JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Multiple Transformations of 2-Alkynyl-1,8-bis(dimethylamino)naphthalenes into Benzo[*g*]indoles. Pd/Cu-Dependent Switching of the Electrophilic and Nucleophilic Sites in Acetylenic Bond and a Puzzle of Porcelain Catalysis

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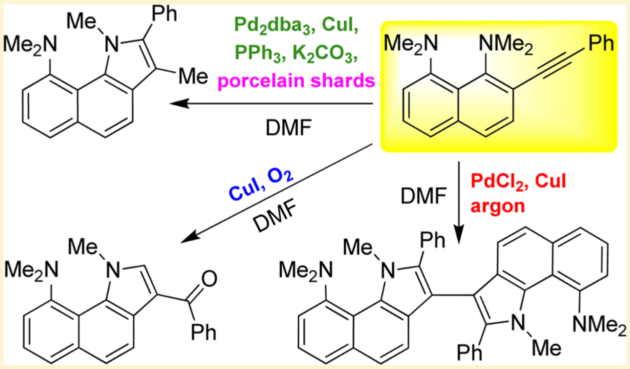
Supporting Information

ABSTRACT: By means of Sonogashira reaction, a series of 2-alkynyl- and 2,7-dialkynyl derivatives of 1,8-bis(dimethylamino)-naphthalene ("proton sponge") have been obtained from the corresponding iodides. It was disclosed that changing the reaction conditions and isolation protocol or conducting the model experiments with the authentic acetylenes results in several types of palladium- and copper-assisted heterocyclizations with the participation of the C≡C bond and 1-NMe$_2$ group. These include: (*i*) a cyclization into isomeric 1*H*-benzo[*g*]indoles with [1,3] migration of the *N*-methyl group into the newly formed pyrrole ring; (*ii*) a similar cyclization with a loss of the methyl group; (*iii*) a tandem process of cyclization into benzo[*g*]indoles and their subsequent 3,3′-dimerization; and (*iv*) a copper-catalyzed oxidative transformation into 3-aroylbenzo[*g*]indoles. In most cases, the reactions occur in parallel, but under certain conditions, one of the above products becomes predominant or even the only one. Remarkably, in Pd-catalyzed cyclizations *i*−*iii*, the acetylenic bond behaves as an electrophile being attacked at the *β*-position by the amine nitrogen atom. In contrast, in transformation *iv*, the C≡C bond attacks by its C$_\alpha$ atom on the aminomethyl radical functionality N(Me)−CH$_2$· presumably arising at copper oxidation/deprotonation of the 1-NMe$_2$ group. Studying rearrangement *i*, some evidence for the porcelain catalysis was obtained.



INTRODUCTION

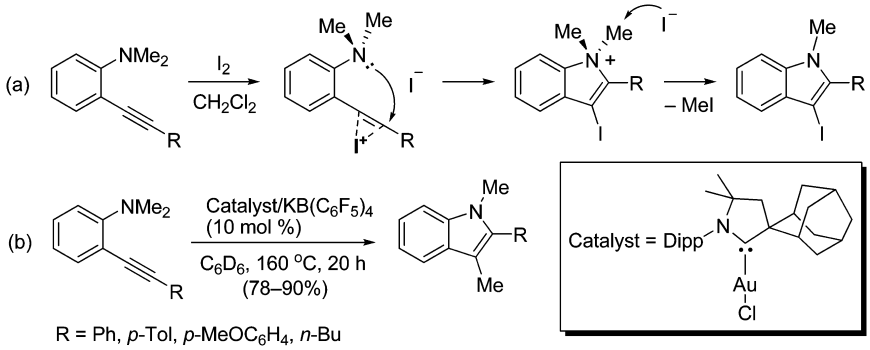
It is well-known that *ortho*-aminoarylacetylenes with primary or secondary amino groups are quite easily cyclized into the corresponding indole derivatives or their numerous condensed analogues.[1] The reaction is generally accelerated under employment of basic catalysts or transition metal complexes. Remarkably, even arylacetylenes having tertiary *ortho*-amino groups under special conditions are able to cyclize with removing one of the *N*-substituents.[1d,2] A typical example is the iodine activated conversion of 2-alkynyl-*N*,*N*-dimethylanilines into 1-methylindoles (Scheme 1a). The reaction starts with the electrophilic activation of the C≡C bond, followed by intramolecular nucleophilic attack and elimination of the *N*-methyl group as methyl iodide.[2]

In some cases, the cyclizations are accompanied by an intramolecular migration of the *N*-substituent into the newly formed heterocyclic ring.[3a] Along with anilines, their oxygen and sulfur analogues can also undergo similar cyclizations. Virtually, in all of these instances, the migratory function was represented by a relatively stable S$_N$1 group: allyl,[3b] propargyl,[3c] acyl,[3d] (*α*-alkoxyalkyl),[3e] (*p*-methoxyphenyl)methyl (MPM),[3f] *α*-phenethyl,[3g] RSO$_2$,[3h] R$_3$Si.[3i] Very often, the exact nature of these migrations remained unexplored, but in a few cases, the preliminary formation of a contact ion pair was registered.[3g] Recently, several examples of migration of the methyl group in such processes have been reported for 2-alkynyl-*N*,*N*-dimethylanilines (Scheme 1b).[4] The reaction proceeded under rather drastic conditions (160 °C) with the assistance of the gold-carbene catalyst. The mechanism of this conversion was not discussed in the original paper.

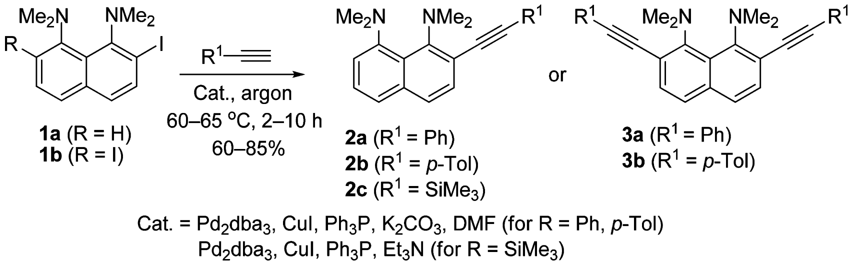
Over the past few years, we were studying the closely related cyclizations of 2-alkynyl- and 2,7-dialkynyl derivatives of 1,8-bis(dimethylamino)naphthalene ("proton sponge"). Our results, mentioned briefly in the conference theses,[5] have brought quite a few new findings into this important field that seems to originate from the specific structure and reactivity of the "proton sponge". In particular, a number of alternative cyclization modes for such compounds were disclosed and the relative importance of different catalytic and oxidative additives was clarified. Now, we report on these findings in more detail.

Received: October 15, 2014
Published: December 8, 2014

Scheme 1. Examples of Electrophile-Activated Cyclization (a) and Metal-Catalyzed Rearrangement (b) of 2-Alkynyl-*N*,*N*-dimethylanilines into *N*-Methylindole Derivatives



Scheme 2. Synthesis of 2-Ethynyl- and 2,7-Diethynyl-1,8-bis(dimethylamino)naphthalenes Using Isolation Protocol *A*

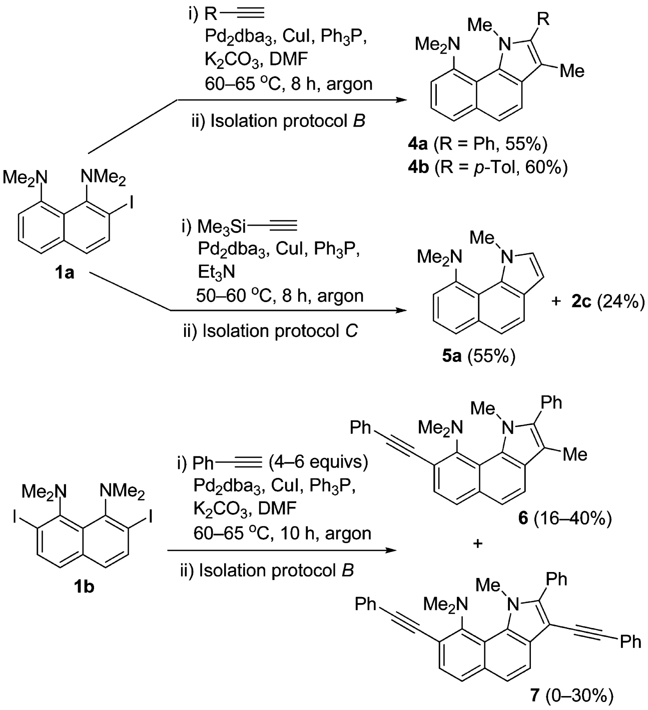


■ RESULTS AND DISCUSSION

Our work started with the synthesis of previously unknown acetylenes **2** and **3** by the Sonogashira coupling of iodides **1a**,**b** and 1-alkynes using the $Pd_2dba_3/CuI/Ph_3P/K_2CO_3$ catalytic system (Scheme 2).[6] Normally, the reactions with phenyl- and *p*-tolylacetylenes were conducted by heating the reactants in DMF solution at 60−65 °C for 8−10 h. The coupling of **1a** with trimethylsilylacetylene (TSA) was carried out with triethylamine as a solvent and a base, simultaneously.

