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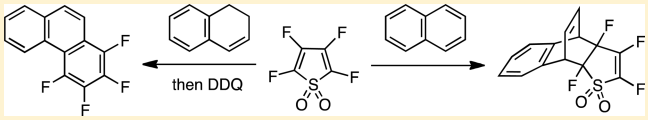
Cycloaddition Chemistry of Tetrafluorothiophene *S*,*S*-Dioxide

David M. Lemal*

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States

Supporting Information

ABSTRACT: Tetrafluorothiophene *S*,*S*-dioxide has been found to be a powerful and versatile cycloaddend that undergoes a wide range of reactions as a Diels–Alder diene, dienophile, and [2 + 2] addend. Because it dimerizes only slowly at high temperatures, a broad range of conditions are available for these transformations. Reactions with terminal alkynes yield products of both Diels–Alder and [2 + 2] cycloaddition. Remarkably, the orbital topology-forbidden [2 + 2] process sometimes dominates over the allowed Diels–Alder reaction.

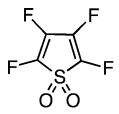


INTRODUCTION

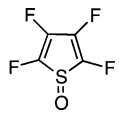
Anticipating that it would be a highly reactive electrophile and cycloaddend, we recently synthesized the title compound tetrafluorothiophene *S*,*S*-dioxide (TFTDO) with plans to explore its chemistry.[1] It was expected to prove capable as a Diels–Alder diene of incorporating a 1,2,3,4-tetrafluorophenyl and/or -cyclohexadienyl fragment into a wide variety of molecular architectures. Given the profound effects that substitution of fluorine for hydrogen has on molecular properties and behavior,[2,3] useful applications could follow, especially in materials chemistry.[4] In the present investigation of TFTDO's cycloaddition chemistry, the promise of potent reactivity is realized, accompanied by surprises.

RESULTS AND DISCUSSION

While developing a route to the sulfone TFTDO (**1**), we generated the corresponding sulfoxide **2** and found it to be a highly reactive Diels–Alder diene.[1] The downside was that it

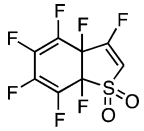


1



2

dimerizes quite rapidly in solution at 0 °C, thus greatly limiting its usefulness as a cycloaddend.[5] It was therefore gratifying to find that the sulfone is a very robust compound. When a 35% (w/v) solution of TFTDO in 1,2-dichloroethane was heated in a pressure vessel at 111–112 °C for 55 h, a 5.8:1 mixture of two dimerization products was obtained in 89% yield.[6] It is noteworthy that 3% of **1** remained unchanged under these forcing conditions. The principal product (**3**) was the result of



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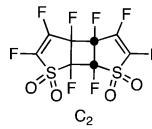
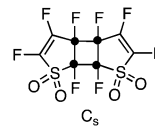
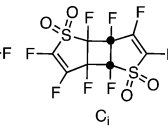
Diels–Alder dimerization accompanied by extrusion of SO_2. The minor one (**4**) was unexpected, a [2 + 2] cycloadduct with 2-fold symmetry. There are four reasonable possibilities (**4a–d**) for its regio- and stereochemistry (highly strained trans 4/5 ring fusions excluded), of which we strongly favor anti dimer **4a**. Presumably, **4a** and **4b** would form via α,α' (or β,β') diradicals, whereas α,β' diradicals would lead to **4c** and **4d**.[7] To model the energy difference, radicals **5** and **6** formed by attack of a hydrogen atom at the α and β positions of TFTDO, respectively, were compared, and the allylic radical **5** was found to be lower in energy by 13.5 kcal/mol.[8] Syn dimer **4b**, which twists a bit to relieve O–O nonbonded repulsion, lies 5.4 kcal/mol above **4a**.



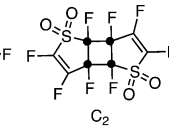
C_2 **4a**



C_s **4b**

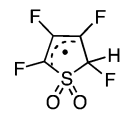


C_i **4c**

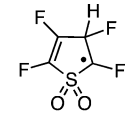


C_2 **4d**

Reaction with Alkenes. TFTDO undergoes Diels–Alder addition to alkenes with extrusion of SO_2. In some cases, the initially formed tetrafluorocyclohexadiene was isolated; in others, it spontaneously underwent further reaction or was treated with DDQ to aromatize it (Table 1).



5



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Styrene adds to TFTDO readily at 50 °C in chloroform with loss of SO_2 to afford **7** (Scheme 1). The calculated reaction coordinate (Figure 1) reveals that the overall reaction is very exothermic, the activation enthalpy for addition is quite low, and the barrier to extrusion of SO_2 is tiny.

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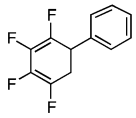
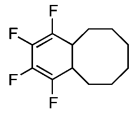
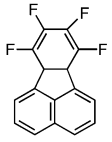
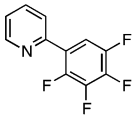
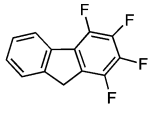
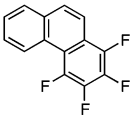
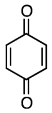
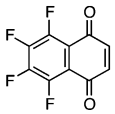
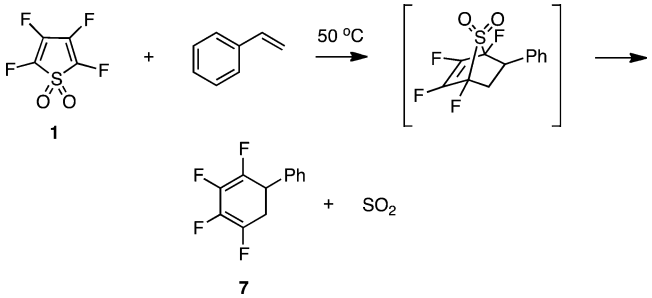
Table 1. Cycloadditions of TFTDO with Alkenes

Addend	Product	Number	Solvent	Conditions	Yield (%)[a]
		7	$CHCl_3$	50 °C, 5.5 h	86
		8	$CDCl_3$	RT, 12 h 50 °C, 3 h	quant.
		9	$PhCH_3$	94 °C, 2 h	97
		10	$ClCH_2CH_2Cl$	RT, 6 h then DDQ	95[b]
		11	$ClCH_2CH_2Cl$	RT, 17 h then DDQ	82[b]
		12	$ClCH_2CH_2Cl$	85 °C, 17 h then DDQ	83[b]
		14	$CDCl_3$	60 °C, 5 h	60
		17	CH_3CN	reflux, 49 h	80

[a]By NMR in this and subsequent tables. [b]For the initial product.

Scheme 1



Cyclooctene reacted with TFTDO under similar conditions to give **8** in quantitative NMR yield, and acenaphthylene afforded dihydrofluoranthene **9** almost quantitatively. The product of 2-vinylpyridine addition to **1**, formed at rt, was aromatized by heating with DDQ at 80 °C in 1,2-dichloroethane to yield **10**. Indene also added at rt, and the initial product was aromatized similarly to afford 1,2,3,4-tetrafluorofluorene (**11**). 1,2-Dihydronaphthalene reacted with TFTDO at 85 °C to give a tetrahydrophenanthrene that was aromatized in stages. Treatment with DDQ at 80 °C for 3 h gave the 9,10-dihydrophenanthrene, and conversion to 1,2,3,4-tetrafluorophenanthrene (**12**) was accomplished with DDQ by prolonged refluxing in chlorobenzene (bp 125 °C).

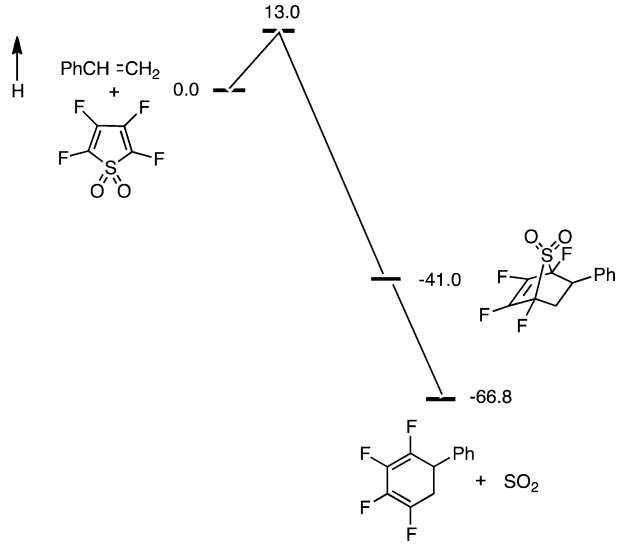
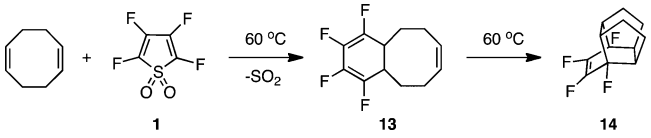


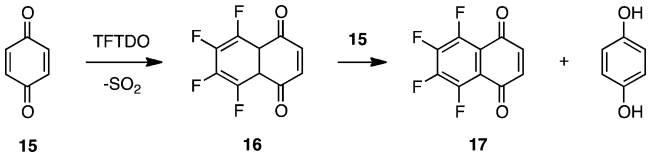
Figure 1. Schematic coordinate for the reaction of TFTDO with styrene. Relative enthalpies are in kcal/mol (B3LYP/cc-PVDZ+). The transition-state value for adduct fragmentation is not shown because at this level of theory, though $\Delta E^{\ddagger}$ is positive, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are actually negative (0.61, −0.40, and −0.96 kcal/mol, respectively). With the 6-311G**+ basis, the corresponding quantities are all positive: 1.47, 0.38, and 0.37 kcal/mol, respectively.

