Palladium–Tetraphosphine Complex Catalysed Heck Reaction of Vinyl Bromides with Alkenes: A Powerful Access to Conjugated Dienes

Mhamed Lemhadri, Ahmed Battace, Florian Berthiol, Touriya Zair, Henri Doucet, Maurice Santelli

Abstract: A wide variety of 1,3-dienes have been prepared by the Heck vinylation of vinyl bromides using [Pd(t-Bu)_2Cl]_2/cis,cis,cis,1,2,3,4-tetrakis(diphenylphosphino)methyl)cyclopentane (Tedicyp) as the catalyst precursor. Both α- and β-substituted vinyl bromides undergo the Heck reaction with functionalised alkenes such as acrylates, enones, styrenes or a vinyl sulfone, and also with nonfunctionalised alkenes such as dec-1-ene, leading stereoselectively, in most cases, to the corresponding E- or E,E-1,3-dienes in good yields. Furthermore, this catalyst can be used at low loading for several reactions.

Key words: catalysis, palladium, tetraphosphine, alkenes, vinyl bromides

The palladium-catalysed so-called Heck reaction is one of the most powerful methods for the formation of carbon–carbon bonds; however, most of the results described so far have been for such reactions performed using aryl halides. The use of vinyl halides to prepare 1,3-dienes has attracted less attention. In fact, in many cases, 1,3-dienes are actually prepared by cross-coupling of organometallic vinyl derivatives [metal = MgX, ZnX, SnX, B(OR)_2] with vinyl halides. The major drawback of these reactions is that they require the preparation of the organometallic derivatives and also provide either an organometallic compound or a salt (MX) as byproduct. The direct coupling of vinyl halides with alkenes, especially at low catalyst loadings, would provide a cost-effective and environmentally attractive procedure for the preparation of 1,3-dienes (only HX as byproduct). In general, these couplings have been performed using palladium catalysts associated with the triphenylphosphine ligand. However, the efficiency of palladium associated with triphenylphosphine as the catalyst precursor is generally low in terms of the substrate-to-catalyst ratio. In recent years, several more stable and efficient palladium catalysts have been successfully used for Heck reactions, but most of the results which have been described with these catalysts were obtained for the coupling of aryl halides. Relatively few results have been reported for vinyl halides. One of the most active catalysts for such substrates is a sulfur-containing palladacycle. With this catalytic system, the coupling of β-bromostyrene with methyl acrylate allowed formation of the corresponding conjugated diene in a high turnover number (TON) of 9000, but in moderate yields (18% and 40%). Tris(dibenzylideneacetone)dipalladium(0) (1 mol%) associated with the electron-rich and sterically hindered phosphine ligand tri-tert-butylphosphine efficiently promotes the reaction of 2-bromobut-2-ene with styrene in 89% yield. Recently, the coupling of a 2-bromocrotylate with a 1,1-disubstituted alkene using palladium(II) acetate (3 mol%) and tri-2-tolylyphosphine (6 mol%) as the catalytic system was described. This reaction allowed the stereoselective synthesis of a 1,3-diene, which is a precursor of a marine natural product, in 84% yield.

Several results have been reported for the coupling of vinyl halides with alkenes, however, the influence of substituents on the vinyl halides on the reaction yields and rates, and also couplings with functionalised alkenes, has not been studied in detail. Thus, an effective and selective method for this reaction, especially using high substrate/catalyst ratios, is still subject to significant improvements.

The coordination of ligands on palladium has an important effect on the rates and selectivities of catalysed reactions. In order to find more efficient palladium catalysts we have prepared the tetradentate phosphine ligand, cis,cis,cis,1,2,3,4-tetrakis[(diphenylphosphino)methyl]cyclopentane (Tedicyp, Scheme 1). The presence of these four phosphines close to the metal centre appears to increase the stability of the catalyst and prevents the formation of ‘palladium black’. We have recently reported several results in allylic substitution reactions, obtained in allylic substitution reactions. The coordination of ligands on palladium has an important effect on the rates and selectivities of catalysed reactions. In order to find more efficient palladium catalysts we have prepared the tetradentate phosphine ligand, cis,cis,cis,1,2,3,4-tetrakis[(diphenylphosphino)methyl]cyclopentane (Tedicyp, Scheme 1). The presence of these four phosphines close to the metal centre appears to increase the stability of the catalyst and prevents the formation of ‘palladium black’. We have recently reported several results in allylic substitution reactions, Suzuki, Sonogashira or Negishi couplings, C–H activation/functionalisation of furans or thiophenes, and also for the Heck vinylation, using Tedicyc as ligand. We have also reported some preliminary results for the Heck reaction using vinyl bromides and alkenes. Here, in order to further establish the requirements for a successful Heck reaction using vinyl halide derivatives, we wish to report on the reaction of α- or β-
substituted vinyl bromides with a variety of alkenes such as acrylates, enones, a vinyl sulfone, simple alkenes or styrene derivatives using Tedicyp as the ligand at moderate to very low catalyst loading.

First, we investigated the Heck reaction of 1,1-dibromostyrene with several alkenes in the presence of the system \([\text{Pd}(\eta^3-\text{C}_3\text{H}_5)\text{Cl}]_2/\text{Tedicyp}\) (Schemes 1 and 2, Tables 1–3). For this study, based on previous results, N,N-dimethylformamide was chosen as the solvent and potassium carbonate or sodium acetate as the base. The reactions were performed at 80–130 °C under argon. Table 1 discloses the results obtained using styrene derivatives as the vinylation reactant. In Table 2, the influence of functional groups on the alkene has been studied. Table 3 describes the Heck reaction of 1,1-dibromostyrene with simple alkenes such as dec-1-ene or cyclic alkenes.

