

# 157 nm Resist Materials: A Progress Report

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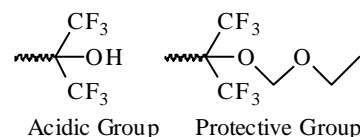
The goal of this work has been to study candidate fluorocarbon materials that might serve as platforms from which to design 157nm resists. A specific goal of the work has been to identify transparent candidate materials that might provide a polymer backbone and acceptable etch resistance. Several model compounds were synthesized and their vacuum UV spectra were measured in the gas phase. Substituted norbornane (bicyclo[2.2.1]heptane) was of significant interest in this regard because we had used this structure successfully in the design systems for 193nm exposure. Surprisingly, 2-monofluoronorbornane is unstable and undergoes spontaneous dehydrohalogenation upon exposure to glass in vacuo. However, 2,2-substitution with fluorine and with other electron withdrawing groups such as trifluoromethyl and even carbonyl groups gives norbornyl derivatives with greatly improved transparency at 157nm. These observations led to the design a variety of novel norbornenes that can be polymerized by metal catalyzed addition polymerization to give etch resistant polymer platforms with greatly improved transparency at 157nm and led to the study of acrylic co-polymers derived from 2-(trifluoromethyl)acrylic acid.

**Keywords:** 157nm Resists, chemically amplified resist, 2-(trifluoromethyl)acrylates, fluoronorbornanes

## 1. Introduction

The design photoresists for exposure at 157 nm is particularly challenging because air, water and most organic compounds are opaque at 157 nm. Recent spectroscopic studies have led to the observation that two classes of organic compounds, organosiloxanes and fluorinated hydrocarbons are relatively transparent in this wavelength regime and are therefore possible candidate platforms from which to design 157nm resists.[1] Our “modular” approach to the design of the resist polymer requires identification of four “modules”: a backbone that tethers the functional substituents and provides basic mechanical properties, an etch barrier that provides RIE resistance, an acidic group that generates TMAH developer solubility, and an acid labile protecting group to enable chemical amplification. All of these modules must be transparent at 157 nm. We fairly quickly identified the hexafluoroisopropyl group as a transparent acidic module and acetal protecting groups (**Figure 1**), were shown to function

effectively with this structure in acid catalyzed, chemically amplified systems.[2]



**Figure 1. Transparent acidic module**

Subsequently, as shown in **Figure 2**, Matsuzawa predicted that trifluoromethyl trifluoroacetate would be quite transparent at 157 nm.[3] This prediction derived from quantum mechanical calculations encouraged us to synthesize a set of esters of trifluoroacetic acid and 3,3,3-trifluoropropionic acid and to measure their absorbance at 157nm. As predicted, these structures have improved transmission at 157nm compared to their hydrocarbon analogs. This corroboration of Matsuzawa's prediction inspired the design and synthesis of a variety of new derivatives of a-trifluoromethylacrylic acid and

certain fluorine substituted poly(norbornane)s that appear to provide the basis for the design of transparent, chemically amplified, dry etch resistant 157nm resist materials.

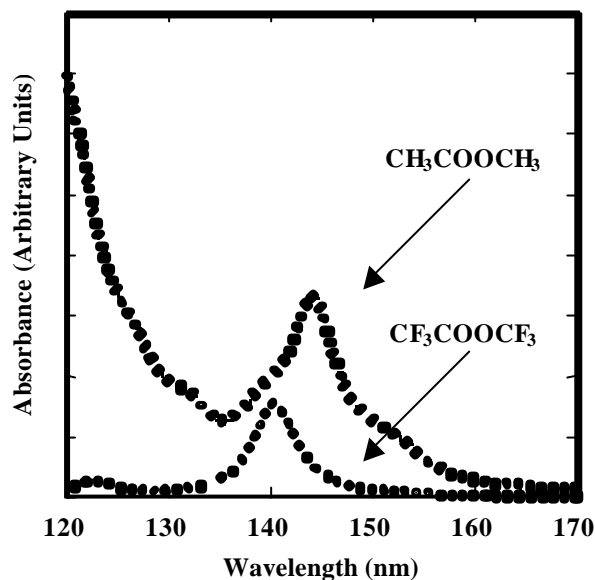


Figure 2. Calculated Spectra [3]

