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Article

KOAc-promoted alkynylation of α-C–H bonds of ethers with alkynyl bromides under transition-metal-free conditions†

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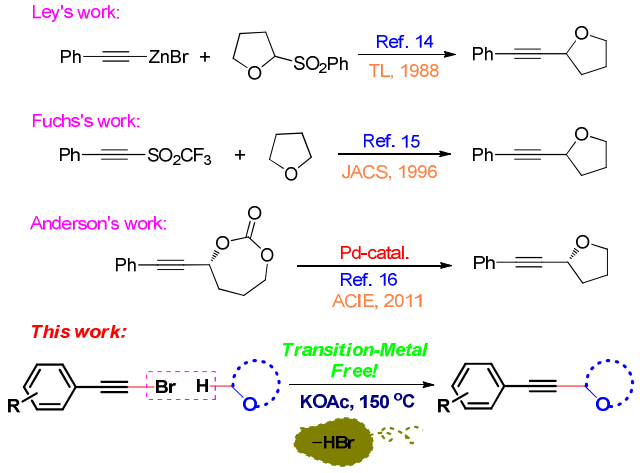
A novel KOAc-promoted α-position C–H activation and alkynylation of ethers with alkynyl bromides to 2-alkynyl ethers has been developed under transition-metal-free and simple reaction conditions. In addition, this methodology can also be extended to the vinylation of ethers with vinyl bromides in excellent regio- and stereo-selectivity. A wide range of direct C(sp)–C(sp^3) and C(sp^2)–C(sp^3) bonds has been formed through this protocol, which offers a new and alternative route.

Introduction

The transition-metal catalyzed direct conversion of C–H bonds into C–C bonds has been one of the most attractive subjects in contemporary organic chemistry. In the past decades, significant efforts have been focused on C–H activation and functionalization, and various high efficiency and versatile protocols have been explored.[1] Despite remarkable advances achieved in this field, critical issues such as stoichiometric amounts of metal waste and the presence of metal impurities in the final product may restrict their practical applicability. Hence, the green and economical platform for mediating organic transformations is demanded. Recently, Itami, Kwong/Lei, Shi, and Shirakawa/Hayashi have reported the astonishing results on the construction of C–C bond from unactivated aromatic rings by direct C–H activation without the aid of transition metal,[2] and these breakthroughs maybe brought a new era of organic synthesis.[3] From the viewpoint of green chemistry, the organic reactions carried out under transition-metal-free conditions with avoiding metal contamination in the final products has been paid much attention in modern organic synthesis, especially in the pharmaceutical industry. In the past two years, a variety of protocols for the direct C–H bond activation and functionalization in the absence of transition-metal have been established.[4] The representative system is KO*t*Bu,[2b,2c,4b,4k,4r–4v] or NaO*t*Bu[2d] in the presence of an effective ligand except one example.[4k]

Substituted tetrahydrofurans are not only valuable building blocks in organic synthesis, but also are ubiquitous motifs present in biological, pharmaceuticals and natural products.[5] In general, they are usually accessible through the α-C(sp^3)–H activation/functionalization of tetrahydrofuran (THF),[6] such as Ni-catalyzed arylation of THF,[7] Fe(II)-catalyzed CDC reaction of THF with malonates,[8] Cu- and Ir-catalyzed carbenoid insertion of ethyl diazoacetate into α-C–H of THF,[9] Cr-promoted reaction of alcohols with THF to 2-tetrahydrofuranyl ethers,[10] AIBN-mediated alkenylation of THF with vinyl triflones,[11] TBHP-promoted reaction of phenylacetylene with THF to allylic ether,[12] and BEt_3- and Me_2Zn-mediated addition of THF with aldehydes and aldimines under air, respectively.[13] 2-Alkynyl cyclic ethers, potential structural motifs of bioactive molecules and materials, have been successfully prepared by region-specific α-position alkynylation of cyclic ethers.[14-16] In 1988, Ley converted 2-benzenesulphonyl cyclic ethers to 2-alkynyl tetrahydrofuran by treatment with the corresponding organozinc agents (Scheme 1).[14] In 1996, Fuchs developed a synthetic strategy of 2-alkynyl cyclic ethers through the alkynylation of α-position C–H bond in cyclic ethers with acetylenic triflones under peroxide or AIBN or UV-irradiation.[15] Most recently, Anderson reported an efficient



Scheme 1 Preparation of 2-alkynyl tetrahydrofurans.

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† Electronic Supplementary Information (ESI) available: Detailed procedures, analytical data, and ^1H, ^{13}C NMR and HRMS spectra of all intermediates and products or other electronic format see DOI: 10.1039/b000000x/

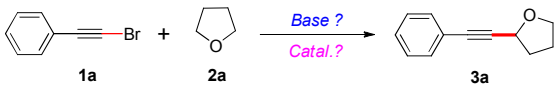
Pd-catalyzed synthesis of 2-alkynyl oxacycles from their cyclic and acyclic carbonates.[16]

Encouraged by the above transformations, and in continuation of our and others interests in transformation of C(sp^3)–H bond into C(sp^3)–C bond,[17] we conceived that alkynylation of α-position C–H bond of ethers with alkynyl bromides without the assistance of transition metal may be possible. Herein, we wish to report an efficient reaction of alkynyl bromides with cyclic ethers for direct C(sp)–C(sp^3) bond formation through KOAc-promoted α-position C–H activation and alkynylation of ethers under transition-metal-free and simple reaction conditions (Scheme 1). Moreover, this methodology can also be extended to the vinylation of α-C–H bonds of ethers with vinyl bromides with excellent regio- and stereo-selectivity.

Results and discussion

In the initial investigation of the reaction of alkynyl bromides to ethers, phenylethynyl bromide (**1a**) and tetrahydrofuran (THF, **2a**) were chosen as model substrates. When the model reaction was carried out in the presence of Na_2CO_3 at 150 °C in a sealed pressure tube for 12 h without additional solvent, a direct alkynylation product (**3a**) of THF via α-position C–H bond activation was isolated in 59% yield (Table 1, entry 1).

