Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 4297–4303

Synthesis of polyarene derivatives of fused aziridines by Suzuki–Miyaura cross-coupling

Alexander I. Zbruyev, Valery V. Vashchenko, Anastasiya A. Andryushchenko, Sergey M. Desenko, Vladimir I. Musatov, Irina V. Knyazeva and Valentin A. Chebanov*

State Scientific Institution 'Institute for Single Crystals' of National Academy of Sciences of Ukraine, Lenin Ave., 60, Kharkiv 61001, Ukraine

Received 25 October 2006; revised 16 February 2007; accepted 8 March 2007
Available online 12 March 2007

Abstract—A convenient and effective synthetic approach to potentially radiochromic polyarene derivatives of bi- and tricyclic aziridines utilizing modified Suzuki–Miyaura cross-coupling with catalysis in micellar media has been developed. A series of polyarene substituents were introduced into 1,5-diaryl-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazoles, 1,6-diaryl-1,3,4,6a-tetrahydroazireno[1,2-*a*]pyrazines, and 1,2-diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines without degradation of the highly reactive aziridine ring system.

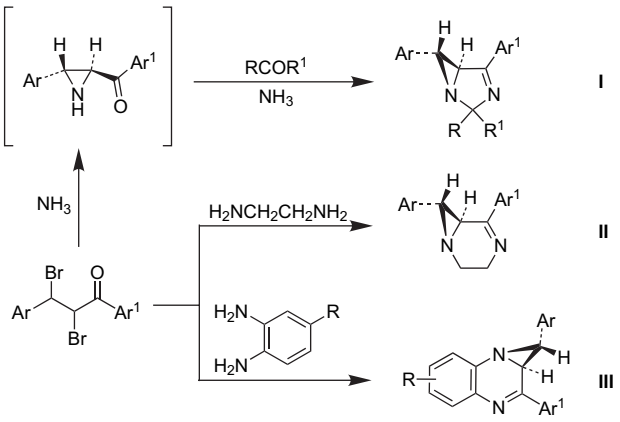
1. Introduction

Derivatives of fused bi- and tricyclic aziridines are of interest due to their chemical and photochromic properties promoted by the presence of sterically strained three-membered heterocycle. Their thermo- and photoinduced cycloaddition reactions with various compounds containing multiple bonds accompanied by cleavage of C–C bond of aziridine ring have been studied.[1,2] The photochromic properties of aziridines are also linked with ring opening of the three-membered cycle.[3]

Among effective photochromes, 1,5-diaryl-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazoles **I**, 1,6-diaryl-1,3,4,6a-tetrahydroazireno[1,2-*a*]pyrazines **II**, and 1,2-diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines **III** containing a 4-nitrophenyl substituent at the aziridine ring should be mentioned. These substances in the crystalline state, initially white or yellow, develop an intense blue color upon irradiation in the UV–vis range (200–700 nm).

Our preliminary experiments showed that aziridines **I**–**III** possessed very low sensitivity toward X-ray and β-radiation.[4] At the same time, various polyarene aromatic compounds are used to transform the energy of absorbed ionizing radiation into an ultraviolet form.[5] Therefore, combining a photochromic (bicyclic aziridine) and a radiophoric (polyarene) fragment in one molecule can give rise to an effective radiochromic compound.[6]

An established method for synthesizing aziridines **I**–**III** is the reaction of 2,3-dibromo-1,3-diarylpropan-1-ones with ammonia and carbonyl compounds or with the corresponding 1,2-diamines (Scheme 1).[1a,b,2,7] In most cases these methods provide good yields of reaction products with high purity. An alternative means to synthesize stereospecific aziridines **I** is based on the microwave-assisted multicomponent reaction of phenacyl chloride with aldehydes in the presence of ammonium acetate, which was reported recently.[8] A serious limitation of the described procedure is the difficulties associated with the preparation of bicyclic aziridines with different substituents in positions 2 and 8.



Scheme 1.

Keywords: Heterocycles; Azireno[1,2-*c*]imidazoles; Azireno[1,2-*a*]pyrazines; Azireno[1,2-*a*]quinoxalines; Cross-coupling; Micellar media.
* Corresponding author. Tel.: +38 057 341 01 91; fax: +38 057 340 93 43; e-mail: chebanov@isc.kharkov.com

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.060

Our attempts to prepare aziridines containing polyarene fragments according to conventionally described procedures in the most were unsuccessful, mainly due to the low solubility of starting materials, intermediates, and final products. In some cases it was not possible to isolate target compounds at all, others required complicated purification, which resulted in a dramatic lowering of the yield. It is worth mentioning that polyarene derivatives of 2,3-dibromopropan-1-ones are also difficult to synthesize by known methods.[9]

An alternative route to bi- and tricyclic aziridines containing polyarene substituents would be use of aryl–aryl cross-coupling reactions after formation of the aziridine fragment. Amongst the wide variety of approaches to Ar–Ar bond formation[10] the Suzuki–Miyaura reaction[11] seems to be most suitable and promising in the case of aziridines taking into account their rather high reactivity and instability at elevated temperature and in the presence of acids or bases.[1b,12] However, there are only a few examples of using Suzuki–Miyaura coupling for compounds containing this heterocycle in non-fused structures.[13]

