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Palladium-catalyzed Arylation of Ureas

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Abstract—Urea arylation with aryl halides in the presence of catalyst precursor Pd_2dba_3–$CHCl_3$/Xantphos and Cs_2CO_3 in dioxane at 100°C affords symmetrical *N,N'*-diarylureas in 64–92% yield. With the same catalytic system the reaction between *N*-phenylurea and aryl bromides containing electron-withdrawing substituents in the *para*-position provided *N*-aryl-*N'*-phenylureas in 64–91% yields.

N,N'-Diarylureas found wide application in agriculture [1, 2], synthesis of pharmaceuticals [2], as receptors for binding anions [3] etc. The most common preparation method for arylureas consists in reacting anilines with highly toxic compounds (phosgene, aryl isocyanates, or carbon monoxide) [2]. As alternative to these classical procedures may be arylation of urea with aryl halides in the presence of transition metal complexes. Similar reactions found recently wide application for building up a C_{Ar}–N bond [4. 5]. Among these are obviously interesting reactions with copper-containing catalysts that provide a possibility of arylation both of amines, amides and imides. However these reactions usually require stringent conditions and in some cases equimolar or more amounts of copper, and the yields often are low [6].

The most efficient catalysts for amines arylation are now palladium complexes [5, 7]. However under these conditions remains uncertain the arylation of compounds with amino group of low basicity, e.g., amides or sulfonamides. The first examples of amides arylation consisted in intramolecular cyclization of amides and carbamates [8]. Also were described several cases of intermolecular N-arylation of lactams [9] and carbamates [10]. And only quite recently was preformed an efficient arylation of amides, sulfonamides, and lactams with the use of a catalytic system $Pd(OAc)_2$/Xantphos [11]. As to ureas, no attempts of its catalytic arylation have been performed up till now.

In order to select an optimal ligand for catalytic arylation of urea we carried out a number of reactions between p-bromobenzotrifluoride with urea at molar ratio 1 : 2 using 1 mol% (2 mol% of Pd) of Pd_2dba_3–$CHCl_3$ and 3 mol% of ligand L in the presence of Cs_2CO_3 as base in dioxane at 100°C (Table 1).

As seen from Table 1, the most efficient ligand was Xantphos: in this case the reaction completed in 4 h and afforded as the main product *N,N'*-di(*p*-trifluoromethylphenyl)urea in 89% yield, and the corresponding monoarylurea formed in a small amount (5%). The prevailing formation of diarylurea in this reaction can result from low solubility of urea in dioxane. Tri(o-tolyl)phosphine was inefficient in this reaction. At the use of bis(2,2'-diphenylphosphino)-

Table 1. Variation of ligands L

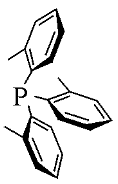
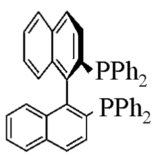
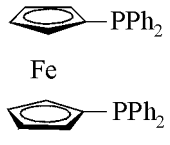
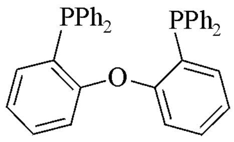
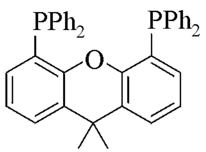
Ligand		 BINAP	 DPPF	 DPE-Phos	 Xantphos
Time, h	18	18	18	18	4
Conversion, %	0	50	58	48	100
(yield, %)		(17)	(22)	(17)	89

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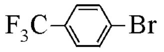
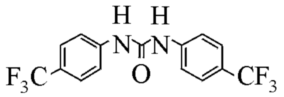
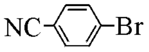
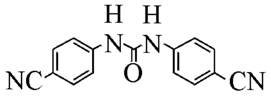
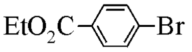
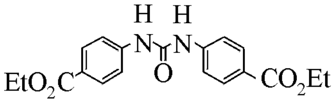
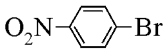
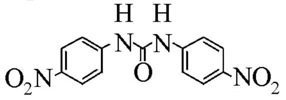
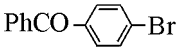
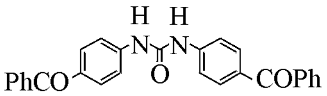
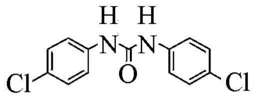
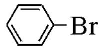
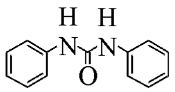
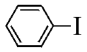
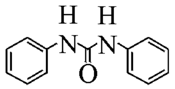
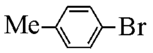
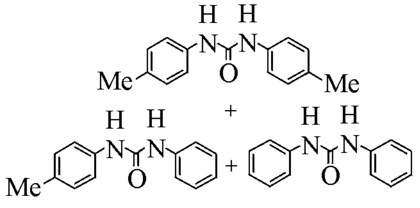
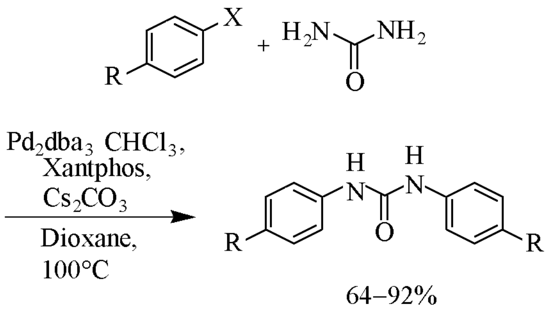
Table 2. Palladium-catalyzed arylation of urea

