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Double elimination protocol for access to unsymmetrically substituted aromatic polyynes starting from sulfones and aldehydes

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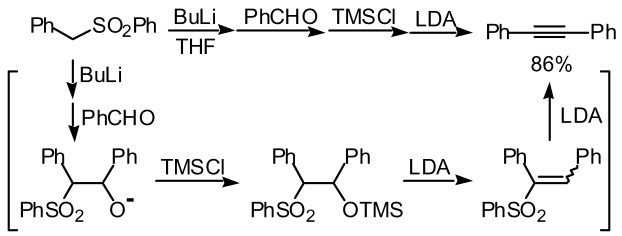
Abstract—A double elimination protocol has been established for access to unsymmetrically substituted aromatic polyynes by use of dialdehyde and substituted benzylic or propargylic sulfones as starting compounds. For this protocol, various substituted sulfones and phthalaldehydes were usable giving rise to the formation of the desired substituted aromatic polyynes.

1. Introduction

Phenylene–ethynylenes have received great attention as organic materials like liquid crystal,[1] photo-[2] and electroluminescent compounds[3] and precursors for carbon-rich materials and polymers.[4] Sonogashira coupling[5] between aryl halides and acetylenes is utilized widely and routinely for access to these compounds. Although this protocol is useful because of facile availability of starting compounds such as terminal alkynes and aryl iodides or triflates, selective preparation of phenylene–ethynylenes with different terminal substituents requires tedious procedures. Bromo iodo arene substrates were employed for selective coupling.[6] In protection–deprotection methodology, TMS- and TIPS-acetylenes were separately deprotected by treatment with K_2CO_3/MeOH and fluoride, respectively.[7] A dialkyltriazene group which is inert to Sonogashira coupling was utilized as an equivalent of iodide, and it is transformed, on demand, to iodide by treatment with MeI.[8] In order to simplify these procedures, various technologies have been developed. A solid-phase synthesis, 'tea bag' technology, enables a combinatorial approach which is indeed useful for access to various substituted patterns of phenylene–ethynylene pentamers: repeating of Sonogashira coupling between polymer-supported terminal alkyne and silylethynylphenyl iodide building blocks followed by deprotection of the resulting silylacetylene.[9] More recently, Grieco succeeded in a one-pot synthesis of triyne by consecutive Sonogashira coupling through in situ deprotection of the intermediate silyl acetylene.[10]

We have already established another approach for acetylene compounds through double elimination protocol of the β-substituted sulfones (Scheme 1).[11] This process is composed of a series of reactions such as aldol type C–C bond formation between sulfone and aldehyde, alcohol protection of the resulting aldolate and double elimination of the β-substituted sulfone, and all these steps could be carried out in one-pot under basic reaction conditions. We postulated that if two kinds of sulfones with different substituents were allowed to react with respective formyl groups of phthalaldehydes separately, unsymmetrically substituted aromatic polyynes would be accessible. This is indeed the case. We report herein a full account of our protocol.[12]



Scheme 1. Double elimination protocol of β-substituted sulfone for acetylene.

2. Results and discussion

In order to prepare unsymmetrically substituted di(phenylethynyl)benzenes **1**, we designed a two-step process shown in Scheme 2. In the first step, sulfone **2** reacts with one of the formyl groups of terephthalaldehyde (**3c**) giving rise to formylvinylsulfone **4**. The second step allows another sulfone to react with the remaining formyl group of **4**, and

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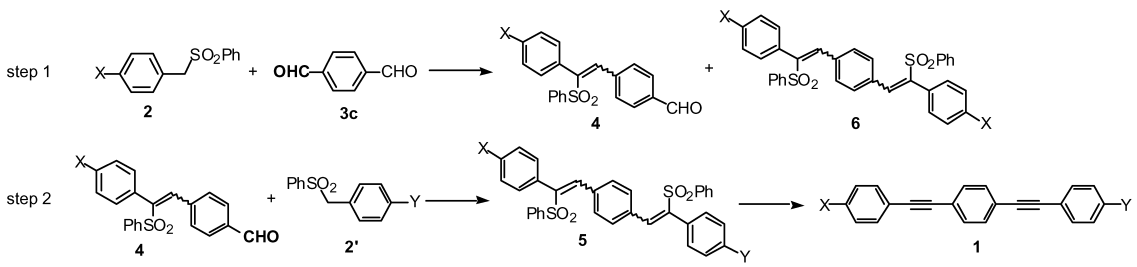
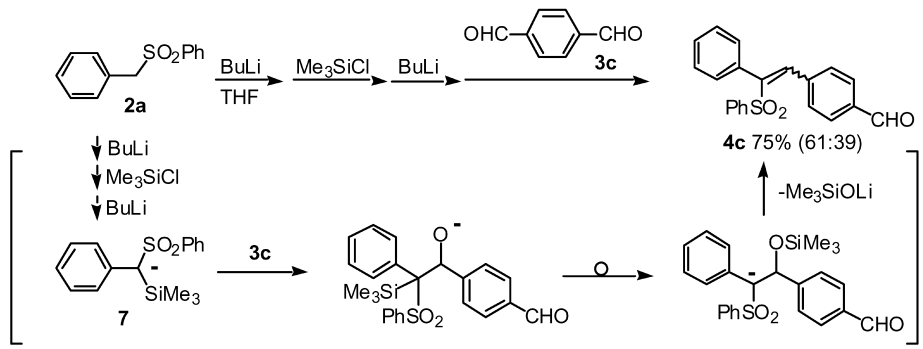


Scheme 2. Two-step process for unsymmetrically substituted phenylene–ethynylene **1**.



Scheme 3. Preparation of formylvinylsulfone **4c** by use of benzylic sulfone **2a** and phthalaldehyde **3c**.

the resulting divinylsulfone **5** was transformed to the desired diacetylene **1** through elimination of sulfinic acid upon treatment with base. Although it may happen in the first step of this process that the desired formylvinylsulfone **4** is contaminated by the starting dialdehyde **3c** and/or a plausible co-product divinylsulfone **6**, **4** would be easily separable because of the high polarity of the phenylsulfonyl group.

