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Palladium-catalyzed direct oxidative vinylation of thiophenes and furans under weakly basic conditions

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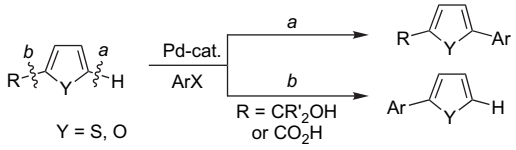
Abstract

The palladium-catalyzed oxidative coupling of thiophenes and furans with alkenes proceeds in the presence of copper and lithium salts as oxidant and additive, respectively, under weakly basic or almost neutral conditions to afford the corresponding vinylated heteroarenes. Under such conditions, diphenyl(hydroxy)methyl and acetal functions on the heteroarene substrates are tolerable. The former function on a thiophene ring can be substituted by palladium-catalyzed arylation via C–C bond cleavage after the vinylation to produce 2-aryl-5-vinylthiophenes.

Keywords: Palladium catalyst; Oxidative vinylation; Heteroarenes; C–H bond cleavage

1. Introduction

Arylated or vinylated thiophenes as well as furans at their 2- and/or 5-position(s) are of interest for their photo- and electrochemical properties and their biological activities.[1] One of the most useful methods for their preparation is the palladium-catalyzed cross-coupling of aryl/vinyl halides with heteroarylmetals or of heteroaryl halides with aryl/vinylmetals.[2] Recently, a number of five-membered heteroarenes including thiophenes and furans have been found to undergo direct intermolecular arylation via C–H bond cleavage at their 2- and 5-position on treatment with aryl halides under the influence of palladium catalysts (Scheme 1, path a).[3] Such reactions can be utilized as effective, straightforward methods for making heteroaryl–aryl linkages. The arylation of heteroarylmethanols and heteroarene carboxylic acids via C–C bond cleavage has also been developed (Scheme 1, path b).[4,5] These reactions have successfully been applied to the synthesis of unsymmetrically 2,5-diarylated thiophenes from diphenyl(2-thienyl)methanol.[5c]



Scheme 1. Arylation of thiophenes and furans via C–H and C–C bond cleavage.

On the other hand, the direct vinylation of thiophenes and furans at the 2- and 5-position using palladium catalysts and oxidants has also been reported.[6–8] However, the reaction is usually conducted in acidic solvents such as acetic and propionic acids,[7] which limits coexisting functional groups in the heteroaryl substrates. Consequently, as part of our study on catalytic vinylation of aromatic substrates,[9] we have explored to develop an effective protocol even for the direct oxidative vinylation of thiophenes and furans possessing acid-sensitive substituents. It was also undertaken to prepare 2-phenyl-5-vinylthiophene derivatives via a successive vinylation–arylation sequence. The results are reported herein.

2. Results and discussion

First, diphenyl(2-thienyl)methanol (**1a**) was reacted with butyl acrylate (**2a**) (3 equiv) under acidic conditions similar to