Table 1 Effect of base and catalyst on the reaction.[a]



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

Entry	Base	Catalyst	Yield (%)[b]
1	Na_2CO_3	–	59
2	Na_2CO_3	$Pd(OAc)_2$	NR
3	Na_2CO_3	CuI	NR
4	Na_2CO_3	$AgBF_4$	NR
5	***KOAc***	–	***93***
6	NaOAc	–	74
7	$NaHCO_3$	–	52
8	$(NH_4)_2CO_3$	–	47
9	K_2CO_3	–	43
10	$KHCO_3$	–	42
11	Cs_2CO_3	–	32
12	K_3PO_4	–	21
13	NaF	–	18
14	KF	–	13
15	LiO^{t}Bu	–	NR
16	NaO^{t}Bu	–	NR
17	KO^{t}Bu	–	NR
18	KOH	–	NR
19	NaOH	–	NR
20	Et_3N	–	NR
21	DBU	–	NR
22	DABCO	–	NR
23	–	–	32

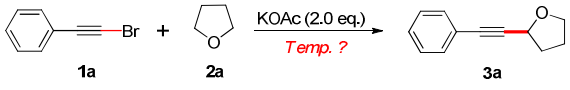
[a] Reaction conditions: **1a** (0.30 mmol), **2a** (2.0 mL, excess, as well as solvent), catalyst (5.0 mol%) if needed, base (0.60 mmol), at 150 °C for 12 h. [b] Isolated yield.

Encouraged by this positive result, further investigation on the addition of transition metal to the reaction was examined. Unfortunately, transition metals, such as $Pd(OAc)_2$, CuI, and $AgBF_4$ completely shut down the reaction (Table 1, entries 2–4). To improve the desired product yield, detail investigation about the effect of base on the reaction was examined. To our delight, KOAc exhibited the highest reactivity to the reaction among the tested bases, providing 93% yield of **3a** (Table 1, entry 5). Other bases, such as NaOAc, $NaHCO_3$, $(NH_4)_2CO_3$, K_2CO_3, $KHCO_3$, Cs_2CO_3, K_3PO_4, NaF, and KF were inferior and generated **3a** in 13–74% yields (Table 1, entries 6–14). However, when the reaction was performed in the presence of LiO^{t}Bu, NaO^{t}Bu, KO^{t}Bu, KOH, NaOH, Et_3N, DBU, or DABCO as base, no **3a** was detected and starting materials were unchanged and recovered (Table 1, entries 15–22). However, only 32% yield of **3a** was generated in the absence of any base, catalyst and additive (Table 1, entry 23).

To further examine the effect of ligand for the improvement of model reaction, L-proline, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), 1,10-phenanthroline (1,10-Phen) and 2,2'-bipyridine (Bipy), 8-hydroxyquinoline (8-HQ), and 1,1'-bis(diphenylphosphino)ferrocene (Dppf) were added to the KO^{t}Bu, NaO^{t}Bu or LiO^{t}Bu system promoted the reaction, but failed (Table S1, Supplementary Information, entries 1–18).

With respect to the base loading, 2 equiv. of KOAc was found to be optimal. When the model reaction was carried out in the presence of KOAc, a significant reaction temperature effect was observed. When the reaction was performed at less than 100 °C, poor yields of **3a** were obtained. The optimal temperature was found to be 150 °C (Table 2, entries 1–7).

Table 2 Effect of temperature on the model reaction.[a]



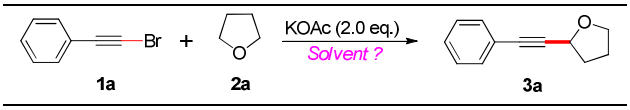
1a **2a** **3a**

Entry	Temp. (°C)	Yield (%)[b]
1	80	22
2	100	40
3	120	64
4	140	80
5	150	93
6	160	93
7	170	90

[a] Reaction conditions: **1a** (0.30 mmol), **2a** (2.0 mL, excess), KOAc (0.60 mmol) at the temperature indicated in this table for 12 h. [b] Isolated yield.

The final investigation revealed that additional solvent, such as DMF, DMA, NMP, DMSO, CH_3CN, HOAc, CH_3CH_2OH, CH_3NO_2, DCE (1,2-dichloroethane) or toluene has a great negative effect on the reaction (Table 3, entries 1–10). The optimized reaction conditions for the model reaction were in the presence of KOAc at 150 °C for 12 h.

Table 3 Effect of solvent on the model reaction.[a]

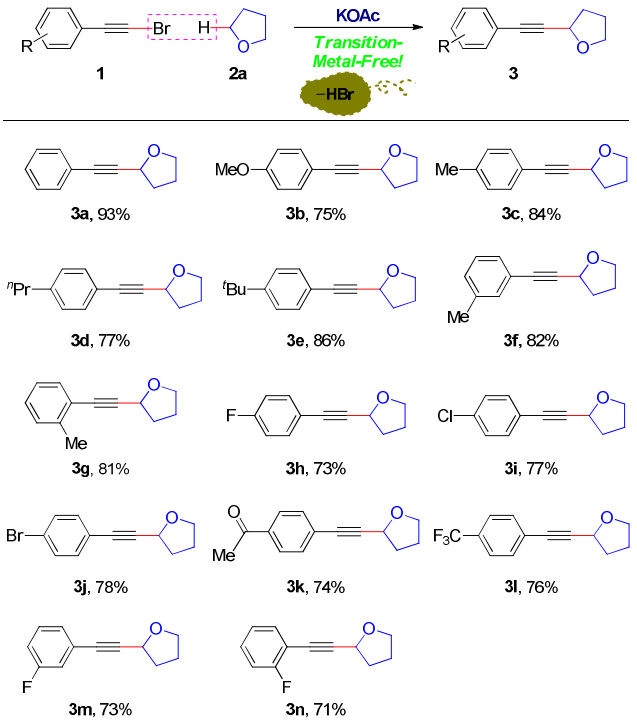


Entry	Solvent/Temp. (°C)	Yield (%)b
1	DMF/150	NR
2	DMA/150	7
3	NMP/150	NR
4	DMSO/150	NR
5	CH_3CN/100	5
6	HOAc/100	NR
7	CH_3CH_2OH/100	NR
8	CH_3NO_2/100	NR
9	DCE/100	13
10	Toluene/150	Trace

