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Various Synthetic Routes to a Gable-Like Bis(porphyrin) Constructed on a 1,10-Phenanthroline Chelate

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Three different synthetic routes to obtain a gable-like bis(porphyrin) are described. The two porphyrins are covalently linked to a 2,9-diphenyl-1,10-phenanthroline chelate. One way to gain access to the bis(porphyrin) relies on the simultaneous construction of two porphyrins on a 2,9-bis(*para*-formylphenyl)-1,10-phenanthroline, whereas the other two are based on Suzuki cross-coupling reactions between a presynthesised porphyrin and an appropriate phenanthroline derivative.

Introduction

Porphyrins are key components in very diverse fields of research because of their well-defined binding sites and interesting chemical and photochemical properties. Their use in the construction of sophisticated multicomponent architectures is related to the development of simple synthetic protocols to nonsymmetrical porphyrin–macrocycle conjugates functionalised either on the *meso* positions or on the pyrrolic sites of the porphyrin.[1] Oblique bis(porphyrin)s have been made and studied since the beginning of the 1980s as models of various natural biological systems related to allostery in haemoglobin or photosynthesis.[2] The first compound of this family was made by the group of Tabushi, and it was named "gable" porphyrin.[3] Later on, several groups embarked on the synthesis and the study of related gable porphyrins with various spacers between the two tetrapyrrolic rings, in relation to biomimetic projects, as already mentioned, and to host–guest chemistry. Our own group has been interested in electron and energy-transfer processes from an early stage, and the first 1,10-phenanthroline-based gable bis(porphyrin) has been at the origin of a large body of studies related to catenanes and rotaxanes, which were made and investigated as models of an important fragment of the bacterial photosynthetic reaction centre,[4] consisting of the special pair (primary electron donor) and bacteriopheophytin (primary electron acceptor).[5] More recently, we have used a metallated zinc(II) bis(porphyrin) constructed on the 1,10-phenanthroline chelate as a receptor for dipyridylporphyrin to build a tris(porphyrinic) macrocycle.[6] The same zinc(II) bis(porphyrin) motif is also the key building block of a new procedure to assemble a [2]catenane by using coordination bonds only.[7] We would now like to describe the different synthetic routes tested to obtain this potentially multipurpose bis(porphyrin) chelate.

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Results and Discussion

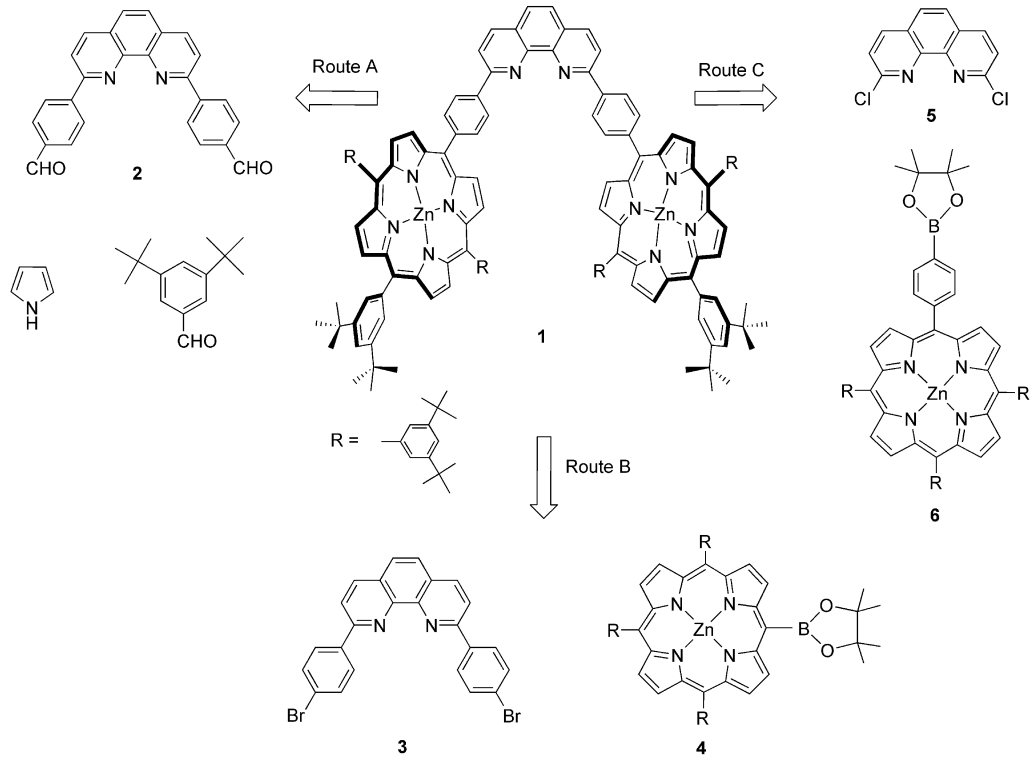
Three different strategies were explored to find a compromise between the number of synthetic steps and the amount of final bis(porphyrin) obtained. The corresponding retrosynthetic schemes are depicted in Scheme 1. They are based on the simultaneous construction (Route A) or attachment (Routes B and C) of two porphyrins on an appropriate functionalised 1,10-phenanthroline.

