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Copper-catalyzed direct cross coupling of 1,3,4-oxadiazoles with *trans*-β-halostyrenes: synthesis of 2-*E*-vinyl 1,3,4-oxadiazoles☆

Biswanath Das *, Gandolla Chinna Reddy, Penagaluri Balasubramanyam, N. Salvanna

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500007, Andhra Pradesh, India

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ABSTRACT

The first direct C–H alkenylation of 1,3,4-oxadiazoles with *trans*-β-halo olefinic system has been carried out using a combination of CuI/DMEDA as a catalyst. A wide range of 2-*E*-vinyl-substituted oxadiazoles were obtained in high yields (85–93%).

1. Introduction

The widespread application of heteroarenes in medicinal chemistry and in material science has driven the development of new synthetic strategies to prepare appropriately substituted heterocyclic cores. Metal-catalyzed direct functionalization of C–H bond of heteroarenes is great importance in recent organic synthesis to generate molecular complexity.[1] In fact, the transformation of C–H to C–C bond in the presence of a metal catalyst is a highly valuable preparative reaction because of its atom economy. Thus various arenes and heteroarenes have been subjected to direct arylation,[2] alkenylation,[3] and alkynylation[4] using different catalyst systems. A wide range of metal catalysts including palladium, rhodium, or ruthenium have been exploited for these transformations. However, the use of copper catalyst remains quite rare, despite clear advantages in their availability and cost-effectiveness. Moreover, to our knowledge, metal-mediated creation of an alkenyl-heteroaryl linkage between an sp^2-hybridized heteroaryl carbon of 1,3,4-oxadiazole and an sp^2-hybridized carbon of alkenyl halide using C–H bond activation has also not yet been reported.

In recent years, replacing the expensive metal catalysts with more abundant and less expensive ones to execute similar C–H activation has attracted great interest.[5a] Daugulis et al. developed a method for the Cu-catalyzed alkenylation of polyfluoroarene C–H bond with alkenyl bromides.[5b] In 2010 Charette's group pursued investigation into the C–H alkenylation of *N*-benzoyliminopyridinium ylides with alkenyl iodides in presence of copper catalyst.[5c] Grierson et al. reported direct alkenylation of oxazoles with vinyl bromides using copper iodide as catalyst.[3a] However, alkenylation of electron deficient heteroarenes such as oxadiazoles by C–H activation still has not been reported.

Oxadiazole derivatives possess a wide range of biological properties.[6] They are known to work as ester and amide bioisosteres.[7] They also exhibit anti-microbial and anti-convulsant activities.[8] Some of the compounds are employed in the field of organic electronics.[9] Thus the synthesis of oxadiazole derivatives is an useful task in pharmaceutical and material science. Herein, we report a copper catalyzed efficient and convenient method for alkenylation of 1,3,4-oxadiazoles.

2. Results and discussion

In continuation of our work on the development of useful synthetic methodologies[10] we have observed that 1,3,4-oxadiazoles underwent direct alkenylation with *trans*-β-iodostyrenes in the presence of CuI using a ligand, *N*,*N*′-dimethylethylene diamine (DMEDA) and LiO-*t*-Bu (Scheme 1).

Initially we considered 2-phenyl 1,3,4-oxadiazole (**1a**; R_1=Ph) and *trans*-β-halostyrene (**2a**; R_2=Ph) as the starting materials for the optimization of the reaction conditions. The reaction was screened with different copper compounds, ligands, and bases

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* Corresponding author. Tel./fax: +91 40 27160512; e-mail address: biswanathdas@yahoo.com (B. Das).

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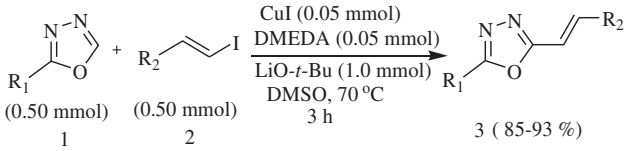
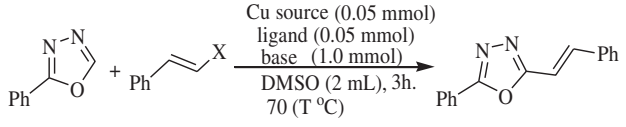


Scheme 1. Copper-catalyzed C–C cross coupling of 1,3,4-oxadiazoles.

