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Diels–Alder Reactions for the Construction of Cyclopropylarenes[‡]

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The straightforward synthesis of new bicyclopropyl-substituted alkynes and 1,3-dienes and their application in cobalt-catalyzed Diels–Alder reactions are described. The cycloaddition processes generated the desired bicyclopropyl-substituted arene derivatives in moderate to good yields, depending on the steric congestion of the reaction partners. The regioselectivity of the cycloaddition was controlled by the ligand coordinated to the cobalt center. The cyclopropyl moiety remained unchanged over the course of the Diels–Alder reaction, indicating that no radical type intermediates were formed. Only in a single case did the DDQ oxidation of the primarily formed dihydroaromatic product lead to ring opening of a cyclopropyl subunit. In all of the other cases, cyclopropyl-modified arenes with various functionalities were obtained.

Introduction

In their ongoing search for biologically active compounds, research laboratories in the pharmaceutical as well as the agrochemical industry always consider the cyclopropyl substituent which, because of its peculiar steric and electronic properties,[1] frequently enhances desired features.[2] In a considerable number of such compounds, the cyclopropyl group is attached to an arene moiety, and in recent years, even cyclopropyl-substituted cyclopropyl groups, that is, 1- and 2-substituted bicyclopropyl substituents attached to arenes, have come into the focus of the search for active compounds.[3] In view of the joint expertise of our two research groups in the areas of catalyzed Diels–Alder reactions[4] and the syntheses of simple cyclopropyl-group containing building blocks for organic synthesis,[5] we set out to test the possibilities of preparing cyclopropyl- and bicyclopropyl-substituted arenes by [4+2] cycloadditions of appropriately substituted alkynes and buta-1,3-dienes with subsequent dehydrogenation. In addition, the incorporation of cyclopropyl-substituted starting materials was conceived as a good test to exclude radical-type intermediates in the mechanism for the cobalt-catalyzed Diels–Alder reaction. Accordingly, we were highly interested to see if the cyclopropyl moiety would stay intact over the course of the cobalt-catalyzed cycloaddition and subsequent oxidation of the dihydroaromatic intermediates by DDQ (2,3-dichloro-5,6-dicyano-1,4-quinone). An electron transfer from the low-valent cobalt catalyst center to the starting materials coordinated to the cobalt could result in a radical opening the cyclopropyl group. Our first results along these lines are reported herein.

Results and Discussion

Synthesis of New Alkynes and Buta-1,3-dienes

In the construction of cyclohexa-1,4-dienes through a [4+2] cycloaddition, the desired cyclopropyl and bicyclopropyl substituents can be introduced with either the correspondingly substituted alkyne or substituted buta-1,3-diene. As both of these possibilities ought to be tested, all of the correspondingly substituted building blocks **1**–**9** were initially considered (Figure 1).

Cyclopropylacetylene (**1**)[6] is now commercially available in bulk quantities,[7] and (1-cyclopropylcyclopropyl)acetylene (**2**) as well as (2-cyclopropylcyclopropyl)acetylene (**3**) were easily prepared from the corresponding aldehydes **11**[8] and **14**, respectively. Aldehydes **11** and **14** were obtained from bromides **10**[8] and **13**,[9] respectively, by using a bromine–lithium exchange with *tert*-butyllithium and then trapping the corresponding cyclopropyllithium species with dimethylformamide (Scheme 1). The treatment of aldehydes

[‡] For one of us (A. de M.), this is considered to be Cyclopropyl Building Blocks for Organic Synthesis, 162. Part 161: A. F. Khlebnikov, S. I. Kozhushkov, D. S. Yufit, H. Schill, M. Reggelin, V. Spohr, A. de Meijere, *Eur. J. Org. Chem.* **2012**, 1530–1545. Part 160: V. A. Rassadin, V. V. Sokolov, A. F. Khlebnikov, N. V. Ulin, S. I. Kozhushkov, A. de Meijere, *Synthesis* **2012**, 372–376.

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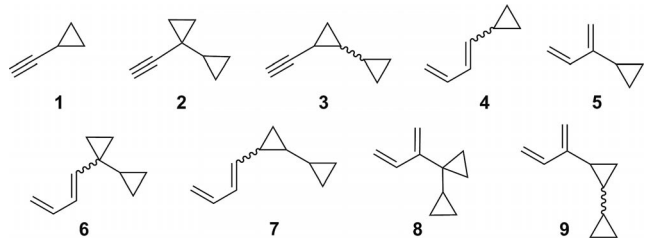
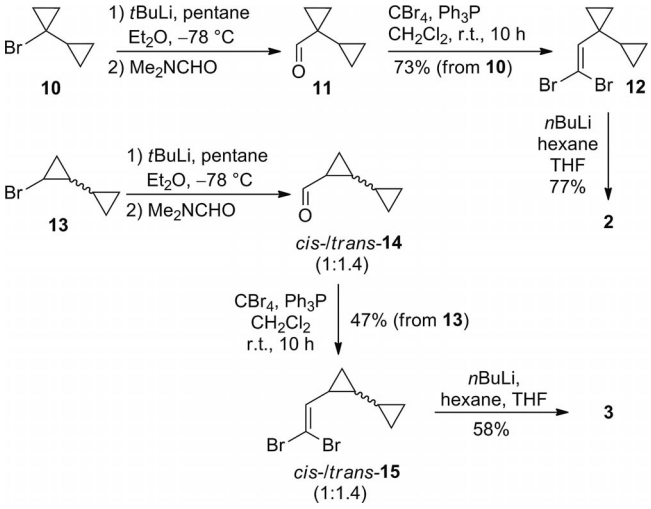


Figure 1. Cyclopropyl-substituted building blocks **1**–**9**.

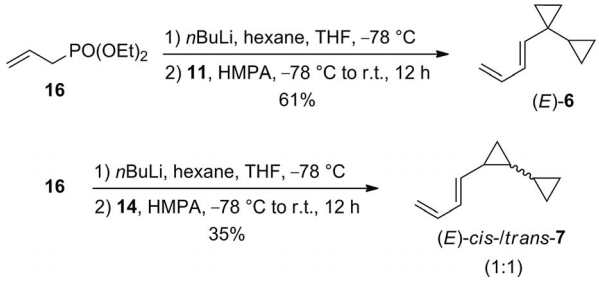
11 and **14** with carbon tetrabromide and triphenylphosphane (Ramirez–Corey–Fuchs alkenation[10]) gave the dibromovinyl derivatives **12** and **15**, respectively.



Scheme 1. Synthesis of (1-cyclopropylcyclopropyl)acetylene (**2**) and (2-cyclopropylcyclopropyl)acetylene (**3**).

The overall yields in the first two steps of these sequences were 73 and 47%, respectively. The conversion of dibromovinyl derivative **12** to alkyne **2** employing the Fritsch–Buttenberg–Wiechell rearrangement[11] was accomplished with a satisfactory yield of 77%.[10b,12]

Although 1-cyclopropylbuta-1,3-diene (**4**)[13] and 2-cyclopropylbuta-1,3-diene (**5**)[14] are known compounds, yet inconveniently prepared, we concentrated on the previously unknown compounds 1-(1′-cyclopropylcyclopropyl)buta-1,3-diene (**6**) and 1-(2′-cyclopropylcyclopropyl)buta-1,3-diene (**7**), as they should be easily accessible from aldehydes

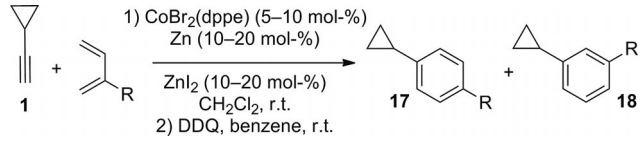


Scheme 2. Preparation of (*E*)-1-(1′-cyclopropylcyclopropyl)buta-1,3-diene (**6**) and (*E*)-1-(2′-cyclopropylcyclopropyl)buta-1,3-diene (**7**).

11 and **14**, which had already been used as precursors to acetylenes **2** and **3**. Indeed, adopting a known procedure for the Horner–Wadsworth–Emmons olefination of aldehydes with diethyl allylphosphonate,[15] we subjected **11** and **14** to the established reaction conditions to give 1,3-butadienes **6** and **7** in 61 and 35% yield, respectively, the latter as a 1:1 mixture of *cis* and *trans* diastereomers (Scheme 2).

