Supporting Information: Atomistic Insights into the Hydrodefluorination of PFAS Using Silylium Catalysts

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Table S1: Geometry comparison

Bond/Angle (Å/ degrees)	Crystal Structure[a] A	Crystal Structure[a] B	DFT Structure
Si–Cl	2.30	2.28	2.28
B–Cl	1.86	1.86	1.90
B–Cl–Si	115.02	114.35	119.51
C–Si–C	119.92	118.06	117.43
C–Si–C	111.32	114.85	114.43
C–Si–C	114.61	115.15	114.88
C–Si–C Ave.	115.28	116.02	115.58

[a] Crystal structure from Douvris, C. *et al.*, *J. Am. Chem. Soc.*, **2010**, 132, 4946–4953

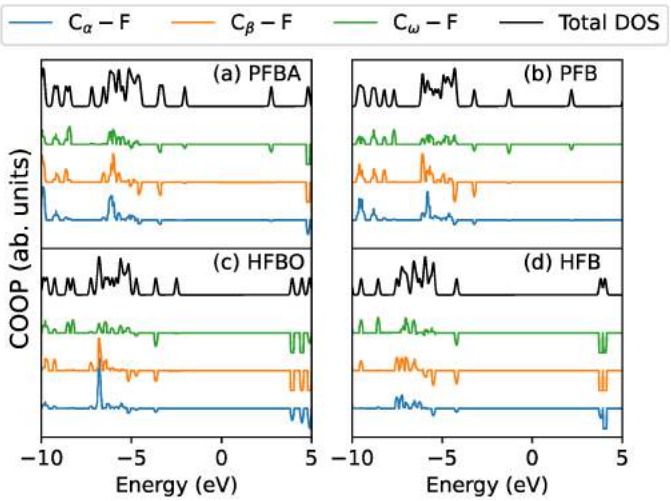


Figure S1: COOP curves for the set of PFAS molecules included in the current study.

Table S2: Reaction energies for the extraction of a fluorine anion (F^-), addition of a hydride (H^-), and their sum for the perfluorinated molecules in Figure 2 with respect to C–F position. Units in electron volts (eV).

Molecule	Position	Reaction Energy (ΔE_{rxn})		
		F^- Extraction	H^- Addition	Total
PFBA	C_α	1.08	−2.62	−1.54
	C_β	1.28	−2.92	−1.64
	C_ω	1.12	−2.37	−1.24
PFB	C_α	0.73	−3.58	−2.78
	C_β	0.75	−3.19	−2.38
	C_ω	0.89	−3.07	−2.18
HFBO	C_α	0.94	−2.22	−1.28
	C_β	1.15	−2.73	−1.58
	C_ω	0.94	−3.10	−2.15
HFB	C_α	0.72	−2.10	−1.38
	C_β	1.09	−2.65	−1.56
	C_ω	0.97	−3.00	−2.03

Table S3: Reaction energetics for the extraction of a fluorine anion (F^-) and the addition of a hydride (H^-) in a concerted reaction mechanism for the perfluorinated molecules in Figure 2 with respect to C–F position. Units in electron volts (eV).

Molecule	Position	Activation Energy (E_a)	Reaction Energy (ΔE_{rxn})
PFBA	C_α	0.63	−3.21
	C_β	0.49	−2.99
	C_ω	0.15	−1.93
PFB	C_α	0.64	−3.14
	C_β	0.42	−3.33
	C_ω	0.09	−1.92
HFBO	C_α	0.81	−3.02
	C_β	0.66	−3.20
	C_ω	0.31	−1.93
HFB	C_α	0.78	−1.45
	C_β	0.76	−2.38
	C_ω	0.41	−1.63

Table S4: Change in reaction energies due to the presence of the carborane anion ($[HCB_{11}H_5F_6]^-$) for the extraction of a fluorine anion (F^-), addition of a hydride (H^-), and their sum for the perfluorinated molecules in Figure 2 with respect to C–F position. Units in electron volts (eV).

Molecule	Position	Change in Reaction Energy ($\Delta\Delta E_{rxn}$)		
		F^- Extraction	H^- Addition	Total
PFBA	C_α	−0.40	−1.17	−1.57
	C_β	−0.33	−0.57	−1.90
	C_ω	−0.18	+0.46	+0.28
PFB	C_α	−0.60	+0.41	−0.19
	C_β	+0.09	+0.63	+0.72
	C_ω	−0.23	+0.08	−0.15
HFBO	C_α	−1.06	−1.74	−2.80
	C_β	−0.22	−1.74	−1.96
	C_ω	+0.03	+0.28	+0.31
HFB	C_α	−0.13	−0.37	−0.50
	C_β	−0.18	−1.54	−1.72
	C_ω	+0.01	+0.00	+0.01

Table S5: Change in reaction energetics for the concerted reaction mechanism for the perfluorinated molecules in Figure 2 with respect to C–F position in the presence of a carborane anion ($[HCB_{11}H_5F_6]^-$). Units in electron volts (eV).

