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Synthesis of New Azole Phosphonate Precursors for Fuel Cells Proton Exchange Membranes

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ABSTRACT: *Herein we present the synthesis and characterization of new phosphonate-, bisphosphonate- and hydroxybisphosphonatebenzimidazole derivatives substituted at the N-1 position and new regioisomers phosphonate-, bisphosphonate-, and hydroxybisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions. The compounds were characterized by NMR and IR spectroscopies, and mass spectrometry (low and high resolution) allowing the assignment of their structure, including the identification of regioisomers. These new azole monomers will be precursors for a mesoporous silica host to produce novel membrane materials with high proton conductivity for intermediate temperature proton exchange membrane fuel cells.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–13, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21254

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INTRODUCTION

In an energy scenario that increasingly demands cleaner and more efficient energy sources, fuel cells are considered promising electrochemical devices since they can provide electric energy with high efficiency and low environmental impact, converting the energy stored in fuels with zero pollution levels. The proton exchange membrane fuel cells (PEMFC) are considered one of the most promising sources among the various kinds of existing fuel cells due to their high power density and high power-to-weight ratio. One of the drawbacks of current cells is related to the electrolytes currently in use, limiting their use to temperatures below 100°C when operating under water-assisted proton conduction.

The temperature operation above 100°C could increase the performance of PEMFC due to a faster electrode reaction without CO poisoning of the Pt electrocatalyst, easier heating, and high energy efficiency [1–8].

The proton exchange membrane is a key component for the operation of PEMFC. During recent years, the study of membrane materials have been focused in obtaining high proton conductivity, low electrical conductivity, low permeability to fuel and oxidant, good chemical and thermal stabilities, good mechanical properties, and low cost [1–8].

Generally, they are made of organic polymers containing acidic functionalities (e.g., Nafion®), but the limitations of current membranes have fostered the research and development of alternative membranes, including doped polybenzimidazole, a composite of Nafion and metal oxides, sulfonated polymers based on aromatic hydrocarbons, and organosiloxane based on inorganic–organic hybrids with various acidic species [1–11].

Usually, some degree of hydration is required to conducting ions. There are new materials combining acceptor and donor ion carrier capabilities of several groups [8]. Phosphonic acids are considered one of the groups that have good proton donor and acceptor properties, with higher proton conductivities, oxidation resistance, and better thermal stability than the sulfonic acid groups. The properties of polymers with phosphonate groups allow their operation at elevated temperatures [12–17]. Heterocycles can act as a proton-conducting species, due to their nitrogen amphoteric behavior and can be used either as dopant or pendant groups in PEMFC without the need of external humidification. The properties of many heterocycles, including benzimidazole and triazole, enable them to be used in materials working above 100°C [1, 9, 18–26].

Facing the importance of developing new materials for fuel cell applications, and taking into account the properties of heterocycles and phosphonic acid groups, it can be conceived that molecules bearing both of these groups can present good properties for PEMFC. Also, the physicochemical and proton conductivity properties of the membranes can be fine-tuned by adjusting the chemical structure and functional groups present at the monomeric units.

Based on the properties of periodic mesoporous silica functionalized with acid groups, including high proton conductivities and high relative humidity [27–29], we envisaged the synthesis of new monomers for the preparation of novel membranes for application in high-temperature PEMFC. These monomers will be used to prepare organic-functionalized materials, including mesoporous silica materials. These materials will be prepared from bridged organosilicon precursors of the general formula $(RO)_3Si\text{-}R'\text{-}Si(RO)_3$, where R represents alkyls groups and R' is a bridge with organic groups, such as benzimidazole or benzotriazole, functionalized with phosphonate or bisphosphonate groups, obtained in this work (Fig. 1). Varying the organic spacer group of the organosilicon precursors allows the fine-tuning of chemical and physical properties of the mesoporous organosilica materials. These types of hybrid compounds can combine the high-temperature stability of polysilsesquioxanes with the proton conductivity of benzimidazole or benzotriazole derivatives and phosphonic groups.

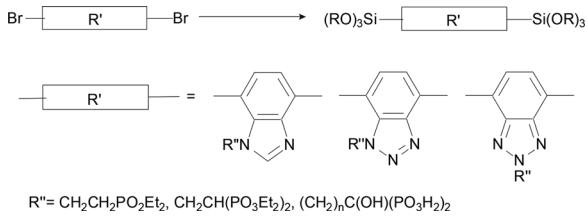
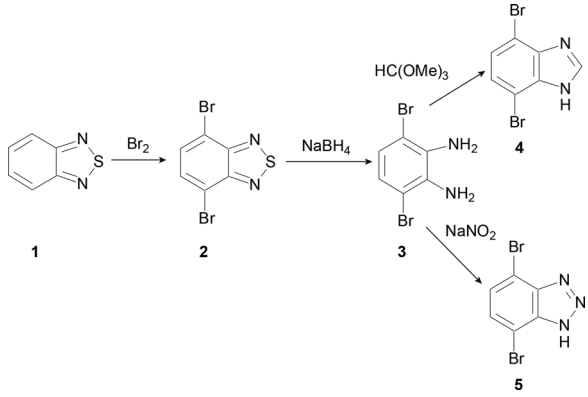


FIGURE 1 General bridged silsesquioxane precursors of the type $(RO)_3Si\text{-}R'\text{-}Si(RO)_3$.



SCHEME 1

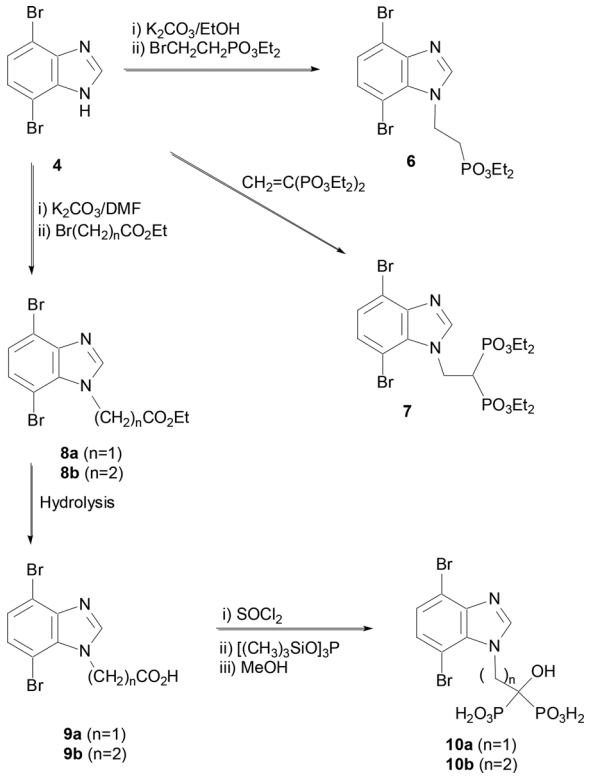
Herein, we report the synthesis and characterization of the new monomers phosphonate-, bisphosphonate-, and hydroxybisphosphonate derived from benzimidazole or benzotriazole and their characterization, including the assignment of regiosiomers.

RESULTS AND DISCUSSION

The new phosphonate monomers were synthesized from 4,7-dibromobenzimidazole **4** and 4,7-dibromobenzotriazole **5** following several strategies and different kinds of reagents and conditions.

The precursor 4,7-dibromobenzimidazole **4** was prepared from 2,1,3-benzothiodiazole **1** in three synthetic steps, modified from literature procedures (Scheme 1). Compound **2** was prepared in high yield by bromination of commercially available 2,1,3-benzothiadiazole **1** [30]. The reduction of **2** with $NaBH_4$ or by an alternative method using $NaBH_4/CoCl_2{\cdot}6H_2O$ (catalytic amount) gave 1,2-diamine **3** in moderated yield [31–34]. Cyclization of 1,2-diamine **3** to 4,7-dibromobenzimidazole **4** was performed by the reaction with trimethylorthoformate in acid conditions, using (±)-camphorsulfonic acid [35].

Benzimidazole phosphonates and bisphosphonates were prepared in good yields using several



SCHEME 2

strategies described in Scheme 2. Compounds **6–10** were fully characterized by NMR (including bidimensional techniques), IR spectroscopy, and mass spectrometry (low and high resolution). The phosphonate and bisphosphonate structure of compounds **6**, **7**, and **10a–b** ($n = 1$ and 2) was easily identified by analysis of NMR data. Electron impact ionization (EI) (compounds **6** – **9**) and electrospray ionization (ESI) (compounds **10a–b)** Mass spectrometry techniques were used to show the molecular ion of compounds and confirmed the proposed molecular formulae.

The reaction of 4,7-dibromobenzimidazole **4** with potassium carbonate, in EtOH, followed by the addition of diethyl 2-bromoethylphosphonate gave phosphonate **6** in excellent yield (Scheme 2). The ^{13}C NMR spectrum of phosphonate **6** shows a doublet at 29.2 ppm ($J_{CP} = 139$ Hz), consistent with a methylene carbon coupling with one phosphorous nuclei, which supported the proposed structure. Also, the proton-decoupled ^{31}P NMR spectrum of **6** shows a singlet at 25.8 ppm.

