Improved Syntheses of *Meso*-Aryl Tetrabenzotriazaporphyrins (TBTAPs)

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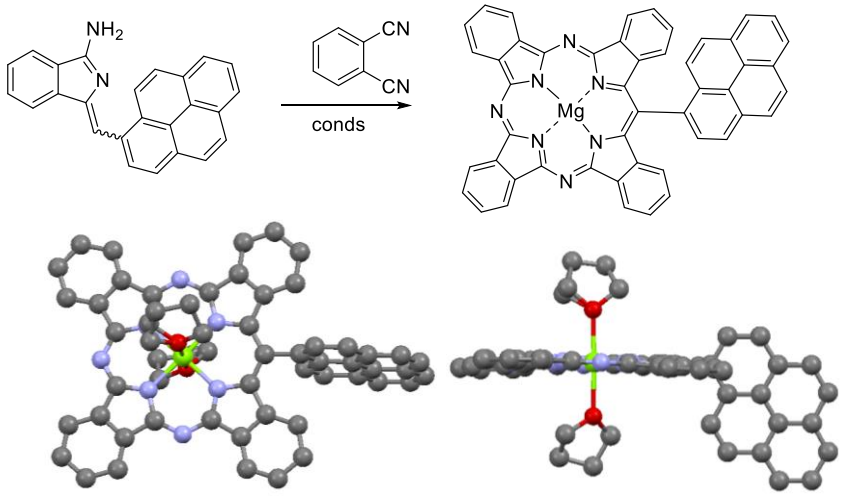
Graphical Abstract



Improved Syntheses of *Meso*-Aryl Tetrabenzotriazaporphyrins (TBTAPs)

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Abstract

New tetrabenzotriazaporphyrins are reported that are functionalised at the *meso*-position. The derivatives functionalised with *meso*-bromophenyl substituents are synthesised using an improved variation on the traditional reaction between phthalonitriles and Grignard reagents. For all other new derivatives, a modern protocol is employed that gives convenient access to these challenging materials by template co-macrocyclisation between phthalonitriles and aryl-aminoisoindoline derivatives like **15**. The newly developed procedure allows design and synthesis of elaborate, functional composites and this is demonstrated by synthesis of *meso*-pyrenylTBTAP **24**, a linked double chromophore in which the two complementary units lie perpendicular to each other and therefore have minimal ground state interaction.

Keywords: Phthalocyanines, Porphyrins, Heterocycles, Synthesis, Hybrids, Pyrene

1. Introduction

The tetrabenzotriazaporphyrin (TBTAP) ring system is one of four types of macrocycle Fig. 1, that can be regarded as hybrids of the much more familiar phthalocyanine (Pc) and tetrabenzoporphyrin (TBP) structures. Molecular orbital calculations for all six molecules,[1,2] the most recent of which utilise TD-DFT methods,[2] show their close inter-relationships but also predict how systematic replacement of the four aza links of the Pc structure by methine carbon atoms leads to an increase in the HOMO-LUMO energy differences. Thus each hybrid structure exhibits a visible region absorption (Q-band) that lies between those of the Pc and TBP structures: that for TBTAP, the molecular type that is the subject of this paper, is the least hypsochromically shifted from that of the Pc ring.

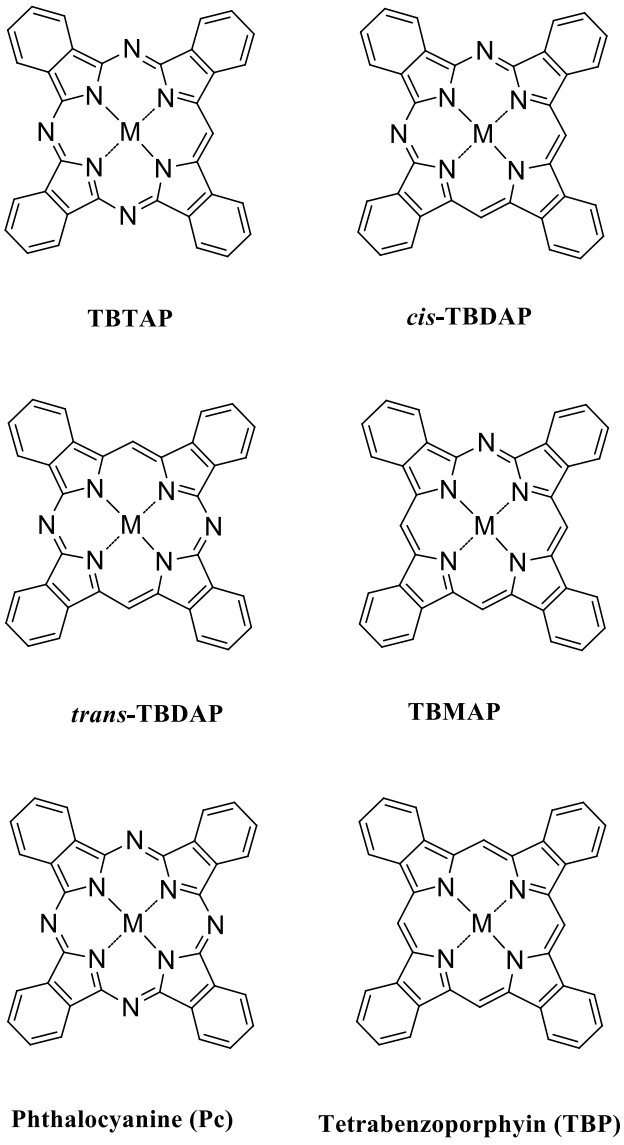


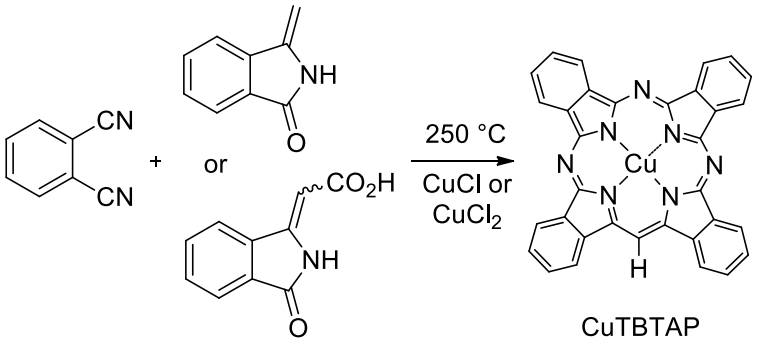
Figure 1. Structures of types of tetrabenzofused 18π electron macrocycles. M = H,H, a metal ion or metalloid element. Tetrabenzotriazaporphyrin, TBTAP; *cis*- and *trans*-tetrabenzodiazaporphyrins, TBDAPs; tetrabenzomonoazaporphyrin, TBMAP; Phthalocyanine and tetrabenzoporphyrin.

Research into the chemistry, properties and applications of Pcs in particular and, to a lesser extent, TBPs has provided the basis of many thousands of papers and these have been discussed in numerous articles and reviews.[3] In contrast, TBTAP compounds, as well as examples of the other hybrids shown in Fig 1, have received much less attention. However, by possessing aspects of the properties of both Pcs and TBPs they have the potential to offer advantages over both. This has been nicely illustrated by Borisov and coworkers.[4] Their research into applications of oxygen quenching of phosphorescence showed that while Pt and Pd metalated Pcs, denoted as PtPc and PdPc, possess remarkable chemical,

thermal and photostability they are only weak emitters of phosphorescence. At the other extreme Pt and PdTBPs show strong emission but poor photostability. In contrast, examples of Pt and PdTBTAPs exhibit both excellent photostability and very satisfactory emission.

As with the Pc and TBP ring system, the TBTAP structure can provide a diversity of derivatives by varying the ion/metalloid at the centre of the macrocycle and through the incorporation of substituents at various points on the macrocycle and, where appropriate, provision of ligands at the metal/metalloid centre. However, from the synthetic chemistry viewpoint, the more significant challenge is the incorporation of the single bridging (*meso*) carbon into the central core and exploiting this as a point for added functionalisation. It is perhaps this issue that has inhibited the potential of the TBTAP series of macrocycles to be fully realised at this time – indeed there are fewer than 50 reports on the synthesis of members of the series.

