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Article

Eco-Friendly Homo- and Cross-Etherification of Benzyl Alcohols Catalyzed by Iron(II/III) Chloride in Propylene Carbonate as a Green and Recyclable Solvent

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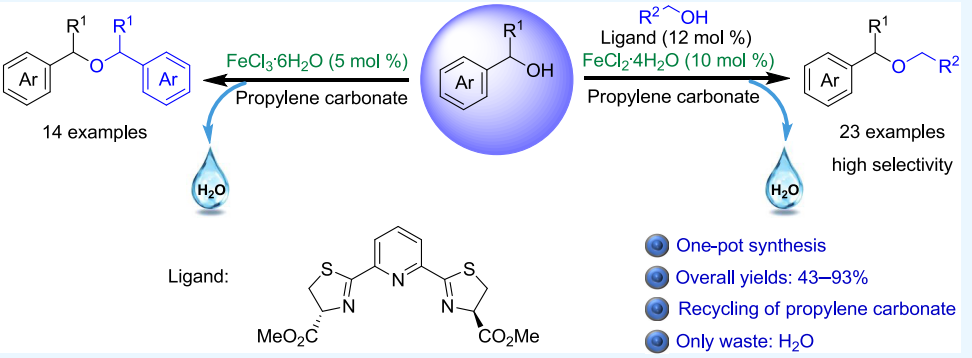

ABSTRACT: A new catalytic approach toward the symmetrical and nonsymmetrical etherification of benzyl alcohols was developed. The symmetrical etherification reaction was carried out in the presence of $FeCl_3·6H_2O$ (5 mol %) as the catalyst and propylene carbonate as a green and recyclable solvent and led to the corresponding symmetrical ethers in 53 to 91% yields. The nonsymmetrical etherification of benzylic alcohols was achieved by using $FeCl_2·4H_2O$ (10 mol %) in the presence of a pyridine bis-thiazoline ligand (12 mol %) and allowed for high selectivity and in 52 to 89% yields. These methods take advantage of eco-friendly conditions.

INTRODUCTION

The development of green methods for the synthesis of ethers has become crucial and necessary to prepare molecules of synthetic and biological interest.[1] Aryl and alkyl ethers are widely present in natural products, biologically important compounds, solvents, agrochemicals, and polymers.[2,3] Etherification is most commonly carried out using Williamson's method,[4] using alkyl halides as reactants. This approach often leads to the formation of hydrogen halide and undesired residual salts, and may give low product yields.[5] Mitsunobu reaction fails in such context due to steric constraints of the S_N2 process.[6] The synthesis of nonsymmetrical ethers from carbonyl compounds and silyl ethers was also achieved.[7] Although these methodologies have benefits, such as selectivity, they have severe limitations, such as the use of stoichiometric quantities or more of bases or oxidants, harsh reaction conditions, formation of salts as waste, use of toxic solvents, and expensive catalysts. In contrast, employing more environmentally friendly substrates, such as alcohols,[8] which produce only water as a byproduct, is a major objective in green chemistry to overcome these limitations.

Currently, significant progress was made using palladium and copper catalysts in Ullman and Buchwald−Hartwig C−O coupling processes, respectively,[9−11] transition metal catalysts in aromatic nucleophilic substitution reactions of aryl halides[12] and catalyzed dehydration of the more active allylic and propargylic alcohols.[13] Further strategies, such as C−H activation reactions, have been described.[14,15] As a result, substantial research employing various metal catalysts, including precious metal complexes, was invested in this field.[16,17] Yi et al. recently reported a remarkable Ru-catalyzed dehydration process of various alcohols to produce nonsymmetrical ethers.[13] The dehydrative homo- and cross-etherification reactions between various alcohols are also known to be successfully catalyzed by organohalides.[16]

Many metal catalysts used in organic synthesis often contain rare and noble metals. Unfortunately, their toxicity and price prevent their use on an industrial scale. From a green chemistry point of view, it is interesting to develop new reactions catalyzed

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by more abundant, inexpensive, and low-toxicity metals, such as iron. Indeed, iron represents one of the most promising transition metals in the field of organic catalysis.[18] Some work using iron catalysts in etherification reactions with alcohols has been described in the literature.[19−23] Yet, we believe that the use of iron salts in etherification reactions is still underinvestigated for the following reasons: (i) the scope of the reactions using Fe^{III} is limited to the cross-etherification of tertiary and secondary allylic, benzylic, and propargylic alcohols, which are more reactive than primary alcohols;[19−23] (ii) some of these methods require the use of a large excess of reagents (up to 150 equiv);[20,22] (iii) these methods use toxic solvents, such as nitromethane, dichloromethane, and dichloroethane.[19,20,23,24] Zhang et al. also developed a very powerful direct Fe^{II}-catalyzed generation of nonsymmetrical benzyl ethers using a combination of $Fe(OTf)_2$ with a pyridine bis-imidazoline ligand.[24] This procedure is attractive due to its high selectivity, together with its performance and group tolerance. However, these methods still require the use of chlorinated solvents, a glovebox, and moisture protection while running the reactions.

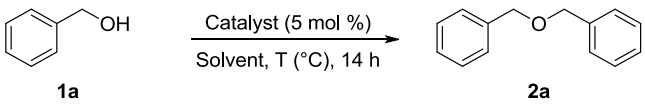
In this work, we developed new approaches using iron(III) chloride and iron(II) chloride as catalysts, respectively, for homo- and cross-etherification of a variety of benzyl alcohols. The reactions are performed under eco-friendly conditions by using propylene carbonate as a green and recyclable solvent.

RESULTS AND DISCUSSION

We started our investigations with optimization of the reaction conditions in the synthesis of symmetrical ethers from benzylic alcohols. In order to study the effect of the solvent, optimization of the reaction was performed at 100 °C for a specified time using benzyl alcohol as the model substrate. The results are listed in Table 1.

First, we found that no reaction occurred without catalyst (Table 1, entry 1). This is clearly an indication that dehydration is a catalyzed process. In addition, $FeCl_3{\cdot}6H_2O$ was studied under the same reaction conditions and yielded the desired product in a full conversion under solvent-free conditions, or in propylene carbonate, dimethyl carbonate, and dichloromethane (Table 1, entries 2, 4, 5, and 8). These reactions gave high yields, except when the reaction was carried out under solvent-free conditions because of the formation of nonidentified impurities together with ether **2a**. The use of other iron salts, such as $Fe_2(SO_4)_3{\cdot}5H_2O$ or anhydrous $FeCl_3$, showed less efficiency than that of $FeCl_3{\cdot}6H_2O$ (Table 1, entries 9 and 10). Unexpectedly, no reaction was observed using other iron catalysts such as $Fe(SO_4){\cdot}7H_2O$, $Fe(TFA)_3$, and $Fe_2(acac)_3$ (Table 1, entries 11−13).

Table 1. Optimization of the Reaction Conditions for the Synthesis of Symmetrical Ethers[a]



1a **2a**

entry	catalyst (5 mol %)	solvent	T (°C)	conv (%)[b]
1			100	NR
2	$FeCl_3{\cdot}6H_2O$		100	100 (63)[c]
3	$FeCl_3{\cdot}6H_2O$	PC[d]	80	90
4	$FeCl_3{\cdot}6H_2O$	DMC[e]	100	100 (90)[c]
5	$FeCl_3{\cdot}6H_2O$	PC	100	**100 (93)**[c]
6	$FeCl_3{\cdot}6H_2O$	AcOEt	100	98 (89)[c]
7	$FeCl_3{\cdot}6H_2O$	CH_3CN	100	98 (84)[c]
8	$FeCl_3{\cdot}6H_2O$	CH_2Cl_2	100	100 (90)[c]
9	$FeCl_3$	PC	100	95 (86)[c]
10	$Fe_2(SO_4)_3{\cdot}5H_2O$	PC	100	85
11	$Fe(SO_4){\cdot}7H_2O$	PC	100	NR
12	$Fe(TFA)_3$	PC	100	NR
13	$Fe_2(acac)_3$	PC	100	NR

[a]Reaction conditions: benzyl alcohol **1a** (2 mmol), catalyst (5 mol %), solvent (1 mL). The mixture was stirred in a pressure tube. The reaction was performed at 100 °C for 14 h. [b]Conversion was determined from the ^1H NMR analysis of the crude product. [c]Isolated yield. [d]PC = propylene carbonate. [e]DMC = dimethyl carbonate.