Molecule	Position	Change in Activation Energy (ΔE_a)	Change in Reaction Energy ($\Delta\Delta E_{rxn}$)
PFBA	C_α	−0.54	+2.08
	C_β	+0.03	+0.50
	C_ω	+0.90	−0.11
PFB	C_α	−0.59	+0.10
	C_β	+0.06	+0.14
	C_ω	+0.78	−0.20
HFBO	C_α	−0.27	+0.58
	C_β	−0.42	+0.26
	C_ω	+0.73	−0.15
HFB	C_α	+0.09	−0.50
	C_β	+0.30	−0.38
	C_ω	+0.79	−0.43

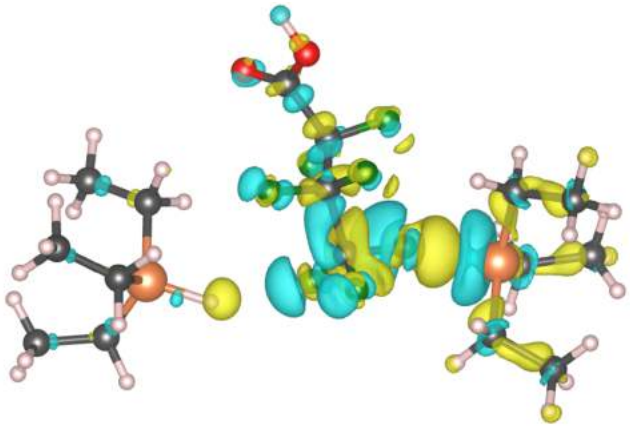


Figure S2: Charge density differences for PFBA at the C_ω position interacting with a Et_3Si^+ and Et_3SiH. Blue regions denote areas of charge depletion, whilst yellow denotes areas of charge accumulation.

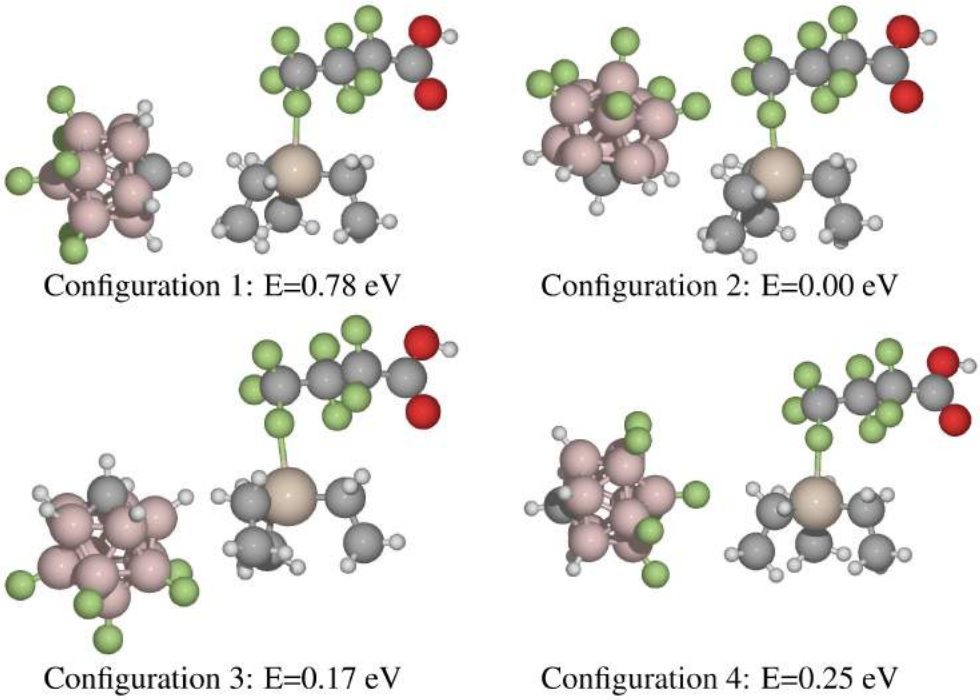
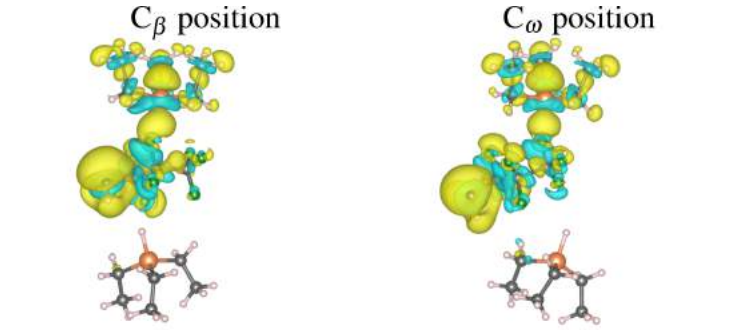


Figure S3: Orientation of the carborane anion relative to PFBA and a silylium cation with relative energies given with respect to the lowest energy conformer (configuration 1).



