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Regioselective, One-Pot, Three-Component Synthesis of 1,3,4- and 1,3,5-Triarylpyrazoles from 1- and 2-Aryl-1-alkenyl Sulfones

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Keywords: Synthetic methods / Multicomponent reactions / Cyclization / Nitrogen heterocycles

A one-pot, three-component coupling of aldehydes with hydrazines and 1-aryl-1-alkenyl sulfones or 2-aryl-1-alkenyl sulfones for the regioselective synthesis of 1,3,4- and 1,3,5-triarylpyrazoles was developed. In our developed procedure, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) worked as an effective oxidant, and the addition of an strong acid was not necessary. We synthesized 1,3,4- and 1,3,5-triarylpyrazoles containing acid-labile functionalities in a one-pot reaction in good yields.

Introduction

One-pot, multicomponent coupling reactions are very powerful synthetic methods for the construction of complex molecules from simple starting materials. In particular, the avoidance of work-up and purification of intermediates when using a one-pot approach improves the efficiency of library synthesis, and this has revolutionized drug discovery.[1]

Pyrazoles are five-membered-ring heteroaromatic compounds that contain two adjacent nitrogen atoms.[2] Triarylpyrazoles are an important subclass of these compounds because these structures are frequently found in biologically active compounds,[3–9] such as antileishmanial and antibacterial agent **1**,[3] fructose-1,6-bisphosphatase (FBPase) inhibitor **2**,[6] cyclooxygenase (COX) I and II inhibitor **3**,[4,5] and fatty-acid-binding protein (FABP) 3 inhibitor **4**,[9] as shown in Figure 1. The most common method for the synthesis of triarylpyrazoles is the Knorr reaction[10] of hydrazines with 1,3-dicarbonyl compounds.[11–14] However, the preparation of the 1,3-dicarbonyl compounds requires multiple synthetic steps, and the control of regiochemistry is usually complicated.[2] Although numerous useful synthetic approaches for the preparation of triaryl-substituted pyrazoles have been reported, the development of a more divergent, protection/deprotection-free short synthetic route from readily available starting materials remains a very important pursuit.[2] From this point of view, a formal [3+2] cycloaddition reaction between hydrazones and nitro alkenes is attractive because both of the substrates are readily available, and the routhe could lead to both 1,3,4- and 1,3,5-triarylpyrazoles regioselectively.[15–25]

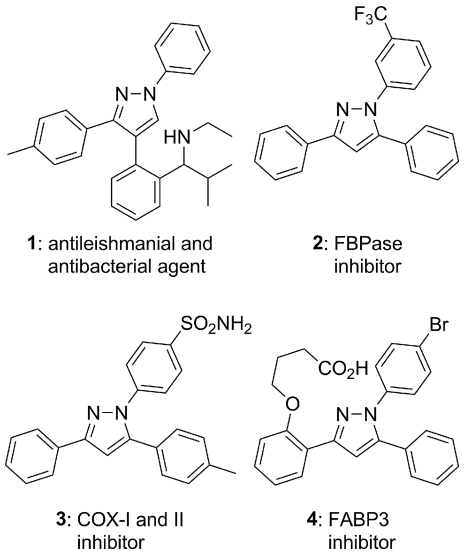

Figure 1. Structures of biologically active triarylpyrazoles.

The Deng group has extensively studied the coupling between various hydrazones and nitroalkenes. Their optimized acidic conditions [10 equiv. of trifluoroacetic acid (TFA) in CF_3CH_2OH, room temp.][23] or neutral conditions

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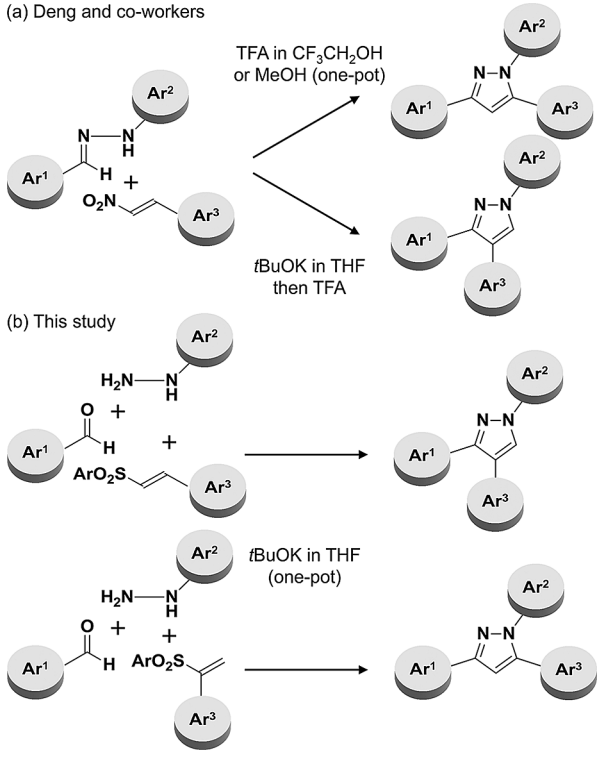
(MeOH or ethylene glycol, reflux)[21] gave 1,3,5-triarylpyrazoles (Scheme 1, a). Their optimized basic/acidic conditions (*t*BuOK, THF, –78 °C, then TFA)[22] gave 1,3,4-triarylpyrazoles. In addition, they reported a beautiful one-pot, three-component synthesis of a 1,3,5-triarylpyrazole under neutral conditions (MeOH, reflux).[21]

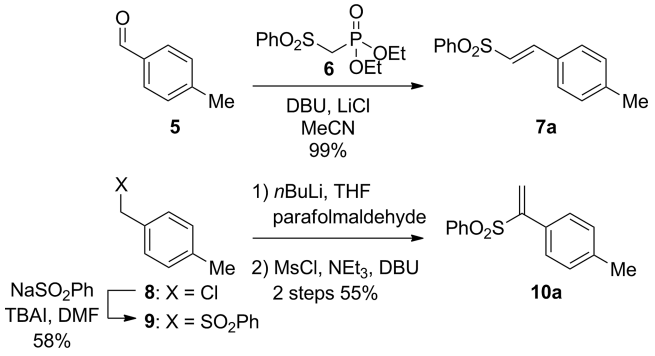


Scheme 1. (a) Formal [3+2] cycloadditions of hydrazones and nitroalkenes under both acidic and basic conditions for the synthesis of 1,3,4- and 1,3,5-triarylpyrazoles, as reported by Deng and coworkers. (b) One-pot, three-component couplings of aldehydes with hydrazines and 2-aryl-1-alkenyl sulfones or 1-aryl-1-alkenyl sulfones for the synthesis of 1,3,4- and 1,3,5-triarylpyrazoles in this study.

