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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 few decades, significant efforts have been made 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 bonds from unactivated aromatic rings by direct C–H activation without the aid of transition metals,[2] and these breakthroughs might bring in a new era of organic synthesis.[3] From the viewpoint of green chemistry, the organic reactions carried out under transition-metal-free conditions, avoiding metal contamination in the final products, have 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 metals have been established.[4] The representative systems are KO*t*Bu,[2b,c,4b,k,r–v] and 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, pharmaceutical 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 to produce 2-alkynyl cyclic ethers through the alkynylation of α-position C–H bonds in cyclic ethers with acetylenic triflones under peroxide or AIBN or UV-irradiation.[15] Most recently, Anderson reported an efficient 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 interest in transformation of C(sp^3)–H bonds into C(sp^3)–C bonds,[17] we conceived that alkynylation of α-position C–H bonds of ethers with alkynyl bromides without the assistance of a 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 for-

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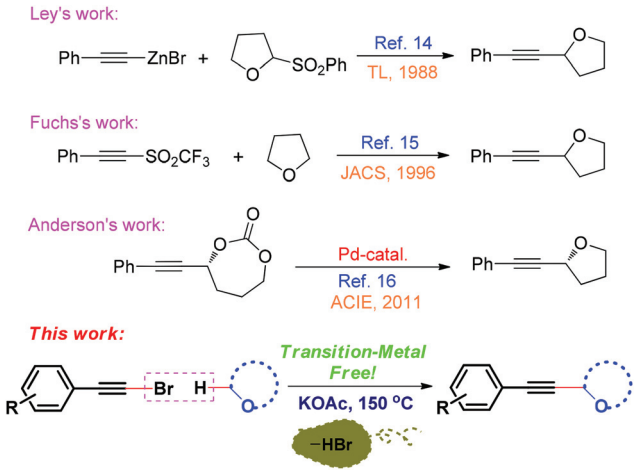


Scheme 1 Preparation of 2-alkynyl tetrahydrofurans.

mation 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 stereoselectivity.

Results and discussion

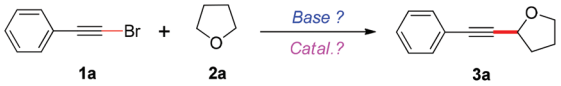
In the initial investigation of the reaction of alkynyl bromides to ethers, phenylethynyl bromide (**1a**) and tetrahydrofuran (THF, **2a**) were chosen as model substrates. When the model reaction was carried out in the presence of Na_2CO_3 at 150 °C in a sealed pressure tube for 12 h without an additional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

Encouraged by this positive result, further investigation on the addition of a 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, detailed investigation on the effect of a 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^tBu, NaO^tBu, KO^tBu, KOH, NaOH, Et_3N, DBU, or DABCO as a 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^tBu, NaO^tBu or LiO^tBu system which promoted the reaction, but failed (Table S1, ESI,† 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).

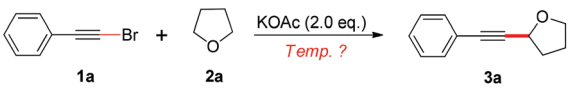
Table 1 Effect of a base and a catalyst on the reaction[a]



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^tBu	—	NR
16	NaO^tBu	—	NR
17	KO^tBu	—	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.

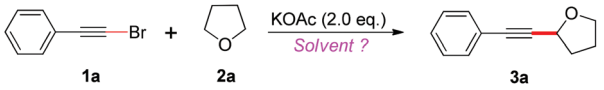
Table 2 Effect of temperature on the model reaction[a]



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.

