Efficient Synthesis of 9,10-Bis(phenylethynyl)anthracene Derivatives by Integration of Sonogashira Coupling and Double-Elimination Reactions

Shinji Toyota,*[a] Daiki Mamiya,[a] Rie Yoshida,[a] Ryo Tanaka,[a] Tetsuo Iwanaga,[a] Akihiro Orita,[b] Junzo Otera[b]

[a] Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-ku, Okayama 700-0005, Japan
Fax +81(86)2569457; E-mail: stoyo@chem.ous.ac.jp

[b] Department of Applied Chemistry, Faculty of Engineering, Okayama University of Science, 1-1 Ridaicho, Kita-ku, Okayama 700-0005, Japan

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Abstract: 9,10-Bis(phenylethynyl)anthracene (BPEA) derivatives were synthesized from 10-bromo-9-anthracenecarbaldehyde by stepwise Sonogashira coupling with phenylethynes and the one-shot double-elimination reaction with benzyl phenyl sulfones. Those two reactions could be integrated in a one-pot process to give unsymmetrically substituted BPEA derivatives in good yields by simple operations. This integrated process was applied to the synthesis of an extended BPEA derivative having an extra phenylethynyl group. The photophysical properties of the BPEA derivatives were investigated by UV/Vis and fluorescence spectroscopy.

Key words: alkynes, anthracenes, Sonogashira coupling, double elimination, one-pot process, reaction integration, fluorescence

9,10-Bis(phenylethynyl)anthracene (BPEA, **1a**; Figure 1) and its derivatives are strongly fluorescent π-conjugated compounds that are employed as fluorophores or light emitters in functional materials chemistry.[1–3] This fluorescent property makes BPEA and its derivatives useful as fluorescent dyes in chemical light sticks.[4] Recently, these compounds have received attention as light-emitting diodes[5] and nonlinear optical materials.[6] Because the chemical structure of BPEA enables extension of the π-conjugation between the two terminal phenyl groups across anthracene and acetylene moieties, this unit is occasionally incorporated in arylene–ethynylene oligomers and polymers.[7–11] The electronic properties of the parent compound are tunable by introducing substituents on the phenyl and anthracene units.[12–17] As for BPEA derivatives with substituted phenyl groups, a large number of compounds have been synthesized using similar methods and the substituent effects on the electronic spectra have been systematically investigated.[2,15] Whereas most of the known compounds have two identically substituted phenyl groups, those with different substituents are less popular because of synthetic limitations. The development of efficient methods for the synthesis of such unsymmetric derivatives would widen the scope of their application as functional materials.

Typical synthetic approaches to BPEA derivatives include (1) the cross-coupling reactions of 9,10-dihaloanthracenes with phenylethynes, (2) the addition of phenylacetylides to anthraquinone followed by reductive aromatization,[2] (3) the conversion of formyl groups in anthracenecarbaldehydes into ethynyl groups, and (4) the elimination from 9,10-bis(phenylethenyl)anthracenes.[15] Previously, unsymmetric BPEA derivatives were prepared from symmetric starting materials by stepwise reactions under statistical conditions. Therefore, the yields were not always high because of the formation of undesired products. For example, Sonogashira coupling (SC)[18] of 9,10-dibromoanthracene (**3**) with phenylethynes gave a singly coupled product in low to moderate yields [Scheme 1 (a)].[7,13,16,19] To overcome this problem, Nesterov and coworkers used 9-bromo-10-iodoanthracene (**4**), which was prepared from 9,10-dibromoanthracene by monolithiation and then iodination, for selective SC.[8] This precursor is now widely used for the synthesis of unsymmetric BPEA derivatives.[9,14] Another practical approach is the stepwise alkynylation of 10-bromo-9-anthracenecarbaldehyde (**5**), which is prepared from 9,10-dibromoanthracene by monolithiation followed by formylation with *N*,*N*-dimethylformamide.[20] The formyl and bromo groups in **5** are converted into ethynyl groups by the Corey–Fuchs reaction and SC, respectively [Scheme 1 (b)]. A 9,10-diethynylanthracene derivative with different terminal silyl groups was prepared by this method. This product is an attractive intermediate for the synthesis of unsymmetric BPEA derivatives, even though the conversion via selective desilylation and SC requires several steps.

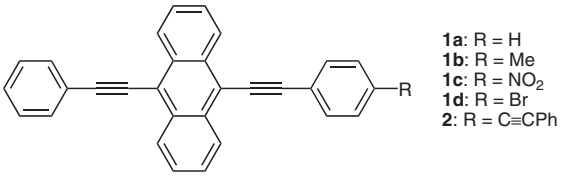

Figure 1 9,10-Bis(phenylethynyl)anthracene (BPEA) derivatives

From these backgrounds, we intended to conduct double-elimination (DE) reactions between arylaldehydes and benzyl phenyl sulfones in the presence of a base, a method which was developed by one of the author's groups, for the synthesis of unsymmetric BPEA derivatives.[21,22] The overall reaction involves the aldol reaction, the formation of phosphate, the elimination of phosphoric acid, and the elimination of sulfinic acid (Scheme 2). The DE protocol is extensively utilized for the synthesis of various alkynes, particularly in cases where other alkyne formation reac-

