DOI: 10.1002/chem.200902221

Palladium(0) versus Nickel(0) Catalysis in Selective Functional-Group-Tolerant sp^3–sp^3 Carbon–Carbon Bond Formations

Emmanuel Ferrer Flegeau, Uwe Schneider, and Shū Kobayashi*[a]

Abstract: We have uncovered Pd^0-catalyzed intermolecular nonsymmetrical Suzuki–Miyaura-type sp^3–sp^3 C–C bond formations between allyl carbonates and nontoxic allyl, allenyl, or propargyl boronates. This report represents the first use of these types of boronic esters in this particular context. The present transformations proceeded with high selectivity under remarkably mild conditions, and various functional groups including an aldehyde function proved to be compatible. In addition, several boronates were found to display very unusual reactivity patterns; the higher reactivity of boron as apposed to silicon was clearly demonstrated as well. Finally, the inherent problem of β-hydride elimination associated with intermediary allyl–Pd species was addressed by employing a commercially available Ni^0 catalyst.

Keywords: boron · carbonates · nickel · palladium · Suzuki–Miyaura reaction

Introduction

Catalytic formation of carbon–carbon bonds with high efficiency and selectivity is of central importance in organic synthesis,[1] in this context catalytic sp^3–sp^3 C–C bond formation is particularly challenging.[2] Among allyl–allyl cross-coupling reactions, effective methods for intramolecular cyclizations have been reported by using allyl stannanes[3,4] or silanes[3b] with allyl acetates[3,4] or trifluoroacetates[3b] under palladium(0),[3] gold(I),[4] or rhodium (I)[4] catalysis. These reactions provide access to valuable 1,5-dienes, which are abundant in naturally occurring terpenes.[5] In addition, these compounds have proved to be highly versatile intermediates and synthetic building blocks.[6] However, the intermolecular nonsymmetrical sp^3–sp^3 allyl–allyl coupling is significantly more challenging.[7] Only sporadic examples of C–C bond formation between allyl metal reagents including magnesium,[8] indium,[9] silicon,[10] or tin[11] and stoichiometric π-allyl–Pd complexes,[8,11c] allyl ethers,[10] halides and acetates,[11] or carbonates[9] have been reported. These reactions proceed without catalyst[8] or under palladium(0)[9,11] or metal-free catalysis.[10] However, with only few exceptions, an excess of toxic or harmful reagents and harsh conditions are required. In addition, a major problem in palladium catalysis may be the propensity of allyl–Pd intermediates to undergo undesired β-hydride elimination. Further, the efficiency of nonsymmetrical allyl–allyl coupling typically suffers from homocoupling and unsatisfactory regioselectivities, such drawbacks may account for low yields and limited scope.

To the best of our knowledge, nontoxic allyl boronates have been exclusively employed for nucleophilic additions to carbonyl compounds and their derivatives.[12] Herein, we report palladium(0)-catalyzed intermolecular sp^3–sp^3 C–C cross-coupling reactions between allyl carbonates and allyl, allenyl, or propargyl boronates, which proceed selectively under remarkably mild conditions. In addition, we propose a nickel(0) catalytic approach as an effective tool to address the intrinsic problem of β-hydride elimination associated with palladium catalysis.

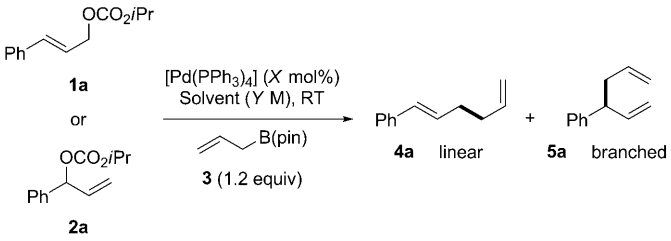
Results and Discussion

Based on our earlier work on In^I-catalyzed allylations of carbonyl derivatives with allyl boronates,[13] we envisioned the use of in situ formed π-allyl–Pd species as electrophiles in a Tsuji–Trost-type reaction[14] with allyl indium(I) nucleophiles, catalytically generated from allyl boronates through boron-to-indium transmetalation. Thus, we initially combined allyl carbonate **1a** and allyl boronate **3** (pin = pinacol-

[a] Dr. E. Ferrer Flegeau, Dr. U. Schneider, Prof. Dr. S. Kobayashi
Department of Chemistry, School of Science
The University of Tokyo
The HFRE Division
ERATO, Japan Science and Technology Agency (JST)
Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5684-0634
E-mail: shu_kobayashi@chem.s.u-tokyo.ac.jp

yl)[13] in the presence of $[Pd(PPh_3)_4]$ (10 mol%) in toluene at room temperature with or without indium(I) iodide (20 mol%; Table 1). Unexpectedly, however, the latter reaction (without indium(I)) proceeded more smoothly and provided almost exclusively the linear 1,5-diene **4a** in quantitative yield (as judged by ^{1}H NMR spectroscopy) after less than 10 min (ratio **4a**/**5a** >32:1, entry 1). The success of allyl boronate **3** in this Pd^0-catalyzed nonsymmetrical sp^3–sp^3 C–C coupling under these mild conditions is striking.[15,16] Indeed, allyl magnesium bromide,[8] allyl trimethylsilane,[10] or allyl trifluoroborate[17,18] provided, in our hands, under the same mild conditions after 16 h reaction time, only the corresponding 1,2-adduct, a complex mixture, or a trace amount of desired product, respectively.

Table 1. Pd^0-catalyzed intermolecular allyl–allyl cross-coupling with allyl boronate **3**.



Entry	Carbonate	Cat. [mol%]	Solvent [M]	t [h]	Yield [%][a]	Ratio **4a**/**5a**
1	**1a**	10	toluene [0.1]	0.1	quant.	>32:1
2	**1a**	10	toluene [0.1][b]	2	57[c]	19:1
3	**1a**	–	toluene [0.1]	16	no reaction	–
4	**1a**	1	toluene [0.1]	2	quant.	>15:1
5	**1a**	1	*n*-hexane [0.1]	6	quant.	nd[d]
6	**1a**	1	CH_2Cl_2 [0.1]	6	89	nd[d]
7	**1a**	1	THF [0.1]	6	trace	–
8	**1a**	1	DMF [0.1]	2	94	nd[d]
9	**1a**	1	EtOAc [0.1]	2	94 (85[c])	>32:1
10	**1a**	2	EtOAc [1]	12	68	11:1
11	**1a**	2	EtOAc [0.5]	12	76	13:1
12	**1a**	2	EtOAc [0.2]	12	90	16:1
13	**1a**	2	EtOAc [0.1]	1	quant.	>32:1
14	**2a**	2	EtOAc [0.1]	1	quant.	>32:1

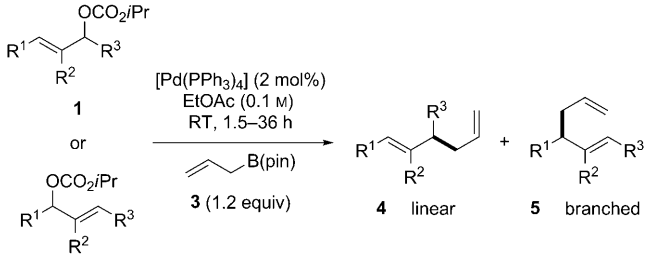
[a] Combined ^{1}H NMR yields and ratios for 1,5-dienes **4a** and **5a** were determined by using 4-methoxytoluene as internal standard. [b] Reaction at 80°C. [c] Isolated yields for **4a** and **5a** after purification on silica gel (PTLC). [d] nd = not determined.

Further experiments dealt with the optimization of several important reaction parameters (Table 1). The palladium-catalyzed transformation at 80°C proved to be both less efficient and less selective (entry 2), whereas the uncatalyzed C–C cross-coupling at room temperature did not proceed at all, even after an extended reaction time (entry 3). Significantly, the catalyst loading could be reduced down to 1 mol% (entry 4). A solvent screening revealed that this C–C bond formation proved to be also very fast in *n*-hexane, dichloromethane, *N*,*N*-dimethylformamide, and ethyl acetate, whereas the reaction in THF essentially did not take place (entries 5–9). Higher reaction concentrations were found to decrease the catalytic activity of the palladium catalyst (entries 10–13), the best concentration was determined to be 0.1 M (entry 13). Importantly, compared with **1a**, the regioisomeric carbonate **2a** showed both identical reactivity and identical selectivity (entry 13 vs. 14), which stands in sharp contrast to the use of allyl–In species, in which substantially different linear/branched ratios were observed with **1a** and **2a**.[9a] Finally, it is noted that homocoupling byproducts were not detected under the present mild conditions.