In terms of green chemistry, our approach is more efficient than the previously described methodologies. We employed a combination of $FeCl_3{\cdot}6H_2O$ as a cheap, less toxic, and harmless to humans and the environment and propylene carbonate (PC) as a green and recyclable solvent. Our approach produces only stoichiometric amounts of H_2O as a waste, associated with a very high atom economy. The etherification reaction was further extended to other benzyl alcohols possessing different substituents in the presence of a catalytic quantity of an Fe^{III} salt in PC as an efficient system for the dehydration of alcohols. This work underlines two greener alternatives than conventional dipolar aprotic solvents, using PC or DMC, but PC was chosen for its nonmiscibility with nonpolar solvents and its high boiling point (242 °C). Surprisingly, the catalyst was dissolved in PC and the products of the reaction are more soluble in petroleum ether than in PC. Accordingly, they are very easily extracted into petroleum ether. This method allowed recycling of the catalyst and regeneration of PC by distillation under reduced pressure, offering up to 80% of pure propylene carbonate.

Noteworthily, benzylic alcohols with electron-withdrawing and -donating substituents on the aromatic ring are successfully reacted in the homocoupling reaction and furnish the desired symmetrical ethers in moderate to good yields (56 to 93%) under mild and green conditions. The results are summarized in Table 2.

Gratifyingly, a variety of primary benzylic alcohols **1a−n** were subjected to the etherification reaction under the optimized conditions to provide the desired products **2a−n** in 43 to 88% yields (Table 2, entries 1−14). On the one hand, we noticed that benzylic alcohols substituted with electron-withdrawing groups on the aromatic ring are less reactive than those substituted with electron-rich groups. Indeed, the etherification of 2-methylbenzylalcohol **1b** and 4-methylbenzylalcohol **1c** in PC at 100 °C led to the formation of complex mixtures of nonidentified byproducts, whereas the selectivity of the reaction run at 70 °C was greatly improved. In this case, we isolated 91% **2b** and 53% **2c** (Table 2, entries 2 and 3). Symmetrical ethers from benzyl alcohols substituted with electron-attracting groups were prepared at 100 and 120 °C as they did not give satisfactory conversions at 70 °C. 2-Trifluoromethyl benzyl alcohol **1j** provided the symmetric ether **2j** in moderate yield (56%) at 120 °C. We noticed that *para*-substituted benzylic alcohols led to the corresponding ethers in higher yields than the *ortho*-substituted ones (with the exception of ether **2c**). This may be due to the steric hindrance of the substituent in the *ortho*-position. Notably, diphenyl methanol was reactive in these conditions and furnished the desired product **2k** in good yield (73%). More sterically congested 1-(naphthalen-6-yl) ethanol **1l** also reacted well and afforded the corresponding symmetrical ether **2l** in good isolated yield (88%). The dehydration of 1-phenylmethanol **1m** led to ether **2m** also with a good yield (74%). As

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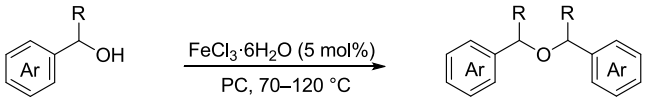
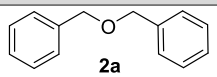
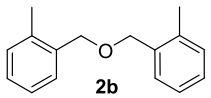
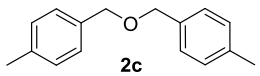
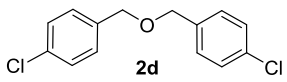
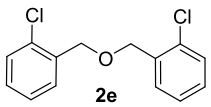
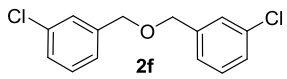
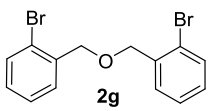
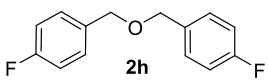
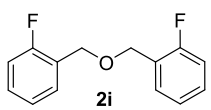
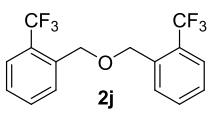
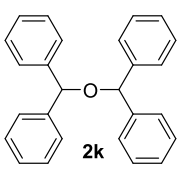
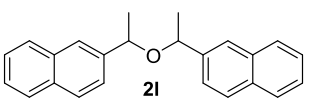
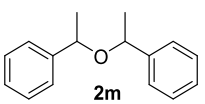
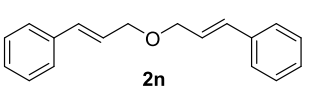
Table 2. Symmetrical Etherification of Substituted Benzylic Alcohol Using Iron(III) Catalyst[a]



1a–n R = H, CH_3, Ph 2a–n

Entry	Product	Time (h)/T(°C)	Yield (%)
1	 2a	14/100	93
2	 2b	24/70	91
3	 2c	24/70	53
4	 2d	24/100	78
5	 2e	24/100	64
6	 2f	24/100	60
7	 2g	48/120	56
8	 2h	24/100	85
9	 2i	24/100	63
10	 2j	48/120	56
11	 2k	14/100	73
12	 2l	14/100	88
13	 2m	14/100	74
14	 2n	14/100	43

[a]Reaction conditions: benzylic alcohol **1a−n** (2 mmol), $FeCl_3·6H_2O$ (5 mol %), PC (1 mL), 70−120 °C, 14−48 h.

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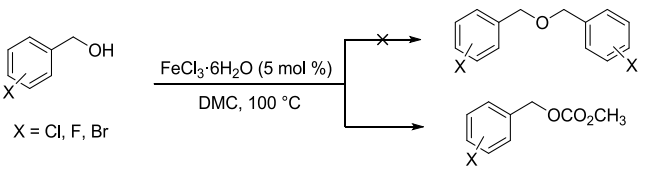
indicated in Table 1 (entry 5), the etherification of benzylic alcohol **1a** in DMC afforded the corresponding symmetric ether **2a** with a full conversion and 90% isolated yield. Surprisingly, we found that the etherification of benzyl alcohols containing electron-withdrawing groups in DMC as the solvent did not lead to the corresponding ethers (Scheme 1). The compounds of interest are listed in Table 3 (entries 1−4). Hence, the reaction may be proceeding via a transesterification process between the benzyl alcohol substituted with an electron-withdrawing group and DMC to afford methyl carbonates **3a−d** in 53 to 85% yield (Scheme 1).

Scheme 1. Reaction of Halogenated Benzyl Alcohols with DMC

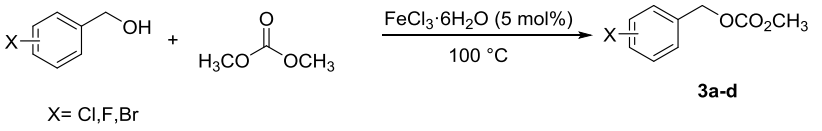


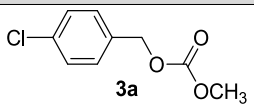
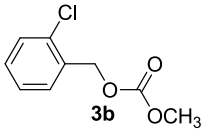
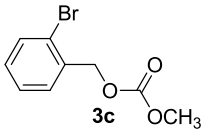
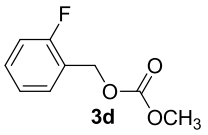
Sahoo et al. described symmetrical etherification from secondary benzylic alcohols and unsymmetrical etherification from secondary and primary alcohols by use of the $Fe(OTf)_3/NH_4Cl/CH_2Cl_2$ system.[23] In their study, the authors demonstrated that the etherification reaction follows an ionic mechanism in which Fe^{III} plays the role of a Lewis acid since the oxidation state of Fe^{III}, measured with EPR analysis, remains unchanged during the reaction. In this work, symmetrical etherification was performed using the $FeCl_3{\cdot}6H_2O$/PC system. The advantage of our reaction is that the reaction works as well with the less reactive benzylic primary alcohols as with benzylic secondary alcohols. By analogy with the work of Sahoo et al.,[23] we believe that the mechanism of the symmetrical etherification using the $FeCl_3{\cdot}6H_2O$/PC system is the same as that using the $Fe(OTf)_3/NH_4Cl/CH_2Cl_2$ system. Accordingly, a radical process in which electron transfer involving the Fe^{III} catalyst does not appear plausible.

We aimed at extending the range of synthesized nonsymmetrical ethers using the same conditions. Unfortunately, the $FeCl_3{\cdot}6H_2O$/PC system did not work to prepare nonsymmetrical ethers (Table 4, entry 10). Importantly, Sahoo et al. demonstrated that the unsymmetrical etherification proceeded via transetherification of symmetrical ethers from benzylic secondary alcohols using the $Fe(OTf)_3/NH_4Cl/CH_2Cl_2$ system.[23] As shown in Scheme 2 (eq 1), we also verified that transetherification did not take place when using the $FeCl_3{\cdot}6H_2O$/PC system. Then, we tried to search for conditions to favor the selective formation of ethers starting from two different alcohols. It is worth noting that in such reactions, the use of metal complexes containing tridentate nitrogen ligand is critical to achieve a good selectivity.[16,17,24] Our new approach for the cross-etherification of alcohols involved using a catalyst generated from iron(II) chloride and a pyridine bis-thiazoline ligand. First, we optimized cross-etherification in the presence of various ligands. Benzyl alcohol **1a** and 1-methyl-1-naphthylmethanol **1l** were chosen as the model substrates (Figure 1). The results of this optimization study are listed in Table 4.

