Rhodium(III)-catalyzed heteroatom-directed C–H allylation with allylic phosphonates and allylic carbonates at room temperature

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**Abstract**

The rhodium(III)-catalyzed mild and site-selective C–H allylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles with allylic phosphonates and allylic carbonates is described. This transformation provides an efficient construction of C2-allylated, crotylated and prenylated 2-arylbenzothiazoles and 2-arylbenzoxazoles. In addition, this protocol can be applied to the formation of 2-arylbenzothiazole scaffolds containing an allylic alcohol group by using of 4-vinyl-1,3-dioxolan-2-one and vinyl oxirane as coupling partners.

**1. Introduction**

2-Arylbenzothiazoles are common structural motifs found in heterocyclic compounds with biological and medicinal applications including anticancer, antibacterial, potassium channels activation, neurotransmission blockade, and neuroprotection. They also serve as versatile building blocks for organic light-emitting diodes (OLEDs), chemosensors, and photosensitizers. Therefore, the development of efficient protocols for the functionalization of these heterocyclic architectures are of great interest in organic synthesis. Recently, the transition-metal-catalyzed C–H functionalization of 2-arylbenzothiazoles and 2-arylbenzoxazoles with diverse coupling partners has been investigated. In this area, arylation, acetoxylation, acylation, hydroxylation, and halogenations under palladium catalysis were explored. In addition, the ruthenium–catalyzed olefination and amination reactions of 2-arylbenzothiazoles were also examined. Moreover, the rhodium-catalyzed C–H alkylation reactions of 2-arylbenzothiazoles with azido compounds were reported. However, to the best of our knowledge, the direct and catalytic C–H allylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles with allylic compounds has been unexplored.

Catalytic C–H allylation reaction has recently emerged as a versatile tool to deliver structurally intricate organic molecules. For example, Oi and Inoue first described the Ru(II)-catalyzed C–H allylation of 2-phenylpyridines with allylic acetates providing a regioisomeric mixture of olefin products. Later, Glorius reported beautiful works on the Rh(III)- or Co(III)-catalyzed regioselective terminal allylations of benzamides and indoles with allylic carbonates. Direct C–H allylations of electron-deficient polyfluoroarenes with allylic phosphonates and allylic carbonates under Cu(0), Cu(I) and Pd(II) catalysis were respectively reported. In addition, allenes were used in the Ir(I)-, Rh(I)- and Rh(III)- catalyzed allylation reactions to give allylated benzamide adducts. More recently, Li and Wang independently applied vinyl oxiranes and 4-vinyl-1,3-dioxolan-2-ones into aryl C–H allylation reaction under rhodium catalysis affording aromatic products with allylic alcohol moieties.

Inspired by our recent studies on the rhodium-catalyzed C–H functionalization of (hetero)aromatic compounds and in consideration of the biological application of functionalized 2-arylbenzothiazoles, we herein present the Rh(III)-catalyzed allylation, crotylation and prenylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles with allylic phosphonates or allylic carbonates to afford ortho-allylated 2-arylbenzothiazoles and 2-arylbenzoxazoles via C–H bond activation.

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2. Results and discussion

In a previous literature, we found that the combination of [Cp*RhCl2]2, AgSbF6 and Cu(OAc)2 in DCE solvent was most effective catalytic system to couple with indoline C–H bonds and allylic substrates. Thus, we used above reaction conditions in our initial study to couple with 1a and allyl acetate (2a) (Table 1), but our desired allylated product 3a was formed in 13% yield (Table 1, entry 1). Additionally, allylic carbonate 2b did not also provide a reasonable yield (Table 1, entry 2). Further investigation revealed that allylic phosphonate 2c as a coupling partner is unique in its ability to facilitate high levels of conversion (Table 1, entry 3). However, cationic ruthenium and cobalt catalysts were found to be ineffective for this transformation (Table 1, entries 4 and 5). Also, exclusion of either [Cp*RhCl2]2 and AgSbF6 resulted in no observation of the desired product 3a (data not shown). Screening of solvents under otherwise identical conditions revealed that THF was found to be an optimal solvent to furnish 3a in 76% yield, but other solvents such as toluene, MeCN, and t-AmOH were less effective (Table 1, entries 6–9). Further screening of additives revealed that Cu(OAc)2 was found to be the most effective in this coupling reaction (Table 1, entries 10 and 11). Furthermore, decreasing amount of Cu(OAc)2 to 50 or 30 mol % provided comparable yields (Table 1, entries 12 and 13). Finally, the coupling reaction was performed under a nitrogen atmosphere leading to a comparable yield (83%) of 3a (Table 1, entry 14). This result indicate that a role of Cu(OAc)2 as an oxidant can be ruled out in the catalytic cycle.

