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Palladium-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids with Benzyl Halides or Aryl Halides

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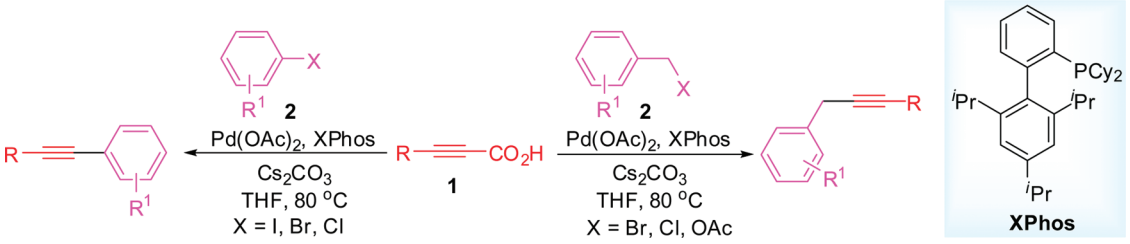

The synthesis of internal benzyl alkynes and 1,2-diarylalkynes has been developed via palladium-catalyzed decarboxylative coupling reactions of alkynyl carboxylic acids with benzyl chlorides or aryl halides. In the presence of $Pd(OAc)_2$ and Xphos (**L3**), alkynyl carboxylic acids smoothly underwent the reaction with various benzyl halides, providing the corresponding benzyl alkynes in moderate to good yields. It is noteworthy that the optimal conditions are compatible with a wide range of aryl halides including less active aryl chlorides.

Introduction

In the past decade transition metal-catalyzed decarboxylative coupling reactions have emerged as useful tools for constructing the carbon−carbon bonds in organic synthesis because acids and their derivatives, one of the reaction partners, are commercially available and inexpensive. These methodologies commonly involve the decarboxylative Heck coupling,[1] aldol additions,[2] decarboxylative enolate alkylation,[3] and decarboxylative cross-coupling reactions.[4−8] Although the decarboxylative coupling reaction with alkynyl carboxylic acid substrates has been rarely explored,[6] these transformations are interesting by comparison with the

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traditionally Sonogashira cross-coupling reaction because they proceed via a CO_2-released process under copper-free conditions, avoiding the occurrence of the homocoupling.[9] In 2008, Lee and co-workers first reported a $Pd_2(dba)_3$/dppf-catalyzed cascade reaction of propiolic acid with aryl halides involving a decarboxylation process (eq 1, Scheme 1).[6a] Subsequently, they found that alkynyl carboxylic acids could undergo the decarboxylative coupling with aryl iodides and bromides with use of the $Pd_2(dba)_3$/dppb catalytic system (eq 2, Scheme 1).[6b] Lee and Kim have also disclosed that $Pd_2(dba)_3$ combined with phosphine ligand (PPh_3 or Xantphos) were effective for the decarboxylative coupling between aryl halides (aryl iodides, bromides, and triflates) and alkynyl carboxylic acids with the aid of Ag_2O and LiX (X = I, Cl) (eq 3, Scheme 1).[6c] As a continuing interest in the decarboxylative coupling reactions,[5k,8] we here report an efficient palladium-catalyzed decarboxylative coupling route to selectively synthesizing internal alkynes using both alkynyl carboxylic acids and benzyl halides as the reaction partners (eq 4, Scheme 1). Moreover, the reaction conditions are compatible with a wide range of aryl halides including less active aryl chlorides.

Results and Discussion

We began our investigation using readily available phenylpropiolic acid (**1a**) and benzyl chloride (**2a**) as the model substrates (Table 1). However, the results demonstrated that the reaction between **1a** and **2a** was not successful under the reported conditions (entry 1).[6a,b] After a series of trials, we found that $Pd(OAc)_2$ combined with dppb (**L1**) afforded the desired decarboxylative coupling product **3** in 8% yield with Cs_2CO_3 base and DMF medium (entries 2−4). To our delight, the yield of **3** was enhanced to 36% when dppb was replaced by PPh_3 (**L2**) (entry 5). Encouraged by these results, both solvents and reaction temperatures were evaluated to obtain the optimal conditions (entries 6−9). It was disclosed that MeCN has no effect on the decarboxylative coupling reaction (entry 6), and THF displayed the highest efficiency (entry 7). Among the reaction temperatures examined, it turned out that the best results were obtained at 80 °C (entries 7−9). Subsequently, the effect of three other ligands