Run no.	Arylhalogenides	Pd, mol%	Time, h	Product	Yield, %
1		2	4		89
2		1	6.5		92
3		1	4		86
4		1	4		75
5		1	2.5		89
6		4	10		64
7		4	10		70
8		4	13		74
9		4	20		22

di-1,1'-naphthyl (BINAP) or DPPF and DPE-Phos the reaction did not go to completion, the yield of diarylurea was low, and arose a significant amount of di(*p*-trifluoromethylphenyl)amine (18–29%) (Table 1).



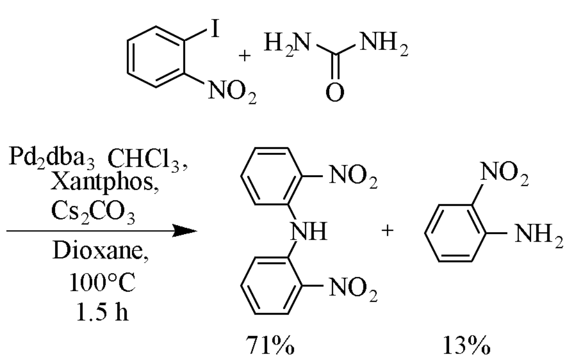
R = CO$_2$Et, CF$_3$, CN, PhC(O), NO$_2$, Cl, H; X = Br, I.

With Xantphos as ligand we performed a number of urea arylation using the latter in slight excess (Table 2).

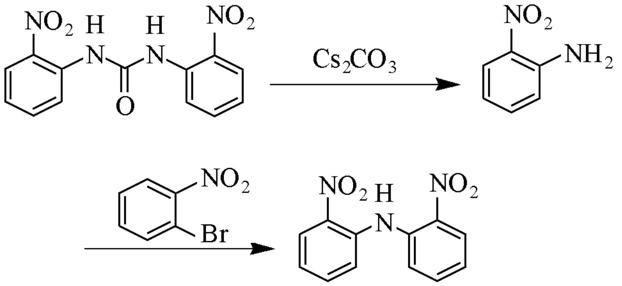
Reactions with aryl bromides having electron-withdrawing groups readily occur in the presence of 1–2 mol% of Pd furnishing *N,N'*-diarylureas in high yield (Table 2, runs nos. 1–5). The reaction with aryl chlorides proceeds with greater difficulty. For instance, with *p*-chlorobenzotrifluoride the conversion was only 25% in 15 h at the use of 2 mol% of the catalyst.

It should be specially mentioned that in reaction of urea with o-iodonitrobenzene the main reaction product was di(*o*-nitrophenyl)amine:

Apparently the arising *N,N'*-di(o-nitrophenyl)urea is cleaved by the base yielding o-nitroaniline that



further is arylated into the corresponding diarylamine:

