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Nickel-Catalyzed Hiyama-type Decarboxylative Coupling of Propiolic Acids and Organosilanes

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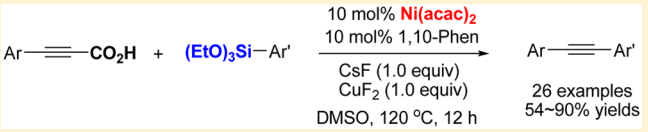
Supporting Information

ABSTRACT: A Ni catalytic system was developed for the decarboxylative coupling reaction of alkynyl carboxylic acids with organosilanes. $Ni(acac)_2$ and 1,10-phenanthroline showed the best result in the presence of CsF and CuF_2 at 120 °C. This system tolerated the presence of alkyl, alkoxy, halogen, nitro, cyano, ketone, and ester functional groups. Moreover, the reaction with but-2-ynedioic acid and organosilane afforded the corresponding symmetrical diarylalkynes.



Efforts have been made to replace precious metals with more abundant and low-cost metals in transition-metal-catalyzed reactions.[1] Compared to Pd, Ni catalytic systems have been less developed for coupling reactions even though Ni is less expensive.[2] Like other coupling reactions, Pd has been successfully introduced in the Sonogashira reaction involving the coupling of aryl halides and terminal alkynes.[3] The Sonogashira reaction is one of the most important methods for the preparation of valuable building blocks in pharmaceuticals, natural products, and polymers.[4] As a terminal alkyne surrogate, alkynyl carboxylic acids have received much attention since we first reported the Pd-catalyzed decarboxylative coupling reaction in 2008.[5] Since then, diverse decarboxylative coupling reactions have been reported by our group and others.[6] Decarboxylative cross-coupling reactions have been studied not only in the formation of carbon−carbon bonds but also in the formation of carbon-heteroatom bonds.[7] However, only one example of a Ni catalyst was found for the sp-carbon decarboxylative coupling reactions (Figure 1a),[8] whereas several examples of Ni-catalyzed decarboxylative reactions with both sp^2 and sp^3 carboxylic acids have been reported.[9]

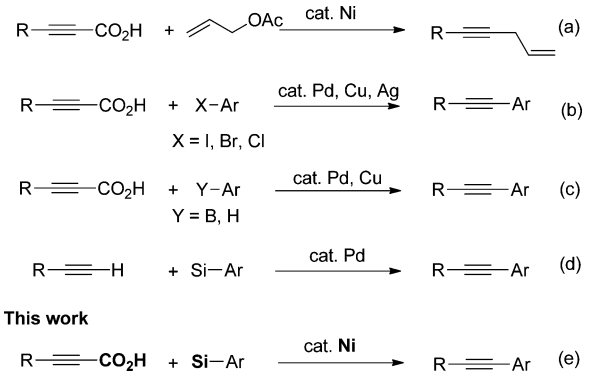


Figure 1. Metal-catalyzed sp carbon coupling reactions.

In the case of the decarboxylative coupling reaction of alkynyl carboxylic acids, aryl halides such as iodides, bromides, and chlorides have mostly been used as the coupling partner; benzyl halides have also been used (Figure 1b).[10] The reactions with terminal alkynes or homocoupling of alkynyl carboxylic acids provided the corresponding diynes.[11] Moreover, oxidative decarboxylative coupling reactions with C−H-activated compounds or aryl boronic acids have also been developed (Figure 1c).[12] However, organosilane compounds have never been used as the coupling partner in decarboxylative coupling reactions with alkynyl carboxylic acids, even though they have several advantages such as storage and handling because of their good stability.[13] Mostly, they have been used as the coupling substrates in Hiyama coupling reactions[14] and recently used in the Ni-catalyzed C−H arylation of heteroarenes.[15] Moreover, only a few examples of Sonogashira−Hiyama-type coupling reactions have been reported, and all of them used Pd as the catalyst.[16] To the best of our knowledge, Ni-catalyzed reactions have not been reported (Figure 1d). Herein, we report a Ni-catalyzed decarboxylative coupling reaction of alkynyl carboxylic acids with organosilanes as the coupling partner for the first time (Figure 1e).

To optimize the reaction conditions, we selected the reaction of phenyl propiolic acid **1a** with triethoxysilylbenzene **2a** as the model reaction as shown in Table 1. Among the Ni sources and solvents investigated, $Ni(acac)_2$ and DMSO showed the best result (see the Supporting Information). With 2,2′-bipyridine as the ligand, several oxidants were investigated. Oxygen and AgF_2 afforded the undesired decarboxylative homocoupled product **4a** in high yields (entries 1 and 2). Among the oxidants, such as Ag_2O, Ag_2CO_3, $Cu(OAc)_2$, $Cu(OTf)_2$, and CuF_2, CuF_2 afforded the highest yield of product **3a** (entry 7). The use of TBAF and KF instead of CsF did not give satisfactory results (entries 8 and 9). Alkyl-substituted 2,2′-bipyridines afforded

