

## SURPRISING SYNTHETIC STRATEGIES FOR SYMMETRIC BODIPY DERIVATIVES

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### ABSTRACT

BODIPY fluorescence dyes represent a captivating area of research in contemporary photochemistry, thanks to the wide array of options their chromophore presents, readily accessible through various synthetic pathways. Indeed, the literature abounds with a vast array of compounds centered around the indacene core. The ability to modulate spectroscopic properties or instigate new photophysical processes through the substitution pattern of BODIPY dyes has significantly expanded the scope of scientific and technological applications for these fluorophores. BODIPY cores, still widely used today and easily derivatized through simple modifications, find extensive application due to their versatile characteristics. These features render BODIPY compounds both workable and appealing. Our research group is interested in conducting studies related to the synthesis of BODIPY compounds, derivatization of the BODIPY core from different positions through Suzuki-Miyaura coupling reactions, and the synthesis of BODIPY derivatives with potential applications in fingerprint detection. The purpose of this investigation is to summarize the fundamental chemistry, synthesis, and spectroscopic properties of common BODIPY derivatives.

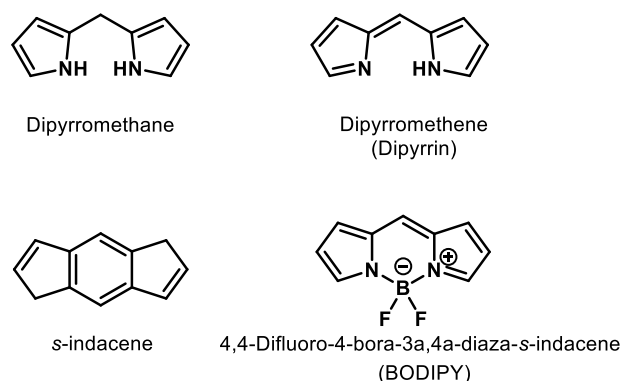
**Keywords:** BODIPYs, Fluorophore, Synthesis, Dyes, Suzuki-Miyaura Coupling, Halogenation.

### Introduction

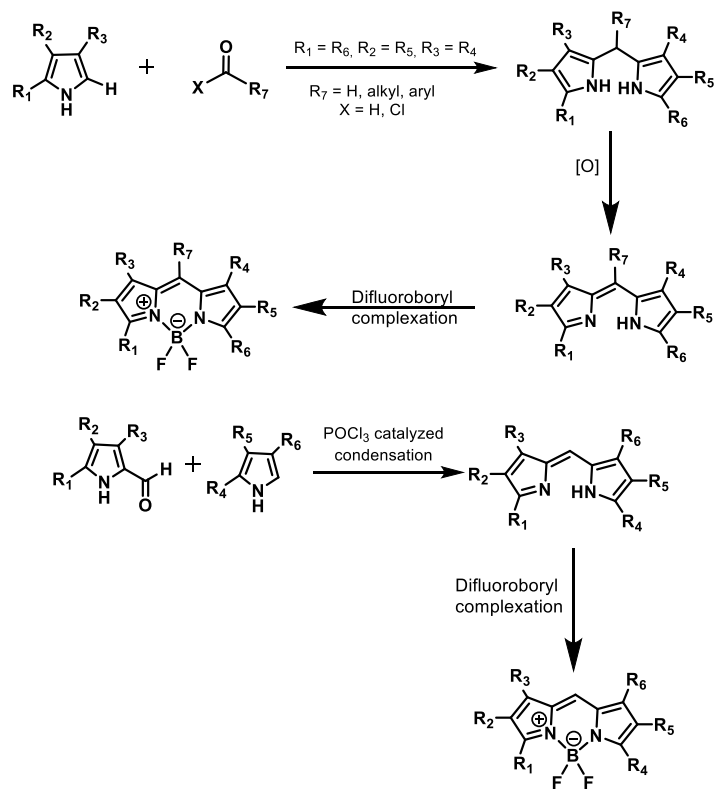
The complexes formed by dipyrromethene ligands with the boron atom are called boron-dipyrromethene or BODIPY (4,4-difluoro-4-boron-3a,4a-diaza-s-indacene). BODIPY compounds are formed by combining the BF<sub>2</sub> unit with a methane bridge at the *meso* position of two pyrrole rings [1,2], (Fig. 1). The synthesis of BODIPY core was first performed by Treibs and Kreuzer in 1968. It has been stated that the BODIPY core obtained by Treibs and Kreuzer is unstable [3]. BODIPY core consist of a group of fluorescent dyes. This category of fluorophores displays intriguing characteristics, including exceptional stability, well-defined fluorescence peaks, adjustable emission wavelengths, and elevated quantum yields. BODIPY (4,4-difluoro-4-boron-3a,4a-diaza-s-indacene) compounds are widely used in both basic and applied sciences due to their fluorescence properties and photochemical and electrochemical properties.

