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Synthesis of 1,3,4-Oxadiazole-Based Aromatic and Heterocyclic/Phenylpyrazole Derivatives

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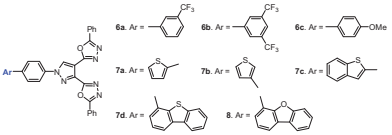
ABSTRACT: *A new series of 1,3,4-oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives* **6a–c**, **7a–d**, *and* **8** *were synthesized via sequential 1,3-dipolar cyclization, hydrazidation, benzoylation, dehydrative cyclization, and the Suzuki coupling reaction. Among the derivatives, compounds* **7a** *and* **7c** *with the corresponding 2-thienyl and 2-benzo[b]thienyl (Ar) at the phenyl group located at the N-1 position of pyrazole showed a better conjugation range.*



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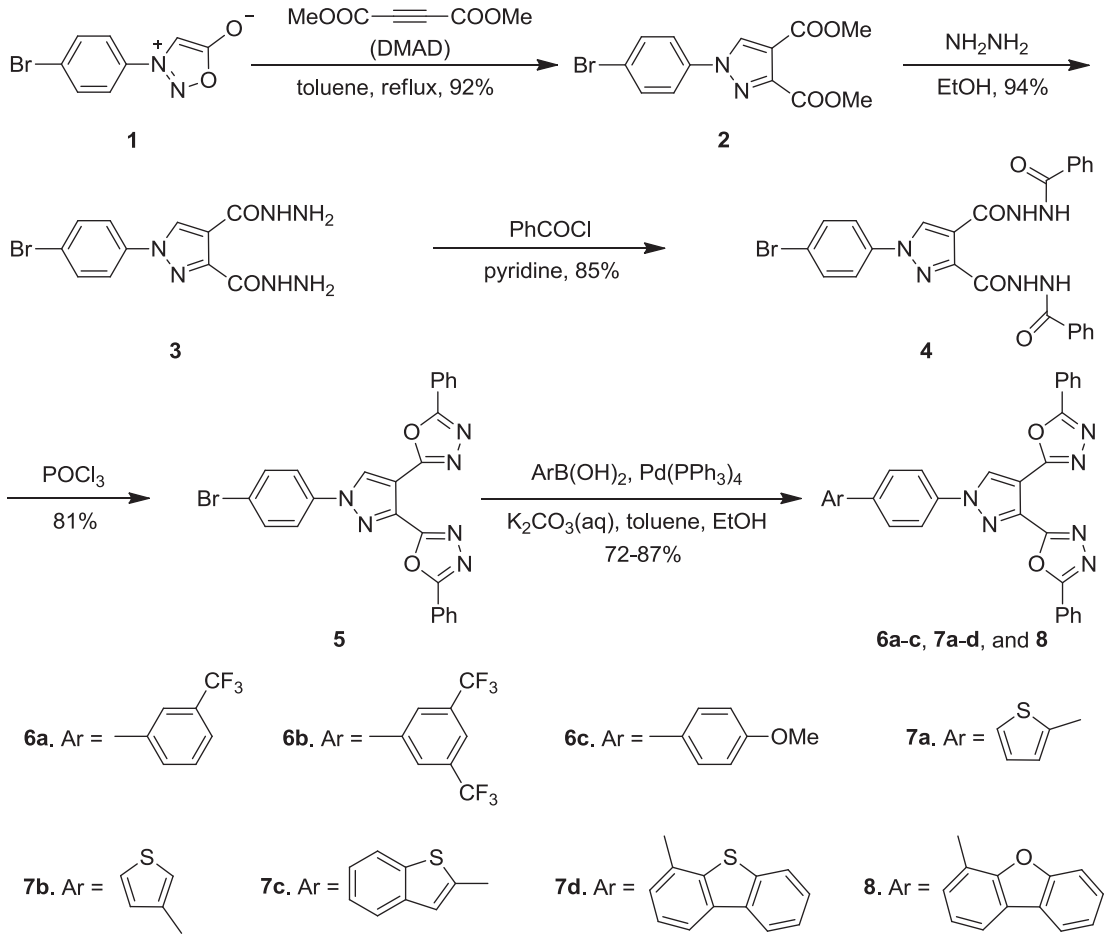
INTRODUCTION

