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

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ABSTRACT

A Highly efficient route for the synthesis of 1,2-disubstituted acetylene derivatives has been developed by palladium catalyzed cross-couplings of alkynyl halides with (hetero)aryl aluminium reagents under mild conditions. This has given corresponding cross-coupling products good to excellent isolated yields of up to 99%. The aryls bearing electron-donating or electron-withdrawing groups in either alkynylhalides or arylaluminum 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. On the basis of the experimental results, a possible catalytic cycle has been proposed.

1. Introduction

Palladium-catalyzed cross-coupling reactions are found to be extremely powerful in constructing new C–X (X = C, N, O, etc.) bonds [1]. Among these reactions, Sonogashira coupling reaction [2], which was discovered in the early 1970s has been emerged as one of the most potent transformations [3]. The corresponding acetylenic products are important synthetic units in the preparation of potential bioactive compounds [4], new materials [5], and natural products as well [6]. 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 [7]. Although, these efforts have provided alternative methods for the synthesis of alkynes, these reactions still suffer from excess bases, co-catalysts, high temperature, relatively long reaction times, and the special reaction medium. The development of more efficient and atom economical approaches for the synthesis of alkynes 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 [8]. Recently, the synthesis of 1, 2-disubstituted acetylenes by copper or nickel-catalyzed cross-coupling of Grignard reagents with alkynyl bromides has been described [9]. In addition to the above reagents, organoalane reagents have been extensively used as nucleophiles for organic reactions [10].

In recent times, metal-catalyzed cross-coupling reactions of electrophiles with alkynylmetallic reagents have provided an alternative route for the preparation of alkyne compounds [11]. Previous studies show that organoalane reagents are a highly efficient nucleophiles for cross-coupling reactions with aromatic halides [12] or benzylic halides. [13] While, the synthesis based on direct coupling of alkynyl halide with organoalane reagents using palladium as catalyst is developed rarely. To continue our efforts in developing coupling reactions using reactive organometallic reagents [9b,10c,13,14], and develop a more efficient and convenient procedures for the preparation of 1, 2-disubstituted acetylenes, herein, we wish to report a new method for the synthesis of 1, 2-disubstituted acetylenes via palladium-catalyzed cross-couplings between 1-bromoalkynes and organoalane reagents in the presence of $Pd(PPh_3)_4$ (1 mol%) and DPPE (2 mol%) at 60 °C. Notably, in our procedure palladium is used as the single catalyst and neither base nor additive is needed to obtain 1,2-disubstituted acetylenes

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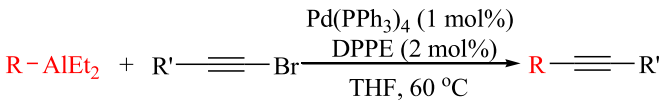


Scheme 1. Palladium-catalyzed cross-coupling reactions of 1-bromoalkyne derivatives with organoalane nucleophiles.

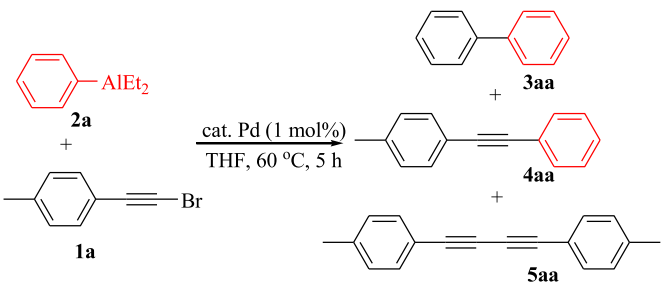
in good to excellent isolated yields (Scheme 1).

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 diethylphenylaluminum ($C_6H_5AlEt_2$) (**2a,** 1.0 mmol) in the presence of $Pd(OAc)_2$ (1 mol%) in THF at 60 °C for 5 h. To our delight, 16% isolated yield of the desired 1-methyl-4-(2-phenylethynyl)-benzene was obtained (**4aa**) (Table 1, entry 1). Then, different palladium salts were examined (Table 1, entries 2–6). Notably, $Pd(PPh_3)_4$ gave the best result among the tested palladium salts (Table 1, entry 3). The product ratio is about 33:66:1 in favor of the coupling product **4aa**. 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 **4aa** using $Pd(PPh_3)_4$ as catalyst is shown in Table 1 (Table 1, entries 7–11). Although the highest isolated yield of coupling product **4aa** (82% yield) was obtained when DPPP was used, the product ratio is only about 16:78:6 (Table 1, entry 9). While, the isolated yield of coupling product **4aa** was only 74% when using DPPE as ligand, but the product ratio is up to 9:90:1 in favor of the coupling product **4aa**. Other ligands such as PPh_3, PCy_3 and DPPB were less effective than DPPE (Table 1, entries 7, 8, 10).

