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Construction of Unusual and Congested Polycyclic Structures via Benzannulated Enediynyl Alcohols Derived from Truxenone

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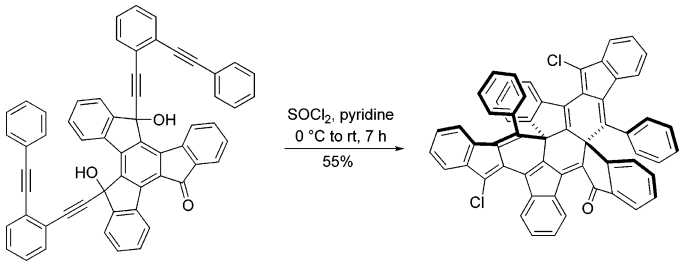

Condensation between truxenone (**8**) and the lithium acetylide derived from 0.9, 2.5, and 5.0 equiv of 1-ethynyl-2-(phenylethynyl)benzene produced the corresponding benzannulated enediynyl alcohol **9**, diol **14**, and triol **16**, respectively. On exposure of these alcohols to thionyl chloride, cascade cyclization reactions occurred to furnish polycyclic compounds **13**, **15**, and **18** in a single operation. The unusual architectures of these polycyclic compounds were established by NMR spectroscopy and X-ray structure analyses.

Introduction

Benzannulated enediynyl alcohols, readily prepared from condensation between ketones and benzannulated enediynes and other related procedures, are excellent precursors of the reactive benzannulated enyne−allenes.[1] The cascade cyclization reactions of the benzannulated enyne−allenes provide new pathways to a variety of highly unusual and congested polycyclic compounds.[2] In particular, condensation between diketone **1** and the lithium acetylide **2**, prepared from treatment of 1-ethynyl-2-(phenylethynyl)benzene as a benzannulated enediyne with *n*-butyllithium, produced diol **3**, which on exposure to thionyl chloride furnished the polycyclic products **4**−**7** (Scheme 1).[2a] It is worth noting that, in producing the twisted 1,1′-dipropyl-9,9′-bifluorenylidene **4**, a rare and unusual process involving the cleavage of the central benzene ring of **3** occurred. The readily available truxenone (**8**)[3] bearing three keto groups provides excellent opportunities for further expanding the use of benzannulated enediynyl alcohols for the synthesis of polycyclic compounds possessing interesting and unusual architectures.

Results and Discussion

Treatment of truxenone (**8**) with 0.90 equiv of **2** furnished the benzannulated enediynyl alcohol **9**, which on exposure to

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(1) (a) Li, H.; Zhang, H.-R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 6662−6668. (b) Wang, K. K. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 1091−1126. (c) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978. (d) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (e) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (f) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem.−Eur. J.* **1997**, *3*, 807−816.

(2) (a) Yang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 5832−5837. (b) Zhang, Y.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2007**, *9*, 1025−1028. (c) Kim, D.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2006**, *8*, 2313−2316. (d) Yang, Y.; Dai, W.; Zhang, Y.; Petersen, J. L.; Wang, K. K. *Tetrahedron* **2006**, *62*, 4364−4371. (e) Yang, H.; Petersen, J. L.; Wang, K. K. *Tetrahedron* **2006**, *62*, 1231−1238. (f) Han, X.; Zhang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2005**, *70*, 2406−2408. (g) Dai, W.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2004**, *6*, 4355−4357. (h) Yang, Y.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 8545−8549. (i) Li, H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804−7810. (j) Zhang, H.-R.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 7996−7999.

(3) (a) Dehmlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021−2031. (b) Gómez-Lor, B.; de Frutos, Ó.; Ceballos, P. A.; Granier, T.; Echavarren, A. M. *Eur. J. Org. Chem.* **2001**, 2107−2114.

