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Highly efficient synthesis of 1,2-disubstituted acetylenes derivatives from the cross-coupling reactions of 1-bromoalkynes with organotitanium reagents

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ABSTRACT

A Highly efficient route for the synthesis of 1,2-disubstituted acetylene derivatives has been developed by nickel catalyzed cross-couplings of alkynyl halides with aryl titanium reagents under mild conditions. This has given corresponding cross-coupling products good to excellent isolated yields of up to 92 %. The aryls bearing electron-donating or electron-withdrawing groups in either alkynylhalides or aryltitanium substrates gave cross-coupling products good yields. This process was simple and easily performed, which provides an efficient method for the synthesis of 1,2-disubstituted acetylenes derivatives.

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1. Introduction

The 1,2-disubstituted acetylenic products are important synthetic units in the preparation of potential bioactive compounds [1], new materials [2], and natural products as well [3]. The synthetic methods of 1,2-disubstituted acetylenic compounds have been widely concerned by chemists. Since the discovery of Sonogashira coupling reaction in 1970s [4], this coupling reaction has become one of the most effective methods to synthesize the 1,2-disubstituted acetylenic compounds [5]. Concerning the importance of this reaction, researchers have directed their efforts towards the development of more efficient or single metal catalyst systems, milder reaction conditions, and other such objectives during the past decades [6]. Among these methods, the typical synthetic protocols for 1,2-disubstituted acetylenic compounds include transition metal (such as Ni, Cu, Pd) catalyzed cross-coupling of Grignard reagents or organoalane with alkynyl bromides [7], transition metal (such as Pd, Ni and Cu) catalyzed cross-coupling reactions of electrophiles with alkynylmetallic reagents [8]. Although, these efforts have provided alternative methods for the synthesis of 1,2-disubstituted acetylenic compounds, these reactions still suffer from excess bases, co-catalysts, high temperature, relatively long reaction time, or the special reaction medium. The development of more efficient and atom economical approaches for the synthesis of 1,2-disubstituted acetylenic compounds remains as desirable work. Aryl halides, especially aryl iodides and bromides, and alkynes are the preferred coupling partners in these reactions. Particularly, 1-bromoalkynes, which is easily synthesized from terminal alkynes, has been widely applied in cross-coupling reactions [9]. In addition to the above reagents, organotitanium reagents have been extensively used as nucleophiles for organic reactions [10].

Previous studies show that organotitanium reagents are a highly efficient nucleophiles for cross-coupling reactions with aromatic halides or benzylic halides [10e,g,i,k,l]. While, the synthesis based on direct coupling of alkynyl halide with organotitanium reagents using nickel as catalyst is developed rarely. To continue our efforts

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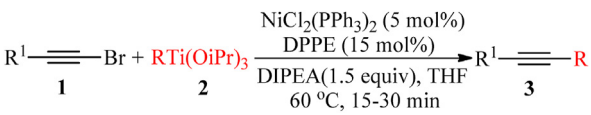
in developing coupling reactions using reactive organometallic reagents [7c,11], and develop a more efficient and convenient procedures for the preparation of 1,2-disubstituted acetylenes compounds, herein, we wish to report a new method for the synthesis of 1,2-disubstituted acetylenes compounds via nickel-catalyzed cross-couplings between 1-bromoalkynes and organotitanium reagents in the presence of $NiCl_2(PPh_3)_2$ (5 mol%)/DPPE (15 mol%) and DIPEA as base at 60 °C for 15–30 min. Notably, nickel is used as the single catalyst to give 1,2-disubstituted acetylenes compounds in good to excellent isolated yields in this procedure (Scheme 1).

2. Results and discussion

In our initial research, we performed the reaction between 1-(2-bromoethynyl)-4-methylbenzene (p-$MeC_6H_4C{\equiv}CBr$)(**1a**, 0.5 mmol) with triisopropoxy(phenyl)titanium ($PhTi(O^iPr)_3$) (**2a**, 0.8 mmol) in the presence of $Ni(acac)_2$ (5 mol%) and 10 mol% DPPE in THF at 60 °C for 0.5 h. To our delight, 32 % isolated yield of the desired 1-methyl-4-(2-phenylethynyl)-benzene(**3aa**) was obtained (Table 1, entry 1). Then, different nickel salts were examined (Table 1, entries 2–4). Notably, $NiCl_2(PPh_3)_2$ gave the best result among the tested nickel salts (Table 1, entry 4). To further understand the nature of this catalysis, we tested the reaction of **1a** with **2a** under various conditions and the results are listed in Tables 1 and 2. The effect of various ligands in the generation of **3aa** using $NiCl_2(PPh_3)_2$ as catalyst is shown in Table 1 (Table 1, entries 5–8). It was found that the DPPE ligand was the best effective for the reactivity (38 % isolated yield, Table 1, entry 4). The other phosphine ligands did not provide satisfactory results (Table 1, entries 5–8). In the same conditions, bases were subsequently surveyed. The isolated yield of coupling product **3aa** was up to 49 % when using DIPEA as base. Other bases such as K_2CO_3, K_3PO_4, Et_3N and ^tBuOK were less effective than DIPEA (Table 1, entries 9–12).

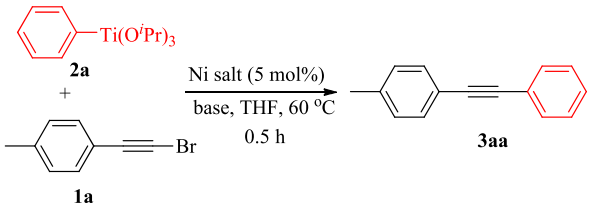
A brief examination of the influence of solvent on the isolated yield of the coupling product **3aa** revealed that THF was the solvent of choice. In toluene, hexane, or DMF, the isolated yield of the coupling product **3aa** was very low (Table 2, entries 1–3). Further studies indicated that the catalyst loading dramatically influenced the isolated yield of the coupling product **3aa**. When the $NiCl_2(PPh_3)_2$ loading increases from 5 mol% to 8 mol%, the isolated yield of the coupling product **3aa** is basically unchanged (Table 1, entry 13, Table 2, entry 5). In contrast, reducing the $NiCl_2(PPh_3)_2$ loading to 2.5 mol% decreased the isolated yield of the coupling product **3aa** to 35 % (Table 2, entry 4).

