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Crown Ether Complex Cation Ionic Liquids: Preparation and Applications in Organic Reactions

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Abstract: A series of crown ether complex cation ionic liquids (CECILs) were designed, synthesised and characterised by NMR spectroscopy, HRMS, thermogravimetric differential thermal analysis (TG-DTA) and elemental analysis. Their applications in various organic reactions were investigated: [15-C-5Na][OH], [15-C-5Na][OAc], [18-C-6K][OH] and [18-C-6K][OAc] (15-C-5 = [15]crown-5; 18-C-6 = [18]crown-6) efficiently catalysed the Michael addition of alkenes and relevant nucleophiles; [18-C-6K][OH] and [15-C-5Na][OH] effectively catalysed the Henry reaction of nitromethane and aromatic aldehydes; [18-C-6K][OH] has excellent catalytic efficiency for Knoevenagel condensation of aromatic aldehydes and malononitrile; $PdCl_2$/[18-C-6K]$_3$[PO_4]/K_2CO_3 efficaciously catalysed the Heck reaction of olefins and aromatic halides; [18-C-6K][BrO_3] can be used as both oxidant and solvent in the oxidation reaction of aromatic alcohols. The CECIL catalysts [15-C-5Na][OH] (Michael addition) and [18-C-6K][OH] (Henry reaction) can be recycled and reused several times without obvious loss of activity and their recovery is very simple.

Keywords: crown compounds · Heck reaction · Henry reaction · ionic liquids · Michael addition

Introduction

Ionic liquids (ILs), defined as molten salts at temperatures lower than 100 °C, have received overwhelming interest because of their unique properties, such as lack of significant vapour pressure, ease of reuse, absence of flammability and tolerance for large temperature variations.[1] ILs have been used in a number of organic reactions, for example, hydrogenation, oxidation and C–C bond-forming reactions.[2] Although thousands of ILs were synthesised in the past decades, they commonly consisted of *N*,*N'*-dialkylimidazolium or *N*-alkylpyridinium cations.[3] Besides these organic cations, could other cations be incorporated into ILs?_It is known that electrostatic interactions between large cations and large anions are relatively weak, whereas the van der Waals forces are strong, which induces a decrease in lattice energy and melting point.[4] Based on these fundamental understandings, we designed and synthesised a series of novel crown ether complex cation ionic liquids (CECILs), which have melting points lower than 200 °C, composed of crown ether chelated alkali metal cations and various anions (Table 1). Furthermore, to demonstrate the practicality of these novel CECILs, they have been applied in various carbon–carbon bond-forming reactions, such as Michael addition, Henry reaction, Knoevenagel condensation and Heck reaction. The excellent results are disclosed in this paper.

Table 1. The properties of the CECILS.

Entry	CECIL	Colour	M.p. [°C][a]	T_d [°C][b]
1	[18-C-6K]$_3$[PO_4]	white	38	145
2	[18-C-6K]$_2$[HPO_4]	white	37	202
3	[18-C-6K][H_2PO_4]	white	39	189
4	[18-C-6K][OAc]	white	77	200
5	[15-C-5Na][OAc]	orange	171	171
6	[18-C-6K][Br]	white	174	192
7	[15-C-5Na][Br]	yellow	153	171
8	[18-C-6K][NO_3]	white	92	213
9	[18-C-6K]$_2$[CO_3]	white	44	197
10	[18-C-6K][HCO_3]	white	113	203
11	[18-C-6K][OH]	white	39	182
12	[15-C-5Na][OH]	orange	−54	147
13	[18-C-6K][ClO_3]	white	179	200
14	[18-C-6K][BrO_3]	yellow	115	174
15	[15-C-5Na][IO_3]	yellow	116	154
16	[15-C-5Na]$_2$[C_2O_4]	colourless	167	167
17	[18-C-6K][biphthalate anion]	white	129	211

[a] All melting points were determined on a XT-4 melting point apparatus without calibration. [b] Decomposition temperatures (T_d) were determined by TG-DTA, heating at 10 °C min^{-1} under nitrogen.

The Michael addition reaction is a useful method for carbon–carbon bond formation and has been efficiently extended for carbon–sulfur and carbon–nitrogen bond formation.[5] The products of Michael addition not only constitute components of biologically active natural products, but also serve as key intermediates for many important organic compounds.[6] Herein, the simple CECIL [15-C-5Na][OH] (15-C-5 = [15]crown-5) was applied in Michael/aza-Michael additions as an efficient catalyst. Another important pathway to construct carbon–carbon bonds is the palladium-catalysed arylation and vinylation of olefins by aryl and vinyl halides

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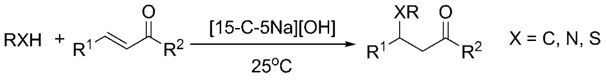
or their derivatives, known as the Heck reaction.[7] In this paper, CECILs [18-C-6K]$_3$[PO$_4$], [18-C-6K]$_2$[HPO$_4$] and [18-C-6K][H$_2$PO$_4$] (18-C-6 = [18]crown-6) were successfully applied in the Heck reactions of olefins and aromatic halides. The Henry (or nitroaldol) reaction, catalysed by organic and inorganic bases, is also a convenient method for direct carbon–carbon bond formation to give bifunctional β-hydroxynitroalkanes.[8] The products are useful intermediates in the preparation of nitroalkenes, α-nitroketones and β-aminoalcohol derivatives, such as ephedrine and norephedrine.[9] Herein, the Henry reaction of nitromethane and aromatic or aliphatic aldehydes catalysed by [18-C-6K][OH] is reported. The Knoevenagel condensation, which is also a very useful reaction and has been widely employed for carbon–carbon bond formation in organic synthesis,[10] is usually catalysed by a base. We found that the CECIL [18-C-6K][OH] showed an excellent catalytic efficiency in the Knoevenagel condensation of aromatic aldehydes and malononitrile. Oxidation reactions are among the most important transformations in synthetic chemistry and are an important tool for the introduction and modification of functional groups.[11] We report our investigation on the oxidation of aromatic alcohols by using [18-C-6K][BrO$_3$] as both oxidant and solvent.