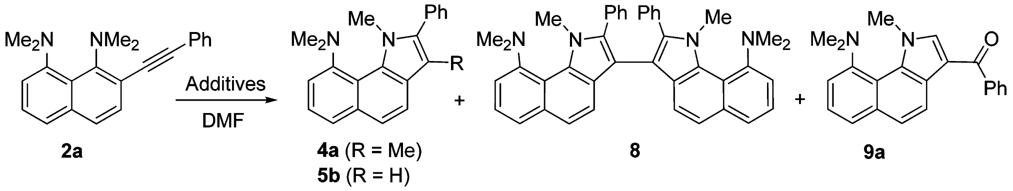
Usually, to isolate compounds **2** and **3**, we added a saturated aqueous solution of NaCl to the reaction mixture and then extracted the products with diethyl ether (isolation protocol *A*).[6] Once, upon synthesizing compound **2a**, the reaction mixture was poured into a porcelain basin and evaporated to dryness on a hot water bath (isolation protocol *B*). Unexpectedly, after flash column chromatography of the residue, *N*,*N*,1,3-tetramethyl-2-phenyl-1*H*-benzo[*g*]indol-9-amine (**4a**) was isolated as a single product in 55% yield. When the similar procedure was applied to the reaction of iodide **1a** with *p*-tolylacetylene, benzo[*g*]indole **4b** was obtained in 60% yield (Scheme 3). The presence of the 1,3-dimethylindole fragment was proved by single-crystal X-ray analysis (Figure S1, Supporting Information). The same isolation protocol in the case of coupling diiodide **1b** with phenylacetylene (4 equiv) gave compound **6** (40%), testifying that the second pyrrole ring was not closed, most likely due to a non-proton sponge nature of **6**. Instead, along with compound **6**, diacetylene **7** was also isolated in 15−30% yield (depending on the amount of phenylacetylene taken) and structurally characterized (Figure S2, Supporting Information).

Scheme 3. Sonogashira Coupling of Iodides 1a,b with 1-Alkynes Using Isolation Protocols *B*,*C*



Obviously, the most intriguing in conversions **1a** → **4** and **1b** → **6** is the migration of one *N*-methyl group into the pyrrole ring of the product under mild conditions that formally represents a rather deep rearrangement of the proton sponge acetylenes. The only exception was the Sonogashira reaction of iodide **1a** with TSA, which resulted in the formation of acetylene **2c** (24% yield) together with benzo[*g*]indole **5a** (55%) without the 3-methyl group in the pyrrole ring (see comment at the final part of this section). It should be noted that, in the last case, to provide the comparable conditions of isolation with **4a**,**b** and **6**, the reaction mixture was poured out into a porcelain basin and evaporated to dryness. Then, a small

Table 1. Influence of Different Additives on Cyclization of 2-Phenylethynyl Derivative 2a (DMF, 90−95 °C)



entry	additive	reaction conditions^a reaction vessel	time, h	atmosphere	yield (%) 2a recov.	4a	5b	8	9a
1	Pd_2dba_3 (5 mol %) porcelain shards (∼1.3 g)	glass flask	3	air	55		7	6	
2	Pd_2dba_3 (5 mol %)	porcelain basin	1.5	air	50		9	5	
3	Pd_2dba_3 (5 mol %) Ph_3P (30 mol %) porcelain shards (∼1.3 g)	glass flask	3	air	50		7	7	
4	Pd_2dba_3 (5 mol %) CuI (20 mol %)	porcelain basin	1.5	air	60		7	23	
5	Pd_2dba_3 (5 mol %) CuI (20 mol %) Ph_3P (30 mol %) porcelain shards (∼1.3 g)	glass flask	3	air	50	1	7	25	
6	Pd_2dba_3 (5 mol %) CuI (20 mol %) Ph_3P (30 mol %)	porcelain basin	1.5	air	65		10	20	
7	Pd_2dba_3 (5 mol %) CuI (20 mol %) Ph_3P (30 mol %) K_2CO_3 (1 equiv) porcelain shards (∼1.3 g)	glass flask	3	air	35	20		16	
8	Pd_2dba_3 (5 mol %) CuI (20 mol %) Ph_3P (30 mol %) K_2CO_3 (1 equiv)	porcelain basin	1.5	air	30	10	5	19	
9	CuI (30 mol %)	glass flask	1.5	air					45
10	CuI (2 equiv)	glass flask	1.5	air					49
11	CuI (2 equiv)	glass flask	2	argon	75				
12	$CuCl_2$ (2 equiv)	glass flask	1.5	air					35
13	$PdCl_2$ (40 mol %)	glass flask	3	air			10	14	
14	$PdCl_2$ (40 mol %)	glass flask	2	argon			13	30	
15	$PdCl_2$ (40 mol %)	porcelain basin	3	air			13	12	
16	$PdCl_2$ (40 mol %) CuI (2 equiv)	glass flask	2	argon				60	
17	$PdCl_2$ (40 mol %) CuI (2 equiv)	glass flask	2	air			6	2	10
18	$PdCl_2$ (40 mol %) $CuCl_2$ (2 equiv)	glass flask	3	air			9	2	10
19	$PdCl_2$ (40 mol %) $CuCl_2$ (2 equiv)	glass flask, rt	24	air			6	2	30

^{a}For a typical load and further details, see the Experimental Section. In most cases, the reaction was conducted at least twice.

amount of DMF was added to the residue and evaporation was repeated (isolation protocol *C*).

At first sight, it looks obvious that benzo[*g*]indoles **4** similar to 1,3-dimethylindoles in Scheme 1b should be formed from acetylenes **2**. However, in reality, the situation turned out to be quite uncertain. To make sense of it, we have conducted a number of control experiments including attempts of direct conversion of authentic acetylenes **2** into benzo[*g*]indoles **4** (see below).

First, we made sure that just the temperature increase at the Sonogashira coupling of **1a** with phenylacetylene from 60−70 to 95−150 °C and subsequent use of isolation protocol *A* does not lead to benzo[*g*]indole **4a**. Along with this, evaporation of DMF from the reaction mixture in a rotary evaporator resulted in the formation of acetylene **2a** and only a trace amount of **4a**. Then, we assumed that air oxygen may be involved into the transformation (for example, via the oxidation of Pd^0 to Pd^{2+} species, which then catalyze the pyrrole ring closure). However, when the reaction mixture after the completion of the Sonogashira coupling was heated for some time under aerobic conditions, followed by isolation protocol *A*, no benzo[*g*]indole **4a** was detected. From this, one can conclude that the evaporation of DMF directly from the reaction vessel is not sufficient for the formation of compounds **4** and **6**. Bringing the reaction mixture into an open porcelain basin and evaporating it to dryness on a hot water bath was the only way that gave selectively benzo[*g*]indole **4a** in appreciable yield. To make the possible catalytic effect of porcelain on the formation of benzo[*g*]indoles **4** more convincing, we have conducted a simple experiment. After completion of the Sonogashira coupling of **1a** with 1-alkyne, the porcelain shards were added into the reaction glass vessel. The resultant mixture was then heated for 3 h under aerobic conditions and treated in accordance with isolation protocol *A*. To our delight, compounds **4a,b** were isolated in this case as the main products in 40−50% yield.

Encouraged by this fact, we then tried to achieve a direct transformation of acetylenes **2** into pyrroles **4**. In a series of control experiments with reference alkyne **2a**, we varied reaction conditions and additives, including porcelain shards (Table 1). Both a glass flask and an open porcelain basin were used as the reaction vessels, and the experiments were conducted either in an inert (argon) or in an air atmosphere.

