Unsymmetrically Substituted 2,7-Dimethyl-1,8-diarylanthracenes[1]

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A synthesis has been developed for 2,7-dimethyl-1,8-di-*o*-tolylanthracene **4**. The cis **4a** and trans **4b** isomers of this hydrocarbon can be separated and are stable to interconversion at temperatures below 200 °C. The two enantiomers of the trans isomer **4b** have chiral cavities and are expected to be useful precursors for chiral reagents or chiral catalysts.

Our earlier study of molecules that might serve as catalysts or reagents for chiral syntheses led us to prepare[2] 1,8-di-*o*-tolylanthracene (**1a**, Chart I), 1,8-bis(2,3-dimethylphenyl)anthracene (**1b**), and several derivatives of these compounds. We were surprised to find that the energy barriers to interconversion of the symmetric cis isomers **2a** and the asymmetric trans isomers **2b** of these compounds **1** were rather low (10–16 kcal/mol, the isomers interconverted slowly at room temperature). The reason for these low interconversion barriers was revealed by X-ray crystal structures that showed a substantial splaying or outward bending of the two substituted phenyl rings which diminished the barrier to rotation of these rings. Since any practical reagents for chiral synthesis would have to be stable to interconversion at temperatures of at least 100 °C, we concluded that the most practical way to increase the interconversion energy barrier for these molecules would be by the addition of additional substituents at positions 2 and 7 on the anthracene ring. This paper describes our preparation of two 2,7-dimethyl-1,8-diarylanthracene derivatives **3** and **4**; the derivative **4** has the desired thermal stability to cis–trans interconversion.

Following a synthetic plan used previously[2] for various 1,8-diarylanthracenes, the required starting material for the dimethyldiarylanthracenes **3** and **4** was the dichloride **5** (Chart II) which we expected[2] to prepare by reduction of the corresponding dichloro quinone **6**. Although the dichloro quinone **6** was reported[3] to be produced in unstated yield by chlorination of the quinone **7**, our subsequent study revealed that the melting point of the pure dichloro quinone **6** did not correspond well with the melting point reported earlier, suggesting that the product reported earlier was not pure. To obtain the starting anthraquinone **7**, we examined several procedures including an Elbs reaction with the benzophenone **8**[4] or a Friedel–Crafts reaction of toluene with methylene chloride[5] to form the anthracene **9** among other products. The quinone **7** could be obtained by oxidation of the anthracene **9** with chromic acid. Our preferred route involved a Diels–Alder reaction of the naphthoquinone **10** with isoprene followed by aromatization of the crude adducts to form a 1:1 mixture of the desired quinone **7** and the higher melting isomer **11**. Extraction of the mixture with a limited volume of acetone separated a soluble fraction enriched in quinone **7** from a residual fraction enriched in quinone **11**. Fractional recrystallization of these enriched fractions afforded each pure quinone. Direct chlorination of each quinone **7** or **11** in sulfuric acid solution afforded mixtures of chlorinated products from which separation of the pure dichloro quinones **6** and **12** was tedious. A more satisfactory route to the dichloro quinone **6** involved nitration of the quinone **7** to form the crude dinitro product **13**;[6] reduction of the

Chart I

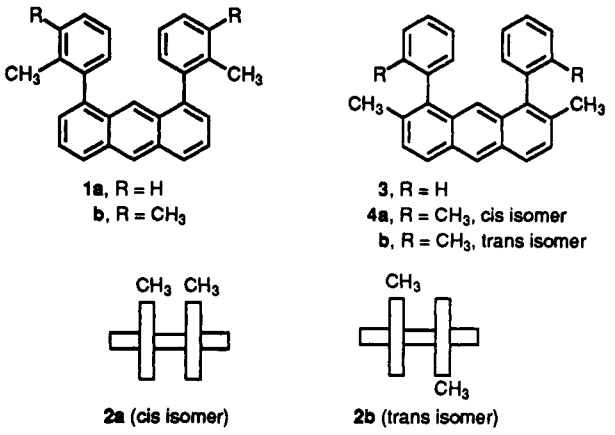
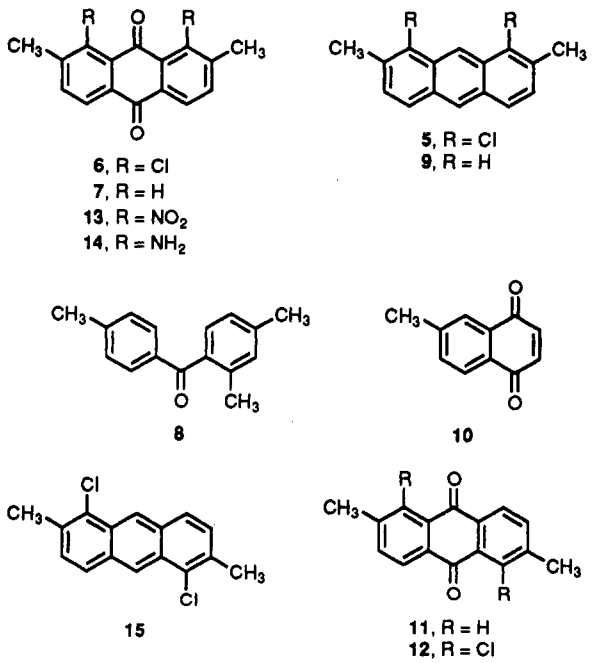


Chart II



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(3) Scholl, R.; Ziegs, K. *Ber.* **1934**, *67*, 1746.

(4) Morgan, G. T.; Coulson, E. A. *J. Chem. Soc.* **1929**, 2203.

(5) Lavaux, J. *Compt. Rend.* **1905**, *140*, 44.

(6) Mayer, F.; Gunther, H. *Ber.* **1930**, *63*, 1455.

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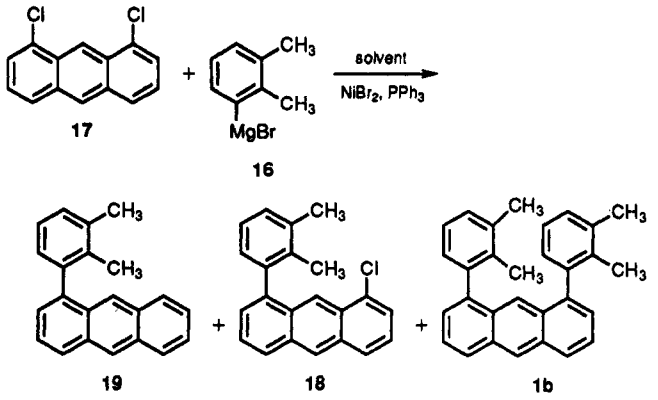
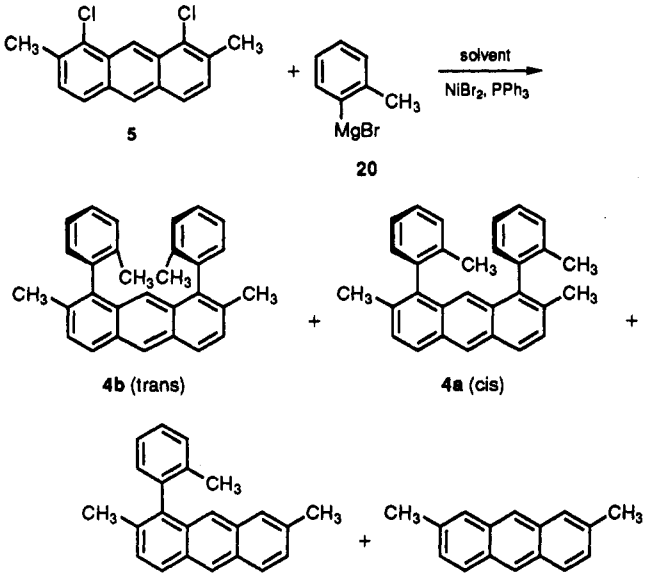
Scheme I



conditions	result
THF–xylene, reflux, 109 °C or xylene (THF removed), reflux, 140 °C	complete within 4 min
THF–xylene, rt	29% of dichloride 17 remained after 3.5 h
THF–xylene, rt, iodine (0.5 equiv)	<1% of dichloride 17 remained after 3.5 h

Scheme II



conditions	ratio of anthracenes (9:21:4)
THF–xylene, reflux, 109 °C, 14 h	1.00:2.53:0.44
THF–xylene, iodine (0.5 equiv), 65 °C, 24 h	1.00:3.23:0.71
THF–xylene, iodine (0.5 equiv), 110 °C, 20 h	1.00:5.65:4.75
xylene (THF removed), iodine (0.5 equiv), 138–140 °C, 30 h	1.00:12.5:18.6

crude dinitro compound **13** and use of a Sandmeyer reaction with the crude diamine **14**[6] afforded the dichloro quinone **6** which was rather easily isolated and purified.