(Table 1). The coupling was also conducted in various solvents at different temperatures (Table 2). The following ligands (Fig. 1) were used to study the present conversion.

Table 1
Standardization of copper source, ligand, and base[a]

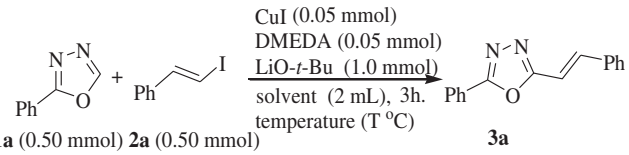


Entry	X	Cu source	Ligand	Base	Yield[b] (%)
1	I	None	None	LiO-*t*-Bu	0
2	Br	CuI	None	LiO-*t*-Bu	0
3	I	CuI	None	LiO-*t*-Bu	0
4	I	CuI	Acac	LiO-*t*-Bu	55
5	Br	CuI	Acac	LiO-*t*-Bu	45
6	Cl	CuI	Acac	LiO-*t*-Bu	0
7	I	CuI	Phen	KO-*t*-Bu	9
8	I	CuI	Phen	LiO-*t*-Bu	62
9	Br	CuI	Phen	LiO-*t*-Bu	56
10	*I*	*CuI*	*DMEDA*	*LiO-t-Bu*	*85*
11	Br	CuI	DMEDA	LiO-*t*-Bu	76
12	I	CuBr	DMEDA	LiO-*t*-Bu	50
13	Br	CuBr	DMEDA	LiO-*t*-Bu	35
14	I	CuCl	DMEDA	LiO-*t*-Bu	10
15	I	CuO	DMEDA	LiO-*t*-Bu	40
16	I	CuI	DMEDA	KO-*t*-Bu	30
17	I	CuI	DMEDA	NaO-*t*-Bu	22
18	I	CuI	TMEDA	LiO-*t*-Bu	65
19	I	CuI	TMEDA	KO-*t*-Bu	26
20	I	CuI	L-Proline	LiO-*t*-Bu	5
21	I	$Cu(OTf)_2$	DMEDA	LiO-*t*-Bu	12
22	I	CuI	DMEDA	Cs_2CO_3	0
23	I	CuI	DMEDA	KHMDS[c]	0

[a] Reaction conditions: 2-phenyl oxadiazole **1** (0.50 mmol), *trans*-β-halostyrene **2** (0.50 mmol), Cu source (0.05 mmol), ligand (0.05 mmol), base (1.0 mmol), DMSO (2 mL) at 70 °C over 3 h.
[b] Isolated yield of **3** after column chromatography.
[c] Potassium bis(trimethyl silyl)-amide.

In absence of the Cu source and ligand the reaction did not proceed (Table 1, entry 1). *trans*-β-Chlorostyrene could not afford any product (entry 6), while *trans*-β-bromostyrene furnished the product with moderate yield in the presence of Cu source and ligand (entries 2, 5, 9, 13). However, *trans*-β-bromostyrene gave the desired product in high yield using the combination of CuI/DMEDA and LiO-*t*-Bu (entry 11). The other olefinic compound, *trans*-β-iodostyrene afforded the product in various yields depending on the application of Cu sources, ligands, and bases. Among various Cu sources, CuI was found to be most effective. The choice of the ligand was also crucial in this alkenylation reaction; DMEDA showed highest efficiency (entry 10). Phen (entry 8) and TMEDA (entry 18) also revealed considerable efficiency. However, among the used bases LiO-*t*-Bu was most effective but other bases were not useful. From this study it was evident that the alkenylation of 2-phenyl 1,3,4-oxadiazole with *trans*-β-iodostyrene in the presence of CuI/DMEDA and LiO-*t*-Bu can proceed efficiently (entry 10).

Table 2
Optimization of solvent and temperature[a]



Entry	Solvent	Temp (°C)	Yield[b] (%)
1	DMSO	rt[c]	45
2	*DMSO*	*70*	*85*
3	DMSO	110	85
4	DMF	rt[c]	30
5	DMF	70	63
6	1,4-Dioxane	rt[c]	25
7	1,4-Dioxane	70	67
8	Toluene	rt[c]	35
9	Toluene	70	70
10	Toluene	Reflux	70
11	THF	rt[c]	10
12	THF	70	25
13	Water	rt[c]	25
14	Water	70	45

[a] Reaction conditions: 2-phenyl 1,3,4-oxadiazole **1** (0.50 mmol), *trans*-β-iodostyrene **2** (0.50 mmol), CuI (0.05 mmol), DMEDA (0.05 mmol), LiO-*t*-Bu (1.0 mmol), solvent (2 mL).
[b] Isolated yield after column chromatography.
[c] Room temperature, approximately 27 °C.

