

**Cascade Radical Cyclizations of Benzannulated Enyne–Allenenes.
Unusual Cleavage of a Benzene Ring Leading to Twisted
1,1'-Dialkyl-9,9'-bifluorenylidenes and
Spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorenes]**

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Treatment of the benzannulated enediynyl propargylic alcohol **16** (isomer ratio = 2:1) with thionyl chloride induced a sequence of reactions leading to the twisted 1,1'-dipropyl-9,9'-bifluorenylidene **17**, the polycyclic compounds **18** and **19**, and the spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] **20** (trans/cis = 5:1). The transformation from **16** to the unexpected **17** presumably involved an initial formation of the benzannulated enyne–allene **21** followed by a C²–C⁶ cyclization reaction and an intramolecular radical–radical coupling reaction, giving rise to the formal Diels–Alder adduct **23**. Repeat of this sequence then furnished **24**. Cleavage of the bond connecting the two carbons having the propyl substituent afforded **25**. A subsequent rotation of the carbon–carbon bond joining the two central five-membered rings then gave the trans isomer **26**. Oxidation of **26**, presumably by oxygen, followed by hydrolysis then produced **17**. Interestingly, the pathway leading to **17** involved an unusual cleavage of a benzene ring. The X-ray crystal structure of **17** reveals that it has a twist angle of 45.2° for the carbon–carbon double bond connecting the two bifluorenylidene fragments. The spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] **20** apparently was produced via two intramolecular [2 + 2] cycloaddition reactions of the benzannulated enyne–allene moieties, generated in situ from the benzannulated enediynyl propargylic alcohols. The twisted 1,1'-dimethyl-9,9'-bifluorenylidene **33** and the spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] **39** (trans/cis = 3:1) were likewise produced from **32** and **38**, respectively.

Introduction

We recently reported the use of thionyl chloride to induce an S_Ni' reaction of the benzannulated enediynyl propargylic alcohol **2**, derived from condensation between 9-fluorenone and the lithium acetylide **1** (Scheme 1).¹ It provided a convenient pathway to produce in situ the benzannulated enyne–allene **4**. A subsequent C²–C⁶ cyclization reaction (Schmittel cyclization) then generated the biradical **5**, which in turn underwent an intramolecular radical–radical coupling to give the formal Diels–Alder adduct **6**. Tautomerization followed by hydrolysis then afforded **8** in 74% yield. Although the transformation from **4** to **6** could also be regarded as a concerted Diels–Alder reaction, the mechanistic,² theoretical,³ and DNA-cleaving⁴ studies suggest a two-step biradical path-

way. Interestingly, in addition to **8**, a minor amount of the [2 + 2] cycloaddition adduct **9** (12%) as a derivative of spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]fluorene] was also isolated. This synthetic strategy was adopted for the synthesis of a C₄₄H₂₆ hydrocarbon having a carbon framework represented on the surface of C₆₀.⁵ Furthermore, by employing a system containing two units of the benzannulated enyne–allene moiety, three highly twisted 4,5-diarylphenanthrenes were obtained.⁶

We were interested in further exploring the use of molecules having two benzannulated enyne–allene units for the synthesis of polycyclic aromatic compounds. It was quite unexpected that this strategy led to the formation of highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes.

Because of overcrowding, the two fluorenylidene fragments of 9,9'-bifluorenylidenes are severely twisted.⁷ The

