Synthesis of Extended 1,3,4-Oxadiazole and 1,3,4-Thiadiazole Derivatives in the Suzuki Cross-coupling Reactions

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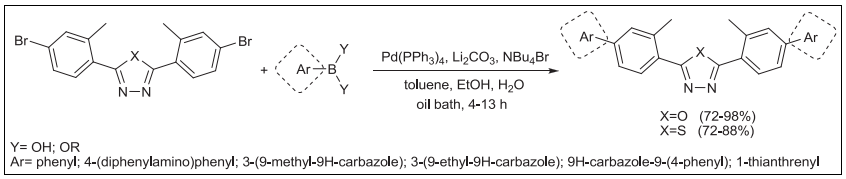

New derivatives of 1,3,4-oxadiazole and 1,3,4-thiadiazole were synthesized by a palladium catalyzed Suzuki cross-coupling reaction under the conditions of the phase transfer catalysis. The structure of the products, the absorption and emission spectra were also studied.

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INTRODUCTION

Heterocyclic compounds have a great contribution to provide valuable reagents for the synthesis of medicines, pesticides, and detergents, as well as in related fields like biochemistry, biotechnology, chemistry of polymers, or materials science. In the area of this group of compounds particularly interesting seems to be 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives. These non-naturally occurring compounds exhibit a broad range of biological activities and therefore are widely used in medicine and agriculture [1–8]. Oxadiazole and thiadiazole derivatives have attracted attention of scientists because of their precious optical properties [9–13]. 1,2-Diazole fragment, which is present in heterocyclic rings such as 1,3,4-oxadiazoles and 1,3,4-thiadiazoles, functions as electron withdrawing group and may be found in many linear conductive systems. Its presence significantly enhances the fluorescence quantum yield and stability of the final product.

Numerous methods for synthesis of the 1,3,4-oxadiazole and 1,3,4-thiadiazole ring are described in literature [14–16]. However, the most common approach towards the preparation of both of them involves reaction making use of diacylhydrazines, which are easy accessible. This particular methodology involves their reactions with a range of cyclodehydrating agents, just to mention boron trifluoride-diethyl etherate, the Burgess reagent, polyphosphoric acid, phosphorus oxychloride, or thionyl chloride, and leads to the formation of 1,3,4-oxadiazole core [17–20]. Further applications of diphosphorus pentasulfide or Lawesson's reagent in the reactions with diacylhydrazines result in formation of 1,3,4-thiadiazole moiety [21–23].

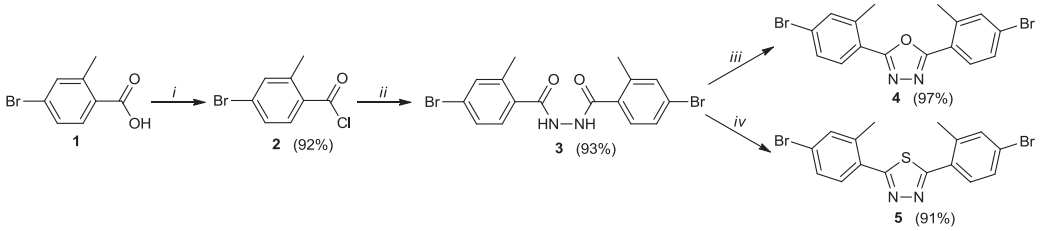
Working earlier on the synthesis of 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives, we obtained new conjugated derivatives which exhibited very high rates of fluorescence quantum yield [20,23]. These findings prompted us to deeper research on these groups of compounds and extending substrate scope searching for the most effective luminophores. This paper describes the efficient synthesis and properties of novel 3,4-diazole derivatives based on one of the most popular catalytic methods of C–C bond construction – the Suzuki cross-coupling reaction [24,25].

RESULTS AND DISCUSSION

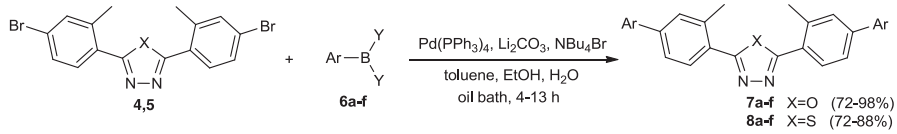
Three step methodology was applied to transform 4-bromo-2-methylbenzoic acid (**1**) to the leading moiety – 2,5-bis(4-bromo-2-methylphenyl)-1,3,4-oxadiazole (**4**) or 2,5-bis(4-bromo-2-methylphenyl)-1,3,4-thiadiazole (**5**). The initial acid **1** was heated in the presence of thionyl chloride in dry toluene giving the corresponding acid chloride **2**. The obtained chloride **2** was treated with hydrazine hydrate in the presence of triethylamine to give the adequate *N*,*N*'-diacylhydrazine **3**. This intermediate heated with appropriate reagent (phosphorus oxychloride for 1,3,4-oxadiazole core or Lawesson's reagent for 1,3,4-thiadiazole core) in non-polar solvent led to the desired compounds **4**,**5** in excellent yields (Scheme 1).

