

***sym*-[5.5.5]Heterocyclophanes: structurally well-defined, mixed  $\pi$ /heteroatom-donor macrobicyclic cages**

**Jens Hansen, Alexander J. Blake, Wan-Sheung Li and Mark Mascall\***

*School of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD*

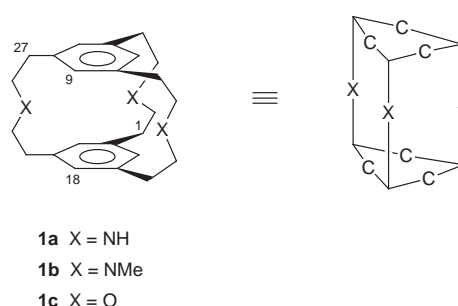
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Structural considerations for achieving conformational stability in cyclophanes are applied as design criteria in the synthesis of *sym*-[5.5.5]triaza- and *sym*-[5.5.5]trioxacyclophane macrobicycles. These compounds act as dynamic hosts in which the metal ion migrates between equivalent, C<sub>3</sub>-related ( $\eta^1$ -C)<sub>2</sub>N<sub>2</sub> coordination sites. The metal–arene interaction may alternatively be described as three centre, two-electron  $\sigma$  complexation to the C–H bond. Crystal structures of the copper(I) and silver(I) complexes show that little reorganization is required on the part of the ligand to accommodate the metal, and the former provides an unusual, structurally characterized example of eta-bonding of an arene to Cu<sup>I</sup>.

The concept of the ‘cyclophane’ was introduced by Cram in 1951,<sup>1</sup> and the prerequisites for achieving conformational stability in ring systems such as these were made clear by Dale in 1966.<sup>2</sup> In the latter work, it was demonstrated that linking planar substructures (such as aromatic rings) diametrically by an *odd* number of methylene units resulted in essentially strain-free molecules, whereas those with an *even* number were conformationally unstable.<sup>3</sup> Despite the fact that Dale’s study comprises the foundations of rational design in a major class of host system where structural definition is a paramount consideration, it is of interest to note that the number of cyclophanes synthesized with odd-membered bridges is no greater than that with even-membered bridges.<sup>4</sup> Even where the odd-number condition has been met, cyclophanes prepared for the purpose of guest complexation have often been designed with the heteroatoms divergent from the cavity.<sup>5</sup> A general consideration for para [*n,n*] or sym-[*n,n,n*] cyclophanes with saturated, odd-membered linking chains is that the odd-numbered positions on the chain ( $\neq 1$  or  $n$ ) will *converge* towards the central aromatic axis, while all even-numbered positions *diverge* from the centre. This is largely supported by the examples of [*n,n*]-paracyclophanes which appear in the Cambridge Structural Database except for those where the chains contain sulfur.<sup>6</sup>

In the *sym*-[*n.n.n*] cyclophanes, the role of the aromatic rings can be debated. These could function simply as anchor points for the intervening chains or, like the bridgehead nitrogens in a cryptand, involve themselves in the binding of a guest. *sym*-[2.2.2], [3.3.3] and [4.4.4]cyclophane systems have been known for some time, but no *endo* metal complexes appear to have been described, even though the well known [3.3]paracyclophane–chromium  $\eta^{12}$  complexes demonstrate the potential for this type of inclusion.<sup>7</sup> For metal ion guests to be involved in eta-complexation the maximum value of *n* is likely to be 5, which situates the rings about 4.8 Å from each other.<sup>8</sup> This puts the midpoint between the rings at 2.4 Å from each phenyl centroid, *i.e.* well beyond the intimate Ar...M distances found in  $\eta^6$  or  $\eta^{12}$  species, but within the range for simple  $\eta^1$  bonding to the periphery of the rings.<sup>9</sup>

With the above considerations in mind and an in-depth study of the conformational preferences of  $[n.n]$  paracyclophane hydrocarbons behind us,<sup>10</sup> we proposed a series of [5.5.5]macrobicycles **1** incorporating parallel aromatic rings as bridgeheads with a heteroatom at the 3-position of each chain. In accordance with the above model, the three heteroatoms are directed towards the cavity, although the distance from each heteroatom



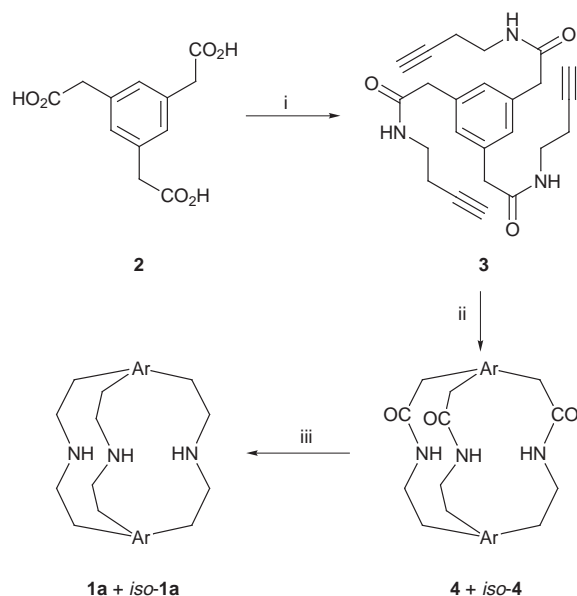
**Fig. 1** Structure of **1** and cartoon where each facet represents an independent  $(\eta^1\text{-C})_2\text{X}_2$  ligand set.

to the centre of the trigonal plane which they define is of the order of 3 Å, thereby ruling out the centre of the cavity as a guest space for most metals. Therefore if neither sandwich-type complexation nor cryptation is possible, this reduces **1** conceptually to three independent, 16-membered azamacrocycles incorporating two heteroatoms and two aromatic *p* orbitals as ligating sites in an approximately square planar arrangement, as represented in Fig. 1. Only one of these  $C_3$ -related ‘facets’ can be occupied at any one time, the consequence of which is dynamic behaviour which is dependent on the identity of the metal. We now report in full on the synthesis and structure of macrobicycles **1** and their interaction with metal ions.<sup>11</sup>

## Results and discussion

The only previous reports of [5.5]cyclophane systems directly comparable to **1** (*i.e.* with a heteroatom at the 3-positions of the chains) were of a thio analogue produced from 1,3,5-tris(bromoacetyl)benzene and sodium sulfide in 0.16% yield<sup>12</sup> and an ester analogue by condensation of benzene-1,3,5-triacetyl chloride with 1,3,5-tris(2-hydroxyethyl)benzene in 3.9% yield.<sup>13</sup> Neither of these approaches seemed attractive to us and we therefore opted for the cobalt-mediated cyclotrimerization method<sup>14</sup> first used by Hubert to access the all-hydrocarbon analogue of **1**.<sup>15</sup>

