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A New Iodovinyl Derivative of Methyl Pyropheophorbide *d* Obtained via Takai Olefination Reaction

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Modification of chlorin derivatives, which leads to extension of the conjugation chain along the y axis, is the most important direction in the field of natural tetrapyrrole compounds. Iodine-containing derivatives of porphyrins are valuable reagents in such Pd-catalyzed reactions as Suzuki, Mizoroki-Heck, Stille, and Sonogashira couplings, as well as Buchwald-Hartwig amination. A new alternative way for functionalization of $C3^2$-position of formyl group of methyl pyropheophorbide d by introducing of iodine has been developed. We have proposed an one-step synthesis of methyl 3-(2-iodovinyl)pyropheophorbide d, including Takai reaction between methyl pyropheophorbide d, iodoform and $CrCl_2$. This functionalized derivative can be useful for further synthesis of derivatives with π-extending system by Pd-catalyzed cross-coupling reaction.

Keywords: Chlorins, chlorophyll *a*, tetrapyrrolic compounds, Takai reaction, Pd-catalyzed cross-coupling reactions.

Новое йодвинильное производное метилового эфира пирофеофорбида *d*, полученное с использованием реакции олефинирования Такаи

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Модификация хлориновых производных, приводящая к увеличению цепи сопряжения вдоль оси y, является важнейшей проблемой в области природных тетрапиррольных соединений. Йодсодержащие порфириновые производные являются ценными реагентами в таких Pd-катализируемых реакциях, как Сузуки, Мизороки-Хека, Стилле, Соногаширы, а также аминировании Бухвальда-Хартвига. В этой статье нами представлена разработка нового альтернативного пути для функционализации формильной группы в $C3^2$-положении метилового эфира пирофеофорбида d через введение атома йода. Таким образом, был предложен одностадийный синтез метилового эфира 3-(2-иодвинил)пирофеофорбида a, который включал в себя реакцию Такаи метилового эфира пирофеофорбида d с йодоформом и $CrCl_2$. Йодвинильное производное открывает широкие возможности для синтеза производных с расширенной π-системой через его использование в Pd-катализируемых реакциях кросс-сочетания.

Ключевые слова: Хлорины, хлорофилл *a*, тетрапиррольные соединения, реакция Такаи, Pd-катализируемые реакции кросс-сочетания.

Introduction

Natural and synthetic tetrapyrrole compounds are widely used in medicine, mainly as drugs for photodynamic therapy (PDT) of cancer[1] and as agents for antimicrobial PDT.[2] They are also used to create materials for solar energy.[3,4] Based on their metal complexes, oxygen and p*H* sensitive sensors are being developed.[5-10] Often, in the field of porphyrin chemistry, the main goal is to improve and impart certain optical, biological, or photophysical properties to the macrocycle. However, obtaining a molecule with the desired properties is not always an easy task. In this regard, there is a need for simple and accessible methods for the functionalization and modification of

tetrapyrrole macrocycles. For chlorophyll *a* derivatives, in particular for phorbine ones, the most important characteristics are the intensity and position of the long-wavelength band Q_y, which significantly affects molecule optical properties.[11] The position of the Q_y band in the electronic absorption spectra depends on the nature and type of binding of the substituents located along the y axis of the macrocycle. The introduction into the C3 and C13 positions of the methyl pyropheophorbide *a*, unsaturated substituents conjugated with the 18-π electronic system of the tetrapyrrole ring is know n to had to a bathochromic shift of the Q_y absorption band whose value depends on the donor or acceptor strength of the substituent.[12] However, methods allowing for the introduction of various substituents with a simultaneous increase of conjugation chain are very rare, and their development is one of the scientific directions of our research group.

Currently, in organic and bioorganic chemistry, extremely popular modification methods are Pd-catalyzed cross-coupling reactions, which allow one to obtain various complex molecules gently and with high yield.[13] The efficiency and relevance of cross-coupling reactions in the chemistry of tetrapyrrole compounds are also evident from the available publications.[14-18] However, in contrast to the great number of publications on the modification of porphyrins by Pd-catalyzed reactions, little attention has been paid to the development and study of similar approaches to the functionalization and modification of natural chlorins.[19,20] One of the most important reagents in such reactions as Suzuki, Mizoroki-Heck, Buchwald-Hartwig amination, Stille and Sonogashira coupling, *etc*., are halogen derivatives, which makes the direct halogenation of some positions of the chlorin macrocycle a very actual task. The introduction of a halogen atom into the macrocycle is possible via the Takai olefination.[21] The reaction mechanism has been studied and described in detail.[22] The main advantage of this reaction is its stereoselectivity, leading to the formation only of the *E*-configuration of the resulting double bond.