Loos et al. described the synthesis of the pyridine bis-thiazoline ligand **L1**.[25] In this work, we prepared ligand **L1** using a different method by reacting 2,6-dicyanopyridine with 2 equiv of L-cysteine methyl ester hydrochloride in water as the solvent, in the presence of $KHCO_3$ and SDS (sodium dodecyl sulfate as a surfactant). This green method afforded ligand **L1** in a 70% yield

Table 3. Etherification of Benzylic Alcohols with Substituted Electron-Withdrawing Groups in DMC[a]



Entry	Product	Time (h)	Yield (%)
1		28	78
2		28	75
3		24	53
4		28	85

[a]Reaction conditions: benzylic alcohol **1** (2 mmol), $FeCl_3{\cdot}6H_2O$ (5 mol %), DMC (1 mL), 100 °C, 24−28 h.

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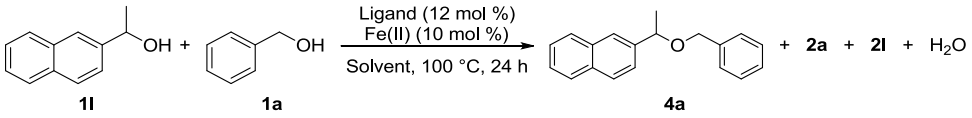
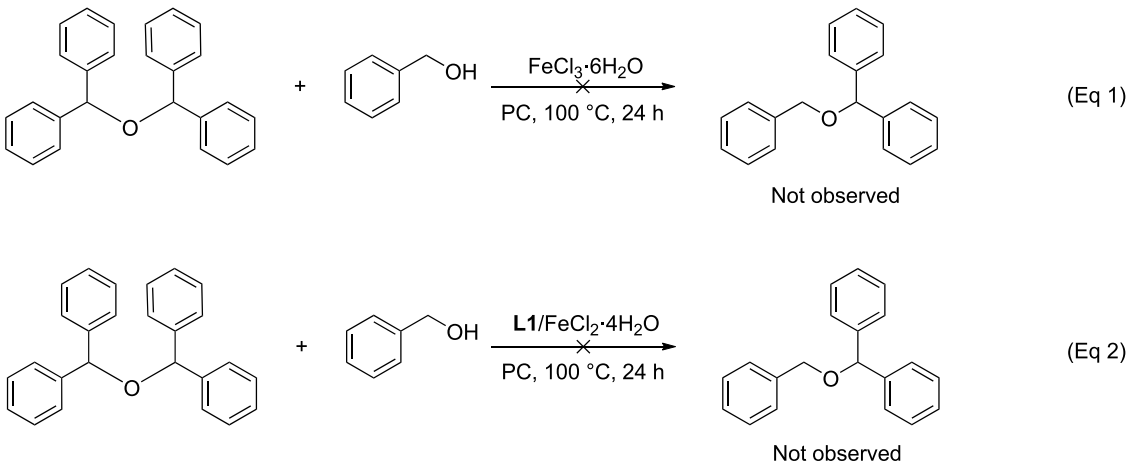
Table 4. Optimization of the Cross-Etherification of Alcohols 1a and 1l[a]



entry	catalyst	ligand	solvent	conv. (%)[b]	yield (%) (4a/2a/2l)
1	$FeCl_2{\cdot}4H_2O$		PC		Nd[c,d]
2	$FeCl_2{\cdot}4H_2O$	**L1**	PC	90	88:0:0
3	$FeCl_2$	**L1**	PC	86	52:0:0
4	$FeCl_2{\cdot}4H_2O$	**L2**	PC	83	80:0:0
5	$FeCl_2{\cdot}4H_2O$	**L3**	PC	84	37:0:16
6	$FeCl_2{\cdot}4H_2O$	**L4**	PC		NR
7	$FeCl_2{\cdot}4H_2O$	**L1**	DMC	85	52:0:0
8	$FeCl_2{\cdot}4H_2O$	**L1**	CH_2Cl_2	89	33:0:0
9	$FeCl_2{\cdot}4H_2O$	**L1**	CH_3CN	62	36:0:0
10	$FeCl_3{\cdot}6H_2O$		PC		Nd[c,d]
11	$FeCl_3{\cdot}6H_2O$	**L1**	PC	81	41:0:0

[a]Reaction conditions: **1l** (1 mmol), **1a** (1.2 mmol), metal salt (10 mol %), ligand (12 mol %), solvent (1 mL), 100 °C, 24 h. [b]Determined by the ^{1}H NMR analysis of the crude product. [c]Not determined. [d]Formation of nonidentified impurities.

Scheme 2. Transetherification of Symmetrical Ethers Catalyzed with $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$/L1



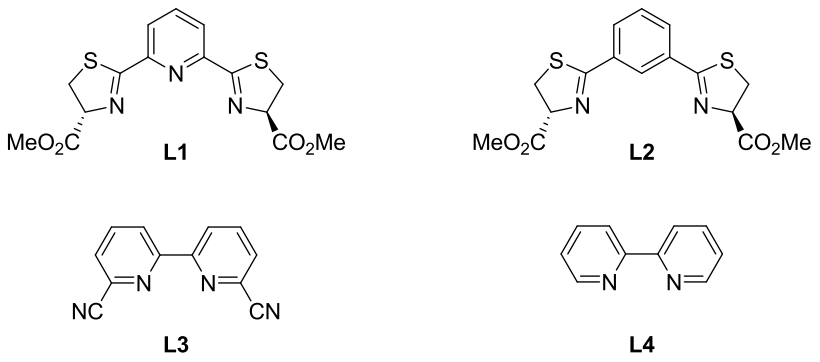


Figure 1. Ligands used in this work.

Scheme 3. Green Synthesis of Pyridine Bis-Thiazoline Ligand L1

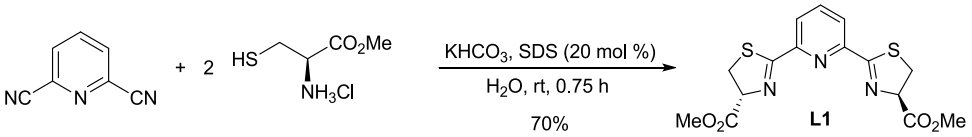


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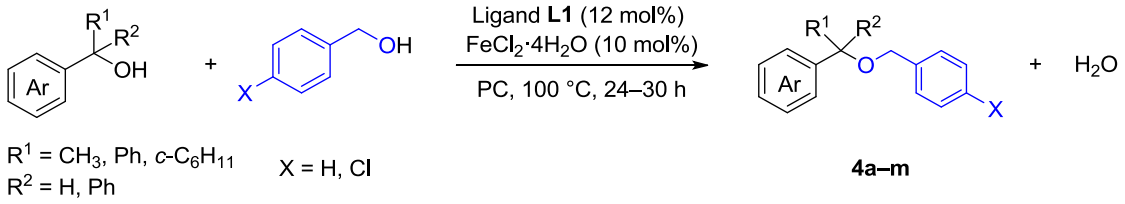
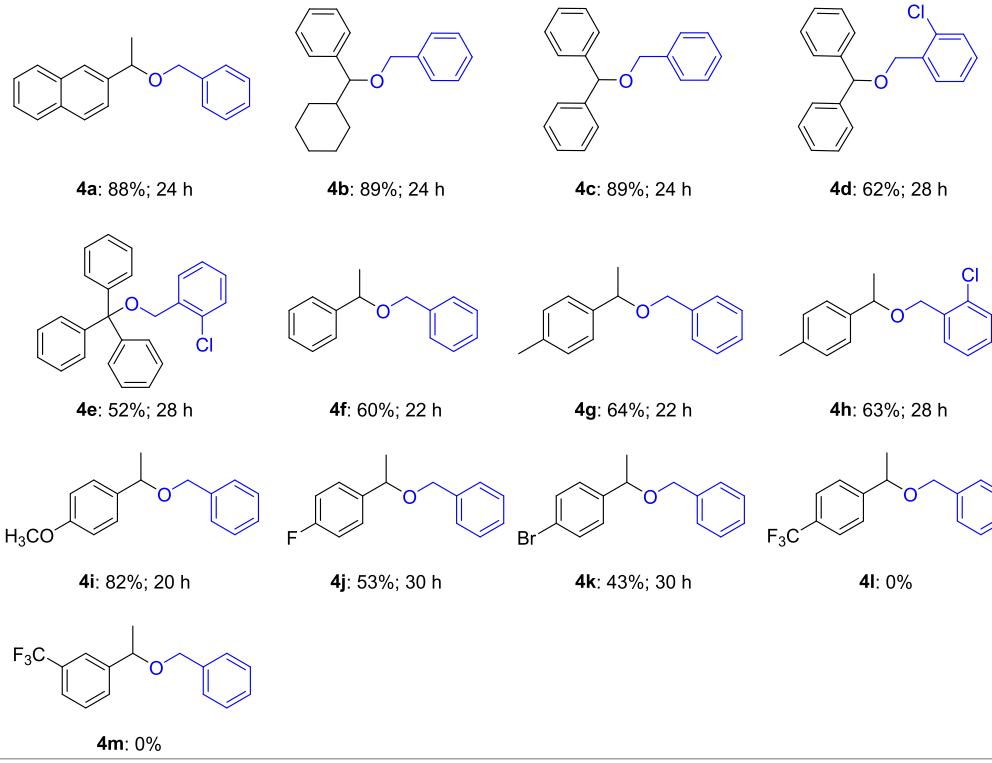
Table 5. $FeCl_2{\cdot}4H_2O$-L1-Catalyzed Etherification of Various Substituted Benzyl Alcohols[a]





[a]Reaction conditions: secondary alcohol (1 mmol), **1a** or **1e** (1.2 mmol), $FeCl_2{\cdot}4H_2O$ (10 mol %), ligand **L1** (12 mol %), PC (1 mL). The mixture was stirred at 100 °C in a pressure tube.

