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Nickel-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylates with Aryl Tosylates and Mesylates

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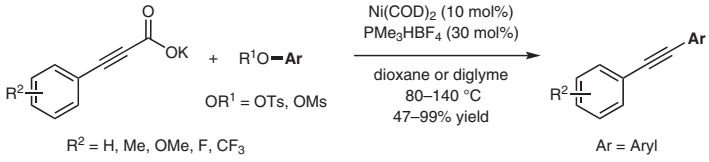

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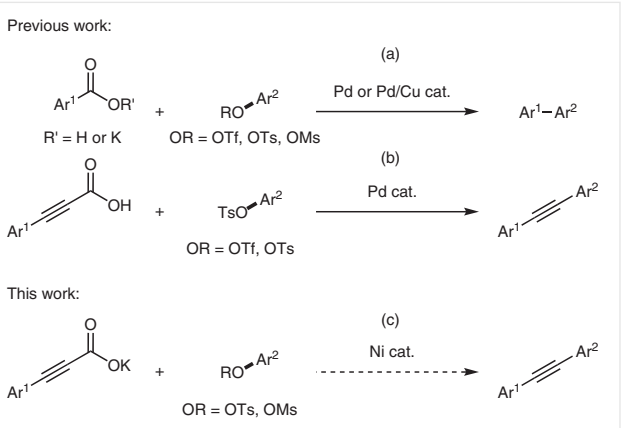
Abstract A method for the nickel-catalyzed coupling of alkynyl carboxylates or acids with aryl tosylates and mesylates is described. Electronically varied carboxylates and aryl electrophiles participate in these transformations to afford the desired diarylalkyne products. In general, electrophiles bearing an extended π-system lead to products in higher yields than sulfonates with only one aromatic ring.

Key words alkynes, arenes, carboxylic acids, cross-coupling, nickel catalysis, decarboxylative

Decarboxylative cross-coupling of aryl electrophiles with carboxylates is a well-established method for the formation of carbon–aryl bonds.[1] The use of carboxylic acids obviates the need for the preparation and use of often sensitive organometallic reagents.[2] Additionally, structurally diverse carboxylic acids are readily available bench-stable compounds. In lieu of these advantages, several reports on decarboxylative cross-couplings with aryl halides have been published.[2–8] In recent years there has been increasing interest in developing cross-coupling methods using phenolic electrophiles in place of aryl halides.[9] However, only a few sporadic reports have detailed decarboxylative cross-couplings using C–O electrophiles.[10] These include the palladium-catalyzed coupling of aryl sulfonates with aryl carboxylates (Scheme 1a) or alkynyl carboxylic acids (Scheme 1b).[1,10] As part of our program on C–C bond formations using C–O electrophiles,[11] herein, we report the first example of nickel-catalyzed decarboxylative couplings of alkynyl carboxylates with aryl tosylates and mesylates (Scheme 1c).[12] A brief scope of these transformations with alkynyl carboxylic acids in place of the corresponding carboxylates is also presented.[13]

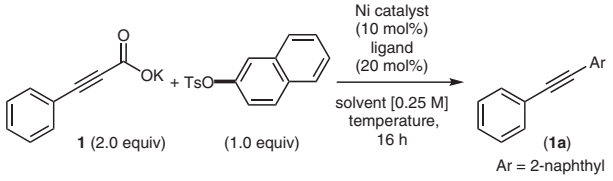


Scheme 1 Decarboxylative cross-couplings with aromatic C–O electrophiles

We commenced our studies with optimization of the cross-coupling of potassium phenylpropiolate with 2-naphthyl tosylate (Table 1). A screen of ligands revealed that PMe_3 (20 mol%) led to the desired product **1a** in 68% yield using $Ni(COD)_2$ as the catalyst and 1,4-dioxane as the solvent at 80 °C (entries 1–4). Increasing the equivalents of PMe_3 enhanced the yield of **1a** (entries 2 and 5). Bench-stable Ni(II) catalysts afforded **1a** in comparable yields to that obtained using $Ni(COD)_2$ (entries 5–7). However, $Ni(COD)_2$ was employed for further studies because it was the most efficient for reactions with electronically varied tosylates. Polar solvents such as 1,4-dioxane, DMSO, and diglyme afforded **1a** in similar yields (entries 5, 9 and 10) while nonpolar solvents such as *p*-xylene gave **1a** in low yield (entry 8). A temperature screen showed that higher temperatures are detrimental to these decarboxylative couplings (entries

5, 11 and 12). Finally, no product was obtained in the absence of the nickel catalyst and the ligand (entries 13 and 14).[14]

Table 1 Optimization of Decarboxylative Alkynylation



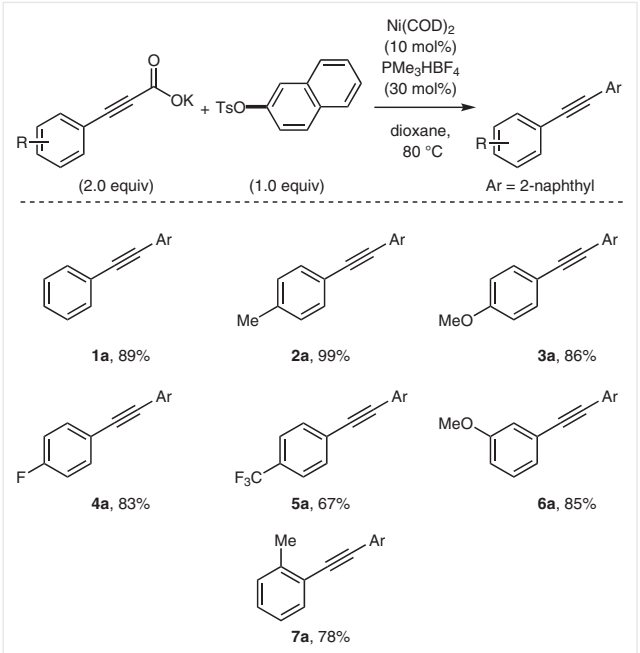
Entry	Solvent	Ligand	Ni catalyst	Temp (°C)	GC yield (%)[a]
1	1,4-dioxane	dppf	$Ni(COD)_2$	80	0
2[b]	1,4-dioxane	PMe_3	$Ni(COD)_2$	80	68
3[b]	1,4-dioxane	PCy_3	$Ni(COD)_2$	80	0
4[b]	1,4-dioxane	P*t*-Bu_3	$Ni(COD)_2$	80	0
5[b,c]	1,4-dioxane	PMe_3	$Ni(COD)_2$	80	84
6[b,c]	1,4-dioxane	PMe_3	$Ni(acac)_2$	80	90
7[b,c]	1,4-dioxane	PMe_3	$NiBr_2$	80	87
8[b,c]	*p*-xylene	PMe_3	$Ni(COD)_2$	80	14
9[b,c]	DMSO	PMe_3	$Ni(COD)_2$	80	72
10[b,c]	diglyme	PMe_3	$Ni(COD)_2$	80	79
11[b,c]	1,4-dioxane	PMe_3	$Ni(COD)_2$	100	83
12[b,c]	1,4-dioxane	PMe_3	$Ni(COD)_2$	120	62
13	1,4-dioxane	none	$Ni(COD)_2$	80	0
14	1,4-dioxane	none	none	80	0

