C(5)H_{ax}$, 2 $C(6)H_2$, 2 $C(7)H_2$, 2 $C(9)H_2$), 1.93 (m, 2H, $C(5)H_{eq}$), 2.74 (m, 4H, $C(10)H_2$), 3.06 (m, 2H, ArC*H*), 3.45 (m, 4H, 2 NCH_2), 3.54 (s, 6H, OMe), 3.97 (br. s, 2H, 2 HN^+), 6.93 (s, 2H, C(1)H), 7.05 (s, 2H, C(4)H). ^{13}C NMR ($CDCl_3$) δ: 16.2, 17.9, 20.9, 23.6, 24.4, 26.0, 28.7, 36.1, 36.6, 37.6, 44.6, 44.7, 45.4, 46.8, 51.7, 115.0, 127.2, 131.5, 134.1, 136.4, 147.8, 177.8 (C=O). Found: C, 64.96; H, 8.58; N, 3.78%. Calcd for $C_{44}H_{64}N_2O_4 2HCl \cdot 3.5H_2O$: C, 64.38; H, 8.96; N, 3.41%.

*1,3-Bis-((4bR,8S,8aS)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-4,5-dihydro-1H-imidazol-3-ium chloride, hydrate (**4**·Cl)*

Suspension of 478 mg (0.59 mmol) of compound **3** was refluxed in 10 mL of ethyl orthoformate and two drops of formic acid (99%) for 30 min, cooled to 70°C, and 10 mL of MeCN was added. Volatiles were distilled (from 80° up to 140°C) until the formation of crystalline compound (**4**·Cl), which was filtered after cooling, washed with 5 mL of ether, and dried in vacuo. Yield 156 mg (37%), white powder, mp 200-204°C (decomp.),$[\alpha]_D^{20}$ + 109 (c 1.56, $CHCl_3$). IR, ν (Nujol): 3370 (br., OH), 1716 (O—C=O), 1622 (C=C), 1308, 1250, 1174, 1132, 1122, 1084, 896 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.17 (s, 6H, Me), 1.19 (d, 6H, J = 6 Hz, Me), 1.20 (d, 6H, J = 6 Hz, Me), 1.23 (s, 6H, Me), 1.36–1.83 (m, 14H, 2 C(5)H_{ax}, 2 C(6)H_2, 2 C(7)H_2, 2 C(9)H_2), 2.07 (m, 2H, C(5)H_{eq}), 2.50 (m, 2H, HC(8a)), 2.85 (m, 4H, C(10)H_2), 2.87 (m, 2H, CHAr), 3.60 (s, 6H, OMe), 4.67 (m, 4H, 2 NCH_2), 6.94 (s, 2H, C(1)H), 7.72 (s, 1H, N = CHN), 7.93 (m, 2H, C(4)H). ^{13}C NMR ($CDCl_3$) δ: 16.2, 17.7, 20.6, 23.7, 23.8, 24.3, 27.0, 28.8, 36.2, 36.7, 37.6, 44.4, 46.7, 51.7, 53.6, 99.4, 122.7, 127.2, 131.3, 137.0, 141.4, 148.4, 177.7 (C = O). Found: C, 66.25; H, 8.34; N, 3.73%. Calcd for $C_{45}H_{63}ClN_2O_4 \cdot 4H_2O$: C, 67.27; H, 8.91; N, 3.49%.

*1,3-Bis-((4bR,8S,8aS)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate (**4**·BF_4)*

Suspension of 320 mg (0.39 mmol) of compound **3** was refluxed in 10 mL of ethyl orthoformate and two drops of formic acid (99%) for 20 min, then 50 mg (0.47 mmol) of NH_4BF_4 and 10 mL of MeCN were added. Volatiles were distilled (from 80° up to 140°C) until the formation of crystalline compound (**4**·BF_4), which was filtered after cooling, washed with 5 mL of ether, and dried in air. Yield 220 mg (67%), white powder, mp 298–300°C. IR, ν (Nujol): 1716 (O—C=O), 1622 (C=C), 1308, 1250, 1174, 1132, 1122, 1084, 896 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.17 (s, 6H, Me), 1.19 (d, 6H, J = 6 Hz, Me), 1.20 (d, 6H, J = 6 Hz, Me), 1.23 (s, 6H, Me), 1.36–1.83 (m, 14H, 2 C(5)H_{ax}, 2 C(6)H_2, 2 C(7)H_2, 2 C(9)H_2), 2.07 (m, 2H, C(5)H_{eq}), 2.50 (m, 2H, HC(8a)), 2.85 (m, 6H, 2 C(10)H_2+CHAr), 3.60 (s, 6H, OMe), 4.67 (m, 4H, 2 NCH_2), 6.94 (s, 1H, C(1)H), 7.72 (s, 1H, NCH=N), 7.93 (m, 2H, C(4)H). ^{13}C NMR ($CDCl_3$) δ: 16.5, 18.4, 21.3, 24.1, 24.4, 24.8, 24.7, 28.0, 29.8, 36.7, 37.3, 44.5, 47.5, 51.9, 54.0, 123.9, 127.2, 130.3, 138.4, 140.7, 150.3, 156.6, 179.0 (C=O). Found: C, 68.98; H, 8.09; N, 3.45%. Calcd for $C_{45}H_{63}BF_4N_2O_4$: C, 69.04; H, 8.11; N, 3.58%.

