Pd-catalyzed Thiophene-Aryl Coupling Reaction *via* C-H bond Activation in Deep Eutectic Solvents

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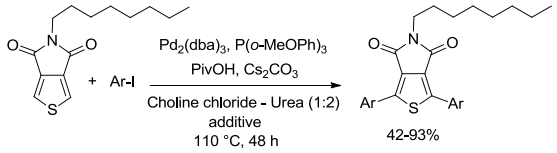
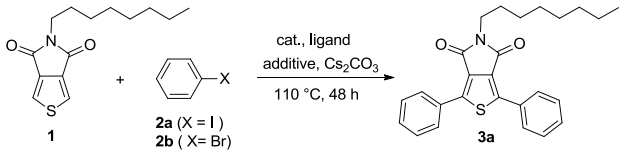
Supporting Information Placeholder



ABSTRACT: Direct arylation of 5-octylthieno[3,4-*c*]pyrrole-4,6-dione with a series of functionalized aryl iodides *via* C-H bond activation is demonstrated in a deep eutectic solvent made of choline chloride and urea in non-anhydrous conditions and without exclusion of air. This is the first demonstration of a thiophene-aryl coupling *via* direct arylation in deep eutectic solvents.

In the last two decades, palladium-catalyzed direct arylation *via* aromatic C-H bond activation[1] has been well recognized as a powerful aryl-aryl bond formation method and a convenient alternative to traditional cross-coupling reactions with organometallic reagents. The direct arylation reaction avoids the use of preformed organometallic reagents, which are sensitivite to air and moisture, expensive and, often, toxic. The major limitation of the direct arylation reaction is related to the use of highly polar but toxic solvents such as N,N-dimethylformamide, N-methyl-2-pyrrolidone and N,N-dimethylacetamide. Recently, research efforts have been spent to combine the advantages of direct arylation procedures with the benefits arising from the use of environmentally friendly reaction media. In this regard, dialkyl carbonates,[2] poly(ethyleneglycol)s (PEGs)[2b] and water[2b,3] have been recently investigated and successfully employed as solvents for palladium-catalyzed aromatic C-H bond activation reactions. Moreover, direct arylation protocols in ionic liquids (ILs) have attracted attention, due to their low vapor pressure and good solvent power towards organic and inorganic reagents.[4] As versatile alternatives to ILs, the deep eutectic solvents (DESs)[5] represent a class of environmentally friendly media that currently attracts considerable attention from the scientific community interested in the development of new green reaction protocols. DESs are mainly composed of quaternary ammonium salts complexed with an organic molecule that is typically a hydrogen bond donor such as urea, amides, acids, or polyols. Mixing these safe and inexpensive components, hydrogen-bond interactions give rise to an eutectic mixture with a melting point lower than those of the individual components and unusual solvent properties that are strongly influenced by hydrogen bonding. DESs have many properties in common with conventional ILs, such as low volatility and insensitivity to water, but they further offer very important advantages in view of large-scale synthetic applications, since they are typically less expensive, more synthetically accessible and less toxic.[6] Recently, DESs have been widely used as green and sustainable media as well as catalysts in many chemical processes,[7,8] including Pd-catalyzed cross-coupling reactions[8d-f] and polar organometallic-based processes.[8a-c] To the best of our knowledge, the direct arylation reaction in DESs has not been reported in the literature so far. In the frame of our studies on organometallic-based routes[9] and, recently, on direct arylation of heterocycles for the synthesis of molecular and polymeric organic semiconductors,[10] here we report the first example of palladium-catalyzed C-H bond arylation reaction using a DES. Here we have used a mixture of choline chloride and urea in 1:2 molar ratio, as a suitable reaction medium with lower environmental impact than conventional organic solvents. We investigated, as a model system, the double aromatic C-H activation reaction of 5-octylthieno[3,4-*c*]pyrrole-4,6-dione (TPD, **1**) with a series of aryl iodides. The TPD core is largely used as an electron withdrawing building block in the synthesis of low-band gap copolymers for organic electronics.[11] As a preliminary investigation, we explored the C-H activation and arylation reaction of **1** with iodo- or bromobenzene (**2a** and **2b**) yielding **3a** (Table 1). Herrmann-Beller catalyst (trans-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)) was initially used as the pre-catalyst due to its well-known high performance and selectivity in direct arylation reactions,[12] in the presence of Cs_2CO_3, P(*o*-MeOPh)$_3$ and pivalic acid (PivOH) as the base, the ligand and the additive, respectively. It is well known that pivalic acid have a beneficial effect on the rate of direct arylation due to the formation, in the basic reaction medium, of corresponding carboxylate anion able to assist the CDM pathway proposed for thiophenes.[13] The outcome of the reaction in different DESs was explored keeping constant the other reaction parameters (Table 1, entries 1-7) in non-anhydrous conditions and without exclusion of air. The use of less expensive "wet" reagents and solvents as well as the tolerance to oxygen are highly attractive features of this protocol.

