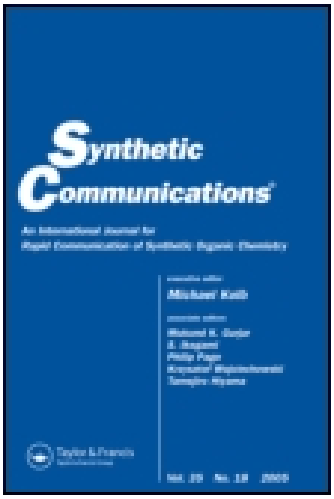

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SYNTHESIS AND STRUCTURE OF 2,3-BIS(5-*TERT*-BUTYL-2-METHOXYPHENYL)BUTA-1,3-DIENE BY BROMINE ELIMINATION OF (*Z*)-1,4-DIBROMO-2,3-BIS(5-*TERT*-BUTYL-2-METHOXYPHENYL)-2-BUTENE

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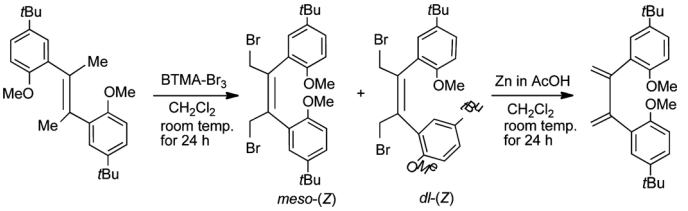
GRAPHICAL ABSTRACT



Abstract *2,3-Bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene was prepared by bromination of (*Z*)- and (*E*)-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene followed by treatment with zinc powder in a mixture of CH_2Cl_2 and acetic acid, which was converted to the corresponding* o*-terphenyl skeleton by the condensation with dimethyl acetylenedicarboxylate followed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone.*

Keywords Bromination; bromine elimination; conformations; diaryl-1,3-butadiene; Diels–Alder reaction

INTRODUCTION

2,3-Diphenylbuta-1,3-diene is a compound of considerable interest to both industrially and academically oriented organic chemists.[1–5] Unfortunately, most of the numerous published syntheses of 2,3-diphenylbuta-1,3-diene are time- and money-consuming multistep reactions that give poor yields or use expensive chemicals. One of the first and simplest procedures for the synthesis of 2,3-diphenylbuta-1,3-diene in good yields was reported by Alder and Haydn using a potassium bisulfate–mediated dehydration of 2,3-diphenylbutane-2,3-diol.[6] Dodson et al.[7]

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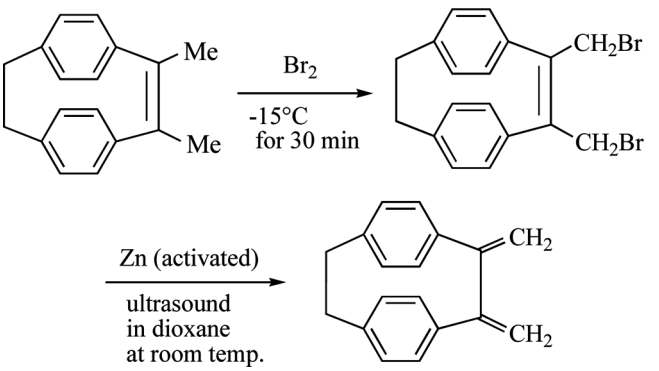
and Baldwin and Lusch,[8] however, were unable to reproduce these results. Wagner and Brinker reported a novel and facile synthesis of 2,3-diphenylbuta-1,3-dienes dehydration of 2,3-diphenylbutane-2,3-diol with hexamethylphosphoramide at 240 °C along with rearrangement products. The separation of the desired 2,3-diphenylbuta-1,3-dienes is quite tedious and not convenient.[9]

On the other hand, König and de Meijere reported the synthesis of 1,2-dimethylene[2.2]paracyclophane using a copper-mediated coupling of 1,2-dibromo-[2.2]-paracyclophan-1-ene with methylmagnesium bromide, followed by bromine addition and bromine elimination with activated zinc promoted by ultrasound.[10]

Recently, we reported the preparation of 1,2-dimethyl[2.*n*]metacyclophan-1-enes[11–14] by using the reductive coupling of carbonyl compounds by low-valent titanium, the McMurry reaction,[15–21] as a key step. These compounds afforded convenient starting materials for the attempted preparation of 1,2-dimethylene[2.*n*]-metacyclophan-1-enes. Thus, there is substantial interest in investigating the convenient preparation of 2,3-diarylbuta-1,3-diene and application to the dienes for Diels–Alder reactions. We report here on a convenient synthesis of 2,3-diarylbuta-1,3-diene by treatment with bromine of 2,3-diaryl-2-butene to afford 1,4-dibromo-2,3-diaryl-2-butenefollowed by bromine elimination with zinc powder. The structural properties of 1,4-dibromo-2,3-diaryl-2-butene are also discussed in solution and solid state.