## 2. Results and Discussion

The synthesis of trifluoromethyl trifluoroacetate requires photochemical reaction with special equipment [4] so we chose to prepare fluorinated ethyl acetates to confirm Matsuzawa's prediction. As shown in **Figure 3**, introduction of fluorine into the molecule causes a peak shift and a significant reduction in extinction at 157 nm. Extending this result to a polymer backbone is nontrivial so we prepared and measured propionate derivatives that are models of poly(methacrylates). The model compounds, 2,2,2-trifluoroethyl 3,3,3-trifluoropropionate (**4**) and ethyl 3,3,3-trifluoropropionate (**5**) were prepared from the corresponding acids and alcohols with dicyclohexylcarbodiimide and dimethylaminopyridine. Solvent was not used in the reaction because complete removal of solvent was difficult due to the low boiling point of the products. **Figure 4** shows the spectra of these models. The fluorination in the ester **5** does not greatly reduce absorbance at 157 nm, but  $\beta$ -fluorination of the alkyl ester generates a hypsochromic shift that reduces absorbance at 157nm.

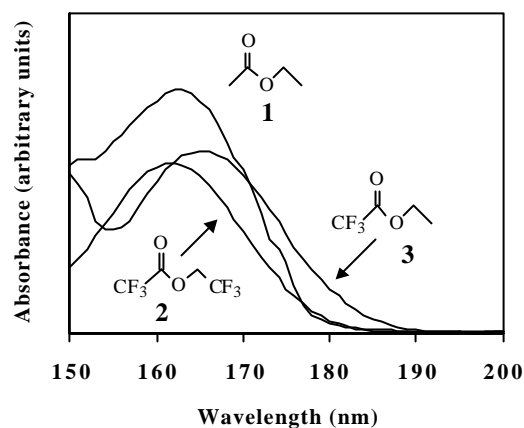


Figure 3. Absorbance of fluorinated ethyl acetates

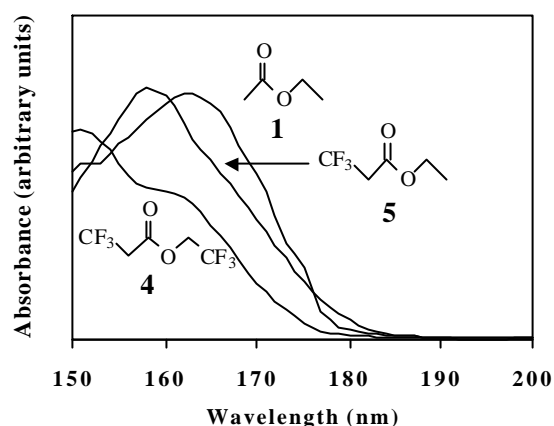
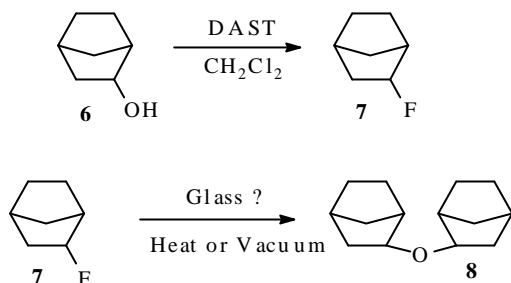


Figure 4. Absorbance of fluorinated esters

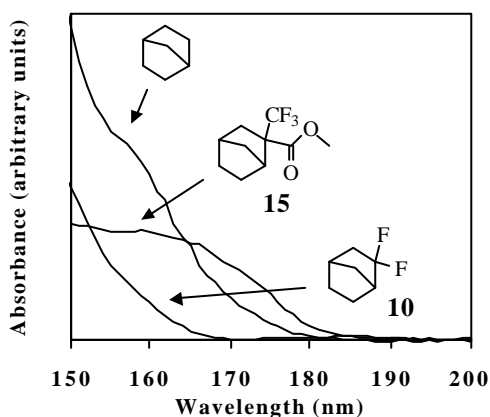
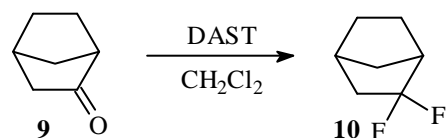
The fluoronorbornane **7** was synthesized from 2-*exo*-bicyclo[2.2.1]heptanol (**6**) and diethylaminosulfur trifluoride (DAST). The product was purified by two sublimations. When this compound was sealed in an evacuated ampoule for VUV spectroscopic studies, it was decomposed in a few days. The sample turned light brown and the glass of the ampoule was etched. Analysis of the decomposition products proved the formation of dibicyclo[2.2.1]heptyl ether (**8**) in over 75% yield. This transformation was also observed when an attempt was made to distill the compound at ambient pressure. We believe that the compound undergoes facile dehydrofluorination and the oxygen source is probably the glassware because the surface of glass was etched when this transformation occurred. This elimination reaction is interesting.