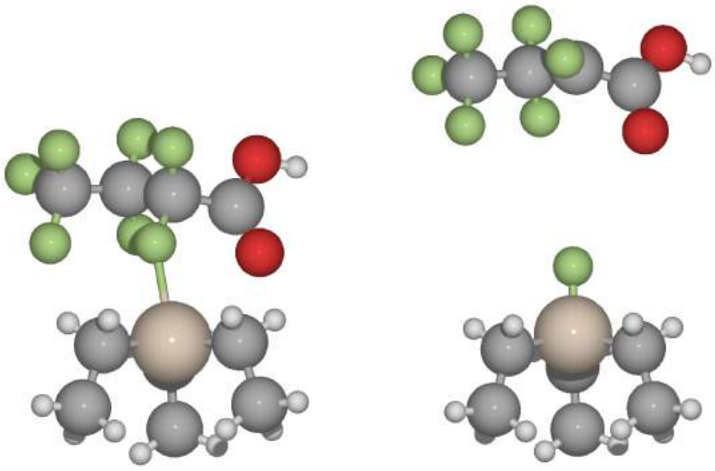
(a) No carborane

(b) With carborane

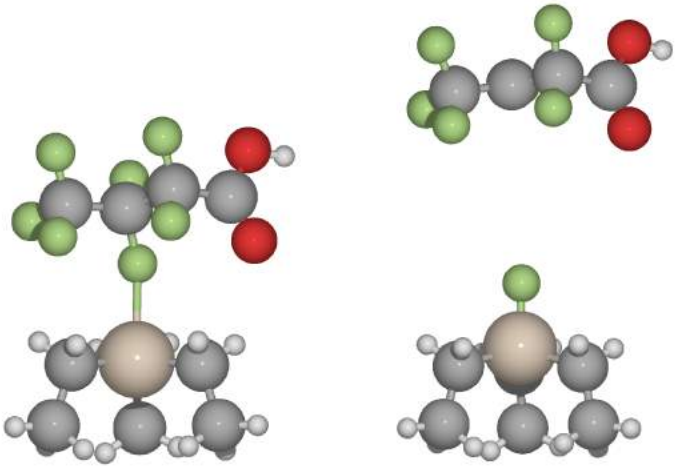
Figure S4: Charge density differences for HFB in the (a) absence of carborane and (b) with it present interacting with a Et_3Si^+ and Et_3SiH. Blue regions denote areas of charge depletion, whilst yellow denotes areas of charge accumulation. Results shown are for the 0.01 e^- Å^{-3} isosurface.

Table S6: Change in reaction energetics for the concerted reaction mechanism for the perfluorinated molecules in Figure 2 with respect to C–F position in the presence of different carborane anions ($[HCB_{11}H_5X_6]^-$, where X=$\{Cl,\ Br,\ I\}$). Reference is $[HCB_{11}H_5F_6]^-$. Units in electron volts (eV).

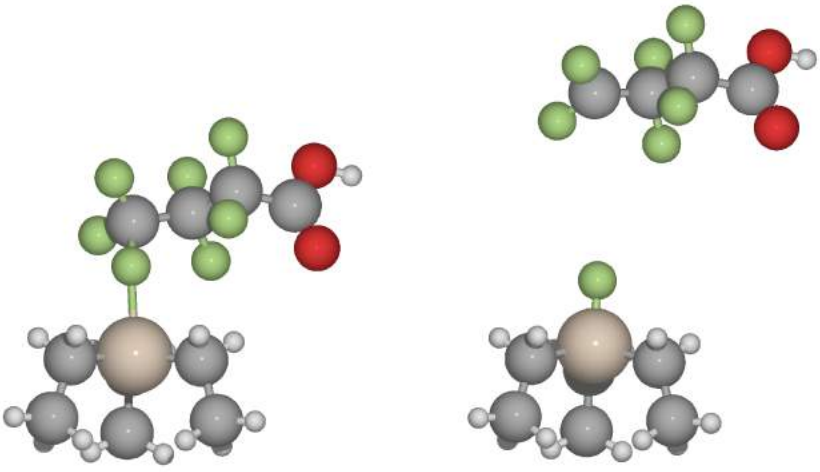
Molecule	Position	$[HCB_{11}H_5Cl_6]^-$		$[HCB_{11}H_5Br_6]^-$		$[HCB_{11}H_5I_6]^-$	
		ΔE_a	$\Delta\Delta E_{rxn}$	ΔE_a	$\Delta\Delta E_{rxn}$	ΔE_a	$\Delta\Delta E_{rxn}$
PFBA	C_α	+0.00	−0.17	+0.02	−0.21	+0.00	−0.09
	C_β	+0.12	−0.02	−0.05	−0.09	−0.38	−0.15
	C_ω	−0.18	−0.04	+0.09	−0.18	−0.38	−0.60
PFB	C_α	−0.09	+0.63	−0.05	+0.69	−0.03	+1.00
	C_β	+0.02	+0.01	−0.03	+0.01	−0.24	−0.14
	C_ω	+0.21	+0.32	+0.07	−0.12	−0.33	−0.68
HFBO	C_α	+0.06	−0.10	−0.03	−0.15	−0.48	+0.67
	C_β	+0.11	−0.06	+0.13	+0.06	−0.20	+0.03
	C_ω	−0.19	−0.14	−0.19	−0.20	−0.34	−0.66
HFB	C_α	−0.08	+0.01	+0.12	−0.11	−0.80	+0.01
	C_β	−0.38	−0.01	−0.48	+0.00	+0.12	−0.30
	C_ω	−0.29	−0.05	−0.15	−0.10	−0.31	−0.49