2. Results and discussion

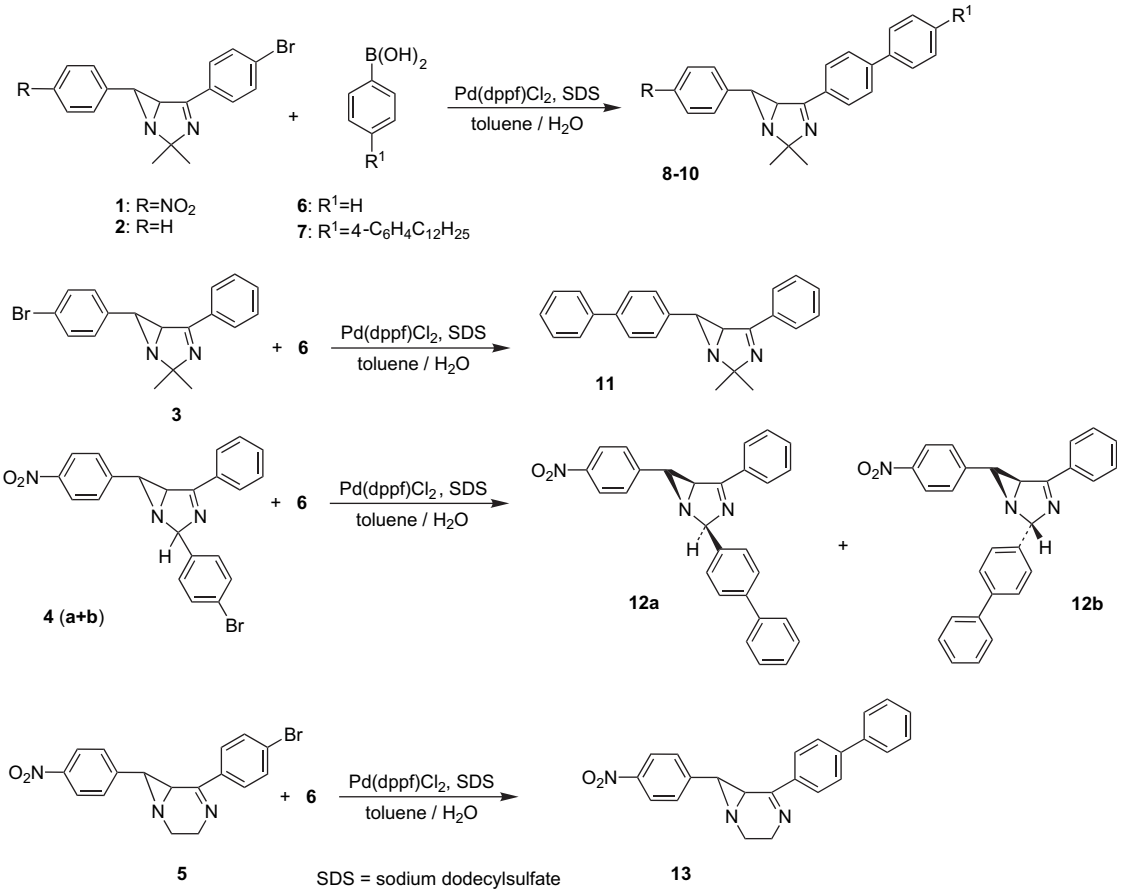
The present work is devoted to the development of a convenient synthetic approach for potentially radiochromic bi- and tricyclic aziridines containing polyarene fragments utilizing Suzuki–Miyaura reaction. One of the main goals of the investigation was elaboration of protocols for cross-coupling reaction, which would be applicable both in case of fused aziridines and for other unstable organic compounds.

2.1. Arylation of azireno[1,2-*c*]imidazole and azireno[1,2-*a*]pyrazine derivatives

For arylation of a sensitive photochrome with a highly reactive three-membered ring as in **1** we initially chose a standard Suzuki–Miyaura reaction protocol providing mild enough reaction conditions: reflux in toluene/water solution with $NaHCO_3$ and $Pd(dppf)Cl_2$ (dppf=1,1′-bis(diphenylphosphino)ferrocene) (Scheme 2).

The course of aziridine **1** treatment with phenylboronic acid **6** was monitored by HPLC. It was established that the concentration of the product **8** was increased for the first 30 min of the reaction; afterward its amount remained almost unchanged (~70% conversion), and only by-products were accumulated after this point, which complicated the work-up procedure and purification of the required product.

To improve the reaction efficiency we used the method described in the preliminary report[14] regarding catalysis in micellar media.[15] Since the reaction is heterogeneous, the presence of a surfactant should promote emulsion formation, bringing together a water-insoluble organic reactant and



Scheme 2.

Table 1. Polyarene derivatives of fused aziridines **8–13** and **19–23**

Entry	R	R^1	Reaction time, min	Yields of crude products, %
8	NO_2	H	5	99
9	H	H	5	83
10	NO_2	4-$C_{12}H_{25}C_6H_4$	5	99
11	—	—	5	88
12 (a+b)	—	—	5	98
13	—	—	5	91
19	—	—	20	85
20 (c+d)	H	H	20	87
21 (c+d)	Et	H	20	83
22 (c+d)	Et	Ph	20	79
23 (c+d)	Ph	H	25	87

a water-soluble inorganic reagent, therefore accelerating the reaction. As the standard Suzuki–Miyaura cross-coupling proceeds in a basic media we have chosen an anionic surfactant—sodium dodecylsulfate (SDS), which is one of the cheapest and most widespread microemulsion forming agents.

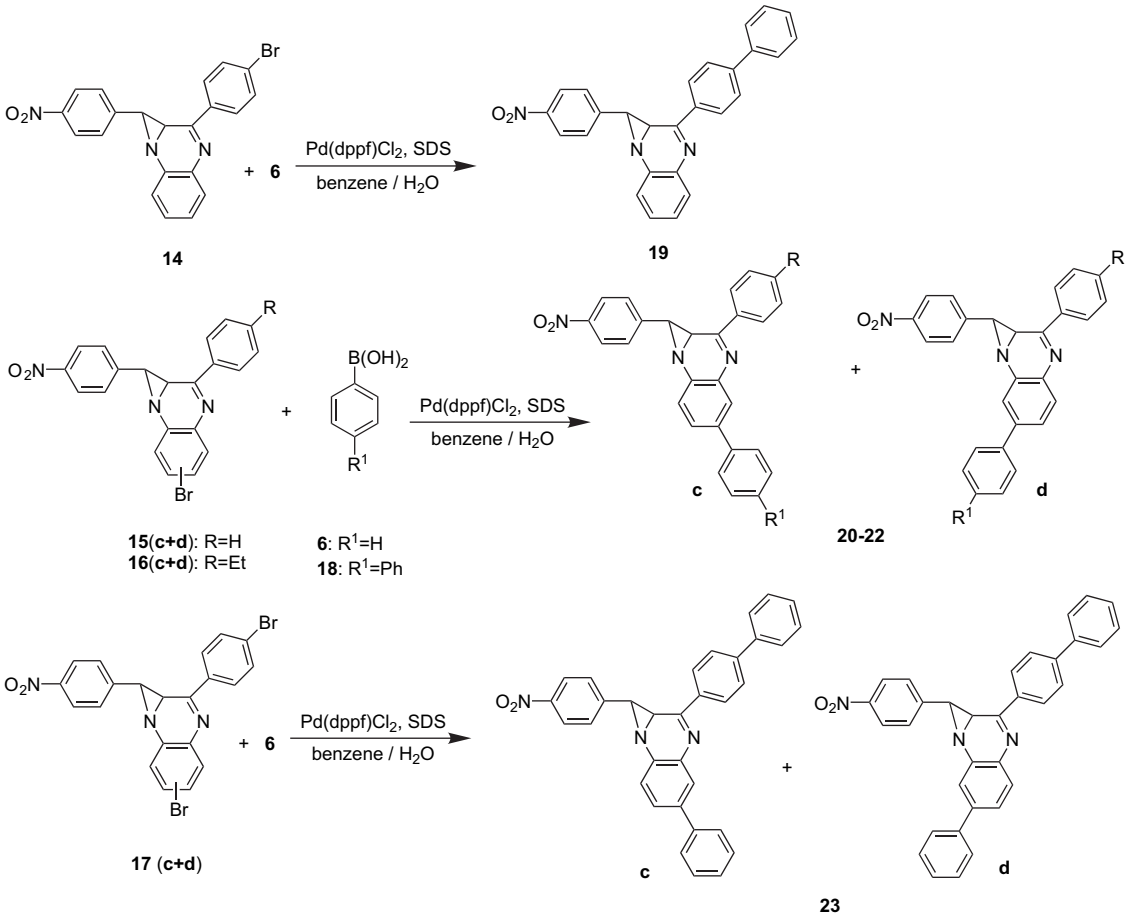
Based on HPLC data the reaction of aziridine **1** with phenylboronic acid **6** in the presence of SDS, about 98% conversion was achieved even in 5 min. At that time, only traces of by-products were detected. After the conventional work-up procedure the product **8** was obtained in more than 95% purity (according to HPLC).