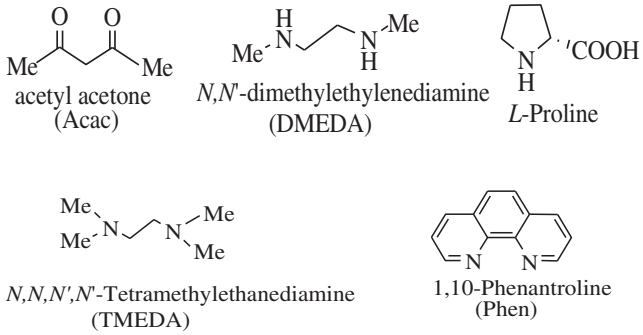


Fig. 1. Ligands used in copper-catalyzed C–C cross coupling of 1,3,4-oxadiazoles.

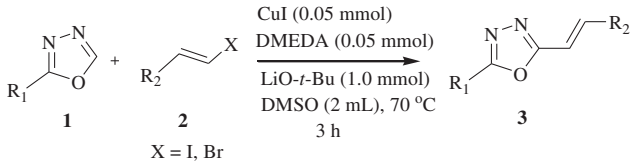
The effect of solvent and temperature was also studied for the above reaction. Among all of the used solvents DMSO was most effective at 70 °C (Table 2). The reaction was complete in 3 h and the alkenylation product **3a** (R_1=R_2=Ph) was formed in a yield of 85%. No side product could be detected.

Following the standardization of the above reaction, with effective reaction conditions (Table 1, entry 10) the C–H functionalization of a series of 1,3,4-oxadiazole derivatives was carried out to prepare several new products using different *trans*-β-iodostyrenes (Table 3).

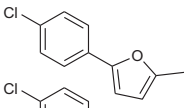
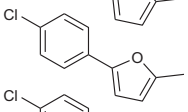
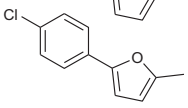
The oxadiazoles containing electron-donating as well as electron-withdrawing groups in the aromatic ring underwent conversion smoothly. The *trans*-β-iodo olefins (**2**) having heteroaromatic moiety also afforded the desired products in high yield. For each conversion the reaction time was 3 h. The structures of the products were established from their spectral (IR, ^{1}H and ^{13}C NMR, and HRMS) data.

Although the exact mechanism still remains unknown for this new process, plausible mechanism[11] is shown in Scheme 2. This mechanism involves the base assisted transmetallation of 1,3,4-oxadiazole to form (heteroaryl) Cu (I) intermediate **A**. Oxidative addition of *trans*-β-iodostyrene to **A** to form the copper(III) complex **B** followed by reductive elimination leads to the formation of expected alkenylated product.

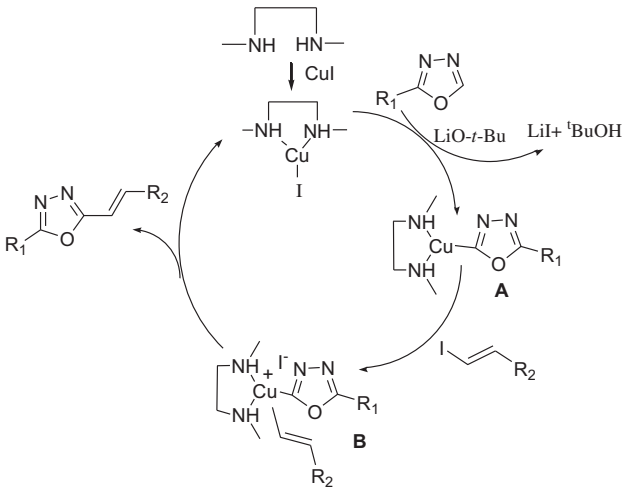
Table 3
Copper-catalyzed direct alkenylation of oxadiazoles with various *trans*-β-halostyrenes[a]