The molar ratio of metal and ligand was examined. It was found that a $Pd(PPh_3)_4$/DPPE ratio of 1.0/2.0 gave the coupling product **4aa** in good isolated yield of 74% with a ratio of 9:90:1 in favor of the coupling product **4aa** (Table 2, entry 2). A brief examination of the influence of solvent on the isolated yield of the coupling product **4aa** and reaction selectivity revealed that THF was the solvent of choice. In toluene, hexane, or DME, the isolated yield of the coupling product **4aa** was low and reaction selectivity was poor (Table 2, entries 5–7). Further studies indicated that the catalyst loading dramatically influenced the isolated yield of the coupling product **4aa**. It was found that the most favorable catalyst loading is 1 mol% $Pd(PPh_3)_4$/2 mol% DPPE (Table 2, entry 2). It is particularly interesting that the addition of K_2CO_3 as a base could somewhat decrease the isolated yield of the coupling product **4aa** and reaction selectivity (Table 2, entry 8). The desired coupling product **4aa** was obtained in 77% isolated yield with good selectivity for the 1,2-disubstituted acetylenes **4aa** when **1a** and **2a** (molar ratio 0.5: 0.8) were stirred in THF in the presence of $Pd(PPh_3)_4$ at 60 °C for 5 h (Table 2, entry 9). It is worth noting that the desired coupling product **4aa** was obtained in 77% isolated yield with excellent selectivity when the reaction time is shortened from 5 h to 4 h (Table 2, entry 12). However, the isolated yield of the coupling product **4aa** and reaction selectivity were decreased when the reaction time was extended to 6 h (Table 2, entry 11). Although excellent selectivity can be obtained at room temperature, the isolated yield of the coupling product **4aa** is only 8% (Table 2, entry 13). Extensive screening showed that the optimized coupling conditions were 1 mol% $Pd(PPh_3)_4$/2 mol% DPPE, 0.5 mmol **1a**, 0.8 mmol **2a** in THF at 60 °C for 4 h (Table 2, entry 9).

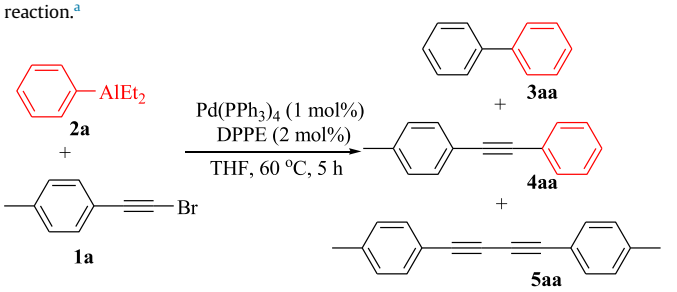
Table 1
Effect of the palladium salt and the ligand on the cross-coupling reaction.[a]



Entry	Cat.	Ligand	Yield **4aa** (%)[b]	**3aa/4aa/5aa**[c]
1	$Pd(OAc)_2$	–	16	55/42/3
2	$Pd(PPh_3)_2Cl_2$	–	37	45/51/4
3	$Pd(PPh_3)_4$	–	78	33/66/1
4	$PdCl_2$	–	16	50/44/6
5	$Pd(dppf)Cl_2$	–	43	41/56/3
6	Pd^{2+}(acac)	–	30	47/48/5
7	$Pd(PPh_3)_4$	PCy_3	43	29/67/4
8	$Pd(PPh_3)_4$	PPh_3	50	37/59/4
9	$Pd(PPh_3)_4$	DPPP	82	16/78/6
10	$Pd(PPh_3)_4$	DPPB	55	18/78/4
11	$Pd(PPh_3)_4$	DPPE	74	9/90/1

[a] **1a**/**2a**/Cat/Ligand = 0.5/1.0/0.005/0.01 mmoL, THF 2 mL.
[b] Isolated.
[c] Ratio of isolated yield.

Table 2
Effect of the solvent and the molar ratio of $Pd(PPh_3)_4$/DPPE on the cross-coupling reaction.[a]



Entry[a]	**2a**(mmol)	Solvent	Yield **4aa** (%)[b]	**3aa/4aa/5aa**[c]
1[d]	1	THF	51	21/74/5
2[e]	1	THF	74	9/90/1
3[f]	1	THF	49	13/78/8
4[g]	1	THF	60	7/90/3
5	1	hexane	37	32/64/4
6	1	toluene	30	23/75/2
7	1	DME	47	34/63/3
8[h]	1	THF	38	3/63/34
9	0.8	THF	77	9/90/1
10	0.5	THF	31	5/79/16
11[i]	0.8	THF	67	10/78/12
12[j]	0.8	THF	77	3/96/1
13[k]	0.8	THF	8	1/98/1

[a] **1a**/$Pd(PPh_3)_4$/Ligand = 0.5/0.005/0.01 mmol, 60 °C, 5 h.
[b] Isolated.
[c] Ratio of isolated yield.
[d] $Pd(PPh_3)_4$/DPPE = 1/1.
[e] $Pd(PPh_3)_4$/DPPE = 1/2.
[f] $Pd(PPh_3)_4$/DPPE = 1/3.
[g] $Pd(PPh_3)_4$/DPPE = 0.01/0.02 mmol.
[h] 2.0 equiv K_2CO_3.
[i] 6 h.
[j] 4 h.
[k] r.t, 4 h.

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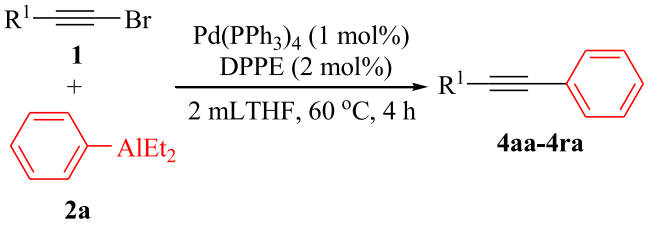
With the optimized conditions in hand, the scope of this reaction was studied by using various 1-bromoalkynes (**1**). The diethylphenylaluminum ($C_6H_5AlEt_2$) (**2a**) reacted smoothly with a series of 1-bromoalkynes **1**(**a**–**r**) at 60 °C for 4 h to give the corresponding coupling products **4**(**aa**–**ra**) in moderate to excellent isolated yields (Table 3, entries 1–18). 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 2–7) and electron-deficient substituents (Table 3, entries 8–10) were tolerated. Notably, methyl, ethyl, propyl, amyl, ^{t}butyl, alkoxyl, bromo, chloro, fluoro and trifluoromethyl groups posed no challenges under the described reaction conditions. Furthermore, even with sterically hindered 1-(2-bromoethynyl)naphthalene (**1r**) (Table 3, entry 18), the coupling reaction underwent smoothly to give good isolated yield of the coupling product **4ra**. Importantly, the reaction also worked well with the 2-(2-bromoethynyl)-thiophene (**1q**) and gave good isolated yield of the coupling product **4qa** (Table 3, entry 17).