Route A (Scheme 1) relies on a double porphyrin-forming reaction carried out on 2,9-bis(4-formylphenyl)-1,10-phenanthroline (**2**) from pyrrole and 3,5-di-*tert*-butylbenzaldehyde. The two other routes are modular: Route B is based on a double Suzuki coupling reaction between 2,9-bis(4-bromophenyl)-1,10-phenanthroline (**3**) and *meso*-boronic ester porphyrin **4**, whereas in Route C the coupling reactions occur directly on the phenanthroline nucleus by using 2,9-dichloro-1,10-phenanthroline (**5**) and *meso*-phenyl boronic ester porphyrin **6** as precursors. The various steps involved in the preparation of the precursors of these three synthetic ways are discussed below.

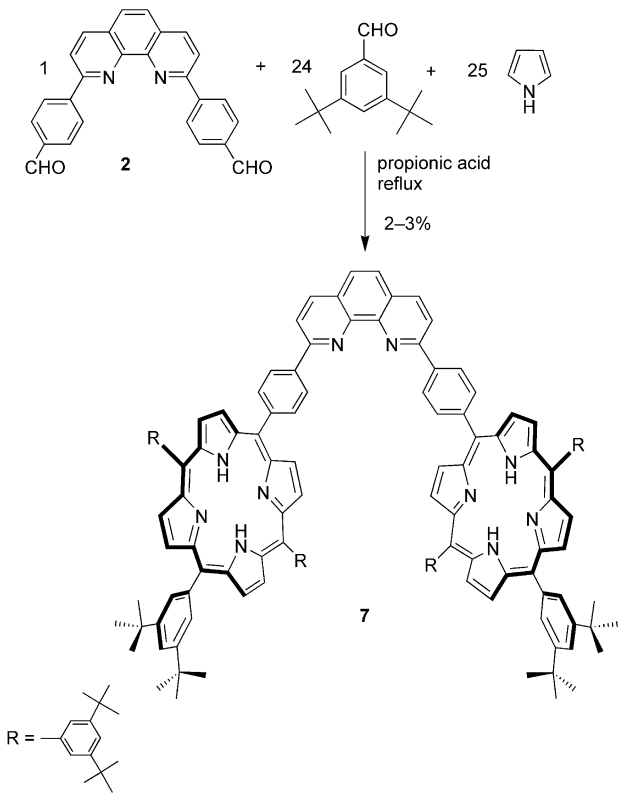
Route A: Synthesis of 1 by a Double Cyclisation Reaction

This is the oldest route explored in our group.[2g] It looks to be the simplest one, as it is based on the direct synthesis of free-base bis(porphyrin) **7** by two simultaneous Rothemund reactions under Adler conditions on phenanthroline **2** (Scheme 2).[8]

Phenanthroline **2** was prepared from 1,10-phenanthroline by a double nucleophilic aromatic substitution with



Scheme 1. Different synthetic routes, A, B, and C, explored to synthesise zinc(II) bis(porphyrin) **1** and the corresponding precursors.



