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Nickel-Catalysed Sonogashira C(sp)–C(sp^2) Coupling Through Visible-Light Sensitization

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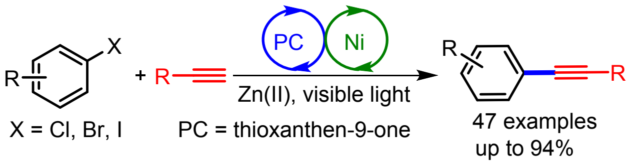


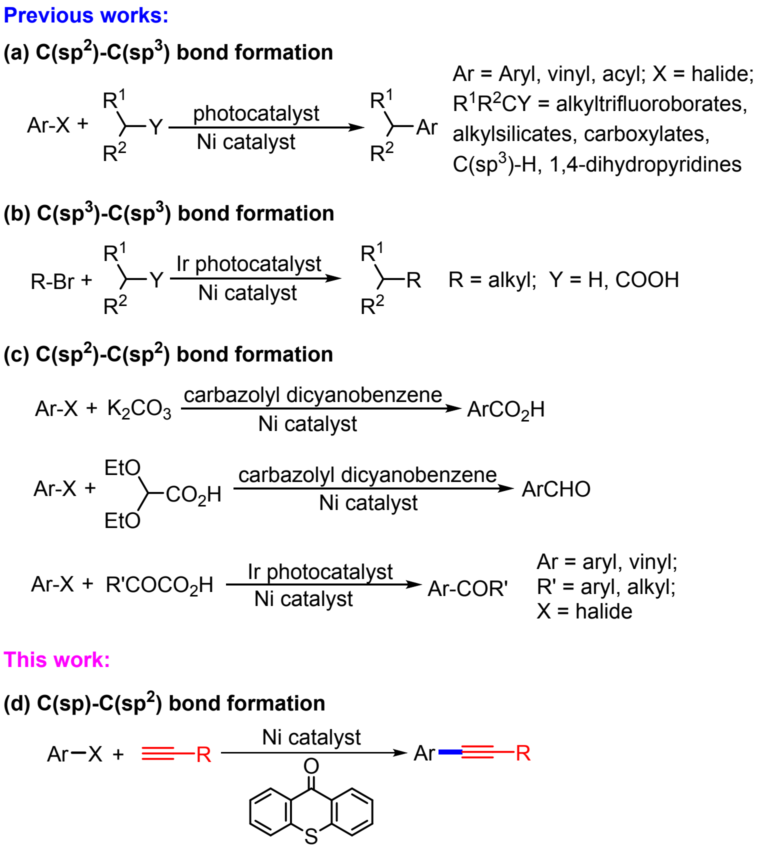
ABSTRACT: An efficient method for visible light-initiated, nickel-catalyzed Sonogashira C(sp)–C(sp^2) coupling has been developed via an energy transfer mode. Thioxanthen-9-one as a photosensitizer could significantly accelerate the arylation of alkynes with a wide range of (hetero)aryl halides in high yields. The cross-coupling reaction undergoes the stepwise oxidative addition of an arylhalide to nickel(0), transmetalation of the resulting aryl–Ni(II) halide species with Zn(II) acetylide into aryl–Ni(II) acetylide species, energy transfer from the excited-state of thioxanthen-9-one to aryl–Ni(II) acetylide and reductive elimination to the aryl alkyne.

INTRODUCTION

Aryl alkynes are important building blocks that widely occur in numerous natural products, pharmaceuticals, agrochemicals, and functional materials.[1-4] To date, the palladium-catalyzed Sonogashira reaction of terminal alkynes with aryl halides with or without copper co-catalyst is a popular method to access these complexes.[5-9] Much effort has also been devoted to the employment of copper,[10-13] cobalt,[14,15] iron,[16-18] and ruthenium[19,20] complexes or nanoparticles as catalysts for the arylation of alkynes.[21-24] Due to its cheap availability and high catalytic activity, nickel catalyst has been used in such conversions.[25-32] In these Ni-catalyzed cases, CuI as a co-catalyst, phosphines as auxiliary ligands and high temperatures were used.

In recent years, initiated by Molander[33] and MacMillan,[34,35] the synergistic combination of metal catalysis with photocatalysis has provided a powerful approach to achieve new chemical reactions.[36-41] In the dual catalysis, nickel catalysts have been commonly used in cross-coupling reactions to forge $C(sp^2)–C(sp^3)$,[42-52] $C(sp^2)–C(sp^2)$,[53-55] and $C(sp^3)–C(sp^3)$[56-60] bonds (Scheme 1). MacMillan, Wu and Chu et al. demonstrated the hydroalkylation or alkylarylation of alkynes using nickel and photoredox dual catalysis.[61-63] However, there is no report on nickel-catalysed C(sp)–$C(sp^2)$ cross-coupling under visible light irradiation. By far, expensive ruthenium and iridium polypyridyl complexes still dominate as photoactive species in the dual-catalysis.[42-65] The utility of cheap and commercially available organic photocatalysts has received much attention in the pursuit of sustainable and green photochemical processes.[66-73] Diarylketones are suitable alternatives due to that their photoexcited states can undergo energy transfer (EnT),[74,75] hydrogen-atom transfer (HAT),[76-81] or electron transfer (ET)[82,83] process. Nevertheless, their applications in combination with nickel catalysts to construct C-C bonds remain significantly limited.[84-87] Herein, we report the nickel-catalysed C(sp)–C(sp^2) coupling of alkynes and (hetero)aryl halides using thioxanthen-9-one (TXO) as a visible-light photosensitizer.

Scheme 1. Visible-Light-Mediated C-C Formations with Nickel and Photoredox Dual Catalysis

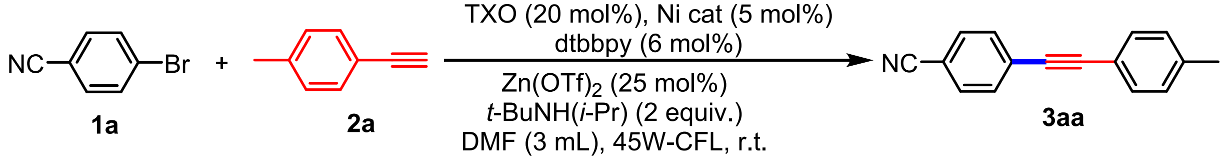


RESULTS AND DISCUSSION

In 2016, Glorius and coworkers described the arylation of alkyl and aromatic alkynes with diazonium salts by a dual photocatalytic system of Au catalyst and $[Ru(bpy)_3](PF_6)_2$.[88] In 2017, MacMillan et al. used $Ir(ppy)_3$ as a triplet photosensitizer to photosensitize nickel-catalyzed aryl esterification.[89] The two dual-catalytic systems required the use of expensive polypyridyl Ru(II) or Ir(III) complexes. Very recently, we have used commercially available thioxanthen-9-one (TXO) as a triplet photosensitizer to promote the nickel-catalyzed esterification of carboxylic acids with aryl bromides to provide aryl esters under visible light.[90] Those results stimulated us to explore TXO to accelerate Sonogashira C(sp)–C(sp^2) cross-coupling reactions. Our initial investigations focused on the coupling of 4-bromobenzonitrile (**1a**) with 1-ethynyl-4-methylbenzene (**2a**) in N,N-dimethylformamide (DMF) with TXO, $Ni(OAc)_2{\cdot}4H_2O$, 4,4′-di-tert-butyl-2,2′-bipyridine (dtbbpy), and *t*-BuNH(*i*-Pr). The irradiation of the mixture with a household 45 W compact fluorescent lamp (45W-CFL, Figure S1) for 24 h resulted in the formation of the desired product 4-(p-tolylethynyl)benzonitrile (**3aa**) in 3% yield with 54% conversion (entry 1, Table 1). The addition of anhydrous $Zn(OTf)_2$ (25 mol%, OTf = trifluoromethylsulfonate) drastically increased the conversion of **1a** and the yield of **3aa** (up to 92%) (entry 2). The in situ formed zinc(II) acetylide might increase transmetallation to form alkynyl nickel species.[91,92] Reducing the amount of TXO to 10 mol% (entry 3) gave a lower, but still respectable yield (85%). The same cross-coupling reaction gave an 83% yield in DMSO, 23% yield in MeCN, and 11% yield in dioxane (entries 1-3, Table S1). The reaction did not work in $CHCl_3$, n-hexane (entries 4 and 5, Table S1). $NiBr_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $NiCl_2$, $Ni(acac)_2$ (acac = acetylacetonate), or

$Ni(COD)_2$ (COD = 1,5-cyclooctadiene) were subsequently examined, and lower yields were observed (entries 4-8, Table 1). For various bases (*t*-BuNH(*i*-Pr), Et_3N, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), (*i*-Pr)$_2$NEt, Cs_2CO_3, Na_2CO_3, K_3PO_4, NaF) (entries 6-12, Table S1), *t*-BuNH(*i*-Pr) was found to be the best one (entry 2, Table 1). The decreasing of $Zn(OTf)_2$ led to the lower yield (entries 13 and 14, Table S1). Control experiments indicated photosensitizer, base, nickel catalyst, dtbbpy, and light irradiation were crucial for the cross coupling (entries 9-13, Table 1). No desired product was observed when the reaction was setup at 60 °C under the exclusion of light (entry 14, Table 1). Under the irradiation of a 300-W Xe lamp equipped with a 400 nm cut-off filter, the same reaction afforded **3aa** in 90% yield (entry 15, Table 1). Visible light could effectively promote this Sonogashira reaction.