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



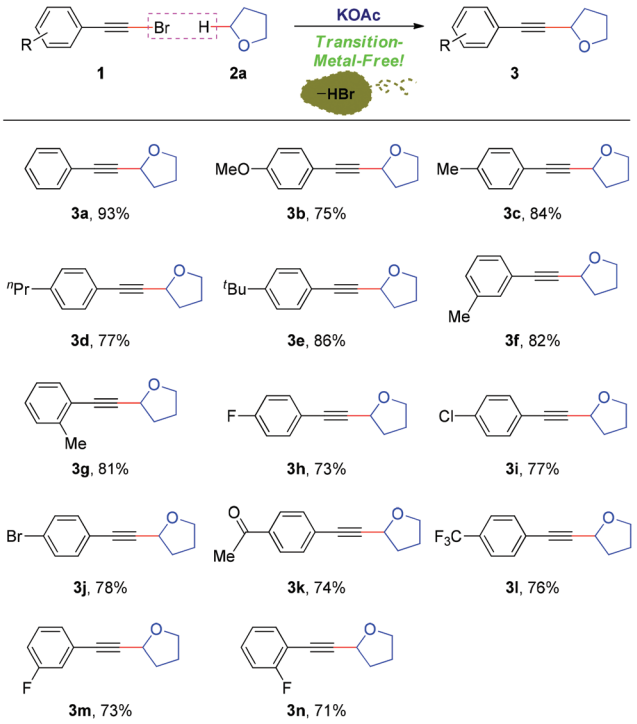
Entry	Solvent/temp. (°C)	Yield[b] (%)
1	DMF/150	NR
2	DMA/150	7
3	NMP/150	NR
4	DMSO/150	NR
5	CH_3CN/100	5
6	HOAc/100	NR
7	CH_3CH_2OH/100	NR
8	CH_3NO_2/100	NR
9	DCE/100	13
10	Toluene/150	Trace

[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.

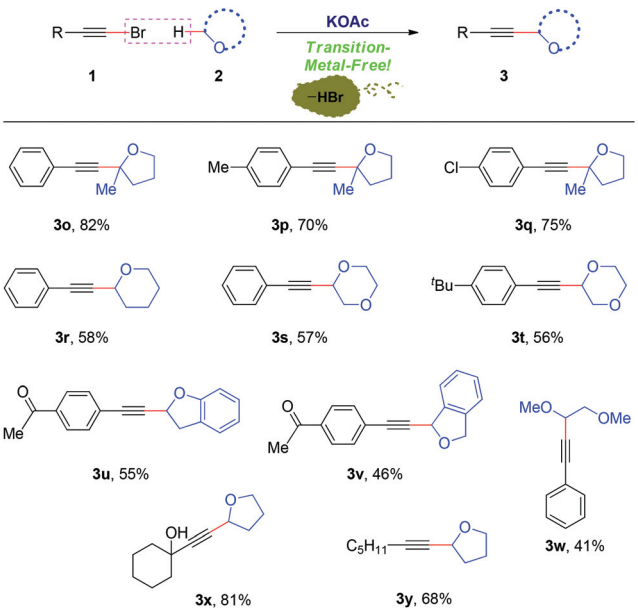
The final investigation revealed that an additional solvent, such as DMF, DMA, NMP, DMSO, CH_3CN, HOAc, CH_3CH_2OH, CH_3NO_2, DCE (1,2-dichloroethane) or toluene has a great negative effect on the reaction (Table 3, entries 1–10). The optimized reaction conditions for the model reaction were in the presence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

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 first tested to couple with different phenylethynyl bromides. We were surprised to find that reaction selectively occurred at the 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



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 a solvent), KOAc (0.60 mmol), at 150 °C for 12 h; isolated product yields after chromatography.

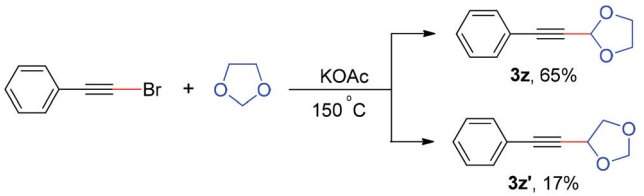


Scheme 3 KOAc-promoted direct alkynylation of other simple ethers under transition-metal free conditions. Reaction conditions: **1** (0.30 mmol), **2** (2.0 mL, excess, as well as solvent), KOAc (0.60 mmol), at 150 °C for 12 h; isolated product yields after chromatography.