The synthesis of bisphosphonate **7** substituted at the N-1 position was performed by the reaction of 4,7-dibromobenzimidazole **4** with tetraethyl ethylidene-1,1-bisphosphonate [36] in THF (Scheme 2), by a Michael addition reaction [37]. Analysis of crude by ^1H NMR shows the characteristic signals of the expected compounds as three multiplets at 3.42, 4.07–4.22, and 4.94–5.08 ppm, consistent with the presence of a methine proton ($CH(PO_3Et_2)_2$) and two methylene groups ($POCH_2CH_3$ and NCH_2CHP), respectively, coupling with phosphorous atoms of 2 equiv phosphonate groups attached to the same carbon. The proton-decoupled ^{31}P NMR spectra of bisphosphonate **7** showed a single signal at 18.8 ppm, which confirmed that two phosphorus atoms are magnetically equivalent. The signals of these spectra are in agreement with the presence of the desired compound **7**, with the proposed structure. However, purification of the crude by column chromatography led to the decomposition of compound **7**, due to a retro-Michael reaction [37], with the regeneration of starting material **4** and a mixture of unidentified compounds.

The most common procedures for the synthesis of hydroxybisphosphonates start from carboxylic acid derivatives, using a classical method with phosphoric or phosphorous acids [38, 39] or by an Arbuzov reaction of a silylphosphite reagent, followed by methanol hydrolysis [40, 41].

The first step to synthesize hydroxybisphosphonates **10a–b** ($n = 1$ and 2) involved the preparation of ester derivatives, followed by their hydrolysis to afford the corresponding carboxylic acids. So, starting from 4,7-dibromobenzimidazole **4**, the benzimidazole ester derivatives **8a–b** ($n = 1$ and 2) were obtained by the nucleophilic substitution reaction of bromo esters ($Br(CH_2)_nCO_2Et$, $n = 1$–2), in good to excellent yields. The hydrolysis of the ester derivatives **8a–b** ($n = 1$ and 2) allowed the synthesis of the corresponding carboxylic acids **9a–b** ($n = 1$ and 2) in excellent yield (Scheme 2). The basic hydrolysis of ester derivative **8a** ($n = 1$) gave the desired carboxylic acid **9a** ($n = 1$) in 99% yield, but these hydrolysis conditions for ester derivative **8b** ($n = 2$) gave a mixture of the carboxylic acid **9b** ($n = 2$) and the starting material 4,7-dibromobenzimidazole **4**, in the ratio of 1.4:1. The hydrolysis of ester derivative **8b** ($n = 2$) was done in acidic conditions, using HCl (1 M) in acetone, to provide the carboxylic acid **9b** ($n = 2$) in 99% yield.

Bisphosphonates **10a–b** ($n = 1$ and 2) were synthesized in good yield by the reaction of carboxylic acids **9a–b** ($n = 1$ and 2) with $SOCl_2$, to produce in situ the corresponding acyl chloride, followed by the reaction with tris(trimethylsilyl)phosphite and subsequent methanolysis (Scheme 2).

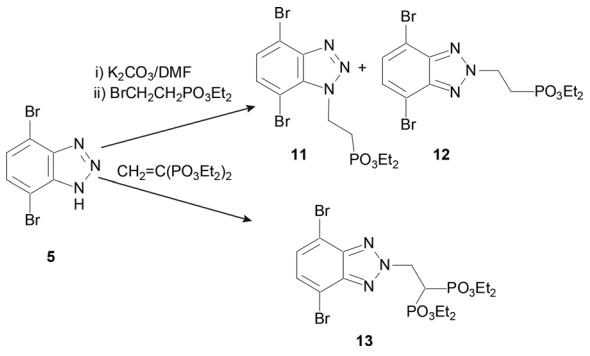
The ^1H NMR spectrum of **10a** ($n = 1$) shows a triplet at 5.19 ($J_{HP} = 10$ Hz) ppm for the protons on carbon NCH_2 due to the coupling with 2 equiv

phosphorous nuclei. The ^{13}C NMR spectra of compounds **10a** ($n = 1$) and **10b** ($n = 2$) show a triplet at 73.9 ppm (J_{CP} = 139 Hz) and 71.3 ppm (J_{CP} = 142 Hz), respectively, consistent with a quaternary carbon (disappearing in DEPT 135 ^{13}C NMR mode) coupling with the 2 equiv phosphorous nuclei, which support the proposed structures with two phosphonate groups attached to the same carbon. The proton-decoupled ^{31}P NMR spectra of compounds **10a** ($n = 1$) and **10b** ($n = 2$) show a singlet at 17.4 and 18.6 ppm, respectively, in agreement with two chemically and magnetically equivalent phosphorus atoms.

Like benzimidazole, the benzotriazole is also a planar and rigid aromatic heterocycle, with one more nitrogen atom, replacing the C-2 methine group of benzimidazole, presenting a moderate electron-deficient character [42]. Since previous studies showed that triazole [19] enhances the proton conductivity with respect to imidazole, it is expected that benzotriazole also presents higher proton conductivity than benzimidazole. Also, the presence of a pendant group bonded to a nitrogen atom of benzotriazole ring create two N-1 and N-2 regioisomers, which present different optical and electrochemical behavior [43]. Moreover, small structural variations at the monomers should be considered since they can fine-tune the electron and proton conductivity properties of the resulting materials.

The precursor 4,7-dibromobenzotriazole **5** was prepared using a different synthetic procedure for cyclization of 1,2-diamine **3** (Scheme 1), in the presence of sodium nitrite in acetic acid in good yield [44]. The synthesis of phosphonate- and bisphosphonate derivatives substituted at N-1 or N-2 positions, starting from the precursor 4,7-dibromobenzotriazole **5**, is presented at Scheme 3.

The reaction of 4,7-dibromobenzotriazole **5** with diethyl 2-bromoethylphosphonate and potassium carbonate, in DMF gave regioisomers **11** and **12**, with the N-2 derivative **12** as a major regioisomer (70% yield) and the N-1 derivative **11** with lower yield (17% yield) (Scheme 3). Compounds **11** and **12** were separated by column chromatography to provide the pure phosphonate regioisomers.



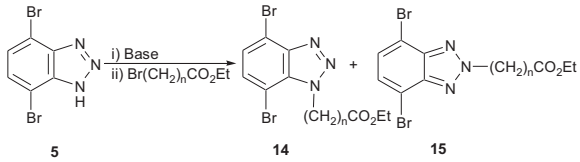
SCHEME 3

The regioisomers of 4,7-dibromobenzotriazoles **11** and **12** present qualitative differences in the NMR spectra, according to their molecular symmetry. The unambiguous assignment of benzotriazole derivatives substituted at N-1 and N-2 was carried out by ^{1}H and ^{13}C NMR spectroscopy, including two-dimensional NMR techniques. The NMR spectra of compound **12** show only one signal for the two 5-H and 6-H protons, and only one signal for each pair: C4 and C7, C5 and C6, and C3a and C7a, showing that the atoms of these pairs are magnetically equivalents, and the compound present molecular symmetry, consistent with the N-2 benzotriazole regioisomer. Spectra of compound **11** present different chemical shifts for each proton or carbon atoms, according to a nonsymmetric molecular structure of N-1 regioisomer. These spectroscopic data are in agreement with the ^{13}C NMR spectra of N-1 and N-2 substituted benzotriazole regioisomers reported in the literature [45–49].

The Michael addition reaction of 4,7-dibromobenzotriazole **5** with tetraethyl ethylidene-1,1-bisphosphonate [36], in THF afforded the bisphosphonate **13** substituted at the N-2 position and unreacted starting material **5** [37]. After column chromatography, compound **13** was isolated in 37% yield (Scheme 3). The NMR spectra of compound **13** are in agreement with a symmetric molecular structure, according to a N-2 benzotriazole regioisomer. Only the N-2 derivative was observed as a product of this reaction probably due to the steric hindrance caused by bromine atoms at 4 and 7 positions of benzotriazole, in contrast with the reaction between benzotriazole and tetraethyl ethylidene-1,1-bisphosphonate already reported, which also afforded the N-1 derivative [50].