Our efforts to convert the dichloro quinone **6** to the anthracene **5** by the previously used[2] direct reduction with excess zinc in aqueous ammonia were complicated by apparent partial overreduction which cleaved one or both C–Cl bonds. Consequently, we used a milder reduction procedure employing zinc in a two-phase solvent system (aqueous ammonia and benzene). The crude product was then treated with $NaBH_4$ to complete the reduction of any residual anthrone. Acidification of the crude product gave the desired anthracene **5**. The most satisfactory method we found for the reduction of the isomeric quinone **12** involved two successive cycles of $NaBH_4$ reduction followed by acidification to form the anthracene **15**.

The previously reported[2] diarylanthracenes **1** were obtained in good yield (83–86%) by the coupling of 1,8-dichloroanthracene (**17**, Scheme I) with the appropriate arylmagnesium bromide in boiling THF in the presence of the catalyst prepared from $Ni(acac)_2$ and Ph_3P (a ligand for Ni). A comparable reaction of the dichloride **5** with PhMgBr in refluxing THF in the presence of $NiBr_2$[7] and Ph_3P produced the diphenyl derivative **3** in 42% yield accompanied by other unidentified byproducts. However, our efforts to effect a similar Ni-catalyzed coupling of the dichloride **5** with the more sterically congested (2,3-dimethylphenyl)magnesium bromide (**16**) failed to form any significant amount of the corresponding diarylanthracene even when the coupling was attempted at higher temperatures with THF–toluene or THF–xylene mixtures.[8] Mass spectra of the three major products found in these trial reactions suggested that the products were 1-chloro-2,7-dimethylanthracene, 1-*o*-xylyl-2,7-dimethylanthracene, and 1-chloro-8-*o*-xylyl-2,7-dimethylanthracene.

To explore the effect of conditions on the rate of these Ni-catalyzed reactions, we studied the known[2] coupling of 1,8-dichloroanthracene (**17**, Scheme I) with the aryl Grignard reagent **16** to form mixtures containing varying amounts of the unchanged dichloride **17**, the diaryl product **1b**, and the intermediate coupling products **18** and **19**. As summarized in Scheme I, this coupling reaction was rapid at elevated temperatures (109–140 °C) and was accelerated at rt by the addition of 0.5 equiv of iodine (which we presume was promptly reduced to iodide ion in the reaction mixture). Although iodide ion has been reported to catalyze the cross-coupling reaction of two aryl halides in the presence of Ni or Zn dust,[9] we are unaware of previous reports that iodide ion catalyzes the Ni-catalyzed coupling of aryl halides with Grignard reagents. We also explored two other catalysts, $NiCl_2(dppp)$[10a] and $PdCl_2(dppf)$,[10b] but found our $NiBr_2$–Ph_3P catalyst system to be more effective.

These observations were supported by a related product study from reaction of the dichloride **5** with *o*-tolylmagnesium bromide (**20**, Scheme II) to form the diaryl product **4** accompanied by products **9** and **21** from intermediates in the coupling reaction. The data tabulated in Scheme II were obtained by running each reaction until periodic sampling revealed no further change in product composition. The best yield (26% isolated) of the diarylan-

(7) We replaced $Ni(acac)_2$ with $NiBr_2$ because of the ease of obtaining $NiBr_2$ in anhydrous form.

(8) These modifications were suggested by an earlier publication: Puckette, T. A. U.S. Patent 4912276, Mar 27, 1990.

(9) (a) Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, *47*, 4089. (b) Takagi, K.; Hayama, N.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3691. (c) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627. (d) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubere, P. *Ibid.* **1989**, *54*, 4840, 4844. (e) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80 and references therein.

(10) (a) The symbol dppp is an abbreviation for 1,3-bis(diphenylphosphino)propane; for examples using this ligand in cross-coupling reactions, see: Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347. (b) The symbol dppf is an abbreviation for 1,1′-bis(diphenylphosphino)ferrocene; for examples of its use as a ligand in cross-coupling reactions, see: Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, *21*, 1871.

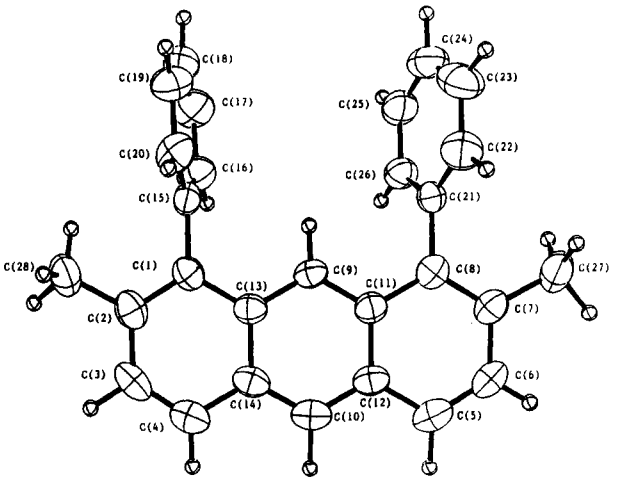


Figure 1. Perspective view of the molecular structure of 2,7-dimethyl-1,8-diphenylanthracene.

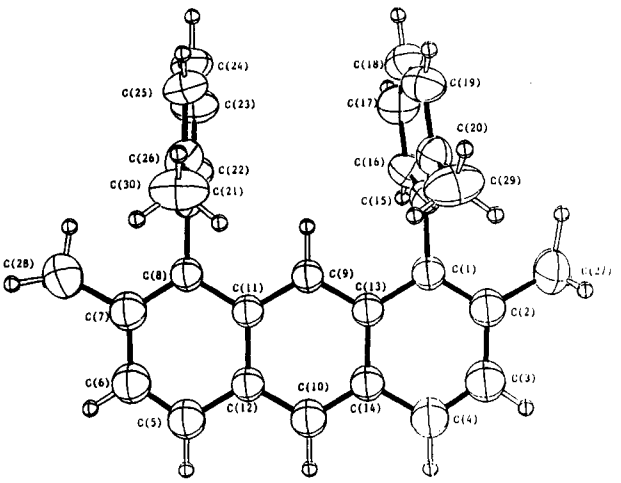


Figure 2. Perspective view of the molecular structure of cis 2,7-dimethyl-1,8-di-*o*-tolylanthracene.

thracene **4** (a mixture of cis and trans isomers) was obtained from a reaction run in refluxing xylene (140 °C) with added I_2 as a catalyst. The principal byproducts **9** and **21** corresponded to reductive cleavage of both C–Cl bonds in the starting dichloride **5** or one C–Cl in the intermediate monocoupled product (analogous to intermediate **18**). The monoaryl byproduct **21** may also be formed by coupling of the Grignard reagent **20** with the partially reduced monochloranthracene formed from dichloride **5**. We presume that these apparent C–Cl bond reductive cleavages are actually the result of forming anthrylnickel(II) intermediates[11] that undergo C–Ni bond homolysis followed by H atom abstraction rather than reductive elimination to form coupled products. Apparently the sterically congested molecules involved in this study require relatively high temperatures to overcome the activation barrier for reductive elimination to form a coupled product. A few exploratory experiments suggested that use of reaction temperatures even higher than 140 °C would not improve the yield of coupled products.

The mixture of diarylanthracene isomers **4** was subjected to a combination of fractional recrystallization and preparative HPLC to separate the higher melting cis isomer **4a** from the lower melting trans isomer **4b** (a racemic mixture). Although both isomers were stable at room temperature for prolonged periods, the lower melting trans isomer **4b** (mp 169.8–170.8 °C) underwent slow isomerization at 200 °C with 7% of the cis isomer **4a** having been formed after 30 min. At 300 °C, each isomer was converted to a 1:1 mixture of cis (**4a**) and trans (**4b**) isomers in less than 5 min. This interconversion offers a practical advantage since the achiral cis isomer **4a** formed in the synthesis can be easily converted to a mixture containing 50% of the more useful racemic trans isomer **4b**.