RESULTS AND DISCUSSION

2,3-Bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene **3** has been prepared according our previous papers.[22] The $TiCl_4$-catalyzed acetylation of 4-*tert*-butylanisole **1** with acetic anhydride at 20 °C gave the desired 2-acetyl-4-*tert*-butylanisole **2** in good yield. 2-Acetyl-4-*tert*-butylanisole **2** was subjected to reductive coupling by the McMurry reaction following the improved Grützmacher procedure[17] (Scheme 1). Thus, the reductive coupling reaction of **2** carried out using $TiCl_4$-Zn in the presence



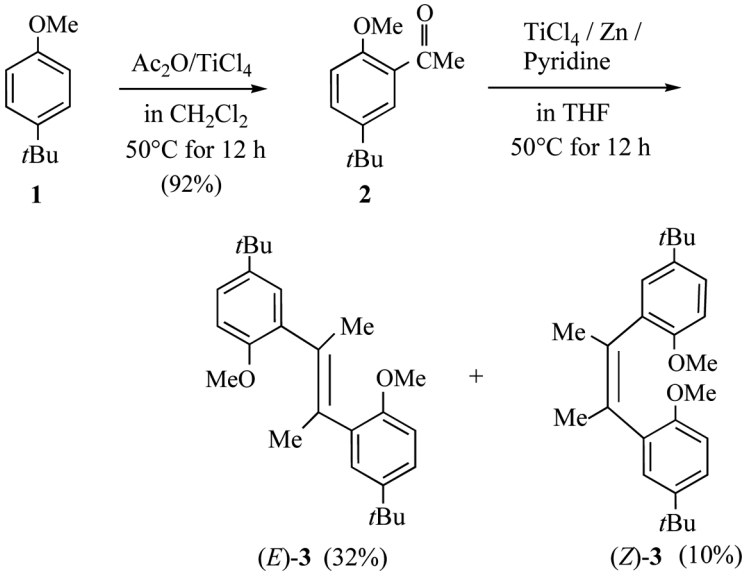
Scheme 1. Synthesis of 1,2-dimethylene[2.2]paracyclophane.

of pyridine in refluxing tetrahydrofuran (THF) afforded the desired compound 2,3-bis(5-*tert*-butyl-2-methoxyl-phenyl)-2-butene **3** in good yield (Scheme 2).

The ^{1}H NMR spectrum of **3** shows two kinds of methoxy protons, each as a singlet. By careful column chromatography (silica gel, Wako C-300), two isomers, (*E*)-**3** and (*Z*)-**3**, are separated in 32% and 10% yields, respectively.

The structures of products (*E*)-**3** and (*Z*)-**3** were also determined on the basis of their elemental analyses and spectral data. ^{1}H NMR signals of the olefinic protons for *E*- and *Z*-olefins should be observed at $\delta > 7.4$ (*E*) and <6.9 (*Z*).[23] ^{1}H NMR spectrum of (*E*)-**3** in $CDCl_3$ shows δ 6.86 (d, $J = 8.4$ Hz), 7.22 (dd, $J = 2.4$, 8.4 Hz), and 7.25 (d, $J = 2.4$ Hz) ppm for the three protons of the aromatic rings. In contrast, ^{1}H NMR spectrum of (*Z*)-**3** in $CDCl_3$ shows at higher field, δ 6.62 (d, $J = 8.3$ Hz), 6.65 (d, $J = 2.4$ Hz), and 6.94 (dd, $J = 2.4$, 8.3 Hz) ppm, for the three protons of the aromatic rings because of the face-to-face arrangement of the phenyl groups. Also the *tert*-butyl proton of (*Z*)-**3** was observed at higher field, δ 1.00 ppm, because of the strong shielding effect of the benzene ring. The structure of the (*Z*)-isomer is also readily assigned from the chemical shift of the methoxy protons at δ 3.83 ppm for (*E*)-**3** and δ 3.77 ppm for (*Z*)-**3**. These data strongly support that the structure of (*E*)-**3** is the (*E*)-configuration and the structure of (*Z*)-**3** is the (*Z*)-configuration.

