Convenient Synthesis of (1-Propynyl)arenes through a One-Pot Double Elimination Reaction, and Their Conversion to Enynes

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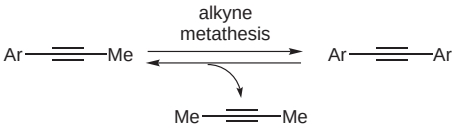
In memory of the late Professor Yoshihiko Ito

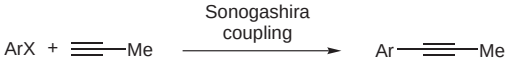
Abstract: A series of (1-propynyl)arenes were prepared by one-pot double elimination reaction of ethyl sulfone, aromatic aldehyde and chloro diethylphosphate in THF with a base such as BuLi and *t*-BuOK. A propargyllithium which was prepared by treatment of (1-propynyl)arene with BuLi in the presence of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) reacted with aromatic aldehyde, chloro diethylphosphate and *t*-BuOK to afford (4-arylbut-3-en-1-ynyl)arene. Photoluminescence of the enynes thus prepared was recorded both in solution and in the solid state.

Key word: alkynes, sulfones, aldehydes, eliminations, enynes

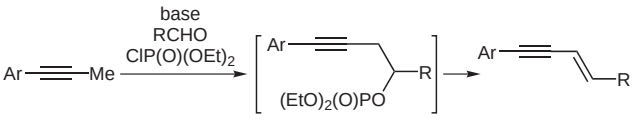
We have long been engaged in the double elimination reaction of β-substituted sulfones, by which a facile one-pot process for the synthesis of various aromatic acetylenes involving mono-, di-, and triyne components has been achieved.[1] Since the acetylenes thus obtained were terminated only by aromatic or trialkylsilyl groups, we became interested in further diversification of the terminal groups. Among them, termination with a methyl group seemed to us of great use because of the following reasons. First, for alkyne metathesis, which has been receiving increasing attention,[2] (1-propynyl)arenes are best employed to bias the reaction in the favored direction as a result of facile release of the co-product 2-butyne from the equilibrium system (Equation 1). However, preparation of (1-propynyl)arenes suffers from inconvenience, because gaseous propyne should be manipulated for Sonogashira coupling with aryl halides (Equation 2).[3] Second, we postulated that the methylethyne component must be readily metallated upon treatment with an organometallic base, so that reaction of the in situ generated propargylic anion with aldehydes could provide a one-pot procedure to produce enynes (Equation 3). Herein, we show that the double elimination protocol is indeed effective for convenient synthesis of (1-propynyl)arenes without use of propyne. Moreover, the (1-propynyl)arenes thus obtained were transformed into enynes, which are another novel motif for electronics materials.



Equation 1

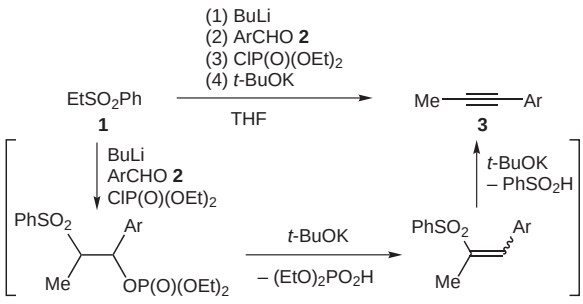


Equation 2



Equation 3

The methyl termination was realized by use of ethyl phenyl sulfone (**1**). Thus, according to the standard double elimination procedure, **1** was treated sequentially with BuLi, aldehyde **2**, $ClP(O)(OEt)_2$, and *t*-BuOK in one-pot manner[4] to afford the desired (1-propynyl)arenes **3** as shown in Scheme 1. A variety of (1-propynyl)arenes were obtained. The yields are satisfactory if it is taken into account that several consecutive reactions are involved in this procedure, i.e., metallation, aldol-type reaction, enolate trapping, and double elimination (Scheme 2). The methoxy group was employable and halogens remained intact.[4a] Not only simple phenylacetylenes but also other aromatics such as naphthyl, thienyl, ferrocenyl, and (phenylethynyl)phenyl derivatives were obtained.



