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Synthesis of Novel Key Chromophoric Intermediates via C-C Coupling Reactions

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Abstract: The fundamentals of Pd-catalyzed Csp^2-Csp^2 Miyaura borylation, Suzuki cross-coupling, and Stille cross-coupling reactions for a variety of borylated precursors based on phenothiazine (PTZ), phenoxazine (POZ), carbazole (Cz), and quinoxaline (QX) units have been explored. Three palladium-based catalysts were chosen for this study: $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(dppf)Cl_2$, applying different reaction conditions. Around 16 desired chromophores were successfully designed and synthesized using C-C cross-coupling reactions in moderate to excellent yields, including PTZ, POZ, and Cz units coupled with QX, indolinium iodide, thienyl, phenyl, or triphenylamine moieties. Additionally, PTZ, POZ, and Cz have been employed in synthesizing various pinacol boronate ester derivatives in good to moderate yields. Interestingly, $Pd(dppf)Cl_2$ was found to be the best catalyst for borylation, and C-C cross-coupling reactions occurred in as little as 30 min, with an excellent yield exceeding 98%. $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ catalyzed the reaction to obtain the desired products in moderate to good yields after a long time (20–24 h). On the other hand, the Suzuki-Miyaura cross-coupling between *N*-(2-methyl)hexyl carbazole pinacol boronate ester derivative **10c** and three halogenated quinoxaline derivatives—4-(3-(5-bromothiophen-2-yl)quinoxalin-2-yl)benzaldehyde (**27**), 4-(5-(3-(5-bromothiophen-2-yl)quinoxalin-2-yl)thiophen-2-yl)benzaldehyde (**30**), and 4-(3-chloroquinoxalin-2-yl)benzaldehyde (**25**) catalyzed by $Pd(PPh_3)_4$—afforded three carbazole-quinoxaline chromophores (**28**, **30**, and **31**, respectively) in 2–3 h, with good to excellent yields reaching 86%. The electron-deficient QX couplers proved to be coupled efficiently using the Stille coupling reaction, which involves the coupling between electron-rich orgaostannane and electron-deficient halide. The synthesized precursors and desired chromophores were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, and HRMS.

Keywords: palladium catalysis; C-C coupling; $Pd(PPh_3)_4$; $Pd(PPh_3)_2Cl_2$; $Pd(dppf)Cl_2$; phenothiazine; phenoxazine; carbazole; quinoxaline; pinacol ester

Citation: Nhari, L.M.; Bifari, E.N.; Al-Marhabi, A.R.; Al-Ghamdi, H.A.; Al-Ghamdi, S.N.; Al-Zahrani, F.A.M.; Al-Footy, K.O.; El-Shishtawy, R.M. Synthesis of Novel Key Chromophoric Intermediates via C-C Coupling Reactions. *Catalysts* **2022**, *12*, 1292. https://doi.org/10.3390/catal12101292

Academic Editors: Mohamed Mokhtar M. Mostafa, Tamer S. Saleh and Nesreen S. Ahmed

Received: 1 October 2022
Accepted: 17 October 2022
Published: 21 October 2022

1. Introduction

In the late 20th century, transition metal-catalyzed reactions became the first choice, while chemistry scientists paid special interest to new strategies for the development of producing promising organic materials. Transition metals can activate several chemical bonds to break easily and catalytically form new bonds. In this regard, palladium was the first transition metal used for the catalysis of C-C bond formation [1]. In 2010, the

prestigious circle of Nobel Laureate chemists hosted Akira Suzuki, Ei-ichi Negishi, and Richard Heck for their brilliant efforts in the field of carbon–carbon bond construction [2]. The organic synthesis methods and strategies were irreversibly changed since their early contributions to the field of palladium-catalyzed cross-coupling reactions in the 1970s [3]. Their efforts revolutionized chemists' way of constructing and conceptualizing molecules.

In the last few decades, the Suzuki–Miyaura cross-coupling reaction (which is simply known as the Suzuki coupling reaction) became the most famous, useful, and applicable palladium-catalyzed C-C bond forming reaction, which involves the coupling between vinyl or aryl boronic acid (or pinacol ester) and vinyl or aryl halides, pseudohalides, alkenes, alkynes, amines organometallic, etc. [4–7]. Due to its milder conditions, commercially available organoboron reagent, less toxicity, sustainability, easier-handling by-products and comparative environmental safety, the Suzuki cross-coupling reaction has gained impressive developments. It has been widely employed for organic synthesis more than other C-C coupling reactions, such as the Heck and Stille coupling reactions [8–10]. Suzuki cross-coupling reactions involve the aryl halide substrate, which is preferred to be bromide or iodide (chloride compounds are less active towards Suzuki cross-coupling [11]) substituted with an electron-withdrawing group, a Pd(0) or Pd(II) catalyst, a degassed aprotic solvent (toluene, THF, dioxane, etc.), and a moderate reaction temperature 60–90 °C. Sodium and potassium carbonate are the most common bases used for Suzuki cross-coupling reactions besides Cs_2CO_3, TlOH, KF, and NaOH, which could also be used. Tetrakis(triphenylphosphine)-palladium(0) ($Pd(PPh_3)_4$) represents the most frequently used heterogeneous catalyst; aryl halide and organoboron molecules adsorb on its surface through the metal–carbon bond. Then, the two carbons couple together to form a new C–C single bond [9]. $Pd(PPh_3)_4$ has been frequently employed as a catalyst in Suzuki coupling reactions in mild conditions and produces moderate to good yields [11,11,12]. Additionally, [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) has been used for Suzuki cross-coupling reactions, producing excellent yields due to its donority character [13]. The mechanism of the Suzuki coupling reaction includes the formation of organopalladium halide (R-Pd-X) via the oxidative addition of the aryl halide to the Pd(0)-catalyst (the rate-determining step). Then, the boron-palladium transmetallation of the main group in an organoboron molecule (R′-B-Y2) forms the diorganopalladium complex (R-Pd-R′). Finally, the (R-R′) molecule is produced by a reductive elimination accompanied by Pd(0)-catalyst regeneration [14].

Arylboronic acids and esters are crucial building blocks for different organic transformations, particularly for Suzuki–Miyaura cross-coupling reactions [14–16]. Although boronic acids and esters are versatile and commercially available, most chemists synthesize aryl pinacol ester derivatives (boronates) in their laboratories using the Miyaura borylation reaction for some points of view. The main reason is that the borylation reaction helps chemists to design molecules with a specific functionality and configuration that serve the aim of this particular work. In addition, boronates have more stability towards isolation and purification by column chromatography. This stability comes from the donating ability of the sigma bond of carbon and the conjugation of the lone pair of oxygen to the electron-deficient boron atom. This reduces the Lewis-acidity of boron and subsequently reduces its reactivity with respect to boronic acids. Moreover, boronates are more soluble in organic solvents and do not tend to oligomerize [17].

Hence, the synthesis of aryl boronates has gained a great deal of attention [18–20]. Miyaura borylation reaction involves the reaction of vinyl or aryl halide with bis(pinacolato)diboron in the presence of Pd-catalysts to form boronates (containing the C–B bond). The reaction is performed in mild conditions of 80–100 °C and in the presence of carboxylate salt, usually KOAc. $Pd(dppf)Cl_2$ [21–23] and $Pd(PPh_3)_2Cl_2$ [24–26] are commonly used as precatalysts for Miyaura borylation reactions.

The second common Pd-catalyzed C-C coupling reaction is the Stille coupling reaction, which involves the reaction between organic or pseudo-halides (electrophiles) with organotin (organostannanes) nucleophiles in the presence of Pd-catalysts [27]. This reaction has

two main advantages, represented in its mild conditions and high yields [28]. $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd_2(dba)_3$ are considered good catalysts for Stille coupling reactions [29–32]. Like organoboron derivatives, organstannanes can tolerate highly sensitive functional groups, which helps eliminate the tedious steps of sensitive group protection and deprotection processes. On the other hand, organostannanes are more toxic than organoboron counterparts.

So far, palladium-catalyzed cross-coupling reactions—particularly Suzuki, Miyaura, and Stille coupling reactions—have found numerous applications in academic, pharmaceutical, and industrial fields for synthesizing promising multifunctional compounds, biologically active molecules, and natural products [33–37].

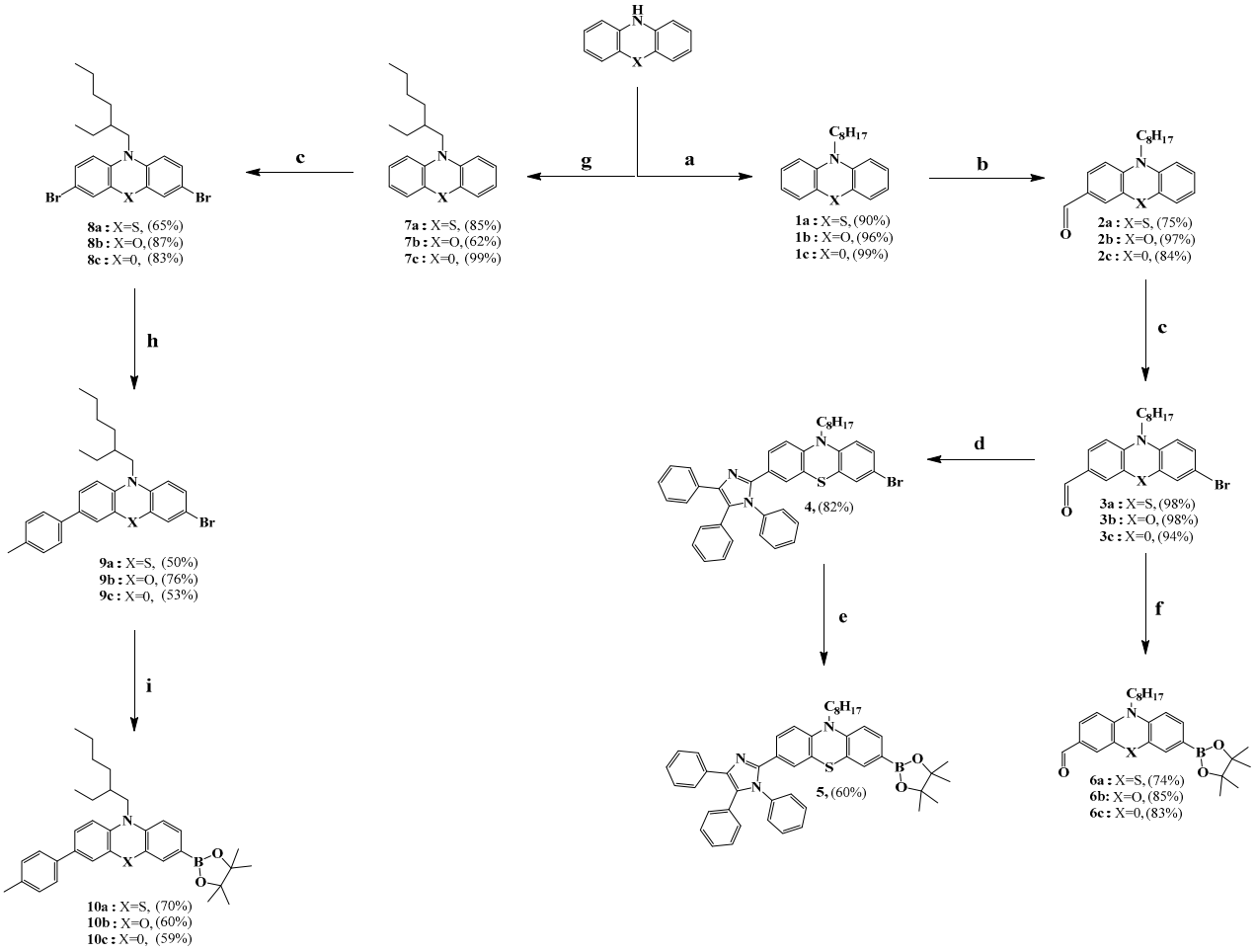
Phenothiazines are tri-heterocyclic donors containing nitrogen and sulfur atoms in their structures. They are easy to be functionalized, have multiple modifiable positions, and are commercially available at cheap prices. The presence of N and S atoms makes them promising electron-donors [38]. Phenoxazines have chemical and electrochemical properties similar to those of phenothiazines due to their similar chemical structures and them replacing the S atom of the phenothiazine core with an oxygen atom. The aromaticity of phenoxazines is somewhat less than that of phenothiazines due to the restrictions of aromaticity caused by the oxygen atom [39]. Additionally, carbazoles are tri-heterocyclic compounds bearing a pyrrole central ring fused to two benzene rings. Carbazole compounds have rigid planar configurations and can be eConverselysily functionalized at C2, C3, C6, C7, and the N atom [40]. Conversely, quinoxalines are di-heterocyclic compounds containing a pyrazine ring fused at C5 and C6 to the benzene ring. These compounds are electron-deficient in nature; they bear two pyridine-like nitrogen atoms [41].

Phenothiazine and phenoxazine [42,43], the two electron-rich compounds with closer electronic structures and rigid butterfly configurations; carbazole [44], the comparatively less electron-rich, more planar, and more p-conjugated compound (with respect to PTZ and POZ); triphenylamine [45], with a high electron density and propeller shape; quinoxaline [46], the electron-deficient building block; imidazole [47], the bipolar unit with two distinctive nitrogen atoms that are potential heteroaromatic units; and indolinium iodide salt [48] have been exploited in Pd-catalyzed cross-coupling reactions for versatile applications. In continuation of our interest in using the above-mentioned heteroaromatic nuclei in designing and synthesizing a variety of donor and donor-acceptor systems applicable for different fields [5,49–53], we started by using $Pd(PPh_3)_2Cl_2$ or $Pd(dppf)Cl_2$ to furnish 17 pinacol boronate esters based on PTZ, POZ, and Cz for the sake of engaging these valuable precursors in different coupling reactions. Quinoxaline was successfully employed for the Stille coupling reaction for more functionalization. Afterward, the synthesized pinacol boronates were coupled with the synthesized halogenated quinoxaline acceptors under Suzuki cross-coupling conditions.

