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# Zirconocene-promoted coupling reaction of terminal acetylenes to geminal enediynes in the presence of *p*-chloranil

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Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

## Abstract

Reaction of alkynyllithium with zirconocene dichloride in the presence of quinones afforded zirconoenediynes in good yields. Treatment of the zirconoenediyne with *p*-chloranil in the presence of CuCl afforded 1,1,4,4-tetraethynyl-1,3-diene in good yield. In the presence of CuCl and/or $Pd(PPh_3)_4$, the zirconoenediynes could be transformed into various enediyne derivatives through coupling reaction with electrophiles.

*Keywords:* Coupling reactions; Alkynes; Zirconium; Quinones; Enediynes

## 1. Introduction

Geminal enediynes (gem-DEEs) have recently received considerable attention due to their extensive applications in molecular wires, switches, and other components for molecular electronics, nonlinear optics (NLO), organic conductors, light-emitting diodes [1–4]. Consequently, there is significant interest in the development of new synthetic methodologies to access geminal enediynes. Although a number of synthetic methods affording geminal enediynes have been reported [5–9], alternative strategies that involve the metal-mediated direct coupling of terminal acetylenes (Scheme 1) remain to be developed.

Organometal-promoted coupling reactions have proved to be an extremely powerful tool to construct carbon–carbon bonds [10]. Among them, interest in organozirconium chemistry has been rapidly increasing and a tremendous number of applications in synthetic chemistry have been found [11]. In a typical process, the carbon–carbon bond formation was reported by Negishi et al. using zirconate complex $Li[Cp_2Zr(C{\equiv}CR)_3]$ [12,13]. Three equivalents of $LiC{\equiv}CPh$ were essential to promote the carbon–carbon bond formation, however, the third $LiC{\equiv}CPh$ did not take part in forming new C–C bond. Considering atomic economics, it is important in maximal use of raw materials. It was reported of oxidative decomposition of organozirconium compounds as a promising method in forming new carbon–carbon bond through coupling reaction of the ligands on the zirconocene species [14]. Recently, it was found out that treatment of zirconacyclopentadienes with quinones in the presence of CuCl gave cyclobutadiene derivatives in our group [15]. As a part of our continuing program on the application of organozirconium and quinones in organic synthesis, herein we would like to report zirconocene-promoted trimerization of terminal acetylenes into zirconoenediynes **1** in the presence of *p*-chloranil (Scheme 2). Moreover, the resulting zirconoenediynes **1** can be converted into various geminal enediynes through coupling reaction with electrophiles.

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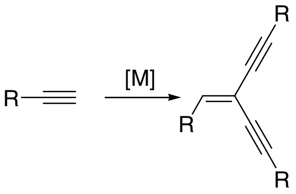
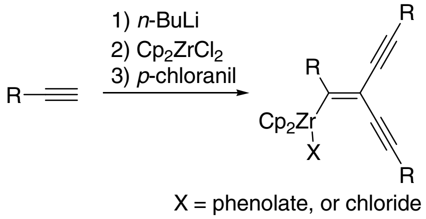


Scheme 1.



Scheme 2.

## 2. Results and discussion

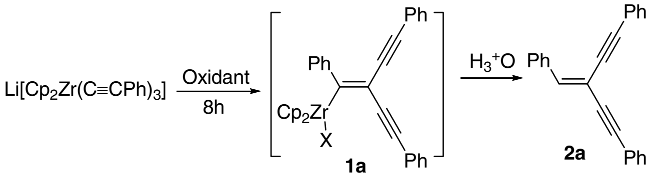
Reaction of $Li[Cp_2Zr(C{\equiv}CPh)_3]$ prepared by the reaction of $Cp_2ZrCl_2$ with 3 equiv. of $LiC{\equiv}CPh$ according to reported literature [12], with oxidants such as 1,4-benzoquinone, tetrachlorobenzoquinone (TCQ) or dichlorodicyanobenzoquinone (DDQ) were carefully examined and quenched with acid to form (2-(phenylethynyl)but-1-en-3-yne-1,4-diyl)dibenzene (**2a**). The product **2a** was characterized by $^{13}$C NMR spectroscopy. Its $^{13}$C NMR($CDCl_3$, $Me_4Si$) spectrum revealed characteristic signals for $=C$-($\equiv$-Ph)$_2$, $=C$H-Ph at 103.3 and 143.2 ppm, and four sp carbons appeared at 86.9, 88.3, 89.2, and 94.6 ppm. Its data were consistent with the literature [7e].