We were successful in obtaining X-ray crystal structures for the diphenyl compound **3** (Figure 1) and the cis di-*o*-tolyl compound **4a** (Figure 2).[22] In both cases, it is noted that the aryl rings at positions 1 and 8 are either approximately parallel or are bent inward slightly unlike the diarylanthracenes **1** studied earlier.[2] A quantitative measure of this distortion is provided by the distance between the 4 positions of the phenyl rings in several materials. The calculated distance, assuming no distortion, is 5.0 Å for all compounds. The actual distance for the relatively uncongested 10-bromo-1,8-diphenylanthracene[2b] is 5.485 Å and the corresponding distance for 9-acetoxy-1,8-di-*o*-xylylanthracene[2a] is 6.833 Å. In the series with methyl groups at positions 2 and 7, the distance for the diphenyl derivative **3** is 5.081 Å and the corresponding distance for the cis di-*o*-tolyl compound **4a** is 4.388 Å, corresponding to the two aryl rings being bent slightly toward one another.

In conclusion, we believe that the trans di-*o*-tolyl compound **4b** possesses properties that recommend it as a desirable precursor for chiral reagents or chiral catalysts. The geometry of the material is well defined and the compound possesses sufficient thermal and chemical stability to be utilized in a number of reaction sequences. Thus, we hope that derivatives of this material will find use in future chiral syntheses.

Experimental Section[12]

Preparation of 2,7-Dimethylanthracene (9) by Pyrolysis of the Trimethylbenzophenone 8. Using modifications of previous procedures,[4] 24.7 g (233 mmol, 3 equiv) of *m*-xylene in 120 mL of CH_2Cl_2 was acylated with 12.0 g (77.6 mmol) of *p*-toluoyl chloride and 12.4 g (93.0 mmol, 1.2 equiv) of $AlCl_3$. The crude neutral product, isolated in the usual way, was distilled twice to separate 11.5 g (66%) of the benzophenone **8** as a colorless liquid: bp 138.5–140.8 °C (1 mm), n^{25}_D 1.5850 [lit.[4] bp 169 °C (4 mm)]; IR (CCl_4) 1662 cm^{-1} (conjugated C=O); ^1H NMR (300 MHz,

(11) For a review of the coupling procedure, see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340–348.

(12) All melting points are corrected and all boiling points are uncorrected. Magnesium sulfate was employed as drying agent unless stated otherwise. Room temperature (rt) is meant to indicate approximately 25 °C. The IR spectra were determined using a Nicolet 520 FT-IR spectrometer. The ^1H NMR spectra were determined at 300 MHz with a Varian Gemini-300 spectrometer. The ^{13}C NMR spectra were determined at 75.5 MHz with a Varian Gemini-300 or at 100.5 MHz with a Varian XL-400 spectrometer. The NMR chemical shift values are expressed in ppm (δ values) relative to a Me_4Si internal standard. The mass spectra were determined using a VG Analytical 70SE instrument. The UV spectra were measured using a Beckman Model 25 or a Gilford Response UV–vis (single beam) spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. All reactions involving organometallic reagents or intermediates were performed under a nitrogen atmosphere. Analytical scale HPLC was performed using a 0.46 × 25 cm column packed with 10-μm silica gel with an eluent flow rate of 2.0 mL/min unless stated othewise. Column chromatography was performed on a low-pressure pump system employing 25 mm × 1.0 m Altex columns (with 15 or 25 × 0.25 m guard columns) packed with 40-μm silica gel (10 mL/min flow rate); eluent compositions are reported elsewhere as appropriate. For further details of this method of chromatography, see: Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2247.

$CDCl_3$) δ 7.70 (2 H, d, J = 8.18 Hz), 7.22 (2 H, d, J = ca. 7.6 Hz), 7.10 (1 H, s), 7.04 (2 H, d, J = ca. 7.7 Hz); mass spectrum, m/e (relative intensity) 225 (4), 224 (19, M^+), 223 (26), 210 (22), 209 (100), 208 (9), 194 (9), 165 (10), 133 (18). A 3.1-g (13.8 mmol) sample of the trimethylbenzophenone **8** was degassed with N_2 and then heated under reflux (N_2 atmosphere) for 30.5 h at 400–450 °C. The resulting black residue (1.9 g) was recrystallized from hexane–benzene to provide 0.56 g (20%) of the anthracene **9** as yellow plates, mp 239–241 °C. Recrystallization from benzene provided the pure anthracene **9** as pale yellow plates, mp 241–242 °C (lit.[4] mp 241 °C); IR (CCl_4), no absorptions in the 3- or 6-μm regions corresponding to OH or C=O; ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (1 H, s), 8.20 (1 H, s), 7.89 (2 H, d, J = ca. 8.5 Hz), 7.72 (2 H, s), 7.27 (2 H, dd, J = ca. 8.8 and 1.77 Hz), 2.54 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$) 135.0, 132.4, 130.1, 128.2, 128.0, 126.5, 125.8, 124.3, 21.78 ppm; mass spectrum, m/e (relative intensity) 207 (19), 206 (100, M^+), 205 (21), 202 (6), 191 (15), 190 (6), 189 (16).

A sample (0.71 g of 3.4 mmol) of 2,7-dimethylanthracene (**9**) was oxidized with 0.95 g (9.5 mmol, 2.8 equiv) of CrO_3 in 65 mL of HOAc during 40 min. The crude, neutral product (0.72 g or 89% of yellow solid, mp 155–164 °C) was recrystallized twice from 95% EtOH and twice from hexane to provide a sample of the anthraquinone **7** as yellow needles, mp 168–169 °C (lit.[4] mp 170 °C), with spectral data corresponding to those described subsequently. Attempts to convert the benzophenone **8** to the anthracene **9** by passing the ketone through a hot (550 °C) tube or by photolysis with a Srinavasan UV reactor were not successful. A study of the photolysis of 2-methylbenzophenone by Wilson and co-workers[13] reveals why the photochemical reaction failed.

Preparation of the 2,6- and 2,7-Dimethylanthraquinones (7 and 11). Adapting a literature[14] procedure, reaction of 66.9 g (619 mmol) of p-benzoquinone with 43.9 g (645 mmol) of freshly distilled isoprene in 190 mL of HOAc for 2 d afforded a solution of the crude Diels–Alder adduct that was aromatized by reaction with 140 g (1.4 mol) of CrO_3 in aqueous HOAc at 70 °C. The crude neutral product was crystallized from hexane to separate 56.3 g (53%) of the naphthoquinone **10** as bright yellow prisms, mp 89–90 °C (lit.[14] mp 90 °C) as well as 8.10 g of less pure quinone **10**, mp 86.5–89 °C (total yield 64.4 g or 61%): IR (CCl_4) 1671 cm^{-1} (conjugated C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (1 H, d, J = ca. 7.9 Hz, aryl CH), 7.89 (1 H, s, aryl CH), 7.56 (1 H, dd, J = 1.37 and ca 8.9 Hz, aryl CH), 6.95 (2 H, s, vinyl CH), 2.51 (3 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT [attached proton test] experiment), 185.5 (s), 185.1 (s), 145.2 (s), 138.8 (d), 138.5 (d), 134.7 (d), 131.8 (s), 129.7 (s), 126.8 (d), 126.6 (d), 21.52 ppm (q); mass spectrum, m/e (relative intensity) 174 (4), 173 (22), 172 (100, M^+), 157 (17), 145 (10), 144 (49), 119 (10), 118 (54), 117 (8), 116 (47), 115 (42); UV maxima, nm (95% EtOH, ε), 343 (3430), 260 (shoulder, 18 600), 285 (20 800).

