

A PEG₁₀₀₀-DAIL[CdCl₃]-toluene temperature-dependent biphasic system that regulates homogeneously catalyzed C–O coupling of organic halides with phenols and alcohols under ligand-free conditions

Yu Lin Hu, Xiao Yun Ma, and Ming Lu

Abstract: An efficient, experimentally simple, and convenient procedure for the C–O coupling of organic halides with phenols and alcohols in a PEG₁₀₀₀-DAIL[CdCl₃]-toluene temperature-dependent biphasic system has been developed. The product can be easily isolated by a simple decantation, and the catalytic system can be recycled and reused without loss of catalytic activity.

Key words: C–O coupling, organic halide, ionic liquid, thermoregulated ionic liquid biphasic system.

Résumé : On a mis au point une méthode commode, efficace et expérimentalement simple de faire un couplage C–O d'halogénures organiques avec des phénols et des alcools dans un système biophysique PEG₁₀₀₀-DAIL[CdCl₃]-toluène qui varie avec la température. Les produits peuvent être facilement isolés par une simple décantation et le système catalytique peut être recyclé et réutilisé sans perte d'activité catalytique.

Mots-clés : couplage C–O, halogénure organique, liquide ionique, système biphasique de liquide ionique soumis à une thermorégulation.

[Traduit par la Rédaction]

Introduction

The carbon–oxygen bond-forming reaction is one of the most fundamental transformations because of the large number of applications of the resulting compounds (ethers) in organic, pharmaceutical, and polymer chemistry.^{1,2} The usual synthetic methods for such a conversion include the Williamson ether synthesis,^{3,4} Ullmann coupling,^{5,6} palladium-catalyzed couplings of aryl halides,^{7–10} C–O couplings of arylboronic acids with phenols,^{11,12} iron-catalyzed couplings,^{13,14} and other coupling reactions.^{15–17} However, these protocols, are generally associated with one or more disadvantages, such as long reaction times, high reaction temperatures, high catalyst loading, tedious work-up procedures, poor substrate scope, moisture sensitivity, costly metal catalysts, difficulty of catalyst recovery, and environmental toxicity. To overcome these limitations, some significant modifications have been made for the Ullmann ether synthesis during the past few years. It has been observed that certain additives, such as 8-hydroxyquinoline,¹⁸ *N,N*-dimethyl glycine,¹⁹ 1-naphthoic acid,²⁰ 2,2,6,6-tetramethylheptane-3,5-dione,²¹ tripod ligands,²² Schiff base,²³ PPAMP,²⁴ triphenylphosphine,²⁵ neocuproine,²⁶ nitrogen-based multidentate ligands,²⁷ phosphorus dendrimer ligands,²⁸ and some cop-

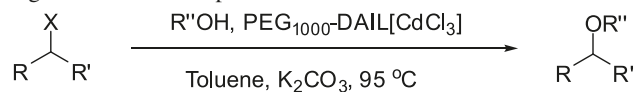
per(I) complexes,²⁹ can accelerate the rate of the reactions, and therefore, the reactions can be performed under milder conditions. Whilst these remarkable advances in the field of Ullmann coupling are exceedingly beneficial, most of the reactions still require long reaction times of more than 24 h, elevated reaction temperatures, and high catalyst loading, and entail difficulties in recycling of the catalyst. Therefore, the introduction of new and environmentally benign procedures that address these drawbacks continues to be of value and interest.

The room-temperature ionic liquid, a kind of environmentally friendly solvent and catalyst because of its adjustable physical and chemical properties, got broad attention from scholars in various fields such as synthesis, catalysis, separation, and electrochemistry.^{30,31} In view of both the advantages and disadvantages of homogeneous and heterogeneous catalysis, and to improve catalyst recovery, some novel temperature-dependent ionic liquid biphasic catalytic systems have been reported recently,^{32–34} and in our research project group, Luo and co-workers very recently reported a new PEG₁₀₀₀-based dicationic ionic liquid (PEG₁₀₀₀-DAIL) exhibiting temperature-dependent phase behavior with toluene, and applied it successfully in a one-pot synthesis of

