Water Compatible Gold(III)-Catalysed Synthesis of Unsymmetrical Ethers from Alcohols

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Dedicated to Professor Dr. Juan Fornies on the occasion of his 60th birthday

Abstract: An efficient and broad-scoped method for the preparation of unsymmetrical ethers from alcohols catalysed by the simplest and least expensive gold catalyst, NaAuCl$_4$, is described for the first time. The procedure enables the etherification of benzylic and tertiary alcohols with moderate to good yields under mild conditions with low catalyst loading. Symmetrical ethers, the usual side products in the etherification of alcohols, were not detected in this case. The formation of the racemic ether from a chiral benzyl alcohol suggests the intermediacy of a carbocation, which has not previously been postulated for gold-catalysed reactions involving alcohols.

Keywords: alcohols · carbocations · gold · homogeneous catalysis · Lewis acids

Introduction

For a long time gold has been overlooked as a catalyst; however, this concept has drastically changed in recent years. This was probably because of its reluctance to participate as other late transition metals do in standard catalytic cycles based on redox principles, such as oxidative addition and reductive elimination. In addition, its ability to act as a Lewis Acid has been undeservedly disregarded. However, gold catalysis has now emerged as one of the most rapidly growing sub-disciplines in this field of research. Thus, gold-catalysed reactions have come to be considered as prominent synthetic methods comprising oxidation, reduction and most commonly addition reactions to multiple bonds.[1] With regard to this last group of reactions, the electrophilic activation of an alkyne towards the addition of a variety of functional groups is a complex process that provides a diverse range of reaction outcomes, the mechanistic rationalisation of which constitutes an interesting, controversial and active field of research. Intramolecular versions of this reaction have allowed the construction of very valuable complex molecules as a result of elegant cascade reactions.[1b] Intermolecular examples are also known but are less frequent, probably because of the difficulties in controlling the coordination of the different reacting species in the metal sphere. Nevertheless, and despite the interest of gold as a π Lewis acid, the exploration of this metal in transformations involving other functional groups is also attractive. In an attempt to extend the scope of the gold-assisted addition of oxygenated nucleophiles to triple bonds, surprisingly, we found that the major product obtained when the couple 1-indanol and phenyl acetylene were used was the symmetric ether of the alcohol. We immediately envisaged exploring what we thought could perhaps be an even more interesting transformation given the possibility of preparing unsymmetrical ethers by alcohol dehydration.

Ethers are fundamental compounds in organic chemistry and are widely used as either fragrance precursors[2] or oxygenates in reformulated gasoline.[3] Preparation of this kind of compound has been developed through a wide variety of procedures, but not without limitations. The Williamson ether synthesis represents the most widely used method. However, it involves converting alcohols into halides or tosylates, and in most cases, the use of hard bases is incompatible with other functionalities present in the substrates.[4a,5] Moreover, high yields are restricted to primary alcohols, while secondary alcohols give low yields and tertiary alcohols tend to mainly give an elimination reaction. Alternative routes to unsymmetrical ethers arising from alcohols and a Brönsted acid catalyst[4b] are often conducted under harsh