[a] Calibrated GC yields against hexadecane as the internal standard.
[b] The HBF_4 salt of the ligand was used.
[c] Ligand (30 mol%) was used.

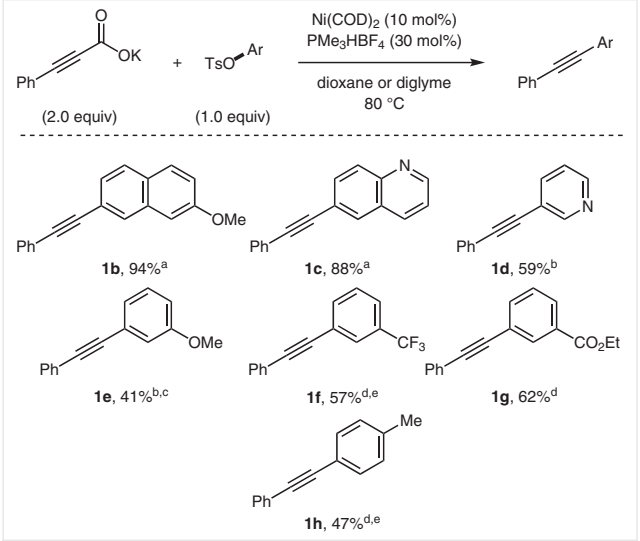
The optimal conditions for the formation of **1a** were applied to the use of electronically diverse alkynyl carboxylates for coupling with 2-naphthyl tosylate. As shown in Scheme 2, the desired diarylalkynes were obtained in good to excellent yields.

Electronically varied tosylates also participate in these reactions (Scheme 3). However, the highest yields were obtained with electrophiles bearing an extended aromatic system, such as for the formation of **1a–c**. Furthermore, electron-deficient tosylates (**1d**, **1f**, and **1g**) afforded the products in somewhat higher yields than electron-rich electrophiles (cf. **1h**). Additionally, reactions leading to products **1d–h** required higher temperatures (120 or 140 °C) than those leading to diarylalkynes **1a–c** (80 °C).[15]

These decarboxylative cross-couplings can be expanded to the use of more atom-economical aryl mesylates. As shown in Scheme 4, in general, electronically varied alkynyl carboxylates coupled with 2-naphthyl mesylate to afford the desired products in comparable yields to those obtained using 2-naphthyl tosylate (Scheme 2).

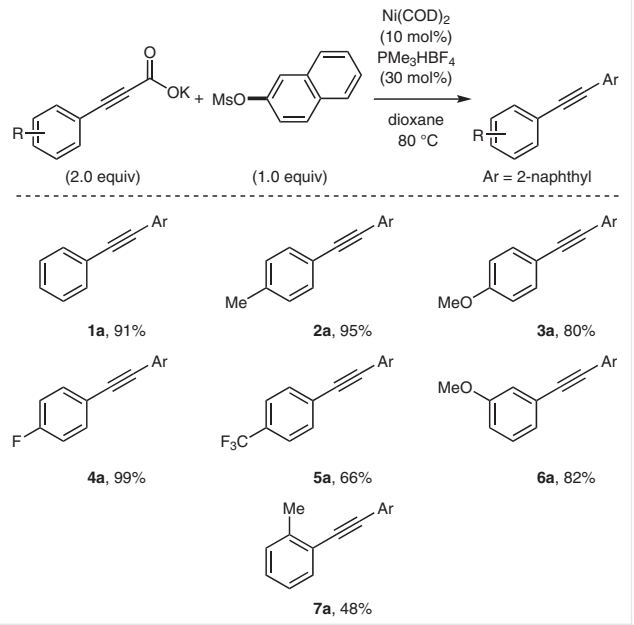


Scheme 2 Scope of salts for cross-coupling with 2-naphthyl tosylate (isolated yields)

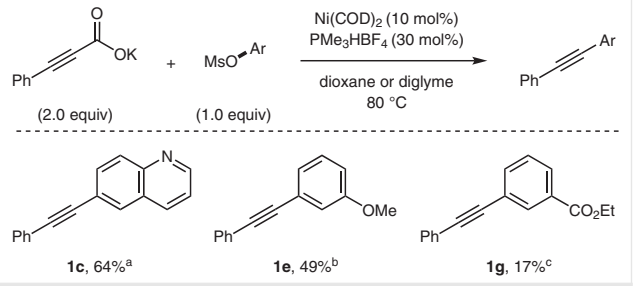


Scheme 3 Scope of tosylates for cross-coupling (isolated yields). [a] Reaction conducted at 80 °C with dioxane as solvent. [b] Reaction conducted at 120 °C with diglyme as solvent. [c] Carboxylate (3.0 equiv) used. [d] Reaction conducted at 140 °C with diglyme as solvent. [e] Carboxylate (4.0 equiv) used.