A solution of 12.6 g (73.3 mmol) of 6-methylnaphthoquinone (**10**) and 20.2 g (297 mmol, 4.05 equiv) of freshly distilled isoprene in 50 mL of HOAc was stirred at rt in a tightly stoppered flask for 2 d. After the unchanged isoprene had been removed with a rotary evaporator, the residual brown mixture was partitioned between H_2O and CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave a brown oil which crystallized on standing. A solution of the residual tan solid (16.3 g) in CH_2Cl_2 was filtered through a bed of silica gel to remove polar impurities and then concentrated to leave the crude tetrahydroanthraquinone adducts as a yellow solid (15.7 g or 89%, mp 76–83 °C). A sample (67.6 g, 281 mmol) of the crude mixture of tetrahydroanthraquinones in 900 mL of 95% EtOH was stirred while a stream of air was passed through the mixture. A 5% solution (550 mL) of KOH in EtOH was added during 30 min and treatment with air was continued for 3.5 h, during which time the mixture gradually changed from black to orange in color. The mixture was diluted with H_2O and acidified to pH 4–5 with HCl, and the resulting precipitate was collected, washed with H_2O, and allowed to dry. The mixture amounted to 63.0 g (95%) of a pale yellow solid, mp 175–228 °C, and contained approximately equal amounts of the isomeric anthraquinones **7** and **11**. The relative amounts of the isomers **7** and **11** in mixtures were determined by quantitative ^{13}C NMR analysis employing $Cr(acac)_3$ (ca. 5 mg/mL of solution) as a paramagnetic relaxation reagent with the spectrometer set for inverse gated decoupling, a 10-s delay between pulses, and a 48.9 ° pulse angle. The areas of peaks at 183.9 (2,7-isomer **7**), 183.6 (2,6-isomer **11**), and 183.1 ppm (2,7-isomer **7**) were used to calculate the relative amounts of the isomers present. The relaxation times associated with these peaks (determined by an inverse recovery T_1 experiment in $CDCl_3$) are as follows: 183.9 (34.8 s), 183.6 (28.4 s), 183.1 ppm (28.1 s).

After a mixture containing approximately equal amounts of the 2,6- and 2,7-dimethylanthraquinones **7** and **11** (64.9 g) had been finely powdered and treated with 1900 mL of acetone, the mixture was stirred for 20 min and then filtered. Concentration of the acetone extract left 27.9 g of yellow solid, mp 159–163 °C, which contained 88% of the 2,7-isomer **7**. This material was recrystallized from an acetone–hexane mixture (1:1 v/v, ca. 1700 mL) with seeding to provide 9.51 g of yellow needles, mp 162–164.5 °C (92% 2,7-isomer **7**). Concentration of the mother liquor and extraction of the residual yellow solid with acetone left 12.1 g of yellow needles, mp 159–162 °C (91% 2,7-isomer **7**). Recrystallization once from acetone–hexane (1:1 v/v), once from EtOH, and twice from hexane provided the pure 2,7-isomer **7** as yellow needles, mp 168.5–169.7 °C (lit. mp 170 °C,[4] 169 °C,[15] 162 °C[6]): IR (CCl_4) 1675 cm^{-1} (conjugated C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (2 H, d, J = ca. 7.9 Hz, aryl CH), 8.09 (2 H, s, aryl CH), 7.58 (2 H, d, J = ca. 8.5 Hz, aryl CH), 2.53 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 183.9 (1 C, s), 183.1 (1 C, s), 145.2 (2 C, s), 135.0 (2 C, d), 133.6 (2 C, s), 131.5 (2 C, s), 127.5 (2 C, d), 127.4 (2 C, d), 21.6 ppm (2 C, q); mass spectrum, m/e (relative intensity) 237 (27), 236 (100, M^+), 235 (13), 221 (28), 208 (43), 207 (13), 193 (12), 179 (17), 178 (20), 165 (49); UV maxima, nm (95% EtOH, ε), 331 (3680), 280 (shoulder, 11 700), 260 (40 700).

The residual yellow solid (35.9 g, mp 220–229 °C) from the initial acetone extraction was again extracted with 1400 mL of acetone to leave 28.6 g of residual yellow solid, mp 230–239 °C, containing none of the 2,7-isomer **7** (^{13}C NMR analysis). A 1.0-g portion of this material was recrystallized from a mixture of acetone–hexane (1:1 v/v) to provide 0.60 g of the quinone **11** as bright yellow needles, mp 239.4–242.6 °C. An additional recrystallization raised the melting point to 240.0–242.7 °C (lit. mp 242 °C,[4] 237–238 °C,[15] or 236–237 °C[6]): IR (CCl_4) 1675 cm^{-1} (conjugated C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (2 H, d, J = ca. 7.9 Hz, aryl CH), 8.08 (2 H, s, aryl CH), 7.57 (2 H, d, J = ca. 7.7 Hz, aryl CH), 2.52 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 183.6 (1 C, s), 145.4 (2 C, s), 134.9 (2 C, d), 133.6 (2 C, s), 131.5 (2 C, s), 127.6 (2 C, d), 127.5 (2 C, d), 21.7 ppm (2 C, q); mass spectrum, m/e (relative intensity) 237 (17), 236 (100, M^+), 221 (26), 208 (28), 207 (10), 193 (9), 179 (15), 178 (17), 165 (43); UV maxima, nm (95% EtOH, ε), 333 (5480), 283 (16 100), 261 (45 800).

Preparation of 1,8-Dichloro-2,7-dimethylanthraquinone (6) by Direct Chlorination. This procedure is a modification of a previous report[3] where no I_2 was added since this additive showed no catalytic activity and gave a more complex product mixture. The experiment used 2,7-dimethylanthraquinone (**7**) that contained 5% of the isomeric 2,6-dimethylanthraquinone (**11**) as an impurity. A red solution of 0.74 g (3.1 mmol) of the quinone **7** in 15 mL of concd H_2SO_4 was heated, with stirring, to 110–120 °C and Cl_2 was passed through the reaction mixture. After 16 h, the quinone **7** was almost completely consumed (HPLC analysis, 4.5% EtOAc–hexane). The red mixture was cooled, diluted with ice–water, and extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 0.94 g of yellow solid, mp 150–160 °C, containing the dichloro quinone **6** (t_R = 9.08 min) as approximately 39% of the total material (uncorrected HPLC peak areas). The observed impurities, believed to contain chlorine, had HPLC retention times (uncorrected peak areas as a percent of total) of 4.44 (24%), 6.18 (6%), 6.72 (12%), and 7.27 min (13%).

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Chromatography (4.5% EtOAc–hexane) of the crude product separated 255 mg (27%) of the quinone **6** as a yellow solid, mp 207–209 °C. Recrystallization from acetone–hexane (1:1 v/v) and then from EtOH afforded the pure quinone **6** as yellow needles, mp 209.3–211.4 °C (lit.[3] mp 196–197 °C, apparently impure): IR (CCl_4) 1691 (quinone C=O), 1676 cm^{-1} (quinone C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (2 H, d, J = 8.00 Hz, aryl H), 7.59 (2 H, d, J = 7.69 Hz, aryl H), 2.56 (6 H, s, methyl); ^{13}C NMR [$CDCl_3$, multiplicity determined by an APT experiment using 5 mg of $Cr(acac)_3$ per 1 mL of solution as a relaxation reagent to decrease the acquisition time] 183.23 (1 C, s), 181.95 (1 C, s), 145.67 (2 C, s), 134.90 (2 C, d), 133.83 (2 C, s), 133.17 (2 C, s), 133.02 (2 C, s), 125.26 (2 C, d), 21.35 ppm (2 C, q); mass spectrum, m/e (relative intensity) 307 (18), 306 (72), 305 (31), 304 (100, M^+), 289 (17), 276 (43), 269 (40), 241 (48), 213 (27), 176 (38); UV maxima, nm (95% EtOH, ϵ), 267 (35 400), 347 (5870).

Anal. Calcd for $C_{16}H_{10}Cl_2O_2$: C, 62.97; H, 3.31; Cl, 23.23. Found: C, 62.79; H, 3.29; Cl, 23.08.