We have developed and reported one-pot, or one-flow, multicomponent coupling methods for the efficient synthesis of organic compounds.[26–33] As part of our drug development research into Alzheimer's disease[31,34,35] based on triarylpyrazoles, we decided to develop a rapid, one-pot approach for the synthesis of a structurally diverse triarylpyrazole library. In this paper, we report the regioselective one-pot, three-component synthesis of 1,3,4- and 1,3,5-triarylpyrazoles from readily available starting materials: aryl aldehydes, aryl hydrazines, and 1- and 2-aryl-1-alkenyl sulfones (Scheme 1, b). As far as we could ascertain, only the Padmavathi group has reported the coupling of various alkenyl sulfones and hydrazones for the synthesis of sulfonyl-linked bispyrazoles,[36–42] however, the elimination of the sulfonyl group has not yet been reported. Key to the success of this approach is whether the aryl sulfonyl group can act as a good leaving group, as was found to be the case for the nitro group.

Results and Discussion

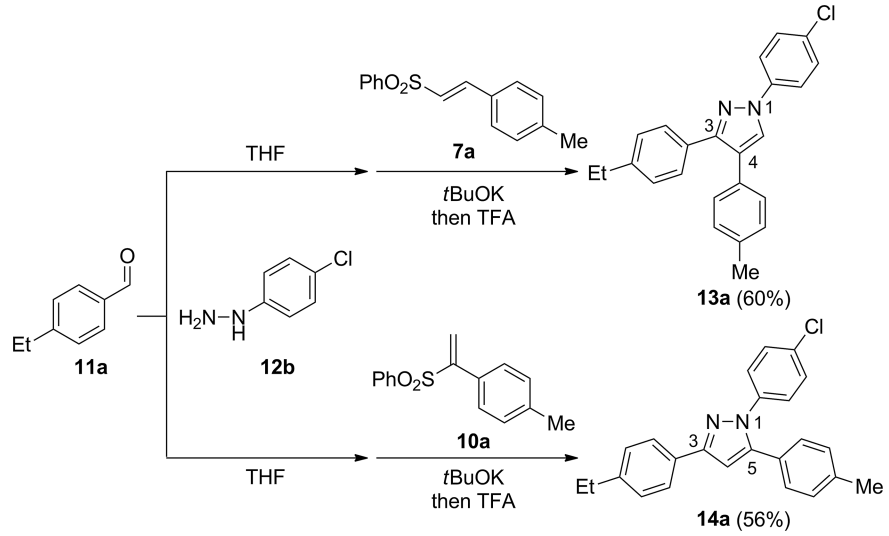
Alkenyl sulfone **7a**[43] was prepared in an excellent yield from 4-tolualdehyde (**5**) following the reported procedure[44] (Scheme 2). Another alkenyl sulfone, **10a**,[45] was prepared by the nucleophilic substitution of 4-methylbenzyl chloride (**8**) with phenylsulfinate anion, followed by *exo*-methylene formation.



Scheme 2. Preparation of phenylsulfonyl alkenes **7a** and **10a**. Me = methyl, Et = ethyl, Ph = phenyl, DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene, TBAI = tetra-*n*-butylammonium iodide, DMF = *N*,*N*-dimethylformamide, Bu = butyl, THF = tetrahydrofuran, Ms = methylsulfonyl.

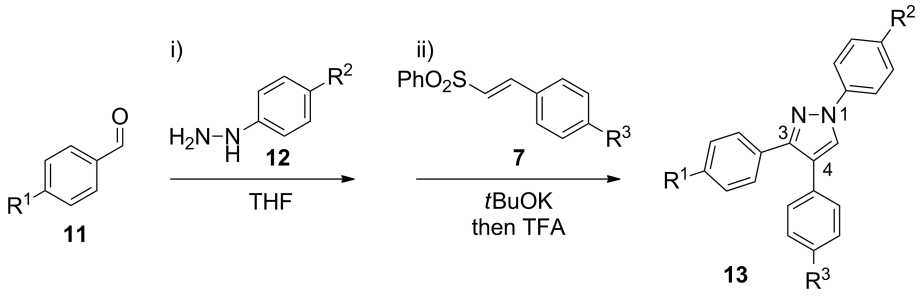
A crucial, one-pot three-component coupling of aldehyde **11a**, hydrazine **12b**, and sulfonyl alkenes **7a** and **10a** was examined following the procedure reported by the Deng group (Scheme 3).[22,23] 4-Ethylbenzaldehyde (**11a**) was coupled with (4-chlorophenyl)hydrazine (**12b**) in THF at room temperature for 1 h. After TLC analysis revealed the consumption of the substrates and the generation of the hydrazone, *t*BuOK was added to the reaction mixture at –78 °C. The mixture was stirred at the same temperature, and then sulfonyl alkene **7a** or **10a** was added, and the mixture was stirred at 50 °C. Then, TFA was added at –78 °C, and the mixture was stirred at room temperature. The desired 1,3,4-triarylpyrazole (i.e., **13a**) and 1,3,5-triarylpyrazole (i.e., **14a**) were both obtained regioselectively in satisfactory yields. As expected, the phenylsulfonyl group acted as a good leaving group.

The substrate scope of the developed one-pot three-component coupling procedure for the synthesis of 1,3,4-triarylpyrazoles was examined using substrates with electron-donating/withdrawing groups (Table 1). The desired products were obtained in moderate to good yields (47–83%) from each of the eight combinations tested, except for 1,3,4-tris(4-chlorophenyl)-1*H*-pyrazole (**13f**), as shown in Table 1, entry 6. A plausible reaction mechanism is shown in Scheme 4. The generation of an undesired product such as **C** was observed in the case of **13f**. We speculated that the electron-poor substituents (Cl) slowed the oxidation of pyrazoline **A** to the desired pyrazole (i.e., **B**; Scheme 4).[22,23] In order to accelerate the oxidation step, an oxidant [2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)] was used in the synthesis of **13f** (Table 1, entry 6), As expected, the desired product was obtained in an improved yield (75%).



