CHAPTER 2

Development of Fluorinated Tricyclononenes: Transparent, Ester-Functionalized Monomers for 157 nm Lithography

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Abstract While metal-catalyzed addition polymers of ester-functionalized norbornenes have the high etch-resistance and glass transition temperatures required for photoresist polymers, they absorb too heavily to be useful for 157 nm lithography. The incorporation of a geminal trifluoromethyl group, while dramatically increasing transparency, renders the monomer unreactive towards metal-catalyzed addition polymerization. The exo-configuration of the additional cyclobutane ring in tricyclo[4.2.1.$0^{2,5}$]non-7-enes serves as a scaffold suitable for the incorporation of additional fluorinated substituents while reducing the steric and electronic effects of these groups on the subsequent polymerization. Novel fluorinated tricyclononene-3-carboxylic acid esters are synthesized via the cycloaddition of quadricyclane with a number of fluorinated acrylic acid esters. Fluorinated tricyclononane esters possess enhanced transparencies at 157 nm relative to non-fluorinated norbornane analogues as determined by gas phase vacuum-ultraviolet (V-UV) spectroscopy. Further extension of this approach to the synthesis of hexafluorocarbinol-functionalized tricyclononenes is limited by the isomerization of quadricyclane to norbornadiene at higher temperatures. As a result, cycloaddition with less reactive dienophiles such as 1-acetoxy-1-trifluoromethyl-ethene is unsuccessful. Additionally, reaction with unsaturated hexafluorocarbinols results in the exclusive formation of norbornenyl ethers.

Introduction

Specialized, alicyclic fluoropolymers are the focus of intense research as the semiconductor industry attempts to develop the functional photoresists required to enable the timely introduction of 157 nm optical lithography, as outlined in the International Technical Roadmap for Semiconductors (ITRS) timeline.[1,2] A prominent concern for 157 nm lithography is the feasibility of employing a practical resist thickness (> 200 nm), which requires a photoresist

with a low absorption coefficient.[3] In order to fulfill this requirement while retaining optimal imaging properties, a critical balance of several, often competing, material properties, such as transparency, etch resistance, glass transition temperature, thermal stability, and dissolution behavior must be achieved. Carbon-rich and heteroatom-deficient norbornene structures such as the norbornene *t*-butyl ester (NTBE, **2.1**, Figure 2.1) were developed for use at 193 nm, proving to be suitable replacements for the heavily absorbing, etch-resistant aromatics used in previous generations of photoresists. Unfortunately, while the majority of the polar functionalities (esters, carbonates, alcohols, and anhydrides) used in resist chemistry are transparent at 193 nm, the absorption coefficients of carbon-carbon double bonds, carbon-oxygen single bonds, carbon-oxygen double bonds, and even some carbon-hydrogen bonds are all too high at 157 nm for these functionalities to be useful.[4]

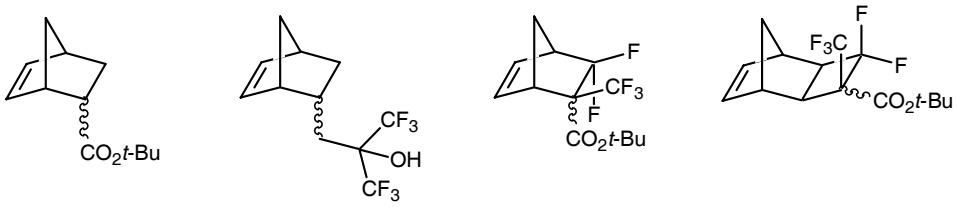
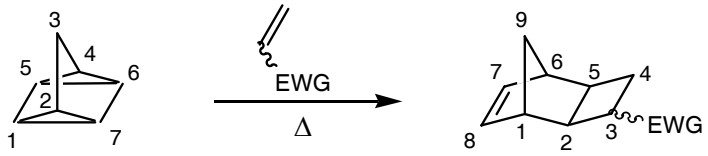


Figure 2.1. Norbornene-type monomers for lithographic applications

Fortunately, through computational[5] and experimental[6] efforts, it was discovered that the incorporation of fluorinated substituents dramatically reduces the absorption of various structures at 157 nm. For example, the hexafluoroisopropyl alcohol functionalized norbornene (NBHFA, **2.2**) was found to be highly transparent.[6] In addition, due to the inductive effects of the two trifluoromethyl groups, the acidity of the this type of fluorinated alcohol is similar to phenol,[7] allowing this polar monomer to replace the highly absorbing phenolic structures used in previous generations of resists. This discovery has renewed interest in resists based on metal-catalyzed addition polymers of functionalized norbornenes, originally developed for 193 nm,[8] as promising

candidates for 157 nm photoresists. Protection of the hexafluoroisopropyl alcohol functionality of **2** with *t*-BOC groups has produced monomers suitable for resist development.[6] Efforts to expand the scope of 157 nm resists to include those based on the more thermally stable *t*-butyl and tetrahydropyranyl esters have achieved only partial success due to the high absorbance of ester-functionalized monomers such as **2.1** at 157 nm. Fortunately, the incorporation of an α-trifluoromethyl group was found to significantly reduce the absorption of these esters.[6] Similarly, the absorbance of norbornane structures could be reduced by the incorporation of judiciously positioned fluorine substituents.[6] The fluorinated monomer **2.3** was subsequently designed as an ideal replacement for the highly absorbing norbornene **2.1**. Unfortunately, norbornene monomers of this type with geminal electron-withdrawing ester and trifluoromethyl substituents were found to be unsuitable for polymerization with common nickel and palladium catalysts.[9] The addition of an α-trifluoromethyl group in **2.3**, while addressing the transparency problem, hinders the polymerization. Thus, alternative approaches towards a polymerizeable monomer incorporating these transparent esters were investigated.

Recently, Grubbs *et al.* reported that, in the copolymerization of ethylene and functionalized norbornene-type monomers to produce functionalized polyethylene, high incorporation (up to 31 mol %) of polar functionalities could be achieved through the use of functionalized tricyclo[4.2.1.$0^{2,5}$]non-7-ene (TCN) monomers.[10] The combination of reduced steric interference due to the 100% exo configuration of the cyclobutane ring (moving the geminal electron-withdrawing functionalities an additional carbon away from the double bond) and increased ring strain improved the reactivity of the tricyclononene monomers towards metal-catalyzed addition polymerization. The use of TCN chemistry in photoresists is a potential solution to the polymerization difficulties of the partially fluorinated norbornenes mentioned previously.



Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (Quadricyclane)

3-EWG-tricyclo[4.2.1.0^{2,5}]non-7-ene

Figure 2.2. Cyclizations of quadricyclane with electron deficient olefins (EWG = electron withdrawing group)

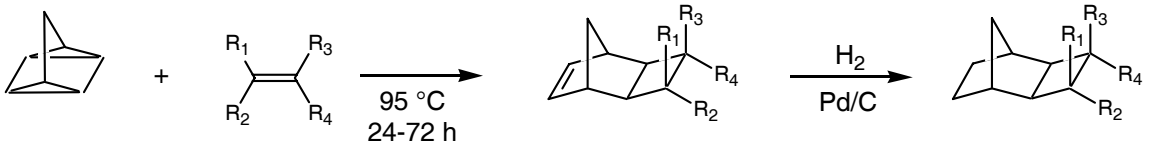
Tricyclo[4.2.1.0^{2,5}]non-7-enes (TCNs) are formed from the [2σ + 2 σ + 2π] cycloaddition of quadricyclane (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane) with electron deficient dienophiles such as alkenes, alkynes, and azo compounds (Figure 2.2).[11,12] The cycloadditions proceed readily at moderate temperature with electron-deficient olefins to produce norbornene-like structures with a fused cyclobutane ring in the exo configuration. While the allowed thermal homo-Diels-Alder [2π + 2π + 2π] reaction between norbornadiene and electron deficient olefins[13] can be catalyzed by nickel and cobalt species[14] to produce deltacyclanes, in certain cases, metal-catalyzed [2π + 2π] cycloadditions can also occur to produce a mixture of tricyclononenes in which the cyclobutane ring appears be in either the exo or the endo configuration.[14b,15] Unfortunately, the tri- and tetra-substituted double bonds of the resulting tricyclononenes,[16] coupled with the complex mixture of exo and endo isomers, renders this route unattractive for the production of valuable monomers. At present, the quadricyclane pathway is the only viable synthetic route towards TCN monomers suitable for metal-catalyzed addition polymerization.

The wide variety of electron-withdrawing groups (nitriles, anhydrides, esters, etc.) able to undergo cyclizations with quadricyclane allows TCNs to retain the versatility of established norbornene chemistry. While most reports of TCN chemistry to date have investigated the regio- and stereospecificity[11] and concertedness of the cyclization reaction,[17] the value of photoresist materials prompted us to consider these compounds for materials development. In this chapter, we report the development of partially fluorinated tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylic acid

esters, such as monomer **2.4**, as transparent, ester-functionalized norbornene-like monomers useful for incorporation into addition-type photoresist polymers.

Results and Discussion

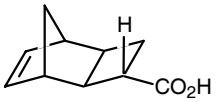
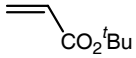
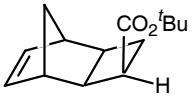
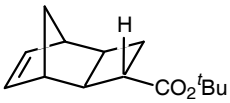
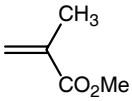
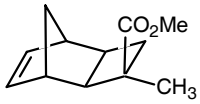
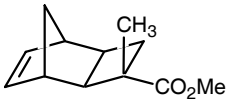
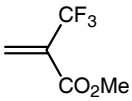
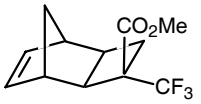
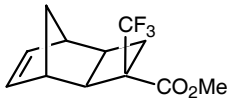
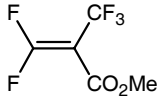
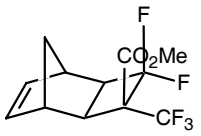
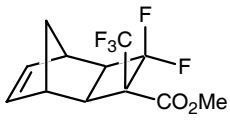
Synthesis of TCN Monomers A series of tricyclononene compounds (**2.5-2.9**, Table 2.1) were synthesized from quadricyclane and the appropriate olefin as shown in Figure 2.3. The numbering system and nomenclature used is shown in Figure 2.2 and Table 2.1, respectively. The methylene bridge (C9) hydrogens will be referred to as either syn or anti to the C(7)-C(8) olefin. The most important substituent (nitrile or ester) at C(3) on the cyclobutane ring will be referred to as being syn or anti to the C(1)-C(2) bond, to avoid confusion with the exo notation used to describe the cyclobutane ring fusion. Since the majority of TCN compounds reported in the literature[11] were made from symmetrical 1,1- or 1,2-disubstituted olefins, less is known about the resultant TCN isomer distribution produced using non-symmetrical 1,1-disubstituted olefins. Particular attention will be paid to the syn/anti isomer distribution as it may significantly affect the rate of polymerization and/or incorporation ratio in copolymerizations. The syn/anti isomer distributions produced by the quadricyclane cyclizations will be compared with the more familiar exo/endo isomer distributions achieved by Diels-Alder reactions with cyclopentadiene. Finally, while esters with readily removable *t*-butyl or cyclic acetal protecting groups are required for use as imageable photoresists, the more synthetically and commercially accessible methyl esters of



R_1,R_2 = H R_3 = H	R_4 = CO_2H	**2.5**	35 % (2 steps from nitrile)
R_1,R_2 = H R_3 = H	R_4 = $CO_2{}^tBu$	**2.6**	80 %
R_1,R_2 = H R_3 = CH_3	R_4 = CO_2Me	**2.7**	8 %
R_1,R_2 = F R_3 = CF_3	R_4 = CO_2Me	**2.8**	94 %
R_1,R_2 = F R_3 = CF_3	R_4 = CO_2Me	**2.9**	73 %

Figure 2.3. Synthesis of tricyclononene monomers and model compounds

Table 2.1. Selectivity in TCN monomer synthesis

Olefin	TCN Products		
	syn		anti
			
	2 %	**2.5***	98 %
			
	57 %	**2.6**	43 %
			
	55 %	**2.7**	45 %
			
	32 %	**2.8**	68 %
			
	49 %	**2.9**	51 %

* After hydrolysis of nitrile

the fluorinated acrylates were employed in this initial study.

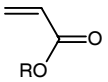
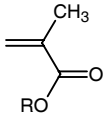
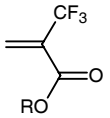
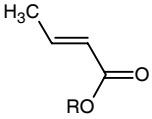
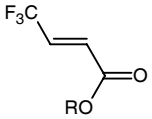
The nitrile-functionalized TCN monomer was synthesized by the cycloaddition of quadricyclane and acrylonitrile using the procedure of Noyori[18] to produce 3-cyano-tricyclo[4.2.1.$0^{2,5}$]non-7-ene with a 2:1 syn:anti ratio and 100% exo cyclobutane ring fusion. Subsequent base catalyzed hydrolysis of the nitrile afforded the carboxylic acid (**2.5**) with a syn:anti ratio of approximately 2:98. During the hydrolysis, epimerization around the C(3)

position converts the syn isomer into the more stable anti isomer, consistent with the results of Tabushi *et al*.[11e] regarding the base-catalyzed isomerization of cis and trans di-ester and di-nitrile-substituted tricyclononenes.

Cycloaddition of quadricyclane with acrylonitrile or *t*-butyl acrylate produced high yields (80%+ with respect to quadricyclane) of TCN products with a preference for the syn product. While this syn structure is formed via a transition state with the maximal orbital overlap on C(2) and C(4) of quadricyclane as is the case in Diels-Alder reactions, the role of electrostatic effects or intermolecular attractive forces remains unknown. The predominant by-products of the reaction are norbornadiene formed by slow isomerization of quadricyclane under the reaction conditions and acrylate or acrylonitrile homopolymer.[19]

t-Butyl methacrylate and methacrylonitrile also undergo cyclizations with quadricyclane, albeit in dramatically reduced yields (~8 % for *t*-butyl methacrylate).[20] Interestingly, no appreciable difference in the syn/anti ratio is observed despite the introduction of the α-methyl group. This is in direct contrast to the cycloaddition behavior of cyclopentadiene, as shown in Table 2.2. In cycloadditions with cyclopentadiene, the presence of an α-methyl group on an acrylate induces a preference for the exo isomer (~70% exo v. ~30% exo for acrylate), while a trans β-methyl group has only a small effect.[21] This deviation from endo selectivity has been attributed either to steric interference between the α-methyl group and the methylene hydrogens of cyclopentadiene or secondary attractive forces between the methyl and the unsaturated carbons.[21] Since the transition state in the quadricyclane cycloaddition is centered on C(6) and C(7) (Figure 2.2), steric interference by the C-3 methylene hydrogens appears to be minimal as exhibited in the small effect on the syn/anti ratio upon incorporation of the α-methyl group (**2.6** and **2.7,** Table 2.1).