To evaluate the scope and limitation of this process, the optimal reaction conditions were applied to a range of 2-aryl substituted heteroarenes 1b–1o (Table 2). The reactions of meta-substituted 2-arylbenzothiazoles 1b–1d were found to be favored for this transformation to afford the desired products 3b–3d in moderate to good yields. Particularly noteworthy were the mono-selectivity and site-selectivity found at the less hindered position, as well as the tolerance of the reaction conditions to the bromo moiety, providing a versatile synthetic handle for further cross-coupling reactions. However, highly electron-rich 2-arylbenzothiazole 1e at the meta-position was found to be relatively less reactive under the present reaction conditions. This reaction was also compatible with ortho-substituted 2-arylbenzothiazole 1f to furnish 3f in 74% yield.

In addition, symmetric 2-phenylbenzoxazole (1g) was coupled with 2c under the optimal reaction conditions, resulting in a mixture of bis-allylated product 3g and mono-allylated product 3a with 1:1 ratio in 51% combined yield. Logically, it was thought that the ratio of 3g and 3a can be controlled by the amount of allylic phosphonate. Indeed, upon use of 3 equiv of 2c, the bis-allylated compound 3g was obtained as a major compound in 63% combined yield, albeit resulting in a low level of bis-selectivity (2:1). Moreover, 2-(p-methoxyphenyl)benzothiazole (1h) underwent smooth the bis-allylation reaction to afford the corresponding product 3h in 61% yield.

However, 2-(4-fluorophenyl)benzothiazole (1i) gave the bis-allylated compound 3i in 37% yield in conjunction with mono-allylated compound 3ia in 36% yield. In sharp contrast, 2-phenylbenzoxazole (1j) displayed a significant bis-selectivity under the identical reaction conditions to furnish the corresponding bis-allylated product 3j in 61% yield, and a trace amount of mono-allylated product was observed by 1H NMR or GC–MS analysis. In addition, meta-substituted 2-arylbenzoxazole 1k was found to be a good substrate in this transformation. Furthermore, we were pleased to observe the allylation reaction at a vinyl C–H bond, which provided the corresponding product 3k in 83% yield. Finally, this reaction was found to be comparable with 2-aryltiazoles 1m and 1n, but in the case of 2-arylmidazole 1o, a relatively low amount of product 3o was formed.

To further explore the scope and limitation of this transformation, substituted allylic phosphonates and allylic carbonates 2d–2g were screened to couple with 2-arylbenzothiazole 1a and 2-arylbenezoxalones 1j and 1k, as shown in Table 3. In sharp contrast to results of allylation reaction with allyl methyl carbonate (2b), both α-methyl-substituted allylic phosphonate 2d and α-methyl-substituted allylic carbonate 2e provided a crotylation product 4a in high yield. In addition, allyl octyl carbonate 2f was smoothly coupled with 1a to give a diastereomic mixture of crotylation product 4b in 42% yield. Notably, these crotylation reactions proceeded readily with complete γ-selectivity in case of branched allylic 

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allyl source</th>
<th>Catalyst (mol %)</th>
<th>Additive (mol %)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>DCE</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>DCE</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>DCE</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>DCE</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>DCE</td>
<td>N.R.</td>
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<tr>
<td>6</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>Toluene</td>
<td>Trace</td>
</tr>
<tr>
<td>7</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>t-AmOH</td>
<td>52</td>
</tr>
<tr>
<td>8</td>
<td>2c</td>
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<td>Cu(OAc)2 (100)</td>
<td>THF</td>
<td>76</td>
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<tr>
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<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>Trace</td>
<td>38</td>
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<tr>
<td>10</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>THF</td>
<td>78</td>
</tr>
<tr>
<td>11</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>THF</td>
<td>83</td>
</tr>
<tr>
<td>12</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (100)</td>
<td>THF</td>
<td>92</td>
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<tr>
<td>13</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (50)</td>
<td>THF</td>
<td>78</td>
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<tr>
<td>14</td>
<td>2c</td>
<td>[RhCp*Cl2]2 (2.5)</td>
<td>Cu(OAc)2 (50)</td>
<td>THF</td>
<td>83</td>
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</table>