*1,3-Bis-((4bR,8S,8aS)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl)-1H-imidazol-3-ium chloride, trihydrate (**5**)*

This compound was synthesized by the method referenced in [10], which is the modification of Arduengo methodology [21]. To 458 mg (0.67 mmol) of bis-imine **2**, 1.5 mL of chloromethyl-propyl ether was added and the brown solution was stirred for 5 min. Afterwards 3 mL of MeCN was added and stirred at room temperature for 1 h. The residue, after evaporation of volatiles in vacuo, was treated by ethyl ether; ether was evaporated and the residue was treated with 5 mL of ethyl acetate to afford 274 mg (56%) of compound **5**. Off-white prisms, mp 235–238°C, $[\alpha]_D^{24}$ +76.4 (*c* 0.5, $CHCl_3$). IR, ν (Nujol): 3400 (br., OH), 1722 (O—C=O), 1632 (C=C), 1546, 1248, 1174, 1132, 1122, 1084, 896 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 1.20 (d, 6H, J = 6.3 Hz, Me), 1.24 (d, 6H, J = 6.3 Hz, Me), 1.25 (s, 6H, Me), 1.28 (s, 6H, Me), 1.42–1.95 (m, 14H, C(5)H_{ax}, 2 C(6)H_2, 2 C(7)H_2, 2 C(9)H_2), 2.08 (m, 2H, C(5)H_{eq}), 2.35 (m, 2H, C(8a)H), 2.63 (m, 2H, CHAr), 3.00 (m, 4H, 2 C(10)H_2), 3.60 (s, 6H, OMe), 7.33 (s, 2H, C(4)H), 7.54 (s, 2H, C(4)H), 8.31 (d, 2H, J = 1.5 Hz, 2 $H_{imidazole}$), 9.91 (t, J = 1.5 Hz, 1H, NCH = N). ^{13}C NMR ($CDCl_3$) δ: 16.3, 18.0, 20.9, 23.5, 23.7, 24.8, 26.4, 28.9, 36.2, 36.7, 37.7, 44.6, 46.9, 52.0, 119.3, 126.6, 127.3, 134.9, 139.1, 147.9, 177.9 (C = O). Found: C, 69.08; N, 8.55; H, 3.85%. Calcd for $C_{45}H_{61}ClN_2O_4 \cdot 3H_2O$: C, 68.99; H, 8.62; N, 3.58%.

General Procedure for Suzuki Coupling Reaction

A 250 mL flask was charged by $Pd(OAc)_2$ (6 mg, 0.028 mmol), 0.028 mmol of appropriate imidazolium salt **1a-i**, 60 mg (0.43 mmol) of K_2CO_3, and 70 mL of DMF, and was heated at 90°C for 15–20 min for the formation of precatalyst in situ. Then 480 mg (2.8 mmol) of 4-bromotoluene was added (2 mL of the working solution in DMF, containing 1 mL, 240 mg of 4-bromotoluene), 380 mg (2.8 mmol) of 4-tolylboronic acid, 770 mg (5.6 mmol) of K_2CO_3, and 0.4 mL of pentadecane as the internal standard. The flask was heated for 5 h at 90°C while stirring in aerobic conditions (at the end of the experiment, some quantity of palladium black was formed). After cooling, inorganic salts were filtered, washed with 20 mL of DMF, and the solvent was

TABLE 2 Crystal Data and Structure Refinement for Compounds **1e** and **2**

	1e	*2*
Empirical formula	$(C_{31}H_{39}N_2O_2)^+$,Cl^-,0.25H_2O	$C_{44}H_{60}N_2O_4$
Formula weight	511.60	680.94
Crystal size, mm	0.43 × 0.37 × 0.29	0.15 × 0.15 × 0.10
Crystal color	colorless	yellow
Temperature, K	295(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a, Å	12.3927(4)	14.893(3)
b, Å	8.7349(3)	7.9435(14)
c, Å	26.3703(9)	17.257(3)
β, deg.	94.766(3)	110.342(4)
Volume Å^3	2844.69(17)	1914.2(6)
Z	4	2
Density (calculated) g/cm^3	1.195	1.181
Absorption coefficient, mm^{-1}	0.165	0.074
Reflections collected	11529	19965
Independent reflections	8870 (R_{int}= 0.0149)	4936 ($R_{int} = 0.1154$)
θ range, deg.	2.80–26.37	1.46–28.00
Completeness to θ, %	98.8	99.7
Refined parameters	667	461
Goodness-of-fit on F^2	1.009	0.978
Reflections with $I > 2\sigma(I)$	5877	2754
$R_1(F)[I > 2\sigma(I)]^a$	0.0359	0.0723
wR_2 (F^2)[all data]	0.0915	0.1122
Largest diff. peak/hole, eÅ^{-3}	0.191/–0.169	0.229/–0.279

$^aR_1 = \sum |F_o - |F_c|| / \sum(F_o)$.

$^bwR_2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$.

evaporated in vacuo until 5–10 mL volume. 70 mL of brine were added, following extraction with CH_2Cl_2 (4 × 25 mL) and drying over $MgSO_4$. The resulting solution was analyzed on a GC-MS system Agilent 6890N.

CRYSTALLOGRAPHY

X-ray experiments were carried out using an Oxford Diffraction Xcalibur S diffractometer (λ(Mo-$K\alpha$) = 0.71073 Å, graphite monochromator, $\omega/2\theta$ scans) for **1e** and SMART 1000 CCD diffractometer (λ(Mo-$K\alpha$) = 0.71073 Å, graphite monochromator, ω-scans) for **2**. All structures were solved by direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for nonhydrogen atoms. Hydrogen atoms connected to carbon atoms were placed in geometrically calculated positions, whereas positions of disordered water hydrogens were found in a difference Fourier synthesis. All the hydrogen atoms were included in the refinement using riding approximation. The details of data collection and crystal structures refinement for which we used SAINT Plus [26], SADABS [27] and SHELXTL-97 [28] program packages are summarized in Table 2.

CCDC 794333 (**1e**) and 794334 (**2**) contain the supplementary crystallographic data for structures **1e** and **2**. These data can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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