Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Improving selectivity in catalytic hydrodefluorination by limiting S_NV reactivity

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1. Reaction conditions for HDF of 3, 4, 5 and additional experiments for HDF of 4

Table S1. Reaction conditions, conversion, E/Z and TOF for HDF of **3**, **4**, **5**.

Substr.	**1a**	**2**	Solvent	t	T	Yield[a]								Conv.	TOF
	[mol %]	[eq.]		[h]	[°C]	**4a**	**4a'**	**4b**	**4b'**	**4c**	**4c'**	**4d**	**4d'**	[%]	[h^{-1}]
4	0.3	1.1	THF	24	rt	20.1	-	5.9	-	8.8	-	5.9	-	100	14
4	0.8	1.0	THF	6	rt	31.3	16.7	10.8	6.3	17.9	4.1	9.9	3.0	100	20
4	0.8	0.9	DME	24	rt	47.6	5.2	14.1	1.3	18.2	1.1	11.6	0.9	100	5
4	1.9	1.0	Dioxane	24	rt	42.4	8.7	9.8	2.4	18.4	2.0	14.4	1.9	100	2
4	2.2	1.2	THF	1	50	28.6	18.9	10.0	7.4	16.9	4.8	9.8	3.6	100	46
4	1.5	0.7	Diglyme	2	rt	18.3	-	5.4	-	8.2	-	5.1	-	37	33
4	2.3	1.7	THF	2	rt	33.2	8.4	12.4	4.5	21.5	3.2	13.1	2.7	99	22
4	2.2	1.0	toluene	24	100	**4e** (E) : **4f** (Z) = 1:100								100	46
5	2.0	1.2	toluene	24	100	main product: CF_3-CH=CH_2								60	30
3	2.0	1.5	toluene	24	40	Z : E : **3c** = 9:1:1								72	1.4

[a] Yields were determined by integration of ^{19}F NMR resonances in the product mixture (versus internal fluorobenzene).

1.1 NMR assignment

To assign the corresponding chemical shifts of the HDF-products **4a-d** it was helpful to compare these data with the ^{19}F NMR of perfluorallylbenzene. Therefore one has a couple of characteristic features:

i) a triplet of triplet of triplet coupling pattern for the *para*-F atom in the aromatic C-F region (Figure S1),

ii) the strong *trans*-F coupling constant ($^3J_{FF}$ = 116.5 Hz), and

iii) the characteristic *gem*-F coupling constant ($^2J_{FF}$ = 57.0 Hz) of the perfluorovinyl group.

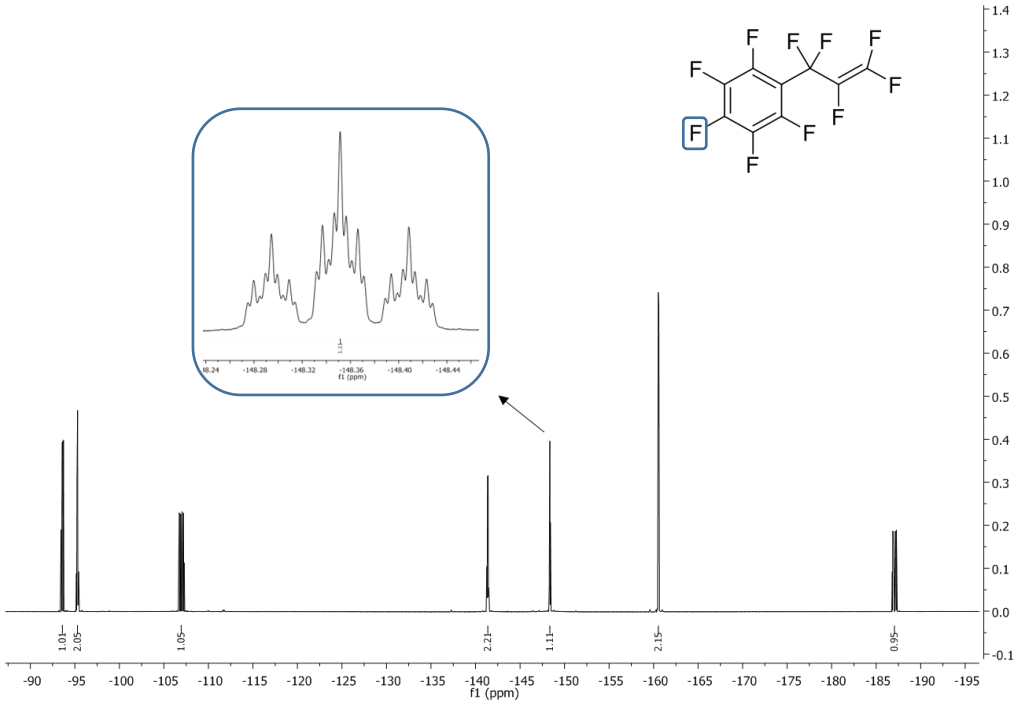


Figure S1: ^{19}F NMR of perfluorallylbenzene, resonance of the *para*-fluorine nuclei expanded.

^{19}F (376 MHz, C_6D_6): δ = -92.7 (1F, ddt, $^2J_{FF}$ = 57.0 Hz, $^3J_{FF}$ = 36.0 Hz, $^4J_{FF}$ = 6.1 Hz, =CF_2), -94.9 (2F, m, -CF_2-), -106.3 (1F, ddtt, $^2J_{FF}$ = 56.9 Hz, $^3J_{FF}$ = 116.5 Hz, $^4J_{FF}$ = 27.3 Hz, $^6J_{FF}$ = 1.7 Hz, =CF_2), -141,4 (2F, m, *meta*-F_{arene}), -147.6 (1F, ttt, $^3J_{FF}$ = 21.4 Hz, $^4J_{FF}$ = 5.5 Hz, $^6J_{FF}$ = 1.8 Hz, *para*-F_{arene}), -159.7 (2F, m, *ortho*-F_{arene}), -186.5 (1F, ddtt, $^3J_{FF}$ = 116.5 Hz, $^3J_{FF}$ = 36.0 Hz, $^3J_{FF}$ = 19.4 Hz, $^5J_{FF}$ = 4.0 Hz, -CF=) ppm.

In combination with the characteristic *para*-F signals (Figure S2), their integrals, the ^{1}H NMR and the following facts:

- characteristic chemical shift (~ -125 ppm) and coupling constant of the CF_2H-group ($^2J_{FH}$ = 51.2 Hz) for **4a**/**b**
- the strong *trans*-F coupling constant ($^3J_{FF}$ = 138.0 Hz) for **4a** and ($^3J_{FF}$ = 136.0 Hz) for **4c**
- the characteristic *gem*-F coupling constant ($^2J_{FH}$ = 71.5 Hz) for **4c** and ($^2J_{FH}$ = 68.9 Hz) for **4d**

it was possible to assign all chemical shifts to the corresponding products (**4a**, **b**, **c**, **d**, **a'**, **c'**, **d'**).

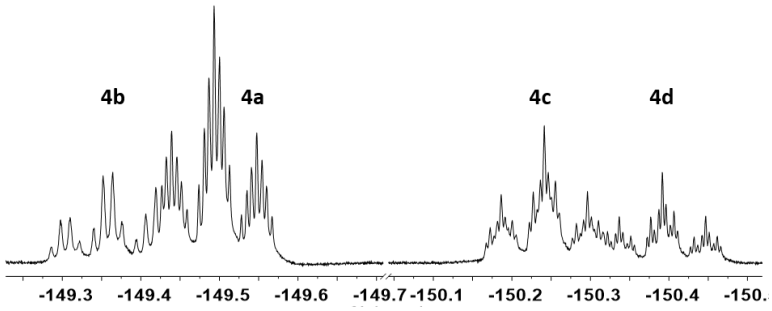


Figure S2: *para*-F region for **4a-d**.

Regarding the 2nd generation HDF-products (**4a'**, **b'**, **c'**, **d'**) all signals in the ^{19}F NMR are doubled except the *para*-F signals (cf. Figure S2), besides the above mentioned characteristic pattern and chemical shifts remain nearly unchanged (Figure S3).