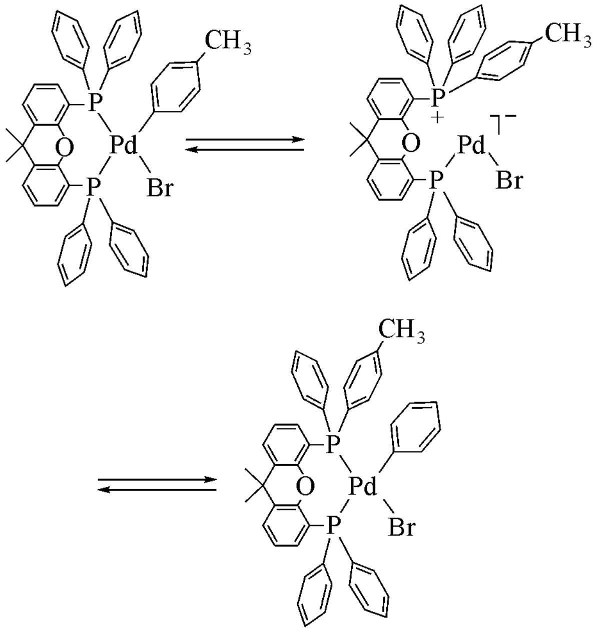


Note that the corresponding *N*,*N*'-di(*p*-nitrophenyl)urea is stable under reaction conditions (Table 2, run no. 4). We observed formation of diarylamines also in reactions with urea of pentafluoropyridine and octafluorotoluene in DMF in the presence of CsF as a base:

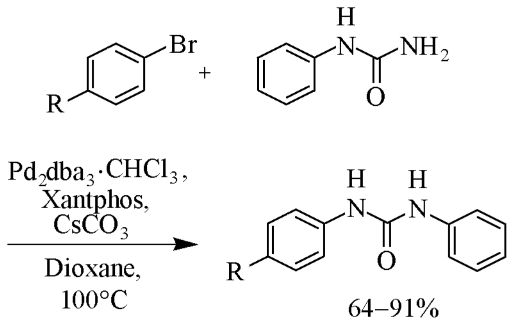
$$Ar_FF + HNC(O)NH_2 \xrightarrow[\text{DMD, } 80°\text{C}]{\text{CsF}} (Ar_F)_2NH \quad 65\text{–}68\%$$

These reactions proceeded as S_NAr processes and did not require any catalyst. In the literature are described similar reactions with hexafluorobenzene [12] and pentafluoropyridine [13] in the presence of a stronger base (NaH). However the heating of *o*-iodonitrobenzene with urea an Cs_2CO_3 in dioxane for 1.5 h did not give rise to notable amounts of products.

Catalyzed reactions with weakly activated or nonactivated aryl halides resulted in lower yields of the target product and required more catalyst (up to 4 mol%) (Table 2, runs nos. 6–8). In these cases we obtained as side products considerable amounts (12–14%) of the corresponding diarylamines. Besides the reaction in run no. 6 was accompanied by formation of a considerable amount of *N*-phenylation product, *N*-phenyl-*N*'-(*p*-chlorophenyl)urea. With *p*-bromotoluene even at 4 mol% of the catalyst the reaction stopped at conversion of 62%, and the products consisted of *N*,*N*-diphenyl, *N*-(*p*-tolyl)-*N*'-phenyl- and *N*,*N*'-di(*p*-tolyl)ureas in molar ratio 5.2 : 10 : 6.8 in an overall yield 22%. The N-phenylated products arise from the exchange of the aryl group bonded to palladium with the phenyl group of phosphine followed by reductive elimination. This process is often observed in the reactions of cross-coupling and amination by aryl halides containing electron-donor substituents [14]. The considerable content of phenyl groups in the arylation product obtained from urea and *p*-bromotoluene corresponds to very high extent of phenyl group migration from Xantphos (85%).



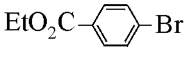
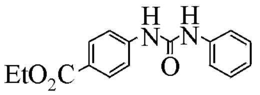
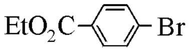
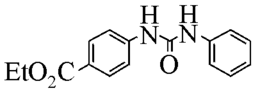
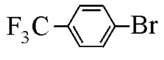
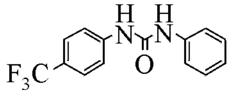
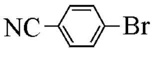
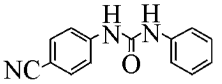
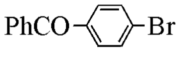
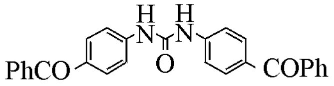
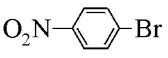
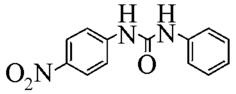
We also demonstrated that the use of XANTphos as ligand provided a possibility of catalytic arylation of phenylurea and opens an easy and efficient way of synthesis of unsymmetrical diarylureas (Table 3).



