DOI: 10.1002/ejoc.200701043

Synthesis of Indene and Naphthalene Derivatives by a Palladium-Catalyzed Domino Carbopalladation/Cyclization/Coupling Process

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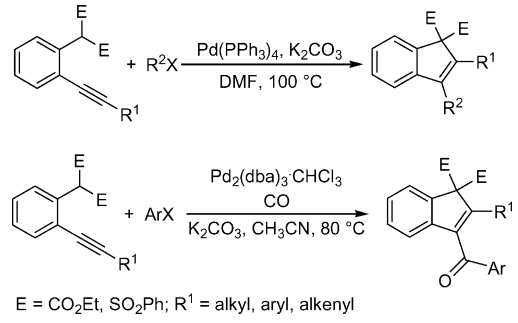
Keywords: Domino reactions / Carbopalladation / Cyclization / C-C coupling

Highly substituted indene and naphthalene derivatives have been readily prepared in good-to-high yields by a palladium-catalyzed domino reaction. This domino reaction involves a Heck carbopalladation/cyclization/coupling process.

Introduction

Transition-metal-catalyzed domino reactions are versatile and powerful tools of contemporary organic synthesis.[1,2] In particular, palladium-catalyzed domino cyclization reactions based on sequences of insertions of organopalladium species into multiple bonds have attracted great interest because these processes allow a considerable increase in the molecular complexity in a single operation and usually proceed with excellent chemo-, regio- and stereoselectivity under mild conditions.[3–5] They also greatly enhance the efficiency of the synthesis and minimize the amount of reagents required.

Carbocycles and heterocycles are extremely important and basic skeletons of many biologically active natural products with specific structures. The palladium-catalyzed annulation of alkynes is particularly effective for the synthesis of a wide variety of carbocycles and heterocycles.[6] On the other hand, domino reactions initiated by intramolecular Heck reactions have been developed and advanced to prepare complex molecules in a single operation.[3–5] The key step in these reactions is the *syn* addition of arylpalladium halide to the triple bond which affords an intermediate that can participate in a wide variety of useful synthetic processes. Recently, we successfully employed the annulation of alkynes in the synthesis of various highly substituted indenes (Scheme 1).[7] Pursuing our interest in constructing carbocycles, we herein wish to report the synthesis of highly substituted indene and naphthalene derivatives by the palladium-catalyzed Heck/Suzuki–Miyaura, Heck/Sonogashira and Heck/Heck domino reactions (Scheme 2).



Scheme 1.

Results and Discussion

To find the optimum reaction conditions, diethyl 2-(2-iodophenyl)-2-(3-phenylprop-2-ynyl)malonate (**1a**) was used as a model compound, and a series of experiments was performed with phenylboronic acid (**2a**). After a brief survey of reaction conditions, it was found that $Pd(PPh_3)_4$ gave the best yield. Among bases such as K_2CO_3, Et_3N, KOAc, Cs_2CO_3 and KO*t*Bu, K_2CO_3 gave the best results. DMF was an excellent solvent.

Subsequently, the reaction with various substrates was examined. The results of the palladium-catalyzed domino cyclization reactions of **1** and boronic acids **2** are shown in Table 1. The reaction of **1a** (0.2 mmol) with 1.2 equiv. of phenylboronic acid (**2a**) in the presence of 5 mol-% $Pd(PPh_3)_4$ in DMF under argon at 100 °C for 2 h gave diethyl 2,3-dihydro-3-(diphenylmethylene)indene-1,1-dicarboxylate (**3a**) in 85% isolated yield (Table 1, entry 1). Phenylboronic acids bearing an electron-donating or

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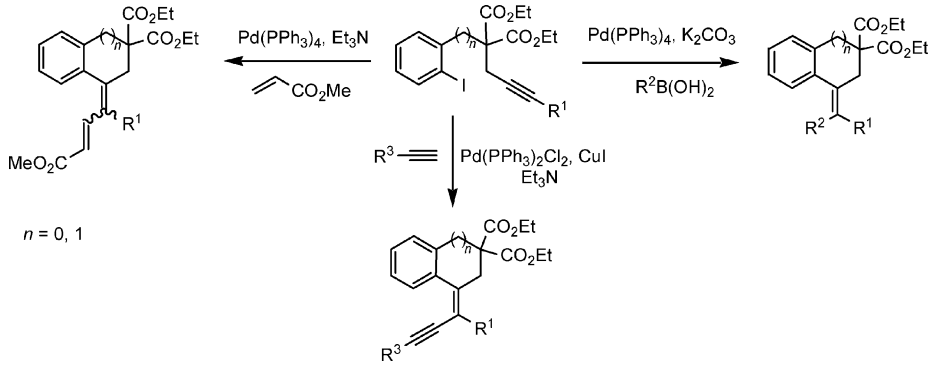


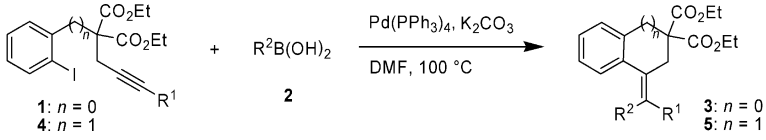
Scheme 2.

-withdrawing group in the *para*, *ortho* or *meta* positions usually gave good yields of the corresponding 3-substituted (*Z*)-2,3-dihydroindenes with high stereoselectivity (entries 2–8). Disubstituted phenylboronic acid **2i** also worked well to give the indene product (*Z*)-**3i** as a single stereoisomer (entry 9). However, no trace of the target product was isolated from the reaction of **1a** with **2j** (entry 10). The reaction of substrates **1** bearing an electron-donating or -withdrawing group on the aromatic ring such as **1b** and **1c** also stereoselectively gave the desired cyclized products (*E*)-**3k** and (*E*)-**3l**, respectively, in high yields (entries 11 and 12). However, when R^1 = H, a mixture of unidentified products was obtained (entry 13). The structure and absolute stereochemistry of (*Z*)-**3d** was unambiguously confirmed by its X-ray crystallographic data.[8] Encouraged by these results, we examined the reaction of substrate **4** with some arylboronic acids **2** under these optimized conditions. Similarly, the corresponding (*Z*)-naphthalene derivatives were obtained in good-to-high yields (entries 15–18).