We found that, in all experiments with Pd_2dba_3 taken either alone or with adding Ph_3P (entries 1−3), the starting compound remained mostly unchanged; at the same time, two new benzo[*g*]indole derivatives were formed: compound **5b** with a missed methyl group and 3,3′-di(benzo[*g*]indole) **8**, each in 5−9% yield. The yield of **8**, whose structure was proved by X-ray study (Figure 1),[7] was markedly increased at the joint presence of Pd_2dba_3 and CuI (entries 4−6). With regard to compound **4a**, the most successful was the experiment in which we applied a full set of additives normally used for Sonogashira coupling of **1**, but with adding porcelain shards (entry 7). In this case, compound **4a** was obtained in 20% yield together with 16% of dimer **8**. The close results were obtained when the above reaction mixture was evaporated in an open porcelain basin with the difference that some amount of compound **5b** was isolated (entry 8). A similar experiment with *p*-tolylethynyl derivative **2b** gave indole **4b** in 22% yield. Apparently, along

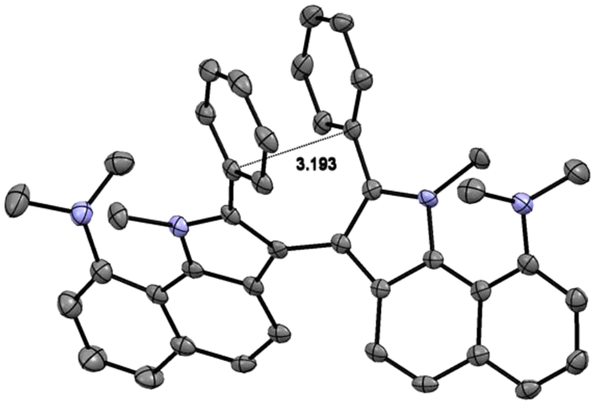
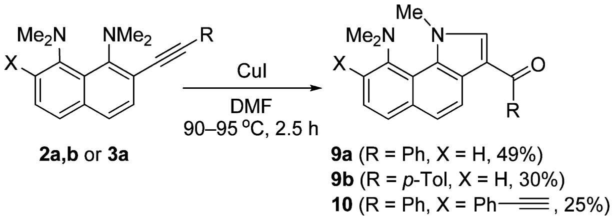


Figure 1. ORTEP plot for X-ray structure of **8** indicating the shortest distance (Å) observed between the *ipso*-carbon atoms of the phenyl rings ($P = 50\%$, 120 K). Hydrogen atoms are omitted for clarity.

with the porcelain catalysis, K_2CO_3 may play here the key role, which is discussed below in more detail. With regard to the formation of **8**, it likely results from the widely spread metal catalyzed oxidative coupling of the electron-rich aromatic and heteroaromatic compounds.[8] The question is which metal (palladium or copper) serves here as a catalyst.

Further, we found that the course of cyclization of acetylene **2a** principally changed when CuI alone was used as an additive (entries 9 and 10). In this case, previously unknown 3-benzoylbenzo[*g*]indole **9a** was obtained in 45–49% yield as the only isolable product. By analogy, treatment of acetylenes **2b** and **3a** with CuI gave ketones **9b** and **10** in 30% and 25% yield, respectively (Scheme 4). The structure of **9b** was proved by X-ray study (Figure S3, Supporting Information). We also found that the reaction with CuI additive carried out in a glass vessel under argon does not produce any products (entry 11). Hence, it was assumed that oxidation of Cu^+ to Cu^{2+} by the air oxygen is a crucial factor for transformation **2a** → **9a**. Indeed, the reaction with $CuCl_2$ additive gave **9a** as the only product in 35% yield (entry 12).

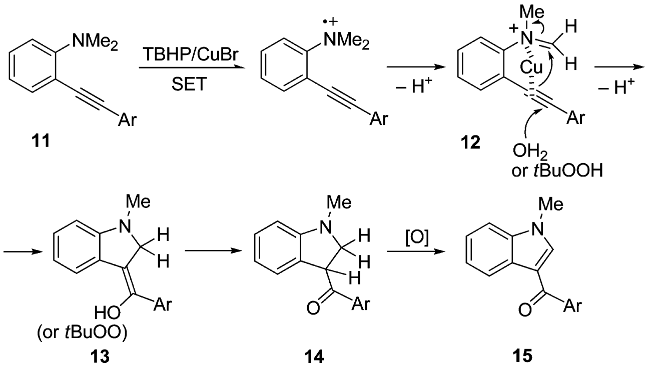
Scheme 4. Synthesis of 3-Aroylbenzo[*g*]indoles 9 and 10



From the results of entries 4–10, we have concluded that transformation **2a** → **8** is Pd^{2+}-catalyzed or palladium–copper cocatalyzed. Noteworthy, the use of $PdCl_2$ without any other additives, especially in air atmosphere, was accompanied by a strong tarring and resulted in a rather modest overall yield of **5b** and **8** (entries 13 and 15). Most likely, this is caused by the high oxidative potential of Pd^{2+}.[9] This should lead to the easier formation of radical species reacting with O_2 and with each other to produce oligomers and resins. The process becomes more controlled under an inert atmosphere as in run 14 producing **5b** and **8** in 13% and 30% yield, respectively. An argument in favor of the palladium–copper cocatalysis was received when acetylene **2a** reacted with a mixture of $PdCl_2$ and CuI under an argon atmosphere (entry 16): the yield of **8** was even more impressive (up to 60%).

Again, the use of $PdCl_2$/CuI and $PdCl_2/CuCl_2$ mixtures under aerobic conditions (entries 17–19) led to the tarring of the reaction mixture, and the reaction products **5b**, **8**, and **9a** were isolated in low yields. Among them, ketone **9a** was predominant. As to the formation of the latter, it should be noted that two groups of researchers have recently reported on the copper-catalyzed[10] and palladium–copper cocatalyzed[11] synthesis of 3-aroylindoles **15** from *ortho*-alkynylated *N*,*N*-dimethylanilines **11** (Scheme 5). They found that, on treatment of these acetylenes with CuBr or $PdBr_2$/CuI in the presence of *tert*-butyl hydroperoxide (TBHP) in DMSO[10] or toluene[11] at 80–100 °C, the 3-aroylindoles **15** were formed in moderate to good yields. Notably, either CuBr or TBHP alone did not give any trace of the indoles. It is believed that TBHP oxidizes the aniline NMe_2 group into methyleneiminium salt **12**, which then undergoes the copper(palladium)-promoted cyclization. It was also shown that the carbonyl oxygen in ketones **15** originates either from water[10] or from TBHP[11] in the result of nucleophilic addition **12** → **13**; the subsequent oxidative aromatization of thus formed indoline **14** gives **15**.

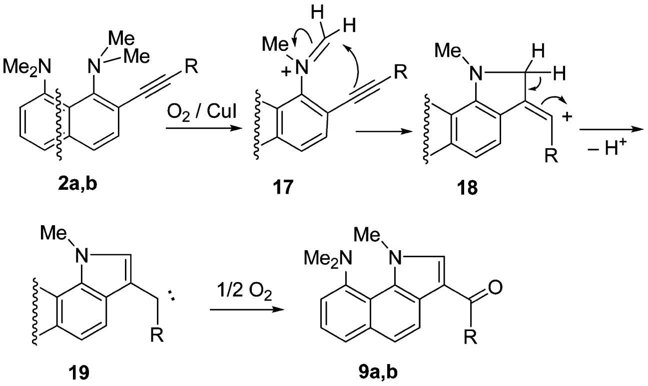
Scheme 5. Oxidative Conversion of 2-Alkynyl-*N*,*N*-dimethylanilines into 3-Aroylindoles[10,11]



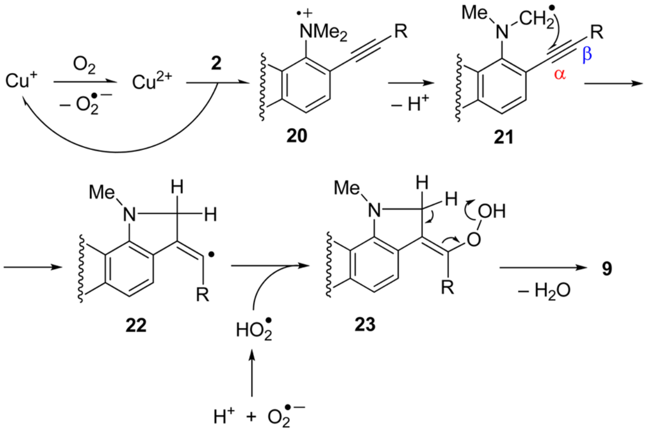
Taking into account this mechanistic approach and a pronounced ability of the proton sponge NMe_2 groups to be oxidized into methyleneiminium salts by some transition metals[12] or under conditions of the so-called *tert*-amino reactions,[13] we first believed that the formation of ketones **9** and **10** could be represented as shown in Scheme 6. However, two points cast doubt on the correctness of this assumption. The first one is an inertness of the proton sponge acetylenes toward air oxygen and copper(I) salts taken separately. The second point is a strongly manifested tendency[13] of the proton sponge methyleneiminium intermediates to cyclize into the dihydroperimidinium salts of type **16**, which has not been registered by us in any case.