(Scheme 3). Ligand **L2** was prepared according to a reported method,[26] whereas ligands **L3** and **L4** are commercially available.

A preliminary study focused on evaluating the catalytic activities of different ligands. We began to investigate the dehydrative reaction of 1-(naphthalen-2-yl) ethanol (**1l**) with benzyl alcohol **1a** (Table 4). First, we have tested the catalytic effect of the ligand **L1**, combined with $FeCl_2{\cdot}4H_2O$ as the catalyst in propylene carbonate as the solvent. The etherification reaction produced the desired nonsymmetrical ether 2-(1-(benzyloxy)ethyl) naphthalene **4a** with 90% conversion, high selectivity, and good isolated yield (88%). The symmetrical ethers **2a** and **2l** were not detected in the crude product (Table 4, entry 2). The use of **L2** as the ligand afforded the nonsymmetrical ethers **4a** in 80% yield of pure product under the same conditions (Table 4, entry 4). Consequently, without ligand, the desired product was not formed (Table 4, entry 1). The performance of **L3** and **L4** was also examined (Table 4, entries 5 and 6). Using **L3**, the dehydrative reaction resulted in a mixture of **4a** (37%) and **2l** (16%) (Table 4, entry 5) and no reaction took place using bipyridine as a ligand (Table 4, entry 6). Thus, we found that the $FeCl_2{\cdot}4H_2O$/**L1** system is the best catalyst to achieve successful and selective cross-etherification. It is meaningful that the solvent medium played an essential role in the etherification of alcohols mediated by Fe^{II}. Within this context, other solvents, including dimethyl carbonate, acetonitrile, and dichloromethane, were employed, but none of them performed better than propylene carbonate. Our investigation showed clearly that PC is the best solvent in this reaction for the following reasons: (i) PC is a green, nontoxic, biodegradable, and recyclable solvent; (ii) also, our products were commonly extracted with petroleum ether using a simple centrifugation, and PC can be reused after purification by distillation under reduced pressure. Interestingly, under the appropriate experimental circumstances, we evaluated the cross-etherification with a variety of aryl and alkyl alcohols, as highlighted in Table 5.

We investigated the etherification of benzyl alcohols **1a** or **1e** with a variety of secondary alcohols under the optimal conditions as indicated in Table 5. The various substrates were successfully converted to the anticipated nonsymmetrical ether in good yields. Notably, 1-(naphthalen-2-yl) ethanol was reactive and provided the required product **4a** in 88% yield. The more bulky cyclohexyl(phenyl)methanol likewise produced the unsymmetrical ether **4b** in a good yield (89%). Similar to this, when diphenyl methanol was etherified with substituted benzylic alcohols, the expected products **4c** and **4d** were preferentially produced in high selectivity and isolated yields of 62 and 89%, respectively. The etherification of triphenylmetha-

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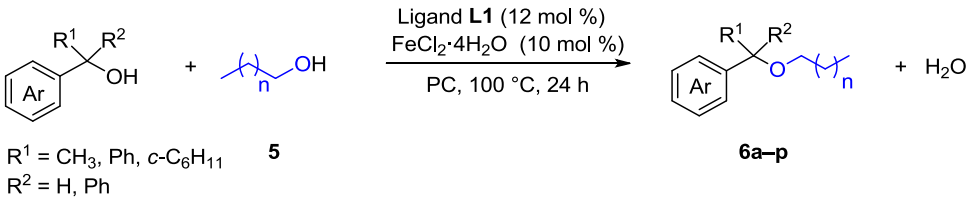
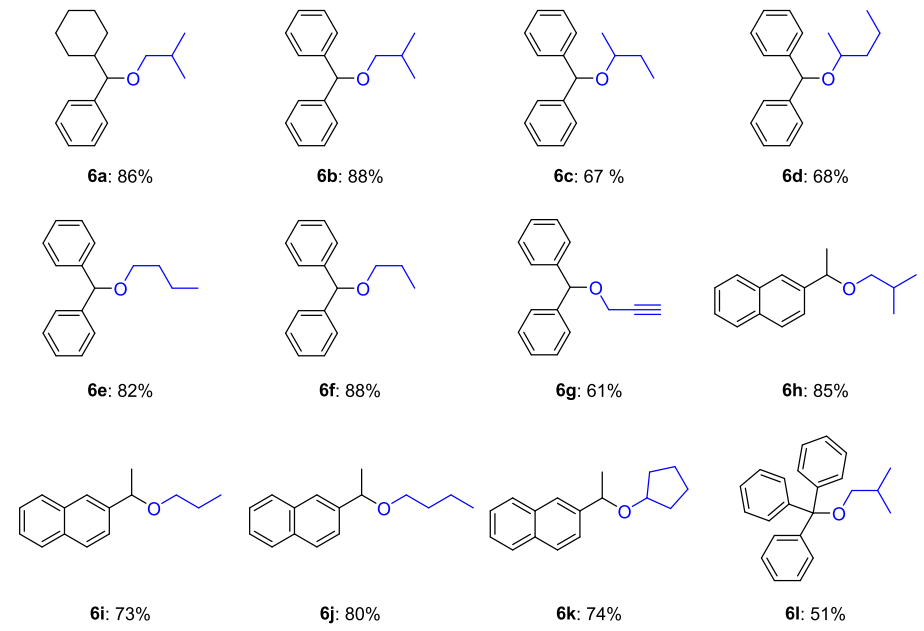
Table 6. $FeCl_2{\cdot}4H_2O$/L1-Catalyzed Etherification of Various Aliphatic Alcohols[a]





[a]Reaction conditions: secondary alcohol (1 mmol), aliphatic alcohol **5** (1.2 mmol), $FeCl_2{\cdot}4H_2O$ (10 mol %), ligand **L1** (12 mol %), PC (1 mL). The mixture was stirred at 100 °C in a pressure tube.

nol was successfully investigated and led to the desired product **4e** with a moderate yield (52%). The same catalytic procedure was applied in the cross-etherification of 1-arylethanols with benzyl alcohol and 2-chlorobenzyl alcohol, producing the nonsymmetrical ethers **4f**, **4g**, and **4h**. The O-alkylation reactions of 1-(1-(benzyloxy)ethyl)-4-fluorobenzene and 1-(1-(benzyloxy)ethyl)-4-bromobenzene afforded the corresponding ethers **4j** and **4k** in moderate isolated yields of 43 and 53%, respectively. Unfortunately, no cross-etherification of 1(1-(benzyloxy)ethyl)-4-(trifluoromethyl)benzene and 1-(1-(benzyloxy)ethyl)-3-(trifluoromethyl) benzenes **4l** and **4m** took place even at 120 °C. Aliphatic alcohols **5** were also appropriate substrates (Table 6). 2-Methylpropan-1-ol was reacted with secondary alcohols such as 1-(naphthalen-2-yl) ethanol, cyclohexyl(phenyl)methanol, diphenyl methanol, and triphenylmethanol to produce the corresponding nonsymmetrical ethers **6a**, **6b**, **6h**, and **6i** in moderate to good yields (58−88%) and high selectivity. In addition, the reaction of diphenyl methanol with a wide range of aliphatic alcohols, including butan-2-ol, pentan-2-ol, butan-1-ol, propan-1-ol, and propargylic alcohol, produced the expected nonsymmetrical ethers **6c−6g** in 61 to 88% yields. Positively, the reaction of 1-(naphthalen-2-yl) ethanol with primary alcohols produced the corresponding ethers **6i−6k** in 73 to 80% yields without producing any byproducts under these conditions. Cyclopentanol afforded the corresponding ether **6l** in a good yield (74%).