Table 1. Optimization of Sonogashira Cross-Coupling Reactions[a]



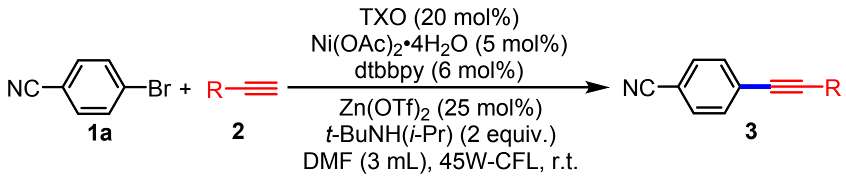
Entry	Cat.	Base	Solvent	Conversio	Yield

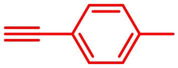
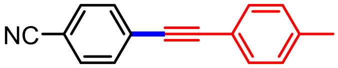
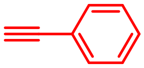
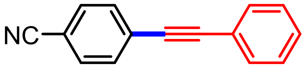
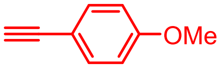
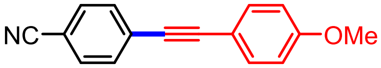
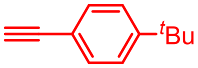
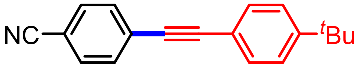
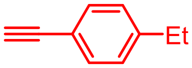
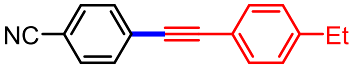
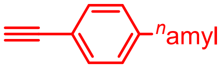
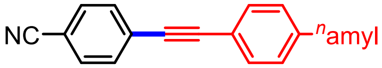
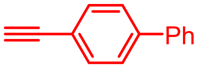
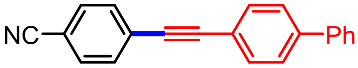
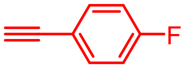
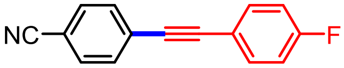
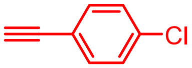
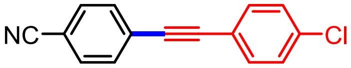
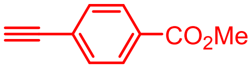
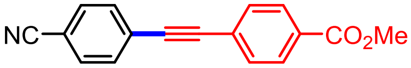
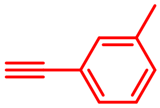
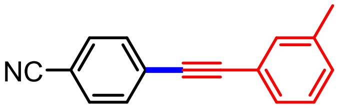
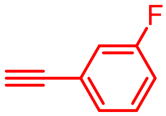
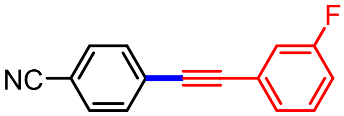
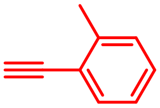
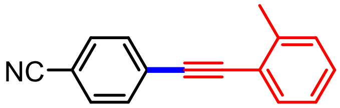
				n	
1[b]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	54%	3%
2	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	93%	92%
3[c]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	87%	85%
4	$NiCl_2$	*t*-BuNH(*i*-Pr)	DMF	85%	73%
5	$NiBr_2\cdot 3H_2O$	*t*-BuNH(*i*-Pr)	DMF	78%	76%
6	$Ni(NO_3)_2\cdot 6H_2O$	*t*-BuNH(*i*-Pr)	DMF	76%	59%
7	$Ni(acac)_2$	*t*-BuNH(*i*-Pr)	DMF	60%	54%
8	$Ni(COD)_2$	*t*-BuNH(*i*-Pr)	DMF	57%	47%
9[d]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	trace	trace
10	$Ni(OAc)_2\cdot 4H_2O$	-	DMF	0	0
11	-	*t*-BuNH(*i*-Pr)	DMF	0	0
12[e]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	7%	<5%
13[f]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	0	0
14[g]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	0	0
15[h]	$Ni(OAc)_2\cdot 4H_2O$	*t*-BuNH(*i*-Pr)	DMF	94%	90%

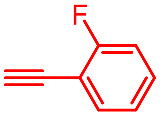
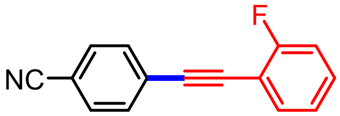
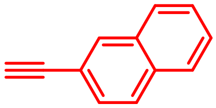
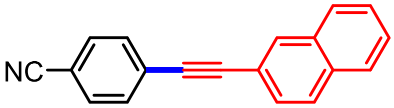
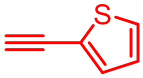
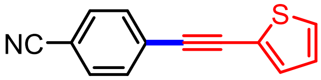
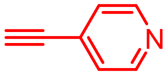
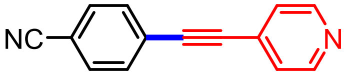
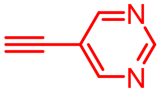
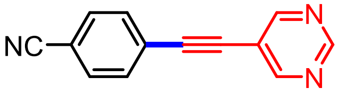
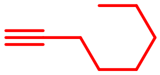
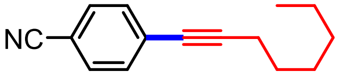
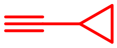
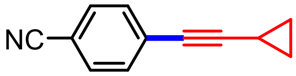
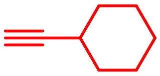
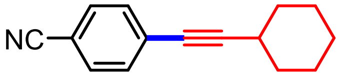
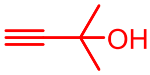
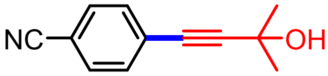
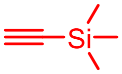
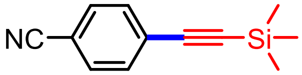
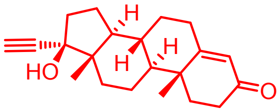
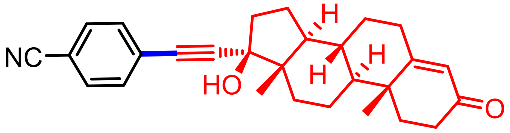
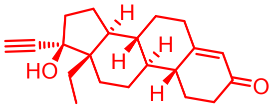
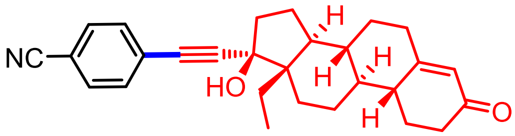
[a] **1a** (0.2 mmol, 1 equiv.), **2a** (0.4 mmol, 2 equiv.), $Ni(OAc)_2\cdot 4H_2O$ (0.01 mmol, 5 mol%), dtbbpy (0.012 mmol, 6 mol%), *t*-BuNH(*i*-Pr) (0.4 mmol, 2.0 equiv.), $Zn(OTf)_2$ (25 mol%), TXO (20 mol%), in 3 mL DMF under an N_2 atmosphere, irradiation under 45W-Compact Fluorescent Lamp (CFL) for 24 h with cooling by fan, HPLC conversion and yield (HPLC = high performance liquid chromatography). [b] Without $Zn(OTf)_2$. [c] TXO (10 mol%). [d] Without TXO. [e] Without dtbbpy. [f] At room temperature and in dark. [g] At 60 °C and in dark. [h] Under 300-W Xe lamp equipped with a 400 nm cut-off filter.

With the optimized conditions in hand, the scopes of the coupling reaction with regard to both alkynes (Table 2) and aryl halides (Table 3) were investigated. Aryl alkynes with electron-deficient and electron-rich groups at *para*- or *meta*-positions of phenyl ring efficiently proceeded to produce diaryl alkynes **3aa-3al** in 84−93% yields. Substrates **2m** and **2n** possessing *ortho* substituents were well tolerated, as evidenced by isolation of **3am** and **3an** in 68-73% yields. The reaction of 2-ethynylnaphthalene with **1a** afforded **3ao** in 62% isolated yield. Heteroatom-containing alkynes such as 2-ethynylthiophene (**2p**), 4-ethynylpyridine (**2q**) and 5-ethynylpyrimidine (**2r**) gave arylated products **3ap-3ar** in good yields (55-63%). Treatment of primary alkyl, secondary alkyl, or hydroxylsubstituted alkynes (**2s-2v**) with **1a** enabled the corresponding coupling in 83-92% yields. Ethynyltrimethylsilane (**2w**) was successfully transformed into 4-((trimethylsilyl)ethynyl)benzonitrile (**3aw**) with 82% yield. To further investigate the synthetic applicability of this method, ethisterone (**2x**) or levonorgestrel (**2y**) reacted with **1a** to give the desired products **3ax** and **3ay** under the standard reaction conditions.

Table 2. Cross-Coupling Reactions of 1a with Alkynes (2).