SCHEME 1

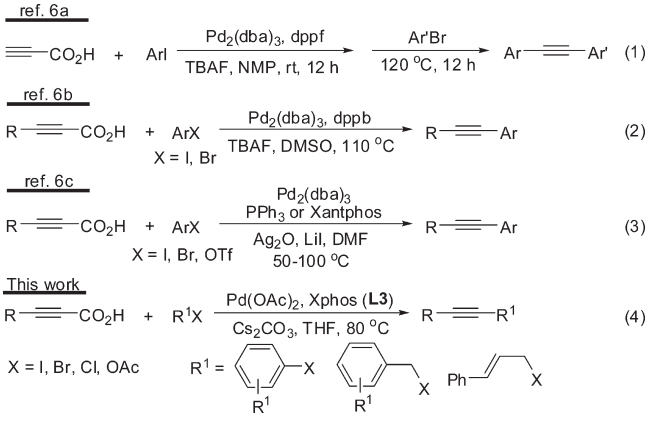
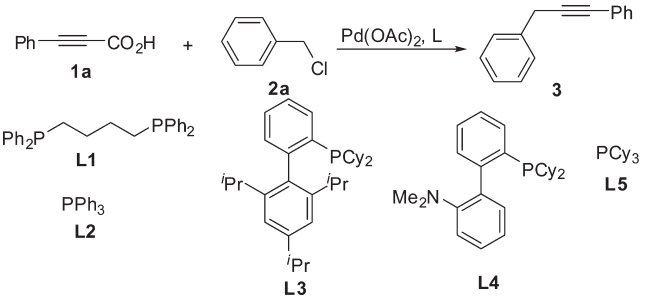


TABLE 1. Screening Optimal Conditions[a]



entry	ligand (mol %)	base	solvent	T (°C)	t (h)	yield (%)
1[b]	**L1** (10)	TBAF	DMSO	100	5	trace
2	**L1** (10)	TBAF	DMSO	100	5	trace
3	**L1** (10)	Cs_2CO_3	DMSO	100	5	trace
4	**L1** (10)	Cs_2CO_3	DMF	100	5	8
5	**L2** (10)	Cs_2CO_3	DMF	100	5	36
6	**L2** (10)	Cs_2CO_3	CH_3CN	100	5	trace
7	**L2** (10)	Cs_2CO_3	THF	100	5	67
8	**L2** (10)	Cs_2CO_3	THF	80	10	72
9	**L2** (10)	Cs_2CO_3	THF	65	10	18
10	**L3** (10)	Cs_2CO_3	THF	80	10	89
11	**L3** (5)	Cs_2CO_3	THF	80	10	86
12	**L4** (5)	Cs_2CO_3	THF	80	10	76
13	**L5** (5)	Cs_2CO_3	THF	80	10	63
14	**L3** (5)	Cs_2CO_3	dioxane	80	10	81
15	**L3** (5)	Et_3N	THF	80	10	78
16	**L3** (5)	K_2CO_3	THF	80	10	65
17	**L3** (5)	Cs_2CO_3	THF	100	10	45
18	**L3** (5)	Cs_2CO_3	THF	60	10	70
19[c]	**L3** (5)	Cs_2CO_3	THF	80	10	85
20[d]	**L3** (2)	Cs_2CO_3	THF	80	10	92
21[d]	**L4** (2)	Cs_2CO_3	THF	80	10	75
22[e]	**L3** (2)	Cs_2CO_3	THF	80	10	0

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), base (1.2 equiv), and solvent (2 mL). [b]$PdCl_2(PPh_3)_2$ (5 mol %) instead of $Pd(OAc)_2$. [c]$Pd(OAc)_2$ (3 mol %) was added. [d]$Pd(OAc)_2$ (1 mol %) was added. [e]Without Pd catalysis.

L3−**5** was tested (entries 10−13). We were pleased to observe that three ligands **L3**−**5** were effective for the reaction, and Xphos (**L3**) was the most active ligand. Moreover, the amount of **L3** affected the reaction slightly (entries 10 and 11). With the $Pd(OAc)_2$/**L3** catalytic system in hand, a number of experimental variables, such as solvent, base, reaction temperature, and the Pd loading, were investigated (entries 14−19). The yield of **3** was lowered by using dioxane

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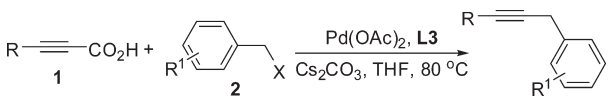
solvent, Et_3N or K_2CO_3 bases (entries 14−16). The reaction temperatures have a fundamental influence on the reaction, and the yield was decreased at either 100 or 60 °C (entries 17 and 18). It was interesting to discover that in the presence of **L3** the highest yield was isolated at a loading of 1 mol % of $Pd(OAc)_2$ (entries 10, 19, and 20), but 1 mol % of $Pd(OAc)_2$ combined **L4** gave the same yield with that of 5 mol % of $Pd(OAc)_2$ (entry 12 vs entry 21). However, the reaction cannot take place without Pd catalysis (entry 22).