Symmetric BODIPY compounds can undergo synthesis through the condensation of two identical pyrrolic units with a carbonyl compound, such as an aldehyde or acyl chloride. This reaction typically employs a strong acid catalyst like hydrobromic acid (HBr) or trifluoroacetic acid (TFA) (Fig. 2). The resulting chemical process yields a dipyrromethane compound with substitution occurring at the *meso* position by the structure previously attached to the carbonyl

reagent. Aromatization of the dipyrromethane is then achieved, often utilizing chloranil or DDQ. This step leads to the formation of dipyrromethene (or dipyrin), which is subsequently converted into BODIPY through a base-catalyzed reaction involving complexation with a difluoroboryl unit. Trifluoroboryl etherate ( $\text{BF}_3 \cdot \text{OEt}_2$ ) is commonly employed for this purpose, often with the assistance of triethylamine (TEA). On the other hand, non-meso-substituted BODIPYs can be synthesized using two distinct pyrrolic units, one of which contains a carboxyaldehyde group at the C2 position of the pyrrolic ring. This reaction, catalyzed by phosphoryl chloride, directly produces the dipyrin intermediate, which is subsequently converted into BODIPY using the same aforementioned method (Fig. 2) [4].



**Fig 1.** Chemical structures of dipyrromethane, dipyrromethene, s-indacene and BODIPYs.



**Fig. 2.** General approaches for the synthesis of BODIPYs.

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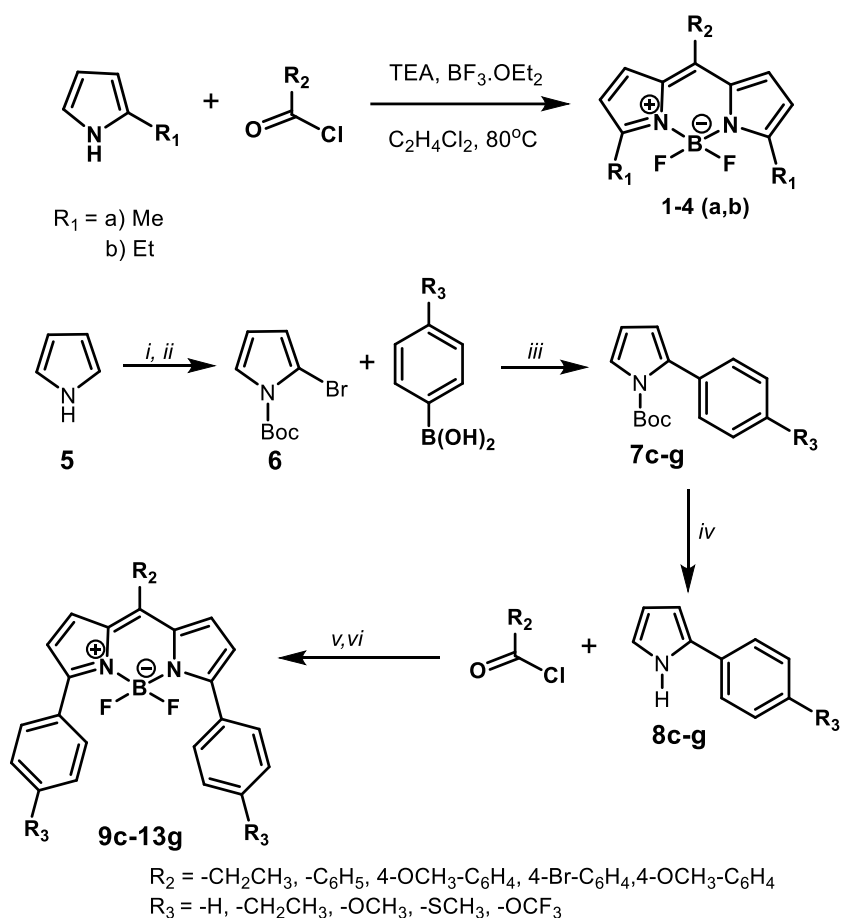
Over the past two decades, researchers have synthesized and utilized thousands of structurally diverse BODIPY compounds in numerous studies [5]. The BODIPY core represents a significant class of fluorescent dyes that have garnered growing interest, owing to their outstanding properties. These include exceptional chemical robustness, virtually insensitive behavior towards environmental polarity, good solubility, intense absorption peaks with high molar absorption coefficients in the visible region, high fluorescence quantum yields, and minimal Stokes shift [6-8]. Moreover, these photophysical characteristics can be readily customized through various synthetic approaches targeting the BODIPY core [5]. As a result, these dyes find myriad applications including fluorescence probes [9-10], bio-labeling reagents [11], laser dyes [12], photosensitizers for photodynamic therapy [13,14], and in solar cells [15]. The photophysical and electrochemical properties of BODIPY dyes are significantly influenced by the substituent groups attached to their structure [1,2].

