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Hydrogenation of nitroarenes bearing aldehyde containing side chains over palladium and platinum catalysts: a new route to medium and large heterocyclic compounds☆

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Abstract—A wide range of nitroarenes bearing aldehyde containing side chains, readily available by hydroformylation of the corresponding alkenes have been hydrogenated over heterogeneous palladium or platinum catalysts to give medium and large heterocycles either resulting from direct cyclisation or by the formation of dimers. The yields of monomers and dimers are discussed as a function of ring size and the pattern of heteroatom substitution in the substrates; in general the greater the number of heteroatoms in the chain, the greater the yield of cyclic compounds. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Hydrogenation of nitroarenes bearing aldehyde or ketone containing side chains (hereafter referred to as nitroaldehydes or nitroketones) over platinum metal catalysts has long been established as a route to 5- and 6-membered cyclic amines.[2] Indoles have been prepared in high yields by hydrogenation of nitroketones over Pd/C[3] or of nitroaldehydes over Rh-catalysts.[4] Pyrrolidines have been prepared by hydrogenation of γ-nitroketones over Raney Ni[5] and a phenanthridine resulted from a related Zn/acetic acid reduction of a nitroaldehyde.[6] The method has also been applied to the synthesis of benzodiazepines,[7] azepine imines[8] (7 ring) and a diazecinone (8 ring).[9] In some cases, e.g. in the hydrogenation of aliphatic α-nitroketones, a piperazine, a dimeric product, is produced.[10]

The high yields of cyclic compounds formed in these reactions prompted us to examine this method as a general route to the preparation of medium and large heterocycles. As the reactions occur on a metal catalyst that is present in relatively low concentrations, it appeared possible that cyclisation could be preferred over oligomerisation or polymerisation without the need to have very low concentrations of the substrate. Some support for this proposal came from a recent report of the synthesis of a 17-membered cyclic amine in good yield (66%) by hydrogenolysis of a Cbz-protected aminoaldehyde.[11] Presumably, the first step of this preparation involves formation of an aminoaldehyde which subsequently cyclises to form an iminium salt or enamine which is hydrogenated to form the amine. In a related sequence, a Boc-protected aminoaldehyde was converted into a 14-ring macrocycle, in modest yield, by treatment with trifluoroacetic acid, triethylamine and subsequent reduction with cyanoborohydride.[12] Ojima has also shown that *N*-protected diallylamines react under hydroformylation/cyclisation conditions to form *N*-protected enamines with a pendant aldehyde.[13] Although all of this evidence points to the involvement of aminoaldehydes, it should be noted that on one occasion in our work an aminoaldehyde was isolated from hydroformylation of an aminoalkene without cyclisation (see below). Aminoaldehydes are again possible intermediates in the hydrogenation of nitroaldehydes and thus this reaction may lead to similar good yields of large and possibly medium heterocycles. Nitroarenes bearing aldehyde containing side chains are readily available by hydroformylation of alkenyl substituted nitroarenes.[14,15]

Further support for the proposed method comes from the reported formation of large ring amines from hydroformylation of aminoalkenes under conditions whereby an intermediate enamine is hydrogenated[16] or trapped by reaction with an appropriately substituted nucleophile.[17]

☆ See Ref. 1.

Keywords: hydrogenation; catalysis; medium-ring heterocycles; macrocycles.

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2. Results and discussion

2.1. Preparation of nitroaldehydes

The nitroaldehydes were all prepared by rhodium-catalysed hydroformylation of nitrobenzenes substituted with alkene containing side chains (Scheme 1). A variety of such alkenes with *o*, *m*, and *p*-substituted nitro groups, with side chains containing only C, with one or more O atoms, with S, with N, or with N and O atoms were prepared by standard methods as described in Section 3. Hydroformylation of the nitroalkenes **1** was carried out using PPh_3 as ligand to give linear and branched aldehydes, **2** and **3** in a ratio of ca. 70:30. In general, the aldehydes were readily separated by column chromatography on silica. Use of the bulky bisphosphite ligand, BIPHEPHOS[18] led to a much greater proportion (≥90:10) of the linear aldehydes.

Aldehydes which were β to an oxygen atom in the chain were prepared by hydroformylation of vinyl ethers which gave linear to branched ratios of ca. 30:70 with either PPh_3 or BIPHEPHOS as ligand.

Some difficulties were encountered in hydroformylation of compounds containing allyloxy substituents, where significant amounts (10–20%) of alcohols arising from hydrogenolysis reactions were formed.

2.2. Hydrogenations of nitroaldehydes

Reaction conditions. The nitroaldehydes **4** were hydrogenated over PtO_2 or 10% Pd/C catalysts at ambient temperature with 1 atm of H_2. A greater quantity (2.6×10^{-4} mol) of PtO_2 was used than palladium (5.6×10^{-5} mol) as reactions using a smaller amount of Pt (5.6×10^{-5} mol) did not go to completion.

2.3. Reduction of *ortho*-nitroaldehydes 4

Both monomeric **5** and dimeric **6** products were formed in these reactions together with varying amounts of polymers (Scheme 2, Table 1). The ratios of monomers to dimers were estimated either by HPLC or from the mass of products isolated by chromatography on silica. Concordant results were obtained for the two methods demonstrating product stability on silica chromatography. The yields quoted in Table 1 are yields of isolated products which in all cases were shown to be pure by a range of analytical techniques.

The effect of hydrogen pressure was evaluated by a hydrogenation of compound **4f** over Pd at ca. 80 atm H_2 which gave the dimeric product in higher yield (74%) than the reaction with 1 atm of H_2 (64%, entry 6). However, as a similar yield of dimeric product (75%, entry 7) could be obtained by the use of a Pt catalyst at 1 atm of H_2, it was felt that the use of high pressure equipment was not justified and subsequent reactions only involved the use of 1 atm H_2.

Hydrogenations of **4f** were carried out over Pd using alternative solvents to methanol. Use of either benzene or ethyl acetate led to reductions in yields of dimer (34 and 33%, respectively) with concomitant increases in polymer formation.

A reaction of compound **4p** over Pd at a higher concentration (×3.3) gave a reduced yield of both monomeric (75 to 34%) and dimeric (6 to 0%) products (cf. entries 19 and 21). Again, more polymeric products were formed. The lower concentration (4.8×10^{-3} M), comparable to that used by Japanese workers in the hydrogenation of the Cbz-protected amino aldehyde[11] was thus adopted.

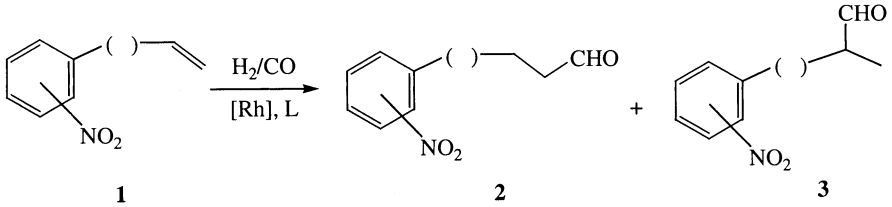
2.4. Effect of ring size on product distribution

The effect of chain length on product distribution for compounds with only one or no heteroatoms in the chain was examined. High yields of 7-membered monomeric products were obtained and no 14-membered dimers were formed (entries 1 and 2). No clear pattern was observed for the formation of 8- and 16-membered compounds (entries 3–5) and polymer formation was >50% in each case. Reactions leading to medium size rings (9- and 10-membered) were as expected unfavourable relative to dimer formation (18- and 20-membered) (entries 6–9 and 11–14) with one substrate **4f** giving up to 75% of the 18-membered ring dimer. Surprisingly, introduction of a NCOPh group into the chain led to formation of the monomeric 9-ring compound in modest yield (22%) with no dimer (entry 10). Larger (15- and 16-membered ring) monomers formed more easily than their corresponding dimers (30- and 32-membered rings) (entries 22–24). In each of these cases overall yields were ca. 50% with monomer to dimer ratios between 1.5 and 3:1.

Thus, in general, the results reflected the well established ease of formation of smaller (7-membered) rings, the difficult formation of medium (9- and 10-membered) rings and the ease of formation of large rings (>15-membered).[19]

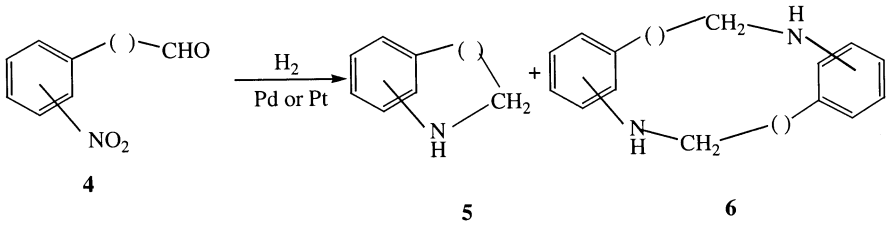
2.5. Effect of increased heteroatom substitution on product distribution

Reactions of a range of nitroaldehydes containing two or three heteroatoms in the side chain were examined. No general improvement in total yields of cyclic products was observed but the introduction of two ethyleneoxy groups led



1 2 3

Scheme 1.



4 **5** **6**

Scheme 2.

Table 1. Isolated yields of heterocycles from hydrogenation of *o*-nitroaldehydes

				Product yield (%)[a]	
Entry	Reactant	( )CHO **4**	Catalyst	Monomer **5**	Dimer **6**
1	**4a**	2-$(CH_2)_2CH(CH_3)CHO$	Pd	67(7)	–(14)
2	**4b**	2-$CH_2OCH(CH_3)CHO$	Pd	56(7)	–(14)
3	**4c**	2-$O(CH_2)_2CH(CH_3)CHO$	Pd	14(8)	30(16)
4	**4d**	2-$CH_2SCH_2CH(CH_3)CHO$	Pt	20(8)	–(16)
5	**4e**	2-$O(CH_2)_3CHO$	Pd	33(8)	8(16)
6	**4f**	2-$O(CH_2)_4CHO$	Pd	–(9)	64(18)
7	**4f**	2-$O(CH_2)_4CHO$	Pt	–	75
8	**4g**	2-$O(CH_2)_3CH(CH_3)CHO$	Pd	–	62(18)
9	**4h**	2-$CH_2O(CH_2)_3CHO$	Pd	–(9)	23(18)
10	**4i**	2-$N(COPh)(CH_2)_4CHO$	Pd	22(9)	–(18)
11	**4j**	2-$O(CH_2)_2OCH(CH_3)CHO$	Pd	–(9)	58(18)
12	**4j**	2-$O(CH_2)_2OCH(CH_3)CHO$	Pt	–(9)	47(18)
13	**4k**	2-$O(CH_2)_5CHO$	Pd	7(10)	20(20)
14	**4l**	2-$O(CH_2)_2OCH_2CH(CH_3)CHO$	Pd	–(10)	37(20)
15	**4m**	2-$O(CH_2)_2O(CH_2)_3CHO$	Pd	19(11)	36(22)
16	**4m**	2-$O(CH_2)_2O(CH_2)_3CHO$	Pt	22	18
17	**4n**	2-$O(CH_2)_2N(SO_2Me)(CH_2)_3CHO$	Pt	36(11)	–(22)
18	**4o**	2-$O[(CH_2)_2O]_2CH_2CH(CH_3)CHO$	Pd	56(13)	–(26)
19	**4p**	2-$O[(CH_2)_2O]_2(CH_2)_3CHO$	Pd	75(14)	6(28)
20	**4p**	2-$O[(CH_2)_2O]_2(CH_2)_3CHO$	Pt	58	–
21	**4p**	2-$O[(CH_2)_2O]_2(CH_2)_3CHO$	Pd[b]	34	–
22	**4q**	2-$O(CH_2)_9CH(CH_3)CHO$	Pt	29(15)	18(30)
23	**4r**	2-$O(CH_2)_{11}CHO$	Pd	27(16)	19(32)
24	**4r**	2-$O(CH_2)_{11}CHO$	Pt	36	11

Reactions at ambient temperature with H_2 (1 atm) using a substrate concentration of 4.76×10^{-3} M in methanol (typically using 100 mg of substrate) with Pd (5.6×10^{-5} mol) as 10% Pd/C and Pt (3×10^{-4} mol) as PtO_2.

[a] Ring size in parentheses.

[b] Reaction at higher concentration (×5).

to a high preference for monomer formation. Thus significant yields (56–75%) of 13- and 14-membered ring compounds were formed at the expense of dimers (entries 18–20). This selectivity is greater than that noted above for the formation of 15- versus 30- and 16- versus 32-membered rings when only one oxygen atom is present in the side chain (entries 22–24). Increased heteroatom substitution led to significant amounts of 11-membered ring formation (entries 15 and 16) and once again introduction of a N-atom in the chain as a sulfonamide gave only 11-ring monomer albeit in modest yield (entry 17). In contrast, the substitution of a further oxygen atom as in compound **4l** led to only dimer formation (20-membered ring) (entry 14) whereas some monomer (7%) was obtained from reaction of the pentamethylene compound **4k** (entry 13).

Table 2. Isolated yields of heterocycles from hydrogenation of *m*- and *p*-nitroaldehydes

				Product yield (%)	
Entry	Reactant	( )CHO **4**	Catalyst	Monomer **5**	Dimer **6**
25	**4s**	3-$O(CH_2)_2CH(CH_3)CHO$	Pd	6(9)	39(18)
26	**4t**	3-$O(CH_2)_4CHO$	Pd	10(10)	17(20)
27	**4u**	4-$O(CH_2)_5CHO$	Pd	–(12)[a]	11(24)
28	**4v**	4-$O(CH_2)_2O(CH_2)_3CHO$	Pt	7(13)	22(26)
29	**4w**	4-$O[(CH_2)_2O]_2(CH_2)_3CHO$	Pt	–(16)	26(32)

Conditions as in Table 1.

[a] Amino alcohol from reduction of CHO and NO_2 groups also formed (45%).

2.6. Reaction of *meta*- and *para*-substituted compounds

A limited number of *meta*- and *para*-substituted nitroaldehydes were hydrogenated. In general, overall recoveries of cyclic products were only modest (Scheme 2 and Table 2). Perhaps surprisingly, small amounts of 9- and 10-membered cyclic compounds were isolated in spite of the additional constraint imposed upon the ring system by the increased number of sp^2 carbon atoms (entries 25 and 26). Reaction of the *para*-substituted compound **4u** was unique in that the major product was the aminoalcohol resulting from reduction of both the nitro and aldehyde groups (entry 27).

2.7. Potential template effects

A series of potential templating agents was added to hydrogenations of nitroaldehyde **4m**. The resulting monomeric and dimeric products had two oxygen and one nitrogen or four oxygen and two nitrogen atoms as potential chelating sites. Addition of $Ag(OTf)_2$ (1 or 2 equiv.), $Ba(NO_3)_2$ (1 equiv.) or $La(OTf)_3$ (1 equiv.) all led to the exclusive formation of monomer in greater yields than when no additive was present (Table 3). Addition of $Ba(OTf)_2$ surprisingly gave only polymeric material with no recoverable cyclic products.

Energy minimisation calculations were carried out using the Insight II program[20] for the potential interactions of one Ag^+ ion with the monomer **5m** and for two Ag^+ ions with the dimer **6m**. The minimum energy conformation of the monomer **5m** with one Ag^+ ion had the Ag^+ ion sitting above the three donor atoms with minimal conformational change in the calculated structure. In contrast, the minimum energy conformation of the dimer with two Ag^+ ions sitting above the plane of the ring required more extensive conformational changes from the free dimer structure.

Table 3. Effects of potential templating agents on the hydrogenations of the nitroaldehyde **4m** (glycine, dissolved in the minimum amount of water, and added to the methanol solution)

Additive	Product yield (%)[a]	
	5m	**6m**
–	19	36
Ag(OTf) 1 equiv.	30	–
Ag(OTf) 2 equiv.	33	–
$Ba(NO_3)_2$ 1 equiv.	30	–
$Ba(OTf)_2$ 1 equiv.	–	–
$La(OTf)_3$ 1 equiv.	45	–
Glycine 1 equiv.	21	33

Reaction over Pd/C in methanol.
[a] Isolated yields.

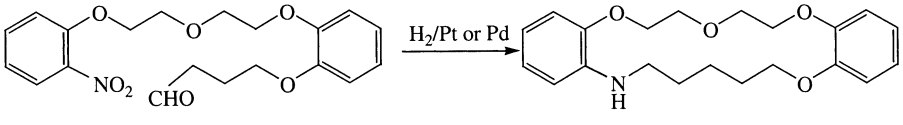
Compound **6j** was prepared in which the two O and one N atoms in each side of an 18-membered ring were all separated by two carbon atoms in an attempt to increase the potential for chelation. Studies were carried out by Professor Lindoy's group who evaluated the stability constant data for the complexation of **6j** with Cu^+ and Ag^+ ions. The measured values of log K of ca. 3 were significantly less than those recorded for 14- and 16-membered rings containing four heteroatoms (N_2O_2, N_2S_2, or N_4) where log K values of 8–15 were obtained.[21] It was concluded that the geometry of **6j** was not conducive to complex formation and no further studies were carried out.

2.8. Mechanistic considerations

The exclusive formation of monomers, dimers and polymers and the absence of trimers and other oligomers was noted in all cases. Other studies have shown that under acid catalysis, facile equilibration between monomers, dimers and oligomers results.[22] It is possible that the imines remain close to the catalyst surface in our reactions and that hydrogenation competes with oligomerisation leading to stable products. It is difficult to see why such high yields of dimer can be obtained, e.g. 75% of dimer **6f** (entry 7, Table 1).

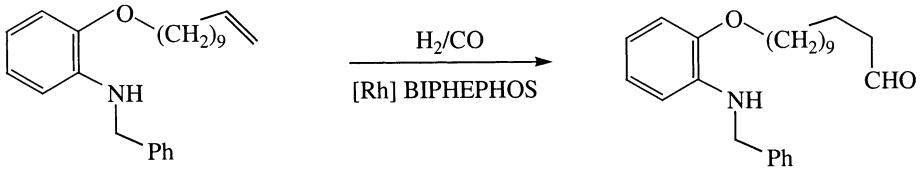
When a further degree of conformational restriction was imposed on the nitroaldehyde in **7**, only the 17-membered cyclic compound **8** was obtained in moderate to good yields (47%, Pt and 65%, Pd) with no trace of any dimeric compounds (Scheme 3).

The possible direct involvement of the Pt or Pd catalysts in the cyclisation step was explored by preparation of the



7 **8**

Scheme 3.



9 **10**

Scheme 4.

aminoaldehyde **10**. Reaction of the aminoalkene **9** with H_2/CO in the presence of Rh/BIPHEPHOS at 80°C gave the aminoaldehyde **10** in moderate yield (40%) (Scheme 4). This result was surprising as both 16- and 32-membered heterocycles form easily (entries 23 and 24, Table 1). In addition, hydroformylation of a related aminoalkene, *N*-benzyl-2-(undec-10-enyloxy)benzylamine gave a 17-membered heterocycle (34%) together with the 34-membered heterocycle (20%).[16]

3. Experimental

Operations involving ligands and catalysts were carried out under an atmosphere of dry N_2 using dry solvents that were distilled prior to use.