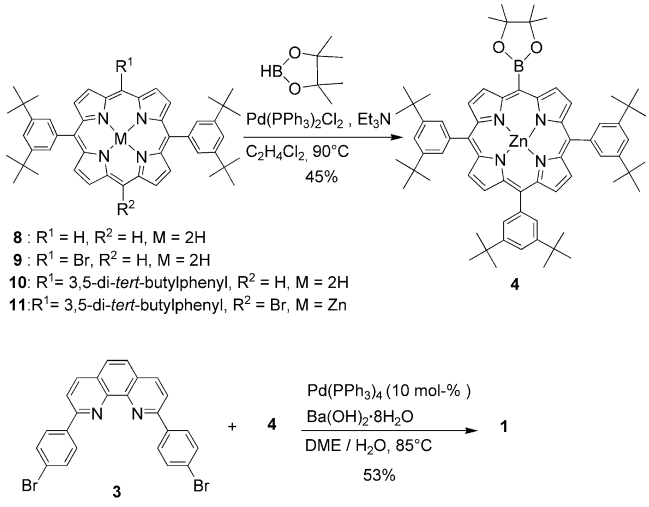
Scheme 2. Route A: Synthesis of free-base bis(porphyrin) **7** by a double cyclisation reaction.

the lithium derivative of *para*-(5,5-dimethyl-1,3-dioxan-2-yl)bromobenzene, followed by acidic hydrolysis of the acetal to restore the aldehyde functional group, as described in the literature.[9] When **2** was treated with 3,5-di-*tert*-butylbenzaldehyde and pyrrole in a 1:24:25 proportion in refluxing propionic acid, free-base porphyrin **7** was obtained with a very poor yield of 2–3% only. This yield was expected, as porphyrins with four identical *meso* substituents are usually obtained with yields not higher than 20% under Adler conditions. Compound **7** can be quantitatively converted into **1** by double metallation of the two free-base porphyrins by using zinc(II) acetate. Difficulties in isolating **7** from the crude product (numerous and delicate chromatographic separations) and the amount obtained (70 mg of **7** from 500 mg of **2**) make this approach unattractive.

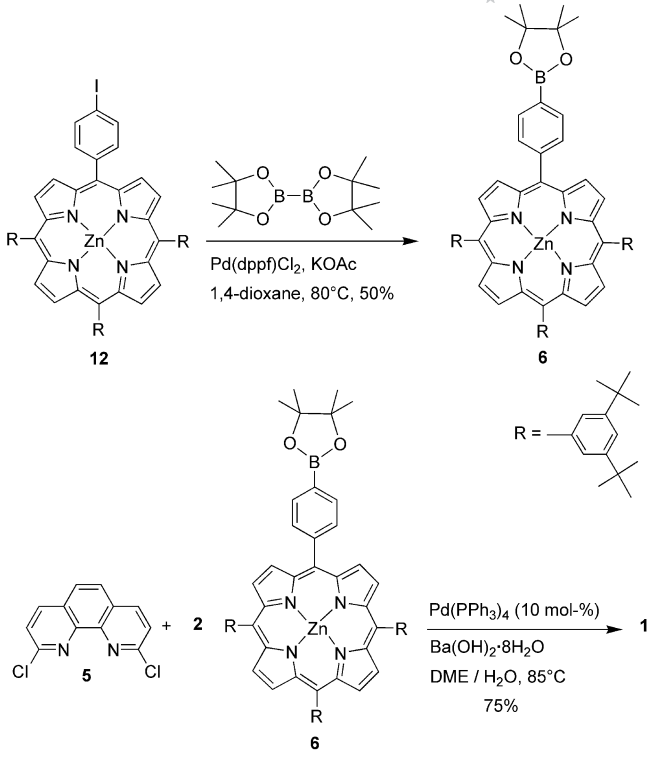
Route B: Synthesis of 1 by a Double Suzuki Cross-Coupling Reaction of *meso*-Boronic Ester Porphyrin 4 and 2,9-Bis(4-bromophenyl)-1,10-phenanthroline (3)

Several synthetic steps were necessary to construct **4**, a porphyrin with three *meso* aryl groups and a boronic ester directly attached to the remaining *meso* position. The synthesis started with the formation of **8** from dipyrrylmethane and 3,5-di-*tert*-butylbenzaldehyde according to a literature procedure.[10] Following a two-step reaction, monobromination and subsequent Suzuki coupling as described by Odobel and co-workers,[11] **8** was converted into porphyrin **10**. After almost quantitative bromination of the remaining free

meso position and zinc metallation of the central core, **11** was obtained (Scheme 3).[12] It was converted into boronic ester **4** in 45% yield by using pinacolborane as the transmetallating reagent as developed by Masuda[13] under reaction conditions described by Therien and co-workers[14] for related porphyrins. Phenanthroline **3** was prepared by a two-step procedure from 1,10-phenanthroline as described by our group.[15] The final double Suzuki reaction involving **3** and **4** (2 equiv.) was performed under classical conditions to give **1** in 53% yield after purification by column chromatography.