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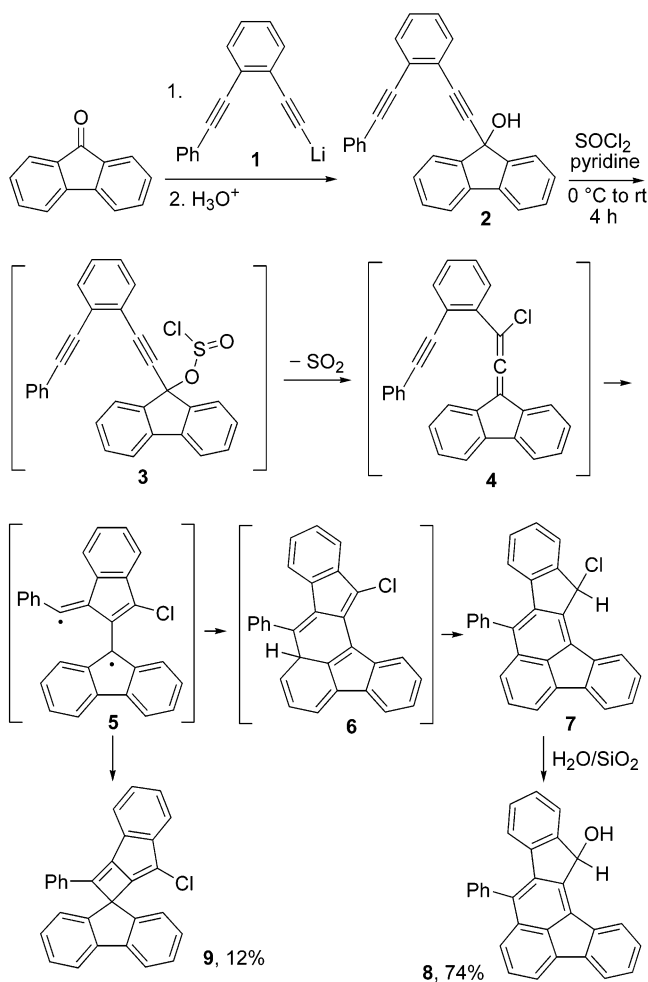
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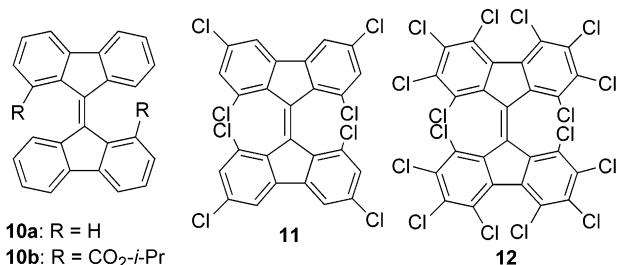
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SCHEME 1



crystal structure of the parent compound **10a** shows a twist angle of ca. 42° while the more crowded 1,1'-disubstituted 9,9'-bifluorenylidene **10b** exhibits a higher twist angle of ca. 52° .^{7a} Remarkable twist angles of 55° and 66° were recently reported for the octachlorobifluorenylidene **11** and the perchlorobifluorenylidene **12**, respectively.^{7b} The reported synthetic methods for 9,9'-bifluorenylidenes generally involve coupling of two fluorenyl fragments.⁷



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Results and Discussion

The diketone **15** was synthesized by treatment of **13**⁸ with 4-octyne to form **14** followed by two intramolecular acylation reactions (Scheme 2). Condensation between **15** and 2 equiv of **1** then provided the benzannulated enediynyl propargylic alcohol **16** as a mixture of the trans and cis isomers (isomer ratio = 2:1). Upon treatment with thionyl chloride, four products, including the 1,1'-dipropyl-9,9'-bifluorenylidene **17**, the polycyclic compounds **18** and **19**, and the spiro[1*H*-cyclobut[*a*]indene-1,9'-[9*H*]-fluorene] **20** as a mixture of the trans and cis isomers (trans/cis = 5:1), were isolated. The structures of **17**, **19**, and the trans isomer of **20** were established by X-ray structure analysis.

The formation of the products **17**, **18**, and **19** was unexpected. Apparently in the case of **17**, the intramolecular radical–radical coupling of the initially formed biradical **22** involved the central benzene ring having the two propyl substituents to form **23** (Scheme 3). It was originally anticipated that such a coupling would occur on one of the peripheral benzene rings, which is sterically less crowded. However, molecular modeling suggests that this pathway suffers from nonbonded steric interactions between the chloro substituent and the neighboring propyl group on the central benzene ring. The effect of such a steric interaction in dictating the course of the reaction was observed previously.¹ A second formal intramolecular Diels–Alder reaction, again promoted by thionyl chloride, then led to **24**. Cleavage of the bond connecting the two carbons having the propyl substituent then gave the valence tautomer **25a**, which could also be regarded as a resonance structure of **25b** having a carbon–carbon single bond joining the two central five-membered rings. Rotation of the carbon–carbon bond joining the two central five-membered rings then gave the trans isomer **26**. The temperature-dependent NMR studies have also shown that the rotational barriers of the cis–trans isomerization of several sterically congested 1,1'-disubstituted 9,9'-bifluorenylidenes are relatively low, allowing rapid interconversion to occur at ambient temperature.⁹ Oxidation of **26**, presumably by oxygen, followed by hydrolysis then produced **17**. The X-ray crystal structure reveals that it has a twist angle of 45.2° for the carbon–carbon double bond connecting the two bifluorenylidene fragments (Figure 1). This carbon–carbon double bond has a bond length of 1.380 Å, which is unusually long for a carbon–carbon double bond indicating a partial diradical character for the bond.

