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New azaheterocyclic aromatic diphosphonates for hybrid materials for fuel cell applications†

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New azaheterocyclic aromatic diphosphonate derivatives of benzimidazole and benzotriazole were synthesized by nickel-catalyzed Arbuzov reaction of 4,7-dibromo-2,1,3-benzothiadiazole with triethyl phosphite, followed by reductive sulfur extrusion reaction and cyclization. This new strategy allowed us to obtain these compounds with high efficiency, with the generation of these azaheterocyclic aromatic diphosphonate derivatives in good to excellent yields, since these compounds could not be synthesized by direct cross-coupling reactions catalyzed by palladium or nickel. All compounds were characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution). NMR studies of compound **9** showed the presence of only one tautomeric form, on the NMR time scale, in different solvents and at different concentrations.

Introduction

The development of cleaner and sustainable sources of energy is one of the major challenges of the 21st century. Alternative energy systems are crucial in order to deal with the environmental threat of global warming and the use of fossil energy sources. Fuel cells are electrochemical devices that convert the chemical energy stored directly into electrical energy. Fuel cells can provide electrical energy with high efficiency and low environmental impact. But, their performance depends crucially on the properties of component materials.[1–7]

Among the various kinds of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) are considered promising power sources, due to their high power density and high power-to-weight ratio. A key material for the operation of PEMFCs is the proton-exchange membrane (PEM). Usually, these membranes are made of organic polymers containing acidic functionalities (*e.g.* Nafion®), but the proton transport properties of these membranes strongly depend on their water content and, consequently, limit their operation temperatures up to 90 °C. These limitations have fostered the interest in research and development of new alternative membranes for the operation of fuel cells at temperatures above 100 °C. Above this temperature, the performance of fuel cells increases, due to faster electrode reaction without CO poisoning of the Pt electro-catalyst.[1–7] New alternative membranes include polybenzimidazole (PBI)-doped membranes, composites of Nafion® and metal oxides, sulfonated polymers based on aromatic hydrocarbons and organosiloxane-based inorganic–organic hybrids with various acidic species.[1–7]

Phosphonic acids are considered to be promising proton carriers because of their good proton donating and accepting properties.[8–10] In addition, phosphonic acids are an alternative to sulfonic acid groups due to their high proton conductivities, oxidation resistance and better thermal stabilities.[9–11]

Arylphosphonates have numerous practical applications, including in the design of fuel cell membranes.[10,12,13] Continuous efforts have been made to construct C–P bonds directly through metal-catalyzed C–P coupling of arylhalides to obtain arylphosphonates.[14] The Hirao reaction[15] and the nickel-catalyzed Arbuzov reaction[16] are widely used methods employed for the synthesis of arylphosphonates.

Phosphonylated azaheterocycles have gained a lot of interest over the years. Direct phosphonylation of aromatic azaheterocycles increased significantly and was reviewed by Van der Jeught and Stevens in 2009.[17] Direct phosphonylation of 6-bromobenzimidazole derivatives by Hirao reaction, using diethyl phosphite in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium, was reported to obtain the (1-ethyl-2-methyl-6-benzimidazolyl)phosphonate and diethyl (1-phenyl-2-methyl-6-benzimidazolyl)phosphonate.[17] Recently Li *et al.* reported the first palladium-catalyzed direct phosphonation

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† Electronic supplementary information (ESI) available: NMR data (^{1}H, ^{13}C and ^{31}P NMR spectra) for new compounds. See DOI: 10.1039/c3nj00585b

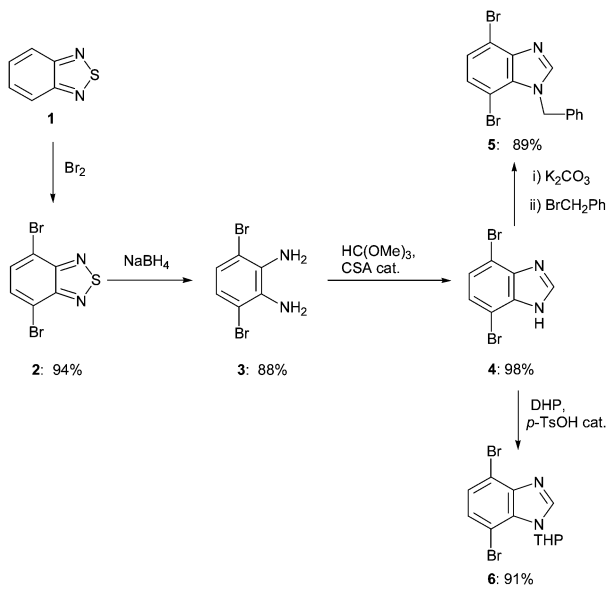
of azoles with dialkyl phosphite without addition of base or acid; however *N*-methylbenzimidazole and *N*-methylindole are inactive for this direct phosphonylation.[18] No synthetic routes are known towards diphosphonylation of 4- and 7-substituted benzimidazoles.

Herein, we report a novel and efficient strategy for the phosphonylation of azaheterocycles of general formula $(EtO)_2(O)P–R–P(O)(OEt)_2$, where R is a benzothiadiazole, benzimidazole or benzotriazole substituted at 4- and 7-positions, which could be used as starting materials to obtain hybrid membranes for PEMFCs with modified properties. This strategy can also be applied to the synthesis of other diverse phosphorylated azoles.

