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Convenient synthesis of photochromic symmetrical or unsymmetrical bis(heteroaryl)maleimides via the Suzuki–Miyaura cross-coupling reaction

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Abstract—A general method for the synthesis of symmetrical or unsymmetrical bis(heteroaryl)maleimides by a one-pot procedure involving Suzuki–Miyaura cross-coupling sequence was developed on the basis of the reaction of 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione with cyclic boronate esters using $PdCl_2$(dppf) as the catalyst. Photochromic properties of the products were examined.

1. Introduction

In recent years, organic photochromic compounds have received increasing attention due to their potential applications for optoelectronic devices.[1] So far, various photochromic families, such as spiropyranes,[2] spirooxazines,[3] azobenzenes,[4] fulgides,[5] and diarylethenes[6] have been developed so as to satisfy the specific needs of each new device. 1,2-Diheteroarylethenes exhibit reversible variations in their physical and chemical characteristics, between their ring-open and ring-closed forms, such as fluorescence emission,[7] infrared absorption,[8] optical rotation,[9] redox potential,[10] and magnetism[11] are considered as promising carriers of three-dimensional optical memory.[12]

In this work, we attempt to prepare symmetrical or unsymmetrical bis(heteroaryl)maleimides by treating of 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione with cyclic boronate esters using $PdCl_2$(dppf) as catalyst, in a one-pot process. The accessibility of new compounds of this class is a steadily growing field due to new possible applications.

2. Results and discussion

This paper describes total synthesis of symmetrical or unsymmetrical substituted diheteroarylmaleimides as having a number of advantages over existing processes and the potential to increase the rate of production.

These processes fall short of the ideal for several reasons: (1) Perkin condensation of aryl acetic acid with glyoxylic acids[13] (or their derivatives[14]), which are relatively expensive complexes and of limited availability, have been plagued with a poor overall yield; (2) same limitation can be noted with base hydrolysis of diheteroarylmaleonitrile (or fumaronitrile), followed by imidization with alkylamine leading to symmetrical and unsymmetrical structures;[15] (3) Friedel–Crafts reaction of thiophene and thieno[3,2-*b*]thiophene derivatives with squaric acid[16] derivative, which is not readily available and of high cost, followed by subsequent oxidation and imidization is limited to symmetrical maleimides.[17] It is worth noting too that accessibility to 2,4,5-trimethylthiophene or 2-methylbenzo[*b*]thiophene analogs was not allowed.

Besides the above classical methods, few examples of palladium-catalyzed reactions, which are one of the most reliable tools to obtain symmetrical or unsymmetrical biaryls, have also been reported.

Correia and co-workers have used an ingenious Heck arylation of maleic anhydrides starting from arenediazonium tetrafluoroborates to perform the synthesis of symmetrical and unsymmetrical arylated maleic anhydrides.[18] To the best of our knowledge, this methodology could not be extended to heteroarylated maleic anhydride due to the difficulty of heteroarenediazonium tetrafluoroborates synthesis.

A method for preparing 3,4-diaryl(or heteroaryl)maleimides by reacting aryl(or heteroaryl)boronic acid with *N*-substituted dibromomaleimides[19] was reported recently by Krayushkin et al. The authors used a wide variety of bases

Keywords: Diheteroarylmaleimides; Suzuki–Miyaura cross-coupling reaction; Palladium; Photochromism.
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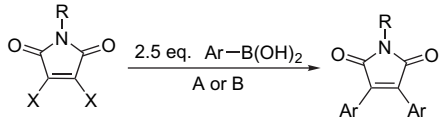
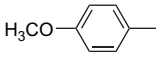
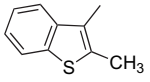
and cesium fluoride seemed to be the most efficient for Suzuki–Miyaura cross-coupling reactions starting from a dibromomaleimide (Table 1, entries 1 and 2).

The application of this protocol (Table 1, entry 3), employing inexpensive and commercial 3-(thiophenyl)boronic acid with 3,4-dibromo-1-benzyl-1*H*-pyrrole-2,5-dione,[20] did not supply the amounts of the desired product, while no starting material was recovered. Therefore, this reaction does not work with a wide range of substrates. The reaction has been performed differently with a variety of solvents (DME, MeOH) and bases (K_3PO_4, Na_2CO_3). So far, none of the used experimental conditions has resulted into a significant yield improvement. Indeed, the poor stability of the maleimide species and protodeboronation process would be accountable for that observed result.