Cobalt-Catalyzed Diels–Alder Reactions of Cyclopropyl-Substituted Alkynes

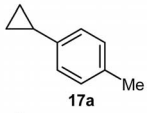
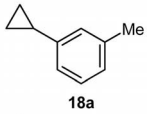
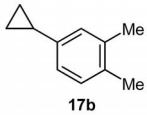
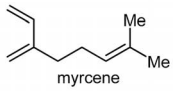
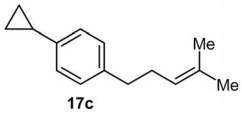
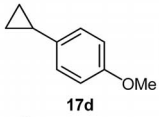
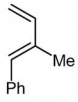
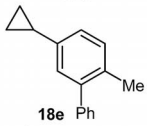
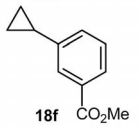
The cobalt-catalyzed Diels–Alder reaction was envisaged to convert the cyclopropyl-substituted 1,3-dienes and acetylenes with nonactivated starting materials under mild conditions.[4] For this purpose, alkyne **1** was treated with different 1,3-dienes in dichloromethane at room temperature utilizing a cobalt catalyst consisting of [1,2-bis(diphenylphosphanyl)ethane]cobalt dibromide [$CoBr_2$(dppe)], zinc powder, and zinc iodide. The cycloaddition process could lead to the two regioisomers **17** and **18**, but by utilizing the cobalt(dppe) dibromide catalyst precursor, regioisomer **17** was formed predominantly (Scheme 3). On the other hand, using catalyst precursor cobalt[2,4,6-trimethylphenyl-*N*-(pyridin-2-ylmethylene)amine] dibromide led to the formation of **18** as the major regioisomer.[4] Thereby, both regioisomers can be obtained from the same starting materials. The results of the reaction of **1** with different 1,3-dienes are summarized in Table 1.



Scheme 3. Cobalt-catalyzed Diels–Alder reaction of **1** (for details see Table 1).

One of the most important observations in terms of the mechanistic interpretation of the cobalt-catalyzed Diels–Alder reaction is that neither the transition-metal-catalyzed cycloaddition process nor the DDQ oxidation led to any significant amount of ring-opened products (<1%), and in all cases, the cyclopropyl subunit remained intact. Accordingly, the low-valent cobalt catalyst did not undergo an electron transfer from the metal to the ligand/substrate, otherwise a radical-type ring opening would have been observed. Also, all types of the 1,3-dienes appeared to be compatible with the catalyst system. Electron-rich 1,3-butadienes such as the 2-methoxy-1,3-butadiene (Table 1, Entry 5) and more electron-neutral 1,3-dienes such as isoprene, 2,3-dimethyl-1,3-butadiene (DMB), and myrcene were applied (Table 1, Entries 1–4). Also, the electron-deficient 1,3-butadiene with a methyl carboxylate group (Table 1, Entry 7) was converted into the desired product **18f** in good yield. In addition, the application of the pyridine-imine-type-derived catalyst system generated *meta*-substituted product **18a** in an excellent yield. However, as it was previously found that the steric bulk of the substituents was very important for

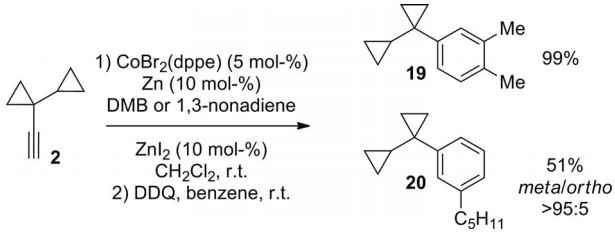
Table 1. Reaction of cyclopropylacetylene (**1**) with substituted 1,3-butadienes (see Scheme 3).

Entry	Diene	Product **17** or **18**	Yield [%] (*para*/*meta*)
1		 **17a**	84 (87:13)
2		 **18a**	97 (24:76)[a]
3		 **17b**	99
4	 myrcene	 **17c**	62 (86:14)
5		 **17d**	83 (>95:5)
6		 **18e**	88 (>95:5)[b]
7		 **18f**	63 (63:37)[b]

[a] The catalyst system cobalt[2,4,6-trimethylphenyl-*N*-(pyridin-2-ylmethylene)amine] dibromide, Zn, ZnI_2, Fe was used. [b] In these cases, the isomeric ratio *meta*/*ortho* is reported.

the regioselectivity,[16] the cyclopropyl substituent, apparently, is only a moderately directing group in this respect.[17] Only for the methoxy-substituted butadiene and the higher substituted butadiene derivative (2-methylbuta-1,3-dienyl)-benzene (Table 1, Entries 5 and 6), excellent levels of regioselectivity were observed.

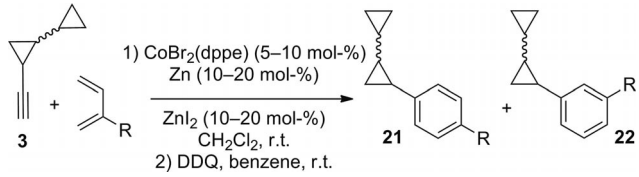
These results encouraged us to investigate the application of more complex cyclopropyl-substituted alkynes such as **2** with a selected number of 1,3-dienes. The reactions with myrcene and (2-methylbuta-1,3-dienyl)benzene gave the [4+2] cycloadducts, but in rather disappointing yields of 14 and 17%, respectively, however, the reactions with DMB and 1,3-nonadiene led to the desired products **19** and **20** in good to excellent yields (Scheme 4).



Scheme 4. Application of **2** in cobalt-catalyzed Diels–Alder reactions.

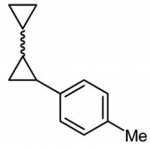
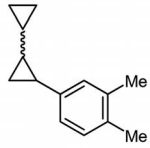
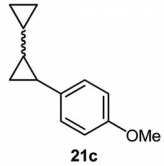
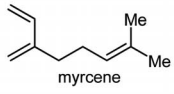
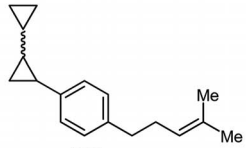
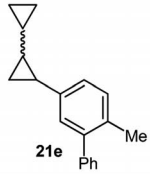
The higher steric encumbrance of **2** apparently reduces its reactivity in the cobalt-catalyzed cycloaddition, so that only a limited number of dienes gave acceptable results. Nevertheless, the cyclopropyl subunits remained intact and no ring-opened side products were observed.

The sterically less encumbered cyclopropyl-substituted alkyne **3** was also applied in the cobalt-catalyzed Diels–Alder reactions with 1,3-dienes (Scheme 5 and Table 2).



Scheme 5. Cobalt-catalyzed Diels–Alder reactions of **3** with 1,3-butadienes (for details see Table 2).

Table 2. Reaction of (2-cyclopropylcyclopropyl)acetylene (**3**) with 1,3-butadienes (see Scheme 5).

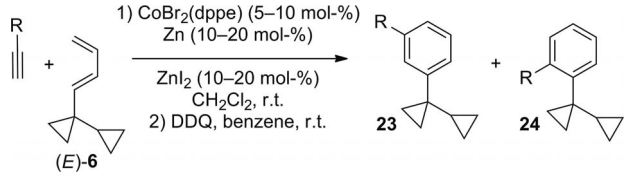
Entry	Diene	Product **21**	Yield [%] (*para*/*meta*) (*cis*/*trans*)
1		 **21a**	53 (92:8) (41:59)
2		 **21b**	75 – (47:53)
3		 **21c**	60 (>95:5) (37:63)
4	 myrcene	 **21d**	44 (92:8) (40:60)
5		 **21e**	32 (>95:5) (40:60)

As described above, alkyne **3** was synthesized as nearly a 1:1 mixture of *cis* and *trans* isomers. Accordingly, the assignments of the NMR signals were less obvious, and in some cases specific assignments were only tentative, as the separation of the four possible regioisomers and diastereomers could not be accomplished by column chromatography on silica gel.

The application of alkyne **3** in the cobalt-catalyzed Diels–Alder reaction gave the desired products mostly in good yields, and generally, the *para*-substituted products **21** (Table 2, Entries 1, 3, and 4) were formed as the main regioisomers. Also, it is noteworthy that in all cases the bicyclopropyl groups stayed intact. These encouraging results showed that alkynes **1** and **3** are well accepted in the cobalt-catalyzed cycloaddition process, whereas the sterically more bulky alkyne **2** led to good results with only a small number of 1,3-dienes.

Cobalt-Catalyzed Diels–Alder Reactions of Cyclopropyl-Substituted 1,3-Dienes

The second phase of our investigation of the cobalt-catalyzed Diels–Alder reactions was performed with bicyclopropyl-modified butadiene derivatives **6** and **7**. For these transformations, one would expect that the conversions with the sterically more congested diene (*E*)-**6** would be as difficult as with alkyne **2**. The reactions of (*E*)-**6** with different alkynes utilizing the $CoBr_2$(dppe) catalyst precursor gave mainly the desired *meta*-substituted products **23**, whereas the more congested *ortho*-substituted regioisomer **24** was formed in only minor amounts (Scheme 6 and Table 3).



