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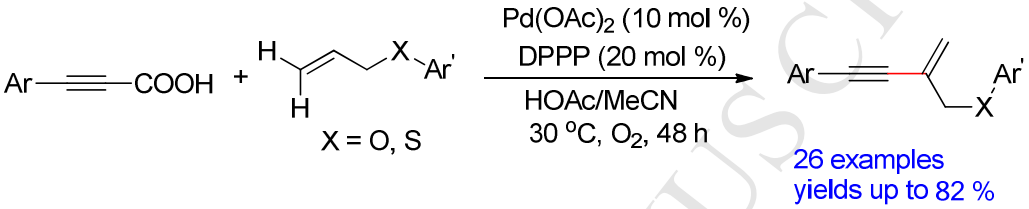

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ABSTRACT

This work reported an efficient and novel method to prepare branched 1, 3-enynes via Pd(II)-catalyzed decarboxylative coupling of arylalkynyl carboxylic acids with allylic ethers under mild conditions. Various arylalkynyl carboxylic acids and allylic ethers could participate in the reaction, regioselectively affording the desired branched 1, 3-enynes in moderate to good yields.

1. Introduction

The 1, 3-enyne moiety attracted much interest owing to its existence in many naturally occurring and pharmaceutically active compounds.[1] For example, terbinafine, containing the 1, 3-enyne moiety, exhibited strong antimycotic activity and was used currently for the treatment of skin mycoses.[2] 1, 3-Enynes were also versatile building blocks for the synthesis of aphthalenes,[3] heterocyclic compounds [4], conjugated alkenes [5] and so on. Therefore, much attention had been paid to the synthesis of 1, 3-enynes. [6] Among various approaches available for 1,3-enynes, by far the most common and convenient method widely used was Sonogashira coupling reaction of terminal alkynes with vinyl halides using palladium-copper,[7] palladium,[8] copper [9] or iron [10] as catalysts. However, these reactions were dependent on preactivation of alkene with halide to form vinyl halide, which required several extra synthetic steps and generated waste. Pd-catalyzed coupling reaction of organometallic alkyne (Cu, Mg, Si, Zn, Sn)[11] with alkene and the alkynylation of alkenylmetals (Al, B, Cu, Mg, Zr)[12] afforded alternative two methods, but suffered from some intrinsic shortcomings, including difficult preparation of organometallic alkyne or alkene, poor functional group compatibility, undesired by-products and low yields. Therefore, it was deserved to seek for more economical and convenient methodologies to provide 1, 3-enynes.

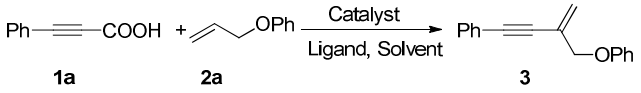
Over the past decade, decarboxylative coupling reactions for the alkynyl carboxylic acid substrates had been successfully applied to construct the C-C,[13] C-N[14] or C-P[15] bonds in organic synthesis. These transformations were attracting due to the usage of much cheap and available alkynyl carboxylic acid as coupling partner, the release of harmless CO_2 and the avoidance of homocoupling products.[16] As part of our ongoing efforts devoted to the synthesis of 1, 3-enynes,[17] we wished to report the Pd-catalyzed decarboxylative coupling protocol for the synthesis of 1, 3-enyne using alkynyl carboxylic acid and unactivated allyl ether as the coupling partner. The reaction could proceed under mild conditions, giving the branched 1, 3-enynes in moderate to good yields. Moreover, O_2 was used as the sole oxidant and therefore only CO_2 and water were formed as the by-products in the reaction, which is a green and environmentally benign procedure. Herein, we reported the results in detail.

