# SUPPORTING INFORMATION

## RATE CONSTANT FOR THE RING OPENING OF THE 2,2-DIFLUOROCYCLOPROPYLCARBINYL RADICAL

Feng Tian and William R. Dolbier, Jr.*

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200

## Experimental Details

General Remarks

High pressure liquid chromatography (HPLC) was performed with a Beckman Instruments (Fullerton, CA) system gold, model 126 pump with a water (Milford, MA) symmetry shield RP18, 2.1 x 150, plus guard column and a Finnigan MAT (San Jose, CA) LCQ in electrospray ionization (ESI) mode mass spectrometry detector. The mobile phases are, A: 0.5% HOAc and 20 mM $NH_4Oac$ in $H_2O$, B: 0.5% HOAc in 1:1 MeOH: iPrOH. The gradient is at 0.2 ml/min. All the kinetic samples were degassed by 3 freeze/thaw cycles (liquid $N_2$) and sealed *in vacuo* in melting point capillary tubes. All of the kinetic studies were performed at 99.3 ± 0.1°C.

## Kinetic Studies

<u>Decomposition of *tert*-butyl perester, **5**, without TEMPO</u>

A cyclohexane solution of perester (**5**) (25 mg in 300μl cyclohexane with 5 % v/v 1,4-cyclohexenadiene) was used for the kinetic study. The disappearance of **5** was monitored with $^{19}$F NMR using another capillary tube sealed with cyclohexane solution of $PhCF_3$ as external standard. The kinetic data are listed in Table 1.

Table 1. Kinetic data of thermal decomposition of perester **5** in cyclohexane

| point | Time (s) | Integration[a] S | $S_0/S$ | $\ln(S_0/S)$ |
|---|---|---|---|---|
| 1 | 0.0 | 25.3100 | 1.0000 | 0.0000 |
| 2 | 10920.0 | 23.2500 | 1.0886 | 0.0849 |
| 3 | 21660.0 | 19.5700 | 1.2933 | 0.2572 |
| 4 | 32520.0 | 14.6200 | 1.7312 | 0.5488 |
| 5 | 43320.0 | 10.7500 | 2.3544 | 0.8562 |
| 6 | 53880.0 | 8.8200 | 2.8696 | 1.0542 |

[a] The peak at –131.1 ppm in $^{19}$F NMR spectrum was used for integration.

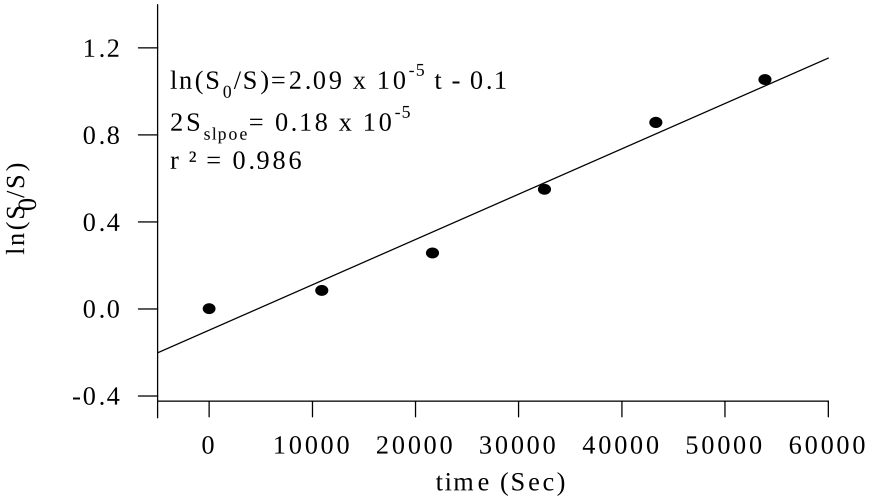

Figure 1. Plot of $\ln(S_0/S)$ vs. time of decomposition of **5** in cyclohexane with 5% v/v 1,4-cyclohexadiene.

Rate constant $k_0 = (2.09 \pm 0.18) \times 10^{-5}\ s^{-1}$

Decomposition of *tert*-butyl perester **5** with 0.6 M TEMPO

A cyclohexane solution of perester (**5**) (10 mg in 1ml cyclohexane with 0.600 M TEMPO) was used for the kinetic study. The disappearance of **5** was monitored with $^{19}F$ NMR using another capillary tube sealed with cyclohexane solution of $PhCF_3$ as external standard. The kinetic data are listed in Table 2.