2. Results and Discussion

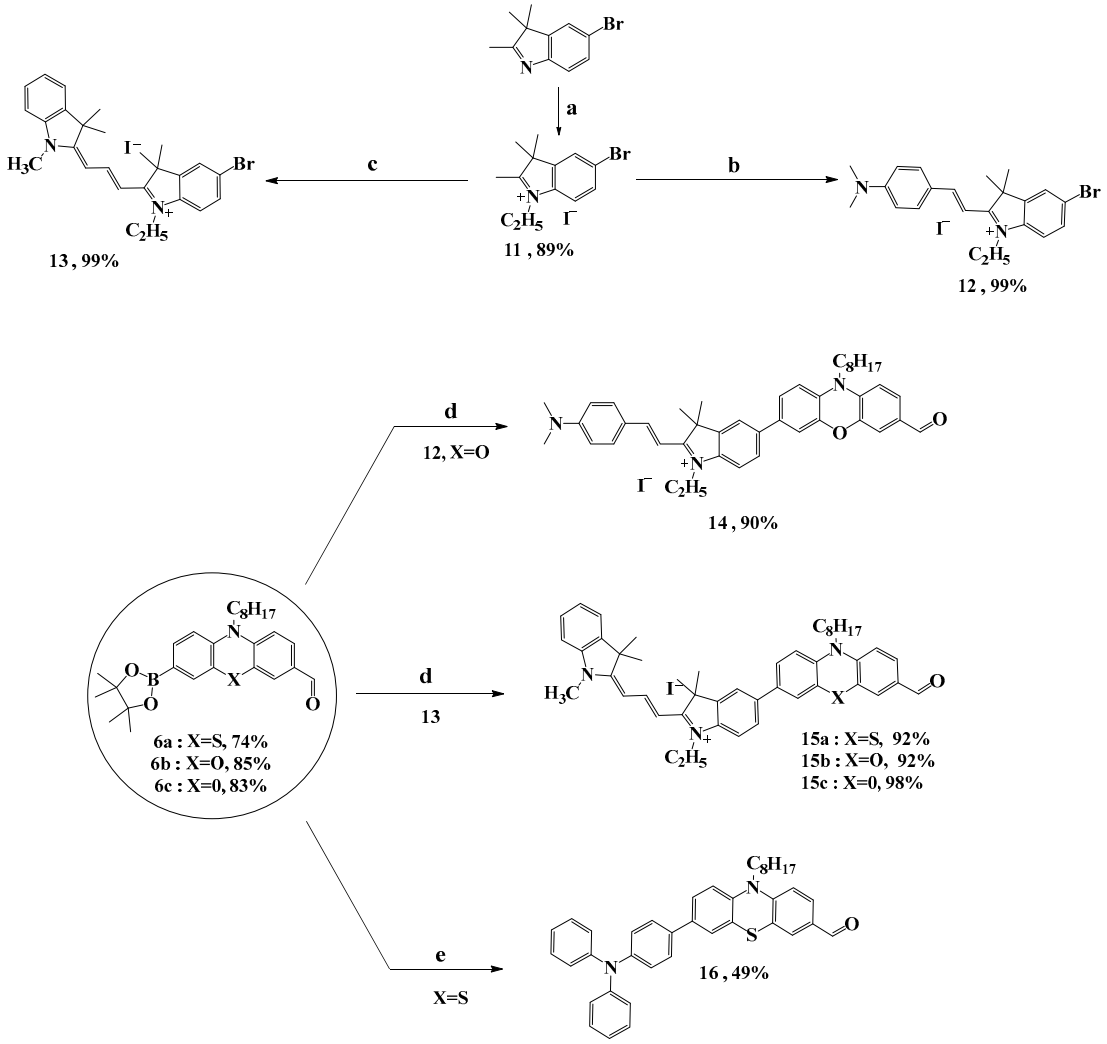
Synthesis

We commenced our work with borylation reaction for heterocyclic donors to end up with a variety of heteroaromatic pinacol boronate precursors ready for C-C coupling reactions (Scheme 1). Our group of researchers recently published the synthesis of **1b,c-4b,c** [51] and **5a-c** to **8a-c** [52] in excellent yields utilizing $Pd(PPh_3)_2Cl_2$ and $Pd(dppf)Cl_2$. Accordingly, borylated *N*-octyl phenothiazine derivative **6a** was synthesized through the *N*-alkylation of phenothiazine followed by Vilsmeier formylation reaction to afford **1a** and **1b**, respectively. Compound **3a** was subjected to a bromination reaction followed by a Miyaura borylation reaction through cross-coupling with B_2Pin_2 catalyzed by $Pd(dppf)Cl_2$ in the presence of KOAc salt to obtain the **6a** precursor in a good yield (74%). The bulky borylated imidazole-phenothiazine precursor **5** was obtained by the cost-effective Debus–Radziszewski synthesis of imidazole moiety (**4**), which underwent Miyaura borylation reaction using $Pd(PPh_3)_2Cl_2$.



Scheme 1. Synthesis of borylated *N*-alkyl PTZ, POZ, Cz derivatives using $Pd(dppf)Cl_2$ or $Pd(PPh_3)_2Cl_2$. a) DMF, NaOH, rt, b) DMF, $POCl_3$, reflux, c) NBS, THF, rt, d) Benzil, $PhNH_2$, $AcONH_4$ AcOH, 110 °C, e) B_2Pin_2, KOAc, $Pd(PPh_3)_2Cl_2$, toluene, 110 °C, f) B_2Pin_2, $Pd(dppf)Cl_2$, KOAc, dioxane, 90 °C, g) 3-(Bromomethyl)heptane, NaOH 50%, TBAI, 70 °C, h) 4-Methylphenylboronic acid, toluene, $Pd(PPh_3)_4$, K_2CO_3, 90 °C, Ar, i) B_2Pin_2, toluene, $Pd(PPh_3)_2Cl_2$, KOAc, 90 °C, Ar.

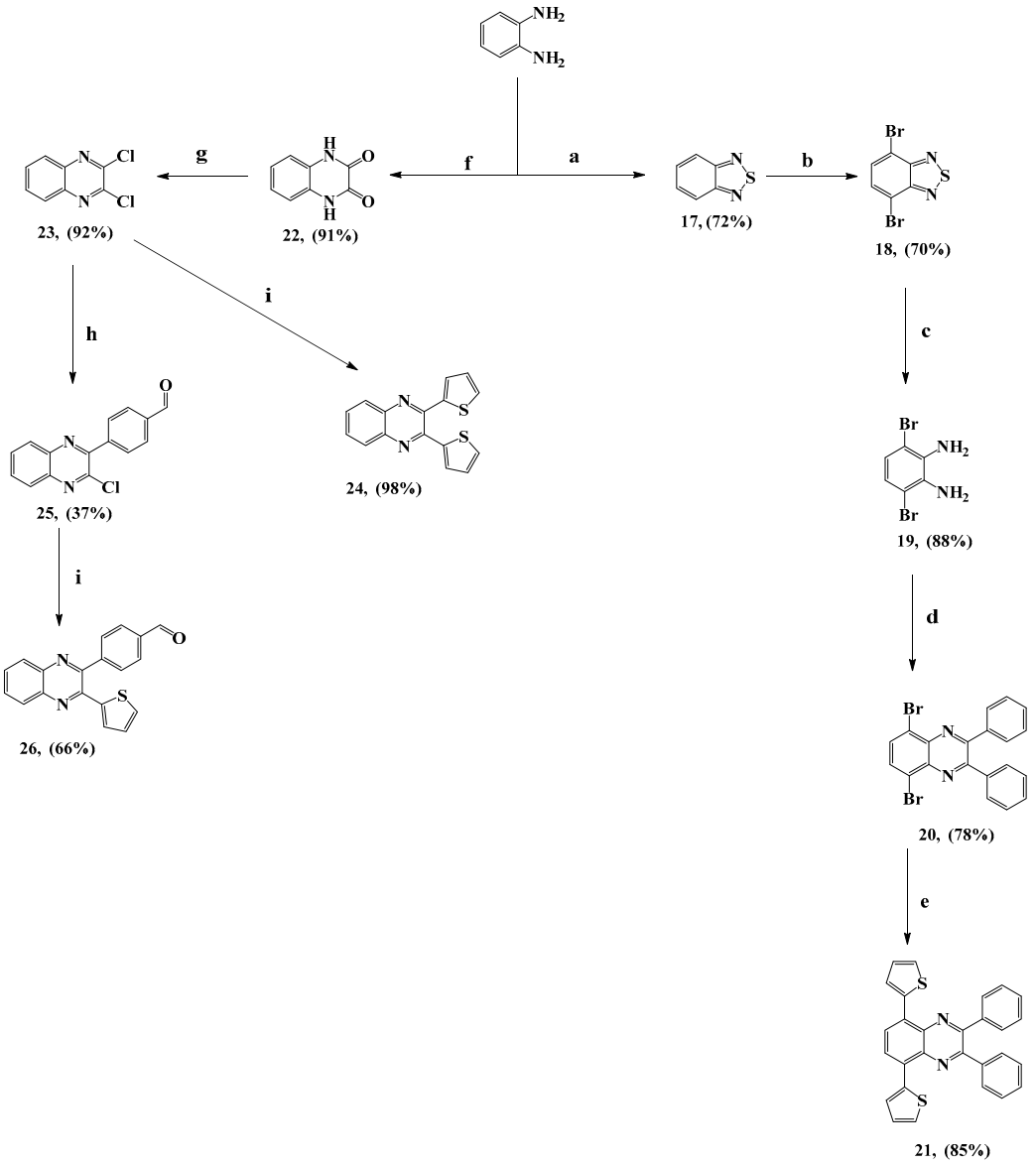
Afterward, the borylated precursors **6a-c** were successfully exploited to introduce indolinium and triphenylamine moieties to phenothiazine, phenoxazine, and carbazole central cores (Scheme 2). BPin (4,4,5,5-pentamethyl-1,3,2-dioxaborolanyl) moiety was incorporated in C-C coupling reactions between borylated phenoxazine precursor **6b** and bromoindolinium coupler **12** to afford chromophore **14** using $Pd(dppf)Cl_2$. Likewise, chromophores **15a-c** were obtained in excellent yields by a C-C coupling reaction between the borylated phenothiazine, phenoxazine, and carbazole with bromoindolinium coupler **13**. As demonstrated in Scheme 2, indolinium iodide derivatives **12** and **13** were synthesized in an excellent yield (99%) via the Knoevenagel condensation reaction of the brominated indolinium iodide salt **11** with 4-(dimethylamino)benzaldehyde and 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde, respectively. Historically, triphenylamine has been widely used in organic synthesis owing to its propeller configuration and electron richness [54]. The C-C coupling reaction of borylated phenothiazine precursor **6a** with the electron-rich 4-bromotriphenylamine afforded chromophore **16** in a comparatively lower yield (49%) by using $Pd(PPh_3)_4$. It has been reported that the Suzuki cross-coupling reaction rate is slightly dependent on electronic factors [55]. This may indicate that the Suzuki cross-coupling reaction preferred an electron-poor coupler, which appears clearly from the high yield of **14** and **15a-c**.



Scheme 2. C-C coupling reactions of *N*-alkyl PTZ, POZ, Cz boronic acid pinacol ester derivatives with indole or TPA precursors using $Pd(dppf)Cl_2$ or $Pd(PPh_3)_4$. a) CH_3CH_2I, CH_3CN, reflux, b) 4-(Dimethylamino)benzaldehyde, EtOH, piperidine, 60 °C, overnight, c) 2-(1,3,3-Trimethylindolin-2-ylidene)acetaldehyde, Ac_2O, 90 °C, d) $Pd(dppf)Cl_2$, K_2CO_3, toluene/MeOH, Ar, 85 °C, e) 4-Bromotriphenylamine, $Pd(PPh_3)_4$, 2M K_2CO_3, CH_3CN, Ar, 90 °C.

Quinoxaline is considered an electron-deficient moiety thanks to the two electron-withdrawing imine (C=N) groups in the pyrazine ring. Subsequently, it was selected to be a good coupler in C-C coupling reactions. Wisely, three quinoxaline derivatives (**21, 24, 26**) have been synthesized utilizing the Suzuki cross-coupling reaction and Stille coupling reaction (Scheme 3) using $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$, respectively. The substituted dibromoquinoxaline coupler **20** was successfully synthesized in four steps, starting from the benzothiadiazole compound **17** obtained from the reaction of *o*-phenylenediamine with thionyl chloride in the presence of pyridine. Then, a di-bromination reaction with *N*-bromosuccimide followed by a sulfur extrusion reaction using the good reducing reagent sodium borohydride afforded **18** and **19**, respectively. Forming 2,3-diphenylquinoxaline moiety was accomplished through the condensation of compound **19** with benzil in an acidic medium. The Stille coupling reaction was performed on coupler **20** for the decoration of chromophore **21** with two thiophene rings. This coupling reaction utilized 2-(tributylstannyl)thiophene in the presence of $Pd(PPh_3)_2Cl_2$, which gives an excellent yield of 85%, owing to the electron deficiency of the quinoxaline central core. On the other hand, the reaction between *o*-phenylenediamine and oxalic acid afforded quinoxalinedione **22**, which underwent a double chlorination reaction using $POCl_3$ in DMF to

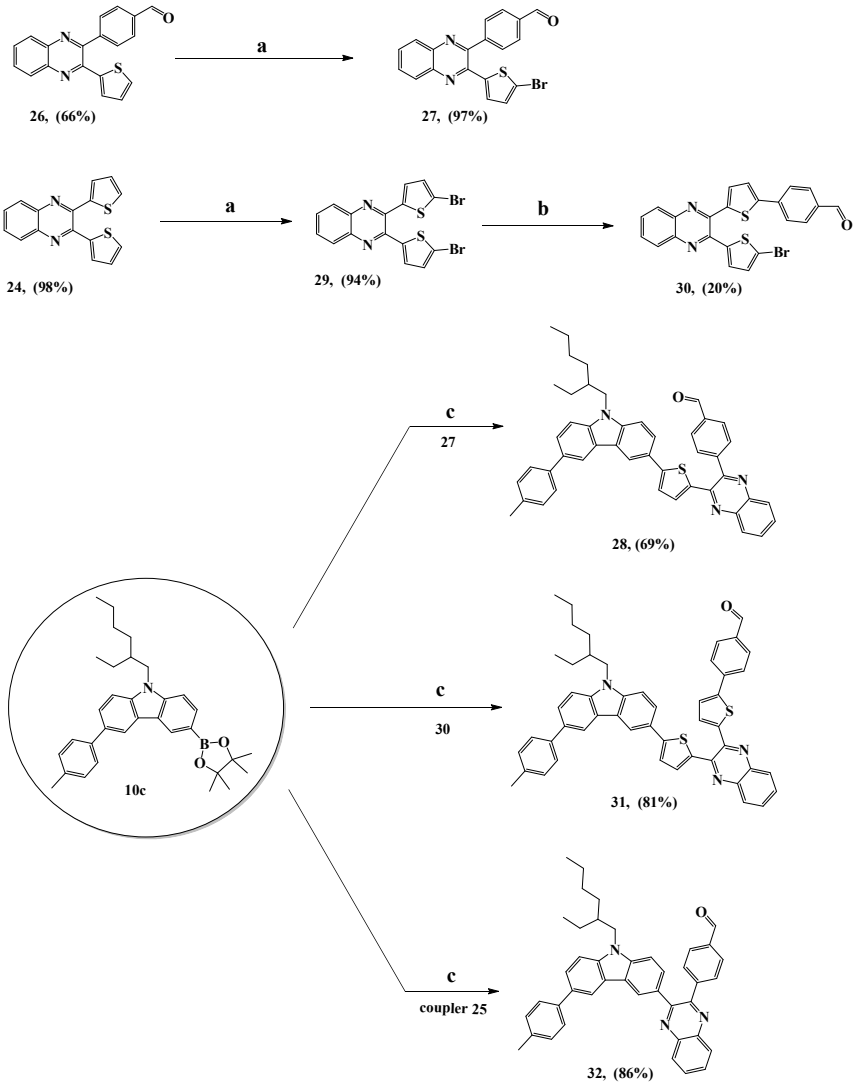
obtain 2,3-dichloroquinoxaline **23**. Then, again, the Stille coupling reaction was performed between coupler **23** and 2-(tributylstannyl)thiophene to obtain 2.3-dithienylquinoxaline **24**. The two Cl in compound **23** were exploited for the synthesis of chromophore **26** in two steps: first, Suzuki cross-coupling with 4-formylphenylboronic acid using $Pd(PPh_3)_4$ to obtain compound **25,** which then coupled with 2-(tributylstannyl)thiophene through a Stille coupling reaction to afford **26** in a moderate yield (66%).



