**Electronic Supplementary Information**

# Experimental and theoretical studies on the thermal decomposition of trans-1-chloro-3,3,3-trifluoropropene/2-chloro-3,3,3-trifluoropropene and their fire-extinguishing performance

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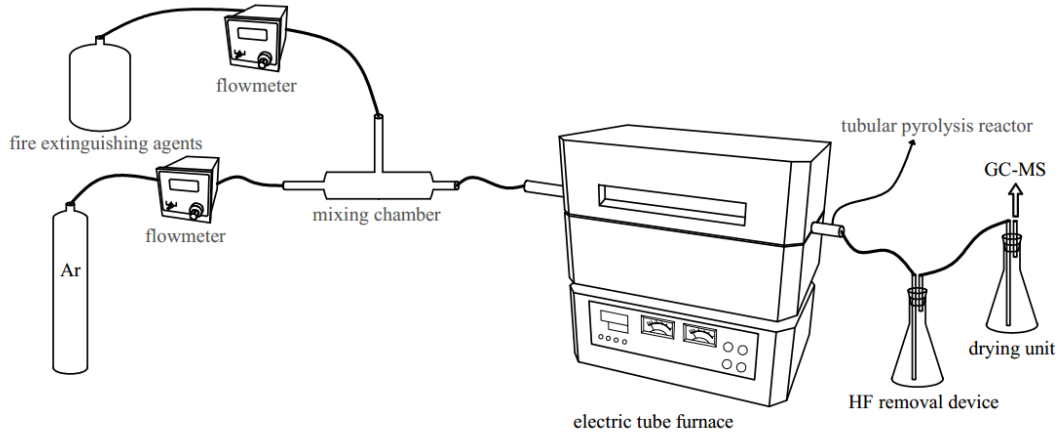



**Fig. S1** Schematic illustration of the thermal decomposition system.

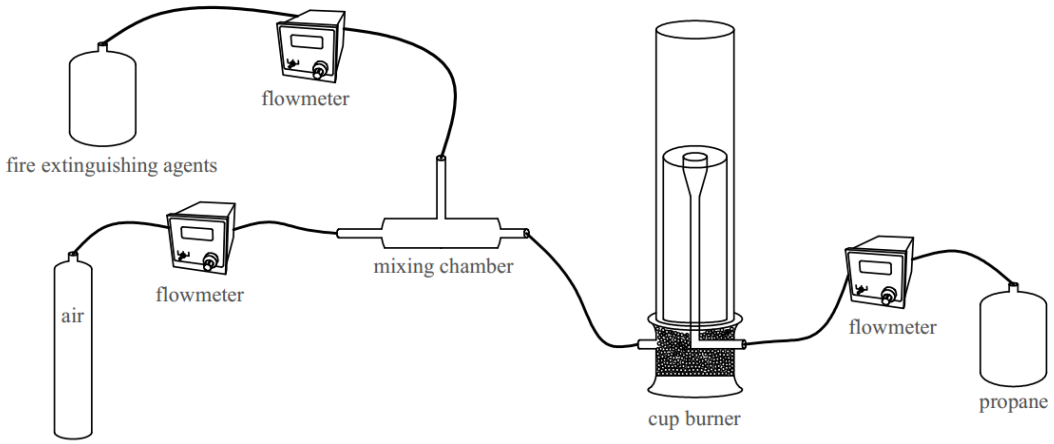
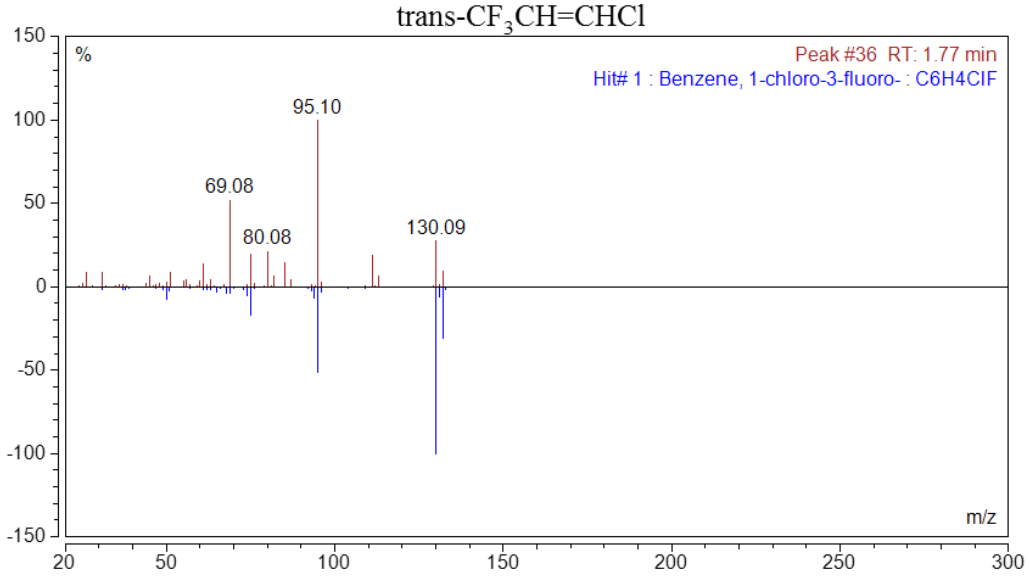
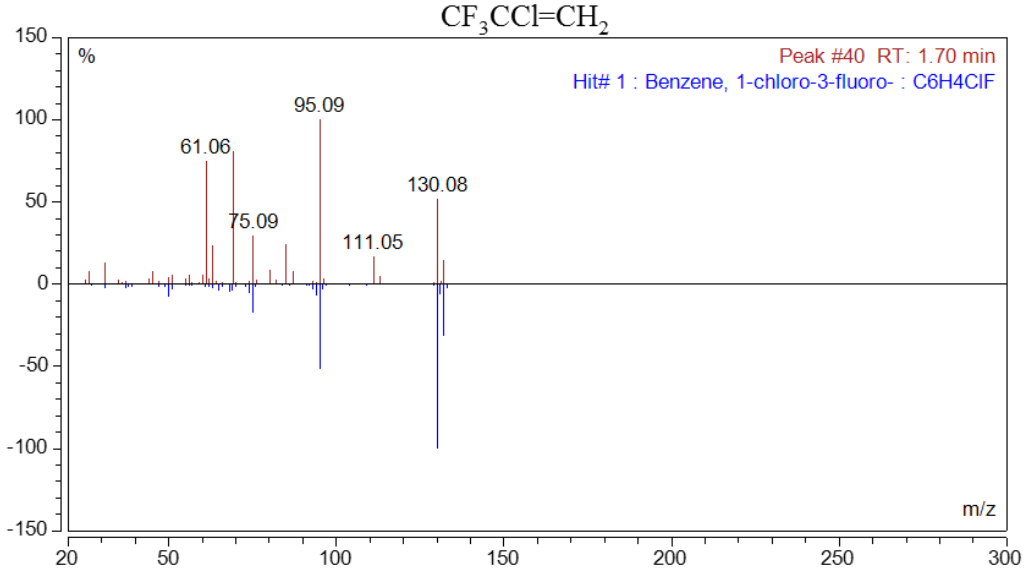



