A recyclable heterogeneous copper(II) Schiff base catalyst for the O-arylation reaction of phenols with aryl halides

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Immobilisation of copper acetate onto a modified polystyrene provided a polymer-supported copper(II) Schiff base catalyst, which is effective in the *O*-arylation reaction of phenols with aryl halides to give diaryl ethers in high yields. This catalyst is air-stable and was recycled for five times with minimal loss of activity.

Keywords: polymer-supported copper(II) Schiff base catalyst, *O*-arylation reaction, aryl halides, diaryl ethers, reusability

A variety of naturally occurring and medicinally important compounds contain a diaryl ether moiety.[1–5] The formation of diaryl ethers via a C–O cross-coupling reaction is a powerful and straightforward method in organic synthesis.[6–8] Of the methods used for the preparation of diaryl ethers, the classic Ullmann ether synthesis is the most important, but it is often limited by the need to employ harsh reaction conditions and stoichiometric amounts of copper, which leads to problems of waste disposal.[9–11] Nowadays palladium-catalysed ether formation reactions have solved some problems in this area.[12,13] A palladium-catalysed coupling reaction between sodium phenoxides and electron-deficient aryl bromides was reported by Mann and Hartwig[14] based on a particular ligand (dppf). Recent work in Buchwald's group with a copper(II) triflate catalyst has made it possible to carry out these reactions under milder conditions with a wider variety of substrates in good yields.[15] Due to the relatively high cost of copper triflate and its air sensitivity, it is still desirable to develop more robust and more cost-effective processes for this important reaction. Later, Buchwald and co-workers described the C–O coupling of aryl halides and phenols by using palladium catalysts in the presence of electron-rich 2-(di-*tert*-butylphosphino)biphenyl as a ligand.[16] The yields are low to moderate, and reactions between electron-rich aryl halides and electron-deficient phenols typically do not work well. Recently, a number of groups have reported using pyridine-type ligands or phosphine-type ligands in catalytic amounts to accelerate or enhance the Ullmann reaction, allowing it to occur under more moderate conditions.[17,18] The high cost of transition-metal catalysts coupled with the toxic effects associated with many transition metals has led to an increased interest in immobilising catalysts onto a support. This class of supported reagent can facilitate both the isolation and recycling of the catalyst by filtration thus providing an environmentally cleaner processes.[19,20] Copper catalysts have the advantage of low cost for large-scale industrial applications. To date, few reports have described reusable copper catalytic systems for this C–O coupling that allow the recycling of the active metal. Of these reports, only some reported leaching measurements of metal toxic residues into final products.[21–24] This feature is of high importance for purity requirements especially in the pharmaceutical industry. Therefore, mild, simple and low-cost reusable methods are highly desirable to avoid toxicity.

Here we report the synthesis and characterisation of a new polymer-supported copper(II) Schiff base catalyst and illustrate its application in a number of diaryl ether coupling reactions between aryl halides and phenols. We have also studied the effect of temperature, solvent and base to obtain optimised reaction conditions. The present work reveals that this polymer-supported Cu(II) Schiff base catalyst has potential applications in the diaryl ether coupling reaction and gives better results than homogeneous catalysts. The experimental results also show that this catalyst can be recycled more than five times without much loss in activity.

The synthesis of the immobilised copper(II) Schiff base catalyst is illustrated in Scheme 1. Thus, aminopolystyrene was reacted with salicylaldehyde in dry toluene at 120 °C for 24 h to afford the polymer-anchored Schiff base ligand. The ligand then reacted with copper(II) acetate in acetic acid at 60 °C for 24 h to generate the polymer-supported copper(II) Schiff base catalyst.