Scheme 3. Synthesis of quinoxaline derivatives by C-C coupling reactions using $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$. a) $SOCl_2$, pyridine, toluene, reflux, b) Br_2, HBr 47%, reflux, c) $NaBH_4$, THF/EtOH, d) Benzil, toluene/AcOH, reflux, e) 2-(Tributylstannyl)thiophene, $Pd(PPh_3)_2Cl_2$, toluene, 110 °C, N_2, f) Oxalic acid, 4N HCl, reflux, g) $POCl_3$, DMF, reflux, h) 4-Formylphenylboronic acid, toluene:MeOH (5:1), $Pd(PPh_3)_4$, K_2CO_3, 80 °C, Ar, i) 2-(Tributylstannyl)thiophene, $Pd(PPh_3)_2Cl_2$, DMF, 110 °C.

Additionally, the synthesized quinoxaline chromophores **24** and **26** and the carbazole-BPin derivative **10c** were used in the synthesis of the three carbazole-quinoxaline chromophores **28**, **31**, and **32**, as shown in Scheme 4. Initially, the thiophene ring in both **24** and **26** were brominated at position 5 using the formal bromination conditions of NBS in DMF to afford two couplers, **27** and **29**. Coupler **30** was obtained from the Suzuki cross-coupling reaction between coupler **29** and 4-formylphenylboronic acid. Finally, cou-

plers **27**, **30**, and **25** were coupled with the carbazole-BPin derivative **10c** for the synthesis of **28**, **31**, and **32** in good yields.



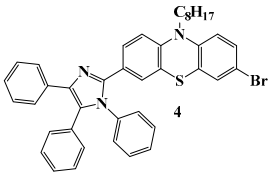
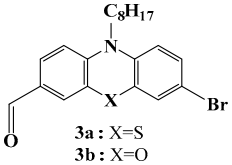
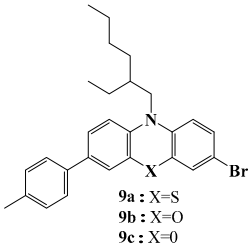
Scheme 4. C-C coupling reactions of *N*-alkyl carbazole boronic acid pinacol ester derivative with the synthesized quinoxaline precursors using $Pd(PPh_3)_4$. a) NBS, DMF, rt, b) 4-Formylphenylboronic acid, toluene, $Pd(PPh_3)_4$, K_2CO_3, 90 °C, Ar, c) Toluene:EtOH:H_2O (2:1:1), $Pd(PPh_3)_4$, K_2CO_3, 80 °C, Ar.

The structures of all of these compounds were confirmed by the spectral data of IR, ^{1}H-NMR, ^{13}C-NMR, DEPT-135, and HRMS (see supplementary data; Figures S1–S83).

To discuss the different conditions of the Miyaura borylation, Suzuki cross-coupling reaction, and Stille coupling reactions, summaries of our work in the field were illustrated in Tables 1–4. The Miyaura borylation reaction has been accomplished for the synthesis of PTZ, POZ, and Cz heteroarylboronates (**4, 6a-c**, and **10a-c**) under the following conditions: $Pd(PPh_3)_2Cl_2$ or $Pd(dppf)Cl_2$ as catalysts and sources for palladium, potassium acetate as a weak base, toluene or dioxane as reaction media, and refluxing from 90 to 110 °C for 12–24 h under N_2 or Ar (Table 1). Obviously, the use of $Pd(PPh_3)_2Cl_2$ in the borylation of PTZ-, POZ-, and Cz-based boronates linked to imidazolyl (**5**) or *p*-tolyl (**10a-c**) moieties afforded the corresponding boronates in moderate yields of Pd-catalyzed borylation reaction (60–70%), even by using two different linking groups of bulky triphenyl imidazole and simple *p*-tolyl units and two different molar ratios (substrate:catalyst:base of 50:1:125 for imidazolyl derivative **5** and 20:1:60 for *p*-tolyl derivatives **10a-c**). Fortunately, the use of $Pd(dppf)Cl_2$ in the borylation reaction catalysis of brominated PTZ, POZ, and Cz compounds was

successfully accomplished in the synthesis of PTZ, POZ, and Cz heteroarylboronates bearing an aldehyde group **6a-c** in excellent yields (94–98%), applying a molar ratio of 20:1:60 but with the same long time of 24 h. It is noteworthy that the yield obtained was much higher for the boronate esters **6a-c** compared with **5** and **10a-c**. This result is mainly attributed to the electronic structure of the substrate. As can be seen, the formyl substrates are much more deactivated due to the formyl group compared with the imidazolyl moiety. This attribution is manifested using the *p*-tolyl analogues **10a-c**, as these compounds are electronically activated; thus, the yield was lower than that of **6a-c**.

Table 1. Summary of the Miyaur borylation reaction of brominated *N*-alkyl PTZ, POZ, and Cz couplers.

Product No	Substrate	Catalyst	Base	Molar Ratio of Substrate:Catalyst:Base	Solvent	Time (h) (Temp (°C))	Yield (%)
5	 4	$Pd(PPh_3)_2Cl_2$	KOAc	1:0.02:2.5	toluene	12 (110)	60
6a	 **3a :** X=S **3b :** X=O **3c :** X=0	$Pd(dppf)Cl_2$		1:0.05:3	dioxane	24 (90)	98
6b							98
6c							94
10a	 **9a :** X=S **9b :** X=O **9c :** X=0	$Pd(PPh_3)_2Cl_2$		1:0.05:3	toluene	24 (90)	70
10b							60
10c							59

By applying Suzuki cross-coupling conditions in reacting brominated electron-donors PTZ, POZ, and Cz with 4-tolylboronic acid in the presence of $Pd(PPh_3)_4$ and potassium carbonate in toluene, compounds **9a-c** were obtained in moderate yields (76–50%) during a reaction period of 24 h. Lower yields (37–20%) were obtained for compounds **25** and **30** from Suzuki coupling between the electron-deficient halogenated QX couplers **23** and **29** and 4-formylphenyl boronic acid using the same conditions of $Pd(PPh_3)_4$ and K_2CO_3 and a reaction time of 20–24 h. The low yields may be attributed to the acidity of compounds **23** and **29**, which makes this compound susceptible to hydrolysis, together with the orthodicholoro steric factor. Furthermore, boronic acids easily undergo side reactions such as oxidation, protodeboronation, or palladium-catalyzed homocoupling during Suzuki coupling reactions [56]. Moreover, in anhydrous conditions, boronic acids tend to be in equilibrium with a trimeric anhydride (boroxine), and this process is not straightforward. Thus, an excess of boronic acids is required in the Suzuki cross-coupling reaction [17].

Interestingly, the electron-deficient QX couplers proved to be coupled efficiently using the Stille coupling reaction, which involves the coupling between electron-rich orgaostannane and electron-deficient halide, without the use of the base. This result confirms that the basic medium is unsuitable for such electron-deficient molecules, owing to their acidity. Thus, di-brominated and di- and mono-chlorinated QX couplers were subjected to Stille coupling conditions in the presence of tributyl stannyl thiophene catalyzed by $Pd(PPh_3)_2Cl_2$. Among the three halogenated couplers demonstrated in Table 3, the most electron-deficient QX derivative, 2,3-dichloroquioxaline **23**, afforded chromophore **24** in an excellent yield

(98%) in only one hour. The di-brominated QX coupler **20**, which is less electron-deficient due to the conjugation with two phenyl groups, gave a good yield (85%) of product **21** in 2 h. Coupler **25**, which has a QX unit linked to the 4-formylphenyl moiety, afforded a moderate yield (66%) of product **26**, which may be attributed to a steric factor. The overall results of QX-based couplers confirm the suitability of the Stille coupling condition compared with the Suzuki one.

Table 2. Summary of Suzuki cross-coupling reactions of halogenated *N*-alkyl PTZ, POZ Cz, and QX couplers with commercial arylboronic acid precursors.

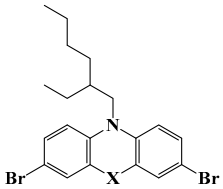
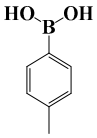
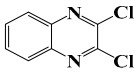
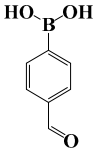
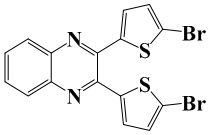
Product No	Halogenated Coupler	Organo-Boron Precursor	Catalyst	Base	Molar Ratio of Coupler:Precursor: Catalyst:Base	Solvent	Time (h) (Temp (°C))	Yield (%)
9a	 **8a :** X=S **8b :** X=O **8c :** X=0		$Pd(PPh_3)_4$	K_2CO_3	1:1.14:0.1:4	toluene	24 (90)	50
9b								76
9c								53
25	 **23**				1:1.57:0.04:1	toluene: MeOH (5:1)	20 (80)	37
30	 **29**				1:1:0.14:9.43	toluene	24 (90)	20

Table 3. Summary of Stille coupling reactions of halogenated QX couplers with commercial arylboronic acid precursors.

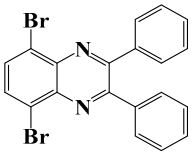
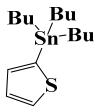
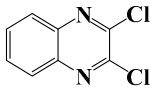
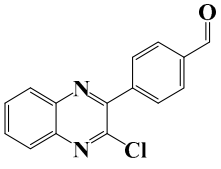
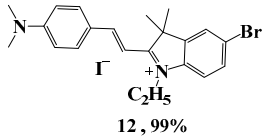
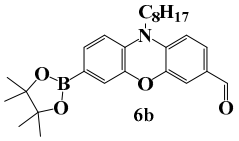
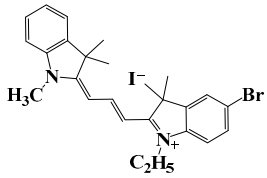
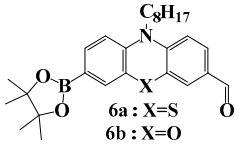
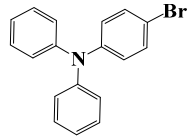
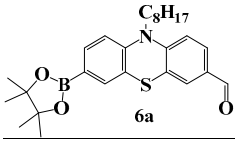
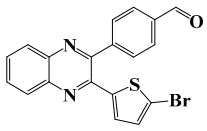
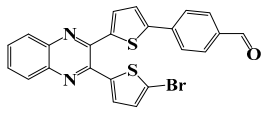
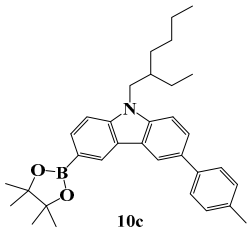
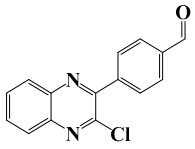
Product No	Haloginated Coupler	Organotin Precursor	Catalyst	Molar Ratio of Coupler:Precursor:Catalyst	Solvent	Time (h) (Temp (°C))	Yield (%)
21	 **20**		$Pd(PPh_3)_2Cl_2$	1:3:0.07	toluene	2 (110)	85
24	 **23**			1:3:0.05		1 (110)	98
26	 **25**			1: 2.11:0.06	DMF	2 (110)	66

Table 4. Summary of Suzuki cross-coupling reactions of borylated *N*-alkyl PTZ, POZ, and Cz precursors with halogenated indolinium, TPA, and QX couplers.

Product No	Halogenated Coupler	Organo-Boron Precursor	Catalyst	Base	Molar Ratio of Coupler:Precursor: Catalyst:Base	Solvent	Time (h) (Temp (°C))	Yield (%)
14	 **12 , 99%**	 **6b**	Pd(dppf)Cl_2	K_2CO_3	1:1.52:0.1:5	toluene/ MeOH 1:1	24 (80)	90
15a	 **13 , 99%**	 **6a : X=S** **6b : X=O** **6c : X=0**					0.5 (80)	92
15b							24 (80)	92
15c							0.5 (80)	98
16		 **6a**		2M K_2CO_3	1:1:0.05:2	CH_3CN	20 (90)	49
28	 **27**				1:1.4:0.05:13.25		2 (80)	69
31	 **30**	 **10c**	Pd(PPh_3)$_4$	K_2CO_3	1:2:0.1:21	toluene/ EtOH/ H_2O 2:1:1	3 (80)	81
32	 **25**				1:0.5:0.03:13		3 (80)	86

The conditions of the Suzuki cross-coupling reactions between the synthesized PTZ, POZ, and Cz boronates and the halogenated indolinium, triphenylamine, and quinoxaline couplers are summarized in Table 4. In terms of catalysis, Pd(dppf)Cl_2 efficiently catalyzed the reaction to afford the desired chromophores **14** and **15a-c** in excellent yields ranging from 90% to 98%. The phenoxazine-based indolinium chromophores **14** and **15b** took a longer reaction time (24 h) in contrast to the phenothiazine and carbazole counterparts, which were obtained in half an hour. This is in contrast to the synthesis of the carbazole-quinoxaline chromophores **28, 31**, and **32**, which were catalyzed by Pd(PPh_3)$_4$ and gave good yields of 69–86% in a comparatively short time (2–3 h). In the case of phenothiazine-triphenylamine chromophore **16**, the low yield of 49% was attributed to the triphenylamine coupler, in which the Br–C bond is very much activated with the electron-donor character of the amine moiety that would hamper the oxidative coupling when compared with the other cationic coupler. It is worth noting that QX-based couplers could afford a higher yield when boronate ester is used (Table 4) instead of boronic acid (Table 2). This result reflects the usefulness of Miyaura boronate ester over boronic acid for the C–C cross-coupling reaction, because boronic acid acts as a proton donor during the coupling condition, which could lower the yield of the reaction.

