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# Arylation of Substituted Anilines Catalyzed by Palladium

**G. A. Artamkina[1], A. R. Petrov[1], O. V. Serushkina[2], M. D. Dutov[2], S. A. Shevelev[2], and I. P. Beletskaya[1]**

[1]*Moscow State University, Moscow, 119992 Russia*
[2]*Zelinsky Institute of Organic Chemistry, Moscow, Russia*

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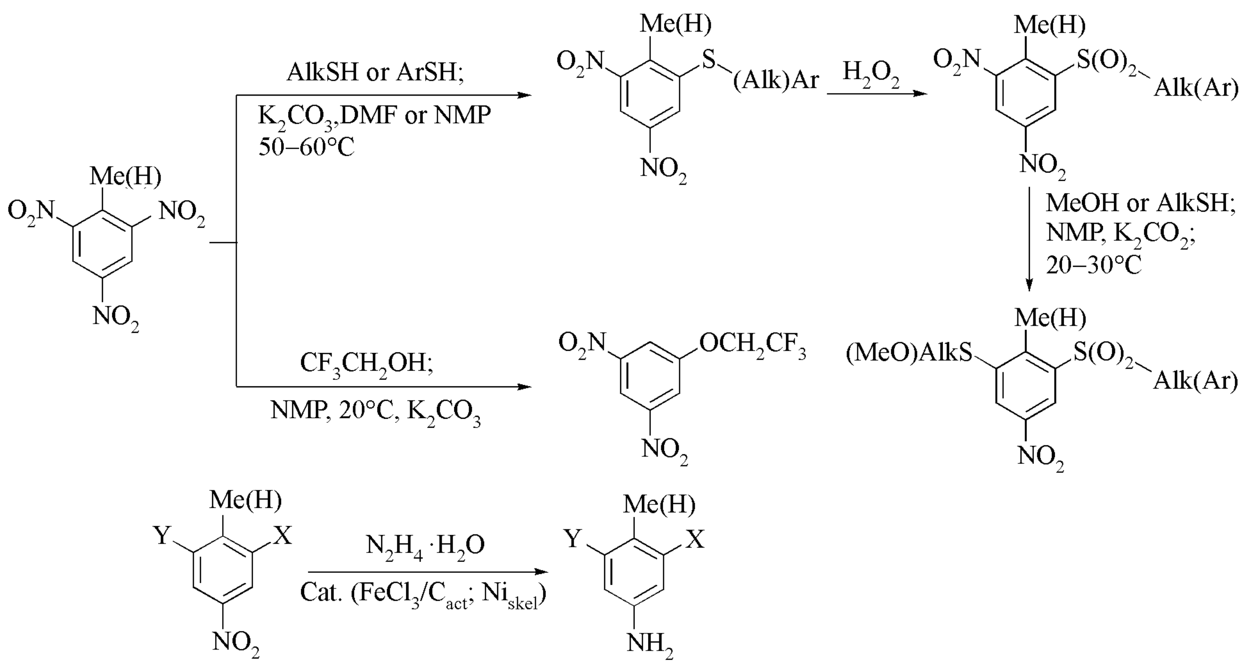
**Abstract**—Arylation catalyzed by palladium complexes of substituted anilines obtained by modification of 2,4,6-trinitrotoluene makes possible preparation of various diaryl- and arylheterylamines in high yields.

This work was carried out in keeping with the program on chemical conversion of an explosive, 2,4,6-trinitrotoluene (trotyl), aimed at transformation the latter and the products of its primary modification (in particular, of 1,3,5-trinitrobenzene) into available chemical raw materials fit for versatile applications [1–3]. The suggestion formerly advanced for solution of this problem consisted in substitution of the nitro group. Using reactions of nucleophilic substitution and reduction of nitro groups procedures were developed for preparation of functionalized aromatic amines. Due to low basicity the latter do not react with nonactivated aryl halides.

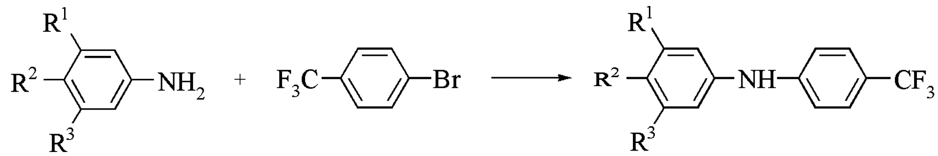



The target of this study was investigation of the possibility to arylate these anilines with various aryl and hetaryl halides under conditions of catalysis with metal complexes. According to PASS program [7] it is forecasted that diaryl- and hetarylamines which would be obtained should possess a wide range of biological activity.

Anilines are known to undergo arylation in Pd-catalyzed reactions easier than aliphatic primary amines [8–14]. However no systematic research was carried out concerning arylation of substituted anilines under catalysis, therefore it was difficult to predict beforehand the result of reaction with anilines obtained from 2,4,6-trinitrotoluene which contained sufficiently strong electron-withdrawing groups reducing the basicity.

## REACTIONS OF ANILINES WITH ARYL HALIDES

The most efficient and accessible ligand used in anilines arylation was 2,2'-bis(diphenylphosphino)-diphenyl ether (DPE-phos) [8]. therefore we started investigating the reactions applying the system $Pd(OAc)_2$/DPE-phos. Toluene was commonly used as solvent save some cases where dioxane was applied to increase the solubility of reagents or reaction products. Preliminary experiments showed that anilines in question are sensitive to the treatment with *t*-BuONa, therefore we used as base $Cs_2CO_3$. Under the chosen conditions anilines **I**–**V** were successfully involved into N-arylation (Table 1).




**I**–**V** 74–87%

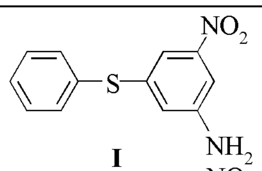
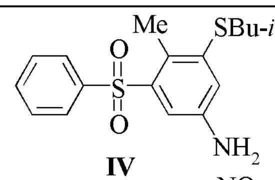
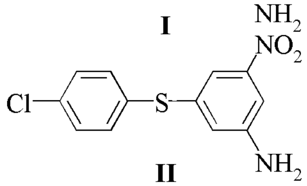
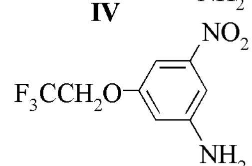
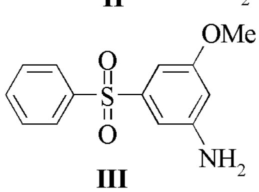
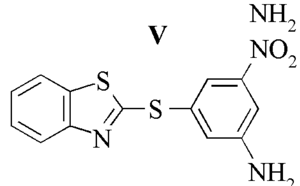
**I**, $R^1$ = PhS, $R^2$ = H, $R^3$ = $NO_2$; **II**, $R^1$ = *p*-$ClC_6H_4S$, $R^2$ = H, $R^3$ = $NO_2$; **III**, $R^1$ = $PhS(O)_2$, $R^2$ = H, $R^3$ = OMe; **IV**, $R^1$ = $PhS(O)_2$, $R^2$ = Me, $R^3$ = SBu-*i*; **V**, $R^1$ = $F_3CCH_2O$, $R^2$ = H, $R^3$ = $NO_2$.

The reactions proceed fast , as a rule within 2 h, yields of arylation products reach 74–87%.

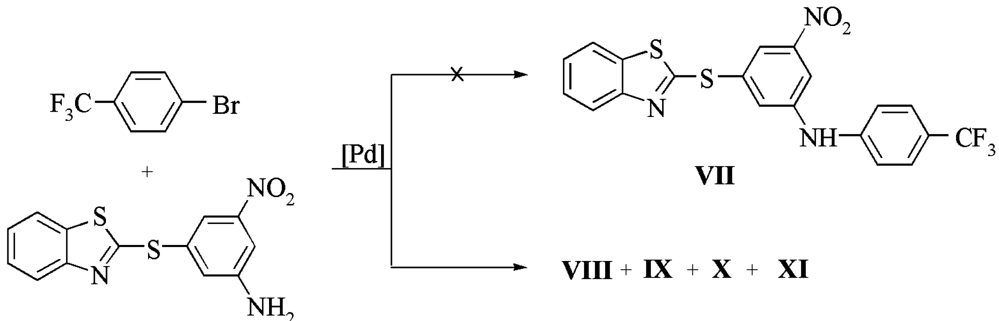
With aniline **VI** containing 2-benzothiazolylthio group the reaction was accompanied by strong tarring (Table 1). After workup of the reaction mixtures compounds **VIII**–**IX** were isolated in small amounts. The substances were identified by mass spectrometry and $^1H$ NMR spectroscopy. The expected product of aniline **VI** arylation was lacking.

It should be noted that this reaction occurred with a cleavage of the $C_{benzothiazole}$–S bond, namely, compound **VI** attacked the arylpalladium complex not by the amino group but by sulfur atom that resulted in compound **VIII** (main product) and probably in palladium complex **XII**.

