Transition-Metal-Catalyzed Synthesis of 1,3-Diynes and Ynamides from 2-Bromo-1-iodoalkenes

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Abstract: Diynes and ynamides are important products in chemical synthesis. An efficient palladium-catalyzed homocoupling reaction of 2-bromo-1-iodoalkenes to give 1,3-diynes has been developed. The reactions are conducted under convenient conditions and provide products in moderate to excellent yields. Moreover, ynamides were synthesized from 2-bromo-1-iodoalkenes and carbamates, and it is noteworthy that this reaction is catalyzed by nanoparticulate copper(I) oxide to give ynamides in high yields.

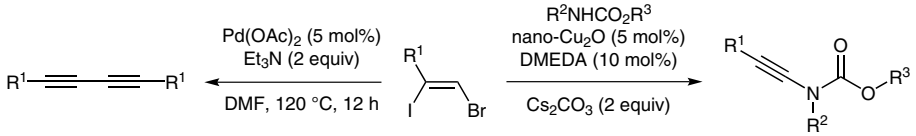
Key words: catalysis, palladium, copper, alkynes, amides, coupling

Diynes have received considerable attention as a result of their use in the construction of carbon-rich materials, organic conductors, macrocyclic annulenes, and supramolecular scaffolds. In addition, diyne moieties are found in numerous natural products, pharmaceuticals, and bioactive compounds.[1] As a consequence, considerable efforts have been made to develop new and effective approaches for the formation of 1,3-diynes. Conventional methods for the synthesis of 1,3-diynes include Glaser coupling, Eglinton coupling, Hay coupling, and Cadiot–Chodkiewicz coupling.[2] Current research is mainly focused on modifying Glaser's original conditions to promote the coupling reaction more effectively, for example, by using copper-mediated conditions[3,4] or palladium- or copper-catalyzed coupling reactions.[5] Recently, copper-[6] and palladium-catalyzed[7] syntheses of 1,3-diynes from internal alkynes have been reported. There are few reports of transition-metal-catalyzed homocoupling reactions of substrates other than terminal alkynes or internal alkynes to give 1,3-diynes.[8] Therefore, the continuation of studies on the formation of 1,3-diynes is still of great significance.

Ynamides have recently been successfully employed in numerous transformations, including nucleophilic addition reactions, cycloadditions, reductions, cycloisomerizations, and metal-catalyzed cross-coupling reactions.[9] The direct synthesis approach is based on copper-catalyzed aerobic coupling of terminal alkynes with amides.[10] Transition-metal-catalyzed coupling of amides with haloalkynes is currently the most widely applied method.[11] Also, 1,1- and 1,2-dibromo-1-alkenes have been used in the preparation of ynamides.[12] Although these well-established methods for the synthesis of ynamides have proved to be very effective,[13] the search for novel routes to ynamides with flexible substrate patterns is an important continuing goal of organic synthesis.

Dihaloalkenes are attracting more and more attention, as it has become possible to construct multifunctional and nonsymmetric compounds.[12a,14,15] We recently reported a simple two-step synthesis of (*Z*)-2-halo-1-iodoalkenes from terminal alkynes in moderate to excellent yields with high regio- and stereoselectivity.[16] During our investigations on 2-halo-1-iodoalkenes, we found that 1,3-diynes were formed in palladium-catalyzed systems, and ynamides were formed in copper-catalyzed conditions. Inspired by these observations, we examined the transition-metal-catalyzed synthesis of 1,3-diynes and ynamides from 2-bromo-1-iodoalkenes (Scheme 1).

We examined the reaction of [(*Z*)-2-bromo-1-iodovinyl]benzene (**1a**) with the aim of optimizing the reaction conditions (Table 1). Our initial investigations focused on attempts to achieve homocoupling of dihaloalkene **1a** by using common metal salts. To our delight, copper salts and palladium salts gave the 1,3-diyne **2a**, albeit in low yields. Palladium catalysts were more efficient in this transformation (Table 1, entries 1–4). We tested a varieties of palladium catalysts (entries 5–7) and we found that palladium(II) acetate is the catalyst of choice (entry 7). The reaction did not proceed in the absence of a catalyst (entry 8). We then examined palladium(II) acetate catalyzed reaction in the presence of various inorganic and organic bases (entries 9–14). Triethylamine was superior to



Scheme 1 Transition-metal-catalyzed synthesis of 1,3-diynes and ynamides from 2-bromo-1-iodoalkenes

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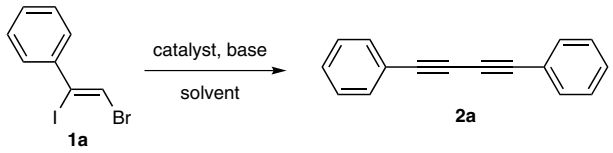
any of the other bases that were tested and gave the desired product in 80% yield (by GC; entry 14). The reaction showed a strong dependence on the nature of the solvent. Among the solvents tested (entries 15–19), *N*,*N*-dimethylformamide was found to be the most appropriate (entry 18). Higher temperatures favored the reaction, and diyne **2a** was obtained in 91% isolated yield after 12 hours at 120 °C (entry 20). Finally, we examined the effect of the reaction time and we found that a shorter time did not favor the reaction (entry 21).