In our initial screening experiments, the Ullmann reaction of iodobenzene and phenol catalysed by the polymer-supported copper(II) Schiff base catalyst was chosen as the model reaction. In the presence of tetra-*tert*-butylammonium bromide (Bu_4^tNBr) and Cs_2CO_3 in NMP medium, the Ullmann diaryl etherification can be catalysed by either Cu(I) or Cu(II) in the absence of any palladium. However, no reaction occurred in the absence of a copper catalyst. As can be seen from Table 1, polymer-anchored Cu(II) catalysts are superior. Among polymer-supported Cu(II) catalysts, which are prepared from different copper(II) sources, polymer-supported Cu(II) Schiff base catalyst from copper(II) acetate is found to be the most effective. The comparison of a heterogeneous Schiff base copper catalyst and a homogeneous Schiff base copper catalyst in the *O*-arylation reaction were carried out under the same reaction conditions. The results (Table 1, entries 7 and 8) clearly show that the polymer-supported copper(II) Schiff base catalyst is more active than the unsupported copper(II) Schiff base catalyst. Additionally, the supported catalyst is expected to have several advantages over the homogenous one. The immobilised catalyst can be removed easily from the reaction mixture by a simple filtration and it is more easily handled. Using $Cu(OAc)_2$ as the source of copper, displacement of acetate would provide an active copper-bound polymer-supported catalyst.[25] So the polymer-supported copper(II) Schiff base from $Cu(OAc)_2$ is used as a catalyst in the following investigation for its high efficiency, easy separation and recycling. Bases such as KOH, Cs_2CO_3, Na_2CO_3, Et_3N, K_3PO_4, and K_2CO_3 are found to facilitate this coupling reaction and among them Cs_2CO_3 is the best (Table 2, entries 1–6). Solvents such as DMF (*N,N*-dimethylformamide), ACN (acetonitrile), NMP (N-methyl-2-pyrrolidinone), MeOH (methanol), DMSO (dimethyl sulfoxide), toluene and water have investigated and it is found that polar solvents are more favoured. With NMP, ACN, DMF, DMSO and MeOH yields are comparatively good (Table 2, entries 1, 7–10). By contrast, the catalytic performance is very low with water and not acceptable when the non-polar solvent toluene is employed (Table 2, entries 11 and 12). Consequently NMP is chosen as the medium of choice for this coupling. This arylation is also found to be highly sensitive to the reaction temperature and time. At lower temperatures (40 and 60 °C) and with lower reaction time (6 and 8 h) only low to moderate yield is obtained (Table 2, entries 13–16). A reaction temperature of 120 °C and reaction time of 12 h are found to be optimal. Thus, the optimised reaction conditions for this Ullmann reaction are

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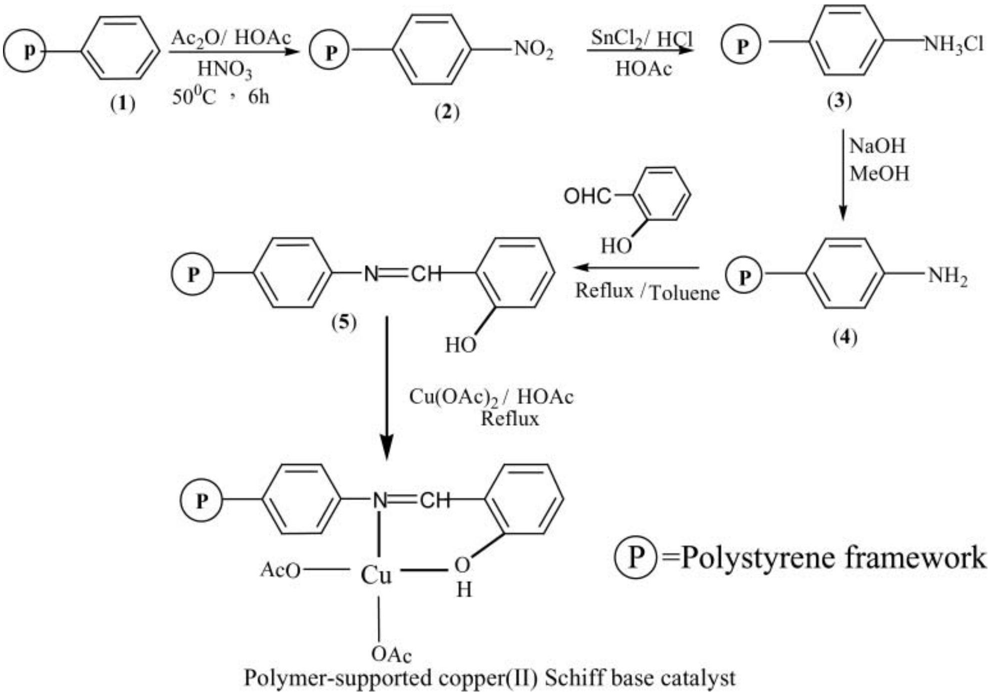
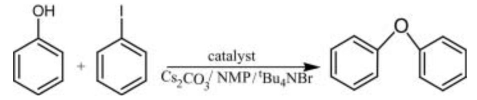


Scheme 1 Synthesis of polymer-supported copper(II) Schiff base catalyst.

