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Synthesis of a family of heterocyclic ligands derived from bisphenols: new flexible bridging ligands for use in metallosupramolecular chemistry

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Abstract

The preparations are described of 35 new bridging ligands from five bisphenols through coupling each with seven different heterocyclic units. X-ray crystal structures of five representative examples revealed different conformations in the solid state with the terminal nitrogen donors being separated by distances ranging from 8 to 23 Å.

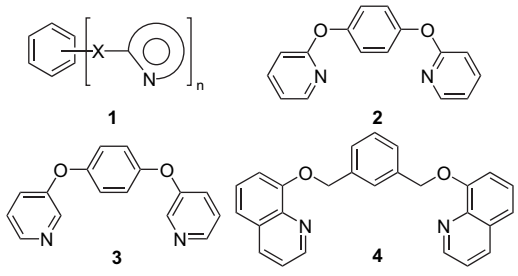
1. Introduction

Metallosupramolecular chemistry[1,2] involves the use of combinations of organic ligands and metallic reagents for the construction of both discrete and polymeric assemblies with diverse architectures.[3–10] The use of rigid, non-flexible bridging ligands allows the rational formation of symmetrical polygons (squares, hexagons, etc.) and polyhedra (cubes, octahedra, dodecahedra, etc.). For some time, we have been engaged in the study of more flexible ligands that provide access to other less symmetrical topologies (helicates, rectangles, boxes, cages, etc.) that are not available to the more rigid ligands.[10] In particular, we have synthesised a large number of ligands that can be represented by the generalised structure **1**.[11] These possess a central arene core to which are appended a number (*n*) of heterocyclic groups via spacer groups (X). For example, the simple ligand **2** was used to form a dimetallomacrocycle with internal π–π stacking by reaction with silver nitrate.[12] The isomeric ligand **3** was used to prepare the first quadruple helicate.[13] In these cases the flexibility is provided by the ether linkages. Variations include the introduction of additional methylene spacer groups and the use of different heterocycles, as in ligand **4** which forms a trinuclear circular helicate.[14] We have also varied the central arene core by using naphthalenes, anthracenes, biphenyls and radialenes.[15,16]

We now describe the synthesis, properties and selected X-ray crystal structures of a family of 35 new ligands that are derived from commercially available bisphenols by reaction with haloazines or chloromethylpyridines. The heterocycles chosen were based on our previous experience with pyridines, pyrazines, quinolines and quinoxalines, which have provided access to a number of interesting supramolecular assemblies.[10] The ligands are all symmetrical in the sense that the two heterocyclic donor groups in each structure are equivalent, which we have found to be important for the efficient self-assembly of metallosupramolecular species as less symmetrical ligands tend to lead to complex mixtures of products.[10]

2. Results and discussion

The 35 new potential ligands were all prepared by nucleophilic substitution reactions using two general procedures. The



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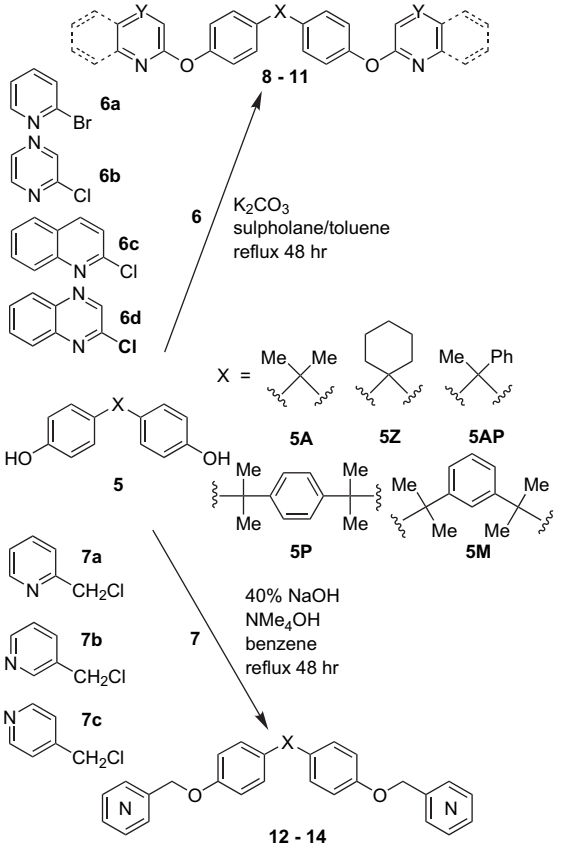
20 ligands **8**–**11** containing diaryl ether linkages were prepared by double nucleophilic aromatic substitution of the bisphenols **5** using the haloazines **6** by reaction in a refluxing sulpholane/toluene mixture. We have found these reaction conditions to be particularly effective for the preparation of related ligands derived from naphthalenediols.[17] The 15 ligands **12**–**14** containing two-atom spacer groups were prepared by phase-transfer-catalysed double alkylation of the bisphenols using the three isomeric chloromethylpyridines **7**, as shown in Scheme 1. Once again we have used these reaction conditions to prepare many structurally related ligands.[18,19]



Scheme 1. Preparations of **8**–**14**.

The products were isolated by standard procedures and purified by recrystallisation or column chromatography. Isolated yields were generally good and are shown along with the full structures in Chart 1. The compounds were all characterised by elemental analysis, mass spectrometry, melting point and by ^{1}H and ^{13}C NMR (see Section 4). Full assignments of the ^{1}H NMR spectra were relatively straightforward, being aided by the symmetrical nature of the compounds. The separate spin systems of the various aromatic rings were readily identified by their integrals and cross couplings and the individual protons of the heterocycles were assigned from their characteristic chemical shifts, spin–spin coupling and by comparison with the spectra from our own library of structurally related ligands containing these heterocycles.[10]

Since we intend to use these compounds as bridging ligands in the construction of metallosupramolecular assemblies, we were interested in their solid state structures. Thus, single crystal X-ray structure determinations were carried out on five representative compounds, each derived from a different bisphenol. This was done in order to (i) confirm their structures, (ii) determine their conformations in the solid state and (iii) measure the distances between the terminal nitrogen donors, which in turn will control the metal–metal separations in their metal complexes.

The X-ray structure of **8AP**, derived from bisphenol AP, is shown in Figure 1. It crystallises in the monoclinic space group $P2_1/c$ with a full molecule in the asymmetric unit. In the solid state the potential mirror symmetry is lost as a consequence of the propeller-like twisting of the three phenyl rings about the central quaternary carbon and the different conformations of the pyridyl ether units. The molecule has a relatively compact structure in which the two nitrogen atoms point towards the internal cavity between the phenyl rings. This is reflected in the two independent N–C–O–C torsional angles having low values of 0.8(2) and 19.1(2)°. The distance between the two potential nitrogen donors is a mere 8.388(2) Å.