It teaches us to avoid incorporation of monofluorinated norbornane derivatives in polymers designed for resist applications. These reactions are shown in **Scheme 1**.



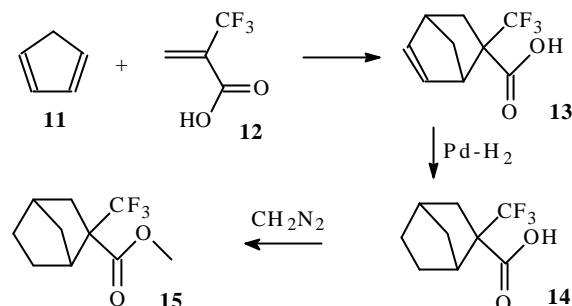
**Scheme 1.** Synthesis and dehydrohalogenation of 2-fluoronorbornane

Compound **10** was synthesized from 2-bicyclo[2.2.1]heptanone (**9**) and DAST and found to be very stable to heat and vacuum in contrast with a compound **7**. The gas phase absorbance spectrum of **10** is shown in **Figure 5**. Introduction of the geminal difluorosubstituents causes a very considerable reduction in the absorbance at 157nm.



**Figure 5.** Absorbance of fluorinated norbornanes

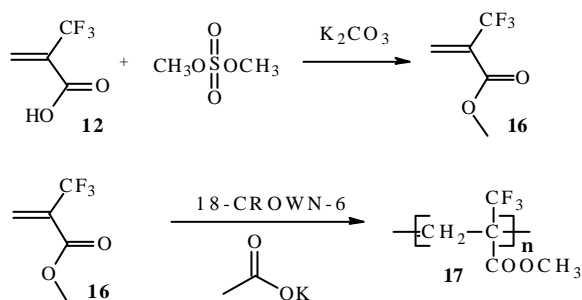
Combining this information with that derived from the study of the esters (**Figure 4**) led to the design of the analogous norbornane **15** (**Scheme 2**). We are pleased to report that this molecule has greatly improved transparency at 157nm even though it incorporates a carboxyl group.



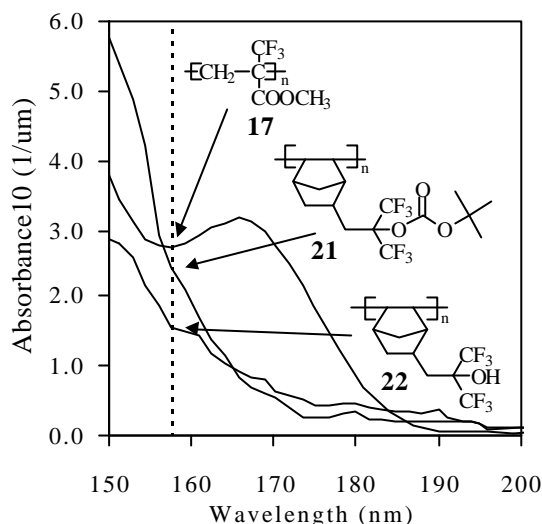
**Scheme 2.** Synthesis of norbornane model compound

The Diels-Alder reaction between cyclopentadiene (**11**) and 2-(trifluoromethyl)acrylic acid (**12**) gave 2-(trifluoromethyl)-5-bicyclo[2.2.1]heptene-2-carboxylic acid (**13**). Hydrogenation followed by esterification with diazomethane gave methyl 2-(trifluoromethyl)bicyclo[2.2.1]heptane-2-carboxylate (**15**). These reactions all proceeded in high yield.

Methyl 2-(trifluoromethyl)acrylate (**16**) was prepared from the corresponding acid **12** by treatment with dimethylsulfate and potassium carbonate as reported.[5] Anionic polymerization of the ester **16** was carried out using potassium acetate and 18-crown-6.[6] The absorbance spectrum of this polymer is fully consistent with the predictions of the model and of the model compounds. The spectrum is provided in **figure 6**.



