Supporting Information

Palladium-Catalyzed Intermolecular [3 + 2] Carbocyclization of Alkynols and Propiolates: An Efficient Entry to Halo-Cyclopentadienes

Yang Gao, Wanqing Wu*, Huawen Huang, Yubing Huang, and Huanfeng Jiang*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China
E-mail: jianghf@scut.edu.cn, cewuwq@scut.edu.cn; Fax and Tel.: (+86) 20-87112906

List of Contents

A. Optimization of Reaction Conditions.............................................................................................................7
B. Experimental Procedures..................................................................................................................................7
  I. General Methods............................................................................................................................................7
  II. General Procedure for Synthesis of the Substrates.......................................................................................7
  III. General Procedure for Synthesis of Halo-cyclopentadienes.................................................................8
  IV. General Procedure for the Further Transformations.................................................................................8
  V. Control Experiments..................................................................................................................................8
C. Characterization Data for Compounds 3aa-8.................................................................................................10
D. NMR Spectra and X-ray Crystallographic Analysis.......................................................................................21
A. Optimization of Reaction Conditions

Table 1. Condition screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Additive</th>
<th>Ligand</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdCl₂</td>
<td>LiBr</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>LiBr</td>
<td>-</td>
<td>86 (83)</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh₃)₂Cl₂</td>
<td>LiBr</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>Pd(PPh₃)₄</td>
<td>LiBr</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Pd₂(dba)₃</td>
<td>LiBr</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pd/C</td>
<td>LiBr</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>Pd(OAc)₂</td>
<td>LiBr</td>
<td>PPh₃</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)₂</td>
<td>LiBr</td>
<td>1,10-Phen</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)₂</td>
<td>TBAB</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>Pd(OAc)₂</td>
<td>NBS</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>Pd(OAc)₂</td>
<td>LiBr</td>
<td>-</td>
<td>81</td>
</tr>
<tr>
<td>12</td>
<td>Pd₂(dba)₃</td>
<td>LiBr</td>
<td>-</td>
<td>35</td>
</tr>
</tbody>
</table>

*Reaction conditions: unless otherwise noted, all reactions were performed with 1a (0.5 mmol), 2a (0.5 mmol), Pd-catalyst (5 mol %), additive (1 mmol) in CH₃CN/HOAc (v/v = 1:1) as solvent at 60 °C for 8h. Determined by GC using dodecane as the internal standard. Data in parentheses is the yield of isolated product. n.d. = not detected. 10 mol % ligands were added in the reaction system. The reactions were performed under N₂ atmosphere.

Table 2. Influence of the solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>Toluene</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>THF</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)₂</td>
<td>DMF</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)₂</td>
<td>DMSO</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)₂</td>
<td>Dioxane</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pd(OAc)₂</td>
<td>MeCN</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Pd(OAc)₂</td>
<td>HOAc</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Pd(OAc)₂</td>
<td>HOAc/CH₃CN = 1:1</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>Pd(OAc)₂</td>
<td>HCOOH/CH₃CN</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>Pd(OAc)₂</td>
<td>α-C₃H₅OOH/CH₃CN</td>
<td>65</td>
</tr>
<tr>
<td>11</td>
<td>Pd(OAc)₂</td>
<td>CH₃CN</td>
<td>31</td>
</tr>
<tr>
<td>12</td>
<td>Pd(OAc)₂</td>
<td>HOAc/THF</td>
<td>80</td>
</tr>
<tr>
<td>13</td>
<td>Pd(OAc)₂</td>
<td>HOAc/Dioxane</td>
<td>66</td>
</tr>
<tr>
<td>14</td>
<td>Pd(OAc)₂</td>
<td>HOAc/DMF</td>
<td>trace</td>
</tr>
</tbody>
</table>

Our initial investigations of this Pd-catalyzed intermolecular carbocyclization focused on the reaction of 2-methylbut-3-yn-2-ol (1a) with ethyl propiolate (2a) in the presence of PdCl₂ and LiBr in MeCN at 60 °C. Experimental results showed that the acidic solvent system played an important role in the success of this transformation and CH₃CN/HOAc (v/v = 1:1) was proved to be the most suitable solvent (see Table 2 for details). Among the palladium catalysts tested, both Pd⁰ and PdII catalysts could promote this transformation and Pd(OAc)₂ gave the best result (entries 1-6). Further investigation on the influence of ligand revealed that the presence of nitrogen or phosphine ligands would inhibit this chemical process (entries 7-8). Other bromine sources such as NBS, TBAB were examined and LiBr gave the best result (entries 2, 9 and 10). In addition, this reaction could perform smoothly under N₂ atmosphere (entries 11-12).
Reaction conditions: unless otherwise noted, all reactions were performed with 1a (0.5 mmol), 2a (0.5 mmol), Pd(OAc)₂ (5 mol%), LiBr (1 mmol) at 60 °C for 8 h. Determined by GC using dodecane as the internal standard. ² 0.1 mmol BF₃·OEt₂ was added to the reaction system.