Table 2. Kinetic data of thermal decomposition of perester **5** in cyclohexane solution of 0.6 M TEMPO

| point | Time (s) | Integration[a] S | $S_0/S$ | $\ln(S_0/S)$ |
|---|---|---|---|---|
| 1 | 0 | 34.68 | 1 | 0 |
| 2 | 9600 | 22.65 | 1.53 | 0.426 |
| 3 | 14400 | 18.66 | 1.86 | 0.620 |
| 4 | 20100 | 13.19 | 2.63 | 0.967 |
| 5 | 25440 | 12.05 | 2.88 | 1.057 |
| 6 | 32280 | 9.85 | 3.52 | 1.259 |

[a] Peaks at –138.0 ppm were used for integration.

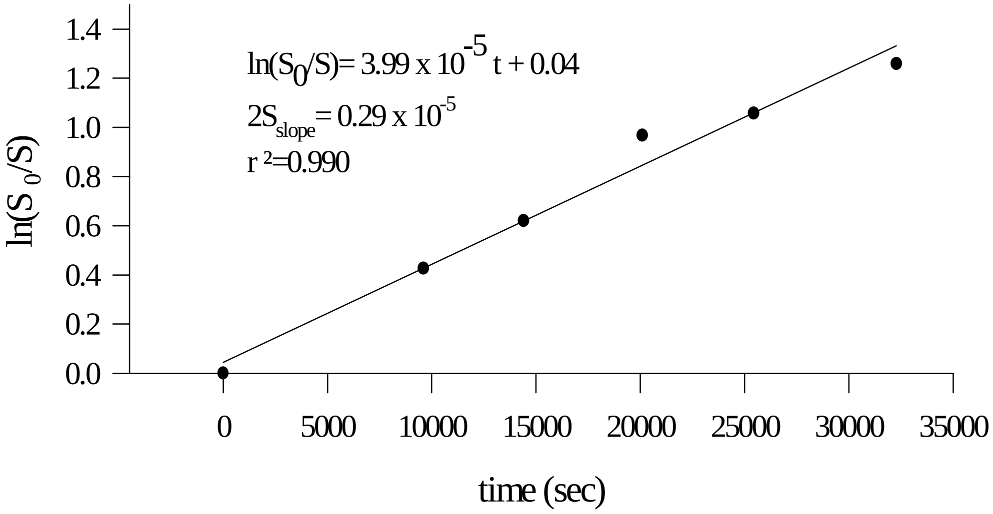

Figure 2. Plot of $\ln(S_0/S)$ vs. time of decomposition of **5** in cyclohexane with 0.6 M TEMPO.

Rate constant $k_{0.6} = (3.99 \pm 0.29) \times 10^{-5}\ s^{-1}$

Decomposition of *tert*-butyl perester **5** cyclohexane with 1.0 M TEMPO

Table 3. Kinetic data of thermal decomposition of perester **5** in cyclohexane solution of 1.0 M TEMPO

| point | Time (s) | Integration[a] S | $S_0/S$ | $\ln(S_0/S)$ |
|---|---|---|---|---|
| 1 | 0.0000 | 41.59 | 1 | 0 |
| 2 | 3600 | 32.93 | 1.263 | 0.233 |
| 3 | 6960 | 25.62 | 1.623 | 0.485 |
| 4 | 11460 | 21.75 | 1.912 | 0.648 |
| 5 | 15120 | 19.54 | 2.129 | 0.755 |
| 6 | 18780 | 16.23 | 2.563 | 0.941 |
| 7 | 22560 | 12.81 | 3.247 | 1.178 |

[a] Peaks at –133.8 ppm were used for integration.

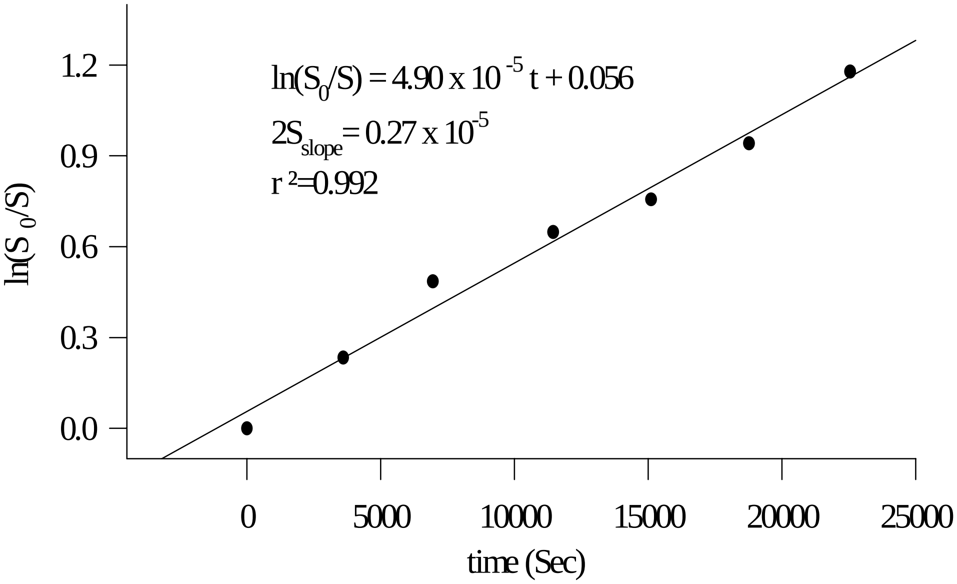

Figure 3. Plot of $\ln(S_0/S)$ vs. time of decomposition of **5** in cyclohexane with 1.0 M TEMPO.

