One-Pot Homo- and Cross-Coupling of Diazanaphthalenes via C-H Substitution: Synthesis of Bis- and Tris-Diazanaphthalenes

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Abstract: The transition metal-free coupling reactions of unactivated diazanaphthalenes were studied using only lithium tetramethylpiperidine (LiTMP) reagent. Symmetrical and nonsymmetrical bis-diazanaphthalenes were synthesized in moderate to high yield by homo- and cross-coupling of related monomers. In addition, the single-step synthesis of diquinoxalino [2,3-a: 2', 3'c] phenazine and 2,2': 3', 2''- terquinoxaline using the appropriate equivalent amount of LiTMP was performed. The products were characterized by means of NMR spectroscopy and HRMS spectrometry.

Introduction

Diazanaphthalenes are a significant class of benzenoid heterocyclic aromatic compounds. There are ten diazanaphthalene derivatives in the isomeric structure (Figure 1) and compounds derived from them have a wide range of applications in material sciences[1] and medicinal chemistry[2] and this has stimulated the discovery and development of novel molecules based on diazanaphthalene and new synthetic methods. On the other hand, dimeric diazanaphthalenes are most widely used in coordination chemistry due to their exceptional ligand capacity.[3] They have been extensively used as versatile building blocks in the fields of analytical, photo-, supra-, nano-, and macromolecular chemistry applications.[1d, 4] For this reason, there has been tremendous interest in synthesis of diazanaphthalene derivatives, especially dimeric forms of these compounds.

Consequently, significant efforts have been made to develop efficient methods for the synthesis of diazanaphthalenes and their derivatives. There are some known methods in the literature for the synthesis of dimeric diazanaphthalenes. However, the numbers of known dimers are limited. The traditional method relies on condensation of 1,2-aminoaldehydes (or 1,2-diamines) with suitable carbonyl compounds.[1a, 3c, e, 4b, 5]

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Although these methods work well for a few derivatives, it is not possible to synthesize many specific dimeric diazanaphthalenes when 1,2-aminoaldehydes (or 1,2-diamines) and suitable carbonyl compounds are used as starting materials.

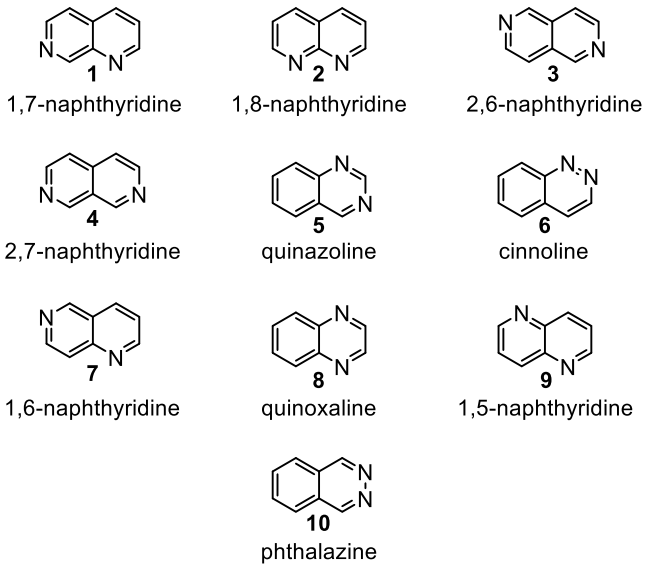
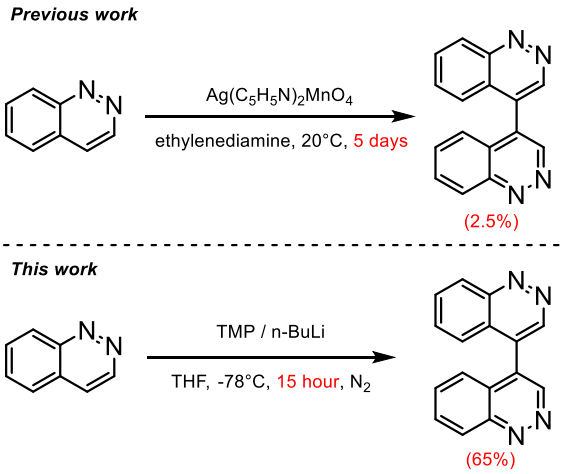


Figure 1. Diazanaphthalene derivatives in the isomeric structure

Another method for the synthesis of dimeric diazanaphthalenes in the literature is coupling reactions using transition metal-containing catalysts and halogen-containing starting compounds.[6] For example, the first and sole synthesis of 2,2'-bi-1,5-naphthyridine was achieved in 22% yield using Ni $(PPh_3)_2Br_2$ over 2-chloro-1,5-naphthyridine.[3b] Likewise, 1,1'-bi-2,7-naphthyridine was synthesized over 1-bromo-2,7-naphthyridine, which was synthesized in several steps, in 49% yield under $Pd(OAc)_2$ catalysis.[3a] The use of transition metals, low yields, and the synthesis of halogenated diazanaphthalenes in several steps make the method useless. Generally, transition metals are expensive and toxic to the environment. Removing traces of transition metals from such dimers is challenging, laborious, and expensive because of the extremely strong metallic coordination. The disadvantages of condensation and coupling reactions used in the synthesis of dimeric diazanaphthalenes have led investigators to study more efficient methods for the synthesis of related compounds. In this context, further methods have been developed in which the unsubstituted starting compounds are dimerized directly.[7] Quinoxaline and cinnoline have been used in related studies, but the synthesis of

other diazanaphthalene dimers was not included. In some reactions, although 2,2'-bi-quinoxaline was synthesized in high yield, synthesis of 4,4'-bi-cinnoline was only achieved in 2.5% yield (Scheme 1).[7b]



