Aryl ether synthesis via Ullmann coupling in non-polar solvents: effect of ligand, counterion, and base

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Abstract
An Ullmann coupling route to diaryl ethers, for use in non-polar solvents, employing 5 mol % of an air stable Cu (I) catalyst, $CuIPPh_3$, has been explored. The *O*-arylation process occurred smoothly in non-polar solvents, toluene or xylene, with the inexpensive base K_2CO_3. The highest yields were achieved with electron poor aryl bromides and electron rich phenols. The reactions were highly selective toward bromide over chloride in multiple halogenated aromatics.

Keywords: Ullmann Coupling, O-arylation, aryl ether synthesis, copper (I) catalyst

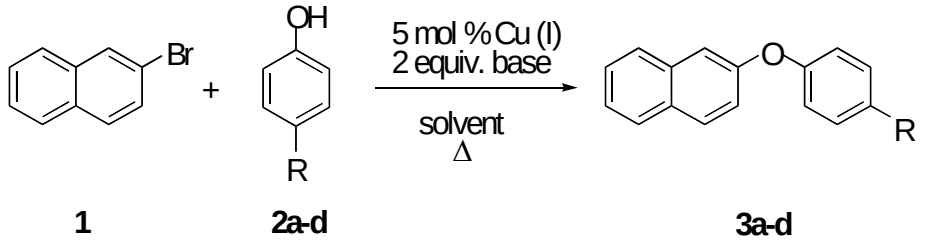
Introduction

The synthesis of aryl ethers is typically achieved via a nucleophilic aromatic substitution, NAS, process or transition metal catalyzed Ullmann-type[1, 2] and Hartwig[3-5] or Buchwald-type[6,7] *O*-arylation reactions. The NAS approach requires the use of phenoxide to displace aryl fluorides or chlorides that are activated by strong electron withdrawing groups, EWG, located in the *ortho*, *para*, or, in rare cases, *meta* positions. The requirement of the presence of an EWG is a severe limitation on the variety of aryl ethers available through NAS chemistry. In contrast, the transition metal catalyzed *O*-arylation reactions of phenoxides with aryl halides typically do not require the presence of an EWG and the reactions are highly efficient with aryl iodides and bromides.

Due to the high costs associated with palladium based catalyst systems, the past decade has seen the development of a multitude of copper catalysts for Ullmann-type *O*-arylation reactions[8-17] and the area has been thoroughly reviewed.[1, 2, 18, 19] The effectiveness of these catalyst systems for the synthesis of aryl ether bonds is highly dependent on the substrate, ligand, solvent, base, and reaction temperature. During the course of a recent investigation of poly(arylene ether)

synthesis, it became necessary to prepare a variety of asymmetric diaryl ether monomers and we chose to take advantage of the versatility of *O*-arylation reactions.

Copper catalyzed *O*-arylation reactions are typically carried out in polar, aprotic solvents, however, given the requirement to utilize non-polar solvents, the use of toluene and xylene was explored. There are limited reports of Cu-catalyzed *O*-arylation reactions being performed in toluene or xylene.[8, 10, 13, 17] To that end we screened the catalytic behavior of a wide range of air stable, readily available and low cost Cu (I) complexes: $CuXPPh_3$ and $CuX(PPh_3)_3$ where X = Cl, Br, or I).[10, 20, 21, 22] (Scheme 1, Table 1). A variety of reaction conditions were studied in order to evaluate the effects of catalyst, base, solvent, reaction temperature and the electronic properties of both the substrate and phenoxide.



Scheme 1. Coupling reactions of 2-Bromonaphthlene and *p*-cresol were used in the screening of Cu(I) catalysts.