Table 1. Optimization of the synthesis of 5-octyl-1,3-diphenyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione 3a.[a]



entry	additive	halide	catalyst	ligand	solvent	yield (%)[b]
1[c]	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	toluene	82
2	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	Decanoic acid - Tetraoctylammonium bromide (2:1)	50
3	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	α-CD (30% w/w) - DMU (70% w/w)	traces
4	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	Choline chloride - Glycerol (1:2)	23
5	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	Choline chloride - Ethylene glycol (1:2)	24
6	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	Choline chloride - 1,4-Butandiol (1:2)	6
7	PivOH	2a	Herrmann-Beller	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	35
8	PivOH	2a	Pd(OAc)$_2$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	6
9	PivOH	2a	$PdCl_2(PPh_3)_2$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	55
10	PivOH	2a	$PdCl_2(CH_3CN)_2$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	traces
11	PivOH	2a	$Pd(PPh_3)_4$	none	Choline chloride - Urea (1:2)	traces
12	**PivOH**	**2a**	**$Pd_2(dba)_3$**	**P(*o*-MeOPh)$_3$**	**Choline chloride - Urea (1:2)**	**82**
13[d]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	79
14[e]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	16
15[f]	none	2a	$CuCl_2$	phenantroline	Choline chloride - Urea (1:2)	5
16	PivOH	2a	$Pd_2(dba)_3$	none	Choline chloride - Urea (1:2)	0
17	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MePh)$_3$	Choline chloride - Urea (1:2)	24
18	PivOH	2a	$Pd_2(dba)_3$	PPh_3	Choline chloride - Urea (1:2)	55
19	PivOH	2a	$Pd_2(dba)_3$	S-Phos	Choline chloride - Urea (1:2)	24
20	PivOH	2b	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	13
21[g]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	43
22[h]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	30
23[i]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Urea (1:2)	20[j]
24[k]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Glycerol (1:2)	25
25[l]	PivOH	2a	$Pd_2(dba)_3$	P(*o*-MeOPh)$_3$	Choline chloride - Ethylene glycol (1:2)	6

[a] Unless specified, the C-H arylation was carried out as follows: TPD **1** (0.38 mmol), aryl halide (1.88 mmol), Pd-catalyst (5 mol %), phosphine (10 mol %), PivOH (30 mol %), Cs_2CO_3 (0.76 mmol) in choline chloride-urea (2.15 g-1.85 g, respectively) at 110 °C for 48 h; [b] Yields refer to isolated products; [c] Reaction carried out in anhydrous conditions and under nitrogen; [d] Reaction performed in the presence of Pd-catalyst (10 mol %); [e] Reaction performed in the presence of Pd-catalyst (2 mol %) and phosphine (4 mol %); [f] Reaction conditions: TPD **1** (0.38 mmol), $CuCl_2$ (40 mol %), phenanthroline (40 mol %), Cs_2CO_3 (1.52 mmol), iodobenzene (1.88 mmol) in choline chloride-urea (2.15 g-1.85 g, respectively) at 110 °C for 48 h; [g] Reaction quenched after 24 h; [h] Reaction performed using 1.14 mmol of aryl halide. [i] Reaction performed using 0.38 mmol of aryl halide. [j] Mono-coupling product was isolated in 15% yield. [k] Reaction performed in choline chloride-glycerol (2.15 g- 2.84 g, respectively). [l] Reaction performed in choline chloride-ethylene glycol (2.15 g- 1.91 g, respectively).