The obtained dibromo 3,4-diazole derivatives **4**,**5** were subjected to Suzuki cross-coupling reaction. They were

Scheme 1. Synthesis of 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (**4**) and 2,5-bis(4-bromophenyl)-1,3,4-thiadiazole (**5**) scaffold. Reagents and conditions: (i) $SOCl_2$, toluene, reflux, 15 h; (ii) $N_2H_4 \bullet H_2O$, TEA, $CHCl_3$, rt, 24 h; (iii) $POCl_3$, toluene, reflux, 8 h; and (iv) Lawesson's reagent, xylene, reflux, 4 h.



Scheme 2. Suzuki cross-coupling reaction. Reagents and conditions: aryl dibromide **4**,**5** (1.00 mmol), boronic acid **6** (2.50 mmol), $Pd(PPh_3)_4$ (0.05 mmol), NBu_4Br (0.10 mmol), Li_2CO_3 (10 mmol), toluene/EtOH/H_2O (10:6:3 mL), oil bath 130°C, 4–13 h.



Y= OH; OR
Ar= phenyl; 4-(diphenylamino)phenyl; 9-methylcarbazol-3-yl; 9-ethylcarbazol-3-yl; 4-(carbazol-9-yl)phenyl; 1-thianthrenyl

refluxed with appropriate boronic acids **6a–f** under a predetermined conditions with similar scaffolds [20,23] (Scheme 2). The reactions were carried out on the oil-bath with an excess amount of the adequate boronic acid **6a–f** in the presence of the Li_2CO_3 as a base to activate boronic acid and to facilitate the transmetallation step. The reaction mixtures were heated under the phase transfer catalysis in a two-phase solvent system (toluene/EtOH/H_2O) using NBu_4Br as the phase transfer catalyst and in the presence of 5 mol% palladium catalyst $Pd(PPh_3)_4$. Reaction times were monitored by TLC until the initial 2,5-bis(4-bromophenyl)-3,4-diazoles **4**,**5** were completely consumed.

The research has led to obtain a new symmetrical 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives in high yields (72–98% for **7a-f**, 72–88% for **8a–f**, Table 1). Interestingly, the lowest yields were obtained for the least conjugated 1,3,4-oxadiazole **7a** and 1,3,4-thiadiazole **8a**, containing a terminal phenyl substituent (72%, Table 1). Other products with extended terminal heterocyclic systems were obtained in relatively higher yields (77–98% for **7b–f**, 77–88% for **8b–f**, Table 1). The structures of all of the resulted derivatives were confirmed by elemental analyses and typical spectroscopic methods (^1H and ^{13}C NMR, UV, IR, HRMS). As expected, NMR spectra showed a reduced number of signals both protons and carbons because these compounds have a symmetrical structure. The symmetrical structure of one from the obtained products was confirmed by X-ray crystal structure analysis (Fig. 1). The oxadiazole **7a** crystallizes in a orthorhombic system forming long unit cell with $a = 41.230(8)$, $b = 7.4842(15)$, $c = 6.6745(13)$ Å with the heterocyclic ring at the plane of symmetry. The central core is almost planar with 7.17(23)° twist of the substituted benzene rings from the plane of the oxadiazole, while the terminal benzene rings are twisted off by 31.45(19)° from the neighboring substituted benzene rings. There are no hydrogen bondings; however, there is a weak intermolecular interaction N1…C1. An interesting comparison with the crystal structures of structurally related compounds NAXDIZ [26], IPODEX [27], and PEDQUM [28] is presented in Figure 2. The methyl substituent in **7a** causes only slight deviation from planarity, similar to the non-substituted benzene ring in PEDQUM, but surprisingly not as twisted as in the meta-substituted IPODEX. Also, the terminal ring is likely twisted to PEDQUM. However, it is worth noting that ortho-disubstituted benzene ring in PEDQUM leads to serious deviation (α') from planarity.

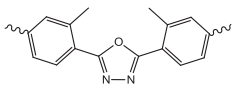
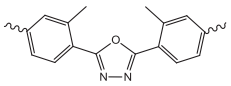
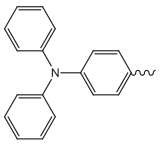
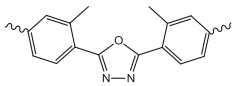
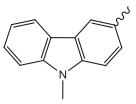
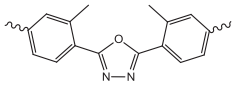
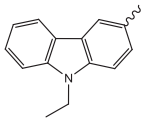
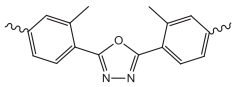
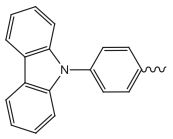
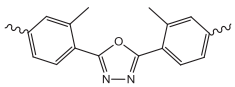
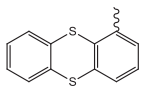
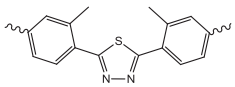
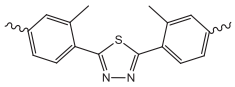
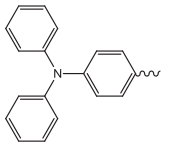
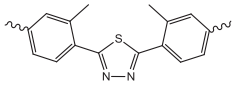
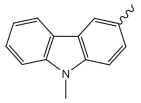
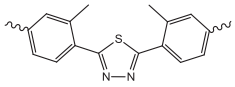
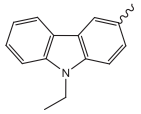
The fluorescence emission spectra were recorded using the excitation maximum. The highest intensity of emission was observed for **7a** compound. The quantum yields were estimated by comparison with a quantum yield standards using comparative method [29–31]. The significant increase of Φ from the 1,3,4-thiadiazole (**8a–f**) moiety to 1,3,4-oxadiazole (**7a–f**) was observed, which can be explained by the heavy atom effect (Table 2).

