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Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles in aqueous solution of anionic surfactant sodium dodecylbenzenesulfonate (SDBS)

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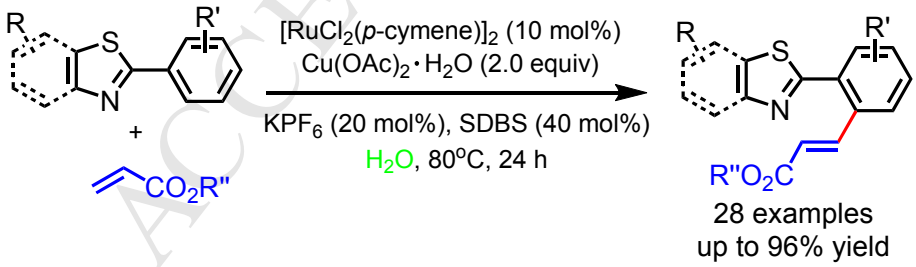
Abstract: A mild and efficient Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles through twofold C-H bond functionalization in aqueous solution of anionic surfactant sodium dodecylbenzenesulfonate (SDBS) has been developed using activated olefins as coupling partner. The protocol could be carried out smoothly on a gram scale, recyclable, and applicable to 2-arylthiazoles.

Graphical Abstract:



Keywords: Alkenylation; C–H functionalization; 2-Arylbenzo[d]thiazoles; 2-Arylthiazoles; Aqueous.

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1. Introduction

Benzo[d]thiazoles are ubiquitous structural scaffolds in biologically natural products, agrochemicals, and pharmaceuticals that exhibit remarkable antitumor, antiviral, and antimicrobial activities.[1] In particular, 2-arylbenzo[d]thiazoles are widely found in a broad range of pharmaceutically active molecules.[2] For example, aryl hydrocarbon receptor agonist 2-(4-amino-3-methylphenyl)-5- fluorobenzothiazole (5F 203) can induce oxidative stress triggering DNA damage and cytoglobin up-regulation in human breast cancer cells (Figure 1).[2a] 2-(4-*N*-[^{11}C]methylaminophenyl)-6-hydroxybenzothiazole (^{11}C PIB), is an β-amyloid PET imaging tracer for Alzheimer's disease diagnosis.[2b] In addition, 2-(3,4-dimethoxyphenyl)-5-fluorobenzothiazole (GW 610) shows potent and selective inhibitory activity against lung, colon, and breast cancer cell lines.[2h]

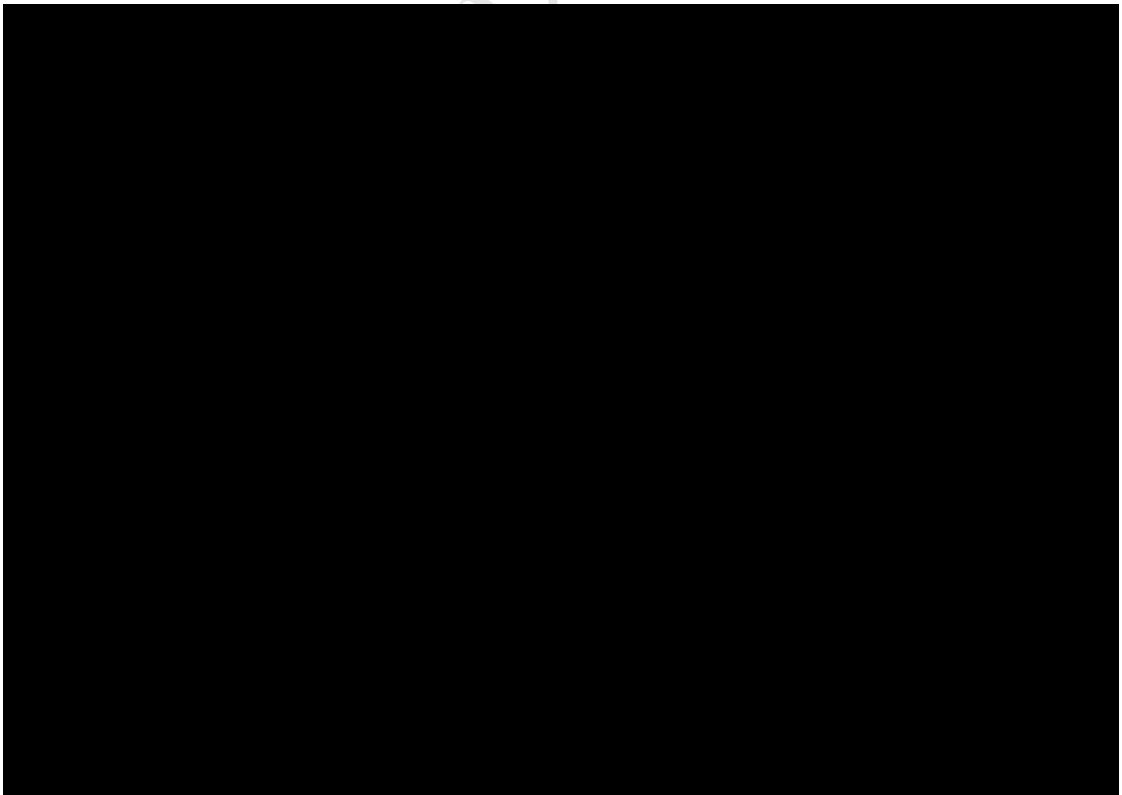


Figure 1 Selected bioactive examples containing 2-aryl-benzothiazole scaffold.

Directing group-assisted transition-metal-catalyzed *ortho* C–H functionalization reactions have been achieved considerable progress in organic and medicinal chemistry in the past decades.[3,4] To date, diverse functional groups including pyridine, amide, anilide, imine, imidazoline, pyrazole, oxazoline, cyano, amine, carboxylic acid, ester, ketone, and hydroxyl groups, have been used as directing groups for various C–H bond functionalizations to construct various C–C and C–X (X = O, N, halogens) bonds. Recently, we and other groups have reported many transition-metal-catalyzed benzothiazole directed *ortho* C–H bond functionalization,[4] including arylation,[4a] alkylation,[4b] acetoxylation,[4c] halogenation,[4d,e] amination,[4f] acylation,[4g-j] hydroxylation,[4k,l] nitration,[4m] trifluoromethylthiolation,[4n] and cyanation.[4o]

During the past decades, transition-metal-catalyzed C–H bond alkenylation have emerged as powerful strategies for the step-economical synthesis of unsaturated and conjugated molecules. In contrast, great success has been achieved with expensive 4d transition-metal catalysts, such as rhodium[5] or palladium[6] complexes. Recently, considerable progress has been made in this field through less expensive ruthenium[7-11] or iron[12] species catalyzed C–H coupling reaction with alkenes, as reported by Miura,[7] Ackermann,[8] Jeganmohan,[9] Dixneuf,[10] and Lei[12b] group.

It is well known that water is the ideal green solvent for organic reaction, because of its abundance, nonflammable, nontoxic, and inexpensiveness. Furthermore, great achievements showed that water could enhance the reactivities and selectivities of some reactions.[13] Given our recent interest in oxidative alkenylation-cyclization of

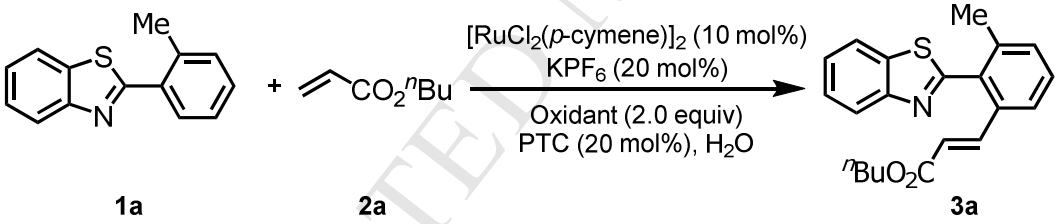
aryl sulfonamides with acrylates,[14] and the Suzuki-Miyaura coupling reaction[15a] and the tandem synthesis 2-aminobenzothiazoles[15b] in aqueous, we would like to report our recent efforts towards Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles through twofold C–H bond functionalization in aqueous solution of anionic surfactant sodium dodecylbenzenesulfonate (SDBS).

