Synthesis of Substituted Fluorenones and Substituted 3′,3′-Dichlorospiro[fluorene-9,2′-thiiranes] and Their Reactivities

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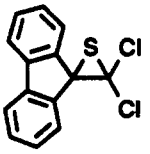
Several novel 9-fluorenones were synthesized and were used as precursors in an attempt to prepare unique substituted 3′,3′-dichlorospiro[fluorene-9,2′-thiiranes]. Several of the thiiranes were unstable and desulfurized during their preparation (**7a–d**, **11**, **12**). 3′,3′-Dichloro(2,5-dimethoxyspiro[fluorene-9,2′-thiirane] (**7f**) was prepared along with 2,2-dichloro-3,3-bis(4-methoxyphenyl)thiirane (**16**), and 3′,3′-dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptane-5,2′-thiirane] (**17**) all of which were stable at room temperature. A study of the reactivity of fluorenyl-substituted thiiranes and other related thiiranes showed that the extent of aromaticity of the substituents at the 3-position of the thiiranes influences their stabilities.

Introduction

As part of our investigation on the mechanism of sulfur extrusion from thiiranes of type **1**,[1] it is necessary to have a general approach to the synthesis of the fluorenones which would serve as precursors to the synthesis of the fluorenyl-substituted thiiranes.



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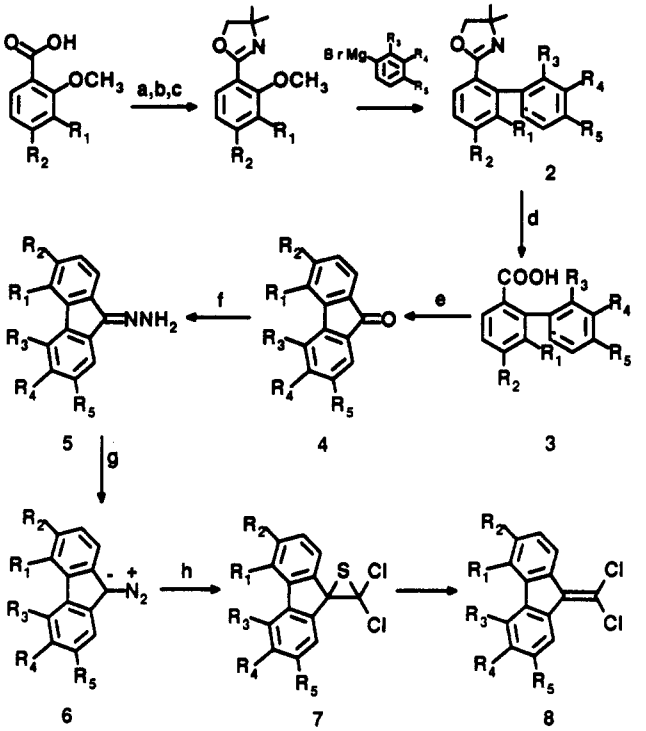
Two known methods for the preparation of fluorenones involve intramolecular cyclization steps. The first is a C–C bond formation from a carbonyl to aryl group and the second from aryl to aryl. Another convenient route to substituted fluorenones was recently described by Snieckus and co-workers and involved a remote aromatic metalation strategy.[2] We have successfully utilized the intramolecular cyclization approaches to the synthesis of substituted fluorenones, and we present our results here as well as attempts to prepare thiiranes with various substitution patterns. A study of the reactivity of these thiiranes was also undertaken.

Results and Discussion

The general method employed is outlined in Scheme I. The synthesis of biphenyloxazolines **2** and biphenylcarboxylic acids **3** is based on that described by Meyers.[3] The 2-oxazoline group was suitable protection for the carboxyl function because of its resistance to Grignard reagents used in a subsequent step in the synthesis.[4] The methodology was recently extended in the synthesis of 2-substituted naphthalenes.[5] The deprotection of the oxazoline moiety was accomplished by alkaline hydrolysis, although a milder method for converting oxazolines to carboxylic acids was recently described by Phillion and co-workers in which trifluoromethanesulfonic anhydride was employed followed by alkali saponification.[6]

Scheme I[a]



a: R_2=OCH_3; R_1=R_3=R_4=R_5=H
b: R_2=OCH_3; R_3=CH_3; R_1=R_4=R_5=H
c: R_2=OCH_3; R_5=CH_3; R_1=R_3=R_4=H
d: R_2=R_4=OCH_3; R_1=R_3=R_5=H
e: R_1=R_3=OCH_3; R_2=R_4=R_5=H
f: R_1=R_5=OCH_3; R_2=R_3=R_4=H

[a] Conditions: (a) $SOCl_2$, 25 °C, 24 h; (b) $NH_2CH_2C(CH_3)_2CH_2OH$, 0 °C; (c) (i) $SOCl_2$; (ii) 20% NaOH; (d) (i) CH_3I, 3 h; (ii) aq NaOH/CH_3OH, reflux 24 h; (e) polyphosphoric acid, 3 h; (f) $NH_2NH_2{\cdot}H_2O$, reflux 24 h; (g) HgO, Na_2SO_4, 10% KOH, 25 °C, 24 h; (h) $CSCl_2$, 0 °C.

With the substituted biphenyls in hand, intramolecular Friedel–Crafts-type acylation was affected by polyphosphoric acid.[7] In the preparation of **4d**, polyphosphoric acid cyclization gave two isomeric compounds, 3,6-

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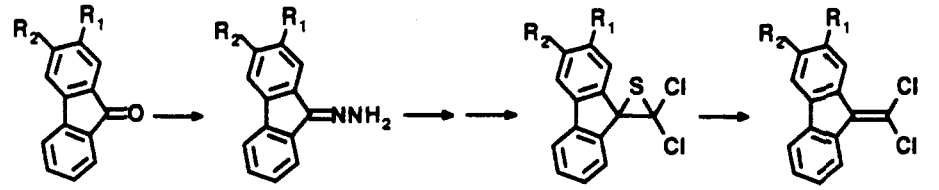
0022-3263/93/1958-4398$04.00/0

Scheme II



9 R_1=H; R_2=CH_3 10 11 R_1=H; R_2=CH_3 13 R_2=H; R_2=CH_3

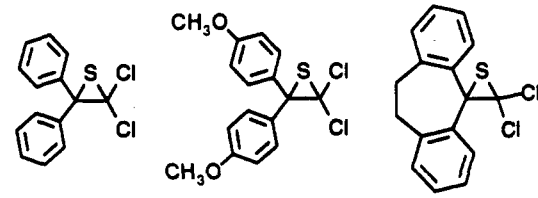
12 R_1=F; R_2=H 14 R_1=F; R_2=H

dimethoxy-9-fluorenone and 1,6-dimethoxy-9-fluorenone, which were easily separated. Conversion of the fluorenones **4** to their hydrazones **5** and then to their diazo derivatives **6** was relatively straightforward following the method described by Baltzly[8] or Schuster.[9] However, under the reaction conditions, fluorenone **4c** could not be converted to its hydrazone.