**Scheme 3.** Synthesis of poly(methyl 2-(trifluoromethyl)acrylate) (**17**)



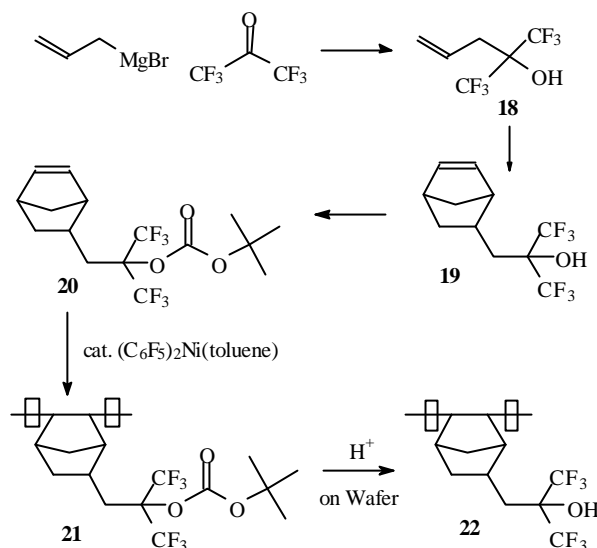
**Figure 6. Absorbance of fluorinated polymers**

We have reported the utility of certain fluoronorbornene polymers in top surface imaging applications [7]. As part of that program we prepared the vinyl addition polymer **21** and measured its absorbance at 157nm. We were pleased and surprised to find that this polymer and its deprotected analog **22** both have good transparency at 157nm. This discovery provides another valuable platform from which to design etch resistant 157nm resists.

The poly(norbornene) monomer (**20**) (Scheme 4) was synthesized by reaction of 3-(5-bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanol (**19**) with di-*t*-butyldicarbonate. The hexafluoroalcohol (**19**) was prepared by the Diels-Alder reaction as previously reported.[8] The monomer **20** was homopolymerized using a nickel catalyst[9] to afford poly(*tert*-Butyl 3-(5-bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propyl carbonate) (**21**). The spectra of (**21**) and its deprotected analog (**22**) are provided in **figure 6**. Deprotection of the polymer **21** to produce (**22**) was carried out on a wafer with photogenerated acid. Hence, the spectrum of (**22**) includes the photoproducts of the PAG.

A detailed description of the gas phase measurements and the apparatus used to make those measurements has been submitted for publication elsewhere [10]. The polymer film spectra were measured by variable angle scanning ellipsometry and in some cases, also by vacuum ultraviolet spectroscopy. The agreement between these measurements was excellent. The

absorbance of **17** at 157nm was measured in film form as  $2.76 \mu\text{m}^{-1}$  by VASE and  $2.68 \mu\text{m}^{-1}$  by spectroscopy [10], while that of poly(methyl methacrylate) is reported to be  $5.69 \mu\text{m}^{-1}$ [1]. The free alcohol polymer **22** is the most transparent we have studied. The absorbance of **22** is less than  $1.67 \mu\text{m}^{-1}$ . Polymer **21** is surprisingly transparent ( $2.53 \mu\text{m}^{-1}$ ), even though it contains a *t*-Boc protecting group.



**Scheme 4. Synthesis of vinyl addition polymer**

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### 3. Conclusion

We found that judicious introduction of a few fluorines into a molecule can cause a very significant reduction in absorbance at 157 nm by both a hypsochromic spectral shift and a reduction in extinction coefficient. These results allowed us

to design many new polymers and co-polymers for evaluation as resists for 157nm lithography.

#### 4. Acknowledgments

The authors gratefully acknowledge International SEMATECH for financial support of this work and Clariant AZ for donation of key monomers. JSR Corporation is gratefully acknowledged for support of Mr. Yamachika and Mr. Chiba. and Everlight Corp. is acknowledged for support of Mr. Lin. We also acknowledge our valuable collaboration with Dr. Nobuyuki Matsuzawa of ASET.

#### 5. Experimental

##### 5.1 Materials

All starting materials were procured from Aldrich except 3,3,3-trifluoropropionic acid (Oakwood) and 2-(trifluoromethyl)acrylic acid (Synquest) and used as received unless noted otherwise. All solvents were dried by standard methods. All liquid reagents used for VUV measurement were distilled from appropriate drying agents, thoroughly degassed by freeze thaw cycles and sealed in glass ampoules under vacuum. Diazomethane was generated from Diazald<sup>®</sup> by the standard procedure [11].

