Tetrahedron 70 (2014) 7380–7387

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Sustainable, mild and efficient *p*-methoxybenzyl ether deprotections utilizing catalytic DDQ

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 26 June 2014
Accepted 1 July 2014
Available online 5 July 2014

Dedicated to the memory of Professor Sandy McKillop, an outstanding organic chemist

Keywords:
Deprotection
Oxidation
Quinone

ABSTRACT

A procedure for the selective deprotection of *p*-methoxybenzyl ethers using catalytic amounts of DDQ and of sodium nitrite, with oxygen as the terminal oxidant, is reported.

1. Introduction

p-Methoxybenzyl (PMB) ethers are one of the most widely used hydroxyl protecting groups in synthetic organic chemistry, mainly owing to their stability, easy application and selective deprotection in the presence of unsubstituted benzyl ethers. They have been used in the synthesis of many natural products,[1,2] for example, discodermolide,[3] a marine natural product with antitumour activity currently in clinical trial. A variety of conditions can be employed to remove PMB ethers, including Brønsted or Lewis acids, such as triflic acid,[4] cerium(III) triflate and chloride,[5,6] silver(I) hexafluoroantimonate[7] and zirconium(IV) chloride.[8] In addition to acidic conditions, they can also be removed by hydrogenolysis[9] or oxidation.[10,11]

One of the most popular methods for deprotection of PMB ethers is oxidative deprotection using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[12,13] This widely used oxidant has been successfully employed in the synthesis of several natural products,[14] such as (+)-indicanone,[15] and operates by via single-electron transfer with formation of *p*-anisaldehyde as a by-product. However, the use of this oxidant in stoichiometric amounts results in large quantities of hydroquinone by-product that make purification difficult. In addition, DDQ is moderately expensive with a cost of $515/mol (at March 2014) and there are some toxicity concerns associated with its use; the compound has an LD_{50} of 82 mg/kg and can release HCN fumes on contact with water. However, this effective organic oxidant is widely used in organic synthesis as a result of its good selectivity, wide applicability and availability.

The use of catalytic DDQ alongside a benign terminal oxidant is a more efficient and sustainable alternative. Previous attempts at oxidations using catalytic quantities of DDQ can be found in the literature. However, these processes have resorted to using several equivalents of metal salts, such as $Mn(OAc)_3$,[16,17] MnO_2[18] and $FeCl_3$[19] in order to reoxidize the hydroquinone. However, there are examples where nitrite co-oxidants, such as *tert*-butyl nitrite[20] or sodium nitrite[21] are employed. These reagents are used in catalytic amounts to generate nitric oxide (NO) in situ, in the presence of acetic acid,[22,23] which is then oxidized to nitrogen dioxide. This species is able to reoxidize the hydroquinone, regenerating DDQ. Two examples are shown in Scheme 1.

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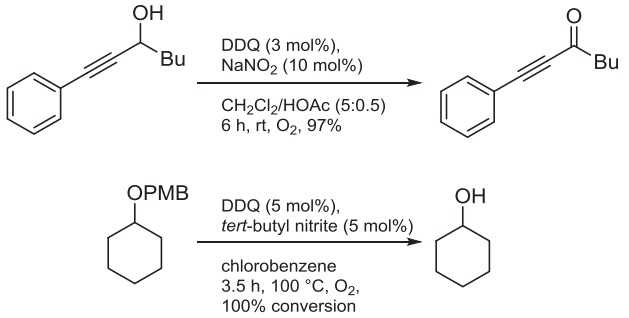
http://dx.doi.org/10.1016/j.tet.2014.07.003
0040-4020/



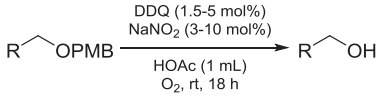
Scheme 1. Literature examples of sodium nitrite and *tert*-butyl nitrite for catalytic DDQ oxidations.

As a result we sought to optimize a procedure in which oxidative deprotection of PMB ethers could be successfully carried out under more 'green' and environmentally sustainable conditions, using catalytic DDQ, catalytic sodium nitrite and oxygen as the terminal oxidant.

2. Results and discussion

A selection of protected alcohols was synthesized and subjected to oxidative deprotection (Table 1). The reactions were found to work best with a 1 M solution of the substrate in acetic acid. Dilution of the mixture with a co-solvent resulted in longer reaction times. Upon completion the product could be extracted by two

Table 1
p-Methoxybenzyl ether deprotections using catalytic DDQ[a]



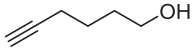
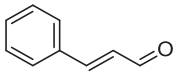
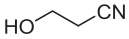
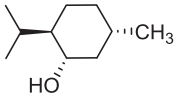
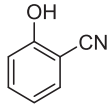
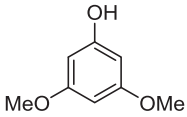
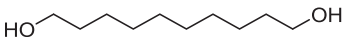
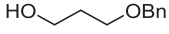
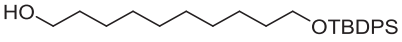
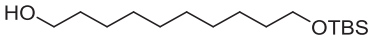
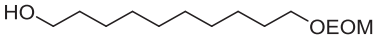
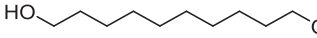
Entry	Product	DDQ/mol %	Yield/%
1		5	93[b]
2		2	77[c] (72)[d]
3		5	81[b]
4		5	86[b]
5		3.5	84[b]
6		1.5	91[c]
7		5	No reaction[e]
8		5	No reaction
9		2.5	87[b]
10		1.5	81[c](83)[d]
11		1.5	89[c]

Table 1 (*continued*)

Entry	Product	DDQ/mol %	Yield/%
12		1.5	90[c]
13		1.5	90[c,f]
14		1.5	92[e]

[a] Reaction conditions: PMB-protected alcohol (1 mmol), DDQ, $NaNO_2$ (2×DDQ mol %), HOAc, O_2, rt, 18 h.
[b] Crude product purified by flash chromatography.
[c] Crude product washed with $NaHSO_3$, no purification necessary.
[d] Yields in brackets correspond to those attained using flash chromatography as opposed to $NaHSO_3$ workup.
[e] Reaction time was 60 h.
[f] Reaction carried out on 0.35 mmol.

methods; flash chromatography or washing with saturated aqueous sodium bisulfite solution to remove the *p*-anisaldehyde by-product. Both methods of extraction worked equally well, although the ability to obtain the desired product without the need for flash chromatography is highly desirable and produces less waste. This often proved beneficial since some products were difficult to separate from the anisaldehyde by-product by chromatography. Catalyst loadings were also kept low for all examples, with most able to achieve complete conversion with just 1.5 mol % DDQ, somewhat lower catalyst loadings than previously reported uses of DDQ. It should be noted that the reactions perform best when carried out under oxygen atmosphere; significantly longer reaction times and reduced yields were observed when the reactions were carried out under air.