(a) C_α

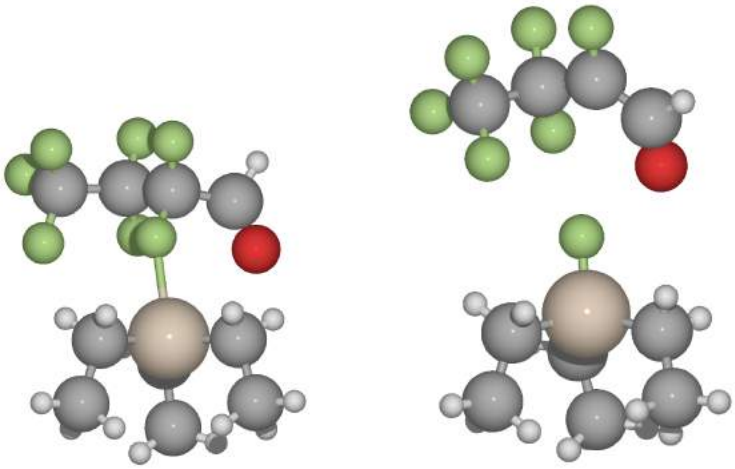


(b) C_β

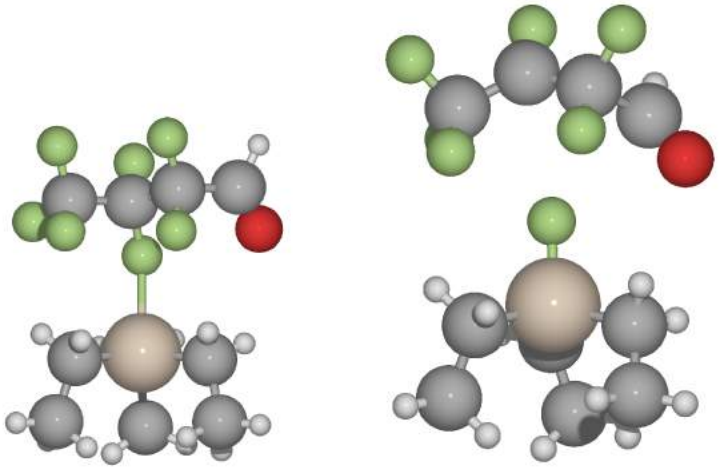


(c) C_ω

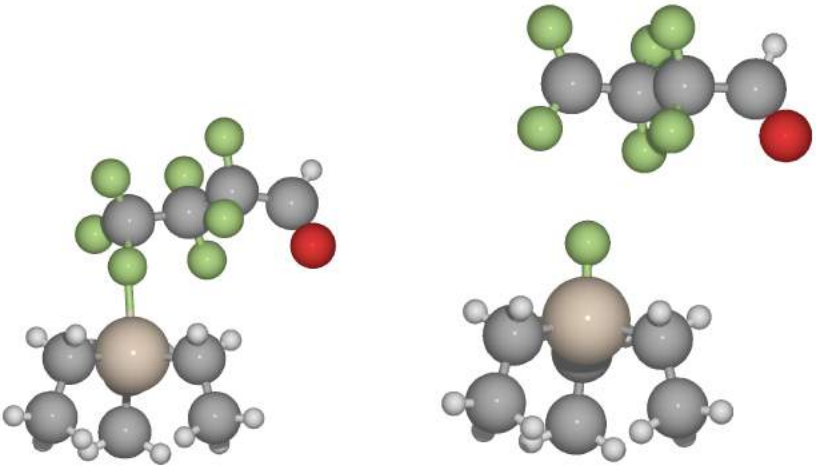
Figure S5: Initial and final states of carbocation formation/defluorination as a function of position for PFBA.