2. Results and Discussion

We commenced the dehydrogenative alkenylation of 2-(*o*-tolyl)benzo[d]thiazole (**1a**) with butyl acrylate (**2a**) under the influence of Ru(II) catalyst, KPF_6, and $Cu(OAc)_2 \cdot H_2O$ in aqueous (Table 1). To our delight, the desired coupling product **3a** was isolated in 14% yield in pure water (Table 1, entry 1). To improve the yield of **3a**, catalytic amount of poly(ethylene glycol) (PEG-200) as an additive was added into the reaction. Expectively, the desired product **3a** was improved to 30% (Table 1, entry 2). Screening of the oxidant indicated that AgOAc, Ag_2CO_3, $K_2S_2O_8$, and CuBr were inferior (Table 1, entries 3-6). Then, the effect of phase transfer catalysts (PTCs) was examined (Table 1, entries 7-11). 18-Crown-6 exhibited the negative result (Table 1, entry 7). Other PTCs, such as tetramethylammonium fluoride (TMAF), hexadecyl trimethyl ammonium chloride (CTAC), sodium dodecyl sulfate (SDS), and sodium dodecylbenzenesulfonate (SDBS) led to a low to moderate yield of the desired product **3a** (Table 1, entries 8-11). Among these PTCs, SDBS turned out to be the best (Table 1, entry 11, 48%). Increasing the amount of $Cu(OAc)_2 \cdot H_2O$ from 2.0 equiv to 3.0 and 4.0 equiv provided **3a** in 60% and 84% yield, respectively (Table 1,

entries 12 and 13). It is worthy to note that better result (90% yield) was achieved by increasing the amount of SDBS (40 mol%) even in the presence of 2.0 equiv of $Cu(OAc)_2 \cdot H_2O$ (Table 1, entry 14). Switching to $AgSbF_6$ as additive instead of KPF_6 provided a lower yield (Table 1, entry 15, 60%). Further investigation indicated that lowering reaction temperature also afforded a slightly lower yield of **3a** (Table 1, entry 16, 80%). In addition, we studied the reaction under catalytic amount of $Cu(OAc)_2 \cdot H_2O$ and using air as terminal oxidant to provide the desired product **3a** in lower yields (Table 1, entries 17 and 18)

Table 1 Optimization of Ru-catalyzed *ortho*-oxidative alkenylation of 2-(*o*-tolyl)benzo[d]thiazole **1a** with butyl acrylate **2a**[a]



1a **2a** **3a**

Entry	Oxidant (x equiv)	PTC[c]	Yield (%)[b]
1	$Cu(OAc)_2 \cdot H_2O$ (2.0)	-	14
2	$Cu(OAc)_2 \cdot H_2O$ (2.0)	PEG 200	30
3	AgOAc (2.0)	PEG 200	20
4	Ag_2CO_3 (2.0)	PEG 200	25
5	$K_2S_2O_8$ (2.0)	PEG 200	Trace
6	CuBr (2.0)	PEG 200	Trace
7	$Cu(OAc)_2 \cdot H_2O$ (2.0)	18-Crown-6	Trace
8	$Cu(OAc)_2 \cdot H_2O$ (2.0)	TMAF	35
9	$Cu(OAc)_2 \cdot H_2O$ (2.0)	CTAC	25
10	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDS	22
11	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	48
12	$Cu(OAc)_2 \cdot H_2O$ (3.0)	SDBS	60
13	$Cu(OAc)_2 \cdot H_2O$ (4.0)	SDBS	84
14[d]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	90
15[e]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	60
16[f]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	80
17	$Cu(OAc)_2 \cdot H_2O$ (0.5)	SDBS	43
18	$Cu(OAc)_2 \cdot H_2O$ (0.2)	SDBS	16

[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (0.2 mmol), butyl acrylate **2a** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), additive (KPF_6, 20 mol%), phase transfer catalyst (PTC, 20 mol%), stirred at 80 ^oC for 24 h in H_2O (2 mL).

[b] Yield based on **1a**.

[c] TMAF: tetramethylammonium fluoride; CTAC: hexadecyl trimethyl ammonium chloride; SDS: sodium dodecyl sulfate; SDBS: sodium dodecylbenzenesulfonate.

[d] SDBS (40 mol%).

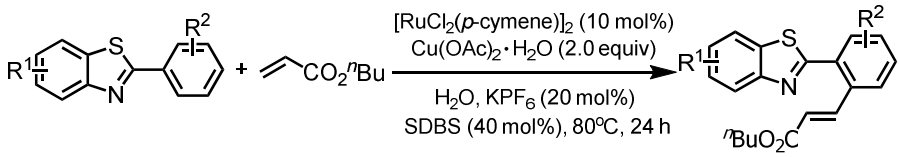
[e] Using $AgSbF_6$ as additive instead of KPF_6.

[f] At 60 ^oC.

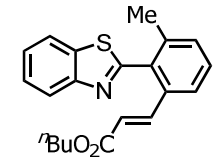
With the optimal reaction conditions in hand, we next examined the scope of 2-arylbenzo[d]thiazoles for this Ru-catalyzed oxidative alkenylation in aqueous (**Scheme 1**). In general, the alkenylation reaction carried out smoothly, providing the

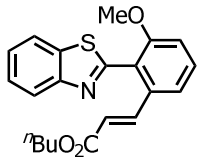
desired products in moderate to excellent yields. Both electron-rich as well as electron-deficient 2-arylbenzo[d]thiazoles are suitable substrates. Different substituents (methoxy, chloro, fluoro, and nitro) at the *ortho* position of the 2-aryl group of substrates were worked well to afford various alkenylated products **3b-3e** in 50-83% yield. The coupling of differently substituted 2-arylbenzo[d]thiazoles (R^1 = Me, F, and Cl) was found to be favored in this alkenylation to give desired products **3f-3l** in 62-86% yields. This catalytic system was also compatible with *meta*-substitued substrates providing only the *mono*-alkenylated products **3m-3q** at the less sterically hindered position in good yields. Subsequently, we examined the coupling reaction of symmetrical substrates (R^2 = 4-OMe, H) under the standard reaction conditions, while we obtained a *mono*- and *di*-alkenylated products (**3r-3t**, **3r'-3t'**) in good yields with moderate regioselectivity.

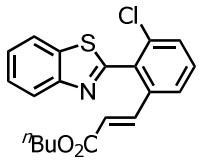
Scheme 1 Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles in aqueous[a,b]

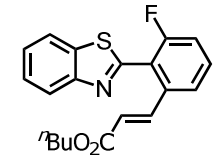


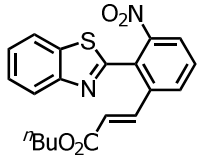
1 **2a** **3**

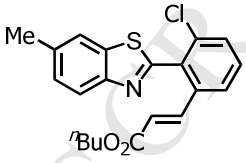

3a, 90%

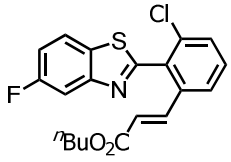

3b, 50%

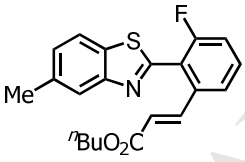

3c, 65%

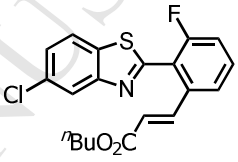

3d, 83%

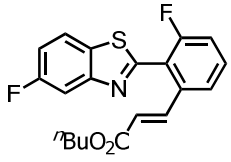

3e, 40%

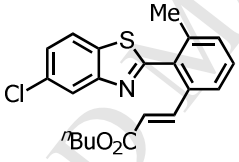

3f, 62%

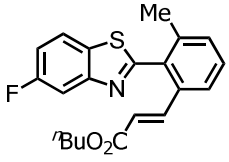

3g, 86%

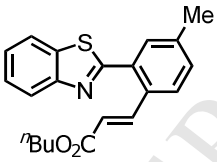

3h, 80%

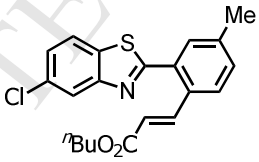

3i, 83%

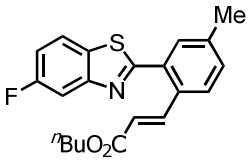

3j, 79%

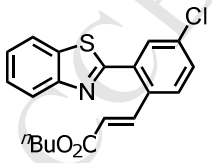

3k, 74%

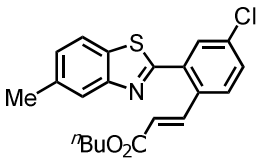

3l, 85%

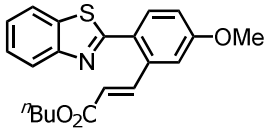

3m, 75%

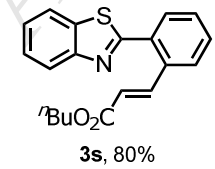

3n, 82%

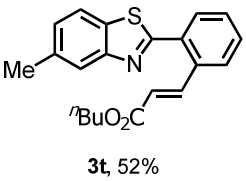

3o, 72%


3p, 55%


3q, 45%


3r, 60%
(mono/di = 2/1)