The initial product **13** formed when TFTDO was allowed to react with 1,5-cyclooctadiene underwent internal Diels–Alder reaction readily at 60 °C to create the cage molecule **14** (Scheme 2). Excess *p*-benzoquinone (**15**) added slowly but in good yield

Scheme 2



Scheme 3



to TFTDO at 80 °C to give naphthoquinone **17** (Scheme 3). This product, along with hydroquinone, resulted from oxidation by benzoquinone of the dihydronaphthoquinone **16** formed initially. Oxidation occurred either directly or following tautomerization of **16** to the corresponding hydroquinone. Because the presence of hydroquinone(s) in the reaction mixture gave rise to quinhydrone formation, the polar solvent acetonitrile was needed to keep things in solution, and the workup included oxidation with persulfate to eliminate the quinhydrones. With its array of electronegative atoms, TFTDO might have been

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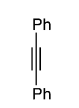
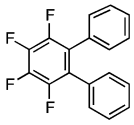
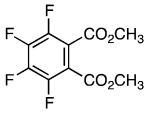
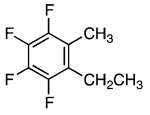
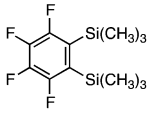
expected to react selectively with electron-rich addends, but its addition to the highly electron-deficient quinone **15** demonstrates that it is *ambiphilic*, capable of reacting across the polarity spectrum.

With Internal Alkynes. Quite vigorous conditions were required for cycloaddition of disubstituted acetylenes to TFTDO, Diels–Alder reactions that yielded tetrafluorobenzenes upon loss of SO_2 (Table 2). Particularly in the case of tolane

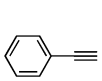
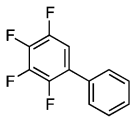
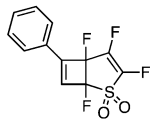
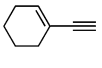
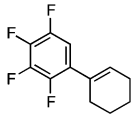
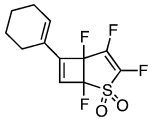
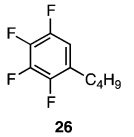
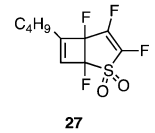
Table 2. Cycloadditions of TFTDO with Internal Alkynes

Addend	Product	Number	Solvent	Conditions	Yield (%)
		**18**	PhCl	105-110 °C 24 h	34
		**19**	$PhCH_3$	100 °C 17 h	53
		**20**	$PhCH_3$	100 °C 17 h	~35
		**21**	$ClCH_2CH_2Cl$	80 °C 28 h	67

(diphenylacetylene) as addend, reaction with TFTDO to give **18** had to compete with dimerization of the sulfone. Obtaining dimethyl tetrafluorophthalate (**19**) under conditions comparable to those for producing **20** and **21** constitutes further evidence for TFTDO's ambiphilic nature.

With Terminal Alkynes. Phenylacetylene reacted readily with TFTDO at 100 °C to afford two products in a 2.8:1 ratio (Table 3). To our surprise, the expected one, tetrafluorobiphenyl **22**, proved to be the minor product; the dominant one (**23**)

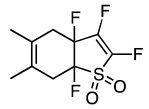
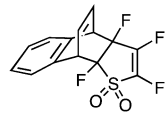
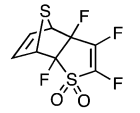
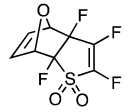
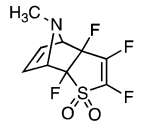
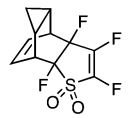
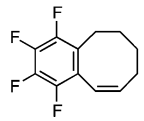
Table 3. Cycloadditions of TFTDO with Terminal Alkynes

Addend	Products	[2 + 2]/[4 + 2]	Conditions	Total Yield (%)
	 **22**  **23**	2.8 : 1	$PhCH_3$ 100 °C 2 h	96
	 **24**  **25**	3.2 : 1	$PhCH_3$ 100 °C 3 h	95
	 **26**  **27**	1 : 1.2	PhCl 100 °C 16 h	80

arose from [2 + 2] cycloaddition. The identity of **23** was confirmed with an X-ray crystal structure. *Here an orbital topology-forbidden process out-competed an allowed one.*[7] The anatomy of these transformations and possible reasons for inversion of the usual relationship between allowed and forbidden processes will be reported elsewhere. A similar result was found with 1-ethynylcyclohexene as addend (Table 3), with [2 + 2] cycloaddition to give **25** again dominant over [4 + 2] to yield **24**. In the case of 1-hexyne, the two modes of reaction competed closely, yielding **26** and **27**.

With Conjugated Dienes. In Diels–Alder reactions with dienes, TFTDO could play the role of dienophile instead of diene. That was found to be the case with a diverse array of dienes, revealing the sulfone to be an unusually powerful dienophile (Table 4). With 2,3-dimethylbutadiene, TFTDO

Table 4. Cycloadditions of TFTDO with Conjugated Dienes

Addend	Product	No.	Endo/Exo	Conditions	Yield (%)
		**28**		CH_2Cl_2 RT, 17 h	93
		**29**	5 :1[a]	PhCl 105 °C, 15 h	**74**
		**30**	3 : 1[a]	neat reflux, ~5 h	62
		**31**	1 : 19	CH_2Cl_2 RT, 6 h	95
		**32**	1.5 : 1	CH_2Cl_2 RT, < 1 h	83
		**34**		$ClCH_2CH_2Cl$ 50 °C, 7 h	**78**
		**35**		$ClCH_2CH_2Cl$ 80 °C, 10 h then DDQ	55[b]

[a]Stereochemistry not assigned. [b]For initial adduct.

afforded **28** in excellent yield at rt. Naphthalene's challenge to TFTDO's dienophilicity was met with the formation of an endo/exo pair of adducts **29**. Like naphthalene, thiophene reacts as a Diels–Alder diene only with potent dienophiles. It does so with TFTDO under reflux to give a 3:1 mixture of stereoisomers **30**.

Furan added readily at rt to afford a 19:1 mixture of stereoisomeric adducts **31**. Here, the ratio was sufficiently lopsided that calculations could be expected to reliably allow assignments of the stereochemistry. The transition state leading to the exo adduct was calculated to lie 1.1 kcal/mol below that for

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J. Org. Chem. 2016, 81, 4931–4938

the endo isomer and the exo adduct itself to lie 3.1 kcal/mol below the endo.[8] Thus, the major, isolated adduct was the exo isomer. *N*-Methylpyrrole added to TFTDO at 0−25 °C, yielding a 1.5:1 mixture of endo/exo isomers **32**. Spin−spin splitting of the fluorines adjacent to the bridgehead hydrogens was much greater for the endo than for the exo isomer in both furan and *N*-methylpyrrole adducts. On this basis, the major isomer obtained from the pyrrole has the endo configuration.

