

## First Examples of Functionalisation of *Meso*-Aryl Tetrabenzotriazaporphyrins (TBTAPs) Through Cross-Coupling Reactions

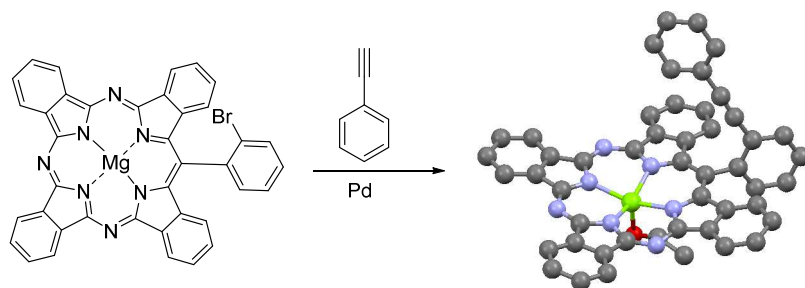
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### Graphical Abstract



# First Examples of Functionalisation of *Meso*-Aryl Tetrabenzotriazaporphyrins (TBTAPs) Through Cross-Coupling Reactions

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## Abstract

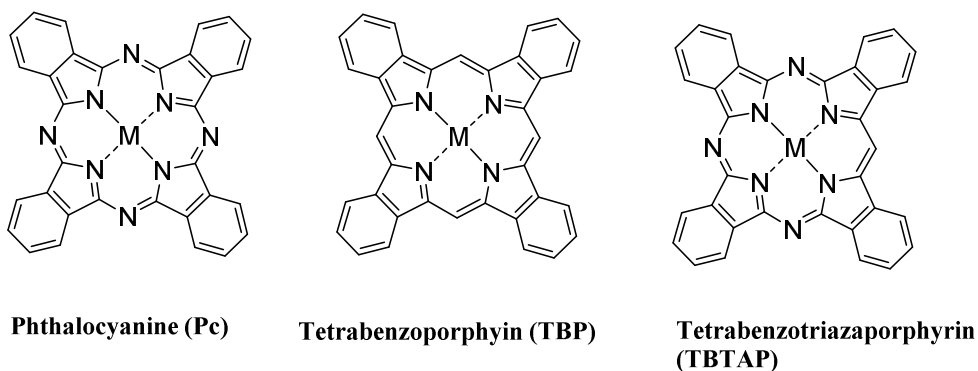
Recent synthetic advances have given convenient access to tetrabenzotriazaporphyrins (TBTAPs) functionalised with *meso*-aryl substituents. In this paper we report the first examples of further functionalization of the *meso*-sites through Suzuki-Miyaura and copper-free Sonagashira cross-coupling reactions of the *meso*-(bromophenyl)TBTAPs, demonstrating the breadth of new materials design now possible in the hybrid macrocycles.

**Keywords:** Phthalocyanines, Porphyrins, Heterocycles, Synthesis, Hybrids, Cross-Coupling

## 1. Introduction

The tetrabenzotriazaporphyrin (TBTAP) ring system can be regarded as a hybrid between the ubiquitous phthalocyanine (Pc) and (tetrabenzo)porphyrin macrocyclic aromatic structures<sup>1</sup> in which a single nitrogen atom bridge is replaced by carbon (Fig 1). The hybrid structures are fascinating and potentially very useful materials; they combine the stability, robustness and intense long-wavelength electronic absorption typical of the phthalocyanines but incorporate a bridging atom (*meso*-site) that can be further functionalised for linking to additional moieties, scaffolds or surfaces. Hybrid systems like TBTAPs were first observed by Linstead<sup>2</sup> and Dent<sup>3</sup> as part of seminal studies that formed the basis for prolonged and extensive investigation into synthetic macrocyclic chromophores. However, whereas research and development in phthalocyanine chemistry has led to many thousands of studies, the chemistry of the hybrids has, until recently, remained relatively underexplored.<sup>4</sup> By far the greatest hindrance to the development of the hybrid materials has been the difficulties associated with their synthesis. Indeed the original method of synthesis developed by Linstead,<sup>2</sup> involving the macrocyclisation of phthalonitrile