The molar ratio of metal and ligand was examined. When the mol ratio of $NiCl_2(PPh_3)_2$ and DPPE was altered to 1:1, the isolated yield of the coupling product **3aa** decreased to 32 % (Table 2, entry 6). While the moral ratio of $NiCl_2(PPh_3)_2$ and DPPE was altered to 1:3, the isolated yield of the coupling product **3aa** increased to 54 % (Table 2, entry 7). When the $PhTi(O^iPr)_3$ (**2a**) loading increases from 0.8 mmol to 1.0 mmol, the isolated yield of the coupling product **3aa** was increased (Table 2, entries 7, 9). In contrast, reducing the $PhTi(O^iPr)_3$ (**2a**) loading to 0.6 mmol decreased the isolated yield of the coupling product **3aa** to 29 % (Table 2, entries 7, 8). It is worth noting that the isolated yield of the desired coupling product **3aa** is basically unchanged when the reaction time is shortened from 10 h to 0.5 h (Table 2, entries 9–12). However, the isolated yield of the coupling product **3aa** were decreased when the reaction time is shortened from 0.5h to 0.25 h (Table 2, entries 12, 13). Furthermore, the isolated yield of the coupling product **3aa** is basically unchanged when the reaction temperature increased from 60 °C to



Scheme 1. Nickel-catalyzed cross-coupling reactions of 1-bromoalkyne derivatives with organotitanium nucleophiles.

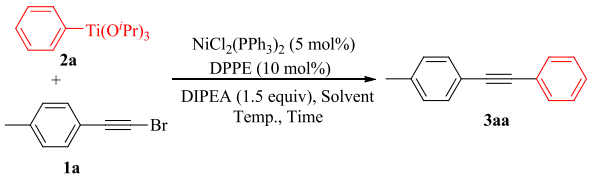
Table 1
Effect of the nickel salt, base and ligand on the cross-coupling reaction. [a].



Entry	Cat.	Base (1.5 equiv)	Ligand	Yield 3aa (%)[b]
1	$Ni(acac)_2$	–	DPPE	32
2	$NiI_2(PPh_3)_2$	–	DPPE	27
3	$Ni(dppf)Cl_2$	–	DPPE	28
4	$NiCl_2(PPh_3)_2$	–	DPPE	38
5	$NiCl_2(PPh_3)_2$	–	PCy_3	16
6	$NiCl_2(PPh_3)_2$	–	TFP	15
7	$NiCl_2(PPh_3)_2$	–	DPPB	21
8	$NiCl_2(PPh_3)_2$	–	Xantphos	23
9	$NiCl_2(PPh_3)_2$	K_2CO_3	DPPE	41
10	$NiCl_2(PPh_3)_2$	K_3PO_4	DPPE	32
11	$NiCl_2(PPh_3)_2$	Et_3N	DPPE	41
12	$NiCl_2(PPh_3)_2$	^tBuOK	DPPE	38
13	$NiCl_2(PPh_3)_2$	DIPEA	DPPE	49

[a] **1a**/**2a**/Cat/Ligand = 0.5/0.8/0.025/0.05 mmoL, THF 3 mL.
[b] Isolated yield.

Table 2
Efffect of the solvent, reaction temperature and the molar ratio of $NiCl_2(PPh_3)_2$/DPPE on the cross-coupling reaction.[a]



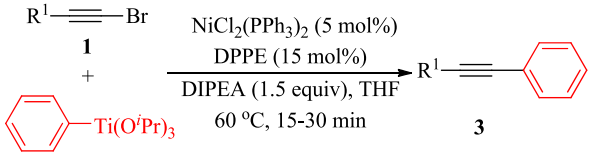
Entry	2a(mmol)	Solvent	Time (h)	Yield 3aa(%)[b]
1	0.8	toluene	10	15
2	0.8	hexane	10	11
3	0.8	DMF	10	trace
4[c]	0.8	THF	10	35
5[d]	0.8	THF	10	48
6[e]	0.8	THF	10	32
7[f]	0.8	THF	10	54
8	0.6	THF	10	29
9	1.0	THF	10	57
10	1.0	THF	5	57
11	1.0	THF	1	56
12	1.0	THF	0.5	56
13	1.0	THF	0.25	50
14[g]	1.0	THF	0.5	55

[a] **1a**/**2a**/$NiCl_2(PPh_3)_2$/DPPE = 0.5/0.8/0.025/0.05 mmol, 60 °C.
[b] Isolated.
[c] **1a**/**2a**/$NiCl_2(PPh_3)_2$/DPPE = 0.5/0.8/0.0125/0.025 mmol, 60 °C.
[d] **1a**/**2a**/$NiCl_2(PPh_3)_2$/DPPE = 0.5/0.8/0.04/0.08 mmol, 60 °C.
[e] $NiCl_2(PPh_3)_2$/DPPE = 1/1.
[f] $NiCl_2(PPh_3)_2$/DPPE = 1/3.
[g] 80 °C.

80 °C (Table 2, entries 12,14). Extensive screening showed that the optimized coupling conditions were 5 mol% $NiCl_2(PPh_3)_2$/15 mol% DPPE, 0.5 mmol **1a**, 1.0 mmol **2a** in THF at 60 °C for 0.5 h (Table 2, entry 12).