The results show that a variety of alcohols containing different functionality can be deprotected successfully. Surprisingly, when deprotecting cyclohex-2-enol (entry 3) the resulting allylic alcohol did not oxidize further to the ketone, as reported in a previous literature example when using manganese acetate to regenerate the DDQ.[16] However, with cinnamyl alcohol (entry 4) the product was immediately oxidized under the reaction conditions, generating cinnamaldehyde. Removal of *p*-methoxybenzyl protecting groups on phenols, both electron rich and electron deficient (entry 7 and 8), proved unsuccessful with recovery of the starting material. A small selection of alcohols containing additional orthogonal protecting groups was also subjected to the conditions. These include benzyl ether (entry 10), silyl ethers (entries 11 and 12), ethoxy methoxy (EOM) (entry 13) and an acetate ester (entry 14), all of which could be selectively deprotected in good yield.

3. Conclusion

An efficient, green and sustainable method for the deprotection of *p*-methoxybenzyl (PMB) ethers, using only catalytic amounts of DDQ has been developed. Good yields could be obtained with a variety of protected alcohols with low catalyst loadings. Chromatography to purify the product was unnecessary in most cases as reactions could be washed with saturated aqueous sodium bisulfite in order to remove the anisaldehyde by-product. Deprotections were also found to be selective against other alcohol protecting groups, such as benzyl ether, silyl ethers, EOM and an acetate ester.

4. Experimental section

4.1. General information

Commercially available compounds were purchased and used without purification unless otherwise stated. All anhydrous

solvents were used as supplied, except tetrahydrofuran and dichloromethane that were freshly distilled according to standard procedures, although drying of solvents was not necessary in the catalytic procedures listed. Reactions were routinely carried out under an atmosphere of argon unless otherwise noted and glassware was oven-dried before use. Light petroleum refers to the fraction with bp 40–60 °C. Ether refers to diethyl ether. Analytical thin layer chromatography was carried out on aluminium-backed plates coated with silica gel, and visualized under UV light at 254 and/or 360 nm and/or by chemical staining. Flash chromatography was carried out using silica gel, with the eluent specified. Infrared spectra were recorded using an FT-IR spectrometer over the range 4000–600 cm^{-1}. NMR spectra were recorded at 400 MHz (^1H frequency, 100 MHz ^{13}C frequency). Chemical shifts are quoted in parts per million (ppm), and are referenced to residual H in the deuterated solvent as the internal standard. Coupling constants, *J*, are quoted in hertz (Hz). In the ^{13}C NMR spectra, signals corresponding to CH, CH_2, or CH_3 groups are assigned from DEPT. Mass spectra were recorded on a time-of-flight mass spectrometer using electrospray ionization (ESI), or an EI magnetic sector instrument.

4.2. General procedure method A

To a microwave vial (35 mL) was added sodium hydride (60% in oil, 8–16 mmol) that was washed with pentane (30 mL) and suspended in THF (10–15 mL) before a solution of alcohol (7.5–10 mmol) in THF (2 mL) was added dropwise with stirring. The mixture was left to stir for 30 min at room temperature before 4-methoxybenzyl chloride (8–16 mmol) was added. The mixture was stirred at room temperature under an argon atmosphere for 20 h, then poured into saturated aqueous sodium hydrogen carbonate (40 mL), and extracted with ethyl acetate (2×30 mL). The organic extracts were washed with brine (40 mL) and dried over sodium sulfate before being concentrated under reduced pressure. Purification of the residue was carried out by flash chromatography.

4.3. General procedure method B

To a microwave vial containing alcohol (7.5–10 mmol) and diisopropylethylamine (9–12 mmol) was added 4-methoxybenzyl chloride (8–16 mmol), the vial sealed under an atmosphere of argon, and heated to 130–150 °C for 3 h. The mixture was poured into saturated aqueous sodium hydrogen carbonate (40 mL) and extracted with ethyl acetate (2×30 mL). The organic extracts were washed with brine (40 mL) and dried over sodium sulfate before being concentrated under reduced pressure. Purification of the residue was carried out by flash chromatography.

4.4. General procedure method C

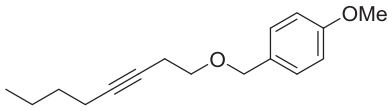
To a Reacti-vial (Thermo Scientific) containing the 4-methoxybenzyl protected alcohol (1 mmol) were added sodium nitrite (3–10 mol %), glacial acetic acid (1 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.5–5 mol %). The resulting mixture was stirred at room temperature under an atmosphere of oxygen for 18 h. The solution was then evaporated under reduced pressure and the residue purified by flash chromatography.

4.5. General procedure method D

To a Reacti-vial (Thermo Scientific) containing 4-methoxybenzyl protected alcohol (1 mmol) were added sodium nitrite (3–10 mol %), glacial acetic acid (1 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.5–5 mol %). The resulting mixture was stirred at room temperature under an atmosphere of oxygen for 18 h. The solution was then diluted with ethyl acetate (30 mL) and washed with saturated aqueous sodium bisulfite solution (3×20 mL), dried over magnesium sulfate and evaporated under reduced pressure.

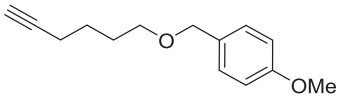
4.6. Preparation of PMB ethers

4.6.1. 1-Methoxy-4-(oct-3-yn-1-yloxy)methylbenzene.



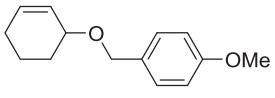
The title compound was synthesized following general procedure method A from 3-octyn-1-ol (1.08 mL, 7.5 mmol), sodium hydride (60% in oil, 335 mg, 8.25 mmol) and *p*-methoxybenzyl chloride (1.02 mL, 7.5 mmol) in THF (10 mL) at room temperature for 20 h. Purification by flash chromatography (0:1 to 1:19 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (651 mg, 35%). Found: $M+Na^+$, 269.1520. $C_{16}H_{22}O_2Na^+$ requires 269.1517; υ_{max} (ATR)/cm^{-1} 2999, 2932, 2860, 2062, 1613, 1513; δ_H (400 MHz; $CDCl_3$) 7.30 (2H, d, *J* 8.8 Hz, ArH), 6.90 (2H, d, *J* 8.8 Hz, ArH), 4.51 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.56 (2H, t, *J* 7.2 Hz, CH_2), 2.48 (2H, tt, *J* 7.0, 2.4 Hz, CH_2), 2.17 (2H, tt, *J* 7.2, 2.4 Hz, CH_2), 1.51–1.39 (4H, m, CH_2), 0.93 (3H, t, *J* 7.2 Hz, CH_3); δ_C (100 MHz; $CDCl_3$) 159.2 (C), 130.4 (C), 129.3 (CH), 113.4 (CH), 81.4 (C), 76.6 (C), 72.6 (CH_2), 68.7 (CH_2), 55.3 (CH_3), 31.1 (CH_2), 21.9 (CH_2), 20.2 (CH_2), 18.5 (CH_2), 13.6 (CH_3).

4.6.2. 1-(Hex-5-yn-1-yloxy)methyl-4-methoxybenzene.