The synthetic route to the aza derivative **1a** is given in Scheme 1. The starting triacid **2** was available in quantity by Willgerodt–Kindler reaction of commercial 1,3,5-triacetylbenzene.<sup>16</sup> Carbonyldiimidazole-induced coupling of **2** with 4-aminobut-1-yne then gave the cyclization precursor **3** in high yield. Intramolecular cyclotrimerization using cyclopentadi-



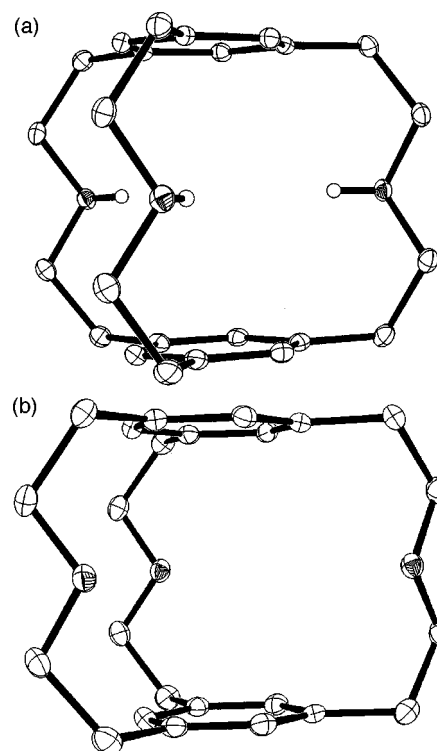
**Scheme 1** Reagents and conditions: i, 1,1'-carbonyldiimidazole, 4-aminobut-1-yne, THF; ii,  $[\text{CpCo}(\text{CO})_2]$ , *o*-xylene, heat; iii,  $\text{BH}_3\text{-SMe}_2$ , THF, heat; then MeOH, heat.

enylcobalt dicarbonyl produced an inseparable mixture of **4** and its 1,2,4-regioisomer (*iso*-**4**) in a 1 : 1.3 ratio (by NMR) in a net 54% yield, or 62% based on recovered **3**. The mixture was finally reduced with borane–dimethyl sulfide complex, whereupon the desired *sym*-macrobicyclic **1a** could be isolated by column chromatography.

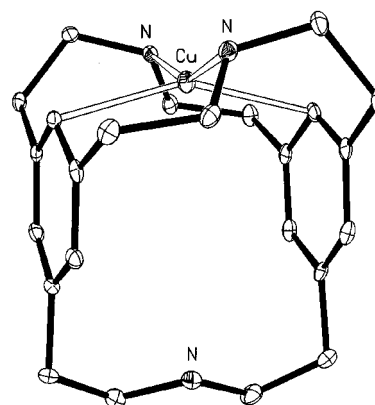
Triaza cage **1a** crystallizes as colourless tablets from hexane, and the determination of the crystal structure [Fig. 2(a)] served to support the above argued structural considerations, *i.e.* that the rings would occupy parallel planes and the heteroatoms would point into the cavity. The actual ring to ring separation is 4.93(3) Å and the N to (molecular)  $\text{C}_3$  axis distance is 3.08(3) Å. An interesting feature of this structure is that the nitrogen H-atoms occupy the cavity in preference to the lone pairs.

Simple mixing of solutions of **1a** and  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  results in the formation of a stable complex. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra of this material show a 2:1 desymmetrization of the ligand resonances consistent with occupation by the metal of one of the three  $(\eta^1\text{-C})_2\text{N}_2$  coordination sites represented in Fig. 1. Final confirmation of this mode of assembly came in the form of an X-ray crystal structure (Fig. 3). The structural similarity of the ligand in the complexed and uncomplexed states indicates favourable preorganization, although the Cu–N bond lengths (2.01 Å) are significantly closer than the midpoint between the two nitrogens in **1a** (2.67 Å) and some puckering of the two chains involved is observed. The third chain however remains undistorted and participates in H-bonding to a molecule of water of crystallization which, along with the  $\text{BF}_4^-$  ion, links the complexes together in chains (Fig. 4). The aromatic rings stack at an interplanar distance of 3.3 Å with centres offset 1.4–1.5 Å.

The relationship of the copper ion to the benzene rings in the  $[\text{Cu1a}]$  complex is a matter of some interest. This may involve either the metal participating in  $\eta^1$  bonds to C, or three centre, two-electron  $\sigma$  complexation to the aromatic C–H bonds.<sup>17</sup> The Cu–C distances are 2.38 and 2.40 Å, and the 0.57 Å displacement of the metal away from the C9–C18 axis puts the contacts to the midpoint of the C–H bonds at 2.37 and 2.39 Å. The 0.59 ppm downfield shift in the  $^1\text{H}$  NMR of the aromatic C–H's associated with the Cu is indicative of electron withdrawal from the hydrogen to the metal bond, whereas the relevant carbon atoms are some 10 ppm upfield of those not involved with the metal. It should be noted that eta interactions between copper(i) and aryl rings are a novelty in any case, with only six



**Fig. 2** (a) Crystal structure of **1a**. Displacement ellipsoids are at the 30% probability level and H-atoms (except for N–H's) are omitted for clarity. (b) Crystal structure of **1c**. Displacement ellipsoids are at the 20% probability level.

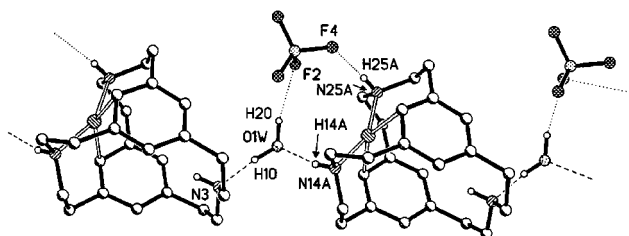


**Fig. 3** Crystal structure of  $[\text{Cu1a}]\text{BF}_4\cdot\text{H}_2\text{O}$ . Displacement ellipsoids are at the 30% probability level. The H-atoms, counterion and water of crystallization are omitted for clarity.