Table 1 Optimization of Reaction Conditions for the Synthesis of 1,1′-Buta-1,3-diyne-1,4-diyldibenzene[a]

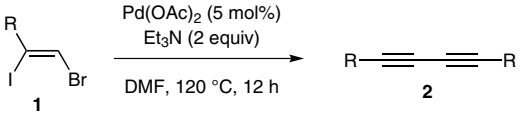


Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	CuI	MeCN	K_2CO_3	5
2	AgOAc	MeCN	K_2CO_3	–
3	$FeCl_3$	MeCN	K_2CO_3	–
4	$Pd(dba)_2$	MeCN	K_2CO_3	48
5	$Pd(PPh_3)_4$	MeCN	K_2CO_3	52
6	$PdCl_2$	MeCN	K_2CO_3	65
7	$Pd(OAc)_2$	MeCN	K_2CO_3	76
8	–	MeCN	K_2CO_3	–
9	$Pd(OAc)_2$	MeCN	NaOAc	64
10	$Pd(OAc)_2$	MeCN	K_3PO_4	58
11	$Pd(OAc)_2$	MeCN	TMEDA	70
12	$Pd(OAc)_2$	MeCN	DABCO	14
13	$Pd(OAc)_2$	MeCN	DBU	26
14	$Pd(OAc)_2$	MeCN	Et_3N	80
15	$Pd(OAc)_2$	1,4-dioxane	Et_3N	35
16	$Pd(OAc)_2$	Ac_2O	Et_3N	14
17	$Pd(OAc)_2$	DMSO	Et_3N	68
18	$Pd(OAc)_2$	DMF	Et_3N	87
19	$Pd(OAc)_2$	toluene	Et_3N	72
20[c]	$Pd(OAc)_2$	DMF	Et_3N	95 (91[d])
21[e]	$Pd(OAc)_2$	DMF	Et_3N	65

[a] Reaction conditions: **1a** (0.5 mmol), solvent (1.0 mL), base (2 equiv), catalyst (5 mol%), 80 °C, 12 h.
[b] Determined by GC.
[c] 120 °C.
[d] Isolated yield.
[e] Reaction for 6 h.

Having determined the optimal conditions, we set out to test the generality of this reaction. The approach to 1,3-diynes was found to be quite versatile (Table 2). In general, aromatic dihaloalkenes with either electron-donating or electron-withdrawing groups attached to the benzene rings underwent smooth homocoupling and gave the corresponding 1,3-diyne products in moderate to good yields. Diaryldiynes containing substituents on the benzene rings gave lower yields than did the unsubstituted analogue 1,1′-buta-1,3-diyne-1,4-diyldibenzene (**1a**), and substrates containing electron-rich groups provided higher yields than did substrates containing electron-deficient groups (entries 2–11). Substituents in the *ortho*-position of the phenyl group had some impact on the yield of the reaction (entries 4, 8, and 10). The bulky *tert*-butyl group was compatible with the conditions (entry 5). For aromatic dihaloalkenes with electron-rich substituents in the *para*-position, the homocoupling yields gradually decreased in the order H > MeO > Me > *t*-Bu (entries 1–6). Note that the carbon–halogen bond was well tolerated, and halogen-containing products were obtained smoothly. In particular, the aryl chloride was capable of being further functionalized (entry 9). It was noteworthy that the 3,5-bis(trifluoromethyl)benzene ring was a suitable substrate under the standard conditions (Table 2, entry 11). However, treatment of alkyl-substituted substrates under

Table 2 Palladium-Catalyzed Synthesis of 1,3-Diynes from 2-Bromo-1-iodoalkene Derivatives[a]



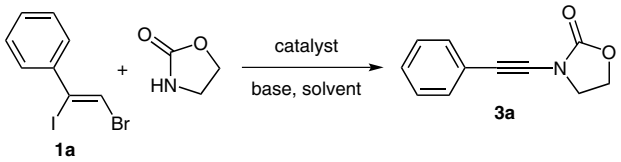
Entry	R	Product	Yield[b] (%)
1	Ph	**2a**	91
2	4-Tol	**2b**	85
3	3-Tol	**2c**	83
4	2-Tol	**2d**	72
5	4-*t*-BuC_6H_4	**2e**	82
6	4-$MeOC_6H_4$	**2f**	88
7	4-FC_6H_4	**2g**	76
8	2-FC_6H_4	**2h**	63
9	3-ClC_6H_4	**2i**	70
10	2-$F_3CC_6H_4$	**2j**	58
11	3,5-$(F_3C)_2C_6H_3$	**2k**	77
12	$(CH_2)_5Me$	**2l**	48
13	CH_2Cy	**2m**	42