It is worth noting that transformation from **16** to **17** involves a rare occurrence of cleavage of a benzene ring. However, the loss of the resonance energy is more than compensated for with the eventual formation of two new benzene rings in **17**.

The chlorosulfite **27**, derived from **23**, could also undergo a different $\text{S}_{\text{N}}1'$ reaction involving the carbon–carbon double bond substituted with a propyl group to produce the chloride **18** (Scheme 4). The structure of **18** was tentatively assigned on the basis of the MS and ^1H NMR spectra. It was observed by ^1H NMR that the

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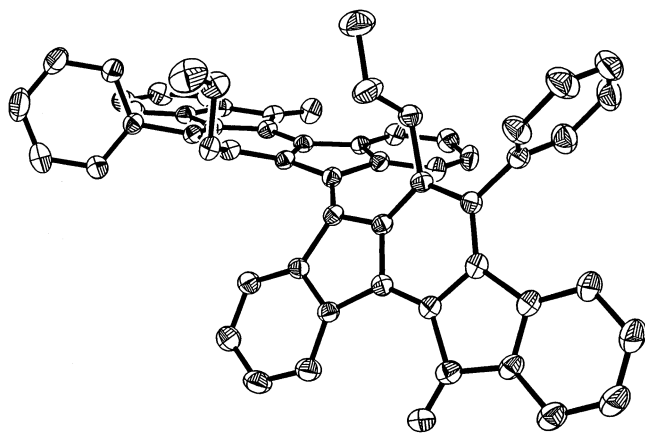
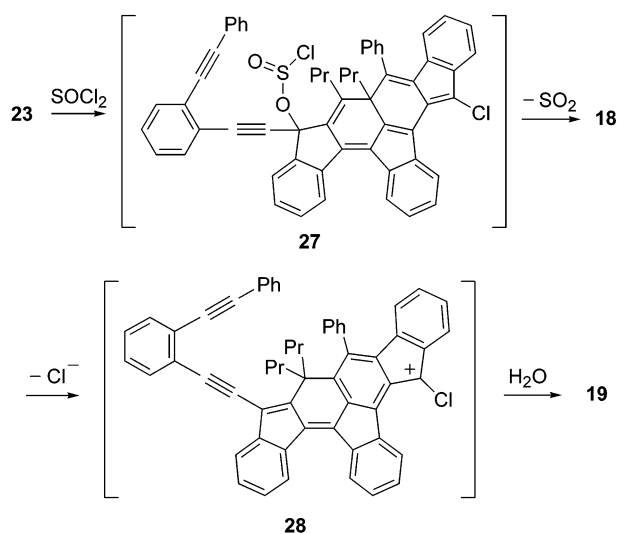


FIGURE 1. ORTEP drawing of the crystal structure of the 1,1'-dipropyl-9,9'-bifluorenylidene **17** with hydrogen atoms omitted for clarity.

SCHEME 4



chloride, **32** was also transformed to the 1,1'-dimethyl-9,9'-bifluorenylidene **33** and the polycyclic compounds **34** and **35**. The structure of **34** was tentatively assigned on the basis of the MS and ^1H NMR spectra. Compared to the case of **16**, elimination of a molecule of hydrogen chloride from **34** to form **35** appears to occur more readily than 1,2-migration of the adjacent methyl group. The structure of **35** was established by X-ray structure analysis. The [2 + 2] cycloaddition adduct was not detected in this case.

