Revised Structures of *N*-Substituted Dibrominated Pyrrole Derivatives and Their Polymeric Products. Termaleimide Models with Low Optical Band Gaps

Dong-Sook Choi, Shenlin Huang, Mingsheng Huang, Thomas S. Barnard, Richard D. Adams,*,† Jorge M. Seminario,* and James M. Tour*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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This paper describes an unexpected rearrangement/oxidation of *N*-substituted 2,5-dibromopyrroles upon treatment with HNO_3. The bromides migrate from the 2,5-positions to the 3,4-positions with subsequent oxidation at the 2,5-positions to afford *N*-substituted 3,4-dibromomaleimides; the structure was confirmed by single-crystal X-ray analysis. The maleimides were then polymerized to the poly(*N*-substituted-3,4-maleimide)s with copper bronze. This constitutes a revision of structure for the monomers and polymers. The propensity for the dibromide migration was further confirmed by treatment of *N*-benzyl-2,5-dibromopyrrole under nonoxidative acidic conditions (*p*-TsOH) to afford *N*-benzyl-3,4-dibromopyrrole; both the starting material and product structures were confirmed by single-crystal X-ray analysis. Several termaleimides were prepared from pyrrole, maleic anhydride, and citraconic anhydride. These trimeric compounds underwent enormous shifts in their optical absorbance maxima (ca. 200 nm) when bases or nucleophilic solvents were added. Therefore, the termaleimides served as excellent models for the polymeric systems that had undergone shifts of 350−400 nm upon treatment with the same additives. Ab initio Hartree−Fock and density functional theory were utilized to assess the minimum conformation of the trimeric system. Both terminal maleimides appear canted 37° relative to the central maleimide unit. As the two end maleimide units were computationally forced into closer proximity, there was a dipolar stabilization that ensued between the two terminal maleimides with the formation of a 1,3-dioxetane. However, it is unlikely that there could be the formation of an isolable 1,3-dioxetane due to the large energy difference between the canted structure and the dioxetane. A significant decrease in the HOMO−LUMO energy of 13 kcal/mol was calculated upon formation of the 1,3-dioxetane, suggesting that nucleophiles likely move the canted structure more toward a planar form via addition to the α,β-unsaturated carbonyl units.

Due to their stable semiconducting characteristics, there has been considerable interest in the preparation and use of pyrrole-derived polymers, especially the parent poly(2,5-pyrrole), which is made by electropolymerization or simple $FeCl_3$-induced oxidative polymerization of pyrrole.[1] Recently, there have been several syntheses of pyrrole-derived polymers from the well-documented *N*-substituted 2,5-dibromopyrroles.[2] Starting from these dibromopyrroles, we previously reported the preparation of polymers with unique sensor-like properties possessing pH, solvent, or ion-induced absorption shifts of λ_{max} from the UV or visible to the near-IR (750−900 nm) spectral regions.[3] We report here a reassignment for the monomer and polymer structures. We also prepared several termaleimides to serve as models for understanding the unique optical properties of the polymers. The model trimers proved to be interesting in their own right, exhibiting enormous optical band gap decreases of 200 nm upon the addition of nucleophiles, an exceptionally large value for simple trimeric systems.

In our initial studies on pyrrole-derived polymers, we had suggested that NBS-induced 2,5-dibromination of *N*-substituted pyrroles followed by HNO_3 oxidation yielded the zwitterionic dibromopyrroles **3a**−**c**.[3] However, recent work has shown that HNO_3 oxidation of *N*-substituted 2,5-dibromopyrroles (**2a**−**c**) does not generate the zwitterionic structures **3a**−**c** but instead generates the constitutional isomers **4a**−**c**, respectively (Scheme 1).[4] This results from an unexpected yet high-yielding transposition of both bromides to the 3,4-position with subsequent oxidation at the 2,5-positions to afford the *N*-substituted 3,4-dibromomaleimides.[5] We confirmed the structure of **4a** by single-crystal X-ray diffraction analysis.[6] The mechanism for the rearrangement could be as

† To whom correspondence regarding crystal structure details should be addressed.

(1) Street, G. B. In *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986. (b) Bureau, J. M.; Gazard, M.; Champagne, M.; Dubois, J. C.; Tourillon, G.; Garnier, F. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 235. (c) Street, G. B.; Lindsey, S. E.; Nazzal, A. I.; Wynne, K. J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 137.

(2) Groenendaal, L.; Peerlings, H. W. I.; van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Macromolecules* **1995**, *28*, 116. (b) Pomerantz, M.; Yang, H.; Cheng, Y. *Macromolecules* **1995**, *28*, 5706.

(3) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437. (b) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7435.

(4) Beddoes, R. L.; Zhao, Y.; Joule, J. A. *Acta Crystallogr.* **1996**, *C52*, 2313. This reference contains the corrected structure for the Diels−Alder adduct, confirmed by X-ray analysis, resulting from the [4 + 2] cycloaddition of **4a** and cyclopentadiene; however, the structures suggested by Beddoes et al. for the NBS-bromination products of *N*-alkylpyrroles are incorrect.

(5) Gilow, H. M.; Burton, D. E. *J. Org. Chem.* **1981**, *46*, 2221. (b) Artico, M. In *Heterocyclic Compounds, Pyrroles*; Jones, R. A., Ed.; Wiley: New York, 1990; Vol. 48, Part I.

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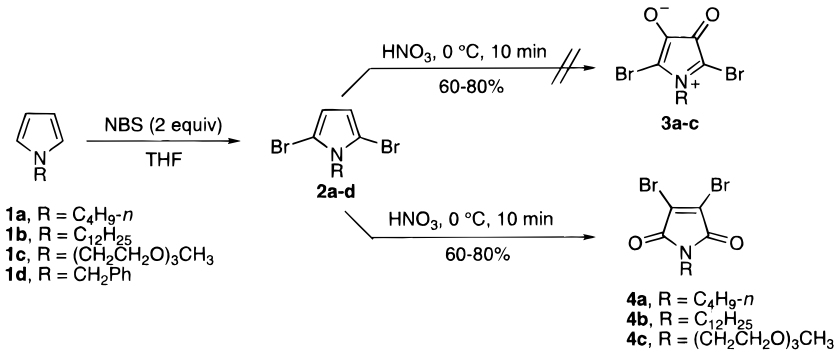
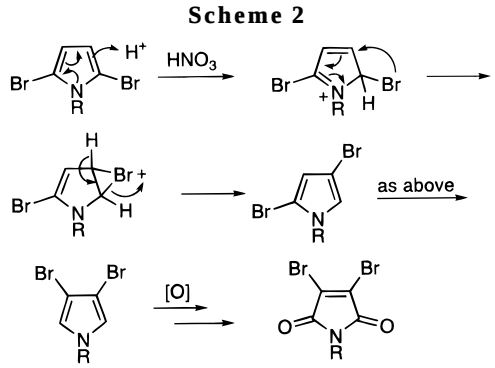
Scheme 1

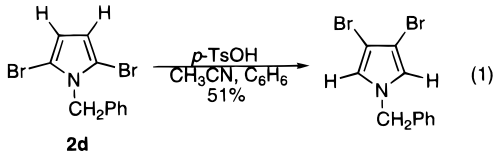


Scheme 2



shown in Scheme 2.[5] Oxidation at the 5-position might precede the second bromide migration; nevertheless, the bis(bromide) rearrangement and oxidation was facile and high yielding even at 0 °C.

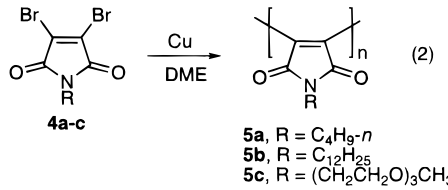
To ensure that the initial NBS-bromination of the *N*-alkylpyrroles occurred at the 2,5-positions, the structure of **2d** was determined by single-crystal X-ray analysis.[6] Furthermore, that acid-induced rearrangement could occur was further confirmed by treatment of **2d** under nonoxidative acidic conditions with *p*-TsOH to afford *N*-benzyl-3,4-dibromopyrrole whose structure was also determined crystallographically (eq 1).[6] The ^{1}H



(1)

NMR chemical shift change for the pyrrole resonances (δ 6.26 for **2d** and δ 6.66 for *N*-benzyl-3,4-dibromopyrrole) provide a useful handle for following the migration. However, the aforementioned crystallographic determinations were necessary to ensure the initial assignments of the bromide locations.

Ullmann polymerization of the dibromides **4a**−**c** afforded, therefore, the poly(*N*-substituted-3,4-maleimide)s (eq 2). The spectroscopic and size-exclusion chromatography data for these polymers have been described previously.[3] In brief, after one fractional precipitation, M_n = 5000−10 000 and PDI = 1.2−1.5. There were only



(2)

small differences between the ^{1}H NMR spectra of the monomers and their corresponding polymers.