We subsequently investigated cross-coupling reactions of substituted arylaluminum reagents with various 1-bromoalkynes using 1 mol% $Pd(PPh_3)_4$ and 2 mol% DPPE conducting in THF at 60 °C for 4–72 h, and results are summarized in Table 4. A series of coupling products 1,2-disubstituted acetylenes (**4**) with electron-withdrawing or electron-donating groups such as methyl, ethyl, fluoro, chloro, bromo and trifluoromethyl on aryl rings were synthesized in moderate to good isolated yields (Table 4, entries 15–23). The diethyl(4-methylphenyl)aluminum (4-$CH_3C_6H_4AlEt_2$) (**2e**) reacted smoothly with (bromoethynyl)- benzene($C_6H_5C{\equiv}CBr$) (**1b**) at 60 °C for 4 h to give the corresponding coupling product **4be** in 89% isolated yield (Table 4, entry 21). Coupling of 1-(2-bromoethynyl)-4-methylbenzene (*p*-$CH_3C_6H_4C{\equiv}CBr$) (**1a**) with diethyl(4-methylphenyl)aluminum (4-$CH_3C_6H_4AlEt_2$) (**2e**) at 60 °C for 5 h to give coupling product **4ae** in only 44% isolated yield (Table 4, entry 15). However, the isolated yield of the coupling product **4oe** was only 40% when 1-(2-bromoethynyl)-4-chlorobenzene (*p*-$ClC_6H_4C{\equiv}CBr$) (**1o**) reacted with diethyl (4-methylphenyl)aluminum (4-$CH_3C_6H_4AlEt_2$) (**2e**) at 60 °C for 72 h. Importantly, the diethyl(2-(thiophen-2-yl)ethynyl)aluminium (**2b**) and diethyl(2-(thiophen-3-yl)ethynyl)aluminium (**2c**) also exhibited good reactivity to give the corresponding coupling products 1,2-disubstituted acetylenes in 44–95% isolated yields (Table 4, entries 1–14). While, coupling of (bromo-ethynyl)benzene ($C_6H_5C{\equiv}CBr$) (**1b**) with diethyl(4-flouro- phenyl)aluminum (4-$FC_6H_4AlEt_2$) (**2d**) at 60 °C for 34 h to give coupling product **4bd** in only 27% isolated yield (Table 4, entry 15). Moreover, the coupling product **4dd** could be obtained in only 26% isolated yield when coupling of 1-(2-bromoethynyl)-4-ethylbenzene (*p*-$C_2H_5C_6H_4C{\equiv}CBr$) (**1d**) with diethyl(4-flourophenyl)aluminum (4-$FC_6H_4AlEt_2$) (**2d**) (Table 4, entry 16).

In order to further explore the reaction mechanism, control experiments were carried out (eq. 6; for details see the Supporting Information). We performed the reaction between 1-(2-bromoethynyl)-4-methylbenzene (*p*-$MeC_6H_4C{\equiv}CBr$)(**1a,** 0.5 mmol) with diethylphenylaluminum ($C_6H_5AlEt_2$) (**2a,** 1.0 mmol) in the presence of $Pd(OAc)_2$ (1 mol%)/DPPE (2 mol%) in THF at 60 °C for 4 h, and 74% isolated yield of the desired 1-methyl-4-(2-phenylethynyl)-benzene was obtained (**4aa**)(Scheme 2). The results are similar to those obtained under the optimal conditions(Table 3, entry 1). The reaction mixture was analyzed by ^{31}P NMR, it was found that the characteristic peak of ^{31}P NMR appeared

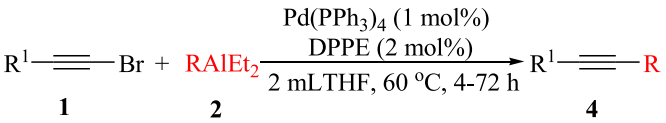
Table 3
$Pd(PPh_3)_4$/DPPE-catalyzed cross-coupling reaction of diethylphenylaluminum (**2a**) with various 1-bromoalkynes.[a]



Entry	1	R^1	Prod.4	Yield 4 (%)[b]
1	**1a**	4-CH_3Ph	**4aa**	77
2	**1b**	Ph	**4ba**	72
3	**1c**	3-CH_3Ph	**4ca**	96
4	**1d**	4-EtPh	**4da**	70
5	**1e**	4-propylPh	**4ea**	66
6	**1f**	4-amylPh	**4fa**	66
7	**1g**	4-^{t}butylPh	**4ga**	71
8	**1h**	4-OCH_3Ph	**4ha**	67
9	**1i**	4-FPh	**4ia**	90
10	**1j**	3-FPh	**4ja**	86
11	**1k**	2-FPh	**4ka**	65
12	**1l**	3,5-F_2Ph	**4la**	96
13	**1m**	3-BrPh	**4ma**	99
14	**1n**	4-BrPh	**4na**	44
15	**1o**	4-ClPh	**4oa**	55
16	**1p**	4-CF_3Ph	**4pa**	95
17	**1q**	2-thienyl	**4qa**	85
18	**1r**	1-Naphthalenyl	**4ra**	85

[a] **1a**/**2a**/$Pd(PPh_3)_4$/Ligand = 0.5/0.8/0.005/0.01 mmoL.
[b] Isolated.