Scheme 6. Cobalt-catalyzed Diels–Alder reactions of (*E*)-**6** with alkynes (for details see Table 3).

As expected, the reactions with terminal alkynes gave the desired products **23** in moderate to good yields. However, the incorporation of the internal alkyne unit as in 1,4-dimethoxy-but-2-yne (Table 3, Entry 4) gave the desired product **23c** in only 19% yield, which indicates that the steric bulk of the alkyne should be minimized to obtain good results.

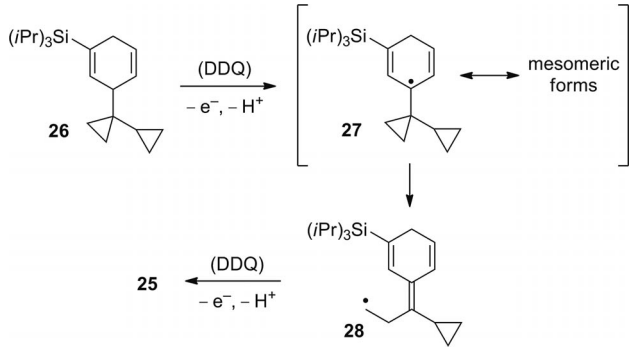
In this investigation, the reaction of (triisopropylsilyl)ethyne with (*E*)-**6** is the only case in which a ring-opened product, such as **25** (Table 3, Entry 3), was obtained, and it is derived most likely from radical-type intermediates. The ring opening of the cyclopropyl substituent, next to the arene moiety, did not take place over the course of the cobalt-catalyzed cycloaddition, as proven by NMR analysis of the crude reaction mixture. Instead, the DDQ oxidation caused the cyclopropyl substituent to open (Scheme 7). This can

Table 3. Reaction of (*E*)-1-(1′-cyclopropylcyclopropyl)buta-1,3-diene [(*E*)-**6**] with alkynes (see Scheme 6).

Entry	Alkyne	Product **23**	Yield [%] (*meta*/*ortho*)
1	Ph—	Ph, **23a**	61[a] (~87:13)
2	Me_3Si—	Me_3Si, **23b**	44 (>95:5)
3	$(iPr)_3Si$—	$(iPr)_3Si$, Me, **25**	53[b] (>99:1) (*Z* only)
4	MeO, MeO	MeO, MeO, **23c**	19[b] (–)

[a] The regioselectivity was estimated by integration of the peaks in the GC–MS recording. The product also contains a small amount (≈10%) of an unidentified side product, exhibiting olefinic signals in the ^{1}H NMR spectrum. [b] $CoBr_2$(dppe) (20 mol-%), Zn (40 mol-%), and ZnI_2 (40 mol-%) were used. The reaction temperature was 40 °C.

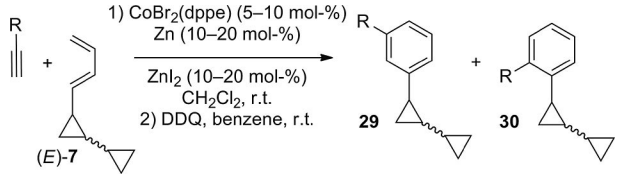
be rationalized in terms of the steric bulk of the TIPS (triisopropylsilyl) group which prohibits the DDQ from coming into close contact with the dihydroaromatic intermediate and thus would be responsible for the reduced rate of the electron-transfer reaction. In particular, the rate of the second electron transfer from radical intermediate **27** to DDQ (or its radical anion) appears to be reduced. Thereby, the lifetime of radical intermediate **27** is increased so that the ring opening to the proposed intermediate **28** can occur. The second oxidation and a proton shift then led to **25**, as the only isolated product, in 53% yield.



Scheme 7. Ring opening of triisopropylsilyl-substituted intermediate **26**.

In the case of phenyl-substituted derivative **23a**, the GC–MS analysis showed the presence of a small amount of another product. The ^{1}H NMR spectrum showed signals of olefinic protons which in this case suggest that a small fraction of the dihydroaromatic intermediate also underwent a ring-opening reaction upon DDQ oxidation. Unfortunately, this side product could not be separated from the main product **23a** by column chromatography.

The application of diene (*E*)-**7** in the cobalt-catalyzed Diels–Alder reactions gave the regioisomers **29** as the main products (Scheme 8 and Table 4).



Scheme 8. Cobalt-catalyzed Diels–Alder reactions of (*E*)-**7** with alkynes (for details see Table 4).

Table 4. Reaction of (*E*)-1-(2′-cyclopropylcyclopropyl)buta-1,3-diene [(*E*)-**7**] with alkynes (see Scheme 8).

Entry	Alkyne	Product **29**	Yield [%] (*meta*/*ortho*) (*cis*/*trans*)
1	Ph—	**29a**	76 (>99:1) (50:50)
2		**29b**	71 (>95:5) (50:50)
3	B(Pin)	**29c**	70 (>99:1) (50:50)

[a] B(Pin) = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

This less sterically encumbered diene (*E*)-**7**, compared to (*E*)-**6**, led to the formation of the desired products in considerably higher yields, even when an internal alkyne was applied (Table 4, Entry 3).

Diene (*E*)-**7** reacted well in the cobalt-catalyzed Diels–Alder reaction with phenylacetylene (Table 4, Entry 1) as well as with the terminal enyne (Table 4, Entry 2), and the desired *meta*-substituted products **29a** and **29b** were formed with excellent regioselectivities. Additionally, the pinacolborane derivative (Table 4, Entry 3) was applied, and **29c** was isolated as a single regioisomer. In all of the cases investigated, both diastereomers were converted into the desired products, meaning that the cobalt catalyst did not differentiate between the two diastereomeric starting materials of (*E*)-**7**.

Conclusions

In conclusion, the straightforward syntheses of alkynes **2** and **3** and butadiene derivatives **6** and **7** and their first applications in cobalt-catalyzed Diels–Alder reactions have been achieved. The use of these cyclopropyl-substituted alkynes and 1,3-dienes reveals they are an appropriate tool for the syntheses of bicyclopropyl-substituted arenes. The mild reaction conditions allowed the generation of various functionalized dihydroaromatic intermediates without the ring opening of the cyclopropyl moieties. In only one case, the cyclopropyl ring opening was observed, when DDQ was used for the oxidation step to generate arene derivative **25**. Accordingly, long-lived radical-type intermediates can be excluded as participants in cobalt catalysis.

Experimental Section

General Remarks: All reagents were used as purchased from commercial suppliers without further purification. All reactions in non-aqueous solvents were carried out using standard Schlenk techniques under dry nitrogen or argon. The solvents were purified and dried according to conventional methods prior to use. ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Varian Unity-300 (300 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR), an Avance 300 (300 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR), a DRX 400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), an Avance 500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR), or an Inova-500 (125.7 MHz for ^{13}C NMR) instrument. Chemical shifts (δ) are given in ppm relative to the residual resonances of the solvents (^{1}H NMR, δ = 7.26 ppm for $CHCl_3$; ^{13}C NMR, δ = 77.0 ppm for $CDCl_3$) or tetramethylsilane (^{1}H NMR, δ = 0.00 ppm; ^{13}C NMR, δ = 0.0 ppm), and coupling constants (J) are presented as absolute values in Hz. The multiplicities of ^{13}C NMR signals were determined by using DEPT techniques. IR spectroscopy was performed with a Bruker IFS 66 (FTIR) spectrometer, a Bruker IFS 200 (FTIR), or a Nicolet Magna IR 750, and the samples were prepared as KBr pellets or oils between KBr plates. EI-MS was performed with a Finnigan MAT 95S (70 eV). High-resolution mass spectrometry (HRMS) was performed with a Finnigan MAT 95S instrument. GC analysis was recorded with a GC-2010 Plus Gas Chromatograph, Shimadzu. GC–MS was accomplished with an Agilent 6890 gas chromatograph with a Hewlett Packard 5973 mass detector. For chromatography, the separations were carried out on Merck Silica 60 (0.063–0.200 mm, 70–230 mesh ASTM) or on Macherey–Nagel Silica 60 (0.040–0.063 mm, 230–400 mesh ASTM). For TLC, Macherey–Nagel TLC plates Alugram® Sil G/UV 254 or Merck TLC plates (Silica 60, F254) were used. Detection of the compounds under UV light was achieved at 254 nm, and the plates were developed with MOPS reagent (10% molybdophosphoric acid, solution in ethanol). The melting points were measured with a Büchi 540 capillary melting point apparatus, and

the elemental analyses were performed with an HP185B CHN analyzer.