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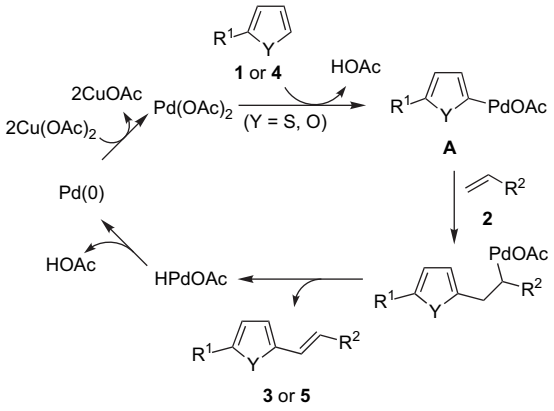
those employed previously in the oxidative direct vinylation of thiophenes and furans.[7] In the presence of $Pd(OAc)_2$ (5 mol %) in acetic acid under air at 120 °C using $Cu(OAc)_2 \cdot H_2O$ (2 equiv)[7a] or a heteropoly acid $H_4PMo_{11}V_1O_{40} \cdot nH_2O$ (1 mol %) and NaOAc (4 mol %),[7d] the desired coupling reaction did not proceed at all (entries 1 and 2 in Table 1). In each case, a large portion of the tertiary alcohol **1a** was consumed for unidentified reactions. It was found that using DMF as a solvent in place of acetic acid in the presence of $Cu(OAc)_2 \cdot H_2O$ under N_2, butyl (*E*)-3-[5-(α,α-diphenyl-α-hydroxymethyl)-2-thienyl]-2-propenoate (**3a**) was formed in 15% yield after 4 h (entry 3). Addition of chloride salts such as $[(PhCH_2)NEt_3]Cl$ and LiCl (3 equiv) enhanced the yield of **3a** to 27 and 44%, respectively (entries 4 and 5). LiOAc was found to be a more effective additive than the chlorides to increase the yield up to 56% (entry 6). When the reaction was conducted using the catalytic system of $Pd(OAc)_2/Cu(OAc)_2 \cdot H_2O$/LiOAc in DMF at 120 °C under air for 4 h, **3a** was formed in 72% yield (entry 7).

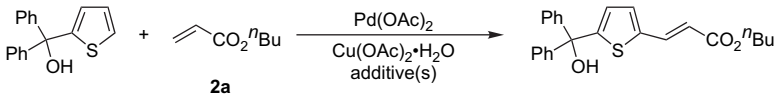
Table 2 summarizes the results for the reactions of a number of thiophenes **1** or furans **4** with alkenes **2**. 2-Methyl- and 2-phenylthiophenes underwent the oxidative coupling with butyl acrylate (**2a**) to give the corresponding 5-vinylated products, **3b** and **3c** (entries 1 and 2). An acid-sensitive acetal function was found to be tolerable under the present conditions.[10] Thus, 2-(1,3-dioxolan-2-yl)thiophene and 2-(1,3-dioxolan-2-yl)furan reacted with **2a** to afford butyl (*E*)-3-[5-(1,3-dioxolan-2-yl)-2-thienyl]-2-propenoate (**3d**) and butyl (*E*)-3-[5-(1,3-dioxolan-2-yl)-2-furyl]-2-propenoate (**5a**), respectively (entries 3 and 4). Since it is known that the electrophilic vinylation of electron-deficient 2-formylthiophene and 2-formyl furan with **2a** is sluggish,[7b,e] the present reaction of the acetals seems to provide a useful synthetic route leading to 5-vinyl-2-formylthiophenes and 5-vinyl-2-formyl furans. It is worth noting that compound **5a** can be used as a precursor in the synthesis of wyerone acid, a phytoalexin from *Vicia faba* L.[7e,11] 2-(*tert*-Butyl)-furan also coupled with **2a** to produce the corresponding 5-vinylated furan **5b** (entry 5). Other alkenes, ethyl acrylate and styrene could be employed for the oxidative coupling with **1a** to give products **3e** and **3f** (entries 6 and 7).

The oxidative coupling is considered to proceed via a sequence similar to that proposed previously.[7] A plausible mechanism for the reaction of 2-substituted thiophenes **1** or furans **4** with alkenes **2** is illustrated in Scheme 2. The first step may involve electrophilic attack of $Pd(OAc)_2$ to **1** or **4** to form a heteroarylpalladium(II) intermediate **A**. Then, alkene insertion into the resulting Pd–C bond of **A** and subsequent β-hydrogen elimination occur to give product **3** or **5** together with HPdOAc. The latter releases HOAc to form Pd(0), which is reoxidized to $Pd(OAc)_2$ by $Cu(OAc)_2$. During palladium-catalyzed oxidation reaction, in general, the regeneration of Pd(II) from Pd(0) is considered to be the crucial step to determine catalyst efficiency.[12] One of the possible roles of added lithium salts, such as lithium acetate and chloride, is to provide the corresponding anions as ligand to prevent the deactivation of Pd(0) to metallic species.[13]



Scheme 2. A plausible mechanism for the reaction of **1** or **4** with **2**.