The diazo derivatives **6** were not isolated but were treated immediately with thiophosgene in situ in an attempt to prepare the fluorenyl-substituted derivatives **7**. The coupling of diazo compounds with thiocarbonyls is one of the easiest methods to prepare thiiranes.[10] This method has been employed with a wide range of both diazo reagents and thioketones and has resulted in a variety of different thiiranes.[11] This route (without isolation of the diazo compound) minimizes generation of azine side products. Azines are known to form readily from diazo compounds[12] and hydrazones.[13] Most of the thiiranes **7** were found to be unstable under the reaction conditions, and they underwent ready desulfurization to their corresponding olefins **8**. Thiirane **7f** was stable long enough to obtain analytical data.

The synthesis of the 3-methylfluorenyl derivative involved C–C bond formation from aryl to aryl. Ring closure was easily effected by Pschorr-type cyclization conditions which have been used to synthesize a variety of substituted fluorenone and azafluorenones.[14] 3-Methylfluorenone (**9**) was obtained which was converted to its hydrazone **10**, oxidized, and then treated with thiophosgene to give thiirane **11**; this thiirane promptly lost sulfur to give the corresponding olefin product **13** (Scheme II). An attempt to prepare the 2-fluorospiro[fluorene-9,2′-thiirane] **12** was also unsuccessful, and only ~1:3 ratio of thiirane to the desulfurized product (**14**) was obtained.

Three other related thiiranes, 2,2-dichloro-3,3-diphenylthiirane (**15**), 2,2-dichloro-3,3-bis(4-methoxyphenyl)-thiirane (**16**), and 3′,3′-dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] (**17**) were successfully prepared using the Staudinger methodology.[10] The 3-membered ring heterocycle in **15** and **17** is likely to be more stable than the fluorenyl-substituted compounds because the degree of aromaticity of the phenyl or benzo groups is less than that of the fluorenyl group (*vide infra*).



15 16 17

A substantial mechanistic study which extends our original observations on the mechanism has been carried out.[15] The major thrust of these proposals is consistent with the structure–activity results obtained here. The essential mechanistic pathway is included for clarity (Scheme III). It should be mentioned that we carried out trapping experiments[15,16] in an effort to intercept the cationic intermediate portrayed in Scheme III. These were unsuccessful, indicating that the concatenation of sulfur atoms is a fast process. There is literature precedent for this process.[17]

The study of the general reactivity of substituted derivatives of **1** entailed measuring the possible loss of sulfur when heated in toluene at 80 °C for 45 min. The unsubstituted thiirane **1**, as expected, was transformed entirely to the corresponding olefin under the reaction conditions. Our proposed mechanism has as the rate-determining step (unimolecular path) the ionization of the C–S bond as shown in intermediate **18** (*vide infra*, Scheme IV).[1,15] Therefore, the reaction would be predicted to lose sulfur much faster in the presence of activating groups on the fluorenyl ring system since these substituents would stabilize the developing cation. In the presence of deactivating groups, the dipolar intermediate would be unfavourable and the compound would not be expected to lose sulfur as easily.

The inability to isolate a pure sample of the fluoro-substituted thiirane derivative **12** is consistent with our

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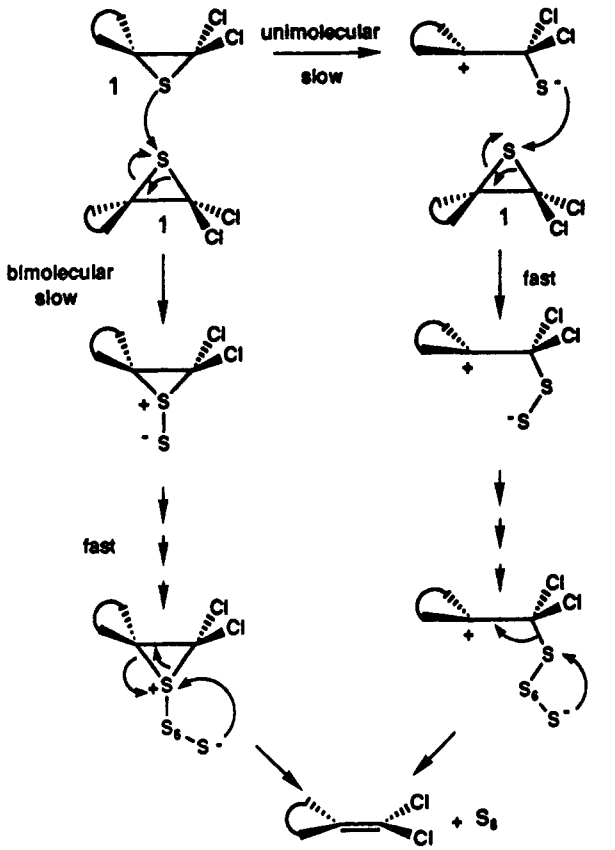
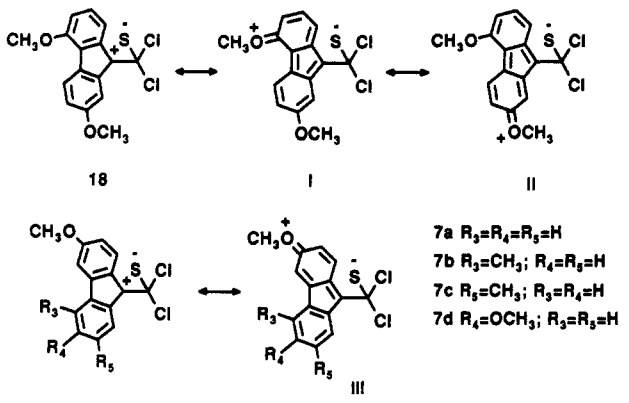
Scheme III



Scheme IV



argument. The fluorine atom could stabilize the dipolar intermediate *via* resonance[18] facilitating desulfurization. Countering this, by its inductive effect, the intermediate would be destabilized and thus inhibit desulfurization. Our experiments show that a mixture of **12** and **14** was obtained, strongly suggesting that the inductive and the resonance effects on the fluorenyl ring system are approximately balanced and episulfide **12** is partially converted to olefin **14**.