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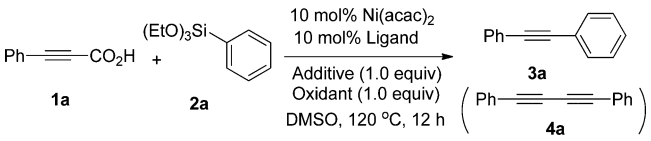
Table 1. Optimization of Decarboxylative Coupling Reaction[a]



				yield (%)[e]	
entry	ligand[b]	additive	oxidant	3a	4a
1	Bipy	CsF	O_2	2	83
2	Bipy	CsF	AgF_2	4	85
3	Bipy	CsF	Ag_2O	6	28
4	Bipy	CsF	Ag_2CO_3	35	35
5	Bipy	CsF	$Cu(OAc)_2$	13	71
6	Bipy	CsF	$Cu(OTf)_2$	28	15
7	Bipy	CsF	CuF_2	79	13
8	Bipy	TBAF	CuF_2	15	30
9	Bipy	KF	CuF_2	41	15
10	$^tBu_2$bipy	CsF	CuF_2	45	21
11	Me_2bipy	CsF	CuF_2	12	33
12	Me_4bipy	CsF	CuF_2	61	45
13	Phen	CsF	CuF_2	90	8
14	Ph_2Phen	CsF	CuF_2	47	19
15	Me_2Phen	CsF	CuF_2	36	18
16	–	CsF	CuF_2	30	19
17	Xantphos	CsF	CuF_2	8	35
18	dppf	CsF	CuF_2	15	34
19[c]	Phen	CsF	CuF_2	63	31
20[d]	Phen	CsF	CuF_2	90	8

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Ni(acac)_2$ (0.03 mmol), ligand (0.03 mmol), CsF (0.3 mmol), and CuF_2 (0.3 mmol) stirred in DMSO (1.5 mL) at 120 °C for 12 h. [b]Ligand: Bipy = 2,2′-bipyridine; tBu_2bipy = 4,4′-di^{t}Bu-2,2′-bipyridine; Me_2bipy = 4,4′-dimethyl-2,2′-bipyridine; Me_4bipy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine; Ph_2Phen = 4,7-diphenyl-1,10-phenanthroline; Me_2Phen = 4,7-dimethyl-1,10-phenanthroline; Phen = 1,10-phenanthroline; Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dppf = 1,1′-bis(diphenylphosphino)-ferrocene. [c]At 100 °C. [d]Under nitrogen atmosphere. [e]Determined by GC with internal standard.

lower yields than 2,2′-bipyridine (entries 10−12). When 1,10-phenanthroline derivatives were used as the ligand, 1,10-phenanthroline provided desired product **3a** in 90% yield (entry 13). However, methyl- or phenyl-substituted 1,10-phenanthroline showed lower yields (entries 14 and 15). In the absence of a ligand, the yield of the product was 30% (entry 16). Phosphine ligands decreased the yield of **3a** (entries 17 and 18). The reaction at 100 °C afforded **3a** in 63% yield (entry 19). The reaction yields were not changed when the reaction was conducted under nitrogen atmosphere (entry 20).

With these optimized reaction conditions in hand, the reactions of diverse alkynyl carboxylic acids with triethoxysilylbenzene were evaluated. The results are summarized in Scheme 1. Arylpropiolic acids were prepared by modified known methods.[17] As expected, phenyl propiolic acid afforded **3a** in 90% isolated yield. Phenyl propiolic acids bearing methyl groups provided **3b−d** in good yields. Alkoxy-substituted phenyl propiolic acids also showed good yields for **3e−g**. 2-Naphthyl group-substituted propiolic acids furnished **3h** and **3i** in 85 and 82% yield, respectively. Halo groups also afforded desired coupling products **3j−l** in good yields. Biphenyl-substituted **3m** was obtained in 77% yield. Phenyl propiolic acids bearing nitro, cyano, ketone, and ester groups at the para position afforded corresponding products **3n−q** in 57, 66, 75, and 69% yield, respectively. The reaction of 2-pyridinyl propiolic acid provided 54% yield. Unfortunately, no desired products **3s** or **3t** were obtained from the alkyl-substituted propiolic acids such as octynoic acid and pentynoic acid.

The reaction with other organosilanes was evaluated for this coupling reaction. As shown in Scheme 2, *p*-tolyl, 4-methoxylphenyl, 4-chlorophenyl, and 2-thiophenyl silanes were coupled with aryl alkynyl carboxylic acids, affording the corresponding products in good yields.

To extend this methodology to the synthesis of symmetrical diaryl alkynes, we reacted 3 equiv of triethoxylsilyl benzene with propiolic acid (**6a**) under the optimized reaction conditions. Unfortunately, no desired product was obtained, as shown in Table 2 (entry 1). However, the reaction with but-2-ynedioic acid (**6b**) provided diphenyl acetylene in 21% yield (entry 2). When the amount of CuF_2 and CsF was doubled, the desired product was obtained in 42% yield (entry 3). Triethoxy(4-methylphenyl)silane and triethoxyl(4-chlorophenyl)silane also afforded corresponding products **7b** and **7c** in 38 and 45% yield, respectively (entry 5).

