CHAPTER 4

Development of Fluorinated Oxatricyclononene Monomers and Oxetane Acetal Structures for 157 nm Lithography

Development of Fluorinated Oxatricyclononene Monomers and Oxetane Acetal Structures for 157 nm Lithography

Abstract Fluorinated 3-oxatricyclo[4.2.1.$0^{2,5}$]non-7-enes, readily obtained via the thermal cycloaddition of trifluoromethyl ketones with quadricyclane, are oxetane-functionalized norbornene monomers potentially amenable to a variety of polymerization pathways to afford new materials for deep ultraviolet lithography. A Lewis acid-catalyzed Wagner-Meerwein rearrangement of the oxetane-functionalized monomers produces a new series of fluorinated alicyclic monomers, 4-oxatricyclo[4.3.$0^{1,6}$.$0^{3,7}$]non-8-enes. This high yielding, 2-step synthesis affords a unique class of highly fluorinated, alicyclic monomers potentially useful to increase etch resistance and mechanical properties in advanced photoresist materials. These novel highly fluorinated structures exhibit high transparency indicating their suitability for use in a number of deep ultraviolet photolithographic applications. Oxetane acetal structures are shown to be highly transparent at 157 nm while being significantly more susceptible to acid-catalyzed ring-opening. Initial studies of a model 2-methoxy-3-oxa-tricyclononane which opens quantitatively to a hexafluorocarbinol-substituted norcamphor derivative are presented.

Introduction

The unique combination of transparency,[1] acidity,[2] and excellent dissolution behavior[3] imparted by hexafluorocarbinols to photoresist polymers has made them the dominant design motif for 157 nm photoresists.[4-8] While most heavily investigated for use in 157 nm lithography, hexafluorocarbinols are being back-integrated into resists for 193 nm and 193 nm immersion lithography. The vast majority of chemically-amplified positive tone photoresists being investigated for 193 nm, 193 nm immersion, and 157 nm lithography (such as the one shown in Figure 4.1) employ a latent acidic functionality with a photoacid-cleavable protecting group.[9] After exposure to deep ultraviolet (UV) radiation, the protecting group is cleaved catalytically by

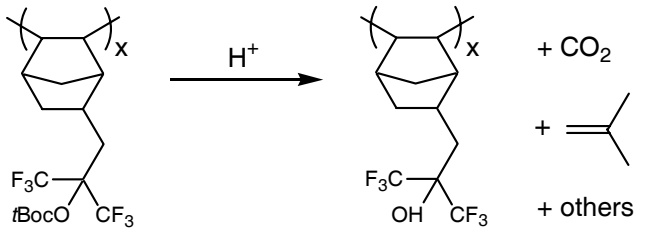


Figure 4.1. 157 nm photoresist with outgassing products

a photogenerated acid, releasing a number of volatile fragments which can outgas from the photoresist film and contaminate optical elements and produce distortions in the imaged features.[10] These issues have prompted the development of low-outgassing or mass-persistent photoresists based on the acid-catalyzed ring-opening of small and medium-sized lactones.[11] Negative tone resists also solve this outgassing problem, however, no negative tone resists based on fluorinated oxiranes or oxetanes suitable for 157nm lithography have been reported. 2,2-Bis(trifluoromethyl) oxetane has been shown to ring-open under acidic conditions in the presence of water or other nucleophiles to produce hexafluorocarbinol-functionalized compounds.[12] We imagined using an olefin-containing annulated oxetane (shown in Figure 4.2) which would remain intact during metal-catalyzed addition or ring-opening metathesis polymerization, yet ring-open under the superacidic conditions of imaging to produce either crosslinked networks (negative tone resists) or possibly hexafluorocarbinol-functionalized polymers (positive tone resists).

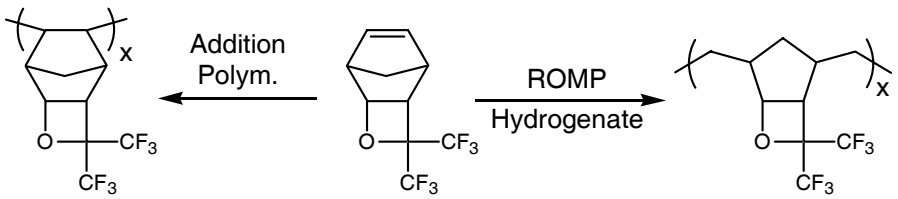


Figure 4.2. Oxetane-functionalized monomer and polymers

A number of 3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-enes similar to the desired monomer have been reported in the literature to be synthesized via the cycloaddition of quadricyclane (**4.1**) with activated carbonyl compounds.[13] With non-activated ketones, photochemical or very high pressure techniques are required. The resultant norbornene-like annulated oxetanes are exclusively exo in configuration, which is ideal for metal-catalyzed polymerization. Given our experience with using quadricyclane cycloadditions with fluorinated olefins to synthesize tricyclo[4.2.1.$0^{2,5}$]non-7-ene monomers for use in 157 nm photoresists,[14] we sought to expand this methodology to include fluorinated ketones such as hexafluoroacetone to produce fluorinated 3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-enes.[15]

Results and Discussion

Monomer Synthesis After condensation of hexafluoroacetone at -78 °C into a Fisher-Porter bottle containing quadricyclane, warming of the mixture to 0 °C resulted in a violent exotherm. This behavior is a marked contrast to quadricyclane cycloadditions with fluorinated olefins which only proceed upon extended heating.[14] On the other hand, this behavior is not so surprising in

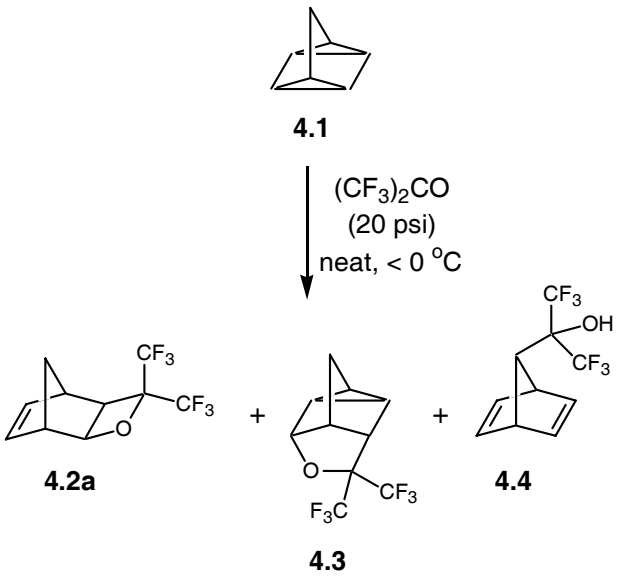


Figure 4.3. Synthesis of 3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-enes

light of the ability of hexafluoroacetone to serve as an excellent dienophile in Diels-Alder reactions.[16,17] Subsequent analysis of the product mixture revealed three major products (Figure 4.3). The major product was the desired 3-oxatricyclononene (**4.2a**). The oxetane was determined to be exclusively in the exo configuration by examination of the ^{1}H coupling of the C-2 endo proton and comparison with the known 4,4-diphenyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene.[18] The second product was a result of a homo-endo type cycloaddition with norbornadiene (either present as an impurity in **4.1** or formed via thermal isomerization during the reaction) leading to compound **4.3**.[19] Modification of the reaction procedure to maintain a reaction temperature below 0 °C eliminated the formation of **4.3**, allowing the use of technical grade quadricyclane without affecting conversions to **4.2a**. Interestingly, the 7-substituted norbornadiene **4.4** was also isolated in small yields (< 1%) during column chromatography. Our preliminary efforts to increase yields of **4.4** in order to examine its optical transparency or potential materials applications have met with little success so far.

Table 4.1 presents the scope of this reaction with a variety of fluorinated ketones. One trifluoromethyl group is sufficient activation for the cycloaddition to proceed; however, higher reaction temperatures are required for the less activated ketones. While these less fluorinated oxatricyclononenes are not sufficiently transparent for use at 157 nm, their aliphatic groups provide excellent handles for ^{1}H NMR NOE experiments.

Table 4.1. Synthesis of 3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-enes

Compound	R_1	R_2	Temp. (°C)	Time (h)	Syn:Anti	Isolated Yield (%)
4.2a	CF_3	CF_3	0	4	-	71
4.2b	Ph	CF_3	90	64	71:28	51
4.2c	CH_2Br	CF_3	60	16	58:42	81
4.2d*	Ph	Ph	rt	16	-	15

* Reaction performed photochemically (see experimental section)

Upon drying **4.2a** over 4 Å molecular sieves in preparation for metal-catalyzed polymerization, a new compound was observed to slowly form. Heating a dichloromethane solution of **4.2a** over flame-activated molecular sieves overnight resulted in complete isomerization of **4.2a** to 5,5-bis(trifluoromethyl)-4-oxa-tricyclo[4.3.$0^{1,6}$.$0^{3,7}$]non-8-ene (**4.5a**) (Figure 4.4). Suspecting the Lewis-acidic nature of the molecular sieves to be responsible, a number of Lewis acids including BF_3, $AlCl_3$, $FeCl_3$, $SnCl_4$ were all found to affect quantitative rearrangement.[20] Structural confirmation was achieved by osmium-catalyzed dihydroxylation of the olefin **4.5a** to produce the crystalline diol **4.6** whose x-ray crystal structure is shown in Figure 4.5.[21] This isomerization behavior is remarkably different than non-fluorinated 3-oxatricyclo[4.2.1.$0^{2,5}$]non-7-enes which retrocyclize to produce unsaturated aldehydes upon exposure to Lewis acids or rhodium complexes (lower pathway, Figure 4.4).[22] The destabilization of the partial positive charge by the highly electron-withdrawing trifluoromethyl groups disfavors this pathway and favors cleavage of the C2-O3 bond to form a non-classical norbornenyl cation which undergoes a Wagner-Meerwein rearrangement. Intramolecular quenching of the cation by the Lewis acid coordinated alkoxide produces **4.5a**. The large relief of ring strain by ring expansion of a strained oxetane to an unstrained tetrahydrofuran provides for a