Bromination of (*E*)-2,3-bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene (*E*)-**3** with excess of bromine in dichloromethane solution at room temperature for 24 h afforded a mixture of the corresponding *meso*-(*Z*)- and *dl*-(*Z*)-1,4-dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene *meso*-(*Z*)-**4** and *dl*-(*Z*)-**4** in 30% and 60% yields along with the recovery of the starting compound (Scheme 3). Similar results were



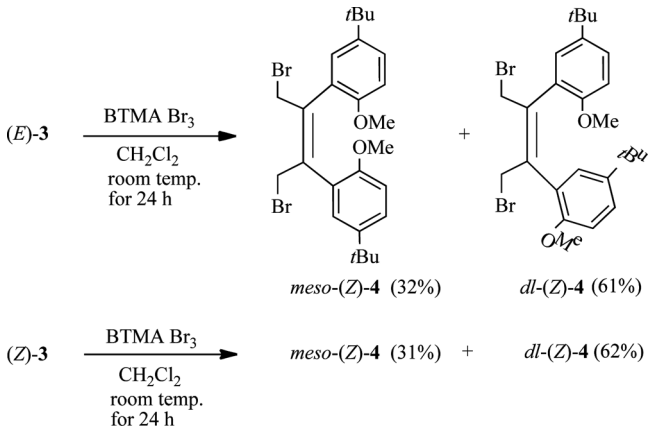
Scheme 2. Synthesis of (*Z*)- and (*E*)-2,3-bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene, (*Z*)-3 and (*E*)-3.

Table 1. Crystal and refinement data for compound *dl*-(*Z*)-**4**

Parameter	*dl*-(*Z*)-**4**
Empirical formula	$C_{26}H_{34}Br_4O_2$
Formula weight	538.33
Crystal system	Triclinic
Space group	P–1
a (Å)	10.154(2)
b (Å)	14.185(2)
c (Å)	9.815(2)
α (deg)	99.27(1)
β (deg)	106.63(1)
γ (deg)	93.32(1)
V (Å^3)	3446.06 (11)
Z	2
D_{calcd} (g cm^{-3})	1.345
T (K)	296
μ(Mo Kα) (mm^{-1})	3.068
Total no. of reflections	6100
Unique reflections	2313
R_{int}	0.0687
Observed reflections	2313
Parameters refined	306
R [I > 2σ(*I*)] and all data	0.087
wR [I > 2σ(*I*)] and all data	0.1010

obtained in the case of (*Z*)-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene (*Z*)-**3** to afford *meso*-(*Z*)-**4** and *dl*-(*Z*)-**4** in the same ratio as in (*E*)-isomer (*E*)-**3**.

The former transformation probably occurred by addition of bromine to the double bond followed by the twofold debromination to diene **5** (discussed later). Interestingly, the compounds (*E*)- and (*Z*)-**3** were treated with 4.5 equiv. of benzyltrimethylammonium tribromide (BTMA Br_3) at room temperature for 24 h



Scheme 3. Bromination of (*E*)- and (*Z*)-2,3-bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene, (*E*)-3 and (*Z*)-3 with BTMA Br_3.

afforded 1,4-dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene *meso*-(*Z*)-**4** and *dl*-(*Z*)-**4** in 32% and 61% yields, respectively. It was also found that the bromination of 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** with an equimolar of BTMA Br_3 at room temperature for 5 min afforded 1,4-dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene *meso*-(*Z*)-**4** and *dl*-(*Z*)-**4** in the same ratio in quantitative yield. This result strongly suggests that the 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** could be an intermediate during the formation of 1,4-dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene **4** in the bromination of 2,3-bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene.