The title compound was synthesized following general procedure method A from 5-hexyn-1-ol (827 μL, 7.5 mmol), sodium hydride (60% in oil, 609 mg, 15 mmol) and *p*-methoxybenzyl chloride (1017 μL, 7.5 mmol) in THF (10 mL) at room temperature for 20 h. Purification by flash chromatography (0:1 to 1:19 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (651 mg, 35%). Found: $M+Na^+$, 241.1183. $C_{14}H_{18}O_2Na^+$ requires 241.1204; ν_{max} (ATR)/cm^{-1} 3294, 2939, 2862, 2116, 1613, 1513; δ_H (400 MHz; $CDCl_3$) 7.28 (2H, d, *J* 8.8 Hz, ArH), 6.90 (2H, d, *J* 8.8 Hz, ArH), 4.45 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.49 (2H, t, *J* 6.2 Hz, CH_2), 2.23 (2H, td, *J* 6.9, 2.6 Hz, CH_2), 1.97 (1H, t, *J* 2.6 Hz, CH), 1.79–1.72 (2H, m, CH_2), 1.68–1.61 (2H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.7 (C), 129.2 (CH), 113.8 (CH), 84.8 (C), 72.5 (CH_2), 69.4 (CH_2), 68.4 (CH), 55.3 (CH_3), 28.7 (CH_2), 25.3 (CH_2), 18.2 (CH_2). Data recorded match literature.[24]

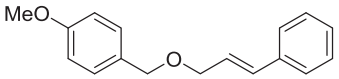
4.6.3. 1-(Cyclohex-2-en-1-yloxy)methyl-4-methoxybenzene.



The title compound was synthesized following general procedure method A using cyclohex-2-enol (736 μL, 7.5 mmol), sodium hydride (60% in oil, 335 mg, 8.25 mmol) and *p*-methoxybenzyl chloride (1.02 mL, 7.5 mmol) in THF (10 mL) at room temperature for 20 h. Purification by flash chromatography (0:1 to 1:19 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (296 mg, 18%). Found: $M+Na^+$, 241.1195. $C_{14}H_{18}O_2Na^+$ requires 241.1204; υ_{max} (ATR)/cm^{-1} 3008, 2939, 2838, 1612, 1586, 1513; δ_H (400 MHz; $CDCl_3$) 7.31 (2H, d, *J* 8.7 Hz, ArH), 6.90 (2H, d, *J* 8.7 Hz, ArH), 5.89 (1H, dtd, *J* 10.1, 3.5, 1.3 Hz, CH), 5.84–5.80 (1H, m, CH),

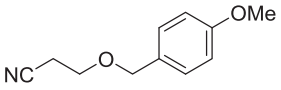
4.57 (1H, d, *J* 11.5 Hz, CH_2), 4.51 (1H, d, *J* 11.5 Hz, CH_2), 3.96 (1H, br s, CH), 3.83 (3H, s, OCH_3), 2.12–2.05 (1H, m, CH_2), 2.01–1.95 (1H, m, CH_2), 1.89–1.72 (3H, m, CH_2), 1.62–1.55 (1H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 131.2 (C), 130.8 (CH), 129.2 (CH), 127.9 (CH), 113.8 (CH), 71.9 (CH), 69.7 (CH_2), 55.3 (CH_3), 28.4 (CH_2), 25.3 (CH_2), 19.3 (CH_2). Data recorded match literature.[25]

4.6.4. 1-(Cinnamyloxy)methyl-4-methoxybenzene.



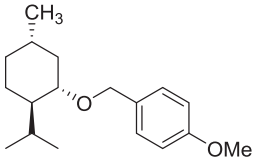
The title compound was synthesized following general procedure method A from cinnamyl alcohol (967 μL, 7.5 mmol), sodium hydride (60% in oil, 609 mg, 15 mmol) and 4-methoxybenzyl chloride (1.02 μL, 7.5 mmol) in THF (10 mL) at room temperature for 20 h. Purification by flash chromatography (0:1 to 1:9 ethyl acetate/light petroleum) gave the *title compound* as a yellow oil (869 mg, 46%). Found: $M+Na^+$, 277.1183. $C_{17}H_{18}O_2Na^+$ requires 277.1204; υ_{max} (ATR)/cm^{-1} 3027, 2836, 1612, 1586, 1513, 1450; δ_H (400 MHz; $CDCl_3$) 7.44–7.41 (2H, m, ArH), 7.37–7.32 (4H, m, ArH), 7.29–7.25 (1H, m, ArH), 6.93 (2H, d, *J* 8.7 Hz, ArH), 6.65 (1H, d, *J* 15.9 Hz, CH), 6.36 (1H, dt, *J* 15.9, 6.1 Hz, CH), 4.54 (2H, s, CH_2), 4.20 (2H, d, *J* 6.1 Hz, CH_2), 3.83 (3H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.3 (C), 136.8 (C), 132.5 (CH), 130.4 (C), 129.5 (CH), 128.6 (CH), 127.7 (CH), 126.5 (CH), 126.2 (CH), 113.8 (CH), 71.9 (CH_2), 70.5 (CH_2), 55.3 (CH_3). Data recorded match literature.[26]

4.6.5. 3-(4-Methoxybenzyloxy)propanenitrile.



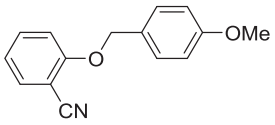
The title compound was synthesized following general procedure method B from 3-hydroxypropanenitrile (684 μL, 10 mmol), 4-methoxybenzyl chloride (1.36 mL, 10 mmol) and diisopropylethylamine (2.10 mL, 12 mmol) at 130 °C for 3 h. Purification by flash chromatography (0:1 to 1:19 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (891 mg, 47%). Found: $M+Na^+$, 214.0845. $C_{11}H_{13}NO_2Na^+$ requires 214.0844; υ_{max} (ATR)/cm^{-1} 3003, 2936, 2872, 2251, 1613, 1585; δ_H (400 MHz; $CDCl_3$) 7.30 (2H, d, *J* 8.8 Hz, ArH), 6.92 (2H, d, *J* 8.8 Hz, ArH), 4.54 (2H, s, CH_2), 3.83 (3H, s, CH_3), 3.68 (2H, t, *J* 6.4 Hz, CH_2), 2.62 (2H, t, *J* 6.4 Hz, CH_2); δ_C (100 MHz; $CDCl_3$) 159.5 (C), 129.4 (CH), 129.3 (C), 117.8 (C), 114.0 (CH), 73.0 (CH_2), 64.3 (CH_2), 55.3 (CH_3), 18.9 (CH_2).

4.6.6. 1-((1S,2R,5S)-2-Isopropyl-5-methylcyclohexyloxy)methyl-4-methoxybenzene.