B. Experimental Procedures

I. General Methods

¹ H NMR spectra were recorded in CDCl₃ at 400 MHz and ¹³C NMR spectra were recorded in CDCl₃ at 100 MHz respectively, and the chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

II. General Procedure for Synthesis of the Substrates

Alkynols 1a-f, 1h and 1i were purchased from Aldrich. 1g, 1j-l were synthesized according to the reported method.¹ Apart from 2a, 2b which were purchased from Aldrich, other propiolates were synthesized according to the reported method.²

Preparation of 2-Phenylbut-3-yn-2-ol

\[
\text{O} \quad \text{MgBr} \quad (0.5 \text{ M in THF, } 1.2 \text{ equiv})
\]

\[
\text{THF, } -10 \text{ °C} \quad \text{rt, } 2 \text{ h}
\]

To a solution of acetophenone (2.00 g, 16.64 mmol) in 30 mL anhydrous THF was added ethynylmagnesium bromide (0.50 M solution in THF 40 mL, 19.97 mmol) at -10 °C. The resulting solution was stirred at -10 °C for 10 min and warmed to room temperature and stirred for 2 h after completion of reaction. The resulting solution was quenched with aqueous NH₄Cl solution (50 mL). The THF was evaporated and the residue was diluted with water (100 mL) and extracted with ether (100 mL × 3) and dried over anhydrous MgSO₄. After the solvent was evaporated, the crude product was purified by column chromatography (hexanes/ethyl acetate = 4/1) to give 2-phenylbut-3-yn-2-ol as a yellow oil (1.70 g, 70 % yield).

Preparation of Phenyl Propiolate

\[\text{O} + \text{O} \quad \text{DAMP, DCC} \]

The arylalcohol (5 mmol) and propionic acid (1.0-1.1 equiv) were dissolved in dichloromethane (5 mL). When the mixture was cooled to 0 °C, a solution of DCC (1.0 equiv.) and DAMP (0.1 equiv), dissolved in dichloromethane (5 mL), was added dropwise, that the temperature of the reaction mixture remained under 5 °C. The mixture was stirred for 4 h. The precipitate was filtered off and the solution was washed with H₂O. The organic layers were combined, dried over Na₂SO₄ and the volatile parts were removed under reduced pressure. The product was purified by flash column chromatography.

III. General Procedure for Synthesis of Halo-Cyclopentadiene

\[\text{HOAc/CH₃CN} = 1:1\]

Alkynol (0.5 mmol), propiolate (0.5 mmol), Pd-catalyst (5 mol %), LiBr (1 mmol) in CH₃CN/HOAc (2 mL, v/v = 1:1) were added to a tube equipped with magnetic stirrer bar. The mixture was stirred at 60 °C (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature and quenched with aqueous Na₂CO₃, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate as eluent to afford the desired product.

IV. General Procedure for the Further Transformations
V. Control Experiments

Two deuterated experiments were carried out to distinguish whether there is proton transfer in this cycloaddition process. As depicted in eq. (1), deuterium product \(3\text{aa}'\) was obtained exclusively in 80% isolated yield and the deuterium atom (98% examined by \(^1\text{H} \) NMR spectroscopy) was still present. However, when deuterated acetic acid was used as the solvent [eq. (2)], there was no deuterium in the product, which indicated that the terminal alkyne hydrogen of alkynol and propiolate remained at the original position.

Furthermore, the possibility of byproducts (E)-3-bromoacrylate (\(2'\)) detected in the reaction system as an intermediate was excluded for \(2'\) could not be transformed to the desired cyclopentadiene products when treated with \(1\text{a}\) under the standard conditions [eq. (3)].

\[
\text{(1)}: \quad \text{HO} + 2\text{a} \quad \xrightarrow{\text{Pd(OAc)}_2, \text{HOAc/CH}_3\text{CN} = 1:1} \quad 3\text{aa}', 80\%
\]

\[
\text{(2)}: \quad \text{HO} + 2\text{a} \quad \xrightarrow{\text{Pd(OAc)}_2, \text{DOAc/CH}_3\text{CN} = 1:1} \quad 3\text{aa}, 82\%
\]

\[
\text{(3)}: \quad \text{Br} + 1\text{a} \quad \xrightarrow{\text{Standard conditions}} \quad 3, \text{not detected}
\]

