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PAPER

Fragmentations observed in the reactions of α-methoxy-γ-alkoxyalkyl iodide substrates with super-electron-donors derived from 4-DMAP and *N*-methylbenzimidazole†‡§

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Reactions of super-electron-donors (SEDs) derived from 4-dimethylaminopyridine and from *N*-methylbenzimidazole with α-methoxy-γ-alkoxyalkyl iodides lead to liberation of the γ-alkoxy groups as their alcohols. This is consistent with generation of alkyl radicals from the alkyl halide precursors, and trapping of these radicals by the radical-cation of the SED, followed by a heterolytic fragmentation.

Introduction

Neutral, ground-state organic electron donors are currently widely studied.[1–5] Whereas the tetrathiafulvalenes[1] have received much attention in materials science and occasionally in synthesis, the tetraazaalkenes,[2–4] including compounds **1** and **3–5**, are considerably more powerful donors and include the most powerful neutral organic ground-state donors known.[5] The commerically available parent compound, *tetrakis*dimethylaminoethene (TDAE) **1**, has been widely used[2] as a two-electron donor to strongly electron-deficient organic systems such as CF_3I, thereby affording the trifluoromethyl anion and the oxidised dication **2**. The stronger donor, benzimidazole-derived **3**,[3a–c,4a] reacted with iodoarenes, *e.g.* **8** and iodoalkanes *e.g.* **10** at high temperature to afford aryl and alkyl radicals respectively after transfer of a single electron; after cyclisation, reductive termination by hydrogen atom abstraction afforded products **9** and **11** respectively in good yield.[4a] This was the first time that a neutral organic ground-state electron donor had achieved the conversion of iodoarenes to aryl radicals, and the term 'super-electron-donor' was applied to such reagents. More powerful organic donors **4**[4d–f,h,j] and **5**,[3a,d] subsequently converted aryl halides to aryl anions[4b,c,g] by donation of two electrons. The presence of the aryl anions derived from iodoarene **12** was shown by cyclisation of the aryl anion derived from substrate **12** onto the ester group to afford ketone **13** (Scheme 1). Whereas aryl anions could be generated in this way, the less stabilised alkyl anions could not.

The driving force for oxidation of the donor is stronger for **4** and **5** than for **3**, likely due to differences in aromatic stabilisation energy in their oxidised forms.[4i] Another factor that impacts on their ease of oxidation is the repulsion that can arise between the two positive charges in their oxidised disalts *e.g.* **2**. It has been shown that for the dication **2** derived from the commercially available donor TDAE **1**, substantial twisting occurs about the central C–C bond to minimise the repulsion between the two positive ends of the molecule.[6] This is also seen in the oxidation of **3**, where the twisted nature of the oxidised dication resulted in the protons within both of the NCH_2 groups being diastereotopic.[4a]

The computed angle between the planes of the two fused planar heterocycles increases from 16° in **3** to 26.3° in the corresponding radical-cation and to 41.3° in the dication.[4b] Likewise, in oxidation of donor **4**, the angle between the two six-membered rings opens to 36° in the radical-cation, while the X-ray structure of the oxidised diaction shows the angle at 53°. However, the donor **5** is constrained by its two trimethylene straps. A computed initial angle of 10.2° between the two planar 5-membered rings in the parent molecule **5** changes only slightly to 12° in the radical-cation **6**, but decreases to 1.5° in the dication **7**.[4b] These small angles might leave the oxidised forms **6** and **7** unusually open to attack by radicals or anions formed in the electron transfer reactions.

In support of this, we recently demonstrated[4g] that the radical-cation **6** can trap alkyl radicals; this was illustrated both by homologation of C_n alkyl halides to the C_{n+1} aldehydes, where the added carbon was derived from the electron donor **5**, and also by fragmentation of a series of α,γ-dialkoxyalkyl halides **14**, from which alcohols ROH **16** and methanol **17** were liberated, as shown in Scheme 2.

The purpose of the investigation leading to this paper was to probe whether this trapping chemistry of the oxidised forms of donor **5** is really an anomaly arising from the almost planar nature of its oxidised forms, **6** and **7**, or whether such trapping occurs routinely in more flexible super-electron-donors; the result would be important for understanding the fundamental chemistry of reactive tetraazaalkenes. The investigation would be carried out

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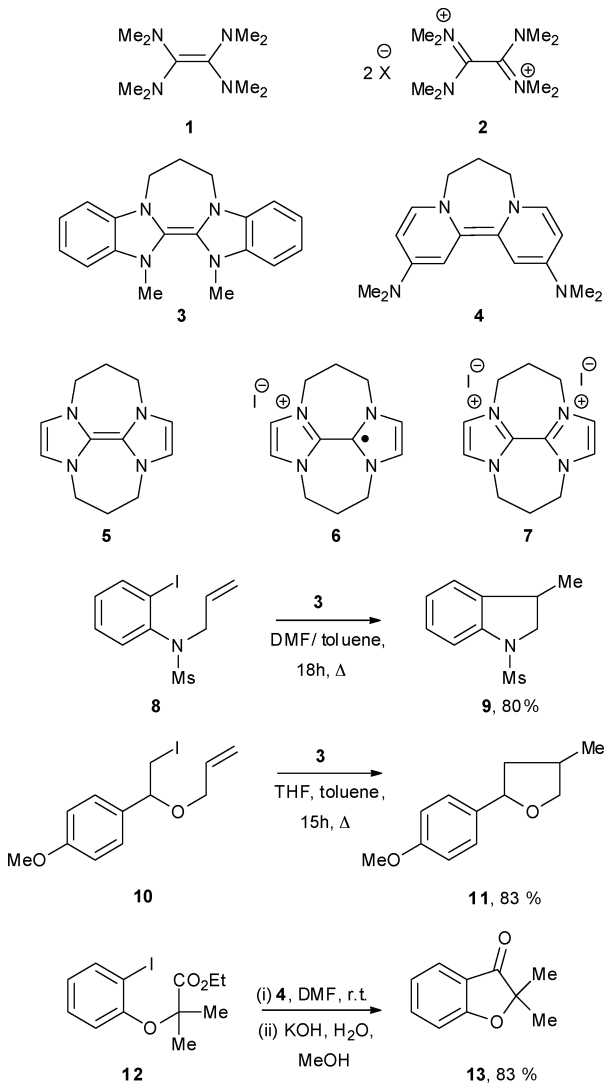


Scheme 1

by exploring the reactions of substrates **14** with donors **3** and **4**, and looking for the liberation of alcohol **16**. Scheme 2 shows a prospective pathway for formation of alcohol **16** from reaction of substrate **14** with donor **4** that is analogous to the mechanism that we proposed earlier with donor **5**.[4g]

Results and Discussion

A series of the desired substrates **14a–h** was prepared.[4g] 3-Methylbut-3-enol **27** was reacted with a range of alkyl bromides RBr, **28a–h**. The alkenyl ethers **29a–h**, produced in this way, were functionalised by reaction with *N*-iodosuccinimide and methanol to afford the α-methoxy-γ-alkoxyalkyl iodides **14a–h** (Scheme 3). The fragmentation reactions proposed to occur on reaction of substrates **14** with super-electron-donors (Scheme 2) would liberate methanol as well as a non-volatile alcohol, ROH **16**. Our plan was to detect isolate and quantify alcohol **16**, if it was produced.

The precursors to the donors **3** and **4**, namely disalts **31** and **32**, were prepared by our previous methods.[4a,4d] The corresponding donors, **3** and **4**, were prepared by the *in situ* method (where the precursor salt is treated with NaH in DMF to form the donor) and reacted with the iodoalkanes **14**. The results of reaction with the DMAP-derived donor **4** are as shown in Table 1. It is clear that alcohols **16a–h** are liberated from these reactions, and generally in good yields. To account for this, we propose the mechanism shown in Scheme 2.

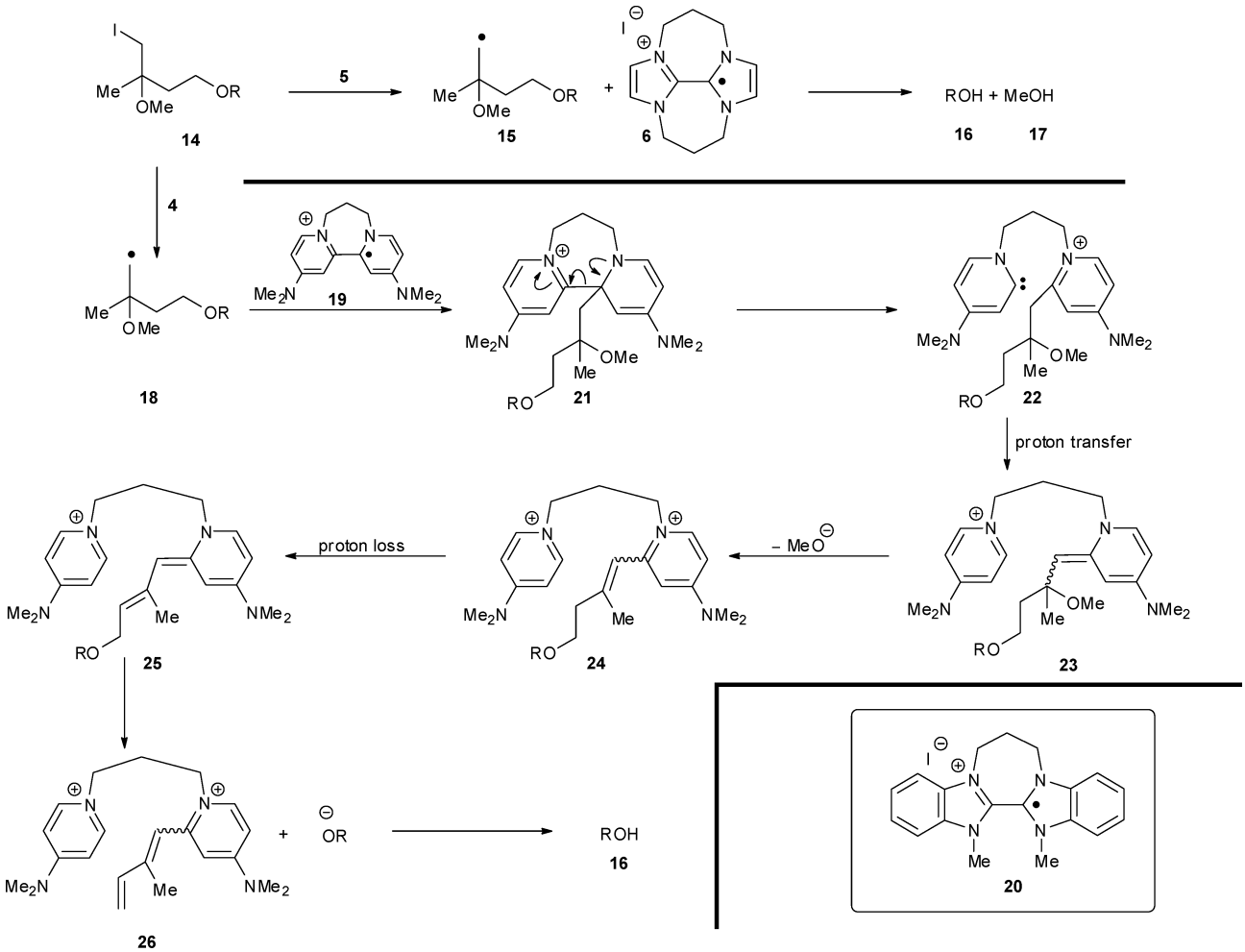
Table 1 Alcohols **16** liberated from ethers **14** on reaction with **4**