To elucidate the reaction mechanism, we investigated the standard conditions by changing the parameters as shown in Table 3. In the presence of TEMPO, the yield of **3a** decreased and that of **4a** increased (entry 2). Without CuF_2, no product was obtained (entry 3). Biphenyl (**8**), a homocoupling product of **2a**, was obtained in the absence of CsF (entry 4). Without the Ni catalyst/ligand, the yield of **3a** decreased to 30% (entry 5). In the absence of both Ni and CsF, the yield of **8** increased to 50% (entry 6). The reaction conducted in the absence of nickel showed 41% yield of product (entry 7).

On the basis of these results, we propose the reaction pathway as shown in Figure 2. Arylsilane is activated by CsF (path **a**)[15] and reacts with Ni(II), providing aryl Ni complex **A**. Alkynyl carboxylic acid is converted to alkynyl copper complex **B** by decarboxylation with Cu. The transmetalation of aryl Ni complex **A** and alkynyl copper complex **B** affords aryl alkynyl Ni complex **C**. The reductive elimination of **C** furnishes the desired product and Ni(0). Ni(II) is regenerated by oxidation.[15] This reaction cycle may involve both radical and ionic processes because the product yield decreased in the presence of TEMPO. Moreover, both Ni-catalyzed path **I** and Cu-mediated path **II** are involved because **3a** was obtained in 30% yield even without Ni. CuF_2 is the most important reagent for this coupling reaction. In the presence of CsF, path **a** dominates and prevents the homocoupling of aryl silane through path **c**.

In summary, an aryl silane was successfully adapted as a coupling partner in the decarboxylative coupling of an alkynyl carboxylic acid in the presence of Ni catalysis for the first time. This cross coupling reaction can take advantage of both easy handling and low cost of the Ni(II) source compared to those of Pd. In the course of our investigation, catalytic activity highly depends on the ligand with 1,10-phenanthroline showing the best result. As an oxidant and activator, CuF_2 seems to be crucial for the transformation, whereas both Ni and CsF can suppress the formation of byproducts. Under the optimal conditions, this catalytic system showed excellent functional group tolerance toward alkyl, alkoxy, halogen, nitro, cyano, ketone, and ester groups. Interestingly, the reaction with but-2-ynedioic acid and organosilane afforded the corresponding symmetrical diarylalkynes. Despite the mechanistic studies, the reaction mechanism has ambiguity and can suggest both Ni-

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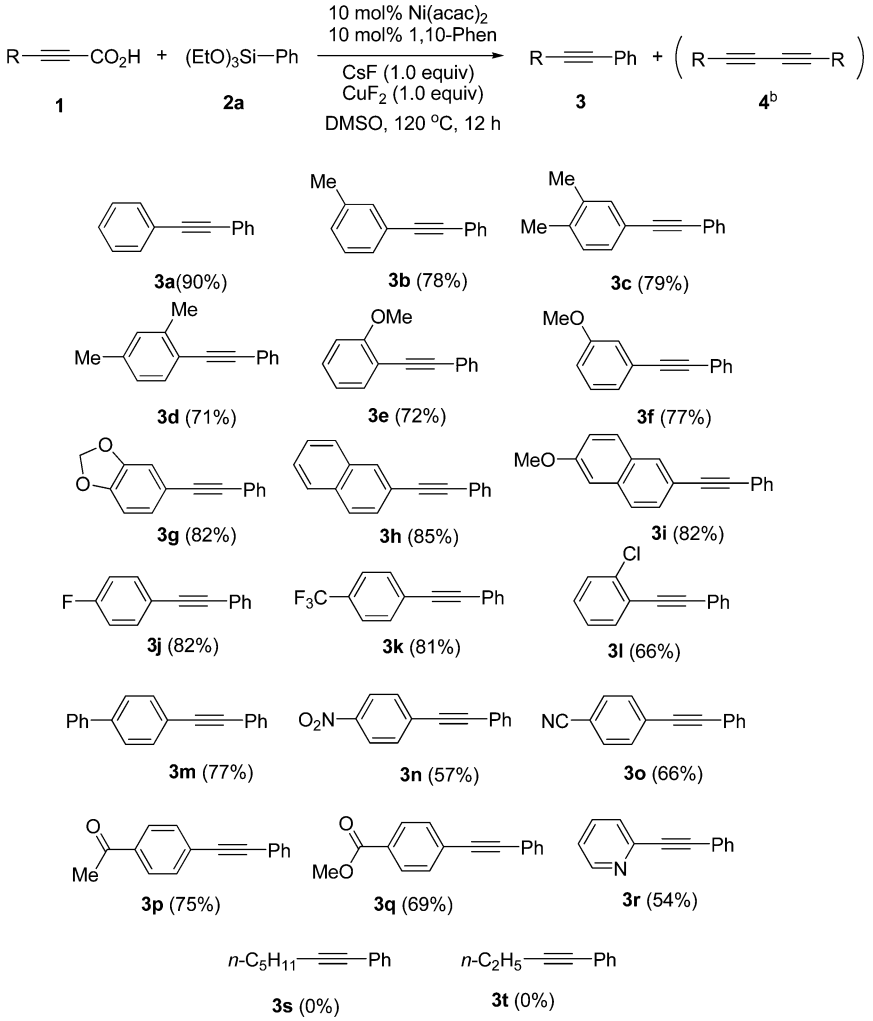
Scheme 1. Decarboxylative Coupling of Aryl Alkynyl Carboxylic Acids and Triethoxysilylbenzene[a]



