

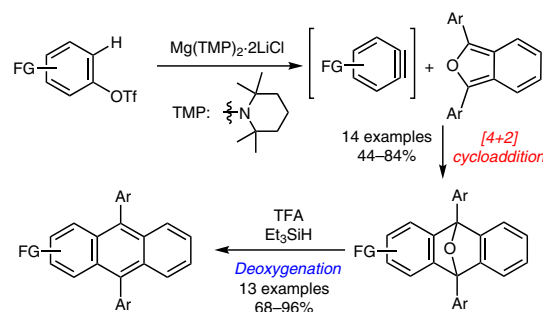
Synthesis of 9,10-Diarylanthracenes via $\text{Mg}(\text{TMP})_2 \cdot 2\text{LiCl}$ -Mediated Benzyne Generation/[4+2] Cycloaddition and Deoxygenation of 9,10-Epoxyanthracene Intermediates

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Received: 01.09.2017

Accepted after revision: 01.10.2017

Published online: 01.12.2017

DOI: 10.1055/s-0036-1591510; Art ID: st-2017-u0659-l

Abstract A new synthetic route to functionalized 9,10-diarylanthracenes has been developed. 9,10-Epoxyanthracene intermediates were prepared by [4+2] cycloaddition of 1,3-diarylisobenzofuran with a variety of functionalized benzyne intermediates, which were obtained by $\text{Mg}(\text{TMP})_2 \cdot 2\text{LiCl}$ -mediated benzyne generation. For the cleavage of the resultant 9,10-epoxyanthracene intermediates, we developed mild deoxygenation conditions using a combination of trifluoroacetic acid and Et_3SiH . The utility of this sequence was demonstrated by application to the synthesis of 5,7,12,14-tetraphenylpentacene.

Key words anthracene, pentacene, arynes, cycloaddition, furanes, deoxygenation

Organic light-emitting diodes (OLEDs) have recently made remarkable progress. OLEDs have been applied to flat panel display in devices such as mobile phones and digital cameras owing to their advantages of high brightness, full-color emission, low driving voltage, rapid response, and self-emitting properties.¹ However, the results regarding their efficiency, stability, and cost have not yet been satisfactory; therefore, tremendous efforts have been devoted to the design and synthesis of new building blocks. Among a variety of functionalized building blocks utilized so far, i.e., triarylamine,² fluorene,³ carbazole,⁴ and anthracene,⁵ anthracene stands out for its unusual photoluminescence, electroluminescence, and excellent electrochemical properties.⁶

Anthracenes having aryl groups at the 9,10-positions, e.g., 2-methyl-9,10-di(1-naphthalenyl)anthracene (MADN),⁷ 4,4'-bis(9-(1-naphthyl)anthracene-10-yl)biphenyl (BUBH-3),⁸ and 9-(10-phenylanthracene-9-yl)spiro[benzo[c]fluorene-

7,9'-fluorene] (BH-9PA),⁹ are currently used as building blocks to prepare OLEDs (Figure 1). There are three general methods to synthesize these 9,10-diarylanthracenes; however, the limited functional group compatibilities hinder their applicability, and the development of a versatile and mild method still remains a challenge.

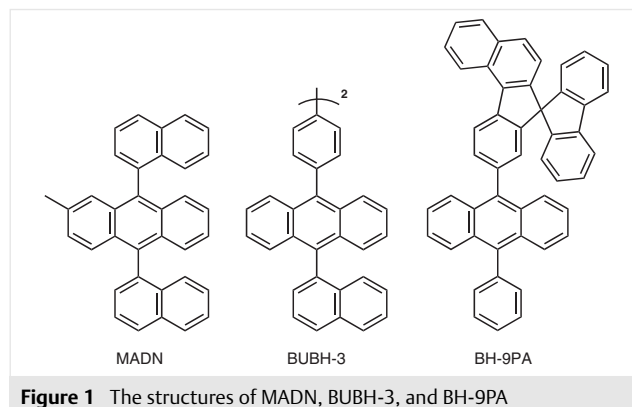
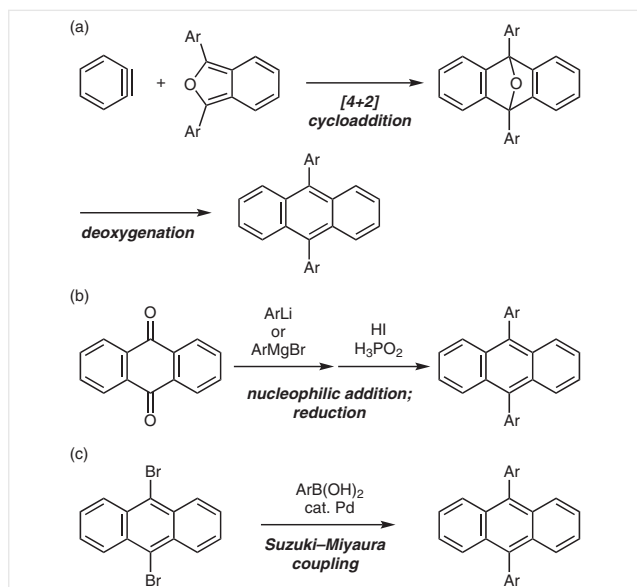