Preparation of 2,7-Dimethyl-1,8-dichloroanthraquinone (6) via the Dinitro Compound 13 and the Diamino Compound 14. The following reactions, based on known procedures,[6] used 2,7-dimethyl quinone sample **7** containing 5% of the 2,6-isomer **11** as an impurity. A stirred, cold (2–5 °C) solution of 4.5 g (19 mmol) of the quinone **7** in 115 mL of concd H_2SO_4 was treated with a solution of 4.6 g of HNO_3 in 5 mL of concd H_2SO_4. After 0.5 h, the solution was allowed to warm to rt during 6 h and then poured into 600 mL of ice–water. The precipitate was collected, washed with water, and dried to leave 6.2 g (100%) of the crude quinone **13** as a pale yellow solid, mp 267–300 °C (lit.[6] mp > 360 °C). A solution of 6.2 g (19 mmol) of the crude dinitroanthraquinone **13** and 19.5 g (75.5 mmol, 4 equiv) of $Na_2S{\cdot}9H_2O$ in 100 mL of EtOH and 400 mL of water was refluxed for 8 h (the mixture turned red soon after the addition of the Na_2S) and then cooled and poured into ice–water. The red precipitate was collected, washed with water, and dried to leave 4.7 g (93%) of the crude diaminoquinone **14**, a red solid, mp 200–210 °C (lit.[6] mp 271 °C). Following a modification of an earlier procedure,[3] a suspension of 1.2 g (4.5 mmol) of the crude diaminoanthraquinone **14** in 80 mL of aqueous 23% HCl was cooled to 15 °C and an aqueous solution of 0.75 g (11 mmol, 2.4 equiv) of $NaNO_2$ was added with stirring during 0.5 h while the temperature was kept at 14–18 °C. The resulting brown solution was added, with stirring during 1 h, to a cold (5 °C) solution of 1.9 g (19 mmol, 4.2 equiv) of CuCl[16] in 60 mL of aqueous 23% HCl while maintaining the reaction mixture at 5–10 °C. After the addition was complete, the reaction mixture was heated on a steam bath for 0.5 h and then cooled and extracted with CH_2Cl_2. The organic layer was washed successively with aqueous 5% NaOH and aqueous NaCl and then dried and concentrated to leave 1.26 g of red-brown solid, mp 183–188 °C, containing about 69% of the dichloroquinone **6** (t_R = 7.44 min, HPLC analysis). The major observed byproducts, believed to contain chlorine, had HPLC retention times (uncorrected peak area as a percent of total) of 3.80 (8%), 5.55 (12%), and 15.7 min (9%). The crude product was chromatographed (2% EtOAc–hexane) to provide 0.60 g (43%) of the pure quinone **6** as yellow needles, mp 209–211 °C (lit.[4] mp 196–197 °C, apparently impure). The spectral properties of product **6** correspond to those of the previously described sample prepared by direct chlorination.

Preparation of 1,5-Dichloro-2,6-dimethylanthraquinone (12). The following reaction is a modification of a published procedure[17] in which no I_2 was added to the reaction mixture. A mixture of 2.82 g (11.9 mmol) of 2,6-dimethylanthraquinone (**11**) and 40 mL of concd H_2SO_4 was heated to 110–115 °C, and Cl_2 was passed through the dark red reaction mixture for 9 h at which time HPLC analysis (4.5% EtOAc–hexane) indicated the quinone **11** to be almost completely consumed. After the mixture had been cooled, poured into ice–water, and extracted with CH_2Cl_2, the organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 3.34 g of yellow solid, mp 180.5–262.5 °C. Recrystallization from $CHCl_3$–hexane (5:1 v/v) and then from acetone–hexane (1:1 v/v) afforded 0.48 g (13%) of the pure dichloro quinone **12** as yellow needles, mp 311–314 °C (lit.[17] mp 295 °C, apparently impure): IR (Nujol mull) 1670 cm^{-1} (conjugated C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (2 H, d, J = ca. 8 Hz, aryl CH), 7.66 (2 H, d, J = ca. 8 Hz, aryl CH), 2.56 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment), 182.0 (2 C, s), 145.3 (2 C, s), 135.8 (2 C, d), 135.7 (2 C, s), 134.3 (2 C, s), 129.5 (2 C, s), 126.4 (2 C, d), 21.8 ppm (2 C, q); mass spectrum, m/e (relative intensity) 308 (12), 307 (12), 306 (66), 305 (21), 304 (100, M^+), 291 (12), 289 (20), 279 (4), 278 (20), 277 (9), 276 (30), 271 (9), 269 (27), 243 (12), 241 (34), 215 (7), 213 (22); UV maxima, nm (95% EtOH, ϵ), 349 (5680), 264 (35 000).

Anal. Calcd for $C_{16}H_{10}Cl_2O_2$: C, 62.97; H, 3.31; Cl, 23.23. Found: C, 62.78; H, 3.36; Cl, 23.12.

Preparation of 1,8-Dichloro-2,7-dimethylanthracene (5). To a stirred solution of 0.23 g (0.75 mmol) of the dichloroanthraquinone **6** in 20 mL of benzene, 10 mL of water, and 90 mL of aqueous 28% ammonia was added 1.0 g (15 mmol, 20 equiv) of Zn dust during 20 min (color changed from yellow to red). The mixture was then refluxed, with vigorous stirring, for 2.5 h at which time reaction of the quinone **6** was complete (HPLC analysis, 4.5% EtOAc–hexane). The hot mixture was filtered and the residual Zn metal and salts were washed with boiling CH_2Cl_2. The filtrate was diluted with 150 mL of water and extracted with CH_2Cl_2. The combined organic layers were dried and concentrated to leave 0.2 g of tan solid, mp 136–185.5 °C. A solution of this crude intermediate in 35 mL of *i*-PrOH was treated with 0.15 g (4.0 mmol) of $NaBH_4$, and the resulting orange mixture was refluxed for 2.5 h. The refluxing mixture was treated with 2.5 mL of concd HCl and reflux was continued for 1 h. After the mixture had been cooled, it was partitioned between H_2O and CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 0.19 g (90%) of the crude anthracene **5** as a yellow solid, mp 162.2–168.3 °C (97% pure by HPLC analysis, 4.5% EtOAc–hexane). A sample of the pure anthracene **5**, mp 179.8–180.8 °C, was obtained as yellow needles by chromatography (EtOAc–hexane eluent, 3:97 v/v) followed by recrystallization from *i*-PrOH and then from acetone–hexane (1:1 v/v): IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 9.19 (1 H, s, aryl CH), 8.29 (1 H, s, aryl CH), 7.78 (2 H, d, J = 8.67 Hz, aryl CH), 7.30 (2 H, d, J = 8.73 Hz, aryl CH), 2.61 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 133.45 (2 C, s), 131.01 (2 C, s), 130.70 (2 C, s), 130.18 (2 C, s), 129.03 (d), 127.16 (d), 126.61 (d), 119.92 (d), 20.88 ppm (2 C, q); mass spectrum, m/e (relative intensity) 278 (15), 277 (16), 276 (71), 275 (28), 274 (100, M^+), 241 (12), 240 (8), 239 (35), 204 (7), 203 (19), 202 (19), 189 (9); UV maxima, nm (95% EtOH, ϵ), 391 (3770), 373 (5020), 352 (3820), 339 (2380), 322 (shoulder, 1430), 264 (127 000).

Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40; Cl, 25.77. Found: C, 69.57; H, 4.35; Cl, 26.05.

Preparation of 1,5-Dichloro-2,6-dimethylanthracene (15). A suspension of 1.25 g (4.1 mmol) of 1,5-dichloro-2,6-dimethylanthraquinone (**12**) in 175 mL of *i*-PrOh was treated with 0.90 g (24 mmol, 5.8 equiv) of $NaBH_4$. After the mixture had been refluxed for 2.5 h, an additional 0.45 g (12 mmol, 2.9 equiv) of $NaBH_4$ was added and reflux was continued for 1.5 h. Then 12 mL of concd HCl was added and the resulting mixture was refluxed 1 h, cooled, and partitioned between H_2O and CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 1.0 g of yellow solid, mp 203–214.2 °C. The crude intermediate in 175 mL of refluxing *i*-PrOH was again treated with 1.2-g (32 mmol) and 0.60-g (16 mmol) portions of $NaBH_4$. Then 12 mL of concd HCl was added and the mixture was worked up as before to provide 1.0 g (88%) of the crude dichloroanthracene **15** as a yellow solid, mp 196–208 °C. Successive recrystallizations from hexane and from EtOH provided the pure anthracene **15** as yellow needles, mp 213.2–214.7 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (2 H, s, aryl CH), 7.88 (2 H, d, J = 8.60 Hz, aryl CH), 7.33 (2 H, d, J = 8.67 Hz, aryl CH), 2.61 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 133.06 (s), 131.79 (s), 129.78 (s), 129.17 (s), 128.97 (d), 127.24 (d), 123.39 (d), 20.90 (q) ppm; mass spectrum, m/e (relative intensity) 278

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(11), 277 (12), 276 (66), 275 (21), 274 (100, M^+), 241 (10), 240 (6), 239 (30), 204 (6), 203 (17), 202 (17), 200 (7), 189 (9); UV maxima, nm (95% EtOH, ϵ), 392 (5500), 370 (6220), 358 (5060), 342 (3100), 322 (1500, shoulder), 266 (197 000), 233 (7225, shoulder).