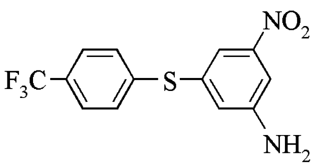
**Table 1.** Arylation of anilines **I**–**VI** with *p*-bromobenzotrifluoride in toluene in the presence of $Pd(OAc)_2$/DPE-phos[a]

| Anilines | Reaction time, h | Yield (conversion), % | Anilines | Reaction time, h | Yield (conversion), % |
|---|---|---|---|---|---|
|  **I** | 3 | 87 |  **IV** | 2 | 78 |
|  **II** | 2 | 83(90) |  **V** | 5.5 | 76(79) |
|  **III** | 2 | 74 |  **VI** | 6 | a |

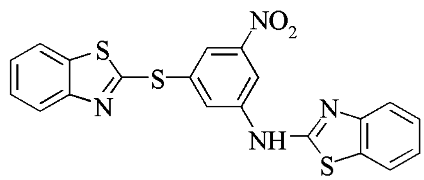
[a] Reaction products are described in the text.



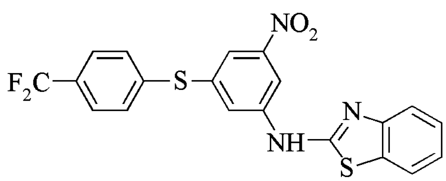

VI



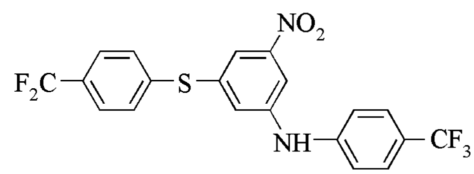
**VIII**, 8%



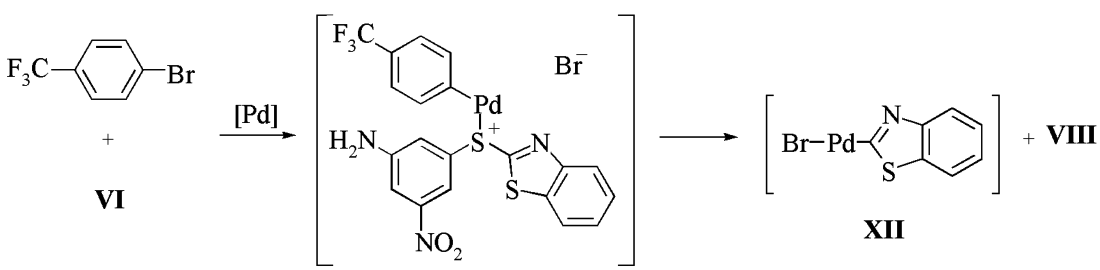
**IX**, 1.4%



**X**, 2.5%



**XI**, 1.7%



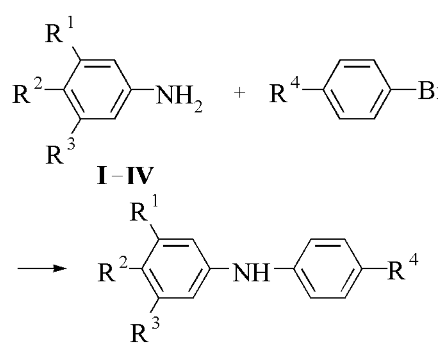

The arylation of sulfur-containing compounds catalyzed by palladium was described [15].

The formation of sulfides **IX** and **X** may be ascribed to reaction of complex **XII** with anilines **VI** and **VIII**. Product **XI** originates from the catalytic N-arylation of aniline **VIII** with *p*-bromobenzotrifluoride.

Note that aniline **VI** does not react with the *p*-bromobenzotrifluoride in the absence of catalyst.

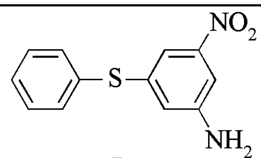
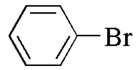
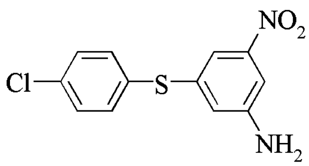
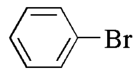
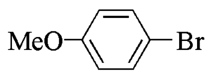
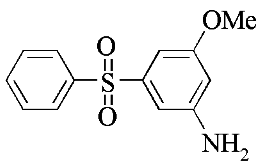
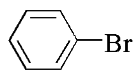
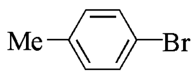
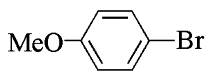
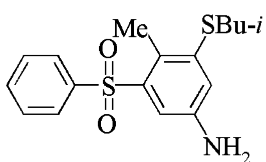
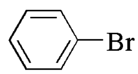
The problem of anilines arylation with nonactivated aryl bromides turned out to be somewhat more difficult (Table 2).

Thus the attempt to use DPE-phos in aniline **I** arylation with bromobenzene failed (Table 2, run no. *1*). Within 9 h conversion was less than 10%. The reaction in the presence of modified DPE-phos, 2,2'-bis(diisopropylphosphino)diphenyl oxide, (Table 2, run no. **2**) was also unsuccessful: The conversion attained within 30 h was only 22%. The best result was obtained in reaction in the presence of




$R^4$ = H, Me, OMe.

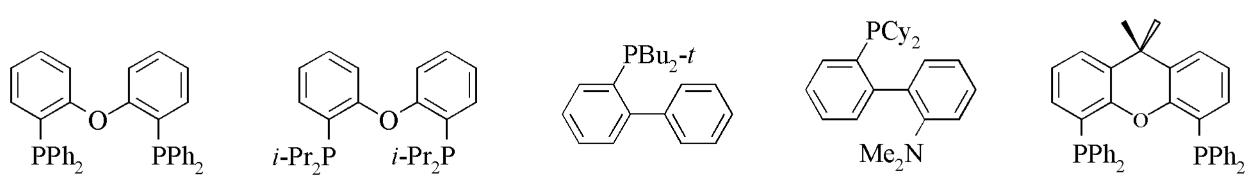
**Table 2.** Arylation of anilines with nonactivated aryl bromides

| Run no. | Anilines | Aryl bromide | Ligand | Reaction time, h | Yield (conversion), % |
|---|---|---|---|---|---|
| *1* |  **I** |  | DPE-phos | 9 | < 10 |
| *2* |  **II** |  | *i*-Pr-DPE-phos | 30 | 22(71 |
| *3* | | | $Me_2N$-Dp-$PCy_2$ | 6.5 | 66(76) |
| *4* | | | Xantphos | 7.5 | 87 |
| *5* | |  | $Me_2N$-Dp-$PCy_2$ | 3 | 81(94) |
| *6* |  **III** |  | $Me_2N$-Dp-$PCy_2$ | 6 | 68(81) |
| *7* | | | DPE-phos | 15.5 | 68(81) |
| *8* | |  | $Me_2N$-Dp-$PCy_2$ | 10 | 90[a] |
| *9* | |  | $Me_2N$-Dp-$PCy_2$ | 2 | 89(95) |
| *10* |  **IV** |  | $Me_2N$-Dp-$PCy_2$ | 6 | 82.6(96) |

[a] In the presence of $Pd_2(dba)_3$ (1 mol%) and $Me_2N$-DP-$PCy_2$ (1.5 mol%) in 3 h conversion was 25%.

($Me_2N$-DP-$PCy_2$): 2-dicyclohexylphosphino-2'-dimethylaminobiphenyl (66%, 6.5 h) (Table 2, run no. 3).

Arylation of anilines **III** and **IV** in the presence of ligand $Me_2N$-DP-$PCy_2$ occurs almost quantitatively within the same time (Table 2, runs nos. *6* and *10*). Presumably the higher products yield is due to the higher basicity of anilines **III** and **IV** compared to that of anilines **I** and **II**. Actually, aniline **III** is arylated with bromobenzene even in the presence of DPE-phos (Table2, cf. run no. *7* and runs nos. *1* and **2**). It should be noted that all arylation reactions at the use of bromobenzene occurred with strong deceleration during the course of the reaction; for instance, in reaction of aniline **II** with bromobenzene (Table 2, run no. *3*) already in 0.5 h after the start of the run the conversion was ~50%, and in 6.5 h it was 76%.



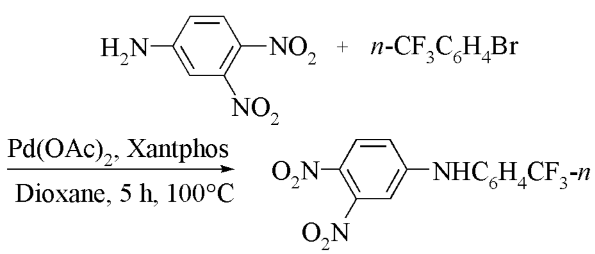
DPE-phos   *i*-Pr-DPE-phos   *t*-$Bu_2$-DP-phos   $Me_2N$-DP-$PCy_2$   Xantphos

Same as in the other catalyzed reactions *p*-bromotoluene is less reactive than bromobenzene (Table 2, run no. *8*). Curiously, but still more deactivated aryl bromide, *p*-bromoanisole, turned out to be more reactive than bromobenzene or *p*-bromotoluene (Table 2, runs nos. *5*, *9*).

