Highly Regio- and Stereoselective Palladium(0)-Catalyzed Addition of Organoboronic Acids with 1,2-Allenic Sulfones, Sulfoxides, or Alkyl- or Aryl-Substituted Allenes in the Presence of Acetic Acid: An Efficient Synthesis of \(E\)-Alkenes

Hao Guo, Shengming Ma*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. of China
Fax +86(21)64167510; E-mail: masm@mail.sioc.ac.cn

Received 2 May 2007; revised 10 June 2007

Abstract: Two sets of reaction conditions were established to enable the palladium(0)-catalyzed addition of organoboronic acids with 1,2-allenic sulfones, sulfoxides, or alkyl- or aryl-substituted allenes in the presence of acetic acid. This reaction provides a new way for the stereoselective synthesis of tri- or tetrasubstituted \(E\)-alkenes. With arylboronic acids, the reactions of 1,2-allenic sulfones, sulfoxides, and alkyl-substituted allenes gave only 1–12\% of specific regioisomers; the reactions of aryl-substituted allenes afforded only \(E\)-alkenes in very high regioselectivity.

Key words: allenenes, sulfones, sulfoxides, palladium, addition reactions, boron

Introduction

The highly stereoselective synthesis of multisubstituted allenenes is one of the most important topics in organic chemistry, since many issues need be considered. Recently, transition-metal-catalyzed addition of organic boronic reagents with allenes has caught the attention of synthetic organic chemists. We1 and Oh et al.2 have reported the palladium-catalyzed reaction of functionalized allenes with organoboronic acids in the presence of acetic acid. It provides a new synthetic method for the formation of tri- or tetrasubstituted \(E\)-alkenes. However, the regio- and stereoselectivities have not been satisfactory. Yoshida and Ishara et al.3 reported the palladium-catalyzed coupling reaction of alkenic alcohols with organoboronic acids, in which the hydroxy group was used as a leaving group, and which yielded substituted dienes and trienes. Oh et al.4 also reported the palladium-catalyzed reaction of 1,6-allenynes with organoboronic acids in the presence of acetic acid, which afforded six-membered-ring products. In the meantime, some palladium-catalyzed three-component coupling reactions involving boronic reagents and allenes have also been reported.5 Very recently, Hayashi et al.6 reported the rhodium-catalyzed asymmetric addition of alkenes with arylboronic acids and allenes have also been reported.7 The highly stereoselective reaction of 1,6-allenynes with organoboronic acids in the presence of acetic acid, which afforded six-membered-ring products. We wish to report here, as part of our research program on the chemistry of allenes,7 the palladium-catalyzed addition of 1,2-allenic sulfones, sulfoxides, or alkyl- or aryl-substituted allenes with organoboronic acids in the presence of acetic acid.

Results and Discussion

Reactions of 1,2-Allenic Sulfones or Sulfoxides

Multisubstituted alk-1-enyl sulfoxides or sulfones are very important in organic synthesis,8 and therefore highly stereoselective methods for their preparation are highly desirable. On the other hand, 1,2-allenic sulfones or sulfoxides show good reactivities.9–11 For example, we have reported the hydrohalogenation of 1,2-allenic sulfones9a and sulfoxides9b and the E-halohydroxylation reaction of 1,2-allenic sulfoxides.9c We have also recently reported the first Heck-type cross-coupling reaction of 1,2-allenic sulfones with aryl halides.10 Mukai et al. have reported the intramolecular nucleophilic addition of 1,2-allenic sulfones.11 Considering their useful reactivities, we were interested to see whether we could control the regio- and stereoselectivities in the addition of 1,2-allenic sulfones or sulfoxides with organoboronic acids in the presence of acetic acid.

1,2-Allenic sulfones 2 are readily available by oxidation of the corresponding sulfoxides 1, which are easily prepared by the reaction of the corresponding propargylic alcohols with benzenesulfonyl chloride (PhSCl) (Scheme 1).12 Six compounds have been synthesized by this literature procedure.12 Under the catalysis of 10 mol\% of tetrakis(triphenylphosphine)palladium, the reaction of phenyl propa-1,2-dienyl sulfone 2a with phenylboronic acid 3a in the presence of 100 mol\% acetic acid failed to afford the addition products in dimethyl sulfoxide, dioxane, \(N,N\)-dimethylformamide, dimethyacetamide (DMA), or ethanol (Table 1, entries 1–5). Fortunately, the same reaction afforded the hydroarylation product in solvents such as, acetone, acetonitrile, diethyl ether, toluene, dichloromethane, and tetrahydrofuran (Table 1, entries 6–11). The best result was obtained in tetrahydrofuran, with product \((E)-4aa\) form-
in a regioselectivity of 91:9 (4aa/5aa) and a stereoselectivity of >99:1 ([E]-4aa/[Z]-4aa) (Table 1, entry 11).

With tetrahydrofuran as the solvent, the same reaction with other catalysts was also studied. Unfortunately, no better results were observed (Table 2).

We next studied the effect of the amount of acetic acid on this reaction (Table 3, entries 1–4), and found that 100 mol% acetic acid was necessary (Table 3, entry 3). The reaction under reflux afforded the product in lower yield (Table 3, entry 5).

The results obtained thus far were combined into conditions A [Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), THF, r.t.] and applied in the regio- and stereoselective formation of E-alkenyl sulfones (E)-4; some of the typical results are summarized in Table 4. The configurations of the C=C bonds in 4 were determined by an X-ray diffraction study of (E)-4ca (Figure 1).

Considering that the reactivities of 1,2-allenic sulfoxides are nearly always the same as those of 1,2-allenic sulfones, we tried the addition of phenyl propa-1,2-dienyl sulfoxide (1a) with phenylboronic acid (3a) under conditions A (Table 5, entry 1). This showed that, fortunately, the reaction can be extended to 1,2-allenic sulfoxides. The reaction of phenyl propa-1,2-dienyl sulfoxide (1a) with different organoboronic acids 3 under conditions A afforded products 6 in slightly lower yields than those of products 4 from 2a (Table 5, cf. Table 4). However, when we tried the reaction of 1,2-allenic sulfoxides 5b and 5c with phenylboronic acid (3a), none of the expected products formed (Scheme 2). Sulfoxide (E)-6ab can be converted into sulfone (E)-4ab in 52% yield by treatment with hydrogen peroxide in acetic acid (Scheme 3).

Biographical Sketches

**Hao Guo** was born in Tianjin, China in 1980. After graduation from Nankai University with a bachelor’s degree in 2003, he joined the graduate school of the Shanghai Institute of Organic Chemistry. He is currently a Ph.D. student in Professor Shengming Ma’s research group.