Table 2.2. Comparison of cyclopentadiene and quadricyclane cycloadditions

Olefin	Cyclopentadiene (% endo, 25 °C)	Cyclopentadiene (% endo, 100 °C)	Quadricyclane (% syn, 97 °C)
	74.3 (R = Me)[21c]	70.5 (R = Me)[21c]	57 (R = ^{t}Bu)
	30.1 (R = Me)[21c]	31.8 (R = Me)[21c]	55 (R = ^{t}Bu)
	67 (R = Me)[25]		32 (R = Me)
	50.9 (R = Me)[21c]	50.8 (R = Me)[21c]	
	26.3 (R = Me)[24d]		

Cyclization of quadricyclane with methyl 2-(trifluoromethyl)acrylate proceeded nearly quantitatively by ^{1}H NMR to produce **2.8** in 94% isolated yield after 72 hours. The inability of the fluorinated methacrylate to undergo radical homopolymerization prevents it from being consumed in the production of polymeric by-products, leading to a high yield. The facile cycloaddition is consistent with the observed behavior of olefins with trifluoromethyl substituents in 1,3-dipolar[22] and Diels-Alder cycloaddition reactions.[23] Unlike the previous acrylate and methacrylate cyclizations, this reaction produced predominantly the anti product (syn/anti = 32:68), similar to the cycloaddition of cyclopentadiene and either *trans*-crotonic acid or *trans*-4,4,4-trifluorocrotonic acid (Table 2.2).[24] In contrast, the cycloaddition of 2-(trifluoromethyl)acrylic acid with cyclopentadiene exhibits little change in exo/endo preference relative to acrylic acid.[25] Since the trifluoromethyl group is more sterically bulky than a methyl

group (being more similar to an isopropyl group),[26] the high yield in the cyclization with the methyl 2-(trifluoromethyl)acrylate (unlike the cyclizations with *t*-butyl methacrylate or methacrylonitrile) demonstrates the importance of the electronics of the dienophile in cyclizations with quadricyclane.

Unfortunately, the cyclization with the methyl 3,3-difluoro-2-(trifluoromethyl)acrylate produced only a moderate yield (~25%) of TCN **2.9** after 72 hours. This was in distinct contrast to the excellent yields obtained in the Diels-Alder reaction of this perfluorinated olefin with cyclopentadiene. The yield was increased to 73% upon allowing the reaction mixture to continue at room temperature for several days. This is similar to some cycloadditions with furan in which high yields are observed after long reaction times at room temperature.[27] Further work is required to explain the reluctance of this fluorinated methacrylate to undergo cyclization with quadricyclane.

Assignment of TCN Isomers As previously mentioned, little has been published on TCN compounds obtained from non-symmetric 1,1-disubstituted olefins. Therefore, we endeavored to find a simple diagnostic to determine the isomeric product distribution in these compounds. Fortunately, due to epimerization during the hydrolysis reaction, the TCN carboxylic acid (**2.5**) is almost exclusively the anti isomer. ^{1}H, ^{13}C, ^{13}C DEPT, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C HMQC and HETCOR NMR experiments were used to assign the carbon and proton resonances in this compound. The spectra were compared with the available published spectral data[10e,16,27] for other tricyclo[4.2.1.0^{2,5}]non-7-ene compounds. The exo configuration of the cyclobutane ring fusion was established by the W-coupling between H(9$_{syn}$) and H(2) and H(5) (^{4}J = 1.7 Hz), that is similar to the reported values for *exo*-3-thiatricyclo[4.2.1.0^{2,5}]non-7-ene-3,3-dioxide.[28]

The bridgehead protons H(1) and H(6) each appear as distinct unresolved multiplets with the H(1) proton appearing about 0.08 ppm downfield from H(6). The $\Delta\delta$ for H(1)-H(6) is diagnostic of syn and anti due to deshielding by the nearby substituents on C(3). For example, in the t-butyl ester TCN compound (**2.6**), H(6) of both the syn and anti isomer are identical;

however, while H(1) of the anti isomer appears 0.07 ppm downfield of H(6), H(1) of the syn isomer is shifted 0.27 ppm downfield due to closer proximity of the ester group, in agreement with the reported NMR assignments for the isolated anti isomer of **2.6**.[10] Since the bridgehead hydrogens in TCNs **2.5-2.9** appear between 2.5 and 3.6 ppm (well resolved from each other and the other protons in these compounds) and agree with the integration of the protons belonging to any ester substituents for the corresponding isomer, the isomer ratio for each compound was determined by integration of the H(1) and H(6) bridgehead protons.

The hydrolysis of the fluorinated TCN methyl ester (**2.9**) produced a mixture of carboxylic acid isomers, one of which was isolated by crystallization. X-ray crystallographic analysis revealed that this isomer is the *syn* compound (**2.10**, Figure 2.4). The crystal structure of **2.10** is similar to that of an imide-functionalized TCN structure reported in the literature.[29] From the crystal structure, the proximity of the carboxylic acid in the syn position to the bridgehead H(1) proton (responsible for significant deshielding of the proton) is apparent. The crystal structure and NMR data from the *syn* isomer of the fluorinated TCN carboxylic acid (**2.10**) complement the NMR data from the anti isomer of the non-fluorinated TCN carboxylic acid

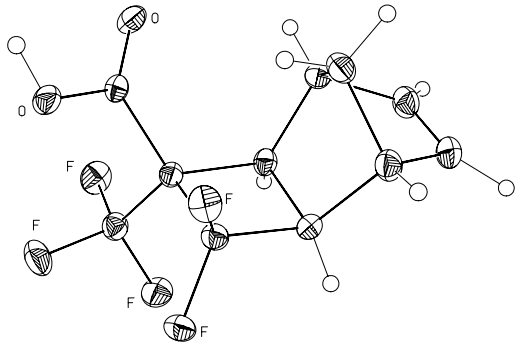


Figure 2.4. X-ray crystal structure of the carboxylic acid **2.10**
Displacement ellipsoids are scaled to the 30% probability level.
Hydrogen atoms are drawn to an arbitrary size.

(**2.5**), confirming the assignments of the isomers and the validity of using the Δδ for H(1)-H(6) as a diagnostic.