### Footnotes

- Reaction conditions: 1a (0.3 mmol), 2a–2c (0.6 mmol), catalyst (quantity noted), AgSbF6 (10 mol %), additive (quantity noted), solvent (1 mL) under air at room temperature for 20 h in reaction tubes.
- Isolated yield by flash column chromatography.
- Under N2 atmosphere.
carbonates, and no migration of double bond on the products was detected. However, linear crotyl phosphonates and \( \beta \)-substituted allylic phosphonates did not yield the corresponding coupling products, presumably due to the increased steric congestion of electrophilic allylic phosphonates, interrupting formal SN-type addition with rhodacycle intermediate. To our delight, \( \alpha,\alpha \)-di-substituted allylic carbonate was found to be reactive under the current reaction conditions to afford ortho-prenylated product \( 4c \) in 40% yield. Moreover, we found that 2-arylbenzoxazoles \( 1j \) and \( 1k \) also participated in crotylation and prenylation reactions, furnishing the corresponding products \( 4d \) (54%, \( E:Z=1:2.6 \)), \( 4e \) (47%, \( E:Z=1.4:1 \)), and \( 4f \) (34%), respectively.

To further investigate the scope of allylation reactions, we first performed the coupling of 2-arylbenzothiazole \( 1a \) with 4-vinyl-1,3-dioxolan-2-one (2h) under the optimized reaction conditions. Fortunately, ortho-C–H allylated product \( 5a \) was formed in high yield (90%) with \( E/Z \) selectivity of 7.5:1 ratio (Scheme 1). In addition, 2-vinylloxirane (2i) was also coupled with \( 1a \) to afford a mixture of allylic alcohol \( 5a \) with 3.5:1 \( E/Z \) ratio in 49% yield as a result of olefin insertion and epoxide ring-opening, which is in agreement with the formal SN-type reaction mechanism.

Based on the previous literature on C–H allylation of arenes using allylic substrates\(^{15c,20} \), a plausible reaction mechanism is shown in Scheme 2. First, a cationic Rh(III) catalyst can coordinate
Table 3
Scope of allylic substrates

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>R₁</th>
<th>R²</th>
<th>Yield</th>
<th>(E:Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>PO(OEt)₂</td>
<td>Me</td>
<td>Me</td>
<td>88%</td>
<td>1:3.5</td>
</tr>
<tr>
<td>O</td>
<td>CO₂Me</td>
<td>Me</td>
<td>Me</td>
<td>42%</td>
<td>1.3:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Me</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Me</td>
<td>54%</td>
<td>1:2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Me</td>
<td>47%</td>
<td>1:4:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Me</td>
<td>Me</td>
<td>34%</td>
<td></td>
</tr>
</tbody>
</table>

* Reaction conditions: 1a, 1j and 1k (0.3 mmol), 2d–2g (0.6 mmol), [RhCp²Cl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), Cu(OAc)₂ (50 mol %), THF (1 mL) at room temperature for 20 h under air in reaction tubes. * Isolated yield by flash column chromatography. * Y = PO(OEt)₂. * Y = CO₂Me. * 2g (1.2 mmol, 4 equiv.).

Scheme 1. Direct allylation using 4-vinyl-1,3-dioxolan-2-one and 2-vinylimidazoline.
a nitrogen atom in 1a and subsequent C–H cleavage affords a rhodacycle intermediate 1.\(^2\) Next, olefin insertion of allylic phosphonate 2c into a Rh–C bond generates a seven-membered Rh(III) intermediate 1, which then undergoes β-oxygen elimination process to provide allylated product 3a and regenerates an active Rh(III) catalyst.