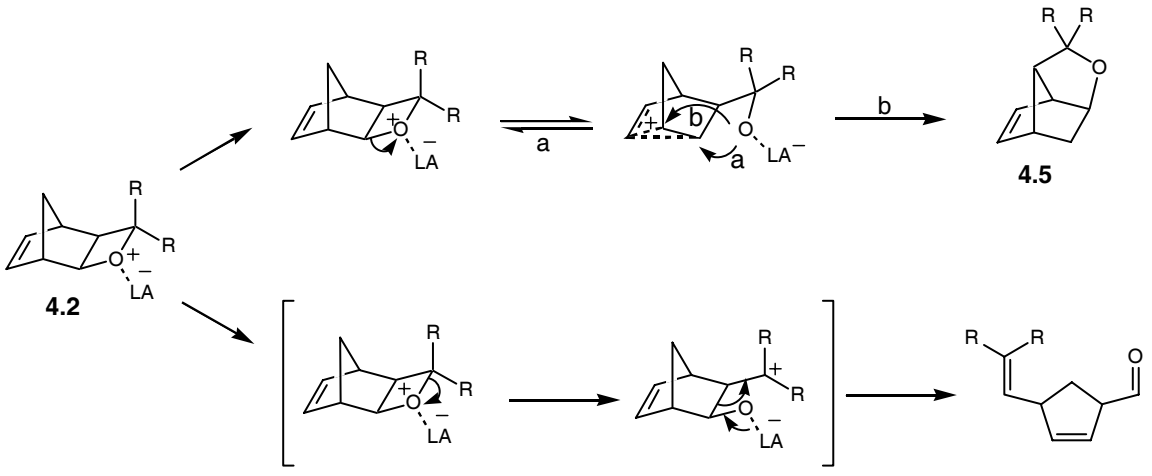


Figure 4.4. Lewis acid-catalyzed isomerizations of 3-oxatricyclononenes

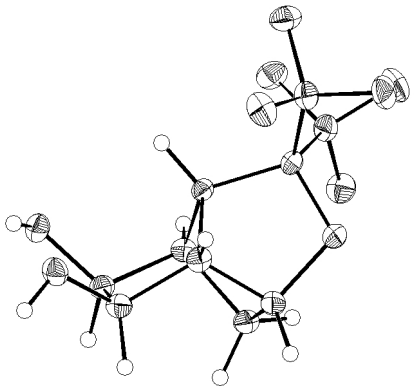


Figure 4.5. X-ray crystallographic structure of **4.6**

Table 4.2. Synthesis of 4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]non-8-enes

4-Oxa-TCN	Parent 3-Oxa-TCN	Lewis acid	Temp. (°C)	Time (h)	Endo:Exo	Isolated Yield (%)
4.5a	**4.2a**	BF_3•OEt_2	rt	6	-	97
4.5a	**4.2a**	4Å MS	40	14	-	90
4.5b	**4.2b**	BF_3•OEt_2	40	21	71:28	76
4.5b	**4.2b**	4Å MS	40	24	71:28	96
4.5c	**4.2c**	BF_3•OEt_2	40	16	52:48*	82
4.5c	**4.2c**	4Å MS	40	16	58:42	98

***** Using **4.2c** with syn:anti ratio 52:48

rapid and irreversible reaction.[23-25]

All fluorinated 3-oxatricyclonenes (**4.2**) underwent clean isomerization to their respective 4-oxatricyclononenes (**4.5**) without polymerization (Table 4.2). ^{1}H NMR NOE experiments confirm that the 4-*anti*-substituent in the oxetane **4.2** always ends up in the endo-configuration in **4.5** after isomerization (Figure 4.6), in agreement with the mechanism shown in Figure 4.4. The necessity of only one trifluoromethyl group for the cycloaddition and subsequent isomerization allows for versatile derivatization of these compounds by simply using a functionalized trifluoromethyl ketone. Since this work was originally intended to develop materials for 157 nm lithography, only the highly fluorinated compounds **4.2a** and **4.5a** are examined further; however,

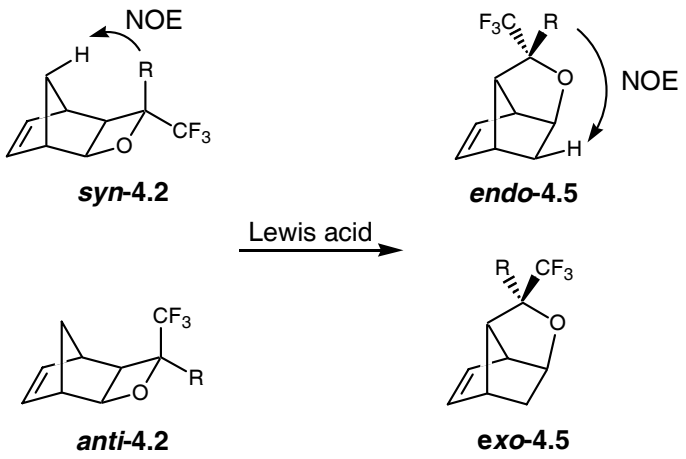


Figure 4.6. Stereochemistry of isomerization products

this methodology provides rapid and facile construction of a new class of fluorinated polycyclic olefins for use as building blocks for other materials and small molecules.

Optical Properties In order to examine the transparency of these fluorinated oxatricyclononenes, compounds **4.2a** and **4.5a** were hydrogenated over palladium on carbon to produce the oxatricyclononanes **4.7** and **4.8**, respectively. 4-Oxatricyclononane **4.8** was also synthesized in quantitative yield via exposure of 3-oxatricyclononane **4.7** to the Lewis acidic conditions used to isomerize **4.2a**. Their vacuum ultraviolet (VUV) spectra are shown in Figure 4.7. Surprisingly, despite the presence of the oxetane oxygen and the lack of fluorination directly on the norbornane skeleton, both oxatricyclononanes display high transparency at 157 nm. 3-Oxatricyclononane **4.7** is one of the most transparent norbornanes examined to date. These promising results prompted us to explore polymerization of these structures to provide confirmation of this high transparency.

Reactivity of Oxetane Ring The oxetane ring in **4.2a** is remarkably stable. Lithium aluminum hydride, lithium triethylborohydride, and lithium tri-*t*-butoxyalumium hydride/triethylborane were all ineffective at opening the oxetane to any useful extent. The oxetane ring proved slightly easier to open under acidic conditions. Reaction with stoichiometric

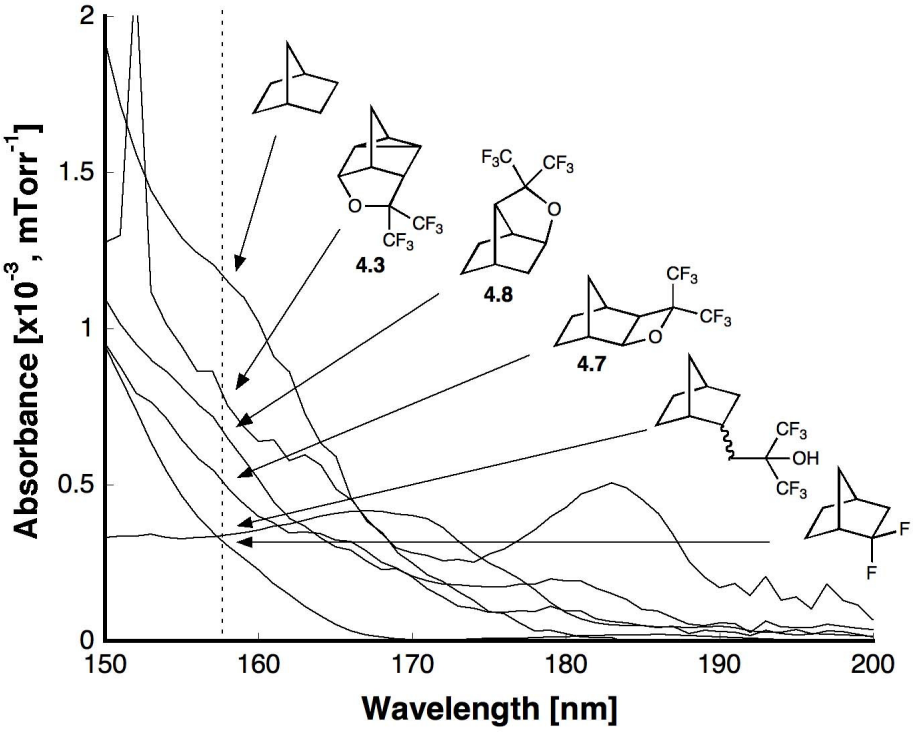


Figure 4.7. Vacuum ultraviolet spectra of oxatricyclononanes

amounts of trifluoroacetic acid afforded conversion to three hexafluorocarbinol-containing products: two nortricyclane structures with trifluoroacetate groups and one trifluoroacetate-free norbornene. Methanolysis resulted in the production of moderate yields of non-olefin ring-opened products (Figure 4.8).

Unfortunately, the saturated oxatricyclononane **4.7** is strongly resistant to ring opening under acidic conditions. Attempted methanolysis with sulfuric acid resulted in only trace reaction after 56 hours of reflux. Reaction with catalytic amounts of triflic acid afforded isomerization to **4.5a**, while reaction with stoichiometric amounts of triflic acid afforded ring-opened products. This is in marked contrast to 2,2-bis(trifluoromethyl)oxetane which ring-opens to afford monomeric and dimeric diols when heated with sulfuric acid for 1 hour.[26] Clearly, the annulated

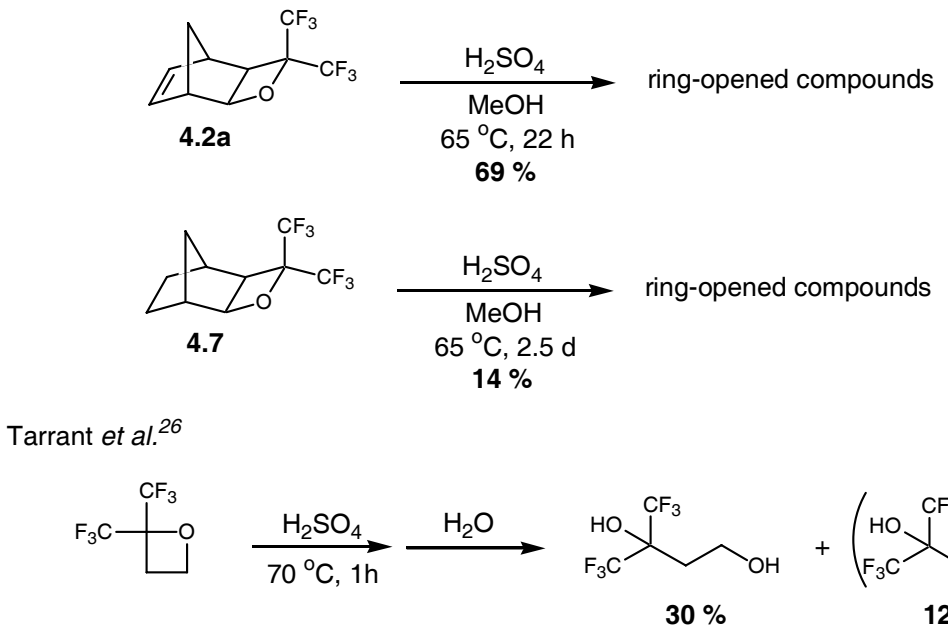


Figure 4.8. Acid-catalyzed ring-opening of **4.2a** and **4.7**

structure affords the oxetane ring a significant amount of stability, presumably by blocking nucleophilic attack which would have to occur from the endo side of the norbornene ring.