Results and Discussion

With the understanding of interaction of the ion pairs, we dissolved the crown ether and relevant inorganic/organic salt or inorganic base in water to generate our desired CECIL. The obtained CECILs have high purity, shown by sharp melting points (Table 1). They have good stabilities measured by TG-DTA. All of the CECILs synthesised are solids at room temperature, except [15-C-5Na][OH], and they range from colourless to orange. It can be seen that almost all of the products prepared with [18]crown-6 are white solids (Table 1, entries 1–4, 6, 8–11, 13, 17), whereas the products prepared with [15]crown-5 have different colours (Table 1, entries 5, 7, 12, 15). CECILs prepared from bromide, chlorate, bromate and iodate have melting points higher than 100 °C, whereas small anion CECILs possess melting points lower than 100 °C. The formation of [18-C-6K][X] and [15-C-5Na][X] is a simple reaction carried out by mixing the correct molar ratio of crown ether and relevant salts in water, followed by evaporation and, finally, desiccation under vacuum. If we define CECILs as molten salts at temperatures lower than 200 °C, all 17 CECILs are consistent with the new concept. The CECILs obtained are thermally stable up to 150–220 °C, a little lower than the thermal stability of imidazolium cation ILs. The decomposition of CECILs might be attributed to damage of their ligands. Impurities in ILs can affect their melting point and reduce their catalytic abilities.

The electrostatic interactions between cations and anions are reduced in CECILs relative to their precursors, thus, we speculate that the anions of CECILs would have stronger nucleophilicities. Therefore, organic reactions traditionally catalysed by a base, such as Michael addition, Henry reaction and Knoevenagel condensation, have been used to test the catalytic abilities of our new ILs [18-C-6K][OH], [15-C-5Na][OH], [18-C-6K][OAc] and [15-C-5Na][OAc]. The CECILs [18-C-6K]$_3$[PO$_4$], [18-C-6K]$_2$[HPO$_4$] and [18-C-6K]-[H$_2$PO$_4$] containing phosphorous anion were used in Heck reactions as additives. And the CECIL [18-C-6K][BrO$_3$] was applied to the oxidation of aromatic alcohols. All these ILs dissolve well in strong polar solvents, such as water, methanol, ethanol, acetone and acetonitrile; we chose methanol as the reaction media in our investigations.

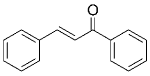
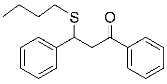
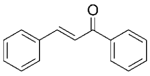
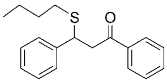
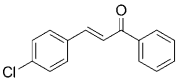
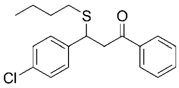
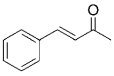
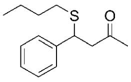
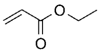
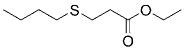
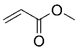
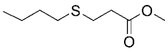
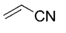
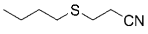
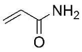
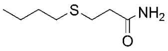
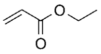
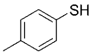
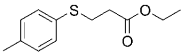
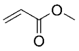
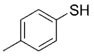
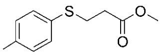
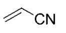
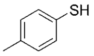
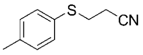
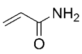
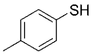
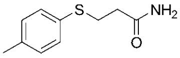
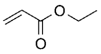
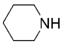
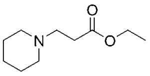
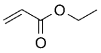
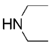
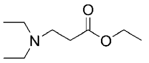
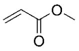
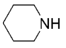
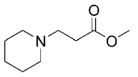
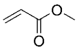
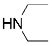
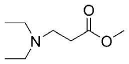
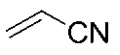
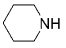
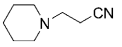
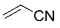
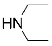
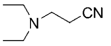
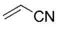
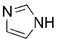
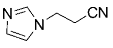
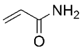
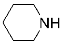
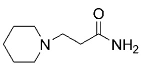
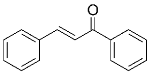
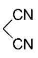
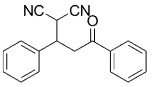
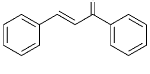
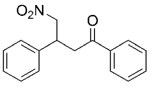
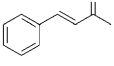
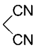
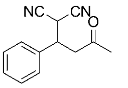
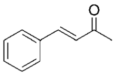
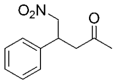
The Michael addition is traditionally catalysed by strong bases.[12] ILs have recently been used as catalysts and solvents in Michael additions.[13] The complexation of a potassium or sodium cation to a crown ether increases the radius of the cation, which decreases the electrostatic interactions between ion pairs and, consequently, enhances the basicity/nucleophilicity of the anion in [15-C-5Na][OH] and [18-C-6K][OH]. Alkaline CECIL of [15-C-5Na][OH] was used to catalyse the Michael/aza-Michael addition of carbon, sulfur and nitrogen nucleophiles and olefins under mild conditions, generating branched carbonyl compounds in high yields (Scheme 1, Table 2). We emphasise that the C−S and C−N bond-forming reactions catalysed by [15-C-5Na][OH] can be achieved within 30 min at 25 °C (Table 2, entries 1, 3–8, 13–18). In particular, the Michael addition of butanethiol to chalcone can be completed within 5 min in the presence of [15-C-5Na][OH] (Table 2, entry 1) or [18-C-6K][OH] (Table 2, entry 2) to generate the product in 98 % yield, which are much more efficient than the traditional IL 1-pentyl-3-methylimidazolium bromide ([pmIm][Br]) (Table 2, entry 2).[13a] For the Michael addition of piperidine to methyl acrylate (Table 2, entry 15), better results were obtained when catalysed by [15-C-5Na][OH] or [15-C-5Na]-[OAc] compared with the conventional IL [DBUH][OAc] (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene). In contrast, the formation of C−C bond was a much slower process, by reason that the C−H bond of the nucleophile is harder to activate (Table 2, entries 21–24). When the olefin was acrylamide, the reaction gave low yields for the conjugation of an amide (Table 2, entries 12, 20). When imidazole was used as the nucleophile a similar phenomenon was observed (Table 2, entry 19).