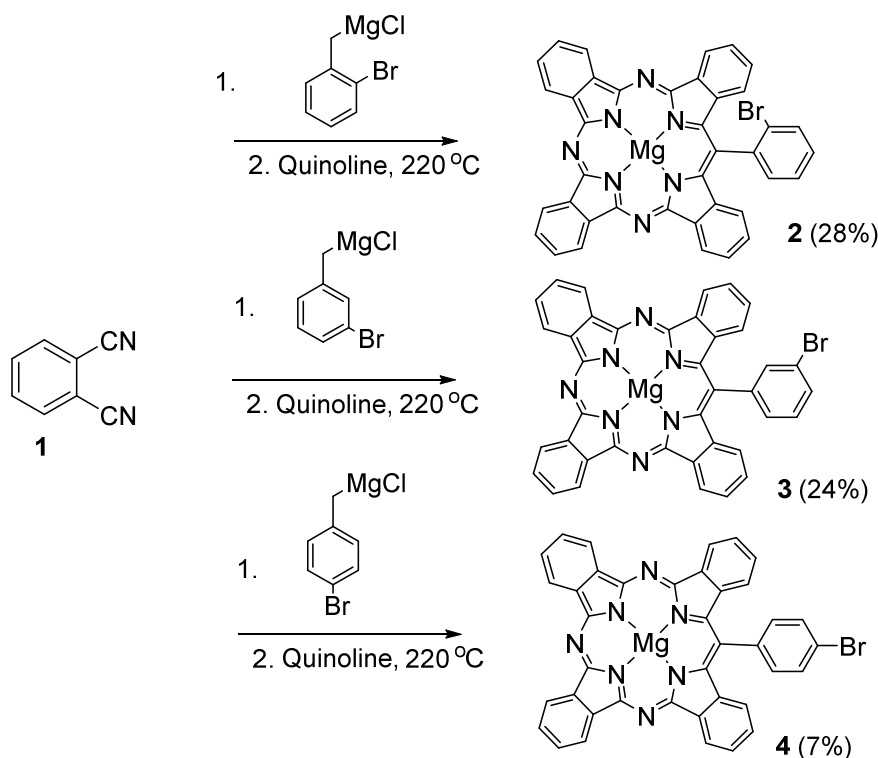
initiated by an organometallic nucleophile (providing the bridging carbon) was employed with little improvement in the majority of studies. Our group has recently reported a new procedure for the controlled synthesis of TBTAP hybrids,<sup>5</sup> and a complementary approach to the *trans*-tetrabenzodiazaporphyrins (*trans*-TBDAPs) has separately been developed by Cepak and co-workers.<sup>6</sup> Alongside the new syntheses we have refined and improved the Grignard reagent initiated macrocyclisation approach, delivering the full range of hybrids in specific cases,<sup>7</sup> and most recently reporting the series of isomeric *meso*-(bromophenyl)TBTAPs.<sup>8</sup> The latter series were targeted as particularly useful intermediates for further functionalisation, and this paper describes the first successful extensions of this chemistry through cross-coupling reactions.



**Figure 1.** Structures Phthalocyanine (Pc), tetrabenzoporphyin (TBP) and tetrabenzotriazaporphyrin (TBTAP).

## 2. Results and Discussion

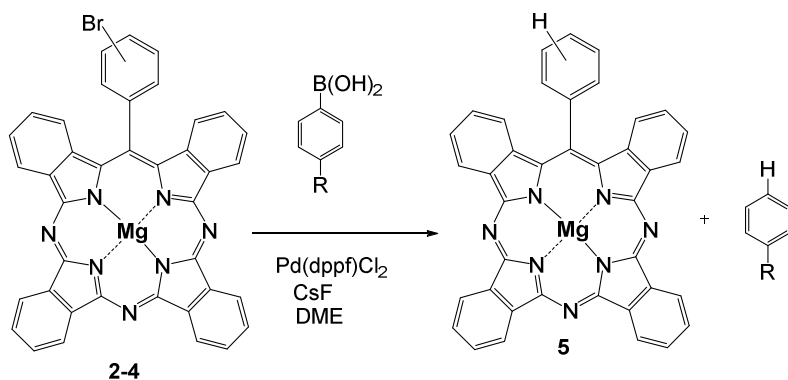
The three isomeric *meso*-(bromophenyl)TBTAPs were prepared as previously reported by initially reacting phthalonitrile with 2-, 3-, or 4-bromobenzylmagnesium chloride in THF at room temperature. Exchange of the solvent for quinoline, followed by heating at 220 °C gave, after chromatographic separation, the TBTAP hybrids **2-4** (Scheme 1).<sup>8</sup>



