Toward Covalently Linked Organic Networks: Model Studies and Connector Syntheses

Ken S. Feldman,* Robert F. Campbell, Joe C. Saunders, Chuljin Ahn, and Katherine M. Masters

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received July 31, 1997[⊗]

A model 1-naphthoic acid bearing a peri-positioned cinnamic acid residue crystallizes as a closed H-bonded dimer. Irradiation of this crystalline solid provides an α-truxillate-type cyclobutane photodimer in quantitative yield. Further synthesis studies have led to more highly functionalized naphthoic/cinnamic acid species capable of (pseudo)centrosymmetric attachment to polyvalent hubs. This system demonstrates the feasibility of designing a covalent molecular connector whose orientation is encoded by its H-bonding pattern.

The organization of functional monomers into periodic higher dimensional arrays remains an enduring challenge in materials research. Self-ordering strategies for polyvalent monomers that encode the assembly instructions with either H-bonding[1] or metal ligation[2] have led to major advances in the preparation of two- and three-dimensional networks of defined and largely predictable architecture. However, the kinetic lability of most of these noncovalent attachments, coupled with the relatively modest connection enthalpies (metal−ligand; $\Delta H_f \leq -10$ kcal/mol,[3a] carboxylic acid dimerization; $\Delta H_f \sim -14$ kcal/mol (gas phase),[3b] pyridone dimerization; $\Delta H_f = -5.4$ kcal/mol[3c]) render them characteristically fragile and susceptible to collapse upon solvent removal. Many downstream applications of these "designer solids" (e.g., shape-selective separations, catalysis) might require a more robust framework than can be delivered by these approaches to monomer connection.

Some of these inherent deficiencies might be overcome by synthesis of a kinetically inert, *completely covalently* linked periodic network, wherein the connection enthalpies exceed H-bonding and metal ligation by substantial margins. Strategies directed toward this goal are still at the formative stages. Promising approaches that rely on either "shot gun" polymerization of directional, polyvalent monomers[4] or complementary "bottom-up" strategies that utilize iterative synthesis have been described.[5]

A third approach currently under development builds upon H-bond-directed monomer assembly for ultimate delivery of covalently linked periodic higher dimensional arrays.[8] Specifically, a two-stage protocol that utilizes (1) monomer preorganization and preorientation in a periodic network by H-bonded encoded crystallization and (2) in situ covalent cross-linking of these monomers in their lattice positions offers the possibility of deliberatively converting molecules into materials of designed architecture. This strategy takes advantage of the self-correcting nature of a kinetically labile but (at least locally) thermodynamically driven crystallization process to bring reactive entities within bonding proximity in the solid state. The critical challenge, then, is to design molecular connectors that (1) have self-complementary H-bonding arrays, (2) bear appropriate reactive functionality poised for intermolecular covalent bond formation only after the H-bond network is in place, and (3) suffer only minimal geometric distortion upon conversion of the H-bond connection to a covalent connection. The design and synthesis of one such connector unit is described herein.

The peri cinnamic acid-substituted naphthoic acid derivate **1** is a plausible candidate for this molecular connector (Scheme 1). When attached to a hub as shown, the well-defined J-shaped geometry bearing two H-bonding termini suggests that a self-complementary H-bond-mediated dimerization will afford a linear connection between two hubs, **2**. The choice of a peri-substituted naphthalene spacer ensures that the cinnamic acid alkene moieties reside within the empirically determined window (≤4.2 Å) for successful solid-state photochemical [$2\pi + 2\pi$] cycloaddition.[6] Topochemical dimerization of a crystalline sample of **2** upon irradiation should then afford the cyclobutane product **3**, in which the two connector modules are now covalently cross-linked. Successful execution of this plan can provide a paradigm for replacing directional but weak intermolecular association with more robust covalent linkages.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) Leading references can be found in: (a) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283. (b) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747. (c) Wang, K.; Simard, M.; and Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119. (d) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737.

(2) Leading references can be found in: (a) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Williams, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 10641. (b) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5963. (c) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, *118*, 295.

(3) (a) Christensen, J. J.; Izatt, R. M. *Handbook of Metal Ligand Heats and Related Thermodynamic Quantities*; Marcel Dekker: New York, 1983. (b) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974; pp 287−288. (c) Hammes, G. G.; Park, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 956.

(4) Leading references can be found in: (a) Rubin, Y.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 698. (b) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988** *53*, 2489. (c) Feldman, K. S.; Mareska, D. A.; Weinreb, C. K.; Chasmawala, M. *J. Chem. Soc., Chem. Commun.* **1996**, 865. (d) Vaid, T. P.; Lobkovsky, E. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 8742.

(5) Leading references can be found in: a) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354. (b) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841. (c) Boldi, A. M.; Anthony, J.; Gramlich, V.; Knobler, C. B.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **1995**, *87*, 779. (d) Jones, L.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388.

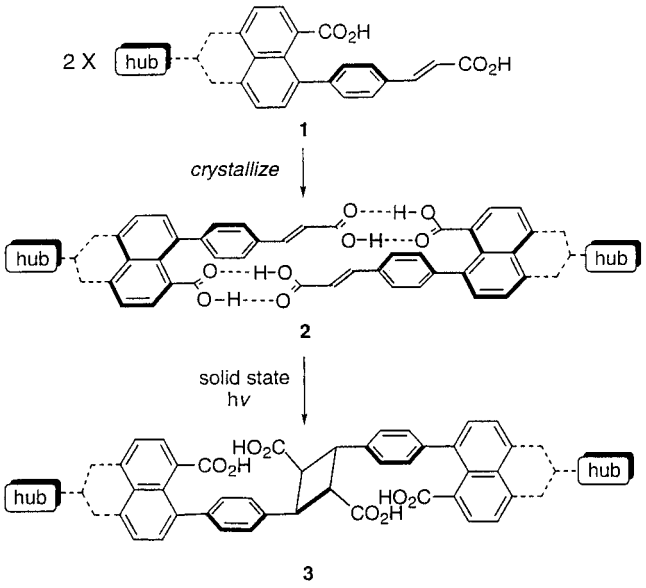
(6) Leading references can be found in: (a) Schmidt, G. M. *Pure Appl. Chem.* **1971**, *27*, 647. (b) Savion, Z.; Wernick, D. L. *J. Org. Chem.* **1993**, *58*, 2424. (c) Enkelmann, V.; Wegner, G.; Novak, K.; Wagener, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 10390.

(7) All molecular mechanics modeling was performed on a Silicon Graphics Power Indigo 2XZ computer with Macromodel 5.5 (mm3* force field). Conformational space about rotatable bonds was searched with a directed 1000-step Monte Carlo algorithm. Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

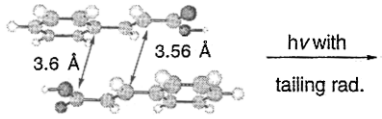
(8) Feldman, K. S.; Campbell, R. F. *J. Org. Chem.* **1995**, *60*, 1924.

S0022-3263(97)01416-3 CCC: $14.00

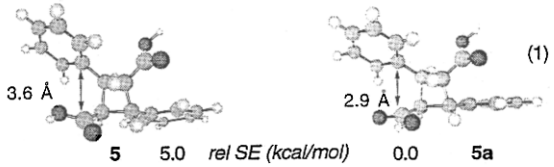
Scheme 1



Maintaining congruence between core atoms of the initial H-bonded connectors and the derived covalently linked species may be critical for sustaining lattice superstructure upon photodimerization. Hence, the consequences of the structural deformations that accompany the cycloaddition-induced decrease of the alkene−alkene gap from ca. 3.62 Å to ca. 1.54 Å on the H-bonded network's integrity are an area of concern. Molecular mechanics calculations[7] on α-cinnamic acid photodimerization in support of crystallographic studies by Enkelmann et al.[6c] give some sense of the magnitude of molecular motion, which results from the tradeoff between accrued strain energy and crystal packing forces. Crystalline α-*trans*-cinnamic acid **4** photodimerizes upon tailing irradiation to furnish the cyclobutane **5**, eq 1.

