Rhodium-Catalyzed Dimerization of Arylacetylenes and Addition of Malonates to 1,3-Enynes

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Abstract: An 8-quinolinolato rhodium catalyst was found to be effective for head-to-tail selective dimerization of arylacetylenes. Formation of substituted cyclopentene and allene derivatives via alkyne dimerization and subsequent addition of malonates was also catalyzed by the 8-quinolinolato rhodium catalyst in the presence of cesium fluoride. One-pot reaction using palladium-catalyzed alkyne dimerization in conjunction with rhodium-catalyzed addition of malonates was also possible.

Key words: rhodium catalyst, aromatic terminal alkynes, head-to-tail dimerization, cyclopentene derivatives, allene derivatives

Conjugated 1,3-enynes are important building blocks in organic synthesis and found in many bioactive natural products.[1] One of the most straightforward, atom-efficient routes to these structural motifs is through dimerization of terminal alkynes.[2] An array of catalysts have been reported to promote the dimerization of terminal alkynes,[3,4] but formation of a mixture of different regio- and stereoisomers as well as higher oligomers is a common drawback with these reactions.

While the 'head-to-head' dimers of terminal alkynes can be prepared using various catalysts, selective dimerization to the 'head-to-tail' dimer is a challenge, with relatively few examples reported. Trost and co-workers, with their $Pd(OAc)_2$/P[2,6-$(MeO)_2C_6H_3]_3$ (TDMPP) catalyst system,[5] have reported a practical dimerization reaction applicable to both aliphatic and aryl terminal alkynes. MAO (methylaluminoxane) was also found to be effective in the selective dimerization of a wide variety of terminal alkynes.[6] A few reports have been made on the use of rhodium catalysts for the formation of the head-to-tail dimers.[7] Goldman and co-workers reported that $[RhCl(PMe_3)_2]_2$ catalyzes head-to-tail dimerization of arylacetylenes,[7a] while Lin and co-workers converted hex-1-yne into the corresponding head-to-tail dimer under the $[RhCl(CO)(PPh_3)_2]/K_2CO_3$/MeI catalysts system.[7b] Li and co-workers also found that N-protected propargyl amines are dimerized in a head-to-tail fashion by a $[RhCl(cod)]_2$/dppf catalyst.[7c] Catalysts of various other transition metals, such as ruthenium,[8] lanthanides,[9] and gold,[10] have also been reported to give the head-to-tail dimers.

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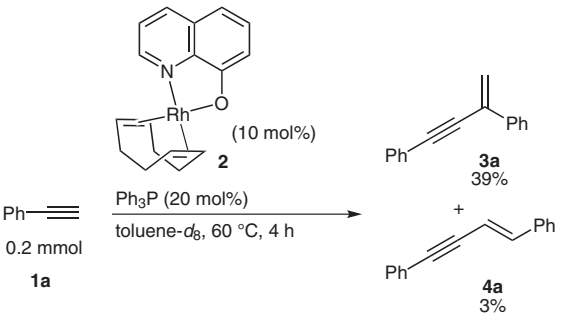
Our group has recently reported anti-Markovnikov addition of alcohols,[11] secondary amines[12] as well as the [2+2] cycloaddition of electron-deficient alkenes[13] to terminal alkynes catalyzed by 8-quinolinolato rhodium complex systems. During the course of these studies, the formation of alkyne oligomers as by-products was observed. Therefore, we decided to look into the structures of these oligomers by investigation on the reactivity of the 8-quinolinolato rhodium catalyst toward terminal alkynes.

When phenylacetylene (**1a**) was reacted in the presence of 8-quinolinolato rhodium cyclooctadiene complex **2** and Ph_3P, formation of the head-to-tail dimer **3a** was observed in 39% NMR yield along with only 3% yield of the *E*-head-to-head dimer **4a** (Scheme 1).

