Synthesis of a Bolaamphiphilic Alkenyl Phosphonic Acid by Ru-catalyzed Olefin Cross Metathesis Reaction

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Abstract: We report the synthesis of bolaamphiphilic alkenyl phosphonic acid (BPC₁₂) through the olefin cross-metathesis reaction of vinylphosphonic acid with 1,11-dodecadiene in the presence of a Ru-carbene catalyst. BPC₁₂ possesses two trans-P-C=⁻C moieties and is thus readily soluble in D₂O up to 3.4 g L⁻¹, as confirmed by ¹H nuclear magnetic resonance (NMR) measurements. Surface tension measurements revealed that BPC₁₂ reduced the surface tension of water from 72.0 to 47.0 mN m⁻¹. The occupied area per molecule (A) of BPC₁₂ (216 Å²) was ten times larger than that of dodecenyl phosphonic acid PC₁₂ (23 Å²). Moreover, dynamic light scattering measurement of an aqueous BPC₁₂ solution (5 mM) revealed the formation of large aggregates with an average estimated diameter of 81.8±27.0 nm.

Key words: bolaamphiphile, phosphonic acid, surface activity, self-assembly

1 Introduction

Bolaamphiphiles are a relatively new class of surfactants in which two polar head groups are connected to a long hydrophobic spacer. They have becoming significant interest owing to their unique self-assembling behavior. Bolaamphiphiles are found in the membranes of archaeabacteria. These membrane-spanning bolaamphiphiles allow bacteria to sustain and thrive in harsh environments, such as high temperatures and acidic conditions.

Phosphorus is a vital element in both living and industrial matter. Phosphonic acids (R-P(O)(OH)) are regarded as structurally analogous to monoalkyl phosphates (R-O-P(O)(OH)). Because of the strong P-C bond, phosphonic acids are resistant to hydrolytic cleavage. Thus, they are incorporated into diverse bi/synthetic compounds. Phosphonic acids have also been debated to play a possible role in protocell membranes. However, the surface properties and self-assembling behavior of phosphonic acids are less understood. This may be due to the difficulty in introducing several phosphonic acid moieties into a surfactant framework, in spite of the recent development of synthetic methodologies. Vercruysse-Moreira et al. reported the synthesis of bolaamphiphilic phosphonic acids, alkyl-bis(α-amino-phosphonic acid) surfactants, via an addition reaction involving the P=⁻H bond of spirophosphorane with diimines. Although they successfully synthesized various substituted surfactants, the products were unstable and decomposed to give P=⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓
2 Experimental

2.1 Materials

Diethyl vinylphosphonate (>98.0%, Tokyo Chemical Industry Co., Ltd.), Grubbs catalyst 2nd generation (Sigma Aldrich), 1,11-dodecadiene (>99.5%, Tokyo Chemical Industry Co., Ltd.), dichloromethane (super dehydrated, FUJIFILM Wako Pure Chemical Co., Ltd.), hexane (>96%, FUJIFILM Wako Pure Chemical Co., Ltd.), ethyl acetate (>99.5%, FUJIFILM Wako Pure Chemical Co., Ltd.), potassium iodide (>99.5%, FUJIFILM Wako Pure Chemical Co., Ltd.), chlorotrimethylsilane (>98.0%, Tokyo Chemical Industry Co., Ltd.), acetonitrile (>99.5%, FUJIFILM Wako Pure Chemical Co., Ltd.), and silica gel (Wakocel C-200, FUJIFILM Wako Pure Chemical Co., Ltd.) were used as received.

2.2 Synthesis and characterization

1H, 13C, and 31P nuclear magnetic resonance (NMR) spectra were recorded on an Avance 400 NMR spectrometer (Bruker Biospin Co., Inc.). Either CDCl3 or D2O was used as the deuterated solvent. Tetramethylsilane served as an internal reference for calibration of the 1H and 13C NMR spectra obtained in CDCl3. The 1H NMR spectra of the samples in D2O were calibrated with the signal from the solvent residue. Dimethyl sulfoxide reference material (>99.0%, FUJIFILM Wako Pure Chemical Co., Ltd.) was used as an internal standard for 1H NMR spectroscopy in D2O. PC12 was synthesized according to the literature procedure.