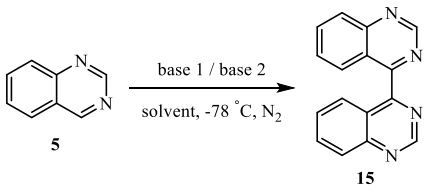
Scheme 1. Method for the synthesis of bis-diazanaphthalenes

Similarly, in the synthesis carried out with Grignard reagent, 2,2':3',2''-terquinoxaline was also synthesized in very low yield.[7a] A similar process was first used in the dimerization of 1,8-naphthyridine and 2,2'-bi-1,8-naphthyridine was synthesized in 69% yield.[8] Recently, a new and efficient method for the homocoupling reactions of inactivated electron-deficient aza arenes has been published by Da and co-workers.[9] In this method, they used TMPMgCl together with tetramethylethylenediamine (TMEDA) (1.0 equiv.) as an additive. The present paper describes modification of the method of Da and co-workers[9] without using any additive and the effective synthesis of new and known bis-diazanaphthalenes. In the present study, LiTMP was freshly prepared in situ by reaction of 2,2,6,6-tetramethylpiperidine (TMPH) with *n*-BuLi before the C-H substitution reaction, and it was used for the coupling of electron-deficient unactivated diazanaphthalenes.

Results and Discussion

In this work, lithium 2,2,6,6-tetramethylpiperidine (LiTMP) was used for the C-H substitution reaction to obtain heteroaromatic dimers and trimers. LiTMP was produced in a reaction flask by treatment of *n*-BuLi with TMP. First, we conducted an optimization study adopting quinazoline (**5**) as a model substrate (Table 1). Initially, the reaction was carried out with *n*-BuLi or *t*-BuLi in THF at -78 °C. No any trace of product formation was observed under these conditions (Table 1, entry 1 and 2). We observed the reaction doesn't work by mixing of DIPA, *t*-BuOK or PPR with *n*-BuLi. (Table 1, entry 3, 4 and 5). The using of TMPH with *n*-BuLi in Et_2O gave the desired product, **15**, in %56 yield (Table 1, entry 6). The using of THF instead of Et_2O increased the efficiency of the reaction (Table 1, entry 7 and 9). We changed bases, and we observed that the efficiency of reaction decreased when *n*-BuLi replaced with *t*-BuLi (Table 1, entry 8). Consequently, the optimized conditions entail the use of TMPH with *n*-BuLi in THF at -78°C.

Table 1. Optimization of reaction conditions.[a]



entry	base 1	base 2[b]	solvent	Yield (%)[c]
1	*n*-BuLi	-	THF	n.d.
2	*t*-BuLi	-	THF	n.d.
3	*n*-BuLi	DIPA	THF	n.d.
4	*n*-BuLi	*t*-BuOK	THF	n.d.
5	*n*-BuLi	PPR	THF	n.d.
6	*n*-BuLi	TMPH	Et_2O	56
7	*n*-BuLi	TMPH	Et_2O/THF	85
8	*t*-BuLi	TMPH	THF	94
9	*n*-BuLi	TMPH	THF	99

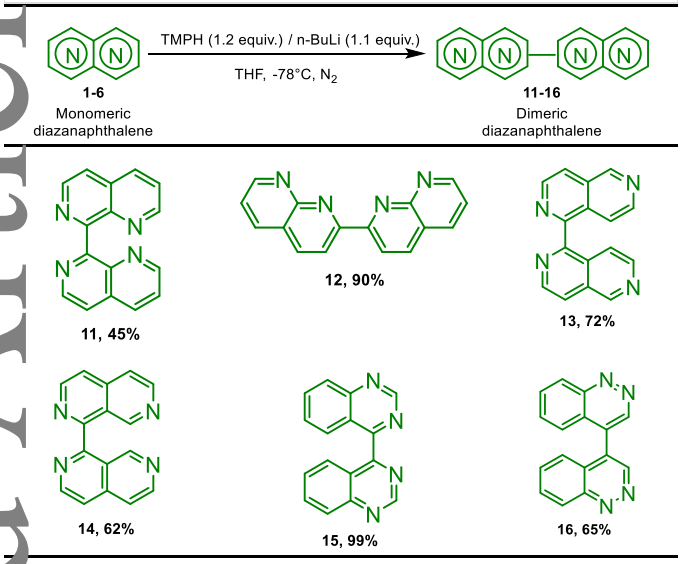
[a] General conditions (unless otherwise specified): **5** (0.38 mmol), base 1 (0.46 mmol), base 2 (0.5 mmol), solvent (10.0 mL), -78°C (2h), rt (12 h). [b] DIPA is diisopropylamine, t-BuOK is potassium tert-butoxide, PPR is piperidine and TMPH is 2,2,6,6-tetramethylpiperidine, respectively. [c] Isolated yield. (n.d.= No detected any trace of target molecule).

Synthesis of Dimeric Diazanaphthalenes Composed of the Same Units

The reaction of isomeric diazanaphthalene derivatives (**1-6**) with LiTMP resulted in the formation of homocoupling products (**11-16**) in 45-99% yields depending on the structures of the monomers as shown in Table 2. As seen in table 2, the reaction yields of dimer is change between 45-99%. This difference is mainly related to count of the active C-H atoms on monomers. Generally, C-H atoms at α position of nitrogen is more active both for nucleophilic attach and C-H activation. Compound **2** has one type active α hydrogen atom, and statically one type dimer is possible, and the yield of dimer is quite higher. Whereas monomers **1** and **3** have more unidentical active α C-H and, thus statistically formation of many kind of by-products is possible. Monomer **5** has also two different active C-H carbon. Formation of only one product in 99% yield show that product via C-H atom between two nitrogen atoms in compound **5** is not favorable due

to crowded four adjacent nitrogen atoms in the possible products. Dimerization via β C-H atom in compound **6** approve this hypothesis.