Meanwhile, we examined the reaction of the easily prepared double aryl halide **1e** under the same conditions by using 0.2 mmol of **1e** and 2.4 equiv. of **2a**. To our delight, the reaction proceeded well at both the triple bonds and afforded the expected product **3m** in 63% isolated yield (Scheme 3). Remarkably, four carbon–carbon bonds were formed in a single step. This result clearly indicates the utility of our tandem cyclization as an efficient method for the synthesis of complex carbocycles.

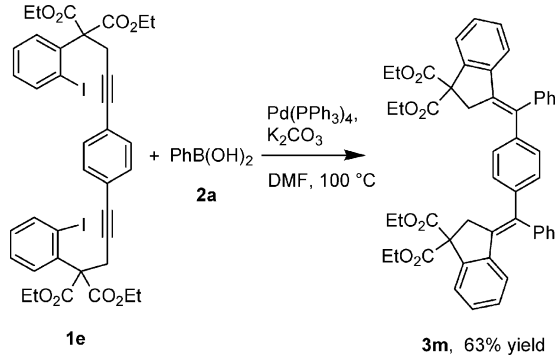
To further explore the scope and versatility of this tandem cyclization reaction, we next investigated the reaction of the substrate **1a** and **4** with a variety of terminal alkynes **6**. As shown in Table 2, the Heck/Sonogashira domino reaction proceeded well with both aliphatic and aromatic alkynes and afforded the corresponding products in good-to-

Table 1. Palladium-catalyzed Heck/Suzuki–Miyaura domino reaction of **1** or **4** with various boronic acids **2**.[a]



Entry	R^1	R^2	Time [h]	**3** or **5**	% Yield[b]
1	Ph (**1a**)	Ph (**2a**)	2	**3a**	85
2	**1a**	*p*-MeO-Ph (**2b**)	3	**3b**	81
3	**1a**	*p*-CH_3-Ph (**2c**)	2	**3c**	83
4	**1a**	*p*-CH_3CO-Ph (**2d**)	5	**3d**	80
5	**1a**	*o*-MeO-Ph (**2e**)	2	**3e**	95
6	**1a**	*o*-CH_3-Ph (**2f**)	2	**3f**	88
7	**1a**	*m*-CH_3-Ph (**2g**)	5	**3g**	87
8	**1a**	*m*-NO_2-Ph (**2h**)	5	**3h**	96
9	**1a**	2,6-dimethoxy (**2i**)	5	**3i**	56
10	**1a**	Bu (**2j**)	5	**3j**	0
11	*p*-CH_3-Ph (**1b**)	**2a**	3	**3k**	87
12	*p*-CH_3CO-Ph (**1c**)	**2a**	2	**3l**	91
13	H (**1d**)	**2a**	5	mixture	–
14	Ph (**4**)	**2a**	5	**5a**	93
15	**4**	**2c**	5	**5c**	92
16	**4**	**2d**	5	**5d**	85
17	**4**	**2f**	5	**5f**	89
18	**4**	**2g**	5	**5g**	92

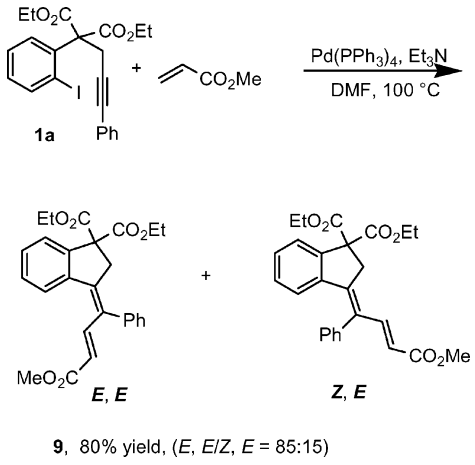
[a] Reaction conditions: **1** or **4** (1.0 equiv.), boronic acid **2** (1.2 equiv.), K_2CO_3 (2.0 equiv.) and $Pd(PPh_3)_4$ (5 mol-%) in DMF at 100 °C. [b] Isolated yield.



Scheme 3.

high yields. The stereoselectivities were very good and only the *Z* stereoisomer was formed during this reaction.[5b,9]

We then applied these methods to the synthesis of compound **9** by a Heck/Heck domino reaction (Scheme 4). On the basis of the above results, the regioselective *syn* insertion of arylpalladium species into the triple bond of the diethyl malonate alkyne was expected. However, after some trials, a separable mixture of two stereoisomers (*E*,*E*/*Z*,*E* = 85:15)



Scheme 4.

was obtained.[10,11] The *E* configuration of the tetrasubstituted double bond in the major diastereomer was deduced from the NOESY spectrum by the interaction between the proton of the double bond and the proton of the methylene in the 2-position of the indene moiety.

Conclusions

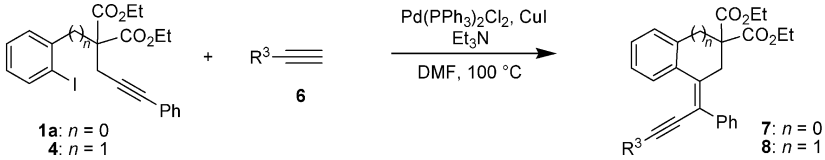
In summary, we have developed an efficient method for the preparation of structurally versatile indene and naphthalene derivatives in good-to-high yields by palladium-catalyzed Heck/Suzuki–Miyaura, Heck/Sonogashira and Heck/Heck domino reactions. This transformation leads to the formation of two C–C bonds in a one-pot process and high selectivity is observed for the sequential process.

Experimental Section

General Remarks: All reactions were performed under argon. Unless otherwise stated, all boronic acids and terminal alkynes were purchased from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel. Melting points were determined with a microscopic apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ with spectrometers operating at 300 or 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ with spectrometers operating at 75 or 100 MHz with TMS as the internal standard. IR spectra were recorded on a FTIR spectrometer and only the major peaks are reported. All products were characterized by element analysis.

General Procedure for the Preparation of Substrates 1a–1c, 1e and 4: K_2CO_3 (4.0 mmol) was added to a solution of diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and (3-bromoprop-1-ynyl)benzene (2.4 mmol) in DMF (5.0 mL). The mixture was stirred for 2 h at room temperature. Then, the reaction mixture was diluted with EtOAc. The EtOAc solution was washed with water and saturated brine. The organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding substrates.