3s, 80%
(mono/di = 5/3)


3t, 52%

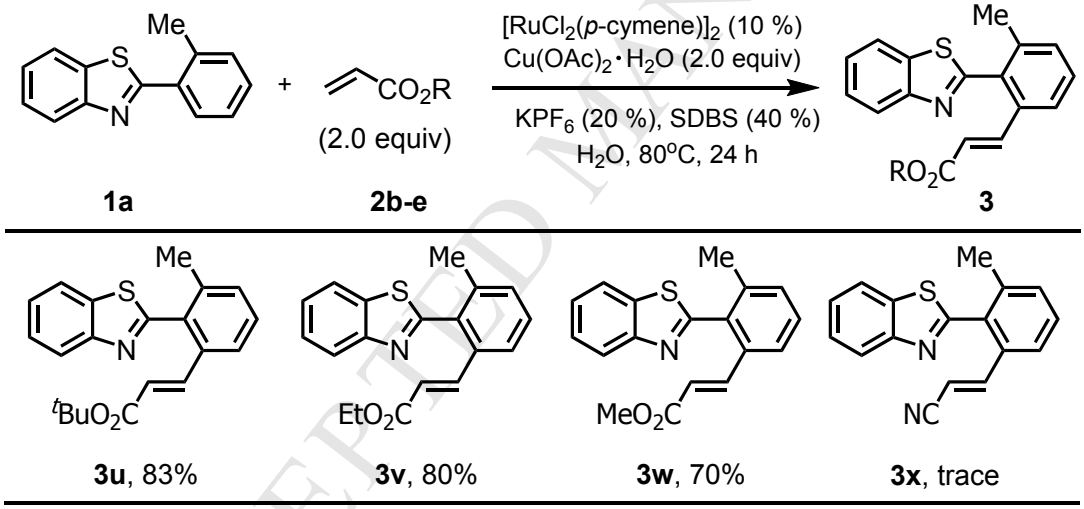
[a] Reaction conditions: 2-arylbenzo[d]thiazole **1** (0.2 mmol), butyl acrylate **2a** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$

(2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 ^oC, 24 h.

[b] Isolated yield.

Furthermore, we investigated the alkenylation of **1a** with several functional alkenes under optimal conditions (**Scheme 2**). Various acrylates **2b-2d** performed smoothly to give corresponding desired products **3u-3w** in good yields (70-83%). Unfortunately, the alkenylation of **1a** with acrylonitrile **2e** failed to offer the alkenlated product **3x** under the same conditions.

Scheme 2 Scope of alkenes[a,b]



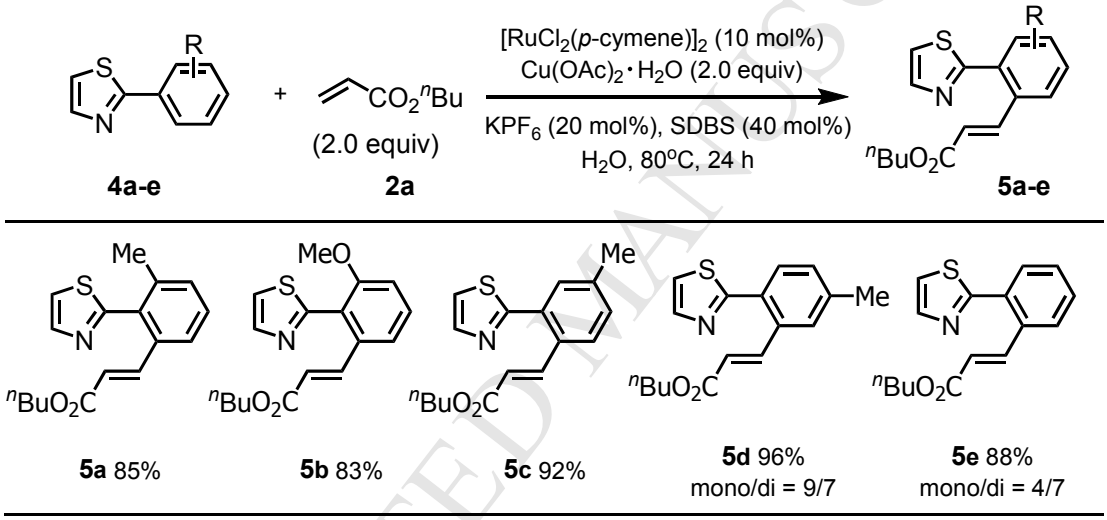
[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (0.2 mmol), acrylates **2b-e** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 ^oC, 24 h.

[b] Isolated yield.

Subsequently, we examined the alkenylation of 2-arylthiazoles **4** with *n*-butyl acrylate **2a** under the same conditions (**Scheme 3**). Notably, 2-(*o*-tolyl)thiazole **4a** was found to undergo the coupling reaction to afford desired product **5a** in 85% yield.

Interesting, to 2-(*m*-tolyl)thiazole **4c** with a methyl group at the *meta*-position of 2-phenyl ring gave product **5c** selectively at the less sterically hindered position in excellent yield (92%). To those *para*-position substituted or unsubstituted 2-phenylthiazoles **4d** and **4e** also reacted with **2a** smoothly under the present conditions and led to the mixtures of *mono*- and *di*-alkenylated products **5d**(**5d'**) and **5e**(**5e'**) in high yields with moderate selectivity.

Scheme 3 Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylthiazoles in aqueous[a,b]

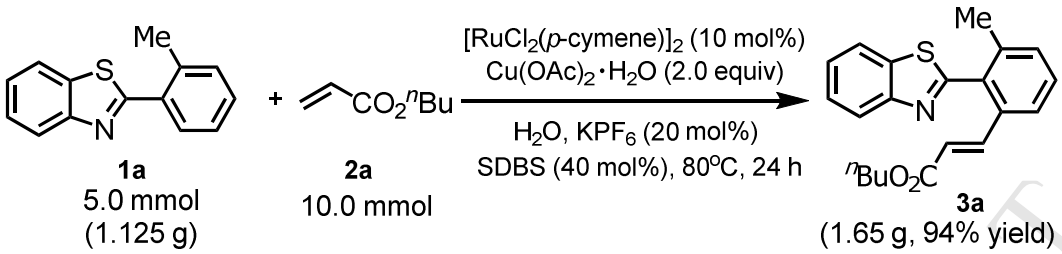


[a] Reaction conditions: 2-arylthiazoles **4** (0.3 mmol), *n*-butyl acrylate **2a** (0.6 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 ^oC, 24 h.

[b] Isolated yield.

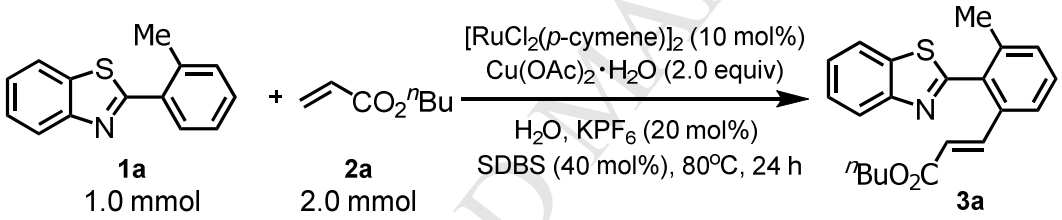
To further investigate the scalability of the present reaction, we proceeded to run a gram-scale reaction of the 2-(*o*-tolyl)benzo[d]thiazole **1a** with *n*-butyl acrylate **2a** (**Scheme 4**). The alkenylated product **3a** was obtained in 94% isolated yield when the reaction was scaled by 25 times to 5.0 mmol.

Scheme 4 Gram-Scale Synthesis



To check the reusability of the reaction medium and catalytic system, the akenylation of 2-(*o*-tolyl)benzo[d]thiazole **1a** with *n*-butyl acrylate **2a** was studied under the standard conditions (**Scheme 5**). We observed that this Ru-catalytic system could be recycled three times without obviously loss of activity.