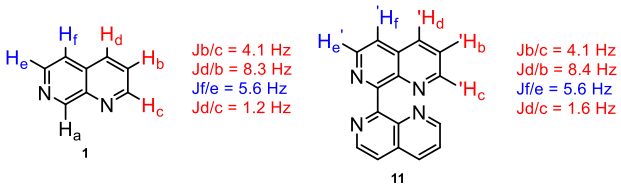
Table 2. Reactions of diazanaphthalenes (1-6) with LiTMP



[a] Isolated yield. No side product was detected.

The structure of 8,8'-bi-1,7-naphthyridine (**11**) obtained from the reaction of 1,7-naphthyridine (**1**) with LiTMP was elucidated by means of NMR spectroscopy. The five different signals observed in the ^{1}H-NMR spectrum of the product and the eight different signals observed in the ^{13}C-NMR spectrum reveal that the product has a symmetrical structure. In these reaction conditions, there are six different possibilities for the open structure of the molecule. The fact that no proton resonating as a singlet is observed in the ^{1}H-NMR spectrum clearly indicates that the binding occurs at the 8-8'- position, because the only proton that can resonate as a singlet in the relevant skeleton is attached to carbon atom number eight. The result of the analysis performed by HRMS spectroscopy is also compatible with the recommended dimeric structure.

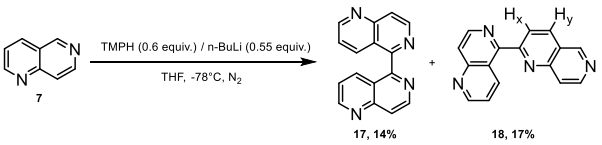
When the ^{1}H-NMR spectra of 1,7-naphthyridine (**1**) and 8-8'-bi-1,7-naphthyridine (**11**) are examined in detail, it is seen that all protons bound to carbon atoms adjacent to electronegative nitrogen atoms in the molecule resonate in lower areas than the others because of the inductive effect of nitrogen atoms. The protons H_a, H_c (H_c') and H_e (H_e') are bound to carbon atoms adjacent to the nitrogen atoms and all of their signals are in the area below around 8.5 ppm. Another remarkable detail about the same spectra is the coupling constants between protons. The coupling constant of proton H_b (H_b') with proton H_c (H_c'), which bonded the carbon that is close to the nitrogen atom, was about 4.0 Hz. However, the coupling constant between proton H_b (H_b') and proton H_d (H_d') was about 8.0 Hz. The coupling constant between visually interacting H_e (H_e') and H_f (H_f') was about 5.5 Hz. In such systems, it is clear that the coupling constant between hydrogen atoms close to electronegative atoms decreases with inductive effect. These generalizations related to chemical shift values and coupling constants played an important role in determining the absolute structures of other diazanaphthalene dimers synthesized in the present study.



Scheme 2. Coupling constants of protons in diazanaphthalene rings.

The dimeric product resulting from the reaction of 1,8-naphthyridine (**2**) with LiTMP is understood to be symmetrical from the number of signals observed in the ^{1}H- (5 signal) and ^{13}C-NMR (8 signal) spectra. In this case, there are three different possible structures (2-2'-, 3,3'-, or 4,4'-bi-1,8-naphthyridine) for the dimeric compound. When the coupling constants of the product were examined, the value was found to be 8.4 Hz. This proves that the structure is strictly 2,2'-bi-1,8-naphthyridine (**12**). If the compound were 3,3'-bi-1,8-naphthyridine, the coupling constant would be about 1.5-2 Hz, and it were 4,4'-bi-1,8-naphthyridine, the value would be about 4-6 Hz. The absolute structure of 1,1'-2,6-naphthyridine (**13**) resulting from the reaction of 2,6-naphthyridine (**3**) with LiTMP was determined based on the observation of one singlet signal in the ^{1}H-NMR spectrum. The structures of 1,1'-2,7-naphthyridine (**14**)[3a], 4,4'-biquinazoline (**15**)[10], and 4,4'-bicinnoline (**16**)[7b] were confirmed by comparing the available spectra with the literature data.

The reaction of 1,6-naphthyridine (**7**) with LiTMP led to the formation of symmetrical and nonsymmetrical dimers by the activation of nonidentical positions in the monomer as shown in Scheme 3. When the corresponding protons were paired with the signals observed in the ^{1}H-NMR spectrum of dimer **18**, it was clearly determined that the vicinal coupling constant between H_x and H_y protons (Scheme 3) was 8.7 Hz. This value indicates that the structure is as shown in Scheme 3.

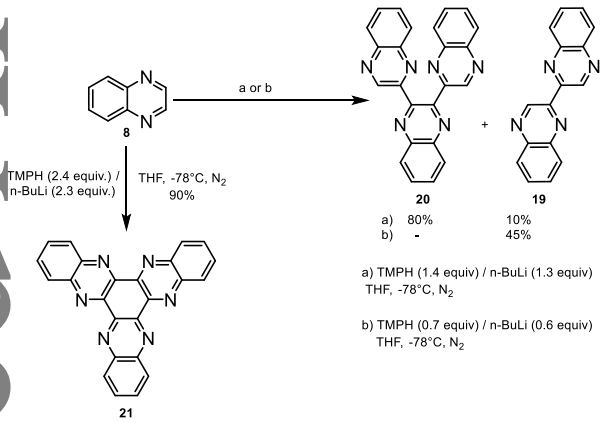


Scheme 3. Reaction of 1,6-naphthyridine with LiTMP.