Anal. Calcd for $C_{16}H_{12}Cl_2$: C, 69.83; H, 4.40; Cl, 25.77. Found: C, 69.73; H, 4.41; Cl, 25.71.

Preparation of 2,7-Dimethyl-1,8-diphenylanthracene (3). A solution of 0.20 g (0.73 mmol) of the dichloroanthracene **5**, 125 mg (0.11 mmol, 0.15 equiv) of PPh_3, and 25 mg (0.11 mmol, 0.15 equiv) of $NiBr_2$ in 15 mL of dry THF was heated to reflux and 2.5 mL of a THF solution containing 4 mmol (5.5 equiv) of PhMgBr was added during 30 min. The resulting black solution was refluxed for 18 h, cooled, and treated with 30 mL of 6 N HCl. After dilution with H_2O, the mixture was extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, filtered through a short column of silica gel, and concentrated to leave 0.57 g of a yellow semisolid containing (HPLC analysis, hexane) the anthracene **3** (t_R = 14.2 min, ca. 48%) along with unidentified impurities with retention times (uncorrected percent of total) of 4.83 (34%), 6.06 (8.3%), and 8.75 min (9.6%). Silica gel chromatography (hexane) separated 60 mg of the anthracene **3**, mp 233.8–235.4 °C, and 50 mg of the anthracene **3**, mp 231.3–233.4 °C; total yield, 110 mg (42%). Two recrystallizations from acetone–hexane (1:1 v/v) furnished the pure anthracene **3** as pale yellow prisms, mp 234.5–235.7 °C: IR (CCl_4), no OH or C=O absorptions in the 3- or 6-μm regions; ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (1 H, s, aryl CH), 7.91 (2 H, d, J = 8.79 Hz, aryl CH), 7.41 (1 H, s, aryl CH), 7.35 (2 H, d, J = 8.67 Hz, aryl CH), 7.29–7.08 (10 H, m, aryl CH), 2.25 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT) 139.57 (2 C, s), 138.03 (2 C, s), 131.94 (2 C, s), 131.89 (2 C, s), 130.18 (d), 129.89 (2 C, s), 128.79 (d), 128.09 (d), 127.15 (d), 126.84 (d), 125.49 (d), 124.17 (d), 20.58 ppm (2 C, q); mass spectrum, m/e (relative intensity), 359 (34), 358 (100, M^+), 342 (9), 341 (9), 265 (6); UV maxima, nm (95% EtOH, ϵ), 390 (5440), 370 (6760), 351 (5140), 336 (shoulder, 2940), 264 (102 000).

Anal. Calcd for $C_{28}H_{22}$: C, 93.80; H, 6.20. Found: C, 93.79; H, 6.19.

Preparation of a Stock Catalyst Solution. A stock solution of PPh_3 and $NiBr_2$ in xylene (a mixture of isomers) was prepared by adding 2.96 g (11.3 mmol) of PPh_3 and 0.25 g (1.14 mmol) of $NiBr_2$ to 150 mL of benzene. The benzene was removed by distillation at atmospheric pressure (to remove H_2O) and then under reduced pressure. The resulting green solid was dissolved in 700 mL of xylene (distilled from $LiAlH_4$) and the resulting homogeneous green solution was stored under nitrogen.

Study of the Effect of Various Conditions on the Coupling of Dichloroanthracene 17 with *o*-Xylylmagnesium Bromide. Authentic samples of the actual and potential byproducts of this reaction were synthesized by the following procedures. A THF solution of (2,3-dimethylphenyl)magnesium bromide (**16**) was prepared as previously described;[2a] the concentration of the Grignard reagent[18] was 1.30 M. A solution of 0.75 mL (1.0 g, 5.5 mmol) of 3-bromo-1,2-dimethylbenzene, 15 mg (0.069 mmol, 0.01 equiv) of $NiBr_2$, and 100 mg (0.38 mmol, 0.07 equiv) of PPh_3 in 12 mL of dry THF was heated to reflux and 5.0 mL of the THF solution containing 6.5 mmol (1.2 equiv) of the Grignard reagent **16** was added, dropwise and with stirring, during 1 h (the solution gradually turned black). After the reaction mixture had been refluxed overnight, cooled, treated with aqueous 6% HCl, and stirred for 30 min, it was partitioned between H_2O and CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, passed through a short column of silica gel to remove colored byproducts, and concentrated to leave 1.37 g of white solid, mp 94.0–114.6 °C. Recrystallization from EtOH gave 0.95 g (83%) of 2,2′,3,3′-tetramethylbiphenyl as white prisms, mp 118.5–120 °C. A second recrystallization sharpened the melting point to 119–120 °C (lit. mp 115–117 °C,[19] 114–115 °C[20]): IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 6.96–7.16 (6 H, m, aryl CH), 2.33 (6 H, s, methyl), 1.95 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 142.5 (2 C, s), 136.8 (2 C, s), 134.7 (2 C, s), 128.7 (2 C, d), 127.4 (2 C, d), 125.2 (2 C, d), 20.3 (2 C, q), 16.2 ppm (2 C, q); mass spectrum, m/e (relative intensity) 211 (18), 210 (86, M^+), 209 (7), 196 (21), 195 (100), 181 (9), 180 (33), 179 (28), 178 (21), 165 (32); UV maxima, nm (95% EtOH, ϵ), 263 (shoulder, 590), 243 (2700).

Anal. Calcd for $C_{16}H_{18}$: C, 91.36; H, 8.64. Found: C, 91.14; H, 8.63.

A solution of 0.52 g (2.4 mmol) of 1-chloroanthracene in 15 mL of the stock catalyst solution (described above) was heated to 120 °C, and 5.7 mL of a THF solution which contained 8.5 mmol (3.5 equiv) of (2,3-dimethylphenyl)magnesium bromide (**16**) was added, dropwise and with stirring, during 20 s. The black mixture was refluxed for 40 min (HPLC analysis indicated complete reaction within 4 min), cooled, treated with 20 mL of aqueous 6% HCl, and stirred for 20 min. The resulting yellow solution was partitioned between H_2O and CH_2Cl_2 and the organic layer was washed with aqueous $NaHCO_3$, dried, and filtered through a short bed of silica gel. Concentration of the filtrate left 0.84 g of pale yellow solid, mp 110–117 °C. Recrystallization of the crude product from acetone–EtOH (1:1 v/v) afforded the hydrocarbon **19** as yellow prisms in two crops: 0.32 g, mp 125–126 °C and 0.12 g, mp 123–125.5 °C (total yield 0.44 g, 64%). Recrystallization from acetone–EtOH (1:1 v/v) afforded tan prisms of the hydrocarbon **19** for analysis, mp 126–127 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 8.49 (1 H, s, aryl CH), 8.00–8.04 (3 H, m, aryl CH), 7.84 (1 H, d, J = 8.61 Hz, aryl CH), 7.19–7.54 (7 H, m, aryl CH), 2.42 (3 H, s, methyl), 1.95 (3 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 140.7 (1 C, s), 140.6 (1 C, s), 137.2 (1 C, s), 135.8 (1 C, s), 132.0 (1 C, s), 131.9 (1 C, s), 131.6 (1 C, s), 131.0 (1 C, s), 129.4 (1 C, d), 128.7 (1 C, d), 128.5 (1 C, d), 128.1 (1 C, d), 127.8 (1 C, d), 126.7 (1 C, d), 126.2 (1 C, d), 125.6 (1 C, d), 125.42 (1 C, d), 125.36 (1 C, d), 125.3 (1 C, d), 125.1 (1 C, d), 20.42 (1 C, q), 16.65 ppm (1 C, q); mass spectrum, m/e (relative intensity) 283 (32), 282 (100, M^+), 281 (37), 268 (10), 267 (37), 266 (31), 265 (42), 263 (12), 253 (11), 252 (25); UV maxima, nm (95% EtOH, ϵ), 260 (43 320), 319 (1366), 331 (3047), 347 (5691), 362 (8903), 381 (8212).