As expected, the oxidants promoted the coupling reaction involving the third $LiC{\equiv}CPh$ for the trimerization of phenylacetylene, and their results relied on the different oxidants and reaction temperature were collected in Table 1. Accordingly to results of entries 1–3, both TCQ and DDQ worked well for this reaction, and the optimized condition is as the following: using TCQ or DDQ as an oxidant, the reaction was carried out at 35 °C for 8 h under nitrogen atmosphere. It was noteworthy that in any of the cases, trace amount of 1,4-diphenyl-1,3-butadiyne was detected by GC–MS even addition of excess amount of oxidants.

The intermediate organozirconium **1a** was assumed in forming product **2a**. To clarify this issue, deuteriolysis and iodinolysis of organozirconium **1a** afforded monodeuterated compound **3a** in 65% yield with 94% deuterium incorporation, and monoiodinated product **4a** in 60% yield, respectively (Scheme 3). The results indicated that zirconium containing complex **1a** formed as an intermediate.

Under the optimized conditions, the coupling reactions of various terminal alkynes were extensively examined and the results are summarized in Table 2. When the aromatic 1-alkynes were used, the desired products were formed in moderated yields (entries 1–4). However, when the aliphatic 1-alkynes were used, only trace amount of desired product was formed (entry 5) and main product was diyne. When 1-ethynylcyclohex-1-ene was used, the corresponding enediyne **2f** was formed in 17% isolated yield (entry 6). Likely the conjugated system of 1-alkyne is necessary for the further coupling of third 1-alkyne.

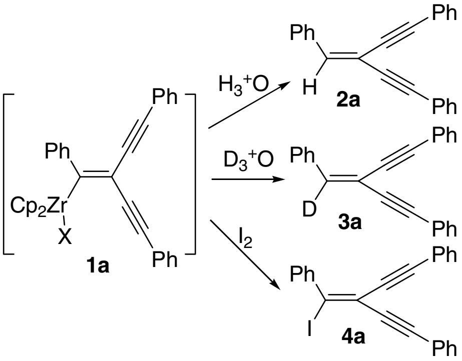
Table 1
Optimization of reaction conditions[a]



| Entry | Oxidant | Temperature (°C) | Yield of **2a** (%)[b] |
|---|---|---|---|
| 1 | 1,4-Benzoquinone | 35 | 10 |
| 2 | TCQ | 35 | 67 |
| 3 | DDQ | 35 | 64 |
| 4 | DDQ | 20 | 24 |
| 5 | DDQ | 10 | 21 |
| 6 | TCQ | 20 | 27 |
| 7 | TCQ | 10 | 25 |

[a] Reaction conditions: ethynylbenzene (3.0 mmol), $Cp_2ZrCl_2$ (1.0 mmol), Oxidant (1.3 mmol).

[b] Isolated yields.

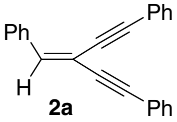
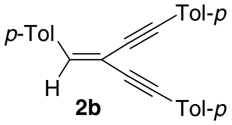
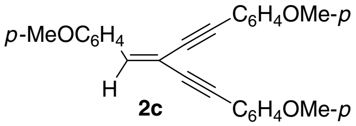
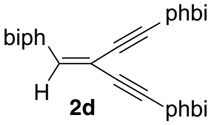
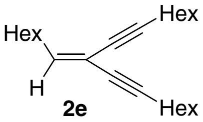
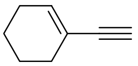
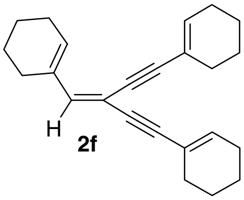


Scheme 3.