The same method was used for introducing various polyarene fragments into different parts of other dihydroazirenoimidazoles. Compounds **9–12** were synthesized according to the procedure developed by the reaction of compounds **1–4** with organoboronic acids **6** and **7** in high yields (see Table 1). It can be noted that compound **4** was used as a mixture of *endo*- and *exo*-isomers and after the cross-coupling reaction the mixture of the corresponding products **12a** (*endo*) and **12b** (*exo*) was isolated and separated.

The protocol is also suitable for introducing polyarene fragments into another class of fused aziridines, 1,6-diaryl-1,3,4,6a-tetrahydroazireno[1,2-*a*]pyrazines. It was found that reaction of **5** with **6** led to the corresponding aziridine **13** in a good yield and high purity.

2.2. Arylation of azireno[1,2-*a*]quinoxaline derivatives

The same reaction conditions were applied to the reaction of 2-(4-bromophenyl) substituted dihydroazirenoquinoxaline **14** with **6**. However, formation of the target biphenyl-substituted aziridine **19** was complicated with rapid appearance of large amounts of by-products within 5 min. Control experiments without **6** and a palladium catalyst in reaction mixture showed that compound **14** was unstable under the selected reaction conditions. As a solution to this problem, reduction of the reaction temperature was used. A replacement of toluene/water mixture with



Scheme 3.

benzene/water allowed compound **19** to be formed in 95% conversion after 15 min (Scheme 3).

To diversify polyarene derivatives of aziridine we also explored the possibility to carry out the cross-coupling reaction on the quinoxaline fragment of dihydroazirenoquinoxalines. Starting bromosubstituted derivatives **15**–**17** were obtained in the reactions of the appropriate 2,3-dibromo-1,3-diarylpropan-1-ones with 4-bromo-1,2-phenylenediamine (see Scheme 1) according to literature procedure.[2,7a] Products **15**–**17** represented mixtures of regioisomeric 5- and 6-bromodihydroazirenoquinoxalines with predominance for the 5-bromoderivative **c**, as previously recorded in an earlier investigation of 4-methyl-1,2-phenylenediamine derivatives.[2] The isomer ratio for **15**–**17** was determined by HPLC and ^{1}H NMR spectroscopic data according to the procedure described[2] (see Section 4). Mixtures of isomers **c** and **d** of the compounds **15**–**17** could not be separated and were introduced into Suzuki–Miyaura coupling giving rise to mixtures of isomeric arylsubstituted compounds **20**–**23**.

It was also determined that both bromine atoms in dihydroazirenoquinoxaline **17** underwent arylation to give a mixture of isomers **23c** and **23d**. No monobromo or dibromosubstituted aziridines were left remaining (as determined by analysis of the crude material by ^{1}H NMR and mass spectroscopy).

All compounds synthesized possess photochromic properties toward UV–vis radiation similar to those of the known aziridines without polyarene fragments[3] and will be studied as possible radiochromic compounds toward X-ray and β-radiation.

3. Conclusions

In summary, this report describes a novel and effective approach to bi- and tricyclic derivatives of fused aziridines containing polyarene fragments based on modified Suzuki–Miyaura cross-coupling. A protocol was developed utilizing catalysis in micellar media for the introduction of polyarene fragments into various positions of the aziridines, which accelerated significantly the reaction rate, increased the yields, and purity of the products. It was shown that micellar-catalyzed procedures were less sensitive to the leakage of air in the course of the reaction in comparison with a more prolonged standard protocol, and allowed avoiding side reactions.

4. Experimental

4.1. General

Melting points were determined with a Boetius apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 or in $CDCl_3$ at 200 MHz (50 MHz for ^{13}C) on a Varian Mercury VX-200 spectrometer or at 500 MHz on a Bruker Avance-500 spectrometer and analyzed with ADVASP™ Analyzer program (Umatek International Inc.). Mass spectra were measured on a GC–MS Varian 1200L instrument (EI, 70 eV). Elemental analysis was made on a EuroVector EA-3000. HPLC experiments were performed on Bischoff module chromatograph. Monitoring of the reaction course for compound **8** and purity analysis for all compounds were carried out on RP C-18 column using 50% acetonitrile–water mixture as eluant. Isomeric composition of compounds **15**–**17** and **20**–**23** was determined using silica column and CH_2Cl_2 as eluant. Separation of the isomeric mixture of **12a** and **12b** was carried out on a Prontosil C18 (250×20 mm) column using acetonitrile (~87%)–water azeotropic mixture as eluant.

Phenylboronic acid (**6**) and Pd(dppf)$Cl_2\cdot CH_2Cl_2$ are commercially available (Aldrich).