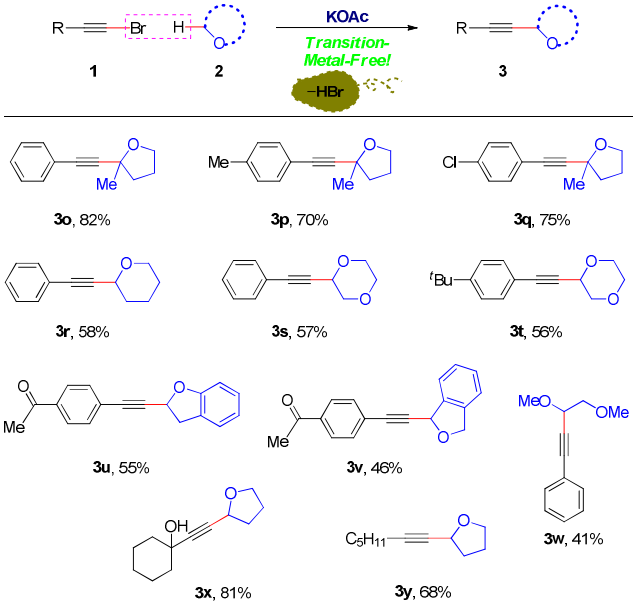
[a] Reaction conditions: **1a** (0.30 mmol), **2a** (2.0 mL, excess), KOAc (0.60 mmol), solvent (2.0 mL) at the temperature indicated in this table for 12 h. [b] Isolated yield.

With the optimized reaction conditions in our hand, a variety of substituted phenylethynyl bromides were selected to couple with tetrahydrofuran for the synthesis of 2-alkynyl-tetrahydrofurans (Scheme 2). Pleasingly, phenylethynyl bromides with electron-donating groups, such as MeO, Me, ^{n}-Pr and ^{t}-Bu, at the *para*-, *meta*-, or *ortho*-positions of phenyl rings, underwent the reaction smoothly with THF (**2a**), generating the corresponding products **3b–g** in good yields (75–86%). Meanwhile, phenylethynyl bromides with electron-withdrawing groups, such as CH_3CO and F_3C also proceeded well with THF to afford the desired products **3k** and **3l** in 74% and 76% yields, respectively. Moreover, substrates with halogen substituents such as F, Cl, and Br could be well transformed into the target products **3h–j** in good yields. In addition, *metal*- and *ortho*-substituents could also be well tolerated in this reaction (**3m** and **3n**).

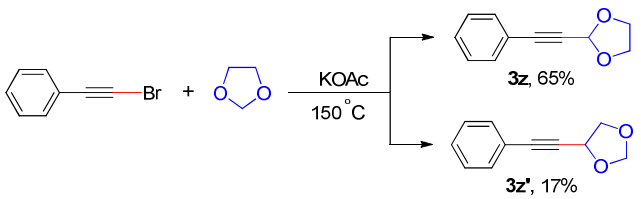
Considering the importance of direct functionalization of different ethers, other simple ethers were also tested to couple with phenylethynyl bromide derivatives under optimized conditions (Scheme 3). 2-Methyl tetrahydrofuran was firstly tested to couple with different phenylethynyl bromides. We were surprised to find that reaction selectively occurred at methyne group, affording the corresponding products in good yields and excellent regio-selectivity (**3o–q**). Tetrahydropyran and 1,4-dioxane were also found to react smoothly with phenylethynyl bromide or (4-*tert*-butylphenyl)ethynyl bromide to generate the alkynylation products **3r–t** in moderate yields. Moreover, when benzene fused tetrahydrofurans, such as 2,3-dihydrobenzofuran and 1,3-dihydroisobenzofuran were employed, the anticipated products, **3u** and **3v** were obtained in 55% and 46% yields, respectively. Notably, this methodology could also be extended to chain-like ethers. 1,2-Dimethoxyethane reacted smoothly with **1a** to afford the corresponding product **3w** in moderate yield, along with excellent regio-selectivity. In addition, the substrate scope of alkyne bromide was extended into aliphatic alkyne bromides, such as 1-(bromoethynyl)cyclohexanol and 1-bromohept-1-yne, and the satisfactory results were achieved (Scheme 3, **3x** and **3y**).



Scheme 2 KOAc-promoted direct alkynylation of tetrahydrofuran under transition-metal free conditions. Reaction conditions: **1** (0.30 mmol), **2a** (2.0 mL, excess, as well as solvent), KOAc (0.60 mmol), at 150 °C for 12 h; isolated product yields after chromatography.



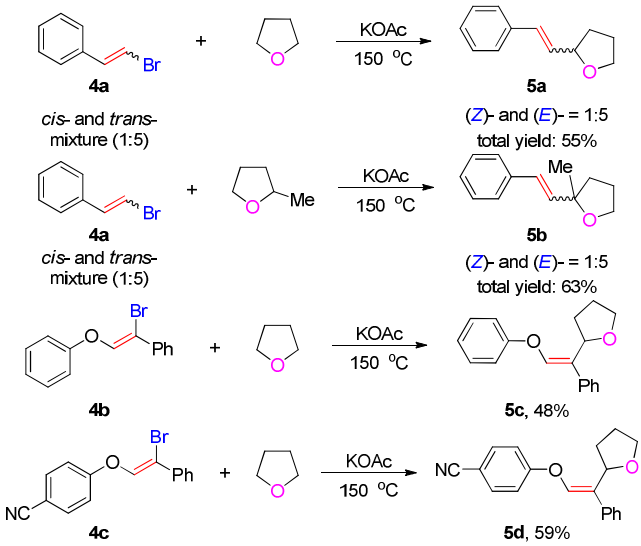
Scheme 3 KOAc-promoted direct alkynylation of other simple ethers under transition-metal free conditions. Reaction conditions: **1** (0.30 mmol), **2** (2.0 mL, excess, as well as solvent), KOAc (0.60 mmol), at 150 °C for 12 h; isolated product yields after chromatography.



Scheme 4 Region-selectivity investigation of direct alkynylation of 1,3-dioxolane with phenylethynyl bromide.