Scheme 3. One-pot, three-component couplings of an aldehyde **11a** with hydrazine **12b** and 2-aryl-1-alkenyl sulfone **7a** or 1-aryl-1-alkenyl sulfone **10a** for the synthesis of 1,3,4- and 1,3,5-triarylpyrazoles.

Table 1. Substrate scope of a one-pot, three-component coupling of aldehydes **11** with hydrazines **12** and 1-aryl-1-alkenyl sulfones **7**, for the synthesis of 1,3,4-triarylpyrazoles **13**.

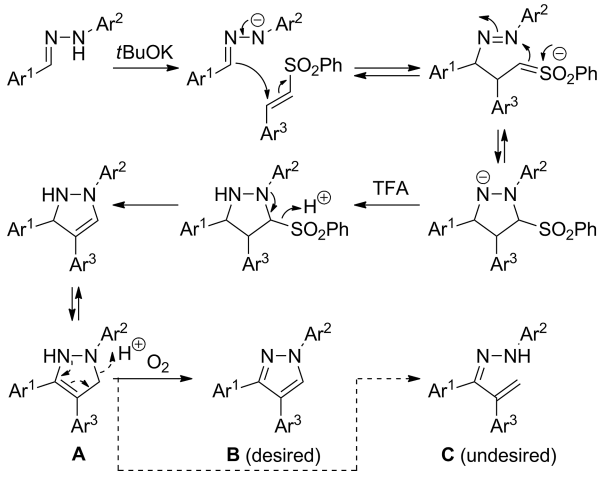


Entry	**11** (R^1)	**12** (R^2)	**7** (R^3)	**13**, Yield [%][a]
1	**11a** (Et)	**12b** (Cl)	**7a** (Me)	**13a**, 60
2	**11a** (Et)	**12b** (Cl)	**7b** (Cl)	**13b**, 50
3	**11a** (Et)	**12a** (OMe)	**7a** (Me)	**13c**, 82
4	**11a** (Et)	**12a** (OMe)	**7b** (Cl)	**13d**, 67
5	**11b** (Cl)	**12b** (Cl)	**7a** (Me)	**13e**, 47
6	**11b** (Cl)	**12b** (Cl)	**7b** (Cl)	**13f**, 19, (75[b])
7	**11b** (Cl)	**12a** (OMe)	**7a** (Me)	**13g**, 83
8	**11b** (Cl)	**12a** (OMe)	**7b** (Cl)	**13h**, 60

[a] Isolated yields. [b] DDQ (2.0 equiv.) and CH_2Cl_2 were added to the crude residue that was obtained from the standard aqueous work-up procedure to accelerate the oxidation step.

Based on these results, the substrate scope of the developed one-pot, three-component coupling procedure for the synthesis of 1,3,5-triarylpyrazoles and a subsequent DDQ oxidation was examined using substrates with electron-donating/withdrawing groups (Table 2). The desired products were obtained in moderate to good yields (41–71%) from each of the eight combinations tested.

To further expand the substrate scope of the procedure, we tried to replace the strong acid, TFA, with a milder one. The procedure described above requires both a strong base, *t*BuOK, and a strong acid, TFA. Therefore, the substrate scope was somewhat limited. Deng and coworkers reported that for the desired 1,3,5-triarylpyrazoles to be obtained the addition of a strong acid (TFA, $PhSO_3H$, or $MeSO_3H$) was necessary, and also that the use of a weaker acid (AcOH) gave an undesired acyclic product.[22] We examined the use of weaker acids, as shown in Table 3. To improve the synthetic efficiency, the acids were added in a one-pot fashion in this examination. To our delight, the use of either CSA (10-camphorsulfonic acid) or AcOH gave the desired prod-

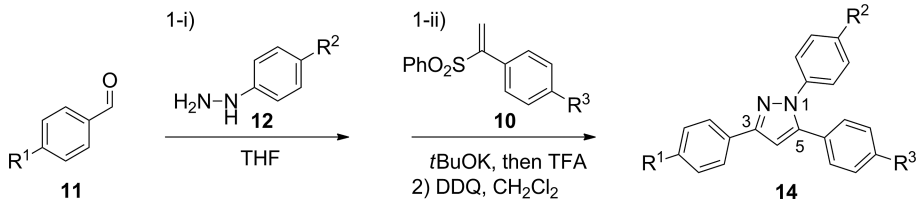


Scheme 4. Plausible reaction mechanism of the synthesis of 1,3,4-triarylpyrazoles.

ucts in comparable yields (Table 3, entries 2 and 3). Based on this result, we anticipated that the 2,3-dichloro-5,6-dicyano-*p*-hydroquinone generated from DDQ might work as a mild acid. As expected, the addition of only DDQ gave the desired product in a good yield (Table 3, entry 4).

The syntheses of several 1,3,4- and 1,3,5-triarylpyrazoles containing acid-labile functionalities were examined based on our developed one-pot procedure (Scheme 5). Aldehyde **11** was coupled with aryl hydrazine **12** in THF at room temperature. After TLC analysis revealed the consumption of the substrates and the generation of the hydrazone, *t*BuOK was added to the reaction mixture at –78 °C. The mixture was stirred at the same temperature, and then sulfonyl alkene **7** or **10** was added, and the mixture was stirred at 50 °C. Then, DDQ was added at room temperature, and the mixture was stirred at the same temperature. The desired 1,3,4-triarylpyrazoles (i.e., **13i** and **13j**) and 1,3,5-tri-

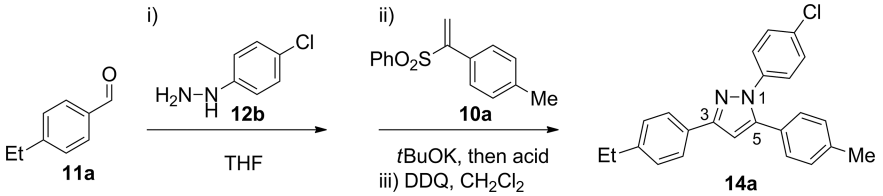
Table 2. Substrate scope of one-pot, three-component coupling of aldehydes **11** with hydrazines **12** and 2-aryl-1-alkenyl sulfones **10** and a subsequent DDQ oxidation, for the synthesis of 1,3,5-triarylpyrazoles **14**.