Scheme 1

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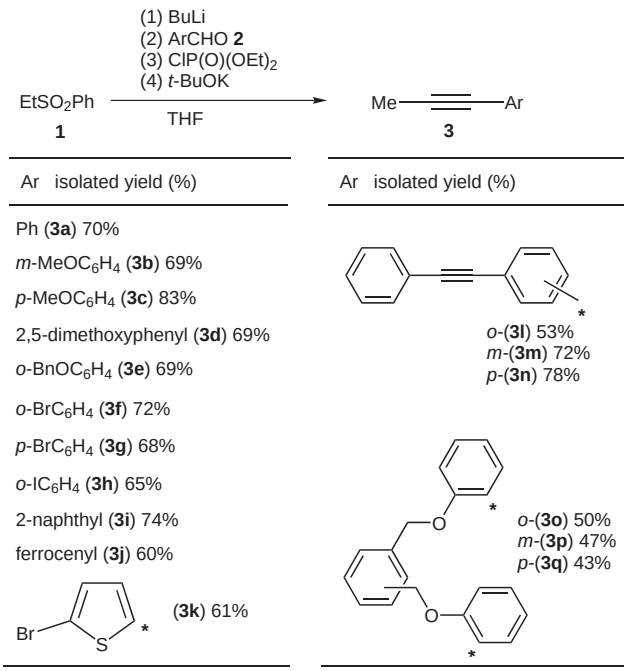
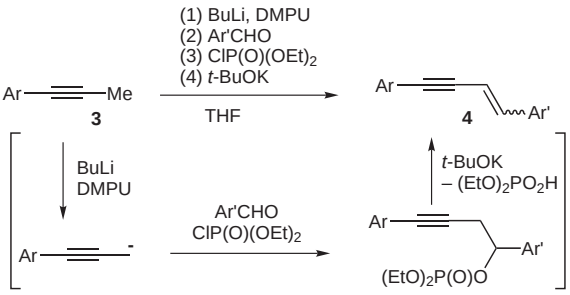


Scheme 2

Notably, bis(1-propynyl) derivatives were also accessible, and these may be employed for ring-closing and polymerization metathesis. Next, the (1-propynyl)arenes thus obtained were subjected to another one-pot procedure involving aldol-type reaction followed by elimination to provide enynes (Table 1).

Table 1 Aldol-Type Reaction of (1-Propynyl)arenes to Enynes



Ar	Ar′		Yield (*E*:*Z*)
2-naphthyl	Ph	**4a**	63 (5:1)
2-naphthyl	*p*-MeOC$_6$H$_4$	**4b**	61 (6:1)
*	Ph	**4c**	68 (2:1)
2-naphthyl	2-naphthyl	**4d**	65 (4:1)
*	*	**4e**	74 (1:1)
MeO *	Ph	**4f**	52 (3:1)

Upon treatment of **3** with BuLi in the presence of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), the corresponding propargylic anion was generated smoothly. To this solution were added aldehyde, ClP(O)(OEt)$_2$, and *t*-BuOK successively. After aqueous workup, the desired enynes **4** were obtained in reasonable yields. Although the C=C bond formation is usually carried out by Wittig reaction[5] or McMurry coupling,[6] the present method is more convenient because neither Wittig reagents nor titanium reagent is necessary.

A number of photoluminescence studies have been reported on arenes connected with vinyl and ethynyl moieties,[7] but few with enynes. We present here the preliminary results of UV–Vis. and photoluminescence spectra of the enynes obtained above. Upon reprecipitation of **4** from hot hexane, the *E*-isomers precipitated first followed by the *E*/*Z* mixtures, and, hence, the pure *E*-isomers were subjected to spectroscopic investigations. The UV–Vis spectra of **4a–c** exhibited strong bands at around 340 nm (Table 1). A strong and medium emission band was observed for **4c** and **4a**, respectively, in CH_2Cl_2, while **4b** was almost nonemissive (Figure 1). This is in parallel with the quantum yields (Table 2). Notably, **4a** and **4b** in the solid state gave higher quantum yields than in solution. This is of great promise for designing electronic devices.

Table 2 Photochemical Data of **4a–c** in Solution and in the Solid State

Compound	λ_{max} UV–Vis[a] (nm)	PL in CH_2Cl_2[b,c] (nm)	PL in the solid state[c] (nm)
4a	331	367 (0.13)	408 (0.55)
4b	341	402 (0.02)	412 (0.22)
4c	341	377 (0.58)	429 (0.50)

[a] In CH_2Cl_2 (1.9×10^{-4} M).
[b] In CH_2Cl_2 (9.4×10^{-7} M).
[c] Quantum yields are shown in parentheses.