When a dilute solution of the pyrrole adducts in deuteriochloroform was allowed to stand at rt, ^{19}F NMR signals for TFTDO slowly appeared. Their identity was confirmed by addition of furan, which caused them to disappear and peaks for the furan adduct to develop. The endo isomer was found to be the principal, if not exclusive, source of the TFTDO. Thus, this pyrrole adduct undergoes retro-Diels−Alder reaction even at rt, a reflection of the aromaticity of pyrroles. The facility of retro-reaction of pyrrole Diels−Alder adducts can be very useful, as illustrated in the synthesis of the very strained fluoroalkene octafluorobicyclohex-1(4)-ene.[9]

To gain a sense of how strongly TFTDO prefers to act as dienophile rather than diene, energetics for the contrasting modes of reaction with furan were compared computationally (Figure 2).[8] Surprisingly, both of the adducts obtained

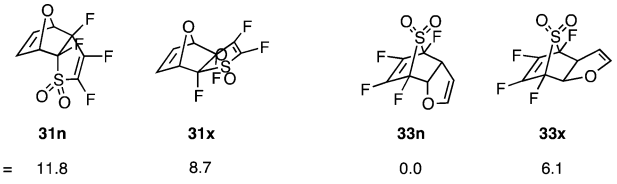
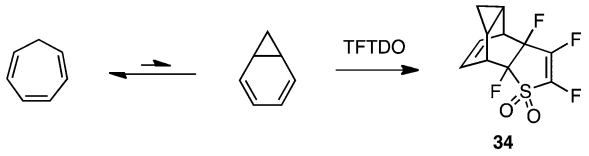


Figure 2. Comparison of possible Diels−Alder adducts of TFTDO and furan. Energies are in kcal/mol.

experimentally (**31n**, **31x**) were found to lie well above the two in which TFTDO serves as the diene (**33n**, **33x**). The transition state leading to **33x** lies 8.6 kcal/mol above that for **31x**. Even with starting geometries strongly biased toward the lowest energy adduct **33n**, calculations intended to locate a transition state for its formation evolved to the transition state for the highest energy adduct **31n**, to which it is related by Cope rearrangement! Clearly, the inherent preference of TFTDO for the dienophile role can overcome large differences in adduct stability.

Cycloheptatriene offered another test of the dienophile vs diene preference of TFTDO. Remarkably, the product of its reaction with the triene had the structrure **34**. TFTDO had again played the dienophile part, not with the triene, but with its bicyclic valence isomer norcaradiene. The pair exists in a very mobile equilibrium (Scheme 4).[10] In light of the triene's nonplanarity,[11] its failure to react as a diene was not unexpected, but it could have served well as a dienophile. No experimental measurement has been made of the energy difference between cycloheptatriene and norcaradiene, but the value we calculate is a full 8.1 kcal/mol at 25 °C.[8] The reaction was carried out at 50 °C,

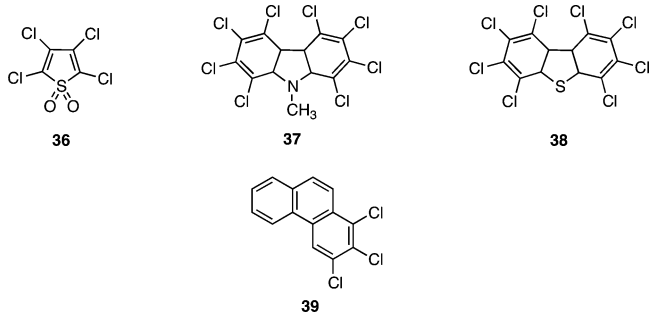
Scheme 4



where the calculated ratio of diene to triene is 3.2×10^{-6}. Thus, TFTDO eschews reaction with a perfectly adequate dienophile, choosing instead a diene present at the level of 3 ppm! By this measure, as with the furan example, the preference at issue is dramatic.

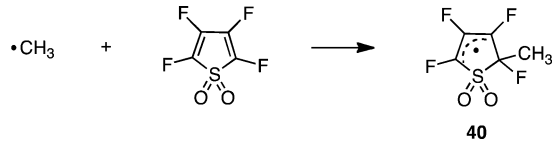
1,3-Cyclooctadiene was chosen as a strongly twisted diene that is quite resistant to flattening.[12] In reacting with this hydrocarbon, TFTDO was finally forced to accept the role of diene. The resulting adduct (−SO_2), formed at 80 °C, was aromatized with DDQ to give benzocyclooctadiene **35.**

In 1980, Raasch reported the synthesis of tetrachlorothiophene *S*,*S*-dioxide (**36**) and an extensive study of its cycloaddition chemistry.[13] For the most part, this chemistry closely parallels that of its perfluoro analogue TFTDO, but there are exceptions. Particularly notable are the Diels−Alder reactions with *N*-methylpyrrole, thiophene, and in a later study,[14] naphthalene. Here, the tetrachloro compound served not as dienophile but as diene to yield **37**−**39**, respectively. Phenanthrene **39** arose from hydrogen migration in and loss of HCl from the initially formed dihydrophenanthrene. Further study will be required to gain an understanding of the strong tendency of TFTDO to play the dienophile role in its reactions with conjugated dienes.



To learn about the energetic price for α-attack on TFTDO to form an allylic radical, the enthalpy change was calculated for formation of radical **40**: ΔH = −52.8 kcal/mol (Scheme 5).

Scheme 5



Because a C−C single bond is worth about 85 kcal/mol,[15] the cost of breaking a double bond of TFTDO is roughly (85−53) = 32 kcal/mol. Even allowing for the resulting allylic stabilization, this is a very low value. It underpins the formation of [2 + 2] dimer **4** and [2 + 2] cycloaddition with terminal alkynes, reactions that presumably proceed via diradicals.

CONCLUSION

Tetrafluorothiophene *S*,*S*-dioxide (TFTDO, **1**) has been shown to be a powerful and versatile electrophilic cycloaddend. It is perhaps better described as ambiphilic, as it reacts with alkenes and alkynes of widely varying polarity. With alkenes it undergoes Diels−Alder reactions with loss of SO_2 to afford tetrafluorocyclohexadiene derivatives; those with hydrogens at the ring juncture can be oxidized with DDQ to tetrafluorobenzenes. With internal alkynes, tetrafluorobenzenes are formed directly.

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J. Org. Chem. 2016, 81, 4931−4938

Terminal alkynes undergo both the expected Diels–Alder reaction and [2 + 2] cycloaddition, an orbital topology-forbidden process that can nonetheless be the dominant reaction pathway. In reaction with conjugated dienes, TFTDO has invariably played the role of dienophile except when the diene is badly twisted. Under sufficiently vigorous conditions, **1** reacts with itself in both Diels–Alder and [2 + 2] fashion. Attack at an α-position of TFTDO to form an allylic radical is quite inexpensive energetically; this fact is important for an understanding of much of the sulfone's cycloaddition chemistry.

EXPERIMENTAL SECTION

NMR spectra were measured on 300, 500, and 600 MHz spectrometers, and, except where noted, all reported here were measured in $CDCl_3$. ^{19}F NMR spectra were referenced to internal trichlorofluoromethane via hexafluorobenzene (δ −162.11 ppm in $CDCl_3$) as internal standard; ^1H and ^{13}C NMR spectra were referenced to TMS via $CHCl_3$ (δ 7.27 and 77.0 ppm, respectively). TFTDO was prepared from its dibromide[1] and assayed by NMR integration versus hexafluorobenzene. For assays, delay time between pulses was 6 s to take into account differential relaxation times. NMR product yields were obtained in the same manner.

2,3,3a,4,5,6,7,7a-Octafluoro-3a,7a-dihydrobenzo[*b*]-thiophene 1,1-Dioxide (3) and 2,3,3a,3b,4,5,6a,6b-Octafluoro-3a,3b,6a,6b-tetrahydrocyclobuta[1,2-*b*:4,3-*b*′]dithiophene 1,1,6,6-Tetroxide (4). Into a heavy-walled glass tube with a threaded Teflon stopper were placed 798 mg of TFTDO (89%, 3.8 mmol) and 2 mL of 1,2-dichloroethane. The pressure vessel was mounted in a vertical pipe wrapped in heating tape and maintained at 111–112 °C for 55 h. Two dimerization products were obtained in the ratio 5.8:1 (Diels–Alder: [2 + 2] dimer). Total yield based on TFTDO consumed was 89%; 3% of the TFTDO was still present. The reaction mixture was transferred to a 10 mL round-bottom flask and subjected to Kugelrohr distillation at 10 Torr up to 100 °C. A 317 mg sample of the 598 mg of distillate was recrystallized from hexane at ∼−25 °C to give the Diels–Alder product **3** as white needles (195 mg). Mp: 27.5–28.5 °C. ^{19}F NMR: δ −138.3 (m, 1F), −144.7 (narrow m, 1F), −146.5 (d, J = 10.8 Hz, 1F), −148.3 (narrow m, 1F), −153.4 (m, 1F), −153.6 (m, 1F), −163.7 (m, 1F), −169.1 (m, 1F). ^{13}C NMR: δ 147.0 ($^1J_{CF}$ = 323 Hz), 141.6 ($^1J_{CF}$ = 309 Hz), 138.1 ($^1J_{CF}$ = ∼274 Hz), 136.7 ($^1J_{CF}$ = ∼273 Hz), 136.1 ($^1J_{CF}$ = ∼297 Hz), 131.0 ($^1J_{CF}$ = 272 Hz), 99.8 ($^1J_{CF}$ = 251 Hz), 83.3 ($^1J_{CF}$ = 227 Hz). Anal. Calcd for $C_8F_8O_2S$: C, 30.78; H, 0.0; F, 48.70. Found: C, 30.50; H, 0.0; F, 48.46.