Therefore, ring-opening must proceed by an E1-process which is extremely slow and can result in isomerization to **4.5a**. In order for these structures to be useful as an active functionality in a photoresist, either the bulk of the annulating structure must be reduced to allow more room for nucleophilic attack on the oxetane (perhaps by using ring-opening metathesis), or the E1 process must be accelerated by stabilizing the resultant positive charge. While the ring-opening metathesis approach will be explored in Chapter 5, we explore the second option in this chapter by taking a look at oxetane acetal structures.

Model Oxetane Acetal Structures While hexafluoroacetone reacts with olefins containing an allylic hydrogen via an ene reaction at elevated temperatures to afford homoallylic hexafluorocarbinols,[27] it reacts with vinyl ethers under mild conditions to produce oxetane acetals.[28] These fluorinated oxetane acetals have been shown to open readily under acidic conditions to afford unsaturated hexafluorocarbinols[28] or β-hydroxy aldehydes[26,29]. Although the

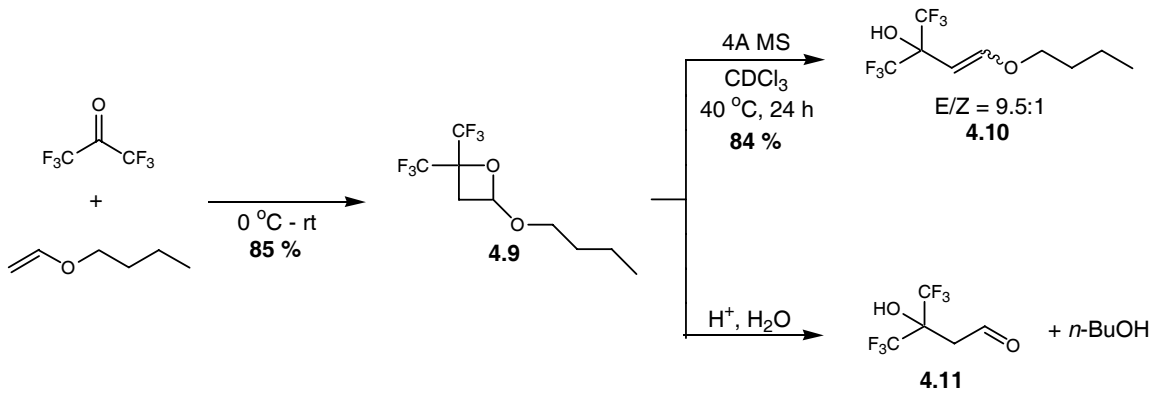


Figure 4.9. Model oxetane acetal synthesis

oxetane acetal structure is significantly more acid-labile, the effect of the additional oxygen on the absorbance of the structure could increase the absorption at 157 nm.

In order to examine the transparency of the oxetane acetal structure, 4-butoxy-2,2-bis(trifluoromethyl)-oxetane was synthesized by treatment of *n*-butyl vinyl ether with hexafluoroacetone (Figure 4.9). Quantitative cycloaddition occurred at 0 °C to afford high yields of oxetane acetal **4.9** after distillation. When the oxetane acetal was heated in the presence of a Lewis acid or sulfuric acid in the absence of water, the predominant ring-opened product is the unsaturated hexafluorocarbinol **4.10**; however, when water is present, aldehyde **4.11** and decomposition products such as the α,β-unsaturated aldehyde[26,29] are the major products in agreement with the literature. These reactions confirmed the high sensitivity of the fluorinated oxetane acetal structure to acidic conditions.

In order to evaluate the potential impact of the oxetane acetal structure on the transparency at 157 nm, the vacuum ultraviolet spectrum of **4.9** was measured and is shown in Figure 4.10. Remarkably, the oxetane acetal structure is extremely transparent despite the hydrocarbon tail and the additional oxygen. It appears to have slightly better transparency than hexafluoroisopropanol.

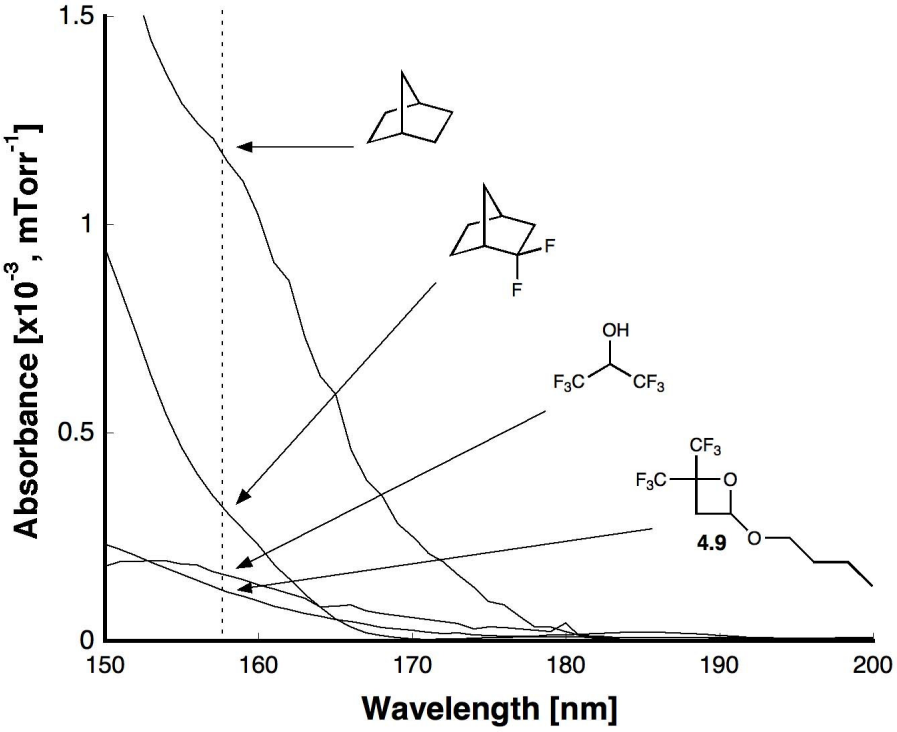
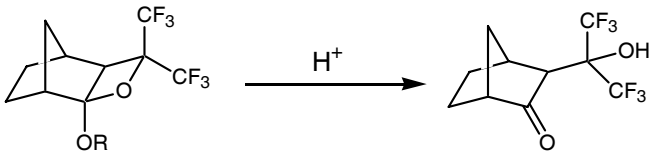


Figure 4.10. Vacuum ultraviolet spectrum of oxetane acetal **4.9**

With these results in hand, we set out to design an oxetane-acetal framework capable of being polymerized. The polymer portion may be connected to the oxetane acetal through 3 different locations: the alkoxy portion of the enol ether, the vinyl portion of the enol ether, or the perfluorinated ketone. An oxetane acetal connected to a polymer backbone through the alkoxy portion would release the hexafluorocarbinol as the volatile aldehyde during deprotection. This is disadvantageous because a non-acidic alcohol is now bound to the polymer backbone which is not base soluble, and the volatile aldehyde and its by-products pose a serious contamination problem to the lens optics. Of the two remaining routes, functionalization of heavily fluorinated ketones is the significantly more difficult endeavor. The most straightforward approach would be to attach the oxetane acetal to the polymer backbone through the olefinic group.

Seeking to maintain the norbornene framework for its high etch resistance and its ability to polymerize via a number of radical and metal-catalyzed pathways, the model 2-alkoxy-3-oxa-



4.12 **4.13**

Figure 4.11. Model 2-alkoxy-3-oxatricyclononane system

tricyclo[4.2.1.$0^{2,5}$]nonane **4.12** was devised (Figure 4.11). This structure combines the alicyclic structure of the 3-oxatricyclononanes shown discussed previously with the acid labile oxetane acetal structure. Upon exposure to acid, it is expected to ring-open to form the hexafluorocarbinol-functionalized norcamphor **4.13**. Hexafluorocarbinol **4.13** has previously been synthesized by the Frechet group for use as a dissolution inhibitor for 157 nm lithography.[30] In addition, synthesis of an unsaturated version capable of being polymerized should be relatively straightforward. However, the combination of the oxetane acetal with the strained oxatricyclononene framework may lead to excessive sensitivity to acid. Fortunately, Kirby *et al.* have shown that incorporation of fluorine on the alkoxy portion of oxetane acetal (from 2,2,2-trifluoroethanol) slows the rate of ring-opening by 3 orders of magnitude.[31] This additional fluorination should also help increase transparency even further.

Synthesis of the non-fluorinated oxetane acetal **4.12a** proceeded in a straightforward manner starting from norcamphor (Figure 4.12). The dimethyl acetal of norcamphor was first converted to the methyl enol ether **4.15a**.[32] Exposure of **4.15a** to hexafluoroacetone afforded the oxetane acetal **4.12a** in good yields. Unfortunately, we were unable to produce the fluorinated enol ether **4.15b** from the fluorinated ketal **4.14b** with the same methodology (likely due to the lower electron density on the oxygens reducing their affinity for the aluminum trichloride). Performing the reaction at higher temperatures or with boron trifluoride diethyl etherate were similarly ineffective. Reaction with trimethylsilyl triflate/diisopropylethylamine, another common method to produce enol ethers from ketals,[33] was also ineffective. It is likely that

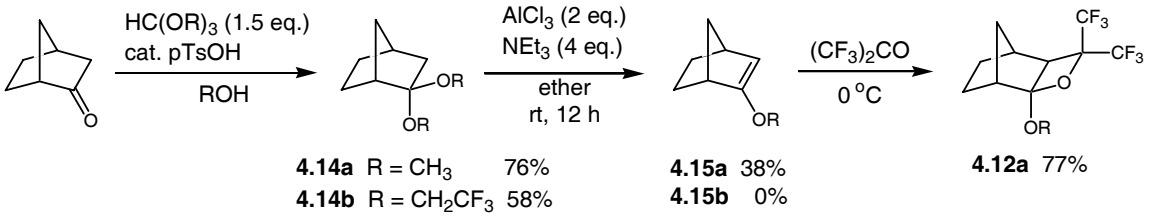


Figure 4.12. Synthesis of model 2-alkoxy-3-oxa-tricyclononanes

thermal cracking[34] of **4.14b** is required to generate the fluorinated enol ether.