Flash chromatography was performed using E.Merck 230–400 mesh silica gel. ^{1}H NMR spectra were measured at 200, 300 or 400 MHz and ^{13}C were recorded at 50 or 100 MHz. Mass spectra including accurate mass measurements (EI) were obtained at 70 eV or by Electrospray Mass Spectroscopy (ESI) with a cone voltage of 25 V and with methanol as the mobile phase. High Performance Liquid Chromatography (HPLC) was performed on a Waters Model 6000A (Column: Deltapak C18 — 100 Å, 3.9 mm×30 cm, 10 μ), Waters gradient programme Model 660 and Waters Model 481 Detector. Unless otherwise stated, the gradient elution involved an initial composition of 20:80% CH_3CN/water, increased to 100% CH_3CN within 40 min with a flow rate of 1 ml/min. Product distributions were obtained from peak areas from a peak printout using HP Chemstation 3365 Series II software.

Rhodium(III) trichloride trihydrate ($RhCl_3{\cdot}nH_2O$, n= approx. 3) was supplied by Johnson Matthey Pty Ltd and converted into tetrakis(acetato)dirhodium(II), $[Rh(OAc)_2]_2$.[23] [6,6′-{[3,3′-bis(1,1-dimethylethyl)-5,5′-dimethoxy-1,1′-biphenyl]-2,2′-diyl}bis(oxy)]bis-dibenzo[*d*,*f*][1,3,2]dioxaphosphepin], BIPHEPHOS, was prepared by a literature procedure.[18] Platinum oxide (PtO_2) was obtained from Johnson Matthey Pty Ltd and 10% Pd/C was obtained from Aldrich. Light petroleum refers to the fraction of petroleum bp 60–80°C.

3.1. Alkenylnitrobenzenes and related compounds

The following were prepared by known literature methods: 2-(but-3-enyloxy)nitrobenzene (precursor to **4a**);[24] 2-(2-oxabut-3-enyl)nitrobenzene (precursor to **4b**);[25] 2-(but-3-enyloxy)nitrobenzene (precursor to **4c** and **4f**);[26] 2-(2-thiapent-4-enyl)nitrobenzene (precursor to **4d**);[15,27] 2-(prop-2-enyloxy)nitrobenzene (precursor to **4e**);[28] 2-(2-oxapent-4-enyl)nitrobenzene (precursor to **4h**);[29] 2-(1,4-dioxahept-6-enyl)nitrobenzene (precursor to **4l** and **4m**);[30] 2-(1,4,7-trioxadec-9-enyl)nitrobenzene (precursor to **4o** and **4p**);[30] 2-(undec-10-enyloxy)nitrobenzene (precursor to **4q** and **4r**)[31] and 4-(but-3-enyloxy)nitrobenzene (precursor to **4u**).[32]

3.1.1. 2-[(*N*-Benzoyl)but-3-enylamino]nitrobenzene (precursor to 4i). Reaction of 2-(but-3-enylamino)nitrobenzene[33] (1.0 g, 5.2 mmol) with benzoyl chloride (2 ml) under standard conditions gave the alkene as a viscous yellow oil after flash chromatography (silica, 20% EtOAc/light petroleum) (1.3 g, 84%). (Found: *m*/*z* 319.1047. $(C_{17}H_{16}N_2O_3+Na)^+$ requires *m*/*z* 319.1059). ν_{max} (film) 3450, 1657, 1603, 1579, 1529, 1389, 1369, 1348, 1317, 785, 735, 704 cm^{-1}. ^{1}H NMR δ (400 MHz) 2.33, m, 2H, H2′; 3.42, m, 1H and 4.15–4.20, m, 1H, H1′; 4.89–4.95, m, 2H, H4′; 5.59, m, 1H, H3′; 6.48–6.50, m, 1H, H5; 6.71–6.74, m, 2H and 6.84, m, 3H, PhH; 7.25, m, 1H, H4; 7.31–7.32, m, 2H, H3,6. ^{13}C NMR δ (100 MHz) 32.59 (C2′); 50.77 (C1′); 116.68 (C4′); 125.39 (C3,5,6); 127.25, 129.76, 132.87 (C4, PhCH);137.38 (C3′). Mass spectrum (ESI$^+$): *m*/*z* 297.2 $(M+H)^+$.

3.1.2. 2-(1,4-Dioxahex-5-enyl)nitrobenzene (precursor to 4j). Reaction of 2-(2-hydroxyethoxy)nitrobenzene (1.0 g, 5.46 mmol) with ethyl vinyl ether (20 ml) and mercuric(II) acetate (0.1 g) at reflux for 24 h as described previously[25] gave the alkene as a yellow oil after flash chromatography (silica, 10% EtOAc/light petroleum) (400 mg, 26%). (Found: C, 57.4; H, 5.4; N, 6.4. $C_{10}H_{11}NO_4$ requires C, 57.4; H, 5.3; N, 6.7%). ν_{max} (film) 2934, 1608, 1584, 1526, 1488, 1453, 1354, 1323, 1279, 1256, 1199, 1167, 1092, 1048, 982, 927, 853, 773, 745 cm^{-1}. ^{1}H NMR δ (300 MHz) 4.06–4.11, m, 3H, H3′ and H6′$_Z$; 4.26, dd, J=14.3, 2.3 Hz, 1H, H6′$_E$; 4.33–4.36, m, 2H, H2′; 6.5, dd, J=14.3, 6.7 Hz, 1H, H5′; 7.03–7.13, m, 2H, H3,5; 7.49–7.55, m, 1H, H4; 7.82, dd, J=8.1, 1.6 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 66.29 (C3′); 68.61 (C2′); 87.52 (C6′); 115.35 (C3); 121.03 (C5); 125.65 (C6); 134.03 (C4); 140.47 (C1); 151.59 (C5′); 152.10 (C2). Mass spectrum (ESI$^+$): *m*/*z* 210.0 ($(M+H)^+$, 8%); 232.1 ($(M+Na)^+$, 100).

3.1.3. 2-[(*N*-Methylsulfonyl)-1-oxa-4-azahept-6-enyl]-nitrobenzene (precursor to 4n). Reaction of 2-(1-oxa-4-azahept-6-enyl)nitrobenzene (0.5 g, 2.25 mmol) with methanesulfonyl chloride (1.29 g, 11 mmol) using standard conditions gave the alkene as a viscous yellow oil which solidified on standing (0.52 g, 76%) mp 59.7–60.3°C. (Found: C, 48.0; H, 5.4; N, 9.5. $C_{12}H_{14}N_2O_5S$ requires C, 48.0; H, 5.4; N, 9.3%). ν_{max} (film) 2935, 1607, 1584, 1525, 1488, 1454, 1329, 1277, 1256, 1148, 1048, 1010m, 776, 746 cm^{-1}. ^{1}H NMR δ (300 MHz) 2.90, s, 3H, CH_3; 3.64, t, J=5.4 Hz, 2H, H3′; 4.03, apparent doublet, J=6.3 Hz, 2H, H5′; 4.27, t, J=5.4 Hz, 2H, H2′; 5.26–5.38, m, 2H, H7′; 5.84, ddt, J=16.6, 10.1, 6.4 Hz, 1H, H6′; 7.03–7.09, m, 2H, H3,5; 7.50–7.56, m, 1H, H4; 7.83, dd, J=8.0, 1.7 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 39.52 (CH_3); 45.78 (C3′); 51.44 (C5′); 68.92 (C2′); 114.49 (C3); 119.77 (C7′); 120.99 (C5); 125.72 (C6); 132.59 (C4); 134.34 (C6′); 139.91 (C1); 151.69 (C2). Mass spectrum (ESI$^+$): *m*/*z* 301.2 $(M+H)^+$.

3.1.4. 2-[(*N*-Benzyl)undec-10-enyloxy]aniline (9). Reaction of 2-(undec-10-enyloxy)aniline (0.2 g, 0.76 mmol) and benzaldehyde (0.16 g, 1.53 mmol) in MeOH (10 ml) at 100°C for 3 h followed by reduction using $NaBH_4$ (86 mg, 2.28 mmol) as described previously[34] gave the alkene as a yellow oil after flash chromatography (silica, 5% EtOAc/light petroleum) (0.13 g, 48%). (Found: *m*/*z* 352.2634. $(C_{24}H_{33}NO+H)^+$ requires *m*/*z* 352.2640). ν_{max} (film) 2926, 2854, 1602, 1519, 1453, 1246, 1214, 1048, 1028, 909, 734, 698 cm^{-1}. ^{1}H NMR δ (200 MHz) 1.21–1.44, bs, 12H, H3′,4′,5′,6′,7′,8′; 1.79, pentet, J=6.5 Hz,

2H, H2′; 1.98–2.08, m, 2H, H9′; 3.99, t, J=6.5 Hz, 2H, H1′; 4.36, s, 2H, PhCH_2; 4.89–5.04, m, 2H, H11′; 5.81, ddt, J=17.1, 10.2, 6.6 Hz, 1H, H10′; 6.54–6.68, m, 2H, H4,6; 6.75- 6.84, m, 2H, H3, 5; 7.21- 7.50, m, 5H, PhH. ^{13}C NMR δ (75 MHz) 25.17, 27.94, 28.12, 28.37, 28.39, 28.42, 28.53 (C2′,3′,4′,5′,6′,7′,8′); 32.80 (C9′); 47.01 (CH_2Ph); 67.40 (C1′); 109.19, 109.59 (C3,6); 113.13 (C11′); 115.59, 120.17 (C4,5); 125.82, 126.32, 126.58 (PhCH); 127.48 (C1); 138.21 (C2); 138.20 (C10′); 145.23 (PhC). Mass spectrum: (ESI$^+$): m/z 352.2 (M+H)$^+$. Mass spectrum (EI): m/z 351 (M$^+$, 23%), 198 (20), 108 (23), 91 (100), 55 (47).

3.1.5. 2-(Undec-10-enyloxy)aniline. Reaction of 2-(undec-10-enyloxy)nitrobenzene (0.5 g, 1.72 mmol) and $SnCl_2\cdot 2H_2O$ (2.48 g, 10.9 mmol) in absolute EtOH (10 ml) at 70°C for 2 h as described prevoiusly[35] gave the alkene as a pale red liquid after flash chromatography (silica, 50% CH_2Cl_2/light petroleum) (0.42 g, 93%). (Found: m/z 262.2165. ($C_{17}H_{27}NO$+H)$^+$ requires m/z 262.2171). ν_{max} (film) 3376, 3381, 3075, 2627, 2854, 1614, 1506, 1460, 1276, 1221, 1142, 1043, 909, 737 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.30–1.46, bs, 12H, H3′,4′,5′,6′,7′,8′; 1.81, pentet, J=6.7 Hz, 2H, H2′; 2.04, q, J=6.7 Hz, 2H, H9′; 3.58, bs, 2H, NH_2; 3.98, t, J=6.5 Hz, 2H, H1′; 4.90–5.03, m, 2H, H11′; 5.81, ddt, J=17.5, 10.3, 6.6 Hz, 1H, H10′; 6.73–6.80, m, 4H, ArH. ^{13}C NMR δ (75 MHz) 26.20, 28.98, 29.17, 29.26, 29.39, 29.46, 29.57, (C2′,3′,4′, 5′,6′,7′,8′); 33.84 (C9′); 68.33 (C1′); 111.59 (C11′); 114.18, 115.09 (C3,6); 118.49 (C4); 120.99 (C5); 136.39 (C1); 139.25 (C10′); 146.84 (C2). Mass spectrum (EI): m/z 261 (M$^+$, 22%), 145 (21), 143 (90), 109 (100), 80 (36), 55 (55).

3.2. Preparation of alkenes by a standard alkylation procedure[26]

3.2.1. 2-(Pent-4-enyloxy)nitrobenzene (precursor to 4g and 4k). A stirred mixture of 2-nitrophenol (2.8 g, 20 mmol), 5-bromopent-1-ene (2.0 g, 13 mmol) and K_2CO_3 (2.8 g, 20 mmol) in DMSO was heated to 110°C for three days. Distillation gave the alkene as a pale yellow oil (2.36 g, 85%), bp (oven) 130°C /0.04 mm. (Found: C, 64.1; H, 6.7; N, 6.9. $C_{11}H_{13}NO_3$ requires C, 63.8; H, 6.3; N, 6.8%). ν_{max} (film) 3078, 2976, 2944, 2882, 1641, 1609, 1583, 1522, 1488, 1451, 1392, 1355, 1280, 1257, 1165, 1150, 1089, 1044, 1005, 917, 855, 772, 745, 670, cm^{-1}. ^{1}H NMR δ (200 MHz) 1.96, pentet, J=6.4 Hz, 2H, H2′; 2.27, q, J=6.5 Hz, 2H, H3′; 4.10, t, J=6.3 Hz, 2H, H1′; 4.95–5.11, m, 2H, H5′; 5.83, ddt, J=16.9, 10.2, 6.7 Hz, 1H, H4′; 6.95–7.09, m, 2H, H3,5; 7.50, m, 1H, H4; 7.80, dd, J=8.0, 1.7 Hz, 1H, H6. ^{13}C NMR δ (50 MHz) 27.88, 29.69 (C2′,3′); 68.46 (C1′), 114.30 (C3); 115.32 (C5′); 119.04 (C5); 125.26 (C6); 133.96 (C4); 137.27 (C4′); 139.71 (C1); 152.18 (C2). Mass spectrum (EI): m/z 207 (M$^+$, 1%), 161 (7), 139 (11), 123 (10), 122 (9), 109 (10), 107 (9), 92 (5), 69 (51), 68 (100), 67 (55), 65 (15).

3.2.2. 3-(But-3-enyloxy)nitrobenzene (precursor to 4s and 4t). This compound was prepared from 3-nitrophenol and 4-bromobut-1-ene as a pale yellow liquid (57%), bp (oven) 70°C /0.02 mm. (Found: C, 62.0; H, 5.9; N, 7.0. $C_{10}H_{11}NO_3$ requires C, 62.2; H, 5.7; N, 7.2%.) ν_{max} (film) 3081, 2981, 2936, 2878, 1643, 1618, 1581, 1540, 1484, 1469, 1390, 1348, 1287, 1246, 1096, 1036, 991, 921, 863, 796, 737, 672 cm^{-1}. ^{1}H NMR δ (200 MHz) 2.56, qt, J=6.7, 1.3 Hz, 2H, H2′; 4.06, t, J=6.6 Hz, 2H, H1′; 5.08–5.23, m, 2H, H4′; 5.89, ddt, J=17.0, 10.2, 6.7 Hz, 1H, H3′; 7.21–7.22, m, 1H, H4; 7.39, t, J=8.2 Hz, 1H, H5; 7.67–7.69, m, 1H, H2; 7.74–7.80, m, 1H, H6. ^{13}C NMR δ (50 MHz) 33.25 (C2′); 67.78 (C1′); 108.72 (C2); 115.58 (C6); 117.40 (C4′); 121.54 (C4); 129.83 (C5); 133.77 (C3′); 149.01 (C1); 159.33 (C2). Mass spectrum (ESI$^+$): m/z 216.1 (M+Na)$^+$.

3.2.3. 2-(1-Oxa-4-azahept-6-enyl)nitrobenzene. This compound was prepared from 2-(2-bromoethoxy)nitrobenzene (1.0 g, 4.08 mmol) and prop-2-enylamine (2.33 g, 41 mmol) in CH_3CN as an orange oil (0.85 g, 94%). (Found: m/z 223.1081. ($C_{11}H_{14}N_2O_3$+H)$^+$ requires m/z 223.1083). ν_{max} (film) 3424, 2884, 1604, 1567, 1520, 1348, 1295, 1046, 746 cm^{-1}. ^{1}H NMR δ (300 MHz) 2.62, t, J=6.1 Hz, 1H, NH; 3.38, t, J=5.3 Hz, 2H, H3′; 3.62–3.67, m, 4H, H 2′,5′; 5.13–5.20, m, 2H, H7′; 5.76, ddt, J=17.5, 9.9, 6.5 Hz, 1H, H6′; 7.05–7.25, m, 1H, H5; 7.27, dd, J=8.3, 1.1 Hz, 1H, H3; 7.44–7.49, m, 1H, H4; 7.69, dd, J=8.1, 1.6 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 53.39 (C3′); 57.78 (C5′); 59.26 (C2′); 118.94 (C7′); 122.63 (C3); 124.47 (C5); 125.51 (C6); 132.97 (C4); 133.43 (C6′); 134.21 (C1); 144.27 (C2). Mass spectrum (ESI$^+$): m/z 223.1 (M+H)$^+$.

3.2.4. 2-{1,4,7-Trioxa-7-[2-(prop-2-enyloxy)phenyl]heptyl}nitrobenzene (precursor to 7). This compound was prepared from 2-(prop-2′-enyloxy)phenol[36] and 2-(6-chloro-1,4-dioxahexyl)nitrobenzene[37] as a pale yellow oil after flash chromatography (silica, 30% EtOAc/light petroleum) (71%). (Found: C, 63.7; H, 5.9; N, 3.9. $C_{19}H_{21}NO_6$ requires C 63.5, H 5.9, N 3.9%). ν_{max} (film) 2932, 2873, 1608, 1526, 1503, 1452, 1355, 1278, 1255, 1215, 1166, 1127, 1047, 928, 852, 772, 744 cm^{-1}. ^{1}H NMR δ (300 MHz) 3.92–3.98, m, 4H, H3′,5′; 4.15–4.19, m, 2H and 4.23–4.26, m, 2H, H2′,6′; 4.55, dt, J=5.2, 1.6 Hz, 2H, H1‴; 5.22, apparent dq, J=10.5, 1.5 Hz, 1H, H3‴$_E$; 5.38, apparent dq, J=17.3, 1.7 Hz, 1H, H3‴$_Z$; 6.04, ddt, J=17.3, 10.5, 5.3 Hz, 1H, H2‴; 6.85–7.10, m, 6H, H3,5, ArCH; 7.43–7.49, m, 1H, H4; 7.78, dd, J=8.1, 1.7 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 68.89, 69.54, 69.78, 70.12, 70.71 (C2′,3′,5′,6′,1‴); 114.40, 114.75, 114.99 (C3,7,ArCH); 117.58 (C3‴); 120.46 (C5); 121.31, 121.48 (C6,ArCH); 125.37 (ArCH); 133.48, 133.98 (C2‴,4); 139.95 (C1); 148.66, 148.69 (ArC); 152.14 (C2). Mass spectrum (ESI$^+$): m/z 360.3 ((M+H)$^+$, 50%); 382.3 ((M+Na)$^+$, 100).

3.3. Preparation of alkenes using phase transfer catalysis[30]

3.3.1. 4-(1,4-Dioxahept-6-enyl)nitrobenzene (precursor to 4v). Reaction of 4-fluoronitrobenzene (1.06 g, 7.48 mmol) and 3-oxahex-5-en-1-ol (1.62 g, 11.2 mmol) in anhydrous benzene (10 ml) with 50% aqueous NaOH (4.5 g) and benzyltriethylammonium chloride (0.09 g, 0.39 mmol) at reflux with vigorous stirring for 4 h gave the alkene as a yellow oil after flash chromatography (silica, 20% EtOAc/light petroleum) (1.90 g, 95%). (Found: C, 59.5; H, 5.8; N, 6.3. $C_{11}H_{14}NO_4$ requires C, 59.2; H, 5.9; N, 6.3.). ν_{max} (film) 3084, 2930, 2864, 1594, 1514, 1453,

1422, 1379, 1342, 1299, 1263, 1174, 1111, 1036, 996, 924, 846, 753, 691, 658 cm^{-1}. ^1H NMR δ (300 MHz) 3.80–3.83, m, 2H, H3′; 4.08, dt J=5.6, 1.3 Hz, 2H, H5′; 4.20–4.23, m, 2H, H2′; 5.18–5.33, m, 2H, H7′; 5.86–5.98, m, 1H, H6′; 6.97, dd, J=9.3, 2.2 Hz, 1H, H3,5; 8.17, dd, J=9.2, 2.2 Hz, 2H, H2,6. ^{13}C NMR δ (75 MHz) 68.10, 68.26 (C1′,3′); 72.42 (C5′); 114.61 (C7′); 117.52 (C3); 125.83 (C2); 134.29 (C6′); 141.63 (C1); 163.87 (C4). Mass spectrum (ESI^+): m/z 246.1 $(M+Na)^+$.