First, we found that the unsymmetrical etherification, using the $FeCl_2{\cdot}4H_2O$/**L1** system, did not occur via a transetherification process (Scheme 2, eq 2). We run some control experiments to elucidate the mechanism of iron(II)-catalyzed unsymmetrical dehydrative reaction (Scheme 4). Two hypotheses are to be discussed: the first one is a mechanism involving the Fe(II)/Fe(III) couple. In this case, the reaction will take place according to an electron transfer between the catalyst and the reactants. The second one is a cationic process in which the catalyst acts as a Lewis acid without changing its oxidation state. TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] and BHT (3,5-di-*tert*-butyl-*p*-hydroxytoluene) are commonly used as free radical trapping or radical inhibitors to provide some useful information on the mechanism of reactions. We found that, when using TEMPO (1.2 equiv) in both reactions, the symmetrical etherification reaction using $FeCl_3{\cdot}6H_2O$ and the nonsymmetrical etherification reaction using $FeCl_2{\cdot}4H_2O$/**L1** were inhibited. However, we believe that this result does not mean that these reactions follow a radical process, but rather that TEMPO, which is a free radical, can be easily oxidized by metal salts,[27,28] and therefore this control experiment leads to an ambiguous result. Instead, we run the nonsymmetrical etherification in the presence of 1.3 equiv of BHT as a radical inhibitor (Scheme 4, eq 1),[29,30] and this did not prevent the formation of ether **4a**. This result supports an ionic mechanism rather than a radical one. We investigated other control experiments such as the *O*-alkylation of **1a** alone under the usual catalytic reaction,

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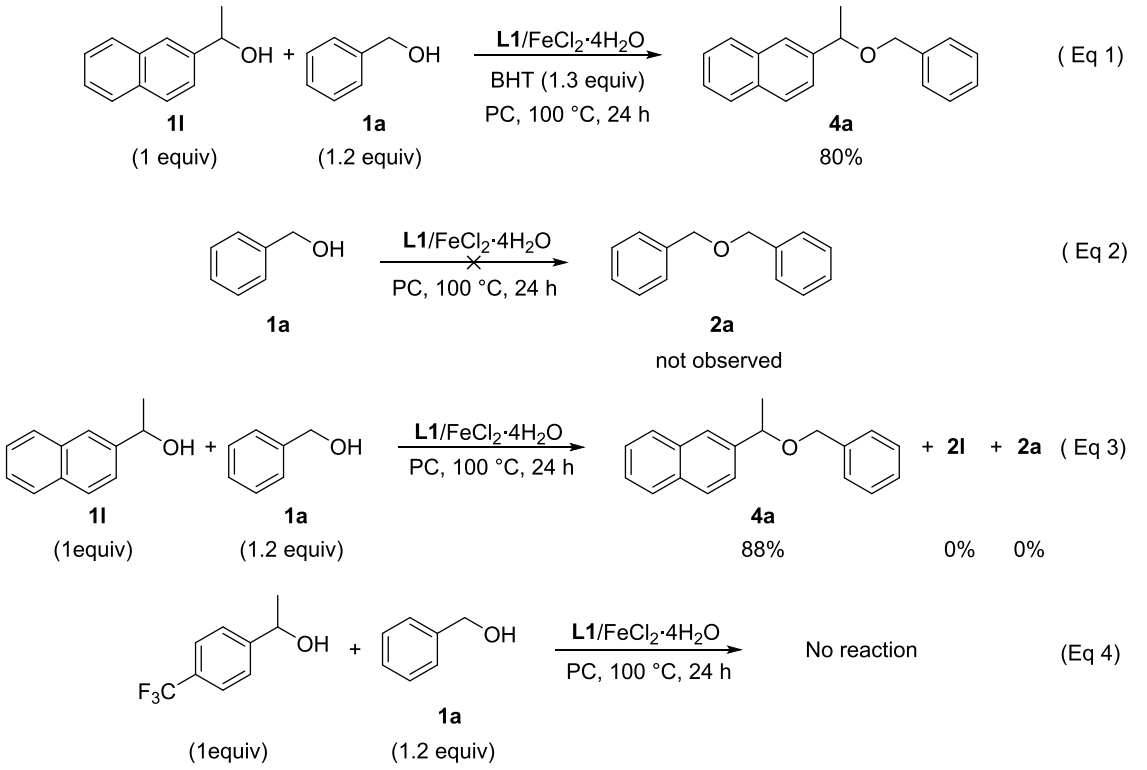
Scheme 4. Control Experiments, Selectivity, and Limitations of the Etherification Catalyzed by the $FeCl_2{\cdot}4H_2O$/L1 System



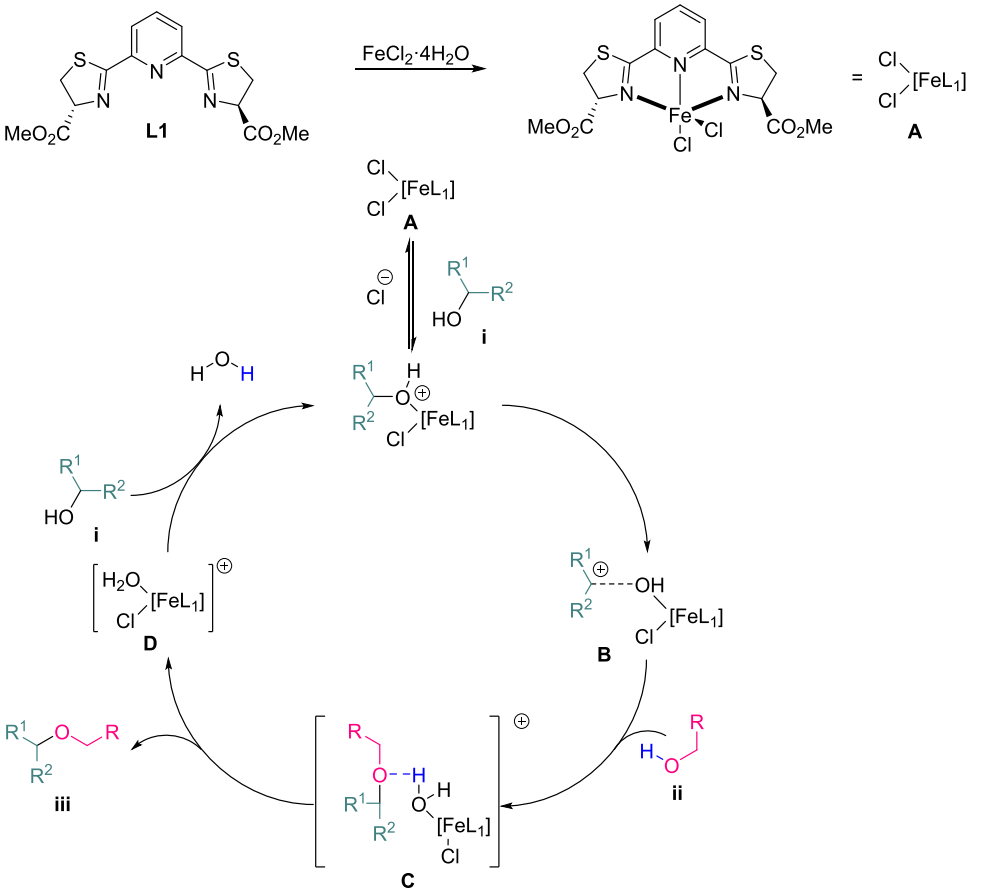


Figure 2. Proposed catalytic cycle for the Fe(II)-ligand-catalyzed cross-etherification.

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and we found that no etherification took place (Scheme 4, eq 2). This highlights why cross-etherification seems to be highly chemoselective. These findings suggested that the development of primary benzyl carbocation is difficult and that the formation of the more stable secondary benzyl alcohol carbocation may be the key step in the synthesis of unsymmetrical ethers.[24,31,32] Afterward, an experiment revealed that the appropriate nonsymmetrical ethers were formed when **1l** reacted with benzyl alcohol offering a high selectivity since no other ether (**2l** or **2a**) was detected in the crude product (Scheme 4, eq 3). Thus, the benzylic alcohol substituted with a more electron-rich group was more reactive. On the other side, the deactivating effect of the trifluoromethyl group prevented the etherification of 1-(4-(trifluoromethyl)phenyl) ethanol from occurring (Scheme 4, eq 4).

Based on our findings and the precedent works,[24,33] a mechanism was postulated (Figure 2). First of all, the interaction of Fe(II) with the *N,N,N*-ligand **L1** produces *in situ* the iron complex **A**.[13,17,31,34] The intermediate **B** is formed by the substitution of a chlorine by the secondary benzyl alcohol (**i**).[24] This interaction promotes the formation of the more stable carbocation ($R^1R^2CH^+$ > RCH_2^+).[20,24] Subsequently, the primary alcohol RCH_2OH acted as a nucleophile on intermediate **B** (the secondary benzylic carbocation) to provide unsymmetrical ether (**iii**) while passing through transition state **C**. Eventually, the regeneration of **A** would be facilitated by the coordination of another alcohol substrate and the release of water as a byproduct. We believe that the selectivity of the reaction is due to the formation of a more stable carbocation ($R^1R^2CH^+$ > RCH_2^+), and steric hindrance linked to the complex **A**, which favors the approach of the primary alcohol (RCH_2OH) rather than the secondary alcohol (R^1R^2CHOH). This mechanism is analogous to that proposed by Zhang et al.[24] for the nonsymmetrical etherification using the $Fe(OTf)_2$/bis-oxazoline system.