Scheme 1. Michael addition of nucleophiles to α, β-unsaturated carbonyl compounds.

The reaction of chalcone and butanethiol was chosen as a model reaction to investigate the recycling of [15-C-5Na] [OH]. The recycling results showed that the catalyst did not lose its activity after five cycles (Table 2, entry 1). For investigation of the solvent effect on catalyst [15-C-5Na][OH],

Table 2. Michael addition catalysed by [15-C-5Na][OH].[a]

Entry	Olefin	Nucleophile	Product	t [min]	Yield [%][b]
1		BuSH		5	98.0 96.2[c] 97.0[c] 98.0[c] 96.5[c]
2		BuSH		5 60	97.5[d] 95.0[e]
3		BuSH		20	99.0
4		BuSH		20	85.0
5		BuSH		30	87.4
6		BuSH		25	99.0
7		BuSH		25	99.0
8		BuSH		30	87.3
9				42	99.7
10				55	94.1
11				115	86.2
12				360	41.3
13				20	83.0
14				20	83.0
15				20 20 90	99.0 95.0[f] 92.0[g]
16				20	84.7
17				20	96.0
18				20	71.0
19				20	10.3
20				30	trace
21				30	64.3
22		CH$_3$NO$_2$		210 140	55.3 82.3[h] 81.3[c] 82.5[c]
23				300	36.5
24		CH$_3$NO$_2$		480	90.0[i]

[a] Reaction conditions: olefin (1 mmol), nucleophile (1.3 mmol), catalyst [15-C-5Na][OH]·H$_2$O (0.1 mmol), CH$_3$OH (1 mL), $T=25$ °C. [b] Isolated yield. [c] Recycled catalyst used. [d] [18-C-6K][OH] (0.1 mmol) was used as catalyst. [e] See reference [13a]. [f] [15-C-5Na][OAc] (0.1 mmol) was used. [g] See reference [13h]. [h] Chalcone (0.2 mmol), CECIL (0.25 g), neat. [i] $T=50$ °C, the amount of [15-C-5Na][OH] 0.5 mmol.

the reaction of chalcone and nitromethane was chosen as a model reaction. Surprisingly, the reaction time was reduced from 210 to 140 min when [15-C-5Na][OH] was used as solvent and catalyst and the yield was enhanced from 55.3 to 82%. This phenomenon was evidence of the positive solvent effect of the novel CECILs (Table 2, entry 22).

We know that Michael addition is usually carried out under strong base catalysis to avoid side reactions. Strangely, our weaker base catalysts [18-C-6K][OAc] or [15-C-5Na][OAc] also gave high yields without any byproducts under mild conditions (Table 3). These phenomena were consistent with our understandings of the enhancements of the basicity/nucleophilicity of the anion of CECILs.

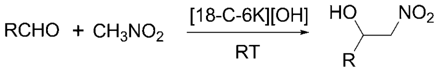
Table 3. Michael addition catalysed by [18-C-6K][OAc].[a]

Type	Olefin	Nucleophile	t [min]	Yield [%][b]
C–S	chalcone	butanethiol	30	99.0 97.0[c]
C–C	chalcone	malononitrile	60	95.0
C–N	ethyl acrylate	piperidine	20	92.0

[a] Reaction conditions: olefin (1 mmol), nucleophile (1.3 mmol), catalyst [18-C-6K][OAc]·2.5H$_2$O (0.1 mmol), CH$_3$OH (1 mL), $T=25$ °C. [b] Isolated yield. [c] [15-C-5Na][OAc]·H$_2$O (0.1 mmol) was used as catalyst.