3.3.2. 4-(1,4,7-Trioxadec-9-enyl)nitrobenzene (precursor to 4w). Reaction of 4-fluoronitrobenzene and 3,6-dioxanon-8-en-1-ol as described above gave the alkene as a yellow oil after distillation, bp (oven) 55°C/0.04 mm (66%). (Found: C, 58.3; H, 6.3; N, 5.3. $C_{13}H_{17}NO_5$ requires C, 58.4; H, 6.4; N, 5.2%). ν_{max} (film) 3082, 2870 m, 1608, 1594, 1513, 1498, 1342, 1299, 1264, 1174, 1111, 1055, 926, 848, 753, 658 cm^{-1}. ^1H NMR δ (300 MHz) 3.61–3.69, m, 2H, 3.72–3.75, m, 2H, and 3.89–3.92, m, 2H, H3′,5′,6′; 4.03, dt, J=5.7, 1.4 Hz, 2H, H8′; 4.22–4.25, m, 2H, H2′; 5.18, apparent dq, J=10.4, 1.3 Hz, 1H, $H10'_E$; 5.27, apparent dq, J=17.2, 1.6 Hz, 1H, $H10'_Z$; 5.91, ddt, J=17.3, 10.4, 5.6 Hz, 1H, H9′; 6.98, dd, J=9.3, 2.2 Hz, 2H, H3,5; 8.18, dd, J=9.3, 2.2 Hz, 2H, H2,6. ^{13}C NMR δ (50 MHz) 68.19, 69.41, 70.96 (C 3′,5′,6′); 72.28 (C 2′,8′); 114.58 (C 3,5); 117.23 (C10′); 125.84 (C 2,6); 134.58 (C9′); 141.56 (C1); 163.86 (C4). Mass spectrum (ESI^+): m/z 268.1 $(M+H)^+$, 7%); 290.2 $(M+Na)^+$, 100).

3.4. General conditions for reaction with H_2/CO

Reactions were carried out in a l00 ml Parr autoclave with a glass sleeve containing a stirrer bead. The substrate (0.3–1 g, ca. 1–5 mmol), rhodium catalyst precursor and ligand (in ratio 200:1:4) were placed in the autoclave under N_2 followed by deoxygenated benzene or EtOAc (10–20 ml). The vessel was flushed and evacuated three times with 200 psi (1.38 mPa) of H_2/CO (1:1 M mixture) and pressurised to 400 psi (2.76 mPa). The vessel was kept at the reaction temperature for 20 h, the autoclave cooled, the gases released and the solvent removed under reduced pressure. In general, ratios of products including regioisomers were determined by relative peak areas of appropriate hydrogens in the ^1H NMR spectra.

Unless otherwise stated, reactions involved the use of $[Rh(OAc)_2]_2$ and BIPHEPHOS as the catalyst system at 80°C for 20 h with H_2/CO, 1:1 at 400 psi.

All aldehyde products were isolated by flash chromatography on silica using EtOAc/light petroleum as eluent (generally 5, 10 or 20%) with the branched isomer having the higher R_f value. In general, it was difficult to obtain analytically pure samples of the aldehydes and thus they were used immediately after spectroscopic characterisation.

3.4.1. 2-(4-Formylbutyloxy)nitrobenzene (4f) and 2-(3-formylbutyloxy)nitrobenzene (4c).[†] A typical procedure involved reaction of 2-(but-3-enyloxy)nitrobenzene (1.0 g, 5.2 mmol), $[Rh(OAc)_2]_2$ (11 mg, 24.8 μmol) and PPh_3 (27 mg, 103 μmol) in EtOAc (20 ml) with H_2/CO (1:1, 400 psi) at 70°C for 20 h. Evaporation of the solvent under reduced pressure gave a brown residue (1.17 g). The ^1H NMR spectrum indicated a 60:40 mixture of the linear and branched aldehydes (**4f**) and (**4c**), respectively. Flash chromatography (silica, 10% EtOAc/light petroleum) gave 2-(3′-formylbutyloxy)nitrobenzene (**4c**) as a yellow liquid (395 mg, 34%) (Found: C, 58.9; H, 5.8; N, 6.1. $C_{11}H_{13}NO_4$ requires C, 59.2; H, 5.9; N, 6.3%). ν_{max} (film) 2965, 2938, 1725, 1608, 1583, 1526, 1489, 1472, 1353, 1309, 1280, 1256, 1166, 1090, 1046, 848, 773, 746, 670 cm^{-1}. ^1H NMR δ (200 MHz) 1.21, d, J=7.3 Hz, 3H, H4′; 1.88, ddt, J=14.5, 6.3, 1.9 Hz, 1H and 2.21–2.38, m, 1H, H2′; 2.77, sextet, J=7.2 Hz, 1H, H3′; 4.18, m, 2H, H1′; 6.99–7.09, m, 2H, H3,5; 7.52, dd, J=8.5, 1.7 Hz, 1H, H4; 7.84, dd, J=8.0, 1.7 Hz, 1H, H6; 9.71,d, J=1.2 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 13.43 (C4′); 29.61 (C2′); 43.08 (C3′); 66.90 (C1′); 114.49 (C3); 120.50 (C5); 125.58 (C6); 134.09 (C4); 133.4 (C1); 152.01 (C2); 204.01 (CHO). Mass spectrum (EI): m/z 222 (M^+-1, <1%), 178(1), 139(10), 113(19), 109(15), 99(14), 92(10), 85(100), 81(16), 78(16), 65(28), 64(20), 63(30), 57(32), 56(20), 55(45).

Further elution gave 2-(4-formylbutyloxy)nitrobenzene (**4f**) as a yellow liquid (406 mg, 35%) (Found: C, 59.2; H, 5.8; N, 6.3. $C_{11}H_{13}NO_4$ requires C, 59.2; H, 5.9; N, 6.3%). ν_{max} (film) 2941, 1710, 1607, 1579, 1526, 1485, 1377, 1352, 1281, 1254, 1167, 1007, 858, 745, 665 cm^{-1}. ^1H NMR δ (400 MHz) 1.82–1.89, m, 4H, H2′,3′; 2.55, td, J=6.8, 1.5 Hz, 2H, H4′; 4.12, t, J=5.7 Hz, 2H, H1′; 6.90–7.01, m, 1H, H5; 7.08, dd, J=8.4, 0.8 Hz, 1H, H3; 7.52, m, 1H, H4; 7.80, dd, J=8.1, 1.7 Hz, 1H, H6; 9.78, t, J=1.5 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 18.50 (C3′); 28.17 (C2′); 43.11 (C4′); 68.96 (C1′); 114.32 (C3); 120.13 (C5); 125.31(C6); 133.98 (C4); 134.10 (C1); 152.07 (C2); 202.03 (CHO). Mass spectrum (EI): m/z 224 (M^++1, <1%), 222 (M^+-1,<1), 193(49), 175(100), 174 (35), 146 (52), 85 (100).

A similar reaction of the alkene (0.3 g, 1.55 mmol) $[Rh(OAc)_2]_2$ (3.4 mg, 7.4 μmol) and BIPHEPHOS (24 mg, 30.5 μmol) gave the linear and branched aldehydes in the ratio of 90:10 with ca. 10% of 2-nitrophenol.

3.4.2. 2-(3-Formylbutyl)nitrobenzene (4a). Reaction of 2-(but-3-enyl)nitrobenzene (260 mg, 1.46 mmol) gave the linear and branched aldehydes (ratio 96:4) as an orange oil (300 mg). Purification gave (**4a**) (10 mg, 3%) and 2-(4-formylbutyl)nitrobenzene (150 mg, 50%).

A similar reaction of the alkene (1.0 g, 5.65 mmol) using PPh_3 as ligand gave the linear and branched aldehydes in a 55:45 ratio. The aldehyde (**4a**) was isolated as a yellow oil (455 mg, 39%). (Found: m/z 162.0554± 0.002. $(C_{11}H_{13}NO3-C_2H_5O)^+$ requires m/z 162.0553). ν_{max} (film) 2935, 2865, 1708, 1681, 1524, 1462, 1349, 911, 786, 733 cm^{-1}. ^1H NMR δ (400 MHz) 1.20, d, J=7.1 Hz, 3H, H4′; 1.69–1.78, m, 1H, and 2.03–2.12, m, 1H, H2′; 2.45, td, J=6.9, 1.7 Hz, 1H, H3′; 2.90–2.95, m, 2H, H1′; 7.34–7.39, m, 2H, H 3,5; 7.51–7.55, m, 1H, H4;

[†] Aldehydes have been named as formyl substituted nitrobenzenes for consistency with the naming of the precursor alkenes; IUPAC nomenclature would name them, e.g. as 5-(2-nitrophenoxy)pentanal (**4f**) and 2-methyl-4-(2-nitrophenoxy)butanal (**4c**).

7.92, dd, J=8.6, 1.5 Hz, 1H, H6; 9.67, d, J=1.7 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 13.38 (C4′); 30.59 (C2′); 31.41 (C1′); 46.09 (C3′); 124.87 (C6); 127.35 (C5); 132.02 (C3); 133.11 (C4); 136.66 (C2); 149.26 (C1); 204.26 (CHO).

2-(4-Formylbutyl)nitrobenzene was isolated as a yellow liquid (506 mg, 43%) (Found: m/z 162.0553±0.002. $(C_{11}H_{13}NO_3-C_2H_5O)^+$ requires m/z 162.0553). ν_{max} (film) 2935, 2866, 1711, 1682, 1524, 1461, 1348, 912, 787, 735 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.69–1.74, m, 4H, H2′, 3′; 2.49, td, J=6.9, 1.6 Hz, 2H, H4′; 2.91, t, J=7.3 Hz, 2H, H1′; 7.32–7.39, m, 2H, H 3,5; 7.49–7.54, m, 1H, H4; 7.89, dd, J=8.6, 1.6 Hz, 1H, H6; 9.78, t, J=1.6 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 21.84 (C3′); 30.10 (C2′); 32.77 (C1′); 43.50 (C4′); 124.72 (C6); 127.09 (C5); 131.87 (C3); 132.94 (C4); 136.89 (C2); 149.27 (C1); 202.24 (CHO).

3.4.3. 2-(3-Formyl-2-oxabutyl)nitrobenzene (4b). Reaction of 2-(2-oxabut-3-enyl)nitrobenzene (230 mg, 1.28 mmol) gave the linear and branched aldehydes (ratio 30:70) as a viscous, orange oil (280 mg). The aldehyde (**4b**) was isolated as a yellow oil (176 mg, 66%). (Found: m/z 123.0317. $(C_{10}H_{11}NO_4-C_4H_6O_2$ requires m/z 123.0321). ν_{max} (film) 2878, 1728, 1613, 1578, 1520, 1448, 1344, 1306, 1108, 859, 792, 730 cm^{-1}. ^{1}H NMR δ (400 MHz) 1.4, d, J=6.9 Hz, 3H, H4′; 4.02, qd, J=6.9, 1.4 Hz, 1H, H3′; 4.96–4.99, m, 2H, H1′; 7.61–7.67, m, 2H, H3,5; 7.82–7.84, m, 1H, H4; 8.06, dd, J=8.2, 1.3 Hz, 1H, H6. ^{13}C NMR δ (75 MHz) 15.11 (C4′); 68.60 (C1′); 80.64 (C3′); 124.79 (C6); 128.39, 128.98 (C3,5); 133.72 (C4); 134.12 (C2); 147.36 (C1); 202.28 (CHO).

2-(4-Formyl-2-oxabutyl)nitrobenzene was isolated as a yellow oil (30 mg, 11%) (Found: m/z 123.0320. $(C_{10}H_{11}NO_4-C_4H_6O_2)^+$ requires m/z 123.0321). ν_{max} (film) 2872, 1730, 1613, 1578, 1525, 1448, 1343, 1306, 1106, 858, 792, 730 cm^{-1}. ^{1}H NMR δ (400 MHz) 2.77, td, J=6.0, 1.8 Hz, 2H, H4′; 3.93, t, J=6.0 Hz, 2H, H3′; 4.91, bs, 2H, H1′; 7.40–7.48, m, 2H, H3,5; 7.72–7.75, m, 1H, H4; 8.07, dd, J=8.2, 1.2 Hz, 1H, H6. ^{13}C NMR δ (75 MHz) 43.79 (C4′); 64.85 (C3′); 69.77 (C1′); 124.68 (C6); 128.12, 128.69 (C3,5); 133.68 (C4); 134.58 (C2); 147.36 (C1); 200.62(CHO).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes in a 30:70 ratio.

3.4.4. 2-(4-Formyl-2-thiapentyl)nitrobenzene (4d). Reaction of 2-(2-thiapent-4-enyl)nitrobenzene (400 mg, 1.91 mmol) with H_2/CO (1:1) (1000 psi) at 80°C for 72 h gave the linear and branched aldehydes (ratio 70:30) as a viscous, light brown oil (513 mg). The aldehyde (**4d**) was isolated as a yellow oil (20 mg, 4%). ν_{max} (film) 2932, 2828, 2726, 1723, 1608, 1577, 1525, 1446, 1421, 1348, 1307, 860, 787, 709 cm^{-1}. ^{1}H NMR δ (200 MHz) 1.08, d, J=7.0 Hz, 3H, H5′; 2.37–2.50, m, 2H, and 2.73, m, 1H, H3′,4′; 4.01, s, 2H, H1′; 7.32–7.50, m, 3H, H3,4,5; 7.90, dd, J=8.1, 1.2 Hz, 1H, H6; 9.54, d, J=1.2 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 13.34 (C5′); 32.38, 33.91 (C1′,3′); 45.95 (C4′); 125.25 (C6); 128.27 (C5); 131.82 (C3); 133.02 (C4); 133.64 (C1); 148.57 (C2); 202.86 (CHO). Mass spectrum (EI): m/z 239 (M^+, 1%), 169 (4), 151(30), 136 (32), 135 (50), 121 (41), 120 (59), 108 (38), 96 (28), 92 (93), 78 (100), 77 (60), 65 (98). The spectral data was consistent with literature data.[15]

2-(5-Formyl-2-thiapentyl)nitrobenzene was isolated as a yellow oil (91 mg, 20%). ν_{max} (film) 2934, 2822, 2726, 1720, 1697, 1577, 1526, 1444, 1349, 788, 710 cm^{-1}. ^{1}H NMR δ (200 MHz) 1.88, m, 2H, H4′; 2.48, t, J=7.1 Hz, 2H, H3′; 2.56, td, J=7.1, 1.2 Hz, H5′; 4.05, s, 2H, H1′; 7.39–7.58, m, 3H, H3,4,5; 7.97, dd, J=7.8, 1.3 Hz, 1H, H6; 9.76, t, J=1.2 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 21.41 (C4′); 31.25 (C1′); 33.17 (C3′); 42.37 (C5′); 125.29 (C6); 128.17 (C5); 131.87 (C3); 132.95 (C4); 134.01 (C1); 148.68 (C2); 201.39 (CHO). Mass spectrum (EI): m/z 239 (M^+, 3%), 168 (3), 136 (25), 135 (51), 121 (32), 120 (53), 108 (28), 92 (95), 89 (41), 79 (38), 78 (80), 77 (48), 65 (100).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes in a ratio of 30:70. Purification gave (**4d**) (126 mg, 37%).

3.4.5. 2-(3-Formylpropyloxy)nitrobenzene (4e). Reaction of 2-(prop-2-enyloxy)nitrobenzene (800 mg, 4.47 mmol) at 70°C gave an orange oil (800 mg) whose ^{1}H NMR spectrum indicated a mixture of the linear and branched aldehydes (ratio ca. 1:1) with ca. 5% of 2-nitrophenol.

A similar reaction of the alkene (3.0 g, 16.8 mmol) using PPh_3 gave 2-nitrophenol and the linear and branched aldehydes in a ratio of 2:1:1 respectively. The aldehyde (**4e**) was isolated as a yellow oil (780 mg, 22%). ν_{max} (film) 1721, 1608, 1583, 1522, 1488, 1490, 1352, 1279, 1256, 1166, 774, 746, 667 cm^{-1}. ^{1}H NMR δ (200 MHz) 2.18, approx. pentet, J=6.0 Hz, 2H, H2′; 2.75, t, J=6.9 Hz, 2H, H3′; 4.16, t, J=6.0 Hz, 2H, H1′; 7.01–7.11, m, 2H, H3,5; 7.53, td, J=7.4, 1.7 Hz, 1H, H4; 7.81, dd, J=8.1, 1.7 Hz, 1H, H6; 9.83, t, J=1.0 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 21.34, 39.91 (C2′, 3′); 67.93 (C1′); 114.22 (C3); 120.15 (C5); 125.25 (C6), 134.05 (C4); 141.78 (C1); 153.27 (C2); 201.51 (CHO). Mass spectrum (EI): m/z 209 (M^+, 1%), 179 (2), 162 (3), 139 (12), 123 (9), 106 (25), 92 (25), 81 (52), 72 (70), 71 (100), 65 (13), 63 (45), 52 (28).

3.4.6. 2-(4-Formylpentyloxy)nitrobenzene (4g) and 2-(5-formylpentyloxy)nitrobenzene (4k). Reaction of 2-(pent-4-enyloxy)nitrobenzene (600 mg, 2.9 mmol) using PPh_3 gave the linear and branched aldehydes (ratio 70:30) as an orange oil (670 mg). The aldehyde (**4g**) was isolated as a pale, yellow oil (158 mg, 23%). ν_{max} (film) 2960, 2877, 1723, 1608, 1583, 1525, 1488, 1469, 1353, 1281, 1256, 1165, 1150, 1089, 1044, 1006, 854, 745 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.35, d, J=7.1 Hz, 3H, H5′; 2.43, sextetd, J=6.9, 1.8 Hz, 2H, H4′; 4.11, t, J=5.9 Hz, 2H, H1′; 6.98–7.06, m, 2H, H3,5; 7.5, td, J=8.5, 1.7 Hz, 1H, H4; 7.81, dd, J=8.1, 1.7 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 13.44 (C5′); 26.40, 26.79 (C2′,3′); 45.83 (C4′); 69.17 (C1′); 114.44 (C3);120.32 (C5); 125.57 (C6); 134.04 (C4); 140.02 (C1); 152.24 (C2); 204.70 (CHO).

