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# *ortho*-Disubstitution reactions of aromatic rings with homo-conjugated bicyclo[2.2.2]octa-2,5-diene derivatives in the presence of palladium(II) acetate

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**Abstract**—Bicyclo[2.2.2]octa-2,5-diene derivatives **5** and **7** reacted with aromatic compounds such as benzene, naphthalene, anthracene, phenanthrene, and tropone in the presence of $Pd(OAc)_2$ to afford *ortho*-disubstituted aromatics **6** and **8**–**12**. Since the yields and regioselectivity were generally low, the reaction conditions were optimized by using iodoarenes as reagents to provide sufficient yields and regioselectivity. In order to investigate reactivities of diene moieties, several kinds of homo-conjugated dienes were surveyed for the reaction. Only dienes containing a bicyclo[2.2.2]octa-2,5-diene skeleton gave the *ortho*-disubstituted aromatics. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Homo-conjugated dienes such as norbornadiene (**1**), bicyclo[2.2.2]octa-2,5-diene (**2**), bicyclo[3.2.2]nona-6,8-diene (**3**), and barrelene (**4**) are highly attractive compounds to investigate through-space interactions and reactivity because their double bonds are fixed close each other. Most studies have been carried out on their photochemical reactions,[1] Diels–Alder reactions with dienophiles,[2] and organometalation.[3] On the other hand, π-allyl palladium complexes are very useful for organic synthesis and much research effort has been conducted.[4] For example, butadiene reacts with Pd salts to afford stable π-allyl palladium complexes, which produce 1,4-disubstituted 2-butene derivatives after reactions with nucleophiles. In this context, reactions of homo-conjugated dienes with Pd salts are of much interest since those provide the possibility of forming homo-π-allyl palladium complexes. At present, several works have been reported on norbornadiene, discussed that homo-π-allyl palladium complexes were considered as a transition state species or a metastable intermediate in the reaction path.[5] However, there is no report on reactions of other homo-conjugated dienes with Pd salts. Therefore, we investigated reactions of several kinds of homo-conjugated dienes with $Pd(OAc)_2$ in dry benzene. When bicyclo[2.2.2]octa-2,5-diene derivatives **5** were employed, a new type of tetracyclic compounds with benzene was obtained. The reactions probably proceeded via homo-π-allyl palladium complexes. We report herein the *ortho*-disubstitution reactions of aromatic compounds with the homo-conjugated dienes using $Pd(OAc)_2$ and properties of the diene moieties.


**1**


**2**


**3**


**4**

## 2. Results and discussion

### 2.1. Reactions of homo-dienes with aromatic compounds

Tricyclo[$3.2.2.0^{2,4}$]nona-6,9-diene derivatives **5a**–**d**[6] were heated at 60–80°C for 20–48 h in dry benzene with $Pd(OAc)_2$ (1 mol equiv.) and NaOAc (5 mol equiv.) to afford compounds **6a**–**d** (Table 1). Molecular structures of **6a**–**d** were determined as follows. In mass spectra molecular ion peaks indicated 1:1 compositions of **5** and benzene. $^1H$ and $^{13}C$ NMR analyses supported *ortho*-disubstituted benzene moieties. Additionally, disappearance of signals for the olefin parts suggested reactions of benzene to the homo-conjugated double bonds.[7] The molecular structure was ultimately determined by an X-ray structural analysis of **6c** (Fig. 1) as indicated in a preliminary report

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*Keywords*: metalation; palladium and compounds; dienes; aryl halides.

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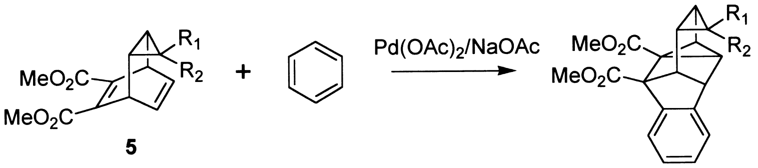
PII: S0040-4020(02)01126-2

**Table 1**. Reactions of dienes **5** with benzene



**5**

**6**

| Diene | $R_1$ | $R_2$ | Temperature (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| **5a** | H | H | 60 | 24 | **6a** 31 |
| **5b** | H | CN | 80 | 48 | **6b** 57 |
| **5c** | CN | H | 80 | 20 | **6c** 43 |
| **5d** | $CO_2Et$ | H | 60 | 20 | **6d** 20 |

Reaction conditions: **5** (3 mmol), $Pd(OAc)_2$ (3 mmol), NaOAc (15 mmol), benzene (30 ml).

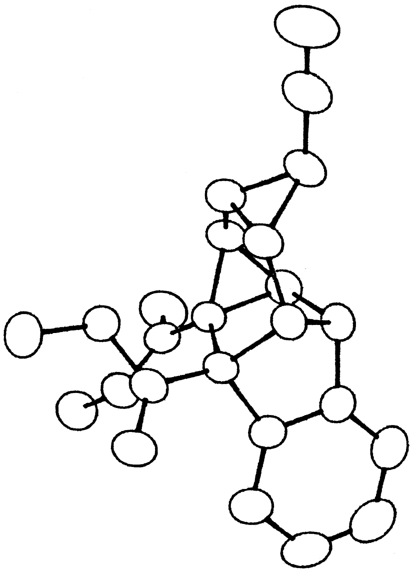


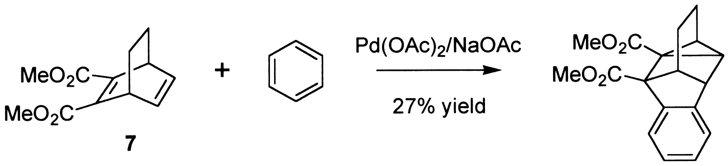
**Figure 1.** Molecular structure of compound **6c** (ORTEP).