Entry	ROH formed	isolated (%)
1	**16a**, R = $Ph(CH_2)_3$	62
2	**16b**, R = $Ph(CH_2)_4$	67
3	**16c**, R = $PhO(CH_2)_3$	69
4	**16d**, R = *p*-$MeOC_6H_4O(CH_2)_3$	92
5	**16e**, R = *p*-$MeC_6H_4O(CH_2)_3$	87
6	**16f**, R = *p*-$MeC_6H_4O(CH_2)_4$	63
7	**16g**, R = β-$C_{10}H_7O(CH_2)_3$	30
8	**16h**, R = β-$C_{10}H_7O(CH_2)_4$	43

A number of features are worth noting. Firstly, as expected from previous reactions with this strong donor, there is no indication of conversion of the alkyl iodide substrates **14** to alkyl anions. This would be expected to result in detection of alkenes **29** (shown in Scheme 3), but none was seen, and this fact reinforces the difficulty in accessing unstabilised naked alkyl anions by electron transfer. The second point is that no product resulting from hydrogen atom abstraction by intermediate radicals **18** is seen. Instead, the sole products seen in the crude organic fractions following work up are the alcohols **16**. Trapping of the initial radical **18** by the radical cation **19** derived from the donor would afford salt **21**. Fragmentation of this salt **21**, would afford the pyridinium salt-carbene **22**. The fragmentation to form a pyridinylidene, as shown here, is not precedented, although corresponding fragmentations to form imidazolylidene carbenes are well precedented.[7] Since this pyridinylidene carbene is expected to be more reactive than an imidazolylidene,[8] it is rewarding to see that it forms quite efficiently. The basic carbene in **22** could then deprotonate the α-position to the pyridinium ring to form enamine **23**, which can then expel methoxide. Deprotonation of **24**, perhaps by methoxide, affords dienamine **25** which, in turn, expels the alkoxide, affording alcohol **16** on work up.

This shows that alkyl radicals can be trapped by radical-cation **19**, which, as already stated, has been computed to have a 36° twist between its two 6-membered rings. Hence, the trapping of alkyl radicals is not confined to the unusual and rigid doubly-strapped radical-cation **6**. Previous reactions [*e.g.* the conversion of **12** to **13**] show that when *aryl* anions are formed from reaction of aryl halides with donor **4**, they can undergo efficient reaction without significant diversion along this trapping pathway.

To explain the products seen, a range of possibilities was considered. Firstly, given that intermediate **21** is the precursor of alcohol **16**, we considered whether such a product (**21**) might have arisen simply by S_N2 reaction of enamine **4** with substrates **14** (Scheme 4). The same point had been considered in our study of donor **5**.[4g] What was needed was to see if the same outcome, the liberation of the alcohol **16**, could arise from a substrate where S_N2 reaction was not possible. The iodoarene **33** was prepared and subjected to the reaction (Scheme 4). Initial electron transfer to **33** would afford an aryl radical **34** plus an iodide anion. Kinetic competition would then arise between (a) further reduction of this radical to an aryl anion **37** and (b) cyclisation of the aryl radical



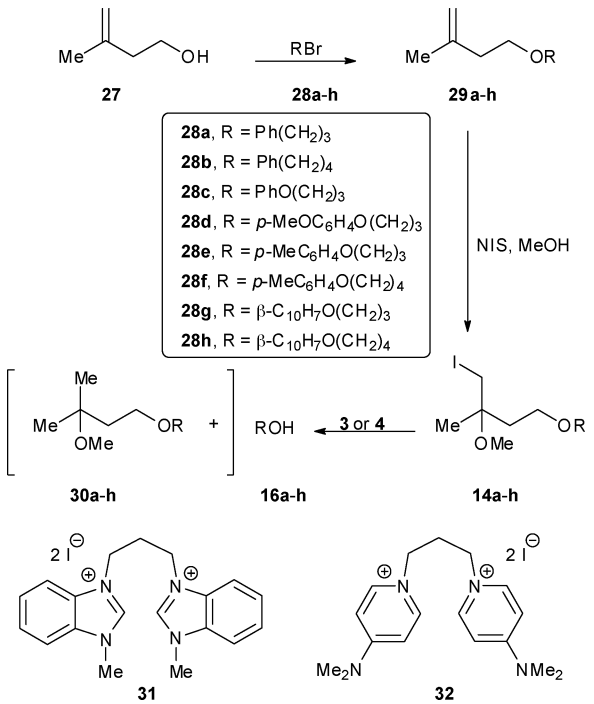
Scheme 2

onto the pendant alkene to form radical **35**. We had previously shown with donor **5** that very little cyclisation occurs in substrates like **33**, because of the speed of transfer of the second electron and, since donor **4** has a greater driving force for transfer of its second electron, we expected the same here. Nevertheless any aryl radicals that cyclised rather than receiving a second electron would afford radical **35** that should be in a position to be intercepted by radical-cation **19** (or by the corresponding dication) and thereby lead to liberation of alcohol **16a**. Alternatively, if trapping is slow, then hydrogen atom abstraction would afford product **36**. When the experiment was conducted, two products were formed: the alcohol **16a** (3%) and the reduced but uncyclised product **38** (14%). The formation of the alcohol shows that under these conditions, an intermediate of the type **21** can be formed, supportive of the trapping of the alkyl radicals by such radical-cation intermediates.

A second possibility for formation of the alcohols **16** was also addressed. In principle, such compounds might be formed by base-induced E2 elimination from a preceding ether, rather than by electron transfer to a halide, if either the donor or the NaH were to act as a base. If such an elimination were to occur in our experiments, it should happen most favourably in unsaturated ethers where an alkene might acidify the proton that needs to be removed to trigger the elimination. Accordingly, the unsaturated ether **29h** was selected as a test substrate, and added to a blank reaction in the presence of **4**, instead of a normal iodoalkyl substrate. When the organic layer was examined following workup, no elimination was seen; instead, only the starting ether **29h** was detected. It was subsequently isolated (82%) but no alcohol **16h** was detected, thereby ruling out this E2 reaction as a possible route to the observed product **16** in the reactions of substrates **14a–h**.

Having examined the behaviour of donor **4**, we were now keen to use these special substrates **14** to see if similar chemistry would be detected using less reactive donor **3**. As shown in the reactions of **8** and **10**, this donor efficiently converts substrates to alkyl radicals, and the principal products isolated, in high yield, are the products of reductive termination of these radicals. It would seem therefore that trapping of alkyl radicals (or indeed of their precursor aryl radicals) should not be a problem with this donor. However, even in the optimised conditions for substrates like **10** (Scheme 1), only 83% of the product is formed, and so we determined to check for evidence of alkyl radical trapping featuring formation of alcohols **16** from substrates **14**.

When the reactions were conducted, the results were as shown in Table 2. Small amounts of alcohols **16** were indeed formed (8–15%), but these were accompanied by the products of reductive termination, **30**, of the intermediate alkyl radicals. Thus, it appears