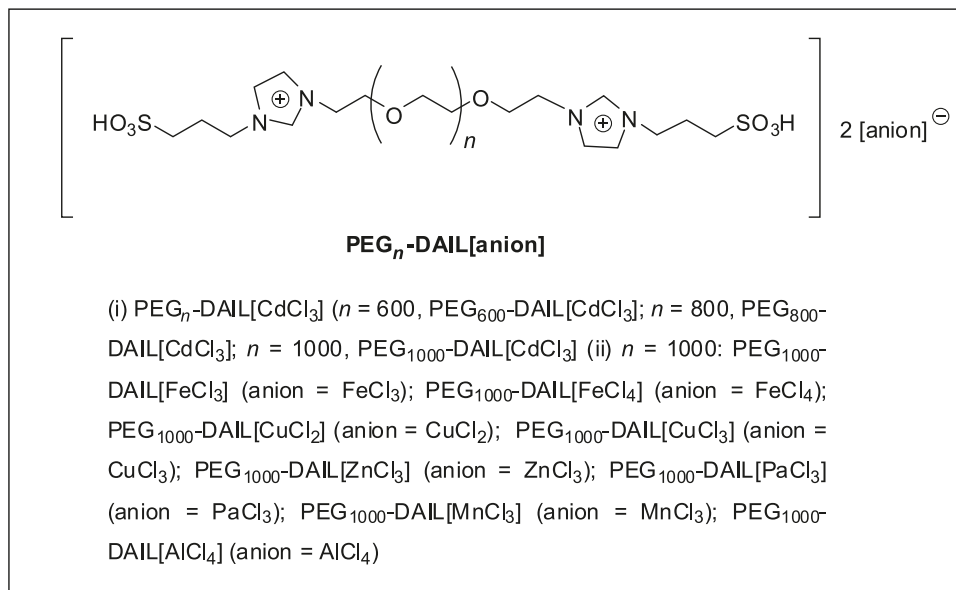
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Scheme 1. Carbon–oxygen coupling of organic halides with phenols and alcohols.

R, R'' = aryls, alkyls; R' = H, aryls, alkyls



benzopyrans.³⁵ They found that the ionic liquid showed some advantages such as high conversions and selectivity, stability at high temperatures, and reusability in the reaction, and it provides a novel route for the separation and recycling of catalysts. Herein, we report a convenient and efficient procedure for the C–O coupling of organic halides with both phenols and alcohols to synthesize aryl ethers catalyzed by PEG₁₀₀₀-based dicationic ionic liquid (PEG₁₀₀₀-DAIL[CdCl₃]) under ligand-free conditions (Scheme 1).

Results and discussion

The investigation was initiated by using the coupling of 4-iodonitrobenzene with phenol as a model reaction (Table 1). At first, catalysts of different types of ionic liquids were tested in this model reaction (Table 1, entries 1–11) with K₂CO₃ as base, and the results showed that PEG₁₀₀₀-DAIL[CdCl₃] demonstrated the best performance (Table 1, entry 3). No product was detected in the absence of ionic liquid as a catalyst (Table 1, entry 12). For comparison on the efficiency of different bases in the couplings (Table 1, entries 3 and 14–18), both K₂CO₃ and Cs₂CO₃ were found to be effective bases for this aryl ether formation (Table 1, entries 3 and 15). Other bases, including K₃PO₄, Na₂CO₃, and some organic bases such as Et₃N and pyridine, gave lower yields (Table 1, entries 14 and 16–18). The bases had a large effect on the reaction and were crucial for achieving high yields because a much lower yield (65%) was obtained in the absence of a base (Table 1, entry 13). Therefore, the combination of less expensive base K₂CO₃ and PEG₁₀₀₀-DAIL[CdCl₃] was chosen as the optimal condition for further exploration.

In addition, the catalytic system could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Fig. 1). The recycling process involved the removal of the top oil layer (toluene, containing product) by decantation. The bottom aqueous layer (PEG₁₀₀₀-DAIL[CdCl₃]) was concentrated under vacuum and then filtered. Fresh substrates and toluene were then recharged with the residual PEG₁₀₀₀-DAIL[CdCl₃] and the mixture was heated to react once again.