Furthermore, the cross-couplings using electronically varied aryl mesylates often afforded the diarylalkyne products in lower yields than those obtained using the corresponding tosylates (Scheme 5).



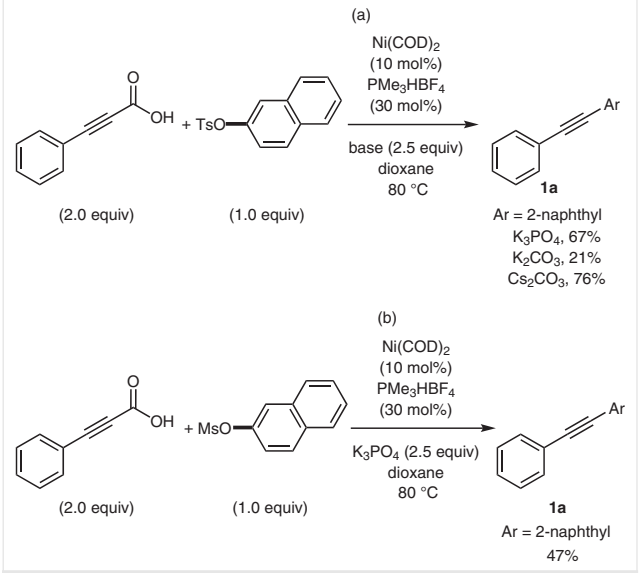
Scheme 4 Scope of salts for cross-coupling with 2-naphthyl mesylate (isolated yields)



Scheme 5 Scope of mesylates for cross-coupling (isolated yields). [a] Reaction conducted at 80 °C with dioxane as solvent. [b] Reaction conducted at 120 °C with diglyme as solvent; carboxylate (3.0 equiv) used. [c] Reaction conducted at 140 °C with diglyme as solvent.

Having explored the scope of these decarboxylative cross-couplings with alkynyl carboxylates, we next examined the use of their precursor alkynyl acids in these transformations. Importantly, the direct use of acids instead of salts enhances the step economy of the process by obviating the synthesis and purification of the carboxylate salts. A screen of bases revealed that both Cs_2CO_3 and K_3PO_4 effected the coupling of phenylpropiolic acid with 2-naphthyl tosylate to afford **1a** in synthetically useful yields (Scheme 6). However, the direct coupling with phenylpropiolic acid was less effective than the reactions using the corresponding carboxylate for couplings with both tosylates and mesylates.

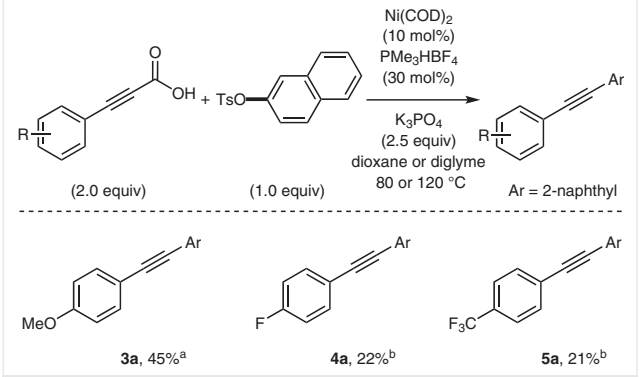
Electronically varied arylpropiolic acids coupled with 2-naphthyl tosylate to afford the diarylalkynes, albeit in lower



Scheme 6 Screen of bases for direct coupling with phenylpropiolic acid

efficiencies than reactions with the corresponding carboxylates (Scheme 7).

In summary, we have described the first general example of nickel-catalyzed decarboxylative cross-couplings of alkynyl carboxylates with aryl tosylates and mesylates. In general, electron-rich carboxylates are more effective for these reactions than their electron-deficient counterparts. Furthermore, aryl electrophiles bearing an extended π-system lead to products in higher yields than aryl electrophiles with only one aromatic ring. The scope of aryl tosylates is broader than aryl mesylates. Finally, arylpropiolic acids can be used in place of the arylpropiolate salts, albeit with lower reaction efficiencies than the latter.



Scheme 7 Cross-couplings with arylpropiolic acids (isolated yields). [a] Reaction conducted at 80 °C with dioxane as solvent. [b] Reaction conducted at 120 °C with diglyme as solvent.

NMR spectra were obtained on a Bruker 400 (399.96 MHz for ^{1}H; 100.57 MHz for ^{13}C) spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), and multiplet/multiple peaks (m). IR spectra were obtained on a Thermo Scientific Nicolet iS5 iD5 ATR spectrophotometer. Melting points were obtained on a Thomas Hoover melting point apparatus. Phenylpropiolic acid was obtained from Aldrich, $Ni(COD)_2$ and ligands were obtained from Strem Chemicals, and anhydrous cesium carbonate, potassium carbonate, and potassium phosphate were obtained from Acros; all materials were used as received. The acids,[13d] carboxylates,[16a] tosylates,[16b] and mesylates[16c] were prepared using literature procedures. Anhydrous *p*-xylene, DMSO, diglyme, and 1,4-dioxane were obtained from Aldrich and used as received. Other solvents were obtained from Fisher Chemical or VWR Chemical and used without further purification. Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and TLC was performed on Analtech TLC plates precoated with silica gel 60 F_{254}.

