Aryl-Aryl Bonds Formation in Pyridine and Diazine Series. Diazines Part 41

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The synthesis of several symmetrical polyaromatic compounds with pyridine or diazine units has been achieved by homocoupling of aryl halides with $Pd(OAc)_2$ as catalyst. Cross-coupling reactions of aryl Grignard reagents with $Fe(acac)_3$ as catalyst allowed the synthesis of various unsymmetrical polyaryl- or polyheteroaryl compounds with π-deficient rings.

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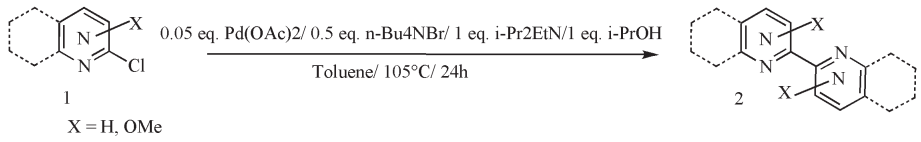
Aryl-aryl bond formation is one of the most important tools of modern organic synthesis. These bonds are very often found in natural products [1] such as alkaloids as well as in numerous biologically active parts of pharmaceutical and agrochemical specialities including pyridine or/and diazine moieties. Polyaromatics also possess original physical properties which could lead to various applications such as organic conductors [2], optoelectronic devices [3] and liquid crystals [4]. Last but not least, di- or triaromatic rings are the backbone of some of the most efficient ligands used as asymmetric catalysts especially when atropoisomery is possible [5], or as complexes with heavy metals [6].

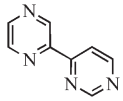
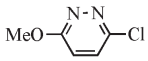
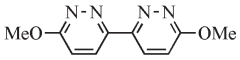
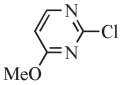
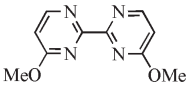
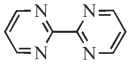
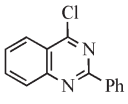
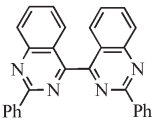
Among the various efficient methods for the construction of carbon-carbon bonds, the transition metal-catalyzed cross-coupling reactions have become an attractive procedure. Biaryls are usually prepared from aryl iodides, bromides or triflates, either by Ullmann coupling [7] or by Palladium-,

Table 1

Homocoupling Reactions of Chlorodiazine

Scheme 1



Entry	Substrate **1**	Product **2**	Compound [Ref.] [a]	Yield
1			**2a**	97% [14]
2			**2b** [15]	95%
3			**2c** [16]	76%
4			**2d** [17]	96%
5			**2e** [18]	39%

[a] All products **2** have been characterized and comparison with already published data are in agreement.

Nickel- or Iron cross-coupling reactions of arylboranes [8], organotins [9] and aryl Grignard reagents [10].

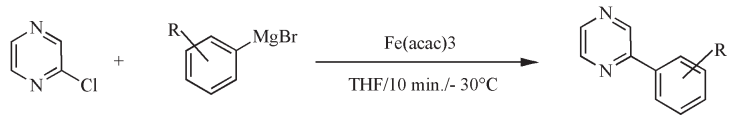
Using these methodologies, we report here syntheses of symmetrical and unsymmetrical di-and poly-arylcompounds with one or several π-deficient heterocycles such as pyridine or diazine.

The most usual way to prepare symmetrical biaryls is the Ullmann [11] synthesis which consists of the condensation of two molecules of aryl halides in the presence of copper, generally at a high temperature. More recently, other methods have been developed based on either a Ni(0)Zn [12] coupling or a Pd/formiate [13,14] coupling and have been reported to synthesize bipyridines.

The association of palladium acetate $Pd(OAc)_2$ and tetrabutylammonium bromide mixture ($Pd(OAc)_2$/(*n*-Bu_4NBr) as a catalyst to induce homocoupling of various chlorodiazines (Table 1, Scheme 1). Using this catalyst, dimers **2a-2d** are obtained in good yields with chlorodiazines (entries 1-4), whereas a lower yield was observed with the 2-phenyl-4-chloroquinazoline (entry 5).