Table 4
$Pd(PPh_3)_4$/DPPE-catalyzed cross-coupling reaction of 1-bromoalkynes(**1**) with organoalane reagents(**2**).[a]



Enter	1 R^1	2 R	Prod.4	Yield 4(%)[b]
1	**1a** 4-CH_3Ph	**2b** 2-thienyl	**4ab**	64
2	**1c** 3-CH_3Ph	**2b** 2-thienyl	**4cb**	61
3	**1b** Ph	**2b** 2-thienyl	**4bb**	74
4	**1i** 4-FPh	**2b** 2-thienyl	**4ib**	89
5	**1j** 3-FPh	**2b** 2-thienyl	**4jb**	84
6	**1k** 2-FPh	**2b** 2-thienyl	**4kb**	44
7	**1m** 3-BrPh	**2b** 2-thienyl	**4mb**	83
8	**1a** 4-CH_3Ph	**2c** 3-thienyl	**4ac**	81
9	**1b** Ph	**2c** 3-thienyl	**4bc**	81
10	**1c** 3-CH_3Ph	**2c** 3-thienyl	**4cc**	53
11	**1i** 4-FPh	**2c** 3-thienyl	**4ic**	95
12	**1j** 3-FPh	**2c** 3-thienyl	**4jc**	76
13	**1k** 2-FPh	**2c** 3-thienyl	**4kc**	64
14	**1m** 3-BrPh	**2c** 3-thienyl	**4mc**	93
15[c]	**1b** Ph	**2d** 4-FPh	**4bd**	27
16[d]	**1d** 4-EtPh	**2d** 4-FPh	**4dd**	26
17[c]	**1i** 4-FPh	**2d** 4-FPh	**4id**	76
18[d]	**1j** 3-FPh	**2d** 4-FPh	**4jd**	69
19[c]	**1k** 2-FPh	**2d** 4-FPh	**4kd**	52
20	**1p** 4-CF_3Ph	**2d** 4-FPh	**4pd**	51
21[e]	**1b** Ph	**2e** 4-CH_3Ph	**4be**	89
22[f]	**1a** 4-CH_3Ph	**2e** 4-CH_3Ph	**4ae**	44
23[g]	**1o** 4-Cl Ph	**2e** 4-CH_3Ph	**4oe**	40

[a] **1**/**2**/$Pd(PPh_3)_4$/DPPE = 0.5/0.8/0.005/0.01 mmoL, 24 h.
[b] Isolated.
[c] 34 h.
[d] 7 h.
[e] 4 h.
[f] 5 h.
[g] 72 h.

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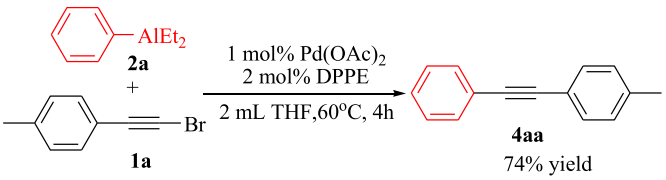
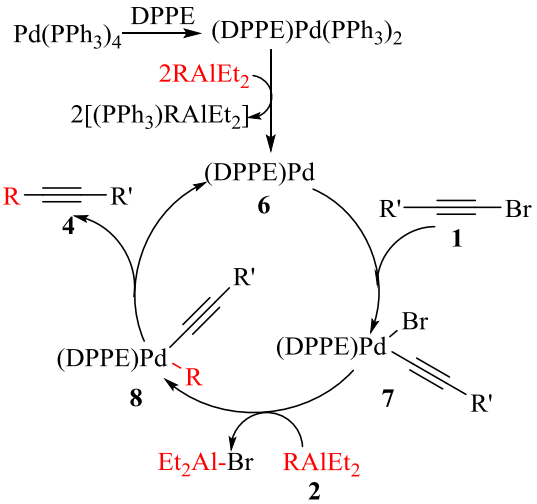


Scheme 2. Cross-coupling reactions of 1-bromoalkyne **1a** with organoalane **2a** catalyzed by 1 mol%$Pd(OAc)_2$/2 mol%DPPE.



Scheme 3. The proposed catalytic cycle for the formation of 1,2-disubstituted acetylenes 4.

around at 55.533 ppm and 56.578 ppm. However, ^{31}P NMR peak of pure DPPE is −12.065 ppm. The results show that dppe work as a ligand of the palladium center. Thus, based on established palladium chemistry, we propose a mechanism to account for the formation of products (Scheme 3). The first step is the oxidative addition of 1-bromoalkyne (**1**) to Pd(0) phosphine complex (**6**) (which in turn from $Pd(PPh_3)_4$, DPPE and $RAlEt_2$) to form the organopalladium (II) bromide intermediate (**7**). Transmetalation of aryl aluminum with **7** gives aryl-(alkynyl)palladium (II) intermediate (**8**) and Et_2AlBr. Finally, complex **8** undergoes reductive elimination to afford the desired product **4** and regenerate the active Pd(0) species for the next catalytic cycle.

3. Conclusions

We have developed an improved procedure for the palladium-catalyzed cross-couplings of alkynyl halides with (hetero)aryl aluminium 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 1 mol % $Pd(PPh_3)_4$/2 mol% DPPE, 1-bromoalkynes reacts smoothly with 1.6 equivalents of (hetero)arylaluminum reagents in THF at 60 °C to generate the corresponding cross-coupled product 1,2-disubstituted acetylenes in moderate to excellent isolated yields of up to 99%. This coupling reaction is compatible with a wide range of functional groups. 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

^1H 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.

4.2. General procedures for the preparation Ar-$AlEt_2$ (**2a**, **2d**, **2e**)

A solution of PhMgBr (10 mL, 1.0 M in hexane) was added to Et_2O (10 mL) at 0 °C under an atmosphere of nitrogen, then added Et_2AlCl (5 mL, 2.0M in hexane) and stirred for 20 min under this temperature. Then the reaction mixture was stirred for 2 h at room temperature. The resulted solution was filtered under an atmosphere of nitrogen, followed by an evaporation of hexane and Et_2O under reduced pressures and then added dry THF to give a solution of $AlArEt_2$(THF) which was used in the coupling reactions.

