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# Synthesis of 2-mesityl-3-methylpyrrole via the Trofimov reaction for a new BODIPY with hindered internal rotation

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**Abstract**—The reaction of *E*-ethylmesitylketoxime with acetylene in the system KOH/DMSO (the Trofimov reaction) (70–74 °C, 3 h, atmosphere pressure) affords 2-mesityl-3-methylpyrrole (23%), 2-mesityl-3-methyl-1-vinylpyrrole (8%), *Z*- (5%) and *E*- (2%) isomers of *O*-vinylethylmesitylketoxime. Initial ethylmesitylketoxime was prepared in two ways: via very slow oximation of ethylmesitylketone in 30% yield after 8 months, and, more efficiently, by oximation of ethylmesitylketimine hydrochloride derived from bromomesitylene in several steps. 2-Mesityl-3-methylpyrrole was used for the synthesis of 4,4-difluoro-2,6-dimethyl-3,5,8-trimesityl-4-bora-3a,4a-diaza-*s*-indacene with mesityl substituents having hindered internal rotation and preventing π-stacking at high concentrations. The latter factor enables the fluorescence of crystals of the prepared BODIPY, a feature that was not previously documented for such molecules.


## 1. Introduction

For more than 30 years since their discovery[1] BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) derivatives have enjoyed wide popularity among experts in chemistry,[2] physics,[3] biology[4] and related fields[5] for their exceptional optical properties.

During the practical realization of various devices based on BODIPY dyes, when high concentrations are needed, intermolecular π-stacking can cancel out their advantages such as high fluorescence quantum yields and intensities.[6] To the best of our knowledge, so far, no fluorescent crystals of BODIPY have been reported, although the pigments (solid dyes) based on them, due to their anticipated high brightness and enhanced resistance to photobleaching, might find extensive application. Therefore, the design of new boradiazaindacenes with hindered π-stacking, which is considered as the principal culprit behind the loss of fluorescence in crystalline form, has remained a challenge.

Herein, we describe a synthesis of the first representatives of boradiazaindacenes, which are fluorescent in a crystalline form. The main idea was to develop an approach to structures with bulky mesityl substituents attached to the BODIPY core, distorting overall planarity and thus hampering the π-stacking at high concentrations. Furthermore, the hindered internal rotation of mesityl rings reduces non-radiative relaxation of excited states, hence decreasing fluorescence quantum yields.[7]

## 2. Results and discussion

As a synthetic target 4,4-difluoro-2,6-dimethyl-3,5,8-trimesityl-4-bora-3a,4a-diaza-*s*-indacene **1** was chosen because its 2,6-methyl groups could additionally hinder internal rotation and force benzene rings out of the molecular plane more efficiently.

The disconnection of **1** (reverse to the synthesis of BODIPY via the reaction of boron trifluoride etherate with dipyrromethenes derived from pyrroles and aldehydes[8]) leads to dipyrromethene **2** and then to 2-mesityl-3-methylpyrrole **3** and 2,4,6-trimethylbenzaldehyde **4** (Scheme 1).

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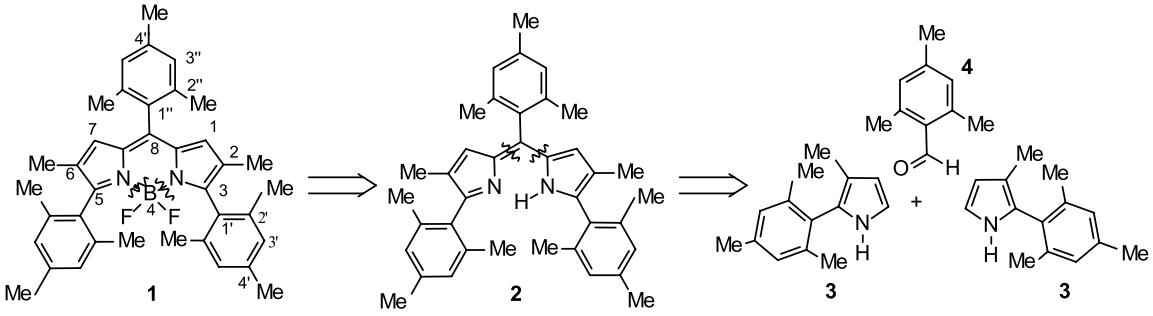
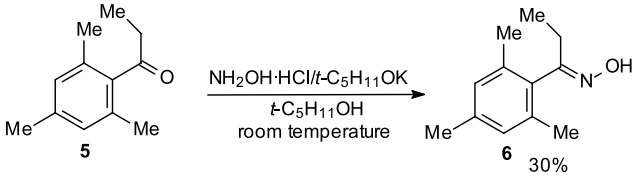