##### 5.2 Instruments and Equipment

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AMX300 or a Bruker DRX500 spectrometer. Shifts for NMR spectra are reported in ppm relative to TMS or to the chemical shift of the solvent (for fluorine <sup>19</sup>F, CFCl<sub>3</sub>). Infrared spectra were recorded on a Mattson Genesis II Fourier transform spectrometer using KBr powder, with a Pike diffuse reflectance accessory. Melting points are uncorrected. Mass spectra were measured on a Finnigan MAT TSQ-70 spectrometer. Molecular weights (Mw) and polydispersity indices (PDI) were measured from THF solutions using a Viscotek GPC equipped with a set of three 5 mm crosslinked polystyrene columns (linear mix, 500 Å, and 100 Å) from American Polymer Standards and are reported relative to polystyrene standards..

##### 5.3 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 are the subject of a separate paper [10]. VUV spectra

of polymer films were calculated from measurements made with a J.A. Woollam VU301 variable angle spectroscopic ellipsometer and/or measured with the Acton CAMS-507 spectrophotometer. The films were cast on calcium fluoride disks from solutions in propylene glycol monomethyl ether acetate and baked at 110 degrees Celsius for at least 5 minutes prior to analysis.

##### 5.4 Syntheses

###### 2,2,2-Trifluoroethyl 3,3,3-trifluoropropionate (4)

To a 50 mL round-bottomed flask was added DMAP (0.53 g, 4.3 mmol), DCC (13.5 g, 65 mmol), and 2,2,2-trifluoroethanol (6.8 g, 68 mmol) under nitrogen at room temperature to afford a clear solution. The mixture was cooled in an ice bath. Then 3,3,3-trifluoropropionic acid (6.6 g, 52 mmol) was added dropwise. Generation of heat and a white precipitate were observed during this addition. After the addition, the mixture was allowed to warm to room temperature and sonicated for 2 h. Distillation of the mixture gave 6.65 g (61% yield) of crude **4**. Washing with water four times and distillation over phosphorous pentoxide gave the pure product (3.9 g). bp 108-110 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.54 (q, <sup>3</sup>J<sub>HF</sub> = 8.2 Hz, -OCH<sub>2</sub>CF<sub>3</sub>, 2H), 3.29 (q, <sup>3</sup>J<sub>HF</sub> = 9.7 Hz, -COCH<sub>2</sub>CF<sub>3</sub>, 2H). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, δ): -64.07 (t, J = 9.9 Hz, -COCH<sub>2</sub>CF<sub>3</sub>, 3F), -74.38 (t, J = 8.2 Hz, -OCH<sub>2</sub>CF<sub>3</sub>, 3F).

###### Ethyl 3,3,3-trifluoropropionate (5)

To a 50 mL round-bottomed flask was added DMAP (0.38 g, 3.1 mmol), DCC (10.1 g, 48.8 mmol), and ethanol (3.60 g, 78.7 mmol) under nitrogen at room temperature to afford a clear solution. The mixture was cooled in an ice bath. Then 3,3,3-trifluoropropionic acid (5.00 g, 39.0 mmol) was added dropwise. Generation of heat and a white precipitate was observed during this addition and the solution was stirred for 2 h. The mixture was distilled, washed three times with water, dried over magnesium sulfate, and distilled again to give pure **5** (0.87 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.24 (q, J = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>, 2H), 3.17 (q, <sup>3</sup>J<sub>HF</sub> = 10 Hz, -COCH<sub>2</sub>CF<sub>3</sub>, 2H), 1.30 (t, J = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>, 3H).

###### 2-*exo*-Fluorobicyclo[2.2.1]heptane (7)

To a 250 mL three-neck round-bottomed flask was added 21.04 g (188 mmol) of 2-*exo*-