Among the synthetic known procedures for the construction of unsymmetrical biaryls with a π-deficient heterocycle, cross-coupling reactions between aryl Grignard reagents and heteroaryl halides provide an efficient method. Such cross-coupling, reactions catalyzed with palladium or nickel. have been reported in the literature [12b,19]. Recently, iron complexes such as Iron III acetylacetonate $Fe(acac)_3$ seemed to be effi-

Scheme 2

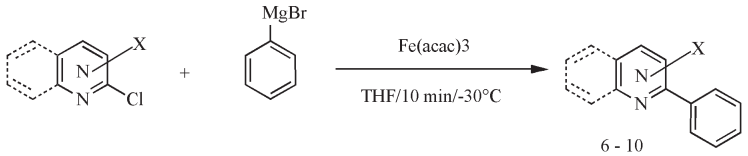


R = o-Me 3 81%
o-OMe 4 75%
p-OMe 5 86%

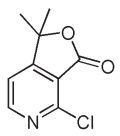
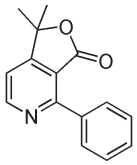
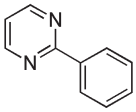
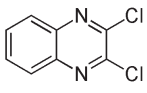
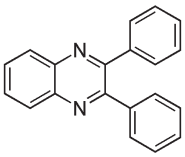
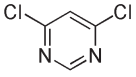
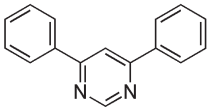
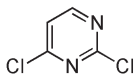
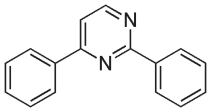
Table 2

Cross-coupling Reactions of Phenylmagnesium Bromide with Heteroaryl Chlorides (Het-Cl)

Scheme 3



6 - 10

Entry	Het-Cl	Product	Compound [Ref]	Yield Isolated
1			**6**	68%
2			**7** [21]	50%
3			**8** [22]	38%
4			**9** [23]	39%
5			**10** [24]	33%

tetra-*n*-butylammonium bromide (*n*-Bu_4NBr) has been used as a convenient catalytic alternative for Ullmann type reactions [14]. We investigated the palladium diacetate/

cient catalysts to achieve cross-coupling reactions of alkyl or aryl Grignard reagents with aryl or heteroaryl chlorides [20]. Using this last methodology, we

describe here the synthesis of different polyaryl- or polyheteroaryl compounds.

First, we have tested the reaction of chloropyrazine with several arylmagnesium bromides leading to the substituted phenylpyrazine derivatives **3-5** in good yields. Nevertheless, the reaction failed with mesitylmagnesium bromide, probably due to steric hindrance (Scheme 2).

Reaction of the π-deficient heteroarl halides with phenylmagnesium bromide under similar experimental conditions gave compounds **6-10** in moderate yields (Scheme 3, Table 2).

In search for new polyaza heterocyclic compounds, we have extended these cross-coupling processes to the reaction of several π-electron-deficient heteroaryl chlorides with pyridylmagnesium chlorides under the above experimental conditions. Reactions with 2- and 4-pyridylmagnesium chlorides failed whereas 3-pyridylmagnesium chloride allowed cross-coupling reaction leading to compounds **11-18** (Scheme 4, Table 3).

In terms of yields, the results compiled in Table 3 are comparable or slightly lower than those obtained in related Palladium- or Nickel catalyzed cross-coupling reactions of aryl Grignard reagents with π-deficient heterocycles previously described in the literature. The high reaction rates at low temperature using $Fe(acac)_3$, a catalyst of low cost, makes this method attractive to access to a wide range of unsymmetrical polyaza heterocyclic compounds.

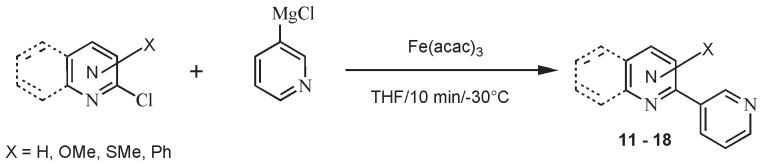
Conclusion.