Scheme 5 Recycle of the catalytic system



	Recycle			
	1	2	3	4
Yield (%)[a,b]	87	86	80	50

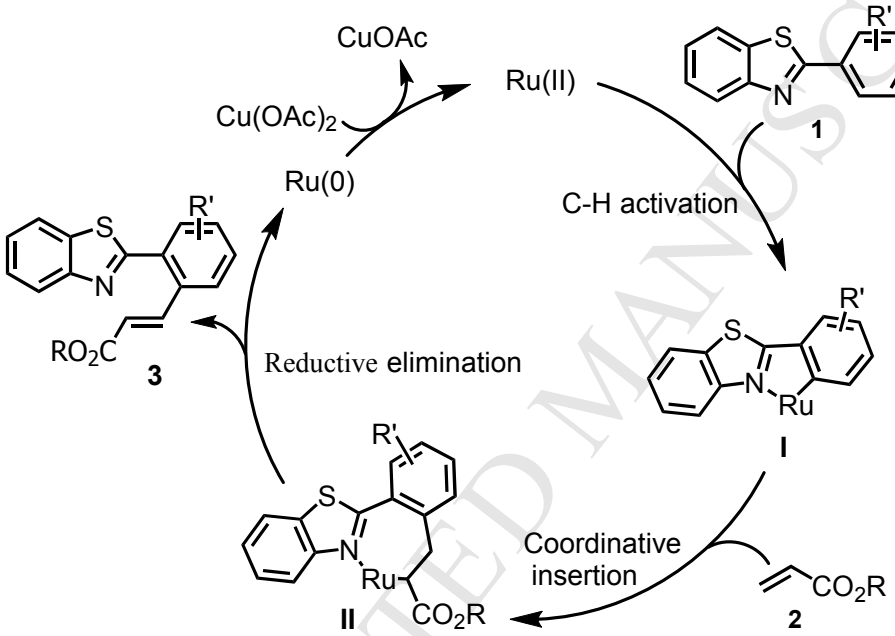
[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (1.0 mmol, 225 mg), butyl acrylate **2a** (2.0 mmol, 290 ul), [$RuCl_2$(*p*-cymene)] (10 mol%, 61 mg), $Cu(OAc)_2 \cdot H_2O$ (2.0 mmol, 399 mg), KPF_6 (20 mol%, 37 mg), SDBS (20 mol%, 140 mg), H_2O (10.0 mL), 80 °C, 24 h.

[b] Isolated yield.

Based on the previous results,[7-11] the mechanism of ruthenium-catalyzed oxidative C–H bond alkenylation may involve the following steps (**Scheme 6**): (i) *ortho*-C–H

bond activation in the presence of ruthenium(□) complexes **I** to form the cyclometallated intermediate; (□) the coordinative insertion of alkene **2** into the metallacycle to give the seven-membered Ru(□)-cycle **II**; (□) *β*-hydride elimination to afford the desired alkenlated product **3** and Ru(0); (□) the reoxidation of Ru(0) by Cu(□) to regenerate the active cationic catalyst Ru(□).

Scheme 6 Possible Mechanism of the Alkenylation



3. Conclusions

In summary, we have developed a highly efficient ruthenium(□)-catalyzed regioselective *ortho*-C–H bond alkenylation of a variety of substituted 2-arylbenzo[d]thiazoles and 2-arylthiazoles with diverse acrylates. The conditions are mild simply with water as a green reaction medium in the presence of catalytic amount of anionic surfactant SDBS at 80 ^{o}C, and using commercially available and

inexpensive $Cu(OAc)_2 \cdot H_2O$ as oxidant. In addition, the catalytic system could be carried out smoothly on a gram scale.

4. Experimental

4.1 General procedure for ruthenium-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles 1 in aqueous solution of anionic surfactant sodium dodecylbenzenesulfonate (SDBS)

A suspension of 2-arylbenzo[d]thiazoles **1** (0.2 mmol), acrylates **2** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (12.2 mg, 10 mol%), KPF_6 (7.4 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (79.8 mg, 2.0 equiv), and SDBS (27.8 mg, 40 mol%) in H_2O (2.0 mL) was stirred at 80 ^oC under air for 24 h. After that, the solution was extracted with EtOAc. The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 10/1) to yield alkenlated product **3**.

4.1.1 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3a***. Yellow oil (90%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.57 (dd, J = 9.5, 4.4 Hz, 1H), 7.54 (s, 1H), 7.53 – 7.48 (m, 1H), 7.48 – 7.42 (m, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 4.06 (t, J = 6.5 Hz, 2H), 2.25 (s, 3H), 1.58 – 1.48 (m, 2H), 1.26 (d, J = 15.1 Hz, 2H), 0.81 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.2, 153.3, 141.8, 138.2, 136.3, 134.6, 133.9, 131.7, 129.9, 126.2, 125.4, 123.9, 123.6, 121.5, 120.5, 64.2, 30.5, 20.1, 19.0, 13.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S$: 352.1366; found: 352.1356.

4.1.2 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-methoxyphenyl)acrylate ***3b***. Pale yellow oil (50%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.55 – 7.39 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 1.56 (d, *J* = 8.0 Hz, 2H), 1.32 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 162.4, 157.9, 153.0, 142.6, 136.5, 136.3, 131.1, 125.9, 125.3, 123.6, 123.2, 121.3, 120.8, 119.3, 112.3, 64.3, 56.0, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$: 368.1315; found: 368.1315.

4.1.3 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-chlorophenyl)acrylate ***3c***. Pale yellow oil (65%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 8.6 Hz , 2H), 7.43-7.50 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.07 (t, *J* = 6.4 Hz, 2H), 1.50-1.57 (m, 2H), 1.22-1.29 (m, 2H), 0.81 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.6, 153.1, 140.7, 140.0, 136.4, 135.0, 133.1, 131.0, 130.9, 126.4, 125.8, 124.9, 124.0, 122.0, 121.6, 64.5, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}ClNO_2S$: 372.0820; Found: 372.0820.

4.1.4 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-fluorophenyl)acrylate ***3d***. Pale yellow oil (83%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.16 (dd, *J* = 0.6, 7.8 Hz, 1H), 7.95 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.91 (d, *J* = 15.6 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.44-7.50 (m, 2H), 7.26 (dt, *J* = 1.2, 8.4 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.56-1.62 (m, 2H), 1.31-1.36 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 160.6 (d, $^1J_{C\text{-}F}$ = 250.8 Hz), 159.2, 153.1, 141.6 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 136.9 (d, $^4J_{C\text{-}F}$ = 1.8 Hz), 136.3 (d, $^3J_{C\text{-}F}$ = 9.5 Hz), 131.5, 131.4, 126.3, 125.8, 123.9, 123.0 (d, $^4J_{C\text{-}F}$ = 3.9 Hz), 121.9 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 121.4,13.7, 117.0 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 64.5, 30.7, 19.2; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{20}H_{19}FNO_2S$: 356.1115; Found: 356.1115.

4.1.5 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-nitrophenyl)acrylate ***3e***. Purple oil (61%); R_f = 0.5 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 13.5, 8.1 Hz, 2H), 7.96 (t, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.53 (ddd, *J* = 26.0, 11.2, 5.6 Hz, 3H), 6.44 (d, *J* = 15.9 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.29 (s, 2H), 0.82 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.3, 153.1, 150.0, 139.3, 137.2, 136.4, 130.9, 130.8, 128.4, 126.6, 126.0, 125.4, 124.0, 123.6, 121.6, 64.7, 30.5, 19.0, 13.6; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{20}H_{19}N_2O_4S$: 383.1060; Found: 383.1069.

4.1.6 (E)-butyl 3-(3-chloro-2-(6-methylbenzo[d]thiazol-2-yl)phenyl)acrylate ***3f***. Pale yellow oil (62%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.66 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.36-7.40 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 6.45 (dd, *J* = 4.8, 15.6 Hz,

1H), 3.99 (t, *J* = 5.6 Hz, 2H), 2.45 (s, 3H), 1.42-1.47 (m, 2H), 1.14-1.25 (m, 2H), 0.74 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 161.4, 151.3, 140.8, 136.9, 136.6, 136.0, 135.0, 133.3, 130.9, 130.8, 128.0, 124.9, 123.4, 121.9, 121.2, 64.5, 30.6, 21.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}ClNO_2S$: 386.0976; Found: 386.0986.

4.1.7 (E)-butyl 3-(3-chloro-2-(6-fluorobenzo[d]thiazol-2-yl)phenyl)acrylate ***3g***. Pale yellow oil (86%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.12 (m, 1H), 7.66 (t, *J* = 7.4 Hz 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.44-7.48 (m, 2H), 7.31 (t, *J* = 8.8 Hz, 1H), 6.40 (d, *J* = 16.4 Hz, 1H), 4.09 (t, *J* = 6.0 Hz, 2H), 1.56 (t, *J* = 6.0 Hz, 2H), 1.25-1.30 (m, 2H), 0.82-0.86 (m, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.3 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 160.8 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 149.7 (d, $^3J_{C\text{-}F}$ = 11.5 Hz), 140.5, 137.5 (d, $^3J_{C\text{-}F}$ = 11.7 Hz), 136.9, 134.9, 132.7, 131.2, 130.9, 125.0, 125.0 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 122.1, 115.2 (d, $^2J_{C\text{-}F}$ = 24.7 Hz), 107.7 (d, $^2J_{C\text{-}F}$ = 27.0 Hz), 64.5, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{18}ClFNO_2S$: 390.0725; Found: 390.0731.