**Shengming Ma** is originally from Zhejiang Province, China. He received a B.S. degree in Chemistry from Hangzhou University (1986), and an M.S. (1988) and a Ph.D. degree (1990) from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. After postdoctoral research at the ETH in Switzerland and the Purdue University in the USA, he joined the faculty of the Shanghai Institute of Organic Chemistry (1997), where he is now the director of the State Key Laboratory of Organometallic Chemistry. Since February 2003 he has been jointly appointed by the SIOC and Zhejiang University, as Research Professor of Chemistry at SIOC and Cheung Kong Scholars Program Professor at Zhejiang University.
FEATURE ARTICLE

Palladium(0)-Catalyzed Addition of Organoboronic Acids with Allenes

The formation of sulfone \((E)\)-4ab from sulfoxide \((E)\)-6ab

Reactions of Alkyl- or Aryl-Substituted Allenes

Non-functionalized allenes are also readily available, but the reaction of deca-1,2-diene with (4-methoxyphenyl)boronic acid afforded the addition products in low selectivities. To further improve the selectivity, we studied the addition of alkyl-substituted allene 8a with phenylboronic acid (3a) under conditions A (Table 6, entry 1).

After some screening (Table 6, entries 2–8), conditions B [Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), dioxane, reflux] (Table 6, entry 4) were established for the highly stereo- selective addition of organoboronic acids with alkyl-

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**Table 1** Tetrakis(triphenylphosphine)palladium-Catalyzed Addition of Phenyl Propa-1,2-diethyl Sulfone (2a) with Phenylboronic Acid (3a) in Different Solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Ratio (^b) 4aa/5aa</th>
<th>Yield(^c) (%) of ((E))-4aa</th>
<th>Ratio(^b) ((E))-4aa/(Z)-4aa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>24</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>dioxane</td>
<td>16</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>9</td>
<td>–</td>
<td>trace</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>DMA</td>
<td>9</td>
<td>–</td>
<td>trace</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>EtOH</td>
<td>40</td>
<td>–</td>
<td>trace</td>
<td>–</td>
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<tr>
<td>6</td>
<td>acetone</td>
<td>65</td>
<td>81:19</td>
<td>70</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>MeCN</td>
<td>40</td>
<td>82:18</td>
<td>23</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>Et₂O</td>
<td>40</td>
<td>83:17</td>
<td>67</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>9</td>
<td>toluene</td>
<td>55</td>
<td>87:13</td>
<td>48</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>10</td>
<td>CH₂Cl₂</td>
<td>40</td>
<td>90:10</td>
<td>48</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>11</td>
<td>THF</td>
<td>22</td>
<td>91:9</td>
<td>68</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^a\) Reagents and conditions: 2a (0.25 mmol), 3a (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), solvent (3 mL), r.t., under N₂.

\(^b\) Determined by \(^1\)H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

\(^c\) Isolated yield.

\(^d\) Allene 2a (32%) was recovered.

\(^e\) Allene 2a (56%) was recovered.
### Table 2  Addition of Phenyl Propa-1,2-dienyl Sulfone (2a) with Phenylboronic Acid (3a) Catalyzed by Different Palladium Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Palladium catalyst</th>
<th>Time (h)</th>
<th>Ratio (^{b\text{ }4\text{aa}/5\text{aa}})</th>
<th>Yield(^{c\text{ }}) of (E)-4aa (^{b\text{ }}) Ratiob</th>
<th>Ratio (^{b\text{ }\text{(E)-4aa}/(Z)-4\text{aa}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(PhCN)(_2)Cl(_2)</td>
<td>65</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)(_2)</td>
<td>61</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>PdCl(_2)</td>
<td>65</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>PdCl(_2)(_x)</td>
<td>65</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PhCN)(_2)Cl(_2)(_x)</td>
<td>61</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>Pd(dba)(_2)</td>
<td>41</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>Pd(dba)(_2)(_x)</td>
<td>9</td>
<td>90:10</td>
<td>61</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)(_2)(_x)</td>
<td>12</td>
<td>90:10</td>
<td>78</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^{a\text{ }}\) Reagents and conditions: 2a (0.25 mmol), 3a (2.0 equiv), Pd catalyst (10 mol%), AcOH (100 mol%), THF (3 mL), r.t., under N\(_2\).

\(^{b\text{ }}\) Determined by \(^{1}\)H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

\(^{c\text{ }}\) Isolated yield.

\(^{d\text{ }}\) Allene 2a (57%) was recovered.

\(^{e\text{ }}\) Allene 2a (67%) was recovered.

\(^{f\text{ }}\) Allene 2a (79%) was recovered.

\(^{g\text{ }}\) PPh\(_3\) (20 mol%) was also used.

\(^{h\text{ }}\) Allene 2a (44%) was recovered.

\(^{i\text{ }}\) Allene 2a (84%) was recovered.

\(^{j\text{ }}\) Complex mixture.

### Table 3  Palladium(0)-Catalyzed Addition of Phenyl Propa-1,2-dienyl Sulfone (2a) with Phenylboronic Acid (3a) in the Presence of Different Amounts of Acetic Acid

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of AcOH (mol%)</th>
<th>Time (h)</th>
<th>Ratio (^{b\text{ }4\text{aa}/5\text{aa}})</th>
<th>Yield(^{c\text{ }}) of (E)-4aa (^{b\text{ }}) Ratiob</th>
<th>Ratio (^{b\text{ }\text{(E)-4aa}/(Z)-4\text{aa}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>24</td>
<td>86:14</td>
<td>65</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>24</td>
<td>87:13</td>
<td>68</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>22</td>
<td>91:9</td>
<td>68</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>24</td>
<td>90:10</td>
<td>57</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5(^{d\text{ }})</td>
<td>100</td>
<td>7</td>
<td>90:10</td>
<td>54</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^{a\text{ }}\) Reagents and conditions: 2a (0.25 mmol), 3a (2.0 equiv), Pd(PPh\(_3\))\(_4\) (10 mol%), AcOH, THF (3 mL), r.t., 24 h, under N\(_2\).

\(^{b\text{ }}\) Determined by \(^{1}\)H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

\(^{c\text{ }}\) Isolated yield.

\(^{d\text{ }}\) The reaction was carried out under reflux.
substituted allenes. The configurations of the C=C bonds in 9 were determined by the $^1$H–$^1$H NOESY spectra of (E)-9aa (Figure 2). The highest regioselectivity observed was 92:8 (Table 6, entry 4).

Some typical results of the reactions between alkyl-substituted allenes 8 and organoboronic acids 3 under conditions B are shown in Table 7. We then tried to extend conditions B to aryl-substituted allenes; typical results are shown in Table 8. It should be noted that both the regio- and stereoselectivities are excellent. Both electron-donating and electron-withdrawing groups can be attached to the aryl group (Table 8, entries 6–8).