On the basis of this, a mechanism of the radical cyclization involving the joint participation of copper and oxygen looks more preferable (Scheme 7). This is supported by the fact that no cyclization **2a** → **9a** occurs in an argon atmosphere, and acetylene **2a** being largely regenerated (Table 1, entry 11). Presumably, the oxygen is involved into two reaction stages. First, it converts Cu^+ into Cu^{2+} ions, which oxidize acetylene **2** into radical-cation **20**. The latter then loses a proton (a tremendous CH acidity of organic radical-cations including those of *N*,*N*-dimethylanilines is well-documented[14]) and thus formed radical **21** is then cyclized on the triple bond. Further

Scheme 6. Ionic Pathway for Copper-Catalyzed Conversion of 2-Alkynyl-1,8-bis(dimethylamino)naphthalenes into 3-Aroylbenzo[*g*]indoles 9



Scheme 7. Radical Pathway for Copper-Catalyzed Conversion of 2-Alkynyl-1,8-bis(dimethylamino)naphthalenes into 3-Aroylbenzo[*g*]indoles 9



conversion of the pyrrole intermediate **22** into **9** demands participation of the superoxide radical-anion, which is typical for the autooxidation processes. Remarkably, unlike the reaction shown in Scheme 5, no TBHP is demanded for conversion **2** → **9**. The absence of TBHP also narrows a range of the possible oxygen atom donors at the formation of the carbonyl group in **9**. As seen, the copper(I)-catalyzed character of the process is provided by the regeneration of the catalyst as the result of one-electron reduction of the Cu(II) species with the highly electron-donor proton sponge system.[15]

One of the striking things in the above findings is a switching of cyclization mode when replacing palladium catalysts by purely copper ones. Indeed, while at the formation of pyrroles **4**–**8**, the C≡C bond behaves as an electrophile, being attacked at the C_β atom by the nitrogen nucleophile, in the case of **9** and **10**, the reaction center is moved to the C_α atom reacting with the *N*-methylene group. Although details of this phenomenon are currently unclear, most likely it results from the different fashion and strength of coordination of palladium and copper ions with the acetylene ligand. Copper possesses weaker coordination ability,[16] and in the presence of more powerful palladium species, it's binding with π-ligands should be essentially suppressed, which is actually observed in many runs listed in Table 1.

Thus, we were almost unsuccessful in modeling the selective and high yield formation of 3-methylbenzo[*g*]indoles **4** directly from acetylenes **2**. Evidently, a very complicated combination of factors operates in the Sonogashira reaction itself (see, for example, ref 17) and at the subsequent conversion of acetylenes **2** into benzo[*g*]indoles. These may include influence of air oxygen, moisture, temperature changes, and diversity of ligands along with character of their coordination with the transition metal species. One can also assume that the proton sponge nature of the substrates may be even more important factor.

In light of the above, an impression arises that acetylenes **2** producing in the Sonogashira coupling are presented in the final reaction mixture in a form, which is incapable to cyclize into benzo[*g*]indoles **4**. Hypothetically, palladium or copper complexes like **24** or **25** (Figure 2; for the related complexes; see refs 18 and 19) as well as protonated acetylenes **26**, in which the unshared electron pair of the 1-NMe_2 group is blocked for heterocyclization, seem the most probable candidates for the nonreactive forms. Of these, we prefer salt **26**, guided by the following considerations. First, palladium and copper catalysts for Sonogashira coupling are normally used in much less than 1 equiv quantity and, therefore, can bind only a small portion of the proton sponge acetylene formed. On the other hand, the protons are evolved in the Sonogashira catalytic cycle (at the formation of a copper acetylenide) in an excessive amount.[17] Because of the abnormally high basicity of the proton sponge (pK_a 12.1, H_2O),[15] which is even higher (by 0.2–0.8 pK_a units)[6] in 2-alkynyl- **2** and 2,7-dialkynyl derivatives **3**, the latter should exist in the crude reaction mixture mainly in the protonated form.[20,21] Obviously, in the presence of porcelain in combination with DMF, high temperature, and some other components, most likely K_2CO_3, the unreactive form of the proton sponge *ortho*-acetylenes becomes capable of the transformation into benzo[*g*]indoles regardless of using the isolation protocols *A* or *B*.

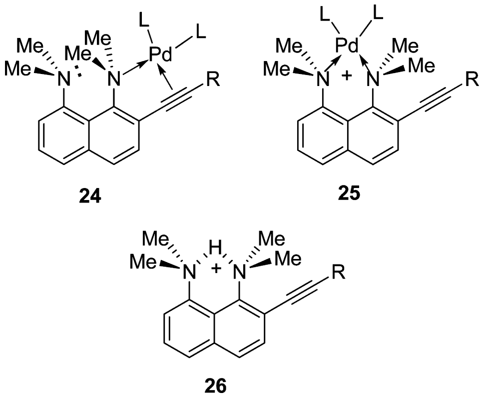
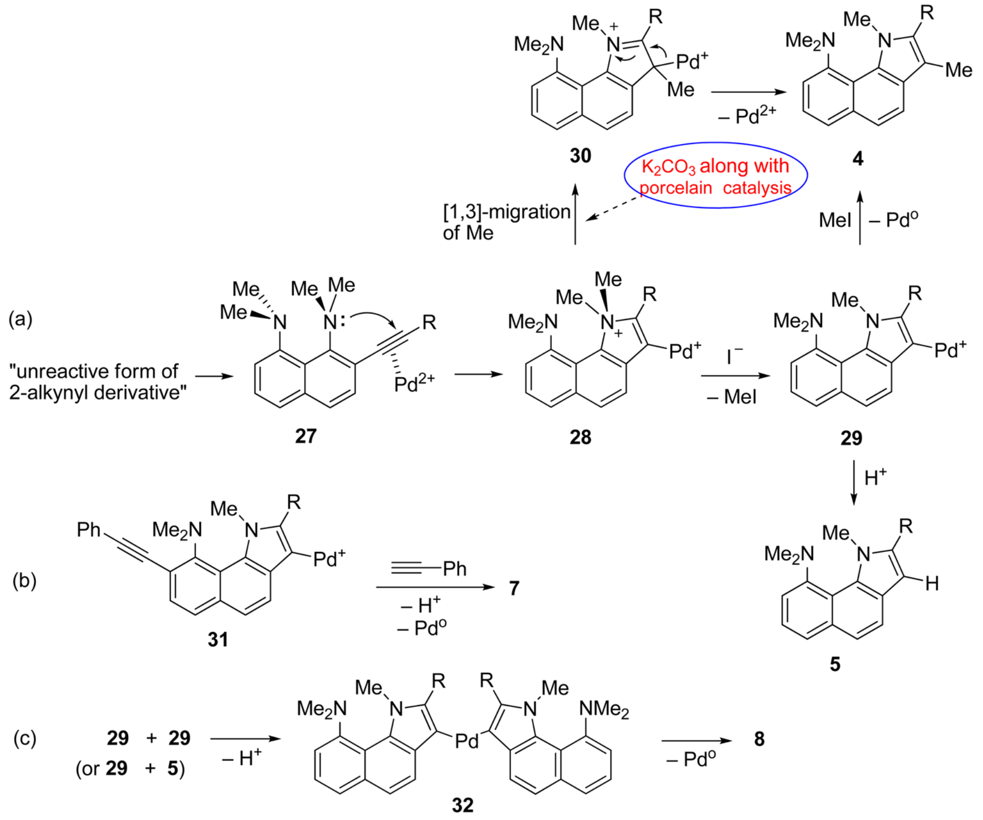


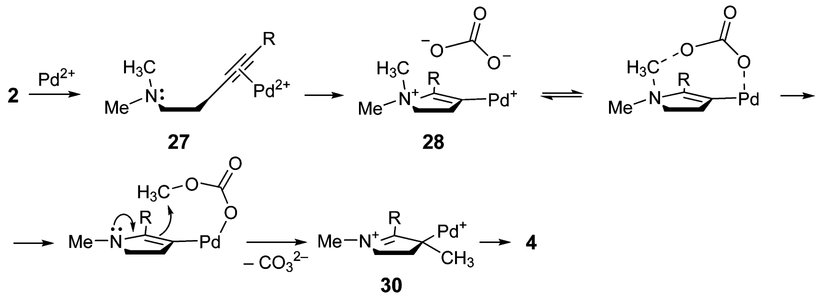
Figure 2. Possible complexes of 2-alkynyl-1,8-bis(dimethylamino)-naphthalenes resisting cyclization into benzo[*g*]indoles under standard conditions of the Sonogashira reaction (L: ligands).