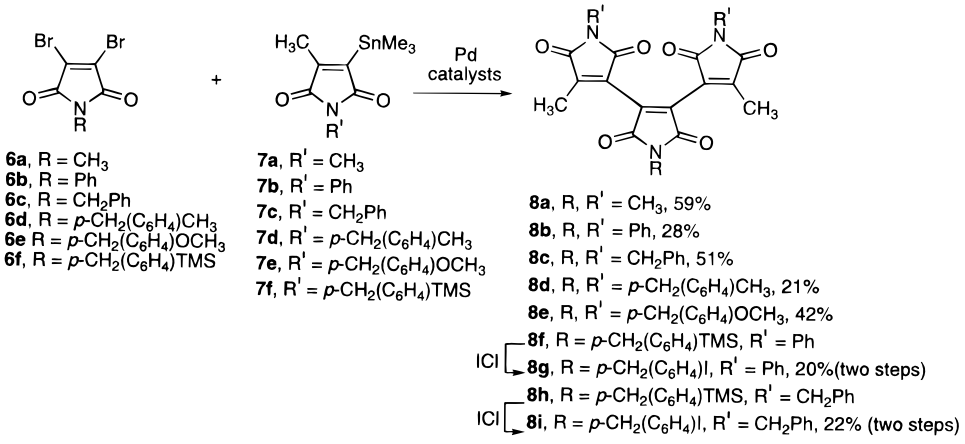
In an effort to understand the unique sensor-like optical properties in the polymers, we sought to make well-defined oligomeric species, specifically trimers, that could be studied optically. Oligomers can often be formed by shortening reaction times and temperatures of the corresponding polymerization reactions.[7] Unfortunately, as is commonly noticed with this method of oligomer synthesis, we were unable to isolate any of the desired homogeneous oligomeric species after fractionation and chromatographic separations. We then proceeded to prepare *N*-butyl-3-bromomaleimide for use as a chain-terminating agent in the Ullmann polymerization; however, again no desired trimeric species could be isolated. Seeking a more controlled cross-coupling approach rather than a homocoupling approach, Stille coupling methods were used to prepare termaleimides; however, it became evident that the α,ω-unsubstituted termaleimides were too unstable to isolate. Therefore, the *N*-substituted 3,4-dibromomaleimides **6a**−**f** were prepared from pyrrole by bromination with NBS followed by rearrangement and oxidation with HNO_3 or, more simply, from maleic anhydride by reaction with a primary amine and a bromonium ion source (Br_2/NaOAc/AcOH or Br_2/$AlBr_3$).[8] Similarly, the *N*-substituted 3-methyl-4-(trimethylstannyl)maleimides **7a**−**f** were prepared from citraconic anhydride by reaction with a primary amine, the same bromonium ion sources listed above, and then conversion of the bromide to the trimethylstannane with $(Me_3Sn)_2$ under Pd-catalyzed conditions.[9] These two components were then cross-coupled with Pd catalysts to afford the methyl-terminated termaleimides **8a**−**i** (Scheme 3). Unfortunately, we have been unable to obtain any of these compounds in a crystalline form suitable for structural analysis by X-ray diffraction.

While the polymaleimides had λ_{max} values ca. 520 nm in THF, the trimers, with their shorter degrees of extended conjugation, understandably had smaller optical absorbance maxima (ca. 390 nm). The polymaleim-

(6) Crystal data for **2d**: space group $P2_1/n$, a = 12.324(5) Å, b = 6.284(3) Å, c = 14.580(6) Å, β = 93.69(3)°, Z = 4, 717 reflections $I > 3\sigma(I)$, R = 0.053, and R_w = 0.052. (b) Crystal data for *N*-benzyl-3,4-dibromopyrrole: space group $P2_1/n$, a = 12.165(7) Å, b = 6.443(4) Å, c = 14.609(6) Å, β = 95.27(4)°, Z = 4, 845 reflections $I > 3\sigma(I)$, R = 0.053, R_w = 0.056. (c) Crystal data for **4a**: space group $P2_1/c$, a = 7.427(2) Å, b = 18.564(3) Å, c = 8.154(2) Å, β = 111.18(2)°, Z = 4, 1097 reflections $I > 3\sigma(I)$, R = 0.039, and R_w = 0.043.

(7) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.
(8) Earl, R. A.; Clough, F. W.; Townsend, L. B. *J. Heterocycl. Chem.* **1978**, *15*, 1479. (b) Brown, J. P. *Chem. Abstr.* **1966**, *65*, 2131a.
(9) Sandosham, J. Undheim, K. *Acta Chem. Scand.* **1989**, *43*, 684.

Scheme 3



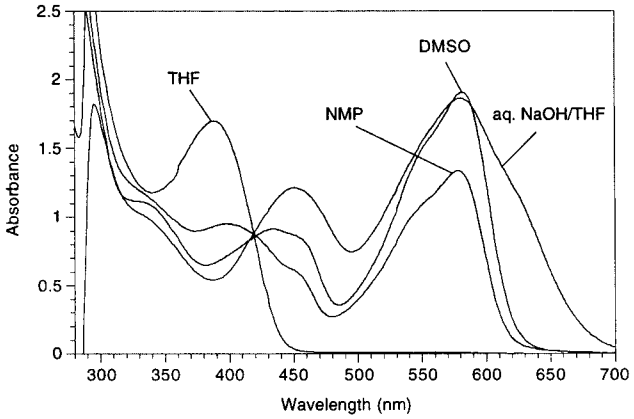


Figure 1. UV−vis spectrum of **8i** in THF, DMSO, NMP, and aqueous NaOH/THF.

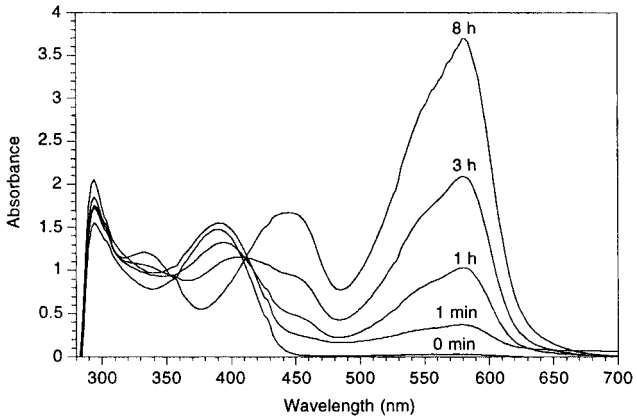


Figure 2. UV−vis spectrum of **8c** (2.5 mL, 0.30 mM in THF) with an added solution of aqueous $NaHCO_3$ (0.03 mL, 0.1 M) and monitoring as a function of time.

ides exhibited bathochromic shifts in their absorption maxima of 350−400 nm when bases or strong donor solvents were added. The trimers similarly showed bathochromic shifts of ca. 200 nm when exposed to the same nucleophilic environments (Figure 1). All of the termaleimides exhibited nearly identical behavior in these various media. None of these solvent systems are likely to act as one-electron donor or acceptor reagents promoting a doped-like state in the trimers; therefore, the bathochromic shifts are probably conformationally induced rather than oxidatively or reductively induced. Although the trimers did not show the low HOMO−LUMO gaps as in the band gaps of the polymers, their bathochromic shifts were unusually pronounced for short conjugated systems; optical band gaps of ca. 1.8 eV were obtained. Therefore, a reduction of ca. 1.0 eV in the HOMO−LUMO gaps was afforded upon treatment of these trimers with nucleophilic solvents.

As typically observed when comparing polymers and small molecules, the trimers were less resilient than the polymers; hence, decomposition of the trimers was observed over a period of 24 h when exposed to aqueous NaOH/THF. However, the trimers were stable in mild alkaline environments such as aqueous $NaHCO_3$/THF, although the response times to these milder bases were slow (Figure 2).

While the polymers showed reversible sensor-like activity with alternating basic and acidic additions, reversibility was not noticed with these less stable oligomeric versions. Addition of sodium bicarbonate gave

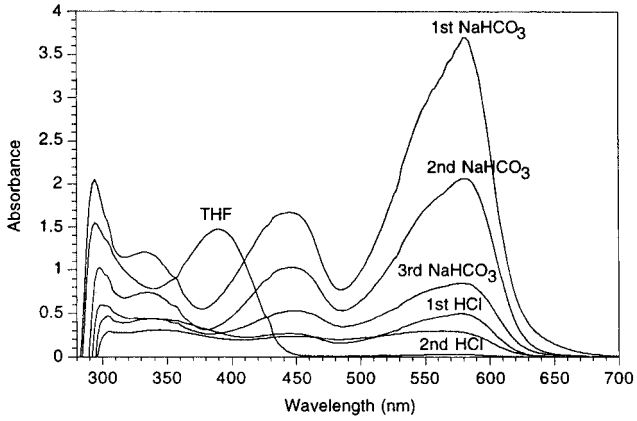


Figure 3. UV−vis spectral trends of **8c** (2.5 mL, 0.30 mM in THF) upon the alternating addition of aqueous $NaHCO_3$ (0.1 M) and aqueous HCl (0.1 M) at 5−10 min cycles.

the expected intense bathochromic shifts to 445 and 580 nm, while addition of aqueous HCl did not restore the original spectral characteristics. Instead, upon acid addition, the absorption intensities plummeted throughout the UV−vis spectral region. Addition of base afforded some recovery of the 445 and 580 nm absorptions, which could again be lost with the addition of acid. By the hypochromicity of the third cycle, it was clear that the material was decomposing (Figure 3). These spectral trends are difficult to rationalize, but they are interesting nonetheless.