The pyrazine-containing compound **9Z** also crystallises in space group $P2_1/c$ with a full molecule in the asymmetric unit. Once again, the symmetry observed in solution is destroyed in the solid state due to the locked conformation of the cyclohexane ring which has one axial and one equatorial phenyl substituent (Fig. 2). The overall structure of this compound is very similar to that of **8AP**, with the two nitrogens adjacent to the ether linkages being twisted inwards with N–C–O–C torsional angles of 6.6(2) and 35.2(2)°. The distance between the internal nitrogens is 8.020(3) Å, while the distal nitrogens are 13.350(3) Å apart. These are the nitrogens most likely to coordinate to metals.[20]

The pyrazine ligand **9M** also crystallises in the monoclinic space group $P2_1/c$ with a full molecule in the asymmetric unit (Fig. 3). It has a much more extended shape and has the pyrazine nitrogens adjacent to the ether linkage again pointing inwards with N–C–O–C torsional angles of 16.2(3) and 17.1(3)°. The internal nitrogens are now separated by 16.257(4) Å, while the less hindered distal nitrogens are 21.373(4) Å apart.

The methylene-extended ligand **13A** crystallises in the triclinic space group *P*-1 with a full molecule in the asymmetric unit (Fig. 4). This exists in a more symmetrical conformation in which each of the two-atom spacers adopts a trans-periplanar arrangement with C–C–O–C torsional angles of 174.8(1) and 169.8(1)°. The pyridine nitrogens now point outwards in order to participate in C–H···N intermolecular interactions about a centre of inversion. These features combine to increase the separation between the two nitrogens to a value of 17.528(2) Å.

Finally, the structure of the doubly extended ligand **13P** was determined. It crystallises in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit, the central ring being positioned on a crystallographic centre of inversion (Fig. 5). As in the previous example the methyleneoxy spacer has its two attached arene rings in a trans-periplanar arrangement with a C–C–O–C torsional angle of 178.3(2)°. The

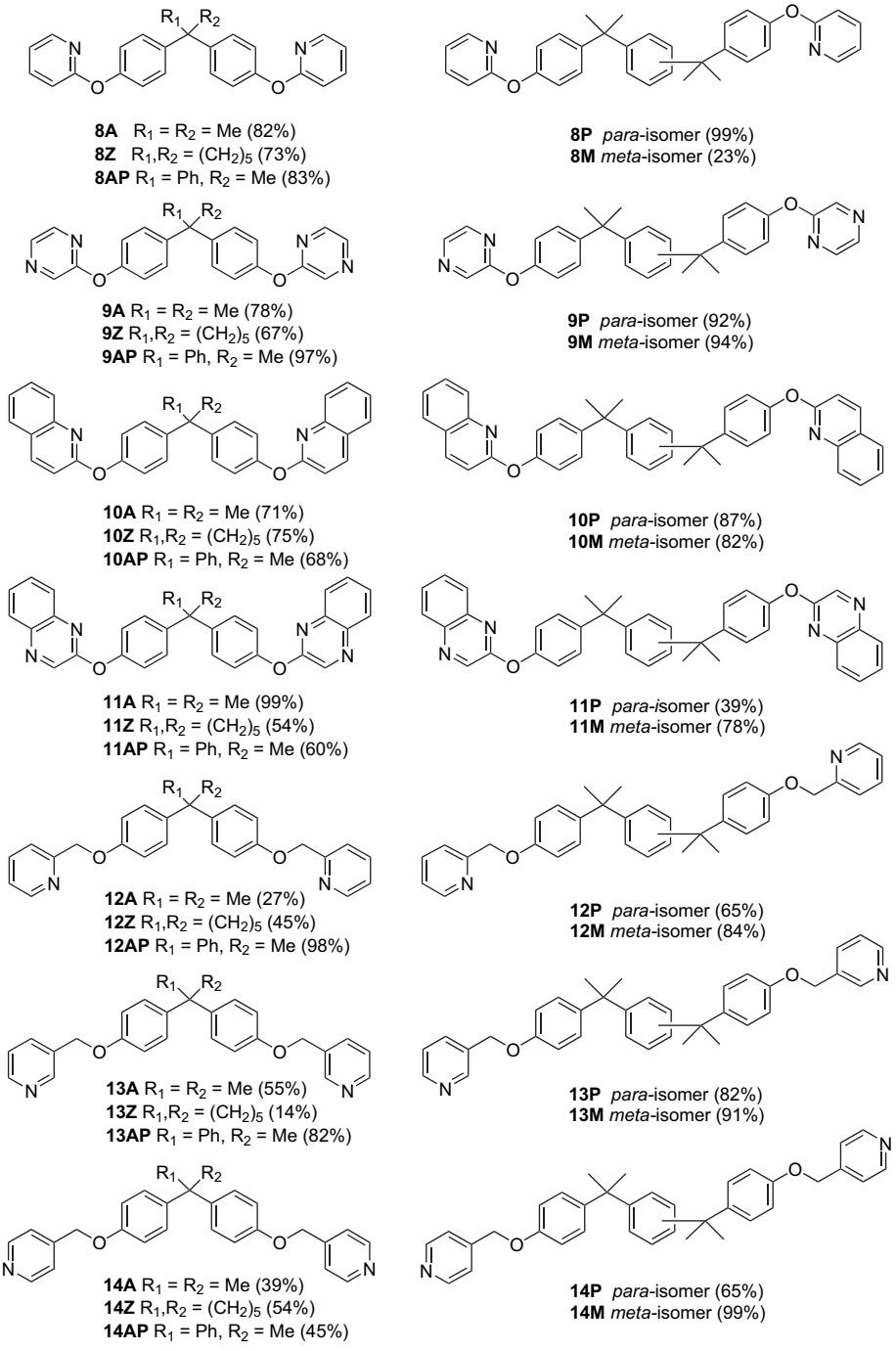


Chart 1. Structures and yields of **8**–**14**.

presence of the extra arene spacer extends the distance between the two nitrogens to 23.132(2) Å.

3. Conclusion

We have prepared 35 new bridging ligands from five commercially available bisphenols by coupling each with seven different heterocyclic units. X-ray crystal structures of five representative examples revealed different conformations in the solid state with the terminal nitrogen donors being separated by distances ranging from 8 to 23 Å. Metallosupramolecular assemblies derived from these ligands will be described elsewhere.