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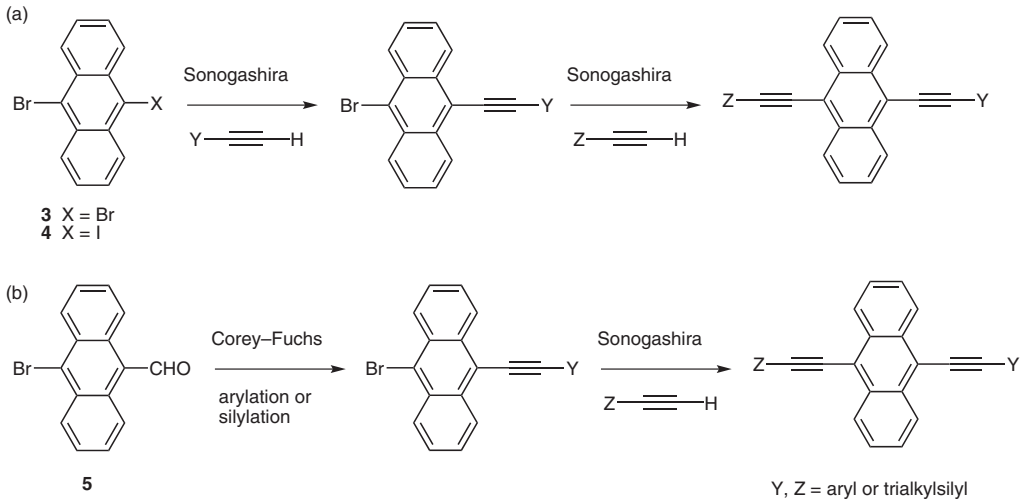
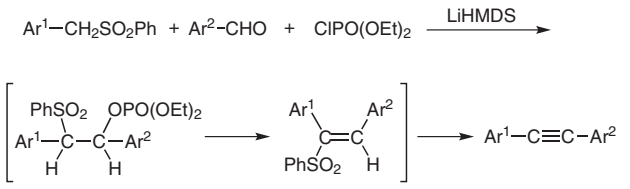


Scheme 1 Examples of synthetic approaches to unsymmetric 9,10-diethynylanthracene derivatives

tions are unsuccessful.[23,24] Whereas the multistep conversion was originally carried out by the sequential addition of reagents into a reaction flask (one-pot process), the procedure was further simplified by mixing all reagents in a reaction flask at once (one-shot process).[25] In terms of the integration of chemical reactions, the one-pot process and the one-shot process are classified as 'time integration' and 'time and space integration', respectively.[26] We have successfully applied the one-shot protocol to the synthesis of anthrylethynes.[27] We introduced one ethynyl group by one-shot DE and another ethynyl group by conventional SC into 10-bromo-9-anthracenecarbaldehyde (**5**). We also tried to integrate the two reactions by the one-pot process to achieve an efficient synthesis. We herein report the optimization of the reaction conditions for the convenient synthesis of unsymmetric BPEA derivatives by the integrated reactions, as well as the photophysical properties of the new fluorescent compounds.



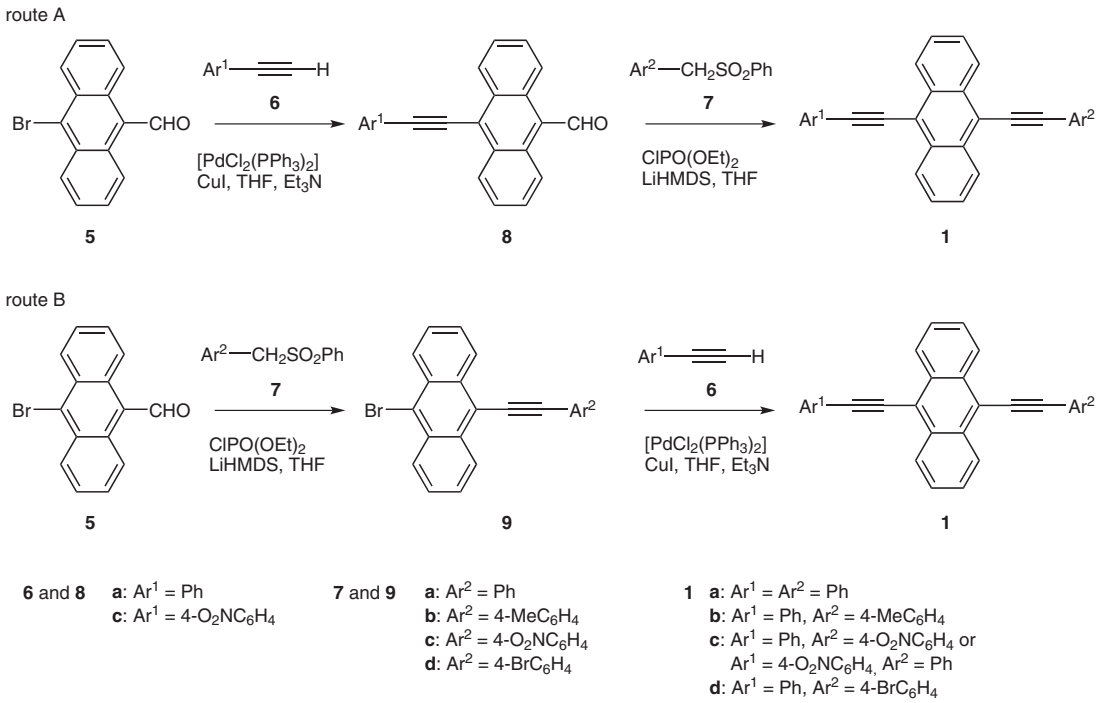
Scheme 2 One-shot DE reaction for the synthesis of unsymmetric diarylethynes

The starting material, 10-bromo-9-anthracenecarbaldehyde (**5**), was prepared from 9,10-dibromoanthracene (**3**) by the literature method.[20] Substituted benzyl phenyl sulfones **7b–d** were prepared by conventional methods. We optimized the conditions for the fundamental processes for substituent-free BPEA (**1a**) and, if necessary, those processes were further optimized for the unsymmetric derivatives **1b–d** which contain a 4-methyl, 4-nitro, or 4-bromo group, respectively, at one phenylethynyl moiety. The isolated yields of the stepwise and one-pot syntheses are compiled in Table 1.