[a]Reaction conditions: **1** (2.0 mmol), **2a** (3.0 mmol), $Ni(acac)_2$ (0.2 mmol), 1,10-phenanthroline (0.2 mmol), CsF (2.0 mmol), and CuF_2 (2.0 mmol) reacted in DMSO (7.0 mL) at 120 °C for 12 h. [b]Less than 5% yield was formed.

catalyzed and Cu-mediated pathways either through radical or ionic processes.

EXPERIMENTAL PROCEDURES

Nickel-Catalyzed Decarboxylative Coupling of Aryl Alkynyl Carboxylic Acid with Triethoxyarylsilane. Aryl alkynyl carboxylic acid (2.0 mmol), 1,10-phenanthroline (36 mg, 0.2 mmol), $Ni(acac)_2$ (51 mg, 0.2 mmol), CuF_2 (203 mg, 2.0 mmol), triethoxyarylsilane (3.0 mmol), CsF (304 mg, 2.0 mmol), and DMSO (10 mL) were added to the reaction vial. The solution was stirred at 120 °C for 12 h. The resulting mixture was cooled and then filtered using a syringe filter. Then, the mass was quenched with saturated ammonium chloride solution. The mixture was extracted with Et_2O (2 × 15 mL), and the combined organic layers were dried over sodium sulfate. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash chromatography on silica gel (eluent = hexane).

*1,2-Diphenylethyne (**3a**).*[3a] 3-Phenylpropiolic acid (**1a**) (292 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1,2-diphenylethyne (**3a**) (321 mg, 1.8 mmol, 90% yield) as a white solid; mp 60−62 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61−7.44 (m, 4H), 7.43−7.30 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 131.6, 128.4, 128.3, 123.3, 89.4; MS (EI) m/z 178 (M^+).

*1-Methyl-3-(phenylethynyl)benzene (**3b**).*[3a] 3-(*m*-Tolyl)propiolic acid (**1b**) (320 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-methyl-3-(phenylethynyl)benzene (**3b**) (300 mg, 1.56 mmol, 78% yield) as a colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−7.55 (m, 2H), 7.44−7.33 (m, 5H), 7.28 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.0, 132.2, 131.6, 129.2, 128.7, 128.4, 128.3, 128.2, 123.4, 123.1, 89.6, 89.1, 21.3; MS (EI) m/z 192 (M^+).

*1,2-Dimethyl-4-(phenylethynyl)benzene (**3c**).*[18] 3-(3,4-Dimethylphenyl)propiolic acid (**1c**) (348 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1,2-dimethyl-4-(phenylethynyl)benzene (**3c**) (326 mg, 1.58 mmol, 79% yield) as a white solid; mp 58−61 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.50 (m, 2H), 7.38−7.31 (m, 4H), 7.29 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.2, 136.7, 132.7, 131.6, 129.7, 129.1, 128.3, 128.0, 123.6, 120.5, 89.7, 88.5, 19.8, 19.6; MS (EI) m/z 206 (M^+).

*2,4-Dimethyl-1-(phenylethynyl)benzene (**3d**).*[19] 3-(2,4-Dimethylphenyl)propiolic acid (**1d**) (348 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 2,4-dimethyl-1-(phenylethynyl)benzene (**3d**) (293 mg, 1.42 mmol, 71% yield) as a pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59−7.55 (m, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.40−7.34 (m, 3H), 7.09 (s, 1H), 7.02 (d, J = 7.8 Hz, 1H), 2.53 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.1, 138.4, 131.8, 131.5, 130.4, 128.4, 128.0, 126.5, 123.8, 120.0, 92.7, 88.6, 21.5, 20.7; MS (EI) m/z 206 (M^+).