Figure 1 The structures of MADN, BUBH-3, and BH-9PA

One of the three mentioned methods that is widely used is the [4+2] cycloaddition¹⁰ of benzyne with 1,3-diarylisobenzofurans, followed by deoxygenation (Scheme 1, a).¹¹ However, the functional group compatibility is limited because of the harsh deoxygenation conditions required. Another method involves the addition of excess aryl Grignard or lithium reagents to anthraquinones (Scheme 1, b),¹² which is limited to the synthesis of simple 9,10-diarylanthracenes due to the low functional group compatibility of the Grignard or lithium reagents. Finally, the Suzuki–Miyaura coupling of 9,10-dibromoanthracenes with arylboronic acids in the presence of catalytic $\text{Pd}(\text{PPh}_3)_4$ and aque-

ous K_2CO_3 (Scheme 1, c)¹³ has a wide range of functional group compatibility although it does not provide access to halogenated derivatives and have the disadvantage of the high cost of palladium catalysts.



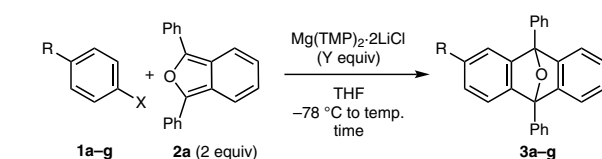
Scheme 1 Conventional approaches to 9,10-diarylanthracenes

Recently, we found that $Mg(TMP)_2 \cdot 2LiCl$ ¹⁴ is a useful base for the generation of benzyne with functional groups, including halogenated moieties.^{15,16} Therefore, we considered that a combination of the benzyne-mediated synthesis of 1,3-diarylisobenzofuran and our newly developed mild deoxygenation conditions should lead to the mild synthesis of 9,10-diarylanthracenes. Herein, we describe the functional group compatibility of the benzyne-mediated [4+2] cycloaddition with 1,3-diarylisobenzofuran¹⁷ and the development of a mild deoxygenation for a versatile synthesis of 9,10-diarylanthracenes.

First, we investigated the synthesis of 2-substituted 9,10-diphenyl-9,10-epoxyanthracene by the [4+2] cycloaddition of 1,3-diphenylisobenzofuran (**2a**) with a variety of benzyne generated from *para*-disubstituted benzyne precursors (Table 1). The [4+2] cycloaddition of unsubstituted benzyne derived from either bromobenzene **1a** or phenyl trifluoromethanesulfonate (triflate, TfO) **1a'** provided 9,10-epoxyanthracene **3a** in comparable yields (Table 1, entries 1 and 2). We used TfO- or Br-substituted benzenes as the benzyne precursor depending on the synthetic accessibility. Methoxy and methyl groups were introduced by the reaction of *p*-bromoanisole (**1b**) and *p*-bromotoluene (**1c**) to give the corresponding epoxyanthracene **3b** and **3c** in 67% and 77% yields, respectively (Table 1, entries 3 and 4). The iodo group was found to be compatible with the reaction conditions. Thus, **1d** was selectively deprotonated at the *ortho* position of the triflate group to produce **3d** in 56% yield (Table 1, entry 5). Significantly, not only the ester function-

ality was compatible with the reaction conditions but also the aldehyde, affording the corresponding cycloadducts **3e–g** in 91%, 70%, and 77% yields, respectively (Table 1, entries 6–8).¹⁸ Comparison with the reaction performed using other bases clearly demonstrated that $Mg(TMP)_2 \cdot 2LiCl$ was the superior base for the generation of functionalized benzyne species. Reaction of **1g** with $Me_2Zn(TMP)Li$ ^{10b,19} or $LiTMP$ gave the desired product **3g** in 10% or 65% yields, respectively (Table 1, entry 8, footnote b).