Results and discussion

Initial studies were carried out in order to obtain new diphosphonylated 4,7-benzimidazoles. The formation of a carbon–phosphorus bond in these compounds was performed starting from the 4,7-dibromobenzimidazole **4**, which was protected, previous to the phosphonylation reactions, at the N-1 position with a benzyl or a tetrahydropyranyl (THP) group. Our strategy for the synthesis of the protected 4,7-dibromobenzimidazoles **5** and **6** is summarized in Scheme 1.

Compound **2** was prepared in high yield by bromination of commercially available 2,1,3-benzothiadiazole **1**.[19] Reduction of **2** with $NaBH_4$ gave 1,2-diamine **3** in moderate yield.[20–22] Cyclization of 1,2-diamine **3** to 4,7-dibromobenzimidazole **4** was performed in excellent yield by reaction with trimethyl orthoformate under catalytic acid conditions, using (±)-camphorsulfonic acid (CSA). Treatment of 4,7-dibromobenzimidazole **4** with benzylbromide and K_2CO_3 in DMF gave compound **5** in 89% yield and treatment of 4,7-dibromobenzimidazole **4** with dihydropyran in CH_2Cl_2 in the presence of a catalytic amount of *p*-TsOH gave compound **6** in 91% yield (Scheme 1).



Scheme 1 Synthesis of new N-1 protected 4,7-dibromobenzimidazoles **5** and **6**.

^1H NMR spectra of compounds **2–4** were in agreement with the literature.[21,23] The NMR spectrum of 4,7-dibromobenzimidazole **4** shows the presence of two tautomeric forms, in a fast equilibrium on the NMR time scale, with equivalent proton atoms 5-H and 6-H, as usually described for benzimidazole.[24,25]

The new N-1 protected 4,7-dibromobenzimidazoles **5** and **6** were fully characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution). After substitution at the N-1 position by the protecting groups benzyl or THP (4,7-dibromobenzimidazoles **5** and **6**, respectively), NMR spectra of compounds **5** and **6** showed different shifts for all hydrogen and carbon atoms.

Electron Impact Ionization (EI) Mass Spectrometry spectra of compounds **5** and **6** show the molecular ion of both compounds, which confirmed the proposed molecular formulae.

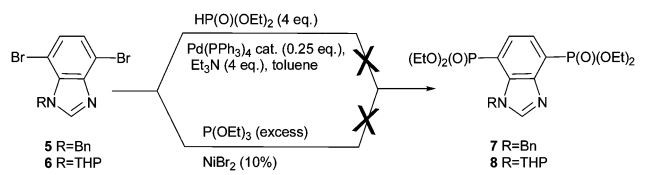
The Hirao reaction and the nickel-catalyzed Arbuzov reaction are widely used methods employed for the synthesis of arylphosphonates.[15,16] Our first studies to achieve the construction of $C(sp^2)$–P bonds were performed by the Hirao cross-coupling reaction of diethyl phosphite with 4,7-dibromobenzimidazole **5** or **6**, using $Pd(PPh_3)_4$ as a catalyst and triethylamine as base (Scheme 2). However these reactions failed under the mentioned conditions and the cross-coupling reaction did not occur. Tolmachev used this procedure for the synthesis of diethyl (1-ethyl-2-methyl-6-benzimidazolyl)phosphonate and diethyl (1-phenyl-2-methyl-6-benzimidazolyl)phosphonate, starting from a 6-bromobenzimidazole derivative, a *meta*-substituted benzimidazole, with no steric effect caused by *ortho*-groups.[17]

A second attempt was made using the Arbuzov nickel-catalyzed cross-coupling reaction of 4,7-dibromobenzimidazole **5** or **6** with triethyl phosphite and $NiBr_2$, but that also failed (Scheme 2). In the case of reaction of 4,7-dibromobenzimidazole **6**, a deprotection occurs and compound **4** was isolated instead.

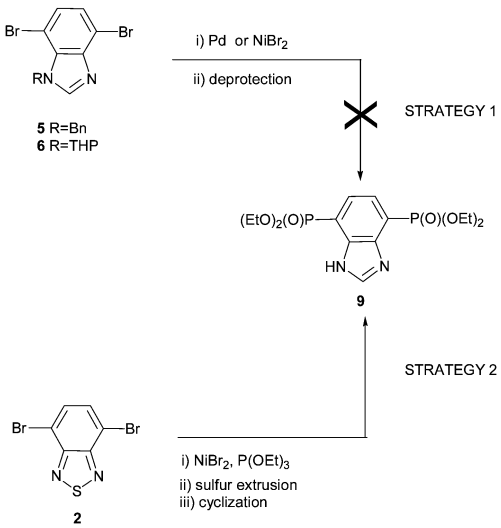
The failure of both reactions probably occurred due to the steric hindrance of *ortho* groups as previously reported for aryl substrates.[16,26–28] It has been observed for Arbuzov reaction that a β branch in the alkyl halide retards the reaction.[27]

In view of these results, an alternative strategy was devised by us. This strategy involved C–P cross coupling bond formation, followed by reductive sulfur extrusion and cyclization, starting from 4,7-dibromo-2,1,3-benzothiadiazole **2** (Scheme 3 – strategy 2). Compound **2** is a very common intermediate in the C–C and C–N cross-coupling reactions, but no C–P cross-coupling reaction was yet described.[29]

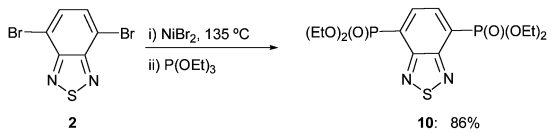
Under Hirao's conditions, no product was observed in the reaction of 2,4-dibromo-2,1,3-benzothiadiazole **2** and diethyl phosphite,



Scheme 2 Attempted synthesis of benzimidazole diphosphonates **7** and **8** by Hirao reaction and Arbuzov nickel-catalyzed reaction.