[a] Reaction conditions: **1** (0.5 mmol), DMF (1.0 mL), Et_3N (2 equiv) and $Pd(OAc)_2$ (5 mol%) at 120 °C for 12 h.
[b] Isolated yield.

these conditions gave lower yields of the corresponding products (entries 12 and 13).

Catalysis by nanoparticles has attracted considerable attention owing to its environmentally benign nature and its high activity in various reactions. Table 3 summarizes results of our studies on the optimization of the reaction of [(*Z*)-(2-bromo-1-iodovinyl)]benzene (**1a**) with 1,3-oxazolidin-2-one. First, we evaluated a series of copper catalysts (Table 3, entries 1–4), and we found that copper(I) oxide promoted the transformation (entry 4). We then examined the effect of nanoparticulate copper(II) oxide (nano-Cu_2O) prepared by a hydrothermal method,[17] and we found that the yield increased to 69% (entry 5). Next, we tried to improve the yields by using various solvents (entries 6–8). Among the solvent surveyed, 1,4-dioxane was found to be the most effective medium for this coupling reaction (entry 9). When we examined the effects of several bases (entries 9–12), we found that ynamide **3a** was obtained in 83% yield when cesium carbonate was used as the base. Optimization of the reaction temperature showed that 110 °C was optimal (entry 13). Finally, when the reaction was carried out under Liang's conditions,[12b] ynamides **3a** was not detected.

Table 3 Optimization of Reaction Conditions for the Synthesis of Ynamide[a]



1a **3a**

Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	CuI	DMF	K_3PO_4	26
2	$CuSO_4 \cdot 5H_2O$	DMF	K_3PO_4	5
3	CuCN	DMF	K_3PO_4	trace
4	Cu_2O	DMF	K_3PO_4	42
5	nano-Cu_2O	DMF	K_3PO_4	69
6	nano-Cu_2O	1,4-dioxane	K_3PO_4	78
7	nano-Cu_2O	toluene	K_3PO_4	65
8	nano-Cu_2O	THF	K_3PO_4	50
9	nano-Cu_2O	1,4-dioxane	*t*-BuOK	72
10	nano-Cu_2O	1,4-dioxane	NaOAc	70
11	nano-Cu_2O	1,4-dioxane	Cs_2CO_3	83
12	nano-Cu_2O	1,4-dioxane	DBU	45
13[c]	nano-Cu_2O	1,4-dioxane	Cs_2CO_3	91 (86[d])

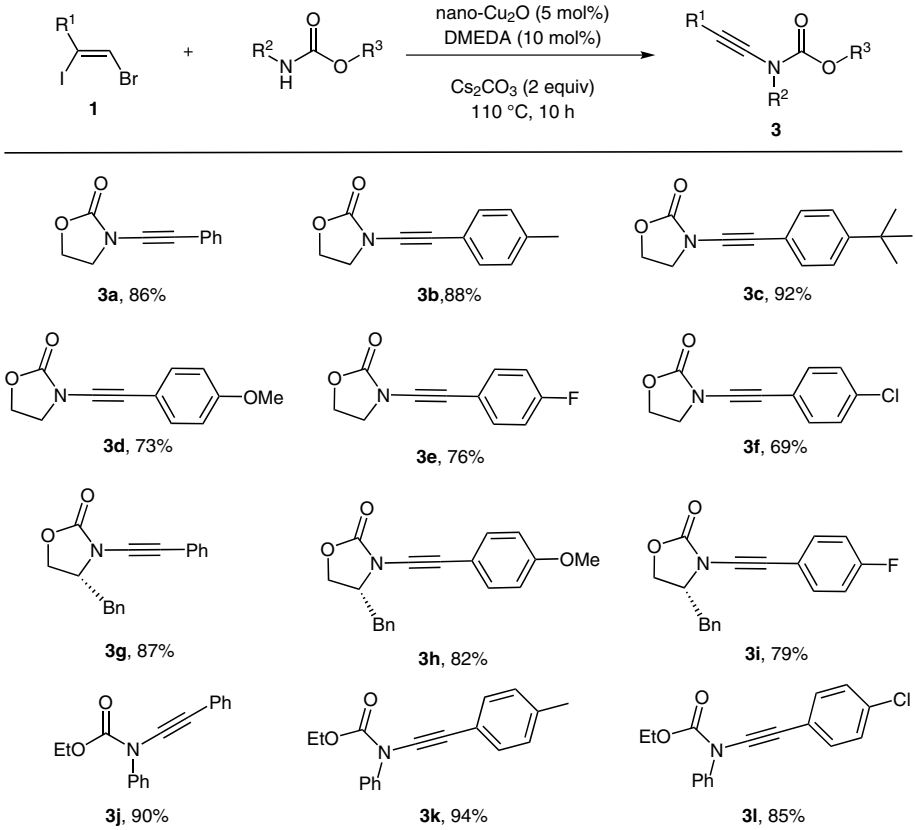
[a] Reaction conditions: alkene **1a** (0.25 mmol), 1,3-oxazolidin-2-one (0.3 mmol), catalyst (5 mol%), DMEDA (10 mol%), base (2 equiv), solvent (1.0 mL), 80 °C, 10 h.
[b] Determined by GC.
[c] 110 °C.
[d] Isolated yield.