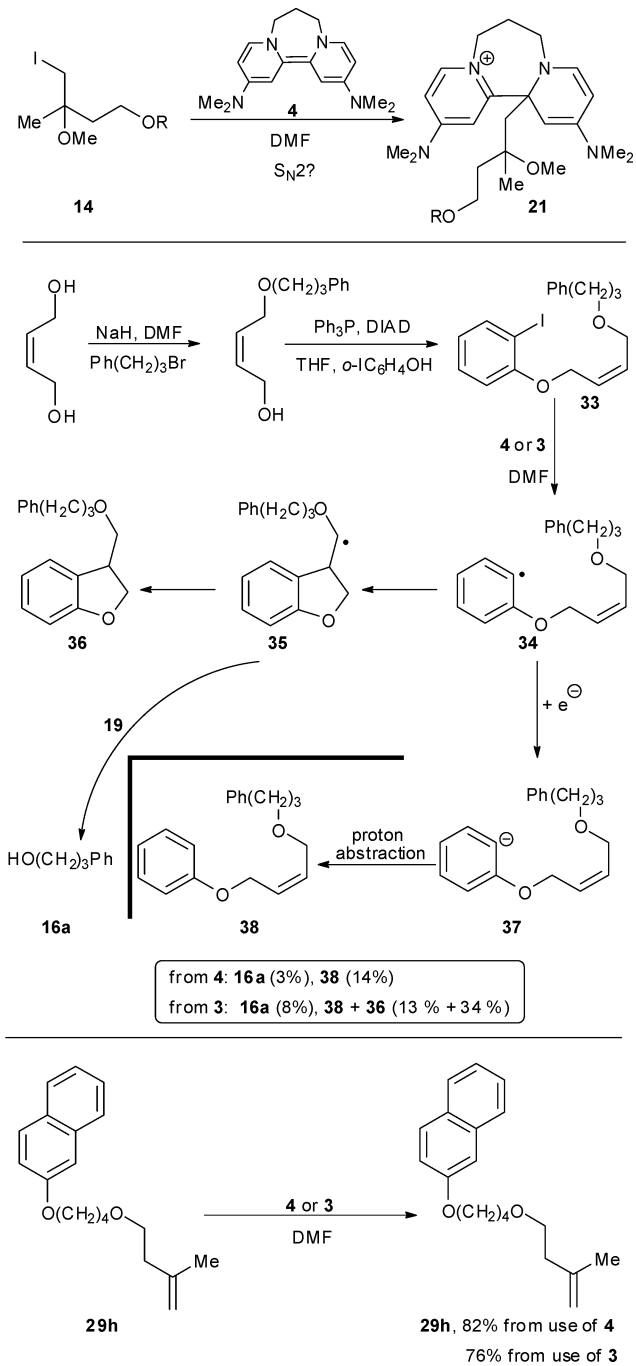
Scheme 3

Table 2 Alcohols **16** liberated from ethers **14** on reaction with **3**

			Products isolated (%)	
Entry	(Substrate)	R	**16**	**30**
1	(**14e**)	p-$MeC_6H_4O(CH_2)_3$	13	29
2	(**14f**)	p-$MeC_6H_4O(CH_2)_4$	8	24
3	(**14g**)	$C_{10}H_7O(CH_2)_3$	15	29
4	(**14h**)	$C_{10}H_7O(CH_2)_4$	12	34

that some trapping of intermediate alkyl radicals occurs even with this donor, leading to the formation of alcohols **16**. The question also arises about why products **30** form with **3** but not with **4**. This suggests that trapping by the radical-cation **20**, derived from **3**, is not so rapid. Although canonical forms **6**, **19** and **20** represent radical-cations as having one heterocyclic aromatic ring and a separate ring containing a radical, the structures are expected to show symmetrical distribution of spin-density across both rings, so that in reality neither heterocyclic ring is markedly aromatic. When these radical-cations trap a radical, *e.g.* in the formation of **21**, the resulting structures can fully express their aromaticity. With **4** (and with **5**), the gain in aromatic stabilisation energy is greater than with **3**, and so we expect that the trapping of a radical by the radical cation carries more driving force, and perhaps therefore more rapid, with **4** than with **3**.

Test reactions were also performed on donor **3** with substrates **33** and **29h** (Scheme 4). With **33**, a small amount of alcohol **16** (8%) was indeed formed together with an inseparable mixture of the two expected products of reductive termination, **36** and **38**. With the blank ether substrate **29h**, once again no alcohol was liberated and the starting compound **29h** was isolated as the sole product (76%).



Scheme 4

Conclusions

These substrates show that alkyl radicals can be trapped during SED reactions of non-rigid donors, and most likely by the radical-cation of the donors. Although we did not look to optimise the reaction outcomes for these substrates, the important point was that alcohols **16** were indeed formed, and so we now know that it does not require an anomalously planar system to afford these products, but that they can be expected from a broad range of super-electron donors.

Experimental Section

A. Preparation of substrates

For preparation of substrates **14a–d**, see ref. 4g.

1-(3-Bromopropoxy)-4-methylbenzene 28e. Sodium carbonate (11.72 g, 110.56 mmol, 2 eq.) was added to a solution of *p*-cresol (6.0 g, 55.6 mmol, 1 eq.) and 1,3-dibromopropane (28.2 mL, 277 mmol, 5 eq.) in acetonitrile (150 mL). The reaction mixture was stirred under reflux (80 °C) for 72 h under argon. The reaction mixture was washed with diethyl ether (3 × 100 mL). The combined organics were then further washed with water (4 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-(3-bromopropoxy)-4-methylbenzene **28e** as a colourless oil (3.54 g, 28%).[9] (Found: $[M+H]^+$ 229.0215. $C_{10}H_{13}BrO$ requires $[M+H]^+$ 229.0223); ν_{max}(neat)/cm^{-1} 2952, 2879, 1451, 1249, 785; δ_H ($CDCl_3$) 2.30–2.36 (2H, m, CH_2), 2.31 (3H, s, CH_3), 3.62 (2H, t, *J* 6.4, CH_2Br), 4.10 (2H, t, *J* 5.8, OCH_2), 6.82 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 20.0 (CH_3), 29.6 (CH_2), 32.0 (CH_2), 64.95 (CH_2), 114.0 (CH), 129.4 (CH), 129.7 (C), 156.1 (C).

1-Methyl-4-(3-((3-methylbut-3-en-1-yl)oxy)propoxy)benzene 29e. Sodium hydride (60% in mineral oil, 0.63 g, 15.79 mmol, 1.2 eq.) was washed three times with anhydrous hexane. The hexane was removed *via* cannula and trace residual amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (25 mL) was then added. 3-Methylbut-3-en-1-ol (1.32 mL, 13.16 mmol, 1 eq.) was added and the resulting orange suspension stirred under argon at room temperature for 1 h. The reaction mixture was cooled to 0 °C and 1-(3-bromopropoxy)-4-methylbenzene **28e** (3.0 g, 13.16 mmol, 1 eq.) was slowly added. The reaction mixture was stirred at room temperature under argon overnight. Water (15 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (2 × 50 mL). The combined organics were then further washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-methyl-4-(3-((3-methylbut-3-en-1-yl)oxy)propoxy)benzene **29e** as a colourless oil (811 mg, 26%). (Found: $[M+H]^+$ 235.1690. $C_{15}H_{22}O_2$ (M) requires $[M+H]^+$ 235.1693); ν_{max}(neat)/cm^{-1} 2941, 2862, 1451, 1440, 1250, 773; δ_H ($CDCl_3$) 1.76 (3H, s, CH_3), 2.02–2.09 (2H, m, CH_2), 2.30–2.34 (2H, m, CH_2), 2.31 (3H, s, CH_3) 3.57 (2H, t, *J* 7.0, CH_2O), 3.63 (2H, t, *J* 6.2, CH_2O), 4.05 (2H, t, *J* 6.3, CH_2O), 4.74 (1H, m, *H*CH═C), 4.78 (1H, m, *H*CH═C), 6.81 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 20.0 (CH_3), 22.2 (CH_3), 29.3 (CH_2), 37.3 (CH_2), 64.5 (CH_2), 66.9 (CH_2), 69.0 (CH_2), 110.9 (CH_2), 114.0 (CH), 129.2 (CH), 129.3 (C), 142.4 (C), 156.4 (C).

1-(3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene 14e. 1-Methyl-4-(3-((3-methylbut-3-en-1-yl)oxy)propoxy)-benzene (0.56 g, 2.34 mmol, 1 eq.) was dissolved in a solution of dry DCM (15 mL) and anhydrous methanol (0.19 mL, 4.68 mmol, 2 eq.). The reaction mixture was cooled to −78 °C. *N*-Iodosuccinimide (0.56 g, 2.51 mmol, 1.5 eq.) was added to the reaction mixture in one portion, and the resultant suspension was stirred at −78 °C for 1 h. The reaction was stirred at room temperature under argon overnight. The reaction mixture was quenched with sodium thiosulfate (30 mL), causing the solution to change from dark purple to colourless. The reaction mixture was extracted with DCM (3 × 60 mL), and the combined organics were washed with brine (3 × 60 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **14e** as a colourless oil (0.80 g, 87%). (Found: $[M+NH_4]^+$ 410.1183. $C_{16}H_{25}IO_3$ (M) requires $[M+NH_4]^+$ 410.1187); ν_{max}(neat)/cm^{-1} 2933, 2870, 1615, 1511, 1243, 1113; δ_H ($CDCl_3$) 1.33 (3H, s, CH_3), 1.90–2.00 (2H, m, CH_2), 2.01–2.06 (2H, m, CH_2), 2.31 (3H, s, CH_3), 3.21 (3H, s, OCH_3), 3.29 (1H, d, *J* 10.8, C*H*HI), 3.34 (1H, d, *J* 10.8, CH*H*I), 3.52 (2H, t, *J* 7.0, CH_2O), 3.60 (2H, t, *J* 6.2, CH_2O), 4.05 (2H, t, *J* 6.4, OCH_3), 6.81 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 15.6 (CH_2), 20.0 (CH_3), 22.2 (CH_3), 29.3 (CH_2), 36.0 (CH_2), 49.0 (CH_3), 64.4 (CH_2), 66.3 (CH_2), 67.1 (CH_2), 73.35 (C), 113.9 (CH), 129.3 (CH), 129.4 (C), 156.4 (C).

1-(4-Bromobutoxy)-4-methylbenzene 28f. Sodium carbonate (11.72 g, 105.5 mmol, 2 eq.) was added to a solution of *p*-cresol (6.0 g, 55.5 mmol, 1 eq.) and 1,4-dibromobutane (33.3 mL, 277 mmol, 5 eq.) in acetonitrile (150 mL). The reaction mixture was stirred under reflux (80 °C) for 72 h under argon. The reaction mixture was washed with diethyl ether (3 × 100 mL). The combined organics were then further washed with water (4 × 100 mL), brine (100 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-(4-bromobutoxy)-4-methylbenzene **28f** as a colourless oil (5.30 g, 39%).[10] (Found: $[M+H]^+$ 243.0374. $C_{11}H_{15}{}^{79}BrO$ (M) requires $[M+H]^+$ 243.0379); ν_{max}(neat)/cm^{-1} 3044, 2998, 2951, 2833, 1616, 1592, 1508, 1451; δ_H ($CDCl_3$) 1.91–1.96 (2H, m, CH_2), 2.05–2.10 (2H, m, CH_2), 2.31 (3H, s, CH_3), 3.50 (2H, t, *J* 6.6, CH_2Br), 3.99 (2H, t, *J* 6.4, OCH_2), 6.89 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 20.0 (CH_3), 27.5 (CH_2), 29.0 (CH_2), 33.0 (CH_2), 66.4 (CH_2), 113.9 (CH), 129.4 (CH), 129.5 (C), 156.2 (C).