*1-Methoxy-2-(phenylethynyl)benzene (**3e**).*[20] 3-(2-Methoxyphenyl)propiolic acid (**1e**) (352 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-methoxy-2-(phenylethynyl)-

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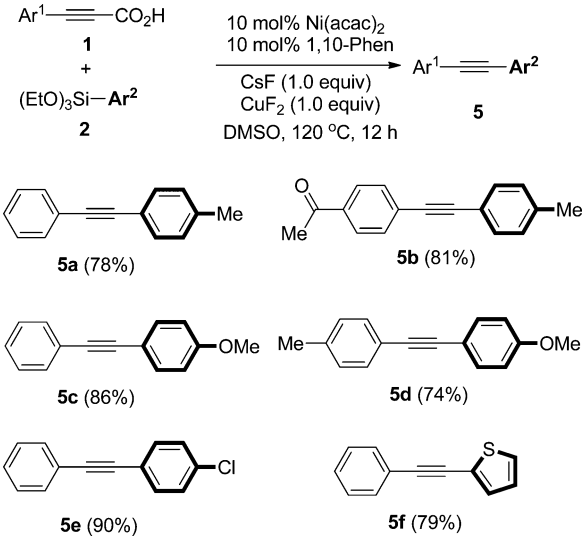
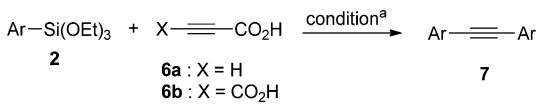
Scheme 2. Decarboxylative Coupling of Aryl Alkynyl Carboxylic Acids with Triethoxyarylsilanes[a]



[a]Reaction conditions: **1** (2.0 mmol), **2** (3.0 mmol), $Ni(acac)_2$ (0.2 mmol), 1,10-phenanthroline (0.2 mmol), CsF (2.0 mmol), and CuF_2 (2.0 mmol) reacted in DMSO (7.0 mL) at 120 °C for 12 h.

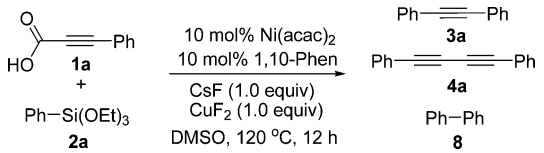
Table 2. Synthesis of Symmetrical Diarylacetylenes[a]



entry	Ar	6	CsF, CuF_2	product	yield(%)
1	C_6H_5	**6a**	1 equiv	–	0
2	C_6H_5	**6b**	1 equiv	**7a** (**3a**)	21
3	C_6H_5	**6b**	2 equiv	**7a** (**3a**)	42
4	4-Me C_6H_4	**6b**	2 equiv	**7b**	38
5	4-Cl C_6H_4	**6b**	2 equiv	**7c**	45

[a]Reaction conditions: **2a** (6.0 mmol), **6b** (2.0 mmol), $Ni(acac)_2$ (0.4 mmol), 1,10-phenanthroline (0.4 mmol), CsF(2.0 or 4.0 mmol), and CuF_2 (2.0 or 4.0 mmol) reacted in DMSO at 120 °C for 12 h.

Table 3. Studies of Reaction Pathway[a]



		yield (%)		
entry	change from standard conditions	**3a**	**4a**	**8**
1	no change	90	8	0
2	with TEMPO	56	30	0
3	no CuF_2	0	0	0
4	no CsF	70	10	5
5	no Ni/ligand	30	19	0
6	no Ni/ligand and CsF	32	12	50
7	no Ni	41	13	0

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Ni(acac)_2$ (0.03 mmol), 1,10-phenanthroline (0.03 mmol), CsF (0.3 mmol), and CuF_2 (0.3 mmol) stirred in DMSO (1.5 mL) at 120 °C for 12 h.

benzene (**3e**) (300 mg, 1.44 mmol, 72% yield) as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.49 (dd, J = 7.6, 1.7 Hz, 1H), 7.35−7.22 (m, 4H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0, 133.6, 131.7, 129.9, 128.3, 128.2, 123.6, 120.7, 112.5, 110.8, 93.5, 85.9, 55.9; MS (EI) m/z 208 (M^+).

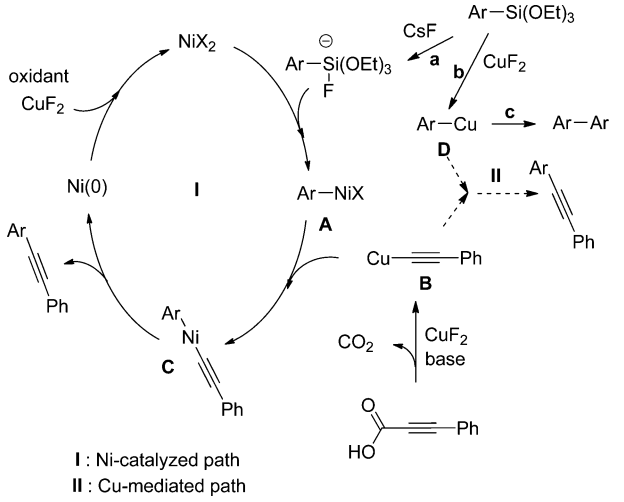


Figure 2. Proposed reaction mechanism.