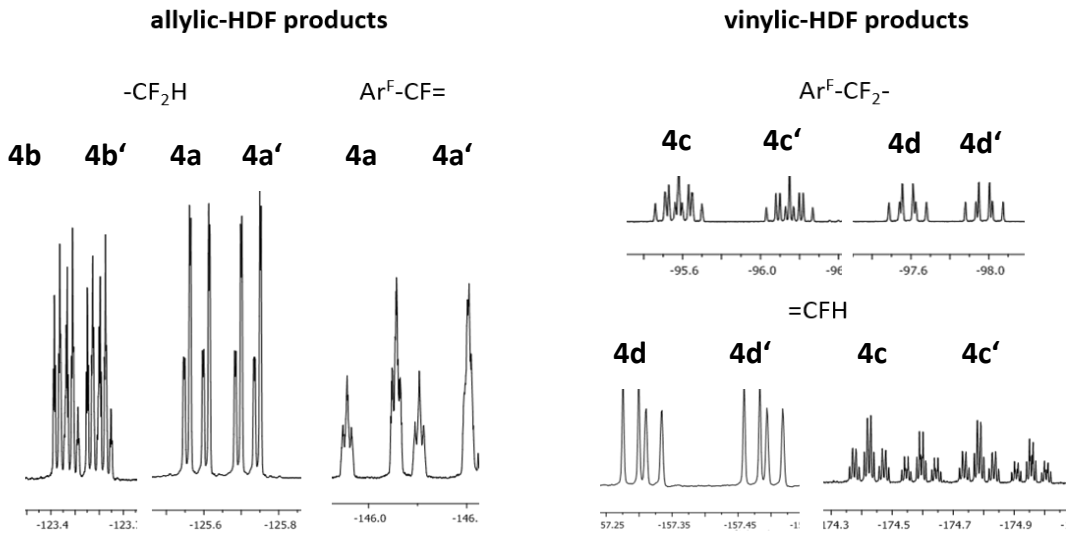


Figure S3. Selection of the doubled characteristically signals for **4a**, **a'**, **b**, **b'**, **c**, **c'**, **d**, **d'**.

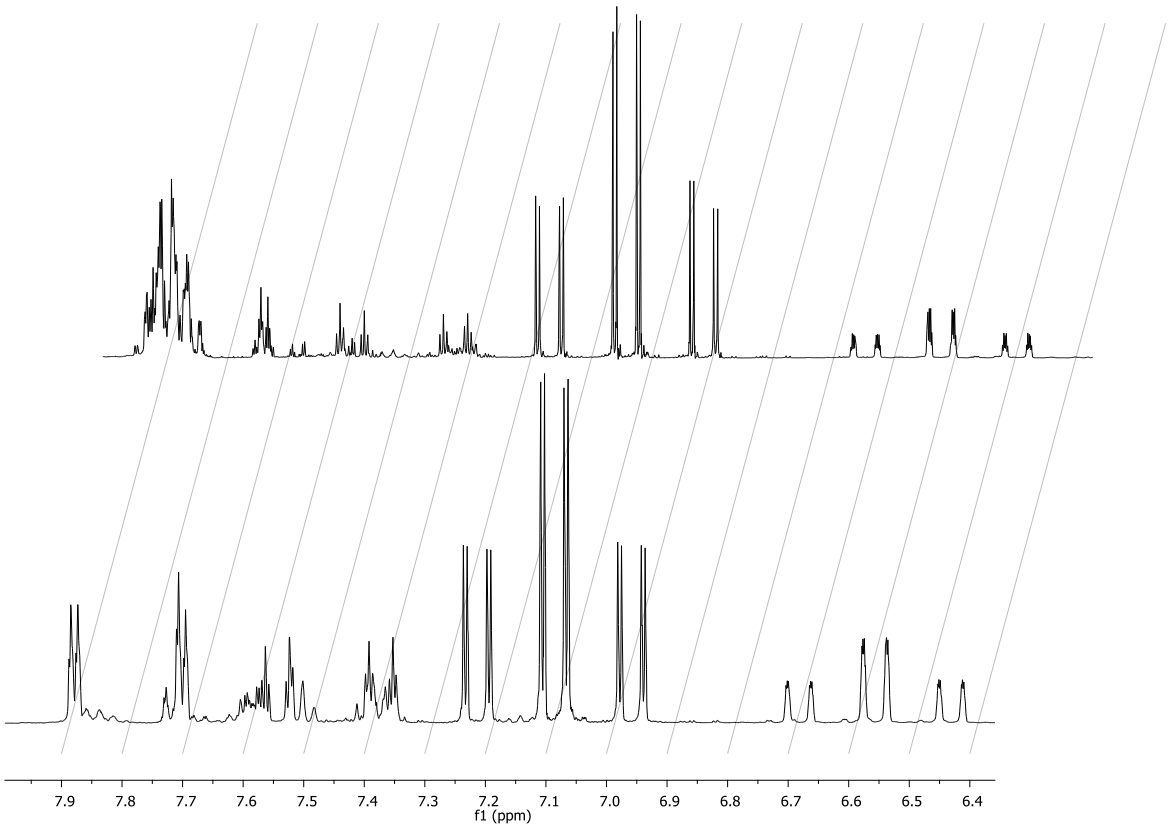


Figure S4. ^{1}H NMR spectra of a reaction mixture containing mainly *top:* 1st generation HDF products (**4a**, **b**, **c**, **d**) and *bottom:* 2nd generation products (**4a'**, **b'**, **c'**, **d'**), additional resonances of the aromatic protons are observed at low field.

1.2 GC-MS

Beside ^{1}H and ^{19}F NMR spectroscopy GC-MS was used for further characterization, therefor we purified the reaction mixture of a catalytic run (Table S1, entry 5) by trap (-30°C) to trap (-196°C) condensation under reduced pressure (5 x 10^{-3} mbar). Figure S5 shows the chromatogram with basically two sets of peaks for 1st (# 4, 6, 7, 8) and 2nd generation HDF products (# 9, 10, 11, 12). Furthermore the measured probe contains small amounts of the substrate (**4**) (Peak 1, Figure S6), Ph_2SiF_2 (Peak 15, Figure S15) and Ph_2SiH_2 (Peak 17, Figure S16). The mass spectra of the 1st and 2nd generation HDF products exhibits the molecular ion with m/z = 280 and m/z = 262, and specific fragmentation for the different constitutional isomers, e.g. the loss of the CF=CFH-group for the vinylic HDF products.

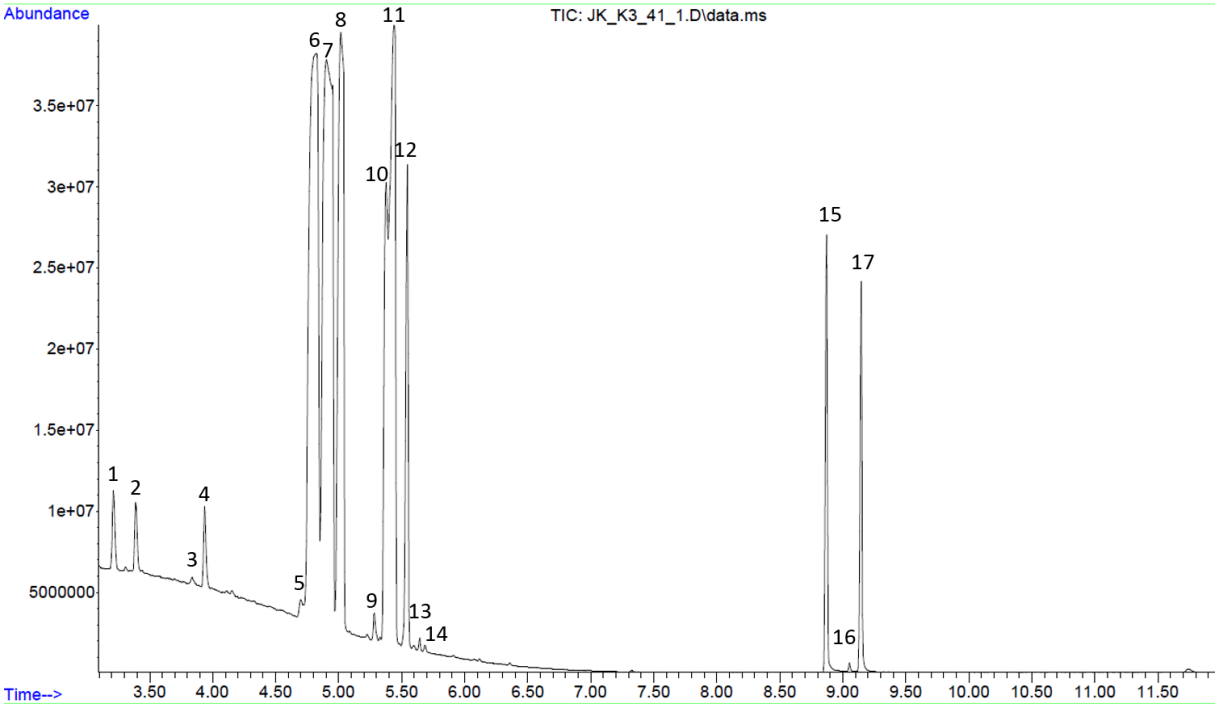


Figure S5. Chromatogram

Peak#	Ret. Time	Type	Width	Area	Start Time	End Time
1	3.216	BV	0.024	75368349	3.169	3.292
2	3.393	VV	0.025	75240795	3.343	9.431
3	3.839	VV	0.053	36390787	3.809	3.912
4	3.939	VV	0.025	88549528	3.912	3.983
5	4.702	VV	0.032	27838002	4.669	4.724
6	4.825	VV	0.067	1808253582	4.724	4.856
7	4.906	VV	0.078	1893255806	4.856	4.973
8	5.020	VV	0.047	1145232408	4.973	5.183
9	5.285	PV	0.019	21370684	5.261	5.317
10	5.378	VV	0.032	579196134	5.338	5.395
11	5.442	VV	0.048	1227905320	5.395	5.497
12	5.547	VV	0.023	411283753	5.497	5.581
13	5.645	VV	0.016	6966730	5.622	5.667
14	5.687	PV	0.015	3489232	5.667	5.886
15	8.872	BV	0.020	363509064	8.802	9.030
16	9.055	VV	0.050	63586677	9.030	9.111
17	9.148	VB	0.018	266512175	9.111	9.160