Entry	**11** (R^1)	**12** (R^2)	**10** (R^3)	**14**, Yield [%][a]
1[b]	**11a** (Et)	**12b** (Cl)	**10a** (Me)	**14a**, 71
2[c]	**11a** (Et)	**12b** (Cl)	**10b** (Cl)	**14b**, 61
3[b]	**11a** (Et)	**12a** (OMe)	**10a** (Me)	**14c**, 42
4[c]	**11a** (Et)	**12a** (OMe)	**10b** (Cl)	**14d**, 68
5[b]	**11b** (Cl)	**12b** (Cl)	**10a** (Me)	**14e**, 55
6[b]	**11b** (Cl)	**12b** (Cl)	**10b** (Cl)	**14f**, 69
7[b]	**11b** (Cl)	**12a** (OMe)	**10a** (Me)	**14g**, 61
8[b]	**11b** (Cl)	**12a** (OMe)	**10b** (Cl)	**14h**, 41

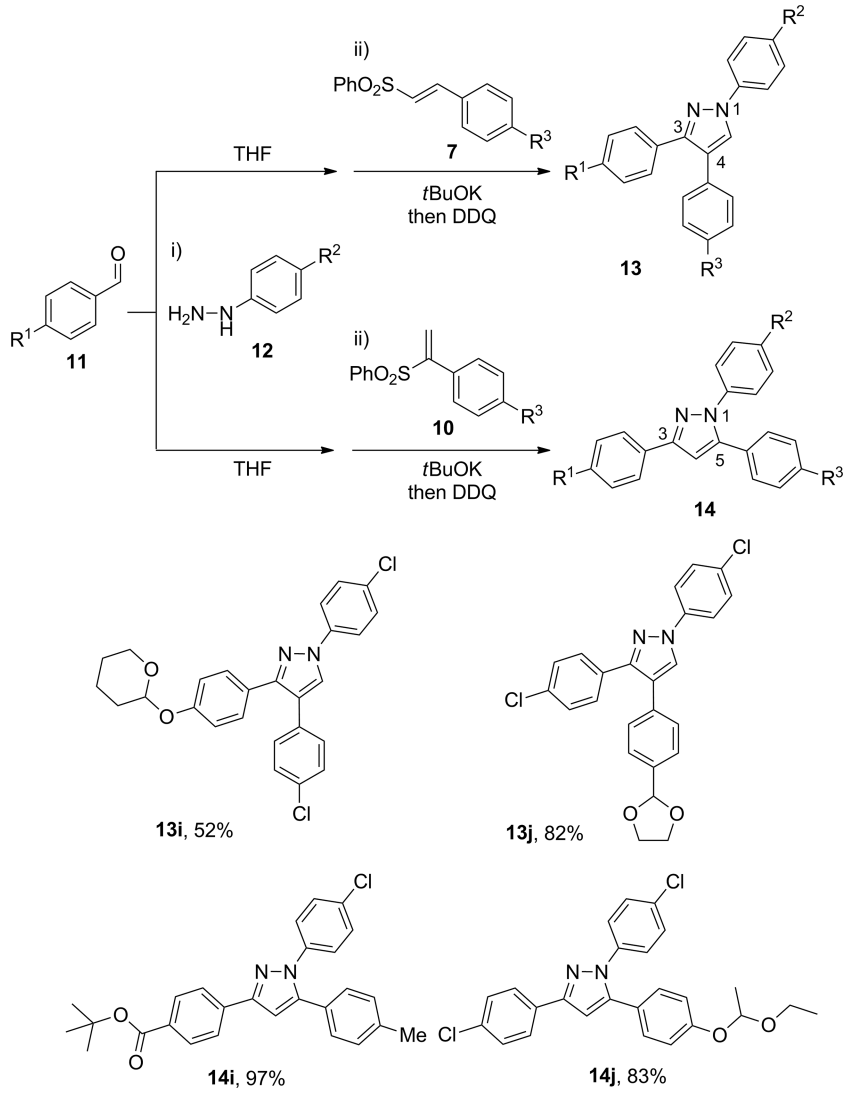
[a] Isolated yields. [b] 1.1 equiv. of DDQ was used for the oxidation step. [c] 2.0 equiv. of DDQ was used for the oxidation step.

Table 3. Examination of acids in a one-pot synthesis of triarylpyrazole **10a**.



Entry	Acid	Yield [%][a]
1	TFA	62
2	CSA	67
3	AcOH	69
4	none	62

[a] Isolated yields (one pot, three steps).



Scheme 5. Synthesis of 1,3,4-triarylpyrazoles **13i** and **13j**, and 1,3,5-triarylpyrazoles **14i** and **14j** containing acid-labile functionalities.

arylpyrazoles (i.e., **14i** and **14j**) were obtained regioselectively in satisfactory to excellent yields (52–97%). Various acid-labile functionalities including tetrahydropyranyl, ethoxyethyl, 1,3-dioxolane-2-yl, and *tert*-butyl ester groups were tolerated under these conditions.

Conclusions

In summary, a one-pot, three-component coupling of aldehydes with hydrazines and phenyl sulfonyl alkenes, for the regioselective synthesis of triarylpyrazoles has been demonstrated. We found that DDQ worked as an efficient oxidant. The developed procedure did not require the addition of a strong acid. This allowed the synthesis of 1,3,4- and 1,3,5-triarylpyrazoles containing acid-labile functionalities in a one-pot reaction in good yields. The developed synthetic approach would be a valuable aid in drug discovery and in materials development based on triarylpyrazoles.