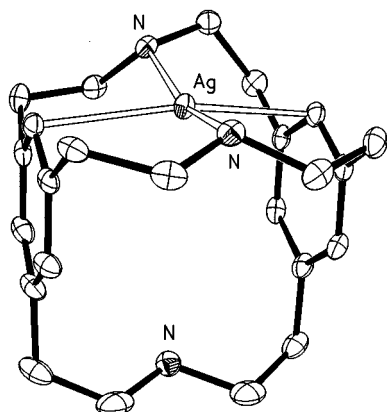
other structurally characterized examples appearing in the literature.<sup>18</sup>

The dynamics of intramolecular exchange between the three coordination sites of **1a** were then examined. The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3/\text{CDCl}_2$ ) of the  $[\text{Cu1a}]$  complex shows temperature dependent fluxional behaviour, with collapse of the two aromatic signals to a single, broad peak occurring around 95 °C. The activation energy for this process estimated from the coalescence temperature and the  $\delta\nu$  value is 72  $\text{kJ mol}^{-1}$ .<sup>19</sup> Migration of the copper nominally involves breaking away from one of the nitrogens and both carbons (or C–H( $\sigma$ )  $\rightarrow$  Cu bonds) of a  $\text{C}_2\text{N}_2$  ligand set before regaining the same from another set, although progression from site to site would take place under the continuous influence of the  $\pi$  system. This in effect constitutes 'dynamic sandwich complexation', with the centre of gravity of the metal coinciding with the molecular  $\text{C}_3$  axis.

Reaction of the macrobicyclic with AgOTf in THF gave the



**Fig. 4** Secondary structure of  $[\text{Cu}(\mathbf{1a})]\text{BF}_4 \cdot \text{H}_2\text{O}$  showing the involvement of the water molecule and counterion. The relevant distances and angles are:  $\text{N3-H1O}$ , 1.78 Å;  $\text{N3-H1O-O1W}$ , 172°;  $\text{O1W-H14A}$ , 2.25 Å;  $\text{O1W-H14A-N14A}$ , 161°;  $\text{F2-H2O}$ , 2.18 Å;  $\text{F2-H2O-O1W}$ , 166°;  $\text{F4-H25A}$ , 2.30 Å;  $\text{F4-H25A-N25A}$ , 159°.

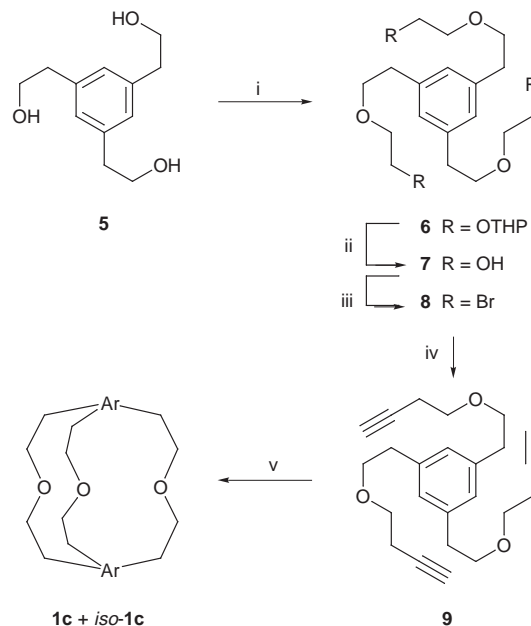


**Fig. 5** Crystal structure of  $[\text{Ag}(\mathbf{1a})]\text{OTf}$ . Displacement ellipsoids are at the 20% probability level and the H-atoms and counterion are omitted for clarity. Only the major component of disorder affecting the free nitrogen ( $\text{N3}$ ) is shown.

corresponding complex  $[\text{Ag}(\mathbf{1a})]\text{OTf}$ . Unlike  $[\text{Cu}(\mathbf{1a})]\text{BF}_4$ , the  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) of this material showed a single resonance in the aromatic region at room temperature. Coalescence occurred at  $-28^\circ\text{C}$  and only on cooling below  $-50^\circ\text{C}$  did two sharp peaks (2:1) appear, separated in this case by 0.27 ppm. This indicated a greater degree of mobility for the  $\text{Ag}^{\text{I}}$  than for  $\text{Cu}^{\text{I}}$ , also reflected in the lower activation energy of 48 kJ  $\text{mol}^{-1}$ .<sup>19</sup> The X-ray crystal structure of  $[\text{Ag}(\mathbf{1a})]\text{OTf}$  (Fig. 5) was comparable to that of  $[\text{Cu}(\mathbf{1a})]\text{BF}_4$ , the major difference being that only one of the two C–C–N–C–C chains needed to distort from the ideal *gauche-anti-anti-gauche* conformation to accommodate the larger silver ion ( $\text{Ag-N}$  distances, 2.32 Å). The outward displacement of the silver from the C9–C18 axis (0.40 Å) is slightly less than that for copper(I), but the same general NMR and structural arguments apply and either  $\eta^1$  complexation<sup>20</sup> or two electron donation from the C–H bonds can be invoked. A longer-range contact to the metal by one of the oxygens (O2) of the triflate ion (2.92 Å) is also observed normal to the (approximate)  $\text{C}_2\text{N}_2$  plane as well as a hydrogen bond from O1 to one of the amine hydrogens ( $\text{H} \cdots \text{O}$  distance, 2.25 Å;  $\text{N-H} \cdots \text{O}$  angle,  $147^\circ$ ).

The alkylation of  $\mathbf{1a}$  by deprotonation with butyllithium and treatment with methyl iodide succeeded in 66% yield to give derivative  $\mathbf{1b}$ . The extreme solubility of  $\mathbf{1b}$  in all solvents from methanol to hexane meant that no single crystals could be grown for X-ray analysis. An analogous silver complex  $[\text{Ag}(\mathbf{1b})]\text{OTf}$  could however be prepared whose NMR spectra showed evidence of dynamic behaviour similar to that of the previous complexes. Coalescence of the aromatic proton signals in  $\text{CD}_2\text{Cl}_2$  occurred at  $-5^\circ\text{C}$ , but a separation of only 0.07 ppm was observed at complete resolution (*ca.*  $-20^\circ\text{C}$ ). In contrast to the other cases, this complex decomposed gradually at room temperature and no X-ray quality crystals were obtained.

The synthetic route to the oxo derivative  $\mathbf{1c}$  is given in Scheme 2. The starting triol  $\mathbf{5}$  was prepared by reduction of the acid  $\mathbf{2}$ .<sup>21</sup> All attempts however to alkylate  $\mathbf{5}$  with homoprop-



**Scheme 2** Reagents and conditions: i, NaH,  $\text{THPOCH}_2\text{CH}_2\text{Br}$ , DMF, heat; ii, HCl, MeOH; iii, methanesulfonyl chloride, TEA,  $\text{CH}_2\text{Cl}_2$  then LiBr, THF; iv, lithium acetylide–ethylenediamine complex, liq.  $\text{NH}_3$ ; v,  $[\text{CpCo}(\text{CO})_2]$ , *o*-xylene, heat.

argylic (but-3-ynyl) halides to directly produce a triyne precursor to  $\mathbf{1c}$  were fruitless. Instead, the alkynyl substituents had to be introduced stepwise, first by alkylation with THP-protected bromoethanol to give  $\mathbf{6}$ , then hydrolysis to the alcohol  $\mathbf{7}$ , conversion to the bromide  $\mathbf{8}$  and finally reaction with acetylide anion to give the cyclization precursor  $\mathbf{9}$ . Cyclotrimerization as described above gave  $\mathbf{1c}$  and its 1,2,4-regioisomer (*iso-1c*) in a 1:1.7 ratio and a net 52% yield, or 72% based on conversion.