1 **2** **3**

Entry	R_1 (**1**)	R_2 (**2**)	Product (**3**)	Yield[b,c] (%)
1	C_6H_5	C_6H_5	**3a**	85 (76)
2	4-CH_3–C_6H_4	C_6H_5	**3b**	91
3	4-OCH_3–C_6H_4	C_6H_5	**3c**	93 (82)
4	4-Cl–C_6H_4	C_6H_5	**3d**	87
5	4-CF_3–C_6H_4	C_6H_5	**3e**	89 (78)
6	C_6H_5	4Ph–C_6H_4	**3f**	86
7	4-CH_3–C_6H_4	4Ph–C_6H_4	**3g**	90
8	4-OCH_3–C_6H_4	4Ph–C_6H_4	**3h**	91
9	4-Cl–C_6H_4	4Ph–C_6H_4	**3i**	85
10	4-CF_3–C_6H_4	4Ph–C_6H_4	**3j**	88
11	3,4,5-$(OMe)_3$–C_6H_2	4Ph–C_6H_4	**3k**	93 (78)
12	C_6H_5	3,4$(OMe)_2$–C_6H_3	**3l**	91 (81)
13	4-OCH_3–C_6H_4	3,4$(OMe)_2$–C_6H_3	**3m**	90
14	4-CF_3–C_6H_4	3,4$(OMe)_2$–C_6H_3	**3n**	88
15	C_6H_5		**3o**	87
16	4-CH_3–C_6H_4		**3p**	88 (71)
17	4-Cl–C_6H_4		**3q**	85

[a] Reaction conditions: 2-aryl 1,3,4-oxadiazole **1** (0.50 mmol), *trans*-β-iodostyrene **2** (0.50 mmol), CuI (0.05 mmol), DMEDA (0.05 mmol), LiO-*t*-Bu (1.0 mmol), DMSO (2 mL).
[b] Yield of isolated product using *trans*-β-iodostyrene.
[c] In parenthesis: yield of isolated product when *trans*-β-bromostyrene was used.



Scheme 2. Plausible mechanism of alkenylation.

3. Conclusions

In conclusion, we have developed for the first time an efficient method for direct alkenylation of 1,3,4-oxadiazoles with *trans*-β-iodo olefinic system using a combination of CuI/DMEDA as a catalyst.

4. Experimental section

4.1. General

Melting points were measured on a Buchi 510 apparatus and are uncorrected. The Spectra were recorded with the following instruments. IR: Perkin–Elmer RX1 FT-IR spectrophotometer; NMR: Varian Gemini 200 MHz (^{1}H) and 50 MHz (^{13}C) spectrometer; ESIMS: VG-Autospec micromass (70 eV) and HRMS: Hybrid MS system (Indian Institute of Chemical Technology). Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp or I_2 stains. Organic extracts were dried over anhydrous Na_2SO_4.

4.2. General procedure for alkenylation of 2-aryl 1,3,4-oxadiazoles (3)

In a 10 mL round bottom flask under nitrogen atmosphere, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-aryl-1,3,4-oxadiazole (0.50 mmol), and *trans*-β-iodostyrene (0.50 mmol) in DMSO (2.0 mL) were taken. The reaction mixture was stirred at 70 °C for 3 h. The progress of the reaction was monitored by TLC. After the consumption of the starting materials, the reaction mixture was allowed to cool, and subsequently extracted with EtOAc (2×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. Concentration in vacuo followed by column chromatography (EtOAc/hexane: 5:95 to 10:90) gave pure compound **3** in 85–93% yield.

4.3. Spectral data of all compounds are given below

*4.3.1. (E)-2-Phenyl-5-styryl-1,3,4-oxadiazole (**3a**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-phenyl-1,3,4-oxadiazole (73 mg, 0.50 mmol), and *trans*-β-iodostyrene (115 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (5% EtOAc/hexane) to give the product **3a** (105 mg, 85%) as a white solid; R_f (15% EtOAc/hexane) 0.52; mp: 125–127 °C; IR (KBr): 2390, 1643, 1521, 1445, 1265 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.12 (2H, d, *J* 8.0 Hz, Ar–H), 7.62–7.50 (6H, m, Ar–H, CH=), 7.49–7.38 (3H, m, Ar–H), 7.11 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 139.0, 135.0, 131.8, 130.1, 129.1, 127.5, 127.2, 123.9, 110.2; ESIMS: *m*/*z* 249 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 249.1030. $C_{16}H_{13}N_2O$ requires 249.1027.