Exposure of oxetane acetal **4.12a** to acidic conditions resulted in its quantitative hydrolysis to **4.13** under moderate conditions (Figure 4.13). The identity of the product was confirmed by independent synthesis from the silyl enol ether **4.16**. After reaction of trimethylsilyl enol ether **4.16** with hexafluoroacetone, three products were observed. The TMS-protected carbinol **4.17**, the deprotected carbinol **4.13,** and what is assigned to be the 2-siloxy-3-oxa-tricyclo[4.2.1.$0^{2,5}$]nonane **4.18** in a 1.9:1.3:1.0 ratio. Rearrangement products and other

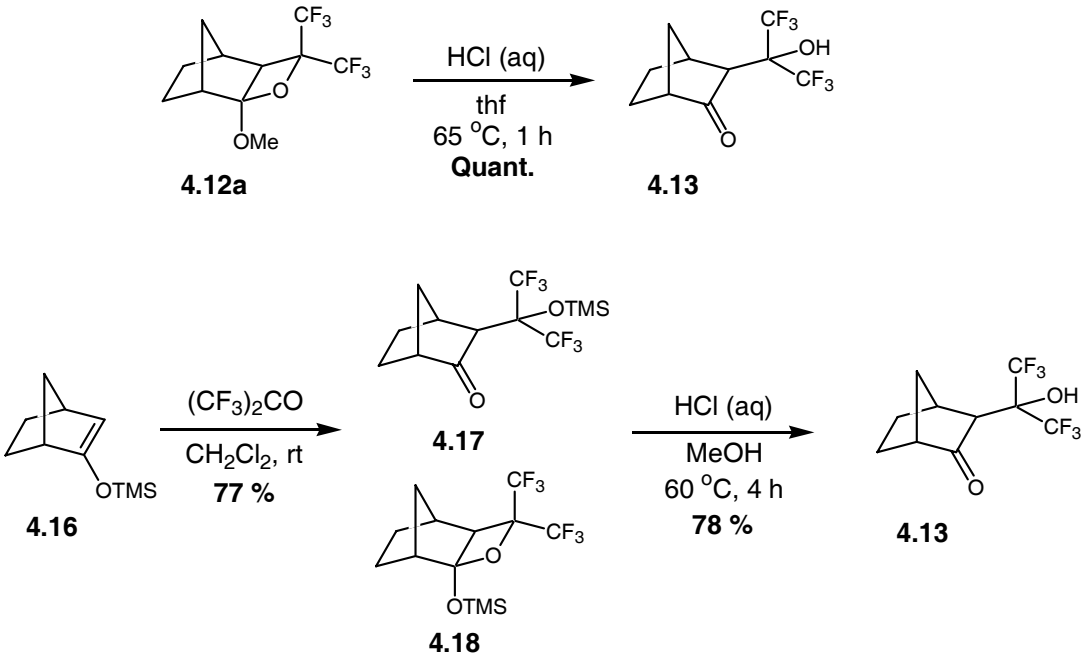


Figure 4.13. Acid-catalyzed ring-opening of model 2-alkoxy-3-oxa-tricyclononane

alkylations can be ruled out by the fact that the three component mixture reduces exclusively to **4.13** under hydrolytic conditions. This oxetane acetal formation is unusual, considering the reaction of silyl enol ethers with hexafluoroacetone usually results only in alkylation with silyl transfer to the oxygen.[35]

Unfortunately, the non-fluorinated oxetane acetal **4.12** has limited stability unless it is stored in the presence of a base such as potassium carbonate. Without a stabilizer, the oxetane acetal converts to **4.13** over the course of a few days, even when stored in the refrigerator. An oxetane acetal this sensitive would be unlikely to survive long term storage in a formulated resist or the baking processes involved in resist processing. However, the fluorinated oxetane acetal bears the promise of increased transparency and more importantly, an increased activation energy for ring-opening.

Conclusions

A wide variety of 3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-enes have been synthesized in high yields via the thermal cycloaddition of quadricyclane with trifluoromethyl ketones. Lewis acid catalyzed rearrangement of these oxetane-functionalized monomers provides easy access to a valuable new class of fluorinated, alicyclic, norbornene-like monomers, 4-oxa-tricyclo[4.3.$0^{1,6}$.$0^{3,7}$]non-8-enes. Both frameworks exhibit good transparency at 193 nm and 157 nm and may be potentially employed in free-radical and metal-catalyzed addition and ring-opening metathesis polymerizations. Such structures could be used in conventional photoresists in place of norbornene to impart transparency and etch resistance or increase thermal and mechanical properties. The high stability of saturated 3-oxatricyclononanes towards acid-catalyzed ring-opening has caused us to explore more labile oxetane acetal structures. While a model oxetane acetal structure exhibits favorable transparency at 157nm, and a model 2-methoxy-3-oxa-tricyclononane opens quantitatively to a hexafluorocarbinol-substituted norcamphor derivative, such oxetane acetals are perhaps too sensitive to acid-catalyzed ring-

opening. Future work into more fluorinated oxetane acetal structures may prove to provide latent hexafluorocarbinols with high transparency and the right activation energy for ring-opening.

Experimental

Materials: All air sensitive manipulations and polymerizations were carried out in an N_2-filled drybox or using standard Schlenk techniques. All solvents were rigorously degassed in 18 L reservoirs and passed through two sequential purification columns consisting of activated alumina.[36] All starting materials were procured from Aldrich except 3-bromo-1,1,1-trifluoroacetone and trifluoroacetophenone (Avocado). Quadricyclane[37] was a gift from Exciton, Inc., Dayton, Ohio and was made available through a Phase II SBIR project that has been sponsored by the Propulsion Directorate of the U.S. Air Force Research Laboratory, AFRL/PR. **WARNING: Quadricyclane has extraordinary toxicity for a hydrocarbon.**[38] Just as with the fluorinated ketones used in this paper, standard chemical safety precautions should be taken to avoid inhalation of quadricyclane vapors. 2,2-Difluoronorbornane was synthesized by colleagues in the Willson group (University of Texas, Austin). All liquid reagents used for vacuum UV measurements were distilled from appropriate drying agents, thoroughly degassed by freeze, pump, thaw cycles and sealed in glass ampoules under vacuum.

Methods: Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300, Varian *Unity Plus 300*, Varian *Gemini 300*, or Varian *Mercury 300* spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, internal C_6F_6 (~ 0.5 %) at -162.2 ppm[39]) or to the chemical shift of the residual proteo solvent.

X-ray Crystallography: X-ray crystallographic analysis on **4.6** was performed by the California Institute of Technology X-ray crystallography facility. See Appendix B for experimental procedure, labeled drawings, table of atomic coordinated, complete bond distances and angles, and anisotropic displacement parameters. Crystallographic data for compound **4.6** have been

deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 203516.

Vacuum UV Spectroscopy: Gas phase VUV measurements were made on an Acton *CAMS-507* spectrophotometer fitted with a custom-made gas cell attachment. The details of the cell design and implementation have been described previously.[1b]

4,4-Bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (4.2a). Quadricyclane (10.2 mL, 10.0 g, 109 mmol) was added to an oven-dried 100 mL Fisher-Porter bottle and degassed via 3 sequential freeze-pump-thaw cycles. After cooling the reaction vessel to 0 °C, the system was exposed to 20 psi of hexafluoroacetone under rapid stirring. After the hexafluoroacetone was consumed over the course of a few minutes, the system was repressurized with hexafluoroacetone. This was repeated until no observable pressure decrease was observed after 20 minutes. Excess hexafluoroacetone was carefully vented through concentrated sodium hydroxide solution. The colorless liquid was purified via silica gel flash column chromatography (20:1 pentane/ether) to produce a colorless liquid. Alternatively, hexafluorocarbinol-containing impurities (such as **4.5**) may be washed away with saturated potassium carbonate solution followed by vacuum distillation (79 °C, 30 Torr). Yield: 71%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.31 (dd, *J* = 5.7, 3.3 Hz), 5.91 (dd, *J* = 5.7, 3.3 Hz), 4.74 (d, *J* = 3.6 Hz), 3.23 (s), 3.20 (s), 2.59 (d, *J* = 4.8 Hz), 2.40 (d, *J* = 9.6 Hz), 1.59 (d, *J* = 9.6 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -69.09 (q, *J* = 10.6 Hz), -78.68 (q, *J* = 10.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 140.84, 132.56, 123.87 (q, *J* = 286 Hz), 121.94 (q, *J* = 286 Hz), 84.33, 80.40 (m), 45.32, 42.24, 42.00, 41.69 (q, *J* = 4.60 Hz). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_8F_6O$, 258.0479; found, 258.0481.

4-Phenyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (4.2b). Quadricyclane (0.831 g, 9.02 mmol) and 2,2,2-trifluoroacetophenone (1.52 mL, 1.88 g, 10.8 mmol) were added to a flame dried 50 mL thick-walled Schlenk tube and degassed via 3 sequential freeze-pump-thaw

cycles. The reaction vessel was sealed under argon and heated at 90 °C for 17 hours. The yellowish liquid was purified via silica gel flash column chromatography (20:1 pentane/ether) to produce a colorless liquid. Yield: 1.16 g (51%). Isomer composition: 73% syn, 27% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.64(dd, *J* = 1.8, 0.9 Hz, 2H, anti), 7.5-7.3(m, 6H), 6.30 (dd, *J* = 5.4, 3.0 Hz, 1H, anti), 6.22 (dd, *J* = 5.7, 3.3 Hz, 1H, syn), 5.91(dd, *J* = 5.7, 3.3 Hz, 1H, syn), 5.83 (dd, *J* = 5.7, 3.3 Hz, 1H, anti), 4.76 (d, *J* = 4.8 Hz, 1H, syn), 4.47 (dd, *J* = 4.8, 2.1 Hz, 1H, anti), 3.34 (s, 1H, anti), 3.19 (d, *J* = 1.5 Hz, 1H, anti), 3.07 (t, *J* = 1.5 Hz, 1H, anti), 2.90-2.82 (m, 2H, syn), 2.75 (d, *J* = 9.3 Hz, 1H, anti, 2.51 (d, *J* = 4.8 Hz, 1H, anti), 1.62 (d, *J* = 9.3 Hz, 2H, syn), 1.20 (d, *J* = 9.6 Hz, 2H, anti). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.58 (s, anti), -82.26 (s, syn) .^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 141.35, 139.82, 139.20, 134.29, 132.98, 132.22, 128.55, 128.38, 128.14, 126.54, 126.47, 125.59 (q, *J* = 285 Hz, syn), 123.90 (q, *J* = 285 Hz, anti), 82.00, 81.42, 48.86, 45.68, 45.20, 42.68, 42.53 (m), 41.92, 41.61, 41.16. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{15}H_{13}F_3O$, 266.0919; found, 266.0920.