1-Bromo-3-methylbuta-1,2-diene (\(1\text{a}'\)) was prepared according to the reported work.\(^3\)

\[
\text{(4)}: \quad 1\text{aa}' + 2\text{a} \quad \xrightarrow{\text{Standard Conditions}} \quad 3\text{aa}, \quad \%
\]
When 1a' was treated with 2a under the standard conditions [eq. (4)], the reaction system became complicated and no desired product 3aa was detected by GC-MS, which could exclude that compound 1a' was the possible intermediate for this transformation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Atmosphere</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd₂(dba)₃</td>
<td>N₂</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>Pd₂(dba)₃</td>
<td>O₂</td>
<td>38</td>
</tr>
</tbody>
</table>

Control experiments showed that both the Pd⁰ and Pd⁸ catalysts could afford the desired products, and even in N₂ atmosphere Pd₂(dba)₃ could afford the desired products without significant influence on the yield (36% compared to 38%). Thus, the active catalyst for this transformation might be Pd⁰.

References

C. Characterization Data for Compounds 3aa-5e

**Ethyl 4-Bromo-3,3-dimethylcyclopenta-1,4-dienecarboxylate (3aa)**

Yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 6.59 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.16 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 153.0, 137.3, 134.9, 127.0, 60.6, 55.7, 21.2, 14.2. IR (KBr, cm⁻¹): 2979, 1721, 1245, 1192, 753; ESI-HRMS calcd for C₁₀H₁₃BrO₂ (M + H)⁺ 245.0172; found, 245.0166.
Ethyl 4-Bromo-3-ethyl-3-methylcyclopenta-1,3-dienecarboxylate (3ab)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (d, $J = 1.2$ Hz, 1H), 6.64 (d, $J = 1.1$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.73 (td, $J = 14.4$, 7.2 Hz, 1H), 1.58 (td, $J = 14.8$, 7.2 Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.12 (s, 3H), 0.65 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 151.7, 136.1, 135.8, 128.2, 60.6, 59.9, 28.5, 20.3, 14.2, 8.7. IR (KBr, cm$^{-1}$): 2976, 2360, 1726, 1258, 1187, 740; ESI-HRMS calcd for C$_{11}$H$_{15}$BrO$_2$ (M + Na)$^+$ 281.0148; found, 281.0139.

Ethyl 4-Bromo-3-hexyl-3-methylcyclopenta-1,3-dienecarboxylate (3ac)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J = 1.6$ Hz, 1H), 6.62 (d, $J = 1.5$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.70 – 1.60 (m, 1H), 1.57 – 1.48 (m, 1H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.28 – 1.18 (m, 6H), 1.14 (s, 3H), 0.99 (d, $J = 6.9$ Hz, 2H), 0.85 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 152.0, 136.1, 135.8, 127.9, 60.6, 59.6, 35.6, 31.5, 29.6, 24.2, 22.5, 20.7, 14.2, 14.0. IR (KBr, cm$^{-1}$): 2989, 1722, 1258, 1184, 756; ESI-HRMS calcd for C$_{15}$H$_{23}$BrO$_2$ (M + H)$^+$ 315.0954; found, 315.0952.

Ethyl 4-Bromo-3-cyclopropyl-3-methylcyclopenta-1,3-dienecarboxylate (3ad)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.93 (d, $J = 1.7$ Hz, 1H), 6.60 (d, $J = 1.7$ Hz, 1H), 4.29 – 4.23 (m, 2H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.17 (s, 3H), 1.01 – 0.91 (m, 1H), 0.55 (tt, $J = 9.0$, 5.4 Hz, 1H), 0.46 (dq, $J = 10.6$, 5.4 Hz, 1H), 0.31 (tt, $J = 9.1$, 5.3 Hz, 1H), 0.02 (dq, $J = 10.9$, 5.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.1, 149.6, 137.2, 136.8, 127.1, 127.1, 60.7, 68.8, 18.5, 16.0, 14.2, 2.2, 0.2. IR (KBr, cm$^{-1}$): 2988, 2027, 1763, 1243, 1108, 618; ESI-HRMS calcd for C$_{12}$H$_{15}$BrO$_2$ (M + H)$^+$ 271.0328; found, 271.0325.