Experimental

General

Reactions were carried out under argon atmosphere, using commercially available reagents that were purchased and used as received. Starting methyl pheophorbide *a* was obtained from commercial sources. Heating reaction vessels was performed with oil bath. Column chromatography was performed using 40-63 μm silica gel, preparative thin layer chromatography (TLC) was performed using glass plates coated with 5-40 μm silica gel (5 mm thick). Control of the reactions was provided by TLC using aluminum-backed Silica Gel 60 F254 pre-coated plates. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance III 600 MHz spectrometer at room temperature in $CDCl_3$. Chemical shifts are reported relative to signals of residual protons of solvents ($CDCl_3$ – 7.26 ppm). Mass spectra were recorded with UltrafleXtreme mass spectrometer (Bruker Daltonics) in a positive-ion mode using reflection mode with 20 MV voltage without matrix. Electronic absorption spectra were recorded with U-2900 (Hitachi) spectrophotometer in quartz rectangular cells of 10 mm path length at concentration 10-5 M in CH_2Cl_2.

Synthesis

Preparation for Takai reaction: The reactions conducted under anhydrous conditions, glassware was dried 10 min in an oven at 250-300 °C. Commercial $CrCl_2$ was also dried under 150-200 °C for 10 min. Reactions were carried out under an atmosphere of argon. THF for Takai reaction was dried over Na and with benzophenone as indicator.

Preparation of $0.98 \cdot 10^{-3}$ M OsO_4 solution. Cleaned of external contaminants a sealed ampoule containing 250 mg of OsO_4 was placed and broken into an Erlenmeyer flask with 100 mL of absolute methylene chloride. The flask contents were thoroughly mixed, after that the solution was ready for use.

Zn^{II} complex of methyl pyropheophorbide d (***8***) was synthesized from the corresponding free base **7** via the standard procedure described in.[23] A methanol solution (1 mL) saturated with $Zn(OAc)_2 \cdot 2H_2O$ was added to a dichloromethane solution (10 mL) of free base **7** (10 μmol) and stirred at room temperature overnight. The reaction mixture was poured into aqueous 4% $NaHCO_3$ and extracted with dichloromethane. The organic layer was washed with water, dried over Na_2SO_4 and filtered. After the solvent was evaporated, the residue was purified with recrystallization from dichloromethane and ethanol to give the corresponding zinc complex **8** which can be used without additional purification.

Methyl pyropheophorbide a (**1**)[24] was obtained using a known procedure.[25] Methyl pheophorbide *a* (1 g) was dissolved in pyridine (80 mL). The mixture was stirred for 2 days at reflux in an oil-bath at 140-160 °C. Then the solvent was thoroughly concentrated *in vacuo*. The residue was diluted with CH_2Cl_2 and extracted with water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography in a CH_2Cl_2/EtOH system (1:100) followed by recrystallization from CH_2Cl_2 and hexane to give 0.82 g of methyl pyropheophorbide *a* **1**. Yield: 91%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.40 (1H, s, 10-H), 9.43 (1H, s, 5-H), 8.58 (1H, s, 20-H), 8.04 (1H, q, J = 11.4 Hz, J = 17.7 Hz, 3^1-H), 6.32 (1H, d, J = 17.7 Hz, 3^2-H), 6.21 (1H, d, J = 11.4 Hz, 3^2-H), 5.29 (1H, d, J = 19.3 Hz, 13^2-H^a), 5.12 (1H, d, J = 19.3 Hz, 13^2-H^b), 4.52 (1H, q, J = 7.5 Hz, 18-H), 4.33 (1H, m, 17-H), 3.72 (2H, q, J = 7.8 Hz, 8^1-CH_2), 3.71 (3H, s, 12-CH_3), 3.64 (3H, s, 17^2-CO_2CH_3), 3.44 (3H, s, 2-CH_3), 3.28 (3H, s, 7-CH_3), 2.73 (1H, m, 17^1-H^a), 2.59 (1H, m, 17^2-H^a), 2.33 (2H, m, 17^1-H^b, 17_2-H^b), 1.84 (3H, d, J = 7.5 Hz, 18-CH_3), 1.73 (3H, t, J = 7.8 Hz, 8^2-CH_3), 0.10 and -1.64 (2H, each s, NH×2). UV-Vis (CH_2Cl_2) λ nm ($A_{rel.}$): 413 (1.00), 508 (0.10), 539 (0.08), 609 (0.07), 667 (0.44).