Synthesis of Saturated TCN Compounds The first concern with these TCN monomers was preservation of the transparency demonstrated in the analogous norbornane structures. It was unknown whether the addition of the fused cyclobutane ring would pose any absorbance problems at 157 nm, similar to those of cyclopropane rings in nortricyclane-based polymers at 193 nm.[30] To investigate this, several tricyclononane compounds were produced by hydrogenating the double bonds of various TCN monomers. Gas-phase vacuum ultraviolet (VUV) spectra of the fluorinated tricyclononane compounds shown in Figure 2.5 reveal promising transparency. In fact, the saturated version of **2.9** exhibits even higher transparency than norbornane. While still more heavily absorbing than 2,2-difluoronorbornane (one of the most transparent norbornanes at 157 nm discovered to date), these results are encouraging enough

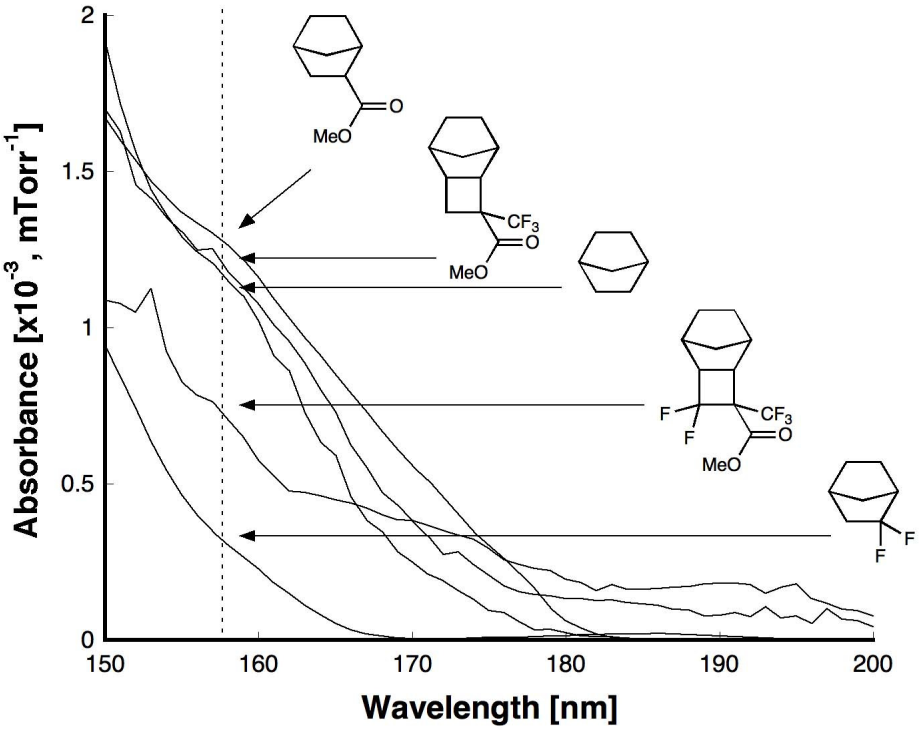


Figure 2.5. Vacuum UV spectra of model tricyclononane structures

to warrant additional experimental verification of transparency through the synthesis of TCN addition polymers for analysis by variable angle spectroscopic ellipsometry (VASE)[31]. The additional cyclobutane ring of the TCN monomer produces only a small increase in absorbance at 157 nm which can be more than compensated for by the incorporation of additional fluorinated groups as shown in Figure 2.6. It should be noted that the lower volatilities of some of the TCN compounds results in the lower signal to noise ratios of the spectra shown in Figures 2.5 and 2.6. Therefore, VASE analysis of TCN homopolymers may be a more accurate determination of the effect of fluorination and the additional cyclobutane ring on the transparency at 157 nm.

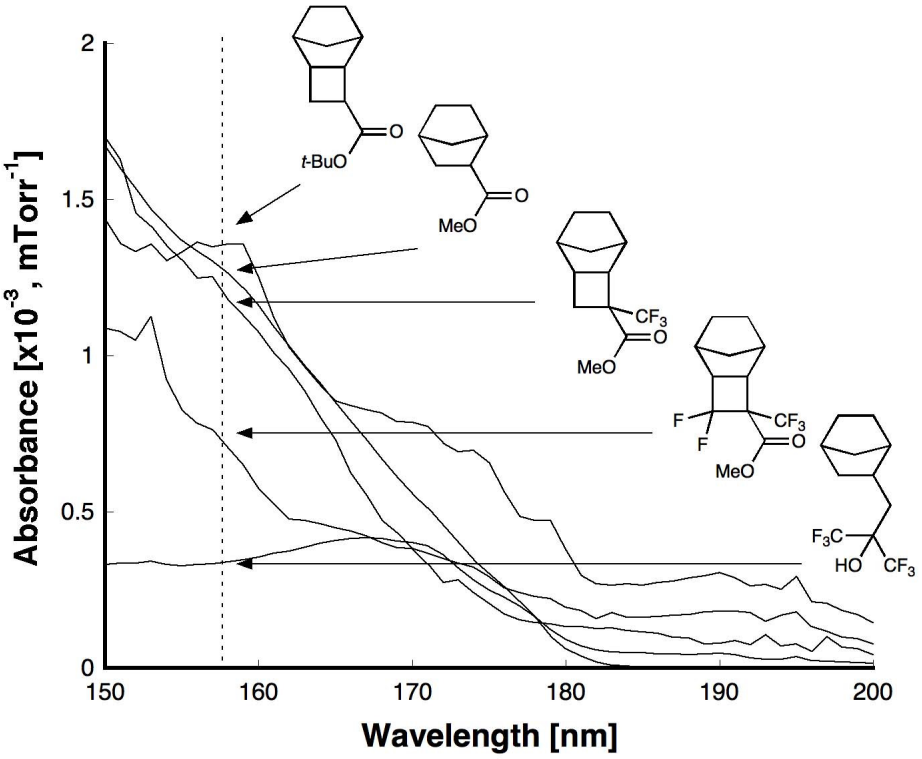


Figure 2.6. Vacuum UV spectra of model tricyclononane structures

Attempted Synthesis of Hexafluorocarbinol-functionalized Tricyclononenes

Given the high transparency of **2.1**, the incorporation of additional fluorine was expected to offer additional transparency enhancements;[6b] however, the more fluorinated analogues **2.11**

and **2.12** were shown to be more absorbing and unreactive towards metal-catalyzed addition polymerization.[32] Similarly, the trifluorocarbinol **2.13** and pentafluorocarbinol **2.14** are easily synthesized via the Diels-Alder reaction with the corresponding vinyl acetate followed by hydrolysis.[6a,33] While alcohol **2.13** does not have sufficient acidity or transparency to be useful, **2.14** offers sufficient acidity and high transparency. Since the additional cyclobutane ring of the TCN framework has little effect on the absorbance at 157 nm and results in superior activity towards metal-catalyzed addition, we sought to synthesize hexafluorocarbinol-functionalized TCN analogues of **2.12 – 2.14**, such as **2.15** and **2.16**.

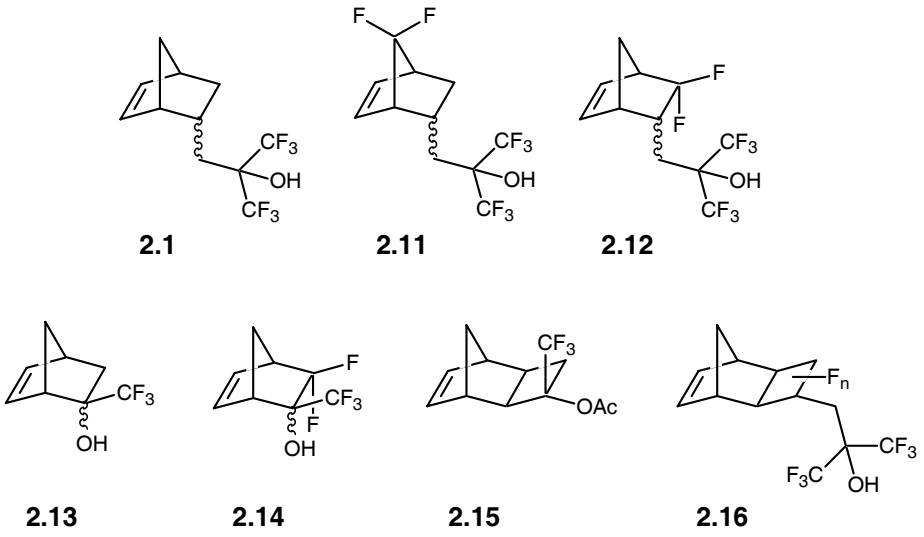


Figure 2.7. Hexafluorocarbinol-functionalized monomers

Unfortunately, reaction of 1-acetoxy-1-trifluoromethyl-ethene with quadricyclane was unsuccessful (Figure 2.8). Extended heating of the reaction mixture at higher temperatures resulted only in the isomerization of quadricyclane back to norbornadiene. Unlike Diels-Alder reactions with cyclopentadiene which can be performed at elevated temperatures for prolonged periods of time in order to achieve acceptable yields of cycloaddition products with moderate dienophiles, reactions with quadricyclane must be performed below 140 °C to prevent isomerization to the unreactive norbornadiene. The lower reactivity of quadricyclane requires