4. Experimental

4.1. General experimental

^{1}H NMR spectra were recorded on Varian Unity 300 or Varian 500 spectrometers at 23 °C with a 3 mm probe operating at 300 MHz or 500 MHz. Spectra were recorded in $CDCl_3$ and referenced relative to the internal standard Me_4Si. ^{13}C NMR

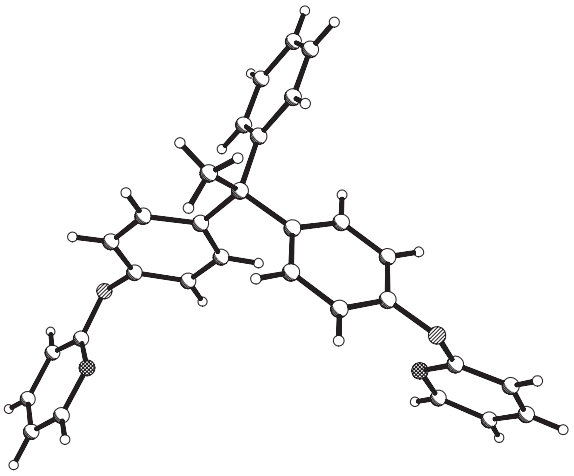


Figure 1. X-ray crystal structure of **8AP**.

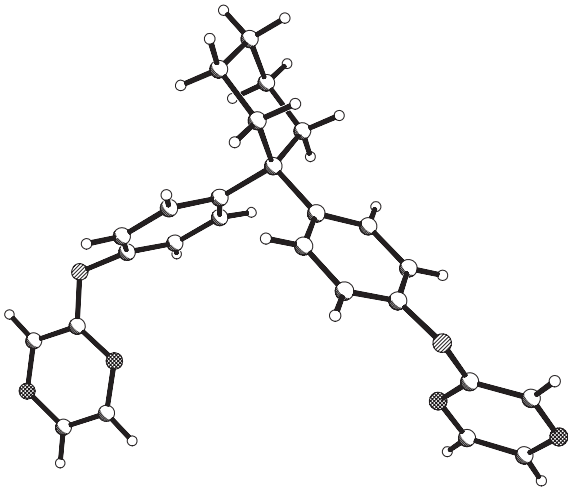


Figure 2. X-ray crystal structure of **9Z**.

spectra were recorded on a Varian Unity 300 spectrometer operating at 75 MHz and referenced against the solvent signal at 77.10 ppm. Electrospray (ES) mass spectra were recorded using a Micromass LCT-TOF mass spectrometer, with a probe operating at 3200 V and a cone voltage of 30 V. Samples were dissolved in 1:1 acetonitrile/water and spectra were acquired using source and desolvation temperatures of 80 and 150 °C, respectively. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell microanalytical laboratory, University of Otago, Dunedin.

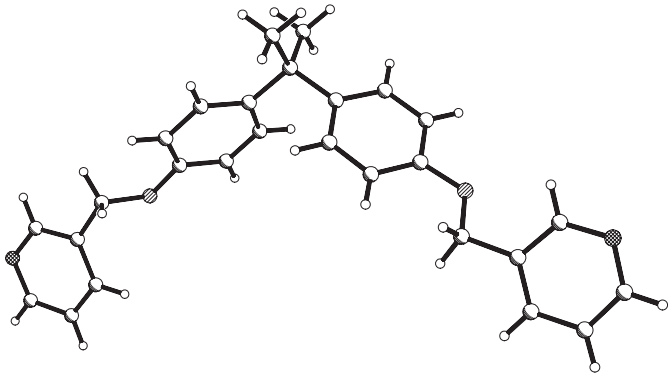


Figure 4. X-ray crystal structure of **13A**.

Unless otherwise stated, reagents were obtained from commercial sources and used as supplied. Solvents were purified by standard literature procedures and freshly distilled as required. 2-Chloroquinoxaline **6d** was prepared by a literature procedure.[21]

4.2. General reaction procedures

4.2.1. Method A

A mixture of bisphenol **5** (1 equiv) and potassium carbonate (4 equiv) was stirred in a solution of sulpholane/toluene (10/5 ml) at room temperature under argon for 45 min. The haloazine **6** (2 equiv) was added and the mixture was heated to reflux at ~180 °C under argon for 48 h. The resulting mixture was poured into a solution of 7% aqueous sodium hydroxide solution (~30 ml). This was then extracted with chloroform and the extracts were combined and reduced in vacuo to give the crude product in a sulpholane solution. This was added to acetone, heated, treated with decolourising charcoal and filtered. The acetone was removed in vacuo to give the product in a saturated sulpholane solution. Just enough water was added to precipitate the crude product, which was subsequently recrystallised from acetone/water solution to give the pure product.

4.2.2. Method B

A mixture of bisphenol **5** (1 equiv), the appropriate chloromethylpyridine·HCl **7** (2 equiv), 40% aqueous tetrabutylammonium hydroxide (6 drops), 40% aqueous sodium hydroxide (7 ml) and benzene (25 ml) was refluxed (~80 °C) for 48 h. The organic layer was then separated, dried over Na_2SO_4 and concentrated in vacuo to give a crude

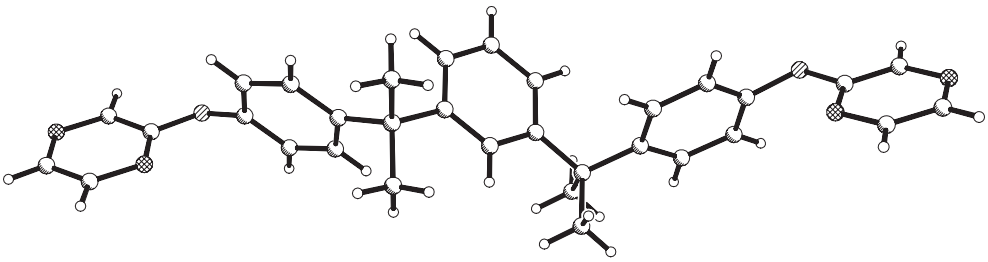


Figure 3. X-ray crystal structure of **9M**.

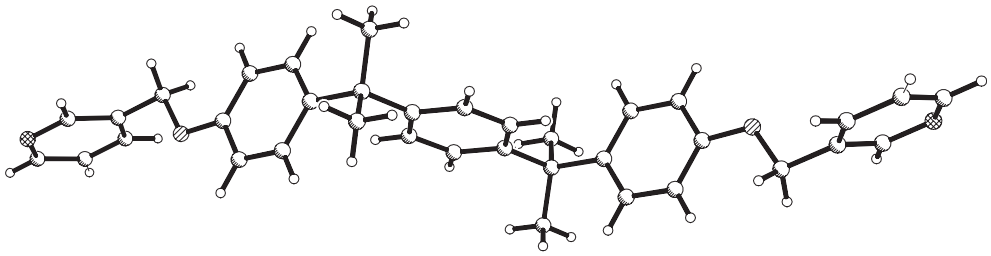


Figure 5. X-ray crystal structure of **13P**.

solid or oil, which was then purified by recrystallisation or column chromatography.

