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Reaction of ene-bis(phosphinylallenes): [2+2] versus [4+2] cycloaddition

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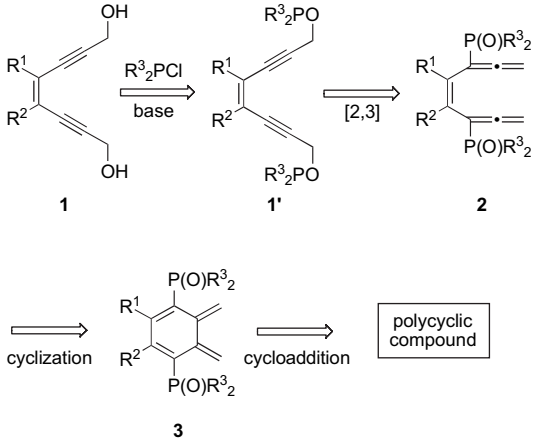
Abstract—Reaction of ene-bis(phosphinylallenes), derived from ene-bis(propargyl alcohols) and chlorodiphenylphosphine, was investigated. Benzene-bridged bis(phosphinylallenes) exclusively gave intramolecular [2+2] cycloadducts in the presence of dimethyl fumarate in sharp contrast to the reaction of benzene-bridged bis(sulfinylallenes), which gave the corresponding [4+2] cycloadducts. On the other hand, substituted ethylene- or five-membered heterocycle-bridged bis(phosphinylallenes) provided [4+2] cycloadducts. Reaction of benzene-bridged diallene bearing both a sulfinyl group and a phosphinyl group on the two allenyl groups was also described.

1. Introduction

Recent efforts from this laboratory[1,2] disclosed that the pericyclic reaction of ene-bis(sulfinylallenes), derived from the reaction of ene-bis(propargyl alcohols), enables the rapid construction of a variety of polycyclic aromatic compounds.[1–3] In our contiguous studies on the utility of the ene-diallene species in organic synthesis, we investigated the pericyclic reaction of ene-bis(phosphinylallene), which is an analogue of ene-bis(sulfinylallene), and should be prepared by the [2,3]-sigmatropic rearrangement[4,5] of a ene-bis(propargyl alcohol) derivative, the same as ene-bis(sulfinylallene)[6] (Scheme 1). This paper describes the unexpected reactivity of the two types of ene-bis(phosphinylallenes); one is the benzene-bridged derivatives, which exclusively underwent [2+2] cycloaddition,[7] while the other is the substituted ethylene derivatives and heterocyclic ones leading to the formation of the [4+2] cycloadducts.



Scheme 1.

2. Results and discussion

According to the previously described procedure for the reaction with PhSCl,[1,6] chlorodiphenylphosphine (Ph_2PCl) was added to the solution of benzene-bridged bis(propargyl alcohol) **4a**, triethylamine, and dimethyl fumarate (**5**) (as a dienophile) in THF at −78 °C, and the resulting mixture was warmed to room temperature to produce the naphtho[*b*]-cyclobutene **6aa**[8] in 85% yield (Scheme 2). The expected cycloadduct **7aa**, predicted on the basis of the reaction of **4a** and **5** in the presence of PhSCl, could not be detected. The reactivity of ene-bis(phosphinylallene) was in sharp contrast to that of bis(sulfinylallene), despite the similarity of the electrical nature between the phosphinyl and sulfinyl groups.[9] On the basis of the experiments in Scheme 2, it was evident that a dienophile did not take part in the formation of **6aa**. Thus, the ring-closing reaction using PhSCl and other chlorophosphines *in the absence of* the dienophile became the next subject of interest (Table 1).

Keywords: Bisallenes; [2+2] Cycloaddition; Naphtho[*b*]cyclobutenes; [4+2] Cycloaddition.
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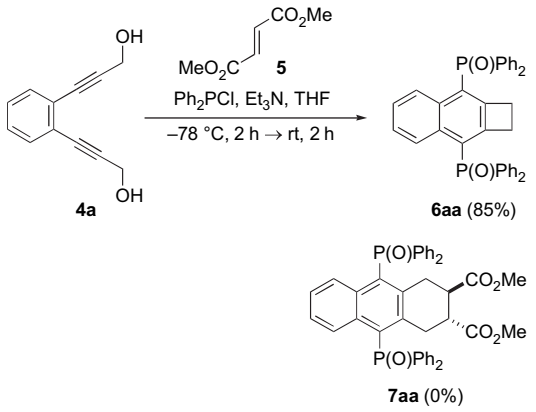
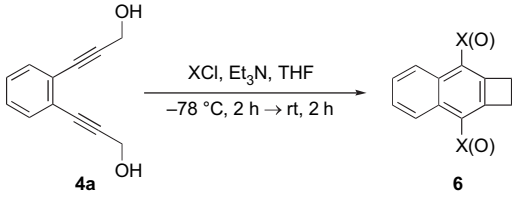
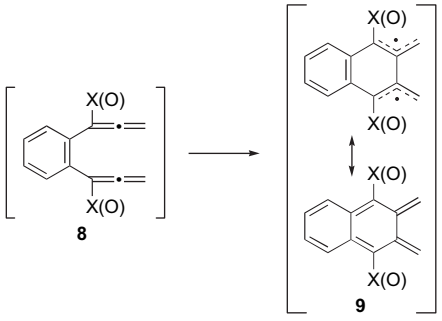


Scheme 2.

Table 1. Synthesis of naphtho[*b*]cyclobutenes **6**[a]



Entry	X	Product	Yield (%)
1	Ph_2P	**6aa**	85
2	Cy_2P	**6ab**	98
3	$^iPr_2P$	**6ac**	81
4	Et_2P	**6ad**	99
5	$(EtO)_2P$	**6ae**	0
6	PhS	**6af**	0



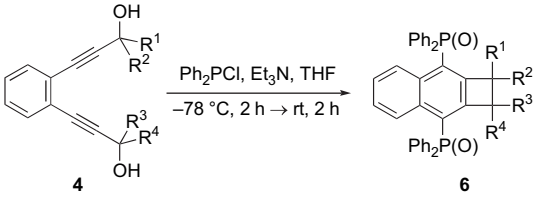
[a] All reactions were performed on a 0.1 mmol scale (0.1 M) with 6 equiv of XCl and 7 equiv of Et_3N.

The reactions with chlorodialkylphosphines instead of Ph_2PCl exclusively afforded the corresponding 3,8-bis(dialkylphosphinyl)naphtho[*b*]cyclobutenes **6ab–6ad** in high yields, regardless of the bulkiness of the alkyl groups on the phosphorus atom (entries 2–4). However, changing chlorodialkylphosphine to PhSCl or diethyl chlorophosphite [$(EtO)_2PCl$] under standard conditions resulted in complex mixtures of products (entries 5 and 6). A comprehensive mechanistic discussion is premature at this point, but it seems reasonable to postulate that the bis(phosphinylallene) **8** [X(O)=phosphinyl], derived from the bis(propargyl phosphinite) by dual [2,3]-sigmatropic rearrangement, would be converted into the biradical (*o*-quinodimethane) species **9**, which spontaneously undergoes intramolecular [2+2] cycloaddition to produce **6**.[10] The production of the naphtho[*b*]-cyclobutene derivative **6aa** as a sole product was observed irrespective of the existence of dimethyl fumarate (**5**) (Scheme 2, Table 1, entry 1). This result may reflect that the intramolecular [2+2] cycloaddition of the plausible biradical intermediate **9** would be much faster than the intermolecular [4+2] cycloaddition with the dienophile. The fact that $(EtO)_2PCl$ could not provide the cyclobutene derivative might be attributable to the comparatively low reactivity in the [2,3]-sigmatropic rearrangement of **1′** to **2** (the second step in Scheme 1).[9]

