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Commercially available liquid enol ethers and acetates as gaseous alkyne equivalents in cationic Rh(I)/BINAP-catalyzed chemo- and regioselective formal cross-alkyne cyclotrimerizations

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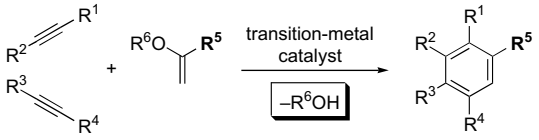
ABSTRACT

A cationic rhodium(I)/BINAP complex catalyzes partial intramolecular [2+2+2] cycloadditions of 1,6- and 1,7-diynes with enol ethers or a ketene acetal giving substituted benzenes in good yields. The same catalyst also catalyzes complete intermolecular [2+2+2] cycloadditions of two different monoynes with enol acetates giving tri- and tetrasubstituted benzenes in good yields with complete regioselectivity. Commercially available liquid enol ethers and acetates can be used as versatile equivalents for gaseous alkynes in the present rhodium-catalyzed formal cross-alkyne cyclotrimerizations.

1. Introduction

Transition-metal-catalyzed alkyne cyclotrimerizations have been shown to be valuable methods for the synthesis of highly substituted benzenes because of their atom economical and convergent nature.[1] Although gaseous alkynes such as acetylene and propyne have been widely employed for the transition-metal-catalyzed cross-alkyne cyclotrimerizations,[2] they are difficult to handle using conventional laboratory equipments due to their explosive and flammable nature. Therefore, alternative easily handled liquid reagents are highly desired. As shown in Scheme 1, if a [2+2+2] cycloaddition between two alkyne units with one enol ether or acetate proceeds through elimination of alcohol or acetic acid, the corresponding substituted benzene is generated.[3–5] Thus, commercially available liquid enol ethers and acetates would be promising equivalents for gaseous alkynes (Fig. 1).[3–5] Our research group has already demonstrated that cationic rhodium(I)/biaryl bisphosphine complexes are highly active and selective catalysts for homo- and cross-alkyne cyclotrimerizations.[6–8] Furthermore, these complexes were also effective catalysts for [2+2+2] cycloadditions between two alkyne units and monoenes.[9] In this article, we wish to present full details of our study on cationic rhodium(I)/BINAP complex-catalyzed chemo- and regioselective formal cross-alkyne cyclotrimerizations using enol ethers and acetates as gaseous alkyne equivalents.[10]



Scheme 1. Use of enol compounds as alkyne equivalents in transition-metal-catalyzed [2+2+2] cycloadditions.

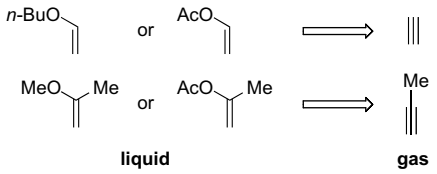


Figure 1. Use of commercially available liquid enol ethers and acetates as gaseous alkyne equivalents.

2. Results and discussion

2.1. Liquid enol ethers as gaseous alkyne equivalents in rhodium-catalyzed formal cross-alkyne cyclotrimerizations with 1,6- and 1,7-diynes

Takeuchi and co-workers reported that a neutral iridium(I)/dppe complex catalyzes a [2+2+2] cycloaddition of 1,6-diyne **1a** with a large excess of *n*-butyl vinyl ether (**2a**, 25 equiv) at elevated

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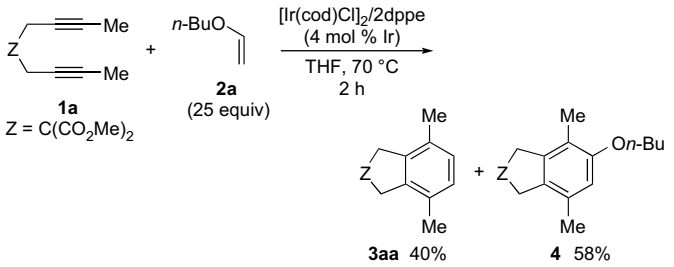
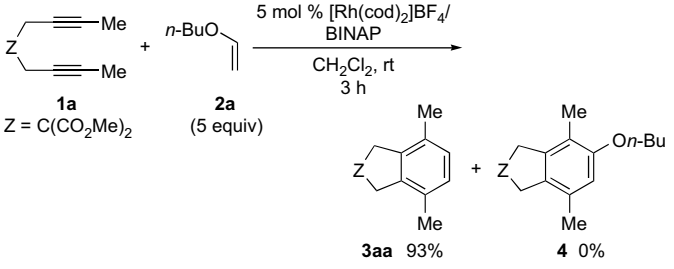
temperature (70 °C).[3a] However, the reaction furnished two different aromatized products **3aa** and **4**, and **4** was generated as the major product (Scheme 2).



Scheme 2. Neutral iridium(I)/dppe complex-catalyzed [2+2+2] cycloaddition of 1,6-diyne **1a** with enol ether **2a**.

We anticipated that as slow elimination of *n*-butanol using the neutral iridium(I) complex may deter the exclusive formation of **3aa**, the use of the highly Lewis acidic cationic rhodium(I)/biaryl bisphosphine complexes would facilitate the elimination of *n*-butanol and thus increase the yield of **3aa**. Gratifyingly, the reaction of **1a** and **2a** (5 equiv) in the presence of a cationic rhodium(I)/BINAP complex (5 mol %) proceeded at room temperature to give **3aa** in 93% isolated yield without the formation of **4** (Scheme 3).[11]



Scheme 3. Cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloaddition of 1,6-diyne **1a** with enol ether **2a**.

Various rhodium(I) complexes with common bisphosphine ligands (Fig. 2) were screened as shown in Table 1. Cationic rhodium(I) complexes with biaryl bisphosphine ligands (BINAP, Segphos, and H_8-BINAP) are highly effective for this transformation, and the desired product **3aa** was obtained in quantitative yields (entries 1–3). On the other hand, the use of non-biaryl bisphosphine ligands (dppb and dppf) significantly lowered the yields of **3aa** (entries 4 and 5). Furthermore, the treatment of the catalyst with hydrogen and the use of the cationic rhodium(I) complex are essential as demonstrated in entries 6 and 7.

Thus, we explored the scope of this process using 5 equiv of enol ethers and 5 mol % of the cationic rhodium(I)/BINAP complex as shown in Table 2. Not only malonate- (**1a**, entry 1) but also

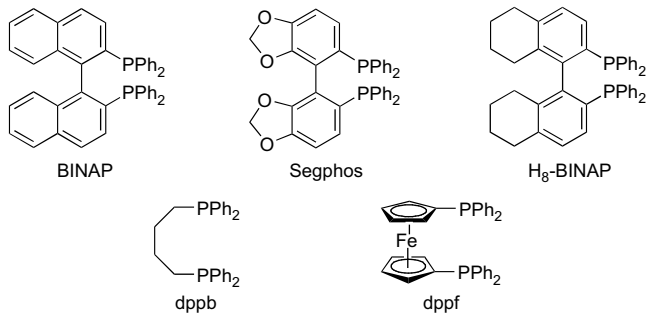
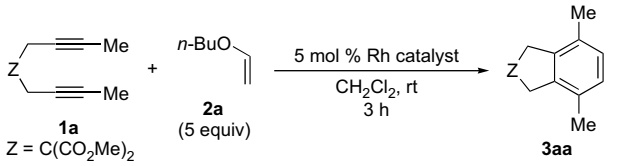


Figure 2. Structures of bisphosphine ligands.

Table 1
Screening of rhodium catalysts for [2+2+2] cycloaddition of 1,6-diyne **1a** with enol ether **2a**[a]



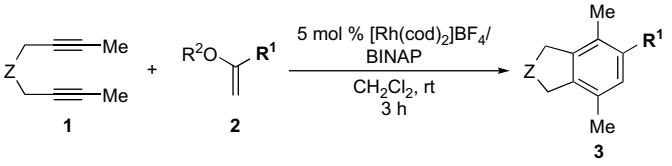
Entry	Catalyst	Yield[b] (%)
1	$[Rh(cod)_2]BF_4$/BINAP	>99
2	$[Rh(cod)_2]BF_4$/Segphos	>99
3	$[Rh(cod)_2]BF_4$/H_8-BINAP	>99
4	$[Rh(cod)_2]BF_4$/dppb	18
5	$[Rh(cod)_2]BF_4$/dppf	78
6[c]	$[Rh(cod)_2]BF_4$/BINAP	15
7	$[Rh(cod)Cl]_2$/2BINAP	0

[a] Rh catalyst (0.010 mmol), **1a** (0.20 mmol), **2a** (1.00 mmol), and CH_2Cl_2 (1.5 mL) were used. The active catalysts were generated in situ by hydrogenation (1 atm, rt).
[b] Determined by ^1H NMR.
[c] Without hydrogenation.

tosylamide- (**1b**, entry 4) and oxygen-linked 1,6-diynes (**1c**, entry 5) reacted with **2a** to give the corresponding tetrasubstituted benzenes in high yields. With respect to enol ethers, not only *n*-butyl vinyl ether (**2a**) but also isopropenyl methyl ether (**2b**) could participate in this reaction, while the yields of the corresponding aromatized products obtained from **2a** (**3aa**–**3ca**, entries 1, 4, and 5) are higher than those obtained from **2b** (**3ab**–**3cb**, entries 6–8). When the amount of **2a** was reduced to 1.1 equiv, the yield of **3aa** decreased to 54% (entry 2). When the reaction of **1a** and **2a** was carried out with 2 mol % of the rhodium catalyst, prolonged reaction time was required (entry 3).