extremely reactive dienophiles for acceptable cycloaddition yields. Consistent with these results, reaction of quadricyclane with the homoallylic hexafluorocarbinol **2.17** did not afford any tricyclononene product; instead however, a 1.4:1 mixture of the norbornenyl and nortricyclyl ethers **2.18a** and **2.18b**, respectively, was isolated. Several iterations of silica gel column chromatography were sufficient to separate the isomers to afford a clean sample of the norbornenyl ether **2.18a** for analysis. These results are similar to those of Dauben *et al.*, who reported the reaction of acetic acid with quadricyclane to afford a mixture of norbornene and nortricyclane esters.[34] When the alcohol is protected (as with the *t*-butyldimethylsilyl-protected hexafluorocarbinol **2.19**), no reaction with quadricyclane is observed. While these failures persuaded us to focus on alternative monomers, the reaction of quadricyclane with fluorinated alcohols was pursued independently with some success by another laboratory.[35]

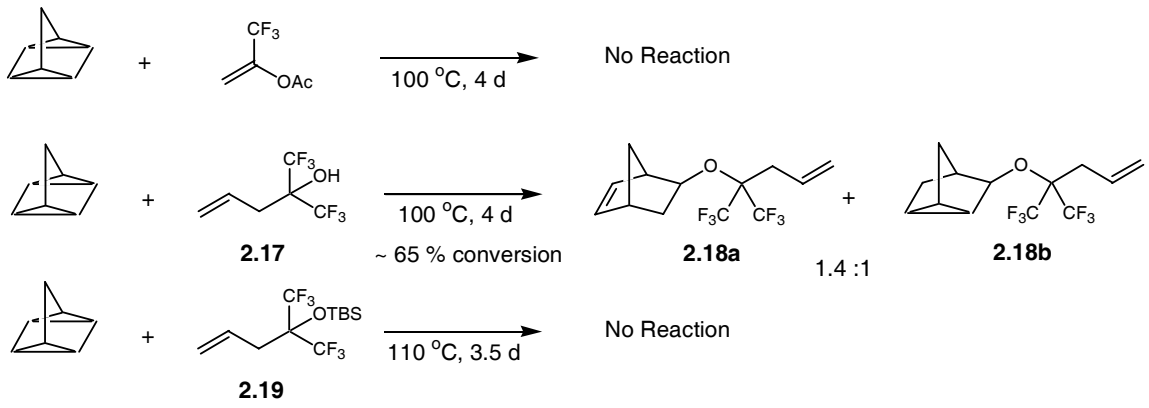


Figure 2.8. Attempted syntheses of hexafluorocarbinol-functionalized tricyclononenes

Conclusions

A number of non- and partially-fluorinated acrylic and methacrylic acid esters undergo cyclizations with quadricyclane to produce tricyclononene structures in moderate to high yield. The *exo*-configuration of the cyclobutane ring relieves steric crowding of the olefin and reduces inductive effects by locating the highly electron-withdrawing fluorine, trifluoromethyl, and carboxylic acid ester functionalities further from the double bond. In this way, the electronic and

steric issues which affect polymerization activity can be balanced with the degree of fluorination required for acceptable transparency. Vacuum-UV measurements on saturated model TCN systems demonstrate the increased transparency imparted by the selective incorporation of trifluoromethyl and fluorine substituents. Further extension of this approach to the synthesis of hexafluorocarbinol-functionalized tricyclononenes is limited by the isomerization of quadricyclane to norbornadiene at higher temperatures. As a result, cycloaddition with less reactive dienophiles such as 1-acetoxy-1-trifluoromethyl-ethene was unsuccessful. Additionally, reaction with unsaturated hexafluorocarbinols resulted in the exclusive formation of norbornenyl and nortricylanyl ethers. Nevertheless, fluorinated tricyclononenes constitute a new viable route towards photoresist materials for 157 nm lithography with enhanced transparencies.

Experimental

Materials: All manipulations and polymerizations were carried out in an N_2-filled drybox or using standard Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å[36] molecular sieves. Dichloromethane was rigorously degassed in 18 L reservoirs and passed through two sequential purification columns consisting of activated alumina. All starting materials were procured from Aldrich except methyl 2-(trifluoromethyl)-3,3,3-trifluoropropenoate (Synquest), (2-trifluoromethyl)acrylic acid (Honeywell), and 1,1,1-trifluoro-2-trifluoromethyl-pent-4-ene-2-ol (**2.17**) (Oakwood) and were used as received unless noted otherwise. Compounds **2.10**, methyl bicyclo[2.2.1]heptane-2-carboxylate, 2,2-difluoronorbornane[6a], and 3-(bicyclo[2.2.1]heptan-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)propan-2-ol were synthesized by colleagues at the 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). Select NMR spectra for compound 2.10 were obtained using a Varian 500 MHz spectrometer (^{13}C: 125 MHz, ^{19}F: 470 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, $CFCl_3$ unless otherwise noted) or to the chemical shift of the residual proteo solvent. Infrared spectra were recorded on either a Nicolet Avatar 360 or a Perkin-Elmer Paragon 1000 IR spectrometer. Mass spectra were measured on a Finnigan *MAT TSQ-700* spectrometer. Gas chromatographs were recorded on a Hewlett Packard *5890 Series II* with an *HP-5* (crosslinked 5% PH ME siloxane) capillary column and flame ionization detector (FID).

X-ray Crystallography: X-ray crystallographic analysis of **2.10** was performed by the X-ray crystallography facility at the University of Texas, Austin. Crystallographic data (experimental procedure, labeled drawings, table of atomic coordinates, complete bond distances and angles, and anisotropic displacement parameters) for compound **2.10** can be found in Appendix A.

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.[37] VUV spectra of polymer films were calculated from measurements made with a J. A. Woollam *VU301* variable angle spectroscopic ellipsometer (VASE) and/or measured with the Acton *CAMS-507* spectrophotometer. The films were cast on either silicon wafers (VASE) or calcium fluoride disks (Acton) from solutions in propylene glycol methyl ether acetate (PGMEA) or cyclohexanone and baked at 100-130°C for at least 5 minutes prior to analysis. All absorbance data reported are in base 10.

General Synthesis Procedure for Tricyclononene Compounds: One equivalent of tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (quadricyclane) and 1-3 equivalents of acrylate were placed in a thick-walled Schlenk tube. The components were degassed and the flask sealed under an atmosphere of argon. For reactions in which radical polymerization of the olefin occurs readily, small amounts (0.001 equiv.) of suitable radical inhibitor such as hydroquinone was added. The reaction mixture was heated to 96 °C for 24-72 hours. The tricyclononene product was separated

from the residual quadricyclane starting material and norbornadiene and polymeric by-products by Kugelrohr vacuum distillation to yield colorless liquids (or solids).

Tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylic acid (2.5). 3-Cyano-tricyclo[4.2.1.0^{2,5}]non-7-ene (prepared by the cycloaddition of quadricyclane with acrylonitrile[18]) (23.6 g, 0.162 mol) was dissolved into 40 mL of ethylene glycol and added to a 250 mL round-bottom flask charged with 1.5 equivalents of potassium hydroxide (13.7 g, 0.244 mol) in 25 mL H_2O. The resulting biphasic system was stirred vigorously while refluxing at 140 °C for 24 hours. The resulting mixture was acidified with 20 mL of HCl (37% solution in H_2O). The product was extracted into ethyl ether and dried over $MgSO_4$. Removal of the solvent *in vacuo* produced a viscous, colorless oil, which crystallized overnight into a white crystalline material. Removal of residual ethylene glycol was achieved via Kugelrohr distillation (80 °C, 60 mTorr) to produce 16.4 g (0.098 mol) of a viscous, colorless oil, which crystallized overnight into a white crystalline material. Yield: 60% (35% over 2 steps from acrylonitrile). Isomer composition: > 98 % anti. Anti isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 11.27 (br s, COOH), 6.01 (dd, *J* = 2.7, 6.0 Hz, 1H, H-7), 5.96 (dd, *J* = 2.7, 6.0 Hz, 1H, H-8), 2.78 (s, 1H, H-1), 2.70 (s, 1H, H-6), 2.50 (m, 1H, H-3), 2.40 (m, 1H, H-4), 2.23 (m, 1H, H-2), 2.05 (m, 1H, H-5), 1.67 (d, *J* = 8.7 Hz, 1H, H-9 anti), 1.62 (m, 1H, H-4), 1.37 (dt, *J* = 1.7, 9.6 Hz, 1H, H-9 syn). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.91 (COOH), 136.07 (CH, C-7), 134.68 (CH, C-8), 44.31 (CH, C-6), 44.13 (CH, C-1), 40.72 (CH, C-2), 40.48 (CH_2, C-9), 37.55 (CH, C-3), 34.47 (CH, C-5), 24.02 (CH_2, C-4). IR (KBr, Nujol, cm^{-1}): 3050, 1700, 1464, 1417, 1267, 1240, 1211, 927, 692. HRMS-EI (*m/z*): $[M + H]^+$ calcd for $C_{10}H_{13}O_2$, 165.0916; found, 165.0903

***t*-Butyl tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (2.6).** Quadricyclane (15 mL, 14.7 g, 0.16 mol) and 4 equiv. *t*-butyl acrylate (92 mL, 80.7 g, 0.63 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 28.0 g (0.13 mol) of colorless liquid. Yield: 80%. Isomer composition: 57 % syn, 43 % anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.94 (m, 4H, H-7+H-8, syn+anti), 3.12 (ddd, *J* = 7.8, 9.6, 11.1 Hz, 1H, H-3, syn),

2.90 (s, 1H, H-1, syn), 2.70 (s, 1H, H-1, anti), 2.63 (s, 2H, H-6, syn+anti), 2.34-2.05 (5H, syn+anti), 2.02-1.87 (2H, H-5 syn+anti), 1.68 (dd, J = 4.8, 7.8 Hz, 1H, H-4, syn), 1.65-1.58 (2H, H-9 anti, syn+anti), 1.57-1.48 (1H, H-4, anti), 1.44 (s, 9H, C(CH_3)$_3$, syn), 1.43 (s, 9H, C(CH_3)$_3$, anti), δ 1.29 (dt, J = 1.5, 8.1 Hz, 1H, H-9 syn, anti), 1.17 (dt, J = 1.5, 9.6 Hz, 1H, H-9 syn, syn). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 175.22 (*C*OOtBu, anti), δ 173.40 (*C*OOtBu, syn), 136.07 (olefin C, syn), 135.81 (olefin C, anti), 135.13 (olefin C, syn), 134.61 (olefin C, anti), 80.03 (*C*(CH$_3$)$_3$, syn), 79.77 (*C*(CH$_3$)$_3$, anti), 44.92 (CH, C-6, syn), 44.17 (CH, C-6, anti), 43.96 (CH, C-1, anti), 42.46 (CH, C-1, syn), 40.57 (CH, C-2, anti), 40.41 (CH_2, C-9, anti), 40.36 (CH_2, C-9, syn), 40.14 (CH, C-2, syn), 38.48 (CH, C-3, anti), 35.56 (CH, C-3, syn), 34.26 (CH, C-5, anti), 33.50 (CH, C-5, syn), 28.30 (COOC(*C*H$_3$)$_3$, syn), 28.18 (COOC(*C*H$_3$)$_3$, anti), 23.79 (CH_2, C-4, anti), 23.07 (CH_2, C-4, syn). IR (KBr, cm^{-1}): 3057 (alkene), 2972, 1723 (C=O), 1456, 1391, 1367, 1349, 1322, 1256, 1228, 1215, 1154, 848, 754, 698. HRMS-EI (*m/z*): [M + H]$^+$ calcd for $C_{14}H_{21}O_2$, 221.1542; found, 221.1546.

***t*-Butyl 3-(methyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (2.7).** Quadricyclane (15 mL, 14.7 g, 0.16 mol) and 3 equiv. *t*-butyl methacrylate (78 mL, 68.2 g, 0.48 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 3.0 g (0.013 mol) of colorless liquid. Yield: 8%. Isomer composition: 55 % syn, 45 % anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.98 (m, 4H, H-7+8, syn+anti), 2.95 (s, 1H, H-1, syn), 2.74 (s, 1H, H-1, anti), 2.65 (s, 2H, H-6, syn+anti), 2.44 (m, 1H), 2.1-1.6 (6H, syn+anti), 1.56-1.48 (m, 1H), 1.46 (s, 9H, C(CH_3)$_3$, syn), 1.45 (s, 9H, C(CH_3)$_3$, anti), 1.40 (d, 3H, -CH_3, syn), 1.36-1.18 (4H, syn+anti), 1.16 (d, 3H, -CH_3, anti). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 178.25 (*C*OOtBu, anti), 176.43 (*C*OOtBu, syn), 136.37 (olefin C, anti), 136.23 (olefin C, syn), 135.71 (olefin C, anti), 135.48 (olefin C, syn), 79.94 (C(CH$_3$)$_3$, syn), 79.79 (C(CH$_3$)$_3$, anti), 48.91 (CH, C-2, syn), 44.63 (CH, C-6, syn), 44.30 (CH, C-2, anti), 43.53 (CH, C-6, anti), 42.99 (CH, C-1, syn), 41.88 (CH_2, C-9, anti), 41.52 (CH, C-1, anti), 41.35 (quat. C, C-3, syn), 41.07 (quat. C, C-3, anti), 40.65 (CH_2, C-9, syn), 33.09 (CH, C-5, anti), 31.36 (CH_2, C-4, anti), 31.08 (CH_2, C-4,

syn), 30.48 (CH, C-5, syn), 28.37 (CH_3, syn), 28.32 ($C(CH_3)_3$, syn), 28.17 ($C(CH_3)_3$, anti), 16.91 (CH_3, anti). IR (KBr, cm^{-1}): 3057 (alkene), 2972, 1720 (C=O), 1470, 1456, 1391, 1367, 1313, 1281, 1256, 1227, 1131, 849, 757, 703. HRMS-EI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{23}O_2$, 235.1698; found, 235.1698.