Table 2. Palladium-catalyzed Heck/Sonogashira domino reaction of **1a** or **4** with various alkynes **6**.[a]



Entry	**1a** or **4**	R^3	Time [h]	**7** or **8**	% Yield[b]
1	**1a**	Ph (**6a**)	5	**7a**	85
2	**1a**	*p*-MeO-Ph (**6b**)	5	**7b**	89
3	**1a**	1-cyclohexenyl (**6c**)	6	**7c**	87
4	**1a**	TMS (**6d**)	6	**7d**	91
5	**1a**	*n*-pentyl (**6e**)	12	**7e**	42[c]
6	**4**	**6a**	5	**8a**	82
7	**4**	**6b**	5	**8b**	73
8	**4**	**6c**	6	**8c**	60

[a] Reaction conditions: **1a** or **4** (1.0 equiv.), alkyne **6** (1.5 equiv.), Et_3N (2.0 equiv.), CuI (10 mol-%) and $Pd(PPh_3)_2Cl_2$ (5 mol-%) in DMF at 100 °C. [b] Isolated yield. [c] The reaction was run at 60 °C.

Diethyl 2-(2-Iodophenyl)-2-(3-phenylprop-2-ynyl)malonate (1a): Compound **1a** was prepared following the above procedure, employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and (3-bromoprop-1-ynyl)benzene (0.47 g, 2.4 mmol) to afford **1a** (0.83 g, 87%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.93 (dd, J = 1.2, 8.1 Hz, 1 H), 7.37–7.24 (m, 2 H), 7.20–7.10 (m, 5 H), 7.00–6.95 (m, 1 H), 4.41–4.21 (m, 4 H), 3.64 (s, 2 H), 1.31–1.26 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 141.8, 139.5, 131.3, 130.8, 129.0, 127.9, 127.5, 123.5, 97.6, 85.8, 83.1, 66.5, 62.4, 26.4, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3450, 2982, 1744, 1466, 1257, 1202, 1013 cm^{-1}.

Diethyl 2-(2-Iodophenyl)-2-[3-(*p*-tolyl)prop-2-ynyl]malonate (1b): Compound **1b** was prepared following the above procedure, employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and 1-(3-bromoprop-1-ynyl)-4-methylbenzene (0.50 g, 2.4 mmol) to afford **1b** (0.86 g, 88%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 1 H), 7.38–7.26 (m, 2 H), 7.04–6.96 (m, 5 H), 4.42–4.21 (m, 4 H), 3.62 (s, 2 H), 2.28 (s, 3 H), 1.32–1.27 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 141.8, 139.6, 137.5, 131.2, 130.8, 129.0, 128.7, 127.6, 120.4, 97.7, 84.9, 83.2, 66.6, 62.5, 26.4, 21.4, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3442, 2982, 1744, 1466, 1256, 1201, 1014 cm^{-1}.

Diethyl 2-[3-(4-Acetylphenyl)prop-2-ynyl]-2-(2-iodophenyl)malonate (1c): Compound **1c** was prepared following the above procedure, employing diethyl (2-iodophenyl)malonate (0.72 g, 2.0 mmol) and 4-(3-bromoprop-1-ynyl)phenylethanone (0.57 g, 2.4 mmol) to afford **1c** (0.95 g, 92%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.95 (m, 1 H), 7.80–7.77 (d, J = 8.7 Hz, 2 H), 7.39–7.34 (m, 1 H), 7.27–7.21 (m, 1 H), 7.19–7.16 (d, J = 8.1 Hz, 2 H), 7.04–6.98 (m, 1 H), 4.42–4.25 (m, 4 H), 3.68 (s, 2 H), 2.55 (s, 3 H), 1.33–1.24 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.3, 168.7, 141.9, 139.3, 135.6, 131.4, 130.7, 129.1, 128.5, 127.9, 127.6, 97.4, 89.9, 82.5, 66.5, 62.6, 26.5, 26.3, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3448, 3349, 2982, 1743, 1683, 1601, 1466, 1361, 1262, 1202, 1014 cm^{-1}.

Compound 1e: Compound **1e** was prepared following the above procedure, employing diethyl (2-iodophenyl)malonate (0.87 g, 2.4 mmol) and 1,4-bis(3-bromoprop-1-ynyl)benzene (0.31 g, 1.0 mmol) to afford **1e** (0.62 g, 71%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.93 (dd, J = 1.2, 7.6 Hz, 1 H), 7.36–7.29 (m, 5 H), 7.24–7.22 (dd, J = 1.6, 8.0 Hz, 1 H), 7.00–6.95 (m, 5 H), 4.39–4.23 (m, 8 H), 3.63 (s, 4 H), 1.32–1.27 (t, J = 7.2 Hz, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 141.8, 139.3, 132.7, 131.1, 130.6, 129.0, 127.5, 122.3, 121.5, 97.4, 87.1, 82.0, 66.4, 62.4, 26.2, 13.7 ppm. IR (neat): $\tilde{\nu}$ = 3449, 2981, 1744, 1484, 1467, 1257, 1202, 1012 cm^{-1}.

Diethyl 2-(2-Iodobenzyl)-2-(3-phenylprop-2-ynyl)malonate (4): Compound **4** was prepared following the above procedure, employing diethyl (2-iodobenzyl)malonate (0.75 g, 2.0 mmol) and (3-bromoprop-1-ynyl)benzene (0.47 g, 2.4 mmol) to afford **4** (0.86 g, 88%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.81 (m, 1 H), 7.44–7.40 (m, 3 H), 7.29–7.23 (m, 4 H), 6.91–6.86 (m, 1 H), 4.30–4.14 (m, 4 H), 3.70 (s, 2 H), 3.03 (s, 2 H), 1.25–1.20 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 139.9, 139.2, 131.5, 130.6, 128.6, 128.1, 127.9, 123.0, 102.1, 84.9, 84.2, 61.6, 58.0, 41.2, 24.1, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3466, 2981, 1732, 1468, 1439, 1276, 1202, 1064 cm^{-1}.