Synthesis of substituted bis(fur-2-yl), bis(fur-3-yl), and bis-(thien-2-yl) maleimides[20] has been described as involving, as a key step, a one-pot Pd/C[21] catalyzed Suzuki cross-coupling between various boron derivatives and the dibromo or diiodomaleimides. These catalysis conditions were not able to promote coupling of 3-thiopheneboronic acid with halogenated maleimides (Table 1, entries 4 and 5).

Table 1. Suzuki–Miyaura cross-coupling of 3,4-dihalogeno-1-(alkyl)-1*H*-pyrrole-2,5-dione and arylboronic acid ester



Entry	R	X	Boronic acid	Reaction conditions	Coupling reaction yield[a] [%]
1	*n*-Bu	Br		A	98[a]
2	*n*-Bu	Br		A	76[a]
3	Bz	Br		A	0
4	Bz	Br		B	0
5	Bz	I		B	0

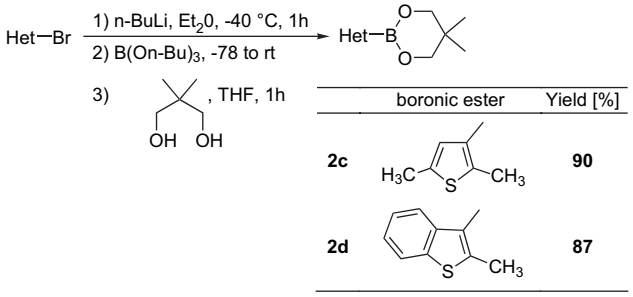
A: CsF, $Pd(PPh_3)_4$, dioxane, reflux, 4 h; B: Pd/C, Et_3N, EtOH, 24 h, reflux.
[a] Ref. 19.

Optimization of the cross-coupling reaction was performed on 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione with arylboronic acid derivatives using $PdCl_2$(dppf) as catalyst. 5,5-Dimethyl-2-(aryl or heteroaryl)-1,3,2-dioxaborinane has often been used as a substitute of arylboronic acids to circumvent protodeboronation[22] and to efficiently couple with aryl halides or aryl triflates in the presence of Pd catalyst.

We applied this strategy to synthesize new bis(heteroaryl)-maleimides as described in Scheme 1.

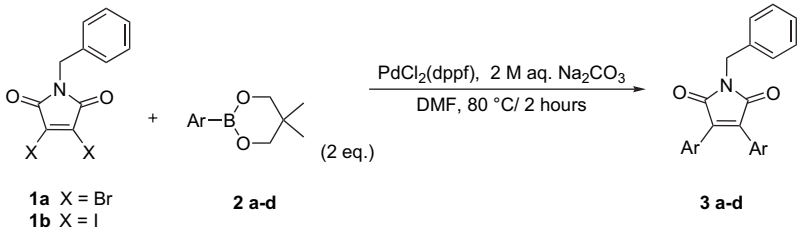
The protection of commercial 3-thienylboronic acid was carried out by esterification with 2,2-dimethylpropane-1,3-diol, according to literature procedure,[23] leading to 5,5-dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane **2a** in excellent yield. Phenylboronate ester **2b** is commercially available.[24]

Heteroarylboronic esters **2c** and **2d** have been prepared by a one-pot procedure as shown in Scheme 2. The initial bromide–lithium exchange step on to 2,5-dimethyl-3-bromothiophene[25] and 3-bromo-2-methylbenzo[*b*]thiophene[26] was easily carried out at −40 °C in ethereal solution on a multigram scale in excellent yield (97%). At −78 °C, an excess amount (2.5 equiv) of tributyl borate was added into the solution of heteroaryl lithium reagents formed. The reaction mixture was allowed to return to room temperature and the solvent was removed by a rotary evaporator. Transesterification of boronate esters intermediates occurred cleanly with 2,2-dimethylpropane-1,3-diol to generate cyclic boronate esters very efficiently (Scheme 2).



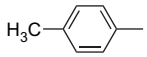
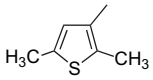
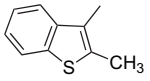
Scheme 2. Synthesis of cyclic boronate esters **2c** and **d**.