CONCLUSION

We have prepared two series of new 3,4-diazole derivatives as extended π-conjugated systems. The leading 1,3,4-oxadiazole or 1,3,4-thiadiazole rings have been coupled at the positions 2 and 5, via a methyl-substituted phenylene linker, with a range of homoaromatic and

Table 1

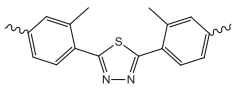
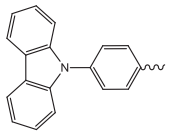
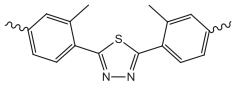
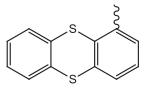
2,5-Bis(4-aryl-2-methylphenyl)-1,3,4-oxadiazoles **7a–f** and 2,5-bis(4-aryl-2-methylphenyl)-1,3,4-thiadiazoles **8a–f** prepared in Suzuki cross-coupling reactions.

Compound	Central core	Substituent Ar	Reaction time [h]	Melting point [°C]	Yield [%]
7a			4	173–174	72
7b			6	249–251	84
7c			9	299–300	77
7d			10	213–214	98
7e			7	306–308	89
7f			12	109–110	87
8a			5	143–144	72
8b			5	291–293	84
8c			13	258–260	78
8d			11	206–209	88

(*Continued*)

Table 1

(*Continued*)

Compound	Central core	Substituent Ar	Reaction time [h]	Melting point [°C]	Yield [%]
8e			8	280–281	85
8f			13	293–295	77

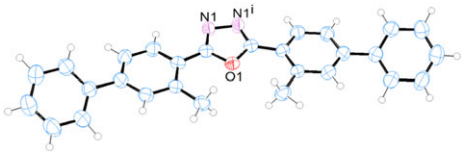


Figure 1. X-ray structure of 2,5-bis(4-phenyl-2-methylphenyl)-1,3,4-oxadiazole (**7a**) with 50% probability ellipsoids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

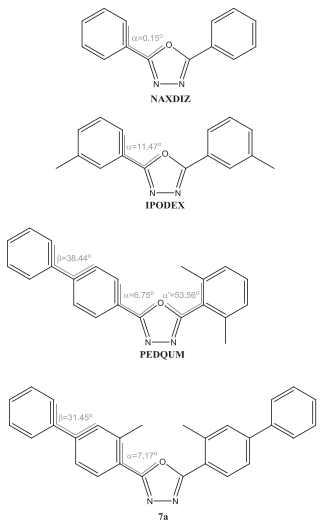


Figure 2. Comparison of the X-ray structures and the torsion angles of the structurally related oxadiazoles to **7a**.

heteroaromatic arrangements. The presence of methyl group on the linker enhances the solubility of these derivatives. It is particularly important for their potential application in the production of optoelectronic devices. Products were obtained in excellent yields at each stage of a few-step methodology. Finally, application of the Suzuki coupling reaction in the final step allows to get the desired products in high yields.

EXPERIMENTAL

Melting points were measured on a Stuart SMP3 melting point apparatus. NMR spectra were recorded at 25°C on an Agilent 400-NMR spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C, using $CDCl_3$ or DMSO as solvents and TMS as the internal standard. UV spectra were recorded on a Jasco V-650 spectrophotometer. FT-IR spectra were recorded between 4000 and 650 cm^{-1} on an FT-IR Nicolet 6700 apparatus with a Smart iTR accessory. Elemental analyses were performed with a VarioEL analyser. High-resolution mass spectra were obtained by means of a Waters ACQUITY UPLC/Xevo G2QT instrument. Thin-layer chromatography was performed on silica gel 60 F_{254} (Merck) thin-layer chromatography plates using benzene/ethyl acetate (9:1 v/v) as the mobile phase. Fluorescence spectra were recorded at room temperature in dichloromethane solution using Hitachi F-2500 fluorescence spectrophotometer.

X-ray single crystal measurement: measurements of the diffraction intensities were performed on a KUMA KM4 four-circle diffractometer, MoK_α radiation, $\omega/2\Theta$ scan mode, Θ range 2.77–25.00°. Crystallographic data for **7a** were deposited with the Cambridge Crystallographic Data Centre as supplementary publications number: CCDC 1465365. A complete listing of the atomic coordinates of *x*, *y*, and *z* can be obtained free of charge, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+int) 44-1223 336 033; e-mail: deposit@ccdc.cam.ac.uk], upon quoting the depository numbers, names of the authors and the journal citation.

4-Bromo-2-methylbenzoyl chloride (2). 4-Bromo-2-methylbenzoic acid (**1**, 4.30 g, 0.02 mol) and thionyl chloride $SOCl_2$ (5.0 mL, 0.06 mol) were refluxed in a dry toluene (20 mL) until the acid was fully consumed (TLC; 15 h). After cooling, the mixture was concentrated on a rotary evaporator. The solid was recrystallized from toluene to give 4-bromo-2-methylbenzoyl chloride (**2**). Beige crystals

Table 2

Absorption and fluorescent properties of compound **7a–f** and **8a–f** in methylene chloride.