General Procedure for the Preparation of 3 and 5: A mixture of diethyl (2-iodophenyl)-2-(3-arylprop-2-ynyl)malonate or diethyl (2-iodobenzyl)-2-(3-phenylprop-2-ynyl)malonate (**1** or **4**; 0.20 mmol), boronic acids **2** (0.24 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol-%) and DMF (2.0 mL) was placed in a 25 mL flask under argon. The resulting mixture was then heated under argon at 100 °C. When the reaction was considered complete, as determined by TLC analysis, the reaction mixture was cooled to room temperature, quenched with a saturated aqueous solution of ammonium chloride and extracted with EtOAc. The combined organic extracts were washed with water and saturated brine. The organic layers were dried with Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding substituted indene (**3**) or naphthalene (**5**) derivatives.

Diethyl 3-(Diphenylmethylene)-2,3-dihydroindene-1,1-dicarboxylate (3a): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 72.4 mg (85%) of the title compound as a solid; m.p. 94–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.58 (d, J = 8.1 Hz, 1 H), 7.33–7.13 (m, 11 H), 6.97–6.92 (m, 1 H), 6.47–6.44 (d, J = 7.5 Hz, 1 H), 4.23–4.16 (m, 4 H), 3.52 (s, 2 H), 1.28–1.22 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 142.9, 142.1, 141.1, 136.7, 135.6, 129.6, 129.0, 128.7, 128.1, 127.9, 127.7, 127.3, 126.9, 126.5, 124.9, 63.1, 61.7, 42.4, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3467, 2982, 1733, 1444, 1259, 1239, 1050 cm^{-1}. $C_{28}H_{26}O_4$ (426.18): calcd. C 78.85, H 6.14; found C 78.72, H 6.04.

Diethyl (*Z*)-3-[(4-Methoxyphenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3b): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 73.9 mg (81%) of the title compound as a solid; m.p. 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.58 (dd, J = 0.8, 7.6 Hz, 1 H), 7.34–7.30 (m, 2 H), 7.27–7.23 (m, 3 H), 7.19–7.13 (m, 3 H), 7.01–6.97 (m, 1 H), 6.88–6.86 (m, 2 H), 6.58–6.56 (m, 1 H), 4.24–4.17 (m, 4 H), 3.82 (s, 3 H), 3.50 (s, 2 H), 1.28–1.23 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 158.9, 143.3, 142.0, 141.4, 136.4, 135.4, 134.4, 130.9, 129.1, 128.1, 127.9, 127.6, 126.9, 126.4, 124.9, 114.1, 63.2, 61.7, 55.2, 42.4, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3468, 2982, 1733, 1603, 1509, 1463, 1244, 1031 cm^{-1}. $C_{29}H_{28}O_5$ (456.19): calcd. C 76.30, H 6.18; found C 76.42, H 6.07.

Diethyl (*Z*)-3-[Phenyl(*p*-tolyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3c): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 73.0 mg (83%) of the title compound as a solid; m.p. 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.58 (d, J = 8.0 Hz, 1 H), 7.33–7.10 (m, 10 H), 7.00–6.96 (m, 1 H), 6.55–6.53 (d, J = 8.0 Hz, 1 H), 4.25–4.18 (m, 4 H), 3.51 (s, 2 H), 2.37 (s, 3 H), 1.27–1.22 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 143.2, 142.1, 141.3, 139.1, 136.9, 136.8, 135.4, 129.5, 129.0, 128.1, 127.9, 127.6, 126.8, 126.5, 125.0, 63.1, 61.7, 42.3, 21.3, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3472, 2983, 1734, 1464, 1260, 1231, 1025 cm^{-1}. $C_{29}H_{28}O_4$ (440.20): calcd. C 79.07, H 6.41; found C 79.12, H 6.37.

Diethyl (*Z*)-3-[(4-Acetylphenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3d): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 74.9 mg (80%) of the title compound as a solid; m.p. 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.93 (dd, J = 2.0, 8.4 Hz, 2 H), 7.63–7.61 (dd, J = 0.8, 8.0 Hz, 1 H), 7.37–7.32 (m, 4 H), 7.28–7.18 (m, 4 H), 7.00–6.96 (m, 1 H), 6.51–6.49 (d, J = 7.6 Hz, 1 H), 4.25–4.19 (m, 4 H), 3.52 (s, 2 H), 2.62 (s, 3 H), 1.28–1.24 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 170.0, 147.2, 142.4, 142.3, 140.6, 136.8, 136.0, 135.5, 130.1, 129.0, 128.8, 128.3, 128.2, 128.1, 127.3, 126.7, 124.8, 63.1, 61.8, 42.4, 26.5, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3466, 3349, 2982, 1732, 1683, 1600, 1362, 1262, 1050, 1022 cm^{-1}. $C_{30}H_{28}O_5$ (468.19): calcd. C 76.90, H 6.02; found C 76.72, H 6.17.

Diethyl (*Z*)-3-[(2-Methoxyphenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3e): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 86.6 mg (95%)

of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.57 (d, J = 7.6 Hz, 1 H), 7.35–7.28 (m, 5 H), 7.22–7.14 (m, 3 H), 6.98–6.90 (m, 3 H), 6.40–6.38 (d, J = 7.6 Hz, 1 H), 4.27–4.14 (m, 4 H), 3.62–3.47 (q, J = 16.4, 45.2 Hz, 2 H), 3.57 (s, 3 H), 1.31–1.20 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 157.2, 142.6, 141.8, 141.4, 136.2, 133.2, 130.9, 128.9, 128.6, 128.1, 127.9, 127.5, 126.6, 126.4, 124.4, 121.1, 111.8, 63.0, 61.7, 55.6, 41.4, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3466, 2982, 1733, 1596, 1463, 1367, 1241, 1049, 1026 cm^{-1}. $C_{29}H_{28}O_5$ (456.19): calcd. C 76.30, H 6.18; found C 76.12, H 6.27.

Diethyl (*Z*)-3-[Phenyl(*o*-tolyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3f): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 77.4 mg (88%) of the title compound as a solid; m.p. 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.59 (d, J = 7.6 Hz, 1 H), 7.31–7.29 (m, 4 H), 7.24–7.14 (m, 6 H), 6.96–6.92 (m, 1 H), 6.20–6.18 (d, J = 8.4 Hz, 1 H), 4.24–4.17 (m, 4 H), 3.70–3.55 (q, J = 16.4, 44.8 Hz, 2 H), 2.08 (s, 3 H), 1.27–1.22 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 170.2, 141.9, 141.7, 141.4, 141.3, 136.4, 135.9, 135.5, 130.6, 129.9, 128.8, 128.3, 128.1, 127.7, 127.5, 126.8, 126.4, 124.3, 63.1, 61.8, 41.8, 19.5, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3466, 2981, 1733, 1463, 1258, 1050 cm^{-1}. $C_{29}H_{28}O_4$ (440.20): calcd. C 79.07, H 6.41; found C 79.14, H 6.29.