3. Experimental

3.1. Materials and Instrumentation

Solvents produced from Sigma, Aldrich, and Fisher were used without purification. All of the used chemicals were of the analytical grade and were used in the synthesis without more purification. The separations of compounds were performed by column chromatography on silica gel (0.063–0.2 mm). The purity of the products was checked by thin layer chromatography (TLC) using an aluminum silica gel F254, and the spot was detected by iodine and/or UV light absorption. NMR spectra were recorded in DMSO–d_6 or $CDCl_3$ on Bruker Avance 600 MHz or 850 MHz spectrometers for ^{1}H-NMR and on a 213 MHz spectrometer for ^{13}C-NMR, using the deuterated solvent signal as the internal standard. Chemical shifts (δ) are given in ppm, and coupling constants are given in Hz. The Fourier transform infrared (FTIR) spectra were carried out on a Thermo Scientific Nicolet iS10 FTIR spectrometer. The Thermo Scientific Orbitrap ID-X Tribrid mass spectrometer was used to obtain high-resolution mass spectra (HRMS).

3.2. Synthetic Procedures

3.2.1. Synthesis of 10-octyl-10H-phenothiazine (**1a**)

Sodium hydroxide (2.0 g, 35.7 mmol) was added to a solution of 10*H*-phenothiazine (2.4 g, 11.9 mmol), 1-bromooctane (3.5 g, 17.9 mmol), and potassium iodide (catalytic) in 50 mL dimethyl formamide (DMF). The reaction mixture was stirred for 5 h at room temperature, and then 200 mL of water was added. The crude product was extracted with chloroform (3 × 50 mL), and the organic layer was washed with saturated ammonium chloride aqueous solution and then water. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent, the residue was purified by column chromatography on silica gel by using *n*-Hexane as an eluent to obtain 3.4 g (90%) of compound **1a** as a colorless oil. ^{1}H-NMR (850 MHz, $CDCl_3$) δ: 7.12–7.14 (m, 4H, ArH), 6.89 (td, 2H, J = 7.65, 0.85 Hz, ArH), 6.85 (d, 2H, J = 7.65 Hz, ArH), 3.83 (t, 2H, J = 7.65 Hz, N-CH_2), 1.79 (qn, 2H, J = 7.65 Hz, CH_2), 1.42 (qn, 2H, J = 7.65 Hz, CH_2), 1.22–1.32 (m, 8H, 4CH_2), 0.86 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ: 145.3, 127.4, 127.1, 124.9, 122.3, 115.4, 47.4, 31.7, 29.2, 29.2, 27.0, 26.9, 22.6, 14.1. IR (cm$^-$1): C-H Olefinic 3066, aliphatic 2923, 2852, C=C stretch 1594, 1571. MS (ESI): m/z calcd for $C_{20}H_{26}NS$ 312.2 $[M+1]^+$, found 312.1.

3.2.2. Synthesis of 10-octyl-10H-phenothiazine-3-carbaldehyde (**2a**)

To an ice-cooled flask containing *N*,*N*-dimethylformamide (0.5 g, 0.5 mL, 7 mmol), phosphoryl chloride (0.3 g, 0.2 mL, 2.1 mmol) was added dropwise with stirring. After the addition, the solution was stirred at room temperature for 90 min. Then, the flask was cooled again in an ice bath, and compound **1a** (0.3 g, 1 mmol) was added. The reaction mixture was warmed gradually to run at 75 °C for 12 h. Then, it was cooled to room temperature, poured into ice water, basified with a saturated aqueous solution of potassium carbonate, extracted with chloroform (4 × 30 mL, washed, dried with magnesium sulfate, evaporated, and purified by column chromatography using petroleum ether:ethyl acetate (98:2) as an eluent to obtain 0.25 g (75%) of compound **2a** as a yellow oil. ^{1}H-NMR (850 MHz, $CDCl_3$) δ: 9.79 (s, 1H, CHO), 7.64 (dd, 1H, J = 8.5, 1.7 Hz, ArH), 7.58 (d, 1H, J = 1.7 Hz, ArH), 7.15–7.17 (m, 1H, ArH), 7.11 (dd, 1H, J = 7.65, 0.85 Hz, ArH), 6.96 (td, 1H, J = 7.65, 0.85 Hz, ArH), 6.87–6.90 (m, 2H, ArH), 3.88 (t, 2H J = 7.65 Hz, N-CH_2), 1.81 (qn, 2H, J = 7.65 Hz, CH_2), 1.43 (qn, 2H, J = 7.65 Hz, CH_2), 1.21–1.33 (m, 8H, 4CH_2), 0.86 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ: 190.1, 150.8, 143.5, 131.0, 130.1, 128.4, 127.6, 127.5, 125.0, 123.8, 123.6, 115.9, 114.8, 48.0, 31.7, 29.7, 29.2, 29.1, 26.8, 26.7, 22.6, 14.1. IR (cm^{-1}): C-H aliphatic 2924, 2853, C-H aldehyde 2723, C=O aldehyde 1683, C=C stretch 1597, 1573. MS (ESI): m/z calcd for $C_{21}H_{26}NOS$ 340.2 $[M+1]^+$, found 340.2.

3.2.3. Synthesis of 7-bromo-10-octyl-10H-phenothiazine-3-carbaldehyde (**3a**)

In an ice bath, compound **2a** (5.8 g, 17 mmol) was dissolved thoroughly in dry THF (85 mL), followed by the addition of *N*-bromosuccinimide (NBS) (3.2 g, 18. Mmol). The

reaction system stirred for 1 h at 0 °C and then left at room temperature to stir until completion. The workup and purification process was handled as described above. The product was extracted with chloroform, dehydrated with Na_2SO_4, and purified by re-crystallization with EtOH to give a yellow-orange oil (7.0 g, 98%). ^{1}H-NMR (850 MHz, $CDCl_3$): δ in ppm 0.86 (t, 3H, J = 7.2 Hz, CH_3), 1.23–1.31 (m, 8H, $4CH_2$), 1.42 (quint, 2H, J = 7.6 Hz, CH_2), 1.78 (quint, 2H, J = 7.4 Hz, CH_2), 3.85 (t, 2H, J = 7.2 Hz, CH_2), 6.71 (d, 1H, J = 8.7 Hz, ArH), 6.9 (d, 1H, J = 8.5 Hz, ArH), 7.22 (d, 1H, J = 2.3 Hz, ArH), 7.25 (dd, 1H, J = 8.6, 2.3 Hz, ArH), 7.57 (d, 1H, J = 1.9 Hz, ArH), 7.65 (dd, 1H, J = 8.5, 1.9 Hz, ArH), 9.8 (s, 1H, CHO). ^{13}C-NMR (214 MHz, $CDCl_3$): δ in ppm 14.07 (CH_3), 22.57 (CH_2), 26.57 (CH_2), 26.7 (CH_2), 29.07 (CH_2), 29.13 (CH_2), 31.66 (CH_2), 48.02 (NCH_2), 114.97 (CH), 115.78 (C), 117.06 (CH), 124.34 (C), 126.09 (C), 128.43 (CH), 129.75 (CH), 130.2 (CH), 130.24 (CH), 131.21 (C), 142.58 (C), 150.3 (C), 189.03 (CHO). IR (cm^{-1}): C-H olefinic 3051, C-H aliphatic 2943, 2852, C-H aldehyde 2725, C=O 1684, C=C 1593, 1563. MS (ESI): m/z calcd for $C_{21}H_{25}BrNOS$ 418.1 $[M+1]^+$ and 420.1 $[M+3]^+$, found 418.0 and 420.0, respectively.

3.2.4. Synthesis of 3-bromo-10-octyl-7-(1,4,5-triphenyl-1H-imidazol-2-yl)-10H-phenothiazine (**4**)

To a solution of compound **3a** (0.4 g, 1 mmol) and phenylamine (0.1 g, 1.5 mmol) in glacial acetic acid, benzil (0.2 g, 1 mmol), and ammonium acetate (0.4 g, 5 mmol) was added. The mixture was stirred at 110 °C for 12 h. After cooling, the solution was poured into a copious amount of water and then neutralized with sodium bicarbonate solution. The dark precipitate was filtered and washed with water. The product was then purified by column chromatography on silica gel by using petroleum ether:ethyl acetate (97:3) as an eluent, affording compound **4** as an off-white powder (0.5 g (82%), m.p. 145 °C). ^{1}H-NMR (850 MHz, DMSO-d_6) δ: 7.47–7.48 (m, 2H, ArH), 7.32–7.37 (m, 5H, ArH), 7.28–7.30 (m, 5H, ArH), 7.23–7.26 (m, 4H, ArH), 7.18 (t, 1H, J = 7.65 Hz, ArH), 7.14 (dd, 1H, J = 8.5, 1.7 Hz, ArH), 7.12 (d, 1H, J = 1.7 Hz, ArH), 6.91–6.94 (m, 2H, ArH), 3.80 (t, 2H, J = 6.8 Hz, N-CH_2), 1.61 (qn, 2H, J = 7.65 Hz, CH_2), 1.33 (qn, 2H, J = 7.65 Hz, CH_2), 1.18–1.23 (m, 8H, $4CH_2$), 0.83 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, DMSO-d_6) δ: 145.4, 144.8, 143.8, 136.1, 131.7, 131.6, 130.7, 130.1, 130.0, 129.7, 129.5, 129.4, 129.2, 128.9, 128.6, 128.1, 126.9, 126.8, 125.9, 122.8, 118.1, 115.9, 114.4, 47.0, 31.5, 29.0, 28.9, 26.4, 22.5, 14.4. IR (cm^{-1}): C-H olefinic 3061, C-H aliphatic 2922, 2854, C=C stretch 1600. MS (ESI): m/z calcd for $C_{41}H_{39}BrN_3S$ 684.2 $[M+1]^+$ and 686.2 $[M+3]^+$, found 684.2 and 686.2, respectively.

3.2.5. Synthesis of 10-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-(1,4,5-triphenyl-1H-imidazol-2-yl)-10H-phenothiazine (**5**)

A solution of **4** (0.7 g, 1 mmol), bis(pinacolato)diboron (0.3 g, 1.1 mmol), potassium acetate (0.3 g, 2.5 mmol), and Bis(triphenylphosphine)palladium(II) dichloride (0.02 g, 0.02 mmol) in dry toluene (40 mL) was refluxed at 110 °C under an N_2 atmosphere for 18 h. After being cooled to room temperature, the mixture was poured into water (40 mL), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 40 mL), and the combined organic layers were dried over anhydrous sodium sulphate. The organic solvent was evaporated to dryness, and the crude product was purified by silica gel column chromatography, eluting with petroleum ether:ethyl acetate (94:6) to obtain 0.4 g (60%) of a yellow solid (m.p.: 140 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ: 7.61 (d, 2H, J = 7.65 Hz, ArH), 7.58 (dd, 1H, J = 8.5, 1.7 Hz, ArH), 7.51 (d, 1H, J = 1.7 Hz, ArH), 7.21–7.34 (m, 10H, ArH), 7.13–7.14 (m, 3H, ArH), 7.07 (m, 2H, ArH), 6.80 (d, 1H, J = 8.5 Hz, ArH), 6.67 (d, 1H, J = 8.5 Hz, ArH), 3.80 (t, 2H, J = 7.65 Hz, NCH_2), 1.76 (qn, 2H, J = 7.65 Hz, CH_2), 1.39 (qn, 2H, J = 7.65 Hz, ArH), 1.34 (s, 12H, $4CH_3$), 1.25–1.30 (m, 8H, $4CH_2$), 0.89 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ: 147.24, 146.09, 144.66, 136.95, 134.11, 133.76, 131.12, 130.67, 130.51, 129.20, 128.43, 128.35, 128.20, 127.97, 127.76, 127.64, 127.47, 126.67, 124.57, 123.50, 114.69, 114.62, 83.73, 47.49, 31.76, 29.21, 29.18, 26.81, 26.64, 24.85, 22.65, 14.15. IR (cm^{-1}): C-H aliphatic 2924, 2854, C=C stretch 1580. MS (ESI): m/z calcd for $C_{47}H_{51}BN_3O_2S$ 732.4 $[M+1]^+$, found 732.6.