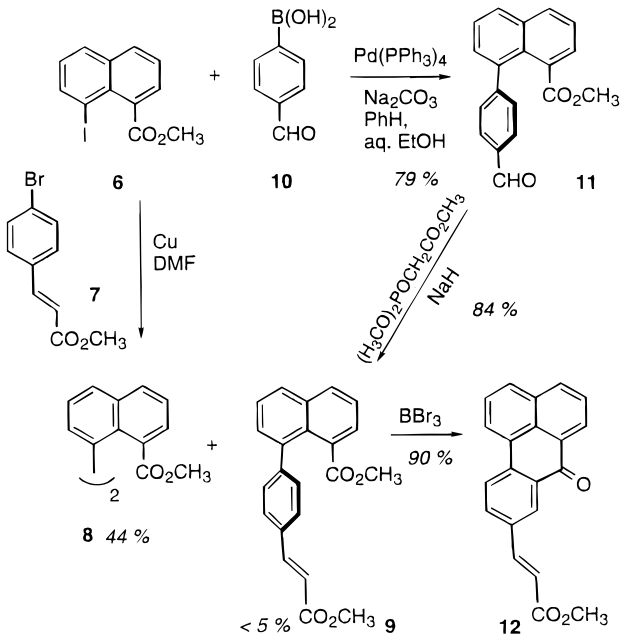


4 crystalline cinnamic acid, α-form



Molecular mechanics calculations on **5**, in which the phenyl ipso carbons and carbonyl carbons are "locked" at their initial precyclcoaddition distances, and also on an unconstrained version of this dimer, **5a**, reveal that an incremental strain of ca. 5.0 kcal/mol accompanies photodimerization without relaxation. Enkelmann has documented that this strain increment apparently can be accommodated in the cinnamic acid lattice without disruptive consequences, as X-ray analysis of the crystal undergoing photodimerization reveals that the carbons noted above *do not change position* (relax) within experimental limits through 67% conversion. Thus, the competition between crystal packing forces and strain resulting from bond angle distortion favors the former in this example, and the "hubs" (e.g., phenyl rings) rotate but do not otherwise suffer significant dislocation.

Scheme 2



A preliminary report describing the successful realization of this two-stage covalent connection strategy in a model system has been disclosed.[8] Full synthesis details and analysis of this model system are provided below. In addition, the design and preparation of a cinnamyl/naphthoic acid derivative that is suitable for attachment to multivalent hubs is detailed. Taken together, these advances provide the foundation for studies directed toward the preparation of two- and three-dimensional covalently linked organic networks.

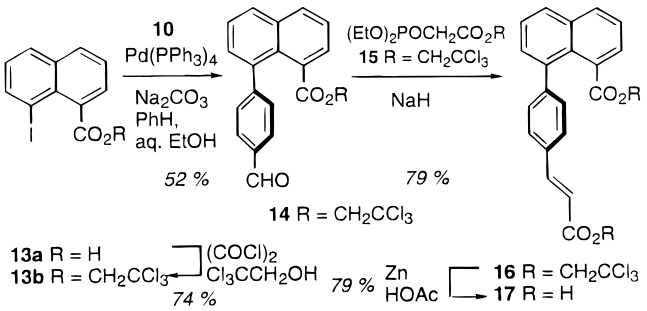
Results and Discussion

The model naphthoic acid/cinnamic acid **17** (Scheme 3) was chosen to test the feasibility of the two-stage crystallization/cross-linking strategy outlined above. This simple species has no functionality to permit attachment with central hub modules. Syntheses of more complex connectors with appropriate (electrophilic) moieties for fastening to polyvalent (nucleophilic) hubs will follow successful execution of the model system chemistry.

The initial route to model diacid **17** commenced with the known iodo methyl ester **6**,[9] available from naphthoic anhydride in three steps (Scheme 2). Initial attempts to effect a mixed Ullmann coupling with cinnamyl bromide **7** afforded mainly the known binaphthyl ester **8**[10] with only a trace (<5%) of the desired product **9**. Biaryl aldehyde **11** was obtained, however, via Suzuki coupling[12] of the known boronic acid **10**[11] with iodide **6**, followed by Emmons−Horner homologation. The diester **9** proved resistant to complete hydrolysis. Basic treatment led to attack at only the cinnamyl ester unit with much attendant decomposition. Attempted S_n2-type ester cleavage was equally unsuccessful, with the results (decomposition or no reaction) varying as per the harsh-

(9) Bailey, R. J.; Card, P. J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096.
(10) Hall, D. M.; Ridgwell, S.; Turner, E. E. *J. Chem. Soc.* **1954**, 2498.
(11) Torssell, K. *Arkiv. Kemi* **1956**, *10*, 507.
(12) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

Scheme 3



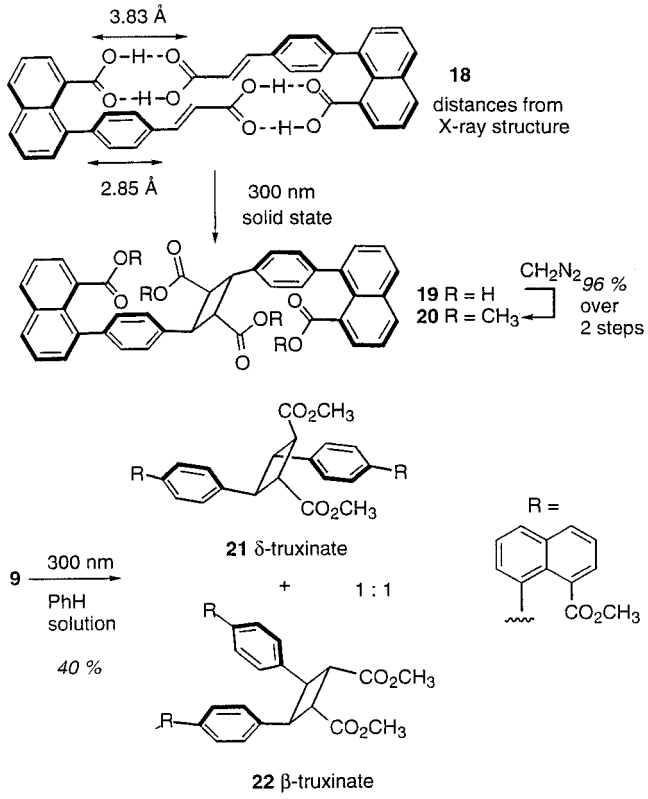
ness of the conditions. Interestingly, treatment of diester **9** with BBr_3 produced the tetracycle **12** resulting, presumably, from internal Friedel−Crafts acylation of an intermediate acyl bromide. Eventually, this dimethyl ester chemistry was abandoned in favor of a related route featuring a more labile protecting group.

The trichloroethyl protecting group appeared to offer advantages in both synthesis and removal for this sterically hindered and nucleophile-sensitive system, and so diester **16** was substituted as a target. The chemistry proceeded as described above from known iodo acid **13**[9] without event (Scheme 3). Deprotection of diester **16** with Zn/HOAc/THF afforded the desired diacid **17** in good yield and free of impurities.