In the presence of styrene derivatives and 1,1-dibromostyrene, the reactions required 0.01–0.1 mol% catalyst in order to obtain high yields of products (Table 1). For example, the coupling of styrene, 3,5-bis(trifluoromethyl)styrene or 3-chlorostyrene gave the \((E,E)-1,4\)-diarylbuta-1,3-dienes \(1, 3\) and \(5\) with high regio- and stereoselectivities, in high TONs of 4300, 3700 and 2500, and also in good yields (Table 1, entries 1, 2, 5, 6, 9 and 10). An electron-donating substituent on the aryl ring of styrene such as a para-methoxy group slightly decreased the reaction rate (TON 640) (Table 1, entries 3 and 4). This catalyst is also highly active for the coupling of 1,1-dibromostyrene with the heteroarylalkenes 2- and 4-vinylpyridine (Table 1, entries 11–14). A higher reaction rate was observed with 4-vinylpyridine (TON 7000) than with 2-vinylpyridine (TON 550). This difference of reactivity could result from a possible interaction between the nitrogen atom of 2-vinylpyridine and the palladium complex, which might have a retarding effect on the reaction rate.

Next, we examined the influence of several functional groups on the alkene, such as an ester, ketone, aldehyde or sulfone group, on the reaction rate for the coupling with 1,1-dibromostyrene (Table 2). The reaction with n-butyl acrylate can be performed with as little as 0.001% catalyst, leading to butyl \((E,E)-5\)-phenylpent-2,4-dienoate \((8)\) in good yield and with high stereoselectivity (Table 2, entries 1 and 2). For this vinylation reaction, a very high TON of 66000 was obtained. The first attempts using conjugated enones, such as but-3-en-2-one or pent-1-en-3-one, as reactants were unsuccessful (Table 2, entries 3 and 6). This is probably due to a fast polymerisation of these enones under the reaction conditions. Commercially available alk-1-en-3-ones are often stabilised with 0.5% S

Table 1  Palladium–Tedicyp Complex Catalysed Heck Reaction of 1,1-Dibromostyrene with Styrene Derivatives (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>styrene</td>
<td>1000</td>
<td>1</td>
<td>(95)</td>
</tr>
<tr>
<td>2</td>
<td>styrene</td>
<td>10000</td>
<td>2</td>
<td>100 (88)</td>
</tr>
<tr>
<td>3</td>
<td>4-methoxystyrene</td>
<td>250</td>
<td>3</td>
<td>100 (90)</td>
</tr>
<tr>
<td>4</td>
<td>4-methoxystyrene</td>
<td>1000</td>
<td>4</td>
<td>100 (82)</td>
</tr>
<tr>
<td>5</td>
<td>3,5-bis(trifluoromethyl)styrene</td>
<td>10000</td>
<td>5</td>
<td>100 (87)</td>
</tr>
<tr>
<td>6</td>
<td>3,5-bis(trifluoromethyl)styrene</td>
<td>10000</td>
<td>6</td>
<td>100 (86)</td>
</tr>
<tr>
<td>7</td>
<td>4-cyanostyrene</td>
<td>250</td>
<td>7</td>
<td>100 (91)</td>
</tr>
<tr>
<td>8</td>
<td>4-cyanostyrene</td>
<td>1000</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>3-chlorostyrene</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>3-chlorostyrene</td>
<td>10000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2-vinylpyridine</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2-vinylpyridine</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>4-vinylpyridine</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>4-vinylpyridine</td>
<td>10000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: 1,1-dibromostyrene (1 equiv), alkene (2 equiv), \(\text{K}_2\text{CO}_3\) (2 equiv), DMF, 130 °C, 20 h.

\(E,E\)-Isomers were obtained selectively (>95%).

GC or NMR yields. Isolated yields are in parentheses.
hydroquinone. We had previously observed that, for Heck reactions with aryl halides, the addition of 8% hydroquinone to the reaction mixture led to the arylation of such enones to give the corresponding (E)-1-arylalk-1-en-3-ones in high yields and TONs.\(^{15e}\) The addition of hydroquinone probably reduces the rate of polymerisation or decomposition of these enones. Using this additive, in the presence of \(\beta\)-bromostyrene, the expected (E,E)-1-phenylalka-1,3-dien-5-ones 9–11 were obtained with high stereoselectivities and in high yields using as little as 0.1–1 mol% catalyst (Table 2, entries 4, 5, and 7–10). Ethyl pent-4-enoate and 2,2-dimethylpent-4-enal also gave the expected E,E-1,3-dienes 12 and 13 in moderate to good yields (Table 2, entries 11–14). With these substrates, the formation of traces of side products arising from the migration of the double bond was observed. Methyl vinyl sulfone was also found to be a suitable reactant for the preparation of the conjugated diene (Table 2, entries 15 and 16); the E,E-1,3-diene 14 was obtained in 81% yield employing 1 mol% catalyst. On the other hand, when 2-methylbut-3-en-2-ol was used, an unexpected reaction was observed. With this substrate a dehydration occurred to give the conjugated triene 15 as the major product, but in moderate yield (Table 2, entries 17 and 18).

Then, we performed some reactions using simple linear, branched or cyclic alkenes (Schemes 1 and 2, Table 3). The vinylation of \(\beta\)-bromostyrylmine performed in the presence of dec-1-ene led to the E,E-1,3-diene 16 in 44% selectivity (Table 3, entries 1 and 2). In the course of this reaction, the formation of several other isomers occurs due to partial migration of the double bond of dec-1-ene. On the other hand, the reaction of \(\beta\)-bromostyrene with the sterically congested 3,3-dimethylbut-1-ene led to the product 17 with a very high regio- and stereoselectivity in favour of the E,E-1,3-diene and in good yield (Table 3, entry 3).