Cross-coupling reaction of dibromomaleimide **1a** with an excess of 5,5-dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane **2a** was first performed in polar solvent (DMF), in presence of base (Na_2CO_3) and catalytic amount of $PdCl_2$(dppf). The desired product **3a** was isolated, for the first time, in moderate yield (48%) as illustrated in Table 2 (entry 1).



Scheme 1.

Table 2. Optimized conditions of Suzuki–Miyaura cross-coupling reaction

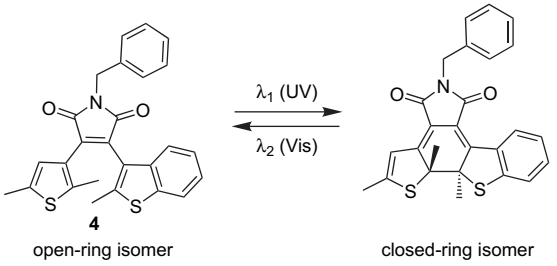
Entry	X	Boronate ester		Coupling reaction product (yield %)
1	Br		**2a**	**3a** (48)
2	I		**2a**	**3a** (64)
3	I		**2b**	**3b** (75)
4	I		**2c**	**3c** (68)
5	I		**2d**	**3d** (43)

When instead of **1a**, diiodomaleimide **1b** was used, a 16% yield increase was observed (entry 2). With the same cross-coupling methodology, the synthesis of 1-benzyl-3,4-bis(4-methylphenyl)-pyrrole-2,5-dione **3b**, 1-benzyl-3,4-bis(2,5-dimethyl-3-thienyl)-pyrrole-2,5-dione **3c** and its 2-methylbenzo[*b*]thiophene analogous **3d** was carried out in moderate to good yield (entries 3–5). Synthesis of **3c** has previously been described, in 3 steps starting from 2,5-dimethylthiophene and expensive 3,4-dichlorocyclobutane-1,2-dione in 40 % overall yields.[27]

The possibility of preparing monoiodo heteroarylated maleimides has been investigated aiming at adding flexibility to this Suzuki–Miyaura cross-coupling methodology and to extend its applicability to the conversion of monoheteroarylated maleimides into the unsymmetrical diheteroarylated compounds (Scheme 3). Treatment of diiodomaleimide **1b** with stochiometric amount of 5,5-dimethyl-2-(2,5-dimethylthien-3-yl)-1,3,2-dioxaborinane **2c**, heating for 1 h in DMF instead of 2 h, furnished only **3c** in 40% yield. The presence of starting material and mono cross-coupling product have not been detected.

Due to the instability of the monoiodo intermediate, unsymmetrical maleimide synthesis has been carried out, in a one-pot procedure, by adding simultaneous the two different cyclic boronate esters **2c** and **2d**. After purification by HPLC, the target unsymmetrical bis(heteroaryl)maleimide **4** was isolated as major product (50%). Symmetric maleimides **3c** and **3d** were separated too (7 and 3%, respectively).

The photocyclisation of new di(heteroaryl)ethenes (**3d** and **4**) was achieved, by irradiation of toluene solution (3×10^{-5} M) in presence of air, at wavelengths corresponding to the absorption band of the open-ring isomer (Scheme 4, Table 3). Both closed isomers are thermally stable for 3 days at 20 °C. Colored forms are also sensitive to visible light, leading to the initial open form.



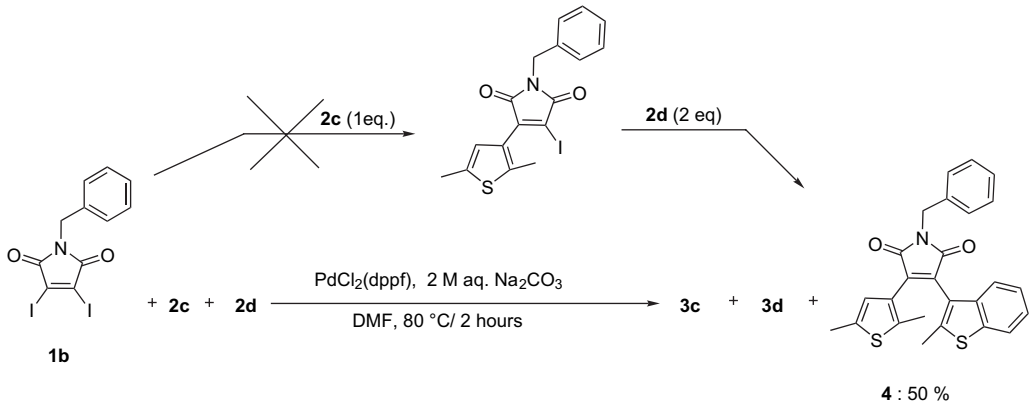
Scheme 4.

