that $y = 0$. Thus, $k_2' \ll k_1'$ and $y = 100lk_2''/[k_1' + l(k_1'' + k_2'')]$. Reformulating this equation we find

$$k_1'y + (k_1'' + k_2'')yl = 100k_2''l$$

$$k_1'\frac{y}{l} + (k_1'' + k_2'')y = 100k_2''$$

$$y = \frac{100k_2''}{k_1'' + k_2''} - \frac{k_1'}{k_1'' + k_2''}\left(\frac{y}{l}\right) \quad (3)$$

Equation 3 defines a hyperbolic function.[15] The data for the dependence of levels of **3a** on concentration from Table I were analyzed by using eq 3, excluding the result at 0.015 M, because the level of **3a** in this case could not be accurately measured. A high degree of statistical significance to the linear relationship of y and y/l was obtained ($r^2 = 0.95$ and $F = 128.7$). Analysis of the slope and intercept of eq 3 gives the following ratios.

$$\frac{100k_2''}{k_2'' + k_1''} = 32 \qquad \frac{k_1''}{k_2''} = 2.1$$

$$\frac{-k_1'}{k_1'' + k_2''} = -0.13 \text{ mol·dm}^{-3}$$

$$\frac{k_1''}{k_1'} = 5.2 \text{ mol}^{-1}\text{·dm}^3 \text{ and } \frac{k_2''}{k_1'} = 2.5 \text{ mol}^{-1}\text{·dm}^3$$

Thus, one can rank the relative order of the four rate constants as follows: $k_1'' = 5.2$ mol^{-2}·dm^6·s^{-1}; $k_2'' = 2.5$ mol^{-2}·dm^6·s^{-1}; $k_1' = 1.0$ mol^{-1}·dm^3·s^{-1}; $k_2' < 0.02$ mol^{-1}·dm^3·s^{-1}.

Note added in proof: The interested reader should note that ylide 1 in THF solution at 0.2 or 1.0 M, in the presence of equimolar lithium bromide, is uncomplexed, as determined by ^{13}C NMR P-C and P-H one-bond coupling constants (for background, see: Albright, T. A.; et al. *J. Am. Chem. Soc.* **1976**, *98*, 6249. Albright, T. A.; Schweizer, E. E. *J. Org. Chem.* **1976**, *41*, 1168). Details will appear in ref 7a.

Registry No. 1, 3728-50-5; LiBr, 7550-35-8; benzaldehyde, 100-52-7; hexanal, 66-25-1.

(15) Eves, H. in *Standard Mathematical Tables*, 24th ed.; CRC Press: Cleveland, OH, 1976; pp 298-300.

Symmetrically Trisubstituted Triptycenes

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A simple synthesis of 1,8,13- and 1,8,16-trisubstituted triptycenes is described. Diels-Alder reaction of 1,8-disubstituted anthracenes with ortho-substituted benzynes gave 15 new triptycene compounds as mixtures of the syn (1,8,13) and anti (1,8,16) trisubstituted triptycenes, which in most cases could be separated by HPLC to afford pure isomeric products. The syn/anti ratio depends on the nature of the substituents on the anthracene and benzyne units. In addition, the improved syntheses of three 1,8-disubstituted anthracenes and a new synthetically useful ortho-substituted aryne are reported.

Rigid carbon frameworks can be used to juxtapose functional groups for a variety of purposes in organic and inorganic chemistry. Potential applications include host-guest complexes, molecular inclusion compounds, and coordination complexes with unusual geometries. Triptycene has a rigid structure with three equivalent benzene rings that provides an ideal framework for systems requiring the imposition of threefold symmetry. Consequently, we became interested in utilizing symmetrically trisubstituted triptycenes as foundations for construction of synthetic model complexes for a variety of metalloprotein active sites that have effective threefold symmetry; these include the P-clusters of nitrogenase,[2] the iron-sulfur cluster of aconitase,[3] and the blue copper proteins.[4] Low molecular weight compounds that mimic ligand types and coordination geometries present in metalloproteins have been used extensively as probes of structure and functions.[5]

Another application of these rigid molecules is the study of molecular inclusion phenomena. Triptycenes have been used as "spacers" leading to crystalline compounds containing channels capable of occluding a variety of other molecules.[6] In addition, trisubstituted triptycenes have the potential for forming clathrate compounds with varying cavity sizes.[7]

Our specific goal was to synthesize symmetrically trisubstituted triptycenes containing functional groups at the 1-, 8-, and 13-positions.[8] Although numerous substituted triptycenes have been prepared,[9] only one symmetrically trisubstituted compound was known prior to this work:

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(2) Averill, B. A. *Structure Bonding* **1983**, *53*, 59.
(3) Emptage, M. H.; Kent, T. A.; Kennedy, M. C.; Beinert, H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 4674.
(4) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180.
(5) Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.
(6) (a) Hart, H.; Lin, L.-T. W.; Ward, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 4043. (b) Toda, F.; Ward, D. L.; Hart, H. *Tetrahedron Lett.* **1981**, *22*, 3865. (c) For a review of host-guest complexes, see: Cram, D. J.; Cram, J. M. *Science (Washington, D.C.)* **1974**, *183*, 803.
(7) For a review of clathrate compounds, see: MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. *Chem. Soc. Rev.* **1978**, *7*, 65.
(8) Note that the numbering scheme of the triptycene structures in this paper is consistent with the 9,10-dihydro-9,10-o-benzenoanthracene nomenclature used by Chemical Abstracts.
(9) For a review of triptycenes, see: Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 951.

0022-3263/86/1951-3308$01.50/0

Table I. Ratios of Anti to Syn Isomers of Trisubstituted Triptycenes

compd	X =	Y =	% anti	% syn	yield,[a] %
9	Cl	CH_3	25	75	74
10	CN	CH_3	28	72	57
11	$COOCH_3$	CH_3	31	69	58
12	Cl	Cl	77	23	27
13	$COOCH_3$	Cl	73	27	20
14	Cl	$COOCH_3$	44	56	47
15	CN	$COOCH_3$	99	1	38
16	$COOCH_3$	$COOCH_3$	76	24	62

[a] Yield is crude yield of both isomers prior to chromatography, based on anthracene starting material. Isomer ratios were obtained by integration of the ^1H NNR spectra of the crude triptycene mixture. Numbers reported are an average of at least two runs.

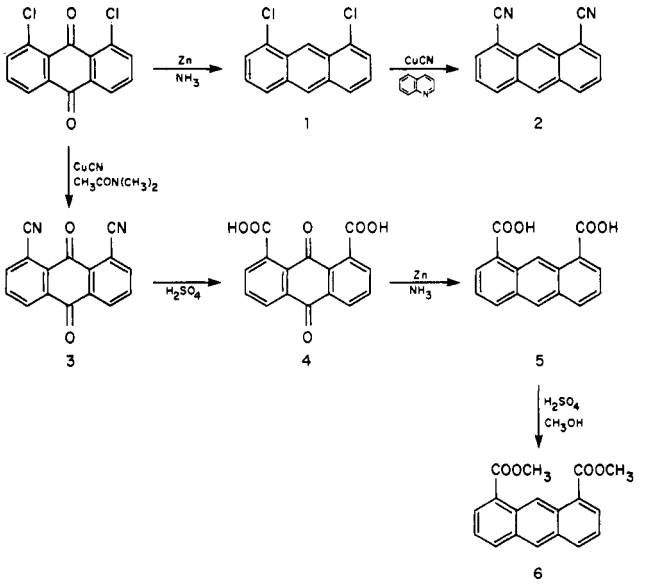
namely, 1,8,13-trichlorotriptycene, obtained in low yield.[10]

We have extended the method of Mori et al.[10] and have found that the Diels–Alder reaction of 1,8-disubstituted anthracenes with benzynes derived from 6-substituted anthranilic acids leads to 1,8,13- and 1,8,16-trisubstituted triptycenes in reasonable yields. We describe herein the synthesis and properties of eight pairs of such isomers with different functional groups, the separation of several pairs into pure isomers, the reactivity of substituents, and the factors important in controlling the stereochemistry of the cycloaddition reaction. In the process of synthesizing these novel triptycenes, we developed a new and potentially useful ortho-functionalized benzyne precursor, 2-amino-6-(methoxycarbonyl)benzoic acid, which is readily accessible from 3-nitrophthalic acid. Additionally, we have reexamined and improved the synthesis of various 1,8-disubstituted anthracenes.