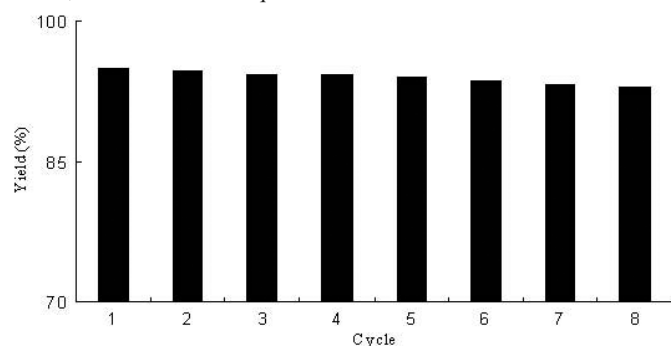
With these optimized reaction conditions in hand, we employed a variety of organic halides in an attempt to synthesize different aryl ethers, as shown in Table 2. Various types of aryl, benzylic, allylic, and aliphatic halides were successfully converted to the corresponding ethers with phenol (Table 2, entries 1–24), whereas the aliphatic halides were less reactive, and higher reaction temperature and longer reaction time were needed to reach good yields (Table 2, entries 16 and 17). Aryl halides with electron-withdrawing substituents (Table 2, entries 6–10, 12, 13, and 15) were more reactive than those with or without electron-donating substituents (Table 2, entries 1–5, 11, and 14). It was also observed that the reactions were faster with benzylic and allylic halides (Table 2, entries 18–24) than with aryl halides (Table 2, entries 1–15). Moreover, the halogen sources greatly influenced the reaction. Taking aryl halides as an example, the reaction activity decreased in the order iodobenzene > bromobenzene > chlorobenzene (Table 2, entries 1, 11, and 14). In addition, to examine a greater range of hydroxy substrates to better illustrate the scope and limitations of this protocol, we investigated the reactions with phenols and alcohols using 4-iodonitrobenzene as a representative organic halide (Table 2, entries 25–30). The experimental

Table 1. Optimization studies for the coupling of 4-iodonitrobenzene with phenol.

Entry	Ionic liquid	Base	Time (h)	Yield (%) ^a
1	PEG ₆₀₀ -DAIL[CdCl ₃]	K ₂ CO ₃	8	87
2	PEG ₈₀₀ -DAIL[CdCl ₃]	K ₂ CO ₃	8	92
3	PEG ₁₀₀₀ -DAIL[CdCl ₃]	K ₂ CO ₃	8	95
4	PEG ₁₀₀₀ -DAIL[FeCl ₃]	K ₂ CO ₃	8	82
5	PEG ₁₀₀₀ -DAIL[FeCl ₄]	K ₂ CO ₃	8	91
6	PEG ₁₀₀₀ -DAIL[CuCl ₂]	K ₂ CO ₃	8	84
7	PEG ₁₀₀₀ -DAIL[CuCl ₃]	K ₂ CO ₃	8	81
8	PEG ₁₀₀₀ -DAIL[ZnCl ₃]	K ₂ CO ₃	8	89
9	PEG ₁₀₀₀ -DAIL[PdCl ₃]	K ₂ CO ₃	8	86
10	PEG ₁₀₀₀ -DAIL[MnCl ₃]	K ₂ CO ₃	8	74
11	PEG ₁₀₀₀ -DAIL[AlCl ₄]	K ₂ CO ₃	8	71
12	—	K ₂ CO ₃	24	0
13	PEG ₁₀₀₀ -DAIL[CdCl ₃]	—	14	65
14	PEG ₁₀₀₀ -DAIL[CdCl ₃]	K ₃ PO ₄	8	88
15	PEG ₁₀₀₀ -DAIL[CdCl ₃]	Cs ₂ CO ₃	8	94
16	PEG ₁₀₀₀ -DAIL[CdCl ₃]	Na ₂ CO ₃	8	85
17	PEG ₁₀₀₀ -DAIL[CdCl ₃]	Et ₃ N	8	76
18	PEG ₁₀₀₀ -DAIL[CdCl ₃]	Pyridine	8	81

Note: DAIL, dicationic ionic liquid. The reactions were carried out with 4-iodonitrobenzene (2.4 mmol), phenol (2 mmol), base (2 mmol), and ionic liquid (0.4 mmol) in toluene (5 mL) at 95 °C.

^aIsolated yield.