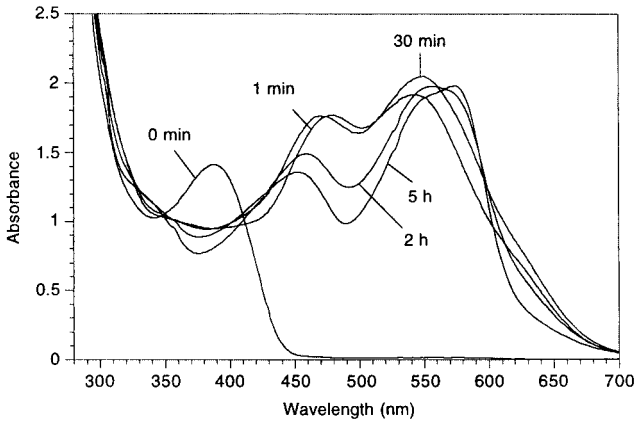


Figure 4. Reaction progress of **8i** (3.0 mL, 0.23 mM in THF) upon the addition of NaSMe (0.1 mL, 0.01 M in methanol) as a function of time.

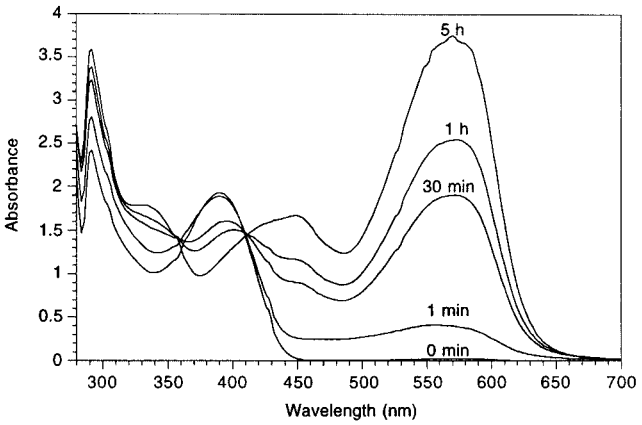


Figure 5. Reaction progress of **8c** (3.0 mL, 0.50 mM in THF) upon the addition of n-C_4H_9Cu (0.05 mL, 0.01 M in diethyl ether) as a function of time.

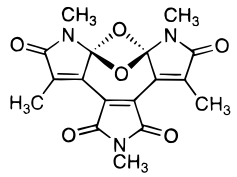
Upon the addition of sodium thiomethoxide or n-butylcopper, both of which are typically 1,4-addition reagents, intense bathochromic shifts were observed that generated stable structures (monitored for 5−24 h) with absorption maxima ca. 580 nm (Figures 4 and 5). This may suggest a 1,4-addition mechanism, though a one-electron addition is possible with the copper reagent.

To rationalize these large changes in the HOMO−LUMO gaps of the trimers, we considered the possible effects of nucleophiles on these compounds. It has been reported that even weak nucleophiles can react with maleimides by a 1,4- or 1,2-addition to one of the α,β-unsaturated carbonyl groups.[11] Therefore, considering 1,2-addition to a maleimide unit on the trimer, the newly generated oxy anion is in position to attack the carbonyl moiety of a maleimide two units away, thus fixing the trimer into a near-planar configuration and maximizing the extended conjugation (Scheme 4, eq 3). 1,2-Addition followed by an intramolecular 1,4-addition would form a spiro-6,5 ring system **10** (Scheme 4, eq 4). Though attack at a β,β-disubstituted system could be slow, 1,4-addition would again lead to an intramolecular reaction to give the near planar trimer **11** or another spiro-6,5 ring system **12** (Scheme 4, eqs 5 and 6). Equations 3 and 5 represent 7-*exo-trig* ring-closure processes, while eqs 4 and 6 have 6-*exo-trig* closures; therefore, all four routes are stereoelectronically favorable by Baldwin's rules.[12] Finally, conjugate addition followed by bond migration would lead to severe buttressing of the carbonyl moieties (Scheme 4, eq 7); thus, this manifold is unlikely to occur to any significant extent. Hence, several nucleophilic routes to highly conjugated structures are possible that would lower the optical band gap of the material, though configurations **9** and **11** appear most likely to afford the highly conjugated systems with low HOMO−LUMO gaps.

Table 1. Total, HOMO, and LUMO Energies for the Two Conformations of 8a (Open, 37°-Canted Terminal Maleimides) and 14 (Closed, 1,3-Dioxetane) Using HF/3-21G

property	open (hartrees)	closed (hartrees)	Δ (kcal/mol)
energy	−1258.030 78	−1257.986 55	27.8
HOMO	−0.356 85	−0.341 68	9.5
LUMO	0.000 15	−0.005 79	−3.7
Δ	0.357 00	0.335 89	13.2

Since no crystal data could be obtained, we proceeded to study **8a** using ab initio Hartree−Fock (HF) and density functional theory (DFT).[13] Compound **8a**, in its minimum energy conformation, had both terminal maleimides canted 37° relative to the central maleimide unit. As the two end maleimide units were computationally forced into closer proximity, there was a dipolar stabilization that ensued between the two terminal maleimides with the formation of a 1,3-dioxetane that had the three original maleimide rings held in a coplanar conformation as in **14**. However, it is unlikely that there could be the



14

formation of an isolable 1,3-dioxetane from the near-planar intermediates resulting from **9** and **11** since the relative stability between the minimized structure for **8a** (37° canted terminal maleimides) and **14** was 28 kcal/mol using HF/3-21G (Table 1) and **14** could readily open to form a less strained intermediate. Using structures similar to **8a** and **14**, except with substitution of the methyl groups with hydrogen atoms to limit the size of the system, and using the more precise B3PW91/6-31G**, which increases the size of the basis, adds polarization functions, and includes electron correlation, the relative

(10) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

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Scheme 4

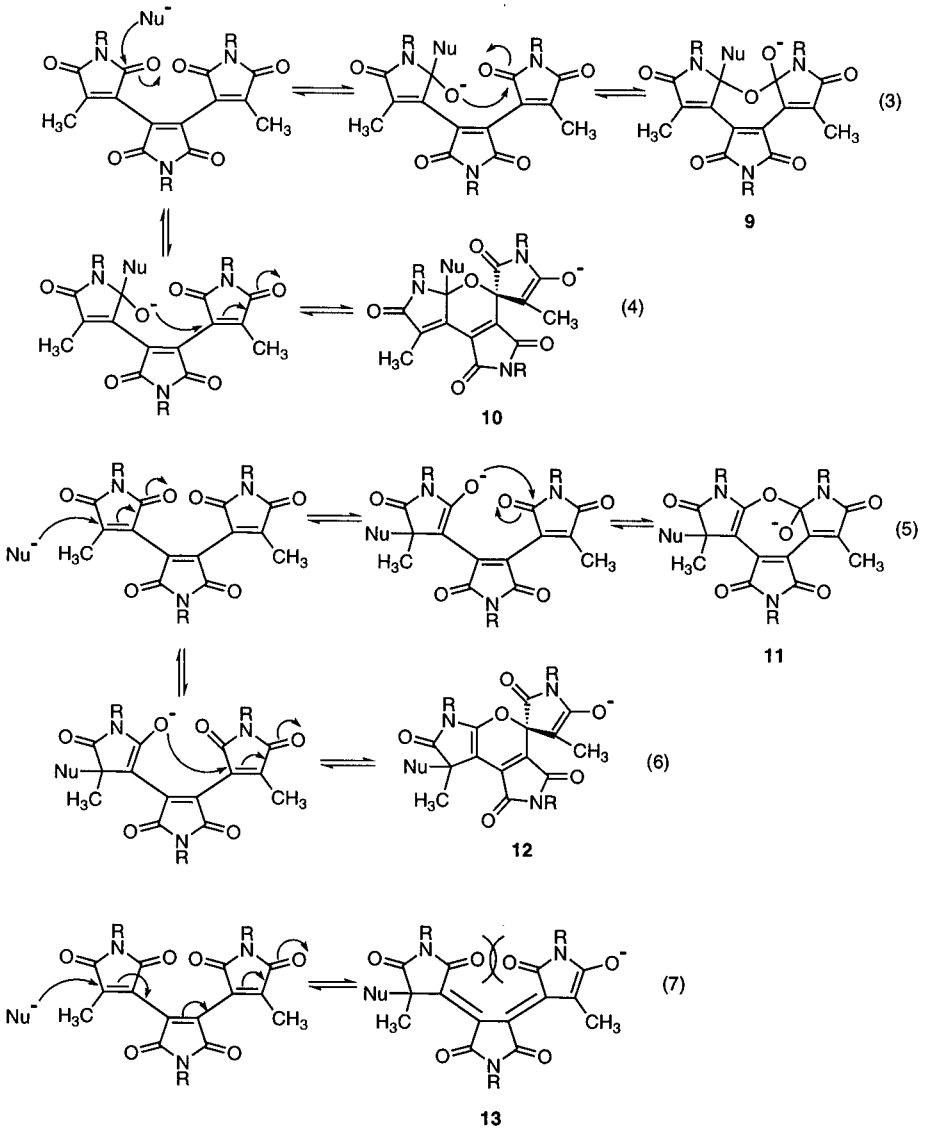

Table 2. Total Energy, Using B3PW91/6-31G, for the Two Conformations of a Termaleimide Analogous to 8a Open (37°-Canted Terminal Maleimides) and 14 (Closed, 1,3-Dioxetane) but with Hydrogen Atoms Replacing All the Methyl Groups**

	open (hartrees)	closed (hartrees)	Δ (kcal/mol)
energy	−1075.520 10	−1075.488 48	19.8

energy difference between the 37° canted structure and the 1,3-dioxetane system was 20 kcal/mol as shown in Table 2. A HOMO−LUMO energy difference between the minimized 37°-canted structure and the 1,3-dioxetane **14** was calculated to be 13 kcal/mol (Table 1), suggesting that minimizing the twisting would cause a significant decrease in the HOMO−LUMO gaps; a trend readily observed experimentally.