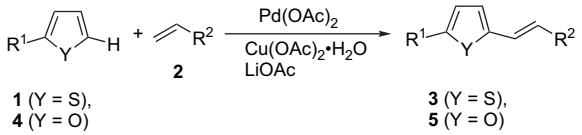
Table 1
Reaction of diphenyl(2-thienyl)methanol (**1a**) with butyl acrylate (**2a**)[a]

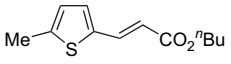
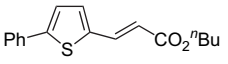
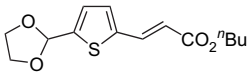
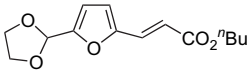
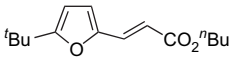
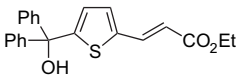
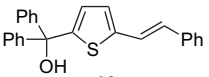


Entry	Additive(s) (mmol)	Solvent	Time (h)	Yield of **3a**[b] (%)
1[c]	—	AcOH	13	0
2[c,d]	$H_4PMo_{11}V_1O_{40} \cdot nH_2O$ (0.004)+NaOAc (0.016)	AcOH	13	0
3	—	DMF	4	15
4	$[(PhCH_2)NEt_3]Cl$ (1.2)	DMF	2	27
5	LiCl (1.2)	DMF	2	44
6	LiOAc (1.2)	DMF	2	56
7[c]	LiOAc (1.2)	DMF	4	72 (65)
8[e]	LiOAc (1.2)	DMF	8	53

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (1.2 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.8 mmol), solvent (3 mL) under N_2 (1 atm) at 120 °C.
[b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification.
[c] Under air (1 atm).
[d] Without $Cu(OAc)_2 \cdot H_2O$.
[e] Under O_2 (1 atm).

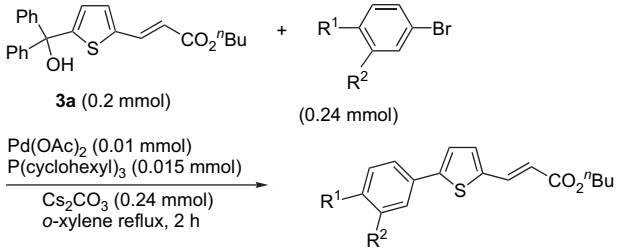
Table 2
Reaction of thiophenes **1** and furans **4** with alkenes **2**[a]



Entry	Y	R^1	R^2	Time (h)	Product	Yield[b] (%)
1	S	Me	$CO_2{}^nBu$	4	 **3b**	52 (32)
2	S	Ph	$CO_2{}^nBu$	4	 **3c**	46
3	S		$CO_2{}^nBu$	8	 **3d**	53 (42)
4	O		$CO_2{}^nBu$	8	 **5a**	53 (40)
5	O	^{t}Bu	$CO_2{}^nBu$	2	 **5b**	67 (57)
6	S		CO_2Et	4	 **3e**	63 (55)
7	S		Ph	1	 **3f**	30

[a] Reaction conditions: **1** or **4** (0.4 mmol), **2** (1.2 mmol), $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2\cdot H_2O$ (0.8 mmol), LiOAc (1.2 mmol), DMF (3 mL) under air (1 atm) at 120 °C.
[b] GC yield based on the amount of **1** or **4** used. Value in parentheses indicates yield after purification.

As described in Section 1, the thiophene **3a**, produced in the reaction of **1a** with **2a**, was subjected to the arylation via C–C bond cleavage to lead to 2-aryl-5-vinylthiophenes. Thus, treatment of **3a** with bromobenzene (1.2 equiv) in the presence of $Pd(OAc)_2$ (5 mol %), $P(cyclohexyl)_3$ (7.5 mol %), and Cs_2CO_3 (1.2 equiv) in refluxing *o*-xylene for 2 h gave **3c** in 74% yield (Scheme 3). The reactions with 4-bromoanisole and 1-bromo-3-(trifluoromethyl)benzene also proceeded effectively to produce the corresponding 2-aryl-5-vinylthiophenes **3g** and **3h**.