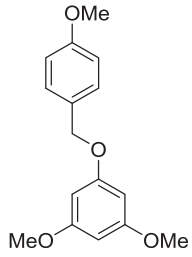
The title compound was synthesized following general procedure method B from (1*S*,2*R*,5*S*)-menthol (1.17 g, 10 mmol), 4-methoxybenzyl chloride (1.02 mL, 10 mmol), sodium iodide (112 mg, 10 mol %) and diisopropylethylamine (2.10 mL, 12 mmol) at 140 °C for 3 h. Purification by flash chromatography (1:99 to 1:49 ethyl acetate/light petroleum) gave the *title compound* as a colourless oil (366 mg, 18%). Found: $M+Na^+$, 299.1964. $C_{18}H_{28}O_2Na^+$ requires 299.1987; υ_{max} (ATR)/cm^{-1} 2953, 2922, 2868, 1613, 1586, 1513; δ_H (400 MHz; $CDCl_3$) 7.29 (2H, d, *J* 8.8 Hz, ArH), 6.89 (2H, d, *J* 8.8 Hz, ArH), 4.61 (1H, d, *J* 11.1 Hz, CH_2), 4.35 (1H, d, *J* 11.1 Hz, CH_2), 3.82 (3H, s, OCH_3), 3.17 (1H, td, *J* 10.4, 4.3 Hz, CH), 2.34–2.29 (1H, m, CH), 2.21 (1H, d, *J* 11.9 Hz, CH), 1.70–1.63 (2H, m, CH_2), 1.41–1.26 (2H, m, CH_2), 1.03–0.83 (3H, m, CH, CH_2), 0.96 (3H, d, *J* 6.7 Hz, CH_3), 0.91 (3H, d, *J* 7.3 Hz, CH_3), 0.73 (3H, d, *J* 6.9 Hz, CH_3); δ_C (100 MHz; $CDCl_3$) 159.0 (C), 131.3 (C), 129.4 (CH), 113.7 (CH), 78.4 (CH), 70.1 (CH_2), 55.3 (CH_3), 48.3 (CH), 40.3 (CH_2), 34.6 (CH_2), 31.6 (CH), 25.5 (CH), 23.3 (CH_2), 22.4 (CH_3), 21.0 (CH_3), 16.1 (CH_3).

4.6.7. 2-(4-Methoxybenzyloxy)benzonitrile.



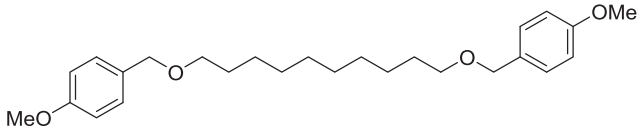
The title compound was synthesized following general procedure method B from 2-hydroxybenzonitrile (1.19 g, 10 mmol), 4-methoxybenzyl chloride (1.02 mL, 10 mmol), sodium iodide (112 mg, 10 mol %) and diisopropylethylamine (2.10 mL, 12 mmol) at 140 °C for 3 h. Purification by flash chromatography (2:3 ethyl acetate/light petroleum) gave the *title compound* as a colourless solid (442 mg, 17%). Found: $M+Na^+$, 262.0817. $C_{15}H_{13}NO_2Na^+$ requires 262.0844; υ_{max} (ATR)/cm^{-1} 3007, 2937, 2839, 2231, 1613, 1599; δ_H (400 MHz; $CDCl_3$) 7.60 (1H, dd, *J* 7.5, 1.6 Hz, ArH), 7.52 (1H, ddd, *J* 8.3, 7.5, 1.6 Hz, ArH), 7.41 (2H, d, *J* 8.7 Hz, ArH), 7.05–7.01 (2H, m, ArH), 6.95 (2H, d, *J* 8.7 Hz, ArH), 5.18 (2H, s, CH_2), 3.85 (3H, s, OCH_3); δ_C (100 MHz; $CDCl_3$) 160.4 (C), 159.6 (C), 134.2 (CH), 133.9 (CH), 128.8 (CH), 127.7 (C), 121.0 (CH), 116.5 (C), 114.1 (CH), 113.1 (CH), 102.5 (C), 70.5 (CH_2), 55.3 (CH_3). Data recorded match literature.[27]

4.6.8. 1,3-Dimethoxy-5-(4-methoxybenzyloxy)benzene.



To a flask containing caesium carbonate (4.89 g, 15 mmol) in dimethylformamide (20 mL) were added 3,5-dimethoxyphenol (2.31 g, 15 mmol) and *p*-methoxybenzyl chloride (1.36 mL, 10 mmol) and the mixture stirred at 20 °C for 24 h. The mixture was diluted with ethyl acetate (40 mL) and washed with lithium chloride (5%; 3×40 mL) and brine (40 mL) before being dried over magnesium sulfate and evaporated under reduced pressure to give the crude product as a yellow oil. Purification by flash chromatography (1:4 ethyl acetate/light petroleum) gave the *title compound* as a colourless solid (971 mg, 35%). Found: $M+Na^+$, 297.1085. $C_{16}H_{18}O_4Na^+$ requires 297.1103; υ_{max} ($CHCl_3$)/cm^{-1} 3010, 2961, 2840, 1602, 1515, 1463; δ_H (400 MHz; $CDCl_3$) 7.38 (2H, d, *J* 8.6 Hz, ArH), 6.94 (2H, d, *J* 8.6 Hz, ArH), 6.20 (2H, d, *J* 2.2 Hz, ArH), 6.13 (1H, t, *J* 2.2 Hz, ArH), 4.97 (2H, s, CH_2), 3.84 (3H, s, OCH_3), 3.79 (6H, s, OCH_3); δ_C (100 MHz; $CDCl_3$) 161.5 (C), 160.8 (C), 159.5 (C), 129.4 (CH), 129.0 (C), 114.0 (CH), 93.8 (CH), 93.2 (CH), 69.9 (CH_2), 55.3 (CH_3), 55.3 (CH_3).

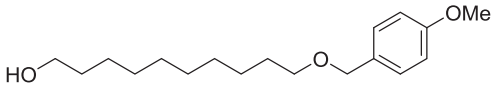
4.6.9. 1,10-Bis(4-methoxybenzyloxy)decane.



The title compound was synthesized following general procedure method B from 1,10-decandiol (8.71 g, 50 mmol), 4-

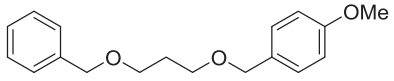
methoxybenzyl chloride (6.78 mL, 50 mmol) and diisopropylethylamine (10.5 mL, 60 mmol) at 140 °C for 3 h. Purification by flash chromatography (0:1 to 1:1 diethyl ether/light petroleum) gave the *title compound* as a colourless crystalline solid (4.48 g, 30%); mp 41–43 °C. Found: M+Na$^+$, 437.2667. $C_{26}H_{38}O_4Na^+$ requires 437.2668; υ_{max} (ATR)/cm^{-1} 3007, 2934, 2857, 1612, 1586, 1513; δ_H (400 MHz; $CDCl_3$) 7.29 (4H, d, *J* 8.8 Hz, ArH), 6.91 (4H, d, *J* 8.8 Hz, ArH), 4.46 (4H, s, CH_2), 3.83 (6H, s, OCH_3), 3.46 (4H, t, *J* 6.7 Hz, CH_2), 1.66–1.58 (4H, m, CH_2), 1.39–1.27 (12H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.9 (C), 129.5 (CH), 113.8 (CH), 72.5 (CH_2), 70.3 (CH_2), 55.3 (CH_3), 29.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 26.2 (CH_2).