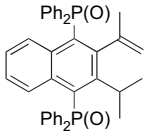
Having identified the effect of the phosphinyl group on the [2+2] cycloaddition, we then synthesized the naphtho[*b*]-cyclobutenes possessing certain substituents on the cyclobutene ring.[11] The results are summarized in Table 2. Treatment of the monomethyl derivative **4b**[1] with Ph_2PCl afforded the naphtho[*b*]cyclobutene **6ba** in 84% yield (entry 1). Similarly, another monosubstituted bis(propargyl alcohol) **4c** furnished **6ca** in a high yield (entry 2). The 1,2-disubstituted naphtho[*b*]cyclobutenes **6da** and **6ea** were obtained as a mixture of two diastereomers from 1,1′-disubstituted bis(propargyl alcohols) **4d** and **4e** in high yields (entries 3 and 4). In addition, the 1,1-disubstituted bis(propargyl alcohol) **4f** provided **6fa** without any difficulties (entry 5). However, fully methyl-substituted bis(propargyl alcohol) **4g** afforded a [1,5] hydrogen-shifted product **10** in 61% yield as the sole isolable product (entry 6).[12]

Stereochemical assignments of **6ea** and **6da** were unambiguously made by a chemical transformation, in particular, using a dephosphinylation reaction,[7] which we have recently developed. Initially, transformation of the major isomer of diphenyl-substituted cycloadduct **6ea** into the known naphtho[*b*]cyclobutene **11**[3c,13] by $LiAlH_4$ in refluxing dioxane was examined; however, an inseparable mixture of the cis- and trans-isomers of **11** and the unknown **12** was obtained (Scheme 3). This result indicated that ring opening of the

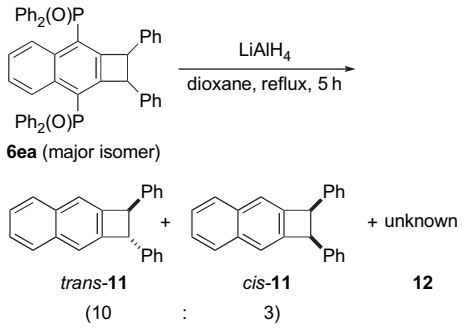
Table 2. Synthesis of substituted naphtho[*b*]cyclobutenes **6**



Entry	Substrate	R^1	R^2	R^3	R^4	Product	Yield (%)
1	**4b**	Me	H	H	H	**6ba**	84
2	**4c**	CH_2OBn	H	H	H	**6ca**	90
3	**4d**	Me	H	Me	H	**6da**	84[a]
4	**4e**	Ph	H	Ph	H	**6ea**	87[b,c]
5	**4f**	Me	Me	H	H	**6fa**	86
6	**4g**	Me	Me	Me	Me	**6ga**	0[b,d]

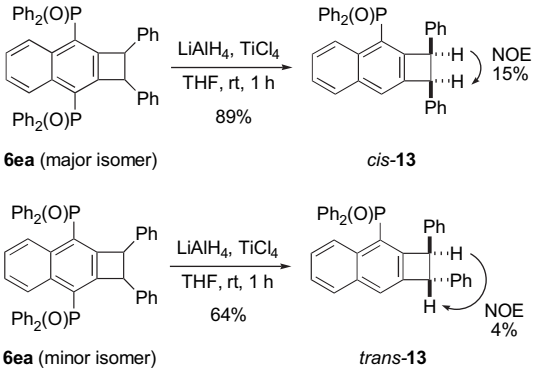


[a] A mixture of trans- and cis-isomers was obtained in a ratio of 3:2.
[b] Reaction mixture was stirred for an additional 15 h at room temperature.
[c] A mixture of trans- and cis-isomers was obtained in a ratio of 1:2.
[d] Compound **10** was obtained in 61% yield.



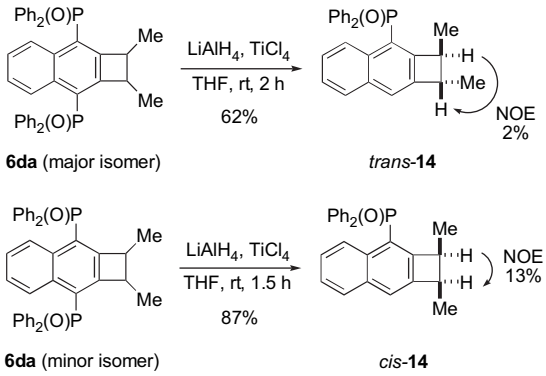
Scheme 3.

cyclobutane framework of **6ea** and/or **11** occurred under the reaction conditions.[14] Thus, a recently developed monodephosphinylation[7] under milder conditions was applied to compound **6ea**. Independent exposure of major and minor isomers of **6ea** to $LiAlH_4$–$TiCl_4$ at room temperature effected the monodephosphinylation without isomerization to provide the *cis*- and *trans*-**13**, respectively (Scheme 4). Their stereochemical assignments were unambiguously established by the NOE experiments as depicted in Scheme 4. As a result, an NOE experiment with *cis*-**13** revealed 15% enhancement between the two benzylic protons, while 4% enhancement was observed by irradiation of one of the two benzylic protons in the NOE experiment with *trans*-**13**. The major and minor isomers of **6da** were transformed to the *trans*- and *cis*-**14**, respectively, under the same reductive conditions (Scheme 5). The stereochemistry of these compounds was also determined on the basis of the NOE experiments. The *cis*-**13** was obtained as a major product in the reaction of the phenyl derivative **4e**, while the major isomer was found to be the *trans*-**14** in the reaction of the methyl congener **4d**. The preferential formation of the *cis*-diphenyl-substituted cycloadduct over the *trans*-one **6ea** in the [2+2] cycloaddition process is uncertain.[15]



Scheme 4.

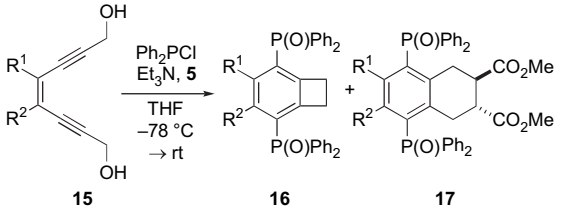
The present [2+2] cycloaddition methodology was found not to be applied to the synthesis of benzocyclobutenes. Indeed, the reaction of ethylene-bridged bis(propargyl alcohol) **15a**[16] with Ph_2PCl in the presence of dimethyl fumarate (**5**) gave neither [2+2] cycloadducts nor [4+2] cycloadducts (Table 3, entry 1). Monosubstituted ethylene **15b**,[1] however, produced the [4+2] cycloadduct **17b** in 88% yield (entry 2). Cycloalkane derivatives **15c**[1] and **15d**[1] (disubstituted ethylene derivatives) also reacted with **5** to give [4+2] cycloadducts **17c** and **17d**, respectively (entries 3 and 4). In

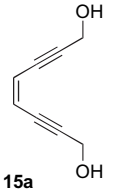
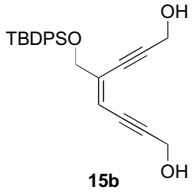
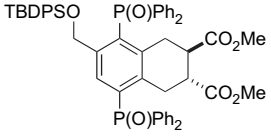
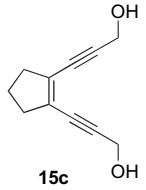
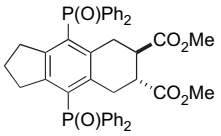
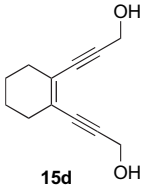
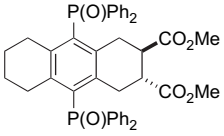
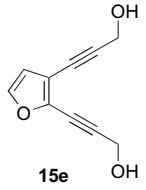
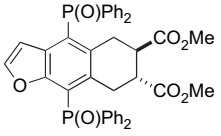
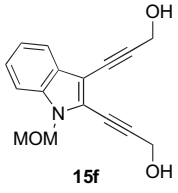
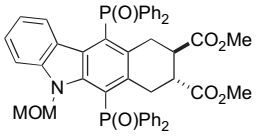
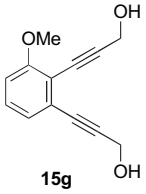
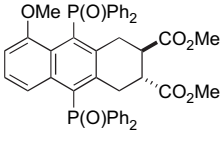