Fig. 1. Repeating reactions using recovered PEG₁₀₀₀-DAIL[CdCl₃]. DAIL, dicationic ionic liquid.

results indicated that substituents on the phenol ring have a great influence on the reaction. For example, substitution of a methyl or methoxy group at the position of phenol incurs a reduction in both yield and reaction rate (Table 2, entries 25 and 26). Finally, the reactions are faster with phenols (Table 2, entries 25–28) than with alcohols (Table 2, entries 29 and 30).

The excellent reaction results of the catalytic system suggest that the coupling among organic halides, phenols, or alcohols, K₂CO₃, toluene, and PEG₁₀₀₀-DAIL[CdCl₃] has a particular catalytic process, which is schematically depicted in Fig. 2. Before the coupling, there exists an obvious biphasic system, and the bottom layer consists of PEG₁₀₀₀-DAIL[CdCl₃] and K₂CO₃, and the top layer consists of toluene and substrates. During the process of coupling, the biphasic system disappears and a homogeneous reaction medium is formed. After the completion of the reaction, a complete phase separation is formed again after being cooled to room temperature. The next process involves the

removal of the oil layer by decantation; the bottom aqueous layer is concentrated by removing the water produced in the reaction under vacuum and then filtered. Fresh substrates and toluene are then recharged to the recovered PEG₁₀₀₀-DAIL[CdCl₃] and then recycled. The PEG₁₀₀₀-DAIL[CdCl₃] plays a very important role in the coupling process to locally concentrate the reacting species by exhibiting a temperature-dependent phase behavior with methylcyclohexane (i.e., the thermoregulated biphasic behavior of monophasic under high temperature and biphasic under room temperature), which leads to a large increase in the effective reactant concentration and excellent results of the coupling.

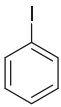
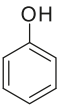
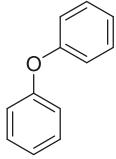
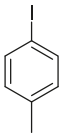
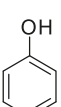
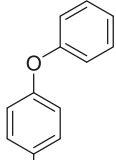
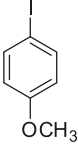
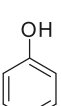
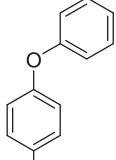
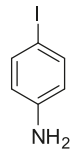
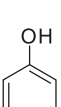
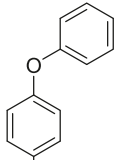
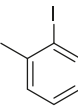
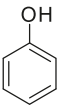
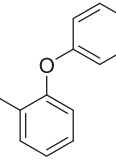
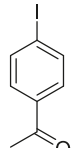
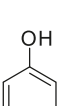
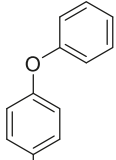
Conclusion

In conclusion, we have developed an experimentally simple and efficient protocol for the C–O coupling of organic halides with phenols and alcohols in a PEG₁₀₀₀-DAIL[CdCl₃]-toluene temperature-dependent biphasic system. A wide range of aryl, benzylic, allylic, and aliphatic halides were found to be applicable to the catalytic system. Advantages of our procedure include simplicity of operation, high yields, easy isolation of products, good thermoregulated biphasic behavior of the ionic liquid, and excellent recyclability of the catalyst. Efforts to define the coupling mechanism and expand the utility of the environmentally benign catalytic system to other organic synthesis are currently under study in our laboratory.

Experimental

All the chemicals were obtained from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to liter-

Table 2. Catalytic coupling of various organic halides.

Entry	Organic halides	R ₃ OH	Time (h)	Products and yields (%) ^a
1			11	 91 1
2			14	 92 2
3			14	 89 3
4			14	 87 4
5			14	 90 5
6			8	 96 6