In summary, an unexpected yet fascinating rearrangement/oxidation of *N*-substituted 2,5-dibromopyrroles results in the formation of *N*-substituted 3,4-dibromomaleimides, which were polymerized to the poly(*N*-substituted 3,4-dibromomaleimide)s under Ullmann conditions. Several model termaleimides were prepared that exhibited a 200 nm bathochromic shift in their optical absorbance maxima upon treatment with nucleophiles; a trend similar to that exhibited by the polymers. Ab initio Hartree−Fock and density functional theories were utilized to assess the minimum energy conformations of the trimeric system, which suggest that there is a dipolar stabilization between the two terminal maleimides with a concomitant decrease in the HOMO−LUMO energy. Nucleophiles probably move the canted structure toward a planar form via addition to the α,β-unsaturated carbonyl units. Therefore, the study of these trimeric systems has afforded a rationale for the extraordinary optical trends exhibited by their polymeric analogues.

Experimental Procedures

General Methods. All nonaqueous operations were carried under a dry, oxygen-free, nitrogen atmosphere. Copper bronze, *N*-methylpyrrole, citraconic anhydride, aluminum tribromide, benzyl bromide, iodine monochloride, *p*-methylbenzylamine, and *p*-methoxybenzylamine were purchased from Aldrich Chemical Co. *N*-Phenylmaleimide was purchased from Fisher Scientific. Hexamethyldistannane was purchased from Aldrich Chemical Co. or Fluka Chemical Co. Reagent-grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent-grade acetonitrile, benzene, dichloromethane, and toluene were distilled under nitrogen from calcium hydride. Bulk-grade hexane was distilled prior to use. Gravity column chroma-

tography and flash chromatography were carried out on silica gel (230−400 mesh from EM Science). The syntheses of **1a**−**c**, **2a**−**c**, **4a**−**c**, and **5a**−**c** have been described previously.[3] Although some small impurity peaks were noted in the ^{1}H NMR or ^{13}C NMR spectra of the new compounds, the purity levels were >94% in all cases. Specific minor impurity peak locations can be noted by referring to the actual spectra in the Supporting Information.

***N*-Benzylpyrrole (1d).**[14] The procedure by Wang et al.[14] was modified as follows. A nitrogen-purged flask equipped with a reflux condenser was charged with dichloromethane (50 mL), tetrabutylammonium bromide (9.69 g, 30.1 mmol), pyrrole (2.10 mL, 30.2 mmol), and benzyl bromide (4.0 mL, 33.6 mmol), and the mixture was cooled to 0 °C using an ice bath. To this solution was added dropwise 50% aqueous sodium hydroxide (30 mL). After the addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (20 mL) and the aqueous phase was extracted with methylene chloride (3×). The combined organic extracts were washed with 3 N hydrochloric acid, water, and brine and dried over magnesium sulfate. The solvent was removed in vacuo, and the crude product was purified by distillation to afford 3.95 g (84%) of the title compound as a colorless liquid: FTIR (neat) 3098, 3061, 3027, 2918, 1497, 1453, 1394, 1355, 1284, 1088, 1067, 1028, 968, 813, 724, 626 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.11 (m, 5 H), 6.71 (t, J = 2.1 Hz, 2 H), 6.21 (t, J = 2.2 Hz, 2 H), 5.08 (s, 2 H).[14]

***N*-Benzyl-2,5-dibromopyrrole (2d).**[15] The procedure used was analogous to Khoury et al.'s[15] method and was modified as follows. To a nitrogen-purged flask charged with THF (100 mL) was added *N*-benzylpyrrole (1.57 g, 10.0 mmol), and the mixture was then cooled to −78 °C. *N*-Bromosuccinimide (3.48 g, 19.6 mmol) was added, and the reaction mixture was allowed to warm to room temperature. After the mixture was stirred at room temperature for 12 h, the solvent was removed in vacuo, and the crude product was dissolved in hexane and filtered. The solvent was removed from the filtrate to give a residue that was purified by flash chromatography on silica gel (hexanes) to afford 2.66 g (84%) of the title compound as a pale yellow solid: FTIR (film) 3114, 3031, 2922, 2852, 1545, 1496, 1442, 1419, 1374, 1357, 1286, 1221, 1150, 1102, 1074, 996, 972, 902, 842, 762, 728, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.26 (m, 3 H), 7.05 (d, J = 7.2 Hz, 2 H), 6.26 (s, 2 H), 5.23 (s, 2 H).[6a,15]

***N*-Benzyl-3,4-dibromopyrrole.** To a nitrogen-purged flask charged with acetonitrile (70 mL) and benzene (70 mL) was added *N*-benzyl-2,5-dibromopyrrole (4.41 g, 14.0 mmol), and the mixture was then cooled to 0 °C. To this solution was added *p*-toluenesulfonic acid (5.33 g, 28.0 mmol), and the reaction mixture was allowed to warm to room temperature. After the mixture was stirred at room temperature for 18 h, the mixture was poured into cold saturated sodium bicarbonate and extracted with ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. Removal of solvent gave the crude product, which was purified by flash chromatography on silica gel (hexanes) to afford 2.30 g (52%) of the title compound as a pale yellow solid: mp 59−62 °C; FTIR (film) 3120, 3032, 3008, 2921, 1604, 1494, 1453, 1438, 1394, 1354, 1304, 1194, 1124, 1109, 1077, 1031, 974, 960, 904, 850, 782, 768, 756, 729, 694, 629 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.11 (m, 5 H), 6.66 (s, 2 H), 4.95 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 129.0, 128.3, 127.3, 121.1, 98.6, 54.5.[6b]

General Procedure for the Bromination of Cyclic Anhydrides (Procedure A).[8b] To a nitrogen-purged screw cap tube was sequentially added maleic anhydride or citraconic anhydride, aluminum tribromide (1.1 mol %), and bromine (1−2 equiv). The reaction mixture was then heated to 120 °C overnight. After cooling to 0 °C, the resulting solid product was collected and purified by recrystallization from benzene. The details are described below for each material.

3,4-Dibromomaleic Anhydride.[8b] See procedure A. Maleic anhydride (9.81 g, 100 mmol), aluminum tribromide (0.302 g, 1.13 mmol), and bromine (10.3 mL, 200 mmol) were used to give 18.2 g (71%) of the title compound as a pale yellow solid after recrystallization: mp 105−111 °C (lit.[8b] mp 105−115 °C); FTIR (film) 1857, 1823, 1778, 1592, 1279, 1237, 1180, 1158, 971, 924, 827, 758, 724, 684 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 131.4.

3-Bromo-4-methylmaleic Anhydride. See procedure A. Citraconic anhydride (4.50 mL, 50.1 mmol), aluminum tribromide (0.151 g, 0.57 mmol), and bromine (2.60 mL, 50.1 mmol) were used to afford 6.59 g (69%) of the title compound as a white solid after recrystallization: mp 74−76 °C; FTIR (film) 2139, 1914, 1857, 1829, 1768, 1485, 1430, 1380, 1275, 1237, 1163, 1048, 1031, 905, 855, 763, 723, 676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 160.1, 145.6, 126.8, 11.4; HRMS calcd for $C_5H_3{}^{79}BrO_3$ 189.9266, found 189.9262.