Methyl 3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (2.8). Quadricyclane (1.5 equiv., 4.25 g, 0.046 mol) and methyl (2-trifluoromethyl)acrylate[6a] (1 equiv., 4.55 g, 0.30 mol) were reacted according to the general procedure mentioned above to produce, after Kugelrohr vacuum distillation, 6.78 g (0.028 mol) of colorless liquid. Yield: 94%. Isomer composition: 32 % syn, 68 % anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 6.1-5.9 (m, 4H, H-7+H-8, syn+anti), 3.80 (s, 3H, COOC*H*$_3$, syn), 3.78 (s, 3H, COOC*H*$_3$, anti), 3.06 (s, 1H, H-1, syn), 2.99 (s, 1H, H-1, anti), 2.82 (s, 1H, H-6, syn), 2.74 (s, 1H, H-6, anti), 2.68 (ddd, *J* = 3.0, 7.5, 13.2 Hz, 1H, anti), 2.5-1.9 (7 H), 1.48-1.24 (4 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 171.16 (d, *J* = 2.9 Hz, *C*OOMe, syn), 168.85 (d, *J* = 2.4 Hz, *C*OOMe, anti), 136.74 (olefin C, anti), 136.62 (olefin C, syn), 135.24 (olefin C, syn), 135.06 (olefin C, anti), 126.32 (q, *J* = 280 Hz, CF_3, anti), 125.16 (q, *J* = 281 Hz, CF_3, syn), 53.30 (COO*C*H3, syn), 52.81 (COO*C*H$_3$, anti), 49.56 (q, *J* = 28.6 Hz, quat. C, C-3, syn), 49.40 (q, *J* = 26.5 Hz, quat. C, C-3, anti), 44.50 (CH, C-6, anti) 44.18 (CH, C-6, syn), 44.15(CH, C-2, syn), 42.86 (CH, C-1, syn), 42.50 (CH, C-1, anti), 41.95 (m, *J* = 2.0 Hz, CH, C-2 anti), 41.14 (m, CH_2, C-9, anti), 40.71 (CH_2, C-9, syn), 32.98 (CH, C-5, syn), 32.83 (CH, C-5, anti), 26.07 (d, *J* = 2.4 Hz, CH_2, C-4, anti), 25.93 (d, *J* = 1.9 Hz, CH_2, C-4, syn). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm) (referenced to external C_6F_6 standard at -166.717 ppm): δ -66.25 (s, 3F, -CF_3, syn), -75.13 (s, 3F, -CF_3,, anti). IR (KBr, cm^{-1}): 3060 (alkene), 2970, 2892, 1742 (C=O), 1473, 1436, 1333, 1322, 1275, 1225, 1163, 1132, 1087, 712, 671. HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{14}F_3O_2$, 246.0868; found, 246.0868 .

Triethylaminoboron trifluoride.[38] To a cooled (dry ice/acetone) 250 mL round-bottom flask equipped with a stir bar and addition funnel was added boron trifluoride diethyl etherate (30 g, 211 mmol). Triethylamine (60 mL) was added dropwise to the flask via an addition funnel. The

formation of white precipitate was immediately observed. After the addition of triethylamine, the reaction was allowed to warm to room temperature, and excess triethylamine was removed *in vacuo*. The white residue was purified by vacuum fractional distillation (85°C / 3 mm Hg) to give a white solid (32.0 g, 91%), which melted at approximately 25°C. The compound was kept in the refrigerator and used in the next step without further purification.

Methyl 3,3-difluoro-2-(trifluoromethyl)acrylate. A slight modification of the literature procedure was used.[39] To a 100 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser were added triethylaminoboron trifluoride (32.0 g, 189 mmol) and methyl 2-(trifluoromethyl)-3,3,3-trifluoropropionate (30.5 g, 145 mmol). The reaction mixture was refluxed for 3 h and then cooled to room temperature. The residue was purified by vacuum transfer (bulb to bulb distillation) to give a clear oil (19.8 g, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.84 (s, 3H, methyl). ^{19}F NMR (CD_3OD, 282 MHz, ppm): δ -58.5 (m, 1F, RC=CF_2), -59.1 (m, 3F, CF_3), -59.5 (m, 1F, RC=CF_2). IR (NaCl, cm^{-1}): 2960, 1767 (C=O), 1710, 1439, 1372, 1152, 1081, 1040, 1024. HRMS-CI (*m/z*): $[M + H]^+$ calcd for $C_5H_3F_5O_2$, 191.0131; found, 191.014.

Methyl 4,4-difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylate (2.9). To a 300 mL Parr pressure reactor equipped with a magnetic stir bar were added quadricyclane (1.5 g, 16.3 mmol) and methyl 3,3-difluoro-2-(trifluoromethyl)acrylate (3.9 g, 20.4 mmol). The pressure vessel was sealed, and the reaction mixture was stirred at 100°C for 72 hours. After cooling to room temperature, the residue was purified by fractional vacuum distillation (39-40°C / 0.30 mm Hg) to yield a clear oil (1.0 g, 22%). In a subsequent synthesis, it was found that if the reaction was allowed to sit at room temperature for 14 days after the initial heating, the isolated yield increased to 73%. Isomer composition: 49% syn, 51% anti. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.27 (dd, *J* = 2.7, 5.7 Hz, olefin H, 1H, anti), 6.05-6.15 (m, olefin H, 3H, 2 syn+1 anti), 3.87 (s, COOCH_3, 3H, anti), 3.86 (s, COOCH_3, 3H, syn), 3.53 (s, 1H, H-1, syn), 3.22 (2H, H-1,

H-6, anti), 3.13 (s, 1H, H-6, syn), 2.84-2.75 (m, 1H, H-5, anti), 2.75-2.6 (m, 1H, H-5, syn), 2.39-2.31 (m, 1H, H-2, syn), 2.10 (d, *J* = 10.2 Hz, 1H, H-2, anti), 1.50-1.30 (m, 4H, H-9 syn, H-9 anti, syn+anti). ^{13}C NMR (C_6D_6, 75 MHz, ppm): 165.11 (COOMe, syn), 162.91 (COOMe, anti), 139.62 (olefin C, anti), 137.82 (olefin C, syn), 136.93 (olefin C, syn), 136.77 (olefin C, anti), 123.97, (q, J = 283 Hz, CF_3, syn), 123.68 (q, J = 280 Hz, CF_3, anti), 116.72 (t, *J* = 292 Hz, C-5), 114.09, (t, *J* = 296 Hz, C-5), 53.32 (COO*C*H$_3$, anti), 52.64 (COO*C*H$_3$, syn), 50.70 (dd, *J* = 19.2, 26 Hz, CH, C-5, anti), 50.36 (t, *J* =23 Hz, CH, C-5, syn), 43.71 (CH, C-1, anti), 43.26 (CH, C-1, syn), 43.11 (dd, *J* = 4.4, 8.2 Hz, CH_2, C-9, anti), 42.82 (d, *J* = 6.6 Hz, CH_2, C-9, syn), 42.08 (CH, C-6, anti), 41.29 (t, *J* = 2.3 Hz, CH, C-6, syn), 37.21(dd, J = 4.9, 12 Hz, CH, C-2, anti), 36.90 (m, CH, C-2, syn). ^{19}F NMR (Acetone, 282 MHz, ppm): δ –61.67 (d, *J* = 6.7 Hz, 3F, CF_3, anti), -68.36 (d, *J* = 2.0 Hz, 3F, CF_3, syn), -85.70 (dm, *J* = 211 Hz, 1F, F-4 syn, anti), -97.15 (dm, *J* = 217 Hz, 1F, F-4 anti, syn), -106.87 (d, *J* = 217 Hz, 1F, F-4 syn, syn), -113.94 (d, *J* = 211 Hz, 1F, F-4 anti, anti). IR (NaCl, cm^{-1}): 3058 (alkene), 2991, 2909, 1752 (C=O), 1429, 1317, 1219, 1045, 897, 794, 697. HRMS-CI (*m/z*): $[M + H]^+$ calcd for $C_{12}H_{12}F_5O_2$, 283.0757; found, 283.0755.