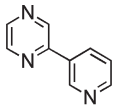
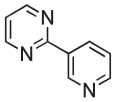
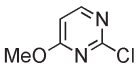
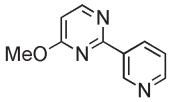
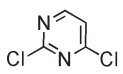
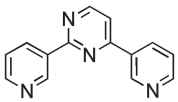
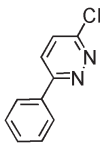
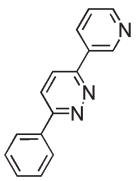
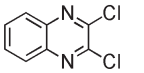
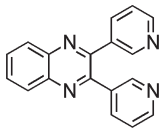
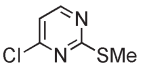
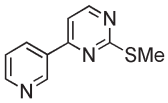
Using $Pd(OAc)_2$ as catalyst, we have developed the syntheses of various symmetrical dimers of π-deficient heterocyclic compounds. Reactions of aryl Grignard reagents catalyzed with $Fe(acac)_3$ provide a promising method to synthesize building blocks, with pyridine and diazine units, which already have a growing interest in supramolecular chemistry and material science. Further

Table 3

Cross-coupling Reactions of 3-Pyridylmagnesium Chloride with Heteroaryl Chlorides (Het–Cl)

Scheme 4



Entry	Het-Cl	Product	Compounds [Ref]	Yield Isolated
1			**11** [19c, 25]	47%
2			**12** [19c, 26]	39%
3			**13**	32%
4			**14** [27]	22%
5			**15** [28]	40%
6			**16** [29]	21%
7			**17** [30]	43%

work along those lines is currently in progress in our laboratory.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are not corrected. ^{1}H, and ^{13}C nmr spectra were recorded on a Bruker AC 300 (300 MHz ^{1}H, 75 MHz ^{13}C) instrument. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus. IR spectra were obtained as potassium bromide pellets with a Perkin-Elmer Paragon 500 spectrophotometer.

For Procedure A, shown below all compounds are known and were characterized by nmr and microanalyses or GC-MS. Mass spectra (MS) were recorded on an ATI-Unicam Automass apparatus.

General Procedure A for Palladium Catalyzed Homocoupling Reaction: Synthesis of Compounds **2a-2e**.

A mixture of diisopropylamine (1.4 ml, 8.0 mmol), palladium acetate (0.4 mmol), tetra-*n*-butylammonium bromide (8.0 mmol), and a solution of heteroaryl chloride (8.0 mmol) in toluene (1.5 ml) was stirred under nitrogen atmosphere. The mixture was refluxed and isopropanol (8.0 mmol) was added. The temperature was maintened at 105 °C for a period of 24 hours. After cooling at room temperature, water (5.0 ml) and diethylether (50 ml) were added. The organic phase was separated, washed with water and dried over magnesium sulfate. The solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel.

General Procedure B for an Iron-catalyzed Aryl-heteroaryl Coupling Reaction: Synthesis of Compounds **3-17**.

A mixture of heteroaryl chloride (1.82 mmol), Iron III acetycatonate complex $Fe(acac)_3$ (29 mg, 0.09 mmol) and THF (10 ml) was stirred under a dry nitrogen atmosphere and cooled to –30 °C. A solution of arylmagnesium bromide or 3-pyridylmagnesium chloride (4.20 mmol) in THF was added *via* a syringe. The resulting mixture was stirred for 10 minutes, then diluted with diethylether (10 ml) and quenched with brine. The aqueous layer was extracted with diethylether (3x20 ml). The combined organic extracts were dried over magnesium sulfate; then the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel.

O-Tolylpyrazine (**3**).

Cross-coupling reaction according to the Procedure B with *o*-tolylmagnesium bromide gave after purification by column chromatography using *n*-heptane/dichloromethane (1:1, v/v) as eluent 250 mg (81%) of **3** as a yellow oil; ^{1}H nmr (deuteriochloroform): δ 2.30 (s, 3H), 7.23 (m, 3H), 7.32 (d, J = 7.0 Hz, 1H), 8.40 (d, J = 2.4 Hz, 1H), 8.54 (s, 1H), 8.60 (s, 1H); ^{13}C nmr: δ 20.7, 126.6, 129.6, 130.2, 131.5, 136.7, 137.1, 142.8, 144.2, 145.5, 156.0; ms(EI): m/z 169 (M^+, 100).

Anal. Calcd. for $C_{11}H_{10}N_2$ (170.22): C, 77.62; H, 5.92, N, 16.46. Found: C, 77.60; H, 5.97; N, 16.39.

2-Methoxyphenylpyrazine (**4**).