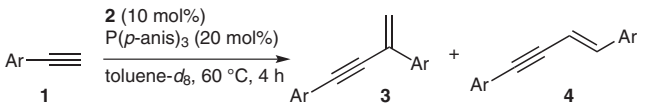


Scheme 1 Rhodium-catalyzed dimerization of phenylacetylene (**1a**)

Phosphine ligands were screened for the alkyne dimerization, and the use of P(*p*-anis)$_3$ improved the yield to 56% (Table 1, entry 1). Various terminal aryl alkynes were then reacted in the presence of catalytic amounts of complex **2** and P(*p*-anis)$_3$. Selective dimerization occurred in moderate to low yields for arylaetylenes with various *para*-substituents such as methoxy, methyl, fluoro, and trifluoromethyl groups (entries 2–5). *m*-Tolylacetylene (**1f**) was dimerized to **3f** in 27% yield (entry 6), while sterically hindered *o*-tolylacetylene (**1g**) dimerized in 47% yield (entry 7). Ferrocenylacetylene (**1h**) also gave the head-to-tail dimer **3h** in 61% yield (entry 8). While the ratios of head-to-tail dimers **3** and the *E*-head-to-head dimers **4** were 4:1 to 9:1 for **1a** and relatively electron-deficient arylacetylenes (entries 1, 4, 5), higher than 10:1 selectivity was achieved for electron-rich arylacetylenes (entries 2, 3, 6–8).

When the alkyne dimerization was conducted in the presence of dimethyl malonate (**5a**), a 2:1 cycloaddition prod-

Table 1 Rhodium-Catalyzed Head-to-Tail Dimerization of Various Arylacetylenes[a]



Entry	1	Ar	3	NMR yield (%)	4	NMR yield (%)
1	**1a**	Ph	**3a**	56	**4a**	8
2	**1b**	4-$MeOC_6H_4$	**3b**	53[b]	**4b**	1
3	**1c**	4-MeC_6H_4	**3c**	35	**4c**	2
4	**1d**	4-FC_6H_4	**3d**	39	**4d**	4
5	**1e**	4-$CF_3C_6H_4$	**3e**	24	**4e**	5
6	**1f**	3-MeC_6H_4	**3f**	27	**4f**	2
7	**1g**	2-MeC_6H_4	**3g**	47	**4g**	2
8	**1h**	ferrocenyl	**3h**	61	**4h**	2

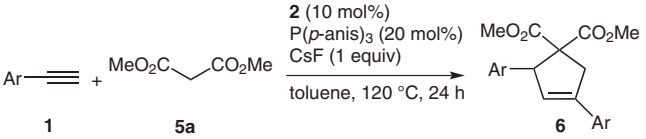
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.02 mmol), P(*p*-anis)$_3$ (0.04 mmol) in toluene-d_8 (0.6 mL), 60 °C, 4 h.
[b] Product **3b** was isolated as a white solid (see Experimental).

uct **6** was obtained (Table 2). The reaction of **1a** with 5 equivalents of **5a** using 10 mol% of **2**, 20 mol% of P(*p*-anis)$_3$, and 1 equivalent of cesium fluoride as a base at 120 °C provided cyclopentene derivative **6a** in 35% isolated yield (Table 2, entry 1). Various *para*-substituted arylacetylenes **1b**–**e** gave the corresponding cyclopentenes **6b**–**e** in 14–32% yields (entries 2–5). *meta*-Substituted arylacetylene **1f** was also converted to cyclopentene **6f** in 32% yield (entry 6). Sterically hindered *o*-tolylacetylene (**1g**) and ferrocenylacetylene (**1h**) did not provide any observable amounts of the corresponding cyclopentene products.

When dimethyl methylmalonate (**5b**) was used as the nucleophile, no cyclopentene product was formed, but an allene containing product **7** was formed in 19% isolated yield (Scheme 2). A similar formation of allenes via nucleophilic addition of malonates to enynes bearing electron-withdrawing groups has been reported,[14] and this led us to propose that allene **7** was formed by rhodium-catalyzed nucleophilic addition of **5b** to enyne **3a**, generated in situ by head-to-tail selective dimerization of **1a**.