Similar to benzimidazolebisphosphonates, for the synthesis of hydroxybenzotriazolebisphosphonate was necessary to prepare the corresponding esters and carboxylic acids. The 4,7-dibromobenzotriazole **5** reacted with a base, followed by addition of the corresponding bromo esters with one or two methylene groups chain length ($Br(CH_2)_nCO_2Et$, $n = 1$–2). Under these conditions, a mixture of N-1 or N-2 substituted regioisomers benzotriazole esters **14a–b** (n = 1 and 2) and **15a–b** (n = 1 and 2) were obtained in different yields and ratios (Table 1). Compounds **14a–b** (n = 1 and 2) and **15a–b** (n = 1 and 2) were separated by column

TABLE 1 Synthesis of Benzotriazole Ester Derivatives Substituted at N-1 and N-2 (**14** and **15**)



5 14 15

n	*Base (solvent)*	*Compound 14 (%)*		*Compound 15 (%)*		*14 + 15 (%)*
1	KO^{t}Bu (EtOH)	**14a**	37	**15a**	53	90
	K_2CO_3 (DMF)		28		50	78
2	KO^{t}Bu (THF)	**14b**	19	**15b**	25	44[a]
	K_2CO_3 (DMF)		37		48	85

[a]56% of starting material **5** remained unreacted.

chromatography to provide pure regioisomers. The identification of the different N-1 and N-2 regioisomers were done according to the observed molecular symmetry or asymmetry, for N-2 derivatives or N-1 derivatives, respectively, at NMR spectra, and are in agreement with NMR data reported in the literature for N-1 and N-2 substituted benzotriazole regioisomers [45–49].

The esters isomers **14a–b** ($n = 1$ and 2) and **15a–b** ($n = 1$ and 2) were subjected to the hydrolysis to afford the corresponding carboxylic acid derivatives **16a–b** ($n = 1$ and 2) and **17a–b** ($n = 1$ and 2), respectively. Using basic hydrolysis conditions, both regioisomers of $n = 1$ derivatives (**16a** ($n = 1$) and **17a** ($n = 1$)) were obtained in excellent yields (Table 2). But the basic hydrolysis of compounds **14b** ($n = 2$) and **15b** ($n = 2$) did not afford the desired compounds. Instead, for compound **14b** ($n = 2$) was obtained a mixture of carboxylic acid **16b** ($n = 2$) and the 4,7-dibromobenzotriazole **5,** and for compound **15b** ($n = 2$) was recovered the starting material **15b** ($n = 2$) and 4,7-dibromobenzotriazole **5**. For $n = 2$ was necessary to use acidic hydrolysis conditions to obtain the desired carboxylic acids **16b** ($n = 2$) and **17b** ($n = 2$) (Table 2).

After preparation of the benzotriazole carboxylic acid derivatives, the synthesis of bisphosphonates **18a–b** ($n = 1$ and 2) and **19a–b** ($n = 1$ and 2) was carried out by the reaction of the carboxylic acids **16a–b** ($n = 1$ and 2) and **17a–b** ($n = 1$ and 2) with $SOCl_2$, to produce in situ the corresponding acyl chloride, followed by the reaction with tris(trimethylsilyl)phosphite and subsequent methanolysis (Table 3).

The NMR spectra allowed the identification of both regioisomers due to the observation of molecular symmetry or asymmetry structure of compounds. The ^{1}H NMR spectra show one signal for 5-H and 6-H pair of protons, and ^{13}C NMR spectra present one signal for each C4–C7, C5–C6, and C3a–C7a pairs, in agreement with the molecular symmetry of N-2 regioisomers **19a–b** ($n = 1$ and 2). The spectra of compounds **18a–b** ($n = 1$ and 2) present distinctive signals to all proton and carbon atoms, in agreement with an asymmetric molecular structure of the N-1 regioisomer.

All compounds **11–19** were characterized by NMR, IR spectroscopy, and mass spectrometry, which confirmed their proposed molecular structures.

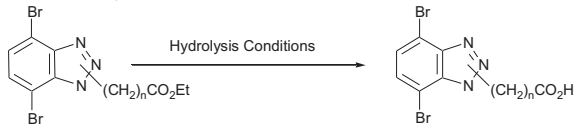
CONCLUSIONS

Several new azole phosphonate derivatives were synthesized to become precursors of membranes for PEMFC. From 4,7-dibromobenzimidazole **4**, new phosphonate-, bisphosphonate- and hydroxybisphosphonatebenzimidazole derivatives substituted at the N-1 position were synthesized in good yields. New regioisomers phosphonate-, bisphosphonate- and hydroxybisphosphonatebenzotriazole derivatives substituted at the N-1 or N-2 position were synthesized in good yields, from 4,7-dibromobenzotriazole **5**. All new compounds were fully characterized by NMR, IR spectroscopy, and mass spectrometry. NMR spectroscopy allowed the identification of both regioisomers due to their molecular symmetric (N-2 regioisomers) or asymmetric structure (N-1 regiosiomers).

EXPERIMENTAL

All the reactions involving air-sensitive reagents were performed under an atmosphere of dry nitrogen, and all solvents were degassed before use. THF was distilled from sodium benzophenone ketyl. Column chromatography was performed on silica gel (230–400 mesh) under a positive pressure of nitrogen.

TABLE 2 Hydrolysis of Benzotriazole Carboxylic Acid Derivatives Substituted at N-1 and N-2 (**16** and **17**)

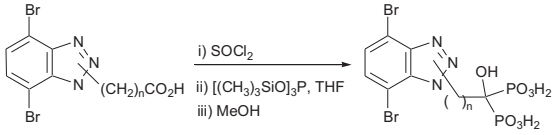


14-15 16-17

Regioisomer	*Reagent*	*n*	*Hydrolysis Conditions*	*Product*	*16 or 17 (%)*
N-1	**14a**	1	NaOH (10 M)	**16a**	99
	14b	2	NaOH (10 M)	**16b**	[a]
	14b	2	HCl (1 M)	**16b**	87
N-2	**15a**	1	NaOH (10 M)	**17a**	99
	15b	2	NaOH (10 M)	**17b**	[b]
	15b	2	HCl (1 M)	**17b**	99

[a]A mixture of carboxylic acid **16b** ($n = 2$) and benzotriazole **5** was obtained in the ratio of 2:1.
[b]A mixture of starting material **15b** ($n = 2$) and benzotriazole **5** was obtained in the ratio of 2.5:1.

TABLE 3 Synthesis of Benzotriazolebisphosphonate Derivatives Substituted at N-1 and N-2 (**18** and **19**)



16-17 18-19

Regioisomer	*Reagent*	*n*	*Product*	*Yield (%)*
N-1	**16a**	1	18a	78
	16b	2	18b	83
N-2	**17a**	1	19a	44
	17b	2	19b	48

2,1,3-Benzothiadiazole **1** is commercially available (Aldrich, 2710-901 Sintra, Portugal). 4,7-Dibromo-1*H*-benzimidazole **4** was synthesized in a three-step synthesis by modifying the synthetic procedures reported [35]. 4,7-Dibromo-1*H*-benzotriazole **5** [44] and tetraethyl ethenylidenebisphosphonate [36] were prepared according to literature procedures.

NMR spectra were recorded on Bruker AMX 300 and on a Bruker Avance II 300 (^{1}H 300 MHz, ^{13}C 75 MHz, ^{31}P 121 MHz), on a 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 spectrum BX Fourier transform spectrometer, using KBr disks or film.

Low resolution and high resolution (HRMS) mass spectra analyses were performed at the 'CACTI, Unidad de Espectrometria de Masas' at the University of Vigo, Spain, on a VG AutoSpect M, MicroTOF (Bruker Daltonics) or APEX-Q (Bruker Daltonics) instruments.

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

General Procedure A: A mixture of 4,7-dibromo-1*H*-benzimidazole **4** or 4,7-dibromo-1*H*-benzotriazole **5** and K_2CO_3 (3 equiv) in DMF (3 mL) was stirred at 80°C during 30 min. The corresponding bromo ester ($Br(CH_2)_nCO_2Et$, n = 1–2) was added, and the reaction mixture was refluxed again. 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 in vacuum. The resulting oil was purified by column chromatography.

General Procedure B: To a solution of 4,7-dibromo-1*H*-benzotriazole **5** and KO^{t}Bu in EtOH, the proper bromo ester ($Br(CH_2)_nCO_2Et$, n = 1–2) was added and the reaction mixture was refluxed. After removing the solvent by evaporation, the residue was washed with H_2O and extracted with dichloromethane. The organic solution was condensed by evaporation, and the product was purified by column chromatography (3:1 dichloromethane/petroleum ether).

General Procedure C: An ester derivative ($n = 1$) (**8a**, **14a**, or **15a**) in an aqueous NaOH solution (10 M) was stirred at reflux for 2 h. The reaction mixture was cooled to room temperature and acidified with 10% aqueous HCl solution, and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed in vacuum.

General Procedure D: To a solution of ester derivative ($n = 2$) (**8b**, **14b**, or **15b**) in acetone, an aqueous HCl solution (1 M) was added. The reaction mixture was refluxed for 18 h. Upon cooling, the mixture was concentrated in vacuum. The obtained solid was dissolved in water, and the aqueous layer was extracted with EtOAc. The combined organic extracts were treated as described in the general procedure C.