**Scheme 1.** Synthesis of *meso*-(bromophenyl)-TBTAPs via the Grignard reagent route.<sup>8</sup>

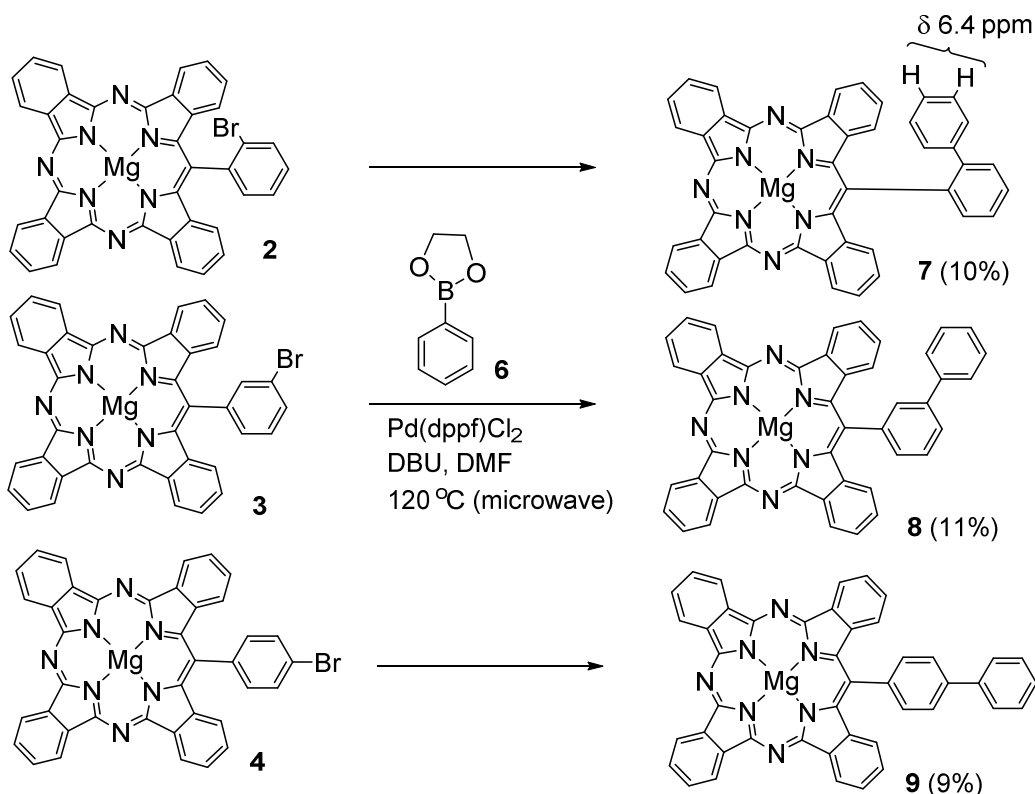
The first attempts at functionalisation through cross-coupling involved treatment of bromides **2-4** with phenyl or 4-methoxyphenyl boronic acid under standard Suzuki-Miyaura<sup>9</sup> conditions. In a typical procedure the TBTAP bromide was treated with excess of boronic acid and CsF in refluxing, dry DME in the presence of Pd(dppf)Cl<sub>2</sub>. Reactions were very slow and took several days to complete. After this time, most of the starting material (**2-4**) had been consumed but the product in each case was the parent *meso*-phenylTBTAP **5** resulting from debromination of the starting materials (Scheme 2). Closer examination of the reaction with 4-methoxyphenyl boronic acid also showed debromination of the

boronic acid reagent was occurring. Both side reactions are well-known in Suzuki-Miyaura cross-coupling chemistry and often dominate when the desired cross-coupling reaction is slow.<sup>10,11</sup>



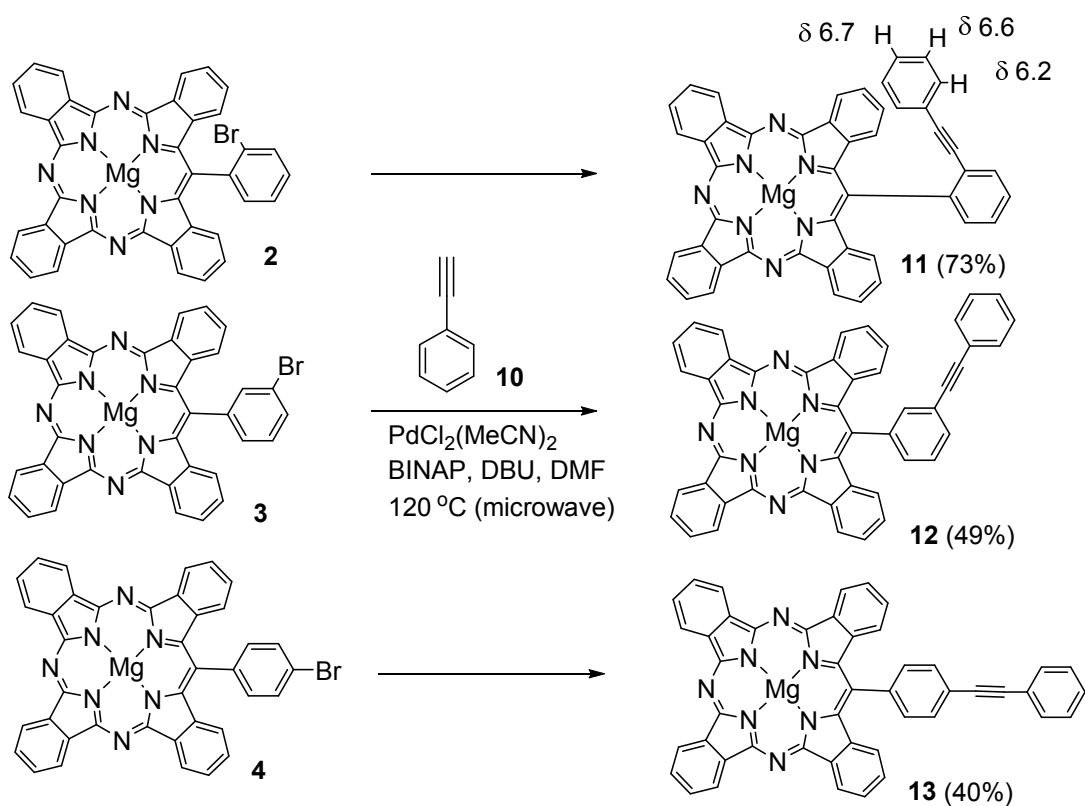
**Scheme 2.** Attempted Suzuki-Miyaura coupling between *meso*-(bromophenyl)-TBTAPs and phenyl boronic acids.