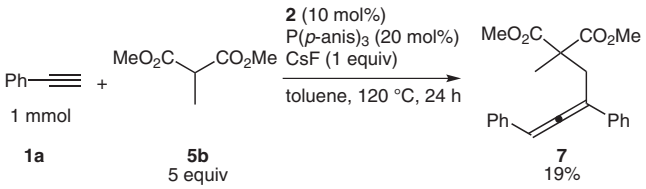
As conjugated enynes **3** were unstable under our reaction conditions, and also was difficult to isolate,[15] a one-pot protocol was devised to explore the efficiency of the addition of malonate species to the head-to-tail dimers. The palladium-catalyzed dimerization of terminal alkynes reported by Trost,[5] which provides the head-to-tail dimers in high yields, was combined with the present rhodium-catalyzed addition of malonates (Table 3). Arylacetylenes **1** were treated with 2 mol% of $Pd(OAc)_2$ and tris(2,6-dimethoxyphenyl)phosphine (TDMPP) at room temperature for 30 minutes, mixed with a solution of **2** and

Table 2 Rhodium-Catalyzed Reaction between Various Arylacetylenes and Dimethyl Malonate[a]



Entry	1	Ar	6	Isolated yield (%)
1	**1a**	Ph	**6a**	35
2	**1b**	4-$MeOC_6H_4$	**6b**	14
3	**1c**	4-MeC_6H_4	**6c**	27
4	**1d**	4-FC_6H_4	**6d**	32
5	**1e**	4-$CF_3C_6H_4$	**6e**	15
6	**1f**	3-MeC_6H_4	**6f**	32

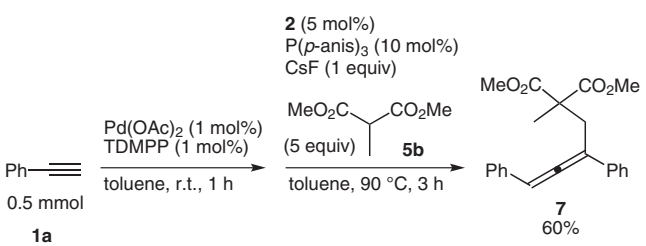
[a] Reaction conditions: **1** (1 mmol), **5a** (5 mmol), **2** (0.10 mmol), P(*p*-anis)$_3$ (0.20 mmol), CsF (1 mmol) in toluene (3 mL), 120 °C, 24 h.



Scheme 2 Rhodium-catalyzed reaction between phenylacetylene (**1a**) and dimethyl methylmalonate (**5b**)

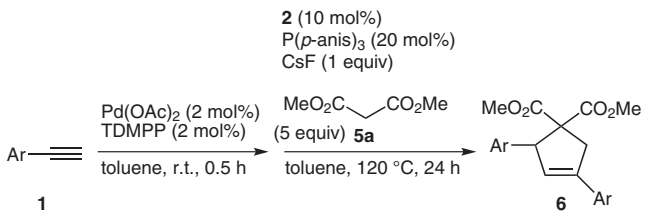
P(*p*-anis)$_3$ in toluene, cesium fluoride, and malonate **5a**, and then heated at 120 °C for 24 hours.[16] This one-pot procedure generally improved the yields of substituted cyclopentene products **6**. For example, arylacetylenes **1a** and **1f** was converted to the corresponding cyclopentenes **6a** and **6f** in 47% and 45% yield, respectively (Table 3, entries 1 and 5). The use of rhodium catalyst **2** is essential to achieve the cyclization; only a trace amount of **6a** was formed in the absence of rhodium catalyst **2**.

The one-pot protocol was applied to the synthesis of allene product **7**. With the reaction conditions reoptimized, the isolated yield of **7** improved to 60% (Scheme 3).