The above success in the use of enol ethers as a cycloaddition partner prompted our investigation into the use of commercially available liquid ketene acetal **2c**, which may furnish the corresponding bicyclic methoxybenzenes. We were pleased to find that the reaction of 1,6-diyne **1a** and **2c** in the presence of the cationic rhodium(I)/BINAP complex (5 mol %) furnished the corresponding methoxybenzene **3ac** in quantitative yield (Table 3, entry 1). The amount of **2c** appeared to have a high impact on the product yield (entry 2). When the reaction of **1a** and **2c** was carried out with

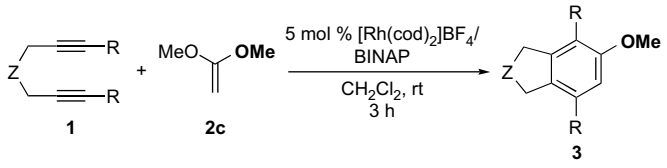
Table 2
Cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloadditions of 1,6-diynes **1a–c** with enol ethers **2a** and **2b**[a]



Entry	**1** (Z)	**2** (R^1, R^2, equiv)	**3**	Yield[b] (%)
1	**1a** [$C(CO_2Me)_2$]	**2a** (H, *n*-Bu, 5)	**3aa**	93
2	**1a** [$C(CO_2Me)_2$]	**2a** (H, *n*-Bu, 1.1)	**3aa**	54
3[c,d]	**1a** [$C(CO_2Me)_2$]	**2a** (H, *n*-Bu, 5)	**3aa**	83
4	**1b** (NTs)	**2a** (H, *n*-Bu, 5)	**3ba**	96
5[d]	**1c** (O)	**2a** (H, *n*-Bu, 5)	**3ca**	95
6	**1a** [$C(CO_2Me)_2$]	**2b** (Me, Me, 5)	**3ab**	85
7	**1b** (NTs)	**2b** (Me, Me, 5)	**3bb**	74
8	**1c** (O)	**2b** (Me, Me, 5)	**3cb**	76

[a] $[Rh(cod)_2]BF_4$ (0.015 mmol), BINAP (0.015 mmol), **1a–c** (0.30 mmol), **2a**,**b** (0.33 or 1.50 mmol), and CH_2Cl_2 (2.0 mL) were used. The active catalyst was generated in situ by hydrogenation (1 atm, rt).
[b] Isolated yield.
[c] Catalyst: 0.0060 mmol (2 mol %).
[d] For 16 h.

Table 3
Cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloadditions of 1,6- and 1,7-diynes **1a–i** with ketene acetal **2c**[a]



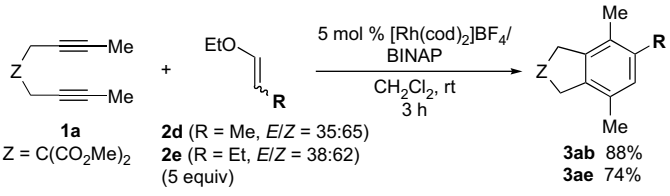
Entry	**1** (Z, R)	**2c** (equiv)	**3**	Yield[b] (%)
1	**1a** [$C(CO_2Me)_2$, Me]	5	**3ac**	>99
2	**1a** [$C(CO_2Me)_2$, Me]	1.1	**3ac**	65
3[c,d]	**1a** [$C(CO_2Me)_2$, Me]	5	**3ac**	99
4	**1b** (NTs, Me)	5	**3bc**	71
5	**1c** (O, Me)	5	**3cc**	91
6[e]	**1d** (O, Ph)	25	**3dc**	52
7	**1e** (O, CO_2Et)	25	**3ec**	<10
8	**1f** [$C(CO_2Me)_2$, H]	25	**3fc**	40
9	**1g** [$(C(CO_2Et)_2)_2$, Me]	5	**3gc**	54
10[d,e]	**1h** (CH_2CH_2, Me)	25	**3hc**	21
11[d]	**1i** (CH_2CH_2, H)	25	**3ic**	26

[a] $[Rh(cod)_2]BF_4$ (0.015 mmol), BINAP (0.015 mmol), **1a–i** (0.30 mmol), **2c** (0.33–7.50 mmol), and CH_2Cl_2 (2.0 mL) were used. The active catalyst was generated in situ by hydrogenation (1 atm, rt).
[b] Isolated yield.
[c] Catalyst: 0.0060 mmol (2 mol %).
[d] For 16 h.
[e] At 80 °C.

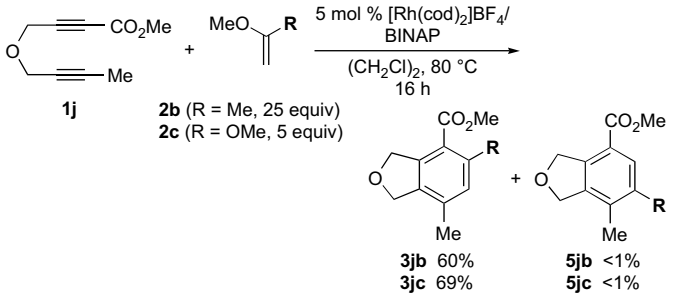
2 mol % of the rhodium catalyst, prolonged reaction time was required (entry 3). The scope of diyne substrates was then examined, which revealed that not only malonate- (**1a**, entry 1) but also tosylamide- (**1b**, entry 4) and oxygen-linked internal 1,6-diynes (**1c**, entry 5), possessing a methyl group at each alkyne terminus, could be employed for this reaction. With respect to the substituents at the alkyne termini, phenyl-substituted 1,6-diyne **1d** (entry 6) and terminal 1,6-diyne **1f** (entry 8) could react with **2c** to give the corresponding methoxybenzenes **3dc** and **3fc**, respectively, in moderate yields, but ethoxycarbonyl-substituted 1,6-diyne **1e** (entry 7) failed to react with **2c** due to the rapid homo-[2+2+2] cycloaddition of **1e**. Although the yields of the corresponding methoxybenzenes were low to moderate, both internal and terminal 1,7-diynes **1g–i** could also participate in this reaction (entries 9–11). A hexane solution of ethyl ethynyl ether is commercially available, but it is unstable.[12] Therefore, the use of commercially available liquid ketene acetal **2c** as a stable equivalent for unstable gaseous ethynyl methyl ether is highly practical.

Next, a [2+2+2] cycloaddition of 1,6-diyne **1a** with 1,2-disubstituted enol ether **2d** (mixture of *E*/*Z* isomers) instead of 1,1-disubstituted enol ether **2b** was examined (Scheme 4). Both *E*- and *Z*-isomers of **2d** reacted with **1a** to give the corresponding pentasubstituted benzene **3ab** in high yield. Furthermore, ethyl-substituted enol ether **2e** (mixture of *E*/*Z* isomers) could also be employed.

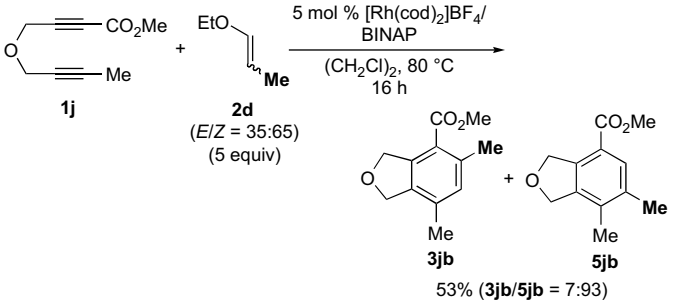
The reactions of unsymmetrical 1,6-diyne **1j**, bearing methyl and methoxycarbonyl at each alkyne terminus, with 1,1-disubstituted enol ethers **2b** and **2c** furnished the corresponding pentasubstituted benzenes **3jb** and **3jc**, respectively, as a sole product (Scheme 5). On the other hand, that with 1,2-disubstituted enol ether **2d** furnished alternative regioisomer **5jb** as a major product (Scheme 6).



Scheme 4. Cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloaddition of 1,6-diyne **1a** with 1,2-disubstituted enol ethers **2d** and **2e**.



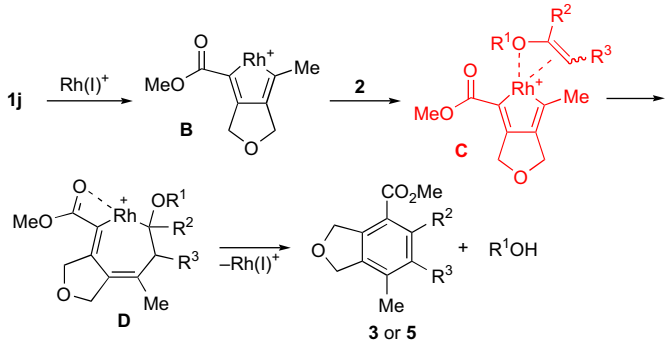
Scheme 5. Cationic rhodium(I)/BINAP complex-catalyzed regioselective [2+2+2] cycloadditions of unsymmetrical 1,6-diyne **1j** with 1,1-disubstituted enol ethers **2b** and **2c**.



Scheme 6. Cationic rhodium(I)/BINAP complex-catalyzed regioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diyne **1j** with 1,2-disubstituted enol ether **2d**.

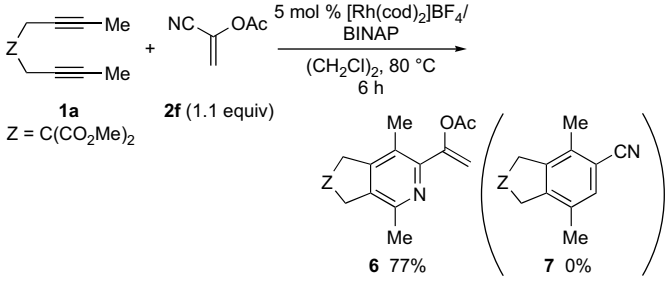
A possible mechanism for the present regioselective [2+2+2] cycloadditions of 1,6-diyne **1j** with enol ethers **2b–d** is shown in Scheme 7. 1,6-Diyne **1j** reacts with rhodium to form rhodacyclopentadiene **B**. Subsequent regioselective insertion of 1,1-disubstituted enol ether **2b** (R^2=Me, R^3=H) or **2c** (R^2=OMe, R^3=H) forms intermediate **D** through intermediate **C**, which is stabilized by coordination of the carbonyl group and/or the alkoxy group to the cationic rhodium. Reductive elimination furnishes substituted benzene **3jb** or **3jc** and an alcohol. Accordingly, the reaction between 1,6-diyne **1j** and 1,2-disubstituted enol ether **2d** furnished regioisomeric product **5jb** as a major product through intermediates **C** and **D**.