The alteration of the molecular configuration of BODIPYs at the indacene core primarily occurs during the formation of dipyrromethene ligands, which serve as precursors for subsequent BODIPY synthesis through interaction with boron trifluoride etherate. Dipyrromethene ligands are synthesized from pyrroles, formylpyrroles, benzene derivatives, and other suitable starting materials. Most dipyrromethene ligands are stable as salts with mineral acids, typically HBr or HCl, and are employed in the creation of coordination compounds. Aryl-substituted dipyrromethenes demonstrate enhanced chemical robustness in their molecular state. Consequently, the more resilient aryl dipyrromethenes can be initially purified and then utilized as starting materials in BODIPY synthesis. On the other hand, less stable aryl dipyrromethenes are not separated from the reaction mixture but are instead utilized directly in solution within the reaction mixture to generate BODIPYs [16-20].

In the realm of modifying the structure of BODIPY, substitutions are observed at positions 1-3, 5-7 (pyrrole positions), 8- (*meso* position), and the boron atom [20,21]. The substituents introduced to the specified positions of pyrrole rings can encompass a wide range, including alkyl -  $C_nH_{2n+1}$ , functional groups featuring O, N, S, phenyl, and other aromatic radicals, as well as halogen atoms (such as F, Cl, Br, I). Additionally, various organic and inorganic ligands have been incorporated onto the boron atom in lieu of the "typical" fluorine atoms [22-24]. Introducing a nitrogen atom in place of the =CH-spacer enables the synthesis of *meso*-aza-analogs of BODIPY [25,26]. Although beyond the scope of this review, substituting boron with phosphorus has given rise to a new class of compounds (PODIPYs) [27-30]. BODIPY molecules may feature both identical and diverse types of peripheral substituents, and the symmetry of substitution degrees at specified positions, along with the arrangement of similar substituents of the same type and nature, can vary. Each type of substitution or their combination imparts a unique set of properties to the compounds. Notably, examples illustrating the effects of well-established, straightforward, and promising structural modification strategies on BODIPY properties have been extensively documented in the research conducted by Bumagina et al. [31].

Diverse synthetic methodologies are available for the fabrication of BODIPY dyes, encompassing halogenation [32,33], introduction of heteroatoms [34-37], fusion of aromatic [38], heteroaromatic [39], and non-aromatic rings [40-42], as well as conjugation with other luminescent dyes [43-44]. Organometallic cross-coupling reactions stand out as a versatile approach for accessing a plethora of essential compounds [45,46]. Employing this synthetic avenue, the  $\pi$ -conjugation network in BODIPY fluorophores can be expanded through aryl,