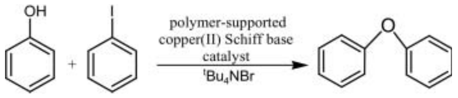
Table 1 Effect of copper source on the O-arylation reaction[a]



Entry	Copper source (amount)	Yield[b]/%
1	None	No reaction
2	CuI (0.05 g)	37
3	$CuCl_2$ (0.05 g)	51
4	$Cu(OAc)_2$ (0.05 g)	66
5	Polymer-supported copper(I)[c](0.05 g)	48
6	Polymer-supported copper(II)[d](0.05 g)	86
7	Polymer-supported copper(II)[e](0.05 g)	94
8	Homogeneous copper(II)[e](0.05 g)	79
9	Polymer-supported copper(II)[e](0.065 g)	94
10	Polymer-supported copper(II)[e] (0.025 g)	65
11	Polymer-supported copper(II)[e] (0.075 g)	95
12	Polymer-supported copper(II)[e] (0.040 g)	74

[a] Reaction conditions: 1 mmol of iodobenzene, 1 mmol of phenol, 1 mmol Cs_2CO_3, Bu_4^tNBr (0.1 mmol), NMP (10 mL), 120 °C, N_2 atmosphere, 12 h. [b] Yield determined by GC and GC-MS analysis using dihexyl ether as internal standard. [c] Catalyst prepared from CuI. [d] Catalyst prepared from $CuCl_2$. [e] Catalyst prepared from $Cu(OAc)_2$.

Table 2 Effect of solvent, base, temperature, reaction time on the O-arylation reaction[a]



Entry	Base	Solvent	Temperature /°C	Time /h	Yield[b] /%
1.	Cs_2CO_3	NMP	120	12	94
2.	K_2CO_3	NMP	120	12	79
3.	Na_2CO_3	NMP	120	12	74
4.	K_3PO_4	NMP	120	12	84
5.	Et_3N	NMP	120	12	67
6	KOH	NMP	120	12	58
7.	Cs_2CO_3	DMF	100	12	82
8.	Cs_2CO_3	DMSO	100	12	85
9.	Cs_2CO_3	ACN	70	14	62
10.	Cs_2CO_3	MeOH	80	15	56
11.	Cs_2CO_3	Water	80	15	40
12.	Cs_2CO_3	Toluene	120	14	26
13.	Cs_2CO_3	NMP	40	12	45
14.	Cs_2CO_3	NMP	60	12	62
15.	Cs_2CO_3	NMP	120	6	60
16.	Cs_2CO_3	NMP	120	8	74

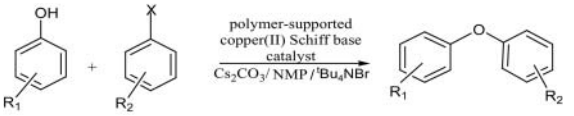
[a] Reaction conditions: 0.05 g of polymer-supported copper(II) Schiff base catalyst, 1 mmol of iodobenzene, 1 mmol of phenol, 1 mmol base, $^tBu_4NBr$ (0.1 mmol), solvent (10 mL), N_2 atmosphere.

[b] Yield determined by GC and GC-MS analysis using dihexyl ether as internal standard.

the polymer supported copper(II) Schiff base catalyst (0.05 g), Bu_4^tNBr (0.1 mmol), Cs_2CO_3 (1 mmol) in NMP at 120 °C for 12 h.