Compound	λ_{max}^{abs} [nm] ($\varepsilon \cdot 10^{-3}$)	λ^{ex} [nm]	λ_{max}^{em} [nm]	Stokes shift[b] Δ [nm]	Quantum yield Φ[c]
7a	314.0 (54.5)	309	361, 379, 398[a]	47	0.92
7b	296.0 (42.3), 373.0 (64.4)	368	465, 493[a]	92	0.70
7c	243.0 (66.6), 302.0 (54.1), 346.0 (64.5)	343	419	73	0.80
7d	243.0 (67.9), 302.5 (54.6), 347.5 (66.6)	341	419	71	0.89
7e	242.0 (75.5), 293.0 (48.9), 342.0 (58.0)	339	424	82	0.85
7f	261.5 (56.9), 307.5 (35.9)	—	—	—	—
8a	246.0 (26.2), 319.0 (43.6)	312	390, 407, 431[a]	71	0.33
8b	299.0 (38.9), 374.0 (50.8)	366	503	129	0.41
8c	244.0 (69.8), 282.5 (46.0), 300.5 (46.1), 352.0 (58.9)	350	454, 490[a]	102	0.44
8d	243.5 (67.5), 284.0 (44.5), 301.0 (45.3), 352.0 (54.6)	351	455	103	0.43
8e	243.0 (96.6), 293.0 (53.1), 342.5 (65.2)	340	446	103	0.58
8f	261.0 (61.8), 310.5 (36.4)	—	—	—	—

[a]Shoulder maximum.
[b]Stokes shift from the equation $\Delta = \lambda_{max}^{em} - \lambda_{max}^{abs}$ [31].
[c]9,10-Diphenylanthracene in cyclohexane (for **7b–e**, **8b–e**) and 1,4-diphenylbutadiene in hexane (for **7a**,**8a**) were used as standards.

(4.30 g, 92% yield); mp 42–44°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3H), 7.47 (s, 1H), 7.49 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 129.6, 129.7, 131.3, 134.9, 135.2, 143.2, 166.9; UV-VIS: λ_{max} (MeOH) 205.0 nm ($\varepsilon \cdot 10^{-3}$ 29.1 $cm^{-1}M^{-1}$), 237.5 (10.3); IR (ATR) ν: 3426, 2996, 1759, 1683, 1588, 1549, 1472, 1458, 1438, 1380, 1327, 1291, 1276, 1202, 1186, 1136, 1091, 1030, 880, 818, 804, 772, 755, 726, 712, 686 cm^{-1}; *Anal*. Calcd for C_8H_6BrClO: C, 41.15; H, 2.59. Found: C, 41.18; H, 2.62; HRMS Calcd. for ($C_8H_6BrClO + H^+$): 232.9363; found: 232.9368.

***N,N′*-Bis(4-bromo-2-methylbenzoyl) hydrazine (3)**. 4-Bromo-2-methylbenzoyl chloride (**2**, 4.30 g, 0.02 mol) dissolved in 20 mL of chloroform was added to a magnetically agitated solution of hydrazine hydrate (0.5 mL, 0.01 mol) and triethylamine (2.9 mL, 0.02 mol) in 40 mL of chloroform placed in an ice bath. After the addition was completed, the mixture was stirred for 20 h at room temperature. The solid precipitate was collected by filtration, washed with hexane, a large quantity of water, air-dried yielding pure *N,N′*-bis(4-bromo-2-methylbenzoyl) hydrazine (**3**). White solid (3.96 g, 93% yield); mp 266–267°C; ^{1}H NMR (400 MHz, DMSO): δ 2.42 (s, 3H), 7.37 (d, J = 8.0 Hz, 1H), 7.50 (dd, J = 8.0 and 1.6 Hz, 1H), 7.55 (d, J = 1.6 Hz, 1H), 10.27 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 18.9, 123.1, 128.5, 129.3, 133.1, 133.9, 138.8, 167.4; UV-VIS: λ_{max} (MeOH) 205.0 nm ($\varepsilon \cdot 10^{-3}$ 56.9 $cm^{-1}M^{-1}$), 235.0 (23.9); IR (ATR) ν: 3427, 3162, 2998, 1600, 1578, 1489, 1456, 1254, 1200, 1099, 868, 833, 820, 810, 772, 753, 728, 669 cm^{-1}; *Anal*. Calcd for $C_{16}H_{14}Br_2N_2O_2$: C, 45.10; H, 3.31; N, 6.57. Found: C, 45.07; H, 3.31; N, 6.55; HRMS Calcd for ($C_{16}H_{14}Br_2N_2O_2 + H^+$): 424.9495; found: 424.9499.