Methyl pyropheophorbide d (**7**) was obtained by oxidation of methyl pyropheophorbide *a* **1** with OsO_4/$NaIO_4$ system.[26] To a solution of methyl pyropheophorbide *a* (100 mg , 0.18 mmol) in THF (25 mL) at 0 °C was added 0.0098 M solution of OsO_4 in anhydrous CH_2Cl_2 (0.4 μL) and 0.11 M solution of $NaIO_4$ in H_2O (10 mL). The mixture was stirred overnight at room temperature. The progress of the reaction was monitored by UV-Vis spectroscopy. The residue was diluted with CH_2Cl_2 and extracted with a water solution of $Na_2S_2O_3$ and then with water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The reaction product did not require further purification. Yield: 95 mg (96 %). ^{1}H NMR ($CDCl_3$) δ ppm: 11.52 (1H, s, 3^1-H), 10.22 (1H, s, 10-H), 9.53 (1H, s, 5-H), 8.83 (1H, s, 20-H), 5.35 (1H, d, J = 19.6 Hz, 13^2-H^a), 5.20 (1H, d, J = 19.6 Hz, 13^2-H^b), 4.59 (1H, m, 18-H), 4.40 (1H, m, 17-H), 3.77 (3H, s, 12-CH_3), 3.68 (5H, m, 8^1-CH_2 and 17^2-CO_2CH_3), 3.65 (3H, s, 2-CH_3), 3.27 (3H, s, 7-CH_3), 2.76 (1H, m, 17^1-H^a), 2.63 (1H, m, 17^2-H^a), 2.34 (2H, m, 17^1-H^b, 17^2-H^b), 1.88 (3H, d, J = 7.3 Hz, 18-CH_3), 1.71 (3H, t, J = 7.7 Hz, 8^2-CH_3), -0.16 and -2.13 (2H, each s, NH × 2). UV-Vis (CH_2Cl_2) λ nm ($A_{rel.}$): 496 (1.00), 521 (0.13), 555 (0.14), 636 (0.08), 695 (0.72).

*(E)-3-(2-Iodovinyl)pyropheophorbide d methyl ester (**10**).* A 25 mL Schlenk 's flask was charged with a stir bar and $CrCl_2$ (166 mg, 0.0014 mol, 8.6 equiv) and dried under 150-200 °C and *in vacuo* for 10 min. It was then stoppered and flushed with argon. Anhydrous THF (5 mL) was added and the suspension was cooled to -5 °C with stirring and bubbled through with argon. CHI_3 (164 mg, 0.4 mmol, 2.5 equiv) and Zn(II) complex of methyl pyropheophorbide *d* (100 mg, 0.16 mmol, 1 equiv) were dis-