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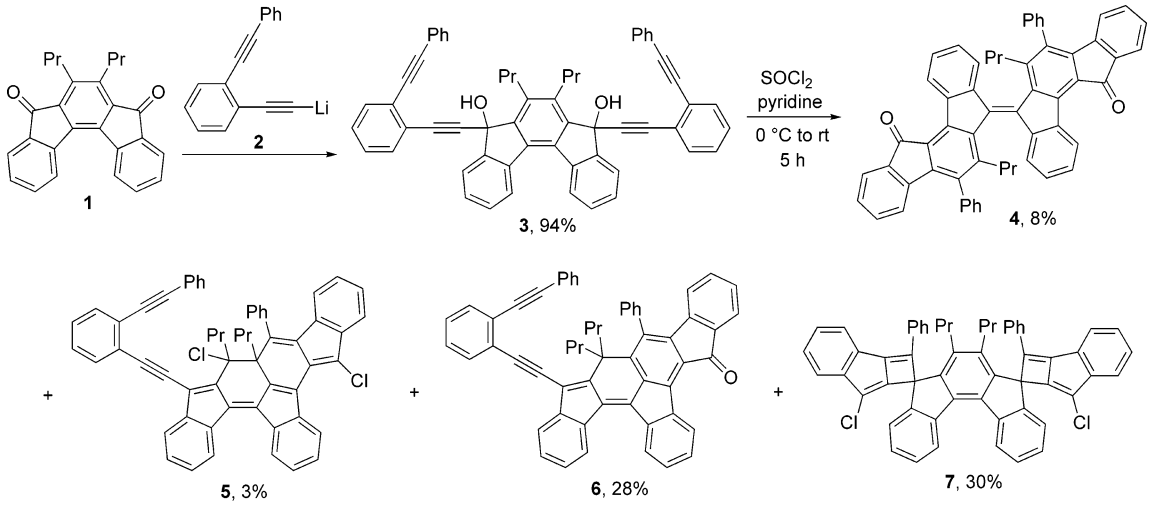
SCHEME 1



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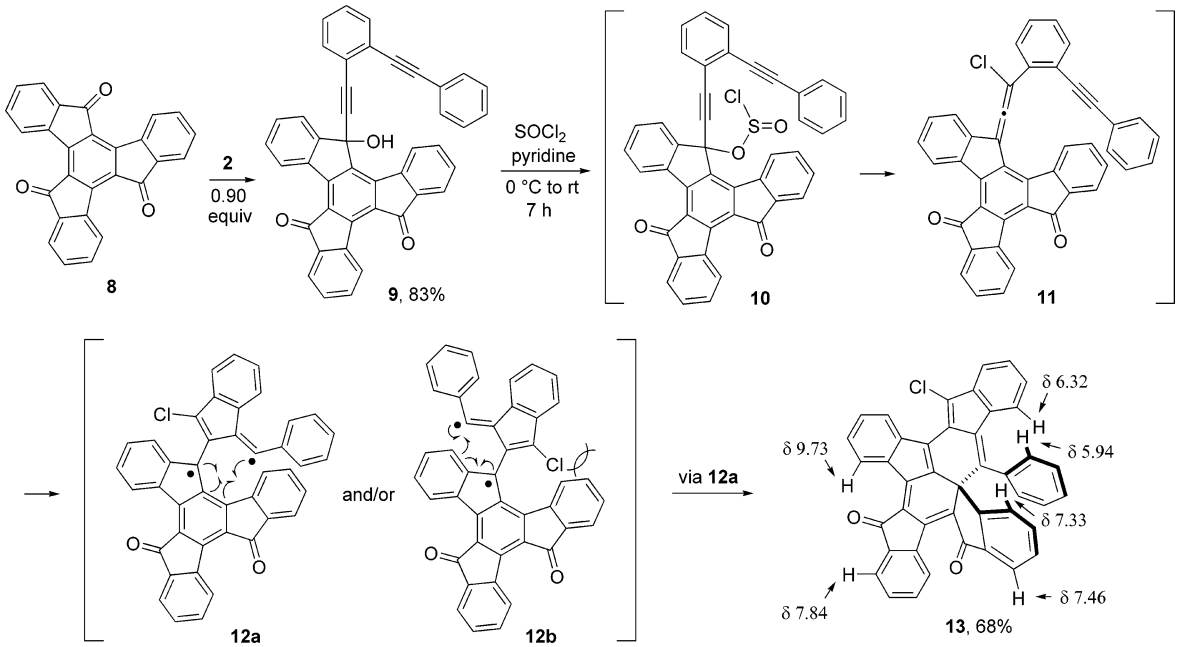
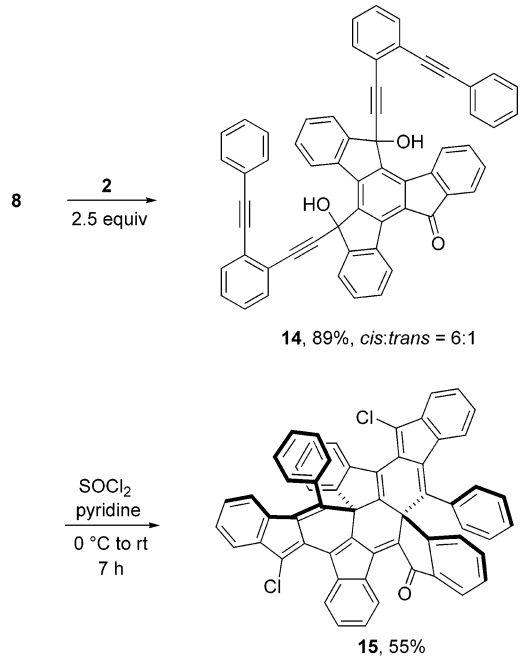