Table 1 Synthesis of 2-substituted 9,10-diphenyl-9,10-epoxyanthracene



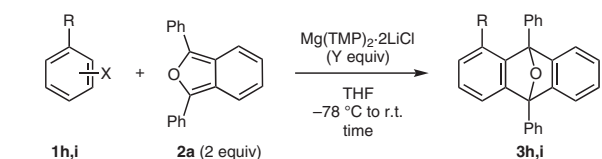
Entry	Substrate R, X	Temp	Y	Time (h)	Yield of 3 (%)
1	1a H, Br	r.t.	3	6	3a 71
2	1a' H, OTf	0 °C	3	4	3a 81
3	1b OMe, Br	reflux	3	8	3b 67
4	1c Me, Br	r.t.	3	2	3c 77
5	1d I, OTf	0 °C	5	2	3d 56
6	1e CO_2t-Bu , OTf	0 °C	5	12	3e 91 ^a
7	1f CO_2Et , OTf	r.t.	5	5	3f 70
8 ^b	1g CHO, OTf	0 °C	5	4	3g 77

^a Gram-scale reaction.

^b In case of the reaction conditions were $Me_2Zn(TMP)Li$ (5.0 equiv), THF, -78 °C to reflux, and 7 h, the yield was 10%. In case of the reaction conditions were $LiTMP$ (5.0 equiv), THF, -78 to 0 °C, and 5 h, the yield was 65%.

We then investigated the synthesis of 1-substituted 9,10-diphenyl-9,10-epoxyanthracene by the [4+2] cycloaddition of benzyne (Table 2). The deprotonation of phenyl triflate bearing a cyclic acetal moiety at the *ortho* position proceeded smoothly to furnish 1-substituted 9,10-epoxyanthracene **3h** in 44% yield (Table 2, entry 1). The deproton-

Table 2 Synthesis of 1-substituted 9,10-diphenyl-9,10-epoxyanthracene **3**

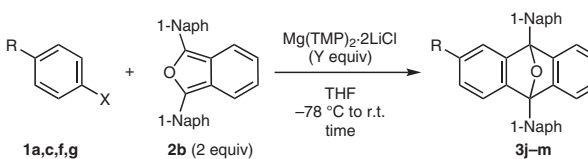


Entry	Substrate (substitution)	Y	Time (h)	Yield of 3 (%)
1	1h 1-OTf, 2-CH(OCH ₂) ₂	5	2	3h 44
2	1i 1-Br, 3-OMe	3	8	3i 84

ation of *m*-bromoanisole occurred selectively at the 2-position to give 1-methoxy-9,10-epoxyanthracene **3i** in 84% yield (Table 2, entry 2).

Next, toward the synthesis of MADN congeners, we conducted the [4+2] cycloaddition of functionalized benzyne with 1,3-dinaphthylisobenzofuran **2b** instead of **2a** (Table 3). 9,10-Dinaphthyl-9,10-epoxyanthracene **3j** was obtained in 54% yield by the reaction of nonsubstituted benzyne with **2b**. The 2-methyl derivative **3k**, the precursor of MADN, was synthesized from *p*-bromotoluene (**1c**) in 62% yield. Ethoxycarbonyl and formyl groups were introduced at the 2-position by reaction of **1f** and **1g**, respectively.

Table 3 Synthesis of 9,10-dinaphthyl-9,10-epoxyanthracene



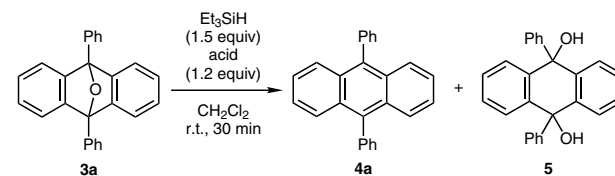
Entry	Substrate R, X	Y	Time (h)	Yield of 3 (%)
1	1a H, Br	3	3	3j 54
2	1c Me, Br	2	3	3k 62
3	1f CO ₂ Et, OTf	5	4	3l 66
4	1g CHO, OTf	5	4	3m 36