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conditions with a consequent erosion in yields and the formation of mixtures of three possible products, thus limiting the utility of the method. Consequently, these approaches predominantly focus on the preparation of symmetrical light alkyl ethers. A sophisticated and broad-scoped method for the preparation of ethers from alcohols has been recently described. However, and in sharp contrast with the above simple procedures, the reactants used (nBuLi, Ph₂PCl) can restrict its use in practice.[6] Alternatively, the use of a catalyst based on a transition metal appears to be a promising method for the etherification of alcohols, even though only a reduced number of metals have been investigated to date. In general, the results show prevalence for a broad scope of selectivity. Therefore, [Yb(OTf)₃][7] has been utilised as an effective and selective catalyst for the preparation of the p-methoxybenzyl ethers of primary and secondary alcohols. On the other hand, FeCl₃[8] catalyses the etherification of allylic alcohols and some benzylic alcohols with primary and secondary aliphatic alcohols. Nonetheless, the method requires a relatively high loading of the catalyst and solvolytic conditions, and an additional concomitant formation of elimination side products is observed. The data on the preparation of protected alcohols, such as benzhydrol ethers, with this same catalyst in the literature are controversial. While one report indicates that no reaction occurs[8] with this substrate, a subsequent communication accounts[9] for good results with no change in the catalyst under milder conditions. The synthesis of unsymmetrical ethers of secondary benzylic alcohols has also been pursued with other metals, such as palladium(II).[10] Complexes of this metal, containing nitrogen and phosphorus bidentate ligands in conjunction with silver triflate (2 equiv) are selective catalysts for the etherification of secondary benzylic alcohols, although the symmetrical ether is a frequent side product. Propargylic alcohols have received individual attention in etherification reactions. The preparation of propargyl ethers by Lewis acid treatment of alcohols with [Co₂(CO)₈]-propargyl alcohols[11] has been described. However, the major drawback of this procedure is that the metal is used in overstoichiometric amounts. Alternative catalytic methods which use a rhenium(V)–oxo complex[12] as an effective catalyst have been reported to accomplish the etherification of both internal and terminal propargyl alcohols. Comparatively, ruthenium was only active with the later substrates.[13] A rhenium-based catalyst has also been applied to the etherification of benzylic alcohols. In this case, the low valent rhenium(I) catalyst[14] has been seen to be more effective for primary benzylic alcohols. Conversely, the high-valent rhenium–oxo complex[15] (very effective with propargylic alcohols) was only active with secondary benzylic alcohols, leading to the corresponding symmetrical or unsymmetrical ethers with moderate yields as elimination and disproportion were significant competitive side reactions.

Other than the homogeneous catalysis, the heterogeneous catalyst has been also developed. For example, AlPW₁₂O₄₀[16] has been shown to be a heterogeneous water resistant Lewis acid that catalyses the etherification of

benzyl alcohols, although solvolytic conditions are required. On the other hand, the synthesis of a variety of ethers from alcohols by using Sn and Zr-containing silicate molecular sieves[17] has been carried out without having to remove water. Nonetheless, this method is alcohol-structure dependent because of the nature of the catalyst and the need to diffuse alcohol within the catalyst channels. Thus, despite the methods reported, the development of new catalysts which are readily available, active at low loadings and which offer a broad scope and selectivity is still an open objective in the synthesis of ethers from alcohols.

Results and Discussion

We report herein, our findings in the synthesis of unsymmetrical ethers from alcohols by using the simplest and least expensive NaAuCl₄ catalyst (Scheme 1). The preparation of

$$R^1OH + R^2OH \xrightarrow{\text{NaAuCl}_4} R^1OR^2 + H_2O$$

R¹: benzylic (primary, secondary)
    alkyl (tertiary)
R²: alkyl (primary, secondary, tertiary)

Scheme 1. Gold-catalysed etherification of alcohols.

unsymmetrical ethers from two different alcohols requires an appropriate catalytic system that is capable of distinguishing between two identical functions and developing a dissimilar role for each partner.

This condition is an essential requisite to control the selectivity in the reaction, otherwise a mixture of the three possible products is potentially expected. As the catalyst must select between two similar substrates, then the stronger the contrast in the components of the alcohol pairs, the greater the possibility that the catalyst has of choosing one of them to play a differentiated role. Initially, we tested the reaction of the highly reactive primary p-methoxybenzyl alcohol **1a** with the less-reactive aliphatic primary, secondary and tertiary alcohols **2a–h**. In a first series of runs, alcohol **1a** was reacted with aliphatic primary alcohols **2a–e** (5 equiv) (Table 1, entries 1–5) and NaAuCl₄ (2%) at 70°C for 1 h.

Aliphatic alcohol was used at a moderately higher concentration than benzyl alcohol to direct the reaction towards the formation of the unsymmetrical ether. Linear (**2d** and **2e**, Table 1, entries 4 and 5) α-branched (**2a** and **2b**, entries 1 and 2) and β-branched (**2c**, entry 3) primary alcohols reacted under the above conditions without the use of dehydrating agents.

The catalyst was also effective in promoting the reaction of **1a** with the secondary alcohol **2f** (Table 1, entry 6) and with the tertiary alcohols **2g** and **2h** (Table 1, entries 7 and 8). Owing to the steric hindrance, however, the catalyst loading had to be increased (5%) to improve the reaction rate, as did the excess of aliphatic alcohol (10 equiv) in the

Table 1. Gold(III)-catalysed etherification of p-methoxy benzyl alcohol.