R^1	R^2	Product, % Yield[a]
H	H	**3c,** 74(69)%
OMe	H	**3g,** 93(88)%
H	CF_3	**3h,** 80(75)%

[a] GC yield. Value in parentheses indicates yield after purification.

Scheme 3. Arylation of **3a**.

3. Conclusions

We have shown that the palladium-catalyzed direct oxidative vinylation of thiophenes and furans can be performed under weakly basic conditions, which allow coexistence of acid-sensitive diphenyl(hydroxy)methyl and acetal functions. The former substituent on a vinylthiophene can be subsequently replaced by aryl groups through cross-coupling via C–C bond cleavage.

4. Experimental

4.1. General

Diphenyl(2-thienyl)methanol (**1a**) was prepared according to the published method.[5b] Other reagents were commercially available. ^1H and ^{13}C NMR spectra were recorded at 400 and

100 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm×1.5 m) or a CBP-1 capillary column (i.d. 0.25 mm×25 m). GC–MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm×25 m).

4.2. Procedure for the palladium-catalyzed oxidative coupling of thiophenes **1** or furans **4** with alkenes **2**

A mixture of **1** or **4** (0.4 mmol), **2** (1.2 mmol), $Pd(OAc)_2$ (0.02 mmol, 4 mg), $Cu(OAc)_2·H_2O$ (0.8 mmol, 160 mg), LiOAc (1.2 mmol, 79 mg), and 1-methylnaphthalene (ca. 50 mg) as internal standard was stirred in DMF (3 mL) at 120 °C under air. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Product **3** or **5** was isolated by thin layer chromatography on silica gel using hexane–ethyl acetate as eluent.

4.3. Procedure for the palladium-catalyzed coupling of butyl (*E*)-3-[5-(α,α-diphenyl-α-hydroxymethyl)-2-thienyl]-2-propenoate (**3a**) with aryl bromides (Scheme 2)

In a flask was placed Cs_2CO_3 (0.24 mmol, 78 mg), which was then dried at 150 °C in vacuo for 2 h. Then, **3a** (0.2 mmol, 78 mg), aryl bromide (0.24 mmol), $Pd(OAc)_2$ (0.01 mmol, 2 mg), P(cyclohexyl)$_3$ (0.015 mmol), 1-methylnaphthalene (ca. 50 mg) as internal standard, and *o*-xylene (3 mL) were added and the resulting mixture was stirred at 170 °C under N_2 for 2 h. After cooling, the reaction mixture was extracted with Et_2O and dried over sodium sulfate. Arylated product **3** was isolated by thin layer chromatography on silica gel using hexane–ethyl acetate as eluent.

4.4. Products

4.4.1. Butyl (*E*)-3-[5-(α,α-diphenyl-α-hydroxymethyl)-2-thienyl]-2-propenoate (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J*=7.3 Hz, 3H), 1.38–1.43 (m, 2H), 1.62–1.67 (m, 2H), 3.02 (s, 1H), 4.16 (t, *J*=6.6 Hz, 2H), 6.14 (d, *J*=15.8 Hz, 1H), 6.69 (d, *J*=3.7 Hz, 1H), 7.09 (d, *J*=3.7 Hz, 1H), 7.31–7.38 (m, 10H), 7.69 (d, *J*=15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.66, 19.09, 30.66, 64.35, 80.08, 116.67, 127.16, 127.47, 127.76, 128.02, 130.53, 137.14, 139.35, 145.86, 155.56, 166.93; HRMS *m/z* (M^+) calcd for $C_{24}H_{24}O_3S$: 392.1463, found 392.1452.