As shown in Table 2, the decarboxylative coupling reactions of alkynyl carboxylic acids with various benzyl chlorides were carried out in the presence of $Pd(OAc)_2$, **L3**, and Cs_2CO_3. Initially, a variety of substituted benzyl chlorides **2b**−**g** were investigated for the reaction with phenylpropiolic acid (**1a**) (entries 1−6). The results indicated that a number of functional groups, including methyl, ether, chloro, and fluoro, on the aryl moiety were tolerated well under the standard conditions, but the electron-deficient NO_2 group was not suitable. Substrate **2b** bearing an *o*-methylphenyl group, for instance, underwent the decarboxylative coupling reaction with acid **1a**, $Pd(OAc)_2$, and **L3** smoothly, affording the corresponding product **4** in 80% yield (entry 1). Moderate yields were still achieved from the reaction of either *p*-chloro-substituted substrates **2e** or *o*-fluoro-substituted **2f** (entries 4 and 5). However, acid **1a** cannot react with 1-(chloromethyl)-4-nitrobenzene (**2g**) under the same conditions and provide the home-coupling product 1,4-diphenylbuta-1,3-diyne in 55% yield (based on alkyne) (entry 6). The reason may be that the electron-withdrawing group deactivated benzyl chloride leading to the home-coupling superior to the cross-coupling process. We were happy to find that benzyl bromide (**2h**) was also consistent with the optimal conditions leading to 88% yield (entry 7), but benzyl acetate (**2i**) was not a suitable substrate (entry 8). Interestingly, cinnamyl halides **2j**−***l***, (*E*)-(3-chloroprop-1-enyl)benzene (**2j**), (*E*)-(3-bromoprop-1-enyl)benzene (**2k**), and cinnamyl acetate (**2*l***), successfully underwent the decarboxylative coupling with acid **1a**, $Pd(OAc)_2$, and **L3** in 72%, 69%, and 80% yields, respectively (entries 9−11). To our delight, the optimal conditions were found to be compatible with various alkynyl carboxylic acids **1b**−**f**, including substituted aryl and aliphatic propiolic acids (entries 12−22). For example, arylalkynyl carboxylic acids **1b**−**d**, with a methyl, chloro or acetyl group on the aryl moiety, were reacted with benzyl chloride (**2a**), $Pd(OAc)_2$, **L3**, and Cs_2CO_3 smoothly in good yields (entries 12−14). Gratifyingly, both oct-2-ynoic acid (**1e**) and but-2-ynoic acid (**1f**) were also successful for the decarboxylative coupling reaction with 5-chloromethylbenzo[1,3]dioxole (**2d**), and afforded the corresponding products **17** and **21** in 88% and 83% yields, respectively (entries 18 and 22). It is noteworthy that NO_2-substituted chloride **2g** is suitable for the reaction with acid **1b** (entry 21). However, an attempt at the decarboxylative coupling reaction of terminal propiolic acid **1g** with chloride **2d** failed (entry 23).

Next, we tested the optimal conditions for the decarboxylative coupling reactions of alkynyl carboxylic acids **1** with numerous aryl halides **2m**−**w**, and the results are summarized in Table 3.[6] In the presence of $Pd(OAc)_2$, **L3**, and Cs_2CO_3, a variety of aryl halides, including less active aryl chloride, successfully underwent the reaction with acid **1a** in moderate to good yields. Initially, the reactions of acid **1a** with iodobenzene (**2m**) or 1-iodo-4-methoxybenzene (**2n**)