Results and Discussion

Initial screening of a series of Cu (I) catalysts (5 mol %) was carried out using 2-bromonaphthalene, **1**, and *p*-cresol, **2a**, as the reaction partners, in toluene at 100 ºC with K_2CO_3 as the base and the results are listed in Table 1. To the best of our knowledge, only a few successful Cu-catalyzed *O*-arylation reactions have been carried out in non-polar solvents such as toluene, however, few of these have utilized the inexpensive K_2CO_3 as the base and typically required at least 10 mol % catalyst to be effective.[8, 17] The use of ultrasound, under solventless conditions, has been reported to provide excellent yields of aryl ether using CuI and K_2CO_3.[23] In the current study, use of CuI, in the absence of any ligand, using toluene as the solvent, afforded **3a** in an unsatisfactorily low yield, 15.5%, however, when the corresponding $CuIPPh_3$ system was applied, a significantly higher yield, 60.2%, was achieved. Although the use of $CuIPPh_3$ for C-C coupling reactions has been reported,[24] it has not previously been applied to the synthesis of aryl ethers. Interestingly, when $CuBrPPh_3$ and $CuClPPh_3$ were utilized under the same conditions the yields decreased significantly to 43.5 and 30.7%, respectively. The use of $CuI(PPh_3)_3$, $CuBr(Ph_3P)_3$ and $CuCl(Ph_3P)_3$ provided only modest yields of **3a**, 6.2, 7.0 and 4.5 %, respectively. These results indicate that the choice of counterion and number of Ph_3P ligands is extremely important when the *O*-arylation reactions are carried out in non-polar solvents. With

optimized conditions in hand ($CuIPPh_3$, toluene, K_2CO_3) we turned our attention to the effects of solvent, counterion for CO_3^{2-}, and phenoxide structure (Table 2).

Table 1. Screening of various copper (I) catalysts for Ullmann coupling of 2-bromonaphtalene **1** and *p*-cresol **2a** at 100 ^oC for 24 hours. All reactions utilized 5 mol % of the copper (I) source

Entry	Base	Catalyst	% Yield (GC/MS)
1	K_2CO_3	CuI	15.5
2	K_2CO_3	$CuIPPh_3$ [a]	60.2
3	K_2CO_3	$CuBrPPh_3$[a]	43.5
4	K_2CO_3	$CuClPPh_3$[a]	30.7
5	K_2CO_3	$CuI(PPh_3)_3$	6.2
6	K_2CO_3	$CuBr(PPh_3)_3$	7.0
7	K_2CO_3	$CuCl(PPh_3)_3$	4.5

[a]Simplified molecular structures of *tetrakis*-[halotriphenyl phosphine copper(I)] were used here and molecular weights were calculated based on the simplified structure.

The carbonate base chosen for the reaction had a tremendous impact on the yield. Entries 1, 2, and 3 (Table 2) indicate that, in toluene at 100 ºC, potassium afforded the highest yield, cesium provided only a 10% yield, and sodium was totally ineffective. The reason for these observations is not well understood, however, it appears that potassium possesses the optimum size, hardness, and solubility for this particular catalyst system. The reaction is much more effective in non-polar solvents such as toluene or *o*-xylene (entries 2 and 8) which afforded 58.3 and 67.9% yield, respectively. It should be noted that the reaction in *o*-xylene was carried at with a reaction temperature of 140 °C which may help to explain the higher yield observed relative to the result in toluene. More polar solvents including NMP and NMP/toluene mixtures (entries 4 and 7) were highly ineffective providing none and 3 % yield, respectively. Solvents with the ability to coordinate to the metal center via oxygen atoms also proved to be less than ideal for $CuIPPh_3$, as anisole and 1,4-dioxane (entries 5 and 6) also provided no perceptible yields of product.

The presence of electron donating groups on the phenoxide typically leads to improved yields while the presence of electron withdrawing groups hampered the reaction (Scheme 1, Table 3). For example, entries 1 (CH_3 - donor), 2 (H - neutral), 3 (F – weak withdrawing), and 6 (CN – strong withdrawing) indicate that strong withdrawing groups decrease the rate of, or hinder the reaction considerably. Some improvements to the yield of **3c**, using 4-fluorophenol, were achieved when the concentrations of the reagents were tripled (29.2 versus 5%) or when *o*-xylene was used as the solvent and the reaction temperature was increased to 140 ºC (with the same concentration as entry 4), which afforded a 46.8% yield of **3c**. The nitrile group, while strongly withdrawing, may also serve to alter the reactivity of the catalyst via a coordination process through its nitrogen atom.