An effective strategy to overcome protonolysis side-reactions is to take all possible steps to remove proton sources. In this case, this involved replacement of the boronic acid starting material with its corresponding boronate ester. We have had particular success in other projects using ethane diol (rather than the more widely employed pinacol) as protective ester.<sup>10,12</sup> Boronate ester **6** was indeed successfully employed in cross-coupling reactions with bromoTBTAPs **2-4**. Reactions were most conveniently performed using microwave heating, and in a typical procedure **2-4** were mixed in a microwave vial with excess of boronate ester **6**, DBU and catalytic Pd(dppf)Cl<sub>2</sub> in dry DMF and degassed with argon. The reaction mixtures were irradiated in a microwave reactor at 120 °C for 1 h. Workup and column chromatography gave the isomeric cross-coupled products **7-9**, albeit in low yields (Scheme 3). As expected, the absorption spectra of the TBTAPs are insensitive to these synthetic modifications, underlining the (ground-state) electronic isolation of the *meso*-aryl substituent due to the perpendicular orientation with respect to the macrocycle. The arrangement places the new benzene ring of 2-substituted derivative **7** above the aromatic macrocycle core so that the *meta* and *para* protons of the new ring experience a shielding effect and appear around  $\delta$  6.4 ppm.

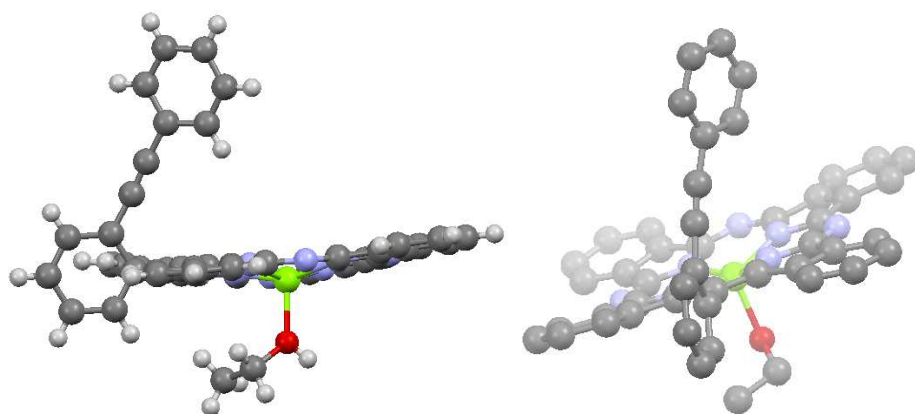


**Scheme 3.** Suzuki-Miyaura coupling between *meso*-(bromophenyl)-TBTAPs and boronate ester **6**.

The second cross-coupling functionalisation strategy employed Sonagashira cross-coupling,<sup>13</sup> selecting phenylacetylene **10** as reactant. In a typical Sonagashira cross-coupling aryl halides are treated with terminal acetylenes, catalysed by palladium and employing copper as co-catalyst. This method has the potential to lead to unwanted incorporation of copper into the macrocyclic ligand (displacing the versatile magnesium) so alternative, copper-free conditions<sup>14</sup> were employed. Cross-coupling to acetylenes, again under microwave heating, proved to be much more straightforward than Suzuki-Miyaura coupling. Treatment of bromo-TBTAPs **2-4** with phenyl acetylene (excess), PdCl<sub>2</sub>(MeCN)<sub>2</sub>/BINAP and DBU in DMF led to cross-coupled TBTAP derivatives **11-13** in good yields (Scheme 4). Once again the 2-substituted derivative **11** shows shielding of the protons lying above the macrocyclic core (6.2-6.7 ppm). Crystals of TBTAP **11** suitable for X-ray crystallography could be grown by slow evaporation from acetone/ethanol and the structure, shown in Figure 2, clearly illustrates the location of the new phenyl unit with respect to the TBTAP core.<sup>15</sup>