4,4-Difluoro-3-(trifluoromethyl)tricyclo-[4.2.1.0^{2,5}]non-7-ene-3-carboxylic acid (2.10). Hydrolysis of **2.9** with KOH and water under standard conditions produced the carboxylic acid. One of the isomers selectively crystallized from solution and was determined to be the syn isomer by x-ray crystallography. Syn isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.6-8.4 (br s, 1H, COOH), 6.16 (m, 2H, H-7+H-8), 3.50 (s, 1H, H-1), 3.16 (s, 1H, H-6), 2.69 (m, *J* = 4.2 Hz, 1H, H-5), 2.35 (m, 1H, H-2), 1.45 (s, 2H, H-9 syn, H-9 anti). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.63 (COOH), 137.94 (C-8), 137.082 (C-7), 122.93 (q, *J* = 282 Hz, CF_3), 116.08 (t, *J* =290 Hz, C-4), 59.5 (quat. C, C-3), 50.25 (t, *J* =23 Hz, CH, C-5), 43.04 (CH, C-1), 42.80 (d, *J* = 6.4 Hz, CH_2, C-9), 41.25 (t, *J* = 1.8 Hz, CH, C-6), 36.77 (m, CH, C-2). ^{19}F NMR ($CDCl_3$, 470 MHz, ppm): δ -68.94 (dd, *J* = 2.4, 17.0 Hz, 3F, CF_3), -97.81 (dm, *J* = 217 Hz, 1F, F-4 anti), -107.95 (d, *J* = 217 Hz, 1F, F-4 syn). HRMS-CI (*m/z*): $[M + H]^+$ calcd for $C_{11}H_{10}F_5O_2$, 269.0601; found, 269.0589.

General Hydrogenation Procedure: Norbornene or tricyclononene monomer (5.86 mmol) was dissolved in 16 mL ethyl acetate in a 250 mL Parr bomb (Parr Instrument Company, MAWP 3000psi at 350 °C). Palladium (10 % on carbon, 0.015g) was added to the bomb, which was pressurized to 50 psi with H_2. The reaction mixture was stirred overnight at room temperature, the catalyst was removed with a 0.45 μm PTFE syringe filter, and the solvent was removed by rotary evaporation to yield a clear oil.

1,1,1-Trifluoro-2-trifluoromethyl-pent-4-ene-2-ol (2.17). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.22 (m, 1H), 5.93 (m, 1H), 5.85 (m, 1 H), 5.24 (dm, 1H), 5.19 (m, 1H), 4.10 (d, 1H, *J* = 6.6 Hz), 2.83 (br s, 2H), 2.76 (d, 2H, *J* = 7.2 Hz), 1.8-1.4 (4H). ^{13}C NMR ($CDCl_3$, 75.46 MHz, ppm): δ 141.78, 132.93, 129.38, 120.23, 48.97, 46.24, 40.58, 36.41, 34.10. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm) (referenced to internal C_6F_6 at -162.2 ppm): δ -77.03 (s).

5-(1,1-Bis-trifluoromethyl-but-3-enyloxy)-bicyclo[2.2.1]hept-2-ene (2.18a). Quadricyclane (0.50g, 5.43 mmol) and 1,1,1-trifluoro-2-trifluoromethyl-pent-4-ene-2-ol (**2.17**) (1.13 g, .43 mmol) were added to a Schlenk tube and degassed via 3 free-pump-thaw cycles. The tube was sealed and heated at 95 °C for3 days. Silica gel column chromatography (20:1 pentane: ether) afforded a 1.4:1 mixture of **2.18a** and 3-(1,1-bis-trifluoromethyl-but-3-enyloxy)-tricyclo[2.2.1.0^{2,6}]heptane (**2.18b**). The norbornenyl ether **2.18a** was separated from **2.18b** via 3 successive silica gel columns (100% pentane) to afford **2.18a** as a colorless liquid. **2.18a** R_f = 0.61 (100% hexane), **2.18b** R_f = 0.56 (100% hexane). Characterization for **2.18a**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.22 (m, 1H), 5.93 (m, 1H), 5.85 (m, 1 H), 5.24 (dm, 1H), 5.19 (m, 1H), 4.10 (d, 1H, *J* = 6.6 Hz), 2.83 (br s, 2H), 2.76 (d, 2H, *J* = 7.2 Hz), 1.8-1.4 (4H). ^{13}C NMR ($CDCl_3$, 75.46 MHz, ppm): δ 141.78, 132.93, 129.38, 120.23, 48.97, 46.24, 40.58, 36.41, 34.10. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.28 (s). *g*HSQC and *g*COSY experiments confirmed the assigned structure. HRMS-EI/GC (*m/z*): $[M\bullet]^+$ calc'd for $C_{13}H_{14}F_6O$, 300.0949; found, 300.0958. Characterization for **2.18b**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.86 (m, 1H), 5.25 (dm, 1H),

5.19 (m, 1H), 4.13 (s, 1H, J = 6.6 Hz), 2.76 (d, 2H, J = 6.9 Hz), 2.0-1.9 (m, 2H), 1.4-1.2 (6H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.75 (m, 3F), -77.19 (m. 3F).

1,1,1-Trifluoro-2-(*t*-butyldimethylsilyloxy)-2-trifluoromethyl-pent-4-ene (2.19). 1,1,1-trifluoro-2-trifluoromethyl-pent-4-ene-2-ol (**2.17**)[6a] (3.0 g, 14.4 mmol) was added slowly to a 30 mL suspension of sodium hydride (0.38 g, 15.8 mmol, 1.1 eq.) in dry tetrahydrofuran. The reaction was stirred at 40 °C for 1 hour to ensure complete reaction. Subsequently, the reaction was cooled to 0 °C and a solution of t-butyldimethylsilyl chloride (2.39g, 15.8 mmol, 1.1 equiv) in 5 mL of tetrahydrofuran was added. The reaction was heated at 40 °C overnight. The reaction mixture was concentrated and the reaction product purified via silica gel chromatography (50:1 pentane:ether) to afford 4.16 g (90 %) of **2.19** as a colorless liquid. R_f = 0.91 (20:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.82 (m, 1 H), 5.23 (dm, 1H), 5.18 (m, 1H), 2.70 (d, 2H, J = 7.2 Hz), 0.91, (s, 9H), 0.19 (s, 6H).). ^{13}C NMR ($CDCl_3$, 75.46 MHz, ppm): δ 129.32, 123.18 (q, J = 289 Hz, CF_3), 120.36, 37.23, 25.62, -3.33. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm) (Referenced to internal C_6F_6 at -162.2 ppm): δ -75.37 (s).

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