The ligand effect is even more evident in arylation of such low-basic aniline as 2,4-dinitroaniline. Even in reaction with an activated substrate, *p*-benzotrifluoride, the system $Pd(OAc)_2/Me_2N$-DP-$PCy_2$ was not sufficiently effective. The conversion within 5 h was 19%, and yield of the target product was therewith 9%. The replacement of the solvent by dioxane did not affect the reaction.

In arylation of amines with strongly reduced electron density on the nitrogen, e.g., amides, sulfonamides, and urea, was successfully applied such phosphine as Xantphos [16, 17]. It was used in arylation with nonactivated aryl bromides of *p*- and *o*-anisidines and *m*-toluidine [11, 13].

It turned out that Xantphos was an efficient ligand for arylation of 2,4-dinitroaniline: A conversion of 95% was attained within 3 h, and the product was isolated in 91% yield.

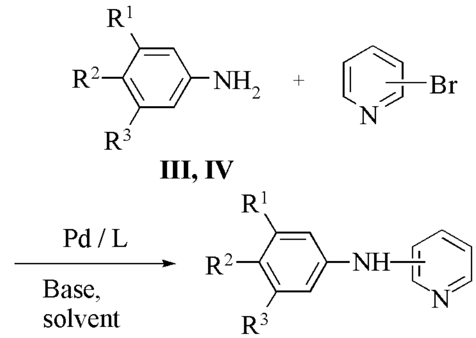



Aniline **II** was also successfully arylated with bromobenzene in the presence of Xantphos. The reaction product was isolated in 87% yield (Table 2, run no. *4*).

## ARYLATION OF ANILINES WITH HETARYL HALIDES

The arylation with hetaryl halides was studied mainly by an example of aniline **III** and to lesser extent on anilines **IV** and **V** (Tables 3, 4).

It turned out that the arylation of anilines **III** and **IV** in the presence of $Me_2N$-DP-$PCy_2$ required a long time, three and two days respectively (Table 3, runs nos. 1 and 10). In contrast to reaction with bromobenzene no significant deceleration in the course of the process was observed, and although the reaction occurred slowly, the yields of products were sufficiently high. Approximately the same pattern was observed in reaction of aniline **III** in the presence of a ligand *t*-$Bu_3P$ (Table 3, run no. *2*). Still less efficient was application of a ligand *t*-$Bu_2$-DP-phos (Table 3, run no. *3*).



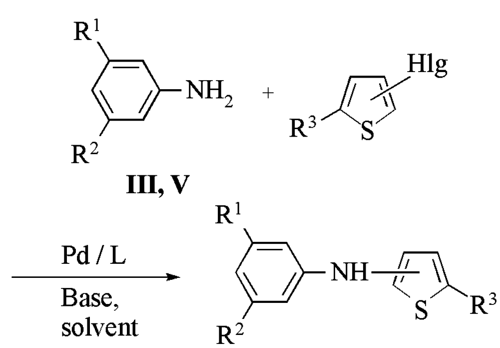

**III**, $R^1$ = $PhS(O)_2$, $R^2$ = H, $R^3$ = MeO; **IV**, $R^1$ = $PhS(O)_2$, $R^2$ = Me, $R^3$ = SBu-*i*.

Low aniline arylation rates with 3-bromopyridine are likely caused by its ability to saturate the palladium coordination sphere and/or by replacement of phosphine in the complex.

As in the case of aryl bromides, Xantphos was the most efficient ligand. For instance, in its presence the reaction of amine **III** with 3-bromopyridine occurs in 2 h with conversion of 89% (Table 3, run no. *4*). The efficiency of Xantphos was also demonstrated on reaction of aniline **III** with 3-bromoquinoline (Table 3, run no. *5*). The process took 1.5 h, and the product was isolated in a quantitative yield.

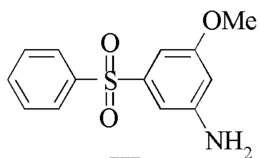
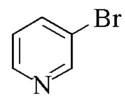
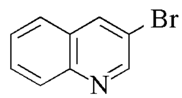
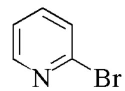
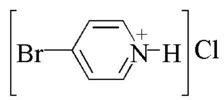
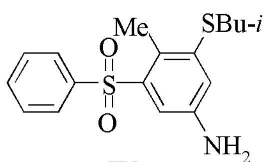
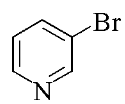
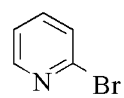
In anilines **III** and **IV** arylation with the more reactive α-bromopyridine the ligand $Me_2N$–DP–$PCy_2$ also turned out to be sufficiently effective (Table 3, runs nos. 6, 11), but the use of Xantphos provided higher yield of the product (80%) and significantly reduced the reaction time (Table 3, run no. *7*).

The diarylamine was obtained in high yield from aniline **III** and 4-bromopyridine hydrochloride; therewith the yields in toluene and dioxane were almost identical (Table 3, runs nos. *8*, *9*), but the process in dioxane was more convenient because of better solubility of reagents and products.



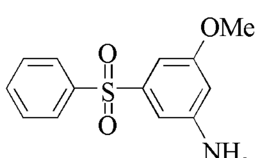
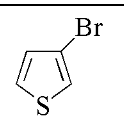
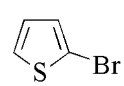
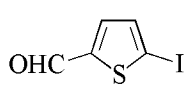
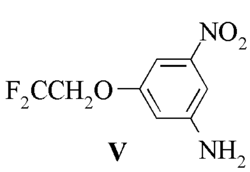
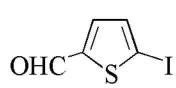

**III**, $R^1$ = $PhS(O)_2$, $R^2$ = MeO; **V**, $R^1$ = $F_3CCH_2O$, $R^2$ = $NO_2$, $R^3$ = H, CHO.

**Table 3.** Anilines arylation with pyridyl bromides and 3-bromoquinoline

| Run no. | Anilines | Hetaryl bromide | Ligand | Reaction time, h | Yield (conversion), % |
|---|---|---|---|---|---|
| *1* |  III |  | $Me_2N$-Dp-$PCy_2$ | 72 | 63(66) |
| *2* | | | | 25 | 46.5(52) |
| *3* | | | *i*-Pr-DPE-phos | 24 | (< 20) |
| *4* | | | Xantphos | 2 | 82(89) |
| *5* | |  | Xantphos | 1.5 | 97 |
| *6* | |  | $Me_2N$-Dp-$PCy_2$ | 9 | 60(81)[a] |
| *7* | | | Xantphos | 4 | 80(96) |
| *8* | |  | Xantphos | 25[b] | 89 |
| *9* | | | Xantphos | 20[b] | 86[c] |
| *10* |  IV |  | $Me_2N$-Dp-$PCy_2$ | 45 | 76(83) |
| *11* | |  | $Me_2N$-Dp-$PCy_2$ | 6 | 73(92) |

[a] 0.015 mmol (3 mol%) of $Pd(OAc)_2$ was used.
[b] Reaction time was not minimized for the moment of reaction completion was difficult to determine.
[c] Reaction in dioxane.

**Table 4.** Anilines arylation with thienyl halides

| Run no. | Anilines | Thiophenyl halides | Ligand | Reaction time, h | Yield (conversion), %[a] |
|---|---|---|---|---|---|
| *1* |  III |  | $Me_2N$-Dp-$PCy_2$ | 6 h | (40) |
| *2* | | | *t*-Pr-DPE-phos | 6 h | (29) |
| *3* | | | Xantphos | 8 h | 53(65) |
| *4* | |  | Xantphos | 11 h | (94) |
| *5* | |  | Xantphos | 2- m | 90in |
| *6* |  | | DPE-phos | 1.5 h | 57(74) |
| *7* | |  | Xantphos | 1.5 h | 85(90) |

[a] The conversion was determined by GLC.

We also studied anilines **III** and **V** arylation with haloderivatives of thiophene: 2- and 3-bromothiophenes and 2-iodo-5-formylthiophene (Table 4).

The application of ligands $Me_2N$-DP-$PCy_2$ and *t*-$Bu_2$-DP-phos in reaction of aniline **III** with 3-bromothiophene as with 3-bromopyridine (Table 3, run no. 1) was inefficient (Table 4, runs nos. *1* and *2*); according to GLC data within 6 h the conversion was 40 and 29% respectively. The yield of the product considerably increased in the presence of Xantphos (Table 4, run no. *3*), although the effect of Xantphos on this reaction was not so crucial as with 3-bromopyridine (Table 3, run no. *4*). The pattern of this reaction reminds that of the process with bromobenzene: the reaction starts with a high rate, the conversion is 58% in 2 h, but then the rate decreases, and after 5 h the conversion no longer grows. The yield of product after 8 h is 53% at conversion of the initial compound of 65%.