With the optimized conditions in hand, the scope of this reaction was studied by using various 1-bromoalkynes (**1**). The triisopropoxy(phenyl)titanium ($PhTi(O^iPr)_3$) (**2a**) reacted smoothly with a series of 1-bromoalkynes **1**(**a**–**o**) at 60 °C for 15–30 min to give the corresponding coupling products **3**(**aa**–**oa**) in moderate to excellent isolated yields (Table 3, entries 1–15). As listed in Table 3, the reaction was not significantly affected by the substituents on the aromatic ring of the 1-bromoalkynes. Both electron-rich (Table 3, entries 1, 3–6) and electron-deficient substituents (Table 3, entries 7–13) were tolerated. Notably, methyl, ethyl, butyl, ^{t}butyl, alkoxyl, bromo, chloro, fluoro and trifluoromethyl groups posed no challenges under the described reaction conditions. Especially, a series of coupling products 1,2-disubstituted acetylenes (**3**) with fluoro and trifluoromethyl on aryl rings of 1-bromoalkynes were synthesized in excellent isolated yields (Table 4, entries 9–11, 13, 86–92 % yields). Furthermore, even with sterically hindered 2-(2-bromoethynyl)naphthalene (**1o**) (Table 3, entry 15), the coupling reaction underwent smoothly to give good isolated yield of the coupling product **3oa** (Table 3, entry 15, 82 % yield). Importantly, the reaction also worked well with the 2-(2-bromoethynyl)thiophene (**1n**) and gave moderate isolated yield of the coupling product **3na** (Table 3, entry 14, 48 % yield). To our delight, 4-(bromoethynyl)benzoate can react with phenyltitanium to obtain isopropoxy 4-(phenylethynyl)benzoate (**4pa**) with 61 % isolated yield, this may be formed by the formation of 4-phenylethynylbenzoate and then exchange with isopropoxy group in the reaction system(Table 3, entry 16). In contrast, under the same conditions, 2-(bromoethynyl)pyridine cannot be coupled with phenyltitanium, this may be due to the coordination between nitrogen and titanium(Table 3, entry 17).

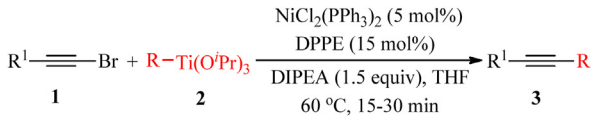
Table 3
$NiCl_2(PPh_3)_2$/DPPE-catalyzed cross-coupling reaction of triisopropoxy(phenyl)titanium ($PhTi(O^iPr)_3$) (**2a**) with various 1-bromoalkynes(**1**).[a]



Entry	1	R^1	Prod.3	Yield 3 (%)[b]
1	**1a**	4-CH_3Ph	**3aa**	56
2	**1b**	Ph	**3ba**	57
3	**1c**	3-CH_3Ph	**3ca**	51
4	**1d**	4-EtPh	**3da**	60
5	**1e**	4-butylPh	**3ea**	71
6	**1f**	4-^{t}butylPh	**3fa**	68
7[c]	**1g**	4-ClPh	**3ga**	78
8[c]	**1h**	4-BrPh	**3ha**	68
9[c]	**1i**	4-FPh	**3ia**	91
10[c]	**1j**	3-FPh	**3ja**	91
11[c]	**1k**	2-FPh	**3ka**	92
12[c]	**1l**	3,5-F_2Ph	**3la**	88
13[c]	**1m**	4-CF_3Ph	**3ma**	86
14	**1n**	2-thienyl	**3na**	48
15[c]	**1o**	2-Naphthalenyl	**3oa**	82
16	**1p**	4-CH_3OOCPh	**3pa**	0(61)[d]
17	**1q**	2-pyridyl	**3qa**	NR

[a] **1**/**2a**/$NiCl_2(PPh_3)_2$/DPPE = 0.5/1.0/0.025/0.075 mmoL, 1.5 equiv DIEPA.
[b] Isolated yield of **3**.
[c] 15 min.
[d] isopropoxy 4-(phenylethynyl)benzoate **(4pa)**.

Table 4
$NiCl_2(PPh_3)_2$/DPPE-catalyzed cross-coupling reaction of 1-bromoalkynes(**1**) with organotitanium reagents(**2**).[a]



Entry	1 R^1	2 R	Prod. 3	Yield 3(%)[b]
1	**1a** 4-CH_3Ph	**2b** 4-FPh	**3 ab**	82
2	**1b** Ph	**2b** 4-FPh	**3bb**	80
3	**1c** 3-CH_3Ph	**2b** 4-FPh	**3 cb**	86
4	**1d** 4-EtPh	**2b** 4-FPh	**3 db**	75
5	**1e** 4-butylPh	**2b** 4-FPh	**3eb**	83
6	**1f** 4-^{t}butylPh	**2b** 4-FPh	**3 fb**	86
7[c]	**1g** 4-ClPh	**2b** 4-FPh	**3gb**	86
8[c]	**1h** 4-BrPh	**2b** 4-FPh	**3 hb**	81
9[c]	**1i** 4-FPh	**2b** 4-FPh	**3ib**	82
10[c]	**1j** 3-FPh	**2b** 4-FPh	**3jb**	89
11[c]	**1k** 2-FPh	**2b** 4-FPh	**3 kb**	87
12[c]	**1l** 3,5-F_2Ph	**2b** 4-FPh	**3lb**	82
13[c]	**1m** 4-CF_3Ph	**2b** 4-FPh	**3mc**	92
14	**1n** 2-thienyl	**2b** 4-FPh	**3 nb**	59
15[c]	**1o** 2-Naphthalenyl	**2b** 4-FPh	**3ob**	77
16[c]	**1a** 4-CH_3Ph	**2c** 4-CH_3Ph	**3ac**	58
17	**1b** Ph	**2c** 4-CH_3Ph	**3bc**	58
18	**1c** 3-CH_3Ph	**2c** 4-CH_3Ph	**3cc**	45
19	**1d** 4-EtPh	**2c** 4-CH_3Ph	**3dc**	68
20	**1e** 4-butylPh	**2c** 4-CH_3Ph	**3ec**	66
21	**1f** 4-^{t}butylPh	**2c** 4-CH_3Ph	**3fc**	60
22[c]	**1g** 4-ClPh	**2c** 4-CH_3Ph	**3gc**	65
23[c]	**1h** 4-BrPh	**2c** 4-CH_3Ph	**3hc**	62
24[c]	**1i** 4-FPh	**2c** 4-CH_3Ph	**3ic**	73
25[c]	**1j** 3-FPh	**2c** 4-CH_3Ph	**3jc**	65
26[c]	**1k** 2-FPh	**2c** 4-CH_3Ph	**3kc**	60
27[c]	**1l** 3,5-F_2Ph	**2c** 4-CH_3Ph	**3lc**	70
28[c]	**1m** 4-CF_3Ph	**2c** 4-CH_3Ph	**3mc**	78
29	**1n** 2-thienyl	**2c** 4-CH_3Ph	**3nc**	41
30[c]	**1o** 2-Naphthalenyl	**2c** 4-CH_3Ph	**3oc**	68

[a] **1**/**2**/$NiCl_2(PPh_3)_2$/DPPE = 0.5/1.0/0.025/0.075 mmoL, 15–30 min, 1.5 equiv DIEPA.
[b] Isolated yield.
[c] 15 min.