(CCDC reference number 186676).[8] The yields were slightly dependent on functional groups ($R_1$, $R_2$) as shown in Table 1. The three-membered ring, however, seemed not to be important in the reactions since diene **7** also reacted with benzene to give compound **8** in 27% yield (Scheme 1). In these reactions no starting material was recovered and other products such as mono-substituted compounds were not obtained at all.[5e,f]

In order to expand applicability to other aromatic compounds, reactions of diene **5d** with condensed aromatic rings were performed (Table 2). Diene **5d** and naphthalene in ethyl acetate were refluxed in the presence of $Pd(OAc)_2$ and NaOAc for 4 days to give three isomers of *ortho*-disubstituted aromatics **9a–c** (entry 1). Molecular structures of **9b** and **9c** were undoubtedly characterized by $^1H$ NMR spectra. Because it was considered that H(f) proton of **9b** was deshielded by ring electrons on the naphthalene moiety, the H(f) proton was used for distinguishing **9b** ($\delta_{Hf}$=3.73 ppm) from the other isomers **9c** ($\delta_{Hf}$=3.30 ppm) and **9a** ($\delta_{Hf}$=3.28 ppm). The major product was **9a**, suggesting that the reaction proceeded to minimize steric hindrance. Anthracene and phenanthrene also reacted under the same conditions to afford mixtures of stereo isomers **10** and **11**, respectively (entries 2 and 3). Tropone was also applied for the reaction as an example of non-benzenoid aromatics. Stereo isomer of product **12** could not be characterized because only a single isomer was obtained in a low yield (entry 4).

### 2.2. Reactions of homo-dienes with iodoarenes

Although several types of aromatic compounds reacted with homo-conjugated diene **5d** as described above, the yields and regioselectivity were generally not high. Therefore, iodoarenes were used for the reaction since insertion of Pd(II) to C–H bonds of aromatics were considered as a crucial step according to many research reports on organometalation.[9] Iodobenzene was allowed to react with diene **5d** in refluxing acetonitrile containing $Pd(OAc)_2$ and NaOAc to give compound **6d** in 52% yield. Furthermore, addition of *n*-$Bu_4NCl$ (1 mol equiv.) increased the yield up to 73%. It has been known that use of *n*-$Bu_4NCl$ is effective for many Pd-catalyzed reactions.[10] Table 3 summarizes yields of products **6a–e** obtained by the reactions of dienes **5a–e** using iodobenzene. The yields are higher than those listed in Table 1 and reaction times are shorter except for **6b**

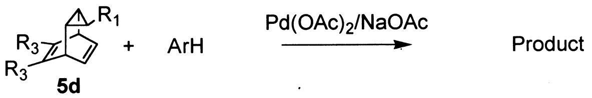


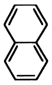
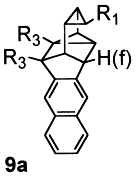
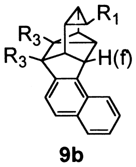
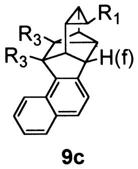
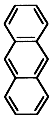
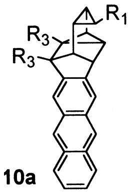
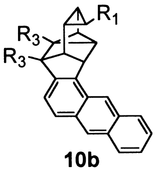
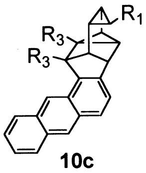
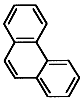
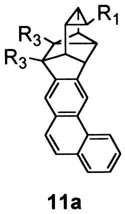
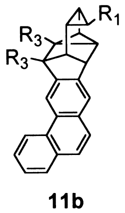
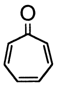
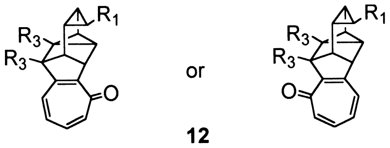
**7**

**8**

**Scheme 1.** Reaction of diene **7** with benzene.

**Table 2**. Reactions of diene **5d** with several types of aromatic compounds



| Entry | ArH | Product | Yield (%) |
|---|---|---|---|
| 1[a] |  |  **9a**  **9b**  **9c** | **9a** 16;<br>**9b** 7;<br>**9c** 3 |
| 2[a] |  |  **10a**  **10b**  **10c** | **10a** 13;<br>**10b** 4;<br>**10c** 3 |
| 3[a] |  |  **11a** and  **11b** | **11** 8 |
| 4[b] |  |  **12** | **12** 4 |

Reaction conditions: **5d** ($R_1$=$CO_2Et$, $R_3$=$CO_2Me$, 1 mmol), ArH (3–9 mmol), $Pd(OAc)_2$ (1 mmol), NaOAc (5 mmol), reflux, 4 days.

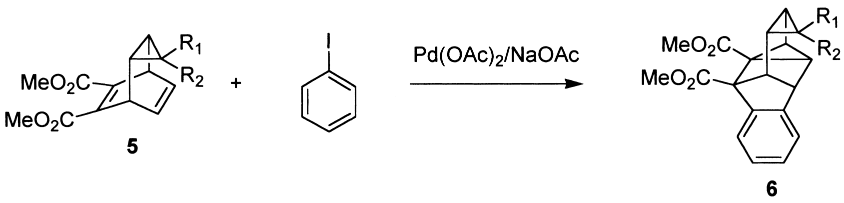
[a] AcOEt (10 ml).