2.2.1 Synthesis of P(O)(OH)2CH = CH(CH2)9CH = CHP(O)(O)(OH)2(BPC12)

In a Schlenk flask equipped with a magnetic stirring bar, 1,11-dodecadiene (0.5 g, 3.0 mmol) and diethyl vinylphosphonate (0.9 g, 6.0 mmol) were dissolved in 5 mL dichloromethane. Grubbs Catalyst™ 2nd generation (0.18 g, 0.2 mmol) was then added, and the mixture was refluxed for 4 h. The solvent was evaporated under reduced pressure, and the crude product was purified by silica gel chromatography by eluting with 10:1 chloroform:methanol. P(O)(O)(CH2CH2)9CH = CH(CH2)9CH = CHP(O)(O)(CH2CH2)9 was thus obtained as a pale brown liquid (0.96 g, 2.2 mmol, 73%).

P(O)(O)(CH2CH2)9CH = CH(CH2)9CH = CHP(O)(O)(CH2CH2)9(2.0 g, 4.6 mmol) and KI (9.0 g, 54.4 mmol) were charged into a two-necked round bottom flask with a magnetic stirring bar and dissolved in MeCN (20 mL). Me3SiCl (5.9 g, 54.4 mmol) was added, and the solution was stirred at 40°C for 12 h. The solvent was then removed under reduced pressure. EtOH (20 mL) and water (10 mL) were added and the mixture was stirred for 12 h. The water was partially evaporated, and the product was extracted into EtOAc to obtain a white solid (2.57 g, 1.56 mmol, 98%). The purity of BPC12 was confirmed by reverse-phase high pressure liquid chromatography (RP-HPLC) using a C18 analytical column (TOSOH TSKgel ODS-100V, 5 μm, 4.6 x 150 mm, flow rate 1.0 mL min⁻¹). Binary gradients comprising solvent A (99% H2O, 0.9% acetonitrile, 0.1% TFA) and solvent B (90% acetonitrile, 9.9% H2O, 0.07% TFA) were employed as follows: 0 min (0% B) to 5 min (0% B) to 20 min (100% B); Rf = 11 min. The structure of BPC12 was characterized by 1H, 13C, and 31P NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Autoflex Speed TOP/TOF, Bruker Daltonics Inc.), where 2,5,6-dihydroxybenzoic acid (DHB) was used as a matrix.

1H-NMR (400 MHz, D2O) δ (ppm): 6.45 (dd, 1H, J = 6.3, 17.6 and 23.1 Hz), 5.70 (br, 2H), 2.11 (m, 2H), 1.37 (br, 2H), 1.18–1.28 (CH3, 4H). 13C-NMR (100 MHz, CDCl3) δ (ppm): 151.0 (J = 3 Hz), 121.3 (J = 199 Hz), 34.4 (J = 20 Hz), 29.3 (2C), 28.3. 31P-NMR (162 MHz, CDCl3) δ (ppm): 15.5. MALDI-TOF-MS analysis of C12H24O6P2: calculated m/z = 326.1; observed m/z = 326.9[M + H]+, 348.9 [M + Na]+.

2.3 Molecular modeling

Conformational analysis of BPC12, PC12, and dodecyl phosphonic acid (DPA) was carried out. For each compound, the initial geometries were generated and subjected to a conformational search using the molecular mechanics force field as implemented in Spartan18. Each of the conformers, generated through the conformational search, was then optimized at the PM6 semi-empirical level of theory in order to generate an energy-based ordering of the conformers. The resulting conformations were used as the input for the calculations at the density functional theory (DFT, B3LYP functional) level using the 6-31G(d) basis set. All quantum mechanical calculations were performed using Spartan18 (Wavefunction, Inc., Irvine, CA, USA).