To investigate the scope of the reaction using this supported copper(II) Schiff base catalyst, we applied similar conditions for Ullmann coupling between a variety of phenols and aryl halides. The results are summarised in Table 3. From Table 3, it can be observed that the Ullmann coupling reactions under these conditions follow the general trend that electron-donating groups on the phenol and electron-withdrawing groups on the halide make the reaction favourable, as indicated by the higher yields (Table 3, entries 1–7 compared to the entries 8 and 9). This has been a well-established trend in copper- and palladium-catalysed ether formation reactions. This coupling is not favourable with electron-withdrawing groups on the phenol and electron- donating groups on the halide. In fact, the palladium-catalysed reactions suffer the same drawback.[26–27] The electron-neutral phenols and aryl halides worked well under the current conditions, as indicated by Table 3, entry 10. Some tolerance of electron-withdrawing groups on the phenol is observed in our reaction conditions, as the reactions with 4-chlorophenol (Table 3, entry 11) gives a reasonable to good yield. Also, even in the presence of an *ortho*-substituted phenol (which is capable of providing scope for steric bias), the reaction proceeded smoothly to give the diaryl ether in good yield (Table 3, entry 12). However, the

Table 3 Polymer-supported copper(II) catalysed O-arylation reaction of aryl halides with phenols[a]



Entry	Phenols	Aryl halides	Product	Isolated yield[b]/%
1	R^1 = H	X = I, R^2 = H	**(3A)**	94
2	R^1 = H	X = I, R^2 = 4-NO$_2$	**(3B)**	97
3	R^1 = 4-OMe	X = I, R^2 = H	**(3C)**	95
4	R^1 = 4-Me	X = I, R^2 = H	**(3D)**	97
5	R^1 = 4-OMe	X = I, R^2 = 4-CN	**(3E)**	94
6	R^1 = H	X = I, R^2 = 4-COMe	**(3F)**	93
7	R^1 = H	X = I, R^2 = 4-CN	**(3G)**	95
8	R^1 = H	X = I, R^2 = 4-Me	**(3D)**	80
9	R^1 = H	X = I, R^2 = 4-OMe	**(3C)**	75
10	R^1 = 4-Cl	X =I, R^2 = 4-Me	**(3H)**	67
11	R^1 = 4-Cl	X = I, R^2 = H	**(3I)**	48
12	R^1 = 2- Me	X = I, R^2 = H	**(3J)**	92
13	R^1 = H	X = I, R^2 =2-Me	**(3J)**	66
14	R^1 = 4-Me	X = I, R^2 = 3-OMe	**(3K)**	98
15	R^1 = 4-Me	X = I, R^2 = 4-OMe	**(3L)**	78
16	R^1 = H	X = Br, R^2 = H	**(3A)**	89
17	R^1 = 4-OMe	X = Br, R^2 = 4-CN	**(3E)**	93
18	R^1 = H	X = Br, R^2 = 4-NO$_2$	**(3B)**	90
19	R^1 = 4-OMe	X = Br, R^2 = H	**(3C)**	92

[a] Reaction conditions: 0.05 g of polymer-supported copper(II) Schiff base catalyst, 1 mmol of aryl halides, 1 mmol of phenols, 1 mmol Cs_2CO_3, $^tBu_4NBr$ (0.1 mmol), NMP (10 mL), 120 °C, N_2 atmosphere, 12 h.

[b] Products were isolated by chromatography on silica gel. All products were characterised by NMR (^1H, ^{13}C).

steric hindrance of aryl iodides is highly disfavoured for this reaction (Table 3, entry 13). The highest yield (quantitative yield) is obtained when *m*-iodomethoxybenzene is reacted with *p*-cresol (Table 3, entry 14). This clearly shows that the presence of an electron-donating methoxy group at the *meta*-position of iodobenzene increases the efficiency of the reaction, whereas the presence of a methoxy group at the *para*-position of iodobenzene decreases the yield of the coupling reaction drastically (Table 3, entry 15). After achieving excellent results with aryl iodides, we further applied this catalytic system for the *O*-arylation of aryl bromides. An excellent yield is observed in the reaction of 4-cyanobromobenzene with 4-methoxyphenol (Table 3, entry 17). For electron-poor aryl bromides and electron-rich phenols, high yields of the desired products are obtained (Table 3, entries 18 and 19).

For any supported catalyst, it is important to know its ease of recovery and possible reuse. The polymer supported copper(II) Schiff base catalyst can be easily separated by filtration. The recovered catalyst after washing with acetone followed by drying at 80 °C was used in the next run. The catalyst was recycled five times to give yields of 94, 94, 93, 92 and 93% consecutively in the reaction of iodobenzene with phenol. This showed that the catalyst retained its activity through recycling and almost consistent activity was observed after five cycles. The copper content of the recovered catalyst after the fifth cycle was 1.68 wt %, remaining unaltered from that of the starting catalyst and indicating no leaching of the metal from the polymer support.