Rate constant $k_{1.0} = (4.90 \pm 0.27) \times 10^{-5}\ s^{-1}$

## Identification of product **3** and **4** and calibration of relative overall response coefficient on HPLC/ESI-MS

The authentic samples of **3** and **4** were analyzed on HPLC/ESI-MS to obtain the values of retention times and ionization patterns. The ring-closed product **3** was easier to elute compared to the ring-opened product **4**. Interestingly, under experimental conditions, only **4** yields m/z 104 and only **3** yields m/z 91.

Three experimental runs were carried out to determine the relative overall response coefficient of **3** and **4** using a 1:1 mixture as measured from its $^{19}$FNMR spectrum. The integration of the total ions on mass spectrum and the ratios were listed in Table 4.

Table 4. Integrations and ratios of **3** and **4** on HPLC/ESI-MS using 1:1 mixture determined with $^{19}$F NMR.

| run | Integration **3** ($10^9$) | Integration of **4** ($10^9$) | Ratio (**3**: **4**) |
|---|---|---|---|
| 1 | 5.496 | 9.868 | 0.5570 |
| 2 | 5.576 | 9.385 | 0.5942 |
| 3 | 6.178 | 10.576 | 0.5841 |
| average | 5.750 | 9.943 | 0.5784 |
| ± std. dev. | 0.3725 | 0.599 | 0.0192 |

Relative overall response coefficient (**3** : **4**) = 0.578 ± 0.019

## Response of integration of product **3** to dilution

The MS integrations of TIC of ring-closed product **3** were measured with its relative concentration varied from 1 (which corresponds to the absolute concentration of **4** in the above experimental kinetic response coefficient experiment), 1/100, 1/200, 1/300. These dilutions correspond to those of **3** that are experimentally observed in the kinetic experiments. The data are listed in Table 5 and least square plot was depicted in Figure 4.

Table 5. Study of conc./integration sensitivity of product **3** using HPLC/ESI-MS

| Rel. [**3**] in sample | Rel. Amount | TIC Integration | Rel. TIC | Rel. TIC / Rel. Amt |
|---|---|---|---|---|
| 1.0000 | 1.0000 | 2901668919 | 1.0000 | |
| 1/100 | 0.0100 | 35586536 | 0.0123 | 1.23 |
| 1/200 | 5.0000e-3 | 18522666 | 6.3000e-3 | 1.26 |
| 1/300 | 3.3000e-3 | 11529730 | 4.0000e-3 | 1.21 |

So the total calibration factor for the ratio of **3**:**4** should therefore be:

0.578 x 1.23= 0.71

Kinetic measurements of the HPLC/ESI-MS ratios of **3** and **4** in the presence of various concentrations of TEMPO

A series of degassed cyclohexane solution of perester (**58**) (25 mg in 10ml cyclohexane with 5 % v/v 1,4-cyclohexenadiene) with the concentrations TEMPO (sublimed) of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 M, respectively, were maintained at 99.3 ± 0.1 °C for 54 hours and were analyzed on HPLC/ESI-MS. The kinetic data are listed in Table 6 and the plot is depicted in Figure 5.

Table 6. HPLC/ESI-MS integrations of total ions of **510** and **59** at different concentration of TEMPO in cyclohexane with 5% v/v of 1,4-cyclohexadiene

| run | [TEMPO] | Integration **510** ($10^7$) | integration **59** ($10^7$) | **510**: **59** |
|---|---|---|---|---|
| 1 | 0.500 | 3.132 | 640.0 | 0.00489 |
| 2 | 0.600 | 5.922 | 911.0 | 0.00650 |
| 3 | 0.700 | 7.990 | 1126.0 | 0.00709 |
| 4 | 0.800 | 5.722 | 837.8 | 0.00683 |
| 5 | 0.900 | 7.251 | 756.7 | 0.00958 |
| 6 | 1.000 | 9.419 | 975.8 | 0.00965 |