(a) C_{α}

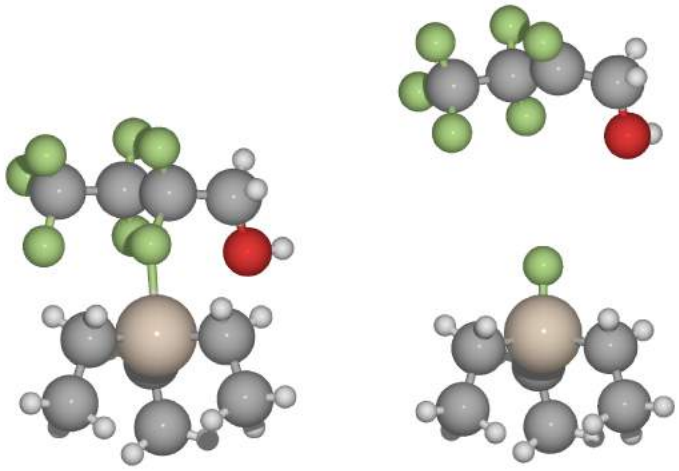


(b) C_{β}

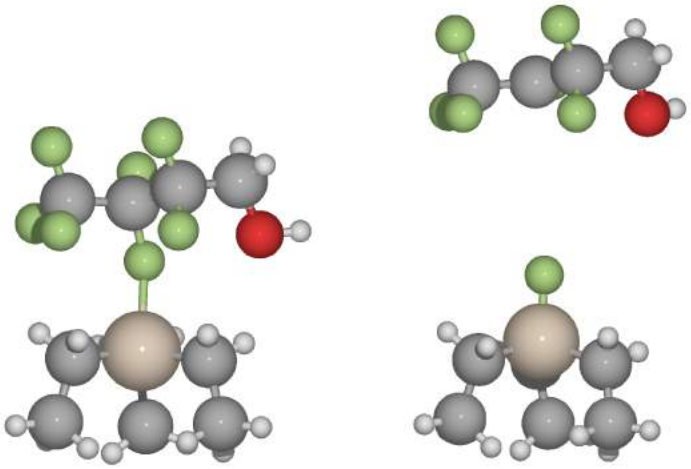


(c) C_{ω}

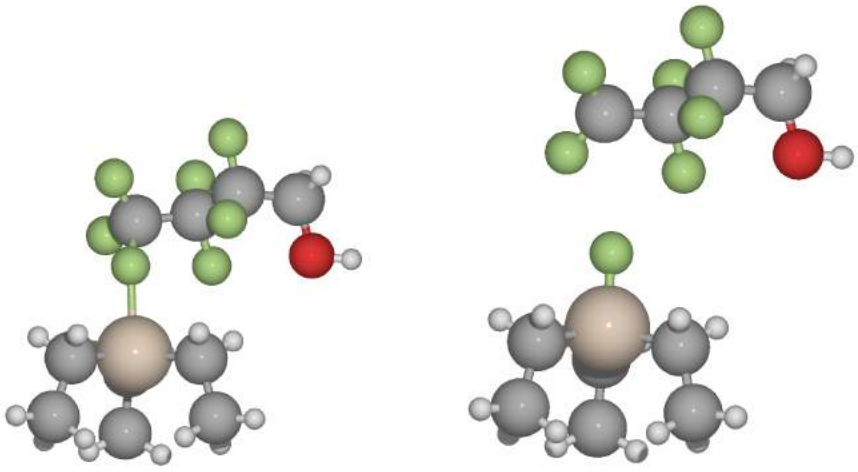
Figure S6: Initial and final states of carbocation formation/defluorination as a function of position for PFB.



