Synthesis of Diarylated Aromatic Hydrocarbons by Dehydroxylation of Diols Using the Titanium(IV) Chloride and Triethylamine Reagent System

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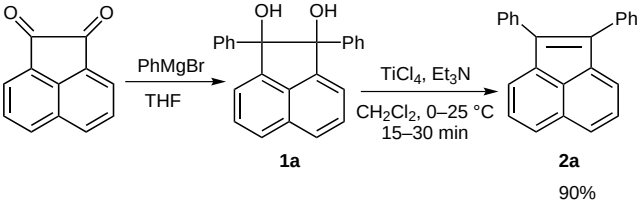
Abstract: 1,2-Diarylacenaphthylene, 9,10-diarylphenanthrene and 9,10-diarylanthracene derivatives were obtained in good yields (61–92%) in short reaction times (5–30 min) from the corresponding diols with the titanium(III) reagent prepared in situ using the $TiCl_4/Et_3N$ reagent system in dichloromethane at 25 °C.

Key words: polycyclic aromatic hydrocarbons, dehydroxylation, diols, titanium tetrachloride, triethylamine

Diaryl derivatives of aromatic systems like acenaphthylene, phenanthrene and anthracene are the most fundamental molecules in the family of fused polycyclic aromatic hydrocarbons. The acenaphthylene derivatives belong to the cyclopentane-fused polycyclic aromatic hydrocarbon family.[1,2] Phenanthrene is an important skeleton of organic compounds as it is a core structure in natural products.[3] Several phenanthrene derivatives exhibit interesting biological activities such as antimalarial,[4] anticancer[5] and emetic activity.[6] Some phenanthrene derivatives also exhibit photoconductivity[7,8] and electroluminescent properties,[9] and hence are useful, common structural motifs in materials science.[10] Many derivatives of anthracene are useful as electron-transfer agents.[11] Some anthracene derivatives exhibit electrochemiluminescence properties[12] and others are useful materials for light-emitting devices.[13] Accordingly, development of a method to readily access these polycyclic aromatic hydrocarbons from easily accessible starting materials under ambient reaction conditions is highly desirable.

Generally, low-valent titanium species are prepared by the reaction of $TiCl_4$ and Cp_2TiCl_2 with reducing agents (e.g., Mg, Mn, Zn, Li, $LiAlH_4$).[14,15] We have previously reported that a titanium(III) species can be easily prepared under ambient conditions by the reaction of titanium tetrachloride with triethylamine.[16] Herein, we report that this reagent system is useful for the synthesis of 1,2-diarylacenaphthylene, 9,10-diarylphenanthrene and 9,10-diarylanthracene derivatives by dehydroxylation of the corresponding diols.

Initially, we examined this transformation with 1,2-diphenyl-1,2-dihydroacenaphthylene-1,2-diol (**1a**, 1 mmol) using $TiCl_4$ (2 mmol) and Et_3N (4 mmol) in dichloromethane solvent. In this experiment, the corresponding 1,2-diphenylacenaphthylene (**2a**) was obtained in 90% yield (Scheme 1).



Scheme 1 Conversion of the readily accessible diol **1a** into **2a** by dehydroxylation using the $TiCl_4/Et_3N$ reagent system

We have carried out this reaction with other amines (Bu_3N, DIPEA) in place of Et_3N for the synthesis of 1,2-diphenylacenaphthylene (**2a**); Et_3N gave the optimum yield. In the case of Bu_3N and DIPEA, the acenaphthylene **2a** was obtained in 78% and 70% yield, respectively. Using this method, we have synthesized several 1,2-diarylacenaphthylene derivatives from the corresponding diols, which are readily accessible via Grignard reaction using the appropriate arylmagnesium halides.[17] Acenaphthylene derivatives containing functional groups such as amino, halo and methoxy groups are readily prepared using this method (Table 1, entries 3–7). Electronic effects play a role in the rate of this transformation. In the case of the *N*,*N*-dialkylaniline derivatives the products were obtained in good yields in a short reaction time (15 min; Table 1, entries 6 and 7), whereas the other 1,2-diarylacenaphthylenes were obtained in 30 minutes (Table 1, entries 1–5). The structure of compound **2f** was confirmed by single-crystal X-ray data (Figure 1).[18]