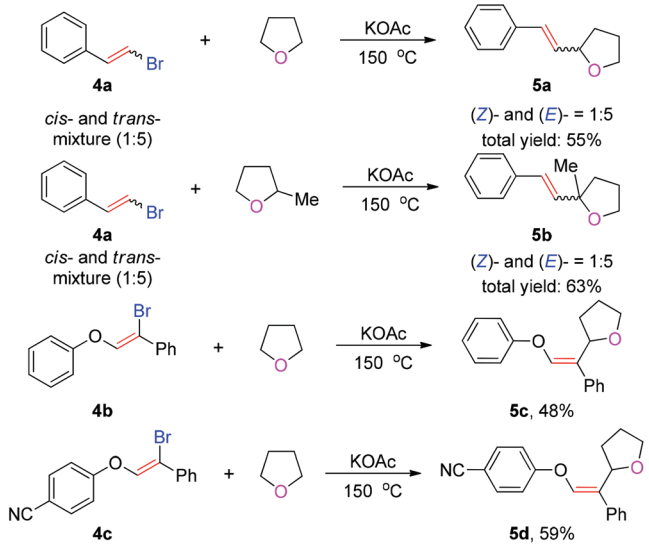
be extended to chain-like ethers. 1,2-Dimethoxyethane reacted smoothly with **1a** to afford the corresponding product **3w** in moderate yield, along with excellent regio-selectivity. In addition, the substrate scope of alkyne bromide was extended to aliphatic alkyne bromides, such as 1-(bromoethynyl)cyclohexanol and 1-bromohept-1-yne, and satisfactory results were achieved (Scheme 3, **3x** and **3y**).

Additionally, the regio-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 the stability of free radicals plays an important role in this reaction.

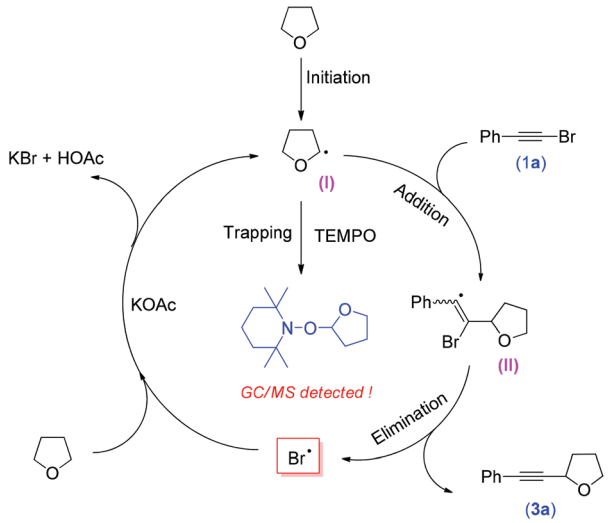
Later on, the vinylation of α-C–H bonds of ethers with vinyl bromides in the presence of KOAc was also examined, and the results are shown in Scheme 4. When a mixture of *cis*- and *trans*-(2-bromovinyl)benzene (1 : 5) reacted with tetrahydrofuran and 2-methyltetrahydrofuran to generate the corresponding products **5a** and **5b** in moderate yields respectively with excellent regio- and stereo-selectivity. The 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



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



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



Scheme 6 Proposed reaction mechanism.

route to vinyl cycloethers with excellent regio- and stereo-selectivity.[12,15b,19] Moreover, the representative structure of **5d** was confirmed by X-ray single crystal analysis.[20]

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 a radical-trapping product, detected by GC/MS (see the ESI† for details), 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 product was detected and only starting materials were recovered, and the added peroxide (such as H_2O_2) could improve the reaction significantly. Based on the experimental results, a proposed mechanism of KOAc-promoted direct C–H alkynylation of simple ethers is depicted in Scheme 6. Firstly, a 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**) occurred 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).