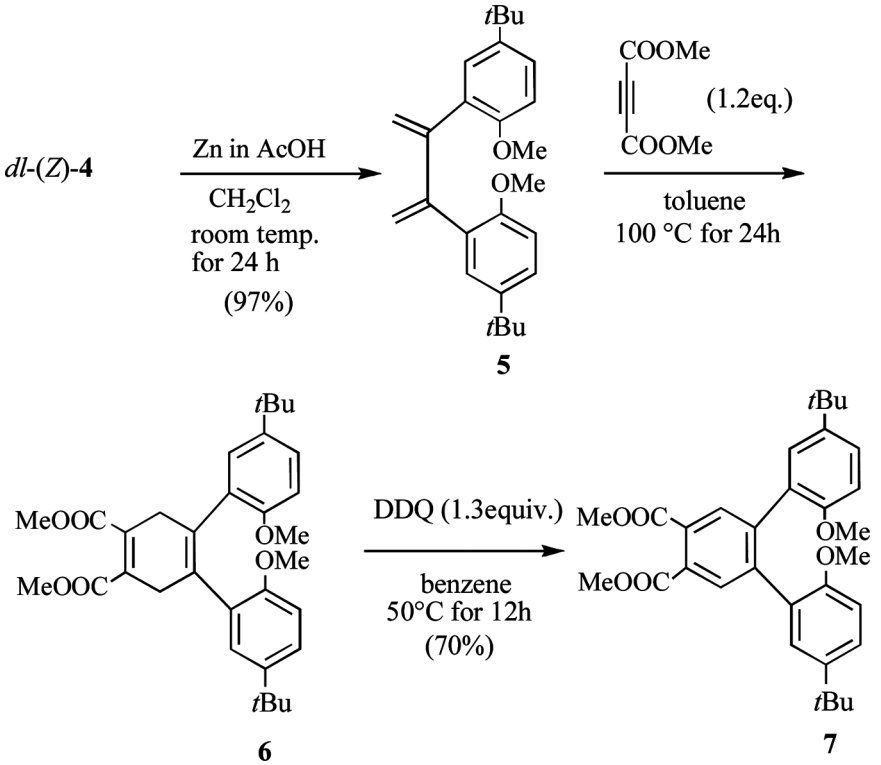
The 300-MHz ^{1}H NMR spectrum of *meso*-(*Z*)-**4** showed a singlet of the methoxy protons at δ 3.79 ppm in addition to the resonances at higher field, δ 6.64 (d, $J = 8.7$ Hz), 6.68 (d, $J = 2.4$ Hz), and 7.03 (dd, $J = 2.4$, 8.7 Hz) ppm, for the three protons of the aromatic rings because of the face-to-face arrangement of the phenyl groups like those of (*Z*)-**3**. The methylene protons of the bromomethyl group were observed as a singlet at δ 4.59 ppm, which indicates the methylene protons in the same environment. In contrast, the 300-MHz ^{1}H NMR spectrum of *dl*-(*Z*)-**4** showed a singlet of the methoxy protons at δ 3.79 ppm in addition to the resonances at lower field, δ 6.86 (d, $J = 8.7$ Hz), 7.35 (dd, $J = 2.4$, 8.7 Hz), and 7.60 (d, $J = 2.4$ Hz) ppm, for the three protons of the aromatic rings. Interestingly, the methylene protons of the bromomethyl group were observed as a set of doublets at δ 3.97 and 4.19 ppm ($J = 9.6$ Hz), which coalesced to a singlet at δ 4.12 ppm above 75 °C in $CDBr_3$. Thus, the introduction of bromo group to methyl group at the double bond in the present 2,3-bis(2-methoxyphenyl)-2-butene skeleton might inhibit the rotation around the single bond of C−CH_2Br, which makes the methylene protons a diasterotopic environment.

The conformation of *dl*-(*Z*)-**4** has also been confirmed by x-ray crystallographic analysis. Single colorless crystals of the *dl*-(*Z*)-1,4-dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene *dl*-(*Z*)-**4** suitable for x-ray crystallography were obtained by recrystallization from methanol–chloroform (1:1). The perspective crystal structure of *dl*-(*Z*)-**4** is illustrated in Fig. 1.

Compound *dl*-(*Z*)-**4** crystallized in triclinic space group, P–1, and is located about a two-fold axis, because this molecule has crystallographic C_2 symmetry. Therefore, the asymmetric unit contains one half of a molecule ($Z = 2$). Both methoxy groups on the benzene ring of *dl*-(*Z*)-**4** point toward the outer side against each bromine atom in the bromomethyl group. This might help avoid the steric crowding with the methoxy group and bromine atom of the bromomethyl group on the each carbon in the double bond.