Scheme 3 One-pot sequential palladium- and rhodium-catalyzed reactions between phenylacetylene (**1a**) and dimethyl methylmalonate (**5b**)

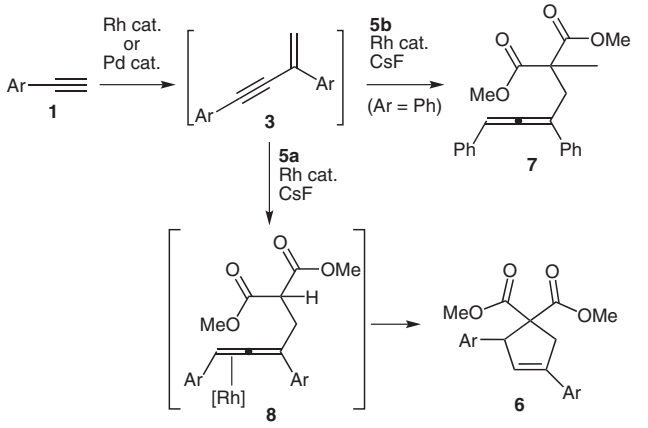
Table 3 One-Pot Sequential Palladium- and Rhodium-Catalyzed Reactions between Arylacetylenes and Dimethyl Malonate[a]



Entry	1	Ar	6	Isolated yield (%)
1	**1a**	Ph	**6a**	47
2	**1b**	4-$MeOC_6H_4$	**6b**	21
3	**1c**	4-MeC_6H_4	**6c**	39
4	**1e**	4-$CF_3C_6H_4$	**6e**	17
5	**1f**	3-MeC_6H_4	**6f**	45

[a] Reaction conditions: **1** (0.50 mmol), $Pd(OAc)_2$ (0.01 mmol), TDMPP (0.01 mmol), toluene (0.5 mL) r.t., 0.5 h, and then **2** (0.50 mmol), P(*p*-anis)$_3$ (0.10 mmol) in toluene (0.5 mL), **5a** (2.5 mmol), CsF (1 mmol), 120 °C, 24 h.

Although the mechanisms for the formations of **6** and **7** remain unclear at the moment, the reactions probably involve head-to-tail dimer **3** as intermediates (Scheme 4), considering that products **6** and **7** can be prepared from **3** generated by rhodium catalyst **2** or Trost's palladium catalyst. The dimerization of alkyne **1** catalyzed by **2** and P(*p*-anis)$_3$ was confirmed to proceed in the presence of cesium fluoride. Formation of allene **7** also suggested that cyclopentene **6** is generated via similar allene intermediate **8**. Because malonate **5a** has one more α-proton than **5b**, intermediate **8** might still undergo nucleophilic addition to the allene moiety in the molecule to form cyclopentene product **6**.



Scheme 4 Possible mechanisms of formation of cyclopentene **6** and allene **7**

In summary, head-to-tail selective dimerization of arylacetylenes **1** was found to be catalyzed by the 8-quinolinolato rhodium-phosphine catalyst system. We also developed a new synthetic route to substituted cyclopentenes **6** and allene **7** using the rhodium catalyst. The yields of **6** and **7** were improved by one-pot procedure employing Trost's palladium catalyst for alkyne dimerization and the 8-quinolinolato rhodium catalyst. Further optimization of the reaction conditions, extension of the scope, and elucidation of the reaction mechanism are now underway.

All procedures were conducted under N_2 using standard Schlenk techniques or a N_2-filled glovebox. Reactions were monitored by TLC (Merck Kieselgel 60 F_{254}), and visualized by exposure to UV light (254 nm) and/or by immersion in Hanessian's stain; by GC (Shimadzu GC-2010); or by ^{1}H NMR recorded on JEOL A400 (400 MHz) or JEOL ECX400 (400 MHz) spectrometer. Flash column chromatography was performed with silica gel 60N (Kanto Chemical Co., Inc.). Toluene was distilled immediately before use from benzophenone ketyl. Catalyst **2** was synthesized by a previously reported method.[12]

Rhodium-Catalyzed Dimerization of Arylacetylenes 1; General Procedure

In a glovebox, 1,3,5-*t*-$Bu_3C_6H_3$ (24.6 mg, 0.1 mmol), **2** (7.1 mg, 0.02 mmol, 10 mol%), P(*p*-anis)$_3$ (14.4 mg, 0.04 mmol, 20 mol%), toluene-d_8 (0.6 mL), and arylacetylene **1** (0.2 mmol, 1 equiv) were added into an NMR tube in this order. The tube was sealed, taken out of the glovebox, and then heated at 60 °C for 4 h. Yields were determined by ^{1}H NMR using 1,3,5-*t*-$Bu_3C_6H_3$ as the internal standard (Table 1).