bicyclo[2.2.1]heptanol (**6**) and 42 mL of dichloromethane under nitrogen. The mixture was cooled to 0 °C with an ice bath and 35 mL (265 mmol) of diethylaminosulfur trifluoride (DAST) was added dropwise during 40 min (exothermic reaction). The ice bath was removed and the mixture was allowed to stir at room temperature for 5 days. During the course of the reaction, the color changed from orange to dark orange. The mixture was then cooled with an ice bath and 50 mL of methanol, 100 mL of water, 300 mL of 5% sodium carbonate, and 200 mL of 5% sodium hydroxide were added slowly in this sequence. The water layer was extracted with dichloromethane (50 mL x 2). The combined organic layers were washed with water (150 mL), dried over magnesium sulfate, filtered, and concentrated. The organics were then purified twice by column chromatography on silica gel in n-pentane and twice by sublimation to afford **7** as an extremely pure, clear but sticky solid (ca. 2.5 g, ca. 12%). mp 88-89 °C (lit.[12] 56-58 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 4.58 (dd, <sup>3</sup>J<sub>HF</sub> = 56.0 Hz, *J* = 5.9 Hz, H-2, 1H), 2.42 (td, *J* = 6.7 Hz, *J* = 1.0 Hz, H-1, 1H), 2.30 (s, H-4, 1H), 1.68-1.58 (m, *endo*-H-3, 1H), 1.62-1.54 (m, H-7, 1H), 1.57-1.51 (m, *exo*-H-3, 1H), 1.55-1.45 (m, *exo*-H-6, 1H), 1.45-1.37 (m, *exo*-H-5, 1H), 1.19-1.13 (m, H-7, 1H), 1.05-0.96 (m, *endo*-H-5, 1H), 1.01-0.92 (m, *endo*-H-6, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ): 96.16 (d, <sup>1</sup>J<sub>CF</sub> = 181.1 Hz, C-2), 42.01 (d, <sup>2</sup>J<sub>CF</sub> = 20.0 Hz, C-1), 39.95 (d, <sup>2</sup>J<sub>CF</sub> = 19.1 Hz, C-3), 34.88 (C-4), 34.62 (C-7), 27.98 (C-5), 22.38 (d, <sup>3</sup>J<sub>CF</sub> = 10.9 Hz, C-6). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, δ): -160.6 (m). HRMS-Cl (m/z): [M - HF + H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>10</sub>, 95; found, 95.

#### Dibicyclo[2.2.1]heptyl ether (**8**)

Pure **7** (0.316 g) was placed in an ampoule and sealed under vacuum. After a week, the material became pale brown. The conversion was ca. 75% by NMR. The brown material was dissolved in ether and transferred to a rotary evaporator. Removing the ether and starting material (**7**) left to give the product **8** (0.22 g, 77% yield). mp 66.0-66.5 °C (lit.[13] 65-66 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 3.37 (m, 2H), 2.27-2.22 (m, 2H), 2.21-2.17 (m, 2H), 1.56-1.22 (m, 10H), 1.09-0.92 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ): 80.01 (C-2 or C-2'), 89.51 (C-2 or C-2'), 41.00 (C-1 or C-1'), 40.82 (C-1 or C-1'), 40.20 (C-3 or C-3'), 40.08 (C-3 or C-3'), 35.19 (C-4 or C-4'), 35.16 (C-4 or C-4'), 34.88 (C-7 or C-7'), 34.82 (C-7 or C-7'),

28.63 (C-5, C-5'), 24.82 (C-6, C-6'). HRMS-Cl (m/z): [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>23</sub>O, 207.1749; found, 207.1740.

#### 2,2-Difluorobicyclo[2.2.1]heptane (**10**)

To a 250 mL three-neck round-bottomed flask were added 22.53 g (205 mmol) of 2-bicyclo[2.2.1]heptanone (**9**) and 45 mL of dichloromethane under nitrogen followed by the dropwise addition of 50 mL (378 mmol) of DAST over 10 min. The mixture was allowed to stir at room temperature for 4 days. During the course of the reaction, the color changed from orange to dark orange. To the mixture cooled with an ice bath were added 130 mL of dichloromethane, 30 mL of water, 250 mL of 5% sodium hydroxide, and 300 mL of 10% sodium hydroxide in this sequence. The water layer was extracted with dichloromethane (50 mL x 3). The combined organic layer was washed with water (100 mL), dried over magnesium sulfate, filtered, and concentrated. The organics were purified twice by column chromatography on silica gel in n-pentane, which afforded 15.45 g (117 mmol, 57%) of the product. Further purification by two sublimations afforded an extremely pure, clear but sticky solid **10**. mp 92.5 °C (lit.[14] 64-66 °C). bp 117.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 2.45 (m, H-1, 1H), 2.37 (m, H-4, 1H), 2.03-1.82 (m, H-3, 1H), 1.75-1.64 (m, H-6, 1H), 1.73-1.65 (m, H-7, 1H), 1.68-1.55 (m, H-3, 1H), 1.65-1.56 (m, H-5, 1H), 1.54-1.45 (m, H-6, 1H), 1.40-1.30 (m, H-5, 1H), 1.38-1.30 (m, H-7, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, δ): 131.31 (t, <sup>1</sup>J<sub>CF</sub> = 253.6 Hz, C-2), 44.68 (t, <sup>2</sup>J<sub>CF</sub> = 20.3 Hz, C-1), 42.90 (t, <sup>2</sup>J<sub>CF</sub> = 23.3 Hz, C-3), 37.01 (d, <sup>3</sup>J<sub>CF</sub> = 5.1 Hz, C-7), 35.82 (d, <sup>3</sup>J<sub>CF</sub> = 1.7 Hz, C-4), 27.47 (C-5), 20.87 (t, <sup>4</sup>J<sub>CF</sub> = 6.0 Hz, C-6). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, δ): -86.4 (dd, *J* = 220 Hz, *J* = 28 Hz), -109.7 (dd, *J* = 220 Hz, *J* = 15 Hz). HRMS-Cl (m/z): [M - HF + H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>10</sub>F, 113.0766; found, 113.0757.