Entry	R−OH (2)	Catalyst[a]	Product (yield [%])[b]
1	HO—⬠ **2a**	A	**3aa** (80)
2	HO— **2b**	B	**3ab** (58)
3	HO— **2c**	A	**3ac** (60)
4	HO— **2d**	A	**3ad** (61)
5	HO— **2e**	A	**3ae** (58)
6	HO— **2f**	B	**3af** (71)
7	HO— **2g**	B	**3ag** (76)[c]
8	HO— **2h**	B	**3ah** (58)[c]

[a] Catalyst loading: 2% NaAuCl₄ (A), 5% NaAuCl₄ (B). [b] Isolated yield. [c] 10 equiv of alcohol **2** were used. Reaction run over 16 h.

Table 2. Gold(III)-catalysed etherification of 1-indanol.

Entry	R−OH (2)	Catalyst[a]	Product (yield [%])[b]
1	HO—⬠ **2a**	A	**3ba** (83)
2	HO— **2d**	A	**3bd** (47)[c]
3	HO— **2f**	A	**3bf** (96)
4	HO—⬡ **2i**	A	**3bi** (86)

[a] Catalyst loading: 2% NaAuCl₄ (A), 5% NaAuCl₄ (B). [b] Isolated yield. [c] 10 equiv of ethanol were used.

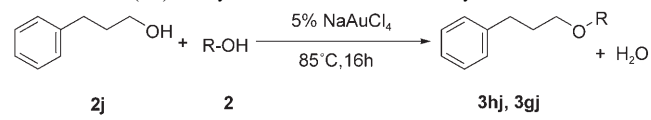Table 3. Gold(III)-catalysed etherification of secondary benzyl alcohols.

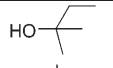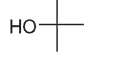| Entry	Substrate	Ether	Yield [%][a]
1	Ph—CH(OH)—Ph **1c**	**3cf**	56
2	**1d**	**3df**	95[b]
3	**1e**	**3ef**	53
4	**1f**	**3ff**	58

[a] Isolated yield unless otherwise specified. [b] Unstable product; yield determined by ¹H NMR spectroscopy.

case of **2g**. It is worth mentioning that in our case, and in sharp contrast with Brönsted acid catalysis[18] or other precedent methods, the unsymmetrical ether was always the main product without any contamination of the symmetrical ether derived from the benzyl alcohol. In addition, the adequate excess of the aliphatic alcohol **2** used was sufficient to preclude the reaction of alcohol **1a** with the water that built up in the system, thus allowing the reaction to take place without the need for dehydrating agents.

The etherification reaction of **1a** with **2f** was selected as a model and further tested with other Au^{III} and Au^I catalysts. The efficiency found for AuCl₃ and NaAuCl₄ was similar but [AuCl(PPh₃)] was only effective when a silver salt (AgSbF₆) was added as co-catalyst. Owing to the low cost of NaAuCl₄, we selected this catalyst for further experiments oriented to determine the scope of the reaction.

Next we tested the synthesis of unsymmetrical ethers with a more difficult substrate, namely the secondary benzyl alcohol **1b** (Table 2). To our delight, however, the etherification of the two secondary alcohols **1b** and **2f** (Table 2, entry 3) was achieved in a very good yield (96%) when using the gold(III) catalyst with a considerably low catalyst loading (2%) under mild conditions. Similar results were obtained with primary (entries 1 and 2) and cyclic secondary alcohols (entry 4).

The reaction could be extended to other secondary benzyl alcohols (Table 3). Benzhydrol **1c** (Table 3, entry 1), methyl D,L-mandelate **1d** (entry 2), *sec*-phenethyl alcohol **1e** (entry 3) and 9-fluorenol **1f** (entry 4) reacted with 2-propanol **2f** to give the corresponding ethers with a moderate yield. NaCl₄Au, therefore, appears to be a suitable general catalyst for the etherification of benzylic alcohols (primary

and secondary) with aliphatic primary and secondary alcohols.