Initial attempts to obtain a suitable sample of **17** for X-ray analysis by crystallization from various solvent mixtures were invariably frustrated by deposition of small and irregular crystals (<0.1 mm largest dimension). However, this deficiency was corrected by inclusion of a small amount of CH_3OH in the otherwise nonprotic solvent (mixtures of hexane/THF or heptane/DME), and well-formed rods (~1 mm × 3 mm) were deposited over several days at 4 °C.[13] In any event, X-ray analysis of crystals of **17** grown from heptane/DME/CH_3OH revealed that the design criteria represented by structure **2** were met.[8] Diacid **17** crystallized as a closed dimer (= **18**) with one molecule of DME per diacid pair. The entire dimer unit spans 19 Å, and these units stack in a herringbone-type pattern in the crystal with no discernible H-bonding interactions between discrete pairs. An examination of the structural details of **18** reveals the mimicry between the aryl ring and the carboxylic acid H-bonded dimer, which underlies the design strategy. These distances are incommensurate (2.85 vs 3.83 Å, respectively), and hence, the alkene moieties are shifted slightly out of register. Nevertheless, the critical alkene−alkene distance in this dimer (3.62 Å) is well within the margin for expected photocycloaddition.

Irradiation of crystalline **17** (= dimer **18**), including samples taken from the same batch that provided the single crystal for X-ray analysis, in a Rayonet photoreactor (300 nm) under ambient conditions for ~45 h led to complete consumption of starting material, Scheme 4. The resulting solid was dissolved in CH_2Cl_2 and methylated (CH_2N_2) for characterization purposes. The ^1H and ^{13}C NMR spectral data of the tetraester **20** were consistent with a single, highly symmetrical cyclobutyl photodimer, but a distinction between the four possible isomers (α-truxillate, *δ*-truxinate, *β*-truxinate, and *ϵ*-truxillate) could not be made. The four isomers noted above

Scheme 4



for the methyl cinnamate photodimerization series were prepared by literature procedures to facilitate independent stereochemical and regiochemical assignment of **20**.[14] In addition, further naphthoate/cinnamate isomeric photodimers were prepared by irradiation of a dilute benzene solution of dimethyl ester **9** at 300 nm, Scheme 4. Control experiments indicated that the diacid **17** did not afford any cyclobutyl-containing products upon extended irradiation in THF solution, nor did crystalline diester **9** yield any photodimers when irradiated as per solid **17**. Examination of the diagnostic methine region in the ^1H NMR spectra for **20**−**22** in comparison with the four known simpler diphenyl cyclobutyl analogues prepared from cinnamate permitted unamibguous structural assignment (see the Supporting Information for copies of the relevant ^1H NMR spectra). Thus, the diacid **17** does in fact photodimerize through the closed H-bonded pair to furnish the α-truxillate stereo- and regioisomer **19**. Unfortunately direct confirmation of this conclusion was not possible, as the irradiated crystals of **18** were not suitable for X-ray analysis.

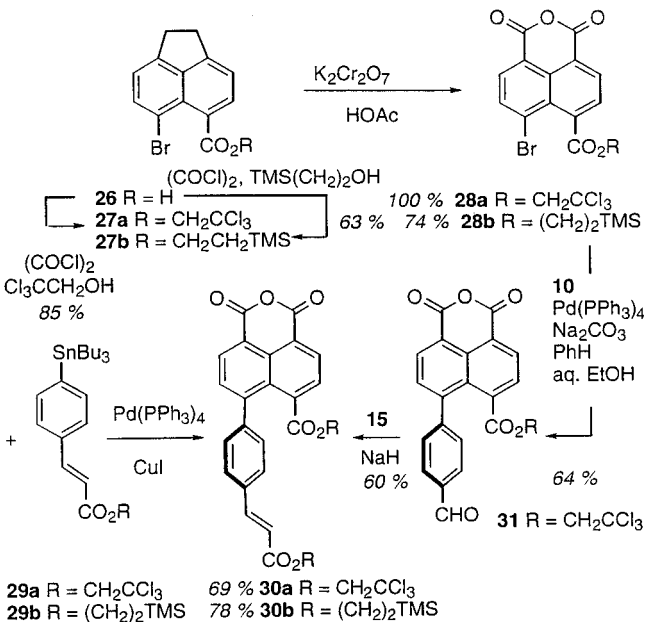
The efficiency of this photodimerization (approaching 100%) is worthy of note. In contrast, a limiting yield (~86%) for photodimerization of α-cinnamic acid has been calculated via a theoretical *independent*-site model.[6b] The unique H-bonding opportunities available to **17** render this model invalid, and the dependent-site photodimerization of **17** is not so constrained.

These encouraging results prompted design of a more advanced molecular connector with hub-attachment capabilities. This new connector would have to meet two specific criteria for success: (1) preservation of the

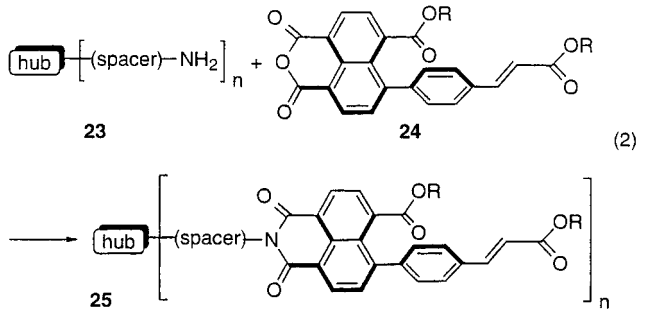
(13) Zerkowski, J. A.; MacDonald, J. C.; Seto, C. T.; Wierda, D. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2382 and references therein.

(14) (a) α-Truxillic and *β*-truxinic acids: Cohen, M. D.; Schmidt, G. M.; Sonntag, F. I. *J. Chem. Soc.* **1964**, 2000. (b) *ϵ*-Truxillic acid: Stoermer, R.; Emmel, E. *Chem. Ber.* **1920**, *53*, 7. (c) *δ*-Truxinic acid: Freedman, M.; Mohadger, Y.; Rennert, J.; Soloway, S.; Waltcher, I. *Org. Prep. Proc.* **1969**, 267.

Scheme 5



attachment linearity implicit in Scheme 1 and (2) facile and high yielding hub-to-naphthalene bond formation. The anhydride **24** appeared to satisfy these requirements, as dehydrative condensation with primary amine-bearing hubs **23** should furnish polyimide-tipped multivalent monomers ready for ester deprotection and then crystallization/photo-cross-linking, eq 2.



The choice of protecting group R in **24** again will play an important role in the outcome of this chemistry. Initial synthesis efforts were directed toward two candidates, CH_2CCl_3 and CH_2CH_2TMS (Scheme 5). Both of these species utilize requisite nonnucleophilic deprotection protocols to unveil their derived acids. However, competition for the nucleophilic primary amines of **23** between the unsaturated cinnamyl ester unit in **24** and the relatively unreactive anhydride moiety is a source of concern, especially in the more electrophilic trichloroethyl ester series.

Synthesis of both diesters **30a** and **30b** began with the known bromo acid **26**[15] available in two steps from acenaphthene (Scheme 5). Conversion of **26** into the bromo esters **27a**/**27b** proceeded without event and set the stage for the key reaction in this sequence, oxidation of the ethylene bridge. Chromic acid oxidation of **27a** and **27b** did indeed deliver the desired anhydrides **28a** and **29a**, respectively, with no evidence for destruction of the ester moieties. Similar oxidation of bromo acid **26** did not furnish the expected anhydride product. The intact cinnamyl ester unit was attached to the bromides **28a** and **28b** via Stille coupling with the stannylcinnamates **29a** and **29b**, respectively. Both of these coupling partners were available from 4-(tri-*n*-butylstannyl)benzaldehyde[16] and the appropriate Emmons–Horner reagent.[17] Stille coupling was superior to the Suzuki procedure in both the anhydride series (**28a** → **31**, 64%) and in the model naphthylene series (cf. Scheme 2, **6** + **29a** → **9**, 52%). In any event, these concise routes provide the desired naphthyl cinnamyl anhydrides in five steps from acenaphthene on a gram scale.

