NMR δ 1.10 (s, 3 H), 1.17 (s, 3 H), 2.53–2.90 (m, 4 H), 2.93–3.27 (m, 2 H), 3.80 (s, 1 H), 7.03–7.50 (m, 9 H); ^{13}C NMR δ 24.3, 28.2, 32.1, 34.8, 45.4, 46.5, 61.4, 124.9, 125.1, 126.5, 126.6, 127.4, 129.1, 130.3, 135.7, 142.3, 143.9; accurate mass calcd for $C_{19}H_{22}S_2$ 314.1163, found 314.1161.

2,2-Dimethylindan-1-yl Vinyl Sulfide (31). A mixture of **32** (103 mg, 0.36 mmol) and *tert*-butoxide (120 mg, 1.08 mmol) in *tert*-butyl alcohol (5 mL) was refluxed for 24 h. The mixture was poured into water (10 mL) and extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo to afford the residue, which was purified by chromatography on silica gel and eluted with hexane–ethyl acetate (20:1) to yield **31** as colorless oil (45.3 mg, 62%): ^{1}H NMR δ 1.09 (s, 3 H), 1.25 (s, 3 H), 2.74 (s, 2 H), 4.09 (s, 1 H), 5.14 (d, J = 10 Hz, 1 H), 5.26 (d, J = 16 Hz, 1 H), 6.38 (dd, J = 10, 16 Hz, 1 H), 7.03–7.46 (m, 4 H). Compound **31** decomposed gradually in chloroform solution.

Reaction of *tert*-Butyl Adamantane-1-peroxycarboxylate (27) with 26. Under a nitrogen atmosphere, a mixture of **26** (326 mg, 1.04 mmol) and **27** (252 mg, 1.00 mmol) in chlorobenzene (5 mL) was refluxed for 24 h. After the mixture was cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give 2,2-dimethylindan-1-one (**28**) (65.6 mg, 42%) and a brown oil, which was further chromatographed on silica gel and eluted with hexane to yield diphenyl disulfide (**29**) (74.1 mg, 34%), mp 53–55 °C (lit.[30] 58–60 °C); 2,2-dimethylindan-1-yl vinyl sulfide (**31**) (16.3 mg, 8%), which exhibited same physical properties as those of the authentic sample; phenyl vinyl sulfide (**30**) (4.1 mg, 3%), ^{1}H NMR δ 5.34 (d, J = 16 Hz, 1 H), 5.35 (d, J = 10 Hz, 1 H), 6.54 (dd, J = 10, 16 Hz, 1 H), 6.90–7.50 (m, 5 H);[31] and a trace amount of **20a**. Starting material **26** (115 mg, 35%) was also recovered.

Reaction of 27 with 2,2-Dimethylindan-1-thione (20a). A mixture of **20a** (210 mg, 1.17 mmol) and **27** (295 mg, 1.17 mmol) in chlorobenzene (5 mL) was refluxed for 24 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to afford 2,2-dimethylindan-1-thione (70 mg, 33%) and 2,2-dimethylindan-1-one (121 mg, 65%), which exhibited the same physical properties as those of the authentic samples.

Acknowledgment. We thank the Croucher Foundation of Hong Kong and the National Science Council of Republic of China for support. L.L.Y. thanks the Croucher Foundation for a studentship.

Registry No. **1**, 6317-10-8; **2**, 7049-31-2; **2b**, 113425-39-1; **2c**, 113425-38-0; **2d**, 113425-37-9; **2e**, 124688-04-6; **3**, 5769-02-8; **4**, 172-16-7; **5**, 124688-02-4; **6**, 42196-84-9; **7**, 5616-55-7; **8**, 19557-70-1; **9**, 41563-48-8; **10**, 632-51-9; **11a**, 746-47-4; **11b**, 27192-91-2; (*Z*)-**11c**, 113425-41-5; (*E*)-**11c**, 113425-42-6; (*Z*)-**11d**, 113425-40-4; (*E*)-**11d**, 113469-17-3; (*Z*)-**11e**, 118477-00-2; (*E*)-**11e**, 124688-05-7; (*E*)-**12**, 782-06-9; (*Z*)-**12**, 782-05-8; **13**, 24536-68-3; **14**, 124688-03-5; **15**, 91590-50-0; **16**, 103-30-0; **17**, 30541-56-1; **18**, 1483-68-7; **19a**, 124688-10-4; **19b**, 124688-11-5; **19c**, 124688-12-6; **19d**, 124688-13-7; **19e**, 124688-14-8; **19f**, 124688-15-9; **19g**, 120932-59-4; **20a**, 100991-60-4; **20b**, 124688-19-3; **20c**, 124688-20-6; **20d**, 124688-21-7; **20e**, 124688-22-8; **20g**, 124688-28-4; **21a**, 124688-18-2; **21g**, 124688-23-9; **22a**, 4773-82-4; **24**, 33735-40-9; **25**, 119-61-9; **26**, 124688-26-2; **28**, 10489-28-8; **29**, 882-33-7; **31**, 124688-27-3; **32**, 124688-25-1; **36**, 124688-17-1; $W(CO)_6$, 14040-11-0; 9-fluorenone-2-carboxylic acid, 784-50-9; 9,9-(ethylenedithio)-fluorene-2-carboxylic acid, 118476-91-8; 2,2-dimethylindan-1-one, 10489-28-8; 2,2-dimethyl-5-methoxyindan-1-one, 124688-06-8; 2,2-dimethyl-6-methoxyindan-1-one, 124688-07-9; 2,2,5-trimethylindan-1-one, 124688-08-0; 2,2,6-trimethylindan-1-one, 57145-24-1; 5-cyano-2,2-dimethylindan-1-one, 124688-09-1; 2,2-dimethyl-1-tetralone, 2977-45-9; 4-bromo-2,2-dimethyl-1-tetralone, 124688-16-0; 2,2-dimethyl-1,2-dihydronaphthalen-1-one, 16020-15-8; 1,2-dimethylnaphthalene, 573-98-8; 2,2-dimethylindan-1-thiol, 124688-24-0.

Supplementary Material Available: 250-MHz ^{1}H NMR spectra of thiones **20a–e** and **20g** (6 pages). Ordering information is given on any current masthead page.

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(*Z*)-2,2′-Disubstituted Bifluorenylidenes by Intramolecular Desulfurdimerization Reactions[1]

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$W(CO)_6$-mediated intramolecular desulfurdimerization reactions have been used in the syntheses of bridged 2,2′-disubstituted bifluorenylidenes in satisfactory yields. Ring sizes from 12 to 24 can be synthesized by this reaction. The extension of this reaction for the synthesis of bifluorenylidene-hinged crown ethers is described. The X-ray structure of **6i** has been determined. The two fluorenylidene moieties are each planar, making a dihedral angle of 44.9°. The first optically active bifluorenylidenes were unequivocally synthesized, and the barriers for the racemization of two such molecules have been determined (12 kcal/mol). The racemization process may arise from the pyramidalization at C_9 and/or $C_{9'}$ followed by rapid twisting along the C_9–$C_{9'}$ bond.

Bifluorenylidene **1** is nonplanar with a twist angle about the C_9–$C_{9'}$ double bond of 43°.[5-7] Accordingly, **1** can be chiral and, indeed, was accidentally obtained in optically pure form, but the absolute configuration is yet unknown.[7] Various attempts to resolve bifluorenylidenes into enantiomeric pure forms have been unsuccessful.[8,9] The

(1) Part 29 of the series "Transition Metal Promoted Reactions".
(2) (a) The Chinese University of Hong Kong. (b) National Taiwan University. (c) To whom correspondence should be addressed at NTU.
(3) (a) On leave from the Institute of Chemistry, Academia Sinica, Beijing. (b) Recipient of the Croucher Foundation studentship, 1988–90.
(4) To whom correspondence should be addressed concerning the X-ray structure of **6i**.
(5) (a) Bailey, N. A.; Hull, S. E. *Acta Crystallogr.* **1978**, *B34*, 3289. (b) Bailey, N. A.; Hull, S. E. *J. Chem. Soc., Chem. Commun.* **1971**, 960.
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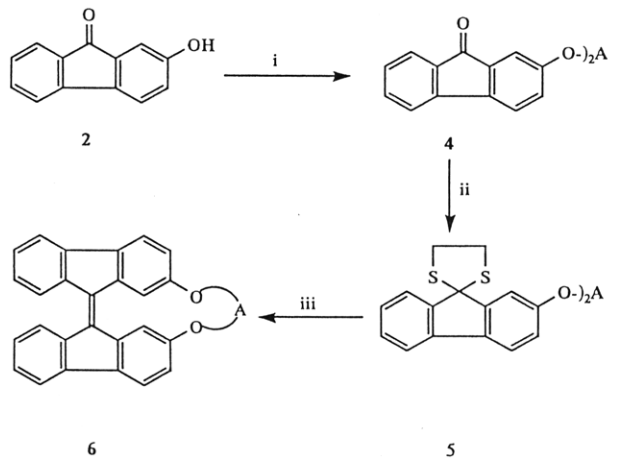
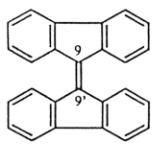
Scheme I[a]



[a] (i) Base, 0.5 equiv of XAX (**3**), PTC catalyst; (ii) $HSCH_2CH_2SH$, BF_3·OEt_2; (iii) $W(CO)_6$, PhCl, reflux.

syntheses of **1** can be achieved by a number of procedures.[10-17] The reaction generally involves the coupling of two fluorene moieties and substrates containing substituents on the aromatic ring normally yield a mixture of *E* and *Z* isomers. To the best of our knowledge, no (*Z*)-2,2′-disubstituted bifluorenylidenes have been isolated in pure form. Rapid *Z*/*E* isomerization upon heating has been reported and the barrier for such equilibrium is relatively low (ca. 20–25 kcal/mol).[8,9,18,19]



1

We recently found that, upon treatment with $W(CO)_6$, dithioketals can undergo desulfurdimerization to give in excellent yields the corresponding dimeric olefins (eq 1).[20,21]

(1)

Table I. Synthesis of Bridged Bifluorenylidenes

3 (A =)	% yield 4	5	6
a $(CH_2)_2$	–	26	37
b $(CH_2)_3$	53	62	66
c $(CH_2)_4$	80	85	64
d $(CH_2)_8$	98	99	70
e $(CH_2)_{11}$	96	94	58
f $(CH_2)_2O(CH_2)_2$	93	100	35
g $(CH_2)_2O(CH_2)_2O(CH_2)_2$	87	79	52
h $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$	85	100	39
i $(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2$	61	79	27

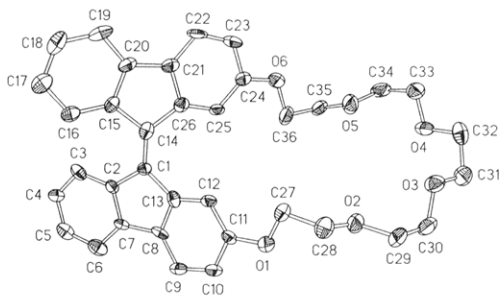


Figure 1. Perspective view of **6i**.