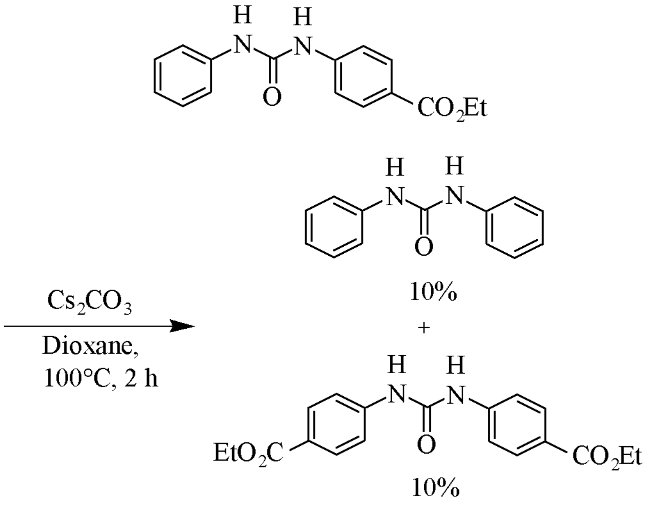
R = CO_2Et, CF_3, CN, PhC(O), NO_2.

The phenylurea arylation with ethyl *p*-bromobenzoate cleanly occurred within 4h in the presence

Table 3. Palladium-catalyzed arylation of phenylurea

Run no.	Arylhalogenides	Pd, mol%	Time, h	Product	Yield, %
1		2	4		58
2		2	1		91
3		2	1		90
4		2	1		80
5		2	1.5		87
6		2	1		64

of 0.5 mol% of the catalyst and resulted in unsymmetrical *N*,*N'*-diarylurea in a moderate yield. The reaction was complicated by formation of symmetrical ureas, *N*,*N'*-diphenylurea and *N*,*N'*-di(*p*-ethoxycarbonylphenyl)urea. We showed that symmetrical diarylureas originated from disproportionation of the reaction product, *N*-(*p*-ethoxycarbonylphenyl)-*N'*-phenylurea, in the presence of base. Thus the heating of *N*-(*p*-ethoxycarbonylphenyl)-*N'*-phenylurea in dioxane to 100°C for 2 h in the presence of Cs_2CO_3 resulted in formation of two symmetrical *N*,*N'*-diarylureas. A longer heating (14 h) gave rise to relatively higher yield of products of disproportionation and decomposition of diarylurea.



In the absence of a base no visible disproportionation occurred even in 6 h. The increase in catalyst amount to 2 mol% reduced the duration of the reaction and the contribution of the symmetrization process thus considerably increasing the yield of the target products (Table 3, runs nos. 2–6). However reaction with *p*-nitrobromobenzene under these conditions provided a large amount of side products, and the desired product was obtained only in 64% yield.

EXPERIMENTAL

Cesium carbonate and fluoride were dried in a vacuum at 150–200°C. Dioxane and DMF were purified and dried by standard procedures. Dioxane was stored in a vacuum over benzophenone ketyl. Pd_2dba_3–$CHCl_3$ was prepared as described in [15]. Xantphos was synthesized along procedure [16]. Aryl halides before use were recrystallized or distilled. The ^1H and ^{19}F NMR spectra were registered on spectrometer Varian VXR 400 at operating frequencies 400 and 376 MHz respectively. The chemical shifts of protons were measured relative the signals of the residual protons of the deuterated solvent, in the ^{19}F NMR spectrum the chemical shifts were measured with respect to the signal of $C_6H_5CF_3$

(δ_F 61.96 ppm from $CFCl_3$). IR spectra were measured on Fourier spectrophotometer Ikar (Joint Stock Co Mikrotekh, Russia). GLC analyses were performed on a device RSI Instruments 910 equipped with flame-ionization detector, capillary column 10000×0.53 mm, carrier gas nitrogen. Mass spectra were registered on Kratos MS-30 instrument, electron impact ionization, ionizing electrons energy 70 eV. For compounds with melting points in disagreement with published data or when published data showed a significant scatter in melting points the results of elemental analysis are presented.

General procedure for urea arylation. Into a reactor filled with argon was charged 0.65 mmol of urea (2.0 mmol in run no. 1), 1.4 mmol of Cs_2CO_3, 0.5–2 mol% ($0.5–2\times10^{-2}$ mmol) of $Pd_2dba_3–CHCl_3$, 1.5–6 mol% ($1.5–6\times10^{-2}$ mmol) of Xantphos, in an argon flow was added 1 mmol of aryl bromide and 0.2 mmol of 1,2,4,5-tetramethylbenzene (as internal reference) in 4 ml of dioxane saturated with argon. The reaction mixture was degassed by evacuation, then the reactor was filled with argon. The reaction was carried out at 100°C while stirring. The reaction progress was monitored by GLC and (or) TLC on Silufol UV-254 plates. On completion of the reaction the mixture was cooled to room temperature, and the content of the reactor was poured into 50 ml of saturated KCl solution. Then the products were extracted into ethyl acetate (3...20 ml), the combined extracts were washed with KCl solution, dried on $MgSO_4$, and evaporated. The residue was subjected to chromatography on silica gel 40–100 μm, using as eluent a mixture ethyl acetate –petroleum ether boiling within 40–70°C.