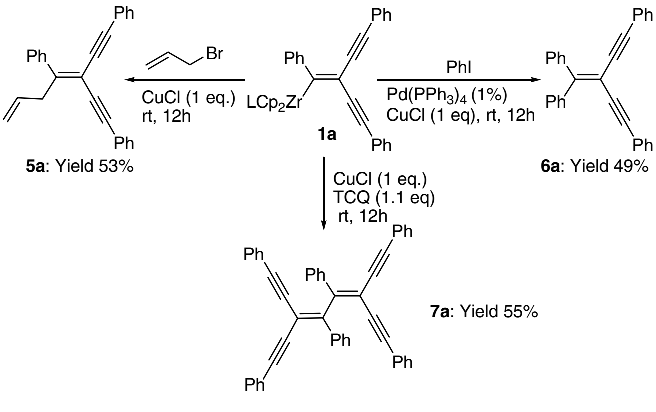
The remaining Zr–C bond of zirconoendiynes **1** could be used in forming functionalized enediynes through coupling reaction with various electrophiles such as iodobenzene, or allyl bromide in the presence of CuCl and/or $Pd(PPh_3)_4$. Typically, **1a** was investigated in reacting with allyl bromide in the presence of CuCl, and one new carbon–carbon bond was formed to give **5a** in 53% yield. In addition, the reaction of **1a** with iodobenzene gave compound **6a** in 49% yield in the presence of CuCl and $Pd(PPh_3)_4$. Moreover, when **1a** was treated with TCQ in the presence of CuCl, dimerized product **7a** was obtained in 55% yield (Scheme 4).

Recently, triethynylethenes have received attention in conjugated organic materials, however, such synthetic reports are rarely reported [16]. The new forming product **4** could be further used in reactions, the reactions of **4** with

Table 2
Homo-coupling reaction of alkynes promoted by zirconocene in the presence of TCQ

| Entry | Alkynes | Time (h) | Product | Yield(%)[a] |
|---|---|---|---|---|
| 1 | Ph—≡ | 8 |  **2a** | 67 |
| 2 | *p*-Tol—≡ | 12 |  **2b** | 56 |
| 3 | *p*-$MeOC_6H_4$—≡ | 8 |  **2c** | 63 |
| 4 | biph—≡ | 12 |  **2d** | 43 |
| 5 | Hex—≡ | 36 |  **2e** | Trace |
| 6 |  | 24 |  **2f** | 17 |

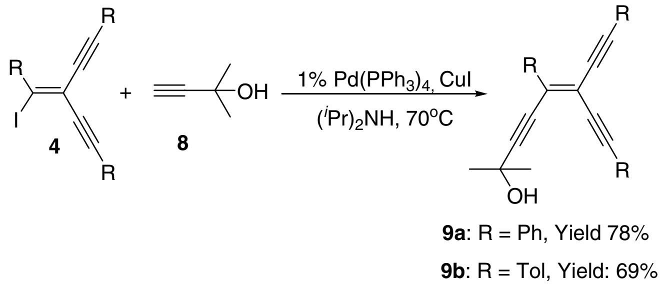
[a] Isolated yields.



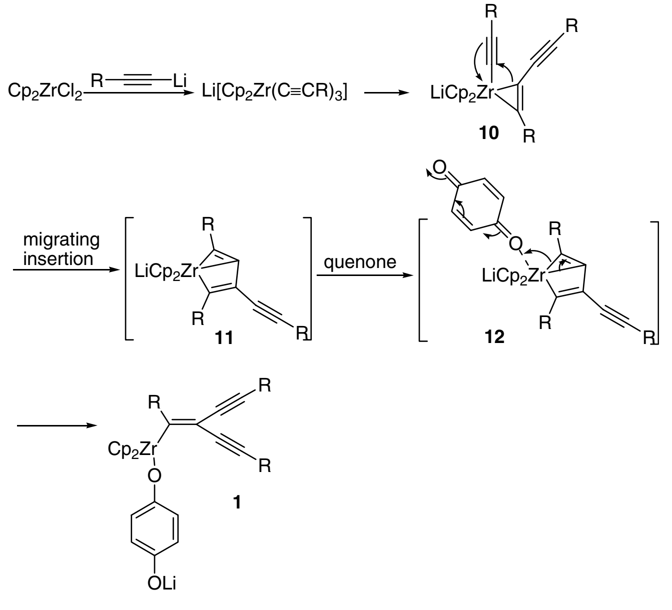
Scheme 4.

alkyne **8** under Sonogashira reaction conditions afforded product **9** in high yields (Scheme 5). Therefore, herein the reaction provides a general methodology for the preparation of triethynylethenes.