2,5-Bis(4-bromo-2-methylphenyl)-1,3,4-oxadiazole (4). A mixture of *N,N′*-bis(4-bromo-2-methylbenzoyl)hydrazine (**3**, 1.70 g, 4.00 mmol) and phosphorous oxychloride (7.4 mL, 0.08 mol) in 20 mL of dry toluene was refluxed until the initial compound **3** was fully consumed (TLC, 8 h). After cooling, the mixture was concentrated on a rotary evaporator and then treated with ethanol (20 mL). The solid precipitate was filtered off, washed with EtOH, and air-dried yielding 2,5-bis(4-bromo-2-methylphenyl)-1,3,4-oxadiazole (**4**). White crystals (1.58 g, 97% yield); mp 158–159°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (s, 3H), 7.47 (dd, J = 8.0 and 1.6 Hz, 1H), 7.53 (d, J = 1.6 Hz, 1H), 7.85 (d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 121.8, 125.9, 129.5, 130.2, 134.8, 140.5, 163.8; UV-VIS: λ_{max} ($CHCl_3$) 289.5 nm ($\varepsilon \cdot 10^{-3}$ 30.9 $cm^{-1}M^{-1}$); IR (ATR) ν: 3073, 2974, 1593, 1537, 1475, 1440, 1382, 1272, 1197, 1099, 1084, 1046, 989, 964, 868, 853, 832, 823, 773, 746, 693 cm^{-1}; *Anal*. Calcd for $C_{16}H_{12}Br_2N_2O$: C, 47.09; H, 2.96; N, 6.86. Found: C, 47.07; H, 3.00; N, 6.89; HRMS Calcd for ($C_{16}H_{12}Br_2N_2O + H^+$): 406.9389; found: 406.9391.

2,5-Bis(4-bromo-2-methylphenyl)-1,3,4-thiadiazole (5). A reaction mixture of *N,N′*-bis(4-bromo-2-methylbenzoyl) hydrazine (**3**, 1.70 g, 4.00 mmol) and Lawesson's reagent (1.62 g, 4.00 mmol) in 30 mL of xylene was refluxed until the initial compound **3** was fully consumed (TLC, 4 h). After cooling, the mixture was evaporated and then alkalized with a 5% solution of NaOH. The residue was subjected to the column chromatography (silica gel, eluent: $CHCl_3$-MeOH 9:1 mixture). The reaction gave the pure 2,5-bis(4-bromo-2-methylphenyl)-1,3,4-thiadiazole (**5**). Beige solid (1.54 g, 91% yield); mp 139–141°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (s, 3H), 7.46 (dd, J = 8.0 and 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 124.9, 128.0, 129.5, 132.1, 134.6, 139.3, 167.0; UV-VIS: λ_{max} ($CHCl_3$) 299.5 nm ($\varepsilon \cdot 10^{-3}$ 24.6 $cm^{-1}M^{-1}$); IR (ATR) ν: 3072,

2971, 2163, 1586, 1439, 1391, 1262, 1190, 1122, 1097, 983, 919, 870, 853, 840, 824, 802, 772, 669 cm^{-1}; *Anal.* Calcd for $C_{16}H_{12}Br_2N_2S$: C, 45.31; H, 2.85; N, 6.60. Found: C, 45.35; H, 2.89; N, 6.58; HRMS Calcd for ($C_{16}H_{12}Br_2N_2S + H^+$): 422.9161; found: 422.9165.

General procedure for Suzuki coupling reactions. 2,5-Bis(4-bromo-2-methylphenyl)-1,3,4-oxadiazole (**4**, 0.20 g, 0.50 mmol) or 2,5-bis(4-bromo-2-methylphenyl)-1,3,4-thiadiazole (**5**, 0.21 g, 0.50 mmol), the appropriate boronic acid/pinacol ester (1.25 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.03 mmol), NBu_4Br (0.02 g, 0.05 mmol), and Na_2CO_3 (0.27 g, 2.50 mmol) were treated with a combination of toluene (10 mL), H_2O (6 mL), and EtOH (3 mL). The mixture was kept under reflux in an oil bath (130°C) for 4–13 h (TLC). After cooling, 200 mL of $CHCl_3$ was added and whole filtered through silica gel (20 mL). The filtrate was separated, and the organic layer was dried over $MgSO_4$ and then concentrated on a rotary evaporator. The residue was treated with a mixture of benzene/ethyl acetate (3:1). The solid precipitate was filtered off, washed with benzene/ethyl acetate (3:1), and air-dried to give pure 2,5-disubstituted-1,3,4-oxadiazole (**7a–f**) or 2,5-disubstituted-1,3,4-thiadiazole (**8a–f**).

2,5-Bis(3-methylbiphenyl-4-yl)-1,3,4-oxadiazole (7a). White solid (0.14 g, 72%); mp 173–174°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (s, 3H), 7.40 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.60 (m, 2H), 7.66 (d, J = 7.6 Hz, 2H), 8.13 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 121.9, 124.9, 127.2, 128.1, 128.9, 129.4, 130.5, 138.9, 139.9, 143.9, 164.3; UV-VIS: λ_{max} ($CHCl_3$) 314.0 nm ($\varepsilon \cdot 10^{-3}$ 54.5 $cm^{-1}M^{-1}$); IR (ATR) ν: 3034, 2994, 1961, 1932, 1607, 1570, 1532, 1470, 1452, 1412, 1281, 1220, 1140, 1079, 1070, 1045, 1034, 1025, 972, 884, 857, 842, 769, 746, 715, 707, 696 cm^{-1}; *Anal.* Calcd for $C_{28}H_{22}N_2O$: C, 83.56; H, 5.51; N, 6.96. Found: C, 83.50; H, 5.53; N, 7.00; HRMS Calcd for ($C_{28}H_{22}N_2O + H^+$): 403.1805; found: 403.1801.