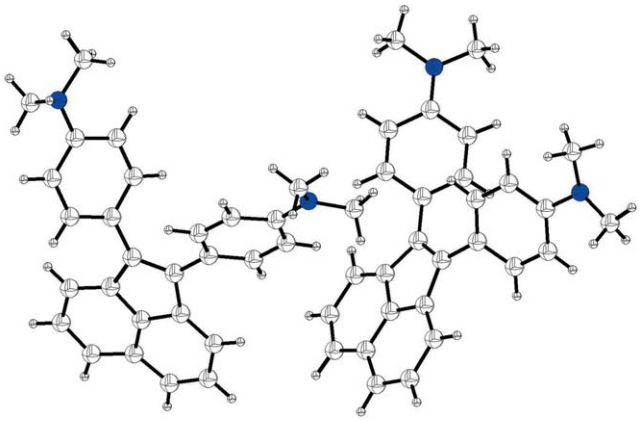


Figure 1 ORTEP diagram of 1,2-bis[4-(dimethylamino)phenyl]acenaphthylene (**2f**)

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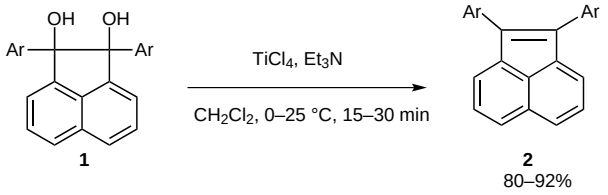
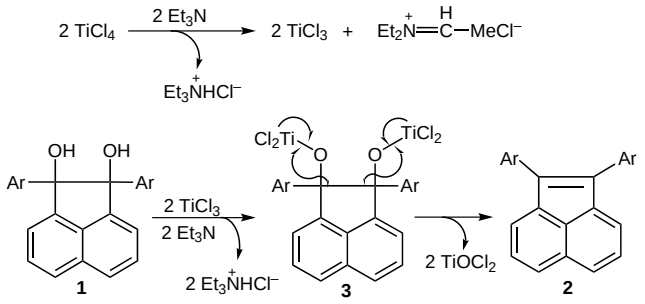
Table 1 Synthesis of 1,2-Diarylacenaphthylenes **2** from 1,2-Diaryl-1,2-dihydroacenaphthylene-1,2-diols **1** Using the $TiCl_4/Et_3N$ Reagent System[a]



Entry	Diol	Ar	Product[b]	Time (min)	Yield[c] (%)
1	**1a**	Ph	**2a**	30	90
2	**1b**	4-MeC_6H_4	**2b**	30	92
3	**1c**	4-$MeOC_6H_4$	**2c**	30	88
4	**1d**	4-$F_3CC_6H_4$	**2d**	30	85
5	**1e**	3,5-$(F_3C)_2C_6H_4$	**2e**	30	83
6	**1f**	4-Me-$_2NC_6H_4$	**2f**	15	80
7	**1g**	4-$Et_2NC_6H_4$	**2g**	15	88

[a] Reaction conditions: diol **1** (1.0 mmol), $TiCl_4$ (2.0 mmol), Et_3N (4.0 mmol), 25 °C.
[b] Identified by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR and MS).
[c] Yield of isolated product, based on the amount of diol **1**.

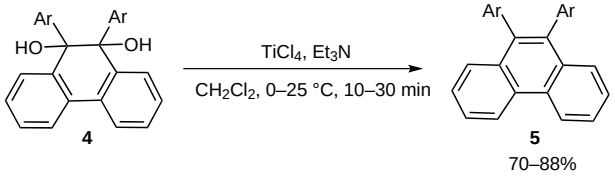
The formation of 1,2-diarylacenaphthylenes **2** from the corresponding diols **1** can be explained by the tentative mechanism outlined in Scheme 2. The reactive titanium(III) species formed in situ by the reaction of $TiCl_4$ with Et_3N would undergo reaction with the diol in the presence of Et_3N[16,19] to give the titanium species **3**, which in turn could give the hydrocarbon **2** and the $TiOCl_2$ species, as envisaged in Scheme 2.