The pathway of the oxidation of $Li[Cp_2Zr(C{\equiv}CR)_3]$ into zirconoenediynes is not clear yet. Possible mechanism is proposed as the following (Scheme 6). First, the zirconate complex $Li[Cp_2Zr(C{\equiv}CR)_3]$ undergoes a 1,2-migratory insertion reaction to give intermediate **10** [12], which was confirmed by Choukroun et al.[17]. Then the $sp^2$ carbon of zirconacyclopropylene reacted with sp carbon of $C{\equiv}CR$ to form another intermediate, proposed as the bicyclic zirconate **11**. The intermediate **11** reacts with quinone to form **1** via intermediate **12**. To understand this



Scheme 5.



Scheme 6.

mechanism, the separation and characterizations of their intermediates are still being in progress.

## 3. Conclusions

In summary, zirconocene-promoted self-coupling reactions of terminal alkynes were successively developed in the presence of *p*-chloranil to afford geminal enediynes. Its intermediates including one Zr–C bond were used to form functionalized enediynes. These reactions provided the convenient methodologies in synthesizing new organic materials with conjugated systems in good yields.

## 4. Experimental

All reactions were carried out in pre-dried Schlenk tube and under nitrogen with a slightly positive pressure. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and distilled from sodium and benzophenone under a nitrogen atmosphere. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on JOEL 300 NMR spectrometer with $CDCl_3$ as the solvent and TMS as internal standard. Flash column chromatography was performed using silica gel (200–300 mesh).

### *4.1. A typical procedure for the preparation of (2-(phenylethynyl)but-1-en-3-yne-1,4-diyl)dibenzene (**2a**)*

The phenylacetylene (3 mmol) was dissolved in THF (5 mL), and then BuLi (3.2 mmol, 2 mL, 1.6 M solution in hexane) was added in the solution at −78 °C. The mixture was stirred at room temperature for 1 h. To the reaction solution, $Cp_2ZrCl_2$ (1 mmol, 292 mg) was added at −78 °C. This mixture was stirred at room temperature for 12 h to afford a dark red solution. Then TCQ (1.3 mmol, 296 mg) was added to the solution and was stirred for another 8 h. The reaction mixture was quenched by 3N HCl solution. Product was extract with $CH_2Cl_2$ and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography silica gel ($CH_2Cl_2$/petroleum ether = 1/10) afforded 204 mg yellow liquid (isolated yield 67%). $^{1}H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.17 (s, 1H), 7.31–7.40 (m, 5H), 7.52–7.55 (m, 8H), 7.93–7.95 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 86.9, 88.3, 89.2, 94.6, 103.3, 122.4, 122.9, 128.3, 128.4, 128.8, 129.1, 129.2, 131.6, 131.7, 135.7, 143.2. HRMS calcd. for $C_{24}H_{16}$ 304.1252, found 304.1256.

#### *4.1.1. 4,4′-(2-(p-tolylethynyl)but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (**2b**)*

A yellow liquid (194 mg, isolated yield 56 %). $^{1}H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 2.28 (s, 3H), 2.29 (s, 6H), 7.03–7.13 (m, 7H), 7.33–7.37 (m, 3H), 7.75–7.78 (d, $^{3}J_{HH} = 7.9$ Hz, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 21.5, 21.5, 21.6, 86.6, 88.1, 88.8, 94.7, 102.4, 120.0, 120.0, 129.0, 129.1, 129.1, 129.2, 131.5, 131.5, 133.2, 138.4, 138.8, 139.3, 142.6. HRMS calcd. for $C_{27}H_{22}$ 346.1722, found 346.1719.

#### *4.1.2. 4,4′-(2-((4-Methoxyphenyl)ethynyl)but-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (**2c**)*

A yellow liquid (248 mg, isolated yield 63 %). $^{1}H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 3.81 (s, 3H), 3.82 (s, 3H), 3.83 (s, 3H), 6.84–7.05 (m, 7H), 7.44–7.50 (m, 4H), 7.89–7.92 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 55.44, 86.3, 87.7, 88.5, 94.4, 101.2, 113.9, 114.1, 114.2, 115.3, 115.4, 129.1, 130.7, 133.2, 141.8, 159.7, 160.0, 160.2. HRMS calcd. for $C_{27}H_{22}O_3$ 394.1569, found 394.1573.