**Scheme 4.** Copper-free Sonagashira cross coupling between *meso*-(bromophenyl)-TBTAPs and phenyl acetylene.



**Figure 2.** X-ray crystal structure of derivative **11** (ball-and-stick representations).

### 3. Conclusions

Porphyrin-phthalocyanine hybrids are intriguing and potentially important organic molecular materials yet challenges associated with their synthesis have prevented development of the area. New and improved synthetic strategies and methods now allow more ambitious, designer molecules to be realised. We have demonstrated here, for the first time, the functionalisation of TBTAP hybrids using cross-coupling chemistry on parent *meso*-bromophenylTBTAPs. Suzuki-Miyaura cross-coupling is challenging, but can be achieved under anhydrous conditions. In contrast, copper-free Sonogashira coupling is straightforward and high yielding. Both strategies demonstrate the potential for engineering multifunctional systems with predictable and fixed relative positioning of the individual components – control that it hard to imagine within phthalocyanines themselves.

### 4. Experimental

**General Methods:** Reagents and solvents were purchased from commercial sources and used without further purification. <sup>1</sup>H (and <sup>13</sup>C-NMR) spectra were recorded at 500 (125.7) on a Bruker Ascend™ 500 spectrometer. The residual solvent peaks were used as references. 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. Additional 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. X-Ray crystallography data was collected by the UK National Crystallography Service at University of Southampton.

#### **General synthetic procedure for the synthesis of *meso*-biphenyl tetrabenzotriazaporphyrins via palladium-catalysed Suzuki cross-coupling reactions**

A mixture of bromophenyl TBTAP **2**, **3** or **4** (1.0 equiv), PdCl<sub>2</sub>(dppf) (0.1 equiv) was sealed in a microwave vessel with a magnetic bar and then evacuated and backfilled with argon three times. A solution of 2-phenyl-[1,3,2]-dioxaborolane **6** (10.0 equiv) and DBU (2.5 equiv) in dry DMF (1.0 mL) was added and stirred under argon for 5 min. The mixture was then irradiated in a microwave reactor at 120 °C for 1 h. After cooling to room temperature, DCM was added and the mixture sonicated for 5



min. After the removal of the solvent under reduced pressure, the resulting material was purified by column chromatography over silica gel to give the desired product.

#### **[20-{2-(1,1'-Biphenyl)}-tetrabenzob[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 7**

Prepared following the procedure described above, a mixture of 2-bromophenyl MgTBTAP **2** (30.0 mg, 0.043 mmol, 1.00 equiv) and PdCl<sub>2</sub>(dppf) (4.0 mg, 4.90 μmol, 0.1 equiv) was sealed in a microwave vessel. A solution of 2-phenyl-[1,3,2]-dioxaborolane **6** (64.0 mg, 0.43 mmol, 10.0 equiv) and DBU (16.5 mg, 0.11 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM → DCM/Et<sub>3</sub>N (20:1) → DCM/Et<sub>3</sub>N/THF (10:1:2) → DCM/THF (1:1) gave the waxy green product. A portion was subjected to a size-exclusion chromatography over Bio-beads SX-3 using THF eluent to obtain a pure sample. Recrystallisation from acetone/EtOH (1:1) yielded the *title compound* as green crystals with a purple reflex (3 mg, 10%); mp > 300 °C; UV-Vis (THF) λ<sub>max</sub>/nm (ε) 672 (1.48×10<sup>4</sup>), 649 (8.59×10<sup>3</sup>), 593 (1.72×10<sup>3</sup>), 446 (1.37×10<sup>3</sup>), 397 (4.47×10<sup>3</sup>). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 298 K): δ (ppm) = 9.58 (d, *J* = 7.5 Hz, 2H), 9.51 – 9.45 (m, 4H), 8.19 – 8.13 (m, 4H), 8.12 (d, *J* = 9.1 Hz, 1H), 8.01 (d, *J* = 7.3 Hz, 1H), 7.97 – 7.91 (m, 3H), 7.89 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 6.7, 3.1 Hz, 2H), 6.42 – 6.37 (m, 3H). <sup>13</sup>C NMR (125.7 MHz, THF-d<sub>8</sub>, 298 K): δ (ppm) = 156.59, 153.49, 152.38, 145.16, 143.30, 142.75, 142.15, 141.19, 141.17, 140.94, 140.23, 134.10, 132.25, 130.43, 130.06, 129.75, 129.61, 129.18, 128.41, 127.87, 127.43, 127.09, 125.83, 125.46, 123.86, 123.74, 123.58. MS (MALDI-TOF) *m/z* 688 [M]<sup>+</sup> (100%). HRMS (ESI) (C<sub>45</sub>H<sub>26</sub>N<sub>7</sub>Mg) [M+H]<sup>+</sup>: calcd: 688.2095; found 688.2092.