The procedure provides an extremely easy entry for the synthesis of bifluorenylidenes. Like other intermolecular coupling reactions,[10-17,20,21] the reaction is nonselective, and a mixture of *E* and *Z* isomers is normally obtained. We felt that, if two fluorenone units are connected with an aliphatic chain, desulfurdimerization would occur intramolecularly. After the removal of the bridging moiety, *Z* isomers could be unequivocally synthesized. Here we report a detailed investigation on such intramolecular coupling reactions and on the synthesis and chemistry of bifluorenylidenes.

Results and Discussion

In the beginning of this study, we tested the generality of the intramolecular desulfurdimerization reaction. Scheme I summarizes the reaction sequence. Thus, reactions of 2-hydroxyfluorenone **2**[22] with 1,ω-dihaloalkanes **3a–e** under basic conditions afforded **4a–e**, which were allowed to react with 1,2-ethanedithiol in the presence of a catalytic amount of BF_3·OEt_2 to yield the corresponding bisdithioketals **5a–e**. Substrates **5a–e** were subjected to intramolecular desulfurdimerization. Hence, upon treatment with $W(CO)_6$ in refluxing chlorobenzene for 24–48 h, bifluorenylidenes **6a–e** were obtained. The results are compiled in Table I.

A series of bifluorenylidene-hinged crown ethers **6f–i** were prepared accordingly (Table I). The X-ray structure of **6i** has been determined.[23] A perspective view of the molecule is shown in Figure 1. The torsion angles in the macrocyclic ring show that the molecule conforms closely to idealized C_2 symmetry. The two 9-fluorenylidene moieties are each planar within experimental error, making a dihedral angle of 44.9° with each other. This value is compatible with that of **1**.[5-7] The six oxygen atoms in **6i** do not lie on the same plane, and accordingly its ability of complexation with alkali metal ions may be somewhat hindered. Nevertheless, preliminary experiments showed that **6h** and **6i** had complexing ability with potassium and sodium ions.[24]

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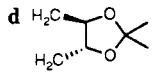
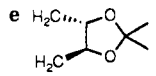
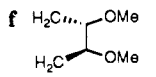
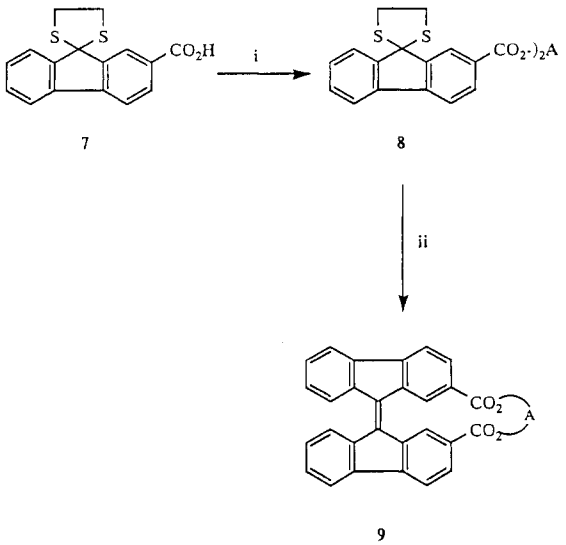
(23) Atomic coordinates, bond angles, and bond lengths are available as the supplementary material.

Table II. Synthesis of Bridged Bifluorenylidene Diesters 9

3 (A =)	% yield 8	% yield 9
a $(CH_2)_2$	80	56
b $(CH_2)_3$	88	63
c $(CH_2)_4$	94	49
d 	84	43
e 	92	40
f 	96	30

Scheme II[a]



[a] (i) K_2CO_3, Bu_4NX, 0.5 equiv of 3; (ii) $W(CO)_6$, PhCl, reflux.

As shown in Table I, the intramolecular coupling reactions generally gave the olefinic products in satisfactory yields. Ring sizes from 12 to 24 essentially did not affect the cyclization. It is particularly noteworthy that no dilution technique was required in these operations.

The absorptions of H_1 and $H_{1'}$ in the ^1H NMR spectrum of **6c–i** appeared at δ 8.00–8.20. Those of **6a** and **6b**, on the other hand, exhibited resonances at δ 8.55 and 8.37, respectively. This is because reducing the number of carbon atoms in the bridging moiety would bring two fluorenylidene moieties in **6** close together, and H_1 and $H_{1'}$ are thus more deshielded. Furthermore, the protons on the ethylene bridge in **6a** exhibited an AA'BB' pattern in the ^1H NMR spectrum at ambient temperature. This observation indicated that **6a** should be relatively rigid.

As described in the preceding paper,[21] esters are stable under the reaction conditions. As such, the bridging moiety of the corresponding dimeric esters could be removed easily and *Z*-substituted bifluorenylidenes could thus be obtained. Accordingly, the strategy similar to that depicted in Scheme I has been applied for the synthesis of **9a–c** with the dithioketal of fluorenone-2-carboxylic acid **7**[21] as the starting material (Scheme II). The results are outlined in Table II.

When the bridging moiety was chiral, the first optically pure bifluorenylidenes **9d** and **9e** were synthesized unequivocally.[25] Compounds **9d** and **9e** are enantiomeric

(24) Wong, K. L.; Luh, T.-Y., unpublished results.

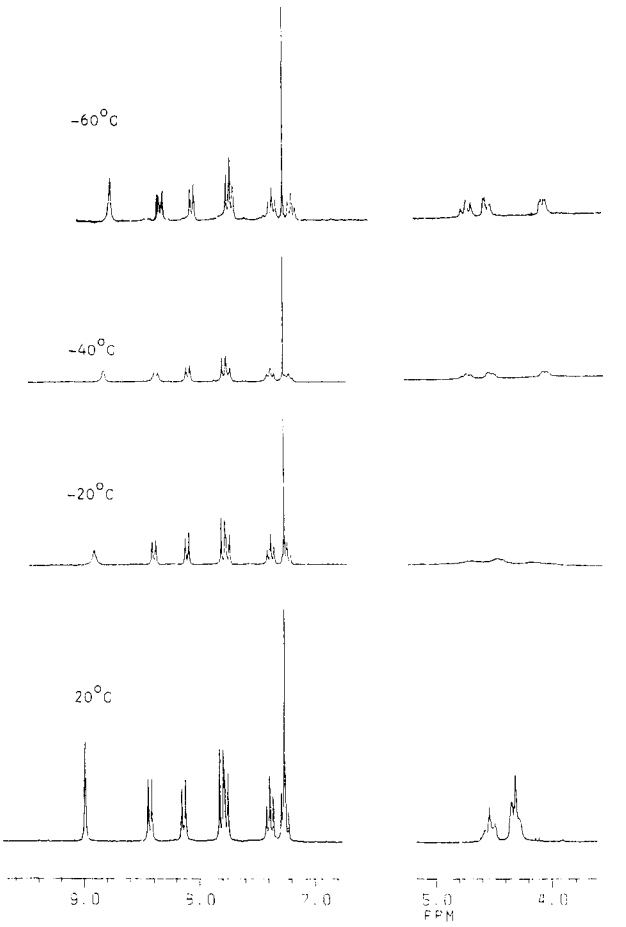


Figure 2. Partial ^1H NMR spectra for **9d** at different temperatures.

isomers which exhibited $[\alpha]^{22}_D$ values at +634° and −690°, respectively. In addition, **9d** and **9e** showed negative and positive Cotton effects, respectively, in CD curves, and the absolute configurations are thus assigned by comparing with related compounds.[25,26] The temperature-dependent ^1H NMR spectra for **9d** is shown in Figure 2. The absorption pattern for the aromatic protons in the ^1H NMR spectra remained unchanged from ambient temperature to −60 °C, but the chemical shifts changed slightly (e.g. H_1 and $H_{1'}$ absorbed at δ 9.00 at 20 °C but at δ 8.85 at −60 °C). The signals broadened slightly at −20 °C ($\omega_{1/2}$ = 9.0 Hz for the singlet at ca. 8.94) but sharper again ($\omega_{1/2}$ = 5.4 and 5.3 Hz at −60 °C and at 20 °C, respectively) at lower and higher temperatures. The two protons of the methylene group on the bridge appeared as multiplet at δ 4.30 at ambient temperature but became nonequivalent at δ 4.02 and 4.50 at −60 °C. The signals coalesce at −20 °C. These results indicate that the bridging group, although rigid, still exhibited fluxional behavior to a certain extent. However, this process does not change the configuration of bifluorenylidene moiety in **9d** and **9e**.

The less rigid "chiral" bridged bifluorenylidene **9f** was synthesized in a similar manner. It is noted that the optical rotation for **9f** ($[\alpha]^{22}_D$ +7.3°) was much less than those for **9d** and **9e**. In addition, **9f** did not exhibit a CD curve in the range from 400 to 220 nm. The partial ^1H NMR spectra for **9f** at different temperatures are shown in

(25) Preliminary communication: Wang, X.-j.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 263.

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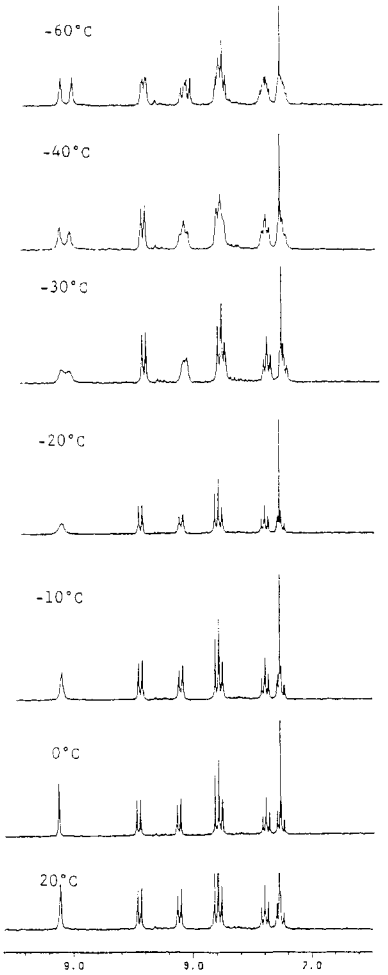
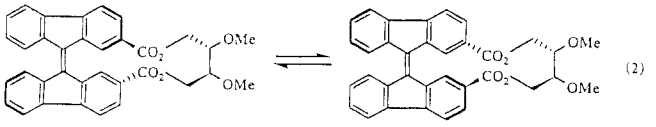


Figure 3. Partial ^{1}H NMR spectra for **9f** at different temperatures.