2. Results and discussion

We chose phenylpropiolic acid **(1a)** and allyl phenyl ether **(2a)** as the model substrates to optimize suitable conditions using $Pd(OAc)_2$ as catalyst, DPPP as ligand at 80 °C under N_2 (**Table 1**). It was found that solvent, catalyst, ligand, oxidant and reaction temperature critically affected the decarboxylative coupling reaction efficiency. Solvents such as HOAc/DCE, HOAc, MeCN, DMSO and Ac_2O were less effective than HOAc/MeCN (entries 2-6), whereas the desired product **3** was obtained in 39 % yield when using a mixed solvent of HOAc/MeCN (entry 1). Three commonly used catalyst precursors, such as $Pd(PPh_3)_4$, $Pd_2(dba)_3$ and $Pd(CF_3COO)_2$ (entries 7-9) were next surveyed to give worse results than $Pd(OAc)_2$ (entry 1). Among the ligands screened, 1,3-bis(diphenylphosphino)propane (**DPPP**) turned out to be the best, while 2,2'-bipyridyl (**bpy**), 1,1'-bis(diphenylphosphino)ferrocene (**DPPF**), bis(diphenylphosphino)ethane (DPPE), bis(diphenylphosphino)butane (DPPB), triphenylphosphine (PPh_3) and 1,10-phenanthroline were not that effective (entries 11-16). Notably, only trace of decarboxylative product can be detected in the absence of ligand (entry 10), showing the ligand played an indispensable role in the reaction. Subsequently, the reaction was tried to proceed under air and O_2, affording the decarboxylative coupling product **3** in 42 and 67 % yields, respectively (entries 17, 18). Encouraged by these results, reaction temperatures were evaluated to obtain the optimal conditions (entries 19-21) and it was interesting to find the yield of decarboxylative product could be dramatically increased to 72

% when the reaction was performed at 30 °C by comparison with 80, 120 and 0 °C. To our delight, the reaction also regioselectively afforded the branched ((2-methylene-4-phenylbut-3-yn-1-yl)oxy)benzene (**3**).[17] Unfortunately, decreasing the amount of allyl phenyl ether **(2a)** to 0.3 mmol (1 equiv) as well as shortening the reaction time to 24 h resulted in lower yields (entries 22, 23). Thus the optimal condition was identified as followings: phenylpropiolic acid (1.0 equiv), allylic ether (2 equiv), $Pd(OAc)_2$ (10 mol%), DPPP (20 mol%), HOAc/MeCN (v/v = 1:3), 30 °C, 48 h under O_2.

Table 1. Modification of the Typical Reaction Conditions [a]



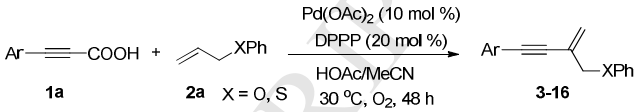
1a **2a** **3**

Entry	Catalyst	Ligand	Solvent [b]	T(°C)	Yield(%) [c]
1	$Pd(OAc)_2$	DPPP	HOAc/MeCN	80	39
2	$Pd(OAc)_2$	DPPP	HOAc/DCE	80	NR
3	$Pd(OAc)_2$	DPPP	HOAc	80	20
4	$Pd(OAc)_2$	DPPP	MeCN	80	trace
5	$Pd(OAc)_2$	DPPP	DMSO	80	NR
6	$Pd(OAc)_2$	DPPP	Ac_2O	80	NR
7	$Pd(PPh_3)_4$	DPPP	HOAc/MeCN	80	NR
8	$Pd_2(dba)_3$	DPPP	HOAc/MeCN	80	25
9	$Pd(CF_3COO)_2$	DPPP	HOAc/MeCN	80	22
10	$Pd(OAc)_2$	-	HOAc/MeCN	80	trace
11	$Pd(OAc)_2$	bpy	HOAc/MeCN	80	NR
12	$Pd(OAc)_2$	DPPF	HOAc/MeCN	80	15
13	$Pd(OAc)_2$	DPPE	HOAc/MeCN	80	31
14	$Pd(OAc)_2$	DPPB	HOAc/MeCN	80	53
15	$Pd(OAc)_2$	PPh_3	HOAc/MeCN	80	11
16	$Pd(OAc)_2$	1,10-phenanthroline	HOAc/MeCN	80	NR
17[d]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	80	42
18[e]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	80	67
19[e]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	120	30
20[e]	**$Pd(OAc)_2$**	**DPPP**	**HOAc/MeCN**	**30**	**72**
21[e]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	0	trace
22[e]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	30	53[f]
23[e]	$Pd(OAc)_2$	DPPP	HOAc/MeCN	30	50[g]