thionyl chloride was smoothly converted to the polycyclic product **13** (Scheme 2). The structure of **13** was established by X-ray structure analysis (Figure 1). Presumably, the initially formed chlorosulfite **10** underwent an S_Ni' reaction[4] to give the benzannulated enyne−allene **11**.[1a,2j] A subsequent Schmittel cyclization reaction[5] to generate biradical **12** followed by an intramolecular radical−radical coupling reaction via **12a** then produced **13** in a single cascade sequence. It is worth noting that the radical−radical coupling step involved the more congested central benzene ring to form the new quaternary carbon center in **13** instead of involving the neighboring less hindered benzene ring on the periphery as depicted in **12b**. Molecular modeling suggests that the pathway involving the attack of the peripheral benzene ring via **12b** suffers from the emergence of nonbonded steric interactions between the chloro substituent and one of the other two peripheral benzene rings.[1a,2a] This observation is reminiscent of what was observed previously for **3** in which the preferential attack of the central benzene ring led to **4**, **5**, and **6**. The aromaticity of the central benzene ring in **11** is disrupted in producing **13**. However, trading two π bonds in **11** for two σ bonds in **13** is more than sufficient to compensate for the loss of aromaticity.

It is worth noting that with the loss of the aromaticity of the central benzene ring in **8** the resultant structure of **13** contains a twisted enone system having four conjugated carbon−carbon double bonds and one keto group at its longest linear extension along with one cross-conjugated carbon−carbon double bond and one cross-conjugated keto group. In addition, the structure could also be regarded as bearing two connected benzofulvene moieties. Furthermore, the original central benzene ring in **8** is transformed to a reactive 5-methylene-1,3-cyclohexadiene moiety.[6] The newly formed chlorofluorenyl group also contains an acid-sensitive 3-methylene-1,4-cyclohexadiene substructure.[7]

(4) Jacobs, T. L.; Fenton, D. M. *J. Org. Chem.* **1965**, *30*, 1808−1812.
(5) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, *1843*−*1845*. (b) Schmittel, M.; Maywald, M. *Chem. Commun.* **2001**, 155−156. (c) Schmittel, M.; Vavilala, C. *J. Org. Chem.* **2005**, *70*, 4865−4868.

SCHEME 3



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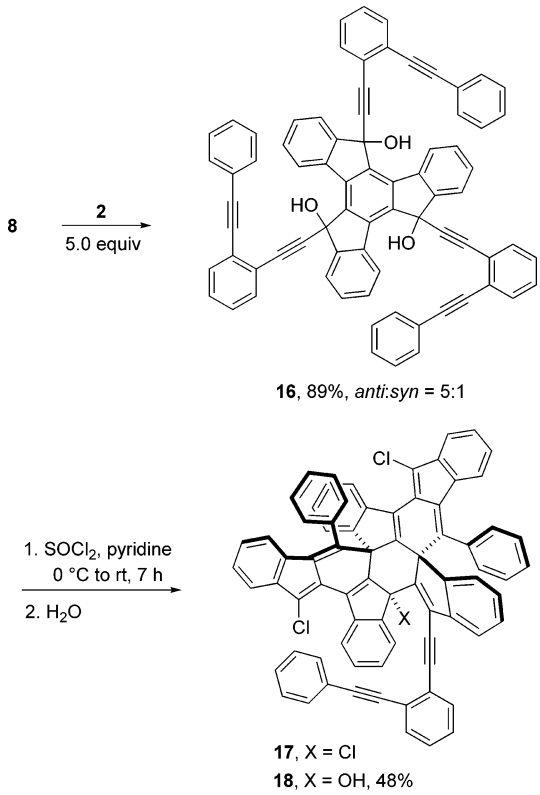

The X-ray structure of **13** indicates that the phenyl substituent is in a sterically congested environment, which could cause a relatively slow rate of rotation. In addition, the phenyl substituent is oriented roughly perpendicular to the newly formed chlorofluorenyl moiety, placing one of the *ortho* hydrogens in the magnetic shielding region of the neighboring indanone group.