4-Bromomethyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (4.2c). Quadricyclane (2.23 mL, 2.19 g, 23.8 mmol) and 1,1,1-trifluoro-3-bromoacetone (2.72 mL, 5.00 g, 26.2 mmol) were added to a flame dried 50 mL thick-walled Schlenk tube and degassed via 3 sequential freeze-pump-thaw cycles. The reaction vessel was sealed under argon and heated at 60 °C for 16 hours. The yellowish liquid was purified via silica gel flash column chromatography (30:1 pentane/ether) to produce a colorless liquid. Yield: 5.50 g (82 %) Isomer composition: 58 % syn, 44% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 6.31 (dd, *J* = 5.4, 3.3 Hz, 1H, anti), 6.27(dd, *J* = 5.4, 3.3 Hz, 1H, syn), 5.92 (dd, *J* = 5.4, 3.3 Hz, 1H, syn), 5.88 (dd, *J* = 5.4, 3.3 Hz, 1H, anti), 4.62 (d, *J* = 4.5 Hz, 1H, syn), 4.59 (d, *J* = 4.8 Hz, 1H, anti), 3.81 (d, *J* = 11.1 Hz, 1H, anti), 3.67 (dm, *J* = 11.1 Hz, 1H, anti), 3.61 (s, 2H, syn), 3.17(s, 2H), 3.13 (s, 2H), 2.50 (d, *J* = 5.1 Hz, 2H), 2.46 (d, *J* = 9.9 Hz, 1H, anti), 2.12 (d, *J* =9.3 Hz, 1H, syn), 1.65(d, *J* = 9.3 Hz, 1H, syn), 1.53 (d, *J* 9.9 Hz, 1H, anti). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -69.23 (s, anti), -80.43 (s, syn). ^{13}C NMR

($CDCl_3$, 75 MHz, ppm): 141.26 (anti), 139.83 (syn), 132.76 (syn), 132.20 (anti), 125.78 (q, *J* = 287 Hz, syn), 81.79 (anti), 81.78 (syn), 80.02 (m, anti), 78.82 (m, syn), 45.51 (anti), 45.15 (anti), 44.95 (syn), 42.34 (syn), 42.26 (anti), 41.61 (m, anti), 40.95 (syn), 40.54 (syn), 32.93 (d, J = 3.1 Hz, anti), 24.21 (d, J = 1.5 Hz, syn). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_{10}F_3OBr$ 281.9866,; found, 281.9867.

4,4-Diphenyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (4.2d). Norbornadiene (2.70 mL, 2.30 g, 25.0 mmol) and benzophenone (3.04 g, 16.7 mmol) in 500 mL benzene were added to a photochemical reaction vessel and degassed via sparging with nitrogen. The reaction vessel was irradiated for 16 hours with a Hanovia 400W medium pressure Hg lamp. The yellowish liquid was purified by recrystallization from ether 2x to yield white crystals. Yield: 0.69 g (15%). Spectra agree with previous reports.[18] ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 7.56 (dt, *J* = 8.4, 1.5 Hz, 2H), 7.4-7.25 (m, 6H), 7.19 (tm, J = 6.9 Hz, 2H), 6.22 (dd, *J* = 5.7, 3.0 Hz, 1H), 5.89 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.57 (dm, *J* = 5.4 Hz, 1H), 3.03 (m, 2H), 2.87 (dt, *J* = 5.1 1.5 Hz, 1H), 1.78 (d, *J* = 9.0 Hz, 1H), 1.20 (dt, *J* = 9.3, 1.5 Hz, 1H). ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm):149.15, 144.72, 139.70, 133.24, 128.82, 128.56, 127.08, 126.83, 125.17, 124.96, 84.84, 79.44, 49.41, 46.14, 42.65, 42.11. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{20}H_{18}O$, 274.1358; found, 274.1359.

4,4-Bis(trifluoromethyl)-3-oxa-tetracyclo[7.1.0.0^{2,6}.0^{5,9}]nonane (4.3). Norbornadiene (4.7 mL, 4.0 g, 43 mmol) was added to an oven dried 100 mL Fisher-Porter bottle and degassed via 3 sequential freeze-pump-thaw cycles. Hexafluoroacetone was condensed into the vessel at -78 °C. The reaction vessel was closed under argon and slowly warmed to room temperature. The reaction was heated at 90 °C for 24 hours. Excess hexafluoroacetone was carefully vented through concentrated sodium hydroxide solution. The colorless liquid was purified via silica gel flash column chromatography (40:1 hexane/ethyl acetate) to produce a colorless liquid. Yield: 2.4 g(22%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 4.58 (s, 1H), 2.80 (s,1H), 2.53 (s, 1H), 1.70 (d, *J* = 1.8 Hz, 2H), 1.57 (t, *J* = 5.2 Hz, 1H), 1.45 (d, *J* = 4.8 Hz, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz,

ppm): δ -68.88 (q, *J* = 11.2 Hz), -75.15 (q, *J* = 10.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 123.51 (q, *J* = 286 Hz), 122.92 (q, *J* = 286 Hz), 87.22, 84.02 (m), 48.54, 40.95 (q, *J* = 4.0 Hz), 28.63, 16.10, 15.87, 12.63. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_8F_6O$, 258.0479; found, 258.0484.

2-(Bicyclo[2.2.1]hepta-2,5-dien-7-yl)-1,1,1,3,3,3-hexafluoro-propan-2-ol (4.4). Column chromatography (20:1 pentane/ether) of the crude reaction mixture of **4.2a** afforded **4.5** as a colorless oil. Yield: < 1 %. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.02 (t, *J* = 2.1 Hz, 2H), 6.96 (t, *J* = 2.1 Hz, 2H), 4.34 (s, 1H), 3.86 (s, 2H), 3.05 (s, H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.81 (s). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 146.11, 142.72, 122.92 (q, *J* = 289 Hz), 78.29, 51.74. HRMS-[EI-GC] (m/z): [M•]+ calc'd for $C_{10}H_8F_6O$, 258.0468; found, 258.0479.

General procedure for Lewis acid catalyzed isomerization of 3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-enes:

Method A. Boron trifluoride diethyl etherate: 3-Oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2**) (1.9 mmol) was added to a flame dried 100 mL round bottom flask with 10 mL anhydrous dichloromethane [0.2M]. Boron trifluoride diethyl etherate (0.19 mmol, 0.1 eq.) was added via syringe at 0 °C and the reaction was slowly warmed to room temperature and stirred for 6-18 hours. The boron trifluoride was quenched with excess anhydrous triethylamine. The dichloromethane was removed *in vacuo* and the crude reaction mixture was purified via silica gel flash column chromatography (20:1 pentane/ether) to afford clean **4.5**.

Method B. Flame activated molecular sieves: 3-Oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2**) (1.9 mmol) in 10 mL anhydrous dichloromethane [0.2M] was added to a flame dried 100 mL round bottom flask with flame activated 4Å molecular sieves (Advanced Specialty Gas Corp, rods). The reaction was heated at 40 °C until isomerization was complete. Filtration of the reaction mixture through a 0.45 μm PTFE syringe filter to remove cloudiness followed by removal of the solvent in vacuo afforded **4.5** in excellent yields.

5,5-Bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]non-8-ene (4.5a). *Method A:* Reaction of 4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2a**) (9.68 g, 37.5 mmol) afforded 9.42 g (97%) of **4.5a**. *Method B:* Reaction of 4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2a**) (1.03 g, 3.9 mmol) afforded 0.92 g (90%) of **4.5a**. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.45 (dd, *J* = 6.0, 3.3 Hz), 5.84 (dd, *J* = 5.4, 3.3 Hz), 4.48 (s), 3.56 9(s), 2.99 (m), 2.93 (s), 2.16 (dd, *J* = 12.6, 4.8 Hz), 1.09 (dm, *J* = 12.6 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -69.72 (q, *J* = 12.5 Hz), -74.97 (q, *J* = 11.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 124.51, 127.72, 123.24 (q, *J* = 288 Hz), 122.73 (q, *J* = 288 Hz), 81.140 (m), 78.13, 64.99, 52.58 (m), 41.93, 36.29 (m). HRMS-[EI+GC] (m/z): [M•]+ calc'd for $C_{10}H_8F_6O$, 258.0479; found, 258.0487.

5-Phenyl-5-trifluoromethyl-4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]non-8-ene (4.5b). *Method A:* Reaction of 4-phenyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2b**) (0.250 g, 0.84 mol) afforded 0.19 (76%) of **4.5a**. *Method B:* Reaction of 4-phenyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2b**) (0.250 g, 0.94 mol) afforded 0.24 g (96%) of **5a**. Composition: 71% endo, 28% exo. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.0-7.0 (m, aromatic, 10H), 6.43 (ddd, *J* = 5.7, 3.3, 0.9 Hz, 1H, exo), 6.26 (ddd, *J* = 5.7, 3.3, 0.96 Hz, 1H, endo), 5.91 (ddd, *J* = 5.7, 3.3, 1.2 Hz, 1H, endo), 5.73 (ddd, *J* = 5.7, 3.3, 0.9 Hz, 1H, exo), 4.50 (m, 1H, exo), 4.43 (t, *J* = 3.0 Hz, 1H, endo), 3.57 (m, 1H, endo), 3.32 (m, 1H, endo), 3.17 (m, 1H, exo), 3.04 (m, 1H, exo), 2.88 (m, 1H, exo), 2.56 (m, 1H, endo), 2.29 (dd, *J* = 12.6, 4.8 Hz, 1H, exo), 1.52 (dd, *J* = 12.6, 4.8 Hz, 1H, endo), 1.12 (dm, *J* = 12.6 Hz, exo), 0.87 (ddd, *J* = 12.6, 3.6, 1.8 Hz, 1H, endo). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.78 (s, exo), -77.02 (s, endo). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 142.87, 140.50, 139.57, 136.07, 128.93, 128.42, 128.38, 128.22, 127.83, 126.48, 125.41 (q, *J* = 285 Hz, exo), 124.60 (q, *J* = 284 Hz, endo), 81.76 (m), 81.13 (m), 77.34, 76.59, 69.32, 67.25, 52.61, 52.11 (m), 42.28, 36.71 (m). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{15}H_{13}F_3O$, 266.0919; found, 266.0926.