1-Methyl-4-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)benzene 29f. Sodium hydride (60% in mineral oil, 1.03 g, 25.66 mmol, 1.2 eq.) was washed three times with anhydrous hexane. The hexane was removed *via* cannula and trace residual amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (25 mL) was then added. 3-Methylbut-3-en-1-ol (2.16 mL, 21.39 mmol, 1 eq.) was added and the resulting orange suspension stirred under argon at room temperature for 1 h. The reaction mixture was cooled to 0 °C and 1-(4-bromobutoxy)-4-methylbenzene **28f** (5.20 g, 21.39 mmol, 1 eq.) was slowly added. The reaction mixture was stirred at room temperature under argon overnight. Water (15 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (2 × 50 mL). The combined organics were then further washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-methyl-4-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)benzene **29f** as a colourless oil (1.22 g, 23%).

(Found: $[M+H]^+$ 249.1851. $C_{16}H_{25}O_2$ requires $[M+H]^+$ 249.1849); ν_{max}(neat)/cm^{-1} 2934, 2872, 1512, 1240; δ_H ($CDCl_3$) 1.78 (3H, s, CH_3), 1.74–1.81 (2H, m, CH_2), 1.83–1.91 (2H, m, CH_2), 2.29–2.35 (2H, m, CH_2), 2.31 (3H, s, CH_3), 3.51 (2H, t, *J* 6.3, CH_2O), 3.55 (2H, t, *J* 7.0, CH_2O), 3.98 (2H, t, *J* 6.3, CH_2O), 4.74 (1H, m, *H*CH=C), 4.78 (1H, m, *H*CH=C), 6.81 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 20.5 (CH_3), 22.8 (CH_3), 26.2 (CH_2), 26.4 (CH_2), 37.9 (CH_2), 67.8 (CH_2), 69.3 (CH_2), 70.5 (CH_2), 111.4 (CH_2), 114.4 (CH), 129.7 (C), 129.9 (CH), 143.0 (C), 157.0 (C).

1-(4-(4-Iodo-3-methoxy-3-methylbutoxy)butoxy)-4-methylbenzene 14f. 1-Methyl-4-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)-benzene **29f** (1.0 g, 4.03 mmol, 1 eq.) was dissolved in a solution of dry DCM (15 mL) and anhydrous methanol (0.33 mL, 8.06 mmol, 2 eq.). The reaction mixture was cooled to −78 °C. *N*-Iodosuccinimide (1.36 g, 6.05 mmol, 1.5 eq.) was added to the reaction mixture in one portion, and the resultant suspension was stirred at −78 °C for 1 h. The reaction was stirred at room temperature under argon overnight. The reaction mixture was quenched with sodium thiosulfate (15 mL), causing the solution to change from dark purple to colourless. The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organics were washed with brine (3 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 1-(4-(4-iodo-3-methoxy-3-methylbutoxy)butoxy)-4-methylbenzene **14f** as a colourless oil (1.04 g, 63%). (Found: $[M+NH_4]^+$ 424.1335. $C_{17}H_{27}IO_3$ (M) requires $[M+NH_4]^+$ 424.1343); ν_{max}(neat)/cm^{-1} 2934, 2863, 1512, 1240, 812; δ_H ($CDCl_3$) 1.33 (3H, s, CH_3), 1.71–1.79 (2H, m, CH_2), 1.81–1.89 (2H, m, CH_2), 1.91–2.02 (2H, m, CH_2), 2.29 (3H, s, CH_3), 3.21 (3H, s, OCH_3), 3.29 (1H, d, *J* 10.8, C*H*HI), 3.34 (1H, d, *J* 10.8, CH*H*I), 3.46–3.53 (4H, m, 2 × CH_2O), 3.96 (2H, t, *J* 6.4, OCH_3), 6.81 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.2, Ar*H*); δ_C ($CDCl_3$) 15.6 (CH_2), 20.0 (CH_3), 22.2 (CH_3), 25.7 (CH_2), 25.9 (CH_2), 36.0 (CH_2), 49.0 (CH_3), 66.2 (CH_2), 67.2 (CH_2), 70.2 (CH_2), 73.4 (C), 113.9 (CH), 129.3 (CH), 129.4 (C), 156.4 (C).

2-(3-Bromopropoxy)naphthalene 28g. Sodium carbonate (6.76 g, 63.76 mmol, 3 eq.) was added to a solution of 2-naphthol (3.0 g, 20.81 mmol, 1 eq.) and 1,3-dibromopropane (16.17 mL, 149 mmol, 7.2 eq.) in acetonitrile (100 mL). The reaction mixture was stirred under reflux (80 °C) for 3 days under argon. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organic layers were then further washed with water (4 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(3-bromopropoxy)naphthalene **28g** as a colourless oil (1.76 g, 32%).[11] (Found: $[M]^+$ 264.0145. $C_{13}H_{13}BrO$ requires $[M]^+$ 264.0144); ν_{max}(neat)/cm^{-1} 2945, 2874, 1567, 1448, 1435, 1248, 786; δ_H ($CDCl_3$) 2.39–2.45 (2H, quintet, *J* 6.0, CH_2), 3.68 (2H, t, *J* 6.4, CH_2Br), 4.26 (2H, t, *J* 6.0, CH_2O), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 29.5 (CH_2), 31.9 (CH_2), 64.9 (CH_2), 106.3 (CH), 118.3 (CH), 123.2 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 128.6 (CH), 129.0 (C), 134.0 (C), 156.1 (C).

2-(3-((3-Methylbut-3-en-1-yl)oxy)propoxy)naphthalene 29g. Sodium hydride (60% in mineral oil, 0.54 g, 13.58 mmol, 1.2 eq.) was washed three times with anhydrous hexane. The hexane was removed *via* cannula and trace residual amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (25 mL) was then added. 3-Methylbut-3-en-1-ol (1.14 mL, 11.32 mmol, 1 eq.) was added and the resulting orange suspension stirred under argon at room temperature for 1 h. The reaction mixture was cooled to 0 °C and 2-(3-bromopropoxy)naphthalene **28g** (3.0 g, 11.32 mmol, 1 eq.) in DMF (5 mL) was slowly added. The reaction mixture was stirred at room temperature under argon overnight. Water (15 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (2 × 50 mL). The combined organics were then further washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(3-((3-methylbut-3-en-1-yl)oxy)propoxy)naphthalene **29g** as a colourless oil (1.06 g, 34%). Found: $[M+H]^+$ 271.1694. $C_{18}H_{22}O_2$ requires $[M+H]^+$ 271.1693); ν_{max}(neat)/cm^{-1} 3059, 2935, 2867, 1630, 1259, 1119, 837; δ_H ($CDCl_3$) 1.76 (3H, s, CH_3), 2.11–2.17 (2H, m, CH_2), 2.32–2.35 (2H, m, CH_2), 3.60 (2H, t, *J* 7.0, CH_2O), 3.68 (2H, t, *J* 6.4, CH_2O), 4.21 (2H, t, *J* 6.4, OCH_3), 4.75 (1H, m, *H*CH=C), 4.79 (1H, m, *H*CH=C), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 22.2 (CH_3), 29.3 (CH_2), 37.3 (CH_2), 64.5 (CH_2), 66.8 (CH_2), 69.0 (CH_2), 110.6 (CH), 111.0 (CH), 118.5 (CH), 123.0 (CH), 125.8 (CH), 126.2 (CH), 127.1 (CH), 128.4 (C), 128.8 (CH), 134.1 (C), 142.4 (C), 156.5 (C).

2-(3-(4-Iodo-3-methoxy-3-methylbutoxy)propoxy)naphthalene 14g. 2-(3-((3-Methylbut-3-en-1-yl)oxy)propoxy)naphthalene **29g** (0.95 g 3.51 mmol, 1 eq.) was dissolved in a solution of dry DCM (15 mL) and anhydrous methanol (0.28 mL, 7.02 mmol, 2 eq.). The reaction mixture was cooled to −78 °C. *N*-Iodosuccinimide (1.19 g, 5.27 mmol, 1.5 eq.) was added to the reaction mixture in one portion, and the resultant suspension was stirred at −78 °C for 1 h. The reaction was stirred at room temperature under argon overnight. The reaction mixture was quenched with sodium thiosulfate (15 mL), causing the solution to change colour from dark purple to colourless. The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organics were washed with brine (3 × 30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)naphthalene **14g** as a colourless oil (0.94 g, 63%) (Found: $[M+NH_4]^+$ 446.1188 $C_{19}H_{25}IO_3$ requires $[M+NH_4]^+$ 446.1187); ν_{max}(neat)/cm^{-1} 2940, 2871, 1629, 1600, 1465, 1258, 1217, 1119, 747; δ_H ($CDCl_3$) 1.34 (3H, s, CH_3), 1.91–2.05 (2H, m, CH_2), 2.10–2.17 (2H, m, CH_2), 3.21 (3H, s, OCH_3), 3.31 (1H, d, *J* 10.8, C*H*HI), 3.35 (1H, d, *J* 10.8, CH*H*I), 3.56 (2H, t, *J* 6.8, CH_2O), 3.64 (2H, t, *J* 6.2, CH_2O), 4.21 (2H, t, *J* 6.4, CH_2O) 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 15.6 (CH_2), 22.2 (CH_3), 29.2 (CH_2), 36.1 (CH_2), 49.0 (CH_3), 64.4 (CH_2), 66.4 (CH_2), 67.0 (CH_2), 73.4 (C), 106.2 (CH), 118.4 (CH), 123.0 (CH), 125.8

(CH), 126.2 (CH), 127.1 (CH), 128.4 (C), 128.8 (CH), 134.1 (C), 156.4 (C).