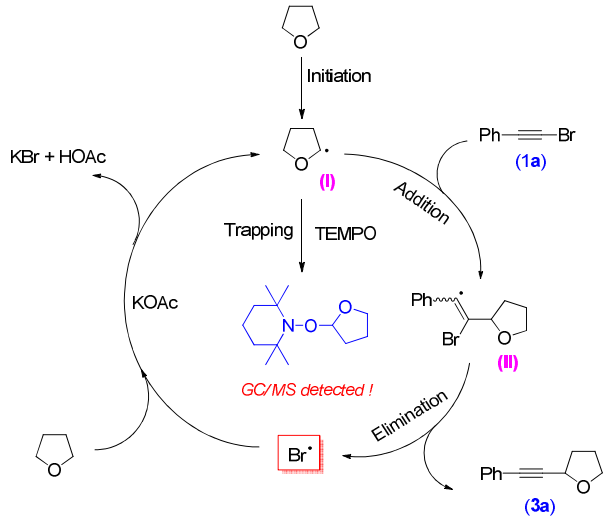
Additionally, the region-selectivity of direct alkynylation of 1,3-dioxolane with phenylethynyl bromide was investigated under the present reaction conditions. The results showed that 82% total yield of **3x** and **3x'** was isolated with a ratio of 65:17 (Scheme 4), which indicated that stability of free radicals plays an important role in this reaction.

Later on, the vinylation of α-C–H bonds of ethers with vinyl bromides in the presence of KOAc was also examined, and the results were shown in Scheme 4. When a mixture of *cis*- and *trans*-(2-bromovinyl)benzene (1:5) reacted with tetrahydrofuran and 2-methyltetrahydrofuran to generate the corresponding products **5a** and **5b** in moderate yields respectively with excellent regio- and stereo-selectivity. When prepared (*Z*)-2-bromovinyl phenyl ethers,[18a] **4b** and **4c** reacted with THF under the optimized reaction conditions, providing the corresponding exclusive (*Z*)-type products **5c** and **5d** (Scheme 5) in moderate yields. It also provides an effective and alternative route to vinyl cycloethers with excellent regio- and stereo-selectivity.[12,15b,19] Moreover, a representative structure of **5d** was confirmed by X-ray single crystal analysis.[20]



Scheme 5 Direct vinylation of α-C–H bonds of ethers with vinyl bromides.

To investigate the reaction mechanism, the related experiments were performed. When a radical scavenger, 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO, 1.5 equiv) was added to the standard reaction system, the reaction was completely shut down, along with formation of radical-trapping product, detected by GC/MS (See ESI for detail), suggesting that a carbon-centered radical of THF is probably involved in this reaction. In addition, when reaction was carried out under strictly anhydrous and anaerobic conditions, no any product was detected and only starting materials were recovered, and added peroxide (such as H_2O_2) could improved the reaction significantly. Based on the experimental results, a proposed mechanism of KOAc-promoted direct C–H alkynylation of simple ethers was depicted in Scheme 6. Firstly, tetrahydrofuran radical (**I**) was generated in the presence of small amounts of peroxide in THF (**2a**). Subsequently, a radical addition of the obtained (**I**) to phenylethynyl bromide (**1a**) underwent smoothly to afford a bromovinyl radical (**II**), which generated a bromine free radical and the final product (**3a**) through a bromine radical elimination process. Finally, the bromine radical abstracted a hydrogen radical from THF (**2a**) to generate intermediate (**I**) with the aid of a suitable base (KOAc).



Scheme 6 Proposed reaction mechanism.

Conclusion

In conclusion, we have established a novel Csp–Csp^3 bond formation through KOAc-promoted direct C–H alkynylation of simple ethers under transition-metal free and simple reaction conditions.[21] Different substituted phenylethynyl bromides and common simple ethers could be cross-coupled smoothly to afford the corresponding products in good to excellent yields. In addition, this methodology can also be extended to the direct C–H vinylation of ethers with excellent regio- and stereo-selectivity. A wide range of direct Csp–Csp^3 and Csp^2–Csp^3 bonds could be constructed through this protocol, offering a brand-new and alternative route for the synthesis of 2-alkynyl- and 2-alkenylethers.[22] Further detailed investigation of reaction mechanism and application of this kind of strategy is underway in our laboratory.

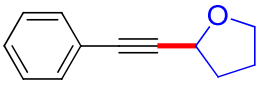
Experimental Section

All the bromoalkynes,[18b] and bromo alkenes,[18a] such as (*Z*)-2-bromovinyl phenyl ethers, **4b** and **4c** as starting materials were

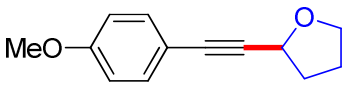
prepared according to the reported procedure in the literatures.[18a,b] All the chemicals and solvents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

Typical procedure for KOAc-promoted alkynylation of α-C–H bonds of ethers with alkynyl bromides

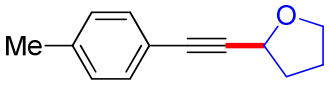
Under air atmosphere, a 10 mL oven-dried sealable reaction vessel equipped with a magnetic stir bar charged with phenylethynyl bromide (**1a**, 54.3 mg, 0.30 mmol), KOAc (59 mg, 0.60 mmol) and tetrahydrofuran (THF, **2a**, 2.0 mL, excess, as well as solvent) were added to the sealed vessel in one-portion. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 150 °C for 12 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 10:1 to 25:1, V/V) to obtain the desired pure product, 2-(phenylethynyl)tetrahydrofuran (**3a**).



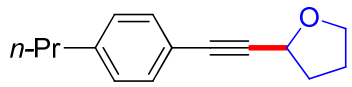
2-(Phenylethynyl)tetrahydrofuran (3a):[16] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.43 (m, 2H), 7.30–7.29 (m, 3H), 4.83–4.80 (m, 1H), 4.05–3.99 (m, 1H), 3.89–3.83 (m, 1H), 2.26–2.19 (m, 1H), 2.13–2.04 (m, 2H), 1.98–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.70, 128.24, 128.21, 122.83, 89.11, 84.46, 68.60, 67.92, 33.42, 25.50. HRMS (EI) ($[M]^+$) Calcd. For $C_{12}H_{12}O$: 172.0888, Found: 172.0883.



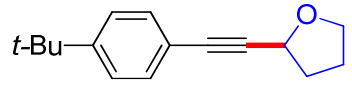
2-((4-Methoxyphenyl)ethynyl)tetrahydrofuran (3b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.82–4.79 (m, 1H), 4.04–3.99 (m, 1H), 3.88–3.85 (m, 1H), 3.80 (s, 3H), 2.25–2.19 (m, 1H), 2.13–2.03 (m, 2H), 1.99–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.55, 133.16, 114.90, 113.82, 87.59, 84.37, 68.69, 67.88, 55.25, 33.45, 25.51. HRMS (EI) ($[M]^+$) Calcd. For $C_{13}H_{14}O_2$: 202.0994, Found: 202.0990.