***N*-Phenyl-3-methylmaleimide.**[16] To a stirred solution of citraconic anhydride (2.70 mL, 30.0 mmol) in an ice-cooled bath in acetic acid (60 mL) was added aniline (2.70 mL, 30.7 mmol) dropwise. The reaction mixture was heated to 90 °C for 2 h. After the mixture was cooled to 0 °C, the solvent was removed to give the crude product, which was purified by recrystallization from ethanol to afford 4.78 g (85%) of the title compound as a pale yellow solid: mp 96−98 °C (lit.[16] mp 98 °C); FTIR (film) 3085, 2989, 2924, 1744, 1704, 1642, 1596, 1506, 1455, 1406, 1290, 1186, 1115, 1072, 1037, 1000, 888, 873, 769, 753, 708, 691, 652, 617 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.31 (m, 5 H), 6.46 (q, J = 1.8 Hz, 1 H), 2.15 (d, J = 1.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 169.6, 145.8, 131.7, 129.1, 127.7, 127.5, 126.0, 11.2; LRMS calcd for $C_{11}H_9NO_2$ 187, found 187.

***p*-(Trimethylsilyl)benzylamine.**[17] The procedure used was analogous to Sakata et al.'s[17] method and was modified as follows. To a stirred suspension of lithium aluminum hydride (1.64 g, 43.2 mmol) in diethyl ether (100 mL) in an ice bath was added dropwise *p*-(trimethylsilyl)benzonitrile (4.81 g, 27.4 mmol) in diethyl ether (20 mL). The reaction mixture was heated to reflux for 3 h. After cooling, mixture was sequentially quenched with ethyl acetate, ethanol, ice chips, and water. The resulting salt was removed by filtration, and the filtrate was extracted with diethyl ether (3×). The combined organic layers were washed with brine and dried over magnesium sulfate. After evaporation, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 9:1) and then distillation (98 °C, 4 mmHg)[17] to afford 2.11 g (43%) of the title compound as a colorless oil: FTIR (neat) 3351, 3067, 3018, 2954, 2896, 2630, 1627, 1602, 1548, 1477, 1396, 1378, 1320, 1296, 1248, 1220, 1107, 1037, 992, 954, 838, 800, 755, 725, 692, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.02 Hz, 2 H), 7.30 (d, J = 8.06 Hz, 2 H), 3.85 (s, 2 H), 0.26 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.8, 133.7, 126.5, 46.5, −1.1; LRMS calcd for $C_{13}H_{12}BrNO_2$ 293; found 293.

General Procedure for the Preparation of Monobromomaleimides from Cyclic Anhydrides (Procedure B).[16] To a stirred solution of citraconic anhydride in acetic acid was added alkylamine (1 equiv) dropwise in an ice-cooled bath. The mixture was then heated to reflux for 2 h. After cooling, sodium acetate and bromine were added. The mixture was then heated to reflux for another 2 h. After cooling, the mixture was poured into water and extracted with ethyl acetate (3×). The combined organic phase was dried over magnesium sulfate, and then solvent was removed to give the crude product, which was purified by recrystallization. The details are described below for each material.

***N*-Methyl-3-bromo-4-methylmaleimide.** See procedure B. Citraconic anhydride (4.5 mL, 50 mmol), acetic acid (50

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mL), methylamine (25 mL, 50 mmol, 2 M in THF), sodium acetate (4.1 g, 50 mmol), and bromine (4.1 mL, 79.7 mmol) were used to afford 6.2 g (61%) of the title compound as a yellow solid after recrystallization from ethyl acetate: mp 44−46 °C; FTIR (film) 1773, 1716, 1646, 1440, 1386, 1244, 1003, 934, 816, 727, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.04 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 165.6, 142.3, 124.8, 24.6, 10.6; HRMS calcd for $C_6H_6{}^{79}BrNO_2$ 202.9582, found 202.9594.

***N*-Benzyl-3-bromo-4-methylmaleimide.** See procedure B. Citraconic anhydride (15.0 mL, 167 mmol), acetic acid (100 mL), benzylamine (18.0 mL, 167 mmol), sodium acetate (13.7 g, 167 mmol), and bromine (12.9 mL, 251 mmol) were used to afford 40.2 g (86%) of the title compound as a yellow solid after recrystallization from ethyl acetate: mp 60−62 °C; FTIR (film) 3470, 3059, 2938, 2848, 1955, 1907, 1776, 1715, 1651, 1600, 1494, 1436, 1402, 1338, 1288, 1255, 1207, 1183, 1156, 1107, 1070, 1030, 963, 925, 897, 860, 824, 754, 731, 701, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.26 (m, 5 H), 4.67 (s, 2 H), 2.02 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 165.1, 142.4, 136.0, 128.8, 128.6, 128.0, 124.9, 42.3, 10.7; HRMS calcd for $C_{12}H_{10}{}^{79}BrNO_2$ 278.9895, found 278.9886.

***N*-(*p*-Methylbenzyl)-3-bromo-4-methylmaleimide.** See procedure B. Citraconic anhydride (0.1 mL, 10 mmol), acetic acid (35 mL), *p*-methylbenzylamine (1.3 mL, 10 mmol), sodium acetate (0.94 g, 10 mmol), and bromine (0.7 mL, 15 mmol) were used to afford 0.91 g (31%) of the title compound as a pale yellow solid after recrystallization from ethanol: mp 81−82 °C; FTIR (film) 3470, 3032, 2939, 1777, 1714, 1651, 1614, 1538, 1512, 1431, 1396, 1344, 1304, 1253, 1206, 1181, 1094, 1037, 990, 962, 900, 850, 829, 802, 756, 725, 709, 693, 634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.9 Hz, 2 H), 7.10 (d, J = 7.9 Hz, 2 H), 4.63 (s, 2 H), 2.30 (s, 3 H), 2.01 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 165.2, 142.3, 137.8, 133.0, 129.4, 128.7, 125.0, 42.1, 21.16 10.7; HRMS calcd for $C_{13}H_{12}{}^{79}BrNO_2$ 293.0051, found 293.0062.

***N*-Phenyl-3-bromo-4-methylmaleimide.** To a stirred solution of *N*-phenyl-3-methylmaleimide (4.78 g, 25.5 mmol) and anhydrous sodium acetate (2.46 g, 30.0 mmol) in glacial acetic acid (30 mL) was added dropwise a solution of bromine (2.30 mL, 45.0 mmol) in acetic acid (45 mL) at 0 °C. The reaction mixture was then heated to reflux for 3 h. The precipitate was removed by filtration, and the filtrate was evaporated to dryness. The residue was extracted with ethyl acetate (3×), and the combined organic layers were washed with brine and dried over magnesium sulfate. Removal of the solvent gave the crude product, which was purified by recrystallization from ethanol to give 4.92 g (72%) of the title compound as a yellow solid: mp 88−89 °C; FTIR (film) 1714, 1646, 1591, 1503, 1454, 1401, 1382, 1284, 1259, 1179, 1128, 1069, 1050, 1030, 964, 913, 892, 824, 783, 755, 730, 703, 687, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46−7.30 (m, 5 H), 2.13 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 164.4, 142.4, 131.4, 129.2, 128.1, 125.9, 125.5, 10.9; HRMS calcd for $C_{11}H_8{}^{79}BrNO_2$ 264.9738, found 264.9738.

General Procedure for the Preparation of Monobromomaleimides from Cyclic Anhydrides (Procedure C). To a stirred solution of 3-bromo-4-methylmaleic anhydride (1.0 equiv) in acetic acid was added the alkylamine (1−2 equiv) in an ice-cooled bath. The mixture was then heated to reflux 2 h. After cooling, the solvent was removed to give the crude product, which was purified by column chromatography. The details are described below for each material.

***N*-(*p*-Methoxybenzyl)-3-bromo-4-methylmaleimide.** See procedure C. 3-Bromo-4-methylmaleic anhydride (2.9 g, 15.3 mmol), acetic acid (50 mL), and *p*-methoxybenzylamine (2.0 mL, 15.3 mmol) were used to afford 4.1 g (82%) of the title compound as a white solid after flash chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (film) 2941, 2838, 1776, 1716, 1649, 1612, 1584, 1511, 1459, 1429, 1397, 1339, 1295, 1248, 1210, 1175, 1091, 1032, 961, 899, 850, 805, 760, 726, 634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.7 Hz, 2 H), 6.83 (d, J = 8.7 Hz, 2 H), 4.61 (s, 2 H), 3.76 (s, 3 H), 2.00 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 165.2, 159.4, 142.3, 130.2, 128.2, 125.0, 114.0, 55.3, 41.8, 10.7; HRMS calcd for $C_{13}H_{12}{}^{79}BrNO_3$ 309.0001, found 308.9996.

***N*-[*p*-(Trimethylsilyl)benzyl]-3-bromo-4-methylmaleimide.** See procedure C. Used were 3-bromo-4-methylmaleic anhydride (0.788 g, 4.40 mmol), acetic acid (6 mL), and *p*-(trimethylsilyl)benzylamine (0.996 g, 5.21 mmol) to give 1.04 g (67%) of the title compound as a white solid after flash chromatography on silica gel (hexane/ether 6:1): FTIR (film) 3070, 3019, 2954, 2896, 1778, 1716, 1645, 1603, 1558, 1502, 1433, 1393, 1348, 1303, 1249, 1211, 1106, 1035, 965, 905, 839, 797, 756, 737, 694, 656, 632 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 4.67 (s, 2 H), 2.02 (s, 3 H), 0.23 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 165.2, 142.3, 140.4, 136.3, 133.8, 127.9, 125.1, 42.3, 10.71, −1.2; HRMS calcd for $C_{15}H_{20}{}^{79}BrNO_2Si$ 351.0290, found 351.0282.