Several reactions were also performed using cyclic alkenes, namely, cyclopentene, cyclohexene, cycloheptene and cyclooctene, as the coupling partners (Scheme 2, Table 3, entries 5–9). Cyclohexene and cycloheptene led to the E-1,5- and E-1,4-dienes 20 and 21 with 94 and 80% selectivity, respectively. With these two substrates, partial migration of the carbon–carbon double bond of the cycloalkene occurs. Such migration has been previously reported.\(^{2h}\) A suitable conformation of the palladium intermediate is necessary for the \(\beta\)-elimination step of the catalytic cycle. These suitable conformations can be favoured by partial migration of the double bond of the cycloalkene. On the other hand, cyclopentene and cy-

### Table 2 Palladium–Tedicyp Complex Catalysed Heck Reaction of \(\beta\)-Bromostyrene with Functionalised Alkenes\(^a\) (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product(^b)</th>
<th>Yield(^c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-butyl acrylate</td>
<td>10000</td>
<td>8</td>
<td>100 (95)(^d)</td>
</tr>
<tr>
<td>2</td>
<td>n-butyl acrylate</td>
<td>1000000</td>
<td></td>
<td>100 (66)(^d)</td>
</tr>
<tr>
<td>3</td>
<td>but-3-en-2-one</td>
<td>250</td>
<td>9</td>
<td>100 (75)(^e)</td>
</tr>
<tr>
<td>4</td>
<td>but-3-en-2-one</td>
<td>250</td>
<td></td>
<td>49(^e)</td>
</tr>
<tr>
<td>5</td>
<td>but-3-en-2-one</td>
<td>1000</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>pent-1-en-3-one</td>
<td>250</td>
<td>10</td>
<td>100 (77)(^e)</td>
</tr>
<tr>
<td>7</td>
<td>pent-1-en-3-one</td>
<td>250</td>
<td></td>
<td>88(^e)</td>
</tr>
<tr>
<td>8</td>
<td>pent-1-en-3-one</td>
<td>1000</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>hex-1-en-3-one</td>
<td>100</td>
<td>11</td>
<td>100 (79)(^e)</td>
</tr>
<tr>
<td>10</td>
<td>hex-1-en-3-one</td>
<td>250</td>
<td></td>
<td>52(^e)</td>
</tr>
<tr>
<td>11</td>
<td>ethyl pent-4-enoate</td>
<td>250</td>
<td>12</td>
<td>100 (66)</td>
</tr>
<tr>
<td>12</td>
<td>ethyl pent-4-enoate</td>
<td>1000</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>13</td>
<td>2,2-dimethylpent-4-enal</td>
<td>100</td>
<td>13</td>
<td>100 (64)</td>
</tr>
<tr>
<td>14</td>
<td>2,2-dimethylpent-4-enal</td>
<td>250</td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>15</td>
<td>methyl vinyl sulfone</td>
<td>100</td>
<td>14</td>
<td>100 (81)</td>
</tr>
<tr>
<td>16</td>
<td>methyl vinyl sulfone</td>
<td>250</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>17</td>
<td>2-methylbut-3-en-2-ol</td>
<td>250</td>
<td>15</td>
<td>100 (48)(^f)</td>
</tr>
<tr>
<td>18</td>
<td>2-methylbut-3-en-2-ol</td>
<td>1000</td>
<td></td>
<td>63(^f)</td>
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</table>

\(^a\) Reaction conditions: \(\beta\)-bromostyrene (1 equiv), alkene (2 equiv), NaOAc (2 equiv), DMF, 110 °C, 20 h.
\(^b\) E,E-Isomers were obtained selectively (>95%).
\(^c\) GC or NMR yields. Isolated yields are in parentheses.
\(^d\) K₂CO₃ (2 equiv) was used as base, at 130 °C.
\(^e\) Hydroquinone (8%) was added to the reaction mixture.
\(^f\) Reaction temperature: 80 °C.
clooctene led mainly to the expected \(E\)-1,3-dienes 19 and 22 (Table 3, entries 5, 8 and 9). It should be noted that a very high selectivity of 93% in favour of \(E\)-1,3-diene 22 was obtained from cyclooctene. Moreover, most of the reactions with these nonfunctionalised linear or cyclic alkenes were performed using as little as 0.1 mol% catalyst.

Next, we studied the formation of 1,3-dienes using four alternative bromoalkenes: 2-bromobut-1-ene, 3-bromo-3-methylbut-1-ol, 1-bromo-2-methylprop-1-ene and 2-bromo-3-methylbut-2-ene (Tables 4–7). With the \(a\)-substituted vinyl bromide, 2-bromobut-1-ene, several reactions were performed using styrene derivatives (Table 4, entries 1–5). With styrene, 4-methoxystyrene, 4-cyanostyrene or 4-vinylpyridine, the \(E\)-1,3-dienes 23–26 were obtained selectively in moderate to good yields using 0.4 mol% catalyst.

The other \(a\)-substituted vinyl bromide, 3-bromo-3-en-1-ol, in the presence of \(n\)-butyl acrylate, styrene, pent-1-en-3-one or oct-1-en-3-one, the reactions gave a simple access to the expected \(E\)-1,3-dien-5-ones 28 and 29. Again, with these unstable substrates, a small amount of hydroquinone had to be added to the reaction mixture in order to reduce the polymerisation side reaction (Table 4, entries 8–11).

The other \(a\)-substituted vinyl bromide, 2-bromobut-1-ene, led to the formation of 1,3-dienes 19 and 22 (Table 3, entries 5, 8 and 9). It should be noted that a very high selectivity of 93% in favour of \(E\)-1,3-diene 22 was obtained from cyclooctene. Moreover, most of the reactions with these nonfunctionalised linear or cyclic alkenes were performed using as little as 0.1 mol% catalyst.

\[ \text{Scheme 2} \]

Next, we studied the formation of 1,3-dienes using four alternative bromoalkenes: 2-bromobut-1-ene, 3-bromo-3-en-1-ol, 1-bromo-2-methylprop-1-ene and 2-bromo-3-methylbut-2-ene (Tables 4–7). With the \(a\)-substituted vinyl bromide, 2-bromobut-1-ene, several reactions were performed using styrene derivatives (Table 4, entries 1–5). With styrene, 4-methoxystyrene, 4-cyanostyrene or 4-vinylpyridine, the \(E\)-1,3-dienes 23–26 were obtained selectively in moderate to good yields using 0.4 mol% catalyst.