4.3. Physical and spectral properties

4.3.1. Compound *8A*

Method A from **5A** and **6a**. White solid. Yield 82%. Mp 110–113 °C. Anal. Found: C, 78.16; H, 5.86; N, 7.16. Calcd for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.21 (2H, H6′), 7.66 (2H, H4′), 7.29 (4H, H3, H5), 7.04 (4H, H2, H6), 6.98 (2H, H5′), 6.88 (2H, H3′), 1.71 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.67, 151.96, 147.69, 146.62, 139.42, 128.08, 120.31, 118.37, 111.52, 42.29, 30.96. ESI-MS: found MH^+=383.1763; $C_{25}H_{23}N_2O_2$ requires MH^+=383.1760.

4.3.2. Compound *8Z*

Method A from **5Z** and **6a**. White solid. Yield 70%. Mp 97–98 °C. Anal. Found: C, 79.61; H, 6.27; N, 6.57. Calcd for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.20 (2H, H6′), 7.66 (2H, H4′), 7.30 (2H, H3, H5), 7.05 (2H, H2, H6), 6.97 (2H, H5′), 6.86 (2H, H3′), 2.28 (4H, H8), 1.58 (4H, H9), 1.51 (2H, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.62, 151.77, 147.68, 144.57, 139.44, 128.43, 120.41, 118.40, 111.52, 45.55, 37.30, 26.32, 22.81. ESI-MS: found MH^+=423.2065; $C_{28}H_{27}N_2O_2$ requires MH^+=423.2073.

4.3.3. Compound *8AP*

Method A from **5AP** and **6a**. White crystalline solid. Yield 84%. Mp 108–111 °C. Anal. Found: C, 80.73; H, 5.51; N, 6.30. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.20 (2H, H6′), 7.67 (2H, H4′), 7.27 (2H, H3″, H5″), 7.20 (1H, H4″), 7.18 (6H, H2″, H6″, H3, H5), 7.13 (4H, H2, H6), 7.03 (2H, H5′), 6.97 (2H, H3′), 2.19 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.50, 152.28, 148.91, 147.68, 145.02, 139.47, 129.97, 128.68, 127.88, 126.02, 120.03, 118.51, 111.65, 51.79, 30.67. ESI-MS: found MH^+=445.1894; $C_{30}H_{25}N_2O_2$ requires MH^+=445.1916.

4.3.4. Compound *8P*

Method A from **5P** and **6a**. Pale yellow solid. Yield 99%. Mp 137–138 °C. Anal. Found: C, 81.32; H, 6.67; N, 5.44. Calcd for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.60. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.20 (2H, H6′), 7.66 (2H, H4′), 7.26 (4H, H3, H5), 7.15 (4H, H2″, H3″, H5″, H6″), 7.02 (4H, H2, H6), 6.98 (2H, H5′), 6.87 (2H, H3′), 1.67 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.68, 151.82, 147.60, 147.60, 146.91, 139.50, 128.09, 126.32, 120.25, 118.34, 111.48, 42.17, 30.84. ESI-MS: found MH^+=501.2553; $C_{34}H_{33}N_2O_2$ requires MH^+=501.2542.

4.3.5. Compound *8M*

Method A from **5M** and **6a**. White solid. Yield 23%. Mp 64–65 °C. Anal. Found: C, 80.61; H, 6.92; N, 5.00. Calcd for $C_{34}H_{32}N_2O_2\cdot 1/2CH_3COCH_3$: C, 80.50; H, 6.66; N, 5.29. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.28 (2H, H6′), 7.76 (2H, H4′), 7.11 (12H, H2, H3, H5, H6, H2″, H4″, H5″, H6″), 6.91 (2H, H5′), 6.69 (2H, H3′), 1.61 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.34, 153.94, 149.92, 147.18, 146.99, 140.18, 128.10, 127.68, 127.28, 123.48, 123.27, 119.50, 114.76, 42.60, 30.75. ESI-MS: found MH^+=501.2542; $C_{34}H_{33}N_2O_2$ requires MH^+=501.2542.

4.3.6. Compound *9A*

Method A from **5A** and **6b**. White crystalline solid. Yield 78%. Mp 130 °C. Anal. Found: C, 71.73; H, 5.31; N, 14.72. Calcd for $C_{23}H_{20}N_4O_2$: C, 71.86; H, 5.24; N, 14.57. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.41 (2H, H3′), 8.27 (2H, H6′), 8.13 (2H, H5′), 7.30 (4H, H3, H5), 7.08 (4H, H2, H6), 1.73 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.11, 150.86, 147.33, 141.08, 138.33, 135.85, 128.17, 120.46, 42.41, 30.90. ESI-MS: found MH^+=385.1648; $C_{23}H_{21}N_4O_2$ requires MH^+=385.1665.

4.3.7. Compound *9Z*

Method A from **5Z** and **6b**. White crystalline solid. Yield 82%. Mp 132–134 °C. Anal. Found: C, 73.62; H, 5.76; N, 13.16. Calcd for $C_{26}H_{24}N_4O_2$: C, 73.56; H, 5.70; N, 13.20. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.38 (2H, H3′), 8.25 (2H, H6′), 8.10 (2H, H5′), 7.33 (4H, H3, H5), 7.08 (4H, H2, H6), 2.30 (4H, H8), 1.59 (4H, H9), 1.52 (2H, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.10, 150.67, 145.26, 141.08, 138.34, 135.82, 128.51, 120.57, 45.65, 37.25, 26.23, 22.76. ESI-MS: found MH^+=425.1981; $C_{26}H_{25}N_4O_2$ requires MH^+=425.1978.

4.3.8. Compound *9AP*

Method A from **5AP** and **6b**. White crystalline solid. Yield 97%. Mp 151–155 °C. Anal. Found: C, 74.93; H, 5.11; N, 12.65. Calcd for $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.41 (2H, H3′), 8.26 (2H,

H6′), 8.11 (2H, H5′), 7.30 (2H, H3″, H5″), 7.22 (1H, H4″), 7.16 (6H, H2″, H6″, H3, H5), 7.07 (4H, H2, H6), 2.22 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.02, 151.19, 148.55, 145.79, 141.09, 138.50, 135.93, 130.07, 128.62, 127.99, 126.18, 120.27, 51.89, 30.66. ESI-MS: found MH^+=447.1838; $C_{28}H_{23}N_4O_2$ requires MH^+=447.1821.

4.3.9. Compound **9P**

Method A from **5P** and **6b**. White crystalline solid. Yield 69%. Mp 133.5–135 °C. Anal. Found: C, 76.20; H, 6.09; N, 11.08. Calcd for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.02; N, 11.15. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.39 (2H, H3′), 8.25 (2H, H6′), 8.12 (2H, H5′), 7.29 (4H, H3, H5), 7.15 (4H, H2″, H3″, H5″, H6″), 7.06 (4H, H2, H6), 1.68 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.14, 150.70, 147.66, 147.44, 141.06, 138.28, 135.80, 128.15, 126.30, 120.30, 42.20, 30.77. ESI-MS: found MH^+=503.2423; $C_{32}H_{31}N_4O_2$ requires MH^+=503.2447.