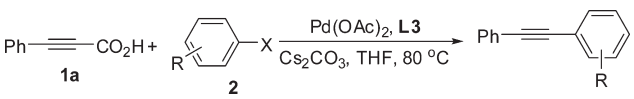
TABLE 2. $Pd(OAc)_2$/L3-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids (1) with Halides or Acetates (2)[a]



entry	acid **1**	substrate **2**	yield (%)
1	Ph−≡−CO_2H (**1a**)	Cl (**2b**)	80 (**4**)
2	Ph−≡−CO_2H (**1a**)	MeO, Cl (**2c**)	88 (**5**)
3	Ph−≡−CO_2H (**1a**)	O, O, Cl (**2d**)	81 (**6**)
4	Ph−≡−CO_2H (**1a**)	Cl, Cl (**2e**)	78 (**7**)
5	Ph−≡−CO_2H (**1a**)	F, Cl (**2f**)	86 (**8**)
6[b]	Ph−≡−CO_2H (**1a**)	O_2N, Cl (**2g**)	trace (**9**)
7	Ph−≡−CO_2H (**1a**)	Br (**2h**)	88 (**3**)
8	Ph−≡−CO_2H (**1a**)	OAc (**2i**)	trace (**3**)
9	Ph−≡−CO_2H (**1a**)	Cl (**2j**)	72 (**10**)
10	Ph−≡−CO_2H (**1a**)	Br (**2k**)	69 (**10**)
11	Ph−≡−CO_2H (**1a**)	OAc (**2l**)	80 (**10**)
12	−≡−COOH (**1b**)	Cl (**2a**)	91 (**11**)
13	Cl−≡−COOH (**1c**)	Cl (**2a**)	85 (**12**)
14	O−≡−COOH (**1d**)	Cl (**2a**)	90 (**13**)
15	*n*-C_5H_{11}−≡−CO_2H (**1e**)	Cl (**2a**)	75 (**14**)
16	*n*-C_5H_{11}−≡−CO_2H (**1e**)	Cl (**2b**)	91 (**15**)
17	*n*-C_5H_{11}−≡−CO_2H (**1e**)	MeO, Cl (**2c**)	85 (**16**)
18	*n*-C_5H_{11}−≡−CO_2H (**1e**)	O, O, Cl (**2d**)	88 (**17**)
19	*n*-C_5H_{11}−≡−CO_2H (**1e**)	Cl, Cl (**2e**)	85 (**18**)
20	*n*-C_5H_{11}−≡−CO_2H (**1e**)	F, Cl (**2f**)	87 (**19**)
21	*n*-C_5H_{11}−≡−CO_2H (**1e**)	O_2N, Cl (**2g**)	42 (**20**)
22	−≡−CO_2H (**1f**)	O, O, Cl (**2d**)	83 (**21**)
23	≡−CO_2H (**1g**)	O, O, Cl (**2d**)	trace (**22**)

[a]Reaction conditions: **1** (0.6 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (1 mol %), **L3** (2 mol %), Cs_2CO_3 (1.2 equiv), and THF (2 mL) at 80 °C for 10 h. [b]The home-coupling product, 1,4-diphenylbuta-1,3-diyne, was obtained in 55% yield (based on alkyne) together with some side products.

TABLE 3. $Pd(OAc)_2$/L3-Catalyzed Decarboxylative Coupling of 3-Phenylpropiolic Acid (1a) with Aryl Halides (2)[a]



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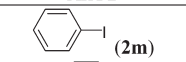
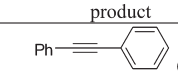
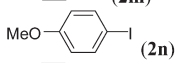
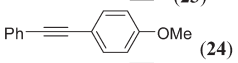
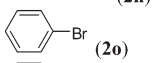
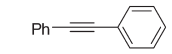
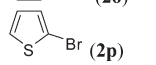
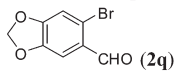
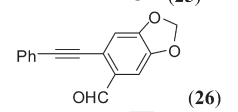
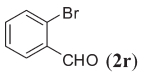
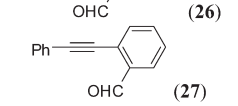
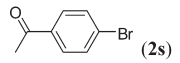
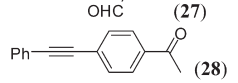
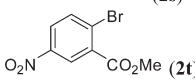
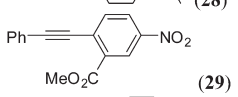
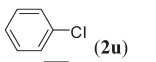
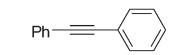
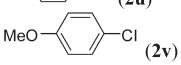
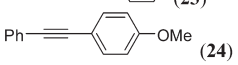
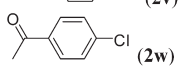
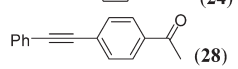
1	 (2m)	 (23)	72
2	 (2n)	 (24)	63
3	 (2o)	 (23)	92
4	 (2p)	 (25)	83
5	 (2q)	 (26)	81
6	 (2r)	 (27)	85
7	 (2s)	 (28)	90
8	 (2t)	 (29)	78
9[b]	 (2u)	 (23)	76
10[b]	 (2v)	 (24)	19
11[b]	 (2w)	 (28)	75