To extend the scope of application of the CECILs, [18-C-6K][OH] and [15-C-5Na][OH] were used as catalysts in the Henry reaction of aldehydes and nitromethane (Table 4). Both aliphatic and aromatic aldehydes, with either electron-withdrawing or electron-donating groups give good yields. Generally, the aromatic aldehydes bearing electron-withdrawing groups revealed higher reaction rates than those with electron-donating groups (Table 4, entries 9–21 versus 1–8). The reactions of highly active aliphatic aldehydes and nitromethane were carried out at −15 °C and gave good yields (Table 4, entries 24 and 25). The CECIL catalyst was much more efficient for aliphatic aldehydes compared with 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]),[8d] 1,1,3,3-tetramethyl guanidine lactate ([TMG][Lac])[8e] and 1-pentyl-3-methylimidazolium bromide -Mg-Al hydrotalcites ([bmIm]BF$_4$-Mg-Al HT) catalysts.[8g] The scope of the reaction was extended to include furfural and cinnamaldehyde (Table 4, entries 22, 23).

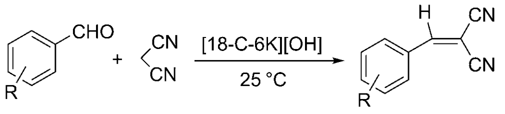
Table 4. Henry reaction catalysed by [18-C-6K][OH].[a]



Entry	R	t [min]	Yield [%][b]
1	Ph	120	71.9
2	2-$CH_3OC_6H_4$	40	95.3
3	4-$CH_3OC_6H_4$	240	52.5
4	2,5-$(CH_3O)_2C_6H_3$	25	99.0
5	2-$CH_3C_6H_4$	240	84.1
6	3-$CH_3C_6H_4$	240	50.9
7	4-$CH_3C_6H_4$	240	72.5
8	3,4-$(CH_3)_2C_6H_3$	120	68.2
9	2-ClC_6H_4	30	97.4
10	3-ClC_6H_4	30	99.5
11	4-ClC_6H_4	120	69.8
12	2,4-ClC_6H_3	40	78.1
13	2-BrC_6H_4	15	96.0
14	2-$NO_2C_6H_4$	10	98.4
15[c]	2-$NO_2C_6H_4$	10	97.2
16[c]	2-$NO_2C_6H_4$	10	96.9
17[c]	2-$NO_2C_6H_4$	10	97.0
18[c]	2-$NO_2C_6H_4$	10	96.0
19[d]	2-$NO_2C_6H_4$	10	98.0
20	3-$NO_2C_6H_4$	20	78.1
21	4-$NO_2C_6H_4$	10	85.9
22	2-furyl	180	99.5
23	(*E*)-cinnamal	60	30.0
24[e]	amyl	170	56.9
25[e]	nonyl	170	63.5

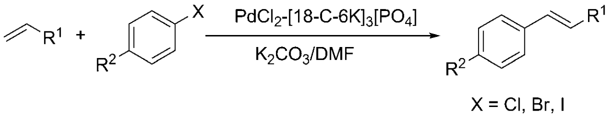
[a] Reaction conditions: aldehyde (4 mmol), nitromethane (10 mmol), catalyst [18-C-6K][OH] (20 mol %), CH_3OH (1 mL), RT. [b] Isolated yield. [c] Recycled [18-C-6K][OH] used. [d] [15-C-5Na][OH]·H_2O (20 mol %) was used as catalyst. [e] $T = -15$ °C.

Table 5. Knoevenagel condensation catalysed by [18-C-6K][OH].[a]



Entry	R	t [min]	Yield [%][b]
1	H	30	61.2
2	2-Br	30	85.0
3	4-Cl	20	86.8
4	2,4-Cl	20	91.7
5	2-OCH_3	25	93.9
		26	95.0[c]

[a] Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1.3 mmol), catalyst [18-C-6K][OH] (30 mol %), CH_3OH (1 mL), $T = 25$ °C. [b] Isolated yield. [c] [15-C-5Na][OH] (30 mol %) was used as catalyst.



Scheme 2. Heck reaction in the presence of $PdCl_2$/$[18\text{-}C\text{-}6K]_3[PO_4]$/$K_2CO_3$.

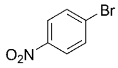
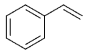
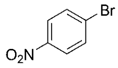
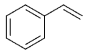
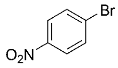
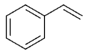
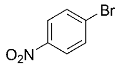
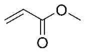
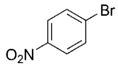
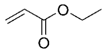
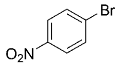
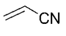
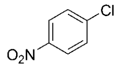
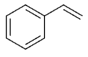
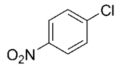
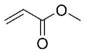
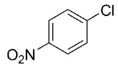
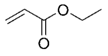
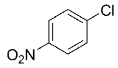
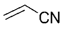
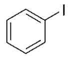
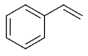
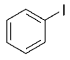
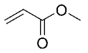
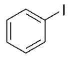
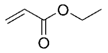
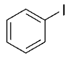
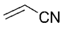
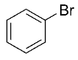
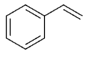
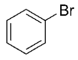
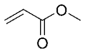
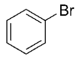
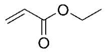
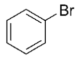
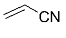
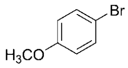
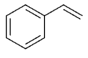
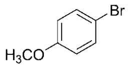
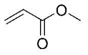
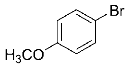
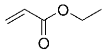
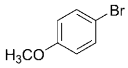
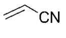
The reaction of 2-nitrobenzaldehyde and nitromethane under optimised reaction conditions was chosen as model to examine the recyclability of catalyst [18-C-6K][OH]. We found that the catalyst can be reused at least five times without significant loss of activity (Table 4, entries 14–18).