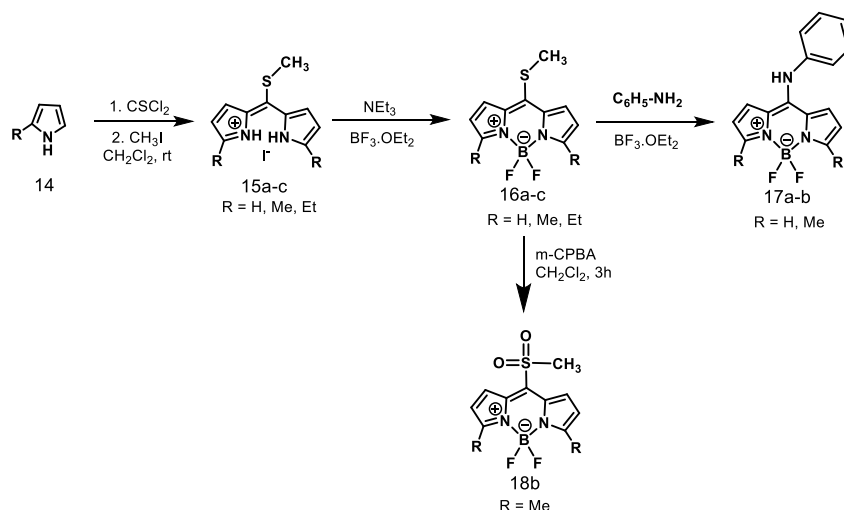
alkenyl, and alkynyl groups, thereby leading to fluorescence at longer wavelengths in comparison to alkylated BODIPYs [47,48], or via Knoevenagel condensation reactions (for alkenyl-substituted BODIPY) [49]. In our prior investigations, we synthesized 3,5-dialkylBODIPY [1-4(a-b)], 3,5-diaryl BODIPY (9c-g), and 3,5,8-triaryl BODIPY (10c-13g) dyes featuring diverse substituents at the 8-position. We prepared aryl BODIPY fluorophores by subjecting the substituent groups of aryl BODIPY fluorophores to Suzuki-Miyaura coupling reactions using various boronic acids. The electrochemical and photophysical properties of BODIPY fluorophores are significantly influenced by the substituent groups within the structure. Tailoring the absorption and emission profiles of BODIPY fluorophores is pivotal for their utility and application [1,2], (Fig. 3). We performed bromination reactions of the obtained BODIPY compounds to use them in further reactions. The article of the relevant study has been prepared for publication.



**Fig. 3.** Synthesis of boronic acids and dialkyl/diaryl/triaryl-BODIPY dyes. Reagents and conditions, i) 1,1'-azobis(cyclohexanecarbonitrile), 1,3-dibromo-5,5-dimethylhydantoin, in THF, -78°C, 3h. ii) DMAP, Et<sub>3</sub>N, Boc<sub>2</sub>O, rt, 8h. iii) 2M K<sub>2</sub>CO<sub>3</sub>(aq), Pd(Ph<sub>3</sub>P)<sub>4</sub> in MeOH/Toluene reflux overnight. iv) NaOCH<sub>3</sub> in MeOH, in THF v) 80°C, 1,2-dichloroethane vi) Et<sub>3</sub>N at 0°C, BF<sub>3</sub>·OEt<sub>2</sub> at rt.

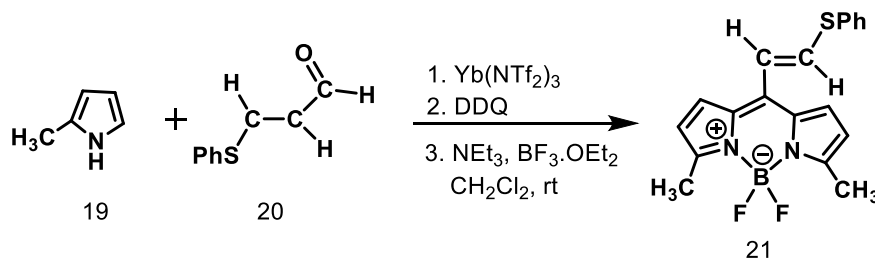
Additionally, the synthesis of heteroatom-containing BODIPY, known as Biemann