At the moment, all the transformations we observed in the present study may be generalized by Scheme 8. The cyclization process itself obviously requires the participation of oxygen to convert Pd^0 into Pd^{2+}. The role of Pd^{2+} consists in activation of the triple bond as shown in Scheme 8. At the beginning, the activated form of *ortho*-ethynyl derivative arbitrarily shown as **27** undergoes cyclization into **28**. The latter can be further transformed into 1,3-dimethylbenzo[*g*]indole **4** either via [1,3] migration of the methyl group (**28** → **30** → **4**; see details in

Scheme 8. Proposed Generalized Mechanism for Pd-Catalyzed Formation of Different Benzo[*g*]indoles



Scheme 9. Proposed Mechanism for the *N*-Methyl Group [1,3] Migration Assisted by Carbonate Ion



Scheme 9) or that is less probable via preliminary loss of methyl, e.g., as MeI, with subsequent methylation of 3-pyrrolylpalladium compound **29** (Scheme 8a). Clearly, intermediate **29** in the case of escaping MeI from the reaction zone undergoes protolytic demetalation to yield benzo[*g*]indole **5**.

Similar to **28** and **29**, the participation of related intermediate **31** can explain the formation of diacetylene 7 (Scheme 8b). As to the formation of di(benzo[*g*]indole) **8**, we believe that it results from transmetalation between two Pd^+–aryl intermediates **29**, followed by reductive elimination of Pd^0 from ArPdAr complex **32** (Scheme 8c). Pd^0 is then reoxidized to Pd^{2+} with air oxygen.[22] Another possible way involves sequential C–H activation of indole **5** by the Pd^+–aryl intermediate **29** and reductive elimination. Recently, on the basis of kinetic studies, H/D exchange experiments, and kinetic isotope effects, it has been shown that Pd-catalyzed aerobic oxidative coupling of arenes proceeds via a bimetallic/transmetalation mechanism.[23] From this, transformation **29** + **29** → **32** → **8** seems to be more probable. The high yield of dimer **8** on heating of **2a** with $PdCl_2$/CuI additives under an argon atmosphere (Table 1, entry 16) may be a consequence of the tendency of Cu^+ to disproportionate to Cu^{2+} and Cu^0. The thus generated Cu^{2+} then triggers reoxidation of Pd^0.[24]

It is known that the ease of the $Pd^0 \rightarrow Pd^{2+}$ air oxidation depends strongly on the ligand surrounding of Pd^0.[22] Apparently, such a surrounding in entries 1–3 is not favorable for the oxidation, which can explain the small yields (13–14% in the sum) of indoles **5b** and **8**. In contrast, in the control experiments (entries 4–8) where CuI and K_2CO_3 additives were used, the benzo[*g*]indole total yield doubles. The addition of potash gives the most notable results. Actually, only in the presence of K_2CO_3 (Table 1, entries 7, 8) benzo[*g*]indole **4a** with the transferred methyl group appears among the reaction products. Effect of this salt may be attributed to the bridging nature of the carbonate ligand that promotes the Me group to be transferred from the nitrogen heteroatom to the C(3) atom, as depicted in Scheme 9.

Another fundamental question is a possible mechanism of the porcelain catalysis, which also plays a crucial role in the

[1,3] methyl group transfer. Porcelain is known to be a solid, porous material made by thermal treatment of clays in the presence of various additives.[25a] Like clays and zeolites,[25b,c] porcelain has an aluminosilicate nature. Two former materials are widely used in the chemical industry, especially in petrol chemistry, as very effective and cheap catalysts for many reactions, in particular for the hydrocarbon isomerizations. Their activity as solid acid catalysts stems primarily from two features: (1) a pronounced ability to ion-exchange and (2) the presence within their structure of a plurality of cracks and cavities of a size that is commensurable with conventional molecules. There are distinct grounds to believe that both of these factors should also work in the case of porcelain. It seems reasonable to suggest that, in our case, the porcelain catalyzes not so much the pyrrole ring closure as the [1,3] migration of the methyl group producing benzo[*g*]indoles **4** and **6**.[26] Presumably, the migration process shown in Scheme 9 occurs inside the tight nanosized cavities of the porcelain matrix[27] that considerably lowers the activation energy for the migration. One can suggest that, in the absence of the effective Me group shuttle, e.g., K_2CO_3, capturing the methyl group from intermediate **28** by other nucleophiles (I^-, Ph_3P) yields the some amount of benzo[*g*]indoles **5a**,**b** without C(3) methyl groups (entries 1−6).

The structural assignment of compounds synthesized, beside elemental analysis and X-ray measurements, was based on spectral data. In this regard, IR and ^1H and ^{13}C NMR spectra were especially informative. In particular, the IR and ^{13}C NMR spectra indicated the absence of the C≡C bonds in most cyclization products (except **6**, **7**, and **10**). Normally, the carbon atoms of the C≡C bond in starting alkynes **2** and **3** give two signals at δ 82−99 ppm, which disappear after cyclization. Even more important are the ^1H NMR spectra, in which the cyclization product manifests itself in the three-proton intensity decrease in the NMe_2 region at δ 2.5−3.0 ppm and the appearance of a singlet around 4 ppm, which is typical for the pyrrolic N−Me group.

■ CONCLUSIONS

In summary, during the Sonogashira synthesis of a number of 2-alkynyl- and 2,7-dialkynyl-1,8-bis(dimethylamino)-naphthalenes, we have disclosed their pronounced ability to cyclize into benzo[*g*]indoles. Four main channels were found for these transformations: (*i*) a palladium and porcelain cocatalyzed rearrangement with [1,3] migration of one of the N−Me groups into the newly formed pyrrole ring, (*ii*) cyclization into benzo[*g*]indoles with elimination of the N−Me group, (*iii*) a palladium-catalyzed cyclization into benzo-[*g*]indoles with their subsequent dimerization, and (*iv*) a copper-assisted oxidative cyclization into 3-aroylbenzo[*g*]-indoles. Of these, only transformations *iii* and *iv* can be selectively achieved with the authentic acetylenes. The transformation *i* is selectively realized only at using a specific isolation procedure (porcelain catalysis) after completion of the Sonogashira coupling of 2-iodo-1,8-bis(dimethylamino)-naphthalenes with 1-alkynes. Notably, in the first three reactions, the 1-NMe_2 group serves as a nucleophile, while the β-carbon atom of the C≡C bond acts as an electrophile. In transformation *iv*, the 1-NMe_2 group is likely oxidized by Cu(I)/air O_2 into aminomethyl radical species and the reaction center of the triple bond is moved to the α-carbon atom. The last conversion differs not only by its mechanism but also by the character of building blocks for the pyrrole ring construction. At the moment, it is rather difficult to elucidate the exact reaction mechanism in each particular case, especially for transformation *i* due to a complex overlapping specific reactivity of the proton sponges[15] and peculiarities of the transition metal catalysis. Under these circumstances, the above findings, especially the porcelain catalysis, little mentioned in the chemical literature, demand further studies, which are now in progress.

■ EXPERIMENTAL SECTION

General Methods. ^1H and ^{13}C NMR spectra were recorded on a 250 MHz spectrometer. Chemical shifts are referred to TMS. Infrared (IR) spectra were recorded in nujol or KBr. Mass spectra were measured in electron impact (EI) mode. CHN analysis was accomplished by combustion analysis (Dumas and Pregl method). Melting points were determined in glass capillaries on a Stuart SMP30 device and are uncorrected. Flash column chromatography was performed on Al_2O_3. Laboratory porcelain ware (see photos S1 and S2 in the Supporting Information) was purchased from Rechitskiy Porcelain Factory (www.rfz.ru).