We subsequently investigated cross-coupling reactions of substituted aryltitanium reagents with various 1-bromoalkynes using 5 mol% $NiCl_2(PPh_3)_2$ and 15 mol% DPPE conducting in THF at 60 °C for 15–30 min, and results are summarized in Table 4. A series of coupling products 1,2-disubstituted acetylenes (**3**) with electron-withdrawing or electron-donating groups such as methyl, ethyl, fluoro, chloro, bromo and trifluoromethyl on aryl rings of 1-bromoalkynes were synthesized in moderate to good isolated yields (Table 4, entries 1, 3–13, 16, 18–28). The triisopropoxy(4-methylphenyl)titanium ($4\text{-}CH_3C_6H_4Ti(O^iPr)_3$) (**2c**) reacted smoothly with various 1-bromoalkynes (**1a-1o**) at 60 °C for 15–30 min to give the corresponding coupling product **3(ac-oc)** in 41–78 % isolated yields (Table 4, entry 16–30). The corresponding coupling product **3**(**ab-ob**) can be obtained by the reaction of triisopropoxy(4-fluorophenyl)titanium ($4\text{-}FC_6H_4Ti(O^iPr)_3$) (**2b**) with 1-bromoalkyne (**1a-1o**) at 60 °C for 15–30 min in 59–92 % isolated yield (Table 4, entries 1–15). The reaction rate of 1-bromoalkynes with electron withdrawing group (Table 4, entries 7–13, 22–28) is faster than that of 1-bromoalkynes with electron donating groups (Table 4, entries 1, 3–6, 16, 18–21). This may be due to the fact that the oxidative addition reaction of alkyne bromide with electron withdrawing group and palladium is easier than that of alkyne bromide with electron donating group. The isolated yield of

the coupling product **3 cc** was only 45 % when 1-(2-bromoethynyl)-3-methylbenzene (*m*-$CH_3C_6H_4C{\equiv}CBr$) (**1c**) reacted with triisopropoxy(4-methylphenyl)titanium (4-$CH_3C_6H_4Ti(O^iPr)_3$) (**2c**) at 60 °C for 30 min. This may be due to the steric hindrance and electron donating effect of 3-methyl, which makes the oxidative addition of 3-methyl phenylethynyl bromide to palladium difficult. Importantly, when 2-(bromoethynyl)thiophene (2-thienylC≡CBr) (**1n**) was reacted with triisopropoxy(4-fluorophenyl)titanium (4-$FC_6H_4Ti(O^iPr)_3$) (**2b**) at 60 °C for 30 min, the corresponding coupling product **3 nb** was obtained in 59 % isolated yield (Table 4, entry 14). Under the same conditions, 2-(bromoalkynyl)naphthalene (**1o**) was coupled with triisopropoxy(4-fluorophenyl)titanium(4-FC_6H_4 $Ti(O^iPr)_3$) (**2b**) for 15 min, the corresponding coupling product **3ob** was obtained in 77 % isolated yield (Table 4, entry 15). Furthermore, the coupling product **3oc** could be obtained in 68 % isolated yield when coupling of 2-(bromoethynyl)naphthalene (**1o**) with triisopropoxy(4-methylphenyl)titanium (4-$CH_3C_6H_4$ $Ti(O^iPr)_3$) (**2c**) (Table 4, entry 30). While, the isolated yield of the coupling product **3nc** was only 41 % when 2-(bromoethynyl)thiophene (2-thienylC≡CBr) (**1n**) reacted with triisopropoxy(4-methylphenyl)titanium (4-$CH_3C_6H_4$ $Ti(O^iPr)_3$) (**2c**) at 60 °C for 30 min (Table 4, entry 29), this may be due to the coordination of sulfur atoms of thiophene with organotitanium reagents.

The reaction was found to be effective in gram-scale synthesis, which indicated its potential for practical application (Scheme 2). 1,2-bis(4-fluorophenyl)ethyne (**3ib**) was synthesized in 1.24 g using this methodology.

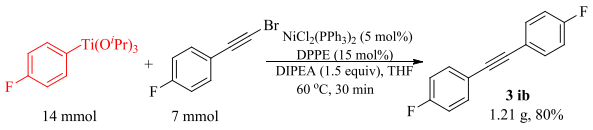
3. Conclusions

We have developed an improved procedure for the nickel-catalyzed cross-couplings of alkynyl halides with aryl titanium reagents under mild conditions and demonstrated that this methodology is a simple and efficient method for the preparation of 1,2-disubstituted acetylenes. In the presence of $NiCl_2(PPh_3)_2$ (5 mol %)/15 mol% DPPE, 1-bromoalkynes reacts smoothly with aryltitaninum reagents in THF at 60 °C for 15–30 min to generate the corresponding cross-coupling products 1,2-disubstituted acetylenes in moderate to excellent isolated yields of up to 92 %. This cross-coupling reaction is compatible with a wide range of functional groups. Moreover, the ready availability of the starting materials, the mild reaction conditions, and the simplicity of the operations involved are additional features making the methodology could therefore serve as a complementary option in the field of 1,2-disubstituted acetylenes. Notably, no other co-catalysts are necessary in the present procedure. Further application of these 1,2-disubstituted acetylenes in organic synthesis is in progress.

4. Experimental section

4.1. General Procedures

General Procedures: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer. The chemical shifts are reported relative to TMS. HRMS were recorded on a Bruker Micro TOF spectrometer equipped with an ESI ion source. Analytical thin-layer chromatography (TLC) was performed on silica 60F-254 plates. Flash column chromatography was carried out on silica gel (300–400 mesh). All reactions were carried out under nitrogen atmosphere. Chemical reagents and solvents were purchased from Damas-beta and Aldrich, and were used without further purification with the exception of these reagents: THF, Et_2O, Hexane and Toluene were distilled from Sodium under Nitrogen. Purification of the coupling products was carried out by flash chromatography. All synthesis and manipulations were carried out under a dry nitrogen atmosphere. Organotitanium compounds of $RTi(O^iPr)_3$(R = Ph (**2a**), 4-MeC_6H_4 (**2b**), or 4-$CF_3C_6H_4$(**2c**)) were prepared according to literature procedures [10d]. Compounds of 1-bromoalkynes **1a-1q** were prepared according to literature procedures [7c,11c].