4.1.8 (E)-butyl 3-(3-fluoro-2-(6-methylbenzo[d]thiazol-2-yl)phenyl)acrylate ***3h***. Pale yellow oil (80%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H), 7.72 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.44-7.47 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 8.8 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 4.14 (t, *J* = 6.2 Hz, 2H), 2.51 (s, 3H), 1.58-1.63 (m, 2H),

1.26-1.37 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 161.6 (d, $^{1}J_{C\text{-}F}$ = 249.6 Hz), 158.1, 151.3, 141.7 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 136.9, 136.5 (d, $^{4}J_{C\text{-}F}$ = 2.4 Hz), 136.0, 131.3 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 128.0, 123.4, 123.0 (d, $^{4}J_{C\text{-}F}$ = 3.9 Hz), 122.2, 121.7, 121.0, 116.9 (d, $^{2}J_{C\text{-}F}$ = 22.2 Hz), 64.4, 30.7, 21.6, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}FNO_2S$: 370.1272; Found: 370.1277.

4.1.9 (E)-butyl 3-(2-(6-chlorobenzo[d]thiazol-2-yl)-3-fluorophenyl)acrylate ***3i***. Pale yellow oil (83%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 3H), 1.26-1.38 (m, 2H), 1.58-1.65 (m, 2H), 2.24 (s, 3H), 4.15 (t, J = 6.4 Hz, 2H), 6.42 (d, J = 15.6 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H), 7.47-7.58 (m,3H), 7.90-7.93 (m, 2H), 8.06 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.7, 64.5, 117.0 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 121.0, 121.4 (d, $^{3}J_{C\text{-}F}$ = 15.0 Hz), 122.0, 123.2 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 124.6, 127.2, 131.7 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 131.9, 136.9, 137.4, 141.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 151.5, 159.8, 160.5 (d, $^{1}J_{C\text{-}F}$ = 250.1 Hz), 166.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{18}ClFNO_2S$: 390.0725; Found: 370.0729.

4.1.10 (E)-butyl 3-(3-fluoro-2-(6-fluorobenzo[d]thiazol-2-yl)phenyl)acrylate ***3j***. Pale yellow oil (79%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (dt, J = 2.0, 7.4 Hz, 3H), 1.25-1.38 (m, 2H), 1.59-1.63 (m, 2H), 4.15 (dt, J = 2.2, 6.4 Hz, 2H), 6.43 (dd, J = 2.2, 16.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.48-7.50 (m, 1H), 7.55 (d, J = 8.0Hz, 1H), 7.63 (d, J = 8.0Hz, 1H), 7.90 (dt, J = 1.8, 15.6 Hz, 1H), 8.08-8.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.7, 64.5, 107.5

(d, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 115.2(d, $^{2}J_{C\text{-}F}$ = 24.6 Hz), 116.9 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz), 121.5 (d, $^{3}J_{C\text{-}F}$ = 13.8 Hz), 121.9, 123.1 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 124.9 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 131.6 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 136.9 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 137.2, 137.4 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 141.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 149.7 (d, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 159.0 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 160.5 (d, $^{1}J_{C\text{-}F}$ = 250.7 Hz), 160.5 (d, $^{1}J_{C\text{-}F}$ = 246.3 Hz), 166.3; HRMS (ESI): m/z $[M + H]^{+}$ calcd for $C_{20}H_{18}F_2NO_2S$: 374.1021; Found: 374.1021.

4.1.11 (E)-butyl 3-(2-(6-chlorobenzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3k***. Yellow oil (78%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.24 (s, 3H), 1.55 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.27 – 1.22 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.8, 151.8, 141.6, 138.2, 137.5, 134.6, 133.4, 131.7, 131.6, 130.1, 127.1, 124.4, 124.0, 121.1, 120.7, 64.3, 30.6, 20.1, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^{+}$ calcd for $C_{21}H_{21}ClNO_2S$: 386.0976; Found: 386.0984.

4.1.12 (E)-butyl 3-(2-(6-fluorobenzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3l***. Yellow oil (85%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.09 (m, 1H), 7.58-7.63 (m, 2H), 7.50 (d, *J* = 16.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.27-7.35 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.25 (s, 3H), 1.50-1.58 (m, 2H), 1.24-1.29 (m, 2H), 0.83 (t, *J* = 7.2Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 166.5, 165.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 160.7 (d, $^1J_{C\text{-}F}$ = 244.9 Hz), 150.0 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 141.7, 138.3, 137.4 (d, $^3J_{C\text{-}F}$ = 10.9 Hz), 134.6, 133.6, 131.8, 130.1, 124.7 (d, $^3J_{C\text{-}F}$ = 9.6 Hz), 124.0, 120.7, 115.0 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 107.7 (d, $^2J_{C\text{-}F}$ = 25.6 Hz), 64.3, 30.6, 20.2, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}FNO_2S$: 370.1272; Found: 370.1272.

4.1.13 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-4-methylphenyl)acrylate ***3m***. Yellow oil (75%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.31(d, *J* = 16.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* =7.6 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.10 (t, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.53-1.58 (m, 2H), 1.28-1.37 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.9, 166.4, 153.9, 143.0, 140.3, 135.9, 133.3, 131.5, 131.3, 127.7, 126.4, 125.4, 123.7, 121.4, 120.1, 64.3, 30.8, 21.3, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S$: 352.1366; Found: 352.1369.

4.1.14 (E)-butyl 3-(2-(6-chlorobenzo[d]thiazol-2-yl)-4-methylphenyl)acrylate ***3n***. Yellow oil (82%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.31 (d, *J* =16.0 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.81 (s, 1H), 7.53-7.57 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.12 (t, *J* = 6.2 Hz, 2H), 2.36 (s, 3H), 1.55-1.62 (m, 2H), 1.18-1.37 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H),; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.0, 166.8, 152.4, 142.8, 140.4,

136.9, 132.8, 131.5, 131.4, 131.3, 127.8, 127.2, 124.4, 121.0, 120.3, 64.4, 30.8, 21.3, 19.2,13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}ClNO_2S$: 386.0976; Found: 386.0976.

4.1.15 (E)-butyl 3-(2-(6-fluorobenzo[d]thiazol-2-yl)-4-methylphenyl)acrylate ***3o***. Yellow oil (72%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 16.0 Hz , 1H), 8.05-8.07 (m, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.60 (s, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 9.2 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.19 (s, 2H), 2.44 (s, 3H), 1.65 (t, *J* = 4.8 Hz, 2H), 1.42 (d, *J* = 6.4 Hz, 2H), 0.93 (dt, *J* = 1.6, 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.2 (d, $^4J_{C\text{-}F}$ = 2.6 Hz), 160.6 (d, $^1J_{C\text{-}F}$ = 244.8 Hz), 150.6 (d, $^4J_{C\text{-}F}$ = 1.4 Hz), 142.9, 140.4, 136.8 (d, $^3J_{C\text{-}F}$ = 10.9 Hz), 133.0, 131.4 (d, $^4J_{C\text{-}F}$ = 6.3 Hz), 131.2, 127.8, 124.7 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 120.2, 115.1 (d, $^2J_{C\text{-}F}$ = 24.2 Hz), 107.7, 107.5, 64.4, 30.8, 21.3, 19.2, 13.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}FNO_2S$: 370.1272; Found: 370.1272.

4.1.16 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-4-chlorophenyl)acrylate ***3p***. Colorless oil (69%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.35 (d, *J* = 15.9 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.55 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.51 – 7.39 (m, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.43 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.5, 164.5, 153.8, 141.9, 135.8, 135.7, 134.7, 132.5, 130.7, 130.4, 129.1, 126.6,

125.8, 123.9, 121.5, 121.4, 64.5, 30.7, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}ClNO_2S$: 372.0820; Found: 372.0820.

4.1.17 (E)-butyl 3-(4-chloro-2-(6-methylbenzo[d]thiazol-2-yl)phenyl)acrylate ***3q***. Pale yellow oil (45%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 16.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.71 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.2 Hz, 2H), 2.51 (s, 3H), 1.64-1.71 (m, 2H), 1.39-1.45 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 163.5, 152.0, 142.1, 136.1, 136.1, 135.7, 134.9, 132.5, 130.6, 130.3, 129.1, 128.3, 123.4, 121.4, 121.2, 64.5, 30.8, 21.6, 19.2, 13.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}ClNO_2S$: 386.0976; Found: 386.0982.