Unsurprisingly, the majority of reported syntheses have focussed on intervention into the cyclotetramerisation of a typical Pc precursor such as phthalonitrile. Pc synthesis is normally undertaken using either strongly basic conditions or by heating in the presence of a metal ion or metal oxide which serves to act as a template and which also mediates a redox process that ultimately provides the Pc core. Thus the majority of syntheses of TBTAP derivatives have exploited the use of Pc precursors but with the inclusion of a reagent, typically containing a potential 'nucleophilic' carbon, to provide the *meso* carbon bridge. This is typified in the first synthesis of a TBTAP derivative by Dent in 1938,[5] a paper published a few months after Helberger[6] reported the first example of a tetrabenzomonoazaporphyrin, TDMAP, and some 4 years after the first of the pioneering papers on Pcs by Linstead and coworkers.[7] Dent obtained copper metalated TBTAP, i.e CuTBTAP, by reacting phthalonitrile with either phthalimidineacetic acid or methylenephthalimidine as providers of the *meso* carbon. The reaction was carried out in the presence of a copper salt in chloronaphthalene at elevated temperatures (Scheme 1)



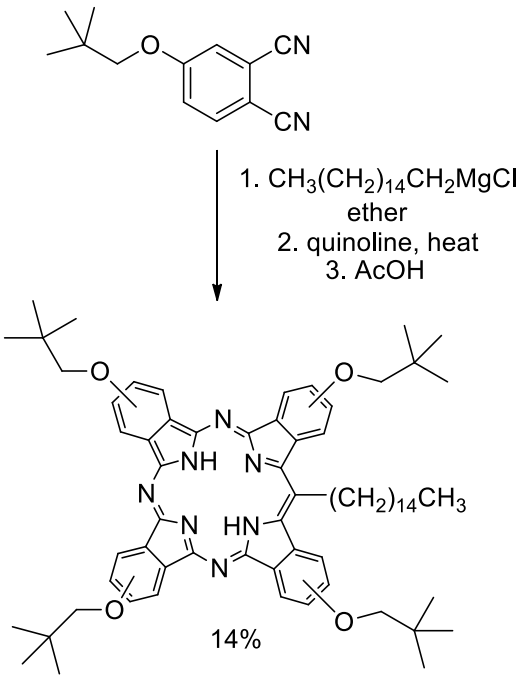
Scheme 1. The early syntheses of CuTBTAP employing mixed cyclizations between a phthalonitrile and methylenephthalimidine or its precursor.

Shortly after, Linstead's group obtained MgTBTAP by reacting phthalonitrile with either the Grignard reagent MeMgI or methyl lithium to provide the *meso* carbon, following a two-stage procedure, initially reacting in cold ether solution followed by heating in a high boiling solvent.[8] Acidic conditions removed the magnesium to allow other metal ions, eg copper, zinc, lithium and iron to be incorporated. Following the same approach several decades later, Hoffman and coworkers added NiTBTAP to this series[9] and Antunes and Nyokong the dihydroxyphosphorus analog.[10] During the 1960s Solov'ev *et al.* obtained the Mg and Cd metallated TBTAPs from mixtures of phthalimidineacetic acid and phthalonitrile or *o*-cyanobenzamide (in the presence of cadmium acetate in the latter case) and found that other hybrid molecules were also formed as conditions were varied.[11,12]

Alternative precursors to TBTAPs were published in the late 1980s and early 1990s. Thus nitrophthalimidine as a *meso* carbon provider was described in a Bayer patent[13] whilst Kospranenkov *et al.*[14] and Kospranenkov, Luk'yanets and coworkers[15] employed adducts from reactions of *t*-butyl substituted phthalamide and iminoisoindoline derivatives with malonic acid in the presence of zinc acetate. Each benzenoid ring was thus substituted with a *t*-Bu group. Berezin and coworkers subsequently refined the purification of the metal-free analogue, (*t*-Bu)$_4$-H$_2$TBTAP.[16]

At about the same time, Leznoff and McKeown reinvestigated the Linstead method, added some refinements to conditions, and undertook reactions using a range of alkyl Grignard reagents with phthalonitrile and substituted phthalonitriles.[17,18] As an example, hexadecylmagnesium chloride was reacted with *neo*-pentyloxyphthalonitrile to give (*neo*-PeO)$_4$-*meso*-*n*-C$_{15}$H$_{31}$-H$_2$TBTAP (after demetalation) in 13% yield, Scheme 3. The reaction also produced significant quantities of the corresponding Pc as a by-product along with trace quantities of the TBDAPs. The use of benzyl

magnesium bromide provided a phenyl group at the *meso* position of the TBTAP ring. Ivanova and coworkers later treated *t*-butylphthalonitrile with MeMgI to form (*t*-Bu)$_4$-MgTBTAP. They also observed the co-formation of the Mg metallated Pc analogue. [19]



(*neo*PeO)$_4$-*meso*-$C_{15}H_{31}$-H_2TBTAP

+

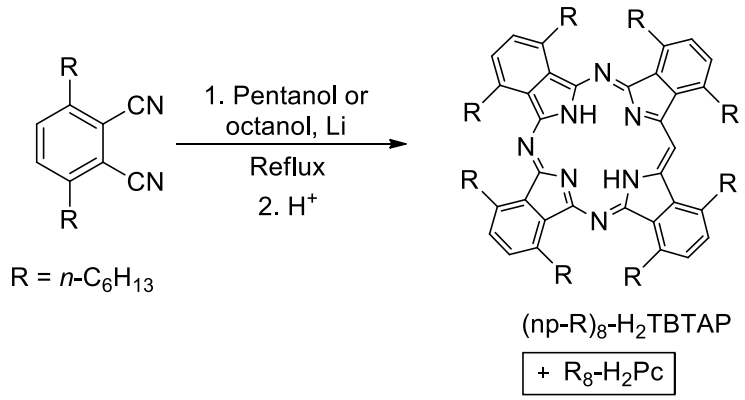
(*neo*PeO)$_4$-H_2Pc and traces of TBDAPs

Scheme 2. Illustrative use of a long chain Grignard reagent to introduce a long chain (minus 1 carbon) at the TBTAP *meso* site.[17]

Further reagents that donate the *meso* carbon have been reported over the last 10 years or so. Thus Galanin and coworkers[20-25] employed the methylene group of carboxylic acids, RCH_2COOH, in mixed cyclization reactions of these with diiminoisoindolines using ZnO or MgO as a template. Their interest was focussed more on developing access to all the hybrids rather than specifically targeting TBTAPs, their products containing the R group (from RCH_2COOH) at the *meso* position(s). The resulting separable mixtures contained the TBTAP derivative along with the other hybrid compounds and, in some cases, the Pc and the TBP analogues as well. The synthesis was employed subsequently by Borisov and coworkers, albeit with much lower reported yields of hybrids.[26] A related mixed cyclization

was reported by Bulavka who used a mixture of potassium phthalimide, the potassium salt of phenyl acetic acid and urea along with MgO as template.[27] Microwave irradiation produced *meso*-Ph-MgTBTAP in 8% yield but the product mixture was dominated by MgPc (65%) along with smaller amounts of the MgTBDAPs, the MgTBMAP and the MgTBP compounds. A further synthesis of *meso*-Ph-MgTBTAP reported by Tomilova and coworkers used phenylacetonitrile as the donor of the *meso*-carbon in reactions with phthalonitrile in the presence of Mg powder.[28] They extended the study using substituted phenylacetonitriles to obtain a number of *meso*-aryl-MgTBTAP compounds in 3-10% yields. The group introduced a further innovation through the reaction of phthalonitrile with quaternary salts of triphenylphosphonium in the presence of Zn powder with gradual heating from 200 to 300^{o}C. The product mixture contained the readily separable ZnPc by-product and *meso*-Ph-ZnTBTAP, the latter in 11% yield. Other hybrid compounds were not detected.[29] *Meso*-Ph-ZnTBTAP has recently been exploited as the precursor for the formation of the first lutetium bis-TBTAP sandwich complex and the corresponding heterolyptic lutetium TBTAP/Pc sandwich complex.[30]

The UEA group's interest in TBTAPs arose from a serendipous finding.[31] The conventional cyclotetramerisation of 3,6-dihexylphthalonitrile into the corresponding non-peripherally (np) substituted (i.e.1,4,8,11,15,18,22,25-) octahexylphthalocyanine using lithium in pentanol as initiator was discovered to give the TBTAP derivative as a by-product under specific conditions (Scheme 3). TBTAP is only formed when lithium metal, in excess, is added to the alcohol solution of phthalonitrile. (Preformed lithium alkoxide leads to production of the phthalocyanine only). The use of 19 equivalents of lithium in pentanol gave a 77:23 ratio of Pc:TBTAP, and the amount of TBTAP formed increased even further when octanol was used in place of pentanol leading to a 53:47 ratio. Remarkably, the origin of the *meso*-carbon was traced to the alcohol solvent. Thus when octanol labelled with ^{13}C at the α-carbon was employed as solvent the isolated TBTAP showed 87% ^{13}C incorporation at the *meso*-site. The mechanism for its incorporation, the evident C-C cleavage reaction involved, the origin of the 13% of unlabelled *meso* carbon and indeed the mechanism for TBTAP formation under these conditions remain unclear. Interestingly, no TBTAP products were observed when the same conditions were applied to 4-*t*-butylphthalonitrile or 4,5-dihexylphthalonitrile.[31]