π-Conjugated 1,3,4-oxadiazole derivatives have been widely exploited as electron-transporting and hole-blocking materials in electroluminescent (EL) devices because of their high florescence efficiency, thermal stability, photoluminescence (PL) quantum yield, and semiconducting property [1]. Therefore, the development of new π-conjugated 1,3,4-oxadiazole-based heterocyclic compounds as EL materials has attracted attention [2–4], particularly in the blue region [1]. Representative examples include 1,3,4-oxadiazole hybridized with pyridine [5], pyrimidine [5], carbazole [6], 1,2,3-triazole [7], 1,2,3-triazole-pyridine [7], triazolopyridinone [8], triazolopyridinone-carbazole [9], and spirobifluorene [10].

In our previous study, we have coupled various arylpyrazoles, the electron-rich heterocycles that have excellent thermal and morphological stability [11]; in the conjugation, main chain of 1,3,4-oxadiazoles generates 1,3,4-oxadiazole-based arylpyrazole derivatives with improved electron-transporting properties [12]. To further improve the conjugation range, we connected the phenyl group in the pyrazole with an additional aryl or heteroaryl group in this study. The aryl and heteroaryl groups included *m*-CF_3-C_6H_4,



SCHEME 1 Synthesis of 1,3,4-oxadiazole-based heterocyclic and aromatic/phenylpyrazole derivatives **6a–c**, **7a–d**, and **8**.

2,6-di-CF_3-C_6H_3, *p*-OMe-C_6H_4, 2-thienyl, 3-thienyl, 2-benzo[*b*]thienyl, dibenzo[*b*,*d*]thiophene-4-yl, and dibenzo[*b*,*d*]furane-4-yl that have important properties to form conducting polymers [13–18]. These new 1,3,4-oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives **6a**–**6c**, **7a**–**7d**, and **8** were obtained by the use of sequential 1,3-dipolar cycloaddition, substitution, benzoylation, dehydrative cyclization, and the Suzuki coupling reaction.

RESULTS AND DISCUSSION

Synthesis of 1,3,4-Oxadiazole-Based Heterocyclic and Aromatic/Phenylpyrazole Derivatives **6a–c**, **7a–d**, *and* **8**

Scheme 1 shows the synthetic route for 1,3,4-oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives **6a**–**c**, **7a**–**d**, and **8**. *N*1-*p*-Bromophenylsydnone **1**, prepared according to the literature procedure [19], was reacted with dimethyl acetylenedicaboxylate (DMAD) to give the corresponding dimethyl 1-(*p*-bromophenyl)-1*H*-pyrazole-3,4-dicarboxylate (**2**) in 92% of the yield [20]. This efficient 1,3-dipolar cycloaddition be able to apply for scale-up manufacture of pyrazole derivatives from sydnones [21, 22]. A treatment of compound **2** with hydrazine hydrate afforded the corresponding dihydrazide **3** in 94% yield [23]. Dihydrazide **3** was then reacted with benzoyl chloride in pyridine to give the corresponding dibenzoyl dihydrazide **4** in 85% yield. A reaction of compound **4** with $POCl_3$ formed the pyrazole–1,3,4-oxadiazole **5** in 81% yield [24].

Compound **5** was then cross-coupled with various arene- and heteroarene-boronic acids, including *m*-CF_3–C_6H_4–, 2,6-di-CF_3–C_6H_3–, *p*-OMe-C_6H_4-, 2-thienyl-, 3-thienyl-, 2-benzo[*b*]thienyl, dibenzo[*b*,*d*]thiophene-4-yl-, and dibenzo[*b*,*d*]furane-4-yl-boronic acids (see Scheme 1) [25] using the Suzuki coupling reaction [26]. The reaction provided the corresponding 1,3,4-oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives **6a**–**c**, **7a**–**d**, and **8** in 72–87% yields (see Scheme 1 and Table 1).