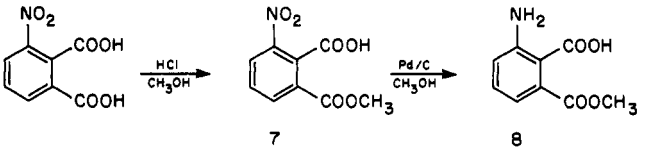
Results and Discussion

Synthesis. Trisubstituted triptycenes were synthesized by the Diels–Alder cycloaddition of disubstituted anthracenes with monosubstituted benzynes. The 1,8-disubstituted anthracenes used were dichloro-, dicyano-, and bis(methoxycarbonyl)anthracene. 1,8-Dichloroanthracene (**1**) was prepared as reported.[11] The literature procedures for other disubstituted anthracenes proved ineffectual, and modifications were made to increase yield and/or product purity. The synthetic routes to the above anthracenes are shown in Scheme I. The literature procedure for the synthesis of 1,8-dicyanoanthracene (**2**)[12] yielded little or no product in our hands. The procedure was improved by treating the crude product **2** with aqueous ammonia to decompose an organocopper intermediate, forming a blue solution of $[Cu(NH_3)_4]^{2+}$. Under these conditions, pure 1,8-dicyanoanthracene was obtained in 41% yield. The synthesis of 1,8-dicyanoanthraquinone[13] was also modified, by changing the solvent from benzyl cyanide to *N,N*-dimethylacetamide (DMA). The organocopper intermediate formed from the substitution reaction with cuprous cyanide was decomposed with nitric acid to give the product in 88% yield. Hydrolysis of the dicyanoanthraquinone with sulfuric acid and subsequent reduction with zinc dust in aqueous NH_3 yielded anthracene-1,8-dicarboxylic acid (**5**). 1,8-Bis(methoxycarbonyl)anthracene was synthesized as described[14] by reaction of **5** with acidic methanol.

Scheme I



Scheme II



Three substituted benzyne precursors were used to react with the anthracenes. 2-Amino-6-methylbenzoic acid was commercially available, 2-amino-6-chlorobenzoic acid was synthesized as previously reported,[15] and 2-amino-6-methoxycarbonylbenzoic acid **8** was synthesized by conversion of 3-nitrophthalic acid to the half methyl ester followed by hydrogenation to the amino acid (Scheme II). The literature procedure[16] for the half methyl ester, 1-methyl-2-hydrogen-3-nitrophthalate (**7**), reported a 56% yield with a reaction time of 16 h. Our procedure gives **7** in 77% yield with a reaction time of 3 h. Hydrogenation of **7** for 8 h in MeOH yielded a gummy yellow solid of **8** (92%). Compound **8** is not stable at room temperature;

(10) Mori, I.; Kadosaka, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1649.
(11) House, H. O.; Koepsell, D.; Jaeger, W. *J. Org. Chem.* **1973**, *38*, 1167.
(12) Akiyama, S.; Misumi, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1293.
(13) Waldmann, H.; Oblath, A. *Chem. Ber.* **1938**, *71*, 366.
(14) Akiyama, S.; Misumi, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1829.
(15) Piper, J. R.; Stevens, F. J. *J. Org. Chem.* **1962**, *27*, 3134.
(16) Nagai, U.; Abe, E.; Sano, R. *Tetrahedron* **1974**, *30*, 25.

it undergoes self-condensation reactions to form amide-linked polymers and MeOH.

The three monosubstituted anthranilic acids were reacted with three different disubstituted anthracenes to yield eight pairs of isomeric substituted triptycenes (Table I). The ninth possible pair of isomers (X = CN; Y = Cl) could not be prepared. Monosubstituted benzynes were generated in situ, by slow addition of the monosubstituted anthranilic acid (dissolved in dimethoxyethane (DME)) to a solution of disubstituted anthracene and isoamyl nitrite in DME. A twofold excess of monosubstituted anthranilic acid and isoamyl nitrite was used to ensure complete reaction. Treatment of the product with aqueous NaOH kept the excess acid in solution and precipitated the product. A mixture of two isomeric triptycenes, which we refer to as anti (1,8,16-trisubstituted) and syn (1,8,13-trisubstituted) structures, was obtained. In a few cases, the parent disubstituted anthracenes were present in the product mixtures. It has been reported that maleic anhydride can be used to scavenge anthracene,[17] but we found that it was easier to separate the anthracene from the triptycenes by sublimation. The yellow starting materials, which have lower melting points (and are more volatile) than the triptycenes, were sublimed off to yield the white mixture of triptycene isomers.

Melting points of the substituted triptycenes were high, usually above 300 °C. The extraordinarily low solubility of many of these triptycenes in common solvents made obtaining analytically pure samples of some compounds difficult; typical preparative HPLC runs produced ≤1 mg/run. Several elemental analyses were somewhat low in carbon, apparently due to occlusion of methylene chloride in the triptycene lattice. The presence of CH_2Cl_2 was verified by NMR; integration gave stoichiometries consistent with the elemental analyses. Heating the compounds at 125 °C under a vacuum of 0.07 torr for 64 h did not remove all the chlorinated solvent present, as evidenced by a positive chloride test (sodium fusion method). For those compounds which analyzed low in carbon, high-resolution mass spectra were obtained to confirm the exact mass.

The lowest yields of triptycenes were obtained by using 3-chlorobenzyne as the dienophile. Yields were apparently a function of the ability of the substituted anthranilic acid to produce benzyne. It has been reported[17] that 3-chlorobenzyne is not easily produced via aprotic diazotization of 3-chloroanthranilic acid or from the isolated 3-chloro-1-diazoniobenzene-2-carboxylate. Attempts to synthesize 1,8-dicyano-13-chlorotriptycene or 1,8-dicyano-16-chlorotriptycene failed, presumably due to the difficulties in generating 3-chlorobenzyne combined with the very low solubility of 1,8-dicyanoanthracene. In comparison, the new aryne made from 3-(methoxycarbonyl)-benzoic acid via aprotic diazotization gave triptycene products in 50–60% yields.

The ratio of syn (s) to anti (a) isomers obtained was determined by integration of the ^1H NMR spectra of the crude triptycene product from at least two separate reactions and is shown in Table I along with combined yields for compounds **9–16**. It is clear from Table I that the substituent Y on the benzyne is the more important in dictating the observed regiochemistry. When Y = CH_3, the syn isomer is formed in a 2 or 3 to 1 ratio relative to the anti, regardless of the anthracene substituent X. Conversely, when Y = Cl, the anti isomer is preferred over the syn structure. Only when Y = CO_2CH_3 does the anti to syn ratio depend noticeably on X.

These results are interpreted as resulting from the effect of the substituents on the polarity of the frontier orbitals of the benzyne and of the anthracene.[18] All three anthracenes examined have electron-withdrawing substituents at the 1- and 8-positions, which are expected to stabilize a partial negative charge at the 9-position and a partial postive charge at the 10-position, with the stabilization being in the order CN > CO_2CH_3 > Cl (based on Hammett σ_p parameters[19]). Because the relevant orbital of the benzyne is the π bond orthogonal to the aromatic system of the benzyne ring, the most important effect of substituents is an inductive one via the σ network, rather than a resonance effect. Qualitatively, an electron-releasing substituent will generate a partial negative charge at the substituted carbon (C-3) of the benzyne, thus stabilizing a polarization of the benzyne as δ^+ at C-2 and δ^- at C-1. An electron-withdrawing substituent will cause exactly the opposite polarization of the benzyne. Simple electrostatic matching of the polarized benzyne and anthracene orbitals satisfactorily accounts for the preferred regiochemistry in **9–13**.