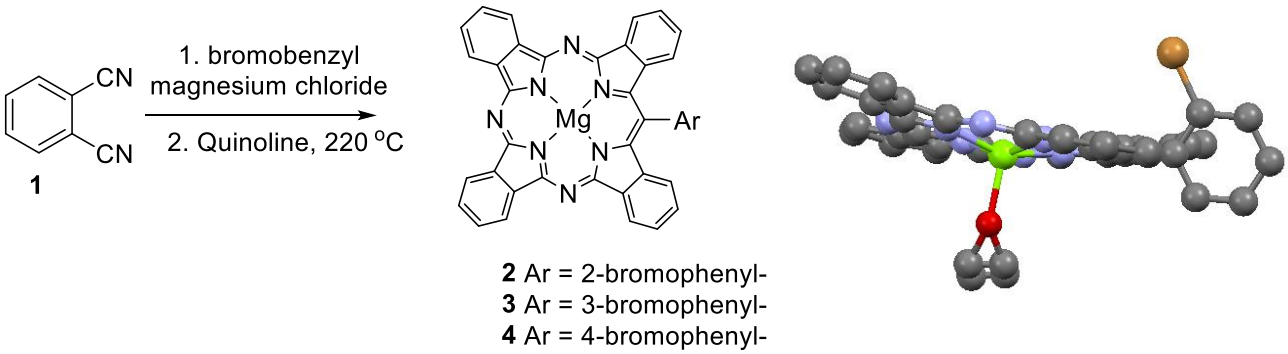
Scheme 3. Unexpected formation of an octakis(alkyl) H_2TBTAP as a side product of the cyclotetramerisation of a 1,4-dialkylphthlonitrile in Li/pentanol to form a Pc.

The disparity in reactivities of the isomeric 3,6-dihexylphthalonitrile and 4,5-dihexylphthalonitrile prompted investigation into reactivities of dialkyl substituted phthalonitriles towards Grignard reagents. Reaction of a 4,5-dialkylphthalonitrile with MeMgBr under modified Leznoff-McKeown conditions gave the corresponding TBTAP and the Pc, broadly as expected on the basis of Leznoff and McKeown's findings.[32] However, application of these conditions to both 3,6-dihexyl and 3,6-didecylphthalonitriles gave quite different results.[32,33] Both substrates gave mixtures of hybrids, the composition dependent on the number of equivalents of MeMgBr that were used. The use of a 1:1 or 2:1 ratio of MeMgBr:3,6-dialkylphthalonitrile gave the corresponding (np)-octaalkyl-MgTBTAP as the dominant product alongside the correspondingly substituted MgTBDAPs and MgTBMAP. Only trace amounts of Pc were detected. Increasing the ratio further to 4:1 gave the MgTBP derivative as essentially the only macrocyclic product. Demetalation of the separated products using acetic acid provided the metal-free analogues that were re-metalated with other ions.[32,34] Columnar liquid crystal behaviour was examined for various examples.[33] Elsewhere, the synthesis has been repeated and the liquid crystal behaviour of the TBMAP and TBP compounds investigated.[35] A remaining anomalous result in reactions of 3,6-dialkylphthalonitriles with Grignard reagents was also uncovered: the use of long chain Grignard reagents provided the *meso* carbon as expected but bound only to hydrogen.[32] The unexpected C-C cleavage is perhaps related to that which occurs using Li in alcohols as discussed above.

2. Results and Discussion

It becomes apparent from the brief review above that the synthetic chemistry of TBTAPs has advanced only modestly since their discovery. Indeed, although a limited number of TBTAP derivatives have been prepared, the investigation of functionalised systems or development of methods for efficient and versatile access to such hybrids has gone essentially unexplored. We are interested in both aspects – functional TBTAPs as potential molecular materials and components of super- and supramolecular structures, and synthetic chemistry development to open the field in a manner parallel to that enjoyed by the parent phthalocyanines and porphyrins.

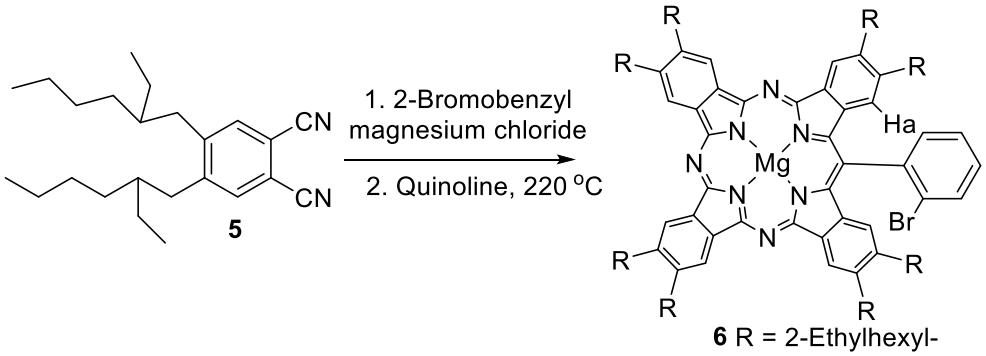
In particular we have been interested in novel TBTAPs bearing aryl substituents at their *meso*-position and our initial investigations focused on the known protocol, exemplified in Scheme 2 above, employing Grignard reagents to induce macrocyclisation. Our first series of functionalised *meso*-phenyl substituted TBTAPs were prepared by reaction between phthalonitrile and the isomeric series of 2-, 3- and 4-bromobenzyl magnesium chlorides, Scheme 4. Reaction conditions were optimised and in a typical procedure the Grignard reagent and phthalonitrile were reacted in THF or ether before changing the reaction solvent to quinoline and heating at 200 ^{o}C. The procedure was later improved further by using diglyme as the only solvent, resulting in a cleaner, more convenient transformation and isolation. It was found that purification of the *meso*-aryl TBTAPs, **2**, **3** and **4** was relatively straightforward so long as the magnesium ion was retained in the macrocycle. Acidic conditions were therefore avoided during workup. Crystals suitable for X-ray diffraction analysis were grown for TBTAP **2**, and the structure is also shown in the scheme.



Scheme 4. Synthesis of *meso*-(bromo-phenyl)-TBTAPs via the Grignard reagent route, plus the X-ray crystal structure of derivative **4** (ball-and-stick representation).

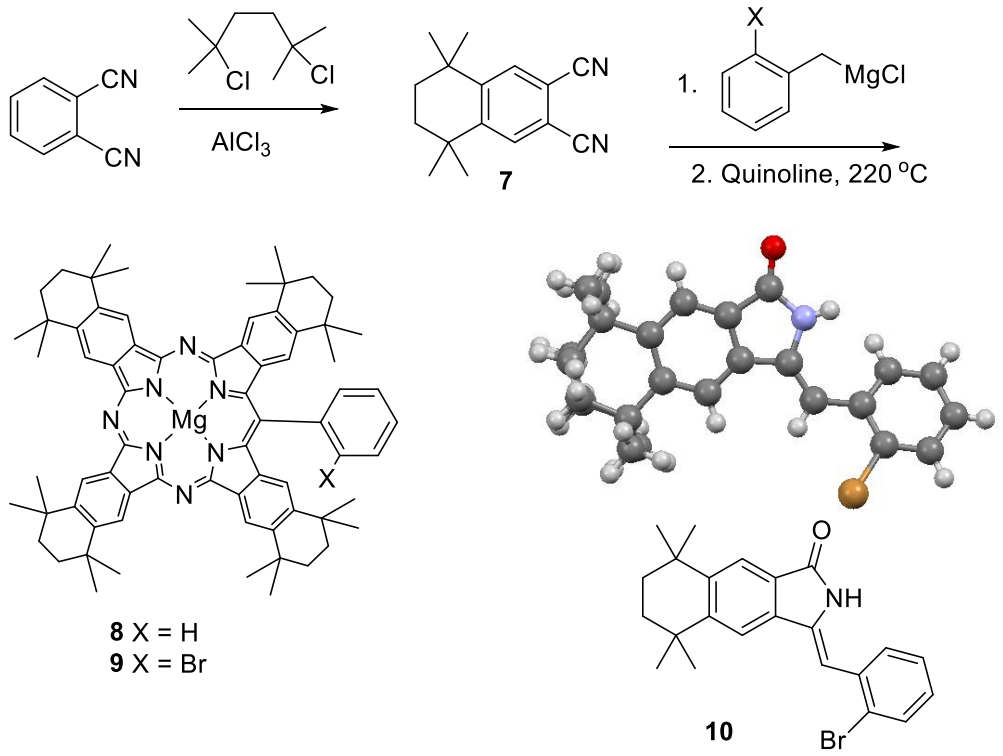
It is well known that solubility and processability in macrocycles such as these can be significantly enhanced by introduction of solubilising groups such as alkyl chains. Our preliminary work

demonstrated that a peripherally substituted octaalkylTBTAP bearing a *meso*-phenyl group could be prepared from benzyl magnesium chloride and a 4,5-dialkylphthalonitrile. The corresponding functionalised-phenyl derivative was similarly synthesised from reaction between 4,5-bis(2-ethylhexyl)phthalonitrile **5** and 2-bromobenzyl magnesium chloride. This phthalonitrile was chosen because the branched (chiral) chains, introduced using racemic 2-ethylhexyl bromide, confer excellent solubility on phthalocyanine macrocycles and this behaviour was observed in TBTAP **6** also (solubility >20 mg/ml in chloroform).