#### **[20-{3-(1,1'-Biphenyl)}-tetrabenzob[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 8**

Prepared following the procedure described above, a mixture of 3-bromophenyl TBTAP **3** (38.0 mg, 0.055 mmol, 1.00 equiv) and PdCl<sub>2</sub>(dppf) (5.0 mg, 6.13 μmol, 0.1 equiv) was sealed in a microwave vessel. A solution of 2-phenyl-[1,3,2]-dioxaborolane **6** (81.4 mg, 0.55 mmol, 10.0 equiv) and DBU (21.0 mg, 0.14 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM → DCM/Et<sub>3</sub>N (20:1) → DCM/Et<sub>3</sub>N/THF (10:1:2) → DCM/THF (1:1) gave a waxy green product. A portion was subjected to a size-exclusion chromatography over Bio-beads SX-3 using THF eluent to obtain a pure material. Recrystallisation from acetone/EtOH (1:1) obtained the *title compound* as green

crystals with a purple reflex (4 mg, 11%); mp > 300 °C; UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 670 ( $4.13 \times 10^3$ ), 647 ( $2.48 \times 10^3$ ), 593 ( $8.26 \times 10^2$ ), 444 ( $4.13 \times 10^2$ ), 396 ( $1.24 \times 10^3$ ).  $^1\text{H}$  NMR (500 MHz, THF- $d_8$ , 298 K):  $\delta$  (ppm) = 9.60 (d,  $J$  = 7.5 Hz, 2H), 9.53 – 9.50 (m, 4H), 8.50 (s, 1H), 8.36 (d,  $J$  = 7.9 Hz, 1H), 8.22 – 8.16 (m, 4H), 8.13 (d,  $J$  = 7.6 Hz, 1H), 8.05 (t,  $J$  = 7.5 Hz, 1H), 7.90 (dd,  $J$  = 14.7, 7.6 Hz, 4H), 7.58 (t,  $J$  = 7.5 Hz, 2H), 7.43 (t,  $J$  = 7.8 Hz, 2H), 7.33 (t,  $J$  = 7.4 Hz, 1H), 7.27 (d,  $J$  = 8.1 Hz, 2H).  $^{13}\text{C}$  NMR (125.7 MHz, THF- $d_8$ , 298 K):  $\delta$  (ppm) = 156.59, 153.49, 152.38, 145.16, 143.30, 142.75, 142.15, 141.19, 141.17, 140.94, 140.23, 134.10, 132.25, 130.43, 130.06, 129.75, 129.61, 129.18, 128.41, 127.87, 127.43, 127.09, 125.83, 125.46, 123.86, 123.74, 123.58. MS (MALDI-TOF)  $m/z$  687 [ $\text{M}$ ] $^+$  (100%).

### **[20-{4-(1,1'-Biphenyl)}-tetrabenzo[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 9**

Prepared following the procedure described above, a mixture of 4-bromophenyl TBAP **4** (21.8 mg, 0.032 mmol, 1.00 equiv) and PdCl<sub>2</sub>(dppf) (3.0 mg, 3.68  $\mu\text{mol}$ , 0.1 equiv) was sealed in a microwave vessel. A solution of 2-phenyl-[1,3,2]-dioxaborolane **6** (46.0 mg, 0.31 mmol, 10.0 equiv) and DBU (12.01 mg, 0.079 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM  $\rightarrow$  DCM/Et<sub>3</sub>N (20:1)  $\rightarrow$  DCM/Et<sub>3</sub>N/THF (10:1:2)  $\rightarrow$  DCM/THF (1:1) gave a waxy green product. A portion was subjected to a size-exclusion chromatography over Bio-beads SX-3 using THF eluent to obtain a pure material. Recrystallisation from acetone/EtOH (1:1) gave the *title compound* as green crystals with a purple reflex (2 mg, 9 %); mp > 300 °C; UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 670 ( $2.27 \times 10^4$ ), 647 ( $1.24 \times 10^4$ ), 592 ( $4.12 \times 10^3$ ), 446 ( $2.06 \times 10^3$ ), 396 ( $6.19 \times 10^3$ ).  $^1\text{H}$  NMR (500 MHz, THF- $d_8$ , 298 K):  $\delta$  (ppm) = 9.60 (d,  $J$  = 8.3 Hz, 2H), 9.53 – 9.50 (m, 4H), 8.32 (d,  $J$  = 6.7 Hz, 2H), 8.25 (d,  $J$  = 7.9 Hz, 2H), 8.21 – 8.13 (m, 6H), 7.91 (t,  $J$  = 7.3 Hz, 2H), 7.66 (t,  $J$  = 7.8 Hz, 2H), 7.59 (t,  $J$  = 7.4 Hz, 2H), 7.52 (t,  $J$  = 6.9 Hz, 1H), 7.29 (d,  $J$  = 8.1 Hz, 2H).  $^{13}\text{C}$  NMR (125.7 MHz, THF- $d_8$ , 298 K):  $\delta$  (ppm) = 156.59, 153.49, 152.38, 145.16, 143.30, 142.75, 142.15, 141.19, 141.17, 140.94, 140.23, 134.10, 132.25, 130.43, 130.06, 129.75, 129.61, 129.18, 128.41, 127.87, 127.43, 127.09, 125.83, 125.46, 123.86, 123.74, 123.58. MS (MALDI-TOF)  $m/z$  687 [ $\text{M}$ ] $^+$  (100%).