4.6.10. 10-(4-Methoxybenzyloxy)decan-1-ol.



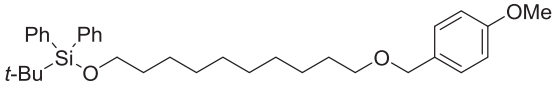
The title compound was synthesized following general procedure method B from 1,10-decandiol (8.71 g, 50 mmol), 4-methoxybenzyl chloride (6.78 mL, 50 mmol) and diisopropylethylamine (10.5 mL, 60 mmol) at 140 °C for 3 h. Purification by flash chromatography (0:1 to 1:1 diethyl ether/light petroleum) gave the *title compound* as a colourless crystalline solid (4.48 g, 30%); mp 44–45 °C. Found: M+Na$^+$, 317.2093. $C_{18}H_{30}O_3Na^+$ requires 317.2093; υ_{max} (ATR)/cm^{-1} 3623, 3009, 2932, 2857, 1612, 1586; δ_H (400 MHz; $CDCl_3$) 7.28 (2H, d, *J* 8.8 Hz, ArH), 6.90 (2H, d, *J* 8.8 Hz, ArH), 4.45 (2H, s, CH_2), 3.82 (3H, s, OCH_3), 3.65 (2H, t, *J* 6.7 Hz, CH_2), 3.45 (2H, t, *J* 6.7 Hz, CH_2), 1.65–1.54 (4H, m, CH_2), 1.50 (1H, s, OH), 1.38–1.27 (12H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.8 (C), 129.2 (CH), 113.7 (CH), 72.5 (CH_2), 70.2 (CH_2), 63.1 (CH_2), 55.3 (CH_3), 30.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 25.7 (CH_2).

4.6.11. 1-Methoxy-4-((3-benzyloxypropoxy)methyl)-benzene.



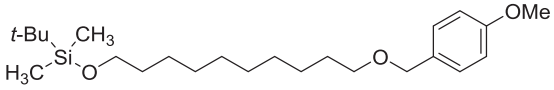
The title compound was synthesized following general procedure method A from 3-benzyloxy-1-propanol (1.19 mL, 7.5 mmol), sodium hydride (60% in oil, 335 mg, 8.25 mmol) and 4-methoxybenzyl chloride (1.02 mL, 7.5 mmol) in THF (10 mL) at room temperature for 20 h. Purification by flash chromatography (0:1 to 1:9 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (1.21 g, 57%). Found: M+Na$^+$, 309.1460. $C_{18}H_{22}O_3Na^+$ requires 309.1467; υ_{max} (ATR)/cm^{-1} 3031, 2858, 1612, 1586, 1513, 1454; δ_H (400 MHz; $CDCl_3$) 7.39–7.30 (5H, m, ArH), 7.27 (2H, d, *J* 8.7 Hz, ArH), 6.90 (2H, d, *J* 8.7 Hz, ArH), 4.53 (2H, s, CH_2), 4.46 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.61 (2H, t, *J* 6.4 Hz, CH_2), 3.59 (2H, t, *J* 6.4 Hz, CH_2), 1.95 (2H, pentet, *J* 6.4 Hz, CH_2); δ_C (100 MHz; $CDCl_3$) 159.2 (C), 138.6 (C), 130.7 (C), 129.3 (CH), 128.4 (CH), 127.7 (CH), 127.5 (CH), 113.8 (CH), 73.0 (CH_2), 72.7 (CH_2), 67.4 (CH_2), 67.0 (CH_2), 55.3 (CH_3), 30.2 (CH_2).

4.6.12. tert-Butyl(10-(4-methoxybenzyloxy)decyloxy) diphenylsilane.



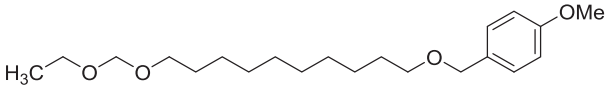
To a flask containing 10-((4-methoxybenzyl)oxy)decan-1-ol (900 mg, 3.06 mmol) and imidazole (230 mg, 3.37 mmol) in dichloromethane (10 mL) was added *tert*-butyldiphenylsilyl chloride (875 μL, 3.37 mmol) and the solution stirred under argon for 20 h at room temperature. The mixture was poured in water (40 mL) and extracted with ethyl acetate (2×30 mL). The organic extracts were washed with brine (40 mL) and dried over magnesium sulfate before being evaporated under reduced pressure. The crude product was purified by elution through a pad of silica to give the *title compound* as a colourless oil (1.58 g, 96%). Found: M+Na$^+$, 555.3259. $C_{34}H_{48}O_3SiNa^+$ requires 555.3270; υ_{max} (ATR)/cm^{-1} 3072, 3008, 2933, 2857, 1612, 1587; δ_H (400 MHz; $CDCl_3$) 7.71–7.69 (4H, m, ArH), 7.48–7.39 (6H, m, ArH), 7.29 (2H, d, *J* 8.8 Hz, ArH), 6.92 (2H, d, *J* 8.8 Hz, ArH), 4.48 (2H, s, CH_2), 3.84 (3H, s, OCH_3), 3.70 (2H, t, *J* 6.6 Hz, CH_2), 3.48 (2H, t, *J* 6.6 Hz, CH_2), 1.66–1.57 (4H, m, CH_2), 1.42–1.27 (12H, m, CH_2), 1.10 (9H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 135.6 (CH), 134.2 (C), 130.9 (C), 129.5 (CH), 129.2 (CH), 127.5 (CH), 113.8 (CH), 72.5 (CH_2), 70.3 (CH_2), 64.0 (CH_2), 55.3 (CH_3), 32.6 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.9 (CH_3), 26.3 (CH_2), 25.8 (CH_2), 19.3 (C).

4.6.13. tert-Butyl(10-(4-methoxybenzyloxy)decyloxy) dimethylsilane.



To a flask containing 10-(4-methoxybenzyloxy)decan-1-ol (900 mg, 3.06 mmol) and imidazole (230 mg, 3.37 mmol) in dichloromethane (10 mL) was added *tert*-butyldimethylsilyl chloride (866 μL, 3.37 mmol) and the solution stirred under argon for 20 h at room temperature. The mixture was poured in water (40 mL) and extracted with ethyl acetate (2×30 mL). The organic extracts were washed with brine (40 mL) and dried over magnesium sulfate before being evaporated under reduced pressure. The crude product was purified by elution through a pad of silica to give the *title compound* as a colourless oil (1.07 g, 86%). Found: M+Na$^+$, 431.2941. $C_{24}H_{44}O_2SiNa^+$ requires 431.2957; υ_{max} (ATR)/cm^{-1} 2929, 2855, 1613, 1586, 1513, 1463; δ_H (400 MHz; $CDCl_3$) 7.29 (2H, d, *J* 8.7 Hz, ArH), 6.90 (2H, d, *J* 8.7 Hz, ArH), 4.45 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.62 (2H, t, *J* 6.6 Hz, CH_2), 3.45 (2H, t, *J* 6.6 Hz, CH_2), 1.63–1.58 (2H, m, CH_2), 1.54–1.51 (2H, m, CH_2), 1.38–1.27 (12H, m, CH_2), 0.92 (9H, s, CH_3), 0.07 (6H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.8 (C), 129.2 (CH), 113.7 (CH), 72.5 (CH_2), 70.2 (CH_2), 63.6 (CH_2), 55.3 (CH_3), 32.9 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 26.0 (CH_3), 25.8 (CH_2), 18.4 (C), −5.3 (CH_3).