Table 3  Palladium–Tedicyp Complex Catalysed Heck Reaction of \(\beta\)-Bromostyrene with Linear, Branched or Cyclic Alkenes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dec-1-ene</td>
<td>1000</td>
<td>16</td>
<td>(68)c</td>
</tr>
<tr>
<td>2</td>
<td>dec-1-ene</td>
<td>10000</td>
<td>100</td>
<td>(79)d</td>
</tr>
<tr>
<td>3</td>
<td>3,3-dimethylbut-1-ene</td>
<td>250</td>
<td>17</td>
<td>100 (82)e</td>
</tr>
<tr>
<td>4</td>
<td>allylbenzene</td>
<td>100</td>
<td>18</td>
<td>98 (82)e</td>
</tr>
<tr>
<td>5</td>
<td>cyclopentene</td>
<td>1000</td>
<td>19</td>
<td>100 (88)d</td>
</tr>
<tr>
<td>6</td>
<td>cyclohexene</td>
<td>1000</td>
<td>20</td>
<td>100 (84)d</td>
</tr>
<tr>
<td>7</td>
<td>cycloheptene</td>
<td>10000</td>
<td>21</td>
<td>92 (81)h</td>
</tr>
<tr>
<td>8</td>
<td>cyclooctene</td>
<td>1000</td>
<td>22</td>
<td>100 (93)j</td>
</tr>
<tr>
<td>9</td>
<td>cyclooctene</td>
<td>10000</td>
<td></td>
<td>54i</td>
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</tbody>
</table>

\[ a \text{ Reaction conditions: } \beta\)-bromostyrene (1 equiv), alkene (2 equiv), K\(_2\)CO\(_3\) (2 equiv), DMF, 130 °C, 20 h. \]

\[ b \text{ GC or NMR yields. Isolated yields are in parentheses.} \]

\[ c \text{ Mixture of isomers; selectivity in favour of (}\text{E,E})\text{-dodeca-1,3-dienylbenzene: 44%}. \]

\[ d \text{ Reaction performed in an autoclave.} \]

\[ e \text{ Mixture of isomers; selectivity in favour of (}\text{E,E})\text{-1,5-diphenylpenta-1,3-diene: 55%}. \]

\[ f \text{ Mixture of isomers; selectivity in favour of (}\text{E})\text{-1-styrylcyclopentene: 55%}. \]

\[ g \text{ Mixture of isomers; selectivity in favour of (}\text{E})\text{-4-styrylcyclohexene: 94%}. \]

\[ h \text{ Mixture of isomers; selectivity in favour of (}\text{E})\text{-3-styrylcycloheptene: 80%}. \]

\[ i \text{ Reaction temperature: 100 °C.} \]

\[ j \text{ Mixture of isomers; selectivity in favour of (}\text{E})\text{-1-styrylcyclooctene: 93%}. \]
dienes 34–37 were obtained in good yields and with high regio- and stereoselectivities. These results were confirmed by the reactivity of the trisubstituted vinyl bromide, 2-bromo-3-methylbut-2-ene (Table 7). An acrylate, styrenes and enones have been successfully employed to give the E-1,3-dienes 38–42 in high yields and TONs of 200–850. Again, these TONs and yields are very similar to those obtained with 2-bromobut-1-ene or 1-bromo-2-methylprop-1-ene. It should be noted that, in the literature, relatively few examples of coupling reactions of trisubstituted vinyl halides with alkenes have been reported. Therefore, the Heck reaction represents a simple and powerful method for the preparation of such compounds.

Table 4 Palladium–Tedicyp Complex Catalysed Heck Reaction of 2-Bromobut-1-eneb (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>styrene</td>
<td>250</td>
<td>23</td>
<td>(58)</td>
</tr>
<tr>
<td>2</td>
<td>4-methoxystyrene</td>
<td>250</td>
<td>24</td>
<td>(76)</td>
</tr>
<tr>
<td>3</td>
<td>4-cyanostyrene</td>
<td>250</td>
<td>25</td>
<td>(83)</td>
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<tr>
<td>4</td>
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<td>25</td>
<td>75</td>
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<td>4-vinylpyridine</td>
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<td>(69)</td>
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<td>1000</td>
<td>27</td>
<td>92 (80)</td>
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<td>7</td>
<td>n-butyl acrylate</td>
<td>10000</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>pent-1-en-3-one</td>
<td>100</td>
<td>28</td>
<td>100 (64)d</td>
</tr>
<tr>
<td>9</td>
<td>pent-1-en-3-one</td>
<td>250</td>
<td></td>
<td>47d</td>
</tr>
<tr>
<td>10</td>
<td>oct-1-en-3-one</td>
<td>100</td>
<td>29</td>
<td>100 (71)d</td>
</tr>
<tr>
<td>11</td>
<td>oct-1-en-3-one</td>
<td>250</td>
<td></td>
<td>33d</td>
</tr>
</tbody>
</table>

a Reaction conditions: 2-bromobut-1-ene (1 equiv), alkene (2 equiv), K2CO3 (2 equiv), DMF, 80 °C, 20 h.
b E-Isomers were obtained selectively (>95%).
c GC or NMR yields. Isolated yields are in parentheses.
d NaOAc (2 equiv) was used as base, and hydroquinone (8%) was added to the reaction mixture.

Table 5 Palladium–Tedicyp Complex Catalysed Heck Reaction of 3-Bromobut-3-en-1-olb (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-butyl acrylate</td>
<td>1000</td>
<td>30</td>
<td>(76)</td>
</tr>
<tr>
<td>2</td>
<td>styrene</td>
<td>100</td>
<td>31</td>
<td>(45)</td>
</tr>
<tr>
<td>3</td>
<td>pent-1-en-3-one</td>
<td>1000</td>
<td>32</td>
<td>77 (62)d</td>
</tr>
<tr>
<td>4</td>
<td>oct-1-en-3-one</td>
<td>250</td>
<td>33</td>
<td>62 (41)d</td>
</tr>
</tbody>
</table>