Compound  $\mathbf{1c}$  is crystallographically isostructural with  $\mathbf{1a}$  [Fig. 2(b)]. The ring to ring separation of 4.74(3) Å is less than in  $\mathbf{1a}$ , while the O to (molecular)  $\text{C}_3$  axis distance of 3.13(1) Å is slightly greater. No characterizable metal complexes of  $\mathbf{1c}$  have yet been obtained, although efforts are continuing.

## Experimental

### Benzene-1,3,5-tris(*N*-but-3-ynylacetamide) **3**

To a stirred solution of benzene-1,3,5-triacetic acid  $\mathbf{2}$ <sup>16</sup> (244 mg, 0.967 mmol) in THF (7  $\text{cm}^3$ ) was added 1,1'-carbonyldiimidazole (518 mg, 3.19 mmol). The mixture was stirred for 3 h after which a solution of 1-aminobut-3-yne (221 mg, 3.20 mmol) in THF (2  $\text{cm}^3$ ) was added dropwise over a 5 min period. Precipitation of the product was observed within 5 min and was complete after 1 h. The solid was filtered off, washed with THF ( $5 \times 1 \text{ cm}^3$ ) and dried to give  $\mathbf{3}$  (240 mg) as colourless crystals. The filtrate was evaporated and the residue was chromatographed on silica (1:1  $\text{CH}_2\text{Cl}_2$ –acetone  $\rightarrow$  acetone) to give additional  $\mathbf{3}$  (127 mg, total 367 mg, 94%), mp (acetone)  $190$ – $193^\circ\text{C}$  (Found: C, 70.94; H, 6.95; N, 10.26.  $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_3$  requires C, 71.09; H, 6.71; N, 10.36%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (KBr) 3290 (NH,  $\text{C}_{\text{sp}}\text{--H}$ ), 3075, 2936, 2118 (C=C), 1642 (C=O), 1549, 1438, 1345, 1251, 1160, 1065, 871 and 640;  $\delta_{\text{H}}$  (400 MHz,  $[\text{H}_6]\text{DMSO}$ ) 2.31 (6 H, dt,  $J$  2.6, 7.1,  $\text{CH}_2\text{--C}\equiv\text{C}$ ), 2.85 (3 H, t,  $J$  2.6, C=CH), 3.18 (6 H, app. q,  $\text{NCH}_2$ ), 3.36 (6 H, s,  $\text{ArCH}_2$ ), 7.00 (3 H, s, ArH) and 8.23 (3 H, t,  $J$  5.5, NH);  $\delta_{\text{C}}$  (100.6 MHz,  $[\text{H}_6]\text{DMSO}$ ) 18.9 ( $\text{CH}_2\text{--C}\equiv\text{C}$ ), 38.0 ( $\text{NCH}_2$ ), 42.3 ( $\text{ArCH}_2$ ), 72.2 (C=CH), 82.4 (C=C), 127.9 (ArH), 136.1 (Ar) and 170.3 (C=O);  $m/z$  (EI) 405 ( $\text{M}^+$ , 18%), 366 (36), 337(8), 310 (42), 297 (9), 267 (11), 241 (27), 212 (21), 70 (100) and 53 (51).

### sym-[5.5.5]Triazacyclophane amides **4** and *iso-4*

*o*-Xylene (700  $\text{cm}^3$ ) was distilled from sodium–benzophenone



directly into a flask containing pulverized triyne **3** (1.90 g, 4.69 mmol) under dry argon. The mixture was degassed by five successive evacuation and flushing cycles with argon while stirring. The suspension was heated at 155 °C and CpCo(CO)<sub>2</sub> (0.250 cm<sup>3</sup>; technical grade) was added. After 4 h additional CpCo(CO)<sub>2</sub> (0.750 cm<sup>3</sup>) was introduced by syringe pump over a 16 h period. The mixture was allowed to come to RT and the solvent was evaporated. The residue was triturated with boiling methanol (2 × 50 cm<sup>3</sup>) and filtered. The combined filtrates were evaporated and the residue was dissolved in hot methanol. The solution was concentrated at the boiling point to *ca.* 2–3 cm<sup>3</sup>, diluted with hot ethyl acetate (10 cm<sup>3</sup>) and immediately chromatographed on silica (10:1→5:1 ethyl acetate–methanol) to give an inseparable mixture of **4** and *iso-4* in a 1:1.3 ratio (1.034 g, 54%). The yield based on recovered **3** (241 mg) was 62%.  $\delta_{\text{H}}$  (400 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO, >6 ppm only) 6.25 (1 H, t, *J* 5.0, NH), 6.31 (3 H, t, *J* 5.1, NH), 6.55 (1 H, t, *J* 5.4, NH), 6.70 (3 H, s, ArH), 6.72 (2 H, s, ArH), 6.76 (1 H, dd, *J* 3.5, 6.9, NH), 6.85 (1 H, d, *J* 7.9, ArH), 6.91 (3 H, s, ArH), 6.97 (1 H, s, ArH), 6.99 (1H, d, *J* 8.2, ArH) and 7.12 (1 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, [<sup>2</sup>H<sub>6</sub>]DMSO) 28.2, 28.9, 33.1, 33.6, 35.5, 37.1, 37.2, 37.9, 43.2, 43.3, 43.5, 43.6, 124.5, 126.4, 126.9, 127.51, 127.57, 127.60, 128.0, 128.5, 134.3, 135.2, 135.7, 136.2, 136.4, 136.5, 136.7, 137.7, 169.69, 169.75 and 170.1.

#### *sym*-[5.5.5]Triazacyclophanes **1a** and *iso-1a*

To a stirred suspension of the above mixture of **4** and *iso-4* (1.016 g, 2.51 mmol) in THF (40 cm<sup>3</sup>) was slowly added a solution of BH<sub>3</sub>·SMe<sub>2</sub> in THF (10 M, 1.65 cm<sup>3</sup>, 16.5 mmol). The mixture was heated at reflux for 24 h and then allowed to cool to RT. Methanol (20 cm<sup>3</sup>) was cautiously added and then evaporated. To the residue was added additional methanol (50 cm<sup>3</sup>) and the mixture was heated at reflux for 12 h. The solvent was evaporated and the residue chromatographed on silica (10:1→3:1 CH<sub>2</sub>Cl<sub>2</sub>–methanol) giving **1a** (235 mg), a mixed fraction of **1a** + *iso-1a* (178 mg) and *iso-1a* (325 mg), total 738 mg (81%), as colourless solids. The mixed fraction was rechromatographed providing additional **1a** (65 mg), and the combined mass of the desired product was recrystallized from hexane to give pure **1a** (274 mg, 30%) as colourless crystals.