Ethyl 4-Bromo-3-methyl-3-phenylcyclopenta-1,4-dienecarboxylate (3ae)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.27 (m, 5H), 7.22 (d, $J = 1.6$ Hz, 1H), 6.78 (d, $J = 1.7$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.64 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.1, 153.8, 137.6, 136.4, 135.4, 128.7, 128.3, 128.0, 127.5, 126.2, 62.8, 60.8, 18.9, 14.2. IR (KBr, cm$^{-1}$): 3058, 2986, 1712, 1243, 1108, 746; ESI-HRMS calcd for C$_{15}$H$_{15}$BrO$_2$ (M + Na)$^+$ 329.0148; found, 329.0139.

Ethyl 4-Bromospiro[4.4]nona-1,3-diene-2-carboxylate (3af)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 1.7$ Hz, 1H), 6.61 (d, $J = 1.7$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.99 (ddd, $J = 11.1$, 8.8, 6.3 Hz, 2H), 1.89 (ddd, $J = 11.7$, 9.3, 6.7 Hz, 4H), 1.67 – 1.62 (m, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.5, 151.5, 134.7, 134.5, 127.6, 66.3, 60.6, 32.5, 26.0, 14.2. IR (KBr, cm$^{-1}$): 2989, 1764, 1242, 1056, 740; ESI-HRMS calcd for C$_{12}$H$_{15}$BrO$_2$ (M + H)$^+$ 271.0328; found, 271.0315.

Ethyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3ag)
Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 1.7$ Hz, 1H), 6.65 (d, $J = 1.7$ Hz, 1H), 4.32 – 4.24 (m, 2H), 1.90 – 1.84 (m, 3H), 1.73 (td, $J = 13.2$, 3.1 Hz, 2H), 1.63 – 1.50 (m, 3H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.19 (d, $J = 12.1$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.5, 149.9, 137.8, 135.8, 127.0, 60.6, 60.0, 31.1, 25.3, 24.2, 14.2. IR (KBr, cm$^{-1}$): 2935, 2878, 1720, 1224, 741; ESI-HRMS calcd for C$_{13}$H$_{17}$BrO$_2$ (M + H)$^+$ 285.0485; found, 285.0483.

Ethyl 4-Bromo-8,8-ethane-diol-spiro[4.5]deca-1,3-diene-2-carboxylate (3ah)

White solid; mp 126-127 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 1.7$ Hz, 1H), 6.66 (d, $J = 1.7$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.00 (s, 4H), 2.11 (td, $J = 13.6$, 4.1 Hz, 2H), 1.84 (ddd, $J = 18.4$, 17.7, 8.7 Hz, 4H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.27 – 1.16 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.4, 148.5, 136.8, 136.6, 127.6, 107.7, 64.5, 64.4, 60.8, 59.0, 33.2, 29.0, 14.2. IR (KBr, cm$^{-1}$): 2989, 1764, 1224, 1056, 753; ESI-HRMS calcd for C$_{15}$H$_{19}$BrO$_4$ (M + H)$^+$ 343.0539; found, 343.0534.

Ethyl 4-Bromo-8-oxaspiro[4.5]deca-1,3-diene-2-carboxylate (3ai)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J = 1.6$ Hz, 1H), 6.71 (d, $J = 1.6$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.09 (dd, $J = 12.0$, 4.7 Hz, 2H), 3.72 (td, $J = 12.8$, 1.8 Hz, 2H), 2.13 (td, $J = 13.4$, 4.8 Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.10 (d, $J = 14.1$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 147.5, 136.7, 136.3, 127.9, 65.6, 60.8, 57.2, 30.2, 14.2. IR (KBr, cm$^{-1}$): 2956, 2369, 1720, 1243, 1108, 747; ESI-HRMS calcd for C$_{12}$H$_{15}$BrO$_3$ (M + Na)$^+$ 309.0097; found, 309.0108.

Ethyl 4-bromospiro[4.7]dodeca-1,3-diene-2-carboxylate (3aj)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 1.8$ Hz, 1H), 6.55 (d, $J = 1.8$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.90 (tt, $J = 4.9$, 4.1 Hz, 2H), 1.81 (ddd, $J = 14.2$, 8.9, 1.5 Hz, 2H), 1.76 – 1.66 (m, 4H), 1.66 – 1.60 (m, 4H), 1.44 – 1.37 (m, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.54, 152.71, 137.99, 135.11, 126.66, 61.63, 60.62, 29.38, 28.30, 24.03, 23.89, 14.24. IR (KBr, cm$^{-1}$): 2935, 2878, 1720, 1243, 1108, 747; ESI-HRMS calcd for C$_{15}$H$_{21}$BrO$_2$ (M + H)$^+$ 313.0797; found, 313.0793.