[b] MeCN (8 ml).

and **6e**. Thus, the rate-determining step governed by organometalation was accelerated. The yield, however, decreased to only 15% when bromobenzene was employed for a reaction with **5d**.

Other types of iodoarenes were applied for the reactions as shown in Table 4. Although a stereo isomer of **13** was not confirmed, entry 1 indicates introduction of functional groups into aromatic rings of products. Entries 2 and 3 show the improved yields and regioselectivity, which demonstrates usefulness of *ortho*-disubstitution reactions for synthesizing unique pentacycles.

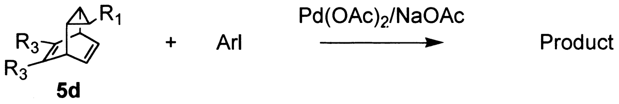
**Table 3**. Reactions of dienes **5** with iodobenzene

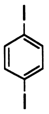
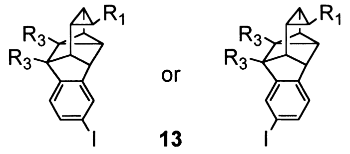
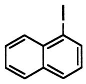
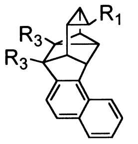
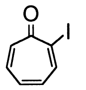
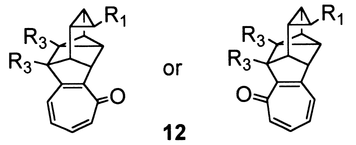


| Diene | $R_1$ | $R_2$ | Time (h) | Yield (%) |
|---|---|---|---|---|
| **5a** | H | H | 6 | **6a** 68 |
| **5b** | H | CN | 48 | **6b** 58 |
| **5c** | CN | H | 6 | **6c** 79 |
| **5d** | $CO_2Et$ | H | 6 | **6d** 73 |
| **5e** | $CO_2Me$ | Me | 6 | **6e** 35 |

Reaction conditions: **5** (1 mmol), PhI (3 mmol), $Pd(OAc)_2$ (1 mmol), NaOAc (5 mmol), *n*-$Bu_4NCl$ (1 mmol), MeCN (6 ml), reflux.

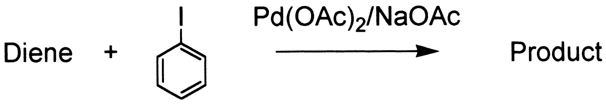
**Table 4**. Reactions of diene **5d** with iodoarenes

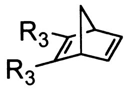
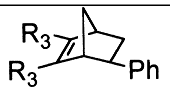
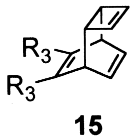
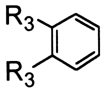
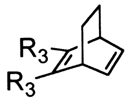
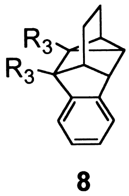
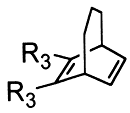
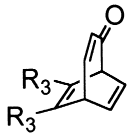


| Entry | ArI | Product | Yield (%) |
|---|---|---|---|
| 1 |  | <br>**13** | **13** 30 |
| 2 |  | <br>**9b** | **9b** 54 |
| 3 |  | <br>**12** | **12** 22 |

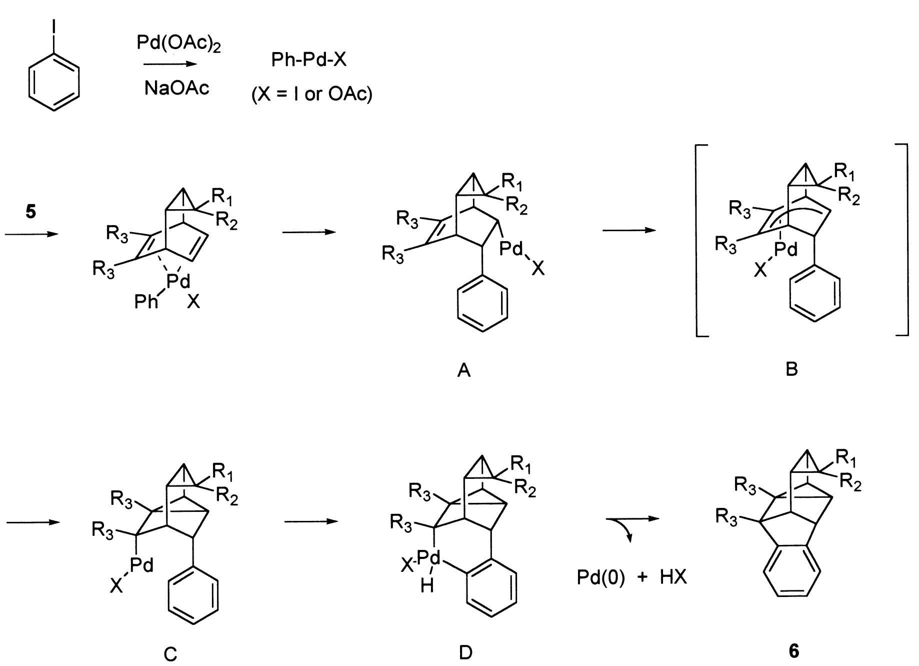
Reaction conditions: **5d** ($R_1$=$CO_2Et$, $R_3$=$CO_2Me$, 1 mmol), ArI (3 mmol), $Pd(OAc)_2$ (1 mmol), NaOAc (5 mmol), *n*-$Bu_4NCl$ (1 mmol), MeCN (6 ml), reflux, 3 days.