Entry[a]	Alkyne	Product		Yield
1			**3aa**	91%
2			**3ab**	90%
3			**3ac**	87%
4			**3ad**	88%
5			**3ae**	86%
6			**3af**	87%
7			**3ag**	84%
8			**3ah**	93%
9			**3ai**	91%
10			**3aj**	92%
11			**3ak**	86%
12			**3al**	88%
13			**3am**	68%

14			**3an**	73%
15			**3ao**	62%
16			**3ap**	63%
17			**3aq**	55%
18			**3ar**	59%
19			**3as**	91%
20			**3at**	89%
21			**3au**	92%
22			**3av**	83%
23			**3aw**	82%
24			**3ax**	45%
25			**3ay**	47%

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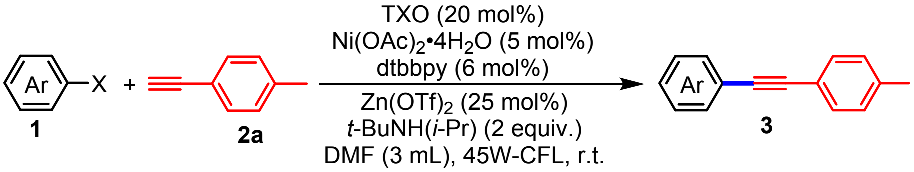
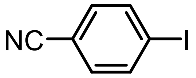
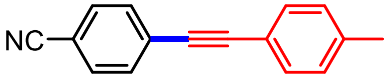
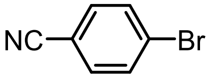
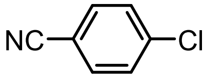
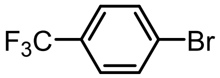
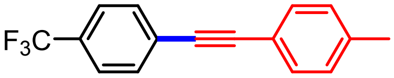
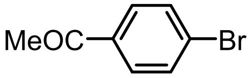
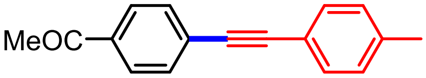
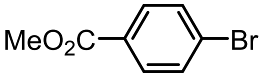
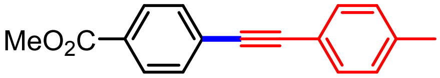
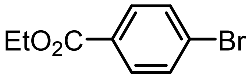
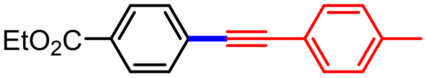
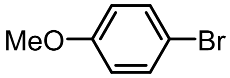
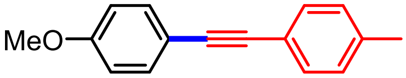
^{a}**1a** (0.2 mmol), **2** (0.4 mmol), Ni(OAc)$_2$·4H$_2$O (5 mol%), dtbbpy (6 mol%), *t*-BuNH(*i*-Pr) (0.4 mmol), Zn(OTf)$_2$ (25 mol%), TXO (20 mol%), 3 mL DMF, N$_2$, 45W-CFL for 24 h with cooling by fan and isolated yields.

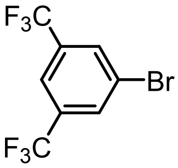
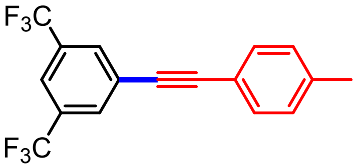
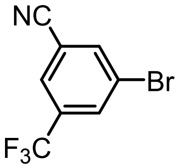
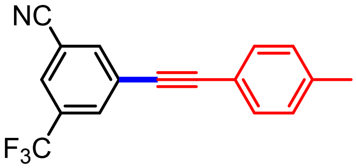
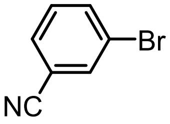
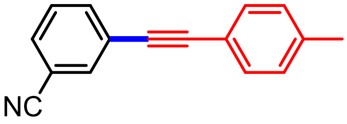
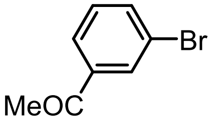
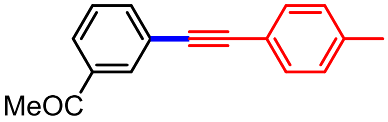
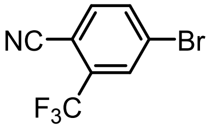
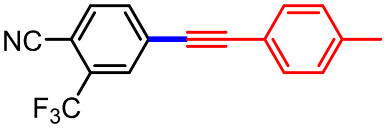
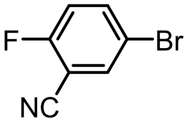
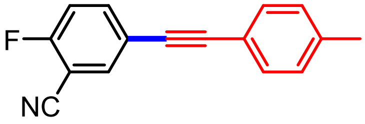
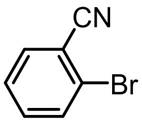
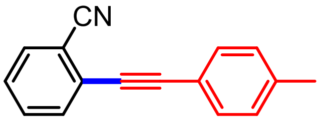
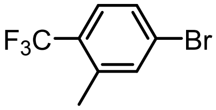
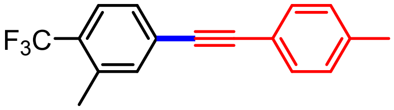
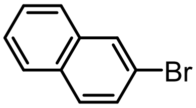
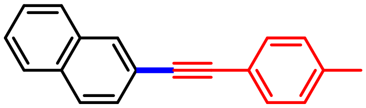
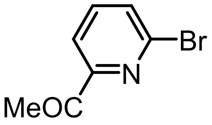
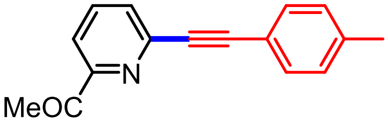
We next examined the reactivity of (hetero)aryl halides with **2a** (Table 3). Aryl bromides (**1a**–**1e**, **1g**–**1l**) bearing electron-deficient groups, including nitrile, carbonyl, fluoro, carboxylic ester or trifluoromethyl at the *para*- or/and *meta*-positions of phenyl ring, offered the products (**3aa**–**3ea**, **3ga**–**3la**) in 70–91% yields. The electron-rich aryl bromide **1f** was treated with **2a** to yield **3fa** in 49% yield. Moderate yield was achieved when the substituent was on the *ortho*-position of the benzene ring (**3ma**). Treatment of **1n** with **2a** afforded **3na** in 67% isolated yield. 2-Bromonaphthalene (**1o**) was smoothly converted into **3oa**. Pyridine substrates **1p-1v** proved to be competent for this transformation and provided products **3pa-3va** in a 66–81% yield range. Disappointingly, 5-bromobenzo[*d*][1,3]dioxole (**1w**) was not found to be a viable substrate for this conversion. However, the arylation of **2a** with 5-iodobenzo[*d*][1,3]dioxole produced **3wa** in 62% yield. Aryl iodides showed higher reactivity than the corresponding aryl bromides (**2a**, **2w**). Reaction of **2a** with 4-chlorobenzonitrile also offered **3aa** in 40% yield. Noteworthy, **3aa** was obtained in 72%

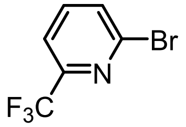
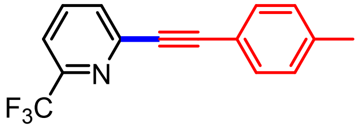
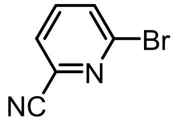
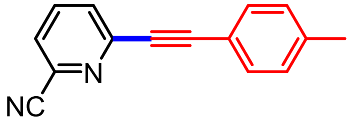
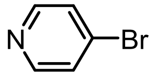
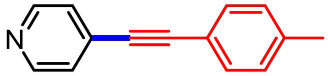
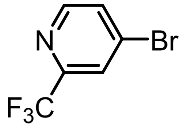
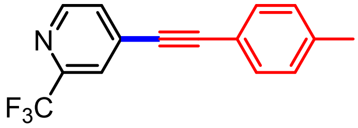
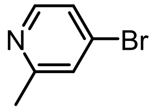
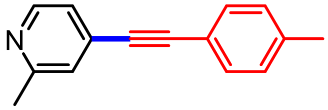
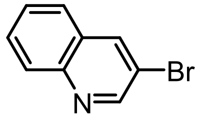
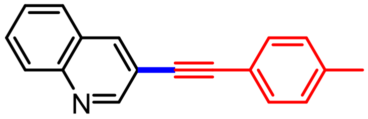
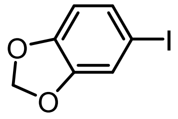
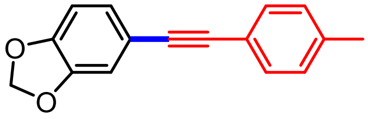
yield (0.9378 g, 4.32 mmol) when the cross-coupling of **1a** (1.092 g, 6.0 mmol) with **2a** (1.392 g, 12.0 mmol) was performed on a gram scale under the irradiation of 2 × 45 W-CFL (Figure S1c) for 72 h.

Table 3. Cross-Coupling Reactions of Aryl Halides (1) with 2a.