Although the 2-bromothiophene shows high activity at nucleophilic substitution its reaction with aniline **III** is relatively slow but without notable deceleration. According to GLC the reaction completed within 11 h (Table 4, run no. 4). To our regret the product was unstable under the reaction conditions, and we failed to isolate it in a pure state. Arylation of aniline **III** with 2-iodo-5-formylthiophene in the presence of Xantphos due to the presence of an electron-withdrawing group proceeded very fast (20 min) and afforded the product in 90% yield (Table 4, run no. 5). Also in the reaction of this substrate with aniline **V** the product was obtained in 85% yield, although the reaction rate was a little slower, apparently because of lower basicity of aniline **V** (Table 4, run no. 7). Note that the use as ligand in the latter reaction of DPE-phos gave less satisfactory results (57%) (Table 4, run no. *6*).

It should be pointed out that only few examples are known of anilines arylation with hetaryl bromides. For instance, the reaction between 3-bromothiophene and *p*-cyclohexylaniline gave rise to a mixture of products originating from mono- and diarylation in 4/1 ratio [$Pd(OAc)_2$/*t*-$Bu_3P$–*t*-BuONa) [18]. Far better result (98%) was obtained in aniline arylation with 2-methoxycarbonyl-3-bromothiophene (36 h) although relatively large amounts of catalyst and ligand were required [5 mol% $Pd_2(dba)_3$–$CHCl_3$, 10 mol% BINAP] [19].

## EXPERIMENTAL

$^1$H NMR spectra were registered on spectrometer Varian VXR-400 (400 MHz) using residual protons of the deuterated solvent as internal reference.

Mass spectra were measured on Kratos MS-30 instrument (electron impact, 70 eV).

GLC analysis was carried out on a chromatograph Agat-9 equipped with a flame-ionization detector, column $3000 \times 3$ mm, stationary phase OV-17 (5%) on Inerton Super, 0.160–0.200 mm (Chemapol), carrier gas nitrogen, flow rate 10–15 ml $min^{-1}$. The conversion in the course of reaction was estimated with the use of an internal reference (naphthalene or *p*-di*tert*-butylbenzene).

The preparative column chromatography was performed on silica gel Fluka 40-65.

The solvents (toluene and dioxane) were purified by standard procedures [20]; dioxane was stored in a vacuum over benzophenone ketyl. Cesium carbonate was dried by heating to 180–200°C in a vacuum ($2.6 \times 10^{-4}$ mm Hg) for 2–3 h.

**General procedure for anilines arylation.** Into a Schlenk vessel was charged anhydrous $Cs_2CO_3$ (2 equiv). The vessel was evacuated and heated for 15–20 min to 180–200°C to remove the residual water from $Cs_2CO_3$. On cooling the reactor was filled with argon, and thereto was charged 2 mol% of $Pd(OAc)_2$, 3 mol% of ligand, 0.5 mmol (1 equiv) of aniline, the reference for GLC analysis, 0.5–0.6 mmol (1–1.2 equiv) of aryl(hetaryl) halide in 2 ml of anhydrous toluene. The reaction mixture was evacuated to remove air, and the reactor was filled with argon. The reaction was carried out at 110°C and at continuous stirring. The reaction progress was monitored by TLC on Silufol UV-254 plates and/or by GLC. On completion of the process the reaction mixture was poured into a saturated KCl solution and extracted into dichloromethane in the case of diarylamines or into EtOAc in the case of arylhetarylamines. The solution was dried with molecular sieves Zeosorb 4Å and evaporated on a rotary evaporator with addition of silica gel (0.6–0.9 g). The products were isolated by preparative column chromatography. In some cases the products were additionally purified by reprecipitation from solution in dichloromethane with petroleum ether. To avoid separation of the product as oil the petroleum ether was added by portions. Reaction time is listed in tables.

### SYNTHESES OF DIARYLAMINES

**3-Nitro-*N*-[4-(trifluoromethyl)phenyl]-5-(phenylthio)aniline**. From 123.0 mg (0.50 mmol) of 3-nitro-5-(phenylthio)aniline (I), 131.0 mg (0.58 mmol, 1.16 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.10 mg (0.015 mmol, 3 mol%) of DPE-phos, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 ml toluene was obtained 168.9 mg (87%) of product as orange fine crystals [eluent benzene, $R_f$ ($ArNH_2$) 0.29, $R_f$ ($Ar_2NH$) 0.54]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (2 ml), mp 140.5–141.5°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.28 d (2H, $CF_3C_6H_4$, *J* 8.9 Hz), 7.29 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.48–7.54 m [4H, $C_6H_3$, $C_6H_5$ (*m*, *p*)], 7.58–7.62 m [4H, $CF_3C_6H_4$, $C_6H_5$(*o*)], 7.80 t (1H, $C_6H_3$, *J* 2.2 Hz), 8.42 br.s (1H, NH). Found, %: C 58.63; H 3.42; N 6.90. $C_{19}H_{13}F_3N_2O_2S$. Calculated, %: C 58.46; H 3.36; N 7.18.

**3-Nitro-N-[4-(trifluoromethyl)phenyl]-5-[(4-chlorophenyl)thio]aniline**. From 140.2 mg (0.50 mmol) of 3-nitro-5-[(4-chlorophenyl)thio]aniline (**II**), 135.0 mg (0.60 mmol, 1.20 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.50 mg (0.016 mmol, 3 mol%) of DPE-phos, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 176 mg (83%) of product as orange powder [eluent benzene, $R_f$ ($ArNH_2$) 0.23, $R_f$ ($Ar_2NH$) 0.53], mp 110–111°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.28 d (2H, $CF_3C_6H_4$, *J* 9.0 Hz), 7.30 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.52 d (2H, $ClC_6H_4$, *J* 8.6 Hz), 7.56 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.58 d (2H, $ClC_6H_4$, *J* 8.6 Hz), 7.60 d (2H, $CF_3C_6H_4$, *J* 9.0 Hz), 7.81 t (1H, $C_6H_3$, *J* 2.2 Hz), 8.42 br.s (1H, NH). Found, %: C 54.08; H 3.01; N 6.39. $C_{19}H_{12}ClF_3N_2O_2S$. Calculated, %: C 53.72; H 2.85; N 6.59.

**3-Methoxy-*N*-[4-(trifluoromethyl)phenyl]-5-(phenylsulfonyl)aniline**. From 130.7 mg (0.49 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 115.0 mg (0.51 mmol, 1.00 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.55 mg (0.016 mmol, 3 mol%) of DPE-phos, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 151.2 mg (74%) of product as colorless crystalline powder [eluent EtOAc–petroleum ether (1 : 1), $R_f$ ($ArNH_2$) 0.24, $R_f$ ($Ar_2NH$) 0.42]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (5 ml), mp 147.9–148.1°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.85 s (3H, $CH_3$), 6.98 t (1H, $C_6H_3$, *J* 2 Hz), 7.07 t (1H, $C_6H_3$, *J* 2 Hz), 7.29 d (2H, $CF_3C_6H_4$, *J* 8.4 Hz), 7.34 t (1H, $C_6H_3$, *J* 2 Hz), 7.60 d (2H, $CF_3C_6H_4$, *J* 8.4 Hz), 7.63–7.72 m [3H, $PhS(O)_2$], 8.01 m [2H, $PhS(O)_2$], 8.28 br.s (1H, NH). Found, %: C 58.55; H 3.56; N 3.10. $C_{20}H_{16}F_3NO_3S$. Calculated, %: C 58.97; H 3.93; N 3.44.

**3-Isobutylthio-4-methyl-N-[4-(trifluoromethyl)-phenyl]-5-(phenylsulfonyl)aniline**. From 167.5 mg (0.50 mmol) of 3-(isobutylthio)-4-methyl-5-(phenylsulfonyl)aniline (**IV**), 115.0 mg (0.51 mmol, 1.05 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.10 mg (0.015 mmol, 3 mol%) of DPE-phos, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml toluene was obtained 186.7 mg (78%) of product as colorless needle crystals [eluent $CH_2Cl_2$–petroleum ether (7:1), $R_f$ ($ArNH_2$) 0.16, $R_f$ ($Ar_2NH$) 0.50]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (6 ml), mp 135.0°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 1.01 d [6H, $(CH_3)_2CH$, *J* 6.7 Hz], 1.87 m [1H, $(CH_3)_2C\mathbf{H}$], 2.38 s (3H, $CH_3Ar$), 2.83 d (2H, $CHCH_2S$, *J* 6.7 Hz), 7.30 d (2H, $CF_3C_6H_4$, *J* 8.6 Hz), 7.42 d (1H, $C_6H_2$, *J* 2.4 Hz), 7.61 d (2H, $CF_3C_6H_4$, *J* 8.6 Hz), 7.61–7.73 m [3H, $PhS(O)_2$], 7.87 d (1H, $C_6H_2$, *J* 2.4 Hz), 7.90–7.94 m [2H, $PhS(O)_2$], 8.25 br.s (1H, NH). Found, %: C 60.50; H 5.09; N 3.20. $C_{24}H_{24}F_3NO_2S_2$. Calculated, %: C 60.13; H 5.01; N 2.92.