A similar explanation can be envisioned for the instability of thiiranes **7**. The presence of methoxy substituents would stabilize the proposed cationic intermediate and enhance its decomposition. The presence of additional activating methyl groups in **7b** and **7c** further increases desulfurization. The synthesis of 2,5-dimethoxy-substituted fluorenylthiirane **7f** was successful, although in poor yield. Initial studies show that when **7f** was heated in toluene at 80 °C for 2 h, no desulfurization occurred. The reaction was followed by ^{1}H NMR and found to be unchanged after heating for 2 h whereas compound **1** completely desulfurized under the same conditions. Although the two methoxy substituents present in **7f** would enhance desulfurization by a resonance effect, a closer examination of the resonance contributors suggests why we do not observe ready desulfurization (Scheme IV).

In order for **7f** to desulfurize, resonance structures **I** or **II** should be strong contributors to the hybrid. However, these contributors destroy the overall aromaticity of the ring system, and therefore, both I and II deliver a small resonance contribution. Conversely, resonance contributor III in compounds **7a–d** does not disrupt the aromaticity of the entire ring system; as a consequence, desulfurization is more likely to occur. Furthermore, it was discovered that introduction of a stabilizing methyl substituent at the 3-position of the fluorenyl group in **1** (thiirane **11**) causes desulfurization. It should be emphasized that in the cases of attempted preparation of **7a–d**, and **11**, the only products isolated were the corresponding alkenes **8a–d** and **13**. The episulfides must have been formed but underwent ready desulfurization.

An interesting result was observed when we studied the reactivity of the diphenyl-substituted thiiranes **15** and **16**. These two compounds are easily prepared in high yield, and the precursors as well as the thiirane are stable for months in the refrigerator without noticeable decomposition. Unlike **1**, **15** does not desulfurize when heated at 80 °C for 45 min. This observation can be explained by the differences in the two aromatic systems which influence their ability to promote the cation generated in the unimolecular rate-determining step.

The planar fluorenyl group in **1** can delocalize the cation more efficiently than the noncoplanar phenyl groups of **15**. It is known from solvolysis reactions of alkyl chlorides containing either the fluorenyl or biphenyl aromatic systems that the fluorenyl substituent is a better transmitter of π electrons in stabilizing carbonium ions.[19] The phenyl groups, meanwhile, are less effective in stabilizing the incipient carbonium ion since the π system is twisted out of the plane. Further supporting this position is the recent observation of Johnston and Lee-Ruff who have demonstrated the comparable stabilities of the two cation systems (fluorenyl and biphenyl).[20] They have reported that when reactivities with the same solvent are compared the diphenylmethyl cation is less reactive than the fluorenyl counterpart.

Conversely, the bis(4-methoxyphenyl)-substituted derivative **16** was found to decompose readily in solution. This would be expected since the *p*-methoxy groups would assist in stabilizing the incipient carbonium ion and facilitate desulfurization.

3′,3′-Dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] (**17**) did not desulfurize under the reaction conditions (2 h, 80 °C) but was found to desulfurize to a 50% extent when heated at 100 °C for 8 days. After 17 days, approximately 75% had decomposed. This is consistent with the overall mechanistic picture because the two methylene groups bridging the phenyl

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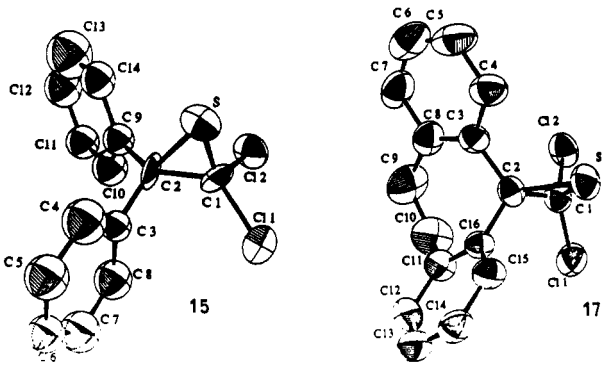

Figure 1. ORTEP representation of thiiranes 15 and 17.

Table I. Atomic Coordinates (x, y, z) and Temperature Factors (B_{eq}) for Compound 15 (Estimated σs Refer to the Last Digit)

atom	x	y	z	B_{eq}
Cl1	0.0877(3)	0.3652(11)	0.0534(3)	5.4(4)
Cl2	−0.0202(3)	0.4118(11)	0.1232(3)	5.5(4)
S	0.0426(3)	0.8129(11)	0.0785(3)	4.4(4)
C1	0.0524(12)	0.543(4)	0.1048(11)	4.4(15)
C2	0.0895(12)	0.685(4)	0.1503(9)	4.2(15)
C3	0.1638(6)	0.676(3)	0.1537(7)	3.6(3)
C4	0.1966(9)	0.8525(22)	0.1334(6)	6.9(3)
C5	0.2647(9)	0.8483(23)	0.1377(6)	6.4(3)
C6	0.3000(6)	0.668(3)	0.1621(7)	5.0(3)
C7	0.2672(9)	0.4909(22)	0.1823(7)	6.8(3)
C8	0.1990(9)	0.4951(23)	0.1781(7)	6.1(3)
C9	0.0665(8)	0.728(3)	0.2127(6)	4.3(3)
C10	0.0771(7)	0.5720(22)	0.2611(9)	6.2(3)
C11	0.0576(7)	0.609(3)	0.3210(7)	5.7(3)
C12	0.0275(8)	0.802(3)	0.3326(6)	6.7(3)
C13	0.0169(7)	0.9581(23)	0.2843(9)	9.6(3)
C14	0.0364(7)	0.9210(25)	0.2243(7)	5.3(3)
Cl1A	0.6579(4)	−0.3601(14)	−0.0320(3)	8.2(5)
Cl2A	0.5726(4)	−0.4533(15)	0.0591(4)	9.5(6)
SA	0.5933(4)	0.0110(14)	0.0270(4)	7.5(5)
C1A	0.6250(15)	−0.252(4)	0.0354(12)	6.3(19)
C2A	0.6619(11)	−0.117(5)	0.0817(12)	5.2(16)
C3A	0.7308(6)	−0.058(3)	0.0698(7)	5.0(3)
C4A	0.7429(8)	0.139(3)	0.0425(7)	6.7(3)
C5A	0.8065(9)	0.1933(21)	0.0342(6)	6.0(3)
C6A	0.8581(6)	0.051(3)	0.0532(7)	5.6(3)
C7A	0.8460(8)	−0.146(3)	0.0805(7)	7.8(3)
C8A	0.7824(9)	−0.2009(21)	0.0888(6)	5.3(3)
C9A	0.6575(7)	−0.143(3)	0.1520(5)	3.4(3)
C10A	0.6796(7)	−0.3271(24)	0.1867(8)	6.6(3)
C11A	0.6777(7)	−0.3386(24)	0.2531(8)	6.2(3)
C12A	0.6536(7)	−0.166(3)	0.2847(5)	6.2(3)
C13A	0.6315(7)	0.018(3)	0.2500(9)	7.8(3)
C14A	0.6334(7)	0.0291(23)	0.1836(8)	8.3(3)