Scheme 3 Two strategies to obtain 4,7-benzimidazole diphosphonate **9** used in this work.



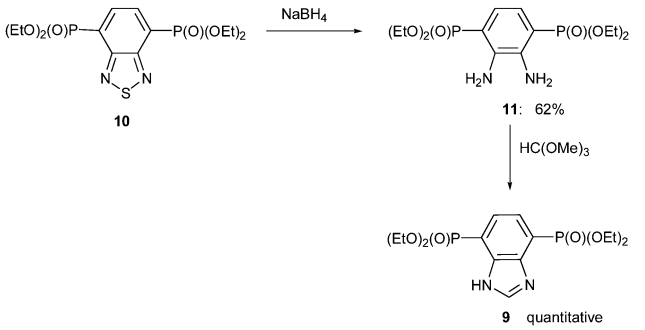
Scheme 4 Synthesis of 2,1,3-benzothiadiazole diphosphonate **10**.

using $Pd(PPh_3)_4$ as the catalyst and triethylamine as base. However, using the Arbuzov reaction conditions in the presence of triethyl phosphite and a catalytic amount of $NiBr_2$, 2,1,3-benzothiadiazole **2** was readily phosphorylated to give the desired 4,7-diphosphonate compound **10** in 86% yield (Scheme 4).

The structure of diphosphonate **10** was confirmed by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of compound **10** reveals that two ethyl ester groups are chemically equivalent, as a triplet (J = 7.1 Hz) and a multiplet centered at 1.38 and 4.24–4.49 ppm, respectively, characteristic of the four methyl groups and eight methylene protons of the two phosphonate groups. The two proton double doublets at 8.31 ppm (J = 13.5 and 5.9 Hz) are attributed to the aromatic ring system (5-H and 6-H), due to the coupling of the 5-H (6-H) proton with one phosphorus atom of the phosphonate groups at *ortho* and *meta* positions.

The ^{13}C NMR spectrum of compound **10** shows a double doublet at 126.8 ppm (J_{CP} = 188.2 and 3.5 Hz), consistent with the signal of a quaternary carbon bearing a phosphonate group, coupling with other phosphorus atoms at *para* positions. Also, the observed carbon triplets signals at 16.4 ppm (J_{CP} = 3.1 Hz) and 63.3 ppm (J_{CP} = 2.7 Hz) are characteristic of the methyl and methylene carbon atoms, respectively, of the ethyl ester phosphonate group.

The ^{31}P NMR spectrum presents a singlet at 11.6 ppm, assigned to the phosphorus atom in the aromatic phosphonate group.



Scheme 5 Synthesis of benzimidazole diphosphonate **9**.

Reduction of azadiphosphonate **10** with $NaBH_4$ gave 1,2-diamine **11** in moderate yield (62%) (Scheme 5). Cyclization reaction of diamine diphosphonate **11** to the desired 4,7-benzimidazole diphosphonate **9** was performed quantitatively by reaction with trimethyl orthoformate in the presence of a catalytic amount of CSA (Scheme 5).

The ^{1}H NMR spectrum of diamine diphosphonate **11** shows a triplet (J = 7.1 Hz) and a multiplet centered at 1.32 and 4.04–4.17 ppm, characteristic of the four methyl groups and eight methylene protons of the phosphonate groups, respectively. The two aromatic protons were observed at 6.94 ppm as a two proton double doublet. In the ^{31}P NMR spectrum a singlet was noted at 20.3 ppm assigned to the phosphorus atom in the aromatic phosphonate group.

The prototropic tautomerism of benzimidazole is well known and seems to be taking place fast enough on the NMR time scale, but the NMR spectra usually presents broad signals because of this tautomeric equilibrium.[24,25,30]

Due to this prototropic tautomerism, compound **9** presents an axis of symmetry with the corresponding proton, carbon and phosphorus atoms appearing as magnetically equivalent. The ^{1}H NMR spectrum in $CDCl_3$ presents a broad singlet at 7.76 ppm, attributed to 5-H and 6-H protons and a singlet at 8.26 ppm attributed to the 2-H proton. The ^{13}C NMR spectrum is in agreement with the ^{1}H NMR spectrum as it presents the carbon atoms C4 and C7, C5 and C6 and C3a and C7a equivalents. The ^{31}P NMR spectrum presents a singlet attributed to the two magnetically equivalent phosphorus atoms at 15.6 ppm.

However, under certain conditions, the NMR spectra of compound **9** also allow the identification of one single tautomer as if the tautomeric equilibrium occurs at slower speed than the NMR time scale. The ^{1}H NMR spectra of compound **9** (with only one tautomeric form, on the NMR time scale) generally present broad signals or multiplets for aromatic protons, due to the asymmetric structure caused by the ''fixed'' position of the N–H proton, as is frequently observed for other benzimidazole derivatives.[31–36] The ^{31}P NMR spectra (Fig. 1 and 2) show two singlets assigned to the two unequivalent phosphorus atoms, which is in agreement with the observed ^{1}H NMR spectra, attributed to an asymmetric molecular structure of compound **9**. The ^{13}C NMR spectrum of compound **9** in acetone-d_6 presents broad signals due to the slow proton exchange between N1 and N3, which allows the identification of carbon atoms as

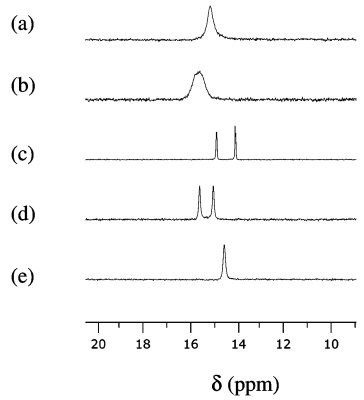


Fig. 1 The ^{31}P NMR spectra of compound **9** in different solvents in 0.01 M solutions: (a) CD_2Cl_2, (b) $CDCl_3$, (c) acetone-d_6, (d) MeOD, (e) DMSO-d_6.