**General synthetic procedure for the synthesis of meso-phenylethynyl-phenyl tetrabenzotriazaporphyrins via palladium-catalysed copper-free Sonogashira cross-coupling reactions.**

A mixture of bromophenyl TBTAP (1.0 eq), BINAP (0.06 equiv) and PdCl<sub>2</sub>(MeCN)<sub>2</sub> (0.07 equiv) was sealed in a microwave vessel with a magnetic bar and then evacuated and backfilled with argon three times. A solution of phenylacetylene (1.6 equiv) and DBU (2.5 equiv) in dry DMF (1.0 mL) was added and stirred under argon for 5 min. The mixture was then irradiated in a microwave reactor at 120 °C for 1 h. After cooling to room temperature, 10 mL of DCM was added and the mixture sonicated. After the removal of the solvent under reduced pressure, the resulting material was purified by column chromatography over silica gel to give the desired product.

### **[20-{2-(Phenylethynyl-phenyl)}-tetrabenzob[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 11**

Prepared following the procedure described above, a mixture of 2-bromophenyl TBTAP **2** (40.0 mg, 0.058 mmol, 1.00 equiv), BINAP (2.16 mg, 3.47 μmol, 0.06 equiv) and PdCl<sub>2</sub>(MeCN)<sub>2</sub> (1.05 mg, 4.05 μmol, 0.07 equiv) was sealed in a microwave vessel. A solution of phenylacetylene (9.46 mg, 0.093 mmol, 1.6 equiv) and DBU (22.0 mg, 0.145 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM → DCM/Et<sub>3</sub>N (20:1) → DCM/Et<sub>3</sub>N/THF (10:1:2) → DCM/THF (1:1) gave the waxy green material which recrystallised from acetone/EtOH (1:1) to yield the *title compound* as green crystals with a purple reflex (30 mg, 73%); mp > 300 °C; UV-Vis (THF) λ<sub>max</sub>/nm (ε) 670 (2.28×10<sup>4</sup>), 648 (1.35×10<sup>4</sup>), 592 (2.61×10<sup>3</sup>), 444 (1.66×10<sup>3</sup>), 395 (7.13×10<sup>3</sup>). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 298 K): δ (ppm) = 9.61 (d, *J* = 7.5 Hz, 2H), 9.52 – 9.50 (m, 4H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.20 – 8.14 (m, 4H), 8.10 (t, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.96 – 7.88 (m, 3H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.1 Hz, 1H), 6.57 (t, *J* = 7.1 Hz, 2H), 6.25 (d, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (125.7 MHz, THF-d<sub>8</sub>, 298 K): δ (ppm) = 145.86, 145.74, 143.23, 143.20, 143.05, 142.75, 141.33, 141.20, 141.08, 141.01, 140.96, 140.27, 139.45, 134.45, 134.43, 134.13, 133.52, 131.73, 130.41, 130.21, 130.04, 129.76, 128.61, 128.52, 128.45, 127.48, 125.22, 125.14, 124.01, 123.87, 123.83, 123.68, 123.66, 123.66. MS (MALDI-TOF) *m/z* 711 [M]<sup>+</sup> (100%). HRMS (ESI) (C<sub>47</sub>H<sub>26</sub>N<sub>7</sub>Mg) [M+H]<sup>+</sup>: calcd: 712.2095; found 712.2094.

### **[20-{3-(Phenylethynyl-phenyl)}-tetrabenzob[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 12**

Prepared following the procedure described above, a mixture of 3-bromophenyl TBTAP **3** (80.0 mg, 0.12 mmol, 1.00 equiv), BINAP (4.33 mg, 6.95 μmol, 0.06 equiv) and PdCl<sub>2</sub>(MeCN)<sub>2</sub> (2.10 mg, 8.10