The aldehyde (**4k**) was isolated as a pale, yellow oil (445 mg, 65%). (Found: C, 60.7; H, 6.7; N, 6.2. $C_{12}H_{15}NO_4$ requires C, 60.8; H, 6.4; N, 5.9%) ν_{max} (film)

2943, 2868, 1719, 1608, 1582, 1523, 1490, 1467, 1390, 1353, 1281, 1256, 1166, 1150, 1089, 1043, 1003, 857, 773, 746 cm^{-1}. ^1H NMR δ (200 MHz) 1.46–1.64, m, 2H, H3′; 1.67–1.75, m, 2H, H4′; 1.85, approx. pentet, J=6.7 Hz, 2H, H2′; 2.49, td, J=6.9, 1.5 Hz, 2H, H5′; 4.11, t, 2H, J=6.2 Hz, 2H, H1′; 6.97–7.09, m, 2H, H3,5; 7.48–7.56, m, 1H, H4; 7.80, dd. J=8.1, 1.7 Hz, 1H, H6; 9.78, t, J=1.6 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 21.42, 25.29, 28.52 (C2′,3′,4′); 43.56 (C5′); 68.98 (C1′); 114.26 (C3); 119.99 (C5); 125.31 (C6); 133.98 (C4); 139.68 (C1); 152.15 (C2); 202.42 (CHO).

A similar reaction under the standard conditions gave (**4k**) and (**4g**) in the ratio 93:7.

3.4.7. 2-(5-Formyl-2-oxapentyl)nitrobenzene (4h). Reaction of 2-(2-oxapent-4-enyl)nitrobenzene (1.0 g, 5.2 mmol) gave the linear and branched aldehydes (ratio 80:20) as a yellow oil (1.10 g). The aldehyde (**4h**) was isolated as an orange oil (324 mg, 28%). ν_{max} (film) 2929, 2871, 2727, 1724, 1613, 1578, 1526, 1479, 1446, 1411, 1341, 1305, 1146, 1114, 1078, 1042, 961, 859, 791, 730 cm^{-1}. ^1H NMR δ (200 MHz) 2.01, pentet, J=6.0, 2H, H2′; 2.60, td, J=6.1, 1.5 Hz, 2H, H3′; 3.62, t, J=6.0 Hz, 2H, H1′; 4.86, s, 2H, $PhCH_2$; 7.44, m, 2H, H3,5; 7.61–7.75, m, 1H, H4; 8.05, dd, J=8.1, 1.1 Hz, 1H, H6; 9.92, t, J=1.5 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 22.41 (C2′); 40.81 (C3′); 69.46, 70.08 ($PhCH_2$, C1′); 124.59 (C6); 127.98, 128.60 (C3,5); 133.58 (C4); 134.84 (C2); 202.08 (CHO).

3.4.8. 2-[(*N*-benzoyl)-4-formylbutylamino]nitrobenzene (4i). Reaction of 2-[(*N*-benzoyl)but-3-enylamino]nitrobenzene (400 mg, 1.35 mmol) gave the linear and branched aldehydes (ratio 90:10) with ca. 17% recovered alkene as a thick, yellow oil (430 mg). The aldehyde (**4i**) was isolated as a yellow, viscous oil (302 mg, 69%). ^{13}C NMR δ (50 MHz): 19.29 (C3′); 27.10 (C2′); 43.28 (C4′); 50.22 (C1′); 125.73, 127.94, 128.30, 128.37, 130.00, 133.89 (C3,4,5,6, PhCH); 202.04 (CHO).

3.4.9. 2-(5-Formyl-1,4-dioxahexyl)nitrobenzene (4j). Reaction of 2-(1,4-dioxahex-5-enyl)nitrobenzene (180 mg, 0.86 mmol) using PPh_3 as ligand gave the linear and branched aldehydes (ratio 30:70) as a viscous, orange oil (225 mg). The aldehyde (**4j**) was isolated as a yellow oil. (145 mg, 73%) (Found: m/z 210.0763. $(C_{11}H_{13}NO_5–CHO)^+$ requires m/z 210.0766). ν_{max} (film) 2933, 1729, 1608, 1583, 1525, 1487, 1451, 1353, 1278, 1256, 1166, 1127, 1046, 924, 852, 745 cm^{-1}. ^1H NMR δ (400 MHz) 1.33, d, J=7.0 Hz, 3H, H6′; 3.97, t, J=4.3 Hz, 2H, H3′; 4.06, qd, J=7.0, 1.2 Hz, 1H, H5′; 4.29, t, J=4.8 Hz, 2H, H2′; 7.01–7.13, m, 2H, H3,5; 7.50–7.55, m, 1H, H4; 7.82, dd, J=7.1, 1.7 Hz, 1H, H6; 9.66, d, J=1.2 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 15.21 (C6′); 68.29, 69.64 (C2′,3′); 81.17 (C5′); 114.98 (C3); 120.88 (C5); 125.71 (C6); 134.13 (C4); 140.39 (C1); 152.18 (C2); 202.74 (CHO).

2-(6-Formyl-1,4-dioxahex-5-enyl)nitrobenzene was isolated as a yellow oil (35 mg, 18%) (Found: m/z 210.0763. $(C_{11}H_{13}NO_5–CHO)^+$ requires m/z 210.0766). ν_{max} (film) 2933, 1729, 1608, 1583, 1525, 1487, 1451, 1353, 1278, 1256, 1166, 1128, 1046, 852, 746 cm^{-1}. ^1H NMR δ (400 MHz) 2.68, td, J=6.0, 1.8 Hz, 2H, H6′; 3.86–3.88, m, 2H, H3′; 3.93, t, J=6.0 Hz, 2H, H5′; 4.23–4.26, m, 2H, H2′; 7.02–7.11, m, 2H, H3,5; 7.51–7.54, m, 1H, H4; 7.84, dd, J=8.1, 1.6 Hz, 1H, H6; 9.78, t, J=1.8 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 43.93 (C6′); 65.41 (C5′); 69.29, 69.63 (C2′,3′); 115.13 (C3); 120.80 (C5); 125.61 (C6); 134.06 (C4); 140.39 (C1); 152.25 (C2); 201.05 (CHO).

A similar ratio of aldehydes was obtained using BIPHEPHOS as ligand

3.4.10. 2-(6-Formyl-1,4-dioxaheptyl)nitrobenzene (4l) and 2-(7-formyl-1,4-dioxaheptyl)nitrobenzene (4m). Reaction of 2-(1,4-dioxahept-6-enyl)nitrobenzene (500 mg, 2.24 mmol) gave the linear and branched aldehydes (ratio 70:30) as a yellow oil (550 mg). The aldehyde (**4l**) was isolated as a yellow oil (101 mg, 18%) (Found: m/z 183.0525±0.002. $(C_{12}H_{15}NO_5–C_4H_6O)^+$ requires m/z 183.0532). ν_{max} (film) 2935, 2877, 1724, 1608, 1584, 1526, 1488, 1452, 1355, 1279, 1256, 1167, 1132, 1096, 1046, 852, 773, 746, 671 cm^{-1}. ^1H NMR δ (400 MHz) 1.09, d, J=7.1 Hz, 3H, H7′; 2.57–2.66, m, 1H, H6′; 3.73–3.78, m, 2H, H5′; 3.81–3.85, m, 2H, H3′; 4.20–4.23, m, 2H, H2′; 6.98–7.04, m, 1H, H5; 7.07–7.09, m, 1H, H3; 7.48–7.52, m, 1H, H4; 7.81, dd, J=8.1, 1.7 Hz, 1H, H6; 9.70, d, J=1.5 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 10.46 (C7′); 46.79 (C6′); 69.41, 69.49 (C3′,4′); 71.64 (C2′); 115.03 (C3); 120.67 (C5); 125.45 (C6); 134.00 (C4); 140.18 (C1); 152.14 (C2); 203.72 (CHO). Mass spectrum $(ESI)^+$: m/z 276.0 $(M+Na)^+$.

The aldehyde (**4m**) was isolated as a yellow oil (348 mg, 61%). (Found: m/z 210.0767. $(C_{12}H_{15}NO_5–C_2H_3O)^+$ requires m/z 210.0766). ν_{max} (film) 2934, 2875, 1722, 1608, 1583, 1526, 1488, 1451, 1356, 1279, 1257, 1166, 1129, 1090, 1046, 852, 774, 746, 670 cm^{-1}. ^1H NMR δ (400 MHz) 1.89, apparent pentet, J=6.6 Hz, 2H, H6′; 2.51, td, J=7.1, 1.5 Hz, 2H, H7′; 3.57, t, J=6.1 Hz, 2H, H5′; 3.78–3.80, m, 2H, H3′; 4.20–4.23, m, 2H, H2′; 6.99–7.04, m, 1H, H5; 7.09, dd, J=8.5, 1.0 Hz, 1H, H3; 7.48–7.52, m, 1H, H4; 7.79, dd, J=8.1, 1.6 Hz, 1H, H6; 9.75, t, J=1.4 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 22.43 (C6′); 40.69 (C7′); 68.82, 69.43 (C3′,5′); 70.51 (C2′); 115.02 (C3); 120.63 (C5); 125.48 (C6); 133.98 (C4); 140.24 (C1); 152.22 (C2); 204.00 (CHO). Mass spectrum (ESI^+): m/z 276.0 $(M+Na)^+$.

3.4.11. 2-[(*N*-Methylsulfonyl)-4-aza-7-formyl-1-oxaheptyl]nitrobenzene (4n). Reaction of 2-[(*N*-methylsulfonyl)-1-oxa-3-azahept-6-enyl]nitrobenzene (400 mg, 1.33 mmol) gave the linear and branched aldehydes (ratio 70:30) as a viscous, yellow oil (448 mg). 2-[(*N*-methylsulfonyl)-4-aza-6-formyl-1-oxaheptyl]nitrobenzene was isolated as a yellow oil which solidified on standing (95 mg, 22%). ν_{max} (CH_2Cl_2) 3054, 2986, 2934, 1725, 1608, 1586, 1527, 1488, 1459, 1422, 1337, 1267, 1149, 1092, 1001 cm^{-1}. ^1H NMR δ (300 MHz) 1.18, d, J=7.2 Hz, 3H, H7′; 2.87–3.02, bs, 4H, SO_2CH_3, H6′; 3.42, dd, J=14.7, 6.0 Hz, 1H and 3.65–3.75, m, 3H, H3′,5′; 4.27–4.33, m, 2H, H2′; 7.05–7.11, m, 2H, H3,5; 7.53–7.58, m, 1H, H4; 7.86, dd, J=8.1, 1.7 Hz, 1H, H6; 9.70, d, J=2.0 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 11.91 (C7′); 38.43 (SO_2CH_3); 46.03, 47.90, 49.65 (C3′,5′,6′); 68.88 (C2′); 114.52 (C3); 121.19

(C5); 125.79 (C6); 134.44 (C4); 139.88 (C1); 151.54 (C2); 203.39 (CHO).

The aldehyde (**4n**) was isolated as a yellow oil which solidified on standing (290 mg, 66%). (Found: *m/z* 273.0576±0.002. $(C_{13}H_{18}N_2O_6S-C_3H_5O)^+$ requires *m/z* 273.0545). ν_{max} (CH_2Cl_2) 3061, 2932, 2877, 1725, 1608, 1585, 1528, 1488, 1459, 1337, 1270, 1260, 1149, 1001 cm^{-1}. ^1H NMR δ (300 MHz) 1.97, pentet, *J*=7.0 Hz, 2H, H6′; 2.57, td, *J*=6.9, 0.9 Hz, 2H, H7′; 2.89, s, 3H, CH_3; 3.36–3.41, m, 2H, H5′; 3.67, t, *J*=5.2 Hz, 2H, H3′; 4.31, t, *J*=5.2 Hz, 2H, H2′; 7.05–7.12, m, 2H, H3,5; 7.53–7.58, m, 1H, H4; 7.85, dd, *J*=8.0, 1.7 Hz, 1H, H6; 9.79, t, *J*=1.0 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 20.92 (C6′); 38.56 (CH_3); 40.48 (C7′); 46.94, 48.30 (C3′,5′); 68.85 (C2′); 114.48 (C3); 121.16 (C5); 125.78 (C6); 134.39 (C4); 139.96 (C1); 151.58 (C2); 201.27 (CHO).

3.4.12. 2-(9-Formyl-1,4,7-trioxadecyl)nitrobenzene (4o) and 2-(10-formyl-1,4,7-trioxadecyl)nitrobenzene (4p). Reaction of 2-(1,4,7-trioxadec-9-enyl)nitrobenzene (500 mg, 1.87 mmol) gave the linear and branched aldehydes (ratio 83:17) as a viscous yellow oil (590 mg). The aldehyde (**4o**) was isolated as a yellow oil (93 mg, 17%).^1H NMR δ (200 MHz) 1.11, d, *J*=7.1 Hz, 3H, H10′; 2.61–2.75, m, 1H, H9′; 3.61–3.69, m, 2H and 3.72–3.76, m, 2H and 3.88–3.92, m, 2H, H3′,5′,6′; 4.24–4.28, m, 2H, H2′; 6.99–7.13, m, 2H, H3,5; 7.49–7.57, m, 1H, H4; 7.83, dd, *J*=8.1, 1.7 Hz, 1H, H6; 9.72, d *J*=1.5 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 10.58 (C10′); 46.72 (C9′); 69.30, 69.43, 69.61, 70.79, 70.95, 71.24 (C2′,3′,5′,6′,8′); 114.93 (C3); 120.57 (C5); 125.51 (C6); 134.04 (C4); 140.11 (C1); 152.22 (C2); 203.99 (CHO).

The aldehyde (**4p**) was isolated as a yellow oil (435 mg, 78%). (Found: C, 56.4; H, 6.6, N, 4.8. $C_{14}H_{19}NO_6$ requires C, 56.6; H, 6.4; N, 4.7%). ν_{max} (film) 2931, 2877, 1723, 1608, 1584, 1526, 1488, 1453, 1357, 1279, 1256, 1166, 1132, 1046, 1001, 926, 852, 774, 746 cm^{-1}. ^1H NMR δ (200 MHz) 1.92, pentet, *J*=6.2 Hz, 2H, H9′; 2.53, td, *J*=6.1, 1.6 Hz, 2H, H10′; 3.51, t, *J*=6.1 Hz, 2H, H8′; 3.56–3.63, m, 2H and 3.69–3.75, m, 2H, and 3.88–3.93, m, 2H, H3′,5′,6′; 4.27, m, 2H, H2′; 6.99–7.14, m, 2H, H 3,5; 7.48–7.57, m, 1H, H4; 7.83, dd, *J*=8.07, 1.7 Hz, 1H, H6; 9.77, t, *J*=1.6 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 22.42 (C9′); 40.83 (C10′); 69.27, 69.60, 70.10, 70.18, 71.06 (C2′,3′,5′,6′,8′); 114.89 (C3); 120.57 (C5); 125.54 (C6); 134.06 (C4); 140.09 (C1); 152.24 (C2); 202.42 (CHO).

3.4.13. 2-(10-Formylundecyloxy)nitrobenzene (4q) and 2-(11-formylundecyloxy)nitrobenzene (4r). Reaction of 2-(undec-10-enyloxy)nitrobenzene (300 mg, 1.0 mmol) gave the linear and branched aldehydes (ratio 90:10) as a yellow oil (354 mg). The aldehyde (**4q**) was isolated as a yellow oil (32 mg, 10%) (Found: *m/z* 344.1835. $(C_{18}H_{27}NO_4+Na)^+$ requires *m/z* 344.1838). ν_{max} (film) 2930, 2856, 1724, 1608, 1583, 1526, 1489, 1466, 1353, 1281, 1256, 1165, 746 cm^{-1}. ^1H NMR δ (400 MHz) 1.08, d, *J*=7.0 Hz, 3H, H11′; 1.30, bs, 12H, H3′,4′,5′,6′,7′,8′; 1.44–1.49, m, 2H, H9′; 1.79–1.86, m, 2H, H2′; 2.29–2.30, m, 1H, H10′; 4.09, t, *J*=6.4 Hz, 2H, H1′; 6.97–7.01, m, 1H, H5; 7.06, dd, *J*=8.5, 0.9 Hz, 1H, H3; 7.47–7.52, m, 1H, H4; 7.80, dd, *J*=8.1, 1.7 Hz, 1H, H6; 9.61, d, *J*=2.0 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz): 13.35 (C11′); 25.85, 26.94, 28.88 (C3′,8′,9′); 29.17, 29.27, 29.44, 29.59 (C 2′,4′,6′,7′); 30.55 (C2′); 46.34 (C10′); 69.67 (C1′); 114.48 (C3); 120.03 (C5); 125.51 (C6); 133.92 (C4); 140.13 (C1); 152.51 (C2); 205.38 (CHO).

The aldehyde (**4r**) was isolated as a yellow oil (225 mg, 70%) (Found: *m/z* 344.1839. $(C_{18}H_{27}NO_4+Na)^+$ requires *m/z* 344.1838). ν_{max} (film) 2927, 2854, 1724, 1608, 1583, 1526, 1489, 1467, 1353, 1281, 1256, 746 cm^{-1}. ^1H NMR δ (200 MHz) 1.29, bs, 14H, H3′,4′,5′,6′,7′,8′,9′; 1.62–1.65, m, 2H, H10′; 1.75–1.85, m, 2H, H2′; 2.42, td, *J*=7.2, 1.7 Hz, 2H, H11′; 4.09, t, *J*=6.4 Hz, 2H, H1′; 6.95–7.10, m, 2H, H3,5; 7.51, td, *J*=7.5, 1.7 Hz, 1H, H4; 7.79, dd, *J*=8.1, 1.6 Hz, 1H, H6; 9.76, t, *J*=1.7 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 21.87, 25.63, 28.74, 28.94, 29.03, 29.15, 29.18, 29.25, 30.21 (C2′,3′,4′,5′,6′,7′,8′,9′,10′); 43.70 (C11′); 69.37 (C1′); 114.25 (C3); 119.78 (C5); 125.23 (C6); 133.88 (C4); 139.69 (C1); 152.27 (C2); 202.78 (CHO).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes (**4q**) and (**4r**) in the ratio 70:30.

3.4.14. 3-(3-Formylbutyloxy)nitrobenzene (4s) and 3-(4-formylbutyloxy)nitrobenzene (4t). Reaction of 3-(but-3-enyloxy)nitrobenzene (300 mg, 1.55 mmol) gave the linear and branched aldehydes (ratio 90:10) as an orange oil (364 mg). The aldehyde (**4s**) was isolated as a pale, yellow oil (17 mg, 5%). (Found: *m/z* 223.0846±0.003. $(C_{11}H_{13}NO_4)^+$ *m/z* 223.0845). ν_{max} (film) 2943, 2866, 1721, 1608, 1582, 1524, 1489, 1469, 1353, 1281, 1256, 1166, 1150, 1089, 1044, 1003, 857, 773, 745 cm^{-1}. ^1H NMR δ (200 MHz) 1.21, d, *J*=7.2 Hz, 3H, H4′; 1.75–1.94, m, 1H and 2.11–2.28, m, 1H, H2′; 2.50–2.65, m, 1H, H3′; 4.03, t, *J*=6.1 Hz, 2H, H1′; 7.08–7.14, m, 1H, H4; 7.33, t, *J*=8.1 Hz, 1H, H5; 7.56–7.58, m, 1H, H6; 7.66–7.71, m, 1H, H2; 9.64, d, *J*=1.4 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 13.06 (C4′); 29.48 (C2′); 43.17 (C3′); 65.72 (C1′); 108.50 (C3); 115.51 (C5); 121.21 (C6); 129.77 (C4); 148.82(C1); 158.89 (C2); 203.77 (CHO).