Scheme 2 Formation of 1,2-diarylacenaphthylenes **2** from diols **1** using the $TiCl_4/Et_3N$ reagent system

We have also examined this transformation using 9,10-diaryl-9,10-dihydrophenanthrene-9,10-diols **4** and the $TiCl_4/Et_3N$ reagent system (Table 2). The resulting 9,10-diarylphenanthrenes **5** were obtained in very good yields (70–88%) under these conditions. In this case also, the amino-substituted derivative, phenanthrene **5d**, was obtained in a shorter reaction time (10 min) than the other 9,10-diarylphenanthrenes (30 min). The 9,10-diaryl-9,10-dihydrophenanthrene-9,10-diols **4** can be readily accessed

Table 2 Synthesis of 9,10-Diarylphenanthrenes **5** from 9,10-Diaryl-9,10-dihydrophenanthrene-9,10-diols **4** Using the $TiCl_4/Et_3N$ Reagent System[a]



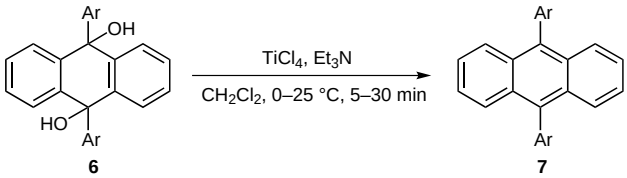
Entry	Diol	Ar	Product[b]	Time (min)	Yield[c] (%)
1	**4a**	Ph	**5a**	30	80
2	**4b**	4-MeC_6H_4	**5b**	30	85
3	**4c**	4-$MeOC_6H_4$	**5c**	30	88
4	**4d**	4-$Et_2NC_6H_4$	**5d**	10	70

[a] Reaction conditions: diol **4** (0.5 mmol), $TiCl_4$ (1 mmol), Et_3N (2 mmol), 25 °C.
[b] Identified by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR and MS).
[c] Yield of isolated product, based on the amount of diol **4**.

by the reaction of 9,10-phenanthrenequinone with aryllithium reagents or Grignard reagents.[17a,20]

9,10-Diaryl-9,10-dihydroanthracene-9,10-diol derivatives **6**, readily accessible by Grignard reaction of the corresponding arylmagnesium bromides with 9,10-anthraquinone,[21] also give similar results (Table 3). In this case, the corresponding 9,10-diarylanthracene derivatives **7** were obtained in good yields (61–85%). Again, the dehydroxylation reaction with the low-valent titanium species is faster with the *N*,*N*-dialkylamine derivative **6c** (5 min).

Table 3 Synthesis of 9,10-Diarylanthracenes **7** from 9,10-Diaryl-9,10-dihydroanthracene-9,10-diols **6** Using the $TiCl_4/Et_3N$ Reagent System[a]



Entry	Diol	Ar	Product[b]	Time (min)	Yield[c] (%)
1	**6a**	Ph	**7a**	30	82
2	**6b**	4-$MeOC_6H_4$	**7b**	30	85
3	**6c**	4-$Et_2NC_6H_4$	**7c**	5	61

[a] Reaction conditions: diol **6** (0.5 mmol), $TiCl_4$ (1 mmol), Et_3N (2 mmol), 25 °C.
[b] Identified by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR and MS).
[c] Yield of isolated product, based on the amount of diol **6**.

The formation of 9,10-diarylphenanthrenes **5** and 9,10-diarylanthracenes **7** from the corresponding diols **4** and **6**,

respectively, would also proceed through a mechanism similar to that outlined for the acenaphthylene derivatives (Scheme 2). We have also examined the reaction of the $TiCl_4/Et_3N$ reagent system with [1,1′-bicyclohexyl]-1,1′-diol under our conditions. Whereas this diol was not affected in dichloromethane at 25 °C, reaction at 75 °C in dichloroethane solvent led to a complex mixture of unidentified products. Presumably, the dehydroxylation readily takes place with the diols **1**, **4** and **6** due to the formation of conjugated aromatic products **2**, **5** and **7**.

In the case of the *N*,*N*-dialkylamino-substituted systems, the products were obtained in relatively shorter reaction times (see Tables 1–3). Presumably, the *N*,*N*-dialkylamino group accelerates fragmentation of the intermediate into the titanium(IV) species which may become coordinated with the *N*,*N*-dialkylamino group in the product (Scheme 2).