Scheme 2. Preparative scale synthesis of selected compounds.

4.2. General Procedures for the coupling reaction of alkynylbromides with organotitaniums reagents

Under a dry nitrogen atmosphere, a mixture of $NiCl_2(PPh_3)_2$ (16.35 mg, 0.025 mmol) and DPPE (29.88 mg, 0.075 mmol) in a reaction vessel was added an aryltitanium compound (1.0 mmol) in 2 mL THF followed by an addition of alkynylbromides (0.50 mmol). The resulted solution was stirred at 60 °C for 15–30 min. After completion the reaction, the mixture was diluted with saturated ammonium chloride solution (5 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuum*. The residue was subjected to flash column chromatography on silica gel (hexane or ethyl acetate and hexane) to afford the corresponding 1, 2-disubstituted acetylenes **3**.

1-methyl-4-(phenylethynyl)benzene**(3aa)** [7c]:Yield: 0.054g (56 %), white solid, m.p. 70–71 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.53–7.50 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.35–7.28 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.51, 131.65, 129.24, 128.44, 128.20, 123.59, 120.30, 89.69, 88.85, 21.65.

1,2-diphenylethyne**(3ba)** [7c]: Yield: 0.051g (57 %), yellow solid, m.p. 61–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 4H), 7.37–7.33 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 131.74, 128.48, 128.39, 123.41, 89.51.

1-methyl-3-(phenylethynyl)benzene**(3ca)** [7c]: Yield: 0.049g (51 %), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.36–7.29 (m, 5H), 7.23 (t, J_1 = 7.6 Hz, J_2 = 7.6 Hz,1H), 7.14 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.14, 132.32, 131.73, 129.30, 128.82, 128.46, 128.38, 128.30,123.51, 123.20, 89.70, 89.17, 21.39.

1-ethyl-4-(phenylethynyl)benzene**(3da)** [7c]: Yield: 0.062g (60 %), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.46–7.44 (m, 2H), 7.35–7.28 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.65 (q, J_1 = 7.6 Hz, J_2 = 15.2 Hz,2H), 1.25–1.21 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.80, 131.72, 131.68, 128.43, 128.19, 128.04, 123.63, 120.55, 89.73, 88.85, 28.97, 15.49.

1-butyl-4-(phenylethynyl)benzene**(3ea)** [11c]: Yield: 0.083g (71 %), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34–7.30 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.61(t, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 2H), 1.63–1.55 (m, 2H), 1.39–1.30 (m, 2H), 0.92 (t, J_1 = 7.2 Hz, J_2 = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.52, 131.68, 131.64, 128.60, 128.44, 128.18, 123.63, 120.50, 89.74, 88.85, 35.7, 33.54, 22.46, 14.09.

1-(*tert*-butyl)-4-(phenylethynyl)benzene**(3fa)** [7c]: Yield: 0.080g (68 %), white solid, m.p. 57–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.37–7.30 (m, 5H), 1.32 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.64, 131.71, 131.47, 128.43, 128.19, 125.48, 123.65, 120.38, 89.68, 88.87, 34.92, 31.32.

1-chloro-4-(phenylethynyl)benzene**(3ga)** [7c]: Yield: 0.083g (78 %), white solid, m.p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.35–7.31 (m, 5H).^{13}C

NMR (101 MHz, $CDCl_3$) δ 134.38, 132.93, 131.73, 128.82, 128.61, 128.52, 123.06, 121.91, 90.46, 88.39.

1-bromo-4-(phenylethynyl)benzene**(3ha)** [7c]: Yield: 0.087g (68 %), white solid, m.p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.38–7.32 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 133.12, 131.71, 131.70, 128.61, 128.51, 123.01, 122.58, 122.33, 90.63, 88.44.

1-fluoro-4-(phenylethynyl)benzene**(3ia)** [7c]: Yield: 0.089g (91 %), white solid, m.p. 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 4H), 7.36–7.32 (m, 3H), 7.05–7.00 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.61 (d, J = 250.5 Hz), 133.60 (d, J = 8.1 Hz), 131.68, 128.48 (d, J = 4.0 Hz), 123.22, 119.50 (d, J = 3.0 Hz), 115.87, 115.65, 89.18, 88.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.88 to −110.94 (m).

1-fluoro-3-(phenylethynyl)benzene**(3ja)** [7c]:Yield: 0.089g (91 %), yellow solid, m.p. 30–33 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.34–7.27 (m, 5H), 7.23–7.21 (m, 1H), 7.05–7.00 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ162.53 (d, J = 247.5 Hz), 131.80, 130.03 (d, J = 9.1 Hz), 128.71, 128.52, 127.61 (d, J = 3.0 Hz), 125.27 (d, J = 9.1 Hz), 122.91, 118.48 (d, J = 22.2 Hz), 115.70 (d, J = 21.2 Hz), 90.40, 88.24 (d, J = 4.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.91 to −112.95 (m).

1-fluoro-2-(phenylethynyl)benzene**(3ka)** [7c]: Yield: 0.090g (92 %), white solid, m.p. 46–48 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 3H), 7.34–7.26 (m, 4H), 7.12–7.06 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.74 (d, J = 252.5 Hz), 133.55, 131.81, 130.08 (d, J = 8.1 Hz), 128.71, 128.48, 124.08 (d, J = 4.0 Hz), 123.02, 115.64 (d, J = 21.2 Hz), 112.04 (d, J = 15.2 Hz), 94.56, 82.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.78 to −109.84 (m).