Synthesis by Stepwise Reactions

Compound **1a** was synthesized from **5** by two routes consisting of SC and one-shot DE in a stepwise manner (Scheme 3). In route A, we first performed SC of **5** and phenylethyne (**6a**). The reaction in the presence of palladium(II) catalyst and copper(I) iodide in tetrahydrofuran and triethylamine gave compound **8a** in 96% yield. This product was then subjected to DE with **7a** (1.2 equiv) following the standard protocol reported in the literature;[27] namely, those two reactants were treated with diethyl chlorophosphate (DECP, 1.2 equiv) and lithium hexamethyldisilazide (LiHMDS, 5.0 equiv) in tetrahydrofuran. The crude product was collected by filtration and then recrystallized from hexane–chloroform to give pure BPEA (**1a**) in 98% yield. The overall yield of the two-step conversion was 94% based on **5**. The same transformation was achieved by the two reactions in the reverse order (route B). One-shot DE with **5** and **7a** gave 9-bromo-10-(phenylethynyl)anthracene (**9a**) in 90% yield, and subsequent SC with **6a** gave BPEA (**1a**) in 93% yield. The overall yield via route B was 84%. We were able to obtain practically pure products by recrystallization, without extraction and chromatography, in the DE step in both routes.

In principle, for the synthesis of unsymmetric BPEA derivatives, substituted phenyl groups can be introduced either by DE with substituted benzyl phenyl sulfones or by SC with substituted phenylethynes. We adopted the former approach in most cases because of the availability and ease of handling of the starting materials. Compound **1b** could be synthesized by both routes with phenylethyne



Scheme 3 Synthesis of BPEA derivatives **1** from **5** by SC and DE reactions

Table 1 Yields for Stepwise and One-Pot Synthesis of BPEA Derivatives **1** from 10-Bromo-9-anthracenecarbaldehyde (**5**) by Sonogashira Coupling (SC) and Double-Elimination (DE) Reactions[a]

Route A 1st reaction (SC)			2nd reaction (DE)			Stepwise	One-pot
Alkyne	Product	Yield (%)	Sulfone	Product	Yield (%)	Overall yield (%)	Yield (%)
6a	**8a**	96	**7a**	**1a**	98	94	90
6a	**8a**	96	**7b**	**1b**	95	91	90
6a	**8a**	96	**7c**	**1c**	<10[b]	low	–
6c	**8c**	87[c]	**7a**	**1c**	94	82	72[c]
6a	**8a**	96	**7d**	**1d**	89	85	35 (91)[d]
Route B 1st reaction (DE)			2nd reaction (SC)			Stepwise	One-pot
Sulfone	Product	Yield (%)	Alkyne	Product	Yield (%)	Overall yield (%)	Yield (%)
7a	**9a**	90	**6a**	**1a**	93	84	7[b,e]
7b	**9b**	76	**6a**	**1b**	98	74	–
7c	**9c**	80	**6a**	**1c**	71	57	–

[a] Isolated yields unless otherwise indicated. Typical conditions for SC: bromide (1.0 equiv), alkyne (1.2 equiv), $[PdCl_2(PPh_3)_2]$ (0.04 equiv), CuI (0.08 equiv) in THF–Et_3N at 70 °C for 2 h. Typical conditions for DE: aldehyde (1.0 equiv), sulfone (1.2 equiv), DECP (1.2 equiv), LiHMDS (5.0 equiv) in THF at r.t. for 20 h.
[b] Estimated yields from ^1H NMR spectra.
[c] Reaction time of 24 h for SC.
[d] LiHMDS (6.5 equiv) for DE.
[e] Reaction time of 16 h for SC.

(**6a**) and 4-methylbenzyl phenyl sulfone (**7b**), and the overall yields via routes A and B were 91% and 74%, respectively. For the synthesis of **1c**, DE of **8a** and 4-nitrobenzyl phenyl sulfone (**7c**) under the standard conditions gave a small amount of the desired product as an inseparable mixture. Therefore, we introduced the 4-nitrophenyl group first by SC with **6c**, even though this reaction required a longer time than SC with **6a**. The product, 10-[(4-nitrophenyl)ethynyl]-9-anthracenecarbaldehyde (**8c**), smoothly formed **1c** by DE with **7a** (82% overall yield). Route B involving DE with **7c** and SC with **6a** produced **1c** in 57% overall yield. For the synthesis of **1d**, route B was far from practical because the bromophenyl unit is also reactive to SC. The only possible approach was route A with **6a** and 4-bromobenzyl phenyl sulfone (**7d**). The stepwise SC and DE worked well to give **1d** in 85% overall yield. Alternatively, **1d** could be synthesized by SC with 9-ethynyl-10-(phenylethynyl)anthracene (**10**) and 1-bromo-4-iodobenzene, although the yield was not high (Scheme 4). In this reaction, we needed to carefully separate the desired product from a small amount of the homocoupling product, the dimer of **10**, as byproduct. The above results showed that the stepwise approaches involving the two reactions gave unsymmetric BPEA derivatives in good overall yields without formation of symmetric derivatives as byproducts.