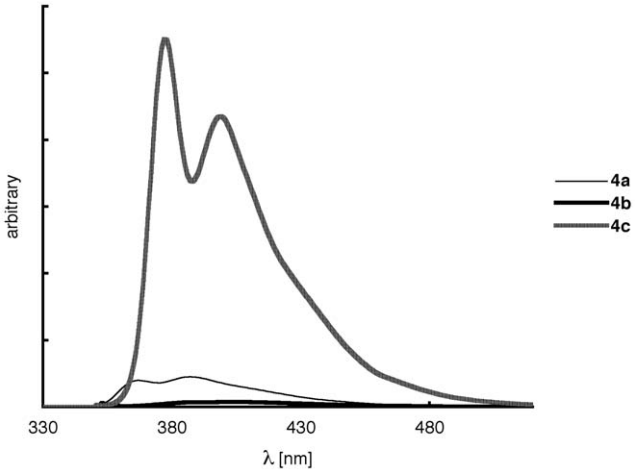


Figure 1 Emission of **4a–c** in CH_2Cl_2 (9.4×10^{-7} M)

In summary, the double elimination protocol has proved to be effective for facile synthesis of (1-propynyl)arenes[8] which are otherwise rather inconvenient to prepare. The (1-propynyl)arenes thus obtained can be transformed into enynes by one-pot addition–elimination reactions. Thus, combination of two one-pot reactions offers a new route for enynes without use of transition-metal catalysts. The enynes free from transition-metal contamination will find practical uses in electronic devices. The applications along this line are now in progress in our group.

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(8) **Typical Procedure of Preparation for 2-(1-Propynyl)naphthalene (3i)**: To a THF solution (15 mL) of ethyl phenyl sulfone (**1**, 204.3 mg, 1.2 mmol) was added BuLi (1.6 M, 0.75 mL, 1.2 mmol) at –78 °C, and the mixture was stirred for 30 min. A THF solution (2 mL) of 2-naphthaldehyde (156.2 mg, 1.0 mmol) was added at –78 °C, and the mixture was stirred for 30 min. Diethyl chlorophosphate (207.1 mg, 1.2 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 3 h. *t*-BuOK (561.1 mg, 5.0 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 15 h. After usual workup with EtOAc and aq NH_4Cl solution, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel to give 2-(1-propynyl)naphthalene (**3i**) as a white powder (123.0 mg, 74%).
2-(1-Propynyl)naphthalene (3i): mp 30–31 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 7.44–7.49 (m, 3 H), 7.74–7.80 (m, 3 H), 7.90 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.4, 80.1, 86.2, 121.3, 126.2, 126.3, 127.5, 127.6, 127.8, 128.6, 131.0, 132.4, 133.0.
(1-Propynyl)benzene (3a): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 7.27–7.29 (m, 3 H), 7.38–7.40 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.3, 79.7, 85.8, 124.0, 127.5, 128.2, 131.5.
1-Methoxy-3-(1-propynyl)benzene (3b): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 3.77 (s, 3 H), 6.82 (d, *J* = 8.2 Hz, 1 H), 6.92 (s, 1 H), 6.98 (d, *J* = 7.7 Hz, 1 H), 7.18 (t, *J* = 7.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.2, 55.1, 79.6, 85.7, 114.0, 116.3, 124.0, 125.0, 129.2, 159.2.
1-Methoxy-4-(1-propynyl)benzene (3c): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 3.78 (s, 3 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 7.32 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.3, 55.2, 79.4, 84.1, 113.8, 116.1, 132.7, 158.9.
1,4-Dimethoxy-2-(1-propynyl)benzene (3d): white powder; mp 61–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 3.75 (s, 3 H), 3.84 (s, 3 H), 6.77–6.81 (m, 2 H), 6.94 (d, *J* = 7.5 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.8, 55.7, 56.3, 75.7, 90.1, 111.6, 113.4, 114.7, 118.3, 153.1, 154.2.
1-Phenylmethyloxy-2-(1-propynyl)benzene (3e): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 5.18 (s, 2 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 6.89 (t, *J* = 7.5 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.30 (t, *J* = 7.2 Hz, 1 H), 7.36–7.40 (m, 3 H), 7.47 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.7, 70.3, 75.8, 90.1, 112.8, 113.9, 120.8, 126.8, 127.6, 128.4, 128.7, 133.1, 159.0.
1-Bromo-2-(1-propynyl)benzene (3f): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 7.11 (t, *J* = 7.7 Hz, 1 H), 7.22 (t, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 7.7 Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.4, 78.4, 90.8, 125.1, 125.8, 126.7, 128.6, 132.1, 133.2.
4-Bromo-1-(1-propynyl)benzene (3g): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.3, 78.7, 87.1, 121.6, 122.9, 131.4, 132.9.
1-Iodo-2-(1-propynyl)benzene (3h): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 6.94 (t, *J* = 8.0 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.5, 82.0, 90.2, 100.8, 127.7, 128.7, 130.4, 132.5, 138.5.
(1-Propynyl)ferrocene (3j): red powder; mp 79–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3 H), 4.13 (t, *J* = 1.8 Hz, 2 H), 4.19 (s, 5 H), 4.35 (t, *J* = 1.8 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.4, 66.0, 68.0, 69.6, 70.9, 77.2, 81.7.
2-Bromo-5-(1-propynyl)thiophene (3k): red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 6.84 (d, *J* = 3.7 Hz, 1 H), 6.88 (d, *J* = 3.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.7, 72.2, 91.3, 111.4, 125.9, 129.7, 131.2.
1-(Phenylethynyl)-2-(1-propynyl)benzene (3l): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.15 (s, 3 H), 7.23–7.26 (m, 2 H), 7.33–7.38 (m, 3 H), 7.42–7.44 (m, 1 H), 7.50–7.52 (m, 1 H), 7.54–7.57 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.5, 78.5, 88.5, 90.3, 92.9, 123.3, 125.5, 126.5, 127.2, 127.9, 128.2, 128.3, 131.5, 131.6, 131.1.