Several attempts using activated zinc powder in dioxane with irradiation by ultrasound, following the reported procedure, to accomplish bromine elimination of *meso*-(*Z*)-**4** and afford 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** failed. Only the recovery of the starting compound or the formation of an intractable mixture of products resulted. Fortunately, we have found that when the present bromine elimination of *meso*-(*Z*)-**4** is carried out in CH_2Cl_2 at room temperature for 24 h in the presence of the commercially available zinc powder and a small amount of the acetic acid, the desired 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** is formed in quantitative yield. Similar treatment of *dl*-(*Z*)-**4** with zinc powder affords the corresponding diene **5** in quantitative yield. Compound **5** is too labile

Figure 1. Crystal structure of *dl*-(*Z*)-**4**. Hydrogen atoms are omitted for clarity. (Figure is provided in color online.)



Scheme 4. Synthesis and Diels–Alder reaction of of 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-buta-1,3-diene 5.

of a solid to purify. Although in solution or exposed to air compound **5** slowly decomposes, the compound is easily trapped by the reaction with dimethyl acetylenedicarboxylate in toluene at reflux for 12 h to afford **6** in good yield (Scheme 4). Diels–Alder adduct **6** was converted to *o*-terphenyl derivative **7** by aromatization with dichlorodicyano-*p*-benzoquinone (DDQ) in 70% yield.

The structures of products **5** and **7** were determined on the basis of their elemental analyses and spectral data. For example, the ^{1}H NMR spectrum of **5** shows two singlets of the *tert*-butyl protons and methoxy protons at δ 1.23 and 3.76 ppm in addition to the resonances at δ 6.72, 7.17, and 7.22 ppm for the three protons of the aromatic rings. The *exo*-methylene protons were observed as singlets at δ 5.12 and 5.14 ppm. These findings suggest that the conformationally flexible structure of **5** adopts an s-*trans* geometry, the same as that of 2,3-diphenylbuta-1,3-diene.[25] On the other hand, the mass spectral data for **7** ($M^+ = 518$) strongly supports the Diels–Alder reaction followed by aromatization product. The ^{1}H-NMR spectrum of **7** shows the *tert*-butyl protons and the methoxy protons at δ 1.11 and 3.52 ppm, which are upfield shifts due to the ring current of the opposite benzene ring.[26,27] The aromatic protons of **7** are observed at δ 6.67, 6.95, and 7.15 ppm in addition to the resonances at δ 7.80 ppm for the newly constructed 3 and 6 aromatic protons.

CONCLUSIONS

In conclusion, we have succeeded for the first time in preparing 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene by bromination of (*Z*)- and (*E*)-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene followed by treatment with zinc powder, which was converted to the corresponding *o*-terphenyl skeleton by the condensation with dimethyl acetylenedicarboxylate followed by oxidation with DDQ. The present method provides excellent yields, easy isolation of product 2,3-diarylbuta-1,3-diene, and overcomes the previously reported problems. Further studies on the reaction of the novel 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** and dimethyl 4,5-bis(5-*tert*-butyl-2-methoxyphenyl)benzene-1,2-dicarboxylate **7** are now in progress.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi Jeol FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. Ultraviolet–visible (UV-VIS) spectra were recorded on a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A ultrahigh-performance mass spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed on a Yanaco MT-5 instrument.

Preparation of 4-*tert*-butylanisole **1** was previously described.[28]

Preparation of 2-Acetyl-4-*tert*-butylanisole (2)

A solution of $TiCl_4$ (57.8 mL, 527 mmol) in CH_2Cl_2 (25 mL) was added to a solution of 4-*tert*-butylanisole **1** (15.0 g, 91.0 mmol) and acetic anhydride (13.2 mL, 140 mmol) in CH_2Cl_2 (200 mL) at 0 °C. After the reaction mixture was stirred at

room temperature for 3 h, it was poured into a large amount of ice water (400 mL) and extracted with CH_2Cl_2 (200 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was distilled under reduced pressure to give 2-acetyl-4-*tert*butylanisole **2** (17.0 g, 93%) as a colorless liquid. Bp 150–158 °C (10 torr). ν_{max}(NaCl)/cm^{-1}: 1676 (C=O). δ_H ($CDCl_3$) 1.31 (s, 9H, *t*Bu), 2.61 (s, 3H, CO*Me*), 3.89 (s, 3H, O*Me*), 6.91 (d, $J = 8.4$ Hz, 1H, Ar*H*), 7.49 (dd, $J = 2.6$, 8.6 Hz, 1H, Ar*H*), 7.76 (d, $J = 2.6$ Hz, 1H, Ar*H*). MS: *m*/*z* [M^+] 206. Elemental analysis calculated for $C_{13}H_{18}O_2$(206.284): C, 75.69; H, 8.8. Found: C, 75.52; H, 8.72.