Having established the mild and versatile synthesis of 9,10-diphenyl- and 9,10-dinaphthylepoxyanthracenes bearing a wide range of functional groups, we then focused on the development of mild deoxygenation conditions. We initially examined trifluoroacetic acid (TFA)-mediated hydride transfer from Et₃SiH on the basis of the reductive cleavage of benzylic alcohols.²⁰ As expected, the deoxygenation proceeded quite smoothly by treatment of **3a** with a 1.5 equiv of Et₃SiH and a 1.2 equiv of TFA in CH₂Cl₂ at room temperature to give the desired 9,10-diphenylanthracene **4a** in 94% yield (Table 4, entry 1). The reactions with weaker acids such as chloroacetic and acetic acid were not effective. Chloroacetic acid provided a substantial amount of hydrated product **5**^{12c} together with starting material **3a** (Table 4, entry 2). The starting material **3a** was recovered almost quantitatively when acetic acid was used (Table 4, entry 3).

A plausible mechanism for the generation of diol **5** is depicted in Scheme 2. After the acidic cleavage of the epoxide, the resultant tertiary cation would be captured by the chloroacetate anion to form ester **7**. Upon aqueous workup, ester **7** would be hydrolyzed to generate diol **5**.

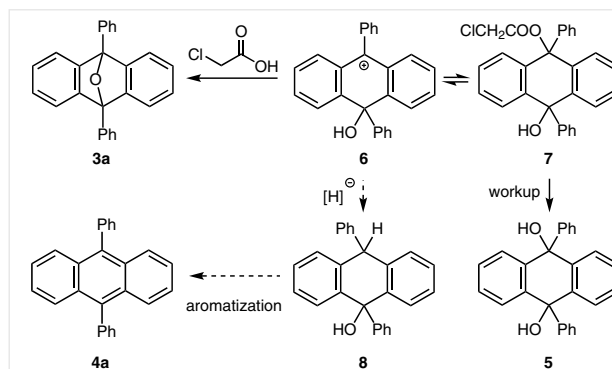
With the deoxygenation conditions in hand, which is milder than the conventional protocols,¹¹ we set to investigate the scope of these conditions for the preparation of functionalized anthracenes (Table 5). Gratifyingly, the combination of TFA and Et₃SiH was proved to be compatible to a

Table 4 Optimization of acid for deoxygenation of 9,10-epoxyanthracene



Entry	Acid	Yield (%)		
		3a	4a	5
1	trifluoroacetic acid	n.d. ^a	94	n.d. ^a
2	chloroacetic acid	61	n.d. ^a	25
3	acetic acid	97	n.d. ^a	n.d. ^a

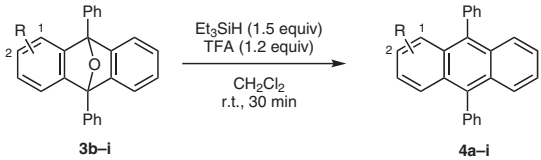
^a n.d. = not detected.



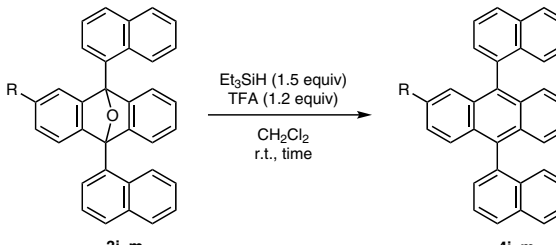
Scheme 2 Proposed mechanism of formation of undesired diol **5**

variety of functionalities. Not only robust functional groups such as methoxy and methyl groups but also relatively labile functional groups such as iodo, alkoxycarbonyl, and even formyl group, remained intact under these conditions, and anthracenes **4b–g,i** were obtained in high yields (Table 5, entries 1–6, 8). Prolonged reaction times were required for the ester substrates **3e** and **3f** (Table 5, entries 4 and 5).²¹ In the case of the aldehyde **3g**, the modified conditions using 1,4-cyclohexadiene as a reductant resulted in a better yield (89%) than that with the standard conditions (62%, Table 5, entry 6). During the reaction of acetal substrate **3h**, deprotection proceeded to furnish the corresponding aldehyde **4h** as the product. The best yield was achieved when the reaction was conducted using 6 equiv of Et₃SiH and 12 equiv of TFA in a diluted CH₂Cl₂ solution (0.01 M, Table 5, entry 7).

Subsequently, we applied the optimal conditions to synthesize a series of MADN congeners (Table 6). The desired transformation proceeded smoothly, and functionalized 9,10-dinaphthylanthracenes **4j–m**, including MADN (**4k**), were obtained in good to high yields.