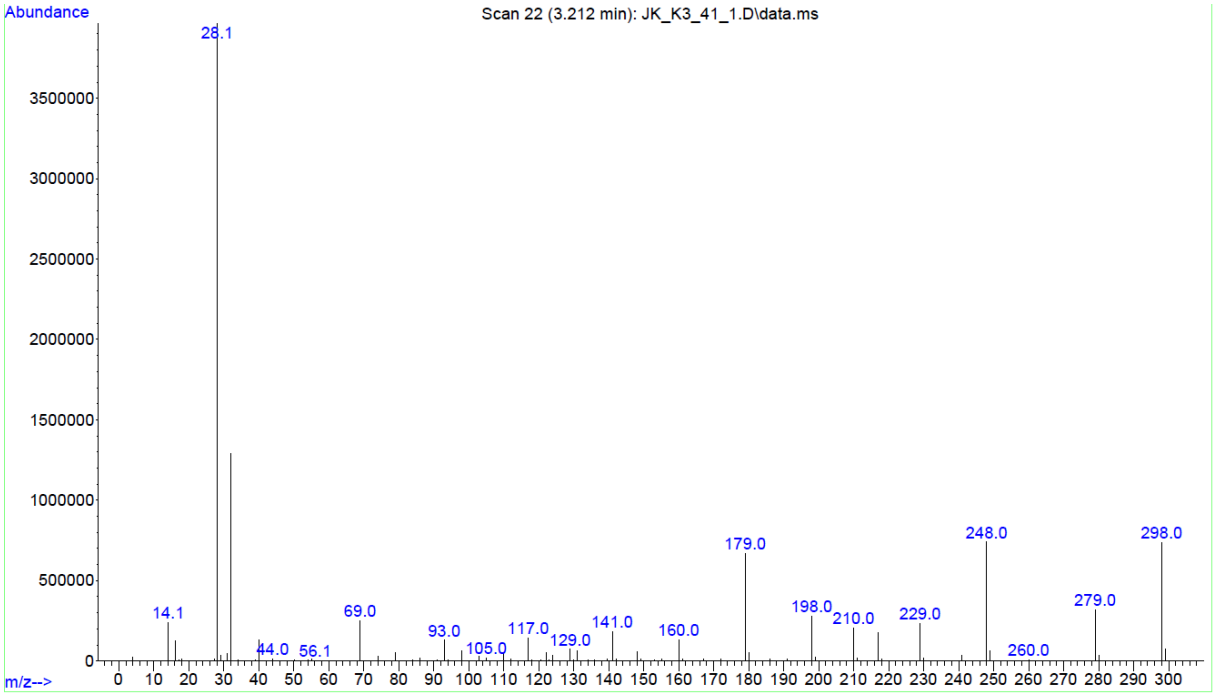


Figure S6. Mass spectra of peak 1.

MS (EI): m/z = 298 (M^+), 279 (M^+-F), 248 (M^+-CF_2), 229 (M^+-CF_2, -F).

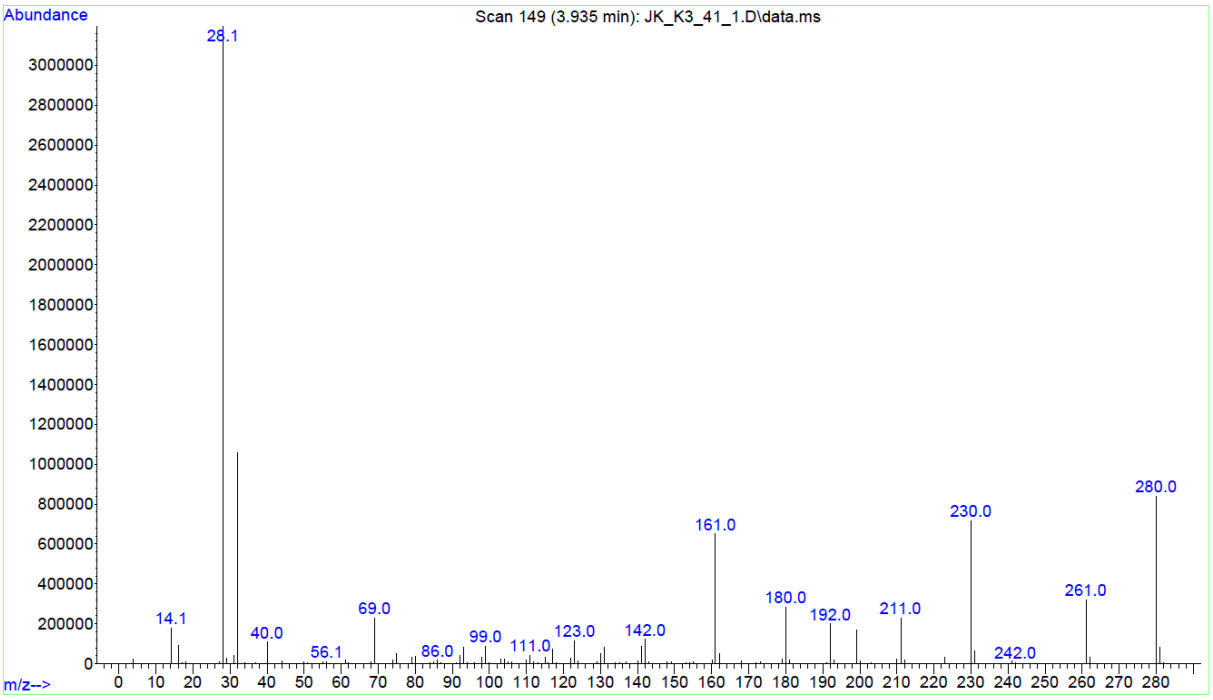


Figure S7. Mass spectra of peak 4.

MS (EI): m/z = 280 (M^+), 261 (M^+-F), 230 (M^+-CF_2).

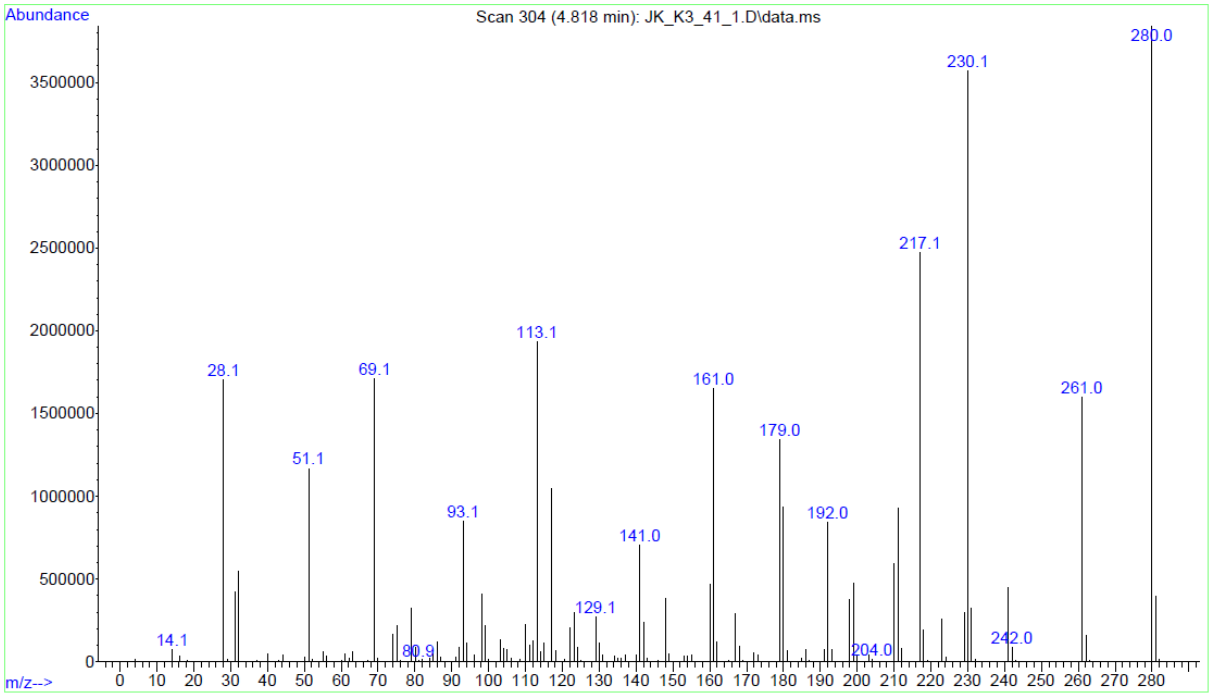


Figure S8. Mass spectra of peak 6.