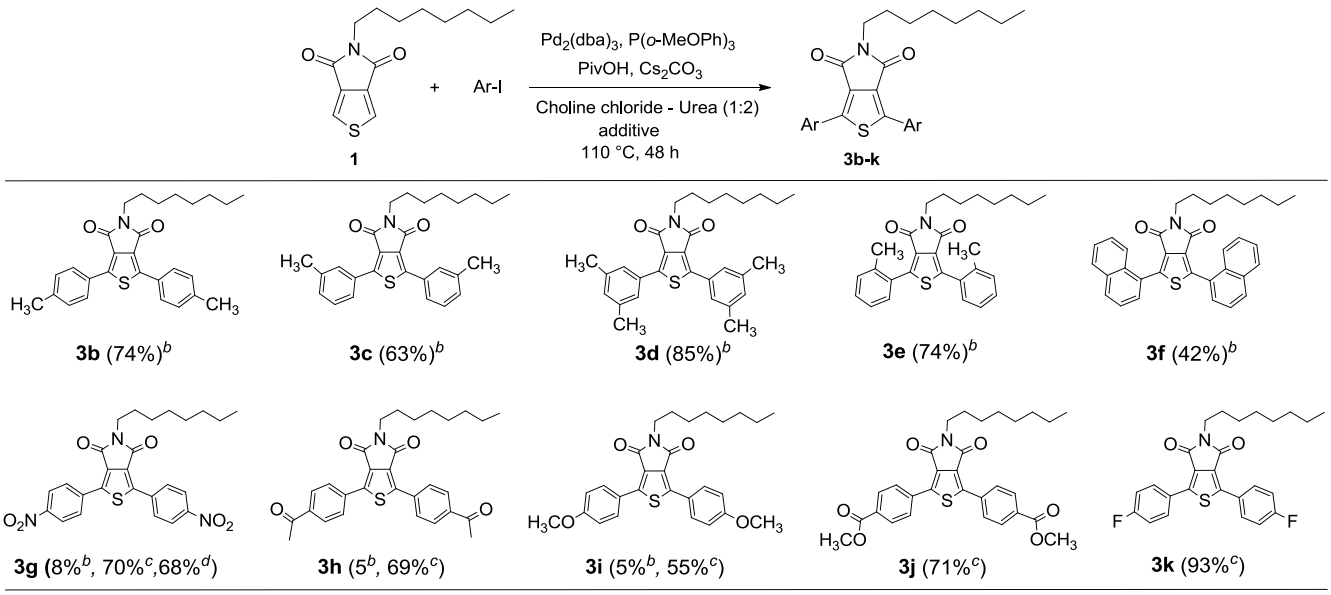
These experimental conditions are similar to those previously reported by Leclerc[14] in an efficient direct (hetero)arylation polymerization protocol in a water/toluene biphasic system. Since the use of non-polar organic conventional solvents is reported to be crucial in the direct C-H arylation of **1**,[15] we firstly used a hydrophobic DES consisting of a mixture of decanoic acid and tetraoctylammonium bromide in 2:1 molar ratio (entry 2). The coupling product **3** was isolated in 50% yield, which is considerably lower than the yield achieved in toluene (82%, entry 1). Furthermore, the use of hydrophobic DES required a complex purification protocol to isolate **3**. As expected, hydrophilic DESs were found to be much less effective, leading to low yields (entries 3-7), with the best results in a mixture of choline chloride and urea in 1:2 molar ratio (35%, entry 7). However, since hydrophilic DESs can be easily removed from the reaction mixture by dissolution in water, we decided to focus anyway on hydrophilic DESs trying to optimize the performances in the mixture of choline chloride and urea in which the higher yield of **3** was obtained. Both choline and urea are naturally occurring biocompatible and not hazardous compounds if released back to the environment, and they are inexpensive. This enables potentially benign, economically viable and scalable processes.[16] Therefore, the subsequent screening of palladium catalysts (entries 8-12, Table 1) was performed in a mixture of choline chloride and urea in relative molar ratio 1:2. Pd(II)- and Pd(0)-complexes, namely Pd(OAc)$_2$, $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, $Pd(PPh_3)_4$ and $Pd_2(dba)_3$, were tested as catalysts in 5 mol % amount with respect to the TPD substrate **1**, keeping the relative quantities of the base and the co-catalyst unalterated. Pd(OAc)$_2$, $PdCl_2(CH_3CN)_2$ and $Pd(PPh_3)_4$ were demonstrated to be much less effective than the Herrmann-Beller catalyst leading to unsatisfactory results (entries 8, 10, 11), whereas $PdCl_2(PPh_3)_2$ and $Pd_2(dba)_3$ exhibited higher efficiencies affording **3** in 55% (entry 9) and 82% yields (entry 12), respectively. No significant enhancement of the yield was observed increasing the amount of $Pd_2(dba)_3$ from 5 to 10 mol% (entry 13), while lowering the $Pd_2(dba)_3$ to 2 mol % loading resulted in a drastic decrease of the reaction yield (16%, entry 14). Cu-catalyzed direct C-H arylation was also explored following a protocol recently reported by Liu,[17] based on $CuCl_2$/phenantroline catalyst. In these conditions the expected product was isolated in very poor yield (5% yield, entry 15). Having selected $Pd_2(dba)_3$ (5 mol %) as the best catalyst, the role of the phosphine ligands was examined (entries 16-19). Under phosphine-ligand-free conditions, the formation of the desired product was not detected (entry 16). Low yields were obtained in the presence of P(*o*-MePh)$_3$, a less electron-rich ligand with steric hindrance similar to P(*o*-MeOPh)$_3$, (24% yield, entry 17), while using the less hindered PPh_3, the desired product was isolated in moderate 55% yield (entry 18). These results suggested that the presence of methoxy electron donating groups as in P(*o*-MeOPh)$_3$ is beneficial for a smooth reaction course, probably due