groups cause the π system to become more planar than the diphenyl system but less than that of the fluorenyl system.

Crystal structure determinations of 15 and 17 were carried out. Figure 1 shows the ORTEP representations of both 15 and 17. Atomic coordinates and temperature factors are reported in Tables I and II. As predicted, the phenyl groups in 15 are not coplanar and are arranged in such a fashion as to minimize their interaction. In 17, a similar nonplanarity of the aromatic rings is also found. The aryl groups in 17 are ~60° out of the plane, and the phenyl groups in 15 are >60° out of the plane; of course, the fluorenyl group in 1 is planar. Since the fluorenyl system decomposes readily while the diphenyl system does not desulfurize, we would expect some decomposition to occur with 17 but at a very slow rate.

Consequently, we can summarize the aromatic systems in increasing order of reactivity: diphenyl < dibenzosuberonyl < fluorenyl and diphenyl ≪ bis(4-methoxyphenyl). Bis(4-methoxyphenyl) would be predicted to be more reactive than fluorenyl since the activating methoxy groups would override the resonance effect of the planar fluorenyl ring system. Qualitatively, we can state that amongst the substituted fluorenyl derivatives the increasing order of reactivity would be as follows: fluorenyl < 2,5-dimethoxyfluorenyl < 2-fluorofluorenyl < 3-methylfluorenyl < 3-methoxyfluorenyl < 3-methoxy-5-methylfluorenyl = 3-methoxy-7-methylfluorenyl < 3,6-dimethoxyfluorenyl.

Table II. Atomic Coordinates (x, y, z) and Temperature Factors (B_{eq}) for Compound 17 (Estimated σs Refer to the Last Digit)

atom	x	y	z	B_{eq}
S	0.62296(19)	0.6257(3)	0.06797(7)	5.15(9)
Cl1	0.54225(18)	1.0721(3)	0.09744(7)	5.68(9)
Cl2	0.75718(18)	1.0136(3)	0.01891(6)	5.54(9)
C1	0.6712(6)	0.8961(10)	0.07392(22)	4.4(3)
C2	0.7574(6)	0.7600(9)	0.11535(23)	3.7(3)
C3	0.9152(7)	0.7150(10)	0.10565(23)	4.0(3)
C4	0.9485(7)	0.5357(12)	0.0762(3)	5.5(4)
C5	1.0918(9)	0.4897(14)	0.0675(3)	7.2(5)
C6	1.1976(9)	0.6260(18)	0.0864(4)	7.7(6)
C7	1.1643(8)	0.8035(15)	0.1158(3)	6.8(5)
C8	1.0231(7)	0.8520(12)	0.1267(3)	5.2(4)
C9	1.0055(8)	1.0434(14)	0.1629(4)	7.7(5)
C10	0.8679(9)	1.1112(11)	0.1805(3)	7.2(4)
C11	0.7803(6)	0.9424(10)	0.2072(3)	4.6(3)
C12	0.7550(7)	0.9529(11)	0.2638(3)	5.2(4)
C13	0.6760(7)	0.8005(13)	0.2879(3)	5.2(4)
C14	0.6217(7)	0.6345(11)	0.2568(3)	4.9(3)
C15	0.6462(6)	0.6201(9)	0.20059(24)	4.1(3)
C16	0.7255(6)	0.7735(9)	0.1759(23)	3.6(3)

Experimental Section

X-Ray Crystallographic Data for 15 and 17. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer using graphite-monochromated CuK$_\alpha$ (γ = 1.540 56 Å) (composed 15) or MoK$_\alpha$ (γ = 0.709 30 Å) (compound 17) radiations using the $\theta/2\theta$ scan mode for 15 and the ω scan mode for 17. Structures were solved by direct methods.[21] Hydrogens were calculated. Solution and refinement were done using NRCVAX system programs.[22] Crystal data, collection and refinement parameters are given in Table III.[23] Crystal 15 decomposed in the beam, and data were collected from four crystals. Phenyl rings in 15 were refined as isotropic rigid groups. For crystal 17 all non-hydrogens were refined anisotropically. Tables of bond lengths and angles, torsion angles, and temperature factors have been deposited as supplementary material.

General Methods. Melting points (mp) were determine using a Gallenkamp melting point apparatus and are uncorrected. Low-resolution electron impact (EI) mass spectra were obtained on a Dupont Instruments 21-492B or Kratos MS25RFA mass spectrometer equipped with a 70-eV ionizing energy source and used in direct-inlet mode. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario). ^{1}H NMR spectra were recorded on either Varian XL200 or XL300 spectrometers using deuteriochloroform as the reference solvent unless otherwise indicated. ^{13}C NMR spectra were obtained at 75.4 MHz using the Varian XL300, at 67.9 MHz using the JEOL CPF-270, or at 50.3 MHz using the Varian Gemini-200 spectrometers. ^{19}F NMR spectra are reported relative to external dichlorodifluoromethane and were not proton decoupled. Infrared spectra were recorded on an Analect Instruments ASQ-18

(21) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M.; Kruger, M., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189.

(22) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* 1989, 22, 384.