1,3-difluoro-5-(phenylethynyl)benzene**(3la)** [7c]: Yield: 0.094g (88 %), yellow solid, m.p. 39–41 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.35–7.34 (m, 3H), 7.03–7.01 (m, 2H), 6.81–6.75 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.91 (d, J = 249.5 Hz), 162.77 (d, J = 250.5 Hz), 131.88, 128.82 (d, J = 47.5 Hz), 126.13, 122.45, 114.77–114.50 (m), 104.50 (t, J_1 = 25.3 Hz, J_2 = 25.8 Hz), 91.44, 87.24. ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.72 (t, J = 7.5 Hz).

1-(phenylethynyl)-4-(trifluoromethyl)benzene**(3ma)** [7c]: Yield: 0.106g (86 %), white solid, m.p. 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.53 (m, 6H), 7.34–7.35 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 131.91 (d, J = 5.1 Hz), 130.02 (d, J = 32.3 Hz), 128.96, 128.59, 127.26, 125.40(q, J_1 = 4.0 Hz, J_2 = 7.1 Hz), 122.71, 91.91, 88.12. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.78.

2-(phenylethynyl)thiophene**(3na)** [7c]: Yield: 0.044g (48 %), yellow solid, m.p. 49–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.35–7.33 (m, 3H), 7.28 (d, J = 4.0 Hz, 2H), 7.00 (t, J_1 = 4.8 Hz, J_2 = 4.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 132.02, 131.54, 128.55, 128.50, 127.38, 127.23, 123.44, 123.04, 93.16, 82.74.

2-(phenylethynyl)naphthalene**(3oa)** [12]: Yield: 0.093g (82 %), white solid, m.p. 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.80–7.77 (m, 3H), 7.58–7.56 (m, 3H), 7.48–7.45 (m, 2H), 7.34 (d, J = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 133.14, 132.91, 131.78, 131.56, 128.54, 128.51, 128.43, 128.13, 127.90, 127.89, 127.78, 127.6,123.41, 120.70, 89.95, 88.89.

isopropoxy4-(phenylethynyl)benzoate **(4pa)**: Yield: 0.079g (61 %), white solid, m.p. 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.00 (m, 2H), 7.59–7.54 (m, 4H), 7.38–7.35 (m, 3H), 5.29–5.23 (m, 1H), 1.38 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.70, 131.86, 131.54, 130.38, 129.58, 128.85, 128.56, 127.88, 122.88, 92.30, 88.87, 68.75, 22.09.

1-fluoro-4-(p-tolylethynyl)benzene**(3 ab)** [13]: Yield: 0.086g (82 %), white solid, m.p. 90–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.03–6.99 (m, 2H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.50 (d, J = 250.5 Hz), 138.59, 133.51 (d, J = 9.1 Hz), 131.56, 129.26, 120.12, 119.69 (d, J = 4.0 Hz), 115.71 (d, J = 22.2 Hz), 89.34, 87.77, 21.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.23 to −111.31(m).

1-fluoro-4-(phenylethynyl)benzene**(3bc)** [7c]: Yield: 0.078g (80 %), white solid, m.p. 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 4H), 7.36–7.32 (m, 3H), 7.05–7.00 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.61 (d, J = 250.5 Hz), 133.60 (d, J = 8.1 Hz), 131.68, 128.48 (d, J = 4.0 Hz), 123.22, 119.50 (d, J = 3.0 Hz), 115.87, 115.65, 89.18, 88.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.88–110.94 (m).

1-((4-fluorophenyl)ethynyl)-3-methylbenzene**(3 cb)** [14]: Yield: 0.090g (86 %), white solid, m.p. 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.33–7.30 (m, 2H), 7.20 (t, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H), 7.11 (t, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 1H), 7.00 (t, J_1 = 8.8 Hz, J_2 = 8.8 Hz, 2H), 2.32 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ162.54 (d, J = 250.5 Hz), 138.15, 133.55 (d, J = 8.1 Hz), 132.24, 129.35, 128.74, 128.38, 123.00, 119.58 (d, J = 3.0 Hz), 115.71 (d, J = 22.2 Hz), 89.37, 88.08, 21.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.09 (d, J = 11.3 Hz).

1-ethyl-4-((4-fluorophenyl)ethynyl)benzene**(3 db)** [7c]: Yield: 0.080g (75 %), white solid, m.p. 49–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 4H), 7.15 (t, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 2H), 7.02–6.98 (m, 2H), 2.66–2.60 (m, 2H), 1.24–1.20 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.48 (d, J = 250.5 Hz), 144.87, 133.50 (d, J = 8.1 Hz), 131.65, 128.06, 120.36, 119.69, 115.68 (d, J = 22.2 Hz), 89.40, 87.77, 28.95, 15.45. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.28 to −111.33 (m).

1-butyl-4-((4-fluorophenyl)ethynyl)benzene**(3eb)** [15]: Yield: 0.105g (83 %), white solid, m.p. 48–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.03–6.99 (m, 2H), 2.60 (t, J_1 = 7.6 Hz, J_2 = 8.0 Hz, 2H), 1.62–1.55 (m, 2H), 1.39–1.29 (m, 2H), 0.92 (t, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.50 (d, J = 250.5 Hz), 143.60, 133.51 (d, J = 8.1 Hz), 131.58, 128.62, 120.33, 119.74 (d, J = 4.0 Hz), 115.70 (d, J = 22.2 Hz), 89.41, 87.77, 35.73, 33.52, 22.45, 14.06. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.36.

1-(*tert*-butyl)-4-((4-fluorophenyl)ethynyl)benzene**(3 fb)** [16]: Yield: 0.108g (86 %), white solid, m.p. 95–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 4H), 7.35–7.33 (m, 2H), 7.01–6.97 (m, 2H), 1.30 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.49 (d, J = 250.5 Hz), 151.71, 133.54 (d, J = 8.1 Hz), 131.43, 125.50, 120.19, 119.74 (d, J = 3.0 Hz), 115.69 (d, J = 22.2 Hz), 89.35, 87.80, 34.90, 31.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.24 to −111.29 (m).

1-chloro-4-((4-fluorophenyl)ethynyl)benzene**(3gb)** [17]: Yield: 0.099g (86 %), white solid, m.p. 111–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 4H), 7.32–7.28 (m, 2H), 7.05–7.00 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.71 (d, J = 251.5Hz), 134.45, 133.61 (d, J = 8.4 Hz), 132.86, 128.83, 121.70, 119.13, 115.82 (d, J = 22.2 Hz), 89.36, 88.07. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.45.