**Scheme 1.**

To accomplish this synthetic sequence, we had to develop an approach to pyrrole **3**. The Trofimov reaction (reaction of ketoximes with acetylene in superbasic media affording pyrroles and *N*-vinyl pyrroles)[9,10] might be useful for approaching **3** from ethylmesitylketoxime **6**. However, until the present work there were no examples of a successful application of this reaction to highly hindered ketoximes and this exploration could shed light on whether such ketoximes are capable of affording pyrroles upon reaction with acetylene.

Meanwhile, at the very beginning of the study we encountered a serious problem of very low reactivity of ethylmesitylketone **5** towards hydroxylamine. Oximation by refluxing mixtures of ketones and hydroxylamine hydrochloride in pyridine, effective in the synthesis of some hindered oximes,[11] proved to be inefficient in the case of **5** (even when microwave activation was applied) and yielded only trace amounts of **6**. The 'lethargic' oximation, although it gave mesitylmethylketoxime from mesitylmethylketone in 98% yield in 28 days,[12] after application to **5** afforded its oxime **6** (mostly *E*-isomer) only in 30% yield after 8 months (Scheme 2).



**Scheme 2.**

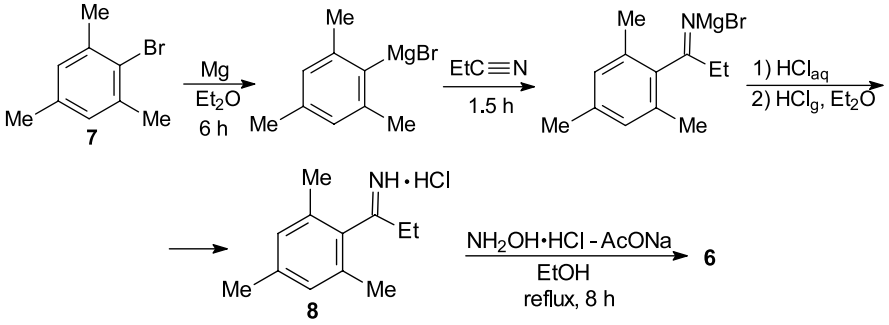
It is obvious that the mesityl group blocks the carbonyl carbon in ketone **5**, and the blockage becomes much more pronounced on passing from mesitylmethylketone to ethylmesitylketone **5**.

To develop a better access to the ketoxime **6** we, therefore, attempted the oximation of ethylmesitylimine hydrochloride **8** similar to that used previously for the synthesis of some other mesityl oximes.[13] This procedure, though multistep, allowed us to approach **6** from bromomesitylene **7** in 39% yield in a matter of 2 days (Scheme 3).

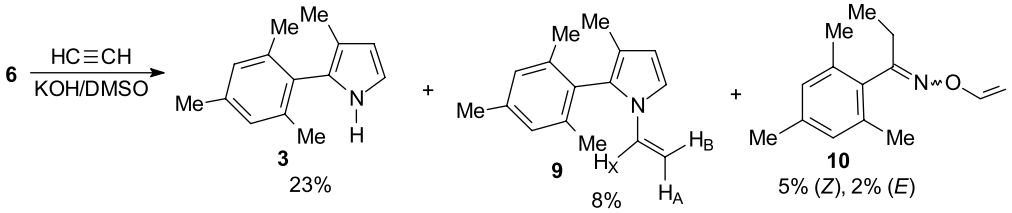
The reaction of the *E*-isomer of oxime **6** with acetylene in the KOH/DMSO superbasic system (70–74 °C, 3 h, atmospheric pressure) gave 2-mesityl-3-methylpyrrole **3** (23%), 2-mesityl-3-methyl-1-vinylpyrrole **9** (8%), *Z*- (5%) and *E*- (2%) isomers of *O*-vinylethylmesitylketoxime **10** (Scheme 4).

A short contact (70 °C, 5 min) of the *E*-isomer of **6** with acetylene in the KOH/DMSO system under increased acetylene pressure (initial pressure 17 atm) led to *O*-vinylketoxime **10** (23%) (*E*–*Z*∼1:2) and pyrrole **3** (12%) ($^1$H NMR).