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

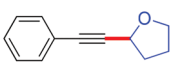
yields. In addition, this methodology can also be extended to the direct C–H vinylation of ethers with excellent regio- and stereo-selectivity. A wide range of direct Csp–Csp^3 and Csp^2–Csp^3 bonds could be constructed through this protocol, offering a brand new and alternative route for the synthesis of 2-alkynyl- and 2-alkenyl ethers.[22] Further detailed investigation of the reaction mechanism and application of this kind of strategy is underway in our laboratory.

Experimental section

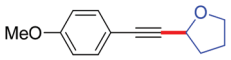
All the bromoalkynes[18b] and bromo alkenes,[18a] such as (*Z*)-2-bromovinyl phenyl ethers, **4b** and **4c**, as starting materials were prepared according to the reported procedure in the literature.[18a,b] All the chemicals and solvents were purchased from commercial suppliers and used without further 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 a solvent and recorded in ppm relative to the internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* values 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 spectroscopy 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.

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

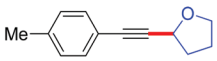
Under an air atmosphere, a 10 mL oven-dried sealable reaction vessel equipped with a magnetic stir bar charged with phenylethynyl bromide (**1a**, 54.3 mg, 0.30 mmol), KOAc (59 mg, 0.60 mmol) and tetrahydrofuran (THF, **2a**, 2.0 mL, excess, as well as solvent) was added to the sealed vessel in one portion. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel was 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**).



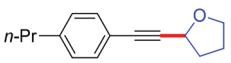
2-(Phenylethynyl)tetrahydrofuran (3a).[16] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.43 (m, 2H), 7.30–7.29 (m, 3H), 4.83–4.80 (m, 1H), 4.05–3.99 (m, 1H), 3.89–3.83 (m, 1H), 2.26–2.19 (m, 1H), 2.13–2.04 (m, 2H), 1.98–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.70, 128.24, 128.21, 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.



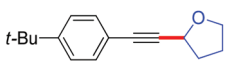
2-((4-Methoxyphenyl)ethynyl)tetrahydrofuran (3b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.82–4.79 (m, 1H), 4.04–3.99 (m, 1H), 3.88–3.85 (m, 1H), 3.80 (s, 3H), 2.25–2.19 (m, 1H), 2.13–2.03 (m, 2H), 1.99–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



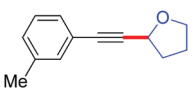
2-(*p*-Tolylethynyl)tetrahydrofuran (3c). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.83–4.80 (m, 1H), 4.05–3.99 (m, 1H), 3.89–3.84 (m, 1H), 2.34 (s, 3H), 2.26–2.20 (m, 1H), 2.13–2.04 (m, 2H), 1.99–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.

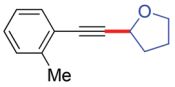


2-((4-(*tert*-Butyl)phenyl)ethynyl)tetrahydrofuran (3e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.83–4.80 (m, 1H), 4.05–4.00 (m, 1H), 3.89–3.84 (m, 1H), 2.26–2.19 (m, 1H), 2.13–2.04 (m, 2H), 1.99–1.92 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (100 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.

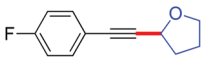


2-(*m*-Tolylethynyl)tetrahydrofuran (3f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.24 (m, 2H), 7.21–7.17 (m, 1H), 7.13–7.11 (m, 1H), 4.84–4.81 (m, 1H), 4.05–4.00 (m, 1H), 3.90–3.84 (m, 1H), 2.32 (s, 3H), 2.26–2.20 (m, 1H), 2.14–2.04 (m, 2H), 2.01–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

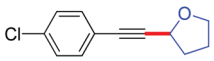
137.86, 132.31, 129.12, 128.76, 128.10, 122.61, 88.71, 84.61, 68.62, 67.90, 33.44, 25.48, 21.18. HRMS (ESI) ([M + H]$^+$) calcd for $C_{13}H_{15}O$: 187.1123, found: 187.1123.