CONCLUSIONS

In summary, we developed a green and efficient method for the homo- and cross-etherification of benzyl alcohols. Symmetrical etherification of benzyl alcohols was achieved by using $FeCl_3 \cdot 6H_2O$ as the catalyst in propylene carbonate as a green and recyclable solvent, whereas cross-etherification of benzyl alcohols was achieved using Fe(II)-pyridine bis-thiazoline complex as the catalyst. This innovative approach requires the use of available, low-cost, and low-toxic catalysts, such as $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$. The pyridine bis-thiazoline ligand **L1**, used for the cross-etherification, was prepared by a novel one-pot method from commercially available reagents under mild and green conditions. Our process is highly selective and generates water as the only byproduct. It gives an operationally simple tool to achieve the synthesis of a variety of symmetrical and nonsymmetrical ethers without using additives or protecting groups and allows the recycling of solvent.

EXPERIMENTAL SECTION

General. All reactions were performed in flame-dried glassware under an atmosphere of argon. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Flash column chromatography was performed on silica gel (230−400 mesh). After isolation and purification of the product, the combined fractions were concentrated by using a rotary evaporator under reduced pressure. ^{1}H, ^{13}C{H}, and ^{19}F NMR spectra were recorded in $CDCl_3$ at 300, 400, and 500 MHz for ^{1}H, and at 75, 100, and 126 MHz for ^{13}C. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sep = septet, br = broad), and coupling constant and integration (in Hz). For ^{13}C{H} NMR, $CDCl_3$ was used as an internal standard (δ = 77.16 ppm) and spectra were obtained with complete proton decoupling. High-resolution mass spectroscopy (HRMS) was performed on a Q Extractive mass Spectrometer (Thermo Fisher). Melting points were measured with a Kofler heating bench. TLC was run on Merck 60F-254 precoated silica gel plates (0.25 mm). Dimethyl carbonate (Reagent plus, 99%) and propylene carbonate (Reagent plus, 99%) were bought from Sigma-Aldrich. All starting materials were bought from commercial suppliers and used without further purification.

Synthesis of Symmetrical Ethers: Typical Procedure. Benzyl alcohol (2.0 mmol) and $FeCl_3 \cdot 6H_2O$ (13.5 mg, 0.050 mmol) in propylene carbonate (1 mL) were charged in a pressure tube with a stirrer bar. The reaction mixture was stirred at 100 °C for the specified time. After completion of the reaction (monitored by TLC), the analytically pure product was isolated by extraction with petroleum ether, then the organic phases were concentrated under reduced pressure and filtered through a short pad of silica gel to yield pure product.

Dibenzyl Ether ***2a***.[34] The product was isolated as a colorless oil (0.184 g, 0.93 mmol, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.32 (m, 10H), 4.59 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 128.4, 128.3, 127.7, 72.0.

Bis(2-methylbenzyl) Ether ***2b***.[34] The product was isolated as a white solid (0.206 g, 0.91 mmol, 91); mp = 50−51 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.39 (m, 2H), 7.26−7.19 (m, 6H), 4.61 (s, 4H), 2.38 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 136.3, 130.3, 128.7, 127.9, 125.9, 70.8, 18.9.

Bis(4-methylbenzyl) Ether ***2c***.[34] The product was isolated as a white solid (0.120 g, 0.53 mmol, 53%); mp = 61−62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 9 Hz, 4H), 7.17 (d, J = 9 Hz, 4H), 4.52 (s, 4 H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 135.5, 129.2, 128.1, 71.5, 20.8.

Bis(4-chlorobenzyl) Ether ***2d***.[34] The product was isolated as a white solid (0.208 g, 0.78 mmol, 78%); mp = 54−55 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35(d, J = 8.5 Hz, 4H), 7.31 (d, J = 8.5 Hz, 4H), 4.58(s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 133.4, 129.0, 128.6, 71.4.

Bis(2-chlorobenzyl) Ether ***2e***.[34] The product was isolated as a white solid (0.171 g, 0.64 mmol, 64%); mp = 48−49°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.5 Hz, 2 Hz, 2H), 7.40 (dd, J = 8 Hz, 1.5 Hz, 2H), 7.32 (td, J = 8 Hz, 1.5 Hz, 2H), 7.26 (td, J = 7.5 Hz, 1.5 Hz, 2H), 4.78 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9, 132.9, 129.3, 129.0, 128.7, 126.8, 69.6.

Bis(3-chlorobenzyl) Ether ***2f***.[34] The product was isolated as a colorless oil (0.160 g, 0.60 mmol, 60%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.24 (m, 8H), 4.54 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 134.5, 129.9, 127.9, 127.8, 125.8, 71.4.

Bis(4-fluorobenzyl) Ether ***2g***.[34] The product was isolated as a colorless oil (0.199 g, 0.85 mmol, 85%); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.34 (t, J = 7.5 Hz, 4H), 7.05 (t, J = 8.5 Hz, 4H), 4.51 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 246.2 Hz), 133.9 (d, J_{C-F} = 3.15 Hz), 129.7 (d, J_{C-F} = 8 Hz), 115.4 (d, J_{C-F} = 22 Hz), 71.5.

Bis(2-fluorobenzyl) Ether ***2h***.[34] The product was isolated as a colorless oil (0.148 g, 0.63 mmol, 63%); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.47 (t, J = 7.5 Hz, 2H), 7.3−7.28 (m, 2H), 7.15 (t, J = 7.5 Hz, 2H), 7.05 (t, J = 7.5 Hz, 2H), 4.66 (s, 4H). ^{13}C NMR

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(126 MHz, $CDCl_3$) δ 160.8 (d, J_{C-F} = 247.4 Hz), 130.0 (d, $J_{C-F'}$ = 4 Hz), 129.5 (d, $J_{C-F'}$ = 8 Hz), 125.4 (d, J_{C-F} = 15 Hz), 124.3 (d, J_{C-F} = 4 Hz), 115.3 (d, $J_{C-F'}$ = 21.5 Hz), 66.1.

Bis(4-(trifluoromethyl)benzyl) Ether **2i**.[35] The product was isolated as a colorless oil (0.131 g, 0.56 mmol, 56%); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.76 (d, J = 8 Hz, 2H), 7.66 (d, J = 8 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 4.83 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 132.1, 129.0, 127.6 (q, $J_{C-F'}$ = 31 Hz), 127.6, 125.8 (q, $J_{C-F'}$ = 5.6 Hz), 124.4 (q, $J_{C-F'}$ = 270 Hz), 68.9.

Bis(2-bromobenzyl) Ether **2j**.[36] The product was isolated as a white solid (0.198 g, 0.56 mmol, 56%); mp = 63−65°C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.56 (t, J = 7.7 Hz, 4H), 7.34 (t, J = 7.5 Hz, 2H), 7.16 (t, J = 7.5 Hz, 2H), 4.71 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 132.5, 129.2, 129.1, 127.5, 122.6, 72.2.

(Oxybis(methanetriyl))tetrabenzene **2k**.[23] The product was isolated as a white solid (0.256 g, 0.73 mmol, 73%); mp = 108−109°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8 Hz, 8H), 7.35 (t, J = 8 Hz, 8H), 7.30−7.27 (m, 4H), 5.45 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 128.4, 127.4, 127.2, 80.0.

2,2′-(Oxybis(ethane-1,1-diyl))dinaphthalene **2l**.[37] The product was isolated as a white solid (0.287 g, 0.88 mmol, 88%); mp = 240−244°C; Mixture of two diastereoisomers 2:1; ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.0−7.85 (m, 20H), 7.76 (s, 4H), 7.65−7.51 (m, 18H), 4.86 (q, J = 6.5 Hz, 2H) min, 4.58 (q, J = 6.5 Hz, 4.6H) maj, 1.71 (d, J = 6.5 Hz, 6H) min, 1.62 (d, J = 6.5 Hz, 13H) maj; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 141.6, 133.4, 133.3, 133.1, 132.9, 128.5, 128.1, 127.9, 127.9, 127.8, 127.7, 126.2, 126.0, 125.8, 125.6, 125.3, 124.9, 124.6, 124.3, 74.9, 74.7,24.7, 23.0.

(Oxybis(ethane-1,1-diyl))dibenzene **2m**.[23] The product was isolated as a yellow oil (0.168 g, 0.74 mmol, 74%); Mixture of two diastereoisomers: 1:1; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.23 (m, 17H), 4.57 (q, J = 6.0 Hz, 1.76H), 4.29 (q, J = 6.0 Hz, 2H), 1.50 (d, J = 6.6 Hz, 6H), 1.42 (d, J = 6.6 Hz, 6.64H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 144.3, 128.6, 128.3, 127.5, 127.2, 126.6, 126.3, 74.7, 74.6, 24.9, 23.1.