**Table 5**. Reactions of homo-conjugated dienes with iodobenzene



| Entry | Diene | Time | Product | Yield (%) |
|---|---|---|---|---|
| 1 | <br>**14** | 3 days | <br>**18** | 11 |
| 2 | <br>**15** | 3 days | <br>**19** | 30 |
| 3 | <br>**7** | 6 h | <br>**8** | 60 |
| 4 | <br>**16** | 20 h | Decomp | |
| 5 | <br>**17** | 3 days | Decomp | |

Reaction conditions: diene ($R_3$=$CO_2Me$, 1 mmol), PhI (3 mmol), $Pd(OAc)_2$ (1 mmol), NaOAc (5 mmol), *n*-$Bu_4NCl$ (1 mmol), MeCN (6 ml), reflux.



**Scheme 2.** Mechanism of *ortho*-disubstitution reaction.

### 2.3. Scope and limitations of *ortho*-disubstitution reactions and mechanisms

The *ortho*-disubstitution reactions were studied using a series of homo-conjugated diene moieties to show the scope and limitations of the reaction (Table 5). Norbornadiene **14** reacted with iodobenzene to afford compound **18** (entry1), and this result was supported by other reports.[11] Diene **15** afforded benzene derivative **19** as a result of elimination of cyclobutadiene like a retro-Diels–Alder reaction (entry 2).[12] Diene **7** produced compound **8** in 60% yield as described above (entry 3). No significant compound was obtained from both reactions using dienes **16** and **17**, respectively (entries 4 and 5). These results demonstrated that only bicyclo[2.2.2]octa-2,5-diene derivatives yielded the products and the *ortho*-disubstitution reactions strongly depended on properties of the homo-conjugated dienes.

The reaction mechanisms were speculated as Scheme 2 from research reports concerning organometalation of $Pd(OAc)_2$ to C–X bonds (X=I, Br, Cl) using inorganic salts[5e,10] and addition to the double bonds.[5,13] The first step was a reaction of $Pd(OAc)_2$ with iodoarene (e.g. iodobenzene) in the presence of NaOAc yielding a Ph-Pd–X (X=I or OAc) complex. This complex followed by addition to homo-conjugated diene (e.g. **5**) to form complex A.[5f] Then complex A was transformed to complex C and/or D, which afforded **6** with release of a Pd(0) complex. In this connection complex B was also consistently thinkable as an intermediate to give complex D. From the mechanistic points of view, the different reactivities of homo-conjugated dienes are not clear yet, and further investigation is under study.

In conclusion, we offered a unique type of *ortho*-disubstitution reactions *via* homo-π-allyl palladium complexes as transition state species or intermediates, which were produced by reactions of bicyclo[2.2.2]octa-2,5-diene derivatives with aromatic compounds in the presence of $Pd(OAc)_2$. Many kinds of aromatic rings were applied to show the scope and limitations of the reaction. After optimizing reaction conditions, the products were obtained in reasonable yields as iodoarenes were employed. These reactions proceeded in only dienes containing a bicyclo[2.2.2]octa-2,5-diene skeleton, which strongly reflected the specific properties of the diene moieties.

## 3. Experimental

### 3.1. General

All solvents were dried and purified by usual methods. Column chromatography was performed using Wakogel C200. Melting points were measured on a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were obtained with a JASCO FT/IR-5300 spectrometer. Mass spectra (EI) were taken with a Hitachi 220A spectrometer operating at 70 eV by a direct inlet system. Elemental analyses were performed on YANACO MT-3 CHN CORDER. $^1H$ and $^{13}C$ NMR spectra were recorded with Varian GEMINI (200 and 300 MHz) spectrometers with tetramethylsilane as an internal standard. In the $^1H$ NMR spectra, protons assigned to pentacyclo-skeletons are described using $H_a$–$H_h$ symbols as shown in Fig. 2.

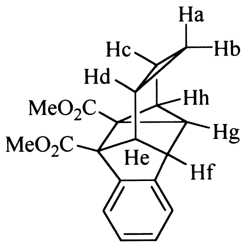


**Figure 2.** Symbols in $^1$HNMR analyses.

**3.1.1. Reactions of dienes (5a–d, 7) with benzene.** A mixture of **5a** (0.70 g, 3.0 mmol), Pd(OAc)$_2$ (0.67 g, 3.0 mmol), and NaOAc (1.23 g, 15.0 mmol) in dry benzene (30 ml) was stirred at 60°C for 24 h under nitrogen. An insoluble solid was removed by filtration and the filtrate was concentrated. To the residue ethyl acetate and water were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic solution was dried over Na$_2$SO$_4$ and concentrated. The obtained solid was recrystallized from benzene–*n*-hexane to give **6a** (0.29 g, 31%) as colorless crystals: mp 159–160°C; IR (KBr) 3005, 2951, 1748, 1738, 1721, 1705, 1441, 1302, 1277, 1258, 1200, 1136, 1061, 758, 681 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 0.13–0.14 (m, 2H, H$_{a,b}$), 0.63 (m, 1H, H$_d$), 1.29 (m, 1H, H$_c$), 1.69 (dt, 1H, $J$=7.7, 1.6 Hz, H$_g$), 2.52 (dt, 1H, $J$=5.0, 2.0 Hz, H$_e$), 2.60 (m, 1H, H$_f$), 2.85 (dd, 1H, $J$=7.7, 4.3 Hz, H$_h$), 3.10 (s, 3H, CH$_3$), 3.59 (s, 3H, CH$_3$), 6.80–7.59 (m, 4H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 6.9, 7.3, 8.6, 37.0, 39.2, 40.5, 44.5, 51.5, 51.8, 57.0, 59.4, 120.5, 124.2, 125.4, 125.5, 147.6, 147.6, 171.7, 172.9; MS *m/z* (rel. intensity) 310 (M$^+$, 2), 263 (78), 219 (65), 191 (100), 165 (36). Found: C, 73.59; H, 5.90%. Calcd for C$_{19}$H$_{18}$O$_4$: C, 73.53; H, 5.85%.