(23) The authors have deposited atomic coordinates for 15 and 17 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table III. Crystal Data for Thiiranes 15 and 17

	compd 15	compd 17
chemical formula	$C_{14}H_{10}SCl_2$	$C_{16}H_{12}SCl_2$
formula wt	281.20	307.23
cryst dimsn (mm)	0.40 × 0.15 × 0.05	0.50 × 0.35 × 0.20
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
lattice constants		
a(Å)	20.646(6)[a]	9.351(4)[b]
b(Å)	6.244(3)	6.3151(19)
c(Å)	20.880(6)	24.077(6)
b(°)	99.263(23)	94.03(3)
Z	8	4
h, k, l ranges	−16 16, 0 5, 0 17	−10 10, 0 6, 0 25
density (cald) (g cm^{-3})	1.406	1.439
no. of parameters	119	172
obsd data $I > 2.5s(I)$	827	1053
for significant reflns	RF = 0.091,[c] R_w = 0.083[d]	RF = 0.045,[c] R_w = 0.040[d]

[a] Cell dimensions were obtained from 20 reflections with 2θ angle in the range 40.00–50.00°. No correction was made for absorption. [b] Cell dimensions were obtained from 25 reflections with 2θ angle in the range 20.00–25.00°. No correction was made for absorption.[c] RF = $\Sigma(F_o - F_c)/\Sigma(F_o)$. [d] $R_w = (\Sigma[w(F_o - F_c)^2/\Sigma(wF_o^2)])^{1/2}$.

FTIR spectrometer. Raman spectra were recorded on a S. A. Ramonor spectrometer equipped with a Spectra-Physics Argon ion laser at 514.5 nm or a Bruker IFS-88 FT Raman spectrometer equipped with a ND:YAG laser.

Synthesis of Biphenyloxazolines 2. General Procedure. The preparation of biphenyl oxazolines **2** is based on the method described by Meyers.[3]

2-(2-Phenyl-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (2a). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (s, 6H, $C(CH_3)_2$), 3.75 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 6.87–6.90 (m, 2H), 7.36–7.39 (m, 5H), 7.70 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.0, 55.4, 67.2, 79.2, 112.5, 115.5, 120.3, 127.2, 127.9, 128.2, 131.8, 141.2, 143.4, 160.9, 163.7. MS m/z (rel intensity) 281 ($M^{\bullet+}$, 25), 280 ($M^{\bullet+}$ − 1, 100), 195 (28), 152 (11), 94 (11).

2-[2-(2-Methylphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2b). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17, 1.19 (2 × s, 6H, $C(CH_3)_2$), 2.11 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 6.73 (d, 1H, J = 2.5 Hz), 6.89 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2.6 Hz), 7.14–7.20 (m, 4H), 7.77 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 20.0, 28.0, 55.3, 66.9, 79.2, 112.6, 115.5, 121.0, 125.0, 127.2, 128.8, 129.3, 131.3, 135.6, 141.2, 143.3, 160.8, 163.3. MS m/z (rel intensity) 295 ($M^{\bullet+}$, 5), 280 ($M^{\bullet+}$ − CH_3, 100), 209 (9).

2-[2-(4-Methylphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2c). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 6H, $C(CH_3)_2$, 2.38 (s, 3H, CH_3), 3.76 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.84–6.87 (m, 2H), 7.23 (dd, 4H, J_1 = 13.0 Hz, J_2 = 7.9 Hz), 9.10 (d, 1H, J = 9.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.2, 28.0, 55.4, 67.1, 79.3, 112.3, 115.5, 120.4, 128.1, 128.7, 131.9, 137.0, 138.3, 143.3, 161.0, 163.8. MS m/z (rel intensity) 295 ($M^{\bullet+}$, 25), 294 ($M^{\bullet+}$ − 1, 100), 280 ($M^{\bullet+}$ − CH_3, 3), 239 (7), 209 (12), 108 (15), 43 (44).

2-[2-(3-Methoxyphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2d). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (s, 6H, $C(CH_3)_2$), 3.77 (s, 2H, CH_2), 3.81 (s, 3H), 3.84 (s, 3H), 6.85–7.68 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 27.8, 55.1, 55.3, 67.1, 79.3, 112.6, 113.0, 113.8, 115.5, 120.4, 120.9, 129.0, 131.9, 142.8, 142.9, 159.5, 161.1, 163.8. MS m/z (rel intensity) 311 ($M^{\bullet+}$, 30) ($M^{\bullet+}$ − 1, 100) 296 ($M^{\bullet+}$ − CH_3, 9), 255 (10), 225 (16).

2-[2-(2-Methoxyphenyl)-3-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2e). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.38 (s, 6H, $C(CH_3)_2$), 3.88 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 6.76–6.98 (m, 4H, aromatic), 7.24 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.6 Hz), 7.52 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.4, 56.1, 56.2, 67.0, 78.4, 111.1, 111.7, 112.1, 115.1, 118.0, 119.5, 121.8, 128.4, 133.3, 148.3, 150.3, 155.9, 163.7. MS m/z (rel intensity) 280 ($M^{\bullet+}$ − OCH_3, 23), 149 (100).

2-[2-(4-Methoxyphenyl)-3-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2f). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20 (s, 6H, $C(CH_3)_2$), 3.69 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.89–7.27 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 27.9, 55.1, 55.8, 60.3, 79.9, 112.8, 113.0, 121.8, 128.0, 128.7, 130.1, 130.7, 130.9, 156.7, 158.6, 163.5. MS m/z (rel intensity) 310 ($M^{\bullet+}$ − 1, 7), 163 (100).

Synthesis of Biphenylcarboxylic Acids 3. General Procedure. The preparation of biphenylcarboxylic acids **3** is based on the method described by Meyers[3] unless otherwise noted.

2-Phenyl-4-methoxybenzoic Acid (3a). Mp: 163–165 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.86 (s 3H, OCH_3), 6.82 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.31–7.35 (m, 5H), 7.98 (d, 1H, J = 8.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 112.6, 116.7, 121.0, 127.3, 127.9, 128.4, 133.4, 141.3, 146.3, 162.4, 172.0. MS m/z (rel intensity) 228 ($M^{\bullet+}$, 100), 211 ($M^{\bullet+}$ − OH, 96), 168 (27), 152 (15), 139 (31).