Anal. Calcd for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.46; H, 6.52.

To a solution of 3.0 g (12 mmol) of 1,8-dichloroanthracene (**17**) in 200 mL of the catalyst stock solution was added, dropwise and with stirring during 30 s, 49.4 mL of a THF solution which contained 74.1 mmol (6 equiv) of (2,3-dimethylphenyl)magnesium bromide (**16**). The red-orange solution was stirred for 3 h and then treated with 60 mL of aqueous 6 M HCl. After being stirred for an additional 0.5 h, the yellow solution was partitioned between H_2O and CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 5.78 g of orange-brown semisolid containing (HPLC analysis, hexane) ca. 50% of the chloroanthracene **18** (t_R = 14.9 min). The major byproducts had retention times of 5.51, 23.1 (one isomer of dixylylanthracene **1b**), 27.8 (one isomer of dixylylanthracene **1b**), and 39.3 min. The crude product was chromatographed (hexane) to provide the anthracene **18** in two fractions: 0.79 of pale yellow solid, mp 90–97.5 °C and 0.42 g of pale yellow semisolid; total yield, 1.2 g (31%). Six recrystallizations from EtOH afforded the pure chloroanthracene **18** as pale yellow prisms, mp 97.5–98.9 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (1 H, s, aryl CH), 8.47 (1 H, s, aryl CH), 8.04 (1 H, d, J = ca. 8.7 Hz, aryl CH), 7.94 (1 H, d, J = ca. 8.2 Hz, aryl CH), 7.21–7.57 (7 H, m, aryl CH), 2.42 (3 H, s, methyl), 1.97 (3 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 141.1 (1 C, s), 139.8 (1 C, s), 137.0 (1 C, s), 135.4 (1 C, s), 132.2 (1 C, s), 132.10 (1 C, s), 132.07 (1 C, s), 131.3 (1 C, s), 129.3 (1 C, d), 129.0 (1 C, s), 128.3 (1 C, d), 127.30 (1 C, d), 127.28 (1 C, d), 127.1 (1 C, d), 126.8 (1 C, d), 125.8 (1 C, d), 125.3 (1 C, d), 125.2 (1 C, d), 124.9 (1 C, d), 122.6 (1 C, d), 20.6 (1 C, q), 17.1 (1 C, q) ppm; mass spectrum, m/e (relative intensity) 319 (11), 318 (44), 317 (36), 316 (100, M^+), 315 (15), 301 (19), 299 (10), 281 (29), 280 (33), 279 (15), 266 (42), 265 (43), 263 (15); UV maxima, nm (95% EtOH, ϵ), 262 (141 000), 322 (shoulder, 1330), 338 (3050), 352 (6390), 373 (9520), 392 (8600).

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Anal. Calcd for $C_{22}H_{17}Cl$: C, 83.39; H, 5.42; Cl, 11.19. Found: C, 83.33; H, 5.47; Cl, 11.09.

The HPLC response factors for dichloroanthracene **17** (0.92), the dixylylanthracenes **1b** (2.36) and the chloroxylylanthracene **18** (1.18) were determined using a UV detector setting of 254 nm and were calculated on the basis of an assigned value of 1.00 for the xylylanthracene **19**. On the basis of these data, the ratio of the chloroxylylanthracene **18** to the 1,8-dixylylanthracenes **1b** in the crude reaction product was 3.4:1.

A solution of 0.15 g (0.62 mmol) of 1,8-dichloroanthracene (**17**) in 8 mL of the stock catalyst solution described above was heated to 120 °C and 2.5 mL of a THF solution which contained 3.7 mmol (6 equiv) of *o*-xylylmagnesium bromide (**16**) was added, dropwise and with stirring, during 30 s. The resulting black solution was refluxed (109 °C), and the reaction progress was monitored by HPLC analysis (hexane) of hydrolyzed aliquots. The dichloroanthracene **17** was completely consumed within 4 min, and the 1,8-dixylylanthracene **1b** and the xylylanthracene **19** were the only observed products. The ratio of the dixylylanthracenes **1b** to the xylylanthracene **19** was 99.4:0.6 (the response factors cited above were employed here and in subsequent calculations). To test the stability of the reagents and intermediates at higher temperatures, the coupling reaction was conducted as described above except the THF was distilled from the reaction mixture as the solution of the Grignard reagent was added. A period of 6 min was required to remove the THF, and a reflux temperature of 140 °C was attained. HPLC analysis of an aliquot removed at this point revealed the same product ratio as reported in the refluxing THF–xylene experiment. The reaction was repeated at rt and additional Grignard reagent (1.2 mL, 2.9 equiv) and stock catalyst solution (2 mL) were added after 6.5 h. Product composition was followed by HPLC analysis (hexane), and after 3.5 h the percentages of anthracenes **1b** and **17–19** were as follows: dichloroanthracene **17** (29%), chloroxylylanthracene **18** (43%), 1-xylylanthracene **19** (3.1%), and dixylylanthracenes **1b** (25%). The experiment was stopped when no further change in product composition was observed (27 h); at this point the dichloroanthracene **17** was not detected and the percentages of products were as follows: xylylanthracene **19** (17%) and dixylylanthracenes **1b** (83%). The room-temperature reaction was repeated as described above except 80 mg (0.32 mmol, 0.5 equiv) of iodine was added immediately before the THF solution of the Grignard reagent was introduced. The resulting red mixture was stirred at rt as above. After 3.5 h the reaction was nearly complete, and the products (HPLC analysis) were dichloroanthracene **17** (0.9%), chloroxylylanthracene **18** (0.9%), xylylanthracene **19** (2.5%), and dixylylanthracenes **1b** (96%).

Preparation of 2,7-Dimethyl-1,8-bis(2-methylphenyl)anthracenes 4. A THF solution of (2-methylphenyl)magnesium bromide (**20**) was prepared from 40.6 g (28.5 mL, 237 mmol) of 2-bromotoluene and 8.65 g (356 mmol, 1.5 equiv) of Mg turnings in 160 mL of dry THF. The concentration of the Grignard reagent[18] was 1.3 M (88% yield). A solution of 2.0 g (7.3 mmol) of the dichloroanthracene **5** in 170 mL of stock catalyst solution (described previously) was heated to reflux, and 0.9 g (3.5 mmol, 0.5 equiv) of iodine in 4 mL of xylene was added followed by the addition of 34 mL of a THF solution which contained 44 mmol (6 equiv) of (2-methylphenyl)magnesium bromide (**20**). The THF was distilled from the resulting black solution, and the reflux temperature was increased to 136 °C. Additional catalyst solution (30 mL), iodine (0.51 g, 0.3 equiv), and Grignard reagent (26 mmol, 3.6 equiv) were added after 3.5, 6.5, and 23 h. After 30 h at reflux, the reaction mixture was cooled to rt, diluted with water, treated with 15 mL of 6 M aqueous HCl, and stirred overnight. The mixture was partitioned between CH_2Cl_2 and water, and the organic layer was washed with saturated aqueous $NaHCO_3$, dried, and concentrated to leave 6.0 g of an orange-red semisolid. The reaction was performed three additional times using 1-g portions of the dichloroanthracene **5**, and the crude product mixtures were combined for purification.