In summary, the feasibility of designing a molecular connector that utilizes labile H-bonds to orient reactive functionality for subsequent covalent attachment in the solid state has been demonstrated. Extension of this chemistry to the two- and three-dimensional polymerization of tri- and tetravalent monomers, respectively, will require the availability of bifunctional connectors capable of both directional H-bonding and covalent linkage to central polyvalent hub units. Naphthalene-based anhydride diesters that might serve in this capacity have been prepared. Hub attachment, deprotection, and crystallization/cross-linking studies are ongoing with these species.

Experimental Section

Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium/benzophenone under Ar immediately before use. Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under Ar. Solvents for chromatography (Et_2O, EtOAc, CH_2Cl_2, hexane) were distilled from CaH_2 prior to use. Flash column chromatography was carried out under positive pressure using 32–63 μm silica gel and the indicated solvents.[18] Melting points are uncorrected. Chemical impact mass spectra (CIMS) were obtained with isobutane as the reagent gas, and electron impact mass spectra (EIMS) were obtained at 50–70 eV. FAB high-resolution mass spectra were obtained from the mass spectrometry laboratory at the University of Texas at Austin. Combustion analyses were performed by either Galbraith Laboratories, Knoxville, TN, or Midwest Microlab, Indianapolis, IN. ^1H and ^{13}C NMR spectra are provided in the Supporting Information to establish purity for those compounds that were not subject to combustion analyses.

Dimethyl (*E*)-8-[4-(2-Propenoyl)phenyl]-1-naphylenecarboxylate (9). Methyl 8-iodo-1-naphthylenecarboxylate (**6**)[9] (377 mg, 1.2 mmol), boronic acid **10**[11] (200 mg, 1.33 mmol, 1.1 equiv), and tetrakis(triphenylphosphine)palladium (46 mg, 0.04 mmol, 0.03 equiv) in 10 mL of benzene, 5 mL of 1 M K_2CO_3, and 2 mL of EtOH were purged with Ar, heated to reflux under Ar, and maintained there for 45 h. At that time, TLC indicated that iodide **6** had been nearly totally consumed. The reaction solution was cooled to room temperature, poured into an equal volume of water, and extracted with 2 × 20 mL of Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash chromatography on silica gel (20% Et_2O/hexane as eluent) to yield 274 mg of methyl 8-(4-formylphenyl)-1-naphthylenecarboxylate (**11**) (79%) following flash chromatography on silica gel with 30% Et_2O/hexane as eluent: IR (CCl_4) 1727, 1706 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 10.05 (s, 1 H), 7.99 (dd, J = 8.2, 1.4 Hz, 1 H), 7.9 (m, 3 H), 7.75 (dd, J = 5.7, 1.6 Hz, 1 H), 7.5 (m, 5 H), 3.09 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.9, 169.8, 149.2, 138.1, 134.9, 134.7, 132.1, 130.7, 130.6, 129.8, 129.5, 129.4, 129.2, 129.1, 125.9, 125.0, 51.5; MS *m*/*z* (relative intensity) 290 (M^+, 100), 231 (55). A sample of this aldehyde (400 mg, 1.38 mmol) in 5

(15) Letsinger, R. L.; Gilpin, J. A.; Vullo, W. J. *J. Org. Chem.* **1962**, *27*, 672.
(16) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418.
(17) (a) **15**: Clayton, J. P.; Luk, K.; Rogers, N. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 312. (b) 2-(Trimethylsilyl)ethyl diethylphosphonoacetate: Taylor, E. C.; Davies, H. M. L. *J. Org. Chem.* **1986**, *51*, 1537.
(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

mL of dry DMF was added dropwise to a stirring suspension of sodium trimethylphosphonoacetate (from 66 mg of 60% NaH, degreased (1.66 mol, 1.2 equiv) and 268 μL of trimethyl phosphonoacetate (1.66 mmol, 1.2 equiv) in 10 mL of dry DMF at 0 °C. The solution was warmed to rt and stirred there until TLC analysis indicated complete consumption of starting aldehyde. The reaction solution was poured into an equal volume of ice-cold 1 M H_3PO_4. This aqueous solution was extracted with 2 × 10 mL of Et_2O, the combined organic phases were washed with saturated brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel, 30% Et_2O/hexane) to furnish 401 mg (84%) of diester **9** as a light yellow solid. Recrystallization from 3:1 Et_2O/hexane afforded 330 mg of the diester as white crystals: mp 108−110 °C; IR (CCl_4) 1725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.3, 1.4 Hz, 1 H), 7.85 (dd, J = 7.9, 1.5 Hz, 1 H), 7.74 (d, J = 15.9 Hz, 1 H), 7.73 (m, 1 H), 7.75 (m, 7H), 6.48 (d, J = 16.0 Hz, 1 H), 3.79 (s, 3 H), 3.09 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.9, 167.3, 144.9, 144.2, 138.6, 134.7, 132.9, 131.9, 130.9, 130.3, 129.1, 129.0, 128.5, 128.0, 127.9, 125.9, 124.8, 117.6, 51.52, 51.46; MS m/z (relative intensity) 346 (M^+, 100), 283 (25).

Attempted BBr_3-Mediated Demethylation of 9. Boron tribromide (2.8 mL of a 1 M CH_2Cl_2 solution, 2.8 mmol, 10 equiv) was added to a solution of diester **9** (96 mg, 0.28 mmol) in 2 mL of CH_2Cl_2 at −10 °C. The dark red solution was warmed to rt and, after 24 h at that temperature, poured into an equal volume of ice-cold 1 M H_3PO_4. The mixture was extracted with 2 × 10 mL of CH_2Cl_2, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to furnish 79 mg (90%) of **12** as a yellow solid that was clean by ^{1}H NMR: IR (CCl_4) 1697 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$ + DMSO-d_6) δ 8.71 (d, J = 6.2 Hz, 1H), 8.59 (d, J = 7.5 Hz, 1H), 8.55 (d, J = 2 Hz, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.00 (dd, J = 8.3, 1.8 Hz, 1H), 7.7 (m, 3H), 6.64 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (90 MHz, $CDCl_3$ + DMSO-d_6) δ 181.7, 165.7, 136.1, 132.8, 131.9, 131.0, 129.8, 128.6, 127.2, 128.1, 126.5, 125.7, 125.0, 124.1, 123.1, 120.1, 117.2, 50.4; MS m/z (relative intensity) 314 (M^+, 35); HRMS calcd for $C_{21}H_{14}O_3$ 314.0943, found 314.0933.