We have introduced the CECIL [18-C-6K][OH] with remarkable effect on Michael additions and Henry reactions. As a part of this program we now report the excellent catalytic efficiency of [18-C-6K][OH] for Knoevenagel condensation of aromatic aldehydes and malononitrile. The results are shown in Table 5. Both the aromatic aldehydes with electron-withdrawing (Table 5, entries 2–4) or electron-donating groups (Table 5, entry 5) generated the respective products in good yields; however, for unsubstituted benzaldehyde the reaction rate is comparatively slow (Table 5, entry 1).

To further extend the scope of application of CECILs, the CECILs of $[18\text{-}C\text{-}6K]_3[PO_4]$, $[18\text{-}C\text{-}6K]_2[HPO_4]$ and $[18\text{-}C\text{-}6K][H_2PO_4]$ were applied in the Heck reaction as additives (Table 6, entry 1). The best additive of $[18\text{-}C\text{-}6K]_3[PO_4]$ was then chosen for further investigations in the Heck reaction of olefins with aryl halides in the presence of $PdCl_2$ and K_2CO_3 in DMF (Scheme 2). From the results in Table 6, it can be seen that the reaction can take place under mild conditions (110 °C) when the active aryl halide iodobenzene is used (Table 6<xtabr6, entries 11–14). When bromobenzene was used as the substrate, the reaction required a higher temperature (140 °C) (Table 6<xtabr6, entries 15–18). When chlorobenzene was used, the reaction cannot occur under the same condition as bromobenzene because of the relatively strong carbon–halogen bond. However, electron-withdrawing groups can activate the carbon–halogen bond, for example, 4-nitrochlorobenzene underwent reaction at 140 °C (Table 6, entries 7–10) and 4-nitrobromobenzene reacted under the more mild conditions of 110 °C (Table 6, entries 1, 4–6). Otherwise, electron-donating group can deactivate the carbon–halogen bond, for example, 4-bromomethoxybenzene underwent reaction at 140 °C with lower yields (Table 6, entries 19–22). In general, $PdCl_2/K_2CO_3$/CECIL in DMF can efficiently initiate the Heck coupling reaction. The reaction of 1-bromo-4-nitrobenzene and styrene can also be achieved without CECIL (Table 6, entry 2) or in toluene (Table 6, entry 3), which suggests that both the CECIL and DMF could act as ligands in the Heck reaction. Considering the solvent effect of CECILs, we chose [18-C-6K][OAc] as both solvent and ligand in the Heck reaction of bromobenzene and styrene. Excitingly, when the reaction temperature was reduced from 140 to 110 °C, the reaction was complete within 70 min and gave 89.2 % yield (Table 6, entry 15). Finally, it is worth noting that this catalytic system is totally insensitive to oxygen and moisture.

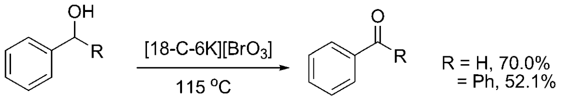
The oxidation of alcohols to their corresponding carbonyl compounds is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing.[14] It is known that bromates are commercially available, inexpensive, stable solids and potential candidates for the oxidation of organic compounds.[15] Accordingly, the CECIL

Table 6. Heck reaction of olefins and aromatic halides.[a]

Entry	Aryl halide	Olefin	*t* [min]	*T* [°C]	Yield[b] [%]
1			120	110	95.0 90.0[c] 91.2[d]
2			150	110	73.5[e]
3			150	110	71.2[f]
4			36	110	80.3
5			60	110	97.1
6			60	110	96.7
7			105	140	43.0
8			217	140	27.0
9			217	140	30.5
10			300	140	–
11			300	110	70.7
12			60	110	98.7
13			12	110	78.2
14			81	110	84.0
15			300 70	140 110	68.0 89.2[g]
16			75	140	86.3
17			32	140	72.0
18			200	140	trace
19			115	140	84.0
20			120	140	21.0
21			96	140	59.1
22			110	140	trace

[a] Reaction conditions: Aryl halide (2 mmol), olefin (2.5 mmol), $PdCl_2$ (2 mol %), additive $[18\text{-}C\text{-}6K]_3[PO_4]\cdot 0.5H_2O$ (4 mol %), K_2CO_3 (3 mmol, 2 equiv), DMF (2 mL). [b] Isolated yield. [c] $[18\text{-}C\text{-}6K]_2[HPO_4]\cdot 0.5H_2O$ (4 mol %) was used as additive. [d] $[18\text{-}C\text{-}6K][H_2PO_4]\cdot 2H_2O$ (4 mol %) was used as additive. [e] No CECIL. [f] Toluene (2 mL). [g] Bromobenzene (1 mmol), [18-C-6K][OAc] (1 g), neat.

$[18\text{-}C\text{-}6K][BrO_3]$ was synthesised as an oxidant, despite its higher melting point of 115 °C. A mixture of benzohydrol and $[18\text{-}C\text{-}6K][BrO_3]$ was stirred at 115 °C in a preheated oil bath and a conversion of 52.1 % was achieved after 120 min Scheme 3. When benzyl alcohol was used as the substrate a 70.0 % yield of benzaldehyde was obtained after 100 min. Most importantly, the oxidation reaction is carried out under neutral conditions and $[18\text{-}C\text{-}6K][BrO_3]$ is both oxidant and solvent for this reaction.



Scheme 3. Oxidation of aromatic alcohols.