|  |  |  |  |  |
|---|---|---|---|---|
| 7 | 1.100 | 8.860 | 900.1 | 0.00984 |

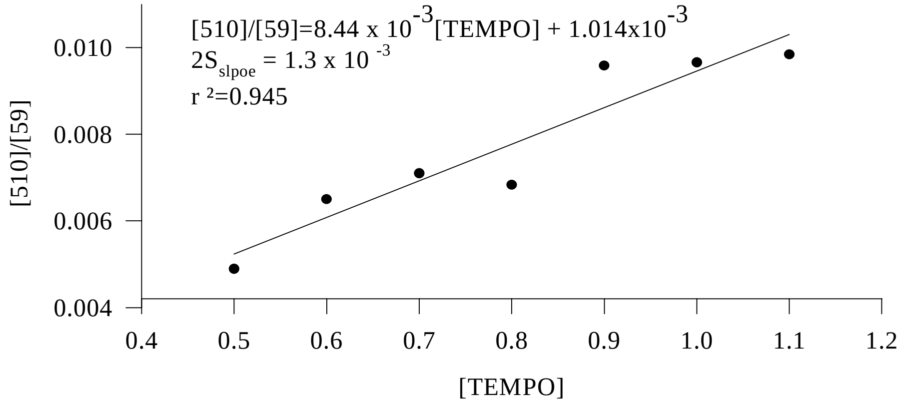

Figure 5. Plot of [**510**]/[**59**] *vs.* concentrations of TEMPO

After corrected by the relative overall respond coefficient: slope = (1.46 ± 0.22) x $10^{-2}$ $M^{-1}$, which is equal to the ratio of TEMPO trapping ($k_T$) and radical ring opening ($k_r$):

$$k_T : k_r = (1.46 \pm 0.22) \times 10^{-2}$$

because $k_T = 1.5 \times 10^{9} M^{-1} s^{-1}$, so

$$k_r = (1.0 \pm 0.15) \times 10^{11} s^{-1}$$

Synthesis of Kinetic Precursor

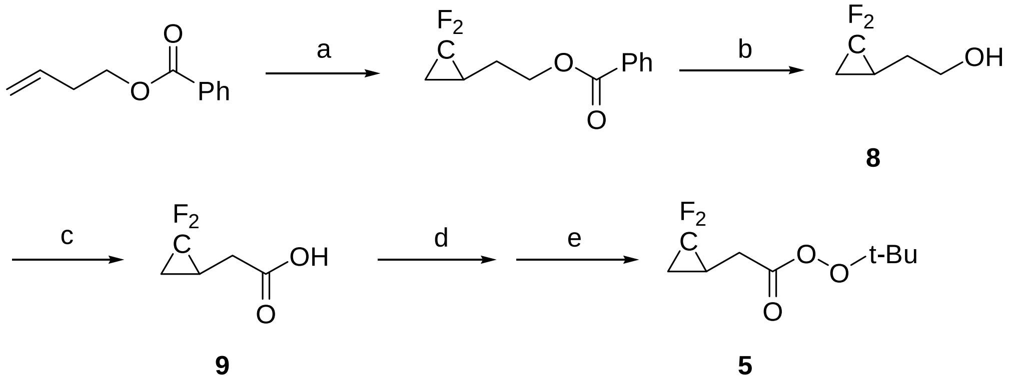

Figure 6. (a). $FSO_2CF_2COOTMS$, NaF, 125°C. (b). NaOH, $H_2O$. (c). $CrO_3$, $H_2SO_4$. (d). ClCOCOCl. (e). HOOt-Bu

1,1-Difluoro-2-(2’-hydroxyl)ethyl-cyclopropane (**8**)

Under $N_2$, a 25 ml two-neck-round bottom flask equipped with a condenser and a magnetic stirring bar was charged with 3.74 g (21 mmol, 1 equivalent) of 3-butenyl benzoate and 10 mg dry NaF. At 125 °C, 8 g (30 mmol, 1.5 equivalent) of trimethylsilyl fluorosulfonyldifluoroacetate was added using a syringe pump with a Teflon® needle. After the addition was completed in 12 hours, the $^1H$ NMR spectrum of the reaction mixture indicated a complete conversion of the starting alkene and that the reaction mixture was nearly the pure cyclopropanated ester except a very little TMS signal. The reaction mixture was transferred into a 100 ml one-neck-round bottom flask equipped with a condenser. Into this flask, charged with 40 ml 10% NaOH/$H_2O$ solution. After refluxing for 3 hours, the reaction mixture was cooled to room temperature and extracted with diethyl ether ( 5 x 20 ml). The combined organic layer was washed with water, 0.1 M HCl, water and brine, and was dried over $Na_2SO_4$. The solvent was vaporized under reduced pressure. The vacuum distillation of the residue (5 mmHg, 55-58 °C) provided