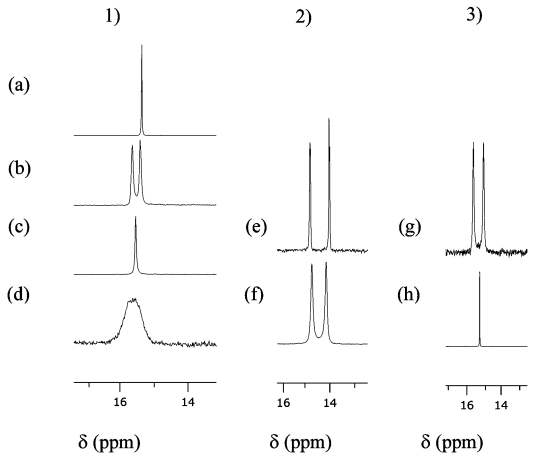
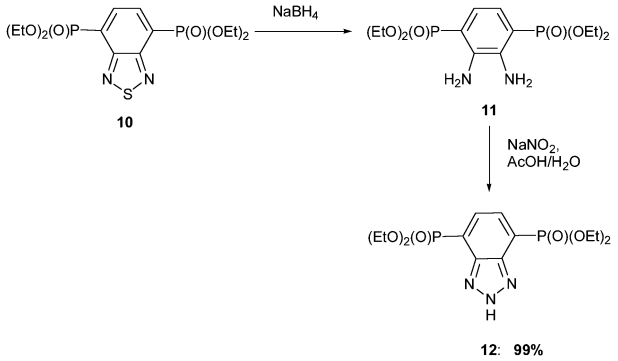


Fig. 2 The ^{31}P NMR spectra of compound **9** at different concentrations: (1) $CDCl_3$: (a) 0.1 M (after redissolution of the sample), (b) 0.1 M, (c) 0.05 M, (d) 0.01 M, (2) acetone-d_6: (e) 0.01 M, (f) 0.1 M and (3) MeOD: (g) 0.01 M, (h) 0.1 M.

magnetically unequivalent corresponding to the presence of only one tautomer on the NMR time scale.

The presence of fast or slow tautomeric equilibria was observed in different solvents (Fig. 1), in the same solvent but at different concentrations (Fig. 2) and even for NMR samples prepared with the same solvents and at the same concentration but at different times (Fig. 2); no relation was observed between temperature and the speed of the tautomeric equilibrium, as observed by other authors for similar compounds.[37,38] The presence of one tautomer was observed in spectra in solvent acetone-d_6 and low concentration MeOD and $CDCl_3$ samples (Fig. 2). NMR spectra of samples with higher concentration in $CDCl_3$ and MeOD show both tautomers as well as the low concentration CD_2Cl_2 and DMSO-d_6 spectra (Fig. 1 and 2). These could be explained by an intermolecular migration of the hydrogen atom in the prototropic tautomerism, which is facilitated in more concentrated solutions or with the assistance of their own solvent, like protic solvents, or the presence of impurities, such as water.[31–33,39,40] The presence of a phosphonate group at the *ortho* position could also slow down the



Scheme 6 Synthesis of benzotriazole diphosphonate **12**.

tautomeric equilibrium probably due to the establishment of a hydrogen bond between the N–H proton and the oxygen atoms, as observed by the other authors for benzimidazole.[33,34,41]

The same strategy regarding the synthesis was used in the preparation of benzotriazole derivatives. Cyclization of the diamine diphosphonate **11** in the presence of sodium nitrite in acetic acid gave the 4,7-benzotriazole diphosphonate **12** in good yield (Scheme 6).

The ^1H NMR spectrum of compound **12** in $CDCl_3$ shows a double doublet at 7.95 ppm attributed to the two aromatic protons. In the ^{31}P NMR spectrum a singlet was observed at 12.8 ppm, assigned to the two equivalent phosphorus atoms in the aromatic phosphonate groups. This is in agreement with the ^1H NMR spectrum, which shows the two aromatic protons to be magnetically equivalent. The ^{13}C NMR spectrum presents broad signals due to the slow proton exchange between N atoms; C4 and C-7, C5 and C6, and C3a and C7a are magnetically equivalent. The ^1H, ^{13}C and ^{31}P NMR spectra recorded in acetone-d_6 present similar signals to those recorded in $CDCl_3$.

It is known that the prototropic tautomerism of the amine proton of benzotriazole, which moves between the N-1 and N-2, and N-3 positions, causes the benzotriazole to exist in three tautomeric forms, the asymmetric N(1)–H and N(3)–H and the symmetric N(2)–H forms.[42–44] Unlike some ^{31}P and ^1H NMR spectra of benzimidazole **9**, in this case, all NMR spectra are in agreement with the three tautomeric forms of benzotriazole equilibrating rapidly on the NMR time scale.

The new diphosphonates **9–12** were also characterized by IR spectroscopy and mass spectrometry (low and high resolution).