Ligand variation. The runs with ligand variation were performed according to procedure for urea arylation using 0.6 mmol of p-bromo-trifluoromethylbenzene, 1.2 mmol of urea, 0.84 of mmol Cs_2CO_3, 0.6×10^{-2} mmol of $Pd_2dba_3CHCl_3$, 1.8×10^{-2} mmol of the ligand, and 0.15 mmol of 1,2,4,5-tetramethylbenzene (internal reference) in 3 ml of dioxane. The reaction mixture was heated at stirring under argon atmosphere for the time indicated in Table 1. The conversion of the original aryl halide was estimated by GLC or from ^1H NMR spectrum of the reaction mixture (the deuterium lock was performed on acetone-d_6 placed in the external tube).

***N,N'*-Di(*p*-trifluoromethylphenyl)urea.** From 129 mg (0.57 mmol) of *p*-bromo-trifluoromethylbenzene, 61 mg (1.01 mmol of urea, 240 mg (0.74 mmol) of Cs_2CO_3, 5.44 mg (0.53×10^{-2} mmol) of $Pd_2dba_3–CHCl_3$ and 8.2 mg (1.42×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 88 mg (89%) of colorless solid, mp 234–236°C (publ.: 239°C [17], 209–210°C [18]). IR spectrum (KBr pellet), cm^{-1}: 3320, 1654, 1326. ^1H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 8.62 s (1H), 7.76 d (2H, 8.6), 7.63 d (2H, 8.6). Found, %: C 52.08; H 3.07; N 7.89. $C_{15}H_{10}F_6N_2O$. Calculated, %: C 51.73; H 2.89; N 8.04.

***N,N'*-Di(*p*-ethoxycarbonylphenyl)urea.** From 139 mg (0.61 mmol) of ethyl *p*-bromobenzoate, 25 mg (0.42 mmol of urea, 275 mg (0.84 mmol) of Cs_2CO_3, 3.44 mg (3.3×10^{-3} mmol) of $Pd_2dba_3–CHCl_3$ and 5.87 mg (1.01×10^{-3} mmol) of Xantphos in 3 ml of dioxane was obtained 93 mg (85%) of colorless solid, mp 225–227°C (publ.: 215°C [19]). IR spectrum (KBr pellet), cm^{-1}: 3336, 1714, 1691. ^1H NMR spectrum (DMSO-d_6), δ, ppm(*J*, Hz): 9.19 s (2H), 7.89 d (4H, 8.8), 7.59 d (4H, 8.8), 4.27 q (4H, 7.0), 1.30 t (6H, 7.0). Found, %: C 64.12; H 5.93; N 7.91. $C_{19}H_{20}N_2O_5$. Calculated, %: C 64.04; H 5.66; N 7.86.

***N,N'*-Di(*p*-cyanophenyl)urea.** From 119 mg (0.65 mmol) of *p*-bromobenzonitrile, 24 mg (0.4 mmol) of urea, 275 mg (0.84 mmol) of Cs_2CO_3, 3.25 mg (3.14×10^{-3} mmol) of $Pd_2dba_3–CHCl_3$, and 5.35 mg (9.25×10^{-3} mmol) of Xantphos in 3 ml of dioxane was obtained 79 mg (92%) of colorless solid mp >300°C (publ.: 240°C [19], 273°C [20], 305°C [21], 275°C [22]). IR spectrum (KBr pellet), cm^{-1}: 3380, 2215, 1735. ^1H NMR spectrum (acetone-d_6 and DMSO-d_6 mixture), δ, ppm (*J*, Hz): 9.23 s (2H), 7.74 d (4H, 9.0), 7.69 d (4H, 9.0). Found, %: C 68.38; H 4.02; N 21.03. $C_{15}H_{10}N_4O$. Calculated, %: C 68.69; H 3.84; N 21.36.

***N,N'*-Di(*p*-nitrophenyl)urea.** From 122 mg (0.6 mmol) of *p*-bromonitrobenzene, 22 mg (0.37 mmol) of urea, 3.16 mg (3.06×10^{-3} mmol) of $Pd_2dba_3–CHCl_3$, and 5.27 mg (9.11×10^{-3} mmol) of Xantphos in 3 ml of dioxane was obtained 69 mg (75%) of yellow solid, mp >300°C (publ. 364–374°C [23]).