1.6 g (131 mmol) of colorless liquid product, **8**, with an overall yield of 62 % for the one-pot-two-step synthesis. $^1$H NMR δ 3.74 (1H, q, *J*=5.1 Hz), 1.7 (3H, m), 1.43 (1H, tdd, $J_t$ = 11.0 Hz, $J_d$ = 7.6 Hz, $J_d$ = 4.2 Hz), 0.97 (1H, dtd, $J_{d\ (H\text{-}F)}$ = 12.9 Hz, $J_t$ = 7.6 Hz, $J_d$ = 3.4Hz); $^{13}$C NMR δ 114.522 (t, $J_{F\text{-}C}$ =282 Hz), 61.973 (d, $J_{F\text{-}C}$ = 2.0 Hz), 30.156 (t, $J_{F\text{-}C}$= 3.5 Hz), 19.719 (t, $J_{F\text{-}C}$ = 10.5 Hz), 16.067 (t, $J_{F\text{-}C}$ = 11.0 Hz); $^{19}$F NMR δ -129.1 (1F, dt, $J_{d\ (F\text{-}F)}$ = 155.7 Hz, $J_{t\ (F\text{-}H)}$ = 12.7 Hz), -144.3 (1F, ddd, $J_{F\text{-}F}$ =155.7 Hz, $J_{F\text{-}H}$ = 13.0 Hz, $J_{F\text{-}H}$ = 4.2 Hz); HRMS $C_5H_9OF_2$ $(M+1)^+$, calculated 123.0621, found 123.0612.

2',2'-Difluorocyclopropyl acetic acid (**9**)

A 250 mol round bottom flask equipped with a magnetic stirring bar was charged with 6 g $CrO_3$ and 100 ml 1.5 M $H_2SO_4$. At 0°C, 100 ml acetone solution of 1.45 g (12 mmol) of alcohol (**8**) was added dropwise. Upon the completion of the addition, the temperature was raised to room temperature. After 4 hour of stirring, the reaction mixture was extracted with diethyl ether (4x50ml). The combined organic layer was washed with brine and then extracted with 2.0 M of NaOH/$H_2O$ (4 x 50 ml). The aqueous layer was acidified with $H_2SO_4$ to pH < 1 and extracted with diethyl ether (4 x 50 ml). The combined organic layer was washed with water, brine and dried over $Na_2SO_4$. The solvent was vaporized under reduced pressure. This afforded 1.8 g (12mmol) colorless liquid with some ether, which later solidified to white solid pure product, **9**, with a 100% yield. $^1$H NMR δ 11.6 (1H, broad), 2.56 [2H, ab pattern, a 2.62 (ddt, $J_d$ = 17.6 Hz, $J_d$ = 7.33, $J_d$ = 1.5 Hz), b 2.51 (dddd, $J_d$ = 17.6 Hz, $J_d$ = 7.6 Hz, $J_d$ = 2.7 Hz, $J_d$ = 1.2 Hz)], 1.87 (1H, ddq, $J_d$ = 13.2 Hz, $J_d$ =11.2Hz, $J_q$ = 7.3 Hz), 1.56 (1H, tdd, $J_t$ = 11.7 Hz, $J_d$ = 7.8 Hz, $J_d$ = 4.6 Hz), 1.09 (1H, dtd, $J_d$ = 12.9 Hz, $J_t$ = 7.8 Hz, $J_d$ = 3.7Hz); $^{13}$C NMR δ 177.822, 113.160 (dd, $J_{d\ (C\text{-}F)}$ = 283 Hz, $J_{d\ (C\text{-}F)}$ = 280 Hz), 31.959 (d, $J_{d\ (C\text{-}F)}$ = 5.0 Hz), 17.843 (t, $J_{t\,(C\text{-}F)}$ = 11.6 Hz), 16.260 (t, $J_{t\,(C\text{-}F)}$ = 11.0 Hz); $^{19}$F NMR δ -130.7 (1F, dt, $J_{d\,(F\text{-}F)}$ = 160.1 Hz, $J_{t\,(H\text{-}F)}$ = 12.8 Hz), -143.9 (1H, ddd, $J_{d\,(F\text{-}F)}$ = 160.1 Hz, $J_{t\,(H\text{-}F)}$ = 12.8 Hz, $J_{t\,(H\text{-}F)}$ = 4.3 Hz); HRMS $C_5H_7O_2F_2$ $(M+1)^+$, calculated 137.0414, found 137.0443; Elemental Analysis, calculated C: 44.13%, H: 4.44%, found C: 44.03%, H: 4.37%.

*tert*-Butyl per(2',2'-difluorocyclopropyl)acetate (**5**)

Under $N_2$, a 10ml two-neck-round-bottom flask equipped with a magnetic stirring bar was charged with 0.70 g (5 mmol, 1 equivalent) of acid (**9**), 5 ml pentane. After the acid was dissolved in pentane, 0.73 g ( 5.7 mmol, 1.1 equivalent) of oxalyl chloride was added dropwise. The reaction mixture was stirred overnight.