MS (EI): m/z = 280 (M^+), 261 (M^+-F), 230 (M^+-CF_2), 217 (M^+-CF=CFH), 113 (M^+-C_6F_5).

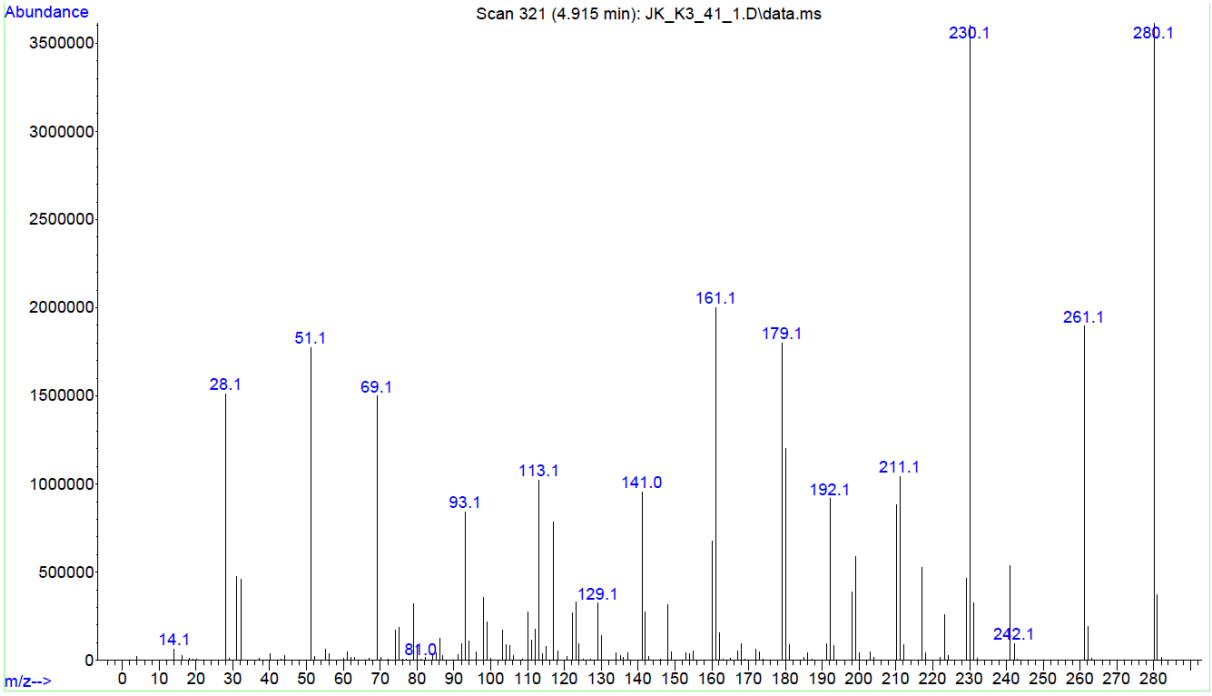


Figure S9. Mass spectra of peak 7.

MS (EI): m/z = 280 (M^+), 261 (M^+-F), 230 (M^+-CF_2), 211 (M^+-CF_2, -F), 113 (M^+-C_6F_5).

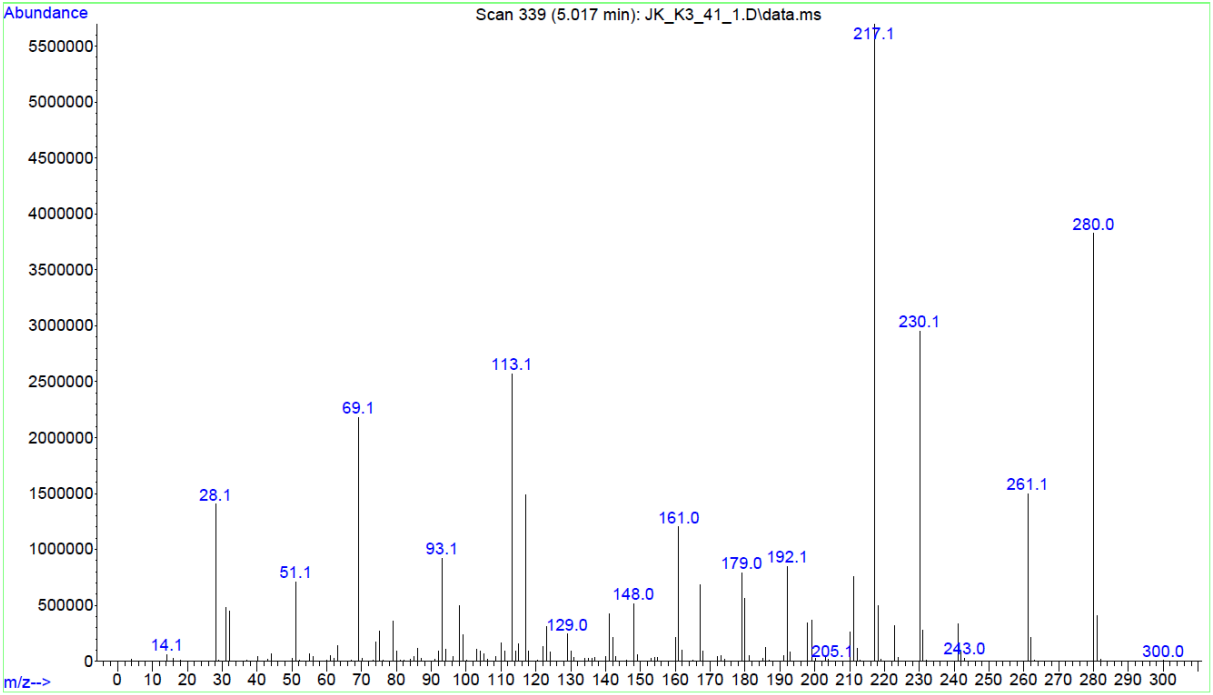


Figure S10. Mass spectra of peak 8.

MS (EI): m/z = 280 (M^+), 261 (M^+-F), 230 (M^+-CF_2), 217 (M^+-CF=CFH), 113 (M^+-C_6F_5).