General Procedure E: A mixture of carboxylic acid (1 equiv) and thionyl chloride was kept under reflux for 2 h. The excess of thionyl chloride was removed under reduced pressure to give the corresponding acyl chloride, which was immediately used without further purification. The crude acyl chloride was dissolved in dry THF and tris(trimethylsilyl)phosphite (2 equiv) was added. Then, the mixture was stirred at room temperature for 1 h. The excess of solvent was removed under reduced pressure. Methanol was added, and the mixture was stirred for 1 h. After solvent removal under reduced pressure, the residue was washed with ethyl ether and precipitated with acetone.

*Diethyl (2-(4,7-dibromo-1H-benzimidazol-1-yl)ethyl)phosphonate (**6**)*

A solution of 4,7-dibromo-1*H*-benzimidazole **4** (300 mg, 1.087 mmol) and K_2CO_3 (450 mg, 3.261 mmol) in EtOH (15 mL) was refluxed during 30 min. An excess of $Br(CH_2)_2PO_3Et_2$ (0.39 mL, 2.174 mmol) was added, and the reaction mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and filtered, and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound **6** (450 mg, 94%) as white solid. mp 40–41°C. ν_{max} (KBr) (cm^{-1}): 3072, 2984, 2906, 1503, 1477, 1453, 1393, 1376, 1364, 1340, 1328, 1317, 1294, 1277, 1232, 1206, 1164, 1140, 1102, 1087, 1053, 1026, 975, 948, 925, 892, 865, 800, 719, 688, 652, 632, 574, 530, 518. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.24 (t, $J = 7.1$, 6H, 2× OCH_2CH_3), 2.39 (dt, $J = 18.6$ and 7.2, 2H, $CH_2PO_3Et_2$), 4.00–4.09 (m, 4H, 2× OCH_2CH_3), 4.74–4.83 (m, 2H, NCH_2), 7.30 (d, $J = 8.3$, 1H, Ar*H*, 5-H or 6-H), 7.33 (d, $J = 8.3$, 1H, Ar*H*, 5-H or 6-H), 8.12 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 16.4 (d, $J_{CP} = 6.0$, CH_3), 29.2 (d, $J_{CP} = 139.1$, $CH_2PO_3Et_2$), 41.2 (d, $J_{CP} = 2.3$, NCH_2), 62.3 (d, $J_{CP} = 6.5$, OCH_2), 102.0, 113.4 (Ar:C4,C7), 126.8, 128.8 (Ar:C5,C6), 131.1 (Ar:C7a), 143.7 (Ar:C3a), 145.9 (Ar:C2). ^{31}P NMR (121 MHz, H_3PO_4/ $CDCl_3$): δ (ppm) = 25.8. MS (ESI): m/z = 465 ($MNa^+ + 4$, 25%), 463 ($MNa^+ + 2$, 52%), 461 (MNa^+, 26%), 443 ($MH^+ + 4$, 54%), 441 ($MH^+ + 2$, 100%), 439 (MH^+, 54%). HRMS (ESI) m/z calcd for $C_{13}H_{18}Br_2N_2O_3P$ 438.9416 (Br-79 isotope) $[MH]^+$, found 438.9416.

*Tetraethyl (2-(4,7-Dibromo-1H-benzimidazol-1-yl)ethane-1,1-diyl)bisphosphonate (**7**)*

A mixture of 4,7-dibromo-1*H*-benzimidazole **4** (100 mg, 0.363 mmol) and tetraethylethenyli denebisphosphonate (109 mg, 0.363 mmol) in THF (5 mL) was stirred under reflux for 18 h. The solvent was evaporated in vacuum to afford a yellow oil. The NMR spectra of crude product show the starting material **4**, $CH_2{=}C(PO_3Et_2)_2$ and compound **7**. Purification by column chromatography led to the decomposition of compound **7** to give the starting material **4** and a mixture of unidentified compounds.

^{1}H NMR spectrum of compound **7** in the crude mixture: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.19 (t, $J = 7.2$, 6H, OCH_2CH_3), 1.28 (t, $J = 7.2$, 6H, OCH_2CH_3), 3.42 (m, 1H, $CH(PO_3Et_2)_2$), 4.07–4.22 (m, 8H, CH_2CH_3), 4.94–5.08 (m, 2H, NCH_2), 7.31 (m, 2H, Ar*H*, 5-H and 6-H), 8.11 (s, 1H, Ar*H*, 2-H). ^{31}P NMR (121 MHz, H_3PO_4/ $CDCl_3$): δ (ppm) = 18.8.

*Ethyl 2-(4,7-Dibromo-1H-benzimidazol-1-yl)acetate (**8a** ($n = 1$))*

Following general procedure A, the reaction of 4,7-dibromo-1*H*-benzimidazole **4** (120 mg, 0.435 mmol) and K_2CO_3 (180 mg, 1.305 mmol) in DMF (3 mL), followed by the addition of $BrCH_2CO_2Et$ (0.10 mL, 0.870 mmol), was refluxed for 45 min and purified by column chromatography (ether) to give compound **8a** ($n = 1$) (144 mg, 91%) as a white solid. mp 110–111°C. ν_{max} (KBr) (cm^{-1}): 3064, 2979, 1745, 1605, 1505, 1476, 1424, 1376, 1364, 1347, 1338, 1317, 1280, 1220, 1168, 1161, 1107, 1027, 975, 923, 892, 793, 777, 711, 634, 537, 426. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.26 (t, $J = 7.2$, 3H, OCH_2CH_3), 4.24 (q, $J = 7.2$, 2H, OCH_2CH_3), 5.22 (s, 2H, NCH_2), 7.26 (d, $J = 8.1$, 1H, Ar*H*, 5-H or 6-H), 7.32 (d, $J = 8.4$, 1H, Ar*H*, 5-H or 6-H), 7.96 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 13.9 (CH_3), 47.7 (NCH_2), 62.2 (OCH_2), 102.1, 113.2 (Ar:C4,C7), 126.4, 128.4 (Ar:C5,C6), 131.4 (Ar:C7a), 143.4 (Ar:C3a), 145.8 (Ar:C2), 169.3 (CO). MS (EI): m/z = 364 ($M^+ + 4$, 17%), 362 ($M^+ + 2$, 40%), 360 (M^+, 19%), 291 (364-COOEt, 35%), 289 (362-COOEt, 100%), 287 (360-COOEt, 40%). HRMS (EI) m/z calcd for $C_{11}H_{10}Br_2N_2O_2$ 359.9109 (Br-79 isotope) $[M]^+$, found 359.9105.

*Ethyl 3-(4,7-Dibromo-1H-benzimidazol-1-yl)propanoate (***8b** *(n = 2))*

Following general procedure A, the reaction of 4,7-dibromo-1*H*-benzimidazole **4** (121 mg, 0.439 mmol) and K_2CO_3 (182 mg, 1.316 mmol) in DMF (3 mL), followed by the addition of $Br(CH_2)_2CO_2Et$ (0.11 mL, 0.877 mmol), was refluxed for 4 h and purified by column chromatography (ether) to give compound **8b** ($n = 2$) (115 mg, 70%) as a white solid. mp 64–65°C. ν_{max} (KBr) (cm^{-1}): 3126, 3079, 2978, 2959, 1727, 1495, 1473, 1443, 1405, 1384, 1374, 1366, 1354, 1336, 1312, 1244, 1204, 1191, 1162, 1103, 1087, 1058, 1025, 983, 946, 916, 890, 869, 852, 790, 626, 593, 572. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.23 (t, J = 7.1, 3H, OCH_2CH_3), 2.95 (t, J = 6.2, 2H, NCH_2CH_2), 4.13 (q, J = 7.1, 2H, OCH_2CH_3), 4.81 (t, J = 6.2, 2H, NCH_2), 7.30 (d, J = 8.7, 1H, Ar*H*, 5-H or 6-H), 7.33 (d, J = 8.2, 1H, Ar*H*, 5-H or 6-H), 8.08 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_3), 36.5 (CH_2), 41.9 (NCH_2), 61.3 (OCH_2), 102.0, 113.7 (Ar:C4,C7), 126.5, 128.5 (Ar:C5,C6), 131.2 (Ar:C7a), 144.2 (Ar:C3a), 146.3 (Ar:C2), 170.6 (CO). MS (EI): m/z = 378 (M^+ + 4, 21%), 376 (M^+ + 2, 49%), 374 (M^+, 23%), 291 (378-CH_2COOEt, 40%), 289 (376-CH_2COOEt, 100%), 287 (374-COOEt, 48%). HRMS (EI) m/z calcd for $C_{12}H_{12}Br_2N_2O_2$ 373.9265 (Br-79 isotope) $[M]^+$, found 373.9259.