Under $N_2$, a 25 ml two-neck-round-bottom flask equipped with a magnetic stirring bar was charged with 0.405 g (4.5 mmol, 0.9 equivalent) *tert*-butyl hydroperoxide anhydrous (obtained by keeping 90% *tert*-butyl hydroperoxide with 4 Å molecular sieve (molecular sieve was changed 4 times)), 0.71g pyridine and 5 ml pentane. At 0°C, the above prepared acyl chloride pentane solution was added dropwise. Upon the completion of the addition, the reaction mixture was stirred at room temperature for an hour, diluted with 20 ml of pentane and washed with water, cold 15% (w/w) $H_2SO_4$, water, saturated sodium bicarbonate, brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure. The crude product was purified using flash column chromatograph (hexane to 10% diethyl ether). The product has a very weak UV absorption on TLC. This provided 0.84 g (4 mmol) of colorless liquid, **5**, with an overall yield of 81%. $^1$H NMR δ 2.51 [2H, ab pattern, a 2.57 (ddt, $J_d$ = 16.8 Hz, $J_d$ = 7.5, $J_d$ = 1.5 Hz), b 2.45 (dddd, $J_d$ = 16.8 Hz, $J_d$ = 7.5 Hz, $J_d$ = 2.4 Hz, $J_d$ = 1.2 Hz)], 1.88 (1H, ddq, $J_d$ = 12.9 Hz, $J_d$ =11.4Hz, $J_q$ = 7.5 Hz), 1.57 (1H, tdd, $J_t$ = 11.9 Hz, $J_d$ = 8.1 Hz, $J_d$ = 4.5 Hz), 1.33 (9H, s), 1.09 (1H, dtd, $J_d$ = 12.9 Hz, $J_t$ = 7.8 Hz, $J_d$ = 3.6Hz); $^{13}$C NMR δ 168.578, 112.750 (t, $J_{t(C\text{-}F)}$= 284 Hz), 83.784, 29.435(d, $J_{d(C\text{-}F)}$ = 4.5 Hz), 26.006, 17.787 (t, $J_{t(C\text{-}F)}$ = 11.0 Hz), 16.157 (t, $J_{t(C\text{-}F)}$ = 11.0 Hz); $^{19}$F NMR δ -130.644 (1F, dt, $J_{d(F\text{-}F)}$ = 157.9 Hz, $J_{t\ (F\text{-}H)}$ = 12.7 Hz), -143.9 (1F, ddd, $J_{d(F\text{-}F)}$ = 157.9 Hz, $J_{d(F\text{-}H)}$ = 12.7 Hz, $J_{d(F\text{-}H)}$ = 4.2 Hz); Elemental analysis calculated C: 51.92%, H: 6.78, found C: 51.86%, H: 6.93%.

Syntheses of Authentic Products

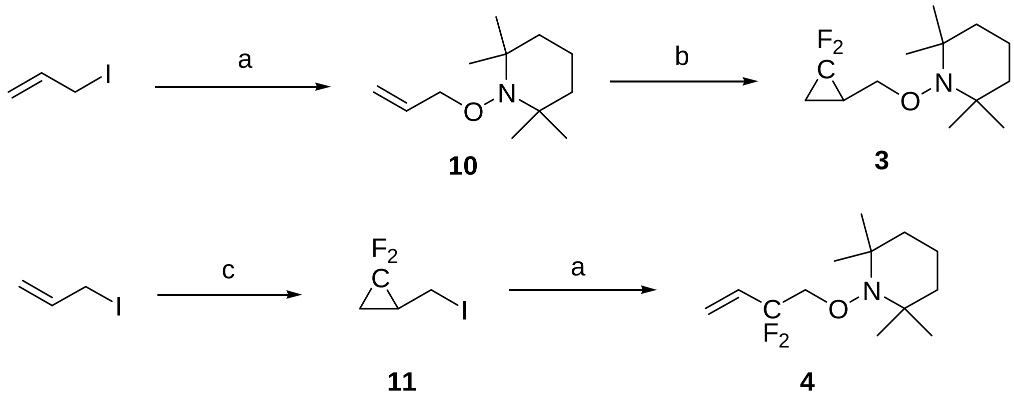

Figure 7. (a). TEMPO, *hv*, $Na_2SO_3$, $CH_3CN$; (b). $FSO_2CF_2COOTMS$, CsF, 90°C PhCOOMe; (c). $FSO_2CF_2COOTMS$, NaF, 105°C, PhCOOMe.