The aldehyde (**4t**) was isolated as a yellow oil (280 mg, 81%). (Found: *m/z* 223.0843±0.003. $(C_{11}H_{13}NO_4)^+$ *m/z* 223.0845). ν_{max} (film) 2944, 2867, 1722, 1608, 1582, 1525, 1489, 1466, 1352, 1281, 1256, 1166, 1150, 1089, 1044, 1002, 857, 773, 746 cm^{-1}. ^1H NMR δ (200 MHz) 1.72–1.82, m, 4H, H2′, 3′; 2.45–2.52, m, 2H, H4′; 3.93–3.99, m, 2H, H1′: 7.09–7.15, m, 1H, H4; 7.33, t, *J*=8.1 Hz, 1H, H5; 7.58–7.60, m, 1H, H6; 7.67- 7.72, m, 1H, H2; 9.72, t, *J*=1.4 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 18.52, 28.23 (C2′,3′); 43.24 (C4′); 67.98 (C1′); 108.54 (C3); 115.49 (C5); 121.39 (C6); 129.82 (C4); 148.97 (C1); 159.28 (C2); 201.97 (CHO).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes (**4s**) and (**4t**) in the ratio 55:45.

3.4.15. 4-(4-Formylbutyloxy)nitrobenzene (4u). Reaction of 4-(but-3-enyloxy)nitrobenzene (500 mg, 2.59 mmol) gave the linear and branched aldehydes (ratio 94:6) as a

viscous, yellow oil (574 mg). 4-(3-Formylbutyloxy)nitrobenzene was isolated as a yellow liquid (23 mg, 4%). (Found: *m/z* 209.0698±0.002. $(C_{11}H_{13}NO_4-CH_2)^+$ requires *m/z* 209.0688). ν_{max} (film) 2936, 1725, 1594, 1514, 1341, 1299, 1263, 1174, 1111, 847, 753 cm^{-1}. ^1H NMR δ (400 MHz) 1.20, d, *J*=7.2 Hz, 3H, H4′; 1.86–1.94, m, 1H and 2.22–2.30, m, 1H, H2′; 2.62–2.67, m, 1H, H3′; 3.60, t, *J*=6.2 Hz, 2H, H1′; 6.92, dd, *J*=9.3, 2.2 Hz, 2H, H3,5; 8.16, dd, *J*=9.3, 2.2 Hz, 2H, H2,6; 9.69, d, *J*=1.4 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 13.41 (C4′); 29.69 (C3′); 43.32 (C2′); 66.10 (C1′); 114.42 (C3,5); 125.88 (C2,6); 141.63 (C1); 163.61 (C4); 203.67 (CHO).

The aldehyde (**4u**) was isolated as a yellow oil (461 mg, 80%). ν_{max} (film) 2944, 1722, 1593, 1514, 1471, 1338, 1299, 1263, 1174, 1111, 846, 753, 654 cm^{-1}. ^1H NMR δ (400 MHz) 1.78–1.88, m, 4H, H2′,3′; 2.53, td, *J*=7.0, 1.4 Hz, 2H, H4′; 4.05, t, *J*=5.9 Hz, 2H, H1′; 6.91, d, *J*=9.3, 2.2 Hz, 2H, H3,5; 8.14, d, *J*=9.3, 2.2 Hz, 2H, H 2,6; 9.78, t, *J*=1.5 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 18.56 (C3′); 28.31 (C2′); 43.28 (C4′); 68.25 (C1′); 114.35 (C3,5); 125.82 (C2,6); 141.40 (C1); 163.93 (C4); 201.81 (CHO).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes in the ratio 55:45.

3.4.16. 4-(7-Formyl-1,4-dioxaheptyl)nitrobenzene (4v). Reaction of 4-(1,4-dioxahept-6-enyl)nitrobenzene (500 mg, 0.23 mmol) gave the linear and branched aldehydes (ratio 70:30) as an orange oil (300 mg). 4-(6-Formyl-1,4-dioxaheptyl)nitrobenzene was isolated as a yellow oil (100 mg, 18%) (Found: *m/z* 183.0532±0.002. $(C_{12}H_{15}NO_5-C_4H_6O)^+$ requires *m/z* 183.0532). ν_{max} (film) 2934, 2878, 1723, 1608, 1594, 1514, 1455, 1342, 1300, 1264, 1175, 1111, 1053, 847, 752, 658 cm^{-1}. ^1H NMR δ (300 MHz) 1.14, d, *J*=7.2 Hz, 3H, H8′; 2.65–2.71, m, 1H, H6′; 3.83–3.86, m, 2H, H3′; 4.19–4.22, m, 2H, H2′; 6.97, dd, *J*=9.3, 2.2 Hz, 2H, H3,5; 8.19, dd, *J*=9.3, 2.2 Hz, 2H, H2,6; 9.72, d, *J*=1.5 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 10.70 (C7′); 46.75 (C6′); 68.09, 69.53 (C3′,5′); 71.52 (C2′); 114.63 (C3,5); 125.91 (C2,6); 141.76 (C1); 163.81 (C2); 203.42 (CHO).

The aldehyde (**4v**) was isolated as a yellow oil (340 mg, 60%). (Found: *m/z* 210.0769±0.002. $(C_{12}H_{15}NO_5-C_2H_3O)^+$ requires *m/z* 210.0766). ν_{max} (film) 2929, 2872, 1721, 1608, 1594, 1513, 1341, 1299, 1264, 1175, 1111, 1052, 847, 753, 657 cm^{-1}. ^1H NMR δ (300 MHz) 1.90–1.99, m, 2H, H6′; 2.55, td, *J*=7.0, 1.5 Hz, 2H, H7′; 3.58, t, *J*=6.1 Hz, 2H, H5′; 3.78–3.81, m, 2H, H3′; 4.16–4.21, m, 2H, H2′; 6.98, dd, *J*=9.3, 2.2 Hz, 2H, H3,5; 8.20, dd, *J*=9.4, 2.3 Hz, 2H, H2,6; 9.78, t, *J*=1.5 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 22.44 (C6′); 40.77 (C7′); 68.17, 68.92 (C3′,5′); 70.48 (C2′); 114.62 (C3,5); 125.90 (C2,6); 141.74 (C1); 163.86 (C4); 201.94 (CHO).

A similar reaction using PPh_3 as ligand gave the linear and branched aldehydes in the ratio 30:70.

3.4.17. 4-(10-Formyl-1,4,7-trioxadecyl)nitrobenzene (4w). Reaction of 4-(1,4,7-trioxadec-9-enyl)nitrobenzene (500 mg, 1.9 mmol) gave to the linear and branched aldehydes (ratio 70:30) as an orange oil (570 mg). 4-(9-Formyl-1,4,7-trioxadecyl)nitrobenzene was isolated as a yellow oil. (90 mg, 16%) (Found: C, 56.9; H, 6.1; N, 5.2. $C_{14}H_{19}NO_6$ requires C, 56.6; H, 6.4; N, 4.7%). (Found: *m/z* 227.0791±0.002. $(M-C_4H_6O)^+$ requires *m/z* 227.0794). ν_{max} (film) 2876, 1723, 1608, 1540, 1514, 1342, 1264, 1111, 848, 753 cm^{-1}. ^1H NMR δ (400 MHz) 1.12, d, *J*=7.1 Hz, 3H, H10′; 2.61–2.68, m, 1H, H9′; 3.63–3.74, m, 6H and 3.86–3.89, m, 2H, H 3′,5′,6′,8′; 4.21–4.22, m, 2H, H2′; 6.99, dd, *J*=9.3, 2.2 Hz, 2H, H3,5; 8.46, dd, *J*=9.3, 2.2 Hz, 2H, H 2,6; 9.72, d, *J*=1.6 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 10.57 (C10′); 46.69 (C9′); 68.13, 69.38 (C5′,6′,8′); 71.07, 71.26 (C2′,3′); 114.57 (C3,5); 125.78 (C2,6); 141.57 (C1); 163.84 (C4); 203.70 (CHO).

The aldehyde (**4w**) was isolated as a yellow oil (352 mg, 62%). (Found: C, 56.8; H, 6.2; N, 4.9%. $C_{14}H_{19}NO_6$ requires C, 56.6; H, 6.4; N, 4.7%). ν_{max} (film) 2877, 1720, 1594, 1517, 1458, 1343, 1300, 1264, 1175, 1111, 1054, 849, 753 cm^{-1}. ^1H NMR δ (200 MHz) 1.92, pentet, *J*=6.1 Hz, 2H, H9′; 2.52, td, *J*=6.0, 1.5 Hz, 2H, H10′; 3.51, t, *J*=6.1 Hz, 2H, H8′; 3.57–3.61, m, 2H and 3.67–3.72, m, 2H and 3.88–3.90, m, 2H, H3′,5′,6′; 4.22–4.24, m, 2H, H2′; 6.98, dd, *J*=9.3, 2.1 Hz, 2H, H3,5; 8.19, dd, *J*=9.3, 2.1 Hz, 2H, H 2,6; 9.77, t, *J*=1.6 Hz, 1H, CHO. ^{13}C NMR δ (75 MHz) 22.50 (C9′); 40.83 (C10′); 68.24, 69.39 70.17, 70.21, 70.89 (C2′,3′,5′,6′,8′); 114.61 (C3,5); 125.84 (C2,6); 141.65 (C1); 163.88 (C4); 202.14 (CHO).

3.4.18. *N*-Benzyl-2-(11-formylundecyloxy)aniline (10). Reaction of *N*-benzyl-2-(undec-10-enyl-oxy)aniline (80 mg, 0.23 mmol) gave the linear aldehyde as a viscous, yellow oil (93 mg). Purification gave (**10**) as a viscous, yellow oil (50 mg, 58%). ^1H NMR δ (200 MHz) 1.30, bs, 14H, H 3′,4′,5′,6′,7′,8′,9′; 1.50–1.68, m, 2H, H 10′; 1.75–1.86, m, 2H, H2′; 2.43, td, *J*=7.3, 1.8 Hz, 2H, H11′; 4.02, t, *J*=6.5 Hz, 2H, H1′; 4.39, s, 2H, PhCH_2; 4.70, bs, 1H, NH; 6.58–6.71, m, 2H, H4,6; 6.70–6.87, m, 2H, H3,5; 7.27–7.43, m, 5H, PhH; 9.77, t, *J*=1.8 Hz, 1H, CHO. ^{13}C NMR δ (50 MHz) 22.04, 26.13, 28.68, 29.13, 29.31, 29.47, 29.51 (C 2′, 3′, 4′, 5′, 6′, 7′, 8′, 9′, 10′); 43.88 (C11′); 47.98 (PhCH$_2$); 110.24, 110.45, 116.63, 121.09 (C3,4,5,6); 127.01, 127.29, 128.30, 128.53 (PhCH); 138.13, 139.67 (C2 and PhC); 146.19 (C1); 202.92 (CHO). Mass spectrum (ESI^+): *m/z* 382.2 $(M+H)^+$.

3.4.19. 2-{7-[2-(3-Formylpropyloxy)phenyl]-1,4,7-trioxaheptyl}nitrobenzene (7). Reaction of 2-{1,4,7-trioxa-7-[2-prop-2-enyloxy)phenyl]heptyl}nitrobenzene (550 mg, 1.5 mmol) gave the linear aldehyde (**7**) and 2-[7-(2-hydroxyphenyl)-1,4,7-trioxaheptyl]nitrobenzene (ratio 1:1) as a viscous, orange oil (575 mg). The aldehyde (**7**) was isolated as a yellow oil (235 mg, 40%). (Found: *m/z* 412.1372. $(C_{20}H_{23}NO_7+Na)^+$ requires *m/z* 412.1372). ν_{max} (film) 2928, 1720, 1608, 1525, 1503, 1452, 1353, 1277, 1255, 1125, 1048, 744 cm^{-1}. ^1H NMR δ (400 MHz) 2.14, pentet, *J*=6.0 Hz, 2H, H2‴; 2.68, td, *J*=7.0, 1.5 Hz, 2H, H3‴; 3.97–4.02, m, 4H, H3′,5′; 4.05, t, *J*=6.0 Hz, 2H, H1‴; 4.17–4.19, m, 2H and 4.29–4.31, m, 2H, H2′,6′; 6.88–6.95, m, 4H, ArCH; 7.02–7.06, m, 1H, H5; 7.14, dd, *J*=8.5, 1.1 Hz, 1H, H3; 7.49–7.54, m, 1H, H4; 7.83, dd, *J*=8.1, 1.7 Hz, 1H, H6; 9.86, t, *J*=1.5 Hz, 1H, CHO. ^{13}C NMR δ (100 MHz) 22.33 (C2‴); 40.67 (C3‴); 68.21, 68.94, 69.54, 69.76, 70.36 (C2′,3′,5′,6′,1‴); 114.49, 114.75,

115.09 (C3,ArCH); 120.65, 121.58, 121.65 (C5,ArCH); 125.52 (C6); 134.03 (C1); 148.92, 148.94 (ArC); 152.28 (C2); 202.23 (CHO).

Further elution gave 2-[7-(2-hydroxyphenyl)-1,4,7-trioxaheptyl]nitrobenzene as a yellow oil. (269 mg, 45%). ν_{max} (film) 3356, 2935, 2876, 1608, 1584, 1528, 1486, 1450, 1352, 1278, 1256, 1166, 1132, 1092, 1044, 852, 746, 670 cm^{-1}. ^1H NMR δ (400 MHz) 3.65, t, J=5.8 Hz, 2H and 3.86, t, J=5.3 Hz, 2H, H3′,5′; 3.92–3.96, m, 2H and 4.26–4.29, m, 2H, H2′,6′; 6.86–6.94, m, 2H, ArCH; 7.00–7.06, m, 2H, H5, ArCH; 7.11, d, J=8.5 Hz, 2H, H3, ArCH; 7.49–7.54, m, 1H, H4; 7.83, dd, J=8.0, 1.6 Hz, 1H, H6. ^{13}C NMR δ (100 MHz) 43.01 (C5′); 69.41, 69.78; 71.89 (C2′,3′,6′); 115.11, 115.45 (C3,ArCH); 120.63, 121.53 (C5,ArCH) 125.52, 125.56 (C6,ArCH); 134.01 (C4); 149.58 (ArC,C1); 152.23 (C2).

3.5. Hydrogenation reactions using 10% Pd/C or PtO_2

Reactions were carried out using standard apparatus for atmospheric pressure hydrogenation (1 atm~15 psi, 0.1 mPa) at ambient temperature (15–20°C) for 24 h in MeOH (50–100 ml) with usually 100 mg substrate and 60 mg PtO_2 or 10% Pd/C (ratio of substrate:catalyst 0.83:1 to 20:1). The catalyst was removed by filtration through a Celite pad and the filter pad washed with MeOH (20 ml) and CH_2Cl_2 (20 ml). The crude product obtained after removal of the solvent under vacuum was purified by flash chromatography on silica (eluent: 5% EtOAc/light petroleum) with monomeric products having a higher R_f value than the corresponding dimers.

Reactions leading to cyclised products were repeated at least once and gave product ratios with ±5% reproducibility.

3.5.1. 3,4,5,6-Tetrahydro-2H-1,6-benzoxazocine (5e) and 7,8,9,10,17,18,19,20-octahydro-6H,16H-dibenzo[*b*,*j*][1,9,4,12]dioxadiazacyclohexadecine (6e). A typical procedure involved reaction of a mixture of 2-(3-formylpropyloxy)nitrobenzene (**4e**) (100 mg, 0.48 mmol) and 10% Pd/C (60 mg) in MeOH (100 ml) with H_2 (1 atm) at ambient temperature for 24 h. Following filtration to remove the catalyst, the solvent was removed under reduced pressure to give a yellow residue (70 mg). Flash chromatography (silica, 5% EtOAc/light petroleum) gave the benzoxazocine (**5e**) as a yellow oil (26 mg, 33%). (Found: m/z 163.100±0.002. $C_{10}H_{13}NO$ requires m/z 163.099). ν_{max} (Nujol) 3052, 2929, 1602, 1513, 1445, 1279, 1260, 1258, 1105, 1048, 762 cm^{-1}. ^1H NMR δ (200 MHz) 1.80–2.05, m, 4H, H3,4; 3.20, t, J=6.6 Hz, 2H, H5; 4.04, t, J=5.4 Hz, 2H, H2; 6.60–6.77, m, 3H, H7,9,10; 6.85, td, J=7.5, 1.6 Hz, 1H, H8. ^{13}C NMR δ (100 MHz) 26.43, 26.55 (C3,4); 42.54 (C5); 67.54 (C2); 109.48, 109.83 (C7,10); 116.02 (C9); 121.26 (C8); 138.63 (C6a); 146.22 (C10a). Mass spectrum (EI): m/z 163 (M^+, 60%), 162(53), 149(11), 148(17), 134(31), 133(12), 132(14), 122(21), 121(16), 120(100), 106(15), 92(21), 91(20), 77(22), 65(30), 55(30). Spectral data was in accordance with that described in the literature.[38]

Further elution gave the dimer (**6e**) as a yellow solid (7 mg, 8%) mp 162.9–163.8°C. (Found: C, 73.5; H 7.7; N, 8.6. $C_{20}H_{26}N_2O_2$ requires C, 73.8; H, 7.7; N, 8.6%). ν_{max} (Nujol) 3052, 2933, 2874, 1603, 1513, 1260, 1250, 1221, 1134, 1140, 761, 744, 738, 711, 698 cm^{-1}. ^1H NMR δ (300 MHz) 1.90–2.10, m, 8H, H7,8,17,18; 3.18, t, J=5.5 Hz, 4H, H9,19, 4.03, t, J=5.1 Hz, 4H, H6,16; 6.59, dd, J=7.7, 1.5 Hz, H1,11; 6.64, td, J=7.6, 1.4 Hz, 2H, H3,13; 6.75, dd, J=7.8, 1.3 Hz, 2H, H4,14; 6.87, td, J=7.6, 1.4 Hz, 2H, H2,12. ^{13}C NMR δ (100 MHz) 26.27, 27.15 (C7,8,17,18); 43.57 (C9,19); 67.39 (C6,16); 107.83, 109.94 (C1,4,11,14); 114.16, 116.46 (C3,13); 121.21 (C2,12); 137.99 (C10a,20a); 145.99 (C4a,14a). Mass spectrum (EI): m/z 326 (M^+, 19%), 253(5), 218(5), 210(8), 198(5), 176(5), 165(12), 164(100), 163(80), 162(55), 134(12), 122(28), 121(10), 120(55), 109(18), 93(13), 80(12), 77(19), 65(19), 55(28).

3.5.2. 3-Methyl-2,3,4,5-tetrahydro-1H-benzazepine (5a). Reaction of 2-(3-formylbutyl)nitrobenzene (**4a**) (100 mg, 0.48 mmol) and 10% Pd/C in MeOH (101 ml) gave a yellow oil (86 mg). Purification gave the benzazepine (**5a**) as a yellow oil (52 mg, 67%). (Found: C, 81.7, H, 9.6, N, 8.7. $C_{11}H_{15}N$ requires C, 81.9, H, 9.4, N, 8.7%). ^1H NMR δ (400 MHz) 0.92, d, J=6.6 Hz, 3H, CH_3; 1.10–1.20, m, 1H, H3; 1.82–1.93, m, 2H, H4; 2.49, dd, J=12.7, 9.5 Hz, 1H and 3.20, dd, J=12.7, 3.3 Hz, 1H, H2; 2.70–2.82, m, 2H, H5; 3.50, bs, 1H, NH; 6.70, dd, J=7.8, 1.0 Hz, 1H, H9; 6.81, td, J=7.4, 1.2 Hz, 1H, H7; 7.02, td, J=7.4, 1.5 Hz, 1H, H8; 7.08, dd, 7.4, 1.3 Hz, 1H, H6; ^{13}C NMR δ (100 MHz) 19.75 (CH_3); 33.96, 34.93, 36.59 (C3,4,5); 55.41 (C2); 119.16, 120.89 (C7,9); 126.59 (C8); 130.62 (C6); 133.53 (C5a); 150.24 (C9a). Mass spectrum (ESI^+): m/z 161.7 $(M+H)^+$.