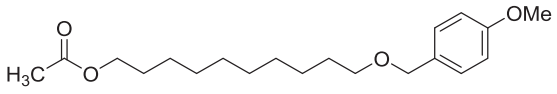
4.6.14. 1-(10-(Ethoxymethoxydecyloxy)methyl)-4-methoxybenzene.



To a flask containing a suspension of sodium hydride (60% in oil, 160 mg, 4 mmol) in tetrahydrofuran (5 mL) was added 10-(4-methoxybenzyloxy)decan-1-ol (588 mg, 2 mmol) in tetrahydrofuran (3 mL) and the resulting mixture stirred for 30 min. Chloromethyl ethylether (372 μL, 4 mmol) was added dropwise before stirring continued for 24 h at room temperature. The mixture was quenched with aqueous ammonium hydroxide (35%; 30 mL) and extracted into ethyl acetate (2×20 mL). The organic layers were combined and washed with brine (30 mL) before being dried over magnesium sulfate and concentrated under reduced pressure to give the crude product as a yellow oil. Purification by flash chromatography (3:17 ethyl acetate/light petroleum) gave the *title compound* as a colourless oil (141 mg, 20%). Found: M+Na$^+$, 375.2510. $C_{21}H_{36}O_4Na^+$ requires 375.2511; υ_{max} (ATR)/cm^{-1} 2933, 2857, 1612, 1513, 1465, 1363; δ_H (400 MHz; $CDCl_3$) 7.28 (2H, d, *J* 8.7 Hz, ArH), 6.90 (2H, d, *J* 8.7 Hz, ArH), 4.69 (2H, s, CH_2), 4.45 (2H, s, CH_2), 3.83 (3H, s, OCH_3), 3.62 (2H, q, *J* 7.0 Hz, CH_2), 3.55 (2H, t, *J*

6.6 Hz, CH_2), 3.45 (2H, t, *J* 6.6 Hz, CH_2), 1.65–1.56 (4H, m, CH_2), 1.40–1.28 (12H, m, CH_2), 1.24 (3H, t, *J* 7.0 Hz, CH_3); δ_C (100 MHz; $CDCl_3$) 159.1 (C), 130.8 (C), 129.2 (CH), 113.7 (CH), 95.1 (CH_2), 72.5 (CH_2), 70.2 (CH_2), 67.9 (CH_2), 63.1 (CH_2), 55.3 (CH_3), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 15.2 (CH_3); 2×CH_2s not observed.

4.6.15. 10-(4-Methoxybenzyloxy)decyl acetate.



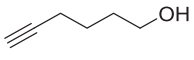
To a flask containing 10-(4-methoxybenzyloxy)decan-1-ol (588 mg, 2 mmol) in pyridine (5 mL) was added acetic anhydride (373 μL, 4 mmol) and the resulting solution stirred for 36 h at room temperature. The mixture was quenched with aqueous hydrochloric acid (1 M; 30 mL) and extracted into ethyl acetate (2×20 mL). The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (30 mL), followed by further aqueous hydrochloric acid (1 M; 30 mL), before being dried over magnesium sulfate and concentrated under reduced pressure to give the crude product as a yellow oil. Purification by flash chromatography (1:4 ethyl acetate/light petroleum) gave the *title compound* as a colourless oil (322 mg, 48%). Found: $M+Na^+$, 359.2194. $C_{20}H_{32}O_4Na^+$ requires 359.2198; υ_{max} (ATR)/cm^{-1} 2933, 2857, 1728, 1612, 1513, 1465; δ_H (400 MHz; $CDCl_3$) 7.29 (2H, d, *J* 8.7 Hz, ArH), 6.90 (2H, d, *J* 8.7 Hz, ArH), 4.45 (2H, s, CH_2), 4.07 (2H, t, *J* 6.9 Hz, CH_2), 3.83 (3H, s, OCH_3), 3.45 (2H, t, *J* 6.7 Hz, CH_2), 2.07 (3H, s, CH_3), 1.65–1.58 (4H, m, CH_2), 1.40–1.27 (12H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 171.3 (CHO), 159.1 (C), 130.8 (C), 129.2 (CH), 113.7 (CH), 72.5 (CH_2), 70.2 (CH_2), 64.7 (CH_2), 55.3 (CH_3), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 26.2 (CH_2), 25.9 (CH_2), 21.0 (CH_3).

4.7. Deprotection reactions

4.7.1. 3-Octyn-1-ol.

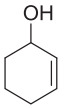
The title compound was synthesized following general procedure method C from 1-methoxy-4-(oct-3-yn-1-yloxy)methylbenzene (246 mg, 1 mmol), sodium nitrite (7 mg, 10 mol %), glacial acetic acid (1 mL) and DDQ (11 mg, 5 mol %). Purification by flash chromatography (0:1 to 1:4 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (117 mg, 93%). Found: $M+Na^+$, 149.0929. $C_8H_{14}ONa^+$ requires 149.0942; υ_{max} (ATR)/cm^{-1} 3550–3200, 2873, 2230, 2071, 1744, 1725; δ_H (400 MHz; $CDCl_3$) 3.69 (2H, t, *J* 6.2 Hz, CH_2), 2.45 (2H, tt, *J* 6.2, 2.4 Hz, CH_2), 2.19 (2H, tt, *J* 7.0, 2.4 Hz, CH_2), 1.84 (1H, br s, OH), 1.53–1.38 (4H, m, CH_2), 0.93 (3H, t, *J* 7.0 Hz, CH_3); δ_C (100 MHz; $CDCl_3$) 82.7 (C), 76.2 (C), 61.4 (CH_2), 31.1 (CH_2), 23.2 (CH_2), 22.0 (CH_2), 18.4 (CH_2), 13.6 (CH_3).

4.7.2. 5-Hexyn-1-ol.