We then explored the scope for allyl carbonates **1** and **2** (Table 2). Gratifyingly, various carbonates, substituted in the α-, β-, or γ-positions, relative to the leaving group, were smoothly and selectively converted into the desired 1,5-dienes. In addition, several important functional groups, such as methoxy, bromo, ester, cyano, and trifluoromethyl were found to be compatible with the mild reaction conditions. Aromatic substrates provided linear products **4** with generally excellent selectivities (entries 1, 2, and 6–8). On the other hand, the nitrile-substituted aromatic compound **2d** and the α,β-unsaturated aliphatic ester **1h** led predominantly to branched 1,5-diene products **5** (entries 3–5 and 9). It is noted that, contrary to most reported procedures,[8–11] the present catalytic cross-coupling can be selectively performed at temperatures as low as −20°C (entry 5). Finally, carbonate **1i**, substituted in both the α- and γ-positions, also proved to be an excellent substrate for this transformation (entry 10).

In addition, more challenging carbonates **1** and **2** were examined (Table 3). Unfortunately, the heteroaromatic sub-

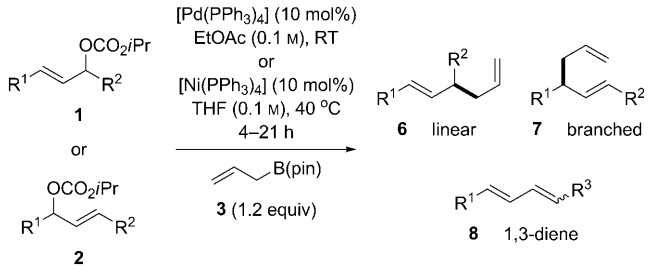
Table 2. Scope for Pd^0-catalyzed allylation of allyl carbonates **1** and **2** with **3**.



Entry	R^1	R^2	R^3	Yield [%][a]	Ratio **4**/**5**
1	**1b**: 4-MeO-C_6H_4	H	H	93	>32:1
2	**2c**: 4-Br-C_6H_4	H	H	88	5.2:1
3	**2d**: 4-NC-C_6H_4	H	H	79	1:2
4[b]	**2d**: 4-NC-C_6H_4	H	H	76	1:7
5[c]	**2d**: 4-NC-C_6H_4	H	H	82	1:15
6	**2e**: 4-F_3C-C_6H_4	H	H	86	4:1
7	**2f**: Ph	Me	H	93	>99:1
8	**2g**: 4-F_3C-C_6H_4	Me	H	89	>32:1
9	**1h**: CO_2iPr	H	H	70[d]	1:>99
10	**1i**: Ph	H	Ph	85	–

[a] Isolated yields of 1,5-dienes **4** and/or **5** after purification on silica gel (PTLC). [b] Reaction with 5 mol%, 0°C. [c] Reaction with 5 mol%, −20°C. [d] ^{1}H NMR yield: 70%; isolated yield: 47% (likely due to the volatility of the branched 1,5-diene **5h**).

Table 3. Pd^0 versus Ni^0: Scope and limitation for challenging carbonates.



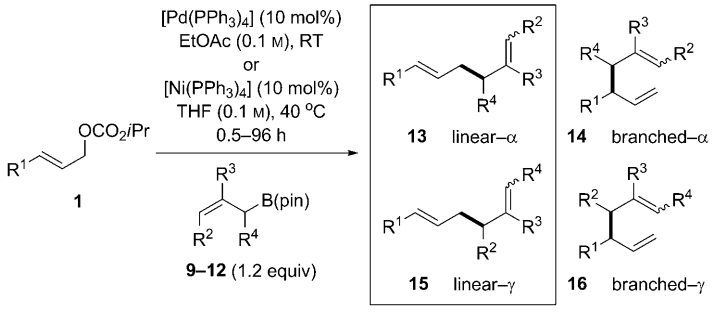
Entry	R^1	R^2	M	Yield [%][a]	Ratio **6**/**7**/**8**
1	**1j**: 3-pyridyl	H	Pd	no reaction	–
2	**1k**: CH_2OTBS	H	Pd	no reaction	–
3	**2l**: $nC_{10}H_{21}$	H	Pd	complex mixture	–[b]
4	**1m**: Ph	Me	Pd	quant.	2.3:nd:1[e]
5	**1n**: $PhCH_2CH_2$	CH_2CH_2Ph	Pd	complex mixture	–[b]
6	**1k**: CH_2OTBS	H	Ni	68	2.9:1:nd[e]
7	**2l**: $nC_{10}H_{21}$	H	Ni	74	1.3:1:nd[e]
8[c]	**1m**: Ph	Me	Ni	76	>99:4:1
9[d]	**1n**: $PhCH_2CH_2$	CH_2CH_2Ph	Ni	90	5.7:nd:1[e]
10	**1j**: 3-pyridyl	H	Ni	72	>99:1:–

[a] Isolated yields of the indicated products after purification on silica gel (PTLC). [b] Due to the complexity of the ^1H NMR spectra, a precise determination of the product distribution proved to be impossible. [c] Reaction in MeCN, RT. [d] Reaction in THF, 40 °C. [e] nd = not detected. R^3: in 1,3-diene byproducts of type **8**, which may be derived from **1**, R^3 corresponds to R^2, but lacks one =CH unit as part of the newly formed C=C double bond (entries 4–5 and 8–9).

strate **1j** (R^1 = 3-pyridyl, R^2 = H) decomposed under the present conditions (entry 1). Moreover, allyl carbonates for which the allyl–Pd derivatives are prone to undergo undesired β-hydride elimination proved to be very difficult (entries 2–5). Typically, the reaction did not proceed (entry 2) or provided a complex mixture of inseparable products, including the undesired 1,3-diene **8** due to β-hydride elimination (entries 3 and 5). Only carbonate **1m** (R^1 = Ph, R^2 = Me) proved to be accessible; however, an inseparable mixture of the desired linear 1,5-diene **6m** and byproduct **8m** was obtained (ratio **6m**/**8m** 2.3:1, entry 4). The use of alternative solvents, such as toluene, *n*-hexane, or dichloromethane resulted in significantly decreased yields for the desired coupling product **6m**, along with more pronounced byproduct formation (1,3-diene **8m**). Unfortunately, our efforts to improve these unsatisfactory results through careful examination of the nature and the amount of phosphine ligands were unsuccessful. The inherent problem of β-hydride elimination associated with intermediary allyl–Pd species has been well studied.[19] In this context, another Group 10 element, nickel, was previously found to enhance the rate of reductive elimination relative to β-hydride elimination.[20] We therefore decided to examine commercially available $[Ni(PPh_3)_4]$ as a catalyst in this reaction system and were pleased to find that β-hydride elimination was effectively suppressed in most cases to selectively provide the desired 1,5-dienes **6** in 68–90% yields (entries 6–9). Particularly noteworthy is the high selectivity observed with the challenging carbonate **1m** (ratio **6m**/**7m**/**8m** >99:4:1, entry 8 vs. 4). Finally, the difficult pyridine-derived carbonate **1j** was converted under our nickel(0) catalysis[21] into the desired linear 1,5-diene **6j** in 72% yield (ratio **6j**/**7j** >99:1, entry 10 vs. 1). The compatibility of this reactive heterocycle with the present catalytic protocol is remarkable and highlights the potential of this carbon–carbon bond formation.

We then turned our attention to the use of allyl boronates **9**–**12**, substituted in the α-, β-, or γ-positions, relative to the boron atom, to examine the scope for boronic esters (Table 4). In principle, four constitutional isomers can be formed in this transformation. Remarkably, however, the initial experiment by using carbonate **1a** and α-methylallyl boronate **9** under palladium(0) catalysis furnished selectively the desired 1,5-diene **13aa** (linear-α), albeit in low yield (entry 1). As indicated in the previous study, the reaction may be hampered by β-hydride elimination of an intermediary allyl–Pd species, which may be derived from **9** in the present case. Nevertheless, it is noted that the exclusive formal α-addition of allyl boronate **9** is very unusual for pal-

Table 4. Pd^0 versus Ni^0: Scope and limitation for allyl boronates.