TABLE 1 Synthesis of 1,3,4-Oxadiazole-Based Aromatic and Heterocyclic/Phenylpyrazole Derivatives **6a–c**, **7a–d**, and **8** from **5** with Various Boronic Acids

Entry	*ArB(OH)$_2$ Ar =*	*Compound*	*Yield (%)*
1	*m*-CF_3–C_6H_4-	**6a**	82
2	2,6-Di-CF_3-C_6H_3-	**6b**	72
3	*p*-OMe-C_6H_4-	**6c**	86
4	2-Thienyl-	**7a**	81
5	3-Thienyl-	**7b**	87
6	2-Benzo[*b*]thienyl-	**7c**	74
7	Dibenzo[*b*,*d*]thiophene-4-yl-	**7d**	83
8	Dibenzo[*b*,*d*]furane-4-yl-	**8**	85

TABLE 2 Spectroscopic Data of **5** and the New 1,3,4-Oxadiazole-Based Aromatic and Heterocyclic/Phenylpyrazole Derivatives **6a–c**, **7a–d**, and **8** in CH_2Cl_2

Entry	*Compound*	*Absorbance λ_{max} (UV–vis, nm)*	*Emission λ_{max} (PL, nm)*	Φ_f[a]
1	**5**	279	361	-
2	**6a**	299	384	0.68
3	**6b**	303	369	0.67
4	**6c**	307	413	0.67
5	**7a**	315	399	0.71
6	**7b**	304	398	0.73
7	**7c**	326	399	0.70
8	**7d**	269	383	0.76
9	**8**	290	387	0.74

[a]Fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene ($\Phi_f = 0.8$).

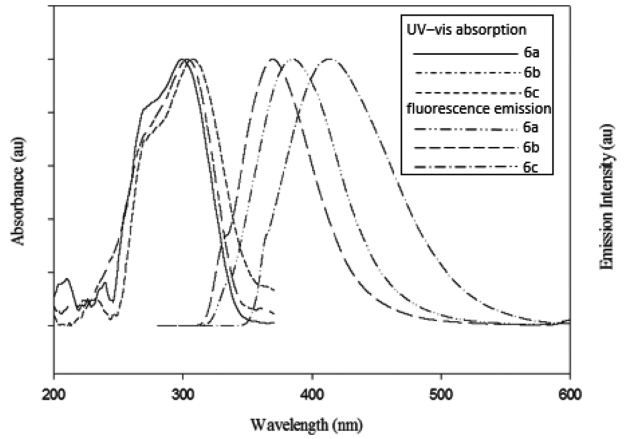


FIGURE 1 The UV–vis and PL spectra of **6a–c** in CH_2Cl_2 solution.

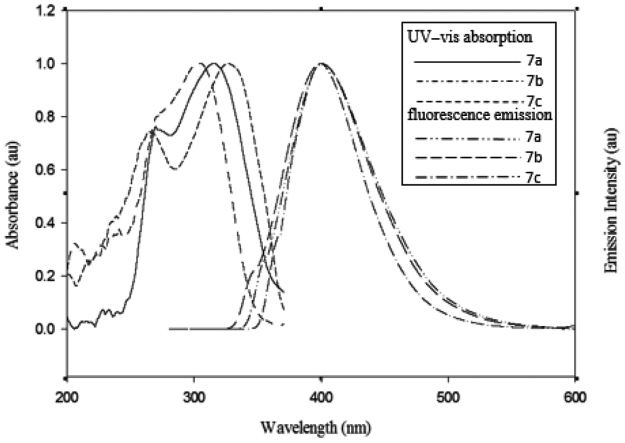


FIGURE 2 The UV–vis and PL spectra of **7a–c** in CH_2Cl_2 solution.