Similar reactions were applied for dienes **5b–d** and **7** to give compounds **6b–d** and **8**.

**6b**: Yield 57%; colorless crystals (benzene); mp 205–206°C; IR (KBr) 2236, 1715 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.44 (m, 1H, H$_d$), 1.60 (t, 1H, $J$=7.7 Hz, H$_a$), 2.10–2.30 (m, 2H, H$_{c,g}$), 2.79 (dt, 1H, $J$=6.0, 1.9 Hz, H$_e$), 2.94 (ddd, 1H, $J$=7.8, 4.3, 1.3 Hz, H$_h$), 3.56 (s, 3H, CH$_3$), 3.89 (s, 3H, CH$_3$), 4.08 (br s, 1H, H$_f$), 7.07–7.25 (m, 3H, Ar), 7.59 (d, 1H, $J$=7.5 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 5.0, 16.0, 16.9, 32.7, 38.8, 39.1, 42.7, 51.8, 52.1, 54.1, 60.6, 119.7, 121.2, 124.5, 126.0, 126.2, 145.2, 147.5, 170.8, 172.0; MS *m/z* (rel. intensity) 335 (M$^+$, 2), 303 (100), 244 (42), 216 (72), 174 (63). Found: C, 71.55; H, 5.05; N, 4.15%. Calcd for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18%.

**6c**: Yield 43%; colorless crystals (benzene); mp 143–144°C; IR (KBr) 2236, 1723 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.42 (t, 1H, $J$=3.5 Hz, H$_b$), 1.71 (m, 1H, H$_d$), 1.87 (dt, 1H, $J$=7.0, 1.5 Hz, H$_g$), 2.28 (m, 1H, H$_c$), 2.73 (dt, 1H, $J$=5.8, 1.8 Hz, H$_e$), 2.91 (ddd, 1H, $J$=7.0, 4.6, 1.1 Hz, H$_h$), 3.11 (br s, 1H, H$_f$), 3.55 (s, 3H, CH$_3$), 3.91 (s, 3H, CH$_3$), 7.03–7.24 (m, 3H, Ar), 7.59 (d, 1H, $J$=7.5 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 6.0, 19.0, 20.0, 35.2, 38.8, 41.3, 45.0, 52.8, 53.1, 54.7, 59.8, 121.0, 121.8, 125.6, 127.0, 127.0, 147.1, 147.3, 171.5, 172.0; MS *m/z* (rel. intensity) 335 (M$^+$, 2), 303 (100), 244 (52), 216 (81), 174 (71). Found: C, 71.38; H, 4.92; N, 4.14%. Calcd for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18%.

**6d**: Yield 20%; colorless crystals (ethyl acetate); mp 205–206°C; IR (KBr) 2951, 1726, 1437 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.50–1.70 (m, 2H, H$_{b,d}$), 1.86 (dt, 1H, $J$=7.5, 1.6 Hz, H$_g$), 2.17 (m, 1H, H$_c$), 2.71 (dt, 1H, $J$=5.6, 1.8 Hz, H$_e$), 2.90 (dd, 1H, $J$=7.5, 1.0 Hz, H$_h$), 3.15 (br s, 1H, H$_f$), 3.55 (s, 3H, CH$_3$), 3.91 (s, 3H, CH$_3$), 4.16 (q, 2H, $J$=7.1 Hz, CH$_2$), 6.90–7.40 (m, 3H, Ar), 7.42–7.65 (m, 1H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.3, 19.0, 19.9, 21.9, 35.2, 38.6, 40.2, 44.7, 51.8, 52.1, 55.3, 59.2, 60.8, 120.8, 124.5, 125.8, 125.9, 146.9, 147.1, 171.1, 172.2, 172.7; MS *m/z* (rel. intensity) 382 (M$^+$, 11), 351 (27), 318 (22), 277 (49), 244 (100). Found: *m/z* 382.1405. Mass calcd for C$_{22}$H$_{22}$O$_6$: 382.1414.

**8**: Yield 27%; colorless crystals (benzene); mp 140–141°C; IR (KBr) 2957, 1734, 1720 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.64 (m, 2H), 2.00 (m, 1H), 2.03 (m, 1H), 2.21 (m, 2H), 2.45 (dt, 1H, $J$=7.7, 2.9 Hz), 3.20 (br s, 1H), 3.51 (s, 3H, CH$_3$), 3.88 (s, 3H, CH$_3$), 7.08 (m, 2H, Ar), 7.18 (d, 1H, $J$=6.9 Hz, Ar), 7.53 (d, 1H, $J$=7.5 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.3, 18.4, 33.8, 38.3, 39.0, 45.5, 51.5, 51.8, 56.3, 59.3, 120.5, 123.9, 125.2, 125.4, 147.4, 149.1, 172.3, 172.9; MS *m/z* (rel. intensity) 298 (M$^+$, 17), 266 (30), 238 (33), 207 (37), 179 (100). Found: C, 72.29; H, 6.01%. Calcd for C$_{18}$H$_{18}$O$_4$: C, 72.47; H, 6.08%.