2-(4-Bromobutoxy)naphthalene 28h. Sodium carbonate (6.76 g, 63.76 mmol, 3 eq.) was added to a solution of 2-naphthol (3.0 g, 20.81 mmol, 1 eq.) and 1,4-dibromobutane (19.04 mL, 159 mmol, 5 eq.) in acetonitrile (100 mL). The reaction mixture was stirred under reflux (80 °C) for 72 h under argon. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organics were then further washed with water (4 × 50 mL), brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(4-bromobutoxy)naphthalene **28h** as a colourless oil (1.80 g, 31%).[12] (Found: $[M]^+$ 278.0301. $C_{14}H_{15}BrO$ requires $[M]^+$ 278.0301); ν_{max}(neat)/cm^{-1} 2952, 2880, 1565, 1451, 1439, 1249, 772; δ_H ($CDCl_3$) 2.02–2.08 (2H, m, C*H*$_2$), 2.12–2.17 (2H, m, C*H*$_2$), 3.54 (2H, t, *J* 6.4, C*H*$_2$Br), 4.15 (2H, t, *J* 6.0, C*H*$_2$O), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.73–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 27.4 (CH_2), 29.0 (CH_2), 32.9 (CH_2), 66.4 (CH_2), 106.1 (CH), 118.4 (CH), 123.1 (CH), 125.9 (CH), 126.2 (CH), 127.1 (CH), 128.5 (C), 128.9 (CH), 134.1 (C), 156.3 (C).

2-(4-((3-Methylbut-3-en-1-yl)oxy)butoxy)naphthalene 29h. Sodium hydride (60% in mineral oil, 1.28 g, 31.81 mmol, 1.2 eq.) was washed three times with anhydrous hexane. The hexane was removed *via* cannula and trace residual amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (40 mL) was then added. 3-Methylbut-3-en-1-ol (2.67 mL, 26.51 mmol, 1 eq.) was added and the resulting orange suspension stirred under argon at room temperature for 1 h. The reaction mixture was cooled to 0 °C and 2-(4-bromobutoxy)naphthalene **28h** (7.40 g, 26.51 mmol, 1 eq.) in DMF (5 mL) was slowly added. The reaction mixture was stirred at room temperature under argon overnight. Water (15 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (2 × 50 mL). The combined organics were then further washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** as a colourless oil (2.2 g, 29%). (Found: $[M+H]^+$ 285.1849. $C_{19}H_{24}O_2$ (M) requires $[M+H]^+$ 285.1849; ν_{max}(neat)/cm^{-1} 3055, 2934, 2857, 1624, 1462, 1254, 1180, 1114, 834; δ_H ($CDCl_3$) 1.82 (3H, s, C*H*$_3$), 1.83–1.86 (2H, m, C*H*$_2$), 1.94–1.99 (2H, m, C*H*$_2$), 2.34 (2H, t, *J* 6.8, C*H*$_2$O), 3.54–3.60 (4H, m, 2 × C*H*$_2$O), 4.14 (2H, t, *J* 6.4, OC*H*$_2$), 4.77 (1H, m, *H*CH═C), 4.81 (1H, m, *H*CH═C), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 22.9 (CH_3), 26.3 (CH_2), 26.7 (CH_2), 38.0 (CH_2), 67.7 (CH_2), 69.5 (CH_2), 70.5 (CH_2), 106.7 (CH), 111.5 (CH_2), 119.0 (CH), 123.6 (CH), 126.3 (CH), 126.8 (CH), 127.7 (CH), 128.9 (C), 129.4 (CH), 134.7 (C), 143.0 (C), 157.1 (C).

2-(4-(4-Iodo-3-methoxy-3-methylbutoxy)butoxy)naphthalene 14h. 2-(4-((3-Methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** (1.40 g, 4.92 mmol, 1 eq.) was dissolved in a solution of dry DCM (15 mL) and anhydrous methanol (0.40 mL, 9.84 mmol, 2 eq.). The reaction mixture was cooled to −78 °C. *N*-Iodosuccinimide (1.66 g, 7.38 mmol, 1.5 eq.) was added to the reaction mixture in one portion, and the resultant suspension was stirred at −78 °C for 1 h. The reaction was stirred at room temperature under argon overnight. The reaction mixture was quenched with sodium thiosulfate (15 mL), causing the solution to change colour from dark purple to colourless. The reaction mixture was extracted with DCM (3 × 30 mL), and the combined organics were washed with brine (3 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford 2-(4-(4-iodo-3-methoxy-3-methylbutoxy)butoxy)naphthalene **14h** as a colourless oil (1.61 g, 74%). (Found: $[M+NH_4]^+$ 460.1332. $C_{20}H_{27}IO_3$ (M) requires $[M+NH_4]^+$ 460.1343); ν_{max}(neat)/cm^{-1} 2940, 2868, 1629, 1465, 1259, 749; δ_H ($CDCl_3$) 1.35 (3H, s, C*H*$_3$), 1.78–1.86 (2H, m, C*H*$_2$), 1.90–2.00 (4H, m, 2 × C*H*$_2$), 3.21 (3H, s, C*H*$_3$O) 3.31 (1H, d, *J* 10.8, C*H*HI), 3.34 (1H, d, *J* 10.8, CH*H*I), 3.54 (4H, m, 2 × C*H*$_2$O), 4.13 (2H, t, *J* 6.4, C*H*$_2$O) 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 16.2 (CH_2), 22.8 (CH_3), 26.2 (CH_2), 26.4 (CH_2), 36.5 (CH_2), 49.5 (CH_3), 66.7 (CH_2), 67.7 (CH_2), 70.7 (CH_2), 73.8 (C), 106.6 (CH), 119.0 (CH), 123.5 (CH), 126.3 (CH), 126.7 (CH), 127.6 (CH), 128.9 (C), 129.3 (CH), 134.6 (C), 157.0 (C).

B. Reactions of substrates with Donor 4

Reaction of substrate 14a with Donor 4. 1,3-Bis (*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (640 mg, 1.19 mmol, 1.8 eq.) was dried under vacuum at 100 °C for 1 h, then cooled. Sodium hydride (60% in mineral oil, 473 mg, 11.90 mmol, 18 eq.) was added, and the mixture was washed with dry hexane three times (3 × 20 mL). The hexane was removed *via* cannula and residual trace amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (15 mL) was then added, causing a purple suspension to form, which was left to stir at room temperature under argon for 4 h. The purple donor suspension was centrifuged at 2000 rpm for 10 min to afford the solution, which was added, *via* cannula, to (3-(4-iodo-3-methoxy-3-methylbutoxy)propyl)benzene **14a** (239 mg, 0.66 mmol, 1 eq.) The reaction mixture was left to stir at room temperature under argon overnight. Water (50 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organics were then further washed with water (4 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–10% diethyl ether in petroleum ether, to afford 3-phenylpropan-1-ol **16a** as a colourless oil (56 mg, 62%).[13] (Found: $[M]^+$ 136.0883. $C_9H_{12}O$ (M) requires $[M]^+$ 136.0883); ν_{max}(neat)/cm^{-1} 3349, 3341, 3027, 2927, 2863, 1667, 1603, 1496, 1454; δ_H ($CDCl_3$) 1.89–1.95 (2H, m C*H*$_2$), 2.73 (2H, t, *J* 7.8, C*H*$_2$Ar), 3.69 (2H, t, *J* 6.4, C*H*$_2$OH), 7.18–7.22 (3H, m, Ar*H*), 7.28– 7.31 (2H, m, Ar*H*); δ_C ($CDCl_3$) 32.1 (CH_2), 34.2 (CH_2), 62.3 (CH_2), 126.0 (CH), 128.4 (CH), 128.5 (CH), 141.8 (C).

Reaction of substrate 14b with Donor 4. Similarly: (4-(4-iodo-3-methoxy-3-methylbutoxy)butyl)benzene **14b** (250 mg, 0.66 mmol, 1 eq.) was reacted with 1,3-*bis*(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (640 mg, 1.19 mmol,

1.8 eq.) to afford 4-phenylbutan-1-ol **16b** as a colourless oil (60 mg, 67%).[14] (Found: $[M+NH_4]^+$ 168.1383. $C_{10}H_{14}O$ (M) requires $[M+NH_4]^+$ 168.1383); ν_{max}(neat)/cm^{-1} 3338, 3027, 2937, 2861, 1666, 1496, 1454; δ_H ($CDCl_3$) 1.60–1.76 (4H, m 2 × CH_2), 2.66 (2H, t, *J* 7.6, CH_2Ar), 3.68 (2H, t, *J* 5.6, CH_2OH), 7.18–7.21 (3H, m, Ar*H*), 7.29–7.31 (2H, m, Ar*H*); δ_C ($CDCl_3$) 27.5 (CH_2), 32.3 (CH_2), 35.7 (CH_2), 62.9 (CH_2), 125.8 (CH), 128.3 (CH), 128.4 (CH), 142.3 (C).

Reaction of substrate 14c with Donor 4. Similarly: (3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)benz-ene **14c** (250 mg, 0.66 mmol, 1 eq.) was reacted with 1,3-*bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide (642 mg, 1.19 mmol, 1.8 eq.) to afford 3-phenoxypropan-1-ol **16c** as a colourless oil (69 mg, 69%).[15] (Found: $[M+NH_4]^+$ 170.1904. $C_9H_{12}O_2$ (M) requires $[M+NH_4]^+$ 170.1904) ν_{max}(neat)/cm^{-1} 3349, 3040, 2950, 1665, 1599, 1496; δ_H ($CDCl_3$) 2.07 (2H, quintet, *J* 5.9, CH_2), 3.88 (2H, t, *J* 5.9, CH_2OH), 4.14 (2H, t, *J* 5.9, CH_2OAr), 6.91–6.98 (3H, m, Ar*H*), 7.28–7.31 (2H, m, Ar*H*). δ_C ($CDCl_3$) 32.1 (CH_2), 60.8 (CH_2), 65.9 (CH_2), 114.7 (CH), 121.0 (CH), 129.6 (CH), 158.7 (C).

Reaction of substrate 14d with Donor 4. Similarly: 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methoxybenzene **14d** (98 mg, 0.25 mmol, 1 eq.) was reacted with 1,3-*bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide (268 mg, 0.5 mmol, 2.0 eq.) to afford 3-(4-methoxyphenoxy)propan-1-ol **16d** as a colourless oil (40 mg, 92%). The compound data were consistent with the reported analytical data;[4g] (Found: $[M+NH_4]^+$ 200.2164. $C_{10}H_{14}O_3$ (M) requires $[M+NH_4]^+$ 200.2164) ν_{max}(neat)/cm^{-1} 3273, 2953, 2872, 1513, 1471, 827; δ_H ($CDCl_3$) 2.00–2.07 (2H, quintet, *J* 5.9, CH_2), 3.88 (2H, t, *J* 5.9, CH_2OH), 4.14 (2H, t, *J* 5.9, CH_2OAr), 6.82–6.88 (4H, m, Ar*H*). δ_C ($CDCl_3$) 32.1 (CH_2), 55.8 (CH_3), 60.8 (CH_2), 66.7 (CH_2), 114.7 (CH), 115.5 (CH), 152.8 (C), 153.9 (C).