1,5-Naphthyridine (**9**) and phthalazine (**10**) could not be dimerized with LiTMP. In 1,5-naphthyridine (**9**), the reason for the failure of the reaction is not that 1,5-naphthyridine (**9**) and

LiTMP do not react, but the resulting litho 1,5-naphthyridine cannot participate in 1,5-naphthyridine, which should act as an electrophile. As a matter of fact, as explained below, cross-dimerization reactions of 1,5-naphthyridine (**9**) with some other diazanaphthalene derivatives were performed and the products were obtained. The reaction of phthalazine (**10**) under different conditions resulted in the formation of a viscous black crude product each time. ^{1}H-NMR analysis of this content revealed that all the phthalazine signals disappeared. However, none of the products formed could be isolated, despite the use of many different separation techniques.

The reaction of quinoxaline (**8**) with LiTMP under different conditions resulted in the formation of a dimer (**19**), a noncyclized trimer (**20**), and a cyclized trimer (**21**) in good yields as shown in Scheme 4.

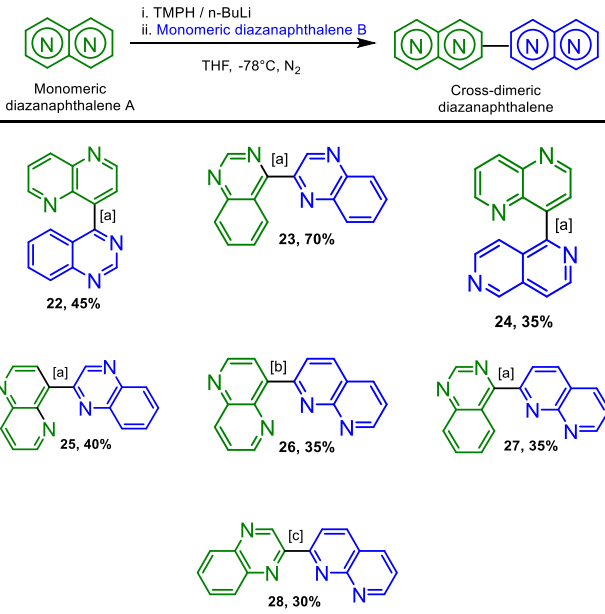


Scheme 4. Reaction of quinoxaline with LiTMP.

Synthesis of Dimeric Diazanaphthalenes Composed of Different Units

Finally, cross-dimerization reactions were studied and the targeted diazanaphthalene dimers were successfully obtained in 30-70% yields by cross-coupling reactions as shown in Table 3. As expected in the reactions, dimeric diazanaphthalenes composed of the same units were formed as side products. Furthermore, noncyclized trimers (**27**, **30**) were formed from the reactions of 1,8-naphthyridine (**2**) with 1,5-naphthyridine (**9**) (Table 3, Entry 5) and quinoxaline (**8**) (Table 3, Entry 7).

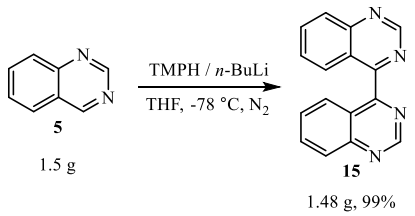
Table 3. Synthesis of cross-dimerization products



[a] The side products were homodimers. [b] The side products were 4,8-di(1,8-naphthyridin-2-yl)-1,5-naphthyridine (15%) (**29**) and 2,2'-bi(1,8-naphthyridine) (10%) (**12**). [c] The side products were 3-(1,8-naphthyridin-2-yl)-2,2'-biquinoxaline (30) and homodimers.

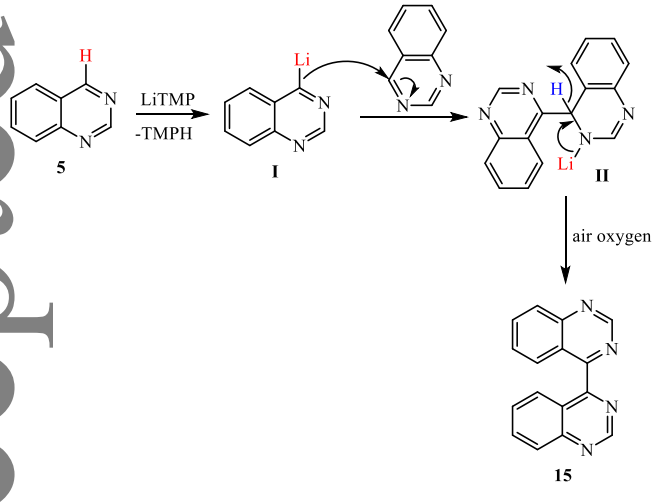
The results of the studies on the synthesis of dimeric diazanaphthalene dimers consisting of the same units were of great benefit in determining the structures of the cross-dimerization products. These results indicate which position of the diazanaphthalene rings is active under the respective reaction conditions. It was therefore understood at which position the rings were attached in the cross dimers. In addition, the coupling constants extracted from the product's ^{1}H-NMR spectra proved the accuracy of the structures. In particular, since the self-dimerization reaction of 1,5-naphthyridine does not work, it is thus determined which position is active in the cross-dimerization reactions, to wit where binding occurs. For example, it was understood from the coupling constant of 4.2 Hz that the 1,5-naphthyridine unit was bonded at carbon 4 in dimer **22**, which was formed by the reaction of 1,5-naphthyridine (**9**) with quinazoline (**5**) (Table 3, Entry 1). Since it is known that carbon 4 of the quinazoline unit is also active, it turns out that the absolute structure is 4-(1,5-naphthyridin-4-yl) quinazoline (**22**). As in this example, in all other cross-dimerization products containing 1,5-naphthyridine units, the coupling was at carbon four. The lack of self-dimerization of 1,5-naphthyridine positively affected the regioselectivity in cross-dimerization reactions. The procedure was modified to ensure this situation. LiTMP was first reacted with 1,5-naphthyridine and then the other diazanaphthalene derivative was reacted.