**3.1.2. Reaction of diene (5d) with naphthalene.** A mixture of **5d** (0.31 g, 1.0 mmol), naphthalene (0.39 g, 3.0 mmol), Pd(OAc)$_2$ (0.23 g, 1.0 mmol), and NaOAc (0.41 g, 5.0 mmol) was refluxed in dry ethyl acetate (10 ml) for 4 days under nitrogen. An insoluble solid was removed by filtration. The organic solution was washed with water and dried over Na$_2$SO$_4$. After removal of the solvent, the residue was separated with column chromatography (silica gel, *n*-hexane–ethyl acetate=6:1) to provide **9a** (41 mg, 16%), **9b** (19 mg, 7%), and **9c** (10 mg, 3%). Both **9a** and **9b** were recrystallized from ethanol.

**9a**: Colorless crystals; mp 233–234°C; IR (KBr) 2953, 1714 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.29 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.66 (m, 1H, H$_d$), 1.73 (t, 1H, $J$=3.0 Hz, H$_b$), 1.86 (dd, 1H, $J$=7.7, 1.9 Hz, H$_g$), 2.18 (m, 1H, H$_c$), 2.75 (dt, 1H, $J$=5.5, 1.9 Hz, H$_e$), 2.82 (ddd, 1H, $J$=7.7, 4.7, 0.8 Hz, H$_h$), 3.28 (br s, 1H, H$_f$), 3.51 (s, 3H, CH$_3$), 3.94 (s, 3H, CH$_3$), 4.16 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.45 (m, 2H, Ar), 7.55 (s, 1H, Ar), 7.74 (m, 1H, Ar), 7.83 (m, 1H, Ar), 7.96 (s, 1H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.2, 19.3, 21.9, 25.8, 36.9, 37.1, 38.9, 44.1, 51.6, 52.2, 58.6, 60.7, 60.9, 118.7, 119.0, 123.1, 123.3, 127.3, 128.2, 132.0, 132.2, 143.7, 144.2, 171.0, 171.8, 172.5; MS *m/z* (rel. intensity) 432 (M$^+$, 87), 401 (28), 369 (64), 327 (52), 294 (100). Found: *m/z* 432.1543. Mass calcd for C$_{26}$H$_{24}$O$_6$: 432.1566.

**9b**: Colorless crystals; mp 164–165°C; IR (KBr) 2953, 1721 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.30 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.70 (m, 1H, H$_d$), 1.82 (t, 1H, $J$=3.2 Hz, H$_b$), 1.95 (dd, 1H, $J$=8.1, 1.9 Hz, H$_g$), 2.22 (m, 1H, H$_c$), 2.86 (dt, 1H, $J$=5.8, 1.9 Hz, H$_e$), 3.02 (dd, 1H, $J$=8.1, 5.8 Hz, H$_h$), 3.49 (s, 3H, CH$_3$), 3.73 (br s, 1H, H$_f$), 3.93 (s, 3H, CH$_3$), 4.18 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.43 (m, 2H, Ar), 7.66 (d, 1H, $J$=8.2 Hz, Ar), 7.78 (d, 1H, $J$=8.2 Hz, Ar), 7.82 (dd, 2H, $J$=7.4, 6.9 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.3, 19.1, 20.5, 22.0, 36.7, 39.4, 42.2, 42.5, 51.7, 52.2, 56.4, 60.2, 60.8, 122.6, 123.1, 125.2, 125.7, 125.9, 127.5, 128.7, 132.1, 144.2, 145.6, 171.1, 172.2, 172.7; MS *m/z* (rel. intensity) 432 (M$^+$, 87), 400 (19), 368 (40), 327 (45), 295 (51), 239 (100). Found: *m/z* 432.1568. Mass calcd for C$_{26}$H$_{24}$O$_6$: 432.1566.

**9c**: $^{1}$H NMR (CDCl$_3$) $\delta$ 1.29 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.64 (m, 1H, H$_d$), 1.70 (t, 1H, $J$=3.1 Hz, H$_b$), 2.04 (dd, 1H, $J$=7.9, 1.9 Hz, H$_g$), 2.20 (m, 1H, H$_c$), 2.75 (m, 2H, H$_{e,h}$), 3.30 (br s, 1H, H$_f$), 3.51 (s, 3H, CH$_3$), 3.94 (s, 3H, CH$_3$), 4.16 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.20–7.96 (m, 6H, Ar).

**3.1.3. Reaction of diene (5d) with anthracene.** By a similar procedure as described for naphthalene, **5d** (0.31 g, 1.0 mmol) was treated with anthracene (0.53 g, 3.0 mmol) in refluxing ethyl acetate (10 ml) with Pd(OAc)$_2$ (0.23 g, 1.0 mmol) and NaOAc (0.41 g, 5.0 mmol) for 4 days to afford three isomers of products.

**10a**: Yield 13%; colorless crystals (ethanol); mp 148–149°C; IR (KBr) 2953, 1723 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.68 (m, 1H, H$_d$), 1.75 (t, 1H, $J$=3.1 Hz, H$_b$), 1.90 (d, 1H, $J$=7.6 Hz, H$_g$), 2.21 (m, 1H, H$_c$), 2.79 (m, 2H, H$_{e,h}$), 3.34 (br s, 1H, H$_f$), 3.51 (s, 3H, CH$_3$), 3.97 (s, 3H, CH$_3$), 4.14 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.43 (m, 2H, Ar), 7.68 (s, 1H, Ar), 7.98 (m, 2H, Ar), 8.08 (s, 1H, Ar), 8.29 (s, 1H, Ar), 8.40 (s, 1H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.3, 19.0, 19.2, 22.0, 32.1, 36.3, 38.3, 44.2, 51.8, 52.3, 52.9, 58.5, 60.8, 118.6, 123.1, 125.1, 125.2, 125.7, 126.8, 127.8, 128.1, 130.7, 130.9, 131.5, 131.6, 142.9, 143.6, 171.1, 171.9, 172.6; MS $m/z$ (rel. intensity) 482 (M$^+$, 100), 451 (7), 404 (6), 377 (9), 289 (21). Found: $m/z$ 482.1711. Mass calcd for C$_{30}$H$_{26}$O$_6$: 482.1722.