McMurry Coupling Reaction of 2

The McMurry reagent was prepared from $TiCl_4$ (13.8 mL, 125 mmol) and Zn powder (18.0 g, 275 mmol) in 300 mL of dry THF, under nitrogen. A solution of 2-acetyl-4-*tert*-butylanisole **2** (5.4 g, 26.0 mmol) and pyridine (22.8 mL, 200 mmol) in dry THF (100 mL) was added within 1 h to the black mixture of the McMurry reagent using a high-dilution technique with continuous refluxing and stirring. The reaction mixture was refluxed for an additional 12 h, cooled to room temperature, and hydrized with aqueous 10% K_2CO_3 (500 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (300 mL × 3). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 500 g) with hexane, hexane–benzene, 3:1, and benzene–EtOAc, 4:1, as eluents to give (*Z*)-**3** (507 mg, 10%) and (*E*)-**3** (1.6 g, 32%), respectively.

(*Z*)-2,3-Bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene (*Z*)-3. Colorless prisms (MeOH). Mp 95–96 °C. ν_{max}(KBr)/cm^{-1}: 2958, 1603, 1502, 1464, 1301, 1247, 1058, 1033, 801. δ_H ($CDCl_3$) 1.00 (s, 18H, *t*Bu), 2.14 (s, 6H, *Me*), 3.77 (s, 6H, O*Me*), 6.62 (d, $J = 8.3$ Hz, 2H, Ar*H*), 6.65 (d, $J = 2.4$ Hz, 2H, Ar*H*), 6.94 (dd, $J = 8.3$, 2.4 Hz, 2H, Ar*H*). δ_C ($CDCl_3$) 21.15, 31.16, 34.12, 55.67, 110.45, 125.59, 125.81, 129.15, 137.17, 143.03, 154.35. MS: *m*/*z* [M^+] 380. Elemental analysis calculated for $C_{26}H_{36}O_2$(380.56): C, 82.06; H, 9.53. Found: C, 81.98; H, 9.45.

(*E*)-2,3-Bis(5-*tert*-butyl-2-methoxylphenyl)-2-butene (E)-3. Colorless prisms (MeOH); mp 88–89 °C. ν_{max}(KBr)/cm^{-1}: 2957, 1601, 1502, 1461, 1299, 1247, 1056, 1030, 807. δ_H ($CDCl_3$) 1.31 (s, 18H, *t*Bu), 1.76 (s, 6H, *Me*), 3.83 (s, 6H, O*Me*), 6.86 (d, $J = 8.4$ Hz, 2H, Ar*H*), 7.22 (dd, $J = 8.4$, 2.4 Hz, 2H, Ar*H*), 7.25 (d, $J = 2.4$ Hz, 2H, Ar*H*). δ_C ($CDCl_3$) 21.24, 31.61, 34.12, 55.69, 110.55, 123.95, 127.60, 131.13, 132.71, 143.13, 154.55. MS: m/z [M^+] 380. Elemental analysis calculated for $C_{26}H_{36}O_2$(380.56): C, 82.06; H, 9.53. Found: C, 81.95; H, 9.56.

Bromination of (*E*)-3 with Br_2

A solution of bromine Br_2 (0.2 mL, 2.6 mmol) in CH_2Cl_2 (1 mL) was added to a solution of (*E*)-**3** (100 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 12 h, it was poured into a large amount of icewater (10 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane

and hexane–benzene, 1:1, as an eluent to give *meso*-(*Z*)-**4** (42 mg, 30%) and *dl*-(*Z*)-**4** (84 mg, 60%), respectively.

***meso*-(*Z*)-1,4-Dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene, meso-(*Z*)-4.** Colorless prisms (hexane). Mp 115–116 °C. ν_{max}(KBr)/cm^{-1}: 2959, 1601, 1502, 1247, 1056, 1030, 809. δ_H ($CDCl_3$) 1.08 (18H, s, *t*Bu), 3.80 (6H, s, O*Me*), 4.59 (4H, s, CH_2), 6.64 (2H, d, $J = 8.7$ Hz, Ar*H*), 6.68 (2H, d, $J = 2.4$ Hz, Ar*H*), 7.03 (dd, $J = 8.7$, 2.4 Hz, 2H, Ar*H*). δ_C ($CDCl_3$) 31.51, 34.12, 35.28, 55.68, 110.44, 125.48, 125.79, 129.31, 137.96, 143.02, 154.29. MS: m/z [M^+] 536, 538, 540. Elemental analysis calculated for $C_{26}H_{34}Br_2O_2$(538.37): C, 58.01; H, 6.37. Found: C, 57.93; H, 6.28.