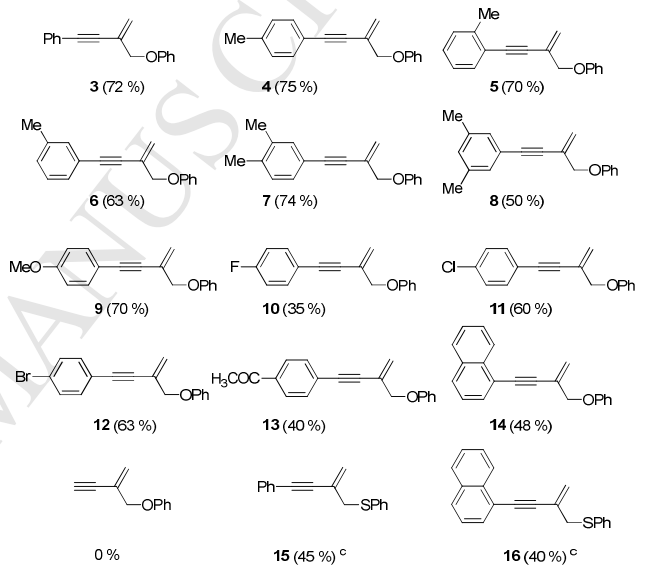
[a] Reaction conditions: phenylpropiolic acid (0.3 mmol), allyl phenyl ether (0.6 mmol), catalyst (10 mol %), ligand (20 mol %), solvent (2 mL), 80 °C, 48 h, under N_2 unless otherwise noted. [b] v / v = 1 : 3, [c] Isolated yields. [d] The reaction was carried out under air. [e] The reaction was carried out under O_2. [f] The amount of allyl phenyl ether was 0.3 mmol. [g] Shorten the reaction to 24 h.

With the optimized conditions in hand, the scope of arylalkynyl carboxylic acids was initially explored (**Table 2**). The results showed that several functional groups on the phenyl moiety, including methyl, methoxyl, fluoro, chloro, bromo, and acetyl groups were tolerated in this decarboxylative coupling procedure. Generally, the electron-donating substituents were beneficial for the transformation, whereas the electron-withdrawing groups decreased the efficiency. For example, methyl substituted arylalkynyl carboxylic acids provided products **4-7** in more than 63 % yields, while 3-(4-methoxyphenyl)propiolic acid gave its corresponding product **9** in 70 % yield. Meanwhile, chloride and bromide products (**11** and **12**) were obtained in 60 % and 63 % yields, respectively. Products **10** and **13** bearing fluoride and acetyl groups were isolated in 35% and 40 % yields, respectively. In the catalytic decarboxylative coupling reaction, steric hindrance affected the efficiency slightly. *o*, *m*, *p* -Methyl and 3,4-dimethyl phenylpropiolic acids afforded their corresponding products in the similar yields except the relatively low yield of compound **8**. Gratifyingly, the bulky 3-(naphthalene-1-yl)propiolic acid underwent the decarboxylative coupling reaction with allyl phenyl ether smoothly, giving 1-(3-(phenoxymethyl)but-3-en-1-ynyl)naphthalene **14** in 48 % yield. It was notable that the coupling reaction of phenylpropiolic acids with allyl phenyl sulfide can also proceed well when the reaction temperature was raised to 80 °C, providing the 1, 3-enyne products **15** and **16** with sulfur atoms in acceptable yields. Unfortunately, the aliphatic carboxylic acid, such as propiolic acid or 2-butynoic acid, was intolerant to the catalytic system.

Table 2. Pd-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids with Allyl Phenyl Ether (Sulfide) [a,b]



1a **2a** X = O, S **3-16**



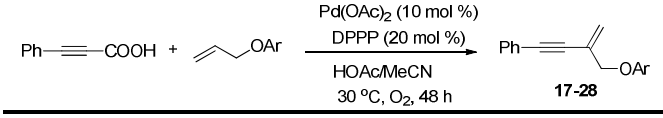
[a] Reaction conditions: alkynyl carboxylic acids (0.3 mmol), allyl phenyl ethers (0.6 mmol), $Pd(OAc)_2$ (10 mol %), DPPP (20 mol %), solvent (2 mL, v / v = 1:3), 30 °C, 48 h, under oxygen. [b] Isolated yields. [c] The reaction was carried under 80 °C.