Cross-coupling reaction according to the Procedure B with 2-methoxyphenylmagnesium bromide gave after purification by column chromatography using *n*-heptane/dichloromethane (1:1, v/v) as eluent 254 mg (75%) of **4** as a yellow oil; ^{1}H nmr (deuteriochloroform): δ 3.81 (s, 3H), 6.95 (d, J = 8.3 Hz, 1H), 7.05 (t, J = 7.55 Hz, 1H), 7.35 (t, J = 7.55 Hz, 1H), 7.73 (d, J = 7.55 Hz, 1H) , 8.38 (s, 1H), 8.57 (s, 1H), 9.07 (s, 1H); ^{13}C nmr δ 56.0, 111.7, 121.7, 126.1, 131.5, 131.6, 142.5, 144.5, 146.9, 152.3, 157.4; ms(EI): m/z 186 (M^+, 100).

Anal. Calcd. for $C_{11}H_{10}N_2O$ (186.21): C, 70.95; H, 5.41, N, 15.04. Found: C, 70.60; H, 5.79; N, 15.39.

4-Methoxyphenylpyrazine (**5**).

Cross-coupling reaction according the Procedure B with 4-methoxyphenylmagnesium bromide gave after purification by column chromatography using *n*-heptane:dichloromethane (1:1, v/v) as eluent 291 mg (86%) of **5** as a yellow solid, mp 86-87°; ^{1}H NMR (deuteriochloroform): δ 3.85 (s, 3H), 7.00 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 7.9 Hz, 2H), 8.42 (s, 1H), 8.56 (s, 1H), 8.69 (s, 1H); ms(EI): m/z 186 (M^+, 100).

Anal. Calcd. for $C_{11}H_{10}N_2O$ (186.21): C, 70.95; H, 5.41, N, 15.04. Found: C, 70.71; H, 5.65; N, 15.22.

4-Phenyl-1,1-dimethyl-3-oxo-1,3-dihyrofuro[3,4-*c*]pyridine (**6**).

Cross-coupling reaction according the Procedure B with phenylmagnesium bromide gave after purification by column chromatography using *n*-heptane/dichloromethane/ethyl acetate (4:5:1, v/v) as eluent 296 mg (68%) of **6** as a yellow solid, mp 149-150°; ^{1}H nmr (deuteriochloroform): δ 1.6 (s, 6H), 7.23 (d, J = 4.9 Hz, 1H), 7.41 (d, J = 3.4 Hz, 3H), 7.85 (d, J = 3.4 Hz, 2H), 8.79 (d, J = 4.9 Hz, 1H); ^{13}C nmr δ 27.4, 83.8, 114.7, 118.1, 128.4, 130.4, 130.5, 136.3, 153.4, 160.1, 165.4, 167.9; ms (EI): m/z 239 (M^+, 100).

Anal. Calcd. for $C_{15}H_{13}NO_2$ (239.27): C, 75.30; H, 5.48, N, 5.48. Found: C, 75.71; H, 5.51; N, 5.16.

2-Phenylpyrimidine (**7**) [21].

Cross-coupling reaction according the Procedure B with phenylmagnesium bromide gave after purification by column chromatography using eluent *n*-heptane/dichloromethane/ethyl acetate (4:5:1, v/v) as eluent 142 mg (50%) of **7** as a yellow solid, mp 75° (lit 73°); ^{1}H NMR (deuteriochloroform): δ 7.04 (t, J = 4.9 Hz, 1H), 7.40 (m, 3H), 8.35 (m, 2H), 8.67 (d, J = 4.9 Hz, 2H); ^{13}C NMR δ 119.0, 128.1, 128.5, 130.7, 137.5, 157.1, 164.7; ms(EI): m/z 156 (M^+, 100).

Anal. Calcd. for $C_{10}H_8N_2$ (156.18): C, 76.90; H, 5.16, N, 17.94. Found: C, 76.99; H, 5.12; N, 17.68.

2,3-Diphenylquinoxaline (**8**) [22].