An example of photochromic behavior is given for compound **4** (Fig. 1).

The fatigue resistance of toluene solution of **4**, determined by the decrease of absorption maximum at 510 nm (where the closed form has an absorption maximum), was observed at room temperature for 7 optical switching cycles upon alternatively irradiation with 404 nm and 510 nm light in presence of air, see Figure 2. An absorbance decrease of 11%

Table 3. Absorption characteristics of photochromic maleimides

Compound	λ_{max} (nm) of the open-ring isomer ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1})	λ_{max} (nm) of the closed-ring isomer
3c	231, 277, 391 (5)	359, 504
3d	406 (2)	510
4	405 (3)	511



Scheme 3. Synthesis of unsymmetrical diheteroarylmaleimide **4**.

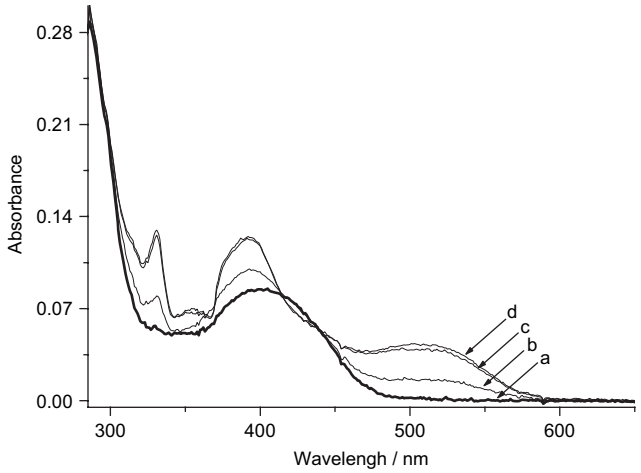


Figure 1. Changes in the UV–vis absorption spectra of a toluene solution of **4** (3×10^{-5} M) upon irradiation with 404 nm light. Irradiation periods are 0 s (a), 60 s (b), 120 s (c), and the photostationary state 180 s (d).

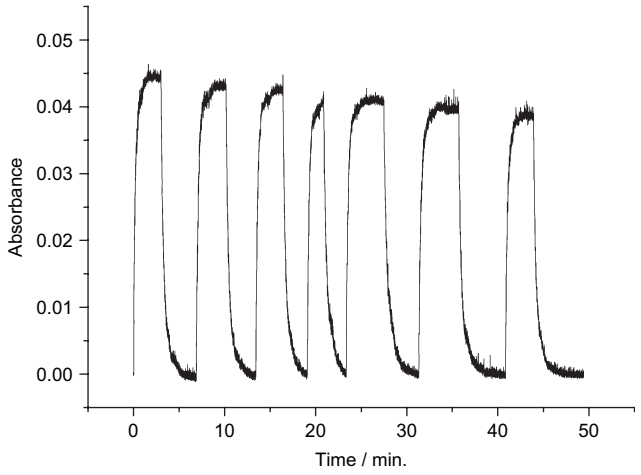


Figure 2. Fatigue resistance of **4** in toluene measured at 510 nm during switching cycles.

occurred. Similar results were obtained for toluene solutions of **3c** and **3d**.

3. Conclusion

In summary, we have shown that the Suzuki–Miyaura cross-coupling methodology can be fruitfully employed to synthesize, in a one-pot procedure, starting from available and low cost starting materials, under mild conditions, symmetrical or unsymmetrical bis(heteroaryl)maleimides, which are not easily available by other routes.

The Suzuki reaction was chosen in part for the large number of commercial boronic acids and esters available.

We have established that the cross-coupling reaction success is highly dependent on the protection of unstable boronic acids into cyclic boronate esters. In an effort to optimize this reaction, the influence of different catalysts, solvents, and bases are in progress.