Entry	R^1	R^2	R^3	R^4	M	Yield [%][a]	Ratio **13**/**14**/**15**/**16**
1[b]	**1a**: Ph	**9**: H	H	Me	Pd	32[d]	>99:nd:1:nd[c]
2	**1a**: Ph	**9**: H	H	Me	Ni	58	1:nd:1.7:nd[c]
3	**1b**: 4-MeO-C_6H_4	**9**: H	H	Me	Pd	57[d]	>99:nd:1:nd[c]
4	**1b**: 4-MeO-C_6H_4	**9**: H	H	Me	Ni	quant.	1:nd:1:nd[c]
5	**1b**: 4-MeO-C_6H_4	**10**: Me	H	H	Ni	quant.	1:nd:1:nd[c]
6[b]	**1a**: Ph	**11**: H	Me	H	Pd	84	>99:1:–:–
7	**1a**: Ph	**11**: H	Me	H	Ni	84	>99:1:–:–
8[e]	**1a**: Ph	**12**: H	H	$SiMe_3$	Pd	78	>99:nd:1:nd[c]
9	**1a**: Ph	**12**: H	H	$SiMe_3$	Ni	87	1:nd:>32:nd[c]

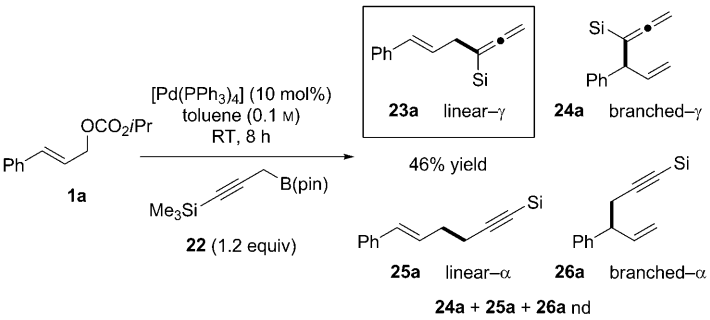
[a] Isolated yields of the indicated products after purification on silica gel (PTLC). [b] Reaction with 2 mol%. [c] nd = not detected. [d] As a side reaction, presumably β-hydride elimination of an intermediary allyl–Pd species (derived from **9**) took place to form 1,3-butadiene, and aromatic olefins were formed from **1** through reductive elimination of a palladium-hydride intermediate. [e] Reaction in *n*-hexane.

ladium(0) catalysis,[17] which may imply a mechanistically distinct process. Further, it is noteworthy that, here again, the corresponding Ni^0-catalyzed reaction led to a significantly higher yield, while maintaining the exclusive linear selectivity, although with a lower α/γ ratio (58% yield; entry 2).

The use of substrate **1b** (R^1 = 4-MeO-C_6H_4) gave better yields, with similar selectivities to **1a**, for both palladium and nickel catalysis (entries 3 and 4 vs. entries 1 and 2). In this context, the Ni^0-catalyzed reaction of **1b** with (*Z*)-crotyl boronate **10** provided an identical result as to the use of α-methylallyl boronate **9**, which suggests the same reactive intermediate (entry 5 vs. 4). The palladium- and nickel-catalyzed cross-coupling between **1a** and methallyl boronate **11** proceeded smoothly with exclusive linear selectivities (entries 6 and 7). Finally, the use of α-(trimethylsilyl)allyl boronate **12** was found to give exclusively the unusual α-adduct **13ac** (linear-α)[17] or the γ-adduct **15ac** (linear-γ) under palladium or nickel catalysis, respectively (entry 8 vs. 9). Here again, distinct reactive intermediates may be considered to explain the opposite regioselective outcome. In addition, these results underscore the higher reactivity of boron as apposed to silicon.

Next, we examined the use of allenyl boronate **17** under palladium catalysis (Table 5). Surprisingly, carbonate **1a** was smoothly converted with excellent linear-γ-selectivity into 1,5-enyne **18a** (entry 1), which reveals a very unusual reactivity pattern for **17**.[22] It is noted that the observed γ/α ratio upon using this boron reagent is comparable with the result when using the corresponding indium compound,[9b] but is substantially better than in case of the allenyl stannanes.[23] Further, it is interesting that our nickel(0) conditions failed to give any reaction, which suggests again that different mechanisms are at play in palladium and nickel catalysis (entry 2). Further selected examples for linear propargylation of allyl carbonates with **17** showed equally good results in favor of linear 1,5-enynes **18** (entries 3–5).

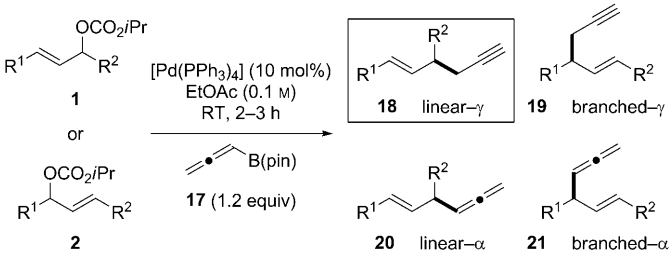
With the aim to selectively generate 1,4-enallenes of type **23**, we examined the use of **1a** with γ-(trimethylsilyl)propargyl boronate **22** (Scheme 1). Gratifyingly, the desired linear-γ-adduct **23a** was exclusively obtained in an acceptable yield. It is noted that unsaturated compounds of type **18** and **23** are potentially interesting substrates for cyclization processes.



Scheme 1. Pd^0-catalyzed selective linear allenylation of **1a** with **22** (Si = $SiMe_3$). Nd = not detected.

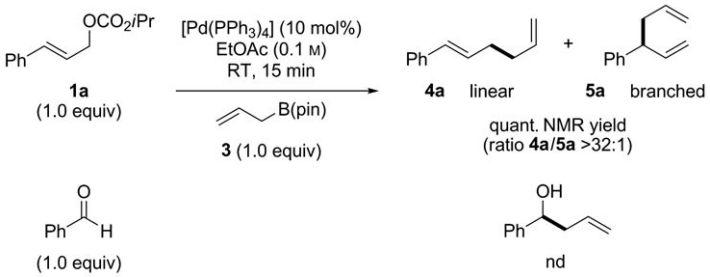
Generally, allyl boronates of type **3** smoothly react with aldehydes, even in the absence of catalysts, to form the corresponding homoallyl alcohols.[12,24] This typical reactivity pattern of allyl boronates may be explained with internal activation of the boron atom by the carbonyl group in a closed, six-membered cyclic chairlike transition state.[12] In this context, the remarkable turnover frequency observed for the present Pd^0-catalyzed C–C cross-coupling between **1a** and **3** (cf. Table 1, entry 1) led us to devise a competition experiment. Thus, allyl carbonate **1a**, benzaldehyde, and allyl boronate **3** (ratio 1:1:1) were combined in ethyl acetate at room temperature in the presence of [$Pd(PPh_3)_4$] (10 mol%; Scheme 2). After 15 min, the reaction was stopped and ^1H and ^{11}B NMR spectroscopic analysis of an aliquot revealed both complete consumption of **3** and full conversion of **1a** into the desired 1,5-dienes **4a** and **5a** (ratio **4a**/**5a** >32:1), whereas benzaldehyde was recovered in an essentially quantitative yield and the corresponding homoallyl alcohol was not detected. This surprisingly chemoselective reaction of allyl boronate **3**[25] strongly suggests the com-

Table 5. Selected examples for Pd^0-catalyzed linear propargylation of **1** and **2** with **17**.



Entry	R^1	R^2	Yield [%][a]	Ratio **18**/**19**/**20**/**21**
1[b]	**1a**: Ph	H	70	50:1:2.1:nd[c]
2[d]	**1a**: Ph	H	no reaction	–
3	**1b**: 4-MeO-C_6H_4	H	70	>99:1:5:nd[c]
4	**2c**: 4-Br-C_6H_4	H	74	>50:1:1.5:nd[c]
5	**1i**: Ph	Ph	50	25:–:1:–

[a] Isolated yields of enynes **18** and **19** after purification on silica gel (PTLC). [b] Reaction with 9 mol%. [c] nd = not detected. [d] Reaction with [$Ni(PPh_3)_4$] (10 mol%), EtOAc (RT–50°C, 48 h).



Scheme 2. Pd^0-catalyzed C–C cross-coupling versus 1,2-allyl boration.

patibility of the present Pd^0-catalyzed cross-coupling with aldehyde functional groups, which may be particularly useful for the synthesis of complex molecules.

Conclusion

We have uncovered Pd^0-catalyzed intermolecular sp^3–sp^3 C–C cross-coupling reactions between allyl carbonates and allyl, allenyl, or propargyl boronates. To the best of our knowledge, these results represent the first use of allyl boronates in this context.[15,16] These overlooked transformations proceeded with high selectivities under remarkably mild conditions, and various functional groups including an aldehyde function were found to be compatible. In addition, the intrinsic problem of β-hydride elimination related to allyl–Pd intermediates was addressed by employing a commercially available Ni^0 catalyst. Considering the facile access to both carbonates and boronic esters, the present Group 10 metal catalysis is expected to have a significant impact on organic synthesis. Further synthetic investigations including asymmetric catalysis and mechanistic studies are underway in our laboratories.