Cross-coupling reaction according the Procedure B with phenylmagnesium bromide gave after purification by column chromatography using eluent *n*-heptane/isopropanol (98:2, v/v) as eluent 154 mg (38%) of **8** as a yellow solid, mp 124-125° (lit 124.5°); ^{1}H nmr (deuteriochloroform): δ 7.44-7.48 (m, 6H), 7.64 (dd, J = 7.2, 1.5 Hz, 4H), 7.88 (d, *J*= 6.4Hz, 2H), 8.31 (d, *J*=6.4Hz, 2H); ^{13}C nmr: δ 128.7, 129.2, 129.6, 130.2, 130.4, 139.4, 141.6; ms(EI): m/z 282 (M^+, 100).

Anal. Calcd. for $C_{20}H_{14}N_2$ (282.34): C, 85.08; H, 5.00, N, 9.92. Found: C, 85.33; H, 5.40; N, 9.56.

4,6-Diphenylpyrimidine (**9**) [23].

Cross-coupling reaction according the Procedure B with phenylmagnesium bromide gave after purification by column chromatography using eluent dichloromethane/ethyl acetate (95:5, v/v) as eluent 164 mg (39%) of **9** as a yellow solid, mp 100-101° (lit 99.5-101°); ^{1}H nmr (deuteriochloroform): δ 7.45 (m, 6H), 7.95 (s, 1H),

8.05 (m, 4H), 8.30 (s, 1H); ^{13}C nmr: δ 113.2, 127.6, 129.1, 131.5, 137.4, 159.6, 165.0; ms(EI): m/z 232 (M^+, 100).

Anal. Calcd. for $C_{20}H_{14}N_2$ (232.28): C, 82.73; H, 5.21, N, 12.06. Found: C, 82.76; H, 5.12; N, 12.12.

2,4-Diphenylpyrimidine (**10**) [24].

Cross-coupling reaction according the Procedure B with phenylmagnesium bromide gave after purification by column chromatography using dichloromethane as eluent 139 mg (39%) of **10** as a yellow solid, mp 64-65 °C (lit 65 °C); ^{1}H nmr (deuteriochloroform): δ 6.70 (dd, 1H), 7.15 (s, 1H), 7.40 (m, 4H), 7.45(d, 1H), 8.10 (dd, 2H), 8.50 (dd, 2H), 8.70 (d, 1H); ^{13}C nmr: δ 114.9, 127.6, 128.7, 129.0, 129.4, 131.2, 131.4, 137.3, 138.2, 158.3, 164.3, 165.0; ms (EI): m/z 232 (M^+, 100).

Anal. Calcd. for $C_{20}H_{14}N_2$ (232.28): C, 82.73; H, 5.21, N, 12.06. Found: C, 82.65; H, 5.35; N, 12.00.

3-Pyridylpyrazine (**11**) [19c,25].

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/methanol (90:10, v/v) as eluent 134 mg (47%) of **11** as a yellow solid, mp 93-94° (lit 92-94°); ^{1}H nmr (deuteriochloroform): δ 7.38 (dd, J = 7.9 Hz, 4.5Hz, 1H), 8.27 (dt, J = 7.9 Hz, 1.9 Hz, 1H), 8.51 (d, J = 1.5 Hz, 1H), 8.61 (d, J =1.5 Hz, 1H), 8.65 (dd, J =4.5 Hz, 1.9 Hz, 1H), 9.00 (s, 1H), 9.18 (d, J = 1.5 Hz, 1H); ^{13}C nmr: δ 124.2, 132.5, 134.7, 142.4, 144.1, 144.9, 148.5, 150.8, 151.2, ms(EI): m/z 157 (M^+, 100).

Anal. Calc for $C_9H_7N_3$ (157.17): C, 68.78; H, 4.49, N, 26.74. Found: C, 68.91; H, 4.32; N, 26.73.

2-(3-Pyridyl)pyrimidine (**12**) [19c,26].

Cross-coupling reaction according the procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/isopropanol (90:10, v/v) as eluent 112 mg (39%) of **12** as a colorless solid, mp 58° (lit 52°); ^{1}H nmr (deuteriochloroform): δ 7.19 (m, 1H), 7.36 (m, 1H), 8.63 (m, 2H), 8.76 (d, J = 4.5 Hz, 2H), 9.60 (s,1H); ^{13}C nmr: δ 120.2, 123.8, 133.5, 135.8, 150.2, 151.8, 157.8, 163.3; ms(EI): m/z MS (EI): 157 (M^+, 100).