4.3.10. Compound **9M**

Method A from **5M** and **6b**. White crystalline solid. Yield 94%. Mp 103–104 °C. Anal. Found: C, 76.51; H, 6.09; N, 11.05. Calcd for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.02; N, 11.15. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.37 (2H, H3′), 8.24 (2H, H6′), 8.11 (2H, H5′), 7.24 (4H, H3, H5), 7.19 (1H, H5″), 7.14 (1H, H2″), 7.09 (2H, H4″, H6″), 7.03 (4H, H2, H6), 1.66 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.13, 150.66, 149.82, 147.69, 141.05, 138.26, 135.71, 128.09, 127.58, 125.31, 124.15, 120.28, 42.72, 30.74. ESI-MS: found MH^+=503.2444; $C_{32}H_{31}N_4O_2$ requires MH^+=503.2447.

4.3.11. Compound **10A**

Method A from **5A** and **6c**. White solid. Yield 71%. Mp 236–238 °C. Anal. Found: C, 77.52; H, 5.25; N, 5.47. Calcd for $C_{33}H_{26}N_2O_2\cdot 11/2H_2O$: C, 77.78; H, 5.74; N, 5.50. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.13 (2H, H4′), 8.10 (2H, H8′), 7.83 (2H, H5′), 7.76 (2H, H7′), 7.62 (2H, H6′), 7.44 (4H, H3, H5), 7.30 (4H, H2, H6), 7.08 (2H, H3′), 1.66 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.62, 151.67, 146.82, 146.42, 139.75, 129.75, 127.97, 127.89, 127.31, 125.64, 124.79, 120.57, 112.68, 42.40, 31.05. ESI-MS: found MH^+=483.2049; $C_{33}H_{27}N_2O_2$ requires MH^+=483.2073.

4.3.12. Compound **10Z**

Method A from **5Z** and **6c**. Yellow crystalline solid. Yield 75%. Mp 174–176 °C. Anal. Found: C, 80.03; H, 6.21; N, 4.88. Calcd for $C_{36}H_{30}N_2O_2\cdot 1/2H_2O$: C, 80.33; H, 6.11; N, 5.00. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.10 (2H, H4′), 7.83 (2H, H8′), 7.75 (2H, H5′), 7.61 (2H, H7′), 7.43 (2H, H6′), 7.37 (4H, H3, H5), 7.19 (4H, H2, H6), 7.06 (2H, H3′), 2.34 (4H, H8), 1.63 (4H, H9), 1.55 (2H, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.61, 151.46, 146.42, 144.77, 139.74, 129.74, 128.33, 127.87, 127.31, 125.64, 124.79, 120.75, 112.68, 45.67, 37.67, 26.38, 22.88. ESI-MS: found MH^+=523.2390; $C_{36}H_{31}N_2O_2$ requires MH^+=523.2386.

4.3.13. Compound **10AP**

Method A from **5AP** and **6c**. Yellow crystalline solid. Yield 69%. Mp 180 °C. Anal. Found: C, 82.19; H, 5.25; N, 4.98. Calcd for $C_{38}H_{28}N_2O_2\cdot 1/2H_2O$: C, 82.44; H, 5.28; N, 5.06. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.07 (2H, H4′), 7.82 (2H, H8′), 7.73 (2H, H5′), 7.59 (2H, H7′), 7.39 (2H, H6′), 7.30 (2H, H3″, H5″), 7.22 (7H, H2″, H4″, H6″, H3, H5), 7.07 (4H, H2, H6), 2.24 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.48, 151.95, 149.02, 146.35, 145.24, 139.81, 129.87, 129.80, 128.73, 127.94, 127.84, 127.33, 126.07, 125.66, 124.85, 120.39, 112.72, 51.89, 30.77. ESI-MS: found MH^+=545.2239; $C_{38}H_{29}N_2O_2$ requires MH^+=545.2229.

4.3.14. Compound **10P**

Method A from **5P** and **6c**. White solid. Yield 87%. Mp 210–211 °C. Anal. Found: C, 83.69; H, 5.91; N, 4.61. Calcd for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04; N, 4.66. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.10 (2H, H4′), 7.82 (2H, H8′), 7.74 (2H, H5′), 7.61 (2H, H7′), 7.40 (2H, H6′), 7.29 (4H, H3, H5), 7.19 (4H, H2″, H3″, H5″, H6″), 7.16 (4H, H2, H6), 7.04 (2H, H3′), 1.71 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.65, 151.57, 147.65, 147.02, 146.39, 139.76, 129.77, 127.97, 127.84, 127.31, 126.37, 125.61, 124.79, 120.48, 112.61, 42.26, 30.92. ESI-MS: found MH^+=601.2825; $C_{42}H_{37}N_2O_2$ requires MH^+=601.2855.

4.3.15. Compound **10M**

Method A from **5M** and **6c**. Yellow crystalline solid. Yield 80%. Mp 134.5–135.5 °C. Anal. Found: C, 83.68; H, 6.12; N, 4.58. Calcd for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04; N, 4.66. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.04 (2H, H4′), 7.79 (2H, H8′), 7.70 (2H, H5′), 7.58 (2H, H7′), 7.38 (2H, H6′), 7.25 (4H, H3, H5), 7.20 (1H, H5″), 7.14 (1H, H2″), 7.12 (6H, H2, H6, H4″, H6″), 1.69 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.61, 151.51, 150.05, 146.98, 146.36, 139.64, 129.69, 127.87, 127.79, 127.55, 127.26, 125.55, 125.44, 124.70, 124.14, 120.48, 112.51, 42.74, 30.85. ESI-MS: found MH^+=601.2849; $C_{42}H_{37}N_2O_2$ requires MH^+=601.2855.

4.3.16. Compound **11A**

Method A from **5A** and **6d**. Yellow crystalline solid. Yield 99%. Mp 181–182 °C. Anal. Found: C, 76.84; H, 5.17; N, 11.48. Calcd for $C_{31}H_{24}N_4O_2$: C, 76.84; H, 4.99; N, 11.56. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.69 (2H, H3′), 8.06 (2H, H8′), 7.79 (2H, H5′), 7.67 (4H, H6′, H7′), 7.37 (4H, H3, H5), 7.23 (4H, H2, H6), 1.77 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.82, 150.63, 147.42, 139.96, 139.48, 139.19, 130.33, 128.83, 128.04, 127.69, 127.39, 120.62, 42.50, 30.99. ESI-MS: found MH^+=485.1991; $C_{31}H_{25}N_4O_2$ requires MH^+=485.1978.