2.4 Titration experiments

Titration requiring pH measurement were carried out with a P-74 pH meter (HORIBA Corp.) that was calibrated regularly using pH 4.0, 7.0, and 9.0 standard buffer solutions. Because phosphonic acids form various self-assembled structures in water depending on the pH, a 2:1 (v/v)
ethanol:water mixed solvent system was used to observe a clear end point. All measurements were performed at room temperature. A fixed volume of BPC₁₂ solution (0.01 M) in ethanol:water was prepared. Aqueous NaOH (0.1 M) was added to this solution in discrete amounts with continuous stirring. The pH was recorded continuously until equilibrium was reached before addition of the next aliquot of titrant. The apparent pKₐ of BPC₁₂ was estimated as the pH of the solution at half the neutralization volume, i.e., half the volume required to reach the neutralization end point.

2.5 Surface activity and self-assembling properties

Surface tension measurements were performed by the Wilhelmy plate method at 25°C with a DY-500 surface tension meter (Kyowa Kaimen Kagaku Co.). Calibration was carried out prior to measurement with ultra-pure water. The Pt plate was cleaned by flaming, and the glassware was rinsed multiple times with ultra-pure water. The critical aggregation concentration (CAC) and surface tension at the CAC (γ₁ᵥ₂) were determined from the break point in the curve of the surface tension versus the logarithm of the concentration. The surface excess concentration (Γ) in mol m⁻² and the area occupied per molecule (A, in Å²) of the surfactant at the air/water interface were calculated using the following Gibbs adsorption isotherm equations:²⁰

\[
\Gamma = -\frac{1}{RT} \frac{dy}{d\ln C}
\]

\[
A = \frac{1}{N_B \Gamma}
\]

where γ represents the surface tension, R is the gas constant, T is the absolute temperature, C is the surfactant concentration, (dy/d ln C) is the slope below the CAC in the surface tension curve, and N_B is Avogadro’s number.

Aqueous solutions of BPC₁₂ at various concentrations were maintained at 25°C overnight for equilibration. The light scattering intensity of the BPC₁₂ solution (5 mM) was measured with a DLS-7000 instrument (Otsuka Electronics Co.) equipped with a 75 mW Ar laser (488 nm) light source, at 25°C.

3 Results and Discussion

3.1 Synthesis

Scheme 1 presents the synthesis of bolaamphiphilic alkenyl phosphonic acid (BPC₁₂) through the cross-metathesis reaction of P(Ο)(ΟH)₂CH₂CH₂CH₂ with ditopic terminal olefin CH₂=CH(CH₂)₈CH=CH₂ in the presence of a Ru-carbene catalyst, (H₂IMes)(PC₅₃)₃ClRu = CHPh (H₂IMes = N,N-bis(mesityl)-4,5-dihydroimidazol-2-yl)ene).¹⁰ Refluxing the mixture in CH₂Cl₂ afforded P(Ο)(ΟH)₂CH₂CH₂CH₂CH=CH(CH₂)₈CH=CH(Ο)(ΟH)₂CH₂ in 73% yield. Subsequent hydration of the esters in the presence of Me₃SiCl (TMSCl) and KI gave P(Ο)(ΟH)₂CH=CH(CH₂)₈CH=CHP(Ο)(ΟH)₂(BPC₁₂) in 98% yield.

Density functional theory at the B3LYP/6-31G(d) level was used for structural analysis. The molecular geometries of BPC₁₂, PC₁₂, and dodecyl phosphonic acid (DPA) in a vacuum were initially optimized at the PM6 level, and the conformations obtained were then used as the starting point for full unconstrained optimization at the B3LYP/6-31G(d) level of theory. BPC₁₂ was characterized by the typical double-bond structure, where two trans-P-C=C moieties were attached to both ends of a methylene spacer (Fig. 1A). PC₁₂ adopted a spoon-shaped molecular geometry with a slightly bent trans-P-C=C moiety and long alky chain handle (Fig. 1B), while DPA adopted a clear linear shape, typical of conventional surfactants (Fig. 1C).