Decarboxylative Cross-Couplings; General Procedures

Couplings with Solid Tosylates or Mesylates; General Procedure A

Carboxylate and electrophile (tosylate or mesylate) were weighed in an oven-dried 4-mL scintillation vial containing a magnetic stir bar. The vial was taken into a glovebox, and $Ni(COD)_2$ and PMe_3HBF_4 were added. Anhydrous 1,4-dioxane or diglyme was added, the vial was sealed with a Teflon-lined cap, then taken out of the glovebox, and the reaction mixture was stirred at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5-inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

Couplings with Mesylates; General Procedure B

Carboxylate was weighed in an oven-dried 4-mL scintillation vial containing a magnetic stir bar. The vial was taken into a glovebox, and mesylate, $Ni(COD)_2$, and PMe_3HBF_4 were added. Anhydrous 1,4-dioxane or diglyme was added, the vial was sealed with a Teflon-lined cap, then taken out of the glovebox, and the reaction mixture was stirred at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5-inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

Couplings with Liquid Tosylates or Mesylates; General Procedure C

Carboxylate was weighed in an oven-dried 4-mL scintillation vial containing a magnetic stir bar. The vial was taken into a glovebox, and $Ni(COD)_2$ and PMe_3HBF_4 were added. Electrophile (tosylate or mesylate) was added as a solution in the solvent (anhydrous 1,4-dioxane or diglyme). The vial was sealed with a Teflon-lined cap, then taken out of the glovebox, and the reaction mixture was stirred at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5-inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

Couplings with Arylpropiolic Acids; General Procedure D

Arylpropiolic acid and electrophile (tosylate or mesylate) were weighed in an oven-dried 4-mL scintillation vial containing a magnetic stir bar. The vial was taken into a glovebox, and $Ni(COD)_2$, PMe_3HBF_4, and base were added. The vial was sealed with a Teflon-lined cap, then taken out of the glovebox, and the reaction mixture was stirred at the indicated temperature for the indicated time. The reaction mixture was cooled to room temperature and filtered through a 1.5-inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

Coupled Products 1a–7a Using 2-Naphthyl Tosylate (Scheme 2)

2-(2-Phenylethynyl)naphthalene (1a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 16 h. Chromatography (hexanes) gave **1a** as a white solid; yield: 50.6 mg (89%).

R_f = 0.32 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 8.06 (s, 1 H), 7.86–7.78 (m, 3 H), 7.61–7.56 (m, 3 H), 7.53–7.47 (m, 2 H), 7.41–7.33 (m, 3 H); the spectroscopic data are consistent with the literature.[17]

2-[2-(4-Methylphenyl)ethynyl]naphthalene (2a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(*p*-tolyl)propiolate (99.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 17 h. Chromatography (hexanes) gave **2a** as a light yellow solid; yield: 60.0 mg (99%).

R_f = 0.44 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 8.04 (s, 1 H), 7.85–7.78 (m, 3 H), 7.57 (d, J = 6.8 Hz, 1 H), 7.53–7.44 (m, 4 H), 7.18 (d, J = 7.6 Hz, 2 H), 2.38 (s, 3 H); the spectroscopic data are consistent with the literature.[17]

2-[2-(4-Methoxyphenyl)ethynyl]naphthalene (3a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(4-methoxyphenyl)propiolate (108 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 14 h. Chromatography (EtOAc/hexanes, 2:98) gave **3a** as a white solid; yield: 55.7 mg (86%).

R_f = 0.30 (EtOAc/hexanes, 2:98).

^{1}H NMR ($CDCl_3$): δ = 8.03 (s, 1 H), 7.83–7.79 (m, 3 H), 7.58–7.46 (m, 5 H), 6.90 (d, J = 8.8 Hz, 2 H), 3.84 (s, 3 H); the spectroscopic data are consistent with the literature.[17]

2-[2-(4-Fluorophenyl)ethynyl]naphthalene (4a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(4-fluorophenyl)propiolate (102 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 16 h. Chromatography (hexanes) gave **4a** as a pale yellow solid; yield: 51.2 mg (83%).

R_f = 0.46 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 8.04 (s, 1 H), 7.85–7.78 (m, 3 H), 7.58–7.47 (m, 5 H), 7.06 (t, *J* = 8.8 Hz, 2 H); the spectroscopic data are consistent with the literature.[17]

2-[2-[4-(Trifluoromethyl)phenyl]ethynyl]naphthalene (5a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-[4-(trifluoromethyl)phenyl]propiolate (126 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 14.5 h. Chromatography (hexanes) gave **5a** as a pale yellow solid; yield: 49.6 mg (67%).

R_f = 0.55 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 8.08 (s, 1 H), 7.91–7.79 (m, 3 H), 7.68–7.51 (m, 7 H); the spectroscopic data are consistent with the literature.[17]

2-[2-(3-Methoxyphenyl)ethynyl]naphthalene (6a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(3-methoxyphenyl)propiolate (107 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (EtOAc/hexanes, 1:99) gave **6a** as a white solid; yield: 55.1 mg (85%); mp 67–68 °C.

R_f = 0.28 (EtOAc/hexanes, 1:99).

IR (neat): 3003, 2960, 2936, 1592, 1579, 1489, 1461, 1443, 1415, 1345, 1323, 1312, 1272, 1249, 1225, 1179, 1157, 1145, 1136, 1109, 1076, 1037, 990, 960, 950, 930, 905, 865, 855, 816, 784, 771, 747, 691, 655 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.06 (s, 1 H), 7.83–7.80 (m, 3 H), 7.58 (dd, *J* = 8.5, 1.6 Hz, 1 H), 7.52–7.48 (m, 2 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.11 (s, 1 H), 6.91 (ddd, *J* = 8.0, 2.5, 0.8 Hz, 1 H), 3.85 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 159.36, 132.98, 132.79, 131.46, 129.42, 128.38, 127.98, 127.74, 126.65, 126.52, 124.25, 124.21, 120.46, 116.35, 114.98, 89.66, 89.60, 55.26.

HRMS: *m*/*z* [M$^+$] calcd for $C_{19}H_{14}O$: 258.1045; found: 258.1040.

2-[2-(2-Methylphenyl)ethynyl]naphthalene (7a)

Following general procedure A, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(*o*-tolyl)propiolate (99.6 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 19 h. Chromatography (hexanes) gave **7a** as a white solid; yield: 46.9 mg (78%); mp 108–109 °C.

R_f = 0.50 (hexanes).

IR (neat): 2920, 1598, 1498, 1483, 1454, 1435, 1142, 944, 899, 863, 819, 754, 743, 717 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.05 (s, 1 H), 7.87–7.77 (m, 3 H), 7.59–7.49 (m, 4 H), 7.30–7.19 (m, 3 H), 2.57 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 140.22, 133.03, 132.75, 131.66, 131.17, 129.46, 128.39, 128.32, 127.96, 127.74, 127.73, 126.57, 126.52, 125.59, 123.01, 120.83, 93.72, 88.68, 20.78.