**3-Nitro-N-[4-(trifluoromethyl)phenyl]-5-(2,2,2-trifluoroethoxy)aniline**. From 118.0 mg (0.50 mmol) of 3-nitro-5-(2,2,2-trifluoroethoxy)aniline (**V**), 115.0 mg (0.50 mmol, 1.00 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.10 mg (0.015 mmol, 3 mol%) of DPE-phos, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 145 mg (76%) of product as yellow powder [eluent benzene, $R_f$ ($ArNH_2$) 0.17, $R_f$ ($Ar_2NH$) 0.50], mp 107–108°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 4.85 q (2H, $CF_3CH_2O$, *J* 8.5 Hz), 7.27 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.39 d (2H, $CF_3C_6H_4$, *J* 8.6 Hz), 7.44 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.64 d (2H, $CF_3C_6H_4$, *J* 8.6 Hz), 7.70 t (1H, $C_6H_3$, *J* 2.0 Hz), 8.45 br.s (1H, NH). Found, %: C 47.50; H 2.75; N 7.31. $C_{15}H_{10}O_3N_2F_6$. Calculated, %: C 47.37; H 2.63; N 7.37.

**Reaction of 3-(2-benzothiazolylthio)-5-nitroaniline with *p*-bromobenzotrifluoride.** We used 150.0 mg (0.50 mmol ) of 3-(2-benzothiazolylthio)-5-nitroaniline (**VI**), 113.0 mg (0.50 mmol, 1.00 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.10 mg (0.015 mmol, 3 mol%) of DPE-phos, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene. Chromatographic separation [eluent benzene, $R_f$ (aniline) 0.05, $R_f$ (**XI**) 0.50, $R_f$ (**VIII**) 0.23, $R_f$ (**X**) 0.14, $R_f$ (**IX**) 0.00]. Product **IX** was eluted with a mixture EtOAc–petroleum ether (1 : 3) with subsequent addition of acetone. Yields of products were as follows:

**VIII**, 18%; **IX**, 1.4%; **X**, 2.5%; **XI**, 1.7%. The compounds were powders of orange, bright yellow, yellow, and lemon-yellow color respectively. Compound **IX** was purified further by recrystallization from a mixture EtOAc–acetone.

**3-Nitro-5-[4-(trifluoromethyl)phenyl]thioaniline (VIII)**, mp 118–120°C. Mass spectrum, *m/z* ($I_{rel}$, %): 314 (100) [$M^+$], 268 (21) [$M^+$–$NO_2$], 267 (15) [$M^+$–$NO_2$–H], 248 (9.3) [$M^+$–$NO_2$–HF], 224 (7.9) [$M^+$–$NO_2$–CS], 199 (33) [$M^+$–$NO_2$–$CF_3$]. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 5.61 br.s (2H, NH), 7.12 t (1H, $C_6H_3$, *J* 1.8 Hz), 7.41 t (1H, $C_6H_3$, *J* 1.8 Hz), 7.51 t (1H, $C_6H_3$, *J* 2 Hz), 7.55 d (2H, $CF_3C_6H_4S$, *J* 8.8 Hz), 7.71 d (2H, $CF_3C_6H_4S$, *J* 8.8 Hz). Found, %: C 50.05; H 2.79; N 9.10. $C_{13}H_9O_2F_3N_2S$. Calculated, %: C 49.68; H 2.87; N 8.92.

**[3-(2-Benzothiazolylthio)-5-nitrophenyl]-2-benzothiazolylamine (IX)**, mp > 220°C. Mass spectrum, *m/z* ($I_{rel}$, %): 436 [$M^+$]. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 7.23 t (1H, $C_7H_4NS$, *J* 7.6 Hz), 7.35 t (1H, $C_7H_4NS$, *J* 7.6 Hz), 7.43 t (1H, $C_7H_4NS$, *J* 7.6 Hz), 7.53 m (2H, $C_7H_4NS$ + $C_7H_4NS_2$), 7.87 d (1H, $C_7H_4NS$, *J* 8.0 Hz), 7.95 d (1H, $C_7H_4NS$, *J* 8.0 Hz), 8.04 d (1H, $C_7H_4NS$, *J* 8.0 Hz), 8.16 m (1H, $C_6H_3$), 8.47 m (1H, $C_6H_3$), 8.88 m (1H, $C_6H_3$), 11.25 br.s (1H, NH). Found, %: C 54.72; H 2.77; N 12.93. $C_{20}H_{12}O_2N_4S_3$. Calculated, %: C 55.05; H 2.75; N 12.84.

**[3-Nitro-5-{[4-(trifluoromethyl)phenyl]thio}-phenyl]-2-benzothiazolylamine (X)**, mp 189–191°C. Mass spectrum, *m/z* ($I_{rel}$, %): 447 (100) [$M^+$], 428 (3.6) [$M^+$–F], 417 (9.8) [$M^+$–NO], 401 (11) [$M^+$–$NO_2$], 400 (9.6) [$M^+$–$NO_2$–H], 256 (4.1) [$M^+$–$NO_2$–$F_3CC_6H_4$], 224 (62) [$M^+$–$NO_2$–$CF_3C_6H_4S$], 223 (17) [$M^+$–$NO_2$–H–$CF_3C_6H_4S$]. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.25 t (1H, $C_7H_4NS$, *J* 8.0 Hz), 7.40 t (1H, $C_7H_4NS$, *J* 8.0 Hz), 7.62 d (1H, $C_7H_4NS$, *J* 8.8 Hz), 7.72 d (2H, $CF_3C_6H_4$, *J* 8.5 Hz), 7.79 d (2H, $CF_3C_6H_4$, *J* 8.5 Hz), 7.80 d (1H, $C_7H_4NS$, *J* 8.8 Hz), 7.85 m (1H, $C_6H_3$), 8.31 m (1H, $C_6H_3$), 8.78 m (1H, $C_6H_3$). Found, %: C 54.02; H 2.62; N 9.37. $C_{20}H_{12}O_2F_3N_3S_2$. Calculated, %: C 53.70; H 2.68; N 9.40.

**3-Nitro-*N*-[4-(trifluoromethyl)phenyl]-5-{[4-(trifluoromethyl)phenyl]thio}aniline (XI)**, mp 98–100°C. Mass spectrum, *m/z* ($I_{rel}$, %): 458 (100) [$M^+$], 439 (6.3) [$M^+$–F], 412 (7.5) [$M^+$–$NO_2$], 343 (8.5) [$M^+$–$NO_2$–$CF_3$], 342 (4.5) [$M^+$–$NO_2$–$CF_3$–H], 252 (7.6) [$M^+$–$NO_2$–$CF_3C_6H_4NH$], 235 (39) [$M^+$–$NO_2$–$CF_3C_6H_4S$]. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.31 d (2H, $CF_3C_6H_4NH$, *J* 9.1 Hz), 7.48 m (1H, $C_6H_3$), 7.60 d (2H, $CF_3C_6H_4NH$, *J* 9.1 Hz), 7.68 d (2H, $CF_3C_6H_4S$, *J* 8.8 Hz), 7.72 m (1H, $C_6H_3$), 7.77 d (2H, $CF_3C_6H_4S$, *J* 8.8 Hz), 7.92 m (1H, $C_6H_3$), 8.50 br.s (1H, NH). Found, %: C 53.58; H 2.97; N 5.12. $C_{20}H_{12}O_2F_6N_2S$. Calculated, %: C 53.40; H 2.62; N 6.11.

**2,4-Dinitro-*N*-4-(trifluoromethyl)phenyl]aniline.** (a) From 91.3 mg (0.50 mmol) of 2,4-dinitroaniline, 115.0 mg (0.59 mmol, 1.00 equiv) of *p*-bromobenzotrifluoride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 14.7 mg (9%) of orange crystalline product. Reaction time 5 h [eluent EtOAc–petroleum ether (1 : 1), $R_f$ ($ArNH_2$) 0.44, $R_f$ ($Ar_2NH$) 0.88]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.5 ml) with petroleum ether (1 ml), mp 128.2–128.5°C.