Experimental Section

General Remarks: NMR spectra were recorded with JEOL Model EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C) and JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) instruments in the indicated solvent. Chemical shifts are reported in units of parts per million (ppm) relative to the signal (δ = 0.00 ppm) for tetramethylsilane. Spectra were calibrated using internal tetramethylsilane for solutions in $CDCl_3$, or by using residual solvent signals: $CDCl_3$ (δ = 7.26 ppm for ^{1}H; δ = 77.1 ppm for ^{13}C), [D_6]DMSO (δ = 2.50 ppm for ^{1}H), or [D_6]acetone (δ = 30.6 ppm for ^{13}C). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; dd, doublet of doublets; q, quartet; t, triplet; m, multiplet; br, broad. Coupling constants (*J*) are given in Hertz (Hz). IR spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer. Only the strongest and/or structurally important peaks are reported, and data are given in cm^{-1}. HRMS (ESI-TOF) data were measured with a Waters LCT Premier™ XE. All reactions were monitored by thin-layer chromatography, which was carried out on 0.25 mm E. Merck silica gel plates (60F-254), visualized with UV light, 4-anisaldehyde solution, ceric sulfate, or phos-

phomolybdic acid (10% in ethanol). Gel permeation chromatography (GPC) for qualitative analysis was carried out with a Japan Analytical Industry Model LC-9210 II NEXT (recycling preparative HPLC), using a Japan Analytical Industry Model RI-700 NEXT refractive index detector, and a Japan Analytical Industry Model UV-254 II NEXT with a polystyrene gel column (JAIGEL-1H, 20 mm × 600 mm), using chloroform as a solvent (3.5 mL/min). Flash column chromatography was carried out on Silica Gel 60N, purchased from Kanto Chemical Co. Dry THF was obtained using a Glasscontour solvent purification system. Dry DMF was prepared by drying over molecular sieves (4 Å).

(*E*)-1-Methyl-4-[2-(phenylsulfonyl)vinyl]benzene (7a): 4-Methylbenzaldehyde (0.282 mL, 2.40 mmol, 1.00 equiv.) was added to a stirred solution of **6** (843 mg, 2.88 mmol, 1.20 equiv.), LiCl (132 mg, 3.12 mmol, 1.30 equiv.), and DBU (0.467 mL, 3.12 mmol, 1.30 equiv.) in dry MeCN (24.0 mL) at room temperature under an argon atmosphere. The mixture was stirred at the same temperature for 2 h, then it was poured into 1 M HCl. The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with saturated aqueous $NaHCO_3$, washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1) to give **7a** (612 mg, 2.37 mmol, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 6.8 Hz, 2 H), 7.66 (d, J = 15.6 Hz, 1 H), 7.61 (t, J = 7.3 Hz, 1 H), 7.54 (t, J = 7.8 Hz, 2 H), 7.38 (d, J = 8.3 Hz, 2 H), 7.20 (d, J = 8.3 Hz, 2 H), 6.80 (d, J = 15.6 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 141.8, 141.0, 133.2, 129.8, 129.6, 129.3, 128.6, 127.6, 126.1, 21.5 ppm.

1-Methyl-4-[1-(phenylsulfonyl)vinyl]benzene (10a): *n*BuLi (1.55 M solution in hexane; 6.28 mL, 9.74 mmol, 1.20 equiv.) was added to a stirred solution of **9** (2.00 g, 8.12 mmol, 1.00 equiv.) in dry THF (85.0 mL) at –78 °C under an argon atmosphere. The mixture was stirred at the same temperature for 30 min, then paraformaldehyde (292 mg, 9.74 mmol, 1.20 equiv.) was added at –78 °C. The mixture was stirred at room temperature for 1 h, then it was poured into saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was used for the next reaction without further purification.

The residue was dissolved in CH_2Cl_2 (32.0 mL), and then triethylamine (3.40 mL, 24.4 mmol, 3.00 equiv.) and DBU (3.64 mL, 24.4 mmol, 3.00 equiv.) were added, and the mixture was cooled to 0 °C under an argon atmosphere. Methanesulfonyl chloride (0.944 mL, 12.2 mmol, 1.50 equiv.) was then added. The mixture was stirred at room temperature for 3 h, then it was poured into HCl (1 M). The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with saturated aqueous $NaHCO_3$, washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 2:1) to give **10a** (1.14 g, 4.43 mmol, 55% over two steps) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.3 Hz, 2 H), 7.52 (t, J = 7.3 Hz, 1 H), 7.40 (t, J = 7.3 Hz, 2 H), 7.21 (d, J = 8.3 Hz, 2 H), 7.07 (d, J = 7.8 Hz, 2 H), 6.59 (s, 1 H), 5.92 (s, 1 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 139.4, 138.9, 133.3, 129.5, 129.0, 128.9, 128.8, 128.3, 125.5, 21.2 ppm.

General One-Pot Procedure for Three-Component Coupling without DDQ: Hydrazine (2.00 equiv.) was added to a stirred solution of aldehyde (2.00 equiv.) in dry THF (3.00 mL/1.00 equiv.) at room temperature under an argon atmosphere. The mixture was stirred at the same temperature for 1 h, then *t*BuOK (2.50 equiv.) was added at –78 °C. The mixture was stirred at the same temperature for 30 min, then phenylsulfonyl alkene (1.00 equiv.) was added at –78 °C. The mixture was stirred at room temperature for 12 h, then TFA (5.00 equiv.) was added at –78 °C. The mixture was stirred at room temperature for 1 d, then it was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified to give the triarylpyrazole.

1-(4-Chlorophenyl)-3-(4-ethylphenyl)-4-(4-tolyl)-1*H*-pyrazole (13a): Purified by chromatography on silica gel (hexane/toluene, 1:2); yield 60%; viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.73 (d, J = 9.1 Hz, 2 H), 7.50 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 9.2 Hz, 2 H), 7.24 (d, J = 8.2 Hz, 2 H), 7.16 (d, J = 7.7 Hz, 2 H), 7.15 (d, J = 7.3 Hz, 2 H), 2.66 (q, J = 7.7 Hz, 2 H), 2.37 (s, 3 H), 1.25 (t, J = 7.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 144.1, 138.6, 136.7, 131.6, 130.3, 129.7, 129.5, 129.2, 128.6, 128.3, 127.8, 126.2, 123.2, 119.9, 28.7, 21.2, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 1719, 1597, 1555, 1508, 1495, 1448, 1395, 1343, 1268, 1220, 1094, 1055, 973, 956, 827 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{24}H_{21}ClN_2$ [M + H]$^+$ 373.1472; found 373.1472.