#### Methyl 2-(trifluoromethyl)bicyclo[2.2.1]heptane-2-carboxylate (**15**)

2-(Trifluoromethyl)-5-bicyclo[2.2.1]heptene-8-carboxylic acid (**13**), synthesized from cyclopentadiene (**11**) and 2-(trifluoromethyl)-acrylic acid (**12**) under typical Diels-Alder conditions [8] was hydrogenated with palladium on charcoal at 50psi. The resulting acid **14** was esterified with diazomethane in ether. Evaporation of the solvent gave **15** as a colorless oil (2.37 g, 83% yield). <sup>1</sup>H NMR (300 MHz,

CDCl<sub>3</sub>,  $\delta$ ): 3.782 (s, -OCH<sub>3</sub>), 3.779 (s, -OCH<sub>3</sub>), 2.85 (m), 2.77 (m), 2.53 (m), 2.48 (m), 2.37 (m), 2.25 (m), 2.20 (m), 1.90-1.74 (m), 1.64-1.45 (m), 1.33-1.07 (m). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>,  $\delta$ ): -65.14 (s), -68.39 (s). IR (cm<sup>-1</sup>) 2967, 2891, 1745. MS-Cl (m/z): [M + H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>14</sub>F<sub>3</sub>O<sub>2</sub>, 223; found, 223.

### Methyl 2-(trifluoromethyl)acrylate (16)

To a 500 mL, 3-neck round bottom flask equipped with a stir bar, condenser, and nitrogen inlet was added 200 mL of dry acetone, 20 g (0.143 mol) of the acid **7**, 23.3 g (0.185 mol) of dimethylsulfate and 25.7 g (0.185 mol) of potassium carbonate that had been dried overnight at 50 °C under high vacuum. The resulting mixture was heated under reflux for 5 h, then cooled to room temperature and 1 g of sodium carbonate was added. After 30 min, the mixture was decanted and the solid products were washed with acetone. Distillation of the combined acetone extracts at atmospheric pressure (101-102 °C) gave 7.04 g (31.9%) of a colorless liquid **16** that was 95% pure by NMR. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.83 (s, 3H), 6.44-6.46 (d, 1H), 6.71-6.73, (d, 1H); <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ) 30.93, 116.42, 120.03, 123.63, 127.25, 131.56, 133.43, 162.00; IR (cm<sup>-1</sup>) 2012, 2960, 1742, 1650. HRMS-Cl (m/z): [M + H]<sup>+</sup> calcd for C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>F<sub>3</sub>, 155.0318; found, 155.0320.

### Poly(methyl 2-(trifluoromethyl)acrylate) (17)

To a 100 mL round bottom flask equipped with a stir bar was added 7.04 g (45 mmol) of monomer **16**, 0.043 g (0.9 mmol) of potassium acetate, and 0.24 g (0.9 mmol) of 18-crown-6. After 15 min the reaction mixture became a thick, colorless mass. After 1 h, the reaction mixture was dissolved in a minimum of THF and the THF solution was added to methanol. The precipitate was filtered, and dried overnight in a vacuum oven at 50 °C, affording 2.93 g of white polymer **17**. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>,  $\delta$ ) 0.49 (s br, 2H), 3.66 (s, 3H); <sup>13</sup>C NMR (75.6 MHz, CDCl<sub>3</sub>,  $\delta$ ) 42.14, 52.74, 54.75, 123.56, 165.94.