1-Methoxy-3-(phenylethynyl)benzene (**3f**).[21] 3-(3-Methoxyphenyl)propiolic acid (**1f**) (352 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-methoxy-3-(phenylethynyl)-benzene (**3f**) (321 mg, 1.54 mmol, 77% yield) as a pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2H), 7.39−7.33 (m, 3H), 7.29−7.24 (m, 1H), 7.16 (m, 1H), 7.09 (m, 1H), 6.91 (qd, J = 8.3, 2.6, 1.0 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.4, 131.6, 129.4, 128.4, 128.3, 124.3, 124.2, 123.2, 116.4, 114.9, 89.3, 89.2, 55.3; MS (EI) m/z 208 (M^+).

5-(Phenylethynyl)benzo[d][1,3]dioxole (**3g**).[22] 3-(Benzo[d][1,3]-dioxol-5-yl)propiolic acid (**1g**) (380 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 5-(phenylethynyl)-benzo[d][1,3]dioxole (**3g**) (364 mg, 1.64 mmol, 82% yield) as a white solid; mp 100−102 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 2H), 7.37−7.30 (m, 3H), 7.07 (dd, J = 8.0, 1.6 Hz, 1H), 6.98 (d, J = 1.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 5.99 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 147.5, 131.5, 128.3, 128.1, 126.3, 123.4, 116.5, 111.5, 108.5, 101.3, 89.3, 87.8; MS (EI) m/z 222 (M^+).

1-(Phenylethynyl)naphthalene (**3h**).[22] 3-(Naphthalen-1-yl)-propiolic acid (**1h**) (392 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-(phenylethynyl)naphthalene (**3h**) (388 mg, 1.70 mmol, 85% yield) as a pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.5 Hz, 1H), 7.98−7.93 (m, 2H), 7.91 (d, J = 7.1 Hz, 1H), 7.81 (m, 2H), 7.73 (m, 1H), 7.64 (m, 1H), 7.55 (m, 1H), 7.50 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 133.5, 133.4, 131.9, 130.6, 128.9, 128.6, 128.5, 126.9, 126.6, 126.4, 125.5, 123.6, 121.1, 94.6, 87.8; MS (EI) m/z 228 (M^+).

2-Methoxy-6-(phenylethynyl)naphthalene (**3i**).[23] 3-(6-Methoxy-naphthalen-2-yl)propiolic acid (**1i**) (452 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 2-methoxy-6-(phenylethynyl)naphthalene (**3i**) (424 mg, 1.64 mmol, 82% yield) as white solid; mp 167−168 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 1H), 7.71 (t, J = 8.3 Hz, 2H), 7.60−7.53 (m, 3H), 7.40−7.31 (m, 3H), 7.17 (dd, J = 8.8, 2.5 Hz, 1H), 7.12 (d, J = 2.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.3, 134.1, 131.6, 131.3, 129.3, 129.0, 128.5, 128.4, 128.1, 126.8, 123.5, 119.4, 118.2, 105.8, 89.9, 89.0, 55.4; MS (EI) m/z 258 (M^+).

1-Fluoro-4-(phenylethynyl)benzene (**3j**).[24] 3-(4-Fluorophenyl)-propiolic acid (**1j**) (328 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-fluoro-4-(phenylethynyl)benzene (**3j**) (322 mg, 1.64 mmol, 82% yield) as an off-white solid; mp 109−111 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.39−7.36 (m, 3H), 7.07 (m, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.5 (d, J = 250 Hz), 133.5 (d, J = 8.4 Hz), 131.6, 128.4, 128.4, 123.1, 119.4 (d, J =

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3.5 Hz), 115.7 (d, J = 22.1 Hz), 89.1, 88.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ −110.9; MS (EI) m/z 196 (M^+).

*1-(Phenylethynyl)-4-(trifluoromethyl)benzene (**3k**).*[25] 3-(4-(Trifluoromethyl)phenyl)propiolic acid (**1k**) (428 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**3k**) (414 mg, 1.68 mmol, 84% yield) as a white solid; mp 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.57 (m, 4H), 7.57−7.52 (m, 2H), 7.38−7.33 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 130.7, 130.7, 128.9 (q, J = 32.7 Hz), 128.2, 127.8, 127.4, 126.9, 126.1, 124.2 (q, J = 3.7 Hz), 121.5, 90.7, 86.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.8; MS (EI) m/z 246 (M^+).

*1-Chloro-3-(phenylethynyl)benzene (**3l**).*[10b] 3-(3-Chlorophenyl)-propiolic acid (**1l**) (361 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-chloro-3-(phenylethynyl)benzene (**3l**) (298 mg, 1.40 mmol, 70% yield) as a pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.50 (m, 3H), 7.40 (m, 1H), 7.37−7.32 (m, 3H), 7.32−7.23 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.2, 131.6, 131.4, 129.7, 129.5, 128.6, 128.5, 128.4, 124.9, 122.7, 90.5, 87.9; MS (EI) m/z 212 (M^+).