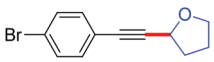
2-(*o*-Tolylethynyl)tetrahydrofuran (3g). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J = 7.6 Hz, 1H), 7.22–7.18 (m, 2H), 7.15–7.11 (m, 1H), 4.89–4.86 (m, 1H), 4.06–4.01 (m, 1H), 3.92–3.86 (m, 1H), 2.43 (s, 3H), 2.28–2.22 (m, 1H), 2.16–2.07 (m, 2H), 2.02–1.93 (m, 1H); ^{13}C NMR (100 MHz,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



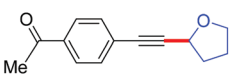
2-((4-Fluorophenyl)ethynyl)tetrahydrofuran (3h). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.39 (m, 2H), 7.00–6.96 (m, 2H), 4.80–4.77 (m, 1H), 4.03–3.97 (m, 1H), 3.88–3.82 (m, 1H), 2.25–2.18 (m, 1H), 2.10–2.05 (m, 2H), 1.98–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.46 (d, J_{CF} = 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.



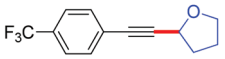
2-((4-Chlorophenyl)ethynyl)tetrahydrofuran (3i). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.81–4.78 (m, 1H), 4.03–3.98 (m, 1H), 3.89–3.83 (m, 1H), 2.26–2.20 (m, 1H), 2.12–2.03 (m, 2H), 2.00–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.28, 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.



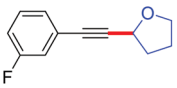
2-((4-Bromophenyl)ethynyl)tetrahydrofuran (3j). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.81–4.78 (m, 1H), 4.04–3.98 (m, 1H), 3.89–3.84 (m, 1H), 2.27–2.20 (m, 1H), 2.13–2.05 (m, 2H), 2.00–1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.15, 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.



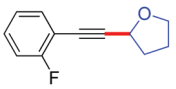
2-((4-Acetyphenyl)ethynyl)tetrahydrofuran (3k). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.83–4.80 (m, 1H), 4.03–3.98 (m, 1H), 3.89–3.83 (m, 1H), 2.58 (s, 3H), 2.28–2.20 (m, 1H), 2.13–2.04 (m, 2H), 1.99–1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



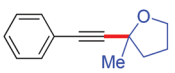
2-((4-(Trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (3l). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57–7.55 (m, 2H), 7.54–7.52 (m, 2H), 4.84–4.81 (m, 1H), 4.05–3.99 (m, 1H), 3.90–3.85 (m, 1H), 2.29–2.22 (m, 1H), 2.14–2.05 (m, 2H), 2.01–1.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.92, 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.



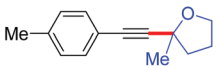
2-((3-Fluorophenyl)ethynyl)tetrahydrofuran (3m). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.25 (m, 1H), 7.24–7.20 (m, 1H), 7.13 (d, J = 9.6 Hz, 1H), 7.04–7.00 (m, 1H), 4.83–4.80 (m, 1H), 4.04–3.99 (m, 1H), 3.90–3.85 (m, 1H), 2.27–2.21 (m, 1H), 2.14–2.06 (m, 2H), 2.00–1.94 (m, 1H); ^{13}C 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.



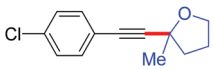
2-((2-Fluorophenyl)ethynyl)tetrahydrofuran (3n). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.41 (m, 1H), 7.31–7.26 (m, 1H), 7.10–7.03 (m, 2H), 4.87–4.84 (m, 1H), 4.05–4.00 (m, 1H), 3.90–3.85 (m, 1H), 2.28–2.22 (m, 1H), 2.16–2.08 (m, 2H), 2.00–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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.



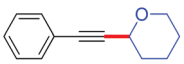
2-Methyl-2-(phenylethynyl)tetrahydrofuran (3o). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.42 (m, 2H), 7.30–7.29 (m, 3H), 4.06–3.95 (m, 2H), 2.34–2.28 (m, 1H), 2.20–2.12 (m, 1H), 2.03–1.98 (m, 1H), 1.90–1.83 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.68, 128.18, 128.07, 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.