3.2.6. Synthesis of 10-octyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine-3-carbaldehyde (**6a**)

Potassium acetate (4.2 g, 0.03 mol) and Pd(dppf)Cl_2 (0.4 g, 5×10^{-4} mol) were added to the mixture of the brominated derivatives **3a** (4.2 g, 0.01 mol) and bis(pinacolato)diboron (3.1 g, 0.012 mol) in dry 1,4-dioxane (100 mL). The reactions took place under a nitrogen atmosphere with reflux at 90 °C for 34 h. The mixtures were left to cool down to room temperature before performing extraction with $CHCl_3$ (20 mL × 5–6 times). After extraction, the organic layers were dried with anhydrous Na_2SO_4 and worked up as usual. Purification with column chromatography, using the system PE/EA (9.5:0.5) as an eluent, afforded the desired pure compound as a yellow oil (3.5 g, 74%). ^{1}H-NMR (850 MHz, $CDCl_3$): δ in ppm 9.78 (s, 1H, CHO), 7.61 (dd, 1H, *J* = 8.4, 1.7 Hz, ArH), 7.58 (dd, 1H, *J* = 8.1, 1.1 Hz, ArH), 7.55 (d, 1H, *J* = 1.7 Hz, ArH), 7.52 (d, 1H, *J* = 1.1 Hz, ArH), 6.88 (d, 1H, *J* = 8.4 Hz, ArH), 6.84 (d, 1H, *J* = 8.2 Hz, ArH), 3.87 (t, 2H, *J* = 7.3 Hz, CH_2), 1.79 (quint, 2H, *J* = 7.4 Hz, CH_2), 1.41 (quint, 2H, *J* = 7.4 Hz, CH_2), 1.32 (s, 12H, $4CH_3$), 1.21–1.3 (m, 8H, $4CH_2$), 0.85 (t, 3H, *J* = 7.3 Hz, CH_3). ^{13}C-NMR (214 MHz, $CDCl_3$): δ in ppm 190.12 (CHO), 150.25 (C), 145.92 (C), 134.39 (CH), 133.9 (CH), 131.18 (C), 129.96 (CH), 128.42 (CH), 125.14 (C), 122.96 (C), 115.26 (CH), 114.92 (CH), 83.88 (2C), 48.01 (NCH_2), 31.72 (CH_2), 29.18 (CH_2), 29.13 (CH_2), 26.75 (CH_2), 26.64 (CH_2), 24.85 ($4CH_3$), 22.63 (CH_2), 14.13 (CH_3). IR cm^{-1}: C-H olefinic 3043, C-H aliphatic 2954, 2853, C-H aldehyde 2724, C=O 1686, C=C 1602, 1578.

3.2.7. Synthesis of 5-bromo-1-ethyl-2,3,3-trimethyl-3H-indolium iodide (**11**)

N-alkylation of the indolenine derivative was carried out through the dissolution of a mixture of 5-bromo-2,3,3-trimethylindolenine (14.3 g, 60 mmol) and iodoethane (28.0 g, 180 mmol) in 150 mL acetonitrile at room temperature, which was then refluxed at 85 °C for 48 h. Then, the CH_3CN was evaporated using a rotary evaporator. Pure brown crystals **11** (21.2 g, 89.6%) with an m.p. of 220.5 °C were obtained by concentrating the residue in acetone and re-precipitating with diethyl ether (five times). ^{1}H-NMR (600 MHz, DMSO-d_6): δ in ppm 8.18 (d, 1H, *J* = 1.7 Hz, ArH), 7.94 (d, 1H, *J* = 8.5 Hz, ArH), 7.85 (dd, 1H, *J* = 8.6, 1.8 Hz, ArH), 4.47 (q, 2H, *J* = 7.3 Hz, CH_2), 2.81 (s, 3H, CH_3), 1.54 (s, 6H, $2CH_3$), 1.42 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C-NMR (214 MHz, DMSO-d_6): δ in ppm 197.08, 144.68, 140.48, 132.37, 127.34, 123.25, 117.71, 54.86, 43.8, 22.11, 14.37, 13.01.IR, cm^{-1}: C-H olefinic 3049,C-H aliphatic 2985, 2969, C=N 1605, C=C 1451.

3.2.8. Synthesis of (E)-5-bromo-2-(4-(dimethylamino)styryl)-1-ethyl-3,3-dimethyl-3H-indolium iodide (**12**)

5-bromo-1-ethyl-2,3,3-trimethyl-3H-indolium iodide (10 mmol, 3.9 g) and 4-dimethylaminobenzaldehyde (12 mmol, 1.6 g) were added to 50 mL ethanol. A catalytic amount of piperidine (1 mmol, 0.1 g, 0.1 mL) was added and refluxed at 60 °C overnight. It was then cooled to room temperature, evaporated, and finally purified by reprecipitation with diethyl ether (3–5 times) to yield 5.2 g (99%) of dark green crystals (m.p.: 219 °C). ^{1}H-NMR (850 MHz, DMSO-d_6): δ (ppm) 8.35 (d, 1H, *J* = 15.5 Hz, =CH), 8.12–8.11 (m, 3H, 3ArH), 7.74 (dd, 1H, *J* = 8.5, 1.9 Hz, ArH), 7.67 (d, 1H, *J* = 8.5 Hz, ArH), 7.22 (d, 1H, *J* = 15.5 Hz, =CH), 6.89 (d, 2H, *J* = 9.1 Hz, 2ArH), 4.5 (q, 2H, *J* = 7.3 Hz, CH_2), 3.18 (s, 6H, $3CH_2$), 1.75 (s, 6H, $3CH_2$), 1.35 (t, 3H, *J* = 7.3 Hz, CH_3). ^{13}C-NMR (213.77 MHz, DMSO-d_6): δ (ppm) 178.55 (C=N), 155.17 (CH), 154.81 (C), 145.01 (C), 140.18 (C), 131.64 (2CH), 126.21 (CH), 122.44 (C), 120.15 (C), 115.19 (2CH), 112.35 (CH), 104.11 (2CH), 51.01 (C), 40.57 (CH_2), 40.01 ($2CH_3$), 26.29 ($2CH_3$), 13.09 (CH_3). IR (cm^{-1}): C-H olefinic 3073, 3016, C-H aliphatic 2972, 2911, C=N 1612, 1591, C=C 1566, 1523. HRMS (ESI): m/z calc. mass for $C_{22}H_{26}BrN_2$ is 397.12739 $[M]^+$ and 399.12534 $[M+2]^+$, found 397.12741 and 399.12519.

3.2.9. Synthesis of 5-bromo-1-ethyl-3,3-dimethyl-2-((E)-3-((E)-1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium iodide (**13**)

5-Bromo-1-ethyl-2,3,3-trimethyl-3H-indolium iodide (11.8 g, 30 mmol) and (*E*)-2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde (7.2 g, 36 mmol) were dissolved in a dry flask

containing 100 mL of acetic anhydride and left under reflux with stirring at 90 °C for 24 h. After cooling to room temperature, the mixture was dried by vacuum. Purification of the product was carried out by reprecipitation with diethyl ether (three times). The product was obtained in a quantitative yield (17.3 g, 99%) as a dark blue powder (293 °C). ^{1}H-NMR (850 MHz, DMSO-d$_6$): δ (ppm) 8.33 (dd, 1H, *J* = 13.5 Hz, =CH), 7.93 (d, 1H, *J* = 2 Hz, ArH), 7.66 (d, 1H, *J* = 7.3 Hz, ArH), 7.63 (dd, 1H, *J* = 8.3, 2 Hz, ArH), 7.51 (d, 1H, *J* = 7.9 Hz, ArH), 7.47 (ddd, 1H, *J* = 8, 8, 1.1 Hz, ArH), 7.41 (d, 1H, *J* = 8.4 Hz, ArH), 7.33 (ddd, 1H, *J* = 7.3, 7.3, 0.9 Hz, ArH), 6.53 (d, 1H, *J* = 13.6 Hz, =CH), 6.47 (d, 1H, *J* = 13.3 Hz, =CH), 4.13 (q, 2H, *J* = 7.2 Hz, CH_2), 3.68 (s, 3H, CH_3), 1.70 (s, 6H, $2CH_3$), 1.69 (s, 6H, $2CH_3$), 1.30 (t, 3H, *J* = 7.3 Hz, CH_3). ^{13}C-NMR (213.77 MHz, DMSO-d$_6$): δ (ppm) 175.05 (C=N), 172.35 (C=N), 149.71 (CH), 142.87 (C), 142.55 (C), 140.93 (C), 140.72 (C), 131.35 (CH), 128.59 (CH), 125.78 (2CH), 125.54 (CH), 122.43 (CH), 117.13 (C), 112.88 (CH), 111.81 (CH), 103.74 (CH), 101.99 (CH), 49.05 (C), 48.82 (C), 38.92 (CH_2), 31.64 (CH_3), 27.24 ($2CH_3$), 27.16 ($2CH_3$), 21.05 (C), 12.06 (CH_3). IR (cm^{-1}): C-H olefinic 3015, C-H aliphatic 2991, 2968, 2941, C=N 1607, C=C 1549, 1403. HRMS (ESI): *m*/*z* calc. mass for $C_{26}H_{30}BrN_2$ is 449.15869 [M]$^+$ and 451.15664 [M+2]$^+$, found 449.15840 and 451.15628, respectively.

3.2.10. General Procedure of the Suzuki Coupling Reaction for the Synthesis of (**14**, **15a**–**c**), (**15a**), (**15b**), (**15c**)

Before adding any of the reactants or reagents, a mixture of toluene/methanol solvents (1:1) was brought to an inert condition by degassing and purging Ar gas for several minutes. The boronic ester, brominated compound, catalyst (Pd(dppf)Cl$_2$), and base (K_2CO_3) were added to the inert mixture of solvents in the following proportions (1.5:1:0.1:5). The mixture was purged again with Ar and then left to reflux at 80 °C until completion.

(E)-2-(4-(dimethylamino)styryl)-1-ethyl-5-(7-formyl-10-octyl-10H-phenoxazin-3-yl)-3,3-dimethyl-3H-indol-1-ium iodide (**14**)

A mixture of **12** (1.3 g, 2.5 mmol), **6b** (1.8 g, 3.8 mmol), Pd(dppf)Cl$_2$ (0.2 g, 0.3 mmol), and K_2CO_3 (1.7 g, 12.5 mmol) was added to the inert solvent mix (Toluene/MeOH, 10:10 mL). The reaction vessel was left to reflux under argon for 24 h. The reaction mixture was then evaporated and filtered by DCM, and the filtrate was finally purified by column chromatography, with a gradual increase in polarity from $CHCl_3$ to $CHCl_3$:MeOH (7:3). The compound was obtained in a low yield (0.5 g, 26%) as a dark blue solid (m.p.: 248 °C). ^{1}H-NMR (850 MHz, DMSO-d$_6$): δ (ppm) 9.69 (s, 1H, CHO), 8.35 (d, 1H, *J* = 15.5 Hz, =CH), 8.12 (d, 1H, *J* = 1.6 Hz, ArH), 8.11 (broad d, 2H, *J* = 6.7 Hz, 2ArH), 7.82 (dd, 1H, *J* = 8.5, 1.7 Hz, ArH), 7.74 (d, 1H, *J* = 8.5 Hz, ArH), 7.47 (dd, 1H, *J* = 8.3, 1.8 Hz, ArH), 7.36 (dd, 1H, *J* = 8.4, 2.1 Hz, ArH), 7.27 (d, 1H, *J* = 15.5 Hz, =CH), 7.24 (d, 1H, *J* = 2.1 Hz, ArH), 7.04 (d, 1H, *J* = 1.8 Hz, ArH), 6.92 (dd, 2H, *J* = 8.5, 5.4 Hz, 2ArH), 6.90 (d, 2H, *J* = 9.1 Hz, 2ArH), 4.56 (q, 2H, *J* = 7.2 Hz, CH_2), 7.71 (t, 2H, *J* = 8.0 Hz, CH_2), 3.18 (s, 6H, $2CH_3$), 1.81 (s, 6H, $2CH_3$), 1.16 (quint, 3H, *J* = 7.4 Hz, CH_3), 1.44 (quint, 2H, *J* = 7.5 Hz, CH_2), 1.40 (t, 3H, *J* = 7.3 Hz, CH_3), 1.36 (quint, 2H, *J* = 7.9 Hz, CH_2), 1.31–1.26 (m, 4H, $2CH_2$), 0.87 (t, 3H, *J* = 7.0 Hz, CH_3). ^{13}C-NMR (213.77 MHz, DMSO-d$_6$): δ (ppm) 189.95 (CHO), 178.43 (C=N)), 154.30 (C), 154.50 (C), 144.22 (C), 144.04 (C), 143.72 (C), 139.86 (C), 138.22 (C), 138.03 (C), 133.09 (C), 130.83 (C), 129.65 (C), 129.63 (C), 129.20 (CH), 126.18 (CH), 122.62 (CH), 122.42 (C), 120.33 (2CH), 113.69 (CH), 113.45 (CH), 113.34 (CH), 113.02 (CH), 112.21 (CH), 111.86 (CH), 104.53 (CH), 50.98 (C), 43.18 (CH_2), 40.56 (CH_2), 39.91 ($2CH_3$), 31.22 (CH_2), 28.80 (CH_2), 28.71 (CH_2), 26.42 ($2CH_3$), 25.97 (CH_2), 24.60 (CH_2), 22.07 (CH_2), 13.97 (CH_3), 13.26 (CH_3). IR (cm^{-1}): C-H olefinic 3052, C-H aliphatic 2922, 2851, C=O 1671, C=N 1608, C=C 1567, 1502. HRMS (ESI): *m*/*z* calc. mass for $C_{44}H_{50}O_2N_3$ is 640.38975 [M]$^+$, found 640.38899.

1-ethyl-5-(7-formyl-10-octyl-10H-phenothiazin-3-yl)-3,3-dimethyl-2-((E)-3-((E)-1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium iodide (**15a**)

The mixture of **13** (1.6 g, 2.7 mmol), **6a** (1.9 g, 4.1 mmol), Pd(dppf)Cl$_2$ (0.2 g, 0.3 mmol), and K_2CO_3 (1.9 g, 13.5 mmol) was refluxed in inert toluene/MeOH (10:10 mL) for half an hour. After completion, the mixture was evaporated, extracted with $CHCl_3$, and then

reprecipitated from DCM by PE. A pure dark violet solid of compound **15a** was obtained with a yield of 2.1 g (93%) and an m.p. of 172 °C. ^{1}H-NMR (850 MHz, DMSO-d$_6$): δ (ppm) 9.81 (s, 1H, CHO), 8.35 (t, 1H, *J* = 13.4 Hz, =CH), 7.98 (d, 1H, *J* = 1.6 Hz, ArH), 7.74 (dt, 2H, *J* = 8.4, 1.7 Hz, 2ArH), 7.64 (d, 1H, *J* = 7.3 Hz, ArH), 7.63 (d, 1H, *J* = 1.9 Hz, ArH), 7.61 (dd, 1H, *J* = 8.5, 2.1 Hz, ArH), 7.59 (d, 1H, *J* = 2.2 Hz, ArH), 7.51 (d, 1H, *J* = 8.4 Hz, ArH), 7.48–7.45 (m, 2H, 2ArH), 7.31 (dt, 1H, *J* = 7.4, 1.8 Hz, ArH), 7.21 (d, 1H, *J* = 8.5 Hz, ArH), 7.17 (d, 1H, *J* = 8.6, ArH), 6.5 (d, 1H, *J* = 13.4 Hz, =CH), 6.50 (d, 1H, *J* = 13.5 Hz, =CH), 4.19 (q, 2H, *J* = 7.1 Hz, CH_2), 4.00 (t, 3H, *J* = 7 Hz, CH_2), 3.66 (s, 3H, CH_3), 1.75 (s, 6H, 2CH_3), 1.71 (s, 6H, 2CH_3), 1.41 (quint, 2H, CH_2), 1.34 (t, 3H, *J* = 7.3 Hz, CH_3), 1.28 (quint, 2H, *J* = 7.8, CH_2), 1.24–1.19 (m, 8H, 4CH_2), 0.82 (t, 3H, *J* = 6.9 Hz, CH_3). ^{13}C-NMR (213.77 MHz, DMSO-d$_6$): δ (ppm) 190.65, 174.45, 173.11, 149.79, 149.49, 142.70, 142.30, 141.63, 140.88, 140.64, 135.87, 134.84, 130.96, 130.42, 128.65, 127.79, 126.55, 126.20, 125.32, 125.11, 123.32, 123.22, 122.46, 120.55, 116.92, 115.69, 111.63, 111.58, 103.11, 102.47, 49.03, 48.93, 47.03, 39.07, 31.12, 28.63, 28.48, 27.42, 27.34, 26.06, 25.94, 22.6, 13.99, 12.32. IR (cm^{-1}): C-H olefinic 3030, C-H aliphatic 2926, 2854, C=N 1682, C=O 1557, C=C 1446, 1413. HRMS (ESI): *m*/*z* calc. mass for $C_{47}H_{54}N_3OS^+$ is 708.3982 [M]$^+$, found 708.3790.