Interestingly, the *E*-isomer of oxime **6** was transformed mainly to the *Z*-isomer of *O*-vinylketoxime **10**. This is a striking contrast to, for example, methylphenylketoxime, which under similar conditions gave only the *E*-isomer of *O*-vinylmethylphenylketoxime.[14] Heating of the *E*-isomer of the oxime **6** at 80 °C for 1 h in KOH/DMSO system resulted in the formation of 1:1 mixture of its *E*- and *Z*-isomers. Thus, the *E*–*Z* isomerization of **6** occurs under the reaction conditions, and steric hindrances imparted on the oxime hydroxyl by both mesityl and ethyl groups in **6** are similar. The specific behaviour of the oxime **6** can be rationalized assuming twisting of mesityl ring out of the C–C=N–O plane. When twisted, it strongly hinders the C=N (C=O) carbon (as evident from the difficulty of oximation of mesityl ketones) and, on the other hand, makes



**Scheme 3.**




**Scheme 4.**

easier the approach of acetylene to the oximate anionic centre generated under superbasic conditions.

The twisted mesityl group might also pre-organize acetylene via either π-stacking or π-hydrogen bonding (Fig. 1),[15] thus making formation of *Z*-isomer of *O*-vinylketoxime **10** entropicaly more favourable.

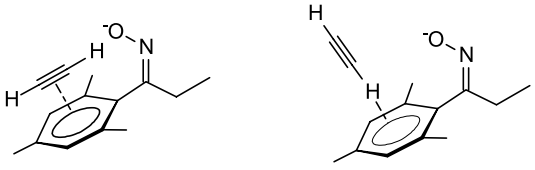


**Figure 1.**

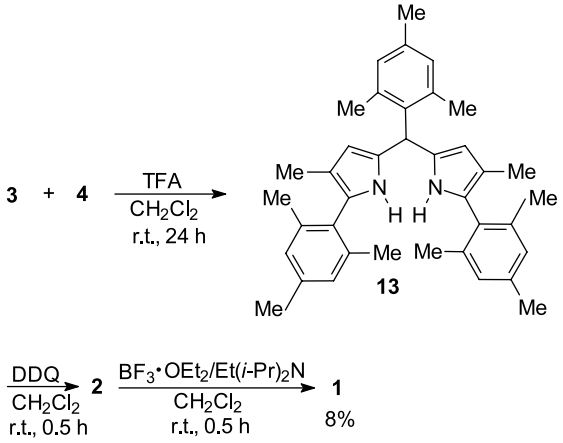
Heating of a DMSO-$d_6$ solution of *O*-vinylketoxime **10** at 120 °C (5 min) leads to its rearrangement to the pyrrole **3** (yield ~50%, $^1$H NMR) in the absence of a base, similar to the rearrangement of 5-(1-vinyloxyiminoethyl)[2,2]paracyclophane to the appropriate pyrrole.[16]

The isolation of the *O*-vinylketoxime **10** from the reaction mixture is remarkable because so far only *O*-vinyl (3-indolyl)ketoximes with an α-methylene group (different from that constituting methyl) have been known to be stable under the reaction conditions.[17] Presumably, the stability of the *O*-vinylketoximes with α-methylene group is due to either increased electron donation of $R^1$ substituent (e.g., 3-indolyl) or a steric effect inhibiting the [1,3] hydrogen shift (Scheme 5) assumed as a key step of the transformation of *O*-vinylketoximes to pyrroles.[10]

Thus, the twisted mesityl group, due to its size, may interfere with the [1,3] hydrogen shift in **10** leading to *O*-vinylhydroxylamine **11** ($R^1$=Mes, $R^2$=Me), as well as [3,3]-sigmatropic rearrangement of the latter to iminoaldehyde **12** by impeding redistribution of electron density during the rearrangement.

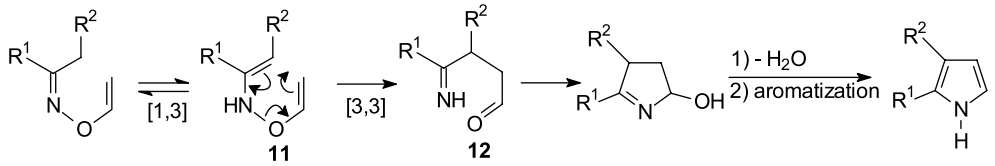
The distinction between the *E*- and *Z*-isomers of oxime **6** and *O*-vinyloxime **10** was made based on the difference in $^1$H NMR shifts of their methylene protons due to the anisotropic influence of the oxime oxygen.[18] These protons in their *E*-isomers (*syn* disposition to oxime oxygen) are shifted downfield (2.65 and 2.70 ppm for oxime and *O*-vinyloxime, respectively) relative to their *Z*-isomers (2.42 and 2.46 for oxime and *O*-vinyloxime, respectively). As compared to other *N*-vinylpyrroles, the resonance of $H_X$ proton in **9** residing in the shielding cone of the twisted mesityl aromatic ring is shifted considerably upfield (6.27 ppm).