Figure 2 shows the NMR spectra of a saturated D₂O solution of BPC₁₂. BPC₁₂ was soluble in D₂O, even under acidic conditions. Sharp signals were observed in the ¹H NMR spectrum (Fig. 2A) at δ 6.39 and 5.60 ppm, assigned to the vinylene hydrogens, with clear multiplet coupling patterns. The trans configuration of the C=C bonds was confirmed by the large ¹H−¹H coupling constant (J = 17 Hz). Methylenic peaks were also observed at δ 2.11, 1.37, and 1.18–1.28 ppm, respectively. Based on the signal intensity of dimethyl sulfoxide as an internal standard, the water solubility of BPC₁₂ was estimated to be 3.35 g L⁻¹ (1.0 × 10⁻² M) at 25°C. This value is higher than that of a similar bolaamphiphile of tetradecanedioic acid having a saturated

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dodecyl spacer $\left(0.2 \text{ g L}^{-1}, 7.7 \times 10^{-4} \text{ M}\right)$\(^{27}\). The \(^{31}\text{P}\) NMR spectrum showed a sharp singlet at $\delta$ 15.5 ppm, corresponding to $\text{P}('\text{OH})_2$, as shown in Fig. 2B. Signals were observed at $\delta$ 151.0 ($J = 3\text{ Hz}$) and 121.3 ($J = 199\text{ Hz}$) ppm in the \(^{13}\text{C}\) NMR spectrum, corresponding to the vinylene carbons (Fig. 2C). Methylene carbons were also observed $\delta$ 34.4 ($J = 2\text{ Hz}$), 29.3 ($2\text{C}$), and 28.3 ppm, respectively. It was also confirmed that $\text{PC}_{12}$ formed a colloidal dispersion in water and did not precipitate at concentrations of up to 40 wt\% in water\(^{27}\). $\text{DPA}$ without the trans-$\text{P}–\text{C}=\text{C}$ moiety was less soluble in $\text{D}_2\text{O}$ ($2.8 \times 10^{-4} \text{ M}$). Flood et al. reported the self-assembling behavior of dodecanediyl-$\text{bis}$ (phosphonic acid) without the trans-$\text{P}–\text{C}=\text{C}$ moiety in organic solvents. They revealed that this compound formed a linear supramolecular polymer via intermolecular hydrogen bonding of the phosphonic acid moieties\(^{28}\). These results suggest that introduction of the trans-$\text{P}–\text{C}=\text{C}$ moiety significantly increases the hydrophilicity, while the two trans-$\text{P}–\text{C}=\text{C}$ moieties at both ends of $\text{BPC}_{12}$ may induce dense packing via hydrogen bond interactions.

Acid-base titration of $\text{BPC}_{12}$ with $\text{NaOH}$ in a 2:1 (v/v) ethanol:water mixed solvent system was also conducted, as shown in Fig. 3. Owing to the four $\text{P}–\text{OH}$ moieties within the molecule, the titration curve showed two break points corresponding to the addition of 2.0 and 4.0 equiv. of $\text{NaOH}$. The apparent $p\text{K}_1$ of $\text{BPC}_{12}$ was estimated as the $\text{pH}$ of the solution at half the neutralization volume, e.g. half the volume required to reach the neutralization end point. The apparent $p\text{K}_1$ and $p\text{K}_2$ of $\text{BPC}_{12}$ were estimated to be 2.7 and 7.9, respectively. These values were slightly lower than those of $\text{PC}_{12}$ ($p\text{K}_1 = 3.9$ and $p\text{K}_2 = 9.3$) and $\text{DPA}$ ($p\text{K}_1 = 4.2$ and $p\text{K}_2 = 8.9$), as shown in Table 1. It was expected that the $\text{P}–\text{OH}$ moieties at both ends of the methylene spacer could interact with each other (e.g., stabilization of the monosodium salt via intramolecular hydrogen bonding to form an acid-soap type complex).