Reaction of substrate 14e with Donor 4. Similarly: 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **14e** (131 mg, 0.33 mmol, 1 eq.) was reacted with 1,3-*bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide (268 mg, 0.5 mmol, 1.5 eq.) to afford 3-(*p*-tolyloxy)propan-1-ol **16e** as a colourless oil (48 mg, 87%). The compound data were consistent with the reported analytical data;[16] ν_{max}(neat)/cm^{-1} 3272, 2936, 2876, 1610, 1512, 1243, 1061; δ_H ($CDCl_3$) 2.00–2.07 (2H, quintet, *J* 5.9, CH_2), 2.31 (3H, s, ArCH_3), 3.89 (2H, t, *J* 5.9, CH_2OH), 4.13 (2H, t, *J* 5.9, CH_2O), 6.83 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*). δ_C ($CDCl_3$) 20.0 (CH_3), 29.3 (CH_2), 37.3 (CH_2), 66.9 (CH_2), 114.0 (CH), 129.4 (CH), 129.6 (C),156.4 (C).

Reaction of substrate 14f with Donor 4. Similarly: 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **14f** (135 mg, 0.33 mmol, 1 eq.) was reacted with 1,3-*bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (268 mg, 0.5 mmol, 1.5 eq.) to afford 4-(*p*-tolyloxy)butan-1-ol **16f** as a colourless oil (38 mg, 63%). ν_{max}(neat)/cm^{-1} 3292, 2935, 2876, 1613, 1512, 1472, 1243, 1062, 813; δ_H ($CDCl_3$) 1.76–1.80 (2H, m, CH_2), 1.88–1.90 (2H, m, CH_2), 2.30 (3H, s, CH_3), 3.74 (2H, t, *J* 5.9, CH_2OH), 4.00 (2H, t, *J* 5.9, CH_2O), 6.83 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*). δ_C ($CDCl_3$) 19.9 (CH_2), 25.4 (CH_2), 29.1 (CH_3), 62.1 (CH_2), 67.4 (CH_2), 113.9 (CH), 129.3 (C), 129.4 (CH).

Reaction of substrate 14g with Donor 4. Similarly: 2-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-naphthalene **14g** (141 mg, 0.33 mmol, 1 eq.) was reacted with 1,3-*bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (268 mg, 0.5 mmol, 1.5 eq.) to afford 3-(naphthalen-2-yloxy)propan-1-ol **16g** as a white solid (60 mg, 30%).[17] M.Pt. 99–100 °C. ν_{max}(neat)/cm^{-1} 3338, 3026, 2936, 2861, 1496, 1453, 1061, 699; δ_H ($CDCl_3$) 2.11–2.20 (2H, quintet, *J* 6.0, CH_2), 3.94 (2H, t, *J* 6.0, CH_2O), 4.27 (2H, t, *J* 6.0, CH_2OH), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 31.7 (CH_2) 60.1 (CH_2), 65.3 (CH_2), 106.3 (CH), 118.3 (CH), 123.2 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 128.5 (C), 128.9 (CH), 134.0 (C), 156.4 (C).

Reaction of substrate 14h with Donor 4. Similarly: 2-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-naphthalene **14h** (147 mg, 0.33 mmol, 1 eq.) was reacted with 1,3-*bis*(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (268 mg, 0.5 mmol, 1.5 eq.) to afford 4-(naphthalen-2-yloxy)butan-1-ol **16h** as a white solid (31 mg, 43%). M.Pt. 118–120 °C. (Found: $[M+H]^+$ 217.1224. $C_{14}H_{16}O_2$ (M) requires $[M+H]^+$ 217.1223); ν_{max}(neat)/cm^{-1} 3238, 2956, 2931, 2878, 1629, 1600, 1389, 1261, 1040, 838, 749; δ_H ($CDCl_3$) 1.82–1.87 (2H, m, CH_2), 1.95–2.07 (2H, m, CH_2), 3.78 (2H, t, *J* 6.2, CH_2O), 4.16 (2H, t, *J* 6.2, CH_2OH), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 25.8 (CH_2), 29.5 (CH_2), 62.7 (CH_2), 67.8 (CH_2), 106.7 (CH), 118.9 (CH), 123.7 (CH), 126.4 (CH), 126.8 (CH), 127.6 (CH), 129.0 (C), 129.4 (CH), 134.6 (C), 156.9 (C).

C. Reactions of substrates with Donor 3

Reaction of substrate 14e with Donor 3. 3,3′-(Propane-1,3-diyl)*bis*(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide **31**(336 mg, 0.6 mmol, 2.1 eq.) was dried under vacuum at 100 °C for 1 h, then cooled. Sodium hydride (60% in mineral oil, 0.24 g, 6.0 mmol, 20 eq.) was added, and the mixture was washed with dry hexane (3 × 20 mL). The hexane was removed *via* cannula and residual trace amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (15 mL) was then added, causing a yellow suspension to form, which was left to stir at room temperature under argon for 4 h. The yellow donor suspension was centrifuged at 2000 rpm for 10 min to afford the solution, which was added, *via* cannula, to 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **14e** (0.143 g, 0.29 mmol, 1.0 eq.) The reaction mixture was heated to 110 °C and left stirring under argon for 18 h. Water (50 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organics were then further washed with water (4 × 50 mL) and brine (50 mL). The organic extract was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography, eluting with 0–10% diethyl ether in petroleum ether, to afford 1-(3-(3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **30e**, (21 mg, 29%) as a colourless oil and (*p*-tolyloxy)propan-1-ol **16e**, (7 mg, 13%) as a colourless oil.

30e (Found: $[M+H]^+$ 267.3758. $C_{16}H_{26}O_3$ (M) requires $[M+H]^+$ 267.3758). ν_{max}(neat)/cm^{-1} 2941, 2867, 1613, 1512, 1243, 1111, 1084, 818; δ_H ($CDCl_3$) 1.17 (6H, s, 2 × CH_3), 2.31 (3H, s, CH_3), 3.21 (3H, s, OCH_3), 3.52 (2H, t, *J* 7.2, CH_2O), 3.59 (2H, t, *J* 7.2,

CH_2), 4.00 (2H, t, *J* 6.3, OCH_3), 6.81 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*). δ_C ($CDCl_3$) 20.4 (CH_3), 25.4 (CH_3), 29.7 (CH_2), 39.2 (CH_2), 49.2 (CH_3), 65.0 (CH_2), 67.2 (CH_2), 67.5 (CH_2), 73.8 (C), 114.3 (CH), 129.8 (CH), 130.0 (C), 156.9 (C).

16e (Found: $[M+NH_4]^+$ 184.2170. $C_{10}H_{14}O_2$ (M) requires $[M+NH_4]^+$ 184.2170) ν_{max}(neat)/cm^{-1} 3273, 2953, 2872, 1513, 1471, 827; δ_H ($CDCl_3$) 2.00–2.07 (2H, quintet, *J* 5.9, CH_2), 3.89 (2H, t, *J* 5.9, CH_2OH), 4.13 (2H, t, *J* 5.9, CH_2O), 6.83 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*). δ_C ($CDCl_3$) 20.0 (CH_3), 29.3 (CH_2), 37.3 (CH_2), 66.9 (CH_2), 114.0 (CH), 129.3 (CH), 142.4 (C), 156.4 (C).

Reaction of Substrate 14f with Donor 3. Similarly: 1-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-4-methylbenzene **14f** (135 mg, 0.33 mmol, 1.0 eq.) was reacted with the 3,3′-(propane-1,3-diyl)*bis*(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide **31** (336 mg, 0.6 mmol, 1.8 eq.) to afford 1-(4-(3-methoxy-3-methylbutoxy)butoxy)-4-methylbenzene **30f** as a colourless oil (22 mg, 24%) and 4-(*p*-tolyloxy)butan-1-ol **16f** as a colourless oil (7 mg, 8%).

30f: ν_{max}(neat)/cm^{-1} 2929, 2868, 1613, 1509, 1240, 1108, 812, 765; δ_H ($CDCl_3$) 1.21 (6H, s, 2 × CH_3), 1.77–1.88 (6H, m, 3 × CH_2), 2.30 (3H, s, CH_3), 3.21 (3H, s, OCH_3), 3.48–3.54 (4H, m, 2 × CH_2O), 3.99 (2H, t, *J* 6.4, OCH_2), 6.81 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*); δ_C ($CDCl_3$) 19.9 (CH_3), 24.9 (CH_3), 25.7 (CH_2), 25.9 (CH_2), 38.7 (CH_2), 48.7 (CH_3), 66.6 (CH_2), 67.2 (CH_2), 70.1 (CH_2), 73.3 (C) 113.9 (CH), 129.3 (CH), 129.4 (C), 156.4 (C).

16f: (Found: $[M+NH_4]^+$ 198.2435. $C_{11}H_{16}O_2$ (M) requires $[M+NH_4]^+$ 198.2435); ν_{max}(neat)/cm^{-1} 3273, 2953, 2872, 1513, 1471, 827; δ_H ($CDCl_3$) 2.00–2.07 (2H, quintet, *J* 5.9, CH_2), 3.89 (2H, t, *J* 5.9, CH_2OH), 4.13 (2H, t, *J* 5.9, CH_2O), 6.83 (2H, d, *J* 8.4, Ar*H*), 7.10 (2H, d, *J* 8.4, Ar*H*). δ_C ($CDCl_3$) 19.9 (CH_2), 25.4 (CH_2), 29.1 (CH_3), 62.1 (CH_2), 67.4 (CH_2), 113.9 (CH), 129.3 (C), 129.4 (CH).