Conclusion

We have discovered a novel type of ionic liquid that consists of a crown ether chelated alkali metal cation and various anions, formed by a simple mixing of the correct molar ratio of crown ether with the relevant salts in water, followed by evaporation and vacuum drying to get the pure crown ether complex cation ionic liquids (CECILs) without any byproducts. These CECILs have shown supreme abilities in organic reactions, exemplified by application in Heck reactions, Michael additions, Henry reactions, Knoevenagel condensations and oxidation reactions. Their excellent catalytic activities might be attributed to enhancement of the basicity of the CECIL anion, along with reduction of the electrostatic interaction between the cation and anion. As with traditional ILs, our new CECILs show a clear solvent effect in various organic reactions. With this novel protocol in hand, further discoveries on the applications of CECILs are underway in our laboratory.

Experimental Section

Materials and methods: All reagents were obtained from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 spectrometer, with TMS as an internal reference ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77$ ppm; D_2O: $\delta_H = 4.80$ ppm). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Thermogravimetric differential thermal analysis (TG-DTA) was carried out on a STA 449 C instrument (Netzsch, Germany). HRMS (ESI) was carried out on a Bruker APEX II mass spectrometer with glycerol as the matrix. Elemental analyses were carried out on Carioel elemental analyser.

General procedure for the synthesis of CECILs: The organic, inorganic potassium or sodium salt (10 mmol) was mixed with [18]crown-6 (10 mmol, 2.6432 g) or [15]crown-5 (10 mmol, 2.2026 g) in water (15 mL). After stirring at RT for 12 h, the excess water was evaporated under reduced pressure. The residue was vacuum dried to generate the desired CECIL in 100 % yield. To obtain the pure CECILs, the substrates must be weighed accurately.

[18-C-6K]$_3$[PO$_4$]·1/2 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.63 ppm (s, 72 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.9 ppm; elemental analysis calcd (%): C 47.04, H 8.00; found: C 47.15, H 8.19.

[18-C-6K]$_2$[HPO$_4$]·1/2 H$_2$O: ^{1}H NMR(300 MHz, D$_2$O, 25 °C, TMS): δ = 3.65 ppm (s, 48 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.7 ppm; elemental analysis calcd (%): C 46.81, H 8.02; found: C 46.86, H 7.95.

[18-C-6K][H$_2$PO$_4$]·2 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.62 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.9 ppm; elemental analysis calcd (%): C 33.02, H 6.93; found: C 33.10, H 6.64.

[18-C-6K][OAc]·2.5 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.65 (s, 24 H), 1.88 ppm (s, 3 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 180.9, 68.9, 23.4 ppm; elemental analysis calcd (%): C 41.26, H 7.92; found: C 41.48, H 7.64.

[15-C-5Na][OAc]·H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.72 (s, 20 H), 1.93 ppm (s, 3 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 180.9, 69.7, 23.4 ppm; elemental analysis calcd (%): C 45.00, H 7.87; found: C 44.81, H 7.48.

[18-C-6K][NO$_3$]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.63 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.7 ppm; elemental analysis calcd (%): C 39.44, H 6.62, N 3.83; found: C 39.05, H 6.54, N 3.66.

[18-C-6K]$_2$[CO$_3$]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.66 ppm (s, 48 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 168.1, 69.6 ppm; elemental analysis calcd (%): C 47.50, H 7.79; found: C 47.69, H 7.89.

[18-C-6K][HCO$_3$]·1/2 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.65 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 161.2, 69.9 ppm; elemental analysis calcd (%): C 41.81, H 7.02; found: C 41.78, H 6.91.

[18-C-6K][OH]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.62 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.6 ppm; elemental analysis calcd (%): C 44.98, H 7.86; found: C 44.81, H 7.77.

[15-C-5Na][OH]·H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.66 ppm (s, 20 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.8 ppm; elemental analysis calcd (%): C 43.16, H 8.33; found: C 43.04, H 8.35.

[15-C-5Na][Br]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.65 ppm (s, 20 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.7 ppm; elemental analysis calcd (%): C 37.17, H 6.24; found: C 37.27, H 6.29.

[18-C-6K][Br]·H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.64 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.6 ppm; elemental analysis calcd (%): C 35.91, H 6.53; found: C 35.58, H 6.25.

[15-C-5Na]$_2$[C$_2$O$_4$]·2 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.72 ppm (s, 40 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 173.1, 69.9 ppm; elemental analysis calcd (%): C 43.28, H 7.26; found: C 43.03, H 7.15.

[18-C-6K][BrO$_3$]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.65 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.6 ppm; elemental analysis calcd (%): C 33.42, H 5.61; found: C 33.48, H 5.33.

[15-C-5Na][IO$_3$]·1/2 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.68 (s, 20 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.7 ppm; elemental analysis calcd (%): C 28.12, H 4.96; found: C 28.15, H 4.99.

[18-C-6K][ClO$_3$]: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 3.64 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 69.8 ppm; elemental analysis calcd (%): C 37.26, H 6.25; found: C 36.97, H 6.05.

[18-C-6K][biphthalate]·1.5 H$_2$O: ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS): δ = 7.73 (q, J(H,H) = 6.0, 3.6 Hz, 2 H), 7.54 (q, J(H,H) = 6.0, 3.6 Hz, 2 H), 3.60 ppm (s, 24 H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS): δ = 174.0, 133.9, 131.0, 129.2, 69.8 ppm; elemental analysis calcd (%): C 48.47, H 6.51; found: C 48.28, H 6.18.