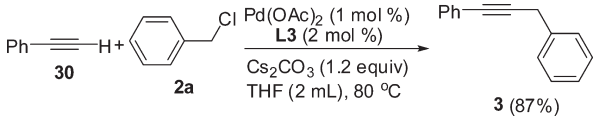
[a]Reaction conditions: **1a** (0.6 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (1 mol %), **L3** (2 mol %), Cs_2CO_3 (1.2 equiv), and THF (2 mL) at 80 °C for 10 h. [b]For 24 h.

were carried out smoothly to afford the target alkynes **23** and **24** in moderate yields together with the homocoupling products (about 10% yields) from aryl iodides (entries 1 and 2). Interestingly, good yields were isolated with use of bromobenzene (**2o**) or 2-bromothiophene (**2p**) as one of the reaction partners under the same conditions (entries 2 and 3). We were pleased to find that several functional groups, such as formyl, acetyl, ester, or nitro group, on the aryl ring were tolerated (entries 5−8). For instance, 6-bromobenzo[1,3]-dioxole-5-carbaldehyde (**2q**) was treated with acid **1a**, $Pd(OAc)_2$, **L3**, and Cs_2CO_3 in 81% yield (entry 5). To our delight, satisfactory yields were still achieved after 24 h for less active aryl chlorides **2u** and **2w** under the optimal conditions (entries 9 and 11). However, deactivated 1-chloro-4-methoxybenzene (**2v**) displayed less efficiency (entry 10).

As shown in Scheme 2, phenylacetylene (**30**) could proceed with the Sonogashira cross-coupling reaction with benzyl chloride providing a good yield in the presence of $Pd(OAc)_2$, **L3**, and Cs_2CO_3.

In summary, we have developed a palladium-catalyzed decarboxylative coupling protocol for selectively preparing internal benzyl alkynes and 1,2-diaryl alkynes. In the presence of $Pd(OAc)_2$ and Xphos (**L3**), alkynyl carboxylic acids smoothly underwent the reaction with benzyl halides and aryl halides in moderate to good yields. Compared with the previous reported results of palladium-catalyzed decarboxylative coupling, two features were established: (1) This reaction

SCHEME 2



is general, and its scope was extended to benzyl halides, cinnamyl halides, and aryl halides including less active aryl chlorides, and (2) this reaction was carried out under relatively low loading $Pd(OAc)_2$ conditions.

Experimental Section

Typical Experimental Procedure for the $Pd(OAc)_2$/Xphos (L3)-Catalyzed Decarboxylative Coupling Reaction. Acid **1** (0.6 mmol), Chloride **2** (0.5 mmol), $Pd(OAc)_2$ (1 mol %, 1.1 mg), **L3** (2 mol %, 3.9 mg), Cs_2CO_3 (1.2 equiv, 195.6 mg), and THF (2 mL) were added to a Schlenk tube in turn. Then the solution was stirred at 80 °C under nitrogen atmosphere for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was washed with brine, extracted with diethyl ether, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to afford the desired product.

Prop-1-yne-1,3-diyldibenzene (3):[10] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.39 (m, 4H), 7.34−7.22 (m, 6H), 3.81 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 131.6, 128.5, 128.2, 127.9, 127.8, 126.6, 123.6, 87.5, 82.6, 25.7; LRMS (EI, 70 eV) *m*/*z* (%) 192 (M^+, 100), 191 (91), 189 (30).

1-Methyl-2-(3-phenylprop-1-ynyl)benzene (4):[10] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.41 (m, 4H), 7.29−7.25 (m, 2H), 7.20−7.15 (m, 2H), 3.72 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 134.9, 131.6, 130.0, 128.3, 128.2, 127.7, 126.8, 126.2, 123.7, 87.2, 82.7, 23.9, 19.3; LRMS (EI, 70 eV) *m*/*z* (%) 206 (M^+, 70), 191 (67), 128 (42), 91 (100).

1-Methoxy-3-(3-phenylprop-1-ynyl)benzene (5):[11] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.43 (m, 2H), 7.30−7.22 (m, 4H), 7.00−6.98 (m, 2H), 6.80−6.79 (m, 1H), 3.80−3.76 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 138.3, 131.6, 129.5, 128.2, 127.8, 123.6, 120.3, 113.7, 120.0, 87.3, 82.7, 55.1, 25.7; LRMS (EI, 70 eV) *m*/*z* (%) 222 (M^+, 100), 207 (64), 178 (63).