We first attempted to prepare formylvinylsulfone **4** through coupling between **2** and **3** (step 1 in Scheme 2). For access to formylvinylsulfones **4**, Peterson olefination[13] served well: α-lithio-α-silylsulfone **7** in situ prepared from **2a** reacted with **3c** to give **4c** in 75% yield (Scheme 3, entry 3 in Table 1). In addition to *p*-phthalaldehyde **3c**, the *o*- and *m*-substituted ones, **3a** and **3b**, also could be used providing the desired vinylsulfones **4**. Although the coupling with **3a** and **3c** proceeded smoothly by use of equimolar **2** and **3**, an excess amount of **3b** was required for good yields of the corresponding vinylsulfones **4b** and **4h** because, otherwise, a considerable amount of bis(vinylsulfone) **6** was produced (entries 2 and 8). The reactions of *o*-phthalaldehyde **3a** with benzylic sulfones **2a** and **2i** resulted in the formation of one of geometrical isomers (entries 1 and 7). When dimethylphthalaldehyde **3d** was employed, the addition of 3 equiv. of **3d** was crucial presumably due to the steric hindrance around the formyl groups (entries 10 and 11). A variety of benzylsulfone derivatives having a functional group such as fluorine **2c**, trifluoromethyl **2g** and methoxy **2i** were usable. It should be noted that bromosulfone **2e** could be successfully incorporated to **4** without reductive-debromination (entry 5) (Fig. 1).

Table 1. Reaction of benzylic sulfones **2** with phthalaldehydes **3** (step 1 in Scheme 2)

Entry	2	3	Products	
			4	Yield[a] (%)
1	**2a**	**3a**	**4a**	32 (one isomer)
2	**2a**	**3b**[b]	**4b**	84 (67:33)
3	**2a**	**3c**	**4c**	75 (61:39)
4	**2c**	**3c**	**4d**	82 (76:24)
5	**2e**	**3c**	**4e**	76 (77:23)
6	**2g**	**3c**	**4f**	67 (75:25)
7	**2i**	**3a**	**4g**	63 (one isomer)
8	**2i**	**3b**[c]	**4h**	83 (93:7)
9	**2i**	**3c**	**4i**	71 (88:12)
10	**2a**	**3d**[d]	**4j**	76 (67:33)
11	**2i**	**3d**[d]	**4k**	79 (81:19)

[a] Isolated yield. Ratio of geometrical isomers is shown in parentheses. *E* and *Z* isomers are not characterized.
[b] **3b** (1.5 equiv.) was used.
[c] **3b** (2.0 equiv.) was used.
[d] **3d** (3.0 equiv.) was used.

With these results in hand, we tackled coupling between **2** and **4** (step 2 in Scheme 2). When **2b** was treated successively with BuLi, **4c**, $ClP(O)(OEt)_2$ and *t*-BuOK, the desired unsymmetrically substituted di(phenylethynyl)-benzene **1i** was obtained in 92% yield (70% total yield in 2 steps) (Scheme 4, entry 9 in Table 2). As shown in Table 2, integration of steps 1 and 2 afforded the desired unsymmetrically substituted di(phenylethynyl)benzenes **1**, respectively. The order to feed the sulfones in this 2-step process have virtually no influence (entries 10 and 16, 15 and 23, 20 and 26, 22 and 28), yet initial addition of sulfones bearing a more electron-withdrawing group resulted in better yields than those of the reversed order except the combination shown in entries 22 and 28 (Fig. 2).

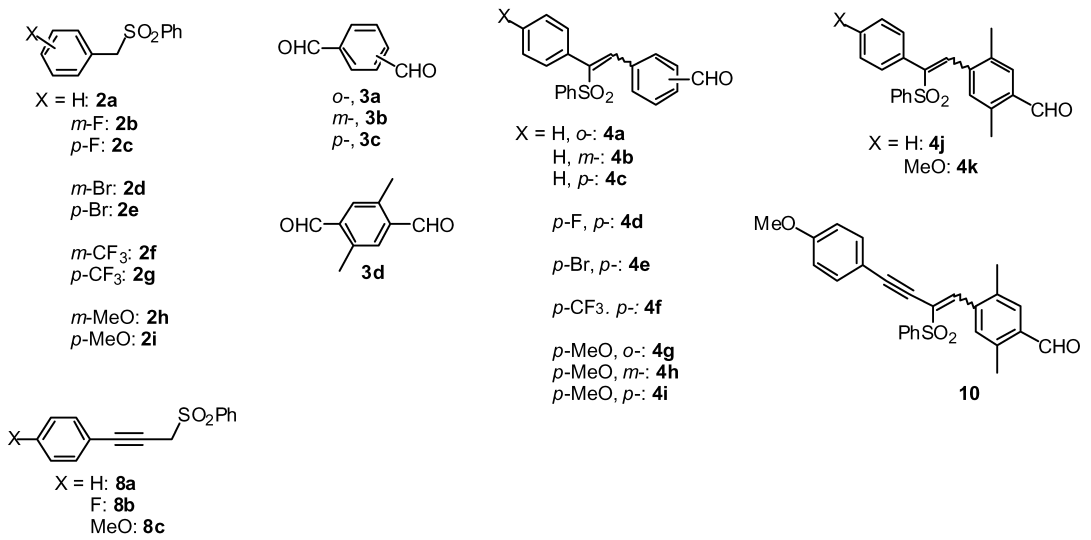
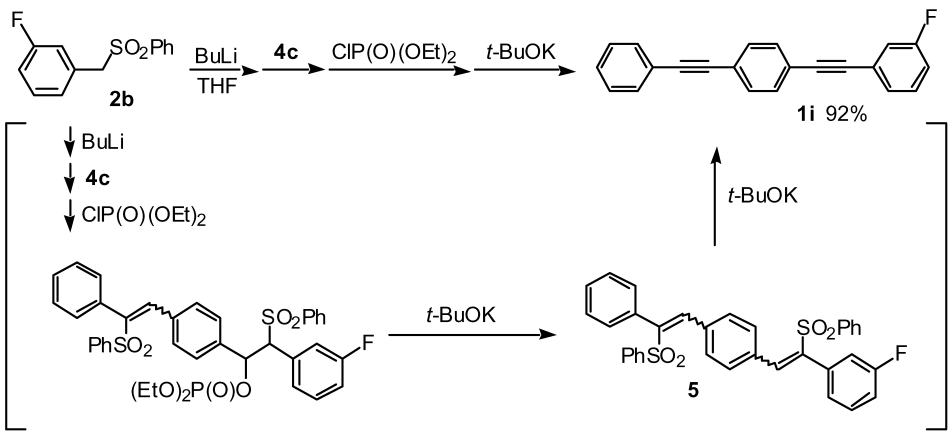


Figure 1. Structures of sulfones **2**-**4**, **8** and **10**.



Scheme 4. Preparation of unsymmetrically substituted phenylene-ethynylene **1i** by use of **2b** and **4c**.