Having determined the optimal conditions (Table 3, entry 13), we examined the scope and utility of this method with other 2-bromo-1-iodoalkenes and carbamates under the standard conditions (Scheme 2). Aromatic dihaloalkenes with either an electron-donating or electron-withdrawing group on the benzene ring gave the corresponding products **3b–l** in good to excellent yield. Clearly, electronic effects play an important role, as electron-rich substituents on the benzene ring favored the transformation. The reaction conditions were compatible with alkyl, alkyloxy, fluoro, or chloro groups (**3b–l**). The bulky *tert*-butyl group afforded the product in 92% yield (**3c**). It should be pointed out that the carbon–halogen bonds were well tolerated, and products containing halogens were obtained smoothly; in particular, the aryl chlorides **3f** and **3l** were capable of being further functionalized. Acyclic carbamates gave better yields of the corresponding ynamide derivatives **3j–l** than did the corresponding cyclic carbamates **3a–i**.

Two plausible mechanisms for the palladium-catalyzed homocoupling reaction (Scheme 3, paths I and II) are proposed on the basis of a previously reported mechanism and the present results. First, intermediate **A** is formed by insertion of palladium(0) into the C–Br bond of the 2-bromo-1-iodoalkene **1**. In path I, the intermediate **A** is transformed into the alkynylpalladium compound **B** by elimination of hydrogen iodide; intermediate **B** is then converted into the 1,3-diyne product **2** by homocoupling.[8a] In path II, elimination of palladium(II) gives the terminal alkyne, from which intermediate **C** is formed by insertion of palladium(0) into the C–H bond; subsequently, 1,3-diyne product **2** is formed by a similar mechanism to one described in the literature.[2,18] To check the feasibility of these routes, we performed control experiments under standard conditions. For example, both the cross-coupling product **2ab** and the homocoupling products **2a** and **2b** were formed when 1-bromo-4-(bromoethynyl)benzene or [(*Z*)-2-bromo-1-iodovinyl]benzene (**1a**) was treated with ethynylbenzene or 1-ethynyl-4-methylbenzene, respectively (Scheme 3, equations 3 and 4). These results support path II as the mechanism.

The nanoparticulate copper(I) oxide catalyzed synthesis of ynamides proceeds by a similar mechanism to that described in the literature.[12]

In conclusion, we have developed a simple and general method for the synthesis of symmetric 1,3-diynes and ynamides in moderate to excellent yields from easily accessible 2-bromo-1-iodoalkenes. Aromatic compounds were more effective substrates than aliphatic compounds. Both electron-donating and electron-withdrawing substituents on the aromatic ring were compatible with the standard conditions. Although the 2-bromo-1-iodoalkenes are more complicated raw materials than terminal alkynes or haloalkynes, the absence of copper salts in the homocoupling reaction and the use of nanoparticulate catalysts for the synthesis of ynamides make the presented methods interesting and valuable. Further utilization of this procedure and studies on its mechanism will continue in our laboratory.



Scheme 2 Nanoparticulate copper(I) oxide-catalyzed synthesis of ynamides from 2-bromo-1-iodoalkenes and carbamates. *Reaction conditions*: alkene **1** (0.25 mmol), carbamate (0.3 mmol), nano-Cu_2O (5 mol%), DMEDA (10 mol%), 1,4-dioxane (1.0 mL), Cs_2CO_3 (2 equiv), 110 °C, 10 h. The reported yields are isolated yields.

All chemicals and solvents were purchased from Aldrich, Fluka, or Merck, and were used without further purification. Melting points were measured with a Büchi B-545 melting point instrument and are uncorrected. IR spectra were obtained for samples prepared either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. $CDCl_3$ was used as solvent, with Me_4Si as internal standard; chemical shifts are referenced to signals at 7.24 ppm (^{1}H NMR) and 77.0 ppm (^{13}C NMR), respectively. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m).