The synthesis of homo-dimer **15** was attempted on a gram scale, where 1.5 g of quinazoline (**5**) was successfully converted into the **15** (1.48 g, 99% yield, Scheme 5). This result clearly demonstrates the practical applicability of the developed methodology.



Scheme 5. Scale-Up experiment for the synthesis of **15**.

We propose following general reaction mechanism for the homo-coupling of **5** as illustrated in scheme 6 in the light of literature. [7]



Scheme 6. Proposed reaction mechanism.

Quinazoline (**5**) is lithiated to form **I** first. The lithiated quinazoline **I** is then added to the *non*-lithiated quinazoline (**5**) to form intermediate **II**. Finally, homo-dimer **15** is formed as a result of aromatization with help of air oxygen.

Conclusions

We have described an efficient and convenient method for the synthesis of homo- and cross- dimeric diazanaphthalenes. All syntheses were performed by low temperature reaction of the aromatic ring with LiTMP. No other additives were used; no halogen-containing starting compounds or transition metal-containing catalysts were needed. The oxidation of the products obtained was carried out with air oxygen. In addition to dimeric products, some non-cyclized and cyclized trimers were also synthesized successfully.

Experimental Section

General Information

All reactions were performed under an argon or nitrogen atmosphere. Solvents were dried according to the established procedures prior to use. Reactions were monitored by thin layer chromatography (TLC) / or ^{1}H NMR spectroscopy, column chromatography purifications were carried out using silica gel. All reagents were purchased from commercial corporations unless otherwise stated. LiTMP was freshly prepared from *n*-BuLi and TMPH (2,2,6,6-tetramethylpiperidine). The high-resolution mass spectrometry (HRMS) analysis was carried out using an atmospheric pressure chemical ionization-time of flight (APCI-TOF) mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal stan-dard at ambient temperature with Bruker and Varian 400 MHz instruments at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR spectroscopy. Apparent splitting is given in all cases in ppm and coupling constants *J* in Hz. While quinoxaline, phthalazine and quinazoline were commercially available, 1,5-[11], 1,6-[12], 1,7-[13], 1,8-[12], 2,6-[13], 2,7-[13] naphthyridines and cinnoline[14] were synthesized using the literature methods.

General Procedure for coupling reactions

LiTMP was freshly prepared from *n*-BuLi in hexane (2.5 M solution) and TMPH (2,2,6,6-tetramethylpiperidine). Under an argon atmosphere, at -10 ºC, TMPH was introduced into a dry two-necked round-bottom flask and *n*-BuLi in hexane were added. THF was introduced. The mixture was cooled to -78ºC by liquid nitrogen-acetone cooling system and stirred for 10 min. Then the diazanaphthalene was added slowly at -78ºC as a THF solution. The reaction mixture was vigorously stirred for 2h. The mixture was allowed to warm to r.t. and stirred for overnight under an argon atmosphere. After completion of the reaction, THF were concentrated in vacuum to give the crude product. The resulting product was purified by silica gel column chromatography or crystallization.

Diazanaphthalene A and Diazanaphthalene B were added as a mixture on LiTMP in cross-dimerization reactions (Table 2, Entry 2,6 and 7). If one of the monomers is 1,5-naphthyridine (Table 2, Entry 1,3,4 and 5), it is added first, stirred for 1 h at -78°C, then the other derivative is introduced.

8,8'-Bi(1,7-naphthyridine) (11):

The product **11** was prepared according to general procedure using TMPH (100.0 mmL, 0.6 mmol), *n*-BuLi (220.0 mmL, 0.55 mmol) and 1,7-naphthyridine (65.0 mg, 0.5 mmol). After column chromatography (CH_2Cl_2/MeOH, 95:5), the product was obtained as a white solid (30.0 mg, 45%; m.p. = 113-115 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.81 (d, *J* = 5.6 Hz, 1H), 8.24 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.82 (d, *J* = 5.6 Hz, 1H), 7.56 (dd, *J* = 8.4, 4.1 Hz, 1H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 160.2, 151.7, 143.1, 142.8, 134.9, 131.8, 124.9, 120.8. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0981.

2,2'-Bi(1,8-naphthyridine) (12):

The product **12** was prepared according to general procedure using TMPH (0.4 mL, 2.3 mmol), *n*-BuLi (0.9 mL, 2.1 mmol) and 1,8-naphthyridine (250.0 mg, 1.9 mmol). After column chromatography (EtOAC/MeOH, 9:1), the product was obtained as a brown solid (225.0 mg, 90%; m.p. = 250-251 °C; Lit.[5a] m.p. =250 ºC). ^{1}H NMR (400 MHz, MeOD) δ 9.18 (d, *J* = 4.2 Hz, 2H), 9.10 (d, *J* = 8.7 Hz, 2H), 8.68 (d, *J* = 8.7 Hz, 2H), 8.59 (d, *J* = 7.9 Hz, 2H), 7.75 (dd, *J* = 7.9, 4.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 155.8, 154.0, 138.0, 137.0, 123.5, 122.6, 121.1. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0920.