to its capacity to increase the electron density and the stability of the Pd complex in the reaction media. For this reason, the C-H arylation reaction was also carried out in the presence of the Buchwald ligand (S-Phos), a highly electron-rich and bulky dialkylarylphosphine bearing methoxy groups on the aryl moiety. However, S-Phos demonstrated to be far less effective than P(*o*-MeOPh)$_3$, affording **3** in 24% yield (entry 19). In this case it is likely that, even if electron rich ligands enhance the catalyst efficiency, steric hindrance on the palladium center suppresses its reactivity. The use of bromobenzene instead of iodobenzene also reduces the reaction yield (entry 20) probably as a result of lower reactivity of aryl bromides than aryl iodides. Similarly, shortening the reaction time to 24 h or decreasing the amount of the halide (3 equiv.) produced a significant decrease of the yield to 43% (entry 21) and 30% (entry 22), respectively. As shown in entry 23, it is not possible to promote the mono C-H activation of **1** using an equimolar ratio of **1** and iodobenzene (**3a** and mono-coupling product are isolated in yield of 20% and 15%, respectively). Finally, using the best catalytic conditions shown in entry 12, the C-H arylation of **1** with iodobenzene was carried out in choline chloride-glycerol (entry 24) and choline chloride-ethylene glycol (entry 25), hydrophilic DESs that have proven to be both markedly less effective than the choline chloride-urea mixture.

To investigate the substrate versatility with the synthetic protocol defined in the entry 12 of Table 1, we reacted TPD **1** in the same conditions with various aryl iodides. The results of this screening are shown in the Scheme 1. The thiophene-aryl coupling reactions *via* C-H activation proceeded with methyl- or dimethyl-benzeneiodides affording expected products in fair to good yields (63-85%). Conversely, only 42% yield was recorded using the sterically hindered 1-iodonaphtalene as the reaction partner. Other iodobenzenes bearing functional polar groups, such as nitro-, acetyl-, methoxy-, were also tested but a drastic decrease of the reaction yields was observed in all these cases. The addition of small amounts of conventional organic solvents to the previously optimized reaction protocol shown in entry 12 of Table 1 allows to overcome this critical issue. Both toluene and a more environmentally friendly additive, namely the cyclopentyl methyl ether (CPME),[18] already employed for Pd-catalyzed direct arylation of heteroaromatics,[19] were proven suitable to increase the reaction yields. As shown in the Scheme 1, a small volume of CPME (0.3 mL *vs* 3 mL of DES), produced a remarkable improvement of the yields in the coupling with *p*-nitroiodobenzene (70% *vs* 8%) and required a lower excess of aryl iodide with respect to reactions in pure choline chloride-urea mixture (3 *vs* 5 equiv). A similar result was obtained using toluene (0.3 mL *vs* 3 mL of DES) as an additive (68% yield). However, the use of CPME as the additive was preferred to preserve the environmentally friendly reaction medium. The expected products **3h** and **3i** were obtained from 1-(4-iodophenyl)ethanone and 1-iodo-4-methoxybenzene in good yields in the presence of CPME (69% and 55%, respectively) while they were isolated in traces in the reactions without additive. Good results (71% and 93%) were also obtained with aryl iodides functionalized with an ester group and a fluorine substituent leading to compounds **3j** and **3k**. Hence, the reaction appears to be tolerant of a variety of functional groups.

In conclusion, we have reported for the first time a thiophene-aryl direct coupling reaction *via* C-H bond activation in a deep eutectic solvent, a choline chloride-urea mixture, which is a green, convenient and inexpensive reaction medium. The reaction is performed in non-anhydrous conditions and without exclusion of air. For our experiments we have used TPD as the C-H activated substrate, in consideration of the interest of this aromatic moiety in the construction of push-pull molecular and polymeric semiconductors of interest in organic electronics and polymer solar cells. The addition of small amounts of CPME to the DES extends the usefulness of the synthetic protocol to coupling reactions with a number of functionalized aryl iodides. Studies aimed at the extension of such synthetic procedure to more complex materials, including small molecules and polymers for organic electronics, are currently underway in our laboratories.

Scheme 1. Synthesis of compounds 3b-k.[a]



[a] Yields refer to isolated products; [b] The C-H arylation was carried out without additive; [c] Reaction carried out in the presence of CPME; for comparison, the synthesis of **3g** was also carried out in pure CPME as the solvent (SI).[d] Reaction carried out in the presence of toluene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental procedures and spectral data for all new compounds (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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