IR spectrum (KBr pellet), cm^{-1}: 3369, 3342, 3322, 3290, 1735. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.79 s (2H), 8.22 d (4H, 9.2), 7.72 d (4H, 9.2). Found, %: C 51.81; H 3.72; N 18.65. $C_{13}H_{10}N_4O_5$. Calculated, %: C 51.66; H 3.33; N 18.54.

***N,N'*-Di(*p*-benzoylphenyl)urea.** From 283 mg (1.08 mmol) of *p*-bromobenzophenone, 48 mg (0.8 mmol) of urea, 500 mg (1.53 mmol) of Cs_2CO_3, 5.82 mg (0.56×10^{-2} mmol) of $Pd_2dba_3–CHCl_3$, and

9.29 mg (1.61×10^{-2} mmol) of Xantphos in 4 ml of dioxane was obtained 206 mg (90%) of solid substance of cream color. Reprecipitation by water from DMF solution provided 203 mg of cream-colored crystals, mp 298–300°C (publ. 189°C [24]). Mass spectrum, *m/z* (I_{rel}, %): 420 (4.4) [*p*-PhC(O)C_6H_4NHC(O)C_6H_4-(O)Ph-*p*]$^{+\cdot}$, 223 (94) [*p*-PhC(O)C_6H_4NCO]$^{+\cdot}$, 197 (100) [*p*-PhC(O)$C_6H_4NH_2$]$^{+\cdot}$. IR spectrum (KBr pellet), cm^{-1}: 3332, 1637, 1699. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.32 s (2H), 7.61–7.84 m (14H), 7.55 t (4H, 7.6). Found, %: C 77.00; H 4.49; N 6.58. $C_{27}H_{20}N_2O_3$. Calculated, %: C 77.13; H 4.79; N 6.66.

***N,N*'-Di(*p*-chlorophenyl)urea.** From 190 mg (0.99 mmol) of *p*-chlorobromobenzene, 39 mg (0.65 mmol) of urea, 450 mg (1.38 mmol) of Cs_2CO_3, 20.46 mg (1.98×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 32.97 mg (5.7×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 110 mg (79%) of colorless solid substance (containing as impurity according to ^{1}H NMR and mass spectra ~14% of *N*-*p*-chlorophenyl-N'-phenylurea). Mass spectrum, *m/z* (I_{rel}, %): 280 (10) [*p*-ClC_6H_4NHC(O)NHC_6H_4Cl-*p*]$^{+\cdot}$, 246 (1.7) [*p*-ClC_6H_4NHC(O)NHC_6H_5)]$^{+\cdot}$, 153 (23) [*p*-ClC_6H_4NCO]$^{+\cdot}$, 127 (100) [*p*-Cl$C_6H_4NH_2$]$^{+\cdot}$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm(*J*, Hz): 8.84 s (H), 7.47 d (4H, 8.9), 7.32 d (4H, 8.9); impurity signals: 8.80 s, 8.69 s, 7.27 t, 6.99 t. After recrystallization from ethanol we obtained 89 mg (64%) of solid substance, mp >300°C (publ.: 292–294°C [21], 303–305°C [25], 318°C [26]). IR spectrum (KBr pellet), cm^{-1}: 3299, 1633. Found,%: C 55.56; H 3.49; N 9.55. $C_{13}H_{10}Cl_2N_2O$. Calculated, %: C 55.54; H 3.54; N 9.96.

***N,N*'-Diphenylurea** (Table 2, run no. 7). From 159 mg (1.01 mmol) of bromobenzene, 43 mg (0.72 mmol) of urea, 495 mg (1.52 mmol) of Cs_2CO_3, 20.80 mg (2.30×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 34.67 mg (6.31×10^{-2} mmol) of Xantphos in 4 ml of dioxane was obtained 75 mg (70%) of colorless solid, mp 239–241°C (publ. 235–236°C [25]). IR spectrum (KBr pellet), cm^{-1}: 3324, 1648. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 8.65 s (2H), 7.45 d (4H, 8.4), 7.27 t (4H, 8.4, 7.4), 6.96 t (2H, 7.4).

***N,N*'-Diphenylurea (Table 2, run no.8).** From 204 mg (1 mmol) of iodobenzene, 43 mg (0.72 mmol) of urea, 475 mg (1.46 mmol) of Cs_2CO_3, 20.7 mg (2×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 34.37 mg (5.94×10^{-2} mmol) of Xantphos in 4 ml of dioxane was obtained 79 mg (70%) of brown solid, mp 238–240°C (publ. 235–236°C [25]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm. (*J*, Hz): 8.65 s (2H), 7.45 d (4H, 8.4), 7.27 t (4H, 8.4, 7.4), 6.96 t (2H, 7.4).