The less volatile [2 + 2] dimer **4** had formed as white crystals on the walls of the Kugelrohr apparatus between the pot and receiver. It was washed out with CH_2Cl_2 and after solvent removal recrystallized from hexane. Mp: 142.5–143.5 °C. ^{19}F NMR: δ −139.6 (d, J = 5.3 Hz, 2F), −140.9 (m, 2F), −168.7 (m, 2F), −182.5 (narrow m, 2F). ^{13}C NMR: δ 148.0 ($^1J_{CF}$ = 275 Hz), 137.1 ($^1J_{CF}$ = 307 Hz), 95.7 ($^1J_{CF}$ = 292 Hz), 89.5 ($^1J_{CF}$ = ∼268 Hz). Anal. Calcd for $C_8F_8O_4S_2$: C, 25.54; H, 0.0; F, 40.40; S, 17.05. Found: C, 25.52; H, 0.0; F, 40.66; S, 17.09.

3,4,5,6-Tetrafluoro-1,2-dihydro-1,1′-biphenyl (7). A combination of 221 mg of TFTDO (91%, 1.1 mmol), 164 mg (1.6 mmol) of freshly distilled styrene, and 3 mL of chloroform was heated at 50 °C; reaction was complete after 5.5 h (86% yield). Product was deposited on 2 g of silica gel, then chromatographed on 6 g of the gel with hexane as eluent. Standing in air at rt, diene **7** degraded rather quickly. ^{19}F NMR: δ −137.6 (s, 1F), −140.3 (s, 1F), −163.8 (s, 1F), 164.6 (s, 1F). ^1H NMR: δ 7.38 (m, 5H), 3.91 (m, 1H), 3.30 (m, 1H), 2.69, (m, 1H). ^{13}C NMR: δ 141.5 ($^1J_{CF}$ = ∼268 Hz), 138.7, 138.2 ($^1J_{CF}$ = ∼267 Hz), 134.2 ($^1J_{CF}$ = 253 Hz), 132.2 ($^1J_{CF}$ = 253 Hz), 129.2, 128.2, 127.0, 39.4, 31.5.

To confirm the identity of the diene, a 24 mg (0.11 mmol) sample in $CDCl_3$ was treated with 30 mg (0.13 mmol) of DDQ. Heated in a bath at ∼65 °C for 7 h, the mixture afforded 2,3,4,5-tetrafluorobiphenyl (**22**).[1,16] Its ^{19}F NMR spectrum was virtually identical with that of **22** reported below.

1,2,3,4-Tetrafluoro-4a,5,6,7,8,9,10,10a-octahydrobenzo[8]-annulene (8).[17] Into an NMR tube were placed 35 mg of TFTDO (86%, 0.16 mmol), 28 mg (0.25 mmol) of freshly distilled cyclooctene, and $CDCl_3$. The tube was immersed in a bath at 50 °C for 3 h and then allowed to stand at rt for 12 h. Yield of diene **8** was quantitative. Solvent was replaced with CD_2Cl_2 for literature comparison, and a bit of CCl_3F was added for calibration. ^{19}F NMR (CD_2Cl_2): δ −145.3 (m, 2F), −167.4 (m, 2F) [lit.[17] −145.2 (m, 2F), −167.3 (m, 2F)].

7,8,9,10-Tetrafluoro-6b,10a-dihydrofluoranthene (9). Technical-grade acenaphthylene was sublimed at atmospheric pressure and temperature up to 135 °C. The resulting bright yellow flakes contained about one-third as much acenaphthene as acenaphthylene plus minor impurities. To a solution of 241 mg of TFTDO (91%, 1.2 mmol) in 3 mL of toluene was added 365 mg of the sublimed acenaphthylene (∼1.8 mmol), and the mixture was heated in a 94 °C bath for 2 h to afford the Diels–Alder adduct (−SO_2) in 97% yield. Toluene was replaced with CH_2Cl_2, 2 g of silica gel was added, and solvent was again evaporated. Residue was poured onto a 10 g column of silica gel and eluted with 5% EtOAc/hexane. Since separation from acenaphthene was poor, early fractions were combined and rechromatographed on 12 g of silica gel with hexane, giving 240 mg of **9** (74% isolated yield). Mp: 131–132 °C. ^{19}F NMR: δ −142.6 (s, 2F), −165.9 (s, 2F). ^1H NMR: δ 7.76 (m, 2H), 7.54 (m, 4H), 4.96 (m, 2H). ^{13}C NMR δ 141.6, 139.8 ($^1J_{CF}$ = 263 Hz), 136.8, 132.1 ($^1J_{CF}$ = 252 Hz), 131.8, 128.3, 124.3, 120.7, 43.2. Anal. Calcd for $C_{16}H_8F_4$: C, 69.57; H, 2.92; F, 27.51. Found: C, 69.56; H, 2.96; F, 27.41.

2-(2,3,4,5-Tetrafluorophenyl)pyridine (10).[18] A solution of 403 mg of TFTDO (90%, 1.9 mmol) and 252 mg of 2-vinylpyridine (2.4 mmol) in 4 mL of 1,2-dichloroethane was allowed to stand at rt for 6 h. Reaction was complete, and the adduct (−SO_2) was present in 95% yield. From a small-scale reaction in $CDCl_3$, ^{19}F NMR: δ −136.7 (m, 1F), −140.6 (m, 1F), −162.6 (apparent 1:3:3:1 q, J_{app} = 6.9 Hz, 1F), −165.1 (apparent 1:4:6:4:1 quin, J_{app} = 7.1 Hz, 1F). DDQ (500 mg, 2.2 mmol) was added to the 1,2-dichloroethane solution, and the mixture was stirred in a bath at 80 °C for 2 h to complete the aromatization. Product was pipetted into a 25 mL round-bottom flask, and the remaining brown syrup was washed with a little CH_2Cl_2. To the combined clear liquid was added 1.5 g of silica gel, solvent was evaporated, and the tan residue was chromatographed on 12 g of silica gel with CH_2Cl_2 as eluent. All but a few late fractions were combined and recrystallized from hexane at −25 °C. Mp of pyridine **10**: 56.5–57.5 °C. ^{19}F NMR: δ −139.3 (m, 1F), −143.4 (m, 1F), −155.1 (m, 1F), −155.8 (m, 1F). ^1H NMR: δ 8.73 (dm, J = 4.7 Hz, 1H), 7.81 (m, 2H), 7.77 (m, 1H), 7.33 (m, 1H). ^{13}C NMR: δ 150.3, 150.0, 147.2 ($^1J_{CF}$ = 247 Hz), 145.9 ($^1J_{CF}$ = 250 Hz), 141.0 ($^1J_{CF}$ = 252 Hz), 140.6 ($^1J_{CF}$ = 256 Hz), 136.8, 124.3, 123.6, 123.4, 111.6. Anal. Calcd for $C_{11}H_5F_4N$: C, 58.16; H, 2.22; F, 33.46; N, 6.17. Found: C, 58.28; H, 2.13; F, 33.21; N, 6.22. The isolated yield was rather low, despite the fact that the DDQ oxidation was quite clean. Presumably some pyridine **10** remained in the brown residue after the reaction, protonated by or H-bonded to the DDQ-derived hydroquinone.

1,2,3,4-Tetrafluorofluorene (11). A mixture of TFTDO (297 mg, 88%, 1.4 mmol), 256 mg of distilled indene, and 3 mL of 1,2-dichloroethane was allowed to stand at rt for 17 h, giving the dihydrofluorene in 82% yield. A small sample was dissolved in $CDCl_3$ for ^{19}F NMR: δ −142.0 (br d, J = 29 Hz, 1F), −143.1 (dm, J = 20 Hz, 1F), −165.2 (m, 1F), −165.7 (m, 1F). To the reaction mixture was added 0.5 g (2.2 mmol) of DDQ, and the flask was immersed in a bath at 75 °C for 8 h. Product was deposited on 1.5 g of silica gel, and the brown powder was placed on a 15 g column of the gel for elution with hexane. Fluorene **11**. Mp: 104–105 °C. ^{19}F NMR: δ −143.2 (dd, J = 20, 17 Hz, 1F), −147.0 (dd J = 20, 17 Hz, 1F), −158.1 (t, J = 20 Hz, 1F), −158.8 (t, J = 20 Hz, 1F). ^1H NMR: δ 7.89 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 3.94 (s, 2H). ^{13}C NMR: δ 143.9 ($^1J_{CF}$ = 246 Hz), 142.6 ($^1J_{CF}$ = 249 Hz), 141.9, 140.1 ($^1J_{CF}$ = 250 Hz), 139.3 ($^1J_{CF}$ = 252 Hz), 137.1, 127.8, 127.6, 125.3, 124.9, 124.4, 123.4, 34.1. Anal. Calcd for $C_{13}H_6F_4$: C, 65.56; H, 2.54; F, 31.91. Found: C, 65.44; H, 2.42; F, 31.65.