Condensation between **13** and benzyne,¹⁰ generated in situ from anthranilic acid, eventually led to the diketone **37** and subsequently the diol **38** as a mixture of the trans and cis isomers (isomer ratio = 3:1) (Scheme 6). Treatment of **38** with 2 equiv of thionyl chloride produced the [2 + 2] cycloaddition adduct **39** as a mixture of the trans and cis isomers (trans/cis = 3:1). In addition, the alcohol **40** as a mixture of the trans and cis isomers (isomer ratio = 2:1) and the ketone **41** were also isolated. The structure of the trans isomer of **39** was established by X-ray structure analysis. Unlike the cases of **16** and **32**, the formation of **40** and **41** indicated that the intramolecular

radical–radical coupling reaction involved one of the peripheral benzene rings. Apparently, the central naphthyl ring with its higher resonance energy is more resistant to being attacked at the ring junction because such an attack would result in the loss of the entire naphthyl aromaticity. The reaction pathway leading to the alcohol **40** is similar to the one described for **8**. It was previously observed that treatment of the chloride **7** and other analogous compounds with NaOH under air produced the corresponding ketones in excellent yields.¹¹ A similar reaction could likewise give rise to the ketone **41**.

Conclusions

The transformations from **16** and **32** to the highly twisted 1,1'-dialkyl-9,9'-bifluorenylidenes **17** and **33**, respectively, represent a novel synthetic pathway to these highly twisted compounds. The cascade sequence involves an unusual cleavage of a benzene ring. Alternatively, the intramolecular [2 + 2] cycloaddition reactions of the benzannulated enyne–allenenes lead to the spiro[1H-cyclobut[a]indene-1,9'-[9H]fluorenes] **20** and **39–41**.

Experimental Section

Diester 14. A mixture of 0.174 g (0.500 mmol) of 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (**13**)⁸ and 0.10 mL (0.68 mmol) of 4-octyne in 3 mL of mesitylene in a sealed tube was heated to 190 °C for 12 h. The solvent was removed in vacuo. Flash column chromatography (silica gel/10% ethyl acetate in hexanes) afforded 0.109 g of **14** (0.253 mmol, 50%) as a waxlike white solid: mp 105–108 °C; IR 1728, 1200, 702 cm^{-1} ; ^1H (270 MHz) δ 7.13–7.06 (6 H, m), 7.03–6.96 (4 H, m), 3.43 (6 H, s), 2.62 (4 H, t, $J = 8.3$ Hz), 1.65 (4 H, sextet, $J = 7.7$ Hz), 1.02 (6 H, t, $J = 7.3$ Hz); ^{13}C (67.9 MHz) δ 170.0, 138.3, 137.0, 136.8, 136.3, 130.0, 127.3, 126.7, 51.7, 33.0, 24.9, 14.9; MS m/z 430 (M^+), 415, 399, 367, 337.