4-(Trifluoromethyl)benzyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3ba)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 1.6$ Hz, 1H), 6.61 (d, $J = 1.5$ Hz, 1H), 5.29 (s, 2H), 1.17 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 154.0, 139.8, 137.7, 134.3, 128.2, 126.7, 125.6 (dd, $J = 7.5$, 3.8 Hz), 65.4, 55.9, 21.1. IR (KBr, cm$^{-1}$): 2987, 2371, 1724, 1245, 1126, 745; APCI-HRMS calcd for C$_{16}$H$_{14}$BrF$_3$O$_2$ (M + H)$^+$ 375.0205; found, 375.0205.

4-Nitrobenzyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3ca)
Phenyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3da)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 1.6$ Hz, 1H), 6.63 (s, 1H), 5.36 (s, 2H), 1.20 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 154.2, 147.8, 143.0, 137.8, 134.0, 128.4, 126.5, 123.8, 64.9, 56.0, 21.1. IR (KBr, cm$^{-1}$): 2964, 2359, 1739, 1530, 1242, 1186, 758; APCI-HRMS calcd for C$_{15}$H$_{14}$BrNO$_4$ (M + H)$^+$ 352.0178; found, 352.0172.

4-(Methylthio)phenyl 4-Bromo-3,3-dimethylcyclopenta-1,4-dienecarboxylate (3ea)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (s, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.69 (s, 1H), 2.48 (s, 3H), 1.22 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.6, 155.0, 148.2, 137.8, 135.8, 134.1, 128.0, 126.7, 122.0, 56.1, 21.1, 16.4. IR (KBr, cm$^{-1}$): 2972, 1738, 1247, 1086, 746; APCI-HRMS calcd for C$_{15}$H$_{15}$BrO$_2$S (M + H)$^+$ 339.0049; found, 339.0051.

Phenyl 4-Bromospiro[4.5]deca-1,3-diene-1-carboxylate (3dg)

White solid; mp 116-117 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 1.7$ Hz, 1H), 7.43 – 7.37 (m, 2H), 7.26 (d, $J = 6.4$ Hz, 1H), 7.17 – 7.14 (m, 2H), 6.75 (d, $J = 1.7$ Hz, 1H), 1.89 (dd, $J = 9.3, 4.9$ Hz, 3H), 1.78 (td, $J = 13.2, 3.4$ Hz, 2H), 1.65 – 1.51 (m, 2H), 1.41 – 1.30 (m, 1H), 1.28 – 1.23 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.8, 152.0, 150.6, 138.2, 135.2, 129.4, 126.8, 125.9, 121.6, 60.4, 31.1, 25.3, 24.2. IR (KBr, cm$^{-1}$): 2984, 2360, 1738, 1248, 1173, 749, 698; APCI-HRMS calcd for C$_{17}$H$_{17}$BrO$_2$ (M + H)$^+$ 333.0485; found, 333.0479.

Benzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3fg)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 1.6$ Hz, 1H), 7.43 – 7.30 (m, 5H), 6.65 (d, $J = 1.6$ Hz, 1H), 5.25 (s, 2H), 1.83 (d, $J = 11.0$ Hz, 3H), 1.71 (td, $J = 13.2, 3.1$ Hz, 2H), 1.53 (ddd, $J = 16.2, 9.4, 2.9$ Hz, 2H), 1.36 – 1.24 (m, 1H), 1.17 (d, $J = 12.3$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.3, 150.5, 137.9, 135.8, 135.5, 128.6, 128.3, 126.9, 66.4, 60.1, 31.0, 25.3, 24.2. IR (KBr, cm$^{-1}$): 2965, 2342, 1721, 1248, 1173, 749, 698; APCI-HRMS calcd for C$_{16}$H$_{19}$BrO$_2$ (M + H)$^+$ 347.0641; found, 347.0640.

4-(Trifluoromethyl)benzyl-4-Bromo-5,5-dimethylcyclopenta-1,3-diene-2-carboxylate (3gg)
Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (s, 1H), 7.41 – 7.37 (m, 2H), 7.06 (t, $J = 8.2$ Hz, 2H), 6.63 (s, 1H), 5.21 (s, 2H), 1.84 (d, $J = 10.9$ Hz, 3H), 1.71 (dd, $J = 21.3$, 8.0 Hz, 2H), 1.53 (dd, $J = 26.6$, 13.0 Hz, 2H), 1.33 (dd, $J = 18.1$, 8.9 Hz, 1H), 1.17 (d, $J = 12.8$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.9, 162.4 (d, $J = 176.8$ Hz), 150.6, 138.0, 135.4, 131.7 (d, $J = 3.3$ Hz), 130.3 (d, $J = 8.3$ Hz), 126.8, 115.5 (d, $J = 21.5$ Hz), 65.7, 60.2, 31.0, 25.3, 24.2. IR (KBr, cm$^{-1}$): 2986, 2359, 1722, 1240, 827, 747; APCI-HRMS calcd for C$_{18}$H$_{18}$BrFO$_2$ (M + H)$^+$ 365.0546; found, 365.0550.