*2-(4,7-Dibromo-1H-benzimidazol-1-yl)acetic acid (***9a** *(n = 1))*

Following general procedure C, the hydrolysis of compound **8a** ($n = 1$) (135 mg, 0.327 mmol) in the aqueous NaOH solution (10 M) (1 mL) gave compound **9a** ($n = 1$) (124 mg, 99%) as a white solid. mp 280–281°C. ν_{max} (KBr) (cm^{-1}): 3500–2300, 3125, 3103, 2998, 2960, 1720, 1604, 1508, 1479, 1424, 1400, 1373, 1347, 1279, 1245, 1224, 1204, 1168, 1112, 981, 938, 894, 808, 797, 678, 644, 629, 598, 569, 540, 530, 440. ^{1}H NMR (300 MHz, MeOD): δ (ppm) = 5.38 (s, 2H, NCH_2), 7.38 (s, 2H, Ar*H*, 5-H and 6-H), 8.27 (s, 1H, Ar*H*, 2-H). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 5.32 (s, 2H, NCH_2), 7.38 (m, 2H, Ar*H*, 5-H and 6-H), 8.37 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 47.7 (NCH_2), 102.4, 112.5 (Ar:C4,C7), 126.0, 128.0 (Ar:C5,C6), 131.8 (Ar:C7a), 143.3 (Ar:C3a), 147.6 (Ar:C2), 169.9 (CO). MS (EI): m/z = 336 (M^+ + 4, 39%), 334 (M^+ + 2, 81%), 332 (M^+, 41%), 291 (336-COOH, 47%), 289 (334-COOH, 100%), 287 (332-COOH, 51%). HRMS (EI) m/z calcd for $C_9H_6Br_2N_2O_2$ 331.8796 (Br-79 isotope) $[M]^+$, found 331.8804.

*3-(4,7-Dibromo-1H-benzimidazol-1-yl)propanoic acid (***9b** *(n = 2))*

Following general procedure D, the hydrolysis of compound **8b** ($n = 2$) (43 mg, 0.114 mmol) in an aqueous HCl solution (1 M) (0.3 mL) gave compound **9b** ($n = 2$) (40 mg, 99%) as a white solid. mp 222–223°C. ν_{max} (KBr) (cm^{-1}): 3400–2300, 3119, 3057, 3032, 3012, 2943, 2913, 1684, 1547, 1497, 1466, 1449, 1418, 1389, 1379, 1362, 1250, 1218, 1190, 1166, 1109, 1089, 934, 908, 870, 820, 794, 660, 628, 610, 538, 480. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 2.90 (t, J = 6.9, 2H, NCH_2CH_2), 4.74 (t, J = 6.9, 2H, NCH_2), 7.47 (s, 2H, Ar*H*, 5-H and 6-H), 8.57 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 35.8 (CH_2), 42.1 (NCH_2), 102.4, 111.9 (Ar:C4, C7), 126.5, 128.7 (Ar:C5, C6), 130.9 (Ar:C7a), 142.2 (Ar:C3a), 147.2 (Ar:C2), 171.8 (CO). MS (EI): m/z = 350 (M^+ + 4, 12%), 348 (M^+ + 2, 28%), 346 (M^+, 13%), 291 (350-CH_2COOH, 13%), 289 (348-CH_2COOH, 34%), 287 (346-CH_2COOH, 16%), 278 (350-$(CH_2)_2COO^+$, 42%), 276 (348-$(CH_2)_2COO^+$, 100%), 274 (346-$(CH_2)_2COO^+$, 52%). HRMS (EI) m/z calcd for $C_{10}H_8Br_2N_2O_2$ 345.8952 (Br-79 isotope) $[M]^+$, found 345.8951.

*(2-(4,7-Dibromo-1H-benzimidazol-1-yl)-1-hydroxyethane-1,1-diyl)bisphosphonic acid (***10a** *(n = 1))*

Following general procedure E, the reaction of carboxylic acid **9a** ($n = 1$) (100 mg, 0.300 mmol), thionyl chloride (2 mL), and tris(trimethylsilyl)phosphite (0.2 mL, 0.600 mmol) gave compound **10a** (n = 1) (125 mg, 87%) as a white solid. mp 214–215°C. ν_{max} (KBr) (cm^{-1}): 3500–2300, 3143, 3081, 3067, 2928, 2864, 1635, 1497, 1387, 1255, 1198, 1134, 1108, 1088, 1054, 1003, 979, 922, 857, 824, 732, 670, 617, 592, 572, 559, 519, 486, 473. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.19 (t, J_{HP} = 10.0, 2H, $NCH_2C(OH)(PO_3H_2)_2$), 7.34 (s, 2H, Ar*H*, 5-H and 6-H), 8.50 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 48.6 (NCH_2), 73.9 (t, J_{CP} = 139, $C(OH)(PO_3H_2)_2$), 104.3, 112.9 (Ar:C4,C7), 126.5, 129.7 (Ar:C5,C6), 133.2 (Ar:C7a), 143.3 (Ar:C3a), 148.9 (Ar:C2). ^{31}P NMR (121 MHz, H_3PO_4/ DMSO-d_6): δ (ppm) = 17.4. MS (ESI): m/z = 483 (MH^+ + 4, 13%), 481 (MH^+ + 2, 21%), 479 (MH^+, 13%). HRMS (ESI) m/z calcd for $C_9H_{11}Br_2N_2O_7P_2$ 478.8403 (Br-79 isotope) $[MH]^+$, found 478.8418.

*(3-(4,7-Dibromo-1H-benzimidazol-1-yl)-1-hydroxypropane-1,1-diyl)bisphosphonic acid (***10b** *(n = 2))*

Following general procedure E, the reaction of carboxylic acid **9b** ($n = 2$) (78 mg, 0.224 mmol), thionyl

chloride (1 mL), and tris(trimethylsilyl)phosphite (0.15 mL, 0.448 mmol) gave compound **10b** (n = 2) (66 mg, 60%) as a white solid. mp 243–244°C. ν_{max} (KBr) (cm^{-1}): 3500–2300, 3147, 3074, 2962, 2924, 1636, 1612, 1578, 1551, 1508, 1500, 1386, 1250, 1201, 1166, 1076, 1039, 979, 951, 928, 882, 836, 774, 755, 670, 637, 615, 593, 567, 535, 523, 481. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.41 (m, 2H, $NCH_2CH_2C(OH)(PO_3H_2)_2$), 4.81 (m, 2H, $NCH_2CH_2C(OH)(PO_3H_2)_2$), 7.39 (s, 2H, Ar*H*, 5-H and 6-H), 8.34 (s, 1H, Ar*H*, 2-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 35.8 (CH_2), 41.9 (t, J_{CP} = 7.6, NCH_2), 71.3 (t, J_{CP} = 142.3, $C(OH)(PO_3H_2)_2$), 102.1, 112.4 (Ar:C4,C7), 125.9, 128.0 (Ar:C5, C6), 131.4 (Ar:C7a), 143.3 (Ar:C3a), 147.1 (Ar:C2). ^{31}P NMR (121 MHz, H_3PO_4/ DMSO-d_6): δ (ppm) = 18.6. MS (ESI): m/z = 497 (MH^+ + 4, 10%), 495 (MH^+ + 2, 17%), 493 (MH^+, 10%). HRMS (ESI) m/z calcd for $C_{10}H_{13}Br_2N_2O_7P_2$ 492.8559 (Br-79 isotope) $[MH]^+$, found 492.8566.

*Diethyl (2-(4,7-dibromo-1H-benzotriazol-1-yl) ethyl)phosphonate (**11**) and Diethyl (2-(4,7-dibromo-2H-benzotriazol-2-yl)ethyl)phosphonate (**12**)*

A solution of 4,7-dibromo-1*H*-benzotriazole **5** (100 mg, 0.376 mmol) and K_2CO_3 (158 mg, 1.143 mmol) in DMF (3 mL) was stirred at 80°C during 30 min. $Br(CH_2)_2PO_3Et_2$ (0.14 mL, 0.752 mmol) was added, and the reaction mixture was stirred for 1 h at 80°C. Upon cooling, the reaction mixture was filtered and the solvent was removed in vacuum The resulting oil was purified by column chromatography (ethyl acetate) to give compound **11** (29 mg, 17%), as a colorless oil and compound **12** (115 mg, 70%), as a white solid.