4.3. General procedures for the preparation (heteroaryl)-$AlEt_2$ (**2b**, **2c**) [13b].

To a solution of a heteroaryl bromide (10 mmol) in Et_2O (10 mL) was added n-BuLi (10 mmol, 2.5 M in hexane, 4 mL) at 0 °C under an atmosphere of nitrogen, and the mixture was stirred for 1 min under this temperature, followed by an addition of $AlEt_2Cl$ (10 mmol, 2.0 M in hexane, 5 mL) at −40 °C. The mixture was stirred for 3 h at the same temperature. The resulted solution was filtered, followed by an evaporation of the solvent under reduced pressures and then added THF to afford a heteroarylaluminum reagent (heteroaryl)-$AlEt_2$(THF) in a quantitative yield, which was directly used in the coupling reactions.

4.4. General procedures for the coupling reaction of alkynylbromides with organoalanes reagents

Under a dry nitrogen atmosphere, a mixture of $Pd(PPh_3)_4$ (5.78 mg, 0.005 mmol) and DPPE (3.98 mg, 0.01 mmol) in a reaction vessel was added an (hetero)arylaluminum compound (0.8 mmol) in 2 mL THF followed by an addition of alkynylbromides (0.50 mmol). The resulted solution was stirred at 60 °C for 4–72 h. 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 overanhydrous Na_2SO_4, filtered and evaporated *in vacuum*. The residue was subjected to flash column chromatography onsilica gel (hexane or ethyl acetate and hexane) to afford the corresponding 1, 2-disubstituted acetylenes **4**.

4.4.1. 1-Methyl-4-(phenylethynyl)benzene(**4aa**) [7e]

Yield: 0.074 g (77%), White solid, m.p.71–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35–7.27 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 131.7 (d, *J* = 4.8 Hz), 129.3, 128.5, 128.2, 123.6, 120.4, 89.7, 88.8, 21.7 ppm.

4.4.2. 1, 2-diphenylethyne(**4ba**) [7e]

Yield: 0.064 g (72%), colourless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.52 (m, 4H), 7.36–7.33 (m, 6H) ppm. ^{13}C NMR (100 MHz,

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$CDCl_3$): δ = 131.7, 128.5, 128.4, 123.4, 89.5 ppm.

*4.4.3. 1-Methyl-3-(phenylethynyl)benzene(**4ca**) [7m]*

Yield: 0.092 g (96%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.35–7.31 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 132.3, 131.7, 130.2, 129.7, 129.3, 128.8, 128.44, 128.36, 128.3, 123.5, 123.2, 89.7, 89.2, 21.4 ppm.

*4.4.4. 1-Ethyl-4-(phenylethynyl)benzene(**4da**) [7n]*

Yield: 0.072 g (70%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.51 (m, 2H), 7.46–7.42 (m, 2H), 7.35–7.29 (m, 3H), 7.22–7.14 (m, 2H), 2.68–2.62 (q, *J* = 6.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 132.6, 131.7 (d, *J* = 3.6 Hz), 128.9, 128.4, 128.2, 128.0, 127.3, 123.6, 120.5, 89.7, 88.8, 29.0, 15.5 ppm.

*4.4.5. 1-(phenylethynyl)-4-propylbenzene(**4ea**) [7g]*

Yield: 0.072 g (66%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.51 (m, 2H), 7.45–7.43 (m, 2H), 7.35–7.28 (m, 3H), 7.16–7.12 (m, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.68–1.59 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 132.5, 131.6 (d, *J* = 5.3 Hz), 128.9, 128.7, 128.7, 128.4, 128.2, 127.4, 127.3, 123.6, 120.5, 89.7, 88.9, 38.1, 24.5, 13.9 ppm.

*4.4.6. 1-Pentyl-4-(phenylethynyl)benzene(**4fa**) [7e]*

Yield: 0.083 g (66%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2H), 7.45–7.41 (m, 2H), 7.35–7.27 (m, 3H), 7.15–7.11 (m, 2H), 2.61–2.56 (m, 2H), 1.64–1.56 (m, 2H), 1.34–1.27 (m, 4H), 0.90–0.87 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 132.5, 131.7, 131.6, 128.9, 128.7, 128.6, 128.4, 128.2, 127.3, 123.6, 120.5, 89.7, 88.8, 36.0, 31.6, 31.1, 22.7, 14.2 ppm.

*4.4.7. 1-(tert-butyl)-4-(phenylethynyl)benzene(**4ga**) [7f]*

Yield: 0.083 g (71%), white solid, m.p. 55–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.51 (m, 2H), 7.48–7.41 (m, 2H), 7.36–7.27 (m, 5H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6, 132.4, 131.7, 131.5, 128.9, 128.4, 128.2, 127.3, 125.6, 125.5, 123.6, 120.3, 89.7, 88.7, 34.9, 31.3 ppm.

*4.4.8. 1-Methoxy-4-(phenylethynyl)benzene(**4ha**) [7e]*

Yield: 0.069 g (67%), white solid, m.p.: 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 4H), 7.29–7.34 (m, 3H), 6.86 (d, *J* = 10.8 Hz, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 133.2, 131.6, 128.4, 128.1, 123.7, 115.4, 114.1, 89.5, 88.2, 55.4 ppm.