Electrospray Ionization (ESI) methods were used to show the molecular ion of all diphosphonates **9–12**, which confirmed the proposed molecular formula of these new compounds.

The IR spectra of compounds **9–12** display intensive bands characteristic of phosphonate groups, including the P=O stretching band at 1227–1250 cm^{-1}, and in the region 1021–1050 cm^{-1} corresponding to stretching bands of the P–O–C group.

Conclusions

New azaheterocyclic aromatic diphosphonate derivatives were synthesized to become precursors for novel membrane materials for PEMFCs with modified properties.

The direct phosphonylation reaction of benzimidazole catalyzed by transition-metals (Pd and Ni) was not successful presumably due to the *ortho*-steric effects of amine groups. A new strategy was idealized with the direct phosphonylation of 4,7-dibromo-2,1,3-benzothiadiazole by nickel Arbuzov reaction, followed by reduction sulfur extrusion and cyclization to afford the new azaheterocyclic diphosphonates derived from benzimidazole and benzotriazole, in good yields. This strategy can be applied to the synthesis of other diverse phosphorylated azoles.

New compounds were fully characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution).

Compound **9** shows, on the NMR time scale, the presence of one or both tautomeric forms according to the solvent and the concentration of the solution.

These azoles will be incorporated into proton conductive inorganic–organic hybrid membranes of mesoporous silica to produce novel membrane materials with potentially high proton conductivity for intermediate temperature PEMFCs.

Experimental section

General remarks

NMR spectra were recorded on Bruker Avance II 300 (^{1}H 300 MHz, ^{13}C 75 MHz, ^{31}P 121 MHz), on Bruker Avance II 400 and Bruker Avance 400 MHz Ultra-shield (^{1}H 400 MHz, ^{13}C 100 MHz, ^{31}P 162 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz.

Infrared spectra were recorded on a Perkin Elmer FT-IR system spectrum BX Fourier Transform spectrometer, using KBr discs or film.

Low resolution and high resolution (HRMS) mass spectra analyses were performed at the 'C.A.C.T.I. – Unidad de Espectrometria de Masas' at the University of Vigo, Spain, on a VG AutoSpect M, MicroTOF (Bruker Daltonics) or APEX-Q (Bruker Daltonics) instrument.

Melting points were determined on a Reichert Thermovar melting point apparatus and are not corrected.

2,1,3-Benzothiadiazole **1** is commercially available (Aldrich) and was used without further purification.

Synthesis of 4,7-dibromobenzothiadiazole 2[19]. A mixture of 1,2,5-benzothiadiazole **1** (5.00 g, 36.72 mmol) in aq. HBr (48%, 15 mL) was heated to reflux with stirring while Br_2 (5.7 mL, 111.25 mmol) was added dropwise for 30 min. The mixture was refluxed for 3 h. The mixture was allowed to cool to room temperature and a saturated solution of $NaHSO_3$ (aq.) was added to consume completely any excess of Br_2. The solid was filtered and washed with water. The solid was then washed once with cold Et_2O and dried under reduced pressure to afford compound **2** (10.11 g, 94%) as a white solid. mp 188–189 °C (lit.[19] 188–189 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.94 (s, 2H, Ar*H*, 5-H and 6-H). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.73 (s, 2H, Ar*H*, 5-H and 6-H).

Synthesis of 3,6-dibromobenzene-1,2-diamine 3[20]. To a suspension of compound **2** (3.50 g, 11.91 mmol) in EtOH (400 mL) and THF (40 mL) at 0 °C, under N_2, was added portion-wise $NaBH_4$ (8.11 g, 211.31 mmol). After stirring at 0 °C for 10 min, the mixture was stirred at room temperature for 3 h. The reaction mixture was cooled to 0 °C and H_2O (100 mL) was added slowly. After removing the solvent under reduced pressure, the residue was diluted with Et_2O (150 mL), washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, resulting in the very air-unstable diamine compound **3** (2.78 g, 88%) as a white solid. Diamine **3** was used immediately in the next step to avoid fast decomposition. mp 94–95 °C (lit.[21] 94–95 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.90 (br s, 4H, NH_2), 6.84 (s, 2H, Ar*H*, 5-H and 6-H).

Synthesis of 4,7-dibromo-1*H*-benzimidazole 4. To a solution of diamine **3** (2.16, 8.11 mmol) in dichloromethane (70 mL) was added $HC(OEt)_3$ (1.06 mL, 9.73 mmol) and the solution was stirred for 10 min. A catalytic quantity of (+)-camphorsulfonic acid (CSA) (20 mg) was added and the solution stirred for 1 h. A white powder precipitate was formed. The precipitate was filtered and washed with Et_2O to afford compound **4** (2.73 g, 98%) as a white solid. mp 264–266 °C (lit.[23] 266–268 °C (decomp.)). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 7.37 (s, 2H, Ar*H*, 5-H and 6-H), 8.39 (s, 1H, Ar*H*, 2-H).