1-ethyl-5-(7-formyl-10-octyl-10H-phenoxazin-3-yl)-3,3-dimethyl-2-((E)-3-((E)-1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium iodide (**15b**)

The starting materials **13** (1.4 g, 2.5 mmol) and **6b** (1.8 g, 3.8 mmol) were mixed with the Pd(dppf)Cl_2 catalyst (0.2 g, 0.3 mmol) and K_2CO_3 base (1.7 g, 12.5 mmol) in toluene/MeOH (10:10 mL) and refluxed at 80 °C under Ar for 24 h. The reaction mixture was then evaporated, extracted with chloroform, and reprecipitated from DCM by PE:EA (1:1). Purified **15b** was obtained with a yield of 1.9 g (93%) as a dark violet-blue powder (m.p: 223 °C). ^{1}H-NMR (850 MHz, $CDCl_3$): δ (ppm) 9.67 (s, 1H, CHO), 8.41 (t, 1H, *J* = 13.3 Hz, =CH), 7.52 (dd, 1H, *J* = 8.2, 1.7 Hz, ArH), 7.46 (d, 1H, *J* = 1.6 Hz, ArH), 7.39 (td, 1H, *J* = 7.9, 1.0 Hz, ArH), 7.36 (d, 1H, *J* = 7.4 Hz, ArH), 7.33 (dd, 1H, *J* = 8.2, 1.8 Hz, ArH), 7.25–7.22 (m, 3H, ArH & 2 = CH), 7.16 (d, 1H, *J* = 8.2 Hz, ArH), 7.13 (d, 1H, *J* = 7.9 Hz, ArH), 7.10 (d, 1H, *J* = 1.8 Hz, ArH), 7.07 (dd, 1H, *J* = 8.2, 2.1 Hz, ArH), 6.90 (d, 1H, *J* = 2.1 Hz, ArH), 6.61 (d, 1H, *J* = 8.3 Hz, ArH), 6.55 (d, 1H, *J* = 8.3 Hz, ArH), 4.32 (q, 2H, *J* = 7.2 Hz, CH_2), 3.79 (s, 3H, CH_3), 3.56 (t, 2H, *J* = 8.1 Hz, CH_2), 1.74 (s, 6H, 2CH_3), 1.72 (s, 6H, 2CH_3), 1.50 (t, 3H, *J* = 7.2 Hz, CH_3), 1.45 (quint, 2H, *J* = 7.5 Hz, CH_2), 1.39 (quint, 2H, *J* = 7.3 Hz, CH_2), 1.34–1.28 (m, 8H, 4CH_2), 0.89 (t, 3H, *J* = 7.0 Hz, CH_3). ^{13}C-NMR (213.77 MHz, $CDCl_3$): δ (ppm) 189.75 (CHO), 174.16 (C=N), 173.00 (C), 150.49 (C), 145.15 (C), 145.01 (C), 142.84 (C), 141.65 (C), 141.06 (C), 140.59 (C), 138.92 (C), 137.33 (C), 134.49 (C), 131.13 (C), 130.14 (C), 129.00 (2CH), 127.01 (CH), 125.42 (CH), 122.37 (CH), 122.13 (CH), 120.05 (CH), 114.20 (CH), 114.05 (CH), 112.64 (CH), 111.21 (CH), 110.94 (CH), 110.81 (CH), 105.16 (CH), 104.88 (CH), 49.10 (C), 48.95 (C), 44.51 (CH_2), 40.43 (CH_2), 32.79 (CH_3), 31.88 (CH_2), 29.45 (CH_2), 29.36 (CH_2), 28.31 (2CH_3), 28.27 (2CH_3), 26.97 (CH_2), 25.20 (CH_2), 22.74 (CH_2), 14.22 (CH_3), 13.11 (CH_3). IR (cm^{-1}): C-H olefinic 3033, C-H aliphatic 2923, 2852, C=N 1672, C=O 1553, C=C 1504, 1416. HRMS (ESI): *m*/*z* calc. mass for $C_{47}H_{54}O_2N_3$ is 694.42105 [M]$^+$, found 694.42011.

1-ethyl-5-(6-formyl-9-octyl-9H-carbazol-3-yl)-3,3-dimethyl-2-((E)-3-((E)-1,3,3-trimethylindolin-2-ylidene)prop-1-en-1-yl)-3H-indol-1-ium iodide (**15c**)

The following amounts of the reactant, catalyst, and base were used: **13** (1.6 g, 2.8 mmol), **6c** (1.8 g, 4.2 mmol), Pd(dppf)Cl_2 (0.2 g, 0.3 mmol), and K_2CO_3 (1.9 g, 14.0 mmol) were mixed with toluene/MeOH (10:10 mL) in an inert environment and refluxed at 80 °C for half an hour. The purification process was conducted after evaporation and extraction with $CHCl_3$ through reprecipitation from DCM by PE. Compound **15c** was obtained as a dark violet solid with a yield of 2.25 g (100%) and an m.p. of 181 °C. ^{1}H-NMR (850 MHz, DMSO-d$_6$): δ (ppm) 10.10 (s, 1H, CHO), 8.89 (d, 1H, *J* = 1.3 Hz, ArH), 8.75 (d, 1H, *J* = 1.6 Hz, ArH), 8.38 (t, 1H, *J* = 13.4 Hz, =CH), 8.14 (d, 1H, *J* = 1.6 Hz, ArH), 8.04 (dd, 1H, *J* = 8.5, 1.4 Hz, ArH), 7.95 (dd, 1H, *J* = 8.5, 1.7 Hz, ArH), 7.91 (dd, 1H, *J* = 8.2, 1.7 Hz, ArH), 7.83 (d, 1H, *J* = 8.5 Hz, ArH), 7.81 (d, 1H, *J* = 8.5 Hz, ArH), 7.65 (d, 1H, *J* = 7.3 Hz, ArH), 7.59 (d, 1H, *J* = 8.3 Hz, ArH), 7.48–7.45 (m, 2H, 2ArH), 7.31 (dt, 1, *J* = 6.8, 1.9 Hz, ArH), 6.55 (d, 1H,

J = 13.4 Hz, =CH), 6.50 (d, 1H, *J* = 13.4 Hz, =CH), 4.52 (t, 2H, *J* = 7.1 Hz, CH_2), 4.24 (quint, 2H, *J* = 7.2 Hz, CH_2), 3.67 (s, 3H, CH_3), 1.81 (s, 6H, $2CH_3$), 1.72 (s, 6H, $2CH_3$), 1.38 (t, 3H, *J* = 7.3 Hz, CH_3), 1.31–1.26 (m, 4H, $2CH_2$), 1.23–1.16 (m, 8H, $4CH_2$), 0.81 (t, 3H, *J* = 7.2 Hz, CH_3). ^{13}C-NMR (213.77 MHz, DMSO-d_6): δ (ppm) 191.92, 174.27, 173.18, 149.41, 144.13, 142.72, 141.69, 140.58, 140.48, 138.17, 131.88, 128.63, 128.42, 127.37, 127.15, 125.86, 125.23, 123.88, 123.06, 122.52, 122.45, 121.09, 119.09, 111.72, 111.50, 110.64, 110.10, 102.93, 102.53, 49.12, 48.86, 42.77, 31.17, 28.73, 28.61, 28.54, 27.48, 27.37, 26.41, 22.03, 13.95, 12.38. IR (cm^{-1}): C-H olefinic 3014, C-H aliphatic 2927, 2854, C=N 1682, C=O 1594, C=C 1557, 1447. HRMS (ESI): *m*/*z* calc. mass for $C_{47}H_{54}N_3O^+$ is 676.4261 $[M]^+$, found 676.4304.

3.2.11. Synthesis of 7-(4-(diphenylamino)phenyl)-10-octyl-10H-phenothiazine-3-carbaldehyde (**16**)

4-Bromo-N,N-diphenylaniline (0.8 g, 2.5 mmol), **6a** (1.2 g, 2.5 mmol), $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol), and 2M of K_2CO_3 (2.5 mL) were mixed with degassed and inert toluene (10 mL). The mixture was refluxed at 90 °C under an Ar atmosphere for 20 h. The mixture underwent evaporation, extraction with DCM, dehydration with Na_2SO_4, and, finally, purification with column chromatography, using PE:EA (9.5:0.5) as an eluent to obtain a yellow semisolid compound (0.7 g, 49%). ^{1}H-NMR (850 MHz, $CDCl_3$): δ (ppm) 9.79 (s, 1H, CHO), 7.64 (dd, 1H, *J* = 8.4, 1.9 Hz, ArH), 7.59 (d, 1H, *J* = 1.9 Hz, ArH), 7.39 (d, 2H, *J* = 8.6 Hz, 2ArH), 7.35 (d, 1H, *J* = 7.7 Hz, ArH), 7.31 (d, 1H, *J* = 2.1 Hz, ArH), 7.27 (dd overlapped with solvent, 4H, *J* = 8.3, 7.4 Hz, 4ArH), 7.12 (d, 4H, *J* = 7.6 Hz, 4ArH), 7.11 (d, 2H, *J* = 8.6 Hz, 2ArH), 7.04 (t, 2H, *J* = 7.4 Hz, 2ArH), 6.90 (dd, 2H, *J* = 8.4, 5.5 Hz, 2ArH), 3.90 (t, 2H, *J* = 7.0 Hz, CH_2), 1.84 (quint, 2H, *J* = 7.5 Hz, CH_2), 1.46 (quint, 2H, *J* = 7.5 Hz, CH_2), 1.34 (quint, 2H, *J* = 7.5 Hz, CH_2), 1.30–1.25 (m, 6H, $3CH_2$), 0.87 (t, 3H, *J* = 7.1 Hz, CH_3). ^{13}C-NMR (213.77 MHz, $CDCl_3$): δ (ppm) 190.13, 150.62, 147.73, 147.31, 142.19, 136.36, 133.55, 131.11, 130.28, 129.42, 128.55, 127.27, 125.76, 125.53, 124.67, 124.57, 124.16, 123.98, 123.12, 116.20, 114.80, 48.21, 31.85, 29.32, 29.28, 26.96, 26.85, 22.74, 14.23. IR (cm^{-1}): C-H olefinic 3033, C-H aliphatic 2952, 2925, C=O 1686, C=C 1581.

3.2.12. Benzo[c][1,2,5]thiadiazole (**17**)

To a suspension of the compound *o*-phenylenediamine (5 g, 46.7 mmol, 1.0 eq) in dry toluene (100 mL), thionyl chloride ($SOCl_2$) (24.6 g, 15 mL, 206.9 mmol, 4.4 eq) was added. It was then refluxed for 3 h, followed by the addition of $SOCl_2$ (5 mL, 1.5 eq) and dry pyridine (1 mL), dropwise. The reaction continued for an additional 19 h while monitoring the reaction by TLC. Toluene and an excess amount of $SOCl_2$ were removed under vacuum, and the residue was collected, poured into water, extracted using EA (50 mL × 4–5 times), washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product. Therefore, the purification of the crude product by silica gel column chromatography, using PE/EA (50:1) as an eluent, gave **17** as white needles (4.6 g, 72%) (m.p.: 43 °C). ^{1}H-NMR (600 MHz, $CDCl_3$) δ ppm: 7.99 (dd, 2H, *J* = 6.6, 3.0 Hz, ArH), 7.57 (dd, 2H, *J* = 6.6, 3.0 Hz, ArH). ^{13}C-NMR (150 MHz, $CDCl_3$) δ ppm: 121.66, 129.40, 154.90. IR (cm^{-1}): C-H olefinic 3061, C=C 1519, 1478.

3.2.13. 4,7-Dibromobenzo[c][1,2,5]thiadiazole (**18**)

Compound **17** (5 g, 36.7 mmol, 1.0 eq) was suspended in hydrobromic acid (HBr, 47%) (100 mL). It was then refluxed with stirring, and bromine (Br_2) (5.7 mL, 110.3 mmol, ~3.0 eq) was added in a dropwise manner for about 3 h. Then, it was refluxed for another 2 h while monitoring the reaction by TLC. The precipitate was filtered off and recrystallized from a mixture of acetic acid (AcOH) and EtOH to yield **18** as white needles (7.5 g, 70%) (m.p.: 189 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 7.73 (s, 2H, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 114.04, 132.52, 153.09. IR (cm^{-1}): C-H olefinic 3079, 3046, C=C 1587, 1498, 1475.