Experimental Section

General: NMR spectra were recorded on a JEOL ECX-400, JEOL ECA-500 spectrometer, or a JEOL ECA-600 spectrometer, operating at 400, 500, or 600 MHz for ^{1}H NMR and at 100, 125, or 150 MHz for ^{13}C NMR spectra. Chemical shifts were reported downfield from tetramethylsilane (TMS). IR spectra were measured by using a JASCO FT/IR-610 spectrometer. HRMS were recorded by using a BRUKER DALTONICS BioTOF II (ESI) spectrometer or a JEOL JMS-T100TD (DART). Preparative Thin Layer Chromatography (PTLC) was carried out by using Wakogel B-5F from WAKO. All organic solvents used were commercially available dry solvents, which were distilled appropriately under an argon atmosphere and stored over molecular sieves prior in an Ar box. Allyl boronate **3**,[26] α-methylallyl boronate **9**,[27] (*Z*)-crotyl boronate **10**,[26] methallyl boronate **11**,[28] α-(trimethylsilyl)allyl boronate **12**,[29] allenyl boronate **17**,[22b] and γ-(trimethylsilyl)propargyl boronate **22**[30] were prepared by slightly modified procedures of reported methods. Allyl carbonates **1a**,[31] **1b**,[31] **1h**,[32] **1j**,[32] **1k**,[32] and **1m**[33] were prepared according to the reported procedures. All other allyl carbonates **1** and **2** are new compounds and were prepared according to general procedure A; their analytical data are shown below (see also copies of NMR spectra). The Pd^0- and Ni^0-catalyzed carbon–carbon cross-coupling reactions with allyl carbonates **1** and **2** were performed according to general procedure B. 1,5-Dienes **4a**,[34] **5a**[35] **4b**,[34] **5b**,[34] **4c**,[11d] **5c**,[11d] **4e**,[34] **5e**,[34] **4i**,[36] **5i**,[36] **6k**,[37] **7k**,[37] **6l**,[38] **7l**[38] **6m**,[39] **7m**,[39] **13aa**,[34] **13ab**,[34] **13ba**,[34] **15ba**,[34] **13ac**,[34] and 1,5-enynes **18a**,[23] **19a**,[23] and 1,4-enallene **20a**[23] are literature-known compounds. Their analyses are in full agreement with the reported data (see also copies of NMR spectra). The analytical data for new C–C cross-coupling products are shown below (see also copies of NMR spectra).

General procedure A (preparation of allyl carbonates): Isopropyl chloroformate (1.0 M in toluene, 3 equiv) was slowly added to a solution of the corresponding allyl alcohol (1 equiv), pyridine (2 equiv), and 4-(dimethylamino)pyridine (cat.) in dry THF at 0 °C under an Ar atmosphere. The reaction mixture was then stirred at room temperature for 24–48 h, before quenching with aqueous HCl (1 M) and dilution with diethyl ether. After phase separation, the organic phase was successively washed with aqueous HCl (1 M; twice), aqueous $NaHCO_3$ (sat), and brine and was dried over $MgSO_4$. After filtration, the organic phase was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel.

Isopropyl 1-phenylallyl carbonate (2a): Prepared from 1-phenylprop-2-en-1-ol (500 mg, 3.73 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/ethyl acetate 19:1). Colorless liquid; yield: 686 mg (83 %); IR (neat): $\tilde{\nu}$ = 1741, 1577, 1363, 1257, 911, 700 cm^{-1}; ^{1}H NMR (400 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.27 (d, *J* = 6.0 Hz, 3H,), 1.31 (d, *J* = 6.0 Hz, 3H), 4.87 (sept, *J* = 6.0 Hz, 1H), 5.25–5.39 (m, 2H), 6.00–6.09 (m, 2H), 7.29–7.40 ppm (m, 5H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 21.8 (2 C), 72.1, 79.8, 117.3, 127.0, 128.3, 128.6, 135.9, 138.4, 153.9 ppm; HRMS (ESI): *m/z*: calcd for $C_{13}H_{16}NaO_3$: 243.0986 $[M+Na]^+$; found: 243.0977.

1-(4-Bromophenyl)allyl isopropyl carbonate (2c): Prepared from 1-(4-bromophenyl)prop-2-en-1-ol (500 mg, 2.35 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 19:1). Colorless liquid; yield: 542 mg (79 %); IR (neat): $\tilde{\nu}$ = 1741, 1640, 1258, 1095 cm^{-1}; ^{1}H NMR (400 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.27 (d, *J* = 6.0 Hz, 3H), 1.31 (d, *J* = 6.0 Hz, 3H), 4.87 (sept, *J* = 6.0 Hz, 1H), 5.26–5.36 (m, 2H,), 5.95–6.04 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.49 ppm (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 21.7 (2C), 72.3, 79.0, 117.8, 122.3, 128.8, 131.7, 135.4, 137.4, 153.7 ppm; HRMS (ESI): *m/z*: calcd for $C_{13}H_{15}{}^{79}BrNaO_3{}^+$: 321.0097 $[M+Na]^+$; found: 321.0105.

1-(4-Cyanophenyl)allyl isopropyl carbonate (2d): Prepared from 4-(1-hydroxy-allyl)benzonitrile (500 mg, 3.14 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 4:1). Colorless liquid; yield: 552 mg (72 %); IR (neat): $\tilde{\nu}$ = 1742, 1644, 1257, 1097, 911, 833 cm^{-1}; ^{1}H NMR (400 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.28 (d, *J* = 6.4 Hz, 3H), 1.32 (d, *J* = 6.4 Hz, 3H), 4.88 (sept, *J* = 6.4 Hz, 1H), 5.32–5.39 (m, 2H), 5.93–6.02 (m, 1H), 6.09 (d, *J* = 6.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.67 ppm (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 21.7 (2 C), 72.6, 78.7, 112.0, 118.5, 118.6, 127.5, 132.4, 134.8, 143.6, 153.6 ppm; HRMS (ESI): *m/z*: calcd for $C_{14}H_{15}NNaO_3{}^+$: 268.0944 $[M+Na]^+$; found: 268.0937.

1-[4-(Trifluoromethyl)phenyl]allyl isopropyl carbonate (2e): Prepared from 1-[4-(trifluoromethyl)phenyl]prop-2-en-1-ol (400 mg, 2.31 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 19:1). Colorless liquid; yield: 383 mg (58 %); IR (neat): $\tilde{\nu}$ = 1643, 1327, 1259, 1067 cm^{-1}; ^{1}H NMR (600 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.27 (d, *J* = 6.2 Hz, 3H), 1.32 (d, *J* = 6.2 Hz, 3H), 4.88 (sept, *J* = 6.2 Hz, 1H), 5.30–5.37 (m, 2H), 5.98–6.03 (m, 1H), 6.11 (d, *J* = 6.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.63 ppm (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 21.7 (2C), 72.5, 78.9, 118.2, 124.0 (q, *J* = 272.2 Hz), 125.6 (d, *J* = 4.4 Hz), 127.2, 130.4 (q, *J* = 33.2 Hz), 135.3, 142.5, 153.7 ppm; HRMS (ESI): *m/z*: calcd for $C_{14}H_{15}F_3NaO_3{}^+$: 311.0866 $[M+Na]^+$; found: 311.0720.

Isopropyl 2-methyl-1-phenylallyl carbonate (2f): Prepared from 2-methyl-1-phenyl-prop-2-en-1-ol (500 mg, 3.38 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 15–16:1). Colorless liquid; yield: 619 mg (78 %); IR (neat): $\tilde{\nu}$ = 1740, 1653, 1455, 1376, 1115, 1087, 914, 790, 762, 699 cm^{-1}; ^{1}H NMR (400 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.20 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 6.4 Hz, 3H), 1.58 (s, 3H), 4.80 (sept, *J* = 6.4 Hz, 1H), 4.93 (s, 1H), 5.10 (s, 1H), 5.91 (s, 1H, s), 7.21–7.32 ppm (m, 5H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 18.6, 21.7, 21.8, 72.1, 81.9, 112.7, 126.9, 128.1, 128.4, 137.9, 142.8, 153.9 ppm; HRMS (ESI): *m/z*: calcd for $C_{14}H_{18}NaO_3{}^+$: 257.1148 $[M+Na]^+$; found: 257.1145.