We subsequently tested the catalytic system in a more challenging case, this being the preparation of ethers arising from the reaction of an aliphatic tertiary alcohol with a primary alcohol (Table 4). The corresponding ethers were obtained (Table 4, entries 1 and 2), but with modest and low yields, respectively. Nevertheless, the examples we present are the first to effectively carry out the etherification reaction from such a mixture of alcohols with a transition-metal-based catalytic system. To test the scope of the reaction further, we attempted an etherification reaction arising from a mixture of cyclooctanol (**2i**), an aliphatic secondary alcohol,

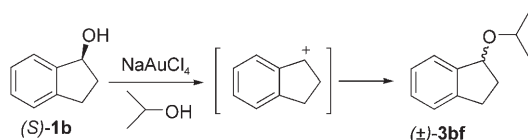Table 4. Gold(III)-catalysed etherification of tertiary alcohols.

Entry	R−OH (2)		Catalyst[a]	Product (yield [%])[b]
1	HO	2h	A	3hj (23)
2	HO	2g	B	3gj (40)

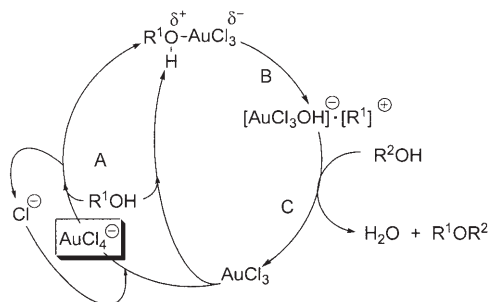[a] Catalyst loading: 5% NaAuCl$_4$ (A), 10% NaAuCl$_4$ (B). [a] Isolated yield.

3-phenylpropanol (2j) and a primary alcohol. Unfortunately, the catalyst (5% NaAuCl$_4$ loading) was ineffective in recovering the initial unchanged materials even under forced conditions. Therefore, the tertiary alcohol represents the borderline point regarding the capacity of the catalyst to generate the electrophilic partner needed to accomplish the etherification reaction. These findings might suggest that the reaction occurs through a carbocation intermediate.[19]

We then analysed the stereochemical outcome of the reaction to correlate this data with either the presence or absence of a carbocation in the reaction course. For this purpose, we ran the reaction with homochiral (S)-1-indanol and 2-propanol. The formation of the corresponding racemic ether, as proved by chiral HPLC, is in agreement with the carbocation intermediacy (Scheme 2). Therefore, the formation of a benzyl or tertiary cation would be the crucial step in the formation of the ether by alcohol dehydration.

Scheme 2. Etherification with racemisation of the chiral alcohol.

The simplified catalytic cycle shown in Scheme 3 contains the following three steps: 1) coordination of the oxygen atom of the benzyl alcohol (or tertiary alcohol) to the catalytic species, which could be either NaAuCl$_4$ or AuCl$_3$

Scheme 3. Catalytic cycle.

(step A); 2) transfer of the hydroxyl group to the metal with concomitant generation of the intermediate carbocation (step B); and 3) trapping of the carbocation by the aliphatic alcohol (step C). This catalytic cycle could account for the results obtained.

Conclusion

We have described the first effective gold(III)-catalysed method for the synthesis of unsymmetrical ethers from alcohols. The results show that primary and secondary benzylic alcohols can be efficiently mixed with primary and secondary aliphatic alcohols to provide the corresponding ethers with moderate to good yields under mild conditions. The catalyst is also active, although less effective, in the most challenging case, that is, the etherification of an aliphatic tertiary alcohol. Indeed, no precedents of this type are reported for other transition-metal-based catalytic systems. The use of a moderate excess of aliphatic alcohol allows the unsymmetrical ether to be prepared with a good yield and with no formation of the symmetrical ether derived from either benzyl or tertiary alcohol. In addition, the water that builds up in the reaction does not compete as a hydroxylic reagent with the aliphatic alcohol, thus allowing a good conversion without the use of dehydrating agents. As far as we are aware, the reaction developed herein represents the first example in which an alcohol acts as an electrophile in gold chemistry. The intermediacy of a carbocation is consistent not only with the profile of the reacting alcohols, but also with the stereochemical outcome of the reaction when chiral alcohols are used.

Experimental Section

General remarks: Proton magnetic resonance and carbon magnetic resonance were recorded at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. Chemical shifts are reported in (δ) ppm relative to the TMS peak at $\delta = 0.0$ ppm (^{1}H spectra) and to the CDCl$_3$ peak at $\delta = 77.0$ ppm (^{13}C spectra). High Resolution Mass Spectra (HRMS) were determined on a Fisons VG Autospec instrument. Reactions were monitored by analytical thin-layer chromatography by using commercial aluminium sheets precoated (0.2 mm layer thickness) with silica gel 60 F254 (E. Merck), and visualisation was effected with short-wavelength UV light (254 nm). Product purification by flash chromatography was performed by using E. Merck silica gel (230–400 mesh).