4.3.17. Compound **11Z**

Method A from **5Z** and **6d**. Yellow solid. Yield 54%. Mp 161–162 °C. Anal. Found: C, 76.15; H, 5.62; N, 10.10. Calcd for $C_{34}H_{28}N_4O_2\cdot 1/2H_2O$: C, 76.53; H, 5.48; N, 10.50. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.66 (2H, H3′), 8.06 (2H, H8′), 7.80 (2H, H5′), 7.62 (4H, H6′, H7′), 7.40 (4H, H3, H5), 7.25

(4H, H2, H6), 2.35 (4H, H8), 1.64 (4H, H9), 1.56 (2H, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.80, 150.45, 145.39, 139.96, 139.56, 139.27, 130.32, 128.87, 128.42, 127.72, 127.39, 120.78, 45.78, 37.36, 26.32, 22.85. ESI-MS: found MH^+=525.2309; $C_{34}H_{29}N_4O_2$ requires MH^+=525.2291.

4.3.18. Compound *11AP*

Method A from **5AP** and **6d**. Yellow crystalline solid. Yield 60%. Mp 136.5 °C. Anal. Found: C, 76.77; H, 5.00; N, 9.08. Calcd for $C_{36}H_{27}N_4O_2\cdot 1/3H_2O\cdot CH_3COCH_3$: C, 76.70; H, 5.39; N, 9.17. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.69 (2H, H3′), 8.07 (2H, H8′), 7.80 (2H, H5′), 7.68 (2H, H6′), 7.63 (2H, H7′), 7.34 (2H, H3″, H5″), 7.27–7.14 (11H, H2, H3, H5, H6, H2″, H4″, H6″), 2.28 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.77, 150.93, 148.72, 145.94, 139.91, 139.09, 130.45, 129.97, 128.81, 128.69, 128.04, 127.73, 127.54, 126.22, 120.49, 104.70, 51.13, 22.78. ESI-MS: found MH^+=547.2112; $C_{36}H_{27}N_4O_2$ requires MH^+=547.2134.

4.3.19. Compound *11P*

Method A from **5P** and **6d**. Yellow solid. Yield 39%. Mp 174–175 °C. Anal. Found: C, 78.51; H, 5.82; N, 8.54. Calcd for $C_{40}H_{34}N_4O_2\cdot CH_3COCH_3$: C, 78.16; H, 6.10; N, 8.48. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.67 (2H, H3′), 8.07 (2H, H8′), 7.79 (2H, H5′), 7.66 (2H, H6′), 7.62 (2H, H7′), 7.32 (4H, H3, H5), 7.20 (4H, H2″, H3″, H5″, H6″), 7.18 (2H, H2, H6), 1.72 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.54, 147.79, 147.60, 140.09, 139.34, 139.05, 130.40, 128.76, 128.07, 127.76, 127.46, 126.40, 120.48, 104.70, 42.34, 30.77. ESI-MS: found MH^+=603.2753; $C_{40}H_{35}N_4O_2$ requires MH^+=603.2760.

4.3.20. Compound *11M*

Method A from **5M** and **6d**. Orange solid. Yield 78%. Mp 143–144 °C. Anal. Found: C, 79.68; H, 5.81; N, 9.05. Calcd for $C_{40}H_{34}N_4O_2$: C, 79.71; H, 5.69; N, 9.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.61 (2H, H3′), 8.02 (2H, H8′), 7.73 (2H, H5′), 7.62 (2H, H6′), 7.57 (2H, H7′), 7.29 (4H, H3, H5), 7.25 (1H, H5″), 7.18 (1H, H2″), 716 (2H, H4″, H6″), 7.14 (4H, H2, H6), 1.71 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.83, 150.47, 149.98, 147.72, 141.98, 139.92, 139.47, 139.16, 130.26, 128.84, 127.96, 127.63, 127.31, 125.60, 124.13, 120.47, 42.81, 30.82. ESI-MS: found M^+=602.2681; $C_{40}H_{34}N_4O_2$ requires M^+=602.2682.

4.3.21. Compound *12A*

Method B from **5A** and **7a**. White solid. Yield 26%. Mp 71–72 °C. Anal. Found: C, 78.73; H, 6.51; N, 6.85. Calcd for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.59 (2H, H6′), 7.72 (2H, H4′), 7.69 (2H, H3′), 7.22 (2H, H5′), 7.15 (4H, H3, H5), 6.88 (4H, H2, H6), 5.18 (4H, CH_2), 1.63 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.46, 156.22, 149.11, 143.52, 136.79, 127.77, 122.52, 121.21, 114.12, 70.56, 41.68, 30.98. ESI-MS: found MH^+=411.2076; $C_{27}H_{27}N_2O_2$ requires MH^+=411.2073.

4.3.22. Compound *12Z*

Method B from **5Z** and **7a**. White solid. Yield 45%. Mp 98–99.5 °C. Anal. Found: C, 79.95; H, 6.72; N, 6.22. Calcd for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.56 (2H, H6′), 7.69 (2H, H4′), 7.52 (2H, H3′), 7.20 (2H, H5′), 7.16 (4H, H3, H5), 6.89 (4H, H2, H6), 5.16 (4H, CH_2), 2.19 (4H, H8), 1.50 (6H, H9, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.27, 155.91, 148.60, 141.54, 137.30, 128.16, 122.67, 121.43, 114.35, 70.19, 45.05, 37.33, 26.37, 22.87. ESI-MS: found MH^+=451.2364; $C_{30}H_{31}N_2O_2$ requires MH^+=451.2386.

4.3.23. Compound *12AP*

Method B from **5AP** and **7a**. Brown oil. Yield 98.1%. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.54 (2H, H6′), 7.65 (2H, H4′), 7.50 (2H, H3′), 7.22 (2H, H5′), 7.15 (1H, H4″), 7.08 (4H, H2″, H3″, H5″, H6″), 7.00 (4H, H3, H5), 6.88 (4H, H2, H6), 5.16 (4H, CH_2), 2.12 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.06, 156.22, 149.21, 148.83, 141.70, 136.62, 129.50, 128.33, 127.58, 125.64, 122.37, 121.05, 113.77, 70.27, 51.01, 30.41. ESI-MS: found MH^+=473.2249; $C_{32}H_{29}N_2O_2$ requires MH^+=473.2229.