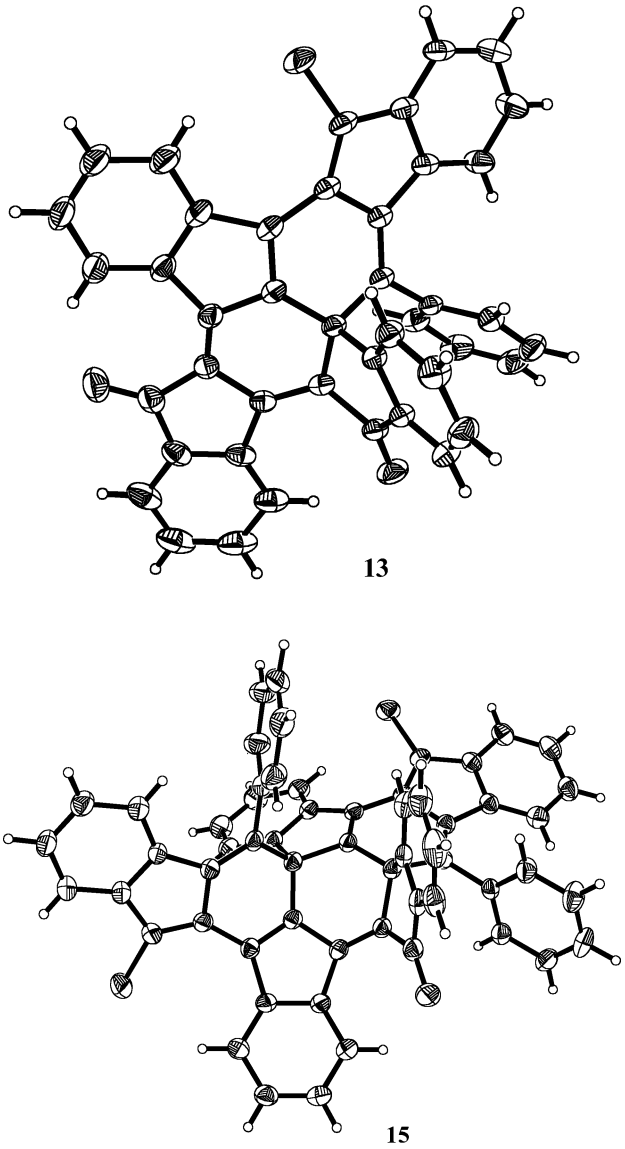

FIGURE 1. ORTEP drawings of the crystal structures of **13** and **15** with thermal ellipsoids scaled to 30% probability.

Indeed, the ^{1}H NMR spectrum of **13** in C_6D_6 using the 1D/2D TOCSY and COSY techniques revealed five distinct signals at δ 5.94 (*ortho*), 6.89 (*meta*), 7.15 (*ortho*), 7.17 (*para*), and 7.24 (*meta*) for the five hydrogens on the phenyl substituent, indicating a slow rate of rotation on the NMR time scale (Figure 2). In addition, the DEPT spectrum exhibited 21 signals for the 21 proton-bearing carbons, including five signals from the phenyl substituent and 16 signals from the rest of the molecule. The magnetic shielding was observed for one of the *ortho* hydrogens, which gave a significantly upfield shift signal at δ 5.94 (Scheme 2). Even at 80 °C, this signal remained virtually unchanged and without significant line broadening. The perpendicular orientation of the phenyl substituent relative to the newly formed chlorofluorenyl moiety is also responsible for upfield shifting the proton signal of the neighboring hydrogen atom on the chlorofluorenyl moiety to δ 6.32 (C_6D_6).[1a,2j] In the contour plot of the COSY spectrum, this signal was also used to locate the remaining three hydrogens on the same benzene ring at δ 6.60 (*ortho*), 6.90 (*meta*), and 7.37 (*para*).