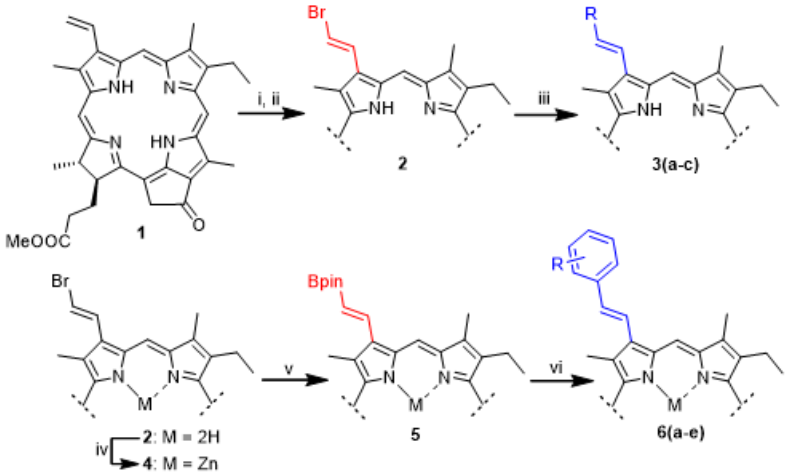
solved in 10 mL of anhydrous THF and added to the THF/$CrCl_2$ suspension dropwise. The reaction was stirred for 3 h under argon, as a deep green solution with suspended chromium. Then the solvent was concentrated *in vacuo*. The residue was diluted in a minimum amount of CH_2Cl_2 and stirring with 1 mL of 37 % HCl for 2 min. The reaction mixture was then diluted with CH_2Cl_2 and extracted with a water solution of $NaHCO_3$ and then with water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by preparative TLC in a CH_2Cl_2/EtOH system (100:4) followed by recrystallization from CH_2Cl_2 and hexane to give 54 mg of (*E*)-3-(2-iodovinyl)pyropheophorbide *d* methyl ester **10**. The reaction overall yield is 49 %. ^{1}H NMR ($CDCl_3$) δ_H ppm: 9.53 (1H, s, 10-H), 9.25 (1H, s, 5-H), 8.71 (1H, d, J = 15.0 Hz, 3^1-H), 8.60 (1H, s, 20-H), 7.40 (1H, d, J = 15.0 Hz, 3^2-H), 5.29 (1H, d, J = 19.2 Hz, 13^2-H^a), 5.14 (1H, d, J = 19.2 Hz, 13^2-H^b), 4.53 (1H, m, 18-H), 4.34 (1H, m, 17-H), 3.70 (5H, m, 12-CH_3 and 8^1-CH_2), 3.64 (3H, s, 17^2-CO_2CH_3), 3.37 (3H, s, 2-CH_3), 3.25 (3H, s, 7-CH_3), 2.73 (1H, m, 17^1-H^a), 2.59 (1H, m, 17^2-H^a), 2.33 (2H, m, 17^1-H^b, 17^2-H^b), 1.84 (3H, d, J = 7.4 Hz, 18-CH_3), 1.72 (3H, t, J = 7.8 Hz, 8^2-CH_3), 0.29 and -1.85 (2H, each s, NH × 2). ^{13}C NMR ($CDCl_3$) δ_C ppm: 196.1 ($C13^1$(>C=O), 173.4 ($C17^3$(>C=O), 171.2 (C19), 160.7 (C16), 154.9 (C6), 151.0 (C9), 149.0 (C14), 145.1 (C8), 140.8 (C1), 138.2 (C11), 137.5 ($C3^1$(-CH=), 136.2(C7), 135.3 (C4), 134.9 (C3), 131.2 (C12), 130.8 (C2), 128.8 (C13), 106.3 (C15), 104.1 (C10), 97.0 (C5), 93.3 (C20), 83.3 ($C3^2$), 51.8 (C17), 51.7 ($C17^4$(-OCH_3), 49.9 (C18), 48.1 ($C13^2$), 31.0 ($C17^2$), 29.9 ($C17^1$), 23.2 ($C18^1$(-CH_3), 19.5 ($C8^1$(-CH_2), 17.4 ($C8^2$(-CH_3), 12.3 ($C2^1$(-CH_3), 12.1 ($C12^1$(-CH_3), 11.3 ($C7^1$(-CH_3). MS (SALDI): *m/z* found 673.1, 674.1, 675.1 calcd. for $C_{34}H_{35}IN_4O_3$: [M]$^+$, 673.18; $^{13}C^{12}C_{33}H_{35}IN_4O_3$: [M]$^+$, 674.18; $^{13}C_2{}^{12}C_{32}H_{35}IN_4O_3$: [M]$^+$, 675.18. UV-Vis ($CH_2Cl_2$) λ nm ($A_{rel.}$): 418 (1.00), 511 (0.12), 541 (0.11), 615 (0.10), 674 (0.42).