In conclusion, we have developed a simple and convenient method for the rapid synthesis of 1,2-diarylacenaphthylene, 9,10-diarylphenanthrene and 9,10-diarylanthracene derivatives by dehydroxylation of the corresponding diols using the simple $TiCl_4/Et_3N$ reagent system under ambient reaction conditions. Previously, these compounds were synthesized via transition-metal-mediated (e.g., Pd, Ni) cross-coupling reactions and multistep rearrangement reactions.[22–25] Recently, some diarylphenanthrene derivatives were synthesized by reaction of the Zn/HCl/AcOH reagent system with the corresponding diols under reflux reaction conditions.[20] Our method of conversion of diarylated diols into the diarylated polycyclic aromatic hydrocarbons **2**, **5** and **7** using the $TiCl_4/Et_3N$ reagent system involves relatively mild reaction conditions. Therefore, the method described here for the synthesis of polycyclic aromatic hydrocarbons from the corresponding readily accessible diols has good synthetic potential.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ with TMS as reference (δ = 0 ppm) on a Bruker Avance 400 spectrometer. Melting points are uncorrected. IR spectra were recorded on a JASCO FT-5300 FT/IR instrument with polystyrene as reference. Mass spectroscopic analysis was carried out on a VG 7070H spectrometer using EI at 70 eV. The quinones and $TiCl_4$ used in the reactions were supplied by Aldrich and Loba Chemicals, respectively. Chromatographic purification was conducted by column chromatography using silica gel (100–200 mesh). All the reported yields are isolated yields of materials, judged homogeneous by TLC analysis. The diols **1a**, **1b**, **1c**, **4a**, **4b**, **4c** and **6b** were synthesized using the reported procedures.[17,20,21]

1,2-Diaryl-1,2-dihydroacenaphthylene-1,2-diols 1d–g; General Procedure[17]

Magnesium turnings (192 mg, 8 mmol) were treated with the appropriate aryl bromide (8 mmol) in THF (30 mL) for 2 h at 25 °C; after the formation of the Grignard reagent, acenaphthenequinone (364 mg, 2 mmol) was added under N_2 atmosphere and the mixture was stirred for 8 h at 25 °C. The reaction was quenched with sat. NH_4Cl soln (10 mL) and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic extract was washed with brine soln (20 mL), dried over anhyd Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (hexane–EtOAc, 85:15).

1,2-Bis[4-(trifluoromethyl)phenyl]-1,2-dihydroacenaphthylene-1,2-diol (1d)

White solid; yield: 739 mg (78%); mp 164–166 °C.

IR (KBr): 3539, 3468 cm^{-1}.

^{1}H NMR: δ = 7.95 (d, *J* = 8.4 Hz, 2 H), 7.69–7.59 (m, 6 H), 7.39–7.26 (m, 6 H), 2.14 (s, 2 H).

^{13}C NMR: δ = 144.9, 144.4, 137.2, 131.4, 130.2 (q, *J* = 32 Hz), 129.1, 128.4, 125.5, 124.7 (q, *J* = 40 Hz), 124.1 (q, *J* = 270 Hz), 121.8, 89.5.

MS (EI): *m*/*z* = 475 $[M + H]^+$.

Anal. Calcd for $C_{26}H_{16}F_6O_2$: C, 65.83; H, 3.40. Found: C, 65.76; H, 3.45.

1,2-Bis[3,5-bis(trifluoromethyl)phenyl]-1,2-dihydroacenaphthylene-1,2-diol (1e)

White solid; yield: 878 mg (72%); mp 172–174 °C.

IR (KBr): 3557, 3433 cm^{-1}.

^{1}H NMR: δ = 8.03 (d, *J* = 8.4 Hz, 2 H), 7.95 (s, 2 H), 7.80–7.73 (m, 6 H), 7.39 (d, *J* = 6.8 Hz, 2 H), 2.29 (s, 2 H).

^{13}C NMR: δ = 143.9, 142.0, 137.5, 132.2, 130.9 (q, *J* = 33 Hz), 129.4, 128.7, 126.8, 123.4 (q, *J* = 271 Hz), 122.2, 121.7, 88.3.

MS (EI): *m*/*z* = 609 $[M - H]^+$.

Anal. Calcd for $C_{28}H_{14}F_{12}O_2$: C, 55.10; H, 2.31. Found: C, 55.21; H, 2.36.

1,2-Bis[4-(dimethylamino)phenyl]-1,2-dihydroacenaphthylene-1,2-diol (1f)

Pale yellow solid; yield: 636 mg (75%); mp 208–210 °C.

IR (KBr): 3528, 1520 cm^{-1}.

^{1}H NMR: δ = 7.88 (d, *J* = 8 Hz, 2 H), 7.66–7.62 (m, 2 H), 7.40 (d, *J* = 7.2 Hz, 2 H), 7.15–7.13 (d, *J* = 8.4 Hz, 4 H), 6.71 (d, *J* = 8.4 Hz, 4 H), 2.98 (s, 12 H), 2.29 (s, 2 H).