**Fig. S2** Schematic illustration of the cup burner system.

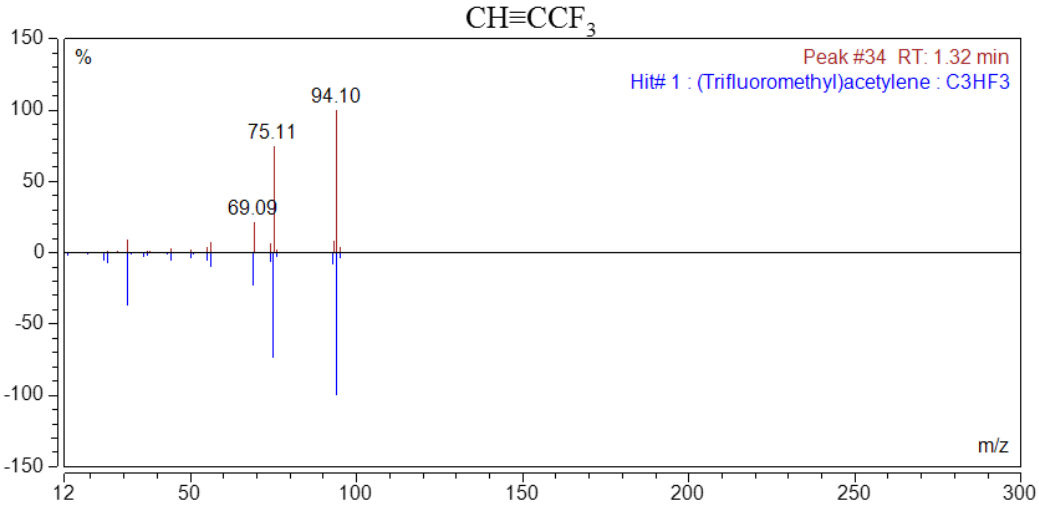
trans-$CF_3CH=CHCl$

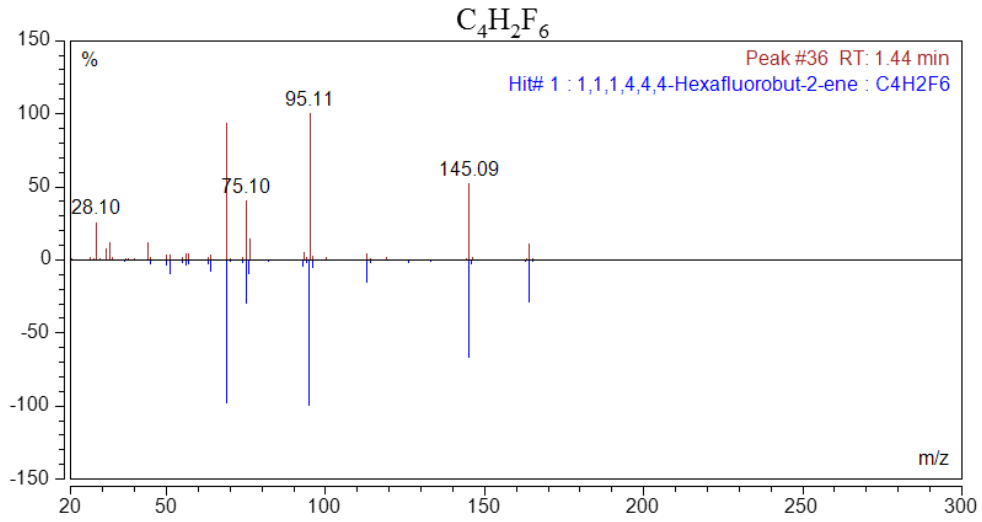


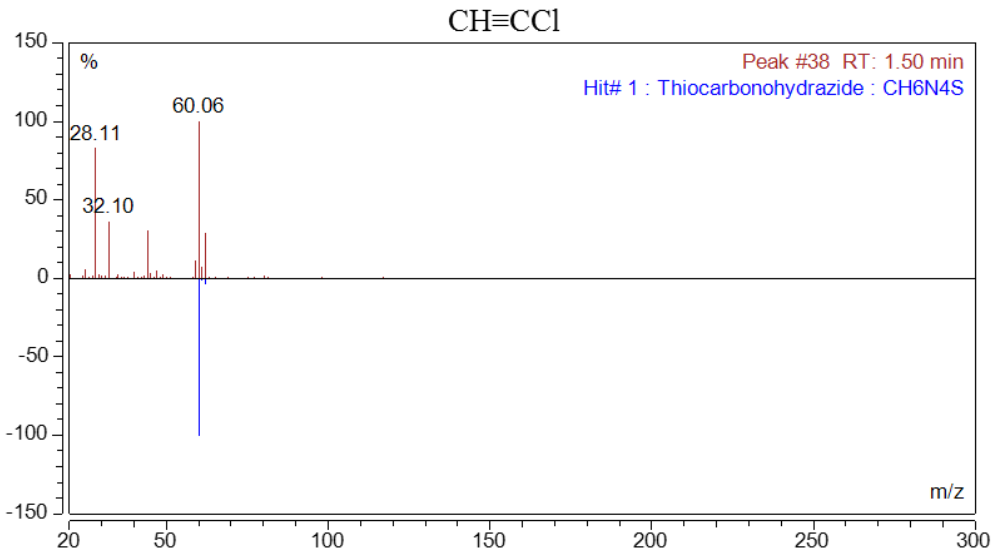

$CF_3CCl=CH_2$