Table 5 Substrate scope of deoxygenation of 9,10-epoxyanthracene


Entry	Substrate R	Position (1 or 2)	Yield of 4 (%)
1	3b OMe	2	4b 95
2	3c Me	2	4c 95
3	3d I	2	4d 86 (96) ^e
4 ^a	3e CO ₂ t-Bu	2	4e 88
5 ^b	3f CO ₂ Et	2	4f 96
6 ^c	3g CHO	2	4g 62 (89) ^f
7 ^d	3h CH(OCH ₂) ₂	1	4h 72 (R = CHO)
8	3i OMe	1	4i 92 (95) ^g

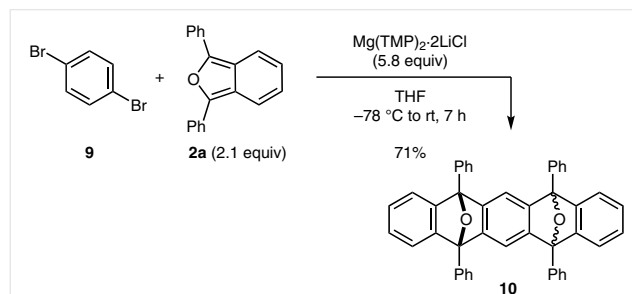
^a Reaction time was 23 h.^b Reaction time was 19 h.^c Reaction time was 24 h.^d Et₃SiH (6 equiv), TFA (12 equiv), and CH₂Cl₂ (0.01 M) were used.^e 1,4-Cyclohexadiene (5.0 equiv) was used as reductant. Reaction time was 3 h.^f 1,4-Cyclohexadiene (5.0 equiv) was used as reductant. Reaction time was 5.5 h.^g 1,4-Cyclohexadiene (5.0 equiv) was used as reductant. Reaction time was 25 min.**Table 6** Synthesis of MADN congeners


Entry	Substrate R	Time	Yield of 4 (%)
1	3j H	10 min	4j 87
2	3k Me	10 min	4k 73
3	3l CO ₂ Et	1 h	4l 95
4 ^a	3m CHO	3 h	4m 82

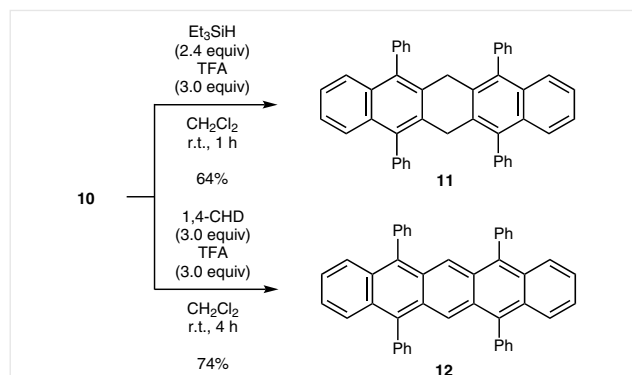
^a 1,4-Cyclohexadiene (4.7 equiv) was used as reductant.

Finally, the established [4+2] cycloaddition/deoxygenation sequence was applied to the construction of a pentacene structure. Initially, 1,4-dibromobenzene (**9**) was subjected to the benzyne generation conditions using 5.8 equiv of Mg(TMP)₂·2LiCl as a substrate in the presence of 1,3-diphenylisobenzofuran (Scheme 3). The sequential benzyne

generation and [4+2] cycloaddition proceeded twice on one benzene ring to furnish diepoxypentacene **10** in 71% yield as a 1:1 mixture of diastereomers.²²

**Scheme 3** Synthesis of pentacene precursor

Next, we examined the deoxygenation of the diepoxypentacene **10** using optimal conditions (Scheme 4). Surprisingly, the initial trial using Et₃SiH produced the unexpected 5,7,12,14-tetraphenyl-6,13-dihydro-pentacene **11** in 64% yield,²³ most likely as a result of the overreduction of the desired 5,7,12,14-tetraphenylpentacene **12**. This overreduction was completely suppressed using 1,4-cyclohexadiene as a milder reductant, which afforded the desired product **12** in 74% yield.²⁴

**Scheme 4** Deoxygenation of pentacene precursor

In summary, we have established a mild sequence for the synthesis of functionalized 9,10-diarylanthracenes by Mg(TMP)₂·2LiCl-mediated benzyne generation/[4+2] cycloaddition, followed by a newly developed mild deoxygenation. The high functional group compatibility of Mg(TMP)₂·2LiCl allows access to a variety of functionalized 9,10-epoxyanthracenes. By choosing appropriate conditions, a broad range of functionalized 9,10-epoxyanthracenes can be converted into 9,10-diarylanthracenes in high yields. Furthermore, the utility of this sequence was demonstrated by the concise synthesis of 5,7,12,14-tetraphenylpentacene.