***N*-Methyl-3,4-dibromomaleimide[18] (6a).** To a nitrogen-purged flask charged with THF (100 mL) was added *N*-methylpyrrole (4.0 mL, 45 mmol), and the mixture was then cooled to −78 °C. To this solution was added *N*-bromosuccinimide (16.0 g, 90.0 mmol), and the mixture was allowed to warm to room temperature. After the mixture was stirred at room temperature for 16 h, the solvent was removed in vacuo from the mixture, and the crude product was dissolved in hexane and filtered. The solvent was removed from the filtrate to give *N*-methyl-3,4-dibromopyrrole, which was cooled to 0 °C immediately, and 5 mL nitric acid (70%) was added dropwise.[3] After addition of nitric acid, the mixture was poured into ice. The aqueous phase was extracted with ethyl acetate (3×), and the combined organic extracts were washed with brine. The organic phase was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate 9:1) to afford 4.5 g (43%) of the title compound as a yellow solid: mp 114−116 °C (lit.[18] mp 120 °C); FTIR (film) 3484, 1783, 1717, 1667, 1596, 1488, 1471, 1449, 1267, 1165, 998, 822, 728, 714 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.12 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 129.4, 25.5; HRMS calcd for $C_5H_3{}^{79}Br_2NO_2$ 266.8531, found 266.8523.

***N*-Phenyl-3-bromomaleimide**.[19a] To a stirred solution of *N*-phenylmaleimide (5.08 g, 29.3 mmol) in glacial acetic acid (6 mL) at 90 °C was added dropwise a solution of bromine (2.20 mL, 42.7 mmol) in acetic acid (6 mL). After being stirred for 15 min, the mixture was cooled to 0 °C, and the solvent was removed to give the crude brominated *N*-alkylsuccinimide, which was treated with triethylamine (11.2 mL, 80.0 mmol) in ether (150 mL) at room temperature for 30 min. The resulting salt was removed by filtration, and the filtrate was evaporated to dryness. The residue was purified by recrystallization from ethanol to give 3.57 g (53%) of the title compound as a pale yellow solid: mp 150−153 °C (lit.[19a] mp 155 °C); FTIR (film) 3098, 3055, 1782, 1710, 1591, 1505, 1454, 1397, 1290, 1243, 1192, 1172, 1149, 1048, 974, 917, 865, 848, 799, 751, 718, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.30 (m, 5 H), 7.01 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.2, 131.9, 131.8, 131.0, 129.3, 128.4, 126.1; HRMS calcd for $C_{10}H_6{}^{79}BrNO_2$ 250.9582, found 250.9577.

***N*-Phenyl-3,4-dibromomaleimide[19b] (6b).** To a stirred solution of the *N*-phenyl-3-bromomaleimide (0.50 g 1.98 mmol) and anhydrous sodium acetate (0.166 g, 2.03 mmol) in glacial acetic acid (2 mL) was added dropwise a solution of bromine (0.17 mL, 3.30 mmol) in acetic acid (5 mL) at 0 °C. The reaction mixture was then heated to reflux for 3 h. The precipitate was removed by filtration, and the filtrate was evaporated to dryness. The residue was extracted with ethyl acetate (3×), and the combined organic layer was washed with brine and dried over magnesium sulfate. Removal of the solvent gave the crude product, which was purified by flash chromatography on silica gel (hexane/ethyl acetate 3:1) to afford 0.66 g (98%) of the title compound as a yellow solid: mp

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160−166 °C (lit.[19b] mp 166−168 °C); FTIR (film) 1722, 1682, 1599, 1503, 1488, 1392, 1288, 1215, 1134, 1115, 1069, 913, 828, 765, 731, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.31 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 130.9, 129.9, 129.4, 128.7, 126.1; LRMS calcd for $C_{10}H_5Br_2NO_2$ 331, found 331.

***N*-Benzyl-3,4-dibromomaleimide[20] (6c).** To a nitrogen-purged flask were added maleic anhydride (15.0 g, 153 mmol), acetic acid (100 mL) and benzylamine (16.7 mL, 153 mmol). The mixture was heated to reflux for 2 h. After cooling using an ice bath, sodium acetate (12.6 g, 153 mmol) and bromine (23.6 mL, 459 mmol) were added to the mixture and heated to reflux for another 2 h. The mixture was poured into water and extracted with ethyl acetate (3×). The combined organic phase was dried over magnesium sulfate. The solvent was removed in vacuo. The residue was crystallized from ethyl acetate to afford 43.8 g (83%) of the title compound as a yellow solid: mp 101−103 °C; FTIR (film) 2941, 1783, 1716, 1599, 1430, 1391, 1335, 1163, 1101, 1065, 909, 813, 754, 729, 700, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5 H), 4.73 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 135.6, 129.9, 129.3, 129.2, 128.7, 43.6; HRMS calcd for $C_{11}H_7{}^{79}Br_2NO_2$ 342.8844, found 342.8829.

General Procedure for the Preparation of Dibromomaleimides from Dibromocyclic Anhydrides (Procedure D).[21] To a stirred solution of 3,4-dibromomaleic anhydride (1.0 equiv) in acetic acid was added the alkylamine (1−2 equiv) in an ice-cooled bath. The mixture was then heated to reflux overnight. After cooling, the solvent was removed to give the crude product, which was purified by column chromatography or recrystallization. The details are described below for each material.

***N*-(*p*-Methylbenzyl)-3,4-dibromomaleimide (6d).** See procedure D. 3,4-Dibromomaleic anhydride (0.986 g, 3.85 mmol), acetic acid (8 mL), and *p*-methylbenzylamine (0.501 g, 3.89 mmol) were used to give 0.90 g (65%) of the title compound as a white solid after recrystallization from ethanol: mp 117−120 °C; FTIR (film) 3034, 2942, 1782, 1726, 1600, 1508, 1429, 1387, 1336, 1304, 1206, 1158, 1086, 1041, 912, 860, 839, 810, 755, 723, 706, 628 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.7 Hz, 2 H), 7.11 (d, J = 7.7 Hz, 2 H), 4.69 (s, 2 H), 2.30 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 138.2, 132.3, 129.52, 129.49, 128.8, 43.0, 21.2; HRMS calcd for $C_{12}H_9{}^{79}Br_2NO_2$ 356.9000, found 356.8982.

***N*-(*p*-Methoxybenzyl)-3,4-dibromomaleimide (6e).** See procedure D. 3,4-Dibromomaleic anhydride (3.90 g, 15.3 mmol), acetic acid (50 mL), and *p*-methoxybenzylamine (2.00 mL, 15.3 mmol) were used to afford 4.9 g (85%) of the title compound as a white solid after flash chromatography on silica gel (hexane/ethyl acetate 9:1): mp 116−118 °C; FTIR (film) 3480, 3008, 2943, 2837, 1781, 1721, 1610, 1598, 1513, 1459, 1430, 1388, 1335, 1302, 1250, 1210, 1176, 1161, 1085, 1031, 915, 856, 814, 760, 725, 628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 4.67 (s, 2 H), 3.76 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 159.6, 130.4, 129.5, 127.5, 114.2, 55.3, 42.7; HRMS calcd for $C_{12}H_9{}^{79}Br_2NO_3$ 372.8949, found 372.8936.

***N*-[*p*-(Trimethylsilyl)benzyl]-3,4-dibromomaleimide (6f).** See procedure D. 3,4-Dibromomaleic anhydride (1.43 g, 7.98 mmol), acetic acid (11 mL), and *p*-(trimethylsilyl)benzylamine (2.55 g, 9.97 mmol) were used to give 2.91 g (87%) of the title compound as a pale yellow solid after column chromatography on silica gel (hexane/ethyl acetate 6:1): mp 87−89 °C; FTIR (film) 3495, 3020, 2954, 1786, 1728, 1594, 1433, 1386, 1343, 1303, 1248, 1211, 1185, 1108, 1086, 1022, 954, 921, 837, 798, 757, 737, 693, 855, 628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 2 H), 7.34 (d, J = 7.8 Hz, 2 H), 4.73 (s, 2 H), 0.23 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 140.8, 135.6, 133.9, 129.5, 128.1, 43.2, −1.2; HRMS calcd for $C_{14}H_{15}Br_2NO_2Si$ 414.9219, found 414.9227.

General Procedure for the Preparation of the (Trimethylstannyl)maleimides (Procedure E).[9,10] A mixture of the *N*-substituted 3-bromo-4-methylmaleimide (1.0 equiv), hexamethyldistannane (1−2 equiv), and bis(triphenylphosphine)palladium(II) chloride (5 mol %) in toluene was heated to 60−70 °C overnight in a nitrogen-purged screw-cap tube. After cooling, the mixture was filtered and washed with ethyl acetate (2×). The filtrate was evaporated to remove the solvent, and the residue was purified by column chromatography on silica gel. The details are described below for each material.