Figure 3. At low temperature, there appeared two sets of signals with equal intensity which coalesced at −20 °C, and at higher temperature only one set of absorptions was observed. These results suggest that **9f** consists of a pair of diastereoisomers which undergo rapid interconversion (eq 2). The barrier for this rapid process was calculated to be 12 kcal/mol based on the NMR results.[27]

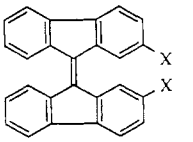


(2)

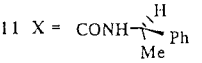
9f

Base hydrolysis of **9c** afforded the diacid **10a**, which was esterified with methanol to give diester **10b** in excellent yield. The stereochemical assignment for **10b** was based on nuclear Overhauser effect experiments. In addition, treatment of diacid **10a** with 1,4-dibromobutane under basic conditions afforded **9c** in 29% yield. This observation further confirmed the stereochemistry of **10a**. It is noted that both **10a** and **10b** were thermally stable, and no E/Z isomerization was observed even at elevated temperature (up to 160 °C). Reduction of **9c** with diisobutylaluminum hydride gave the corresponding diol **10c** in excellent yields. Again, **10c** was thermally stable.

In a similar manner, **9d** and **9e** were hydrolyzed with base followed by esterification with methanol to yield **10b**,

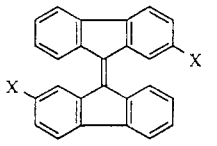


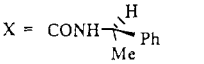
10 a X = CO_2H
b X = CO_2Me
c X = CH_2OH

11 X = 

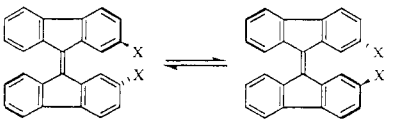
which was optically inactive. In addition, the reaction of **9d** and **9e** with diisobutylaluminum hydride afforded optically inactive **10c**. These observations are consistent with the results just depicted, namely, that the bifluorenylidene moiety would undergo rapid racemization if the molecules are not rigid. For a rigid system such as **9d** and **9e**, such interconversion would not occur, and hence optically pure enantiomers were obtained.

Treatment of **9d** with trimethylaluminum in the presence of (*R*)-(+)-(1-phenylethyl)amine in refluxing dichloromethane[28] for 48 h afforded **11** and **12** in 14 and 77% yields, respectively. It is noted that **11** was relatively unstable in solution and rapidly rearranged to **12** in boiling ethanol. Presumably, the bulky substituents would lower the barrier for the *Z* to *E* conversion. Both compounds were optically active, and amide **12** showed $[\alpha]^{22}_D$ −20.3°. The stereochemical assignments were based on the nuclear Overhauser effect experiments. In the experiment with **11**, no enhancement of other aromatic protons was observed upon irradiation at δ 8.98. On the other hand, the intensity of the signals at δ 8.28 attributed to H_8 and $H_{8'}$ in **12** was enhanced upon irradiation at δ 8.80. Based on these observations, **11** and **12** were assigned to be *Z* and *E* isomers, respectively. Furthermore, the amidic protons in **11** and **12** appeared at δ 7.15 and 6.28. This is understandable because intramolecular hydrogen bonding may occur in **11**, which would result in lower field absorption of this amidic proton.



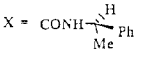
12 X = 

The ^{1}H NMR spectrum for **11** was again temperature dependent. It showed one set of absorptions at 20 °C but two sets of signals as low temperature (Figure 4). The coalescent temperature was −30 °C, which corresponds to a barrier of 11.5 kcal/mol.[27] This result again demonstrates that rapid equilibrium between two diastereomers **11a** and **11b** occurred in this acyclic substrate (eq 3). The ratio of these two isomers was about 3 to 2, but it is dif-



(3)

11a 11b

X = 

(27) Atta-ur-Rahman *Nuclear Magnetic Resonance. Basic Principles*; Springer: New York, 1986; p 133.

(28) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, 4172.

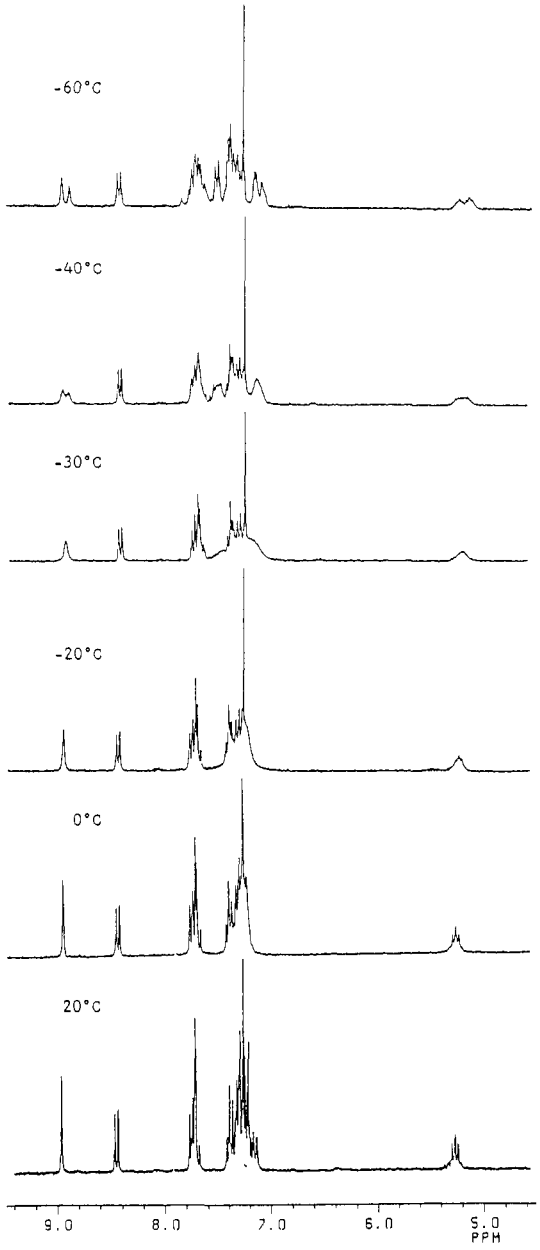


Figure 4. Partial ^1H NMR spectra for **11** at different temperatures.

ficult to assign which one is the major isomer. This result is somewhat different from that of **9f** where 1:1 isomer distribution was observed. Presumably, the sterically crowded amidic substituent may play an interesting role here. It is noted that the amidic group sometimes gives very complicated temperature-dependent NMR spectra, and several processes may occur simultaneously.[29] However, the barrier from this experiment is in agreement with that for the isomerization of **9f** depicted earlier.

The mechanism for the racemization of the bifluorenylidene moiety is intriguing. A planar bifluorenylidene transition state seems highly unlikely due to severe steric interaction between peripheral hydrogens. It is noted that pyramidalization of olefinic carbons may occur in crowded olefins.[30] Such rehybridization may relieve steric strain and hence lower the barrier for twisting about the C_9–$C_{9'}$ bond. This latter process might result in racemization of bifluorenylidene moieties.

In conclusion, we have demonstrated the first intramolecular desulfurdimerization of dithioketals which have been used in the unambiguous synthesis of (*Z*)-2,2′-disubstituted bifluorenylidenes. The activation barrier of the racemization of some of these molecules have been determined. Our results indicated that bifluorenylidene molecules could be chiral in certain rigid systems. This observation may imply that other strained olefins may behave similarly.

Experimental Section

Melting points are uncorrected. All ^1H NMR spectra were recorded at 250 MHz in $CDCl_3$. All ^{13}C NMR spectra were taken at 62.5 MHz. Reagent-grade tungsten hexacarbonyl (Aldrich or Fluka) was used without further purification. Chromatographic separation was performed on silica gel (Merck, 70–230 mesh). All solvents were purified by standard procedure[31] prior to use. Chlorobenzene was distilled from calcium hydride and stored over molecular sieve (4A).

1,3-Bis[(9′-oxofluoren-2′-yl)oxy]propane (4b). A mixture of **2**[22] (1.37 g, 7.0 mmol), 1,3-dibromopropane **3b** (0.7 g, 3.5 mmol), potassium hydroxide (0.6 g, 11.0 mmol), and a catalytic amount of 18-crown-6 in THF (30 mL) was heated with stirring at 60 °C overnight. The mixture was poured into water (200 mL), and the yellow precipitate was collected and washed with aqueous hydrochloric acid (5%, 50 mL) and then water (2 × 200 mL). The filter cake was dried under vacuum to give diketone **4b** (0.8 g, 53%): mp 231–232 °C; IR (KBr) ν 3020, 2920, 730 cm^{-1}; ^1H NMR δ 2.3 (quint, J = 6 Hz, 2 H), 4.2 (t, J = 6 Hz, 4 H), 7.00 (dd, J = 2, 8 Hz, 2 H), 7.23 (m, 4 H), 7.40 (m, 6 H), 7.60 (d, J = 8 Hz, 2H); accurate mass calcd for $C_{29}H_{20}O_4$ 432.1361, found 432.1362. This product was used for the next reaction without further purification.

1,4-Bis[(9′-oxofluoren-2′-yl)oxy]butane (4c). By use of the similar procedure for the preparation of **4b**, a mixture of **2** (2.2 g, 11.2 mmol), 1,4-dibromobutane **3c** (1.2 g, 5.5 mmol), potassium hydroxide (0.80 g, 14.0 mmol), and a catalytic amount of 18-crown-6 (100 mg, 0.38 mmol) in THF (50 mL) was converted to diketone **4c** (2.0 g, 80%): mp 242–243 °C; IR (KBr) ν 3020, 2920, 1700, 760 cm^{-1}; ^1H NMR δ 2.00 (m, 4 H), 4.10 (m, 4 H), 6.97 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 4 H), 7.42 (m, 6 H), 7.60 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{30}H_{22}O_4$ 446.1518, found 446.1521. This product was used for the next reaction without further purification.

1,8-Bis[(9′-oxofluoren-2′-yl)oxy]octane (4d). A solution of **2** (0.98 g, 5.0 mmol), 1,8-dibromooctane **3d** (0.68 g, 2.5 mmol), and sodium hydroxide (220 mg, 5.5 mmol) in HMPA–THF (15 mL, 1:4) was refluxed for 6 h, and then cooled to room temperature. The mixture was diluted with water, and the crude product was obtained by filtration and then recrystallized from acetone to give **4d** as yellow crystal (1.23 g, 98%): mp 178–180 °C; IR (KBr) ν 3059, 2940, 2861, 1717, 1601, 1455, 1286, 1130, 760, 730 cm^{-1}; ^1H NMR δ 1.43 (m, 8 H), 1.82 (m, 4 H), 4.02 (t, J = 6 Hz, 4 H), 6.98 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 4 H), 7.40 (m, 6 H), 7.59 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{34}H_{30}O_4$ 502.2144, found 502.2131. Anal. Calcd: C, 81.25; H, 6.24. Found: C, 81.72; H, 5.89.