^{13}C NMR: δ = 150.2, 146.2, 137.2, 131.0, 128.7, 128.6, 128.0, 124.9, 121.7, 111.9, 89.9, 40.5.

MS (EI): *m*/*z* = 425 $[M + H]^+$.

Anal. Calcd for $C_{28}H_{28}N_2O_2$: C, 79.22; H, 6.65; N, 6.60. Found: C, 79.06; H, 6.57; N, 6.71.

1,2-Bis[4-(diethylamino)phenyl]-1,2-dihydroacenaphthylene-1,2-diol (1g)

Pale yellow solid; yield: 672 mg (70%); mp 168–170 °C.

IR (KBr): 3528, 2966, 1520 cm^{-1}.

^{1}H NMR: δ = 7.89 (d, *J* = 8.4 Hz, 2 H), 7.66–7.62 (m, 2 H), 7.40 (d, *J* = 6.8 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 4 H), 6.65 (d, *J* = 8.4 Hz, 4 H), 3.40 (q, *J* = 6.8 Hz, 8 H), 2.44 (s, 2 H), 1.22 (t, *J* = 6.8 Hz, 12 H).

^{13}C NMR: δ = 147.3, 146.1, 137.0, 130.9, 128.7, 128.5, 126.9, 124.5, 121.5, 110.8, 89.8, 44.1, 12.5.

MS (EI): *m*/*z* = 481 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83. Found: C, 79.86; H, 7.61; N, 5.75.

9,10-Bis[4-(diethylamino)phenyl]-9,10-dihydrophenanthrene-9,10-diol (4d)

Diol **4d** was synthesized via reaction of the Grignard reagent prepared from 4-bromo-*N*,*N*-diethylaniline (1.82 g, 8 mmol) and magnesium turnings (192 mg, 8 mmol) with 9,10-phenanthrenequinone (416 mg, 2 mmol) in THF (30 mL).

White solid; yield: 556 mg (55%); mp 170–172 °C.

IR (KBr): 3528 cm^{-1}.

^{1}H NMR: δ = 7.91 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 7.6 Hz, 2 H), 7.42–7.38 (m, 2 H), 7.28–7.25 (m, 6 H), 6.48 (d, *J* = 8.4 Hz, 4 H), 3.26 (q, *J* = 7.2 Hz, 8 H), 2.37 (s, 2 H), 1.10 (t, *J* = 7.2 Hz, 12 H).

^{13}C NMR: δ = 147.0, 142.5, 133.7, 128.9, 128.7, 128.0, 126.8, 126.1, 122.7, 111.1, 80.7, 44.1, 12.6.

MS (EI): *m*/*z* = 507 [M + H]$^+$.

Anal. Calcd for $C_{34}H_{38}N_2O_2$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.48; H, 7.49; N, 5.65.

9,10-Diaryl-9,10-dihydroanthracene-9,10-diols 6a and 6c; General Procedure

Diols **6a** and **6c** were synthesized via reaction of the Grignard reagent prepared from the appropriate aryl bromide (8 mmol) and magnesium turnings (192 mg, 8 mmol) in THF (30 mL) with 9,10-anthraquinone (416 mg, 2 mmol) in 1,4-dioxane (60 mL).

9,10-Diphenyl-9,10-dihydroanthracene-9,10-diol (6a)

White solid; yield: 328 mg (45%); mp 242–244 °C.

IR (KBr): 3576 cm^{-1}.

^{1}H NMR: δ = 7.51–7.23 (m, 18 H), 2.69 (s, 2 H).

^{13}C NMR: δ = 148.1, 140.6, 128.5, 128.4, 128.1, 126.8, 126.6, 74.4.

MS (EI): *m*/*z* = 365 [M + H]$^+$.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.52; H, 5.48.

9,10-Bis[4-(diethylamino)phenyl]-9,10-dihydroanthracene-9,10-diol (6c)

White solid; yield: 556 mg (55%); mp 222–224 °C.

IR (KBr): 3553, 3427 cm^{-1}.

^{1}H NMR: δ = 7.52–7.49 (m, 4 H), 7.29–7.27 (m, 4 H), 7.21 (d, *J* = 8 Hz, 4 H), 6.61 (d, *J* = 8 Hz, 4 H), 3.34 (q, *J* = 7.2 Hz, 8 H), 2.59 (s, 2 H), 1.17 (t, *J* = 7.2 Hz, 12 H).