5-(3-Phenylprop-1-ynyl)benzo[*d*][1,3]dioxole (6): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.42−7.26 (m, 3H), 6.91−6.82 (m, 2H), 6.76 (d, J = 7.9 Hz, 1H), 5.91 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 146.2, 131.6, 130.4, 128.2, 127.8, 123.5, 120.7, 108.5, 108.1, 100.9, 87.6, 82.6, 25.3; LRMS (EI, 70 eV) *m*/*z* (%) 236 (M^+, 100), 178 (80), 206 (29); HRMS (EI) for $C_{16}H_{12}O_2$ (M^+) calcd 236.0837, found 236.0835.

1-Chloro-4-(3-phenylprop-1-ynyl)benzene (7):[10] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.42 (m, 2H), 7.34−7.27 (m, 7H), 3.77 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 132.4, 131.6, 129.3, 128.6, 128.2, 127.9, 123.8, 86.8, 83.0, 25.1; LRMS (EI, 70 eV) *m*/*z* (%) 226 (M^+, 28), 189 (30), 191 (100).

1-Fluoro-2-(3-phenylprop-1-ynyl)benzene (8): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59−7.45 (m, 3H), 7.30−7.02 (m, 6H), 3.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6 (d, $^1J_{C,F}$ = 245 Hz, 1C), 131.6, 129.9 (d, $^3J_{C,F}$ = 3.8 Hz, 1C), 128.4 (d, $^3J_{C,F}$ = 8.8 Hz, 1C), 128.2, 127.9, 124.2, (d, $^4J_{C,F}$ = 2.5 Hz, 1C), 123.8

(10) (a) Li, C.; Li, W.; Wang, J. *Tetrahedron Lett.* **2009**, *50*, 2533. (b) Adjabeng, G.; Brenstrum, T.; Frampton, C. S.; Robertson, A. J.; Hillhous, J.; McNulty, J.; Capretta, A. *J. Org. Chem.* **2004**, *69*, 5082. (c) Li, C.; Wang, J. *J. Org. Chem.* **2007**, *72*, 7431.

(11) Oku, M.; Arai, S.; Katayama, K.; Shioiri, T. *Synlett* **2000**, 493.

(d, $^2J_{C,F}$ = 15 Hz, 1C), 123.4, 115.0 (d, $^2J_{C,F}$ = 21.3 Hz, 1C), 86.0, 83.0, 19.1; LRMS (EI, 70 eV) *m*/*z* (%) 210 (M^+, 100), 209 (78), 189 (29); HRMS (EI) for $C_{15}H_{11}F$ (M^+) calcd 210.0845, found 210.0844.

(*E*)-Pent-1-en-4-yne-1,5-diyldibenzene (10):[12] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.20 (m, 10H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.25−6.20 (dt, *J* = 5.6 Hz, 15.7 Hz, 1H), 3.39 (dd, *J* = 1.8 Hz, 5.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 131.6, 131.4, 128.5, 128.2, 127.8, 127.3, 126.3, 124.2, 123.7, 86.7, 82.8, 23.0; LRMS (EI, 70 eV) *m*/*z* (%) 218 (M^+, 100), 202 (94), 217 (91).

1-Methyl-4-(3-phenylprop-1-ynyl)benzene (11):[10] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.41 (d, *J* = 7.2 Hz, 2H), 7.36−7.25 (m, 5H), 7.11−7.08 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 136.9, 131.5, 123.0, 128.5, 127.9, 126.6, 120.6, 86.7, 82.7, 25.7, 21.4; LRMS (EI, 70 eV) *m*/*z* (%) 206 (M^+, 100), 205 (73), 176 (48).

1-Chloro-4-(3-phenylprop-1-ynyl)benzene (12):[13] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.25 (m, 9H), 3.82 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 133.8, 132.9, 128.6, 127.9, 126.7, 122.2, 88.6, 81.5, 25.7; LRMS (EI, 70 eV) *m*/*z* (%) 226 (M^+, 50), 191 (100), 190 (25).