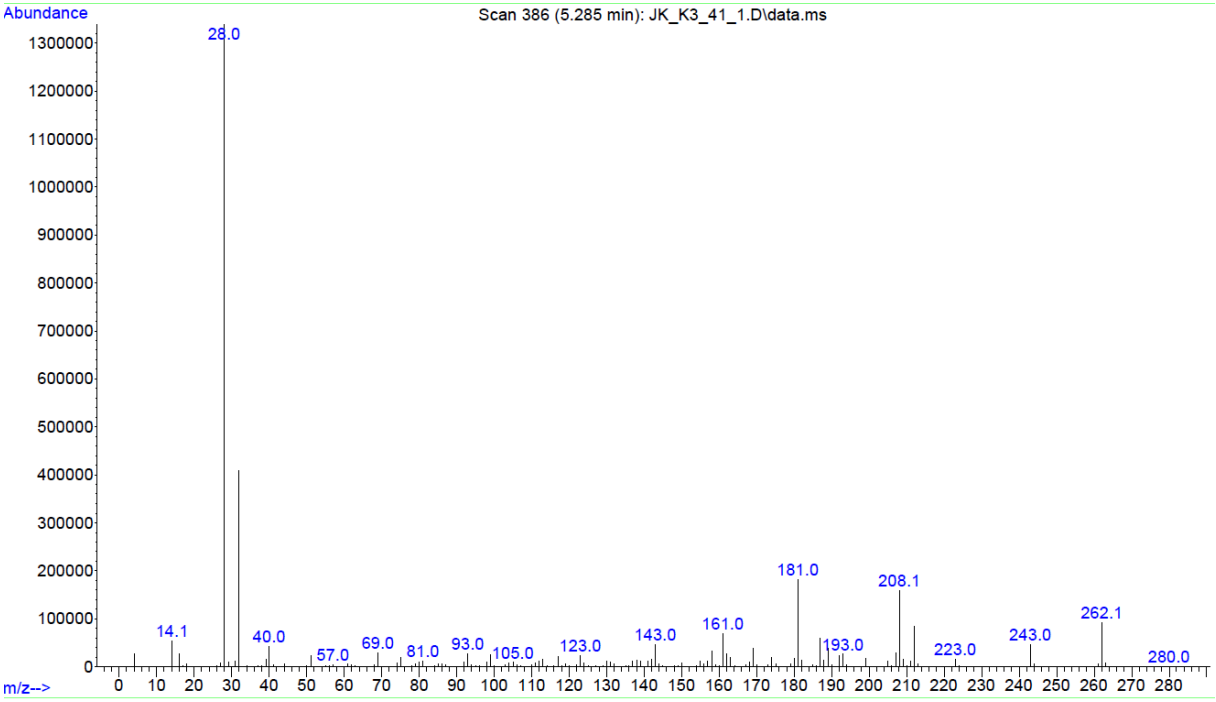


Figure S11. Mass spectra of peak 9.

MS (EI): m/z = 262 (M^+), 243 (M^+-F).

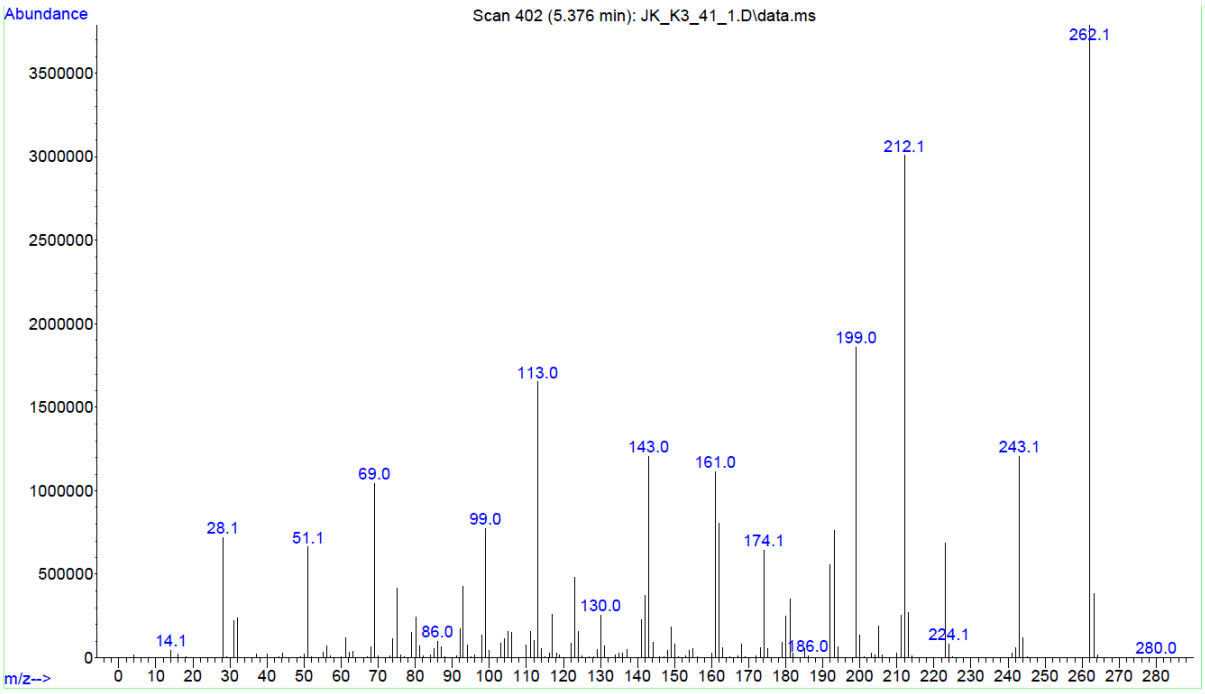


Figure S12. Mass spectra of peak 10.

MS (EI): m/z = 262 (M^+), 243 (M^+-F), 212 (M^+-CF_2), 199 (M^+-CF=CFH), 113 (M^+-C_6F_4H).

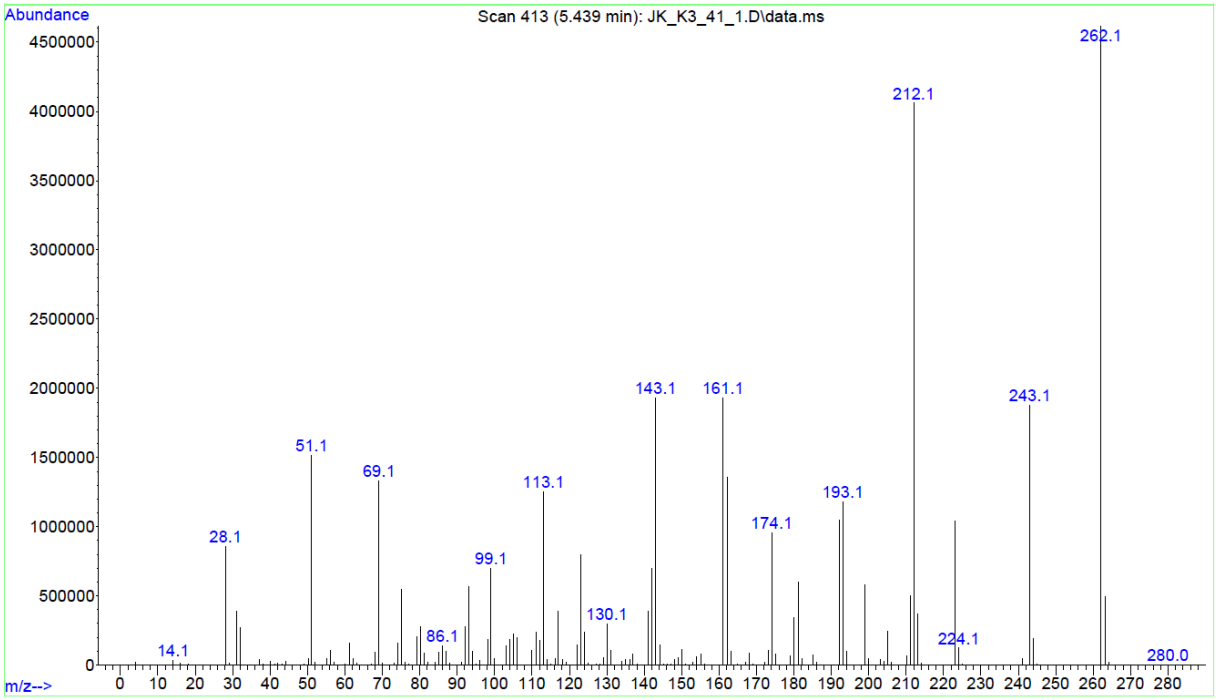


Figure S13. Mass spectra of peak 11.

MS (EI): m/z = 262 (M^+), 243 (M^+-F), 212 (M^+-CF_2), 113 (M^+-C_6F_4H).