Pyrrole **3** was introduced into the reaction with 2,4,6-trimethylbenzaldehyde **4** catalysed by trifluoroacetic acid (TFA). Generated dipyrromethane **13** was further oxidized in situ with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to dipyrromethene **2**. The reaction of **2** with boron trifluoride etherate in the presence of diisopropylethylamine afforded the target BODIPY **1** in 8% yield.




Interestingly, the bulky mesityl substituent in aldehyde **4** did not block its reaction with pyrrole **3**, although the reaction actually involves attack of secondary 2-pyrrolic nucleophile at the hindered carbonyl carbon in **4**.

The optical absorption of the BODIPY **1**, dissolved in spectrometric grade dichloromethane (DCM), had the $S_0$–$S_1$ transition maximum at 543 nm with an extinction coefficient 40,150 $LM^{-1}\,cm^{-1}$. The emission maximum was observed at 559 nm with a fluorescence quantum yield 95% (Rhodamine in ethanol was used as a reference). The fluorescence lifetime was 8.5 ns, which is longer than any




**Scheme 5.**

reported lifetime for such molecules. Submicrometric crystals of **1** obtained after evaporation of DCM exhibited fluorescence with lifetime of 1.5 ns that is in striking contrast to previously known boradiazaindacenes for which fluorescence in crystals had not been reported. The use of 1,2-dichlorobenzene as a solvent gave slower evaporation and smaller crystallized fluorescent particles with longer lifetimes (3–4 ns). The detailed description of the study of the fluorescent properties of the synthesized BODIPY **1** will be described elsewhere.

## 3. Conclusion

An approach to a new BODIPY with bulky mesityl substituents preventing the molecule from π-stacking at high concentrations and possessing hindered internal rotation decreasing non-radiative relaxation of excited states was developed. The precursor of the boradiazaindacene **1**, 2-mesityl-3-methylpyrrole **3**, was prepared via the Trofimov reaction. It was demonstrated that the mesityl group imposes less steric hindrance on the nucleophilic addition of ethylmesitylketoxime to acetylene than phenyl group. However, the presence of mesityl in *O*-vinylethylmesitylketoxime inhibits its rearrangement to appropriate pyrrole. This was not the case for most known *O*-vinylketoximes with α-methylene groups.

## 4. Experimental

### 4.1. General

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 400 (400.13 and 100.61 MHz, respectively) and a Bruker ultrashield 300 AC (300.1 and 75.4 MHz, respectively) instruments in $CDCl_3$ using HMDS as an internal standard. IR spectra were recorded on a Bruker IFS 25 instrument. Absorption spectra were obtained using a UV–vis Varian CARY 500 spectrophotometer. Steady-state excitation and emission spectra were measured on a SPEX Fluorolog-3 (Jobin-Yvon). A right-angle configuration was used. Optical density of the samples was less than 0.1 to avoid reabsorption artefacts. The fluorescence decay curves were obtained with a time-correlated single-photon-counting method using a titanium-sapphire laser pumped by an argon ion laser. The Levenberg–Marquardt algorithm was used for non-linear least squares fits.

**4.1.1. Ethylmesitylketone (5).** The ketone **5** was prepared in 84% yield according to the procedure.[19] Transparent colourless liquid; bp 116–121 °C (5 mm); $n_D^{22}=1.5093$; $^1$H NMR δ (ppm) 6.80 (s, 2H, $H_m$), 2.67 (q, 2H, $^3J_{H1H2(Et)}=7.4$ Hz, C$H_2$Me), 2.25 (s, 3H, $Me_p$), 2.15 (s, 6H, $Me_o$), 1.17 (t, 3H, $CH_2Me$); $^{13}$C NMR δ (ppm) 211.4 (C=O), 140.0 ($C_i$), 138.2 ($C_o$), 132.5 ($C_p$), 128.5 ($C_m$), 38.0 (*C*$H_2$Me), 21.1 ($Me_p$), 19.1 ($Me_o$), 7.7 ($CH_2Me$); IR (cm$^{-1}$, film) 2975, 2936, 2878, 2735, 1700, 1611, 1575, 1457, 1413, 1378, 1342, 1297, 1265, 1224, 1156, 1077, 1036, 1014, 961, 930, 851, 801, 740, 723, 592.