4.1.18 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)-5-methoxyphenyl)acrylate ***3r(mono)***. Colorless oil (40%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 16.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.22 (d , *J* = 6.0 Hz, 2H), 3.90 (s, 3H), 1.68 (s, 2H), 1.44 (t, *J* = 6.6 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.2, 161.0, 154.0, 143.4, 135.6, 132.6, 126.3, 126.2, 125.2, 123.5, 121.3, 121.2, 115.8, 112.6, 64.5, 55.6, 30.8, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$: 368.1315; Found: 368.1318.

4.1.19 (2E,2'E)-dibutyl 3,3'-(2-(benzo[d]thiazol-2-yl)-5-methoxy-1,3-phenylene)diacrylate ***3r(di)***. Colorless oil (20%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.55-7.59 (m, 3H), 7.46 (s, 1H), 7.25 (s, 2H), 6.38 (d, *J* = 15.6 Hz, 2H), 4.09 (d, *J* = 3.2 Hz, 4H), 3.93 (s, 3H), 1.26 (s, 8H), 0.82-0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.3, 160.6, 141.4, 136.9, 136.7, 127.0, 126.5, 125.7, 123.9, 121.6, 121.4, 113.2, 64.5, 55.7, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{28}H_{32}NO_5S$: 494.1995; Found: 494.1996.

4.1.20 (E)-butyl 3-(2-(benzo[d]thiazol-2-yl)phenyl)acrylate ***3s(mono)***. Pale yellow oil (50%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 16.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.68-7.78 (m, 2H), 7.43-7.49 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 1.59-1.63 (m, 2H), 1.34-1.39 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.3, 154.0, 143.2, 135.9, 134.1, 133.4, 131.0, 130.4, 129.9, 127.8, 126.4, 125.5, 123.8, 121.4, 121.1, 64.4, 30.8, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{20}NO_2S$: 338.1209; Found: 338.1214.

4.1.21 (2E,2'E)-dibutyl 3,3'-(2-(benzo[d]thiazol-2-yl)-1,3-phenylene)diacrylate ***3s(di)***. Pale yellow oil (30%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.6 Hz,

2H), 7.53-7.59 (m, 4H), 7.49 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 2H), 4.09 (t, *J* = 6.8 Hz, 4H), 1.51-1.58 (m, 4H), 1.25-1.29 (m, 4H), 0.75 (t, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.2, 153.2, 141.2, 136.5, 135.5, 134.1, 130.4, 127.8, 126.6, 125.9, 124.0, 121.6, 121.5, 64.4, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{30}NO_4S$: 464.1890; Found: 464.1890.

4.1.22 (E)-butyl 3-(2-(6-methylbenzo[d]thiazol-2-yl)phenyl)acrylate ***3t(mono)***. Yellow oil (60%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 15.9 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.79 (m, 1H), 7.76 – 7.70 (m, 2H), 7.49 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.33 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 2.52 (s, 3H), 1.72 – 1.64 (m, 2H), 1.42 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 165.2, 152.1, 143.3, 136.0, 135.7, 134.0, 133.5, 130.9, 130.2, 129.8, 128.0, 127.7, 123.3, 121.1, 120.9, 64.4, 30.8, 21.6, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{21}NO_2S$: 352.1366; found: 352.1373.

4.1.23 (2E,2'E)-dibutyl 3,3'-(2-(6-methylbenzo[d]thiazol-2-yl)-1,3-phenylene)diacrylate ***3t(di)***. Orange oil (30%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 3H), 7.60 – 7.51 (m, 3H), 7.37 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 4H), 2.54 (s, 3H), 1.54 (dd, *J* = 14.7, 6.8 Hz, 4H), 1.32 – 1.16 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 166.2, 162.0, 151.4, 141.3, 136.7, 136.0, 135.5, 134.2, 130.2, 128.2, 127.8, 123.4, 121.4, 121.1, 64.4, 30.6, 21.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{28}H_{31}NO_4S$: 478.2046; found: 478.2054.

4.1.24 (E)-tert-butyl 3-(2-(benzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3u***. Colorless oil (83%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.49 (m, 2H), 7.50 – 7.35 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 2.24 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.4, 153.3, 140.8, 138.2, 136.4, 134.7, 134.0, 131.5, 129.9, 126.3, 125.5, 123.8, 123.7, 122.2, 121.5, 80.4, 28.1, 20.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S$: 374.1185; Found: 374.1185.

4.1.25 (E)-ethyl 3-(2-(benzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3v***. Yellow oil (80%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 8.2Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 7.2 Hz, 2H), 2.25 (s, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.3, 153.4, 142.0, 138.3, 136.4, 134.6, 134.0, 131.7, 129.9, 126.3, 125.5, 124.0, 123.7, 121.6, 120.6, 60.4, 20.2, 14.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{18}NO_2S$: 324.1053; Found: 324.1053.

4.1.26 (E)-methyl 3-(2-(benzo[d]thiazol-2-yl)-3-methylphenyl)acrylate ***3w***. Yellow oil

(70%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.61 – 7.37 (m, 5H), 7.34 (d, J = 7.6 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 3.67 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.2, 153.3, 142.1, 138.4, 136.4, 134.5, 133.9, 131.8, 129.9, 126.3, 125.5, 124.1, 123.7, 121.6, 120.2, 51.6, 20.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{16}NO_2S$: 310.0896; Found: 310.0904.

4.2 General procedure for ruthenium-catalyzed *ortho*-oxidative alkenylation of 2-arylthiazoles 4 in aqueous solution of anionic surfactant sodium dodecylbenzenesulfonate (SDBS)

A suspension of 2-arylthiazoles **4** (0.3 mmol), acrylates **2** (0.6 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (18.3 mg, 10 mol%), KPF_6 (11.1 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (119.7 mg, 2.0 equiv), and SDBS (41.7 mg, 40 mol%) in H_2O (3.0 mL) was stirred at 80 ^{o}C under air for 24 h. After that, the solution was extracted with EtOAc. The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 10/1) to yield alkenlated product **5**.

*4.2.1 (E)-butyl 3-(3-methyl-2-(thiazol-2-yl)phenyl)acrylate **5a***. Yellow oil (85%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 3.3 Hz, 1H), 7.54 (t, J = 6.3 Hz, 2H), 7.39 (dd, J = 19.8, 11.9 Hz, 2H), 7.31 (d, J = 7.5 Hz, 1H), 6.30 (d, J = 15.9 Hz, 1H), 4.11 (t, J = 6.6 Hz, 2H), 2.19 (s, 3H), 1.61 (dt, J = 14.5, 6.7 Hz, 2H), 1.36 (dq, J = 14.6, 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 166.6, 164.6, 143.1, 142.2, 138.6, 135.0, 133.9, 131.6, 129.6, 124.0, 121.0, 120.2, 64.3, 30.6, 20.2, 19.1, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}NO_2S$: 302.1209; found: 302.1210.

4.2.2 (E)-butyl 3-(3-methoxy-2-(thiazol-2-yl)phenyl)acrylate ***5b***. Yellow oil (83%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 3.3 Hz, 1H), 7.77 (d, *J* = 15.9 Hz, 1H), 7.52 (d, *J* = 3.3 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 1.65 – 1.59 (m, 3H), 1.39 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.3, 157.6, 143.5, 142.5, 136.3, 130.4, 122.9, 120.9, 120.2, 119.6, 112.1, 64.3, 56.0, 30.7, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}NO_3S$: 318.1158; found: 318.1160.

4.2.3 (E)-butyl 3-(4-methyl-2-(thiazol-2-yl)phenyl)acrylate ***5c***. Yellow oil (92%); R_f = 0.3 (petroleum ether/ethyl acetate = 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 15.9 Hz, 1H), 7.95 (d, *J* = 3.3 Hz, 1H), 7.66 – 7.52 (m, 2H), 7.44 (d, *J* = 3.3 Hz, 1H), 7.32 – 7.15 (m, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.67 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.43 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 143.7, 143.2, 140.2, 133.3, 131.1, 130.8, 130.6, 127.6, 120.4, 119.7, 64.3, 30.7, 21.2, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}NO_2S$: 302.1209; found: 302.1211.

4.2.4 (E)-butyl 3-(5-methyl-2-(thiazol-2-yl)phenyl)acrylate ***5d(mono)***. Colorless oil (52%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 15.9 Hz, 1H), 7.94 (d, *J* = 3.3 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.51 (s, 1H), 7.41 (d, *J* = 3.3 Hz, 1H), 7.28 (s, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.73 – 1.64 (m, 2H), 1.44 (dq, *J* = 14.6, 7.4 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.5, 143.7, 143.6, 139.8, 133.4, 130.7, 130.6, 130.4, 128.3, 120.4, 120.1, 64.4, 30.7, 21.3, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}NO_2S$: 302.1209; found: 302.1212.