[18-C-6K][X]: HRMS (ESI): m/z calcd for [18-C-6K]: 303.1204; found: 303.1209.

[15-C-5Na][X]: HRMS (ESI): m/z calcd for [15-C-5Na]: 243.1203; found: 243.1200.

General procedure for the Michael addition: A mixture of olefin (2 mmol), nucleophile (2.6 mmol) and [15-C-5Na][OH] or [18-C-6K][OAc] (10 mol%) was stirred at 25 °C in CH$_3$OH (1 mL). After completion of the reaction, monitored by TLC, the mixture was added to water (15 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and evaporated. The products were purified by flash column chromatography, if necessary.

Catalyst recycling procedure: A mixture of chalcone (1 mmol), butanethiol (1.3 mmol) and [15-C-5Na][OH] (10 mol%) were stirred for 5 min at 25 °C. After completion of the reaction, the mixture was added to water (10 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were concentrated under reduced pressure to give the desired product. The aqueous phase was evaporated and dried under vacuum to recover the catalyst.

3-(Butylthio)-1, 3-diphenylpropan-1-one: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.91 (d, J(H,H) = 6.9 Hz, 2 H), 7.54 (t, J(H,H) = 6.9, 7.5 Hz, 1 H), 7.43 (t, J(H,H) = 9.0, 7.5 Hz, 4 H), 7.30 (t, J(H,H) = 6.9, 7.8 Hz, 2 H), 7.18 (q, J(H,H) = 7.2, 6.9, 7.5 Hz, 1 H), 4.56 (t, J(H,H) = 6.9, 7.2 Hz, 1 H), 3.53 (d, J(H,H) = 6.9 Hz, 2 H), 2.25–2.42 (m, 2 H), 1.43–1.62 (m, 2 H), 1.24–1.37 (m, 2 H), 0.83 ppm (t, J(H,H) = 6.9, 7.8 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 196.9, 142.2, 136.7, 133.2, 128.6, 128.5, 128.1, 127.8, 127.1, 45.4, 44.2, 31.2, 31.1, 21.9, 13.6 ppm.

Ethyl 3-(piperidin-1-yl)propanoate: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.10 (q, J(H,H) = 7.5, 6.9, 7.2 Hz, 2 H), 2.63 (t, J(H,H) = 5.7, 8.1 Hz, 2 H), 2.46 (t, J(H,H) = 7.5, 7.8 Hz, 2 H), 2.44 (m, 4 H), 1.55 (m, 4 H), 1.40 (m, 2 H) 1.23 ppm (t, J(H,H) = 6.9, 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 172.7, 60.3, 54.2, 54.2, 32.2, 25.9, 24.2, 14.2 ppm.

2-(3-Oxo-1,3-diphenyl-propyl)malononitrile: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.96 (d, J(H,H) = 7.2 Hz, 2 H), 7.62 (t, J(H,H) = 7.5, 7.8 Hz, 1 H), 7.49 (t, J(H,H) = 7.8, 6.9 Hz, 2 H), 7.43 (m, 5 H), 4.63 (d, J(H,H) = 5.1 Hz, 1 H), 3.93–3.99 (m, 1 H), 3.63–3.69 ppm (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 196.6, 136.4, 135.6, 134.1, 129.2, 129.1, 128.8, 128.0, 127.9, 111.9, 111.7, 41.0, 39.9, 28.7 ppm.

General procedure for the Henry reaction: A mixture of aromatic aldehyde (4 mmol), nitromethane (10 mmol), [18-C-6K][OH] (20 mol%) and CH$_3$OH (1 mL) were stirred for 1–6 h at RT. After completion of the reaction, monitored by TLC, the mixture was added to water (10 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum to give the desired product, which was then purified by flash column chromatography (petroleum ether/ethyl acetate).

Catalyst recycling procedure: After completion of the reaction between 2-nitrobenzaldehyde (4 mmol) and nitromethane (10 mmol) catalysed by [18-C-6K][OH] (20 mol%) at RT, the mixture was added to water (10 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were collected and concentrated to give the target product. The aqueous phase was evaporated and then the residue was dried under vacuum to recover [18-C-6K][OH] for the next cycle.

2-Nitro-1-phenylethanol: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.38 (m, 5 H), 5.44 (dd, J(H,H) = 9.3, 3.3 Hz, 1 H), 4.47–4.64 (m, 2 H), 2.93 ppm (br, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 138.1, 129.0, 128.9, 125.9, 81.2, 70.9 ppm.

(*E*)-1-Nitro-4-phenylbut-3-en-2-ol: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.24–7.39 (m, 5 H), 6.75 (dd, J(H,H) = 16.2, 1.2 Hz, 1 H,), 6.12 (dd, J(H,H) = 15.9, 6.3 Hz, 1 H), 5.01 (m, 1 H), 4.6 (d, J(H,H) = 6.0 Hz, 2 H,), 2.91 ppm (d, J(H,H) = 4.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 135.4, 133.5, 128.7, 128.4, 126.6, 124.9, 79.8, 69.5 ppm.

1-(Furan-2-yl)-2-nitroethanol: ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.40 (d, J(H,H) = 6.9 Hz, 1 H), 6.38 (m, 2 H), 5.45 ppm (dd, J(H,H) = 9.0, 3.6 Hz, 1 H), 4.68–4.81 (m, 2 H), 3.29 ppm (br, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS): δ = 150.8, 143.1, 110.6, 108.1, 78.4, 64.7 ppm.