4.1.1. General procedure for the synthesis of arylboronic acids 7 and 18. Grignard reagent was obtained from magnesium and the corresponding aryl bromide in absolute THF, refluxed for 4 h, and cooled to 0 °C. Trimethylborate was added dropwise to the obtained solution. Reaction mixture was mixed for 1 h, allowed to warm up to 20 °C, and to stand overnight. Then it was decomposed with 16% HCl solution and mixed for 2 h. The precipitate obtained was filtered, washed with water and heptane, and dried in vacuum.

4.1.1.1. 4-(4-Dodecylphenyl)phenylboronic acid (7). Quantities used: magnesium (0.56 g, 22.9 mmol), 4-bromo-4′-dodecylbiphenyl (8.5 g, 21.2 mmol), absolute THF (55 mL), trimethylborate (7.1 mL, 63.6 mmol), and HCl solution (400 mL). Yield: 6.55 g (84.4%) of white crystals. ^{1}H NMR (DMSO-d_6): δ 0.82 (t, J=7.0 Hz, 3H, CH_3), 1.13–1.33 (m, 18H, $(CH_2)_9$), 1.48–1.65 (m, 2H, CH_2), 2.58 (t, J=7.4 Hz, 2H, CH_2), 7.25 (d, J=8.2 Hz, 2H$_{arom}$), 7.57 (d, J=8.2 Hz, 2H$_{arom}$), 7.58 (d, J=8.2 Hz, 2H$_{arom}$), 7.84 (d, J=8.2 Hz, 2H$_{arom}$), 8.05 (s, 1.9H (exchangeable), $(OH)_3$).

4.1.1.2. 4-Phenylphenylboronic acid (18).[16] Quantities used: magnesium (0.169 g, 7.0 mmol), 4-bromobiphenyl (1.5 g, 6.4 mmol), absolute THF (25 mL), trimethylborate (2.2 mL, 19.2 mmol), and HCl solution (130 mL). Yield: 0.847 g (67%) of white crystals.

4.1.2. Synthesis of the starting aziridines. Starting aziridines **1**–**5** and **14**–**17** were obtained by known methods.[1b,2,7a]

4.1.2.1. 5(6)-Bromo-1-(4-nitrophenyl)-2-phenyl-1,1a-dihydroazireno[1,2-*a*]quinoxaline (15c+d). Yield: 68% (73% (**c**) and 27% (**d**)) of yellowish crystals. ^{1}H NMR ($CDCl_3$): δ 2.95 (d, J=2.7 Hz, 1H, 1-CH (**c**)), 2.98 (d, J=2.7 Hz, 1H, 1-CH (**d**)), 3.41 (d, J=2.7 Hz, 1H, 1a-CH (**d**)), 3.43 (d, J=2.7 Hz, 1H, 1a-CH (**c**)), 7.15 (d, J=8.2 Hz, 1H, 7-CH (**c**)), 7.25 (dd, J=1.8, 8.2 Hz, 1H, 6-CH (**c**)), 7.28 (dd, J=1.7, 8.4 Hz, 1H, 5-CH (**d**)), 7.31 (d, J=8.4 Hz, 1H, 4-CH (**d**)), 7.38–7.42 (m, 2H$_{arom}$ (**c+d**)), 7.45 (br s, 1H, 7-CH (**d**)), 7.46–7.48 (m, 3H$_{arom}$ (**c+d**)), 7.60 (d, J=1.8 Hz, 1H, 4-CH (**c**)), 7.84 (d, J=7.7 Hz, 2H$_{arom}$ (**c+d**)), 8.20 (d, J=8.5 Hz, 2H$_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=419 (2%) [M$^+$], 421 (2%) [M$^+$], 284 (10%), 286 (10%), 257 (19%), 259 (22%); 156 (22%), 154 (17%). Anal. Calcd for $C_{21}H_{14}BrN_3O_2$: C, 60.02; H, 3.36; N, 10.00. Found: C, 60.15; H, 3.45; N, 9.97.

4.1.2.2. 5(6)-Bromo-2-(4-ethylphenyl)-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (16c+d). Yield: 63% (72% (**c**) and 28% (**d**)) of yellowish crystals.

^{1}H NMR ($CDCl_3$): δ 1.18 (t, J=7.6 Hz, 3H, CH_3 (**c+d**)), 2.64 (quart, J=7.6 Hz, 2H, CH_2 (**c+d**)), 2.93 (d, J=2.9 Hz, 1H, 1-CH (**c**)), 2.96 (d, J=2.9 Hz, 1H, 1-CH (**d**)), 3.41 (d, J=2.9 Hz, 1H, 1a-CH (**d**)), 3.42 (d, J=2.9 Hz, 1H, 1a-CH (**c**)), 7.14 (d, J=8.2 Hz, 1H, 7-CH (**c**)), 7.22 (d, J=8.2 Hz, $2H_{arom}$ (**c+d**)), 7.23 (dd, J=2.3, 8.2 Hz, 1H, 6-CH (**c**)), 7.27 (dd, J=2.0, 8.3 Hz, 1H, 5-CH (**d**)), 7.30 (d, J=8.3 Hz, 1H, 4-CH (**d**)), 7.44 (d, J=2.0 Hz, 1H, 7-CH (**d**)), 7.46 (d, J=8.7 Hz, $2H_{arom}$ (**c+d**)), 7.59 (d, J=2.2 Hz, 1H, 4-CH (**c**)), 7.77 (d, J=8.2 Hz, $2H_{arom}$ (**c+d**)), 8.20 (d, J=8.8 Hz, $2H_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=449 (29%) [M^+], 447 (31%) [M^+], 314 (100%), 312 (95%), 300 (9%), 298 (12%), 287 (5%), 285 (8%), 156 (23%), 154 (18%), 105 (24%). Anal. Calcd for $C_{23}H_{18}BrN_3O_2$: C, 61.62; H, 4.05; N, 9.37. Found: C, 61.50; H, 4.20; N, 9.34.