Scheme 5. Synthesis of the peripherally substituted analogue **6**.

However, phthalonitrile **5** does have some drawbacks. Its preparation and purification are tedious, and ^{1}H NMR spectra can be complicated and broadened due to the formation of mixtures of diasteriomers. We therefore turned our attention to an alternative 4,5-dialkylphthalonitrile, namely **7**. Phthalonitrile **7** is relatively easy to synthesise, has high symmetry yet is heavily branched, conferring solubility and preventing aggregation. TBTAP formation was therefore investigated using this derivative as precursor, and benzyl magnesium chloride and 2-bromobenzyl magnesium chloride as Grignard reagents. The corresponding *meso*-aryl TBTAPs, **8** and **9**, were isolated, Scheme 6, albeit in relatively low yields, and characterisation was reasonably straightforward. ^{1}H NMR spectroscopy is particularly informative, showing distinct signals for the protons labelled Ha (*ca*. 7.0 ppm) that lie in the shielding ring current of the *meso*-aryl substituent.

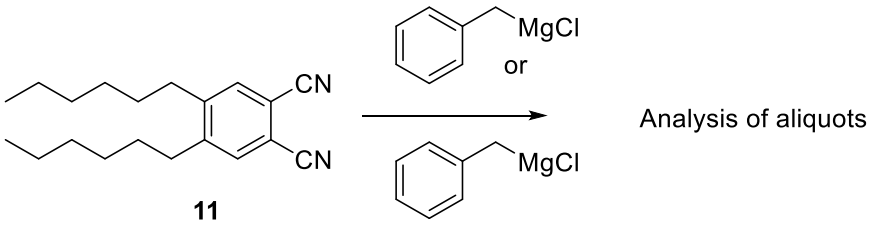


Scheme 6. TBTAP synthesis employing phthalonitrile **7** and the isolated side product **10** (ball-and-stick representation of the structure obtained by X-ray crystallography).

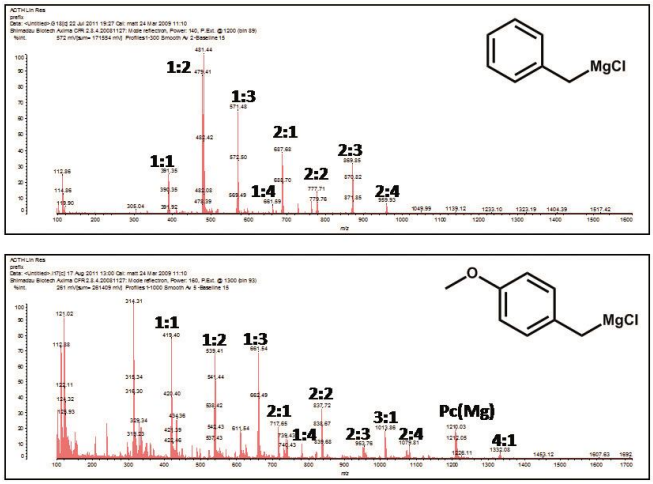
The reaction between phthalonitrile **7** and 2-bromobenzyl magnesium chloride was given particular attention, and in one experiment a side-product was isolated and identified as phthalimidine **10**. Crystals suitable for X-ray diffraction analysis were grown and its structure was unambiguously confirmed. Phthalimidine **10** is a direct analogue of Dent's original precursor to TBTAPs, see Scheme 1. However, in our case its origin is likely to be through hydrolysis of the initial addition product formed between phthalonitrile **7** and the Grignard reagent.

Isolation of phthalimidine **10** stimulated a closer examination of the reaction course from phthalonitrile and Grignard reagent through to TBTAP. In order to facilitate analysis of the reaction mixture by mass spectrometry, the reaction between 4-methoxybenzyl magnesium chloride and 4,5-dihexylphthalonitrile **11** was selected (Scheme 7). Aliquots from the reaction were examined by mass spectrometry, Fig. 2, and clearly revealed that the initial steps of the reaction result in formation of a complex mixture of oligomers. Heating with a template ion leads to macrocyclisation. However, closer examination of the mass spectrum indicates that the growing oligomers are themselves susceptible to attack by Grignard reagent and it is difficult to see how such intermediates can lead to useful

macrocyclic products. Unfortunately this cannot be solved by modification of the addition of Grignard reagent (reduced quantity, slower addition); when only a low quantity of Grignard reagent initiator is present, the most favourable cyclisation (and therefore the most abundant product) would lead to simple phthalocyanine. Although this investigation revealed fundamental problems with the Grignard initiation route to TBTAPs, close examination of the mass spectra identified a peak that most likely corresponds to (protonated) intermediate **12**. We reasoned that this intermediate, if accessed discretely, could initiate TBTAP formation without the complications described above.



Scheme 7. Examination of the reaction between phthalonitrile **11** and benzyl Grignard reagents.



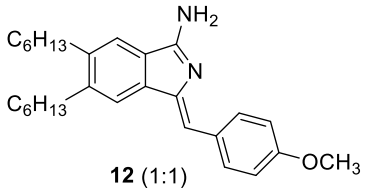
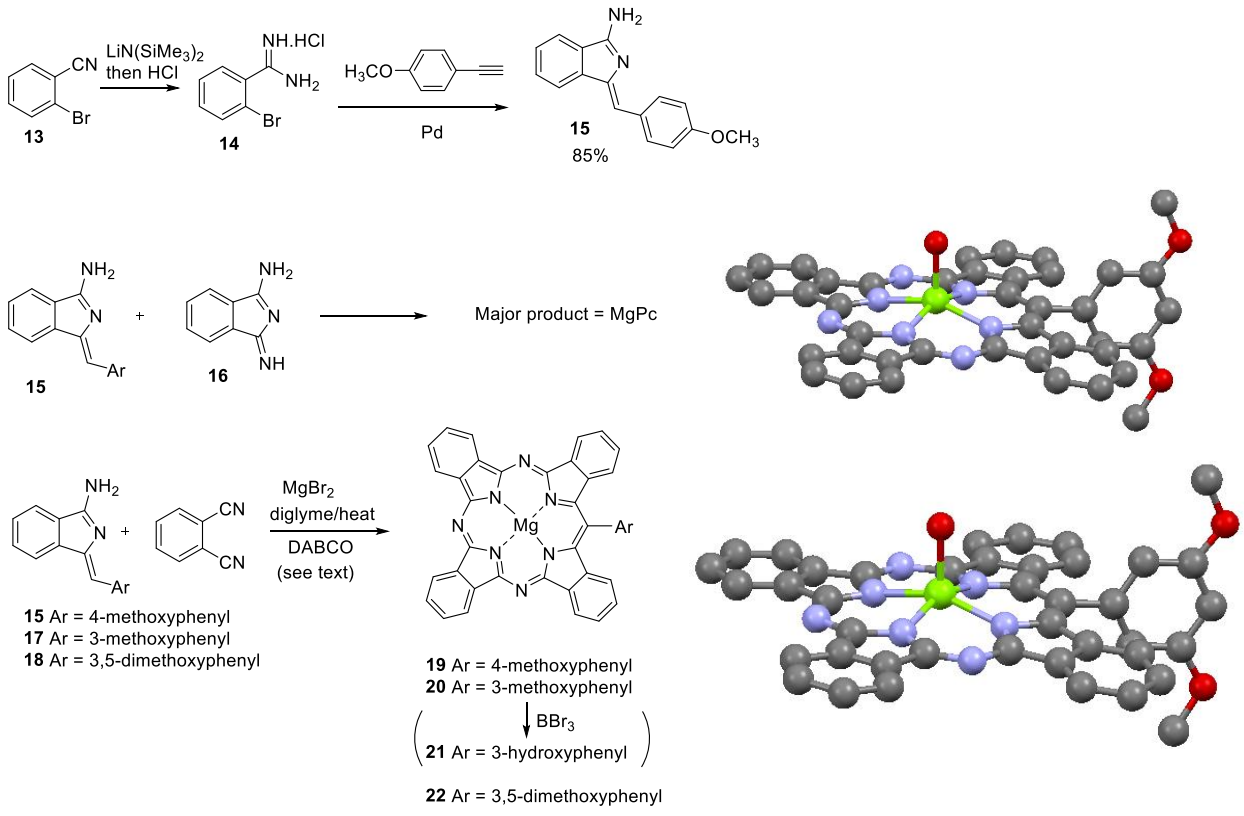


Figure 2. Mass spectra of crude mixtures from the reaction between benzyl Grignard reagents and 4,5-dihexylphthalonitrile.