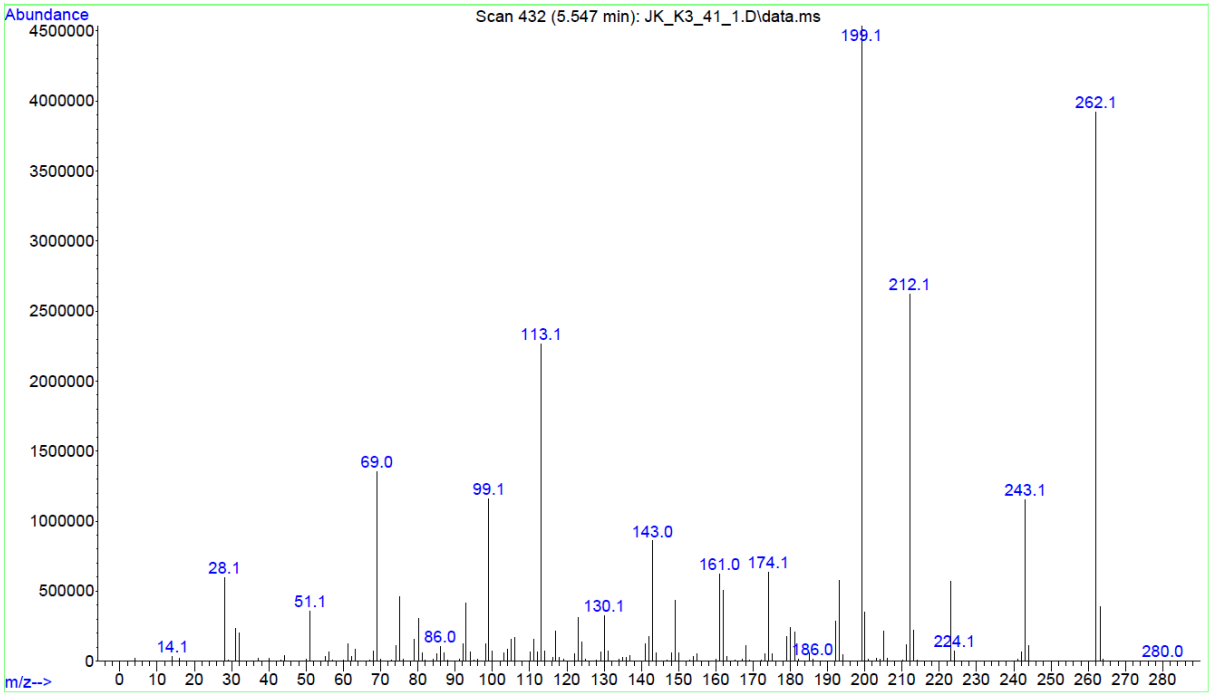


Figure S14. Mass spectra of peak 12.

MS (EI): m/z = 262 (M^+), 243 (M^+-F), 212 (M^+-CF_2), 199 (M^+-CF=CFH), 113 (M^+-C_6F_4H).

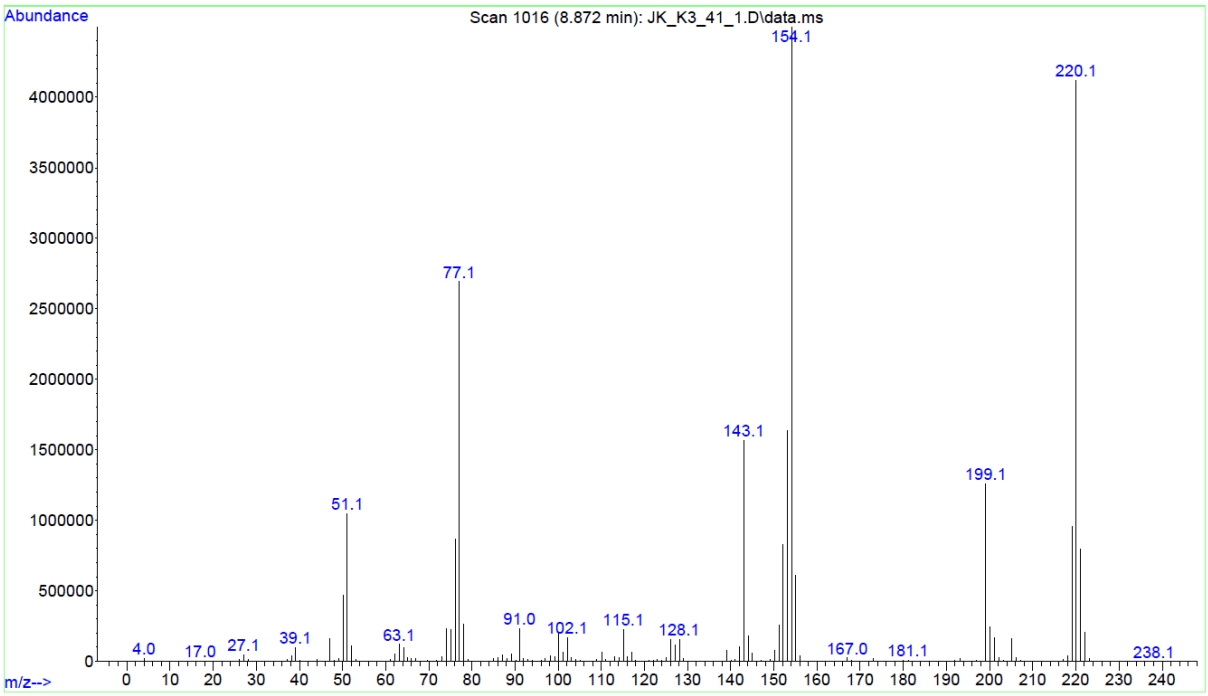


Figure S15. Mass spectra of peak 15.

MS (EI): m/z = 220 (M^+), 143 (M^+-Ph), 77 (M^+-$PhSiF_2$).

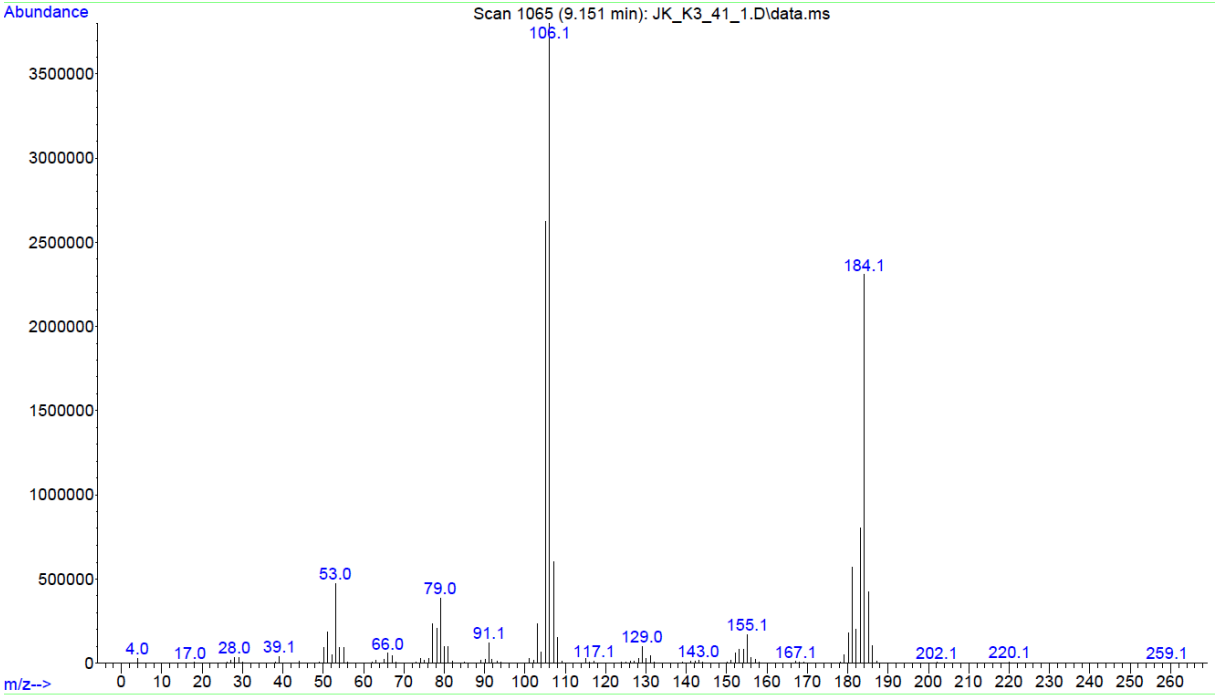
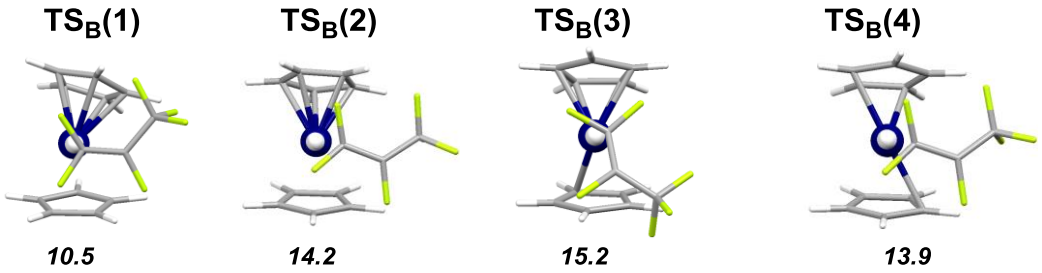


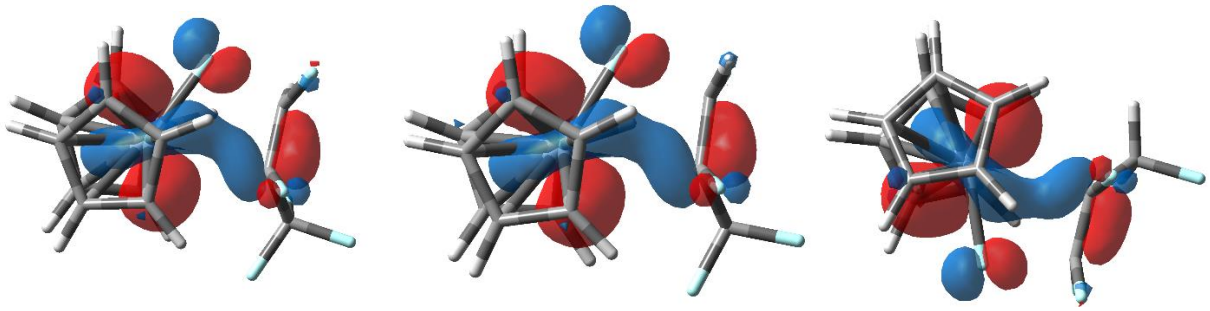
Figure S16. Mass spectra of peak 17.