dl-(*Z*)-1,4-Dibromo-2,3-bis(5-*tert*-butyl-2-methoxyphenyl)-2-butene, dl-(*Z*)-4. Colorless prisms (hexane). Mp 146–147 °C. ν_{max}(KBr)/cm^{-1}: 2952, 1605, 1502, 1244, 1100, 1026, 805. δ_H ($CDCl_3$) 1.39 (s, 18H, *t*Bu), 3.79 (s, 6H, O*Me*), 3.97 (d, $J = 9.6$ Hz, 2H, CH_2), 4.19 (2H, d, $J = 9.6$ Hz, CH_2), 6.86 (2H, d, $J = 8.7$ Hz, Hz, Ar*H*), 7.35 (2H, dd, $J = 8.7$, 2.4 Hz, Ar*H*), 7.60 (2H, d, $J = 2.4$ Hz Ar*H*). δ_C ($CDCl_3$) 31.48, 34.15, 35.33, 55.71, 110.48, 125.51, 125.82, 129.36, 137.92, 143.96, 154.25. MS: m/z [M^+] 536, 538, 540. Elemental analysis calculated for $C_{26}H_{34}Br_2O_2$(538.37): C, 58.01; H, 6.37. Found: C, 57.97; H, 6.37.

Bromination of (*Z*)-3 with Br_2

A solution of bromine Br_2 (0.2 mL, 2.6 mmol) in CH_2Cl_2 (1 mL) was added to a solution of (*Z*)-**3** (100 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 12 h, it was poured into a large amount of ice water (10 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane and hexane–benzene (1:1) as an eluent to give *meso*-(*Z*)-**4** (42 mg, 30%) and *dl*-(*Z*)-**4** (84 mg, 60%), respectively.

Bromination of (*E*)-3 with BTMA Br_3

BTMA Br_3 (440 mg, 1.2 mmol) was added to a solution of (*E*)-**3** (100 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 24 h, it was poured into a large amount of ice water (100 mL) and extracted with CH_2Cl_2 (50 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was treated as described previously to give *meso*-(*Z*)-**4** (45 mg, 32%) and *dl*-(*Z*)-**4** (85 mg, 61%), respectively.

Bromination of (*Z*)-3 with BTMA Br_3

BTMA Br_3 (440 mg, 1.2 mmol) was added to a solution of (*E*)-**3** (100 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 24 h, it was poured into a large amount of ice water (100 mL) and extracted with CH_2Cl_2 (50 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was treated as

described previously to give *meso*-(*Z*)-**4** (44 mg, 31%) and *dl*-(*Z*)-**4** (87 mg, 62%), respectively.

Bromination of 5 with BTMA Br_3

BTMA Br_3 (98 mg, 0.26 mmol) was added to a solution of **5** (98 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the reaction mixture was stirred at room temperature for 12 h, it was poured into a large amount of icewater (10 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane and hexane–benzene (1:1) as an eluent to give *meso*-(*Z*)-**4** (45 mg, 32%) and *dl*-(*Z*)-**4** (87 mg, 62%), respectively.

Debromination of 4 with Zinc Powder

Acetic acid (0.28 mL, 4.8 mmol) was gradually added to a suspension of *meso*-(*Z*)-**4** (130 mg, 0.24 mmol) and Zn powder (317 mg, 4.9 mmol) in CH_2Cl_2 (6 mL) and stirred at room temperature for 24 h. The reaction mixture was filtered and washed with CH_2Cl_2 (5 mL × 3). The filtrate was condensed under the reduced pressure to leave the crude 2,3-bis(5-*tert*-butyl-2-methoxyphenyl)buta-1,3-diene **5** (91 mg, 100%) as a colorless solid. Mp 115–116 °C. ν_{max}(KBr)/cm^{-1}: 2966, 1505, 1459, 1247, 1034, 805. δ_H ($CDCl_3$) 1.23 (s, 18H, *t*Bu), 3.76 (s, 6H, O*Me*), 5.12 (s, 2H, *CH*$_2$), 5.14 (s, 2H, *CH*$_2$), 6.72 (d, $J = 8.4$ Hz, 2H, Ar*H*), 7.17 (dd, $J = 8.4$, 2.4 Hz, 2H, Ar*H*), 7.22 (d, $J = 2.4$ Hz, 2H, Ar*H*). δ_C ($CDCl_3$) 31.55, 34.02, 55.90, 110.53, 116.00, 124.88, 128.37, 130.29, 142.84, 147.74, 154.74. MS: m/z [M^+] 378. Elemental analysis calculated for $C_{26}H_{34}O_2$(378.56): C, 82.49; H, 9.05. Found: C, 82.63; H, 9.18.