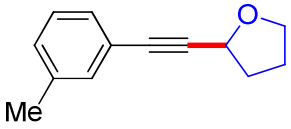
2-(*p*-Tolylethynyl)tetrahydrofuran (3c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.83–4.80 (m, 1H), 4.05–3.99 (m, 1H), 3.89–3.84 (m, 1H), 2.34 (s, 3H), 2.26–2.20 (m, 1H), 2.13–2.04 (m, 2H), 1.99–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.33, 131.61, 128.97, 119.71, 88.31, 84.59, 68.66, 67.91, 33.44, 25.51, 21.46. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{13}H_{15}O$: 187.1123, Found: 187.1123.



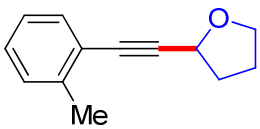
2-((4-*n*-Propylphenyl)ethynyl)tetrahydrofuran (3d): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.83–4.80 (m, 1H), 4.05–3.99 (m, 1H), 3.89–3.84 (m, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.26–2.19 (m, 1H), 2.12–2.06 (m, 2H), 1.99–1.92 (m, 1H), 1.67–1.60 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.08, 131.59, 128.36, 119.98, 88.35, 84.62, 68.66, 67.87, 37.90, 33.45, 25.48, 24.29, 13.71. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{15}H_{19}O$: 215.1436, Found: 215.1441.



2-((4-(*tert*-Butyl)phenyl)ethynyl)tetrahydrofuran (3e): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.83–4.80 (m, 1H), 4.05–4.00 (m, 1H), 3.89–3.84 (m, 1H), 2.26–2.19 (m, 1H) , 2.13–2.04 (m, 2H), 1.99–1.92 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.44, 131.42, 125.20, 119.80, 88.36, 84.56, 68.67, 67.87, 34.72, 33.47, 31.17, 25.48. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{16}H_{21}O$: 229.1592, Found: 229.1588.

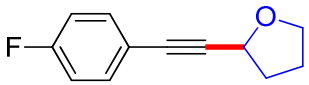


2-(*m*-Tolylethynyl)tetrahydrofuran (3f): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.24 (m, 2H), 7.21–7.17 (m, 1H), 7.13–7.11 (m, 1H), 4.84–4.81 (m, 1H), 4.05–4.00 (m, 1H), 3.90–3.84 (m, 1H), 2.32 (s, 3H), 2.26–2.20 (m, 1H), 2.14–2.04 (m, 2H), 2.01–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.86, 132.31, 129.12, 128.76, 128.10, 122.61, 88.71, 84.61, 68.62, 67.90, 33.44, 25.48, 21.18. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{13}H_{15}O$: 187.1123, Found: 187.1123.

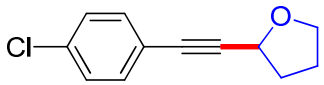


2-(*o*-Tolylethynyl)tetrahydrofuran (3g): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 1H), 7.22–7.18 (m, 2H), 7.15–7.11 (m, 1H), 4.89–4.86 (m, 1H), 4.06–4.01 (m, 1H), 3.92–3.86 (m, 1H), 2.43 (s, 3H), 2.28–2.22 (m, 1H), 2.16–2.07 (m, 2H), 2.02–1.93 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ: 140.21, 132.00, 129.34, 128.27, 125.45, 122.56, 93.07, 83.34,

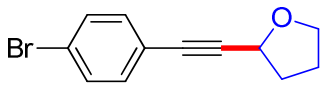
68.72, 67.83, 33.59, 25.41, 20.65. HRMS (EI) ([M]$^+$) Calcd. For $C_{13}H_{14}O$: 186.1045, Found: 186.1044.



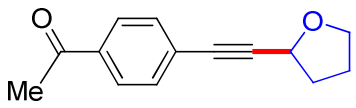
2-((4-Fluorophenyl)ethynyl)tetrahydrofuran (3h): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.39 (m, 2H), 7.00–6.96 (m, 2H), 4.80–4.77 (m, 1H), 4.03–3.97 (m, 1H), 3.88–3.82 (m, 1H), 2.25–2.18 (m, 1H), 2.10–2.05 (m, 2H), 1.98–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.46 (d, J_{CF} = 247.8 Hz), 133.58 (d, J_{CF} = 8.3 Hz), 118.90 (d, J_{CF} = 3.5 Hz), 115.45 (d, J_{CF} = 21.9 Hz), 88.78, 83.39, 68.51, 67.93, 33.36, 25.49. HRMS (EI) ([M]$^+$) Calcd. For $C_{12}H_{11}FO$: 190.0794, Found: 190.0789.



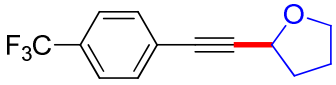
2-((4-Chlorophenyl)ethynyl)tetrahydrofuran (3i): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.81–4.78 (m, 1H), 4.03–3.98 (m, 1H), 3.89–3.83 (m, 1H), 2.26–2.20 (m, 1H), 2.12–2.03 (m, 2H), 2.00–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.28, 132.93, 128.54, 121.32, 90.10, 83.35, 68.51, 67.99, 33.34, 25.50. HRMS (EI) ([M]$^+$) Calcd. For $C_{12}H_{11}ClO$: 206.0498, Found: 206.0501.



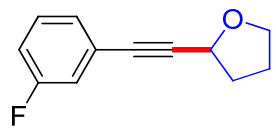
2-((4-Bromophenyl)ethynyl)tetrahydrofuran (3j): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.81–4.78 (m, 1H), 4.04–3.98 (m, 1H), 3.89–3.84 (m, 1H), 2.27–2.20 (m, 1H), 2.13–2.05 (m, 2H), 2.00–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.15, 131.48, 122.49, 121.79, 90.30, 83.41, 68.52, 68.00, 33.32, 25.50. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{12}H_{12}BrO$: 251.0072, Found: 251.0072.