(a) C_α

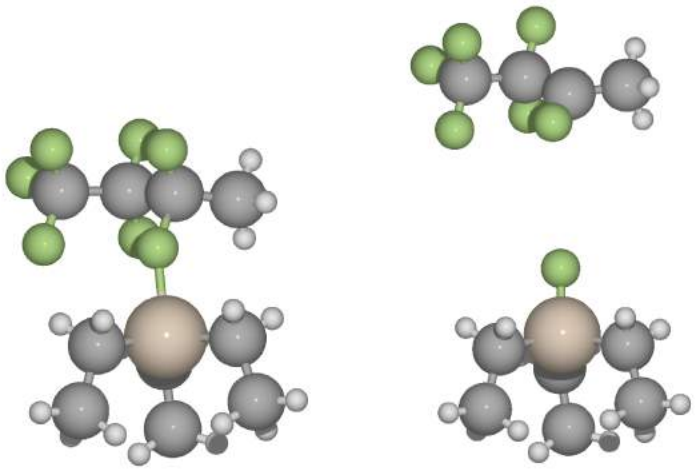


(b) C_β

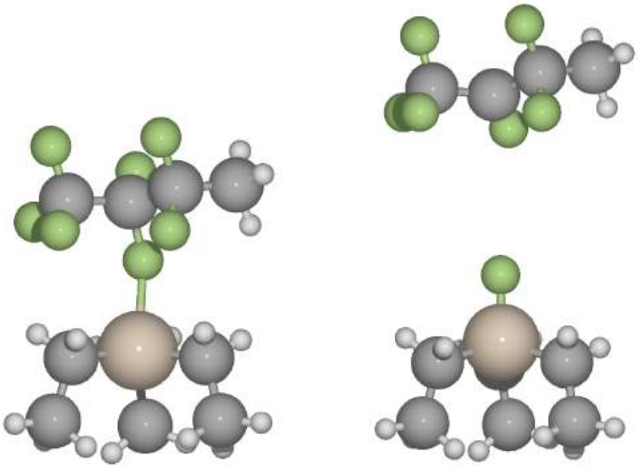


(c) C_ω

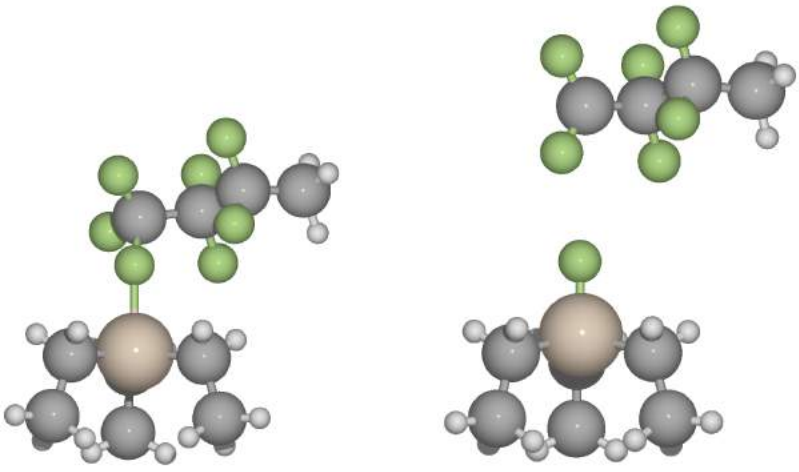
Figure S7: Initial and final states of carbocation formation/defluorination as a function of position for HFBO.



(a) C_α

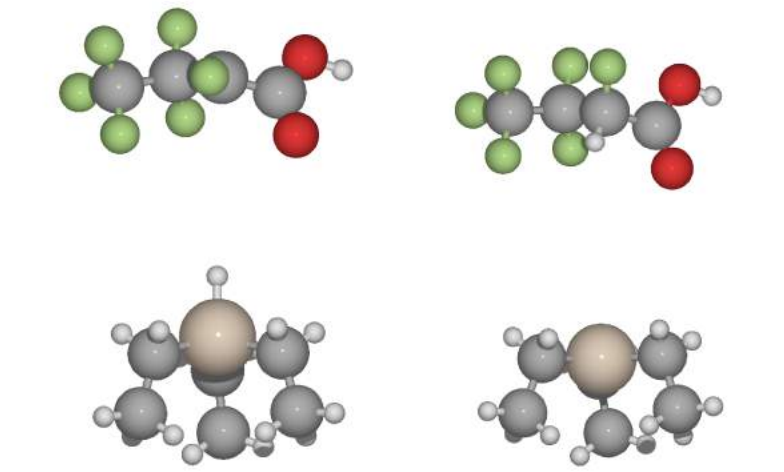


(b) C_β

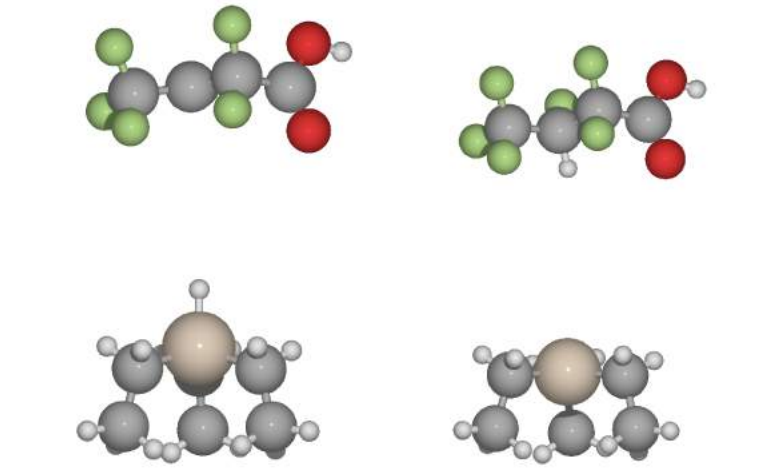


(c) C_ω

Figure S8: Initial and final states of carbocation formation/defluorination as a function of position for HFB.