Diethyl (*Z*)-3-[Phenyl(*m*-tolyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3g): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 76.6 mg (87%) of the title compound as a solid; m.p. 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.58 (m, 1 H), 7.34–7.27 (m, 4 H), 7.24–7.11 (m, 4 H), 7.05–6.94 (m, 3 H), 6.48–6.46 (d, J = 8.0 Hz, 1 H), 4.24–4.18 (m, 4 H), 3.51 (s, 2 H), 2.30 (s, 3 H), 1.27–1.23 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 143.0, 141.9, 141.1, 138.3, 136.8, 135.4, 130.0, 128.9, 128.6, 128.1, 128.0, 127.6, 126.8, 126.6, 126.4, 124.9, 63.0, 61.7, 42.1, 21.3, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3467, 2982, 1733, 1464, 1259, 1050 cm^{-1}. $C_{29}H_{28}O_4$ (440.20): calcd. C 79.07, H 6.41; found C 79.01, H 6.37.

Diethyl (*Z*)-3-[(3-Nitrophenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3h): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 90.1 mg (96%) of the title compound as a solid; m.p. 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20–8.10 (m, 2 H), 7.66–7.61 (m, 2 H), 7.53–7.49 (m, 1 H), 7.38–7.20 (m, 6 H), 7.00–6.96 (m, 1 H), 6.43–6.41 (d, J = 8.0 Hz, 1 H), 4.26–4.20 (m, 4 H), 3.53 (s, 2 H), 1.28–1.24 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 148.7, 143.7, 142.5, 141.7, 140.1, 137.8, 136.3, 133.8, 129.7, 129.0, 128.5, 128.1, 127.5, 126.9, 124.7, 124.4, 122.3, 63.0, 61.9, 42.5, 13.9 ppm. IR (KBr): $\tilde{\nu}$ = 3466, 2926, 1733, 1530, 1465, 1347, 1260, 1051 cm^{-1}. $C_{28}H_{25}NO_6$ (471.17): calcd. C 71.33, H 5.34, N 2.97; found C 71.23, H 5.41, N 2.87.

Diethyl (*Z*)-3-[(2,6-Dimethoxyphenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3i): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 54.4 mg (56%) of the title compound as a solid; m.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.50 (dd, J = 0.8, 8.0 Hz, 1 H), 7.42–7.39 (m, 2 H), 7.31–7.24 (m, 3 H), 7.21–7.14 (m, 2 H), 7.00–6.96 (m, 1 H), 6.60–6.58 (d, J = 8.8 Hz, 2 H), 6.45–6.43 (d, J = 8.0 Hz, 1 H), 4.23–4.16 (m, 4 H), 3.58 (s, 6 H), 3.54 (s, 2 H), 1.25–1.22 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 157.8, 143.0, 141.9, 141.6, 136.7, 128.9, 128.5, 128.3, 127.8, 127.4, 126.4, 123.3, 119.8, 104.8, 63.1, 61.6, 55.9, 40.9, 13.9 ppm. IR (KBr): $\tilde{\nu}$ = 3423, 2981, 1733, 1588, 1468, 1249, 1110, 1049 cm^{-1}. $C_{30}H_{30}O_6$ (486.20): calcd. C 74.06, H 6.21; found C 73.94, H 6.19.

Diethyl (*E*)-3-[Phenyl(*p*-tolyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3k): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 76.6 mg (87%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.58 (d, J = 7.8 Hz, 1 H), 7.34–7.27 (m, 3 H), 7.24–7.11 (m, 7 H), 6.96–6.91 (m, 1 H), 6.45–6.42 (d, J = 8.1 Hz, 1 H), 4.24–4.15 (m, 4 H), 3.54 (s, 2 H), 2.33 (s, 3 H), 1.27–1.22 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.2, 142.2, 141.9, 141.3, 140.0, 136.7, 136.6, 135.1, 129.7, 128.9, 128.8, 128.7, 127.9, 127.5, 127.2, 126.4, 124.9, 63.1, 61.7, 42.3, 21.2, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3468, 2982, 1733, 1464, 1258, 1231, 1050 cm^{-1}. $C_{29}H_{28}O_4$ (440.20): calcd. C 79.07, H 6.41; found C 78.93, H 6.27.

Diethyl (*E*)-3-[(4-Acetylphenyl)(phenyl)methylene]-2,3-dihydroindene-1,1-dicarboxylate (3l): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 85.2 mg (91%) of the title compound as a solid; m.p. 77–79 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.92 (d, J = 8.4 Hz, 2 H), 7.63–7.61 (d, J = 7.8 Hz, 1 H), 7.39–7.34 (m, 5 H), 7.25–7.18 (m, 3 H), 7.00–6.95 (m, 1 H), 6.48–6.45 (d, J = 8.1 Hz, 1 H), 4.25–4.18 (q, J = 7.2 Hz, 4 H), 3.51 (s, 2 H), 2.59 (s, 3 H), 1.28–1.23 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.6, 170.0, 147.7, 142.2, 141.3, 140.7, 137.2, 135.5, 135.4, 129.7, 129.2, 128.9, 128.3, 128.2, 128.0, 127.6, 126.5, 125.1, 63.0, 61.8, 42.2, 26.6, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 3467, 3348, 2982, 1732, 1683, 1600, 1465, 1362, 1264, 1050 cm^{-1}. $C_{30}H_{28}O_5$ (468.19): calcd. C 76.90, H 6.02; found C 76.83, H 6.11.

Compound 3m: The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 97.5 mg (63%) of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.59 (d, J = 8.0 Hz, 2 H), 7.46–7.43 (m, 4 H), 7.35–7.32 (m, 4 H), 7.22–7.13 (m, 8 H), 6.98–6.94 (m, 2 H), 6.45–6.43 (d, J = 8.0 Hz, 2 H), 4.25–4.19 (m, 8 H), 3.48 (s, 4 H), 1.28–1.23 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 142.1, 141.8, 141.5, 140.9, 136.3, 135.5, 131.3, 130.8, 129.7, 128.9, 128.0, 127.6, 126.6, 125.0, 120.9, 63.1, 61.9, 42.3, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3465, 2982, 1733, 1485, 1391, 1259, 1240, 1070, 1011 cm^{-1}. $C_{50}H_{46}O_8$ (774.32): calcd. C 77.50, H 5.98; found C 77.34, H 6.13.