**Figure 2** $^1$H–$^1$H NOESY interaction of (E)-9aa

**Table 4** Palladium(0)-Catalyzed Addition Reactions of 1,2-Allenic Sulfones 2 with Organoboronic Acids 3 under Conditions A

<table>
<thead>
<tr>
<th>Entry</th>
<th>R$^1$</th>
<th>2</th>
<th>R$^2$</th>
<th>3</th>
<th>Time (h)</th>
<th>Product 4</th>
<th>Ratio$^b$ 4/5</th>
<th>Yield$^b$ (%) of (E)-4</th>
<th>Ratio$^b$ (E)-4(Z)-4</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>2a</td>
<td>Ph</td>
<td>3a</td>
<td>22</td>
<td>4aa</td>
<td>91:9</td>
<td>68</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>2a</td>
<td>4-Tol</td>
<td>3b</td>
<td>22</td>
<td>4ab</td>
<td>&gt;99:1</td>
<td>62</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>2a</td>
<td>3-MeOC$_6$H$_4$</td>
<td>3c</td>
<td>59</td>
<td>4ac</td>
<td>&gt;97:3</td>
<td>35</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>2a</td>
<td>4-MeOC$_6$H$_4$</td>
<td>3d</td>
<td>17.5</td>
<td>4ad</td>
<td>93:7</td>
<td>78</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>2a</td>
<td>3-O$_2$NC$_6$H$_4$</td>
<td>3e</td>
<td>19</td>
<td>4ae</td>
<td>94:6</td>
<td>66</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td>2a</td>
<td>3-AcC$_6$H$_4$</td>
<td>3f</td>
<td>22</td>
<td>4af</td>
<td>&gt;99:1</td>
<td>80</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>2a</td>
<td>4-AcC$_6$H$_4$</td>
<td>3g</td>
<td>22</td>
<td>4ag</td>
<td>94:6</td>
<td>80</td>
<td>&gt;99:1</td>
</tr>
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<td>1-Naph</td>
<td>3h</td>
<td>21.5</td>
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<td>9</td>
<td>H</td>
<td>2a</td>
<td>(E)-CH=CH(CH$_2$)$_2$Me</td>
<td>3i</td>
<td>25</td>
<td>4ai</td>
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<td>10</td>
<td>H</td>
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<td>(E)-CH=CHPh</td>
<td>3j</td>
<td>11</td>
<td>4aj</td>
<td>94:6</td>
<td>52</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>11</td>
<td>Me</td>
<td>2b</td>
<td>Ph</td>
<td>3a</td>
<td>72</td>
<td>4ba</td>
<td>&gt;99:1</td>
<td>50</td>
<td>&gt;99:1</td>
</tr>
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<td>12</td>
<td>n-Bu</td>
<td>2c</td>
<td>Ph</td>
<td>3a</td>
<td>96</td>
<td>4ca</td>
<td>&gt;99:1</td>
<td>55</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

$^a$ Reagents and conditions (conditions A): 2 (0.25 mmol), 3 (2.0 equiv), Pd(PPh$_3$)$_4$ (10 mol%), AcOH (100 mol%), THF, r.t., under N$_2$.

$^b$ Determined by $^1$H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

$^c$ Isolated yield.

**Conclusion**

We have succeeded in establishing two sets of reaction conditions for the addition reaction of allenes with organoboronic acids: conditions A for the addition of organoboronic acids with 1,2-allenic sulfones or sulfoxides affording E-alkenyl sulfones or sulfoxides; conditions B for the addition of organoboronic acids with alkyl- or aryl-substituted allenes affording E-alkenes. The generality of this reaction was studied, with some typical results reported. Further studies in this area and the synthetic applications of this reaction are being carried out in our laboratory.

Melting points were determined on a SGW X-4 apparatus. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. $^1$H (300 MHz) and $^{13}$C (75.4 MHz) NMR spectra of samples in CDCl$_3$ (unless stated otherwise) were recorded on a Varian Mercury VX300 spectrometer. MS (EI, 70 eV) determinations were carried out on a HP 5973 spectrometer. HRMS (MALDI) determinations were carried out on a Ionspec MALDI-FTMS spectrometer. HRMS (EI) determinations were carried out on a Water GCT CA176 spectrometer. Elemental analyses were carried out on a Elementar Vario EL instrument. Column chromatography was performed on silica gel (10–40 u). The starting materials 1a,$^{12}$ 1b,$^{12}$ 1c,$^{12}$ 2a,$^{12}$ 2b,$^{12}$ 8a,$^{12}$ 8b,$^{14}$ 8c,$^{14}$ 8d,$^{14}$ 8e,$^{14}$ 11a,$^{13}$ 11b,$^{13}$ 11c,$^{13}$ and 11d,$^{13}$ were prepared according to literature procedures.
Table 5  Palladium(0)-Catalyzed Addition Reaction of Phenyl Propa-1,2-dienyl Sulfoxide (1a) with Different Organoboronic Acids 3 under Conditions A

\[
\text{PhOS} + \text{R-B(OH)_2} \xrightarrow{\text{Pd(PPh}_3\text{)}_4 (10 \text{ mol\%}), \text{AcOH (100 mol\%)}, \text{THF, r.t.}} \text{6a} + \text{7}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>3</th>
<th>Time (h)</th>
<th>Product 6</th>
<th>Ratio(^b) 6/7</th>
<th>Yield(^c) (%) of (E)-6</th>
<th>Ratio(^d) (E)-6/(Z)-6(^b)</th>
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<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>3a</td>
<td>72</td>
<td>6aa</td>
<td>94:6</td>
<td>50</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>4-Tol</td>
<td>3b</td>
<td>36</td>
<td>6ab</td>
<td>&gt;97:3</td>
<td>58</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>3-MeOCH(_2)H(_4)</td>
<td>3c</td>
<td>12</td>
<td>6ac</td>
<td>99:1</td>
<td>59</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>4-MeOCH(_2)H(_4)</td>
<td>3d</td>
<td>24.5</td>
<td>6ad</td>
<td>95:5</td>
<td>52</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>3-O(_2)NC(_6)H(_4)</td>
<td>3e</td>
<td>48</td>
<td>6ae</td>
<td>&gt;96:4</td>
<td>49</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6</td>
<td>4-Ac(_6)H(_4)</td>
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<td>48</td>
<td>6ag</td>
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</tr>
<tr>
<td>7</td>
<td>1-Naph</td>
<td>3h</td>
<td>24</td>
<td>6ah</td>
<td>&gt;94:6</td>
<td>41</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>(E)-CH=CH(CH(_2))(_3)Me</td>
<td>3k</td>
<td>72</td>
<td>6ak</td>
<td>&gt;92:8</td>
<td>53</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>9</td>
<td>(E)-CH=CHPh</td>
<td>3j</td>
<td>50</td>
<td>6aj</td>
<td>&gt;94:6</td>
<td>46</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^a\) Reagents and conditions (conditions A): 1a (0.25 mmol), 3 (2.0 equiv), Pd(PPh\(_3\))\(_4\) (10 mol\%), AcOH (100 mol\%), THF, r.t., under N\(_2\).

\(^b\) Determined by \(^\text{H}\) NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

\(^c\) Isolated yield.