1-[4-(Trifluoromethyl)phenyl]-2-methallyl isopropyl carbonate (2g): Prepared from 1-[4-(trifluoromethyl)phenyl]-2-methylprop-2-en-1-ol (400 mg, 1.85 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 15–16:1). Colorless liquid; yield: 395 mg (71 %); IR (neat): $\tilde{\nu}$ = 1637, 1327, 1260, 1125, 1067, 788 cm^{-1}; ^{1}H NMR (600 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 1.29 (d, *J* = 6.0 Hz, 3H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.65 (s, 3H), 4.89 (sept, *J* = 6.0 Hz, 1H), 5.04 (s, 1H), 5.20 (s, 1H), 6.04 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.62 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20 °C, TMS): δ = 18.3, 21.7 (2C), 71.4, 72.4, 81.2, 114.0, 124.0 (q, *J* =

271.7 Hz), 125.3–125.4 (m), 127.1, 130.3 (q, J=31.8 Hz), 142.1, 153.8 ppm; HRMS (ESI): m/z: calcd for $C_{15}H_{17}F_3NaO_3^+$: 325.1022 $[M+Na]^+$; found: 325.1028.

Isopropyl (*E*)-1,3-diphenylallyl carbonate (1i): Prepared from (*E*)-1,3-diphenylprop-2-en-1-ol (4.84 g, 23.0 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 19:1). Pale-yellow liquid; yield: 1.41 g (21%); IR (neat): $\tilde{\nu}$=1739, 1257, 1108, 1032, 745, 695 cm^{-1}; ^1H NMR (400 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.28 (d, J=6.0 Hz, 3H), 1.31 (d, J=6.0 Hz, 3H), 4.88 (sept, J=6.0 Hz, 1H), 6.25 (d, J=7.0 Hz, 1H), 6.34–6.40 (m, 1H), 6.68 (d, J=16.0 Hz, 1H), 7.22–7.45 ppm (m, 10H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20°C, TMS): δ=21.8 (2C), 72.2, 79.8, 126.7, 126.9, 127.0, 128.1, 128.3, 128.5, 128.6, 132.8, 136.0, 138.7, 153.9 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{20}NaO_3^+$: 319.1305 [M<M+>Na]$^+$; found: 319.1326.

Isopropyl tridec-1-en-3-yl carbonate (2l): Prepared from tridec-1-en-3-ol (700 mg, 3.80 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 19:1). Colorless liquid; yield: 933 mg (86%); IR (neat): $\tilde{\nu}$=1740, 1640, 1261, 1100 cm^{-1}; ^1H NMR (400 MHz, [D$_1$]chloroform, 20°C, TMS): δ=0.89–0.86 (m, 3H), 1.21–1.36 (m, 25H), 1.55–1.74 (m, 3H), 4.87, (sept, J=6.0 Hz, 1H), 5.00–5.05 (m, 1H), 5.18–5.31 (m, 2H), 5.75–5.84 ppm (m, 1H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20°C, TMS): δ=14.1, 21.7, 21.8, 22.7, 25.0, 29.3, 29.4, 29.5, 29.6, 31.9, 34.2, 71.6, 78.7, 117.2, 136.2, 154.1 ppm; HRMS (ESI): m/z: calcd for $C_{17}H_{32}O_3Na^+$: 307.2238 $[M+Na]^+$; found: 307.2237.

Isopropyl (*E*)-4-phenylbut-3-en-2-yl carbonate (1m): Prepared from (*E*)-phenylbut-3-en-2-ol (10.3 g, 64.4 mmol) according to general procedure A (eluant for flash column chromatography: *n*-hexane/EtOAc 19:1). Colorless liquid; yield: 14.4 g (95%); IR (neat): $\tilde{\nu}$=1735, 1648, 1262, 1113, 1036, 792, 749, 693 cm^{-1}; ^1H NMR (400 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.31 (t, J=6.4 Hz, 3H), 1.47 (d, J 6.4 Hz, 3H), 4.88 (sept, J=6.4 Hz, 1H), 5.33–5.39 (m, 1H), 6.18–6.23 (m, 1H), 6.65 (d, J=16 Hz, 1H), 7.23–7.40 ppm (m, 5H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20°C, TMS): δ=20.5, 21.8 (2C), 71.7, 74.8, 126.6, 128.0, 128.2, 128.3, 128.4, 128.5, 132.0, 136.2, 153.9 ppm; HRMS (ESI): m/z: calcd for $C_{14}H_{18}NaO_3^+$: 257.1148 $[M+Na]^+$; found: 257.1154.

General procedure B (Pd^0- or Ni^0-catalyzed sp^3–sp^3 C–C cross-coupling reactions): The corresponding catalyst [Pd(PPh$_3$)$_4$] (1–10 mol%) or [Ni(PPh$_3$)$_4$] (5–10 mol%) and the indicated solvent (2 mL, 0.1 M) were added to an oven-dried 5 mL microwave-type vial with a magnetic stirring bar in an Ar box. Under an Ar atmosphere (outside the Ar box), the corresponding allyl carbonate **1** or **2** (0.20 mmol, 1.0 equiv) was introduced into the vial at room temperature, before setting the indicated reaction temperature. The corresponding boronate **3**, **9**–**12**, **17**, or **22** (0.24 mmol, 1.2 equiv) was added dropwise to the stirred mixture and the reaction was monitored by TLC on silica gel until complete conversion of **1** or **2**. The reaction mixture was filtered through Celite (when using **17** or **22**) and concentrated in vacuo. The residue was purified by PTLC on silica gel to afford the corresponding cross-coupling products **4**–**7**, **13**–**15**, **18**–**20**, or **23**.

4-[(*E*)-Hexa-1,5-dienyl]benzonitrile (4d)/4-(hexa-1,5-dien-3-yl)benzonitrile (5d; cf. Table 2, entry 5): Prepared from allyl carbonate **2d** and allyl boronate **3** according to general procedure B with [Pd(PPh$_3$)$_4$] (5 mol%) in ethyl acetate at −20°C for 4 h (eluant for PTLC: *n*-hexane/EtOAc 4:1). Colorless liquid; yield: 82%; ratio **4d**/**5d** 1:15; IR (neat): $\tilde{\nu}$=2227, 1639, 1606, 1503, 1412, 993, 917, 836, 560 cm^{-1}; ^1H NMR (600 MHz, [D$_1$]chloroform, 20°C, TMS): δ=2.23–2.27 (m, 2H; **4d**), 2.34–2.37 (m, 2H; **4d**), 2.43–2.55 (m, 2H; **5d**), 3.41–3.44 (m, 1H; **5d**), 4.98–5.12 (m, 2H; **4d**; m, 4H; **5d**), 5.65–5.70 (m, 1H; **5d**), 5.80–5.95 (m, 2H; **4d**; m, 1H; **5d**), 6.35–6.45 (m, 1H; **4d**), 7.26–7.30 (m, 2H; **4d**; m, 2H; **5d**), 7.41 (d, J=8.2 Hz, 2H; **4d**), 7.59 ppm (d, J=8.2 Hz, 2H; **5d**); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20°C, TMS): δ=32.4 (**4d**), 33.1 (**4d**), 39.3 (**5d**), 49.5 (**5d**), 110.0 (**4d**), 110.1 (**5d**), 115.3 (**4d**), 115.6 (**5d**), 116.9 (**5d**), 118.9 (**5d**), 119.1 (**4d**), 126.4 (**4d**), 128.6 (**5d**), 128.9 (**4d**), 132.2 (**5d**), 132.3 (**4d**), 134.4 (**4d**), 135.4 (**5d**), 137.5 (**4d**), 140.0 (**5d**), 142.1 (**4d**), 149.2 ppm (**5d**); HRMS (ESI): m/z: calcd for $C_{13}H_{14}N^+$: 184.1121 $[M+H]^+$; found: 184.1126.

1-[(*E*)-2-Methylhexa-1,5-dienyl]benzene (4f; cf. Table 2, entry 7): Prepared from allyl carbonate **2f** and allyl boronate **3** according to general procedure B with [Pd(PPh$_3$)$_4$] (2 mol%) in ethyl acetate at room temperature for 3 h (eluant for PTLC: *n*-hexane). Colorless liquid; yield: 93%; IR (neat): $\tilde{\nu}$=1640, 1444, 912, 740, 698 cm^{-1}; ^1H NMR (600 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.86 (d, J=0.8 Hz, 3H), 2.23–2.29 (m, 4H), 4.97–5.09 (m, 2H), 5.81–5.91 (m, 1H), 6.28 (s, 1H), 7.16–7.33 ppm (m, 5H); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20°C, TMS): δ=17.8, 32.3, 40.0, 114.6, 125.1, 125.8, 128.0, 128.8, 138.3, 138.4, 138.5 ppm; HRMS (ESI): m/z: calcd for $C_{13}H_{16}^+$: 172.1252 $[M+H]^+$; found: 172.1240.