3.5.3. 3-Methyl-1,2,3,5-tetrahydro-4,1-benzoxazepine (5b). Reaction of 2-(3-formyl-2-oxabutyl)nitrobenzene (**4b**) (86 mg, 0.41 mmol) and 10% Pd/C (52 mg) in MeOH (86 ml) gave a white solid (68 mg). Purification gave the benzoxazepine as (**5b**) as a yellow crystalline solid (37 mg, 56%) mp 62.3–64.7°C. (Found: C, 73.5; H, 8.2; N, 8.6. $C_{10}H_{12}NO$ requires C, 73.6; H, 8.0; N, 8.6%). ν_{max} (CH_2Cl_2): 3380, 3053, 2975, 2949, 2884, 2840, 1606, 1590, 1503, 1483, 1442, 1371, 1314, 1280, 1260, 1096 cm^{-1}. ^1H NMR δ (300 MHz) 1.20, d, J=6.4 Hz, 3H, CH_3; 2.76, dd, J=13.3, 9.1 Hz, 1H and 3.22, dd, J=13.2, 1.8 Hz, 1H, H2, 3.71–3.78, m, 1H, H3; 3.94, bs, 1H, NH; 4.55, d, J=13.4 Hz, 1H and 4.71, d, J=13.4 Hz, 1H, H5; 6.76–6.78, m, 1H and 6.83–6.87, m, 1H, H7,9; 7.10–7.15, m, 2H, H6,8. ^{13}C NMR δ (100 MHz) 19.36 (CH_3); 55.52 (C2); 73.12 (C5); 78.08 (C3); 118.41 (C9); 120.61 (C7); 128.46, 129.43 (C6,8); 130.31 (C5a); 149.79 (C9a). Mass spectrum (ESI^+): m/z 164.0 $(M+H)^+$.

3.5.4. 4-Methyl-3,4,5,6-tetrahydro-2H-1,6-benzoxazocine (5c) and 8,18-dimethyl-7,8,9,10,17,18,19,20-octahydro-6H,16H-dibenzo[*b*,*j*][1,9,4,12]dioxadiazacyclohexadecine (6c). Reaction of 2-(3-formylbutyloxy)nitrobenzene (**4c**) (150 mg, 0.67 mmol) and 10% Pd/C in MeOH (150 ml) gave a pink solid (132 mg). HPLC analysis indicated that the cyclohexadecine (**6c**) and the benzoxazocine (**5c**) were present in a ratio of 5:3, respectively. The benzoxazocine (**5c**) was isolated as a colourless film (16 mg, 14%) mp (HCl salt) 162.3–166.1°C. (Found: C, 74.4; H, 8.5; N, 7.9. $C_{11}H_{15}NO$ requires C, 74.6; H, 8.5; N, 7.9%). HPLC 46.79 min (40–100% CH_3CN/H_2O). ν_{max}

(film) 3416, 2854, 2869, 1602, 1502, 1456, 1382, 1354, 1248, 1193, 1112, 1048, 1017, 975, 753, 736 cm^{-1}. ^1H NMR δ (200 MHz) 0.99, d, J=6.9 Hz, 3H, CH_3; 1.44–1.69, m, 1H and 1.71–1.83, m, 1H, H3; 1.95–2.06, m, 1H, H4; 3.25, dd, J=14.3, 6.5 Hz, 1H and 3.74, dd, J=14.3, 4.6 Hz, 1H, H5; 4.07, ddd. J=11.4, 8.3, 3.3 Hz, 1H and 4.20, ddd, J=11.4, 6.5, 3.7 Hz, 1H, H2; 6.54–6.63, 2H, H 7,9; 6.87, td, J=6.5, 1.5 Hz, 2H, H8,10. ^{13}C NMR δ (50 MHz) 19.11 (CH_3); 31.16 (C3); 35.72 (C4); 49.78 (C5); 73.37 (C2); 116.33, 117.60 (C7,10); 124.59, 124.79 (C8,9); 138.54 (C6a); 146.02 (C10a). Mass spectrum (EI): m/z 177 (M^+, 68%), 176 (M^+-1, 28), 162(3), 149(13), 148(12), 134(30), 133(10), 132(20), 122(28), 121(15), 120(100), 106(10), 93(12), 77(13), 65(31), 55(33).

The dimer (**6c**) was isolated as a white solid (42 mg, 36%) mp 183.9–186.8°C. (Found: C, 74.2; H, 8.4; N, 7.9. $C_{22}H_{30}N_2O_2$ requires C, 74.6; H, 8.5; N, 7.9%). HPLC 43.2 and 43.8 min (40–100% CH_3CN/H_2O). ν_{max} (Nujol) 3054, 1604, 1513, 1265, 1248, 1217, 1114, 1047, 994, 896, 738, 705 cm^{-1}. ^1H NMR δ (400 MHz) 1.07, d, J=7.0 Hz, 3H and 1.08, d, J=7.1 Hz, 3H, 2×CH_3; 1.50–1.57, m, 1H 1.62–1.74, m, 1H, 2.21–2.27, m, 1H and 2.34–2.39, m, 1H, H7,17; 2.06–2.09, m, 2H, H8,18; 2.84–2.96, m, 2H and 3.03–3.06, m, 2H, H9,19; 3.96–4.02, m, 2H, 4.04–4.06, m, 1H and 4.07–4.11, m, 1H, H6,16; 4.22, bs, 1H and 4.41, bs, 1H, NH; 6.55–6.66, m, 4H, 6.73–6.81, m, 2H and 6.85–6.89, m, 2H, H1,2,3,4,11,12,13,14. ^{13}C NMR δ (100 MHz) 19.01,19.07 (CH_3); 31.32, 31.33 (C8,18); 34.44, 34.85 (C7,17); 49.81 (C9,19); 65.23, 65.78 (C6,16); 109.06, 109.18, 109.69, 109.90, 115.90, 116.03, 121.11, 121.27 (C1,2,3,4,11,12, 13,14); 138.33, 138.64 (C10a,20a); 145.92, 146.33 (C4a,14a). Mass spectrum (EI): m/z 354 (M^+, 12%), 179(15), 178 (100), 177(90), 176(50), 134(15), 122(35), 120(50), 93(10), 60(10), 77(18), 65(18), 55(18).

A similar reaction of (**4c**) (163 mg, 0.73 mmol) and 10% Pd/C (17 mg) in MeOH (35 ml) gave a white solid (99 mg). HPLC analysis of the crude indicated the cyclohexadecine (**6c**) and the benzoxazocine (**5c**) were present in a ratio of 4:1 with the dimeric compound (**6c**) being present as a mixture of two isomers, possibly *meso* and *racemic*. Purification of the crude gave (**5c**) as a yellow liquid (31 mg, 26%) followed by (**6c**) as a white solid (48 mg, 37%). The HCl salt of the monomer (**5c**) was prepared from ether/HCl (1.3 M).

3.5.5. 3-Methyl-1,3,4,6-tetrahydro-2H-5,1-benzothiazocine (5d). Reaction of 2-(4-formyl-2-thiapentyl)nitrobenzene (**4d**) (50 mg, 0.21 mmol) and PtO_2 (30 mg) in MeOH (47 ml) gave a dark brown residue (40 mg). Purification gave the thiazocine (**5d**) as a yellow oil (6 mg, 20%). ν_{max} (film) 3082, 3046, 3016, 2927, 2854, 1672, 1634, 1608, 1584, 1489, 1452, 1404, 1281, 1252, 1165, 1090, 1047, 1007, 924, 860 cm^{-1}. ^{13}C NMR δ (50 MHz) 18.56 (CH_3); 33.62, 34.73 (C3,4); 40.08 (C2); 51.59 (C6); 118.28, 119.89, 128.21, 132.33 (C7,8,9,10); 122.30 (C6a); 148.10 (C10a). Mass spectrum (ESI^+): m/z 161.8 $(M+H)^+$.

3.5.6. 6,7,8,9,10,11,17,18,19,20,21,22-Dodecahydrodibenzo[*b*,*k*][1,10,4,13]dioxadiazacyclooctadecine (6f). Reaction of 2-(4-formylbutyloxy)nitrobenzene (**4f**) (100 mg, 0.45 mmol) and PtO_2 (60 mg) in MeOH (100 ml) gave a white solid (89 mg). Purification gave the dimer (**6f**) as a white solid (53 mg, 75%) mp 198.5–200.7°C. (Found: C, 74.5; H, 8.4; N, 7.8. $C_{22}H_{30}N_2O_2$ requires C, 74.6; H, 8.5; N, 7.9%). HPLC 26.7 min. ν_{max} (Nujol) 3425, 3062, 2923, 1602, 1519, 1458, 1377, 1365, 1249, 1214, 1142, 1051, 728, 717 cm^{-1}. ^1H NMR δ (400 MHz) 1.70–1.90,m, 12H, H7,8,9,18,19,20; 3.20, t, J=5.1 Hz, 4H, H10,21; 4.04, t, J=5.6 Hz, 4H, H6,17; 4.2, bs, 2H, NH; 6.57–6.63, m, 3H, H1,12,14; 6.67–6.75, apparent td, J=7.7, 1.5 Hz, 3H, H3,4,15; 6.81–6.90, td, J=7.5, 1.6 Hz, 2H, H2,13. ^{13}C NMR δ (100 MHz) 24.66, 28.74, 29.51 (C7,8,9,18,19,20); 42.87 (C10,21); 67.06 (C6,17); 109.16, 109.30, (C1,4,12,15); 116.12 (C3,14), 120.95 (C2,13), 138.20 (C11a,22a); 145.66 (C4a,15a). Mass spectrum (EI): m/z 354 (M^+, 38%), 179(12), 178(100), 177(50), 176(58), 148(13), 122(38), 120(57), 109(10), 93(10), 77(15), 65(12).

Reactions of (**4f**) in benzene and EtOAc gave (**6f**) in 34 and 33% yields, respectively.

A similar reaction using 10% Pd/C with H_2 (1200 psi) at ambient temperature for 24 h using a stainless steel Parr autoclave gave a solid residue (85 mg) which was purified to give (**6f**) (59 mg, 74%).

A reaction of (**4f**) (105 mg, 0.47 mmol) and 10% Pd/C (60 mg) in MeOH (105 ml) gave a white solid (72 mg). Purification gave (**6f**) as a white solid (53 mg, 64%).

3.5.7. 9,20-Dimethyl-6,7,8,9,10,11,17,18,19,20,21,22-dodecahydrodibenzo[*b*,*k*][1,10,4,13]dioxadiazacyclooctadecine (6g). Reaction of 2-(4-formylpentyloxy)nitrobenzene (**4g**) (50 mg, 0.22 mmol) and 10% Pd/C (30 mg) in MeOH (49 ml) gave the dimer (**6g**) as a white solid (26 mg, 62%) mp 138.5–140.5°C. (Found: C, 75.6; H, 8.9; N 7.2. $C_{24}H_{34}N_2O_2$ requires C 75.4; H 8.9; N 7.2%). ν_{max} (CH_2Cl_2) 3429, 2931, 2875, 1602, 1514, 1476, 1444, 1269, 1247, 1216, 1139, 1049, 1003 cm^{-1}. ^1H NMR δ (300 MHz) 1.08, d, J=6.7 Hz, 6H, 2×CH_3; 1.20–1.32, m, 1H, 1.35–1.46, m, 1H, 1.74–1.87, m, 2H, 1.88–2.07, m, 5H and 2.10–2.21, m, 1H, H7,8,9,18,19,20; 2.84–2.92, m, 2H and 3.19, dt, J=11.5, 3.1 Hz, 2H, H10,21; 3.99, dq, J=8.7, 2.8 Hz, 2H and 4.06–4.14, m, 2H, H6,17; 4.27, bs, 2H, NH; 6.58–6.67, m, 4H, H1,3,12,14; 6.74, d, J=7.8 Hz, 2H, H4,15; 6.87, td, J=7.6, 1.4 Hz, 2H, H2,13. ^{13}C NMR δ (75 MHz) 17.87, 17.97 (CH_3); 26.50, 26.70 (C8,19); 30.92, 31.16 (C7,18); 32.16, 32.26 (C9,20); 49.57, 49.96 (C10,21); 67.29, 67.46 (C6,17); 109.21, 109.34 (C1,12); 115.94, 115.97 (C3,4,14,15); 120.98, 121.02 (C2,13); 138.21, 138.29 (C11a,22a); 146.07, 146.10 (C4a,15a). Mass spectrum (ESI^+): m/z 382 $(M+H)^+$.

3.5.8. 5,6,7,8,9,11,16,17,18,19,20,22-Dodecahydrodibenzo[*c*,*l*][1,10,5,14]dioxadiazacyclooctadecine (6h). Reaction of 2-(5-formyl-2-oxapentyl)nitrobenzene (**4h**) (150 mg, 0.57 mmol) and 10% Pd/C in MeOH (140 ml) gave a white solid (100 mg). Purification gave the dimer (**6h**) as a fine, crystalline solid (28 mg, 23%). (Found: C, 74.6; H, 8.5; N 7.7. $C_{22}H_{30}N_2O_2$ requires C, 74.6; H, 8.5; N, 7.9%). ν_{max} (CH_2Cl_2) 3421, 2987, 2954, 1601, 1524, 1268, 1256 cm^{-1}. ^1H NMR δ (300 MHz) 1.68–1.85, m, H7,8,18,19; 3.08–3.13, m, 4H, H6,17; 3.50, t, J=5.5 Hz, 4H, H9,20; 4.52, s,

4H, H11,22; 4.93, bs, 2H, NH; 6.59–6.65, m, 4H, H2,4,13,15; 7.02, dd, J=7.3, 1.4 Hz, 2H, H1,12; 7.19, td, J=7.9, 1.6 Hz, 2H, H3,14. ^{13}C NMR δ (75 MHz) 26.82, 27.51 (C7,8,18,19); 43.11 (C6,17); 69.41 (C9,20); 73.15 (C11,22); 110.10 (C4,15); 116.07 (C2,13); 121.63 (C12a,22a); 129.62, 129.76 (C1,3,12,14); 147.99 (C5a,15a). Mass spectrum (ESI$^+$): m/z 355.3 $(M+H)^+$.

3.5.9. 1-Benzoyl-2,3,4,5,6,7-hexahydro-1H-1,7-benzodiazonine (5i). Reaction of 2-[(*N*-benzoyl)-4-formylbutylamino]nitrobenzene (**4i**) (100 mg, 0.30 mmol) and 10% Pd/C in MeOH (70 ml) gave a white solid (83 mg). Purification gave the benzodiazonine (**5i**) as a yellow oil (18 mg, 22%). (Found: m/z 303.1473. $(C_{18}H_{20}N_2O+Na)^+$ requires m/z 303.1473). ν_{max} (CH_2Cl_2) 3422, 3055, 2934, 1633, 1499, 1447, 1400, 1315, 1278, 1259 cm^{-1}. ^{1}H NMR δ (200 MHz) 1.49–1.67, m, 4H, H4,5; 1.76–1.89, m, 2H, H3; 2.97–3.13, m, 1H and 3.23–3.37, m, 1H, H6; 3.62–3.81, m, 1H and 4.61–4.74, m, 1H, H2; 6.48–6.56, m, 1H, H8; 6.72, dd, J=7.6, 1.4 Hz, 1H, H10; 6.86–6.94, m, 1H, H9; 7.04–7.35, m, 6H, PhH, H11. ^{13}C NMR δ (50 MHz) 24.19 (C4); 27.10 (C3); 30.67 (C5); 44.36 (C2); 52.74 (C6); 118.43, 119.20, 127.18, 127.57, 128.04, 128.30, 128.54, 129.54, 129.68 (C8,9,10,11,PhCH); 130.25 (PhC); 131.87(C11a), 136.27 (C7a), 171.21 (C=O). Mass spectrum (ESI$^+$): m/z 281.2 $(M+H)^+$.

3.5.10. 9,20-Dimethyl-6,7,10,11,17,18,21,22-octahydro-9H,20H-dibenzo[*e*,*h*][1,4,10,13,7,16]tetraoxadiazacyclooctadecine (6j). Reaction of 2-(5-formyl-1,4-dioxahexyl)-nitrobenzene (**4j**) (75 mg, 0.31 mmol) and 10% Pd/C (45 mg) in MeOH (66 ml) gave a yellow residue (54 mg). Purification gave the dimer (**6j**) as a white solid (32 mg, 51%). (Found: m/z 387.2277. $(C_{22}H_{30}N_2O_4+H)^+$ requires m/z 387.2284). ν_{max} (CH_2Cl_2) 3410, 3056, 2924, 1603, 1513, 1422, 1269, 1259, 1215, 1130 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.27, d, J=6.2 Hz, 6H, 2×CH_3; 3.05–3.15, m, 2H and 3.29–3.33, m, 2H, H10,21; 3.81–3.93, m, 6H, 4.04–4.07, m, 1H, 4.08–4.10, m, 1H, 4.17–4.15, m, 1H and 4.16–4.26, m, 1H, H6,7,9,17,18,20; 6.57–6.71, m, 4H, H1,3,12,14; 6.74, td, J=7.9, 1.9 Hz, 2H, H2,13; 6.77–6.90, m, 2H, H4,15. ^{13}C NMR δ (75 MHz) 17.49, 17.65 (CH_3); 48.91 (C10,21); 66.86, 67.41, 68.25, 68.51, 73.46, 73.82 (C6,7,9,17,18,20); 109.89, 110.11, 110.45, 111.25 (C1,4,12,15); 116.33, 116.40 (C3,14); 121.41, 121.68 (C2,13); 138.33, 138.62 (C11a,22a); 146.46, 146.50 (C4a,15a). Mass spectrum (ESI$^+$): m/z 387.3 $(M+H)^+$.

3.5.11. 3,4,5,6,7,8-Hexahydro-2H-1,8-benzoxazecine (5k) and 7,8,9,10,11,12,19,20,21,22,23,24-dodecahydro-6H,18H-dibenzo[*b*,*l*][1,11,4,14]dioxadiazacycloeicosine (6k). Reaction of 2-(5-formylpentyloxy)nitrobenzene (**4k**) (100 mg, 0.44 mmol) and 10% Pd/C in MeOH (97 ml) gave a white solid (75 mg). The benzoxazecine (**5k**) was isolated as a white solid (6 mg, 7%). HPLC 52.1 min. (Found: m/z 191.1309. $C_{12}H_{17}NO$ requires m/z 191.1310). ν_{max} (CH_2Cl_2) 3429, 3055, 2936, 2859, 1602, 1513, 1444, 1269, 1268, 1216, 1047 cm^{-1}. ^{1}H NMR δ (200 MHz) 1.53–1.56, m, 4H, H4,5; 1.69–1.76, m, 2H, H6; 1.80–1.87, m, 2H, H3; 3.13, t, J=6.8 Hz, 2H, H7; 3.98, t, J=6.3 Hz, 2H, H2; 4.16, bs, 1H, NH; 6.58–6.66, m, 2H, H9,12; 6.74, dd, J=7.8, 1.2 Hz, 1H, H11; 6.85, td, J=7.5, 1.3 Hz, 1H, H10. ^{13}C NMR δ (50 MHz) 26.17, 27.08, 29,30, 29.47 (C3,4,5,6); 43.75 (C7); 67.94 (C2); 109.82 (C9); 110.16 (C12); 116.19 (C11); 121.16 (C10); 138.48 (C8a); 146.09 (C12a). Mass spectrum (ESI$^+$): m/z 192.0 $(M+H)^+$.