Table 6  Palladium(0)-Catalyzed Addition of Alkyl-Substituted Allene 8a with Phenylboronic Acid (3a) in the Presence of Acetic Acid

\[
\text{n-C}_8\text{H}_{17} + \text{B(OH)_2} \xrightarrow{\text{Pd(PPh}_3\text{)}_4 (10 \text{ mol\%)}, \text{AcOH, dioxane}} \text{(E)-9aa} + \text{(Z)-9aa} + \text{10aa}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of AcOH (mol%)</th>
<th>Temperature</th>
<th>Time (h)</th>
<th>Yield(^d) (%) of 9aa + 10aa</th>
<th>Ratio(^e) 9aa/10aa</th>
<th>Ratio(^f) (E)-9aa/(Z)-9aa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^d)</td>
<td>100</td>
<td>r.t.</td>
<td>60</td>
<td>38</td>
<td>91:9</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2(^d)</td>
<td>100</td>
<td>reflux</td>
<td>8</td>
<td>75</td>
<td>90:10</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>reflux</td>
<td>18</td>
<td>64</td>
<td>90:10</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>reflux</td>
<td>9</td>
<td>75</td>
<td>92:8</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>reflux</td>
<td>5</td>
<td>68</td>
<td>90:10</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>reflux</td>
<td>9</td>
<td>42</td>
<td>90:10</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>reflux</td>
<td>9</td>
<td>45</td>
<td>92:8</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>reflux</td>
<td>9</td>
<td>44</td>
<td>91:9</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

\(^a\) Reagents and conditions: 8a (0.25 mmol), 3a (2.0 equiv), Pd(PPh\(_3\))\(_4\) (10 mol\%), dioxane (3 mL), under N\(_2\).

\(^b\) Isolated yield; the isomers could not be separated by flash chromatography (silica gel).

\(^d\) Determined by \(^\text{H}\) NMR (300 MHz) analysis of the crude reaction mixture obtained after evaporation.

\(^e\) THF was used as solvent.

\(^f\) The reaction was conducted in a Schlenk tube with a screw cap.
A solution of Hepta-1,2-dien-3-yl Phenyl Sulfone (2c) (441 mg, 2 mmol) and 30% H2O2 (0.6 mL) in AcOH (5 mL) was stirred at room temperature and monitored by 1H NMR spectroscopy, from which the ratio of 9:10 was determined (see Table 4). Purification of the residue by flash chromatography (silica gel, PE–Et2O, 20:1) gave (E)-4aa. Yield: 44 mg (68%); solid; mp 70–72 °C (Et2O–PE).

IR (neat): 1601, 1541, 1460, 1314, 1239, 1124 cm–1.

1H NMR (300 MHz, CDCl3): δ = 8.01–7.94 (m, 2 H), 7.65–7.51 (m, 3 H), 7.45–7.30 (m, 5 H), 6.61 (q, J = 1.2 Hz, 1 H), 2.53 (d, J = 1.2 Hz, 3 H).

IR (neat): 1541, 1460, 1314, 1239, 1124, 1011 cm–1.

1H NMR (300 MHz, CDCl3): δ = 5.73–5.64 (m, 10 H), 5.30–5.21 (m, 6 H), 5.07–5.00 (m, 4 H), 1.22–1.13 (m, 12 H), 1.02–0.93 (m, 10 H), 0.84–0.75 (m, 12 H), 0.71–0.62 (m, 10 H), 0.59–0.50 (m, 8 H), 0.50–0.41 (m, 8 H), 0.39–0.30 (m, 8 H), 0.29–0.20 (m, 8 H), 0.20–0.11 (m, 8 H), 0.11–0.02 (m, 8 H).

IR (neat): 3327, 2976, 1601, 1541, 1460, 1314, 1239, 1124 cm–1.

1H NMR (300 MHz, CDCl3): δ = 7.65–7.51 (m, 3 H), 7.45–7.30 (m, 5 H), 6.61 (q, J = 1.2 Hz, 1 H), 2.53 (d, J = 1.2 Hz, 3 H).

IR (neat): 3327, 2976, 1601, 1541, 1460, 1314, 1239, 1124 cm–1.

1H NMR (300 MHz, CDCl3): δ = 7.65–7.51 (m, 3 H), 7.45–7.30 (m, 5 H), 6.61 (q, J = 1.2 Hz, 1 H), 2.53 (d, J = 1.2 Hz, 3 H).

Phenylation (E)-2-(4-Tolyl)prop-1-en-1-yl Sulfone [(E)-4ab]

Compounds (E)-4aa and (E)-4bb were prepared similarly to compound (E)-4aa by conditions A. The reaction of (E)-4aa and (E)-4bb afforded crude (E)-4aa after evaporation of the solvent, filtration through a pad of silica gel, and evaporation to dryness, the resulting mixture was analyzed by 1H NMR spectroscopy, from which the ratio of (E)-4aa/(Z)-4aa was determined.

IR (neat): 3327, 2976, 1601, 1541, 1460, 1314, 1239, 1124 cm–1.

1H NMR (300 MHz, CDCl3): δ = 7.65–7.51 (m, 3 H), 7.45–7.30 (m, 5 H), 6.61 (q, J = 1.2 Hz, 1 H), 2.53 (d, J = 1.2 Hz, 3 H).

IR (neat): 3327, 2976, 1601, 1541, 1460, 1314, 1239, 1124 cm–1.
**Table 8** Palladium(0)-Catalyzed Addition of Aryl-Substituted Allenes 11 with Organoboronic Acids 3 under Conditions B

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>11</th>
<th>R</th>
<th>3</th>
<th>Product 12</th>
<th>Yield (%) of (E)-12</th>
<th>Ratio (%)</th>
<th>Ratio (%) (E)-12/(Z)-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>11a</td>
<td>Ph</td>
<td>3a</td>
<td>12aa</td>
<td>41</td>
<td>99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>11a</td>
<td>4-Tol</td>
<td>3b</td>
<td>12ab</td>
<td>73</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>11a</td>
<td>4-MeOC₆H₄</td>
<td>3d</td>
<td>12ad</td>
<td>79</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>11a</td>
<td>1-Naph</td>
<td>3h</td>
<td>12ah</td>
<td>87</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>11a</td>
<td>4-MeOC₆H₄</td>
<td>3d</td>
<td>12bd</td>
<td>60</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>6</td>
<td>Ph</td>
<td>11a</td>
<td>4-MeOC₆H₄</td>
<td>3d</td>
<td>12cd</td>
<td>66</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>11a</td>
<td>4-MeOC₆H₄</td>
<td>3d</td>
<td>12dd</td>
<td>62</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

*a* Reagents and conditions (conditions B): 11 (0.25 mmol), 3 (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), dioxane, reflux, 5 h, under N₂.

*b* Isolated yield.

¹ Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after evaporation.

² Reaction time: 2 h.