As we have demonstrated that a chemoselective [2+2+2] cycloaddition of the cyano group of acrylonitrile with a 1,6-diyne



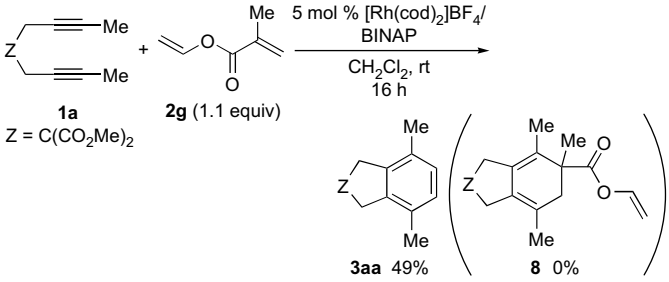
Scheme 7. Possible mechanism for the regioselective formation of **3jb** (R^2=Me, R^3=H), **3jc** (R^2=OMe, R^3=H), and **5jb** (R^2=H, R^3=Me).

proceeded to give a bicyclic 2-vinylpyridine in good yield,[13] chemoselectivity between the enol double bond and the cyano group of commercially available 1-cyanovinyl acetate (**2f**) in a [2+2+2] cycloaddition with 1,6-diyne **1a** is of interest. Like acrylonitrile, the cyano group of **2f** selectively reacted with **1a** to give bicyclic 2-(1-acetoxyvinyl)pyridine **6** in high yield without formation of cyanopyridine **7** (Scheme 8).



Scheme 8. Chemoselectivity between the enol double bond and the cyano group.

Chemoselectivity between two different double bonds of commercially available vinyl methacrylate (**2g**) in a [2+2+2] cycloaddition with 1,6-diyne **1a** was also examined. Although double bonds of methacrylates are highly reactive toward rhodium-catalyzed [2+2+2] cycloadditions,[9a] the double bond of the enol moiety selectively reacted with **1a** to give tetrasubstituted benzene **3aa** without the formation of cyclohexadiene **8** (Scheme 9).

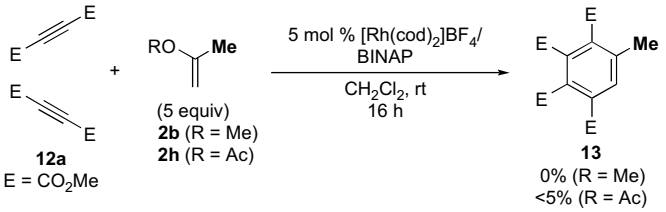


Scheme 9. Chemoselectivity between two different double bonds.

2.2. Liquid enol esters as gaseous alkyne equivalents in rhodium-catalyzed formal cross-alkyne cyclotrimerizations with monoynes

Having succeeded the partial intramolecular cross-[2+2+2] cycloaddition of 1,6-diynes with enol ethers, we turned our attention to a complete intermolecular cross-[2+2+2] cycloaddition of monoynes with enol ethers. Interestingly, terminal monoyne **9a** failed to react with enol ether **2b** in the presence of the cationic rhodium(I)/BINAP complex (5 mol %) due to the rapid homocyclotrimerization of **9a**, but the reaction of **9a** with enol acetate **2h** proceeded to give the corresponding trisubstituted benzenes in 28% yield as a mixture of two regioisomers **10** and **11** (Scheme 10).

The reactions of an electron-deficient internal monoyne, dimethyl acetylenedicarboxylate (**12a**), with enol ether **2b** and enol acetate **2h** were also examined, but both **2b** and **2h** failed to react with **12a** in the presence of the cationic rhodium(I)/BINAP complex (5 mol %) due to the rapid homo-cyclotrimerization of **12a** (Scheme 11).[4]

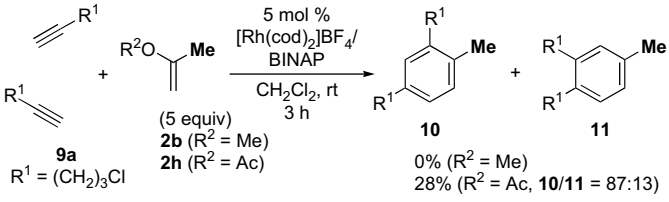


Scheme 11. Cationic rhodium(I)/BINAP complex-catalyzed intermolecular [2+2+2] cycloadditions of dimethyl acetylenedicarboxylate (**12a**) with enol ether **2b** and enol acetate **2h**.

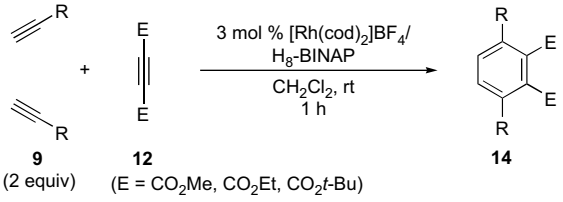
On the other hand, we have already reported that two molecules of terminal monoyne **9** react with one molecule of dialkyl acetylenedicarboxylate **12** in the presence of the cationic rhodium(I)/H_8-BINAP complex (3 mol %) to give the corresponding tetrasubstituted benzene **14** in high yield with high regioselectivity (Scheme 12).[8a,c]

As enol acetate **2h** showed no reactivity to electron-deficient internal monoyne **12a** and moderate reactivity to terminal monoyne **9a**, a cross-[2+2+2] cycloaddition of **12a**, 1-dodecyne (**9b**), and **2h** was investigated in the presence of the cationic rhodium(I)/BINAP complex (10 mol %).[14,15] Gratifyingly, the desired three-component cycloaddition reaction proceeded at room temperature to give the corresponding tetrasubstituted benzene **15abh** in good yield with perfect regioselectivity (Table 4, entry 1). Thus, we explored the scope of this process as shown in Table 4. With respect to terminal monoynes, primary alkyl- (**9b** and **9c**, entries 1 and 3), chloropropyl- (**9a**, entry 4), phenylpropyl- (**9d**, entry 5), benzyl- (**9e**, entry 6), cyclohexyl- (**9f**, entry 7), cyclohexenyl- (**9g**, entry 8), phenyl- (**9h**, entry 9), and trimethylsilyl-substituted terminal monoynes (**9i**, entry 10) could participate in this reaction to give the corresponding tetrasubstituted benzenes in moderate to good yields with perfect regioselectivity. Not only dimethyl (**12a**, entry 1) but also di-*tert*-butyl acetylenedicarboxylate (**12b**, entry 2) could be employed for this reaction. When the reactions were carried out using 1.1 equiv of enol acetate **2h** (entry 11) or 5 mol % of the rhodium catalyst (entry 12), the yields of the desired product significantly decreased.

Commercially available trifluoromethyl-substituted enol acetate **2i** is a possible equivalent for gaseous trifluoromethylacetylene. Unfortunately, **2i** is much less reactive than isopropenyl acetate (**2h**) toward the present rhodium-catalyzed [2+2+2] cycloaddition. The intermolecular reaction of **12a**, **9b**, and **2i** did not furnish the desired cycloaddition product **15abi** at all due to the cross-cyclotrimerization between **12a** and **9b** (Scheme 13), while the partial

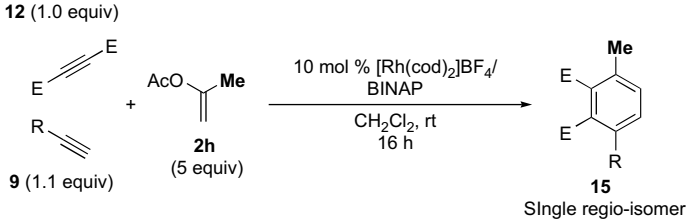


Scheme 10. Cationic rhodium(I)/BINAP complex-catalyzed complete intermolecular [2+2+2] cycloadditions of terminal monoyne **9a** with enol ether **2b** and enol acetate **2h**.



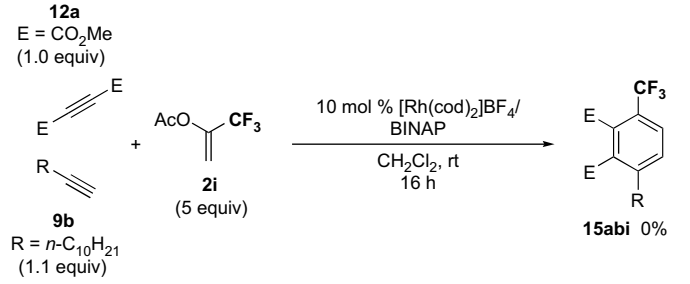
Scheme 12. Cationic rhodium(I)/H_8-BINAP complex-catalyzed intermolecular [2+2+2] cycloadditions of dialkyl acetylenedicarboxylate **12** with terminal monoyne **9**.