Synthesis of 1-benzyl-4,7-dibromo-1*H*-benzimidazole 5. A solution of 4,7-dibromo-1*H*-benzimidazole **4** (200 mg, 0.724 mmol) and K_2CO_3 (300 mg, 2.171 mmol) in DMF (3 mL) was stirred at 80 °C. After 30 min, $BrCH_2Ph$ (0.17 mL, 145 mmol) was added and the reaction mixture was refluxed for 2.5 h. Upon cooling, the mixture was acidified with 10% aqueous HCl solution and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (1 : 1 EtOAc:petroleum ether) to give compound **5** (237 mg, 89%) as a white solid. mp 155 °C. ν_{max} (KBr) (cm^{-1}): 3069, 3029, 2969, 2923, 1600, 1495, 1476, 1448, 1391, 1369, 1354, 1334, 1310, 1274, 1227, 1209, 1162, 1104, 1073, 1029, 969, 919, 899, 880, 799, 769, 754, 729, 690, 656, 634, 534, 454. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.77 (s, 2H, NCH_2), 7.07 (d, J = 6.8, 2H, Ar*H*, 5-H and 6-H), 7.27–7.36 (m, 5H, Ph*H*), 7.97 (s, 1H, Ar*H*, 2-H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 49.9 (NCH_2), 102.5, 113.6 (Ar:C4,C7), 126.5, 129.1 (Ph:C$_{ortho}$, C$_{meta}$), 126.6, 128.3, 128.8 (Ph:C$_{para}$, Ar:C5,C6), 131.7 (Ar:C7a), 136.5 (Ph:C$_{ipso}$), 144.2 (Ar:C3a), 145.0 (Ar:C2). MS (EI): m/z = 368 (M^+ + 4, 13%), 366 (M^+ + 2, 29%), 364 (M^+, 14%), 91 ($PhCH_2^+$, 100%). HRMS (EI) m/z calcd for $C_{14}H_{10}Br_2N_2$ 363.9211 (Br-79 isotope) $[M]^+$, found 363.9205.

Synthesis of 4,7-dibromo-1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-benzimidazole 6. To a solution of 4,7-dibromo-1*H*-benzimidazole **4** (400 mg, 1.450 mmol) in dichloromethane (15 mL) were added 3,4-dihydro-2*H*-pyran (0.4 mL, 4.384 mmol) and *p*-TsOH (28 mg, 0.145 mmol). The solution was stirred for 3 h at room temperature. The solution was further diluted with dichloromethane, washed with saturated Na_2HCO_3 and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (1 : 1 EtOAc : petroleum ether) to give compound **6** (477 mg, 91%) as a white solid. mp 119–121 °C. ν_{max} (KBr) (cm^{-1}): 3119, 3084, 3018, 2965, 2939, 2870, 2849,

1600, 1490, 1475, 1454, 1440, 1388, 1342, 1319, 1280, 1250, 1218, 1185, 1168, 1125, 1105, 1080, 1054, 1044, 995, 943, 922, 898, 871, 849, 824, 786, 759, 722, 693, 654, 634, 620, 559, 484, 454. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.64–1.80 (m, 3H, C*H*), 1.94–2.10 (m, 2H, C*H*), 2.26 (d, J = 12.1, 1H, C*H*), 3.81 (t, J = 11.2, 1H, C*H*), 4.16 (d, J = 11.3, 1H, C*H*), 6.24 (d, J = 10.5, 1H, C*H*), 7.32 (m, 2H, Ar*H*, 5-H and 6-H), 8.26 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.2, 24.9, 32.2, 68.5 (CH_2), 83.2 (CH), 102.4, 113.6 (Ar:C4,C7), 126.5, 129.1 (Ar:C5,C6), 131.0 (Ar:C7a), 141.9 (Ar:C2), 144.3 (Ar:C3a). MS (EI): m/z = 362 (M^+ + 4, 1.5%), 360 (M^+ + 2, 3%), 358 (M^+, 1.5%), 278 (362-C_5H_9O + H^+, 68%), 276 (360-C_5H_9O + H^+, 100%), 274 (358-C_5H_9O + H^+, 77%). HRMS (EI) m/z calcd for $C_{12}H_{12}Br_2N_2O$ 357.9316 (Br-79 isotope) $[M]^+$, found 357.9322.

Synthesis of tetraethyl benzo[*c*][1,2,5]thiadiazole-4,7-diylbis-(phosphonate) 10. A mixture of 4,7-dibromobenzothiadiazole **2** (1.00 g, 3.345 mmol) and nickel(II) bromide (73 mg, 0.334 mmol) was heated at 135 °C under N_2. Triethyl phosphite (3 mL, 17.495 mmol) was added dropwise. The mixture was heated at the same temperature and stirred under N_2 for 24 h. After cooling to room temperature, the mixture was filtered through Celite. The solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (1 : 1 EtOAc : acetone) to give compound **10** (1.18 g, 86%) as a white solid. mp 74–75 °C. ν_{max} (KBr) (cm^{-1}): 3132, 3084, 3054, 2984, 2938, 2905, 2868, 1655, 1560, 1535, 1476, 1444, 1391, 1366, 1295, 1246, 1209, 1165, 1099, 1047, 1023, 973, 941, 887, 854, 794, 754, 731, 664, 622, 570, 550, 528, 514, 491, 455, 422. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.38 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.24–4.49 (m, 8H, 4× OCH_2CH_3), 8.31 (dd, J = 13.5 and 5.9, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 16.4 (t, J_{CP} = 3.1, CH_3), 63.3 (t, J_{CP} = 2.7, OCH_2), 126.8 (dd, J_{CP} = 188.2 and 3.5, Ar:C4,C7), 135.3 (m, Ar:C5,C6), 153.5 (t, J_{CP} = 7.8, Ar:C3a,C7a). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 11.6. MS (ESI): m/z = 431 (MNa^+, 100%), 409 (MH^+, 44%). HRMS (ESI) m/z calcd for $C_{14}H_{23}N_2O_6P_2S$ 409.07466 $[MH]^+$, found 409.07470.