Diethyl 4-(Diphenylmethylene)-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (5a): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 81.8 mg (93%) of the title compound as a solid; m.p. 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 3 H), 7.16–7.10 (m, 6 H), 7.04–6.97 (m, 3 H), 6.79–6.69 (m, 2 H), 4.18–4.11 (m, 2 H), 4.04–3.98 (m, 2 H), 3.34 (s, 2 H), 3.13 (s, 2 H), 1.13–1.09 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 143.6, 143.1, 141.2, 135.9, 135.1, 131.0, 130.6, 130.4, 128.2, 128.0, 127.0, 126.7, 124.8, 61.4, 55.0, 35.2, 34.9, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 3463, 2958, 1733, 1445, 1367, 1255, 1184, 1053 cm^{-1}. $C_{29}H_{28}O_4$ (440.20): calcd. C 79.07, H 6.41; found C 79.01, H 6.43.

Diethyl (*Z*)-4-[Phenyl(*p*-tolyl)methylene]-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (5c): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 83.5 mg (92%) of the title compound as a solid; m.p. 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.23 (m, 3 H), 7.15–7.10 (m, 4 H), 7.04–6.81 (m, 5 H), 6.75–6.71 (m, 1 H), 4.17–4.11 (m, 2 H), 4.04–3.98 (m, 2 H), 3.33 (s, 2 H), 3.11 (s, 2 H), 2.27 (s, 3 H), 1.14–1.09 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 143.3, 141.1, 140.6, 136.4, 136.2, 135.0, 131.0, 130.9, 130.4, 130.1, 128.7, 128.2, 127.9, 126.9, 126.7, 124.8, 61.4, 55.1, 35.3, 35.0, 21.2, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 3464, 2982, 1732, 1446, 1367, 1255, 1184, 1053 cm^{-1}. $C_{30}H_{30}O_4$ (454.21): calcd. C 79.27, H 6.65; found C 79.34, H 6.53.

Diethyl (*Z*)-4-[(4-Acetylphenyl)(phenyl)methylene]-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (5d): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 81.9 mg (85%) of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.72 (dd, *J* = 0.8, 8.8 Hz, 2 H), 7.35–7.26 (m, 3 H), 7.15–7.06 (m, 6 H), 6.74–6.72 (m, 2 H), 4.18–4.14 (m, 2 H), 4.03–3.98 (m, 2 H), 3.35 (s, 2 H), 3.14 (s, 2 H), 2.53 (s, 3 H), 1.14–1.10 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 170.9, 148.8, 142.3, 139.9, 135.5, 135.3, 132.6, 131.2, 130.5, 130.4, 128.3, 128.1, 127.5, 127.3, 125.0, 61.4, 55.0, 35.3, 34.8, 26.5, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3462, 3346, 2983, 1731, 1682, 1600, 1445, 1362, 1260, 1184, 1053 cm^{-1}. $C_{31}H_{30}O_5$ (482.21): calcd. C 77.16, H 6.27; found C 77.01, H 6.34.

Diethyl (*Z*)-4-[Phenyl(*o*-tolyl)methylene]-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (5f): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 81.1 mg (89%) of the title compound as a solid; m.p. 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 2 H), 7.22–7.15 (m, 3 H), 7.09–6.91 (m, 6 H), 6.72–6.65 (m, 2 H), 4.19–4.09 (m, 3 H), 3.89–3.84 (m, 1 H), 3.51–3.45 (m, 2 H), 3.16–3.02 (m, 2 H), 1.94 (s, 3 H), 1.18–1.14 (m, 3 H), 1.04–1.01 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 170.8, 143.0, 142.0, 140.6, 136.7, 136.1, 134.8, 131.2, 130.9, 130.2, 130.0, 129.2, 128.1, 127.9, 127.0, 126.7, 125.8, 125.0, 61.3, 54.9, 34.9, 34.5, 20.2, 13.9, 13.7 ppm. IR (KBr): $\tilde{\nu}$ = 3464, 2982, 1732, 1446, 1367, 1256, 1185, 1117, 1053 cm^{-1}. $C_{30}H_{30}O_4$ (454.21): calcd. C 79.27, H 6.65; found C 79.01, H 6.55.

Diethyl (*Z*)-4-[Phenyl(*m*-tolyl)methylene]-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (5g): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 83.5 mg (92%) of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 3 H), 7.16–7.09 (m, 3 H), 7.03–6.94 (m, 3 H), 6.80–6.72 (m, 4 H), 4.17–4.11 (m, 2 H), 4.04–3.98 (m, 2 H), 3.33 (s, 2 H), 3.11 (s, 2 H), 2.17 (s, 3 H), 1.13–1.09 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 143.5, 143.2, 141.3, 137.5, 136.1, 135.0, 131.4, 131.0, 130.4, 128.1, 127.9, 127.8, 127.6, 126.9, 124.8, 61.4, 55.1, 35.3, 35.0, 21.3, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3464, 2982, 1732, 1600, 1446, 1367, 1255, 1185, 1053 cm^{-1}. $C_{30}H_{30}O_4$ (454.21): calcd. C 79.27, H 6.65; found C 79.09, H 6.47.

General Procedure for the Preparation of 7 and 8: $Pd(PPh_3)_2Cl_2$ (7 mg, 5 mol-%) and CuI (3.8 mg, 10 mol-%) were added to a solution of diethyl (2-iodophenyl)-2-(3-arylprop-2-ynyl)malonate or diethyl (2-iodobenzyl)-2-(3-phenylprop-2-ynyl)malonate (**1** or **4**; 0.20 mmol), alkyne (0.30 mmol) and Et_3N (40.4 mg, 0.40 mmol) in DMF (2.0 mL). The resulting mixture was then heated under argon at 100 °C. The work-up procedure was the same as that described for the Heck/Suzuki–Miyaura domino reaction. The residue was purified by chromatography on silica gel to afford the corresponding substituted indene (**7**) or naphthalene (**8**) derivatives.