The crude product (17 g) was chromatographed (hexane) to give fractions enriched in 2,7-dimethylanthracene (**9**), the tolylanthracene **21**, and the ditolylanthracenes **4**. The fraction enriched in 2,7-dimethylanthracene (**9**) (0.26 g of pale yellow solid) was recrystallized from benzene to give 32 mg of the anthracene **9** as pale yellow plates (mp 241–242 °C). This byproduct was identified with material obtained via the Elbs reaction (see above) by a comparison of spectral data and by a mixture melting point determination. The fraction enriched in the tolylanthracene **21** (1.3 g of pale yellow semisolid) was recrystallized three times from hexane to give 380 mg of the tolylanthracene **21** as colorless prisms, mp 150–151 °C. Two additional recrystallizations from hexane provided a sample of the pure tolylanthracene **21**, mp 152–152.5 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (1 H, s, aryl CH), 7.87–7.94 (2 H, m, aryl CH), 7.66 (1 H, s, aryl CH), 7.54 (1 H, s, aryl CH), 7.17–7.41 (6 H, m, aryl CH), 2.45 (3 H, s, methyl), 2.18 (3 H, s, methyl), 1.94 (3 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 139.4 (1 C, s), 137.0 (1 C, s), 136.7 (1 C, s), 134.6 (1 C, s), 132.2 (1 C, s), 132.1 (1 C, s), 131.5 (1 C, s), 130.20 (1 C, d), 130.18 (1 C, s), 130.1 (1 C, d), 129.5 (1 C, s), 128.3 (1 C, d), 127.9 (1 C, d), 127.6 (1 C, d), 127.41 (1 C, d), 127.39 (1 C, d), 126.7 (1 C, d), 126.0 (1 C, d), 125.8 (1 C, d), 123.2 (1 C, d), 21.8 (1 C, q), 20.4 (1 C, q), 19.5 ppm (1 C, q); mass spectrum, *m/e* (relative intensity) 297 (26), 296 (100, M^+), 282 (11), 281 (38), 280 (9), 279 (14), 267 (9), 266 (37), 265 (33); UV maxima, nm (95% EtOH, ε), 384 (5290), 364 (6690), 347 (5260), 332 (2980), 317 (shoulder, 1440), 262 (146 000), 254 (shoulder, 84 000).

Anal. Calcd for $C_{23}H_{20}$: C, 93.19; H, 6.81. Found: C, 93.26; H, 6.75.

The ditolylanthracenes **4**, collected in five fractions during chromatography, amounted to 1.8 g (26% yield based on the 4.9 g of the anthracene **5** used in the four coupling reactions). Three of the fractions were yellow semisolids and were enriched in the lower melting trans isomer **4b**. The remaining two fractions were pale yellow solids (mp 85–172 °C and mp 180–200 °C) and were enriched in the higher melting cis isomer **4a**. In the following separations, fraction compositions were measured by analytical HPLC techniques employing a commercial chiral column (Pirkle type 1-A)[21] with 0.01% *i*-PrOH in hexane as eluent (1.25 mL/min). The retention times for the diastereomers **4** were 5.6 min (lower melting trans isomer **4b**) and 6.2 min (higher melting cis isomer **4a**); there was no evidence from the peak shapes that indicated the enantiomers of the trans isomer **4b** could be resolved to any extent using either a Pirkle type 1-A or an Astec Cyclobond I Ac chiral HPLC column.[21]

The fraction most enriched in the lower melting isomer was subjected to two recrystallizations from ethanol to provide 12 mg of the lower melting trans isomer **4b** as colorless needles, mp 167–168 °C. The remaining two fractions enriched in the lower melting trans isomer were recrystallized from hexane several times, until the mother liquors contained the lower melting isomer as 80% of the total. The mother liquors were concentrated and the resulting solid was subjected to preparative HPLC employing a Dynamax Macro column (21.4 mm i.d. × 25 cm, 8-μm silica gel) and hexane as eluent (14 mL/min) to provide an additional 42 mg of the lower melting trans isomer, mp 159–163 °C. Two recrystallizations from ethanol furnished the pure lower melting trans isomer **4b** as colorless needles, mp 169.8–170.8 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions corresponding to OH or C=O groups; ^1H NMR (300 MHz, $CDCl_3$) δ 8.39 (1 H, s, aryl CH), 7.92 (2 H, d, J = 8.8 Hz, aryl CH), 7.36 (2 H, d, J = 8.7 Hz, aryl CH), 7.10–7.16 (6 H, m, aryl CH), 6.91–6.96 (3 H, m, aryl CH), 2.17 (6 H, s, methyl), 1.74 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 138.7 (2 C, s), 137.3 (2 C, s), 136.5 (2 C, s), 131.7 (2 C, s), 131.4 (2 C, s), 129.8 (2 C, s), 129.7 (d), 129.6 (d), 128.5 (d), 127.0 (d), 126.9 (d), 125.5 (d), 125.4 (d), 123.1 (d), 20.4 (2 C, q), 19.3 (2 C, q) ppm; mass spectrum, *m/e* (relative intensity) 387 (35), 386 (100, M^+), 372

(21) The Astec Cyclobond chiral HPLC columns are available from Rainin Instrument Company (Woburn, MA). The Pirkle type 1-A column was obtained from Alltech Associates (Deerfield, IL). For information concerning chiral stationary phases for HPLC, see: Pirkle, W. H.; Finn, J. M.; Schreiner, J. L.; Hamper, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3964.

(22) The authors have deposited atomic coordinates for **3** and **4a** with the Camridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2, 1EZ, UK.

(6), 371 (18), 356 (18), 355 (14), 339 (6); UV maxima, nm (95% EtOH, ϵ), 392 (6300), 372 (7770), 354 (5890), 341 (3313), 321 (shoulder, 1300), 268 (126 000).

Anal. Calcd for $C_{30}H_{26}$: C, 93.21; H, 6.79. Found: C, 93.10; H, 6.81.

The fractions enriched in the higher melting cis isomer **4a** were recrystallized repeatedly from hexane to furnish 80 mg of the higher melting cis isomer as fine white needles, mp 227–227.5 °C (six to seven recrystallizations were required to purify fractions that contained the higher melting isomer as 60–70% of the total material). Two additional recrystallizations from hexane provided the pure higher melting cis isomer **4a** as fine white needles, mp 229.5–229.9 °C: IR (CCl_4), no absorption in the 3- or 6-μm regions attributable to OH or C=O groups; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (1 H, s, aryl CH), 7.92 (2 H, d, J = 8.8 Hz, aryl CH), 7.36 (2 H, d, J = 8.7 Hz, aryl CH), 7.07–7.16 (6 H, m, aryl CH), 6.89–6.94 (3 H, m, aryl CH), 2.17 (6 H, s, methyl), 1.76 (6 H, s, methyl); ^{13}C NMR ($CDCl_3$, multiplicity determined by an APT experiment) 138.7 (2 C, s), 137.3 (2 C, s), 136.4 (2 C, s), 131.7 (2 C, s), 131.4 (2 C, s), 129.80 (2 C, s), 129.75 (d), 129.5 (d), 128.5 (d), 127.0 (d), 126.9 (d), 125.53 (d), 125.50 (d), 122.9 (d), 20.4 (2 C, q), 19.3 (2 C, q); mass spectrum, m/e (relative intensity), 387 (32), 386 (100, M^+), 371 (15), 356 (17), 355 (14), 339 (6); UV maxima, nm (95% EtOH, ϵ), 392 (5730), 373 (7160), 355 (5380), 340 (3050), 322 (shoulder, 1230), 268 (108 000).

Anal. Calcd for $C_{30}H_{26}$: C, 93.21; H, 6.79. Found: C, 93.05; H, 6.89.

The HPLC response factors for the tolylanthracene **21** (1.85) and the mixture of ditolylanthracenes **4** (3.57) were determined for a UV detector setting of 254 nm and were calculated on the basis of an assigned value of 1.00 for 2,7-dimethylanthracene (**9**). On the basis of these data, the crude reaction mixture from a typical experiment contained dimethylanthracene **9** (t_R = 9.90 min), tolylanthracene **21** (t_R = 20.4 min), and a mixture of ditolylanthracenes **4** (t_R = 33.1 min) in a ratio of 1:12.5:18.6. Unidentified impurities appeared at retention times of 7.69, 12.93, and 35.8 min but comprised a relatively small percentage of the product as judged by the uncorrected ratio of peak areas.

Thermal Interconversion of *cis*- and *trans*-Ditolylanthracenes 4. To explore the thermal interconversion of the ditolylanthracenes **4**, samples of the isomers were sealed in melting point capillaries under nitrogen and heated in a Mel-Temp apparatus. After a specified period of time, the capillary tubes were cooled in an ice–water bath, and the samples were dissolved in hexane and subjected to HPLC analysis using a chiral column (Pirkle type 1-A) with 0.01% *i*-PrOH in hexane as eluent (1.25 mL/min). After the higher melting cis isomer **4a** was heated to 300 °C for 5 min, an approximately 1:1 ratio of cis **4a** and trans **4b** isomers was observed. The same isomer composition was observed for samples heated for 1 h, indicating thermal equilibrium had been reached within 5 min. Identical results were obtained for the lower melting trans isomer **4b**. After 30 min at 200 °C, the lower melting trans isomer **4b** was converted to a 93:7 mixture of isomers **4b**:**4a**.