Anal. Calcd. for $C_9H_7N_3$ (157.17): C, 68.78; H, 4.49, N, 26.74. Found: C, 68.71; H, 4.42; N, 26.65.

4-Methoxy-2-(3-pyridyl)pyrimidine (**13**).

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/dichloromethane (50:50, v/v) as eluent 109 mg (32%) of **13** as a colorless solid, mp 74°; ^{1}H NMR (deuteriochloroform): δ 4.05 (s, 3H), 6.83 (m, 1H), 7.14 (dd, J = 8.1, 4.5 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 8.47 (d, J = 4.5 Hz, 1H), 8.63 (s, 1H); ms(EI): m/z 177 (M^+, 100).

Anal. Calcd. for $C_{10}H_9N_3O$ (187.20): C, 64.16; H, 4.85, N, 22.45. Found: C, 64.18; H, 4.42; N, 22.26.

2,4-Di(3-pyridyl)pyrimidine (**14**) [27].

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/isopropanol (90:10, v/v) as eluent 91 mg (22%) of **14** as a yellow solid, mp 141-143°; ^{1}H nmr (deuteriochloroform): δ 7.50 (m, 2H), 7.74 (d, J = 5.3 Hz, 1H) 8.58 (d, J =7.9 Hz, 1H), 8.80 (m, 3H), 8.96 (d, J = 5.3 Hz, 1H), 9.42 (s, 1H), 9.82 (s, 1H); ms(EI): m/z 234 (M^+, 100).

Anal. Calcd. for $C_{14}H_{10}N_4$ (234.26): C, 71.78; H, 4.30, N, 23.92. Found: C, 71.64; H, 4.42; N, 23.92.

3-Phenyl-6-(3-pyridyl)pyridazine (**15**) [28].

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/isopropanol (90:10, v/v) as eluent 169 mg (40%) of **15** as a colorless solid, mp 189-190° (litt 190°); ^{1}H nmr (deuteriochloroform): δ 7.45 (m, 4H), 7.92 (m, 2H), 8.10 (m, 2H), 8.49 (d, J = 7.9 Hz, 1H), 8.68 (d, J = 4.9Hz, 1H), 9.23 (s, 1H); ^{13}C NMR: δ 90.4, 124.4, 124.6, 124.8, 127.4, 129.5, 130.8, 134.9, 148.4, 151.3

Anal. Calcd. for $C_{15}H_{11}N_3$ (233.27): C, 77.23; H, 4.75, N, 18.01 Found: C, 77.20; H, 4.77; N, 18.05.

2,3-Di(3-pyridyl)quinoxaline (**16**) [29].

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate:isopropanol (90:10, v/v) as eluent 109 mg (21%) of **16** as a colorless solid, mp 200 °C (dec.); ^{1}H nmr (deuteriochloroform): δ 7.34 (m, 2H), 7.44 (m, 2H), 8.40 (d, J = 7.9 Hz, 2H), 8.70 (d, J = 4.5 Hz, 2H), 9.01 (s, 2H), 9.30 (d, J = 1.5 Hz, 2H);

Anal. Calcd. for $C_{18}H_{12}N_4$ (284.11): C, 76.O4; H, 4.25, N, 19.71. Found: C, 76.40; H, 4.03; N, 19.57.

2-Methlythio-4-(3-pyridyl)pyrimidine (**17**) [30].

Cross-coupling reaction according the Procedure B with 3-pyridylmagnesium chloride gave after purification by column chromatography using ethyl acetate/isopropanol (90:10, v/v) as eluent 159 mg (43%) of **17** as a yellow solid, mp 94-95°; ^{1}H NMR (deuteriochloroform): δ 2.56 (s, 3H), 7.37 (m, 2H), 8.32 (d, J = 7.9 Hz, 1H), 8.52 (d, J =5.3 Hz, 1H), 8.65 (d, J = 3.8 Hz, 1H), 9.20 (s, 1H); ^{13}C nmr: δ 14.6, 112.2, 124.1, 132.4, 135.0, 148.8, 152.1, 158.3, 161.9, 173.7; ms (EI): m/z 203 (M^+, 100).

Anal. Calcd. for $C_{10}H_9N_3S$ (203.26): C, 59.09; H, 4.46, N, 20.67 Found: C, 59.57; H, 4.67; N, 20.38.

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