1-(4-Chlorophenyl)-3-(4-ethylphenyl)-5-(4-tolyl)-1*H*-pyrazole (14a): Purified by chromatography on silica gel (toluene); yield 56%; pale orange solid; m.p. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.3 Hz, 2 H), 7.28 (br. s, 4 H), 7.24 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 7.11 (d, J = 8.3 Hz, 2 H), 6.73 (s, 1 H), 2.67 (q, J = 7.8 Hz, 2 H), 1.25 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 144.3, 144.2, 138.8, 138.4, 132.7, 130.3, 129.3, 128.9, 128.6, 128.1, 127.5, 126.2, 125.8, 105.2, 28.7, 21.2, 15.5 ppm. IR (KBr): $\tilde{\nu}$ = 1497, 1441, 1359, 1093, 1015, 971, 832, 798 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{24}H_{21}ClN_2$ [M + H]$^+$ 373.1472; found 373.1466.

1,4-Bis(4-chlorophenyl)-3-(4-ethylphenyl)-1*H*-pyrazole (13b): Purified by chromatography on silica gel (hexane/toluene, 1:3); yield 50%; yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.8 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H), 7.26 (d, J = 8.8 Hz, 2 H), 7.18 (d, J = 8.8 Hz, 2 H), 2.67 (q, J = 7.8 Hz, 2 H), 1.25 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 152.0, 145.9, 140.4, 134.0, 133.5, 132.8, 132.1, 131.8, 131.1, 130.2, 129.9, 129.5, 129.2, 123.4, 121.5, 30.0, 16.6 ppm. IR (KBr): $\tilde{\nu}$ = 2966, 1597, 1549, 1501, 1487, 1219, 1093, 832, 505 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{23}H_{19}Cl_2N_2$ [M + H]$^+$ 393.0925; found 393.0903.

3-(4-Ethylphenyl)-1-(4-methoxyphenyl)-4-(4-tolyl)-1*H*-pyrazole (13c): Purified by chromatography on silica gel (hexane/ethyl acetate, 3:1); yield 82%; brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.66 (d, J = 8.8 Hz, 2 H), 7.51 (d, J = 8.3 Hz, 2 H), 7.23 (d, J = 8.3 Hz, 2 H), 7.15 (d, J = 8.3 Hz, 2 H), 7.12 (d, J = 8.3 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 3.80 (s, 3 H), 2.64 (q, J = 7.8 Hz, 2 H), 1.23 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 149.9, 143.7, 136.3, 133.8, 130.7, 130.1, 129.1, 128.5, 128.3, 127.7, 126.4, 122.3, 120.4, 114.5, 55.5, 28.6, 21.1, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 1516, 1445, 1247, 1182, 1060, 973, 828, 662, 525 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{25}H_{25}N_2O$ [M + H]$^+$ 369.1967; found 369.1946.

4-(4-Chlorophenyl)-3-(4-ethylphenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (13d): Purified by chromatography on silica gel (hexane/toluene, 1:2); yield 67%; grey solid; m.p. 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.65 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.3 Hz, 2 H), 7.27 (d, J = 9.3 Hz, 2 H), 7.25 (d, J = 9.3 Hz, 2 H), 7.16 (d, J = 8.3 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 3.81 (s, 3 H), 2.65 (q, J = 7.8 Hz, 2 H), 1.24 (t, J = 7.8 Hz, 3 H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 150.0, 144.0, 133.6, 132.5, 131.6, 130.3, 129.8, 128.6, 128.3, 127.8, 126.5, 121.1, 120.5, 114.5, 55.5, 28.6, 15.4 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 1548, 1516, 1248, 833 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{24}H_{22}ClN_2O$ $[M + H]^+$ 389.1421; found 389.1389.

1,3-Bis(4-chlorophenyl)-4-(4-tolyl)-1*H*-pyrazole (13e): Purified by chromatography on silica gel (hexane/toluene, 1:1); yield 47%; white solid; m.p. 137–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.71 (d, J = 8.8 Hz, 2 H), 7.52 (d, J = 8.8 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.29 (d, J = 8.8 Hz, 2 H), 7.20 (d, J = 8.3 Hz, 2 H), 7.15 (d, J = 8.3 Hz, 2 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 138.4, 137.1, 133.9, 131.9, 131.5, 129.6, 129.5, 129.4, 129.3, 128.6, 128.5, 126.5, 123.3, 120.0, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1597, 1554, 1495, 1218, 1093, 827, 734, 505 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{22}H_{17}Cl_2N_2$ $[M + H]^+$ 379.0769; found 379.0741.

1,3,4-Tris(4-chlorophenyl)-1*H*-pyrazole (13f): Purified by GPC; yield 19%; yellow solid; m.p. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.69 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.27–7.34 (m, 4 H), 7.18 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 138.2, 134.2, 133.2, 132.2, 131.1, 130.8, 129.9, 129.6, 128.9, 128.7, 126.6, 122.1, 120.0 ppm. IR (KBr): $\tilde{\nu}$ = 2927, 1704, 1596, 1489, 1093, 1014, 831, 501 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{21}H_{14}Cl_3N_2$ $[M + H]^+$ 399.0223; found 399.0187.

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-4-(4-tolyl)-1*H*-pyrazole (13g): Purified by chromatography on silica gel (toluene); yield 83%; white solid; m.p. 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.66 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 2 H), 7.28 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 8.3 Hz, 2 H), 7.14 (d, J = 8.3 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 148.7, 136.7, 133.6, 133.5, 131.9, 129.7, 129.6, 129.3, 128.6, 128.4, 126.8, 122.5, 120.6, 114.5, 55.5, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2935, 1574, 1553, 1520, 1508, 1253, 828, 801, 733, 654, 589, 516 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{23}H_{20}ClN_2O$ $[M + H]^+$ 375.1264; found 375.1238.

3,4-Bis(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (13h): Purified by chromatography on silica gel (hexane/toluene, 1:3); yield 60%; grey solid; m.p. 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.64 (d, J = 9.3 Hz, 2 H), 7.48 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.22 (d, J = 8.3 Hz, 2 H), 6.97 (d, J = 9.3 Hz, 2 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 148.7, 133.8, 133.4, 132.9, 131.5, 131.2, 129.9, 129.6, 128.8, 128.6, 126.8, 121.3, 120.7, 114.6, 55.5 ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2836, 1573, 1547, 1519, 1487, 1252, 1094, 832, 733, 642, 502 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{22}H_{17}Cl_2N_2O$ $[M + H]^+$ 395.0718; found 395.0701.