Materials: Commercial reagents were supplied by Aldrich and they were used without further purification. Ethers 3ac,[20] 3ad,[16] 3ae,[18] 3af,[16] 3ag,[16] 3bd,[21] 3cf,[22] 3ef[20] and 3ff[10] have been described previously.

Representative general procedure for the etherification reaction: A mixture of alcohol 1 (0.4 mmol), alcohol 2 (2 mmol) and NaAuCl$_4$ (2 mol%) was added to a flask sealed with a Teflon screw-cap and was heated to 70°C. After being refluxed for 1 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (5 mL), and filtered over activated aluminium oxide. The solution was then evaporated under reduced pressure. The crude material was purified by flash column chromatography (hexane).

1-[(Cyclopentylmethoxy)methyl]-4-methoxybenzene (3aa): Yield: 80%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.19$ (d, $J = 8.4$ Hz), 6.78 (d, $J =$

8.4 Hz), 4.37 (s, 2H), 3.73 (s, 3H), 3.23 (d, $J = 7.1$ Hz, 2H), 2.00 (sept., $J = 7.5$ Hz, 1H), 1.61–1.70 (m, 2H), 1.41–1.42 (m, 4H), 1.12–1.21 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 159.1$, 131.0, 129.2, 113.8, 74.8, 72.6, 55.3, 39.5, 29.7, 25.5 ppm; HMRS (EI): m/z: calcd for $C_{13}H_{14}O$: 220.1463 $[M]^+$; found: 220.1469.

1-Methoxy-4-(neopentyloxymethyl)benzene (3ab): Yield: 58%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.18$ (d, $J = 8.4$ Hz), 6.78 (d, $J = 8.4$ Hz), 4.38 (s, 2H), 3.73 (s, 3H), 3.01 (s, 2H), 0.84 ppm (s, 9H); ^{13}C NMR (CDCl$_3$): $\delta = 158.8$, 131.1, 128.8, 113.6, 80.5, 72.8, 55.2, 32.0, 26.7 ppm; HMRS (EI): m/z: calcd for $C_{13}H_{20}O$: 208.1463 $[M]^+$; found: 208.1463.

1-(Isopentyloxymethyl)-4-methoxybenzene (3ac): Yield: 60%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.19$ (d, $J = 8.4$ Hz), 6.80 (d, $J = 8.4$ Hz), 4.36 (s, 2H), 3.73 (s, 3H), 3.39 (t, $J = 6.7$ Hz, 2H), 1.65 (sept., $J = 6.6$ Hz, 1H), 1.42 (m, 2H), 0.82 ppm (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl$_3$): $\delta = 159.0$, 130.7, 129.1, 113.7, 72.5, 68.5, 55.2, 38.5, 25.0, 22.6 ppm; HMRS (EI): calcd for $C_{13}H_{20}O$: 208.1463 $[M]^+$; found: 208.1463.

1-(Ethoxymethyl)-4-methoxybenzene (3ad): Yield: 61%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.19$ (d, $J = 8.4$ Hz), 6.78 (d, $J = 8.4$ Hz), 4.20 (q, $J = 7.0$ Hz, 2H), 3.71 (s, 3H), 1.15 ppm (t, $J = 7.0$ Hz, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 158.7$, 132.0, 128.7, 113.6, 72.7, 65.8, 55.6, 15.6 ppm; HMRS (EI): calcd for $C_{10}H_{14}O$: 166.0993 $[M]^+$; found: 166.0983.

1-Methoxy-4-(pentyloxymethyl)benzene (3ae): Yield: 58%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.18$ (d, $J = 8.4$ Hz), 6.79 (d, $J = 8.4$ Hz), 4.35 (s, 2H), 3.72 (s, 3H), 3.36 (t, $J = 6.7$ Hz, 2H), 1.50–1.55 (m, 2H), 1.23–1.28 (m, 4H), 0.79–0.84 ppm (m, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 159.0$, 130.7, 129.1, 113.6, 72.4, 70.1, 55.2, 29.4, 28.3, 22.5, 14.0 ppm; HMRS (EI): calcd for $C_{13}H_{20}O$: 208.1463 $[M]^+$; found: 208.1457.