Bis(cinnamyl) Ether **2n**.[38] The product was isolated as a colorless oil (0.108 g, 0.43 mmol, 43%); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39−7.17 (m,10H), 6.48 (d, J = 16 Hz, 2H), 6.29 (td, J = 16 Hz, J = 6.6 Hz, 2H), 3.15−3.11 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 131.2, 128.6, 128.3, 127.2, 126.2, 100.1.

Preparation of Benzyl Methyl Carbonates. *4-Chlorobenzyl Methyl Carbonate* **3a**.[39] The product was isolated as a colorless oil (0.156 g, 0.78 mmol, 78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36:7.27 (m, 4H), 5.12 (s, 2H), 3.8 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.8, 134.6, 133.8, 129.8, 128.9, 68.8, 55.4.

2-Chlorobenzyl Methyl Carbonate **3b**.[40] The product was isolated as a colorless oil (0.150 g, 0.75 mmol, 75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.27 (m, 4H), 5.29 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.6, 133.6, 133.1, 129.9, 129.8, 129.7, 127.0, 66.8, 54.9.

2-Bromobenzyl Methyl Carbonate **3c**.[41] The product was isolated as a colorless oil (0.129 g, 0.53 mmol, 53%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H) 7.44 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.2 (t, J = 7.5 Hz, 1H), 5.22 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 134.7, 132.9, 130.0, 129.9, 127.6, 123.3, 68.8, 55.1.

2-Fluorobenzyl Methyl Carbonate **3d**.[42] The product was isolated as a colorless oil (0.156 g, 0.85 mmol 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, J = 7.5 Hz, 1H), 7.33(q, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 5.24 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0 (d, J_{C-F} = 246 Hz), 155.7, 130.7 (d, J_{C-F} = 3.6 Hz), 124.3 (d, J_{C-F} = 4 Hz), 122.5 (d, J_{C-F} = 14 Hz), 115.5 (d, J_{C-F} = 21 Hz), 63.3 (d, J_{C-F} = 4.2 Hz), 54.8.

Synthesis of Nonsymmetrical Ethers: Typical Procedure. In a pressure tube were sequentially added $FeCl_2{\cdot}4H_2O$ (19.8 mg, 10 mol %) and pyridine bis-thiazoline ligand (43.8 mg, 12 mol %) in propylene carbonate (1 mL). The mixture was stirred for 1 h at room temperature. Then, secondary benzyl alcohol (1.0 mmol) and primary benzyl alcohol or aliphatic alcohol (1.2 mmol) were added. The reaction mixture was stirred at 100 °C for a specified time. After completion of the reaction (monitored by TLC), the mixture was extracted with petroleum ether (30 mL). We used centrifugation to accelerate the separation between petroleum ether and PC. The product goes into the petroleum ether phase, and the iron salt and the ligand remain in the PC phase. The crude product was then filtered through a short pad of silica gel and concentrated under reduced pressure to yield pure unsymmetrical ether.

Preparation of 2,6-Bis(4-methoxycarbonyl-4,5-dihydrothiazol-2-yl)-pyridine.[25] Pyridine-2,6-diacarbonitrile (0.129 g, 1.0 mmol, 1.0 equiv), L-cysteine methyl hydrochloride (0.377 g, 2.2 mmol, 2.2 equiv), potassium bicarbonate (0.220 g, 2.2 mmol, 2.2 equiv), and sodium lauryl sulfate (0.057 g, 0.20 mmol, 20 mol %) were added to H_2O (3 mL) in a Schlenk tube. The mixture was stirred for 45 min at rt, extracted with ethyl acetate (3 × 10 mL), and then concentrated in *vacuo*. The crude product was purified by recrystallization with diethyl ether to give the ligand as a white solid (255.5 mg, 70%). *Rf* = 0.57 (CH_2Cl_2/MeOH 20:1); mp: 152 °C (lit. 152 °C); $[\alpha]^D$ = +127.3 (c = 1 in CH_3Cl); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 2H), 7.87 (t, J = 7.8 Hz, 1H), 5.40 (t, J = 9.5 Hz, 2H), 3.84 (s, 6H), 3.62 (2 dd, J = 11.5 Hz, 9.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 170.9, 150.1, 137.0, 123.4, 79.5, 53.1, 34.1; HRMS (ESI) m/z: $[MH]^+$: calcd for $C_{15}H_{16}N_3O_4S_2$: 366,0577: found: 366.0581.

2-(1-(Benzyloxy)ethyl) Naphthalene **4a**.[37] The product was isolated as a colorless oil (0.231 g, 0.88 mmol, 88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90−7.27 (m, 12H), 4.68 (q, J = 6.5 Hz, 1H), 4.49 (d, J = 12 Hz, 1H), 4.35 (d, J = 12 Hz, 1H), 1.57 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.7, 133.4, 133.2, 128.6, 128.5, 127.9, 127.6, 126.2, 126.1, 125.9, 125.4, 124.4, 77.4, 70.4, 24.1.

((Benzyloxy)(cyclohexyl)methyl) Benzene **4b**. The product was isolated as a colorless oil (0.249 g, 0.89 mmol, 89%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.19 (m, 10 H), 4.45 (d, J = 12 Hz, 1H), 4.25 (d, J = 12 Hz, 1H), 4.00 (d, J = 7.5 Hz, 1H), 2.19−2.15 (m, 1H), 1.77−0.77 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 139.0, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4, 86.4, 70.5, 44.5, 29.8, 29.5, 26.6, 26.2, 26.1; HRMS (TOF MS Cl^+) calculated for: $C_{20}H_{23}O$ $[M^+]$: 279.1749, found: 279.1744.

Benzyl Diphenylmethyl Ether **4c**.[37] The product was isolated as a colorless oil (0.244 g, 0.89 mmol, 89%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70−7.19 (m, 15H), 5.61 (s, 1 H), 4.70 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 138.4, 128.4, 128.5, 127.8, 127.7, 127.5, 127.1, 82.5, 70.5.

(((2-Chlorobenzyl)oxy) Methylene) Dibenzene **4d**.[43] The product was isolated as a colorless oil (0.191 g, 0.62 mmol, 62%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.22 (m, 14H), 5.61 (s, 1 H), 4.74 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 136.4, 129.3, 128.6, 128.5, 128.0, 127.6, 127.3, 127.2, 126.8, 83.5, 68.0.

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2-Chlorobenzyl Trityl Ether ***4e***.[44] The product was isolated as a white solid (0.200 g, 0.52 mmol, 52%); (mp = 147−149 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.13 (m, 19 H), 4.32 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 137.1, 129.6, 129.5, 129.1, 128.9, 128.4, 128.0, 127.2, 126.8, 87.5, 63.3.

(1-(Benzyloxy)ethyl) Benzene ***4f***.[37] The product was isolated as a colorless oil (0.127 g, 0.60 mmol, 60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.27 (m, 10H) 4.55−4.45(m, 2H), 4.32 (d, J = 12 Hz, 1H), 1.51 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 138.7, 128.6, 128.4, 127.8, 127.6, 127.5, 126.4, 70.0, 69.9, 24.2.

1-(1-(Benzyloxy)ethyl)-4-methylbenzene ***4g***.[37] The product was isolated as a colorless oil (0.145 g, 0.64 mmol, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 9H), 4.51−4.44 (m, 2H), 4.29 (d, J = 12 Hz, 1H), 2.40 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.7, 137.2, 129.2, 128.4, 127.9, 127.4, 126.4, 74.1, 70.3, 24.2, 21.0.

1-Chloro-2-((1-(p-tolyl)ethoxy)methyl) Benzene ***4h***. The product was isolated as a colorless oil (0.164 g, 0.63 mmol, 63%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.53 (m, 1 H), 7.36−7.16 (m, 8H), 4.54 (q, J = 6.3 Hz, 1H), 4.48 (s, 2H), 2.38 (s, 3H), 1.52 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 137.3, 136.7, 133.0, 129.3, 128.5, 126.6, 126.5, 126.3, 77.9, 67.9, 24.2, 21.2; HRMS (TOF MS Cl^{+}) calculated for: $C_{16}H_{16}OCl$ [M]$^{+}$: 259.0890, found: 259.0885.

1-(1-(Benzyloxy)ethyl)-4-methoxybenzene ***4i***.[37] The product was isolated as a colorless oil (0.194 g, 0.82 mmol, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.31(m, 7 H), 6.98−6.95 (m, 2H), 4.53−4.47 (m, 2H), 4.32 (d, J = 12 Hz, 1H), 3.86 (s, 3H), 1.52 (d, J = 6.5, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 138.7, 135.7, 128.3, 127.7, 127.6, 127.4, 113.8, 76.8, 70.1, 55.2, 24.0.