1,2,3,4-Tetrafluorophenanthrene (12).[19] TFTDO (307 mg, 85%, 1.4 mmol) and 157 mg (1.21 mmol) of 1,2-dihydronaphthalene were dissolved in 3 mL of 1,2-dichloroethane. Here, the hydrocarbon is the limiting reagent because if present in excess, separation of the product from naphthalene formed after aromatization is problematic.

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Mixture was heated in a bath at ~85 °C for 17 h, with loss of much of the solvent. The tetrahydrophenanthrene was formed in 83% yield. ^{19}F NMR: δ −137.7 (s, 1F), −146.4 (s, 1F), −164.3 (unresolved d, J = ~5.3 Hz, 1F), −165.4 (unresolved d, J = ~6.0 Hz, 1F). DDQ (304 mg, 1.3 mmol) and 2 mL of 1,2-dichloroethane were added and heating was resumed for 3 h at 80 °C. The reaction mixture was partitioned between 15 mL of ether and 10 mL of water containing 0.50 g (2.0 mmol) of $Na_2S_2O_3{\cdot}5H_2O$. The ether layer was extracted with 10 mL of satd aq $NaHCO_3$, a little brine, and then dried over Na_2SO_4. Silica gel (1.5 g) was added, solvent was evaporated, and the light brown powder was poured onto a 15 g column of silica gel for elution with hexane. The DDQ oxidation had produced a little phenanthrene **12** along with the dihydrophenanthrene. For the dihydro compound, ^{19}F NMR: δ −144.0 (m, 1F), −145.2 (dd, J = 22, 13.0 Hz, 1F), −158.2 (dd, J = 21, 3.2 Hz, 1F), −159.9 (t, J = 20 Hz, 1F). To the combined fractions in 4 mL of chlorobenzene was added ~50% excess of DDQ, and the mixture was refluxed for 22 h. Since a bit of dihydro compound still remained, some additional DDQ was introduced, and refluxing was continued for another 6 h. Chlorobenzene was replaced with CH_2Cl_2, 1.5 g of silica gel was added, and solvent was evaporated again. The resulting brown powder was chromatographed on 15 g of silica gel with hexane as eluent, affording pure phenanthrene **12**. Mp: 172.5−173 °C. ^{19}F NMR: δ −140.0 (unresolved ddm, 1F), −149.3 (dd, J = 21, 14.1 Hz, 1F), −158.6 (unresolved dd, J = 19, 21 Hz, 1F), −158.9 (td, J = 21, 3.8 Hz, 1F). ^{1}H NMR: δ 8.95 (d, J = 8.1 Hz, 1H), 7.93 (dd, J = 7.4, 1.7 Hz, 1H), 7.89 (dd, J = 9.1, 1.7 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.71 (m 2H). ^{13}C NMR: δ 145.9 ($^1J_{CF}$ = ~261 Hz), 142.4 ($^1J_{CF}$ = ~248 Hz), 139.4 ($^1J_{CF}$ = ~245 Hz), 137.8 ($^1J_{CF}$ = ~245 Hz), 132.3, 129.0, 128.9, 128.0, 127.8, 127.0, 126.9, 118.2, 116.8, 115.8. Anal. Calcd for $C_{14}H_6F_4$: C, 67.21; H, 2.42; F, 30.38. Found: C, 66.97; H, 2.56; F, 30.16.

5,6,7,7a-Tetrafluoro-2,3,3a,4,5,7a-hexahydro-1*H*-1,5,4-(epipropane[1,1,3]triyl)indene (14). Into an NMR tube were placed 37 mg of TFTDO (89% pure, 0.18 mmol), several drops of 1,5-cyclooctadiene, and $CDCl_3$. After 5 h in a bath at 60 °C, the tube contained **14** in 60% yield. An oven-dried 10 mL round-bottom flask was charged with 297 mg of TFTDO (~90%, 1.4 mmol), 184 mg (1.7 mmol) of freshly distilled diene, and 3 mL of chloroform. Solution was refluxed for 3 h, then 1.5 g of silica was added and the solvent was evaporated. Residue was chromatographed on 9 g of silica gel with hexane as eluent. Mp of **14**: 105.5−106.5 °C. ^{19}F NMR: δ −156.3 (m, 2F), −190.9 (m, 2F). ^{1}H NMR: δ 2.15 (s, 4H), 1.91 (m, 8H). ^{13}C NMR: δ 131.0 ($^1J_{CF}$ = 276 Hz), 96.4 ($^1J_{CF}$ = 202 Hz), 44.6, 22.5. Anal. Calcd for $C_{12}H_{12}F_4$: C, 62.06; H, 5.21. Found: C, 62.07; H, 5.30.

5,6,7,8-Tetrafluoro-1,4-naphthalene-1,4-dione (17). A solution containing 292 mg of TFTDO (95%, 1.5 mmol), 397 mg of *p*-benzoquinone (3.7 mmol), and 3 mL of acetonitrile was refluxed for 49 h. The dominant product was the quinone **17**, but some of the initial adduct (−SO_2) was also present. Solvent was evaporated, and the black residue (color due to quinhydrone formation) was transferred with 20 mL of hot CH_2Cl_2 to a 50 mL round-bottom flask. Potassium persulfate (0.50 g, 1.9 mmol) in 10 mL of water was added, and the mixture was stirred for 1 h at rt, then allowed to stand overnight. The two-phase mixture was separated, the aqueous layer was washed with 10 mL of CH_2Cl_2, and the golden brown combined organic phase was dried over Na_2SO_4. The yield of product was 80%, but that included 8% of unoxidized initial product that had survived the persulfate treatment, presumably because it had not enolized. Chromatography on 8 g of silica gel with 20% EtOAc/hexane failed to achieve adequate separation of the naphthoquinone from the slightly faster eluting benzoquinone. TLC experimentation with a variety of solvents finally led to benzene, which was tried in the hope that preferential π-complexation with the naphthoquinone would cause it to elute significantly faster than benzoquinone. In benzene, R_f values were 0.22 and 0.16, respectively, so the combined fractions from above were chromatographed on 10 g of silica with that eluent. The isolated yield of clean quinone **17** was 220 mg (65%). Mp was obtained on a sample sublimed at 100 °C and aspirator pressure: 191−192 °C. ^{19}F NMR: δ −138.1 (narrow m, 2F), −144.0 (narrow m, 2F). ^{1}H NMR: δ 6.92 (s, 2H). ^{13}C NMR: δ 180.5, 147.0 ($^1J_{CF}$ = 273 Hz), 144.6 ($^1J_{CF}$ = 266 Hz), 138.7, 116.0. Anal. Calcd for $C_{10}H_2F_4O_2$: C, 52.19; H, 0.88; F, 33.03. Found: C, 52.26; H, 0.92; F, 32.93.

3′,4′,5′,6′-Tetrafluoro-1,1′,2′,1″-terphenyl (18).[16,20] A mixture of 402 mg of TFTDO (90%, 1.9 mmol), 1.2 g (6.7 mmol) of tolane, and 4 mL of chlorobenzene was heated in a bath at 105−110 °C for 24 h, after which ~2% of the TFTDO remained. The terphenyl (34% yield) and TFTDO dimers were present in a 3:1 ratio. Solvent was evaporated and the residue was chromatographed with hexane on 15 g of silica gel. Separation from unreacted tolane was poor, but two low temperature recystallizations of selected fractions from hexane gave terphenyl **18**, mp 104.5−105.5 °C (lit.[20] mp 107−108 °C). ^{19}F NMR: δ −141.5 (m, 2F), −157.5 (m, 2F) [20.6 (m), 4.6 (m) rel. to hexafluorobenzene; lit.[16] (1:1 $CDCl_3/CCl_4$) 20.8 (m), 4.7 (m)]. ^{1}H NMR: δ 7.23 (m, 6H), 7.05 (m, 4H) [lit.[18] (CCl_4) 7.25−6.87 (m)]. ^{13}C NMR: δ 144.9 ($^1J_{CF}$ = 245 Hz), 139.9 ($^1J_{CF}$ = 255 Hz), 131.4, 130.7, 128.0, 127.9, 125.4.