Crystal data for compound (7a). The crystal chosen for X-ray analysis, obtained from recrystallization from toluene, was a clear colorless block with the approximate dimensions of 0.8 × 0.6 × 0.3 mm. $C_{28}H_{22}N_2O$ (402.48 g mol^{-1}) crystallizes in the orthorhombic system, space group $Cmc2_1$, with a = 41.230(8), b = 7.4842(15), c = 6.6745(13) Å, V = 2059.6(7) $Å^3$, Z = 4, μ(MoKα) = 0.079 mm^{-1}, and D_{calcd} = 1.298 cm^{-3}. A total of 2170 reflections were collected to $2\Theta_{max}$ = 50.00° (h: 0 → 49 k: 0 → 8, l: −7 → 0), of which 1002 were unique. In refinements, weights were used according to the scheme $w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 0.20P]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement of 187 parameters (data-to-parameter ratio being 11.6) converged to the final agreement factors R = 0.0405 for 801 reflections with Fo > 4σ (Fo) and R_w = 0.1280, and S = 1.042 for all observed reflections. The electron density of the largest difference peak was found to be 0.19 e $Å^{-3}$, while that of the largest difference hole was 0.27 e $Å^{-3}$.

2,5-Bis[4'-(N,N-diphenylamino)-3-methylbiphenyl-4-yl]-1,3,4-oxadiazole (7b). Yellow solid (0.31 g, 84%); mp 249–251°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84 (s, 3H), 7.04 (t, J = 7.2 Hz, 2H), 7.13 (m, 6H), 7.27 (t, J = 7.2 Hz, 4H), 7.52 (d, J = 7.2 Hz, 2H), 7.55 (m, 2H), 8.10 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 121.3, 123.3, 123.5, 124.3, 124.7, 127.8, 129.4, 129.5, 129.8, 133.3, 138.9, 143.3, 147.5, 148.1, 164.3; UV-VIS: λ_{max} ($CHCl_3$) 296.0 nm ($\varepsilon \cdot 10^{-3}$ 42.3 $cm^{-1}M^{-1}$), 373.0 (64.4); IR (ATR) ν: 3034, 2921, 2156, 1587, 1535, 1484, 1450, 1330, 1273, 1198, 1185, 1158, 1048, 1032, 888, 822, 749, 729, 693 cm^{-1}; *Anal.* Calcd for $C_{52}H_{40}N_4O$: C, 84.75; H, 5.47; N, 7.60. Found: C, 84.78; H, 5.43; N, 7.63; HRMS Calcd for ($C_{52}H_{40}N_4O + H^+$): 737.3275; found: 737.3271.

2,5-Bis[4-(9-methylcarbazol-3-yl)-2-methylphenyl]-1,3,4-oxadiazole (7c). Beige solid (0.22 g, 77%); mp 299–300°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 (s, 3H), 3.92 (s, 3H), 7.31 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.6, 29.3, 108.7, 108.9, 119.0, 119.3, 121.3, 122.9, 124.9, 125.1, 126.1, 128.2, 129.1, 129.5, 130.4, 130.9, 138.8, 139.9, 141.5, 144.8, 167.4; UV-VIS: λ_{max} ($CHCl_3$) 243.0 nm ($\varepsilon \cdot 10^{-3}$ 66.6 $cm^{-1}M^{-1}$), 302.0 (54.1), 346.0 (64.5); IR (ATR) ν: 3426, 3044, 2578, 2161, 2014, 1606, 1474, 1458, 1439, 1418, 1327, 1236, 1044, 844, 824, 771, 755, 742, 730, 712 cm^{-1}; *Anal.* Calcd for $C_{42}H_{32}N_4O$: C, 82.87; H, 5.30; N, 9.20. Found: C, 82.84; H, 5.29; N, 9.22; HRMS Calcd for ($C_{42}H_{32}N_4O + H^+$): 609.2649; found: 609.2652.

2,5-Bis[4-(9-ethylcarbazol-3-yl)-2-methylphenyl]-1,3,4-oxadiazole (7d). White solid (0.31 g, 98%); mp 213–214°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (t, J = 6.8 Hz, 3H), 2.93 (s, 3H), 4.41 (q, J = 6.8 Hz, 2H), 7.28 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.51 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.6, 37.7, 108.7, 108.8, 119.2, 120.6, 121.0, 123.0, 123.6, 124.9, 125.1, 126.0, 129.0, 129.5, 130.4, 130.8, 138.9, 139.9, 140.5, 144.8, 164.4; UV-VIS: λ_{max} ($CHCl_3$) 243.0 nm ($\varepsilon \cdot 10^{-3}$ 67.9 $cm^{-1}M^{-1}$), 302.5 (54.6), 347.5 (66.6); IR (ATR) ν: 2974, 2162, 2020, 1596, 1468, 1447, 1382, 1332, 1247, 1232, 1155, 1125, 1054, 1038, 798, 766, 743, 727, 704 cm^{-1}; *Anal.* Calcd for $C_{44}H_{36}N_4O$: C, 82.99; H, 5.70; N, 8.80. Found: C, 82.97; H, 5.73; N, 8.83; HRMS Calcd for ($C_{44}H_{36}N_4O + H^+$): 637.2962; found: 637.2961.