**10b**: Yield 4%; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.68 (m, 1H, H$_d$), 1.75 (m, 1H, H$_b$), 2.02 (m, 1H, H$_g$), 2.21 (m, 1H, H$_c$), 2.94 (m, 1H, H$_e$), 3.05 (m, 1H, H$_h$), 3.50 (s, 3H, CH$_3$), 3.91 (br s, 1H, H$_f$), 3.96 (s, 3H, CH$_3$), 4.17 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.43 (m, 2H, Ar), 7.80 (d, 1H, $J$=8.1 Hz, Ar), 7.86 (d, 1H, $J$=8.1 Hz, Ar), 7.98 (m, 2H, Ar), 8.25 (s, 1H, Ar), 8.38 (s, 1H, Ar).

**10c**: Yield 3%; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.70 (m, 1H, H$_d$), 1.74 (m, 1H, H$_b$), 1.94 (d, 1H, $J$=7.6 Hz, H$_g$), 2.20 (m, 1H, H$_c$), 2.88 (d, 1H, $J$=7.6 Hz, H$_h$), 2.94 (m, 1H, H$_e$), 3.47 (br s, 1H, H$_f$), 3.51 (s, 3H, CH$_3$), 3.94 (s, 3H, CH$_3$), 4.17 (q, 2H, $J$=7.1 Hz, CH$_2$), 7.21 (m, 2H, Ar), 7.40 (m, 2H, Ar), 7.47 (d, 1H, $J$=8.1 Hz, Ar), 7.84 (m, 2H, Ar), 8.01 (d, 1H, $J$=7.7 Hz, Ar).

**3.1.4. Reaction of diene (5d) with phenanthrene.** By a similar procedure as described for naphthalene, **5d** (0.31 g, 1.0 mmol) was treated with phenanthrene (1.60 g, 9.0 mmol) in refluxing ethyl acetate (10 ml) with Pd(OAc)$_2$ (0.23 g, 1.0 mmol) and NaOAc (0.41 g, 5.0 mmol) for 4 days to afford a mixture of two isomers **11a** and **11b** (7:3) in 8% yield. **11**: IR (KBr) 2953, 1723, 1437, 1308, 1181 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.30 (t, 3H, $J$=7.0 Hz, CH$_3$), 1.70 (m, 1H, H$_d$), 1.76 (m, 1H, H$_b$), 1.89–1.92 (m, 1H, H$_g$), 2.20–2.22 (m, 1H, H$_c$), 2.81 (m, 1H, H$_e$), 2.88 (m, 1H, H$_h$), 3.32 (br s, 0.3H, H$_f$), 3.37 (br s, 0.7H, H$_f$), 3.49 (s, 0.9H, CH$_3$), 3.50 (s, 2.1H, CH$_3$), 3.95 (s, 2.1H, CH$_3$), 3.98 (s, 0.9H, CH$_3$), 4.17 (q, 2H, $J$=7.0 Hz, CH$_2$), 7.56 (m, 1H, Ar), 7.61–7.64 (m, 1H, Ar), 7.66 (d, 0.3H, $J$=8.9 Hz, Ar), 7.72 (d, 1H, $J$=8.3 Hz, Ar), 7.76 (d, 0.7H, $J$=8.8 Hz, Ar), 7.87–7.88 (m, 1H, Ar), 8.04 (s, 0.7H, Ar), 8.43 (s, 0.7H, Ar), 8.60 (d, 0.7H, $J$=8.3 Hz, Ar), 8.75 (d, 0.3H, $J$=8.3 Hz, Ar), 8.85 (s, 0.3H, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.8, 19.5, 20.1, 22.5, 22.5, 34.6, 38.2, 40.1, 44.8, 45.3, 52.3, 52.8, 52.8, 55.2, 55.2, 59.4, 59.7, 61.3, 114.9, 119.1, 120.6, 123.0, 123.5, 124.8, 126.7, 126.7, 126.8, 126.8, 126.9, 127.2, 128.0, 128.9, 129.0, 129.1, 129.3, 130.7, 131.0, 131.1, 131.2, 132.4, 132.6, 145.3, 145.5, 145.6, 145.9, 171.6, 171.7, 172.4, 173.1; MS $m/z$ (rel. intensity) 482 (M$^+$, 87), 418 (51), 377 (47), 345 (85), 317 (48), 289 (100), 274 (59). Found: $m/z$ 482.1737. Mass calcd for C$_{30}$H$_{26}$O$_6$: 482.1722.