Synthesis of 2-Alkynyl-1,8-bis(dimethylamino)naphthalenes 2a,b (General Procedure). CuI (76 mg, 0.4 mmol), Pd_2dba_3 (73 mg, 0.08 mmol), Ph_3P (210 mg, 0.8 mmol), and K_2CO_3 (345 mg, 2.5 mmol) were added to 2-iodo-1,8-bis(dimethylamino)naphthalene (**1a**)[28] (680 mg, 2.00 mmol) in dry DMF (11 mL) under a slow stream of argon. After stirring for 10 min under argon at 40 °C, 1-alkyne (5.0 mmol) was added dropwise. The stirring was continued for 8 h at 60−65 °C. The reaction mixture was then mixed with saturated solution of NaCl (20 mL) and extracted with ether (3 × 20 mL). The organic phase was evaporated to dryness. The residue was purified by flash column chromatography on Al_2O_3 (2 × 20 cm) with $CHCl_3$/hexane (1:3, v/v) as eluent. The yellow fraction with R_f 0.2−0.4 was separated, and the crude product was purified additionally by flash column chromatography on Al_2O_3 (2 × 20 cm) with the same eluent. Finally, the yellow fraction with R_f 0.2 gave **2**.

*1,8-Bis(dimethylamino)-2-(phenylethynyl)naphthalene (**2a**).* **2a** was obtained in 75% yield as a yellow solid, mp 98−100 °C (EtOH). EIMS (*m*/*z*) (rel intensity) 314 (M^+; 90), 299 (24), 282 (72), 268 (77), 254 (29), 226 (35), 207 (37), 196 (27), 167 (26), 157 (25), 149 (29), 141 (29), 133 (25), 127 (53), 113 (38), 103 (26), 91 (70), 77 (68), 58 (72), 51 (35), 44 (100). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.87; H, 7.23; N, 9.03. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.78 (s, 6H), 3.16 (s, 6H), 6.94 (dd, J = 6.0, 2.8 Hz, 1H), 7.24−7.40 (m, 7H), 7.53 (dd, J = 7.7, 1.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 45.0, 45.2, 91.5, 94.5, 114.2, 114.7, 122.2, 123.0, 124.9, 126.8, 128.2, 128.8, 131.0, 131.3, 138.3; 152.1, 152.4.

*1,8-Bis(dimethylamino)-2-(p-tolylethynyl)naphthalene (**2b**).* **2b** was obtained in 75% yield as yellow solid, mp 89−92 °C (EtOH). EIMS (*m*/*z*) (rel intensity) 328 (M^+; 100), 313 (25), 296 (74), 282 (66), 268 (17), 206 (18), 196 (20), 164 (21), 149 (22), 141 (17), 134 (18), 127 (20). Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.11; H, 7.37; N, 8.53. Found: C, 84.24; H, 7.26; N, 8.37. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.36 (s, 3H), 2.79 (s, 6H), 3.16 (s, 6H), 6.95 (dd, J = 6.3, 2.4 Hz, 1H), 7.15 (d, J = 7.9 Hz, 2H), 7.25−7.46 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.9, 45.0, 45.2, 90.1, 94.7, 114.2, 115.0, 121.8, 122.3, 123.0, 123.1, 126.7, 129.6, 131.0, 131.2, 138.2, 138.3, 152.0, 152.1.

Synthesis of 1,8-Bis(dimethylamino)-2-(trimethylsilylethynyl)naphthalene (2c). CuI (0.19 g, 1.0 mmol), Pd_2dba_3 (0.46 g, 0.5 mmol), and Ph_3P (0.79 g, 3.0 mmol) were added to 2-iodonaphthalene **1a** (3.40 g, 10.0 mmol) in dry Et_3N (35 mL) under a slow stream of argon. After stirring for 10 min under argon, trimethylsilylacetylene (3.2 mL, 2.24 g, 23.0 mmol) was added. The flask was hermetically sealed, and the stirring was continued for 4 h at 50 °C. The reaction mixture was then evaporated to dryness. The residue was purified by flash column chromatography on Al_2O_3 (2 × 20 cm) with *n*-hexane as eluent. The yellow fraction with R_f 0.2−0.4 was separated, and the crude product was purified additionally by flash column chromatography on Al_2O_3 (2 × 20 cm) with Et_2O/hexane

(1:3, v/v) as eluent. The yellow fraction with R_f 0.2 gave 2.59 g (83%) of **2c** as a dark yellow oil. **2c**: IR (Nujol) 2140 (C≡C), 1553 (ring) cm^{-1}; EIMS (*m*/*z*) (rel intensity) 310 (M^+, 51), 295 (29), 279 (24), 264 (22), 238 (30), 221 (17), 206 (51), 192 (30), 73 (100). Anal. Calcd for $C_{19}H_{26}N_2Si$: C, 73.49; H, 8.44; N, 9.02. Found: C, 73.58; H, 8.29; N, 9.23. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.29 (s, 9H), 2.78 (s, 6H), 3.13 (s, 6H), 6.92−6.98 (m, 1H), 7.25−7.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 0.5, 45.0, 45.1, 82.4, 99.1, 107.3, 114.0, 122.0, 122.1, 122.7, 126.8, 131.3, 138.4, 152.1, 153.1.

Synthesis of 2,7-Dialkynyl-1,8-bis(dimethylamino)naphthalenes 3a,b (General Procedure). CuI (40 mg, 0.21 mmol), Pd_2dba_3 (46 mg, 0.05 mmol), Ph_3P (131 mg, 0.50 mmol), and K_2CO_3 (280 mg, 2.02 mmol) were added to 2,7-diiodo-1,8-bis(dimethylamino)naphthalene (**1b**)[28] (466 mg, 1.00 mmol) in dry DMF (12 mL) under a slow stream of argon. After stirring for 10 min under argon at 40 °C, 1-alkyne (4.00 mmol) was added dropwise. The stirring was continued for 10 h at 60−65 °C. The reaction mixture was then evaporated to dryness. The residue was purified by flash column chromatography on Al_2O_3 (2 × 20 cm) with $CHCl_3$/hexane (1:3, v/v for **3a**; 1:2, v/v for **3b**) as eluent. The yellow-orange fraction with R_f 0.2 gave **3**.

*1,8-Bis(dimethylamino)-2,7-bis(phenylethynyl)naphthalene (**3a**).* **3a** was obtained in 64% yield as a yellow solid, mp 156−157 °C (EtOH or *n*-octane); IR (Nujol) 2211 cm^{-1} (C≡C); EIMS (*m*/*z*) (rel intensity) 414 (M^+; 94), 399 (39), 382 (100), 368 (31), 307 (25), 91 (29), 58 (23). Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.09; H, 6.17; N, 6.84. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.17 (s, 12H), 7.31−7.42 (m, 10H), 7.53−7.57 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 45.0, 90.8, 94.6, 116.8, 123.5, 124.3, 126.3, 128.1, 128.5, 131.1, 131.5, 137.7, 152.8.

*1,8-Bis(dimethylamino)-2,7-bis(p-tolylethynyl)naphthalene (**3b**).* **3b** was obtained in 50% yield as yellow solid, mp 155−156 °C (*i*-PrOH); IR (Nujol) 2210 cm^{-1} (C≡C); EIMS (*m*/*z*) (rel intensity) 442 (M^+; 100), 427 (40), 410 (89), 396 (33), 320 (22), 221 (20), 205 (21), 191 (17), 175 (26). Anal. Calcd for $C_{32}H_{30}N_2$: C, 86.84; H, 6.83; N, 6.33. Found: C, 87.00; H, 6.95; N, 6.13. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.38 (s, 6H), 3.17 (s, 12H), 7.17 (d, *J* = 7.9 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 4H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.0, 45.2, 90.4, 95.0, 117.5, 121.6, 123.8, 126.8, 129.6, 131.3, 131.7, 137.8, 138.5, 152.9.

Synthesis of *N*,*N*,1,3-Tetramethyl-2-phenyl-1*H*-benzo[*g*]indol-9-amine (4a). CuI (76 mg, 0.4 mmol), Pd_2dba_3 (73 mg, 0.08 mmol), Ph_3P (210 mg, 0.8 mmol), and K_2CO_3 (345 mg, 2.5 mmol) were added to 2-iodonaphthalene **1a** (680 mg, 2.0 mmol) in dry DMF (11 mL) under a slow stream of argon. After 10 min stirring under argon at 40 °C, phenylacetylene (0.55 mL, 510 mg, 5.0 mmol) was added dropwise. The stirring was continued for 8 h at 60−65 °C. The reaction mixture was poured into a porcelain basin and evaporated to dryness on the water bath. The residue was purified by flash column chromatography on Al_2O_3 with hexane as eluent. The colorless fraction with R_f 0.7 gave **4a** (345 mg, 55%) as off-white crystals. **4a**: mp 110−112 °C (hexane); IR (Nujol) 1600, 1549 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 314 (M^+; 100), 298 (15), 283 (23), 270 (18), 254 (13), 157 (22), 149 (16), 127 (13). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.21; H, 7.19; N, 8.76. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3H), 2.80 (s, 6H), 3.64 (s, 3H), 7.08 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.34−7.41 (m, 1H), 7.46−7.55 (m, 6H), 7.63 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 10.2, 39.3, 43.4, 111.2, 113.9, 118.5, 119.3, 121.9, 123.2, 124.2, 127.7, 127,8, 128.9, 131.0, 133.4, 134.6, 135.6, 141.1, 148.9.