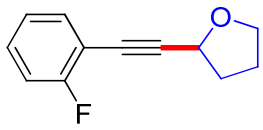
2-((4-Acetyphenyl)ethynyl)tetrahydrofuran (3k): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.83–4.80 (m, 1H), 4.03–3.98 (m, 1H), 3.89–3.83 (m, 1H), 2.58 (s, 3H), 2.28–2.20 (m, 1H), 2.13–2.04 (m, 2H), 1.99–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.25, 136.29, 131.80, 128.12, 127.70, 92.55, 83.68, 68.48, 68.06, 33.30, 26.55, 25.51. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{14}H_{15}O_2$: 215.1072, Found: 215.1071.



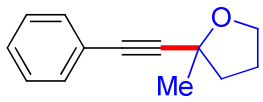
2-((4-(Trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (3l): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.55 (m, 2H), 7.54–7.52 (m, 2H), 4.84–4.81 (m, 1H), 4.05–3.99 (m, 1H), 3.90–3.85 (m, 1H), 2.29–2.22 (m, 1H), 2.14–2.05 (m, 2H), 2.01–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.92, 129.99 (q, J_{CF} = 32.4 Hz), 126.64, 125.14 (q, J_{CF} = 3.8 Hz), 123.88 (q, J_{CF} = 270.4 Hz), 91.66, 83.12, 68.42, 68.07, 33.29, 25.50. HRMS (EI) ([M]$^+$) Calcd. For $C_{13}H_{11}F_3O$: 240.0762, Found: 240.0763.



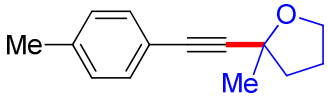
2-((3-Fluorophenyl)ethynyl)tetrahydrofuran (3m): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.25 (m, 1H), 7.24–7.20 (m, 1H), 7.13 (d, J = 9.6 Hz, 1H), 7.04–7.00 (m, 1H), 4.83–4.80 (m, 1H), 4.04–3.99 (m, 1H), 3.90–3.85 (m, 1H), 2.27–2.21 (m, 1H), 2.14–2.06 (m, 2H), 2.00–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.28 (d, J_{CF} = 244.8 Hz), 129.77 (d, J_{CF} = 8.6 Hz), 127.58 (d, J_{CF} = 3.1 Hz), 124.66 (d, J_{CF} = 9.5 Hz), 118.50 (d, J_{CF} = 22.7 Hz), 115.60 (d, J_{CF} = 21.0 Hz), 90.09, 83.23 (d, J_{CF} = 3.4 Hz), 68.46, 68.01, 33.33, 25.49. HRMS (EI) ([M]$^+$) Calcd. For $C_{12}H_{11}FO$: 190.0794, Found: 190.0793.



2-((2-Fluorophenyl)ethynyl)tetrahydrofuran (3n): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.41 (m, 1H), 7.31–7.26 (m, 1H), 7.10–7.03 (m, 2H), 4.87–4.84 (m, 1H), 4.05–4.00 (m, 1H), 3.90–3.85 (m, 1H), 2.28–2.22 (m, 1H) , 2.16–2.08 (m, 2H), 2.00–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.77 (d, J_{CF} = 250.1 Hz), 133.62 (d, J_{CF} = 1.3 Hz), 129.97 (d, J_{CF} = 7.9 Hz), 123.81 (d, J_{CF} = 3.7 Hz), 115.41 (d, J_{CF} = 20.8 Hz), 111.38 (d, J_{CF} = 15.6 Hz), 94.41 (d, J_{CF} = 3.4 Hz), 77.82 (d, J_{CF} = 0.9 Hz), 68.58, 67.97, 33.36, 25.42. HRMS (EI) ([M]$^+$) Calcd. For $C_{12}H_{11}FO$: 190.0794, Found: 190.0798.

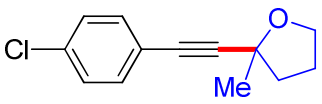


2-Methyl-2-(phenylethynyl)tetrahydrofuran (3o): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.42 (m, 2H), 7.30–7.29 (m, 3H), 4.06–3.95 (m, 2H), 2.34–2.28 (m, 1H), 2.20–2.12 (m, 1H), 2.03–1.98 (m, 1H), 1.90–1.83 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.68, 128.18, 128.07, 123.01, 92.36, 82.73, 76.40, 67.65, 40.18, 27.72, 25.72. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{13}H_{15}O$: 187.1123, Found: 187.1124.

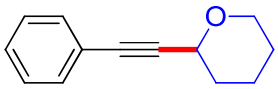


2-Methyl-2-(*p*-tolylethynyl)tetrahydrofuran (3p): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 4.06–3.94 (m, 2H), 2.34 (s, 3H), 2.31–2.27 (m, 1H), 2.22–2.11 (m, 1H), 2.05–1.95 (m, 1H), 1.90–1.83 (m, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

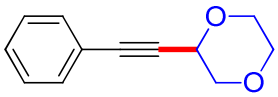
137.99, 131.46, 128.82, 119.82, 91.48, 82.72, 76.32, 67.50, 40.08, 27.65, 25.61, 21.32. HRMS (EI) ([M]$^+$) Calcd. For $C_{14}H_{16}O$: 200.1201, Found: 200.1199.



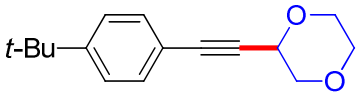
2-((4-Chlorophenyl)ethynyl)-2-methyltetrahydrofuran (3q): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 4.03–3.94 (m, 2H), 2.31–2.26 (m, 1H), 2.18–2.09 (m, 1H), 2.03–1.97 (m, 1H), 1.90–1.83 (m, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.96, 132.80, 128.39, 121.39, 93.28, 81.51, 76.23, 67.61, 39.99, 27.56, 25.62. HRMS (EI) ([M]$^+$) Calcd. For $C_{13}H_{13}ClO$: 220.0655, Found: 220.0654.



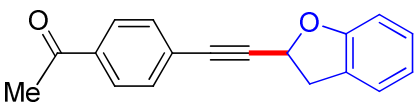
2-(Phenylethynyl)tetrahydro-2H-pyran (3r):[16] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.46 (m, 2H), 7.32–7.27 (m, 3H), 4.53–4.51 (m, 1H), 4.09–4.04 (m, 1H), 3.63–3.57 (m, 1H), 1.95–1.87 (m, 2H), 1.84–1.77 (m, 1H) , 1.65–1.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.76, 128.29, 128.22, 122.77, 88.15, 85.19, 67.46, 66.64, 32.20, 25.69, 21.84.