1-(Trifluoromethyl)-4-[(*E*)-2-methylhexa-1,5-dienyl]benzene (4g)/1-(trifluoromethyl)-4-(2-methylhexa-1,5-dien-3-yl)benzene (5g; cf. Table 2, entry 8): Prepared from allyl carbonate **2g** and allyl boronate **3** according to general procedure B with [Pd(PPh$_3$)$_4$] (2 mol%) in ethyl acetate at room temperature for 3 h (eluant for PTLC: *n*-hexane). Colorless liquid; yield: 89%; ratio **4g**/**5g** >32:1); IR (neat): $\tilde{\nu}$=1642, 1325, 1123, 1068 cm^{-1}; ^1H NMR (600 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.86 (d, J=1.6 Hz, 3H), 2.22–2.32 (m, 4H), 4.99–5.10 (m, 2H), 5.76–5.93 (m, 1H), 6.29 (s, 1H), 7.32 (d, J=8.4 Hz, 2H), 7.55 ppm (d, J=8.4 Hz, 2H); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20°C, TMS): δ=111.4, 114.9 (2C), 116.4, 121.7, 122.6, 122.7, 123.5, 124.9 (4C), 125.0 (3C), 125.1, 125.2, 125.3, 125.7, 127.4, 127.5, 127.7, 127.9, 128.1, 128.2, 128.7, 128.8, 129.0, 130.1, 135.9, 137.8, 138.0 (2C), 138.9 (2C), 140.8, 141.0, 142.0, 142.1 ppm; HRMS: mass spectroscopic analyses (DART, ESI, FAB, MALDI) failed to give the desired molecular signal, resulting only in fragmentation; in addition, preparation of a sample for elemental analysis failed due to the volatility of these compounds.

Isopropyl 2-vinylpent-4-enoate (5h; cf. Table 2, entry 9): Prepared from allyl carbonate **1h** and allyl boronate **3** according to general procedure B with [Pd(PPh$_3$)$_4$] (2 mol%) in ethyl acetate at room temperature for 4 h (eluant for PTLC: *n*-hexane/EtOAc 9:1). Colorless liquid; NMR yield: 70% (use of 4-methoxytoluene (0.1 equiv) as internal standard), isolated yield: 42% (due to volatility of **5h**); IR (neat): $\tilde{\nu}$=1639 cm^{-1}; ^1H NMR (600 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.20 (d, J=6.4 Hz, 3H), 1.23 (d, J=6.4 Hz, 3H), 2.30–2.34 (m, 1H), 2.47–2.52 (m, 1H), 3.04–3.07 (m, 1H), 4.98–5.09 (m, 3H), 5.13–5.16 (m, 2H), 5.71–5.78 (m, 1H), 5.80–5.86 ppm (m, 1H); ^{13}C NMR (150 MHz, [D$_1$]chloroform, 20°C, TMS): δ=21.7, 21.8, 36.4, 50.1, 67.9, 116.9, 117.1, 135.0, 135.7, 172.9 ppm; HRMS (ESI): m/z: calcd for $C_{10}H_{16}NaO_2^+$: 191.1043 $[M+Na]^+$; found: 191.1047.

3-[(*E*)-Hexa-1,5-dienyl]pyridine (6j; cf. Table 3, entry 10): Prepared from allyl carbonate **1j** and allyl boronate **3** according to general procedure B with [Ni(PPh$_3$)$_4$] (10 mol%) in THF at 40°C for 4 h (eluant for PTLC: diethyl ether). Additional purification: a solution of the obtained compound in diethyl ether was successively washed with aqueous NaOH (1 M, twice) and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the pure product **6j**. Colorless liquid; yield: 72%; IR (neat): $\tilde{\nu}$=1640, 1444, 912, 740, 698 cm^{-1}; ^1H NMR (400 MHz, [D$_1$]chloroform, 20°C, TMS): δ=2.22–2.28 (m, 2H), 2.38–2.31 (m, 2H), 5.00–5.10 (m, 2H), 5.81–5.91 (m, 1H), 6.26–6.41 (m, 2H), 7.20–7.23 (m, 1H), 7.64–7.67 (m, 1H), 8.42–8.43 (m, 1H), 8.55–8.56 ppm (m, 1H); ^{13}C NMR (100 MHz, [D$_1$]chloroform, 20°C, TMS): δ=32.4, 33.2, 115.2, 123.3, 126.7, 132.4, 132.6, 133.2, 137.7, 147.9, 148.0 ppm; HRMS (ESI): m/z: calcd for $C_{11}H_{14}N^+$: 160.1121 $[M+H]^+$; found: 160.1113.

(*E*)-5-Allyl-1,7-diphenylhept-3-ene (6n)/(2*E*,4*E*)-1,7-diphenylhepta-2,4-diene (8n; cf. Table 3, entry 9): Prepared from allyl carbonate **1n** and allyl boronate **3** according to general procedure B with [Ni(PPh$_3$)$_4$] (10 mol%) in THF at 40°C for 21 h (eluant for PTLC: *n*-hexane). Colorless liquid; yield: 90%; ratio **6n**/**8n** 5.7:1; IR (neat): $\tilde{\nu}$=1638, 1495, 1454, 910, 745, 698 cm^{-1}; ^1H NMR (500 MHz, [D$_1$]chloroform, 20°C, TMS): δ=1.42–1.50 (m, 1H), 1.65–1.72 (m, 1H), 2.00–2.11 (m, 3H), 2.33–2.41 (m, 2H), 2.41–2.47 (m, 1H), 2.54–2.60 (m, 1H), 2.68–2.71 (m, 2H), 4.94–4.97 (m, 2H), 5.20–5.24 (m, 1H), 5.40–5.46 (m, 1H), 5.64–5.73 (m, 1H), 7.11–7.20 (m, 5H), 7.23–7.28 ppm (m, 5H); ^{13}C NMR (125 MHz, [D$_1$]chloroform, 20°C, TMS): δ=33.4, 34.4, 36.1, 36.4, 40.0, 42.1, 115.6, 125.5, 125.7, 128.2 (2 C), 128.4, 128.5, 130.0, 134.5, 137.1, 142.0, 142.8 ppm; HRMS: mass spectroscopic analyses (DART, ESI, FAB, MALDI) failed to give the desired molecular signal, resulting only in

fragmentation; in addition, preparation of a sample for elemental analysis failed, because the two compounds could not be fully separated.

1-[(*E*)-Hex-1-en-5-ynyl]-4-methoxybenzene (18b)/1-(hex-1-en-5-yn-3-yl)-4-metho-xybenzene (19b)/1-[(*E*)-hexa-1,4,5-trienyl]-4-methoxybenzene (20b; cf. Table 5, entry 3): Prepared from allyl carbonate **1b** and allenyl boronate **17** according to general procedure B with $[Pd(PPh_3)_4]$ (10 mol%) in ethyl acetate at room temperature for 3 h (eluant for PTLC: *n*-hexane/EtOAc 9:1). Colorless liquid; yield: 70%; ratio **18b**/**19b**/**20b** >99:1:5; 1,5-enynes **18b** (linear-γ) and **19b** (branched-γ) could be separated from the minor byproduct **20b** (linear-α); IR (neat): $\tilde{\nu}$= 1642, 1252, 1030, 804 cm^{-1}; ^1H NMR (500 MHz, $[D_1]$chloroform, 20°C, TMS): δ=1.98–1.99 (m, 1H), 2.32–2.36 (m, 2H), 2.40–2.44 (m, 2H), 3.79 (s, 3H), 6.08–6.14 (m, 1H), 6.39 (d, J=15.9 Hz, 1H), 6.84 (d, J=9.1 Hz, 2H), 7.29 ppm (d, J=9.1 Hz, 2H); ^{13}C NMR (125 MHz, $[D_1]$chloroform, 20°C, TMS): δ=18.8, 32.0, 55.2, 68.7, 83.9, 113.9, 126.2, 127.2, 130.2, 130.4, 158.8 ppm; HRMS: mass spectroscopic analyses (DART, ESI, FAB, MALDI) failed to give the desired molecular signal, resulting only in fragmentation; elemental analysis: calcd (%) for $C_{13}H_{14}O$: C 83.83, H 7.58; found: C 83.41, H 7.76.