1,3-Diynes 2a–m; General Procedure

The mixture of 2-bromo-1-iodoalkene **1** (0.5 mmol), Et_3N (1 mmol), and $Pd(OAc)_2$ (5 mol%) in DMF (1 mL) was stirred in a 25 mL Schlenk tube at 120 °C for 12 h. When the reaction was complete, H_2O (8 mL) was added and the mixture was extracted with Et_2O (3 × 5 mL). The extracts were combined, dried ($MgSO_4$), and concentrated to give a crude product that was purified by column chromatography [silica gel, PE–EtOAc (100:1 to 10:1)].

1,1′-Buta-1,3-diyne-1,4-diyldibenzene (2a)[5a]
White solid; yield: 46 mg (91%); mp 86–87 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.53 (m, 4 H), 7.30–7.36 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 129.1, 128.4, 121.7, 81.5, 75.8.

MS (EI): *m/z* = 202, 174, 150, 126, 101, 88.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-methylbenzene) (2b)[5a]
White solid; yield: 49 mg (85%); mp 137–138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 4 H), 7.12 (d, *J* = 8.0 Hz, 4 H), 2.34 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 132.3, 129.1, 118.7, 81.5, 73.3, 21.5.

MS (EI): *m/z* = 230, 215, 189, 163, 115, 101, 88.

1,1′-Buta-1,3-diyne-1,4-diylbis(3-methylbenzene) (2c)[5a]
White solid; yield: 48 mg (83%); mp 68–70 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.33 (m, 4 H), 7.15–7.22 (m, 4 H), 2.32 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 132.9, 130.0, 129.5, 128.2, 121.5, 81.5, 73.5, 21.1.

MS (EI): *m/z* = 230, 215, 202, 163, 115, 101, 88.

1,1′-Buta-1,3-diyne-1,4-diylbis(2-methylbenzene) (2d)[5a]
White solid; yield: 41 mg (72%); mp 72–74 °C.

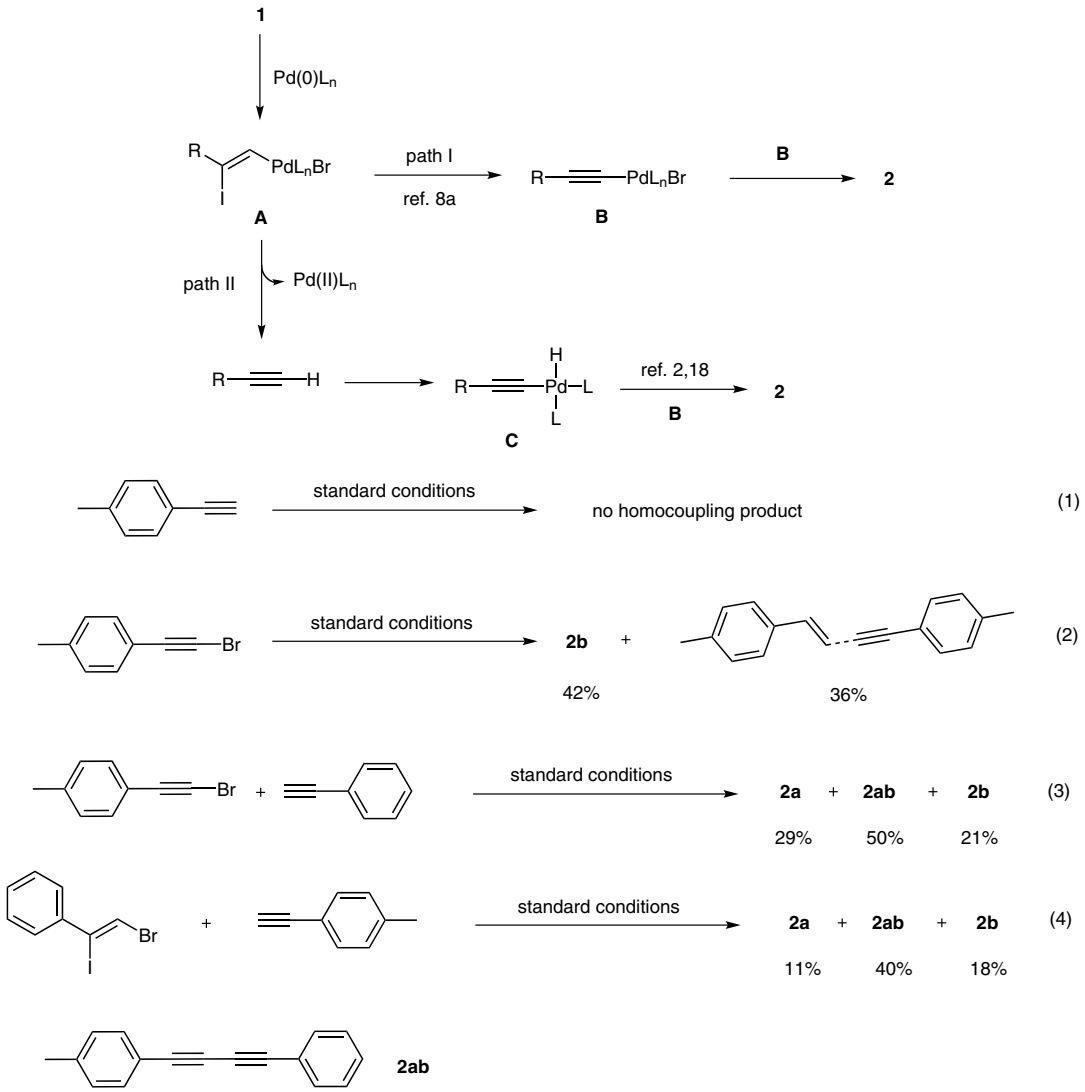
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.2 Hz, 2 H), 7.20–7.27 (m, 4 H), 7.13–7.17 (m, 2 H), 2.49 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 132.9, 129.6, 129.1, 125.7, 121.7, 81.2, 77.5, 20.7.