***N*-Methyl-3-Methyl-4-(trimethylstannyl)maleimide (7a).** See procedure E. *N*-Methyl-3-bromo-4-methylmaleimide (1.6 g, 7.8 mmol), hexamethyldistannane (1.7 mL, 7.8 mmol), bis(triphenylphosphine)palladium(II) chloride (0.55 g, 0.78 mmol), and toluene (4 mL) were used to give 1.5 g (61%) of the title compound as a colorless liquid after flash chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (film) 3437, 2984, 2918, 1756, 1698, 1611, 1438, 1385, 1274, 1244, 1191, 1119, 1041, 990, 924, 778, 734, 673, 628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (s, 3 H), 2.07 (s, 3 H), 0.35 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 172.1, 154.6, 144.3, 24.0, 12.3, −8.7; HRMS calcd for $C_8H_{12}NO_2{}^{116}Sn$ 269.9885, found 269.9899.

***N*-Phenyl-3-methyl-4-(trimethylstannyl)maleimide (7b).** See procedure E. *N*-Phenyl-3-bromo-4-methylmaleimide (1.07 g, 4.02 mmol), hexamethyldistannane (2.75 g, 8.39 mmol), bis(triphenylphosphine)palladium(II) chloride (0.103 g, 0.147 mmol), and toluene (9 mL) were used to afford 1.06 g (76%) of the title compound as a pale yellow solid after flash chromatography on silica gel (hexane/ethyl acetate 8:1): mp 65−69 °C; FTIR (film) 3060, 2989, 2919, 1777, 1756, 1698, 1614, 1596, 1503, 1454, 1424, 1387, 1289, 1196, 1114, 1073, 1012, 910, 886, 775, 747, 694, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.24 (m, 5 H), 2.17 (s, 3 H), 0.41 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 170.7, 154.7, 144.9, 132.4, 129.0, 127.3, 125.7, 12.6, −8.5; HRMS calcd for $C_{14}H_{17}NO_2Sn$ 347.0277, found 347.0264.

***N*-Benzyl-3-methyl-4-(trimethylstannyl)maleimide (7c).** See procedure E. *N*-Benzyl-3-bromo-4-methylmaleimide (5.53 g, 19.7 mmol), hexamethyldistannane (4.20 mL, 19.7 mmol), bis(triphenylphosphine)palladium(II) chloride (0.69 g, 0.99 mmol), and toluene (10 mL) were used to give 5.0 g (70%) of the title compound as a colorless liquid after flash chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (neat) 3440, 3033, 2985, 2919, 1763, 1697, 1610, 1496, 1456, 1434, 1398, 1348, 1263, 1192, 1124, 1069, 1030, 962, 921, 886, 778, 735, 698, 670, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 4.61 (s, 2 H), 2.07 (s, 3 H), 0.35 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 172.0, 155.0, 144.9, 137.3, 129.0, 128.9, 128.0, 42.2, 12.8, −8.3; HRMS calcd for $C_{14}H_{16}NO_2{}^{116}Sn$ (M − CH_3) 346.0198, found 346.0190.

***N*-(*p*-Methylbenzyl)-3-methyl-4-(trimethylstannyl)-maleimide (7d).** See procedure E. *N*-(*p*-Methylbenzyl)-3-bromo-4-methylmaleimide (0.303 g, 1.03 mmol), hexamethyldistannane (0.568 g, 1.73 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.0406 g, 0.0578 mmol), and toluene (2.4 mL) were used to afford 0.19 g (50%) of the title compound as a pale yellow solid after flash chromatography on silica gel (hexane/ethyl acetate 8:1): mp 92−97 °C; FTIR (film) 3439, 2984, 2920, 1761, 1698, 1610, 1515, 1433, 1395, 1347, 1305, 1263, 1192, 1126, 1090, 1023, 961, 892, 844, 778, 756, 731, 670, 634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.97 Hz, 2 H), 7.09 (d, J = 7.81 Hz, 2 H), 4.56 (s, 2 H), 2.29 (s, 3 H), 1.56 (s, 3 H), 0.34 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 171.7, 154.6, 144.4, 137.3, 133.9, 129.3, 128.6, 41.6, 21.2, 12.4, −8.6; HRMS calcd for $C_{14}H_{17}NO_2Sn$ 360.0355, found 360.0330.

***N*-(*p*-Methoxybenzyl)-3-methyl-4-(trimethylstannyl)-maleimide (7e).** See procedure E. *N*-(*p*-Methoxybenzyl)-3-bromo-4-methylmaleimide (1.6 g, 4.9 mmol), hexamethyldistannane (1.1 mL, 5.2 mmol), bis(triphenylphosphine)palladium(II) chloride (0.34 g, 0.48 mmol), and toluene (4 mL) were used to afford 1.1 g (58%) of the title compound as a

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colorless liquid after flash chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (neat) 3436, 2918, 2835, 1759, 1693, 1612, 1586, 1513, 1433, 1395, 1347, 1292, 1248, 1176, 1125, 1088, 1035, 960, 892, 780, 731, 670, 632 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.7 Hz, 2 H), 6.82 (d, J = 8.7 Hz, 2 H), 4.54 (s, 2 H), 3.76 (s, 3 H), 2.05 (s, 3 H), 0.34 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 171.7, 159.6, 154.6, 144.4, 130.0, 129.2, 113.9, 55.2, 41.3, 12.4, −8.7; HRMS calcd for $C_{16}H_{21}NO_3{}^{116}Sn$ 391.0539, found 391.0522.

***N*-[*p*-(Trimethylsilyl)benzyl]-3-methyl-4-(trimethylstannyl)maleimide (7f).** See procedure E. *N*-[*p*-(Trimethylsilyl)-benzyl]-3-bromo-4-methylmaleimide (0.610 g, 1.73 mmol), hexamethyldistannane (0.858 g, 2.62 mmol), bis(triphenylphosphine)palladium(II) chloride (0.122 g, 0.173 mmol), and toluene (3 mL) were used to afford 0.52 g (69%) of the title compound as a colorless oil after flash chromatography on silica gel (hexane/ether 5:1): FTIR (neat) 2955, 2921, 1762, 1698, 1609, 1431, 1394, 1302, 1248, 1192, 1108, 1087, 963, 892, 839, 779, 739, 693, 656, 633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.11 Hz, 2 H), 7.34 (d, J = 8.08 Hz, 2 H), 4.61 (s, 2 H), 2.08 (s, 3 H), 0.37 (s, 9 H), 0.24 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 171.7, 154.6, 144.5, 139.8, 137.3, 133.7, 127.9, 41.8, 12.4, −1.1, −8.6; HRMS calcd for $C_{17}H_{24}NO_2SiSn$ 418.0594, found 418.0590.

General Procedure for the Preparation of the Termaleimides (Procedure F).[10] To a nitrogen-purged screw-cap tube was added the *N*-alkyl-3,4-dibromomaleimide (1 equiv), *N*-alkyl-3-methyl-4-(trimethylstannyl)maleimide (1 equiv), and bis(triphenylphosphine)palladium(II) chloride (10 mol %) in THF. The mixture was then stirred at room temperature 1−2 days. The mixture was filtered and washed with ethyl acetate (2×), and then the filtrate was concentrated to dryness. The crude product was purified with column chromatography on silica gel and/or preparative TLC. The details are described below for each material.

***N*,*N*′,*N*″-Trimethyl-4,4″-dimethyltermaleimide (8a).** See procedure F. *N*-Methyl-3,4-dibromomaleimide (1.4 g, 5.2 mmol), *N*-methyl-3-methyl-4-(trimethylstannyl)maleimide (1.5 g, 5.2 mmol), bis(triphenylphosphine)palladium(II) chloride (0.37 g, 0.52 mmol), and THF (5 mL) were reacted for 2 d to afford 0.55 g (59%) of the title compound as a yellow solid after gravity column chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (film) 3470, 2951, 1774, 1704, 1439, 1386, 1276, 1196, 1163, 1090, 1009, 940, 805, 722, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.17 (s, 3 H), 2.97 (s, 6 H), 2.25 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 169.2, 167.8, 144.7, 131.6, 128.3, 24.8, 24.4, 11.7; HRMS calcd for $C_{17}H_{15}N_3O_6$ 357.0961, found 357.0956.

***N*,*N*′,*N*″-Triphenyl-4,4″-dimethyltermaleimide (8b).** See procedure F. *N*-Phenyl-3,4-dibromomaleimide (0.18 g, 0.53 mmol), *N*-phenyl-3-methyl-4-(trimethylstannyl)maleimide (0.19 g, 0.53 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.157 mmol), and THF (7 mL) were reacted for 1 d to give 0.080 g (28%) of the title compound as a yellow solid after gravity column chromatography on silica gel (hexane/ethyl acetate 9:1) and then preparative TLC (hexane/methylene chloride 2:1): FTIR (film) 2923, 2851, 1774, 1709, 1654, 1597, 1502, 1457, 1388, 1289, 1198, 1130, 1080, 1068, 1028, 898, 851, 827, 760, 714, 690, 676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.19 (m, 15 H), 2.39 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 169.3, 167.4, 145.7, 131.9, 130.1, 129.9, 129.9, 129.4, 129.1, 129.0, 128.8, 126.8, 126.6, 12.9; HRMS calcd for $C_{32}H_{21}N_3O_6$ 543.1430, found 543.1429.