Table 2. Effects of solvent and base on the $CuIPPh_3$ catalyzed Ullmann coupling reactions of 2-bromonaphthalene with *p*-cresol at 100 °C for 24 hours

Entry	Base	Solvent	Isolated Yield (%)
1	Na_2CO_3	Toluene	0
2	K_2CO_3	Toluene	58.3
3	Cs_2CO_3	Toluene	10.7
4	K_2CO_3	Toluene/NMP (10:1)	3.0
5	K_2CO_3	Anisole	0
6	K_2CO_3	1,4-dioxane	0
7	K_2CO_3	NMP	0
8	K_2CO_3	*o*-Xylene	67.9 [a]

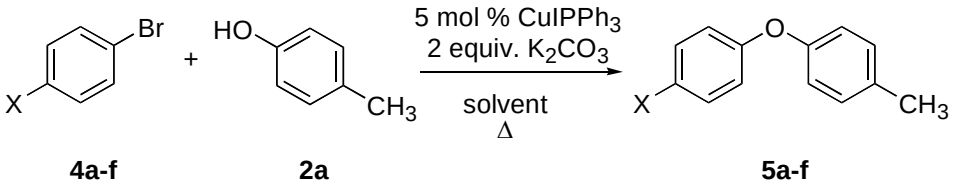
[a]Reaction was carried out at 140 °C.

Table 3. Results of $CuIPPh_3$ catalyzed Ullmann coupling reaction of 2-bromonaphthalene with various phenols at 100 °C for 24 hours

Entry	R	Base	Solvent	Product	Isolated Yield (%)
1	*p*-CH_3 (**2a**)	K_2CO_3	Toluene	**3a**	58.3
2	H (**2b**)	K_2CO_3	Toluene	**3b**	14.8
3	*p*-F (**2c**)	K_2CO_3	Toluene	**3c**	5.2
4	*p*-F (**2c**)	K_2CO_3	Toluene	**3c**	29.4 [a]
5	*p*-F (**2c**)	K_2CO_3	*o*-Xylene	**3c**	46.8[b]
6	*p*-CN (**2d**)	K_2CO_3	Toluene	**3d**	0

[a]Reaction was carried out at 100 °C with triple the normal concentration.
[b]Reaction was carried out at 140 °C with triple the normal concentration.

The electronic properties of the aryl bromide also played a critical role in the success of the *O*-arylation process and the results of reactions using **2a** with a variety of aryl bromides are summarized in Table 4 (Scheme 2). Electron withdrawing groups (entries 1-2) lead to higher yields of diaryl ethers while the weakly donating methyl group (entry 6) afforded only a 21.4 % yield. The lower yield for bromobenzene **4d** versus bromotoluene **4f** may have resulted from the loss of starting material via evaporation. The strongly withdrawing nitrile group did not lead to a significant enhancement of yield, possibly due to a competing coordinative process with the copper catalyst. Interestingly, the presence of a conjugated biphenyl system (entry 3) afforded a substantially higher yield, 67.9%, than aryl bromides with stronger electron withdrawing groups. At this point it is not possible to differentiate between inductive effects and resonance effects as evidenced by the reasonable yield provided with 4-bromoanisole which carries the inductively withdrawing, but donating by resonance methoxy group.



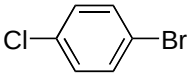
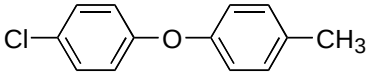
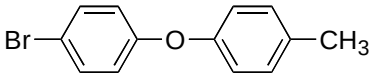
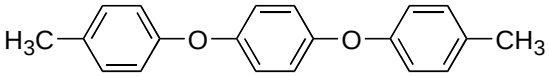
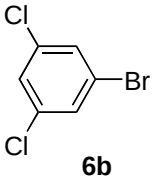
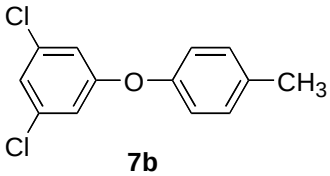
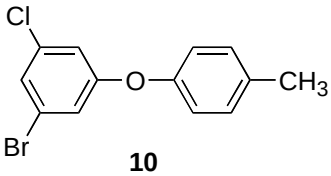
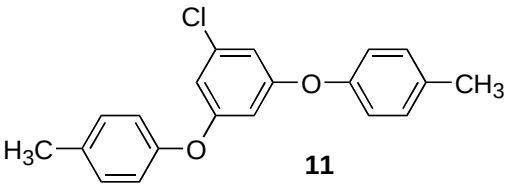
Scheme 2. Ullmann Coupling reactions of various aryl bromides with *p*-cresol.