(a) C_α



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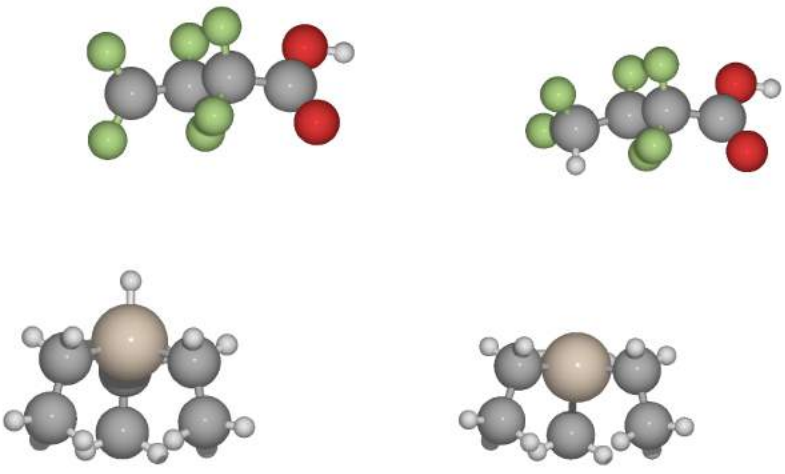
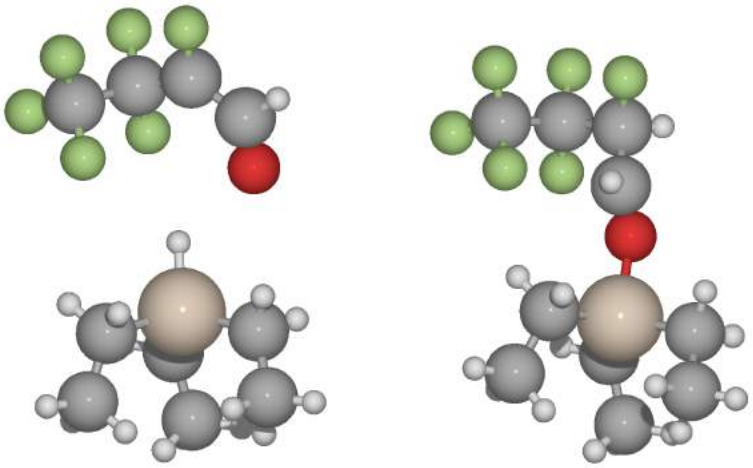
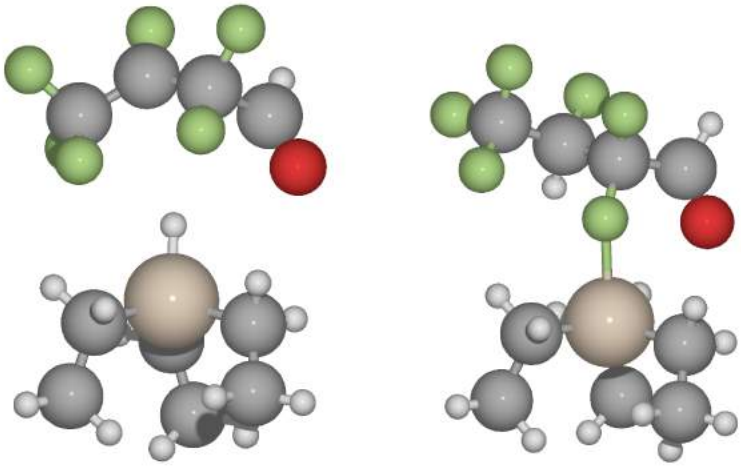


(c) C_ω

Figure S9: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for PFBA.



(a) C_α



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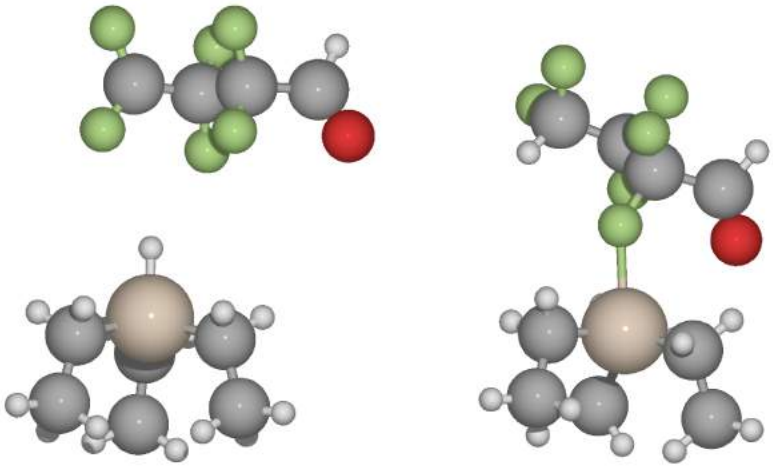
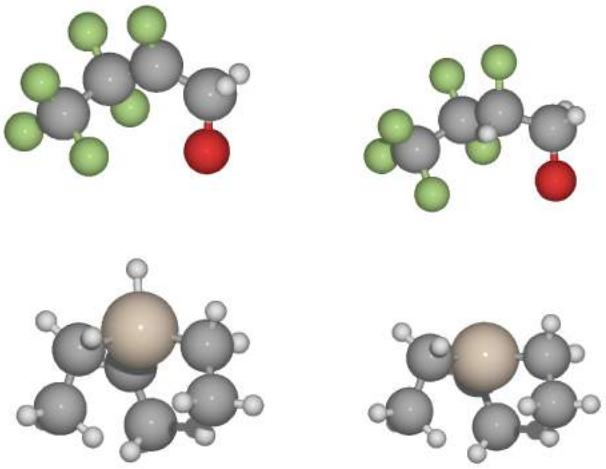
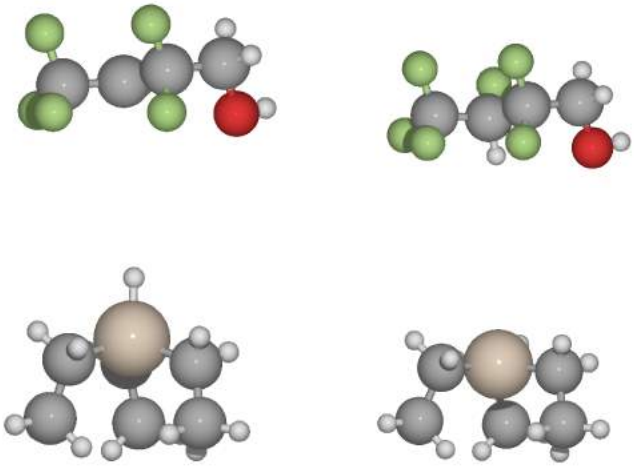


(c) C_ω

Figure S10: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for PFB.