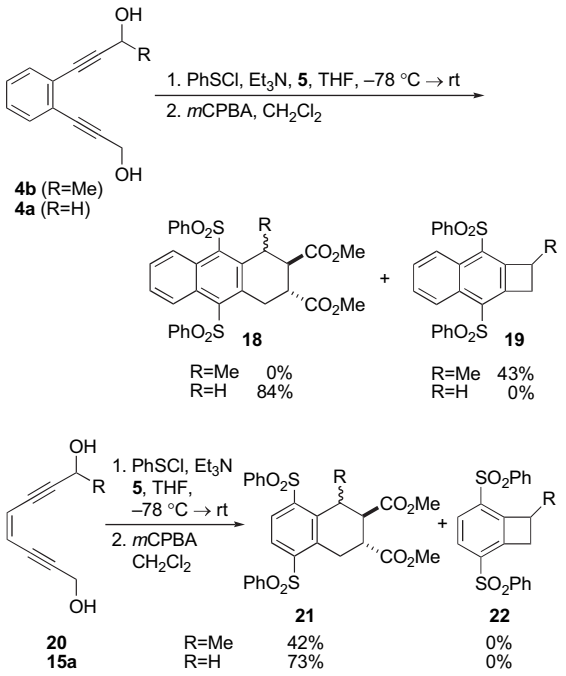
Scheme 5.

addition, the reaction of furan and indole derivatives **15e**[1] and **15f**[1] afforded [4+2] cycloadducts **17e** and **17f** as the sole isolable products in 48% and 77% yields, respectively (entries 5 and 6). The anisole derivative **15g** produced the [4+2] cycloadduct **17g** in 44% yield (entry 7), which was an unexpected result, because the corresponding benzene derivatives **4** consistently afforded naphtho[*b*]cyclobutenes **6** in high yields (see Scheme 2 and Table 2). It should be mentioned that [2+2] cycloadducts could not be detected in the reaction mixture even though the reaction ran in the absence of **5**. Cava and Shirley reported that the 2,3-naphthoquinodimethane (without a sulfinyl or phosphinyl group) is subject to the intramolecular [2+2] cycloaddition in the absence of dienophiles, whereas the *o*-quinodimethane generally tends to undergo dimerization (a kind of [4+2] cycloaddition) under similar conditions. On the basis of these experiments, they claimed that the formation of the naphtho[*b*]cyclobutene framework might be attributed to a higher degree of diradical character of the 2,3-naphthoquinodimethane than that of the *o*-quinodimethane.[17] Thus, the formation of the [4+2] cycloadducts in the reaction of **15b**, **15c**, and **15d** via the corresponding *o*-quinodimethane species (entries 2–4) would be tentatively rationalized by Cava and Shirley's interpretation, although we have no clues yet to understand the result of **15a**. A similar tendency was recorded in the reaction of benzene- and ethylene-bis(propargyl alcohols) **4b** and **20**, having a methyl group at the propargylic position, with PhSCl (Scheme 6).[1] The benzene derivative **4b** gave [2+2] cycloadduct **19** (R=Me) via the 2,3-naphthoquinodimethane intermediate, while ethylene derivative **20** provided a [4+2] cycloadduct **21** (R=Me) via the *o*-quinodimethane intermediate. However, the reaction of both **4a** and **15a** with PhSCl gave the corresponding [4+2] cycloadducts **18** (R=H) and **21** (R=H) in high yields. As aforementioned, the 2,3-naphthoquinodimethane having a bis(diphenylphosphinyl) group, derived from the reaction of **4a** with Ph_2PCl, furnished the [2+2] cycloadduct **6aa** (Scheme 2), whereas the corresponding phenylsulfinyl congener, derived from the reaction of **4a** with PhSCl, provided the [4+2] cycloadduct **18** (R=H). The significant difference in the reactivity observed in these two reactions cannot be rationalized on the basis of Cava and Shirley's results. By taking the similarity of the electrical nature between the phosphinyl and sulfinyl groups into account, we tentatively assumed that the much bulkier diphenylphosphinyl groups might inhibit the approach of dienophiles to the 1,3-diene moiety of the 2,3-naphthoquinodimethane having

Table 3. Reaction of various ene-bis(propargyl alcohols) with Ph_2PCl



Entry	Substrate	Product
1	 **15a**	Complex mixture
2	 **15b**	 **17b** (88%)
3	 **15c**	 **17c** (64%)
4	 **15d**	 **17d** (87%)
5	 **15e**	 **17e** (48%)
6	 **15f**	 **17f** (77%)
7	 **15g**	 **17g** (44%)

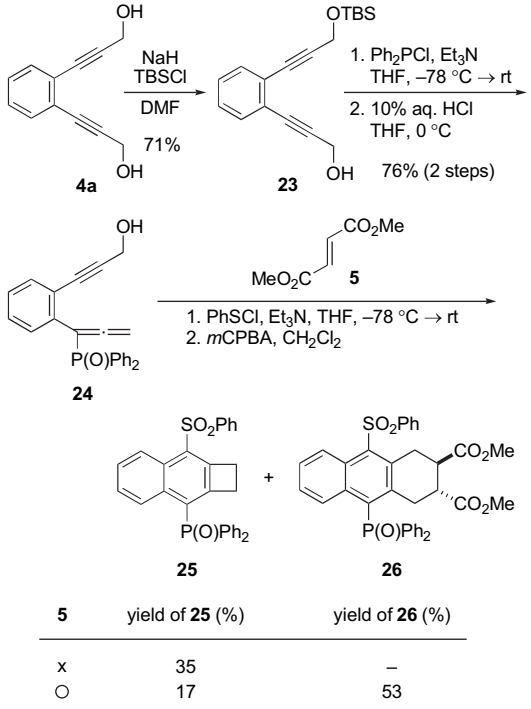


Scheme 6.

a bis(diphenylphosphinyl) group resulting in the exclusive formation of the [2+2] cycloadduct. This would not be the case with the naphthoquinodimethane having a bis(phenylsulfinyl) group where the less sterically hindered circumstances might allow the [4+2] cycloaddition to occur. In the case of other aromatic compounds **15e** and **15f** (Table 3, entries 5 and 6), the plausible furanoquinodimethane and carbazoloquinodimethane intermediates might no longer suffer from the serious non-bonding interaction between the diphenylphosphinyl group and the *peri*-hydrogen atom, which should be associated with the case of the naphthoquinodimethane intermediate derived from **4**. Thus, the rather bulky diphenyl moiety on the phosphorus atom of **15e** and **15f** would be allowed to orient opposite to the quinodimethane moiety. As a result, dimethyl fumarate (**5**) would approach to the 1,3-diene moiety resulting in the [4+2] cycloaddition. This speculation, however, cannot be used to explain the result obtained in the reaction of **15g** (Table 3, entry 7), because the naphthoquinodimethane intermediate from **15g** has a bulkier methoxy group than a hydrogen atom at the *peri*-position.

Independent treatment of the benzene-bis(propargyl alcohol) **4a** with Ph_2PCl (Scheme 2) and PhSCl (Scheme 6) gave the respective formation of the [2+2] cycloadduct **6aa** and the [4+2] cycloadduct **18** (R=H). In other words, the naphthoquinodimethane having a bis(diphenylphosphinyl) group afforded the naphthocyclobutene derivative ([2+2] product), while the bis(phenylsulfinyl) derivative furnished the tetrahydroanthracene derivative ([4+2] product). The outcome of these reactions seems to depend on the property of the substituent on the allenyl moiety. Thus, it would be interesting to examine the reaction of a benzene-bridged diallene bearing both a sulfinyl group and a phosphinyl group on the two allenyl groups. Monosilylation of bis(propargyl alcohol) **4a** under the conventional conditions gave **23**, which was subsequently treated with Ph_2PCl and 10%

aqueous HCl to give phosphinylallene derivative **24** (Scheme 7). The sequential reaction of **24** with PhSCl was carried out in the absence of **5** to give, after *m*CPBA oxidation, the naphtho[*b*]cyclobutene **25** in 35% yield. When **4a** was directly exposed to PhSCl, no characteristic products could be detected, whereas upon treatment with Ph_2PCl, **4a** provided **6aa** in 85% yield as mentioned in Table 1. On the other hand, similar treatment of **24** in the presence of **5** furnished the [4+2] cycloadduct **26** in 53% yield along with the [2+2] cycloadduct **25** (17%) as a by-product. These results may reflect both the natures of the sulfinyl group being susceptible to [4+2] cycloaddition and the phosphinyl group, which is subject to [2+2] cycloaddition.