*4-(Phenylethynyl)-1,1′-biphenyl (**3m**).*[26] 3-([1,1′-Biphenyl]-4-yl)-propiolic acid (**1m**) (445 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 4-(phenylethynyl)-1,1′-biphenyl (**3m**) (392 mg, 1.54 mmol, 77% yield) as a white solid; mp 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.53 (m, 8H), 7.47 (t, J = 7.6 Hz, 2H), 7.41−7.33 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.9, 140.3, 132.0, 131.6, 128.7, 128.4, 128.3, 127.6, 127.0, 123.3, 122.2, 90.1, 89.3; MS (EI) m/z 254 (M^+).

*1-Nitro-4-(phenylethynyl)benzene (**3n**).*[10a] 3-(4-Nitrophenyl)-propiolic acid (**1n**) (382 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-nitro-4-(phenylethynyl)benzene (**3n**) (254 mg, 1.14 mmol, 57% yield) as a light yellow solid; mp 115−117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (m, 2H), 7.67 (m, 2H), 7.59−7.54 (m, 2H), 7.42−7.36 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.9, 132.3, 131.8, 130.3, 129.3, 128.5, 123.6, 122.1, 94.7, 87.5; MS (EI) m/z 223 (M^+).

*4-(Phenylethynyl)benzonitrile (**3o**).*[22] 3-(4-Cyanophenyl)propiolic acid (**1o**) (342 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 4-(phenylethynyl)benzonitrile (**3o**) (268 mg, 1.32 mmol, 66% yield) as a light yellow solid; mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.58 (m, 4H), 7.58−7.50 (m, 2H), 7.41−7.35 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.0, 131.0, 130.8, 128.1, 127.5, 127.2, 121.2, 117.5, 110.4, 92.7, 86.7; MS (EI) m/z 203 (M^+).

*1-(4-(Phenylethynyl)phenyl)ethanone (**3p**).*[25] 3-(4-Acetylphenyl)-propiolic acid (**1p**) (376 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 1-(4-(phenylethynyl)phenyl)-ethanone (**3p**) (330 mg, 1.50 mmol, 75% yield) as a light yellow solid; mp 96−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.55 (m, 2H), 7.39−7.34 (m, 3H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.3, 136.2, 131.7, 131.7, 128.8, 128.5, 128.3, 128.2, 122.6, 92.7, 88.6, 26.6; MS (EI) m/z 220 (M^+).

*Methyl 4-(Phenylethynyl)benzoate (**3q**).*[22] 3-(4-(Methoxycarbonyl)phenyl)propiolic acid (**1q**) (408 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded methyl 4-(phenylethynyl)benzoate (**3q**) (326 mg, 1.38 mmol, 69% yield) as a light yellow solid; mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.55 (m, 2H), 7.39−7.34 (m, 3H), 3.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.6, 131.8, 131.5, 129.5, 129.5, 128.8, 128.5, 128.0, 122.7, 92.4, 88.6, 52.3; MS (EI) m/z 236 (M^+).

*3-(Phenylethynyl)pyridine (**3r**).*[22] 3-(Pyridin-3-yl)propiolic acid (**1r**) (294 mg, 2.0 mmol) and triethoxyphenylsilane (**2a**) (721 mg, 3.0 mmol) afforded 3-(phenylethynyl)pyridine (**3r**) (194 mg, 1.08 mmol, 54% yield) as a light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (dd, J = 2.1, 0.9 Hz, 1H), 8.47 (dd, J = 4.9, 1.7 Hz, 1H), 7.70 (ddd, J = 7.9, 4.9, 1.75 Hz, 1H), 7.49 (m, 2H), 7.30−7.25 (m, 3H), 7.15 (ddd, J = 7.9, 4.9, 0.9 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.2, 148.5, 138.3, 131.7, 128.8, 128.4, 122.9, 122.5, 120.4, 92.7, 86.0; MS (EI) m/z 179 (M^+).

*1-Methyl-4-(phenylethynyl)benzene (**5a**).*[22] 3-Phenylpropiolic acid (**1a**) (292 mg, 2.0 mmol) and triethoxy(*p*-tolyl)silane (**2b**) (763 mg, 3.0 mmol) afforded 1-methyl-4-(phenylethynyl)benzene (**5a**) (300 mg, 1.56 mmol, 78% yield) as a light yellow solid; mp 67−69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.37−7.31 (m, 3H), 7.16 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5; MS (EI) m/z 192 (M^+).

*1-(4-(p-Tolylethynyl)phenyl)ethanone (**5b**).*[27] 3-(4-Acetylphenyl)-propiolic acid (**1p**) (376 mg, 2.0 mmol) and triethoxy(*p*-tolyl)silane (**2b**) (763 mg, 3.0 mmol) afforded 1-(4-(*p*-tolylethynyl)phenyl)-ethanone (**5b**) (380 mg, 1.62 mmol, 81% yield) as a light yellow solid; mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 2.58 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 139.1, 135.9, 131.6, 131.6, 129.2, 128.4, 128.2, 119.5, 93.0, 88.1, 26.6, 21.5; MS (EI) m/z 234 (M^+).