1-(Isopropoxymethyl)-4-methoxybenzene (3af): Yield: 71%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.19$ (d, $J = 8.4$ Hz), 6.79 (d, $J = 8.4$ Hz), 4.3 (s, 2H), 3.71 (s, 3H), 3.58 (sept., $J = 6.1$ Hz, 1H), 1.12 ppm (t, $J = 6.1$ Hz, 6H); ^{13}C NMR (CDCl$_3$): $\delta = 158.9$, 131.1, 129.0, 113.6, 70.5, 69.6, 55.2, 22.0 ppm; HMRS (EI): calcd for $C_{11}H_{16}O$: 180.1150 $[M]^+$; found: 180.1146.

1-(tert-Butoxymethyl)-4-methoxybenzene (3ag): Yield: 76%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.18$ (d, $J = 8.4$ Hz), 6.79 (d, $J = 8.4$ Hz), 4.30 (s, 2H), 3.71 (s, 3H), 1.21 ppm (s, 9H); ^{13}C NMR (CDCl$_3$): $\delta = 158.8$, 131.9, 128.9, 113.7, 73.2, 63.7, 55.3, 27.7 ppm; HMRS (EI): calcd for $C_{12}H_{18}O$: 194.1306 $[M]^+$; found: 194.1297.

1-Methoxy-4-(tert-pentyloxymethyl)benzene (3ah): Yield: 58%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.19$ (d, $J = 8.4$ Hz), 6.78 (d, $J = 8.4$ Hz), 4.20 (s, 2H), 3.71 (s, 3H), 1.52 (q, $J = 7.5$ Hz, 1H), 1.15 (s, 6H), 0.85 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 158.7$, 132.0, 128.7, 113.6, 75.2, 63.2, 55.2, 32.7, 25.2, 8.3 ppm; HMRS (EI): calcd for $C_{13}H_{20}O$: 208.1463 $[M]^+$; found: 208.1461.

1-(Cyclopentylmethoxy)-2,3-dihydro-1H-indene (3ba): Yield: 83%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.11$–7.32 (m, 4H), 4.18–4.85 (m, 1H), 3.26–3.37 (m, 2H), 2.29–3.03 (m, 1H), 2.62–2.76 (m, 1H), 2.21–2.32 (m, 1H), 2.05–2.15 (m, 1H), 1.91–2.02 (m, 1H), 1.62–1.72 (m, 2H), 1.44–1.51 (m, 4H), 1.16–1.21 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 143.6$, 143.1, 128.0, 126.2, 124.9, 124.7, 83.1, 73.2, 39.6, 32.3, 30.1, 29.6, 29.6, 25.3 ppm; HMRS (EI): calcd for $C_{15}H_{20}O$: 216.1514 $[M]^+$; found: 216.1515.

1-Ethoxy-2,3-dihydro-1H-indene (3bd): Yield: 47%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.31$–7.33 (m, 2H), 7.10–7.18 (m, 2H), 4.48 (dd, $J = 6.6$, 4.3 Hz, 1H), 3.53 (q, $J = 7.0$ Hz, 2H), 2.95–3.06 (m, 1H), 2.68–2.78 (m, 1H), 2.22–2.33 (m, 1H), 1.94–2.04 (m, 1H), 1.15 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 143.8$, 143.0, 128.1, 126.2, 124.9, 124.8, 82.9, 63.9, 32.4, 30.1, 15.5 ppm; HMRS (EI): m/z: calcd for $C_{11}H_{14}O$: 162.1044 $[M]^+$; found: 162.1050.

1-Isopropoxy-2,3-dihydro-1H-indene (3bf): Yield: 96%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.27$–7.30 (m, 1H), 7.10–7.17 (m, 3H), 4.91 (t, $J = 6.2$ Hz, 1H), 3.78 (sept., $J = 6.1$ Hz, 1H), 2.92–3.02 (m, 1H), 2.71 (quint., $J = 7.7$ Hz, 1H), 2.25–2.36 (m, 1H), 1.86–1.97 (m, 1H), 1.15 ppm (dd, $J = 6.1$, 1.0, (6H)); ^{13}C NMR (CDCl$_3$): $\delta = 143.8$, 143.3, 127.9, 126.3, 124.7, 124.6, 80.9, 70.2, 33.6, 29.9, 23.1, 22.5 ppm; HMRS (EI): calcd for $C_{12}H_{16}O$: 176.1201 $[M]^+$; found: 176.1204.