a Reaction conditions: 3-bromobut-3-en-1-ol (1 equiv), alkene (2 equiv), K2CO3 (2 equiv), DMF, 130 °C, 20 h.
b E-Isomers were obtained selectively (>95%).
c GC or NMR yields. Isolated yields are in parentheses.
d NaOAc (2 equiv) was used as base, at 110 °C, and hydroquinone (8%) was added to the reaction mixture.
In summary, in the presence of the palladium–Tedicyp complex, the Heck reaction of vinyl bromides can be performed with a wide variety of alkenes such as acrylates, enones, styrene derivatives, sulfones or simple linear and cyclic alkenes. Moreover, both $\alpha$- and $\beta$-substituted vinyl bromides can be employed, and relatively similar TONs are obtained indicating a minor steric effect of the vinyl bromide substituents on the reaction rate. A wide range of $E$- and $E,E,1,3$-dienes have been selectively prepared in good yields. The high levels of regio- and stereoselection for most of the reactions, as well as the functional group tolerance, are worthy of note. Most of these reactions can be performed with as little as 0.01–1 mol% catalyst. To date, few other catalytic systems have achieved this objective. Due to the high price of palladium, the practical advantage of such low catalyst loadings is increasingly important for industrial processes.

DMF analytical grade (99%) was not distilled before use. $\text{K}_2\text{CO}_3$ and NaOAc (99+%) were used. All reactions were run under argon using vacuum lines, in Schlenk tubes with oven-dried glassware. $^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in CDCl$_3$ solution. Chemical shifts (δ) are reported in ppm relative to CDCl$_3$. Elemental analyses were performed on a Thermo Finnigan EA 1112 apparatus. Flash chromatography was performed on silica gel (230–400 mesh).

**Palladium–Tedicyp Complex Catalyst**

An oven-dried 40-mL Schlenk tube equipped with a magnetic stirrer bar, under argon atmosphere, was charged with [Pd($\eta^1$-C$_5$H$_5$)Cl]$_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol).

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### Table 6 Palladium–Tedicyp Complex Catalysed Heck Reaction of 1-Bromo-2-methylprop-1-ene\(^a\) (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product $^b$</th>
<th>Yield $^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$n$-butyl acrylate</td>
<td>250</td>
<td>$^34$</td>
<td>100 (89)</td>
</tr>
<tr>
<td>2</td>
<td>$n$-butyl acrylate</td>
<td>1000</td>
<td>$^35$</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>styrene</td>
<td>250</td>
<td>$^36$</td>
<td>(75)</td>
</tr>
<tr>
<td>4</td>
<td>4-cyanostyrene</td>
<td>250</td>
<td>$^37$</td>
<td>(85)</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 1-bromo-2-methylprop-1-ene (1 equiv), alkene (2 equiv), $\text{K}_2\text{CO}_3$ (2 equiv), DMF, 100 °C, 20 h.

$^b$ $E$-Isomers were obtained selectively (>95%).

$^c$ GC or NMR yields. Isolated yields are in parentheses.

### Table 7 Palladium–Tedicyp Complex Catalysed Heck Reaction of 2-Bromo-3-methylbut-2-ene\(^a\) (Scheme 1)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Ratio substrate/catalyst</th>
<th>Product $^b$</th>
<th>Yield $^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$n$-butyl acrylate</td>
<td>250</td>
<td>$^38$</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>styrene</td>
<td>250</td>
<td>$^39$</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>4-vinylpyridine</td>
<td>250</td>
<td>$^40$</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>pent-1-en-3-one</td>
<td>1000</td>
<td>$^41$</td>
<td>57$^d$</td>
</tr>
<tr>
<td>5</td>
<td>oct-1-en-3-one</td>
<td>1000</td>
<td>$^42$</td>
<td>62$^d$</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 2-bromo-3-methylbut-2-ene (1 equiv), alkene (2 equiv), $\text{K}_2\text{CO}_3$ (2 equiv), DMF, 100 °C, 20 h.

$^b$ $E$-Isomers were obtained selectively (>95%).

$^c$ Isolated yields.

$^d$ NaOAc (2 equiv) was used as base, at 110 °C, and hydroquinone (8%) was added to the reaction mixture.
Anhyd DMF (2.5 mL) was added, then the solution was stirred at r.t. for 10 min. This catalyst solution was used directly for the catalyzed reactions.

**Butyl (E,E)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2)**

**Typical Procedure**

The reaction of β-bromostyrene (1.83 g, 10 mmol), n-butyl acrylate (2.56 g, 20 mmol) and K₂CO₃ (2.80 g, 20 mmol) in anhyd DMF (10 mL) in the presence of the palladium–Tedicyp complex (0.0001 mmol) under argon at 130 °C for 20 h afforded the corresponding product 8, after extraction with CH₂Cl₂ (20 mL), concentration and flash chromatography (pentane–Et₂O, 1:1); yield: 1.52 g (66%).

**1H NMR (300 MHz, CDCl₃); δ = 7.85–7.25 (m, 8 H), 7.09 (dd, J = 15.1, 10.6 Hz, 1 H), 6.95 (dd, J = 15.1, 10.6 Hz, 1 H), 6.78 (d, J = 15.0 Hz, 1 H), 6.67 (d, J = 15.0 Hz, 1 H).**

**Butyl (E,E)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2)** See typical procedure.

**Butyl (E,E)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2)**

The reaction of β-bromostyrene (0.183 g, 1 mmol), but-3-en-1-one (0.140 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded 9; yield: 0.129 g (75%).

**1H NMR (300 MHz, CDCl₃); δ = 7.49 (d, J = 7.7 Hz, 2 H), 7.38–7.17 (m, 4 H), 6.90 (d, J = 16.5 Hz, 1 H), 6.81 (dd, J = 15.7, 9.6 Hz, 1 H), 6.19 (d, J = 15.7 Hz, 1 H), 2.60 (q, J = 7.7 Hz, 2 H), 1.14 (t, J = 7.7 Hz, 3 H).**

**Butyl (E,E)-5-Phenylpenta-2,4-dienoate (8) (Table 2, Entry 2)**

The reaction of β-bromostyrene (0.183 g, 1 mmol), 3,5-bis(trifluoromethyl)styrene (0.183 g, 1 mmol), pent-1-en-3-one (0.210 g, 2 mmol) and K₂CO₃ (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded 6; yield: 0.178 g (86%).