The dimer (**6k**) was isolated as a fine, white solid (17 mg, 20%). HPLC 40.5 min (Conditions A). (Found: C, 75.3; H, 9.1; N, 7.3. $C_{24}H_{34}N_2O_2$ requires C, 75.4; H, 9.0; N, 7.3%). ν_{max} (CH_2Cl_2) 3424, 3060, 2924, 1604, 1517, 1454, 1374, 1362, 1247, 1213, 1142, 1054 cm^{-1}. ^{1}H NMR δ (400 MHz) 1.49–1.67, m, 8H, H8,9,20,21; 1.74, apparent pentet, J=6.3 Hz, 4H, H10,22; 1.77–1.85, m, 4H, H7,19; 3.13, t, J=6.2 Hz, 4H, H11,23; 4.01, t, J=5.5 Hz, 4H, H6,18; 4.17, bs, 2H, NH; 6.59–6.66, m, 4H, H1,3,13,15; 6.75, dd, J=7.8, 1.3 Hz, 2H, H4,16; 6.86, td, J=7.6, 1.4 Hz, 2H, H2,14. ^{13}C NMR δ (100 MHz) 26.78, 26.95 (C8,9,20,21); 29.47, 29.79 (C7,10,9,22); 43.44 (C11,23); 68.56 (C6,18); 110.21 (C1,13); 111.22 (C4,16); 116.34 (C3,15); 121.52 (C2,14); 139.13 (C12a,4a); 146.36 (C4a,16a). Mass spectrum (ESI$^+$): m/z 383.3 $(M+H)^+$.

3.5.12. 10,22-Dimethyl-6,7,9,10,11,12,18,19,21,22,23,24-dodecahydrodibenzo[*e*,*o*][1,4,11,14,7,17]tetraoxadiazacycloeicosine (6l). Reaction of 2-(6-formyl-1,4-dioxaheptyl)nitrobenzene (**4l**) (50 mg, 0.19 mmol) and 10% Pd/C gave a yellow film (39 mg). Purification gave the dimer (**6l**) as a white solid (15 mg, 37%) mp 92.2–94.1°C. (Found: C, 69.5; H, 8.2; N, 6.6. $C_{24}H_{34}N_2O_4$ requires C 69.5, H 8.3, N 6.7%). ν_{max} (CH_2Cl_2) 3398, 2961, 2930, 2876, 1603, 1514, 1458, 1269, 1250, 1215, 1124 cm^{-1}. ^{1}H NMR δ (400 MHz) 1.03, d, J=6.9 and 1.04 Hz, d, J=6.9 Hz, 6H, 2×CH_3; 2.12–2.19, m, 2H, H10,22; 3.07–3.15, m, 2H and 3.18–3.26, m, 2H, H11,23; 3.49–3.60, m, 4H, and 3.76–3.85, m, 4H, H7,9,19,21; 4.12–4.19, m, 4H, H6,18; 6.60–6.64, m, 4H, H1,3,13,15; 6.80, dd, J=8.4, 1.5 Hz, 2H, H4,16; 6.88–6.93, m, 2H, H2,14. ^{13}C NMR δ (75 MHz) 15.73 (CH_3); 33.30, 33.67 (C10,22); 47.45, 47.72 (C11,23); 68.57, 68.77 (C9,21); 70.14 (C7,19); 74.77, 75.28 (C6,18); 109.91, 109.95 (C1,13); 112.21, 112.42 (C4,16): 115.67, 115.70 (C3,15); 122.06, 122.15 (C2,14); 139.53, 139.74 (C12a,24a); 145.87 (C4a,16a). Mass spectrum (ESI$^+$): m/z 415.0 $(M+H)^+$.

3.5.13. 2,3,6,7,8,9-Hexahydro-5H-1,4,9-benzodioxaazacycloundecine (5m) and 6,7,10,11,12,13,19,20,23,24,25,26-dodecahydro-9H,22H-dibenzo[*e*,*p*][1,4,12,15,7,18]-tetraoxadiazacyclodocosine (6m). Reaction of 2-(7-formyl-1,4-dioxaheptyl)nitrobenzene (**4m**) (100 mg, 0.39 mmol) and PtO_2 in MeOH (88 ml) gave a viscous oil (90 mg). The monomer (**5m**) was isolated as a yellow oil (18 mg, 22%). (Found: C, 69.7; H, 8.4; N, 6.6. $C_{12}H_{17}NO_2$ requires C, 69.5; H, 8.3; N, 6.8%). ν_{max} (film) 3362, 2926, 2858, 1603, 1520, 1471, 1338, 1252, 1189, 1121, 1099, 1041, 740 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.68–1.75, m, 2H and 1.77–1.85, m, 2H, H6,7; 3.18–3.21, m, 2H, H8; 3.44–3.51, m, 2H, and 3.52–3.54, m, 2H, H3,5; 4.13–4.17, m, 2H, H2; 6.56–6.65, m, 2H, H10,12; 6.93–7.01, m, 2H, H11,13. ^{13}C NMR δ (50 MHz) 25.69, 27.31 (C6,7); 44.51 (C8); 66.84, 69.24, 72.34 (C2,3,5); 111.086 (C10); 115.46 (C13); 119.89 (C12); 124.14 (C11); 142.91 (C9a); 145.48 (C13a). Mass spectrum (ESI$^+$): m/z 207.84 $(M+H)^+$.

The dimer (**6m**) was isolated as a white solid (15 mg, 18%) mp 136.7–138.6°C. (Found: C, 69.1; H, 8.4; N, 6.7.

$C_{24}H_{34}N_2O_4$ requires C, 69.5; H, 8.3; N, 6.8%). ν_{max} (CH_2Cl_2) 3422, 3054, 2937, 2870, 1603, 1514, 1444, 1276, 1256, 1215, 1127 cm^{-1}. ^1H NMR δ (300 MHz) 1.7–1.83, m, 8H, H10,11,23,24; 3.15, t, J=6.6 Hz, 4H, H 12,25; 3.29, t, J=5.9 Hz, 4H, H9,22; 3.76–3.79, m, 4H, H7,20; 4.10–4.13, m, 4H, H6,19; 4.40, bs, 2H, NH; 6.58–6.63, m, H1,3,14,16; 6.77, dd, J=8.4, 1.5 Hz, 2H, H4,17; 6.88, td, J=7.7, 1.5 Hz, 2H, H2,15; ^{13}C NMR δ (50 MHz) 26.29, 27.66 (C10,11,23,24); 43.55 (C12,25); 68.91, 69.34 (C7,9,20,22); 71.25 (C6,19); 109.99 (C1,14); 112.27 (C4,17); 115.97 (C3,16); 122.19 (C2,15); 139.29 (C13a,26a); 145.74 (C4a,17a). Mass spectrum (ESI^+): m/z 415.4 $(M+H)^+$.

A similar reaction using 10% Pd/C gave the monomer (**5m**) (15 mg, 19%) followed by the dimer (**6m**) (29 mg, 36%).

3.5.14. 4-(Methylsulfonyl)-2,3,4,5,6,7,8,9-octahydro-1,4,9-benzoxadiazacycloundecine (5n). Reaction of 2-[(*N*-methylsulfonyl)-3-aza-6-formyl-1-oxaheptyl]nitrobenzene (**4n**) (100 mg, 0.30 mmol) and PtO_2 gave the monomer (**5n**) as a white solid (31 mg, 36%). ν_{max} (CH_2Cl_2) 3462, 3061, 2932, 2877, 1610, 1582, 1508, 1452, 1444, 1363, 1255, 1242, 1135, 1013 cm^{-1}. ^{13}C NMR δ (50 MHz) 24.35, 24.76 (C6,7); 35.76 (CH_3); 49.60, 49.73, 50.33 (C3,5,8); 70.35 (C2); 113.31, 122.06, 122.36, 122.68 (C10,11, 12,13); 139.19 (C9a); 151.65 (C13a). Mass spectrum (ESI^+): m/z 285.5 $(M+H)^+$.

3.5.15. 9-Methyl-2,3,5,6,8,9,10,11-octahydro-1,4,7,11-benzotrioxaazacyclotridecine (5o). Reaction of 2-(9-formyl-1,4,7-trioxadecyl)nitrobenzene (**4o**) (46 mg, 0.15 mmol) and 10% Pd/C (28 mg) in MeOH (32 ml) gave a yellow oil (37 mg). Purification gave the monomer (**5o**) as a colourless oil (26 mg, 30%). (Found: C, 67.4; H, 8.9; N, 5.4. $C_{14}H_{21}NO_3$ requires C, 66.9; H, 8.4; N, 5.6%). (Found: m/z 252.1594. $(C_{14}H_{21}NO_3+H)^+$ requires m/z 252.1600). ν_{max} (CH_2Cl_2) 3364, 2960, 2912, 2874, 1603, 1515, 1459, 1278, 1258, 1216, 1141, 1112, 1049 cm^{-1}. ^1H NMR δ (300 MHz) 0.98, d, J=7.3 Hz, 3H, CH_3; 2.22–2.33, m, 1H, H9; 2.89, dd, J=11.5, 9.6 Hz, 1H and 3.33, dd, J=11.5, 2.3 Hz, 1H, H10; 3.39, t, J=8.8 Hz, 1H, 3.56–3.58, m, 1H, 3.65–3.67, m, 1H, 3.68–3.70, m, 1H 3.70–3.77, m, 1H and 3.78–3.81, m, 1H, H3,5,6,8; 4.04, ddd, J=10.8, 7.2, 2.4 Hz, 1H and 4.21, ddd, J=10.8, 5.0, 2.4 Hz, 1H, H2; 6.55–6.61, m, 2H, H12,14; 6.84, dd, J=8.1, 1.3 Hz, 1H, H15; 6.91, td, J=7.7, 1.4 Hz, 1H, H13. ^{13}C NMR δ (75 MHz) 15.74 (CH_3); 32.53 (C9); 51.64 (C10); 70.10, 70.41, 71.34, 71.45 (C2,3,5,6,8); 109.99 (C12); 115.60, 115.80 (C14,15); 123.09 (C13); 141.64 (C11a); 146.78 (C15a). Mass spectrum (ESI^+): m/z 252.1 $(M+H)^+$.

3.5.16. 2,3,5,6,9,10,11,12-Octahydro-8H-1,4,7,12-benzotrioxaazacyclotetradecine (5p) and 6,7,9,10,13,14,15,16,22,23,25,26,29,30,31,32-hexadecahydro-12H,28H-dibenzo[*h*,*v*][1,4,7,15,18,21,10,24]hexaoxadiazacyclooctacosine (6p). Reaction of 2-(10-formyl-1,4,7-trioxadecyl)nitrobenzene (**4p**) (100 mg, 0.34 mmol) and 10% Pd/C in MeOH (71 ml) gave a yellow residue (75 mg). The monomer (**5p**) was isolated as a yellow oil (63 mg, 75%). (Found: C, 67.1; H, 8.6; N, 5.7. $C_{14}H_{21}NO_3$ requires C, 66.9; H, 8.4; N, 5.6%). ν_{max} (CH_2Cl_2) 3384, 3054, 2986, 2936, 2873, 1604, 1517, 1447, 1422, 1265, 1133, 1112 cm^{-1}. ^1H NMR δ (300 MHz) 1.73–1.81, m, 2H and 1.83–1.91, m, 2H, H9,10; 3.11–3.15, m, 2H, H11; 3.53–3.57, m, 2H, 3.63–3.69, m, 2H and 3.76–3.81, m, 4H, H3,5,6,8; 4.05–4.09, m, 2H, H2; 5.25, bs, 1H, NH; 6.53–6.59, m, 2H, H13,15; 6.84, dd, J=8.2, 1.6 Hz, 1H, H16; 6.88–6.94, m, 1H, H14,. ^{13}C NMR δ (50 MHz) 25.26, 28.16 (C9,10); 44.16 (C11); 69.27, 70.01, 70.27, 70.71, 71.14 (C2,3, 5,6,8); 110.19, 115.32, 115.45, 123.16 (C13,14,15,16); 142.80 (C12a), 145.73 (C16a). Mass spectrum (ESI^+): m/z 251.0 $(M+H)^+$.

The dimer (**6p**) was isolated as a yellow solid (5 mg, 6%). (Found: C, 67.1; H, 8.6; N, 5.5. $C_{28}H_{42}N_2O_6$ requires C 66.9, H 8.4, N 5.6%). ν_{max} (CH_2Cl_2) 3379, 3048, 2933, 2872, 1604, 1518, 1478, 1448, 1368, 1336, 1278, 1258, 1226, 1215, 1133, 1113, 1048 cm^{-1}. ^1H NMR δ (400 MHz) 1.75–1.82, m, 4H and 1.85–1.91, m, 4H, H13,14,29,30; 3.13–3.16, m, 4H, H15,31; 3.57, t, J=5.4 Hz, 4H, 3.65–3.67, m, 4H, 3.78–3.80, m, 4H and 3.81–3.83, m, 4H, H7,9,10,12,23,25,26,28; 4.08–4.10, m, 4H, H6,22; 6.56–6.59, m, 4H, H1,3,17,19; 6.85, dd, J=8.1, 1.5 Hz, 2H, H4,20; 6.90–6.94, m, 2H, H2,18. ^{13}C NMR δ (100 MHz) 25.37 (C14,30); 28.26 (C13,29); 44.12 (C15,31); 69.41, 70.12, 70.42, 70.79, 71.25 (C6,7,9,10,12,22,23,25,26,28); 110.15 (C1,17); 115.39, 115.43 (C3,4,19,20); 123.24 (C2,18); 141.06 (C16a, 32a); 145.80 (C4a,20a). Mass spectrum (ESI^+): m/z 503.1 $(M+H)^+$.

An identical reaction of (**4p**) using PtO_2 gave a yellow residue (65 mg). Purification gave only the monomer (**5p**) as a yellow oil (48 mg, 58%).

A similar reaction of (**4p**) (70 mg, 0.24 mmol) and 10% Pd/C (42 mg) in MeOH (15 ml) gave the monomer (**5p**) (20 mg, 34%).

3.5.17. 11-Methyl-2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-1,13-benzoxaazacyclopentadecine (5q) and 15,32-dimethyl-6,7,8,9,10,11,12,13,14,15,16,17,23,24,25,26,27,28,29,30,31,32,33,34-tetracosahydrodibenzo[*b*,*q*][1,16,4,19]dioxadiazacyclotriacontine (6q). Reaction of 2-(10-formylundecyloxy)nitrobenzene (**4q**) (100 mg, 0.31 mmol) and PtO_2 in MeOH (70 ml) gave a yellow oil (82 mg). The monomer (**5q**) was isolated as a clear liquid (25 mg, 29%). (Found C, 78.3; H, 10.5: N, 5.1. $C_{18}H_{29}NO$ requires C, 78.5; H 10.6; N, 5.1%). ν_{max} (film) 3429, 3062, 2926, 2855, 1714, 1603, 1520, 1463, 1378, 1354, 1247, 1214, 1114, 1047, 732 cm^{-1}. ^1H NMR δ (200 MHz) 0.99, d, J=6.8 Hz, 3H, CH_3; 1.25–1.56, m, 12H, H 4,5,6,7,8,9; 1.63–1.79, m, 5H, H3,10,11; 2.70–2.81, m, 1H and 3.08–3.13, m, 1H, H12; 3.88–4.10, m, 2H, H2; 4.26, bs, 1H, NH; 6.53–6.66, m, 2H, H14,17; 6.73, dd, J=7.8, 1.5 Hz, 1H, H16; 6.85, td, J=7.5, 1.6 Hz, 1H, H15. ^{13}C NMR δ (50 MHz) 18.94 (CH_3); 24.54, 24.81, 25.87, 26.52, 26.52, 26.84, 27.14, 28.23, 32.10 (C3,4,5,6,7,8,9,10); 32.36 (C11); 50.01 (C12); 67.89 (C2); 109.41 (C14); 110.11 (C17); 115.80 (C16); 121.14 (C15); 138.79 (C13a); 146.11 (C17a). Mass spectrum (ESI^+): m/z 276.3 $(M+H)^+$.

The dimer (**6q**) was isolated as a white solid (15 mg, 18%). (Found C, 78.5; H, 10.6; N, 5.0. $C_{36}H_{58}N_2O_2$ requires C, 78.5; H 10.6; N, 5.1%). ν_{max} (CH_2Cl_2) 3431, 3054, 2929,

2856, 1602, 1514, 1270, 1200, 1248, 1215 cm^{-1}. ^1H NMR δ (200 MHz) 0.99, d, J=6.7 Hz, 6H, 2×CH_3; 1.09–1.46, m, 20H, H8,9,10,11,12,25,26,27,28,29; 1.49–1.73, m, 8H, H13,14,30,31; 1.76–1.83, m, 4H, H 7,24; 2.86–2.96, m, 2H, H15,32; 3.04, d, J=5.0 Hz, 2H and 3.10, d, J=4.8 Hz, 2H, H16,33; 3.99, t, J=5.7 Hz, 4H, H6,23; 6.61–6.68, m, 4H, H1,3,18,20; 6.73–6.76, m, 2H, H4,21; 6.77–6.89, m, 2H, H2,19. ^{13}C NMR δ (50 MHz) 18.15 (CH_3); 26.69, 26,99, 29.48, 29.67, 29.73, 29.91, 30.18 (C7,8,9,10, 11,12,13,14,24,25,26,27,28,29,30,31); 32.67 (C15,32); 56.39 (C16,33); 68.14 (C6,23), 110.55 (C1,3,18,20); 116.44 (C4,21); 121.26 (C2,19); 138.52 (C17a, 34a); 146.36 (C4a, 21a). Mass spectrum (ESI^+): m/z 551.4 $(M+H)^+$.

