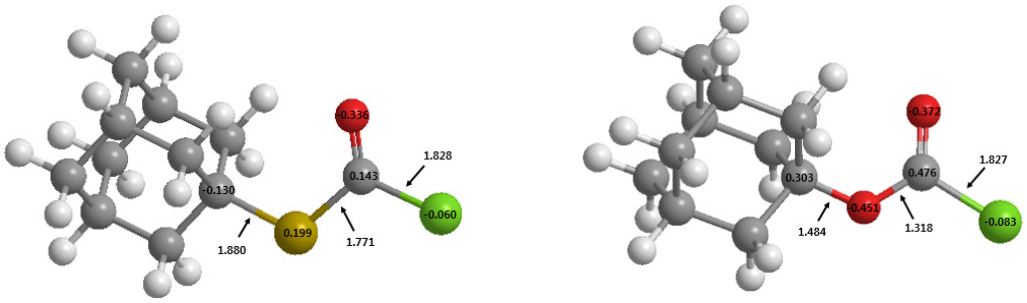
Supporting Materials

Table S1. Calculated energy, charge and distance for 1-adamantyl chlorothioformate (**1**) and chloroformate (**2**), as calculated at B3LYP/6-31G(d) level theory

Sub.[a]	Energy[b]	Charge[c]					Distance (Å)			
1	-361.838028	**(R)C*-S**	**S*-C=O**	**C*=O**	**C=O***	**C-X***	**(R)C-S**	**(S-C)=O**	**(C=O)**	**C-X**
		-0.130	0.199	0.143	-0.336	-0.06	1.880	1.771	1.19106	1.828
2	-038.874069	**(R)C*-O**	**O*-C=O**	**C*=O**	**C=O***	**C-X***	**(R)C-O**	**(O-C)=O**	**(C=O)**	**C-X**
		0.303	-0.451	0.478	-0.372	-0.083	1.484	1.3176	1.19149	1.82654

[a] 1-Adamantyl chlorothioforamte and 1-adamantyl chloroformate in the gas phase. [b] hartree (HF) = 627.5095 kcal/mol. [c]Mulliken charge.



(a) **(b)**

Figure S2. Optimized molecular structures of (a) 1-AdSCOCl and (b) 1-AdOCOCl using B3LYP/6-31G(d).

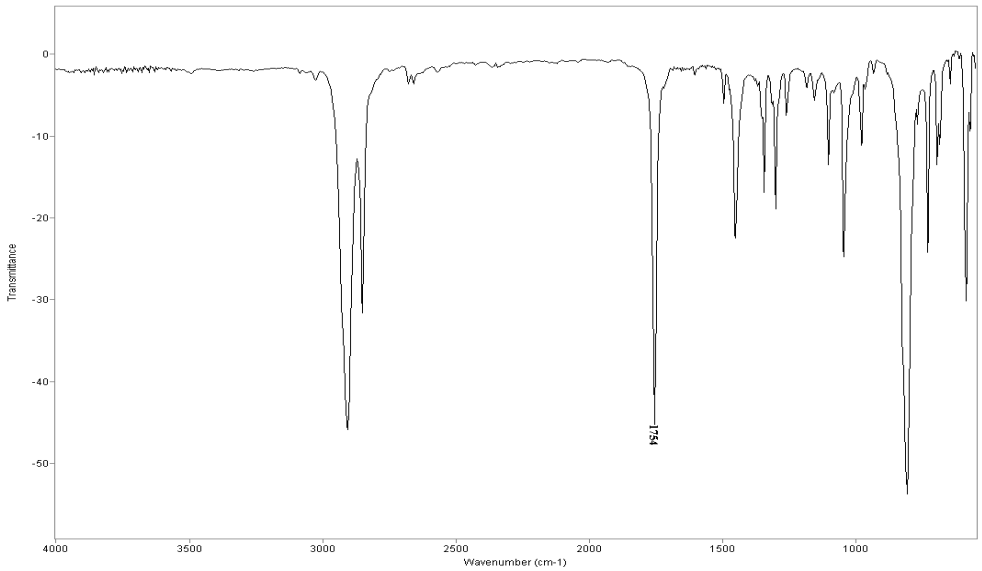


Figure S3. IR spectrum of 1-adamantyl chlorothioformate showing characteristic C=O peak at 1754 cm^{-1}.

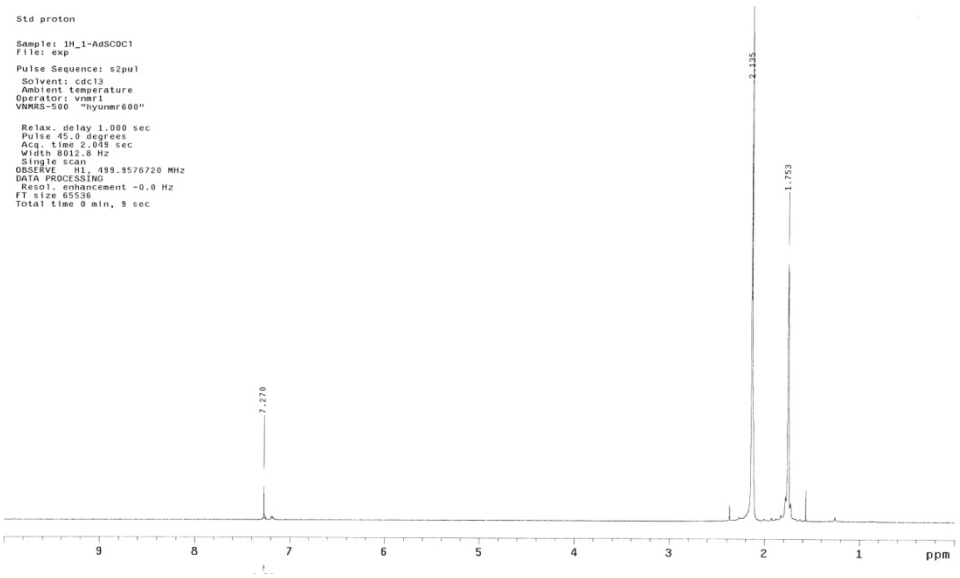


Figure S4. ^{1}H NMR spectrum of 1-adamantyl chlorothioformate.