General procedure for the Knoevenagel condensation: A mixture of aldehyde (1 mmol), malononitrile (1.3 mmol), [18-C-6K][OH] (30 mol%) and CH$_3$OH (1 mL) were stirred at 25 °C until the reaction was complete (TLC). The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated under vacuum. The product was purified by flash column chromatography (petroleum ether/ethyl acetate).

2-Benzylidenemalononitrile: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.91$ (d, J(H,H) = 7.5 Hz, 2 H), 7.78 (s, 1 H), 7.64 (t, J(H,H) = 7.8, 6.9 Hz, 1 H), 7.55 ppm (t, J(H,H) = 7.8, 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 159.9$, 134.6, 130.9, 130.7, 129.6, 113.7, 112.5, 83.1 ppm.

2-(4-Chlorobenzylidene)-malononitrile: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.85$ (d, J(H,H) = 7.2 Hz, 2 H), 7.74 (s, 1 H), 7.52 ppm (dd, J(H,H) = 6.6, 1.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.2$, 141.1, 131.8, 130.0, 129.3, 113.4, 112.3, 84.0 ppm.

2-(2-Bromobenzylidene)malononitrile: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.22$ (s, 1 H), 8.12 (dd, J(H,H) = 6.9, 2.7 Hz, 1 H), 7.74 (dd, J(H,H) = 7.5, 2.1 Hz, 1 H), 7.42–7.53 ppm (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.7$, 134.9, 134.0, 130.7, 129.8, 128.3, 126.4, 113.1, 111.7, 86.0 ppm.

2-(2-Methoxybenzylidene)malononitrile: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.30$ (s, 1 H), 8.18 (dd, J(H,H) = 7.8, 1.2 Hz, 1 H), 7.58 (t, J(H,H) = 8.1, 7.5 Hz, 1 H), 7.08 (t, J(H,H) = 7.5 Hz, 1 H), 6.99 (d, J-(H,H) = 8.4 Hz, 1 H), 3.93 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.9$, 154.4, 136.5, 128.8, 121.1, 120.1, 114.3, 112.9, 111.5, 81.3, 55.9 ppm.

2-(2,4-Dichlorobenzylidene)malononitrile: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.18$ (s, 1 H), 8.14 (d, J(H,H) = 8.7 Hz, 1 H), 7.57 (d, J-(H,H) = 1.8 Hz, 1 H), 7.44 ppm (d, J(H,H) = 5.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 154.5$, 141.0, 137.1, 130.7, 130.1, 128.3, 127.4, 113.0, 111.7, 86.0 ppm.

General procedure for the Heck Reaction: $[18\text{-C-6K}]_3[PO_4]\cdot 0.5H_2O$ (0.08 g, 4 mol %), K_2CO_3 (0.414 g, 3 mmol) and $PdCl_2$ (0.0035 g, 2 mol %) was added sequentially to a mixture of aryl halide (2 mmol) and olefin (2.5 mmol) in DMF (2 mL). The mixture was stirred and heated at 110 or 140 °C (see Table 6<xtabr6). After completion of the reaction, monitored by TLC, the mixture was added to water (15 mL) and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to give the desired product, which was then purified by flash column chromatography (petroleum ether/ethyl acetate).

(*E*)-1-Phenyl-2-(4-nitrophenyl)-ethylene: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.22$ (d, J(H,H) = 9.0 Hz, 2 H), 7.63 (d, J(H,H) = 8.4 Hz, 2 H), 7.55 (d, J(H,H) = 7.5 Hz, 2 H), 7.36 (m, 4 H), 7.14 ppm (d, J(H,H) = 16.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 146.7$, 143.8, 136.1, 133.2, 128.9, 128.8, 127.0, 126.8, 126.2, 124.1 ppm.

(*E*)-1, 2-Diphenyl-ethylene: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.50$ (d, J(H,H) = 7.8 Hz, 2 H), 7.34 (t, J(H,H) = 6.6, 7.5 Hz, 2 H), 7.24 (t, J(H,H) = 7.5, 7.2 Hz, 2 H), 7.10 ppm (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 137.2$, 128.6, 128.6, 127.6, 126.5 ppm.

(*E*)-Methyl cinnamate: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.71$ (d, J(H,H) = 16.2 Hz, 2 H), 7.50–7.53 (m, 2 H), 7.36–7.38 (m, 3 H), 6.44 (d, J(H,H) = 15.9 Hz, 1 H), 3.79 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 167.3$, 144.8, 134.2, 130.2, 128.8, 128.0, 117.7, 51.6 ppm.

(*E*)-Methyl 3-(4-nitrophenyl)-2-propenoate: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.25$ (d, J(H,H) = 8.7 Hz, 2 H), 7.70 (d, J(H,H) = 17.7 Hz, 1 H), 7.67 (d, J(H,H) = 7.8 Hz, 2 H), 6.57 ppm (d, J(H,H) = 15.9 Hz, 1 H), 3.84 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.5$, 148.5, 141.9, 140.4, 128.6, 124.2, 122.0, 52.1 ppm.

General procedure for the oxidation reaction: An oven-dried round-bottom flask equipped with a stirrer bar was charged with aromatic alcohol (2 mmol) and $[18\text{-C-6K}][BrO_3]$ (0.862 g, 2 mmol). The mixture was stirred at 115 °C in a preheated oil bath. Upon completion (TLC) the reaction mixture was added to water (15 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to obtain the crude product, which was purified by flash column chromatography (petroleum ether/Et_2O).

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