Entry^a	Aryl halide	Product		Yield
1			**3aa**	94%
2				91%
3				40%
4			**3ba**	85%
5			**3ca**	89%
6			**3da**	87%
7			**3ea**	89%
8			**3fa**	49%

9			**3ga**	76%
10			**3ha**	70%
11			**3ia**	81%
12			**3ja**	77%
13			**3ka**	76%
14			**3la**	75%
15			**3ma**	50%
16			**3na**	67%
17			**3oa**	62%
18			**3pa**	67%

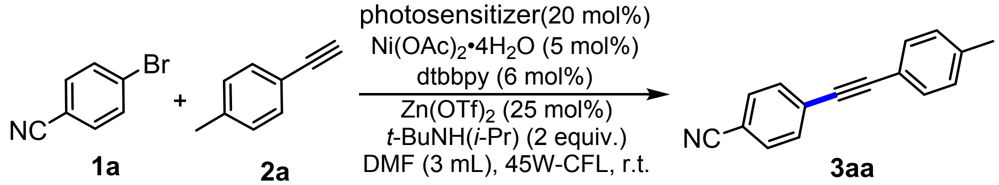
19			**3qa**	66%
20			**3ra**	72%
21			**3sa**	73%
22			**3ta**	81%
23			**3ua**	69%
24			**3va**	72%
25			**3wa**	62%

[a] **1** (0.2 mmol), **2a** (0.4 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (5 mol%), dtbbpy (6 mol%), *t*-BuNH(*i*-Pr) (0.4 mmol), $Zn(OTf)_2$ (25 mol%), TXO (20 mol%), 3 mL DMF, N_2, 45W-CFL for 24 h with cooling by fan and isolated yields.

We then moved on to examine the mechanism of this reaction system. Cyclic voltammetry (CV) of TXO revealed a reduction potential at E = -1.66 V vs. saturated calomel electrode (SCE) in DMF (Figure S2). Based on the electrochemical and spectroscopic data of TXO (Figure S3 and S4), the redox potentials of excited-states TXO* is estimated to be +1.34 V vs. SCE. So TXO* could engage one electron from (dtbbpy)-arylNi^{II} acetylide (E(Ni^{III}/Ni^{II}) = 0.83 V vs. SCE[35]) to generate a (dtbbpy)Ni^{III}-aryl acetylide and TXO$^{\bullet-}$. The Ni(III) species may then undergo reductive elimination[34,35] to afford an expected product and a (dtbbpy)Ni^{I} intermediate. The Ni(I) species would be readily reduced to [(dtbbpy)Ni^{0}] (E(Ni^{II}/Ni^{0}) = −1.20 V vs. SCE[34,35]) by TXO$^{\bullet-}$ (E(TXO/TXO$^{\bullet-}$) = -1.66 V vs. SCE in DMF). Such Ni-catalyzed coupling reaction might undergo electron transfer process (Scheme S1). To test this pathway, we performed a series of experiments with some other photocatalysts (entries 1-5, Table 4). The utilization of Eosin Y or Rose Bengal with similar oxidizing potentials instead of TXO drastically reduced the efficacy of the C−C cross coupling in our model system (entries 3 and 4). 9-Mesityl-10-methylacridinium perchlorate [Mes^{+}-Acr]ClO_4 with a much higher oxidizing potential than TXO (entry 5) did not provide any product under the identical conditions. These experiments suggest that a mechanism involving oxidation of Ni(II) to Ni(III) may not be operative in this transformation.

In light of the above experiments, we suspected that a mechanism involving triplet−triplet energy transfer from the excited-state of TXO (TXO*) to the Ni(II) complex might be operative. As displayed in Table 4, the reactivity was correlated with triplet state energy (E_T) of photocatalysts rather than with excited-state oxidation potential. TXO with highest E_T (63.4 kcal·mol^{-1}) proved most effective (entry 1). $Ir(ppy)_3$ with E_T of 55.2 kcal·mol^{-1} was a moderately efficient photocatalyst in combination with the nickel catalyst (entry 2). Rose Bengal (40.9 kcal·mol^{-1}) and [Mes$^+$-Acr]ClO_4 with lower triplet energy almost shut down the arylation reaction. On this basis of the information, this cross coupling possibly proceeded via an EnT manner.

Table 4. The Effect of Photosensitizer on the Coupling of 1a and 2a.



Entry^a	Photosensitizer	E* M/M (V)	E_m (nm)	E_T (kcal/mol)	Yield
1	TXO	1.34	414	63.4	92%
2	$Ir(ppy)_3$	0.31	518	55.2	44%

3	Eosin Y	1.18	539	-	6%
4	Rose Bengal	0.99	559	40.9	<1%
5	[Mes$^+$-Acr]ClO_4	2.05	590	-	0

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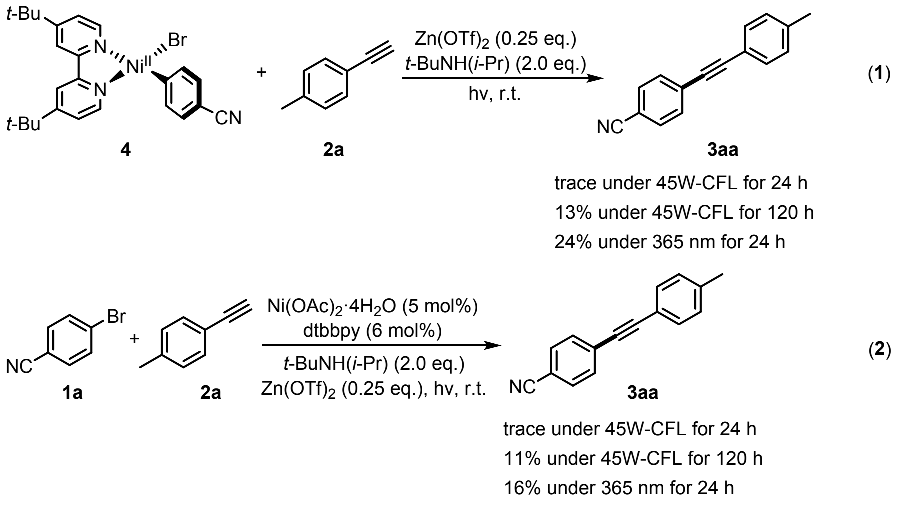
[a]**1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (5 mol%), dtbbpy (6 mol%), *t*-BuNH(*i*-Pr) (0.4 mmol), $Zn(OTf)_2$ (25 mol%), photosensitizer (20 mol%), 3 mL DMF, N_2, 45W-CFL for 24 h with cooling by fan and HPLC yields.

To further verify the EnT mechanism, we carried out the reaction of $Ni(COD)_2$ and dtbbpy with **1a** to offer (dtbbpy)-4-cyanophenylnickel(II) bromide (**4**). Compound **4** shows only a weak absorption at wavelengths of more than 400 nm (Figure S5). The visible light irradiation of the cross-coupling reaction of **4** and **2a** in the absence of TXO resulted in no conversion, suggesting that the operative triplet state is not accessible from the excited state of Ni(II) intermediate (eq 1, Scheme 2). UV irradiation (λ = 365 nm) of **4** and **2a** for 24 h led to the formation of the cross-coupling product **3aa** in 24% yield. In addition, the irradiation of the reaction of **1a** and **2a** in DMF without TXO under 45W-CFL for 24 h could not afford **3aa**. Only 11% yield of **3aa** could be achieved by prolonging the irradiation time to 120 h. The same reaction offered **3aa** in 16% yield after 24 h of λ = 365 nm irradiation (eq 2, Scheme 2). These experiments suggest a mechanism involving an energy-transfer pathway in which an excited-state of (dtbbpy)-4-cyanophenyl-(p-tolylethynyl)nickel(II) species (confirmed by electrospray ionization mass spectrometry (Figure S7)) underwent reductive elimination to form the desired product **3aa**. As discussed above, the 47% yield of **3aa** was achieved using Ni(COD)$_2$ as a catalyst (entry 8, Table 1), thus suggesting the involvement of a Ni(0) species in this transformation. These above results implied that the excited-state Ni(II) species generated by energy transfer from excited TXO underwent reductive elimination to form aryl alkyne and a reactive Ni(0) intermediate.

Scheme 2. The Studies of Reductive Elimination

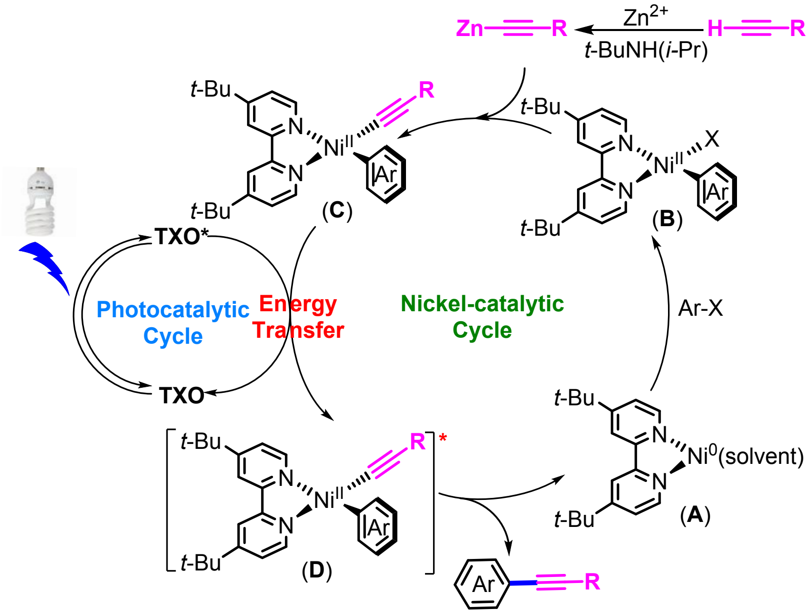


trace under 45W-CFL for 24 h
13% under 45W-CFL for 120 h
24% under 365 nm for 24 h

trace under 45W-CFL for 24 h
11% under 45W-CFL for 120 h
16% under 365 nm for 24 h

Based on the combination of above experiments and literature reports,[37,74,75,90-93] a plausible catalytic cycle is delineated in Scheme 3. The initial oxidative addition of [dtbbpyNi^0] (**A**) with aryl halide gives aryl-Ni(II)-halide complex **B**. Transmetallation of **B** with Zn(II) acetylide affords aryl-Ni(II) acetylide **C**. Simultaneously, the irradiation of TXO produces the triplet photoexcited state TXO* under visible light. The subsequent triplet-triplet energy transfer can occur between TXO* and **C**, affording the excited state of **C**. The resulting excited-state Ni(II) species (**D**) undergoes the reductive elimination to generate **3** and **A**, thereby completing the catalytic cycle.