4-Chlorobenzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3hg)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 1.5$ Hz, 1H), 7.37 – 7.32 (m, 4H), 6.63 (d, $J = 1.5$ Hz, 1H), 5.21 (s, 2H), 1.84 (d, $J = 11.0$ Hz, 3H), 1.72 (td, $J = 13.3$, 3.0 Hz, 2H), 1.53 (td, $J = 13.0$, 3.1 Hz, 2H), 1.35 – 1.25 (m, 1H), 1.17 (d, $J = 12.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.2, 150.8, 138.0, 135.3, 134.3, 134.2, 129.7, 128.8, 126.8, 65.6, 60.2, 31.0, 25.3, 24.2. IR (KBr, cm$^{-1}$): 2967, 2359, 1739, 1247, 745; ESI-HRMS calcd for C$_{18}$H$_{18}$BrClO$_2$ (M + Na)$^+$ 403.0071; found, 403.0065.

4-Bromobenzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3ig)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 1.6$ Hz, 1), 7.50 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 1.6$ Hz, 1H), 5.19 (s, 2H), 1.84 (d, $J = 11.0$ Hz, 3H), 1.72 (td, $J = 13.2$, 3.1 Hz, 2H), 1.60 – 1.47 (m, 2), 1.36 – 1.24 (m, 1H), 1.17 (d, $J = 12.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.1, 150.4, 138.0, 135.3, 134.8, 131.7, 130.0, 126.8, 122.4, 65.6, 60.2, 31.0, 25.3, 24.2. IR (KBr, cm$^{-1}$): 2932, 2359, 1727, 1246, 810; ESI-HRMS calcd for C$_{18}$H$_{18}$Br$_2$O$_2$ (M + Na)$^+$ 446.9566; found, 446.9562.

$p$-Tolyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3jg)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 (s, 1H), 7.30 (d, $J = 7.8$ Hz, 2H), 7.18 (d, $J = 7.7$ Hz, 2H), 6.64 (s, 1H), 5.20 (s, 2H), 2.36 (s, 3H), 1.83 (d, $J = 10.6$ Hz, 3H), 1.75 – 1.66 (m, 2H), 1.52 (dd, $J = 26.6$, 13.0 Hz, 2H), 1.35 – 1.25 (m, 1H), 1.17 (d, $J = 12.9$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.4, 150.4, 138.2, 137.8, 135.6, 132.8, 129.2, 128.5, 127.0, 66.4, 60.1, 31.0, 25.3, 24.2, 21.2. IR (KBr, cm$^{-1}$): 2969, 2342, 1720, 1248, 1173, 749, 688; APCI-HRMS calcd for C$_{19}$H$_{21}$BrO$_2$ (M + H)$^+$ 361.0798; found, 361.0809.

4-Bromo-3,3-dimethyl-N-phenylcyclopenta-1,3-dienecarboxamide (3ka)

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.02 (d, $J = 1.8$ Hz, 1H), 6.69 (d, $J = 1.8$ Hz, 1H), 1.22 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.5, 147.2, 138.5, 138.3, 137.5, 129.1, 126.6, 124.6, 120.1, 55.9, 21.4. IR (KBr, cm$^{-1}$): 3256, 2987, 2359, 1699, 1273, 746; APCI-HRMS calcd for C$_{14}$H$_{14}$BrNO (M + H)$^+$ 292.0331; found, 292.0335.

4-Bromo-N-(4-chlorophenyl)-3,3-dimethylcyclopenta-1,3-dienecarboxamide (3la)
Yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, \(J = 8.7\) Hz, 3H), 7.30 (d, \(J = 8.8\) Hz, 2H), 6.99 (d, \(J = 1.7\) Hz, 1H), 6.65 (d, \(J = 1.7\) Hz, 1H), 1.20 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.4, 147.5, 138.5, 138.3, 136.1, 129.6, 129.1, 126.5, 121.3, 56.0, 21.4. IR (KBr, cm\(^{-1}\)): 3258, 2988, 2359, 1699, 1273, 746; APCI-HRMS calcd for C\(_{14}\)H\(_{13}\)BrClNO (M + H\(^+\)) 325.9942; found, 325.9940.