4.2.5 (2E,2'E)-dibutyl 3,3'-(5-methyl-2-(thiazol-2-yl)-1,3-phenylene)diacrylate ***5d(di)***. Yellow oil (42%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 3.3 Hz, 1H), 7.57 (d, *J* = 3.3 Hz, 1H), 7.54 (s, 2H), 7.47 (d, *J* = 15.9 Hz, 2H), 6.34 (d, *J* = 15.9 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 4H), 2.46 (s, 3H), 1.64 – 1.57 (m, 4H), 1.36 (dt, *J* = 14.6, 7.4 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.9, 143.4, 141.8, 140.0, 135.5, 131.3, 128.6, 121.8, 120.9, 64.4, 30.6, 21.4, 19.1, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{24}H_{29}NO_4S$: 428.1890; found: 428.1889.

4.2.6 (E)-butyl 3-(2-(thiazol-2-yl)phenyl)acrylate ***5e(mono)***. Yellow oil (32%); R_f = 0.4 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 15.9 Hz, 1H), 7.96 (d, *J* = 3.3 Hz, 1H), 7.73 (ddd, *J* = 16.6, 5.5, 3.4 Hz, 2H), 7.47 (ddd, *J* = 10.8, 8.2, 4.9 Hz, 3H), 6.43 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H),

1.72 – 1.63 (m, 2H), 1.48 – 1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.4, 143.8, 143.4, 133.6, 133.3, 130.5, 129.8, 129.7, 127.7, 120.7, 120.5, 64.4, 30.7, 19.2, 13.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{17}NO_2S$: 288.1053; found: 288.1050.

4.2.7 (2E,2'E)-dibutyl 3,3'-(2-(thiazol-2-yl)-1,3-phenylene)diacrylate ***5e(di)***. Yellow oil (56%); R_f = 0.2 (petroleum ether/ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 3.3 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 3.3 Hz, 1H), 7.50 (dd, *J* = 19.7, 11.9 Hz, 3H), 6.35 (d, *J* = 15.9 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 4H), 1.62 (dt, *J* = 14.5, 6.6 Hz, 4H), 1.44 – 1.30 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.6, 143.4, 141.5, 135.7, 133.9, 130.0, 127.9, 121.9, 121.2, 64.4, 30.6, 19.1, 13.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{27}NO_4S$: 414.1734; found: 414.1737.

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Graphical Abstract:

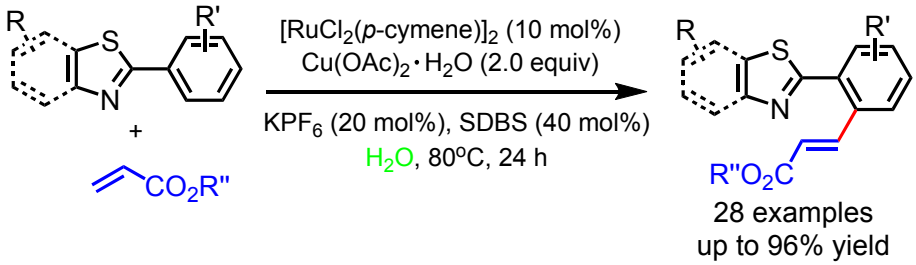
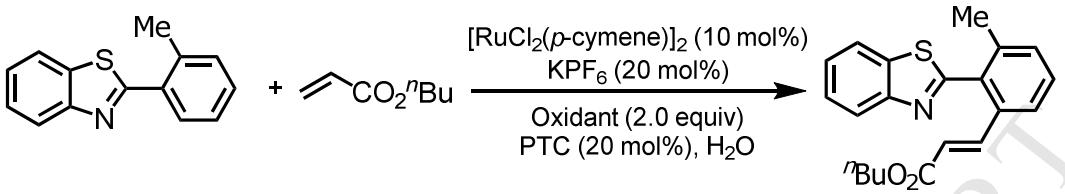


Figure 1 Selected bioactive examples containing 2-aryl-benzothiazole scaffold.

Table 1 Optimization of Ru-catalyzed *ortho*-oxidative alkenylation of 2-(*o*-tolyl)benzo[d]thiazole **1a** with butyl acrylate **2a**[a]



1a **2a** **3a**

Entry	Oxidant (x equiv)	PTC[c]	Yield (%)[b]
1	$Cu(OAc)_2 \cdot H_2O$ (2.0)	-	14
2	$Cu(OAc)_2 \cdot H_2O$ (2.0)	PEG 200	30
3	AgOAc (2.0)	PEG 200	20
4	Ag_2CO_3 (2.0)	PEG 200	25
5	$K_2S_2O_8$ (2.0)	PEG 200	Trace
6	CuBr (2.0)	PEG 200	Trace
7	$Cu(OAc)_2 \cdot H_2O$ (2.0)	18-Crown-6	Trace
8	$Cu(OAc)_2 \cdot H_2O$ (2.0)	TMAF	35
9	$Cu(OAc)_2 \cdot H_2O$ (2.0)	CTAC	25
10	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDS	22
11	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	48
12	$Cu(OAc)_2 \cdot H_2O$ (3.0)	SDBS	60
13	$Cu(OAc)_2 \cdot H_2O$ (4.0)	SDBS	84
14[d]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	90
15[e]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	60
16[f]	$Cu(OAc)_2 \cdot H_2O$ (2.0)	SDBS	80
17	$Cu(OAc)_2 \cdot H_2O$ (0.5)	SDBS	43
18	$Cu(OAc)_2 \cdot H_2O$ (0.2)	SDBS	16

[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (0.2 mmol), butyl acrylate **2a** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), additive (KPF_6, 20 mol%), phase transfer catalyst (PTC, 20 mol%), stirred at 80 °C for 24 h in H_2O (2 mL).

[b] Yield based on **1a**.

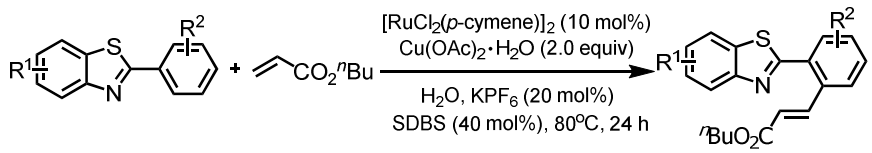
[c] TMAF: tetramethylammonium fluoride; CTAC: hexadecyl trimethyl ammonium chloride; SDS: sodium dodecyl sulfate; SDBS: sodium dodecylbenzenesulfonate.

[d] SDBS (40 mol%).

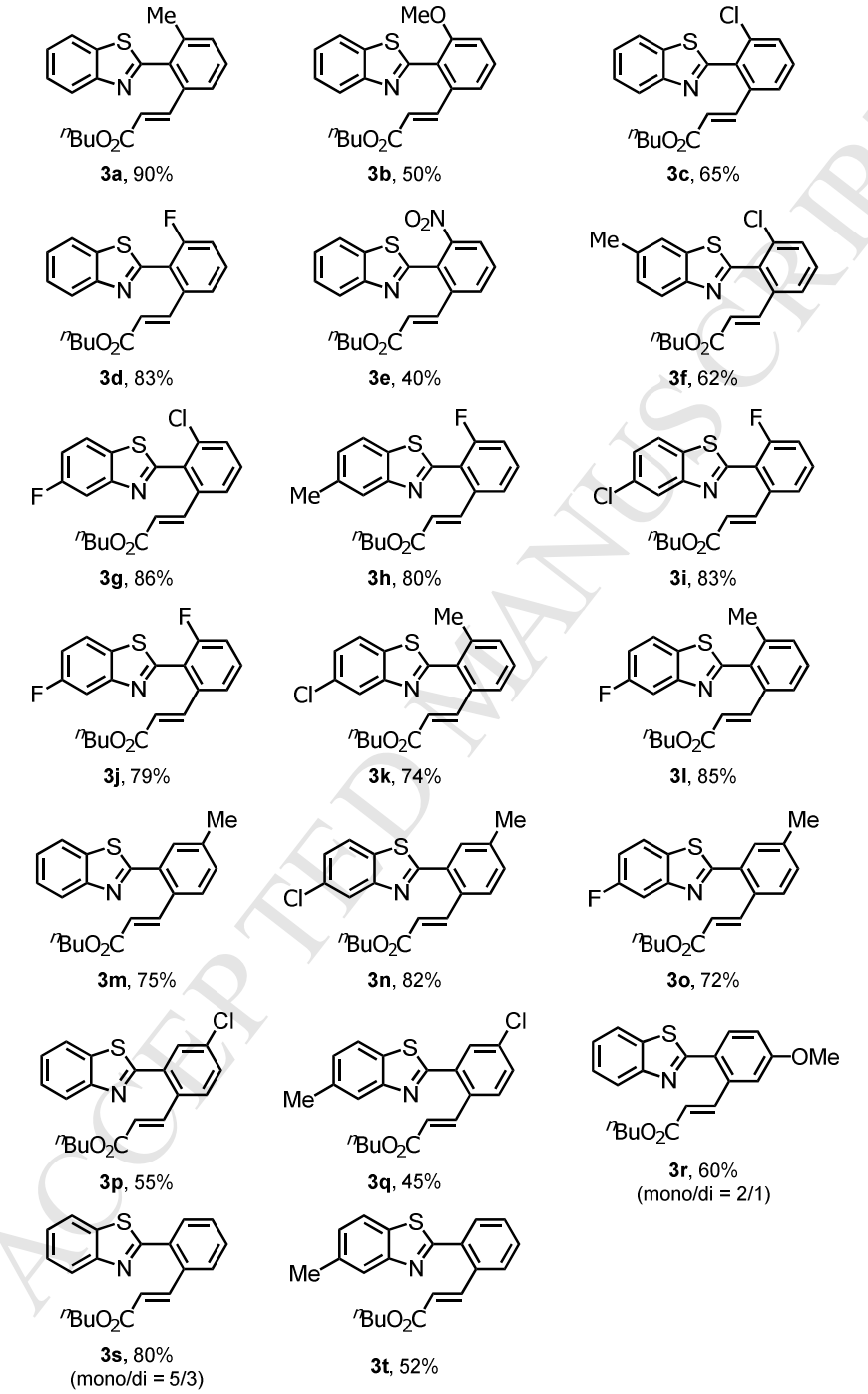
[e] Using $AgSbF_6$ as additive instead of KPF_6.