General Stepwise Procedure for Three-Component Coupling and Subsequent Oxidation Using DDQ for the Synthesis of 1,3,5-Triarylpyrazoles: Hydrazine (2.00 equiv.) was added to a stirred solution of aldehyde (2.00 equiv.) in dry THF (3.00 mL/equiv.) at room temperature under an argon atmosphere. The mixture was stirred at the same temperature for 1 h, then *t*BuOK (2.50 equiv.) was added at –78 °C. The mixture was stirred at the same temperature for 30 min, then phenylsulfonyl alkene (1.00 equiv.) was added at –78 °C. The mixture was stirred at 50 °C for 3 h, then TFA (5.00 equiv.) was added at –78 °C. The mixture was stirred at room temperature for 24 h, then it was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was used in the next reaction without further purification.

The residue was dissolved in CH_2Cl_2, and DDQ was added at room temperature under an argon atmosphere. The mixture was stirred at room temperature for 1 h, then it was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (2×). The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified to give the 1,3,5-triarylpyrazole.

1,5-Bis(4-chlorophenyl)-3-(4-ethylphenyl)-1*H*-pyrazole (14b): DDQ (2.00 equiv.); purified by chromatography on silica gel (hexane/ethyl acetate, 3:1); yield 61%; yellow solid; m.p. 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.3 Hz, 2 H), 7.29–7.36 (m, 8 H), 7.20 (d, J = 8.8 Hz, 2 H), 6.77 (s, 1 H), 2.69 (q, J = 7.8 Hz, 2 H), 1.27 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 144.5, 143.1, 138.5, 134.6, 133.2, 130.1, 130.0, 129.2, 128.9, 128.9, 128.2, 126.3, 125.8, 105.6, 28.7, 15.5 ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2930, 1496, 1093, 832, 797, 501 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{23}H_{19}Cl_2N_2$ $[M + H]^+$ 393.0925; found 393.0887.

3-(4-Ethylphenyl)-1-(4-methoxyphenyl)-5-(4-tolyl)-1*H*-pyrazole (14c): DDQ (1.10 equiv.); purified by chromatography on silica gel (toluene); yield 42%; brown solid; m.p. 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 9.3 Hz, 2 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.16 (d, J = 8.3 Hz, 2 H), 7.11 (d, J = 8.3 Hz, 2 H), 6.86 (d, J = 9.3 Hz, 2 H), 6.74 (s, 1 H), 3.81 (s, 3 H), 2.68 (q, J = 7.8 Hz, 2 H), 1.26 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 151.7, 144.3, 143.9, 138.0, 133.7, 130.7, 129.1, 128.5, 128.1, 127.8, 126.7, 125.8, 114.1, 104.3, 55.5, 28.7, 21.2, 15.5 ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2931, 1515, 1250, 833, 794, 588 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{25}H_{25}N_2O$ $[M + H]^+$ 369.1967; found 369.1928.

5-(4-Chlorophenyl)-3-(4-ethylphenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (14d): DDQ (2.00 equiv.); purified by chromatography on silica gel (hexane/ethyl acetate, 3:1); yield 68%; brown solid; m.p. 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.8 Hz, 2 H), 7.23–7.29 (m, 4 H), 7.20 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 9.3 Hz, 2 H), 6.76 (s, 1 H), 3.83 (s, 3 H), 2.69 (q, J = 7.8 Hz, 2 H), 1.27 (t, J = 7.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 151.8, 144.1, 143.0, 134.2, 133.2, 130.4, 129.9, 129.1, 128.7, 128.1, 126.8, 125.7, 114.2, 104.6, 55.5, 28.7, 15.5 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 2928, 1513, 1250, 835, 722 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{24}H_{22}ClN_2O$ $[M + H]^+$ 389.1421; found 389.1385.

1,3-Bis(4-chlorophenyl)-5-(4-tolyl)-1*H*-pyrazole (14e): DDQ (1.10 equiv.); purified by chromatography on silica gel (hexane/toluene, 1:1); yield 55%; brown solid; m.p. 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2 H), 7.37 (d, J = 8.3 Hz, 2 H), 7.29 (br. s, 4 H), 7.13 (br. s, 4 H), 6.72 (s, 1 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 144.7, 138.7, 138.6, 133.8, 133.0, 131.4, 129.3, 129.0, 128.8, 128.6, 127.2, 127.0, 126.2, 105.2, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1495, 1435, 1357, 1091, 833, 794, 504 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{22}H_{17}Cl_2N_2$ $[M + H]^+$ 379.0769; found 379.0745.

1,3,5-Tris(4-chlorophenyl)-1*H*-pyrazole (14f): DDQ (2.00 equiv.); purified by chromatography on silica gel (hexane/toluene, 1:3); yield 69%; red-brown solid; m.p. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2 H), 7.40 (d, J = 8.3 Hz, 2 H), 7.03–7.36 (m, 4 H), 7.27 (d, J = 8.8 Hz, 2 H), 7.19 (d, J = 8.8 Hz, 2 H), 6.77 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 143.4, 138.3, 134.8, 134.0, 133.5, 131.2, 129.9, 129.2, 129.0, 128.9, 128.5, 127.0, 126.3, 105.5 ppm. IR (KBr): $\tilde{\nu}$ = 1596, 1496, 1483, 1436, 1357, 1094, 1015, 971, 833, 798, 505 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{21}H_{14}Cl_3N_2$ $[M + H]^+$ 399.0223; found 399.0191.

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-5-(4-tolyl)-1*H*-pyrazole (14g): DDQ (1.10 equiv.); purified by chromatography on silica gel (toluene); yield 61%; red-brown solid; m.p. 175–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H), 7.26 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 8.8 Hz, 2 H), 6.72 (s, 1 H), 3.80 (s, 3 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 150.4, 144.6, 138.2, 133.5, 133.4, 131.8, 129.2, 128.7, 128.5, 127.5, 127.0, 126.7, 114.1, 104.2, 55.4, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 2933, 1512, 1492, 1250, 834, 794, 588, 514 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{23}H_{20}ClN_2O$ [M + H]$^+$ 375.1264; found 375.1223.