We have also synthesised the complex of free aminopolystyrene with copper acetate. This complex shows the catalytic activity for the *O*-arylation reaction but gives a lower yield than was obtained from the Schiff base complex. The metal in the free aminopolystyrene copper acetate complex is leached out into the solvent during the catalytic run.

Further we have compared the activity of the polymer supported copper(II) Schiff base catalyst in the O-arylation reaction with the other reported catalysts (Table 4). From Table 4, it can be seen that the activity of this copper(II) catalyst is comparable than the other reported systems and in the present system the reaction is conducted at lower reaction time (12 h).

Table 4 Comparison of activity of different copper catalysts in the O-arylation reaction

Entry	Catalyst	Reaction conditions	Yield/%	Ref.
1	Polymer-supported copper(II) Schiff base catalyst	NMP, $^tBu_4NBr$, Cs_2CO_3, 120 °C, 12 h	94	This study
2	2 mol of CuI and 2mmol of N,N-dimethylglycine HCl salt.	Dioxane, Cs_2CO_3, 90 °C, 22 h	86	36
3	BINAM–Cu(OTf)$_2$ catalyst	Dioxane,Cs_2CO_3, 110 °C,18 h	70	41
4	Cu(OAc)$_2$.H$_2$O	NMP, K_3PO_4, 180 °C, 22 h	78	43
5	Cu(bpy)$_2$BF$_4$	DMF, K_3PO_4, 90–110 °C, 22 h	85	44

In summary, we have developed an experimentally simple method for the efficient coupling of aryl halides and phenols. Further studies into the scope and mechanism of this and related copper-catalysed C–O bond formation methodologies are currently under way in our laboratories.

Experimental

Analytical grade reagents and distilled solvents were used throughout the investigation. The liquid substrates were predistilled and dried over the appropriate molecular sieve and the solid substrates were recrystallised before use. The chemical analysis was done by the usual procedure.[28] Macroporous polystyrene beads cross linked with 2% divinylbenzene were supplied by the Aldrich Chemical Company, USA. Copper salts and other organic reagents were purchased from Merck and used without further purification.

The FTIR spectra of the samples were recorded from 400–4000 cm^{-1} on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). All NMR spectra were recorded at 400 MHz for ^1H and 100 MHz for ^{13}C. The characterisations of the products were carried out by ^1H NMR spectroscopy in $CDCl_3$ with TMS as internal standard using a Bruker DPX-400 instrument. Chemical shifts are given as δ value with reference to TMS as the internal standard. The reaction products were quantified (GC data) by a Varian 3400 gas chromatograph equipped with a 30m CP-SIL8CB capillary column and a flame ionisation detector and identified by a Trace DSQ II GC-MS equipped with a 60m TR-50MS capillary column.

Synthesis of metal complexes

p-*nitro-polystyrene* (**2**): A suspension of macroporous polystyrene beads (1) (5.0 g) in a mixture of acetic anhydride (20 mL), nitric acid (~ 70%, 2 mL) and glacial acetic acid (4 mL) was constantly stirred for 30 min at 5 °C and for 5 h at 50 °C.[29] The corresponding *p*-nitropolystyrene was washed successively with acetic acid, water and methanol and finally dried under reduced pressure.

CAUTION: Mixtures of fuming nitric acid and acetic anhydride are dangerously unstable and can explode (see refs 45–47). Although, in the present case, conditions are different, caution is advised.

p-Amino-polystyrene (**4**): A suspension of *p*-nitropolystyrene (5.0 g) in a mixture of acetic acid (20 mL), stannous chloride (5 g), concentrated hydrochloric acid (6 mL) was stirred for 72 h at room temperature to reduce the nitro-compound to the corresponding aminehydrochloride (**3**).[29] The residue was washed several times with hydrochloric acid (12 M) and glacial acetic acid (1:4) mixture and then with methanol. The product on repeated treatment with dilute alcoholic NaOH (5%) produced the corresponding free amine. This was washed with alcohol and dried under reduced pressure.

Polymer-supported Schiff base ligand (**5**): The suspension of macroporous aminopolystyrene (2 g) in toluene (50 mL) was taken in a round bottom flask. Salicylaldehyde (5 mL) was added dropwise to the stirring suspension of aminopolystyrene. The reaction mixture was refluxed for 24 h, when the polymer suspension turned into light yellow in colour. After cooling to room temperature, the light yellow polymer-anchored Schiff base ligand was filtered off, washed successively with toluene, methanol and finally dried under reduced pressure.