Scheme 3. Proposed Mechanism



CONCLUSIONS

In summary, we have shown the Ni-catalyzed C(sp)–C(sp^2) couplings of alkynes with (hetero)aryl halides using the quite inexpensive photosensitizer thioxanthen-9-one as an energy transfer agent at ambient temperature and under the illumination of a household light bulb. The arylation of alkynes are compatible with a wide range of functional groups to provide aryl alkynes in moderate to excellent yields. The combination of a cheap, readily available organic photocatalyst with an earth-abundant metal catalyst provides a highly economical route to construct C-C and C-heteroatom bonds.

EXPERIMENTAL SECTION

General Information. All reagents were used as purchased without further purification. All solvents were obtained from commercial sources and were purified according to standard procedures. Column chromatography was performed on silica gel. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. The LC-MS (liquid chromatography mass spectroscopy) was recorded using a Rapid Resolution HT-3 chromatographic column on an Agilent 1260 Infinity Liquid Chromatograph with 6120 Quadrupole Mass Spectrometer and MeCN as mobile phase. High performance liquid chromatography (HPLC) was conducted on a LC-20AT with MeOH and H_2O as the mobile phase. High resolution mass spectra (HRMS) were obtained with a GCT Premier (Micromass UK Limited) chemical ionization time-of-flight mass spectrometer (CI-TOF). The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000-400 cm^{-1}).

Preparation of (dtbbpy)-4-cyanophenylnickel(II) bromide (4). This complex was synthesized by adapting the literature report.[90] In a nitrogen filled glove box, an ovendried 10 mL test tube was charged with Ni(COD)$_2$ (0.0550 g, 0.2 mmol), dtbbpy (0.0536 g, 0.2 mmol) and THF (3 mL). The mixture was stirred for 2 h at room temperature and the color of solution was turned into deep purple. 4-Bromobenzonitrile (0.1092 g, 0.6 mmol) was added and the reaction was left to stir for 20 min. The resulting dark red solution was triturated with pentane (10 mL). The precipitate was collected on a frit, rinsed with pentane and residual solvent was removed under vacuum to give an orange powder. The product was used without further purification. The complex was stored in a nitrogen filled glove box at -35 ºC. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, ppm) δ = 9.18 (s, 1H), 7.82 (m, 4H), 7.55 (d, *J* = 5.6, 1H), 7.18 (s, 4H), 1.41 (s, 9 H), 1.35 (s, 9H).

The Studies of Reductive Elimination. The (dtbbpy)-4-cyanophenylnickel(II) bromide (**4**) (0.1521 mg, 0.3 mmol) and 6 mL dried, degassed DMF, *t*-BuNH(*i*-Pr) (0.0690 mg, 0.6 mmol) and 1-ethynyl-4-methylbenzene (0.1044 g, 0.9 mmol) were added. The suspension was then stirred for 15min and 2 mL of this mixture was weighed into the other two 10 mL test tubes. These three test tubes were added with Zn(OTf)$_2$ (0.0092 g, 25 mol%) independently. The resulting mixture was stirred under

45W-CFL (Philips) and 365 nm irradiation for 24 h or 120 h with cooling by fan. Next, biphenyl was added as an internal standard, followed by water (10 mL) and the aqueous solution extracted with ethyl acetate (3 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4, and concentrated in vacuum. The crude product was dissolved in acetonitrile for monitoring by HPLC.

Experimental Procedures and Analytical Data. *Typical Reaction (Table 1, Entry 2).* A 10 mL test tube was weighted with **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (2.49 mg, 0.01 mmol), dtbbpy (3.22 mg, 0.012 mmol) and TXO (8.4 mg, 0.04 mmol), *t*-BuNH(*i*-Pr) (46.0 mg, 0.4 mmol), and $Zn(OTf)_2$ (18.2 mg, 25 mol%) in 3 mL degased, dried DMF. The reaction was stirred under a nitrogen atmosphere and irradiated with a household 45W CFL (Philips) for 24 h with cooling by fan. Next, 3 mL water was added and the mixture was extracted three times with ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate (EtOAc) as the eluent.

*4-(p-Tolylethynyl)benzonitrile (**3aa**).*[94] **3aa** was obtained in 91% yield (39.5 mg) based on 4-bromobenzonitrile, 94% yield (40.8 mg) based on 4-iodobenzonitrile, 40% yield (17.4 mg) based on 4-chlorobenzonitrile according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.60 (q, *J* = 8.2 Hz, 4H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm) δ = 139.7, 132.2, 132.2, 131.9, 129.5, 128.7, 119.3, 118.8, 111.4, 94.3, 87.4, 21.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NNa^+$ 240.0784; Found 240.0792.

*4-(Phenylethynyl)benzonitrile (**3ab**).*[95] **3ab** was obtained in 90% yield (36.5 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.61 (q, *J* = 8.3 Hz, 4H), 7.58–7.52 (m, 2H), 7.43–7.34 (m, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): *δ* 132.2, 132.2, 132.0, 129.3, 128.7, 128.4, 122.4, 118.7, 111.6, 94.0, 87.9. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_9NNa^+$ 226.0627; Found 226.0645.

*4-((4-Methoxyphenyl)ethynyl)benzonitrile (**3ac**).*[96] **3ac** was obtained in 87% yield (40.6 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.58 (dd, *J* = 17.6, 8.3 Hz, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 160.4, 133.5, 132.1, 132.0, 128.8, 118.8, 114.4, 114.3, 111.1, 94.3, 86.9, 55.5. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NONa^+$ 256.0733; Found 256.0721.

*4-((4-(Tert-butyl)phenyl)ethynyl)benzonitrile (**3ad**).*[97] **3ad** was obtained in 88% yield (45.6 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64–7.61 (m, 2H), 7.60–7.57 (m, 2H), 7.51–7.47 (m, 2H), 7.43–7.38 (m, 2H), 1.34 (s, 9H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 152.7, 132.2, 132.2, 131.7, 128.7, 125.7, 119.3, 118.7, 111.4, 94.4, 87.4, 35.1, 31.3. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{19}H_{17}NNa^+$ 282.1253; Found 282.1260.

*4-((4-Ethylphenyl)ethynyl)benzonitrile (**3ae**).* **3ae** was obtained in 86% yield (39.7 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid, mp = 105.8−106.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34 (q, J = 8.1 Hz, 4H), 7.21 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 2H), 2.42 (q, J = 7.5 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 145.9, 132.2, 132.2, 132.0, 128.7, 128.3, 119.6, 118.8, 111.4, 94.4, 87.4, 29.1, 15.5. IR (KBr disc, cm^{-1}): 2957, 2926, 2852, 2225, 2213, 1918, 1640, 1597, 1511, 1459, 1407, 1377, 1271, 1177, 1133, 1105, 1060, 1017, 973, 835, 556, 543. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{13}NNa^+$ 254.0940; Found 254.0955.

*4-((4-Pentylphenyl)ethynyl)benzonitrile (**3af**).* **3af** was obtained in 87% yield (47.5 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid, mp 77.5−78.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60 (q, J = 8.1 Hz, 4H), 7.46 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.63 (dd, J = 14.2, 7.2 Hz, 2H), 1.33 (d, J = 3.1 Hz, 5H), 0.90 (t, J = 6.5 Hz, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 144.7, 132.2, 132.1, 131.9, 128.8, 128.7, 119.5, 118.7, 111.4, 94.4, 87.4, 36.1, 31.6, 31.0, 22.7, 14.2. IR (KBr disc, cm^{-1}): 2958, 2926, 2856, 2217, 1910, 1674, 1600, 1512, 1456, 1405, 1377, 1262, 1183, 1103, 1019, 838, 802, 727, 555, 544. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{20}H_{19}NNa^+$ 296.1410; Found 296.1410.