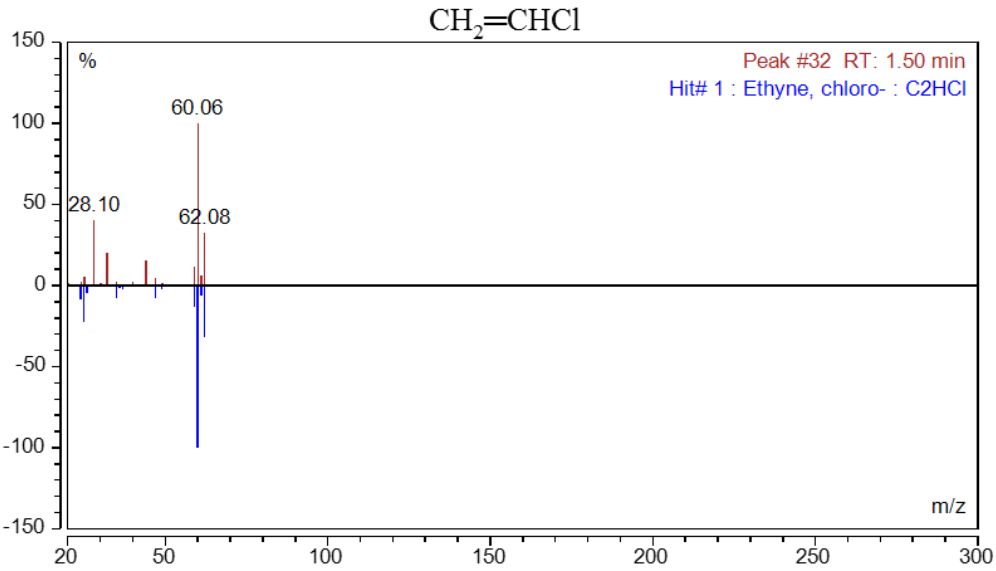



$CH{\equiv}CCF_3$

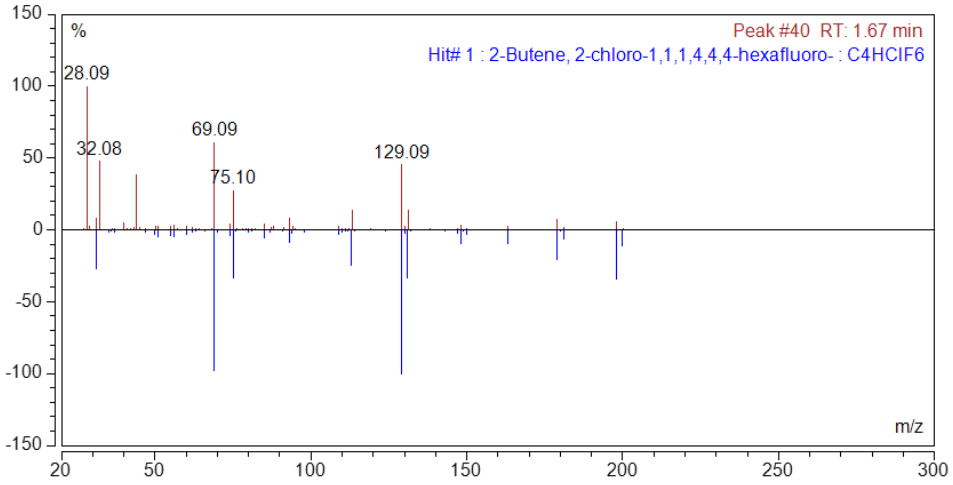



$C_4H_2F_6$
%
Peak #36 RT: 1.44 min
Hit# 1 : 1,1,1,4,4,4-Hexafluorobut-2-ene : C4H2F6
95.11
145.09
75.10
28.10
m/z