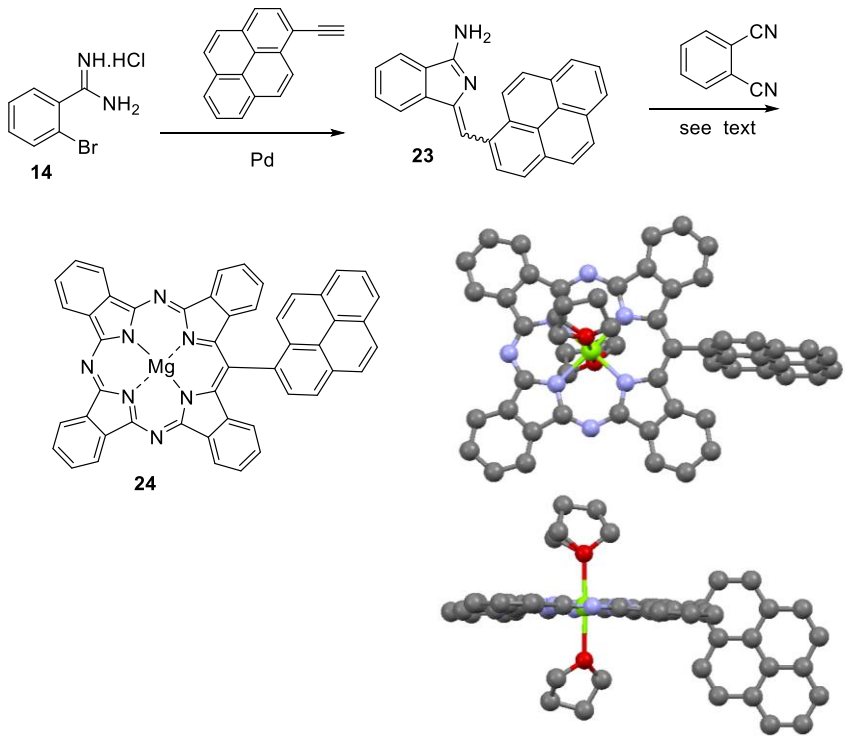
In light of this finding, aminoisoindoline **15**, Scheme 8, was selected for investigation as a new TBTAP precursor. The 4-methoxyphenyl substituent was chosen to demonstrate introduction of functionality, but also to simplify characterisation by ^{1}H NMR spectroscopy. Synthesis of **15**, via **13** and **14**[36] was straightforward and followed the method developed by Hellal and Cuny (Scheme 8).[37] Initial reactions to form a TBTAP from aminoisoindoline **15** and diiminoisoindoline **16** as co-reactant under the high temperature conditions (220 ^{o}C, $MgBr_2$) required for the reaction demonstrated TBTAP

formation but the dominant product was the simple magnesium phthalocyanine resulting from macrocyclisation of diiminoisoindoline alone. Switching the co-reactant from diiminoisoindoline to phthalonitrile (which does not readily cyclise to phthalocyanine under these conditions) improved the reaction outcome considerably. Furthermore, subtle optimisation led to development of an efficient protocol for formation of *meso*-(4-methoxyphenyl)TBTAP **19**.[38] Specifically, a mixture of aminoisoindoline **15** and phthalonitrile (1:1) is added slowly to a heated mixture of phthalonitrile (3 eq) and $MgBr_2$ in diglyme at 220 ^oC, followed by addition of DABCO and more phthalonitrile (1 eq). Adding DABCO to the reaction mixture results in release of unreacted **15** from its complex with the MgTBTAP product. Complete consumption of starting **15** is then observed with corresponding improvement in the overall yield. Alternative precursor aminoisoindolines **17** and **18** provided access to the isomeric *meso*-(3-methoxyphenyl)TBTAP **20** and *meso*-(3,5-dimethoxyphenyl)TBTAP **22**, the latter providing crystals suitable for X-ray diffraction; its structure is also shown in Scheme 8. *Meso*-(3-methoxyphenyl)TBTAP was smoothly hydrolysed using BBr_3, giving *meso*-(3-hydroxyphenyl)TBTAP **21**.



Scheme 8. Improved synthesis protocol for *meso*-aryl TBTAPs, and the X-ray crystal structure of **22** (ball-and-stick representations).

The new synthetic route therefore opens the way for design and synthesis of new families of *meso*-aryl TBTAPs, and their further elaboration into complex, functional molecular materials. As in *meso*-aryl porphyrins, the *meso*-aryl moiety on the new TBTAPs lies essentially perpendicular to the macrocycle plane, minimising ground state electronic interaction. Intriguing arrays become possible, where multiple chromophores/fluorophores lie in close proximity but without interaction. To illustrate the potential of the new synthetic protocol we selected pyrene as complementary aromatic unit. Thus, 1-ethynylpyrene was reacted with bromoamidine **14** to give the corresponding aminoisoindoline **23,** Scheme 8. In this case the product **23** was isolated as a mixture of stereoisomers. Macrocyclisation of the mixture of isomers with phthalonitrile using our previously developed conditions proceeded smoothly, leading to isolation of *meso*-(1-pyrenyl)TBTAP **24**. Crystals suitable for X-ray diffraction were eventually grown and the structure is shown in Scheme 9.



Scheme 9. Synthesis and crystal structure of *meso*-pyrenyl TBTAP **24** (ball-and-stick representations).

The absorption and fluorescence spectra for *meso*-(1-pyrenyl)TBTAP **24** are shown in the Figure 3. As expected the absorption spectrum shows no significant perturbation of the individual chromophores – the spectrum is essentially identical to other members of the MgTBTAP series (**19**-**22**) in the TBTAP (350-700 nm) range, and shows additional absorptions associated with the pyrene fragment between 250-350 nm. Energy transfer between the two mutually perpendicular chromophores is expected to be forbidden and weak. Examination of the fluorescence spectrum (exciting into the pyrene absorption at 246 nm) shows that energy transfer from the (excited) pyrene fragment to the TBTAP is observed but incomplete. Emission occurs from both the pyrene and TBTAP. This conclusion is further supported by the excitation spectrum where, recording emission at 674 nm from the TBTAP only, we see the profile following the absorption of both the pyrene and TBTAP fragments of the molecule.

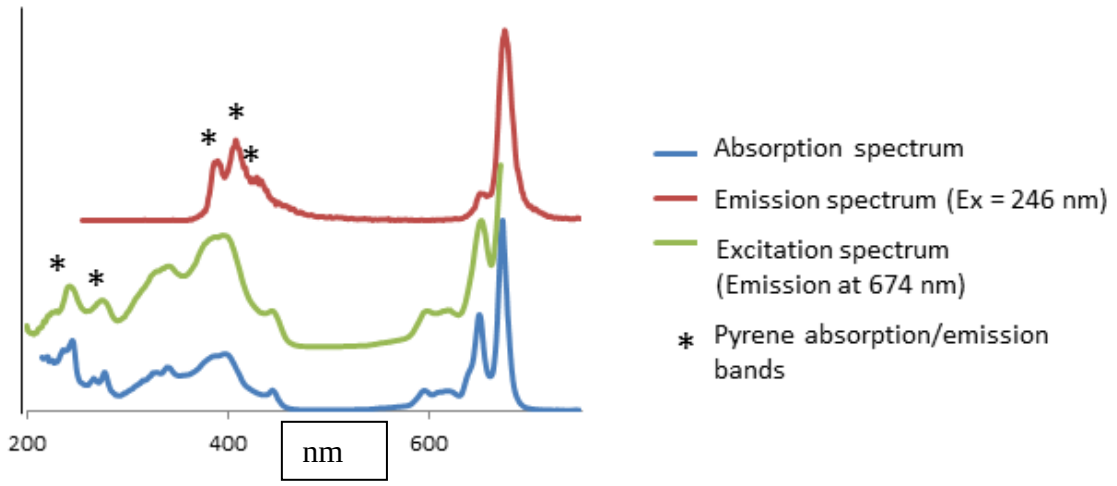


Figure 3. Absorption, Fluorescence and Excitation spectra for pyrenyl-TBTAP **24**.

3. Conclusions

New tetrabenzotriazaporphyrins are reported that are functionalised at the *meso*-position. In particular, a versatile protocol is employed that gives convenient access to these challenging materials by template co-macrocyclisation between phthalonitriles and aryl-aminoisoindoline derivatives like **15**. The newly developed procedure allows design and synthesis of elaborate, functional composites and this is demonstrated by synthesis of *meso*-pyrenylTBTAP **24**, a linked chromophores dyad in which the two complementary units lie perpendicular to each other and therefore have minimal ground state interaction.