Table 4
Cationic rhodium(I)/BINAP complex-catalyzed intermolecular [2+2+2] cycloadditions of two different monoynes **12a**,**b** and **9a**–**i** with isopropenyl acetate (**2h**)[a]



Entry	**12** (E)	**9** (R)	**15**	Yield[b] (%)
1	**12a** (CO_2Me)	**9b** (n-$C_{10}H_{21}$)	**15abh**	69
2	**12b** (CO_2t-Bu)	**9b** (n-$C_{10}H_{21}$)	**15bbh**	66
3	**12a** (CO_2Me)	**9c** (n-C_6H_{13})	**15ach**	44
4	**12a** (CO_2Me)	**9a** [$Cl(CH_2)_3$]	**15aah**	41
5	**12a** (CO_2Me)	**9d** [$Ph(CH_2)_3$]	**15adh**	67
6	**12a** (CO_2Me)	**9e** (Bn)	**15aeh**	44
7	**12a** (CO_2Me)	**9f** (Cy)	**15afh**	72
8	**12a** (CO_2Me)	**9g** (1-Cyclohexenyl)	**15agh**	35
9	**12a** (CO_2Me)	**9h** (Ph)	**15ahh**	51
10	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aih**	73
11[c]	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aih**	60
12[d]	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aih**	63

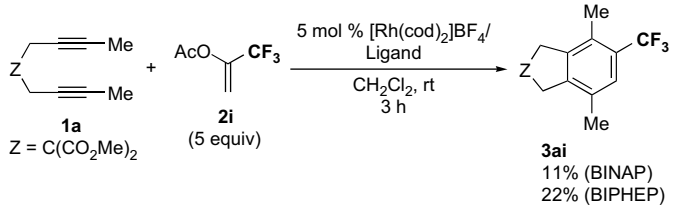
[a] $[Rh(cod)_2]BF_4$ (0.030 mmol), BINAP (0.030 mmol), **12a**,**b** (0.30 mmol), **9a**–**i** (0.33 mmol), **2h** (1.50 mmol), and CH_2Cl_2 (2.0 mL) were used. The active catalyst was generated in situ by hydrogenation (1 atm, rt).
[b] Isolated yield.
[c] Compound **2h**: 0.33 mmol (1.1 equiv).
[d] Catalyst: 0.015 mmol (5 mol %).



Scheme 13. Cationic rhodium(I)/BINAP complex-catalyzed intermolecular [2+2+2] cycloaddition of two different monoynes **12a** and **9b** with enol acetate **2i**.

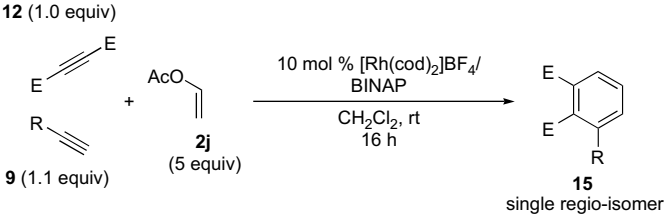
intramolecular reaction of **1a** and **2i** furnished the desired cycloaddition product **3ai** in low yields (Scheme 14).

Not only isopropenyl acetate (**2h**) but also vinyl acetate (**2j**) could be employed for the present intermolecular three-component cycloaddition reaction as shown in Table 5. The reaction of **12a**, **9b**, and **2j** furnished the corresponding trisubstituted benzene **15abj** in moderate yield with perfect regioselectivity (entry 1). A variety of terminal alkynes **9** could participate in this reaction (entries 1, 3, 4–7, 9, and 10) while 1-ethynylcyclohexene (**9g**) reacted with **12a** and **2j** in very low yield (entry 8) and di-*tert*-butyl acetylenedicarboxylate (**12b**) failed to react with **9b** and **2j** (entry 2). Like the reactions involving isopropenyl acetate (**2h**, Table 4),

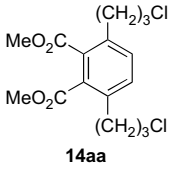


Scheme 14. Cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloaddition of 1,6-diyne **1a** with enol acetate **2i**.

Table 5
Cationic rhodium(I)/BINAP complex-catalyzed intermolecular [2+2+2] cycloadditions of two different monoynes **12a**,**b** and **9a**–**i** with vinyl acetate (**2j**)[a]



Entry	**12** (E)	**9** (R)	**15**	Yield[b] (%)
1	**12a** (CO_2Me)	**9b** (n-$C_{10}H_{21}$)	**15abj**	49
2	**12b** (CO_2t-Bu)	**9b** (n-$C_{10}H_{21}$)	**15bbj**	0
3	**12a** (CO_2Me)	**9c** (n-C_6H_{13})	**15acj**	59
4	**12a** (CO_2Me)	**9a** [$Cl(CH_2)_3$]	**15aaj**	66[c]
5	**12a** (CO_2Me)	**9d** [$Ph(CH_2)_3$]	**15adj**	72
6	**12a** (CO_2Me)	**9e** (Bn)	**15aej**	56
7	**12a** (CO_2Me)	**9f** (Cy)	**15afj**	80
8	**12a** (CO_2Me)	**9g** (1-Cyclohexenyl)	**15agj**	<10
9	**12a** (CO_2Me)	**9h** (Ph)	**15ahj**	40
10	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aij**	84
11[d]	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aij**	57
12[e]	**12a** (CO_2Me)	**9i** (Me_3Si)	**15aij**	57

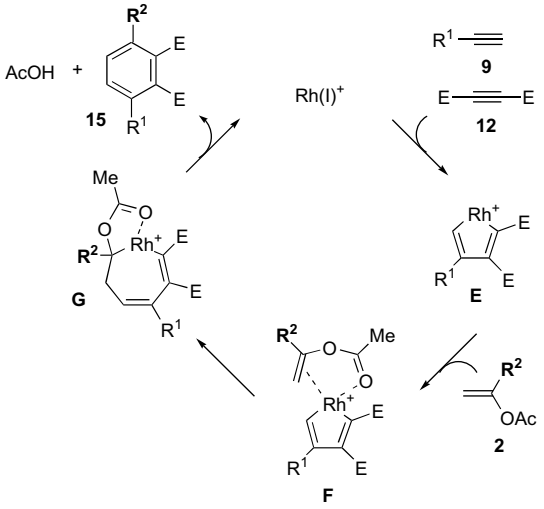


14aa

[a] $[Rh(cod)_2]BF_4$ (0.030 mmol), BINAP (0.030 mmol), **12a**,**b** (0.30 mmol), **9a**–**i** (0.33 mmol), **2j** (1.50 mmol), and CH_2Cl_2 (2.0 mL) were used. The active catalyst was generated in situ by hydrogenation (1 atm, rt).
[b] Isolated yield.
[c] Isolated as a mixture of **15aaj** and **14aa**. Yield of **15aaj** was determined by ^1H NMR.
[d] Compound **2j**: 0.33 mmol (1.1 equiv).
[e] Catalyst: 0.015 mmol (5 mol %).

decreasing the amount of **2j** (entry 11) or the catalyst loading (entry 12) significantly lowered the yields of the desired product.

A possible mechanism for the present chemo- and regioselective cross-[2+2+2] cycloaddition of two different monoynes with an enol acetate is shown in Scheme 15. Terminal monoyne **9** and electron-deficient internal monoyne **12** react with rhodium to form



Scheme 15. Possible mechanism for chemo- and regioselective formation of **15** (E=CO_2Me or CO_2t-Bu).

rhodacyclopentadiene **E** due to the steric repulsion between R^1 and the BINAP ligand. Bidentate coordination of enol acetate **2h** or **2j** (intermediate **F**) followed by regioselective insertion forms intermediate **G**, which is stabilized by coordination of the carbonyl group to the cationic rhodium through five-membered chelation. Reductive elimination furnishes substituted benzene **15** and acetic acid.

3. Conclusions

In conclusion, we have demonstrated that commercially available and cheap liquid enol ethers can be used as gaseous alkyne equivalents in the cationic rhodium(I)/BINAP complex-catalyzed partial intramolecular cross-[2+2+2] cycloadditions with 1,6- and 1,7-diynes. Especially, the use of a commercially available liquid ketene acetal as a stable equivalent for unstable gaseous ethynyl methyl ether is highly practical. On the other hand, commercially available and cheap liquid enol acetates can be used not only as the gaseous alkyne equivalents but also as suitable cycloaddition partners in the cationic rhodium(I)/BINAP complex-catalyzed complete intermolecular cross-[2+2+2] cycloadditions with terminal monoynes and dialkyl acetylenedicarboxylates.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on 300 MHz JEOL AL 300. ^{13}C NMR spectra were obtained with complete proton decoupling on 75 MHz JEOL AL 300. HRMS data were obtained on a Bruker micrOTOF Focus II and a JEOL JMS-700. Infrared spectra were obtained on a JASCO FT/IR-4100. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

4.2. Materials

Anhydrous CH_2Cl_2 (No. 27,099-7) was obtained from Aldrich and used as received. H_8-BINAP and Segphos were obtained from Takasago International Corporation. Rhodium complexes were obtained from Umicore. Diynes **1a**,[16] **1b**,[17] **1c**,[9e] **1d**,[18] **1e**,[19] **1f**,[16] **1g**,[20] and **1j**[21] were prepared according to literature procedures. All other reagents were obtained from commercial sources and used as received.

4.3. Representative procedure for cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloadditions of α,ω-diynes 1 with enol ethers 2 (Table 2, entry 1)

BINAP (9.3 mg, 0.015 mmol) and $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at room temperature for 5 min. H_2 (1 atm) was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (0.8 mL). To this solution was added a solution of **1a** (70.9 mg, 0.300 mmol) and **2a** (150.2 mg, 1.50 mmol) in CH_2Cl_2 (1.2 mL) at room temperature. The solution was stirred at room temperature for 3 h. The resulting solution was concentrated and purified by a silica gel column chromatography (hexane/EtOAc=10:1), which furnished **3aa** (73.3 mg, 0.279 mmol, 93% yield) as a colorless solid.