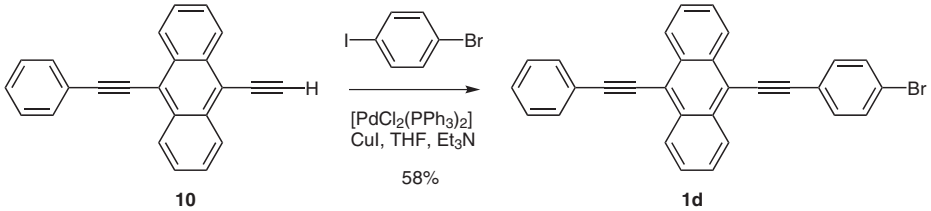
One-Pot Synthesis

We then integrated the two reactions to simplify the experimental operations. We first synthesized BPEA (**1a**) by the one-pot process based on the conditions for the stepwise synthesis. For the integration of route A, SC of **5** with **6a** was carried out by the standard method and then **7a** and other reagents for DE were added to the reaction flask. After the mixture was stirred for 20 hours at room temperature, we obtained practically pure BPEA in 90% yield, even without extraction and chromatographic purification. Although the SC step formed one equivalent of triethylammonium bromide, the subsequent DE step required no extra amount of LiHMDS as base, a part of which should be consumed by reaction with the ammonium salt. For the integration of route B, DE with **5** and **7a** was carried out by the standard method and then **6a**, the catalysts, and the base for SC were added to the reaction flask. Because SC required a long time to complete, the reaction mixture was heated for as long as 16 hours. Unfortunately, the product was a mixture of **1a** and **9a** in the ratio of 7:93 and thus we abandoned isolation of the desired product from the mixture. We also tried to integrate the two reactions by the one-shot process. The starting materials and all reagents for the two reactions were put into a reaction flask at once, and the whole was stirred for 2 hours at room temperature and then heated at 70 °C for 16 hours. The product was a mixture of **1a** and **9a** in the ratio of 15:85. These unsuccessful results, the one-pot process of route B and the one-shot process, indicated that the reagents and products involving salts of the DE reaction deactivated the catalytic system of SC. Thereafter, we adopted the one-pot protocol following the reaction order of route A for the synthesis of unsymmetric BPEA derivatives.

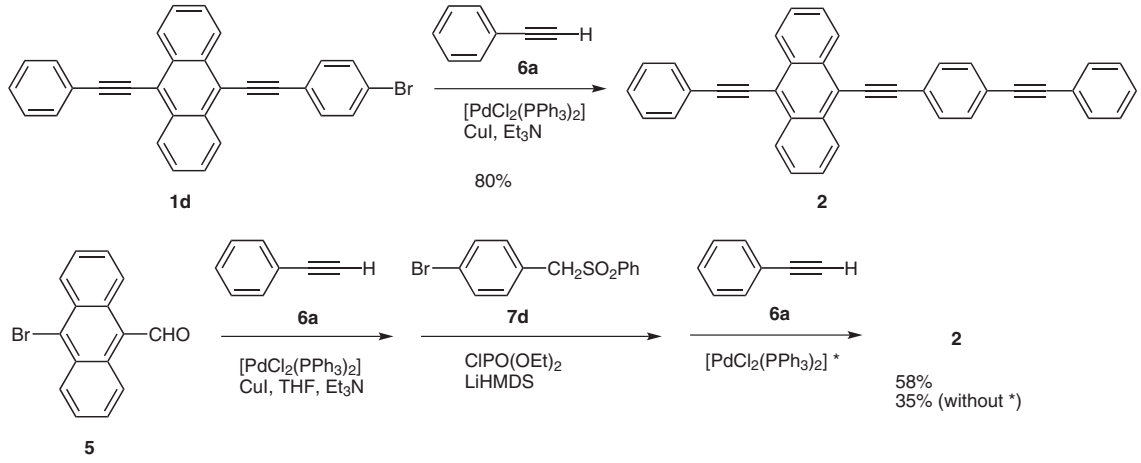
Methyl derivative **1b** was synthesized by the one-pot process with **6a** and then **7b** in 90% yield. Nitro derivative **1c** was similarly synthesized with **6c** (reaction time: 24 h) and then **7a** in 72% yield. For bromo derivative **1d**, the standard procedure with **6a** and **7d** gave the final product in only 35% yield with the recovery of a large amount of **8a**. After several trials, the conversion efficiency of DE was found to be improved by the use of an additional amount of LiHMDS rather than long reaction times and high reaction temperatures. On treatment with 6.0 and 6.5 equivalents of LiHMDS (5.0 equiv for the standard procedure), the isolated yields increased to 79% and 91%, respectively. These one-pot procedures proved that unsymmetric BPEA derivatives can be effectively synthesized by simple operations. Both extraction and chromatographic purification were not always essential even though the final reaction mixture contained several chemical species. Therefore, the overall process can be realized with the least amount of solvents and other chemicals.

Synthesis of an Extended Derivative

The introduction of an extra arylethynyl unit into the parent BPEA structure can extend the π-conjugation and yield candidates for photovoltaic and other functional materials.[9,28] Bromo derivative **1d** is a convenient precursor to construct such structures by using cross-coupling reactions. As an example of this application, we introduced an extra phenylethynyl group into the BPEA core. SC of **1d** and **6a** (2.0 equiv) was performed in triethylamine with-



Scheme 4 An alternative synthesis of **1d** by SC of **10** and 1-bromo-4-iodobenzene



Scheme 5 Synthesis of BPEA derivative **2** with extended π-conjugation

out tetrahydrofuran for 16 hours at 100 °C to give the desired product **2** in 80% yield (Scheme 5). We also attempted to integrate this step with the one-pot process from **5**. After the one-pot process for the synthesis of **1d**, phenylethyne (**6a**) was charged into the reaction flask. The whole mixture was heated at 70 °C for 16 hours to give **2** in 35% yield along with the recovery of **1d** (50%). When the palladium catalyst was also charged in addition to **6a**, the yield of the desired product was increased to 58%. Accordingly, although the palladium catalyst charged in the first step was still active in the last step, the use of additional catalyst improved the result. This highly integrated process consisting of two SC steps and one one-shot DE step gave the final product in moderate yield, thereby proving the flexibility of the integration of multiple alkynylations.