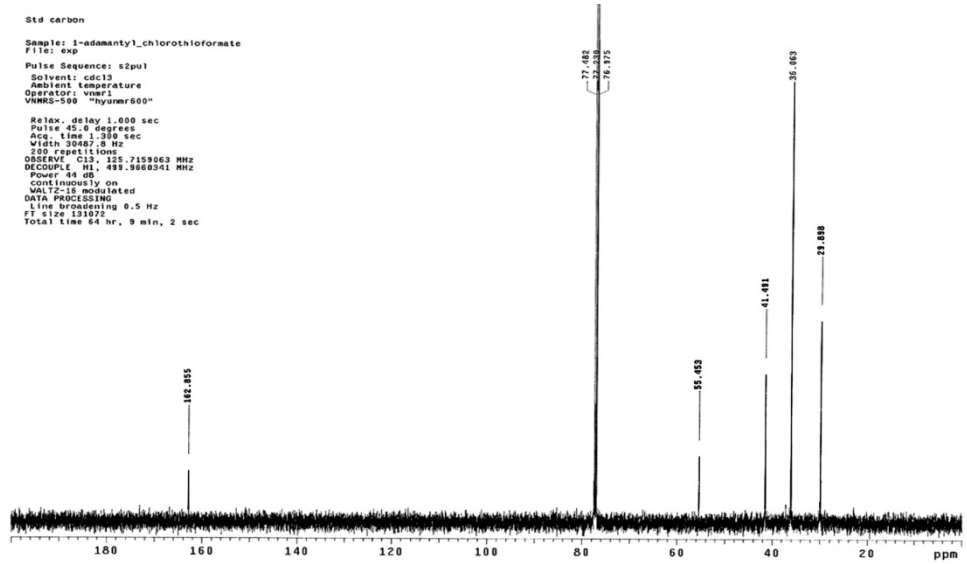


Figure S5. ^{13}C NMR spectrum of 1-adamantyl chlorothioformate.

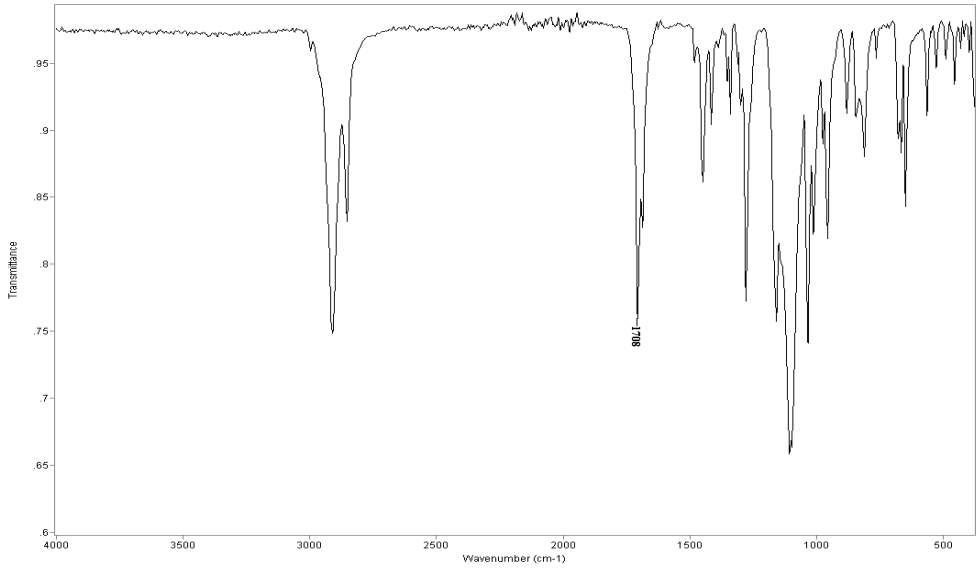


Figure S6. IR spectrum of 1-adamantyl ethyl thiocarbonate showing characteristic C=O peak at 1708 cm^{-1}.