3. Conclusion

In conclusion, we disclosed the rhodium(III)-catalyzed direct C–H allylation of 2-arylbenzo[d]thiazoles and 2-arylbenzo[d]oxazoles with allylic phosphonates and allylic carbonates. These transformations have been applied to a wide range of substrates, and allow the generation of an array of ortho-allylated, ortho-crotylated, and ortho-prenylated 2-arylbenzothiazoles and 2-arylbenzoxazoles, which may find the application in the preparation of bioactive compounds.

4. Experimental

4.1. General

Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes (13 × 100 mm\(^2\)) were purchased from Fischer Scientific and dried in oven for overnight and cooled under a stream of nitrogen prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel 60F\(^2\) (Merck.). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (\(^1\)H and \(^13\)C NMR) were recorded on a Bruker Avance III 600 MHz spectrometer for CDCl\(_3\) solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual CHCl\(_3\) \(\delta_H (7.24 \text{ ppm})\) and CDCl\(_3\) \(\delta_C (77.2 \text{ ppm})\) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), sp (septet) and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (\(J\)) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm\(^{-1}\). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

4.2. General procedure for the allylation of 2-arylbenzothiazoles and 2-arylbenzoxazoles

To an oven-dried sealed tube charged with 2-m-tolybenzo[d]thiazole (1a) (67.6 mg, 0.3 mmol, 100 mol %), [RhCp\(_2\)Cl\(_2\)] (4.6 mg, 0.0075 mmol, 2.5 mol %), AgSbF\(_6\) (10.3 mg, 0.03 mmol, 10 mol %) and Cu(OAc)\(_2\) (27.2 mg, 0.15 mmol, 50 mol %) in THF (1 mL) was added allyl diethyl phosphate (2c) (116.5 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, \(n\)-hexanes/EtOAc = 100:1) to afford 1a in 92% yield.

4.2.1. 2-(2-Allyl-5-methylphenyl)benzo[d]thiazole (3a). Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.01 \text{ (d, } J=8.1 \text{ Hz, 1H)}, 7.83 \text{ (d, } J=7.9 \text{ Hz, 1H)}, 7.44–7.40 \text{ (m, 2H)}, 7.32 \text{ (dt, } J=8.1, 1.1 \text{ Hz, 1H}), 7.19–7.14 \text{ (m, 2H)}, 5.93–5.88 \text{ (m, 2H)}, 4.92–4.87 \text{ (m, 2H)}, 3.70 \text{ (d, } J=6.4 \text{ Hz, 2H}), 2.32 \text{ (s, 3H)}; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 165.8, 138.2, 136.5, 135.7, 134.8, 133.4, 133.1, 121.4, 115.4, 37.4, 20.9\); IR (KBr) \(\nu 3062, 2920, 2851, 1636, 1434, 1312, 1261, 1251, 1234, 1154, 1086, 970, 804, 755 \text{ cm}^{-1}\); HRMS (EI) calcd for C\(_{17}\)H\(_{15}\)NS [M]\(^+\) 265.0927, found 265.0925.

4.2.2. 2-(2-Allyl-5-bromophenyl)benzo[d]thiazole (3b). Light yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.10 \text{ (d, } J=8.1 \text{ Hz, 1H)}, 7.93 \text{ (d, } J=8.0 \text{ Hz, 1H}), 7.85 \text{ (d, } J=2.0 \text{ Hz, 1H}), 7.55–7.51 \text{ (m, 2H)}, 7.45–7.41 \text{ (m, 1H)}, 7.25 \text{ (d, } J=8.1 \text{ Hz, 1H}), 5.99–5.89 \text{ (m, 1H)}, 5.04–4.96 \text{ (m, 2H)}, 3.77 \text{ (d, } J=6.4 \text{ Hz, 2H}); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 165.8, 153.7, 138.2, 136.5, 135.7, 134.8, 133.4, 133.1, 121.4, 124.6, 125.5, 123.6, 121.5, 120.0, 116.5, 37.3; IR (KBr) \(\nu 3062, 2920, 2851, 1636, 1508, 1477, 1312, 1219, 1086, 970, 804, 755 \text{ cm}^{-1}\); HRMS (quadru-pole, EI) \(m/z\) calcd for C\(_{16}\)H\(_{12}\)BrNS \([M+H]^+\) 328.9874, found 328.9873.