2,2,2-Trichloroethyl 8-Iodo-1-naphthylenecarboxylate (13b). 8-Iodonaphthylenecarboxylic acid (**13a**)[9] (1.53 g, 5.1 mmol) suspended in 5 mL of CH_2Cl_2 was treated sequentially with oxalyl chloride (527 μL, 6.2 mmol, 1.2 equiv) and then 1 drop of DMF. A vigorous reaction ensued that resulted in a homogeneous yellow solution after 5 min at rt. This solution was concentrated in vacuo, and the residue was redissolved in 10 mL of CH_2Cl_2, and (dimethylamino)pyridine (756 mg, 6.2 mmol, 1.2 equiv) followed by 2,2,2-trichloroethanol (596 μL, 6.2 mmol, 1.2 equiv) were added with efficient stirring at rt. TLC indicated complete consumption of intermediate acid chloride after 22 h, and so the reaction solution was poured into an equal volume of ice-cold 1 M H_3PO_4. The aqueous layer was extracted with 3 × 20 mL of CH_2Cl_2, and the combined organic phases were washed with saturated brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to furnish a yellow oil. Crystallization of the oil from 2:1 hexane/CH_2Cl_2 afforded 1.06 g of a yellow solid. Flash column chromatography (silica gel) on the filtrate (10% Et_2O/hexane as eluent) furnished an additional 556 mg of ester **13b** as a yellow solid (total = 1.62 g, 74%). A sample for elemental analysis was prepared by vapor diffusion crystallization from THF/hexane: mp 85−86 °C; IR (CCl_4) 1745 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.24 (dd, J = 7.3, 1.1 Hz, 1 H), 7.91 (td, J = 7.7, 1.2 Hz, 2 H), 7.81 (dd, J = 7.2, 1.4 Hz, 1 H), 7.50 (dd, J = 8.1, 7.2 Hz, 1 H), 7.20 (t, J = 7.8 Hz, 1 H), 5.11 (s, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.8, 141.9, 135.4, 132.8, 132.7, 131.3, 129.7, 129.6, 127.6, 125.2, 94.8, 92.5 75.4; MS m/z (relative intensity) 428 (M^+, 11), 281 (82). Anal. Calcd for $C_{13}H_8Cl_3IO_2$: C, 36.34; H, 1.88. Found: C, 36.48; H, 1.89.

2,2,2-Trichloroethyl 8-(4-Formylphenyl)-1-naphthylenecarboxylate (14). Bromide **13b** (629 mg, 1.46 mmol), (4-formylphenyl)boronic acid (**10**)[12] (235 mg, 1.56 mmol, 1.07 equiv), and $Pd(PPh_3)_4$ (87 mg, 0.08 mmol, 0.05 equiv) were added to 5 mL of benzene, 3 mL of 1 M K_2CO_3, and 2 mL of EtOH. This heterogeneous mixture was purged with Ar, heated to reflux under Ar, and maintained there for 45 h. At that time, TLC indicated that bromide **13b** had been nearly totally consumed. The reaction solution was cooled to rt, poured into an equal volume of water, and extracted with 2 × 20 mL of Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by the flash chromatography on silica gel (20% Et_2O/hexane as eluent) to yield 309 mg of aldehyde **14** as a white solid (52%). A sample for elemental analysis was prepared by vapor diffusion crystallization with THF/hexane: mp 130−132 °C; IR (CCl_4) 1743, 1701 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.09 (s, 1 H), 8.09 (dd, J = 8.2, 1.3 Hz, 1 H), 7.96 (d, J = 8.1 Hz, 2 H), 7.9 (m, 1 H), 7.89 (dd, J = 7.1, 1.3 Hz, 1H), 7.6 (m, 5H), 4.17 (s, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 191.7, 166.9, 149.1, 138.0, 135.0, 134.8, 132.8, 130.8, 129.9, 129.8, 129.4, 129.14, 129.08, 127.9, 126.2, 125.0, 94.6, 74.0; MS m/z (relative intensity) 408 (M^+, 14), 406 (13), 231 (78). Anal. Calcd for $C_{20}H_{13}Cl_3O_3$: C, 58.89; H, 3.21; Cl, 26.61. Found: C, 58.90; H, 3.19; Cl 27.10.

2,2,2-Trichloroethyl (*E*)-8-[4-[[(2,2,2-Trichloroethoxy)-carbonyl]ethenyl]phenyl]-1-naphthylenecarboxylate (16). 2,2,2-Trichloroethyl diethoxyphosphonoacetate (**15**)[17] (145 mg, 0.44 mmol, 1.2 equiv) was added dropwise to a stirring suspension of degreased NaH (60% suspension in oil, 189 mg, 0.44 mmol, 1.2 equiv) in 1 mL of dry DMF. After gas evolution had ceased, solid aldehyde **14** (150 mg, 0.37 mmol) was added in one portion, resulting in a homogeneous, light orange solution. After 30 min, TLC indicated consumption of starting aldehyde, and so the reaction solution was poured into an equal volume of ice-cold 1 M H_3PO_4. This aqueous solution was extracted with 2 × 10 mL of Et_2O, the combined organic phases were washed with saturated brine, dried over Na_2SO_4, filtered, concentrated in vacuo, and the white solid residue was purified by crystallization from 20% Et_2O in hexane to furnish 170 mg of diester **16** as a white powdery solid (79%). A sample for elemental analysis was prepared by vapor diffusion crystallization from THF/hexane: mp 181−182 °C; IR (CCl_4) 1740 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) 8.08 (dd, J = 8.3, 1.3 Hz, 1 H), 7.94 (dd, J = 8.1, 1.3 Hz, 1 H), 7.88 (d, J = 16.0 Hz, 1H), 7.87 (dd, J = 7.0, 1.3 Hz, 1 H), 7.6 (m, 5 H), 7.44 (d, J = 8.2 Hz, 2 H), 6.60 (d, J = 16.0 Hz, 1 H), 4.90 (s, 2 H), 4.18 (s, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.7, 165.2, 146.4, 145.4, 138.4, 134.7, 132.8, 131.2, 130.6, 129.6, 129.5, 129.4, 128.83, 128.77, 128.4, 126.6, 124.9, 116.5, 95.2, 94.7, 74.2; MS m/z (relative intensity) 580 (M^+, 100), 283 (75). Anal. Calcd for $C_{24}H_{16}Cl_6O_4$: C, 49.61; H, 2.78; Cl, 36.61. Found: C, 50.01; H, 2.86; Cl, 36.67.

From Stannane 29a. Ester **13b** (4.0 g, 9.3 mmol) and CuI (89 mg, 0.47 mmol, 0.47 equiv) was dissolved in toluene (100 mL), and a solution of $Pd(PPh_3)_4$ (269 mg, 0.23 mmol, 0.025 equiv) in 50 mL of toluene was added followed by the cinnamic ester **29a** (8.0 g, 14 mmol, 1.5 equiv) in toluene (50 mL). After 20 h at reflux, TLC analysis indicated complete consumption of starting material. The reaction mixture was cooled, filtered through Celite, and washed with Et_2O (3 × 50 mL). The organic phase was washed with water (100 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo to afford a yellow oil that was purified as above to yield 2.8 g of diester **16** as a yellow solid (52%).

(*E*)-8-[4-(Carboxyethenyl)phenyl)-1-naphthylenecarboxylic Acid (17). Diester **16** (415 mg, 0.72 mmol) and activated Zn (700 mg, 10.7 mmol, 15 equiv) were added to a solution of 4 mL of HOAc and 40 mL of THF. After vigorous stirring at rt for 1.5 h, TLC analysis indicated complete consumption of starting material. The reaction solution was filtered through Celite, and the zinc-containing residue was washed with 3 × 20 mL of THF. The filtrate was concentrated in vacuo to give a white solid that was dissolved in 20 mL of 1 N NaOH. This homogeneous basic solution was washed with 3 × 20 mL of Et_2O, treated with activated charcoal, filtered, and acidified with 1 M H_2SO_4 until a white precipitate formed. The aqueous acidic solution was extracted with 3 × 50 mL of EtOAc, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to furnish pure diacid **17** as a white solid (180 mg, 79%). Vapor

diffusion crystallization with THF/hexane afforded a sample that decomposed without melting at 322−326 °C: IR (KBr) 3457, 1690 cm^{-1}; ^1H NMR (200 MHz, 1:1 $CDCl_3$/DMSO-d_6) δ 12.1 (brs, 2 H), 8.04 (dd, J = 7.9, 1.2 Hz, 1 H), 7.93 (dd, J = 8.0, 1.3 Hz, 1 H), 7.75 (dd, J = 8.0, 7.0 Hz, 1 H), 7.6−7.4 (m, 8 H), 6.47 (d, J = 16.0 Hz, 1 H); ^{13}C NMR (50 MHz, 1:1 $CDCl_3$/DMSO-d_6) δ 169.4, 167.0, 143.9, 142.8, 137.7, 133.5, 131.6, 131.1, 130.2, 129.0, 128.0, 127.5, 127.2, 126.7, 126.6, 124.6, 123.7, 117.5; MS m/z (relative intensity) 318 (M^+, 100); HRMS calcd for $C_{20}H_{14}O_4$ 318.0892, found 318.0901.