5	yield of **25** (%)	yield of **26** (%)
x	35	–
○	17	53

Scheme 7.

3. Conclusions

We have shown that benzene-bis(phosphinylallenes), derived from benzene-bis(propargyl alcohols) and Ph_2PCl, underwent intramolecular [2+2] cycloaddition leading to the naphtho[*b*]cyclobutene derivatives in sharp contrast to the reaction of benzene-bis(sulfinylallenes), which gave the corresponding [4+2] cycloadducts. On the other hand, ethylene-bis(phosphinylallenes) afforded the [4+2] cycloadducts instead of the [2+2] cycloadducts. Thus, the reaction pathway could be controlled by proper choice of the reagent (Ph_2PCl and PhSCl) for the [2,3]-sigmatropic rearrangement of the propargyl alcohol moiety. Further studies on the scope and limitations of this method are currently in progress.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were measured in $CHCl_3$. ^1H NMR spectra were taken in $CDCl_3$. $CHCl_3$ (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230–400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

4.2. General procedure for reaction of ene-bis(propargyl alcohols) with chlorodialkylphosphine

To a solution of bis(propargyl alcohol) (0.100 mmol) in THF (1 mL) were successively added Et_3N (0.10 mL, 0.72 mmol) and chlorodialkylphosphine (0.56 mmol) at −78 °C. After being stirred for 2 h, the reaction mixture was allowed to warm to room temperature. After 2 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with AcOEt–MeOH gave the cycloadduct. To the reaction in the presence of dienophile, to a solution of bis(propargyl alcohol), dienophile (4 equiv), and Et_3N were added chlorodialkylphosphine.

4.2.1. 3,8-Bis(diphenylphosphinyl)-1,2-dihydrocyclobuta[*b*]naphthalene (6aa). Colorless prisms: mp >300 °C (AcOEt–MeOH); IR 1439, 1180 cm^{-1}; ^1H NMR δ 8.59–8.55 (2H, m), 7.70–7.25 (22H, m), 2.06 (4H, s); ^{13}C NMR δ 150.4 (dd, J_{C-P}=11.7, 11.7 Hz), 134.4 (J_{C-P}=7.8 Hz), 133.0 (J_{C-P}=105 Hz), 132.2–131.8 (m), 128.8–128.6 (m), 128.3 (dd, J_{C-P}=3.4, 3.4 Hz), 126.1 (J_{C-P}=191 Hz), 30.0; MS *m*/*z* 554 (M^+, 32). Anal. Calcd for $C_{36}H_{28}O_2P_2 \cdot 1/2H_2O$: C, 76.72; H, 5.19. Found: C, 76.78; H, 5.30.

4.2.2. 3,8-Bis(dicyclohexylphosphinyl)-1,2-dihydrocyclobuta[*b*]naphthalene (6ab). Colorless powders: mp >300 °C (AcOEt–MeOH); IR 1448, 1150 cm^{-1}; ^1H NMR δ 9.10 (2H, br s), 7.54–7.50 (2H, m), 3.46 (4H, s), 2.20–1.10 (44H, m); ^{13}C NMR δ 145.4 (br), 136.2 (dd, J_{C-P}=8.3, 6.1 Hz), 127.8, 125.9 (J_{C-P}=0.6 Hz), 124.6 (dd, J_{C-P}=77.1, 2.2 Hz), 37.6 (J_{C-P}=69.3 Hz), 32.2 (J_{C-P}=3.1 Hz), 26.5 (dd, J_{C-P}=13.4, 3.1 Hz), 25.8, 25.3; MS *m*/*z* 578 (M^+, 55); HRMS calcd for $C_{36}H_{52}O_2P_2$ 578.3443, found 578.3436.

4.2.3. 3,8-Bis(diisopropylphosphinyl)-1,2-dihydrocyclobuta[*b*]naphthalene (6ac). Colorless prisms: mp 223–225 °C (AcOEt); IR 1464, 1173, 1140 cm^{-1}; ^1H NMR δ 9.12 (2H, br s), 7.54–7.50 (2H, m), 3.50 (4H, s), 2.50–2.37 (4H, m), 1.33 (6H, d, J=7.1 Hz), 1.28 (6H, d, J=7.1 Hz), 1.15 (6H, d, J=7.1 Hz), 1.09 (6H, d, J=7.1 Hz); ^{13}C NMR δ 148.0 (br), 135.8 (br), 127.5, 125.8, 124.4 (dd, J_{C-P}=77.0, 2.8 Hz), 32.1, 27.6 (J_{C-P}=66.5 Hz), 16.3, 15.5; MS *m*/*z* 418 (M^+, 89). Anal. Calcd for $C_{24}H_{36}O_2P_2$: C, 68.88; H, 8.67. Found: C, 68.53; H, 8.75.

4.2.4. 3,8-Bis(diethylphosphinyl)-1,2-dihydrocyclobuta[*b*]naphthalene (6ad). A colorless oil: IR 1458, 1155 cm^{-1}; ^1H NMR δ 9.02–8.98 (2H, m), 7.58–7.54 (2H, m), 3.51 (4H, s), 2.19–2.06 (8H, m), 1.21 (6H, t, J=7.6 Hz), 1.15 (6H, d, J=7.6 Hz); selected characteristic data for ^{13}C NMR δ 31.9 (dd, J_{C-P}=1.7, 1.7 Hz), 23.4

(J_{C-P}=68.7 Hz), 5.9 (J_{C-P}=5.0 Hz); MS *m/z* 362 (M^+, 100); HRMS calcd for $C_{20}H_{28}O_2P_2$ 362.1565, found 362.1567.

4.2.5. 3,8-Bis(diphenylphosphinyl)-1-methyl-1,2-dihydrocyclobuta[*b*]naphthalene (6ba). Colorless prisms: mp >300 °C (AcOEt–MeOH); IR 1437, 1173 cm^{-1}; ^1H NMR δ 8.59 (1H, d, *J*=7.6 Hz), 8.38 (1H, d, *J*=8.3 Hz), 7.81–7.20 (22H, m), 2.90–2.86 (1H, m), 2.46–2.38 (1H, m), 1.71–1.65 (1H, m), 0.75 (3H, d, *J*=6.9 Hz); selected characteristic data for ^{13}C NMR δ 155.6 (dd, J_{C-P}=13.5, 8.6 Hz), 148.9 (dd, J_{C-P}=13.4, 8.5 Hz), 39.4 (d, J_{C-P}=4.3 Hz), 38.3 (J_{C-P}=3.9 Hz), 20.3; MS *m/z* 568 (M^+, 100); HRMS calcd for $C_{37}H_{30}O_2P_2$ 568.1721, found 568.1725.

4.2.6. 1-(Benzyloxymethyl)-3,8-bis(diphenylphosphinyl)-1,2-dihydrocyclobuta[*b*]naphthalene (6ca). Pale yellow solid: mp 288–293 °C (AcOEt–MeOH); IR 1437, 1173 cm^{-1}; ^1H NMR δ 8.66 (1H, d, *J*=8.5 Hz), 8.22 (1H, d, *J*=8.5 Hz), 7.74–7.02 (27H, m), 4.13 (2H, s), 3.21–3.12 (3H, m), 2.29–2.15 (2H, m); selected characteristic data for ^{13}C NMR δ 151.6 (dd, J_{C-P}=7.2, 7.2 Hz), 149.6 (dd, J_{C-P}=9.3, 4.1 Hz), 72.6, 71.4, 44.4 (d, J_{C-P}=3.1 Hz), 34.7 (J_{C-P}=4.1 Hz); MS *m/z* 674 (M^+, 5.4); HRMS calcd for $C_{44}H_{36}O_3P_2$ 674.2140, found 674.2132. Anal. Calcd for $C_{44}H_{36}O_3P_2 \cdot 1/2H_2O$: C, 77.29; H, 5.45. Found: C, 77.64; H, 5.16.