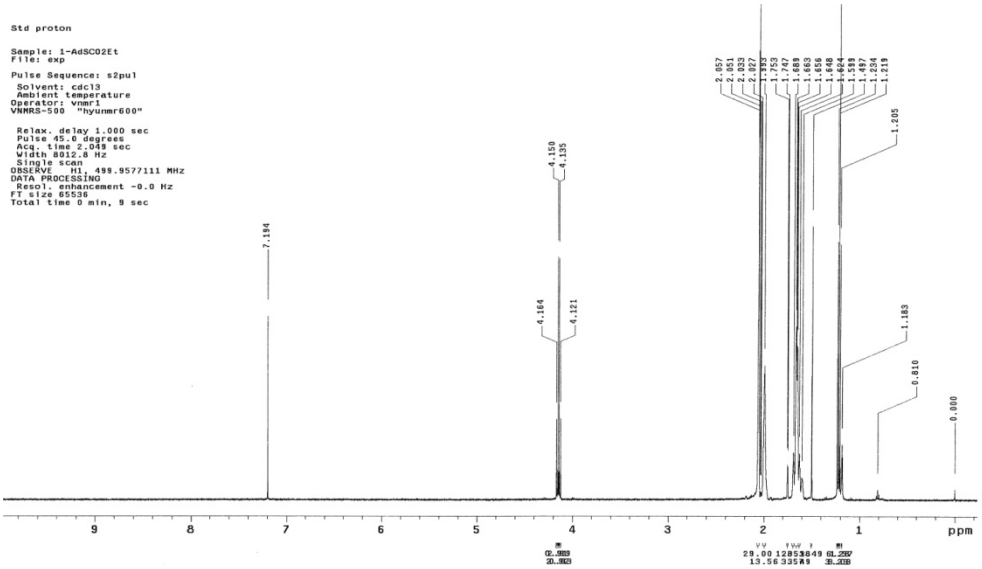


Figure S7. ^{1}H NMR spectrum of 1-adamantyl ethyl thiocarbonate.

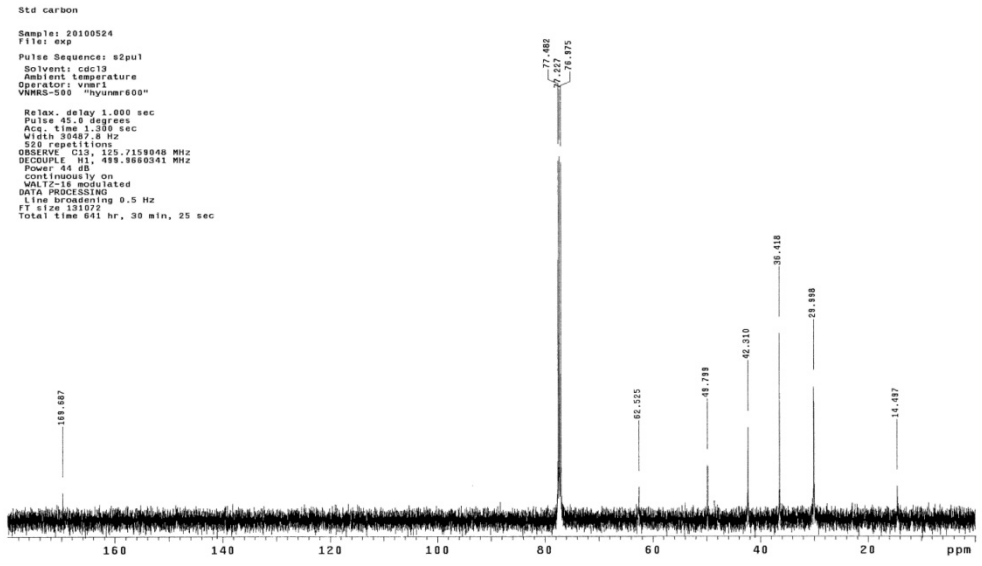
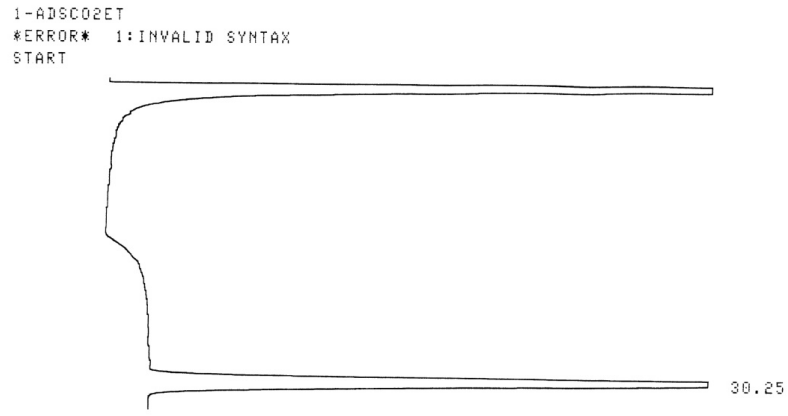


Figure S8. ^{13}C NMR spectrum of 1-adamantyl ethyl thiocarbonate.

Substrate: 1-adamantyl ethyl thiocarbonate (5.699×10^{-3}M)	**Gas chromatography :** GC-9A (Shimadzu)
Solvent: *n*-Pentane	**Column :** glass (length: 2.1m, O.D: 5mm, I.D: 3mm)
Injection Temp. : 210 °C	**Stationary phase :** Carbowax 20M 10% Chromosorb WAW 80/100
Column Temp. : 170 °C	**Detector :** FID, **Carrier gas:** N_2
Injection volume : 1μL	



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 711

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	30.25	131551			100	
	TOTAL	131551			100	

Figure S9. G.C. analysis sheet of 1-adamantyl ethyl thiocarbonate.