A complete assignment of the ^{1}H NMR chemical shifts to the remaining hydrogens of **13** and the ^{13}C NMR chemical shifts

(6) Dytnerski, D.; Ranganayakulu, K.; Singh, B. P.; Sorensen, T. S. *J. Org. Chem.* **1983**, *48*, 309−315.
(7) Lukáč, J.; Heimgartner, H. *Helv. Chim. Acta* **1985**, *68*, 335−370.

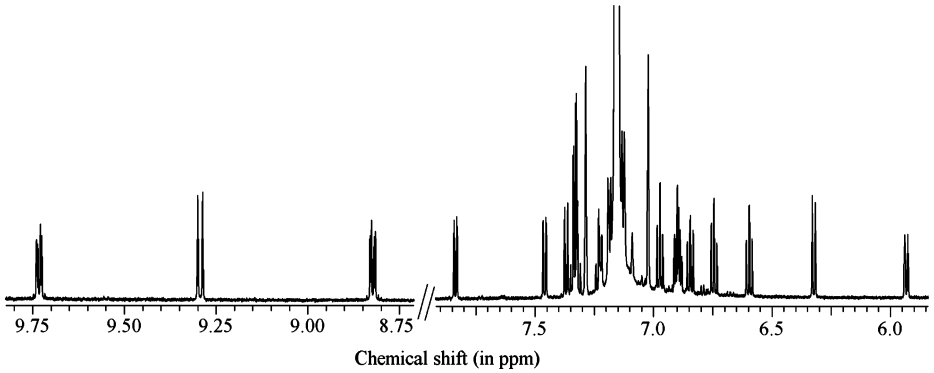

FIGURE 2. ^{1}H NMR spectrum of **13** in C_6D_6.

to the 43 carbons was made by an analysis strategy based on the application of several gradient-selected two-dimensional experiments, such as gHSQC, gHMBC, and gHSQC-TOCSY. The 2D and simulated NMR spectra are included in the Supporting Information. Again, the proton connectivities were identified from the COSY and 1D/2D TOCSY spectra. The gHSQC correlations were used to confirm the proton-bearing carbons, and the gHMBC cross-peaks were used to define the locations of the quaternary carbons. The gHMBC correlation with the quaternary sp^3 carbon resonance at δ 57.6 allowed the assignment of the proton signal at δ 7.33 to the hydrogen three bonds away, which in turn allowed the assignment of the remaining three hydrogens on the same benzene ring at δ 6.84 (*ortho*), 6.75 (*meta*), and 7.46 (*para*) based on 2D TOCSY and COSY correlations. Using the gHMBC technique, the proton signal at δ 7.46 was used to locate the ^{13}C chemical shift of the neighboring carbonyl carbon at δ 187.7. Similarly, the chemical shift of the hydrogen three bonds away from the other carbonyl carbon at δ 190.3 was identified at δ 7.84, which in turn allowed the assignment of the remaining three hydrogens on the same benzene ring at δ 6.97 (*ortho*), 7.19 (*meta*), and 9.29 (*para*). The most downfield proton signal at δ 9.73 was assigned to the hydrogen on the remaining benzene ring closest to the carbonyl carbon with a chemical shift at δ 190.3. The last three proton signals at δ 7.32 (*ortho*), 7.34 (*meta*), and 8.82 (*para*) were then assigned by COSY.

Treatment of truxenone with 2.5 equiv of **2** allowed the isolation of the *cis*-diol of **14** in 76% yield along with the corresponding *trans*-diol in 13% yield (Scheme 3). The structure of the *cis*-diol was established by X-ray structure analysis. On exposure of a mixture of the *cis* and *trans* isomers of diol **14** to thionyl chloride, the product **15** bearing two quaternary carbon centers was produced. In addition, the two chlorinated fluorenyl moieties are *trans* to each other with respect to the central six-membered ring. The structure of **15** was established by X-ray structure analysis (Figure 1). Apparently, the second cascade cyclization reaction also involved a carbon−carbon double bond of the central six-membered ring. In addition, the second radical−radical coupling reaction occurred from the direction *trans* to the first chlorinated fluorenyl unit. As observed in **13**, several ^{1}H NMR signals of **15** in C_6D_6 showed significant upfield shifts, with the most upfield signal appearing at δ 5.62.