4.2.7. 3,8-Bis(diphenylphosphinyl)-1,2-dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene (6da): *trans*-6da. Colorless prisms: mp >300 °C (AcOEt–MeOH); IR 1437, 1175 cm^{-1}; ^1H NMR δ 8.46–8.42 (2H, m), 7.82–7.23 (22H, m), 2.39–2.37 (2H, m), 0.82 (6H, d, *J*=6.9 Hz); selected characteristic data for ^{13}C NMR δ 154.7 (dd, J_{C-P}=11.2, 11.2 Hz), 48.1 (dd, J_{C-P}=2.2, 2.2 Hz), 20.1; MS *m/z* 582 (M^+, 100); HRMS calcd for $C_{38}H_{32}O_2P_2$ 582.1878, found 582.1891.

cis-**6da**. Colorless prisms: mp >300 °C (AcOEt–MeOH); IR 1437, 1173 cm^{-1}; ^1H NMR δ 8.32–8.28 (2H, m), 7.85–7.17 (22H, m), 3.26–3.20 (2H, m), 0.71 (6H, d, *J*=6.6 Hz); selected characteristic data for ^{13}C NMR δ 154.8 (dd, J_{C-P}=11.0, 11.0 Hz), 48.2 (J_{C-P}=2.5 Hz), 20.0; MS *m/z* 582 (M^+, 100); HRMS calcd for $C_{38}H_{32}O_2P_2$ 582.1878, found 582.1875.

4.2.8. 3,8-Bis(diphenylphosphinyl)-1,2-diphenyl-1,2-dihydrocyclobuta[*b*]naphthalene (6ea): *trans*-6ea. Pale yellow solid: mp >300 °C (AcOEt–MeOH); IR 1437, 1171 cm^{-1}; ^1H NMR δ 8.68–8.66 (2H, m), 7.71–7.06 (28H, m), 6.50 (4H, d, *J*=6.9 Hz), 3.64 (2H, s); selected characteristic data for ^{13}C NMR δ 150.0 (dd, J_{C-P}=11.2, 11.2 Hz), 135.5 (dd, J_{C-P}=7.3, 7.3 Hz), 60.8 (dd, J_{C-P}=2.2, 2.2 Hz); MS *m/z* 706 (M^+, 72); HRMS calcd for $C_{48}H_{36}O_2P_2$ 706.2191, found 706.2191.

cis-**6ea**. Colorless solid: mp >300 °C (AcOEt–MeOH); IR 1437, 1171 cm^{-1}; ^1H NMR δ 8.61–8.58 (2H, m), 7.56–7.18 (22H, m), 6.71–6.61 (6H, m), 6.22–6.20 (4H, m), 4.39 (2H, s); selected characteristic data for ^{13}C NMR δ 150.1 (dd, J_{C-P}=11.2, 11.2 Hz), 138.0, 135.2 (dd, J_{C-P}=7.3, 7.3 Hz), 55.8; MS *m/z* 706 (M^+, 83); HRMS calcd for $C_{48}H_{36}O_2P_2$ 706.2191, found 706.2185.

4.2.9. 3,8-Bis(diphenylphosphinyl)-1,1-dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene (6fa). Colorless prisms: mp >300 °C (AcOEt–MeOH); IR 1437, 1167 cm^{-1}; ^1H NMR δ 8.62–8.59 (1H, m), 7.73–7.47 (22H, m), 7.27–7.21 (1H, m), 7.09–7.03 (1H, m), 2.09 (2H, s), 1.49 (6H, s); selected characteristic data for ^{13}C NMR δ 47.3 (J_{C-P}=4.7 Hz), 45.8, 26.8; MS *m/z* 582 (M^+, 100); HRMS calcd for $C_{38}H_{32}O_2P_2$ 582.1878, found 582.1893. Anal. Calcd for $C_{38}H_{32}O_2P_2$: C, 78.34; H, 5.54. Found: C, 78.17; H, 5.57.

4.2.10. 1,4-Bis(diphenylphosphinyl)-2-(1-methylethenyl)-3-(1-methylethyl)naphthalene (10). A colorless oil: IR 1437, 1169 cm^{-1}; ^1H NMR δ 8.26 (1H, d, *J*=8.8 Hz), 8.00 (1H, d, *J*=8.8 Hz), 7.79–7.31 (20H, m), 7.02 (1H, t, *J*=7.4 Hz), 6.94 (1H, t, *J*=7.4 Hz), 4.94 (1H, s), 4.81 (1H, s), 3.57 (1H, sep, *J*=6.8 Hz), 1.90 (3H, s), 0.95 (3H, d, *J*=6.9 Hz), 0.67 (3H, d, *J*=6.9 Hz); selected characteristic data for ^{13}C NMR δ 38.3 (J_{C-P}=8.4 Hz), 29.1, 23.7, 20.4; MS *m/z* 610 (M^+, 45); HRMS calcd for $C_{40}H_{36}O_2P_2$ 610.2191, found 610.2192.

4.2.11. Dimethyl *trans*-6-(*tert*-butyldiphenylsiloxy)-methyl-5,8-bis(diphenylphosphinyl)-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (17b). A pale yellow oil: IR 1734, 1437, 1175 cm^{-1}; ^1H NMR δ 7.76–7.19 (31H, m), 4.22 (2H, s), 3.52–3.46 (1H, m), 3.49 (3H, s), 3.45 (3H, s), 3.23–3.06 (3H, m), 2.90–2.82 (2H, m), 0.70 (9H, s); selected characteristic data for ^{13}C NMR δ 174.1, 174.0, 64.7 (J_{C-P}=4.1 Hz), 51.9, 51.8, 40.9, 40.3, 31.0 (J_{C-P}=5.2 Hz), 29.8 (J_{C-P}=5.2 Hz), 26.7, 18.9; FABMS *m/z* 917 (M^++1, 40); FABHRMS calcd for $C_{55}H_{55}O_7P_2Si$ 917.3192, found 917.3164.

4.2.12. Dimethyl *trans*-4,9-bis(diphenylphosphinyl)-2,3,5,6,7,8-hexahydro-1*H*-cyclopenta[*b*]naphthalene-6,7-dicarboxylate (17c). A pale yellow oil: IR 1732, 1437, 1171 cm^{-1}; ^1H NMR δ 7.70–7.47 (20H, m), 3.42 (6H, s), 3.17–3.07 (4H, m), 2.81–2.79 (2H, m), 2.24–2.19 (2H, m), 1.48 (2H, quin, *J*=7.1 Hz); selected characteristic data for ^{13}C NMR δ 174.2, 51.8, 40.6, 34.2 (dd, J_{C-P}=1.7, 1.7 Hz), 30.5 (dd, J_{C-P}=2.8, 2.8 Hz), 25.8; MS *m/z* 688 (M^+, 100); HRMS calcd for $C_{41}H_{38}O_6P_2$ 688.2144, found 688.2140.

4.2.13. Dimethyl *trans*-9,10-bis(diphenylphosphinyl)-1,2,3,4,5,6,7,8-octahydroanthracene-2,3-dicarboxylate (17d). A pale yellow oil: IR 1732, 1437, 1165 cm^{-1}; ^1H NMR δ 7.70–7.47 (20H, m), 3.40 (6H, s), 2.99–2.97 (4H, m), 2.81–2.78 (2H, m), 2.44–2.41 (4H, m), 1.13–1.05 (4H, m); selected characteristic data for ^{13}C NMR δ 174.3, 51.8, 40.6, 30.2 (dd, J_{C-P}=2.8, 2.8 Hz), 28.9 (dd, J_{C-P}=2.8, 2.8 Hz), 19.6; MS *m/z* 702 (M^+, 100); HRMS calcd for $C_{42}H_{40}O_6P_2$ 702.2300, found 702.2304.