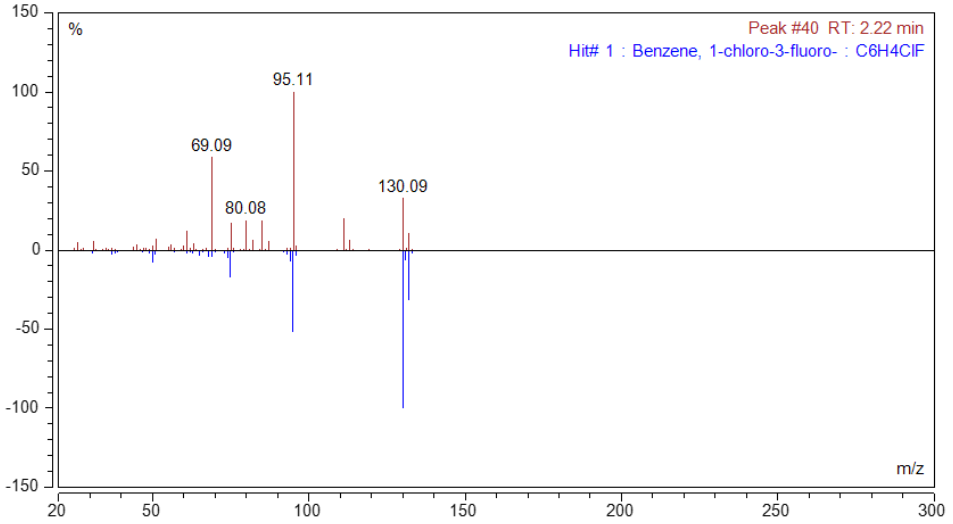

CH≡CCl
%
Peak #38 RT: 1.50 min
Hit# 1 : Thiocarbonohydrazide : CH6N4S
60.06
28.11
32.10
m/z


$CH_2$=CHCl
%
Peak #32 RT: 1.50 min
Hit# 1 : Ethyne, chloro- : C2HCl
60.06
28.10
62.08
m/z

$C_4HF_6Cl$




Isomer of trans-$CF_3CH=CHCl$




Isomer of $CF_3CCl=CH_2$

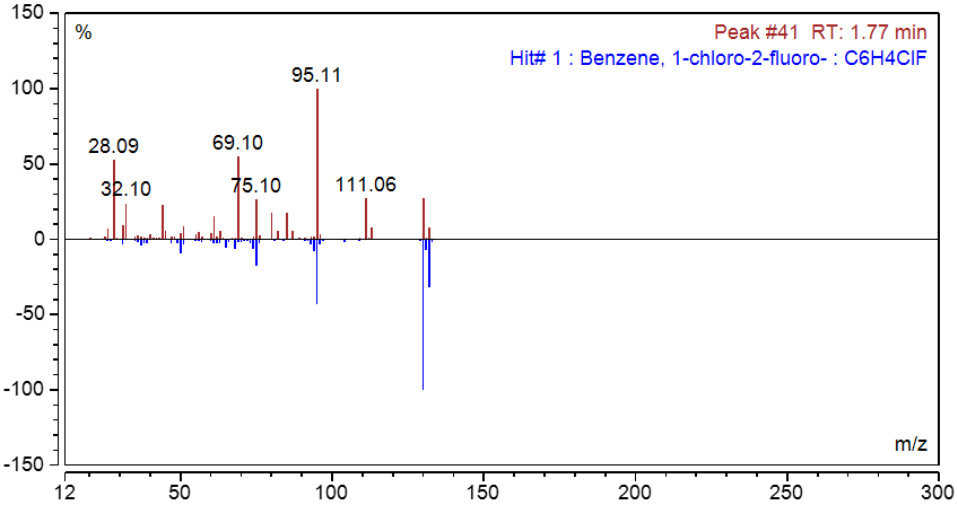
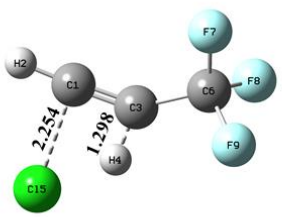



**Fig. S3** Molecular ion peaks of reactants and thermal decomposition products.

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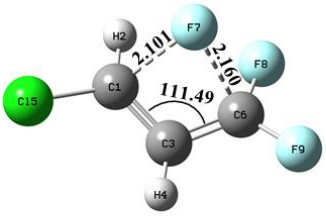


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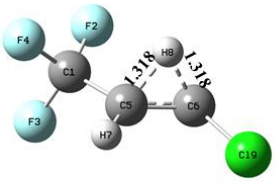


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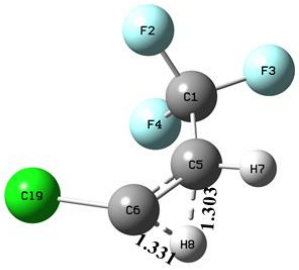


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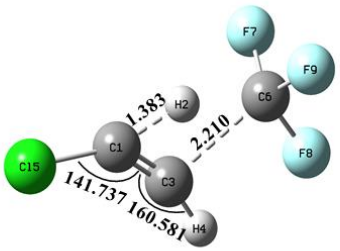


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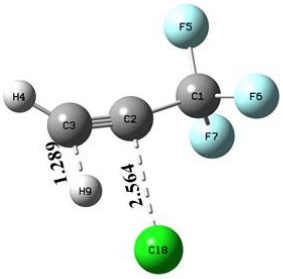


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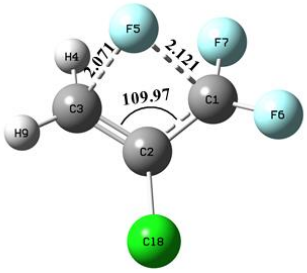


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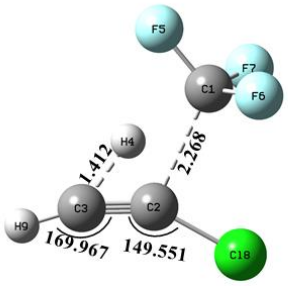


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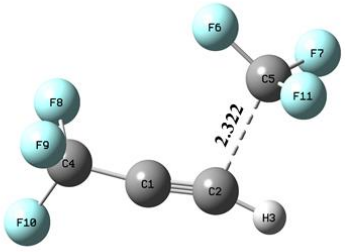