Compound **11:** ν_{max} (film) (cm^{-1}): 3063, 2983, 2931, 2909, 1486, 1446, 1394, 1369, 1252, 1200, 1163, 1124, 1098, 1054, 1026, 961, 907, 865, 828, 793, 690, 648, 585, 568. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.32 (t, J = 7.1, 6H, 2× OCH_2CH_3), 2.45–2.57 (m, 2H, $CH_2PO_3Et_2$), 4.09–4.19 (m, 4H, 2× OCH_2CH_3), 5.19–5.27 (m, 2H, NCH_2), 7.42 (d, J = 8.0, 1H, Ar*H*, 5-H or 6-H), 7.52 (d, J = 8.0, 1H, Ar*H*, 5-H or 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 16.6 (d, J_{CP} = 6.0, CH_3), 28.6 (d, J_{CP} = 139.0, $CH_2PO_3Et_2$), 44.4 (NCH_2), 62.4 (d, J_{CP} = 6.4, OCH_2), 101.6, 113.3 (Ar:C4,C7), 128.3, 132.5 (Ar:C5, C6), 131.9 (Ar:C7a), 146.1 (Ar:C3a). ^{31}P NMR (121 MHz, H_3PO_4/ $CDCl_3$): δ (ppm) = 24.9. MS (ESI): m/z = 466 (MNa^+ + 4, 13%), 464 (MNa^+ + 2, 26%), 462 (MNa^+, 13%), 444 (MH^+ + 4, 46%), 442 (MH^+ + 2, 100%), 440 (MH^+, 50%). HRMS (ESI) m/z calcd for $C_{12}H_{17}Br_2N_3O_3P$ 439.9369 (Br-79 isotope) $[MH]^+$, found 439.9370.

Compound **12:** mp 54°C. ν_{max} (KBr) (cm^{-1}): 3061, 2979, 2930, 2907, 1498, 1476, 1448, 1391, 1366, 1311, 1256, 1239, 1219, 1198, 1162, 1136, 1099, 1054, 1018, 982, 952, 834, 814, 796, 782, 755, 719, 671, 654, 583, 552, 516. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.30 (t, J = 7.1, 6H, 2× OCH_2CH_3), 2.60–2.72 (m, 2H, $CH_2PO_3Et_2$), 4.08–4.18 (m, 4H, 2× OCH_2CH_3), 4.99–5.07 (m, 2H, NCH_2), 7.44 (s, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 16.5 (d, J_{CP} = 6.0, CH_3), 27.2 (d, J_{CP} = 140.8, $CH_2PO_3Et_2$), 51.8 (NCH_2), 62.3 (d, J_{CP} = 6.4, OCH_2), 110.1 (Ar:C4, C7), 130.0 (Ar:C5, C6), 144.0 (Ar:C3a, C7a). ^{31}P NMR (121 MHz, H_3PO_4/$CDCl_3$): δ (ppm) = 24.8. MS (ESI): m/z = 466 (MNa^+ + 4, 19%), 464 (MNa^+ + 2, 36%), 462 (MNa^+, 17%), 444 (MH^+ + 4, 51%), 442 (MH^+ + 2, 100%), 440 (MH^+, 53%). HRMS (ESI) m/z calcd for $C_{12}H_{17}Br_2N_3O_3P$ 439.9369 (Br-79 isotope) $[MH]^+$, found 439.9357.

*Tetraethyl (2-(4,7-dibromo-2H-benzotriazol-2-yl)ethane-1,1-diyl)bisphosphonate (**13**)*

A mixture of compound **5** (100 mg, 0.376 mmol) and tetraethyl ethenylidene-1,1-bisphosphonate (113 mg, 0.376 mmol) in THF (5 mL) was stirred under reflux for 18 h. The solvent was evaporated in vacuum, and the crude material was purified by column chromatography (1:3 ethyl acetate/acetone) to give compound **13** (81 mg, 37%) as a colorless oil. ν_{max} (film) (cm^{-1}): 2986, 2935, 2911, 1715, 1652, 1622, 1479, 1445, 1394, 1370, 1249, 1165, 1098, 1026, 974, 856, 802. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.17 (t, J = 7.0, 6H, OCH_2CH_3), 1.26 (t, J = 7.0, 6H, OCH_2CH_3), 3.72 (tt, J_{HP} = 23.0 and 7.1, 1H, $CH(PO_3Et_2)_2$), 4.07–4.22 (m, 8H, CH_2CH_3), 5.27 (dt, J_{HP} = 13.8 and 7.1, 2H, NCH_2), 7.43 (s, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 16.2 (t, J_{CP} = 6.9, CH_3), 38.2 (t, J_{CP} = 132.2, $CH(PO_3Et_2)_2$), 53.3 (t, J_{CP} = 2.9, NCH_2), 63.4 (t, J_{CP} = 7.0, OCH_2), 110.1 (Ar:C4,C7), 129.9 (Ar:C5,C6), 143.7 (Ar:C3a,C7a). ^{31}P NMR (121 MHz, H_3PO_4/ $CDCl_3$): δ (ppm) = 18.5. MS (ESI): m/z = 602 (MNa^+ + 4, 46%), 600 (MNa^+ + 2, 86%), 598 (MNa^+, 48%), 580 (MH^+ + 4, 20%), 578 (MH^+ + 2, 44%), 576 (MH^+, 20%). HRMS (ESI) m/z calcd for $C_{16}H_{26}Br_2N_3O_6P_2$ 575.9658 (Br-79 isotope) $[MH]^+$, found 575.9650.

*Ethyl 2-(4,7-dibromo-1H-benzotriazol-1-yl)acetate (**14a** (n = 1)) and Ethyl 2-(4,7-dibromo-2H-benzotriazol-2-yl)acetate (**15a** (n = 1))*

1. Following general procedure B, to a mixture of 4,7-dibromo-1*H*-benzotriazole **5** (150 mg, 0.561 mmol) and KO^{t}Bu (69 mg, 0.617 mmol)

in EtOH (6 mL), $BrCH_2CO_2Et$ (0.07 mL, 0.620 mmol) was added and refluxed for 3 h to afford compound **14a** ($n = 1$) (75 mg, 37%) and compound **15a** ($n = 1$) (109 mg, 53%) as a white solids.

2. Following general procedure A, to a mixture of 4,7-dibromo-1*H*-benzotriazole **5** (100 mg, 0.376 mmol) and K_2CO_3 (156 mg, 1.128 mmol) in DMF (3 mL). $BrCH_2CO_2Et$ (0.045 mL, 0.414 mmol) was added and refluxed for 30 min. to afford compound **14a** ($n = 1$) (38 mg, 28%) and compound **15a** ($n = 1$) (68 mg, 50%) as white solids.

Compound **14a** ($n = 1$): mp 79–80°C. ν_{max} (KBr) (cm^{-1}): 3068, 3002, 2964, 2942, 2903, 1741, 1489, 1472, 1468, 1459, 1445, 1420, 1407, 1394, 1375, 1351, 1287, 1265, 1240, 1208, 1132, 1101, 1083, 1022, 969, 906, 875, 820, 814, 787, 711, 594, 544, 428. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.27 (t, $J = 7.1$, 3H, OCH_2CH_3), 4.27 (q, $J = 7.1$, 2H, OCH_2CH_3), 5.70 (s, 2H, NCH_2), 7.43 (d, $J = 8.0$, 1H, Ar*H*, 5-H or 6-H), 7.51 (d, $J = 8.1$, 1H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_3), 51.0 (NCH_2), 62.7 (OCH_2), 101.8, 113.4 (Ar:C4,C7), 128.4, 132.5 (Ar:C5,C6), 132.7 (Ar:C7a), 146.0 (Ar:C3a), 166.8 (CO). MS (EI): $m/z = 365$ ($M^+ + 4$, 19%), 363 ($M^+ + 2$, 40%), 361 (M^+, 20%), 292 (365-COOEt, 45%), 290 (363-COOEt, 100%), 288 (361-COOEt, 45%). HRMS (EI) m/z calcd for $C_{10}H_9Br_2N_3O_2$ 360.9061 (Br-79 isotope) $[M]^+$, found 360.9056.

Compound **15a** ($n = 1$): mp 140–142 °C. ν_{max} (KBr) (cm^{-1}): 3066, 3010, 2978, 2934, 1743, 1498, 1464, 1446, 1408, 1396, 1374, 1348, 1321, 1310, 1283, 1239, 1198, 1174, 1168, 1108, 1095, 1020, 1002, 974, 948, 874, 820, 788, 711, 656, 552, 534. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.29 (t, $J = 7.1$, 3H, OCH_2CH_3), 4.28 (q, $J = 7.1$, 2H, OCH_2CH_3), 5.58 (s, 2H, NCH_2), 7.49 (s, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.1 (CH_3), 57.6 (NCH_2), 62.7 (OCH_2), 110.3 (Ar:C4,C7), 130.3 (Ar:C5,C6), 144.3 (Ar:C3a,C7a), 146.0 (Ar:C3a), 165.4 (CO). MS (EI): $m/z = 365$ ($M^+ + 4$, 34%), 363 ($M^+ + 2$, 100%), 361 (M^+, 43%), 292 (365-COOEt, 15%), 290 (363-COOEt, 35%), 288 (361-COOEt, 16%). HRMS (EI) m/z calcd for $C_{10}H_9Br_2N_3O_2$ 360.9061 (Br-79 isotope) $[M]^+$, found 360.9056.