#### *4.1.3. 4,4′-(2-(Diphenyl-4-ylethynyl)but-1-en-3-yne-1,4-diyl)-bis(diphenyl) (**2d**)*

A yellow liquid (229 mg, isolated yield 43 %). $^{1}H$ NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.21 (s, 1H), 7.30–7.36 (m, 3H), 7.40–7.44 (m, 6H), 7.55–7.64 (m, 16H), 8.02–8.06 (d, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 88.0, 88.7, 90.3, 95.1, 103.4, 121.9, 122.0, 127.1, 127.3, 127.8, 127.9, 129.0, 129.7, 132.2, 132.3, 135.0, 140.3, 140.4, 140.4, 141.2, 141.6, 141.8, 142.9. HRMS calcd. for $C_{42}H_{28}$ 532.219, found 532.221.

### *4.1.4. 1,1′-(2-(Cyclohexenylethynyl)but-1-en-3-yne-1,4-diyl)-dicyclohex-1-ene **(2f)***

A yellow liquid (54 mg, isolated yield 17 %). $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 1.56–1.66 (m, 12H), 2.10–2.16 (m, 12H), 6.01 (s, 1H), 6.09–6.12 (m, 2H), 6.44 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 21.6, 21.9, 22.2, 22.4, 22.7, 25.8, 26.6, 27.0, 28.7, 29.2, 85.4, 87.8, 88.4, 95.1, 100.2, 120.8, 121.1, 134.7, 134.9, 136.9, 145.8. HRMS calcd. for $C_{24}H_{28}$ 316.2191, found 316.2197.

### *4.1.5. (2-(Phenylethynyl)but-1-deuterium-1-en-3-yne-1,4-diyl)dibenzene **(3a)***

The reaction was carried out in a similar way to that described above using DCl instead of 3N HCl to quench the reaction mixture. Isolated yield: 65%. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.38–7.48 (m, aromatic, 9H), 7.59–7.61 (m, aromatic, 4H), 8.00–8.03 (m, aromatic, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 87.0, 88.5, 89.3, 94.7, 103.3, 122.9, 123.0, 128.4, 128.5, 128.9, 129.2, 129.3, 131.8, 131.8, 135.8, 142.9 (t, $^1J_{DC} = 23.7$ Hz). Calcd. for $C_{24}H_{15}D$ 305.1315, found 305.1319.

### *4.1.6. (1-Iodo-2-(phenylethynyl)but-1-en-3-yne-1,4-diyl)-dibenzene **(4a)***

After addition of CuCl (1.0 mmol, 99 mg) to the reaction mixture of **1a** at room temperature, $I_2$ (1.2 mmol, 305 mg) was added and the reaction mixture was stirred at room temperature for 3 h. The resulting mixture was treated with 3N HCl at 0 °C. Product was extract with $CH_2Cl_2$ and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography silica gel ($CH_2Cl_2$/petroleum ether = 1/10) yield 258 mg of the title compound in 60% isolated yield. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.28–7.29 (m, 10H), 7.34–7.41 (m, 2H), 7.63–7.71 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 86.0, 92.1, 92.5, 93.9, 114.1, 118.0, 122.6, 122.7, 127.8, 128.4, 128.5, 128.8, 129.0, 129.3, 130.0, 131.5, 131.9, 142.0. Calcd. for $C_{24}H_{15}I$ 430.0218, found 430.0221.

### *4.1.7. (3-(Phenylethynyl)hepta-3,6-dien-1-yne-1,4-diyl)-dibenzene **(5a)***

The reaction was carried out in a similar way to that described above using allyl bromide instead of $I_2$. After adding the allyl bromide, the reaction mixture was stirred for 12 h at room temperature. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 3.66–3.69 (d, $^3J_{HH} = 6.5$ Hz, 2H), 5.03–5.07 (d, $^3J_{HH} = 10.0$ Hz, 1H), 5.13–5.19 (d, $^3J_{HH} = 17.1$ Hz, 1H), 5.81–5.90 (m, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 10.3$ Hz, $^3J_{HH} = 16.8$ Hz, 1H), 7.21–7.62 (m, 15H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 40.7, 87.1, 87.7, 90.8, 93.4, 103.2, 116.9, 123.2, 123.3, 127.9, 128.3, 128.4, 128.5, 128.6, 128.6, 131.5, 131.7, 134.5, 139.8, 155.2. Calcd. for $C_{27}H_{20}$ 344.1565, found 344.1567.