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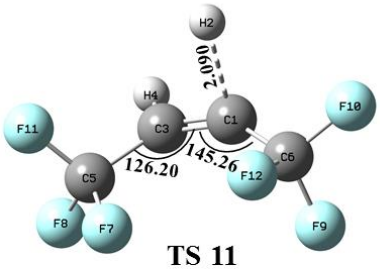


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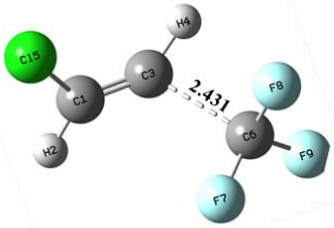


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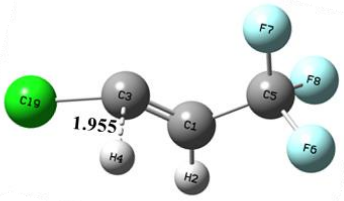


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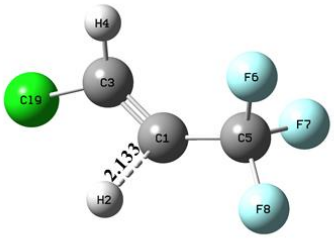


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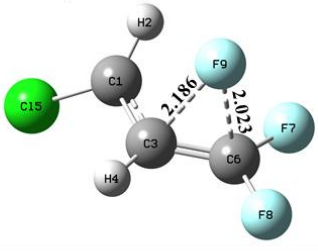


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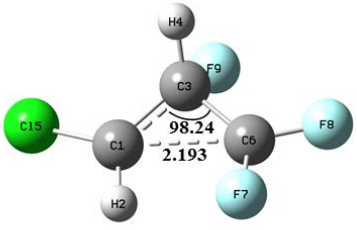


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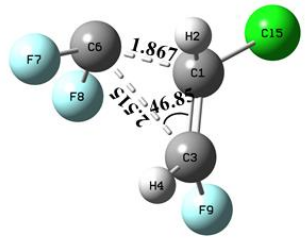


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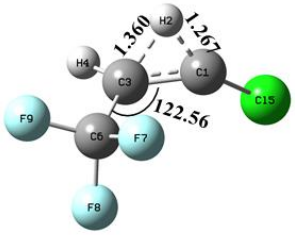


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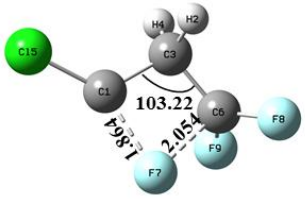


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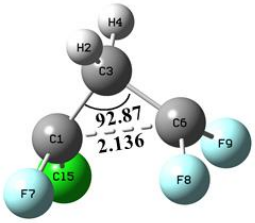


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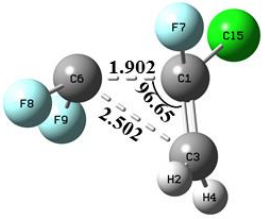


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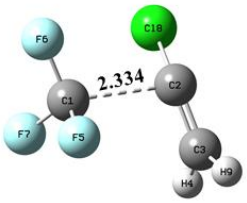


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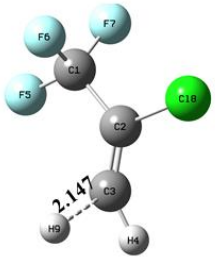


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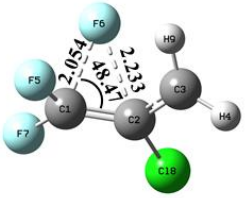


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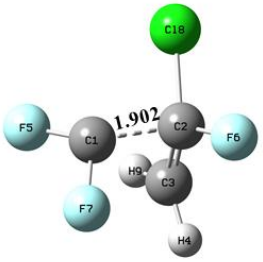


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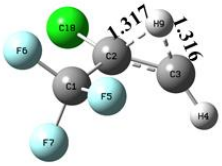


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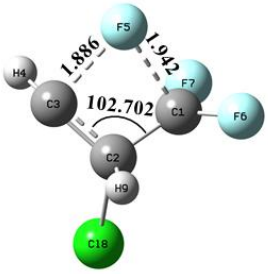


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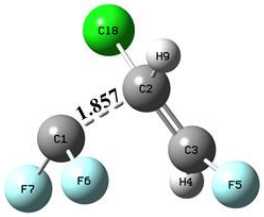


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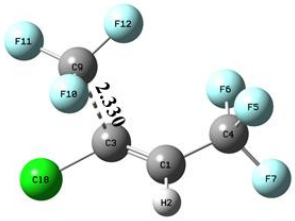


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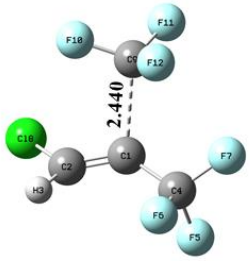


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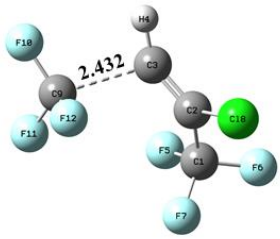


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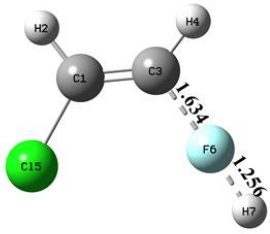


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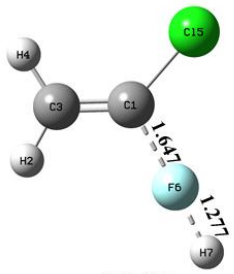