Results and Discussion

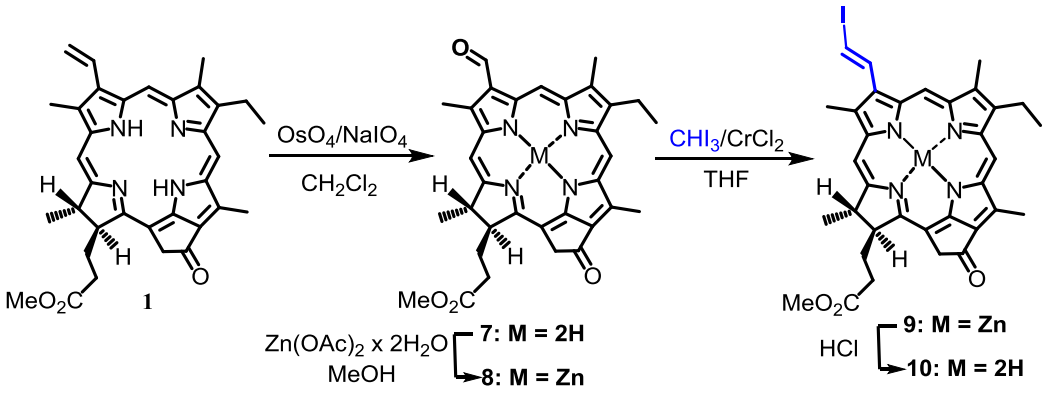
Recently, we have shown two-step regioselective one-pot bromination of vinyl group of methyl pyropheophorbide *a* and examined its reactivity in Pd(0)-catalyzed cross coupling reactions.[19] Moreover, our research group has examined bromovinyl derivative of methyl pyropheophorbide *a* as a reagent in Suzuki-Miyaura reaction, resulted in the formation of methyl ester (*E*)-3^2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl) pyropheophorbide *a*, a useful compound for further synthesis of π-extended macroheterocyclic systems (Scheme 1).[20]

In this article we have developed a new approach for modification of C3-position of methyl pyropheophorbides, allowing to significantly increase the yield of C3-substituted methyl pyropheophorbide *a* derivatives. Generally, we proposed a method for introducing the iodine atom in $C3^2$-position of methyl pyropheophorbide *d* to obtain (*E*)-3-(2-iodovinyl)pyropheophorbide *d* methyl ester. As a raw material we used methyl pyropheophorbide *a* which, according to a well-known method,[26] was converted to corresponding methyl pyropheophorbide *d*. First, the Takai reaction was carried out on a free base of methyl pyropheophorbide *d*, however, this pathway led to the formation of a large number of by-products that could not be separated. To prevent side reactions at nitrogen atoms in the macrocycle ring, metalation of chlorin **7** was carried out using zinc(II) acetate. Zinc complex **8** was further introduced into the Takai reaction using a large excess of $CrCl_2$ (8.6 equiv) and 2.5 equiv CHI_3 in absolute THF under argon atmosphere. Since zinc complex **9** is unstable under the conditions of chromatography on silica gel, after the reaction, *in situ* demetalation was carried out with concentrated HCl. As a result, the desired product was obtained with a total yield of 47 % (Scheme 2).

The structure of the resulting iodovinyl derivative **10** was confirmed by NMR spectroscopy (Figure 1). In the ^{1}H NMR spectrum, we observed the disappearance of the formyl group proton and formation of two characteristic doublets, which indicates the AX spin system formation. The double bond has *E*-configuration which is confirmed by coupling constant J = 15.0 Hz of the 3-iodovinyl group protons. Signal at 83.3 ppm in the ^{13}C NMR spectrum (Figure 2) belongs to the iodine substituted vinylic carbon atom, the high field shift of which is due to the heavy atom effect of iodine atom, while $C3^1$ atom possesses low field shift possibly due to the higher mesomeric effect of iodine atom compared to the corresponding bromine substituted vinyl group in **2**.