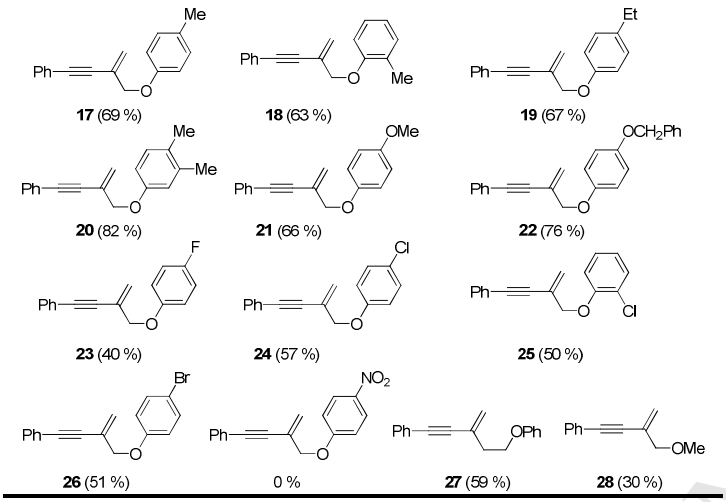
Subsequently, phenylpropiolic acids were examined with respect to various allyl aryl ethers to afford 1, 3-enynes derivatives **(Table 3)**. The results demonstrated that allyl aryl ethers having electron-donating groups favored the decarboxylative coupling reaction than those with electron-withdrawing groups. Methyl, ethyl, methoxy or benzyloxy ethers provided 1, 3-enynes **17-22** in 63 %-82 % yields. Meanwhile, fluoride, chloride and bromide ethers afforded **23-26** in 40 %-57 % yields. And trace of desired product could be obtained when 1-(allyloxy)-4-nitrobenzene was reacted with phenylpropiolic acid. To our delight, phenyl homoallylic ether such as (but-3-en-1-yloxy)benzene could smoothly undergo the coupling reaction, giving the aimed product **27** in good yield. But only 30 % yield of (3-(methoxymethyl)but-3-en-1-yn-1-yl)benzene **28** could be isolated when allyl methyl ether was reacted with phenylpropiolic acid, which showed that the optimal reaction condition was more compatible to the aromatic ether.

A possible mechanism for the present palladium (II)-catalyzed decarboxylative coupling of phenylpropiolic acid with allyl phenyl ether is proposed in Scheme 1. First, the reaction of

$Pd(OAc)_2$ with phenylpropiolic acid by releasing HOAc and CO_2 affords an arylpalladium (II) species **A**.[18] The insertion of the double bond of allyl phenyl ether to **A** generates intermediate **B**, which would be followed by β-H elimination to produce the desired product 1,3-enyne **3** and Pd (0) with loss of a molecule of HOAc. The resulting Pd (0) is then oxidized by O_2 to regenerate the Pd (II) catalyst.[19]

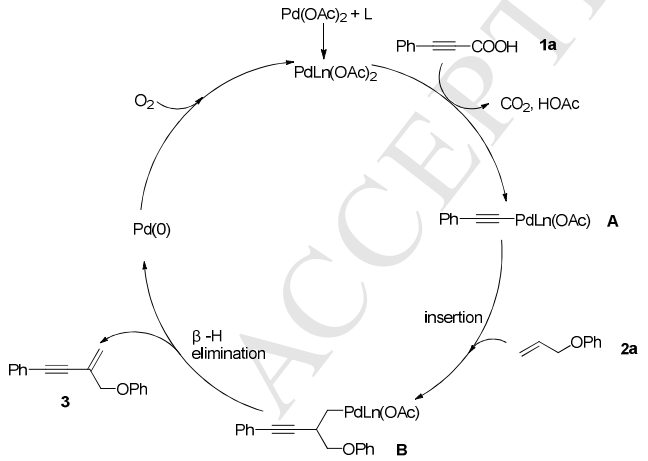
Table 3. Pd-Catalyzed Decarboxylative Coupling of Phenylpropiolic Acids with Allyl Aryl Ether [a,b]





[a] Reaction conditions: phenylpropiolic acids (0.3 mmol), allyl aryl ether (0.6 mmol), $Pd(OAc)_2$ (10 mol %), DPPP (20 mol %), solvent (2 mL, v / v = 1:3), 30 °C, 48 h, under oxygen. [b] Isolated yields.

Scheme 1 Plausible mechanism pathway



3. Conclusions

In conclusion, we had developed an efficient and mild protocol to synthesize 1, 3-enyne compounds at low temperature (30 °C) *via* $Pd(OAc)_2$-catalyzed direct decarboxylative coupling of alkynyl carboxylic acids with unactived allyl ether. This method did not require the preactivation of alkene with halide to form vinyl halide and exemplified the ideals of atom and step economy. Moreover, the procedure was also green and environmentally because only CO_2 and water were formed as the by-products. Various alkynyl carboxylic acids could participate in the reaction, regioselectively affording the desired branched 1, 3-enynes in moderate to good yield. The proposed mechanism was described.

4. Experimental Section

4.1 General

Chemicals were either purchased or purified by standard techniques. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^{1}H at 500 MHz, ^{13}C at 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants *J* are given in hertz. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. All reactions under oxygen atmosphere were conducted using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus (Beijing Tech. Instrument) and uncorrected. Column chromatography was performed using EM silica gel 60 (300-400 mesh).