3.5.18. 3,4,5,6,7,8,9,10,11,12,13,14-Dodecahydro-2H-1,14-benzoxaazacyclohexadecine (5r) and 7,8,9,10,11,12, 13,14,15,16,17,18,25,26,27,28,2930,31,32,33,34,35,36-tetracosahydro-6H,24H-dibenzo[*b,r*][1,17,4,20]dioxadiazacyclodotriacontine (6r). Reaction of 2-(11-formylundecyloxy)nitrobenzene (**4r**) (100 mg, 0.31 mmol) and 10% Pd/C in MeOH (70 ml) gave a white solid (74 mg). The monomer (**5r**) was obtained as a colourless film (23 mg, 27%). (Found: C, 78.2; H, 10.4; N, 5.3. $C_{18}H_{29}NO$ requires C, 78.5; H, 10.6; N, 5.1%). HPLC 41.68 min. ν_{max} (film) 3431, 2927, 2856, 1602, 1521, 1445, 1246, 1213, 1048, 731 cm^{-1}. ^1H NMR δ (200 MHz) 1.31, bs, 4H and 1.41, bs, 10H, H5,6,7,8,9,10,11; 1.49–1.56, m, 2H, H4; 1.64–1.74, m, 2H, H12; 1.75–1.82, m, 2H, H3; 3.18, t, J=5.4 Hz, 2H, H13; 4.03, t, J=5.2 Hz, 2H, H2; 4.30, bs, 1H, NH; 6.59–6.65, m, 2H, H15,18; 6.70–6.75, m, 1H, H17; 6.84, td, J=7.6, 1.3 Hz, H16. ^{13}C NMR δ (50 MHz) 24.77, 25.19, 25.64, 25.83, 26.73, 27.12, 27.61, 28.52, 29.42 (C3,4,5,6,7,8,9,10,11,12); 42.40 (C13); 67.56 (C2); 109.48, 109.78 (C15,18); 115.85 (C17); 120.99 (C16); 138.62 (C14a); 146.19 (C18a). Mass spectrum (EI): m/z 276 (M+1, 20%), 275(85), 148(12), 123(30), 122(100), 120(68), 109(48), 95(20), 94(11), 93(11), 78(12), 77(15), 69(11), 67(12), 65(12), 55(43); (ESI^+): m/z 276.2 $(M+H)^+$.

The dimer (**6r**) was isolated as a white solid (17 mg, 19%). HPLC 39.09 min. (Found: C, 78.2; H, 10.6; N, 5.1. $C_{38}H_{66}N_2O_2$ requires C, 78.3; H, 11.4; N, 4.8%). ν_{max} (CH_2Cl_2) 3425, 3054, 2929, 2855, 1602, 1513, 1280, 1230, 1215 cm^{-1}. ^1H NMR δ (300 MHz) 1.29, bs, 28H, 1.47–1.50, m, 4H, 1.61–1.68, m, 4H and 1.74–1.81, m, 4H, H7,8,9,10,11,12,13,14,15,16, 25, 26,27, 28,29, 30, 31, 32, 33,34; 3.13, t, J=6.3 Hz, 4H, H17,35; 3.99, t, J=5.7 Hz, 4H, H6,24; 6.61–6.66, m, 4H, H1,3,19,21; 6.74–6.76, m, 2H, H4,22; 6.83–6.88, m, 2H, H2,20. ^{13}C NMR δ (200 MHz) 26.65, 27.14, 29.27, 29.38, 29.51, 29.62, 29.73 (C7,8,9,10,11,12,13,14,15,16,25,26,27,28,29,30,31,32, 33,34); 43.52 (C17,35); 68.38 (C6,24); 109.94, 110.71 (C1,3,19,21); 116.09 (C4,22); 121.27 (C2,20); 138.91 (C18a,36a); 146.26 (C4a, 22a). Mass spectrum (EI): m/z 552 (M^++1, 20%), 551(M^+, 60), 123(13), 122(100), 120(22), 110(15), 109(15), 91(10), 69(18), 55(42).

A similar reaction using PtO_2 gave a yellow film (88 mg). Purification gave the monomer (**5r**) (31 mg, 36%) followed by the dimer (**6r**) (9 mg, 11%).

3.5.19. 5-Methyl-2-oxa-7-azabicyclo[6.3.1]dodeca-1(12), 8,10-triene (5s) and 5,16-dimethyl-2,13-dioxa-7,18-diazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8,10,12(24),19,21-hexaene (6s). Reaction of 3-(3-formylbutyloxy)nitrobenzene (**4s**) (100 mg, 0.45 mmol) and 10% Pd/C in MeOH (100 ml) gave a white solid (67 mg). The monomer (**5s**) was isolated as a yellow liquid (5 mg, 6%). (Found: m/z 178.1225. $(C_{11}H_{16}NO+H)^+$ requires m/z 178.1232). ν_{max} (CH_2Cl_2) 3429, 2959, 2930, 2874, 1602, 1514, 1446, 1271, 1236, 1215, 1141, 1114, 1048 cm^{-1}. ^1H NMR δ (300 MHz) 0.95, d, J=6.8 Hz, 3H, CH_3; 1.51–1.72, m, 2H, H4; 2.01–2.18, m, 1H, H5; 2.60–2.76, m, 1H and 3.15–3.25, m, 1H, H6; 3.82–4.01, m, 2H, H3; 6.10–6.17, m, 3H, H9,10,11; 6.89, td, J=8.1, 2.6 Hz, 1H, H12. ^{13}C NMR δ (75 MHz) 18.34 (CH_3); 27.95 (C5); 33.69 (C4,6); 49.36 (C3); 64.98 (C3); 99.11, 101.49, 107.39 (C9,10,11); 129.45 (C12); 149.21 (C8); 159.95 (C1).

The dimer (**6s**) was isolated as a fine, white solid (31 mg, 39%). HPLC 48.14 min. (Found: C 74.5, H 8.5, N 7.9. $C_{22}H_{30}N_2O_2$ requires C 74.5, H 8.5, N 7.9%). ν_{max} (CH_2Cl_2) 3448, 3054, 2931, 1616, 1511, 1269, 1262, 11196, 1165, 1062 cm^{-1}. ^1H NMR δ (200 MHz) 0.84, d, J=6.7 Hz, 6H, 2×CH_3; 1.50–1.71, m, 4H, H4,15; 1.99–2.18, m, 2H, H5,16; 2.62–2.78, m, 2H and 3.11–3.20, m, 2H, H6,17; 3.82–4.01, m, 8H, H3,14, NH; 6.06–6.20, m, 6H, H9,10,11,20,21,22; 6.89, td, J=8.0, 2.6 Hz, 2H, H23,24. ^{13}C NMR δ (50 MHz) 18.34 (CH_3); 27.91, 28.23 (C4,15); 33.77 (C5,16); 49.31, 49.55 (C6,17); 64.88, 65.35 (C3,14); 99.11, 99.83, 101.49, 107.39, 107.67 (C9,10, 11,20,21,22); 129.42, 129.53 (C23,24); 149.08 (C8,19); 159.89 (C1,12). Mass spectrum: (ESI^+): m/z 355.2 $(M+H)^+$.

3.5.20. 2-Oxa-8-azabicyclo[7.3.1]trideca-1(13),9,11-triene (5t) and 2,14-dioxa-8,20-diazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),9,11,13(26),21,23-hexaene (6t). Reaction of 3-(4-formylbutyloxy)nitrobenzene (**4t**) (150 mg, 0.67 mmol) and 10% Pd/C in MeOH (150 ml) gave an orange solid (120 mg). The monomer (**5t**) was isolated as a colourless liquid (12 mg, 10%). HPLC 43.61 min. (Found: m/z 178.1227. $(C_{11}H_{15}NO+H)^+$ requires m/z 178.1232). ν_{max} (CH_2Cl_2) 3438, 3044, 2921, 2854, 1613, 1602, 1508, 1475, 1286, 1268, 1201, 1165 cm^{-1}. ^1H NMR δ (200 MHz) 1.52–1.71, m, 4H, and 1.79, pentet, J=6.2 Hz, 2H, H4,5,6; 3.74, bs, 1H, NH; 3.17, t, J=6.6 Hz, 2H, H7; 3.98, t, J, 6.0 Hz, 2H, H3; 6.10–6.18, m, 3H, H10,11,12; 7.02, t, J=8.0 Hz, 1H, H13. ^{13}C NMR δ (50 MHz) 24.05, 29.14, 29.27 (C4,5,6); 43.95 (C7); 67.54 (C3); 99.28, 102.24, 106.83 (C10,11,12); 129.85 (C13); 149.89 (C9); 160.42 (C1).

The dimer (**6t**) was isolated as a white solid (20 mg, 17%). HPLC 35.8 min. (Found: m/z 355.2387. $(C_{22}H_{30}N_2O_2+H)^+$ requires m/z 355.2386). ν_{max} (CH_2Cl_2) 3436, 3055, 2941, 2864, 1616, 1601, 1510, 1475, 1339, 1299, 1296, 1268, 1200, 1163 cm^{-1}. ^1H NMR δ (400 MHz) 1.46–1.62, m, 8H and 1.71, pentet, J=6.4 Hz, 4H, H4,5,6,16,17,18; 3.10, t, J=6.7 Hz, 4H, H7,19; 3.67, bs, 2H, NH; 3.91, t, J=6.1 Hz, 2H, H3,15; 6.07–6.15, m, 6H, H10,11,12,22,23,24; 6.94, t, J=8.0 Hz, 2H, H25,26. ^{13}C NMR δ (100 MHz) 23.07, 28.19, 28.46 (C4,5,6,16,17,18); 43.53 (C7,19); 66.88 (C3,15); 99.00, 102.78, 106.74 (C10,11,12,22,23,24); 129.91 (C25,26); 147.68 (C9,21); 160.19 (C1,13). Mass spectrum (ESI^+): m/z 355.3 $(M+H)^+$.

3.5.21. 2,13-Dioxa-8,19-diazatricyclo[18.2.2.2^{9,12}]hexacosa-10,11,20,22,23,25-hexaene (6u). Reaction of 4-(4-formylbutyloxy)nitrobenzene (**4u**) (100 mg, 0.48 mmol) and PtO_2 in MeOH (100 ml) gave a colourless residue (90 mg). The dimer (**6u**) was obtained as a white solid (9 mg, 11%). (Found: *m/z* 355.2382. $(C_{22}H_{30}N_2O_2+H)^+$ requires *m/z* 355.2386). ν_{max} (CH_2Cl_2) 3430, 3054, 2936, 2862, 1734, 1604, 1513, 1480, 1278, 1259, 1235, 1128, 1106, 1076 cm^{-1}. ^{1}H NMR δ (400 MHz) 1.53–1.55, m, 8H, and 1.72, apparent pentet, *J*=5.8 Hz, 4H, H4,5,6,15,16,17; 2.91, bs, 2H, NH; 3.12, t, *J*=6.2 Hz, 4H, H7,18; 3.84, t, *J*=5.9 Hz, 4H, H3,14; 6.44, dd, *J*=8.8, 2.3 Hz, 4H, H10,21,23,26; 6.59, dd, *J*=8.9, 2.2 Hz, 4H, H11,22,24,25. ^{13}C NMR δ (100 MHz) 21.37, 25.45, 27.02 (C4,5,6,15,16,17); 44.08 (C7,18); 67.21 (C3,14); 115.23, 115.83 (C10,11,21,22,23,24,25,26); 141.10 (C9,20); 151.07 (C1,12). Mass spectrum (ESI$^+$): *m/z* 355.0 $(M+H)^+$.

Further elution gave 4-(5-hydroxypentyloxy)aniline as a yellow liquid which solidified on standing (40 mg, 45%). (Found: *m/z* 196.1330. $(C_{11}H_{17}NO_2+H)^+$ requires *m/z* 196.1338). ν_{max} (CH_2Cl_2) 3616, 3448, 3373, 3054, 2939, 2870, 1610, 1512, 1475, 1260, 1237, 1058, 1029 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.49–1.56, m, 2H and 1.57–1.68, m, 2H, H3′,4′; 1.72–1.82, m, 2H, H2′; 3.32, bs, 1H, OH; 3.66, t, *J*=6.3 Hz, 2H, H5′; 3.89, t, *J*=6.4 Hz, 2H, H1′; 6.63, dd, *J*=8.8, 2.3 Hz, 2H, H2,6; 6.73, dd, *J*=8.9, 2.3 Hz, 2H, H3,5. ^{13}C NMR δ (100 MHz) 22.39 (C3′); 29.20 (C4′); 32.50 (C2′); 62.85 (C5′); 68.57 (C1′); 115.75 (C3,5); 116.45 (C4,6); 139.94 (C1); 152.29 (C4).

3.5.22. 2,5-Dioxa-10-azabicyclo[9.2.2]pentadeca-11,13,14-triene (5v) and 2,5,15,18-tetraoxa-10,23-diazatricyclo-[22.2.2.2^{11,14}]triaconta-11,13,24,26,27,29-hexaene (6v). Reaction of 4-(7-formyl-1,4-dioxaheptyl)nitrobenzene (**4v**) (95 mg, 0.38 mmol) and PtO_2 in MeOH (79 ml) gave a yellow residue (77 mg). The monomer (**5v**) was obtained as a yellow film (4 mg, 7%). (Found: C, 69.8; H, 8.2; N, 6.8. $C_{12}H_{18}NO_2$ requires C, 69.5; H, 8.3; N, 6.8%). (Found: *m/z* 208.1329. $(C_{12}H_{18}NO_2+H)^+$ requires *m/z* 208.1338). ν_{max} (CH_2Cl_2) 3360, 3049, 2929, 2869, 1603, 1519, 1471, 1457, 1330, 1278, 1256, 1236, 1189, 1121, 1109, 1041 cm^{-1}. ^{1}H NMR δ (400 MHz) 1.67–1.73, m, 2H and 1.74–1.80, m, 2H, H7,8; 3.13, t, *J*=6.9 Hz, 2H, H9; 3.59, t, *J*=5.6 Hz, 2H, 3.71–3.73, m, 2H and 4.01–4.03, m, 2H, H3,4,6; 6.47, dd, *J*=8.9, 2.3 Hz, 2H, H12,14; 6.66, dd, *J*=9.0, 2.3 Hz, 2H, H13,15. ^{13}C NMR δ (100 MHz) 26.78, 26.97 (C7,8); 44.72 (C9); 69.19, 69.52, 70.91 (C3,4,6); 114.37 (C12,14); 116.66 (C13,15); 143.07 (C11); 151.16 (C1).

The dimer (**6v**) was obtained as a yellow film (25 mg, 32%). (Found: C, 69.6; H, 8.5; N, 5.1. $C_{24}H_{34}N_2O_4$ requires C, 69.5, H, 8.3, N, 6.8%). (Found: 415.2580. $(C_{24}H_{34}N_2O_4+H)^+$ requires 415.2597). ν_{max} (CH_2Cl_2) 2929, 2871, 1723, 1608, 1514, 1458, 1358, 1265, 1260, 1235, 1127, 1069 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.68–1.82, m, 8H, H7,8,20,21; 3.13, t, *J*=6.8 Hz, 4H, H9,22; 3.59, t, *J*=5.2 Hz, 4H, 3.71–3.74, m, 4H and 3.99–4.03, m, 4H, H3,4,6,16,17,19; 6.48, dd, *J*=8.9, 2.3 Hz, 4H, H12,25,27,30; 6.65, dd, *J*=8.9, 2.3 Hz, 4H, H13,26,28,29. ^{13}C NMR δ (75 MHz) 26.78, 27.01 (C7,8,20,21); 44.90 (C9,22); 69.13, 69.54, 70.95 (C3,4,6, 16,17,19); 114.54 (C12,25,27,30); 116.59 (C13,26,28,29); 142.82 (C11,24); 151.28 (C1,14). Mass spectrum (ESI$^+$): *m/z* 415.3 $(M+H)^+$.

3.5.23. 2,5,8,18,21,24-Hexaoxa-13,29-diazatricyclo-[28.2.2.2^{14,17}]hexatriaconta-4,16,30,32,33,35-hexaene (6w). Reaction of 4-(10-formyl-1,4,7-trioxadecyl)nitrobenzene (**4w**) (100 mg, 0.34 mmol) and PtO_2 gave a yellow residue (80 mg). Purification gave the dimer (**6w**) as a colourless film (22 mg, 26%). (Found: C, 66.8; H, 8.3; N, 5.7. $C_{28}H_{42}O_6N_2$ requires C, 66.9; H, 8.4; N, 5.6%). ν_{max} (CH_2Cl_2) 3055, 2928, 2869, 1648, 1604, 1514, 1457, 1353, 1278, 1256, 1236, 1109, 1068 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.67–1.81, m, 8H, H10,11,26,27; 3.13, t, *J*=6.8 Hz, 4H, H12,28; 3.59, t, *J*=5.2 Hz, 4H, 3.71–3.74, m, 8H and 3.99–4.03, m, 8H, H3,4,6,7,9,19,20,22,23,25; 6.48, dd, *J*=8.9, 2.3 Hz, 4H, H15,31,33,36; 6.65, dd, *J*=8.9, 2.3 Hz, 4H, H16,32,34,35. ^{13}C NMR δ (75 MHz) 26.78, 27.01 (C10,11,26,27); 44.90 (C12,28); 69.13, 69.54, 70.95 (C3,4,6,7,9,19,20,22,23,25); 114.54 (C15,31, 33,36); 116.59 (C16,32,34,35); 142.82 (C14,30); 151.28 (C1,17). Mass spectrum (ESI$^+$): *m/z* 503 $(M+H)^+$.

3.5.24. 6,7,9,10,18,19,20,21-Octahydro-5H-dibenzo[*b*,*k*]-[1,4,7,10,13]tetraoxaazacycloheptadecine (8). Reaction of 2-{7-[2-(3-formylpropyloxy)phenyl-1,4,7-trioxaheptyl}-nitrobenzene (**7**) (100 mg, 0.26 mmol) and 10% Pd/C in MeOH (54 ml) gave a solid residue (71 mg). Purification gave (**8**) as a white, crystalline solid (58 mg, 65%) mp 133.8–135.3°C. (Found: C, 69.3; H, 7.3; N, 4.0. $C_{20}H_{25}NO_4$ requires C, 69.5; H, 7.3; N, 4.1%). ν_{max} (CH_2Cl_2) 3421, 3048, 2932, 2874, 1603, 1506, 1470, 1453, 1453, 1271, 1253, 1222, 1125, 1064, 1048 cm^{-1}. ^{1}H NMR δ (300 MHz) 1.81–1.98, m, 4H, H7,8; 3.34, t, *J*=5.5 Hz, 2H, H6; 3.81–3.84, m, 2H and 3.93–3.96, m, 2H, H17,19; 4.07, t, *J*=5.3 Hz, 2H and 4.18–4.20, m, 4H, H 9,6,20; 4.91, bs, 1H, NH; 6.57–6.65, m, 2H, H4,13; 6.84–6.96, m, 6H, H1,3,11,12,13,14. ^{13}C NMR δ (75 MHz) 25.90, 26.63 (C7,8); 42.34 (C6); 68.59, 69.42, 69.70, 69.90, 70.37 (C9,16,17,19,20); 110.31 (C4); 113.60, 113.62, 114.95, 115.59 (C1,2,11,14); 120.94, 121.41, 122.95 (C3,12,13); 140.67 (C4a); 145.765 (C21a); 148.97, 149.34 (C10a,15a). Mass spectrum (ESI$^+$): *m/z* 383.4 $(M+K)^+$.

A similar reaction using PtO_2 gave (**8**) 47% yield.

3.6. Template-assisted reactions with H_2

The general procedure for hydrogenation of (**4m**) using 10% Pd/C was followed.

Reaction of 2-(2-formyl-1,4-dioxaheptyl)nitrobenzene (**4m**) (46 mg, 0.18 mmol), 10% Pd/C (30 mg) and Ag(OTf) (45 mg, 0.17 mmol) in MeOH (37 ml) gave an orange residue (66 mg) which was dissolved in a mixture of CH_2Cl_2/MeOH. 10% NaCl (aq.) solution was added to give AgCl as a white precipitate and the residue was chromatographed to give the monomer (**5m**) (11 mg, 30%).

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