*Ethyl 3-(4,7-dibromo-1H-benzotriazol-1-yl)propanoate (**14b** (n = 2)) and Ethyl 3-(4,7-dibromo-2H-benzotriazol-2-yl)propanoate (**15b** (n = 2))*

1. Following general procedure B, to a mixture of 4,7-dibromo-1*H*-benzotriazole **5** (500 mg, 1.88 mmol) and KO^tBu (232 mg, 2.068 mmol) EtOH (12 mL), $Br(CH_2)_2CO_2Et$ (0.27 mL, 2.068 mmol) was added and refluxed for 24 h to give compound **14b** ($n = 2$) (176 mg, 25%) and compound **15b** ($n = 2$) (134 mg, 19%) and unreacted starting material **5**.
2. Following general procedure A, to a mixture of 4,7-dibromo-1*H*-benzotriazole **5** (337 mg, 1.267 mmol) and K_2CO_3 (350 mg, 2.534 mmol) in DMF (3 mL), $Br(CH_2)_2CO_2Et$ (0.18 mL, 1.394 mmol) was added and refluxed for 3 h to afford compound **14b** ($n = 2$) (179 mg, 37%) as a colorless oil and compound **15b** ($n = 2$) (220 mg, 48%) as a white solid.

Compound **14b** ($n = 2$): ν_{max} (film) (cm^{-1}): 3084, 2981, 2935, 2905, 1738, 1732, 1599, 1562, 1487, 1446, 1393, 1379, 1355, 1319, 1297, 1252, 1192, 1124, 1103, 1087, 1019, 1008, 980, 943, 907, 858, 815, 694, 666, 644. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.22 (t, $J = 7.2$, 3H, OCH_2CH_3), 3.08 (t, $J = 7.3$, 2H, NCH_2CH_2), 4.15 (q, $J = 7.2$, 2H, OCH_2CH_3), 5.24 (t, $J = 7.3$, 2H, NCH_2),7.40 (d, $J = 8.0$, 1H, Ar*H*, 5-H or 6-H), 7.49 (d, $J = 8.1$, 1H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_3), 35.5 (CH_2), 45.4 (NCH_2), 61.3 (OCH_2), 101.7, 113.2 (Ar:C4,C7), 128.2, 132.4 (Ar:C5,C6), 132.0 (Ar:C7a), 146.0 (Ar:C3a), 169.9 (CO). MS (ESI): m/z = 380 ($MH^+ + 4$, 48%), 378 ($MH^+ + 2$, 100%), 376 (MH^+, 41%). HRMS (ESI) m/z calcd for $C_{11}H_{12}Br_2N_3O_2$ 375.9291 (Br-79 isotope) $[MH]^+$, found 375.9288.

Compound **15b** ($n = 2$): mp 70–72°C. ν_{max} (KBr) (cm^{-1}): 3066, 2989, 2940, 2910, 1727, 1691, 1420, 1397, 1382, 1355, 1311, 1282, 1263, 1210, 1194, 1152, 1115, 1065, 1041, 1020, 952, 868, 821, 703, 670, 653, 588, 552, 464. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.24 (t, $J = 7.2$, 3H, OCH_2CH_3), 3.19 (t, $J = 7.2$, 2H, NCH_2CH_2), 4.17 (q, $J = 7.2$, 2H, OCH_2CH_3), 5.07 (t, $J = 7.2$, 2H, NCH_2), 7.42 (s, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_3), 34.2 (CH_2), 52.6 (NCH_2), 61.3 (OCH_2), 110.1 (Ar:C4,C7), 129.9 (Ar:C5,C6), 143.9 (Ar:C3a,C7a), 169.9 (CO). MS (ESI): m/z = 402 ($MNa^+ + 4$, 7%), 400 ($MNa^+ + 2$, 13%), 398 (MNa^+, 7%), 380 ($MH^+ + 4$, 51%), 378 ($MH^+ + 2$, 100%), 376 (MH^+, 48%). HRMS (ESI) m/z calcd for $C_{11}H_{12}Br_2N_3O_2$ 375.9291 (Br-79 isotope) $[MH]^+$, found 375.9289.

*2-(4,7-Dibromo-1H-benzotriazol-1-yl)acetic acid (**16a** (n = 1))*

Following general procedure C, the hydrolysis of compound **14a** ($n = 1$) (73 mg, 0.201 mmol) in the aqueous NaOH solution (10 M) (2 mL) gave compound **16a** ($n = 1$) (67 mg, 99%) as a white

solid. mp 191–193°C. ν_{max} (KBr) (cm^{-1}): 3550–3100, 3317, 3237, 3089, 3070, 3009, 2956, 1720, 1647, 1492, 1415, 1401, 1359, 1290, 1264, 1252, 1215, 1188, 1138, 1113, 1090, 1004, 974, 943, 907, 829, 812, 685, 660, 645, 598, 541, 526. ^{1}H NMR (400 MHz, MeOD): δ (ppm) = 5.80 (s, 2H, NC*H*$_2$), 7.53 (d, J = 8.0, 1H, Ar*H*, 5-H or 6-H), 7.65 (d, J = 8.1, 1H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 51.9 (NCH_2), 103.5, 113.3 (Ar:C4,C7), 129.7, 133.8 (Ar:C5,C6), 134.0 (Ar:C7a), 146.6 (Ar:C3a), 170.3 (CO). MS (EI): m/z = 337 (M^+ + 4, 43%), 335 (M^+ + 2, 95%), 333 (M^+, 47%), 292 (337-COOH, 50%), 290 (335-COOH, 100%), 288 (333-COOH, 50%). HRMS (EI) m/z calcd for $C_8H_5Br_2N_3O_2$ 332.8748 (Br-79 isotope) $[M]^+$, found 332.8748.

*2-(4,7-Dibromo-2H-benzotriazol-2-yl)acetic acid (***17a** *(n = 1))*

Following general procedure C, the hydrolysis of compound **15a** (n = 1) (60 mg, 0.165 mmol) in the aqueous NaOH solution (10 M) (2 mL) gave compound **17a** (n = 1) (55 mg, 99%) as a white solid. mp 215–216°C. ν_{max} (KBr) (cm^{-1}): 3550–3200, 3514, 3377, 3070, 3006, 2962, 1727, 1648, 1542, 1501, 1468, 1416, 1351, 1312, 1285, 1260, 1200, 1168, 1104, 1010, 985, 952, 900, 833, 822, 697, 653, 589, 552, 534. ^{1}H NMR (400 MHz, MeOD): δ (ppm) = 5.67 (s, 2H, NC*H*$_2$), 7.54 (s, 2H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 58.5 (NCH_2), 111.0 (Ar:C4,C7), 131.4 (Ar:C5,C6), 145.3 (Ar:C3a,C7a), 169.0 (CO). MS (EI): m/z = 337 (M^+ + 4, 43%), 335 (M^+ + 2, 90%), 333 (M^+, 47%), 293 (337-COO^+, 46%), 291 (335-COO^+, 100%), 289 (333-COO^+, 50%). HRMS (EI) m/z calcd for $C_8H_5Br_2N_3O_2$ 332.8748 (Br-79 isotope) $[M]^+$, found 332.8743.

*3-(4,7-Dibromo-1H-benzotriazol-1-yl)propanoic acid (***16b** *(n = 2))*

Following general procedure D, the hydrolysis of compound **14b** (n = 2) (110 mg, 0.291 mmol) in an aqueous HCl solution (1 M) (0.35 mL) gave compound **16b** (n = 2) (98 mg, 97%) as a white solid. mp 178–180°C. ν_{max} (KBr) (cm^{-1}): 3500–2500, 3086, 3063, 2958, 2930, 1734, 1493, 1482, 1440, 1406, 1388, 1353, 1302, 1261, 1233, 1213, 1184, 1132, 1040, 976, 950, 938, 905, 831, 782, 717, 670, 640, 566, 548, 536, 521, 493. ^{1}H NMR (400 MHz, MeOD): δ (ppm) = 3.12 (t, J = 7.1, 2H, NCH_2CH_2), 5.26 (t, J = 7.1, 2H, NC*H*$_2$), 7.51 (d, J = 8.0, 1H, Ar*H*, 5-H or 6-H), 7.65 (d, J = 8.1, 1H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 35.7 (CH_2), 47.0 (NCH_2), 103.2, 113.2 (Ar:C4,C7), 129.6, 133.9 (Ar:C5,C6), 133.4 (Ar:C7a), 146.7 (Ar:C3a), 173.5 (CO). MS (ESI): m/z = 352 (MH^+ + 4, 50%), 350 (MH^+ + 2, 100%), 348 (MH^+, 49%). HRMS (ESI) m/z calcd for $C_9H_8Br_2N_3O_2$ 347.8978 (Br-79 isotope) $[MH]^+$, found 347.8977.