1-(4-(3-Phenylprop-1-ynyl)phenyl)ethanone (13): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89−7.87 (m, 2H), 7.52−7.49 (m, 2H), 7.41−7.34 (m, 4H), 7.32−7.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 136.2, 135.9, 131.7, 128.6, 128.5, 128.1, 127.9, 126.8, 91.3, 82.0, 26.5, 25.8; LRMS (EI, 70 eV) *m*/*z* (%) 234 (M^+, 71), 219 (100), 191 (52); HRMS (EI) for $C_{17}H_{14}O$ (M^+) calcd 234.1045, found 234.1041.

Oct-2-ynylbenzene (14):[14] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.27 (m, 4H), 7.23−7.21 (m, 1H), 3.58 (t, *J* = 2.2 Hz, 2H), 2.23−2.19 (m, 2H), 1.56−1.51 (m, 2H), 1.39−1.31 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 128.3, 127.8, 126.3, 82.7, 77.4, 31.1, 28.7, 25.1, 22.2, 18.8, 14.0; LRMS (EI, 70 eV) *m*/*z* (%) 186 (M^+, 28), 130 (67), 129 (100).

1-Methyl-2-(oct-2-ynyl)benzene (15): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.42 (m, 1H), 7.23−7.12 (m, 3H), 3.48 (t, *J* = 2.2 Hz, 2H), 2.30 (s, 3H), 2.22−2.19 (m, 2H), 1.52−1.50 (m, 2H), 1.40−1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.8, 129.9, 128.1, 126.6, 126.0, 82.7, 77.1, 31.1, 28.7, 23.3, 22.2, 18.8, 13.9; LRMS (EI, 70 eV) *m*/*z* (%) 200 (M^+, 24), 128, (43), 129 (100); HRMS (EI) for $C_{15}H_{20}$ (M^+) calcd 200.1565, found 200.1561.

1-Methoxy-3-(oct-2-ynyl)benzene (16): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.19 (m, 1H), 6.93−6.91 (m, 2H), 6.78−6.74 (m, 1H), 3.80 (s, 3H), 3.56 (t, *J* = 2.2 Hz, 2H), 2.23−2.19 (m, 2H), 1.53−1.50 (m, 2H), 1.38−1.33 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 139.2, 129.3, 120.2, 113.4, 111.8, 82.8, 77.3, 55.1, 31.1, 28.7, 25.1, 22.2, 18.8, 14.0; LRMS (EI, 70 eV) *m*/*z* (%) 216 (M^+, 100), 115 (53), 116 (40); HRMS (EI) for $C_{15}H_{20}O$ (M^+) calcd 216.1514, found 216.1516.

5-(Oct-2-ynyl)benzo[*d*][1,3]dioxole (17): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85−6.71 (m, 3H), 5.91 (s, 2H), 3.48 (t, *J* = 2.4 Hz, 2H), 2.22−2.17 (m, 2H), 1.54−1.50 (m, 2H), 1.39−1.31 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 146.0, 131.4, 120.5, 108.4, 108.0, 100.8, 82.6, 77.6, 31.1, 28.7, 24.8, 22.2, 18.7, 13.9; LRMS (EI, 70 eV) *m*/*z* (%) 230 (M^+, 100), 115 (53), 116 (40); HRMS (EI) for $C_{15}H_{18}O_2$ (M^+) calcd 230.1307, found 230.1304.

1-Chloro-4-(oct-2-ynyl)benzene (18):[14] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 4H), 3.53 (t, *J* = 2.4 Hz, 2H), 2.23−2.19 (m, 2H), 1.54−1.50 (m, 2H), 1.40−1.30 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 132.1, 129.8, 128.4, 83.1, 76.9, 31.1, 28.6, 24.5, 22.2, 18.7, 13.9; LRMS (EI, 70 eV) *m*/*z* (%) 220 (M^+, 22), 129 (100), 128 (42).

1-Fluoro-2-(oct-2-ynyl)benzene (19): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54−7.53 (m, 1H), 7.18−7.10 (m, 2H), 7.02−6.98 (m, 1H), 3.59 (s, 3H), 2.24−2.20 (m, 2H), 1.54−1.51 (m, 2H), 1.39−1.31 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, (d, $^1J_{C,F}$ = 245 Hz, 1C), 129.8, (d, $^3J_{C,F}$ = 3.8 Hz, 1C), 128.1 (d, $^3J_{C,F}$ = 7.5 Hz, 1C), 124.8 (d, $^2J_{C,F}$ = 16.3 Hz, 1C), 124.0, (d, $^4J_{C,F}$ = 3.8 Hz, 1C), 114.9 (d, $^2J_{C,F}$ = 21.8 Hz, 1C), 83.1, 76.0, 31.1, 28.7, 22.4, 18.8, 18.5, 14.0; LRMS (EI, 70 eV) *m*/*z* (%) 204 (M^+, 31), 147 (98), 95 (100); HRMS (EI) for $C_{14}H_{17}F$ (M+) calcd 204.1314, found 204.1310.