Scheme 1. Different ways for modification C3-position of pyropheophorbides. i: Br_2, -90 ℃, CH_2Cl_2; ii: 80 ℃; iii: *a* – Pd^0, base, tributyl(vinyl)tin, *b* – Pd^0, base, phenylboronic acid, *c* – Pd^0, base, methyl acrylate; iv: MeOH, $Zn(OAc)_2$; v: B_2pin_2, $Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane; vi: *a* – $PdCl_2(CH_3CN)_2$, dppp, Cs_2CO_3, 1,4-dioxane, iodobenzene; *b* – $Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane, 1-iodo-3-nitrobenzene, *c* – $Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane, 4-iodophenol, *d* – $Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane, 4-iodoacetophenon, *e* – $Pd(PPh_3)_4$, Cs_2CO_3, 1,4-dioxane, 4-iodotoluene.



Scheme 2. Synthesis of (*E*)-3-(2-iodovinyl)pyropheophorbide *d* methyl ester using Takai reaction.

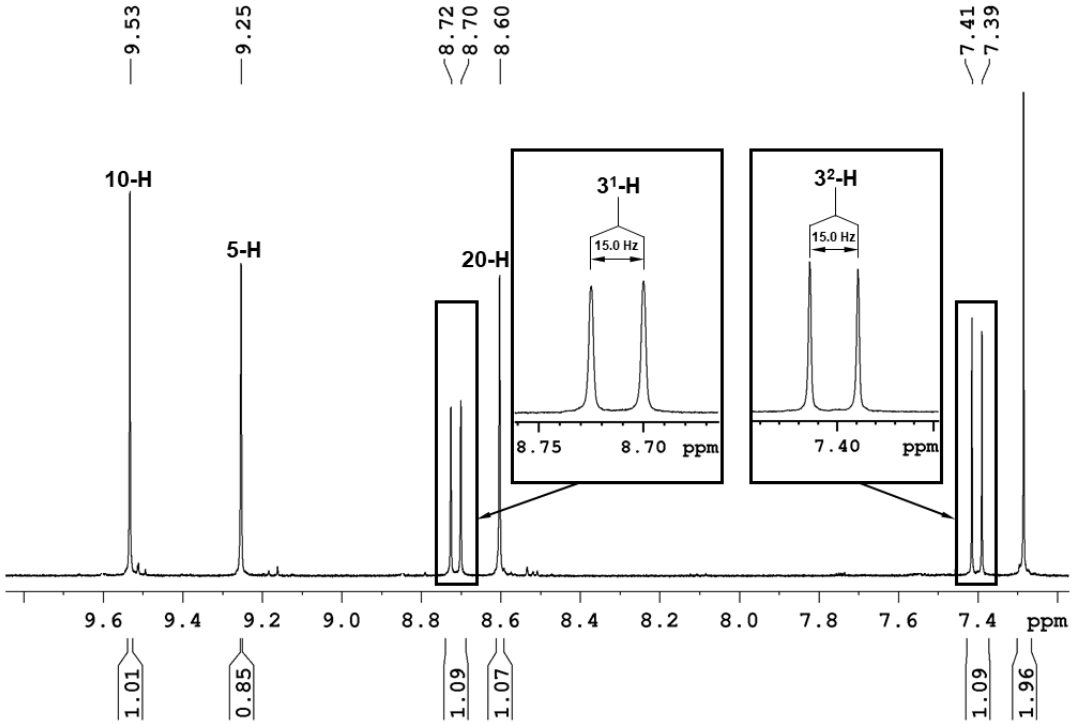


Figure 1. Fragment of ^{1}H NMR spectrum of (*E*)-3-(2-iodovinyl)pyropheophorbide *d* methyl ester.

We believe that such moderate reaction yield is associated with a steric factor, as well as a multi-stage metalation - demetalation process, leading to losses at all stages of the proposed protocol. However, iodine derivatives are known to be significantly more effective in the Pd-catalyzed reactions than the corresponding bromine and chlorine derivatives.[27-30] For this reason, the resulting iodovinyl derivative **10** is expected to be more active than it bromvinyl analog **2**. This suggests further research to optimize this approach.