1,1-Dibromo-2-(1-cyclopropylcyclopropyl)ethene (12): A three-necked flask, equipped with a magnetic stir bar, a rubber septum, and a nitrogen inlet, was charged with zinc (9.46 g, 144.6 mmol), triphenylphosphane (39.4 g, 150.2 mmol), carbon tetrabromide (49.8 g, 150.2 mmol), and anhydrous CH_2Cl_2 (300 mL) at 0 °C. The mixture was then stirred for 30 h at room temperature. 1-Cyclopropylcyclopropanecarbaldehyde[8] (8.07 g, 73 mmol) was added, and the reaction mixture was stirred for an additional 72 h. The reaction mixture was then poured into pentane (400 mL), and the insoluble materials were removed by filtration. The insoluble fraction was taken through two additional cycles of dichloromethane extraction and pentane precipitation to remove all of the olefinic product. Evaporation of the solvent under reduced pressure and distillation (54–56 °C, 0.01 Torr) gave pure 1,1-dibromo-2-(1-cyclopropylcyclopropyl)ethene (15.3 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.63 (s, 1 H), 1.20–1.11 (m, 1 H), 0.66–0.62 (m, 2 H), 0.52–0.48 (m, 2 H), 0.39–0.32 (m, 2 H), 0.12–0.07 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 141.2, 137.4, 91.7, 24.0, 14.6, 11.2, 2.3 ppm.

(1-Cyclopropylcyclopropyl)ethyne (2): Under nitrogen, a solution of 1,1-dibromo-2-(1-cyclopropylcyclopropyl)ethene (15.0 g, 56.4 mmol) in tetrahydrofuran (200 mL) at –78 °C was treated with *n*BuLi (2.5 M in hexane, 48.2 mL, 120.5 mmol). After stirring at –78 °C for 1 h, the reaction mixture was warmed to 25 °C and maintained at this temperature for 1 h. Water was added, and the resulting mixture was extracted with pentane. Fractional distillation (113–114 °C, 760 Torr) afforded **2** (3.00 g, 50%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 1 H), 0.93–0.89 (m, 1 H), 0.87–0.84 (m, 2 H), 0.62–0.58 (m, 2 H), 0.45–0.39 (m, 2 H), 0.30–0.25 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 88.8, 64.1, 15.6, 14.0, 12.6, 2.7 ppm. $C_8H_{10}O$ (122.17): calcd. C 90.5, H 9.5; found C 90.6, H 9.3. The fraction with b.p. 105–112 °C (3.89 g) contained two compounds that according to ^{1}H NMR spectroscopic data were 1-chlorobutane (2.28 g) and (1-cyclopropylcyclopropyl)ethyne (1.61 g), that is, the total yield of **2** was 77%.

2-Cyclopropylcyclopropanecarbaldehyde (14): *tert*-Butyllithium (1.5 M in pentane, 42 mL, 63.1 mmol) was added dropwise (60 min) to a solution of 1-cyclopropylcyclopropyl bromide (9.96 g, 60 mmol) in diethyl ether (140 mL) at –78 °C. After 50 min at –78 °C, dimethylformamide (4.82 g, 5.11 mL, 66 mmol) was added with a syringe (10 min), and the mixture was allowed to slowly warm to room temperature over 1.3 h. The reaction was quenched with diluted HCl [H_2O (250 mL) + conc. HCl (12 mL)], the water layer was separated and extracted with diethyl ether (3 × 100 mL) and pentane (2 × 50 mL). The combined organic phases were washed with aqueous Na_2HCO_3 and brine and then dried with Na_2SO_4. The solution was concentrated on a rotary evaporator at 0 °C (52 mbar) to give **14** (6.59 g, 100%) which was contaminated with some impurities originating from the starting bromide. The purification of the crude product by flash chromatography (silica gel, pentane/diethyl ether, 1:2) was accompanied by partial decomposition to give **14** (4.23 g, 64%) as an approximate 1:1 mixture of *cis* and *trans* isomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.31 (d, J = 5.6 Hz, 0.5 H), 9.02 (d, J = 5.6 Hz, 0.5 H), 1.85–1.42 (m, 1 H), 1.15–1.05 (m, 2 H), 0.95–0.80 (m, 2 H), 0.60–0.05 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.9, 200.9, 29.4, 29.2, 26.7, 25.0, 13.3, 13.0, 11.3, 9.1, 5.5, 5.2, 3.8, 2.7 ppm. MS (EI): m/z = 110 $[M]^+$, 109, 95, 81, 79, 77, 69, 68, 67, 54, 53. A different preparation for aldehyde **14** has been published in patents, yet without spectroscopic characterization.[3e,3f]

***cis/trans*-1,1-Dibromo-2-(2′-cyclopropylcyclopropyl)ethane (15):** A three-necked flask, equipped with a magnetic stir bar, a rubber septum, an addition funnel fitted with a rubber septum, and a nitrogen inlet, was charged with carbon tetrabromide (49.8 g, 150 mmol), and anhydrous dichloromethane (250 mL) was added with a syringe. The solution was cooled in an ice-water bath, and a solution of triphenylphosphane (78.7 g, 300 mmol) in anhydrous dichloromethane (250 mL) was then added dropwise from the addition funnel over 30 min. The reaction mixture was stirred at 0 °C for 10 min, and then a solution of 2-cyclopropylcyclopropanecarbaldehyde (8.26 g, 75.0 mmol, *cis/trans*, approximately 1:1.4) in anhydrous dichloromethane (20 mL) was added over 10 min with a syringe. The solution was stirred at 0 °C for 5 h and at room temperature for 10 h, and then water (500 mL) was added. The resulting mixture was transferred to a separatory funnel, and the aqueous layer was separated and then extracted with dichloromethane (3 × 200 mL). The combined organic layers were washed with brine (200 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure using a rotary evaporator. To the residue was added diethyl ether (200 mL), and the resulting suspension was filtered to remove triphenylphosphane oxide. The collected solid was washed with diethyl ether (3 × 100 mL), and the combined ethereal extracts were concentrated under reduced pressure using a rotary evaporator. The residue (oil, 11.56 g) was purified by column chromatography (250 mL of silica gel, pentane) to give **15** (9.38 g, 47%, *cis/trans*, approximately 1:1.4) as a yellowish oil which was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (d, J = 9.2 Hz, 0.4 H), 5.78 (d, J = 9.2 Hz, 0.6 H), 1.73–1.62 (m, 0.4 H), 1.43–1.34 (m, 0.6 H), 1.18–0.99 (m, 1.0 H), 0.96–0.81 (m, 1.2 H), 0.73–0.51 (m, 2.4 H), 0.49–0.33 (m, 1.6 H), 0.29–0.04 (m, 1.8 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 139.1, 86.0, 84.9, 22.7, 21.8, 21.3, 21.1, 11.9, 11.4, 9.6, 4.5, 4.2, 3.4, 2.7 ppm. MS (EI): m/z = 264 $[M]^+$, 224, 212, 146, 133, 121, 105, 93, 77, 67, 51.

***cis/trans*-(2-Cyclopropylcyclopropyl)ethyne (3):** A solution of 1,1-dibromo-2-(2-cyclopropylcyclopropyl)ethene (9.34 g, 35.3 mmol, *cis/trans*, approximately 1:1.4) in tetrahydrofuran (250 mL) at –78 °C under nitrogen was treated with *n*BuLi (2.5 M in hexane, 41 mL, 102.8 mmol) for 50 min. After stirring at –78 °C for 1 h, the reaction mixture was warmed to 25 °C and maintained at this temperature for 1 h. Water (250 mL) was added, and the resulting mixture was extracted with pentane (4 × 50 mL). Column chromatography (100 mL of silica gel, pentane), and distillation (118–120 °C, 760 mm) afforded of **3** (2.18 g, 58%, *cis/trans*, approximately 1:1.4) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.81 (d, J = 2.2 Hz, 0.4 H), 1.73 (d, J = 2.2 Hz, 0.6 H), 1.38–1.34 (m, 0.4 H), 1.24–1.20 (m, 0.6 H), 1.19–1.15 (m, 0.6 H), 0.99–0.95 (m, 0.4 H), 0.82–0.70 (m, 2.2 H), 0.58–0.42 (m, 1.4 H), 0.40–0.36 (m, 0.6 H), 0.34–0.29 (m, 0.6 H), 0.26–0.19 (m, 1 H), 0.11–0.07 (m, 0.6 H), 0.04–0.00 (m, 0.6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.3, 85.3, 65.7, 63.5, 24.1, 21.8, 13.0, 12.9, 11.6, 10.0, 5.5, 5.1, 4.2, 3.6, 3.3, 2.3 ppm. MS (EI): m/z = 106 $[M]^+$, 105, 91, 78, 65, 54. $C_8H_{10}O$ (122.17): calcd. C 90.5, H 9.5; found C 90.2, H 9.8. IR (film): $\tilde{\nu}$ = 3310, 3081, 2117 cm^{-1}.