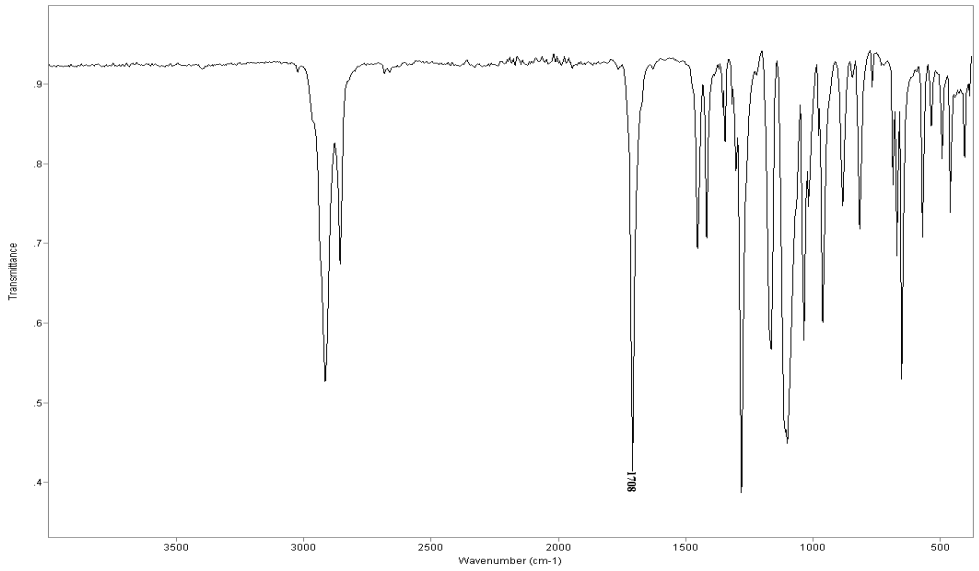


Figure S10. IR spectrum of 1-adamantyl 2,2,2-trifluoroethyl thiocarbonate showing characteristic C=O peak at 1708 cm^{-1}.

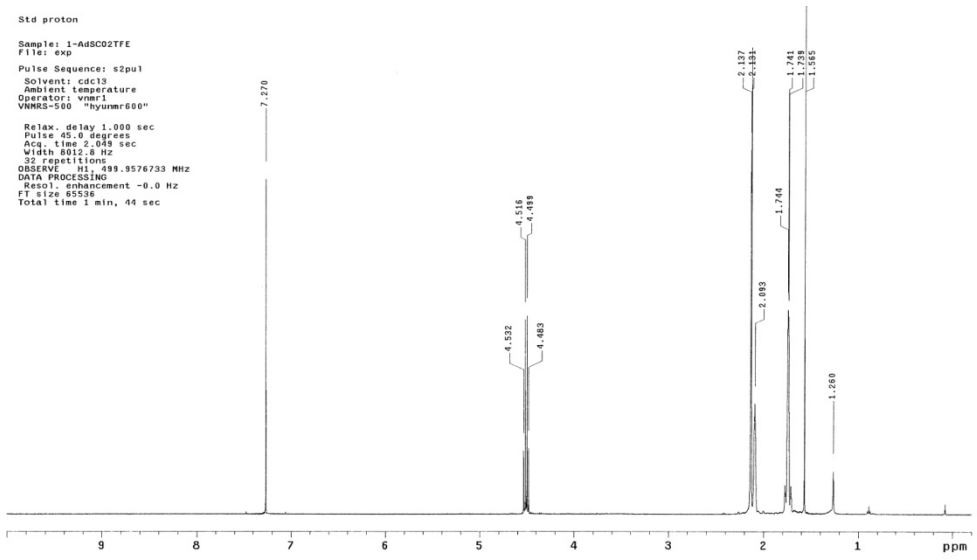


Figure S11. ^{1}H NMR spectrum of 1-adamantyl 2,2,2-trifluoroethyl thiocarbonate.

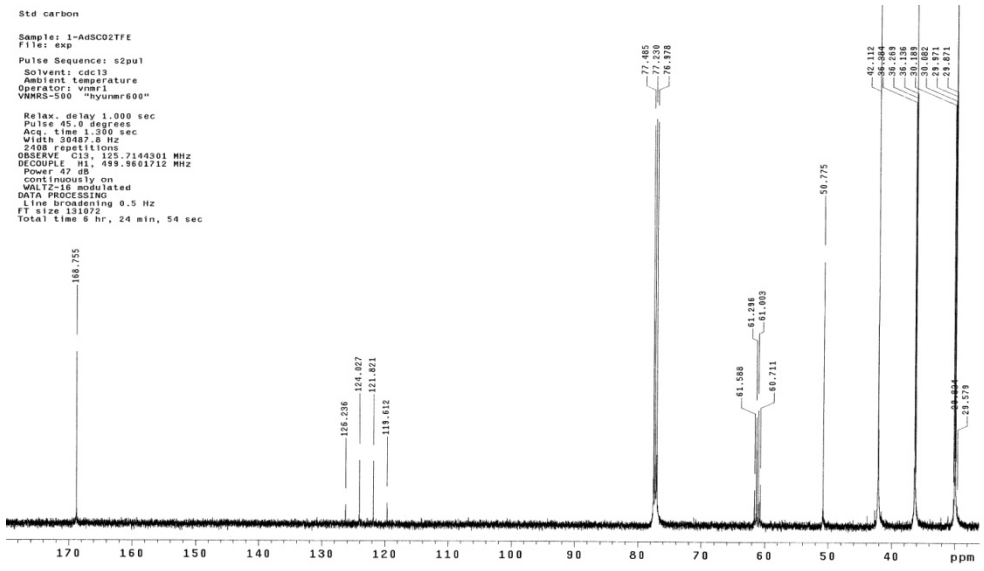
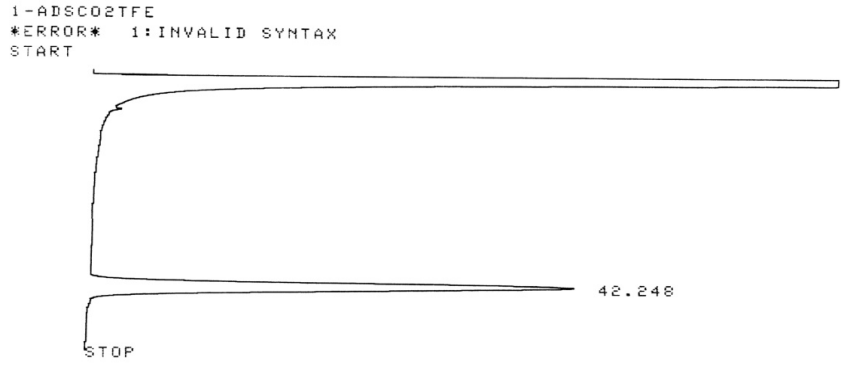