Propargylsulfones **8a**–**c** can serve as building blocks as well, and a butadiyne unit was constructed in these cases. For instance, when a THF solution of propargylsulfone **8c**, formylvinylsulfone **4j** and $ClP(O)(OEt)_2$ was consecutively treated with bases such as LiHMDS and LDA, triyne **9a** was obtained in 64% yield (49% total yield in two steps) (Scheme 5, entry 1 in Table 3). Other yne–diyne derivatives **9** could be prepared through the same procedure (entries 2 and 3 in Table 3). It should be noted that addition order of sulfones **2** and **8** plays a crucial role for access to **9**: subjection of benzylsulfone **2a** and formylvinylsulfone **10**, prepared from propargylsulfone **8c**, to double elimination protocol (step 2) resulted in a considerably lower yield of the desired product **9a** because of the formation of many unidentified byproducts (Scheme 6).

3. Conclusion

We have presented herein a practical route to unsymmetrically substituted aromatic polyynes by using double elimination of β-substituted sulfones. This process is useful for synthesis of aromatic polyynes bearing various functional groups such as F, Br, CF_3 and MeO, and will find a broad range of applications in the synthesis of aromatic acetylenes.

4. Experimental

4.1. General procedure for the preparation compounds 4

To a THF solution (5 mL) of benzyl phenyl sulfone (**2a**) (232 mg, 1.0 mmol) was added a hexane solution of BuLi (1.60 M, 0.69 mL, 1.1 mmol) at −78°C, and the mixture was stirred for 0.5 h. Trimethylsilyl chloride (0.14 mL, 1.1 mmol) was added, and the mixture was stirred at room temperature for 1 h. BuLi (1.60 M, 0.69 mL, 1.1 mmol) was added at −78°C, and the mixture was stirred for 0.5 h. Terephthalaldehyde (**3c**) (134 mg, 1.0 mmol) was added and the mixture was stirred for 2 h. After usual workup with ethyl acetate and NH_4Claq, drying over $MgSO_4$ and evaporation, the residue was subjected to column chromatography to furnish **4c** as a 61:39 mixture of geometrical isomers (261 mg, 75%).

Table 2. Reaction of vinylsulfone with benzylsulfone (step 2 in Scheme 3)

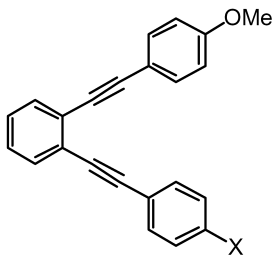
Entry	4	2	Products		
			1	Yield[a] (%)	Total yield through steps 1 and 2 (%)
1[b]	**4a**	**2i**	**1a**	91	32×91=29
2[b]	**4g**	**2c**	**1b**	77	63×77=49
3[b]	**4g**	**2e**	**1c**	65	63×65=41
4[b]	**4b**	**2i**	**1d**	79	84×79=66
5[b]	**4h**	**2b**	**1e**	86	83×86=71
6[b]	**4h**	**2c**	**1f**	87	83×87=72
7[b]	**4h**	**2d**	**1f**	73	83×73=61
8[b]	**4h**	**2e**	**1h**	76	83×76=63
9	**4c**	**2b**	**1i**	92	75×92=70
10	**4c**	**2c**	**1j**	80	75×80=60
11	**4c**	**2d**	**1k**	90	75×90=68
12	**4c**	**2e**	**1l**	83	75×83=62
13	**4c**	**2f**	**1m**	88	75×88=66
14	**4c**	**2h**	**1o**	75	75×75=56
15	**4c**	**2i**	**1p**	91	75×91=68
16	**4d**	**2a**	**1j**	89	82×89=73
17	**4d**	**2h**	**1r**	91	82×91=75
18	**4d**	**2i**	**1s**	72	82×72=59
19	**4e**	**2h**	**1u**	90	76×90=68
20	**4e**	**2i**	**1v**	87	76×87=66
21	**4f**	**2a**	**1n**	85	67×85=57
22	**4f**	**2i**	**1x**	67	67×67=45
23	**4i**	**2a**	**1p**	75	71×75=53
24	**4i**	**2b**	**1q**	76	71×76=54
25	**4i**	**2d**	**1t**	79	71×79=56
26	**4i**	**2e**	**1v**	69	71×69=49
27	**4i**	**2f**	**1w**	89	71×89=63
28	**4i**	**2g**	**1x**	86	71×86=61

[a] Isolated yield.
[b] LiHMDS was used instead of *t*-BuOK.

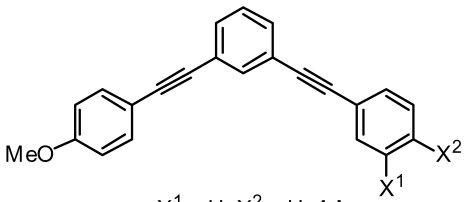
4.1.1. 2-[2-Phenyl-2-(phenylsulfonyl)vinyl]benzaldehyde (4a). One geometrical isomer: geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, *J*=7.7 Hz, 1H), 7.01 (d, *J*=7.3 Hz, 2H), 7.12 (t, *J*=7.8 Hz, 2H), 7.21 (t, *J*=7.5 Hz, 1H), 7.29 (td, *J*=7.5 Hz, 0.9 Hz, 1H), 7.39–7.43 (m, 3H), 7.52 (t, *J*=7.5 Hz, 1H), 7.78–7.81 (m, 3H), 8.55 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.2, 128.5, 128.7, 128.9, 129.1, 130.2, 130.5, 131.0, 133.0, 133.2, 133.4, 134.6, 134.9, 138.1, 138.7, 143.7, 192.0; HRMS (EI): calcd for 348.0820, found: 348.0836.

4.1.2. 3-[2-Phenyl-2-(phenylsulfonyl)vinyl]benzaldehyde (4b). 67:33. Geometry *E* or *Z* was not determined. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01–8.02 (m, 15H), 9.76, 10.05 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 129.0, 129.2, 129.5, 129.6, 129.7, 130.1, 130.2, 130.4, 130.6, 131.9, 133.2, 133.4, 133.7, 134.7, 135.0, 135.3, 135.6, 135.7, 135.8, 136.4, 138.1, 139.5, 139.7, 143.3, 145.4, 191.3, 191.8. HRMS (EI): calcd for 348.0820, found: 348.0833.

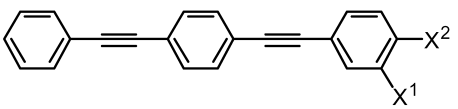
4.1.3. 4-[2-Phenyl-2-(phenylsulfonyl)vinyl]benzaldehyde (4c). 61:39. Geometry *E* or *Z* was not determined): ^{1}H NMR (500 MHz, acetone-d_6) δ 7.04–8.07 (m, 15H), 9.97, 10.09 (s, 1H): ^{13}C NMR (125 MHz, acetone-d_6) δ 128.9, 129.0, 129.4, 129.5, 129.6, 129.7, 129.8, 129.9, 130.1, 130.3, 130.6, 130.7, 131.5, 131.8, 132.0, 134.2, 134.5, 136.4, 137.0, 137.1, 137.9, 139.5, 139.6, 141.1, 141.2, 141.4, 145.6, 146.3, 192.3, 192.6. HRMS (EI): calcd for 348.0820, found: 348.0844.