*4.3.2. (E)-2-Styryl-5-p-tolyl-1,3,4-oxadiazole (**3b**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-*p*-tolyl-1,3,4-oxadiazole (80 mg, 0.50 mmol), and *trans*-β-iodostyrene (115 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (5% EtOAc/hexane) to give the product **3b** (118 mg, 91%) as a white solid; R_f (15% EtOAc/hexane) 0.49; mp: 127–129 °C; IR (KBr): 2378, 1642, 1492, 1443, 1258 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.99 (2H, d, *J* 8.0 Hz, Ar–H), 7.60–7.52 (3H, m, Ar–H, CH=), 7.41–7.28 (5H, m, Ar–H), 7.05 (1H, d, *J* 14.0 Hz, =CH), 2.42 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 142.3, 138.8, 134.9, 130.1, 130.0, 129.2, 127.6, 126.9, 121.1, 110.0, 21.2; ESIMS: *m*/*z* 263 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 263.1185. $C_{17}H_{15}N_2O$ requires 263.1184.

*4.3.3. (E)-2-(4-Methoxyphenyl)-5-styryl-1,3,4-oxadiazole (**3c**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-methoxyphenyl)-1,3,4-oxadiazole (88 mg, 0.50 mmol), and *trans*-β-iodostyrene (115 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (7% EtOAc/

hexane) to give the product **3c** (129 mg, 93%) as a white solid; R_f (20% EtOAc/hexane) 0.51; mp: 135–137 °C; IR (KBr): 2382, 1609, 1493, 1449, 1257 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.07 (2H, d, *J* 8.0 Hz, Ar–H), 7.65–7.52 (3H, m, Ar–H, CH=), 7.48–7.31 (4H, m, Ar–H, =CH), 7.02 (2H, d, *J* 8.0 Hz, Ar–H), 3.90 (3H, s, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.9, 138.8, 135.1, 130.0, 129.1, 128.9, 127.8, 116.3, 114.8, 110.2, 55.7; ESIMS: *m*/*z* 279 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 279.1136. $C_{17}H_{15}N_2O_2$ requires 279.1133.

*4.3.4. (E)-2-(4-Chlorophenyl)-5-styryl-1,3,4-oxadiazole (**3d**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-chlorophenyl)-1,3,4-oxadiazole (90 mg, 0.50 mmol), and *trans*-β-iodostyrene (115 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (6% EtOAc/hexane) to give the product **3d** (122 mg, 87%) as a white solid; R_f (15% EtOAc/hexane) 0.42; mp: 140–142 °C; IR (KBr): 2386, 1643, 1519, 1480, 1263 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* 8.0 Hz, Ar–H), 7.63–7.31 (8H, m, Ar–H, CH=), 7.02 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.1, 139.3, 138.1, 134.5, 130.2, 129.8, 128.9, 128.2, 127.4, 125.5, 122.6, 109.8; ESIMS: *m*/*z* 283, 285 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 283.0646. $C_{16}H_{12}N_2OCl$ $[MH]^+$ 283.0638.

*4.3.5. (E)-2-Styryl-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (**3e**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (107 mg, 0.50 mmol), and *trans*-β-iodostyrene (115 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (7% EtOAc/hexane) to give the product **3e** (140 mg, 89%) as a white solid; R_f (20% EtOAc/hexane) 0.42; mp: 146–148 °C; IR (KBr): 2382, 1643, 1518, 1329, 1163 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.26 (2H, d, *J* 8.0 Hz, Ar–H), 7.79 (2H, d, *J* 8.0 Hz, Ar–H), 7.64–7.52 (3H, m, Ar–H, CH=), 7.46–7.38 (3H, m, Ar–H), 7.09 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.9, 139.9, 134.4, 130.1, 129.2, 127.5, 127.2, 126.1, 109.2; ESIMS: *m*/*z* 317 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 317.0904. $C_{17}H_{12}N_2OF_3$ requires 317.0901.

*4.3.6. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-phenyl-1,3,4-oxadiazole (**3f**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-phenyl-1,3,4-oxadiazole (73 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (5% EtOAc/hexane) to give the product **3f** (139 mg, 86%) as a white solid; R_f (15% EtOAc/hexane) 0.48; mp: 130–132 °C; IR (KBr): 2391, 1643, 1549, 1477, 1278 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.18–8.02 (3H, m, Ar–H), 7.70–7.31 (12H, m, Ar–H, CH=), 7.12 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.3, 142.8, 140.2, 138.7, 133.9, 132.8, 129.0, 128.9, 127.8, 127.6, 127.4, 126.7, 124.1, 109.9; ESIMS: *m*/*z* 325 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 325.1346. $C_{22}H_{17}N_2O$ requires 325.1340.