Conclusions

In conclusion, a new method for synthesis of a halogenated derivative – (*E*)-3-(2-iodovinyl)pyropheophorbide *d* methyl ester has been elaborated. This strategy included 4 stages: the stage of oxidation of the vinyl group, metalation, Takai reaction and demetalation. Takai reaction occurs with 100 % stereoselectivity, and the double bond has *E*-configuration, which is confirmed by coupling constant J = 15.0 Hz of the 3-iodovinyl group protons. The developed approach opens up a broad possibility for introduction of numerous aromatic and unsaturated substituents along the *y*-axis of the macrocycle to form extended π-conjugated chlorin systems.

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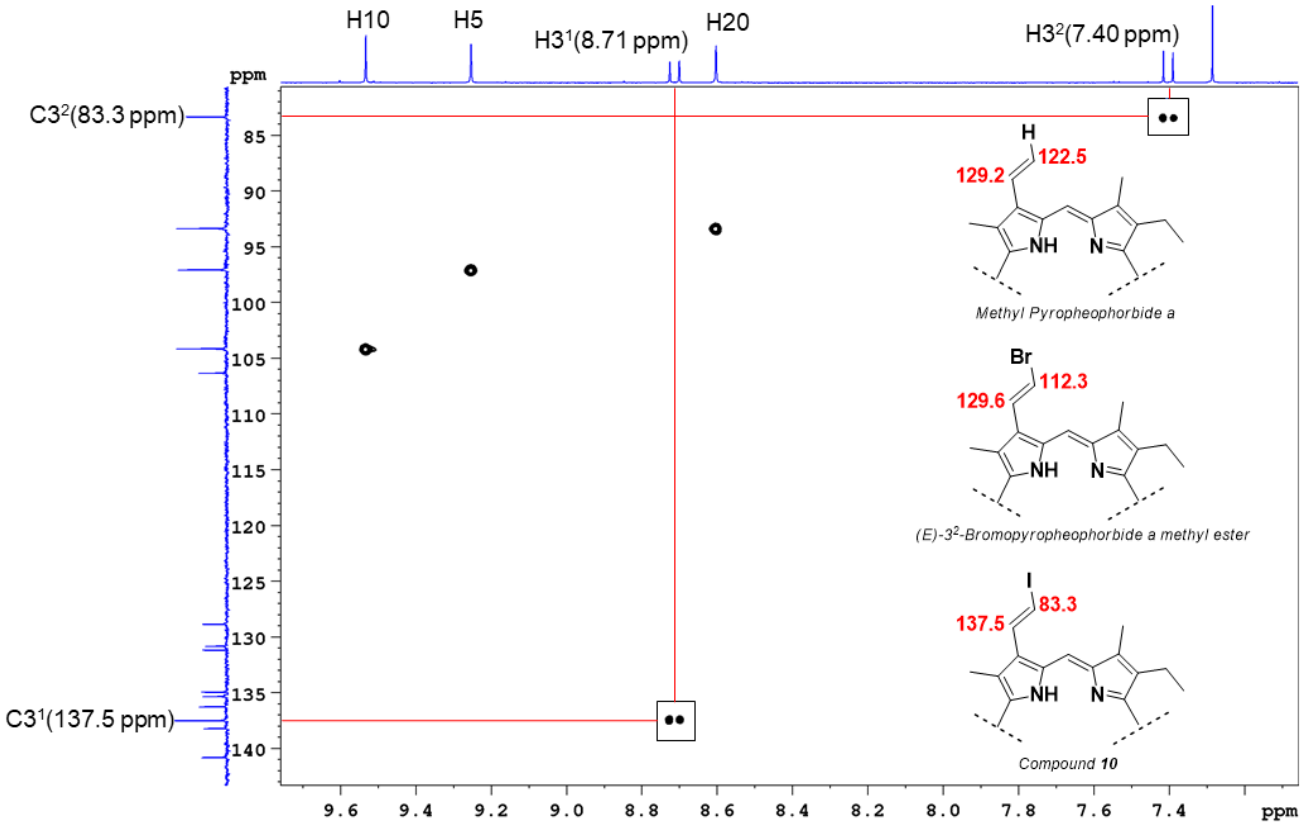

Figure 2. Fragment of ^{1}H–^{13}C HSQC spectrum of compound **10**. Right inset: ^{13}C NMR shifts value of $C3^{1}$ and $C3^{2}$ carbon atoms of variously substituted vinyl groups showing the influence iodine atom on the carbon signals.

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