Optical Properties

1,3,4-Oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives **6a–c**, **7a–d**, and **8** showed similar λ_{max} (at 299–307, 269–326, and 290 nm, respectively) in the UV–vis spectra measured in CH_2Cl_2 (Table 2). For the UV–vis spectra of **6a–c** and **7a–c** as shown in Figs. 1 and 2, the main absorption bands at ~290 nm were contributed by the conjugation of phenyl and pyrazole moieties as indicated in our previously published results [12]. Compounds **6a–c** have a slightly redshift (299–307 nm) in comparison with **5**, possibly due to the conjugation resulting from the additional aryl group connected to the *N*1-phenyl group in the pyrazolic ring. Compounds **7a–c** with 2-thienyl, 3-thienyl, and 2-benzo[*b*]thienyl groups at the paraposition of the *N*1-phenylpyrazole also showed a slightly redshift with λ_{max} values of 304–326 nm. For compounds **7d** and **8**, they showed very similar absorption peaks (at 269 and 290 nm, respectively) to that of the starting material **5** in the visible region (see Fig. 3). We thought that the steric repulsion between bulky dibenzo[*b*,*d*]thiophene-4-yl or dibenzo[*b*,*d*]furane-4-yl substituents with an 1,3,4-oxadiazole-based phenylpyrazole core structure may exist. As a result, dibenzo[*b*,*d*]thiophene-4-yl and dibenzo[*b*,*d*]furane-4-yl groups may not favor conjugation with phenylpyrazole.

Table 2 also shows the emission λ_{max} of compounds **5**, **6a–c**, **7a–d**, and **8** in their PL spectra measured in CH_2Cl_2. Except for compound **6b**, these compounds showed a redshift in λ_{max} by ≥15 nm in comparison with **5** (λ_{max} for **5**: 361 nm). For **6a–c** bearing the substituted phenyl group at the phenylpyrazole moiety, the emission λ_{max} was observed at 369–413 nm (see Fig. 1). Compound **6c** bearing two strong electron-withdrawing CF_3 groups showed the strongest redshift in the PL emission spectrum (at ~413 nm; see Fig. 1). For compounds **7a–d** and **8** containing the corresponding 2-thienyl, 3-thienyl, 2-benzo[*b*]thiophenyl, dibenzofuranyl, and dibenzothiophenyl groups, their PL showed a slightly

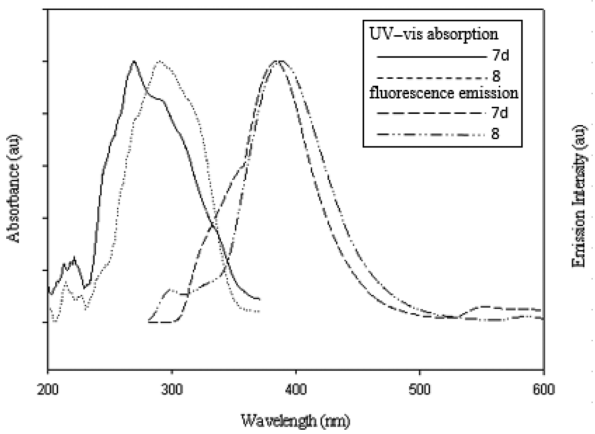


FIGURE 3 The UV–vis and PL spectra of **7d** and **8** in CH_2Cl_2 solution.

redshift with λ_{max} at 383–399 nm. Following the results from UV–vis and PL, we assumed that the different substituents at the paraposition of the phenyl ring located at the phenylpyrazole group, including aryl, 4-dibenzofuranyl, 2- or 3-thiophenyl, 2-benzo[*b*]thiophenyl, 4-dibenzofuranyl, and 4-dibenzothiophenyl groups, seemed to conjugate with a 1,3,4-oxadiazole-based phenylpyrazole core backbone, especially for 2-thiophenyl and 2-benzo[*b*]thiophenyl groups. On the other hand, the solution fluorescence quantum yields (Φ_f) of **5**, **6a–c**, **7a–d**, and **8**, all of which fall in the range of 0.67–0.76, were determined relative to that of 2-phenyl-5-(4-biphenyl)-1,3,4-oxzdiazole in benzene ($\Phi_f = 0.80$; see Table 2).