**1a**. Mp (*n*-hexane) 247–249 °C (Found: C, 79.43; H, 9.35; N, 11.48. C<sub>24</sub>H<sub>33</sub>N<sub>3</sub> requires C, 79.29; H, 9.15; N, 11.56%);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 3291 (NH), 2917, 2827, 2744, 1601, 1458, 1120 and 909;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 1.90 (3 H, br s, NH), 2.74 (12 H, t, *J* 5.7, ArCH<sub>2</sub>), 2.91 (12 H, t, *J* 5.7, NCH<sub>2</sub>) and 6.81 (6 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 35.0 (ArCH<sub>2</sub>), 49.9 (NCH<sub>2</sub>), 127.1 (ArH) and 139.7 (Ar); *m/z* (EI) 363 (M<sup>+</sup>, 53%) and 335 (100).

*iso-1a*. Mp (*n*-hexane) 135–140 °C (Found: C, 79.49; H, 9.33; N, 11.62. C<sub>24</sub>H<sub>33</sub>N<sub>3</sub> requires C, 79.29; H, 9.15; N, 11.56%);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 3294 (NH), 2911, 2829, 2743, 1600, 1460 and 1120;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 0.09 (3 H, br s, NH), 2.45–2.91 (24 H, m, CH<sub>2</sub>), 6.54 (1 H, s, ArH), 6.75 (1 H, s, ArH), 6.79 (1H, s, ArH), 6.83 (1 H, dd, *J* 1.6, 7.8, ArH), 6.86 (1 H, s, ArH) and 6.97 (1 H, d, *J* 7.8, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 30.4, 31.4, 34.6, 34.8, 34.9, 35.2, 48.1, 49.0, 49.6, 49.8, 50.1, 50.3, 126.09, 126.14, 126.6, 127.77, 127.84, 130.4, 135.2, 136.8, 137.2, 138.7, 139.1 and 139.6; *m/z* (EI) 363 (M<sup>+</sup>, 100%), 335 (57), 320 (16), 244 (14), 203 (30), 172 (19), 160 (28), 145 (16), 117 (12), 91 (12) and 42 (28).

#### [Cu**1a**]BF<sub>4</sub>·H<sub>2</sub>O complex

To a solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> (15.7 mg, 50.0 μmol) in acetonitrile (0.5 cm<sup>3</sup>) was added a solution of cyclophane **1a** (18.2 mg, 50.0 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 cm<sup>3</sup>). The solvent was evaporated giving [Cu**1a**]BF<sub>4</sub>·H<sub>2</sub>O (25.7 mg, 97%) as a colour-

less solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–ether at −20 °C gave [Cu**1a**]BF<sub>4</sub>·H<sub>2</sub>O as colourless crystals, mp 210–230 °C (decomp.) (HRFABMS: M<sup>+</sup>, 426.1962. C<sub>24</sub>H<sub>33</sub><sup>63</sup>CuN<sub>3</sub> requires 426.1970);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 3266 (NH), 2925, 1600, 1457, 1076 (B-F) and 980;  $\delta_{\text{H}}$  (250 MHz, [<sup>2</sup>H<sub>6</sub>]acetone) 1.58 (1 H, br s, NH), 2.6–3.0 (20 H, m, CH<sub>2</sub>), 3.26 (4 H, m, CH<sub>2</sub>), 3.97 (2 H, br s, CuNH), 6.75 (4 H, s, ArH) and 7.34 (2 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, [<sup>2</sup>H<sub>6</sub>]acetone) 33.1 (ArCH<sub>2</sub>), 35.5 (ArCH<sub>2</sub>, br), 48.9 (NCH<sub>2</sub>, br), 50.4 (NCH<sub>2</sub>), 118.1 (ArH–Cu), 128.2 (ArH), 138.1 (Ar) and 142.1 (Ar); *m/z* (FAB) 426 ([Cu**1a**], 20%) and 364 (**1a** + H, 7).

#### [Ag**1a**]OTf complex

All operations were performed with exclusion of light. To a solution of cyclophane **1a** (18.2 mg, 50.0 μmol) in THF (1 cm<sup>3</sup>) was added a solution of silver triflate in THF (33.5 mM, 1.50 cm<sup>3</sup>, 50.0 μmol). The solvent was evaporated giving [Ag**1a**]OTf (31.0 mg, 100%) as a colourless solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–ether at −20 °C gave pure [Ag**1a**]OTf as colourless crystals, mp 220–225 °C (decomp.) (Found: C, 48.13; H, 5.33; N, 6.46. C<sub>24</sub>H<sub>33</sub>N<sub>3</sub> requires C, 48.39; H, 5.36; N, 6.77%);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 3269 (NH), 2924, 2859, 1597, 1454, 1282, 1028 and 638 (m);  $\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 1.93 (3 H, br s, NH), 2.72 (12 H, t, *J* 5.8, ArCH<sub>2</sub>), 2.89 (12 H, br s, NCH<sub>2</sub>) and 6.86 (6 H, s, ArH);  $\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, −50 °C, >6 ppm only) 6.72 (4 H, s, ArH) and 6.99 (2 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 34.5 (ArCH<sub>2</sub>), 50.6 (NCH<sub>2</sub>), 124.4 (br, ArH) and 139.2 (br, Ar); *m/z* (FAB) 620 ([Ag**1a**] + TfOH, 7%), 470 ([Ag**1a**], 100) and 364 (**1a** + H, 18).

#### Tri-*N*-methyl-*sym*-[5.5.5]triazacyclophane **1b**

To a solution of **1a** (36.4 mg, 100 μmol) in THF (2 cm<sup>3</sup>) at −78 °C was added a solution of *n*-butyllithium in hexane (1.57 M, 0.210 cm<sup>3</sup>, 330 μmol) over a 5 min period. The pale yellow mixture was allowed to warm to −20 °C over a 30 min period. After an additional 10 min the mixture was recooled to −78 °C and methyl iodide (56.8 mg, 400 μmol) was added over a period of 3 min. The reaction was warmed to RT and the solvent was evaporated. The residue partitioned between CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and water (3 cm<sup>3</sup>) and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 2 cm<sup>3</sup>). The combined extracts were dried over MgSO<sub>4</sub> and the solvent evaporated. Chromatography on silica (ether saturated with NH<sub>3</sub>) gave **1b** (27 mg, 66%) as a waxy white solid (HREIMS: M<sup>+</sup>, 405.3142. C<sub>27</sub>H<sub>39</sub>N<sub>3</sub> requires 405.3144);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 2937, 2845, 2790, 1602, 1459, 1350, 1127 and 1048;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.30 (9 H, s, CH<sub>3</sub>), 2.46 (12 H, t, *J* 6.3, NCH<sub>2</sub>), 2.58 (12 H, t, *J* 6.3, ArCH<sub>2</sub>) and 6.57 (6 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 33.6 (ArCH<sub>2</sub>), 40.6 (CH<sub>3</sub>), 59.6 (NCH<sub>2</sub>), 125.9 (ArH) and 140.3 (Ar); *m/z* (EI) 405 (M<sup>+</sup>, 24%), 116 (3) and 58 (100).