(b) Reaction was carried out with the same amounts of reagents save as ligand was used Xantphos, 8.70 mg (0.015 mmol, 3 mol%), and as solvent dioxane (2 ml). We obtained 148.9 mg (91%) of product as orange needle crystals. Reaction time 5 h [eluent EtOAc–petroleum ether (1 : 1)]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (4.5 ml), mp 127.8–128.5°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.50 d (1H, $C_6H_3$, *J* 9.6 Hz), 7.73 d (2H, $CF_3C_6H_4$, *J* 8.5 Hz), 7.86 d (2H, $CF_3C_6H_4$, *J* 8.5 Hz), 8.33 d.d (1H, $C_6H_3$, *J* 9.6, 2.7 Hz), 9.04 d (1H, $C_6H_3$, *J* 2.7 Hz), 10.16 br.s (1H, NH). Found, %: C 47.92; H 2.74; N 12.90. $C_{13}H_8F_3N_3O_4$. Calculated, %: C 47.72; H 2.46; N 12.84.

**3-Nitro-N-phenyl-5-(phenylthio)aniline**. A mixture of 123.0 mg (0.50 mmol) of 3-nitro-5-(phenylthio)aniline (**I**), 78.5 mg (0.50 mmol, 1.00 equiv) of bromobenzene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.10 mg (0.015 mmol, 3 mol%) of DPE-phos, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was stirred at 110°C for 9 h. According to GLC data the conversion was ≤ 10%. The product was not isolated.

**3-Nitro-N-phenyl-5-[4-(chlorophenyl)thio]aniline**. (a) From 140.2 mg (0.50 mmol) of 3-nitro-5-[(4-chlorophenyl)thio]aniline (**II**), 78.5 mg (0.50 mmol, 1.00 equiv) of bromobenzene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 6.10 mg (0.015 mmol, 3 mol%) of *i*-Pr-DPE-phos, 326 mg (2 equiv) of

$Cs_2CO_3$, and 2 ml of toluene was obtained 40.0 mg (22%) of the product as orange powder [eluent benzene, $R_f$ ($ArNH_2$) 0.32, $R_f$ (Ar2NH) 0.50], mp 143–144°C.

(b) From the same reagents but taking as ligand $Me_2N$-DP-$PCy_2$, 5.90 mg (0.015 mmol, 3 mol%) we obtained 117.5 mg (66%) of product as orange fine crystals. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (3.5 ml).

(c) From the same reagents but taking as ligand Xantphos, 8.70 mg (0.015 mmol, 3 mol%) we obtained 155.0 mg (87%) of product. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1.5 ml) with petroleum ether (3.5 ml). $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 7.04 m (1H, Ph), 7.17 m (3H, $C_6H_3$, Ph), 7.32 m (2H, Ph), 7.43 m (1H, $C_6H_3$), 7.53 m (4H, $ClC_6H_4$), 7.70 m (1H, $C_6H_3$), 8.06 br.s (1H, NH). Found, %: C 60.23; H 3.44; N 7.83. $C_{18}H_{13}ClN_2O_2S$. Calculated, %: C 60.60; H 3.65; N 7.85.

**N-(4-Methoxyphenyl)-3-nitro-5-[4-(chlorophenyl)thio]aniline**. From 140.2 mg (0.50 mmol) of 3-nitro-5-[(4-chlorophenyl)thio]aniline (**II**), 93.8 mg (0.50 mmol, 1.00 equiv) of *p*-bromoanisole, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 155.7 mg (81%) of product as bright orange powder [eluent benzene, $R_f$ ($ArNH_2$) 0.44, $R_f$ ($Ar_2NH$) 0.60]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (7 ml), mp 120–121°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.80 s (3H, $CH_3$), 6.92 d (2H, $MeOC_6H_4$, *J* 9 Hz ), 7.03 m (1H, $C_6H_3$), 7.12 d (2H, $CH_3OC_6H_4$, *J* 9 Hz), 7.34 m (1H, $C_6H_3$), 7.48–7.54 m (5H, $ClC_6H_4$, $C_6H_3$), 7.78 br.s (1H, NH). Found, %: C 58.96; H 3.59; N 7.33. $C_{19}H_{15}ClN_2O_3S$. Calculated, %: C 59.00; H 3.88; N 7.24.

**3-Methoxy-N-phenyl-5-(phenylsulfonyl)aniline**. (a) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 78.5 mg (0.50 mmol, 1.00 equiv) of bromobenzene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 336 mg (2 equiv) of $Cs_2CO_3$,and 2 ml of toluene was obtained 154.7 mg (91%) of colorless crystalline powder [eluent EtOAc–petroleum ether (1 : 1), $R_f$ ($ArNH_2$) 0.19, $R_f$ ($Ar_2NH$) 0.41]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.9 ml) with petroleum ether (3 ml) mp 128–129°C.

(b) From the same reagents but taking as ligand DPE-phos, 8.10 mg (0.015 mmol, 3 mol%), was obtained 115.6 mg (68%) of product as colorless crystalline powder The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (5 ml), mp 128.5–129.0°C.

$^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.80 s (3H, $CH_3O$), 6.83 t (1H, $C_6H_3$, *J* 2.2 Hz), 6.93 d.t (1H, $C_6H_3$, *J* 2.2, 1.8 Hz), 6.99 t.t (1H, Ph, *J* 7.4, 1.1 Hz), 7.17 d.d (2H, Ph, *J* 8.5, 1.1 Hz), 7.25 t (1H, $C_6H_3$, *J* 1.8 Hz), 7.31 m (2H, Ph), 7.59–7.69 m [3H, $PhS(O)_2$], 7.84 br.s (1H, NH), 7.87–8.00 m [2H, $PhS(O)_2$]. Found, %: C 67.20; H 5.16; N 3.81. $C_{19}H_{17}NO_3S$. Calculated, %: C 67.26; H 5.01; N 4.31.

**3-Methoxy-N-(4-methylphenyl)-5-(phenylsulfonyl)aniline**. (a) From 130.7 mg (0.49 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 86.0 mg (0.50 mmol, 1.00 equiv) of *p*-bromotoluene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 170.2 mg (96%) of light-yellow oil [eluent EtOAc–petroleum ether (1:1), $R_f$ $ArNH_2$ 0.21, $R_f$ $Ar_2NH$ 0.38]. The light-yellow oil obtained was dissolved in $CH_2Cl_2$ (1.1 ml) and precipitated with petroleum ether (5 ml). We obtained a colorless powder of fine crystals, mp 109–110°C.

(b) The reagents were taken in the same amounts, but $Pd_2(dba)_3$ 5.20 mg (0.005 mmol, 1 mol%) was used. We obtained 66 mg (25%) of product. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 2.28 s (3H, $C_2H_3C_6H_4$), 3.79 s (3H, $CH_3O$), 6.76 m (1H, $C_6H_3$), 6.88 m (1H, $C_6H_3$), 7.06 d (2H, $CH_3C_6H_4$, *J* 8.3 Hz), 7.14 d (2H, $MeC_6H_4$, *J* 8.3 Hz), 7.19 m (1H, $C_6H_3$), 7.59–7.69 m [3H, $PhS(O)_2$], 7.69 br.s (1H, NH), 7.95–7.98 m [2H, $PhS(O)_2$]. Found, %: C 67.68; H 5.21; N 3.75. $C_{20}H_{19}NO_3S$. Calculated, %: C 67.98; H 5.38; N 3.97.

**3-Methoxy-*N*-(4-methoxyphenyl)-5-(phenylsulfonyl)aniline**. From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 93.7 mg (0.50 mmol, 1.00 equiv) of *p*-bromoanisole, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 164.8 mg (89%) of product as lightly colored powder of small crystals [eluent EtOAc–petroleum ether (1 : 1), $R_f$ ($ArNH_2$) 0.23, $R_f$ ($Ar_2NH$) 0.42]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1.1 ml) with petroleum ether (4 ml), mp 142–143°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.77 s (3H, $CH_3O$), 3.79 s (3H, $CH_3O$), 6.64 t (1H, $C_6H_3$, *J* 2.2 Hz), 6.83 t (1H, $C_6H_3$, *J* 1.9 Hz), 6.93 d (2H, $CH_3OC_6H_4$, *J* 8.9 Hz), 7.09 t (1H, $C_6H_3$, *J* 1.7 Hz), 7.12 d (2H, $CH_3OC_6H_4$, *J* 8.9 Hz), 7.54 br.s (1H, NH), 7.59–7.69 m [3H, $PhS(O)_2$], 7.94–7.97 m [2H, $PhS(O)_2$]. Found, %: C 64.92; H 5.07; N 3.70. $C_{20}H_{19}NO_4S$. Calculated, %: C 65.04; H 5.15; N 3.79.