Synthesis of tetraethyl (2,3-diamino-1,4-phenylene)bis-(phosphonate) 11. To a solution of compound **10** (200 mg, 0.490 mmol) in EtOH (10 mL) at 0 °C, under N_2, was added portion-wise $NaBH_4$ (334 mg, 8.829 mmol). After stirring at 0 °C during 10 min, the mixture was stirred at room temperature for 2 h. The reaction mixture was cooled to 0 °C and H_2O (5 mL) was added slowly. After removing the solvent under reduced pressure, the residue was diluted with Et_2O, washed with brine and dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting oil was purified by column chromatography (1 : 1 EtOAc : acetone) to give compound **11** (116 mg, 62%) as a pale yellow oil. ν_{max} (film) (cm^{-1}): 3421, 3310, 3244, 3073, 2984, 2945, 2914, 1678, 1652, 1623, 1533, 1454, 1448, 1393, 1371, 1301, 1233, 1164, 1151, 1099, 1049, 1021, 966, 789, 769, 756, 632. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.32 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.02–4.17 (m, 8H, 4× OCH_2CH_3), 5.06 (br s, 4H, N*H*), 6.94 (dd, J = 10.8 and 6.6, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 16.4 (t, J_{CP} = 3.4, CH_3), 62.4 (t, J_{CP} = 2.7, OCH_2), 112.4 (dd, J_{CP} = 179.7 and 2.6, Ar:C1,C4), 120.9 (Ar:C5,C6), 141.1 (dd, J_{CP} = 16.3 and 9.3, Ar:C2,C3). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 20.3. MS (ESI): m/z = 381 (MH^+, 100%). HRMS (ESI) m/z calcd for $C_{14}H_{27}N_2O_6P_2$ 381.13389 $[MH]^+$, found 381.13474.

Synthesis of tetraethyl 1*H*-benzo[*d*]imidazole-4,7-diylbis-(phosphonate) 9. To a solution of diamine **11** (150 mg, 0.394 mmol) in dichloromethane (10 mL) was added $HC(OEt)_3$ (0.05 mL, 0.473 mmol) and the solution was stirred for 10 min. A catalytic quantity of (+)-camphorsulfonic acid (10 mg) was added and the solution stirred for 24 h at room temperature. The solvent was removed and the resulting oil was purified by column chromatography (1 : 1 EtOAc : acetone) to give compound **9** (154 mg, 100%) as a pale white solid. mp 158–159 °C. ν_{max} (KBr) (cm^{-1}): 3147, 3095, 2985, 2936, 2905, 1598, 1478, 1460, 1443, 1393, 1370, 1334, 1294, 1250, 1240, 1201, 1165, 1124, 1100, 1049, 967, 920, 805, 760, 685, 645, 604, 579, 530, 477, 446. MS (ESI): m/z = 391 (MH^+, 100%). HRMS (ESI) m/z calcd for $C_{15}H_{25}N_2O_6P_2$ 391.11824 $[MH]^+$, found 391.11826.

1st attempt: ^{1}H NMR (400 MHz, $CDCl_3$) (0.1 M): δ (ppm) = 1.32 (m, 12H, 4× OCH_2CH_3), 4.06–4.29 (m, 8H, 4× OCH_2CH_3), 7.58 (m, 1H, Ar*H*, 5-H or 6-H), 7.92 (m, 1H, Ar*H*, 5-H or 6-H), 8.25 (s, 1H, Ar*H*, 2-H), 11.30 (br s, 1H, N*H*). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 15.4, 15.7.

2nd attempt: ^{1}H NMR (400 MHz, $CDCl_3$) (0.1 M): δ (ppm) = 1.32 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.11–4.26 (m, 8H, 4× OCH_2CH_3), 7.75 (dd, J = 11.6 and 5.9, 2H, Ar*H*, 5-H and 6-H), 8.32 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 16.4 (t, J_{CP} = 3.1, CH_3), 62.9 (t, J_{CP} = 2.4, OCH_2), 119.4 (d, J_{CP} = 184, Ar:C4,C7), 126.5 (m, Ar:C5,C6), 139.5 (Ar:C3a,C7a), 143.4 (Ar:C2). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 15.4.

^{1}H NMR (400 MHz, $CDCl_3$) (0.05 M): δ (ppm) = 1.33 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.14–4.27 (m, 8H, 4× OCH_2CH_3), 7.76 (br s, 1H, Ar*H*, 5-H and 6-H), 8.26 (s, 1H, Ar*H*, 2-H). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 15.6 (br s).

^{1}H NMR (400 MHz, $CDCl_3$) (0.01 M): δ (ppm) = 1.34 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.15–4.23 (m, 8H, 4× OCH_2CH_3), 7.65 (br s, 1H, Ar*H*, 5-H or 6-H), 7.88 (br s, 1H, Ar*H*, 5-H or 6-H), 8.25 (s, 1H, Ar*H*, 2-H), 10.9 (br s, 1H, N*H*). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 15.7 (br s).

^{1}H NMR (400 MHz, DMSO-d_6) (0.01 M): δ (ppm) = 1.24 (t, J = 7.0, 12H, 4× OCH_2CH_3), 4.03–4.12 (br m, 8H, 4× OCH_2CH_3), 7.69 (br s, 2H, Ar*H*, 5-H and 6-H), 8.37 (s, 1H, Ar*H*, 2-H), 12.59 (br s, 1H, N*H*). ^{31}P NMR (162 MHz, H_3PO_4/DMSO-d_6): δ (ppm) = 14.5.