For **3b**, the mixture was cooled to r.t., and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane–EtOAc, 20:1) to afford a pure product.

Rhodium-Catalyzed Reaction Between Arylacetylenes 1 and Malonates 5; General Procedure

In a glovebox, **2** (35.5 mg, 0.1 mmol, 10 mol%), P(*p*-anis)$_3$ (70.4 mg, 0.2 mmol, 20 mol%), toluene (3 mL), CsF (76.0 mg, 1 mmol, 1 equiv), malonate **5** (5 mmol, 5 equiv), and **1** (1 mmol, 1 equiv) were added into a 10 mL Schlenk tube in this order. The tube was sealed, taken out of the glovebox, and then heated at 120 °C for 24 h. The mixture was cooled to r.t., and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane–EtOAc, 20:1) to afford substituted cyclopentene **6** or allene **7** (Table 2).

One-Pot Sequential Rhodium- and Palladium-Catalyzed Reactions Between Arylacetylenes 1 and Dimethyl Malonate (5a); General Procedure

In a glovebox, $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 2 mol%), TDMPP (4.4 mg, 0.01 mmol, 2 mol%), toluene (0.5 mL), and arylacetylene **1** (0.5 mmol, 1 equiv) were added into a 10 mL Schlenk tube in this order. The solution was stirred for 0.5 h, after which a solution of **2** (17.8 mg, 0.05 mmol, 10 mol%) and P(*p*-anis)$_3$ (35.5 mg, 0.1 mmol, 20 mol%) in toluene (0.5 mL), CsF (76.0 mg, 0.5 mmol, 1 equiv), and **5a** (330 mg, 2.5 mmol, 5 equiv) were added. The tube was sealed, taken out of the glovebox, and then heated at 120 °C for 24 h. The mixture was cooled to r.t., and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane–EtOAc, 20:1) to afford substituted cyclopentene **6** (Table 3).

1,1′-(3-Methyleneprop-1-yne-1,3-diyl)bis(4-methoxybenzene) (3b)
Yield: 66 mg (50%); white solid; mp 77 °C.

IR (KBr): 2961w, 2939w, 2908w, 2840w, 1654m, 1604m, 1559w, 1507s, 1289m, 1248s, 1180m, 1030s, 899m, 837s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.829 (s, 3 H), 3.833 (s, 3 H), 5.62 (s, 1 H), 5.84 (s, 1 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.66 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 55.30, 55.33, 87.5, 90.5, 113.7, 114.0, 115.3, 118.1, 127.3, 130.0, 130.1, 133.1, 159.7, 159.7.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{17}O_2$: 265.12285; found: 265.12236.

Dimethyl 2,4-Diphenylcyclopent-3-ene-1,1-dicarboxylate (6a)
Yield: 59 mg (35%); colorless oil.

IR (KBr): 3032w, 2953m, 2849w, 1733s, 1601w, 1495m, 1436m, 1250s, 1077w, 756w, 699w cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.15 (s, 3 H), 3.17 (d, *J* = 16.9 Hz, 1 H), 3.78 (s, 3 H), 3.92 (d, *J* = 16.9 Hz, 1 H), 5.05 (s, 1 H), 6.14 (s, 1 H), 7.20–7.52 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 40.6, 52.0, 53.0, 57.2, 65.0, 125.8, 126.2, 127.4, 127.9, 128.0, 128.5, 129.0, 134.9, 139.0, 140.2, 169.7, 172.4.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{20}O_4$ + Na: 359.12593; found: 359.12570.

Dimethyl 2,4-Bis(4-methoxyphenyl)cyclopent-3-ene-1,1-dicarboxylate (6b)
Yield: 21 mg (21%); yellow solid; mp 36 °C.