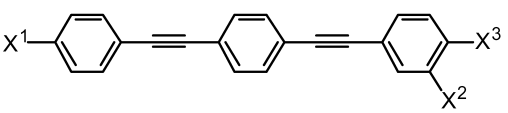
X = H: **1a**
F: **1b**
Br: **1c**



X^1 = H, X^2 = H: **1d**
X^1 = F, X^2 = H: **1e**
X^1 = H, X^2 = F: **1f**
X^1 = Br, X^2 = H: **1g**
X^1 = H, X^2 = Br: **1h**

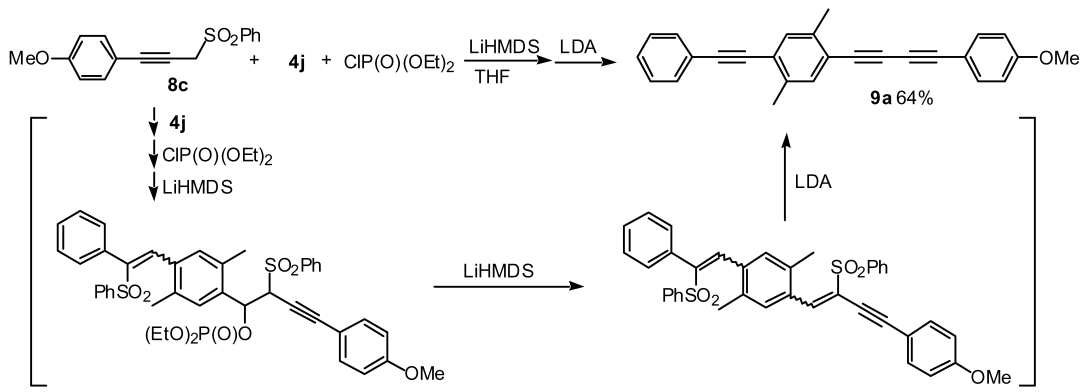


X^1 = F, X^2 = H: **1i**
X^1 = H, X^2 = F: **1j**
X^1 = Br, X^2 = H: **1k**
X^1 = H, X^2 = Br: **1l**
X^1 = CF_3, X^2 = H: **1m**
X^1 = H, X^2 = CF_3: **1n**
X^1 = OMe, X^2 = H: **1o**
X^1 = H, X^2 = OMe: **1p**



X^1 = MeO, X^2 = F, X^3 = H: **1q**
X^1 = F, X^2 = MeO, X^3 = H: **1r**
X^1 = F, X^2 = H, X^3 = MeO: **1s**
X^1 = MeO, X^2 = Br, X^3 = H: **1t**
X^1 = Br, X^2 = MeO, X^3 = H: **1u**
X^1 = Br, X^2 = H, X^3 = MeO: **1v**
X^1 = MeO, X^2 = CF_3, X^3 = H: **1w**
X^1 = MeO, X^2 = H, X^3 = CF_3: **1x**

Figure 2. Structures of **1**.

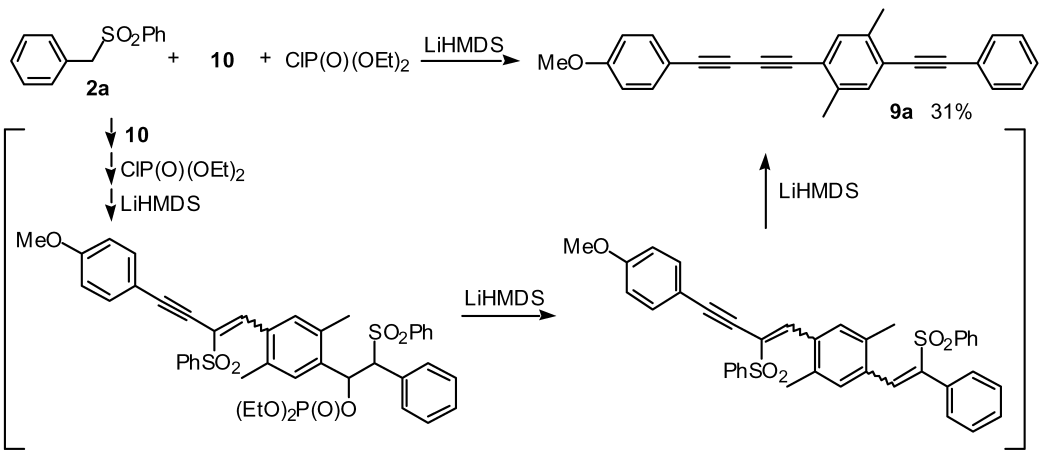


Scheme 5. Preparation of aromatic polyyne **9a** by use of **8c** and **4j**.

Table 3. Reaction of vinylsulfone **4** with propargylsulfone **8** (Scheme 5)

Entry	4	8	Products		
			9	Yield[a] (%)	Total yield (%)
1	**4j**	**8c**	**9a**	64	76×64=49
2	**4k**	**8a**	**9b**	21	79×21=17
3	**4k**	**8b**	**9c**	42	79×42=33

[a] Isolated yield.



Scheme 6. Preparation of aromatic polyyne **9a** by use of **2a** and **10**.

4.1.4. 4-[2-(4-Fluorophenyl)-2-(phenylsulfonyl)vinyl]-benzaldehyde (4d). 76:24. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.11–8.08 (m, 14H), 9.98, 10.08 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 115.8, 116.0, 116.7, 116.9, 128.0, 128.1, 128.9, 129.4, 129.5, 129.7, 130.0, 130.1, 130.7, 131.7, 132.5, 132.6, 132.9, 133.0, 133.7, 133.8, 134.3, 134.5, 137.1, 137.6, 137.9, 139.4, 139.5, 141.0, 141.2, 141.4, 141.5, 144.5, 145.1, 162.9, 163.2, 164.9, 165.2, 192.3, 192.5. Elemental analysis calcd (%) for $C_{21}H_{15}FO_3S$: C 68.84, H 4.13; found: C 68.96, H 4.01.

4.1.5. 4-[2-(4-Bromophenyl)-2-(phenylsulfonyl)vinyl]-benzaldehyde (4e). 77:23. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90–8.02 (m, 14H), 9.94, 10.05 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.7, 124.2, 128.1, 128.6, 128.7, 129.0, 129.1, 129.5, 129.6, 129.7, 130.8, 131.1, 132.1, 133.5, 133.7, 133.8, 136.0, 136.4, 136.7, 137.8, 138.1, 139.4, 139.7, 140.0, 143.3, 144.7, 191.2, 191.7. Elemental analysis calcd (%) for $C_{21}H_{15}BrO_3S$: C 59.03, H 3.54; found: C 59.30, H 3.50.