1-bromo-4-((4-fluorophenyl)ethynyl)benzene**(3 hb)** [18]: Yield: 0.111g (81 %), white solid, m.p. 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 4H), 7.36–7.34 (m, 2H), 7.05–7.00 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.71 (d, J = 250.5 Hz), 133.60 (d, J = 8.1 Hz), 133.06, 131.75, 122.67, 122.16, 119.13 (d, J = 3.0 Hz), 115.83 (d, J = 22.2 Hz), 89.55, 88.13. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.38 to −110.42 (m).

1,2-bis(4-fluorophenyl)ethyne**(3ib)** [7c]: Yield: 0.088g (82 %), white solid, m.p. 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 4H), 7.04–6.99 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.65 (d, J = 250.5 Hz), 133.56 (d, J = 8.1 Hz), 119.33, 115.80 (d, J = 22.2 Hz), 88.09. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.76 to −110.84 (m).

1-fluoro-3-((4-fluorophenyl)ethynyl)benzene**(3jb)** [7c]: Yield: 0.095g (89 %), white solid, m.p. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.51–7.47 (m, 2H), 7.28 (s, 2H), 7.20 (d, J = 8.4 Hz, 1H), 7.03 (t, J_1 = 8.8 Hz, J_2 = 8.6 Hz,3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80 (d, J = 251.5 Hz), 162.52 (d, J = 248.5 Hz), 133.70 (d, J = 8.1 Hz), 130.06 (d, J = 9.1 Hz), 127.55 (d, J = 3.0 Hz), 125.08 (d, J = 9.1 Hz), 119.02 (d,

J = 3.0 Hz), 118.43 (d, J = 23.2Hz), 115.81 (q, J_1 = 7.1 Hz, J_2 = 21.7 Hz), 89.31, 87.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ-110.32 to −110.38 (m), −112.85 to −112.90 (m).

1-fluoro-2-((4-fluorophenyl)ethynyl)benzene**(3 kb)** [7c]: Yield: 0.093g (87 %), white solid, m.p. 108–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 3H), 7.31–7.26 (m, 1H), 7.12–7.01 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80 (d, J = 250.5 Hz), 162.73 (d, J = 253.5 Hz), 133.65 (t, J_1 = 8.1 Hz, J_2 = 14.7 Hz), 130.16 (d, J = 8.1 Hz), 124.10 (d, J = 4.0 Hz), 119.13 (d, J = 3.0 Hz), 115.90–115.55 (q, J_1 = 14.1 Hz, J_2 = 21.7 Hz), 111.86 (d, J = 15.2 Hz), 93.43, 82.53. ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.91, −110.41.

1,3-difluoro-5-((4-fluorophenyl)ethynyl)benzene**(3lb)**: Yield: 0.095g (82 %), white solid, m.p. 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.06–6.99 (m, 4H), 6.81–6.75 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ163.02 (d, J = 251.5 Hz), 162.79 (d, J = 250.5 Hz), 133.84 (d, J = 9.1 Hz), 125.94, 118.55, 115.95 (d, J = 22.2 Hz), 114.73–114.47 (m), 104.84–104.34 (m), 90.35, 86.95. Anal. calcd for $C_{14}H_7F_3$: C 72.42, H 3.04; found C 72.66, H 3.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.67 (t, J = 7.5 Hz), −109.74.

1-fluoro-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene**(3 mb)** [7c]: Yield: 0.121g (92 %), white solid, m.p. 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 4H), 7.53–7.49 (m, 2H), 7.07–7.03 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ162.97 (d, J = 251.5 Hz), 133.83 (d, J = 8.1 Hz), 131.89, 130.12(d, J = 32.3 Hz), 127.09, 125.49–125.38 (m), 122.73, 118.82 (d, J = 4.0 Hz), 115.93(d, J = 22.2 Hz), 90.81, 87.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.84, −109.90 to −109.94 (m).

2-((4-fluorophenyl)ethynyl)thiophene**(3 nb)** [7c]: Yield: 0.060g (59 %), white solid, m.p. 73–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.49–7.46 (m, 2H), 7.26 (d, J = 5.2 Hz, 2H), 7.04–6.98 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.69 (d, J = 250.5 Hz), 133.45 (d, J = 8.1 Hz), 132.05, 127.43, 127.23, 123.24, 119.16 (d, J = 4.0 Hz), 115.81 (d, J = 22.2 Hz), 92.07, 82.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.48 to −110.52 (m).

2-((4-fluorophenyl)ethynyl)naphthalene**(3ob)** [19]: Yield: 0.095g (77 %), white solid, m.p. 109–110 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.79–7.76 (m, 3H), 7.56–7.45 (m, 5H), 7.03 (t, J_1 = 8.4 Hz, J_1 = 8.6 Hz, 2H).^{13}C NMR (101 MHz,$CDCl_3$) δ162.62 (d, J = 250.5 Hz), 133.64 (d, J = 8.1 Hz), 133.02 (d, J = 19.2 Hz), 131.53, 128.42, 128.16, 127.89, 126.76 (d, J = 12.1 Hz), 120.50, 119.49, 115.79 (d, J = 22.2 Hz), 89.63, 88.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.79.

1,2-di-p-tolylethyne**(3ac)** [7c]: Yield: 0.060g (58 %), white solid, m.p. 132–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 7.6 Hz, 4H), 2.35 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.29, 131.56, 129.21, 120.51, 89.01, 21.62.

1-methyl-4-(phenylethynyl)benzene**(3bc)** [7c]: Yield: 0.056g (58 %), white solid, m.p. 70–71 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.53–7.50 (m, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.35–7.28 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.51, 131.65, 129.24, 128.44, 128.20, 123.59, 120.30, 89.69, 88.85, 21.65.

1-methyl-3-(p-tolylethynyl)benzene**(3 cc)** [20]: Yield: 0.046g (45 %), white solid, m.p. 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.27–7.24 (m, 2H), 7.14 (t, J_1 = 7.6 Hz, J_2 = 7.6 Hz,1H), 7.06 (t, J_1 = 8.0 Hz, J_2 = 7.8 Hz, 3H), 2.27 (d, J = 6.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.41, 138.10, 132.26, 131.61, 129.23, 129.11, 128.75, 128.34, 123.40, 120.42, 89.35, 89.03, 21.64, 21.38.