¹¹H NMR (300 MHz, CDCl₃): δ = 8.01–7.94 (m, 2 H), 7.67–7.50 (m, 3 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.60 (q, J = 1.2 Hz, 1 H), 2.51 (d, J = 1.2 Hz, 3 H), 2.35 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 153.4, 142.3, 140.3, 137.0, 133.1, 129.4, 129.2, 127.2, 126.4, 126.2, 21.2, 17.1.

MS (EI, 70 eV): m/z (%) = 272 [M⁺] (92.36), 115 (100).

Analytical Calcd for C₁₆H₁₆O₃S: C, 70.56; H, 5.92. Found: C, 70.16; H, 5.90.

(E)-2-(4-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfone [(E)-4ad]

Compound (E)-4ad was prepared similarly to compound (E)-4aa by conditions A. The reaction of 2a (45 mg, 0.25 mmol), 3d (77 mg, 0.51 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μL, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 4ad and 5ad after evaporation of the solvent, filtration through a pad of silica gel, and evaporation to dryness [4ad/5ad = 93:7, (E)-4ad/(Z)-4ad > 99:1; by ¹H NMR analysis]. Pure (E)-4ad was isolated by flash chromatography (silica gel). Yield: 56 mg (78%); liquid.

IR (neat): 1599, 1568, 1511, 1424, 1329, 1319, 1278, 1271, 1253, 1140, 55.4, 16.9.

MS (EI, 70 eV): m/z (%) = 288 [M⁺] (100).

HRMS (MALDI): m/z calc for C₁₆H₁₆O₃SNa⁺ [M⁺ + Na⁺] = 311.0712; found: 311.0712.

(E)-2-(4-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfone [(E)-4ad]

Compound (E)-4ad was prepared similarly to compound (E)-4aa by conditions A. The reaction of 2a (45 mg, 0.25 mmol), 3d (77 mg, 0.51 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μL, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 4ac and 5ac after evaporation of the solvent, filtration through a pad of silica gel, and evaporation to dryness [4ac/5ac = 94:6, (E)-4ae/(Z)-4ae > 99:1; by ¹H NMR analysis]. Pure (E)-4ae was isolated by flash chromatography (silica gel). Yield: 50 mg (66%); liquid.

IR (neat): 1611, 1530, 1479, 1446, 1352, 1306, 1148, 1085 cm⁻¹.
Compound \( (E)-4af \) was prepared similarly to compound \( (E)-4aa \) by conditions A. The reaction of \( 2a \) (45 mg, 0.25 mmol), \( 3g \) (82 mg, 0.50 mmol), Pd(PPh\( _3 \))\( _2 \) (29 mg, 0.025 mmol), and AcOH (14 \( \mu l, 0.24 \) mmol) in THF (3 mL) afforded crude \( 4af \) after evaporation of the solvent. Filtration through a pad of silica gel, and evaporation to dryness \( [4af 5af 6af > 99:1, (E)-4af / (Z)-4af > 99:1; by \( ^1H \) NMR analysis]. Pure \( (E)-4af \) was isolated by flash chromatography (silica gel). Yield: 60 mg (80%); liquid.

IR (neat): 1686, 1608, 1449, 1446, 1424, 1305, 1147 cm\(^{-1}\).

\( ^1H \) NMR (300 MHz, CDCl\( _3 \)): \( \delta = 8.01–7.96 \) (2H, 7.94 (d, \( J = J_{1H, 2H} = 6.6 \) Hz, 1H), 7.20–7.15 (4H, \( J = J_{1H, 2H} = 7.9 \) Hz, 3H), 7.15–7.10 (4H, 6.64 (q, \( J = J_{1H, 2H} = 1.2 \) Hz, 3H), 2.60 (d, \( J = J_{1H, 2H} = 1.3 \) Hz, 3H), 2.57 (d, \( J = J_{1H, 2H} = 1.1 \) Hz, 3H), 1.86 (q, \( J = J_{1H, 2H} = 6.6 \) Hz, 3H).

\( ^13C \) NMR (75.4 MHz, CDCl\( _3 \)): \( \delta = 197.3, 152.1, 144.5, 141.7, 137.5, 133.4, 130.7, 129.6, 129.3, 129.1, 128.6, 127.3, 125.9, 26.7, 17.3.

MS (EL, 70 eV): m/z (\%) = 300 [M\(^+\)] (28.66), 280 (100).

HRMS (MALDI): \( m/z \) calc for \( C_{31}H_{26}O_3SNa^+ [M + Na]^+ \): 331.0783; found: 331.0783.

IR (neat): 1637, 1587, 1461, 1446, 1305, 1145, 1085 cm\(^{-1}\).

\( ^1H \) NMR (300 MHz, CDCl\( _3 \)): \( \delta = 7.95–7.88 \) (2H, 7.63–7.48 (m, 3H), 6.20 (s, 1H), 6.17 (dt, \( J = J_{1H, 2H} = 6.6 \), 15.0 Hz, 1H), 5.98 (d, \( J = J_{1H, 2H} = 15.0 \) Hz, 2H), 2.11 (d, \( J = J_{1H, 2H} = 6.6 \) Hz, 3H).

\( ^1C \) NMR (75.4 MHz, CDCl\( _3 \)): \( \delta = 154.6, 141.9, 139.6, 133.6, 133.4, 130.9, 129.3, 128.9, 128.5, 127.2, 126.7, 126.2, 125.1, 124.5, 124.2, 20.6.

MS (EL, 70 eV): \( m/z \) (%): 308 [M\(^+\)] (6.07), 167 (100).

HRMS (MALDI): \( m/z \) calc for \( C_{31}H_{26}O_3SNa^+ [M + Na]^+ \): 331.0763; found: 331.0783.

\( (E,3E)-2-Methylmethyla-1,3-dien-1-yl Phenyl Sulfone \) \( (E)-4ai \)

Compound \( (E)-4ai \) was prepared similarly to compound \( (E)-4aa \) by conditions A. The reaction of \( 2a \) (45 mg, 0.25 mmol), \( 3m \) (72 mg, 0.51 mmol), Pd(PPh\( _3 \))\( _2 \) (29 mg, 0.025 mmol), and AcOH (14 \( \mu l, 0.24 \) mmol) in THF (3 mL) afforded crude \( 4ai \) after evaporation of the solvent. Filtration though a pad of silica gel, and evaporation to dryness \( [4ai 5ai 6ai > 99:1, (E)-4ai / (Z)-4ai > 99:1; by \( ^1H \) NMR analysis]. Pure \( (E)-4ai \) was isolated by flash chromatography (silica gel). Yield: 50 mg (72%); liquid.

IR (neat): 1614, 1508, 1442, 1308, 1148 cm\(^{-1}\).