HRMS: *m*/*z* [M$^+$] calcd for $C_{19}H_{14}$: 242.1096; found: 242.1089.

Coupled Products 1b–h Using Aryl Tosylates (Scheme 3)

2-Methoxy-7-(2-phenylethynyl)naphthalene (1b)

Following general procedure A, a mixture of 7-methoxy-2-naphthyl tosylate (82.0 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (hexanes) gave **1b** as a light yellow solid; yield: 61.1 mg (94%); mp 104–106 °C.

R_f = 0.30 (hexanes).

IR (neat): 3011, 2924, 1625, 1593, 1569, 1508, 1489, 1458, 1450, 1409, 1391, 1371, 1329, 1269, 1249, 1214, 1171, 1143, 1130, 1114, 1072, 1030, 968, 952, 919, 889, 843, 835, 824, 806, 754, 724, 693 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.95 (s, 1 H), 7.74–7.71 (m, 2 H), 7.60–7.54 (m, 2 H), 7.44 (d, *J* = 7.8 Hz, 1 H), 7.40–7.33 (m, 3 H), 7.16 (dd, *J* = 9.3, 2.8 Hz, 1 H), 7.11 (s, 1 H), 3.93 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 158.06, 134.19, 131.61, 130.21, 129.21, 128.33, 128.23, 127.70, 126.24, 123.32, 121.02, 119.44, 105.57, 89.91, 89.62, 55.31.

HRMS: *m*/*z* [M$^+$] calcd for $C_{19}H_{14}O$: 258.1045; found: 258.1049.

6-(2-Phenylethynyl)quinoline (1c)

Following general procedure A, a mixture of quinolin-6-yl 4-methylbenzene sulfonate (74.8 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (EtOAc/hexanes, 20:80) gave **1c** as a tan solid; yield: 50.4 mg (88%).

R_f = 0.32 (EtOAc/hexanes, 20:80).

^{1}H NMR ($CDCl_3$): δ = 8.92 (d, *J* = 3.0 Hz, 1 H), 8.15–8.03 (m, 3 H), 7.82 (d, *J* = 8.6 Hz, 1 H), 7.58 (d, *J* = 3.6 Hz, 2 H), 7.44–7.38 (m, 4 H); the spectroscopic data are consistent with the literature.[18]

3-(2-Phenylethynyl)pyridine (1d)

Following general procedure A, a mixture of 3-pyridyl tosylate (62.3 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 120 °C for 4 h. Chromatography (EtOAc/hexanes, 20:80) gave **1d** as a tan solid; yield: 26.6 mg (59%).

R_f = 0.22 (EtOAc/hexanes, 20:80).

^{1}H NMR ($CDCl_3$): δ = 8.77 (s, 1 H), 8.55 (d, *J* = 4.0 Hz, 1 H), 7.81 (d, *J* = 7.8 Hz, 1 H), 7.56–7.54 (m, 2 H), 7.38–7.36 (m, 3 H), 7.30–7.26 (m, 1 H); the spectroscopic data are consistent with the literature.[19]

1-Methoxy-3-(2-phenylethynyl)benzene (1e)

Following general procedure A, a mixture of *m*-methoxyphenyl tosylate (69.6 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (138.2 mg, 0.750 mmol, 3.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 120 °C for 15 h. Chromatography (EtOAc/hexanes, 1:99) gave **1e** as an orange oil; yield: 21.4 mg (41%).

R_f = 0.35 (EtOAc/hexanes, 1:99).

^{1}H NMR ($CDCl_3$): δ = 7.55–7.53 (m, 2 H), 7.35–7.34 (m, 3 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 7.06 (s, 1 H), 6.90 (d, *J* = 7.4 Hz, 1 H), 3.83 (s, 3 H); the spectroscopic data are consistent with the literature.[20]

1-(2-Phenylethynyl)-3-(trifluoromethyl)benzene (1f)

Following general procedure A, a mixture of *m*-(trifluoromethyl)phenyl tosylate (79.0 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (184.2 mg, 1.00 mmol, 4.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 140 °C for 4 h. Chromatography (hexanes) gave **1f** as a pale yellow solid; yield: 35.1 mg (57%).

R_f = 0.60 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 7.80 (s, 1 H), 7.70 (d, *J* = 7.7 Hz, 1 H), 7.60–7.54 (m, 3 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.38–7.36 (m, 3 H); the spectroscopic data are consistent with the literature.[21]

Ethyl 3-(2-Phenylethynyl)benzoate (1g)

Following general procedure C, a mixture of ethyl 3-(tosyloxy)benzoate (80.0 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.50 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 140 °C for 4 h. Chromatography (EtOAc/hexanes, 1:99) gave **1g** as an orange oil; yield: 38.8 mg (62%).

R_f = 0.16 (EtOAc/hexanes, 1:99).

^{1}H NMR ($CDCl_3$): δ = 8.21 (s, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.58–7.51 (m, 2 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.39–7.34 (m, 3 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 1.41 (t, *J* = 7.1 Hz, 3 H); the spectroscopic data are consistent with the literature.[19]

1-Methyl-4-(2-phenylethynyl)benzene (1h)

Following general procedure A, a mixture of *p*-tolyl tosylate (65.6 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (184 mg, 1.00 mmol, 4.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 140 °C for 15.5 h. Chromatography (hexanes) gave **1h** as a light orange solid; yield: 22.4 mg (47%).

R_f = 0.60 (hexanes).