4.3.24. Compound *12P*

Method B from **5P** and **7a**. White crystalline solid. Yield 80%. Mp 171 °C. Anal. Found: C, 81.73; H, 7.03; N, 5.28. Calcd for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.58 (2H, H6′), 7.72 (2H, H4′), 7.69 (2H, H3′), 7.54 (2H, H5′), 7.15 (4H, H3, H5), 7.09 (4H, H2″, H3″, H5″, H6″), 6.88 (4H, H2, H6), 5.18 (4H, CH_2), 1.63 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.45, 156.18, 149.02, 147.73, 143.41, 136.85, 127.82, 126.17, 122.52, 121.23, 114.07, 70.49, 41.83, 30.84. ESI-MS: found MH^+=529.2855; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

4.3.25. Compound *12M*

Method B from **5M** and **7a**. White crystalline solid. Yield 84%. Mp 81–82 °C. Anal. Found: C, 80.64; H, 7.21; N, 5.28. Calcd for $C_{36}H_{36}N_2O_2\cdot 1/2H_2O$: C, 80.42; H, 6.94; N, 5.21. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.56 (2H, H6′), 7.66 (2H, H4′), 7.51 (2H, H3′), 7.18 (2H, H5′), 7.17 (1H, H5″), 7.10 (4H, H3, H5), 7.08 (1H, H2″), 7.01 (2H, H4″, H6″), 6.86 (4H, H2, H6), 5.17 (4H, CH_2), 1.60 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.39, 156.08, 150.14, 149.03, 143.41, 136.71, 127.73, 127.33, 125.14, 123.97, 122.45, 121.17, 114.00, 70.48, 42.32, 30.81. ESI-MS: found MH^+=529.2876; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

4.3.26. Compound *13A*

Method B from **5A** and **7b**. Yellow solid. Yield 53%. Mp 127–128.5 °C. Anal. Found: C, 78.74; H, 6.43; N, 6.79. Calcd for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.67 (2H, H2′), 8.58 (2H, H6′), 7.77 (2H, H4′), 7.31 (2H, H5′), 7.16 (4H, H3, H5), 6.88 (4H, H2, H6), 5.04 (4H, CH_2), 1.64 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.20, 149.22, 148.83, 143.72, 135.36, 132.73,

127.81, 123.51, 114.11, 67.45, 41.72, 30.97. ESI-MS: found MH^+=411.2059; $C_{27}H_{27}N_2O_2$ requires MH^+=411.2073.

*4.3.27. Compound **13Z***

Method B from **5Z** and **7b**. Orange solid. Yield 16%. Mp 117–118 °C. Anal. Found: C, 79.90; H, 6.78; N, 6.25. Calcd for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.66 (2H, H2′), 8.57 (2H, H6′), 7.76 (2H, H4′), 7.32 (2H, H5′), 7.17 (4H, H3, H5), 6.89 (4H, H2, H6), 5.03 (4H, CH_2), 2.22 (4H, H8), 1.53 (6H, H9, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.97, 149.13, 148.74, 141.69, 135.47, 132.81, 128.19, 123.56, 114.33, 67.40, 45.08, 37.32, 26.34, 22.86. ESI-MS: found MH^+=451.2365; $C_{30}H_{31}N_2O_2$ requires MH^+=451.2386.

*4.3.28. Compound **13AP***

Method B from **5AP** and **7b**. Brown solid. Yield 82%. Mp 98–99 °C. Anal. Found: C, 80.63; H, 6.22; N, 5.84. Calcd for $C_{32}H_{28}N_2O_2\cdot 1/3H_2O$: C, 80.31; H, 6.04; N, 5.85. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.66 (2H, H2′), 8.57 (2H, H6′), 7.76 (2H, H4′), 7.30 (2H, H5′), 7.26 (2H, H3″, H5″), 7.20 (1H, H4″), 7.09 (2H, H2″, H6″), 7.01 (4H, H3, H5), 6.86 (4H, H2, H6), 5.03 (4H, CH_2), 2.13 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.37, 149.25, 148.84, 142.04, 135.25, 132.54, 129.75, 129.69, 128.46, 127.77, 125.83, 123.44, 113.88, 67.38, 51.19, 30.57. ESI-MS: found MH^+=473.2207; $C_{32}H_{29}N_2O_2$ requires MH^+=473.2229.

*4.3.29. Compound **13P***

Method B from **5P** and **7b**. White crystalline solid. Yield 82.0%. Mp 176–177 °C. Anal. Found: C, 81.93; H, 6.87; N, 5.36. Calcd for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.67 (2H, H2′), 8.57 (2H, H6′), 7.76 (2H, H4′), 7.31 (2H, H5′), 7.16 (4H, H3, H5), 7.09 (4H, H2″, H3″, H5″, H6″), 6.86 (4H, H2, H6), 5.04 (4H, CH_2), 1.63 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.19, 149.24, 148.85, 147.74, 143.67, 135.35, 132.75, 127.88, 126.19, 123.51, 114.05, 67.45, 41.87, 30.84. ESI-MS: found MH^+=529.2846; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

*4.3.30. Compound **13M***

Method B from **5M** and **7b**. Brown solid. Yield 90.4%. Mp 72–73 °C. Anal. Found: C, 81.49; H, 7.07; N, 5.32. Calcd for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.65 (2H, H2′), 8.55 (2H, H6′), 7.74 (2H, H4′), 7.27 (2H, H5′), 7.12 (4H, H3, H5), 7.14 (1H, H5″), 7.12 (4H, H3, H5), 7.10 (1H, H2″), 7.02 (2H, H4″, H6″), 6.84 (4H, H2, H6), 5.02 (4H, CH_2), 1.61 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.03, 150.06, 149.19, 148.82, 143.60, 135.14, 132.56, 127.73, 127.33, 125.12, 123.92, 123.35, 113.94, 67.36, 42.30, 30.77. ESI-MS: found MH^+=529.2828; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

*4.3.31. Compound **14A***

Method B from **5A** and **7c**. Yellow solid. Yield 39%. Mp 135–136 °C. Anal. Found: C, 78.88; H, 6.48; N, 6.86. Calcd for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.62 (4H, H2′, H6′), 7.36 (4H, H3′, H5′), 7.15 (4H, H3, H5), 6.85 (4H, H2, H6), 5.06 (4H, CH_2), 1.63 (6H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.97, 149.46, 147.00, 143.85, 127.86, 121.62, 114.13, 68.08, 41.75, 30.96. ESI-MS: found MH^+=411.2092; $C_{27}H_{27}N_2O_2$ requires MH^+=411.2073.

*4.3.32. Compound **14Z***

Method B from **5Z** and **7c**. White crystalline solid. Yield 14%. Mp 130–132 °C. Anal. Found: C, 79.70; H, 6.80; N, 6.18. Calcd for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300 MHz, $CHCl_3$): δ 8.59 (4H, H2′, H6′), 7.33 (4H, H3′, H5′), 7.18 (4H, H3, H5), 6.85 (4H, H2, H6), 5.02 (4H, CH_2), 2.21 (4H, H8), 1.52 (6H, H9, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.74, 149.66, 146.65, 141.74, 128.17, 121.52, 114.31, 68.03, 45.03, 37.27, 26.29, 22.81. ESI-MS: found MH^+=451.2381; $C_{30}H_{31}N_2O_2$ requires MH^+=451.2386.