2,5-Bis[4'-(carbazol-9-yl)-3-methylbiphenyl-4-yl]-1,3,4-oxadiazole (7e). White solid (0.33 g, 89%); mp 306–308°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (s, 3H), 7.32 (t, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.72 (m, 4H), 7.91 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 8.23 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.6, 109.8, 120.1, 120.4, 122.2, 123.5, 124.9, 126.0, 127.5, 128.6, 129.7, 130.5, 137.7, 138.9, 139.2, 140.8, 142.9, 164.3; UV-VIS: λ_{max} ($CHCl_3$) 242.0 nm (ε·10^{-3} 75.5 cm^{-1}M^{-1}), 293.0 (48.9), 342.0 (58.0); IR (ATR) ν: 3053, 2182, 1604, 1535, 1489, 1477, 1449, 1385, 1361, 1334, 1307, 1225, 1171, 1042, 1015, 826, 815, 750, 740, 724, 718, 703, 658 cm^{-1}; *Anal*. Calcd for $C_{52}H_{36}N_4O$: C, 85.22; H, 4.95; N, 7.64. Found: C, 85.26; H, 4.97; N, 7.60; HRMS Calcd for ($C_{52}H_{36}N_4O + H^+$): 733.2962; found: 733.2966.

2,5-Bis[4-(thiantren-1-yl)-2-methylphenyl]-1,3,4-oxadiazole (7f). Beige solid (0.29 g, 87%); mp 109–110°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.90 (s, 3H), 7.20 (m, 2H), 7.29 (m, 2H), 7.39 (dd, J = 7.6 and 1.2 Hz, 1H), 7.43 (m, 2H), 7.50 (dd, J = 7.6 and 1.2 Hz, 1H), 7.56 (dd, J = 7.6 and 1.2 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 122.4, 127.2, 127.4, 127.7, 127.9, 128.3, 128.6, 128.8, 128.9, 129.0, 132.9, 135.0, 135.6, 135.9, 136.3, 138.5, 141.4, 143.1, 164.3; UV-VIS: λ_{max} ($CHCl_3$) 261.5 nm (ε·10^{-3} 56.9 cm^{-1}M^{-1}), 307.5 (35.9); IR (ATR) ν: 34258, 3044,2 2162, 2036, 1607, 1474, 1458, 1439, 1327, 1236, 1063, 1044, 843, 824, 771, 754, 742, 727, 712 cm^{-1}; *Anal*. Calcd for $C_{40}H_{26}N_2OS_4$: C, 70.76; H, 3.86; N, 4.13; S, 18.89. Found: C, 70.72; H, 3.82; N, 4.09; S, 18.90; HRMS Calcd for ($C_{40}H_{26}N_2OS_4 + H^+$): 679.1001; found: 679.0997.

2,5-Bis(3-methylbiphenyl-4-yl)-1,3,4-thiadiazole (8a). White solid (0.15 g, 72%); mp 143–144°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 125.0, 127.2, 127.9, 128.1, 128.9, 130.4, 131.4, 137.7, 140.0, 143.1, 167.6; UV-VIS: λ_{max} ($CHCl_3$) 246.0 nm (ε·10^{-3} 26.2 cm^{-1}M^{-1}), 319.0 (43.6); IR (ATR) ν: 3031, 2982, 2926, 2162, 1959, 1607, 1556, 1487, 1445, 1437, 1391, 1220, 1097, 1077, 1024, 988, 882, 835, 763, 730, 714, 697 cm^{-1}; *Anal*. Calcd for $C_{28}H_{22}N_2S$: C, 80.35; H, 5.30; N, 6.69; S, 7.66. Found: C, 80.37; H, 5.31; N, 6.63; S, 7.68; HRMS Calcd for ($C_{28}H_{22}N_2S + H^+$): 419.1576; found: 419.1572.

2,5-Bis[4'-(N,N-diphenylamino)-3-methylbiphenyl-4-yl]-1,3,4-thiadiazole (8b). Yellow solid (0.32 g, 84%); mp 291–293°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (s, 3H), 7.05 (t, J = 7.6 Hz, 2H), 7.14 (m, 6H), 7.27 (t, J = 7.6 Hz, 4H), 7.51 (m, 3H), 7.56 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 123.2, 123.5, 124.4, 124.7, 127.8, 128.3, 129.3, 129.8, 131.4, 137.7, 142.6, 146.6, 147.5, 147.9, 167.4; UV-VIS: λ_{max} ($CHCl_3$) 299.0 nm (ε·10^{-3} 38.9 cm^{-1}M^{-1}), 374.0 (50.8); IR (ATR) ν: 3033, 2157, 1950, 1587, 1519, 1484, 1444, 1329, 1317, 1273, 1194, 1178, 1075, 1028, 985, 816, 769, 753, 724, 685 cm^{-1}; *Anal*. Calcd for $C_{52}H_{40}N_4S$: C, 82.95; H, 5.35; N, 7.44; S, 4.26. Found: C, 82.98; H, 5.39; N, 7.41 S, 4.25; HRMS Calcd for ($C_{52}H_{40}N_4S + H^+$): 753.3046; found: 753.3041.