IR (KBr): 2952w, 2837w, 1734s, 1609m, 1513s, 1436m, 1251s, 1178s, 1031s, 829m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.12 (d, *J* = 16.8 Hz, 1 H), 3.21 (s, 3 H), 3.76 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H), 3.85 (d, *J* = 16.8 Hz, 1 H), 4.97 (s, 1 H), 5.97 (s, 1 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 7.12 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 40.5, 52.0, 53.0, 55.2, 55.3, 56.4, 65.0, 113.4, 113.8, 124.4, 127.0, 127.8, 130.1, 131.1, 139.3, 158.8, 159.3, 169.9, 172.6.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{24}O_6$ + Na: 419.14706; found: 419.14757.

Dimethyl 2,4-Bis(4-methylphenyl)cyclopent-3-ene-1,1-dicarboxylate (6c)
Yield: 50 mg (27%); colorless oil.

IR (neat): 3026w, 2952m, 2922w, 2864w, 1734s, 1514m, 1436m, 1249s, 1062w, 813m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.29 (s, 3 H), 2.36 (s, 3 H), 3.14 (d, *J* = 16.8 Hz, 1 H), 3.18 (s, 3 H), 3.76 (s, 3 H), 3.88 (d, *J* = 16.8 Hz, 1 H), 4.98 (s, 1 H), 6.05 (s, 1 H), 7.05 (d, *J* = 8.1 Hz, 2 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 7.40 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 21.0, 21.2, 40.5, 51.9, 52.9, 56.7, 65.0, 125.5, 125.7, 128.7, 128.9, 129.1, 132.1, 135.9, 136.9, 137.6, 139.8, 169.8, 172.5.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{24}O_4$ + Na: 387.15723; found: 387.15790.

Dimethyl 2,4-Bis(4-fluorophenyl)cyclopent-3-ene-1,1-dicarboxylate (6d)
Yield: 12 mg (34%); white solid; mp 138 °C.

IR (KBr): 3059w, 3000w, 2951w, 2843w, 1728s, 1602w, 1510s, 1507s, 1437m, 1302w, 1280s, 1257m, 1217w, 1201m, 1181m, 1165s, 1104m, 1060m, 964w, 951w, 939w, 826m, 788w cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.13 (d, *J* = 16.8 Hz, 1 H), 3.20 (s, 3 H), 3.79 (s, 3 H), 3.85 (d, *J* = 16.8 Hz, 1 H), 5.04 (s, 1 H), 6.02 (s, 1 H), 6.95 (dd, *J* = 8.8, 8.6 Hz, 2 H), 7.05 (dd, *J* = 8.8, 8.8 Hz, 2 H), 7.18 (dd, *J* = 8.8, 5.4 Hz, 2 H), 7.46 (dd, *J* = 8.8, 5.4 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 40.8, 52.1, 53.1, 56.4, 64.9, 114.9 (d, $J_{C,F}$ = 20.7 Hz), 115.4 (d, *J* = 21.6 Hz), 125.6, 127.5 (d, *J* = 8.5 Hz), 130.6 (d, $J_{C,F}$ = 7.5 Hz), 131.0 (d, $J_{C,F}$ = 3.8 Hz), 134.7 (d, $J_{C,F}$ = 2.8 Hz), 139.4, 162.1 (d, $J_{C,F}$ = 246.2 Hz), 162.5 (d, $J_{C,F}$ = 248.0 Hz), 169.6, 172.2.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{18}F_2O_4$ + Na: 395.10709; found: 395.10702.

Dimethyl 2,4-Bis(4-trifluoromethylphenyl)cyclopent-3-ene-1,1-dicarboxylate (6e)
Yield: 40 mg (15%); white solid; mp 126 °C.