\( ^1H \) NMR (300 MHz, CDCl\( _3 \)): \( \delta = 8.00–7.92 \) (2H, 7.66–7.49 (m, 3H), 7.46–7.39 (m, 2H), 7.38–7.28 (m, 3H), 6.96 (d, \( J = J_{1H, 2H} = 16.1 \) Hz, 1H), 6.68 (d, \( J = J_{1H, 2H} = 16.1 \) Hz, 1H), 6.42 (s, 1H), 2.56 (s, 3H).

\( ^1C \) NMR (75.4 MHz, CDCl\( _3 \)): \( \delta = 149.7, 142.4, 135.8, 135.53, 135.51, 133.1, 129.4, 129.2, 129.1, 128.8, 127.2, 127.1, 13.2. 

MS (EL, 70 eV): \( m/z \) (%): 284 [M\(^+\)] (11.6), 55 (100).

\( (E,1E)-3-Phenylbut-2-en-2-yl Sulfone \) \( (E)-4ba \)

Compound \( (E)-4ba \) was prepared similarly to compound \( (E)-4aa \) by conditions A. The reaction of \( 2b \) (49 mg, 0.25 mmol). \( 3a \) (61 mg, 0.50 mmol), Pd(PPh\( _3 \))\( _2 \) (29 mg, 0.025 mmol), and AcOH (14 \( \mu l, 0.24 \) mmol) in THF (3 mL) afforded crude \( 4ba \) after evaporation of the solvent. Filtration though a pad of silica gel, and evaporation to dryness \( [4ba 5ba 6ba > 99:1, (E)-4ba / (Z)-4ba > 99:1; by \( ^1H \) NMR analysis]. Pure \( (E)-4ba \) was isolated by flash chromatography (silica gel). Yield: 34 mg (50%); liquid.

IR (neat): 1620, 1598, 1490, 1447, 1303, 1144 cm\(^{-1}\).

\( ^1H \) NMR (300 MHz, CDCl\( _3 \)): \( \delta = 8.00–7.92 \) (2H, 7.66–7.49 (m, 3H), 7.46–7.39 (m, 2H), 7.38–7.28 (m, 3H), 6.96 (d, \( J = J_{1H, 2H} = 16.1 \) Hz, 1H), 6.68 (d, \( J = J_{1H, 2H} = 16.1 \) Hz, 1H), 6.42 (s, 1H), 2.56 (s, 3H).

\( ^1C \) NMR (75.4 MHz, CDCl\( _3 \)): \( \delta = 149.8, 142.8, 141.4, 133.7, 133.1, 129.1, 128.5, 127.7, 127.1, 126.2, 22.6, 17.7.

MS (EL, 70 eV): \( m/z \) (%): 272 [M\(^+\)] (27.39), 91 (100).
Phenyl (E)-2-Phenylethyl-2-en-3-yl Sulfoxide ([E]-4ca)

Compound (E)-4ca was prepared similarly to compound (E)-4aa by conditions A. The reaction of 2c (59 mg, 0.25 mmol), 3a (61 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded crude 4ca after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness ([4ca]不安 = 99:1, (E)-4ca ([E]-4ca) > 99:1; by 1H NMR analysis). Pure (E)-4ca was isolated by flash chromatography (silica gel). Yield: 43 mg (55%); solid; mp 83–85 °C (Et₂O).

HRMS (MALDI): m/z calc'd for C₁₈H₂₁O₂S⁺ [M⁺ + H]: 273.0944; found: 273.0945.

Phenyl (E)-2-Phenylethyl-2-en-3-yl Sulfone ([E]-4ca)

Compound (E)-4ca was prepared similarly to compound (E)-4aa by conditions A. The reaction of 2d (91 mg, 0.4 mmol), 3a (61 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded crude 4ca after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness ([4ca]不安 = 99:1, (E)-4ca ([E]-4ca) > 99:1; by 1H NMR analysis). Pure (E)-4ca was isolated by flash chromatography (silica gel). Yield: 41 mg (59%); liquid.

IR (neat): 1601, 1547, 1485, 1443, 1428, 1039 cm⁻¹.

IR (neat): 1601, 1547, 1485, 1443, 1428, 1039 cm⁻¹.

MS (70 eV): m/z (%) = 272 [M⁺] (1.91), 244 (100).

HRMS (MALDI): m/z calc'd for C₁₈H₂₁O₂SNa⁺ [M⁺ + Na]: 295.0763; found: 295.0759.

Phenyl (E)-2-Phenylethyl-2-en-3-yl Sulfoxide ([E]-6ad)

Compound (E)-6ad was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3d (76 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded crude 6ad after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness ([6ad]不安 > 99:1; by 1H NMR analysis). Pure (E)-6ad was isolated by flash chromatography (silica gel). Yield: 35 mg (52%); liquid.

IR (neat): 1604, 1567, 1513, 1463, 1442, 1255, 1183, 1034 cm⁻¹.

IR (neat): 1604, 1567, 1513, 1463, 1442, 1255, 1183, 1034 cm⁻¹.

MS (70 eV): m/z (%) = 273 (3.15), 272 [M⁺] (1.82), 224 (100).

HRMS (MALDI): m/z calc'd for C₁₉H₁₉O₂Sn⁺ [M⁺ + Na]: 273.0944; found: 273.0961.

(3S,4S)-2-(3-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfoxide ([E]-6ac)

Compound (E)-6ac was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3e (76 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded crude 6ac after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness ([6ac]不安 > 99:1; (E)-6ac ([E]-6ac) > 99:1; by 1H NMR analysis). Pure (E)-6ac was isolated by flash chromatography (silica gel). Yield: 41 mg (59%); liquid.

IR (neat): 1615, 1530, 1476, 1443, 1351, 1083, 1038 cm⁻¹.

IR (neat): 1615, 1530, 1476, 1443, 1351, 1083, 1038 cm⁻¹.

MS (70 eV): m/z (%) = 288 (5.97), 287 [M⁺] (2.64), 239 (100).

HRMS (MALDI): m/z calc'd for C₁₉H₁₉O₂Sn⁺ [M⁺ + H]: 288.0689; found: 288.0672.

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(E)-2-(4-Acetylphenyl)prop-1-en-1-yl Phenyl Sulfoxide [(E)-6a]

Compound (E)-6a was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3g (83 mg, 0.51 mmol), Pd(PPh3)4 (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded crude 6ag after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6af/7ag > 99:1; (E)-6af/Z-6af > 99:1; by 1H NMR analysis]. Pure (E)-6af was isolated by flash chromatography (silica gel). Yield: 34 mg (48%); liquid.

IR (neat): 1613, 1590, 1579, 1494, 1474, 1443, 1082, 1036 cm⁻¹.


(1E,3E)-2-Methyl-4-phenylbuta-1,3-dien-1-yl Phenyl Sulfoxide [(E)-6aj]

Compound (E)-6aj was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (40 mg, 0.24 mmol), 3j (78 mg, 0.50 mmol), Pd[PPh3]4 (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 6aj and 7aj after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6aj/7aj > 99:1; (E)-6aj/Z-6aj > 99:1; by 1H NMR analysis]. Pure (E)-6aj was isolated by flash chromatography (silica gel). Yield: 31 mg (46%); liquid.