1-Nitro-4-(oct-2-ynyl)benzene (20): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.19−8.16 (m, 2H), 7.54−7.51 (m, 2H), 3.69−3.68 (m, 2H), 2.26−2.21 (m, 2H), 1.55−1.52 (m, 2H), 1.38−1.32 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.6, 123.6, 84.2, 75.7, 31.1, 28.5, 25.6, 22.2, 18.7, 14.0; LRMS (EI, 70 eV) *m*/*z* (%) 231 (M^+, 3), 128 (86), 95 (100); HRMS (EI) for $C_{14}H_{17}NO_2$ (M^+) calcd 231.1259, found 231.1257.

5-(But-2-ynyl)benzo[*d*][1,3]dioxole (21): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.78−6.72 (m, 2H), 5.92 (s, 2H), 3.45 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 146.0, 131.3, 120.6, 108.5, 108.0, 100.8, 77.74, 76.87, 24.7, 3.5; LRMS (EI, 70 eV) *m*/*z* (%) 174 (M^+, 100), 115 (93), 116 (59); HRMS (EI) for $C_{11}H_{10}O_2$ (M^+) calcd. 174.0681, found 174.0680.

1,2-Diphenylethyne (23):[10] white solid, mp 58.5−60.8 (lit. mp 59−60 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.51 (m, 4H), 7.39−7.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0, 128.7, 128.6, 123.7, 89.7; LRMS (EI, 70 eV) *m*/*z* (%) 178 (M^+, 100).

1-Methoxy-4-(2-phenylethynyl)benzene (24):[10] white solid, mp 55.1−57.8 (lit. mp 56−58 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.51 (m, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.34−7.32 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3; LRMS (EI, 70 eV) *m*/*z* (%) 208 (M^+, 100).

2-(Phenylethynyl)thiophene (25):[15] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.50 (d, *J* = 3.9 Hz, 2H), 7.34−7.24 (m, 5H), 7.02−6.99 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.8, ;131.4, 128.4, 127.2, 127.1, 123.3, 122.9, 93.0, 82.3; LRMS (EI, 70 eV) *m*/*z* (%) 184 (M^+, 100), 139 (28), 152 (24).

6-(Phenylethynyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (26):[16] yellow solid, mp 128.1−130.2 °C (lit. mp 128−130 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.54−7.52 (m, 2H), 7.39−7.37 (m, 4H), 7.03 (s, 1H), 6.09 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 152.4, 148.7, 132.1, 131.6, 128.9, 128.5, 123.3, 111.9, 106.1, 102.4, 95.1, 84.8; LRMS (EI, 70 eV) *m*/*z* (%) 250 (M^+, 100), 163 (53), 164 (33).

2-(Phenylethynyl)benzaldehyde (27):[17] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.96−7.30 (d, *J* = 7.8 Hz, 1H), 7.65−7.55 (m, 4H), 7.46−7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 135.8, 133.7, 133.2, 131.6, 129.0, 128.6, 128.5, 127.2, 126.8, 122.3, 96.3, 84.9; LRMS (EI, 70 eV) *m*/*z* (%) 206 (M^+, 100), 178 (47), 176 (43).

1-(4-(Phenylethynyl)phenyl)ethanone (28):[10] yellow solid, mp 95.5−98.0 (lit. mp 95−97 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96−7.93 (d, *J* = 8.4 Hz, 2H), 7.63−7.55 (m, 4H), 7.38−7.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 136.2, 131.7, 131.6, 128.8, 128.4, 128.3, 128.2, 122.6, 92.7, 88.6, 26.6; LRMS (EI, 70 eV) *m*/*z* (%) 220 (M^+, 70), 205 (100), 176 (46).

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Methyl 5-nitro-2-(phenylethynyl)benzoate (29):[18] yellow solid; mp 71.9−74.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.33 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.62−7.61 (m, 2H), 7.41 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 146.3, 134.9, 132.7, 132.0, 130.3, 129.6, 128.5, 126.0, 125.8, 122.2, 100.4, 86.9, 52.8; LRMS (EI, 70 eV) m/z (%) 281 (M^+, 100), 266 (60), 220 (34).

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Supporting Information Available: Copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.