4.3.1. 4,7-Dimethylindan-2,2-dicarboxylic acid dimethyl ester (*3aa*)

Colorless solid; mp 102.5–103.3 °C; ^{1}H NMR ($CDCl_3$) δ 6.91 (s, 2H), 3.77 (s, 6H), 3.55 (s, 4H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 172.3, 138.3, 130.7, 127.9, 59.3, 52.9, 39.6, 18.6.

4.3.2. 4,7-Dimethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (*3ba*)

Colorless solid; mp 147.5–148.2 °C; IR (KBr) 3089, 2918, 2846, 2736, 1939, 1874, 1673, 1596, 1397, 1049, 808 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J=8.1 Hz, 2H), 7.32 (d, J=8.1 Hz, 2H), 6.93 (s, 2H), 4.56 (s, 4H), 2.41 (s, 3H), 2.16 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 143.5, 134.6, 133.7, 129.7, 129.6, 128.6, 127.4, 53.3, 21.4, 18.1; HRMS (EI) calcd for $C_{17}H_{19}NO_2S$ $[M]^+$ 301.1136, found 301.1117.

4.3.3. 4,7-Dimethyl-1,3-dihydroisobenzofuran (*3ca*)[22]

Colorless oil; ^{1}H NMR ($CDCl_3$) δ 6.96 (s, 2H), 5.10 (s, 4H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 137.5, 128.3, 73.6, 18.4.

4.3.4. 4,5,7-Trimethylindan-2,2-dicarboxylic acid dimethyl ester (*3ab*)

Colorless solid; mp 79.1–80.5 °C; IR (KBr) 2950, 1736, 1436, 1377, 1250, 1083, 875, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 1H), 3.75 (s, 6H), 3.55 (s, 2H), 3.51 (s, 2H), 2.20 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.4, 138.6, 135.8, 135.2, 130.3, 129.7, 129.2, 59.6, 52.9, 40.1, 39.5, 19.4, 18.5, 15.5; HRMS (EI) calcd for $C_{16}H_{20}O_4$ $[M]^+$ 276.1362, found 276.1352.

4.3.5. 4,5,7-Trimethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (*3bb*)

Colorless solid; mp 179.4–180.3 °C; IR (KBr) 3089, 2918, 2853, 2734, 1937, 1596, 1463, 1302, 1096, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J=8.1 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 6.83 (s, 1H), 4.57 (s, 2H), 4.55 (s, 2H), 2.40 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 143.5, 136.1, 135.0, 133.8, 132.2, 130.3, 129.7, 129.2, 128.0, 127.5, 53.7, 53.4, 21.4, 19.1, 18.1, 15.3; HRMS (EI) calcd for $C_{18}H_{21}NO_2S$ $[M]^+$ 315.1293, found 315.1280.

4.3.6. 4,5,7-Trimethyl-1,3-dihydroisobenzofuran (*3cb*)

Colorless solid; mp 68.8–69.9 °C; IR (KBr) 2847, 1948, 1618, 1488, 1365, 1232, 1048, 904 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.87 (s, 1H), 5.10 (s, 4H), 2.25 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 138.0, 135.7, 135.1, 130.0, 128.0, 126.7, 73.8, 73.7, 19.0, 18.3, 15.5; HRMS (EI) calcd for $C_{11}H_{14}O$ $[M]^+$ 162.1045, found 162.1072.

4.3.7. 5-Methoxy-4,7-dimethylindan-2,2-dicarboxylic acid dimethyl ester (*3ac*)

Colorless solid; mp 101.9–102.5 °C; IR (KBr) 3006, 2956, 2737, 2114, 1731, 1610, 1449, 1346, 1163, 948, 871, 838, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.51 (s, 1H), 3.77 (s, 3H), 3.75 (s, 6H), 3.53 (s, 2H), 3.48 (s, 2H), 2.22 (s, 3H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.3, 157.0, 139.8, 130.8, 130.1, 119.2, 110.4, 59.7, 55.7, 52.8, 39.7, 39.0, 19.0, 12.0; HRMS (EI) calcd for $C_{15}H_{17}O_4$ $[M-OMe]^+$ 261.1127, found 261.1120.

4.3.8. 5-Methoxy-4,7-dimethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (*3bc*)

Colorless solid; mp 162.3–164.0 °C; IR (KBr) 2910, 2845, 1920, 1738, 1598, 1500, 1343, 1283, 1236, 1116, 832 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J=8.1 Hz, 2H), 7.32 (d, J=8.1 Hz, 2H), 6.53 (s, 1H), 4.54 (s, 2H), 4.52 (s, 2H), 3.77 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 157.4, 143.5, 136.1, 133.7, 130.1, 129.8, 127.5, 126.4, 118.1, 110.9, 55.8, 53.4, 53.0, 21.5, 18.7, 11.9; HRMS (EI) calcd for $C_{17}H_{18}NO_3S$ $[M-Me]^+$ 316.1007, found 316.0986.

4.3.9. 5-Methoxy-4,7-dimethyl-1,3-dihydroisobenzofuran (*3cc*)

Colorless solid; mp 67.3–68.5 °C; IR (KBr) 2845, 2119, 1950, 1728, 1618, 1496, 1325, 1281, 1124, 957, 903, 781 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.56 (s, 1H), 5.05 (s, 4H), 3.82 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 157.3, 139.2, 129.3, 128.6, 116.7, 110.6, 73.4, 73.2, 55.8, 18.8, 12.1; HRMS (EI) calcd for $C_{11}H_{14}O_2$ $[M]^+$ 178.0994, found 178.1006.

*4.3.10. 5-Methoxy-4,7-diphenyl-1,3-dihydroisobenzofuran (**3dc**)*

Pale yellow solid; mp 148.5–149.7 °C; IR (KBr) 2934, 2359, 1956, 1895, 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49–7.31 (m, 10H), 6.96 (s, 1H), 5.20 (s, 2H), 4.99 (s, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.6, 140.7, 140.2, 135.9, 135.6, 129.4, 129.3, 128.7, 128.2, 127.8, 127.6, 127.3, 124.0, 110.8, 73.5, 73.4, 56.2; HRMS (APCI) calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ 303.1380, found 303.1374.

*4.3.11. 5-Methoxy-indan-2,2-dicarboxylic acid dimethyl ester (**3fc**)*

Colorless solid; mp 46.0–47.1 °C; IR (KBr) 3476, 2952, 1727, 1610, 1431 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (d, J=7.1 Hz, 1H), 6.79–6.67 (m, 2H), 3.76 (s, 3H), 3.74 (s, 6H), 3.56 (s, 2H), 3.52 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 172.1, 159.1, 141.3, 131.7, 124.7, 113.0, 109.5, 60.7, 55.3, 52.9, 40.7, 39.7; HRMS (ESI) calcd for $C_{14}H_{16}O_5Na$ $[M+Na]^+$ 287.0890, found 287.0892.

*4.3.12. 6-Methoxy-5,8-dimethyl-1,4-dihydronaphthalene-2,2,3,3-tetracarboxylic acid tetraethyl ester (**3gc**)*

Colorless solid; mp 104.8–105.9 °C; IR (KBr) 2982, 1724, 1601, 1457 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.58 (s, 1H), 4.28–4.10 (m, 8H), 3.77 (s, 3H), 3.38 (s, 2H), 3.32 (s, 2H), 2.22 (s, 3H), 2.10 (s, 3H), 1.22 (t, J=7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 170.1, 170.1, 155.1, 133.3, 132.2, 123.2, 121.0, 110.8, 61.7, 61.6, 57.3, 57.1, 55.5, 33.0, 32.2, 19.9, 13.7, 10.8; HRMS (ESI) calcd for $C_{25}H_{34}O_9Na$ $[M+Na]^+$ 501.2095, found 501.2082.

*4.3.13. 6-Methoxy-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (**3hc**)[23]*

Colorless solid; mp 34.0–34.9 °C; ^1H NMR ($CDCl_3$) δ 6.59 (s, 1H), 3.79 (s, 3H), 2.71–2.60 (m, 2H), 2.60–2.49 (m, 2H), 2.21 (s, 3H), 2.08 (s, 3H), 1.78 (quint, J=3.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 136.7, 134.1, 127.8, 122.0, 110.2, 55.8, 27.7, 26.8, 23.1, 23.0, 19.9, 10.7.

*4.3.14. 6-Methoxy-1,2,3,4-tetrahydronaphthalene (**3ic**)[24]*

Pale yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.97 (d, J=8.1 Hz, 1H), 6.67 (d, J=8.1 Hz, 1H), 6.61 (s, 1H), 3.77(s, 3H), 2.84–2.64 (m, 2H), 2.78–2.62 (m, 2H), 1.79–1.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.3, 138.1, 129.9, 129.2, 113.6, 111.7, 55.2, 29.7, 28.5, 23.4, 23.2.

*4.3.15. 5-Ethyl-4,7-dimethylindan-2,2-dicarboxylic acid dimethyl ester (**3ae**)*

Colorless solid; mp 88.1–89.0 °C; IR (neat) 2968, 1733, 1434, 1248, 1066, 882 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.81 (s, 1H), 3.75 (s, 6H), 3.56 (s, 2H), 3.52 (s, 2H), 2.57 (q, J=7.5 Hz, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 1.16 (t, J=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.41, 141.19, 138.8, 135.8, 130.5, 128.5, 128.2, 59.5, 52.9, 40.2, 39.5, 26.0, 18.6, 14.94, 14.90; HRMS (ESI) calcd for $C_{17}H_{22}O_4Na$ $[M+Na]^+$ 313.1410, found 313.1422.