Reaction of urea with *p*-bromotoluene. From 102 mg (0.6 mmol) of *p*-bromotoluene, 24 mg (0.4 mmol) of urea, 275 mg (0.84 mmol) of Cs_2CO_3, 12.8 mg (1.24×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 21.05 mg (3.64×10^{-2} mmol) of Xantphos in 2.5 ml of dioxane was obtained 16 mg (22%) of light-brown solid, consisting of *N,N*'-diphenylurea, *N*-*p*-tolyl-*N*-phenylurea, and *N,N*'-di(p-tolyl)urea in 5.2 : 10 : 6.8 ratio as calculated from the integral intensity ratio of the corresponding amide proton signals in the ^{1}H NMR spectrum (the respective chemical shifts were consistent with the published values [22]). Mass spectrum, *m/z* (I_{rel}, %): 240 (54) [*p*-TolNHC(O)NHTol-*p*]$^{+\cdot}$, 226 (72) [PhNHC(O)NHTol-*p*]$^{+\cdot}$, 212 (28) [PhNHC(O)–NHPh]$^{+\cdot}$, 133 (23) [*p*-TolNCO]$^{+\cdot}$, 119 (23) [PhNCO]$^{+\cdot}$, 107 (100) [*p*-TolNH_2]$^{+\cdot}$, 93 (98) [PhNH_2]$^{+\cdot}$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.65 s (PhN*H*C(O)N*H*Ph), 8.60 s (PhN*H*C(O)NHTol-*p*), 8.54 s (PhNHC(O)–N*H*Tol-*p*), 8.48 s (*p*-TolN*H*C(O)N*H*Tol-*p*), 8.40–8.47 m, 7.29–7.35 m, 7.23–7.29 m, 7.04–7.10 m, 6.92–6.99 m.

Reaction of urea with *o*-iodonitrobenzene. From 257 mg (1.03 mmol) of *o*-iodonitrobenzene, 43 mg (0.72 mmol) of urea, 490 mg (1.50 mmol) of Cs_2CO_3, 5.77 mg (0.56×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 9.13 mg (3.64×10^{-2} mmol) of Xantphos in 4 ml of dioxane was obtained 95 mg (71%) of di(*o*-nitrophenyl)amine as orange solid substance, mp 168–170°C (publ.: 172.1–172.5°C [27], 171–171.5°C [28]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 10.62 s (1H), 8.18 d.d (2H, 8.5, 1.4), 7.68 m (2H), 7.60 d.d (2H, 8.4, 1.2), 7.2 m (2H).

General procedure for phenylurea arylation. Into a reactor filled with argon was charged 0.6 mmol of phenylurea 0.84 mmol of Cs_2CO_3, 1 mol% of Pd_2dba_3–$CHCl_3$, 3 mol% of Xantphos, in an argon flow was added 0.6 mmol of aryl bromide in 3 ml of dioxane saturated with argon. The reaction mixture was degassed by evacuation, then the reactor was filled with argon. The reaction was carried out at 100°C while stirring. The reaction progress was monitored by TLC on Silufol UV-254 plates. On completion of the reaction the mixture was cooled to room temperature and diluted with ethyl acetate (40 ml), filtered, and evaporated. The residue was subjected to chromatography on silica gel 40–100 μm, using as eluent a mixture ethyl acetate –petroleum ether boiling within 40–70°C.

***N*-(*p*-Ethoxycarbonylphenyl)-*N*'-phenylurea.** From 143 mg (0.62 mmol) of ethyl *p*-bromobenzoate, 81 mg (0.59 mmol) of phenylurea, 280 mg (0.86 mmol) of Cs_2CO_3, 6.28 mg (0.61×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 11.01 mg (1.90×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 156 mg (91%) of colorless solid, mp 168–170°C (publ.: 169°C [29], 163°C [30]). IR spectrum (KBr pellet), cm^{-1}: 3351, 3315, 3307, 1716, 1699. ^1H NMR spectrum (d_6 DMSO), δ, ppm (*J*, Hz): 9.09 s (1H), 8.78 s (1H), 7.89 d (2H, 8.8), 7.59 d (2H, 8.8), 7.46 d (2H, 8.5), 7.29 d.d (2H, 8.5, 7.4), 6.99 t (1H, 7.4).