3.2.14. 3,6-Dibromobenzene-1,2-diamine (**19**)

Compound **18** (2 g, 6.8 mmol, 1.0 eq) was dissolved in THF (108 mL) and EtOH (40 mL). It was then cooled to 0 °C, and sodium borohydride ($NaBH_4$) (4.4 g, 116 mmol, 17.0 eq) was added in a portion wise manner. Then, the mixture was stirred at RT for 20 h while monitoring the reaction by TLC. The solvent under vacuum was removed after the reaction was complete; the mixture was extracted with diethyl ether (Et_2O) (40 mL × 4–5 times), washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product. Then, purification by silica gel column chromatography, using PE/EA (5:1) as an eluent, gave **19** as a pale-yellow solid (1.6 g, 88%) (m.p. 89 °C). ^{1}H-NMR (600 MHz, $CDCl_3$) δ ppm: 6.84 (s, 2H, ArH), 3.79 (br, s, 4H, $2NH_2$). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 109.83, 123.40, 133.86. IR (cm^{-1}): NH_2 3396, 3366, N-H bend 1647, C=C 1444.

3.2.15. 5,8-Dibromo-2,3-diphenylquinoxaline (**20**)

Compound **19** (13.1 g, 49.4 mmol, 1.0 eq) and benzil (10.4 g, 49.7 mmol, 1.0 eq) were mixed in toluene (180 mL) and glacial AcOH (120 mL). It was then refluxed with stirring for 3 h while monitoring the reaction by TLC. It was then cooled to room temperature, followed by solvent removal under vacuum. The residue obtained was extracted from an aqueous solution using $CHCl_3$ (100 mL × 4–5 times), followed by the usual work-up above to afford the crude product. Recrystallization from a mixture of $CHCl_3$/ MeOH (1:4) afforded **20** as white needles (16.9 g, 78%) (m.p. 216 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 7.92 (s, 2H, ArH), 7.66 (d, 4H, *J* = 7.65 Hz, ArH), 7.41 (t, 2H, *J* = 7.65 Hz, ArH), 7.36 (t, 4H, *J* = 7.65 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 123.85, 128.52, 129.72, 130.38, 133.24, 138.04, 139.48, 154.28. IR (cm^{-1}): C-H olefinic 3064, 3061, C=C 1584, 1454.

3.2.16. 2,3-Diphenyl-5,8-di(thiophen-2-yl)quinoxaline (**21**)

To a mixture of compound **20** (0.7 g, 1.5 mmol, 1.0 eq) and tributyl(thiophen-2-yl)stannane (1.7 g, 4.5 mmol, 3.0 eq) in dry toluene (20 mL), $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.1 mmol, 0.05 eq) was added under a nitrogen atmosphere. It was then refluxed for 2 h at 110 °C while monitoring the reaction by TLC. After reaction was complete, the mixture was cooled to room temperature, followed by solvent removal under vacuum. The residue obtained was extracted from an aqueous solution using $CHCl_3$ (20 mL × 4–5 times), followed by the usual work-up to afford the crude product. Therefore, the crude product was purified by silica gel column chromatography, using PE/DCM (3:1) as an eluent, to obtain **21** as an orange solid (0.6 g, 85%) (m.p. 208 °C). R_f = 0.395 (eluent: PE/DCM, 3:1). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 8.14 (s, 2H, ArH), 7.88 (dd, 2H, *J* = 3.4, 0.85 Hz, ArH), 7.75 (dd, 4H, *J* = 7.65, 0.85 Hz, ArH), 7.52 (dd, 2H, *J* = 5.1, 0.85 Hz, ArH), 7.38–7.41 (m, 6H, ArH), 7.19 (dd, 2H, *J* = 5.1, 3.4 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 126.58, 126.77, 127.22, 128.37, 129.03, 129.15, 130.62, 131.44, 137.37, 138.82, 138.89, 151.87. IR (cm^{-1}): C-H olefinic 3064, C=C 1633, 1467, 1421.

3.2.17. Quinoxaline-2,3(1H,4H)-dione (**22**)

The compound *o*-phenylenediamine (10. 5 g, 96.6 mmol, 1.0 eq) and oxalic acid dihydrate (13.6 g, 107.6 mmol, 1.1 eq) were refluxed in aqueous HCl (4 N, 100 mL) for 2 h at 100 °C while monitoring the reaction by TLC. It was then cooled to room temperature; then, the precipitate was filtered, washed several times with water, and dried to obtain **22** as a gray microcrystalline solid (14.2 g, 91%) (m.p. > 400 °C). ^{1}H-NMR (600 MHz, DMSO-d_6) δ ppm: 11.90 (s, 2H, 2NH), 7.12 (dd, 2H, *J* = 6.0, 3.6 Hz, ArH), 7.07 (dd, 2H, *J* = 6.0, 3.6 Hz, ArH). ^{13}C-NMR (213 MHz, DMSO-d_6) δ ppm: 115.15, 123.02, 125.62, 155.20. IR (cm^{-1}): C-H olefinic 3034, C=O 1671, C=C 1500, 1473.

3.2.18. 2,3-Dichloroquinoxaline (**23**)

To a solution of compound **22** (11.8 g, 72.5 mmol, 1.0 eq) in $POCl_3$ (77.9 g, 508.1 mmol, 47.5 mL, ~7.0 eq), DMF (1.2 g, 16.1 mmol, 1.3 mL, 0.22 eq) was added. It was then refluxed

for 3 h at 110 °C while monitoring the reaction by TLC. Then, it was cooled to room temperature and slowly poured into ice water. Then, the precipitate was filtered, washed with water, and dried to obtain pure **23** as a gray solid (13.3 g, 92%) (m.p. 154 °C). ^{1}H-NMR (600 MHz, $CDCl_3$) δ ppm: 8.03 (dd, 2H, J = 6.6, 3.6 Hz, ArH), 7.81 (dd, 2H, J = 6.6, 3.6 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 128.36, 131.38, 140.71, 145.50. IR (cm^{-1}): C-H olefinic 3043, C=C 1557, 1530, 1485.

3.2.19. 2,3-Di(thiophen-2-yl)quinoxaline (**24**)

To a mixture of **23** (5.9 g, 30 mmol, 1.0 eq) and tributyl(thiophen-2-yl)stannane (33.6 g, 90 mmol, 3.0 eq) in dry DMF (250 mL), $Pd(PPh_3)_2Cl_2$ (1.0 g, 1.5 mmol, 0.05 eq) was added under nitrogen atmosphere. It was then refluxed for 1 h at 110 °C while monitoring the reaction by TLC. After the reaction was complete, the temperature was lowered to get the mixture to room temperature, followed by the addition of water to stop the reaction. Following $CHCl_3$ extraction of the product (50 mL × 4–5 times), it was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure to obtain the crude product, and it was purified by column chromatography on silica gel, using PE/DCM (5:2) as an eluent, to obtain compound **24** as a yellow solid (8.7 g, 98%) (m.p. 14^5 °C). ^{1}H-NMR (600 MHz, $CDCl_3$) δ ppm: 8.08 (dd, 2H, J = 6.6, 3.6 Hz, ArH), 7.72 (dd, 2H, J = 6.6, 3.6 Hz, ArH), 7.50 (dd, 2H, J = 4.8, 1.2 Hz, ArH), 7.25 (dd, 2H, J = 3.6, 1.2 Hz, ArH), 7.04 (dd, 2H, J = 4.8, 3.6 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 127.72, 128.98, 129.04, 129.49, 130.29, 140.75, 141.56, 146.79. IR (cm^{-1}): C-H olefinic 3094, C=C 1550, 1521, 1474.

3.2.20. 4-(3-Chloroquinoxalin-2-yl)benzaldehyde (**25**)

Compound **23** (0.5 g, 2.5 mmol, 1.0 eq), 4-formylphenylboronic acid (0.6 g, 3.8 mmol, 1.5 eq), K_2CO_3 (0.3 g, 2.5 mmol, 1.0 eq), and $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol, 0.03 eq) were mixed in mixture solvent of dry toluene/MeOH 5:1 (60 mL) under an argon atmosphere and a drying system of $CaCl_2$ with stirring at ambient temperature. Then, the reaction mixture was heated for 20 h at 80 °C and monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and extracted by distilled water and EA (30 mL × 4–5 times). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed at reduced pressure to afford the crude product and was purified by silica gel column chromatography, using PE/EA (9:1) as an eluent, to remove the residue of the start. This was followed by increasing the polarity of the eluent gradually until 8:2 to obtain the desired compound **25** as a white powder (0.3 g, 37%) (m.p. 167 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.14 (s, 1H, CHO), 8.17 (dd, 1H, J = 7.65, 0.85 Hz, ArH), 8.09 (dd, 1H, J = 7.65, 1.7 Hz, ArH), 8.04–8.07 (m, 4H, ArH), 7.83–7.86 (m, 2H, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 128.38, 129.48, 129.67, 130.60, 130.97, 131.67, 136.97, 141.04, 141.46, 142.49, 145.77, 151.73, 191.92. IR (cm^{-1}): C-H olefinic 3042, C-H aldehyde 2819, 2733, C=O 1698, C=C 1604, 1558, 1479. HRMS (ESI): m/z cacld for $C_{15}H_{10}ClN_2O$ 269.0482 $[M+1]^+$ and 271.0638 $[M+3]^+$, found 269.0485 and 271.0458, respectively.

3.2.21. 4-(3-(Thiophen-2-yl)quinoxalin-2-yl)benzaldehyde (**26**)

To a mixture of compound **25** (0.2 g, 0.7 mmol, 1.0 eq) and tributyl(thiophen-2-yl)stannane (0.6 g, 1.5 mmol, 2.0 eq) in dry DMF (30 mL), $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol, 0.05 eq) was added under an argon atmosphere. It was then refluxed for 2 h at 110 °C while monitoring the reaction by TLC. After the reaction was complete, the temperature was lowered to get the mixture to room temperature, followed by the addition of water to stop the reaction. Following $CHCl_3$ extraction of the product (30 mL × 4–5 times), it was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure to obtain the crude product and was purified by column chromatography on silica gel, using PE/EA (9:1) as an eluent, to obtain **26** as a yellow powder (0.2 g, 66%) (m.p. 157 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.13 (s, 1H, CHO), 8.15 (dd,

1H, *J* = 8.5, 0.85 Hz, ArH), 8.12 (dd, 1H, *J* = 8.5, 0.85 Hz, ArH), 8.01 (d, 2H, *J* = 8.5 Hz, ArH), 7.82 (d, 2H, *J* = 8.5 Hz, ArH), 7.79–7.80 (m, 1H, ArH), 7.75–7.77 (m, 1H, ArH), 7.44 (dd, 1H, *J* = 4.25, 0.85 Hz, ArH), 6.90 (dd, 1H, *J* = 5.1, 4.25 Hz, ArH), 6.79 (dd, 1H, *J* = 3.4, 0.85 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 128.04, 129.00, 129.12, 129.95, 130.13, 130.28, 130.30, 130.40, 131.06, 136.77, 140.31, 141.38, 141.95, 145.09, 146.67, 151.13, 191.97. IR (cm^{-1}): C-H olefinic 3082, C-H aldehyde 2851, 2754, C=O 1694, C=C 1603, 1530. HRMS (ESI): *m*/*z* cacld for $C_{19}H_{13}N_2OS$ 317.0749 $[M+1]^+$, found 317.0740.

3.2.22. 4-(3-(5-Bromothiophen-2-yl)quinoxalin-2-yl)benzaldehyde (**27**)

To a solution of compound **26** (0.3 g, 0.9 mmol, 1.0 eq) in DMF (12 mL), a solution of NBS (0.2 g, 1.3 mmol, 1.5 eq) in DMF (3 mL) was added in a dropwise manner. It was then stirred for 24 h in the dark at room temperature while monitoring the reaction by TLC. After completion, the reaction was stopped by adding ice. The precipitate was filtered off and washed several times with distilled water to obtain compound **27** as a yellow powder (0.3 g, 97%) (m.p. 177 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.14 (s, 1H, CHO), 8.10 (t, 2H, *J* = 7.65 Hz, ArH), 8.03 (d, 2H, *J* = 7.65 Hz, ArH), 7.82 (d, 2H, *J* = 7.65 Hz, ArH), 7.80 (t, 1H, *J* = 7.65 Hz, ArH), 7.76 (t, 1H, *J* = 7.65 Hz, ArH), 6.83 (d, 1H, *J* = 4.25 Hz, ArH), 6.45 (d, 1H, *J* = 4.25 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 117.90, 128.98, 129.25, 130.14, 130.21, 130.26, 130.50, 130.97, 131.13, 136.87, 140.47, 141.33, 144.00, 144.96, 145.54, 150.67, 191.91. IR (cm^{-1}): C-H olefinic 3057, C-H aldehyde 2832, 2738, C=O 1698, C=C 1602, 1530. HRMS (ESI): *m*/*z* cacld for $C_{19}H_{12}BrN_2O_S$ 394.9854 $[M+1]^+$ and 397.0010 $[M+3]^+$ found 394.9854 and 396.9837, respectively.

3.2.23. 4-(3-(5-(9-(2-Ethylhexyl)-6-p-tolyl-9H-carbazol-3-yl)thiophen-2-yl)quinoxalin-2-yl)benzaldehyde (**28**)

Compound **27** (0.3 g, 0.8 mmol, 1.0 eq), 9-(2-ethylhexyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-*p*-tolyl-9*H*-carbazole **10c** (0.6 g, 1.1 mmol, 1.5 eq), K_2CO_3 (1.5 g, 10.6 mmol, 14.0 eq), and $Pd(PPh_3)_4$ (0.04 g, 0.04 mmol, 0.05 eq) were mixed in a degassed aqueous solvent of toluene/EtOH/H_2O 2:1:1 (80 mL) under an argon atmosphere with stirring at ambient temperature. Then, the reaction mixture was heated for 2 h at 80 °C and monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and extracted by distilled water and DCM (30 mL × 4–5 times). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed at reduced pressure to afford the crude product and was purified by silica gel column chromatography, using PE/EA (9:1) as an eluent, to remove the undesired low polar fractions, followed by increasing the polarity of the eluent gradually until 8:2 to obtain the desired compound **28** as an orange powder (0.4 g, 69%) (m.p. 227 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.16 (s, 1H, CHO), 8.41 (d, 1H, *J* = 0.85 Hz, ArH), 8.32 (d, 1H, *J* = 1.7 Hz, ArH), 8.21 (d, 1H, *J* = 7.65 Hz, ArH), 8.14 (d, 1H, *J* = 8.5 Hz, ArH), 8.06 (d, 2H, *J* = 7.65 Hz, ArH), 7.91 (d, 2H, *J* = 7.65 Hz, ArH), 7.82 (t, 1H, *J* = 7.65 Hz, ArH), 7.74–7.76 (m, 2H, ArH), 7.72 (dd, 1H, *J* = 8.5, 1.7 Hz, ArH), 7.63 (d, 2H, *J* = 7.65 Hz, ArH), 7.44 (d, 1H, *J* = 8.5 Hz, ArH), 7.39 (d, 1H, *J* = 8.5 Hz, ArH), 7.31 (d, 2H, *J* = 7.65 Hz, ArH), 7.14 (d, 1H, *J* = 4.25 Hz, ArH), 6.75 (d, 1H, *J* = 4.25 Hz, ArH), 4.16–4.21 (m, 2H, N-CH_2), 2.44 (s, 3H, CH_3), 2.09 (sept, 1H, *J* = 6.8 Hz, CH), 1.36–1.46 (m, 4H, 2CH_2), 1.26–1.35 (m, 4H, 2CH_2), 0.94 (t, 3H, *J* = 7.65 Hz, CH_3), 0.88 (t, 3H, *J* = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 11.05, 14.19, 21.24, 23.20, 24.53, 28.95, 31.14, 39.62, 47.81, 109.63, 109.66, 118.19, 118.83, 122.98, 123.32, 123.59, 124.25, 124.93, 125.72, 127.22, 128.71, 129.06, 129.70, 130.09, 130.26, 130.28, 131.13, 131.93, 132.90, 136.39, 136.85, 139.09, 139.45, 140.00, 140.89, 141.32, 141.55, 145.25, 146.61, 150.73, 151.01, 192.01. IR (cm^{-1}): C-H olefinic 3060, C-H aliphatic 2957, 2857, C-H aldehyde 2724, C=O 1699, C=C 1603, 1537. HRMS (ESI): *m*/*z* cacld for $C_{46}H_{42}N_3OS$ 684.3049 $[M+1]^+$, found 684.3048.