*4.3.7. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-p-tolyl-1,3,4-oxadiazole (**3g**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-*p*-tolyl-1,3,4-oxadiazole (80 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (5% EtOAc/hexane) to give the product **3g** (152 mg, 90%) as a white solid; R_f (15% EtOAc/hexane) 0.46; mp: 150–152 °C; IR (KBr): 2394, 1638, 1490, 1410, 1268 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* 8.0 Hz, Ar–H), 7.68–7.57 (7H, m, Ar–H, CH=), 7.49–7.30 (5H, m, Ar–H), 7.10 (1H, d, *J* 14.0 Hz, =CH), 2.43 (3H, m, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.5, 142.8, 142.5, 140.2, 138.4, 133.9, 129.9, 129.1, 128.0, 127.9, 127.8, 127.0, 121.1, 110.0, 21.8; ESIMS: *m*/*z* 339 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 339.1511. $C_{23}H_{19}N_2O$ requires 339.1497.

*4.3.8. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**3h**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-methoxyphenyl)-1,3,4-oxadiazole (88 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (8% EtOAc/hexane) to give the product **3h** (161 mg, 91%) as a white solid; R_f (20% EtOAc/hexane) 0.42; mp: 164–166 °C; IR (KBr): 2394, 1610, 1494, 1451, 1256 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.05 (2H, d, *J* 8.0 Hz, Ar–H), 7.72–7.54 (7H, m, Ar–H, CH=), 7.49–7.30 (3H, m, Ar–H), 7.10 (1H, d, *J* 14.0 Hz, =CH), 7.01 (2H, d, *J* 8.0 Hz, Ar–H), 3.91 (3H, s, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.7, 142.9, 140.0, 137.9, 134.1, 128.9, 128.8, 128.0, 127.9, 127.7, 127.1, 116.6, 114.5, 109.9, 55.2; ESIMS: *m*/*z* 355 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 355.1460. $C_{23}H_{19}N_2O_2$ requires 355.1446.

*4.3.9. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-(4-chlorophenyl)-1,3,4-oxadiazole (**3i**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (107 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (6% EtOAc/hexane) to give the product **3i** (152 mg, 85%) as a white solid; R_f (15% EtOAc/hexane) 0.51; mp: 158–160 °C; IR (KBr): 2396, 1639, 1509, 1476, 1275 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.09 (2H, d, *J* 8.0 Hz, Ar–H), 7.72–7.61 (7H, m, Ar–H), 7.54–7.35 (5H, m, Ar–H, CH=), 7.12 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.8, 143.2, 140.1, 139.0, 138.2, 133.7, 129.3, 128.9, 128.0, 127.9, 127.3, 126.6, 122.9, 109.5; ESIMS: *m*/*z* 359, 361 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 359.0963. $C_{22}H_{16}N_2OCl$ requires 359.0951.

*4.3.10. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (**3j**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (107 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (7% EtOAc/hexane) to give the product **3j** (172 mg, 88%) as a white solid; R_f (15% EtOAc/hexane) 0.43; mp: 201–203 °C; IR (KBr): 2372, 1636, 1414, 1331, 1124 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.26 (2H, d, *J* 8.0 Hz, Ar–H), 7.82 (2H, d, *J* 8.0 Hz, Ar–H), 7.73–7.55 (7H, m, Ar–H, CH=), 7.49–7.31 (3H, m, Ar–H), 7.12 (1H, d, *J* 14.0 Hz, =CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.9, 143.1, 140.0, 139.3, 133.2, 128.9, 128.1, 128.0, 127.8, 127.2, 127.0, 126.1, 111.9, 109.3; ESIMS: *m*/*z* 393 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 393.1218. $C_{23}H_{16}N_2OF_3$ requires 393.1214.