4.2.14. Dimethyl *trans*-4,9-bis(diphenylphosphinyl)-5,6,7,8-tetrahydronaphtho[2,3-*b*]furan-6,7-dicarboxylate (17e). A pale yellow oil: IR 1734, 1437, 1172 cm^{-1}; ^1H NMR δ 7.76–7.43 (20H, m), 6.94 (1H, d, *J*=2.3 Hz), 5.72 (1H, dd, *J*=2.3, 2.1 Hz), 4.00 (1H, dd, *J*=16.0, 6.4 Hz), 3.49 (3H, s), 3.45–3.32 (3H, m), 3.43 (3H, s), 3.00–2.91 (1H, m), 2.83–2.75 (1H, m); selected characteristic data for ^{13}C NMR δ 174.4, 174.2, 51.9, 40.5, 30.4 (J_{C-P}=5.6 Hz), 29.0 (J_{C-P}=5.0 Hz); MS *m/z* 688 (M^+, 100); HRMS calcd for $C_{40}H_{34}O_7P_2$ 688.1780, found 688.1776.

4.2.15. Dimethyl *trans*-6,11-bis(diphenylphosphinyl)-5-(methoxymethyl)-7,8,9,10-tetrahydro-5*H*-benzo[*b*]carbazole-8,9-dicarboxylate (17f). A pale yellow oil: IR 1734, 1437, 1172 cm^{-1}; ^1H NMR δ 8.38 (1H, d, J=7.9 Hz), 7.81–7.13 (22H, m), 6.92 (1H, t, J=6.3 Hz), 5.50 (1H, d, J=10.9 Hz), 5.23 (1H, d, J=10.9 Hz), 3.59–3.41 (1H, m), 3.59 (3H, s), 3.41 (3H, s), 2.95–2.56 (5H, m), 2.56 (3H, s); selected characteristic data for ^{13}C NMR δ 173.9, 79.3, 55.8, 52.1, 51.9, 40.3 (J_{C-P}=2.8 Hz), 31.9 (J_{C-P}=6.7 Hz), 30.1; FABMS m/z 782 (M^++1, 2.4); FABHRMS calcd for $C_{46}H_{42}NO_7P_2$ 782.2437, found 782.2440.

4.2.16. Dimethyl *trans*-9,10-bis(diphenylphosphinyl)-5-methoxy-1,2,3,4-tetrahydroanthracene-2,3-dicarboxylate (17g). A pale yellow oil: IR 1732, 1437, 1175 cm^{-1}; ^1H NMR δ 8.00–7.03 (22H, m), 6.33 (1H, d, J=7.7 Hz), 3.89–2.92 (6H, m), 3.47 (3H, s), 3.41 (3H, s), 2.99 (3H, s); selected characteristic data for ^{13}C NMR δ 174.2, 173.9, 53.3, 52.2, 52.0, 40.0, 39.9; MS m/z 728 (M^+, 16); HRMS calcd for $C_{43}H_{38}O_7P_2$ 728.2093, found 728.2089.

4.3. Dephosphinylation of *cis*-6ea with $LiAlH_4$

To a suspension of $LiAlH_4$ (30.4 mg, 0.800 mmol) in 1,4-dioxane (2 mL) was added *cis*-**6ea** (141 mg, 0.200 mmol), and the mixture was refluxed for 5 h. The mixture was cooled to room temperature and quenched by addition of water. Aqueous HCl 10% was added, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated. Chromatography of the residue with hexane afforded an inseparable mixture of the cis- and trans-isomers of **11**[3c,13] and the unknown **12** (38.0 mg, *cis*-**11**: *trans*-**11**=10:3) as colorless solid: ^1H NMR δ 7.88–6.96 (>16H, m), 5.37 (0.46H, s, for *cis*-**11**), 4.67 (1.54H, s, for *trans*-**11**), 4.05 (2.5H, s, for **12**); MS m/z 306 (M^+, 70); HRMS calcd for $C_{24}H_{18}$ 306.1409, found 306.1410.

4.4. Typical procedure for dephosphinylation with $LiAlH_4$–$TiCl_4$

To a suspension of $LiAlH_4$ (20.6 mg, 0.544 mmol) in THF (1 mL) were successively added $TiCl_4$ (0.03 mL, 0.3 mmol) and *cis*-**6ea** (48.1 mg, 6.80×10^{-2} mmol), and the mixture was stirred for 1 h at room temperature. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated. Chromatography of the residue with hexane–AcOEt (1:3) afforded *cis*-**13** (30.8 mg, 89%) as a colorless oil.

4.4.1. *cis*-3-(Diphenylphosphinyl)-1,2-diphenyl-1,2-dihydrocyclobuta[*b*]naphthalene (*cis*-13). A colorless oil: IR 1437, 1169 cm^{-1}; ^1H NMR δ 8.56 (1H, d, J=8.5 Hz), 7.91 (2H, s), 7.57–6.70 (20H, m), 6.29 (2H, d, J=7.3 Hz), 5.17 (1H, d, J=6.6 Hz), 4.58 (1H, d, J=6.6 Hz); selected characteristic data for ^{13}C NMR δ 151.2 (J_{C-P}=8.9 Hz), 143.7 (J_{C-P}=14.0 Hz), 60.9 (J_{C-P}=3.9 Hz), 58.2; MS m/z 506 (M^+, 2.5); HRMS calcd for $C_{36}H_{27}OP$ 506.1800, found 506.1802.

4.4.2. *trans*-3-(Diphenylphosphinyl)-1,2-diphenyl-1,2-dihydrocyclobuta[*b*]naphthalene (*trans*-13). A colorless oil: IR 1437, 1169 cm^{-1}; ^1H NMR δ 8.57 (1H, d, J=8.8 Hz), 7.89 (1H, d, J=8.3 Hz), 7.85 (1H, s), 7.55–7.04 (20H, m), 6.63 (2H, d, J=7.1 Hz), 4.34 (1H, d, J=2.4 Hz), 4.02 (1H, d, J=2.4 Hz); selected characteristic data for ^{13}C NMR δ 151.2 (J_{C-P}=9.3 Hz), 143.7 (J_{C-P}=13.4 Hz), 57.3 (J_{C-P}=4.1 Hz), 53.2; MS m/z 506 (M^+, 1.1); HRMS calcd for $C_{36}H_{27}OP$ 506.1800, found 506.1792.

4.4.3. *trans*-3-(Diphenylphosphinyl)-1,2-dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene (*trans*-14). A colorless oil: IR 1437, 1167 cm^{-1}; ^1H NMR δ 8.38 (1H, d, J=8.4 Hz), 7.85–7.26 (14H, m), 3.02–3.00 (1H, m), 2.71–2.68 (1H, m), 1.39 (3H, d, J=6.9 Hz), 0.85 (3H, d, J=6.9 Hz); selected characteristic data for ^{13}C NMR δ 155.5 (J_{C-P}=8.9 Hz), 146.6 (J_{C-P}=14.0 Hz), 49.2 (J_{C-P}=3.9 Hz), 45.2, 19.3, 18.7; MS m/z 382 (M^+, 100); HRMS calcd for $C_{26}H_{23}OP$ 382.1487, found 382.1486.

4.4.4. *cis*-3-(Diphenylphosphinyl)-1,2-dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene (*cis*-14). A colorless oil: IR 1437, 1169 cm^{-1}; ^1H NMR δ 8.35 (1H, d, J=8.6 Hz), 7.86–7.24 (14H, m), 3.66 (1H, quin, J=7.3 Hz), 3.26 (1H, quin, J=7.3 Hz), 1.23 (3H, d, J=7.3 Hz), 0.75 (3H, d, J=7.3 Hz); selected characteristic data for ^{13}C NMR δ 156.7 (J_{C-P}=8.3 Hz), 147.7 (J_{C-P}=14.5 Hz), 43.6 (J_{C-P}=7.2 Hz), 39.2, 14.5, 13.7; MS m/z 382 (M^+, 100); HRMS calcd for $C_{26}H_{23}OP$ 382.1487, found 382.1485.