4.2 Typical experimental procedure for the $Pd(OAc)_2$-catalyzed direct decarboxylative coupling of alkynyl carboxylic acids with allyl ethers

Arylalkynyl carboxylic acids (0.3 mmol), allyl ethers (0.6 mmol), $Pd(OAc)_2$ (10 mol %), and DPPP (20 mol %) were added to a two necked flask, and then a mixed solvent of CH_3CN (1.5 mL) and HOAc (0.5 mL) was added. The mixture was then stirred at 30 °C for 48 h under oxygen. After the reaction was complete, the mixture was washed with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 three times. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated in vacuum. The resulting crude product was purified by flash chromatography on silica gel using hexane or hexane/ethyl acetate (150:1) as the eluent to give the pure products.

4.3. Characterization data

4.3.1 ((2-Methylene-4-phenylbut-3-yn-1-yl)oxy)benzene (**3**).[17] Yellow oil, 72% yield (50.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.47 (m, 2H), 7.34-7.29 (m, 5H), 6.99-6.98 (m, 3H), 5.71 (s, 1H), 5.68 (s, 1H), 4.65 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 131.8, 129.6, 128.7, 128.5, 127.3, 122.9, 122.2, 121.3, 115.1, 90.9, 87.1, 69.7. LRMS (EI, 70 eV) m/z (%): 234 (M^+, 51), 191 (16), 141 (23), 115 (100), 77 (17).

4.3.2 1-Methyl-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**4**).[17] Yellow oil, 75% yield (55.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.34-7.30 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02-6.97 (m, 3H), 5.70 (s, 1H), 5.67 (s, 1H), 4.66 (s, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 138.8, 131.7, 129.6, 129.2, 127.5, 121.7, 121.3, 119.9, 115.2, 91.1, 86.5, 69.8, 21.6. LRMS (EI, 70 eV) m/z (%): 248 (M^+, 100), 233 (40), 153 (83), 139 (55), 129 (63).

4.3.3 1-Methyl-2-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**5**). Yellow oil, 70% yield (52.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.24-7.19 (m, 2H), 7.17-7.13 (m, 1H), 7.00-6.97 (m, 3H), 5.70 (d, *J* = 1.0 Hz, 1H), 5.67 (s, 1H), 4.66 (s, 2H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 140.4, 132.1, 129.62, 129.61, 128.7, 127.6, 125.7, 122.8, 121.8, 121.3, 115.2, 91.0, 89.9, 69.9, 20.8. HRMS (ESI): calcd for $C_{18}H_{17}O^+$ ([M + H]$^+$) 249.1274, Found: 249.1277.

4.3.4 1-Methyl-3-(3-phenoxymethyl-but-3-en-1-ynyl)-benzene (**6**): [17] Yellow oil, 63 % yield (46.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.99-6.96 (m, 3H), 5.69 (d, *J* = 1.5 Hz, 1H), 5.66 (d, *J* = 1.5 Hz, 1H), 4.63 (s, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 138.2, 132.4, 129.61, 129.55, 128.9, 128.4, 127.4, 122.8, 122.0, 121.3, 115.2, 91.1, 86.8, 69.8, 21.3. LRMS (EI, 70 eV) m/z (%): 248 (M^+, 100), 153 (76), 152 (45), 139 (49), 129 (60).

4.3.5 1,2-Dimethyl-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**7**). Colourless oil, 74 % yield (58.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.26 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 3H), 5.68 (s, 1H), 5.65 (s, 1H), 4.64 (s, 2H), 2.27 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 137.6, 136.8, 132.9, 129.8, 129.6, 129.3, 127.5, 121.6, 121.3, 120.2, 115.2, 91.3, 86.2, 69.7, 19.9, 19.7. HRMS (ESI): calcd for $C_{19}H_{19}O^+$ ([M + H]$^+$) 263.1430, Found: 263.1438.

4.3.6 1,3-Dimethyl-5-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**8**). Yellow oil, 50 % yield (39.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.10 (s, 2H), 6.98-6.97 (m, 4H), 5.68 (s, 1H), 5.65 (s, 1H), 4.64 (s, 2H), 2.30 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 138.0, 130.6, 129.6, 129.5, 127.4, 122.5, 121.9, 121.3, 115.1, 91.3, 86.4, 69.7, 21.2. HRMS (ESI): calcd for $C_{19}H_{19}O^+$ ([M + H]$^+$) 263.1430, Found: 263.1437.