*4.4.9. 1-Fluoro-4-(phenylethynyl)benzene(**4ia**) [7e]*

Yield: 0.089 g (90%), white solid, m.p.: 104–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 4H), 7.35–7.34 (m, 3H), 7.06–7.01 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 248.2 Hz), 134.7(d, *J* = 8.6 Hz), 133.6(d, *J* = 8.3 Hz), 131.7, 128.5 (d, *J* = 3.9 Hz), 123.2, 116.1(d, *J* = 22.2 Hz), 115.8(d, *J* = 20.0 Hz), 89.2, 88.4 ppm.

*4.4.10. 1-Fluoro-3-(phenylethynyl)benzene(**4ja**) [7h]*

Yield: 0.085 g (86%), white solid, m.p. 28–30 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.34–7.26 (m, 5H), 7.23–7.18 (m, 1H), 7.06–7.00 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245.0 Hz), 131.8, 130.0 (d, *J* = 8.7 Hz), 128.7, 128.5, 127.6 (d, *J* = 3.0 Hz), 125.2 (d, *J* = 9.5 Hz), 122.9, 118.5 (d, *J* = 22.6 Hz) 115.7 (d, *J* = 21.1 Hz), 90.4, 88.2 (d, *J* = 3.4 Hz) ppm.

*4.4.11. 1-Fluoro-2-(phenylethynyl)benzene(**4ka**) [7d]*

Yield: 0.063 g (65%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.50 (m, 3H), 7.36–7.27 (m, 4H), 7.14–7.07 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 250.2 Hz), 133.6, 131.8, 130.1 (d, *J* = 8.1 Hz), 128.7, 128.5, 124.1 (d, *J* = 3.6 Hz), 123.03, 115.7 (d, *J* = 20.8 Hz), 94.6, 82.8 ppm.

*4.4.12. 1,3-Difluoro-5-(phenylethynyl)benzene(**4la**) [7n]*

Yield: 0.103 g (96%), white solid, m.p. 38–39 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.37–7.35 (m, 2H), 7.04–7.02 (m, 3H), 6.89–6.76 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (dd, J_1 = 247.4 Hz, J_2 = 13.4 Hz), 131.7, 128.9, 128.4, 126.0, 123.9, 122.3, 115.6–115.4 (m), 114.6–114.4 (m), 106.0 (t, *J* = 25.2 Hz), 104.4 (t, *J* = 25.3 Hz), 91.3, 87.1 ppm.

*4.4.13. 1-Bromo-3-(phenylethynyl)benzene(**4ma**) [7c]*

Yield: 0.127 g (99%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 1H), 7.52–7.50 (m, 2H), 7.44–7.41 (m, 2H), 7.33–7.32 (m, 3H), 7.16 (t, *J* = 8.0 Hz,1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 131.6, 131.3, 130.1, 129.7, 128.6, 128.3, 125.2, 122.7, 122.1, 90.7, 87.8 ppm.

*4.4.14. 1-Bromo-4-(phenylethynyl)benzene(**4na**) [7f]*

Yield: 0.0570 g (44%), white solid, m.p.: 83–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.48–7.45 (m, 2H), 7.39–7.33 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.2, 131.7 (d, *J* = 2.1 Hz), 128.6, 128.5, 127.3, 123.1, 122.6, 122.4, 90.6, 88.4 ppm.

*4.4.15. 1-Chloro-4-(phenylethynyl)benzene(**4oa**) [7f]*

Yield: 0.058 g (55%), white solid, m.p.: 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 2H), 7.46–7.44 (d, *J* = 8.4 Hz, 2H), 7.35–7.30 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 132.9, 131.7, 128.8, 128.6, 128.5, 123.1, 121.9, 90.5, 88.4 ppm.

*4.4.16. 1-(phenylethynyl)-4-(trifluoromethyl)benzene(**4pa**) [7e]*

Yield: 0.117 g (95%), white solid, m.p.: 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 4H), 7.58–7.54 (m, 2H), 7.39–7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.93, 131.89, 130.0(q, *J* = 32.4 Hz), 128.9, 128.6, 127.3, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 270.6 Hz), 122.7, 91.8, 88.1 ppm.

*4.4.17. 2-(phenylethynyl)thiophene(**4qa**) [7k]*

Yield: 0.078 g (85%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.6 Hz, 1H), 7.52–7.49 (m, 2H), 7.45–7.41 (t, *J* = 7.2 Hz, 1H), 7.36–7.30 (m, 3H), 6.99 (t, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.0, 131.5, 128.9, 128.53, 128.50, 127.4, 127.3, 127.2, 123.4, 123.0, 93.2, 82.8 ppm.

*4.4.18. 1-(phenylethynyl)naphthalene(**4ra**) [7m]*

Yield: 0.094 g (85%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.0 Hz, 1H), 7.83–7.74 (m, 3H), 7.65–7.63 (d, *J* = 6.8 Hz, 2H), 7.59–7.56 (t, *J* = 7.2 Hz, 1H), 7.51–7.48 (t, *J* = 7.6 Hz, 1H), 7.43–7.34 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.4, 133.3, 131.8, 130.5, 128.9, 128.5, 128.5, 128.4, 126.9, 126.5, 126.3, 125.9, 123.5, 121.0, 94.5, 87.7 ppm.

*4.4.19. 2-(p-tolylethynyl)thiophene(**4ab**)*

Yield: 0.063 g (64%), white solid, m.p.: 59–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 4.4 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 4.4 Hz, 1H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 131.8, 131.4, 129.3, 127.2, 127.1, 123.6, 119.9, 93.3, 82.1, 21.7 ppm. HRMS (ESI) *m*/*z* calcd for $C_{13}H_{11}S^+$ $(M+H)^+$ 199.05760, found 199.05775.