Polymer supported copper(II) Schiff base catalyst: The polymer-anchored Schiff base ligand (2 g) was taken in acetic acid (20mL) in a round bottom flask. Copper acetate(50 mg) in acetic acid (5 mL) was added to the above suspension with constant stirring and the mixture was then refluxed on an oil bath for 24 h. After cooling the reaction mixture to room temperature, the separated brownish-yellow colour polymer complex was filtered off, washed thoroughly with methanol, and dried under reduced pressure.

Due to the insolubility of the polymer-anchored Cu(II) Schiff base catalyst in all common organic solvents, its structural investigation was limited to physicochemical properties, chemical analysis, SEM, IR, TGA-DTA and UV-Vis spectroscopic data only. Chemical analysis results suggested 1.68 wt % Cu in the copper catalyst. The morphological change in the polymer-anchored Schiff base ligand and immobilised copper(II) complex is quite evident from the SEM images, suggesting the loading of copper metal on the surface of the polymer matrix. Thermogravimetric study suggests that the polymer anchored Cu(II) complex is stable up to 250 °C and degrades at a considerably higher temperature. The peaks at 1630 cm^{-1} and 1310 cm^{-1} due to monodentate acetate group,[30] 1605 cm^{-1} due to νC=N of azomethine group, a weak peak at 628 cm^{-1} (νCu-O)[31] and a νCu-N[32] stretching vibration at 530 cm^{-1} are present in the spectra of the complex. There is also a weak band in the 3435 cm^{-1} region, indicating the presence of an OH group. The copper(II) complex shows a characteristic frequency νCu-O$_{\text{acetate oxygen}}$ around 430 cm^{-1}.[30] The UV-spectrum exhibits a band at *ca* 270 nm due to intra-ligand charge transfer and bands at 350 and 450 nm arise due to ligand to metal charge transfer. The band at 450 nm indicates the phenolic oxygen to copper charge transfer.[33–34] The expected d–d bands are not observed in the polymer-anchored copper catalyst. Possibly poor loading of the metal on the polymer matrix has prevented the exhibit of the d–d band, which is a low-energy and less-intense band.[35]

General procedure for O-arylation phenols with aryl halides

Under a nitrogen atmosphere, a 100 mL round bottomed flask was charged with the polymer- supported copper(II) catalyst (0.05 g), aryl halide (1.0 mmol), phenol (1.0 mmol), Cs$_2$CO$_3$ (1.0 mmol), Bu$_4^t$NBr (0.1 mmol), dihexyl ether (0.425 mmol) and NMP (10 mL). The reaction mixture was refluxed at 120 °C for 12 h. To study the progress of the reaction, samples of the reaction mixtures were collected at different time intervals and quantified by GC analysis using dihexyl ether as internal standard. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous Na$_2$SO$_4$. The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Diphenylether[**36**] (**3A**): Colourless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09–7.15 (m, 4H), 7.16–7.22(m, 2H); 7.39–7.46 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 119, 123.4, 129.9, 157.4. MS *m/z*: 170(M+), 141, 77, 65, 51, 39.

4-Nitrodiphenylether[37] (**3B**): Yellow solid, m.p. 57–60 °C (lit. [37] 60 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.99–7.02 (m, 2H), 7.05–7.10 (m, 2H), 7.22–7.29 (m, 1H), 7.40–7.44 (m, 2H), 8.16–8.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 117.2, 120.6, 125.5, 126, 130.4, 142.7, 154.8, 163.4. MS *m/z*: 215 (M+), 185, 141, 129, 115, 77, 63, 51.

4-Methoxydiphenylether[38] (**3C**): Colourless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.73 (s, 3H), 6.78–6.82 (m, 2H), 6.85–6.92 (m, 4H), 6.93–6.98 (m, 1H), 7.16–7.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.8, 115, 117.8, 121, 122.6, 129.7, 150.3, 156.1, 158.7. MS *m/z*: 200 (M+), 185, 169, 155, 141, 128, 115, 91, 77, 65, 51, 39.