1,11-Bis[(9′-oxofluoren-2′-yl)oxy]undecane (4e). By use of the similar procedure for the preparation of **4d**, a solution of **2** (1.96 g, 10.0 mmol), 1,11-dibromoundecane (1.57 g, 5.0 mmol), and sodium hydroxide (440 mg, 11.0 mmol) in HMPA–THF (30 mL, 1:4) was transformed into **4e** (2.60 g, 96%): mp 121–123 °C (acetone); IR (KBr) ν 3054, 2920, 2895, 1711, 1601, 1455, 1288, 1250, 1224, 760, 729 cm^{-1}; ^1H NMR δ 1.43 (m, 14 H), 1.80 (m, 4 H), 4.00 (t, J = 6 Hz, 4 H), 6.97 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 4 H), 7.40 (m, 6 H), 7.59 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{37}H_{36}O_4$ 544.2613, found 544.2610.

(29) le Noble, W. J. *Highlights of Organic Chemistry*; Dekker: New York, 1974; Chapter 6.

(30) (a) Kahn, A. Z.-Q.; Sandström, J. *J. Am. Chem. Soc.* **1988**, *110*, 4843 and references therein. (b) Sakurai, H.; Ebata, K.; Sakamoto, K.; Nakadaira, Y.; Kabuto, D. *Chem. Lett.* **1988**, 965. (c) For a recent review, see: Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

(31) Perrin, D. R.; Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.

1,5-Bis[(9′-oxofluoren-2′-yl)oxy]-3-oxapentane (4f). To a mixture of **2** (0.98 g, 5.0 mmol) and sodium hydroxide (0.3 g, 7.5 mmol) in THF (25 mL) was added diethylene glycol ditosylate (1.04 g, 2.5 mmol) in HMPA (5 mL). The mixture was refluxed for 48 h. Yellow solid was precipitated after the addition of water (200 mL). The crude product was collected by filtration, washed with acetone (20 mL), and recrystallized from cyclohexane–chloroform to give **4f** (1.08 g, 93%): mp 175–177 °C; ^{1}H NMR δ 3.96 (t, J = 5 Hz, 4 H), 4.22 (t, J = 5 Hz, 4 H), 7.02 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 4 H), 7.40 (m, 6 H), 7.62 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 68.3, 70.0, 110.5, 119.6, 121.1, 121.3, 124.4, 127.9, 134.6, 134.8, 136.1, 137.4, 144.9, 160.2, 193.6; m/z 462, 223, 196, 195, 151.

1,8-Bis[(9′-oxofluoren-2′-yl)oxy]-3,6-dioxaoctane (4g). To a mixture of **2** (0.98 g, 5.0 mmol) and NaOH (0.3 g, 7.5 mmol) in THF (25 mL) was added triethylene glycol dichloride (0.46 g, 2.5 mmol) in HMPA (5 mL). The mixture was refluxed for 48 h, cooled to room temperature, and poured into water (200 mL). The mixture was then extracted with chloroform (3 × 100 mL). The combined organic layers were washed with aqueous KOH (5%, 4 × 100 mL) and water (2 × 150 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo to give a deep red solution, which was allowed to stand until precipitation was completed. Yellow solid was collected by filtration and was washed with acetone (20 mL) and recrystallized from cyclohexane–chloroform to afford **4g** (1.11 g, 87%): mp 134–135 °C; ^{1}H NMR δ 3.77 (s, 4 H), 3.88 (t, J = 5 Hz, 4 H), 4.18 (t, J = 5 Hz, 4 H), 7.00 (dd, J = 2, 8 Hz, 2 H), 7.17 (m, 4 H), 7.37 (m, 6 H), 7.56 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 68.3, 69.8, 71.1, 110.5, 119.6, 121.0, 121.3, 124.3, 127.9, 134.6, 134.8, 136.1, 137.3, 144.9, 160.3, 193.5; accurate mass calcd for $C_{32}H_{26}O_6$ 506.1729, found 506.1739. Anal. Calcd: C, 75.88; H, 5.17. Found: C, 75.50; H, 5.19.

1,11-Bis[(9′-oxofluoren-2′-yl)oxy]-3,6,9-trioxaundecane (4h). To a mixture of **2** (0.98 g, 5.0 mmol) and NaOH (0.3 g, 7.5 mmol) in THF (25 mL) was added tetraethylene glycol dichloride (0.58 g, 2.5 mmol) in HMPA (5 mL). The mixture was refluxed for 48 h, cooled to room temperature, and then poured into water (200 mL). The mixture was extracted with chloroform (3 × 100 mL). The combined organic layers were washed with aqueous KOH (5%, 4 × 100 mL) and water (2 × 150 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo to give a deep red solution, which was allowed to stand until precipitation was completed. The yellow solid was filtered, washed with acetone (20 mL), and recrystallized from cyclohexane–chloroform to give **4h** (1.17 g, 85%): mp 120–122 °C; ^{1}H NMR δ 3.72 (m, 8 H), 3.88 (t, J = 5 Hz, 4 H), 4.16 (t, J = 5 Hz, 4 H), 7.00 (dd, J = 2, 8 Hz, 2 H), 7.18 (m, 4 H), 7.40 (m, 6 H), 7.58 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 68.1, 69.7, 70.8, 71.0, 110.2, 119.6, 121.0, 121.3, 124.3, 127.9, 134.4, 134.8, 135.9, 137.2, 144.9, 160.1, 193.7; m/z 550, 223, 196, 195, 151, 45.

1,14-Bis[(9′-oxofluoren-2′-yl)oxy]-3,6,9,12-tetraoxatetradecane (4i). To a mixture of **2** (0.98 g, 5.0 mmol) and NaOH (0.3 g, 0.75 mmol) in THF (25 mL) was added pentaethylene glycol ditosylate (1.37 g, 2.5 mmol) in HMPA (5 mL). The mixture was refluxed for 24 h. Water (200 mL) was added, and the mixture was extracted with chloroform (3 × 100 mL). The combined organic solutions were washed with aqueous KOH (5%, 4 × 100 mL) and water (2 × 150 mL), dried (Na_2SO_4), and filtered. The filtrate was evaporated in vacuo to give the residue, which was chromatographed on silica gel using hexane–ethyl acetate (3:1) as eluent to give **4i** (0.91 g, 61%): mp 99–101 °C (cyclohexane–chloroform); ^{1}H NMR δ 3.66 (s, 4 H), 3.72 (m, 8 H), 3.88 (t, J = 5 Hz, 4 H), 4.16 (t, J = 5 Hz, 4 H), 6.96 (dd, J = 2, 8 Hz, 2 H), 7.16 (m, 4 H), 7.36 (m, 6 H), 7.56 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 68.3, 69.7, 70.8 (2 C's), 71.0, 110.4, 119.6, 121.0, 121.3, 124.3, 127.9, 134.5, 134.8, 136.0, 137.2, 144.9, 160.3, 193.5; m/z 594, 223, 196, 195, 151, 45.

1,2-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]ethane (5a). A mixture of **2** (1.06 g, 5.4 mmol), 1,2-dibromoethane **3a** (0.48 g, 2.6 mmol), potassium hydroxide (0.4 g, 7.1 mmol), and a catalytic amount of 18-crown-6 in THF (50 mL) was heated with stirring at 50 °C overnight. The mixture was poured into water (200 mL), and the yellow precipitate was collected and washed with aqueous hydrochloric acid (5%, 50 mL) and then water (200 mL). The solid (crude **4a**) was dried under vacuum and then dissolved in glacial acetic acid (50 mL). To the above mixture were added 1,2-ethanedithiol (0.5 g, 5.3 mmol) and a catalytic amount of BF_3·Et_2O. The resulted mixture was then heated at 100 °C for 10 h and poured into water (200 mL). The precipitate was collected and dissolved in chloroform (50 mL). The filtrate was extracted with chloroform (2 × 30 mL), and the organic solutions were combined and washed with aqueous sodium hydroxide (10%, 2 × 50 mL) and then water (3 × 100 mL). The organic layer was dried and evaporated in vacuo to give **5a** (0.4 g, 26%): mp 255–257 °C (hexane–ethyl acetate); IR (KBr) ν 3020, 2920, 730 cm^{-1}; ^{1}H NMR δ 3.80 (s, 8 H), 4.42 (s, 4 H), 6.95 (dd, J = 2, 8 Hz, 2 H), 7.25–7.35 (m, 6 H), 7.55 (d, J = 8 Hz, 4 H), 7.67 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{32}H_{26}O_2S_4$ 570.0816, found 570.0815.

1,3-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]propane (5b). A mixture of **4b** (0.6 g, 1.4 mmol), 1,2-ethanedithiol (0.16 g, 1.7 mmol), and a catalytic amount of BF_3·Et_2O in glacial acetic acid (20 mL) was heated at 100 °C for 10 h until a red clear solution was obtained. After being cooled to room temperature, the mixture was poured into water (200 mL). The precipitate was collected, dissolved in chloroform (50 mL), and filtered. The filtrate was extracted with chloroform (2 × 30 mL), and the organic solutions were combined and washed with aqueous sodium hydroxide (10%, 2 × 50 mL) and then water (3 × 100 mL). The organic layer was dried and evaporated to give **5b** (0.5 g, 62%): mp 209–210 °C (chloroform); IR (KBr) ν 3020, 2900, 760 cm^{-1}; ^{1}H NMR δ 2.30 (quint, J = 6 Hz, 2 H), 3.80 (s, 8 H), 4.25 (t, J = 6 Hz, 4 H), 6.90 (dd, J = 2, 8 Hz), 7.24–7.36 (m, 6 H), 7.51 (m, 4 H), 7.64 (d, J = 8 Hz); accurate mass calcd for $C_{33}H_{28}O_2S_4$ 584.0972, found 584.0969.

1,4-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]butane (5c). To a slurry of the diketone **4c** (1.5 g, 3.0 mmol) in glacial acetic acid (30 mL) was added 1,2-ethanedithiol (0.8 g, 8.5 mmol) and a catalytic amount of BF_3·Et_2O. The mixture was treated in the same manner as described above to give **5c** (1.7 g, 85%): mp 188–189 °C (chloroform); IR (KBr) ν 3020, 2920, 750 cm^{-1}; ^{1}H NMR δ 2.00 (br s, 4 H), 3.8 (s, 8 H), 4.1 (br s, 4 H), 6.91 (dd, J = 2, 8 Hz, 2 H), 7.21–7.35 (m, 4 H), 7.50 (m, 6 H), 7.68 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{34}H_{30}O_2S_4$ 598.1129, found 598.1128.