**Ethyl 4-Chloro-3,3-dimethylcyclopenta-1,3-dienecarboxylate (4a)**

Yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.07 (d, \(J = 1.8\) Hz, 1H), 6.40 (d, \(J = 1.7\) Hz, 1H), 4.26 (q, \(J = 7.1\) Hz, 2H), 1.33 (t, \(J = 7.1\) Hz, 3H), 1.19 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.6, 151.7, 146.9, 133.9, 122.6, 60.6, 54.6, 20.7, 14.2. IR (KBr, cm\(^{-1}\)): 2989, 2309, 1726, 1258, 1192, 786; APCI-HRMS calcd for C\(_{10}\)H\(_{13}\)ClO\(_2\) (M + Na\(^+\)) 223.0496; found, 223.0504.

**Ethyl 4-Bromo-3-methyl-3-phenylcyclopenta-1,3-dienecarboxylate (4b)**

Yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.25 (m, 4H), 7.20 (d, \(J = 1.4\) Hz, 1H), 7.18 (s, 1H), 6.55 (d, \(J = 1.6\) Hz, 1H), 4.27 (q, \(J = 7.1\) Hz, 2H), 1.63 (s, 3H), 1.33 (t, \(J = 7.1\) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.3, 152.2, 147.2, 136.5, 134.6, 128.8, 127.5, 126.2, 124.4, 61.7, 60.8, 18.7, 14.2. IR (KBr, cm\(^{-1}\)): 2986, 2362, 1738, 1243, 764; APCI-HRMS calcd for C\(_{15}\)H\(_{15}\)ClO\(_2\) (M + H\(^+\)) 263.0833; found, 263.0839.

**Ethyl 4-Bromo-7,7-dimethyl-5-phenylbicyclo[2.2.1]hept-2-ene-2-carboxylate (5a)**

Light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 – 7.24 (m, 3H), 7.12 – 7.08 (m, 2H), 6.48 (s, 1H), 4.35 – 4.25 (m, 2H), 3.63 (dd, \(J = 9.1, 4.6\) Hz, 1H), 2.99 (d, \(J = 3.6\) Hz, 1H), 2.60 (ddd, \(J = 13.0, 9.1, 3.9\) Hz, 1H), 1.67 (dd, \(J = 12.9, 4.6\) Hz, 1H), 1.34 (t, \(J = 7.0\) Hz, 3H), 1.14 (s, 3H), 1.02 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.9, 145.8, 140.1, 139.6, 129.59, 127.8, 127.0, 77.6, 63.2, 60.7, 59.9, 48.5, 34.0, 20.6, 19.6, 14.3. IR (KBr, cm\(^{-1}\)): 2979, 2356, 1712, 1598, 1255, 1081, 748; ESI-HRMS calcd for C\(_{18}\)H\(_{21}\)BrO\(_2\) (M + H\(^+\)) 349.0798; found, 349.0798.

**Ethyl 4-Bromo-5-(4-bromophenyl)-7,7-dimethylbicyclo[2.2.1]hept-2-ene-2-carboxylate (5b)**

Light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (d, \(J = 8.1\) Hz, 2H), 6.97 (d, \(J = 8.1\) Hz, 2H), 6.43 (s, 1H), 4.35 – 4.24 (m, 2H), 3.58 (dd, \(J = 9.0, 4.4\) Hz, 1H), 2.99 (d, \(J = 2.8\) Hz, 1H), 2.63 – 2.55 (m, 1H), 1.63 – 1.59 (m, 1H), 1.33 (t, \(J = 7.1\) Hz, 3H), 1.12 (s, 3H), 1.01 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.7, 145.4, 140.4, 138.7, 131.1, 130.9, 121.1, 77.2, 63.4, 60.8, 50.4, 48.5, 33.9, 20.5, 19.6, 14.3. IR (KBr, cm\(^{-1}\)): 2982, 2362, 1710, 1600, 1254, 1081, 740; ESI-HRMS calcd for C\(_{18}\)H\(_{29}\)Br\(_2\)O \(_2\) (M + Na\(^+\)) 448.9722; found, 448.9720.
**Ethyl 1-Bromo-6-phenylspiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclohexane]-3-carboxylate (5c)**