*4.3.16. 5,7-Dimethyl-1,3-dihydroisobenzofuran-4-carboxylic acid methyl ester (**3jb**)*

Pale yellow solid; mp 101.5–102.9 °C; IR (KBr) 2924, 2848, 1710, 1605, 1447, 1363, 1269, 1152, 1066, 914, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.97 (s, 1H), 5.30 (s, 2H), 5.06 (s, 2H), 3.87 (s, 3H), 2.57 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.5, 141.7, 139.9, 136.7, 135.1, 132.1, 121.3, 75.8, 72.6, 51.5, 21.7, 18.8; HRMS (EI) calcd for $C_{11}H_{11}O_3$ $[M-Me]^+$ 191.0708, found 191.0706.

*4.3.17. 5-Methoxy-7-methyl-1,3-dihydroisobenzofuran-4-carboxylic acid methyl ester (**3jc**)*

Pale yellow solid; mp 89.7–91.5 °C; IR (KBr) 2951, 2849, 1944, 1695, 1610, 1438, 1197, 903, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.70 (s, 1H), 5.26 (s, 2H), 5.03 (s, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.0, 159.4, 142.7, 136.5, 130.7, 112.4, 111.7, 75.2, 72.3, 56.5, 51.7, 19.3; HRMS (EI) calcd for $C_{12}H_{14}O_4$ $[M]^+$ 222.0892, found 222.0873.

*4.3.18. 5,7-Dimethyl-1,3-dihydroisobenzofuran-4-carboxylic acid methyl ester (**3jb**) and 6,7-dimethyl-1,3-dihydroisobenzofuran-4-carboxylic acid methyl ester (**5jb**)*

Ratio **3jb**/**5jb**=7:93; colorless solid; mp 86.3–87.2 °C; IR (KBr) 2972, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74 (s, 1H), 5.38 (s, 2H), 5.10 (s, 2H), 3.89 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H); aryl protons of minor isomer **3ib**: 6.97 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 166.7, 139.6, 138.8, 136.0, 135.3, 130.3, 121.4, 75.5, 72.8, 51.8, 19.0, 16.3; HRMS (APCI) calcd for $C_{12}H_{15}O_3$ $[M+H]^+$ 207.1016, found 207.1025.

*4.3.19. 3-(1-Acetoxyvinyl)-1,4-dimethyl-5,7-dihydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (**6**)*

Pale yellow solid; mp 123.1–124.3 °C; IR (KBr) 3469, 2955, 2848, 2743, 2554, 2039, 1717, 1588, 1366, 903, 801 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.34 (d, J=1.8 Hz, 1H), 5.12 (d, J=1.8 Hz, 1H), 3.78 (s, 6H), 3.57 (s, 4H), 2.42 (s, 3H), 2.33 (s, 3H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.6, 169.1, 151.9, 150.5, 150.3, 149.4, 133.5, 125.0, 106.5, 59.1, 53.1, 40.0, 39.0, 21.7, 20.9, 15.8; HRMS (FAB) calcd for $C_{18}H_{22}O_6N$ $[M+H]^+$ 348.1447, found 348.1405.

*4.3.20. 2,4-Bis-(3-chloropropyl)-1-methylbenzene (**10**) and 1,2-bis-(3-chloropropyl)-4-methylbenzene (**11**)*

Ratio **10**/**11**=87:13; colorless oil; IR (neat) 2955, 1614, 1502, 1442, 1291, 972, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.14–6.89 (m, 2H), 6.85 (d, J=9.9 Hz, 1H), 3.62–3.46 (m, 4H), 2.79–2.69 (m, 4H), 2.30 (s, 3H), 2.11–1.98 (m, 4H); methyl proton of minor isomer **7**: 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 139.0, 138.5, 138.3, 135.9, 135.5, 133.7, 130.5, 130.2, 129.4, 129.3, 127.2, 126.3, 44.7, 44.64, 44.62, 44.4, 44.3, 34.1, 34.0, 32.9, 32.3, 30.3, 29.6, 29.1, 21.0, 18.8; HRMS (EI) calcd for $C_{13}H_{18}Cl_2$ $[M]^+$ 244.0786, found 244.0775.

*4.3.21. 4,7-Dimethyl-5-trifluoromethylindan-2,2-dicarboxylic acid dimethyl ester (**3ai**)*

Colorless solid; mp 78.2–79.5 °C; IR (KBr) 2961, 1729, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (s, 1H), 3.77 (s, 6H), 3.59 (s, 2H), 3.56 (s, 2H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.9, 142.2 (d, J_{CF}=1.2 Hz), 140.6, 130.8, 128.1 (q, J_{CF}=242.8 Hz), 127.6 (t, J_{CF}=6.5 Hz), 125.8 (q, J_{CF}=5.6 Hz), 122.9, 59.2, 53.1, 39.9, 39.7, 18.6, 15.47 (q, J_{CF}=1.8 Hz); HRMS (ESI) calcd for $C_{16}H_{17}F_3O_4Na$ $[M+H]^+$ 353.0971, found 353.0980.

4.4. Representative procedure for cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloadditions of two different monoynes 12 and 9 with enol acetates 2 (Table 4, entry 1)

BINAP (18.7 mg, 0.030 mmol) and $[Rh(cod)_2]BF_4$ (12.2 mg, 0.030 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at room temperature for 5 min. H_2 (1 atm) was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (0.8 mL). To this solution was added a solution of **12a** (42.6 mg, 0.300 mmol), **9b** (54.9 mg, 0.330 mmol), and **2h** (150.2 mg, 1.50 mmol) in CH_2Cl_2 (1.2 mL) at room temperature. The solution was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by preparative TLC (hexane/CH_2Cl_2=1:2), which furnished **15abh** (71.8 mg, 0.206 mmol, 69% yield) as a colorless oil.

*4.4.1. 3-Decyl-6-methylphthalic acid dimethyl ester (**15abh**)*

Colorless oil; IR (neat) 2925, 2854, 1737, 1437, 1269, 1200, 1114, 1035, 795, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21(s, 2H), 3.864 (s, 3H), 3.858 (s, 3H), 2.66 (t, J=7.8 Hz, 2H), 2.39 (s, 3H), 1.60–1.45 (m, 2H), 1.40–1.24 (m, 14H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.7, 139.1, 134.4, 132.4, 131.80, 131.76, 131.4, 52.2, 33.3, 31.8, 31.5,

29.6, 29.5, 29.42, 29.37, 29.3, 22.6, 19.8, 14.1; HRMS (EI) calcd for $C_{21}H_{32}O_4$ $[M]^+$ 348.2301, found 348.2311.

*4.4.2. 3-Decyl-6-methylphthalic acid di-tert-butyl ester (**15bbh**)*

Colorless oil; IR (neat) 2927, 2855, 1719, 1458, 1368, 1295, 1155, 910, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.11 (s, 2H), 2.64 (t, J=7.8 Hz, 2H), 2.36 (s, 3H), 1.59 (s, 18H), 1.60–1.54 (m, 2H), 1.42–1.21 (m, 14H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.1, 168.0, 137.8, 133.23, 133.16, 132.9, 131.4, 130.8, 82.1, 82.0, 33.5, 31.8, 31.7, 29.8, 29.6, 29.5, 29.3, 28.14, 28.05, 27.8, 22.6, 19.9, 14.1; HRMS (ESI) calcd for $C_{27}H_{44}O_4Na$ $[M+Na]^+$ 455.3137, found 455.3130.

*4.4.3. 3-Hexyl-6-methylphthalic acid dimethyl ester (**15ach**)*

Colorless oil; IR (neat) 2929, 1736, 1436 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21(s, 2H), 3.864 (s, 3H), 3.858 (s, 3H), 2.66 (t, J=7.8 Hz, 2H), 2.39 (s, 3H), 1.60–1.46 (m, 2H), 1.44–1.22 (m, 6H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.8, 139.1, 134.4, 132.4, 131.8, 131.5, 52.2, 33.3, 31.6, 31.4, 29.1, 22.5, 19.9, 14.0; HRMS (ESI) calcd for $C_{17}H_{24}O_4Na$ $[M+Na]^+$ 315.1567, found 315.1556.

*4.4.4. 3-(3-Chloropropyl)-6-methylphthalic acid dimethyl ester (**15aah**)*

Colorless oil; IR (neat) 2951, 1733, 1437, 1281, 1202, 1109, 1035, 795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (s, 2H), 3.87 (s, 6H), 3.52 (t, J=6.6 Hz, 2H), 2.85 (t, J=7.2 Hz, 2H), 2.39 (s, 3H), 2.12–2.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 168.6, 137.1, 135.1, 132.7, 132.03, 131.96, 131.8, 52.4, 52.3, 44.3, 34.0, 30.4, 19.9; HRMS (EI) calcd for $C_{13}H_{14}ClO_3$ $[M-OMe]^+$ 253.0631, found 253.0642.

*4.4.5. 3-Methyl-6-(3-phenylpropyl)phthalic acid dimethyl ester (**15adh**)*

Colorless oil; IR (neat) 2950, 1734, 1437, 1277 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–7.23 (m, 2H), 7.23–7.08 (m, 5H), 3.85 (s, 3H), 3.77 (s, 3H), 2.70 (t, J=7.5 Hz, 2H), 2.64 (t, J=7.5 Hz, 2H), 2.38 (s, 3H), 1.89 (quint, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 168.8, 168.7, 141.9, 138.5, 134.6, 132.5, 131.9, 131.8, 131.6, 128.4, 128.2, 125.7, 52.21, 52.17, 35.6, 33.0, 32.9, 19.8; HRMS (ESI) calcd for $C_{20}H_{22}O_4Na$ $[M+Na]^+$ 349.1410, found 349.1400.