### *4.1.8. (2-(Phenylethynyl)but-1-en-3-yne-1,1,4-triyl)-tribenzene **(6a)***

The reaction was carried out in a similar way to that described above using iodobenzene instead of $I_2$. After adding the iodobenzene and catalytic amount of $Pd(PPh_3)_4$, the reaction mixture was stirred for 12 h at 50 °C. $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.25–8.20 (m, 20H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 88.9, 91.9, 102.1, 123.3, 127.8, 128.1, 128.3, 128.4, 128.6, 128.9, 129.1, 130.6, 131.6, 131.8, 140.5, 156.0. Calcd. for $C_{30}H_{20}$ 380.1565, found 380.1569.

### *4.1.9. (5-Phenyl-3,6-bis(phenylethynyl)octa-3,5-dien-1,7-diyne-1,4,8-triyl)tribenzene **(7a)***

To the reaction mixture of **1a** at room temperature, CuCl and *p*-chloranil were added and the reaction mixture was stirred at room temperature for 12 h. The resulting mixture was treated with 3N HCl at 0 °C. Product was extract with $CH_2Cl_2$ and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography silica gel ($CH_2Cl_2$/petroleum ether = 1/10) yield 168 mg of the title compound in 55% isolated yield.

$^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 7.34–7.38 (m, aromatic, 6H), 7.43–7.54 (m, aromatic, 16H), 7.66–7.71 (m, aromatic, 4H), 7.99–8.02 (m, aromatic, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 86.1, 86.5, 92.9, 95.7, 104.1, 122.6, 122.7, 127.9, 128.4, 128.5, 128.8, 129.0, 129.2, 130.0, 131.5, 131.9, 136.7, 146.0. Calcd. for $C_{48}H_{30}$ 606.2348, found 606.2353.

## *4.2. A typical procedure for the preparation of 2-methyl-5,8-diphenyl-6-(phenylethynyl)octa-5-en-3,7-diyn-2-ol **(9a)***

A mixture of **4a** (1 mmol, 430 mg), $Pd(PPh_3)_4$ (30 mg), CuI (2 mg), 2-methylbut-3-yn-2-ol (2 mmol, 194 μL), and $NEt_3$ (5 mL) was stirred for 12 h at 50 °C. The mixture was filtrated under reduced pressure, affording a clarifying solution, which was washed with 2N HCl solution to remove $NEt_3$. The product was extracted with $CH_2Cl_2$ and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography silica gel (diethyl ether/petroleum ether = 1/1) afforded 302 mg product (isolated yield 78%). $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 1.69 (s, 6H), 2.87 (br, 1H), 7.34–8.02 (m, 15H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 31.4, 66.0, 82.7, 87.4, 88.7, 94.4, 96.4, 105.7, 109.4, 122.7, 123.0, 128.0, 128.4, 128.5, 128.8, 128.9, 129.0, 129.1, 131.6, 131.8, 135.4, 136.7. Calcd. for $C_{29}H_{22}O$ 386.1671, found 386.1673.

### *4.2.1. 2-Methyl-5,8-dip-tolyl-6-(p-tolylethynyl)octa-5-en-3,7-diyn-2-ol **(9b)***

A yellow liquid (295 mg, isolated yield 69%). $^1$H NMR (300 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 1.61(s, 6H), 2.32 (s, 3H), 2.33(s, 3H), 2.36 (s, 3H), 7.08–7.11 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.12–7.15 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.17–7.20 (t,

$^3J_{HH} = 8.2$ Hz, 2H), 7.29–7.32 (d, $^3J_{HH} = 7.9$ Hz, 2H), 7.45–7.47 (d, $^3J_{HH} = 7.9$ Hz, 2H), 7.84–7.87 (d, $^3J_{HH} = 7.9$ Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$, $Me_4Si$) $\delta$ 21.5, 21.6, 31.5, 66.0, 83.0, 87.2, 88.5, 94.4, 96.6, 105.1, 108.9, 119.9, 120.1, 128.7, 128.9, 129.2, 129.3, 131.5, 131.7, 134.0, 134.4, 138.9, 139.1, 139.1. Calcd. for $C_{32}H_{28}O$ 428.2140, found 428.2140.

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