(*E*)-1-(1′-Cyclopropylcyclopropyl)buta-1,3-diene (6): *n*-Butyllithium (2.5 M in hexane, 23.7 mL, 59.2 mmol) was added dropwise at –78 °C to a solution of diethyl allylphosphonate (10.6 g, 10.3 mL, 59.2 mmol) in anhydrous tetrahydrofuran (120 mL). After stirring for 15 min, a solution of 1-cyclopropylcyclopropanecarbaldehyde (5.43 g, 49.3 mmol) in hexamethylphosphoric triamide (HMPA, 20.1 g, 20.7 mL, 118 mmol) was added dropwise with a syringe. The resulting solution was stirred at –78 °C for 2 h and then warmed to room temperature. The stirring was continued for an

additional 12 h, and then the reaction was quenched with a saturated aqueous NH_4Cl solution. The mixture was extracted with diethyl ether (3 × 100 mL). The combined organic phases were washed with brine (100 mL), dried with $NaSO_4$, and concentrated to afford the crude product. Purification by flash chromatography (silica gel, pentane) gave the desired diene **6** (4.03 g, 61%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.40–6.26 (m, 2 H), 5.48–5.39 (m, 1 H), 5.18–5.07 (m, 1 H), 4.95–4.90 (m, 1 H), 1.24–1.14 (m, 1 H), 0.53–0.50 (m, 2 H), 0.48–0.45 (m, 2 H), 0.45–0.42 (m, 2 H), 0.04–0.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 137.4, 127.2, 113.9, 22.7, 13.3, 12.0, 2.2 ppm. MS (EI): *m*/*z* = 134 $[M]^+$, 133, 119, 105, 103, 93, 91, 79, 77, 67. $C_{10}H_{14}O$ (150.22): calcd. C 89.5, H 10.5; found C 89.7, H 10.2.

(*E*)-1-(*cis*/*trans*-2′-Cyclopropylcyclopropyl)buta-1,3-diene (7): *n*-Butyllithium (2.5 M in hexane, 15.8 mL, 39.9 mmol) was added dropwise at –78 °C to a solution of diethyl allylphosphonate (8.11 g, 7.88 mL, 45.2 mmol) in anhydrous tetrahydrofuran (95 mL). After stirring for 15 min, a solution of 2-cyclopropylcyclopropanecarbaldehyde (4.15 g, 37.7 mmol, *cis*/*trans*, ≈1:1) in hexamethylphosphoric triamide (15.3 g, 15.8 mL, 90.5 mmol) was added dropwise with a syringe. The resulting solution was stirred at –78 °C for 2 h and then warmed to room temperature. The stirring was continued for an additional 12 h, and then the reaction was quenched with a saturated aqueous NH_4Cl solution. The mixture was extracted with diethyl ether (3 × 100 mL). The combined organic phases were washed with brine (100 mL), dried with Na_2SO_4, and concentrated to afford the crude product. Purification by flash chromatography (silica gel, pentane) gave the desired diene **7** (1.77 g, 35%, *cis*/*trans*, ≈1:1) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.40–6.05 (m, 2 H), 5.60–5.52 (m, 0.5 H), 5.30–5.22 (m, 0.5 H), 5.10–5.08 (m, 0.5 H), 5.04–5.02 (m, 0.5 H), 4.92–4.90 (m, 0.5 H), 4.89–4.87 (m, 0.5 H), 1.58–1.47 (m, 0.5 H), 1.26–1.15 (m, 0.5 H), 1.01–0.76 (m, 2 H), 0.72–0.63 (m, 0.5 H), 0.58–0.28 (m, 3.5 H), 0.20–0.15 (m, 1 H), 0.12–0.01 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 137.2, 137.0, 136.0, 130.3, 128.2, 113.7, 113.5, 23.4, 22.3, 20.3, 20.2, 12.3, 12.1, 11.0, 9.4, 4.6, 4.4, 3.3, 2.4 ppm. MS (EI): *m*/*z* = 134 $[M]^+$, 119, 105, 93, 91, 79, 77, 67, 65. $C_{10}H_{14}O$ (150.22): calcd. C 89.5, H 10.5; found C 89.8, H 10.4.

General Procedure for the Cobalt-Catalyzed Diels–Alder Reaction: Anhydrous zinc iodide (10–20 mol-%), zinc powder (10–20 mol-%), and [1,2-bis(diphenylphosphanyl)ethane]cobalt dibromide (5–10 mol-%) were suspended in dichloromethane (1.0 mL) under an argon atmosphere. Then, the 1,3-butadiene (0.5–0.6 mmol) and the alkyne (0.5 mmol) were added, and the mixture was stirred at room temperature or at 40 °C until the complete conversion of the starting materials was observed as monitored by GC–MS (14–30 h). The mixture was filtered through a small pad of silica gel (diethyl ether), and the solvent was removed under reduced pressure. The residual dihydroaromatic intermediate was oxidized with DDQ (1.1 equiv.) in benzene (5 mL). After 1 h at room temperature, the mixture was filtered through a short pad of deactivated silica gel (diethyl ether), and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel. The ratios of regioisomers were determined by integration of the GC and ^{1}H NMR signals.

1-Cyclopropyl-4-methylbenzene (17a): After purification by column chromatography (pentane), the product (**17a**/**18a**, 87:13, 111 mg, 84%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, **17a**): δ = 7.11–7.04 (m, 2 H), 7.02–6.94 (m, 2 H), 2.31 (s, 3 H), 1.87 (tt, *J* = 8.5, 5.1 Hz, 1 H), 0.98–0.85 (m, 2 H), 0.72–0.61 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, **17a**): δ = 140.8, 134.8, 128.9, 125.6, 20.9, 15.0, 8.8 ppm. Only the resolved signals of **18a** are listed. ^{1}H NMR (300 MHz, $CDCl_3$, **18a**): δ = 7.15 (t, *J* = 7.6 Hz, 1 H), 6.92–6.85 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, **18a**): δ = 126.1 ppm. MS (EI): *m*/*z* = 132 $[M]^+$, 129, 117, 115, 105, 91, 77, 65. The analytical data are consistent with those in the literature.[18]

1-Cyclopropyl-3-methylbenzene (18a): For the *meta*-selective Diels–Alder reaction, the catalyst precursor cobalt[2,4,6-trimethylphenyl-*N*-(pyridin-2-ylmethylene)amine] dibromide was used, and iron powder (10 mol-%) was added to the catalyst system. After purification by column chromatography (pentane), the product (**18a**/**17a**, 76:24, 129 mg, 97%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, **18a**): δ = 7.19 (t, *J* = 7.5 Hz, 1 H), 7.04–6.97 (m, 1 H), 6.96–6.88 (m, 2 H), 2.36 (s, 3 H), 1.90 (tt, *J* = 8.4, 5.1 Hz, 1 H), 1.02–0.89 (m, 2 H), 0.77–0.66 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, **18a**): δ = 143.9, 137.8, 128.2, 126.5, 126.1, 122.6, 21.4, 15.3, 9.0 ppm. Only the resolved signals of **17a** are listed. ^{1}H NMR (300 MHz, $CDCl_3$, **17a**): δ = 7.11 (d, *J* = 8.0 Hz, 2 H), 7.04–6.98 (m, 2 H), 2.35 (s, 3 H), 1.95–1.84 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, **17a**): δ = 140.8, 134.8, 128.9, 125.6, 20.9, 15.0, 8.8 ppm. MS (EI): *m*/*z* = 132 $[M]^+$, 129, 117, 115, 105, 91, 77, 65. The analytical data are consistent with those in the literature.[18a]

4-Cyclopropyl-1,2-dimethylbenzene (17b): After purification by column chromatography (pentane), the product (73 mg, 99%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (d, *J* = 7.7 Hz, 1 H), 6.88 (s, 1 H), 6.83 (d, *J* = 7.7 Hz, 1 H), 2.24 (s, 3 H), 2.23 (s, 3 H), 1.85 (ddd, *J* = 13.4, 8.6, 5.1 Hz, 1 H), 0.97–0.86 (m, 2 H), 0.70–0.61 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3, 136.3, 133.5, 129.5, 127.2, 123.0, 19.7, 19.2, 14.9, 8.8 ppm. MS (EI): *m*/*z* = 146 $[M]^+$, 131, 127, 119, 115, 105, 91, 77, 65. HRMS (EI): calcd. for $C_{11}H_{14}$ 146.1096; found 146.1098. IR (film): $\tilde{\nu}$ = 3081, 3007, 2967, 2921, 1615, 1507, 1462, 1045, 1018, 995, 813 cm^{-1}.