For **14–16**, the observed regiochemistry depends on the anthracene substituents X. This is rationalized by the recognition that the substituent-induced polarization of the benzyne π electrons by the methoxycarbonyl group (σ_I = 0.20) is intermediate between those of the methyl and chloro groups (σ_I = −0.04 and 0.46, respectively).[20] Consequently, an increased sensitivity to subtle changes in the electronic structure of the anthracene would be expected. For Y = CO_2CH_3, the anti preference correlates with the ability of the anthracene to stabilize negative charge at C-9 and positive charge at C-10. For X = CN and CO_2CH_3, σ_p and σ_R values are both positive; therefore these substituents strongly favor the anti isomer. For X = Cl, σ_p and σ_R have opposite signs, and it appears as if the resonance effect, which places a partial negative charge at C-10, dominates, giving a slight excess of the syn isomer. The almost exclusive formation of the anti isomer for X = CN is readily explained by the stronger combined σ_p and σ_R effects of CN vs. CO_2CH_3. Alternatively, the favorable alignment of opposed dipoles in the transition state may be significant in determining the final orientation of substituents. For example, the lowest energy arrangement of dipoles[21] of the benzyne and anthracene to produce **15** yields the anti isomer and may account for the virtually exclusive formation of this isomer. None the results suggests that steric effects are significant with the substituents examined.

Separation of the six pairs of structural isomers was carried out by using a semipreparative HPLC equipped with a silica gel column. The pairs of isomers formed by using *o*-(methoxycarbonyl)benzyne were easiest to separate. The polarity difference made 1,8,13- and 1,8,16-tris(methoxycarbonyl)triptycenes separable by column chromatography, although radial thin-layer chromatography was used as an efficient way to perform the separation. The radical chromatograph was equipped with a quartz cover which allowed the evolution of bands to be followed with a UV light source. Two sets of isomers could not be separated by HPLC: trichlorotriptycene (**12**) and dichloro(methyl)triptycene (**9**). 1,8,13- and 1,8,16-Tri-

(17) Freidman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089.

(18) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(19) Exner, O. *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 439–540.

(20) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

(21) Topsom, R. D. *Acc. Chem. Res.* **1983**, *16*, 292.

chlorotriptycenes have been reported[10] to be separable on an alumina column by using benzene as the eluent. TLC on alumina plates showed no separation in benzene or other solvents. No separation was observed by using HPLC conditions similar to those used with other pairs of isomers. 1,8-Dichloro-13- and 1,8-dichloro-16-methyltriptycene were also inseparable by using similar HPLC conditions. The 1,8-dichloro-13-methyltriptycene was, however, separated from the anti isomer by slow evaporation of an ethyl acetate (EtOAc) solution of the mixture of compounds, whereupon the syn isomer selectively crystallized. Recrystallization from EtOAc gave the syn isomer in 95% isomeric purity.

Reactivity. Manipulation of the triptycene substituents proved difficult due to the low solubility of the triptycenes in common organic solvents. The nitrile groups of **10** were converted to carboxylic acids upon treatment with KOH in ethylene glycol for 4 days at 150 °C. Attempts to oxidize the methyl substituent of **10** using the pyridine-soluble oxidant tetrabutylammonium permanganate failed; even at temperatures as high as 100 °C and with prolonged reaction times, starting material was recovered. A stronger oxidant, such as $KMnO_4$, yielded methyl-substituted anthraquinone.

The substituents of the tris(methoxycarbonyl)-triptycenes (**16s**, **16a**) provided increased solubility and circumvented many reaction condition problems. Hydrolysis to the triptycenetricarboxylic acids (**17s**, **17a**) in KOH/MeOH was easily performed. This provided a synthetic route to a totally symmetrically substituted triptycene framework suitable for use in synthesis of a model for metalloprotein active sites.[22] Conversion of the syn and anti isomers of **17** to the corresponding tris(carbonylchlorides) **18s** and **18a** was achieved by reaction with $SOCl_2$. The water-sensitive products **18s** and **18a** were reacted immediately with amines, forming triptycene amides in excellent yields. The amines used were propylamine, *p*-toluidine, and *p*-aminophenol.

Physical Properties. The most effective way to differentiate the isomeric pairs of triptycenes was by their ^1H NMR spectra. The triptycene structure shows a characteristic pattern composed of four doublets, two doublets of doublets, and two singlets. The singlets are due to the bridgehead protons, and their shifts vary depending upon the substituents on the aromatic rings. The ^1H NMR of triptycene was studied by Kidd et al.[23] with the conclusion that the observed shifts were due to a combination of ring current, bond anisotropy, and ring current contributions. Our data confirm these results; the triptycenes with polar substituents show the largest $\Delta\delta$ for the bridgehead protons. In each case, the syn isomer bridgehead proton signals show a larger $\Delta\delta$ than those for the anti isomer. The ABC spin system on each aromatic ring shows $J_{AB} = J_{BC}$ and $J_{AC} \approx 0$. In some instances, the overlap of peaks made it necessary to decouple protons selectively in order to assign coupling constants. For **9a**, **9s**, **12a**, **12s**, and **20a**, two-dimensional homonuclear chemical shift correlation (COSY) spectra were recorded in addition to the one-dimensional ^1H NMR to determine coupling constants. The ^{13}C NMR spectra typically showed two bridgehead signals in the region of 43.4–54.7 ppm, four signals between 147.8–141.4 ppm due to the carbons next to the bridgeheads, and eight aromatic ring signals at ~126 ppm. In a few cases, fewer signals were observed than predicted, presumably due to coincidental overlap of resonances. Characterization of **16s**, **17s**, and **21s** by ^1H and ^{13}C NMR was simplified due to a decrease in the number of signals owing to their threefold symmetry and resulting magnetic equivalence of the identically substituted aromatic rings.

(22) Rogers, M. E.; Averill, B. A., unpublished results.
(23) Kidd, K. G.; Kotowycz, G.; Schaeffer, T. *Can. J. Chem.* **1967**, *45*, 2155.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NTC-360 instrument. Chemical shifts are reported in parts per million (δ) relative to internal $(CH_3)_4Si$. IR spectra were determined on a Perkin-Elmer Model 1430 ratio recording spectrophotometer, using polystyrene for calibration. Mass spectra were measured at 70 eV on a Finnegan MAT model 4600 GC/MS operated by departmental personnel. High-resolution mass spectra were obtained on a Finnegan MAT Model 8230 GC/MS. Uncorrected melting points (<200 °C) were determined on a Thomas-Hoover capillary apparatus; melting points (>200 °C) were determined on a Laboratory Device Mel-Temp apparatus. HPLC analyses, using a Waters Associates μ-Porasil column, were performed with a Waters Associates Model M-45 solvent delivery system equipped with a Model U6K injector and Model 440 absorbance detector. Semipreparative-scale HPLC separations were done with a Whatman Partisil 10 Magnum 9 (50-cm length) silica column. Radial thin-layer chromatography was performed on a 4-mm silica plate by using a Harrison Research Model 7924 Chromatotron. Microanalyses were performed by Atlantic Microlab Inc., Atlanta, GA. The silica gel used for column chromatography was 230–400 mesh. All chemicals used were reagent grade, unless otherwise stated.

1,8-Dicyanoanthracene (2). The procedure of Akiyama et al.[12] was followed with modifications. 1,8-Dichloroanthracene 1[11] (6.7 g, 30 mmol) and CuCN (8.1 g, 90 mmol) were slurried in distilled quinoline (70 mL) and refluxed for 24 h under Ar. The warm black solution was poured into 1 M HCl (600 mL), producing a black solid that was filtered and washed with water. The solid product was partitioned between 1 M NH_4OH (300 mL) and CH_2Cl_2 (300 mL) and stirred vigorously for 6 h. The blue aqueous layer was separated, and fresh 1 M NH_4OH (300 mL) was added to the organic phase and allowed to stir for another 6 h. This procedure was repeated until the aqueous layer was no longer blue. Rotary evaporation of the organic layer left a brown oil, which was chromatographed (R_f 0.32, silica gel, CH_2Cl_2) to afford pure **2** as a yellow solid (2.5 g, 41%): mp 300–303 °C (lit.[12] mp 304–306 °C); ^1H NMR ($CDCl_3$) δ 9.16 (1 H, s), 8.65 (1 H, s), 8.31 (2 H, d, J = 10.8 Hz), 8.08 (2 H, d, J = 7.2 Hz), 7.63 (2 H, dd, J = 10.8 , 10.8 Hz); IR (KBr) 2216 (s, CN) cm^{-1}; MS (EI), m/e (relative intensity) 228 (M^+, 100), 201 (11), 175 (5), 100 (10), 87 (11), 74 (5).