Table 4. Effect of the electronic properties of the aryl bromide on the $CuIPPh_3$ catalyzed Ullmann coupling reaction with *p*-cresol at 100 ^oC for 24 hours

Entry	X		Product	Isolated Yield (%)
1	p-F	**4a**	**5a**	54.4
2	p-CN	**4b**	**5b**	44.0
3	p-Ph	**4c**	**5c**	67.9
4	H	**4d**	**5d**	16.3
5	p-OCH_3	**4e**	**5e**	53.7
6	p-CH_3	**4f**	**5f**	21.4

The selectivity in aryl halides containing both chloride and bromide groups was probed via the reaction of **2a** with 1-bromo-4-chlorobenzene, **6a**, as well as 1-bromo-3,5-dichloro benzene, **6b** (Table 5). With **6a,** the selectivity of coupling at the bromide site was approximately 35:1, while with **6b**, the selectivity was > 50:1 despite the presence of two chloro groups; only 1 % or less of any disubstituted products was observed. In part, these observations may be due to relative positions of the chloro groups to the bromo group. In **6a**, the chloro group is inductively electron withdrawing, but donating via resonance whereas in **6b**, the chloro groups can only participate via an inductive pathway. Thus, it appears that the reaction yield and selectivity can be enhanced significantly by the presence of inductively withdrawing groups.

Table 5. Selectivity toward the bromo site over the chloro site in Ullmann coupling reactions of multiple halogenated aromatic compounds with *p*-cresol

Entry	Aryl Halide	Product	GC-Yield[a] (%)	Isolated Yield (%)
1	 **6a**	 **7a**	66.9	48.3
		 **8**	1.9	0
		 **9**	Trace (<1)	0
2	 **6b**	 **7b**	90.2	64.8
		 **10**	Trace (<1)	0
		 **11**	1.02	0

[a] GC yield was uncalibrated.

Conclusions

In summary, we have thoroughly explored the effect of ligand, counterion, and base on an *O*-arylation procedure carried out in non-polar solvents. A procedure that utilizes 5 mol % of a readily available catalyst, $CuIPPh_3$, proceeded in moderate to good yields with the inexpensive base, K_2CO_3, in non-polar solvents such as toluene or xylenes. The presence of electron withdrawing groups on the aryl bromide component enhances the reaction while their presence on the phenol retards it. The new procedure provides the corresponding symmetrical or unsymmetrical diaryl ethers in moderate to good yields. The preference for reaction of aryl bromides versus aryl chlorides was quite high. Significant improvements in product yield can be achieved by increasing the reaction temperature and concentration of reagents.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 300 MHz instrument operating at 300 and 75.5 MHz, respectively; samples were dissolved in chloroform-*d*. Unless otherwise noted, all reagents were used without any further purification. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN. Melting points were determined using a MEL-TEMP and are uncorrected. GC/MS spectra were obtained using a Hewlett Packard HP 6890 GC- system with an HP 5972 mass selective detector.

Iodo-*tris*-(triphenylphosphine)copper(I) $Cu(PPh_3)_3I$ was synthesized according to the reported literature procedure.[22] In a 25 mL flask were placed 0.7866 g (3.0 mmol) of triphenylphosphine and 10 mL of chloroform. The resulting mixture was heated to reflux at which point 0.1904 g (1.0 mmol) of copper (I) iodide was added slowly in small portions. After the addition of copper (I) iodide, the mixture was held at reflux for 2 hours, cooled to room temperature and 0.93 g (95 % yield) of white crystals were collected via filtration. The product was used without further purification.

Bromo-*tris*-(triphenylphosphine)copper(I) $Cu(PPh_3)_3Br$ was synthesized by a slightly modified literature procedure.[20] In a 1000 mL Erlenmeyer flask equipped with a Teflon stir bar were placed 380 mL of ethanol and 22.28 g (85 mmol) of triphenylphospine. The mixture was slowly heated until all of the triphenylphosphine dissolved, at which point 4.46 g (20 mmol) of Cu (II) bromide was added in small portions. The resulting heterogeneous mixture was stirred for 10 minutes and the flask was allowed to cool to ambient temperature. The reaction mixture was then filtered via a Buchner funnel to isolate the desired compound as a white solid. After washing repeatedly with ethanol and then diethyl ether the resultant white solids were dried under vacuum to give 18.4 grams (99%, based on $CuBr_2$) of product with a m.p. 166-168 ^oC (lit. [20] 167 ^oC.)