In conclusion, a series of 1,3,4-oxadiazole-based aromatic and heterocyclic/phenylpyrazole derivatives were successfully synthesized by sequential 1,3-dipolar cycloaddition, hydrazidation, benzoylation, dehydrative cyclization, and the Suzuki coupling reaction. Aryl, dibenzofuranyl, 2-thiophenyl, 3-thiophenyl, 2-benzo[*b*]thiophenyl, and dibenzothiophenyl were introduced to the 1,3,4-oxadiazole-phenylpyrazole main structure to promote the conjugation range. Based on spectroscopic studies including UV–vis and PL, compounds **7c** and **7d** with the respective 2-thiophenyl and 2-benzo[*b*]thiophenyl groups possessed the more conjugation efficiency.

EXPERIMENTAL

General

All chemicals were reagent grade and used as purchased. All reactions were carried out under nitrogenous atmosphere and monitored by thin-layer chromatography. Flash column chromatography was carried out on silica gel (230–400 mesh). Tetrakis(triphenylphosphine)palladium, toluene, silica gel and *p*-xylene were purchased from Merck Chemical Co. Dichloromethane, chloroform, ethanol, hydrazine hydrate, methanol, and tetrahydrofuran were purchased from Fluka & Aldrich. Benzoyl chloride, benzo[b]thien-2-ylboronic acid, 4-dibenzothienylboronic acid, 4-(dibenzofuranyl)boronic acid, dimethyl acetylenedicaboxylate, diphenylacetylene, phenylacetylene, potassium carbonate, pyridine, phosphorus oxychloride, 2-thienylboronic acid, and 3-thienylboronic acid were purchased from Acros Chemical Co. Potassium carbonate was purchased from TCI Chemical Co.

Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wave numbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. UV–visible spectra were measured with a HP 8452A diode-array spectrophotometer. PL spectra were obtained on a PerkinElemer fluorescence spectrophotometer (LS 55). Proton NMR spectra were obtained on a Bruker AC-300 (300 MHz) spectrometer by the use of DMSO-d_6 as the solvent. Carbon-13 NMR spectra were obtained on a Bruker AC-300 (75 MHz) spectrometer by using of DMSO-d_6 as a solvent. Carbon-13 chemical shifts are referenced to the center of the DMSO-d_6 sextet (δ 39.6 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz).

The UV–vis spectra of the samples were measured in NMP by a Shimadzu model UV-160 spectrophotometer. The fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. Elemental analyses were carried out on a Heraeus CHN–O RAPID element analyzer.

*Synthesis of Dimethyl 1-(4-Bromophenyl)-1H-pyrazole-3,4-dicarboxylate (**2**)*

A solution of sydnone **1** (0.20 g, 1.0 equiv) in 4.0 mL *p*-xylene was added DMAD (1.05 equiv). The reaction mixture was heated at reflux for 6.0 h. After the reaction was completed, the solution was concentrated under reduced pressure to remove *p*-xylene. The residue was purified by column chromatography on silica gel to give **2** in 92% yield [20]: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 7.66 (d, J = 7.8 Hz, 2H, ArH), 7.83 (d, J = 7.8 Hz, 2H, ArH), 9.08 (s, 1H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 52.1, 52.7, 115.6, 120.9, 121.6,

132.7, 132.9, 137.7, 144.7, 161.6, 162.2; Anal. calcd for $C_{13}H_{11}BrN_2O_4$: C 46.04; H 3.27; N 8.26; found: C 46.10; H 3.24; N 8.21.