**4.1.2. Ethylmesitylketimine hydrochloride (8).** This protocol represents a modified method.[13] To a stirred solution of mesityl magnesium bromide prepared from magnesium turnings (5.00 g, 205.8 mmol) and bromomesitylene **7** (30.00 g, 150.7 mmol),[20] a mixture of propionitrile (8.25 g, 149.8 mmol) and diethyl ether (10 mL) was added over 30 min and the obtained white suspension was additionally stirred for 1 h at room temperature. After that a 13% solution of hydrochloric acid (100 mL) was added for 1 h to the stirred reaction mixture cooled in a water bath with subsequent stirring for 1 h. The acid was neutralized with a solution of NaOH (14.00 g, 350.1 mmol) in water (30 mL), and from the resultant mixture ethylmesitylketone imine was extracted with diethyl ether (5×40 mL). The combined extracts were dried over $K_2CO_3$ and evaporated to the volume of 70 mL. Dry hydrogen chloride was passed through the etheral solution to precipitate the ketimine hydrochloride **8** which was collected by filtration and dried. As a result, **8** (15.01 g, 47%) was obtained as a yellowish solid; mp 194–196 °C; $^1$H NMR δ (ppm) 13.73 (broad s, 1H, $NH_E$), 13.36 (broad s, 1H, $NH_Z$), 6.90 (s, 2H, $H_m$), 3.09 (q, 2H, $^3J_{H1H2(Et)}=7.6$ Hz, C$H_2$Me), 2.27 (s, 9H, $Me_o$, $Me_p$), 1.32 (t, 3H, $^3J_{H1H2(Et)}=7.6$ Hz, $CH_2Me$); $^{13}$C NMR δ (ppm) 196.3 (C=N), 141.3 ($C_i$), 133.7 ($C_o$, $C_p$), 129.4 ($C_m$), 32.6 (*C*$H_2$Me), 21.2 ($Me_p$), 19.9 ($Me_o$), 10.4 (*C*$H_2$Me); IR (cm$^{-1}$, KBr) 3372, 3250-2250, 2017, 1687, 1611, 1556, 1456, 1382, 1297, 1187, 1120, 1020, 909, 854, 717.

**4.1.3. Ethylmesitylketoxime (6).** This procedure represents a modified protocol.[13] A mixture of **8** (10.00 g, 47.2 mmol), $NH_2OH\cdot HCl$ (6.56 g, 94.5 mmol), $CH_3COONa$ (9.68 g, 118.0 mmol) and 96% ethanol (160 mL) was refluxed for 8 h. After cooling, $K_2CO_3$ (10.00 g, 72.4 mmol) and water (5 mL) were added to the solution with subsequent stirring for 1 h to neutralize nascent acetic acid. Then diethyl ether (200 mL) was added; the precipitate was filtered off and washed with diethyl ether. The organic solutions were combined and evaporated to dryness in vacuo to give viscous amber coloured liquid (7.37 g, 82%) consisting of the *E*- and *Z*-isomers of ethylmesitylketoxime **6** (*E*–*Z*∼3:1) ($^1$H NMR) and crystallizing in several hours. The *E*-isomer of **6** was isolated by column chromatography (basic $Al_2O_3$, petroleum ether–diethyl ether).

**4.1.4. *E*-isomer of 6.** White crystals, mp 80–82 °C; $^1$H NMR δ (ppm) 9.0 (broad s, 1H, OH), 6.83 (s, 2H, $H_m$), 2.65 (q, 2H, $^3J_{H1H2(Et)}=7.6$ Hz, C$H_2$Me), 2.26 (s, 3H, $Me_p$), 2.18 (s, 6H, $Me_o$), 0.93 (t, 3H, $^3J_{H1H2(Et)}=7.6$ Hz, $CH_2Me$); $^{13}$C NMR δ (ppm) 162.0 (C=N), 137.6 ($C_i$), 136.2 ($C_o$), 132.8 ($C_p$), 128.3 ($C_m$), 22.8 (*C*$H_2$Me), 21.1 ($Me_p$), 19.8 ($Me_o$), 9.7 ($CH_2Me$); IR (cm$^{-1}$, KBr) 3240, 2968, 2920, 1649, 1612, 1574, 1488, 1458, 1374, 1321, 1302, 1283, 1171, 1071, 1038, 972, 955, 892, 851, 764, 744, 726, 668, 592, 579.