Chloro-*tris*-(triphenylphosphine)copper(I) $Cu(PPh_3)_3Cl$ was obtained by the same procedure as the synthesis of bromo-*tris*-(triphenylphosphine) copper (I) with the exception that copper (II) chloride dihydrate was used instead of copper (II) bromide. The resulting white solid (98% yield) had a m.p. 166-168 ^oC (lit. [20] 172 ^oC).

Tetrakis-[iodotriphenylphosphinecopper(I)] $[CuIPPh_3]_4$ was synthesized according to the literature procedure.[21] A solution of 5.350 g (20.4 mmol) of triphenylphosphine, dissolved in 80 mL acetonitrile, was slowly added to a solution of 3.809 g (20.0 mmol) of copper (I) iodide dissolved in 400 mL of acetonitrile. After a few seconds, the desired compound started to precipitate. The mixture was stirred for 1 h further and the solid was isolated by filtration, washed with acetonitrile, and dried under vacuum to afford 8.72 g (87% yield) of the desired product as a white solid with a mp of 263-265 ^oC.

Tetrakis-[bromotriphenylphosphinecopper(I)] $[CuBrPPh_3]_4$. The title compound was obtained by a slightly modified literature procedure.[20] In a 100 mL round-bottomed flask were placed 0.669 g (3 mmol) of copper (II) bromide and 30 mL of ethanol. The reaction mixture was heated to reflux and 1.180 g (4.5 mmol) of triphenyl phosphine were added in small portions. Upon complete addition, the mixture was kept at reflux for an additional 30 minutes. After cooling to room temperature, the resulting white solids were collected by filtration to afford 1.06 g (87.2% yield) of the desired product, mp 240 ^oC (lit. [20] 248 ^oC).

Tetrakis-[chlorotriphenylphosphinecopper(I)] $[CuClPPh_3]_4$. was obtained by a slightly modified literature procedure.[20] In a 100 mL round-bottomed flask were placed 1.71 g (10 mmol) of copper (II) chloride dihydrate and 90 mL of ethanol. The resulting mixture was heated to reflux and 3.93 g (15 mmol) of triphenyl phosphine was added in small portions. After complete addition, the mixture was maintained at reflux for 30 minutes. After cooling to room temperature, the resulting white solids were collected by filtration to afford 3.60 g (99% yield) of product, mp 240-242 ^oC (lit. [20] 240 ^oC).

General procedure for the synthesis of aromatic ethers

To a 100 mL three necked round-bottomed flask equipped with a Teflon stir bar, reflux condenser and nitrogen inlet were added 2 mmol aromatic bromide, 3 mmol phenol, 0.1 mmol catalyst, 4 mmol base and 5 mL solvent. The flask was purged with nitrogen for 10 minutes before being immersed into an oil bath which was preheated to 100 °C. The reaction mixture was allowed to stir at 100 °C for 24 hours. After cooling to room temperature, 50 mL of hexanes were added and the mixture was allowed to stir for 1 hour at which point the mixture was filtered to remove any remaining solids. The solvents were removed via rotary evaporation to provide a colorless oil, which was purified via column chromatography (silica gel) using hexanes as the eluent. The final product was obtained after removing the hexanes and drying *in vacuo*.

2-(*p*-Tolyloxy)naphthalene (3a). (58.3 %) was obtained as a white solid, mp 41-42 ^oC (lit. [25] 41-42.3 ^oC). ^1H NMR (300 MHz, $CDCl_3$) *δ:* 2.32 (s, 3H), 6.96 (d, *J*= 8Hz, 2H), 7.13 (d, *J*=8 Hz, 2H), 7.21-7.41 (m, 4H), 7.61-7.64 (m, 1H), 7.74-7.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ:*

20.7,113.2, 119.3, 119.7, 124.4, 126.4, 127.0, 127.7, 129.7, 129.9, 130.3, 133.1, 134.3, 154.6, 155.7. The ^{1}H and ^{13}C NMR data were consistent with the literature data. [25]