*Synthesis of 1-(p-Bromophenyl)-1H-pyrazole-3,4-dicarbohydrazide (**3**)*

A solution of **2** (0.51 g, 1.5 mmol, 1.0 equiv) and hydrazine monohydrate (0.76 g, 6.0 mmol, 4.0 equiv) in EtOH was heated at reflux for 12 h. After the reaction was completed, the solution was concentrated under reduced pressure and precipitated by EtOAc (15 mL). The resulting solution was kept at –5°C for 4 h. The precipitate was filtered and washed with cold EtOH (10 mL). The solids were dried in a vacuum oven for 12 h to give the desired **3** in 94% yield [23]: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 4.68 (br, 4H, NH_2), 7.61 (d, $J = 8.9$ Hz, 2H, ArH), 8.06 (d, $J = 8.9$ Hz, 2H, ArH), 9.09 (s, 1H, ArH), 10.36 (br, 2H, NH), 11.19 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 119.3, 120.6, 121.4, 132.6, 132.2, 138.0, 141.9, 160.1, 161.1; Anal. calcd for $C_{11}H_{11}BrN_6O_2$: C 38.96; H 3.27; N 24.78; found: C 38.89; H 3.22; N 24.85.

*Synthesis of Dibenzoyl-1-(4-bromophenyl)-1H-pyrazole-3,4-dicarbohydrazide (**4**)*

To a solution of **3** (2.0 g, 5.9 mmol, 1.0 equiv) in pyridine (20 mL) in an ice bath, benzoyl chloride (2.7 g, 23.7 mmol, 4.0 equiv) was added. The reaction mixture was stirred at 80°C for 5 h. After the reaction was completed, the reaction mixture was concentrated under reduced pressure. The residue was recrystallized from EtOH to give the desired **4** in 85% yield: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.48–7.56 (m, 6H, ArH), 7.80–7.96 (m, 4H, ArH), 8.05 (d, $J = 8.4$ Hz, 2H, ArH), 8.18 (d, $J = 8.7$ Hz, 2H, ArH), 9.33 (s, 1H, ArH), 10.73 (s, 1H, NH), 10.76 (s, 1H, NH), 11.20 (s, 1H, NH), 11.90 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 117.0, 119.2, 121.7, 127.7, 128.7, 128.8, 132.1, 132.7, 132.4, 134.3, 134.7, 137.7, 137.8, 141.0, 141.3, 159.7, 162.1, 165.9, 167.0; Anal. calcd for $C_{25}H_{19}BrN_6O_4$: C 54.86; H 3.50; N 15.35; found: C 54.81; H 3.51; N 15.38.

*Synthesis of 5,5′-(1-(4-Bromophenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**5**)*

Compound **4** (2.3 g, 4.2 mmol, 1.0 equiv) was dissolved in $POCl_3$ (10 mL), and the resultant solution was heated at 90°C for 12 h. After the reaction was completed, the reaction mixture was added with cold water (10 mL) and neutralized with aqueous $NaHCO_3$ (10 mL). The precipitate was filtrated and washed with cold water (5.0 mL). The solids were recrystallized from EtOH to give the desired **5** in 81% yield [25]: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.60–7.83 (m, 10H, ArH), 7.86 (d, $J = 7.5$ Hz, 2H, ArH), 8.07 (d, $J = 7.5$ Hz, 2H, ArH), 9.69 (s, 1H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 109.1, 122.1, 123.5, 123.6, 127.0, 127.4, 129.1, 129.6, 130.0, 131.8, 132.0, 132.1, 135.0, 136.2, 137.0, 158.1, 158.3, 165.0, 166.2; Anal. calcd for $C_{25}H_{15}BrN_6O_2$: C 58.72; H 2.96; N 16.44; found: C 58.67; H 2.92; N 16.50.

Standard Procedure for the Synthesis of 1,3,4-Oxadiazole-Based Aromatic and Heterocyclic/Phenylpyrazole Derivatives **6a–c**, **7a–d**, *and* **8**

Compound **5** (~5.0 mmol, 1.0 equiv), aryl- or heteroaryl-boronic acid (~10 mmol, 2.0 equiv), tetrakis(triphenylphosphine)palladium (~0.20 mmol, 0.04 equiv), and potassium carbonate (2.0 M in H_2O, ~15 mmol, 3.0 equiv) in *p*-xylene/EtOH (40/20 mL) were heated at reflux for 24 h under N_2. The solution was concentrated, added with water (10 mL), and extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with a saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL). The solution was dried over $MgSO_4$(s) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexanes as an eluent. The collected compounds were recrystallized from a mixture of EtOAc and EtOH to afford the corresponding **6a–c**, **7a–d**, and **8** [25].