Irradiation of Crystalline Diacid 17. A sample of recrystallized diacid **17** (48 mg, 0.15 mmol) in a Pyrex flask was irradiated in a Rayonet photoreactor equipped with 300 nm bulbs (ambient temperature ~45 °C). TLC monitoring of small portions quenched with ethereal diazomethane indicated clean conversion of diacid to a single photoproduct. After 45 h, no starting diacid remained, and so the slightly yellow solid was suspended in 5 mL of CH_2Cl_2 and treated with excess ethereal diazomethane. A few drops of HOAc were added to quench any remaining diazomethane, the solution was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel (20% Et_2O/CH_2Cl_2) to afford 30 mg of cyclobutane product **20** as a white solid (57%). A sample obtained by vapor diffusion crystallization with 1,2-dichloroethane/hexane melted at 238−239 °C: IR ($CDCl_3$) 1715 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.3, 1.3 Hz, 2 H), 7.88 (dd, J = 8.2, 1.2 Hz, 2 H), 7.72 (dd, J = 7.1, 1.4 Hz, 2 H), 7.6 (m, 4 H), 4.53 (dd, J = 10.6, 7.2 Hz, 2 H), 4.08 (dd, J = 10.3, 7.1 Hz, 2 H), 3.57 (s, 6 H), 3.17 (s, 6 H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.4, 170.2, 141.8, 139.1, 137.5, 134.8, 131.9, 131.3, 130.6, 129.0, 128.8, 128.1, 127.4, 125.9, 124.7, 51.9, 51.8, 46.7, 41.5; MS m/z (relative intensity) 692 (M^+, 90), 346 (100); HRMS calcd for $C_{44}H_{36}O_8$ 692.2410, found 692.2356.

A sample of crystalline diacid **17** (12.0 mg) *taken from the batch of crystals used for the X-ray structural determination* yielded 12.6 mg of diester **19** (96%) after similar reaction.

Irradiation of Dimethyl Ester 9 in Benzene Solution. A sample of recrystallized diester **9** (10 mg, 29 μmol) in 1.5 mL of C_6D_6 was purged with Ar and irradiated in a Rayonet photochemical reactor equipped with 300 nm bulbs at rt with periodic ^1H NMR monitoring. After 6 days of exposure, ^1H NMR indicated that all but ~10% of the starting diester was consumed. The reaction was concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel, 50% Et_2O/hexane) to afford 2 mg (20%) of the δ-truxinate cyclobutane dimer **21** followed by 2 mg (20%) of the β-truxinate isomer **22**. No other cyclobutane-containing products were detected (^1H NMR, TLC).

21: IR (CCl_4) 1715 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.2, 1.4 Hz, 2 H), 7.89 (dd, J = 8.0, 1.6 Hz, 2 H), 7.70 (dd, J = 7.0, 1.4 Hz, 2 H), 7.5 (m, 6 H), 7.4 (m, 8 H), 3.77 (m, 8 H), 3.58 (m, 2 H), 3.11 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.8, 170.1, 141.9, 139.4, 134.8, 131.8, 131.3, 130.5, 129.1, 129.0, 128.2, 126.8, 126.0, 124.7, 70.4, 52.2, 51.6, 47.9, 44.5, MS m/z (relative intensity) 692 (M^+, 50), 548 (80), 346 (100); HRMS calcd for $C_{44}H_{36}O_8$ 692.2410, found 692.2391.

22: IR (CCl_4) 1712 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.2, 1.2 Hz, 2 H), 7.83 (dd, J = 8.1, 1.4 Hz, 2 H), 7.68 (dd, J = 7.1, 1.4 Hz, 2 H), 7.4 (m, 8 H), 7.2 (m, 6 H), 4.50 (d, J = 6.4 Hz, 2 H), 3.92 (d, J = 6.3 Hz, 2 H), 3.78 (s, 6 H), 2.79 (s, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.0, 170.2, 141.4, 139.2, 137.6, 134.9, 132.0, 131.3, 130.7, 129.2, 128.7, 128.2, 127.5, 126.1, 124.8, 63.6, 52.3, 51.5, 45.0, 43.7; MS m/z (relative intensity) 692 (M^+, 45), 346 (100); HRMS calcd for $C_{44}H_{36}O_8$ 692.2410, found 692.2441.

2,2,2-Trichloroethyl 5-Bromo-6-acenaphthenecarboxylate (27a). 5-Bromo-6-acenaphthenecarboxylic acid (**26**)[15] (1.77 g, 6.4 mmol) was suspended in CH_2Cl_2 (20 mL). Oxalyl chloride (664 μL, 7.7 mmol, 1.2 equiv) was added followed by DMF (2 drops), resulting in immediate gas evolution. The mixture was stirred at room temperature for 20 min, at which time the homogeneous solution was concentrated in vacuo and the residue was redissolved in CH_2Cl_2 (20 mL). 4-(Dimethylamino)pyridine (939 mg, 7.7 mmol, 1.2 equiv) was added followed by 2,2,2-trichloroethanol (760 μL, 7.7 mmol, 1.2 equiv). After 8 d, the mixture was poured into an equal volume of ice-cold 1 M H_3PO_4 and extracted with CH_2Cl_2 (3 × 40 mL). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated in vacuo, and the resulting solid was purified by flash chromatography on silica gel (20% CH_2Cl_2/hexane as eluent) to afford 2.21 g of ester **27a** as a white solid (85%): mp 174−176 °C; IR ($CHCl_3$) 1738 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.77 (d, J = 7.4 Hz, 1 H), 7.71 (d, J = 7.2 Hz, 1 H), 7.33 (d, J = 7.2 Hz, 1 H), 7.20 (d, J = 7.4 Hz, 1 H), 5.07 (s, 2 H), 3.39 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.2, 150.3, 146.5, 140.8, 134.4, 130.5, 127.2, 125.9, 121.3, 119.2, 114.1, 94.9, 75.1, 30.6, 29.9; MS m/z (relative intensity) 406 (M^+,18), 152 (100); HRMS calcd for $C_{15}H_{11}O_2Cl_3Br$ 406.9008, found 406.9005.

4-Bromo-5-[(2,2,2-trichloroethoxy)carbonyl]-1,8-naphthalic Anhydride (28a). $K_2Cr_2O_7$ (7.4 g, 25 mmol, 7 equiv) was added to a hot solution of the ester **27a** (1.42 g, 3.5 mmol) in 50 mL of 85% aqueous acetic acid. The mixture was refluxed for 24 h and cooled, and water (300 mL) was added. The resulting solution with white precipitate was cooled in ice, filtered, and washed with copious amounts of water to give 0.90 g of **28a** as a white powder (100%): mp 152−153 °C; IR (CCl_4) 1785, 1745 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.74 (d, J = 7.5 Hz, 1 H), 8.53 (d, J = 7.9 Hz, 1 H), 8.24 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.5 Hz, 1 H), 5.10 (s, 2 H); ^{13}C (50 MHz, $CDCl_3$) δ 166.3, 159.3, 159.1, 137.3, 134.7, 133.7, 133.1, 131.8, 129.3, 128.7, 127.4, 121.4, 118.6, 94.0, 75.6; MS m/z (relative intensity) 450 (M^+, 3.4), 241 (100); HRMS calcd for $C_{15}H_7O_5Cl_3Br$ 450.8542, found 450.8539.