2-Phenoxynaphthalene (3b). (14.8 %) was obtained as a white solid, mp 45-46 ^{o}C (lit. [25] 46-47 ^{o}C); The ^{1}H and ^{13}C NMR spectra matched the literature data. [26]

2-(4-Fluorophenoxy)naphthalene (3c). (46.8 %) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ:* 7.02-7.04 (m, 4H), 7.21-7.24 (m, 2H), 7.35-7.46 (m, 2H), 7.21-7.41 (m, 2H), 7.65-7.68 (m, 1H), 7.79-7.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ:* 113.3, 116.4 (d, *J*=23Hz), 119.5, 120.8 (d, *J*=8Hz), 124.7, 126.7, 127.1, 127.7, 129.9, 130.1, 134.3, 152.8 (d, *J*=2.5Hz), 155.5, 158.9 (d, *J*=240Hz). Anal. Calc. for $C_{16}H_{11}FO$: C, 80.66%; H, 4.65%. Found: C, 80.99%; H, 5.08%.

4-Fluoro-4'-methyldiphenyl ether (5a). (54.4 %) was obtained as a nearly colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ:* 2.27 (s, 3H), 6.83 (d, J=8.7Hz, 2H) 6.89-6.93 (m, 4H), 7.07 (d, *J*=8.7 Hz, 2H). The ^{13}C NMR spectrum matched the literature data.[27]

4-(*p*-Tolyloxy)benzonitrile (5b). (44.0 %) was obtained as a light yellow solid with a mp of 71.5-73.5 ^{o}C. The ^{1}H and ^{13}C NMR spectra match literature data. [28]

4-*p*-Tolyloxybiphenyl (5c). (67.9 %) was obtained as a white solid, mp 97-98 ^{o}C (lit. [29] 96-98 ^{o}C). ^{1}H NMR (300 MHz, CDCl3) *δ:* 2.32 (s, 3H), 6.95 (d, *J*=8.4 Hz, 2H), 7.02 (d, *J*=8.7Hz, 2H), 7.13 (d, *J*=8.1 Hz, 2H), 7.26-7.32 (m, 1H), 7.37-7.43(m, 2H), 7.49-7.55(m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ:* 20.7, 118.4, 119.2, 126.8, 126.9, 128.3, 128.7, 130.3, 133.0, 135.8, 140.5, 154.6, 157.4.

4-Methyldiphenyl ether (5d). (16.3 %) was obtained as a colorless oil; the ^{1}H and ^{13}C NMR spectra matched the literature data. [30]

4-Methoxy-4'-methyldiphenyl ether (5e). (53.7%) was obtained as a white solid, mp 49-50 ^{o}C (lit. [31] 49-50 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) *δ:* 2.28 (s, 3H), 3.73 (s, 3H), 6.81-6.85 (m, 4H), 6.91-6.94 (m, 2H), 7.06 (d, J=8.4Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ:* 20.5, 55.4, 114.7, 117.7, 120.2, 130.0, 131.8,150.7, 155.5, 156.0.

Di(*p*-Tolyl) ether (5f). (21.4 %) was obtained as a white solid, mp 47-49 ^{o}C (lit. [32] 50 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$) *δ:* 2.32 (s, 6H), 3.73 (s, 3H), 6.87 (d, *J*=8.4Hz, 4H), 7.06 (d, *J*=8.4Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ:* 20.6, 118.5, 130.1, 132.3, 155.3.

4-Chloro-4'-methyldiphenyl ether (7a). (48.3 %) was obtained as a white solid, mp 53-54^{o}C (lit. [6] 47.5-49 ^{o}C). The ^{1}H and ^{13}C NMR spectra matched the literature data.[6]

3,5-Dichloro-4'-methyldiphenyl ether (7b). (64.8 %) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ:* 2.32 (s, 3H), 6.91 (d, *J*=1.8 Hz, 2H), 6.89 (d, *J*=8.4 Hz, 2H), 6.98 (t, *J*=1.8 Hz, 1H), 7.13 (d, *J*=8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ:* 20.7, 116.2, 119.9, 122.6, 130.5, 134.4, 135.5, 152.9, 159.4. Anal. Calc. for $C_{13}H_{10}Cl_2O$: C, 61.68%; H, 3.98%. Found: C, 62.01%; H, 4.15%.

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