Diethyl (*Z*)-3-(1,3-Diphenylprop-2-ynylidene)-2,3-dihydroindene-1,1-dicarboxylate (7a): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 76.5 mg (85%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68–8.65 (d, *J* = 7.5 Hz, 1 H), 7.70–7.68 (d, *J* = 7.8 Hz, 1 H), 7.59–7.30 (m, 12 H), 4.26–4.16 (m, 4 H), 3.55 (s, 2 H), 1.26–1.22 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 144.4, 142.3, 140.6, 139.9, 131.4, 129.2, 128.8, 128.6, 128.4, 128.2, 127.5, 126.8, 124.7, 123.5, 115.9, 95.2, 90.4, 62.8, 62.0, 41.1, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3466, 2981, 1734, 1489, 1444, 1367, 1258, 1241, 1195, 1050 cm^{-1}. $C_{30}H_{26}O$ (450.18): calcd. C 79.98, H 5.82; found C 79.79, H 5.87.

Diethyl (*Z*)-3-[3-(4-Methoxyphenyl)-1-phenylprop-2-ynylidene]-2,3-dihydroindene-1,1-dicarboxylate (7b): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 85.5 mg (89%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68–8.65 (d, *J* = 7.5 Hz, 1 H), 7.70–7.67 (d, *J* = 8.1 Hz, 1 H), 7.59–7.56 (m, 2 H), 7.46–7.32 (m, 7 H), 6.89–6.86 (d, *J* = 8.7 Hz, 2 H), 4.23–4.15 (m, 4 H), 3.80 (s, 3 H), 3.55 (s, 2 H), 1.26–1.21 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 159.5, 143.5, 142.2, 140.7, 140.0, 132.8, 129.0, 128.8, 128.5, 128.3, 127.4, 126.8, 124.5, 116.2, 115.6, 114.0, 95.3, 89.1, 62.7, 61.9, 55.2, 41.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3459, 2981, 1733, 1605, 1509, 1463, 1367, 1249, 1027 cm^{-1}. $C_{31}H_{28}O_5$ (480.19): calcd. C 77.48, H 5.87; found C 77.69, H 5.77.

(3*Z*)-Diethyl 3-(3-Cyclohexenyl-1-phenylprop-2-ynylidene)-2,3-dihydroindene-1,1-dicarboxylate (7c): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 78.6 mg (87%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61–8.58 (d, *J* = 7.5 Hz, 1 H), 7.67–7.65 (d, *J* = 6.9 Hz, 1 H), 7.52–7.50 (d, *J* = 7.8 Hz, 2 H), 7.45–7.25 (m, 5 H), 6.18–6.17 (d, *J* = 4.2 Hz, 1 H), 4.24–4.13 (m, 4 H), 3.50 (s, 2 H), 2.25–2.14 (m, 4 H), 1.72–1.59 (m, 4 H), 1.25–1.20 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 142.9, 142.0, 140.7, 140.2, 135.2, 128.8, 128.6, 128.5, 128.2, 127.2, 126.7, 124.5, 121.0, 116.3, 97.4, 87.9, 62.7, 61.9, 40.9, 28.9, 25.7, 22.2, 21.4, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3466, 2934, 1734, 1598, 1463, 1444, 1366, 1257, 1240, 1050 cm^{-1}. $C_{30}H_{30}O_4$ (454.21): calcd. C 79.27, H 6.65; found C 79.19, H 6.77.

Diethyl (*Z*)-3-[1-phenyl-3-(trimethylsilyl)prop-2-ynylidene]-2,3-dihydroindene-1,1-dicarboxylate (7d): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 81.2 mg (91%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77–8.75 (d, *J* = 7.2 Hz, 1 H), 7.76–7.73 (dd, *J* = 1.5, 7.8 Hz, 1 H), 7.59–7.56 (d, *J* = 8.1 Hz, 2 H), 7.50–7.38 (m, 5 H), 4.29–4.22 (q, *J* = 7.2 Hz, 4 H), 3.57 (s, 2 H), 1.33–1.28 (t, *J* = 7.2 Hz, 6 H), 0.34 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8, 145.4, 142.3, 140.3, 139.6, 129.2, 128.8, 128.5, 128.3, 127.4, 126.8, 124.9, 115.9, 105.5, 101.0, 62.6, 61.9, 41.0, 13.9, –0.2 ppm. IR (neat): $\tilde{\nu}$ = 3470, 2960, 2126, 1735, 1464, 1367, 1250, 1049 cm^{-1}. $C_{27}H_{30}O_4Si$ (446.19): calcd. C 72.61, H 6.77; found C 72.49, H 6.57.

Diethyl (*Z*)-3-(1-Phenyloct-2-ynylidene)-2,3-dihydroindene-1,1-dicarboxylate (7e): The reaction was run at 60 °C. The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 37.3 mg (42%) of the title compound as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62–8.60 (d, *J* = 7.8 Hz, 1 H), 7.67–7.64 (d, *J* = 7.5 Hz, 1 H), 7.51–7.48 (d, *J* = 7.5 Hz, 2 H), 7.41–7.25 (m, 5 H), 4.21–4.14 (q, *J* = 7.2 Hz, 4 H), 3.47 (s, 2 H), 2.51–2.46 (t, *J* = 7.2 Hz, 2 H), 1.67–1.58 (m, 2 H), 1.48–1.27 (m, 4 H), 1.25–1.20 (t, *J* = 7.5 Hz, 6 H), 0.94–0.89 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0, 142.5, 141.9, 140.8, 128.8, 128.5, 128.3, 127.2, 126.7, 124.3, 116.5, 97.2, 81.4, 62.7, 61.9, 40.8, 31.2, 28.3, 22.2, 19.9, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3470, 2960, 2932, 1735, 1463, 1367, 1261, 1239, 1049 cm^{-1}. $C_{29}H_{32}O_4$ (444.23): calcd. C 78.35, H 7.26; found C 78.29, H 7.17.