4.1.6. 4-[2-(4-Trifluoromethylphenyl)-2-(phenylsulfonyl)vinyl]benzaldehyde (4f). 75:25. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.30–8.15 (m, 14H), 10.09, 9.98 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 123.3, 125.8, 125.9, 126.0, 126.1, 126.6, 126.7, 126.9, 128.9, 129.3, 129.4, 129.8, 130.0, 130.1, 130.2, 130.5, 130.7, 130.9, 131.2, 131.4, 131.5, 131.8, 132.5, 132.7, 134.5, 134.8, 137.3, 138.1, 138.3, 139.1, 139.4, 140.4, 140.5, 140.8, 140.9, 142.4, 144.2, 145.1, 192.3, 192.6. Elemental analysis calcd (%) for $C_{22}H_{15}F_3O_3S$: C 63.45, H 3.63; found: C 63.32, H 3.36.

4.1.7. 2-[2-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl]-benzaldehyde (4g). One geometrical isomer. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.64 (d, J=8.6 Hz, 2H), 6.93–7.00 (m, 3H), 7.31–7.34 (m, 1H), 7.39–7.44 (m, 3H), 7.52 (t, J=7.6 Hz, 1H), 7.80 (t, J=6.6 Hz, 3H), 8.50 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.1, 113.8, 122.1, 128.5, 128.8,

129.0, 130.5, 132.4, 132.8, 133.1, 133.4, 134.5, 135.2, 137.5, 138.9, 143.5, 159.9, 191.9. HRMS (EI): calcd for 378.0926, found: 378.0892.

4.1.8. 3-[2-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl]-benzaldehyde (4h). 93:7. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.87–8.05 (m, 14H), 9.80, 10.04 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 55.7, 114.4, 115.3, 123.5, 128.7, 129.2, 129.3, 129.6, 129.8, 130.0, 130.1, 130.9, 131.0, 132.2, 132.4, 132.8, 134.0, 134.3, 135.1, 135.2 135.9, 136.2, 136.4, 137.0, 137.7, 137.8, 140.0, 140.5, 144.4, 161.5, 192.2, 192.7. HRMS (EI): calcd for 378.0926, found: 378.0901.

4.1.9. 4-[2-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl]-benzaldehyde (4i). 88:12. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, acetone-d_6) δ 3.81 (s, 3H), 6.80–7.97 (m, 14H), 9.92, 10.04 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.1, 55.2, 113.6, 114.4, 122.3, 125.9, 128.0, 128.5, 128.6, 128.7, 129.0, 129.5, 129.6, 130.8, 131.1, 131.8, 133.1, 133.3, 135.7, 136.4, 138.2, 138.8, 139.2, 139.8, 140.3, 144.2, 145.3, 160.2, 160.4, 191.3, 191.7. HRMS (EI): calcd for 378.0926, found: 378.0955.

4.1.10. 4-[2-Phenyl-2-(phenylsulfonyl)vinyl]-2,5-dimethylbenzaldehyde (4j). 67:33. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25, 2.22 (s, 3H), 2.45, 2.68 (s, 3H), 6.62–8.14 (m, 13H), 10.13, 10.27 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 128.0, 128.3, 128.4, 128.5, 128.8, 129.1, 129.2, 129.8, 130.4, 130.6, 132.4, 132.5, 133.1, 133.2, 133.4, 133.5, 133.7, 133.9, 134.8, 135.1, 135.9, 137.1, 137.2, 137.3, 138.4, 139.2, 139.6, 139.9, 144.7, 146.0, 192.1, 192.3. HRMS (EI): calcd for 376.1133, found: 376.1119.

4.1.11. 4-[2-(4-Methoxyphenyl)-2-(phenylsulfonyl)-vinyl]-2,5-dimethylbenzaldehyde (4k). 81:19. Geometry *E* or *Z* was not determined. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30, 2.20 (s, 3H), 2.42, 2.67 (s, 3H), 3.77, 3.84 (s, 3H), 6.69–8.09 (m, 12H), 10.14, 10.26 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 18.8, 18.9, 19.3, 19.4, 55.2, 55.3, 113.7, 114.0, 122.3, 126.9, 128.0, 128.5, 128.8, 131.3, 132.0, 132.4, 132.5, 132.6, 133.1, 133.2, 133.3, 133.6, 133.7, 133.9, 135.0, 135.8, 137.2, 137.4, 137.6, 138.6, 139.1, 139.5, 140.1, 144.5, 145.5, 160.2, 160.3, 192.2, 192.4. HRMS (EI): calcd for 406.1239, found: 406.1246.

4.2. General procedure for the preparation of compounds 1

To a THF solution (5 mL) of *p*-methoxybenzyl phenyl sulfone (**2i**) (79 mg, 0.30 mmol) was added BuLi (1.60 M, 0.21 mL, 0.35 mmol), and the mixture was stirred for 0.5 h. A THF solution (3 mL) of **4c** (87 mg, 0.25 mmol) was added, and the mixture was stirred for 1 h. At −78°C, $ClP(O)(OEt)_2$ (0.05 mL, 0.30 mmol) was added, and the mixture was stirred at room temperature for 2 h. *t*-BuOK (421 mg, 3.75 mmol) was added at −78°C, and the mixture was stirred at −78°C for 1 h and at room temperature for 2 h. After usual workup with ethyl acetate and NH_4Claq, drying over $MgSO_4$ and evaporation, the residue was subjected to column chromatography to furnish **1p** (70 mg, 91%).

4.2.1. 1-(4-Methoxyphenylethynyl)-2-phenylethynyl-benzene (1a). Liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.86 (d, *J*=8.9 Hz, 2H), 7.26–7.36 (m, 5H), 7.48–7.58 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.1, 88.5, 93.4, 93.7, 114.0, 115.4, 123.4, 125.6, 126.2, 127.6, 128.0, 128.3, 131.5, 131.6, 131.7, 133.1, 159.8. HRMS (EI) calcd for 308.1201; found: 308.1204.

4.2.2. 1-(4-Fluorophenylethynyl)-2-(4-methoxyphenyl-ethynyl)benzene (1b). Liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.86 (d, *J*=8.9 Hz, 2H), 7.03 (d, *J*=8.7 Hz, 2H), 7.23–7.30 (m, 2H), 7.47–7.55 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.0, 88.1, 88.2, 92.3, 93.7, 114.1, 115.4, 115.6, 115.7, 119.4, 119.5, 125.4, 126.2, 127.6, 128.0, 131.5, 131.6, 133.1, 133.4, 133.5, 159.8, 161.6, 163.6. HRMS (EI) calcd 326.1107; found: 326.1107.