3.2.24. 2,3-Bis(5-bromothiophen-2-yl)quinoxaline (**29**)

To a solution of **24** (0.4 g, 1.5 mmol, 1.0 eq) in DMF (10 mL), a solution of NBS (0.6 g, 3.5 mmol, 2.3 eq) in DMF (4 mL) was added in a dropwise manner. It was then stirred for 36 h in the dark at room temperature while monitoring the reaction by TLC. After completion, the reaction was stopped by adding ice. The precipitate was filtered off and washed several times with distilled water to obtain compound **29** as a yellow solid (0.6 g, 94%) (m.p. 136 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 8.02 (dd, 2H, *J* = 6.8, 3.4 Hz, ArH), 7.73 (dd, 2H, *J* = 6.8, 3.4 Hz, ArH), 7.12 (d, 2H, *J* = 4.25 Hz, ArH), 7.01 (d, 2H, *J* = 4.25 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 116.93, 128.95, 129.73, 130.69, 130.71, 140.68, 143.00, 145.11. IR (cm^{-1}): C-H olefinic 3076, C=C 1519, 1475. HRMS (ESI): *m*/*z* cacld for $C_{16}H_9Br_2N_2S_2$ 450.8574 $[M+1]^+$ and 452.8730 $[M+3]^+$, found 450.8576 and 454.8548, respectively.

3.2.25. 4-(5-(3-(5-Bromothiophen-2-yl)quinoxalin-2-yl)thiophen-2-yl)benzaldehyde (**30**)

Compound **29** (0.3 g, 0.7 mmol, 1.0 eq), 4-formylphenylboronic acid (0.1 g, 0.7 mmol, 1.1 eq), K_2CO_3 (0.9 g, 6.6 mmol, 10.0 eq), and $Pd(PPh_3)_4$ (0.1 g, 0.1 mmol, 0.1 eq) were mixed in dry toluene (30 mL) under an argon atmosphere and a drying system of $CaCl_2$ with stirring at ambient temperature. Then, the reaction mixture was heated for 24 h at 90 °C and monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and extracted by distilled water and DCM (30 mL × 4–5 times). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed at reduced pressure to afford the crude product and was purified by silica gel column chromatography, using PE/DCM (2:1) as an eluent, to remove the residue of the start and the impurities, followed by increasing the polarity of the eluent gradually until 1:1 to obtain the desired compound **30** as an orange powder (0.1 g, 20%) (m.p. 111 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.03 (s, 1H, CHO), 8.08 (dd, 1H, *J* = 6.8, 2.55 Hz, ArH), 8.06 (dd, 1H, *J* = 6.8, 2.55 Hz, ArH), 7.93 (d, 2H, *J* = 7.65 Hz, ArH), 7.84 (d, 2H, *J* = 8.5 Hz, ArH), 7.75–7.76 (m, 2H, ArH), 7.42 (d, 1H, *J* = 3.4 Hz, ArH), 7.38 (d, 1H, *J* = 4.25 Hz, ArH), 7.16 (d, 1H, *J* = 4.25 Hz, ArH), 7.02 (d, 1H, *J* = 3.4 Hz, ArH). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 117.03, 125.58, 126.33, 128.18, 128.98, 128.99, 129.85, 130.52, 130.69, 130.73, 130.79, 135.74, 139.53, 140.73, 140.79, 142.51, 143.22, 145.42, 145.56, 146.10, 191.55. IR, (cm^{-1}): C-H olefinic 3057, C-H aldehyde 2848, 2732, C=O 1695, C=C 1599, 1565. HRMS (ESI): *m*/*z* cacld for $C_{23}H_{14}BrN_2OS_2$ 476.9731 $[M+1]^+$ and 478.9887 $[M+3]^+$ found 476.9733 and 478.9718, respectively.

3.2.26. 4-(5-(3-(5-(9-(2-Ethylhexyl)-6-p-tolyl-9H-carbazol-3-yl)thiophen-2-yl)quinoxalin-2-yl)thiophen-2-yl)benzaldehyde (**31**)

Compound **30** (0.1 g, 0.1 mmol, 1.0 eq), 9-(2-ethylhexyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-*p*-tolyl-9*H*-carbazole **10c** (0.1 g, 0.2 mmol, 1.5 eq), K_2CO_3 (0.3 g, 2.1 mmol, 14.0 eq), and $Pd(PPh_3)_4$ (0.01 g, 0.01 mmol, 0.05 eq) were mixed in a degassed aqueous solvent of toluene/EtOH/H_2O 2:1:1 (60 mL) under an argon atmosphere with stirring at ambient temperature. Thereafter, the reaction mixture was heated for 3 h at 80 °C and monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and extracted by distilled water and $CHCl_3$ (20 mL × 4–5 times). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure to afford the crude product and was purified by silica gel column chromatography, using PE/EA (9:1) as an eluent, to produce compound **31** as an orange powder (0.1 g, 81%) (m.p. 74 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.02 (s, 1H, CHO), 8.45 (s, 1H, ArH), 8.33 (s, 1H, ArH), 8.13 (d, 1H, *J* = 8.5 Hz, ArH), 8.10 (d, 1H, *J* = 8.5 Hz, ArH), 7.92 (d, 2H, *J* = 7.65 Hz, ArH), 7.85 (d, 2H, *J* = 7.65 Hz, ArH), 7.80 (d, 1H, *J* = 8.5 Hz, ArH), 7.72–7.76 (m, 3H, ArH), 7.63 (d, 2H, *J* = 7.65 Hz, ArH), 7.50 (d, 1H, *J* = 4.25 Hz, ArH), 7.45 (d, 1H, *J* = 8.5 Hz, ArH), 7.43 (dd, 1H, *J* = 3.4, 0.85 Hz, ArH), 7.41–7.42 (m, 2H, ArH), 7.31 (dd, 1H, *J* = 3.4, 0.85 Hz, ArH), 7.30 (d, 2H, *J* = 7.65 Hz, ArH), 4.16–4.22 (m, 2H, N-CH_2), 2.43 (s, 3H, CH_3), 2.10 (sept, 1H, *J* = 6.8 Hz, CH), 1.35–1.46 (m, 4H,

$2CH_2$), 1.26–1.34 (m, 4H, $2CH_2$), 0.94 (t, 3H, J = 7.65 Hz, CH_3), 0.89 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 11.05, 14.20, 21.24, 23.20, 24.53, 28.96, 31.14, 39.63, 47.82, 109.65, 109.69, 118.22, 118.85, 122.82, 123.31, 123.62, 124.35, 124.92, 125.65, 125.74, 126.35, 127.22, 128.35, 128.71, 128.94, 129.69, 130.56, 130.68, 131.03, 131.36, 131.95, 132.58, 132.91, 135.71, 136.40, 137.87, 139.09, 139.56, 140.13, 140.18, 140.90, 141.55, 142.26, 145.92, 146.26, 150.85, 191.55. IR (cm^{-1}): C-H olefinic 3058, C-H aliphatic 2956, 2851, C-H aldehyde 2732, C=O 1696, C=C 1600. HRMS (ESI): m/z cacld for $C_{50}H_{44}N_3OS_2$ 766.2926 $[M+1]^+$, found 766.2927.

3.2.27. 4-(3-(9-(2-ethylhexyl)-6-(p-tolyl)-9H-carbazol-3-yl)quinoxalin-2-yl)benzaldehyde (**32**)

Compound **25** (0.1 g, 0.4 mmol, 1.0 eq), 9-(2-ethylhexyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-*p*-tolyl-9*H*-carbazole **10c** (0.3 g, 0.2 mmol, 1.5 eq), K_2CO_3 (0.7 g, 5.2 mmol, 14.0 eq), and $Pd(PPh_3)_4$ (0.01 g, 0.01 mmol, 0.05 eq) were mixed in a degassed aqueous solvent of toluene/EtOH/H_2O 2:1:1 (40 mL) under an argon atmosphere with stirring at ambient temperature. Then, the reaction mixture was heated at 80 °C for 3 h and monitored by TLC. After the reaction was complete, the solvent was removed under vacuum and extracted by distilled water and DCM (20 mL × 4–5 times). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed at reduced pressure to afford the crude product and was purified by silica gel column chromatography, using PE/EA (9:1) as an eluent, to remove the undesired low polar fractions, followed by increasing the polarity of the eluent gradually until 8:2 to obtain the desired compound **32** as a yellow powder (0.2 g, 86%) (m.p. 99 °C). ^{1}H-NMR (850 MHz, $CDCl_3$) δ ppm: 10.01 (s, 1H, CHO), 8.49 (s, 1H, ArH), 8.44 (d, 1H, J = 7.65 Hz, ArH), 8.26 (d, 1H, J = 8.5 Hz, ArH), 8.21 (d, 1H, J = 0.85 Hz, ArH), 7.86–7.88 (m, 1H, ArH), 7.83–7.85 (m, 3H, ArH), 7.77 (d, 2H, J = 8.5 Hz, ArH), 7.71 (dd, 1H, J = 8.5, 1.7 Hz, ArH), 7.57 (d, 2H, J = 8.5 Hz, ArH), 7.50 (dd, 1H, J = 8.5, 1.7 Hz, ArH), 7.45 (d, 1H, J = 8.5 Hz, ArH), 7.30 (d, 1H, J = 8.5 Hz, ArH), 7.28 (d, 2H, J = 7.65 Hz, ArH), 4.16–4.21 (m, 2H, N-CH_2), 2.42 (s, 3H, CH_3), 2.07 (sept, 1H, J = 6.8 Hz, CH), 1.33–1.42 (m, 4H, $2CH_2$), 1.22–1.32 (m, 4H, $2CH_2$), 0.92 (t, 3H, J = 7.65 Hz, CH_3), 0.86 (t, 3H, J = 7.65 Hz, CH_3). ^{13}C-NMR (213 MHz, $CDCl_3$) δ ppm: 11.04, 14.17, 21.23, 23.18, 24.50, 28.88, 31.11, 39.56, 47.83, 109.21, 109.71, 118.99, 122.94, 123.44, 123.51, 125.88, 127.30, 128.19, 128.36, 128.69, 129.36, 129.67, 129.78, 130.46, 130.74, 131.37, 133.27, 136.30, 136.45, 139.08, 140.26, 140.87, 141.05, 142.23, 145.11, 152.68, 153.42, 191.95. IR (cm^{-1}): C-H olefinic 3057, C-H aliphatic 2956, 2857, C-H aldehyde 2731, C=O 1701, C=C 1602, 1477. HRMS (ESI): m/z cacld for $C_{42}H_{40}N_3O$ 602.3171 $[M+1]^+$, found 602.3170.

4. Conclusions

Three palladium-catalyzed coupling reactions—the Suzuki-Miyaura coupling reaction, Suzuki cross-coupling reaction, and Stille cross-coupling reaction—have been investigated utilizing three palladium catalysts—$Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(dppf)Cl_2$—under mild conditions. PTZ, POZ, and Cz were utilized in the Miyaura borylation reaction to synthesize 17 heteroaromatic pinacol boronate esters decorated with imidazolyl, *p*-tolyl, or carbaldehyde groups. The best yields of the borylated species were obtained using $Pd(dppf)Cl_2$ as a catalyst. The electron-deficient QX was decorated with the phenyl and/or thienyl ring utilizing the Suzuki cross-coupling reaction and the Stille cross-coupling reaction, achieving moderate to excellent yields. $Pd(PPh_3)_4$ and $Pd(dppf)Cl_2$ were employed in the Suzuki cross-coupling reaction for the synthesis of 16 PTZ, POZ, and Cz chromophores using commercial boronic acids or synthesized pinacol boronate esters. Among the three Pd-catalysts, $Pd(dppf)Cl_2$ gives the best yields. A few borylated derivatives have been coupled here with halogenated couplers. The electron-deficient QX couplers could be coupled efficiently using the Stille coupling reaction. Future studies are in progress for synthesizing new PTZ, POZ, and Cz boronate derivatives using novel catalysts, and the outcome of this work will be published elsewhere.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101292/s1, Figures S1−S83: contains the NMR, ATR-FTIR, HRMS charts for the synthesized compounds.

Author Contributions: L.M.N. Synthesis, methodology and writing the draft, E.N.B., A.R.A.-M., H.A.A.-G., S.N.A.-G. and F.A.M.A.-Z. synthesis and methodology, K.O.A.-F. resources and supervision, R.M.E.-S. conceptualization, writing the manuscript and supervision. All authors have read and agreed to the published version of the manuscript.

Funding: Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant no. KEP-PhD: 73-130-1443.

Data Availability Statement: The data presented in this study is available in Supplementary Material.

Acknowledgments: The Deanship of Scientific Research (DSR) at King Abdulaziz University (KAU), Jeddah, Saudi Arabia, has funded this project, under grant no. KEP-PhD: 73-130-1443.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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