MS (EI): m/z = 184 (M^+), 106 (M^+-Ph, -F).

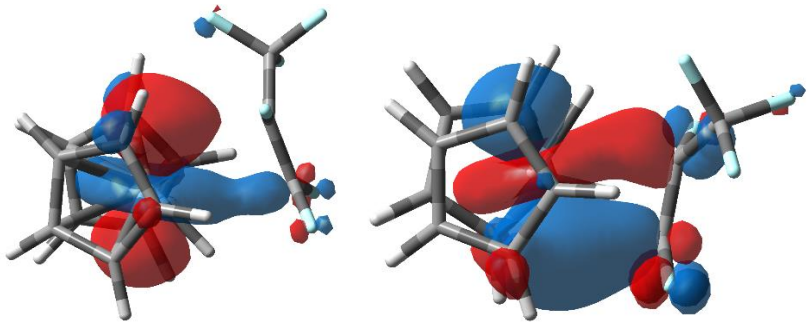
2. Other possible TS for S_NV TS (TS_B3-IP1)



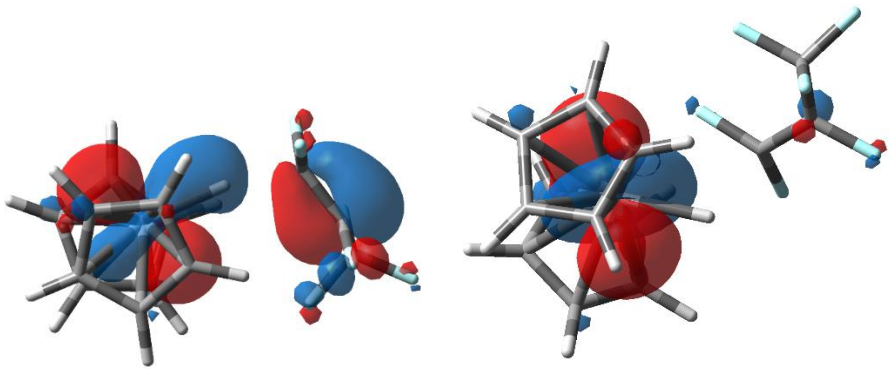
3. SOMO pictures for all HDF-TS for 3.



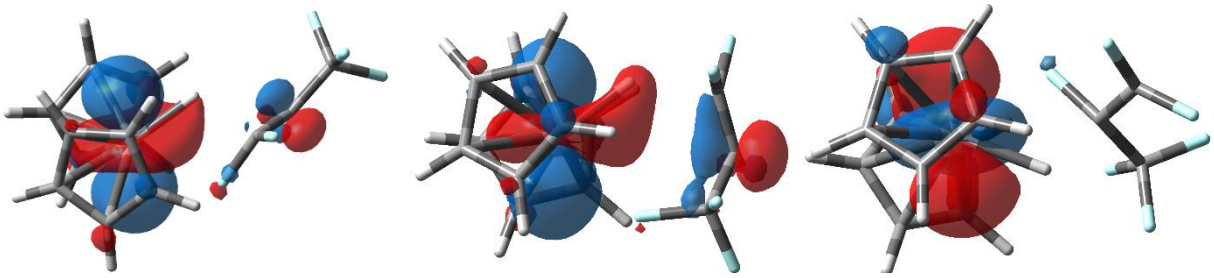
TS5a-3a TS5b-3b TS5c-3c



TS-A-3-5d TS-A-C2_attack



TS-B-3-IP1 TS-B-3-IP2



TS-C-3-3b **TS-C-3-3c** **TS-C-C2_attack**

4. Tables for energies, enthalpy and entropy corrections (T = 298 K, 1 bar) perfluoropropene (3)

THF

Name	M06-2X DZ	M06-2X TZ	M06-2X TZ+D3	S2	ZPE	EnthalpyCorr	EntropyCorr	H	G	ΔH	ΔG
1	-445.5659121	-445.696266	-445.6969973	0.7625	0.1755678	0.184745746	0.046543206	-445.5122516	-445.5587948		
3a_cis_HFCCFCF3	-613.9171124	-614.1418234	-614.1419252	0	0.042750815	0.049746799	0.040252735	-614.0921784	-614.1324312		
3b_trans_HFCCFCF	-613.912899	-614.1381959	-614.1382866	0	0.042500845	0.049516542	0.040528462	-614.0887701	-614.1292986		
3_C3F6	-713.1231448	-713.3857426	-713.3858334	0	0.034851065	0.042501583	0.042405561	-713.3433318	-713.3857374		
3c_F2CCFCF2H	-613.9000803	-614.1244213	-614.1245171	0	0.04325847	0.050422812	0.04086798	-614.0740943	-614.1149622		
1b	-544.8873167	-545.0532995	-545.0540579	0.7586	0.171810346	0.181787941	0.048813186	-544.8722699	-544.9210831		
3+1	-1158.689057	-1159.082009	-1159.082831		0.210418865	0.227247329	0.088948767	-1158.855583	-1158.944532	0.0	0.0
3-1_contact_pair	-1158.695883	-1159.091043	-1159.093001	0.7636	0.21168447	0.229173872	0.071239515	-1158.863827	-1158.935066	-5.2	5.9
TS-C-3-3b	-1158.692984	-1159.084958	-1159.086724	0.7627	0.211282001	0.228011995	0.068462664	-1158.858712	-1158.927174	-2.0	10.9
TS-B-3-IP2	-1158.691993	-1159.083552	-1159.085357	0.7627	0.211391876	0.228013049	0.067018448	-1158.857344	-1158.924362	-1.1	12.7
TS-C-3_C2_attack	-1158.677874	-1159.069178	-1159.070984	0.7706	0.211182265	0.230470078	0.06633296	-1158.840514	-1158.906847	9.5	23.6
TS-C-3-3c	-1158.69411	-1159.086574	-1159.088509	0.7645	0.211094406	0.22772845	0.067062589	-1158.86078	-1158.927843	-3.3	10.5
TS-A-3-5d	-1158.700282	-1159.093138	-1159.095096	0.7639	0.212622885	0.228752781	0.064686216	-1158.866343	-1158.93103	-6.8	8.5
TS-A-3_C2_contact	-1158.692886	-1159.084238	-1159.08613	0.7623	0.212448572	0.23128501	0.065249868	-1158.854845	-1158.920095	0.5	15.3
TS-B-3-IP1	-1158.689775	-1159.083071	-1159.084983	0.7623	0.210267095	0.227441318	0.070188703	-1158.857542	-1158.92773	-1.2	10.5
TS-B-3-IP1(2)	-1158.686004	-1159.079619	-1159.081571	0.7644	0.21078417	0.227634626	0.067997049	-1158.853937	-1158.921934	1.0	14.2
TS-B-3-IP1(3)	-1158.684865	-1159.078027	-1159.079916	0.7668	0.210438002	0.22668348	0.067153587	-1158.853233	-1158.920387	1.5	15.2
TS-B-3-IP1(4)	-1158.68595	-1159.079606	-1159.08157	0.7648	0.210799381	0.227655896	0.068526654	-1158.853914	-1158.922441	1.0	13.9
TS-B-3-IP1(5)	-1158.686004	-1159.079617	-1159.08157	0.7644	0.210782222	0.227632854	0.067998656	-1158.853937	-1158.921936	1.0	14.2
TS-B-3-IP1(6)	-1158.686001	-1159.07953	-1159.081479	0.7645	0.211104874	0.230365576	0.066305089	-1158.851114	-1158.917419	2.8	17.0
IP4_anion	-713.8511705	-714.109084	-714.1091983		0.043891948	0.051794147	0.042993179	-714.0574041	-714.1003973		
IP4_cation	-444.8319751	-444.9618139	-444.9624742	0.7577	0.170469025	0.179001112	0.051156354	-444.7834731	-444.8346295		
IP4	-1158.683146	-1159.070898	-1159.071672		0.214360973	0.230795258	0.094149534	-1158.840877	-1158.935027	9.2	6.0
IP1	-1158.710015	-1159.101701	-1159.103594	0.7605	0.215422894	0.235131363	0.06896906	-1158.868463	-1158.937432	-8.1	4.5