Figure S12. ^{13}C NMR spectrum of 1-adamantyl 2,2,2-trifluoroethyl thiocarbonate.

Substrate: 1-adamantyl 2,2,2-trifluoroethyl thiocarbonate (5.436×10^{-3}M)	**Gas chromatography :** GC-9A (Shimadzu)
Solvent: *n*-Pentane	**Column :** glass (length: 2.1m, O.D: 5mm, I.D: 3mm)
Injection Temp. : 210 °C	**Stationary phase :** Carbowax 20M 10% Chromosorb WAW 80/100
Column Temp. : 170 °C	**Detector :** FID, **Carrier gas:** N_2
Injection volume : 1μL	



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 683

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1	42.248	76001			100	
	TOTAL	76001			100	

Figure S13. G.C. analysis sheet of 1-adamantyl 2,2,2-trifluoroethyl thiocarbonate.

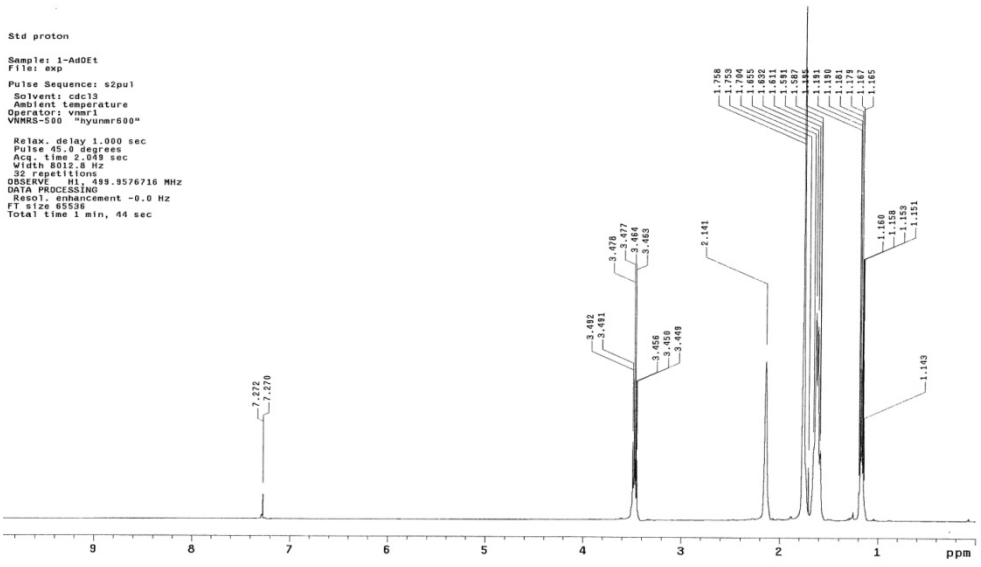


Figure S14. ^{1}H NMR spectrum of 1-adamantyl ethyl ether.

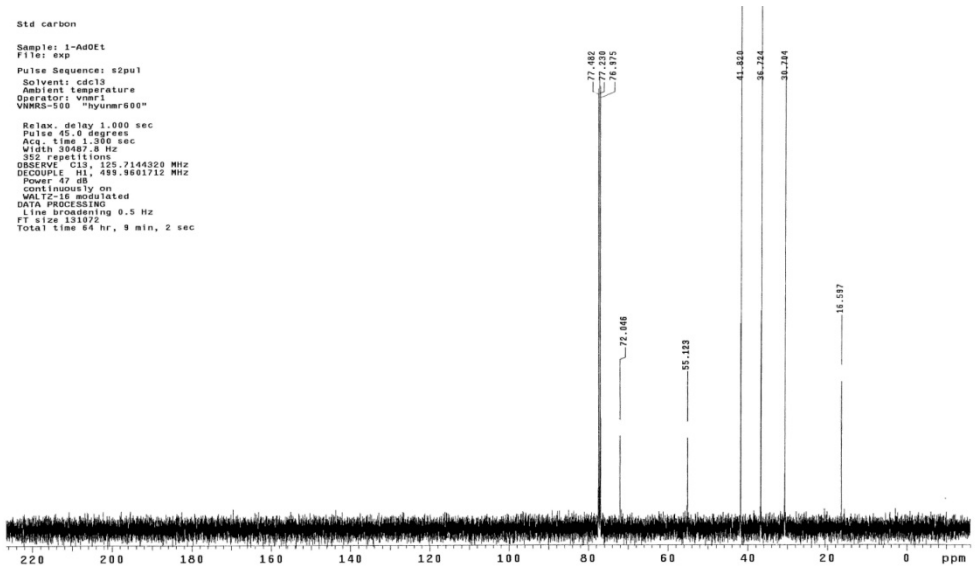
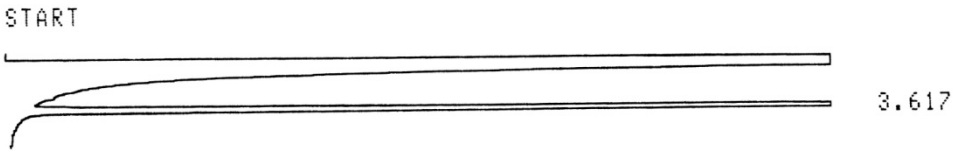


Figure S15. ^{13}C NMR spectrum of 1-adamantyl ethyl ether.