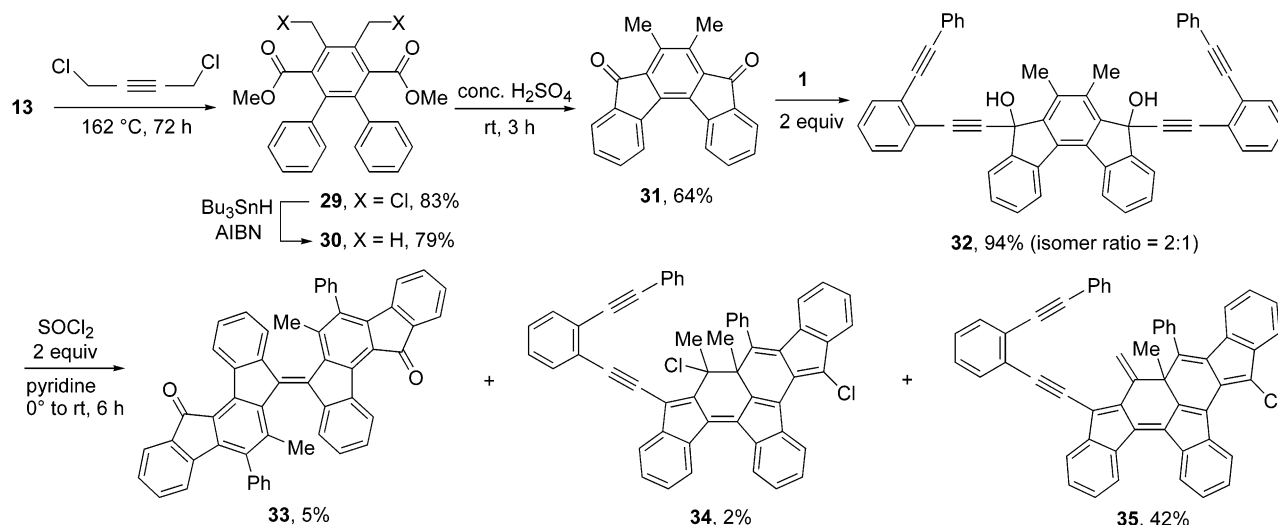
Diketone 15. To a flask containing 0.088 g (0.205 mmol) of **14** was added 4 mL of concentrated sulfuric acid. The mixture was swirled periodically until the solid was dissolved in the sulfuric acid at rt. After 3 h, the reaction mixture was poured into an ice–water mixture and then was extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated. Recrystallization of the crude yellow solid from 95% ethanol afforded 0.059 g of **15** (0.161 mmol, 79%) as bright-yellow crystals: mp 182–184 °C; IR (KBr) 1700, 757, 721 cm^{-1} ; ^1H (270 MHz) δ 8.09 (2 H, d, $J = 7.7$ Hz), 7.75 (2 H, d, $J = 7.4$ Hz), 7.59 (2 H, td, $J = 7.5, 1.0$ Hz), 7.38 (2 H, t, $J = 7.4$ Hz), 3.12 (4 H, t, $J = 8.0$ Hz), 1.55 (4 H, sextet, $J = 7.6$ Hz), 1.10 (6 H, t, $J = 7.3$ Hz); ^{13}C (67.9 MHz) δ 193.8, 146.0, 143.0, 136.9, 135.9, 135.4, 134.7, 129.1, 124.5, 123.5, 28.3, 24.4, 14.6; MS m/z 366 (M^+), 351, 337.

Diol 16. To a solution of 0.18 g (0.89 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne⁶ in 10 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.31 mL of a 2.5 M solution of *n*-butyllithium (0.78 mmol) in hexanes. The reaction mixture was then allowed to warm to rt. After 30 min at rt, a solution of 0.099 g (0.271 mmol) of **15** in 40 mL of diethyl ether was introduced via cannula. After an additional 12 h, 5 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/30% diethyl ether in hexanes) provided 0.197 g of **16** (0.256 mmol, 94%, a mixture of the trans and cis isomers,

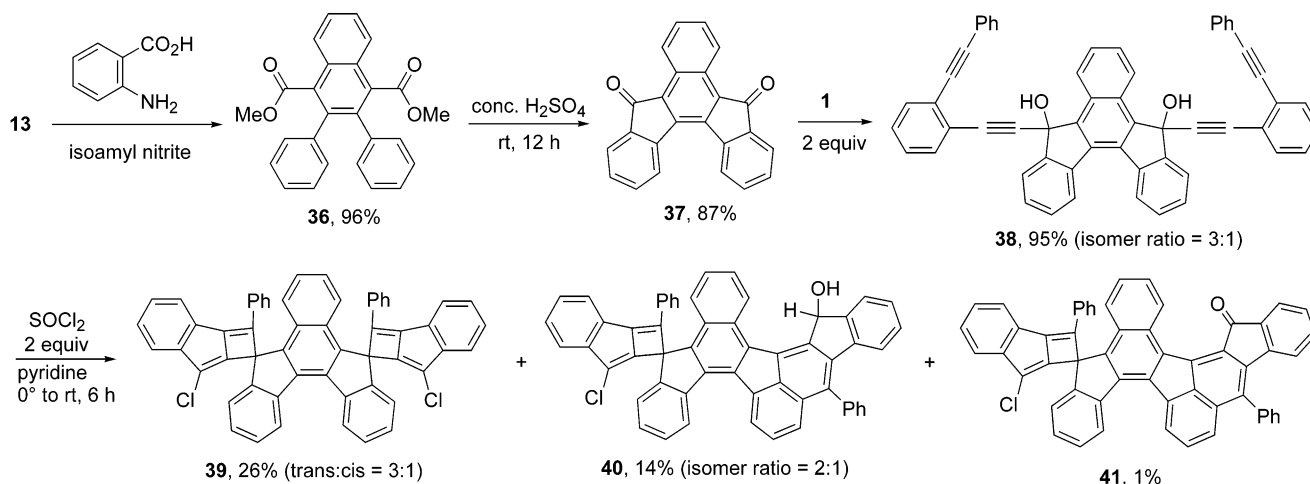
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SCHEME 5