1,1'-Bi(2,6-naphthyridine) (13):

The product **13** was prepared according to general procedure using TMPH (315.0 mmL, 1.85 mmol), *n*-BuLi (675.0 mmL, 1.7 mmol) and 2,6-naphthyridine (200.0 mg, 1.55 mmol). After crystallization (CH_2Cl_2/EtOH, 95:5), the product was obtained as a white solid (143.0 mg, 72%; m.p. = >> 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 0.8 Hz, 2H), 8.93 (d, *J* = 5.7 Hz, 2H), 8.68 (d, *J* = 6.0 Hz, 2H), 7.98 (d, *J* = 5.7 Hz, 2H), 7.86 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 152.3, 145.3, 143.4, 131.4, 129.6, 120.2, 118.7. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0990.

1,1'-Bi(2,7-naphthyridine) (14):

The product **14** was prepared according to general procedure using TMPH (160.0 mmL, 0.95 mmol), *n*-BuLi (340.0 mmL, 0.85 mmol) and 2,7-naphthyridine (100.0 mg, 0.77 mmol). After column chromatography (CH_2Cl_2/MeOH, 9:1), the product was obtained as a white solid (62.0 mg, 62%; m.p. = >> 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.92 (d, *J* = 5.7 Hz, 1H), 8.78 (d, *J* = 5.7 Hz, 1H), 7.84 (d, *J* = 5.7 Hz, 1H), 7.79 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 152.5, 146.9, 145.5, 139.7, 123.0, 120.1, 119.3. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0927.

4,4'-Biquinazoline (15):

The product **15** was prepared according to general procedure using TMPH (2.5 mL, 15.0 mmol), *n*-BuLi (5.5 mL, 14.0 mmol) and quinazoline (1.5 g, 11.5 mmol). After crystallization (EtOAc), the product was obtained as a white solid (1.48 g, 99%; m.p. = 210 °C; Lit.[10] m.p. = 210-212 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 2H), 8.23 (d, *J* = 8.4 Hz, 2H), 8.00 (t, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 154.1, 151.4, 134.6, 129.1, 128.6, 126.4, 123.5. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0933.

4,4'-Bicinnoline (16):

The product **16** was prepared according to general procedure using TMPH (157.0 mmL, 0.92 mmol), *n*-BuLi (340.0 mmL, 0.85 mmol) and cinnoline (100.0 mg, 0.77 mmol). After column chromatography (CH_2Cl_2/MeOH, 49:1), the product was obtained as a black solid (65.0 mg, 65%; m.p. = 235 °C; Lit.[7b] m.p.= 235-236 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 2H), 8.75 (d, *J* = 8.6 Hz, 2H), 8.02 – 7.90 (m, 2H), 7.78 – 7.66 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 144.5, 132.5, 131.3, 130.7, 128.0, 124.6, 124.0. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0975.

5,5'-Bi(1,6-naphthyridine) (17) and 2,5'-Bi(1,6-naphthyridine) (18):

The products **17** and **18** were prepared according to general procedure using TMPH (0.41 mL, 2.4 mmol), *n*-BuLi (0.87 mL, 2.2 mmol) and 1,6-naphthyridine (520.0 mg, 4.0 mmol). After column chromatography (CH_2Cl_2/MeOH, 19:1), in the firs fraction, the product **18** was obtained as a white solid (88.0 mg, 17%; m.p. = 259-261 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.7 Hz, 1H), 9.40 (s, 1H), 9.15 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.93 (d, *J* = 5.9 Hz, 1H), 8.86 (d, *J* = 5.9 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 1H), 8.48 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 6.0 Hz, 1H), 8.05 (d, *J* = 6.0 Hz, 1H), 7.62 (dd, *J* = 8.7, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 156.5, 154.7, 152.8, 151.6, 149.5, 147.5, 145.6, 136.6, 136.5, 124.2, 123.7, 123.1, 122.9, 122.7, 122.3. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0984. In the second fraction, the product **17** was obtained as a white solid (72.0 mg, 14%; m.p. = >> 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.94 (d, *J* = 5.9 Hz, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 5.9 Hz, 1H), 7.51 (dd, *J* = 8.6, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 154.9, 151.5, 145.3, 135.6, 123.4, 123.0, 122.9. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0979.

2,2'-Biquinoxaline (19):

The product **19** was prepared according to general procedure using TMPH (0.45 mL, 2.7 mmol), *n*-BuLi (0.92 mL, 2.3 mmol) and quinoxaline (500.0 mg, 3.85 mmol). After column chromatography (EtOAc/hexane, 3:7), the product was obtained as a yellow solid (220.0 mg, 45%; m.p. = 293-295 °C; Lit.[7e] m.p.= 293-295 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 2H), 8.30 – 8.24 (m, 2H), 8.24 – 8.19 (m, 2H), 7.89 – 7.82 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 144.3, 142.9, 141.7, 130.9, 130.6, 130.0, 129.5. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0921.