Funding Information

This work was financially supported by JSPS KAKENHI Grant Numbers 16H01127, 16H00999, 17K05773, 16K04864, a Grant-in aid for Scientific Research (A) (26253001), JST ERATO (JPMJER1301), MEXT (Interdepartmental Doctoral Degree Program for Multidimensional Material Science Leaders), and JSPS predoctoral fellowship (for N.M.).

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0036-1591510>.

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- (17) A preliminary result of [4+2] cycloaddition of 1,3-(4-bromophenyl)isobenzofuran with benzyne generated by treatment of PhOTf with Mg(TMP)₂·2LiCl was reported by our group (ref. 16b).
- (18) **A Gram-Scale Preparation of tert-Butyl 9,10-Diphenyl-9,10-epoxy-2-anthracenecarboxylate (3e)**
A flame-dried 500 mL three-necked round-bottomed flask equipped with a 200 mL dropping funnel, a magnetic stirring bar, a rubber septum, and an inlet adapter with a three-way stopcock was charged with 1,3-diphenylisobenzofuran (**2a**, 2.16 g, 8.00 mmol), dry THF (20.0 mL), and tert-butyl 4-(trifluoromethylsulfonyloxy)benzoate (**1e**, 1.23 g, 3.77 mmol). After cooling to -78 °C, Mg(TMP)₂·2LiCl (0.16 M in THF, 130 mL, 20 mmol) was added dropwise to the flask, and the resulting mixture was stirred at -78 °C for 1 h. The flask was then immersed in an ice bath, and the mixture was stirred for 11 h, after which time TLC (hexanes–EtOAc = 2:1) indicated complete consumption of tert-butyl 4-(trifluoromethylsulfonyloxy)benzoate (**1e**). The reaction was quenched by addition of sat. aq. NH₄Cl, and the aqueous layer was extracted with EtOAc three times. The combined organic extracts were successively washed with H₂O and brine, dried over anhydrous Na₂SO₄, and filtered. The organic solvents were removed under reduced pressure to give a crude epoxyanthracene, which was purified by flash column chromatography on silica gel (hexanes–dichloromethane = 1:1) to afford **3e** (1.53 g, 3.43 mmol, 91%) as a white solid. R_f = 0.18 (hexanes–dichloromethane = 1:1). The spectral data of **3e** were in complete agreement with those reported in the literature (ref. 19).
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- (21) **tert-Butyl 9,10-Diphenyl-2-anthracenecarboxylate (4e)**
A 10 mL test tube equipped with a magnetic stirring bar and a cap was charged with tert-butyl 9,10-diphenyl-9,10-epoxy-2-anthracenecarboxylate (**3e**, 100 mg, 224 μmol), wet CH₂Cl₂ (448 μL), Et₃SiH (53.7 μL, 336 μmol), and TFA (20.0 μL, 269 μmol). The mixture was stirred for 23 h, after which time TLC (hexanes–EtOAc = 3:1) indicated complete consumption of tert-butyl 9,10-diphenyl-9,10-epoxy-2-anthracenecarboxylate (**3e**). The reaction was quenched by addition of H₂O, and the aqueous

layer was extracted with CH_2Cl_2 three times. The combined organic extracts were successively washed with sat. aq. NaHCO_3 and brine, dried over anhydrous Na_2SO_4 , and filtered. The organic solvents were removed under reduced pressure to give a crude anthracene, which was purified by flash column chromatography on silica gel (hexanes- CH_2Cl_2 = 4:1) to afford **4e** (85.3 mg, 198 μmol , 88%) as a pale yellow solid. R_f = 0.73 (hexanes-EtOAc = 3:1). For the spectral data of **4e**, see the Supporting Information.

- (22) In the case of LiTMP was used as the base, the yield (14%) was lower than using $\text{Mg}(\text{TMP})_2 \cdot 2\text{LiCl}$ as the base.
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