1-Cyclopropyl-4-(4-methylpent-3-enyl)benzene (17c): After purification by column chromatography (pentane), the product (**17c**/**18c**, 86:14, 63 mg, 62%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12–7.04 (m, 2 H), 7.03–6.94 (m, 2 H), 5.22–5.13 (m, 1 H), 2.64–2.53 (m, 2 H), 2.27 (dt, *J* = 7.9, 7.4 Hz, 2 H), 1.87 (tt, *J* = 8.4, 5.0 Hz, 1 H), 1.69 (s, 3 H), 1.58 (s, 3 H), 0.97–0.86 (m, 2 H), 0.72–0.60 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.2, 139.5, 132.0, 128.3, 125.6, 123.9, 35.7, 30.1, 25.7, 17.7, 15.0, 8.9 ppm. MS (EI): *m*/*z* = 200 $[M]^+$, 165, 141, 131, 115, 91, 77. HRMS (EI): calcd. for $C_{15}H_{20}$ 200.1565; found 200.1570. IR (film): $\tilde{\nu}$ = 3081, 3008, 2968, 2922, 2856, 1516, 1452, 1378, 1019, 816 cm^{-1}.

1-Cyclopropyl-4-methoxybenzene (17d): After purification by column chromatography (pentane/methyl *tert*-butyl ether, 50:1), the product (**17d**/**18d**, >95:5, 62 mg, 83%) was obtained as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06–6.99 (m, 2 H), 6.85–6.79 (m, 2 H), 3.79 (s, 3 H), 1.86 (tt, *J* = 8.4, 5.1 Hz, 1 H), 0.91 (ddd, *J* = 8.4, 6.3, 4.4 Hz, 2 H), 0.66–0.59 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 135.8, 126.8, 113.8, 55.3, 14.6, 8.4 ppm. The analytical data are consistent with those in the literature.[19]

5-Cyclopropyl-2-methylbiphenyl (18e): After purification by column chromatography (pentane → pentane/diethyl ether, 50:1), the product (**18e**/**17e**, >95:5, 92 mg, 88%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.39 (m, 2 H), 7.39–7.31 (m, 3 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.04–6.96 (m, 2 H), 2.25 (s, 3 H), 1.92 (tt, *J* = 8.4, 5.1 Hz, 1 H), 1.01–0.92 (m, 2 H), 0.75–0.68 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.2, 141.8, 141.3, 132.3, 130.2, 129.2, 128.0, 127.2, 126.7, 124.5, 19.9, 15.0, 9.0 ppm. MS (EI): *m*/*z* = 208 $[M]^+$, 193, 178, 165, 152, 139, 128, 115, 89, 77.

HRMS (EI): calcd. for $C_{16}H_{16}$ 208.1252; found 208.1261. IR (film): $\tilde{\nu}$ = 3079, 2922, 1601, 1489, 1443, 1020, 909, 816, 770, 703 cm^{-1}.

Methyl 3-Cyclopropylbenzoate (18f) and Methyl 2-Cyclopropylbenzoate (17f): After purification by column chromatography (pentane/methyl *tert*-butyl ether, 50:1), the product (**18f/17f**, 63:38, 55 mg, 63%) was obtained as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.71 (m, 3 H), 7.39 (t, J = 7.6 Hz, 1 H), 7.35–7.25 (m, 2 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.01 (d, J = 7.9 Hz, 1 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 2.65 (tt, J = 8.6, 5.4 Hz, 1 H), 1.94 (tt, J = 8.5, 5.1 Hz, 1 H), 1.05–0.96 (m, 4 H), 0.77–0.72 (m, 2 H), 0.71–0.66 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 167.3, 144.6, 144.4, 131.7, 131.2, 130.5, 130.1, 130.0, 128.2, 126.7, 126.6, 125.6, 125.2, 52.03, 51.95, 15.3, 13.4, 9.3, 8.7 ppm. MS (EI): m/z = 176 $[M]^+$, 161, 148, 144, 133, 115, 105, 91, 77. HRMS (EI): calcd. for $C_{11}H_{12}O_2$ 176.0837; found 176.0828. IR (film): $\tilde{\nu}$ = 3083, 3004, 2951, 1723, 1491, 1434, 1281, 1262, 1218, 1128, 1076, 754 cm^{-1}. The analytical data for methyl 3-cyclopropylbenzoate (**18f**) are consistent with those in the literature.[20]

4-(Bicyclopropyl)-1,2-dimethylbenzene (19): After purification by column chromatography (pentane), the product (92 mg, 99%) was obtained as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.04 (m, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H), 1.27 (tt, J = 8.2, 5.2 Hz, 1 H), 0.73–0.64 (m, 2 H), 0.64–0.56 (m, 2 H), 0.46–0.37 (m, 2 H), 0.17–0.08 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 136.1, 133.9, 129.4, 129.2, 125.3, 24.8, 19.9, 19.3, 17.4, 11.2, 2.7 ppm. MS (EI): m/z = 186 $[M]^+$, 171, 156, 143, 128, 115, 105, 91, 77. HRMS (EI): calcd. for $C_{14}H_{18}$ 186.1409; found 186.1398. IR (film): $\tilde{\nu}$ = 3078, 3003, 2967, 2921, 1505, 1453, 1017, 996, 817 cm^{-1}.

1-(Bicyclopropyl)-3-pentylbenzene (20): After purification by column chromatography (pentane), the product [**20**/1-(bicyclopropyl)-2-pentylbenzene, >95:5, 59 mg, 51%] was obtained as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.14 (m, 3 H), 7.00 (dt, J = 6.7, 1.8 Hz, 1 H), 2.62–2.54 (m, 2 H), 1.68–1.55 (m, 5 H), 0.90 (t, J = 6.8 Hz, 3 H), 0.74–0.66 (m, 2 H), 0.66–0.58 (m, 2 H), 0.46–0.38 (m, 2 H), 0.16–0.08 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6, 142.7, 127.9, 127.8, 125.8, 125.0, 36.0, 31.6, 31.2, 25.0, 22.5, 17.2, 14.0, 11.6, 2.7 ppm. MS (EI): m/z = 228 $[M]^+$, 213, 200, 171, 157, 143, 129, 115, 91, 77. HRMS (EI): calcd. for $C_{17}H_{24}$ 228.1878; found 228.1864. IR (film): $\tilde{\nu}$ = 3078, 3004, 2957, 2928, 2857, 1605, 1487, 1459, 1383, 1017, 784, 705 cm^{-1}.

Note on Characterizations of 21a–21e: As described above, alkyne **3** was synthesized as nearly a 1:1 mixture of *cis* and *trans* isomers. Accordingly, the assignments of the NMR signals of products **21a–21e** were less obvious, and in some cases specific assignments are only tentative, as a separation of the four possible regioisomers and diastereomers could not be accomplished by column chromatography on silica gel.

1-(Bicycloprop-2-yl)-4-methylbenzene (21a): After purification by column chromatography (pentane), the product (**21a/22a**, 92:8, 46 mg, 53%) was obtained in a diastereomeric ratio of 41:59 as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.16 (m, 2 H), 7.14–7.04 (m, 4 H), 6.98–6.92 (m, 2 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.09 (dt, J = 8.7, 6.2 Hz, 1 H), 1.64 (dt, J = 8.9, 5.0 Hz, 1 H), 1.17–1.07 (m, 1 H), 1.01–0.67 (m, 7 H), 0.50–0.08 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6, 137.0, 134.9, 134.7, 129.1, 128.9, 128.5, 125.6, 25.8, 25.1, 21.3, 21.1, 21.0, 20.9, 13.5, 12.4, 9.8, 9.6, 4.7, 4.5, 3.3, 2.6 ppm. MS (EI): m/z = 172 $[M]^+$, 157, 143, 129, 118, 105, 91, 77, 65. The analytical data of the *trans* isomer are consistent with those in the literature.[21]

4-(Bicycloprop-2-yl)-1,2-dimethylbenzene (21b): After purification by column chromatography (pentane), the product (69 mg, 75%) was obtained in a diastereomeric ratio of 47:53 as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.08–6.99 (m, 4 H), 6.84–6.82 (m, 1 H), 6.78 (dd, J = 7.7, 1.7 Hz, 1 H), 2.25 (s, 3 H), 2.24 (s, 3 H), 2.23 (s, 3 H), 2.22 (s, 3 H), 2.05 (dt, J = 8.8, 6.1 Hz, 1 H), 1.61 (dt, J = 9.0, 5.0 Hz, 1 H), 1.13–1.05 (m, 1 H), 0.97–0.89 (m, 2 H), 0.82–0.74 (m, 2 H), 0.74–0.67 (m, 2 H), 0.46–0.34 (m, 2 H), 0.33–0.27 (m, 1 H), 0.27–0.10 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 137.4, 136.3, 135.8, 133.5, 133.3, 130.7, 129.5, 129.1, 127.1, 126.5, 122.9, 25.0, 22.5, 21.2, 21.0, 19.8, 19.7, 19.3, 19.2, 13.5, 12.4, 9.8, 9.6, 4.8, 4.6, 3.3, 2.6 ppm. MS (EI): m/z = 186 $[M]^+$, 171, 157, 143, 132, 127, 119, 105, 91, 77. HRMS (EI): calcd. for $C_{14}H_{18}$ 186.1409; found 186.1427. IR (film): $\tilde{\nu}$ = 3076, 3001, 2968, 2921, 1614, 1507, 1452, 1017, 815 cm^{-1}. The analytical data of the *trans* isomer are consistent with those in the literature.[21]