**3-Isobutylthio-4-methyl-*N*-phenyl-5-(phenylsulfonyl)aniline**. From 167.5 mg (0.50 mmol) of 3-isobutylthio-4-methyl-5-(phenylsulfonyl)aniline (**IV**), 78.5 mg (0.50 mmol, 1.00 equiv) of bromobenzene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 170.2 mg (82.6%) of product as colorless needle crystals [eluent $CH_2Cl_2$–petroleum ether (7 : 1), $R_f$ ($ArNH_2$) 0.08, $R_f$ ($Ar_2NH$) 0.35]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.8 ml) with petroleum ether (2.5 ml), mp 133.0–133.5°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 1.00 d [6H, $(CH_3)_2CH$, *J* 6.7 Hz], 1.85 m [1H, $(CH_3)_2CH$], 2.35 s (3H, $CH_3C_6H_2$), 2.78 d (2H, $CHCH_2S$, *J* 6.7 Hz), 6.97 t (1H, Ph, *J* 7.4 Hz), 7.20 d (2H, Ph, *J* 8.1 Hz), 7.31 d (1H, $C_6H_2$, *J* 2.4 Hz), 7.33 m (2H, Ph), 7.61–7.72 m [3H, $PhS(O)_2$], 7.79 d (1H, $C_6H_2$, *J* 2.4 Hz), 7.82 br.s (1H, NH), 7.88–7.92 m [2H, $PhS(O)_2$]. Found, %: C 67.09; H 6.54; N 2.99. $C_{23}H_{25}NO_2S_2$. Calculated, %: C 67.15; H 6.08; N 3.41.

## PREPARATION OF ARYLHETARYLAMINES

**[3-Methoxy-5-(phenylsulfonyl)phenyl]-3-pyridylamine**. (a) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 95.0 mg (0.60 mmol, 1.20 equiv) of 3-bromopyridine, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 18.3 mg *p*-di-*tert*-butylbenzene, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 107 mg (63%) of product as colorless powder of small crystals [eluent EtOAc–petroleum ether (6 : 1), $R_f$ ($ArNH_2$) 0.55, $R_f$ (ArHetNH) 0.15]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.5 ml) with petroleum ether (1 ml), mp 138.0–138.5°C.

(b) The reaction was carried out with the same amounts of reagents but using as ligand *t*-$Bu_2$-DP-phos, 4.45 mg (0.015 mmol, 3 mol%), internal reference naphthalene, 23.4 mg. According to GLC the conversion of initial product was 18–20%. The reaction product was not isolated.

(c) The reaction was carried out with the same amounts of reagents but using as ligand *t*-$Bu_3P$, 3.06 mg (0.015 mmol, 3 mol%), internal reference naphthalene, 21.3 mg. We obtained 79 mg (46.5%) of product.

(d) The reaction was carried out with the same amounts of reagents but using as ligand Xantphos, 8.70 mg (0.015 mmol, 3 mol%), internal reference naphthalene, 20.9 mg. We obtained 136.3 mg (88%) of product. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.83 s (3H, $CH_3O$), 6.85 m (1H, $C_6H_3$), 6.98 m (1H, $C_6H_3$), 7.24 m (1H, $C_6H_3$), 7.30 d.d (1H, Py-3, *J* 8.3 Hz, 4.6 Hz), 7.58 d.m (1H, Py-3, *J* 8.3 Hz), 7.60–7.71 m [3H, $PhS(O)_2$], 7.97–8.02 m [3H, $PhS(O)_2$, NH], 8.20 d.d (1H, Py-3, *J* 4.6 Hz, 1.1 Hz), 8.43 d (1H, Py-3, *J* 2.5 Hz). Found, %: C 63.37; H 4.78; N 8.42. $C_{18}H_{16}N_2O_3S$. Calculated, %: C 63.51; H 4.74; N 8.23.

**[3-Methoxy-5-(phenylsulfonyl)phenyl]-2-pyridylamine**. (a) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 93.0 mg (0.62 mmol, 1.24 equiv) of 2-bromopyridine, 3.50 mg (0.016 mmol, 3 mol%) of $Pd(OAc)_2$, 8.70 mg (0.022 mmol, 4.4 mol%) of $Me_2N$-DP-$PCy_2$, 330 mg (2 equiv) $Cs_2CO_3$, and 2 ml of toluene was obtained 101.6 mg (60%) of product as colorless powder [eluent $CH_2Cl_2$–MeOH–EtOAc (50 : 1 : 1), $R_f$ ($ArNH_2$) 0.34, $R_f$ (ArHetNH) 0.20]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.5 ml) with petroleum ether (1.5 ml), mp 129–132°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.85 s (3H, $CH_3O$), 6.83 d.d (1H, Py-2, *J* 7.0, 5.5 Hz), 6.87 d (1H, Py-2, *J* 8.5 Hz), 7.02 m (1H, $C_6H_3$), 7.57– 7.69 m [4H, $PhS(O)_2$, Py-2], 7.83 m (1H, $C_6H_3$), 7.93 m (1H, $C_6H_3$), 7.98–8.01 m [2H, $PhS(O)_2$], 8.25 d.d (1H, Py-2, *J* 5.0, 1.5 Hz), 8.64 br.s (1H, NH).

(b) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 84.7 mg (0.53 mmol, 1.07 equiv) of 2-bromopyridine, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.70 mg (0.015 mmol, 3 mol%) of Xantphos, 200 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 136 mg (80%) of product. The conversion of the initial product 96%. Found, %: C 63.52; H 4.91; N 7.78; S 9.48. $C_{18}H_{16}N_2O_3S$. Calculated, %: C 63.51; H 4.74; N 8.23; S 9.41.

**[3-Methoxy-5-(phenylsulfonyl)phenyl)]-4-pyridylamine**. (a) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 116.6 mg (0.60 mmol, 1.20 equiv) of 4-bromopyridine hydrochloride, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.70 mg (0.015 mmol, 3 mol%) of Xantphos, 0.50 g (1.5 mmol, 3 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained by gradient elution through a small bed of silica gel (4 cm) 150.2 mg (88.7%) of product as colorless powder. As eluent was used a mixture petroleum ether–ethyl acetate (1 : 4). The initial aniline was isolated, and then the product was back-washed with acetone. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1.0 ml) with petroleum ether (1 ml), mp 169–170°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.87 s (3H, $CH_3O$), 7.00 m (2H, Py-4), 7.03 m (1H, $C_6H_3$), 7.13 m (1H, $C_6H_3$), 7.37 m (1H, $C_6H_3$), 7.61–7.72 m [3H, $PhS(O)_2$], 7.99– 8.02 m [2H, $PhS(O)_2$], 8.30 m (2H, Py-4), 8.34 br.s (1H, NH). Found, %: C 63.73; H 4.53; N 8.00. $C_{18}H_{16}N_2O_3S$.Calculated, %: C 63.51; H 4.74; N 8.23.

(b) The reaction was carried out with the same amounts of reagents but using dioxane (2 ml) as solvent. Yield of the product 146.4 mg (86%).

**[3-(Isobutylthio)-4-methyl-5-(phenyl sulfonyl)phenyl]-3-pyridylamine**. From 167.5 mg (0.50 mmol) of 3-(isobutylthio)-4-methyl-5-(phenylsulfonyl)aniline (**IV**), 80.0 mg (0.51 mmol, 1.01 equiv) of 3-bromopyridine, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 157.5 mg (76%) of product [eluent petroleum ether–ethyl acetate (1/6), $R_f$ ($ArNH_2$) 0.70, $R_f$ (ArHetNH) 0.36). The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (2.0 ml) with petroleum ether (7 ml), mp 162.5–163.0°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 1.01 d [6H, $(CH_3)_2CH$, $J$ 6.7 Hz], 1.86 m [1H, $(CH_3)_2CH$], 2.35 s (3H, $CH_3C_6H_2$), 2.80 d (2H, $CHCH_2S$, $J$ 6.7 Hz), 7.30 m (1H, Py-3), 7.32 m (1H, $C_6H_2$), 7.60 m (1H, $C_6H_2$), 7.61–7.73 m [3H, $PhS(O)_2$], 7.79 m (1H, Py-3), 7.89–7.92 m [2H, $PhS(O)_2$], 7.97 br.s (1H, NH), 8.18 d.d (1H, Py-3, $J$ 4.7, 1.2 Hz), 8.47 d (1H, Py-3, $J$ 2.6 Hz). Found, %: C 63.81; H 5.48; N 6.74. $C_{21}H_{22}N_2O_2S_2$. Calculated, %: C 64.05; H 5.86; N 6.79.