Electronic Spectra

The UV/Vis and fluorescence spectra of the BPEA derivatives were measured in chloroform. The spectral data are compiled in Table 2. In the UV/Vis spectra, all compounds show structured absorption bands at around 450 nm in the *p*-band region. The peak at the longest wavelength was observed at 464 nm for BPEA (**1a**) and its methyl and bromo derivatives **1b** and **1d**. The corresponding peak was shifted to longer wavelength by ca. 15 nm by the substitution of nitro and phenylethynyl groups (**1c** and **2**, respectively). In the fluorescence (FL) spectra, intense emission peaks were observed at ca. 480 nm, except for the nitro derivative **1c** that showed no emission. The fluorescence quantum yields (ca. 0.80) were not affected by the substitution of the methyl, bromo, or phenylethynyl group. The effective quenching by the nitro group is attributed to intramolecular charge transfer, which facilitates nonradiative decay.[29] Compound **1a** has the longest fluorescence lifetime (2.5 ns) among the four compounds, and the substituents tend to shorten the lifetime.

Table 2 Electronic Spectral Data of BPEA Derivatives **1a**–**d** and **2** in Chloroform

Compound	UV		FL			Stokes shift
	λ_{max} (nm)[a]	ε[a]	λ_{em} (nm)	Φ_f[b]	τ_f (ns)[c]	(nm)
1a	464	41000	475, 506	0.81	2.5	11
1b	463	53100	478, 509	0.83	2.3	15
1c	480	52000	–[d]	–	–	–
1d	464	60500	478, 509	0.80	2.2	14
2	479	41200	487, 519	0.75	1.8	8

[a] Wavelength and molar extinction coefficient of the peak at the longest wavelength in the *p*-band region.
[b] Absolute fluorescence quantum yield.
[c] Fluorescence lifetime.
[d] No emission peak was observed.

In conclusion, the combination of DE and SC starting from 10-bromo-9-anthracenecarbaldehyde offers an efficient approach toward BPEA derivatives by both the stepwise and one-pot processes in good overall yields. In particular, unsymmetric BPEA derivatives can be synthesized by simple operations without the formation of symmetric analogues as byproducts. Because a large number of substituted phenylethynes and substituted benzyl phenyl sulfones are commercially available or readily prepared from ordinary compounds, these protocols are efficient for the synthesis of various BPEA derivatives involving oligomers, dendrimers, and functional materials.

Melting points are uncorrected. Elemental analyses were performed with a Perkin-Elmer 2400 series analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Jeol JNM-ECS400 spectrometer at 400 and 100 MHz, respectively. High-resolution FAB mass spectra were measured on a Jeol MStation-700 spectrometer. UV/Vis spectra were measured on a Hitachi U-3000 spectrometer with a 10-mm cell. Fluorescence spectra were measured on a Jasco FP-6500 spectrofluorometer with a 10-mm cell; samples were degassed with argon gas immediately before measurements. The absolute fluorescence quantum yields were recorded on a Hamamatsu Photonics C9920-02 system. The fluorescence lifetimes were measured on a Spectra-Physics time-resolved spectrofluorometer system (Tsunami 3960/50-M2S) with a Ti:Sapphire laser. Phenylethyne, 4-nitrophenylethyne, benzyl phenyl sulfone, and 1-bromo-4-iodobenzene are commercially available. 10-Bromo-9-anthracenecarbaldehyde was prepared from 9,10-dibromoanthracene according to the known method.[20] 4-Methylbenzyl phenyl sulfone,[23d] 4-nitrobenzyl phenyl sulfone,[30] and 4-bromobenzyl phenyl sulfone[23c] were prepared from sodium benzenesulfinate and the corresponding benzyl bromides by a standard method. All reactions were carried out under atmosphere of argon. LiHMDS soln (1.0 M in THF) and THF (super dehydrated) were purchased from Sigma-Aldrich and Wako Pure Chemical Industries, respectively.

10-(Phenylethynyl)-9-anthracenecarbaldehyde (8a); Typical Procedure for SC

To a soln of 10-bromo-9-anthracenecarbaldehyde (**5**) (114 mg, 0.40 mmol) and phenylethyne (**6a**) (49 mg, 0.48 mmol) in a degassed mixture of anhyd THF (8 mL) and Et_3N (8 mL) were added $[PdCl_2(PPh_3)_2]$ (11 mg, 16 μmol) and CuI (6.1 mg, 32 μmol). The reaction mixture was stirred at 70 °C for 2 h under argon (reaction mixture A). The solvent was removed, and the crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the desired product as an orange solid.

Yield: 117 mg (96%); mp 198–200 °C (Lit.[31] 179–180 °C); R_f = 0.26 (hexane–$CHCl_3$, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.53 (m, 3 H), 7.65–7.74 (m, 4 H), 7.79–7.82 (m, 2 H), 8.79 (d, *J* = 8.7 Hz, 2 H), 8.97 (d, *J* = 8.7 Hz, 2 H), 11.53 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.1, 104.6, 122.8, 123.8, 124.9, 125.5, 126.5, 127.6, 128.6, 128.9, 129.2, 131.1, 131.7, 131.8, 192.9.