*5,5′-(1-(3′-(Trifluoromethyl)-[1,1′-biphenyl]-4-yl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**6a**).* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44–7.57 (m, 6H, ArH), 7.62–7.67 (m, 2H, ArH), 7.76–7.82 (m, 3H, ArH), 7.86 (s, 1H, ArH), 7.98 (d, $J = 8.4$ Hz, 2H, ArH), 8.11 (d, $J = 7.2$ Hz, 2H, ArH), 8.18 (d, $J = 7.2$ Hz, 2H, ArH), 8.78 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.9, 120.3, 123.4, 123.5, 123.7, 123.8, 124.6, 127.0, 127.3, 128.5, 129.1, 129.5, 130.0, 130.3, 131.2, 131.6, 131.9, 132.1, 136.3, 138.2, 140.0, 140.2, 158.1, 158.5, 165.0, 165.3; Anal. calcd for $C_{32}H_{19}F_3N_6O_2$: C 66.67; H 3.32; N 14.58; found: C 66.71; H 3.22; N 14.65.

*5,5′-(1-(3′,5′-Bis(trifluoromethyl)-[1,1′-biphenyl]-4-yl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**6b**).* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45–7.60 (m, 6H, ArH), 7.82 (d, $J = 8.4$ Hz, 2H, ArH), 7.92 (s, 1H, ArH), 8.04–8.06 (m, 4H, ArH), 8.12 (d, $J = 7.2$ Hz, 2H, ArH), 8.19 (d, $J = 7.2$ Hz, 2H, ArH), 8.90 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.1, 120.5, 121.6, 123.4, 123.5, 125.0,

127.1, 127.3, 128.7, 129.1, 130.1, 131.9, 132.1, 132.7, 136.5, 138.4, 138.9, 141.6, 153.1, 154.1, 158.1, 158.4, 165.1, 165.3; Anal. calcd for $C_{33}H_{18}F_6N_6O_2$: C 61.50; H 2.81; N 13.04; found: C 61.59; H 2.85; N 13.01.

5,5′-(1-(4′-Methoxy-[1,1′-biphenyl]-4-yl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**6c**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H, OCH_3), 7.01 (d, J = 8.4 Hz, 2H, ArH), 7.48–7.60 (m, 8H, ArH), 7.73 (d, J = 8.1 Hz, 2H, ArH), 7.92 (d, J = 8.1 Hz, 2H, ArH), 8.13 (d, J = 7.2 Hz, 2H, ArH), 8.20 (d, J = 7.2 Hz, 2H, ArH), 8.83 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.0, 108.2, 114.0, 119.8, 123.0, 123.1, 125.8, 126.7, 126.9, 127.4, 127.7, 128.7, 129.6, 131.4, 131.5, 131.6, 135.7, 136.7, 140.9, 148.9, 158.1, 159.3, 164.5, 164.8; Anal. calcd for $C_{32}H_{22}N_6O_3$: C 71.37; H 4.12; N 15.60; found: C 71.29; H 4.16; N 15.51.

5,5′-(1-(4-(Thiophen-2-yl)phenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**7a**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.13 (m, 1H, ArH), 7.34–7.39 (m, 2H, ArH), 7.47–7.57 (m, 6H, ArH), 7.77 (d, J = 7.2 Hz, 2H, ArH), 7.89 (d, J = 7.5 Hz, 2H, ArH), 8.12 (d, J = 6.6 Hz, 2H, ArH), 8.19 (d, J = 7.2 Hz, 2H, ArH), 8.83 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.7, 120.3, 123.4, 123.5, 124.0, 125.8, 127.0, 127.1, 127.3, 128.3, 128.6, 129.1, 130.0, 131.9, 132.1, 134.8, 136.1, 137.4, 142.5, 158.2, 158.5, 164.9, 165.2; Anal. calcd for $C_{29}H_{18}N_6O_2S$: C 67.69; H 3.53; N 16.33; found: C 67.62; H 3.47; N 16.41.