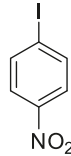
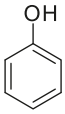
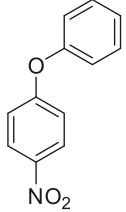
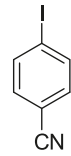
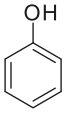
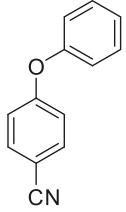
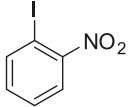
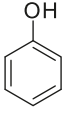
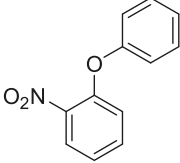
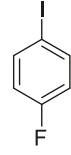
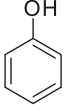
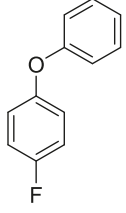
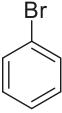
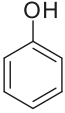
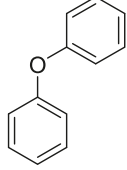
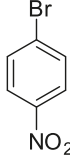
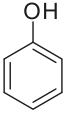
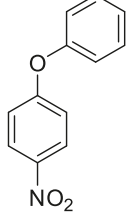
ature procedures.^{30,35} ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer using CDCl₃ as the solvent with tetramethylsilane (TMS) as an internal standard. High-performance liquid chromatography (HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America), consisting of a pump (P680) and UV-vis

light detector (UVD) system (170U). Elemental analyses were performed on a Vario EL III instrument (Elementar Analysen Systeme GmbH, Germany).

General procedure for coupling reactions

To a stirred solution of organic halide (2.4 mmol), R₃OH

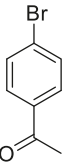
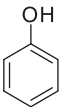
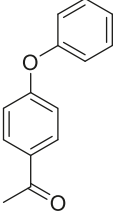
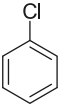
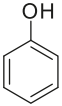
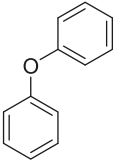
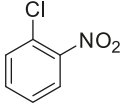
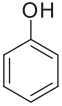
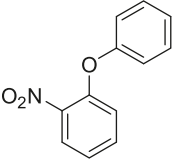
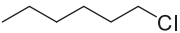
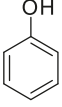
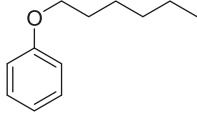
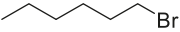
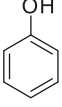
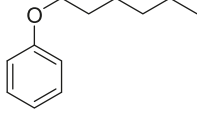

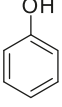
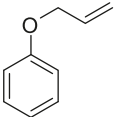
Table 2. (continued).

Entry	Organic halides	R ₃ OH	Time (h)	Products and yields (%) ^a
7			8	 95 7
8			8	 95 8
9			8	 94 9
10			8	 92 10
11			14	 86 11
12			10	 90 12

(2 mmol), and PEG₁₀₀₀-DAIL[CdCl₂] (0.4 mmol) in toluene (5 mL) was added K₂CO₃ (2 mmol). Stirring was continued at 95 °C for an appropriate time, the reaction progress being monitored by HPLC. Upon completion, the mixture was

cooled to room temperature. The organic phase was separated by decantation and then rinsed with water (3 × 10 mL) and dried with anhydrous sodium sulfate. The crude mixture was purified by column chromatography on silica

Table 2. (continued).

Entry	Organic halides	R ₃ OH	Time (h)	Products and yields (%) ^a
13			10	 91 13
14			18	 82 14
15			14	 89 15
16			24 ^b	 81 16
17			24 ^b	 84 17
18			7	 89 18

gel to afford the product with high purity. The next run was performed under identical reaction conditions. All the products were confirmed by ¹H NMR or elemental analysis or compared with their authentic samples.

Spectral data of selected products

1-Methyl-4-phenoxybenzene (2)

¹H NMR (400 MHz, CDCl₃) δ: 2.31 (s, CH₃, 3H), 6.89–7.01 (m, Ar-H, 4H), 7.05–7.09 (m, Ar-H, 1H), 7.12–7.16 (m, Ar-H, 2H), 7.29–7.35 (m, Ar-H, 2H). Anal. calcd for C₁₃H₁₂O: C 84.73, H 6.56, O 8.69; found: C 84.75, H 6.57, O 8.68.