1,8-Dicyanoanthraquinone (3). The procedure for synthesis of 1-cyanoanthraquinone from 1-chloroanthraquinone was followed,[24] with 1,8-dichloroanthraquinone as the starting material. 1,8-Dichloroanthraquinone (10.0 g, 36 mmol) and CuCN (9.2 g, 0.10 mol) were slurried in DMA (50 mL) and refluxed under Ar for 3 h. The hot brown solution was poured onto ice (700 g), and the brown-green precipitate was filtered and washed with water. The copper complex was decomposed with 3 N HNO_3 (500 mL) at 60 °C for 4 h. The brown solid was filtered, washed with water and air-dried. This procedure afforded crude **3** (8.2 g, 88%): mp 402–406 °C (lit.[13] mp >390 °C); ^1H NMR (Me_2SO-d_6) δ 8.51 (2 H, d, J = 7.92 Hz), 8.44 (2 H, d, J = 7.56 Hz), 8.12 (2 H, dd, J = 7.74, 7.74 Hz); IR (KBr) 2216 (m, CN), 1678 (s, C=O) cm^{-1}; MS (EI), m/e (relative intensity) 258 (M^+, 100), 230 (55), 211 (82), 175 (44), 149 (11), 101 (31), 87 (13), 75 (41).

Anthraquinone-1,8-dicarboxylic Acid (4). The procedure of Waldmann et al.[13] was followed with modifications. Crude **3** (8.2 g, 30 mmol) was refluxed in 70% H_2SO_4 (500 mL) for 1 h. The hot solution was poured onto ice (800 g) to precipitate crude **4** as a brown solid (8.2 g, 87%): mp 294–300 °C (lit.[13] mp 316 °C); ^1H NMR (Me_2SO-d_6) δ 13.40–13.10 (2 H, br, s), 8.28 (2 H, d, J = 7.56 Hz), 7.96 (2 H, dd, J = 7.92, 7.92 Hz), 7.85 (2 H, d, J = 7.20 Hz); IR (KBr) 3400–2750 (s, OH), 1710–1665 (br, s, C=O) cm^{-1}; MS (EI), m/e (relative intensity) 296 (M^+, 0.5), 279 (7), 252 (71), 234 (100), 208 (16), 180 (32), 150 (47), 139 (27), 75 (39).

(24) Golden, R.; Stock, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 3080.

Anthracene-1,8-dicarboxylic Acid (5). The procedure of Waldmann et al.[13] was followed with modifications. Crude **4** (8.2 g, 30 mmol) and Zn dust (30 g, 0.5 mol) were refluxed with stirring in 20% NH_4OH (350 mL) for 4 h, during which time the color changed from dark red to yellow. The solution was filtered to remove excess Zn, and water (500 mL) was added to the yellow filtrate. The filtrate was cooled to 0 °C, and 10% HCl was slowly added until a yellow precipitate formed. Filtration of the solid and air-drying yielded crude **5** (5.9 g, 79%): mp 345–347 °C dec (lit.[13] mp 345 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 13.30–13.00 (2 H, br, s), 10.47 (1 H, s), 8.78 (1 H, s), 8.34 (2 H, d, J = 8.28 Hz), 7.62 (2 H, dd, J = 7.74, 7.74 Hz); IR (KBr) 3300–2450 (br, s, OH), 17.17 (s, C=O) cm^{-1}; MS (EI) m/e (relative intensity) 266 (M^+, 100), 249 (7), 236 (2), 221 (14), 204 (40), 192 (5), 176 (4), 165 (27), 150 (6), 139 (4), 124 (4), 110 (6), 97 (5), 82 (9), 69 (6).

1,8-Bis(methoxycarbonyl)anthracene (6). The procedure of Akiyama et al.[14] was followed with modifications. Compound **5** (2.9 g, 10 mmol) was refluxed in MeOH (400 mL) with concentrated H_2SO_4 (4 mL) for 16 h. Water (100 mL) was added to the warm brown solution, and the product was extracted with CH_2Cl_2 until the organic layer was no longer yellow. Concentration of solvent by rotary evaporation left a brown oil, which was chromatographed (R_f 0.57, silica gel, CH_2Cl_2) to yield pure **6** (1.8 g, 61%): mp 101–103 °C (lit.[14] mp 104–105 °C); ^{1}H NMR ($CDCl_3$) δ 10.71 (1 H, s), 8.49 (1 H, s), 8.28 (2 H, d, J = 6.84 Hz), 8.18 (2 H, d, J = 8.28 Hz), 7.52 (2 H, dd, J = 7.20, 7.20 Hz); ^{13}C NMR ($CDCl_3$) δ 167.35, 133.10, 130.97, 130.89, 129.14, 127.31, 127.10, 123.90, 123.65, 51.95; IR (KBr) 1707 (s, C=O) cm^{-1}; MS (EI), m/e (relative intensity) 294 (M^+, 100), 263 (52), 235 (25), 220 (19), 203 (18), 176 (16), 164 (9), 150 (4), 131 (5), 123 (11), 116 (19), 102 (20), 88 (27), 75 (8).

1-Methyl 2-Hydrogen 3-Nitrophthalate (7). The procedure reported by Nagai et al.[16] was followed with some modifications. Reagent grade 3-nitrophthalic acid (50 g, 0.24 mol) was dissolved in anhydrous MeOH (200 mL) and was filtered through a fine-glass frit to remove small black impurities present in the starting material. The resulting yellowish solution was cooled to 0 °C, and dry HCl gas was bubbled through at a rate of approximately 1 bubble per s for 20 min. The resulting colorless solution was refluxed for 2–3 h and poured while hot into ice–water (900 mL) to precipitate the product 1. The white microcrystals were filtered, washed with cold water, and dried in vacuo at 60 °C. This procedure afforded pure **7** (41.3 g, 77%): mp 162–164 °C (lit.[16] mp 160–162 °C); ^{1}H NMR (Me_2SO-d_6) δ 14.10–13.75 (1 H, br, s), 8.33 (1 H, d, J = 8.17 Hz), 8.22 (1 H, d, J = 7.72 Hz) 7.82 (1 H, dd, J = 8.01, 8.01 Hz); IR (KBr) 3400–3000 (br, s, OH), 1766 (s, C=O ester), 1700 (s, C=O acid), 1541 (s, NO_2), 1352 (s, NO_2) cm^{-1}; MS (EI), m/e (relative intensity) 225 (M^+, 2), 208 (68), 194 (100), 181 (37), 164 (22), 151 (79), 136 (46), 119 (36), 104 (63), 92 (41), 75 (68), 63 (30).

2-Amino-6-(methoxycarbonyl)benzoic Acid (8). Compound **7** (30.0 g, 0.13 mol) was dissolved in MeOH (125 mL) and placed in a heavy-walled Pyrex bottle, to which was added 5% Pd on charcoal (0.30 g).[25] The reaction flask was pressurized to 40 psi with H_2 and allowed to shake on a Parr pressure reaction apparatus for 8 h at room temperature. The resultant bright yellow solution was filtered to remove the catalyst. Rotary evaporation of the solvent and subsequent drying in vacuo yielded **8** as a gummy solid[26] (23.8 g, 92%): ^{1}H NMR (Me_2SO-d_6) δ 9.20–8.00 (3 H, br, s), 7.21 (1 H, dd, J = 7.56, 7.56 Hz), 6.87 (1 H, d, J = 8.2 Hz), 6.61 (1 H, J = 6.84 Hz), 3.71 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 170.64, 170.40, 135.51, 132.55, 119.31, 116.79, 109.96, 52.56; IR (NaCl) 3490 (w, NH_2), 3380 (w, NH_2), 1712 (m, C=O ester), 1615 (m, C=O acid) cm^{-1}; MS (EI), m/e (relative intensity) 195 (M^+, 1), 177 (12), 163 (44), 147 (13), 119 (75), 90 (100).