1-Bromo[(*E*)-hex-1-en-5-ynyl]benzene (18c)/1-bromo-4-(hex-1-en-5-yn-3-yl)benzene (19c)/1-bromo-4-[(*E*)-hexa-1,4,5-trienyl]benzene (20c; cf. Table 5, entry 4): Prepared from allyl carbonate **2c** and allenyl boronate **17** according to general procedure B with $[Pd(PPh_3)_4]$ (10 mol%) in ethyl acetate at room temperature for 2 h (eluant for PTLC: *n*-hexane/EtOAc 9:1). Colorless liquid; yield: 74; ratio **18c**/**19c**/**20c** >50:1:1.5; 1,5-enynes **18c** (linear-γ) and **19c** (branched-γ) could be separated from the minor byproduct **20c** (linear-α); IR (neat): $\tilde{\nu}$=1643, 1487, 1072, 798, 639 cm^{-1}; ^1H NMR (500 MHz, $[D_1]$chloroform, 20°C, TMS): δ=1.95–2.01 (m, 1H), 2.34–2.37 (m, 2H), 2.41–2.45 (m, 2H), 6.22–6.28 (m, 1H), 6.39 (d, J= 15.9 Hz, 1H), 7.21 (d, J=8.5 Hz, 2H), 7.41 ppm (d, J=8.5 Hz, 2H); ^{13}C NMR (125 MHz, $[D_1]$chloroform, 20°C, TMS): δ=18.6, 31.9, 69.0, 83.6, 120.8, 127.6, 129.25, 130.0, 131.6, 136.3 ppm; HRMS: mass spectroscopic analyses (DART, ESI, FAB, MALDI) failed to give the desired molecular signal, resulting only in fragmentation; elemental analysis: calcd (%) for $C_{12}H_{11}Br$: C 61.30, H 4.72; found: C 61.59, H 4.85.

(*E*)-1,3-Diphenylhex-1-en-5-yne (18i)/(*E*)-4,6-diphenylhexa-1,2,5-triene (20i; cf. Table 5, entry 5): Prepared from allyl carbonate **1i** and allenyl boronate **17** according to general procedure B with $[Pd(PPh_3)_4]$ (10 mol%) in ethyl acetate at room temperature for 3 h (eluant for PTLC: *n*-hexane). Colorless liquid; yield: 50%; ratio **18i**/**20i** 25:1; the desired 1,5-enyne **18i** (γ) could be separated from the minor byproduct **20i** (α); IR (neat): ν=1645, 1494, 744, 695 cm^{-1}; ^1H NMR (400 MHz, $[D_1]$chloroform, 20°C, TMS): δ=1.98–1.99 (m, 1H), 2.68–2.71 (m, 2H) 3.69–3.73 (m, 1H), 6.39–6.49 (m, 2H), 7.18–7.39 ppm (m, 10H); ^{13}C NMR (100 MHz, $[D_1]$chloroform, 20°C, TMS): δ=25.5, 47.6, 70.2, 82.3, 126.3, 126.8, 127.3, 127.7, 128.5 (2 C), 130.6, 131.7, 137.1, 142.6 ppm; HRMS: mass spectroscopic analyses (DART, ESI, FAB, MALDI) failed to give the desired molecular signal, resulting only in fragmentation; elemental analysis: calcd (%) for $C_{18}H_{16}$: C 93.06, H 6.94; found: C 92.90, H 7.09.

Trimethyl[(*E*)-6-phenylhexa-1,2,5-trien-3-yl]silane (23a; cf. Scheme 1): Prepared from allyl carbonate **1a** and γ-(trimethylsilyl)propargyl boronate **22** according to general procedure B with $[Pd(PPh_3)_4]$ (10 mol%) in toluene at room temperature for 8 h (eluant for PTLC: *n*-hexane). Colorless liquid; yield: 46%; the desired 1,4-enallene **23a** (linear-γ) was obtained as a single isomer, but exists as a mixture of two rotamers in $CDCl_3$ at 40°C (ratio major/minor 24:1); IR (neat): $\tilde{\nu}$=1928, 1645, 1249, 962, 840, 745, 693 cm^{-1}; ^1H NMR (600 MHz, $[D_1]$chloroform, 40°C, TMS): δ=0.02 (s, 9H; minor), 0.14 (s, 9H; major), 2.91–2.93 (m, 2H; major), 2.98–2.99 (m, 2H; minor), 4.39 (t, J=2.8 Hz, 2H; major), 4.46 (t, J=2.8 Hz, 2H; minor), 6.26 (dt, J=6.8, 15.8 Hz, 1H; major + minor), 6.43 (d, J=15.8 Hz, 1H; major + minor), 7.19–7.21 (m, 1H; major + minor), 7.28–7.31 (m, 2H; major + minor), 7.35–7.36 ppm (m, 2H; major + minor); ^{13}C NMR (150 MHz, $[D_1]$chloroform, 40°C, TMS): δ= −1.53 (3C; major), 0.03 (3C; minor), 33.1 (major), 69.1 (major), 70.0 (minor), 86.3 (minor), 93.4 (major), 126.1 (major), 126.9 (major), 128.5 (major), 129.1 (major), 130.5 (major), 137.8 (major), 209.4 ppm (major); HRMS (ESI): *m*/*z*: calcd for $C_{15}H_{21}Si^+$: 229.1407 $[M+H]^+$; found: 229.1407.

Competition experiment: Pd^0-catalzyed C–C coupling versus 1,2-allyl boration: $[Pd(PPh_3)_4]$ (10 mol%), ethyl acetate (2 mL, 0.1 M), dibenzyl ether (0.10 mmol, 0.50 equiv), allyl carbonate **1a** (0.20 mmol, 1.0 equiv), and benzaldehyde (0.20 mmol, 1.0 equiv) were added successively to an oven-dried 5 mL microwave-type vial with a magnetic stirring bar in an Ar box. Allyl boronate **3** (0.20 mmol, 1.0 equiv) was then added in one portion to the vigorously stirred reaction mixture at room temperature. After 15 min, TLC analysis showed complete conversion of allyl carbonate **1a**. The reaction mixture was quenched with aqueous HCl (1 M, 1 drop) and an aliquot of the mixture (100 μL) was analyzed in $CDCl_3$ (500 μL). ^1H NMR spectral analysis showed full conversion of allyl carbonate **1a** into the desired 1,5-dienes **4a** and **5a** (ratio **4a**/**5a** >32:1; quantitative NMR yield based on dibenzyl ether as internal standard). In addition, benzaldehyde was recovered in essentially quantitative yield and the potentially formed homoallylic alcohol or any related allyl borated materials were not detected.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) .

[1] a) *Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis* (Ed.: J. Tsuji), Wiley, New York, **2000**; b) *Catalytic Asymmetric Catalysis* (Ed.: I. Ojima), Wiley-VCH, Weinheim, **2000**.

[2] For a recent review, see: D. J. Cárdenas, *Angew. Chem.* **2003**, *115*, 398; *Angew. Chem. Int. Ed.* **2003**, *42*, 384.

[3] a) B. M. Trost, K. M. Pietrusiewicz, *Tetrahedron Lett.* **1985**, *26*, 4039; b) J. M. Cuerva, E. Gómez-Bengoa, M. Méndez, A. M. Echavarren, *J. Org. Chem.* **1997**, *62*, 7540; c) M. Méndez, J. M. Cuerva, E. Gómez-Bengoa, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2002**, *8*, 3620.

[4] S. Porcel, V. López-Carrillo, C. García-Yebra, A. M. Echavarren, *Angew. Chem.* **2008**, *120*, 1909; *Angew. Chem. Int. Ed.* **2008**, *47*, 1883.

[5] a) E. Breitmaier, *Terpenes—Flavors, Fragrances, Pharmaca, Pheromones*, Wiley-VCH, Weinheim, **2006**; b) K. C. Nicolaou, T. Montagnon, *Molecules that Changed the World*, Wiley-VCH, Weinheim, **2008**.

[6] For selected examples of organic synthesis by using 1,5-dienes, see: a) L. E. Overman, F. M. Knoll, *J. Am. Chem. Soc.* **1980**, *102*, 865; b) R. C. D. Brown, J. F. Keily, *Angew. Chem.* **2001**, *113*, 4628; *Angew. Chem. Int. Ed.* **2001**, *40*, 4496; c) H. Nakamura, Y. Yamamoto in *Handbook of Organopalladium Chemistry for Organic Synthesis, Vol. 2* (Eds.: E.-i. Negishi, A. de Meijere), Wiley-Interscience, West Lafayette, **2002**, p. 2919; d) T. J. Donohoe, S. Butterworth, *Angew. Chem.* **2003**, *115*, 978; *Angew. Chem. Int. Ed.* **2003**, *42*, 948; e) Y.-J. Zhao, S.-S. Chng, T.-P. Loh, *J. Am. Chem. Soc.* **2007**, *129*, 492; f) J. A. Feducia, M. R. Gagné, *J. Am. Chem. Soc.* **2008**, *130*, 592.