4.1.2.3. 5(6)-Bromo-2-(4-bromophenyl)-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (17c+d). Yield: 57% (73% (**c**) and 27% (**d**)) of yellowish crystals. ^{1}H NMR ($CDCl_3$): δ 2.94 (d, J=2.9 Hz, 1H, 1-CH (**c**)), 2.97 (d, J=2.9 Hz, 1H, 1-CH (**d**)), 3.36 (d, J=2.9 Hz, 1H, 1a-CH (**d**)), 3.37 (d, J=2.9 Hz, 1H, 1a-CH (**c**)), 7.15 (d, J=8.2 Hz, 1H, 7-CH (**c**)), 7.26 (dd, J=2.3, 8.2 Hz, 1H, 6-CH (**c**)), 7.28 (m, 2H, 5-CH (**d**)+4-CH (**d**)), 7.45 (d, 1H, 7-CH (**d**)), 7.46 (d, J=8.8 Hz, $2H_{arom}$ (**c+d**)), 7.52 (d, J= 8.8 Hz, $2H_{arom}$ (**c+d**)), 7.58 (d, J=2.2 Hz, 1H, 4-CH (**c**)), 7.71 (d, J=8.8 Hz, $2H_{arom}$ (**c+d**)), 8.20 (d, J=8.8 Hz, $2H_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=501 (2%) [M^+], 499 (3%) [M^+], 497 (2%) [M^+], 366 (37%), 364 (77%), 362 (33%), 339 (3%), 337 (6%), 335 (3%), 183 (12%), 181 (14%), 156 (14%), 154 (14%). Anal. Calcd for $C_{21}H_{13}Br_2N_3O_2$: C, 50.53; H, 2.63; N, 8.42. Found: C, 50.59; H, 2.51; N, 8.39.

4.1.3. Non-micellar procedure for synthesis of 3,3-dimethyl-1-(4-nitrophenyl)-5-(4-phenylphenyl)-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole 8. A mixture of aziridine **1** (1.00 g, 2.59 mmol), phenylboronic acid **6** (0.379 g, 3.1 mmol), toluene (30 mL), water (15 mL), and 1-butanol (3 mL) in a three-necked flask was degassed in vacuum and flashed with argon under vigorous stirring, then $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (56 mg, 0.069 mmol) was added. The degassing was repeated again, and the mixture was heated to reflux under argon atmosphere and solution of $NaHCO_3$ (870 mg, 10.36 mmol) in water (15 mL) was added in one portion. The reflux was continued whereas samples of reaction mixture for HPLC analysis were taken after 3, 5, 10, 30, 70, and 140 min after addition of the base.

4.1.4. General procedure for micellar-catalyzed synthesis of aziridines 8–13. Procedure with micellar catalysis is similar to the one described above, except addition of surfactant to mixture of reactants. Quantities used: an appropriate bromosubstituted aziridines **1**–**5** (2.59 mmol), phenylboronic acid **6** (0.379 g, 3.1 mmol), SDS (0.300 g), toluene (30 mL), water (15 mL), 1-butanol (3 mL), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (56 mg, 0.069 mmol), and a solution of $NaHCO_3$ (870 mg, 10.36 mmol) in water (15 mL). After addition of the base, the reaction mixture was refluxed for 5 min and cooled to room temperature. The organic layer was separated, water layer was extracted with CH_2Cl_2 (2×15 mL), the combined organic extract was washed with water (50 mL), dried over Na_2SO_4, filtered through short plug of silica gel (20 cc), evaporated to dryness, and stored in vacuum desiccator to afford products **8**–**13**.

4.1.4.1. 3,3-Dimethyl-1-(4-nitrophenyl)-5-(4-phenylphenyl)-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole (8). Yield: 99% of colorless crystals, mp 198 °C (from acetone). ^{1}H NMR ($CDCl_3$): δ 1.60 and 1.62 (2s, 6H, CH_3), 2.63 (d, J=1.6 Hz, 1H, 1-CH), 3.64 (d, J=1.6 Hz, 1H, 5a-CH), 7.38–7.53 (m, $5H_{arom}$), 7.60–7.70 (m, $4H_{arom}$), 7.93 (d, J=8.4 Hz, $2H_{arom}$), 8.20 (d, J=8.8 Hz, $2H_{arom}$). Anal. Calcd for $C_{24}H_{21}N_3O_2$: C, 75.18; H, 5.52; N, 10.96. Found: C, 75.10; H, 5.41; N, 10.93. ^{13}C NMR ($CDCl_3$): δ 23.7, 31.3, 43.8, 56.2, 95.9, 123.7, 127.2, 127.4, 127.4, 128.0, 128.7, 129.0, 130.7, 140.1, 144.3, 146.0, 147.4, 167.3.

4.1.4.2. 3,3-Dimethyl-1-phenyl-5-(4-phenylphenyl)-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole (9). Yield: 83% of colorless crystals, mp 108 °C (from hexane). ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 6H, CH_3), 2.60 (d, J=1.7 Hz, 1H, 1-CH), 3.66 (d, J=1.7 Hz, 1H, 5a-CH), 7.27–7.53 (m, $8H_{arom}$), 7.62–7.71 (m, $4H_{arom}$), 7.98 (d, J=8.2 Hz, $2H_{arom}$). Anal. Calcd for $C_{24}H_{22}N_2$: C, 50.53; H, 2.63; N, 8.42. Found: C, 50.44; H, 2.78; N, 8.39. ^{13}C NMR ($CDCl_3$): δ 23.7, 31.5, 44.9, 55.6, 95.5, 126.6, 127.2, 127.4, 127.6, 128.0, 128.5, 128.8, 129.0, 131.0, 138.4, 140.2, 144.0, 168.1. MS (EI, 70 eV): m/z (%)=338 (81%) [M^+], 323 (100%), 296 (7%), 261 (30%), 234 (41%), 180 (30%).

4.1.4.3. 5-{4-[4-(4-Dodecylphenyl)phenyl]phenyl}-3,3-dimethyl-1-(4-nitrophenyl)-3,5a-dihydro-1*H*-azireno-[1,2-*c*]imidazole (10). Yield: 99% of white solid, mp 168 °C (from acetone). ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 3H, Alk-CH_3), 1.13–1.42 (m, 20H, $(CH_2)_{10}$), 1.51–1.73 (m, 8H, $2CH_3$+ CH_2), 2.57–2.70 (m, 3H, 1-CH+ArCH_2), 3.64 (d, J=1.6 Hz, 1H, 5a-CH), 7.20–7.30 (m, $2H_{arom}$), 7.45–7.60 (m, $4H_{arom}$), 7.62–7.75 (m, $6H_{arom}$), 7.92 (d, J=8.4 Hz, $2H_{arom}$), 8.20 (d, J=8.8 Hz, $2H_{arom}$). Anal. Calcd for $C_{42}H_{49}N_3O_2$: C, 80.34; H, 7.87; N, 6.69. Found: C, 80.44; H, 7.79; N, 6.67. ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 23.7, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.3, 31.4, 31.9, 35.7, 43.8, 56.2, 95.9, 123.7, 126.9, 127.2, 127.4, 127.5, 127.5, 128.8, 128.9, 130.7, 137.7, 138.5, 141.0, 142.5, 143.8, 146.0, 147.4, 167.3. MS (EI, 70 eV): m/z (%)=627 (32%) [M^+], 492 (49%), 478 (92%), 465 (34%), 424 (22%), 335 (46%), 323 (63%), 268 (100%).