#### [Ag**1b**]OTf complex

All operations were performed with exclusion of light. To a solution of cyclophane **1b** (8.11 mg, 20.0 μmol) in ether (1 cm<sup>3</sup>) was added a solution of silver triflate in THF (33.5 mM, 0.596 cm<sup>3</sup>, 20.0 μmol) in THF. The solvent was evaporated and the resulting tan solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–ether at −20 °C giving [Ag**1b**]OTf (12.4 mg, 94%) as colourless crystals, mp 140–180 °C (decomp.) (HRFABMS: M<sup>+</sup>, 512.2209. C<sub>27</sub>H<sub>39</sub><sup>107</sup>AgN<sub>3</sub> requires 512.2195);  $\nu_{\text{max}}$ /cm<sup>−1</sup> (CHCl<sub>3</sub>) 2960, 2860, 2795, 1599, 1456, 1282, 1158, 1100, 1030 and 638;  $\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 2.55 (9 H, br s, CH<sub>3</sub>), 2.74 (24 H, br m, CH<sub>2</sub>) and 6.78 (6 H, s, ArH);  $\delta_{\text{H}}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, −20 °C, >6 ppm only) 6.71 (4 H, s, ArH) and 6.78 (2 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>, 323 K) 32.2 (ArCH<sub>2</sub>), 43.2 (br, CH<sub>3</sub>), 59.4 (NCH<sub>2</sub>), 122.8 (br, ArH) and 139.2 (br, Ar); *m/z* (FAB) 662 ([Ag**1b**] + TfOH, 2%), 512 ([Ag**1b**], 32) and 406 (**1b** + H, 17).

### 1,3,5-Tris[2-(2-(tetrahydropyran-2-yloxy)ethoxy)ethyl]benzene **6**

To a suspension of sodium hydride (60% in paraffin oil, 480 mg, 12.0 mmol) and 1,3,5-tris(2-hydroxyethyl)benzene **5** (210 mg, 1.00 mmol) in DMF (5 cm<sup>3</sup>) was added 2-(2-bromoethoxy)-tetrahydropyran (1.89 g, 9.04 mmol). The mixture was stirred at 50 °C for 5 h and allowed to cool to RT. Sat. aq. NH<sub>4</sub>Cl (5 cm<sup>3</sup>) and ether (10 cm<sup>3</sup>) were added carefully with vigorous stirring. The aqueous phase was extracted with ether (3 × 10 cm<sup>3</sup>) and the combined organic extracts were washed with sat. aq. NaCl (10 cm<sup>3</sup>) and dried over MgSO<sub>4</sub>. The residue was chromatographed on silica (2:1 petroleum ether–ether–ether) to give **6** (483 mg, 81%) as a colourless oil (Found: C, 66.38; H, 9.27. C<sub>33</sub>H<sub>54</sub>O<sub>9</sub> requires C, 66.64; H, 9.15%;  $\nu_{\max}/\text{cm}^{-1}$  (neat) 2940, 2867, 1604, 1455, 1352, 1201, 1124, 1078, 1036, 987, 871 and 815;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 1.40–1.87 (18 H, m, THP-3,4,5-H), 2.82 (6 H, t, *J* 7.3, ArCH<sub>2</sub>), 3.46 (3 H, m, OCH<sub>2</sub>), 3.52–3.70 (15 H, m, OCH<sub>2</sub>), 3.83 (6 H, m, OCH<sub>2</sub>), 4.60 (3 H, t, *J* 3.7, 3 H, THP-2-H) and 6.90 (3 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 19.3 (THP-C-4), 25.3 (THP-C-5), 30.4 (THP-C-3), 36.0 (ArCH<sub>2</sub>), 62.0 (OCH<sub>2</sub>), 66.5 (OCH<sub>2</sub>), 70.1 (OCH<sub>2</sub>), 72.2 (OCH<sub>2</sub>), 98.7 (THP-C-2), 127.3 (ArH) and 138.8 (Ar); *m/z* (EI) 333 (5%), 331 (8), 290 (4), 218 (22), 199 (15), 156 (23), 144 (100), 129 (32), 85 (65), 84 (90), 55 (83) and 41 (43).

### 1,3,5-Tris[2-(2-hydroxyethoxy)ethyl]benzene **7**

To a solution of the tris-THP-ether **6** (4.98 g, 8.37 mmol) in methanol (200 cm<sup>3</sup>) was added conc. HCl (10 drops). After standing for 14 h solid K<sub>2</sub>CO<sub>3</sub> (1.0 g) was added. The mixture was stirred for 0.5 h, filtered and the solvent evaporated. The residue was chromatographed on silica (10:1→7:1 ether–MeOH) to give **7** (2.77 g, 97%) as a colourless oil (HRFABMS: *M* + *H*, 343.2087. C<sub>18</sub>H<sub>31</sub>O<sub>6</sub> requires 343.2121;  $\nu_{\max}/\text{cm}^{-1}$  (neat) 3398 (OH), 2928, 2865, 1604, 1458, 1358, 1119, 1052, 890, 869 and 713;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.53 (3 H, t, *J* 6.2, OH), 2.86 (6 H, t, *J* 6.5, ArCH<sub>2</sub>), 3.54 (6 H, m, OCH<sub>2</sub>), 3.65 (6 H, m, CH<sub>2</sub>OH), 3.72 (6 H, t, *J* 6.5, OCH<sub>2</sub>) and 6.97 (3 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 35.9 (ArCH<sub>2</sub>), 61.4 (CH<sub>2</sub>OH), 71.7 (OCH<sub>2</sub>), 71.9 (OCH<sub>2</sub>), 127.3 (ArH) and 139.0 (Ar); *m/z* (FAB) 343 (*M* + 1, 92%), 219 (53), 157 (78), 154 (100) and 136 (72).