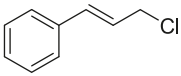
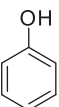
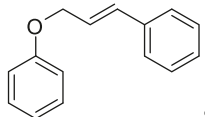
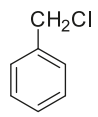
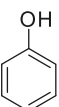
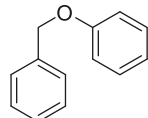
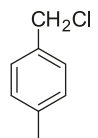
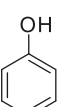
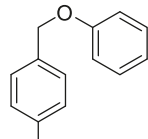
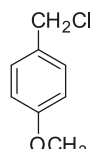
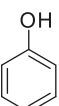
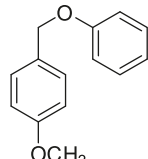
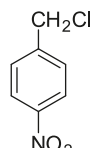
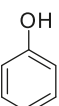
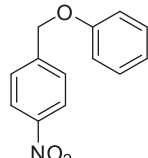
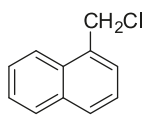
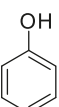
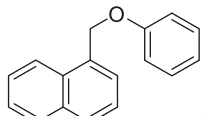
1-Methoxy-4-phenoxybenzene (3)

¹H NMR (400 MHz, CDCl₃) δ: 3.78 (s, CH₃, 3H), 6.86–6.93 (m, Ar-H, 2H), 6.96–7.02 (m, Ar-H, 4H), 7.05–7.11 (m, Ar-H, 1H), 7.27–7.33 (m, Ar-H, 2H). Anal. calcd for C₁₃H₁₂O₂: C 77.95, H 6.04, O 15.99; found: C 77.98, H 6.04, O 15.98.

1-Nitro-4-phenoxybenzene (7)

¹H NMR (400 MHz, CDCl₃) δ: 6.93–6.97 (m, Ar-H, 2H), 7.01–7.05 (m, Ar-H, 2H), 7.24–7.27 (m, Ar-H, 1H), 7.47–7.54 (m, Ar-H, 2H), 8.11–8.16 (m, Ar-H, 2H). Anal. calcd for C₁₂H₉NO₃: C 66.94, H 4.23, N 6.50, O 22.32; found: C 66.97, H 4.22, N 6.51, O 22.30.

Table 2. (continued).

Entry	Organic halides	R ₃ OH	Time (h)	Products and yields (%) ^a
19			7	 19 92
20			7	 20 94
21			7	 21 96
22			7	 22 97
23			9	 23 90
24			7	 24 96

4-Phenoxybenzotrile (8)

¹H NMR (400 MHz, CDCl₃) δ: 6.89–6.93 (m, Ar-H, 2H), 6.97–7.01 (m, Ar-H, 2H), 7.17–7.21 (m, Ar-H, 1H), 7.34–7.38 (m, Ar-H, 2H), 7.71–7.76 (m, Ar-H, 2H). Anal. calcd for C₁₃H₉NO: C 79.96, H 4.66, N 7.17, O 8.21; found: C 79.98, H 4.65, N 7.17, O 8.20.

1-Methyl-4-(phenoxyethyl)benzene (21)

¹H NMR (400 MHz, CDCl₃) δ: 2.32 (s, CH₃, 3H), 5.13 (s, CH₂, 2H), 6.92–7.03 (m, Ar-H, 3H), 7.08–7.17 (m, Ar-H, 4H), 7.27–7.34 (m, Ar-H, 2H). Anal. calcd for C₁₄H₁₄O: C 84.77, H 7.13, O 8.09; found: C 84.81, H 7.12, O 8.07.

1-Methoxy-4-(phenoxyethyl)benzene (22)

¹H NMR (400 MHz, CDCl₃) δ: 3.81 (s, CH₃, 3H), 5.12 (s,

CH₂, 2H), 6.89–7.06 (m, Ar-H, 7H), 7.29–7.35 (m, Ar-H, 2H). Anal. calcd for C₁₄H₁₄O₂: C 78.46, H 6.59, O 14.94; found: C 78.48, H 6.59, O 14.93.

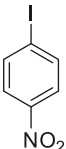
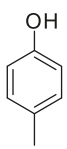
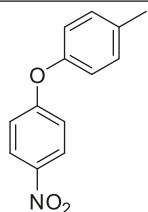
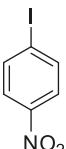
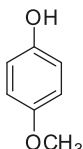
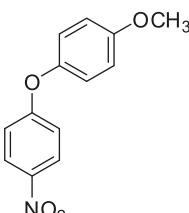
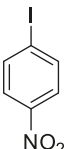
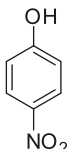
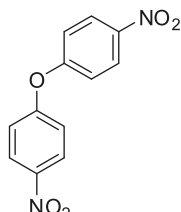
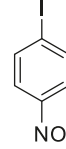
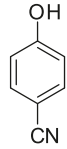
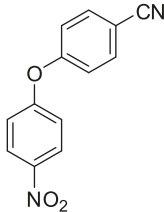
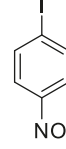
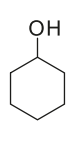
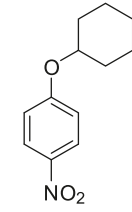
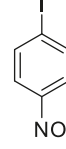
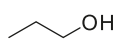
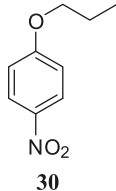
1-Methoxy-4-(4-nitrophenoxy)benzene (26)