Similar treatment of *dl*-(*Z*)-**4** with zinc powder afforded the corresponding diene **5** in quantitative yield.

Diels–Alder Reaction of 5 with Dimethyl Acetylenedicarboxylate

A solution of crude **5** (285 mg, 0.75 mmol) and dimethyl acetylenedicarboxylate (128 mg, 0.90 mmol) in toluene (5 mL) was heated at 100 °C for 24 h. After the reaction mixture was cooled to room temperature, the solvent was condensed under reduced pressure to leave the residue. The residue was column chromatographed over silica gel with benzene as eluent to give compound **6** (285 mg, 73%) as a pale yellow oil. δ_H ($CDCl_3$) 1.01 (s, 18H, *t*Bu), 3.76 (s, 6H, O*Me*), 3.80 (s, 10H, *CH*$_2$, COO*Me*), 6.63 (d, $J = 8.6$ Hz, 2H, Ar*H*), 6.72 (d, $J = 2.3$ Hz, 2H, Ar*H*), 6.99 (dd, $J = 8.6$, 2.3 Hz, 2H, Ar*H*). MS: m/z [M^+] 520. Elemental analysis calculated for $C_{32}H_{40}O_6$(520.66): C, 73.82; H, 7.74. Found: C, 73.93; H, 7.68.

Oxidation of 6 with DDQ

A solution **6** (100 mg, 0.19 mmol) and DDQ (44 mg, 0.25 mmol) in benzene (5 mL) was heated at 50 °C for 12 h. After the reaction mixture was cooled to rt, the solvent was condensed under the reduced pressure to leave the residue. The residue was column chromatographed over silica gel with ethyl acetate as eluent to give

a colorless solid. Recrystallization from methanol afforded dimethyl 4,5-bis(5-*tert*-butyl-2-methoxyphenyl)benzene-1,2-dicarboxylate **7** (68 mg, 70%) as colorless prisms (MeOH). Mp 123–124 °C. ν_{max}(KBr)/cm^{-1}: 2959, 1730 (C=O), 1502, 1432, 1288, 1255, 1126, 1070, 812. δ_H ($CDCl_3$) 1.11 (18H, s, *t*Bu), 3.52 (6H, s, O*Me*), 3.92 (6H, s, COO*Me*), 6.67 (2H, d, $J = 8.6$ Hz, Ar-*H*), 6.95 (2H, d, $J = 2.4$ Hz, Ar*H*), 7.15 (2H, dd, $J = 8.6$, 2.4 Hz Ar*H*), 7.80 (2H, s, Ar*H*). δ_C ($CDCl_3$) 31.38, 33.85, 52.52, 55.20, 109.98, 125.33, 128.20, 128.50, 130.02, 131.59, 141.92, 142.66, 153.92, 168.26. MS: m/z [M$^+$] 518. Elemental analysis calculated for $C_{32}H_{38}O_6$(518.64): C, 74.11; H, 7.39. Found: C, 74.27; H, 7.36.

Crystallographic Data for *dl*-(*Z*)-4

Crystal data for *dl*-(*Z*)-**4**: $C_{26}H_{34}Br_4O_2$, $M = 538.33$, triclinic, P–1, $a = 10.154(2)$, $b = 14.185(2)$, $c = 9.815(2)$ Å, $V = 1328.8(4)$ Å^3, $\alpha = 99.27(1)$, $\beta = 106.63(1)$, $\gamma = 93.32(1)$, $Z = 2$, $D_c = 1.345$ g cm^{-3}, μ(Mo-K$_\alpha$) = 3.068 mm^{-1}, $T = 296$ K, colorless prisms; 6100 reflections measured on a Rigaku AFC5S CCD diffractometer, of which 2313 were independent, data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.9987, 0.9987) and Lp effects, $R_{int} = 0.06870$, structure solved by direct methods (version 3.5.1. Rigaku/MSC), F^2 refinement, $R_1 = 0.0870$ for 2313 data with $F^2 > 2s(F^2)$, $wR_2 = 0.1010$ for all data, 306 parameters. Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 702663. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 144-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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