^{1}H NMR ($CDCl_3$): δ = 7.54–7.50 (m, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.37–7.30 (m, 3 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 2.37 (s, 3 H); the spectroscopic data are consistent with the literature.[12b]

Coupled Products 1a–7a Using 2-Naphthyl Mesylate (Scheme 4)

2-(2-Phenylethynyl)naphthalene (1a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 14 h. Chromatography (hexanes) gave **1a** as a yellow solid; yield: 51.7 mg (91%); R_f = 0.32 (hexanes). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-(4-Methylphenyl)ethynyl]naphthalene (2a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(*p*-tolyl)propiolate (99.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 16 h. Chromatography (hexanes) gave **2a** as a light yellow solid; yield: 57.4 mg (95%); R_f = 0.44 (hexanes). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-(4-Methoxyphenyl)ethynyl]naphthalene (3a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(4-methoxyphenyl)propiolate (107 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (EtOAc/hexanes, 1:99) gave **3a** as a light yellow solid; yield: 51.9 mg (80%); R_f = 0.30 (EtOAc/hexanes, 2:98). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-(4-Fluorophenyl)ethynyl]naphthalene (4a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(4-fluorophenyl)propiolate (101 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 14 h. Chromatography (hexanes) gave **4a** as a yellow solid; yield: 61.5 mg (99%); R_f = 0.46 (hexanes). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-[4-(Trifluoromethyl)phenyl]ethynyl]naphthalene (5a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-[4-(trifluoromethyl)phenyl]propiolate (126 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (hexanes) gave **5a** as a pale yellow solid; yield: 48.5 mg (66%); R_f = 0.55 (hexanes). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-(3-Methoxyphenyl)ethynyl]naphthalene (6a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(3-methoxyphenyl)propiolate (107 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15.5 h. Chromatography (EtOAc/hexanes, 1:99) gave **6a** as a white solid; yield: 52.7 mg (82%); R_f = 0.28 (EtOAc/hexanes, 1:99). The spectroscopic data are consistent with those of the product obtained using the tosylate.

2-[2-(2-Methylphenyl)ethynyl]naphthalene (7a)

Following general procedure A, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-(*o*-tolyl)propiolate (99.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 17 h. Chromatography (hexanes) gave **7a** as a white solid; yield: 29.0 mg (48%); R_f = 0.50 (hexanes). The spectroscopic data are consistent with those of the product obtained using the tosylate.

Coupled Products 1c, 1e, 1g Using Aryl Mesylates (Scheme 5)

6-(2-Phenylethynyl)quinoline (1c)

Following general procedure A, a mixture of quinolin-6-yl-methane sulfonate (55.8 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 19 h. Chromatography (EtOAc/hexanes, 20:80) gave **1c** as a yellow solid; yield: 36.8 mg (64%); R_f = 0.31 (EtOAc/hexanes, 20:80). The spectroscopic data are consistent with those of the product obtained using the tosylate.

1-Methoxy-3-(2-phenylethynyl)benzene (1e)

Following general procedure C, a mixture of *m*-methoxyphenyl mesylate (50.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (138.2 mg, 0.750 mmol, 3.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 120 °C for 16 h. Chromatography (EtOAc/hexanes, 1:99) gave **1e** as a yellow oil; yield: 25.4 mg (49%); R_f = 0.35 (EtOAc/hexanes, 1:99). The spectroscopic data are consistent with those of the product obtained using the tosylate.

Ethyl 3-(2-Phenylethynyl)benzoate (1g)

Following general procedure B, a mixture of ethyl 3-(mesyloxy)benzoate (60.5 mg, 0.250 mmol, 1.0 equiv), potassium 3-phenylpropiolate (92.1 mg, 0.500 mmol, 2.0 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 140 °C for 4 h. Chromatography (EtOAc/hexanes, 1:99) gave **1g** as an orange oil; yield: 10.8 mg (17%); R_f = 0.21 (EtOAc/hexanes, 1:99). The spectroscopic data are consistent with those of the product obtained using the tosylate.

Coupled Products 1a, 3a–5a Using Acids (Schemes 6 and 7)

2-(2-Phenylethynyl)naphthalene (1a)

Following general procedure D, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), 3-phenylpropiolic acid (73.1 mg, 0.500 mmol, 2.0 equiv), K_3PO_4 (133 mg, 0.625 mmol, 2.5 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 17 h. Chromatography (hexanes) gave **1a** as a white solid; yield: 32.0 mg (67%); R_f = 0.38 (hexanes). The spectroscopic data are consistent with those of the product obtained using the carboxylate.

2-(2-Phenylethynyl)naphthalene (1a)

Following general procedure D, a mixture of 2-naphthyl mesylate (55.5 mg, 0.250 mmol, 1.0 equiv), 3-phenylpropiolic acid (73.1 mg, 0.500 mmol, 2.0 equiv), K_3PO_4 (133 mg, 0.625 mmol, 2.5 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 14.5 h. Chromatography (hexanes) gave **1a** as a white solid; yield: 26.9 mg (47%); R_f = 0.38 (hexanes). The spectroscopic data are consistent with those of the product obtained using the carboxylate.

2-[2-(4-Methoxyphenyl)ethynyl]naphthalene (3a)

Following general procedure D, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), 3-(4-methoxyphenyl)propiolic acid (88.1 mg, 0.500 mmol, 2.0 equiv), K_3PO_4 (133 mg, 0.625 mmol, 2.5 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous dioxane (1.0 mL) was stirred at 80 °C for 15 h. Chromatography (EtOAc/hexanes, 1:99) gave **3a** as a white solid; yield: 29.3 mg (45%); R_f = 0.30 (EtOAc/hexanes, 2:98). The spectroscopic data are consistent with those of the product obtained using the carboxylate.

2-[2-(4-Fluorophenyl)ethynyl]naphthalene (4a)

Following general procedure D, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), 3-(4-fluorophenyl)propiolic acid (82.1 mg, 0.500 mmol, 2.0 equiv), K_3PO_4 (133 mg, 0.625 mmol, 2.5 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 120 °C for 14 h. Chromatography (hexanes) gave **4a** as a pale yellow solid; yield: 13.4 mg (22%); R_f = 0.46 (hexanes). The spectroscopic data are consistent with those of the product obtained using the carboxylate.