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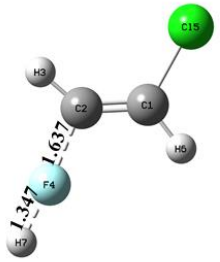


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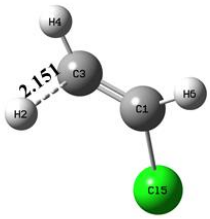


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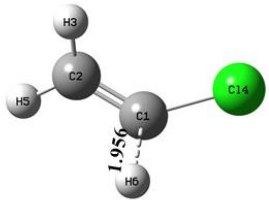


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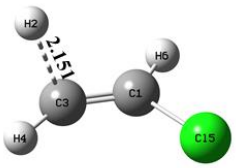


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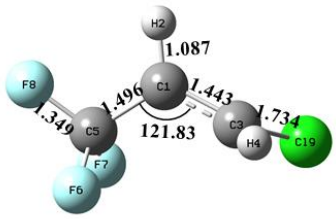
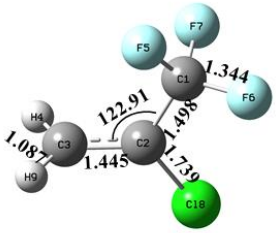



**$CF_3CH{-}CHCl$**

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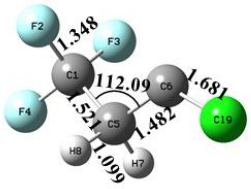


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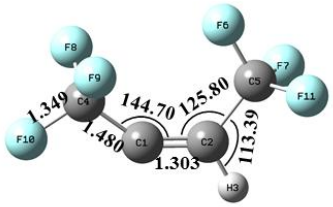


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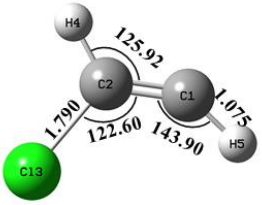


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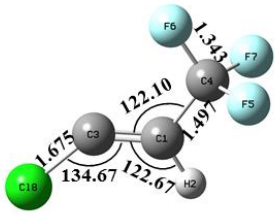


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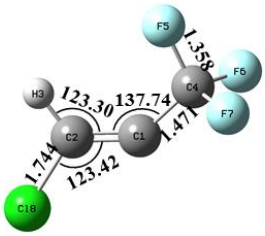


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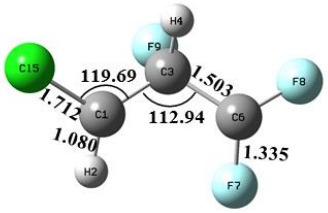
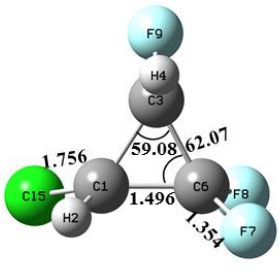
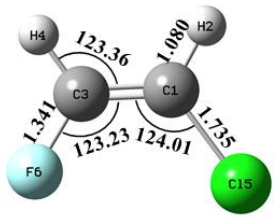



**IM 6**




**IM 7**

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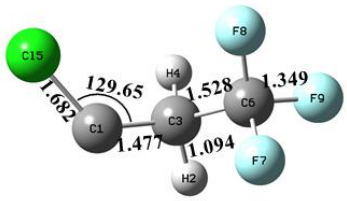


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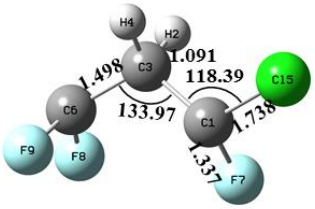


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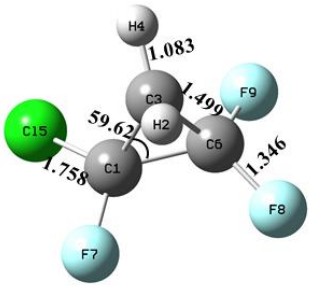


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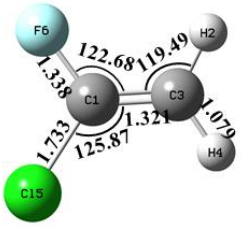
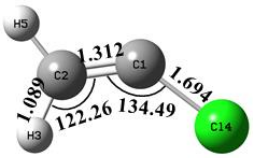
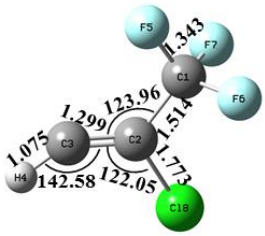


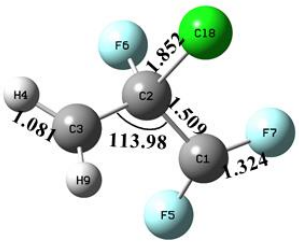

**IM 12**



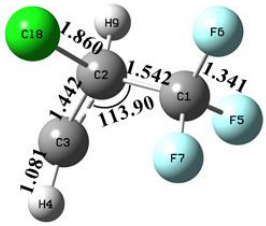

**IM 13**




**IM 14**




**IM 15**

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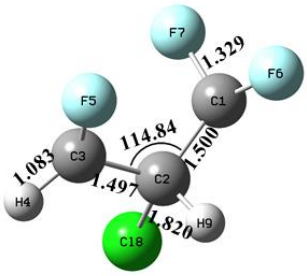
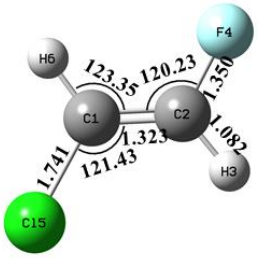
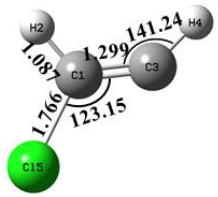