3,4,5,6-Dimethyl Tetrafluorophthalate (19).[21] Into an NMR tube were placed 43 mg of TFTDO (86%, 0.20 mmol), 147 mg of dimethyl acetylenedicarboxylate (1.0 mmol), and toluene. The tube was immersed in a bath at 100 °C for 17 h. The reaction was essentially complete, giving the phthalate in 53% yield. ^{19}F NMR: δ −137.0 (d, J = 12 Hz, 2F), −149.2 (d, J = 12 Hz, 2F) [lit.[21] −137.0 (2F), −149.2 (2F)]. ^{1}H NMR: δ 3.91 (6H) [lit.[21] 3.94 (6H)].

1-Ethyl-2,3,4,5-tetrafluoro-6-methylbenzene (20).[17] A solution of TFTDO (46.0 mg, 86%, 0.21 mmol), 2-pentyne (72 mg, 1.1 mmol), and toluene in an NMR tube was heated at 100 °C for 17 h. The yield of **20** was ~35% averaged over two runs. The reaction mixture was chromatographed on 2 g of silica gel with hexane as eluent. ^{19}F NMR: δ −143.2 (m, 1F), −146.2 (m, 1F), −161.4 (m, 2F) [lit.[17] −143.1 (m, 1F), −146.1 (m, 1F), −161.4 (m, 2F). ^{1}H NMR: δ 2.70 (m, 2H), 2.24 (m, 3H), 1.17 (m, 3H)] [lit.[17] 2.67 (m, 2H), 2.21 (m, 3H), 1.14 (m, 3H)].

1,2,3,4-Tetrafluoro-5,6-bis(trimethylsilyl)benzene (21).[17] Into an NMR tube were placed 44 mg of TFTDO (91%, 0.21 mmol), 57 mg (0.33 mmol) of bis(trimethylsilyl)acetylene, and 1,2-dichloroethane. After immersion in a bath at ~80 °C for 28 h, the solution produced **21** in 67% yield. ^{19}F NMR: δ −120.5 (m, 2F), −155.4 (m, 2F) [lit.[17] −120.3 (m, 2F), −155.1 (m, 2F)]. ^{1}H NMR: δ 0.42 (s, 18H) [lit.[17] 0.43 (18H)].

2,3,4,5-Tetrafluorobiphenyl (22)[1,16] and 1,3,4,5-Tetrafluoro-6-phenyl-2-thiabicyclo[3.2.0]hepta-3,6-diene 2,2-Dioxide (23). A solution of 348 mg of TFTDO (93%, 1.7 mmol) and 193 mg (1.9 mmol) of phenylacetylene in 2 mL of toluene was heated at 100 °C. The reaction was complete after 2 h, producing in 96% yield a [2 + 2] adduct and the biphenyl in the ratio 2.8:1. Toluene was evaporated and replaced with CH_2Cl_2; silica gel (2 g) was added, and solvent was removed again. The resulting powder was placed on a 3.5 g column of silica gel and eluted with hexane to obtain the biphenyl (26% isolated yield). Elution was then continued with 25% CH_2Cl_2/hexane to afford the [2 + 2] adduct (60% isolated yield). For the biphenyl **22**, mp 69−69.5 °C (lit.[1] 65−66 °C). ^{19}F NMR: δ −140.0 (m, 1F), −144.1 (s, 1F), −155.6 (m, 1F), 157.5 (d, J = 18.6 Hz, 1F). ^{1}H NMR: δ 7.48 (m, 5H), 7.08 (m, 1H) [lit.[16] (1:1 $CDCl_3/CCl_4$) 7.52 (s, 5H), 7.09 (m, 1H)].

For the [2 + 2] adduct **23**, mp 106−107 °C. ^{19}F NMR: δ −137.2 (d, J = 25 Hz, 1F), −154.6 (s, 1F), −162.3 (s, 1F), −167.7 (d, J = 25 Hz, 1F). ^{1}H NMR: δ 7.58 (m, 5H), 6.85 (d, J = 3 Hz, 1H). ^{13}C NMR: δ 159.8, 142.6 ($^1J_{CF}$ = 321 Hz), 142.3 ($^1J_{CF}$ = 305 Hz), 133.0, 129.4, 127.7, 126.9, 126.1, 100.2 ($^1J_{CF}$ = 283 Hz), 89.8 ($^1J_{CF}$ = 248 Hz). Anal. Calcd for $C_{12}H_6F_4O_2S$: C, 49.66; H, 2.08; S, 11.05. Found: C, 49.69; H, 2.12; S, 11.16. A sample allowed to crystallize slowly from methanol/water gave prisms suitable for X-ray crystal structure analysis.

2′,3′,4′,5′-Tetrafluoro-2,3,4,5-tetrahydro-1,1′-biphenyl (24)[17] and 6-(Cyclohex-1-en-1-yl)-1,3,4,5-tetrafluoro-2-thiabicyclo[3.2.0]hepta-3,6-diene 2,2-Dioxide (25). To an NMR tube were added 46 mg of TFTDO (86%, 0.21 mmol), 25 mg (0.24 mmol) of 1-ethynylcyclohexene, and toluene. The tube was placed in a bath at 100 °C, and the reaction was complete within 3 h. The [2 + 2] adduct **25** and Diels−Alder product **24** were obtained in 95% yield in the ratio 3.2:1. After the reaction had been scaled up by a factor of 7, the toluene was evaporated and replaced with CH_2Cl_2. Silica gel (2 g) was added, solvent was again removed, and the residual powder was placed on a 4 g column of silica gel. The column was initially eluted with hexane to afford benzene **24** in 18% isolated yield and then with 25% CH_2Cl_2/

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hexane to obtain [2 + 2] adduct **25** in 64% isolated yield. For benzene **24**, ^{19}F NMR: δ −141.1 (m, 1F), −142.6 (m, 1F), −156.8 (1F), 159.4 (m, 1F) [lit.[17] −140.9 (m, 1F), −142.3 (m, 1F, −156.6 (m, 1F), −159.3 (m, 1F)]. ^{1}H NMR: δ 6.84 (m, 1H), 6.00 (br s, 1H), 2.30 (s, 2H), 1.72 (m, 4H), 1.20 (m, 2H) [lit.[17] 6.83 (s, 1H), 5.97 (s, 1H), 2.31−0.88 (m, 8H)].

For [2 + 2] adduct **25**, mp 67−69 °C. ^{19}F NMR: δ −136.1 (d, J = 21 Hz, 1F), −155.7 (s, 1F), −161.7 (s, 1F), −167.5 (m, 1F). ^{1}H NMR: δ 6.46 (s, 1H), 6.29 (unresolved m, 1H), 2.29 (s, 2H), 2.17 (s, 2H), 1.69 (m, 4H). ^{13}C NMR: δ 161.1, 142.4 ($^1J_{CF}$ = 306 Hz), 142.4 ($^1J_{CF}$ = 321 Hz), 140.2, 128.6, 123.3, 100.5 ($^1J_{CF}$ = 283 Hz), 89.5 ($^1J_{CF}$ = 248 Hz), 26.1, 23.7, 21.3, 21.1. Anal. Calcd for $C_{12}H_{10}F_4O_2S$: C, 48.98; H, 3.43; S, 10.90. Found: C, 49.38, H, 3.27; S, 11.12.

1-Butyl-2,3,4,5-tetrafluorobenzene (26)[16] and 1,3,4,5-Tetrafluoro-6-butyl-2-thiabicyclo[3.2.0]hepta-3,6-diene 2,2-Dioxide (27). Into a glass pressure tube with threaded Teflon stopper were placed 296 mg of TFTDO (88%, 1.4 mmol), 281 mg (3.43 mmol) of 1-hexyne, and 3 mL of chlorobenzene. The vessel was maintained at ∼100 °C for 16 h in a pipe wrapped with heating tape. Two products were obtained in 80% yield in a ratio of 1.2:1 (Diels−Alder: [2+ 2] adduct). Solvent was evaporated and replaced with CH_2Cl_2; silica gel (1.5 g) was added and solvent was again removed. The resulting tan powder was chromatographed on 15 g of silica gel with 20% CH_2Cl_2/hexane as eluent to obtain the [2 + 2] adduct **27**. ^{19}F NMR: δ −140.4 (dd, J = 23, 4.3 Hz, 1F), −154.6 (s, 1F), −163.9 (unresolved m, 1F), −169.1 (ddd, J = 23, 10.1, 4.1 Hz, 1F). ^{1}H NMR: δ 6.52 (d, J = 4.3 Hz, 1H), 2.42 (m, 2H), 1.61 (m, 2H) 1.42 (sextet, J = 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR: δ 166.4, 142.3 ($^1J_{CF}$ = 305 Hz), 142.2 ($^1J_{CF}$ = ∼324 Hz), 131.9, 100.3 ($^1J_{CF}$ = 284 Hz), 90.1 ($^1J_{CF}$ = 247 Hz), 28.0, 27.3, 22.2, 13.5. Anal. Calcd for $C_{10}H_{10}F_4O_2S$: C, 44.44; H, 3.73; S, 11.87. Found: C, 44.33; H, 3.72; S, 11.66.