¹H NMR (400 MHz, CDCl₃) δ: 3.81 (s, CH₃, 3H), 6.94–6.97 (m, Ar-H, 2H), 7.16–7.19 (m, Ar-H, 2H), 7.38–7.42 (m, Ar-H, 2H), 8.14–8.18 (m, Ar-H, 2H). Anal. calcd for C₁₃H₁₁NO₄: C 63.63, H 4.52, N 5.71, O 26.12; found: C 63.67, H 4.52, N 5.71, O 26.10.

1-(Cyclohexyloxy)-4-nitrobenzene (29)

¹H NMR (400 MHz, CDCl₃) δ: 1.32 (m, CH₂, 2H), 1.46 (m, CH₂, 4H), 1.87 (m, CH₂, 4H), 3.72 (m, CH, 1H), 7.32–7.38 (m, Ar-H, 2H), 8.12–8.16 (m, Ar-H, 2H). Anal. calcd

Table 2. (concluded).

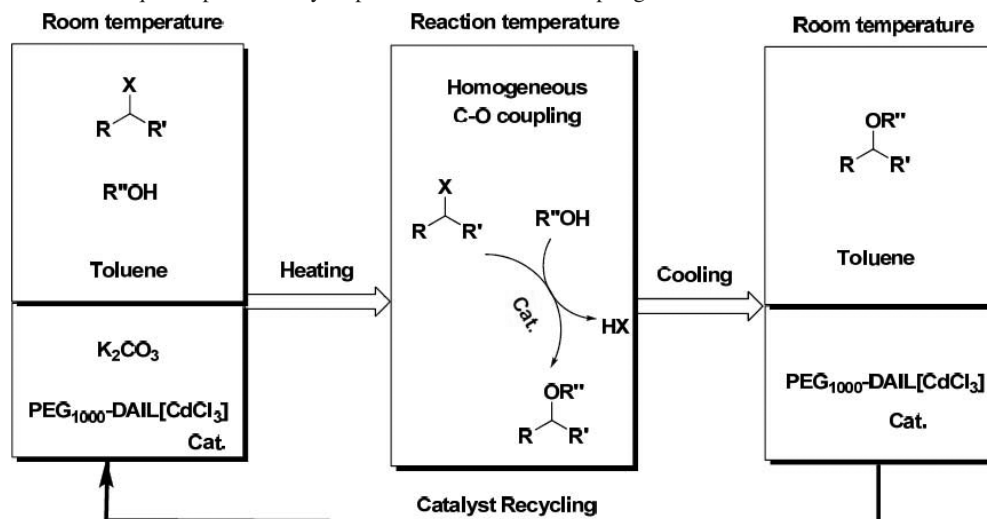
Entry	Organic halides	R ₃ OH	Time (h)	Products and yields (%) ^a
25			14	 25 91
26			14	 26 89
27			8	 27 98
28			8	 28 97
29			24 ^c	 29 84
30			24 ^c	 30 82

Note: Unless otherwise noted, the reactions were carried out with organic halide (2.4 mmol), R₃OH (2 mmol), K₂CO₃ (2 mmol), PEG₁₀₀₀-DAIL[CdCl₂] (0.4 mmol), in toluene (5 mL) at 95 °C.

^a Isolated yield.

^b The reaction was carried out at 105 °C.

Fig. 2. Thermoregulated ionic liquid biphase catalytic process for the C–O coupling.



for $C_{12}H_{15}NO_3$: C 65.10, H 6.83, N 6.34, O 21.71; found: C 65.14, H 6.83, N 6.33, O 21.69.

Acknowledgements

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