**[3-(Isobutylthio)-4-methyl-5-(phenylsulfonyl)-phenyl]-2-pyridylamine**. From 167.5 mg (0.50 mmol) of 3-(isobutylthio)-4-methyl-5-(phenylsulfonyl)aniline (**IV**), 79.0 mg (0.50 mmol, 1.00 equiv) of 2-bromopyridine, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 5.90 mg (0.015 mmol, 3 mol%) of $Me_2N$-DP-$PCy_2$, 320 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 150.0 mg (73%) of product as colorless powder [eluent $CH_2Cl_2$–MeOH–EtOAc (50 : 1 : 1), $R_f$ ($ArNH_2$) 0.67, $R_f$ (ArHetNH) 0.44]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1.0 ml) with petroleum ether (5 ml), mp 166.5–167.2°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 1.05 d [6H, $(CH_3)_2CH$, $J$ 6.7 Hz], 1.96 m [1H, $(CH_3)_2CH$], 2.36 s (3H, $CH_3C_6H_2$), 2.86 d (2H, $CHCH_2S$, $J$ 6.7 Hz), 6.82 d.d.d (1H, Py-2, $J$ 7.2, 5.1, 1.0 Hz), 6.90 d.t (1H, Py-2, $J$ 8.4, 1.0 Hz), 7.59–7.72 m [4H, $PhS(O)_2$, $C_6H_2$], 7.88–7.92 m [2H, $PhS(O)_2$], 8.23 m (2H, Py-2, $C_6H_2$), 8.44 t (1H, Py-2, $J$ 2.8 Hz), 8.67 br.s (1H, NH). Found, %: C 64.00; H 5.95; N 6.94; S 15.28. $C_{22}H_{24}N_2O_2S_2$. Calculated, %: C 64.05; H 5.86; N 6.79; S 15.54.

**[3-Methoxy-5-(phenylsulfonyl)phenyl]-3-quinolylamine**. From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 125.0 mg (0.60 mmol, 1.20 equiv) of 3-bromoquinoline, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.70 mg (0.015 mmol, 3 mol%) of Xantphos, 326 mg (2 equiv) of $Cs_2CO_3$, and 2 m¨ of toluene was obtained 189.0 mg (97%) of product as yellow crystalline powder [eluent EtOAc–petroleum ether (3 : 1), $R_f$ ($ArNH_2$) 0.50, $R_f$ (ArHetNH) 0.31]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1.5 ml) with petroleum ether (1.5 ml), mp 109–111°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.86 s (3H, $CH_3O$), 7.02 m (1H, $C_6H_3$), 7.05 m (1H, $C_6H_3$), 7.36 m (1H, $C_6H_3$), 7.50–7.72 m [5H, $PhS(O)_2$, $C_9H_6N$], 7.81 m (1H, $C_9H_6N$), 7.94–8.04 m [4H, $PhS(O)_2$, $C_9H_6N$], 8.28 br.s (1H, NH), 8.75 d (1H, $C_9H_6N$, $J$ 2.5 Hz). Found, %: C 67.37; H 4.49; N 7.07. $C_{22}H_{18}N_2O_3S$. Calculated, %: C 67.68; H 4.65; N 7.17.

**[3-Methoxy-5-(phenylsulfonyl)phenyl]-3-thienylamine**. (a) From 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 97.0 mg (0.60 mmol, 1.20 equiv) of 3-bromothiophene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.50 mg (0.015 mmol, 3 mol%) of Xantphos, 250 mg (1.50 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 89.8 mg (52.6%) of product as colorless powder of fine crystals [eluent petroleum ether–ethyl acetate (1 : 1), $R_f$ ($ArNH_2$) 0.35, $R_f$ (ArHetNH) 0.70]. Internal reference naphthalene (monitoring by GLC and TLC). The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (0.3 ml) with petroleum ether (0.5 ml), mp 143.8–144.0°C. $^1$H NMR spectrum (acetone-$d_6$), δ, ppm: 3.81 s (3H, $CH_3O$), 6.77 m (1H, $C_6H_3$), 6.88 m (1H, $C_6H_3$), 6.95 d.d (1H, $C_4H_3S$, $J$ 3.1, 1.5 Hz), 6.98 d.d (1H,

$C_4H_3S$, *J* 5.2, 1.5 Hz), 7.18 m (1H, $C_6H_3$), 7.44 d.d (1H, $C_4H_3S$, *J* 5.2, 3.1 Hz), 7.58–7.69 m [3H, $PhS(O)_2$], 7.94 br.s (1H, NH), 7.96–8.00 m [2H, $PhS(O)_2$]. Found, %: C 58.91; H 4.22; N 3.86. $C_{17}H_{15}NO_3S_2$. Calculated, %: C 59.13; H 4.35; N 4.06.

(b) The reaction was carried out with the same amounts of reagents but using as ligand $Me_2N$-DP-$PCy_2$, 5.80 mg (0.015 mmol, 3 mol%). Internal reference naphthalene, 20.5 mg. The conversion of the initial product 40% (GLC). The product was not isolated.

(c) The reaction was carried out with the same amounts of reagents but using as ligand *t*-$Bu_2$-DP-phos, 4.45 mg (0.015 mmol, 3 mol%). Internal reference naphthalene, 21.1 mg. The conversion of the initial product 29% (GLC). The product was not isolated.

**[3-Methoxy-5-(phenylsulfonyl)phenyl]-2-thienylamine**. A mixture of 131.5 mg (0.50 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 97.8 mg (0. 60 mmol, 1.20 equiv) of 2-bromothiophene, 2.25 mg (0.010 mmol, 2 mol%) of $Pd(OAc)_2$, 8.70 mg (0.015 mmol, 3 mol%) of Xantphos, 330 mg (2 equiv) of $Cs_2CO_3$, and 2 ml of toluene (internal reference naphthalene, 20.0 mg) was stirred for 11 h. The conversion of the initial product 94% (GLC). The product was unstable, and we failed to isolate it in an individual state.

**5-[3-Methoxy-5-(phenylsulfonyl)anilino]-2-thiophenecarbaldehyde**. From 79.0 mg (0.30 mmol) of 3-methoxy-5-(phenylsulfonyl)aniline (**III**), 72.0 mg (0.30 mmol, 1.00 equiv) of 2-iodo-5-formylthiophene, 1.35 mg (0.006 mmol, 2 mol%) of $Pd(OAc)_2$, 5.20 mg (0.009 mmol, 3 mol%) of Xantphos, 200 mg (0.6 mmol, 2 equiv) of $Cs_2CO_3$, and 2 ml of toluene was obtained 101 mg (90%) of product as dark-brown powder [eluent petroleum ether–ethyl acetate (1 : 3)]. The product was additionally purified by reprecipitation from a solution in $CH_2Cl_2$ (1 ml) with petroleum ether (1.5 ml), mp 152–153°C. $^1H$ NMR spectrum (acetone-$d_6$), δ, ppm: 3.87 s (3H, $CH_3O$), 6.73 d (1H, OHC–$C_4H_2S$, *J* 4.2 Hz), 7.03 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.11 t (1H, $C_6H_3$, *J* 2.1 Hz), 7.45 t (1H, $C_6H_3$, *J* 2.1 Hz), 7.58–7.71 m [3H, $PhS(O)_2$], 7.74 d (1H, OHC–$C_4H_2S$, *J* 4.2 Hz), 8.00–8.02 m [2H, $PhS(O)_2$], 9.60 br.s (1H, NH), 9.70 s (1H, CHO). Found, %: C 57.50; H 3.90; N 3.95; S 16.70. $C_{18}H_{15}N_2O_4S_2$. Calculated, %: C 57.89; H 4.05; N 3.75; S 17.17.

**5-[3-Nitro-5-(2,2,2-trifluoroethoxy)phenyl]-2-thiophenecarbaldehyde**. (a) From 94.4 mg (0.40 mmol) of 3-nitro-5-(2,2,2-trifluoroethoxy)-aniline (**V**), 96.0 mg (0.41 mmol, 1.02 equiv) of 2-iodo-5-formylthiophene, 1.60 mg (0.006 mmol, 2 mol%) of $Pd(OAc)_2$, 6.50 mg (0.012 mmol, 3 mol%) of DPE-phos, 220 mg (1.70 equiv) of $Cs_2CO_3$, and 1.6 ml of toluene was obtained 79.0 mg (57%) of product as brown powder [eluent benzene, $R_f$ ($ArNH_2$) 0.33, $R_f$ (ArHetNH) 0.20].

(b) The reaction was carried out with the same amounts of reagents but using as ligand Xantphos, 6.90 mg (0.015 mmol, 3 mol%). We obtained 117.0 mg (85%) of product, that was additionally purified by reprecipitation from solution in $CH_2Cl_2$ (1 ml) with petroleum ether (2 ml), mp 162–163°C. $^1H$ NMR spectrum (acetone-$d_6$), δ, ppm: 4.91 q (2H, $CF_3CH_2O$, *J* 8.4 Hz), 6.88 d (1H, OHC–$C_4H_2S$, *J* 4.2 Hz), 7.32 t (1H, $C_6H_3$, *J* 2.2 Hz), 7.52 t (1H, $C_6H_3$, *J* 2.1 Hz), 7.80 d (1H, OHC–$C_4H_2S$, *J* 4.2 Hz), 7.81 t (1H, $C_6H_3$, *J* 2.1 Hz), 9.42 br.s (1H, NH), 9.75 s (1H, CHO). Found, %: C 45.08; H 2.80; N 7.86. $C_{13}H_9N_2O_4F_3S$. Calculated, %: C 45.09; H 2.62; N 8.09.

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