4.1.4.4. 3,3-Dimethyl-1-(4-phenylphenyl)-5-phenyl-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole (11). Yield: 88% of colorless crystals, mp 116 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 1.60 and 1.62 (2s, 6H, CH_3), 2.72 (d, J=1.6 Hz, 1H, 1-CH), 3.89 (d, J=1.6 Hz, 1H, 5a-CH), 7.34–7.50 (m, $8H_{arom}$), 7.57–7.65 (m, $4H_{arom}$), 7.88 (d, J=7.1 Hz, $2H_{arom}$). Anal. Calcd for $C_{24}H_{22}N_2$: C, 50.53; H, 2.63; N, 8.42. Found: C, 50.40; H, 2.71; N, 8.39. ^{13}C NMR ($CDCl_3$): δ 23.7, 31.5, 44.6, 55.7, 95.6, 127.0, 127.1, 127.3, 127.4, 128.3, 128.7, 128.8, 131.3, 132.2, 137.5, 140.6, 140.9, 168.4. MS (EI, 70 eV): m/z (%)=338 (78%) [M^+], 323 (100%), 220 (13%), 185 (35%), 158 (28%).

4.1.4.5. *endo*-1-(4-Nitrophenyl)-5-phenyl-3-(4-phenylphenyl)-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole (12a). Colorless crystals, mp 174 °C. ^{1}H NMR (DMSO-d_6): δ 2.68 (d, J=1.9 Hz, 1H, 1-CH), 4.22 (d, J=1.9 Hz, 1H, 5a-CH), 6.76 (s, 1H, 3-CH), 7.30–7.68 (m, $14H_{arom}$), 8.02

(d, J=6.7 Hz, 2H$_{arom}$), 8.15 (d, J=8.4 Hz, 2H$_{arom}$). ^{13}C NMR (DMSO-d_6): δ 41.6, 57.7, 95.6, 124.1, 127.3, 127.4, 128.2, 128.5, 129.2, 129.6, 129.7, 132.0, 132.4, 138.6, 140.1, 140.3, 146.8, 147.4, 171.5. Anal. Calcd for $C_{28}H_{21}N_3O_2$: C, 77.94; H, 4.91; N, 9.74. Found: C, 77.88; H, 5.01; N, 9.71.

4.1.4.6. *exo*-1-(4-Nitrophenyl)-5-phenyl-3-(4-phenylphenyl)-3,5a-dihydro-1*H*-azireno[1,2-*c*]imidazole (12b). Colorless crystals, mp 196 °C. ^{1}H NMR (DMSO-d_6): δ 2.68 (d, J=1.8 Hz, 1H, 1-CH), 3.09 (d, J=1.8 Hz, 1H, 5a-CH), 6.33 (s, 1H, 3-CH), 7.30–7.69 (m, 14H$_{arom}$), 7.99 (d, J=7.1 Hz, 2H$_{arom}$), 8.20 (d, J=8.1 Hz, 2H$_{arom}$). ^{13}C NMR (DMSO-d_6): δ 47.2, 56.7, 96.8, 124.1, 127.4, 128.1, 128.2, 128.5, 129.2, 129.5, 129.6, 132.0, 132.3, 140.5, 140.6, 141.2, 147.1, 147.4, 170.1. Anal. Calcd for $C_{28}H_{21}N_3O_2$: C, 77.94; H, 4.91; N, 9.74. Found: C, 77.87; H, 4.99; N, 9.70.

4.1.4.7. 1-(4-Nitrophenyl)-6-(4-phenylphenyl)-1,3,4,6a-tetrahydroazireno[1,2-*a*]pyrazine (13). Yield: 91% of yellowish crystals, mp 145 °C (from acetone). ^{1}H NMR (DMSO-d_6): δ 2.69–2.84 (m, 1H, CH$_2$), 3.16–3.27 (m, 2H, 1-CH+CH$_2$), 3.25 (d, J=2.2 Hz, 1H, 6a-CH), 3.67–3.84 (m, 2H, CH$_2$), 3.95, 7.31–7.50 (m, 3H$_{arom}$), 7.59–7.72 (m, 6H$_{arom}$), 7.85 (d, J=8.5 Hz, 2H$_{arom}$), 8.21 (d, J=8.8 Hz, 2H$_{arom}$). ^{13}C NMR (DMSO-d_6): δ 39.6, 39.8, 43.7, 124.2, 127.2, 127.3, 127.4, 128.3, 128.6, 129.7, 138.0, 140.0, 142.3, 147.4, 147.7, 162.6. Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.70; H, 5.29; N, 11.36.

4.1.5. General procedure for micellar-catalyzed synthesis of dihydroazirenoquinoxalines 19–22. A mixture of the corresponding bromosubstituted dihydroazirenoquinoxaline (2.59 mmol), phenylboronic acid (3.1 mmol), SDS (0.300 g), benzene (30 mL), water (15 mL), and 1-butanol (3 mL) in a three-necked flask was degassed in vacuum and flashed with argon under vigorous stirring, then Pd(dppf)Cl$_2\cdot$CH$_2$Cl$_2$ (56 mg, 0.069 mmol) was added. The degassing was repeated again, and the mixture was heated to reflux under argon atmosphere and the solution of Na_2CO_3 (10.36 mmol) in water (15 mL) was added in one portion. After addition of the base, the reaction mixture was refluxed for 20 min and cooled to room temperature. The organic layer was separated, water layer was extracted with CH_2Cl_2 (2×15 mL), the combined organic extract was washed with water (50 mL), dried over Na_2SO_4, filtered through short plug of silica gel (20 cc), evaporated to dryness, and dried in vacuum desiccator. The residue was recrystallized from acetone to afford products **19**–**22**.