1-ethyl-4-(p-tolylethynyl)benzene**(3dc)** [18]: Yield: 0.075g (68 %), white solid, m.p. 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J_1 = 9.6 Hz, J_2 = 9.0 Hz, 4H), 7.14 (t, J_1 = 10.4 Hz, J_2 = 9.2 Hz, 4H), 2.67–2.61 (m, 2H), 2.34 (s, 3H), 1.23 (t, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.60, 138.28, 131.66, 131.58, 129.21, 128.01, 120.78, 120.57, 89.05, 89.01, 28.97, 21.63, 15.48.

1-butyl-4-(p-tolylethynyl)benzene**(3ec)**: Yield: 0.082g (66 %), white solid, m.p. 30–31 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.44–7.40 (m, 4H), 7.15–7.12 (m, 4H), 2.60 (t, J_1 = 8.0 Hz, J_2 = 7.8 Hz, 2H), 2.35 (s, 3H), 1.63–1.53 (m, 2H),1.37–1.30 (m, 2H), 0.92 (t, J_1 = 7.2 Hz, J_2 = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.32, 138.28, 131.58, 129.21, 128.57, 120.74, 120.58, 89.06, 89.02, 35.74, 33.55, 22.46, 21.64, 14.08. HRMS (ESI) m/z calcd for $C_{19}H_{21}^+$ $(M + H)^+$ 249.16378, found 249.16393.

1-(*tert*-butyl)-4-(p-tolylethynyl)benzene**(3fc)** [21]: Yield: 0.074g (60 %), white solid, m.p. 115–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.46–7.40 (m, 4H), 7.35 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.32 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46, 138.29, 131.60, 131.41,129.21, 125.45, 120.60, 89.03, 89.00, 34.92, 31.34, 21.64.

1-chloro-4-(p-tolylethynyl)benzene**(3gc)** [7c]: Yield: 0.073g (65 %), white solid, m.p. 147–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 4H), 7.33–7.29 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.80, 134.17, 132.87, 131.62, 129.30, 128.78, 122.14, 119.98, 90.67, 87.75, 21.67.

1-bromo-4-(p-tolylethynyl)benzene**(3hc)** [22]: Yield: 0.083g (62 %), white solid, m.p. 127–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.38–7.35 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.82, 133.08, 131.70, 131.61, 129.30, 122.59, 122.37, 119.95, 90.86, 87.82, 21.67.

1-fluoro-4-(p-tolylethynyl)benzene**(3ic)** [23]: Yield: 0.077g (73 %), white solid, m.p. 90–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.03–6.99 (m, 2H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.50 (d, J = 250.5 Hz), 138.59, 133.51 (d, J = 9.1 Hz), 131.56, 129.26, 120.12, 119.69 (d, J = 4.0 Hz), 115.71 (d, J = 22.2 Hz), 89.34, 87.77, 21.62.

1-fluoro-3-(p-tolylethynyl)benzene**(3jc)** [24]: Yield: 0.068g (65 %), white solid, m.p. 60–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42–7.33 (m, 2H), 7.27–7.13 (m, 5H), 7.03–6.99 (m, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.55 (d, J = 247.5 Hz), 138.92, 131.71, 129.98 (d, J = 9.1 Hz), 129.30, 127.55 (d, J = 3.0 Hz), 125.52 (d, J = 9.1 Hz), 119.86, 118.42 (d, J = 22.2 Hz), 115.51 (d, J = 21.2 Hz), 90.64, 87.66, 21.67.

1-fluoro-2-(p-tolylethynyl)benzene**(3kc)** [25]: Yield: 0.063g (60 %), white solid, m.p. 55–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.44 (m, 3H), 7.30–7.26 (m, 1H), 7.17–7.06 (m, 4H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.70 (d, J = 252.5 Hz), 138.90, 133.52, 131.72, 129.81 (d, J = 8.1 Hz), 129.26, 124.05 (d, J = 4.0 Hz), 119.96, 115.62 (d, J = 21.2 Hz), 112.17, 94.77, 82.17, 21.65.

1,3-difluoro-5-(p-tolylethynyl)benzene**(3lc)** [26]: Yield: 0.080g (70 %), yellow solid, m.p. 68–70 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.15–6.99 (m, 4H), 6.78–6.73 (m, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89 (d, J = 250.5 Hz), 162.76 (d, J = 249.5 Hz), 139.30, 131.77, 129.34, 126.36, 119.37, 114.53(q, J_1 = 7.1 Hz, J_2 = 15.2 Hz), 110.10, 104.27 (t, J_1 = 25.3 Hz, J_1 = 25.8 Hz), 91.72, 86.68, 21.64.

1-methyl-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene **(3mc)** [27]: Yield: 0.101g (78 %), white solid, m.p. 140–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 7.08–7.06 (m, 2H), 2.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.22, 131.82 (d, J = 6.1 Hz), 130.00, 129.67, 129.36, 127.49, 125.37 (d, J = 3.0 Hz), 122.78, 119.63, 92.18, 87.55, 21.66.

2-(p-tolylethynyl)thiophene**(3nc)** [7c]: Yield: 0.041g (41 %), yellow solid, m.p. 59–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 7.19–7.16 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.93–6.90 (m, 1H), 2.29 (d, J = 9.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.73, 131.77, 131.45, 129.56, 129.27, 127.18, 127.13, 126.93, 123.70, 119.96, 93.36, 82.06, 21.67.

2-(p-tolylethynyl)naphthalene**(3oc)** [28]: Yield: 0.082g (68 %), white solid, m.p. 130–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.81–7.77 (m, 3H), 7.58–7.55 (m, 1H), 7.47 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.58, 133.17, 132.85, 131.68, 131.41, 129.29, 128.58, 128.09,

127.88, 126.68, 127.63, 120.92, 120.33, 90.09, 89.29, 21.67.

Declaration of competing interest

There are no conflicts to declare.

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Appendix A. Supplementary data

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