4.2.3. 2-(2-Allyl-5-nitrophenyl)benzo[d]thiazole (3c). Light yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.58 \text{ (d, } J=2.4 \text{ Hz, 1H}), 8.26 \text{ (dd,}
2.4. 2-(3-Allylnaphthalene-2-yl)benz[d]thiazole (3d). Light yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.22 (s, 1H), 8.14 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.83–7.84 (m, 2H), 7.71–7.73 (m, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H, 7.24 (m, 2H), 7.01 (d, J = 7.8, 1H, 6.03–5.93 (m, 1H), 4.93–4.87 (m, 2H), 1.38 (s, 3H), 0.97 (d, J = 6.2 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 167.7, 158.2, 153.7, 136.8, 135.9, 134.4, 128.0, 127.2, 126.1, 125.1, 125.3, 123.0, 121.3, 114.9, 55.9, 30.6; IR (KBr) v 3071, 2915, 2848, 2360, 1708, 1609, 1571, 1496, 1359, 1260, 1041, 983, 758 cm⁻¹; HRMS (quadrupole, EI) m/z m/e ccalc for C20H15NS [M]+ 301.0925, found 301.0928.

2.4.1. 2-(2-Allyl-4-tert-butylcyclohex-1-enyl)benz[d]thiazole (3f). Colorless oil; 1H NMR (400 MHz, CDCl3) δ 8.70 (s, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.44–7.37 (m, 2H), 6.96 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.93–5.82 (m, 1H), 4.97–4.89 (m, 2H), 3.78 (s, 3H), 3.38 (d, J = 6.6 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 164.3, 157.9, 153.2, 141.4, 136.7, 136.6, 130.9, 127.5, 125.0, 123.4, 122.5, 122.0, 121.4, 116.0, 109.0, 55.9, 37.6; IR (KBr) v 3062, 2937, 2835, 1637, 1577, 1477, 1311, 1264, 1064, 952, 767, 688 cm⁻¹; HRMS (quadrupole, EI) m/z m/e ccalc for C19H15NOS [M]+ 281.0874, found 281.0875.

2.4.1. 2-(3-Allyl-5-methoxyphenyl)benz[d]thiazole (3g). Colorless oil; 1H NMR (400 MHz, CDCl3) δ 8.05 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 5.90–5.80 (m, 2H), 5.04–4.92 (m, 4H), 3.25 (d, J = 6.6 Hz, 4H); 13C NMR (100 MHz, CDCl3) δ 165.7, 163.5 (d, Jc-F = 2472 Hz), 153.2, 142.5 (d, Jc-F = 8.0 Hz), 136.3, 135.9, 128.7 (d, Jc-F = 3.1 Hz), 126.2, 125.5, 123.6, 121.5, 116.9, 114.2 (d, Jc-F = 21.8 Hz), 37.8; IR (KBr) v 3077, 2979, 2857, 2355, 1658, 1597, 1433, 1311, 1240, 1126, 983, 863, 759 cm⁻¹; HRMS (quadrupole, EI) m/z m/e ccalc for C19H16FNS [M]+ 309.0987, found 309.0986.

2.4.2. 2-(2-Allyl-4-fluorophenyl)benz[d]thiazole (3i). Colorless oil; 1H NMR (400 MHz, CDCl3) δ 8.12 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 5.90–5.80 (m, 2H), 5.04–4.92 (m, 4H), 3.25 (d, J = 6.6 Hz, 4H); 13C NMR (100 MHz, CDCl3) δ 165.7, 163.5 (d, Jc-F = 2472 Hz), 153.2, 142.5 (d, Jc-F = 8.0 Hz), 136.3, 135.9, 128.7 (d, Jc-F = 3.1 Hz), 126.2, 125.5, 123.6, 121.5, 116.9, 114.2 (d, Jc-F = 21.8 Hz), 37.8; IR (KBr) v 3077, 2979, 2857, 2355, 1658, 1597, 1433, 1311, 1240, 1126, 983, 863, 759 cm⁻¹; HRMS (quadrupole, EI) m/z m/e ccalc for C19H16FNS [M]+ 309.0987, found 309.0986.