Diels−Alder product **26** obtained in a separate experiment was dissolved in 1:1 CCl_4/$CDCl_3$ for literature comparison. ^{19}F NMR (ppm relative to hexafluorobenzene): 2.4 (m, 1F), 5.5 (m, 1F), 17.5 (m, 1F), 21.3 (m, 1F) [lit.[16] 2.5 (td, 1F), 5.7 (m, 1F), 17.6 (m, 1F), 21.6, (m, 1F)].

2,3,3a,7a-Tetrafluoro-5,6-dimethyl-3a,4,7,7a-tetrahydrobenzo[*b*]thiophene 1,1-Dioxide (28). A mixture of 102 mg of TFTDO (95%, 0.51 mmol), 64 mg (0.78 mmol) of 2,3-dimethyl-1,3-butadiene, and 2 mL of CH_2Cl_2 was allowed to stand at rt for 17 h. Reaction was complete, giving the adduct in 93% yield. Silica gel (0.7 g) was added, solvent was evaporated, and the gel was chromatographed on a 4 g column of silica gel with 10% CH_2Cl_2/hexane as eluent. Mp of adduct **28**: 39−40.5 °C. ^{19}F NMR: δ −144.5 (d, J = 25 Hz, 1F), −152.8 (s, 1F), −156.1 (m, 1F), −158.8 (m, 1F). ^{1}H NMR: δ 3.04 (dd, J = 12.9, 5.1 Hz, 1H), 2.80 (m, 3H), 1.78 (s, 3H), 1.76 (s, 3H). ^{13}C NMR: δ 143.4 ($^1J_{CF}$ = 321 Hz), 143.2 ($^1J_{CF}$ = 298 Hz), 125.1, 124.4, 102.7 ($^1J_{CF}$ = 252 Hz), 89.1 ($^1J_{CF}$ = 211 Hz), 35.0, 34.9, 18.8, 18.4. HRMS calcd for $C_{10}H_{10}F_4O_2S$: 270.0338, found 270.0336.

2,3,3a,9a-Tetrafluoro-3a,4,9,9a-tetrahydro-4,9-ethenonaphtho[2,3-*b*]thiophene 1,1-Dioxide (29). Into a glass pressure vessel with threaded Teflon stopper were placed 300 mg of TFTDO (85%, 1.4 mmol), 300 mg of naphthalene (2.3 mmol), and 3 mL of chlorobenzene. Solution was maintained at 105 °C for 15 h in a vertical pipe wrapped with heating tape, affording adduct **29** in 62% yield. Solvent was replaced with a few milliliters of ether, 1.5 g of silica gel was added, and the ether was evaporated. The off-white residue was chromatographed on 12 g of silica gel, initially with hexane as eluent to remove naphthalene. Solvent was then switched to 20% CH_2Cl_2/hexane. Selected fractions were combined and recrystallized from hexane. Adduct **29**, mp 134.5−135 °C. ^{19}F NMR: δ −143.9 (d, J = 26 Hz, 1F), −149.6 (s, 1F), −154.5 (dm, J = 13.8 Hz, 1F), −158.0 (ddm, J = 26, 13.8 Hz, 1F). ^{1}H NMR: δ 7.43 (m, 2H), 7.34 (m, 2H), 6.70 (m, 1H), 6.57 (m, 1H), 4.66 (unresolved m, 1H), 4.61 (unresolved m, 1H). ^{13}C NMR: δ 144.9 ($^1J_{CF}$ = 321 Hz), 143.3 ($^1J_{CF}$ = 297 Hz), 136.0, 134.9, 134.8, 132.5, 128.1, 128.0, 126.6, 126.5, 102.4 ($^1J_{CF}$ = 226 Hz), 90.3 ($^1J_{CF}$ = 222 Hz), 45.2, 45.1. Anal. Calcd for $C_{14}H_8F_4O_2S$: C, 53.16; H, 2.55; F, 24.03; S, 10.14. Found: C, 53.30; H, 2.57; F, 23.92; S, 10.04. It was clear from ^{19}F spectra on chromatographic fractions that major "impurity" peaks eliminated in the recrystallization represented the other stereoisomer (endo or exo) of the principal adduct. ^{19}F NMR: δ −144.9 (d, J = 25 Hz, 1F), −150.6 (d, J = 2.1 Hz, 1F), −156.9 (dm, J = 11.6 Hz, 1F), 158.3 (m, 1F). This isomer was formed in 12% yield (isomer ratio 5:1).

2,3,3a,7a-Tetrafluoro-3a,4,7,7a-tetrahydro-4,7-epithiobenzo[*b*]thiophene 1,1-Dioxide (30). A solution of 238 mg of TFTDO (95%, 1.2 mmol) in 2.0 mL (25 mmol) of thiophene was boiled under reflux for 5.3 h, affording a mixture of products that included in 62% yield two 1:1 adducts in the ratio 3:1. Silica gel (1.5 g) was added, solvent was evaporated, and the residue was chromatographed on 10 g of silica gel with 20% CH_2Cl_2/hexane as eluent. The endo and exo adducts eluted together. ^{19}F NMR: major adduct, δ −143.5 (d, J = 25 Hz, 1F), −147.7 (s, 1F), −148.8 (s, 1F), −152.6 (d, J = 25 Hz, 1F); minor adduct, δ −142.7 (d, J = 25 Hz, 1F), −146.5 (s, 1F), −152.0 (s, 1F), −156.1 (d, J = 25 Hz, 1F). ^{1}H NMR: major adduct, δ 6.82 (dd, J = 5.5, 3.9 Hz, 1H), 6.70 (dd, J = 5.5, 3.9 Hz, 1H), 4.48 (narrow m, 1H), 4.36 (narrow m, 1H); minor adduct, δ 6.72 (m, 1H), 6.53 (m 1H), 4.41 (m, 1H), 4.34 (m, 1H). ^{13}C NMR: major adduct, δ 144.9 ($^1J_{CF}$ = ∼322 Hz), 142.9 ($^1J_{CF}$ = 298 Hz), 138.4, 136.0, 105.1 ($^1J_{CF}$ = 267 Hz), 94.7 ($^1J_{CF}$ = 228 Hz), 51.6, 51.1; minor adduct (CH only), 139.8, 136.7, 55.2, 54.6. Anal. Calcd for $C_8H_4F_4O_2S_2$: C, 35.29; H, 1.48; F, 27.92. Found: C, 35.30; H, 1.36; F, 28.09.

2,3,3a,7a-Tetrafluoro-3a,4,7,7a-tetrahydro-4,7-epoxybenzo[*b*]thiophene 1,1-Dioxide (31). Into an oven-dried 10 mL round-bottom flask were placed 329 mg of TFTDO (88%, 1.5 mmol) and 3 mL of CH_2Cl_2. Flask was cooled in ice and 0.50 mL (470 mg, 6.9 mmol) of freshly distilled furan was added with stirring through a cotton plug. After 0.5 h, the colorless solution was allowed to warm to rt, and reaction was complete after 6 h. The product comprised two stereoisomeric adducts, the major one in 90% and the minor in ∼5% yield. Silica gel (1.5 g) was added to the solution, solvent was removed, and the white residue was chromatographed on a 15 g column of silica gel with 30% CH_2Cl_2/hexane as eluent. All nonempty fractions were colorless and crystalline, and all contained both isomers (total isolated yield, 91%). To obtain the major (exo) isomer in pure form, selected fractions were combined and recrystallized from hexane. Mp: 97.5−98 °C. ^{19}F NMR: major (exo) isomer, δ −142.3 (dd, J = 25, 3.1 Hz, 1F), −148.0 (unresolved dd, 1F), −163.6 (s, 1F), −168.6 (d, J = 25 Hz, 1F); minor (endo) isomer, δ −141.4 (dd, J = 25, 3.2 Hz, 1F), −145.9 (m, 1F), −171.3 (br dd, J = 18.1, ∼ 5 Hz, 1F), −173.8 (ddd, J = 25, 18.1, 5.9 Hz, 1F). ^{1}H NMR: exo isomer, δ 6.81 (d, J = 5.8 Hz, 1H), 6.73 (d, J = 5.8 Hz, 1H), 5.55 (br s, 1H), 5.28 (br d, J = 1.5 Hz, 1H); endo isomer, δ 6.76 (dd, J = 5.8, 1.4 Hz, 1H), 6.55 (d, J = 5.8 Hz, 1H), 5.38 (d, J = ∼7 Hz, 1H), 5.37 (d, J = 7 Hz, 1H). ^{13}C NMR: exo isomer, δ 143.4 ($^1J_{CF}$ = ∼320 Hz), 141.5 ($^1J_{CF}$ = 296 Hz), 136.3, 134.2, 101.5 ($^1J_{CF}$ = 267 Hz), 90.4 ($^1J_{CF}$ = 229 Hz), 79.1, 78.8. Anal. Calcd for $C_8H_4F_4O_3S$: C, 37.51; H, 1.57; S, 12.52. Found: C, 37.47; H, 1.62; S, 12.48.