2-(2-Methylphenyl)-4-methoxybenzoic Acid (3b). Mp: 141–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.70 (d, 1H, J = 2.5 Hz), 6.92 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.09–7.25 (m, 4H), 8.05 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.9, 55.5, 112.8, 116.3, 120.8, 125.3, 127.3, 128.2, 129.5, 133.4, 135.3, 141.4, 162.6, 170.1. MS m/z (rel intensity) 242 ($M^{\bullet+}$, 97), 227 ($M^{\bullet+}$ − CH_3, 51), 225 ($M^{\bullet+}$ − OH, 100), 197 (19), 181 (22), 165 (35), 152 (28), 120 (23).

2-(4-Methylphenyl)-4-methoxybenzoic Acid (3c). Mp: 167–169 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.81 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.21 (s, 4H), 7.97 (d, 1H, J = 8.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.2, 55.5, 112.5, 116.6, 121.0, 128.3, 128.7, 133.4, 137.1, 138.3, 146.2, 162.3, 171.4. MS m/z (rel intensity) 242 ($M^{\bullet+}$, 100), 225 ($M^{\bullet+}$ − OH, 67), 182 (10), 165 (9), 152 (11), 120 (14).

2-(3-Methoxyphenyl)-4-methoxybenzoic Acid (3d). The preparation of **3d** was based on the method described by Schuster.[9] Mp: 128–129 °C (lit.[9] mp 130–131 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.84 (s, 3H), 6.79–7.84 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.1, 55.4, 112.6, 112.8, 114.2, 116.4, 121.1, 123.2, 129.0, 132.9, 143.2, 145.3, 159.3, 162.0, 172.8. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 83), 241 ($M^{\bullet+}$ − OH, 42), 86 (34), 72 (100).

2-(2-Methoxyphenyl)-3-methoxybenzoic Acid (3e). Mp: 194–196 °C (lit.[3] 196–197 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.92 (d, 1H, J = 8.2 Hz), 7.01 (d, 1H, J = 7.4 Hz), 7.15 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.1 Hz), 7.33 (t, 1H, J = 8.3 Hz), 7.38 (t, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.6, 56.2, 110.9, 115.1, 120.3, 122.2, 125.2, 128.2, 128.3, 128.9, 131.0, 131.8, 156.7, 157.3, 169.8. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 100), 227 ($M^{\bullet+}$ − OCH_3, 48), 211 (12), 197 (7), 184 (9), 168 (21), 165 (58), 139 (12).

2-(4-Methoxyphenyl)-3-methoxybenzoic Acid (3f). Mp: 170–172 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.90–7.55 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.1, 56.0, 113.3, 114.5, 122.1, 128.1, 128.2, 130.7, 131.2, 131.8, 157.2, 158.8, 172.3. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 100), 225 (9), 197 (12), 184 (7), 122 (11).

Synthesis of Fluorenones 4. General Procedure. The preparation of fluorenones **4** is based on the method described by Schuster.[9]

3-Methoxy-9-fluorenone (4a). Mp: 95–96 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.85 (s, 3H, OCH_3), 6.67 (dd, H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.94 (d, 1H, J = 2.2 Hz), 7.20–7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.8, 107.0, 112.9, 120.0, 123.8, 126.2, 127.1, 129.2, 134.1, 135.3, 143.3, 146.9, 165.3, 192.5. MS m/z (rel intensity) 210 ($M^{\bullet+}$, 100), 180 (13), 167 (15), 152 (9), 139 (28).

3-Methoxy-5-methyl-9-fluorenone (4b). Mp: 138–140 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.72 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.2 Hz), 7.14–7.22 (m, 3H), 7.50 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 20.1, 55.7, 111.0, 111.4, 121.6, 126.2, 127.6, 128.9, 133.5, 135.7, 136.9, 140.9, 147.6, 165.1, 192.8. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 181 (15), 170 (6), 165 (17), 152 (20).

3-Methoxy-7-methyl-9-fluorenone (4c). Mp: 118–120 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.69 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.5, 55.8, 106.8, 112.4, 119.9, 124.6, 126.1, 127.2, 134.4, 135.5, 139.4, 140.6, 147.1, 170.0. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 181 (15), 165 (11), 153 (13).

3,6-Dimethoxy-9-fluorenone (4d). Mp: 141–143 °C (lit.[9] mp 142–144 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 6H, OCH_3), 6.73 (dd, 2H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.98 (s, 2H), 7.57 (d, 2H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.7, 107.0, 112.9, 125.7, 128.3, 145.9, 164.9, 191.4. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 100), 211 (9), 197 (17), 169 (17), 126 (9).

4,5-Dimethoxy-9-fluorenone (4e). Mp: 184–137.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.06 (s, 6H, 2 × OCH_3), 7.51 (t, 2H, J = 8.0 Hz), 8.06 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.2 Hz), 8.93 (dd, 2H, J_1 = 8.3 Hz, J_2 = 1.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 56.0, 116.8, 117.2, 122.6, 124.3, 128.5, 129.2, 129.6. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 6), 226 (100), 211 (49), 155 (19), 139 (8), 127 (13). IR (cm^{-1}): 1724 (C=O).

2,5-Dimethoxy-9-fluorenone (4f). Mp: 160–163 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.90–7.55 (m, 5H), 7.66 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 55.6, 109.4, 116.5, 117.9, 119.9, 125.1, 127.2, 128.1, 129.2, 135.2, 135.8, 136.3, 154.7, 160.0. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 100), 225 (63), 197 (20), 126 (11).

Synthesis of Hydrazones 5. General Procedure. The preparation of hydrazones **5** is based on the method of described by Schuster.[9]

3-Methoxy-9-fluorenone Hydrazone (5a). Mp: 118–125 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89, 3.91 (2 × s, 6H, OCH_3, both isomers), 6.81–7.94 (m, 14H, both isomers). ^{13}C NMR (75.4, MHz, $CDCl_3$): major isomer δ 55.6, 106.4, 112.6, 119.5, 120.7, 123.6, 126.8, 128.1, 128.4, 138.3, 140.2, 141.0, 143.5, 161.1, minor isomer δ 74.7, 104.9, 113.9, 120.4, 121.8, 125.6, 127.9, 129.6, 131.0, 138.6, 139.8, 141.6, 145.9, 160.7. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 209 ($M^{\bullet+}$ – NH, 23), 195 (30), 180 (19), 165 (11), 152 (43).