**4.1.5. *Z*-isomer of 6.** White crystals. $^1$H NMR δ (ppm) 8.7 (broad s, 1H, OH), 6.86 (s, 2H, $H_m$), 2.43 (q, 2H, $^3J_{H1H2(Et)}=7.3$ Hz, C$H_2$Me), 2.26 (s, 3H, $Me_p$), 2.15 (s, 6H, $Me_o$), 1.15 (t, 3H, $CH_2Me$); $^{13}$C NMR δ (ppm) 160.3 (C=N), 137.8 ($C_i$), 134.1 ($C_o$), 132.1 ($C_p$), 128.2 ($C_m$), 28.6 (*C*$H_2$Me), 21.1 ($Me_p$), 19.5 ($Me_o$), 10.3 ($CH_2Me$)

The 'lethargic' oximation of **5** was carried out similarly to mesitylmethylketone.[12] However, 8 months were required

for the reaction to afford the oxime **6** (mainly *E*-isomer) in only 30% preparative yield.

### 4.2. 2-Mesityl-3-methylpyrrole (3), 2-mesityl-3-methyl-1-vinylpyrrole (9) and *O*-vinylethylmesitylketoxime (10)

A mixture of ethylmesitylketoxime **6** (1.00 g, 5.2 mmol), fine-powdered $KOH \cdot 0.5H_2O$ (0.34 g, 5.2 mmol) and DMSO (15 mL) was stirred under acetylene atmosphere at 70–74 °C for 3 h. After cooling to room temperature the mixture was diluted with water (10 mL) and extracted with diethyl ether (4×10 mL). The ether extracts were washed with water (4×5 mL) and dried over anhydrous $K_2CO_3$. The residue obtained after distilling off the solvent was chromatographed on column (basic $Al_2O_3$, petroleum ether–diethyl ether) to yield 2-mesityl-3-methylpyrrole **3** (23%), 2-mesityl-3-methyl-1-vinylpyrrole **9** (8%), *Z*- (5%) and *E*-(2%) isomers of **10**.

The reaction of oxime **6** with acetylene under high pressure was carried out as follows: ethylmesitylketoxime **6** (0.50 g, 2.6 mmol), $KOH \cdot 0.5H_2O$ (0.34 g, 5.2 mmol) and DMSO (20 mL) were charged in a 250-mL steel rotating autoclave, saturated with acetylene at room temperature (initial acetylene pressure 17 atm), heated to 70 °C and kept at this temperature for 5 min. After cooling and discharge, the reaction mixture was diluted with 40 mL of water and extracted with diethyl ether (5×10 mL). The extracts were washed with water (4×5 mL) and dried over $K_2CO_3$. After evaporation of the ether, a red liquid (0.50 g) containing ($^1$H NMR) pyrrole **3** (12%) and *O*-vinylketoxime **10** (*E*–*Z*∼1:2) (23%) was obtained.

**4.2.1. Compound 3.** White crystals, mp 74–76 °C; $^1$H NMR $\delta$ (ppm) 7.65 (broad s, 1H, NH), 6.91 (s, 2H, $H_m$), 6.73 (t, 1H, $J_{H1H4H5}$=2.7 Hz, $H_5$), 6.12 (t, 1H, $J_{H1H4H5}$=2.7 Hz, $H_4$), 2.30 (s, 3H, $Me_p$), 2.03 (s, 6H, $Me_o$), 1.86 (s, 3H, $Me_{Pyr}$); $^{13}$C NMR $\delta$ (ppm) 139.2 ($C_p$), 137.7 ($C_o$), 130.1 ($C_i$), 127.9 ($C_m$), 126.8 ($C_2$), 116.2 ($C_3$), 115.9 ($C_5$), 109.8 ($C_4$), 21.1 ($Me_p$), 20.1 ($Me_o$), 11.2 ($Me_{Pyr}$); IR (cm$^{-1}$, KBr) 3423, 2917, 2868, 1640, 1610, 1582, 1569, 1539, 1509, 1488, 1467, 1452, 1375, 1278, 1249, 1157, 1099, 1081, 1063, 1052, 1000, 897, 852, 821, 745, 719, 689, 631, 570, 554, 531, 494; EIMS: *m*/*z* calculated for $C_{14}H_{17}N$: 199.3, found: 199 ($M^+$).