10-[(4-Nitrophenyl)ethynyl]-9-anthracenecarbaldehyde (8c)

To a soln of **5** (114 mg, 0.40 mmol) and 4-nitrophenylethyne (**6c**) (70 mg, 0.48 mmol) in a degassed mixture of anhyd THF (8 mL) and Et_3N (8 mL) were added $[PdCl_2(PPh_3)_2]$ (11 mg, 16 μmol) and CuI (6.1 mg, 32 μmol). The reaction mixture was stirred at 70 °C for 24 h under argon (reaction mixture A′). The solvent was removed, and the crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the desired product as a red solid.

Yield: 122 mg (87%); mp 221–224 °C; R_f = 0.42 (hexane–$CHCl_3$, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (m, 2 H), 7.65–7.74 (m, 4 H), 7.81 (m, 2 H), 8.79 (d, *J* = 8.7 Hz, 2 H), 8.97 (d, *J* = 8.7 Hz, 2 H), 11.53 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 90.9, 101.7, 123.8, 123.9, 124.1, 127.2, 127.3, 129.1, 131.0, 132.2, 132.6, 133.4, 134.1, 147.6, 193.2.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_{23}H_{13}NO_3$: 351.0895; found: 351.0993.

Anal. Calcd for $C_{23}H_{13}NO_3$: C, 78.62; H, 3.73; N, 3.99. Found: C, 78.44; H, 3.34; N, 4.15.

9-Bromo-10-(phenylethynyl)anthracene (9a); Typical Procedure for One-Shot DE

To a soln of **5** (114 mg, 0.40 mmol), benzyl phenyl sulfone (**7a**) (112 mg, 0.48 mmol), and DECP (70 μL, 0.48 mmol) in anhyd THF (12 mL) was slowly added the LiHMDS soln (2.0 mL, 2.0 mmol) with a syringe at 0 °C under argon. This solution was stirred at 0 °C for 10 min, and then at r.t. for 20 h (reaction mixture B). The reaction was quenched with aq NH_4Cl (12 mL), and the organic materials were extracted with $CHCl_3$ (3 × 20 mL). The combined organic solution was dried over $MgSO_4$ and concentrated. The residue was recrystallized (hexane–$CHCl_3$) to give the pure product as yellow crystals.

Yield: 129 mg (90%); mp 167–169 °C (Lit.[7,8] 170–171 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.49 (m, 3 H), 7.63–7.66 (m, 4 H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 2 H), 8.57 (m, 2 H), 8.72 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.0, 101.8, 118.2, 123.4, 124.2, 126.8, 127.2, 127.4, 128.2, 128.6, 128.8, 130.2, 131.6, 133.0.

9,10-Bis(phenylethynyl)anthracene (1a)

This compound was synthesized by DE with **8a** (123 mg, 0.40 mmol) and **7a** (112 mg, 0.48 mmol) according to the typical procedure. The formed solid was collected by filtration, washed with water, and dried. Recrystallization (hexane–$CHCl_3$) gave the desired product.

Yield: 148 mg (98%); mp 242–248 °C (dec) (Lit.[32] 257–258 °C, Lit.[2d] 253 °C, Lit.[33] 249–250 °C). This sample slowly decomposed >240 °C and showed a sharp endothermic peak at 258 °C on DTA measurement.

R_f = 0.41 (hexane–$CHCl_3$, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.48 (m, 6 H), 7.66 (m, 4 H), 7.78 (dd, *J* = 1.6, 8.0 Hz, 4 H), 8.70 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.4, 102.4, 118.5, 123.3, 126.8, 127.2, 128.6, 128.7, 131.7, 132.1.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 275 (105000), 313 (43300), 439 (38900), 464 nm (41000).

FL ($CHCl_3$): λ_{max} = 475, 506 nm (λ_{ex} 458 nm, Φ_f 0.81, τ_f 2.5 ns).

The same compound was also synthesized by SC with **9a** (143 mg, 0.40 mmol) and **6a** (49 mg, 0.48 mmol) by the typical procedure. Chromatographic purification (hexane–$CHCl_3$, 10:1) gave **1a**; yield: 141 mg (93%).

9-Bromo-10-[(4-methylphenyl)ethynyl]anthracene (9b)

This compound was synthesized by DE with **5** (114 mg, 0.40 mmol) and 4-methylbenzyl phenyl sulfone (**7b**) (118 mg, 0.48 mmol) according to the typical procedure. Recrystallization (hexane) gave the desired compound as yellow needles.

Yield: 113 mg (76%); mp 160–161 °C; R_f = 0.71 (hexane–$CHCl_3$, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.62–7.69 (m, 6 H), 8.58 (m, 2 H), 8.72 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 85.4, 102.1, 118.5, 120.2, 123.9, 126.7, 127.3, 127.4, 128.2, 129.3, 130.2, 131.5, 132.9, 139.0.

HRMS–FAB: *m/z* $[M]^+$ calcd for $C_{23}H_{15}{}^{79}Br$: 370.0357; found: 370.0373.

Anal. Calcd for $C_{23}H_{15}Br$: C, 74.60; H, 4.08. Found: C, 74.52; H, 7.24.

9-Bromo-10-[(4-nitrophenyl)ethynyl]anthracene (9c)
This compound was synthesized by DE with **5** (114 mg, 0.40 mmol) and 4-nitrobenzyl phenyl sulfone (**7c**) (133 mg, 0.48 mmol) according to the typical procedure. Recrystallization (hexane) gave the desired compound as a red solid.