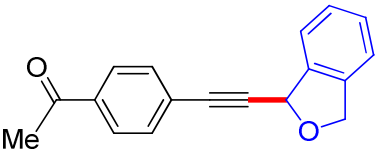
2-(Phenylethynyl)-1,4-dioxane (3s):[15a] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.32–7.31 (m, 3H), 4.59–4.57 (m, 1H), 3.96–3.92 (m, 2H), 3.78–3.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.87, 128.70, 128.27, 122.07, 86.56, 84.32, 70.41, 66.46, 66.40, 65.80.



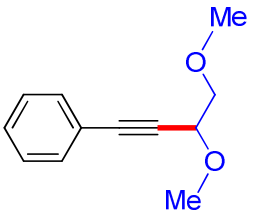
2-((4-(*tert*-Butyl)phenyl)ethynyl)-1,4-dioxane (3t): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.59–4.56 (m, 1H), 3.96–3.92 (m, 2H), 3.79–3.67 (m, 4H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.98, 131.60, 125.27, 119.01, 86.70, 83.59, 70.49, 66.55, 66.38, 65.84, 34.78, 31.13. HRMS (EI) ([M]$^+$) Calcd. For $C_{16}H_{20}O_2$: 244.1463, Found: 244.1468.



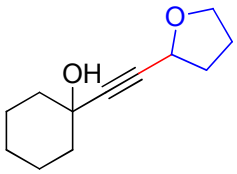
1-(4-((2,3-Dihydrobenzofuran-2-yl)ethynyl)phenyl)ethanone (3u): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.23–7.19 (m, 1H), 6.98–6.95 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.87–4.83 (m, 1H), 4.65–4.61 (m, 1H), 4.56–4.52 (m, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.16, 159.33, 136.15, 131.74, 129.04, 128.07, 127.79, 126.85, 124.63, 121.08, 109.99, 91.35, 82.05, 76.22, 34.48, 26.47. HRMS (EI) ([M]$^+$) Calcd. For $C_{18}H_{14}O_2$: 262.0994, Found: 262.0999.



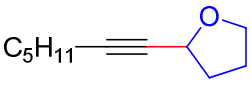
1-(4-((1,3-Dihydroisobenzofuran-1-yl)ethynyl)phenyl)ethanone (3v): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.45–7.43 (m, 1H), 7.37–7.35 (m, 2H), 7.29–7.27 (m, 1H), 6.14 (s, 1H), 5.31–5.28 (m, 1H), 5.16–5.13 (m, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.16, 138.74, 138.60, 136.39, 131.85, 128.24, 128.02, 127.78, 127.22, 121.75, 121.06, 90.39, 85.10, 73.69, 72.91, 26.48. HRMS (EI) ([M]$^+$) Calcd. For $C_{18}H_{14}O_2$: 262.0994, Found: 262.0993.



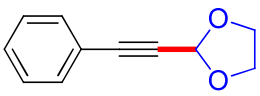
(3,4-Dimethoxybut-1-yn-1-yl)benzene (3w): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.33–7.32 (m, 3H), 4.45–4.41 (m, 1H), 3.69–3.66 (m, 2H), 3.54 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.82, 128.56, 128.28, 122.34, 86.85, 84.86, 74.92, 71.07, 59.37, 56.89. HRMS (ESI) ([M+H]$^+$) Calcd. For $C_{12}H_{15}O_2$: 191.1072, Found: 191.1075.



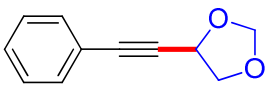
1-((Tetrahydrofuran-2-yl)ethynyl)cyclohexanol (3x):[22] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.63–4.61 (m, 1H), 3.97–3.92 (m, 1H), 3.83–3.80 (m, 1H), 2.27 (br, s, 1H), 2.17–2.15 (m, 1H), 2.05–1.88 (m, 5H), 1.68–1.66 (m, 2H), 1.58–1.50 (m, 4H), 1.24–1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 88.04, 83.90, 68.42, 68.03, 67.64, 39.74, 33.32, 25.21, 25.04, 23.21.



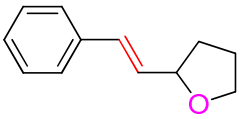
2-(Hept-1-yn-1-yl)tetrahydrofuran (3y):[23] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.57–4.55 (m, 1H), 3.98–3.93 (m, 1H), 3.82–3.76 (m, 1H), 2.21 (t, J = 7.0 Hz, 2H), 2.15–2.08 (m, 1H), 2.04–2.00 (m, 1H), 1.96–1.87 (m, 2H), 1.54–1.47 (m, 2H), 1.33–1.26 (m, 4H), 0.90 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 85.21, 79.74, 68.33, 67.56, 33.42, 30.94, 28.23, 25.31, 22.09, 18.63, 13.88.



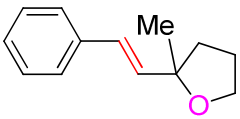
2-(Phenylethynyl)-1,3-dioxolane (3z):[24] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.46 (m, 2H), 7.36–7.32 (m, 3H), 5.90 (s, 1H), 4.17–4.13 (m, 2H), 4.01–3.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.94, 128.99, 128.31, 121.60, 93.45, 85.21, 84.45, 64.61.



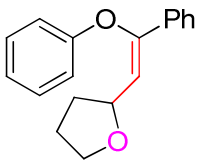
4-(Phenylethynyl)-1,3-dioxolane (3z'): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.34–7.32 (m, 3H), 5.11 (s, 1H), 5.08 (s, 1H), 4.95 (t, J = 6.0 Hz, 1H), 4.21–4.18 (m, 1H), 3.95–3.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.81, 128.73, 128.29, 122.08, 95.20, 86.22, 85.65, 70.59, 65.81. HRMS (EI) ($[M]^+$) Calcd. For $C_{11}H_{10}O_2$: 174.0681, Found: 174.0677.