**4.2.2. Compound 9.** A transparent colourless liquid, $n_D^{19}$=1.6815; $^1$H NMR $\delta$ (ppm) 7.02 (d, 1H, $^3J_{H4H5}$=3.0 Hz, $H_5$), 6.91 (s, 2H, $H_m$), 6.27 (dd, 1H, $H_X$, $^3J_{AX}$=9.0 Hz, $^3J_{BX}$=15.8 Hz), 6.15 (d, 1H, $^3J_{H4H5}$=3.0 Hz, $H_4$), 4.90 (d, 1H, $^3J_{BX}$=15.8 Hz, $H_B$), 4.33 (d, 1H, $^3J_{AX}$=9.0 Hz, $H_A$), 2.31 (s, 3H, $Me_p$), 1.95 (s, 6H, $Me_o$), 1.79 (s, 3H, $Me_{Pyr}$); $^{13}$C NMR $\delta$ (ppm) 139.7 ($C_p$), 138.1 ($C_o$), 131.2 ($C_\alpha$), 128.9 ($C_i$), 128.1 ($C_2$), 127.9 ($C_m$), 117.4 ($C_5$), 115.0 ($C_3$), 111.5 ($C_4$), 95.2 ($C_\beta$), 22.8 ($Me_p$), 21.2 ($Me_o$), 14.2 ($Me_{Pyr}$); IR (cm$^{-1}$, film) 2922, 2856, 1640, 1613, 1582, 1491, 1472, 1419, 1388, 1370, 1305, 1229, 1201, 1160, 1073, 1034, 1015, 989, 966, 851, 761, 723, 693, 677, 593. EIMS: *m*/*z* calculated for $C_{16}H_{19}N$: 225.3, found: 225 ($M^+$).

**4.2.3. *Z*-isomer of 10.** A transparent colourless liquid, $n_D^{19}$=1.5218; $^1$H NMR $\delta$ (ppm) 6.86 (s, 2H, $H_m$), 6.80 (dd, 1H, $^3J_{AX}$=6.7 Hz, $^3J_{BX}$=14.1 Hz, $H_X$), 4.52 (dd, 1H, $^3J_{BX}$=14.1 Hz, $^2J_{AB}$=1.3 Hz, $H_B$), 4.01 (dd, 1H, $^3J_{AX}$=6.7 Hz, $^2J_{AB}$=1.3 Hz, $H_A$), 2.46 (q, 2H, $^3J_{H1H2(Et)}$=7.5 Hz, C*H*$_2$Me), 2.27 (s, 3H, $Me_p$), 2.13 (s, 6H, $Me_o$), 1.15 (t, 3H, $^3J_{H1H2(Et)}$=7.5 Hz, CH$_2$*Me*); $^{13}$C NMR $\delta$ (ppm) 163.0 (C=N), 152.5 ($C_\alpha$), 137.7 ($C_p$), 133.7 ($C_o$), 132.4 ($C_i$), 128.1 ($C_m$), 87.5 ($C_\beta$), 28.8 ($CH_2$), 21.1 ($Me_p$), 19.5 ($Me_o$), 10.4 (CH$_2$*Me*); IR (cm$^{-1}$, film) 2975, 2922, 1643, 1620, 1576, 1459, 1380, 1306, 1187, 1152, 1088, 1055, 981, 949, 933, 873, 850, 833, 693, 604. Anal. calcd for $C_{14}H_{19}NO$: C 77.38, H 8.81, N 6.45; found: C 77.51, H 8.92, N 6.80.

**4.2.4. *E*-isomer of 10.** A transparent colourless liquid; $^1$H NMR $\delta$ (ppm) 6.98 (dd, 1H, $^3J_{AX}$=6.8 Hz, $^3J_{BX}$=14.2 Hz, $H_X$), 6.86 (s, 2H, $H_m$), 4.58 (dd, 1H, $^3J_{BX}$=14.2 Hz, $^2J_{AB}$=1.4 Hz, $H_B$), 4.09 (dd, 1H, $^3J_{AX}$=6.8 Hz, $^2J_{AB}$=1.4 Hz, $H_A$), 2.70 (q, 2H, $^3J_{H1H2(Et)}$=7.6 Hz, C*H*$_2$Me), 2.26 (s, 3H, $Me_p$), 2.20 (s, 6H, $Me_o$), 0.96 (s, 3H, CH$_2$*Me*); $^{13}$C NMR $\delta$ (ppm) 164.6 (C=N), 153.1 ($C_\alpha$), 138.1 ($C_p$), 136.0 ($C_o$), 132.0 ($C_i$), 128.5 ($C_m$), 87.4 ($C_\beta$), 24.1 (*C*H$_2$Me), 21.1 ($Me_p$), 19.9 ($Me_o$), 9.9 (CH$_2$*Me*).