1,8-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]octane (5d). A solution of **4d** (0.50 g, 1.0 mmol), 1,2-ethanedithiol (0.2 mL, 2.4 mmol), and BF_3·Et_2O (0.5 mL) in glacial acetic acid (20 mL) was refluxed for 12 h. After being cooled to room temperature, the mixture was treated in a similar manner as described above to yield **5d** as a colorless solid (0.64 g, 99%): mp 181–182 °C (MeOH); IR (KBr) ν 3060, 2930, 2860, 1620, 1585, 1495, 1280, 745 cm^{-1}; ^{1}H NMR δ 1.42 (m, 4 H), 1.50 (m, 4 H), 1.80 (m, 4 H), 3.77 (s, 8 H), 4.02 (t, J = 6 Hz, 4 H), 6.86 (dd, J = 2, 8 Hz, 2 H), 7.26 (m, 6 H), 7.49 (m, 4 H), 7.63 (d, J = 8 Hz, 2 H); m/z 654, 470, 244, 212. Anal. Calcd for $C_{38}H_{38}O_2S_4$: C, 69.69; H, 5.85. Found: C, 69.70; H, 5.93.

1,11-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]undecane (5e). A solution of **4e** (1.10 g, 2.0 mmol), 1,2-ethanedithiol (0.4 mL, 4.8 mmol), and BF_3·Et_2O (0.5 mL) in glacial acetic acid (40 mL) was converted in a similar manner as described above to **5e** as a colorless solid (1.31 g, 94%): mp 163–165 °C (chloroform); IR (KBr) ν 3055, 2930, 2860, 1620, 1585, 1495, 1450, 1285, 750 cm^{-1}; ^{1}H NMR δ 1.38 (m, 10 H), 1.50 (m, 4 H), 1.80 (m, 4 H), 3.76 (s, 8 H), 4.00 (t, J = 6 Hz, 4 H), 6.87 (dd, J = 2, 8 Hz, 2 H), 7.26 (m, 6 H), 7.50 (m, 4 H), 7.63 (d, J = 8 Hz, 2 H); m/z 696, 512, 484, 212. Anal. Calcd for $C_{41}H_{44}O_2S_4$: C, 70.65; H, 6.36. Found: C, 70.76; H, 6.43.

1,5-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]-3-oxapentane (5f). A solution of **4f** (1.39 g, 3.0 mmol), 1,2-ethanedithiol (0.3 mL, 3.6 mmol), and BF_3·OEt_2 (0.4 mL) in glacial acetic acid (40 mL) was refluxed for 6 h. The mixture was poured into ice (50 g) and extracted with chloroform (3 × 100 mL). The combined organic layers were washed with aqueous NaOH (5%, 3 × 150 mL) and water (2 × 150 mL). Then it was dried (Na_2SO_4) and filtered, and the filtrate was evaporated in vacuo to give **5f** (1.84 g, 100%): mp 137–140 °C (cyclohexane–chloroform); ^{1}H NMR δ 3.76 (s, 8 H), 3.98 (t, J = 5 Hz, 4 H), 4.26 (t, J = 5 Hz, 4 H), 6.90 (dd, J = 2, 8 Hz, 2 H), 7.28 (m, 6 H), 7.48 (m, 4 H), 7.64 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 42.2, 68.0, 68.5, 70.1, 111.7, 115.4, 119.0, 120.6, 125.0, 127.1, 128.5, 131.6, 138.4, 150.2, 152.2, 159.5; m/z 615, 430, 195. Anal. Calcd for $C_{34}H_{30}O_3S_4$: C, 66.42; H, 4.92. Found: C, 66.48; H, 4.97.

1,8-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]-3,6-dioxaoctane (5g). According to the procedure for the preparation of **5f** described above, **4g** (1.52 g, 3.0 mmol) was transformed into **5g** (1.57 g, 79%): mp 158–161 °C (cyclohexane–chloroform); ^{1}H NMR δ 3.75 (s, 8 H), 3.79 (s, 4 H), 3.90 (t, J = 5 Hz, 4 H), 4.19 (t, J = 5 Hz, 4 H), 6.88 (dd, J = 2.4, 8.4 Hz, 2 H), 7.26 (m, 6 H), 7.47 (m, 4 H), 7.63 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 42.2, 67.8, 68.5, 69.9, 71.0, 111.7, 115.2, 119.0, 120.6, 125.0, 127.1, 128.5, 131.6, 138.4, 150.2, 152.2, 159.5; m/z 474, 239, 212, 211, 195, 45. Anal. Calcd for $C_{36}H_{34}O_4S_4$: C, 65.62; H, 5.20. Found: C, 66.06; H, 5.25.

1,11-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]-3,6,9-trioxadecane (5h). According to the procedure described for the preparation of **5f**, **4h** (1.65 g, 3.0 mmol) was transformed into crude **5h**, which was subjected to chromatographic separation using hexane–ethyl acetate (3:1) as eluent to give **5h** as oil (2.11 g, 100%): ^{1}H NMR δ 3.73 (m, 8 H), 3.75 (s, 8 H), 3.87 (t, J = 5 Hz, 4 H), 4.18 (t, J = 5 Hz, 4 H), 6.88 (dd, J = 2.4, 8.3 Hz, 2 H), 7.27 (m, 6 H), 7.48 (m, 4 H), 7.63 (d, J = 7 Hz, 2 H). This material was used directly for the next operation without further purification.

1,14-Bis[[9′,9′-(ethylenedithio)fluoren-2′-yl]oxy]-3,6,9,12-tetraoxatetradecane (5i). By use of the procedure for the preparation of **5f**, **4i** (1.78 g, 3.0 mmol) was converted to an oil which was chromatographed on silica gel and eluted with hexane–ethyl acetate (3:1) to give **5i** (1.77 g, 79%), which was used for the next operation without further purification; ^{1}H NMR δ 3.64 (s, 4 H), 3.68 (m, 8 H), 3.76 (s, 8 H), 3.86 (t, J = 5 Hz, 4 H), 4.16 (t, J = 5 Hz, 4 H), 6.86 (dd, J = 2, 8 Hz, 2 H), 7.26 (m, 6 H), 7.49 (m, 4 H), 7.64 (d, J = 7 Hz, 2 H); ^{13}C NMR δ 42.2, 68.1, 68.7, 69.9, 70.8, 71.0, 111.9, 115.4, 119.1, 120.6, 125.1, 127.2, 128.6, 131.7, 138.6, 150.3, 152.3, 159.6.

General Procedure for the Intramolecular Desulfurdimerization of Dithioketals. The dithioketal and excess tungsten hexacarbonyl were mixed in chlorobenzene, and the mixture was flushed with nitrogen. The mixture was then refluxed under nitrogen for 12–48 h with stirring. After being cooled to room temperature, the blackish mixture was filtered and the residue was washed with chlorform. The filtrate was evaporated in vacuo, and the excess tungsten hexacarbonyl was removed by sublimation (90 °C, 0.3 mm) to give, after filtering through silica gel, bifluorenylidene, which was recrystallized from hexane–ethyl acetate to give the desired product.

1,2-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]ethane (6a). According to the general procedure described above, compound **5a** (0.12 g, 0.21 mmol) and $W(CO)_6$ (0.47 g, 1.3 mmol) were refluxed for 24 h to afford **6a** (0.03 g, 37%): mp 259–261 °C (hexane–ethyl acetate); ^{1}H NMR δ 4.02 (m, 2 H), 4.50 (m, 2 H), 6.78 (dd, J = 2, 8 Hz, 2 H), 7.30 (m, 6 H), 7.58 (d, J = 8 Hz, 2 H), 8.35 (d, J = 8 Hz, 2 H), 8.55 (d, J = 2 Hz, 2 H); ^{13}C NMR δ 65.1 (C-1, C-2), 117.0, 119.6, 119.9, 120.0, 125.6, 126.8, 129.6 (C-1′, C-1″, C-3′ to C-8′, C-3″ to C-8″), 135.2, 136.5, 139.0, 140.6, 141.6 (C-9′ to C-13′, C-9″ to C-13″), 153.2 (C-2′, C-2″); accurate mass calcd for $C_{28}H_{18}O_2$ 386.1307, found 386.1306. Anal. Calcd: C, 87.03; H, 4.69. Found: C, 86.90; H, 4.74.

1,3-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]propane (6b). A mixture of **5b** (1.02 g, 1.74 mmol) and $W(CO)_6$ (3.06 g, 8.7 mmol) in chlorobenzene (25 mL) was converted according to the general procedure to yield **6b** (0.46 g, 66%): mp 231–233 °C (hexane–ethyl acetate); IR (KBr) ν 3070, 2920, 1610, 1580, 1485, 1450, 1220, 760, 720 cm^{-1}; ^{1}H NMR δ 2.25 (q, J = 6 Hz, 2 H), 4.02 (t, J = 6 Hz, 4 H), 6.83 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 4 H), 7.45 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H), 8.35 (d, J = 8 Hz, 2 H), 8.37 (d, J = 2 Hz, 2 H); ^{13}C NMR δ 28.5 (C-2), 69.8 (C-1, C-3), 118.5, 119.7, 120.4, 121.0, 126.0, 126.6, 129.5 (C-1′, C-1″, C-3′ to C-8′, C-3″ to C-8″), 136.1, 137.2, 138.8, 140.7, 141.3 (C-9′ to C-13′, C-9″ to C-13″), 156.9 (C-2′, C-2″); accurate mass calcd for $C_{29}H_{20}O_2$ 400.1469, found 400.1469. Anal. Calcd: C, 86.98; H, 5.03. Found: C, 86.85; H, 4.99.

1,4-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]butane (6c). According to the general procedure described above, a mixture of **5c** (0.81 g, 1.35 mmol) and $W(CO)_6$ (3.01 g, 8.6 mmol) in chlorobenzene (30 mL) was allowed to react to give **6c** (0.35 g, 64%): mp 143–145 °C; IR (KBr) ν 3050, 2920, 1610, 1485, 760, 720 cm^{-1}; ^{1}H NMR δ 1.78 (br s, 4 H), 4.10 (br s, 4 H), 6.95 (dd, J = 2, 8 Hz, 2 H), 7.20 (m, 2 H), 7.30 (m, 2 H), 7.58 (d, J = 8 Hz, 2 H), 7.60 (m, 2 H), 8.00 (d, J = 2 Hz, 2 H), 8.40 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 22.2 (C-2, C-3), 68.4 (C-1, C-4), 115.4, 118.5, 119.4, 119.8, 125.3, 125.4, 128.4 (C-1′, C-1″, C-3′ to C-8′, C-3″ to C-8″), 134.7, 136.7, 137.8, 140.1, 140.3 (C-9′ to C-13′, C-9″ to C-13″), 154.7 (C-2′, C-2″); m/z 414. Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.92; H, 5.35. Found: C, 87.13; H, 5.42.