*4.4.20. 2-(m-tolylethynyl)thiophene(**4cb**)*

Yield: 0.060 g (61%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.31 (m, 2H), 7.28–7.21 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H),

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7.01–6.99 (m, 1H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 132.1, 131.9, 129.5, 128.6, 128.4, 127.6, 127.2, 123.6, 122.8, 93.5, 82.4, 21.4 ppm. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}S^+$ $(M+H)^+$ 199.05760, found 199.05766.

*4.4.21. 2-((4-fluorophenyl)ethynyl)thiophene(**4ib**)*

Yield: 0.090 g (89%), white solid, m.p.: 74–76 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 3H), 7.28–7.26 (m, 1H), 7.05–6.98 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 248.5 Hz), 133.5, 133.4, 132.0, 127.4, 127.2, 123.2, 119.1(d, *J* = 3.5 Hz), 115.9, 115.7, 92.1, 82.5(d, *J* = 1.5 Hz) ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03233.

*4.4.22. 2-((3-fluorophenyl)ethynyl)thiophene(**4jb**)*

Yield: 0.085 g (84%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 4H), 7.21–7.18 (m, 1H), 7.04–6.98 (m, 2H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245. Hz), 132.5, 130.1(d, *J* = 8.6 Hz), 127.8, 127.4 (d, *J* = 3.1 Hz), 127.3, 124.9 (d, *J* = 9.5 Hz), 122.9, 118.2 (d, *J* = 22.7 Hz), 115.8(d, *J* = 21.0 Hz), 91.9(d, *J* = 3.5 Hz), 83.7 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03279.

*4.4.23. 2-((2-fluorophenyl)ethynyl)thiophene(**4kb**)*

Yield: 0.045 g (44%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (t, *J* = 7.2 Hz, 1H), 7.32–7.28 (m, 3H), 7.10 (q, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 250.5 Hz), 133.3 (d, *J* = 1.1 Hz), 132.5, 130.3 (d, *J* = 7.9 Hz), 127.8, 127.3, 124.1 (d, *J* = 3.8 Hz), 122.9, 115.6 (d, *J* = 20.7 Hz), 111.7 (d, *J* = 15.5 Hz), 87.7, 86.5 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03241.

*4.4.24. 2-((3-bromophenyl)ethynyl)thiophene(**4mb**) [7y]*

Yield: 0.108 g (83%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (t, *J* = 1.6 Hz, 1H), 7.44–7.39 (m, 2H), 7.28–7.27 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.99(dd, J_1 = 4.0 Hz, J_1 = 0.8 Hz,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1, 132.5, 131.6, 130.0, 129.9, 127.9, 127.3, 125.0, 122.8, 122.3, 91.6, 84.1. HRMS (ESI) *m/z* calcd for $C_{12}H_8BrS^+$ $(M+H)^+$ 262.95246, found 262.95218.

*4.4.25. 3-(p-tolylethynyl)thiophene(**4ac**) [7a]*

Yield: 0.080 g (81%), white solid, m.p.: 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.27–7.25 (m, 1H), 7.18 (d, *J* = 4.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 131.4, 129.9, 129.1, 128.3, 125.3, 122.5, 120.1, 89.1, 83.9, 21.5 ppm. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}S^+$ $(M+H)^+$ 199.05760, found 199.05733.

*4.4.26. 3-(phenylethynyl)thiophene(**4bc**) [7j]*

Yield: 0.075 g (81%), white solid, m.p.: 37–39 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 3H), 7.33–7.31 (m, 3H), 7.28–7.26 (m, 1H), 7.18 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.6, 129.9, 128.7, 128.5, 128.3, 126.4, 126.2, 125.5, 123.3, 122.4, 89.0, 84.6 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_9S^+$ $(M+H)^+$ 185.04195, found 185.04193.

*4.4.27. 3-(m-tolylethynyl)thiophene(**4 cc**)*

Yield: 0.052 g (53%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 2.8 Hz, 1H), 7.34–7.31 (m, 2H), 7.28–7.26 (m, 1H), 7.22–7.18 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 132.2, 130.0, 129.2, 128.7, 128.6, 128.4, 125.4, 123.1, 122.5, 89.2, 84.3, 21.4 ppm. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}S^+$ $(M+H)^+$ 199.05760, found 199.05791.

*4.4.28. 3-((4-fluorophenyl)ethynyl)thiophene(**4ic**)*

Yield: 0.096 g (95%), white solid, m.p.: 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 2H), 7.36–7.27 (m, 2H), 7.17 (d, *J* = 4.8 Hz, 1H), 7.02 (t, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 248.1 Hz), 134.6 (d, *J* = 8.5 Hz), 133.5 (d, *J* = 8.3 Hz), 129.9, 128.8, 126.5, 126.2, 125.6, 119.9, 115.7 (d, *J* = 22.0 Hz), 87.9, 84.3 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03212.

*4.4.29. 3-((3-fluorophenyl)ethynyl)thiophene(**4jc**)*

Yield: 0.077 g (76%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 2.4 Hz, 1H), 7.32–7.27 (m, 3H), 7.21–7.18 (m, 2H), 7.05–6.98 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245.0 Hz), 130.1, 130.0, 129.9, 129.2, 127.5 (d, *J* = 2.8 Hz) 125.6, 121.9, 118.4 (d, *J* = 22.7 Hz), 115. 6 (d, *J* = 21.1 Hz), 87.8, 85.6 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03242.

*4.4.30. 3-((2-fluorophenyl)ethynyl)thiophene (**4kc**)*

Yield: 0.065 g (64%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 2.4 Hz, 1H), 7.51–7.48 (m, 1H), 7.32–7.27 (m, 2H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 250 Hz), 133.5 (d, *J* = 1.3 Hz), 130.1, 130.0, 129.3, 125.6, 124.1, 124.07, 115.7, 115.5, 89.7, 82.4 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8FS^+$ $(M+H)^+$ 203.03253, found 203.03239.