When truxenone was treated with 5.0 equiv of **2**, triol **16** was obtained as a mixture of the *anti* and *syn* isomers (5:1) in 89% combined yield (Scheme 4). On exposure of a mixture of the *anti* and *syn* isomers of **16** to thionyl chloride, the product **18** was produced in 48% yield. The structure of **18** was established by X-ray structure analysis. Clearly, the third benzannulated enediynyl alcohol unit did not undergo the anticipated cascade cyclization reaction. Instead, an S_Ni' reaction involving the remaining carbon−carbon double bond of the central six-membered ring might have occurred to give **17**, which on hydrolytic workup then furnished **18**.

Conclusions

Benzannulated enediynyl alcohols **9**, **14**, and **16**, derived from condensations of truxenone and the lithium acetylide **2**, were readily converted to the polycyclic compounds **13**, **15**, and **18** by thionyl chloride-promoted cascade cyclization reactions. The aromaticity of the central benzene ring of truxenone is disrupted in all three of the resultant products. Transformation of two π bonds to two σ bonds in each of the cascade cyclization sequences provides the necessary driving force for the construction of these unusual and congested polycyclic structures.

Experimental Section

Benzannulated Enediynyl Alcohol 9. To 0.049 g (0.243 mmol) of 1-ethynyl-2-(phenylethynyl)benzene in 5 mL of THF under a nitrogen atmosphere at 0 °C was added 0.15 mL of a 1.6 M solution of *n*-butyllithium (0.24 mmol) in hexanes. After 30 min of stirring, a solution of 0.102 g of truxenone (**8**; 0.266 mmol) in 10 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 18 h, 15 mL of water was introduced, and the reaction mixture was extracted with methylene chloride. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash chromatography (silica gel/methylene chloride) to afford 0.129 g (0.220 mmol, 83%) of **9** as a pale yellow solid: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.18−9.17 (1 H, m), 9.03 (1 H, d, J = 7.2 Hz), 8.82 (1 H, d, J = 7.8 Hz), 7.93−7.92 (1 H, m), 7.64 (2 H, d, J = 6.6 Hz), 7.56−7.52 (2 H, m), 7.44−7.41 (3 H, m), 7.37−7.32 (3 H, m), 7.24−7.15 (7 H, m), 3.35 (1 H, br); MS *m*/*z* 569 (M^+ − OH); HRMS *m*/*z* calcd for $C_{43}H_{21}O_2$ (M^+ − OH) 569.1542, found 569.1543.

Diketone 13. To a solution of 0.102 g (0.174 mmol) of **9** in 10 mL of THF under a nitrogen atmosphere at 0 °C was added slowly via cannula a solution of 0.1 mL (1.4 mmol) of thionyl chloride and 0.16 mL (2.0 mmol) of pyridine in 5 mL of THF. The reaction mixture then was allowed to warm to room temperature. After 7 h, 10 mL of water was introduced, and the organic layer was separated. The aqueous layer was back-extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash chromatography (silica gel/50% methylene chloride in hexanes) to afford 0.071 g (0.118 mmol, 68%) of **13** as a green solid: IR 1701, 1434 cm^{-1}; ^{1}H (C_6D_6, 600 MHz) δ 9.73 (1 H, ddd, J = 7.4, 1.2, 0.7 Hz), 9.29 (1 H, dt, J = 7.9, 0.9 Hz), 8.82 (1