*Ethyl 3-(4,7-dibromo-2H-benzotriazol-2-yl)propanoate (***17b** *(n = 2))*

Following general procedure D, the hydrolysis of compound **15b** (n = 2) (189 mg, 0.501 mmol) in an aqueous HCl solution (1 M) (0.35 mL) gave compound **17b** (n = 2) (174 mg, 99%) as a white solid. mp 152–155°C. ν_{max} (KBr) (cm^{-1}): 3550–2500, 3134, 3127, 2990, 2928, 1743, 1696, 1692, 1497, 1452, 1443, 1414, 1389, 1376, 1349, 1312, 1293, 1281, 1262, 1226, 1193, 1183, 1154, 1078, 1062, 1044, 1014, 953, 816, 796, 687, 654, 620, 560, 552, 480, 459, 407. ^{1}H NMR (400 MHz, MeOD): δ (ppm) = 3.23 (t, J = 6.8, 2H, NCH_2CH_2), 5.05 (t, J = 6.8, 2H, NC*H*$_2$), 7.49 (s, 2H, Ar*H*, 5-H and 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 34.2 (CH_2), 53.7 (NCH_2), 110.9 (Ar:C4,C7), 131.0 (Ar:C5,C6), 144.8 (Ar:C3a,C7a), 173.6 (CO). MS (ESI): m/z = 352 (MH^+ + 4, 49%), 350 (MH^+ + 2, 100%), 348 (MH^+, 49%). HRMS (ESI) m/z calcd for $C_9H_8Br_2N_3O_2$ 347.8978 (Br-79 isotope) $[MH]^+$, found 347.8975.

*(2-(4,7-Dibromo-1H-benzotriazol-1-yl)-1-hydroxyethane-1,1-diyl)bisphosphonic acid (***18a** *(n = 1))*

Following general procedure E, the reaction of carboxylic acid **16a** (n = 1) (50 mg, 0.149 mmol), thionyl chloride (1 mL), and tris(trimethylsilyl)phosphite (0.10 mL, 0.299 mmol) gave compound **18a** (n = 1) (56 mg, 78%) as a white solid. mp 155–156°C. ν_{max} (KBr) (cm^{-1}): 3600–2300, 3398, 3180, 3032, 2984, 1672, 1485, 1396, 1262, 1179, 1152, 1131, 1088, 1032, 1011, 956, 931, 921, 864, 818, 687, 670, 662, 590, 571, 554, 539, 509, 460. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.52 (J_{HP} = 9.6, 2H, NC*H*$_2$C(OH)(PO_3H_2)$_2$), 7.54 (d, J = 8.0, 2H, Ar*H*, 5-H or 6-H), 7.66 (d, J = 7.9, 2H, Ar*H*, 5-H or 6-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 51.1 (NCH_2), 72.8 (t, J_{CP} = 141.6, C(OH)(PO_3H_2)$_2$), 103.3, 111.5 (Ar:C4,C7), 127.6, 132.8 (Ar:C5,C6), 133.0 (Ar:C7a), 144.5 (Ar:C3a). ^{31}P NMR (161 MHz, H_3PO_4/ DMSO-d_6): δ (ppm) = 15.3. MS (ESI): m/z = 506 (MNa^+ + 4, 8%), 504 (MNa^+ + 2, 17%), 502 (MNa^+, 8%), 484 (MH^+ + 4, 50%), 482 (MH^+ + 2, 100%), 480 (MH^+, 49%). HRMS (ESI) m/z calcd for $C_8H_{10}Br_2N_3O_2P_2$ 479.8355 (Br-79 isotope) $[MH]^+$, found 479.8352.

*(2-(4,7-Dibromo-2H-benzotriazol-2-yl)-1-hydroxyethane-1,1-diyl)bisphosphonic acid (**19a** (n = 1))*

Following general procedure E, the reaction of carboxylic acid **17a** (n = 1) (100 mg, 0.275 mmol), thionyl chloride (1 mL), and tris(trimethylsilyl)phosphite (0.18 mL, 0.551 mmol) gave compound **19a** (n = 1) (58 mg, 44%) as a white powder. mp 200–201°C. ν_{max} (KBr) (cm^{-1}): 3550–2400, 3422, 3020, 2964, 2923, 1685, 1499, 1356, 1314, 1306, 1282, 1261, 1191, 1162, 1081, 1045, 1017, 958, 943, 900, 819, 804, 689, 656, 647, 592, 552, 538, 510, 454. ^{1}H NMR (400 MHz, MeOD): δ (ppm) = 5.41 (t, J_{HP} = 10.0, 2H, NCH_2C(OH)(PO_3H_2)$_2$), 7.55 (s, 2H, ArH, 5-H and 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 60.2 (NCH_2), 74.2 (t, J_{CP} = 146.5, C(OH)(PO_3H_2)$_2$), 111.0 (Ar:C4,C7), 131.3 (Ar:C5,C6), 144.8 (Ar:C3a,C7a). ^{31}P NMR (121 MHz, H_3PO_4/ MeOD): δ (ppm) = 14.7. MS (ESI): m/z = 506 (MNa^+ + 4, 24%), 504 (MNa^+ + 2, 50%), 502 (MNa^+, 21%), 484 (MH^+ + 4, 50%), 482 (MH^+ + 2, 100%), 480 (MH^+, 63%). HRMS (ESI) m/z calcd for $C_8H_{10}Br_2N_3O_2P_2$ 479.8355 (Br-79 isotope) $[MH]^+$, found 479.8375.

*(3-(4,7-Dibromo-1H-benzotriazol-1-yl)-1-hydroxypropane-1,1-diyl)bisphosphonic acid (**18b** (n = 2))*

Following general procedure E, the reaction of carboxylic acid **16b** (n = 2) (50 mg, 0.143 mmol), thionyl chloride (1 mL), and tris(trimethylsilyl)phosphite (0.1 mL, 0.286 mmol) gave compound **18b** (n = 2) (59 mg, 83%) as a white powder. mp 204–205°C. ν_{max} (KBr) (cm^{-1}): 3550–2300, 3377, 3068, 2957, 2936, 2869, 1639, 1508, 1490, 1458, 1322, 1304, 1261, 1210, 1173, 1136, 1080, 1045, 1000, 980, 965, 951, 882, 824, 813, 790, 766, 682, 670, 660, 644, 586, 570, 556, 541, 524, 456, 428. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.54 (m, 2H, NC$H_2$$CH_2$), 5.25 (m, 2H, NCH_2CH_2), 7.59 (d, J = 8.0, 2H, ArH, 5-H or 6-H), 7.71 (d, J = 8.0, 2H, ArH, 5-H or 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 34.8 (CH_2), 45.7 (t, J_{CP} = 7.5, NCH_2), 71.0 (t, J_{CP} = 142.9, C(OH)(PO_3H_2)$_2$), 101.9, 111.7 (Ar:C4,C7), 128.2, 132.5 (Ar:C5,C6), 131.8 (Ar:C7a), 145.0 (Ar:C3a). ^{31}P NMR (121 MHz, H_3PO_4/ DMSO-d_6): δ (ppm) = 18.4. MS (ESI): m/z = 498 (MH^+ + 4, 7%), 496 (MH^+ + 2, 16%), 494 (MH^+, 7%). HRMS (ESI) m/z calcd for $C_9H_{12}Br_2N_3O_7P_2$ 493.8512 (Br-79 isotope) $[MH]^+$, found 493.8532.

*(3-(4,7-Dibromo-2H-benzotriazol-2-yl)-1-hydroxypropane-1,1-diyl)bisphosphonic acid (**19b** (n = 2))*

Following general procedure E, the reaction of carboxylic acid **17b** (n = 2) (100 mg, 0.287 mmol), thionyl chloride (2 mL), and tris(trimethylsilyl)phosphite (0.19 mL, 0.573 mmol) gave compound **19b** (n = 2) (68 mg, 48%) as a white powder. mp 204–205°C. ν_{max} (KBr) (cm^{-1}): 3600–2300, 3386, 2962, 2926, 2854, 1640, 1498, 1458, 1312, 1183, 1097, 1059, 1008, 955, 817, 789, 761, 682, 655, 585, 549, 514. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.82–2.92 (m, 2H, NC$H_2$$CH_2$), 5.19–5.23 (m, 2H, NCH_2CH_2), 7.52 (s, 2H, ArH, 5-H and 6-H). ^{13}C NMR (100 MHz, MeOD): δ (ppm) = 35.2 (CH_2), 54.2 (t, J_{CP} = 7.6, NCH_2CH_2), 72.8 (t, J_{CP} = 146.5, C(OH)(PO_3H_2)$_2$), 110.9 (Ar:C4,C7), 131.0 (Ar:C5,C6), 144.9 (Ar:C3a,C7a). ^{31}P NMR (121 MHz, H_3PO_4/ DMSO-d_6): δ (ppm) = 18.0. MS (ESI): m/z = 498 (MH^+ + 4, 49%), 496 (MH^+ + 2, 100%), 494 (MH^+, 48%). HRMS (ESI) m/z calcd for $C_9H_{12}Br_2N_3O_7P_2$ 493.8512 (Br-79 isotope) $[MH]^+$, found 493.8507.

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