2.5. 2-(3-Allyl-5-methoxyphenyl)benz[d]thiazole (3g). Colorless oil; 1H NMR (400 MHz, CDCl3) δ 8.12 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 5.90–5.80 (m, 2H), 5.04–4.92 (m, 4H), 3.25 (d, J = 6.6 Hz, 4H); 13C NMR (100 MHz, CDCl3) δ 165.7, 163.5 (d, Jc-F = 2472 Hz), 153.2, 142.5 (d, Jc-F = 8.0 Hz), 136.3, 135.9, 128.7 (d, Jc-F = 3.1 Hz), 126.2, 125.5, 123.6, 121.5, 116.9, 114.2 (d, Jc-F = 21.8 Hz), 37.8; IR (KBr) v 3077, 2979, 2857, 2355, 1658, 1597, 1433, 1311, 1240, 1126, 983, 863, 759 cm⁻¹; HRMS (quadrupole, EI) m/z m/e ccalc for C19H16FNS [M]+ 309.0987, found 309.0986.
2.4.21. 2-(5-Methyl-2-(3-methylbut-2-enyl)phenyl)benz[d]thiazole (4d). Light yellow oil; 1H NMR (400 MHz, CDCl3) δ 8.12 (d, J=6.1 Hz, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.56–7.52 (m, 2H), 7.45–7.42 (m, 1H), 7.32–7.24 (m, 2H), 5.54–5.35 (m, 2H), 3.73 (d, J=6.4 Hz, 2H), 2.42 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H). HRMS (quadrupole, El) m/z calculated for C25H21NO [M]+ 361.2406, found 361.2409.

4.3. Experimental procedure and characterization for the alkylation of 1a with 4-vinyl-1,3-dioxolan-2-one and 2-vinylloxirane

To an oven-dried sealed tube charged with 2-m-tolybenzo[d]thiazole (1a) (67.6 mg, 0.3 mmol, 100 mol %), [RhCp2Cl2]2 (4.6 mg, 0.0075 mmol, 2.5 mol %), AgSbF6 (10.3 mg, 0.03 mmol, 100 mol %) and Cu(OAc)2 (27.2 mg, 0.15 mmol, 50 mol %) in THF (1 mL) was
added 4-vinyl-1,3-dioxolan-2-one (2h) (68.5 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, n-hexanes/EtOAc=6:1) to afford 79.8 mg of 5a in 90% yield.

4.3.1. 4-[(2-Benzylthiazol-2-yl)-4-methylphenyl]but-2-en-1-ol (5a). Light yellow oil, E/Z ratio=7:5:1. 1H NMR (400 MHz, CDCl3) E-isomer: δ 8.17–8.11 (m, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.56–7.52 (m, 2H), 7.45–7.42 (m, 1H), 7.31–7.24 (m, 2H), 5.89–5.81 (m, 1H), 5.62–5.55 (m, 1H), 4.02 (d, J=5.7 Hz, 2H), 3.79 (d, J=6.5 Hz, 2H), 2.42 (m, 3H); Z-isomer: δ 8.17–8.11 (m, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.56–7.52 (m, 2H), 7.45–7.42 (m, 1H), 7.31–7.24 (m, 2H), 5.70–5.67 (m, 2H), 4.22 (d, J=5.0 Hz, 2H), 3.86 (d, J=5.8 Hz, 2H), 2.42 (m, 3H); 13C NMR (100 MHz, CDCl3) E-isomer: δ 167.9, 153.8, 136.3, 136.1, 135.7, 132.7, 131.6, 131.4, 131.1, 130.8, 130.3, 126.2, 125.2, 123.4, 121.4, 63.6, 36.0, 20.9; Z-isomer: δ 168.3, 153.8, 136.5, 136.3, 135.5, 132.4, 131.7, 131.4, 131.2, 130.6, 129.1, 126.3, 125.3, 123.3, 121.4, 58.3, 51.2, 20.9; IR (KBr) ν 3379, 3016, 2922, 2855, 2339, 1656, 1495, 1435, 1312, 1239, 1168, 1010, 982, 814, 758 cm⁻¹; HRMS (quadrupole, EI) m/z calcd for C21H₂2N₂Os [M⁺] 295.1031, found 295.1032.

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Supplementary data
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References and notes