4. Experimental section

4.1. General

All the reactions were conducted out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. All solvents (Carlo Erba Company, France) for reactions were purified before use and were dried if necessary. Et_2O and THF were distilled under nitrogen from sodium benzophenone ketyl and used immediately. Metallations were performed under an argon atmosphere and reagents were handled with syringes through septa. Column liquid chromatographies were carried out on Merck silica gel 60 (70–230 mesh). Analytical thin-layer chromatography (TLC) was done on Merck $60F_{254}$ silica gel plates. Detection of TLC components was accomplished using a 254/366 nm UV lamp. Melting points were determined on a Buchi 510 apparatus in open glass capillaries and were uncorrected.

Reagents and starting materials were used as received without further purification from Avocado, Aldrich or Acros. Starting materials 2,5-dimethyl-3-bromothiophene,[25] 5,5-dimethyl-2-(thien-3-yl)-1,3,2-dioxaborinane (**2a**),[23] 5,5-dimethyl-2-(4-methylphenyl)-1,3,2-dioxaborinane (**2b**),[24] and 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione (**1**)[20] were prepared according to literature procedures.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brücker AC 250 spectrometer (250 and 62.5 MHz, respectively) in deuteriochloroform as solvent with tetramethylsilane as the internal standard. The electron impact mass spectra (EIMS) were obtained on a spectrometer HP 5973 Masse Selective Detector. HPLC Analyses were performed on a Shimadzu HPLC system using a Chromatorex C-18 column (250 mm×4.6 mm i.d.), a Shimadzu LC-10AT solvent delivery system, Shimadzu SPD-10A UV/VIS Detector, with isocratic elution with acetonitrile/water (80:20, v/v), at a flow rate of 1.0 mL min^{-1}.

Absorption spectra were measured on a Varian Cary 50 UV–vis spectrophotometer. Photoirradiation was carried out by using a Xenon lamp (150 W) equipped with a monochromator.

4.1.1. 5,5-Dimethyl-2-(2,5-dimethylthien-3-yl)-1,3,2-dioxaborinane (2c). *n*-BuLi (7.5 mL, 18.75 mmol, 2.5 M in hexane) was added dropwise via syringe to a solution of 2,5-dimethyl-3-bromothiophene (3 g, 15.7 mmol) in dry ether (30 mL) at −40 °C under argon. After 1 h, at −78 °C, tributyl borate (12.5 mL, 47.1 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 h. The solvent was evaporated in vacuo and the residue was dissolved in anhydrous THF (30 mL). 2,2-Dimethylpropane-1,3-diol (8.17 g, 78.5 mmol) was added in one portion. The resulting mixture was stirred for a further 1 h and concentrated. The obtained crude product was dissolved in diethyl ether and washed several times with water. The organic phase was then dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography with cyclohexane/ethyl acetate (10:1) as eluant, yielding 3.16 g (90%) of the corresponding boronic ester as a white solid. Mp: 73–74 °C; ^{1}H NMR δ=1.00 (s, 6H), 2.38 (s, 3H), 2.58 (s, 3H), 3.71 (s,

4H), 6.81 (s, 1H); ^{13}C NMR δ=14.77, 15.53, 31.71, 72.01, 130.72, 35.39, 149.07, quaternary $C_{thiophene}B$ not visible; EIMS, *m/z*: 224 $[M]^+$. Anal. Calcd for $C_{11}H_{17}BO_2S$: C, 58.95; H, 7.65; S, 14.31. Found: C, 59.22; H, 7.88; S, 13.79.

4.1.2. 3-Bromo-2-methylbenzo[*b*]thiophene.[26] A solution of bromine (0.34 mL, 6.75 mmol) in chloroform (10 mL) was added to a stirring solution of 2-methyl-benzo[*b*]thiophene (1 g, 6.75 mmol) in chloroform (30 mL) at 0 °C. After 2 h of stirring, the reaction was quenched by the successive addition of the aqueous solutions of 10% $Na_2S_2O_3$ and 10% $NaHCO_3$, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with satd aq NaCl, dried over anhydrous $MgSO_4$, and filtered. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using cyclohexane as eluant, to give the title product (4.046 g, 99%) as a colorless oil. ^{1}H NMR δ=2.56 (s, 3H), 7.35–7.44 (m, 2H), 7.70–7.74 (m, 2H); ^{13}C NMR δ=138.48, 137.22, 135.23, 124.93, 124.79, 122.61, 122.21, 122.18, 106.66, 15.54; EIMS, *m/z*: 226, 227 $[M]^+$.