4.1.5.1. 1-(4-Nitrophenyl)-2-(4-phenylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (19). Yield: 85% of yellowish crystals, mp 147–148 °C (from acetone). ^{1}H NMR (DMSO-d_6): δ 3.47 (d, J=2.6 Hz, 1H, 1-CH), 3.94 (d, J=2.6 Hz, 1H, 1a-CH), 7.21–7.51 (m, 7H$_{arom}$), 7.67–7.73 (m, 4H$_{arom}$), 7.81 (d, J=8.4 Hz, 2H$_{arom}$), 8.03 (d, J=8.4 Hz, 2H$_{arom}$), 8.27 (d, J=8.7 Hz, 2H$_{arom}$). Anal. Calcd for $C_{27}H_{19}N_3O_2$: C, 77.68; H, 4.59; N, 10.07. Found: C, 77.59; H, 4.66; N, 10.05.

4.1.5.2. 2,5(2,6)-Diphenyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (20c+d). Yield: 87% (85% (**c**) and 15% (**d**)) of yellowish crystals. ^{1}H NMR (CDCl$_3$): δ 3.01 (d, J=2.8 Hz, 1H, 1-CH (**c**)), 3.02 (d, J=2.8 Hz, 1H, 1-CH (**d**)), 3.46 (d, J=2.7 Hz, 1H, 1a-CH (**c+d**)), 7.27–7.57 (m, 12H$_{arom}$), 7.72 (d, J=2.1 Hz, 1H, 4-CH (**c**)), 7.88 (d, J=7.6 Hz, 2H$_{arom}$ (**c+d**)), 8.21 (d, J=8.6 Hz, 2H$_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=417 (3%) [M$^+$], 282 (73%), 255 (5%), 152 (25%), 103 (24%), 102 (100%). Anal. Calcd for $C_{27}H_{19}N_3O_2$: C, 77.68; H, 4.59; N, 10.07. Found: C, 77.57; H, 4.68; N, 10.04.

4.1.5.3. 2-(4-Ethylphenyl)-1-(4-nitrophenyl)-5(6)-phenyl-1,1a-dihydroazireno[1,2-*a*]quinoxaline (21c+d). Yield: 83% (77% (**c**) and 23% (**d**)) of yellowish crystals. ^{1}H NMR (CDCl$_3$): δ 1.19 (t, J=7.7 Hz, 3H, CH$_3$ (**c+d**)), 2.65 (quart, J=7.7 Hz, 2H, CH$_2$ (**c+d**)), 2.99 (d, J=2.9 Hz, 1H, 1-CH (**c**)), 3.00 (d, J=2.9 Hz, 1H, 1-CH (**d**)), 3.46 (d, J=2.9 Hz, 1H, 1a-CH (**c+d**)), 7.23 (d, J=7.9 Hz, 2H$_{arom}$ (**c+d**)), 7.27–7.42 (m, 4H$_{arom}$ (**c+d**)), 7.49–7.57 (m, 5H$_{arom}$ (**c+d**)), 7.71 (d, J=2.1 Hz, 1H, 4-CH (**c**)), 7.80 (d, J=8.2 Hz, 2H$_{arom}$ (**c+d**)), 8.21 (d, J=8.7 Hz, 2H$_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=445 (2%) [M$^+$], 310 (99%), 283 (3%), 152 (25%), 102 (100%). Anal. Calcd for $C_{29}H_{23}N_3O_2$: C, 78.18; H, 5.20; N, 9.43. Found: C, 78.27; H, 5.29; N, 9.40.

4.1.5.4. 2-(4-Ethylphenyl)-1-(4-nitrophenyl)-5(6)-(4-phenylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (22). Yield: 79% (80% (**c**) and 20% (**d**)) of yellowish crystals. ^{1}H NMR (CDCl$_3$): δ 1.19 (t, J=7.7 Hz, 3H, CH$_3$ (**c+d**)), 2.65 (quart, J=7.7 Hz, 2H, CH$_2$ (**c+d**)), 2.99 (d, J=2.8 Hz, 1H, 1-CH (**c**)), 3.00 (d, J=2.8 Hz, 1H, 1-CH (**c**)), 3.46 (d, J=2.9 Hz, 1H, 1a-CH (**c+d**)), 7.21–7.68 (m, 15H$_{arom}$ (**c+d**)), 7.75 (d, J=1.9 Hz, 1H, 4-CH (**c**)), 7.81 (d, J=8.2 Hz, 2H$_{arom}$ (**c+d**)), 8.22 (d, J=8.7 Hz, 2H$_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=493 (100%) [M$^+$], 494 (46%) [M$^+$], 358 (65%), 359 (18%), 228 (12%), 178 (21%). Anal. Calcd for $C_{33}H_{23}N_3O_2$: C, 80.31; H, 4.70; N, 8.51. Found: C, 80.22; H, 4.79; N, 8.47.

4.1.6. Micellar-catalyzed synthesis of 1-(4-nitrophenyl)-5(6)-phenyl-2-(4-phenylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline 23. The procedure is similar to the one described above (Section 4.1.5), except the quantity of the starting dibromosubstituted aziridine **17** (mixture of **c** and **d**) was 1.28 mmol and reaction time was 25 min.

4.1.6.1. 1-(4-Nitrophenyl)-5(6)-phenyl-2-(4-phenylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (23). Yield: 87% (80% (**c**) and 20% (**d**)) of yellowish crystals. ^{1}H NMR (CDCl$_3$): δ 2.97 (d, J=2.7 Hz, 1H, 1-CH (**c**)), 2.99 (d, J=2.7 Hz, 1H, 1-CH (**d**)), 3.47 (d, J=2.7 Hz, 1H, 1a-CH (**c+d**)), 7.28–7.65 (m, 17H$_{arom}$ (**c+d**)), 7.92 (d, J=8.3 Hz, 2H$_{arom}$ (**c+d**)), 8.22 (d, J=8.6 Hz, 2H$_{arom}$ (**c+d**)). MS (EI, 70 eV): m/z (%)=493 (1%) [M$^+$], 358 (100%), 179 (26%), 152 (29%), 102 (70%). Anal. Calcd for $C_{33}H_{23}N_3O_2$: C, 80.31; H, 4.70; N, 8.51. Found: C, 80.24; H, 4.65; N, 8.48.