2-[2-[4-(Trifluoromethyl)phenyl]ethynyl]naphthalene (5a)

Following general procedure D, a mixture of 2-naphthyl tosylate (74.5 mg, 0.250 mmol, 1.0 equiv), 3-[4-(trifluoromethyl)phenyl]propiolic acid (108 mg, 0.500 mmol, 2.0 equiv), K_3PO_4 (133 mg, 0.625 mmol, 2.5 equiv), $Ni(COD)_2$ (6.90 mg, 0.025 mmol, 0.10 equiv), PMe_3HBF_4 (12.3 mg, 0.075 mmol, 0.30 equiv), and anhydrous diglyme (1.0 mL) was stirred at 120 °C for 16 h. Chromatography (hexanes) gave **5a** as a pale yellow solid; yield: 15.4 mg (21%); R_f = 0.55 (hexanes). The spectroscopic data are consistent with those of the product obtained using the carboxylate.

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Supporting Information

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References

(1) (a) Schwarz, J.; König, B. *Green Chem.* **2018**, *20*, 323. (b) Wei, Y.; Hu, P.; Zhang, M.; Su, W. *Chem. Rev.* **2017**, *117*, 8864. (c) Font, M.; Quibell, J. M.; Perry, G. J. P.; Larrosa, I. *Chem. Commun.* **2017**, *53*, 5584. (d) Hoover, J. M. *Comments Inorg. Chem.* **2017**, *37*, 169. (e) Guo, L.-N.; Wang, H.; Duan, X.-H. *Org. Biomol. Chem.* **2016**, *14*, 7380. (f) Huang, H.; Jia, K.; Chen, Y. *ACS Catal.* **2016**, *6*, 4983. (g) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898. (h) Miao, J.; Ge, H. *Synlett* **2014**, *25*, 911. (i) Gooßen, L. J.; Gooßen, K. *Top. Organomet. Chem.* **2013**, *44*, 121. (j) Park, K.; Lee, S. *RSC Adv.* **2013**, *3*, 14165. (k) Cornella, J.; Larrosa, I. *Synthesis* **2012**, *44*, 653. (l) Dzik, W. I.; Lange, P. P.; Gooßen, L. J. *Chem. Sci.* **2012**, *3*, 2671. (m) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846. (n) Rodríguez, N.; Gooßen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030. (o) Gooßen, L. J.; Rodríguez, N.; Gooßen, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 3100.

(2) (a) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A.; Diederich, F., Ed.; Wiley-VCH: Weinheim, **2004**, 2nd ed.. (b) Seechurn, C. C. C. J.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062.

(3) For representative examples of Pd-catalyzed decarboxylative reactions, see: (a) Hu, P.; Zhang, M.; Jie, X.; Su, W. *Angew. Chem. Int. Ed.* **2012**, *51*, 227. (b) Zhang, F.-Z.; Greaney, M. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 2768. (c) Xie, K.; Yang, Z.; Zhou, X.; Li, X.; Wang, S.; Tan, Z.; An, X.; Guo, C.-C. *Org. Lett.* **2010**, *12*, 1564. (d) Wang, C.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 4194. (e) Cornella, J.; Lu, P.; Larrosa, I. *Org. Lett.* **2009**, *11*, 5506. (f) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. *Chem. Commun.* **2008**, 6312.

(4) For representative examples of Rh- and Ru-catalyzed reactions, see: (a) Neely, J. M.; Rovis, T. *J. Am. Chem. Soc.* **2014**, *136*, 2735. (b) Zhang, J.; Liu, J.-F.; Ugrinov, A.; Pillai, A. F. X.; Sun, Z.-M.; Zhao, P. *J. Am. Chem. Soc.* **2013**, *135*, 17270. (c) Wang, J.; Liu, B.; Zhao, H.; Wang, J. *Organometallics* **2012**, *31*, 8598. (d) Sun, Z. M.; Zhang, J.; Zhao, P. *Org. Lett.* **2010**, *12*, 992. (e) Austeri, M.; Linder, D.; Lacour, J. *Adv. Synth. Catal.* **2010**, *352*, 3339. (f) Austeri, M.; Linder, D.; Lacour, J. *Chem. Eur. J.* **2008**, *14*, 5737. (g) Burger, E. C.; Tunge, J. A. *Org. Lett.* **2004**, *6*, 2603.

(5) For representative examples of Cu-catalyzed decarboxylative reactions, see: (a) Chen, L.; Ju, L.; Bustin, K. A.; Hoover, J. M. *Chem. Commun.* **2015**, *51*, 15059. (b) Ponpandian, T.; Muthusubramanian, S. *Tetrahedron Lett.* **2012**, *53*, 4248. (c) Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H.-Z.; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 9350.

(6) For representative examples of Fe-catalyzed decarboxylative cross-couplings, see: (a) Rong, G.; Liu, D.; Lu, L.; Yan, H.; Zheng, Y.; Chen, J.; Mao, J. *Tetrahedron* **2014**, *70*, 5033. (b) Zhao, J.; Zhou, W.; Han, J.; Li, G.; Pan, Y. *Tetrahedron Lett.* **2013**, *54*, 6507. (c) Zhao, J.; Fang, H.; Han, J.; Pan, Y. *Beilstein J. Org. Chem.* **2013**, *9*, 1718. (d) Yang, H.; Yan, H.; Sun, P.; Zhu, Y.; Lu, L.; Liu, D.; Rong, G.; Mao, J. *Green Chem.* **2013**, *15*, 976. (e) Bi, H.-P.; Chen, W.-W.; Liang, Y.-M.; Li, C.-J. *Org. Lett.* **2009**, *11*, 3246.

(7) For Ni-catalyzed decarboxylative cross-couplings, see: (a) Yang, K.; Zhang, C.; Wang, P.; Zhang, Y.; Ge, H. *Chem. Eur. J.* **2014**, *20*, 7241. (b) Wu, Y.; Liu, L.; Yan, K.; Xu, P.; Gao, Y.; Zhao, Y. *J. Org. Chem.* **2014**, *79*, 8118. (c) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. *Science* **2014**, *345*, 437. (d) Choe, J.; Yang, J.; Park, K.; Palani, T.; Lee, S. *Tetrahedron Lett.* **2012**, *53*, 6908.