*4.4.31. 3-((3-bromophenyl)ethynyl)thiophene(**4mc**)*

Yield: 0.123 g (93%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.27 (q, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.19–7.15 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 131.4, 130.1, 129.90, 129.86, 129.3, 125.6, 125.3, 122.3, 121.9, 87.5, 86.0 ppm. HRMS (ESI) *m/z* calcd for $C_{12}H_8BrS^+$ $(M+H)^+$ 262.95246, found 262.95203.

*4.4.32. 1-Fluoro-4-(phenylethynyl)benzene(**4bd**)[7e]*

Yield: 0.026 g (27%), white solid, m.p.: 104–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 4H), 7.37–7.33 (m, 3H), 7.06–7.01 (m, 2H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6(d, *J* = 248.2 Hz), 134.7(d, *J* = 8.6 Hz), 133.6(d, *J* = 8.3 Hz), 131.7, 128.5 (d, *J* = 3.9 Hz), 123.2, 116.1(d, *J* = 22.2 Hz), 115.8(d, *J* = 22.0 Hz), 89.2, 88.4 ppm.

*4.4.33. 1-Ethyl-4-(p-tolylethynyl)benzene(**4dd**) [7n]*

Yield: 0.030 g (26%), white solid, m.p.: 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2H), 7.45–7.43 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.06–7.00 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.24 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 247.8 Hz), 144.9, 133.6, 133.5, 131.7, 128.1, 120.4, 119.7, 115.8, 115.6, 89.4, 87.8, 29.0, 15.5 ppm.

*4.4.34. 1,2-bis(4-fluorophenyl)ethyne(**4id**) [7z]*

Yield: 0.081 g (76%), white solid, m.p.: 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (m, 4H), 7.02 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 248.2 Hz), 133. 5(d, *J* = 8.4 Hz), 119.3 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.1 Hz), 88.1 ppm. HRMS (ESI) *m/z* calcd for $C_{14}H_9F_2^+$ $(M+H)^+$ 215.06668, found 215.06625.

*4.4.35. 1-Fluoro-3-((4-fluorophenyl)ethynyl)benzene(**4jd**)*

Yield: 0.074 g (69%), white solid, m.p.: 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 2H), 7.29–7.27 (m, 2H), 7.22–7.19 (m, 1H), 7.06–7.00 (m, 1H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 248.7 Hz), 162.5(d, *J* = 245.2 Hz), 133.7 (d, *J* = 8.4 Hz), 130.1 (d, *J* = 8.7 Hz), 127.6 (d, *J* = 3.1 Hz), 125.1 (d, *J* = 9.5 Hz), 119.0 (d, *J* = 3.5 Hz), 118.4 (d, *J* = 22.6 Hz), 115.85 (d, *J* = 22.2 Hz), 115.78 (d, *J* = 21.1 Hz), 89.3, 87.9 ppm. HRMS (ESI) *m/z* calcd for $C_{14}H_9F_2^+$ $(M+H)^+$ 215.06668, found 215.06665.

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*4.4.36. 1-Fluoro-2-((4-fluorophenyl)ethynyl)benzene(**4kd**)*

Yield: 0.055 g (52%), white solid, m.p.: 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.48 (m, 3H), 7.34–7.29 (m, 1H), 7.15–7.11 (m, 2H), 7.08–7.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8(d, J = 248.6 Hz), 162.7(d, J = 250.1 Hz), 133.7(d, J = 8.4 Hz), 133.5 (d, J = 1.1 Hz), 130.2 (d, J = 7.9 Hz), 124.1 (d, J = 3.7 Hz), 119.1(d, J = 3.5 Hz), 115.8 (d, J = 22.0 Hz), 115.7 (d, J = 20.8 Hz), 111.9(d, J = 15.6 Hz), 93.4 (d, J = 3.3 Hz), 82.5 ppm. HRMS (ESI) m/z calcd for $C_{14}H_9F_2^+$ $(M+H)^+$ 215.06668, found 215.06622.

*4.4.37. 1-Fluoro-4-((4-(trifluoromethyl)phenyl)ethynyl) benzene(**4pd**)*

Yield: 0.081 g (51%), white solid, m.p.: 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 4H), 7.52–7.48 (m, 2H), 7.06–7.00 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0 (d, J = 249.2 Hz), 133.8 (d, J = 8.4 Hz), 131.9, 130.1 (q, J = 32.5 Hz), 127.1, 125.4 (q, J = 3.8 Hz), 122.7, 118.8 (d, J = 3.5 Hz), 116.0(d, J = 22.0 Hz), 90.8, 87.8 ppm. HRMS (ESI) m/z calcd for $C_{15}H_9F_4^+$ $(M+H)^+$ 265.06349, found 265.06360.

*4.4.38. 1-Methyl-4-(phenylethynyl)benzene(**4be**)[7e]*

Yield: 0.085 g (89%), White solid, m.p.71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52(dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.36–7.31 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H)ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5, 131.7, 131.6, 129.2, 128.4, 128.2, 123.6, 120.3, 89.7, 88.8, 21.6 ppm.

*4.4.39. 1,2-Di-p-tolylethyne(**4ae**) [7c]*

Yield: 0.046 g (44%), white solid, m.p.: 122–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.0 Hz, 4H), 7.14–7.11 (m, 4H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 131.6, 129.2, 120.5, 89.0, 21.6 ppm.

*4.4.40. 1-Chloro-4-(p-tolylethynyl)benzene(**4oe**) [7c]*

Yield: 0.045 g (40%), white solid, m.p.: 144-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.40 (m, 4H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 134.2, 132.9, 131.6, 129.6, 128.8, 122.1, 120.0, 90.7, 87.8, 21.7 ppm.

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Appendix A. Supplementary data

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