IR (neat): 1623, 1599, 1579, 1494, 1474, 1443, 1082, 1036 cm⁻¹.

HRMS (MALDI): m/z calcd for C17H14OS+: [M+H]+: 268.0922; found: 268.0923.

(1E,3E)-2-(1-Naphthyl)prop-1-en-1-yl Phenyl Sulfoxide [(E)-6ah]

Compound (E)-6ah was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3h (86 mg, 0.50 mmol; should be recrystallized from H2O immediately before use), Pd[PPh3]4 (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 6ah and 7ah after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6ah/7ah > 99:1; by 1H NMR analysis]. Pure (E)-6ah was isolated by flash chromatography (silica gel). Yield: 30 mg (41%); liquid.

IR (neat): 1512, 1465, 1445, 1378 cm⁻¹.

HRMS (MALDI): m/z calcd for C17H17OS+: [M+H]+: 292.0891.

(1E,3E,5E)-2-Methylocta-1,3-dien-1-yl Phenyl Sulfoxide [(E)-6ak]

Compound (E)-6ak was prepared similarly to compound (E)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3k (64 mg, 0.50 mmol), Pd[PPh3]4 (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 6ak and 7ak after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6ak/7ak > 99:1; by 1H NMR analysis]. Pure (E)-6ak was isolated by flash chromatography (silica gel). Yield: 33 mg (53%); liquid.

IR (neat): 1512, 1465, 1378 cm⁻¹.

HRMS (MALDI): m/z calcd for C17H14OS+: [M+H]+: 268.0922; found: 268.0923.
(E)-2-(2-Methoxyphenyl)undec-2-ene [(E)-9al]

Compound (E)-9al was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3i (76 mg, 0.50 mmol), 8a (38 mg, 0.25 mmol), Pd(PPh3)4 (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9al and 10al after evaporation [9al/10al = 91:9, (E)-9al/(Z)-9al > 99:1; by 1H NMR analysis]. A mixture of (E)-9al and 10al was isolated by flash chromatography (silica gel). Yield: 43 mg (66%); (E)-9al/10al = 91:9; liquid.

IR (neat): 1530, 1465, 1349 cm⁻¹.

HRMS (EI): m/z calc for C17H23NO+ [M+]: 275.1888; found: 275.1888.

(2)-2-(4-Acetylphenyl)undec-2-ene [(E)-9ag]

Compound (E)-9ag was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3g (82 mg, 0.50 mmol), 8a (38 mg, 0.25 mmol), Pd(PPh3)4 (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9ag and 10ag after evaporation [9ag/10ag = 93.7, (E)-9ag/(Z)-9ag > 99:1; by 1H NMR analysis]. Pure (E)-9ag was isolated by flash chromatography (silica gel). Yield: 42 mg (62%); liquid.

IR (neat): 1684, 1602, 1466, 1408, 1267 cm⁻¹.


(2)-1-Naphthylundec-2-ene [(E)-9ah]

Compound (E)-9ah was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3h (86 mg, 0.50 mmol), 8a (38 mg, 0.25 mmol), Pd(PPh3)4 (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9ah and 10ah after evaporation [9ah/10ah = 90:10, (E)-9ah/(Z)-9ah > 99:1; by 1H NMR analysis]. A mixture of (E)-9ah and 10ah was isolated by flash chromatography (silica gel). Yield: 52 mg (74%); (E)-9ah/10ah = 92:8; liquid.

IR (neat): 1591, 1578, 1506, 1465, 1394, 1376 cm⁻¹.


(2)-2-Phenylpentadec-2-ene [(E)-9ba]

Compound (E)-9ba was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3i (84 mg, 0.50 mmol), 8a (38 mg, 0.25 mmol), Pd(PPh3)4 (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9ba and 10ae after evaporation [9ba/10ae = 99:1, (E)-9ba/(Z)-9ba > 99:1; by 1H NMR analysis]. A mixture of (E)-9ba and 10ae was isolated by flash chromatography (silica gel). Yield: 46 mg (67%); (E)-9ba/10ae = 93:7; liquid.

IR (neat): 1530, 1465, 1349 cm⁻¹.

(E)-2-(4-Methoxyphenyl)monadec-2-ene [(E)-9cd] Compound (E)-9cd was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3d (76 mg, 0.50 mmol), 8c (66 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9cd and 10cd after evaporation [9cd/10cd = 93:7. (E)-9cd/(Z)-9cd > 99:1; by ¹H NMR analysis]. A mixture of (E)-9cd and 10cd was isolated by flash chromatography (silica gel); yield: 32 mg (34%); [(E)-9cd/10cd = 95.5. Pure (E)-9cd was obtained by recrystallization (Et₂O); solid; mp 45–47 °C (Et₂O).

IR (neat): 1609, 1516, 1471, 1464 cm⁻¹.

¹H NMR (300 MHz, CDCl₃); δ = 7.73 (d, J = 9.2 Hz, 2 H), 6.86 (d, J = 9.2 Hz, 2 H), 5.70 (t, J = 6.9 Hz, 1 H), 3.80 (s, 3 H), 2.24–2.12 (m, 2 H), 2.00 (s, 3 H), 1.51–1.18 (m, 28 H), 0.88 (t, J = 6.9 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃); δ = 158.3, 136.6, 133.7, 127.3, 126.5, 113.4, 55.2, 31.9, 29.70, 29.66, 29.60, 29.43, 29.37, 28.8, 22.7, 15.8, 14.1.

MS (EI, 70 eV); ml/c (%) = 372 [M⁺] (36.55), 161 (100). Anal. Calcd for C₂₉H₄₀O: C, 83.80; H, 11.90. Found: C, 83.52; H, 11.82.

(E)-1-Cyclohexyl-2-(4-methoxyphenyl)prop-1-ene [(E)-9dd] Compound (E)-9dd was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3d (76 mg, 0.50 mmol), 8d (31 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9dd and 10dd after evaporation [9dd/10dd = 88:12. (E)-9dd/(Z)-9dd > 99:1; by ¹H NMR analysis]. A mixture of (E)-9dd and 10dd was isolated by flash chromatography (silica gel); yield: 25 mg (44%); [(E)-9dd/10dd = 92.8; liquid.

IR (neat): 1607, 1511, 1463, 1447, 1426 cm⁻¹.

¹H NMR (300 MHz, CDCl₃); δ (E)-9dd = 7.33 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 2 H), 5.56 (d, J = 9.0 Hz, 1 H), 3.81 (s, 3 H), 2.40–2.26 (m, 1 H), 2.02 (s, 2 H), 1.81–1.50 (m, 4 H), 1.42–1.04 (m, 6 H), δ (10dd) = 5.20 (s, 1 H), 4.93 (s, 1 H).