*4.3.33. Compound **14AP***

Method B from **5AP** and **7c**. Brown solid. Yield 48%. Mp 124 °C. Anal. Found: C, 80.34; H, 6.18; N, 6.04. Calcd for $C_{32}H_{28}N_2O_2\cdot 1/3H_2O$: C, 80.31; H, 6.04; N, 5.85. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.61 (4H, H2′, H6′), 7.35 (4H, H3′, H5′), 7.27 (2H, H3″, H5″), 7.21 (1H, H4″), 7.19 (2H, H2″, H6″), 7.07 (4H, H3, H5), 6.84 (4H, H2, H6), 5.06 (4H, CH_2), 2.13 (3H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.20, 149.84, 149.22, 146.31, 142.16, 129.74, 128.48, 127.81, 125.90, 121.47, 113.92, 68.05, 51.23, 30.58. ESI-MS: found MH^+=473.2234; $C_{32}H_{29}N_2O_2$ requires MH^+=473.2229.

*4.3.34. Compound **14P***

Method B from **5P** and **7c**. Cream solid. Yield 68%. Mp 76–77 °C. Anal. Found: C, 81.65; H, 6.70; N, 5.29. Calcd for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.61 (4H, H2′, H6′), 7.35 (4H, H3′, H5′), 7.15 (4H, H3, H5), 7.09 (4H, H2″, H3″, H5″, H6″), 6.84 (4H, H2, H6), 5.05 (4H, CH_2), 1.63 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.98, 149.81, 147.73, 146.57, 143.78, 127.91, 126.19, 121.51, 114.06, 68.11, 41.88, 30.83. ESI-MS: found MH^+=529.2846; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

*4.3.35. Compound **14M***

Method B from **5M** and **7c**. Brown solid. Yield 98%. Mp 91–92 °C. Anal. Found: C, 80.45; H, 7.56; N, 5.18. Calcd for $C_{36}H_{36}N_2O_2\cdot 1/2CH_3CO_2C_2H_5$: C, 80.82; H, 7.14; N, 7.08. ^{1}H NMR (500 MHz, $CHCl_3$): δ 8.59 (4H, H2′, H6′), 7.33 (4H, H3′, H5′), 7.14 (1H, H5″), 7.11 (5H, H3, H5, H2″), 7.02 (2H, H4″, H6″), 6.82 (4H, H2, H6), 5.05 (4H, CH_2), 1.60 (12H, H8). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.81, 150.03, 149.74, 146.34, 143.71, 127.75, 127.34, 125.12, 123.91, 121.37, 113.92, 67.96, 42.29, 30.75. ESI-MS: found MH^+=529.2870; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855.

Table 1
Crystal data and X-ray experimental details

Compound	**8AP**	**9Z**	**9M**	**13A**	**13P**
Empirical formula	$C_{30}H_{24}N_2O_2$	$C_{26}H_{24}N_4O_2$	$C_{32}H_{30}N_4O_2$	$C_{27}H_{26}N_2O_2$	$C_{36}H_{36}N_2O_2$
Formula weight	444.51	424.49	502.60	410.50	528.67
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1	$P2_1/n$
Unit cell dimensions					
a (Å)	13.5894(7)	15.6096(10)	11.1220(6)	6.3060(2)	6.0100(4)
b (Å)	11.9003(5)	9.3870(7)	6.6592(3)	12.2921(3)	6.8165(5)
c (Å)	15.2111(7)	14.6695(11)	35.002(2)	14.2864(4)	34.162(3)
α (°)	90	90	90	92.837(1)	90
β (°)	105.038(3)	100.607(3)	95.294(3)	99.980(1)	90.981(2)
γ (°)	90	90	90	96.315(1)	90
Volume (Å^3)	2375.67(19)	2112.8(3)	2581.4(2)	1081.36(5)	1399.32(17)
Z	4	4	4	2	2
Density (calculated) (Mg/m^3)	1.243	1.335	1.293	1.261	1.255
Absorption coefficient (mm^{-1})	0.078	0.087	0.082	0.080	0.077
F(000)	936	896	1064	436	564
Crystal size (mm^3)	0.34×0.21×0.08	0.48×0.40×0.12	0.35×0.18×0.01	0.62×0.30×0.30	0.48×0.45×0.04
θ Range for data collection (°)	2.20–25.05	1.33–25.05	3.11–25.05	1.67–25.05	1.19–25.05
Reflections collected	22,115	18,254	32,280	12,392	8856
Independent reflections [R(int)]	4213 [0.0489]	3742 [0.0559]	4565 [0.1694]	3830 [0.0103]	2461 [0.0358]
Observed reflections [$I>2\sigma(I)$]	2982	2574	1818	3519	1877
Data/restraints/parameters	4213/0/308	3742/0/289	4565/0/343	3830/0/280	2461/0/181
Goodness-of-fit on F^2	0.996	0.997	0.803	1.057	1.042
R_1 [$I>2\sigma(I)$]	0.0391	0.0460	0.0479	0.0322	0.0468
wR_2 (all data)	0.0968	0.1041	0.0900	0.0860	0.1048

4.4. Crystallography

Crystal data and experimental details of the data collections and structure refinements are listed in Table 1. Data were collected with an APEX CCD area detector, using graphite monochromatised Mo Kα radiation (λ=0.71073 Å). Almost complete spheres of data were collected. The structures were solved by direct methods using SHELXS,[22] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[23] Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 665094–665098). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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References and notes

1. Constable, E. C. *Chem. Ind.* **1994**, 56–59.
2. Steel, P. J. *Chem. N.Z.* **2003**, *67*, 57–60.
3. Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908.
4. Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3537.
5. Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043.
6. Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509–518.
7. Siedel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983.
8. Janiak, C. *Dalton Trans.* **2003**, 2781–2804.
9. Gavrilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, *104*, 349–383.
10. Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250.
11. Sumby, C. J.; Steel, P. J. *Inorg. Chim. Acta* **2007**, *360*, 2100–2114 and references therein.
12. Hartshorn, C. M.; Steel, P. J. *Inorg. Chem.* **1996**, *35*, 6902–6903.
13. McMorran, D. A.; Steel, P. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3295–3297.
14. Al-Mandhary, M. R. A.; Steel, P. J. *Inorg. Chem. Commun.* **2002**, *5*, 954–957.
15. O'Keefe, B. J.; Steel, P. J. *CrystEngComm* **2007**, *9*, 222–227.
16. Steel, P. J.; Sumby, C. J. *Chem. Commun.* **2002**, 322–323.
17. O'Keefe, B. J.; Steel, P. J. *Molecules* **2006**, *11*, 684–692.
18. Hartshorn, C. M.; Steel, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3927–3934.
19. Hartshorn, C. M.; Steel, P. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 2655–2657.
20. Steel, P. J.; Fitchett, C. M. *Coord. Chem. Rev.*, in press. doi:10.1016/j.ccr.2007.07.018
21. Gowenlock, A. H.; Newbold, G. T.; Spring, F. S. *J. Chem. Soc.* **1945**, 622–625.
22. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
23. Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.