MS (EI): *m/z* = 230, 215, 202, 189, 115, 89.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-*tert*-butylbenzene) (2e)[19a]
Off-white solid; yield: 64 mg (82%); mp 195–196 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 4 H), 7.34 (d, *J* = 8.4 Hz, 4 H), 1.30 (s, 18 H).



Scheme 3 Possible mechanisms for the palladium-catalyzed homocoupling reaction

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 132.2, 125.4, 118.7, 81.4, 73.4, 34.8, 31.0.

MS (EI): *m/z* = 314, 299, 271, 239, 215, 165, 142, 114.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-methoxybenzene) (2f)[5a]
White solid; yield: 58 mg (88%); mp 141–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.8 Hz, 4 H), 6.83 (d, *J* = 8.8 Hz, 4 H), 3.80 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 133.9, 114.0, 113.8, 81.1, 72.8, 55.2.

MS (EI): *m/z* = 262, 247, 219, 204, 176, 131, 110.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-fluorobenzene) (2g)[5a]
White solid; yield: 45 mg (76%); mp 189–190 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.51 (m, 4 H), 6.99–7.04 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0 (d, *J* = 251.0 Hz), 134.5 (d, *J* = 8.0 Hz), 117.7, 115.9 (d, *J* = 22.0 Hz), 80.4, 73.4.

MS (EI): *m/z* = 238, 218, 192, 168, 144, 119, 74.

1,1′-Buta-1,3-diyne-1,4-diylbis(2-fluorobenzene) (2h)[5a]
White solid; yield: 37 mg (63%); mp 120–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.52 (m, 2 H), 7.31–7.37 (m, 2 H), 7.06–7.12 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6 (d, *J* = 252.0 Hz), 134.2, 131.0 (d, *J* = 8.0 Hz), 124.1, 115.6 (d, *J* = 20.0 Hz), 110.3 (d, *J* = 15.0 Hz), 78.3, 75.8.

MS (EI): *m/z* = 238, 218, 207, 192, 135, 119, 106, 80.

1,1′-Buta-1,3-diyne-1,4-diylbis(3-chlorobenzene) (2i)[5a]
White solid; yield: 47 mg (70%); mp 138–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 2 H), 7.38 (d, *J* = 7.6 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.23–7.27 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 132.2, 130.6, 129.6, 129.0, 123.1, 80.5, 74.6.

MS (EI): *m/z* = 270, 200, 174, 135, 100, 32, 28.

1,1′-Buta-1,3-diyne-1,4-diylbis[2-(trifluoromethyl)benzene] (2j)[19a]
White solid; yield: 49 mg (58%); mp 70–71 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.70 (m, 4 H), 7.43–7.53 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.6, 132.3, 132.0, 130.9, 128.6, 125.6, 125.5, 124.1, 121.4, 119.3, 78.2, 78.1.

MS (EI): *m/z* = 338, 319, 287, 269, 159, 135.

1,1'-Buta-1,3-diyne-1,4-diylbis[3,5-bis(trifluoromethyl)benzene] (2k)[19b]
Reddish-brown semisolid; Yield: 91 mg (77 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 4 H), 7.87 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4 (q, *J* = 20.0 Hz), 126.8, 124.1, 123.8 (d, *J* = 42.0 Hz), 120.1 (d, *J* = 272.0 Hz), 79.8, 76.2.

MS (EI): *m/z* = 474, 405, 355, 285, 237, 203, 193, 168, 158.