***N*-(*p*-Trifluoromethylphenyl)-*N*'-phenylurea.** From 145 mg (0.62 mmol) of *p*-trifluoromethylbromobenzene, 85 mg (0.62 mmol) of phenylurea, 285 mg (0.87 mmol) of Cs_2CO_3, 6.47 mg (0.63×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 11.07 mg (1.91×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 157 mg (90%) of colorless solid, mp 223–225°C (publ.: 225°C [17]). IR spectrum (KBr pellet), cm^{-1}: 3311, 1645, 1328. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.09 s (1H), 8.79 s (1H), 7.64 m (4H), 7.59 d (2H, 8.8), 7.46 d (2H, 8.3), 7.29 d.d (2H, 8.3, 7.7), 7.00 t (1H, 7.4).

***N*-(*p*-Cyanophenyl)-*N*'-phenylurea.** From 115 mg (0.63 mmol) of ethyl *p*-bromobenzonitrile, 82 mg (0.6 mmol) of phenylurea, 285 mg (0.87 mmol) of Cs_2CO_3, 6.45 mg (0.623×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 10.85 mg (1.877×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 115 mg (80%) of colorless solid, mp 208–210°C (publ.: 198°C [21], 210°C [22]). IR spectrum (KBr pellet), cm^{-1}: 3301, 2225, 1643, 1594, 1552, 1500. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.19 s, (1H), 8.85 s, (1H), 7.73 d, (2H, 8.6), 7.62 d, (2H, 8.6), 7.45 d (2H, 8.0), 7.29 d.d (2H, 8.0, 7.4), 7.00 t (1H, 7.4).

***N*-(*p*-Benzoylphenyl)-*N*'-phenylurea.** From 169 mg (0.65 mmol) of *p*-bromobenzophenone, 86 mg (0.63 mmol) of phenylurea, 280 mg (0.86 mmol) of Cs_2CO_3, 6.61 mg (0.64×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 11.50 mg (2.0×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 175 mg (87%) of white solid, mp 201– 203°C (publ.: 203°C [26]). IR spectrum (mineral oil), cm^{-1}: 3370, 1710, 1640, 1610. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.15 s (1H), 8.81 s (1H), 7.79–7.60 m (7H), 7.55 t (2H, 7.6, 7.2), 7.47 d (2H, 8.0), 7.29 d.d (2H, 8.0, 7.4), 6.99 t (1H, 7.4).

***N*-(*p*-Nitrophenyl)-*N*'-phenylurea.** From 121 mg (0.6 mmol) of *p*-nitrobromobenzene, 83 mg (0.61 mmol) of phenylurea, 275 mg (0.84 mmol) of Cs_2CO_3, 6.43 mg (0.62×10^{-2} mmol) of Pd_2dba_3–$CHCl_3$, and 10.81 mg (1.87×10^{-2} mmol) of Xantphos in 3 ml of dioxane was obtained 99 mg (64%) of light-yellow solid, mp 225–227°C (publ. 213–218°C [22], 207–220°C [23]). IR spectrum (KBr pellet), cm^{-1}: 3301, 1650, 1560, 1346. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.43 s (1H), 8.92 s (1H), 8.19 d (2H, 9.2), 8.69 d (2H, 9.2), 7.47 d (2H, 8.3), 7.30 d.d (2H, 8.3, 7.4), 7.01 t (1H, 7.4).

Urea arylation with pentafluoropyridine. Into a two-neck reactor was charged 405 mg (2.68 mmol) of CsF, 175 mg (1.03 mmol) of pentafluoropyridine, 25.6 mg (0.43 mmol) of urea, and 2.5 ml of DMF. The reaction mixture was degassed by evacuation and heated for 7 h to 80°C. The reaction progress was monitored by ^{19}F NMR spectra. On completion of the reaction the mixture was cooled to room temperature, and the content of the reactor was poured saturated KCl solution. Then the products were thrice extracted into ethyl acetate, the combined extracts were washed with KCl solution, dried, and evaporated. The residue was subjected to chromatography on silica gel to afford 105 mg (65%) of bis(tetrafluoropyridyl)amine as colorless solid, mp 148–150°C (publ.: 144–146°C [13], 149–150°C [31]). Yield according to ^{19}F NMR data was 68%.

Urea arylation with octafluorotoluene. The reaction was carried out as with pentafluoropyridine. From 450 mg (2.98 mmol) of CsF, 285 mg (1.2 mmol) of octafluorotoluene, 31 mg (0.52 mmol) of urea after 41 h of heating was separated 125 mg (46%) of bis(4-perfluorotolyl)amine as colorless solid, mp 73–75°C (publ.: 76–77°C [31]). Yield according to ^{19}F NMR data was 65%.

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