4.5. Reaction of 24 with PhSCl in the presence of 5

To a solution of **24** (91.9 mg, 0.248 mmol) in THF (2.5 mL) were successively added **5** (71.5 mg, 0.497 mmol), Et_3N (0.21 mL, 1.5 mmol), and a solution of PhSCl (108 mg, 0.747 mmol) in THF (0.5 mL) at −78 °C. After being stirred for 2 h, the reaction mixture was allowed to warm to room temperature. After 13 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (1:3) to afford the crude sulfoxides. To a solution of the crude sulfoxides in CH_2Cl_2 (2 mL) was added *m*CPBA (66.7 mg, 0.386 mmol) at 0 °C, and the reaction mixture was allowed to warm to room temperature. After 12 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ and aqueous $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:2) afforded **26** (83.7 mg, 53%) and **25** (21.3 mg, 17%) as a colorless oils.

4.5.1. 3-(Diphenylphosphinyl)-8-(phenylsulfonyl)-1,2-dihydrocyclobuta[*b*]naphthalene (25). IR 1437, 1148 cm^{-1}; ^1H NMR δ 8.66–8.61 (2H, m), 7.96 (2H, d, J=6.9 Hz), 7.72–7.34 (15H, m), 3.50–3.46 (2H, m), 2.39–2.36 (2H, m); selected characteristic data for ^{13}C NMR δ 150.7 (J_{C-P}=9.5 Hz), 147.7 (J_{C-P}=14.5 Hz), 141.7, 31.1, 31.0; MS m/z 494 (M^+, 70); HRMS calcd for $C_{30}H_{23}O_3PS$ 494.1106, found 494.1101.

4.5.2. Dimethyl *trans*-9-(diphenylphosphinyl)-10-(phenylsulfonyl)-1,2,3,4-tetrahydroanthracene-2,3-dicarboxylate (26). IR 1732, 1437, 1175 cm^{-1}; ^1H NMR δ 8.94

(1H, d, J=8.7 Hz), 8.26 (1H, d, J=8.7 Hz), 7.94 (2H, d, J=6.9 Hz), 7.71–7.12 (15H, m), 4.05 (1H, dd, J=15.3, 6.3 Hz), 3.61 (3H, s), 3.56–3.34 (2H, m), 3.45 (3H, s), 3.14–3.07 (2H, m), 2.91–2.84 (1H, m); selected characteristic data for ^{13}C NMR δ 173.9, 173.7, 144.3 (J_{C-P}=7.8 Hz), 143.3, 140.0 (J_{C-P}=11.2 Hz), 52.2, 52.0, 39.9, 39.6, 30.4 (J_{C-P}=6.1 Hz), 27.9; MS m/z 638 (M^+, 46); HRMS calcd for $C_{36}H_{31}O_7PS$ 638.1528, found 638.1526.

4.6. Preparation of propargyl alcohols

4.6.1. 1-(4-Benzyloxy-3-hydroxy-1-butynyl)-2-(3-hydroxy-1-propynyl)benzene (4c). To a solution of 1-bromo-2-iodobenzene (1.06 g, 3.75 mmol) and 3-(tetrahydropyran-2-yl)-oxy-1-propyne (1.05 g, 7.50 mmol) in THF (15 mL) were successively added $Pd(PPh_3)_2Cl_2$ (52.6 mg, 7.50×10^{-2} mmol), CuI (71.4 mg, 0.375 mmol), and Et_3N (5.2 mL, 37 mmol) at room temperature. The mixture was stirred for 8 h, and the resulting precipitates were filtered off. The filtrate was concentrated to leave the residue, which was chromatographed with hexane–AcOEt (20:1) to afford 1-bromo-2-[3-(tetrahydropyran-2-yl)oxy-1-propynyl]benzene (988 mg, 89%) as a pale yellow oil: IR 3012, 2237 cm^{-1}; ^{1}H NMR δ 7.59–7.46 (2H, m), 7.28–7.13 (2H, m), 4.99 (1H, t, J=3.2 Hz), 4.55 (2H, s), 3.95–3.86 (1H, m), 3.62–3.54 (1H, m), 1.91–1.54 (6H, m); ^{13}C NMR δ 133.6, 132.4, 129.5, 126.9, 125.5, 96.7, 89.9, 84.3, 62.1, 54.6, 30.3, 25.4, 19.1; MS m/z 294 (M^+, 6.9); HRMS calcd for $C_{14}H_{15}O_2Br$ 294.0255, found 294.0252.

To a solution of the above bromobenzene (295 mg, 1.00 mmol) and (trimethylsilyl)acetylene (0.28 mL, 2.0 mmol) in Et_3N (5 mL) were successively added $Pd(PPh_3)_2Cl_2$ (35.0 mg, 5.00×10^{-2} mmol), CuI (19.0 mg, 0.100 mmol), and PPh_3 (26.3 mg, 0.100 mmol) at room temperature. The mixture was heated under reflux for 15 h, and the resulting precipitates were filtered off. The filtrate was concentrated to leave the residue, which was passed through a short pad of silica gel with hexane–AcOEt (20:1) to afford the crude diyne (311 mg) as a pale yellow oil. To a solution of the above diyne (311 mg) in MeOH (10 mL) was added K_2CO_3 (152 mg, 1.10 mmol) at room temperature. After 30 min, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (20:1) gave 1-ethynyl-2-[3-(tetrahydropyran-2-yl)oxy-1-propynyl]benzene (192 mg, 80% for two steps) as a colorless oil: IR 3308, 2230 cm^{-1}; ^{1}H NMR δ 7.50–7.45 (2H, m), 7.30–7.25 (2H, m), 5.00 (1H, t, J=3.4 Hz), 4.55 (2H, s), 3.93–3.88 (1H, m), 3.59–3.55 (1H, m), 3.28 (1H, s), 1.87–1.55 (6H, m); ^{13}C NMR δ 132.5, 132.1, 128.4, 128.0, 125.7, 124.6, 96.5, 89.3, 84.1, 82.0, 80.9, 62.0, 54.6, 30.2, 25.4, 19.1; MS m/z 240 (M^+, 12); HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1153.

To a solution of the above ethynylbenzene (243 mg, 1.01 mmol) in THF (8 mL) was added EtMgBr in THF (0.50 M, 2.2 mL, 1.1 mmol) at 0 °C. After 10 min, benzyloxyacetaldehyde (0.16 mL, 1.1 mmol) was added, and the mixture was stirred for 2 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (7:3) to afford the crude alcohol (193 mg, 49%) and to recover the ethynylbenzene (125 mg, 51%). To a solution of the above alcohol (193 mg) in MeOH (10 mL) was added $TsOH\cdot H_2O$ (9.5 mg, 5.0×10^{-2} mmol) at room temperature. After 30 min, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) gave **4c** (125 mg, 82%) as a yellow oil: IR 3421, 2231 cm^{-1}; ^{1}H NMR δ 7.37–7.21 (9H, m), 4.82 (1H, br s), 4.62 (2H, s), 4.39 (2H, s), 3.85–3.62 (4H, m); ^{13}C NMR δ 137.4, 131.2, 130.9, 128.4, 128.1, 127.9, 125.7, 125.1, 92.2, 91.2, 84.3, 84.1, 73.5, 73.4, 62.2, 51.2; FABMS m/z 307 (M^++1, 3.2); FABHRMS calcd for $C_{20}H_{19}O_3$ 307.1334, found 307.1347.