4.1.3. 5,5-Dimethyl-2-(2-methylbenzo[*b*]thiophen-3-yl)-1,3,2-dioxaborinane (2d). *n*-BuLi (4 mL, 9.9 mmol, 2.5 M in hexane) was added dropwise via syringe to a solution of 3-bromo-2-methylbenzo[*b*]thiophene (1.5 g, 6.6 mmol) in dry ether (45 mL) at −40 °C under argon. After 1 h, at −78 °C, tributyl borate (5.25 mL, 19.8 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 h. The solvent was evaporated in vacuo and the residue was dissolved in anhydrous THF (45 mL). 2,2-Dimethylpropane-1,3-diol (3.43 g, 33 mmol) was added in one portion. The resulting mixture was stirred for a further 1 h and concentrated. The obtained crude product was dissolved in diethyl ether and washed several times with water. The organic phase was then dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography with cyclohexane/ethyl acetate (10/1) as eluant, yielding 1.5 g (87%) of the corresponding boronic ester as a white solid. Mp: 76–77 °C; ^{1}H NMR δ=1.00 (s, 6H), 2.71 (s, 3H), 3.76 (s, 4H), 7.13–7.28 (m, 2H), 7.68 (d, *J*=7.9 Hz, 1H), 8.21 (d, *J*=7.74 Hz, 1H); ^{13}C NMR δ=16.75, 21.87, 31.71, 72.07, 121.20, 123.01, 123.84, 124.77, 139.26, 144.69, 152.98, quaternary $C_{thiophene}B$ not visible; EIMS, *m/z*: 260 $[M]^+$. Anal. Calcd for $C_{14}H_{17}BO_2S$: C, 64.63; H, 6.59; S, 12.33. Found: C, 64.94; H, 6.78; S, 11.82.

4.2. Suzuki–Miyaura cross-coupling reaction of 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione (1) with cyclic boronate ester (2a–c). General procedure for preparation of compounds (3 and 4)

A mixture of the required cyclic boronate ester **2a–d** (0.684 mmol), 3,4-diiodo-1-benzyl-1*H*-pyrrole-2,5-dione **1b** (100 mg, 0.228 mmol), and 2 M Na_2CO_3 (0.34 mL, 0.68 mmol) was degassed and flushed with a nitrogen flow for 30 min. Then, the catalyst [1,1′-bis(diphenylphosphino)-ferrocene]dichloropalladium(II) (10 mg, 1.36×10^{-5} mol) was added, and the mixture was stirred at 80 °C, under nitrogen and tested by TLC to check the completion of the reaction (2 h). The solution was cooled to room temperature and was extracted with ethyl acetate (15 mL). The combined organic layers were washed with water (15 mL), brine, and dried over anhydrous $MgSO_4$. Finally, purification by flash chromatography on silica gel (eluant: cyclohexane/CH_2Cl_2 1:1) furnished bis(heteroaryl)maleimides below.

4.2.1. 1-Benzyl-3,4-bis(thien-3-yl)-pyrrole-2,5-dione (3a). This compound was prepared by general method, from **2a** (134 mg) in 64% (51 mg) yield as an orange solid after chromatography and recrystallization from pentane. Mp: 115 °C; ^{1}H NMR δ=4.73 (s, 2H, CH_2N), 7.16 (dd, *J*=5, 1.26 Hz, 2H), 7.20–7.29 (m, 5H, H_{arom}), 7.36 (m, 2H), 7.91 (dd, *J*=3, 1.26 Hz, 2H); ^{13}C NMR δ=41.94, 125.85, 127.58, 127.88, 128.69, 128.72, 129.19, 129.26, 129.59, 136.41, 170.69; EIMS, *m/z*: 351 $[M]^+$. Anal. Calcd for $C_{19}H_{13}NO_2S_2$: C, 64.93; H, 3.73; N, 3.99; S, 18.25. Found: C, 64.92; H, 3.91; N, 3.79; S, 18.27.