Acknowledgements

The present work was supported by grant of National Academy of Sciences of Ukraine. We thank Dr. Thomas Gurley for the editorial contribution.

References and notes

1. (a) Heine, H. W.; Smith, A. B., III; Bower, D. *J. Org. Chem.* **1968**, *33*, 1097; (b) Heine, H. W.; Henzel, R. P. *J. Org. Chem.* **1969**, *34*, 171; (c) Padwa, A.; Glazer, E. *J. Org. Chem.* **1973**, *38*, 284.
2. Zbruyev, A. I.; Yaremenko, F. G.; Chebanov, V. A.; Desenko, S. M.; Shishkin, O. V.; Lukinova, E. V.; Knyazeva, I. V. *Izv. Akad. Nauk, Ser. Khim.* **2006**, *2*, 350; *Russ. Chem. Bull. Int. Ed.* **2006**, *2*, 362.
3. (a) Trozzolo, A. M.; Sarpotdar, A. S.; Leslie, T. M. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 201; (b) Sheng, S. J.; Leslie, T. M.; Trozzolo, A. M. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 175; (c) Orlov, V. D.; Vorob'eva, N. P.; Tischenko, A. A.; Pikalev, O. M.; Popov, V. I.; Yagupol'skii, L. M. *Khim. Geterotsikl. Soedin.* **1991**, *9*, 1179; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1991**, *27*, 942; (d) Orlov, V. D.; Vorob'eva, N. P.; Tischenko, A. A.; Krainov, I. P. *Zh. Prikl. Spektrosk.* **1991**, *54*, 638; *J. Appl. Spectrosc. (Engl. Transl.)* **1991**, *54*, 403.
4. Chebanov, V. A.; Zbruyev, A. I.; Desenko, S. M.; Vaschenko, V. V. *Abstracts of Autumn Meeting of Korean Association of Radiation Protection*, Cheju, Korea, Nov 10–12, 2004; Korean Association of Radiation Protection: Cheju, Korea, 2004; p 278.
5. Galunov, N. Z.; Seminozhenko, V. P. *Theory and Practice of Radioluminescence of Organic Condensed Media*; Naukova Dumka: Kiev, 1997.
6. Chebanov, V. A.; Zbruyev, A. I.; Desenko, S. M.; Doroshenko, A. O.; Vaschenko, V. V. *J. Korean Assoc. Radiat. Prot.* **2005**, *30*, 31.
7. (a) Heine, H. W.; Weese, R. H.; Cooper, R. A. *J. Org. Chem.* **1967**, *32*, 2708; (b) Padwa, A.; Clough, S.; Glazer, E. *J. Am. Chem. Soc.* **1970**, *92*, 1778; (c) DoMinh, T.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 4046; (d) DoMinh, T.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6997; (e) Padwa, A.; Gehrlein, L. *J. Am. Chem. Soc.* **1972**, *94*, 4933; (f) Kaluski, Z.; Gresyak-Figas, E.; Vorob'eva, N. P.; Bakumenko, A. I.; Yaremenko, F. G.; Orlov, V. D. *Khim. Geterotsikl. Soedin.* **1989**, *8*, 1064; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1989**, *25*, 888; (g) Orlov, V. D.; Kaluski, Z.; Figas, E.; Vorob'eva, N. P.; Bakumenko, A. I.; Yaremenko, F. G. *Khim. Geterotsikl. Soedin.* **1991**, *8*, 1060; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1991**, *27*, 849; (h) Orlov, V. D.; Vorob'eva, N. P.; Demenkova, N. N.; Chesnovskii, V. S.; Yaremenko, F. G. *Khim. Geterotsikl. Soedin.* **1988**, *3*, 328; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1988**, *24*, 267; (i) Pashkevich, K. I.; Khomutov, O. G. *Zh. Org. Khim.* **1999**, *35*, 106; *Russ. J. Org. Chem.* **1999**, *35*, 100.
8. Risitano, F.; Grassi, G.; Foti, F.; Moraci, S. *Synlett* **2005**, 1633.
9. Dhar, D. N. *The Chemistry of Chalcones and Related Compounds*; John Wiley & Sons: New York, NY, 1981.
10. (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359; (b) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263.
11. See, for example: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457; (b) Suzuki, A. *J. Organomet. Chem.* **1998**, *576*, 147; (c) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633.
12. (a) Padwa, A.; Gehrlein, L.; Kinnel, R. B. *J. Org. Chem.* **1975**, *40*, 1683; (b) Orlov, V. D.; Yaremenko, F. G.; Lavrushin, V. F. *Khim. Geterotsikl. Soedin.* **1979**, *4*, 536; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1979**, *15*, 438; (c) Orlov, V. D.; Yaremenko, F. G.; Kolos, N. N.; Pivnenko, N. S.; Lavrushin, V. F. *Khim. Geterotsikl. Soedin.* **1980**, *4*, 544; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1980**, *16*, 424; (d) Orlov, V. D.; Yaremenko, F. G.; Tlakhun, M.; Vorob'eva, N. P.; Zolotarev, B. M. *Khim. Geterotsikl. Soedin.* **1984**, *5*, 673; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1984**, *20*, 542.
13. (a) Lapinsky, D. J.; Bergmeier, S. C. *Tetrahedron Lett.* **2001**, *42*, 8583; (b) Lapinsky, D. J.; Bergmeier, S. C. *Tetrahedron* **2002**, *58*, 7109; (c) Bergmeier, S. C.; Katz, S. J.; Huang, J.; McPherson, H.; Donoghue, P. J.; Reed, D. D. *Tetrahedron Lett.* **2004**, *45*, 5011.
14. Vashchenko, V. V.; Goodby, J. W.; Petrenko, A. S. *Abstracts of Papers, XIX Ukrainian Conference for Organic Chemistry*, Lviv, Ukraine, Sept 10–14, 2001; Lvivs'ka politechnika: Lviv, Ukraine, 2001; p 134.
15. The detailed study of the scope and limitation of micellar catalysis in Suzuki–Miyaura cross-coupling is now underway.
16. (a) Bowie, R. A.; Musgrave, O. C. *J. Chem. Soc. C* **1966**, 566; (b) Vollmann, K.; Mueller, C. E. *Heterocycles* **2002**, *57*, 871.