4-(4-Formylphenyl)-5-[(2,2,2-trichloroethoxy)carbonyl]-1,8-naphthalic Anhydride (31). Anhydride **28a** (1.16 g, 2.6 mmol) and $Pd(OAc)_2$ (60 mg, 0.26 mmol, 0.1 equiv) were suspended in THF (2.5 mL). To this mixture was added a solution containing (4-formylphenyl)boronic acid (**10**) (585 mg, 3.89 mmol, 1.5 equiv), 1 M K_2CO_3 (7.3 mL, 3 equiv), and 2.5 mL of THF. The mixture was brought to reflux and held there for 20 h, cooled, filtered through Celite, and washed with water (2 × 10 mL). The aqueous layer was washed with EtOAc (50 mL), and the organic layers were discarded. The aqueous layer was acidified with 1 M H_2SO_4, extracted with EtOAc (6 × 50 mL), dried with Na_2SO_4, and concentrated in vacuo. The solid residue was titurated with EtOAc and filtered. The filtrate was concentrated in vacuo and subjected to flash chromatography on silica gel (30% EtOAc/hexane as eluent) to afford the desired aldehyde **31** as a yellow solid. Additional material was obtained by refluxing the undissolved solid from the EtOAc trituration in water (50 mL) and DMSO (5 mL) for 24 h followed by extracting the aqueous solution with CH_2Cl_2 (4 × 100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated in vacuo to provide a yellow oil that was dissolved in $CHCl_3$ and concentrated to afford a yellow solid. Flash chromatography on silica gel (2% EtOAc/CH_2Cl_2 as eluent) produced a total of 0.7 g of a yellow solid (64%): mp 198−200 °C; IR ($CHCl_3$) 1786, 1742, 1705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 10.12 (s, 1 H), 8.75 (d, J = 7.6 Hz, 1 H), 8.73 (d, J = 7.6 Hz, 1 H), 8.11 (d, J = 7.6 Hz, 1 H), 8.02 (d, J = 8.2 Hz, 2 H), 7.87 (d, J = 7.6 Hz, 1 H), 7.61 (d, J = 8.2 Hz, 2 H), 4.16 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 165.1, 159.6, 159.5, 145.8, 136.2, 133.3, 132.6, 131.5, 130.0, 129.9, 129.5, 126.9, 121.8, 118.7, 93.9, 74.4; MS m/z (relative intensity) 476 (M^+,100); HRMS calcd for $C_{22}H_{11}O_6Cl_3$ 475.9621, found 475.9624.

2,2,2-Trichloroethyl (*E*)-4-Carboxy-5-[4-[[(2,2,2-Trichloroethoxy)carbonyl]ethenyl]phenyl)-1,8-naphthalic Anhydride (30a). From Aldehyde 31. 2,2,2-Trichloroethyl diethoxyphosphonoacetate[17a] (667 mg, 2.0 mmol, 1.7 equiv) was dissolved in 5 mL of DMF and added via cannula to a stirring suspension of degreased NaH (60% suspension in oil, 110 mg, 4.6 mmol, 3.8 equiv) in 5 mL of dry DMF at rt. After gas evolution had ceased, aldehyde **31** was added in one portion. After 5 h, TLC indicated complete consumption of **31**, and so the reaction mixture was poured into ice-cold 1 M H_3PO_4 (5 mL) and extracted with EtOAc (4 × 100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated in vacuo. The resulting oil was purified by flash chromatography on silica gel (30% EtOAc/hexane as eluent) to afford 468 mg of **30a** as a yellow solid (60%): mp 112−114 °C; IR ($CHCl_3$)

1784, 1742, 1638 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.76 (d, $J = 7.6$ Hz, 1 H), 8.74 (d, $J = 7.5$ Hz, 1 H), 8.10 (d, $J = 7.5$ Hz, 1 H), 7.90 (m, 2 H), 7.73 (d, $J = 8.2$ Hz, 2 H), 7.51 (d, $J = 8.2$ Hz, 2 H), 6.66 (d, $J = 16.0$ Hz, 1 H), 4.91 (s, 2 H), 4.20 (s, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 165.3, 164.8, 146.5, 145.4, 142.4, 136.5, 134.6, 133.3, 132.5, 131.7, 131.4, 129.7, 128.7, 127.2, 121.8, 118.4, 118.0, 95.0, 94.1, 74.5, 74.3; MS *m/z* (relative intensity) 648 (M^+, 16); HRMS calcd for $C_{26}H_{15}O_7Cl_6$ 648.8949, found 648.8954.

From Bromide 28a. Anhydride **28a** (1.12 g, 2.5 mmol) was mixed with CuI (48 mg, 0.25 mmol, 0.1 equiv), and then a solution of $Pd(PPh_3)_4$ (145 mg, 0.125 mmol, 0.05 equiv) dissolved in 30 mL of toluene, followed by the cinnamic ester **29a** in toluene (10 mL), was added. The mixture was heated to reflux, and after 15 h at reflux, the solution was cooled to rt, filtered through Celite, and washed with Et_2O (2 × 50 mL). The combined organic phases were washed with water (2 × 50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo, and the resulting orange oil was purified by flash chromatography on silica gel (30% EtOAc/hexane as eluent). Residual tin compounds were removed by hexane trituration to provide 1.12 g of **30a** as yellow solid (69%).

2,2,2-Trichloroethyl (*E*)-3-[4-(Tri-*n*-butylstannyl)phenyl]prop-2-enoate (29a). 2,2,2-Trichloroethyl diethoxyphosphonoacetate (274 mg, 0.84 mmol, 1.2 equiv) was dissolved in 2 mL of DMF and transferred via cannula to a stirring suspension of degreased NaH (60% suspension in oil, 40 mg, 1 mmol, 1.4 equiv) in 1.5 mL of DMF at rt. After gas evolution had ceased, 4-(tri-*n*-butylstannyl)benzaldehyde[16] (283 mg, 0.7 mmol) dissolved in 2 mL of DMF was added. The reaction mixture was stirred for 6 h, at which time TLC analysis indicated complete consumption of the aldehyde. The mixture was poured into an equal volume of ice-cold 1 M H_3PO_4 and extracted with Et_2O (2 × 50 mL). The organic phase was washed with brine (50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Silica gel flash chromatography (40% ether/hexane as eluent) afforded 355 mg of **29a** as an orange oil (89%): IR ($CHCl_3$) 1723, 1634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, $J = 16.0$ Hz, 1 H), 7.51 (m, 4 H), 6.54 (d, $J = 16.0$ Hz, 1 H) 4.87 (s, 2 H), 1.53 (m, 6 H), 1.35 (m, 6 H), 1.07 (m, 6 H), 0.88 (t, $J = 7.2$ Hz, 9 H); ^{13}C (90 MHz, $CDCl_3$) δ 165.2, 147.5, 147.1, 137.0, 133.5, 127.4 ($J_{C-Sn} = 19.9$ Hz), 115.8, 95.2, 74.1, 29.8, 27.3 ($J_{C-Sn} = 27.8$ Hz), 13.6, 9.7 ($J_{C-^{119}Sn} = 170.8$ Hz, $J_{C-^{117}Sn} = 163.2$ Hz); MS *m/z* (relative intensity) 511 ($M^+ - Bu$, 100); HRMS calcd for $C_{19}H_{26}O_2Cl_3Sn$ ($M^+ - Bu$) 511.0042, found 511.0020.