**3.1.5. Reaction of diene (5d) with tropone.** By a similar procedure as described for naphthalene, **5d** (0.31 g, 1.0 mmol) was treated with tropone (0.53 g, 5.0 mmol) in refluxing acetonitrile (8 ml) with Pd(OAc)$_2$ (0.23 g, 1.0 mmol) and NaOAc (0.41 g, 5.0 mmol) for 4 days to afford a single isomer of product in 4% yield. **12**: IR (NaCl) 2955, 1724, 1572 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.54 (m, 1H, H$_d$), 1.70 (m, 1H, H$_b$), 2.05–2.17 (m, 2H, H$_{c,g}$), 2.65 (dt, 1H, $J$=6.7, 3.3 Hz, H$_e$), 2.97 (ddd, 1H, $J$=7.7, 4.3, 1.2 Hz, H$_h$), 3.58 (s, 3H, CH$_3$), 3.60 (br s, 1H, H$_f$), 3.89 (s, 3H, CH$_3$), 4.14 (q, 2H, $J$=7.1 Hz, CH$_2$), 6.97 (m, 1H, Ar), 7.09–7.21 (m, 2H, Ar), 7.51 (d, 1H, $J$=11.0 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.2, 18.3, 19.2, 21.5, 35.9, 38.5, 41.5, 44.0, 51.9, 52.6, 53.3, 60.9, 63.9, 132.1, 134.8, 136.1, 142.2, 156.4, 159.5, 170.0, 171.9, 172.5, 182.7; MS $m/z$ (rel. intensity) 410 (M$^+$, 100), 379 (35), 351 (51), 305 (96), 277 (41). Found: $m/z$ 410.1383. Mass calcd for C$_{23}$H$_{22}$O$_7$: 410.1359.

**3.1.6. Reactions of dienes (5a–e, 7) with iodobenzene.** A mixture of **5a** (0.23 g, 1.0 mmol) and iodobenzene (0.61 g, 3.0 mmol) in dry acetonitrile (6 ml) with Pd(OAc)$_2$ (0.23 g, 1.0 mmol), NaOAc (0.41 g, 5.0 mmol), and $n$-Bu$_4$NCl (0.28 g, 1.0 mmol) was refluxed for 6 h under nitrogen. An insoluble solid was removed by filtration and the filtrate was concentrated. To the residue ethyl acetate and water were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic solution was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography (silica gel, $n$-hexane–ethyl acetate=4:1) and was recrystallized from ethanol to give **6a** in 68% yield.

Similar reactions were applied for dienes **5b–e** and **7** to afford compounds **6b–e** and **8**, respectively.

**6b**: Yield 58%.

**6c**: Yield 79%.

**6d**: Yield 73%.

**6e**: Yield 35%; colorless crystals (ethanol); mp 130–131°C; IR (KBr) 2953, 1721 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$) $\delta$ 1.50 (dd, 1H, $J$=10.2, 5.8 Hz, H$_d$), 1.68 (s, 3H, CH$_3$), 2.03 (dt, 1H, $J$=7.7, 1.9 Hz, H$_g$), 2.24 (dd, 1H, $J$=10.2, 4.1 Hz, H$_c$), 2.68 (dt, 1H, $J$=5.8, 1.9 Hz, H$_e$), 2.76 (dd, 1H, $J$=7.7, 4.1 Hz, H$_h$), 3.45 (br s, 1H, H$_f$), 3.55 (s, 3H, CH$_3$), 3.67 (s, 3H, CH$_3$), 3.89 (s, 3H, CH$_3$), 7.06–7.17 (m, 3H, Ar), 7.51 (d, 1H, $J$=7.4 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 11.4, 22.1, 23.8, 26.0, 33.3, 37.4, 39.7, 43.8, 51.7, 52.0, 52.2, 56.4, 61.3, 120.9, 124.4, 125.6, 125.9, 145.5, 147.8, 171.0, 172.8, 175.1; MS $m/z$ (rel. intensity) 382 (M$^+$, 12), 351 (18), 318 (52), 291 (57), 258 (100). Found: $m/z$ 382.1405. Mass calcd for C$_{22}$H$_{22}$O$_6$: 382.1414.

**8**: Yield 60%.

**3.1.7. Reactions of diene (5d) with iodoarenes.** By a similar procedure as described for iodobenzene, **5d** (0.31 g, 1.0 mmol) was treated with 1,4-diiodobenzene (0.99 g, 3 mmol), 1-iodonaphthalene (0.76 g, 3.0 mmol), or 2-iodotropone (0.70 g, 3.0 mmol) to afford compounds **13**, **9b**, and **12**, respectively.

**13**: Yield 30%; colorless crystals (*n*-hexane–ethyl acetate); mp 177–178°C; IR (KBr) 2953, 1726 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.28 (t, 3H, $J$=7.1 Hz, CH$_3$), 1.61 (m, 1H, H$_d$), 1.65 (m, 1H, H$_b$), 1.83 (d, 1H, $J$=7.8 Hz, H$_g$), 2.15 (m, 1H, H$_c$), 2.68 (d, 1H, $J$=5.3 Hz, H$_e$), 2.88 (dd, 1H, $J$=7.8, 4.9 Hz, H$_h$), 3.11 (br s, 1H, H$_f$), 3.57 (s, 3H, CH$_3$), 3.89 (s, 3H, CH$_3$), 4.18 (q, 2H, $J$=7.1 Hz, CH$_2$), 6.91 (d, 1H, $J$=7.6 Hz, Ar), 7.43 (dd, 1H, $J$=7.6, 1.9 Hz, Ar), 7.88 (d, 1H, $J$=1.9 Hz, Ar); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.1, 18.7, 19.5, 21.8, 35.1, 38.2, 39.9, 44.2, 51.8, 52.2, 55.1, 59.0, 60.7, 90.7, 122.7, 133.6, 134.8, 146.6, 148.9, 170.4, 171.7, 172.4; MS *m/z* (rel. intensity) 508 (M$^+$, 43), 444 (100), 403 (51), 370 (91), 300 (28). Found: *m/z* 508.0369. Mass calcd for $C_{22}H_{21}IO_6$: 508.0377.

**9b**: Yield 54%.

**12**: Yield 22%. This $^1$H NMR spectrum was coincident with that of the material obtained in the reaction of diene **5d** and tropone.

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