1-(Phenylethynyl)-3-(1-propynyl)benzene (3m): colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 7.23 (t, *J* = 7.9 Hz, 1 H), 7.31–7.34 (m, 4 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.50–7.52 (m, 2 H), 7.57 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.3, 78.9, 86.6, 88.6, 89.7, 123.0, 123.3, 124.3, 128.2, 128.3, 130.6, 131.2, 131.6, 134.5.

1-(Phenylethynyl)-4-(1-propynyl)benzene (3n): white powder; mp 99–101 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 7.32–7.34 (m, 3 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 8.2 Hz, 2 H), 7.51–7.53 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.4, 79.5, 87.9, 89.1, 90.7, 122.3, 123.0, 123.9, 128.3, 131.3, 131.4, 131.5.

1,2-Bis[2-(1-propynyl)phenyloxymethyl]benzene (3o): white powder; mp 99–100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.04 (s, 6 H), 5.33 (s, 4 H), 6.89 (t, *J* = 7.5 Hz, 2 H), 6.97 (d, *J* = 8.3 Hz, 2 H), 7.21 (t, *J* = 7.8 Hz, 2 H), 7.34–7.36 (m, 2 H), 7.38 (d, *J* = 7.6 Hz, 2 H), 7.61 (s, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.6, 68.7, 75.9, 90.1, 112.4, 113.7, 120.8, 128.0, 128.2, 128.8, 133.4, 134.9, 158.8.

1,3-Bis[2-(1-propynyl)phenyloxymethyl]benzene (3p): pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 6 H), 5.18 (s, 4 H), 6.85 (d, *J* = 8.3 Hz, 2 H), 6.89 (t, *J* = 7.5 Hz, 2 H), 7.17 (t, *J* = 7.9 Hz, 2 H), 7.36–7.42 (m, 5 H), 7.59 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.7, 70.4, 75.8, 90.2, 113.0, 114.0, 120.9, 125.4, 126.2, 128.6, 128.7, 133.5, 137.4, 159.0.

1,4-Bis[2-(1-propynyl)phenyloxymethyl]benzene (3q): white powder; mp 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 6 H), 5.15 (s, 4 H), 6.84–6.89 (m, 2 H), 7.17 (t, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 7.6 Hz, 4 H), 7.46 (s, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.7, 70.2, 75.8, 90.1, 112.8, 113.9, 120.8, 127.0, 128.7, 133.5, 136.5, 159.0.

Typical Procedure of Preparation for 2-(4-Phenylbut-3-en-1-ynyl)naphthalene (4a): To a THF solution (10 mL) of 2-(1-propynyl)naphthalene (83.1 mg, 0.5 mmol) and DMPU (64.1 mg, 0.5 mmol) was added BuLi (1.6 M, 0.31 mL, 0.5 mmol) at –78 °C, and the mixture was stirred for 30 min. A THF solution (2 mL) of benzaldehyde (53.1 mg, 0.5 mmol) was added at –78 °C, and the mixture was stirred for 30 min. Diethyl chlorophosphate (103.5 mg, 0.6 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 2 h. *t*-BuOK (140.3 mg, 1.25 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 2 h. After usual workup with EtOAc and aq NH_4Cl solution, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel and recrystallization (from hexane) to afford (*E*)-2-(4-phenylbut-3-en-1-ynyl)naphthalene (**4a**) as a white powder (59.0 mg, 46%). Recrystallization of the second crop from hexane gave a 3:5 mixture of *E*- and *Z*-isomers (21.1 mg, 17%).