General Procedure for the Preparation of 1,8,13- and 1,8,16-Trisubstituted Triptycenes. The 1,8-disubstituted anthracene (5 mmol) was dissolved in a minimal amount of hot DME (10–300 mL). Isoamyl nitrite (1.3 mL, 10 mmol) was added to the refluxing solution, and the substituted anthranilic acid (10 mmol), dissolved in DME (10–20 mL), was added dropwise over a 20-min period. The solution was refluxed 20 min, and another charge of isoamyl nitrite (1.3 mL, 10 mmol) was added. A second aliquot of anthranilic acid (10 mmol), dissolved in DME (10–20 mL), was added over a 20-min period. The solution was refluxed another 40 min and cooled to 0 °C, and 95% EtOH (20 mL) was added. Cold 7.5% NaOH was added until a precipitate formed. The solid was filtered, washed with cold MeOH–H_2O (4:1) until there was no brown color in the filtrate, and dried in vacuo at 60 °C. Purification was performed in some cases by subliming off unreacted anthracene. Separation of some isomers by chromatography was performed as indicated.

1,8-Dichloro-13-methyltriptycene (9s) and 1,8-Dichloro-16-methyltriptycene (9a). Reaction of **1** with 2-amino-6-methylbenzoic acid (recrystallized from 95% EtOH), by the general procedure above, yielded 74% **9a** and **9s**. Pure **9s** was obtained by selective crystallization from EtOAc.

9a and 9s:[27] mp 332–335 °C; ^{1}H NMR (Me_2SO-d_6) δ 7.51 (2 H, d, J = 7.20 Hz), 7.46 (2 H, d, J = 7.20 Hz), 7.36 (1 H, d, J = 7.20 Hz), 7.35 (1 H, dd, J = 6.48, 6.48 Hz), 7.16 (2 H, d, J = 7.20 Hz), 7.15 (2 H, d, J = 7.20 Hz), 7.08 (2 H, dd, J = 7.20, 7.20 Hz), 7.07 (2 H, dd, J = 7.20, 7.20 Hz), 6.92 (4 H, m), 6.60 (1 H, s), 6.28 (1 H, s), 6.06 (1 H, s), 5.84 (1 H, s), 2.49 (3 H, s), 2.48 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 147.79, 147.34, 144.82, 143.10, 142.97, 142.19, 141.88, 141.81, 133.03, 132.10, 129.91, 129.84, 127.26, 127.13, 126.45, 126.40, 125.97, 125.81, 125.25, 122.36, 122.01, 121.51, 54.67, 50.77, 47.32, 43.39, 18.60, 18.49; MS (EI), m/e (relative intensity) 340 (M^+ + 4, 4), 338 (M^+ + 2, 47), 336 (M^+, 80), 301 (66), 286 (45), 266 (100), 250 (17), 189 (8), 132 (30), 125 (8); high-resolution mass spectrum, exact mass calcd for $C_{21}H_{14}Cl_2$ (M^+) 336.0473, found 336.0479. Anal. Calcd for $C_{21}H_{14}Cl_2 \cdot {}^1/_2CH_2Cl_2$: C, 68.00; H, 3.98. Found: C, 67.72; H, 3.73.

9s: mp 355–357 °C; ^{1}H NMR ($CDCl_3$) δ 7.26 (2 H, d, J = 6.84 Hz), 7.23 (1 H, d, J = 7.20 Hz), 7.04 (2 H, d, J = 7.92 Hz), 6.93 (2 H, dd, J = 7.56, 7.56 Hz), 6.92 (1 H, dd, J = 7.56, 7.56 Hz), 6.89 (1 H, d, J = 6.84 Hz), 6.73 (1 H, s), 5.43 (1 H, s), 2.60 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 147.81, 141.90, 133.04, 129.86, 126.76, 126.09, 125.45, 124.89, 121.64, 121.14, 54.68, 43.40, 18.59; MS (EI), m/e (relative intensity) 340 (M^+ + 4, 6), 338 (M^+ + 2, 32), 336 (M^+, 61), 301 (75), 286 (37), 266 (100), 250 (15), 176 (4), 150 (8), 143 (10), 131 (37), 118 (11); high-resolution mass spectrum, exact mass calcd for $C_{21}H_{14}Cl_2$ (M^+) 336.0473, found 336.0479. Anal. Calcd for $C_{21}H_{14}Cl_2 \cdot {}^1/_8CH_2Cl_2$: C, 72.94; H, 4.13. Found: C, 73.44; H, 4.29.

1,8-Dicyano-13-methyltriptycene (10s) and 1,8-Dicyano-16-methyltriptycene (10a). Reaction of **2** with 2-amino-6-methylbenzoic acid (recrystallized from 95% EtOH), by the general procedure above, yielded **10a** and **10s** and some unreacted 1,8-dicyanoanthracene. Sublimation of the mixture separated the lower melting anthracene from the triptycenes to yield 57% of an off-white solid of **10a** and **10s**. Separation by semipreparative HPLC afforded **10a** and **10s** as white solids.

10a: mp 365–368 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.59 (2 H, d, J = 7.20 Hz), 7.45 (1 H, d, J = 7.20 Hz), 7.33 (2 H, d, J = 7.92 Hz), 7.14 (2 H, dd, J = 7.56, 7.56 Hz), 7.00 (1 H, dd, J = 7.56, 7.56 Hz), 6.93 (1 H, d, J = 7.56 Hz), 6.26 (1 H, s), 5.77 (1 H, s), 2.51 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 147.54, 145.95, 141.66, 141.53, 132.45, 128.76, 127.96, 127.70, 126.34, 125.93, 122.84, 116.60, 108.83, 50.48, 49.91, 18.49; MS (EI), m/e (relative intensity) 318 (M^+, 72), 303 (100), 288 (6), 275 (8), 158 (5), 151 (9), 144 (8), 138 (10), 130 (9), 124 (7); high-resolution mass spectrum, exact mass calcd for $C_{23}H_{14}N_2$ (M^+) 318.1157, found 318.1144; HPLC (CH_2Cl_2) t_r 10.8 min, flow rate 8.0 mL/min. Anal. Calcd for $C_{23}H_{14}N_2$: C, 86.77; H, 4.43; N, 8.80. Found: C, 85.67; H, 4.55; N, 8.65.

10s: mp 408–411 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.50 (2 H, d, J = 7.20 Hz), 7.33 (2 H, d, J = 7.92 Hz), 7.26 (1 H, d, J = 6.12 Hz), 7.14 (2 H, dd, J = 7.56, 7.56 Hz), 6.97 (1 H, dd, J = 7.02, 7.02 Hz), 6.94 (1 H, d, J = 6.12 Hz), 6.58 (1 H, s), 5.54 (1 H, s), 2.66 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 147.27, 146.36, 143.52, 140.13, 133.75, 128.55, 127.83, 127.70, 126.38, 125.97, 121.79, 116.59, 108.83, 53.73, 46.58, 18.58; MS (EI), m/e (relative intensity) 318 (M^+, 100), 303 (84), 288 (5), 275 (8), 158 (4), 144 (7), 138 (7), 132 (8), 124 (5); high-resolution mass spectrum, exact mass calcd for $C_{23}H_{14}N_2$ (M^+) 318.1157, found 318.1144; HPLC (CH_2Cl_2) t_r 9.2 min, flow rate

(25) The rubber stopper used to cover the bottle was lined with Parafilm to insure that sulfur in the stopper would not poison the catalyst.

(26) The compound slowly reacts with itself, producing polymers; storage under inert atmosphere below 0 °C is suggested.

(27) Data reported are for a 25:75 mixture of **9a** and **9s**.

8.0 mL/min. Anal. Calcd. for $C_{23}H_{14}N_2 \cdot {}^1/_8CH_2Cl_2$: C, 84.29; H, 4.36; N, 8.51. Found: C, 83.90; H, 4.74; N, 8.22.

1,8-Bis(methoxycarbonyl)-13-methyltriptycene (11s) and 1,8-Bis(methoxycarbonyl)-16-methyltriptycene (11a). Reaction of **6** with 2-amino-6-methylbenzoic acid (recrystallized from 95% EtOH), by the general procedure above, yielded 58% **11a** and **11s**. Separation by semipreparative HPLC afforded pure **11a** and pure **11s** as white solids.