SCHEME 6



isomer ratio = 2:1) as a soil-colored solid: mp 107–113 °C; IR 3528, 3426, 2215, 753 cm^{-1} ; ^1H (270 MHz) δ 8.24 (2 H, d, J = 7.9 Hz), 7.85 (2 H, d, J = 7.4 Hz), 7.51–7.4 (6 H, m), 7.4–7.09 (16 H, m), 3.32–3.13 (2 H, m), 3.13–2.98 (2 H, m), 2.48 (2 H, br), 1.92–1.76 (2 H, m), 1.76–1.52 (2 H, m), 1.03 (6 H, t, J = 7.2 Hz); ^{13}C (67.9 MHz) δ 148.6, 146.9, 140.9, 138.5, 132.7, 131.9, 131.8, 131.7, 129.2, 128.4, 128.1, 127.8, 125.9, 124.9, 124.5, 123.1, 93.3, 93.2, 87.9, 82.0, 75.5, 31.1, 25.0, 15.2; MS m/z 770 (M^+), 753, 736; HRMS calcd for $\text{C}_{58}\text{H}_{42}\text{O}_2$ 770.3185, found 770.3160.

Compounds 17–20. To a flask containing 0.05 mL (0.7 mmol) of thionyl chloride in 10 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.08 mL (1.0 mmol) of pyridine in 5 mL of diethyl ether via cannula. After 10 min, 0.094 g (0.122 mmol) of **16** in 20 mL of diethyl ether was introduced slowly via cannula. After 5 h at 0 °C, the reaction mixture was allowed to warm to rt. After an additional 2 h at rt, 10 mL of water was introduced, and the organic layer was separated. The aqueous layer was back extracted with methylene chloride. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) provided 0.008 g of **17** (0.010 mmol, 8%) as a pink solid, 0.0030 g of **18** (0.0037 mmol, 3%) as a dark solid, 0.026 g of **19** (0.035 mmol, 28%) as a dark brown solid, and 0.029 g of **20** (0.036 mmol, 30%, trans/cis = 5:1) as an orange solid. Compound **17**: mp 266–269 °C; IR 1701, 749 cm^{-1} ; ^1H (270 MHz) δ 9.35 (2 H, dd, J = 7.9, 1.2 Hz), 7.93 (2 H, d, J = 7.2