1,8-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]octane (6d). A chlorobenzene solution (30 mL) of **5d** (0.60 g, 0.92 mmol) and $W(CO)_6$ (1.30 g, 3.68 mmol) was refluxed for 36 h. The mixture was cooled to room temperature and filtered; the filter cake was washed with chloroform. After the solvent was evaporated in vacuo, the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give **6d** (0.30 g, 70%): mp 103–105 °C; IR (KBr) ν 3060, 2930, 2860, 1620, 1580, 1450, 1290, 1240, 1220, 765, 725 cm^{-1}; ^{1}H NMR δ 1.45 (m, 4 H), 1.56 (m, 4 H), 1.78 (m, 4 H), 3.98 (t, J = 6 Hz, 4 H), 6.88 (dd, J = 2, 8 Hz, 2 H), 7.10 (m, 2 H), 7.25 (m, 2 H), 7.52 (d, J = 8 Hz, 2 H), 7.55 (d, J = 8 Hz, 2 H), 8.06 (d, J = 2 Hz, 2 H), 8.33 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 25.3, 27.6, 28.1, 68.3, 113.3, 115.8, 119.1, 120.4, 125.8, 126.7, 129.3, 134.6, 138.2, 139.6, 141.4, 141.6, 158.9; m/z 470, 342; accurate mass calcd for $C_{34}H_{30}O_2$ 470.2246, found 470.2241. Anal. Calcd: C, 86.78; H, 6.43. Found: C, 86.66; H, 6.43.

1,11-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]undecane (6e). A chlorobenzene solution (30 mL) of **5e** (0.69 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 36 h. The mixture was cooled to room temperature and filtered; the filter cake was washed with chloroform. After the solvent was evaporated in vacuo, the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give **6e** (246 mg, 58%): mp 145–148 °C; IR (KBr) ν 3060, 2940, 2860, 1620, 1580, 1485, 1290, 1240, 765, 725 cm^{-1}; ^{1}H NMR δ 1.36 (m, 10 H), 1.50 (m, 4 H), 1.87 (m, 4 H), 3.96 (t, J = 6 Hz, 4 H), 6.85 (dd, J = 2, 8 Hz, 2 H), 7.10 (m, 2 H), 7.24 (m, 2 H), 7.58 (d, J = 8 Hz, 4 H), 8.04 (d, J = 2 Hz, 2 H), 8.28 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 24.9, 26.3, 27.2, 27.4, 29.0, 68.2, 113.3, 115.0, 119.1, 120.4, 125.7, 126.9, 129.2, 134.6, 138.5, 139.9, 141.5, 141.8, 159.3; m/z 512, 342; accurate mass calcd for $C_{37}H_{36}O_2$ 512.2715, found 512.2709. Anal. Calcd: C, 86.68; H, 7.08. Found: C, 86.14; H, 6.95.

1,5-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]-3-oxapentane (6f). A mixture of bridged dithioketal **5f** (0.31 g, 0.5 mmol) and $W(CO)_6$ (0.72 g, 2.0 mmol) in chlorobenzene (40 mL) was refluxed for 36 h under nitrogen atmosphere. After being cooled to room temperature, the mixture was filtered and the filter cake was washed with chloroform (10 mL). The combined organic solutions were evaporated in vacuo, and the residue was subjected to chromatographic separation using hexane–ethyl acetate (6:1) as eluent to give **6f** (0.08 g, 35%): mp 274–275 °C (EtOH); ^{1}H NMR δ 3.75 (t, J = 4 Hz, 4 H), 4.29 (m, 4 H), 6.89 (dd, J = 2.3, 8 Hz, 2 H), 7.09 (t, J = 8 Hz, 2 H), 7.26 (t, J = 8 Hz, 2 H), 7.55 (two overlapping sets of doublet, 4 H), 8.19 (d, J = 2.3 Hz, 2 H), 8.31 (d, J = 8 Hz, 2 H); ^{13}C NMR δ 66.3, 73.3, 110.4, 119.0, 120.4, 125.6, 127.0, 129.2, 134.6, 138.5, 141.8, 159.4; accurate mass calcd for $C_{30}H_{22}O_3$ 430.1569, found 430.1558.

1,8-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]-3,6-dioxaoctane (6g). The bridged dithioketal **5g** (0.33 g, 0.5 mmol) was allowed to react with $W(CO)_6$ (0.72 g, 2.0 mmol) in chlorobenzene (40 mL) according to the procedure described for the preparation of **6f**. The pure olefinic dimer **6g** was collected after chromatographic separation, employing hexane–ethyl acetate (4:1) as eluent (0.12 g, 52%): mp 214–216 °C (EtOH); ^{1}H NMR δ 3.75 (s, 4 H), 3.88 (t, J = 4 Hz, 4 H), 4.17 (t, J = 4 Hz, 4 H), 6.87 (dd, J = 2.3, 8 Hz, 2 H), 7.13 (t, J = 7.5 Hz, 2 H), 7.28 (t, J = 7.5 Hz, 2 H), 7.56 (two overlapping sets of doublet, 4 H), 8.15 (d, J = 2.3 Hz, 2 H), 8.35 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 68.5, 70.2, 71.7, 113.8, 116.2, 119.4, 120.6, 126.1, 126.9, 129.6, 135.1, 138.4, 139.7, 141.9, 158.8; accurate mass calcd for $C_{32}H_{26}O_4$ 474.1831, found 474.1831.

1,11-[(Z)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]-3,6,9-trioxaundecane (6h). The bridged dithioketal **5f** (0.28 g, 0.4 mmol) was allowed to react with $W(CO)_6$ (0.58 g, 1.6 mmol) in chlorobenzene (30 mL) according to the procedure for the preparation of **6f**. The pure olefinic dimer **6h** was collected after chromatographic separation using hexane–ethyl acetate (2:1) as eluent (0.08 g, 39%): mp 198–200 °C (EtOH); ^{1}H NMR δ 3.72 (s, 8 H), 3.81 (t, J = 4 Hz, 4 H), 4.14 (t, J = 4 Hz, 4 H), 6.89 (dd, J = 2.2, 8 Hz, 2 H), 7.12 (t, J = 7.5 Hz, 2 H), 7.26 (t, J = 7.5 Hz, 2 H), 7.56 (two overlapping sets of doublet, 4 H), 8.05 (d, J = 2.2 Hz,

2 H), 8.31 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 68.3, 69.7, 70.7 (2 C's), 112.8, 116.2, 119.2, 120.5, 125.9, 126.8, 129.3, 135.0, 138.4, 139.7, 141.4, 141.7, 158.7; accurate mass calcd for $C_{34}H_{30}O_5$ 518.2093, found 518.2086.

1,14-[(*Z*)-9′,9″-Bifluorenylidene-2′,2″-diyldioxy]-3,6,9,12-tetraoxatetradecane (6i). The bridged dithioketal **5i** (0.25 g, 0.33 mmol) was treated with $W(CO)_6$ (0.48 g, 1.3 mmol) in chlorobenzene (30 mL) according to the procedure for the preparation of **6f**. The pure olefinic dimer **6i** was collected after chromatographic separation using hexane–ethyl acetate (2:1) as eluent (51 mg, 27%): mp 158–160 °C (EtOH); ^{1}H NMR δ 3.67 (s, 4 H), 3.73 (s, 8 H), 3.88 (t, J = 4.8 Hz, 4 H), 4.09 (t, J = 4.8 Hz, 4 H), 6.93 (dd, J = 2.2, 8 Hz, 2 H), 7.11 (t, J = 7.5 Hz, 2 H), 7.27 (t, J = 7.5 Hz, 2 H), 7.56 (d, J = 8.5 Hz, 4 H), 8.01 (d, J = 2.2 Hz, 2 H), 8.30 (d, J = 7.5 Hz, 2 H); ^{13}C NMR δ 68.2, 69.9, 70.8 (2 C's), 71.1, 111.7, 117.1, 119.2, 120.6, 125.9, 126.8, 129.3, 135.0, 138.3, 139.6, 141.4, 141.6, 158.6; accurate mass calcd for $C_{36}H_{34}O_6$ 562.2355, found 562.2329.

1,2-Ethanediyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8a). A DMF solution (30 mL) of **7**[21] (1.5 g, 5.0 mmol), 1,2-dibromoethane (0.47 g, 2.5 mmol), anhydrous potassium carbonate (0.8 g, 6.0 mmol), and $Bu_4NCl{\cdot}H_2O$ (200 mg, 1.6 mmol) was stirred at 60 °C for 5 h. After being cooled to room temperature, the mixture was poured into water. The solid was filtered and washed with water, and air-dried to yield **8a** (1.25 g, 80%): mp 218–220 °C (acetone); IR (KBr) ν 3070, 2930, 1725, 1620, 1455, 1420, 1285, 1260, 1215, 1170, 1120, 1100, 750 cm^{-1}; ^{1}H NMR δ 3.78 (m, 8 H), 4.73 (s, 4 H), 7.40 (m, 4 H), 7.66 (d, J = 8 Hz, 4 H), 7.71 (m, 2 H), 8.09 (dd, J = 2, 8 Hz, 2 H), 8.37 (d, J = 2 Hz, 2 H). Anal. Calcd for $C_{34}H_{26}O_4S_4$: C, 65.15; H, 4.18. Found: C, 65.61; H, 4.29.

1,3-Propanediyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8b). A DMF solution (30 mL) of **7** (0.90 g, 3.0 mmol), 1,3-dibromopropane (0.30 g, 1.5 mmol), anhydrous potassium carbonate (0.55 g, 4.0 mmol), and $Bu_4NCl{\cdot}H_2O$ (200 mg, 1.6 mmol) was stirred at 60 °C for 8 h. After being cooled to room temperature, the mixture was poured into water. The precipitate was collected by filtration, washed with water, and then dried to yield **8b** (0.84 g, 88%): mp 198–200 °C (acetone); IR (KBr) ν 3060, 2975, 2930, 1715, 1620, 1290, 1260, 750 cm^{-1}; ^{1}H NMR δ 2.33 (quint, J = 6.5 Hz, 2 H), 3.84 (m, 8 H), 4.56 (t, J = 6.5 Hz, 4 H), 7.31–7.44 (m, 4 H), 7.60 (m, 4 H), 7.73 (dd, J = 2, 8 Hz, 2 H), 8.00 (dd, J = 2, 8 Hz, 2 H), 8.34 (d, J = 2 Hz, 2 H). Anal. Calcd for $C_{35}H_{28}O_4S_4$: C, 65.58; H, 4.40. Found: C, 65.18; H, 4.12.