Yield: 129 mg (80%); mp 254–256 °C (Lit.[17] 255.0–255.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 4 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 8.34 (d, *J* = 8.4 Hz, 2 H), 8.60–8.67 (m, 4 H).

9-[(4-Methylphenyl)ethynyl]-10-(phenylethynyl)anthracene (1b)
This compound was synthesized by SC with **9b** (149 mg, 0.40 mmol) and **6a** (49 mg, 0.48 mmol). Chromatographic purification (hexane–$CHCl_3$, 10:1) gave **1b** as orange crystals.

Yield: 154 mg (98%); mp 216–217 °C; R_f = 0.45 (hexane–$CHCl_3$, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 7.25 (d, *J* = 7.7 Hz, 2 H), 7.41–7.49 (m, 3 H), 7.60–7.68 (m, 6 H), 7.78 (dd, *J* = 1.6, 8.1 Hz, 2 H), 8.66–8.70 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 85.9, 86.5, 102.3, 102.7, 118.1, 118.7, 120.3, 123.4, 126.7, 126.8, 127.2, 127.3, 128.6, 128.7, 129.3, 131.6, 131.7, 132.0, 132.1, 138.9.

HRMS–FAB: *m/z* $[M]^+$ calcd for $C_{31}H_{20}$: 392.1565; found: 392.1550.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 275 (123000), 314 (49100), 441 (50100), 463 nm (53100).

FL ($CHCl_3$): λ_{max} = 478, 509 nm (λ_{ex} 458 nm, Φ_f 0.83, τ_f 2.3 ns).

Anal. Calcd for $C_{31}H_{20}$: C, 94.86; H, 5.14. Found: C, 94.48; H, 5.19.

This compound was also synthesized by DE with **8a** (123 mg, 0.40 mmol) and **7b** (118 mg, 0.48 mmol). The product was purified by recrystallization (CH_2Cl_2) to give pure material **1b**; yield: 149 mg (95%).

9-[(4-Nitrophenyl)ethynyl]-10-(phenylethynyl)anthracene (1c)
This compound was synthesized by SC with **9c** (161 mg, 0.40 mmol) and **6a** (49 mg, 0.48 mmol). Chromatographic purification (hexane–$CHCl_3$, 10:1) gave **1c** as a red solid.

Yield: 120 mg (71%); mp 256–258 °C; R_f = 0.61 (hexane–$CHCl_3$, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.49 (m, 3 H), 7.66–7.71 (m, 4 H), 7.79 (dd, *J* = 1.6, 8.0 Hz, 2 H), 7.92 (d, *J* = 9.2 Hz, 2 H), 8.33 (d, *J* = 9.2 Hz, 2 H), 8.65 (m, 2 H), 8.74 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.2, 91.9, 100.2, 103.2, 116.8, 120.1, 123.2, 123.9, 126.8, 127.0, 127.4, 127.5, 128.6, 129.0, 130.3, 131.8, 132.0, 132.3, 132.4, 147.1.

HRMS–FAB: *m/z* $[M]^+$ calcd for $C_{30}H_{17}NO_2$: 423.1216; found: 423.1259.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 275 (91300), 309 (41700), 457 (52900), 480 nm (52000).

Anal. Calcd for $C_{30}H_{17}NO_2$: C, 85.09; H, 4.05; N, 3.31. Found: C, 85.22; H, 4.04; N, 3.29.

This compound was also synthesized by DE with **8c** (141 mg, 0.40 mmol) and **7a** (112 mg, 0.48 mmol). The product was purified by recrystallization (CH_2Cl_2) to give pure material **1c**; yield: 159 mg (94%). The reaction was also carried out with **8a** (122 mg, 0.40 mmol) and **7c** (133 mg, 0.48 mmol). Chromatographic separation of the crude product (hexane–$CHCl_3$, 10:1) gave 54 mg of a mixture containing **1c** (<10%) and other byproducts.

9-[(4-Bromophenyl)ethynyl]-10-(phenylethynyl)anthracene (1d)
The DE reaction was carried out with **8a** (123 mg, 0.40 mmol) and 4-bromobenzyl phenyl sulfone (**7d**) (149 mg, 0.48 mmol). Chromatographic purification (hexane–$CHCl_3$, 10:1) gave **1d** as orange crystals.

Yield: 163 mg (89%); mp 223–224 °C; R_f = 0.63 (hexane–$CHCl_3$, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.49 (m, 3 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 7.63–7.68 (m, 6 H), 7.79 (dd, *J* = 1.6, 7.8 Hz, 2 H), 8.65 (m, 2 H), 8.74 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.4, 87.7, 101.2, 102.6, 117.9, 118.8, 122.4, 122.9, 123.4, 126.8, 126.9, 127.1, 127.3, 128.6, 128.8, 131.7, 131.8, 132.1, 132.1, 133.0.

HRMS–FAB: *m/z* $[M]^+$ calcd for $C_{30}H_{17}{}^{79}Br$: 456.0514; found: 456.0518.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 275 (147000), 317 (66600), 442 (58200), 464 nm (60500).

FL ($CHCl_3$): λ_{max} = 478, 509 nm (λ_{ex} 458 nm, Φ_f 0.80, τ_f 2.2 ns).

Anal. Calcd for $C_{30}H_{17}Br$: C, 78.78; H, 3.75. Found: C, 79.00; H, 3.87.

Alternative Synthesis of 1d
To a soln of 9-ethynyl-10-(phenylethynyl)anthracene[8,16] (**10**) (121 mg, 0.40 mmol) and 1-bromo-4-iodobenzene (170 mg, 0.60 mmol) in a degassed mixture of anhyd THF (6 mL) and Et_3N (6 mL) were added $[PdCl_2(PPh_3)_2]$ (11 mg, 16 μmol) and CuI (6.1 mg, 32 μmol). After the reaction mixture was stirred at r.t. for 17 h under argon, the solvent was removed. The crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the desired product; yield: 106 mg (58%).