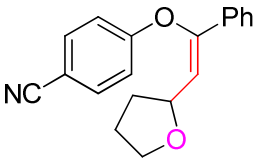
(*E*)-2-Styryl-tetrahydrofuran (*E*-5a):[12] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.39 (m, 2H), 7.33–7.30 (m, 2H), 7.27–7.22 (m, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 16.0, 6.0 Hz, 1H), 4.52–4.47 (m, 1H), 4.02–3.97 (m, 1H), 3.89–3.83 (m, 1H), 2.18–2.10 (m, 1H), 2.03–1.94 (m, 2H), 1.77–1.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.76, 130.43, 130.32, 128.40, 127.39, 126.36, 79.56, 68.08, 32.30, 25.82.



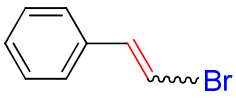
(*E*)-2-Methyl-2-styryl-tetrahydrofuran (*E*-5b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.39 (m, 2H), 7.34–7.30 (m, 2H), 7.25–7.21 (m, 1H), 6.57 (d, J = 16.0 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 3.97–3.94 (m, 2H), 2.03–1.96 (m, 3H), 1.83–1.76 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.10, 135.43, 128.38, 127.08, 126.69, 126.27, 82.29, 67.54, 37.76, 26.68, 25.63. HRMS (EI) ($[M]^+$) Calcd. For $C_{13}H_{16}O$: 188.1201, Found: 188.1202.



(*Z*)-4-((1-Phenyl-2-(tetrahydrofuran-2-yl)vinyl)oxy)benzonitrile (5c): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.50 (m, 2H), 7.30–7.27 (m, 3H), 7.25–7.21 (m, 2H), 6.99–6.93 (m, 3H), 5.92 (d, J = 8.0 Hz 1H), 4.80–4.74 (m, 1H), 3.97–3.92 (m, 1H), 3.80–3.75 (m, 1H), 2.12–2.07 (m, 1H), 2.01–1.87 (m, 2H), 1.72–1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.11, 149.90, 134.59, 129.41, 128.33, 125.71, 121.59, 118.83, 115.70, 74.04, 67.82, 32.33, 26.04. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{18}H_{19}O_2$: 267.1385, Found: 267.2382.



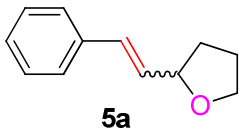
(*Z*)-4-((1-Phenyl-2-(tetrahydrofuran-2-yl)vinyl)oxy)benzonitrile (5d): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, J = 8.0 Hz, 2H), 7.46–7.45 (m, 2H), 7.31–7.27 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 8.0 Hz 1H), 4.70–4.65 (m, 1H), 3.96–3.91 (m, 1H), 3.80–3.74 (m, 1H), 2.11–2.05 (m, 1H), 2.02–1.96 (m, 1H), 1.94–1.89 (m, 1H), 1.72–1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.49, 149.13, 134.03, 133.49, 128.87, 128.62, 125.43, 119.62, 118.70, 116.49, 105.27, 73.67, 67.94, 32.33, 26.03. HRMS (ESI) ($[M+H]^+$) Calcd. For $C_{19}H_{18}NO_2$: 292.1338, Found: 292.1338.



4a

cis- and *trans*-mixture

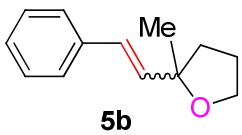
(*E*/*Z*)-(2-Bromovinyl)benzene (*E*-4a and *Z*-4a) [*E*/*Z* = 5/1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.39 (m, 1H), 7.37–7.34 (m, 5H), 7.15 (d, J = 14.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 0.2H), 6.81 (d, J = 14.0 Hz, 1H), 6.48 (d, J = 8.4 Hz, 0.2H).



5a

(*Z*)- and (*E*)-mixture

(*E*/*Z*)-2-Styryltetrahydrofuran (*E*-5a and *Z*-5a) [*E*/*Z* = 5/1]:[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.38 (m, 2H), 7.35–7.30 (m, 2.8H), 7.28–7.22 (m, 1.2H), 6.61 (d, J = 11.6 Hz, 0.2H), 6.60 (d, J = 15.6 Hz, 1H), 6.22 (dd, J = 16.0, 6.4 Hz, 1H), 5.72 (dd, J = 11.6, 8.8 Hz, 0.2H), 4.71–4.65 (m, 0.2H), 4.52–4.47 (m, 1H), 4.01–3.96 (m, 1.2H), 3.88–3.79 (m, 1.2H), 2.17–2.12 (m, 1.2H), 2.03–1.94 (m, 2.4H), 1.75–1.71 (m, 1.2H).



5b

(*Z*)- and (*E*)-mixture

(*E*/*Z*)-2-Methyl-2-styryltetrahydrofuran (*E*-5b and *Z*-5b) [*E*/*Z* = 5/1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.38 (m, 2.4H), 7.33–7.29 (m, 2.6H), 7.24–7.21 (m, 1H), 6.61 (d, J = 8.4 Hz, 0.2H), 6.56 (d, J = 16.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.20 (d, J = 7.2 Hz, 0.2H), 4.26–4.21 (m, 0.2H), 3.97–3.94 (m, 2H),

2.01–1.80 (m, 4.8H), 1.62 (s, 0.6H), 1.42 (s, 3H).

Acknowledgements

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Notes and reference

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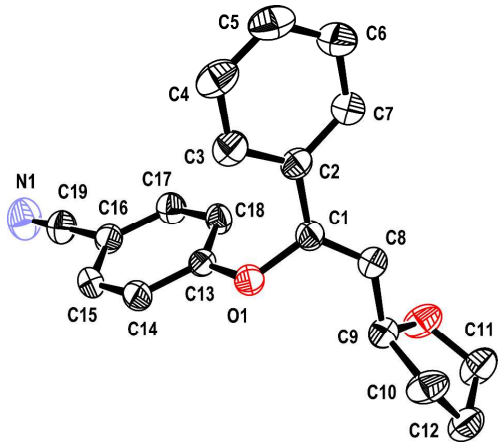
20 X-ray single crystal structure of **5d**, which is numbered CCDC 955471 at The Cambridge Crystallographic Data Centre.



21 KOAc (99.96%) was purchased from Aladdin Co. The reaction solution was analysis by ICP-MS, and the determination data indicated that Cu, Pd, Ni, Fe, Co, Ru, and Rh are less than 0.2 ppm (under detection limit).

22 During revision of this manuscript, a similar work was reported using NaF by Liang, and see: Y. Yang, H. Huang, X. Zhang, W. Zeng and Y. Liang, *Synthesis*, 2013, 3137–3146 for detail.

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