4. Experimental

General Methods: Reagents and solvents were purchased from commercial sources and used without further purification. IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR spectrometer. ^{1}H (and ^{13}C-NMR) spectra were recorded at 500 (125.7) or 400 (100.6) MHz using a Bruker Ascend^{TM} 500 or an Ultrashield Plus^{TM} 400 spectrometer. Poor solubility and aggregation prevented acquisition of useful ^{13}C NMR data for several final compounds. The residual solvent peaks were used as references.[1] 2D COSY, NOESY, HSQC and HMBC experiments were used to assist with the NMR spectroscopy assignments. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with

Alugram® Sil G/UV254 (Macherey-Nagel), with visualization by UV light and by charring with 0.1% ninhydrin in EtOH when necessary. Column chromatography was carried out on silica gel Davisil® LC60A 40-63 micron (Grace GmbH & Co). MALDI-TOF mass spectra were obtained using a Shimadzu Biotech Axima instrument, and isotopic patterns were compared with theoretical prediction to confirm sample identity. High resolution mass spectrometry was performed by the ESPRC UK National Mass Spectrometry Service Centre at Swansea. UV-Vis spectra were recorded in a Hitachi U-3000 spectrophotometer. Melting points were measured using a Reichert Thermovar microscope with a thermopar based temperature control. Fluorescence excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrometer, using compound concentrations that give 0.1 units of maximum UV-Vis absorbance. X-Ray crystallography data was collected by the UK National Crystallography Service at University of Southampton.

General synthetic procedure for the synthesis of substituted *meso*-aryl TBTAPs *via* the Grignard reagent route using quinoline as solvent

(Substituted) phthalonitrile was dissolved in dry THF and stirred at room temperature, under an argon atmosphere. A solution of arylmagnesium halide was added dropwise *via* a syringe and the mixture was heated under reflux for 2 h. The reaction underwent a colour change from a yellow solution, to a dark brown colour. A stream of argon was passed through the reaction flask for 20 min to remove the THF. After removal of the solvent, distilled/degassed quinoline was added to the hot vessel *via* syringe, and the reaction mixture was heated at 200 °C for 24 h under argon. During this time the colour of the reaction mixture changed gradually from dark brown to green. Then, the majority of the quinoline was removed under a stream of argon. The crude product was cooled to room temperature and MeOH was added to the mixture. After sonication, the resulting suspension was poured onto a column of dry silica gel. MeOH was initially eluted through the column to remove the remaining quinoline and other polar by-products, then the eluent was changed to THF leading to collection of the product as a dark green fraction. The solvent was removed under reduced pressure and the resulting green material further purified by column chromatography eluting with PE:THF (15:1) to obtain a green (TBTAP) and then a blue fraction (Pc). Finally, the green material was subjected to a second chromatographic separation using DCM:PE (1:15).

(2,3,9,10,15,16,23,24-Octakis(2-ethylhexyl)-27-(2-bromophenyl)tetrabenzo-[*b*,*g*,*l*,*q*][5,10,15]triazaporphinato) magnesium **6**

Synthesised following the general procedure described above from 4,5-bis(2-ethylhexyl) phthalonitrile **5**[32,38] (200.0 mg, 0.567 mmol, 1 eq) and 2-bromobenzylmagnesium bromide (4.54 mL, 0.25 M in Et_2O, 1.13 mmol, 2 eq) in distilled/degassed quinoline (3.0 mL). The final material was recrystallised from acetone/EtOH (1:1) yielding the ***title compound*** as a green solid (35.0 mg, 16%); mp >300 ^oC; UV-vis (THF) λ_{max} / nm (ε) 685 ($3.57 \cdot 10^3$), 662 ($2.62 \cdot 10^3$), 606 ($7.14 \cdot 10^2$), 450 ($4.76 \cdot 10^2$), 390 ($1.67 \cdot 10^3$); ν_{max} / cm^{-1} (ATR) 2926, 1463, 1376; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.32 (br s, 2H), 9.25 (br s, 4H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.16 (br s, 1H), 7.99 – 7.92 (m, 2H), 6.99 (s, 2H), 3.25 – 3.24 (m, 16H), 2.12 (m, 8H), 1.72 – 1.59 (m, 64H), 1.03 – 0.87 (m, 48H); MS (MALDI-TOF) *m/z* 1589 $[M]^+$ (100%).

General synthetic procedure for the synthesis of substituted *meso*-aryl TBTAPs *via* the Grignard reagent route using diglyme as solvent

A suspension of phthalonitrile in dry diglyme was refluxed at 220 °C for 10 min under an argon atmosphere, in a preheated mantle. A solution of bromobenzylmagnesium bromide was added dropwise via a syringe. The reaction mixture was heated at 220 °C under argon for 3 h. A stream of argon was passed through the reaction vessel in order to remove the solvent. After the reaction mixture cooled to room temperature, a mixture of DCM:MeOH (50 ml, 1:1) was added to the reaction mixture and sonicated. After removal of the solvent under reduced pressure, the crude solid was loaded on a silica-gel column and eluted with DCM:Et_3N:THF (10:1:4) in order to initially remove the yellow-brown impurities and then green/blue fractions which were subjected to a second column chromatographic separation using PE:THF:MeOH (10:3:1) as elutent to obtain the pure green product.

20-(2-Bromophenyl)-tetrabenzo[*b*,*g*,*q*,*l*][5,10,15]triazaporphyrinato) magnesium **2**

Synthesised following the general procedure described above from phthalonitrile (280 mg, 2.19 mmol) and 2-bromobenzylmagnesium bromide (2.92 mL, 0.25 M in Et_2O, 0.73 mmol) in diglyme (1.0 mL). The final material was recrystallised from acetone/EtOH (1:1) yielding the ***title compound*** as as green crystals with a purple reflex (140 mg, 28%); mp >300 ^oC; UV-vis (THF) λ_{max} / nm (ε) 671 ($2.12 \cdot 10^3$), 650 ($1.11 \cdot 10^3$), 594 ($2.33 \cdot 10^2$), 443 ($1.55 \cdot 10^2$), 396 ($5.96 \cdot 10^3$); ν_{max} / cm^{-1} (ATR) 3050, 1462, 1374; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.61 (d, *J* = 7.5 Hz, 2H), 9.53 – 9.48 (m, 4H), 8.31 (d, *J*

= 8.3 Hz, 1H), 8.18 – 8.16 (m, 5H), 7.98 (t, *J* = 7.9 Hz, 1H), 7.93-7.90 (m, 3H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) = 177.06, 156.67, 153.74, 152.68, 144.36, 142.51, 141.26, 141.03, 140.79, 140.31, 135.27, 134.70, 132.18, 130.15, 129.87, 129.64, 128.59, 127.60, 125.14, 124.71, 123.93, 123.83, 123.74, 108.57, 108.28, 107.83, 102.09, 98.92; MS (MALDI-TOF) *m/z* 692 $[M]^+$ (100%); HRMS (ESI) ($C_{39}H_{20}$Br Mg N_7) M^+: Calc.: 689.0807; Found: 689.0808.

20-(3-Bromophenyl)-tetrabenzo[*b*,*g*,*q*,*l*][5,10,15]triazaporphyrinato) magnesium **3**

Synthesised following the general procedure described above from phthalonitrile (280 mg, 2.19 mmol) and 3-bromobenzylmagnesium bromide (2.92 mL, 0.25 M in Et_2O, 0.73 mmol) in diglyme (1.0 mL). The final material was recrystallised from acetone/EtOH (1:1) yielding the ***title compound*** as as green crystals with a purple reflex (120 mg, 24%); mp >300 ºC; UV-vis (THF) λ_{max} / nm (ε) 671 ($3.29\cdot10^3$), 648 ($1.91\cdot10^3$), 593 ($4.15\cdot10^2$), 442 ($2.90\cdot10^2$), 396 ($1.09\cdot10^3$); ν_{max} / cm^{-1} (ATR) 3050, 1462; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.61 (d, *J* = 7.6 Hz, 2H), 9.53 – 9.47 (m, 4H), 8.37 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.19 – 8.15 (m, 5H), 7.94 – 7.87 (m, 3H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H); ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) = 176.28, 166.35, 160.34, 157.98, 155.83, 154.80, 153.38, 152.27, 151.68, 150.48, 147.92, 146.41, 146.35, 145.95, 144.27, 143.15, 141.08, 140.88, 140.63, 140.14, 139.55, 139.40, 138.13, 133.19, 133.07, 130.15, 129.84, 128.32, 127.38, 125.16, 123.83, 123.80, 123.59; MS (MALDI-TOF) *m/z* 692 $[M]^+$ (100%); HRMS (ESI) ($C_{39}H_{20}BrMgN_7$) M^+: Calc.: 689.0817; Found: 689.0808.