4.4.2. Butyl (*E*)-3-(5-methyl-2-thienyl)-2-propenoate (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.3 Hz, 3H), 1.38–1.47 (m, 2H), 1.64–1.71 (m, 2H), 2.49 (s, 3H), 4.18 (t, *J*=6.6 Hz, 2H), 6.10 (d, *J*=15.8 Hz, 1H), 6.70–6.71 (m, 1H), 7.04 (d, *J*=3.7 Hz, 1H), 7.69 (d, *J*=15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.73, 15.78, 19.18, 30.79, 64.28, 115.58, 126.43, 131.52, 137.37, 137.61, 143.85, 167.15; MS *m/z* 224 (M^+). Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.54; H, 7.11; S, 13.82.

4.4.3. Butyl (*E*)-3-(5-phenyl-2-thienyl)-2-propenoate (**3c**)

Mp 53–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.3 Hz, 3H), 1.39–1.49 (m, 2H), 1.65–1.72 (m, 2H), 4.20 (t, *J*=6.6 Hz, 2H), 6.23 (d, *J*=15.8 Hz, 1H), 7.21 (d, *J*=3.7 Hz, 1H), 7.25 (d, *J*=3.7 Hz, 1H), 7.30–7.34 (m, 1H), 7.37–7.42 (m, 2H), 7.59–7.62 (m, 2H), 7.74 (d, *J*=15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.75, 19.20, 30.79, 64.42, 116.63, 123.92, 125.96, 128.37, 129.03, 132.19, 133.60, 137.03, 138.76, 147.27, 167.00; MS *m/z* 286 (M^+). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.20. Found: C, 71.19; H, 6.29; S, 11.27.

4.4.4. Butyl (*E*)-3-[5-(1,3-dioxolan-2-yl)-2-thienyl]-2-propeonate (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J*=7.3 Hz, 3H), 1.38–1.47 (m, 2H), 1.64–1.71 (m, 2H), 4.01–4.14 (m, 4H), 4.19 (t, *J*=6.6 Hz, 2H), 6.07 (s, 1H), 6.21 (d, *J*=15.6 Hz, 1H), 7.08 (d, *J*=3.6 Hz, 1H), 7.13 (d, *J*=3.6 Hz, 1H), 7.71 (d, *J*=15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.68, 19.13, 30.71, 64.41, 65.27, 99.88, 117.43, 126.81, 130.41, 136.92, 140.21, 144.81, 166.76; HRMS *m/z* (M^+) calcd for $C_{14}H_{18}O_4S$: 282.0926, found 282.0920.

4.4.5. Ethyl (*E*)-3-[5-(α,α-diphenyl-α-hydroxymethyl)-2-thienyl]-2-propenoate (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J*=7.0 Hz, 3H), 3.13 (s, 1H), 4.20 (q, *J*=7.0 Hz, 2H), 6.12 (d, *J*=15.8 Hz, 1H), 6.68 (d, *J*=3.7 Hz, 1H), 7.07 (d, *J*=3.7 Hz, 1H), 7.30–7.37 (m, 10H), 7.68 (d, *J*=15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.27, 60.44, 80.19, 116.80, 127.18, 127.53, 127.87, 128.11, 130.55, 137.16, 139.46, 145.84, 155.44, 166.83; HRMS *m/z* (M^+) calcd for $C_{22}H_{20}O_3S$: 364.1133, found 364.1108.

4.4.6. (*E*)-1-[5-(α,α-Diphenyl-α-hydroxymethyl)-2-thienyl]-2-phenylethene (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 1H), 6.62 (d, *J*=3.7 Hz, 1H), 6.84 (d, *J*=16.1 Hz, 1H), 6.89 (d, *J*=3.7 Hz, 1H), 7.14 (d, *J*=16.1 Hz, 1H), 7.21–7.42 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.13, 121.75, 125.61, 126.28, 127.25, 127.39, 127.59, 127.69, 128.02, 128.45, 128.67, 136.88, 143.17, 146.18, 150.90; HRMS *m/z* (M^+) calcd for $C_{25}H_{20}OS$: 368.1235, found 368.1230.