IP2	-1158.725332	-1159.114492	-1159.11626	0.7603	0.216434471	0.233138682	0.067361037	-1158.883121	-1158.950482	-17.3	-3.7
5d	-1158.781834	-1159.173285	-1159.175197	0.7583	0.217549109	0.236938807	0.068044689	-1158.938258	-1159.006303	-51.9	-38.8
5a	-1158.789154	-1159.178973	-1159.180888	0.7602	0.217909331	0.234195047	0.065457578	-1158.946693	-1159.012151	-57.2	-42.4
5b	-1158.787972	-1159.177969	-1159.179882	0.7601	0.217712265	0.233954981	0.064943347	-1158.945927	-1159.01087	-56.7	-41.6
5c	-1158.782973	-1159.172582	-1159.174475	0.7603	0.217753171	0.234087072	0.065529229	-1158.940388	-1159.005918	-53.2	-38.5
TS5a_3a	-1158.772989	-1159.162611	-1159.16455	0.7593	0.216385714	0.232509305	0.064437356	-1158.932041	-1158.996478	-48.0	-32.6
TS5b_3b	-1158.769747	-1159.159712	-1159.161648	0.7593	0.216335527	0.232414692	0.064116929	-1158.929234	-1158.99335	-46.2	-30.6
TS5c_3c	-1158.760689	-1159.149724	-1159.151641	0.7591	0.216519877	0.23276532	0.064861877	-1158.918875	-1158.983737	-39.7	-24.6
1b-3b_contact pair	-1158.80763	-1159.198979	-1159.20064	0.7583	0.214974533	0.235942926	0.075940096	-1158.964697	-1159.040637	-68.5	-60.3
1b-3c_contact pair	-1158.794394	-1159.186532	-1159.188492	0.7588	0.216152697	0.236910272	0.072363737	-1158.951582	-1159.023945	-60.2	-49.8
1b-3a_contact pair	-1158.813	-1159.20578	-1159.207748	0.7589	0.215711353	0.236373923	0.071685502	-1158.971374	-1159.04306	-72.7	-61.8
1b-3b_contact pair(2)	-1158.809684	-1159.202808	-1159.204762	0.7583	0.215395944	0.236071814	0.071618632	-1158.96869	-1159.040309	-71.0	-60.1
1b-3c_contact pair(2)	-1158.794393	-1159.186531	-1159.188491	0.7588	0.216162002	0.236914588	0.072276198	-1158.951576	-1159.023853	-60.2	-49.8
4+3a	-1158.804429	-1159.195123	-1159.195983		0.214561161	0.23153474	0.089065921	-1158.964448	-1159.053514	-68.3	-68.4
4+3b	-1158.800216	-1159.191495	-1159.192345		0.214311191	0.231304483	0.089341647	-1158.96104	-1159.050382	-66.2	-66.4
4+3c	-1158.787397	-1159.177721	-1159.178575		0.215068816	0.232210753	0.089681166	-1158.946364	-1159.036045	-57.0	-57.4
Pentafluoropropene Elimination E isomer	-1059.578891	-1059.932221	-1059.934101		0.224175504	0.239660108	0.055366287		-1059.749807	-0.71	
Pentafluoropropene Elimination Z isomer	-1059.578042	-1059.931158	-1059.933026		0.224186705	0.239604757	0.05502741		-1059.748449		
4 anion radical A	-1341.442662	-1341.442662	-1341.443433	0.7615	0.079750149	0.094901325	0.055437719	-1059.694441	-1341.403969	-4.55	
4 anion radical B	-1341.436393	-1341.436393	-1341.43717	0.7554	0.080064539	0.094976307	0.054527776	-1059.693422	-1341.396721		

Toluene

Name	M06-2X DZ	M06-2X TZ	M06-2X TZ+D3	S2	ZPE	EnthalpyCorr	EntropyCorr	H	G	ΔH	ΔG
1	-445.5615783	-445.691867	-445.6926011		0.1756556	0.18646902	0.046185776				
3	-713.1224048	-713.3850046	-713.3850954		0.034987506	0.043734003	0.042364902				
3+1	-1158.683983	-1159.076872	-1159.077697		0.210643106	0.230203023	0.088550677	-1158.847493	-1158.936044	0.0	0.0
TS-C-3-3b	-1158.690287	-1159.082275	-1159.084043	0.763	0.211639443	0.231035738	0.06813611	-1158.853007	-1158.921143	-3.5	9.4
TS-C-3-3a	-1158.689201	-1159.080839	-1159.082644	0.7631	0.211634939	0.230970903	0.066874357	-1158.851673	-1158.918548	-2.6	11.0
TS-C-3-3c	-1158.692021	-1159.084648	-1159.086583	0.7647	0.211024099	0.230527786	0.068202938	-1158.856056	-1158.924258	-5.4	7.4
TS-A-3-5d	-1158.697847	-1159.090724	-1159.092683	0.7641	0.212924853	0.231775148	0.064575767	-1158.860908	-1158.925484	-8.4	6.6
TS-B-3-IP1	-1158.681768	-1159.075078	-1159.077032	0.765	0.210951368	0.230526187	0.067600389	-1158.846506	-1158.914106	0.6	13.8
TS5a_3a	-1158.769596	-1159.15897	-1159.160909	0.7593	0.216413014	0.235327757	0.065006794	-1158.925581	-1158.990588	-49.0	-34.2
TS5b_3b	-1158.766609	-1159.156318	-1159.158253	0.7592	0.21639341	0.235244315	0.064451041	-1158.923009	-1158.98746	-47.4	-32.3
TS5c_3c	-1158.757062	-1159.146129	-1159.148046	0.759	0.216585097	0.235614518	0.065096178	-1158.912431	-1158.977528	-40.7	-26.0

5. Tables for energies, enthalpy and entropy corrections (T = 298 K, 1 bar) perfluoroallylbenzene (4)

THF

Name	M06-2X DZ	M06-2X TZ	M06-2X TZ+D3	S2	ZPE	EnthalpyCorr	EntropyCorr	H	G	ΔG
1	-445.5659121	-445.696266	-445.6969973	0.7625	0.1755678	0.186332	0.046543	-445.5564767	-445.5572081	
4	-1340.890354	-1341.366934	-1341.367685	0	0.083722117	0.100699	0.061642	-1341.327876	-1341.328628	
4+1	-1786.456266	-1787.0632	-1787.064683		0.259289918	0.287031	0.108185	-1786.884353	-1786.885836	0.0
TS_C4_4a	-1786.462241	-1787.068658	-1787.071925	0.7646	0.259699545	0.287378	0.085835	-1786.867115	-1786.870382	9.7
TS_C4_4b	-1786.461872	-1787.067712	-1787.071133	0.7647	0.259620195	0.287306	0.085782	-1786.866188	-1786.869609	10.2
TS_B4_IP1c	-1786.462549	-1787.067892	-1787.071441	0.7631	0.260433485	0.287957	0.085049	-1786.864984	-1786.868533	10.9
TS_B4_IP2	-1786.458603	-1787.064084	-1787.066907	0.763	0.259957907	0.287722	0.087012	-1786.863374	-1786.866197	12.3
TS_C4_4e	-1786.453216	-1787.059539	-1787.062359	0.7639	0.260132064	0.287839	0.086126	-1786.857827	-1786.860647	15.8
TS_A4_4e_HM	-1786.451634	-1787.0576171973	-1787.060887	0.7635	0.260021207	0.287704	0.08612	-1786.856034	-1786.859303	16.6
TS_A4-HM)	-1786.468308	-1787.075202	-1787.078367	0.7641	0.261346128	0.288583	0.084077	-1786.870696	-1786.87386	7.5
TS_B4_IP3	-1786.454548	-1787.061743	-1787.064725		0.258883746	0.287104	0.088731	-1786.77464	-1786.863371	12.2
A/E pathway	-1786.461387									
4d	-1786.539665	-1787.143431	-1787.146603	0.7594	0.265048476	0.2923	0.08408	-1786.935211	-1786.938384	0.0
4c	-1786.535146	-1787.139682	-1787.142862	0.7594	0.2647358	0.291992	0.083896	-1786.931586	-1786.934766	2.3
4a	-1786.52878	-1787.1323	-1787.135633	0.7594	0.264889333	0.292292	0.084961	-1786.924968	-1786.928302	6.3
4b	-1786.529155	-1787.132348	-1787.135677	0.7596	0.265219498	0.292434	0.083081	-1786.922995	-1786.926325	7.6