4.3.7 1-Methoxy-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**9**). [17] Yellow oil, 70% yield (55.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.33-7.28 (m, 2H), 6.99-6.96 (m, 3H), 6.87-6.84 (m, 2H), 5.66 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.63 (d, *J* = 1.5 Hz, 1H), 4.64 (t, *J* = 1.5 Hz, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.0, 158.6, 133.3, 129.6, 127.5, 121.4, 121.3, 115.2, 115.1, 114.2, 91.0, 85.8, 69.8, 55.4. LRMS (EI, 70 eV) m/z (%): 264 (M^+, 69), 141 (22), 128 (100), 127 (23), 102 (19).

4.3.8 1-Fluoro-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**10**). [17] Yellow oil, 35% yield (26.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.32-7.29 (m, 2H), 7.04-6.96 (m, 5H), 5.70 (d, *J* = 1.5 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.63 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.8 Hz), 158.5, 133.8 (d, *J* = 8.75 Hz), 129.6, 127.2, 122.4, 121.4, 119.1, 115.8 (d, *J* = 22.5 Hz), 115.2, 89.8, 86.8, 69.7. LRMS (EI, 70 eV) m/z (%): 252 (M^+, 54), 209 (15), 157 (20), 133 (100), 123 (12).

4.3.9 1-Chloro-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**11**). [17] Yellow oil, 60% yield (48.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.31-7.29 (m, 4H), 6.99-6.97 (m, 3H), 5.72 (s, 1H), 5.68 (s, 1H), 4.64 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 134.8, 133.1, 129.6, 128.9, 127.2, 122.7, 121.5, 121.4, 115.2, 89.8, 88.1, 69.7. LRMS (EI, 70 eV) m/z (%): 268 (M^+, 46), 205 (22), 149 (59), 139 (100), 65 (27).

4.3.10 1-Bromo-4-(3-phenoxymethyl-but-3-en-1-ynyl)benzene (**12**). [17] Yellow solid, mp: 79-80 °C, 63% yield (59.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 4H), 7.00-6.97 (m, 3H), 5.72 (s, 1H), 5.69 (s, 1H), 4.64 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 133.3, 131.8, 129.6, 127.2, 123.0, 122.8, 122.0, 121.4, 115.2, 89.8, 88.2, 69.7. LRMS (EI, 70 eV) m/z (%): 312 (M^+, 29), 205 (25), 140 (98), 139 (100), 114 (20).

4.3.11 1-[4-(3-Phenoxymethyl-but-3-en-1-ynyl)-phenyl]ethanone (**13**). Yellow oil, 40% yield (33.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.32-7.29 (m, 2H), 7.00-6.97 (m, 3H), 5.76 (d, *J* = 1.5 Hz, 1H), 5.73 (d, *J* = 1.5 Hz, 1H), 4.65 (s, 2H), 2.60 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.3, 158.5, 136.7, 132.0, 129.7, 128.4, 127.8, 127.2, 123.5, 121.5, 115.2, 90.3, 90.1, 69.6, 26.7. HRMS (ESI): calcd for $C_{19}H_{17}O_2^+$ ([M + H]$^+$) 277.1223, Found: 277.1236.

4.3.12 1-(3-Phenoxymethyl-but-3-en-1-ynyl)-naphthalene (**14**). Yellow oil, 48 % yield (40.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.59-7.52 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.36-7.31 (m, 2H), 7.05-6.99 (m, 3H), 5.81 (s, 1H), 5.79 (d, *J* = 1.0 Hz, 1H), 4.77 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 133.4, 133.3, 130.7, 129.7, 129.2, 128.4, 127.7, 127.0, 126.6, 126.3, 125.3, 122.4, 121.4, 120.6, 115.2, 92.0, 89.2, 69.9. HRMS (ESI): calcd for $C_{21}H_{17}O^+$ ([M + H]$^+$) 285.1274, Found: 285.1264.

4.3.13 (2-methylene-4-phenylbut-3-yn-1-yl)(phenyl)sulfane (**15**). Yellow oil, 45 % yield (33.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 4H), 7.33-7.31 (m, 3H), 7.29-7.28 (m, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 5.49 (s, 1H), 5.41 (s, 1H), 3.71 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.0, 131.9, 130.6, 129.0, 128.5, 128.4, 128.3, 126.7, 123.3, 123.1, 90.4, 88.8, 40.9. HRMS (ESI): calcd for $C_{17}H_{15}S^+$ ([M + H]$^+$) 251.0889, Found: 251.0894.