4.2.3. 1-(4-Bromophenylethynyl)-2-(4-methoxyphenyl-ethynyl)benzene (1c). Mp 117–119°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.87 (d, *J*=8.9 Hz, 2H), 7.26–7.32 (m, 2H), 7.39–7.42 (m, 2H), 7.44–7.49 (m, 4H), 7.52–7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.0, 89.6, 92.3, 93.9, 114.1, 115.3,122.4, 122.6, 126.2, 126.3, 127.7, 128.2, 131.5, 131.6, 131.7, 133.0, 133.1, 159.9. Elemental analysis calcd (%) for $C_{23}H_{15}BrO$: C 71.33, H 3.90; found: C 71.61, H 3.51.

4.2.4. 1-(4-Methoxyphenylethynyl)-3-phenylethynyl-benzene (1d). Mp 118–120°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.88 (d, *J*=8.8 Hz, 2H), 7.28–7.36 (m, 4H), 7.45–7.55 (m, 6H), 7.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.3, 88.6, 89.9, 90.0, 114.0, 115.1, 123.0, 123.6, 124.0, 128.36, 128.40, 128.41, 130.9, 131.1, 131.6, 133.1, 134.4, 159.7. Elemental analysis calcd (%) for $C_{23}H_{16}O$: C 89.58, H 5.23; found: C 89.18, H 5.07.

4.2.5. 1-(3-Fluorophenylethynyl)-3-(4-methoxyphenyl-ethynyl)benzene (1e). Mp 86–88°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (d, *J*=8.8 Hz, 2H), 7.01–7.08 (m, 1H), 7.20–7.25 (m, 1H), 7.30–7.35 (m, 3H), 7.44–7.49 (m, 4H), 7.70 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.2, 88.5, 88.6, 89.5, 90.2, 114.0, 115.1, 115.6, 115.9, 118.2, 118.5, 123.1, 124.1, 124.8, 125.0, 127.5, 127.6, 128.5, 129.9, 130.0, 131.0, 131.4, 133.1, 134.5, 159.8, 160.8, 164.0. Elemental analysis calcd (%) for $C_{23}H_{15}FO$: C 84.64, H 4.63; found: C 84.32, H 4.44.

4.2.6. 1-(4-Fluorophenylethynyl)-3-(4-methoxyphenyl-ethynyl)benzene (1f). Mp 105–107°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.88 (d, *J*=8.6 Hz, 2H), 7.05 (t, *J*=8.6 Hz, 2H), 7.31 (t, *J*=7.8 Hz, 1H), 7.43–7.53 (m, 6H), 7.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.2, 88.3, 88.4, 88.8, 90.1, 114.0, 115.1, 115.5, 115.8, 119.1,119.2, 123.4, 124.0, 128.4, 130.9, 131.2, 133.1, 133.5, 133.6, 134.4, 159.8, 160.9, 164.2. Elemental analysis calcd (%) for $C_{23}H_{15}FO$: C 84.64, H 4.63; found: C 84.42, H 4.52.

4.2.7. 1-(3-Bromophenylethynyl)-3-(4-methoxyphenyl-ethynyl)benzene (1g). Mp 121–123°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (d, *J*=8.9 Hz, 2H),

7.22 (t, J=7.8 Hz, 1H), 7.32 (t, J=7.8 Hz, 1H), 7.44–7.54 (m, 6H), 7.67–7.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 87.4, 88.5, 90.2, 90.4, 114.3, 115.3, 122.5, 123.3, 124.4, 125.4, 128.7, 130.1, 130.4, 131.2, 131.7, 131.8, 133.4, 134.6, 134.8, 160.1. HRMS (EI) calcd 386.0306; found: 386.0297.

4.2.8. 1-(4-Bromophenylethynyl)-3-(4-methoxyphenylethynyl)benzene (1h). Mp 127–129°C: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.88 (d, J=8.8 Hz, 2H), 7.32 (t, J=7.8 Hz, 1H), 7.38 (d, J=8.6 Hz, 2H), 7.44–7.50 (m, 6H), 7.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.2, 88.8, 89.8, 90.1, 114.1, 115.1, 122.0, 122.7, 123.2, 124.1, 128.5, 130.9, 131.4, 131.7, 133.0, 133.1, 134.4, 159.8. Elemental analysis calcd (%) for $C_{23}H_{15}BrO$: C 71.33, H 3.90; found: C 70.94, H 3.67.

4.2.9. 1-(3-Fluorophenylethynyl)-4-phenylethynylbenzene (1i). Mp 167–169°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03–7.08 (m, 1H), 7.23 (d, J=8.3 Hz, 1H), 7.29–7.38 (m, 5H), 7.48–7.55 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 88.98, 89.84, 89.87, 89.93, 91.42, 115.70, 115.87, 118.27, 118.45, 122.54, 122.95, 123.48, 124.84, 124.91, 127.49, 127.51, 128.39, 128.51, 129.92, 129.99, 131.56, 131.59, 131.63, 161.41, 163.37; Elemental analysis calcd (%) for $C_{22}H_{13}F$: C 89.17, H 4.42; found: C 88.80, H 4.29.

4.2.10. 1-(4-Fluorophenylethynyl)-4-phenylethynylbenzene (1j). Mp 225–227°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (t, J=8.6 Hz, 2H), 7.35–7.37 (m, 3H), 7.49–7.54 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.7, 88.8, 89.0, 90.1, 91.3, 115.6, 115.9, 119.1, 119.1, 122.9, 123.0, 123.2, 128.4, 128.5, 131.4, 131.5, 131.6, 133.5, 133.6, 160.9, 164.2. Elemental analysis calcd (%) for $C_{22}H_{13}F$: C 89.17, H 4.42; found: C 89.02, H 4.08.

4.2.11. 1-(3-Bromophenylethynyl)-4-phenylethynylbenzene (1k). Mp 164–166°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, J=7.9 Hz, 1H), 7.35–7.37 (m, 3H), 7.45–7.55 (m, 8H), 7.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 89.0, 89.6, 90.4, 91.5, 122.2, 122.5, 123.0, 123.5, 125.1, 128.4, 128.5, 129.8, 130.1, 131.56, 131.57, 131.59, 131.63, 134.3. Elemental analysis calcd (%) for $C_{22}H_{13}Br$: C 73.97, H 3.67; found: C 74.03, H 3.38.

4.2.12. 1-(4-Bromophenylethynyl)-4-phenylethynylbenzene (1l). Mp 208–210°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.39 (m, 3H), 7.40 (d, J=8.5 Hz, 2H), 7.49–7.55 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 89.0, 90.1, 90.2, 91.4, 122.0, 122.6, 122.7, 122.9, 123.4, 128.4, 128.5, 131.5, 131.6, 131.61, 131.7, 133.0. Elemental analysis calcd (%) for $C_{22}H_{13}Br$: C 73.97, H 3.67; found: C 73.69, H 3.43.