**1H NMR (300 MHz, CDCl₃); δ = 8.57 (d, J = 4.1 Hz, 1 H), 7.62 (dd, J = 7.5, 1.7 Hz, 1 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.43–7.20 (m, 5 H), 7.10 (dd, J = 7.4, 4.9 Hz, 1 H), 6.98 (dd, J = 15.5, 10.7 Hz, 1 H), 6.78 (d, J = 15.8 Hz, 1 H), 6.72 (d, J = 15.5 Hz, 1 H).**

**2-(E,E)-4-Phenyl-1,3-dienyl]pyridine (6) (Table 1, Entry 11)**

The reaction of β-bromostyrene (0.183 g, 1 mmol), 2-vinylpyridine (0.210 g, 2 mmol) and K₂CO₃ (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 130 °C afforded 6; yield: 0.188 g (91%).

**1H NMR (300 MHz, CDCl₃); δ = 8.53 (d, J = 6.0 Hz, 2 H), 7.45 (d, J = 8.2 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.30–7.20 (m, 3 H), 7.12 (dd, J = 15.5, 10.2 Hz, 1 H), 6.94 (dd, J = 15.5, 10.2 Hz, 1 H), 6.77 (d, J = 15.5 Hz, 1 H), 6.57 (d, J = 15.5 Hz, 1 H).**

The reaction of β-bromostyrene (0.183 g, 1 mmol), 2,2-dimethyl-
pent-4-enol (0.224 g, 2 mmol) and NaOAc (0.164 g, 2 mmol)
with the palladium complex (0.01 mmol) at 110 °C afforded
the palladium complex (0.01 mmol) at 130 °C afforded a mixture of product 18
with other regio- and stereoisomers in 82% (1.81 g) isolated yield
and in 55% selectivity in favour of 18.

1H NMR (300 MHz, CDCl3): δ = 7.30–7.15 (m, 10 H), 6.80 (dd,
J = 15.0, 10.2 Hz, 1 H), 6.51 (d, J = 15.0 Hz, 1 H), 6.29 (dd,
J = 15.0, 10.2 Hz, 1 H), 6.01 (dt, J = 15.0, 7.5 Hz, 1 H), 3.51 (d,
J = 7.5 Hz, 2 H).

(E)-1-Styrylcyclohexene (19) (Table 3, Entry 5)
The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclohexene
(1.50 g, 20 mmol) and K2CO3 (2.80 g, 20 mmol) with the palladium
complex (0.01 mmol) at 130 °C in an autoclave afforded a mixture of product 19
with other regio- and stereoisomers in 84% (1.55 g)
isolated yield and in 94% selectivity in favour of 19.

1H NMR (300 MHz, CDCl3): δ = 7.43 (d, J = 8.2 Hz, 2 H), 7.39–
7.25 (m, 3 H), 7.04 (d, J = 16.0 Hz, 1 H), 6.43 (d, J = 16.0 Hz, 1 H),
5.89 (m, 1 H), 2.65–2.40 (m, 4 H), 2.00 (quin, J = 7.5 Hz, 2 H).

(E)-4-Styrylcyclohexene (20) (Table 3, Entry 6)
The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclohexene
(1.50 g, 20 mmol) and K2CO3 (2.80 g, 20 mmol) with the palladium
complex (0.01 mmol) at 130 °C in an autoclave afforded a mixture of product 20
with other regio- and stereoisomers in 93% (1.60 g)
isolated yield and in 94% selectivity in favour of 20.

1H NMR (300 MHz, CDCl3): δ = 7.40 (d, J = 8.2 Hz, 2 H), 7.35–
7.15 (m, 3 H), 6.43 (d, J = 16.0 Hz, 1 H), 6.26 (dd, J = 16.0, 7.1 Hz,
1 H), 5.73 (m, 2 H), 2.55–1.45 (m, 7 H).

(E)-3-Styrylcyclooctene (21) (Table 3, Entry 7)
The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclooctene
(1.64 g, 20 mmol) and K2CO3 (2.80 g, 20 mmol) with the palladium
complex (0.01 mmol) at 100 °C afforded a mixture of product 21
with other regio- and stereoisomers in 81% (1.60 g)
isolated yield and in 80% selectivity in favour of 21.

1H NMR (300 MHz, CDCl3): δ = 7.35–7.28 (m, 4 H), 7.22 (t,
J = 7.5 Hz, 1 H), 6.44 (d, J = 15.8 Hz, 1 H), 6.28 (dd, J = 15.8, 7.3
Hz, 1 H), 5.83 (dt, J = 11.2, 5.1 Hz, 1 H), 5.69 (dd, J = 11.2, 4.5 Hz,
1 H), 3.17 (m, 1 H), 2.30–1.40 (m, 8 H).

(E)-1-Styrylcyclooctene (22) (Table 3, Entry 8)
The reaction of β-bromostyrene (1.83 g, 10 mmol), cyclooctene
(1.78 g, 20 mmol) and K2CO3 (2.80 g, 20 mmol) with the palladium
complex (0.01 mmol) at 130 °C afforded a mixture of product 22
with other regio- and stereoisomers in 93% (1.97 g)
isolated yield and in 93% selectivity in favour of 22.

1H NMR (300 MHz, CDCl3): δ = 7.29 (t, J = 7.2 Hz, 2 H), 7.17 (t,
J = 7.2 Hz, 1 H), 6.74 (d, J = 16.2 Hz, 1 H), 6.47 (d, J = 16.2 Hz, 1 H),
5.86 (t, J = 8.3 Hz, 1 H), 2.51 (m, 2 H), 2.25 (m, 2 H), 1.70–1.40 (m, 8 H).

13C NMR (75 MHz, CDCl3): δ = 139.3, 138.0, 133.8, 132.2, 128.5,
126.8, 126.1, 125.1, 30.4, 28.6, 27.4, 26.9, 26.0, 24.3.