$\mu\text{mol}$ , 0.07 equiv) was sealed in a microwave vessel. A solution of phenylacetylene (18.92 mg, 0.185 mmol, 1.6 equiv) and DBU (44.10 mg, 0.289 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM  $\rightarrow$  DCM/Et<sub>3</sub>N (20:1)  $\rightarrow$  DCM/Et<sub>3</sub>N/THF (10:1:2)  $\rightarrow$  DCM/THF (1:1) gave a waxy green material which recrystallised from acetone/EtOH (1:1) to afford the *title compound* as green crystals with a purple reflex (42 mg, 49%); mp > 300 °C; UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 670 ( $1.62 \times 10^4$ ), 647 ( $8.84 \times 10^3$ ), 593 ( $1.83 \times 10^3$ ), 443 ( $9.15 \times 10^2$ ), 393 ( $4.88 \times 10^3$ ). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 298 K):  $\delta$  (ppm) = 9.61 (d,  $J = 7.5$  Hz, 2H), 9.52 – 9.50 (m, 4H), 8.37 (s, 1H), 8.24 (d,  $J = 8.0$  Hz, 1H), 8.22 – 8.15 (m, 5H), 8.01 (t,  $J = 7.7$  Hz, 1H), 7.93 (t,  $J = 7.1$  Hz, 2H), 7.63 (t,  $J = 7.0$  Hz, 2H), 7.54 (dd,  $J = 7.2, 2.3$  Hz, 2H), 7.36 – 7.29 (m, 3H), 7.21 (d,  $J = 8.0$  Hz, 2H). <sup>13</sup>C NMR (125.7 MHz, THF-d<sub>8</sub>, 298 K):  $\delta$  (ppm) = 148.51, 147.76, 147.29, 146.20, 144.85, 144.42, 143.19, 141.77, 141.58, 141.30, 141.19, 140.97, 140.96, 140.94, 140.44, 140.23, 139.67, 137.98, 137.95, 137.22, 133.30, 133.06, 132.55, 130.22, 130.15, 130.07, 129.85, 129.48, 129.43, 129.40, 128.36, 128.26, 127.93, 127.43, 126.90, 125.70, 125.53, 125.42, 124.24, 123.91, 123.76, 123.67, 123.65. MS (MALDI-TOF)  $m/z$  711 [M]<sup>+</sup> (100%). HRMS (ESI) (C<sub>47</sub>H<sub>26</sub>N<sub>7</sub>Mg) [M+H]<sup>+</sup>: calcd: 712.2095; found 712.2092.

### [20-{4-(Phenylethynyl-phenyl)}-tetrabenzob[*b,g,q,l*][5,10,15]triazaporphyrinato] magnesium 13

Prepared following the procedure described above, a mixture of 4-bromophenyl TBTAP **190** (45.50 mg, 0.066 mmol, 1.00 equiv), BINAP (2.46 mg, 3.95  $\mu\text{mol}$ , 0.06 equiv) and PdCl<sub>2</sub>(MeCN)<sub>2</sub> (1.19 mg, 4.61  $\mu\text{mol}$ , 0.07 equiv) was sealed in a microwave vessel. A solution of phenylacetylene (10.75 mg, 0.105 mmol, 1.6 equiv) and DBU (25.04 mg, 0.165 mmol, 2.5 equiv) in dry DMF (1.0 mL) was added, stirred and then irradiated in a microwave reactor at 120 °C for 1 h. Purification by chromatography on silica gel using DCM  $\rightarrow$  DCM/Et<sub>3</sub>N (20:1)  $\rightarrow$  DCM/Et<sub>3</sub>N/THF (10:1:2)  $\rightarrow$  DCM/THF (1:1) gave a waxy green material which recrystallised from acetone/EtOH (1:1) to afford the *title compound* as green crystals with a purple reflex (18.9 mg, 40%); mp > 300 °C; UV-Vis (THF)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 669 ( $3.42 \times 10^3$ ), 646 ( $1.71 \times 10^3$ ), 592 ( $2.14 \times 10^2$ ), 444 ( $1.06 \times 10^2$ ), 394 ( $8.33 \times 10^2$ ). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 298 K):  $\delta$  (ppm) = 9.61 (d,  $J = 7.5$  Hz, 2H), 9.52 – 9.50 (m, 4H), 8.23 – 8.17 (m, 6H), 8.15 (d,  $J = 8.2$  Hz, 2H), 7.93 (t,  $J = 7.2$  Hz, 2H), 7.75 (dd,  $J = 8.0, 1.4$  Hz, 2H), 7.65 (t,  $J = 7.5$  Hz, 2H), 7.52 – 7.44 (m, 3H), 7.24 (d,  $J = 8.1$  Hz, 2H). <sup>13</sup>C NMR (125.7 MHz, THF-d<sub>8</sub>, 298 K):  $\delta$  (ppm) = 148.51, 147.76, 147.29, 146.20, 144.85, 144.42, 143.19, 141.77, 141.58, 141.30, 141.19, 140.97, 140.96, 140.94, 140.44,

140.23, 139.67, 137.98, 137.95, 137.22, 133.30, 133.06, 132.55, 130.22, 130.15, 130.07, 129.85, 129.48, 129.43, 129.40, 128.36, 128.26, 127.93, 127.43, 126.90, 125.70, 125.53, 125.42, 124.24, 123.91, 123.76, 123.67, 123.65. MS (MALDI-TOF)  $m/z$  711 [M]<sup>+</sup> (100%). MS (MALDI-TOF)  $m/z$  711 [M]<sup>+</sup> (100%). HRMS (ESI) (C<sub>47</sub>H<sub>26</sub>N<sub>7</sub>Mg) [M+H]<sup>+</sup> :calcd: 712.2095; found 712.2092.

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15. CCDC 1044515 contain the supplementary crystallographic data for TBTAP **11**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).