*4-([1,1'-Biphenyl]-4-ylethynyl)benzonitrile (**3ag**).* **3ag** was obtained in 84% yield (46.9 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid, mp 177.8−178.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64 (d, J = 12.3 Hz, 9H), 7.57–7.43 (m, 3H), 7.39 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 142.0, 140.2, 133.6, 132.8, 132.4, 132.2, 129.1, 128.4, 128.1, 127.3, 127.2, 121.2, 118.7, 111.6, 94.0, 88.6. IR (KBr disc, cm^{-1}): 2957, 2925, 2853, 2231, 2215, 1637, 1598, 1500, 1459, 1483, 1406, 1378, 1261, 1178, 1098, 1020, 841, 803, 765, 690, 554. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{21}H_{13}NNa^+$ 302.0940; Found 302.0954.

*4-((4-Fluorophenyl)ethynyl)benzonitrile (**3ah**).*[96] **3ah** was obtained in 93% yield (41.1 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.56–7.49 (m, 2H), 7.07 (t, J = 8.5 Hz, 2H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ

163.1 (d, *J* = 252.2 Hz), 162.3, 133.9 (d, *J* = 8.5 Hz), 132.2, 132.1, 128.2, 118.6, 118.5 (d, *J* = 3.0 Hz), 116.1 (d, *J* = 21.1 Hz), 111.7, 92.8, 87.5. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_8FNNa^+$ 244.0533; Found 244.0517.

*4-((4-Chlorophenyl)ethynyl)benzonitrile (**3ai**).*[96] **3ai** was obtained in 91% yield (43.1 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.49–7.44 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 135.4, 133.2, 132.2, 132.2, 129.1, 128.0, 120.9, 118.6, 111.9, 92.7, 88.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_8ClNNa^+$ 260.0237; Found 260.0263.

*Methyl 4-((4-cyanophenyl)ethynyl)benzoate (**3aj**).* **3aj** was obtained in 92% yield (48.0 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 149.0−149.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.71–7.54 (m, 6H), 3.93 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 166.6, 132.4, 132.3, 131.9, 130.5, 129.8, 127.8, 127.0, 118.6, 112.2, 92.9, 90.5, 52.5. IR (KBr disc, cm^{-1}): 2954, 2924, 2851, 2225, 1938, 1721, 1604, 1559, 1514, 1494, 1446, 1433, 1405, 1308, 1290, 1281, 1173, 1136, 1109, 1015, 963, 857, 843, 823, 768, 692, 555, 527. QTOF-MS *m/z* m/z [M + Na]$^+$ Calcd for $C_{17}H_{11}NO_2Na^+$ 284.0682; Found 284.0687.

*4-(m-Tolylethynyl)benzonitrile (**3ak**).*[98] **3ak** was obtained in 86% yield (37.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): *δ* 7.60 (q, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 11.7 Hz, 2H), 7.26 (dd, *J* = 9.2, 5.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): *δ* 138.4, 132.5, 132.2, 132.2, 130.2, 129.1, 128.2, 128.5, 122.2, 118.7, 111.5, 94.2, 87.6, 21.4. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NNa^+$ 240.0784; Found 240.0793.

*4-((3-Fluorophenyl)ethynyl)benzonitrile (**3al**).* **3al** was obtained in 88% yield (38.9 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 108.2−108.9 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): *δ* 7.54 (q, *J* = 8.1 Hz, 4H), 7.31–7.21 (m, 2H), 7.20–7.11 (m, 1H), 7.01 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): *δ* 163.5 (d, *J* = 247.2 Hz), 132.3, 132.2, 130.3 (d, *J* = 8.6 Hz), 127.9, 127.8, 124.2 (d, *J* = 9.4 Hz), 118.8, 118.7 (d, *J* = 34.6 Hz), 116.7 (d, *J* = 21.2 Hz), 112.0, 92.4 (d, *J* = 3.3 Hz), 88.6. IR (KBr disc, cm^{-1}): 3070, 2963, 2229, 2206, 1607, 1577, 1501, 1481, 1431, 1407, 1317, 1262, 1207, 1174, 1098, 1021, 941, 862, 844, 800, 681, 552, 521, 455. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_8FNNa^+$ 244.0533; Found 244.0559.

*4-(o-Tolylethynyl)benzonitrile (**3am**).*[99] **3am** was obtained in 68% yield (29.5 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (q, *J* = 8.1 Hz, 4H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.32–7.23 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 2.51 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 140.7, 132.3, 132.2, 132.1, 129.8, 129.4, 128.7, 125.9, 122.2, 118.7, 111.6, 93.0, 91.8, 20.9. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NNa^+$ 240.0784; Found 240.0753.

*4-((2-Fluorophenyl)ethynyl)benzonitrile (**3an**).*[100] **3an** was obtained in 73% yield (32.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (s, 4H), 7.52 (t, *J* = 6.9 Hz, 1H), 7.37 (dd, *J* = 13.3, 6.3 Hz, 1H), 7.20–7.08 (m, 2H). $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$, ppm): δ 163.0 (d, *J* = 252.8 Hz), 133.7, 132.3 (d, *J* = 10.8 Hz), 131.1 (d, *J* = 8.0 Hz), 128.0, 124.3 (d, *J*

= 3.7 Hz), 118.6, 115.9 (d, *J* = 20.9 Hz), 112.1, 111.3, 111.1, 92.8 (d, *J* = 3.4 Hz), 87.2. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_8FNNa^+$ 244.0533; Found 244.0556.

*4-(Naphthalen-2-ylethynyl)benzonitrile (**3ao**).*[98] **3ao** was obtained in 62% yield (31.4 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.09 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 3H), 7.65 (s, 4H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 5.9, 3.0 Hz, 2H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): *δ* 133.3, 133.1, 132.3, 132.3, 128.4, 128.3, 128.1, 128.0, 127.4, 127.0, 119.7, 118.7, 111.7, 94.4, 88.3. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{19}H_{11}NNa^+$ 276.0784; Found 276.0792.

*4-(Thiophen-2-ylethynyl)benzonitrile (**3ap**).*[101] **3ap** was obtained in 63% yield (26.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.63 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.34 (d, *J* = 3.1 Hz, 1H), 7.07–7.03 (m, 1H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): *δ* 133.3, 132.3, 131.9, 128.7, 128.1, 127.6, 122.3, 118.7, 111.7, 91.7, 87.4. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{13}H_7NSNa^+$ 232.0191; Found 232.0167.

*4-(Pyridin-4-ylethynyl)benzonitrile (**3aq**).* **3aq** was obtained in 55% yield (22.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid, mp 110.6−111.4 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.64 (d, J = 5.5 Hz, 2H), 7.65 (q, J = 8.2 Hz, 4H), 7.39 (d, J = 5.6 Hz, 2H). ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$, ppm): δ 150.2, 132.6, 132.4, 130.6, 127.2, 125.7, 118.4, 112.8, 91.9, 90.7. IR (KBr disc, cm^{-1}): 3072, 3059, 2957, 2924, 2852, 2232, 1925, 1736, 1637, 1605, 1590, 1518, 1503, 1459, 1406, 1378, 1320, 1270, 1221, 1187, 1082, 1025, 986, 855, 842, 820, 630, 558, 547, 493, 460. QTOF-MS m/z [M + Na]$^+$ Calcd for $C_{14}H_8N_2Na^+$ 227.0580; Found 227.0578.

*4-(Pyrimidin-5-ylethynyl)benzonitrile (**3ar**).* **3ar** was obtained in 59% yield (24.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid, mp 195.5−196.3 °C. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 9.19 (s, 1H), 8.88 (s, 2H), 7.67 (q, J = 8.2 Hz, 4H). ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$, ppm): δ 159.0, 157.6, 132.5, 132.4, 126.8, 119.2, 118.3, 113.0, 94.4, 86.5. IR (KBr disc, cm^{-1}): 2924, 2225, 1601, 1575, 1543, 1497, 1426, 1413, 1272, 1186, 1178, 1104, 1041, 1013, 920, 847, 839, 718, 633, 559, 531, 459. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{13}H_7N_3Na^+$ 228.0532; Found 228.0540.

*4-(Oct-1-yn-1-yl)benzonitrile (**3as**).*[98] **3as** was obtained in 91% yield (38.4 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.65–1.55 (m, 2H), 1.44 (dt, *J* = 14.1, 7.2 Hz, 2H), 1.32 (d, *J* = 3.2 Hz, 4H), 0.90 (t, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 132.3, 132.1, 129.4, 118.8, 110.9, 95.9, 79.6, 31.5, 28.8, 28.6, 22.7, 19.7, 14.2. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_{17}NNa^+$ 234.1253; Found 234.1267.

*4-(Cyclopropylethynyl)benzonitrile (**3at**).*[102] **3at** was obtained in 89% yield (29.7 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 1.53–1.39 (m, 1H), 0.96–0.88 (m, 2H), 0.87–0.79 (m, 2H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 132.2, 132.1, 129.2, 118.8, 110.8, 99.0, 74.8, 9.1, 0.4. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{12}H_9NNa^+$ 190.0627; Found 190.0634.

*4-(Cyclohexylethynyl)benzonitrile (**3au**).*[103] **3au** was obtained in 92% yield (38.5 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 2.60 (dd, J = 10.6, 7.2 Hz, 1H), 1.93–1.82 (m, 2H), 1.74 (d, J = 4.5 Hz, 2H), 1.53 (d, J = 11.1 Hz, 3H), 1.35 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 132.3, 132.0, 129.4, 118.8, 110.9, 99.7, 79.6, 32.6, 29.9, 25.99, 25.0. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{15}NNa^+$ 232.1097; Found 232.1073.