Scheme 3. Route B: Synthesis of porphyrin precursor **4** and the coupling reaction of **4** with phenanthroline derivative **3**.



Scheme 4. Route C: Synthesis of *meso*-phenyl boronic ester porphyrin **6** followed by Suzuki cross-coupling reaction with **5**.

Route C: Synthesis of 1 by a Double Suzuki Cross-Coupling Reaction between *meso*-Phenyl Boronic Ester Porphyrin 6 and 2,9-Dichloro-1,10-phenanthroline (5)

This route required the synthesis of porphyrin **12**, a *meso* substituted porphyrin similar to **4**, which can be obtained easily in a one-step reaction by condensation of the appropriate aromatic aldehydes and pyrrole under Adler reaction conditions.[8] Metallation with zinc(II) was performed directly on the crude product obtained after workup. The yield of the isolated compound (10%) was better than that obtained under Lindsey conditions.[16] The moderate yield was counterbalanced by the amount of **12**, which can be obtained in one batch (typically 500 mg) and purification of the iodo porphyrin derivative is easier than that of the bromo derivative (i.e., **9**; Scheme 3, Route B). From **12**, *meso*-phenyl boronic ester zinc(II) porphyrin **6** was obtained by using the approach of Miyaura with pinacol diboron as the transmetallating reagent, as represented in Scheme 4.[17]

Phenanthroline **5** was prepared on a gram scale in three steps from 1,10-phenanthroline monohydrate as already described.[18] Pd-catalysed cross-coupling of **5** with **6** (2 equiv.) gave desired zinc(II) bis(porphyrin) **1** in 75% yield, which is a better yield than that obtained in the last step of Route B also based on a double Suzuki cross-coupling reaction to form **1**.

Conclusions

Three different routes to a zinc(II) bis(porphyrin) were discussed. Whereas Route A might seem attractive because the number of steps is limited, the low yield, the limited amount of compound obtained, and the extreme separation and purification difficulties make it almost useless. Routes B and C are based on a double Suzuki cross-coupling reaction with various halogenated 1,10-phenanthroline and boronic ester porphyrin precursors. Route C is the most efficient one, as the number of steps to construct the functionalised porphyrin is significantly less than that of Route B. This new strategy paves the way to the construction of more complex multiporphyrin assemblies based on this readily available ligand. The zinc(II) porphyrins can coordinate nitrogen-bearing ligands, and the phenanthroline chelates can be used to assemble several such bis(porphyrin)s around a given transition-metal centre. A noncovalent tetraporphyrinic catenane was recently reported in the literature[7] and other noncovalent multiporphyrinic edifices are actually elaborated by using this zinc(II) bis(porphyrin).

Experimental Section

General Methods: Dry solvents were distilled from suitable drying agents: 1,2-dimethoxyethane from sodium/benzophenone and 1,2-dichloroethane from calcium hydride. Commercial anhydrous dioxane was purchased from Aldrich and used as received. Flash column chromatography was carried out by using Combi Flash Retrieve (alumina neutral chromatography columns by Teledyne Isco). Column chromatography was carried out by using silica gel (Merck Kieselgel, silica gel 60, 0.063–0.200 mm). All chemicals were of best commercially available grade and used without further purification (except when mentioned). NMR spectra for ^1H were acquired with a Bruker Avance 300 spectrometer. The spectra were referenced to residual proton-solvent references (^1H: CD_2Cl_2 at δ = 5.32 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet, br. d: broad doublet), the value of the coupling constants in Hertz if applicable, the number of protons implied, and finally the assignment. Mass spectra were obtained with a Bruker MicroTOF spectrometer.