4-*Methyldiphenylether*[36] (**3D**): Colourless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.42 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.05–7.1 (m, 2H), 7.12–7.18 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.8, 118.5, 119.3, 122.9, 129.8, 130.4, 133.0, 154.9, 157.9. MS *m/z*: 184 (M+), 169, 155, 141, 128, 115, 91, 77, 65, 51, 41.

4-Cyano-4-methoxydiphenylether[39] (**3E**): White solid, m.p. 108–110 °C (lit.[39] 109 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.75 (s, 3 H), 6.84–6.89 (m, 4H), 6.91–6.95 (m, 2H), δ 7.47–7.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.8, 105.4, 115.4, 117.3, 119.1, 122, 134.2, 148, 157.2, 162.6

4-Acetyldiphenylether[37] (**3F**): White solid, m.p. 47 °C (lit.[37] 49–51 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94(d, *J* = 10.4Hz, 2H), 7.39(m, 2H), 7.20(t, *J* = 7.2Hz, S10 1H), 7.07(d, *J* = 7.8Hz, 2H), 7.00(d, *J* = 9.0Hz, 2H), 2.57(s, 3H). ^{13}C NMR (100MHz, CDCl$_3$): δ 196.7, 161.9, 155.5, 131.9, 130.6, 130.0, 124.6, 120.2, 117.3, 26.4. MS *m/z*: 212(M+), 197, 141, 115, 99, 77, 63, 51, 43, 39.

4-Phenoxybenzonitrile[40] (**3G**): Oil: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55(d, *J* = 8.6 Hz, 2H), 7.43(t, *J* = 7.9 Hz, 2H), 7,20 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H).^{13}C NMR (100MHz, CDCl$_3$) δ 160.8, 151.6, 136.8, 131.5, 123.0, 119.4, 116.5, 120.3, 102.6.

4-Methyl-4′-chlorodiphenylether[15] (**3H**): White solid, m.p. 46.3 °C (lit.[15] 47.5–49 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.85–6.94 (m, 4H), 2.30 (s,3H).^{13}C NMR (100MHz, CDCl$_3$) δ 155.1, 153.8, 130.9, 129.3, 128.4, 127.4, 118.4, 120.2, 20.5. MS *m/z*: 220, 218 (M+), 169, 155, 141, 128, 115, 91, 77, 51, 41, 39.

4-Chlorodiphenylether[37] (**3I**): Colourless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.82–6.87 (m, 2H), 6.89–6.93 (m, 2H), 7.01–7.06 (m, 1H), 7.15–7.21 (m, 2H), 7.22–7.28 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 119.1, 120.2, 123.8, 128.3, 129.8, 130, 156.1, 157. MS *m/z*: 206, 204 (M+), 169, 141, 115, 77, 51, 39.

2-Methyldiphenylether[36] (**3J**): Colourless liquid:^{1}H NMR (400 MHz, CDCl$_3$) δ 2.23 (s, 3H), 6.87–6.92 (m, 3H), 6.98–7.08 (m, 2H), 7.12–7.18 (m, 1H), 7.22–7.31 (m, 3H); ^{13}CNMR (100 MHz, CDCl$_3$) δ 16.3, 117.4, 119.9, 122.4, 124.1, 127.3, 129.8, 130.1, 131.6,154.6, 158.1. MS *m/z*: 184(M+), 165, 141, 106, 91, 78, 65, 51, 39.

4-Methyl-3-methoxydiphenylether[41] (**3K**): Colourless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.33 (s, 3H), 3.76 (s, 3H), 6.53–6.56 (m, 2H), 6.61 (d, *J* = 8.4 Hz,1H), 6.90–6.95 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR(100 MHz, CDCl3) δ 20.8, 55.4, 104.5, 108.6, 110.6, 119.4, 130.1, 130.3, 133.2, 154.6,159.2, 161. MS *m/z*: 214 (M+), 199, 171, 143, 128, 91, 77, 65, 51, 41.

4-*Methyl-4′-methoxydiphenylether*[42] (**3L**): White solid, m.p. 48–50 °C (lit.[6] 49–50 °C): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 3H), 3.82 (s, 3H), 6.90 (d, *J* = 8.9 Hz, 4H), 7.0 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.7, 55.7, 114.9, 117.9, 120.4, 130.2, 132.1, 150.9 , 155.8, 156.2. MS *m/z*: 214 (M+), 199, 171, 143, 128, 91, 77, 65, 39.

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