4.2.2. 1-Benzyl-3,4-bis(4-methylphenyl)-pyrrole-2,5-dione (3b). This compound was prepared by general method, from **2b** (139 mg) in 75% (61 mg) yield as a yellow solid after chromatography and recrystallization from pentane. Mp: 131 °C; ^{1}H NMR δ=2.33 s (6H), 4.77 (s, 2H, CH_2N), 7.11–7.46 (m, 13H, H_{arom}); ^{13}C NMR δ=21.49, 41.89, 125.84, 127.80, 128.65, 128.83, 129.25, 129.73, 135.40, 136.54, 140.04, 170.72; EIMS, *m/z*: 367 $[M]^+$, 353 $[M-Me]^+$. Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.68; H, 5.91; N, 3.69.

4.2.3. 1-Benzyl-3,4-bis(2,5-dimethylthien-3-yl)-pyrrole-2,5-dione (3c).[27] This compound was prepared by general method, from **2c** (153 mg) in 68% (63 mg) yield as an orange solid after chromatography and recrystallization from isopropylic alcohol. Mp: 161 °C; ^{1}H NMR δ=1.86 (s, 6H, 5-CH_3, 5′-CH_3), 2.41 (s, 6H, 2-CH_3, 2′-CH_3), 4.78 (s, 2H, CH_2N), 6.75 (s, 2H, 4-H, 4′-H), 7.30–7.40 (m, 3H, H_{arom}), 7.41–7.51 (m, 2H, H_{arom}); ^{13}C NMR δ=14.72, 15.16, 41.94, 126.26, 126.53, 127.80, 128.64, 128.94, 132.60, 136.51, 136.75, 139.50, 170.74; EIMS, *m/z*: 407 $[M]^+$, 392 $[M-Me]^+$. Anal. Calcd for $C_{23}H_{21}NO_2S_2$: C, 67.78; H, 5.19; N, 3.44; S, 15.74. Found: C, 67.48; H, 4.97; N, 3.32; S, 15.83.

4.2.4. 1-Benzyl-3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-pyrrole-2,5-dione (3d). This compound was prepared by general method, from **2d** (178 mg) in 43 % (47 mg) yield as an yellow solid after chromatography and recrystallization from pentane. Mp: 181 °C; ^{1}H NMR δ=1.98 (s, 3H), 2.24 (s, 3H), 4.89 (s, 2H, CH_2N), 7.04–7.69 (m, 13H, H_{arom}); ^{13}C NMR δ=15.46, 15.51, 42.27, 121.80, 121.86, 121.98, 122.19, 122.33, 124.13, 124.24, 124.38, 124.50, 127.93, 128.72, 128.81, 135.57, 136.04, 136.36, 137.61, 138.09, 138.14, 143.02, 143.49, 169.57; EIMS, *m/z*: 479 $[M]^+$. Anal. Calcd for $C_{29}H_{21}NO_2S_2$: C, 72.62; H, 4.41; N, 2.92; S, 13.37. Found: C, 72.51; H, 4.61; N, 3.11; S, 13.08.

4.2.5. 1-Benzyl-3-(2-methylbenzo[*b*]thiophen-3-yl)-4-(2,5-dimethyl-3-thienyl)-pyrrole-2,5-dione (4). This compound was prepared by general method, from a mixture of **2c** (50 mg, 0.228 mmol) and **2d** (71 mg, 0.274 mmol) in 50% (50 mg) yield as an orange solid after HPLC. Mp: 176 °C; ^{1}H NMR δ=1.64 (s, 3H), 2.21 (s, 3H), 2.37 (s, 3H), 4.82 (s, 2H, CH_2N), 6.77 (s, 1H, $H_{thiophene}$), 7.22–7.49 (m, 8H, H_{arom}), 7.69–7.73 (m, 1H, H_{arom}); ^{13}C NMR δ=14.72,

15.09, 15.48, 121.83, 122.47, 122.54, 124.15, 124.38, 126.13, 126.20, 127.85, 128.72, 128.84, 131.76, 136.16, 136.46, 136.92, 138.08, 138.15, 140.58, 142.42, 169.86, 170.48; EIMS, *m/z*: 443 $[M]^+$, 428 $[M-Me]^+$. Anal. Calcd for $C_{26}H_{21}NO_2S_2$: C, 70.40; H, 4.77; N, 3.16; S, 14.46. Found: C, 70.18; H, 4.54; N, 3.01; S, 14.57.

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