### 1,3,5-Tris[2-(2-bromoethoxy)ethyl]benzene **8**

To a stirred solution of triol **7** (2.745 g, 8.02 mmol) and triethylamine (9.73 g, 96.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) at –40 °C was added mesyl chloride (5.51 g, 48.1 mmol) over a period of 10 min. The mixture was allowed to warm to RT. After stirring for 20 h and then an additional 4.5 h at 45 °C, sat. aq. NH<sub>4</sub>Cl (50 cm<sup>3</sup>) was added. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 75 cm<sup>3</sup>) and the combined organic extracts were washed with sat. aq. NaCl (50 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and the solvent evaporated. THF (50 cm<sup>3</sup>) was added to the residue followed by LiBr (18.8 g, 216 mmol) in five portions with stirring and cooling so that the temperature did not rise above 40 °C. After 20 h the solvent was evaporated and the residue partitioned between sat. aq. NH<sub>4</sub>Cl (50 cm<sup>3</sup>) and ether (100 cm<sup>3</sup>). The aqueous phase was extracted with ether (3 × 100 cm<sup>3</sup>) and the combined organic extracts were washed with sat. aq. NaCl (50 cm<sup>3</sup>) and dried over MgSO<sub>4</sub>. Chromatography on silica (2:1 petroleum ether–ether) gave the tribromide **8** (3.63 g, 85%) as a colourless oil (Found: C, 40.98; H, 5.41. C<sub>33</sub>H<sub>54</sub>O<sub>9</sub> requires C, 40.71; H, 5.12%;  $\nu_{\max}/\text{cm}^{-1}$  (neat) 3017, 2916, 2864, 2791, 1604, 1458, 1361, 1275, 1118 (C–O), 1043, 712 and 667;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.87 (6 H, t, *J* 7.1, ArCH<sub>2</sub>), 3.46 (6 H, t, *J* 6.1, CH<sub>2</sub>Br), 3.71 (6 H, t, *J* 7.1, OCH<sub>2</sub>CH<sub>2</sub>Ar), 3.78 (6 H, t, *J* 6.1, OCH<sub>2</sub>CH<sub>2</sub>Br) and 6.97 (3 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 30.4 (CH<sub>2</sub>Br), 36.1 (ArCH<sub>2</sub>), 70.7 (OCH<sub>2</sub>), 72.1 (OCH<sub>2</sub>), 127.5 (ArH) and 138.8 (Ar); *m/z* (EI) 532 (*M* + 4, 1.1%), 530 (*M* + 2, 1.1), 528 (*M*<sup>+</sup>, 0.2), 405 (7), 281 (58), 157 (62), 107 (70), 83 (41), 74 (63), 59 (100) and 45 (78).

### 1,3,5-Tris[2-(but-3-ynoxy)ethyl]benzene **9**

Ammonia (10 cm<sup>3</sup>) was condensed in a flask containing lithium acetylide–ethylenediamine complex (807 mg, 8.77 mmol) with stirring at –78 °C. Tribromide **8** (512 mg, 0.964 mmol) was then added over a period of 10 min. Stirring was continued at a bath temperature between –40 and –30 °C for 3.5 h. The ammonia was allowed to evaporate and the residue was partitioned between sat. aq. NH<sub>4</sub>Cl (15 cm<sup>3</sup>) and ether (20 cm<sup>3</sup>). The aqueous phase was extracted with ether (2 × 25 cm<sup>3</sup>) and the combined organic extracts were washed with sat. aq. NaCl (15 cm<sup>3</sup>) and dried over MgSO<sub>4</sub>. Chromatography on silica (4:1→3:1 petroleum ether–ether) gave the triyne **9** (260 mg, 74%) as a colourless oil (HREIMS: *M*<sup>+</sup>, 366.2188. C<sub>24</sub>H<sub>30</sub>O<sub>3</sub> requires 366.2195;  $\nu_{\max}/\text{cm}^{-1}$  (neat) 3289 (C<sub>sp</sub>–H), 3017, 2916, 2864, 2794, 2120 (C≡C), 1604, 1459, 1364, 1112 (C–O), 868 and 642;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 2.00 (3 H, t, *J* 2.7, C≡CH), 2.46 (6 H, dt, *J* 2.7, 6.9, CH<sub>2</sub>C≡C), 2.85 (6 H, t, *J* 7.2, ArCH<sub>2</sub>), 3.58 (6 H, t, *J* 6.9, OCH<sub>2</sub>), 3.67 (6 H, t, *J* 7.3, OCH<sub>2</sub>) and 6.95 (3 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 19.7 (CH<sub>2</sub>C≡CH), 36.0 (ArCH<sub>2</sub>), 68.8 (OCH<sub>2</sub>), 69.3 (C≡CH), 71.8 (OCH<sub>2</sub>), 81.3 (C≡CH), 127.4 (ArH) and 138.8 (Ar); *m/z* (EI) 366 (*M*<sup>+</sup>, 3%), 296 (5), 283 (5), 268 (5), 257 (7), 227 (12), 213 (32), 187 (20), 157 (14), 129 (12), 91 (17), 83 (20) and 53 (100).

### syn-[5.5.5]Trioxacyclophanes **1c** and *iso-1c*

*o*-Xylene (900 cm<sup>3</sup>) was distilled from sodium–benzophenone into a flask under dry argon and degassed by seven successive evacuation and flushing cycles with argon while stirring. CpCo(CO)<sub>2</sub> (0.700 cm<sup>3</sup>; technical grade) was added and the mixture was heated at 155 °C. A solution of triyne **9** (1.49 g, 4.07 mmol) in the degassed *o*-xylene (20 cm<sup>3</sup>) was added *via* syringe pump over an 18 h period. Additional CpCo(CO)<sub>2</sub> (1.05 cm<sup>3</sup>) was also added over a period of 15 h, starting 3 h after the addition of triyne was begun. The mixture was kept stirring for further 3 h and then allowed to cool to RT. The solvent was evaporated and the residue triturated with 1:1 ether:CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) and filtered. The solid was then washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 cm<sup>3</sup>) and the combined filtrates evaporated. Chromatography of the crude product on silica (4:1→1:1 petroleum ether–ether) gave the starting material **9** (414 mg), a mixed fraction of **1c**:*iso-1c* (5:95, 466 mg) and a second mixed fraction of **1c**:*iso-1c* (86:14, 307 mg). The pure isomers could be isolated by recrystallization from *n*-hexane, giving **1c** (231 mg, 16%) and *iso-1c* (410 mg, 28%) as colourless crystals. The overall yield of the mixture was 52% (19% of **1c**, 33% of *iso-1c*, ratio: 1:1.7) or 72% based on conversion.