Substrate: 1-adamantyl ethyl ether (5.547×10^{-3}M)	**Gas chromatography :** GC-9A (Shimadzu)
Solvent: *n*-Pentane	**Column :** glass (length: 2.1m, O.D: 5mm, I.D: 3mm)
Injection Temp. : 210 °C	**Stationary phase :** Carbowax 20M 10% Chromosorb WAW 80/100
Column Temp. : 170 °C	
Injection volume : 1μL	**Detector :** FID, **Carrier gas:** N_2



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 712

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	3.617	195621			100	
	TOTAL	195621			100	

Figure S16. G.C. analysis sheet of 1-adamantyl ethyl ether.

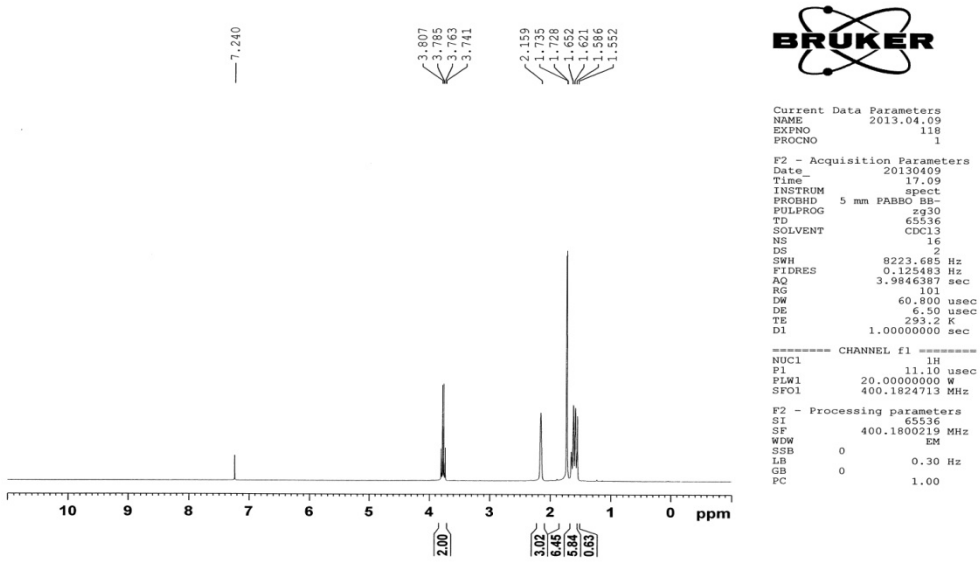


Figure S17. [1]H NMR spectrum of 1-adamantyl 2,2,2-trifluoroethyl ether.

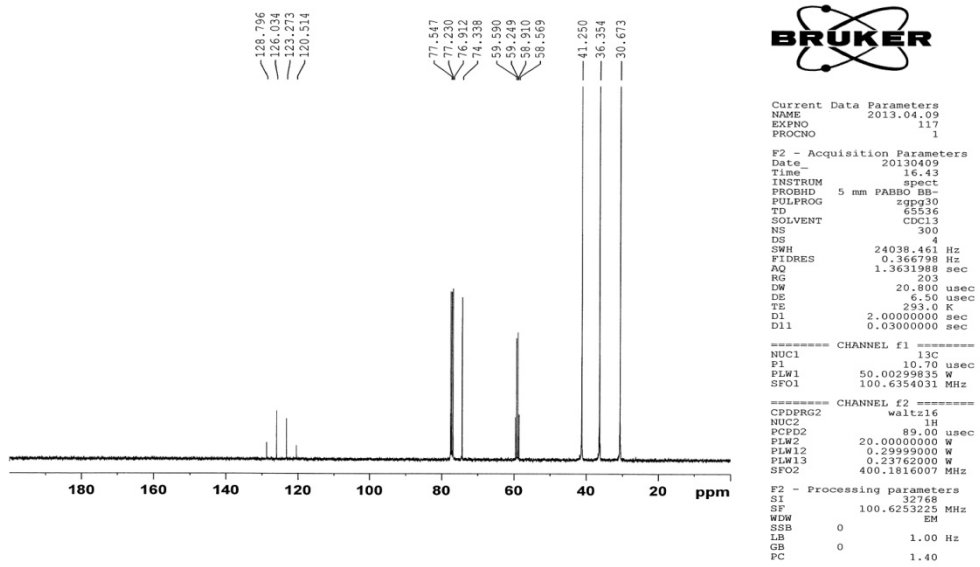
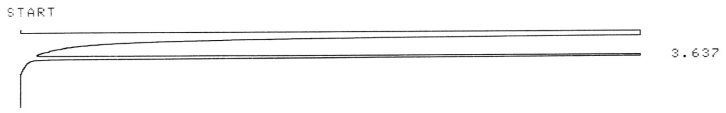


Figure S18. [13]C NMR spectrum of 1-adamantyl 2,2,2-trifluoroethyl ether.