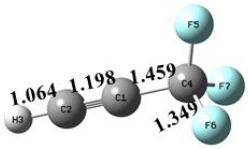

**IM 17**



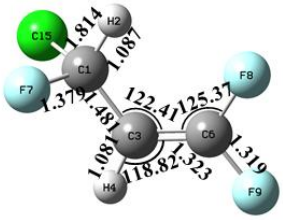

**IM 18**



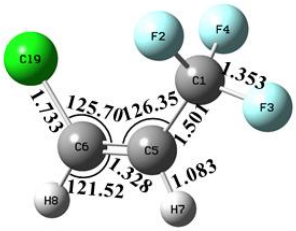

**IM 19**




**$CF_3C{\equiv}CH$**




**$CHFClCH{=}CF_2$**




**cis-$CF_3CH{=}CHCl$**

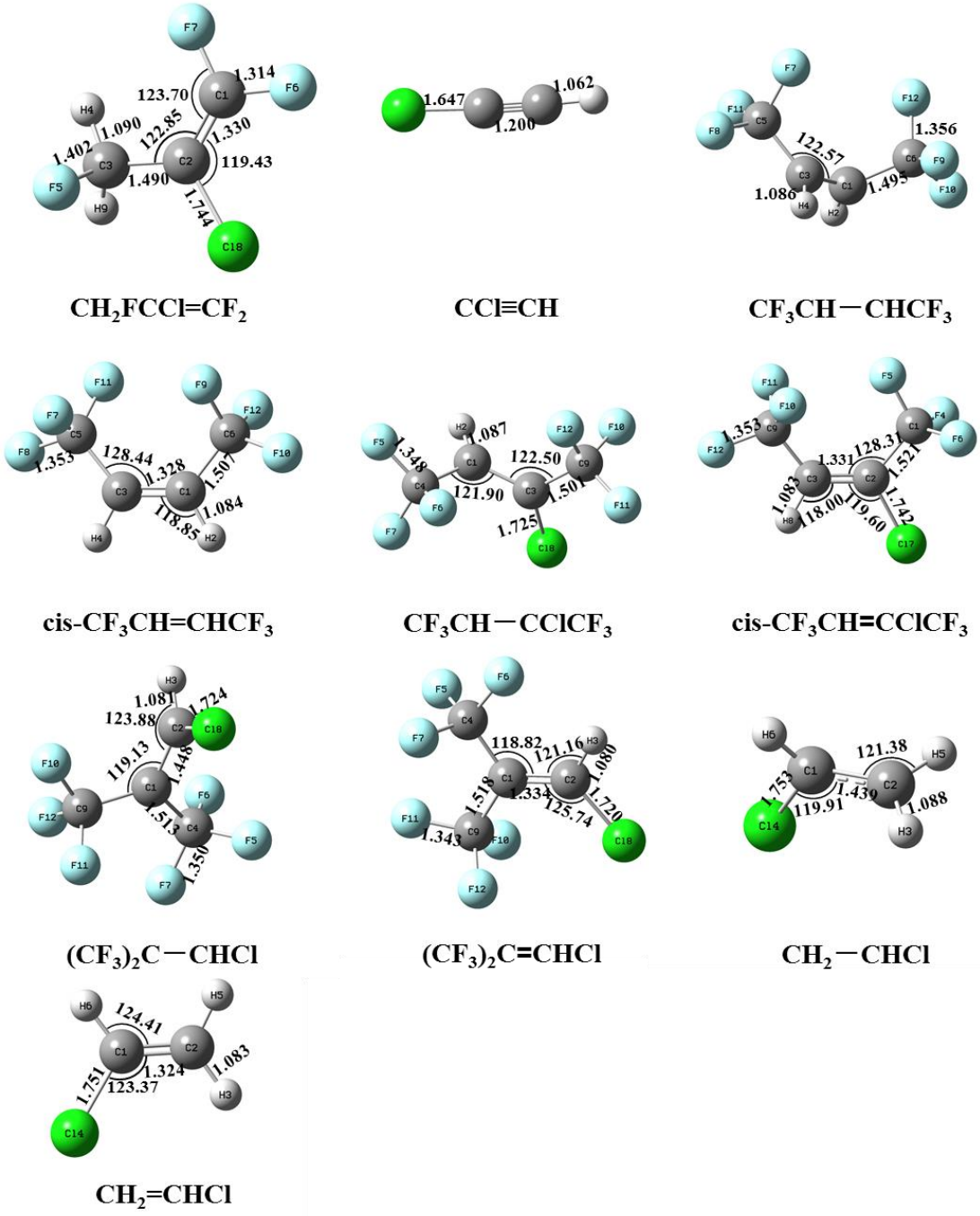



**Fig. S4** Optimized geometries of reactants, intermediates and transition states in thermal decomposition mechanism calculations of HCFO-1233zd(E) and HCFO-1233xf.