2,2':3',2''-Terquinoxaline (20):

The product **20** was prepared according to general procedure using TMPH (0.92 mL, 5.4 mmol), *n*-BuLi (2.0 mL, 5.0 mmol) and quinoxaline (500.0 mg, 3.85 mmol). After column chromatography (EtOAc/hexane, 1:4), in the firs fraction, the product **19** was obtained (50.0 mg, 10%). In the second fraction the product **20** was obtained as a orange solid (400.0 mg, 80%; m.p. = 234 °C; Lit.[15] m.p.= 234-235 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 2H), 8.33 (AA' part of AA'BB' system, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.94 (BB'' part of AA'BB' system, 2H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 150.3, 146.0, 141.9, 141.5, 141.1, 131.8, 130.7, 130.4, 129.9, 129.5, 129.3. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{24}H_{14}N_6$ 387.1358; found 387.1281.

Diquinoxalino[2,3-a:2',3'-c]phenazine (21):

The product **21** was prepared according to general procedure using TMPH (1.6 mL, 9.2 mmol), *n*-BuLi (3.55 mL, 8.85 mmol) and quinoxaline (500.0 mg, 3.85 mmol). After crystallization (MeOH), the product was obtained as a green solid (450.0 mg, 90%; m.p. = >> 300 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (AA' part of AA'BB' system, 6H), 8.06 (BB' part of AA'BB' system, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.8, 132.5, 130.9. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{24}H_{12}N_6$ 385.1202; found 385.1199.

4-(1,5-Naphthyridin-4-yl)quinazoline (22):

The product **22** was prepared according to general procedure using TMPH (0.78 mL, 4.6 mmol), *n*-BuLi (1.7 mL, 4.25 mmol), 1,5-naphthyridine (500.0 mg, 3.85 mmol) and quinazoline (500.0 mg, 3.85 mmol). After column chromatography (Et_2O/EtOAc, 1:1), in the first fraction roduct **15** was obtained (149.0 mg, 15%). In the second fraction the product **22** was obtained as a white solid (446.5 mg, 45%; m.p. = 169-170 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 9.20 (d, *J* = 4.2 Hz, 1H), 8.87 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.56 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.89 (m, 1H), 7.78 (d, *J* = 4.2 Hz, 1H), 7.71 (dd, *J* = 8.6, 4.2 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 154.6, 151.65, 151.0, 150.4, 144.4, 144.2, 141.9, 137.8, 134.1, 128.9, 127.9, 127.0, 124.9, 124.7, 124.5. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0999.

4-(Quinoxalin-2-yl)quinazoline (23):

The product **23** was prepared according to general procedure using TMPH (0.35 mL, 1.9 mmol), *n*-BuLi (0.70 mL, 1.8 mmol), quinoxaline (100.0 mg, 0.77 mmol) and quinazoline (100.0 mg, 0.77 mmol). After column chromatography (Et_2O/hexane, 3:7), in the first fraction roduct **23** was obtained as a white solid (140.0 mg, 70%; m.p. = 197 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 9.53 (s, 1H), 9.15 (d, *J* = 8.5 Hz, 1H), 8.25 – 8.29 (m, 2H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.76 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.3, 151.9, 150.6, 146.3, 142.4, 141.0, 134.1, 131.3, 130.7, 130.0, 129.5, 129.1, 128.7, 127.5, 123.2. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0927. In the second fraction the product **15** was obtained (30.0 mg, 15%).

4-(2,6-Naphthyridin-1-yl)-1,5-naphthyridine (24):

The product **24** was prepared according to general procedure using TMPH (0.6 mL, 3.5 mmol), *n*-BuLi (1.32 mL, 3.3 mmol), 1,5-naphthyridine (330.0 mg, 2.5 mmol) and 2,6-naphthyridine (330.0 mg, 2.5 mmol). After column chromatography (CH_2Cl_2/EtOH, 19:1), in the first fraction roduct **24** was obtained as a white solid (230.0 mg, 35%; m.p. = 181-183 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 9.20 (d, *J* = 4.2 Hz, 1H), 8.91 (d, *J* = 5.8 Hz, 1H), 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.56 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.55 (d, *J* = 5.9 Hz, 1H), 7.94 (d, *J* = 5.9 Hz, 1H), 7.80 (d, *J* = 4.2 Hz, 1H), 7.70 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.22 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 152.3, 151.5, 151.1, 145.5, 144.7, 144.2, 144.1, 142.2, 137.8, 130.5, 129.8, 125.3, 124.8, 119.8, 119.2. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0996. In the second fraction the product **13** was obtained (32.0 mg, 5%).

2-(1,5-Naphthyridin-4-yl)quinoxaline (25):

The product **25** was prepared according to general procedure using TMPH (0.78 mL, 4.6 mmol), *n*-BuLi (1.7 mL, 4.25 mmol), 1,5-naphthyridine (500.0 mg, 3.85 mmol) and quinoxaline (500.0 mg, 3.85 mmol). After column chromatography (Et_2O/EtOAc, 9:1), in the first fraction roduct **19** was obtained (100.0 mg, 10%). In the second fraction the product **25** was obtained as a white solid (400.0 mg, 40%; m.p. = 205 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 9.21 (d, *J* = 4.3 Hz, 1H), 9.06 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.5, 1.6 Hz, 1H), 8.25 (d, *J* = 4.3 Hz, 1H), 8.21-8.23 (m, 2H), 7.88 – 7.81 (m, 2H), 7.75 (dd, *J* = 8.5, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 150.5, 148.0, 144.5, 143.6, 142.6, 141.9, 141.4, 137.9, 130.5, 130.2, 129.8, 129.3, 125.0, 124.6. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0991.