H, ddd, J = 7.6, 1.1, 0.7 Hz), 7.84 (1 H, ddd, J = 7.5, 1.2, 0.7 Hz), 7.46 (1 H, ddd, J = 7.5, 1.2, 0.7 Hz), 7.37 (1 H, ddd, J = 7.5, 1.1, 1.0 Hz), 7.34 (1 H, td, J = 7.6, 1.2 Hz), 7.33 (1 H, ddd, J = 7.9, 1.1, 0.7 Hz), 7.32 (1 H, ddd, J = 7.6, 7.4, 1.1 Hz), 7.24 (1 H, td, J = 7.5, 1.2 Hz), 7.19 (1 H, ddd, J = 7.9, 7.3, 1.2 Hz), 7.17 (1 H, m), 7.15 (1 H, m), 6.97 (1 H, td, J = 7.4, 1.0 Hz), 6.90 (1 H, td, J = 7.5, 0.9 Hz), 6.89 (1 H, m), 6.84 (1 H, ddd, J = 7.9, 7.3, 1.2 Hz), 6.75 (1 H, td, J = 7.7, 1.1 Hz), 6.60 (1 H, td, J = 7.5, 1.1 Hz), 6.32 (1 H, dt, J = 7.6, 0.9 Hz), 5.94 (1 H, dt, J = 7.2, 1.2 Hz); ^{1}H ($CDCl_3$, 600 MHz) δ 9.22 (1 H, d, J = 7.2 Hz), 8.99 (1 H, d, J = 7.8 Hz), 8.69 (1 H, d, J = 7.8 Hz), 7.93 (1 H, d, J = 7.8 Hz), 7.72 (1 H, t, J = 7.8 Hz), 7.59 (1 H, t, J = 7.2 Hz), 7.53−7.47 (7 H, m), 7.44 (1 H, t, J = 7.2 Hz), 7.30 (1 H, t, J = 7.8 Hz), 7.25−7.22 (2 H, m), 7.18−7.16 (1 H, m), 6.88 (1 H, t, J = 7.8 Hz), 6.16 (1 H, d, J = 7.8 Hz), 5.88 (1 H, d, J = 6.6 Hz); ^{13}C (C_6D_6, 150 MHz) δ 190.3, 187.7, 150.0, 147.5, 145.1, 142.6, 142.2, 142.0, 141.6, 140.1, 139.7, 137.9, 135.7, 135.4, 134.88, 134.79, 134.36, 134.28, 133.9, 133.3, 131.33, 131.24, 131.20, 130.22, 130.11, 129.63, 129.59, 129.3, 129.15, 129.11, 128.8, 128.56, 128.37, 128.15, 127.91, 127.83, 124.5, 123.5, 123.02, 122.96, 122.8, 120.0, 57.6; ^{13}C ($CDCl_3$, 150 MHz) δ 190.6, 188.1, 149.7, 146.9, 145.3, 142.0, 141.8, 141.6, 140.8, 139.5, 139.1, 138.1, 135.2, 135.0, 134.9, 134.4, 133.9, 133.1, 132.9, 131.6, 131.4, 131.1, 129.9, 129.7, 129.10, 129.07, 128.97, 128.8, 128.54, 128.52, 128.47, 128.3, 128.1, 127.83, 127.77, 124.3, 123.5, 122.93, 122.87, 122.5, 119.8, 57.3; HRMS m/z calcd for $C_{43}H_{21}ClO_2$ (M^+) 604.1230, found 604.1231. Recrystallization of **13** from a mixture of methylene chloride and 2-propanol produced a single crystal suitable for X-ray structure analysis.

Ketone 15. To a solution of 0.097 g (0.123 mmol) of a mixture of the *cis* and *trans* isomers of diol **14** in 8 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added slowly via cannula a solution of 0.09 mL (1.2 mmol) of thionyl chloride and 0.14 mL (1.7 mmol) of pyridine in 7 mL of diethyl ether. The reaction mixture was then allowed to warm to room temperature. After 7 h, 15 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 brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash chromatography (silica gel/50% methylene chloride in hexanes) to afford 0.056 g (0.068 mmol, 55%) of **15** as a red solid and ca. 0.004 g of an unidentified green solid. Data for **15**: ^{1}H (C_6D_6, 600 MHz) δ 8.73−8.71 (1 H, m), 8.68−8.66 (1 H, m), 8.62 (1 H, d, J = 7.8 Hz), 7.83 (1 H, d, J = 7.8 Hz), 7.45 (1 H, d, J = 7.8 Hz), 7.43 (1 H, d, J = 7.8 Hz), 7.31 (1 H, d, J = 7.8 Hz), 7.27 (1 H, d, J = 7.2 Hz), 7.25−7.23 (2 H, m), 7.19−7.13 (2 H, m), 7.10 (1 H, d, J = 6.6 Hz), 7.06 (1 H, t, J = 7.2 Hz), 7.03−7.01 (1 H, m), 6.98 (1 H, t, J = 7.8 Hz), 6.91 (1 H, t, J = 7.5 Hz), 6.85 (1 H, t, J = 7.8 Hz), 6.81 (1 H, t, J = 7.5 Hz), 6.76 (1 H, t, J = 7.2 Hz), 6.74 (1 H, t, J = 7.2 Hz), 6.68 (1 H, t, J = 7.8 Hz), 6.66 (1 H, t, J = 7.8 Hz), 6.59 (1 H, t, J = 7.8 Hz), 6.49 (1 H, t, J = 7.8 Hz), 6.25 (1 H, d, J = 7.8 Hz), 6.23 (1 H, d, J = 7.8 Hz), 6.15 (1 H, d, J = 7.8 Hz), 6.07 (1 H, d, J = 7.8 Hz), 5.62 (1 H, d, J = 7.8 Hz); ^{13}C (C_6D_6, 150 MHz) δ 185.1, 151.4, 149.5, 147.1, 146.74, 146.57, 145.1, 143.7, 142.84, 142.65, 142.52, 142.1, 141.6, 139.9, 138.6, 137.2, 136.4, 135.6, 134.7, 134.5, 134.2, 133.3, 131.9, 131.7, 131.3, 130.4, 130.2, 129.6, 128.90, 128.77, 128.6, 127.5, 126.9, 125.8, 125.4, 125.1, 124.4, 124.1, 123.2, 122.7, 122.4, 119.9, 119.5, 64.8, 58.2; HRMS m/z calcd for $C_{59}H_{31}Cl_2O$ (MH^+) 825.1752, found 825.1755. Recrystallization of **15** from a mixture of methylene chloride and hexanes produced a single crystal suitable for X-ray structure analysis.