[7] E.-i. Negishi, B. Liao in *Handbook of Organopalladium Chemistry for Organic Synthesis, Vol. 1* (Eds.: E.-i. Negishi, A. de Meijere), Wiley-Interscience, West Lafayette, **2002**, p. 591.

[8] a) A. Goliaszewski, J. Schwartz, *J. Am. Chem. Soc.* **1984**, *106*, 5028; b) A. Goliaszewski, J. Schwartz, *Tetrahedron* **1985**, *41*, 5779.

[9] a) P. H. Lee, S.-y. Sung, K. Lee, S. Chang, *Synlett* **2002**, 146; b) P. H. Lee, E. Shim, K. Lee, D. Seomoon, S. Kim, *Bull. Korean Chem. Soc.* **2005**, *26*, 157.

[10] M. Murakami, T. Kato, T. Mukaiyama, *Chem. Lett.* **1987**, 1167.

[11] a) B. M. Trost, E. Keinan, *Tetrahedron Lett.* **1980**, *21*, 2595; b) J. Godschalx, J. K. Stille, *Tetrahedron Lett.* **1980**, *21*, 2599; c) A. Goliaszewski, J. Schwartz, *Organometallics* **1985**, *4*, 417; d) H. Nakamura, M. Bao, Y. Yamamoto, *Angew. Chem.* **2001**, *113*, 3308; *Angew. Chem. Int. Ed.* **2001**, *40*, 3208.

[12] a) For a recent review, see: J. W. J. Kennedy, D. G. Hall, *Angew. Chem.* **2003**, *115*, 4880; *Angew. Chem. Int. Ed.* **2003**, *42*, 4732; b) for an account, see: D. G. Hall, *Synlett* **2007**, 1644; for recent exceptions that use an allyl boronate in 1,4-additions, see: c) J. D. Sieber, S. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2007**, *129*, 2214; d) J. D. Sieber, J. P. Morken, *J. Am. Chem. Soc.* **2008**, *130*, 4978; e) M. B. Shaghafi, B. L. Kohn, E. R. Jarvo, *Org. Lett.* **2008**, *10*, 4743.
[13] a) U. Schneider, S. Kobayashi, *Angew. Chem.* **2007**, *119*, 6013; *Angew. Chem. Int. Ed.* **2007**, *46*, 5909; b) U. Schneider, I.-H. Chen, S. Kobayashi, *Org. Lett.* **2008**, *10*, 737; c) S. Kobayashi, H. Konishi, U. Schneider, *Chem. Commun.* **2008**, 2313.
[14] Pd^0-catalyzed cross-coupling between allyl carbonates and allyl–indium species (THF, reflux, 24 h), in situ generated from allyl bromides with a stoichiometric amount of In^0, has been reported; see reference [9].
[15] A 1,5-diene has been observed as a symmetrical coupling side product in Pd^0-catalyzed borylation of an allyl carbonate with $B_2(pin)_2$ (DMSO, 50 °C; 80 % yield); only a single example has been reported, see: T. Ishiyama, T.-a. Ahiko, N. Miyaura, *Tetrahedron Lett.* **1996**, *37*, 6889.
[16] 1,5-Dienes have been observed as symmetrical coupling side products in Pd^0-catalyzed allylation of aldehydes with allyl carbonates and BEt_3 (THF, RT, 6–21 % yield), see: M. Kimura, I. Kiyama, T. Tomizawa, Y. Horino, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **1999**, *40*, 6795.
[17] Pd^0-catalyzed sp^3–sp^2 cross-coupling between allyl trifluoroborates and aryl or alkenyl bromides with γ-selectivity has been reported, see: a) Y. Yamamoto, S. Takada, N. Miyaura, *Chem. Lett.* **2006**, *35*, 704; b) Y. Yamamoto, S. Takada, N. Miyaura, T. Iyama, H. Tachikawa, *Organometallics* **2009**, *28*, 152.
[18] S_N2 reactions between primary allyl halides and allyl trialkylborates have been reported, see: a) Y. Yamamoto, K. Maruyama, *J. Am. Chem. Soc.* **1978**, *100*, 6282; b) Y. Yamamoto, H. Yatagai, K. Maruyama, *J. Am. Chem. Soc.* **1981**, *103*, 1969.
[19] a) E. Keinan, S. Kumar, V. Dangur, J. Vaya, *J. Am. Chem. Soc.* **1994**, *116*, 11151; b) L. H. Shultz, M. Brookhart, *Organometallics* **2001**, *20*, 3975.
[20] a) H. Kurosawa, H. Ohnishi, M. Emoto, Y. Kawasaki, S. Murai, *J. Am. Chem. Soc.* **1988**, *110*, 6272; b) H. Kurosawa, H. Ohnishi, M. Emoto, N. Chatani, Y. Kawasaki, S. Murai, I. Ikeda, *Organometallics* **1990**, *9*, 3038.
[21] Ni^0-catalyzed activation of allyl carbonates for retroallylation with homoallyl alcohols has been reported, see: Y. Sumida, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, *10*, 1629.
[22] Typically, allenyl boronate **17** has been shown to display other reactivity patterns under Ru or Pd catalysis, see: a) Ru: E. Bustelo, C. Guérot, A. Hercouet, B. Carboni, L. Toupet, P. H. Dixneuf, *J. Am. Chem. Soc.* **2005**, *127*, 11582; Pd: b) K. Tonogaki, K. Itami, J.-i. Yoshida, *J. Am. Chem. Soc.* **2006**, *128*, 1464; c) K. Tonogaki, K. Itami, J.-i. Yoshida, *Org. Lett.* **2006**, *8*, 1419; d) O. B. Locos, K. Dahms, M. O. Senge, *Tetrahedron Lett.* **2009**, *50*, 2566.
[23] Pd^0-catalyzed cross-coupling between an allenyl stannane and allyl acetates has been shown to provide product mixtures, see: E. Keinan, M. Peretz, *J. Org. Chem.* **1983**, *48*, 5302.
[24] H. C. Brown, U. S. Racherla, P. J. Pellechia, *J. Org. Chem.* **1990**, *55*, 1868.
[25] Pd^0-catalyzed chemoselective cross-coupling between an allyl stannane and allyl chlorides in the presence of aldehydes has been reported; see reference [11d].
[26] W. R. Roush, M. A. Adam, A. E. Walts, D. J. Harris, *J. Am. Chem. Soc.* **1986**, *108*, 3422.
[27] R. W. Hoffmann, J. J. Wolff, *Chem. Ber.* **1991**, *124*, 563.
[28] P. G. M. Wuts, P. A. Thompson, G. R. Callen, *J. Org. Chem.* **1983**, *48*, 5398.
[29] D. J. S. Tsai, D. S. Matteson, *Organometallics* **1983**, *2*, 236.
[30] R. W. Hoffmann, H. Brinkmann, G. Frenking, *Chem. Ber.* **1990**, *123*, 2387.
[31] D. J. Weix, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 7720.
[32] S. B. J. Kan, R. Matsubara, F. Berthiol, S. Kobayashi, *Chem. Commun.* **2008**, 6354.
[33] T. Nemoto, T. Masuda, Y. Akimoto, T. Fukuyama, Y. Hamada, *Org. Lett.* **2005**, *7*, 4447.
[34] Y. Sumida, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2008**, *10*, 1629.
[35] M. J. S. Dewar, L. E. Wade, Jr., *J. Am. Chem. Soc.* **1977**, *99*, 4417.
[36] G. C. Kabalka, M.-L. Yao, S. Borella, Z. Wu, Y.-H. Ju, T. Quick, *J. Org. Chem.* **2008**, *73*, 2668.
[37] a) For compound **6k** (linear), see: M. E. Krafft, T. F. N. Haxell, *J. Am. Chem. Soc.* **2005**, *127*, 10168; b) for compound **7k** (branched), see: K. Urabe, K. Suzuki, F. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 10014.
[38] a) For compound **6l** (linear), see: P. Bertrand, J.-P. Gesson, *Tetrahedron Lett.* **1992**, *33*, 5177; b) for compound **7l** (branched), see: T. Nishikawa, T. Shinokubo, K. Oshima, *Org. Lett.* **2003**, *5*, 4623.
[39] a) For compounds **6m** (linear) and **7m** (branched), see: Y. Kataoka, I. Makihira, H. Akiyama, K. Tani, *Tetrahedron* **1997**, *53*, 9525; b) for compound **8m** (1,3-diene), see: D. A. Mundal, K. E. Lutz, R. J. Thompson, *Org. Lett.* **2009**, *11*, 465.

Received: August 10, 2009
Published online: October 15, 2009