*4-(3-Hydroxy-3-methylbut-1-yn-1-yl)benzonitrile (**3av**).*[104] **3av** was obtained in 83% yield (30.7 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 2.30 (s, 1H), 1.61 (s, 6H). $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$, ppm): δ 132.3, 132.1, 127.9, 118.6, 111.8, 98.5, 80.8, 65.8, 31.5. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{12}H_{11}NONa^+$ 208.0733; Found 208.0757.

*4-((Trimethylsilyl)ethynyl)benzonitrile (**3aw**).*[105] **3aw** was obtained in 82% yield (32.6 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): orange solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.58 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 0.26 (s, 9H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 132.6, 132.1, 128.2, 118.6, 111.9, 103.2, 99.7, 1.2. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{12}H_{13}NSiNa^+$ 222.0709; Found 222.0702.

*4-(((8R,9S,10R,13S,14S,17S)-17-Hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethynyl)benzonitrile (**3ax**).* **3ax** was obtained in 45% yield (37.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid, mp 201.2−201.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 5.73 (s, 1H), 2.44–2.25 (m, 5H), 2.21–1.98 (m, 3H), 1.87 (d, J = 12.2 Hz, 1H), 1.76–1.64 (m, 5H), 1.45 (dd, J = 11.8, 6.4 Hz, 2H), 1.30 (d, J = 19.3 Hz, 1H), 1.21 (s, 4H), 0.95 (s, 4H), 0.90–0.78 (m, 1H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 199.6, 171.0, 132.4, 132.2, 127.9, 124.2, 118.6, 111.9, 97.3, 84.9, 80.4, 53.7, 50.6, 47.5, 39.2, 38.9, 36.5, 35.9, 34.2, 33.1, 32.9, 31.7, 23.4, 21.0, 17.7, 13.1. IR (KBr disc, cm^{-1}): 2948, 2917, 2887, 2854, 2224, 1658, 1615, 1602, 1500, 1453, 1437, 1376, 1361, 1335, 1272, 1231, 1183, 1147, 1126, 1105, 1070, 1046, 1025, 965, 868, 841, 804, 557. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{28}H_{31}NO_2Na^+$ 436.2247; Found 436.2268.

4-(((8R,9S,10R,13S,14S,17S)-13-ethyl-17-hydroxy-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethynyl)benzonitrile (**3ay**). **3ay** was obtained in 47% yield (38.8 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid, mp 145.6–146.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60 (d, J = 7.8, 2H), 7.50 (d, J = 8.0, 2H), 5.84 (s, 1H), 2.46 (dd, J = 30.6, 15.4, 3H), 2.35–2.17 (m, 5H), 2.10 (d, J = 12.6, 3H), 2.03–1.80 (m, 4H), 1.71 (s, 2H), 1.57–1.46 (m, 5H), 1.18–1.08 (m, 2H), 1.04 (t, J = 7.1, 4H), 0.93–0.83 (m, 2H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$, ppm): δ 200.1, 166.6, 132.3, 132.2, 127.9, 124.9, 118.6, 111.9, 97.8, 84.9, 82.1, 51.5, 49.2, 48.9, 42.7, 41.1, 39.9, 36.7, 35.7, 30.9, 29.1, 26.8, 26.4, 22.8, 19.3, 9.8. IR (KBr disc, cm^{-1}): 2934, 2871, 2226, 1660, 1501, 1450, 1384, 1262, 1210, 1130, 1060, 875, 842, 559, 467, 457. QTOF-MS m/z [M + Na]$^+$ Calcd for $C_{28}H_{31}NO_2Na^+$ 436.2247; Found 436.2229.

*1-Methyl-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene (**3ba**).*[95] **3ba** was obtained in 85% yield (44.2 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.68–7.54 (m, 4H), 7.46 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): δ 139.3, 131.9, 131.8, 129.9 (q, J = 32.6 Hz), 129.4, 127.6, 125.4 (q, J = 3.7 Hz), 124.3 (q, J = 272.1 Hz), 119.7, 92.3, 87.6, 21.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}F_3Na^+$ 283.0705; Found 283.0711.

*1-(4-(p-Tolylethynyl)phenyl)ethan-1-one (**3ca**).*[94] **3ca** was obtained in 89% yield (41.7 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.93 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.7 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 2.61 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): δ 197.5, 139.2, 136.2, 131.8, 131.8, 129.4, 128.6, 128.4, 119.7, 93.2, 88.2, 26.8, 21.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{14}ONa^+$ 257.0937; Found 257.0925.

*Methyl 4-(p-tolylethynyl)benzoate (**3da**).*[106] **3da** was obtained in 87% yield (43.5 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 3.93 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 166.7, 139.2, 131.8, 131.6, 129.6, 129.4, 129.3, 128.4, 119.8, 92.8, 88.2, 52.4, 21.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{14}O_2Na^+$ 273.0886; Found 273.0864.

*Ethyl 4-(p-tolylethynyl)benzoate (**3ea**).*[107] **3ea** was obtained in 89% yield (47.0 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, J = 7.9 Hz, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 2.38 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 166.3, 139.1, 131.8, 131.5, 129.8, 129.6, 129.4, 128.3, 119.8, 92.7, 88.3, 61.3, 21.7, 14.5. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{18}H_{16}O_2Na^+$ 287.1043; Found 287.1047.

*1-Methoxy-4-(p-tolylethynyl)benzene (**3fa**).*[95] **3fa** was obtained in 49% yield (21.8 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.46 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$, ppm): δ 159.7, 138.2, 133.2, 131.5, 129.3, 120.8, 115.9, 114.2, 88.9, 88.4, 55.5, 21.7. QTOF-MS m/z [M + Na]$^+$ Calcd for $C_{16}H_{14}ONa^+$ 245.0937; Found 245.0913.

*1-(p-Tolylethynyl)-3,5-bis(trifluoromethyl)benzene (**3ga**).* **3ga** was obtained in 76% yield (49.9 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 79.5−80.1 ℃. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.95 (s, 2H), 7.80 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.24–7.17 (m, 2H), 2.40 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): δ 139.8, 132.1 (q, J = 33.7 Hz), 131.9, 131.6 (d, J = 2.3 Hz), 129.8, 129.5, 126.1, 125.2 (q, J = 272.8 Hz), 121.5 (q, J = 7.1 Hz), 119.0, 93.3, 86.0, 21.8. IR (KBr disc, cm^{-1}): 3091, 2922, 2228, 2201, 1796, 1615, 1515, 1464, 1386, 1284, 1174, 1127, 1106, 906, 890, 845, 816, 734, 696, 683, 533, 520, 500. QTOF-MS m/z [M + Na]$^+$ Calcd for $C_{17}H_{10}F_6Na^+$ 351.0579; Found 351.0572.

*3-(p-Tolylethynyl)-5-(trifluoromethyl)benzonitrile (**3ha**).* **3ha** was obtained in 70% yield (39.9 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 70.4−70.9 ℃. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.95 (d, J = 8.9 Hz, 2H), 7.82 (s, 1H), 7.45 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): δ 140.1, 137.8, 132.6 (q, J = 34.0 Hz), 132.3 (q, J = 3.5 Hz), 131.9, 129.5, 127.7 (q, J = 3.6 Hz), 126.6, 122.8 (q, J = 273.0 Hz), 118.7, 116.9, 114.1, 94.4, 85.2, 21.8. IR (KBr disc, cm^{-1}): 3071, 3026, 2961, 2924, 2234, 2207, 1837, 1599, 1509, 1445, 1365, 1288, 1262, 1173, 1127, 1109, 1018, 945, 915, 892, 877, 813, 721, 690, 682, 641, 605, 527, 500, 514, 434. QTOF-MS m/z [M + Na]$^+$ Calcd for $C_{17}H_{10}F_3NNa^+$ 308.0658; Found 308.0660.

*3-(p-Tolylethynyl)benzonitrile (**3ia**).* **3ia** was obtained in 81% yield (35.2 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 103.8−104.7 ℃. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.79 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 8.3 Hz, 3H), 7.18 (d, J = 7.7 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$, ppm): δ 139.4, 135.7, 134.9, 131.8, 131.3, 129.4, 129.4, 125.3, 119.3, 118.3, 113.0, 92.2, 86.5, 21.7. IR (KBr disc, cm^{-1}): 3068, 2962, 2923, 2360, 2233, 2206, 1913, 1637, 1592, 1570, 1508, 1475, 1412, 1383, 1261, 1170, 1089, 1018, 908, 817, 808, 710, 685, 528, 485, 465. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NNa^+$ 240.0784; Found 240.0784.

*1-(3-(p-Tolylethynyl)phenyl)ethan-1-one (**3ja**).* **3ja** was obtained in 77% yield (36.1 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 68.8−69.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.10 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.48–7.40 (m, 3H), 7.17 (d, *J* = 7.7 Hz, 2H), 2.62 (s, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): *δ* 197.6, 139.0, 137.3, 135.9, 131.8, 131.7, 129.4, 128.8, 127.8, 124.3, 119.9, 90.8, 87.9, 26.8, 21.7. IR (KBr disc, cm^{-1}): 2962, 2919, 2218, 1684, 1591, 1508, 1473, 1422, 1352, 1300, 1273, 1243, 1107, 1019, 973, 921, 880, 815, 794, 685, 588, 516, 503, 447. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{14}ONa^+$ 257.0937; Found 257.0940.