4.6.2. 1,2-Bis(3-hydroxy-3-phenyl-1-propynyl)benzene (4e). To a solution of *o*-diiodobenzene (387 mg, 1.17 mmol) and 1-phenyl-2-propyn-1-ol (0.90 mL, 7.0 mmol) in THF (8.5 mL) were successively added $Pd(PPh_3)_2Cl_2$ (16.0 mg, 2.34×10^{-2} mmol), CuI (22.0 mg, 0.117 mmol), and $^iPr_2NH$ (1.3 mL, 12 mmol) at room temperature. The mixture was stirred for 16 h, and the resulting precipitates were filtered off. The filtrate was concentrated to leave the residue, which was chromatographed with hexane–AcOEt (8:1→1:3) to afford **4e** (380 mg, 96%) as yellow solid: IR 3587, 3384, 2199 cm^{-1}; ^{1}H NMR δ 7.54–7.22 (14H, m), 5.59 (2H, s), 3.58 (2H, br s); ^{13}C NMR δ 140.4, 140.3, 131.3, 131.2, 128.7, 128.6, 128.5, 128.5, 128.3, 128.2, 128.1, 126.9, 126.8, 126.6, 125.4, 125.3, 93.2, 85.2, 65.0, 64.8; FABMS m/z 339 (M^++1, 0.1); FABHRMS calcd for $C_{24}H_{19}O_2$ 339.1385, found 339.1368.

4.6.3. 1-(3-Hydroxy-3-methyl-1-propynyl)-2-(3-hydroxy-1-propynyl)benzene (4f). To a solution of 1-(3-hydroxy-1-propynyl)-2-iodobenzene[18] (50.0 mg, 0.194 mmol) and 2-methyl-3-butyn-2-ol (0.06 mL, 0.6 mmol) in THF (2 mL) were successively added $Pd(PPh_3)_2Cl_2$ (2.7 mg, 3.9×10^{-3} mmol), CuI (3.7 mg, 1.9×10^{-2} mmol), and Et_3N (0.3 mL, 2 mmol) at room temperature. The mixture was stirred for 3 d, and the resulting precipitates were filtered off. The filtrate was concentrated to leave the residue, which was chromatographed with hexane–AcOEt (3:1) to afford **4f** (35.3 mg, 85%) as yellow solid: IR 3597, 3383, 2230 cm^{-1}; ^{1}H NMR δ 7.39–7.20 (4H, m), 4.53 (2H, s), 3.91 (2H, br s), 1.63 (6H, s); ^{13}C NMR δ 131.1, 131.0, 127.9, 127.8, 125.5, 125.4, 98.2, 91.7, 84.2, 80.8, 65.7, 51.2, 31.2; MS m/z 214 (M^+, 25); HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0998.

4.6.4. 2,3-Bis(3-hydroxy-1-propynyl)anisole (15g). To a biphasic mixture of 3-methoxycatechol (700 mg, 5.00 mmol) in toluene (10 mL) and 30% aqueous K_3PO_4 (20 mL) was added Tf_2O (2.02 mL, 12.0 mmol) at 0 °C. After the mixture was stirred for 3 h at room temperature, the layer was separated. The toluene layer was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (8:1) to afford 2,3-bis(trifluoromethanesulfonyloxy)anisole (2.05 g, quant.) as pale yellow solid: ^{1}H NMR δ 7.41–7.38 (1H, m), 7.10–7.04 (2H, m), 3.97 (3H, s).

To a solution of the above bis(triflate) (992 mg, 2.45 mmol) in Et_3N–DMF (24 mL, 1:5) were successively added tetrabutylammonium iodide (2.71 g, 7.35 mmol), (trimethylsilyl)-acetylene (1.38 mL, 9.80 mmol), $Pd(PPh_3)_2Cl_2$ (172 mg, 0.245 mmol) and CuI (140 mg, 0.735 mmol) at room temperature. After being stirred for 8 h at 70 °C, the mixture was cooled, diluted with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (20:1) to afford the crude bis[(trimethylsilyl)acetylene] (720 mg) as a brown oil. To a solution of the above bis[(trimethylsilyl)acetylene] (720 mg) in MeOH (15 mL) was added K_2CO_3 (728 mg, 5.28 mmol) at room temperature. After 3 h, MeOH was evaporated off, and the residue was dissolved in water and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (20:1) to afford the crude diyne (97.1 mg). To a solution of the above diyne (97.1 mg) in THF (5 mL) was added ^{n}BuLi in hexane (1.35 M, 1.01 mL, 1.36 mmol) at −40 °C. After 30 min, paraformaldehyde (188 mg, 12.8 mmol) was added to the reaction mixture, which was stirred for an additional 3 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (3:1) to afford **15g** (38.5 mg, 7% for three steps) as pale yellow solid: IR 3367, 3022 cm^{-1}; ^1H NMR δ 7.22 (1H, t, J=7.9 Hz), 7.03 (1H, d, J=7.9 Hz), 6.85 (1H, d, J=7.9 Hz), 4.60 (2H, s), 4.54 (2H, s), 3.89 (3H, s), 2.37 (2H, br s); ^{13}C NMR δ 129.1, 123.4, 110.7, 96.1, 91.8, 56.0, 52.1, 51.8; MS *m/z* 216 (M^+, 100); HRMS calcd for $C_{13}H_{12}O_3$ 216.0787, found 216.0790.

4.6.5. 1-[1-(Diphenylphosphinyl)-1,2-propadienyl]-2-(3-hydroxy-1-propynyl)benzene (24). To a suspension of NaH (60% in oil, 44.0 mg, 1.1 mmol) in THF (5 mL) was added a solution of **4a** (186 mg, 1.00 mmol) in THF (5 mL) at 0 °C. After 20 min, TBSCl (166 mg, 1.10 mmol) was added to the mixture, which was stirred for an additional 1 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (5:1) to afford 1-[3-(*tert*-butyldimethylsiloxy)-1-propynyl]-2-(3-hydroxy-1-propynyl)benzene (**23**) (213 mg, 71%) as a pale yellow oil: IR 3607, 3421, 2233, 2189 cm^{-1}; ^1H NMR δ 7.43–7.41 (2H, m), 7.27–7.24 (2H, m), 4.59 (2H, s), 4.52 (2H, br s), 2.37 (1H, br s), 0.94 (9H, s), 0.18 (6H, s); ^{13}C NMR δ 131.8, 131.7, 128.0, 127.9, 125.4, 125.1, 91.7, 91.5, 84.2, 83.4, 52.4, 51.5, 25.8, 14.1, −5.1; MS *m/z* 243 ($M^+-{}^t$Bu, 99); HRMS calcd for $C_{14}H_{15}O_2Si$ 243.0841, found 243.0846.

To a solution of the above propargyl alcohol **23** (30.0 mg, 0.100 mmol) and Et_3N (0.05 mL, 0.4 mmol) in THF (1 mL) was added Ph_2PCl (0.05 mL, 0.3 mmol) at −78 °C. After 45 min, the reaction was quenched by addition of saturated aqueous $NaHCO_3$, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (1:1) to afford the crude phosphinylallene (41.3 mg) as a yellow oil. To a solution of the above crude phosphinylallene (21.6 mg) in THF (1 mL) was added 10% aqueous HCl (0.1 mL) at 0 °C. The reaction mixture was stirred for 2 h at that temperature and then diluted with water. The mixture was extracted with Et_2O, and the extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane–AcOEt (1:3) to afford **24** (14.9 mg, 76% for two steps) as a yellow oil: IR 3306, 1958, 1927, 1439, 1173 cm^{-1}; ^1H NMR δ 7.83–7.13 (14H, m), 4.88 (2H, d, J_{P-H}=10.6 Hz), 4.50 (2H, s), 1.26 (1H, s); characteristic data for ^{13}C NMR δ 213.9 (J_{C-P}=5.6 Hz), 99.4 (J_{C-P}=100.6 Hz), 93.1, 84.4, 78.0 (J_{C-P}=12.3 Hz), 51.3; MS *m/z* 370 (M^+, 82); HRMS calcd for $C_{24}H_{19}O_2P$ 370.1123, found 370.1129.

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