5,5′-(1-(4-(Thiophen-3-yl)phenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**7b**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44–7.59 (m, 9H, ArH), 7.78 (d, J = 8.4 Hz, 2H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH), 8.13 (d, J = 7.2 Hz, 2H, ArH), 8.20 (d, J = 7.2 Hz, 2H, ArH), 8.83 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.6, 120.4, 120.6, 123.8, 123.8, 126.8, 127.0, 127.5, 127.7, 128.1, 128.3, 128.7, 130.1, 131.4, 133.6, 134.7, 136.6, 136.9, 140.6, 158.2, 158.9, 165.2, 165.5; Anal. calcd for $C_{29}H_{18}N_6O_2S$: C 67.69; H 3.53; N 16.33; found: C 67.60; H 3.58; N 16.25.

5,5′-(1-(4-(Benzo[b]thiophen-2-yl)phenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**7c**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26–7.60 (m, 8H, ArH), 7.64 (s, 1H, ArH), 7.80–8.01 (m, 6H, ArH), 8.13 (d, J = 7.2 Hz, 2H, ArH), 8.20 (d, J = 7.2 Hz, 2H, ArH), 8.84 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.7, 119.3, 120.9, 122.4, 123.7, 123.8, 124.0, 124.2, 125.0, 127.5, 127.7, 127.9, 128.8, 130.2, 132.1, 132.5, 132.6, 133.2, 138.2, 139.1, 140.3, 141.4, 143.2 158.3, 158.7, 164.4, 164.7; Anal. calcd for $C_{33}H_{20}N_6O_2S$: C 70.20; H 3.57; N 14.88; found: C 70.11; H 3.48; N 14.96.

5,5′-(1-(4-(Dibenzothiophen-4-yl)phenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**7d**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44–7.61 (m, 10H, ArH), 7.86–7.89 (m, 1H, ArH), 7.96 (d, J = 8.7 Hz, 2H, ArH), 8.05 (d, J = 8.4 Hz, 2H, ArH), 8.15 (d, J = 7.2 Hz, 2H, ArH), 8.22 (d, J = 8.1 Hz, 4H, ArH), 8.90 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.5, 120.3, 121.1, 121.8, 122.7, 123.5, 123.6, 124.6, 125.3, 126.9, 127.0, 127.1, 127.3, 129.1, 129.8, 130.2, 131.9, 132.1, 132.3, 135.3, 135.6, 136.5, 138.1, 138.4, 139.3, 141.1, 158.1, 158.5, 164.8, 165.0; Anal. calcd for $C_{37}H_{22}N_6O_2S$: C 72.30; H 3.61; N 13.67; found: C 72.26; H 3.67; N 13.74.

5,5′-(1-(4-(Dibenzofuran-4-yl)phenyl)-1H-pyrazole-3,4-diyl)bis(2-phenyl-1,3,4-oxadiazole) (**8**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.44 (m, 2H, ArH), 7.49–7.55 (m, 5H, ArH), 7.62–7.67 (m, 3H, ArH), 7.97–8.05 (m, 5H, ArH), 8.11–8.15 (m, 4H, ArH), 8.21 (d, J = 6.9 Hz, 2H, ArH), 8.88 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.4, 111.4, 119.6, 120.0, 120.3, 122.6, 122.9, 123.5, 123.7, 124.7, 126.1, 126.7, 126.9, 127.0, 128.2, 128.7, 129.7, 131.4, 131.5, 131.6, 131.7, 136.5, 137.4, 152.8, 153.7, 155.7, 157.8, 158.1, 164.6, 164.8; Anal. calcd for $C_{37}H_{22}N_6O_3$: C 74.24; H 3.70; N 14.04; found: C 74.28; H 3.65; N 14.10.

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