Hz), 7.70–7.26 (16 H, m), 7.21 (2 H, td, J = 7.3, 1.0 Hz), 7.12 (2 H, td, J = 7.7, 1.2 Hz), 5.96 (2 H, d, J = 7.7 Hz), 3.55 (2 H, br), 2.64 (2 H, m), 1.25 (4 H, m), 0.49 (6 H, t, J = 6.8 Hz); ^{13}C (67.9 MHz) δ 193.7, 149.3, 144.2, 143.7, 141.5, 141.2, 140.7, 138.6, 138.3, 137.6, 136.9, 135.6, 134.1, 130.2, 129.4, 129.1, 128.94, 128.87, 128.7, 128.2, 127.0, 126.7, 123.7, 123.5, 35.1, 25.1, 14.3; MS m/z 769 (MH^+), 768; HRMS calcd for $\text{C}_{58}\text{H}_{40}\text{O}_2$ 768.3028, found 768.3021. Recrystallization of **17** from CH_2Cl_2 /2-propanol produced a crystal suitable for X-ray structure analysis. Compound **18**: IR 1447, 753, 691 cm^{-1} ; ^1H (270 MHz) δ 8.73 (1 H, d, J = 7.2 Hz), 8.40 (1 H, d, J = 6.9 Hz), 8.29 (1 H, d, J = 7.4 Hz), 7.85 (1 H, d, J = 7.2 Hz), 7.67–7.16 (19 H, m), 7.01 (1 H, t, J = 7.5 Hz), 6.86 (1 H, t, J = 7.7 Hz), 5.48 (1 H, d, J = 7.7 Hz), 2.32–2.22 (1 H, m), 2.2–2.0 (1 H, m), 1.8–1.4 (4 H, m), 1.12–0.96 (1 H, m), 0.9–0.8 (1 H, m), 0.69 (3 H, t, J = 7.3 Hz), 0.46 (3 H, t, J = 7.1 Hz); MS m/z 790, 771 ($\text{M}^+ - \text{Cl}$), 728. Compound **19**: mp 275–277 °C; IR (KBr) 2211, 1695, 761 cm^{-1} ; ^1H (270 MHz) δ 9.44 (1 H, dd, J = 6.9, 1.7 Hz), 8.64 (1 H, dd, J = 6.9, 1.5 Hz), 8.38 (1 H, d, J = 7.7 Hz), 7.78 (1 H, d, J = 7.4 Hz), 7.68 (1 H, d, J = 7.2 Hz), 7.64–7.31 (16 H, m), 7.26 (1 H, td, J = 7.5, 1.0 Hz), 7.17 (1 H, td, J = 7.4, 0.7 Hz), 7.03 (1 H, td, J = 7.7, 1.2 Hz), 6.96 (1 H, td, J = 7.4, 0.7 Hz), 5.20 (1 H, d, J = 7.7 Hz), 2.71 (2 H, m), 2.12 (2 H, m), 1.02 (4 H, sextet, J = 7.9 Hz), 0.68 (6 H, t, J = 7.3 Hz); ^{13}C (67.9 MHz) δ 193.8, 153.3, 145.3, 145.0, 144.4, 144.3, 141.2, 140.0, 139.4, 137.2, 137.0, 136.5, 136.3, 135.2, 134.2, 132.4, 132.0, 131.8, 131.6, 130.7, 130.1, 129.1, 128.94, 128.87, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 126.9, 126.1,

125.8, 125.3, 125.0, 124.3, 123.7, 123.6, 123.1, 120.5, 118.5, 102.6, 93.7, 89.0, 88.4, 51.6, 42.5, 18.5, 14.1; MS m/z 753 (MH⁺), 752, 709; HRMS calcd for C₅₈H₄₀O 752.3079, found 752.3048. Recrystallization of **19** from CH₂Cl₂/2-propanol produced a crystal suitable for X-ray structure analysis. Compound **20**: mp >340 °C; IR 1640, 1424, 1196, 753 cm⁻¹; ¹H (270 MHz) δ (trans isomer) 8.67 (2 H, d, $J = 7.7$ Hz), 7.87 (2 H, t, $J = 7.4$ Hz), 7.56–7.20 (22 H, m), 2.54 (2 H, m), 2.42 (2 H, m), 1.27 (2 H, m), 1.03 (2 H, m), 0.44 (6 H, t, $J = 7.2$ Hz); ¹³C (67.9 MHz) δ (trans isomer) 152.4, 148.8, 148.1, 145.7, 144.0, 141.1, 140.4, 139.3, 134.9, 131.9, 130.2, 129.3, 129.0, 128.5, 128.2, 127.8, 127.3, 125.0, 124.5, 123.7, 123.2, 120.0, 111.5, 65.6, 30.2, 25.2, 14.5; ¹³C (67.9 MHz) δ (cis isomer, partial) 151.9, 149.0, 145.9, 144.01, 140.97, 139.2, 135.0, 132.1, 130.0, 129.4, 128.8, 127.6, 120.1, 112.0, 65.55, 14.54; MS m/z 807 (MH⁺), 763, 720; HRMS calcd for C₅₈H₄₁Cl₂ 807.2585, found 807.2569. Recrystallization of **20** from CH₂Cl₂/2-propanol produced a crystal of the trans isomer suitable for X-ray structure analysis.

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Supporting Information Available: Experimental procedures and spectroscopic data for **29–35** and **37–41**; ¹H and/or ¹³C NMR spectra for **14–20**, **29–35**, and **37–41**; and ORTEP drawings and tables of crystallographic data for the X-ray diffraction analyses of **17**, **19**, **20**, **35**, and **39**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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