¹³C NMR (75.4 MHz, CDCl₃); δ = 158.3, 136.6, 133.1, 132.0, 126.5, 113.4, 55.3, 37.7, 33.2, 26.1, 26.0, 15.8.

MS (EI, 70 eV); ml/c (%) = 230 [M⁺] (100). HRMS (EI): ml/c calcd for C₁₉H₂₇O⁺ [M⁺]*: 230.1671; found: 230.1683.

(E)-3-(4-Methoxyphenyl)-1-phenylbut-2-ene [(E)-9ed] Compound (E)-9ed was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3d (76 mg, 0.50 mmol), 8e (33 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 µL, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9ed and 10ed after evaporation [9ed/10ed > 93:7. (E)-9ed/(Z)-9ed > 95.5; by ¹H NMR analysis]. Pure (E)-9ed was isolated by flash chromatography (silica gel); yield: 45 mg (76%); liquid.

IR (neat): 1607, 1574, 1511, 1449, 1453, 1441, 1245 cm⁻¹.

¹H NMR (300 MHz, CDCl₃); δ = 7.41–7.17 (m, 7 H), 6.84 (d, J = 8.7 Hz, 2 H), 5.92 (t, J = 7.5 Hz, 1 H), 3.81 (s, 3 H), 3.56 (d, J = 7.5 Hz, 2 H), 2.13 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃); δ = 144.0, 134.4, 128.8, 128.1, 126.4, 125.6, 31.9, 29.69, 29.66, 29.63, 29.60, 29.43, 29.37, 28.8, 22.7, 15.7, 14.1.

MS (EI, 70 eV); ml/c (%) = 286 [M⁺] (37.23), 118 (100).

HRMS (EI): ml/c calcd for C₁₉H₂₆O⁺ [M⁺]*: 286.2661; found: 286.2651.
mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded crude 12ad after evaporation [12ag/13ag > 99:1; (E)-12ag/(Z)-12ag > 99:1; by ¹H NMR analysis]. Pure (E)-12ag was isolated by flash chromatography (silica gel). Yield: 26 mg (44%); solid; mp 104–106 °C (Et₂O).

IR (neat): 1677, 1599, 1450, 1410, 1357, 1272 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 7.96 (d, J = 8.7 Hz, 2 H), 7.61 (d, J = 8.4 Hz, 2 H), 7.45–7.35 (m, 4 H), 7.32–7.25 (m, 1 H), 6.95 (q, J = 1.5 Hz, 1 H), 2.63 (s, 3 H), 2.31 (s, 3 J, 3 H).
¹C NMR (75.4 MHz, CDCl₃): δ = 197.7, 148.5, 137.7, 136.3, 135.7, 129.6, 129.1, 128.8, 128.2, 126.9, 120.6, 26.0, 17.3.

MS (EL, 70 eV): m/z (%) = 236 [M⁺] (93.22), 43 (100).


(E)-1-(2-(1-Naphthyl)-1-phenylprop-1-ene [(-E)-12ah]) Compound (E)-12ah was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3d (75 mg, 0.49 mmol), 11a (29 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded crude 12ah after evaporation [12ah/13ah > 99:1, (E)-12ah/(Z)-12ah > 99:1; by ¹H NMR analysis]. Pure (E)-12ah was isolated by flash chromatography (silica gel). Yield: 53 mg (87%); liquid.

IR (neat): 1605, 1597, 1514, 1462, 1262 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 8.21–8.13 (m, 1 H), 8.00–7.87 (m, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 7.62–7.46 (m, 8 H), 7.41–7.34 (m, 1 H, 6.70 (q, J = 1.2 Hz, 1 H), 2.48 (d, J = 1.2 Hz, 3 H).
¹C NMR (75.4 MHz, CDCl₃): δ = 144.1, 137.9, 137.9, 133.8, 131.0, 130.4, 129.0, 128.4, 128.3, 127.2, 126.2, 126.5, 125.82, 125.75, 125.7, 124.8, 20.9.

MS (EL, 70 eV): m/z (%) = 244 [M⁺] (94.3), 229 (100).

HRMS (EI): m/z calcd for C₂₀H₂₀O [M⁺]: 224.1252; found: 224.1252.

(E)-1,2-Bis(4-methoxyphenyl)prop-1-ene (-E)-12bd⁻¹⁻) Compound (E)-12bd was prepared similarly to compound (E)-9aa by conditions B. The reaction of 3d (75 mg, 0.49 mmol), 11a (29 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μL, 0.24 mmol) in dioxane (3 mL) afforded crude 12bd after evaporation [12bd/13bd > 99:1, (E)-12bd/(Z)-12bd > 99:1; by ¹H NMR analysis]. Pure (E)-12bd was isolated by flash chromatography (silica gel). Yield: 38 mg (60%); solid; mp 121–122 °C (Et₂O).

IR (neat): 1580, 1511, 1452, 1252 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 7.47 (d, J = 8.7 Hz, 2 H), 7.31 (d, J = 8.7 Hz, 2 H), 6.96–6.87 (m, 4 H), 6.74 (s, 1 H), 3.84 (s, 6 H), 2.26 (s, 3 H).
¹C NMR (75.4 MHz, CDCl₃): δ = 158.7, 158.0, 136.6, 135.3, 131.1, 130.3, 126.9, 129.5, 113.6, 113.5, 55.3, 55.2, 17.4.

MS (EL, 70 eV): m/z (%) = 254 [M⁺] (100).

Synthesis of Sulfone (-E)-4a from Sulfoxide (E)-6a As a soln of (E)-6a (101 mg, 0.4 mmol) and 30% H₂O₂ (5 mL) in AcOH (5 mL) was stirred at 40 °C for 24 h. After complete conversion of the starting material as monitored by TLC (PE–Et₂O, 1:1), the mixture was quenched with H₂O (15 mL), and extracted with CHCl₃ (6 × 25 mL). The organic layer was then neutralized by washing with sat. aq NaHCO₃. The combined organic layer was dried (MgSO₄). Evaporation of the solvent and flash chromatography (silica gel, PE–Et₂O, 3:1) afforded of 4a; yield: 57% (52%).

Acknowledgment
We are grateful to the National Natural Science Foundation of China (Grant No. 20121202 and 20332060).

References


(13) Crystal structure data for (E)-4ca: C_{19}H_{22}O_{2}S, MW = 314.43, triclinic, space group P-1, Mo Kα, final R indices [I > 2σ(I)], R1 = 0.0464, wR2 = 0.1016, a = 9.5661 (11) Å, b = 9.9879 (11) Å, c = 10.6025 (12) Å, α = 102.675 (2)°, β = 101.020 (2)°, γ = 116.035 (2)°, V = 838.98 (16) Å³, T = 293 (2) K, Z = 2, reflections collected/unique: 5004/3565 (Rint = 0.0485), no observation [I > 2σ(I)] 3565, parameters 234. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under CCDC 613372.