3,5-Bis(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (14h): DDQ (1.10 equiv.); purified by chromatography on silica gel (hexane/toluene, 1:3); yield 41%; red-brown solid; m.p. 157–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 2 H), 7.38 (d, J = 8.8 Hz, 2 H), 7.28 (d, J = 8.8 Hz, 2 H), 7.24 (d, J = 8.8 Hz, 2 H), 7.18 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.75 (s, 1 H), 3.81 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 150.6, 143.3, 134.4, 133.7, 132.9, 131.5, 129.8, 128.8, 128.7, 127.0, 126.7, 114.2, 104.6, 55.5 ppm. IR (KBr): $\tilde{\nu}$ = 2933, 1725, 1516, 1483, 1250, 1092, 834, 796, 519 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{22}H_{17}Cl_2N_2O$ [M + H]$^+$ 395.0718; found 395.0691.

General One-Pot Procedure for Three-Component Coupling and Subsequent Oxidation Using DDQ for the Synthesis of Triarylpyrazoles with Acid-Labile Functionalities: Hydrazine (2.00 equiv.) was added to a stirred solution of aldehyde (2.00 equiv.) in dry THF (3.00 mL/equiv.) at room temperature under an argon atmosphere. The mixture was stirred at the same temperature for 30 min, then *t*BuOK (2.50 equiv.) was added at –78 °C. The mixture was stirred at the same temperature for 30 min, then phenylsulfonyl alkene (1.00 equiv.) was added at –78 °C. The mixture was stirred at 50 °C for time 1, then DDQ was added to the reaction mixture at room temperature. The mixture was stirred at the same temperature for time 2, then it was poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (3×). The combined extracts were washed with brine, dried with Na_2SO_4, and concentrated in vacuo. The residue was purified to give the triarylpyrazole.

1,4-Bis(4-chlorophenyl)-3-{4-[(tetrahydro-2*H*-pyran-2-yl)-oxy]phenyl}-1*H*-pyrazole (13i): Time 1: 2 h; DDQ (2.00 equiv.); time 2: 50 min; purified by chromatography on silica gel (hexane/ethyl acetate, 17:3); yield 52%; white solid; m.p. 156–158 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.57 (s, 1 H), 7.99 (d, J = 8.8 Hz, 2 H), 7.56 (d, J = 9.2 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.40 (s, 4 H), 7.06 (d, J = 8.8 Hz, 2 H), 5.48 (t, J = 3.4 Hz, 1 H), 3.86 (ddd, J = 11.7, J = 8.3, J = 3.4 Hz, 1 H), 3.60 (ddd, J = 9.2, J = 4.9, J = 4.4 Hz, 1 H), 1.98–1.57 (m, 6 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 158.3, 151.0, 139.6, 133.2, 132.8, 131.9, 131.1, 130.3, 130.2, 129.5, 128.4, 127.1, 122.4, 120.7, 117.2, 97.1, 62.6, 31.1, 25.9, 19.7 ppm. IR (KBr): $\tilde{\nu}$ = 2943, 1610, 1501, 1237, 1094, 955, 833, 506 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{26}H_{22}Cl_2N_2O_2$ [M + H]$^+$ 465.1137; found 465.1151.

4-[4-(1,3-Dioxolan-2-yl)phenyl]-1,3-bis(4-chlorophenyl)-1*H*-pyrazole (13j): Time 1: 2 h; DDQ (3.00 equiv.); time 2: 40 min; purified by chromatography on silica gel (hexane/ethyl acetate, 2:1); yield 82%; yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.70 (d, J = 8.8 Hz, 2 H), 7.50 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.3 Hz, 2 H), 7.42 (d, J = 9.3 Hz, 2 H), 7.32 (d, J = 8.3 Hz, 2 H), 7.29 (d, J = 8.8 Hz, 2 H), 5.81 (s, 1 H), 4.18–4.12 (m, 2 H), 4.09–4.03 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 138.2, 136.7, 134.0, 133.2, 132.0, 131.2, 129.6, 129.5, 128.6, 126.9, 126.7, 122.8, 119.9, 103.5, 65.4 ppm. IR (KBr): $\tilde{\nu}$ = 2887, 1598, 1496, 1395, 1218, 1094, 957, 832, 500 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{24}H_{18}Cl_2N_2O_2$ [M + H]$^+$ 437.0824; found 437.0837.

***tert*-Butyl 4-[1-(4-Chlorophenyl)-5-(4-tolyl)-1*H*-pyrazol-3-yl]benzoate (14i):** Time 1: 30 min; DDQ (4.00 equiv.); time 2: 10 h; purified by chromatography on silica gel (hexane/ethyl acetate, 5:1); yield 97%; yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.3 Hz, 2 H), 7.94 (d, J = 8.3 Hz, 2 H), 7.31 (s, 4 H), 7.15 (s, 4 H), 6.82 (s, 1 H), 2.36 (s, 3 H), 1.62 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 151.2, 144.8, 138.7, 138.6, 136.8, 133.1, 131.3, 129.8, 129.4, 129.0, 128.6, 127.1, 126.3, 125.3, 105.7, 80.9, 28.2, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 1711, 2979, 1711, 1614, 1497, 1368, 1296, 1166, 1120, 833, 758, 505 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{27}H_{25}ClN_2O_2$ [M + H]$^+$ 445.1683; found 445.1705.

1,3-Bis(4-chlorophenyl)-5-[4-(1-ethoxyethoxy)phenyl]-1*H*-pyrazole (14j): Time 1: 50 min; DDQ (4.00 equiv.); time 2: 50 min; purified by chromatography on silica gel (hexane/ethyl acetate, 3:1); yield 83%; brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 2 H), 7.38 (d, J = 8.8 Hz, 2 H), 7.30 (s, 4 H), 7.16 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 6.71 (s, 1 H), 5.41 (q, J = 5.4 Hz, 1 H), 3.77 (dq, J = 2.4, J = 7.3 Hz, 1 H), 3.55 (dq, J = 2.4, J = 6.8 Hz, 1 H), 1.51 (d, J = 5.4 Hz, 3 H), 1.21 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 151.0, 144.4, 138.6, 133.8, 133.0, 131.4, 129.9, 129.0, 128.8, 127.0, 126.2, 123.3, 117.2, 105.0, 99.3, 61.2, 20.0, 15.1 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 1726, 1613, 1494, 1244, 1092, 834, 501 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{25}H_{22}Cl_2N_2O_2$ [M + H]$^+$ 453.1137; found 453.1130.

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