3-Methoxy-5-methyl-9-fluorenone Hydrazone (5b). In some cases, hydrazone **5b** was contaminated by the Wolff–Kishner reduction product (3-methoxy-5-methylfluorene) which was removed by column chromatography (1:1 CH_2Cl_2/hexanes eluent). Mp: 128–134 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): major isomer (NNH_2 syn to H_1) δ 2.65 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 6.19 (s, 2H, NNH_2), 6.83 (m, 2H, both isomers), 7.12–7.23 (m, 4H, both isomers), 7.43, (d, 1H, J = 2.4 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 8.5 Hz), minor isomer (NNH_2 syn to H_8) δ 2.69 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.24 (s, 2H, NNH_2), 7.32, (d, 1H, J = 2.2 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): major isomer δ 20.8, 55.6, 110.6, 110.9, 118.3, 124.0, 126.5, 127.7, 131.3, 131.4, 132.8, 139.1, 140.9, 146.0, 160.4, minor isomer δ 21.2, 55.6, 109.7, 111.9, 121.4, 123.3, 127.6, 131.1, 132.4, 133.8, 136.2, 138.8, 144.5, 145.9, 160.8. MS m/z (rel intensity) 238 ($M^{\bullet+}$, 100), 223 ($M^{\bullet+}$ – CH_3, 19), 209 (32), 195 (17), 165 (27), 152 (19).

3-Methoxy-7-methyl-9-fluorenone Hydrazone (5c). Mp: 118–123 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.69 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, ^{1}H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.5, 55.8, 106.8, 112.4, 119.9, 124.6, 126.1, 127.2, 134.4, 135.5, 139.4, 140.6, 147.1, 165.2, 170.0. MS m/z (rel intensity) 238 ($M^{\bullet+}$, 100), 223 ($M^{\bullet+}$ – CH_3, 18), 209 (29), 195 (16), 165 (26), 152 (25).

3,6-Dimethoxy-9-fluorenone Hydrazone (5d). Mp: 204–204.5 °C (lit.[9] mp 202–203 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.10 (s, 2H, NNH_2), 6.85 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.13 (s, 1H), 7.23, (s, 1H), 7.62 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.9 (2 × CH_3), 106.5, 106.8, 113.9, 114.7, 124.0, 126.3, 131.3, 131.8, 143.4, 144.8, 154.7, 163.2, 163.3. MS m/z (rel intensity) 254 ($M^{\bullet+}$, 100), 239 ($M^{\bullet+}$ – NH, 21), 225 (17), 210 (17), 139 (11), 129 (27), 112 (11).

2,5-Dimethoxy-9-fluorenone Hydrazone (5f). In somes cases, hydrazone **5f** was contaminated by the Wolff–Kishner reduction product (2,5-dimethoxyfluorene) which was removed by column chromatography (CH_2Cl_2 eluent). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.88 (d, 1H, J = 8.2 Hz), 6.97 (d, 1H, J = 8.2 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.28 (s, 1H), 7.48 (d, 1H, J = 8.0 Hz), 7.87 (d, 1H, J = 8.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): major isomer δ 55.4, 55.5, 104.8, 112.7, 115.3, 117.9, 124.5, 127.7, 129.0, 131.7, 138.9, 145.7, 155.2, 159.4, 169.8, minor isomer δ 55.3, 55.7, 110.9, 112.6, 113.2, 113.7, 122.3, 124.9, 128.2, 131.0, 133.5, 139.3, 154.8, 158.9, 169.8.

Synthesis of Diazo Compounds 6. General Procedure. The preparation of diazo compounds **6** is based on the method described by Schuster.[9] Hydrazones **5** were dissolved in 10 mL of anhydrous THF, and 0.25 g sodium sulfate was added to the solution. Yellow mercuric oxide (2 equiv) was then added followed by 3 drops of ethanolic KOH. The mixture was stirred at room temperature for 45 min, decanted from the mercuric sludge, and immediately cooled to 0 °C. In some cases, a second portion of mercuric oxide was necessary and the mixture stirred until a violet of reddish tint was obtained.

Attempted Synthesis of Substituted Thiiranes 7. General Procedure. The cooled diazo compounds **6** (1 equiv) were treated dropwise with thiophosgene (1.5 equiv, *caution: toxic*) until the evolution of nitrogen ceased. After the solvent was evaporated followed by flash chromatography, the products were identified and characterized.

Dichloro(3-methoxy-9-fluorenylidene)methane (8a). Flash chromatography was performed using 1:1 CH_2Cl_2/hexanes eluent: mp 86–89 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.91 (s, 3H, OCH_3), 6.74 (dd, 1H, J_1 = 8.20 Hz, J_2 = 2.2 Hz), 7.03 (d, 1H, J = 2.4 Hz), 7.15–7.50 (m, 4H), 7.62 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.8, 107.1, 112.9, 120.1, 123.9, 126.3, 127.2, 128.3, 129.3, 134.1, 135.4, 137.8, 143.4, 147.0, 165.4. MS m/z (rel intensity) 280 (11), 278 (64), 276 ($M^{\bullet+}$, 100), 233 (41), 198 (12), 163 (29).

Dichloro(3-methoxy-5-methyl-9-fluorenylidene)methane (8b). Flash chromatography was performed using 3:2 hexanes/CH_2Cl_2 eluent. Mp: 96–96.5 °C. R_f: 0.75. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.79 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.15 (d, 1H, J = 2.5 Hz), 7.19 (d, 1H, J = 7.8 Hz), 7.53 (d, 1H, J = 7.7 Hz), 8.10 (s, 1H), 8.18 (d, 1H, J = 8.8 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 22.0, 55.5, 104.8, 112.4, 119.3, 119.7, 119.8, 126.5, 126.9, 129.4, 129.7, 133.8, 137.3, 137.6, 142.2, 160.7. MS m/z (rel intensity) 294 (11), 292 (65), 290 ($M^{\bullet+}$, 100), 247 (44), 212 (21), 176 (36), 88 (17).

Dichloro(3-methoxy-7-methyl-9-fluorenylidene)methane (8c). Flash chromatography was performed using 3:2 hexanes/CH_2Cl_2 eluent. Mp: 82–85 °C. R_f: 0.64. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.67 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.82 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.5 Hz), 7.17–7.22 (m, 2H), 7.40 (d, 1H, J = 2.5 Hz), 8.23 (d, 1H, J = 8.6 Hz), 8.31 (d, 1H, J = 7.6 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 21.3, 55.5, 110.0, 110.8, 119.3, 123.4, 126.6, 127.1, 129.8, 131.9, 132.9, 133.6, 137.6, 137.8, 142.9, 160.3. MS m/z (rel intensity) 294 (11), 292 (65), 290 ($M^{\bullet+}$, 100), 247 (36), 212 (25), 176 (40).