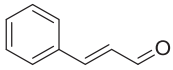
The title compound was synthesized following general procedure method C from 1-(hex-5-yn-1-yloxy)methyl-4-methoxybenzene (218 mg, 1 mmol), sodium nitrite (3 mg, 4 mol %), glacial acetic acid (1 mL) and DDQ (5 mg, 2 mol %) gave the *title compound* as a colourless oil (71 mg, 72%); υ_{max} (ATR)/cm^{-1} 3550–3200, 2943, 2116, 1434, 1062, 990; δ_H (400 MHz; $CDCl_3$) 3.70 (2H, t, *J* 6.3 Hz, CH_2), 2.26 (2H, td, *J* 6.8, 2.7 Hz, CH_2), 1.98 (1H, t, *J* 2.7 Hz, CH), 1.75–1.60 (4H, m, CH_2), 1.52 (1H, s, OH); δ_C (100 MHz; $CDCl_3$) 84.3 (C), 68.5 (CH), 62.4 (CH_2), 31.7 (CH_2), 24.7 (CH_2), 18.2 (CH_2). Data recorded match literature.[28]

4.7.3. Cyclohex-2-enol.



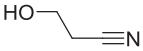
The title compound was synthesized following general procedure method C from 1-(cyclohex-2-en-1-yloxy)methyl-4-methoxybenzene (218 mg, 1 mmol), sodium nitrite (7 mg, 10 mol %), glacial acetic acid (1 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (11 mg, 5 mol %). Purification by flash chromatography (0:1 to 1:9 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (79 mg, 81%); υ_{max} (ATR)/cm^{-1} 3550–3200, 3024, 2936, 1650, 1435, 1286; δ_H (400 MHz; $CDCl_3$) 5.85 (1H, dtd, *J* 10.0, 3.7, 1.0 Hz, CH), 5.77 (1H, ddd, *J* 10.0, 4.8, 1.9 Hz, CH), 4.21 (1H, br s, CH), 2.10–1.84 (3H, m, CH_2), 1.80–1.55 (4H, m, CH_2); OH not observed; δ_C (100 MHz; $CDCl_3$) 130.6 (CH), 129.9 (CH), 65.5 (CH), 32.0 (CH_2), 25.0 (CH_2), 18.9 (CH_2). Data recorded match literature.[29]

4.7.4. Cinnamaldehyde.



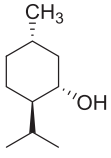
The title compound was synthesized following general procedure method C from 1-(cinnamyloxy)methyl-4-methoxybenzene (254 mg, 1 mmol), sodium nitrite (7 mg, 10 mol %), glacial acetic acid (1 mL) and DDQ (11 mg, 5 mol %). Purification by flash chromatography (10–20% ethyl acetate/light petroleum) gave the *title compound* as a colourless oil (113 mg, 86%); δ_H (400 MHz; $CDCl_3$) 9.75 (1H, d, *J* 7.8 Hz, CHO), 7.62–7.59 (2H, m, ArH), 7.52 (1H, d, *J* 15.9 Hz, CH), 7.49–7.45 (3H, m, ArH), 6.76 (1H, dd, *J* 15.9, 7.8 Hz, CH); δ_C (100 MHz; $CDCl_3$) 193.7 (CHO), 152.8 (CH), 134.0 (C), 131.3 (CH), 129.1 (CH), 128.5 (CH), 128.3 (CH). Data recorded match literature.[30]

4.7.5. 3-Hydroxypropanenitrile.



The title compound was synthesized following general procedure method C from 3-(4-methoxybenzyloxy)propanenitrile (191 mg, 1 mmol), sodium nitrite (5 mg, 7 mol %), glacial acetic acid (1 mL) and DDQ (8 mg, 3.5 mol %). Purification by flash chromatography (1:1 ethyl acetate/light petroleum) gave the *title compound* as a colourless oil (60 mg, 84%); υ_{max} (ATR)/cm^{-1} 3600–3300, 2961, 2899, 2253, 1474, 1413; δ_H (400 MHz; $CDCl_3$) 3.92 (2H, t, *J* 6.1 Hz, CH_2), 2.64 (2H, t, *J* 6.1 Hz, CH_2), 2.27 (1H, br s, OH); δ_C (100 MHz; $CDCl_3$) 118.2 (C), 57.8 (CH_2), 21.5 (CH_2).

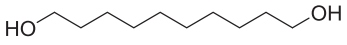
4.7.6. (1S,2R,5S)-Menthol.



The title compound was synthesized following general procedure method D from 1-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyloxy)methyl-4-methoxybenzene (276 mg, 1 mmol), sodium nitrite (2 mg, 3 mol %), glacial acetic acid (1 mL)

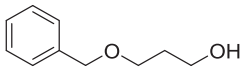
and DDQ (3 mg, 1.5 mol %) gave the *title compound* as a pale yellow solid (142 mg, 91%); mp 39–41 °C (lit.[31] mp 40–41.5 °C). Found: $M+Na^+$, 179.1411. $C_{10}H_{20}ONa^+$ requires 179.1412; υ_{max} (ATR)/cm^{-1} 3607, 3008, 2959, 2926, 2850, 1456; δ_H (400 MHz; $CDCl_3$) 3.43 (1H, td, *J* 10.3, 4.3 Hz, CH), 2.23–2.15 (1H, m, CH), 2.02–1.96 (1H, m, CH_2), 1.71–1.61 (2H, m, CH_2), 1.51–1.40 (1H, m, CH), 1.13 (1H, ddt, *J* 12.9, 10.3, 3.1 Hz, CH), 1.05–0.85 (3H, m, CH_2), 0.95 (3H, t, *J* 6.7 Hz, CH_3), 0.93 (3H, t, *J* 6.7 Hz, CH_3), 0.83 (3H, d, *J* 6.9 Hz, CH_3); OH not observed; δ_C (100 MHz; $CDCl_3$) 71.6 (CH), 50.2 (CH), 45.1 (CH_2), 34.5 (CH_2), 31.6 (CH), 25.9 (CH), 23.2 (CH_2), 22.2 (CH_3), 21.0 (CH_3), 16.1 (CH_3). Data recorded match literature.[32]

4.7.7. 1,10-Decanediol.



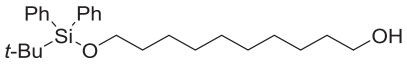
The title compound was synthesized following general procedure method C from 1,10-bis((4-methoxybenzyl)oxy)decane (414 mg, 1 mmol), sodium nitrite (4 mg, 5 mol %), glacial acetic acid (1 mL) and DDQ (6 mg, 2.5 mol %). Purification by flash chromatography (1:1 diethyl ether/light petroleum) gave the *title compound* as a colourless oil (151 mg, 87%); mp 69–71 °C (lit.[33] mp 70–71 °C). Found: $M+Na^+$, 197.1917. $C_{10}H_{22}O_2Na^+$ requires 197.1917; υ_{max} (ATR)/cm^{-1} 3623, 3010, 2931, 2857, 1465, 1389; δ_H (400 MHz; $CDCl_3$) 3.66 (4H, t, *J* 6.6 Hz, CH_2), 1.58 (4H, quintet, *J* 7.2 Hz, CH_2), 1.45 (2H, s, OH), 1.38–1.32 (12H, m, CH_2); δ_C (100 MHz; $CDCl_3$) 63.1 (CH_2), 32.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 25.7 (CH_2).

4.7.8. 3-Benzyloxy-1-propanol.