*4.3.11. (E)-2-(2-(Biphenyl-4-yl)vinyl)-5-(3,4,5-trimethoxyphenyl)-1,3,4-oxadiazole (**3k**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(3,4,5-trimethoxyphenyl)-1,3,4-oxadiazole (118 mg, 0.50 mmol), and *trans*-β-iodo-(4-phenyl)styrene (152 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (10% EtOAc/hexane) to give the product **3 k** (192 mg, 93%) as a white solid; R_f (20% EtOAc/hexane) 0.41; mp 154–156 °C; IR: 2382, 1643, 1594, 1493, 1321 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.72–7.52 (7H, m, Ar–H), 7.42 (2H, m, Ar–H, CH=), 7.35–7.26 (3H, m, Ar–H), 7.09 (1H, d, *J* 14.0 Hz, =CH), 3.94 (6H, s, 2×OCH_3), 3.88 (3H, s, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.2, 153.8, 142.7, 140.0, 138.3, 133.5, 129.1, 128.1, 128.0, 127.8, 127.1, 118.6, 110.0, 104.2, 61.6, 56.5; ESIMS: *m*/*z*

415 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 415.1669. $C_{25}H_{23}N_2O_4$ requires 415.1657.

*4.3.12. (E)-2-(3,4-Dimethoxystyryl)-5-phenyl-1,3,4-oxadiazole (**3l**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-phenyl-1,3,4-oxadiazole (73 mg, 0.50 mmol), and *trans*-β-iodo-(3,4-dimethoxy)styrene (145 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (9% EtOAc/hexane) to give the product **3l** (140 mg, 91%) as a white solid; R_f (20% EtOAc/hexane) 0.52; mp: 102–104 °C; IR (KBr): 2408, 1638, 1592, 1523, 1266 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.13 (2H, d, *J* 8.0 Hz, Ar–H), 7.58–7.47 (4H, m, Ar–H, CH=), 7.19–7.12 (2H, m, Ar–H), 6.99 (1H, d, *J* 14.0 Hz, =CH), 6.90 (1H, d, *J* 8.0 Hz, Ar–H), 3.97 (3H, s, OCH_3), 3.95 (3H, s, $-OCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 151.1, 149.8, 138.9, 132.0, 129.1, 127.8, 127.0, 124.2, 122.1, 111.2, 109.1, 107.9, 56.1, 56.0; ESIMS: *m*/*z* 309 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 309.1238. $C_{18}H_{17}N_2O_3$ requires 309.1239.

*4.3.13. (E)-2-(3,4-Dimethoxystyryl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**3m**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-methoxyphenyl)-1,3,4-oxadiazole (88 mg, 0.50 mmol), and *trans*-β-iodo-(3,4-dimethoxy)styrene (145 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (9% EtOAc/hexane) to give the product **3m** (152 mg, 90%) as a white solid; R_f (20% EtOAc/hexane) 0.49; mp: 142–144 °C; IR (KBr): 2401, 1608, 1496, 1457, 1249 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.01 (2H, d, *J* 8.0 Hz, Ar–H), 7.46 (1H, d, *J* 14.0 Hz, CH=), 7.11–6.82 (6H, m, Ar–H, =CH), 3.93 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 3.86 (3H, s, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 162.2, 150.9, 149.0, 138.0, 128.2, 127.9, 121.8, 116.5, 114.8, 111.1, 108.9, 107.8, 55.6, 55.5, 55.2; ESIMS: *m*/*z* 339 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 339.1335. $C_{19}H_{19}N_2O_4$ requires 339.1344.

*4.3.14. (E)-2-(3,4-Dimethoxystyryl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (**3n**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (107 mg, 0.50 mmol), and *trans*-β-iodo-(3,4-dimethoxy)styrene (145 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (8% EtOAc/hexane) to give the product **3m** (165 mg, 88%) as a white solid; R_f (20% EtOAc/hexane) 0.53; mp: 136–138 °C; IR (KBr): 2238, 1633, 1591, 1572, 1325 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.22 (2H, d, *J* 8.0 Hz, Ar–H), 7.80 (2H, d, *J* 8.0 Hz, Ar–H), 7.57 (1H, d, *J* 14.0 Hz, CH=), 7.14–7.05 (2H, m, Ar–H), 6.92 (1H, d, *J* 14.0 Hz, =CH), 6.84 (1H, d, *J* 8.0 Hz, Ar–H), 3.95 (3H, s, OCH_3), 3.90 (3H, s, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.8, 151.1, 149.5, 139.9, 133.2, 133.0, 127.2, 127.1, 126.0, 125.9, 122.0, 111.1, 109.1, 107.0, 55.9, 55.8; ESIMS: *m*/*z* 377 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 377.1123. $C_{19}H_{16}N_2O_3F_3$ requires 377.1113.