***N*,*N*′,*N*″-Tribenzyl-4,4″-dimethyltermaleimide (8c).** See procedure F. *N*-Benzyl-3,4-dibromomaleimide (3.96 g, 11.5 mmol), *N*-benzyl-3-methyl-4-(trimethylstannyl)maleimide (4.18 g, 11.5 mmol), bis(triphenylphosphine)palladium(II) chloride (0.81 g, 1.15 mmol), and THF (10 mL) were reacted for 2 days to afford 1.73 g (51%) of the title compound as a yellow solid after gravity column chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (film) 3468, 3033, 2929, 1771, 1714, 1645, 1497, 1456, 1434, 1398, 1350, 1143, 1125, 1067, 1030, 984, 921, 888, 822, 723, 698, 669, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 15 H), 4.76 (s, 2 H), 4.50 (s, 4 H), 2.27 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.0, 167.5, 144.5, 135.8, 135.4, 131.4, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 127.9, 42.1, 42.0, 12.0; HRMS calcd for $C_{35}H_{27}N_3O_6$ 585.1900, found 585.1919.

***N*,*N*′,*N*″-Tris(*p*-methylbenzyl)-4,4″-dimethyltermaleimide (8d).** See procedure F. *N*-(*p*-Methylbenzyl)-3,4-dibromomaleimide (0.116 g, 0.323 mmol), *N*-(*p*-methylbenzyl)-3-methyl-4-(trimethylstannyl)maleimide (0.148 g, 0.392 mmol), bis(triphenylphosphine)palladium(II) chloride (0.0296 g, 0.0422 mmol), and THF (5 mL) were reacted for 2 d to give 0.036 g (21%) yield of the title compound as a yellow solid after gravity column chromatography on silica gel (hexane/ethyl acetate, 9:1) and then preparative TLC (hexane/methylene chloride 2:1): FTIR (neat) 2924, 2855, 1772, 1708, 1644, 1516, 1434, 1398, 1347, 1307, 1184, 1073, 1022, 987, 900, 845, 806, 756, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−7.05 (m, 12 H), 4.70 (s, 2 H), 4.44 (s, 4 H), 2.30 (s, 3 H), 2.26 (s, 6 H), 2.23 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.7, 167.3, 144.3, 138.0, 137.5, 132.7, 132.4, 131.2, 129.4, 129.2, 128.47, 128.2, 128.0, 42.4, 41.8, 21.3, 21.3, 12.2; HRMS calcd for $C_{38}H_{33}N_3O_6$ 627.2369, found 627.2363.

***N*,*N*′,*N*″-Tri(*p*-methoxybenzyl)-4,4″-dimethyltermaleimide (8e).** See procedure F. *N*-(*p*-Methoxybenzyl)-3,4-dibromomaleimide (0.53 g, 1.4 mmol), *N*-(*p*-methoxybenzyl)-3-methyl-4-(trimethylstannyl)maleimide (1.1 g, 2.8 mmol), bis(triphenylphosphine)palladium(II) chloride (0.20 g, 0.28 mmol), and THF (4 mL) were reacted for 2 d to afford 0.55 g (59%) of the title compound as a yellow solid after gravity column chromatography on silica gel (hexane/ethyl acetate 9:1): FTIR (film) 2936, 2837, 1772, 1712, 1613, 1586, 1514, 1435, 1398, 1347, 1294, 1249, 1178, 1103, 1033, 899, 820, 765, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (d, J = 8.5 Hz, 2 H), 7.16 (d, J = 8.6 Hz, 4 H), 6.83 (d, J = 8.5 Hz, 2 H), 6.79 (d, J = 8.6 Hz, 4 H), 4.67 (s, 2 H), 4.43 (s, 4 H), 3.76 (s, 3 H), 3.72 (s, 6 H), 2.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 169.0, 167.5, 159.5, 159.3, 144.4, 131.4, 130.1, 129.6, 128.4, 128.0, 127.7, 114.21, 114.0, 55.3, 55.3, 42.1, 41.5, 12.0; HRMS calcd for $C_{38}H_{33}N_3O_9$ 675.2217, found 675.2231.

General Procedure for the Preparation of the Iodotermaleimides (Procedure G).[10,22] To a nitrogen-purged screw-cap tube was added the *N*-alkyl-3,4-dibromomaleimide (1 equiv), the *N*-substituted 3-methyl-4-(trimethylstannyl)-maleimide (1−2 equiv), and bis(triphenylphosphine)palladium(II) chloride (10 mol %) in THF. The mixture was then stirred at 23−60 °C for 1−2 days. After cooling, the mixture was filtered and washed with methylene chloride. The filtrate was concentrated to dryness, and the residue was purified by flash chromatography on silica gel to remove the unreacted compounds along with the catalyst. The collected product portions (dimer and trimer mixture) were then treated with iodine monochloride (1.5−4.5 equiv) in carbon tetrachloride at room temperature. The mixture was heated to reflux overnight. After cooling, it was concentrated to dryness. The crude product was purified by column chromatography and then preparative TLC. The details are described below for each material.

***N*,*N*″-Diphenyl-*N*′-(*p*-iodobenzyl)-4,4″-dimethyltermaleimide (8g).** See procedures F and G. *N*-[(Trimethylsilyl)benzyl]-3,4-dibromomaleimide (0.224 g, 0.537 mmol), *N*-phenyl-3-methyl-4-(trimethylstannyl)maleimide (0.223 g, 0.637 mmol), bis(triphenylphosphine)palladium(II) chloride (0.0453 g, 0.0645 mmol), and THF (3 mL) were used to afford the crude *N*,*N*″-diphenyl-*N*′-[*p*-(trimethylsilyl)benzyl]-4,4″-dimethyltermaleimide (**8f**) that was enhanced in purity using silica gel (hexane/ethyl acetate 3:1) and then treated directly with iodine monochloride (0.260 g, 1.60 mmol) and carbon tetrachloride (5 mL) to give 0.0734 g (20%) of the title compound as a yellow sticky oil after gravity column chromatography on silica gel (hexane/ethyl acetate 5:1) and then preparative TLC (hexane/methylene chloride 1:1): FTIR (neat) 2923, 2851, 1774, 1709, 1654, 1597, 1502, 1457, 1388, 1289, 1198, 1130, 1080, 1068, 1028, 898, 851, 827, 760, 714, 690, 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2 H), 7.48−7.15 (m, 12 H), 4.75 (s, 2 H), 2.34 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 168.5, 167.4, 144.7, 138.1, 134.9, 131.6, 131.2, 130.7, 129.2,

128.33 128.30, 126.1, 94.0, 42.2, 12.2; HRMS calcd for $C_{33}H_{22}IN_3O_6$ 683.0553, found 683.0546.

***N,N′′*-Dibenzyl-*N′*-(*p*-iodobenzyl)-4,4′′-dimethyltermaleimide (8i).** See procedures F and G. *N*-[(Trimethylsilyl)benzyl]-3,4-dibromomaleimide (0.420 g, 1.01 mmol), *N*-benzyl-3-methyl-4-(trimethylstannyl)maleimide (0.731 g, 2.01 mmol), bis(triphenylphosphine)palladium(II) chloride (0.144 g, 0.205 mmol), and THF (9 mL) were used to afford crude *N,N′′*-dibenzyl-*N′*-[*p*-(trimethylsilyl)benzyl]-4,4′′-dimethyltermaleimide (**8h**) that was enhanced in purity using silica gel (hexane/ethyl acetate 3:1) and then treated with iodine monochloride (0.200 g, 1.23 mmol) and carbon tetrachloride (15 mL) to give 0.158 g (22%) of the title compound as a yellow sticky oil after gravity column chromatography on silica gel (hexane/ethyl acetate 5:1) and then preparative TLC (hexane/methylene chloride 1:1): FTIR (neat) 3467, 3063, 3032, 2926, 2845, 1772, 1707, 1643, 1588, 1486, 1434, 1398, 1348, 1267, 1143, 1125, 1068, 1008, 984, 918, 888, 844, 797, 735, 723, 698, 668, 637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2 H), 7.61−7.23 (m, 10 H), 7.10 (d, J = 8.3 Hz, 2 H), 4.67 (s, 2 H), 4.48 (s, 4 H), 2.24 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 168.8, 167.4, 144.6, 138.1, 135.7, 135.0, 131.4, 130.6, 128.7, 128.3, 128.1, 127.9, 94.1, 42.1, 42.0, 12.0; HRMS calcd for $C_{35}H_{26}IN_3O_6$ 711.0866, found 711.0873.

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Supporting Information Available: Detailed crystallographic data for **2d**, **4a**, and *N*-benzyl-3,4-dibromopyrrole in addition to ^1H NMR or ^{13}C NMR spectra for all new compounds (49 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.

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