Reaction of Substrate 14g with Donor 3. Similarly: 2-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-naphthalene **14g** (143 mg, 0.33 mmol, 1.0 eq.) was reacted with 3,3′-(propane-1,3-diyl)*bis*(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide **31** (336 mg, 0.6 mmol, 1.8 eq.) to afford 2-(3-(3-methoxy-3-methylbutoxy)propoxy)naphthalene **30g** as a colourless oil (32 mg, 29%) and 3-(naphthalen-2-yloxy)propan-1-ol **16g** as a white solid (8 mg, 15%).

30g (Found: $[M+H]^+$ 303.4079. $C_{19}H_{26}O_3$ (M) requires $[M+H]^+$ 303.4079); ν_{max}(neat)/cm^{-1} 2923, 2868, 1509, 1246, 1114, 815. δ_H ($CDCl_3$) 1.17 (6H, s, 2 × CH_3), 1.83 (2H, t, *J* 7.3, CH_2), 2.09–2.13 (2H, quintet, *J* 7.3, CH_2), 3.19 (3H, s, CH_3), 3.55 (2H, t, *J* 6.0, CH_2O), 3.64 (2H, t, *J* 6.0, CH_2O), 4.19 (2H, t, *J* 6.3, CH_2), 7.14–7.16 (2H, m, ArH), 7.34 (1H, t, *J* 6.0, ArH), 7.42 (1H, t, *J* 6.9, ArH), 7.71–7.78 (3H, m, ArH); δ_C ($CDCl_3$) 25.4 (CH_3), 29.8 (CH_2), 39.2 (CH_2), 49.2 (CH_3), 65.0 (CH_2), 67.2 (CH_2), 67.4 (CH_2), 73.8 (C), 106.7 (CH), 119.0 (CH), 123.5 (CH), 126.3 (CH), 126.7 (CH), 127.6 (CH), 128.9 (C), 129.3 (CH), 134.7 (C), 157.0 (C).

16g;[17] M.Pt. 99–100 °C. ν_{max}(neat)/cm^{-1} 3273, 2953, 2872, 1513, 1471, 827; δ_H ($CDCl_3$) 2.11–2.20 (2H, m, CH_2), 3.94 (2H, t, *J* 6.0 CH_2O), 4.27 (2H, t, *J* 6.0, CH_2OH), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 31.5 (CH_2), 60.1 (CH_2), 65.3 (CH_2), 106.2 (CH), 118.3 (CH), 123.2 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 128.5 (C), 128.9 (CH), 134.0 (C), 156.4 (C).

Reaction of Substrate 14h with Donor 3. Similarly: 2-(3-(4-iodo-3-methoxy-3-methylbutoxy)propoxy)-naphthalene **14h** (147 mg, 0.33 mmol, 1 eq.) was reacted with 3,3′-(propane-1,3-diyl)*bis*(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide **31** (336 mg, 0.6 mmol, 1.8 eq.) to afford 2-(4-(3-methoxy-3-methylbutoxy)butoxy)naphthalene **30h** (36 mg, 38%) as a colourless oil and 4-(naphthalen-2-yloxy)butan-1-ol **16h** (9 mg, 12%) as a white solid.

30h (Found: $[M+H]^+$ 317.2114. $C_{20}H_{28}O_3$ (M) requires $[M+H]^+$ 317.2111). ν_{max}(neat)/cm^{-1} 2926, 2856, 1629, 1601, 1465, 1217, 1118, 1084, 836; δ_H ($CDCl_3$) 1.20 (6H, s, 2 × CH_3), 1.82–1.98 (6H, m, 3 × CH_2), 3.21 (3H, s, OCH_3), 3.51–3.55 (4H, m, 2 × CH_2O), 4.16 (2H, t, *J* 6.2, CH_2OH) 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 24.9 (CH_3), 25.7 (CH_2), 26.0 (CH_2), 38.7 (CH_2), 48.7 (CH_2), 66.6 (CH_2), 67.3 (CH_2), 70.2 (CH_2), 73.2 (C), 106.0 (CH), 118.4 (CH), 123.0 (CH), 125.7 (CH), 126.1 (CH), 127.2 (CH), 128.4 (C), 128.8 (CH), 134.1 (C).

16h M.Pt. 118–120 °C. (Found: $[M+H]^+$ 217.1224. $C_{14}H_{16}O_2$ (M) requires $[M+H]^+$ 217.1223); ν_{max}(neat)/cm^{-1} 3238, 2956, 2931, 2878, 1629, 1600, 1389, 1261, 1040, 838, 749; δ_H ($CDCl_3$) 1.82–1.87 (2H, m, CH_2), 1.95–2.07 (2H, m, CH_2), 3.78 (2H, t, *J* 6.2, CH_2O), 4.16 (2H, t, *J* 6.2, CH_2OH), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 25.8 (CH_2), 29.5 (CH_2), 62.7 (CH_2), 67.8 (CH_2), 106.7 (CH), 118.9 (CH), 123.7 (CH), 126.4 (CH), 126.8 (CH), 127.6 (CH), 129.0 (C), 129.4 (CH), 134.6 (C), 156.9 (C).

D. Preparation and Reactions of Substrate 33

(*Z*)-4-(3-phenylpropoxy)-but-2-en-1-ol. (*Z*)-But-2-ene-1,4-diol (16.5 mL, 200 mmol, 1.1 eq) was added dropwise to a stirred suspension of sodium hydride (60% in mineral oil, 0.88 g, 22 mmol, 10 eq) in dry DMF (10 mL) at 0 °C and under argon. After 20 min, 1-bromo-3-phenylpropane (3.04 mL, 20 mmol, 1 eq) was added dropwise and the reaction was left to stir at 0 °C for 1 h and heated to 90 °C for 24 h. The reaction mixture was poured into water (30 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with water (2 × 100 mL), brine (100 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The crude product was purified using silica gel chromatography, eluting with diethyl ether/PE (1 : 1), to afford (*Z*)-4-(3-phenylpropoxy)-but-2-en-1-ol as a yellow oil (2.84 g, 68%);[1] ν_{max}(neat)/cm^{-1} 3393, 2931, 2861, 1454, 1102, 699; δ_H ($CDCl_3$) 1.93 (2H, m, CH_2), 2.70 (2H, t, *J* 7.9, CH_2Ar), 3.46 (2H, t, *J* 6.8, CH_3O), 4.05 (2H, t, *J* 6.6, CH_2O), 4.22 (2H, t, *J* 7.0, CH_2O), 5.71–5.75 (1H, m, C*H* = CH), 5.80–5.84 (1H, m, C*H* = CH), 7.24–7.27 (3H, m, ArH), 7.33–7.37 (2H, m, ArH); δ_C ($CDCl_3$) 31.3 (CH_2), 32.3 (CH_2), 58.8 (CH_2), 66.5 (CH_2), 69.9 (CH_2), 125.8 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 132.1 (CH), 141.8 (C). *m*/*z* (CI^+) 224 [(M+ NH_4)$^+$, 100%] 207 (95), 189 (50), 118 (30).

1-(3-((Z)-4-(2-iodophenoxy)but-2-enyloxy)propyl)benzene 33. To a stirred solution of (*Z*)-4-(3-phenylpropoxy)but-2-en-1-ol (1.50 g, 7.27 mmol, 1 eq), 2-iodophenol (1.92 g, 8.73 mmol, 1.2 eq) and triphenylphosphine (2.86 g, 10.91 mmol, 1.5 eq) in THF (20 mL) at 0 °C was added diisopropyl azodicarboxylate (2.16 mL, 10.91 mmol, 1.5eq) and the mixture was allowed to warm to rt overnight. After evaporation of the solvent under

reduced pressure, the remaining solid was dissolved in DCM (100 mL). The solution was sequentially washed with 2 N NaOH (3 × 75 mL), 2 N hydrochloric acid (75 mL), sat. aqueous $NaHCO_3$ (75 mL) and brine (75 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The crude product was purified using silica gel chromatography, eluting with a solvent system of 12% diethyl ether/PE to afford 1-(3-((Z)-4-(2-iodophenoxy)but-2-enyloxy)propyl)benzene **33** as a colourless oil (2.26 g, 76%). (Found: $[M+NH_4]^+$ 426.0920. $C_{19}H_{21}IO_2$ (M) requires $[M+NH_4]^+$ 409.0924); ν_{max}(neat)/cm^{-1} 3060, 3025, 2938, 2859, 1581, 1471, 1017, 747; δ_H ($CDCl_3$) 1.93 (2H, m, CH_2), 2.70 (2H, t, *J* 7.9, CH_2Ar), 3.47 (2H, t, *J* 6.8, CH_2O), 4.10 (2H, d, *J* 6.6, CH_2O), 4.70 (2H, t, *J* 6.9, CH_2O), 5.81–5.88 (1H, m, C*H* = CH), 5.89–5.91 (1H, m, C*H* = CH), 6.72 (1H, dt, *J* 1.3, 7.6, ArH) 6.82 (1H, dd, *J* 6.6, 1.0, ArH), 7.21–7.26 (3H, m, ArH), 7.33–7.37 (3H, m, ArH), 7.8 (1H, dd, *J* 6.2, 1.3, ArH); δ_C ($CDCl_3$) 31.3 (CH_2), 32.4 (CH_2), 65.4 (CH_2), 67.0 (CH_2), 69.9 (CH_2), 112.6 (CH), 122.8 (CH), 125.8 (CH), 127.3 (CH), 128.3 (CH), 128.5 (CH), 129.4 (CH), 130.3 (CH), 139.7 (CH), 141.9 (C), 157.2 (C).