1,4-Butanediyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8c). A DMF solution (30 mL) of **7** (1.5 g, 5.0 mmol), 1,4-dibromobutane (0.54 g, 2.5 mmol), anhydrous potassium carbonate (0.8 g, 6.0 mmol), and $Bu_4NCl{\cdot}H_2O$ (200 mg, 1.6 mmol) was stirred at 60 °C for 5 h. After being diluted with water, the mixture was filtered and the filter cake was washed with water and dried to give **8c** (1.53 g, 94%): mp 202–204 °C (acetone); IR (KBr) ν 3050, 2960, 2930, 1715, 1620, 1290, 1260, 750 cm^{-1}; ^{1}H NMR δ 2.00 (br s, 4 H), 3.80 (m, 8 H), 4.44 (br s, 4 H), 7.40 (m, 4 H), 7.66 (d, J = 8 Hz, 4 H), 7.71 (dd, J = 2, 8 Hz, 2 H), 8.06 (dd, J = 2, 8 Hz, 2 H), 8.37 (d, J = 2 Hz, 2 H). Anal. Calcd for $C_{36}H_{30}O_4S_4$: C, 66.02; H, 4.59. Found: C, 65.97; H, 4.61.

1,2-Ethanediyl (*Z*)-9′,9″-Bifluorenylidene-2′,2″-dicarboxylate (9a). A chlorobenzene solution (50 mL) of **8a** (0.52 g, 0.83 mmol) and $W(CO)_6$ (1.18 g, 3.32 mmol) was refluxed for 36 h. The mixture was cooled and filtered; the filter cake was washed with chloroform. Evaporation of solvent in vacuo gave the residue, which was chromatographed on silica gel and eluted with hexane–ethyl acetate (4:1) to afford **9a** as a red powder (0.21 g, 56%): mp 271–273 °C (MeOH); IR (KBr) ν 3070, 2970, 1725, 1465, 1450, 1420, 1260, 1190, 760, 725 cm^{-1}; ^{1}H NMR δ 4.57 (s, 4 H), 7.30 (t, J = 8 Hz, 2 H), 7.42 (t, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H), 8.06 (dd, J = 2, 8 Hz, 2 H), 8.56 (d, J = 8 Hz, 2 H), 9.37 (s, 2 H); ^{13}C NMR δ 166.4, 145.2, 140.9, 140.5, 138.2, 137.0, 131.2, 130.5, 130.0, 128.6, 128.3, 127.0, 121.0, 119.6, 61.3; accurate mass calcd for $C_{30}H_{18}O_4$ 442.1205, found 442.1205. Anal. Calcd: C, 81.44; H, 4.10. Found: C, 81.50; H, 4.03.

1,3-Propanediyl (*Z*)-9′,9″-Bifluorenylidene-2′,2″-dicarboxylate (9b). A chlorobenzene solution (50 mL) of **8b** (0.64 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 36 h. The mixture was cooled and filtered. The filter cake was washed with chloroform. Evaporation of solvent in vacuo gave the residue, which was chromatographed on silica gel and eluted with hexane–ethyl acetate (4:1) to afford **9b** as a red powder (0.29 g, 63%): mp 166–168 °C (MeOH); IR (KBr) ν 3090, 2970, 1715, 1460, 1425, 1395, 1295, 1265, 1210, 760, 725 cm^{-1}; ^{1}H NMR δ 2.10 (quint, 2 H), 4.54 (t, J = 6 Hz, 4 H), 7.27 (t, J = 8 Hz, 2 H), 7.38 (t, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H), 8.10 (dd, J = 2, 8 Hz, 2 H), 8.52 (d, J = 8 Hz, 2 H), 9.32 (s, 2 H); ^{13}C NMR δ 166.8, 145.3, 141.1, 140.6, 138.8, 137.4, 131.3, 129.9, 129.2, 128.3, 127.9, 127.6, 120.8, 119.6, 64.7, 29.2; accurate mass calcd for $C_{31}H_{20}O_4$ 456.1361, found 456.1368. Anal. Calcd: C, 81.57; H, 4.42. Found: C, 81.57, H, 4.40.

1,4-Butanediyl (*Z*)-9′,9″-Bifluorenylidene-2′,2″-dicarboxylate (9c). A chlorobenzene solution (50 mL) of **8c** (0.65 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 36 h. The mixture was cooled and filtered; the filter cake was washed with chloroform. Evaporation of solvent in vacuo gave the residue, which was chromatographed on silica gel and eluted with hexane–ethyl acetate (4:1) to afford **9c** as red powder (0.23 g, 49%): mp 215–217 °C (MeOH); IR (KBr) ν 3070, 2970, 1715, 1610, 1475, 1425, 1290, 1270, 1110, 755, 720 cm^{-1}; ^{1}H NMR δ 1.87 (br s, 4 H), 4.35 (br s, 4 H), 7.26 (t, J = 8 Hz, 2 H), 7.38 (t, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H), 7.82 (d, J = 8 Hz, 2 H), 8.14 (dd, J = 2, 8 Hz, 2 H), 8.44 (d, J = 8 Hz, 2 H), 9.14 (s, 2 H); ^{13}C NMR δ 166.9, 145.4, 141.2, 140.6, 139.1, 137.8, 131.4, 129.8, 129.3, 127.9, 127.7, 127.4, 120.7, 119.8, 63.8, 24.9; accurate mass calcd for $C_{32}H_{22}O_4$ 470.1518, found 470.1511. Anal. Calcd: C, 81.68; H, 4.71. Found: C, 81.19; H, 4.54.

(+)-*trans*-2,2-Dimethyl-1,3-dioxolane-4,5-dimethyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8d). A mixture of **7** (1.5 g, 5.0 mmol), (+)-*trans*-4,5-bis[(tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (1.17 g, 2.5 mmol), anhydrous potassium carbonate (0.83 g, 6.0 mmol), and Bu_4NBr (100 mg, 0.7 mmol) in DMF (40 mL) was heated at 60 °C for 6 h. The cooled mixture was diluted with water and filtered. The filter cake was recrystallized from acetone to give bisdithioketal **8d** (1.53 g, 84%): mp 174–175 °C; $[\alpha]^{22}_D$ +9.0° (c 0.20, $CHCl_3$); ^{1}H NMR δ 8.37 (s, 2 H), 8.08 (dd, J = 2, 8 Hz, 2 H), 7.72 (dd, J = 2, 8 Hz, 2 H), 7.65 (m, 4 H), 7.35 (m, 4 H), 4.60 (m, 4 H), 4.40 (m, 2 H), 3.80 (m, 8 H), 1.50 (s, 6 H).

(−)-*trans*-2,2-Dimethyl-1,3-dioxolane-4,5-dimethyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8e). By use of an identical procedure described for the preparation of **8d**, the reaction of **7** (1.5 g, 5.0 mmol) with (−)-*trans*-4,5-bis[(tosyloxy)-methyl]-2,2-dimethyl-1,3-dioxolane (1.17 g, 2.5 mmol), anhydrous potassium carbonate (0.83 g, 6.0 mmol), and Bu_4NBr (100 mg, 0.7 mmol) in DMF (40 mL) to give **8e** (1.67 g, 92%): mp 173–175 °C (acetone); $[\alpha]^{22}_D$ −10.2° (c 0.17, $CHCl_3$); IR (KBr) ν 3080, 2990, 2930, 1725, 1625, 1425, 1290, 1260, 1215, 1170, 750 cm^{-1}; ^{1}H NMR δ 8.37 (s, 2 H), 8.08 (dd, J = 2, 8 Hz, 2 H), 7.72 (dd, J = 2, 8 Hz, 2 H), 7.65 (m, 4 H), 7.35 (m, 4 H), 4.60 (m, 4 H), 4.40 (m, 2 H), 3.80 (m, 8 H), 1.50 (s, 6 H). Anal. Calcd for $C_{39}H_{34}O_6S_4$: C, 64.45; H, 4.79. Found: C, 64.44; H, 4.71.

(+)-(2*S*,3*S*)-2,3-Dimethoxybutane-1,4-diyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8f). A mixture of **7** (3.0 g, 10.0 mmol), (+)-(2*S*,3*S*)-1,4-bis(tosyloxy)-2,3-dimethoxybutane (2.30 g, 5.0 mmol), anhydrous potassium carbonate (1.5 g, 11.0 mmol), and Bu_4NBr (200 mg, 1.3 mmol) in DMF (50 mL) was stirred at 60 °C for 6 h. The cooled mixture was diluted with water and filtered. The filter cake was washed with water, dried, and recrystallized from acetone to give **8f** (3.4 g, 96%): mp 202–204 °C; $[\alpha]^{22}_D$ +1.6° (c 0.384, $CHCl_3$); ^{1}H NMR δ 8.38 (s, 2 H), 8.08 (dd, J = 2, 8 Hz, 2 H), 7.64–7.75 (m, 6 H), 7.35–7.44 (m, 4 H), 4.80 (dd, J = 5, 12 Hz, 2 H), 4.46 (dd, J = 5, 12 Hz, 2 H), 3.84 (m, 8 H), 3.78 (m, 2 H), 3.60 (s, 6 H).

Desulfurdimerization of (−)-*trans*-2,2-Dimethyl-1,3-dioxolane-4,5-dimethyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8e). A chlorobenzene solution (30 mL) of **8e** (0.726 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 48 h. The mixture was cooled to room temperature and filtered; the filter cake was washed with dichloromethane. The residue from the removal of solvent was chromatographed and eluted with hexane–ethyl acetate (4:1) to yield **9e** (212 mg, 40%): mp 274–277 °C; $[\alpha]^{22}_D$ +634° (c 0.1, $CHCl_3$); ^{1}H NMR δ 9.00 (s, 2 H), 8.42 (d, J = 8 Hz, 2 H), 8.16 (dd, J = 2, 8 Hz, 2 H), 7.80 (d, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H), 7.36 (m, 2 H), 7.24 (m, 2 H), 4.52

(m, 2 H), 4.30 (m, 4 H), 1.48 (s, 6 H); ^{13}C NMR δ 166.1, 145.6, 141.0, 140.3, 138.9, 137.6, 131.7, 129.9, 128.3, 128.0, 127.4, 127.3, 120.8, 120.0, 114.4, 77.5, 64.0, 28.7; accurate mass calcd for $C_{35}H_{26}O_6$ 542.1748, found 542.1753.