1-(Bicycloprop-2-yl)-4-methoxybenzene (21c): After purification by column chromatography (pentane/methyl *tert*-butyl ether, 50:1), the product (**21c/22c**, >95:5, 58 mg, 60%) was obtained in a diastereomeric ratio of 37:63 as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, J = 8.8 Hz, 2 H), 6.85–6.78 (m, 2 H), 6.70–6.60 (m, 4 H), 3.64 (s, 3 H), 3.62 (s, 3 H), 1.89 (dt, J = 8.6, 6.2 Hz, 1 H), 1.46 (dt, J = 8.5, 5.1 Hz, 1 H), 0.96–0.86 (m, 1 H), 0.84–0.71 (m, 2 H), 0.67–0.44 (m, 4 H), 0.16–0.10 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 157.5, 135.7, 132.1, 130.2, 126.7, 113.7, 113.3, 55.3, 55.2, 24.7, 22.1, 20.9, 20.5, 13.2, 12.4, 9.8, 9.6, 4.7, 4.5, 3.3, 2.6 ppm. MS (EI): m/z = 188 $[M]^+$, 173, 159, 144, 134, 128, 121, 115, 103, 91, 77. HRMS (EI): calcd. for $C_{13}H_{16}O$ 188.1201; found 188.1186. IR (film): $\tilde{\nu}$ = 3075, 3000, 2954, 2834, 1613, 1515, 1463, 1291, 1247, 1178, 1038, 825 cm^{-1}. The analytical data of the *trans* isomer are consistent with those in the literature.[21]

1-(Bicycloprop-2-yl)-4-(4-methylpent-3-enyl)benzene (21d): After purification by column chromatography (pentane), the product (**21d/22d**, 92:8, 53 mg, 44%) was obtained in a diastereomeric ratio of 40:60 as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (d, J = 7.9 Hz, 2 H), 7.14–7.05 (m, 4 H), 6.97 (d, J = 7.9 Hz, 2 H), 5.24–5.13 (m, 2 H), 2.62 (t, J = 7.1 Hz, 2 H), 2.59 (t, J = 7.8 Hz, 2 H), 2.35–2.22 (m, 4 H), 2.09 (dt, J = 8.6, 6.0 Hz, 1 H), 1.70 (s, 6 H), 1.68–1.61 (m, 1 H), 1.59 (s, 3 H), 1.57 (s, 3 H), 1.19–1.08 (m, 1 H), 1.01–0.89 (m, 2 H), 0.87–0.67 (m, 4 H), 0.50–0.08 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0, 139.5, 139.3, 137.3, 132.0, 129.0, 128.3, 127.9, 125.5, 123.9, 35.74, 35.66, 30.12, 30.10, 25.7, 25.1, 22.4, 21.4, 21.1, 17.7, 17.6, 13.6, 12.4, 9.7, 9.6, 4.8, 4.6, 3.3, 2.6 ppm. MS (EI): m/z = 240 $[M]^+$, 207, 186, 171, 155, 141, 129, 117, 105, 91, 77, 69. HRMS (EI): calcd. for $C_{18}H_{24}$ 240.1878; found 240.1861. IR (film): $\tilde{\nu}$ = 3076, 3001, 2968, 2924, 2856, 1516, 1451, 1376, 1107, 1033, 1017, 887, 820 cm^{-1}.

5-(Bicycloprop-2-yl)-2-methylbiphenyl (21e): After purification by column chromatography (pentane), the product (**21e/22e**, >95:5, 39 mg, 32%) was obtained in a diastereomeric ratio of 40:60 as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.29 (m, 10 H), 7.23–7.14 (m, 4 H), 7.00–6.90 (m, 2 H), 2.27 (s, 3 H), 2.23 (s, 3 H), 2.19–2.04 (m, 1 H), 1.74–1.63 (m, 1 H), 1.23–1.10 (m, 1 H), 1.03–0.90 (m, 2 H), 0.89–0.69 (m, 4 H), 0.52–0.07 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3, 142.1, 141.7, 141.3, 141.1, 137.5, 132.3, 132.1, 130.7, 130.2, 129.8, 129.22, 129.15, 128.1, 128.00, 127.98, 127.2, 126.7, 126.6, 124.5, 25.2, 22.5, 21.3, 21.1, 20.0, 19.9, 13.6, 12.4, 9.8, 9.7, 4.8, 4.7, 3.3, 2.6 ppm. MS (EI): m/z = 248 $[M]^+$, 233, 219, 205, 194, 181, 165, 152, 141, 128, 115, 91, 77. HRMS (EI): calcd. for $C_{19}H_{20}$ 248.1565; found 248.1549. IR (film): $\tilde{\nu}$ = 3075, 3000, 2923, 1601, 1574, 1504, 1489, 1443, 1139, 1073, 1017, 896, 818, 771, 703 cm^{-1}.

3-(Bicyclopropyl)biphenyl (23a) and 2-(Bicyclopropyl)biphenyl (24a): After purification by column chromatography (pentane/dichloro-

methane, 10:1), the product (71 mg, 61%) was obtained as a mixture of regioisomers and an unidentified side product (approximately 10%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.57 (m, 3 H), 7.51–7.33 (m, 6 H), 1.43–1.30 (m, 1 H), 0.84–0.77 (m, 2 H), 0.73–0.66 (m, 2 H), 0.52–0.43 (m, 2 H), 0.24–0.14 (m, 2 H) ppm. All of the signals could not be assigned in the ^{13}C NMR spectrum. The resolved signals are listed. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3, 141.6, 141.1, 128.7, 128.5, 127.2, 127.1, 126.7, 124.6, 25.2, 24.9, 18.9, 17.2, 12.1, 11.7, 3.5, 2.8 ppm. MS (EI): *m*/*z* = 234 $[M]^+$, 219, 205, 191, 178, 165, 152, 141, 128, 115, 101, 91, 77. HRMS (EI): calcd. for $C_{18}H_{18}$ 234.1409; found: 234.1408.

[3-(Bicyclopropyl)phenyl]trimethylsilane (23b): After purification by column chromatography (pentane), the product (**23b/24b**, >95:5, 51 mg, 44%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.52 (m, 1 H), 7.41–7.27 (m, 3 H), 1.31 (tt, *J* = 8.1, 5.3 Hz, 1 H), 0.74–0.71 (m, 2 H), 0.71–0.63 (m, 2 H), 0.51–0.40 (m, 2 H), 0.29 (s, 9 H), 0.19–0.12 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 140.1, 132.6, 130.7, 128.5, 127.5, 25.2, 17.3, 11.4, 2.8, –1.1 ppm. MS (EI): *m*/*z* = 230 $[M]^+$, 215, 202, 187, 171, 156, 141, 128, 115, 105, 91, 73, 59. HRMS (EI): calcd. for $C_{15}H_{22}Si$ 230.1491; found 230.1494. IR (film): $\tilde{\nu}$ = 3078, 3004, 2955, 2896, 1589, 1393, 1249, 1128, 1017, 859, 837, 753, 706 cm^{-1}.

(*Z*)-[3-(1-Cyclopropylprop-1-enyl)phenyl]triisopropylsilane (25): After purification by column chromatography (pentane) and bulb-to-bulb distillation (0.1 mbar, 70 °C), the product {**25**/(*Z*)-[2-(1-cyclopropylprop-1-enyl)phenyl]triisopropylsilane, >99:1, 83 mg, 53%} was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 2 H), 6.90 (d, *J* = 7.8 Hz, 1 H), 6.73 (dd, *J* = 11.4, 1.3 Hz, 1 H), 5.86 (dq, *J* = 11.6, 6.9 Hz, 1 H), 1.93 (tt, *J* = 8.6, 5.3 Hz, 1 H), 1.78 (dd, *J* = 7.0, 1.7 Hz, 3 H), 1.38 (sept, *J* = 7.6 Hz, 3 H), 1.08 (d, *J* = 7.4 Hz, 18 H), 0.93 (ddd, *J* = 8.4, 6.2, 4.3 Hz, 2 H), 0.74–0.65 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7, 136.2, 136.0, 133.9, 130.5, 129.5, 126.4, 123.2, 18.6, 14.5, 12.9, 10.8, 8.0 ppm. MS (EI): *m*/*z* = 314 $[M]^+$, 271, 243, 229, 215, 201, 187, 169, 155, 141, 128, 115, 93, 73. HRMS (EI): calcd. for $C_{21}H_{34}Si$ 314.2430; found 314.2412. IR (film): $\tilde{\nu}$ = 3082, 3011, 2943, 2865, 1592, 1463, 1383, 1366, 1094, 1044, 1016, 995, 883, 677, 666, 651 cm^{-1}.