11a: mp 215–216 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (1 H, s), 7.58 (2 H, d, J = 7.92 Hz), 7.50 (2 H, d, J = 7.20 Hz), 7.39 (1 H, d, J = 7.20 Hz), 7.03 (2 H, dd, J = 7.56, 7.56 Hz), 6.92 (1 H, dd, J = 7.56, 7.56 Hz), 6.85 (1 H, d, J = 7.56 Hz), 5.71 (1 H, s), 4.01 (3 H, s), 2.50 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 167.41, 146.80, 146.35, 143.86, 143.23, 131.69, 128.94, 127.26, 127.03, 126.90, 126.63, 125.22, 124.90, 122.85, 52.02, 50.63, 47.02, 18.35; MS (EI), m/e (relative intensity) 384 (M^+, 71), 362 (5), 353 (14), 337 (13), 331 (4), 324 (16), 310 (4), 303 (4), 293 (100), 278 (5), 265 (25), 263 (29), 250 (19), 239 (7), 189 (7), 176 (5), 146 (5), 132 (19), 125 (10), 75 (4); HPLC (CH_2Cl_2) t_r 13.3 min, flow rate 8.0 mL/min. Anal. Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.15; H, 5.26.

11s: mp 231–233 °C; ^{1}H NMR ($CDCl_3$) δ 8.32 (1 H, s), 7.58 (2 H, d, J = 7.92 Hz), 7.49 (2 H, d, J = 7.20 Hz), 7.22 (1 H, d, J = 7.20 Hz), 7.02 (2 H, dd, J = 7.56, 7.56 Hz), 6.90 (1 H, dd, J = 7.20, 7.20 Hz), 6.87 (1 H, d, J = 7.20 Hz), 5.47 (1 H, s), 4.01 (3 H, s), 2.68 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 167.40, 147.31, 145.98, 145.03, 142.25, 134.04, 127.26, 127.14, 126.84, 126.70, 125.13, 124.93, 121.19, 54.51, 52.00, 42.94, 18.59; MS (EI), m/e (relative intensity) 384 (M^+, 100), 352 (59), 324 (37), 309 (12), 292 (91), 278 (7), 265 (59), 263 (57), 250 (29), 239 (12), 226 (4), 189 (16), 176 (10), 161 (13), 146 (7), 132 (24), 125 (10), 118 (6), 84 (21), 75 (6); HPLC (CH_2Cl_2) t_r 9.7 min, flow rate 8.0 mL/min. Anal. Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 77.70; H, 5.20.

1,8,13-Trichlorotriptycene (12s) and 1,8,16-Trichlorotriptycene (12a). Reaction of **1**[11] with 2-amino-6-chlorobenzoic acid,[15] by the general procedure above, yielded 27% **12a** and **12s**. This pair of isomers was not separated.

12a and 12s: mp 355–358 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 7.58 (2 H, d, J = 7.92 Hz), 7.55 (3 H, d, J = 7.92 Hz), 7.51 (1 H, d, J = 7.20 Hz), 7.21 (2 H, d, J = 8.64 Hz), 7.20 (1 H, d, J = 8.64 Hz), 7.20 (3 H, d, J = 7.92 Hz), 7.12 (1 H, dd, J = 7.92, 7.92 Hz), 7.12 (3 H, dd, J = 7.92, 7.92 Hz), 7.11 (2 H, dd, J = 7.92, 7.92 Hz), 6.82 (1 H, s), 6.38 (1 H, s), 6.17 (1 H, s), 5.98 (1 H, s); MS (EI), m/e (relative intensity) 360 (M^+ + 4, 9), 358 (M^+ + 2, 27), 356 (M^+, 33), 321 (42), 286 (100), 250 (34), 176 (8), 160 (7), 143 (20), 125 (22), 112 (5); high-resolution mass spectrum, exact mass calcd for $C_{20}H_{11}Cl_3$ (M^+) 355.9926, found 355.9950. Anal. Calcd for $C_{20}H_{11}Cl_3 \cdot {}^1/_8CH_2Cl_2$: C, 65.63; H, 3.07. Found: C, 65.14; H, 2.98.

1,8-Bis(methoxycarbonyl)-13-chlorotriptycene (13s) and 1,8-Bis(methoxycarbonyl)-16-chlorotriptycene (13a). Reaction of **6** with 2-amino-6-chlorobenzoic acid,[15] by the general procedure above, yielded 20% **13a** and **13s**. Separation by semipreparative HPLC yielded **13a** and **13s** as white solids.

13a: mp 218–219 °C; ^{1}H NMR ($CDCl_3$) δ 7.99 (1 H, s), 7.62 (2 H, d, J = 7.92 Hz), 7.57 (2 H, d, J = 7.20 Hz), 7.44 (1 H, d, J = 7.20 Hz), 7.08 (1 H, d, J = 7.92 Hz), 7.05 (2 H, dd, J = 8.28, 8.28 Hz), 6.95 (1 H, dd, J = 7.56, 7.56 Hz), 5.97 (1 H, s), 4.02 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 167.25, 146.61, 146.01, 145.94, 142.59, 129.30, 127.75, 127.23, 127.01, 126.72, 126.04, 125.26, 123.48, 52.07, 50.69, 46.94; MS (EI), m/e (relative intensity) 406 (M^+ + 2, 38), 404 (M^+, 100), 373 (61), 368 (11), 344 (54), 337 (45), 312 (83), 301 (6), 293 (13), 286 (57), 278 (41), 273 (6), 266 (34), 249 (67), 238 (34), 223 (12), 210 (9), 186 (12), 175 (30), 169 (11), 142 (13), 138 (21), 124 (37), 118 (29), 111 (11), 85 (9), 83 (78); high-resolution mass spectrum, exact mass calcd for $C_{24}H_{17}O_4Cl$ (M^+) 404.0815, found 404.0796; HPLC (CH_2Cl_2) t_r 17.3 min, flow rate 6.0 mL/min. Anal. Calcd for $C_{24}H_{17}O_4Cl \cdot {}^1/_8CH_2Cl_2$: C, 69.74; H, 4.18. Found: C, 69.73; H, 4.33.

13s: mp 204–205 °C; ^{1}H NMR ($CDCl_3$) δ 8.41 (1 H, s), 7.63 (2 H, d, J = 7.56 Hz), 7.52 (2 H, d, J = 7.20 Hz), 7.28 (1 H, d, J = 7.20 Hz), 7.08 (2 H, dd, J = 7.56, 7.56 Hz), 7.07 (1 H, d, J = 7.56 Hz), 6.95 (1 H, dd, J = 7.56, 7.56 Hz), 5.51 (1 H, s), 4.06 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 146.81, 144.85, 127.76, 127.31, 127.25, 126.73, 126.69, 126.41, 125.35, 121.86, 54.53, 52.17, 51.90; MS (EI), m/e (relative intensity) 406 (M^+ + 2, 40), 404 (M^+, 100), 373 (80), 367 (25), 344 (42), 336 (66), 312 (67), 305 (7), 300 (24), 293 (34), 286 (74), 277 (32), 273 (8), 265 (43), 249 (58), 237 (43), 223 (14), 209 (12), 185 (16), 175 (30), 161 (8), 142 (17), 138 (28), 131 (29), 124 (35), 118 (26), 111 (24), 83 (78), 71 (9); high-resolution mass spectrum, exact mass calcd for $C_{24}H_{17}O_4Cl$ (M^+) 404.0815, found 404.0796; HPLC (CH_2Cl_2) t_r 18.1 min, flow rate 6.0 mL/min. Anal. Calcd for $C_{24}H_{17}O_4Cl \cdot {}^1/_4CH_2Cl_2$: C, 68.36; H, 4.14. Found: C, 68.65; H, 4.29.

1,8-Dichloro-13-(methoxycarbonyl)triptycene (14s) and 1,8-Dichloro-16-(methoxycarbonyl)triptycene (14a). Reaction of **1**[11] with **8** by the general procedure above, yielded **14a** and **14s** and some unreacted **1**. Sublimation of the mixture separated the more volatile anthracene from the triptycenes to yield 47% **14a** and **14s**. Separation by semipreparative HPLC yielded pure **14a** and pure **14s** as white solids.