(E)-3-Ethylbuta-1,3-diene (23) (Table 4, Entry 1)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), styrone (0.208
2 g, 2 mmol) and K2CO3 (0.280 g, 2 mmol) with the palladium
complex (0.004 mmol) at 80 °C afforded 23: yield: 0.092 g (58%).

1H NMR (300 MHz, CDCl3): δ = 7.29 (t, J = 7.2 Hz, 2 H), 7.17 (t,
J = 7.2 Hz, 1 H), 6.74 (d, J = 16.2 Hz, 1 H), 6.47 (d, J = 16.2 Hz, 1 H),
6.57 (d, J = 16.1 Hz, 1 H), 5.12 (s, 1 H), 5.07 (s, 1 H), 2.36 (q,
J = 7.3 Hz, 2 H), 1.15 (t, J = 7.3 Hz, 3 H).
1-(E)-3-Ethylbuta-1,3-dienyl]-4-methoxybenzene (24) (Table 4, Entry 2)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), 4-methoxy-
styrene (0.268 g, 2 mmol) and K$_2$CO$_3$ (0.280 g, 2 mmol) with the
palladium complex (0.004 mmol) at 80 °C afforded 24; yield: 0.143 g (76%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 7.34 (d, $J$ = 8.7 Hz, 2 H), 6.86 (d, $J$ = 8.7 Hz, 2 H), 6.70 (d, $J$ = 16.2 Hz, 1 H), 6.53 (d, $J$ = 16.2 Hz, 1 H), 5.07 (s, 1 H), 5.01 (s, 1 H), 3.80 (s, 3 H), 2.34 (q, $J$ = 7.3 Hz, 2 H), 1.15 (t, $J = 7.3$ Hz, 3 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 159.1, 147.8, 130.2, 129.1, 127.5, 127.2, 114.1, 114.0, 55.3, 24.7, 12.8.

Anal. Calcd for C$_{12}$H$_{18}$O: C, 72.61; H, 8.68.

4-(E)-3-Ethylbuta-1,3-dienyl]benzonitrile (25) (Table 4, Entry 3)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), 4-cyanostyrene (0.260 g, 2 mmol) and K$_2$CO$_3$ (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded 25; yield: 0.152 g (83%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 7.58 (d, $J$ = 8.5 Hz, 2 H), 7.48 (d, $J$ = 8.5 Hz, 2 H), 6.90 (d, $J$ = 16.4 Hz, 1 H), 6.55 (d, $J$ = 16.4 Hz, 1 H), 5.22 (s, 1 H), 5.19 (s, 1 H), 2.36 (q, $J$ = 7.3 Hz, 2 H), 1.16 (t, $J = 7.3$ Hz, 3 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 147.1, 142.0, 134.8, 132.4, 126.7, 125.9, 119.0, 117.7, 110.3, 24.5, 12.6.

Anal. Calcd for C$_{12}$H$_{13}$N: C, 82.99; H, 8.23.

Butyl (E)-4-(2-Hydroxyethyl)penta-2,4-dienoate (27) (Table 4, Entry 6)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), n-butyl acrylate (0.256 g, 2 mmol) and K$_2$CO$_3$ (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 80 °C afforded 27; yield: 0.110 g (69%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 8.52 (d, $J$ = 6.4 Hz, 2 H), 7.26 (d, $J$ = 6.4 Hz, 2 H), 6.99 (d, $J$ = 16.4 Hz, 1 H), 6.47 (d, $J$ = 16.4 Hz, 1 H), 5.23 (s, 1 H), 5.20 (s, 1 H), 2.34 (q, $J$ = 7.3 Hz, 2 H), 1.16 (t, $J = 7.3$ Hz, 3 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 149.8, 147.0, 145.0, 135.7, 125.1, 120.8, 118.1, 24.4, 12.5.

Anal. Calcd for C$_{13}$H$_{20}$O: C, 79.94; H, 9.15. Found: C, 79.87; H, 9.34.

(E)-3-Methylene-5-phenylpent-4-en-1-ol (31) (Table 5, Entry 2)
The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), styrene (0.280 g, 2 mmol) and K$_2$CO$_3$ (0.280 g, 2 mmol) with the palladium complex (0.001 mmol) at 130 °C afforded 31; yield: 0.151 g (76%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 7.29 (d, $J$ = 16.0 Hz, 1 H), 5.92 (d, $J$ = 16.0 Hz, 1 H), 5.48 (s, 1 H), 5.41 (s, 1 H), 4.15 (t, $J = 7.5$ Hz, 2 H), 3.76 (t, $J = 7.5$ Hz, 2 H), 2.52 (t, $J = 7.5$ Hz, 2 H), 1.64 (m, 2 H), 1.41 (m, 2 H), 0.93 (t, $J = 7.5$ Hz, 3 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 167.1, 145.9, 141.0, 125.0, 118.7, 64.4, 60.8, 34.9, 30.7, 19.1, 13.7.


Butyl (E)-4-(2-Hydroxyethyl)hepta-4,6-dien-3-one (32) (Table 5, Entry 3)
The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), pent-1-en-3-one (0.164 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 80 °C afforded 32; yield: 0.088 g (64%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 7.18 (d, $J$ = 16.3 Hz, 1 H), 6.19 (d, $J$ = 16.3 Hz, 1 H), 5.39 (s, 1 H), 5.36 (s, 1 H), 2.61 (q, $J = 7.5$ Hz, 2 H), 2.24 (q, $J = 7.5$ Hz, 2 H), 1.11 (m, 6 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 201.5, 146.5, 144.3, 125.8, 122.7, 33.7, 24.3, 12.3, 8.2.

Anal. Calcd for C$_{12}$H$_{18}$O: C, 78.21; H, 10.21. Found: C, 78.30; H, 10.07.

(E)-2-Ethyldeca-1,3-dien-5-one (29) (Table 4, Entry 10)
The reaction of 2-bromobut-1-ene (0.135 g, 1 mmol), oct-1-en-3-one (0.206 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.01 mmol) at 80 °C afforded 29; yield: 0.128 g (71%).