^{1}H NMR (400 MHz, MeOD) (0.01 M): δ (ppm) = 1.33 (t, J = 7.0, 12H, 4× OCH_2CH_3), 4.18–4.26 (m, 8H, 4× OCH_2CH_3), 7.79–7.87 (br m, 2H, Ar*H*, 5-H and 6-H), 8.37 (s, 1H, Ar*H*, 2-H). ^{31}P NMR (162 MHz, H_3PO_4/MeOD): δ (ppm) = 15.0, 15.6.

^{1}H NMR (400 MHz, MeOD) (0.1 M): δ (ppm) = 1.33 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.16–4.23 (m, 8H, 4× OCH_2CH_3), 7.85 (dd, J = 11.7 and 6.1, 2H, Ar*H*, 5-H and 6-H), 8.49 (s, 1H, Ar*H*, 2-H). ^{31}P NMR (162 MHz, H_3PO_4/MeOD): δ (ppm) = 15.2.

^{1}H NMR (400 MHz, acetone-d_6) (0.01 M): δ (ppm) = 1.29 (dt, J = 7.0 and 3.0, 12H, 4× OCH_2CH_3), 4.07–4.29 (m, 8H, 4× OCH_2CH_3), 7.67 (ddd, J = 13.8, 7.5 and 3.1, 1H, Ar*H*, 5-H or 6-H), 7.85 (ddd, J = 14.2, 7.5 and 3.5, 1H, Ar*H*, 5-H or 6-H), 8.37 (s, 1H, Ar*H*, 2-H).

^{31}P NMR (162 MHz, H_3PO_4/acetone-d_6): δ (ppm) = 14.0 (d, J = 4.9), 14.8 (d, J = 4.9).

^{1}H NMR (400 MHz, acetone-d_6) (0.1 M): δ (ppm) = 1.29 (t, J = 7.0, 12H, 4× OCH_2CH_3), 4.22 (br m, 8H, 4× OCH_2CH_3), 7.70 (br s, 1H, Ar*H*, 5-H or 6-H), 7.85 (br s, 1H, Ar*H*, 5-H or 6-H), 8.43 (s, 1H, Ar*H*, 2-H), 12.00 (br s, 1H, N*H*). ^{13}C NMR (100 MHz, acetone-d_6): δ (ppm) = 16.6 (CH_3), 63.1 (d, J_{CP} = 24.5, OCH_2), 116.4 (d, J_{CP} = 186, Ar:C4 or C7), 125.4 (d, J_{CP} = 183, Ar:C4 or C7), 126.3, 127.2 (Ar:C5,C6), 135.8 (Ar:C3a or C7a), 145.0 (Ar:C2). ^{31}P NMR (162 MHz, H_3PO_4/acetone-d_6): δ (ppm) = 14.2, 14.8.

^{1}H NMR (400 MHz, CD_2Cl_2) (0.01 M): δ (ppm) = δ 1.31 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.12–4.21 (m, 8H, 4× OCH_2CH_3), 7.72 (br s, 2H, Ar*H*, 5-H and 6-H), 8.22 (s, 1H, Ar*H*, 2-H), 11.33 (br s, 1H, N*H*). ^{31}P NMR (162 MHz, H_3PO_4/CD_2Cl_2): δ (ppm) = 14.9 (br s).

Synthesis of tetraethyl 1*H*-benzo[*d*][1,2,3]triazole-4,7-diylbis-(phosphonate) 12. To a solution of diamine **11** (116 mg, 0.304 mmol) in AcOH (1.2 mL) was added a solution of $NaNO_2$ (23 mg, 0.335 mmol) in H_2O (0.6 mL). After 30 min stirring at room temperature, the solution was diluted with H_2O and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed under reduce pressure. The resulting oil was purified by column chromatography (1 : 1 EtOAc : acetone) to give compound **12** (118 mg, 99%) as a white solid. mp 172–174 °C; ν_{max} (KBr) (cm^{-1}): 3042, 2985, 2912, 2828, 1599, 1560, 1479, 1460, 1444, 1394, 1370, 1354, 1270, 1254, 1227, 1165, 1099, 1050, 1025, 974, 941, 874, 798, 756, 684, 587, 530, 487, 444. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.34 (t, 12H, 4× OCH_2CH_3), 4.18–4.40 (m, 8H, 4× OCH_2CH_3), 7.95 (dd, J = 12.0 and 5.6, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 16.4 (t, J_{CP} = 3.1, CH_3), 63.5 (t, J_{CP} = 2.7, OCH_2), 120.4 (br d, J_{CP} = 180, Ar:C4,C7), 130.0 (t, J_{CP} = 10.6, Ar:C5,C6), 139.1 (br s, Ar:C3a,C7a). ^{31}P NMR (162 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 12.8. ^{1}H NMR (400 MHz, acetone-d_6): δ (ppm) = 1.31 (t, J = 7.1, 12H, 4× OCH_2CH_3), 4.21–4.30 (m, 8H, 4× OCH_2CH_3), 8.03 (dd, J = 11.9 and 5.6, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, acetone-d_6): δ (ppm) = 16.6 (t, J_{CP} = 3.1, CH_3), 63.6 (t, J_{CP} = 2.7, OCH_2), 121.8 (br d, J_{CP} = 200, Ar:C4,C7), 130.8 (t, J_{CP} = 9.7, Ar:C5,C6), 139.7 (br s, Ar:C3a,C7a). ^{31}P NMR (162 MHz, H_3PO_4 acetone-d_6): δ (ppm) = 12.2. MS (ESI): m/z = 414 (MNa^+, 28%), 392 (MH^+, 100%). HRMS (ESI) m/z calcd for $C_{14}H_{24}N_3O_6P_2$ 392.11348 $[MH]^+$, found 392.11420.

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