Dichloro(3,6-dimethoxy-9-fluorenylidene)methane (8d). The product was obtained by filtration. Mp: 122–123 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 (s, 6H, OCH_3), 6.84 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.17 (d, 2H, J = 2.3 Hz), 8.20 (d, 2H, J = 8.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 105.1, 113.1, 118.1, 126.8, 130.2, 133.2, 141.6, 160.6. MS m/z (rel intensity) 310 (11), 308 (65), 306 ($M^{\bullet+}$, 100), 263 (29), 220 (11), 153 (15), 129 (27), 112 (10).

3′,3′-Dichloro-2,5-dimethoxyspiro[fluorene-9,2′-thiirane] (7f). Flash chromatography was performed using 1:1 hexanes/CH_2Cl_2 eluent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.87 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.91 (d, 1H, J = 8.5 Hz), 6.92 (d, 1H, J = 8.5 Hz), 7.20 (t, 1H, J = 8.1 Hz), 7.91 (s, 1H), 7.92 (d, 1H, J = 8.0 Hz), 8.17 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.4, 55.6, 65.5, 91.6, 111.7, 112.2, 114.0, 118.3, 124.5, 127.1, 132.7, 134.7, 137.3, 138.2, 154.7, 158.7. MS m/z (rel intensity) 310 (2), 309 (12), 308 (12), 307 (65), 306 ($M^{\bullet+}$ – S, 65), 305 ($M^{\bullet+}$ – SH, 100), 290 (59), 262 (12), 247 (10), 150 (13), 76 (15).

Dichloro(3-methyl-9-fluorenylidene)methane (13). Flash chromatography was performed using hexanes eluent. Mp: 67–70 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 7.11 (d, 1H, J = 7.2 Hz), 7.29–7.38 (m, 2H), 7.48 (s, 1H), 7.65 (d, 1H, J = 6.9 Hz), 8.16 (d, 1H, J = 7.9 Hz), 8.29 (d, 1H, J = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.6, 119.4, 120.2, 121.2, 125.5, 125.7, 127.3, 128.3, 128.6, 133.9, 134.1, 136.8, 139.2, 140.2, 140.3. MS m/z (rel intensity) 264 (11), 262 (64), 260 ($M^{\bullet+}$, 100), 225 ($M^{\bullet+}$ – Cl, 37), 190 (34), 189 (71), 163 (10), 94 (36). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 68.90; H, 3.73.

Dichloro(2-fluoro-9-fluorenylidene)methane (14). Flash chromatography (4:1 hexanes/CH_2Cl_2 eluent) yielded a ~1:3 mixture of 12 and 14 determined by ^{13}C NMR analysis. The mixture could not be separated as both compounds have identical R_f values. Mp: 114–120 °C. ^1H NMR of 14 only (200 MHz, $CDCl_3$): δ 7.06–7.68 (m, 5H, aromatic), 8.02 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.5 Hz), 8.30 (d, 1H, J = 7.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 113.4 (d, J = 26.3 Hz), 116 (d, J = 23.3 Hz), 119.4, 120.4 (d, J = 9.0 Hz), 123.6, 125.8, 127.2, 129.4, 133.6, (d, J = 2.8 Hz), 136.2, 136.5, 138.1 (d, J = 9.2 Hz), 139.4, 162.5 (d, J = 243.9). ^{19}F NMR (282.2 MHz, $CDCl_3$): δ 63.68. MS m/z (rel intensity) 268 (11), 266 (64), 264 ($M^{\bullet+}$, 100), 229 ($M^{\bullet+}$ – Cl, 7), 194 ($M^{\bullet+}$ – 2 × Cl, 53), 183 (11), 168 (6), 132 (10), 114 (8), 97 (21).

2,2-Dichloro-3,3-bis(4-methoxyphenyl)thiirane (16). Flash chromatography was performed using 1:1 CH_2Cl_2/hexanes eluent. Mp: 86–87 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 3.79 (s, 6H, OCH_3), 6.87 (d, 4H, J = 8.9 Hz), 7.51 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 55.6, 66.4, 82.0, 113.7, 131.1, 131.6, 159.6. MS m/z (rel intensity) 311 (2), 309 (13), 308 ($M^{\bullet+}$ – S, 4), 307 ($M^{\bullet+}$ – SH, 20), 238 ($M^{\bullet+}$ – SCl_2, 16), 223 (7), 69 (18), 66 (100), 57 (88), 41 (30). Raman: 665 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2SCl_2$: S, 9.39. Found: S, 9.37. **1,1-Dichloro-2,2-bis(4-methoxyphenyl)ethylene.** The second fraction was identified as the desulfurized product. Mp: 128–132 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 3.88 (s, 6H, OCH_3), 6.95 (d, 4H, J = 8.9 Hz), 7.78 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 55.4, 113.4, 113.7, 128.4, 130.7, 132.2, 162.8. MS m/z (rel intensity) 308 ($M^{\bullet+}$, 0.2) 242 (23), 227 (24), 211 (10), 135 (100), 107 (12), 92 (17), 77 (20).

3′,3′-Dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] (17). Flash chromatography was performed using 2:1 hexanes/CH_2Cl_2 eluent. Mp: 113–114 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 2.98–3.16 (m, 2H), 3.64–3.82 (m, 2H), 7.11–7.41 (m, 8H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 31.9, 69.0, 82.8, 126.2, 128.9, 129.5, 129.7, 136.5, 138.8. MS m/z (rel intensity) 306 ($M^{\bullet+}$, 3), 277 (2), 276 (3), 275 (5), 274 ($M^{\bullet+}$ – S, 14), 273 ($M^{\bullet+}$ – SH, 38), 272 ($M^{\bullet+}$ – H_2S, 23), 271 ($M^{\bullet+}$ – Cl, 100), 236 (63), 221 (11), 202 (31), 191 (41). Raman: 627, 685 cm^- Anal. Calcd for $C_{16}H_{12}SCl_2$: C, 62.54; H, 3.94. Found: C, 62.14; H, 3.60.

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Supplementary Material Available: ^1H NMR spectra (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page or ordering information.