Alcohol 18. To a solution of 0.089 g (0.090 mmol) of the *anti* and *syn* isomers of **16** in 10 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added slowly via cannula a solution of 0.07 mL (0.9 mmol) of thionyl chloride and 0.11 mL (1.4 mmol) of pyridine in 5 mL of diethyl ether. The reaction mixture then was allowed to warm to room temperature. After 7 h, 15 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 brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash chromatography (silica gel/40% methylene chloride in hexanes) to afford 0.044 g (0.043 mmol, 48%) of **18** as a bright yellow solid: IR 1643, 1600 cm^{-1}; ^{1}H (C_6D_6, 600 MHz) δ 8.88 (1 H, d, J = 7.8 Hz), 8.85 (1 H, d, J = 7.8 Hz), 7.99 (1 H, d, J = 7.2 Hz), 7.77 (1 H, d, J = 7.2 Hz), 7.57 (1 H, d, J = 7.2 Hz), 7.48−7.46 (2 H, t, J = 6.3 Hz), 7.42 (1 H, t, J = 7.5 Hz), 7.34 (1 H, d, J = 7.8 Hz), 7.31 (1 H, t, J = 7.2 Hz), 7.27−7.21 (6 H, m), 7.03−6.84 (10 H, m), 6.76−6.69 (3 H, m), 6.66−6.61 (3 H, m), 6.53 (1 H, t, J = 7.5 Hz), 6.45 (1 H, d, J = 7.8 Hz), 6.34 (1 H, d, J = 7.8 Hz), 6.27 (1 H, d, J = 7.8 Hz), 6.14 (1 H, d, J = 7.8 Hz), 6.01 (1 H, d, J = 7.8 Hz), 5.83 (1 H, d, J = 7.8 Hz), 1.07 (1 H, s); ^{13}C (C_6D_6, 150 MHz) δ 152.2, 151.6, 148.7, 148.3, 147.9, 147.0, 146.25, 146.18, 144.3, 142.4, 142.2, 141.7, 141.4, 139.0, 136.7, 136.42, 136.36, 134.2, 133.9, 133.8, 133.3, 132.2, 132.1, 131.1, 130.82, 130.79, 129.8, 129.4, 127.4, 127.2, 127.1, 126.9, 126.7, 126.5, 126.1, 126.0, 125.8, 125.7, 125.4, 125.0, 124.6, 124.48, 124.43, 123.6, 122.9, 122.6, 122.0, 121.6, 119.7, 119.4, 100.2, 93.7, 89.1, 86.1, 85.4 (the ^{13}C NMR signals of the two sp^3-hybridized quaternary carbons without a hydroxyl substituent are too weak to be discerned); MS m/z 1009 (M^+ − OH); HRMS m/z calcd for $C_{75}H_{40}Cl_2ONa(MNa^+)$ 1049.2354, found 1049.2361. Recrystallization of **18** from a mixture of methylene chloride and 2-propanol produced a single crystal suitable for X-ray structure analysis.

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Supporting Information Available: Experimental procedures and/or spectroscopic data for **13**, **14**, and **16**, ^{1}H and ^{13}C NMR spectra of compounds **9**, **13**−**16**, and **18**, and ORTEP and ball and stick drawings of the crystal structures of **13**, *cis*-**14**, **15**, and **18** (PDF) and X-ray crystallographic data of **13**, *cis*-**14**, **15**, and **18** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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