BODIPY, has also been introduced into the literature [36]. According to Biellmann et al.'s study, 8-(thiomethyl)-4,4-difluoro-3,5-disubstitue-4-bora-3a,4a-diaza-s-indacene 16a-c was synthesized [36]. Oxidizing 8-(thiomethyl)-4,4-difluoro-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene 16b with m-CPBA resulted in the formation of methylsulfonyl product 18b, yielding 10%. The thiomethyl group of compounds 16a and 16b is substituted by aniline, resulting in the formation of 8-(anilino) compounds, initially designated as 17a and 17b in our study. (Fig. 4)



**Fig. 4.** Synthesis pathway for Biellmann BODIPYs and their derivatives.

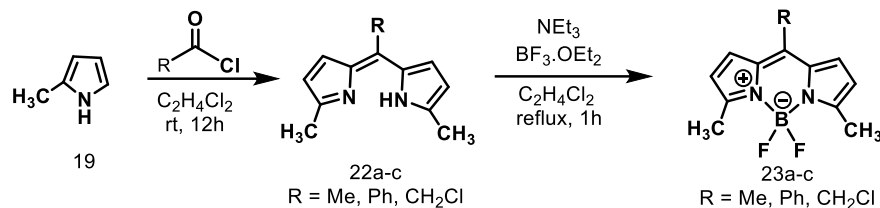
To assess the spectral characteristics of vinylic thioether, we synthesized 8-(2-thiophenylethene)-4,4-difluoro-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene 21 (Fig 5). The reaction of 2-methylpyrrole 19 with 3-(phenylthio)-propenal 20 in the presence of catalytic ytterbium (III) trifluoromethanesulfonamide yielded the non-isolated dipyrrolomethane, which was subsequently oxidized to the pyrrolomethene using DDQ. Indacene 21 was obtained in low yield through the reaction of boron trifluoride etherate in the presence of triethylamine. However, the spectral properties of vinylic thioether 21 did not meet our expectations, prompting us to make only limited attempts to synthesize compound 21 and its derivatives [36].



**Fig. 5.** Synthesis of 8-(2-thiophenylethene)-4,4-difluoro-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene.

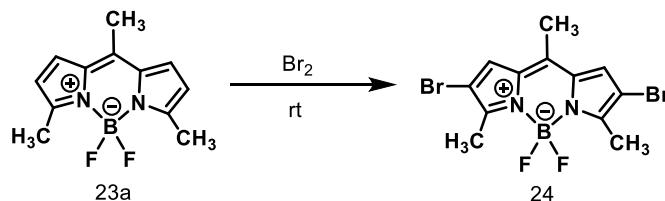
Treating pyrrolomethane 19 with acetyl chloride and boron trifluoride etherate in the presence of triethylamine produced 4,4-Difluoro-3,5,8-trimethyl-4-bora-3a,4a-diaza-s-indacene 22a. When benzoyl chloride and chloroacetyl chloride were substituted for acetyl chloride,

corresponding compounds 4,4-Difluoro-8-phenyl-3,5-dimethyl-4-bora-3a,4a-diazas-indacene 22b and 4,4-difluoro-8-chloromethyl-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene 22c were formed, respectively [36], (Fig. 6).



**Fig. 6.** Synthesis of 4,4-difluoro-8-substituted-3,5-dimethyl-4-bora-3a,4a-diaza-s-indacene 23a-c.

Bromination reactions hold prominence in synthetic chemistry [50-52]. Given the importance of brominated compounds as precursors in preparing organometallic reagents [53] and metal-mediated coupling reactions [54], we carried out bromination on 4,4-difluoro-3,5,8-trimethyl-4-bora-3a,4a-diaza-s-indacene 23a in a tube. This process yielded 1,2,6,7-tetrabromo-4,4-difluoro-3,5,8-trimethyl-4-bora-3a,4a-diaza-s-indacene 24 [36], (Fig. 7).