*4.4.6. 3-Benzyl-6-methylphthalic acid dimethyl ester (**15aeh**)*

Colorless oil; IR (neat) 3085, 3027, 2951, 1732, 1603, 1436, 1281, 1203, 1109, 1032, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31–7.06 (m, 7H), 4.09 (s, 2H), 3.86 (s, 3H), 3.74 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.69, 168.65, 140.0, 137.2, 135.1, 132.7, 132.5, 132.1, 131.7, 129.0, 128.4, 126.2, 52.33, 52.30, 38.8, 19.9; HRMS (EI) calcd for $C_{17}H_{15}O_3$ $[M-OMe]^+$ 267.1021, found 267.1037.

*4.4.7. 3-Cyclohexyl-6-methylphthalic acid dimethyl ester (**15afh**)*

Colorless solid; mp 55.7–56.5 °C; IR (KBr) 2940, 1734, 1714, 1441 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (d, J=8.1 Hz, 1H), 7.24 (d, J=8.1 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.80–2.55 (m, 1H), 2.39 (s, 3H), 1.87–1.65 (m, 5H), 1.44–1.16 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 169.2, 168.6, 143.4, 134.4, 132.4, 132.0, 130.7, 128.5, 52.2, 52.1, 40.9, 34.2, 26.8, 26.0, 19.9; HRMS (ESI) calcd for $C_{17}H_{22}O_4Na$ $[M+Na]^+$ 313.1410, found 313.1401.

*4.4.8. 3-Cyclohex-1-enyl-6-methylphthalic acid dimethyl ester (**15agh**)*

Colorless oil; IR (neat) 2930, 1733, 1436 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23 (d, J=7.8 Hz, 1H), 7.17 (d, J=7.8 Hz, 1H), 5.61–5.48 (m, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.39 (s, 3H), 2.28–2.17 (m, 2H), 2.16–2.05 (m, 2H), 1.82–1.68 (m, 2H), 1.68–1.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 169.2, 168.6, 141.5, 137.3, 134.9, 132.0, 131.4, 131.3, 130.2, 126.6, 52.3, 52.1, 29.8, 25.5, 22.9, 21.8, 19.8; HRMS (ESI) calcd for $C_{17}H_{20}O_4Na$ $[M+Na]^+$ 311.1254, found 311.1256.

*4.4.9. 4-Methylbiphenyl-2,3-dicarboxylic acid dimethyl ester (**15ahh**)*[25]

Colorless solid; mp 81.5–91.3 °C; ^1H NMR ($CDCl_3$) δ 7.43–7.33 (m, 5H), 7.33–7.28 (m, 2H), 3.89 (s, 3H), 3.58 (s, 3H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.1, 168.5, 139.9, 138.7, 135.8, 132.3, 132.0, 131.8, 128.4, 128.3, 128.2, 127.5, 52.4, 52.2, 19.9.

*4.4.10. 3-Methyl-6-(trimethylsilanyl)phthalic acid dimethyl ester (**15aih**)*

Colorless solid; mp 48.2–49.0 °C; IR (KBr) 2951, 2901, 1747, 1582, 1434, 1384, 1235, 1161, 1102, 1022, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.56 (d, J=7.8 Hz, 1H), 7.30 (d, J=7.8 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.39 (s, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 169.4, 169.3, 137.5, 136.9, 136.3, 136.2, 132.9, 132.0, 52.24, 52.19, 19.6, −0.22; HRMS (FAB) calcd for $C_{13}H_{17}O_4Si$ $[M-Me]^+$ 265.0896, found 265.0924.

*4.4.11. 3-Decylphthalic acid dimethyl ester (**15abj**)*

Colorless oil; IR (neat) 2925, 2854, 1731, 1594, 1460, 1433, 1281, 1150, 1106, 1070, 763 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (dd, J=7.2, 1.8 Hz, 1H), 7.46–7.35 (m, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 2.60 (t, J=7.8 Hz, 2H), 1.70–1.46 (m, 2H), 1.43–1.08 (m, 14H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.8, 166.3, 140.4, 134.9, 133.7, 129.0, 127.7, 127.5, 52.39, 52.36, 33.2, 31.8, 31.2, 29.54, 29.48, 29.4, 29.34, 29.27, 22.6, 14.1; HRMS (EI) calcd for $C_{20}H_{30}O_4$ $[M]^+$ 334.2144, found 334.2151.

*4.4.12. 3-Hexylphthalic acid dimethyl ester (**15acj**)*

Colorless oil; IR (neat) 2952, 1461, 1731, 1461, 1280, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (d, J=7.2 Hz, 1H), 7.46–7.32 (m, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 2.61 (t, J=7.8 Hz, 2H), 1.68–1.52 (m, 2H), 1.48–1.17 (m, 6H), 0.88 (t, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.8, 166.3, 140.4, 134.9, 133.6, 129.0, 127.7, 127.5, 52.4, 52.3, 33.2, 31.5, 31.2, 29.0, 22.5, 14.0; HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ $[M+Na]^+$ 301.1410, found 301.1418.

*4.4.13. 3-(3-Chloropropyl)phthalic acid dimethyl ester (**15aaj**)*

Colorless oil; IR (neat) 2950, 1731, 1593, 1431, 1282, 959, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (d, J=7.5 Hz, 1H), 7.47 (d, J=7.5 Hz, 1H), 7.42 (t, J=7.5 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.53 (t, J=6.3 Hz, 2H), 2.79 (t, J=6.3 Hz, 2H), 2.07 (quint, J=6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 169.5, 166.2, 138.4, 137.8, 135.1, 133.9, 132.2, 129.3, 128.09, 128.05, 52.6, 52.5, 44.2, 44.1, 33.9, 33.8, 30.5, 30.3; HRMS (ESI) calcd for $C_{13}H_{15}ClO_4Na$ $[M+Na]^+$ 293.0551, found 293.0552.

*4.4.14. 3-(3-Phenylpropyl)phthalic acid dimethyl ester (**15adj**)*

Colorless oil; IR (neat) 2950, 1728, 1593, 1496, 1455, 1433 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (d, J=6.9 Hz, 1H), 7.47–7.08 (m, 7H), 3.87 (s, 3H), 3.84 (s, 3H), 2.71–2.55 (m, 4H), 1.93 (quint, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 169.6, 166.2, 141.7, 139.9, 135.0, 133.6, 129.1, 128.4, 128.3, 127.8, 127.7, 125.8, 52.4, 52.3, 35.6, 32.7; HRMS (ESI) calcd for $C_{19}H_{20}O_4Na$ $[M+Na]^+$ 335.1254, found 335.1242.

*4.4.15. 3-Benzylphthalic acid dimethyl ester (**15aej**)*

Colorless solid; mp 58.2–59.5 °C; IR (KBr) 2999, 2952, 1717, 1591, 1464 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.86 (d, J=7.5 Hz, 1H), 7.39 (d, J=7.5 Hz, 1H), 7.37–7.11 (m, 6H), 4.01 (s, 2H), 3.89 (s, 3H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.6, 166.3, 139.4, 138.8, 135.1, 134.4, 129.3, 129.1, 128.5, 128.0, 126.4, 52.5, 52.4, 38.6; HRMS (ESI) calcd for $C_{17}H_{16}O_4Na$ $[M+Na]^+$ 307.0941, found 307.0938.

*4.4.16. 3-Cyclohexylphthalic acid dimethyl ester (**15afj**)*

Colorless oil; IR (neat) 2928, 1732, 1593, 1433 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, J=7.8 Hz, 1H), 7.53 (d, J=7.8 Hz, 1H), 7.42 (t, J=7.8 Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 2.62–2.39 (m, 1H), 1.88–1.63 (m, 5H), 1.44–1.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.0, 166.3, 145.2, 134.7, 130.8, 129.2, 127.6, 127.3, 52.41, 52.40, 41.6, 34.2,

26.8, 26.0; HRMS (ESI) calcd for $C_{16}H_{20}O_4Na$ $[M+Na]^+$ 299.1254, found 299.1254.

*4.4.17. Biphenyl-2,3-dicarboxylic acid dimethyl ester (**15ahj**)*

Pale yellow solid; mp 92.1–93.8 °C; IR (KBr) 2953, 1963, 1911, 1719, 1587, 1497, 1436 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (d, J=6.9 Hz, 1H), 7.58–7.48 (m, 2H), 7.45–7.41 (m, 5H), 3.91 (s, 3H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.2, 166.2, 140.6, 139.2, 134.7, 134.2, 129.1, 128.8, 128.6, 128.3, 128.1, 127.9, 52.6, 52.3; HRMS (ESI) calcd for $C_{16}H_{14}O_4Na$ $[M+Na]^+$ 293.0784, found 293.0784.

*4.4.18. 3-(Trimethylsilanyl)phthalic acid dimethyl ester (**15aij**)*

Colorless oil; IR (neat) 2952, 2900, 1732, 1573, 1441, 1282, 1107, 961, 842, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (d, J=7.8 Hz, 1H), 7.57 (d, J=7.8 Hz, 1H), 7.47 (t, J=7.8 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 0.31 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.5, 166.9, 140.0, 138.8, 138.3, 130.2, 128.6, 128.4, 52.4, 52.3, −0.5; HRMS (EI) calcd for $C_{12}H_{15}O_4Si$ $[M-Me]^+$ 251.0739, found 251.0701.