**Table S1.** The relative energies of HCFO-1233zd(E) and HCFO-1233xf decomposition mechanism calculations.

| | **Species** | **ZPVE (Kcal/Mol)** | **E(CORR) (Hartree)** |
|---|---|---|---|
| Reactants | trans-$CF_3CH=CHCl$ | 30.01 | -873.82 |
| | $CF_3CClCH_2$ | 29.89 | -873.82 |
| Intermediates | IM 1 | 29.13 | -873.72 |
| | IM 2 | 30.43 | -750.45 |
| | IM 3 | 17.97 | -536.74 |
| | IM 4 | 21.88 | -873.14 |
| | IM 5 | 21.64 | -873.13 |
| | IM 6 | 28.31 | -873.70 |
| | IM 7 | 30.31 | -873.76 |
| | IM 8 | 22.25 | -636.48 |
| | IM 9 | 29.13 | -873.72 |
| | IM 10 | 28.85 | -873.70 |
| | IM 11 | 29.89 | -873.77 |
| | IM 12 | 21.86 | -636.48 |
| | IM 13 | 18.29 | -536.75 |
| | IM 14 | 21.32 | -873.13 |
| | IM 15 | 27.10 | -873.69 |
| | IM 16 | 27.87 | -873.71 |
| | IM 17 | 28.16 | -873.69 |
| | IM 18 | 22.01 | -636.48 |
| | IM 19 | 17.76 | -536.74 |
| Diradicaloid transition states | $CF_3CH-CHCl$ | 27.28 | -873.72 |
| | $CF_3CCl-CH_2$ | 27.31 | -873.72 |
| | $CF_3CH-CHCF_3$ | 36.10 | -751.04 |

| | **Species** | **ZPVE (Kcal/Mol)** | **E(CORR) (Hartree)** |
|---|---|---|---|
| | $CF_3CH$-$CClCF_3$ | 30.82 | -1210.11 |
| | $(CF_3)_2C$-$CHCl$ | 30.59 | -1210.10 |
| | $CH_2$-$CHCl$ | 23.58 | -537.33 |
| Transition states | TS 1 | 24.17 | -873.68 |
| | TS 2 | 28.67 | -873.70 |
| | TS 3-1 | 26.44 | -873.70 |
| | TS 3-2 | 26.59 | -873.70 |
| | TS 4 | 23.54 | -873.58 |
| | TS 6 | 24.12 | -873.67 |
| | TS 7 | 28.45 | -873.68 |
| | TS 8 | 23.28 | -873.58 |
| | TS 10 | 28.12 | -750.38 |
| | TS 11 | 31.34 | -750.93 |
| | TS 12 | 25.68 | -873.64 |
| | TS 13 | 22.86 | -873.63 |
| | TS 14 | 22.52 | -873.62 |
| | TS 15-1 | 26.89 | -873.65 |
| | TS 15-2 | 28.20 | -873.66 |
| | TS 15-3 | 27.57 | -873.68 |
| | TS 16-1 | 25.15 | -873.64 |
| | TS 16-2 | 26.94 | -873.59 |
| | TS 16-3 | 28.45 | -873.69 |
| | TS 16-4 | 26.87 | -873.68 |
| | TS 17 | 25.87 | -873.64 |
| | TS 18 | 22.01 | -873.63 |
| | TS 19-1 | 26.366 | -873.64 |

| | **Species** | **ZPVE (Kcal/Mol)** | **E(CORR) (Hartree)** |
|---|---|---|---|
| | TS 19-2 | 26.87 | -873.68 |
| | TS 20-1 | 24.29 | -873.63 |
| | TS 20-2 | 26.37 | -873.59 |
| | TS 20-3 | 27.54 | -873.68 |
| | TS 21 | 29.31 | -1210.03 |
| | TS 22 | 29.23 | -1210.02 |
| | TS 23 | 28.82 | -1210.02 |
| | TS 24 | 21.74 | -636.91 |
| | TS 25 | 21.83 | -636.92 |
| | TS 26 | 21.68 | -636.92 |
| | TS 27 | 18.56 | -537.24 |
| | TS 28 | 18.74 | -537.24 |
| | TS 29 | 19.37 | -537.24 |
| Products | $CH{\equiv}CCF_3$ | 20.70 | -413.49 |
| | $CHFClCH{=}CF_2$ | 30.42 | -873.79 |
| | cis-$CF_3CH{=}CHCl$ | 30.01 | -873.81 |
| | $CH_2FCCl{=}CF_2$ | 30.54 | -873.78 |
| | $CCl{\equiv}CH$ | 23.54 | -873.58 |
| | cis-$CF_3CH{=}CHCF_3$ | 38.80 | -751.13 |
| | cis-$CF_3CH{=}CClCF_3$ | 32.88 | -1210.20 |
| | $(CF_3)_2C{=}CHCl$ | 32.96 | -1210.20 |
| | $CH_2{=}CHCl$ | 26.64 | -537.43 |

**Table S2.** Imaginary frequency (in cm-1) of all TSs at B3LYP/6-311++G(d, p) level of theory.

| **Transition state** | **Imaginary frequency** |
|---|---|
| TS 1 | 1764.11i |
| TS 2 | 484.49i |
| TS 3-1 | 1284.23i |
| TS 3-2 | 1321.75i |
| TS 4 | 2032.81i |
| TS 6 | 1751.40i |
| TS 7 | 590.24i |
| TS 8 | 1912.87i |
| TS 10 | 319.25i |
| TS 11 | 698.57i |
| TS 12 | 278.21i |
| TS 13 | 918.00i |
| TS 14 | 613.87i |
| TS 15-1 | 238.35i |
| TS 15-2 | 189.37i |
| TS 15-3 | 397.98i |
| TS 16-1 | 1965.88i |
| TS 16-2 | 874.38i |
| TS 16-3 | 453.95i |
| TS 16-4 | 431.24i |
| TS 17 | 458.37i |
| TS 18 | 558.90i |
| TS 19-1 | 324.66i |
| TS 19-2 | 431.24i |
| TS 20-1 | 2059.14i |

| **Transition state** | **Imaginary frequency** |
|---|---|
| TS 20-2 | 854.35i |
| TS 20-3 | 379.64i |
| TS 21 | 448.46i |
| TS 22 | 258.46i |
| TS 23 | 272.83i |
| TS 24 | 1545.04i |
| TS 25 | 1494.91i |
| TS 26 | 1509.59i |
| TS 27 | 516.41i |
| TS 28 | 893.55i |
| TS 29 | 517.19i |