### 3.2 Surface activity and self-assembling properties

The self-assembling behavior of the bolaamphiphilic alkenyl phosphonic acid in water was confirmed by the Wilhelmy plate method. Surface tension measurement of $\text{BPC}_{12}$ showed two break points in the surface tension curve (Fig. 4). Above the concentration of the first break point ($6.7 \times 10^{-4} \text{ M}$), a gentle slope was observed, and the surface tension of water became constant after the second break point. The critical aggregation concentration (CAC) of $\text{BPC}_{12}$ was estimated to be $9.2 \times 10^{-3} \text{ M}$. This value is almost equal to the solubility of $\text{BPC}_{12}$ in $\text{D}_2\text{O}$. The CAC was higher than that of $\text{PC}_{12}$ ($4.8 \times 10^{-4} \text{ M}$\(^{24}\)). Two break points are often observed in the surface tension curve of bolaamphiphilic surfactants\(^{29–31}\). This is expected due to...
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the formation of aggregates or conformational change at the air/water interface before the real CAC is reached. Indeed, DLS measurement of BPC_{12} before the CAC (5.0 × 10^{-3} M) revealed the formation of large aggregates with an estimated d value of 81.8 ± 27.0 nm, as shown in Fig. 5. This value is almost equal to that of PC_{12b} (75.9 ± 22.7 nm). The γ_{CAC} of BPC_{12} (47.0 mN m^{-1}) was higher than that of PC_{12b} (23.6 mN m^{-1}). Notably, the CAC of PC_{12b} (CAC = 4.8 × 10^{-4} M) is one order of magnitude lower than that of DPA_{32} and BPC_{12} (Table 2). It is well known that the ability of bolaamphiphilic surfactants to decrease the surface tension of water is weaker than that of conventional surfactants because of the reverse U-shaped conformation at the air/water interface. The occupied area per molecule, A, of BPC_{12} was estimated from the slope between the two break points (216 Å^2). Note that this value is significantly larger than that of PC_{12b} (A = 23 Å^2). We assumed that BPC_{12} could adopt an extended conformation and both polar ends could attach to water. PC_{12b} having one trans-P-C = C moiety exhibits more dense packing at the air/water interface, where the polar head attaches to water and the alkenyl chain points to the other side.

4 Conclusion

In conclusion, the bolaamphiphilic alkenyl phosphonic acid BPC_{12} was synthesized by the Ru-catalyzed cross-metathesis reaction. The two trans-P-C = C moieties of BPC_{12} confer remarkable water solubility and colloidal dispersity to the molecule. ^1H NMR analysis in D_{2}O revealed that BPC_{12} is readily soluble in water (3.35 g L^{-1}, 1.0 × 10^{-2} M at 25°C). BPC_{12} exhibits surface activity, where it reduces the surface tension of water from 72.0 to 47.0 mN m^{-1}. The surface tension curve showed two break points, suggesting characteristic self-assembly behavior, as is often observed in the case of bolaamphiphilic surfactants. The occupied area per molecule (A) calculated from the slope of the surface tension curve revealed that the A value of BPC_{12} (216 Å^2) was approximately ten times larger than that of PC_{12b} (23 Å^2). Thus, we expected that BPC_{12} could adopt an extended conformation and both polar ends could attach to water. DLS measurement of an aqueous solution of BPC_{12} showed the presence of large aggregates (d = 81.8 ± 27.0 nm) with a size almost equal to that of PC_{12b} (75.9 ± 22.7 nm).

Bolaamphiphiles are found in the membrane of archaeobacteria. Owing to the presence of membrane-spanning bolaamphiphiles, these bacteria can sustain harsh environments. In the same line, phosphonic acids have also been debated as playing a possible role in protocell membranes, since they are the only phosphorus-containing molecules found in the carbonaceous Murchison meteorite. Thus, this work can contribute to the development of functional surfactants with distinctive self-assembling

Table 2  Surface properties of BPC_{12}, PC_{12b}, and DPA.

| Phosphonic acid | CMC (M) | γ_{CMC} (mN/m) |
|-----------------|---------|----------------|
| BPC_{12}        | 7.0 × 10^{-3} | 47.0          |
| PC_{12b}        | 4.8 × 10^{-4} | 23.6          |
| DPA_{32}        | 1.0 × 10^{-3} | 19            |

Data are taken from a) Ref. 24 and b) Ref. 32.
properties, and can also provide insight into the possible role of bolaamphiphilic alkenyl phosphonic acids in the formation of protocell membranes.

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Conflicts of Interest
There are no conflicts of interest to declare.

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