N-Allyloxy-2,2,6,6-tetramethylpiperidine (**10**) (CAS 131531-08-3)

A quartz tube was charged with 1.67 g (10mmol, 1 equivalent) of allyl iodide, 1.9 g (12 mmol, 1.2 equivalent) of TEMPO, 2.52 g of $Na_2SO_3$ and 100 ml $CH_3CN$. The reaction mixture was thoroughly purged with $N_2$ and then irritated in UV reactor with occasionally shaking. After one day's irritation, the color of the reaction mixture faded from red-brown to light orange and the $^1$H NMR indicated a complete conversion. Into the reaction, 200 ml of water was added and the mixture was extracted with diethyl ether

(50ml x 6). The combined organic layer was washed with water, brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure. The crude produce was distilled (~ 1 mmHg, 65 °C-75°C) to afford 0.8 g of colorless product, **10**, which was further purified on silica gel flash chromatograph column (10% diethyl ether/ hexanes, $R_f$ = 0.64). $^1H$ NMR $\delta$ 5.91 (1H, ddt, $J_d$ = 17.3 Hz, $J_d$ = 10.5 Hz, $J_d$ = 5.6 Hz), 5.28 (1H, dq, $J_d$ = 17.3 Hz, $J_q$ = 2.0 Hz), 5.13 (1H, dtd, $J_d$ =10.5 Hz, $J_t$ = 1.5 Hz, $J_d$ =2.0), 4.29 (2H, dt, $J_d$ = 5.4 Hz, $J_t$ = 1.7), 1.46 (4H, m), 1.34 (2H, m), 1.17 (6H, s), 1.12 (6H, s); $^{13}C$ NMR $\delta$ 134.347, 116.252, 59.943, 39.844, 33.134, 20.360, 17.342; HRMS $C_{12}H_{24}NO$ $(M+1)^+$ calculated 198.1858, found 198.1867.

N-(2',2'-Difluorocyclopropyl)methoxy-2,2,6,6-tetramethylpiperidine (**3**)

Under $N_2$, a 5 ml two-neck-pear-shape flask equipped with a magnetic stirring bar was charged with 200 mg (1mmol) of **10**, 136 mg (1mmol) of methyl benzoate and 2 mg of CsF. At 90°C, after 1 g (4 equivalent) of trimethylsilyl fluorosulfonyldifluoroacetate (**21**) was added the complete conversion of reaction was achieved. The reaction mixture was purified on silica gel flash chromatograph column (1:1 hexanes/benzene, $R_f$= 0.5) to remove methyl benzoate. The crude product was further purified on silica gel flash chromatograph column (3% ethyl acetate /hexanes) to provide relative pure light yellow liquid product, **3**, which is unstable on silica gel. $^1H$ NMR 3.80 [2H, ab pattern, a 3.85 (dddd, $J_d$ = 10 Hz, $J_d$ = 6.8 Hz, $J_d$ = 3.2 Hz, $J_d$ = 1.5 Hz), b 3.75 (ddd, $J_d$ = 10 Hz, $J_d$ = 8.3 Hz, $J_d$ = 2.0 Hz)], 1.81 (1H, m), 1.46 (1H, M), 1.45 (4H, m), 1.33 (2H, m), 1.15 (6H, s), 1.12(6H, s), 1.11(1H, m); $^{13}C$ NMR $\delta$ 113.854 (t, $J_{t\ (C\text{-}F)}$ = 281 Hz), 59.993 (d, $J_{d\ (C\text{-}F)}$ = 12.5 Hz), 39.798, 33.174, 21.395 (t, $J_{t\ (C\text{-}F)}$ = 11.0 Hz), 20.260, 17.289, 14.785 (t, $J_{d\ (C\text{-}F)}$ = 11.0 Hz); $^{19}F$ NMR $\delta$ -129.6 (1F, dtt, $J_{d\ (F\text{-}F)}$ = 157.9 Hz, $J_{t\ (F\text{-}H)}$ = 12.8 Hz, $J_{t\ (F\text{-}H)}$ = 8.5

Hz), -143.3 (1F, ddd, $J_{d\ (F\text{-}F)}$ = 157.9 Hz, $J_{d\ (F\text{-}H)}$ = 12.8 Hz, $J_{d\ (F\text{-}H)}$ = 4.3 Hz); HRMS $C_{13}H_{23}NOF_2$ $M^+$, calculated 247.1748, found 247.1689.