1-Bicyclopropyl-2,3-bis(methoxymethyl)benzene (23c): After purification by column chromatography (pentane/methyl *tert*-butyl ether, 20:1), the product (23 mg, 19%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (dd, *J* = 6.9, 2.2 Hz, 1 H), 7.25–7.17 (m, 2 H), 4.76 (s, 2 H), 4.58 (s, 2 H), 3.47 (s, 3 H), 3.44 (s, 3 H), 1.08 (tt, *J* = 8.2, 5.3 Hz, 1 H), 0.78–0.72 (m, 2 H), 0.70–0.64 (m, 2 H), 0.35–0.27 (m, 2 H), 0.09–0.02 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9, 138.4, 135.2, 130.9, 128.0, 127.1, 72.2, 68.4, 58.7, 58.5, 24.8, 18.8, 11.0, 2.7 ppm. MS (EI): *m*/*z* = 246 $[M]^+$, 231, 217, 201, 182, 167, 154, 141, 128, 115, 102, 91, 77. HRMS (EI): calcd. for $C_{16}H_{22}O_2$ 246.1620; found 246.1618. IR (film): $\tilde{\nu}$ = 3074, 2994, 2924, 2881, 2816, 1686, 1458, 1378, 1190, 1097, 1022, 954, 914, 792, 754 cm^{-1}.

3-(Bicycloprop-2-yl)biphenyl (29a): After purification by column chromatography (pentane/diethyl ether, 100:1), the product (**29a/30a**, >99:1, 89 mg, 76%) was obtained in a diastereomeric ratio of 50:50 as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.55 (m, 4 H), 7.54 (s, 1 H), 7.50–7.40 (m, 5 H), 7.40–7.31 (m, 5 H), 7.31–7.25 (m, 2 H), 7.03 (dt, *J* = 6.8, 1.6 Hz, 1 H), 2.19 (dt, *J* = 8.7, 6.4 Hz, 1 H), 1.75 (dt, *J* = 8.6, 5.0 Hz, 1 H), 1.30–1.17 (m, 1 H), 1.06–0.76 (m, 6 H), 0.52–0.11 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.2, 141.53, 141.45, 141.3, 140.7, 140.6, 128.7, 128.6, 128.2, 128.1, 127.20, 127.16, 127.1, 124.7, 124.5, 124.4, 124.2, 25.5, 22.6, 21.8, 21.6, 13.9, 12.4, 9.82, 9.78, 4.8, 4.6, 3.4, 2.6 ppm. MS (EI): *m*/*z* = 234 $[M]^+$, 219, 205, 191, 180, 165, 152, 139, 128, 115, 102, 91, 77. HRMS (EI): calcd. for $C_{18}H_{18}$ 234.1409; found 234.1416. IR (film): $\tilde{\nu}$ = 3063, 2999, 1600, 1481, 1449, 1420, 1075, 1017, 894, 758, 699 cm^{-1}.

1-(Bicycloprop-2-yl)-3-cyclohexenylbenzene (29b): After purification by column chromatography (pentane), the product (**29b/30b**, >95:5, 78 mg, 71%) was obtained in a diastereomeric ratio of 50:50 as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (s, 1 H), 7.23–7.10 (m, 5 H), 7.06 (s, 1 H), 6.88 (d, *J* = 7.3 Hz, 1 H), 6.14–6.10 (m, 1 H), 6.10–6.06 (m, 1 H), 2.46–2.37 (m, 4 H), 2.25–2.17 (m, 4 H), 2.11 (dt, *J* = 8.6, 6.3 Hz, 1 H), 1.83–1.74 (m, 4 H), 1.70–1.62 (m, 5 H), 1.19–1.12 (m, 1 H), 0.98–0.91 (m, 2 H), 0.87–0.78 (m, 2 H), 0.77–0.71 (m, 2 H), 0.47–0.33 (m, 3 H), 0.33–0.27 (m, 1 H), 0.27–0.10 (m, 5 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 142.8, 142.1, 139.9, 136.81, 136.77, 128.0, 127.8, 127.5, 125.9, 124.6, 124.4, 123.7, 122.5, 122.2, 122.1, 27.52, 27.47, 25.89, 25.85, 25.2, 23.11, 23.08, 22.5, 22.21, 22.18, 21.8, 21.6, 13.7, 12.4, 9.8, 9.7, 4.8, 4.6, 3.3, 2.6 ppm. MS (EI): *m*/*z* = 238 $[M]^+$, 223, 209, 184, 171, 165, 155, 141, 129, 105, 91, 81. HRMS (EI): calcd. for $C_{18}H_{22}$ 238.1722; found 238.1723. IR (film): $\tilde{\nu}$ = 3072, 3000, 2929, 2858, 2834, 1601, 1486, 1435, 1345, 1017, 891, 787, 699 cm^{-1}.

2-{2-[Bicycloprop-2-yl]-6-cyclohexenylphenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29c): After purification by column chromatography (pentane/methyl *tert*-butyl ether, 100:1), the product (**29c/30c**, >99:1, 129 mg, 70%) was obtained in a diastereomeric ratio of 50:50 as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 7.7 Hz, 1 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 6.92 (dd, *J* = 7.6, 0.8 Hz, 1 H), 6.63 (d, *J* = 7.7 Hz, 1 H), 5.66–5.60 (m, 2 H), 2.38–2.32 (m, 4 H), 2.29 (dt, *J* = 8.7, 6.2 Hz, 1 H), 2.17–2.10 (m, 4 H), 1.85 (dt, *J* = 8.9, 5.1 Hz, 1 H), 1.80–1.72 (m, 4 H), 1.69–1.62 (m, 4 H), 1.36 (s, 12 H), 1.35 (s, 12 H), 1.30–1.21 (m, 1 H), 1.06–0.98 (m, 1 H), 0.95–0.83 (m, 2 H), 0.81–0.76 (m, 2 H), 0.66 (dt, *J* = 8.8, 5.3 Hz, 1 H), 0.46–0.29 (m, 4 H), 0.20–0.09 (m, 4 H), 0.06 to –0.01 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.8, 148.7, 146.6, 142.9, 141.5, 141.4, 128.5, 127.7, 125.4, 125.31, 125.28, 123.9, 123.6, 120.4, 83.5, 83.3, 30.3, 30.2, 25.5, 25.4, 25.34, 25.28, 25.26, 24.9, 23.1, 23.0, 22.6, 22.02, 22.00, 21.9, 21.6, 13.5, 12.3, 9.3, 9.1, 4.5, 4.1, 3.4, 2.1 ppm. MS (EI): *m*/*z* = 364 $[M]^+$, 335, 310, 295, 280, 264, 249, 235, 223, 210, 193, 181, 167, 153, 141, 128, 115, 101, 83. HRMS (EI): calcd. for $C_{24}H_{33}BO_2$ 364.2574; found 364.2554. IR (film): $\tilde{\nu}$ = 3070, 2991, 2929, 2858, 2835, 1587, 1566, 1442, 1371, 1323, 1303, 1145, 1111, 1053, 858, 750, 675 cm^{-1}.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra of all key intermediates and products.

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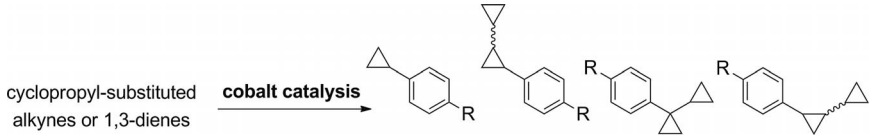

The application of cyclopropyl-substituted alkynes and 1,3-dienes in cobalt-catalyzed Diels–Alder reactions led to various cyclopropyl-substituted arenes. In only one case, the ring-opened product was isolated. This shows that the cyclopropyl subunits were generally compatible with the conditions of the cobalt catalysis and of the subsequent DDQ oxidation of the dihydroaromatic intermediates.

Keywords: Cycloaddition / Arenes / Small ring systems / Cobalt / Dehydrogenation