Hexadeca-7,9-diyne (2l)[19a]
Colorless oil; yield: 26 mg (48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (t, *J* = 6.8 Hz, 4 H), 1.45–1.52 (m, 4 H), 1.30–1.39 (m, 4 H), 1.20–1.27 (m, 8 H), 0.86 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.5, 65.1, 31.2, 28.5, 28.2, 22.4, 19.1, 14.0.

MS (EI): *m/z* = 218, 203, 189, 147, 133, 119, 105, 91, 79, 67, 41.

1,1′-Hexa-2,4-diyne-1,6-diyldicyclohexane (2m)[19a]
Colorless oil; yield: 25 mg (42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (d, *J* = 6.4 Hz, 4 H), 1.74–1.78 (m, 4 H), 1.66–1.70 (m, 4 H), 1.59–1.63 (m, 2 H), 1.41–1.49 (m, 2 H), 1.05–1.26 (m, 6 H), 0.90–1.00 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.3, 66.0, 37.2, 32.6, 26.9, 26.0, 26.0.

MS (EI): *m/z* = 242, 199, 159, 145, 131, 117, 91, 83, 55.

Ynamides 3a–l; General Procedure
A mixture of the 2-bromo-1-iodoalkene **1** (0.25 mmol), the appropriate carbamate (0.3 mmol), Cs_2CO_3 (2 equiv), DMEDA (10 mol%), and nano-Cu_2O (5 mol%) in 1,4-dioxane (1 mL) was stirred in a 25 mL Schlenk tube at 110 °C for 10 h. When the reaction was complete, H_2O (8 mL) was added and the mixture was extracted with Et_2O (3 × 5 mL). The extracts were combined, dried ($MgSO_4$), and concentrated to give a crude product that was purified by column chromatography [silica gel, PE–EtOAc (4:1 to 1:2)].

3-(Phenylethynyl)-1,3-oxazolidin-2-one (3a)[20a]
White solid; yield: 40 mg (86%); mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.43 (m, 2 H), 7.26–7.30 (m, 3 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 3.95 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 131.5, 128.3, 128.2, 122.1, 79.0, 71.1, 63.2, 47.0.

MS (EI): *m/z* = 187, 143, 128, 115, 88, 77, 65, 51.

3-[(4-Tolyl)ethynyl]-1,3-oxazolidin-2-one (3b)[20a]
White solid; yield: 44 mg (88%); mp 114–115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 4.43 (t, *J* = 8.0 Hz, 2 H), 3.95 (t, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 138.4, 131.5, 129.1, 119.0, 78.3, 71.1, 61.1, 47.0, 21.4.

MS (EI): *m/z* = 201, 157, 142, 129, 115, 102, 91, 77, 65, 51.

3-[(4-*tert*-Butylphenyl)ethynyl]-1,3-oxazolidin-2-one (3c)[20b]
Colorless solid; yield: 56 mg (92%); mp 131–133 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 4.45 (t, *J* = 8.0 Hz, 2 H), 3.97 (t, *J* = 8.0 Hz, 2 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 151.5, 131.3, 125.3, 119.0, 78.3, 71.1, 63.0, 47.1, 34.7, 31.1.

MS (EI): *m/z* = 243, 228, 184, 156, 128, 115, 78, 51.

3-[(4-Methoxyphenyl)ethynyl]oxazolidin-2-one (3d)[20a]
Colorless solid; yield: 40 mg (73%); mp 90–91 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 9.2 Hz, 2 H), 4.47 (t, *J* = 8.0 Hz, 2 H), 3.98 (t, *J* = 8.0 Hz, 2 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 156.0, 133.4, 114.0, 113.9, 77.5, 70.9, 62.9, 55.2, 47.1.

MS (EI): *m/z* = 217, 173, 158, 145, 130, 116, 102, 90, 76, 63, 51.

3-[(4-Fluorophenyl)ethynyl]-1,3-oxazolidin-2-one (3e)[20c]
White solid; yield: 39 mg (76%); mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.42 (m, 2 H), 6.96–7.01 (m, 2 H), 4.48 (t, *J* = 8.0 Hz, 2 H), 3.99 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 248.0 Hz), 155.9, 133.6 (d, *J* = 9.0 Hz), 118.1 (d, *J* = 3.0 Hz), 115.6 (q, *J* = 13.0 Hz), 78.5, 70.1, 63.0, 46.9.

MS (EI): *m/z* = 205, 161, 146, 133, 106, 81, 57.

3-[(4-Chlorophenyl)ethynyl]-1,3-oxazolidin-2-one (3f)[20c]
White solid; yield: 38 mg (69%); mp 134–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.8 Hz, 2 H), 7.28 (d, *J* = 8.8 Hz, 2 H), 4.50 (t, *J* = 8.0 Hz, 2 H), 4.01 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 134.2, 132.7, 128.6, 120.6, 79.8, 70.2, 63.1, 46.9.