4.2.13. 1-Phenylethynyl-4-(3-trifluoromethylphenylethynyl)benzene (1m). Mp 155–157°C: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.37 (m, 3H), 7.46–7.61 (m, 8H), 7.69 (d, J=7.6 Hz, 1H), 7.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 88.94, 89.52, 90.57, 91.54, 122.33, 122.62, 122.94, 123.68, 124.02, 124.78, 124.89, 124.92, 124.95, 124.98, 128.35, 128.39, 128.40, 128.41, 128.45, 128.54, 128.92, 128.99, 130.90, 131.16, 131.52, 131.60, 131.62, 131.64, 134.62, 134.63, 134.64. Elemental analysis calcd (%) for $C_{23}H_{13}F_3$: C 79.76, H 3.78; found: C 79.58, H 3.61.

4.2.14. 1-Phenylethynyl-4-(4-trifluoromethylphenylethynyl)benzene (1n). Mp 214–216°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.37 (m, 3H), 7.53–7.55 (m, 6H), 7.63 (d, J=3.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 88.9, 89.7, 91.4, 91.6, 122.1, 122.3, 122.9, 123.8, 125.2, 125.2, 125.3, 125.4, 125.7, 126.8, 126.9, 128.4, 128.6, 129.4, 129.9, 130.3, 130.7, 131.6, 131.64, 131.7, 131.8. Elemental analysis calcd (%) for $C_{23}H_{13}F_3$: C 79.76, H 3.78; found: C 79.39, H 3.54.

4.2.15. 1-(3-Methoxyphenylethynyl)-4-phenylethynylbenzene (1o). Mp 137–139°C: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.89–6.92 (m, 1H), 7.06–7.07 (m, 1H), 7.13 (d, J=7.7 Hz, 1H), 7.23–7.29 (m, 1H), 7.32–7.38 (m, 3H), 7.47–7.54 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 88.9, 89.1, 91.2, 91.3, 115.2, 116.4, 123.0, 123.1, 123.2, 124.0, 124.2, 128.4, 128.5, 129.5, 131.53, 131.56, 131.63, 159.4. Elemental analysis calcd (%) for $C_{23}H_{16}O$: C 89.58, H 5.23; found: C 89.24, H 5.15.

4.2.16. 1-(4-Methoxyphenylethynyl)-4-phenylethynylbenzene (1p). Mp 175–177°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (d, J=8.9 Hz, 2H), 7.34–7.37 (m, 3H), 7.46–7.54 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.9, 89.2, 91.1, 91.3, 114.0, 115.1, 122.7, 123.1, 123.4, 128.4, 128.4, 131.3, 131.5, 131.6, 133.1, 159.8. Elemental analysis calcd (%) for $C_{23}H_{16}O$: C 89.58, H 5.23; found: C 89.53, H 5.06.

4.2.17. 1-(3-Fluorophenylethynyl)-4-(4-methoxyphenylethynyl)benzene (1q). Mp 175–177°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (d, J=8.6 Hz, 2H), 7.05 (t, J=8.6 Hz, 2H), 7.45–7.52 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.8, 88.8, 88.9, 89.9, 91.4, 114.0, 115.1, 115.6, 115.8, 119.1, 119.2, 122.5, 123.5, 131.3, 131.4, 133.1, 133.4, 133.5, 159.8, 161.6, 163.6. Elemental analysis calcd (%) for $C_{23}H_{15}FO$: C 84.64, H 4.63; found: C 84.50, H 4.50.

4.2.18. 1-(4-Fluorophenylethynyl)-4-(3-methoxyphenylethynyl)benzene (1r). Mp 163–165°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89–6.92 (m, 1H), 7.03–7.07 (m, 3H), 7.13 (d, J=7.7 Hz, 1H), 7.24–7.28 (m, 1H), 7.46–7.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 88.75, 88.77, 88.8, 90.1, 91.2, 115.2, 115.6, 115.9, 116.3, 119.0, 119.1, 122.9, 123.1, 124.0, 124.2, 129.5, 131.5, 131.6, 133.5, 133.6, 159.4, 161.0, 164.3. Elemental analysis calcd (%) for $C_{23}H_{15}FO$: C 84.64, H 4.63; found: C 84.30, H 4.49.

4.2.19. 1-(4-Fluorophenylethynyl)-4-(4-methoxyphenylethynyl)benzene (1s). Mp 200–202°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.89 (d, J=9.0 Hz, 2H), 7.06 (t, J=8.7 Hz, 2H), 7.45–7.54 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.8, 88.8, 88.9, 89.9, 89.94, 91.4, 114.0, 115.0, 115.6, 115.8, 119.1, 119.2, 122.5, 123.5, 131.4, 131.4, 133.1, 133.4, 133.5, 159.8, 160.9, 164.2. Elemental analysis calcd (%) for $C_{23}H_{15}FO$: C 84.64, H 4.63; found: C 84.41, H 4.69.

4.2.20. 1-(3-Bromophenylethynyl)-4-(4-methoxyphenylethynyl)benzene (1t). Mp 175–177°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.89 (d, J=8.9 Hz, 2H), 7.22 (t, J=7.9 Hz, 1H), 7.44–7.48 (m, 8H), 7.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.8, 89.4, 90.5, 91.6, 114.1, 115.0, 122.1, 122.2, 123.9, 125.1, 129.8, 130.1, 131.4, 131.5, 131.6, 133.1, 134.3. Elemental analysis calcd (%) for $C_{23}H_{15}BrO$: C 71.33, H 3.90; found: C 70.98, H 3.62.

4.2.21. 1-(4-Bromophenylethynyl)-4-(3-methoxyphenylethynyl)benzene (1u). Mp 196–198°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.90–6.92 (m, 1H), 7.06 (s, 1H), 7.13 (d, J=7.7 Hz, 1H), 7.23–7.28 (m, 1H), 7.39 (d, J=8.2 Hz, 2H), 7.48–7.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 88.8, 90.1, 90.2, 91.3, 115.2, 116.4, 122.0, 122.7, 122.8, 123.3, 124.0, 124.2, 129.5, 131.5, 131.6, 131.7, 133.0, 159.4. Elemental analysis calcd (%) for $C_{23}H_{15}BrO$: C 71.33, H 3.90; found: C 71.21, H 3.73.