4.4.7. Butyl (*E*)-3-[5-(4-methoxyphenyl)-2-thienyl]-2-propenoate (**3g**)

Mp 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.3 Hz, 3H), 1.39–1.49 (m, 2H), 1.65–1.72 (m, 2H), 3.84 (s, 3H), 4.20 (t, *J*=6.6 Hz, 2H), 6.19 (d, *J*=15.4 Hz, 1H), 6.91–6.94 (m, 2H), 7.14 (d, *J*=3.7 Hz, 1H), 7.19 (d, *J*=3.7 Hz, 1H), 7.52–7.56 (m, 2H), 7.73 (d, *J*=15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.66, 21.11, 32.71, 57.29, 66.27, 116.35, 117.96, 124.75, 128.35, 129.20, 134.30, 139.09, 139.72, 149.31, 161.81, 169.02; HRMS *m/z* (M^+) calcd for $C_{18}H_{20}O_3S$: 316.1133, found 316.1138.

*4.4.8. Butyl (E)-3-[5-(3-trifluoromethylphenyl)-2-thienyl]-2-propenoate (**3h**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J=7.3 Hz, 3H), 1.40–1.49 (m, 2H), 1.66–1.73 (m, 2H), 4.21 (t, J=6.6 Hz, 2H), 6.26 (d, J=15.4 Hz, 1H), 7.24 (d, J=3.7 Hz, 1H), 7.31 (d, J=3.7 Hz, 1H), 7.52 (t, J=7.7 Hz, 1H), 7.57 (d, J=7.7 Hz, 1H), 7.74 (d, J=15.4 Hz, 1H), 7.76 (d, J=7.7 Hz, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.73, 19.18, 30.76, 64.52, 117.47, 122.56 (q, J=3.8 Hz), 123.83 (q, J=271 Hz), 124.77 (q, J=3.8 Hz), 124.92, 129.06, 129.58, 131.53 (q, J=31.9 Hz), 132.04, 134.39, 136.62, 139.79, 145.07, 166.79; HRMS *m/z* (M^+) calcd for $C_{18}H_{17}F_3O_2S$: 354.0901, found 354.0904.

*4.4.9. Butyl (E)-3-[5-(1,3-dioxolan-2-yl)-2-furyl]-2-propenoate (**5a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J=7.3 Hz, 3H), 1.37–1.47 (m, 2H), 1.63–1.70 (m, 2H), 4.01–4.15 (m, 4H), 4.18 (t, J=6.5 Hz, 2H), 5.94 (s, 1H), 6.35 (d, J=15.9 Hz, 1H), 6.49 (d, J=3.3 Hz, 1H), 6.55 (d, J=3.3 Hz, 1H), 7.39 (d, J=15.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.68, 19.14, 30.72, 64.37, 65.23, 97.48, 110.73, 114.79, 116.77, 130.62, 151.33, 153.53, 166.95; HRMS *m/z* (M^+) calcd for $C_{14}H_{18}O_5$: 266.1154, found 266.1158.

*4.4.10. Butyl (E)-3-[5-(1,1-dimethylethyl)-2-furyl]-2-propenoate (**5b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J=7.3 Hz, 3H), 1.30 (s, 9H), 1.38–1.48 (m, 2H), 1.64–1.71 (m, 2H), 4.18 (t, J=6.9 Hz, 2H), 6.05 (d, J=3.3 Hz, 1H), 6.25 (d, J=15.6 Hz, 1H), 6.49 (d, J=3.3 Hz, 1H), 7.37 (d, J=15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.71, 19.18, 28.91, 30.81, 32.97, 64.18, 105.11, 114.04, 115.91, 131.22, 149.22, 167.31, 167.44; HRMS *m/z* (M^+) calcd for $C_{15}H_{22}O_3$: 250.1569, found 250.1575.

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