*4-(p-Tolylethynyl)-2-(trifluoromethyl)benzonitrile (**3ka**).* **3ka** was obtained in 76% yield (43.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1):

yellow solid, mp 150.7−151.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.90 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): *δ* 140.3, 134.8, 134.7, 133.2 (q, *J* = 32.9 Hz), 132.1, 129.7 (q, *J* = 4.7 Hz), 129.6, 129.3, 127.3, 122.3 (q, *J* = 274.2 Hz), 118.7, 115.5, 108.7, 96.4, 86.3, 21.9. IR (KBr disc, cm^{-1}): 2963, 2230, 2210, 1601, 1556, 1513, 1419, 1337, 1261, 1166, 1096, 1019, 909, 865, 848, 800, 683, 557, 528. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{10}F_3NNa^+$ 308.0658; Found 308.0664.

*2-Fluoro-5-(p-tolylethynyl)benzonitrile (**3la**).* **3la** was obtained in 75% yield (35.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid, mp 83.9−84.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.77 (d, *J* = 5.6 Hz, 1H), 7.74–7.68 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.20 (dd, *J* = 14.0, 8.2 Hz, 3H), 2.38 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): *δ* 162.4 (d, *J* = 261.9 Hz), 139.5, 138.1 (d, *J* = 8.4 Hz), 136.4, 131.8, 129.5, 121.4 (d, *J* = 4.0 Hz), 119.2, 117.0 (d, *J* = 20.4 Hz), 113.4, 102.3 (d, *J* = 16.3 Hz), 91.8, 85.4, 21.8. IR (KBr disc, cm^{-1}): 2963, 2925, 2850, 2233, 1629, 1560, 1513, 1492, 1261, 1097, 1022, 802, 701, 529, 487. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{10}FNNa^+$ 258.0689; Found 258.0699.

*2-(p-Tolylethynyl)benzonitrile (**3ma**).*[108] **3ma** was obtained in 50% yield (21.7 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 139.7, 132.8, 132.5, 132.2, 132.1, 129.4, 128.2, 127.6, 119.1, 117.8, 115.3, 96.5, 85.3, 21.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{11}NNa^+$ 240.0784; Found 240.0798.

*2-Methyl-4-(p-tolylethynyl)-1-(trifluoromethyl)benzene (**3na**).* **3na** was obtained in 67% yield (36.7 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid, mp 101.4−101.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, J = 8.0 Hz, 1H), 7.48–7.37 (m, 4H), 7.18 (d, J = 7.7 Hz, 2H), 2.48 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 139.2, 137.0, 134.8, 132.6, 131.8, 129.4, 128.9, 128.4 (q, J = 30.1 Hz), 127.2, 126.0 (q, J = 5.6 Hz), 124.6 (q, J = 273.5 Hz), 119.8, 91.8, 87.7, 21.8, 19.4. IR (KBr disc, cm^{-1}): 2955, 2924, 2850, 2209, 1730, 1644, 1606, 1565, 1459, 1377, 1313, 1273, 1173, 1122, 1041, 892, 837, 818, 753, 615, 528, 446. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{13}F_3Na^+$ 297.0862; Found 297.0854.

*2-(p-Tolylethynyl)naphthalene (**3oa**).*[96] **3oa** was obtained in 62% yield (30.0 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.05 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 3H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$, ppm): δ 138.7, 133.3, 132.9, 131.8, 131.5, 129.4, 128.7, 128.2, 127.9, 126.8, 126.7, 121.1, 120.1, 90.2, 89.3, 21.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{19}H_{14}Na^+$ 265.0988; Found 265.0990.

*1-(6-(p-Tolylethynyl)pyridin-2-yl)ethan-1-one (**3pa**).*[109] **3pa** was obtained in 67% yield (31.5 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 7.96 (d, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 2.77 (s, 3H), 2.39 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): *δ* 200.1, 154.0, 143.3, 139.8, 137.2, 132.2, 130.7, 129.4, 120.6, 119.1, 90.4, 87.9, 26.1, 21.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{13}NONa^+$ 258.0889; Found 258.0862.

*2-(p-Tolylethynyl)-6-(trifluoromethyl)pyridine (**3qa**).* **3qa** was obtained in 66% yield (34.5 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): yellow solid, mp 108.1−108.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (151 MHz, $CDCl_3$, ppm): δ 148.8 (q, J = 34.9 Hz), 144.4, 140.0, 137.7, 132.3, 129.9, 129.4, 121.3 (q, J = 274.5 Hz), 119.2 (q, J = 2.5 Hz), 118.8, 91.7, 87.2, 21.8. IR (KBr disc, cm^{-1}): 3069, 2963, 2223, 2194, 1588, 1567, 1509, 1461, 1419, 1382, 1346, 1305, 1261, 1248, 1191, 1110, 1020, 993, 899, 818, 744, 711, 686, 652, 526, 507. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_{10}F_3NNa^+$ 284.0658; Found 284.0670.

*6-(p-Tolylethynyl)picolinonitrile (**3ra**).*[109] **3ra** was obtained in 72% yield (31.4 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.62 (d, J =

7.6 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$, ppm): *δ* 145.6, 140.4, 137.5, 134.5, 132.4, 130.3, 129.5, 127.1, 118.5, 116.9, 92.4, 86.7, 21.9. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{10}N_2Na^+$ 241.0736; Found 241.0739.

*4-(p-Tolylethynyl)pyridine (**3sa**).*[110] **3sa** was obtained in 73% yield (28.2 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^1H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.58 (d, *J* = 4.7 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 4.7 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H). $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$, ppm): *δ* 149.9, 139.7, 132.0, 131.9, 129.5, 125.7, 119.3, 94.5, 86.3, 21.8. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}NNa^+$ 216.0784; Found 216.0754.

*4-(p-Tolylethynyl)-2-(trifluoromethyl)pyridine (**3ta**).* **3ta** was obtained in 81% yield (42.3 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): yellow solid, mp 79.3−80.1 ℃. ^1H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.69 (d, *J* = 4.8 Hz, 1H), 7.75 (s, 1H), 7.53 (d, *J* = 4.6 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): *δ* 150.2, 148.6 (q, *J* = 34.8 Hz), 140.4, 133.7, 132.1, 129.6, 128.1, 122.5 (q, *J* = 2.7 Hz), 121.5 (q, *J* = 274.5 Hz), 118.5, 96.6, 85.3, 21.8. IR (KBr disc, cm^{-1}): 2963, 2928, 2238, 2218, 2199, 1917, 1598, 1541, 1511, 1422, 1339, 1308, 1262, 1212, 1188, 1175, 1129, 1103, 1087, 1019, 898, 852, 819, 802, 690, 665, 526, 495, 482, 465. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{15}H_{10}F_3NNa^+$ 284.0658; Found 284.0674.

*2-Methyl-4-(p-tolylethynyl)pyridine (**3ua**).* **3ua** was obtained in 69% yield (28.6 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): brown solid, mp 88.4−88.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 8.45 (d, *J* = 5.0 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.23 (s, 1H), 7.15 (d, *J* = 7.3 Hz, 3H), 2.54 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$NMR (151 MHz, $CDCl_3$, ppm): δ 158.5, 149.1, 139.5, 132.0, 131.9, 129.4, 125.1, 122.7, 119.3, 93.9, 86.5, 24.4, 21.7. IR (KBr disc, cm^{-1}): 2959, 2923, 2851, 2209, 1925, 1644, 1594, 1535, 1510, 1465, 1379, 1261, 1215, 1180, 1097, 1019, 888, 832, 819, 589, 530, 493, 479, 450. QTOF-MS *m/z* [M + H]$^+$ Calcd for $C_{15}H_{13}NH^+$ 208.1120; Found 208.1151.

*3-(p-Tolylethynyl)quinoline (**3va**).*[111] **3va** was obtained in 72% yield (35.0 mg) according to the general procedure (petroleum ether/EtOAc, 10:1): white solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): *δ* 8.99 (s, 1H), 8.29 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$, ppm): *δ* 152.4, 146.9, 139.3, 138.3, 131.8, 130.2, 129.6, 129.4, 127.8, 127.5, 127.5, 119.7, 117.9, 93.1, 86.2, 21.8. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{18}H_{13}NNa^+$ 266.0940; Found 266.0963.

*5-(p-Tolylethynyl)benzo[d][1,3]dioxole (**3wa**).*[95] **3wa** was obtained in 62% yield (29.3 mg) according to the general procedure (petroleum ether/EtOAc, 100:1): white solid. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): *δ* = 7.41 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), 2.37 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$, ppm): δ 148.0, 147.6, 138.4, 131.6, 129.3, 126.3, 120.5, 117.0, 111.7, 108.7, 101.5, 88.8, 88.2, 21.7. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{16}H_{12}O_2Na^+$ 259.0730; Found 259.0713.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

^{1}H NMR and ^{13}C NMR spectra of products

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Notes

The authors declare no competing financial interests.

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