5-Bromomethyl-5-trifluoromethyl-4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]non-8-ene (4.5c). *Method A:* Reaction of 4-bromomethyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**2c**) (1.11, 3.92 mmol) afforded 0.913 g (82%) of **4.5a**. *Method B:* Reaction of 4-bromomethyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2c**) (1.20 g, 4.24 mmol) 4-phenyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2b**) (0.50 g, 1.9 mol) afforded 1.17 g (98%) of **5a**. Composition: 58% endo, 42% exo. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.44 (dd, *J* = 6.0, 3.0 Hz, 1H, exo), 6.38 (dd, *J* = 6.0, 3.0 Hz, 1H, endo), 5.88 (dd, *J* = 6.0, 3.0 Hz, 1H, endo), 5.83 (dd, *J* = 6.0, 3.0 Hz, 1H, exo), 4.41 (d, *J* = 3.3 Hz, 1H, endo), 4.40 (d, *J* = 3.0 Hz, 1H, exo), 3.61 (d, *J* = 11.4 Hz, 1H, endo), 3.49 (m, 1H, endo), 3.46 (d, *J* = 11.4 Hz, 1H, endo), 3.45 (dm, *J* = 11.7 Hz, 1H, exo), 3.36 (dm, *J* = 11.4 Hz, 1H, exo), 3.29 (m, 1H, exo), 3.11 (m, 1H, endo), 3.00 (m, 3H,) 2.13 (dd, *J* = 12.6, 4.5 Hz, 1H, exo), 1.90 (dd, *J* = 12.9, 4.5 Hz, 1H, endo), 1.18 (dq, *J* = 12.9, 1.8 Hz, 1H, endo), 1.00 (dm, *J* = 12.6 Hz, 1H, exo). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -70.46 (s, exo), -75.44 (s, endo). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 143.41, 141.12, 128.81, 127.40, 125.28 (q, *J* = 287 Hz), 124.74 (q, *J* = 287 Hz), 79.13 (m), 78.21 (d, 2.0 Hz), 77.48 (d, J = 2.0 Hz) 66.44, 66.25, 52.48 (m), 41.80, 40.84, 36.68, 35.82, 31.33, 28.14. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_{10}F_3OBr$, 281.9867; found, 281.9873.

5,5-Bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]nonane-8,9-diol (4.6). To a solution of **4.5a** (0.53 g, 2.1 mmol) and *n*-methyl morpholine oxide (0.29 g, 2.5 mmol) in 20 mL tetrahydrofuran/water (9;1) was added osmium tetroxide (2.5 wt% solution in *t*-butanol, 257 μL, 0.02 mmol). The reaction was stirred at room temperature for 30 minutes, after which TLC indicated consumption of **4.5a** was complete. Silica gel chromatography (1:2 pentane/ether) afforded **4.6** as a white crystalline solid. Slow recrystallization from hexanes/ether produced crystals suitable for x-ray crystallographic analysis. Yield: 0.300g (49 %). ^{1}H NMR (Acetone-d_6, 300 MHz, ppm): δ 4.51 (m, 2H), 4.35 (d, *J* = 6.6 Hz, 1H), 3.94 (t, *J* = 6.0 Hz, 1H), 3.88 (m, 1H), 3.19 (s, 1H), 2.72 (m, 1H), 2.43 (dm, *J* = 7.5 Hz, 1H), 1.74 (dd, *J* = 14.1, 6.3 Hz, 1H), 1.06 (d, J = 14.1 Hz, 1H). ^{19}F NMR (Acetone-d_6, 282 MHz, ppm): δ -70.66 (q, *J* = 11.9 Hz), -75.32 (q, *J* =

11.9 Hz). ^{13}C NMR (Acetone-d_6, 75 MHz, ppm): δ 124.34 (q, *J* = 288 Hz), 123.76 (q, *J* = 288 Hz), 84.44 (m), 81.58, 74.99, 66.97, 55.54 (m), 48.09, 43.80, 30.08. HRMS-[FAB-gly] (m/z): [M + H]+ calc'd for $C_{10}H_{11}F_6O_3$, 293.0612; found, 293.0609.

4,4-Bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]nonane (4.7). 4,4-Bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**4.2a**) (0.97 g, 3.8 mmol) and palladium on carbon (10 wt% Pd, 150 mg) were added to a 100 mL round bottom flask with 15 mL diethyl ether. The solution was degassed via 3 freeze-pump-thaw cycles. After attaching a balloon of hydrogen, the reaction was stirred overnight at room temperature. Subsequent filtration through a 0.45 μm PTFE filter and removal of the solvent in vacuo afforded **4.7** as a colorless liquid. Yield: 0.98g (100 %). ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 4.99 (dd, *J* = 3.0, 1.2 Hz, 1H), 2.71 (d, *J* = 4.5 Hz, 1H), 2.61 (s, 1H), 2.52 (d, *J* = 11.1 Hz, 1H), 2.44 (m, 1H), 1.7-1.5 (m, 2H), 1.44 (d, *J* = 11.1 Hz, 1H), 1.08 (m 1H), 0.93 (m, 1H). ^{19}F NMR (CD_2Cl_2, 282 MHz, ppm): δ -70.39 (m), -79.50 (m). ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): 124.06 (q, *J* = 288 Hz), 122.20 (q, *J* = 288 Hz), 89.03 46.27, 39.39, 36.50, 33.33 (m), 28.86, 22.18. HRMS- (m/z): [M•]+ calc'd for $C_{10}H_{10}F_6O$, 260.0636; found, 260.0632.

5,5-Bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0^{1,6}.0^{3,7}]nonane (4.8). 5,5-Bis(trifluoromethyl)-4-oxa-tricyclo[4.3.0.0^{3,7}]non-8-ene (**4.5a**) (0.75 g, 2.9 mmol) and palladium on carbon (10 wt% Pd, 150 mg) were added to a 100 mL round bottom flask with 50 mL diethyl ether. The solution was degassed via three freeze-pump-thaw cycles. After attaching a balloon of hydrogen, the reaction was stirred for 12 hours at room temperature. Subsequent filtration through a 0.45 μm PTFE filter and removal of the solvent in vacuo afforded **4.8** as a colorless liquid. Yield; 0.75g (100 %). ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 4.41 (s, 1H), 2.85 (dd, *J* = 3.0, 1.5 Hz, 1H), 2.56 (s, 1H), 2.41 (dd, *J* = 3.9, 1.8 Hz, 1H), (dd, *J* = 13.8, 5.4 Hz, 1H), 1.75-1.60 (m, 2H), 1.5-1.35 (m, 2H), 1.18 (dm, *J* = 12.3 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -70.39 (q, *J* = 11.9 Hz), -75.05 (q, *J* = 11.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 123.87 (q, *J* = 287 Hz), 123.26 (q, *J* =

287 Hz), 84.46, 51.03, 47.09 (m), 37.04, 33.93 (m), 32.19, 18.84. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_{10}F_6O$, 260.0636; found, 260.0640.

4-Butoxy-2,2-bis-trifluoromethyl-oxetane (4.9). *n*-Butyl vinyl ether (3.0 g mL, 3.0 mmol) was added to an oven dried 100 mL Fisher-Porter bottle and degassed via three sequential freeze-pump-thaw cycles. The vessel was pressurized with 20 psi of hexafluoroacetone at 0 °C while rapidly stirring. When the pressure fell to < 5 psi, an additional 20 psi of hexafluoroacetone was added. This procedure was repeated until the pressure did not decrease after 20 minutes. Excess hexafluoroacetone was carefully vented through concentrated sodium hydroxide solution. NMR analysis showed quantitative conversion to product. The colorless liquid was unstable to silica gel flash column chromatography, so Kugelrohr distillation (rt, 20 mTorr) was used to afford a colorless liquid. The product was stored over potassium carbonate. Yield: 6.6 g (85 %). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.59 (t, *J* = 5.0 Hz, 1H), 3.79 (m, 1H), 3.56 (m, 1H), 3.07 (dd, *J* = 5.7, 13.5 Hz, 1H), 2.83 ddd, *J* = 1.5, 4.5, 13.5 Hz, 1H), 1.61 (m, 2H), 1.40 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). Spectrum agrees with previously reported compound (see Ref. 28a). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -79.08 (m), -79.20 (m). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 122.98 (q, *J* = 282 Hz), 121.62 (q, *J* = 282 Hz), 102.12, 76.14, 69.73, 32.33, 31.73, 19.22, 13.82. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_9H_{12}F_6O_2$, 266.0741; found, 266.0750.

4-Butoxy-1,1,1-trifluoro-2-trifluoromethyl-but-3-en-2-ol (4.10). 4-Butoxy-2,2-bis-trifluoromethyl-oxetane (**4.9**). (0.02 g, 0.08 mmol) in 1 mL $CDCl_3$ was added to an NMR tube with flame activated 4Å molecular sieves (3.0 g mL, 3.0 mmol) and heated for 24 hours at 40 °C. NMR analysis indicated the formation of 4 major products: 85% 4-Butoxy-1,1,1-trifluoro-2-trifluoromethyl-but-3-en-2-ol (4.x) (E/Z = 9.5:1), 3% aldehyde-containing species, and 13% of an unidentified compound. ***E*-4.10x:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.95 (d, *J* = 12.6 Hz, 1H), 4.82 (d, *J* = 12.6 Hz, 1H), 3.78 (t, *J* = 6.6 Hz, 2H), 2.86 (s, 1H), 1.68 (m, 2H), 1.40 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -79.30 (m). ^{13}C NMR ($CDCl_3$, 75

MHz, ppm): 154.24, 124.38, 91.82, 70.01, 30.98, 19.02, 13.73. Spectrum agrees with previously reported compound (see Ref. 28a). ***Z*-4.10x:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.45 (d, *J* = 6.6 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.05 (s, 1H), 1.67 (m, 2H), 1.40 m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -79.12 (m). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_9H_{12}F_6O_2$, 266.0741; found, 266.0748.

2-Methoxy-4,4-bis-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]nonane (4.12a). To a dry pressure reaction vessel was added 2-methoxy-norborn-2-ene (1.74 g, 14 mmol) and deoxygenated at –78 °C. The vessel was warmed to 0 °C and hexafluoroacetone was added to 20 psi. When the vessel pressure decreased to 5 psi, hexafluoroacetone was added to 20 psi and this procedure repeated until the pressure remained at 5 psi for 30 minutes. A vacuum line was used to remove remaining hexafluoroacetone to afford a yellow oil which was added to ether and successively washed with 0.5M sodium hydroxide solution, saturated potassium carbonate solution, and brine. The ether phase was dried over anhydrous potassium carbonate and distilled at 55 °C and 10 mTorr. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.37 (s, 3H), 2.63 (m, 2H), 2.57 (s, 1H), 1.8-1.2 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 122.56 (q, *J* = 287 Hz), 51.94, 50.51, 39.64, 37.06, 34.78 (m), 27.75, 23.06. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ –67.00 (q, *J* = 12.0 Hz), -76.91 (q, *J* = 11.2 Hz). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{11}H_{12}F_6O_2$, 290.0741; found, 290.0749.