4-(1,8-Naphthyridin-2-yl)-1,5-naphthyridine (26):

The product **26** was prepared according to general procedure using TMPH (0.78 mL, 4.6 mmol), *n*-BuLi (1.7 mL, 4.25 mmol), 1,5-naphthyridine (500.0 mg, 3.85 mmol) and 1,8-naphthyridine (500.0 mg, 3.85 mmol). After column chromatography (CH_2Cl_2/MeOH, 24:1), in the first fraction the product **26** was obtained as a white solid (350.0 mg, 35%; m.p. = 206-207 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 4.2, 2.0 Hz, 1H), 9.18 (d, *J* = 4.5 Hz, 1H), 9.05 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.54 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.44 (d, *J* = 4.5 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.31 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.72 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.57 (dd, *J* = 8.2, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 156.2, 153.9, 151.5, 150.9, 145.1, 144.5, 141.6, 138.0, 136.8, 136.3, 126.1, 125.6, 124.2, 122.6, 122.5. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0993. In the second fraction the product **29** was obtained as a white solid (110.0 mg, 15%; m.p. = >>300 °C; Lit.[3c] m.p. = >> 300 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 4.3 Hz, 1H), 9.21 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 4.3 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.33 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.59 (dd, *J* = 8.1, 4.1 Hz, 1H). ^{13}C NMR (could not be obtained because of poor solubility). HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{24}H_{15}N_6$ 387.1358; found 387.1365. In the third fraction product **12** was obtained (100.0 mg, 10%).

4-(1,8-Naphthyridin-2-yl)quinazoline (27):

The product **27** was prepared according to general procedure using TMPH (0.3 mL, 1.75 mmol), *n*-BuLi (0.65 mL, 1.6 mmol), 1,8-naphthyridine (150.0 mg, 1.15 mmol) and quinazoline (150.0 mg, 1.15 mmol). After column chromatography (EtOAc), in the first fraction product **15** was obtained (75.0 mg, 25%). In the second fraction the product **27** was obtained as a white solid (105.0 mg, 35%; m.p. = 159 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 9.45 (d, *J* = 8.5 Hz, 1H), 9.26 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.34 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.97 (ddd, *J* = 8.5, 7.0, 1.2 Hz, 1H), 7.75 (ddd, *J* = 8.5, 7.0, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.2, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.5, 155.1, 154.4, 154.1, 151.9, 138.3, 137.1, 134.0, 128.8, 128.6, 128.5, 123.4, 123.2, 123.2, 122.9. HRMS (APCI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0927. In the third fraction product **12** was obtained (15.0 mg, 5%).

2-(1,8-Naphthyridin-2-yl)quinoxaline (28):

The product **28** was prepared according to general procedure using TMPH (1.0 mL, 5.75 mmol), *n*-BuLi (2.15 mL, 5.4 mmol), 1,8-naphthyridine (500.0 mg, 3.85 mmol) and quinoxaline (500.0 mg, 3.85 mmol). After column chromatography (EtOAc/hexane, 4:1), in the first fraction product **19** was obtained (59.0 mg, 12%). In the second fraction the product **28** was obtained as a white solid (300.0 mg, 30%; m.p. = 290-291 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 9.22 (dd, *J* = 4.2, 1.9 Hz, 1H), 8.93 (d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.30 (dd, *J* = 8.1, 1.9 Hz, 1H), 8.18-8.24 (m, 2H), 7.88 – 7.76 (m, 2H), 7.58 (dd, *J* = 8.1, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 155.8, 154.2, 149.4, 144.9, 143.0, 141.7, 138.2, 137.1, 130.7, 130.3, 129.9, 129.5, 123.3, 122.8, 120.4. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{11}N_4$ 259.0984; found 259.0997. In the third fraction the product **30** was obtained as a white solid (60.0 mg, 8%; m.p. = 230-232 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.92 (dd, *J* = 4.3, 2.0 Hz, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.3Hz, 1H), 8.36 – 8.32 (m, 1H), 8.30 – 8.26 (m, 1H), 8.24 (dd, *J* = 8.1, 2.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.70 – 7.64 (m, 1H), 7.50-7.54 (m, 1H), 7.46 – 7.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 155.0, 153.8, 152.5, 151.3, 150.3, 145.9, 141.7, 141.3, 141.0, 141.0, 137.8, 136.7, 131.3, 131.1, 130.1, 129.8, 129.7, 129.5, 129.3, 129.2, 122.8, 122.4, 122.1. HRMS (APCI-TOF) (m/z): $[M + H]^+$ calcd for $C_{24}H_{15}N_6$ 387.1358; found 387.1384. In the fourth fraction product **12** was obtained (49.0 mg, 10%).

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Keywords: diazanaphthalene • naphthyridine • C-H substitution • bi-naphthyridine • benzodiazine

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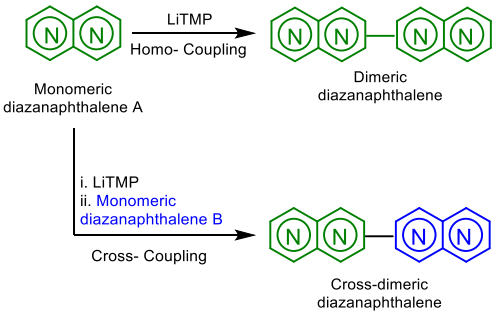
Layout 1:

FULL PAPER

The transition metal-free coupling reactions of unactivated diazanaphthalenes were studied using only lithium tetramethylpiperidine (LiTMP) reagent. Symmetrical and nonsymmetrical bis-diazanaphthalenes were synthesized by homo- and cross-coupling of related monomers.



Research Assistant Sefa Uçar

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One-Pot Homo- and Cross-Coupling of Diazanaphthalenes via C-H Substitution: Synthesis of Bis- and Tris-Diazanaphthalenes

Graphical abstract

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