Light yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.22 (m, 3H), 7.13 – 7.06 (m, 2H), 6.47 (s, 1H), 4.36 – 4.23 (m, 2H), 3.65 (dd, $J$ = 9.1, 4.4 Hz, 1H), 3.33 (d, $J$ = 3.4 Hz, 1H), 2.51 (ddd, $J$ = 12.9, 9.2, 3.8 Hz, 1H), 1.86 – 1.60 (m, 7H), 1.34 (t, $J$ = 7.1 Hz, 3H), 1.31 – 1.12 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.9, 145.9, 139.6, 139.2, 129.6, 127.7, 127.0, 77.9, 67.4, 60.6, 50.4, 43.3, 33.2, 28.5, 28.3, 26.5, 24.1, 23.2, 14.3. IR (KBr, cm$^{-1}$): 2928, 2858, 2355, 1712, 1597, 1246, 1080, 748; ESI-HRMS calcd for C$_{21}$H$_{25}$BrO$_2$ (M + Na)$^+$ 389.1111; found, 389.1107.

**tert-Butyl 3,3-dimethyl-4-phenylcyclopenta-1,3-dienecarboxylate (6a)**

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 7.6 Hz, 2H), 7.35 (t, $J$ = 7.6 Hz, 2H), 7.25 (dd, $J$ = 8.4, 6.2 Hz, 1H), 7.03 (d, $J$ = 1.3 Hz, 1H), 6.80 (d, $J$ = 1.2 Hz, 1H), 1.56 (s, 9H), 1.37 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.8, 155.2, 155.0, 135.4, 135.2, 128.4, 127.0, 126.6, 124.2, 80.6, 53.9, 28.2, 22.0. IR (KBr, cm$^{-1}$): 2988, 2209, 1726, 1248, 1192, 697; ESI-HRMS calcd for C$_{18}$H$_{22}$O$_2$ (M + H)$^+$ 271.1692; found, 271.1697.

**Ethyl 3,3-dimethyl-4-(naphthalen-2-yl)cyclopenta-1,3-dienecarboxylate (6b)**

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 – 7.77 (m, 4H), 7.71 (d, $J$ = 8.7, 1.7 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.18 (d, $J$ = 1.6 Hz, 1H), 7.03 (d, $J$ = 1.5 Hz, 1H), 4.31 (q, $J$ = 7.1 Hz, 2H), 1.47 (s, 6H), 1.37 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.4, 156.3, 154.9, 133.7, 133.4, 132.4, 132.4, 128.2, 128.0, 127.5, 126.2, 125.9, 125.1, 124.9, 124.5, 60.5, 54.1, 22.3, 14.3. IR (KBr, cm$^{-1}$): 2988, 2210, 1726, 1243, 1192, 680; ESI-HRMS calcd for C$_{20}$H$_{20}$O$_2$ (M + H)$^+$ 293.1536; found, 293.1543.

**5-(4-Bromo-3,3-dimethylcyclopenta-1,3-dienyl)nonan-5-ol (7)**

Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.21 (d, $J$ = 1.9 Hz, 1H), 6.13 (d, $J$ = 1.9 Hz, 1H), 1.63 – 1.56 (m, 4H), 1.28 (m, 8H), 1.10 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.9, 138.1, 137.4, 128.3, 74.7, 54.1, 40.1, 25.5, 23.0, 22.1, 14.0. IR (KBr, cm$^{-1}$): 3380, 2988, 2876, 2309, 1726, 1358, 1192, 797; ESI-HRMS calcd for C$_{16}$H$_{23}$BrO (M + H)$^+$ 315.1318; found, 315.1316.

**4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylic acid (8)**
White solid; mp 138-139 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 1.5$ Hz, 1H), 6.62 (d, $J = 1.5$ Hz, 1H), 1.21 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 155.7, 137.7, 134.2, 126.6, 56.1, 21.1. IR (KBr, cm$^{-1}$): 2988, 2878, 2310, 1698, 1258, 1192, 796; ESI-HRMS calcd for C$_8$H$_9$BrO$_2$ (M + H)$^+$ 216.9858; found, 216.9864.
D. NMR Spectra and X-ray Crystallographic Analysis
X-ray Crystallographic Analysis of 3ah and 8

Summary of Data CCDC 935031
---------------
Formula: C15 H20 Br1 O4
Unit cell parameters: a 5.76610(10) b 11.1691(2) c 22.7520(5)
alpha 90.00 beta 91.966(2) gamma 90.00
space group P21/n

Summary of Data CCDC 935030
---------------
Formula: C8 H9 Br O2
Unit cell parameters: a 5.8136(2) b 20.7534(8) c 7.4685(3)
alpha 90.00 beta 103.620(4) gamma 90.00
space group P21/c