IR (KBr): 2955w, 1732s, 1617m, 1434w, 1418w, 1327s, 1271m, 1251m, 1229w, 1167s, 1109s, 1068s, 1017m, 967w, 908w, 857w, 842m, 828m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.15 (s, 3 H), 3.21 (d, *J* = 16.8 Hz, 1 H), 3.81 (s, 3 H), 3.92 (d, *J* = 16.8 Hz, 1 H), 5.16 (s, 1 H), 6.21 (s, 1 H), 7.35 (d, *J* = 8.3 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.60 (d, *J* = 8.3 Hz, 2 H), 7.63 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 41.0, 52.4, 53.5, 57.1, 65.2, 124.3 (q, *J* = 272.5 Hz), 124.3 (q, *J* = 272.5 Hz), 125.3 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 3.8 Hz), 126.3, 128.0, 129.6, 130.0 (q, *J* = 32.6 Hz), 130.1 (q, *J* = 32.9 Hz), 138.2, 140.4, 143.2, 169.5, 172.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{18}F_6O_4$ + Na: 495.10070; found: 495.09946.

Dimethyl 2,4-Bis(3-methylphenyl)cyclopent-3-ene-1,1-dicarboxylate (6f)
Yield: 58 mg (32%); yellow oil.

IR (neat): 3032m, 2953m, 1735s, 1700m, 1652w, 1604w, 1437m, 1253s, 1156w, 1057w, 784m, 703m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.29 (s, 3 H), 2.37 (s, 3 H), 3.5 (d, *J* = 16.8 Hz, 1 H), 3.17 (s, 3 H), 3.77 (s, 3 H), 3.90 (d, *J* = 16.8 Hz, 1 H), 5.00 (s, 1 H), 6.10 (s, 1 H), 6.99–7.33 (m, 8 H).

^{13}C NMR ($CDCl_3$): δ = 21.3, 21.4, 40.6, 51.9, 52.9, 57.0, 65.0, 122.9, 126.1, 126.2, 126.5, 127.9, 128.0, 128.4, 128.5, 129.7, 134.9, 137.5, 138.0, 138.9, 140.1, 169.7, 172.4.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{24}O_4$ + Na: 387.15723; found: 387.15724.

One-Pot Rhodium- and Palladium-Catalyzed Reaction between Phenylacetylene (1a) and Malonate 5b; Dimethyl 2-(2,4-Diphenylbuta-2,3-dienyl)-2-methylmalonate (7)
In a glovebox, $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 1 mol%), TDMPP (2.2 mg, 0.005 mmol, 1 mol%), toluene (0.5 mL), and phenylacetylene (**1a**; 51 mg, 0.5 mmol, 1 equiv) were added into a 10 mL Schlenk tube in this order. The solution was stirred for 1 h, after which a solution of **2** (8.9 mg, 0.025 mmol, 5 mol%) and P(*p*-anis)$_3$ (17.8 mg, 0.05 mmol, 20 mol%) in toluene (0.5 mL), CsF (76.0 mg, 0.5 mmol, 1 equiv), and **5b** (365 mg, 2.5 mmol, 5 equiv) were added. The tube was sealed, taken out of the glovebox, and then heated at 90 °C for 3 h. The mixture was cooled to r.t., and hexane (10 mL) was added, which gave a white precipitate. The precipitate was removed by filtration, and the solution was concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane–EtOAc, 25:1) to afford allene **7** mixed with **5b**. Bulb-to-bulb distillation of the mixture gave pure **7**; yield: 54 mg (60%); colorless oil.

IR (neat): 2998s, 2953w, 2844w, 1936w, 1735s, 1597w, 1494w, 1458w, 1447w, 1435w, 1378w, 1300w, 1247m, 1202m, 1161m, 1101m, 1029w, 986w, 914w, 873w, 828w, 762w, 746s, 718w, 693m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.50 (s, 3 H), 3.19 (dd, *J* = 15.1, 2.7 Hz, 1 H), 3.30 (dd, *J* = 15.1, 2.7 Hz, 1 H), 3.46 (s, 3 H), 3.57 (s, 3 H), 6.49 (t, *J* = 2.7 Hz, 1 H), 7.20–7.45 (m, 10 H).

^{13}C NMR ($CDCl_3$): δ = 20.1, 35.7, 52.5, 52.5, 53.6, 98.3, 105.2, 126.4, 127.1, 127.3, 127.4, 128.5, 128.7, 133.7, 136.3, 172.0, 172.3, 207.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{22}O_4$ + Na: 373.14158; found: 373.14129.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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