**1c**. Mp (*n*-hexane) 185–186 °C (Found: C, 78.47; H, 8.25. C<sub>24</sub>H<sub>30</sub>O<sub>3</sub> requires C, 78.65; H, 8.25%;  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3016, 2934, 2896, 2852, 2789, 1605, 1459, 1360, 1256, 1229, 1128 (C–O), 1046, 836 and 700;  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 2.68 (12 H, t, *J* 5.5, ArCH<sub>2</sub>), 3.69 (12 H, t, *J* 5.5, OCH<sub>2</sub>) and 6.66 (6 H, s, ArH);  $\delta_{\text{C}}$  (100.6 MHz, CDCl<sub>3</sub>) 35.7 (ArCH<sub>2</sub>), 70.4 (OCH<sub>2</sub>), 126.1 (ArH) and 138.6 (Ar); *m/z* (EI) 366 (*M*<sup>+</sup>, 100%).

*iso-1c*. Mp (*n*-hexane) 117–119 °C (Found: C, 78.74; H, 8.52. C<sub>24</sub>H<sub>30</sub>O<sub>3</sub> requires C, 78.65; H, 8.25%;  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3014, 2905, 2859, 2785, 1603, 1458, 1360, 1258, 1121 (C–O), 1040, 820 and 704;  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 2.38–2.48 (2 H, m, ArCH<sub>2</sub>), 2.60–2.75 (6 H, m, ArCH<sub>2</sub>), 2.79 (2 H, m, ArCH<sub>2</sub>), 2.85–2.95 (2 H, m, ArCH<sub>2</sub>), 3.29 (1H, m, OCH<sub>2</sub>), 3.44 (1 H, m, OCH<sub>2</sub>), 3.52–3.58 (2 H, m, OCH<sub>2</sub>), 3.62 (2 H, m, OCH<sub>2</sub>), 3.75 (2 H, m, OCH<sub>2</sub>), 3.77–3.86 (2 H, m, OCH<sub>2</sub>), 3.92–3.98 (2 H, m, OCH<sub>2</sub>), 6.48 (1 H, s, ArH), 6.63 (1 H, s, ArH), 6.84 (1 H, d, ArH), 6.85 (1 H, s, ArH), 6.89 (1 H, s, ArH) and 6.94 (1 H, dd, ArH);  $\delta_{\text{C}}$  (125.8 MHz, CDCl<sub>3</sub>) 30.4, 31.8, 35.8, 35.9, 36.3, 37.0 (ArCH<sub>2</sub>), 69.6, 70.2, 70.5, 71.0, 71.8, 72.5 (OCH<sub>2</sub>), 125.0, 126.2, 126.7, 127.3, 127.8, 128.0 (ArH), 135.7, 136.7, 137.7, 138.8, 139.26 and 139.33 (Ar); *m/z* (EI) 366 (*M*<sup>+</sup>, 100%), 348 (4), 321

(11), 204 (32), 186 (67), 175 (50), 174 (48), 159 (72), 156 (80), 145 (74), 131 (59), 129 (67), 117 (58), 105 (27) and 91 (69).

### Single crystal structure determination of 1a

$C_{24}H_{33}N_3$ ,  $M = 363.53$ , colourless tablet  $0.50 \times 0.50 \times 0.30$  mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14),  $a = 12.736(6)$ ,  $b = 15.371(6)$ ,  $c = 10.676(5)$  Å,  $\beta = 94.12(8)^\circ$ ,  $U = 2084.7(16)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.158$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.068$  mm<sup>-1</sup>,  $T = 150(2)$  K. Data were collected on a Stoe Stadi-4 four-circle diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and  $\omega/\theta$  scans to  $2\theta_{\text{max}} = 50^\circ$ . Of a total of 5202 reflections measured, 3683 were unique ( $R_{\text{int}} = 0.092$ ): of these 2412 had  $F_o \geq 4\sigma(F_o)$  and 3680 were used in all calculations. No crystal decay was observed and no corrections were applied for absorption. The structure was solved by automatic direct methods (all non-H atoms)<sup>22</sup> and refined<sup>23</sup> by full-matrix least-squares on  $F^2$  with all non-H atoms assigned anisotropic displacement parameters. Amine H atoms were located from  $\Delta F$  syntheses; other hydrogen atoms were placed geometrically, thereafter these were refined freely and constrained to ride on their parent C atoms, respectively. The weighting scheme  $w^{-1} = [\sigma^2(F_o^2) + (0.062P)^2 + 1.03P]$ ,  $P = \frac{1}{3}[\text{MAX}(F_o^2, 0) + 2F_c^2]$ , gave satisfactory agreement analyses and final  $R_1 [F_o \geq 4\sigma(F_o)] = 0.0585$ ,  $wR_2$  (all data) = 0.1578,  $S(F^2) = 1.04$ , for 253 refined parameters. The final  $\Delta F$  synthesis showed no features outside the range  $\pm 0.21$  e Å<sup>-3</sup>.

### Single crystal structure determination of 1c

$C_{24}H_{30}O_3$ ,  $M = 366.48$ , colourless hexagonal tablet  $0.47 \times 0.47 \times 0.19$  mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14),  $a = 12.592(7)$ ,  $b = 15.123(13)$ ,  $c = 10.737(7)$  Å,  $\beta = 95.50(7)^\circ$ ,  $U = 2035(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.196$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.077$  mm<sup>-1</sup>,  $T = 150(2)$  K. Data were collected on a Stoe Stadi-4 four-circle diffractometer using graphite-monochromated Mo-K $\alpha$  X-radiation ( $\lambda = 0.71073$  Å) and  $\omega/\theta$  scans. Of a total of 4266 reflections measured to  $2\theta_{\text{max}} = 50^\circ$ , 3552 were unique ( $R_{\text{int}} = 0.059$ ), giving 2673 with  $F \geq 4\sigma(F)$  and 3552 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption. The structure was solved by automatic direct methods (all non-H atoms)<sup>22</sup> and refined by full-matrix least squares<sup>23</sup> with all non-H atoms anisotropic; hydrogen atoms were introduced at geometrically calculated positions and thereafter constrained to ride on their parent C with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The weighting scheme  $w^{-1} = [\sigma^2(F_o^2) + (0.027P)^2 + 1.38P]$ ,  $P = \frac{1}{3}[\text{MAX}(F_o^2, 0) + 2F_c^2]$  gave satisfactory agreement analyses. Final  $R_1 [F \geq 4\sigma(F)] = 0.0493$ ,  $wR_2$  [all data] = 0.1139,  $S[F^2] = 1.18$  for 245 refined parameters. An extinction correction refined to 0.0045(6) and the final  $\Delta F$  synthesis showed no features outside the range  $\pm 0.20$  e Å<sup>-3</sup>.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC Web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/261.

Fig. 2–5 were produced using SHELXTL/PC.<sup>24</sup>

For the crystal data for  $[\text{Cu}1\text{a}]\text{BF}_4 \cdot \text{H}_2\text{O}$  and  $[\text{Ag}1\text{a}]\text{OTf}$  consult ref. 11.

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