Compound 4: A round-bottom flask was charged with compound **11** (115 mg, 0.11 mmol), pinacolborane (140 μL, 0.95 mmol), triethylamine (200 μL, 1.49 mmol), dichlorobis(triphenylphosphane)-palladium(II) (2.4 mg, 0.003 mmol), and freshly distilled 1,2-dichloroethane (20 mL). The mixture was degassed by three vacuum–argon cycles and then stirred at 90 °C under an atmosphere of argon. After 2 h, thin-layer chromatography showed complete conversion of **11**. The solvent was evaporated; the residue was taken up in dichloromethane and washed with water. The organic layer was dried with magnesium sulfate. The solvent was evaporated, and the crude product was purified by a quick column chromatography (silica gel; pentane/CH_2Cl_2, 70:30) to yield **4** as a purple solid (53 mg, 45%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.91 (d, ^3J = 4.5 Hz, 2 H, $H_{pyrrolic}$), 9.10 (d, ^3J = 4.8 Hz, 2 H, $H_{pyrrolic}$), 9.00 (d, ^3J = 4.8 Hz, 2 H, $H_{pyrrolic}$), 8.99 (d, ^3J = 4.8 Hz, 2 H, $H_{pyrrolic}$), 8.12 (d, ^4J = 1.8 Hz, 4 H, H_{opx}), 8.09 (d, ^4J = 1.8 Hz, 2 H, H_{opz}), 7.87 (t, ^4J = 1.8 Hz, 2 H, H_{ppx}), 7.84 (t, ^4J = 1.8 Hz, 1 H, H_{ppz}), 1.86 (s, 12 H, $H_{Me\text{-}boronic}$), 1.56 (s, 36 H, $H_{t\text{Bux}}$), 1.53 (s, 18 H, $H_{t\text{Buz}}$) ppm. MS (ES): m/z = 1065.58 $[M + H]^+$.

Zn^{II} Bis(porphyrin) 1 by Route B: A Schlenk flask was charged with porphyrin derivative **4** (137 mg, 0.13 mmol), **3** (21 mg, 0.043 mmol), barium hydroxide octahydrate (40.6 mg, 0.13 mmol), freshly distilled 1,2-dimethoxyethane (3.5 mL), and deionised water (0.35 mL). The mixture was freeze–pump–thaw degassed before tetrakis(triphenylphosphane)palladium (5 mg, 0.0043 mmol) was added, and the mixture was then stirred at reflux under an atmosphere of argon overnight. The solvents were evaporated, and the residue was taken up in dichloromethane and washed with water. The organic layer was dried under vacuum. The crude product was then purified by column chromatography three times (2 × silica gel; pentane/CH_2Cl_2, 100:0 to 50:50; then 1 × silica gel; cyclohexane/CH_2Cl_2, 80:20 to 50:50) to give **1** as a purple solid (50 mg, 53%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.06 (d, ^3J = 4.6 Hz, 4 H, $H_{pyrrolic}$), 8.94 (d, ^3J = 4.6 Hz, 8 H, $H_{pyrrolic}$), 8.92 (d, ^3J = 4.6 Hz, 4 H, $H_{pyrrolic}$), 8.92 (d, ^3J = 8.3 Hz, 4 H, H_o), 8.56 (br. d, 4 H, $H_{3,4,7,8}$), 8.50 (d, ^3J = 8.1 Hz, 4 H, H_m), 8.11 (d, ^4J = 1.7 Hz, 4 H, H_{opz}), 8.06 (d, ^4J = 1.8 Hz, 8 H, H_{opx}), 8.01 (s, 2 H, $H_{5,6}$), 7.86 (t, ^4J = 1.7 Hz, 2 H, H_{ppz}), 7.79 (t, ^4J = 1.7 Hz, 4 H, H_{ppx}), 1.55 (s, 36 H, $H_{t\text{Buz}}$), 1.47 (s, 72 H, $H_{t\text{Bux}}$) ppm. MS (ES): m/z = 2206.09 $[M + H]^+$.