One-Pot Synthesis of 1a; Typical Procedure
After reaction mixture A was cooled to r.t., **7a** (112 mg, 0.48 mmol) and DECP (70 μL, 0.48 mmol) were added to the mixture. To the solution was slowly added the LiHMDS soln (2.0 mL, 2.0 mmol) with a syringe at 0 °C. This solution was stirred at 0 °C for 10 min, and then at r.t. for 20 h. The reaction was quenched with aq NH_4Cl (12 mL). The formed solid was collected by filtration, washed with water, and dried. Recrystallization (hexane–$CHCl_3$) gave the pure product as yellow crystals; yield: 136 mg (90%).

One-Pot Synthesis of 1a (Reverse Order)
To reaction mixture B were added **6a** (49 mg, 0.48 mmol), $[PdCl_2(PPh_3)_2]$ (11 mg, 16 μmol), CuI (6.1 mg, 32 μmol), and Et_3N (8 mL). The mixture was stirred at 70 °C for 16 h and the reaction was quenched with aq NH_4Cl (12 mL). The organic materials were extracted with $CHCl_3$ (3 × 20 mL). The combined organic solution was dried over $MgSO_4$, and concentrated. ^{1}H NMR spectra revealed that the crude product was a mixture of **1a** and **9a** in 7:93 ratio.

One-Shot Synthesis of 1a
To a soln of **5** (114 mg, 0.40 mmol) and **6a** (49 mg, 0.48 mmol) in a degassed mixture of anhyd THF (8 mL) and Et_3N (8 mL) were added **7a** (112 mg, 0.48 mmol), DECP (70 μL, 0.48 mmol), $[PdCl_2(PPh_3)_2]$ (11 mg, 16 μmol), and CuI (6.1 mg, 32 μmol). To the solution was slowly added the LiHMDS soln (2.0 mL, 2.0 mmol) with a syringe at 0 °C under argon. This mixture was stirred at 0 °C for 10 min, at r.t. for 2 h, and then at 70 °C for 16 h. The reaction was similarly quenched with aq NH_4Cl. ^{1}H NMR spectra revealed that the crude product was a mixture of **1a** and **9a** in 15:85 ratio.

One-Pot Synthesis of 1b
This reaction was carried out with reaction mixture A and **7b** (118 mg, 0.48 mmol). The crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the pure product; yield: 141 mg (90%).

One-Pot Synthesis of 1c
This reaction was carried out with reaction mixture A′ and **7a** (112 mg, 0.48 mmol). The crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the pure product; yield: 121 mg (72%).

One-Pot Synthesis of 1d
This reaction was carried out with reaction mixture A and **7d** (149 mg, 0.48 mmol). The LiHMDS soln (2.6 mL, 2.6 mmol) was added to the reaction mixture, which was stirred at r.t. for 12 h (reaction mixture C). The crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 10:1) to give the pure product; yield: 166 mg (91%). When 2.0 mL (2.0 mmol) and 2.4 mL (2.4 mmol) of the LiHMDS soln were used, the isolated yields were 35% and 79%, respectively.

9-(Phenylethynyl)-10-{[4-(phenylethynyl)phenyl]ethynyl}anthracene (2)
To a soln of **1d** (60 mg, 0.13 mmol) and **6a** (27 mg, 0.26 mmol) in degassed Et_3N (8 mL) were added $[PdCl_2(PPh_3)_2]$ (3.6 mg, 5.2 μmol) and CuI (1.9 mg, 10 μmol). The reaction mixture was stirred at 100 °C for 16 h under argon, and the solvent was removed. The crude product was purified by chromatography on silica gel (hexane–$CHCl_3$, 5:1) to give the desired product as a yellow solid.

Yield: 50 mg (80%); mp 250–252 °C (dec); R_f = 0.30 (hexane–CH_2Cl_2, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.26 (m, 3 H), 7.47 (t, J = 7.8 Hz, 3 H), 7.62–7.68 (m, 8 H), 7.78 (m, 4 H), 8.67–8.72 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 86.5, 88.5, 89.2, 91.7, 102.2, 102.7, 118.2, 118.9, 123.1, 123.3, 123.5, 123.7, 126.9, 127.0, 127.2, 127.4, 128.4, 128.5, 128.6, 128.8, 131.6, 131.7, 131.8, 132.20, 132.23.

HRMS–FAB: m/z $[M]^+$ calcd for $C_{38}H_{22}$: 478.1722; found: 478.1686.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 284 (90000), 316 (30600), 336 (27200), 350 (31100), 457 (41400), 479 nm (41200).

FL ($CHCl_3$): λ_{max} = 487, 519 nm (λ_{ex} 457 nm, Φ_f 0.75, τ_f 1.8 ns).

One-Pot Synthesis of 2
To reaction mixture C were added **6a** (123 mg, 1.20 mmol) and $[PdCl_2(PPh_3)_2]$ (11.2 mg, 16 μmol) at r.t. The reaction mixture was heated at 70 °C for 16 h, and then quenched with aq NH_4Cl. The organic materials were extracted with $CHCl_3$ (3 × 20 mL). The combined organic solution was washed with water, dried over $MgSO_4$, and concentrated. The crude product was similarly purified to give **2** (111 mg, 58% based on **5**) and **1d** (22%). When only **6a** was added, the reaction gave **2** and **1d** in 35% and 50%, respectively.

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