^{13}C NMR: δ = 146.6, 141.7, 134.1, 127.9, 127.8, 127.7, 110.9, 74.5, 44.2, 12.6.

MS (EI): *m*/*z* = 507 [M + H]$^+$.

Anal. Calcd for $C_{34}H_{38}N_2O_2$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.68; H, 7.51; N, 5.75.

1,2-Diphenylacenaphthylene (2a); Typical Procedure

To a soln of diol **1a** (338 mg, 1 mmol) and Et_3N (0.56 mL, 4 mmol) in CH_2Cl_2 (15 mL), $TiCl_4$ (0.44 mL of 1:1 $TiCl_4$–CH_2Cl_2 soln, 2 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min at 0 °C under N_2 atmosphere. The mixture was stirred for 0.5 h at 0–25 °C, then the reaction was quenched with sat. NH_4Cl soln (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic extract was washed with brine soln (10 mL) and dried over anhyd Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column (hexane–EtOAc, 97:3) to give **2a**.

Orange solid; yield: 274 mg (90%); mp 162–163 °C (Lit.[22d] 161–163 °C).

IR (KBr): 3059, 1479, 1427 cm^{-1}.

^{1}H NMR: δ = 7.88 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.63–7.59 (m, 2 H), 7.47–7.44 (m, 4 H), 7.39–7.29 (m, 6 H).

^{13}C NMR: δ = 139.9, 138.0, 135.2, 130.8, 128.4, 128.2, 128.1, 127.8, 127.3, 127.1, 124.0.

MS (EI): *m*/*z* = 305 [M + H]$^+$.

1,2-Bis(4-methylphenyl)acenaphthylene (2b)

Orange solid; yield: 305 mg (92%); mp 120–122 °C.

IR (KBr): 3036, 2914, 1481, 1431 cm^{-1}.

^{1}H NMR: δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 6.8 Hz, 2 H), 7.63–7.59 (m, 2 H), 7.40–7.39 (m, 4 H), 7.23–7.20 (m, 4 H), 2.43 (s, 6 H).

^{13}C NMR: δ = 140.2, 137.7, 136.8, 132.4, 129.9, 129.2, 128.4, 128.3, 127.8, 127.1, 123.8, 21.4.

MS (EI): *m*/*z* = 333 [[M + H]$^+$.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.76; H, 6.12.

1,2-Bis(4-methoxyphenyl)acenaphthylene (2c)

Red solid; yield: 320 mg (88%); mp 106–108 °C (Lit.[22a] 106–107 °C).

IR (KBr): 3040, 2955, 1541, 1491 cm^{-1}.

^{1}H NMR: δ = 7.84 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 6.8 Hz, 2 H), 7.60–7.56 (m, 2 H), 7.39 (d, *J* = 8.8 Hz, 4 H), 6.92 (d, *J* = 8.8 Hz, 4 H), 3.85 (s, 6 H).

^{13}C NMR: δ = 158.7, 140.3, 136.9, 131.2, 128.3, 128.2, 127.8, 127.7, 127.0, 123.6, 113.9, 55.2.

MS (EI): *m*/*z* = 365 [M + H]$^+$.

1,2-Bis[4-(trifluoromethyl)phenyl]acenaphthylene (2d)

Yellow solid; yield: 374 mg (85%); mp 166–168 °C.

IR (KBr): 3057, 1614, 1433, 1323 cm^{-1}.

^{1}H NMR: δ = 7.95 (d, *J* = 8 Hz, 2 H), 7.76 (d, *J* = 6.8 Hz, 2 H), 7.67–7.65 (m, 6 H), 7.54 (d, *J* = 8 Hz, 4 H).

^{13}C NMR: δ = 138.9, 138.5, 137.8, 130.2, 129.4 (q, *J* = 32 Hz), 128.6, 128.1, 128.0, 125.6, 125.5, 124.4, 124.3 (q, *J* = 271 Hz).

MS (EI): *m*/*z* = 441 [M + H]$^+$.

Anal. Calcd for $C_{26}H_{14}F_6$: C, 70.91; H, 3.20. Found: C, 70.85; H, 3.28.

1,2-Bis[3,5-bis(trifluoromethyl)phenyl]acenaphthylene (2e)

Yellow solid; yield: 478 mg (83%); mp 160–162 °C.

IR (KBr): 3057, 1618, 1539 cm^{-1}.

^{1}H NMR: δ = 8.02 (d, *J* = 8.4 Hz, 2 H), 7.90–7.70 (m, 10 H).