### 1,1,1-Trifluoro-2-(trifluoromethyl)pent-4-ene-2-ol (18) ether complex

Allyl magnesium bromide (1 M in ether, 500 ml) was placed in a 1 L three neck round bottom flask and cooled with an ice bath. To this was added dropwise 83 mL of condensed hexafluoroacetone (HFA). The ice bath was

removed after the addition of HFA and the reaction was stirred at room temperature for 17 h. The resulting solution was cooled with an ice bath and then 3 N HCl was added until the pH was ~5. The organic phase was separated and washed with water until the pH of the aqueous phase was ~7. Excess ether solvent was removed at 30 torr. The desired product was obtained by distillation at room pressure to yield a clear liquid (111.49 g complexed with ether, 81.8%). Different ratios of ether and the alcohol were obtained across a wide range of head temperatures (56-95 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.67 (d, *J* = 7.5 Hz, allylic, 2H), 3.11 (s, OH, 1H); 5.29-5.40 (m, vinylic, 2H), 5.76-5.90 (m, vinylic, 1H). IR (cm<sup>-1</sup>) 3600, 3472, 3196, 2980, 2878, 1644, 1449, 1388, 1280, 1019, 958, 722, 681. HRMS-Cl (m/z): [M + H]<sup>+</sup> calcd for C<sub>6</sub>H<sub>7</sub>F<sub>6</sub>O, 209.040; Found: 209.040.

### 3-(5-Bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propanol (19)

Alcohol **18** (0.17 mol), freshly cracked cyclopentadiene (23 ml), and hydroquinone (0.2 g) were added to a Parr bomb (Parr Instrument Company, MAWP 3000Psi). The bomb was heated at 175 °C for 17 hrs. The unreacted ether complex of **18** was recovered (0.07 mol, 41%) by distillation. The residue was then purified by column chromatography (eluent: hexane/ethyl acetate 10/1) and vacuum distillation (105-106 °C at 55 torr) to yield the product as a clear oil (8.97 g, 32.7 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 0.63 (m, 1H), 1.22-1.50 (m, 3H), 1.61-2.12 (m, 3H), 2.37 (bs, 1H), 2.75-2.92 (m, 2H), 5.92-6.22 (m, 2H). IR (cm<sup>-1</sup>) 3598, 3487, 3061, 2965, 2868, 1214, 1141, 716. HRMS-Cl (m/z): [M + H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>F<sub>6</sub>O, 275.087; Found: 275.086.

### tert-Butyl 3-(5-bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propyl carbonate (20)

Sodium hydride (2.39 g, 59.7 mmol, 60% dispersed in mineral oil) was suspended in 80 ml THF, in a 250 ml three neck round bottom flask, and cooled with an ice bath. Alcohol **19** (18.6 g, 54.3 mmol) dissolved in 20 ml THF was added to the reaction flask dropwise. Hydrogen gas was evolved during the addition of the alcohol. When the gas ceased to evolve, di-*tert*-butyl dicarbonate (13.0 g, 5.97 mmol) in 50 ml of THF was added and the resulting mixture was stirred overnight at room temperature. Cold water was then added to quench excess NaH and additional ether was

then added. The organic phase was separated, and washed with water until the aqueous phase was neutral. The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, hexanes as an eluent) to yield a clear oil (19.3 g, 95%) that is a mixture of *endo*- and *exo*- product **20**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.21 (m), 6.07 (m), 5.97 (m), 2.85 (m), 2.79 (m), 2.63 (m), 2.48 (m), 2.43 (m), 2.06-1.92 (m), 1.56 (s), 1.52 (d, *J*=1.2 Hz, *t*-Bu), 1.50 (d, *J*=1.2 Hz, *t*-Bu), 1.45-1.23 (m), 0.68 (m), 0.64 (m). IR (cm<sup>-1</sup>) 2974, 1774, 1287, 1249, 1218, 1132, 1092.

**Poly(*tert*-Butyl 3-(5-bicyclo[2.2.1]hepten-2-yl)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propyl carbonate) (21)**

To a 100 mL flask, was added monomer **20** (5.61 g), bis(pentafluorophenyl)nickel toluene complex (73 mg) [9], and oxygen-free toluene (20 mL) at room temperature. After stirring for 15 h, the mixture was added to methanol dropwise to precipitate the polymer. Filtration and drying under vacuum afforded the product as a white solid **21** (3.0 g, 54% yield). GPC: Mw = 98,400, Pd = 4.08.

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