### 4.3. Thermal *E*–*Z* isomerisation of ethylmesitylketoxime (6)

A mixture of *E*-isomer of **6** (0.05 g, 0.3 mmol), fine-powdered $KOH \cdot 0.5H_2O$ (0.05 g, 0.8 mmol) and DMSO (5 mL) was stirred at 80 °C for 1 h. After cooling, the mixture was neutralized with dry ice, diluted with water (5 mL) and extracted with diethyl ether (3×10 mL). The ether extracts were washed with water (3×3 mL) and dried over $K_2CO_3$. After evaporation of the ether, a viscous mass (0.04 g) consisting of *E*- and *Z*-isomers of **6** (*E*:*Z*∼1:1) ($^1$H NMR) was obtained.

### 4.4. Thermal rearrangement of *Z*-isomer of *O*-vinylethylmesitylketoxime (10) into 2-mesityl-3-methylpyrrole (3)

An NMR ampule containing a solution of *Z*-isomer of **10** (∼0.05 g) in DMSO-$d_6$ (0.5 mL) was heated in the NMR spectrometer at 120 °C for 10 min and kept at this temperature until disappearance of the signals of the vinyl group of **10** (5 min). During the heating the intensity of the *O*-vinyl group signals decreased with a simultaneous increase in the intensity of the signals of pyrrole **3**. In addition to signals of **3** (yield ∼50%, $^1$H NMR) heating gave rise to unidentified singlets at 9.72 and 7.06 ppm with half intensities of the pyrrole ring protons in **3** and singlet at 2.44 ppm with the threefold intensity of the latter.

**4.4.1. 4,4-Difluoro-2,6-dimethyl-3,5,8-trimesityl-4-bora-3a,4a-diaza-*s*-indacene (1).** Pyrrole **3** (0.35 g, 1.8 mmol) and 2,4,6-trimethylbenzaldehyde **4** (0.13 g, 0.9 mmol) were dissolved in degassed $CH_2Cl_2$ (50 mL), then two drops of TFA were added, and the obtained orange solution was stirred for 24 h under argon at room temperature. TLC analysis ($SiO_2$ on aluminium plates, $CH_2Cl_2$–petroleum ether=1:1) of the reaction mixture showed the presence of initial pyrrole **3**, so an additional 0.025 g of aldehyde **4** and two drops of TFA were added and stirring was continued for some time until TLC showed no stain of pyrrole **3**. Then DDQ (0.19 g, 0.8 mmol) was added and the reaction mixture was stirred for 0.5 h. After that, diisopropylethylamine

(2 mL, 1.48 g, 11.5 mmol) and boron trifluoride etherate (2 mL, 2.24 g, 15.8 mmol) were added with subsequent stirring of the obtained fluorescent solution for 0.5 h. After evaporation of the solvent at ambient temperature in vacuo the residue (was flash chromatographed under nitrogen on silica ($CH_2Cl_2$–petroleum ether = 1:3) to afford 0.04 g (8%) of BODIPY **1**. A red powder, it does not melt but decomposes above 280–300 °C; $^1$H NMR $\delta$ (ppm) 7.00 (s, 2H, $H_{3''}$), 6.84 (s, 4H, $H_{3'}$), 6.42 (s, 2H, $H_{1,7}$), 2.40 (s, 3H, $Me_{4''}$), 2.26 (s, 6H, $Me_{2''}$ or $Me_{4'}$), 2.24 (s, 6H, $Me_{4'}$ or $Me_{2''}$), 2.06 (s, 12H, $Me_{2'}$), 1.65 (s, 6H, $Me_{2,6}$); $^{13}$C NMR $\delta$ (ppm) 157.8, 141.6, 138.3, 137.4 ($CH_{arom}$), 136.8, 134.2, 131.1, 129.0, 128.5, 128.1 ($CH_{arom}$), 127.8 ($CH_{arom}$), 127.0, 29.8 ($Me_{4''}$), 21.4 ($Me_{4'}$), 20.1 ($Me_{2'}$ or $Me_{2''}$), 20.0 ($Me_{2''}$ or $Me_{2'}$), 11.0 ($Me_{2,6}$). EIMS: *m/z* calculated for $C_{38}H_{41}BF_2N_2$: 574.6, found: 526 $[M-BF_2]^+$.

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