**Fig. 7.** Bromination of 4,4-difluoro-3,5,8-trimethyl-4-bora-3a,4a-diaza-s-indacene 23a.

## Conclusions

This study briefly discusses several important synthesis methodologies, significance, and applications of BODIPY compounds. The ease of derivatization of BODIPY compounds allows them to find various applications and uses. As a result, these types of BODIPY compounds, encountered in many fields, excite scientists for the production and application of new derivatives. In this preface, readers will encounter several important studies related to the derivatization of BODIPY compounds. Detailed synthesis steps, the diversity of application areas, and information regarding the photophysical and electrochemical properties of BODIPY compounds can be found in referenced articles. This brief article provides information on heteroatom-containing BODIPYs, synthesis and halogenation of the symmetrical BODIPY core, and Suzuki-Miyaura coupling reactions used to form substituent groups, which are the most studied and important aspects in derivatization.

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## SİMMETRİK BODIPY TÖRƏMƏLƏR ÜÇÜN İNNOVATİV SİNTEZ STRATEGİYƏLƏRİ

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### XÜLASƏ

BODIPY flüoresan boyalar, müxtəlif sintetik yollarla asanlıqla əldə edilə bilən xromoforların təqdim etdiyi geniş seçimlər sayəsində müasir fotokimyada cazibədar tədqiqat sahəsini təmsil edir. Həqiqətən də, ədəbiyyat indasən nüvəsi ətrafında cəmlənmiş çoxlu birləşmələrlə zəngindir. BODIPY boyalarının əvəzedici nümunəsi vasitəsilə spektroskopik xassələri modulyasiya etmək və ya yeni fotofiziki prosesləri başlatmaq qabiliyyəti bu flüoroforlar üçün elmi və texnoloji tətbiqlərin əhatəsini əhəmiyyətli dərəcədə genişləndirmişdir. Bu gün də geniş şəkildə istifadə edilən və sadə modifikasiyalarla asanlıqla əldə edilən BODIPY nüvələri çox yönlü xüsusiyyətlərinə görə geniş tətbiq tapır. Bu xüsusiyyətlər BODIPY birləşmələrini həm tətbiq yönümlü, həm də cəlbedici edir. Tədqiqat qrupumuz BODIPY birləşmələrinin sintezi, Suzuki-Miyaura birləşmə reaksiyaları vasitəsilə BODIPY nüvəsinin müxtəlif mövqələrdən törəməsi və barmaq izinin aşkarlanmasında potensial tətbiqlərlə BODIPY törəmələrinin sintezi ilə bağlı

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tədqiqatların aparılmasında maraqlıdır. Bu araşdırmanın məqsədi ümumi BODIPY törəmələrinin əsas kimyası, sintezi və spektroskopik xüsusiyyətlərini ümumiləşdirməkdir.

**Açar sözlər:** BODIPY, Fluorofor, Sintez, Boyalar, Suzuki-Miyaura Coupling, Halogenləşmə.

## УДИВИТЕЛЬНЫЕ СИНТЕТИЧЕСКИЕ СТРАТЕГИИ ДЛЯ ПРОИЗВОДНЫХ СИММЕТРИЧНЫХ ТЕЛОВ

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### РЕЗЮМЕ

Флуоресцентные красители BODIPY представляют собой увлекательную область исследований в современной фотохимии благодаря широкому спектру возможностей их хромофора, легко доступных различными синтетическими путями. Действительно, литература изобилует обширным набором соединений, сосредоточенных вокруг индаценового ядра. Способность модулировать спектроскопические свойства или инициировать новые фотофизические процессы посредством схемы замещения красителей BODIPY значительно расширила сферу научного и технологического применения этих флуорофоров. Ядра BODIPY, которые до сих пор широко используются и легко модифицируются посредством простых модификаций, находят широкое применение благодаря своим универсальным характеристикам. Эти особенности делают составы BODIPY работоспособными и привлекательными. Наша исследовательская группа заинтересована в проведении исследований, связанных с синтезом соединений BODIPY, дериватизацией ядра BODIPY из разных положений посредством реакций сочетания Сузуки-Мияуры, а также синтезом производных BODIPY с потенциальным применением в обнаружении отпечатков пальцев. Целью данного исследования является обобщение фундаментальной химии, синтеза и спектроскопических свойств распространенных производных BODIPY.

**Ключевые слова:** BODIPY, флуорофор, синтез, красители, соединение Сузуки-Мияуры, галогенирование.