Diethyl (*Z*)-4-(1,3-Diphenylprop-2-ynylidene)-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (8a): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 76.1 mg (82%) of the title compound as a solid; m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56–8.53 (dd, *J* = 3.6, 5.4 Hz, 1 H), 7.48–7.38 (m, 4 H), 7.34–7.17 (m, 9 H), 4.14–3.98 (m, 4 H), 3.29 (s, 2 H), 3.15 (s, 2 H), 1.12–1.07 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.6, 139.9, 138.9, 135.1, 134.9, 131.3, 129.2, 128.6, 128.5, 128.3, 128.2, 127.9, 127.4, 125.6, 123.7, 120.7, 93.4, 92.0, 61.5, 54.7, 35.4, 35.1, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 3462,

2982, 1733, 1489, 1444, 1258, 1184, 1071, 1049 cm^{-1}. $C_{31}H_{28}O_4$ (464.20): calcd. C 80.15, H 6.08; found C 80.29, H 6.17.

Diethyl (*Z*)-4-[3-(4-Methoxyphenyl)-1-phenylprop-2-ynylidene]-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (8b): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 72.1 mg (73%) of the title compound as a solid; m.p. 134–136 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.57–8.55 (m, 1 H), 7.47–7.38 (m, 4 H), 7.34–7.18 (m, 6 H), 6.81–6.79 (dd, J = 1.2, 6.6 Hz, 2 H), 4.15–3.99 (m, 4 H), 3.77 (s, 3 H), 3.28 (s, 2 H), 3.14 (s, 2 H), 1.12–1.08 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 159.5, 140.1, 137.9, 135.1, 132.8, 129.3, 128.6, 128.3, 127.4, 125.6, 120.9, 115.9, 113.9, 93.7, 90.9, 61.5, 55.2, 54.7, 35.5, 35.1, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 2984, 2254, 1729, 1606, 1509, 1370, 1248, 1030 cm^{-1}. $C_{32}H_{30}O_5$ (494.21): calcd. C 77.71, H 6.11; found C 77.58, H 6.13.

Diethyl (4*Z*)-4-(3-Cyclohexenyl-1-phenylprop-2-ynylidene)-1,2,3,4-tetrahydronaphthalene-2,2-dicarboxylate (8c): The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 56.2 mg (60%) of the title compound as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.51–8.49 (m, 1 H), 7.40–7.35 (m, 4 H), 7.30–7.14 (m, 4 H), 6.01–6.00 (t, J = 1.2 Hz, 1 H), 4.12–3.97 (m, 4 H), 3.25 (s, 2 H), 3.09 (s, 2 H), 2.10–2.06 (m, 4 H), 1.61–1.54 (m, 4 H), 1.11–1.07 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 140.4, 137.3, 135.1, 134.8, 129.2, 128.5, 128.2, 127.2, 125.5, 121.2, 121.1, 95.8, 89.5, 61.4, 54.7, 35.5, 35.1, 28.6, 25.7, 22.2, 21.5, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 2933, 2254, 1730, 1443, 1393, 1368, 1260, 1050 cm^{-1}. $C_{31}H_{32}O_4$ (468.23): calcd. C 79.46, H 6.88; found C 79.58, H 6.75.

General Procedure for the Preparation of 9: A mixture of diethyl 2-(2-iodophenyl)-2-(3-phenylprop-2-ynyl)malonate (**1a**; 0.20 mmol), methyl acrylate (0.24 mmol), Et_3N (40.4 mg, 0.40 mmol), Pd-$(PPh_3)_4$ (11.5 mg, 5 mol-%) and DMF (2.0 mL) was placed in a 25 mL flask under argon. The resulting mixture was then heated under argon at 100 °C. The work-up procedure was the same as that described for Heck/Suzuki–Miyaura domino reaction. The residue was purified by chromatography on silica gel to afford the corresponding substituted indene derivatives **9**.

Diethyl 3-[(*E*,*E*)-3-(Methoxycarbonyl)-1-phenylallylidene]-2,3-dihydroindene-1,1-dicarboxylate [(*E*,*E*)-9]: The reaction mixture was purified by chromatography with 20:1 hexanes/EtOAc to afford 69.4 mg (80%) of the title compound as a solid; m.p. 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.44–8.40 (d, J = 15.6 Hz, 1 H), 7.84–7.83 (d, J = 7.6 Hz, 1 H), 7.71–7.69 (d, J = 7.2 Hz, 1 H), 7.49–7.36 (m, 5 H), 7.23–7.21 (m, 2 H), 5.56–5.52 (d, J = 15.6 Hz, 1 H), 4.20–4.13 (m, 4 H), 3.75 (s, 3 H), 3.20 (s, 2 H), 1.26–1.21 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 167.9, 145.1, 143.5, 143.1, 139.7, 139.4, 133.3, 129.3, 129.2, 128.8, 127.6, 127.3, 126.0, 121.5, 62.9, 61.9, 51.5, 43.0, 13.9 ppm. IR (KBr): $\tilde{\nu}$ = 3407, 2925, 1731, 1612, 1461, 1368, 1260, 1170, 1092, 1048, 1028 cm^{-1}. $C_{26}H_{26}O_6$ (434.17): calcd. C 71.87, H 6.03; found C 71.69, H 6.15.

Supporting Information (see also the footnote on the first page of this article): Typical experimental characterization for all products.

Acknowledgments

We thank the Chinese National Science Foundation (NSF) (NSF-20621091, NSF-20672049) and the "Hundred Scientist Program" of the Chinese Academy of Sciences for financial support.

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[8] Crystal data for (*Z*)-**3d**: $C_{30}H_{28}O_5$, M_w = 468.52, T = 294(2) K, λ = 0.71073 Å, monoclinic space group $P1$, a = 8.5245(5), b = 36.609(2), c = 16.3840(9) Å, α = 90.00, β = 91.0620(10), γ = 90.00°, V = 5112.2(5) $Å^3$, Z = 4, D_c = 1.217 $mg\,m^{-3}$, μ =

0.082 mm^{-1}, $F(000)$ = 1984, crystal size 0.28 × 0.24 × 0.20 mm, independent reflections 9510 [R(int) = 0.0433], 26615 reflections collected, refinement method, full-matrix least-squares on F^2, goodness-of-fit on F^2 1.054, final R indices [$I > 2\sigma(I)$] R_1 = 0.1176, wR_2 = 0.1607, R indices (all date) R_1 = 0.0554, wR_2 = 0.1295, extinction coefficient 0.0017(6), largest diff. peak and hole 0.275 and –0.204 e $Å^{-3}$. CCDC-650940 contains the supplementary crystallographic data for (*Z*)-**3d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: November 5, 2007
Published Online: January 15, 2008