*4.3.15. (E)-2-(2-(5-(4-Chlorophenyl)furan-2-yl)vinyl)-5-phenyl-1,3,4-oxadiazole (**3o**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-phenyl-1,3,4-oxadiazole (73 mg, 0.50 mmol), and (*E*)-2-(4-chlorophenyl)-5-(2-iodovinyl)furan (165 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (8% EtOAc/hexane) to give the product **3m** (151 mg, 87%) as a white solid; R_f (20% EtOAc/hexane) 0.43; mp: 150–152 °C; IR (KBr): 2376, 1624, 1550, 1460 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.17–8.04 (4H, m, Ar–H), 7.69–7.30 (6H, m, Ar–H, CH=), 7.02 (1H, d, *J* 14.0 Hz, =CH), 6.72 (1H, d, *J* 2.0 Hz, Ar–H), 6.68 (1H, d, *J* 2.0 Hz, Ar–H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.8, 155.0, 150.8, 133.1, 132.1, 132.0, 129.5, 129.2, 127.8, 127.1, 127.0, 125.5, 125.3, 116.2, 108.2, 107.6; ESIMS: *m*/*z* 349, 351 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 349.0742. $C_{20}H_{14}N_2O_2Cl$ requires 349.0743.

*4.3.16. (E)-2-(2-(5-(4-Chlorophenyl)furan-2-yl)vinyl)-5-p-tolyl-1,3,4-oxadiazole (**3p**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-*p*-tolyl-1,3,4-oxadiazole (80 mg, 0.50 mmol), and (*E*)-2-(4-chlorophenyl)-5-(2-iodovinyl)furan (165 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (8% EtOAc/hexane) to give the product **3m** (161 mg, 88%) as a white solid; mp: 197–199 °C; IR (KBr): 2385, 1619, 1488, 1463, 1259 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.98 (2H, d, *J* 2.0 Hz, Ar–H), 7.65 (2H, d, *J* 8.0 Hz, Ar–H), 7.41–7.23 (5H, m, Ar–H, CH=), 7.02 (1H, d, *J* 14.0 Hz, =CH), 6.71 (1H, d, *J* 2.0 Hz, Ar–H), 6.65 (1H, d, *J* 2.0 Hz, Ar–H), 2.46 (3H, s, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.2, 155.0, 150.9, 142.2, 134.1, 130.0, 129.1, 126.8, 125.9, 125.0, 121.2, 118.9, 116.2, 107.9, 107.3, 21.5; ESIMS: *m*/*z* 363, 365 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 363.0882. $C_{21}H_{16}N_2O_2Cl$ requires 363.0900.

*4.3.17. (E)-2-(4-Chlorophenyl)-5-(2-(5-(4-chlorophenyl)furan-2-yl)vinyl)-1,3,4-oxadiazole (**3q**).* Following Section 4.2, CuI (9 mg, 0.05 mmol), DMEDA (4.5 mg, 0.05 mmol), LiO-*t*-Bu (80 mg, 1.0 mmol), 2-(4-chlorophenyl)-1,3,4-oxadiazole (90 mg, 0.50 mmol), and (*E*)-2-(4-chlorophenyl)-5-(2-iodovinyl)furan (165 mg, 0.50 mmol) in DMSO (2.0 mL) to give crude product, which was purified by column chromatography (9% EtOAc/hexane) to give the product **3m** (164 mg, 85%) as a white solid; mp: 192–194 °C; IR (KBr): 2380, 1605, 1475, 1407, 1255 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 8.02 (2H, d, *J* 8.0 Hz, Ar–H), 7.68 (2H, d, *J* 8.0 Hz, Ar–H), 7.55–7.47 (2H, m, Ar–H), 7.44–7.30 (3H, m, Ar–H, CH=), 7.04 (1H, d, *J* 14.0 Hz, =CH), 6.73 (1H, d, *J* 2.0 Hz, Ar–H), 6.69 (1H, d, *J* 2.0 Hz, Ar–H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.8, 155.2, 150.3, 133.9, 129.8, 129.2, 128.2, 125.4, 125.2, 119.1, 116.2, 108.8, 107.2; ESIMS: *m*/*z* 383, 385, 387 $[MH]^+$; HRMS (ESI): $[MH]^+$, found 383.0353. $C_{20}H_{13}N_2O_2Cl_2$ requires 383.0354.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.10.049.

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