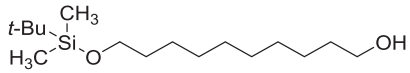
The title compound was synthesized following general procedure method D from 1-methoxy-4-(3-(phenylmethoxy)propoxy) methylbenzene (286 mg, 1 mmol), sodium nitrite (2 mg, 3 mol %), glacial acetic acid (1 mL) and DDQ (3 mg, 1.5 mol %) gave the *title compound* as a colourless oil (133 mg, 81%). Found: $M+Na^+$, 189.0878. $C_{10}H_{14}O_2Na^+$ requires 189.0891; υ_{max} (ATR)/cm^{-1} 3600–3200, 3031, 2944, 2865, 1496, 1454; δ_H (400 MHz; $CDCl_3$) 7.40–7.29 (5H, m, ArH), 4.55 (2H, s, CH_2), 3.81 (2H, t, *J* 5.8 Hz, CH_2), 3.69 (2H, t, *J* 5.8 Hz, CH_2), 2.27 (1H, br s, OH), 1.90 (2H, quintet, *J* 5.8 Hz, CH_2); δ_C (100 MHz; $CDCl_3$) 138.1 (C), 128.5 (CH), 127.7 (CH), 127.7 (CH), 73.3 (CH_2), 69.4 (CH_2), 61.9 (CH_2), 32.1 (CH_2). Data recorded match literature.[34]

4.7.9. 10-(tert-Butyldiphenylsilyloxy)decan-1-ol.



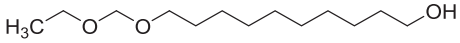
The title compound was synthesized following general procedure method D from *tert*-butyl(10-(4-methoxybenzyl)oxy) decyloxydiphenylsilane (533 mg, 1 mmol), sodium nitrite (2 mg, 3 mol %), glacial acetic acid (1 mL) and DDQ (3 mg, 1.5 mol %) gave the *title compound* as a colourless oil (366 mg, 89%). Found: $M+Na^+$, 435.2692. $C_{26}H_{40}SiO_2Na^+$ requires 435.2695; υ_{max} (ATR)/cm^{-1} 3550–3300, 3070, 2929, 2856, 1471, 1427; δ_H (400 MHz; $CDCl_3$) 7.70 (4H, dd, *J* 7.6, 1.5 Hz, ArH), 7.45–7.38 (6H, m, ArH), 3.68 (4H, td, *J* 6.6, 2.6 Hz, CH_2), 1.62–1.55 (4H, m, CH_2), 1.38–1.27 (12H, m, CH_2), 1.08 (9H, s, CH_3); OH not observed; δ_C (100 MHz; $CDCl_3$) 135.6 (CH), 134.2 (C), 129.5 (CH), 127.6 (CH), 64.0 (CH_2), 63.1 (CH_2), 32.8 (CH_2), 32.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 26.9 (CH_3), 25.8 (CH_2), 25.7 (CH_2), 19.2 (C). Data recorded match literature.[35]

4.7.10. 10-(tert-Butyldimethylsilyloxy)decan-1-ol.



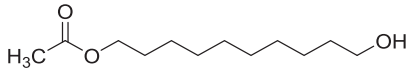
The title compound was synthesized following general procedure method D from *tert*-butyl(10-(4-methoxybenzyloxy) decyl)dimethylsilane (409 mg, 1 mmol), sodium nitrite (2 mg, 3 mol %), glacial acetic acid (1 mL) and DDQ (3 mg, 1.5 mol %) gave the *title compound* as an orange oil (259 mg, 90%). Found: $M+Na^+$, 311.2366. $C_{16}H_{36}SiO_2Na^+$ requires 311.2382; υ_{max} (ATR)/cm^{-1} 3622, 3011, 2931, 2857, 1471, 1464; δ_H (400 MHz; $CDCl_3$) 3.64 (4H, dt, *J* 19.1, 6.6 Hz, CH_2), 1.61–1.50 (4H, m, CH_2), 1.39–1.29 (12H, m, CH_2), 0.92 (9H, s, CH_3), 0.08 (6H, s, CH_3); OH not observed; δ_C (100 MHz; $CDCl_3$) 63.4 (CH_2), 63.1 (CH_2), 32.9 (CH_2), 32.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 26.0 (CH_3), 25.8 (CH_2), 25.7 (CH_2), 25.6 (CH_2), 18.4 (C), −5.2 (CH_3). Data recorded match literature.[36]

4.7.11. 10-(Ethoxymethoxy)decan-1-ol.



The title compound was synthesized following general procedure method D from 1-((10-(ethoxymethoxy)decyloxy)methyl)-4-methoxybenzene (123 mg, 0.35 mmol), sodium nitrite (1 mg, 3 mol %), glacial acetic acid (350 μL) and DDQ (1 mg, 1.5 mol %) gave the *title compound* as a yellow oil (72 mg, 90%). Found: $M+Na^+$, 255.1918. $C_{13}H_{28}O_3Na^+$ requires 255.1936; υ_{max} (ATR)/cm^{-1} 3500–3300, 2926, 1465, 1387, 1260; δ_H (400 MHz; $CDCl_3$) 4.69 (2H, s, CH_2), 3.65 (2H, t, *J* 6.6 Hz, CH_2), 3.61 (2H, q, *J* 7.1 Hz, CH_2), 3.54 (2H, t, *J* 6.6 Hz, CH_2), 1.61–1.54 (4H, m, CH_2), 1.40–1.28 (12H, m, CH_2), 1.24 (3H, t, *J* 7.1 Hz, CH_3); OH not observed; δ_C (100 MHz; $CDCl_3$) 95.0 (CH_2), 67.9 (CH_2), 63.1 (CH_2), 63.0 (CH_2), 32.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 25.7 (CH_2), 15.2 (CH_3).

4.7.12. 1-Hydroxydecyl acetate.



The title compound was synthesized following general procedure method D from 10-(4-methoxybenzyloxy)decyl acetate (322 mg, 0.95 mmol), sodium nitrite (2 mg, 3 mol %), glacial acetic acid (1 mL) and DDQ (3 mg, 1.5 mol %) gave the *title compound* as a yellow oil (198 mg, 92%). Found: $M+Na^+$, 239.1608. $C_{12}H_{24}O_3Na^+$ requires 239.1623; υ_{max} (ATR)/cm^{-1} 3600–3300, 2928, 1739, 1601, 1366, 1242; δ_H (400 MHz; $CDCl_3$) 4.07 (2H, t, *J* 6.7 Hz, CH_2), 3.65 (2H, t, *J* 6.7 Hz, CH_2), 2.06 (3H, s, CH_3), 1.66–1.54 (4H, m, CH_2), 1.40–1.29 (12H, m, CH_2); OH not observed; δ_C (100 MHz; $CDCl_3$) 171.3 (C), 64.7 (CH_2), 63.0 (CH_2), 32.8 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 25.9 (CH_2), 25.7 (CH_2), 21.0 (CH_3). Data recorded match literature.[37]

Acknowledgements

We thank the Engineering and Physical Sciences Research Council and GlaxoSmithKline for an Industrial CASE award (to K.W.).

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