2,3,3a,7a-Tetrafluoro-8-methyl-3a,4,7,7a-tetrahydro-4,7-epiminobenzo[*b*]thiophene 1,1-Dioxide (32). A solution of 340 mg of TFTDO (100%, 1.8 mmol) in 5 mL of CH_2Cl_2 was cooled in ice, and 0.20 mL (2.3 mmol) of freshly distilled *N*-methylpyrrole was added dropwise with stirring. After 5 min more in the bath, the yellow mixture was allowed to warm to rt, and 50 min after the addition the reaction was complete. Two stereoisomeric adducts were present in the ratio 1.5:1 (83% yield). Solvent was evaporated and the oily residue was chromatographed on 13 g of silica gel with 10% EtOAc/hexane as eluent. The minor adduct eluted first in fractions that were mostly yellow or orange. Several were combined and sublimed at ≤1 Torr and temperatures up to 52 °C to give off-white crystals. Mp: 76.5−77.5 °C. The major adduct appeared in fractions that were colorless or nearly so, mp 84.5−85.5 °C. ^{19}F NMR: major (endo) adduct, δ −141.7 (d, J = 26 Hz, 1F), −148.2 (s, 1F), −166.7 (dd, J = 12.3, 4.9 Hz, 1F), −169.7 (ddd, J = 26, 12.3, 5.4 Hz, 1F); minor (exo) adduct, δ −143.2 (dd, J = 25, 3.7 Hz, 1F), −150.4 (s, 1F), −165.0 (s, 1F), −170.3 (dd, J = 25, 3.5 Hz, 1F). ^{1}H NMR: endo adduct, δ 6.51 (d, J = 5.4 Hz, 1H), 6.30 (d, J = 5.4 Hz, 1H), 4.33 (m, 2H), 2.37 (s, 3H); exo adduct, δ 6.57 (d, J = 5.2 Hz, 1H), 6.45 (d, J = 5.2 Hz, 1H), 4.45 (s, 1H), 4.26 (s, 1H), 2.19 (s, 3H). ^{13}C NMR: endo adduct, δ 144.2 ($^1J_{CF}$ = 321 Hz), 142.4 ($^1J_{CF}$ = 299 Hz), 134.5, 132.0, 103.9 ($^1J_{CF}$ = ∼270 Hz), 92.7 ($^1J_{CF}$ = 231 Hz), 72.1, 71.8, 33.7; exo adduct, δ 143.4 ($^1J_{CF}$ = ∼320 Hz), 142.3 ($^1J_{CF}$ = 296 Hz),

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134.2, 131.4, 102.5 ($^1J_{CF}$ = 259 Hz), 91.8 ($^1J_{CF}$ = 221 Hz), 69.1, 68.9, 32.5. Anal. Calcd for $C_9H_7F_4NO_2S$: C, 40.15; H, 2.62; N, 5.20; S, 11.91. Found: C, 40.38; H, 2.67; N, 5.32; S, 11.87.

^{19}F NMR signals for TFTDO slowly appear at rt in $CDCl_3$ solutions of the endo adduct, signifying retro-Diels–Alder reaction. This was confirmed by addition of furan, which resulted in disappearance of the TFTDO signals, appearance of those of the furan adduct, and further slow growth of the latter over time. The exo adduct dissociates much more slowly, if at all, at rt.

2,3,3a,6a-Tetrafluoro-3a,4a,5,5a,6,6a-hexahydro-4*H*-4,6-ethenocyclopropa[4,5]benzo[1,2-*b*]thiophene 1,1-Dioxide (34). A solution of 270 mg of TFTDO (87%, 1.2 mmol) and 209 mg (2.3 mmol) of distilled 90% cycloheptatriene in 3 mL of 1,2-dichloroethane was heated for 7 h at 50 °C, giving an adduct in 78% yield. Solvent was evaporated and the residue mostly dissolved in a little 20% CH_2Cl_2/hexane, leaving behind brown insoluble material. The solution was chromatographed on a 10 g column of silica gel with that solvent as eluent. Most of the nonempty fractions were combined and recrystallized from hexane, affording the adduct **34** as small prisms. Mp: 83.5–85 °C. ^{19}F NMR: δ −143.8 (dd, J = 26, 2.3 Hz, 1F), −153.3 (s, 1F), −162.9 (dm, J = 18.5 Hz, 1F), −167.8 (dd, J = 26, 18.5 Hz, 1F). ^{1}H NMR: δ 5.91 (m, 1H), 5.77 (m, 1H), 3.71 (m, 1H), 3.65 (m, 1H), 1.53 (m, 1H), 1.44 (m, 1H), 0.61 (m, 1H), 0.44 (m, 1H). ^{13}C NMR: δ 144.5 ($^1J_{CF}$ = 314 Hz), 143.6 ($^1J_{CF}$ = 297 Hz), 128.3, 125.5, 103.2 ($^1J_{CF}$ = 263 Hz), 89.7 ($^1J_{CF}$ = 218 Hz), 37.3, 37.1, 4.5, 4.0, 3.9. Anal. Calcd for $C_{11}H_8F_4O_2S$: C, 47.14; H, 2.88. Found: C, 47.08; H, 2.64.

(*Z*)-1,2,3,4-Tetrafluoro-5,6,7,8-tetrahydrobenzo[8]annulene (35). A combination of 569 mg of TFTDO (90%, 2.7 mmol), 419 mg (3.9 mmol) of distilled 1,3-cyclooctadiene, and 5 mL of 1,2-dichloroethane was heated at 80 °C for 10 h to produce an adduct (−SO_2) in 55% yield. For a sample in $CDCl_3$, ^{19}F NMR: δ −139.9 (m, 1F), −147.6 (m, 1F), −164.7 (m, 1F), −165.8 (m, 1F). DDQ (700 mg, 3.1 mmol) was added to the reaction mixture, which was then heated at ∼80 °C for 21 h. Solvent was evaporated from the resulting thick, dark brown slurry, and the residue was slurried with a few mL of CH_2Cl_2. Silica gel (2.0 g) was added and solvent was again evaporated, leaving a brown powder that was placed on a 15 g column of silica gel for elution with hexane. All fractions were colorless, viscous oils. ^{19}F NMR of **35**: δ −142.0 (dd, J = 21.7, 12.3 Hz, 1F), −145.6 (dd, J = 21, 12.3 Hz, 1F), −159.3 (t, J = 21 Hz, 1F); −161.4 (t, J = 21 Hz, 1H). ^{1}H NMR: δ 6.28 (d, J = 11.9 Hz, 1H), 6.10 (dt, J = 11.9, 6.1 Hz, 1H), 2.80 (br s, 2H), 2.20 (br s, 2H), 1.69 (br s, 2H), 1.52 (m, 2H). ^{13}C NMR: δ 145.2 ($^1J_{CF}$ = 241 Hz), 144.5 ($^1J_{CF}$ = 244 Hz), 139.5 ($^1J_{CF}$ = 252 Hz), 138.3 ($^1J_{CF}$ = 250 Hz), 137.4, 123.9, 121.8, 117.8, 29.9, 27.0, 24.1, 21.7. Anal. Calcd for $C_{12}H_{10}F_4$: C, 62.61; H, 4.38; F, 33.01. Found: C, 62.42;, H, 4.42; F, 32.89.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00848.

X-ray data for **23** (CIF)

^{1}H, ^{19}F, and ^{13}C NMR spectra; total energies and Cartesian coordinates for calculated structures; X-ray crystal data plus ORTEP for **23** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: david.m.lemal@dartmouth.edu.

Notes

The authors declare no competing financial interest.

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