20-(4-Bromophenyl)-tetrabenzo[*b*,*g*,*q*,*l*][5,10,15]triazaporphyrinato) magnesium **4**

Synthesised following the general procedure described above from phthalonitrile (4.41 mg, 34.45 mmol) and 4-bromobenzylmagnesium bromide (11.98 mL, 2.13 M in Et_2O, 25.52 mmol) in diglyme (6.0 mL). The final material was recrystallised from acetone/EtOH (1:1) yielding the ***title compound*** as as green crystals with a purple reflex (400 mg, 5%); mp >300 ºC; UV-vis (THF) λ_{max} / nm (ε) 671 ($1.75\cdot10^3$), 648 ($1.00\cdot10^3$), 594 ($2.50\cdot10^2$), 443 ($2.14\cdot10^2$), 394 ($6.79\cdot10^2$); ν_{max} / cm^{-1} (ATR) 3050, 1463, 1373; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm9.60 (d, *J* = 7.5 Hz, 2H), 9.52 – 9.48 (m, 4H), 8.19 – 8.13 (m, 6H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.91 (t, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H); ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) 157.87, 154.69, 153.61, 143.25, 143.17, 141.06, 140.86, 140.68, 140.13, 135.23, 133.26, 130.13, 129.81, 128.28, 127.36, 125.22, 124.15, 123.82,

123.76, 123.57, 121.81, 108.56; MS (MALDI-TOF) *m/z* 692 $[M]^+$ (100%); HRMS (ESI) ($C_{39}H_{21}Br\ Mg\ N_7$) $[M+H]^+$: Calc.: 690.0888; Found: 690.0887.

General synthetic procedure for the synthesis of aminoisoindolines

Following the reported procedure[37] a mixture of amidine **14**, BINAP (0.055 eq) and $PdCl_2(MeCN)_2$ (0.05 eq) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with N_2 thrice. Then, a solution of arylethyne (1.2 eq) and DBU (2.5 eq) in dry DMF (12 ml) was added. The mixture was stirred under N_2 for 5 min to give a clear yellow solution with a white solid. Finally, the mixture was irradiated in a microwave reactor at 120 °C for 1 h. After cooling, 50 ml of AcOEt were added and the mixture washed three times with a saturated solution of $NaHCO_3$ (75 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated. The residue was finally purified by column chromatography using AcOEt, AcOEt:EtOH:H_2O (90:5:3) and finally AcOEt:EtOH:H_2O (45:5:3).

(*Z*)-1-(3-Methoxybenzylidene)-1*H*-isoindol-3-amine **17**

Synthesised following the general procedure described above using a solution of 3-ethynylanisole (0.67 g, 5.09 mmol) and DBU (1.62 g, 10.64 mmol) in dry DMF (12 ml) and adding amidine **14** (1.00 g, 4.25 mmol), BINAP (0.13 g, 0.21 mmol) and $PdCl_2(MeCN)_2$ (0.06 g, 0.21 mmol). After purification, the yellow solid was recrystallized from a DCM:petroleum ether (1:1) to yield the ***title compound*** as yellow needles (440 mg, 41%); mp 183-184 °C; ; UV-vis (DCM) λ_{max} / nm (ε) 367 ($2.93 \cdot 10^3$), 292 ($9.01 \cdot 10^2$); ν_{max} / cm^{-1} (ATR) 3600-3050 (br), 2930, 1593, 1423; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.83 (br s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.73 (s, 1H), 5.74 – 5.35 (br s, 2H, NH_2), 3.88 (s, 3H); ^{13}C-NMR (125.7 MHz, $CDCl_3$, 298 K): δ (ppm) 165.04, 159.85, 159.84, 159.80, 138.10, 131.11, 129.47, 129.36, 127.40, 126.85, 123.40, 119.97, 119.02, 115.58, 113.64, 55.45; MS (MALDI-TOF) *m/z* 251 $[M]^+$ (100%); HRMS (ESI) ($C_{16}H_{15}N_2O$) $[M+H]^+$: Calc.: 251.1179; Found: 251.1180.

(*Z*)-1-(3,5-Dimethoxybenzylidene)-1*H*-isoindol-3-amine **18**

Synthesised following the general procedure described above using a solution of 1-ethynyl-3,5-dimethoxybenzene (0.83 g, 5.12 mmol) and DBU (1.62 g, 10.64 mmol) in dry DMF (12 ml) and adding amidine **14** (1.00 g, 4.25 mmol), BINAP (0.13 g, 0.21 mmol) and $PdCl_2(MeCN)_2$ (0.06 g, 0.21 mmol).

After purification, the yellow solid was recrystallized from a DCM:petroleum ether (1:1) to yield the ***title compound*** as yellow needles (300 mg, 25%); mp 167-168 °C; ; UV-vis (DCM) λ_{max} / nm (ε) 367 ($1.18 \cdot 10^3$), 290 ($3.36 \cdot 10^2$); ν_{max} / cm^{-1} (ATR) 3600-3050 (br), 1589, 1416; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) 7.79 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 2H), 6.70 (s, 1H), 6.42 (t, *J* = 2.3 Hz, 1H), 3.87 (s, 6H); ^{13}C-NMR (125.7 MHz, $CDCl_3$, 298 K): δ (ppm) 164.76, 160.91, 159.76, 154.32, 153.83, 152.80, 138.20, 131.11, 129.80, 128.82, 127.64, 127.30, 120.05, 119.39, 108.49, 100.66, 55.61; MS (MALDI-TOF) *m/z* 281 $[M]^+$ (100%); HRMS (ESI) ($C_{17}H_{17}N_2O_2$) $[M+H]^+$: Calc.: 281.1285; Found: 281.1287.

(*Z/E*)-1(1-Pyrenylmethylene)-1H-isoindol-3-amine **23**.

Synthesised following the general procedure described above using a solution of 1-ethynylpyrene (500 mg, 2.2 mmol) and DBU (0.7 mL) in dry DMF (10 ml) and adding amidine **14** (435 mg, 1.85 mmol), BINAP (69 mg, 0.11 mmol) and $PdCl_2(MeCN)_2$ (24 mg, 0.092 mmol). The crude product was purified by column chromatography using DCM then DCM:MeOH (9:1 to 2:1) as solvent gradient to afford the ***title compound*** a bright yellow solid, an approximate 3:1 mixture of stereoisomers, (455 mg, 72%); mp 280-282 °C; ; UV-vis (DCM) λ_{max} / nm (ε) 403 ($7.64 \cdot 10^3$); 238 ($1.62 \cdot 10^4$); ν_{max} / cm^{-1} (ATR) 3600-2900 (br), 1652, 1543, 1436; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) major isomer 8.97 (d, 1H, *J* = 8.1); 8.45 (d, 1H, *J* = 9.2); 8.22 – 7.98 (m, 6H); 7.97 (t, 1H, *J* = 7.6); 7.93 (d, 1H, *J* = 7.6); 7.65 (s, 1H, H-a); 7.50 (br td, 1H, *J* = 7.5, 1.1); 7.45 (br dt, 1H, *J* = 7.6, 0.9); 7.37 (br td, 1H, *J* = 7.4, 0.9); 5.4 – 4.2 (br s, 2H, NH_2); minor isomer 8.23 (d, 1H, *J* = 9.1); 8.22 – 7.98 (m, 8H); 7.69 (s, 1H, H-a); 7.54 (d, 1H, *J* = 7.8); 7.22 (br td, 1H, *J* = 7.4, 1.1); 7.02 (br td, 1H, *J* = 7.6, 1.0); 6.96 (br dt, 1H, *J* = 7.9, 0.9); 5.4 – 4.2 (br s, 2H, NH_2); MS (MALDI-TOF) *m/z* 344 $[M]^+$ (100%); HRMS (ESI) ($C_{25}H_{17}N_2$) $[M+H]^+$: Calc.: 345.1386; Found: 345.1386.

General synthetic procedure for the synthesis of *meso*-aryl TBTAPs *via* aminoisoindoline intermediates

A suspension of phthalonitrile (ca 150 mg, 3 eq) and $MgBr_2$ (1.5 eq) in dry diglyme (0.5 mL) was heated at 220 °C for 10 min under an argon atmosphere, in a preheated mantle. A solution of aminoisoindoline (1 eq) and phthalonitrile (1 eq) in dry diglyme (1 ml) was added dropwise over 1 h using a syringe pump. After finishing the first addition, the reaction mixture was left to reflux at 220 °C for 30 min. Finally, a solution of phthalonitrile (1 eq) and DABCO (1.5 eq) in dry diglyme (0.5 ml) was

added dropwise over 1 h. The reaction mixture was then refluxed at 220 °C under argon for further 30 min. A stream of argon was passed through the reaction vessel in order to remove the solvent. The reaction mixture was cooled to room temperature and a mixture of DCM:MeOH (50 ml, 1:1) was added and the mixture sonicated. After removal the solvent under reduced pressure, the resulting material was purified by two consecutive flash chromatographies. Firstly, the crude was loaded on a silica-gel column and eluted with DCM:Et_3N:THF (10:1:4) in order to remove the yellow-brown impurities and obtain a green fraction. The green fraction was then subjected to a second column chromatography using PE:THF:MeOH (10:3:1) as elutent to obtain the pure green product. Alternatively, analytically pure material could be obtained by size-exclusion chromatography over Bio-beads SX-3 using THF eluent.