Synthesis of *N*,*N*,1,3-Tetramethyl-2-*p*-tolyl-1*H*-benzo[*g*]indol-9-amine (4b). The reaction was carried out similarly to the synthesis of **4a** with *p*-tolylacetylene (580 mg, 5.0 mmol). Compound **4b** (394 mg, 60%) was obtained as beige crystals, mp 152−154 °C (hexane); IR (Nujol) 1550 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 328 (M^+; 66), 164 (100), 156 (57), 149 (41), 141 (38), 134 (43), 127 (50), 121 (20), 115 (15), 91 (16). Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.11; H, 7.37; N, 8.53. Found: C, 84.00; H, 7.29; N, 8.38. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3H), 2.45 (s, 3H), 2.81 (s, 6H), 3.64 (s, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.27−7.33 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 10.2, 21.8, 39.2, 43.4, 110.8, 113.8, 118.5, 119.3, 121.7, 123.1, 124.0, 127.7, 129.6, 130.4, 130.9, 134.5, 135.3, 137.5, 141.1, 148.8.

Synthesis of *N*,*N*,1-Trimethyl-1*H*-benzo[*g*]indol-9-amine (5a) and N^1,N^1,N^8,N^8-Tetramethyl-2-((trimethylsilyl)ethynyl)naphthalene-1,8-diamine (2c). CuI (57 mg, 0.3 mmol), Pd_2dba_3 (128 mg, 0.14 mmol), and Ph_3P (262 mg, 1.0 mmol) were added to 2-iodonaphthalene **1a** (1.02 g, 3.0 mmol) in dry Et_3N (13 mL) under a slow stream of argon. After 15 min stirring under argon, trimethylsilylacetylene (1 mL, 0.7 g, 7.2 mmol) was added. The flask was hermetically sealed, and the stirring was continued for 8 h at 50−60 °C. The reaction mixture was then evaporated to dryness. To the residue was added DMF (5 mL). The resultant mixture was poured into a porcelain basin and evaporated to dryness on the water bath. The residue was purified by flash column chromatography on Al_2O_3 with $CHCl_3$/hexane (1:2, v/v) as eluent. The colorless fraction with R_f 0.9 gave **5a** (370 mg, 55%) as beige crystals. The yellow fraction with R_f 0.2 gave **2c** (220 mg, 24%) as dark yellow oil.

5a: mp 73−75 °C (hexane); IR (KBr) 2959, 2926, 2853, 2790, 1600, 1594, 1556, 1525, 1510 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 224 (M^+; 68), 208 (28), 193 (35), 180 (49), 166 (29), 152 (39), 139 (50), 127 (25), 112 (63), 104 (63), 97 (57), 90 (41), 83 (48), 77 (49), 69 (25), 63 (57), 57 (29), 51 (30), 42 (100). Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.18; H, 7.03; N, 12.64. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.73 (s, 6H), 4.06 (s, 3H), 6.64 (d, *J* = 3.0 Hz, 1H), 7.12−7.15 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 40.1, 43.7, 103.5, 114.1, 118.9, 121.5, 121.8, 123.5, 124.1, 127.4, 131.2, 132.7, 134.3, 148.8.

Synthesis of *N*,*N*,1,3-Tetramethyl-2-phenyl-8-(phenylethynyl)-1*H*-benzo[*g*]indol-9-amine (6) and *N*,*N*,1-Trimethyl-2-phenyl-3,8-bis(phenylethynyl)-1*H*-benzo[*g*]indol-9-amine (7). CuI (40 mg, 0.21 mmol), Pd_2dba_3 (46 mg, 0.05 mmol), Ph_3P (131 mg, 0.5 mmol), and K_2CO_3 (280 mg, 2.02 mmol) were added to 2,7-diiodonaphthalene **1b** (466 mg, 1.0 mmol) in dry DMF (12 mL) under a slow stream of argon. After 10 min stirring under argon at 40 °C, 1-alkyne (4.0 mmol) was added dropwise. The stirring was continued for 10 h at 60 °C. The reaction mixture was poured into a porcelain basin and evaporated to dryness on the water bath. The residue was purified by flash column chromatography on Al_2O_3 with Et_2O/hexane (1:4, v/v) as eluent. The yellow fraction with R_f 0.5 was separated, and the crude product was purified additionally by flash column chromatography on Al_2O_3 with Et_2O/hexane (1:4, v/v) as eluent. The yellow fraction with R_f 0.5 gave **6** (165 mg, 40%) as yellow crystals. **6**: mp 159−160 °C (hexane); IR (Nujol) 2205, 1596, 1536 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 414 (M^+; 100), 397 (24), 321 (13), 91 (14), 77 (27). Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.78; H, 6.49; N, 6.61. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3H), 3.15 (s, 6H), 3.56 (s, 3H), 7.32−7.56 (m, 13H), 7.65 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 10.1, 39.9, 44.0, 91.2, 94.7, 111.0, 115.6, 120.2, 121.1, 121.6, 124.6, 124.7, 127.9, 128.3, 128.7, 128.8, 128.9, 129.4, 130.9, 131.3, 133.2, 134.5, 135.7, 141.5, 150.0.

The same protocol with 6.0 mmol of 1-alkyne gave a mixture of products **6** and **7**. After evaporation of the reaction mixture, the residue was purified by flash column chromatography on Al_2O_3 with Et_2O/hexane (1:4, v/v) as eluent. The yellow fraction within R_f 0.3−0.6 was separated. PTLC on Al_2O_3 with CH_2Cl_2/hexane (1:2, v/v) elution gave **6** (R_f 0.5, 66 mg, 16%) and **7** (R_f 0.4, 150 mg, 30%).

7: yellow crystals, mp 176−178 °C (hexane); IR (Nujol) 2202 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 500 (M^+; 100), 483 (15), 423 (13), 407 (19), 250 (24), 241 (14), 234 (13), 212 (12), 203 (12), 250 (24), 241 (14), 234 (13), 212 (12), 203 (12), 77 (22). Anal. Calcd for $C_{37}H_{28}N_2$: C, 88.77; H, 5.64; N, 5.60. Found: C, 88.62; H, 5.59; N, 5.78. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.17 (s, 6H), 3.71 (s, 3H), 7.28−7.60 (m, 16H), 7.86−7.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 41.2, 44.1, 84.4, 90.8, 92.9, 95.1, 99.1, 116.2, 120.9, 121.1, 123.2, 124.5, 124.7, 124.8, 127.9, 128.5, 128.7, 128.8, 128.87, 128.90, 129.1, 130.1, 130.5, 131.4, 131.7, 131.9, 135.0, 135.5, 147.1, 149.9.

General Procedure for the Cyclization of 2a in the Presence of Additives (Table 1). *Reaction in a Glass Flask.* A stirred mixture of phenylethynylnaphthalene **2a** (157 mg, 0.5 mmol), DMF (10 mL), and additives listed in Table 1 was heated at 90−95 °C in a glass flask for the indicated time. The reaction mixture was then mixed with a saturated aqueous solution of NaCl (30 mL) and extracted with ether (4 × 20 mL). The solvent was evaporated to dryness, and the residue was purified by flash column chromatography on Al_2O_3 with Et_2O/hexane (1:4, v/v) as eluent. The colorless fraction with R_f 0.7−0.9 was first collected. It contained a mixture of compounds **4a** and **8**. The next fraction with R_f 0.5 gave starting compound **2a** (entries 1−7) or compound **9a** (entries 9, 10, 12, 17−19). The first isolated fraction was additionally chromatographed on Al_2O_3 with hexane as eluent collecting compound **4a** (entry 7) or compound **5b** (entries 1−6, 13−15, 17−19). Compound **8** was isolated after changing hexane into Et_2O/hexane (1:4, v/v) mixture.