2,5-Bis[4-(9-methylcarbazol-3-yl)-2-methylphenyl]-1,3,4-thiadiazole (8c). Green solid (0.24 g, 78%); mp 258–260°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 (s, 3H), 3.89 (s, 3H), 7.27 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 29.3, 108.7, 108.8, 118.9, 119.2, 120.4, 122.9, 123.4, 125.0, 125.1, 126.1, 127.2, 130.4, 131.0, 131.4, 137.7, 140.9, 141.5, 144.1, 167.7; UV-VIS: λ_{max} ($CHCl_3$) 244.0 nm (ε·10^{-3} 69.8 cm^{-1}M^{-1}), 282.5 (46.0), 300.5 (46.1), 352.0 (58.9); IR (ATR) ν: 3048, 2924, 2156, 2022, 1596, 1493, 1479, 1469, 1443, 1393, 1363, 1325, 1260, 1246, 1154, 1124, 1104, 1019, 986, 878, 816, 793, 764, 744, 725, 693 cm^{-1}; *Anal*. Calcd for $C_{42}H_{32}N_4S$: C, 80.74; H, 5.16; N, 8.97; S, 5.13. Found: C, 80.70; H, 5.18; N, 9.00; S, 5.10; HRMS Calcd for ($C_{42}H_{32}N_4S + H^+$): 625.2420; found: 625.2427.

2,5-Bis[4-(9-ethylcarbazol-3-yl)-2-methylphenyl]-1,3,4-thiadiazole (8d). Yellow solid (0.29 g, 88%); mp 206–209°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (t, J = 6.8 Hz, 3H), 2.81 (s, 3H), 4.40 (q, J = 6.8 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.49 (m, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 37.7, 108.7, 108.8, 119.0, 120.6, 123.0, 123.6, 125.0, 125.1, 126.0, 127.1, 128.3, 130.4, 130.9, 131.4, 137.7, 139.8, 140.5, 144.1, 167.8; UV-VIS: λ_{max} ($CHCl_3$) 243.5 nm (ε·10^{-3} 67.5 cm^{-1}M^{-1}), 284.0 (44.5), 301.0 (45.3), 352.0 (54.6); IR (ATR) ν: 3050, 2923, 2179, 2021, 1596, 1478, 1470, 1443, 1393, 1363, 1326, 1305, 1285, 1259, 1247, 1233, 1155, 1125, 986, 878, 814, 793, 765, 745, 725, 694 cm^{-1}; *Anal*. Calcd for $C_{44}H_{36}N_4S$: C, 80.95; H, 5.56; N, 8.58; S, 4.91. Found: C, 80.98; H, 5.53; N, 8.54; S, 4.90; HRMS Calcd for ($C_{44}H_{36}N_4S + H^+$): 653.2733; found: 653.2730

2,5-Bis[4'-(carbazol-9-yl)-3-methylbiphenyl-4-yl]-1,3,4-thiadiazole (8e). Grey solid (0.32 g, 85%); mp 280–281°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (s, 3H), 7.30 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.71 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 109.8, 120.1, 120.4,

123.5, 125.0, 126.0, 127.5, 128.3, 128.4, 128.6, 130.4, 131.6, 137.6, 138.0, 140.8, 142.2, 167.6; UV-VIS: λ_{max} ($CHCl_3$) 243.0 nm ($\varepsilon \cdot 10^{-3}$ 96.6 $cm^{-1}M^{-1}$), 293.0 (53.1), 342.5 (65.2); IR (ATR) ν: 3047, 3924, 2156, 2018, 1596, 1521, 1494, 1479, 1444, 1392, 1364, 1335, 1317, 1260, 1232, 1154, 1120, 1019, 986, 878, 816, 792, 746, 724, 695 cm^{-1}; *Anal*. Calcd for $C_{52}H_{36}N_4S$: C, 83.39; H, 4.84; N, 7.48; S, 4.28. Found: C, 83.35; H, 4.80; N, 7.43; S, 4.31; HRMS Calcd for ($C_{52}H_{36}N_4S + H^+$): 749.2733; found: 749.2737.

2,5-Bis[4-(thiantren-1-yl)-2-methylphenyl]-1,3,4-thiadiazole (8f). Beige solid (0.27 g, 77%); mp 293–295°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (s, 3H), 7.21 (m, 2H), 7.29 (m, 2H), 7.40 (m, 3H), 7.50 (dd, J = 7.6 and 1.2 Hz, 1H), 7.54 (dd, J = 7.6 and 1.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 122.3, 127.2, 127.5, 127.7, 127.9, 128.3, 128.7, 128.9, 129.1, 130.7, 132.8, 135.1, 135.6, 136.0, 136.3, 138.5, 141.2, 143.1, 167.3; UV-VIS: λ_{max} ($CHCl_3$) 261.0 nm ($\varepsilon \cdot 10^{-3}$ 61.8 $cm^{-1}M^{-1}$), 310.5 (36.4); IR (ATR) ν: 3046, 2914, 2168, 1970, 1607, 1559, 1441, 1376, 1278, 1246, 1107, 1066, 1033, 990, 885, 840, 790, 753, 731, 722 cm^{-1}; *Anal*. Calcd for $C_{40}H_{26}N_2S_5$: C, 69.13; H, 3.77; N, 4.03; S, 23.07. Found: C, 69.09; H, 3.72; N, 4.07; S, 23.00; HRMS Calcd for ($C_{40}H_{26}N_2S_5 + H^+$): 695.0772; found: 695.0777.

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