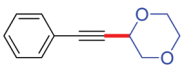
2-Methyl-2-(*p*-tolylethynyl)tetrahydrofuran (3p). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 4.06–3.94 (m, 2H), 2.34 (s, 3H), 2.31–2.27 (m, 1H), 2.22–2.11 (m, 1H), 2.05–1.95 (m, 1H), 1.90–1.83 (m, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)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



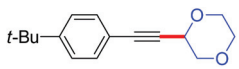
2-((4-Chlorophenyl)ethynyl)-2-methyltetrahydrofuran (3q). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 4.03–3.94 (m, 2H), 2.31–2.26 (m, 1H), 2.18–2.09 (m, 1H), 2.03–1.97 (m, 1H), 1.90–1.83 (m, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 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.



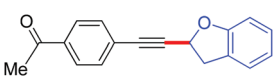
2-(Phenylethynyl)tetrahydro-2*H*-pyran (3r).[16] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.46 (m, 2H), 7.32–7.27 (m, 3H), 4.53–4.51 (m, 1H), 4.09–4.04 (m, 1H), 3.63–3.57 (m, 1H), 1.95–1.87 (m, 2H), 1.84–1.77 (m, 1H), 1.65–1.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.76, 128.29, 128.22,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



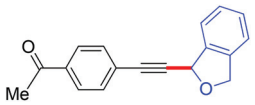
2-(Phenylethynyl)-1,4-dioxane (3s).[15a] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.32–7.31 (m, 3H), 4.59–4.57 (m, 1H), 3.96–3.92 (m, 2H), 3.78–3.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.87, 128.70, 128.27, 122.07, 86.56, 84.32, 70.41, 66.46, 66.40, 65.80.



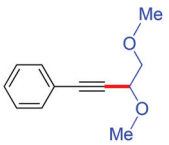
2-((4-(*tert*-Butyl)phenyl)ethynyl)-1,4-dioxane (3t). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.59–4.56 (m, 1H), 3.96–3.92 (m, 2H), 3.79–3.67 (m, 4H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.98, 131.60, 125.27, 119.01, 86.70, 83.59, 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.



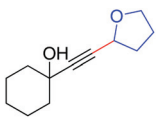
1-(4-((2,3-Dihydrobenzofuran-2-yl)ethynyl)phenyl)ethanone (3u). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 7.23–7.19 (m, 1H), 6.98–6.95 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.87–4.83 (m, 1H), 4.65–4.61 (m, 1H), 4.56–4.52 (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.



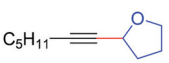
1-(4-((1,3-Dihydroisobenzofuran-1-yl)ethynyl)phenyl)ethanone (3v). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.45–7.43 (m, 1H), 7.37–7.35 (m, 2H), 7.29–7.27 (m, 1H), 6.14 (s, 1H), 5.31–5.28 (m, 1H), 5.16–5.13 (m, 1H), 2.59 (s, 3H); ^{13}C NMR (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.



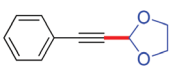
(3,4-Dimethoxybut-1-yn-1-yl)benzene (3w). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.33–7.32 (m, 3H), 4.45–4.41 (m, 1H), 3.69–3.66 (m, 2H), 3.54 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.82, 128.56, 128.28, 122.34, 86.85, 84.86, 74.92, 71.07, 59.37, 56.89. 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.

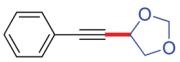


2-(Hept-1-yn-1-yl)tetrahydrofuran (3y).[23] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.57–4.55 (m, 1H), 3.98–3.93 (m, 1H), 3.82–3.76 (m, 1H), 2.21 (t, J = 7.0 Hz, 2H), 2.15–2.08 (m, 1H), 2.04–2.00 (m, 1H), 1.96–1.87 (m, 2H), 1.54–1.47 (m, 2H), 1.33–1.26 (m, 4H), 0.90 (t, J = 6.4 Hz, 3H); ^{13}C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

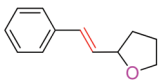


2-(Phenylethynyl)-1,3-dioxolane (3z).[24] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48–7.46 (m, 2H), 7.36–7.32 (m, 3H), 5.90 (s, 1H), 4.17–4.13 (m, 2H), 4.01–3.98 (m, 2H); ^{13}C

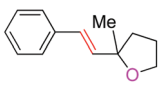
NMR (100 MHz, $CDCl_3$) δ: 131.94, 128.99, 128.31, 121.60, 93.45, 85.21, 84.45, 64.61.