2-(Trimethylsilyl)ethyl 5-Bromo-6-acenaphthenecarboxylate (27b). 5-Bromo-6-acenaphthenecarboxylic acid (**26**) (1.90 g, 6.8 mmol) was suspended in 25 mL of thionyl chloride (343 mmol, 50 equiv) at rt. After 3 h of vigorous stirring, the now homogeneous orange solution was concentrated in vacuo. 4(-Dimethylamino)pyridine (1.16 g, 9.5 mmol, 1.4 equiv) was added followed by 9 mL of CH_2Cl_2 and 2-(trimethylsilyl)ethanol (1.1 mL, 7.5 mmol, 1.1 equiv). After 60 h at rt, the dark brown solution was poured into 15 mL of 1 M H_3PO_4. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to furnish 2.09 g of a brown residue. Flash column chromatography of this material on silica gel (5% EtOAc/hexane as eluent) afforded 1.81 g of ester **27b** as a light yellow solid (63%): mp 96−98 °C (recryst EtOAc); IR (CH_2Cl_2) 1719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, $J = 7.4$ Hz, 1 H), 7.45 (d, $J = 7.1$ Hz, 1 H), 7.08 (d, $J = 7.1$ Hz, 1 H), 6.93 (d, $J = 7.4$ Hz, 1 H), 4.43 (m, 2 H), 3.12 (m, 4H), 1.09 (m, 2 H), 0.00 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 148.9, 146.1, 140.4, 133.8, 129.5, 127.8, 126.8, 120.7, 118.9, 114.0, 63.8, 30.2, 29.5, 17.0, −1.6; MS *m/z* (relative intensity) 378 (M^+, 7), 269 (52).

4-Bromo-5-[[2-(trimethylsilyl)ethoxy]carbonyl]-1,8-naphthalic Anhydride (28b). Ester **27b** (2.99 g, 7.9 mmol) in 89 mL of 85% aqueous HOAc was treated with $K_2Cr_2O_7$ (12.2 g, 41.3 mmol, 5.2 equiv), and the mixture was heated to 95 °C for 5 h. The orange solution was cooled to rt and then poured into 200 mL of ice-water. The resulting white solution/suspension was extracted with EtOAc (3 × 200 mL). The combined organic phases were washed with saturated $NaHCO_3$ (3 × 200 mL) and then brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford 2.46 g of **28b** as an orange solid (74%): mp 176−179 °C; IR(CH_2Cl_2) 1783, 1743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, $J = 7.5$ Hz, 1 H), 8.46 (d, $J = 7.9$ Hz, 1 H), 8.18 (d, $J = 7.9$ Hz, 1 H), 7.86 (d, $J = 7.5$ Hz, 1 H), 4.53 (m, 2 H), 1.15 (m, 2 H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 159.5, 159.3, 139.6, 134.5, 133.4, 133.2, 131.8, 129.1, 128.7, 127.4, 120.6, 118.5, 65.6, 17.1, <1.5; MS *m/z* (relative intensity) 422 (M^+, 5) 231 (49). Anal. Calcd for $C_{18}H_{17}O_5BrSi$: C, 51.48; H, 4.08; Br, 18.81. Found: C, 51.56; H,4.13; Br, 18.86.

2-(Trimethylsilyl)ethyl (*E*)-3-[4-(Tri-*n*-butylstannyl)-phenyl]prop-2-enoate (29b). 2-(Trimethylsilyl)ethyl diethoxyphosphanoacetate[17b] (2.00 g, 6.75 mmol, 1.1 equiv) was dissolved in 10 mL of DMF and transferred to a stirring suspension of degreased NaH (60% suspension in oil, 162 mg, 6.75 mmol, 1.1 equiv) in 10 mL of DMF at 0 °C. After gas evolution had ceased and the reaction mixture turned clear yellow (ca. 10 min), 4-(tri-*n*-butylstannyl)benzaldehyde (2.43 g, 6.14 mmol) in 10 mL of DMF was added. The solution was allowed to warm to rt and stirred for 2 h, at which time TLC analysis indicated consumption of the aldehyde. The mixture was poured into an equal volume of ice-cold 1 M H_3PO_4 and extracted with Et_2O (3 × 25 mL). The organic phase was washed with brine (75 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. The resulting yellow oil was purified by flash chromatography on silica gel (1% Et_2O/hexane as eluent) to afford 2.30 g of **29b** as a colorless oil (70%): IR ($CDCl_3$) 1702 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.66 (d, $J = 16.0$ Hz, 1H), 7.47 (m, 4H), 6.43 (d, $J = 16.0$ Hz, 1H), 4.29 (t, $J = 8.3$ Hz, 2H), 1.32 (m, 6H), 1.29 (m, 8H), 1.10 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 9H), 0.067 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.1, 145.9, 144.8, 136.9 ($J_{Sn-C} = 15.1$ Hz), 134.0, 127.2 ($J_{Sn-C} = 20.1$ Hz), 118.0, 62.6, 29.0 ($J_{C-Sn} = 10.2$ Hz), 27.3 ($J_{C-Sn} = 27.7$ Hz), 17.4, 13.6, 9.59 ($J_{C-^{119}Sn} = 170.6$, $J_{C-^{117}Sn} = 163.0$ Hz), −1.50; MS *m/z* (relative intensity) 537 (M^+, 1); HRMS calcd for $C_{26}H_{46}O_2SiSn$ 537.4242, found 537.4756.

2-(Trimethylsilyl)ethyl (*E*)-4-[[2-(Trimethylsilyl)ethoxy]carbonyl]-5-[4-[[[2-(trimethylsilyl)ethoxy]carbonyl]ethenyl]phenyl]-1,8-naphthalic Anhydride (30b). Anhydride **28b** (0.97 g, 2.3 mmol), copper(I) iodide (61 mg, 0.32 mmol, 0.14 equiv), and stannylcinnamic ester **29b** (1.48 g, 2.8 mmol, 1.2 equiv) were combined in 15 mL of toluene. $Pd(PPh_3)_4$ (185 mg, 0.16 mmol, 0.07 equiv) in 15 mL of toluene was added to the reaction mixture, and the red solution was heated to reflux and held there for 22 h. At that time, the solution was cooled to rt and filtered through Celite. The filtrate was washed with water (2 × 40 mL) and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The red-brown solid was triturated with 50 mL of hexane. The solid residue was dried in vacuo to afford 1.06 g of the diester **30b** as a red-brown solid (78%). Vapor diffusion crystallization from CH_2Cl_2/hexane resulted in a sample melting at 188−190 °C: IR (CH_2Cl_2) 1781, 1741, 1716 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.71 (d, $J = 7.6$ Hz, 1 H), 8.69 (d, $J = 7.5$ Hz, 1 H), 7.96 (d, $J = 7.5$ Hz, 1 H), 7.82 (d, $J = 7.6$ Hz, 1 H), 7.71 (d, $J = 16.1$ Hz, 1 H), 7.65 (d, $J = 8.2$ Hz, 2 H), 7.45 (d, $J = 8.2$ Hz, 2 H), 6.50 (d, $J = 16.0$ Hz, 1 H), 4.33 (m, 2 H), 3.55 (m, 2 H), 1.08 (m, 2 H), 0.81 (m, 2 H), 0.08 (s, 9 H), −0.04 (s, 9 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.6, 166.7, 159.9, 147.0, 142.9, 142.0, 139.0, 134.8, 133.1, 132.7, 131.6, 131.2, 129.4, 129.2, 128.2, 127.1, 120.8, 119.8, 118.0, 64.7, 62.9, 17.3, 17.0, −1.5, −1.6; MS *m/z* (relative intensity) 589 (M^+, 0.9) 518 (10).

Acknowledgment. This work was supported by the NSF under the auspices of CHE9321787.

Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra for compounds **9**, **11**, **12**, **17**, **20**−**22**, **27a**,**b**, **28a**, **29a**,**b**, **30a**,**b**, and **31** and copies of diagnostic regions of the ^1H NMR spectra of the methyl esters of α-truxillic, ϵ-truxillic, β-truxinic, and δ-truxinic acids (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9714167