Reaction in a Porcelain Basin. A mixture of **2a** (157 mg, 0.5 mmol), DMF (10 mL), and additives listed in Table 1 was placed into a porcelain basin and evaporated to dryness at heating on a water bath (90−95 °C, 1.5 h). Isolation of the reaction products was carried out similarly to the above procedure.

Reaction in a Glass Flask, Inert Atmosphere. A stirred mixture of **2a** (157 mg, 0.5 mmol), DMF (10 mL), and additives listed in Table 1 was heated at 90−95 °C for 2 h in a glass flask under argon. Isolation of the reaction products was carried out similarly to the above procedures.

*N,N,1-Trimethyl-2-phenyl-1H-benzo[g]indol-9-amines (**5b**).* **5b** was obtained as beige crystals, mp 83−85 °C; IR (Nujol) 1600, 1578, 1560 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 300 (M^+, 100), 284 (20), 269 (30), 256 (25), 150 (30), 142 (23), 128 (18). Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 84.11; H, 6.59; N, 9.18. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.83 (s, 6H), 3.78 (s, 3H), 6.79 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.30−7.41 (m, 2H), 7.47−7.57 (m, 4H), 7.65−7.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 39.8, 43.4, 104.3, 114.1, 118.6, 121.1, 122.6, 123.2, 124.3, 127.0, 127.9, 129.0, 129.4, 133.7, 134.5, 136.6, 145.0, 148.7.

*N^9,N^9,$N^{9'}$,$N^{9'}$,1,1′-Hexamethyl-2,2′-diphenyl-1H,1′H-3,3′-bibenzo[g]indole-9,9′-diamine (**8**).* **8** was obtained as off-white crystals, mp 284−286 °C (heptane); R_f 0.3 (hexane); IR (Nujol) 1599, 1552 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 598 (M^+; 64), 299 (100), 291 (21), 283 (24), 277 (16), 268 (26), 260 (18), 254 (22), 215 (13), 168 (21), 118 (17). Anal. Calcd for $C_{42}H_{38}N_4$: C, 84.25; H, 6.40; N, 9.36. Found: C, 84.09; H, 6.27; N, 9.57. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.73 (s, 6H), 2.93 (s, 6H), 3.67 (s, 6H), 6.86 (dd, *J* = 8.4, 1.5 Hz, 4H), 6.95−7.07 (m, 6H), 7.11 (dd, *J* = 7.6, 1.0 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 39.7, 42.3, 44.3, 110.5, 113.9, 118.5, 121.0, 122.1, 123.2, 124.2, 126.9, 128.0, 128.6, 130.3, 133.0, 134.4, 135.8, 142.8, 148.8.

*(9-(Dimethylamino)-1-methyl-1H-benzo[g]indol-3-yl)(phenyl)methanone (**9a**).* **9a** was obtained as off-white crystals, mp 129−130 °C (octane); IR (Nujol) 1625 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 328 (M^+; 100), 312 (15), 284 (13), 223 (36), 208 (37), 192 (24), 105 (68), 77 (67). Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.33; H, 5.96; N, 8.47. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.71 (s, 6H), 4.08 (s, 3H), 7.15 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.45−7.60 (m, 5H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.85−7.89 (m, 2H), 8.51 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 41.2, 43.7, 114.9, 117.0, 118.2, 121.9, 123.6, 124.8, 125.2, 126.4, 128.7, 129.3, 131.6, 133.9, 134.9, 139.8, 141.4, 148.9, 191.7.

Synthesis of (9-(Dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-3-yl)(*p*-tolyl)methanone (9b). A stirred mixture of *p*-tolylethynylnaphthalene **2b** (164 mg, 0.5 mmol) and CuI (29 mg, 0.15 mmol) in DMF (15 mL) was heated at 90−95 °C for 2.5 h. The reaction mixture was then mixed with a saturated aqueous solution of NaCl (30 mL) and extracted with ether (3 × 20 mL). The solvent was evaporated to dryness. The residue was purified by flash column chromatography on Al_2O_3 with Et_2O/CH_2Cl_2 (1:1, v/v) as eluent. The colorless fraction with R_f 0.1 gave **9b** (51 mg, 30%) as beige crystals. **9b**: mp 159−160 °C (hexane); IR (Nujol) 1621 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 342 (M^+; 100), 223 (20), 208 (18), 192 (12), 119 (35), 91 (30). Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48; N, 8.18. Found: C, 80.45; H, 6.33; N, 8.00. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.44 (s, 3H), 2.71 (s, 6H), 4.07 (s, 3H), 7.15 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.58 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.0, 41.1, 43.8, 114.8, 117.1, 118.2, 121.9, 123.6, 124.6, 125.1, 126.5, 129.3, 129.5, 133.8, 134.9, 138.6, 139.4, 142.1, 148.9, 191.4.

Synthesis of (9-(Dimethylamino)-1-methyl-8-(phenylethynyl)-1*H*-benzo[*g*]indol-3-yl)(phenyl)methanone (10). The reaction was carried out similarly to the synthesis of **9b** with 2,7-bis(phenylethynyl)naphthalene **3a** (207 mg, 0.5 mmol). Compound **10** was obtained in 25% yield (54 mg) as yellowish crystals with mp 163−165 °C (heptane); IR (Nujol) 2200 cm^{-1}; EIMS (*m*/*z*) (rel intensity) 428 (M^+; 83), 351 (17), 321 (15), 307 (18), 105 (100), 77 (63). Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.23; H, 5.49; N, 6.71. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.04 (s, 6H), 4.00 (s, 3H), 7.33−7.41 (m, 3H), 7.46−7.57 (m, 7H), 7.62 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.87 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.55 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 42.2, 44.2, 90.3, 95.6, 116.7, 117.5, 121.5, 122.8, 124.3, 124.7, 125.4, 127.7, 128.6, 128.7, 128.9, 129.3, 130.5, 131.3, 131.7, 133.8, 134.9, 140.2, 141.3, 149.9, 191.6.

X-ray Diffraction Analysis. Crystals suitable for X-ray studies were grown by slow evaporation from solutions of compounds in the appropriate solvents or solvent mixtures: **4b** (*n*-hexane), **7** (EtOAc), **8** ($PhMe-CH_2Cl_2$), **9b** (Et_2O). X-ray experiments were carried out using a SMART APEX2 CCD [λ(Mo−Kα) = 0.71073 Å, graphite monochromator, ω-scans] diffractometer. Collected data were analyzed by the SAINT and SADABS programs incorporated into the APEX2 program package.[29a] All structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model. The refinement was carried out with the SHELXTL program.[29b] The details of data collection and crystal structures refinement are summarized in Table S1 (Supporting Information). CCDC 1029140−1029143 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra for the products, photos of porcelain basins, ORTEP plots for crystal structures, and crystal data and structure refinement for compounds **4b**, **7**, **8**, and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (projects 11-03-00073 and 14-03-00010). We thank Drs. Z. A. Starikova (deceased on September 5, 2013) and K. Y. Suponitsky (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russian Federation) for X-ray experiments.

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(26) The fact that all readily migrating groups belong to the so-called S_N1 type can indicate that, in the transition state (TS), they form the corresponding cation or some kind of ionic pair, followed by the C−C bond formation. Convincing arguments in favor of this mechanism are given in ref 3g. Since methyl cation is not stabilized, the methyl group transfer most likely occurs as the direct [1,3] migration (actually as two consecutive [1,2] migrations).[3g] It is well-known that the TS of [1,3] migrations is sterically highly demanded (Mikhailov, I. E.; Dushenko, G. A.; Minkin, V. I. *Molecular Rearrangements of Cyclopolyenes* (in Russian); Nauka: Moscow, 2008; p 19). Probably, this is a reason why [1,3] migrations of the Me group in the reactions under consideration occur only under specific conditions and with high activation energy (see ref 4 along with our case). This view also elucidates why compound **2c** regardless of using isolation protocols *B* or *C* is converted into benzo[*g*]indole **5a**. Apparently, the bulky $SiMe_3$ group strongly inhibits both intra- and intermolecular migration of the methyl group and the latter is eliminated from **28** reacting with other nucleophiles.

(27) By request of one of the reviewers, we have carried out the following experiment. After completion of Sonogashira reaction of **1** with phenylacetylene, molecular sieves 3Å and 4Å (Sigma−Aldrich) were added into the reaction mixture instead of porcelain shards. The subsequent use of isolation protocol *A* gave **4a** in 8% and 16%, respectively. The major part of the reaction products seems to be oligomers. Clearly, such experiments involving different kinds of zeolites and clays deserve further studies.

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