14a: mp 256–258 °C; ^{1}H NMR ($CDCl_3$) δ 7.67 (1 H, d, J = 7.92 Hz), 7.65 (1 H, d, J = 7.92 Hz), 7.36 (2 H, d, J = 7.20 Hz), 7.10 (1 H, dd, J = 7.56, 7.56 Hz), 7.06 (2 H, d, J = 7.20 Hz), 6.95 (2 H, dd, J = 7.56, 7.56 Hz), 6.91 (1 H, s), 6.45 (1 H, s), 3.98 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 167.20, 147.07, 146.94, 145.14, 141.84, 129.76, 128.51, 127.29, 126.71, 126.11, 125.78, 125.21, 122.84, 52.10, 50.10, 50.42, 47.10; MS (EI), m/e (relative intensity) 384 (M^+ + 4, 9), 382 (M^+ + 2, 51), 380 (M^+, 96), 349 (22), 345 (8), 320 (33), 313 (89), 286 (100), 278 (12), 266 (16), 250 (63), 224 (6), 211 (6), 176 (20), 156 (9), 143 (13), 139 (16), 125 (61), 112 (11), 84 (13); HPLC (CH_2Cl_2) t_r 7.8 min, flow rate 4.0 mL/min. Anal. Calcd for $C_{22}H_{14}O_2Cl_2$: C, 69.31; H, 3.70. Found: C, 69.30; H, 4.01.

14s: mp 322–323 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (1 H, s), 7.69 (1 H, d, J = 7.92 Hz), 7.54 (1 H, d, J = 7.20 Hz), 7.27 (2 H, d, J = 7.92 Hz), 7.10 (1 H, dd, J = 7.56, 7.56 Hz), 7.07 (2 H, d, J = 7.92 Hz), 6.95 (2 H, dd, J = 7.56, 7.56 Hz), 5.48 (1 H, s), 4.08 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 167.22, 147.47, 146.60, 144.59, 141.42, 130.56, 127.65, 127.43, 126.71, 126.26, 125.42, 122.85, 121.96, 54.52, 52.29, 43.82; MS (EI), m/e (relative intensity) 384 (M^+ + 4, 8), 382 (M^+ + 2, 44), 380 (M^+, 91), 349 (20), 344 (8), 320 (34), 313 (91), 286 (100), 278 (11), 266 (11), 250 (83), 246 (8), 224 (6), 211 (5), 176 (14), 157 (10), 143 (11), 139 (10), 125 (37), 112 (7); HPLC (CH_2Cl_2) t_r 8.1 min, flow rate 4.0 mL/min. Anal. Calcd for $C_{22}H_{14}O_2Cl_2$: C, 69.31; H, 3.70. Found: C, 69.05; H, 3.78.

1,8-Dicyano-13-(methoxycarbonyl)triptycene (15s). Reaction of **2** with **8**, by the general procedure above, yielded **15s** and some unreacted **2**. Sublimation of the mixture separated the anthracene from the triptycene to yield 38% of **15s**. The compound was further purified by semipreparative HPLC. This procedure afforded **15s** as white crystals: mp 366–369 °C; ^{1}H NMR ($CDCl_3$) δ 7.77 (1 H, d, J = 7.92 Hz), 7.73 (1 H, d, J = 7.92 Hz), 7.69 (2 H, d, J = 7.56 Hz), 7.36 (2 H, d, J = 7.56 Hz), 7.17 (1 H, dd, J = 7.56, 7.56 Hz), 7.16 (2 H, dd, J = 7.56, 7.56 Hz), 7.08 (1 H, s), 6.32 (1 H, s), 4.00 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 161.40, 149.38, 147.21, 145.84, 145.63, 143.63, 129.03, 128.98, 128.61, 127.97, 126.65, 125.95, 116.52, 108.79, 52.25, 50.23, 49.47; MS (EI), m/e (relative intensity) 362 (M^+, 83), 347 (20), 330 (30), 302 (100), 275 (16), 201 (5), 181 (5), 165 (6), 151 (21), 138 (29), 124 m (35), 11 (8), 84 (8), 75 (11); high-resolution mass spectrum, exact mass calcd for $C_{24}H_{14}N_2O_2$ (M^+) 362.1055, found 362.1055. Anal. Calcd for $C_{24}H_{14}N_2O_2$: C, 79.55; H, 3.89; N, 7.73. Found: C, 78.77; H, 4.46; N, 7.39.

1,8,13-Tris(methoxycarbonyl)triptycene (16s) and 1,8,16-Tris(methoxycarbonyl)triptycene (16a). Reaction of **6** with **8**, by the general procedure above, yielded 62% **16a** and **16s**. Separation by radial chromatography (R_f 0.24 (**16a**), 0.10 (**16s**), silica gel, CH_2Cl_2) and subsequent recrystallization from 1:1 CH_2Cl_2–EtOAc afforded colorless crystals of pure **16a** and pure **16s**.

16a: mp 256–257 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (1 H, s), 7.70 (1 H, d, J = 7.20 Hz), 7.65 (1 H, d, J = 7.92 Hz), 7.61 (4 H, d, J = 7.92 Hz), 7.08 (1 H, dd, J = 7.56, 7.56 Hz), 7.07 (2 H, dd, J = 7.56, 7.56 Hz), 6.95 (1 H, s), 4.02 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 167.32, 147.40, 146.38, 146.05, 145.94, 129.14, 128.15, 127.10, 126.73, 125.40, 125.20, 52.06, 52.02, 50.23, 46.75; MS (EI), m/e (relative intensity) 428 (M^+, 100), 413 (4), 397 (36), 381 (6), 368 (22), 337 (85), 309 (11), 305 (8), 293 (17), 278 (19), 266 (6), 250 (29), 237 (7), 183 (22), 176 (4), 161 (4), 153 (5), 147 (4), 139 (8), 125 (33), 118 (7), 84 (9). Anal. Calcd for $C_{26}H_{20}O_6$: C, 72.89; H, 4.71. Found: C, 72.80; H, 4.69.

16s: mp 287–289 °C; ^{1}H NMR ($CDCl_3$) δ 8.69 (1 H, s), 7.57 (3 H, d, J = 7.92 Hz), 7.52 (3 H, d, J = 7.20 Hz), 7.07 (3 H, dd,

J = 7.92, 7.92 Hz), 5.53 (1 H, s), 4.05 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 167.40, 146.73, 144.72, 127.86, 126.97, 126.92, 125.19, 54.23, 52.02, 43.63; MS (EI), m/e (relative intensity) 428 (M^+, 100), 413 (3), 397 (31), 368 (19), 337 (27), 310 (13), 293 (13), 278 (12), 266 (5), 250 (19), 237 (7), 198 (13), 183 (9), 147 (5), 125 (26), 118 (9). Anal. Calcd for $C_{26}H_{20}O_6$: C, 72.89; H, 4.71. Found: C, 72.43; H, 4.66.

Triptycene-1,8,13-tricarboxylic Acid (17s) and Triptycene-1,8,16-tricarboxylic Acid (17a). Compound **16a** or **16s** (2.5 g, 5.8 mmol) was dissolved in MeOH (625 mL). KOH (10%, 125 mL) was added to the solution, which was then refluxed for 12 h. The reaction mixture was cooled to room temperature, water (200 mL) was added, and the solution was concentrated by rotary evaporation to half the volume. HCl (6 N) was added with stirring until a white precipitate formed. The solid was collected on a fine-glass frit and dried in vacuo at 60 °C overnight to yield **17a** or **17s** (2.1 g, 95%).

17a: mp 426–428 °C; ^{1}H NMR (Me_2SO-d_6) δ 13.12 (3 H, s), 7.87 (1 H, s), 7.64 (2 H, d, J = 7.20 Hz), 7.60 (1 H, d, J = 7.20 Hz), 7.57 (1 H, d, J = 7.92 Hz), 7.50 (2 H, d, J = 7.92 Hz), 7.15 (1 H, dd, J = 7.20, 7.20 Hz), 7.13 (2 H, dd, J = 7.20, 7.20 Hz), 6.90 (1 H, s); ^{13}C NMR (Me_2SO-d_6) δ 167.85, 167.81, 146.43, 146.16, 145.68, 145.26, 128.20, 127.91, 127.58, 126.72, 126.45, 125.26, 49.64, 46.19; MS (EI), m/e (relative intensity) 386 (M^+, 100), 368 (12), 340 (25), 323 (50), 295 (14), 279 (44), 250 (29), 239 (15), 237 (10), 184 (6), 124 (14), 119 (11), 75 (5). Anal. Calcd for $C_{23}H_{14}O_6$: C, 71.50; H, 3.65. Found: C, 71.40; H, 3.76.