[f] At 60 °C.

Scheme 1 Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylbenzo[d]thiazoles in aqueous[a,b]



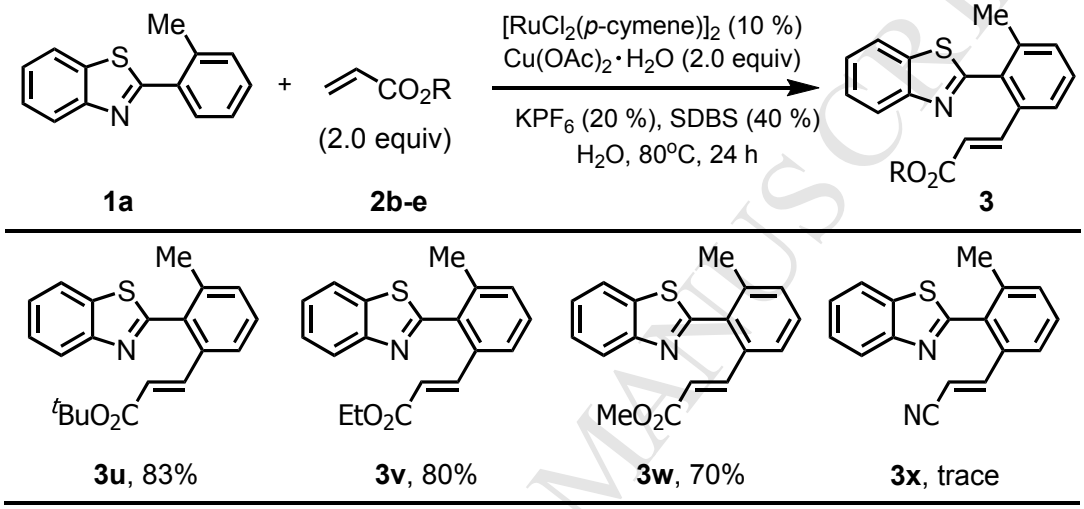
1 2a 3



[a] Reaction conditions: 2-arylbenzo[d]thiazole **1** (0.2 mmol), butyl acrylate **2a** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 °C, 24 h.

[b] Isolated yield.

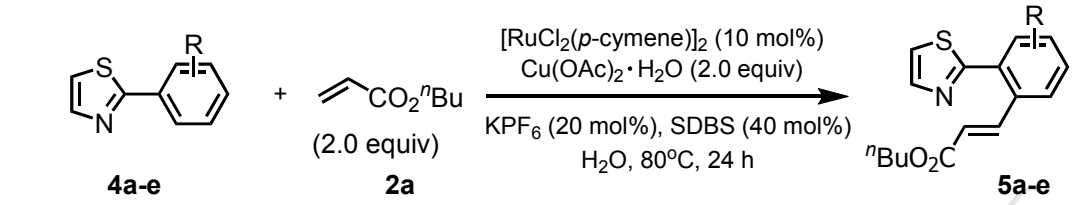
Scheme 2 Scope of alkenes[a,b]



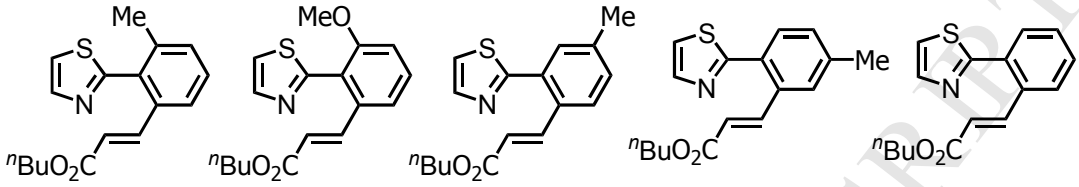
[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (0.2 mmol), acrylates **2b-e** (0.4 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 °C, 24 h.

[b] Isolated yield.

Scheme 3 Ru-catalyzed *ortho*-oxidative alkenylation of 2-arylthiazoles in aqueous[a,b]



4a-e **2a** **5a-e**

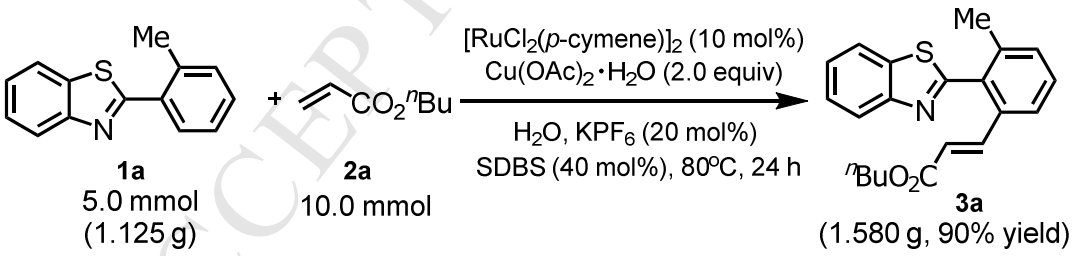


5a 85% **5b** 83% **5c** 92% **5d** 96% mono/di = 9/7 **5e** 88% mono/di = 4/7

[a] Reaction conditions: 2-arylthiazoles **4** (0.3 mmol), *n*-butyl acrylate **2a** (0.6 mmol, 2.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (10 mol%), KPF_6 (20 mol%), $Cu(OAc)_2 \cdot H_2O$ (2.0 equiv), SDBS (40 mol%), H_2O (2.0 mL), 80 °C, 24 h.

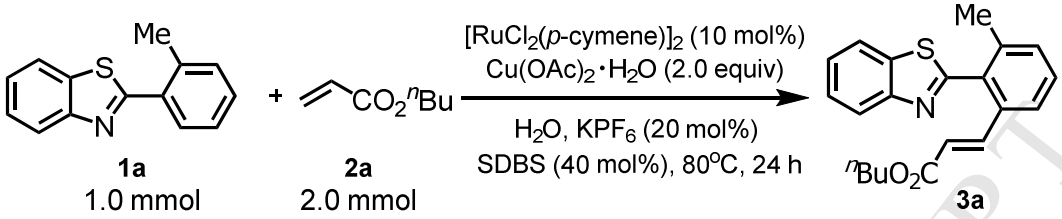
[b] Isolated yield.

Scheme 4 Gram-Scale Synthesis



1a 5.0 mmol (1.125 g) **2a** 10.0 mmol **3a** (1.580 g, 90% yield)

Scheme 5 Recycle of the catalytic system



	Recycle			
	1	2	3	4
Yield (%)[a,b]	87	86	80	50

[a] Reaction conditions: 2-(*o*-tolyl)benzo[d]thiazole **1a** (1.0 mmol, 225 mg), butyl acrylate **2a** (2.0 mmol, 290 ul), [$RuCl_2$(*p*-cymene)] (10 mol%, 61 mg), $Cu(OAc)_2 \cdot H_2O$ (2.0 mmol, 399 mg), KPF_6 (20 mol%, 37 mg), SDBS (20 mol%, 140 mg), H_2O (10.0 mL), 80 °C, 24 h.

[b] Isolated yield.

Scheme 6 Possible Mechanism of the Alkenylation