4.3.14 1-(3-Phenylsulfanylmethyl-but-3-en-1-ynyl)naphthalene (**16**). Yellow oil, 40 % yield (36.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 9.0 Hz, 2H), 7.69-7.67 (m, 1H), 7.60-7.56 (m, 1H), 7.55-7.51 (m, 1H), 7.49-7.43 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24-7.21 (m, 1H), 5.60 (s, 1H), 5.47 (d, *J* = 1.0 Hz, 1H), 3.82 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 135.8, 133.5, 133.4, 130.8, 130.7, 129.1, 129.0, 128.4, 128.0, 127.0, 126.8, 126.6, 126.5, 125.3, 123.5, 120.8, 93.6, 88.6, 41.2. HRMS (ESI): calcd for $C_{21}H_{17}S^+$ ([M + H]$^+$) 301.1045, Found: 301.1048.

4.3.15 1-Methyl-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**17**). Yellow oil, 69 % yield (51.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.35-7.33 (m, 3H), 7.11-7.10 (m, 2H), 6.91-6.85 (m, 2H), 5.70 (d, *J* = 1.5 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.62 (t, *J* = 1.5 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.5, 131.9, 130.6, 130.1, 128.6, 128.5, 127.5, 123.0, 122.1, 115.1, 90.9, 87.2, 70.0, 20.6. LRMS (EI, 70 eV) m/z (%): 248 (M^+, 29), 233 (28), 205 (18), 141 (26), 115 (100). HRMS (ESI): calcd for $C_{18}H_{17}O^+$ ([M + H]$^+$) 249.1274, Found: 249.1270.

4.3.16 1-Methyl-2-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**18**). Yellow oil, 63 % yield (46.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.34-7.33 (m, 3H), 7.18-7.15 (m, 2H), 6.92-6.86 (m, 2H), 5.74 (d, *J* = 1.5 Hz, 1H), 5.69 (s, 1H), 4.65 (s, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.6, 131.8, 130.9, 128.6, 128.5, 127.7, 127.3, 126.9, 123.1, 121.8, 121.0, 111.9, 90.8, 87.2, 69.8, 16.4. HRMS (ESI): calcd for $C_{18}H_{17}O^+$ ([M + H]$^+$) 249.1274, Found: 249.1266.

4.3.17 1-Ethyl-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**19**). Yellow oil, 67 % yield (52.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.34-7.33 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.71 (d, *J* = 1 Hz, 1H), 5.68 (s, 1H), 4.63 (s, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.6, 137.1, 131.9, 128.9, 128.6, 128.5, 127.6, 123.1, 122.1, 115.1, 90.9, 87.2, 70.0, 28.1, 15.9. HRMS (ESI): calcd for $C_{19}H_{19}O^+$ ([M + H]$^+$) 263.1430, Found: 263.1438.

4.3.18 1,2-Dimethyl-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**20**). Yellow oil, 82 % yield (64.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.35-7.34 (m,

3H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.82-6.81 (m, 1H), 6.75-6.73 (m, 1H), 5.72 (d, *J* = 1.5 Hz, 1H), 5.68 (d, *J* = 1.5 Hz, 1H), 4.63 (s, 2H), 2.26 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.7, 137.9, 131.8, 130.5, 129.3, 128.6, 128.5, 127.6, 123.1, 122.0, 116.8, 112.1, 90.8, 87.2, 69.9, 20.1, 18.9. HRMS (ESI): calcd for $C_{19}H_{19}O^+$ ([M + H]$^+$) 263.1430, Found: 263.1436.

4.3.19 1-Methoxy-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**21**). Yellow oil, 66 % yield (52.3 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.34-7.32 (m, 3H), 6.94-6.91 (m, 2H), 6.87-6.83 (m, 2H), 5.69 (d, *J* = 1.5 Hz, 1H), 5.67 (s, 1H), 4.60 (s, 2H), 3.78 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.4, 152.7, 131.8, 128.6, 128.5, 127.6, 123.0, 122.2, 116.3, 114.8, 90.9, 87.2, 70.7, 55.9. LRMS (EI, 70 eV) m/z (%): 264 (M$^+$, 48), 178 (22), 139 (12), 123 (100), 115 (54).