17s: mp 432–435 °C; ^{1}H NMR (Me_2SO-d_6) δ 12.91 (3 H, s), 8.35 (1 H, s), 7.63 (3 H, d, J = 7.20 Hz), 7.40 (3 H, d, J = 7.92 Hz), 7.11 (3 H, d, J = 7.56 Hz), 5.87 (1 H, s); ^{13}C NMR (Me_2SO-d_6) δ 167.85, 146.96, 129.31, 126.62, 125.85, 125.06, 52.58, 43.45; MS (EI), m/e (relative intensity) 386 (M^+, 24), 324 (21), 279 (10), 250 (10), 239 (8), 84 (100); high-resolution mass spectrum, exact mass calcd for $C_{22}H_{12}O_3$ ($M^+ - (CO_2 + H_2O)$) 324.0786, found 324.0775. Anal. Calcd for $C_{23}H_{14}O_6$: C, 71.50; H, 3.65. Found: C, 70.64; H, 3.72.

Triptycene-1,8,13-tricarbonyl Trichloride (18s) and Triptycene-1,8,16-tricarbonyl Trichloride (18a). Compound **17a** or **17s** (0.2 g, 0.52 mmol) and $SOCl_2$ (10 mL) were mixed under Ar, and the slurry was refluxed for 12 h. $SOCl_2$ was removed under reduced pressure to yield **18a** or **18s** as a white solid (0.23 g, 98%).

General Procedure for the Preparation of N,N′,N″-Trisubstituted 1,8,13- and 1,8,16-Triptycenetricarboxamides. The tricarbonyl trichloride **18a** or **18s** (0.23 g, 0.51 mmol) was made in situ and kept under Ar. The appropriate amine (1.5 mmol) in CH_2Cl_2 (20 mL) or CH_3CN (30 mL) was syringed into the reaction flask, followed by Et_3N (0.22 mL, 1.5 mmol). Upon addition of the reagents, some reaction mixtures formed solutions, while others remained as slurries. Each reaction mixture was refluxed 18 h under an inert atmosphere and allowed to cool and the volume reduced to 15 mL under reduced pressure. A white precipitate was collected on a fine-glass frit and washed with water, followed by 10% HCl. The products were dried in vacuo overnight at 60 °C.

***N,N′,N″*-Tripropyl-1,8,16-triptycenetricarboxamide (19a).** Reaction of **18a** with propylamine in CH_2Cl_2, by the general procedure above, yielded **19a** as a white solid (0.25 g, 96%): mp 369–402 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 8.48 (2 H, t, J = 5.40 Hz), 8.33 (1 H, t, J = 5.40 Hz), 7.48 (2 H, d, J = 6.84 Hz), 7.38 (1 H, d, J = 7.20 Hz), 7.13 (3 H, d, J = 7.56 Hz), 7.06 (3 H, dd, J = 7.20, 7.20 Hz), 6.63 (1 H, s), 6.25 (1 H, s), 3.32 (6 H, m), 1.62 (6 H, m), 0.97 (6 H, t, J = 7.20 Hz), 0.95 (3 H, t, J = 7.20 Hz); ^{13}C NMR (Me_2SO-d_6) δ 167.46, 145.73, 145.27, 143.90, 142.39, 133.11, 132.55, 125.46, 125.34, 124.85, 124.68, 124.10, 123.57, 49.85, 46.72, 41.00, 40.74, 22.41, 22.35, 11.51, 11.43; MS (EI), m/e (relative intensity) 509 (M^+, 24), 451 (14), 424 (16), 394 (18), 365 (10), 279 (10), 250 (13), 168 (20), 125 (15), 100 (8), 86 (29), 73 (100); high-resolution mass spectrum, exact mass calcd for $C_{32}H_{35}N_3O_3$ (M^+) 509.2678, found 509.2680. Anal. Calcd for $C_{32}H_{35}N_3O_3$: C, 75.41; H, 6.92; N, 8.24. Found: C, 74.66; H, 6.80; N, 8.08.

***N,N′,N″*-Tris(4-methylphenyl)-1,8,16-triptycenetricarboxamide (20a).** Reaction of **18a** with *p*-toluidine in CH_3CN, by the above procedure, yielded **20a** as a white solid (0.32 g, 97%): mp 371–374 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 10.28 (3 H, s), 10.17 (3 H, s), 7.72 (2 H, d, J = 7.92 Hz), 7.59 (2 H, d, J = 6.48 Hz), 7.57 (4 H, d, J = 7.92 Hz), 7.52 (1 H, d, J = 7.20 Hz), 7.33 (1 H, d, J = 7.56 Hz), 7.27 (2 H, d, J = 9.00 Hz), 6.78 (1 H, s), 6.29 (1 H, s), 3.35 (6 H, s), 2.31 (3 H, s); ^{13}C NMR (Me_2SO-d_6) δ 166.19, 166.09, 145.89, 145.36, 144.10, 143.27, 136.72, 136.49, 133.28, 132.59, 132.42, 128.99, 128.73, 126.31, 125.60, 124.81, 124.04, 123.80, 120.52, 119.98, 49.86, 46.68, 20.55, 20.52; MS (EI), m/e (relative intensity) 653 (M^+, 10), 547 (81), 413 (10), 394 (5), 384 (10), 366 (5), 355 (7), 341 (6), 307 (5), 278 (5), 250 (38), 239 (5), 221 (15), 207 (11), 198 (8), 184 (10), 176 (22), 171 (20), 149 (10), 133 (5), 125 (19), 106 (100), 91 (37), 86 (46), 79 (51), 64 (23); high-resolution mass spectrum, exact mass calcd for $C_{44}H_{35}N_3O_3$ (M^+) 653.2678, found 653.2681. Anal. Calcd for $C_{44}H_{35}N_3O_3 \cdot {}^1/_4CH_2Cl_2$: C, 78.74; H, 5.30; N, 6.23. Found: C, 79.07; H, 5.37; N, 6.21.

***N,N′,N″*-Tris(4-hydroxyphenyl)-1,8,13-triptycenetricarboxamide (21s).** Reaction of **18s** with *p*-aminophenol in CH_2Cl_2, by the general procedure above, yielded **21s** as a white solid (0.32 g, 95%): mp 420–424 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 10.18 (3 H, s), 9.29 (3 H, s), 7.94 (3 H, d, J = 7.20 Hz), 7.50 (1 H, s), 7.40 (6 H, d, J = 8.64 Hz), 7.29 (3 H, d, J = 7.56 Hz), 7.15 (3 H, dd, J = 7.56, 7.56 Hz), 6.63 (6 H, d, J = 8.28 Hz), 5.93 (1 H, s); ^{13}C NMR (Me_2SO-d_6) δ 165.90, 153.99, 146.44, 141.84, 133.43, 129.93, 125.43, 125.10, 124.61, 123.81, 114.56, 52.72, 43.42; MS (EI), m/e (relative intensity) 659 (M^+, 7), 551 (59), 442 (8), 282 (4), 250 (40), 109 (100), 86 (17), 80 (79); high-resolution mass spectrum, exact mass calcd for $C_{41}H_{29}N_3O_6$ (M^+) 659.2056, found 659.2042. Anal. Calcd for $C_{41}H_{29}N_3O_6$: C, 74.65; H, 4.43; N, 6.37. Found: C, 73.92; H, 4.55; N, 6.38.

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Registry No. C=O—BeH^+, 102869-81-8; C=O—$BeMe^+$, 102869-82-9; C=O—BF_2^+, 102920-08-1; C=O—BMe_2^+, 102869-83-0; C=O—AlF_2^+, 102869-84-1; C=O—$AlMe_2^+$, 102869-85-2; C=O—BeH_2, 102869-86-3; C=O—$BeMe_2$, 102869-87-4; C=O—BF_3, 102869-88-5; C=O—BMe_3, 102869-89-6; C=O—AlF_3, 102869-90-9; C=O—$AlMe_3$, 102869-91-0; *trans*-dimethylcyclopropanone, 102869-92-1.