1-(1-(Benzyloxy)ethyl)-4-fluorobenzene ***4j***.[37] The product was isolated as a colorless oil (0.122 g, 0.53 mmol, 53%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−6.94 (m, 9H), 4.63−4.47 (m, 2H), 4.33 (d, J = 12 Hz, 1H), 1.48 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, J_{C-F} = 243 Hz), 146.7 (d, J_{C-F} = 6.4 Hz), 138.6, 130.0 (d, J_{C-F} = 8 Hz), 128.5, 125.6 (d, J_{C-F} = 7 Hz), 122.0 (d, J_{C-F} = 3 Hz), 114.5 (d, J_{C-F} = 21 Hz), 113.2 (d, J_{C-F} = 21 Hz), 76.8, 70.7, 24.1. ^{19} F NMR (282 MHz; $CDCl_3$) δ − 113.0.

1-(1-(Benzyloxy)ethyl)-4-bromobenzene ***4k***. The product was isolated as a colorless oil (0.125 g, 0.43 mmol 43%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.11 (m, 9 H), 4.52−4.50 (m, 2H), 4.29 (d, J = 12 Hz, 1H), 1.45 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 138.4, 131.7, 128.5, 128.2, 127.8, 127.7, 121.3, 74.3, 70.4, 24. 0. HRMS (TOF MS Cl^{+}) calculated for: $C_{15}H_{15}BrO$ [M]$^{+}$:290.0306, found: 290. 0307.

(Cyclohexyl(isobutoxy)methyl) Benzene ***6a***. The product was isolated as a colorless oil (0.212 g, 0.86 mmol 86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.10 (m, 5 H), 3.85 (d, J = 7.5 Hz, 1H), 3.08 (dd, J = 2.4 Hz, 9 Hz, 1H), 2.93 (dd, J = 2.4 Hz, 9 Hz, 1H), 2.11−2.07 (m, 1H), 1.88−1.53 (m, 1H) 1.77−1.53 (m, 5H), 1.37−0.94 (m, 6H), 0.90(d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) (75 MHz, $CDCl_3$) δ 142.1, 128.0, 127.6, 127.2, 87.9, 76.1, 44.7, 29.5, 28.8, 26.7, 26.3, 26.2, 19.7, 19.6. HRMS (TOF MS Cl^{+}) calculated for: $C_{17}H_{26}O$ [M]$^{+}$: 245.1905, found: 245.1897.

(iso-Butoxymethylene) Dibenzene ***6b***. The product was isolated as a colorless oil (0.212 g, 0.88 mmol, 88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.26 (m, 10H), 5.38 (s, 1H), 3.30 (d, J = 6.6 Hz, 2H), 2.09−1.96 (m, 1H), 1.02 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 128.4, 127.3, 127.1, 83.9, 76.1, 28.9, 19.6. HRMS (TOF MS Cl^{+}) calculated for: $C_{17}H_{20}O$ [M]$^{+}$: 240.1514, found: 240.1516.

(sec-Butoxymethylene) Dibenzene ***6c***.[45] The product was isolated as a colorless oil (0.161 g, 0.67 mmol, 67%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.27 (m, 10H), 5.58 (s, 1H), 3.61−3.51 (m, 1H), 1.82−1.54 (m, 2H), 1.26 (d, J = 6.3 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 128.3, 127.4, 127.1, 80.7, 74.1, 29.6, 19.3, 9.8.

((Pentan-2-yloxy)methylene) Dibenzene ***6d***.[45] The product was isolated as a colorless oil (0.173 g, 0.68 mmol, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.27 (m, 10H), 5.56 (s, 1H), 3.65−3.54 (m, 1 H), 1.78−1.33 (m, 4H), 1.25 (d, J = 6.3 Hz, 3H), 0.95 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 128.4, 127.3, 127.1, 80.8, 72.7, 39.3, 19.8, 18.8, 14.3.

(Butoxymethylene) Dibenzene ***6e***.[45] The product was isolated as a colorless oil (0.197 g, 0.82 mmol, 82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56−7.28 (m, 10 H), 5.42 (s, 1 H), 3.55 (t, J = 6.3 Hz, 2H), 1.73 (quint, J = 6.3 Hz, 2H), 1.58−1.46 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 128.3, 127.3, 127.1, 83.7, 69.0, 32.1, 19.6, 14.0.

(Propoxymethylene) Dibenzene ***6f***.[45] The product was isolated as a colorless oil (0.199 g, 0.88 mmol, 88%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.26 (m, 10H), 5.42 (s, 1H), 3.51 (t, J = 6.6 Hz, 2H), 1.81−1.72 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 128.3, 127.3, 127.1, 83.7, 70.8, 23.2, 10.8.

((Prop-2-yn-1-yloxy)methylene) Dibenzene ***6g***.[45] The product was isolated as a colorless oil (0.135 g, 0.61 mmol, 61%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.26 (m, 10H), 5.70 (s, 1H), 4.18 (d, J = 2.4 Hz, 2H), 2.48 (t, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 128.5, 127.7, 127.4, 81.7, 79.9, 74.7, 55.9.

2-(1-Isobutoxyethyl) Naphthalene ***6h***. The product was isolated as a colorless oil (0.194 g, 0.85 mmol, 85%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89−7.45 (m, 7H), 4.58 (q, J = 6.6 Hz, 1H), 3.20 (dd, J = 9 Hz, 6.3 Hz, 1H), 3.15 (dd, J = 9 Hz, 6.3 Hz, 1H), 2.01−1.88 (m, 1 H), 1.58 (d, J = 6.6 Hz, 3H), 0.96 (dd, J = 1.8 Hz, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 133.5, 133.1, 128.3, 127.9, 127.7, 126.0, 125.7, 125.0, 124.4, 78.3, 76.0, 29.1, 24.1, 19.5; HRMS (TOF MS Cl^{+}) calculated for: $C_{16}H_{20}O$ [M]$^{+}$: 228.1514, found: 228.1518.

2-(1-Propoxyethyl) Naphthalene ***6i***. The product was isolated as a colorless oil (0.156 g, 0.73 mmol, 73%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88−7.26 (m, 7H), 4.59 (q, J = 6.6 Hz, 1 H), 3.36 (t, J = 6.6 Hz, 2 H), 1.71−1.59 (m, 2 H), 1.56 (d, J = 6.6 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 133.5, 133.2, 128.3, 127.9, 127.8, 126.1, 125.7, 125.0, 124.4, 78.1, 70.6, 23.6, 23.1, 10.5. HRMS (TOF MS Cl^{+}) calculated for: $C_{15}H_{18}O$ [M]$^{+}$: 214.1358, found: 214.1356.

2-(1-Butoxyethyl) Naphthalene ***6j***. The product was isolated as a colorless oil (0.183 g, 0.80 mmol, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88−7.45 (m, 7 H), 4.58 (q, J = 6.6 Hz, 1H), 3.38 (t, J = 6.3 Hz, 2H), 1.67−1.60 (m, 2H), 1.55 (d, J = 6.3 Hz, 3H), 1.48−1.31 (m, 2 H), 0.94 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 133.3, 133.2, 128.2, 128.0, 127.7, 126.1, 125.6, 125.0, 124.3, 78.1, 68.7, 32.2, 24.2, 19.5, 14.1. HRMS (TOF MS Cl^{+}) calculated for: $C_{16}H_{20}O$ [M]$^{+}$:228.1514, found: 228.1516.

2-(1-(Cyclopentyloxy)ethyl) Naphthalene ***6k***. The product was isolated as a colorless oil (0.178 g, 0.747 mmol, 74%); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.85−7.43 (m, 7H), 4.65 (q, J = 6.6 Hz, 1 H), 3.92−3.85 (m, 1 H), 1.76−1.59 (m, 8 H), 1.50 (d, J = 6.3 Hz, 3H);^{13}C NMR (75 MHz; $CDCl_3$) δ 142.4, 133.5, 133.1,

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128.1, 127.9, 127.8, 126.1, 125.7, 125.0, 124.6, 79.0, 75.8, 32.9, 32.1, 24.4, 23.8. HRMS (TOF MS Cl$^+$) calculated for: $C_{17}H_{20}O$ $[M]^+$: 240.1514, found: 240.1512.

(Isobutoxymethanetriyl) Tribenzene ***6l.*** The product was isolated as a colorless oil (0.162 g, 0.51 mmol, 51%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.28 (m, 15 H), 2.99 (d, J = 6.6 Hz, 2H), 2.09−1.95 (m, 1H), 1.04 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 129.1, 127.7, 126.6, 86.1, 69.5, 29.02, 19.8; HRMS (TOF MS Cl$^+$) calculated for: $C_{23}H_{24}O$ $[M]^+$: 316.1827, found: 316.1823.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03803.

Recycling procedures and copies of the NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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