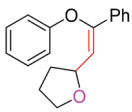
4-(Phenylethynyl)-1,3-dioxolane (3z′). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.45 (m, 2H), 7.34–7.32 (m, 3H), 5.11 (s, 1H), 5.08 (s, 1H), 4.95 (t, J = 6.0 Hz, 1H), 4.21–4.18 (m, 1H), 3.95–3.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.81, 128.73, 128.29, 122.08, 95.20, 86.22, 85.65, 70.59, 65.81. HRMS (EI) ([M]$^+$) calcd for $C_{11}H_{10}O_2$: 174.0681, found: 174.0677.



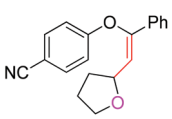
(*E*)-2-Styryl-tetrahydrofuran (*E*-5a).[12] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.39 (m, 2H), 7.33–7.30 (m, 2H), 7.27–7.22 (m, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 16.0, 6.0 Hz, 1H), 4.52–4.47 (m, 1H), 4.02–3.97 (m, 1H), 3.89–3.83 (m, 1H), 2.18–2.10 (m, 1H), 2.03–1.94 (m, 2H), 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.



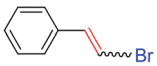
(*E*)-2-Methyl-2-styryl-tetrahydrofuran (*E*-5b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.39 (m, 2H), 7.34–7.30 (m, 2H), 7.25–7.21 (m, 1H), 6.57 (d, J = 16.0 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 3.97–3.94 (m, 2H), 2.03–1.96 (m, 3H), 1.83–1.76 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 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.



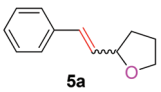
(*Z*)-4-((1-Phenyl-2-(tetrahydrofuran-2-yl)vinyl)oxy)benzonitrile (5d). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, J = 8.0 Hz, 2H), 7.46–7.45 (m, 2H), 7.31–7.27 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 8.0 Hz, 1H), 4.70–4.65 (m, 1H), 3.96–3.91 (m, 1H), 3.80–3.74 (m, 1H), 2.11–2.05 (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

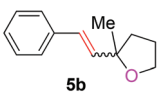
(*E*/*Z*)-(2-Bromovinyl)benzene (*E*-4a and *Z*-4a) [*E*/*Z* = 5/1]. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.39 (m, 1H), 7.37–7.34 (m, 5H), 7.15 (d, J = 14.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 0.2H), 6.81 (d, J = 14.0 Hz, 1H), 6.48 (d, J = 8.4 Hz, 0.2H).



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 references

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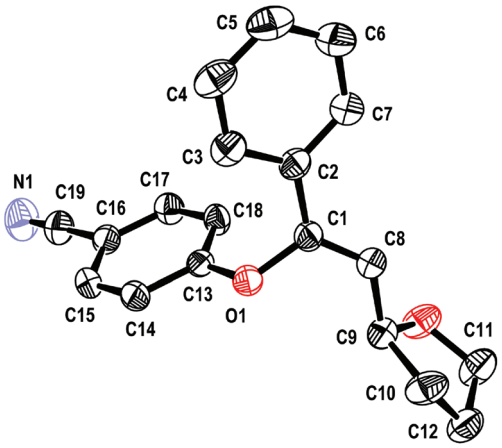
20 X-ray single crystal structure of **5d**, which is numbered CCDC 955471 at The Cambridge Crystallographic Data Centre.



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21 KOAc (99.96%) was purchased from Aladdin Co. The reaction solution was analysed 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 limits).

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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24 A. R. Katritzky, H. H. Odens and M. V. Voronkov, *J. Org. Chem.*, 2000, **65**, 1886.