$^1$H NMR (300 MHz, CDCl$_3$): δ = 7.21 (d, $J = 16.3$ Hz, 1 H), 6.22 (d, $J = 16.3$ Hz, 1 H), 5.43 (s, 1 H), 5.40 (s, 1 H), 2.60 (t, $J = 7.5$ Hz, 2 H), 2.27 (q, $J = 7.5$ Hz, 2 H), 1.75–0.78 (m, 12 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 202.0, 147.3, 145.2, 126.9, 123.5, 41.3, 32.3, 25.1, 24.8, 23.2, 14.7, 13.1.

Anal. Calcd for C$_{12}$H$_{15}$O: C, 79.94; H, 9.18. Found: C, 79.87; H, 11.34.
(E)-2-(2-Hydroxyethyl)deca-1,3-dien-5-one (33) (Table 5, Entry 4)

The reaction of 3-bromobut-3-en-1-ol (0.151 g, 1 mmol), oct-1-en-3-one (0.206 g, 2 mmol), hydroquinone (0.009 g, 0.08 mmol) and NaOAc (0.164 g, 2 mmol) with the palladium complex (0.004 mmol) at 110 °C afforded 33; yield: 0.080 g (41%).

[^1] H NMR (300 MHz, CDCl₃): δ = 7.17 (d, J = 16.0 Hz, 1 H), 6.21 (d, J = 16.0 Hz, 1 H), 5.52 (s, 1 H), 5.45 (s, 1 H), 3.76 (t, J = 7.5 Hz, 2 H), 2.59 (t, J = 7.5 Hz, 2 H), 1.61 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, J = 7.5 Hz, 3 H).

[^1] C NMR (75 MHz, CDCl₃): δ = 150.2, 143.4, 141.5, 125.9, 115.4, 64.0, 30.8, 22.5, 20.9, 19.2, 14.0, 13.7.

Anal. Calcd for C₁₃H₁₄O: C, 84.02; H, 8.55. Found: C, 83.17; H, 8.52.

Butyl (E)-5-Methylhexa-2,4-dienoate (34) (Table 6, Entry 1)

The reaction of 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), n-butyl acrylate (0.256 g, 2 mmol) and K₂CO₃ (0.280 g, 2 mmol) with the palladium complex (0.004 mmol) at 100 °C afforded 34; yield: 0.162 g (89%).

[^1] H NMR (300 MHz, CDCl₃): δ = 7.54 (dd, J = 11.7, 15.2 Hz, 1 H), 5.97 (d, J = 11.7 Hz, 1 H), 5.75 (d, J = 15.2 Hz, 1 H), 4.15 (t, J = 6.8 Hz, 2 H), 1.88 (s, 3 H), 1.86 (s, 3 H), 1.65 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3 H).

13C NMR (75 MHz, CDCl₃): δ = 153.4, 142.3, 34.1, 22.7, 20.9, 14.1, 8.5.


[^1] H NMR (300 MHz, CDCl₃): δ = 7.86 (d, J = 15.5 Hz, 1 H), 5.77 (d, J = 15.5 Hz, 1 H), 4.15 (t, J = 6.8 Hz, 2 H), 1.95 (s, 3 H), 1.86 (s, 3 H), 1.78 (s, 3 H), 1.65 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3 H).

[^1] C NMR (75 MHz, CDCl₃): δ = 150.2, 143.4, 141.5, 125.9, 115.4, 64.0, 30.8, 22.5, 20.9, 19.2, 14.0, 13.7.

Anal. Calcd for C₁₃H₂₂O: C, 73.43; H, 10.27. Found: C, 73.61; H, 10.31.

[^1] H NMR (300 MHz, CDCl₃): δ = 7.51 (m, 2 H), 7.48 (d, J = 15.9 Hz, 1 H), 7.25 (m, 3 H), 6.35 (d, J = 15.9 Hz, 1 H), 1.96 (s, 3 H), 1.88 (s, 6 H).

[^1] C NMR (75 MHz, CDCl₃): δ = 142.8, 142.6, 141.1, 126.2, 123.8, 134.1, 22.7, 20.9, 14.1, 8.5.


[^1] H NMR (300 MHz, CDCl₃): δ = 7.77 (d, J = 15.9 Hz, 1 H), 6.11 (d, J = 15.9 Hz, 1 H), 2.60 (q, J = 7.4 Hz, 2 H), 1.97 (s, 3 H), 1.88 (s, 3 H), 1.79 (s, 3 H), 1.12 (t, J = 7.4 Hz, 3 H).

[^1] C NMR (75 MHz, CDCl₃): δ = 128.1, 128.0, 126.9, 126.7, 125.1, 119.2, 109.7, 26.4, 18.7.


[^1] H NMR (300 MHz, CDCl₃): δ = 7.55 (d, J = 7.5 Hz, 2 H), 7.42 (d, J = 7.5 Hz, 2 H), 7.08 (dd, J = 15.5, 10.9 Hz, 1 H), 6.38 (d, J = 15.5 Hz, 1 H), 6.01 (d, J = 10.9 Hz, 1 H), 1.87 (s, 3 H), 1.86 (s, 3 H).


[^1] H NMR (300 MHz, CDCl₃): δ = 7.85 (m, 2 H), 7.17 (dd, J = 11.0, 15.5 Hz, 1 H), 7.15 (m, 2 H), 6.32 (d, J = 15.5 Hz, 1 H), 6.02 (d, J = 11.0 Hz, 1 H), 1.88 (s, 3 H), 1.87 (s, 3 H).

[^1] H NMR (300 MHz, CDCl₃): δ = 7.75 (d, J = 15.9 Hz, 1 H), 6.09 (d, J = 15.9 Hz, 1 H), 2.54 (t, J = 7.4 Hz, 2 H), 1.96 (s, 3 H), 1.87 (s, 3 H), 1.78 (s, 3 H), 1.62 (m, 2 H), 1.30 (m, 4 H), 0.88 (t, J = 7.4 Hz, 3 H).

[^1] C NMR (75 MHz, CDCl₃): δ = 128.1, 128.0, 126.9, 126.7, 125.1, 119.2, 109.7, 26.4, 18.7.


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