*1-Methoxy-4-(phenylethynyl)benzene (**5c**).*[22] 3-Phenylpropiolic acid (**1a**) (292 mg, 2.0 mmol) and triethoxy(4-methoxyphenyl)silane (**2c**) (811 mg, 3.0 mmol) afforded 1-methoxy-4-(phenylethynyl)-benzene (**5c**) (358 mg, 1.72 mmol, 86% yield) as a light yellow solid; mp 58−60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.51 (m, 2H), 7.39−7.32 (m, 3H), 6.90 (m, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 133.1, 131.5, 128.4, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3; MS (EI) m/z 208 (M^+).

*1-Methoxy-4-(p-tolylethynyl)benzene (**5d**).*[22] 3-(*p*-Tolyl)propiolic acid (**1s**) (320 mg, 2.0 mmol) and triethoxy(4-methoxyphenyl)silane (**2c**) (811 mg, 3.0 mmol) afforded 1-methoxy-4-(*p*-tolylethynyl)-benzene (**5d**) (329 mg, 1.48 mmol, 74% yield) as a light yellow solid; mp 119−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.5, 137.9, 132.9, 131.3, 129.1, 120.5, 115.6, 113.9, 88.7, 88.2, 55.2, 21.5; MS (EI) m/z 222 (M^+).

*1-Chloro-4-(phenylethynyl)benzene (**5e**).*[27] 3-Phenylpropiolic acid (**1a**) (292 mg, 2.0 mmol) and (4-chlorophenyl)triethoxysilane (**2d**) (824 mg, 3.0 mmol) afforded 1-chloro-4-(phenylethynyl)benzene (**5e**) (383 mg, 1.80 mmol, 90% yield) as a light yellow solid; mp 78−80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.54 (m, 2H), 7.45−7.41 (m, 3H), 7.41−7.37 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.4, 132.9, 131.7, 128.8, 128.6, 128.5, 123.1, 121.9, 90.6, 88.5; MS (EI) m/z 212 (M^+).

*2-(Phenylethynyl)thiophene (**5f**).*[22] 3-Phenylpropiolic acid (**1a**) (292 mg, 2.0 mmol) and triethoxy(thiophen-2-yl)silane (**2e**) (691 mg, 3.0 mmol) afforded 2-(phenylethynyl)thiophene (**5f**) (291 mg, 1.58 mmol, 79% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (m, 2H), 7.38−7.32 (m, 3H), 7.29 (m, 2H), 7.02 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.9, 131.4, 128.5, 128.4, 127.3, 127.1, 123.3, 122.9, 93.0, 82.6; MS (EI) m/z 184 (M^+).

Symmetrical Diarlalkynes from Silanes. *Nickel-Catalyzed Decarboxylative Coupling of But-2-ynedioic Acid (**6b**) with Triethoxyarylsilane.* But-2-ynedioic acid (**6b**) (228 mg, 2.0 mmol), 1,10-phenanthroline (72 mg, 0.4 mmol), $Ni(acac)_2$ (103 mg, 0.4 mmol), CuF_2 (406 mg, 4.0 mmol), triethoxyarylsilane (6.0 mmol), CsF (608 mg, 4.0 mmol), and DMSO (10 mL) were added to the reaction vial. The solution was stirred at 120 °C for 12 h. The resulting mixture was cooled and then filtered using a syringe filter. Then, the mass was quenched with saturated ammonium chloride solution. The mixture was extracted with Et_2O (2 × 15 mL), and then the combined organic layers were dried over sodium sulfate. The solvent was removed under reduced pressure, and the resulting crude product was purified by flash chromatography on silica gel (eluent = hexane).

*1,2-Di-p-tolylethyne (**7b**).*[10b] But-2-ynedioic acid (**6b**) (228 mg, 2.0 mmol) and triethoxy(*p*-tolyl)silane (**2a**) (1526 mg, 6.0 mmol) afforded 1,2-di-*p*-tolylethyne (**7b**) (157 mg, 0.76 mmol, 38% yield) as a white solid; mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 4H), 7.16 (d, J = 7.9 Hz, 4H), 2.38 (s, 6H); ^{13}C{^{1}H}

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NMR (101 MHz, $CDCl_3$) δ 138.2, 131.5, 129.1, 120.4, 88.9, 21.5; MS (EI) m/z 206 (M^+).

*1,2-Bis(4-chlorophenyl)ethyne (**7c**).*[28] But-2-ynedioic acid (**6b**) (228 mg, 2.0 mmol) and (4-chlorophenyl)triethoxysilane(**2a**) (1649 mg, 6.0 mmol) afforded 1,2-bis(4-chlorophenyl)ethyne (**7c**) (222 mg, 0.9 mmol, 45% yield) as a white solid; mp 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 4H), 7.33 (d, J = 8.7 Hz, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.5, 132.8, 128.7, 121.4, 89.2; MS (EI) m/z 246 (M^+).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00883.

Screening data of the nickel source and solvent and copies of ^{1}H and ^{13}C{^{1}H} NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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