^{13}C NMR: δ = 137.7, 136.9, 136.4, 132.3 (q, *J* = 33 Hz), 129.9, 129.0, 128.8, 128.3, 127.8, 124.8, 123.0 (q, *J* = 271 Hz), 121.4.

MS (EI): *m*/*z* = 577 [M + H]$^+$.

Anal. Calcd for $C_{28}H_{12}F_{12}$: C, 58.36; H, 2.10. Found: C, 58.45; H, 2.16.

1,2-Bis[4-(dimethylamino)phenyl]acenaphthylene (2f)

Dark red solid; yield: 312 mg (80%); mp 206–208 °C.

IR (KBr): 3040, 2922, 1606 cm^{-1}.

^{1}H NMR: δ = 7.81 (d, *J* = 8 Hz, 2 H), 7.76 (d, *J* = 8 Hz, 2 H), 7.60–7.56 (m, 2 H), 7.46–7.43 (m, 4 H), 6.79 (d, *J* = 8.4 Hz, 4 H), 3.02 (s, 12 H).

^{13}C NMR: δ = 149.3, 141.0, 136.4, 130.9, 128.6, 128.3, 127.7, 126.5, 123.9, 123.2, 112.3, 40.5.

MS (EI): *m*/*z* = 391 [M + H]$^+$.

Anal. Calcd for $C_{28}H_{26}N_2$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.08; H, 6.65; N, 7.25.

1,2-Bis[4-(diethylamino)phenyl]acenaphthylene (2g)

Dark red semisolid; yield: 392 mg (88%).

IR (KBr): 3038, 2970, 1608 cm^{-1}.

^{1}H NMR: δ = 7.85–7.83 (m, 4 H), 7.65–7.61 (m, 2 H), 7.52–7.49 (m, 4 H), 6.77 (d, *J* = 8.4 Hz, 4 H), 3.45 (q, *J* = 6.8 Hz, 8 H), 1.27 (t, *J* = 6.8 Hz, 12 H).

^{13}C NMR: δ = 146.5, 141.0, 135.9, 131.0, 128.5, 128.1, 127.5, 126.2, 123.0, 122.7, 111.4, 44.2, 12.7.

MS (EI): *m*/*z* = 447 [M + H]$^+$.

Anal. Calcd for $C_{32}H_{34}N_2$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.15; H, 7.72; N, 6.37.

9,10-Diarylphenanthrenes 5 and 9,10-Diarylanthracenes 7; General Procedure

To a soln of the diol **4** (or **6**) (0.5 mmol) and Et_3N (0.28 mL, 2 mmol) in CH_2Cl_2 (10 mL), $TiCl_4$ (0.22 mL of 1:1 $TiCl_4$–CH_2Cl_2 soln, 1 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise over 5 min at 0 °C under N_2 atmosphere. The mixture was stirred for 0.5 h at 0–25 °C, then the reaction was quenched with sat. NH_4Cl soln (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extract was washed with brine soln (10 mL) and dried over anhyd Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column (hexane–EtOAc, 98:2) to give **5** (or **7**).

9,10-Diphenylphenanthrene (5a)

White solid; yield: 132 mg (80%); mp 242–244 °C (Lit.[20] 238–239 °C).

IR (KBr): 3047, 1485, 1439 cm^{-1}.

^1H NMR: δ = 8.84 (d, *J* = 8 Hz, 2 H), 7.71–7.50 (m, 6 H), 7.26–7.18 (m, 10 H).

^{13}C NMR: δ = 139.6, 137.2, 131.9, 131.1, 130.0, 127.9, 127.6, 126.6, 126.5, 126.4, 122.5.

MS (EI): *m*/*z* = 331 $[M + H]^+$.

9,10-Bis(4-methylphenyl)phenanthrene (5b)

White solid; yield: 152 mg (85%); mp 256–258 °C (Lit.[20] 261–263 °C).

IR (KBr): 3026, 2922, 1682, 1504 cm^{-1}.

^1H NMR: δ = 8.82 (d, *J* = 8.4 Hz, 2 H), 7.67–7.47 (m, 6 H), 7.08 (m, 8 H), 2.35 (s, 6 H).

^{13}C NMR: δ = 137.2, 136.6, 135.8, 132.2, 130.9, 129.9, 128.4, 127.9, 126.5, 126.2, 122.5, 21.3.

MS (EI): *m*/*z* = 359 $[M + H]^+$.