(*E*)-2-(4-Phenylbut-3-en-1-ynyl)naphthalene (4a): white powder; mp 135–136 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.44 (d, *J* = 16.2 Hz, 1 H), 7.09 (d, *J* = 16.2 Hz, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 8.6 Hz, 1 H), 7.44–7.50 (m, 4 H), 7.53 (d, *J* = 8.2 Hz, 1 H), 7.78–7.82 (m, 3 H), 8.00 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 89.3, 92.2, 108.1, 120.7, 126.3, 126.5, 126.6, 127.7, 127.8, 128.0, 128.3, 128.6, 128.7, 131.3, 132.7, 133.0, 136.3, 141.4. ESI–MS: *m*/*z* [M^+] calcd for $C_{20}H_{14}$: 254.1; found: 254.8.

(*E*)-2-[4-(4-Methoxyphenyl)but-3-en-1-ynyl]naphthalene (4b): pale yellow powder; mp 145–147 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.29 (d, *J* = 16.2 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 16.2 Hz, 1 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 7.47–7.55 (m, 3 H), 7.78–7.82 (m, 3 H), 7.98 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 89.7, 91.4, 105.7, 114.2, 120.9, 126.5, 126.6, 127.6, 127.7, 127.8, 127.9, 128.3, 129.2, 131.1, 132.6, 133.0, 141.0, 160.1. ESI–MS: *m*/*z* [M^+] calcd for $C_{21}H_{16}O$: 284.1; found: 284.8.

(*E*)-1-(4-Phenylbut-3-en-1-ynyl)-4-phenylethynylbenzene (4c): white powder; mp 171–173 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.40 (d, *J* = 16.5 Hz, 1 H), 7.06 (d, *J* = 16.5 Hz, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.34–7.37 (m, 5 H), 7.44 (d, *J* = 8.3 Hz, 2 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 7.51 (d, *J* = 8.6 Hz, 2 H), 7.53–7.55 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 89.1, 90.8, 91.3, 91.5, 107.9, 122.9, 123.0, 123.2, 126.4, 128.4, 128.5, 128.8, 131.4, 131.5, 131.6, 136.2. ESI–MS: *m*/*z* [M^+] calcd for $C_{24}H_{16}$: 304.1; found: 304.8.

(*E*)-2-[4-(2-Naphthyl)but-3-en-1-ynyl]naphthalene (4d): yellow powder; mp 157–158 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.56 (d, *J* = 16.3 Hz, 1 H), 7.26 (d, *J* = 16.3 Hz, 1 H), 7.47–7.52 (m, 4 H), 7.55 (d, *J* = 8.6 Hz, 1 H), 7.65 (d, *J* = 8.6 Hz, 1 H), 7.80–7.86 (m, 7 H), 8.02 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 89.5, 92.6, 108.4, 120.7, 122.7, 126.4, 126.5, 126.6, 126.7, 127.0, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 131.3, 132.8, 133.0, 133.5, 133.8, 141.5. ESI–MS: *m*/*z* [M^+] calcd for $C_{24}H_{16}$: 304.1; found: 304.8.

(*E*)-1-(Phenylethynyl)-4-{4-[4-(phenyl-ethynyl)phenyl]but-3-en-1-ynyl}benzene (4e): yellow powder; mp 263–266 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 16.4 Hz, 1 H), 7.04 (d, *J* = 16.4 Hz, 1 H), 7.35–7.37 (m, 7 H), 7.43 (d, *J* = 8.3 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.50 (d, *J* = 8.3 Hz, 2 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.53–7.55 (m, 3 H). ESI–MS: *m*/*z* [M^+] calcd for $C_{32}H_{20}$: 404.2; found: 404.9. ^{13}C NMR could not be measured because of poor solubility.

(*E*)-1-(4-Methoxyphenylethynyl)-3-(4-phenylbut-3-en-1-ynyl)benzene (4f): mp 104–106 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.39 (d, *J* = 16.2 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.06 (d, *J* = 16.2 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 7.7 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.40–7.46 (m, 4 H), 7.48 (d, *J* = 8.9 Hz, 2 H), 7.63 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 87.3, 89.4, 90.0, 90.9, 107.9, 114.0, 123.7, 123.9, 126.3, 128.3, 128.4, 128.7, 128.8, 130.8, 131.0, 133.1, 134.3, 136.2, 141.6, 159.7. ESI–MS: *m*/*z* [M^+] calcd for $C_{25}H_{18}O$: 334.1; found: 334.9.