Desulfurdimerization of (+)-*trans*-2,2-Dimethyl-1,3-dioxolane-4,5-dimethyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8d). A chlorobenzene solution (30 mL) of **8d** (0.726 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 48 h. The mixture was cooled to room temperature and filtered; the filter cake was washed with dichloromethane. The residue from the removal of solvent was chromatographed and eluted with hexane–ethyl acetate (4:1) to yield **9d** (230 mg, 43%): mp 275–277 °C; $[\alpha]^{22}_D$ −690° (*c* 0.11, $CHCl_3$); ^{1}H NMR δ 9.00 (s, 2 H), 8.42 (d, *J* = 8 Hz, 2 H), 8.16 (dd, *J* = 2, 8 Hz, 2 H), 7.80 (d, *J* = 8 Hz, 2 H), 7.74 (d, *J* = 8 Hz, 2 H), 7.36 (m, 2 H), 7.24 (m, 2 H), 4.52 (m, 2 H), 4.30 (m, 4 H), 1.48 (s, 6 H); ^{13}C NMR δ 166.1, 145.6, 141.0, 140.3, 138.9, 137.6, 131.7, 129.9, 128.3, 128.0, 127.4, 127.3, 120.8, 120.0, 114.4, 77.5, 64.0, 28.7. Anal. Calcd for $C_{35}H_{26}O_6$: C, 77.48; H, 4.83. Found: C, 77.37; H, 4.74.

Desulfurdimerization of (+)-(2*S*,3*S*)-2,3-Dimethoxybutane-1,4-diyl Bis[9′,9′-(ethylenedithio)fluorene-2′-carboxylate] (8f). A chlorobenzene solution (30 mL) of **8f** (0.712 g, 1.0 mmol) and $W(CO)_6$ (1.40 g, 4.0 mmol) was refluxed for 48 h. The mixture was cooled to room temperature and filtered; the filter cake was washed with dichloromethane. The residue from the removal of solvent was chromatographed and eluted with hexane–ethyl acetate (4:1) to yield **9f** (145 mg, 30%): mp 265–285 °C; $[\alpha]^{22}_D$ +7.3° (*c* 0.191, $CHCl_3$); ^{1}H NMR δ 9.12 (s, 2 H), 8.45 (d, *J* = 8 Hz, 2 H), 8.12 (dd, *J* = 2, 8 Hz, 2 H), 7.80 (dd, *J* = 2, 8 Hz, 4 H), 7.40 (m, 2 H), 7.24 (m, 2 H), 4.50 (m, 4 H), 3.70 (m, 2 H), 3.42 (s, 6 H); ^{13}C NMR δ 166.3, 145.4, 141.1, 140.6, 139.0, 137.7, 131.4, 129.9, 128.9, 128.3, 128.0, 127.4, 120.8, 120.0, 70.0, 61.6, 58.7; accurate mass calcd for $C_{34}H_{26}O_6$ 530.1729, found 530.1670. Anal. Calcd: C, 76.98; H, 4.94. Found: C, 77.20; H, 4.85.

(*Z*)-Bifluorenylidene-2,2′-dicarboxylic Acid (10a). A mixture of **9b** (100 mg, 0.22 mmol) and sodium hydroxide (2.0 g, 50.0 mmol) in ethanol–water solution (5:1, 10 mL) was refluxed overnight. After neutralized with concentrated hydrochloric acid, the crude solid was collected by filtration and then recrystallized from DMF to afford **10a** (90 mg, 98%): mp >300 °C; accurate mass calcd for $C_{28}H_{16}O_4$ 416.1048, found 416.1021.

Hydrolysis of 9d or 9e. A mixture of **9d** or **9e** (50 mg, 0.09 mmol) and sodium hydroxide (2.0 g, 50.0 mmol) in ethanol–water solution (5:1, 10 mL) was refluxed overnight. After neutralizing with concentrated hydrochloric acid, the crude solid was collected by filtration and then recrystallized from DMF to afford optically inactive **10a** (35 mg, 92%): mp >300 °C; *m*/*z* 416.

Esterification of 10a. A methanolic solution (10 mL) of **10a** (100 mg, 0.24 mmol) containing three drops of concentrated sulfuric acid was refluxed overnight. After being cooled to room temperature, the ester **10b** was crystallized from methanol (100 mg, 94%): mp >300 °C; ^{1}H NMR δ 9.05 (s, 2 H), 8.35 (d, *J* = 8 Hz, 2 H), 8.06 (dd, *J* = 2, 8 Hz, 2 H), 7.80–7.76 (m, 4 H), 7.44–7.30 (m, 4 H), 3.48 (s, 6 H); accurate mass calcd for $C_{30}H_{20}O_4$ 444.1361, found 444.1360.

Reduction of 1,3-Propanediyl (*Z*)-9′,9″-Bifluorenylidene-2′,2″-dicarboxylate (9b). To a solution of cyclic diester **9b** (110 mg, 0.24 mmol) in toluene was added dropwise DIBAL-H (1.0 mL, 1.2 mmol, 1.2 M in toluene) at 0 °C. After addition, TLC showed no trace of starting material. The solution was quenched with 1 N hydrochloric acid and extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4) and filtered. Evaporation of the solvent yielded (*Z*)-2,2′-bis(hydroxymethyl)-9,9′-bifluorenylidene **10c** (93 mg, 99%): mp 245–246 °C; IR (KBr) ν 3600–3100, 2910, 2860, 1610, 1490, 1450, 1430, 1050, 770, 720 cm^{-1}; ^{1}H NMR δ 8.55 (s, 2 H), 8.41 (d, *J* = 8 Hz, 2 H), 7.70 (d, *J* = 8 Hz, 2 H), 7.65 (d, *J* = 8 Hz, 2 H), 7.35 (m, 2 H), 7.23 (m, 2 H), 4.67 (s, 4 H); accurate mass calcd for $C_{28}H_{20}O_2$ 388.1463, found 388.1473. Anal. Calcd: C, 86.57; H, 5.19. Found: C, 86.20; H, 4.97.

Reduction of 9d and 9e. To a solution of **9d** or **9e** (110 mg, 0.20 mmol) in toluene was added dropwise diisobutylaluminum hydride (1.0 mL, 1.2 mmol, 1.2 M in toluene) at 0 °C. After addition, TLC showed no trace of starting material. The solution was quenched with 1 N hydrochloric acid and extracted with dichloromethane. The combined organic layers were dried (Na_2SO_4) and filtered. Evaporation of solvent yielded optically inactive **10c** (75 mg, 95%), which was identical in every respect with the authentic sample.

Cyclization of (*Z*)-9,9′-Bifluorenylidene-2,2′-dicarboxylic Acid (10a). A solution of **10a** (52 mg, 0.13 mmol), 1,4-dibromobutane (27 mg, 0.13 mmol), potassium carbonate (41 mg, 0.3 mmol), and Bu_4NBr (50 mg) in DMF (15 mL) was stirred at 60 °C for 48 h. The mixture was diluted with water and extracted with dichloromethane. After removal of solvent, the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (4:1) to give **9c** (17 mg, 29%), which exhibited identical physical properties with those of the sample prepared by intramolecular desulfurdimerization described above.

***N*,*N*′-Bis(1-phenylethyl)-(*Z*)-9,9′-bifluorenylidene-2,2′-dicarboxamide (11).** A mixture of **9d** (110 mg, 0.20 mmol), (*R*)-(+)-(1-phenylethyl)amine (200 mg, 1.60 mmol), and trimethylaluminum (1.0 mL, 2.0 M in toluene, 2.0 mmol) in dichloromethane (10 mL) was heated under reflux for 48 h. The mixture was poured into water. The organic layer was separated and washed with dilute hydrochloric acid and then with water. The organic solution was dried ($MgSO_4$) and filtered, and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (3:1) to give **11** (18 mg, 14%): ^{1}H NMR δ 8.98 (s, 2 H), 8.42 (d, *J* = 8 Hz, 2 H), 7.70–7.80 (m, 4 H), 7.10–7.41 (m, 8 H), 5.27 (quint, *J* = 7 Hz, 2 H), 1.52 (d, *J* = 7 Hz, 6 H). The second portion **12** (97 mg, 77%): mp 231–233 °C; $[\alpha]^{22}_D$ −20.3° (*c* 0.000 67, $CHCl_3$); ^{1}H NMR δ 8.80 (s, 2 H), 8.28 (d, *J* = 8 Hz, 2 H), 7.66–7.77 (m, 4 H), 7.14–7.26 (m, 6 H), 7.17 (t, *J* = 7.5 Hz, 2 H), 6.28 (d, *J* = 7 Hz, 2 H, NH), 5.29 (quint, *J* = 7 Hz, 2 H), 1.56 (d, *J* = 7 Hz, 6 H); accurate mass calcd for $C_{44}H_{34}N_2O_2$ 622.2620, found 622.2633. Compound **11** was unstable in solution and rapidly rearranged to **12**.

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Registry No. **2**, 6949-73-1; **3a**, 106-93-4; **3b**, 106-93-4; **3c**, 110-52-1; **3d**, 4549-32-0; **4a**, 124755-70-0; **4b**, 124779-86-8; **4c**, 124755-71-1; **4d**, 124779-87-9; **4e**, 124779-88-0; **4f**, 120342-79-2; **4g**, 120368-17-4; **4h**, 120342-80-5; **4i**, 120342-81-6; **5a**, 124755-72-2; **5b**, 124755-73-3; **5c**, 124755-74-4; **5d**, 124755-75-5; **5e**, 124755-76-6; **5f**, 120342-82-7; **5g**, 120342-83-8; **5h**, 120342-84-9; **5i**, 120342-85-0; **6a**, 124755-77-7; **6b**, 124755-78-8; **6c**, 124755-79-9; **6d**, 124755-80-2; **6e**, 124755-81-3; **6f**, 124755-82-4; **6g**, 124755-83-5; **6h**, 124755-84-6; **6i**, 124755-85-7; **7**, 118476-91-8; **8a**, 124755-86-8; **8b**, 124755-87-9; **8c**, 124755-88-0; **8d**, 118476-97-4; **8e**, 124755-89-1; **8f**, 118476-99-6; **9a**, 124755-90-4; **9b**, 124755-91-5; **9c**, 118476-95-2; **9d**, 118574-07-5; **9e**, 118476-93-0; **9f**, 118476-96-3; **10a**, 118476-98-5; **10b**, 118477-00-2; **10c**, 118476-94-1; **11**, 124755-92-6; **12**, 124755-93-7; 1,11-dibromoundecane, 16696-65-4; diethylene glycol ditosylate, 7460-82-4; triethylene glycol dichloride, 112-26-5; tetraethlene glycol dichloride, 638-56-2; pentaethylene glycol ditosylate, 41024-91-3; tungsten hexacarbonyl, 14040-11-0; (+)-*trans*-4,5-bis[(tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane, 51064-65-4; (−)-*trans*-4,5-bis[(tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane, 37002-45-2; (+)-(2*S*,3*S*)-1,4-bis(tosyloxy)-2,3-dimethoxybutane, 55933-41-0.

Supplementary Material Available: Tables 1–4 containing atomic coordinates, equivalent isotropic temperature factors, bond angles, bond lengths, torsion angles, anisotropic thermal parameters, and H-atom coordinates (6 pages). Ordering information is given on any current masthead page.