9,10-Bis(4-methoxyphenyl)phenanthrene (5c)

White solid; yield: 172 mg (88%); mp 264–268 °C (Lit.[20] 274–275 °C).

IR (KBr): 3059, 2951, 1608, 1506 cm^{-1}.

^1H NMR: δ = 8.80 (d, *J* = 8.4 Hz, 2 H), 7.68–7.47 (m, 6 H), 7.06 (d, *J* = 8.8 Hz, 4 H), 6.80 (d, *J* = 8.8 Hz, 4 H), 3.80 (s, 6 H).

^{13}C NMR: δ = 157.9, 137.1, 132.3, 132.1, 132.0, 129.9, 127.8, 126.5, 126.3, 122.5, 113.1, 55.1.

MS (EI): *m*/*z* = 391 $[M + H]^+$.

9,10-Bis[4-(diethylamino)phenyl]phenanthrene (5d)

White solid; yield: 165 mg (70%); mp 214–216 °C.

IR (KBr): 2964, 1612, 1514 cm^{-1}.

^1H NMR: δ = 8.79 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.65–7.46 (m, 4 H), 6.98 (d, *J* = 8.0 Hz, 4 H), 6.61 (d, *J* = 8.0 Hz, 4 H), 3.33 (q, *J* = 6.8 Hz, 8 H), 1.14 (t, *J* = 6.8 Hz, 12 H).

^{13}C NMR: δ = 146.2, 137.7, 132.8, 132.0, 129.9, 128.1, 127.3, 126.3, 125.8, 122.3, 111.7, 44.4, 12.5.

MS (EI): *m*/*z* = 473 $[M + H]^+$.

Anal. Calcd for $C_{34}H_{36}N_2$: C, 86.40; H, 7.68; N, 5.93. Found: C, 86.25; H, 7.76; N, 5.85.

9,10-Diphenylanthracene (7a)

White solid; yield: 135 mg (82%); mp 242–244 °C (Lit.[25] 248–250 °C).

IR (KBr): 3024, 1489, 1386 cm^{-1}.

^1H NMR: δ = 7.74–7.71 (m, 4 H), 7.65–7.50 (m, 10 H), 7.37–7.34 (m, 4 H).

^{13}C NMR: δ = 139.1, 137.1, 131.4, 129.9, 128.4, 127.5, 126.9, 125.0.

MS (EI): *m*/*z* = 331 $[M + H]^+$.

9,10-Bis(4-methoxyphenyl)anthracene (7b)

White solid; yield: 166 mg (85%); mp 270–272 °C (Lit.[25] 274 °C).

IR (KBr): 1604, 1512, 1390 cm^{-1}.

^1H NMR: δ = 7.75–7.73 (m, 4 H), 7.40–7.32 (m, 8 H), 7.14 (d, *J* = 8.8 Hz, 4 H), 3.97 (s, 6 H).

^{13}C NMR: δ = 159.0, 136.7, 132.4, 131.1, 130.3, 127.0, 124.9, 113.9, 55.4.

MS (EI): *m*/*z* = 391 $[M + H]^+$.

9,10-Bis[4-(diethylamino)phenyl]anthracene (7c)

Pale yellow solid; yield: 144 mg (61%); mp >250 °C.

IR (KBr): 2972, 1606, 1518 cm^{-1}.

^1H NMR: δ = 7.89–7.87 (m, 4 H), 7.33–7.30 (m, 8 H), 6.90 (d, *J* = 8.8 Hz, 4 H), 3.50 (q, *J* = 7.2 Hz, 8 H), 1.30 (t, *J* = 7.2 Hz, 12 H).

^{13}C NMR: δ = 147.0, 137.2, 132.3, 130.5, 127.4, 125.6, 124.5, 111.4, 44.4, 12.8.

MS (EI): *m*/*z* = 473 $[M + H]^+$.

Anal. Calcd for $C_{34}H_{36}N_2$: C, 86.40; H, 7.68; N, 5.93. Found: C, 86.22; H, 7.61; N, 6.03.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are characterization data and copies of the ^1H and ^{13}C NMR spectra for all products, as well as crystallographic data for compound **2f**.

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(18) The crystal data of compound **2f** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 911781. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk] or via www.ccdc.cam.ac.uk/data_request/cif. Unit cell parameters: a = 16.397(2) Å, b = 9.4410(13) Å, c = 26.943(4) Å, α = 90°, β = 94.170(2)°, γ = 90°, space group P21/c.
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