Substrate: 1-adamantyl 2,2,2-trifluoroethyl ether (5.588×10^{-3}M)	**Gas chromatography :** GC-9A (Shimadzu)
Solvent: *n*-Pentane	**Column :** glass (length: 2.1m, O.D: 5mm, I.D: 3mm)
Injection Temp. : 210 °C	**Stationary phase :** Carbowax 20M 10% Chromosorb WAW 80/100
Column Temp. : 170 °C	
Injection volume : 1μL	**Detector :** FID, **Carrier gas:** N_2

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CHROMATOPAC   C-R3A                  FILE        0
SAMPLE NO   0                        METHOD        41
REPORT NO   697

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   1      3.637     125972                 100
                  ---------            -------------
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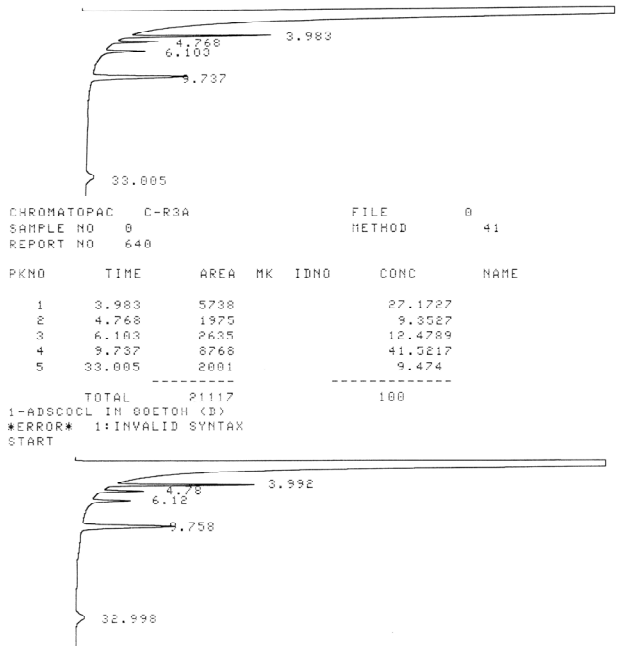
```

Figure S19. G.C. analysis sheet of 1-adamantyl 2,2,2-trifluoroethyl ether.

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SAMPLE NO   0                        METHOD        41
REPORT NO   640

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   3      6.103       2635                12.4789
   4      9.737       8768                41.5217
   5     33.005       2001                 9.474
                  ---------            -------------
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START
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AMPLE NO   0                         METHOD        41
EPORT NO   641

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  1      3.992       5557                27.3626
  2      4.78        1903                 9.3706
  3      6.12        2502                12.3182
  4      9.758       8428                41.5016
  5     32.998       1919                 9.4475
                  ---------            -------------