(20-(3-Methoxyphenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato) magnesium **20**

Synthesised following the general procedure described above using a solution of phthalonitrile (154.0 mg, 1.20 mmol) and $MgBr_2$ (110.0 mg, 0.60 mmol) in dry diglyme (0.5 ml), heating at 220 °C for 10 min under argon and initially adding aminoisoindoline **17** (100.0 mg, 0.40 mmol) and phthalonitrile (51.0 mg, 0.40 mmol) in dry diglyme (1.0 ml) over 1 h. Finally, a solution of phthalonitrile (51.0 mg, 0.40 mmol) and DABCO (67.0 mg, 0.60 mmol) in dry diglyme (0.5 ml) was added dropwise over 1 h. The purified product was recrystallized from acetone/EtOH (1:1) gave the ***title compound*** as green crystals with purple reflex (50 mg, 20%); mp >300 ^oC; UV-vis (THF) λ_{max} / nm (ε) 670 ($7.35 \cdot 10^3$), 647 ($4.41 \cdot 10^3$), 592 ($1.03 \cdot 10^2$), 442 ($1.03 \cdot 10^2$), 397 ($2.50 \cdot 10^2$); ν_{max} / cm^{-1} (ATR) 2930, 1463, 1379; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.59 (d, *J* = 7.5 Hz, 2H), 9.53 – 9.50 (m, 4H), 8.23 – 8.15 (m, 4H), 7.92 (t, *J* = 7.1 Hz, 2H), 7.88 – 7.84 (m, 1H), 7.77 – 7.68 (m, 2H), 7.63 – 7.59 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 3H); ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) 169.56, 161.75, 156.84, 153.81, 152.87, 145.09, 143.05, 141.13, 141.00, 140.90, 140.20, 134.79, 134.51, 133.67, 132.79, 130.86, 130.09, 129.80, 128.24, 127.39, 126.63, 125.81, 125.69, 123.86, 123.76, 123.64, 123.58, 122.46, 118.90, 115.86, 108.56, 98.90, 56.04; MS (MALDI-TOF) *m/z* 642 $[M]^+$ (100%); HRMS (ESI) ($C_{40}H_{23}MgN_7O$) $[M+H]^+$: Calc.: 642.1887; Found: 642.1885.

(20-(3,5-Dimethoxyphenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato) magnesium **22**

Synthesised following the general procedure described above using a solution of phthalonitrile (210 mg, 1.64 mmol) and $MgBr_2$ (148 mg, 0.80 mmol) in dry diglyme (0.5 ml), heating at 220 °C for 10 min under argon and initially adding aminoisoindoline **18** (150 mg, 0.54 mmol) and phthalonitrile (69 mg,

0.54 mmol) in dry diglyme (1.0 ml) over 1 h. Finally, a solution of phthalonitrile (69 mg, 0.54 mmol) and DABCO (90 mg, 0.80 mmol) in dry diglyme (0.5 ml) was added dropwise over 1 h. The purified product was recrystallized from acetone/EtOH (1:1) gave the ***title compound*** as green crystals with purple reflex (30 mg, 8%); mp >300 ºC; UV-vis (THF) λ_{max} / nm (ε) 670 ($6.45 \cdot 10^3$), 647 ($4.23 \cdot 10^3$), 594 ($1.21 \cdot 10^2$), 443 ($1.41 \cdot 10^2$), 395 ($2.82 \cdot 10^3$); ν_{max} / cm^{-1} (ATR) 2934, 1470; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.59 (d, *J* = 7.5 Hz, 2H), 9.53 – 9.50 (m, 4H), 8.20 – 8.15 (m, 4H), 7.93 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 2.3 Hz, 2H), 7.18 (t, *J* = 2.3 Hz, 1H), 3.95 (s, 6H); ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) 162.77, 156.73, 153.72, 152.83, 145.37, 142.92, 142.14, 141.16, 140.93, 140.21, 130.07, 129.78, 128.35, 127.41, 126.68, 125.97, 123.85, 123.65, 123.54, 111.75, 102.25, 56.14; MS (MALDI-TOF) *m/z* 672 $[M]^+$ (100%); HRMS (ESI) ($C_{41}H_{25}MgN_7O_2$) $[M+H]^+$: Calc.: 671.1915; Found: 671.1923 $[M+H]^+$.

(20-(1-Pyrenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato) magnesium **24**

Synthesised following the general procedure described above using a solution of phthalonitrile (154.0 mg, 1.20 mmol) and $MgBr_2$ (110.0 mg, 0.60 mmol) in dry diglyme (1.0 ml), heating at 220 °C for 10 min under argon and initially adding aminoisoindoline **23** (138 mg, 0.40 mmol) and phthalonitrile (51.0 mg, 0.40 mmol) in dry diglyme (1.5 ml) over 30 min. Finally, a solution of phthalonitrile (51.0 mg, 0.40 mmol) and DABCO (6 mg, 0.60 mmol) in dry diglyme (0.5 ml) was added dropwise over 30 min and the mixture heated for a further 1.5 h. The crude product was purified by column chromatography using AcOEt:PE (1:3) then AcOEt:PE:THF (3:10:1) as eluent gradient. Recrystallization from THF and hexane gave **24** as green-purple crystals (35 mg. 12%); mp >300 ºC; UV-vis (THF) λ_{max} / nm (ε) 670 ($7.35 \cdot 10^3$), 647 ($4.41 \cdot 10^3$), 592 ($1.03 \cdot 10^2$), 442 ($1.03 \cdot 10^2$), 397 ($2.50 \cdot 10^2$); ν_{max} / cm^{-1} (ATR) 3054, 1606, 1512, 1481, 1328; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.55-9.50 (m, 6H); 8.79 (d, 1H, *J* = 7.6,); 8.75 (d, 1H, *J* = 7.6); 8.59 (d, 1H, *J* = 9.2); 8.46 (d, 1H, *J* = 9.2); 8.42 (dd, 1H, *J* = 7.3, 1.6); 8.20-8.17 (m, 4H); 8.09 (dd, 1H, *J* = 7.3, 1.6); 8.06 (t, 1H, *J* = 7.3); 7.71 (ddd, 2H, *J* = 7.5, 7.0, 0.7); 7.61 (d, 1H, *J* = 9.4); 7.50 (d, 1H, *J* = 9.4); 7.09 (ddd, 2H, *J* = 8.1, 7.0, 1.1); 6.23 (br dt, 2H, *J* = 8.1, 0.7).; ^{13}C-NMR (125.7 MHz, THF-d_8, 298 K): δ (ppm) 156.7, 153.6, 153.2, 152.6, 143.5, 141.1, 140.8, 140.6, 140.1, 138.2, 133.5, 133.3, 133.2, 133.0, 132.1, 131.7, 130.0, 129.7, 129.3, 128.8, 128.7, 128.1, 127.4, 127.1, 126.6, 126.2, 126.1, 126.0, 126.0, 125.9, 125.0, 123.8, 123.6, 123.4; MS (MALDI-TOF) *m/z* 735.5 $[M]^+$ (100%); HRMS (MALDI) ($C_{49}H_{25}N_7Mg$) $[M]^+$: Calc.: 735.2016; Found: 735.2024.

(20-(3-Hydroxyphenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato) magnesium **21**

A solution of TBTAP **20** (40 mg, 0.062 mmol) in distilled DCM (5 mL) was stirred at 0 °C for 5 min under an argon atmosphere. A solution of BBr_3 (1.25 mL, 1.25 mmol, 20 eq, 1 M in DCM) was added dropwise over 1 h using a syringe pump. After finishing the addition, the reaction mixture was left to warm to room temperature and stirred for further 1 h. MeOH (5 ml) was added and the mixture sonicated for 5 min. The solvents were removed under reduced pressure and the crude product was purified by column chromatography on silica gel using DCM:Et_3N:THF (20:1:3) as eluent. Recrystallisation from acetone/EtOH gave the ***title compound*** as green crystals with purple reflex (19 mg, 50%); mp >300 ^oC; UV-vis (THF) λ_{max} / nm (ε) 670 ($4.14\cdot10^3$), 646 ($2.26\cdot10^3$), 592 ($5.65\cdot10^2$), 444 ($1.88\cdot10^2$), 428 ($3.77\cdot10^2$), 383 ($1.32\cdot10^3$); ν_{max} / cm^{-1} (ATR) 3600-3100 (br), 1455, 1348; ^{1}H-NMR (500 MHz, THF-d_8, 298 K): δ (ppm) 9.59 (d, *J* = 7.5 Hz, 2H), 9.53 – 9.50 (m, 4H), 8.82 (br s, 1H, OH), 8.21 – 8.15 (m, 4H), 7.92 (t, *J* = 7.0 Hz, 2H), 7.79 – 7.74 (m, 1H), 7.66 – 7.61 (m, 3H), 7.54 (s, 1H), 7.46 (ddd, *J* = 8.4, 2.4, 0.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H); MS (MALDI-TOF) *m/z* 628 $[M]^+$ (100%); HRMS (ESI) ($C_{39}H_{21}MgN_7O$) $[M]^+$: Calc.: 627.1653; Found: 627.1654.

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