Reaction of Substrate 33 with donor 3. 3,3′-(Propane-1,3-diyl)bis(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide (554 mg, 1.00 mmol, 1.6 eq.) was heated to 110 °C for 1 h under vacuum. Once cooled, sodium hydride (0.475 g, 11.88 mmol, 18 eq.) was added and the reaction mixture washed three times with dry hexane, and then DMF (15 mL) was added. The reaction mixture was left stirring at room temperature under argon for 4 h. The yellow donor suspension was centrifuged at 2000 rpm for 10 min. The yellow solution was added to 1-(3-((*Z*)-4-(2-iodophenoxy)but-2-enyloxy)propyl)benzene **33** (269 mg, 0.66 mmol, 1 eq.) *via* cannula. The reaction mixture was heated to 110 °C overnight. After cooling, the reaction mixture was poured into water (100 mL). The reaction mixture was extracted with diethyl ether (3 × 75 mL), and the organic layers were combined and washed with water (3 × 75 mL), brine (75 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified using column chromatography, eluting with a solvent system of 50 : 50 diethyl ether/PE to afford 3-(2-(3-phenylpropoxy)ethyl)-2,3-dihydrobenzofuran **36** and (*Z*)-(3-((4-phenoxybut-2-en-1-yl)oxy)propyl)benzene **38** as an inseparable mixture as a colourless oil (88 mg; the ratio of 5 : 2 is seen in the ^{1}H-NMR spectrum; since the products have the same MW, this would equate to 34% of **36** and 13% of **38**), and 3-phenylpropan-1-ol **16a** as a colourless oil (7 mg, 8%); (Found: $[M + H]^+$ 137.0883. $C_9H_{12}O$ (M) requires $[M + H]^+$ 137.0883); ν_{max}(neat)/cm^{-1} 3349, 3341, 3027, 2927, 2863, 1667, 1603, 1496, 1454; δ_H ($CDCl_3$) 1.89–1.95 (2H, m CH_2), 2.73 (2H, t, *J* 7.8, CH_2Ar), 3.69 (2H, t, *J* 6.4, CH_2OH), 7.18–7.22 (3H, m, Ar*H*), 7.28–7.31 (2H, m, Ar*H*); δ_C ($CDCl_3$) 32.1 (CH_2), 34.2 (CH_2), 62.3 (CH_2), 126.0 (CH), 128.4 (CH), 128.5 (CH), 141.8 (C).

Reaction of Substrate 33 with donor 4. 1,3-*Bis*-(*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide **32** (641 mg, 1.19 mmol, 1.8 eq.) was heated to 110 °C for 1 h under vacuum. Once cooled, sodium hydride (0.475 g, 11.88 mmol, 18 eq.) was added and the reaction mixture washed three times with dry hexane, then dried and DMF (15 mL) was added. The reaction mixture was left stirring at room temperature under argon for 4 h. The yellow donor suspension was centrifuged at 2000 rpm for 10 min. The yellow solution was added to 1-(3-((*Z*)-4-(2-iodo-phenoxy)but-2-enyloxy)propyl)benzene **33** (269 mg, 0.66 mmol, 1 eq.) *via* cannula. The reaction mixture was left stirring at rt overnight, under argon. After cooling, the reaction mixture was poured into water (100 mL). The reaction mixture was extracted with diethyl ether (3 × 75 mL), and the organic layers were combined and washed with water (3 × 75 mL), brine (75 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified using column chromatography, eluting with 50 : 50 diethyl ether/PE to afford (*Z*)-(3-((4-phenoxybut-2-en-1-yl)oxy)propyl)benzene **38** as a colourless oil (25 mg, 14%), and 3-phenylpropan-1-ol **16a** as a colourless oil (6 mg, 3%);

((Z)-(3-((4-phenoxybut-2-en-1-yl)oxy)propyl)benzene **38**. Found: $[M + H^+]$ 283.1688. $C_{19}H_{22}O_2$ (M) requires $[M + H^+]$ 283.1693); ν_{max}(neat)/cm^{-1} 3027, 2937, 2858, 1598, 1495, 1241, 1104, 752; δ_H ($CDCl_3$) 1.93 (2H, m, CH_2), 2.75 (2H, t, *J* 7.9, CH_2Ar), 3.40 (2H, t, *J* 6.8, CH_2O), 4.15 (1H, d, *J* 5.3, C*H* = CH), 4.60 (1H, d, *J* 6.4, C*H* = CH), 6.94–7.01 (3H, m, ArH), 7.22–7.24 (3H, m, ArH), 7.3–7.32 (4H, m, ArH); δ_C ($CDCl_3$) 30.8 (CH_2), 31.9 (CH_2), 63.5 (CH_2), 66.3 (CH_2), 69.3 (CH_2), 114.2 (CH), 120.4 (CH), 125.3 (CH), 127.4 (CH), 127.8 (CH), 128.0 (CH), 129.0 (CH), 129.6 (CH), 141.4 (C), 158 (C).

Phenylpropan-1-ol **16a**. Found: $[M + H]^+$ 137.0883. $C_9H_{12}O$ (M) requires $[M + H]^+$ 137.0883); ν_{max}(neat)/cm^{-1} 3349, 3341, 3027, 2927, 2863, 1667, 1603, 1496, 1454; δ_H ($CDCl_3$) 1.89–1.95 (2H, m CH_2), 2.73 (2H, t, *J* 7.8, CH_2Ar), 3.69 (2H, t, *J* 6.4, CH_2OH), 7.18–7.22 (3H, m, Ar*H*), 7.28–7.31 (2H, m, Ar*H*); δ_C ($CDCl_3$) 32.1 (CH_2), 34.2 (CH_2), 62.3 (CH_2), 126.0 (CH), 128.4 (CH), 128.5 (CH), 141.8 (C).

Test for E2 elimination with alkene 29h using Donor 4. 1,3-*Bis*-*N*,*N*-dimethyl-4-aminopyridinium)propane diiodide (641 g, 1.19 mmol, 1.8 eq.) was dried under vacuum at 100 °C for 1 h, then cooled. Sodium hydride (60% in mineral oil, 475 mg, 11.90 mmol, 18 eq.) was added, and the mixture was washed with dry hexane three times. The hexane was removed *via* cannula and residual trace amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (15 mL) was then added, causing a purple suspension to form, which was left to stir at room temperature under argon for 4 h. The purple donor suspension was centrifuged at 2000 rpm for 10 min to afford the solution, which was added, *via* cannula, to 2-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** (187 mg, 0.66 mmol, 1 eq.) The reaction mixture was left to stir at room temperature under argon overnight. Water (50 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organic layers were then further washed with water (4 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The ^{1}H NMR taken of the crude NMR indicated only starting material was present. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford the starting material, 2-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** as a colourless oil (154 mg, 82% recovery). (Found: $[M+NH_4]^+$ 302.1775. $C_{19}H_{24}O_2$ (M) requires $[M+NH_4]^+$ 302.1776); ν_{max}(neat)/cm^{-1} 2934, 2872, 1600, 1497, 1471, 754; δ_H ($CDCl_3$) 1.82 (3H, s, CH_3), 1.83–1.86 (2H, m, CH_2), 1.94–1.99 (2H, m, CH_2), 2.34 (2H, t, *J* 6.8, CH_2O), 3.54–3.60 (4H, m, 2 × CH_2O), 4.14 (2H, t, *J* 6.4, OCH_2), 4.77 (1H, m, *H*CH═C), 4.81 (1H, m, *H*CH═C), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*);

δ_C ($CDCl_3$) 22.2 (CH_3), 25.7 (CH_2), 25.9 (CH_2), 37.3 (CH_2), 67.2 (CH_2), 68.9 (CH_2), 70.0 (CH_2), 106.1 (CH), 110.9 (CH_2), 118.5 (CH), 123.0 (CH), 125.8 (CH), 126.2 (CH), 127.1 (CH), 128.4 (C), 128.8 (CH), 134.1 (C), 142.5 (C), 156.5 (C).

Test for E2 elimination with alkene 29h using Donor 3. 3,3′-(Propane-1,3-diyl)*bis*(1-methyl-1*H*-benzo[d]imidazol-3-ium) iodide (547 mg, 0.6 mmol, 1.8 eq.) was dried under vacuum at 100 °C for 1 h, then cooled. Sodium hydride (60% in mineral oil, 475 mg, 11.90 mmol, 18 eq.) was added, and the mixture was washed with dry hexane three times. The hexane was removed *via* cannula and residual trace amounts of hexane were removed using a flow of argon. Anhydrous *N*,*N*-dimethylformamide (15 mL) was then added, causing a purple suspension to form, which was left to stir at room temperature under argon for 4 h. The purple donor suspension was centrifuged at 2000 rpm for 10 min to afford the solution, which was added, *via* cannula, to 2-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** (187 mg, 0.66 mmol, 1 eq.) The reaction mixture was heated to 110 °C, under argon, for 18 h. Water (50 mL) was slowly added to quench the reaction mixture. The reaction mixture was washed with diethyl ether (3 × 50 mL). The combined organic layers were then further washed with water (4 × 50 mL), brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The ^{1}H NMR taken of the crude NMR indicated only starting material was present. The crude product was purified by silica gel chromatography, eluting with 0–5% diethyl ether in petroleum ether, to afford the starting material, 2-(4-((3-methylbut-3-en-1-yl)oxy)butoxy)naphthalene **29h** as a colourless oil (142 mg, 76% recovery). (Found: $[M+NH_4]^+$ 302.1775. $C_{19}H_{24}O_2$ (M) requires $[M+NH_4]^+$ 302.1776); ν_{max}(neat)/cm^{-1} 2934, 2872, 1600, 1497, 1471, 754; δ_H ($CDCl_3$) 1.82 (3H, s, CH_3), 1.83–1.86 (2H, m, CH_2), 1.94–1.99 (2H, m, CH_2), 2.34 (2H, t, *J* 6.8, CH_2O), 3.54–3.60 (4H, m, 2 × CH_2O), 4.14 (2H, t, *J* 6.4, OCH_2), 4.77 (1H, m, *H*CH═C), 4.81 (1H, m, *H*CH═C), 7.15–7.19 (2H, m, Ar*H*), 7.44 (1H, t, *J* 6.0, Ar*H*), 7.48 (1H, t, *J* 6.9, Ar*H*), 7.74–7.80 (3H, m, Ar*H*); δ_C ($CDCl_3$) 22.2 (CH_3), 25.7 (CH_2), 25.9 (CH_2), 37.3 (CH_2), 67.2 (CH_2), 68.9 (CH_2), 70.0 (CH_2), 106.1 (CH), 110.9 (CH_2), 118.5 (CH), 123.0 (CH), 125.8 (CH), 126.2 (CH), 127.1 (CH), 128.4 (C), 128.8 (CH), 134.1 (C), 142.5 (C), 156.5 (C).

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