MS (EI): *m/z* = 221, 177, 162, 149, 114, 88, 63, 50.

(4*R*)-4-Benzyl-3-(phenylethynyl)-1,3-oxazolidin-2-one (3g)[20b]
Light-tan solid; yield: 60 mg (87%); mp 87–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.46 (m, 2 H), 7.27–7.36 (m, 6 H), 7.22–7.24 (m, 2 H), 4.33–4.35 (m, 2 H), 4.12–4.17 (m, 1 H), 7.24–7.28 (m, 1 H), 2.97–3.03 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 134.2, 131.6, 129.4, 129.0, 128.3, 128.2, 127.5, 122.2, 77.9, 73.3, 67.5, 58.5, 38.0.

MS (EI): *m/z* = 277, 216, 172, 145, 117, 91, 76, 65, 51.

(4*R*)-4-Benzyl-3-[(4-methoxyphenyl)ethynyl]-1,3-oxazolidin-2-one (3h)[20a]
White solid; yield: 63 mg (82%); mp 89–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.42 (m, 2 H), 7.32–7.35 (m, 2 H), 7.27–7.29 (m, 1 H), 7.22–7.26 (m, 2 H), 6.84–6.86 (m, 2 H), 4.31–4.36 (m, 2 H), 4.12–4.16 (m, 1 H), 3.80 (s, 3 H), 3.23–3.27 (m, 1 H), 2.96–3.02 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 155.7, 134.3, 133.5, 129.4, 129.0, 127.4, 114.1, 113.9, 76.6, 73.0, 67.4, 58.5, 55.3, 37.9.

MS (EI): *m/z* = 307, 262, 216, 172, 145, 117, 91, 76, 65, 51.

(*R*)-4-Benzyl-3-((4-fluorophenyl)ethynyl)oxazolidin-2-one (3i)[20d]
Yellow oil; yield: 58 mg (79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.44 (m, 2 H), 7.33–7.37 (m, 2 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.23–7.25 (m, 2 H), 7.01 (t, *J* = 8.8 Hz, 2 H), 4.35–4.37 (m, 2 H), 4.16–4.17 (m, 1 H), 3.24–3.28 (m, 1 H), 2.98–3.03 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 248.0 Hz), 155.5, 134.2, 133.7, 133.7, 129.2 (d, *J* = 35.0 Hz), 127.5, 118.2 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.0 Hz), 77.6, 72.2, 67.5, 58.4, 38.0.

MS (EI): *m/z* = 295, 250, 204, 160, 145, 133, 117, 107, 91, 65, 51.

Ethyl Phenyl(phenylethynyl)carbamate (3j)
Yellow oil; yield: 60 mg (90%).

IR (KBr): 3415, 2252, 1738, 1620, 1278, 1127, 755, 619 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.57 (m, 2 H), 7.40–7.45 (m, 4 H), 7.29–7.31 (m, 4 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 139.5, 131.2, 128.9, 128.2, 127.7, 126.9, 124.6, 123.0, 83.0, 70.1, 63.7, 14.3.

MS (EI): *m/z* = 265, 206, 192, 165, 115, 103, 89, 77, 63, 51.

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.72; H, 5.77; N, 5.33.

Ethyl Phenyl[(4-tolyl)ethynyl]carbamate (3k)
Yellow oil; yield: 66 mg (94%).

IR (KBr): 3428, 2253, 1737, 1635, 1279, 1125, 511 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.58 (m, 2 H), 7.40–7.44 (m, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.27–7.31 (m, 1 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 2.35 (s, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 139.7, 137.8, 131.3, 129.0, 128.9, 126.8, 124.6, 119.9, 82.3, 70.1, 63.7, 21.4, 14.4.

MS (EI): *m/z* = 279, 220, 206, 165, 117, 103, 77, 51.

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.23; H, 6.18; N, 5.07.

Ethyl [(4-Chlorophenyl)ethynyl]phenylcarbamate (3l)
Yellow oil; yield: 64 mg (85%).

IR (KBr): 3415, 2253, 1738, 1490, 1369, 1277, 1125, 755, 693, 512 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.54 (m, 2 H), 7.40–7.43 (m, 2 H), 7.33–7.36 (m, 2 H), 7.26–7.30 (m, 3 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 139.4, 133.6, 132.4, 129.0, 128.5, 127.1, 124.7, 121.5, 83.9, 69.1, 63.8, 14.3.

MS (EI): *m/z* = 299, 240, 226, 191, 165, 137, 123, 77, 51.

Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67. Found: C, 67.86; H, 4.79; N, 4.61.

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