1-(Cycloheptyloxy)-2,3-dihydro-1H-indene (3bi): Yield: 86%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.26$–7.29 (m, 1H), 7.11–7.16 (m, 3H), 4.90 (t,

$J = 6.1$ Hz, 1H), 3.61 (sept, $J = 6.0$ Hz, 1H), 2.64–2.74 (m, 1H), 2.24–2.35 (m, 1H), 1.84–1.93 (m, 2H), 1.56–1.68 (m, 4H), 1.46–1.51 (m, 4H), 1.31–1.38 ppm (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 143.9$, 143.2, 127.8, 126.3, 124.7, 124.6, 80.8, 78.9, 35.1, 34.2, 33.6, 29.9, 28.4, 28.2, 23.0, 22.8 ppm; HMRS (EI): m/z: calcd for $C_{16}H_{22}O$: 230.1670 $[M]^+$; found: 230.1668.

(Isopropoxymethylene)dibenzene (3cf): Yield: 56%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.15$–7.32 (m, 10H), 5.43 (s, 1H), 3.62 (sept., $J = 6$ Hz, 1H); 1.16 ppm (d, $J = 6$ Hz, 6H); ^{13}C NMR (CDCl$_3$): $\delta = 142.2$, 128.2, 127.2, 127.0, 80.4, 69.0, 22.2 ppm; HMRS (EI): m/z: calcd for $C_{16}H_{18}O$: 226.1357 $[M]^+$; found: 226.1362.

(1-Isopropoxyethyl)benzene (3ef): Yield: 53%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.20$–7.30 (m, 8H), 4.50 (q, $J = 6$ Hz, 1H), 3.44 (sept., $J = 6$ Hz, 1H), 1.37 (d, $J = 6$ Hz, 3H), 1.11 (d, $J = 6$ Hz, 3H), 1.06 ppm (d, $J = 6$ Hz, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 144.8$, 128.2, 127.1, 126.0, 74.5, 68.4, 24.7, 23.3, 21.3 ppm; HMRS (EI): calcd for C_8H_9O: 121.0653 $[M-43]^+$; found: 121.0640.

(9-Isopropoxy)fluorene (3ff): Yield: 58%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.53$–7.59 (m, 4H), 7.18–7.33 (m, 4H), 5.50 (s, 1H), 3.74 (sept., $J = 6$ Hz, 1H), 1.13 ppm (d, $J = 6$ Hz, 6H); ^{13}C NMR (CDCl$_3$): $\delta = 144.3$, 140.4, 128.7, 127.4, 125.4, 119.8, 79.7, 69.9, 23.7 ppm; HMRS (EI): m/z: calcd for $C_{16}H_{16}O$: 224.1201 $[M]^+$; found: 224.1202.

[3-(tert-Pentyloxy)propyl]benzene (3hj): Yield: 23%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.07$–7.22 (m, 5H), 3.25 (t, $J = 6.4$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 1.73–1.82 (m, 2H), 1.42 (q, $J = 7.5$ Hz, 2H), 1.05 (s, 6H), 0.80 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl$_3$): $\delta = 142.3$, 128.4, 128.2, 125.5, 74.4, 60.2, 32.7, 32.5, 32.1, 25.0, 8.2 ppm; HMRS (EI): m/z: calcd for $C_{14}H_{22}O$: 205.1592 $[M]^+$; found: 205.1548.

(3-tert-Butoxypropyl)benzene (3gj): Yield: 40%; colourless oil; ^{1}H NMR (CDCl$_3$): $\delta = 7.09$–7.24 (m, 4H), 3.30 (t, $J = 6.4$ Hz, 2H), 2.63 (t, $J = 8.1$ Hz, 2H), 1.75–1.85 (m, 2H), 1.13 ppm (s, 9H); ^{13}C NMR (CDCl$_3$): $\delta = 142.2$, 128.4, 128.2, 125.6, 72.5, 60.7, 32.4, 32.1, 27.6 ppm; HMRS (EI): calcd for $C_{12}H_{17}O$: 177.1279 $[M-15]^+$; found: 177.1259.

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