3-(2,2,2-Trifluoro-1-hydroxy-1-trifluoromethyl-ethyl)-bicyclo[2.2.1]heptan-2-one (4.13). To a solution of 2-methoxy-4,4-bis-trifluromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]nonane (200 mg, 0.69 mmol) in 15 mL tetrahydrofuran was added 14 mL (0.042 mmol) of 10% hydrochloric acid. The mixture was stirred over an oil bath at 65 °C for 1 hour, and then cooled to room temperature. The mixture was diluted with 50 mL ether, extracted with ether three times, washed with sodium bicarbonate solution, and washed in water. The organic layers were dried over sodium sulfate and concentrated by rotary evaporation to yield 1.128 g clear liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.31 (s, 1H), 2.95 (s, 1H), 2.75 (d, *J* = 3.3 Hz, 1H), 2.41 (d, *J* = 3.3 Hz, 1H), 2.12 (d, *J* =

11.4 Hz, 1H), 2.1-1.95 (m, 2H), 1.7-1.5 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.92 (q, J = 9.3 Hz), -77.38 (q, J = 9.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 123.26 (q, J = 286 Hz), 122.10 (q, J = 286 Hz), 50.18, 48.44, 36.84, 35.74, 30.63, 23.14. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_{10}F_6O_2$, 276.0585; found, 276.0585.

2,2-Dimethoxynorbornane (4.14a). To a flask containing norcamphor (5.0 g, 45.4 mmol) and p-toluenesulfonic acid monohydrate (125 mg, 0.657 mmol) was added 25 mL dry methanol by cannula, followed by addition of dry trimethyl orthoformate (7.22 g, 68.1 mmol) by syringe. The solution was refluxed overnight at 65 °C and quenched with 30 mL of 10% potassium hydroxide solution. The product was extracted with 40% pentane in dichloromethane solution and dried with potassium carbonate. Distillation at 450 mTorr pressure yielded 5.76 g (81%) 2, 2-dimethoxynorbornane. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.17 (s, 3H), 3.15 (s, 3H), 2.35 (m, 1 H), 2.24 (m, 1H), 1.8-1.2 (m, 6H). Spectrum agrees with literature: San Filippo J., Jr.; Anderson, G. M. *J. Org. Chem.* **1974**, *39*, 473-477. Wiberg, K. B.; Cunningham, W.C., Jr. *J. Org Chem.* **1990**, *55*, 679-684.

2,2-Bis-(2,2,2-trifluoroethoxy)norbornane (4.14b). To a flask containing norcamphor (g (45.4 mmol) and *p*-toluenesulfonic acid monohydrate (124 mg, 0.66 mmol) was added 2,2,2-trifluoroethanol (30 mL, 400 mmol) with a syringe. The flask was attached to a reverse Dean-Stark trap containing activated molecular sieves. The mixture was refluxed at 85 °C overnight. A solution of 30 mL of 10% potassium hydroxide in water was added, followed by extraction with 40% pentane in dichloromethane. The extracts were washed with water and brine, and then dried with potassium carbonate. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.9-3.7 (m, 4H), 2.36 (d, J = 3.3, 1H), 2.30 (s, 1H), 1.7-1.2 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): 124.29 (q, J = 277 Hz), 124.10 (q, J = 277 Hz), 112.31, 61.44 (q, J = 35 Hz), 59.56 (q, J = 35 Hz), 43.65, 41.17, 37.3, 36.23, 28.53, 21.72. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -74.34 (t, J = 8.9 Hz), -74.47 (q, J = 8.1 Hz). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{11}H_{14}F_6O_2$, 292.0898; found, 292.0895.

2-Methoxy-norborn-2-ene (4.15a). To a dry flask containing aluminum trichloride (8.5 g, 64 mmol) was added 75 mL anhydrous ether by cannula, followed by addition of triethylamine (12.9 g, 128 mmol) by syringe. After stirring at room temperature for one hour, a solution of 2,2-dimethoxynorbornane (5.0 g, 32 mmol) in 5 mL ether was added via a cannula. The reaction mixture was stirred in a cold water bath overnight, and then stirred with 150 mL of 5N sodium hydroxide solution. The mixture was extracted with ether and dried over potassium carbonate. The oily residue was distilled to yield 3.42 g of 2-methoxy-2-norbonene. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 4.54 (d, *J* = 3.3 Hz, 1H), 3.50 (s, 3H), 2.82 (s, 1 H), 2.68 (s, 1H), 1.8-1.6 (m, 2H), 1.49 (m, 2H), 1.19 (m, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm):167.48, 99.07, 56.20, 47.30, 44.04, 40.87, 28.39, 24.98. Spectra agree with literature (see Ref 32).

Bicyclo[2.2.1]hept-2-en-2-yloxy)trimethyl silane (4.16). To a flask was added norcamphor (3.0 g, 27.2 mmol), 25 mL of n-pentane, triethylamine (3.44 g, 34.0 mmol), and trimethylsilyl chloride (3.70 g, 34.0 mmol). To this flask was slowly added a mixture of sodium iodide (5.11 g, 34.0 mmol) in 45 mL of acetonitrile. The reaction mixture was stirred overnight at room temperature. The pentane layer was removed by cannula, then the mixture extracted with dry n-pentane. Anhydrous potassium carbonate was added to the extracts, and then filtered. The dried solution was concentrated and distilled to 4.42 g (89.1%) of product. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 4.70 (d, *J* = 2.7 Hz, 1H), 2.77 (m, 1H), 2.57 (m, 1H), 1.68 (m, 2H), 1.48 (dm, *J* = 8.1 Hz, 1H), 2.12 (m, 2H), 1.04 (dd, *J* = 1.8, 7.2 Hz, 2H), 0.20 (m, 9H). Spectrum matches literature: Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075-2083.

3-[2,2,2-Trifluoro-1-trifluoromethyl-1-(trimethylsilanyloxyl)-ethyl]-bicyclo[2.2.1]heptan-2-one (4.17). A modified version of the synthetic procedure of Burger and Helmreich was used. To a pressure reaction vessel was added a solution of bicyclo[2.2.1]hept-2-en-2-yloxy)trimethyl silane (2.0 g, 10.9 mmol) in 10 mL of dichloromethane. A regulator was attached and the system degassed. Hexafluoroacetone was added to reach a pressure of 20 psi, and added each time the pressure dropped. When the pressure remained constant for 10 minutes, the reaction was

quenched with 30 mL of ice water. The reaction mixture was extracted with dichloromethane, and the organic extracts were washed with first water and then brine. The extracts were dried over magnesium sulfate and concentrated, then dried over potassium carbonate and concentrated to recover 2.94 g (77.4%) of a 1.9:1.3:1.0 mixture of **4.17**:**4.13**:**4.18**. 3-[2,2,2-Trifluoro-1-trifluoromethyl-1-(trimethylsilanyloxyl)-ethyl]-bicyclo[2.2.1]heptan-2-one (**4.17**): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.95 (s, 1H), 2.62 (s, 1H), 2.30 (d, J = 3.3 Hz, 1H), 2.0-1.2 (m, 6H), 0.23 (m, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.91 (q, 3H), -73.36 (q, 3H). 2-trimethylsiloxy-4,4-bis-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]nonane (**4.18**): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.53 (s, 1H), 2.30 (d, J = 3.3 Hz, 1H), 2.14(s, 1H), 2.11 (s, 1H), 2.0-1.2 (m, 6H), 0.21 (m, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -67.38 (q, 3H), -76.82 (q, 3H).

References and Notes

(1) (a). Patterson, K.; Yamachika, M.; Hung, R. J.; Brodsky, C. J.; Yamada, S.; Somervell, M. H.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G. *Proc. SPIE* **2000**, *3999*, 365-374. (b). Brodsky, C.; Byers, J.; Conley, W.; Hung, R.; Yamada, S.; Patterson, K.; Somervell, M.; Trinque, B.; Tran, H. V.; Cho, S.; Chiba, T.; Lin, S-H.; Jamieson, A.; Johnson, H.; Vander Heyden, T.; Willson, C. G. *J. Vac. Sci. Technol.* B **2000**, *18*, 3396-3401.

(2) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937-51.

(3) (a). Ito, H. *IBM J. Res. Dev.* **2001**, *45*, 683-695. (b). Hoskins, T.; Chung, W. J.; Agrawal, A.; Ludovice, P. J.; Henderson, C. L.; Seger, L. D.; Rhodes, L. F.; Shick, R. A. *Macromolecules* **2004**, *37*, 4512-4518.

(4) (a). Trinque, B. C.; Chambers, C. R.; Osborn, B. P.; Callahan, R. P.; Lee, G. S.; Kusumoto, S.; Sanders, D. P.; Grubbs, R. H.; Conley, W. E.; Willson, C. G. *J. Fluor. Chem.* **2003**, *122*, 17-26. (b). Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y-T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; MacDonald, S. A.; Willson,

C. G.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W. *Macromolecules* **2002**, *35*, 6539-6549. (c). Willson, C. G.; Trinque, B. C.; Osborn, B. P.; Chambers, C. R.; Hsieh, Y-T.; Chiba, T.; Zimmerman, P.; Miller, D.; Conley, W. *J. Photopolym. Sci. Technol.* **2002**, *15*, 583-590. (d). Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y-T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W.; MacDonald, S. A.; Willson, C. G. *J. Photopolym. Sci. Technol.* **2001**, *14*, 669-674. (e). Chiba, T.; Hung, R. J.; Yamada, S.; Trinque, B.; Yamachika, M.; Brodsky, C.; Patterson, K.; Vander Heyden, A.; Jamison, A.; Lin, S-H.; Somervell, M.; Byers, J.; Conley, W; Willson, C. G. *J. Photopolym. Sci. Technol.* **2000**, *13*, 657-664.

(5) (a). Ito, H.; Wallraff, G. M.; Brock, P. J.; Fender, N.; T., Hoa D.; Breyta, G.; Miller, D. C.; Sherwood, M. H.; Allen, R. D. *Proc. SPIE* **2001**, *4345*, 273-284. (b). Trinque, B. C.; Chiba, T.; Hung, R. J.; Chambers, C. R.; Pinnow, M. J.; Osborn, B. P.; Tran, H. V.; Wunderlich, J.; Hsieh, Y-T.; Thomas, B. H.; Shafer, G.; DesMarteau, D. D.; Conley, W.; Willson, C. G. *J. Vac. Sci. & Technol. B*. **2002**, *20*, 531-536. (c). Trinque, B. C.; Osborn, B. P.; Chambers, C. R.; Hsieh, Y-T.; Corry, S. B.; Chiba, T.; Hung, Raymond J-P.; Tran, H. V.; Zimmerman, P.; Miller, D.; Conley, W.; Willson, C. G. *Proc. SPIE* **2002**, *4690*, 58-68.

(6) (a). Kodama, S.; Kaneko, I.; Takebe, Y.; Okada, S.; Kawaguchi, Y.; Shida, N.; Ishikawa, S.; Toriumi, M.; Itani, T. *Proc. SPIE* **2002**, *4690*, 76-83. (b). Irie, S.; Ishikawa, S.; Hagiwara, T.; Yamazaki, T.; Furukawa, T.; Itani, T.; Kawaguchi, Y.; Kodama, S.; Yokokoji, O.; Kaneko, I.; Takebe, Y.; Okada, S. *Jap. J. Appl. Phys. Pt. 1*. **2003**, *42*(6B), 3743-3747.