4.2.22. 1-(4-Bromophenylethynyl)-4-(4-methoxyphenylethynyl)benzene (1v). Mp 256–258°C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.89 (d, J=8.5 Hz, 2H), 7.39 (d, J=8.3 Hz, 2H), 7.49 (t, J=8.70 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.8, 89.9, 90.3, 91.5, 114.0, 115.0, 122.0, 122.3, 122.7, 123.7, 131.4, 131.5, 131.7, 133.0, 133.1, 159.8. Elemental analysis calcd (%) for $C_{23}H_{15}BrO$: C 71.33, H 3.90; found: C 71.16, H 3.76.

4.2.23. 1-(4-Methoxyphenylethynyl)-4-(3-trifluoromethylphenylethynyl)benzene (1w). Mp 164–166°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.89 (d, J=8.9 Hz, 2H), 7.47–7.53 (m, 7H), 7.59 (d, J=8.0 Hz, 1H), 7.70 (d, J=7.7 Hz, 1H), 7.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 87.7, 89.4, 90.6, 91.6, 114.0, 115.0, 121.9, 122.6, 124.0, 124.1, 124.7, 124.8, 124.9, 128.3, 128.4, 128.9, 130.8, 131.1, 131.4, 131.6, 133.1, 134.5, 134.6, 159.8. Elemental analysis calcd (%) for $C_{24}H_{15}F_3O$: C 76.59, H 4.02; found: C 76.67, H 3.88.

4.2.24. 1-(4-Methoxyphenylethynyl)-4-(4-trifluoromethylphenylethynyl)benzene (1x). Mp 244–246°C: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.89 (d, J=8.9 Hz, 2H), 7.47–7.51 (m, 6H), 7.60–7.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 87.7, 89.5, 91.5, 91.7, 114.1, 115.0, 121.6, 122.1, 124.1, 125.2, 125.3, 125.3, 125.4, 125.7, 126.8, 126.9, 129.8, 130.2, 131.4, 131.6, 131.8, 133.1, 159.8. Elemental analysis calcd (%) for $C_{24}H_{15}F_3O$: C 76.59, H 4.02; found: C 76.39, H 3.71.

4.3. General procedure for the preparation of compound 9

To a THF solution (5 mL) of **4j** (75 mg, 0.20 mmol), **8c** (69 mg, 0.24 mmol) and $Cl(O)P(OEt)_2$ (0.04 mL, 0.24 mmol) was added LiHMDS (1.0 M in THF, 0.44 mL, 0.44 mmol) at −78°C, and the mixture was stirred for 2 h. Then, to this solution was added toluene (10 mL) followed by LiHMDS (1.0 M in THF, 4.0 mL, 4.0 mmol) at −78°C, and the mixture was stirred for 3 h at room temperature. After usual workup with NH_4Claq and ethyl acetate, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel to give **9a** (46 mg, 64%).

4.3.1. 1-(4-Methoxyphenylbuta-1,3-diynyl)-2,5-dimethyl-4-(phenylethynyl)benzene (9a). Mp 150–152°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.44 (s, 3H), 3.82 (s, 3H), 6.86 (d, J=8.6 Hz, 2H), 7.34–7.38 (m, 5H), 7.48 (d, J=8.6 Hz, 2H), 7.52–7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.0, 20.1, 55.3, 72.8, 78.8, 80.0, 83.0, 88.1, 95.2, 113.7, 114.1, 121.6, 123.2, 123.7, 128.3, 128.4, 131.5, 132.6, 133.5, 134.1, 137.3, 138.7, 160.3. Elemental analysis calcd (%) for $C_{27}H_{20}O$: C 89.97, H 5.59; found: C 89.69, H 5.43.

4.3.2. 1-(4-Methoxyphenylethynyl)-2,5-dimethyl-4-(phenylbuta-1,3-diynyl)benzene (9b). Mp 149–151°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 6H), 3.83 (s, 3H), 6.88 (d, J=8.9 Hz, 2H), 7.32–7.38 (m, 5H), 7.47 (d, J=8.9 Hz, 2H), 7.53–7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.02, 20.03, 55.3, 74.0, 78.4, 80.6, 82.7, 86.9, 95.4, 114.0, 115.3, 121.0, 121.9, 124.3, 128.4, 129.2, 132.4, 132.5, 133.0, 133.6, 137.1, 138.7, 159.7. HRMS (EI) calcd 360.1514; found: 360.1514.

4.3.3. 1-(4-Fluorophenylbuta-1,3-diynyl)-4-(4-methoxyphenylethynyl)-2,5-dimethyl benzene (9c). Mp 156–158°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.43 (s, 3H), 3.83 (s, 3H), 6.88 (d, J=8.6 Hz, 2H), 7.04 (t, J=8.7 Hz, 2H), 7.33 (t, J=9.5 Hz, 2H), 7.46 (d, J=8.9 Hz, 2H), 7.51–7.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.0, 20.1, 55.3, 73.80, 73.81, 78.2, 80.6, 81.5, 86.8, 95.5, 114.0, 115.3, 115.8, 116.0, 117.9, 118.0, 120.8, 124.4, 132.5, 133.0, 133.6, 134.4, 134.5, 137.1, 138.7, 159.8, 162.0, 164.0. Elemental analysis calcd (%) for $C_{27}H_{19}FO$: C 85.69, H 5.06; found: C 85.82, H 4.77.

4.4. Procedure for the preparation of compounds 10

To a THF solution (5 mL) of **3d** (324 mg, 2.0 mmol), **8c** (143 mg, 0.5 mmol), $Cl(O)P(OEt)_2$ (0.09 mL, 0.6 mmol) was added LiHMDS (1.0 M in THF, 1.1 mL, 1.1 mmol) at −78°C. The mixture was stirred at −78°C for 3 h. After usual work-up with NH_4Claq and ethyl acetate, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel to give **10** (166 mg, 77%).

4.4.1. 4-[4-(4-Methoxyphenyl)-2-(phenylsulfonyl)but-1-en-3-ynyl]-2,5-dimethylbenzaldehyde (10). Mp 180–182°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.51 (s, 3H), 2.63 (s, 3H), 3.83 (s, 3H), 6.87 (d, J=8.9 Hz, 2H), 7.31 (d, J=8.9 Hz, 2H), 7.58 (t, J=7.8 Hz, 2H), 7.67 (t, J=7.5 Hz, 2H), 8.05–8.07 (m, 2H), 8.12 (s, 1H), 8.18 (s, 1H), 10.2 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 19.3, 55.4, 80.6, 103.2, 113.4, 114.3, 128.0, 128.9, 129.1, 131.4, 133.2, 133.7, 133.8, 134.9, 136.3, 136.6, 136.7, 137.6, 138.7, 160.8, 192.1. Elemental analysis calcd (%) for $C_{26}H_{22}O_4S$: C 72.54, H 5.15; found: C 72.36, H 4.83.

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