2,2-Difluorocyclopropylcarbinyl iodide (**11**)

Under $N_2$, a 25 ml two-neck-round-bottom flask equipped with a magnetic stirring bar was charged with 2.5 g (15 mmol, 1 equivalent) of allyl iodide, 2.04 g (15mmol, 1 equivalent) of methyl benzoate and 2 mg of NaF. At 105°C, 7.5 g (30 mmol, 2 equivalent) of trimethylsilyl fluorosulfonyldifluoroacetate was added using a syringe pump with a Teflon® needle in a period of 10 hours. The reaction mixture was distilled twice (130mmHg, 76°C- 92°C) to afford 1.9 g purple curd product. The color of the reaction mixture changed from light brown to deep purple. The crude product was further purified by a fast silica gel flash chromatograph purification (pentane, $R_f$ = 0.34, TLC UV light visualization). Pentane was removed at 160 mmHg at room temperature. This to afford relative pure colorless liquid product, **11**, which is sensitive to light and unstable on silica gel. $^1$H NMR δ 3.21 [2H, ab pattern, a 3.27 (m), b 3.13 (dddd, $J_d$ = 10.5 Hz, $J_d$ = 8.6 Hz, $J_d$ = 2.4 Hz, $J_d$ = 1.2 Hz)], 2.09 (1H, dddt, $J_d$ = 12.1 Hz, $J_d$ = 11.2 Hz, $J_d$ =8.6Hz, $J_d$ = 7.3 Hz), 1.59 (1H, tdd, $J_t$ = 11.5 Hz, $J_d$ = 8.1 Hz, $J_d$ = 5.1 Hz), 1.03 (1H, dtd, $J_d$ = 13.4 Hz, $J_t$ = 7.8 Hz, $J_d$ = 3.9Hz); $^{13}$C NMR δ 115.838 (t, $J_{(C\text{-}F)}$ = 282 Hz), 26.410 (t, $J_{(C\text{-}F)}$ = 11.0 Hz), 20.314 (t, $J_{(C\text{-}F)}$ = 10.5 Hz), -0.536 (d, $J_{(C\text{-}F)}$ = 5.6 Hz); $^{19}$F NMR δ -126.5 (1F, dt, $J_{d\ (F\text{-}F)}$ = 157.9 Hz, $J_{d(H\text{-}F)}$ = 10.7Hz ), -145.8 (1F, ddd, $J_{(F\text{-}F)}$ = 157.9 Hz, $J_{(H\text{-}F)}$ = 12.8 Hz, $J_{(H\text{-}F)}$ = 4.3 Hz); HRMS (CI pos methane),$C_4H_5IF$ $(M+1\text{-}HF)^+$, calculated 198.9420, found 198.9410, $C_4H_5F_2$ $(M+1\text{-}HI)^+$ calculated 91.0359, found 91.0379 (100).

N-(2’,2’-difluoro)-3-butenoxy-2,2,6,6-tetramethylpiperidine (**4**)

A quartz tube was charged with 217 mg (1mmol, 1 equivalent) of 2,2-difluorocyclopropylcarbinyl iodide, **11**, 188 mg (1.2 mmol, 1.2 equivalent) of TEMPO, 252 mg of $Na_2SO_3$ and 10 ml $CH_3CN$. The reaction mixture was thoroughly purged with $N_2$ and then irritated in UV reactor with occasionally shaking. After one day’s irritation, the color of the reaction mixture faded from red-brown to light orange and the $^{19}F$ NMR spectrum of reaction showed two quartet peaks indicated a complete conversion. Into the reaction mixture, 20 ml of water was added and the mixture was extracted with diethyl ether (5ml x 6). The combined organic layer was washed with water, brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure. The crude product was further purified on silica gel flash chromatograph column (3% ethyl acetate /hexanes, $R_f$ =5.2 for 10% ethyl acetate/hexanes) to provide relative pure colorless liquid product, **4**, which is unstable on silica gel. $^1H$ NMR $\delta$ 6.03 (1H, dq, $J_d$ = 17.8 Hz, $J_q$ = 11.2 Hz), 5.72 (1H, dtd, $J_d$ = 17.6 Hz, $J_t$ = 2.4 Hz, $J_d$ = 1.0 Hz), 5.50 (1H, d, $J_d$ = 11.0 Hz), 4.02 (2H, t, $J_{t(H\text{-}F)}$= 12.5 Hz), 1.46 (4H, m), 1.34 (2H, m), 1.17 (6H, s), 1.11 (6H, s); $^{13}C$ NMR $\delta$ 131.542 (t, $J_{d\ (C\text{-}F)}$ = 25.7 Hz), 120.164 (t, $J_{d\ (C\text{-}F)}$ = 9.6 Hz), 118.388 (t, $J_{d\ (C\text{-}F)}$ = 239.7 Hz), 60.537, 39.864, 32.940, 20.240, 17.162; $^{19}F$ NMR $\delta$ -105.6 (q, $J_q$ = 12.8 Hz); HRMS $C_{13}H_{24}ONF_2$ $(M+1)^+$, calculated 248.1826, found 248.1783.