(7) (a). Feiring, A. E.; Crawford, M.; Feldman, J.; Farnham, W. B.; Feldman, J.; French, R. H.; Leffew, K. W.; Petrov, V. A.; Schadt, F. L., III; Whelanad, R.C.; Zumsteg, F. C. *J. Fluorine Chem.* **2003**, *122*, 11-16. (b). Toriumi, M.; Ishikawa, T.; Kodani, T.; Koh, M.;

Moriya, T.; Araki, T.; Aoyama, H.; Yamashita, T.; Yamazaki, T.; Itani, T.; *J. Photopolym. Sci. Technol.* **2003**, *16*, 607-614. (c). Sharif, I.; DesMarteau, D.; Ford, L.; Shafer, G. J.; Thomas, B.; Conley, W.; Zimmerman, P.; Miller, D.; Lee, G. S.; Chambers, C. R.; Trinque, B. C.; Chiba, T.; Osborn, B. P.; Willson, C. G. *Proc. SPIE* **2003**, *5039*, 33-42.

(8) (a). Bae, Y. C.; Douki, K.; Yu, T.; Dai, J.; Schmaljohann, D.; Koerner, H.; Ober, C. K.; Conley, W. *Chem. Mater.* **2002**, *14*, 1306-1313. (b). Schmaljohann, D.; Young, C. B.; Dai, J.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *J. Photopolym. Sci. Technol.* **2000**, *13*, 451-458.

(9) (a). Stewart, M. D.; Patterson, K.; Sommervell, M. H.; Willson, C. G. *J. Phys. Org. Chem.* **2000**, *13*, 767-774. (b). Ito, H. *IBM J. Res. Dev.* **2000**, *44*, 119-130. (b). MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151-158.

(10) (a). Bloomstein, T. M.; Sedlacek, Jan H. C.; Palmacci, Stephen T.; Hardy, D. E.; Liberman, V.; Rothschild, M. *Proc. SPIE* **2003**, *5040*, 650-661. (b). Rothschild, M.; Bloomstein, T. M.; Fedynyshyn, T. H.; Liberman, V.; Mowers, W.; Sinta, R.; Switkes, M.; Grenville, A.; Orvek, K. *J. Fluorine Chem.* **2003**, *122*, 3-10. (c). Matsui, Y.; Umeda, S.; Seki, S.; Tagawa, S.; Ishikawa, S.; Itani, T. *Jap. J. Appl. Phys., Pt. 1*. **2003**, *42*(6B), 3894-3899. (d). Hien, S.; Angood, S.; Ashworth, D.; Basset, S.; Bloomstein, T. M.; Dean, K. R.; Kunz, R. R.; Miller, D. A.; Patel, S.; Rich, G. *Proc. SPIE* **2001**, *4345*, 439-447. (e). Fedynyshyn, T. H.; Kunz, R. R.; Sinta, R. F.; Goodman, R. B.; Doran, S. P. *J. Vac. Sci. Technol.* B **2000**, *18*, 3332-3339. (f). Cefalas, A. C.; Sarantopoulou, E.; Gogolides, E.; Argitis, P. *Microelectronic Eng.* **2000**, *53*, 123-126.

(11) (a). Pinnow, M. J.; Noyes, B. F., III; Tran, H. V.; Tattersall, P. I.; Cho, S.; Klopp, J. M.; Bensel, N.; Frechet, J. M. J.; Sanders, D. P.; Grubbs, R. H.; Willson, C. Grant. *PMSE Prepr.* ***2002***, *87*, 403-404. (b). Klopp, J. M.; Bensel, N.; Fresco, Z. M.; Frechet, J. M. J. *Chem. Comm.* **2002**, *24*, 2956-2957. (c). Kim, J-B.; Lee, J-J. *Polymer* **2002**, *43*, 1963-1967.

(12) Tarrant, P.; Bull, R. N. *J. Fluorine Chem.* **1988**, *40*, 201-215.

(13) (a). Papadopoulos, M.; Jost, R.; Jenner, G. *J. Chem. Soc., Chem. Comm.* **1983**, *5*, 221-222. (b). Papadopoulos, M.; Jenner, G. *Nouv. J. Chim.* **1984**, *8*, 729-732. (c). Jenner, G.; Papadopoulos, M. *Tetrahedron Lett.* **1985**, *26*, 725-726. (d). Jenner, G.; Papadopoulos, M. *Physica* **1986**, *139-140*, 729-731.

(14) Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Hung, R. J.; Osborn, B. P.; Chiba, T.; MacDonald, S. A.; Willson, C. G.; Conley, W. *Macromolecules* **2003**, *36*, 1534-1542.

(15) Recently, DuPont independently published the cycloaddition of fluorinated ketones with quadricyclane. (a). Petrov, V. A.; Davidson, F.; Smart, B. E. *J. Fluor. Chem.* **2004**, *125*, 1543-1552. (b). Feiring, A. E.; Schadt, F. L., III.; Petrov, V. A.; Smart, B. E.; Farnham, W. B. *PCT Int. Appl. WO 2004/014960*, **2004**.

(16) Patterson, V. A. *J. Org. Chem.* **1969**, *34*, 3650-3651.

(17) Hexafluoroacetone readily undergoes a Diels-Alder reaction with cyclopentadiene; however, the resulting adduct retrocyclizes at room temperature. (a). Linn, W. J. *J. Org. Chem.* **1964**, *29*, 3111-3114. (b). Martynov, B. I., Lantseva, L. T.; Dyatkin, B. L. *Zhurnal Organicheskoi Khimii* **1975**, *11*, 2282-2285.

(18) (a). Gorman, A. A.; Leyland, R. L. *Tetrahedron Lett.* **1972**, *52*, 5345-5348. (b). Kubota, T.; Shima, K.; Sakurai, H. *Chem. Lett.* **1972**, *5*, 343-346. (c). Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Parekh, C. T.; Smith, P. G. *Tetrahedron* **1980**, *36*, 397-407.

(19) Homo-endo adduct **4.3a** was independently synthesized in modest yield via the extended heating of norbornadiene in the presence of hexafluoroacetone (see experimental section).

(20) UV irradiation, weak Bronsted acidic conditions (acetic acid), and elevated temperatures were ineffective in accelerating the formation of the new compound.

(21) Compound **4.5a** displays the opposite regiochemistry of compounds formed via photochemical reactions of aromatic ketones with norbornadiene (such as 4,4-diphenyl-5-

oxa-tricyclo[4.3.$0^{1,6}$.$0^{3,7}$]non-8-ene) in which the oxygen is attached to the single carbon bridge.[17]

(22) Adames, G.; Bibby, C.; Grigg, R. *J. Chem. Soc., Chem. Commun.* **1972**, *8*, 491-492.

(23) Lewis acid-catalyzed ring expansions of oxetanes have been reported in the literature. Carless, H. A. J.; Trivedi, H. S.; *J. Chem. Soc., Chem. Comm.* **1979**, *8*, 382-383.

(24) A similar ring expansion has been reported in the literature for norbornene oxide,[25] although the conversion of an epoxide to an oxetane is less energetically favorable. Kas'jan, L. A.; Gnedenko, L. Y.; Galafeeva, M. F.; Kornilov, M. Y.; Krasutsky, P. A.; Averina, N. V.; Zefirov, N. S. *Tetrahedron Lett.* **1986**, *27*, 2921-2922.

(25) Similar Lewis-acid catalyzed rearrangements are likely responsible for the formation of other 4-oxatricyclo[4.3.$0^{1,6}$.$0^{3,7}$]non-8-enes (a). von Hans Fritz, C. D. W.; Winkler, T. *Helv. Chim. Acta* **1975**, *58*, 1345-1357. (b). Becherer, J.; Hauel, N.; Hoffmann, R. W. *Justus Liebigs Ann. Chem.* **1978**, *2*, 312-19.

(26) Tarrant, P.; Bull, R. N. *J. Fluor. Chem.* **1998**, *40*, 201-215.

(27) (a). Pattison, V. A. *J. Org. Chem.* 1969, *34*, 3650-3651. (b). Gambaryan, N. P.; Rokhlin, E. M.; Zeifman, Y. V.; Ching-Yun, C.; Knunyants, I. L. *Angew. Chem. Int. Ed.* **1966**, *5*, 947-956.

(28) (a). Gambaryan, N. P.; Simonyan, L. A.; Petrovskii, P. V. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1967**, 886-888. (b). Karakhanov, E. A.; Lysenko, S. V.; Kovaleva, N. F.; Brezhnev, L. Yu.; Glukhovtsev, V. G.; Karakhanov, R. A. *Moscow Universitet. A.* **1982**, *23*, 159-163.

(29) (a). Patton, J. R. *Ph.D. Dissertation* University of Florida, **1974**. (b). Davis, H. R. *US Pat. 3,169,610*, **1964**.

(30) Fresco, Z. M.; Bensel, N.; Suez, I.; Backer, S. A.; Frechet, J. M. J.; Conley, W. *J. Photopolym. Sci. Technol* **2003**, *16*, 27-36.

(31) Kirby, A. J.; Ryder, H.; Matasa, V. *J. Chem. Soc. Perkin Trans. 2* **1990**, *5*, 825-831.

(32) Barbot, F.; Miginiac, P. *Helvetica Chimica Acta* **1979**, *62*, 1451-1457.

(33) Gassman, P. G.; Burns, S. J.; Pfister, K. B. *J. Org. Chem.* **1993**, *58*, 1449-1457.

(34) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437-6445.

(35) Burger, K.; Helmreich, B. *J. Prakt. Chem.* **1992**, *334*, 219-226.

(36) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K. Trimmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

(37) Quadricyclane (tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane) can be synthesized photochemically from norbornadiene. (a). Hammond, G. S.; Turro, N. J.; Fischer, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674-4675. (b). Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532-2533. (c). Smith, C. D.; Taggi, A. J.; Meinwald, J. *Org. Synth.* **1971**, *51*, 133-138. (d). Alberici, F.; Cassar, L.; Monti, F.; Neri, C.; Nodarai, N. *US Pat. 5076813*, **1991**.

(38) Kinkead, E. R.; Wolfe, R. E.; Salins, S. A.; Grabau, J. H. Report (1993), (Order No. AD-A272694). CAN 123:190700.

(39) Everett, T. S. In *ACS Monograph*, vol. 187(*Chemistry of Organic Fluorine Compounds II*), American Chemical Society: Washington, D.C. **1995**, pp. 1037-1086.