4.3.20 1-Benzyloxy-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**22**). Yellow solid, mp: 88-89 °C, 76 % yield (77.6 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.45-7.43 (m, 2H), 7.41-7.38 (m, 2H), 7.34-7.33 (m, 4H), 6.93 (s, 4H), 5.70 (d, *J* = 1.5 Hz, 1H), 5.68 (d, *J* = 1.5 Hz, 1H), 5.03 (s, 2H), 4.60 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.6, 152.9, 137.5, 131.8, 128.7, 128.6, 128.47, 128.46, 128.0, 127.6, 123.0, 122.2, 116.2, 116.0, 90.9, 87.2, 70.9, 70.6. LRMS (EI, 70 eV) m/z (%): 340 (M$^+$, 35), 249 (17), 221 (14), 178 (15), 91 (100).

4.3.21 1-Fluoro-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**23**). Yellow oil, 40 % yield (30.3 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.35-7.34 (m, 3H), 7.03-6.98 (m, 2H), 6.95-6.91 (m, 2H), 5.70 (s, 2H), 4.62 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ157.7 (d, *J* = 237.5 Hz), 154.6, 131.8, 128.7, 128.5, 127.3, 122.9, 122.3, 116.3 (d, *J* = 7.5 Hz), 116.0 (d, *J* = 23.8 Hz), 91.0, 87.0, 70.5. HRMS (ESI): calcd for $C_{17}H_{14}FO^+$ ([M + H]$^+$) 253.1023, Found: 253.1037.

4.3.22 1-Chloro-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**24**). Yellow oil, 57 % yield (45.8 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.34-7.32 (m, 3H), 7.26-7.24 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.67 (d, *J* = 3.0 Hz, 2H), 4.61 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.1, 131.8, 129.5, 128.7, 128.5, 126.9, 126.3, 122.8, 122.4, 116.5, 91.1, 86.8, 70.0. HRMS (ESI): calcd for $C_{17}H_{14}ClO^+$ ([M + H]$^+$) 269.0728, Found: 269.0737.

4.3.23 1-Chloro-2-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**25**). Yellow oil, 50% yield (40.2 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.40 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.35-7.33 (m, 3H), 7.24-7.20 (m, 1H), 6.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.95-6. 91 (m, 1H), 5.79 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.70 (dd, *J* = 3.0, 1.5 Hz, 1H), 4.72 (t, *J* = 1.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.0, 131.89, 130.6, 128.7, 128.5, 127.8, 126.7, 123.5, 122.9, 122.2, 122.1, 114.4, 91.1, 86.8, 70.4. HRMS (ESI): calcd for $C_{17}H_{14}ClO^+$ ([M + H]$^+$) 269.0728, Found: 269.0738.

4.3.24 1-Bromo-4-(2-methylene-4-phenyl-but-3-ynyloxy)benzene (**26**). Yellow oil, 51% yield (47.7 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.40-7.39 (m, 2H), 7.35-7.32 (m, 3H), 6.88-6.84 (m, 2H), 5.68 (d, *J* = 1.0 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.61 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.6, 132.5, 131.8, 128.7, 128.5, 127.0, 126.8, 122.4, 117.1, 113.6, 91.1, 86.8, 70.0. HRMS (ESI): calcd for $C_{17}H_{14}BrO^+$ ([M + H]$^+$) 313.0223, Found: 313.0218.

4.3.25 (3-Methylene-5-phenoxypent-1-yn-1-yl)benzene (**27**). Yellow oil, 59 % yield (44.0 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.31-7.26 (m, 5H), 6.95-6.93 (m, 3H), 5.55-5.54 (m, 1H), 5.45 (d, *J* = 1.5 Hz, 1H), 4.21 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.0, 131.8, 129.6, 128.4, 127.8, 123.5, 123.2, 120.9, 114.9, 89.9, 89.2, 66.3, 37.2. HRMS (ESI): calcd for $C_{18}H_{17}O^+$ ([M + H]$^+$) 249.1274, Found: 249.1273.

4.3.26 (3-(Methoxymethyl)but-3-en-1-yn-1-yl)benzene (**28**).[17] Yellow oil, 30 % yield (15.5 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.32-7.31 (m, 3H), 5.62 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.58 (dd, *J* = 3.0, 1.5 Hz, 1H), 4.04 (t, *J* = 1.5 Hz, 2H), 3.43 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 131.8, 128.52, 128.49, 128.4, 123.1, 122.1, 90.3, 87.7, 74.7, 58.4. LRMS (EI, 70 eV) m/z (%): 172 (M$^+$, 25), 142 (100), 127 (58), 115 (21), 77 (18).

Supporting Information:

Copies of ^1H and ^{13}C NMR spectra for the products.

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