(8) For Ni-catalyzed decarbonylative and decarboxylative C–H arylations, see: (a) Crovak, R. A.; Hoover, J. M. *J. Am. Chem. Soc.* **2018**, *140*, 2434. (b) Honeycutt, A. P.; Hoover, J. M. *ACS Catal.* **2017**, *7*, 4597. (c) Crawford, J. M.; Shelton, K. E.; Sadarananda, B. K.; Reeves, E. K.; Kalyani, D. *Org. Chem. Front.* **2015**, *2*, 726. (d) Yang, K.; Wang, P.; Zhang, C.; Kadi, A. A.; Fun, H.-K.; Zhang, Y.; Lu, H. *Eur. J. Org. Chem.* **2014**, 7586. (e) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 13573.

(9) (a) Mesganaw, T.; Garg, N. K. *Org. Process Res. Dev.* **2013**, *17*, 29. (b) Kozhushkov, S. I.; Potukuchi, H. K.; Ackermann, L. *Catal. Sci. Technol.* **2013**, *3*, 562. (c) So, C. M.; Kwong, F. Y. *Chem. Soc. Rev.* **2011**, *40*, 4963. (d) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev.* **2011**, *111*, 1346. (e) Li, B.-J.; Yu, D.-G.; Sun, C.-L.; Shi, Z.-J. *Chem. Eur. J.* **2011**, *17*, 1728. (f) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486. (g) Antoft-Finch, A.; Blackburn, T.; Snieckus, V. *J. Am. Chem. Soc.* **2009**, *131*, 17750.

(10) (a) Lee, J.-H.; Raja, G. C. E.; Yu, S.; Lee, J.; Song, K. H.; Lee, S. *ACS Omega* **2017**, *2*, 6259. (b) Fujino, T.; Hinoue, T.; Usuki, Y.; Satoh, T. *Org. Lett.* **2016**, *18*, 5688. (c) Sardzinski, L. W.; Wertjes, W. C.; Schnaith, A. M.; Kalyani, D. *Org. Lett.* **2015**, *17*, 1256. (d) Song, B.; Knauber, T.; Gooßen, L. J. *Angew. Chem. Int. Ed.* **2013**, *52*, 2954. (e) Gooßen, L. J.; Rodríguez, N.; Lange, P. P.; Linder, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 1111. (f) Kim, H.; Lee, P. H. *Adv. Synth. Catal.* **2009**, *351*, 2827. (g) Gooßen, L. J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248.

(11) (a) Steinberg, D. F.; Turk, M. C.; Kalyani, D. *Tetrahedron* **2017**, *73*, 2196. (b) Yi, Z.; Aschenaki, Y.; Daley, R.; Davick, S.; Schnaith, A.; Wander, R.; Kalyani, D. *J. Org. Chem.* **2017**, *82*, 6946. (c) Ferguson, D. M.; Rudolph, S. R.; Kalyani, D. *ACS Catal.* **2014**, *4*, 2395. (d) Wang, J.; Ferguson, D. M.; Kalyani, D. *Tetrahedron* **2013**, *69*, 5780. (e) Nervig, C. S.; Waller, P. J.; Kalyani, D. *Org. Lett.* **2012**, *14*, 4838.

(12) For Ni-catalyzed synthesis of diarylalkynes via decarboxylative cross-coupling, see: (a) Son, Y.; Kim, H.-S.; Lee, J.-H.; Jang, J.; Lee, C.-F.; Lee, S. *Tetrahedron Lett.* **2017**, *58*, 1413. (b) Raja, G. C. E.; Irudayanathan, F. M.; Kim, H.-S.; Kim, J.; Lee, S. *J. Org. Chem.* **2016**, *81*, 5244.

(13) For Pd-catalyzed synthesis of diarylalkynes via decarboxylative cross-coupling, see: (a) Jang, J.; Raja, G. C. E.; Lee, J.-H.; Son, Y.; Kim, J.; Lee, S. *Tetrahedron Lett.* **2016**, *57*, 4581. (b) Lee, J.-H.; Raja, G. C. E.; Son, Y.; Jang, J.; Kim, J.; Lee, S. *Tetrahedron Lett.* **2016**, *57*, 4824. (c) Li, X.; Yang, F.; Wu, Y. *J. Org. Chem.* **2013**, *78*, 4543. (d) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. J. *J. Org. Chem.* **2010**, *75*, 6244.

(14) The reactions are heterogeneous. The carboxylate is less soluble in *p*-xylene than in dioxane or diglyme. The lower yields at higher temperature might be in part due to decarboxylative dimerization (mass consistent with this byproduct was observed by GCMS). The Aldrich specification sheet for dioxane or diglyme did not mention the presence of any inhibitors.

(15) The carboxylate equivalence is largely empirical. The products were isolated using reaction conditions that showed highest conversion and least byproducts by GCMS. The reaction using *p*-methoxyphenyl tosylate led to the product in low yield and we were unable to isolate a clean sample of the desired product.

(16) (a) Shang, R.; Xu, Q.; Jiang, Y.-Y.; Wang, Y.; Liu, L. *Org. Lett.* **2010**, *12*, 1000. (b) Ogata, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 13848. (c) Lei, X.; Jalla, A.; Shama, M. A. A.; Stafford, J. M.; Cao, B. *Synthesis* **2015**, *47*, 2578.

(17) Liu, L.; Zhao, D.; Liu, M.; Zhou, Y.; Chen, T. *Org. Lett.* **2018**, *20*, 2741.

(18) Nishida, T.; Ida, H.; Kuninobo, Y.; Kanai, M. *Nat. Commun.* **2014**, *5*, 1.

(19) Okura, K.; Kawashima, H.; Tamakuni, F.; Nishida, N.; Shirakawa, E. *Chem. Commun.* **2016**, *52*, 14019.

(20) Tian, Z.-Y.; Wang, S.-M.; Jia, S.-J.; Song, H.-X.; Zhang, C.-P. *Org. Lett.* **2017**, *19*, 5454.

(21) Zhang, M.; Jia, T.; Wang, C. Y.; Walsh, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 10346.