        TOTAL       20309                 100
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Figure S20. G.C. analysis sheets of products of 1-adamantyl chlorothioformate solvolysis in 80% EtOH.

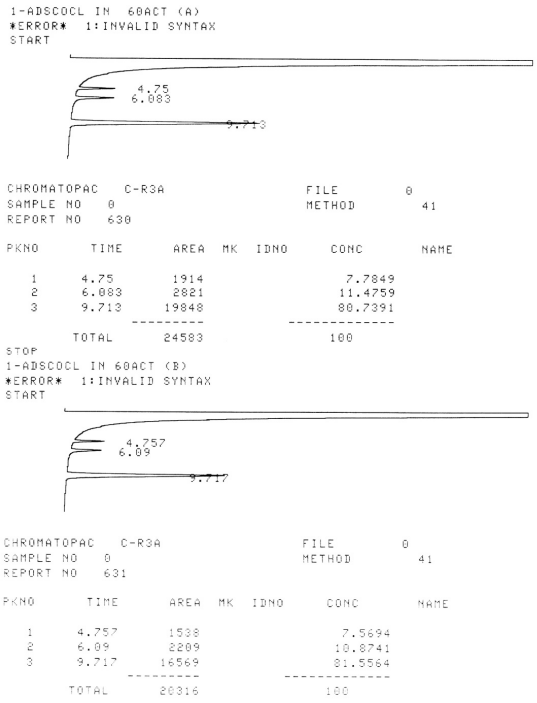


Figure S21. G.C. analysis sheets of products of 1-adamantyl chlorothioformate solvolysis in 60% Me_2CO.

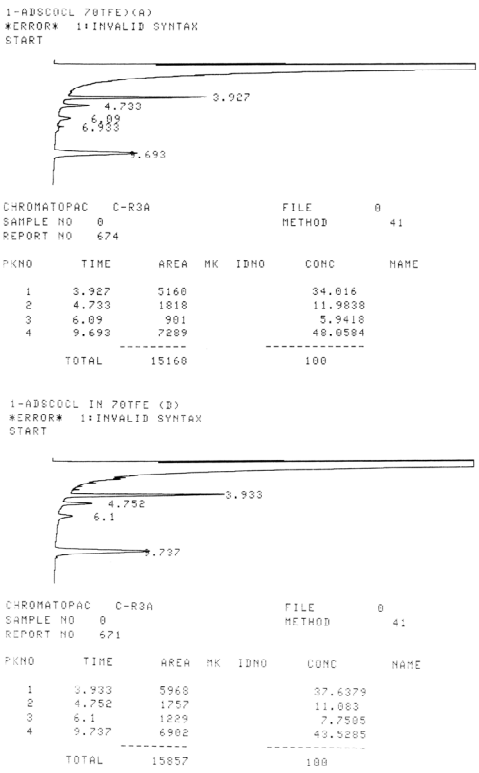
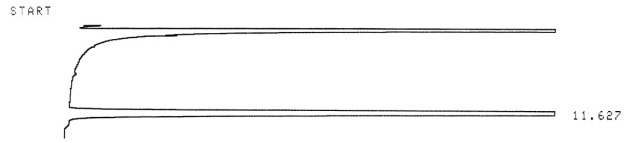


Figure S22. G.C. analysis sheets of products of 1-adamantyl chlorothioformate solvolysis in 70% TFE.



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 949

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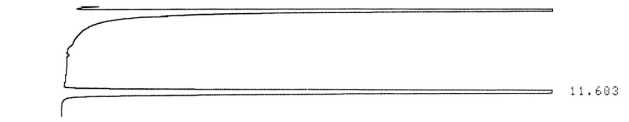
	TOTAL	134277			100	



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 950

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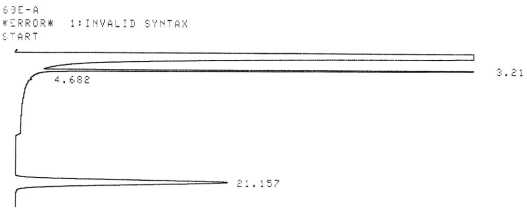
1	11.603	102519			100	
	TOTAL	102519			100	

Figure S23. G.C. analysis sheets of products of 1-adamantyl fluorothioformate solvolysis in 100% EtOH.



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 742

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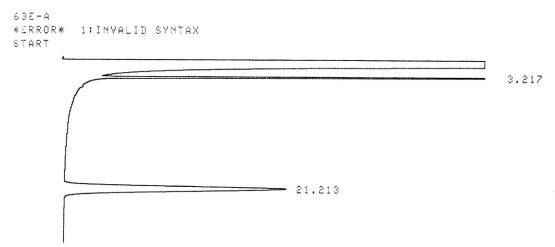
2	21.157	54280			59.5099	
	TOTAL	91212			100	



CHROMATOPAC C-R3A FILE 0
SAMPLE NO 0 METHOD 41
REPORT NO 733

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1	3.217	38027			40.2068	
2	21.213	56552			59.7932	
	TOTAL	94579			100	

Figure S24. G.C. analysis sheets of products of 1-adamantyl fluorothioformate solvolysis in 60% EtOH.

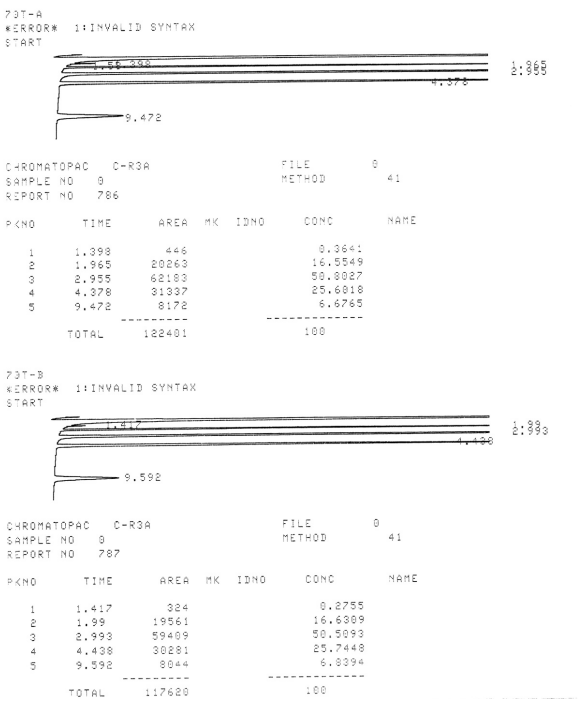

Figure S25. G.C. analysis sheets of products of 1-adamantyl fluorothioformate solvolysis in 70% TFE.

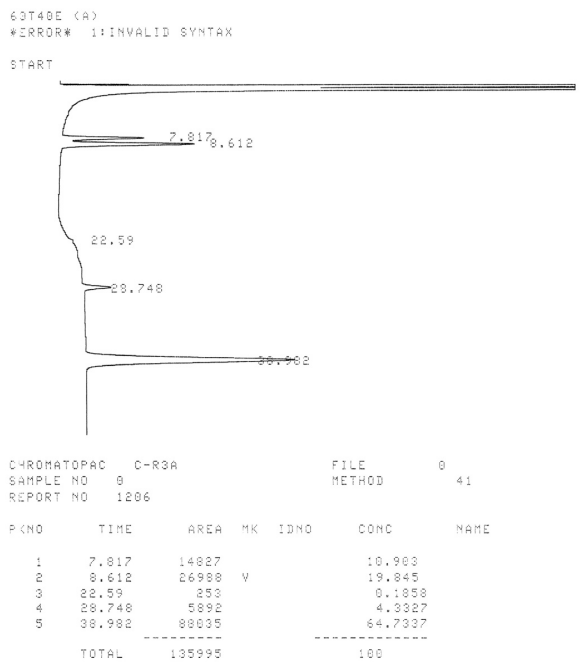

Figure S26. G.C. analysis sheet of products of 1-adamantyl fluorothioformate solvolysis in 60T-40E.