Compound 12: In a round-bottom flask, 4-iodobenzaldehyde (1.1 g, 0.0047 mmol), 3,5-di-*tert*-butylbenzaldehyde (4.9 g, 0.023 mmol), and pyrrole (1.3 mL, 0.02 mmol) were dissolved in propionic acid (70 mL), and the mixture was heated at reflux for 6 h. The solvent was removed by adding the same amount of toluene and by evaporating the mixture under reduced pressure. The crude product was taken up in dichloromethane and triethylamine (100 mL) was added. Then, the mixture was washed with water (3 × 50 mL), and the organic layer was evaporated under reduced pressure and dried under vacuum. The crude product was again taken up in dichloromethane and filtered by a column of silica gel in order to remove the black polymers. The fractions containing the desired product were then precipitated in CH_2Cl_2/EtOH and purified by column chromatography (silica gel; cyclohexane/CH_2Cl_2, 100:0 to 80:20). The desired porphyrin contaminated with impurities was metallated with zinc acetate. The mixture was dissolved in dichloromethane, and $Zn(OAc)_2{\cdot}2H_2O$ (175 mg) dissolved in methanol (20 mL) was added. The mixture was heated at reflux for 1 h, and then the solvents were evaporated under reduced pressure. The crude was taken up in dichloromethane and washed with water. The organic layer was evaporated and dried under vacuum. Finally, flash column chromatography (several elutions; alumina; cyclohexane/CH_2Cl_2, 98:2 to 90:10) gave **12** as a purple solid (490 mg, 10%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.00 (d, ^3J = 4.6 Hz, 2 H, $H_{pyrrolic}$), 8.99 (s, 4 H, $H_{pyrrolic}$), 8.94 (d, ^3J = 4.6 Hz, 2 H, $H_{pyrrolic}$), 8.12 (d, ^3J = 8.2 Hz, 2 H, H_o), 8.09 (d, ^4J = 1.8 Hz, 6 H, $H_{opx,opz}$), 7.98 (d, ^3J = 8.2 Hz, 2 H, H_m), 7.84 (m, ^4J = 1.8 Hz, 3 H, $H_{ppx,ppz}$), 1.53 (s, 54 H, $H_{t\text{Bux},t\text{Buz}}$) ppm. MS (ES): m/z = 1040.43 $[M]^+$.

Compound 6: A round-bottom flask was charged with compound **12** (200 mg, 0.18 mmol), bis(pinacolato)diboron (67 mg, 0.26 mmol), potassium acetate (52 mg, 0.53 mmol), [1,1′-bis(diphenylphosphanyl)ferrocene]dichloropalladium(II) (7.2 mg, 0.009 mmol), and commercial anhydrous dioxane (2 mL). The mixture was degassed by three vacuum–argon cycles and then stirred at 80 °C under an atmosphere of argon. The reaction was monitored by thin-layer chromatography, and after 5 d, no more evolution could be detected. The solvent was removed under reduced pressure, and the crude product was taken up in dichloromethane and washed with water (3 × 10 mL). The crude product was then purified by flash column chromatography (silica gel; cyclohexane/CH_2Cl_2, 65:35) to yield 50% of **6** as a purple solid. ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.06 (s, 4 H, $H_{pyrrolic}$), 9.05 (d, ^3J = 4.5 Hz, 2 H, $H_{pyrrolic}$), 8.99 (d, ^3J = 4.8 Hz, 2 H, $H_{pyrrolic}$), 8.31 (d, ^3J = 8.1 Hz, 2 H, H_o), 8.20 (d, ^3J = 7.8 Hz, 2 H, H_m), 8.17 (d, ^4J = 1.8 Hz, 6 H, $H_{opx,opz}$), 7.91 (t, ^4J = 1.8 Hz, 3 H, $H_{ppx,ppz}$), 1.60 (s, 54 H, $H_{t\text{Bux},t\text{Buz}}$), 1.53 (s, 12 H, $H_{Me\text{-}boronic}$) ppm. MS (ES): m/z 1141.53 $[M + H]^+$.

Zn^{II} Bis(porphyrin) 1 by Route C: A Schlenk flask was charged with compound **6** (133.2 mg, 0.12 mmol), **5** (13.6 mg, 0.056 mmol), barium hydroxide octahydrate (36 mg, 0.12 mmol), freshly distilled 1,2-dimethoxyethane (2.6 mL), and deionised water (0.26 mL). The mixture was freeze–pump–thaw degassed before tetrakis(triphenylphosphane)palladium (13.5 mg, 0.012 mmol) was added, and the mixture was stirred at reflux under an atmosphere of argon overnight. The solvents were evaporated, and the residue was taken up in dichloromethane and washed with water (3 × 10 mL). The organic layer was dried under vacuum. The crude product was then purified by column chromatography (silica gel; cyclohexane/CH_2Cl_2, 60:40 to 20:80) and precipitated with CH_2Cl_2/MeOH to yield **1** as a purple solid (93 mg, 75%). Compound **1** was characterised as described in Route B.

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