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References and notes

1. For reviews of transition-metal-catalyzed [2+2+2] cycloadditions, see: (a) Tanaka, K. *Chem. Asian J.*, in press. doi:10.1002/asia.200800378; (b) Varela, J. A.; Saá, C. *Synlett* **2008**, 2571; (c) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, 1317; (d) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085; (e) Agenet, N.; Buisine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. In *Organic Reactions*; RajanBabu, T. V., Ed.; John Wiley & Sons: Hoboken, 2007; Vol. 68, p 1; (f) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307; (g) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209; (h) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741; (i) Gandon, V.; Aubert, C.; Malacria, M. *Curr. Org. Chem.* **2005**, *9*, 1699; (j) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503; (k) Varela, J.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787; (l) Malacria, M.; Aubert, C.; Renaud, J. L. In *Science of Synthesis: Houben-Weyl Methods for Molecular Transformations*; Lautens, M., Trost, B. M., Eds.; Georg Thieme: New York, NY, 2001; Vol. 1, p 439; (m) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901; (n) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 741; (o) Boese, R.; Sickle, A. P. V.; Vollhardt, K. P. C. *Synthesis* **1994**, 1374; (p) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1129; (q) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
2. For selected recent examples, see: (a) Heller, B.; Gutnov, A.; Fischer, C.; Drexler, H.-J.; Spannenberg, A.; Redkin, D.; Sundermann, C.; Sundermann, B. *Chem.—Eur. J.* **2007**, *13*, 1117; (b) Ramana, C. V.; Salian, S. R.; Gonnade, R. G. *Eur. J. Org. Chem.* **2007**, 5483; (c) Young, D. D.; Senaiar, R. S.; Deiters, A. *Chem.—Eur. J.* **2006**, *12*, 5563; (d) Yamamoto, Y.; Hashimoto, T.; Hattori, K.; Kikuchi, M.; Nishiyama, H. *Org. Lett.* **2006**, *8*, 3565; (e) Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Nishiyama, H.; Itoh, K. *Org. Biomol. Chem.* **2004**, *2*, 1287; (f) Yamamoto, Y.; Hata, K.; Arakawa, T.; Itoh, K. *Chem. Commun.* **2003**, 1290; (g) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143; (h) Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281; (i) Witulski, B.; Zimmermann, A. *Synlett* **2002**, 1855; (j) Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun.* **2000**, 549; (k) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 2426; (l) Sato, Y.; Ohashi, K.; Mori, M. *Tetrahedron Lett.* **1999**, *40*, 5231; (m) McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605; (n) Sato, Y.; Nishimata, T.; Mori, M. *J. Org. Chem.* **1994**, *59*, 6133.
3. (a) Kezuka, S.; Tanaka, S.; Ohe, T.; Nakaya, Y.; Takeuchi, R. *J. Org. Chem.* **2006**, *71*, 543; For their works on neutral iridium(I)/diphosphine complex-catalyzed [2+2+2] cycloadditions, see: (b) Takeuchi, R.; Tanaka, S.; Nakaya, Y. *Tetrahedron Lett.* **2001**, *42*, 2991; (c) Takeuchi, R.; Nakaya, Y. *Org. Lett.* **2003**, *5*, 3659; (d) Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, R. *Org. Lett.* **2005**, *7*, 1711; (e) Onodera, G.; Matsuzawa, M.; Aizawa, T.; Kitahara, T.; Shimizu, Y.; Kezuka, S.; Takeuchi, R. *Synlett* **2008**, 755; For a review of neutral iridium(I)/diphosphine complex-catalyzed enantioselective [2+2+2] cycloadditions, see: Ref. 1c.
4. Although palladium-catalyzed [2+2+2] cycloadditions of dimethyl acetylenedicarboxylate with vinyl ethers and esters were reported, the reactions required a large excess of the vinyl compounds (100 equiv) and a long reaction time (3–5 days), see: Stephan, C.; Munz, C.; Dieck, H. T. *J. Organomet. Chem.* **1993**, *452*, 223.
5. For the use of ethyl vinyl ether as a synthetic equivalent of acetylene in a DABCO-catalyzed microwave-assisted Diels–Alder–elimination reaction sequence, see: Kranjc, K.; Koevar, M. *Synlett* **2008**, 2613.
6. For our accounts, see: (a) Tanaka, K. *Synlett* **2007**, 1977; (b) Tanaka, K.; Nishida, G.; Suda, T. *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 862.
7. For a review of rhodium-catalyzed cyclotrimerization reactions, see: Fujiwara, M.; Ojima, I. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005; p 129.
8. (a) Tanaka, K.; Shirasaka, K. *Org. Lett.* **2003**, *5*, 4697; (b) Tanaka, K.; Nishida, G.; Wada, A.; Noguchi, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6510; (c) Tanaka, K.; Toyoda, K.; Wada, A.; Shirasaka, K.; Hirano, M. *Chem.—Eur. J.* **2005**, *11*, 1145; (d) Tanaka, K.; Nishida, G.; Ogino, M.; Hirano, M.; Noguchi, K. *Org. Lett.* **2005**, *7*, 3119; (e) Tanaka, K.; Sagae, H.; Toyoda, K.; Noguchi, K. *Eur. J. Org. Chem.* **2006**, 3575; (f) Nishida, G.; Suzuki, N.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2006**, *8*, 3489; (g) Tanaka, K.; Takeishi, K.; Noguchi, K. *J. Am. Chem. Soc.* **2006**, *128*, 4586; (h) Tanaka, K.; Suda, T.; Noguchi, K.; Hirano, M. *J. Org. Chem.* **2007**, *72*, 2243; (i) Tanaka, K.; Sagae, H.; Toyoda, K.; Noguchi, K.; Hirano, M. *J. Am. Chem. Soc.* **2007**, *129*, 1522; (j) Tanaka, K.; Osaka, T.; Noguchi, K.; Hirano, M. *Org. Lett.* **2007**, *9*, 1307; (k) Tanaka, K.; Hara, H.; Nishida, G.; Hirano, M. *Org. Lett.* **2007**, *9*, 1907; (l) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3951; (m) Tanaka, K.; Kamisawa, A.; Suda, T.; Noguchi, K.; Hirano, M. *J. Am. Chem. Soc.* **2007**, *129*, 12078; (n) Tanaka, K.; Sagae, H.; Toyoda, K.; Hirano, M. *Tetrahedron* **2008**, *64*, 831; (o) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3410; (p) Nishida, G.; Ogaki, S.; Yusa, Y.; Yokozawa, T.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2008**, *10*, 2849; (q) Suda, T.; Noguchi, K.; Hirano, M.; Tanaka, K. *Chem.—Eur. J.* **2008**, *14*, 6593.
9. (a) Tsuchikama, K.; Kuwata, Y.; Shibata, T. *J. Am. Chem. Soc.* **2006**, *128*, 13686; (b) Tanaka, K.; Nishida, G.; Sagae, H.; Hirano, M. *Synlett* **2007**, 1426; (c) Shibata, T.; Kawachi, A.; Ogawa, M.; Kuwata, Y.; Tsuchikama, K.; Endo, K. *Tetrahedron* **2007**, *63*, 12853; (d) Shibata, Y.; Noguchi, K.; Hirano, M.; Tanaka, K. *Org. Lett.* **2008**, *10*, 2825; (e) Tanaka, K.; Takahashi, M.; Imase, H.; Osaka, T.; Noguchi, K.; Hirano, M. *Tetrahedron* **2008**, *64*, 6289.
10. The preliminary communication of this work has been reported, see: Hara, H.; Hirano, M.; Tanaka, K. *Org. Lett.* **2008**, *10*, 2537.
11. Although the reaction of **1a** with vinyl acetate (**2j**) was also examined, **3aa** was obtained in lower yield (47%) than that with **2a**.
12. For cationic rhodium(I)/BINAP complex-catalyzed [2+2+2] cycloadditions of diynes with alkynyl ethers en route to aryl ethers, see: Clayden, J.; Moran, W. J. *Org. Biomol. Chem.* **2007**, *5*, 1028.
13. Tanaka, K.; Suzuki, N.; Nishida, G. *Eur. J. Org. Chem.* **2006**, 3917.
14. For examples of transition-metal-catalyzed intermolecular three-component cocyclotrimerizations, see: (a) Mori, N.; Ikeda, S.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2722; (b) Mori, N.; Ikeda, S.; Odashima, K. *Chem. Commun.* **2001**, 181; (c) Chouraqui, G.; Petit, M.; Aubert, C.; Malacria, M. *Org. Lett.* **2004**, *6*, 1519; (d) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2004**, *126*, 3712; (e) Ura, Y.; Sato, Y.; Tsujita, H.; Kondo, T.; Imachi, M.; Mitsudo, T. *J. Mol. Catal. A* **2005**, *239*, 166; (f) Deng, L.; Giessert, A. J.; Gerlitz, O. O.; Dai, X.; Diver, S. T.; Davies, H. M. L. *J. Am. Chem. Soc.* **2005**, *127*, 1342; (g) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 9625; (h) Komagawa, S.; Saito, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2446.
15. For examples of intermolecular three-component cocyclotrimerizations using stoichiometric transition-metal complexes, see: (a) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123; (b) Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 361; (c) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672; (d) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093; (e) Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 7925; (f) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059; (g) Tanaka, R.; Nakano, Y.; Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, *124*, 9682.
16. Atkinson, R. S.; Grimshir, M. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1215.
17. Nishida, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 8606.
18. Kudoh, T.; Mori, T.; Shirahama, M.; Yamada, M.; Ishikawa, T.; Saito, S.; Kobayashi, H. *J. Am. Chem. Soc.* **2007**, *129*, 4939.
19. Matano, Y.; Miyajima, T.; Nakabuchi, T.; Matsutani, Y.; Imahori, H. *J. Org. Chem.* **2006**, *71*, 5792.
20. James, W. M.; Xiang, W.; Ross, A. W. *Org. Lett.* **2001**, *3*, 385.
21. Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem.—Eur. J.* **2003**, 2469.
22. Grubbs, R. H.; Pancoast, T. A. *J. Am. Chem. Soc.* **1977**, *99*, 2382.
23. Yanagita, M.; Futaki, R. *J. Org. Chem.* **1956**, *21*, 949.
24. Park, I. S.; Kwon, M. S.; Kang, K. Y.; Lee, J. S.; Park, J. *Adv. Synth. Catal.* **2007**, *349*, 209.
25. Alder, K.; Gunzl-Schumacher, M. *Chem. Ber.* **1959**, *92*, 822.