(a) C_α



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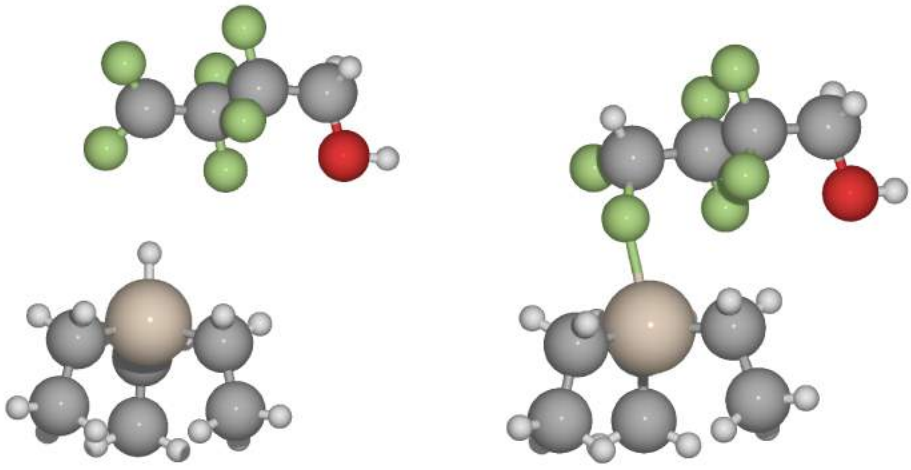
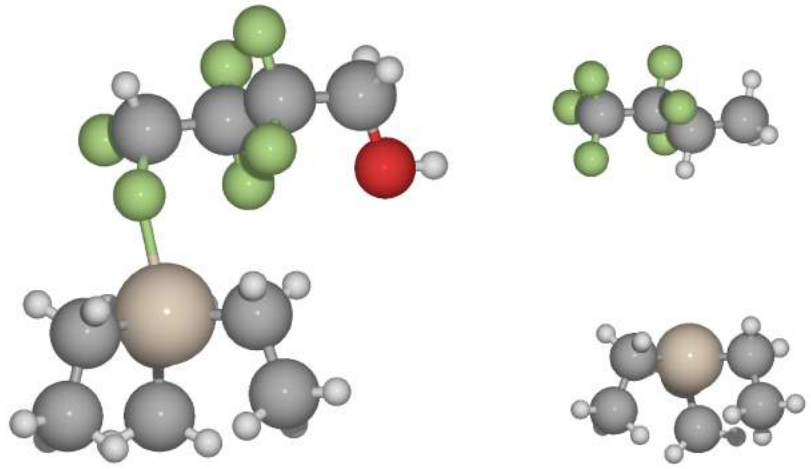
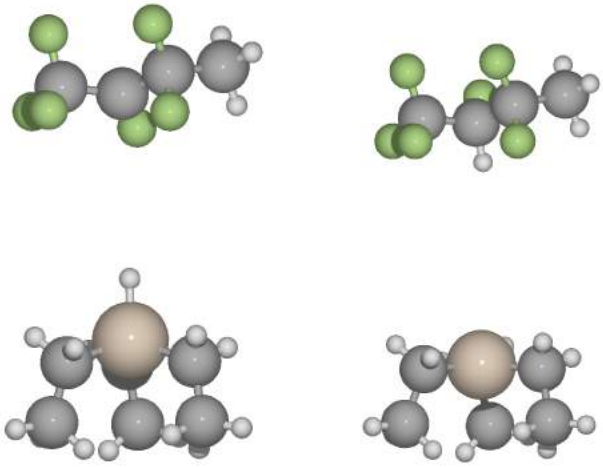


(c) C_ω

Figure S11: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for HFBO.



(a) C_α



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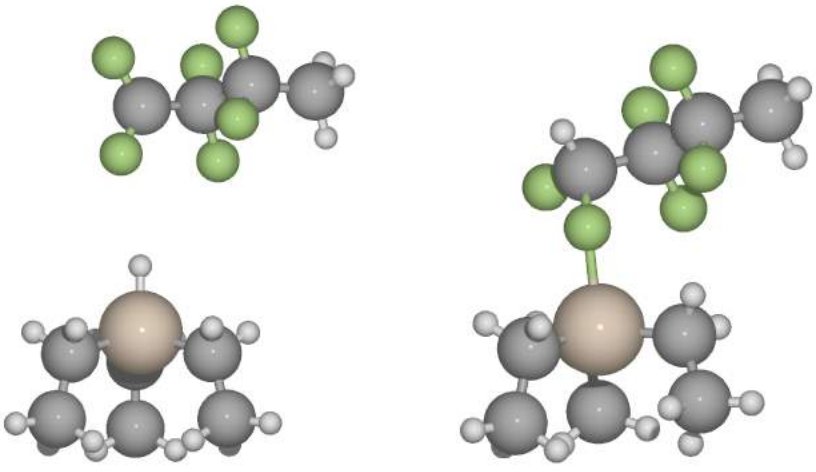
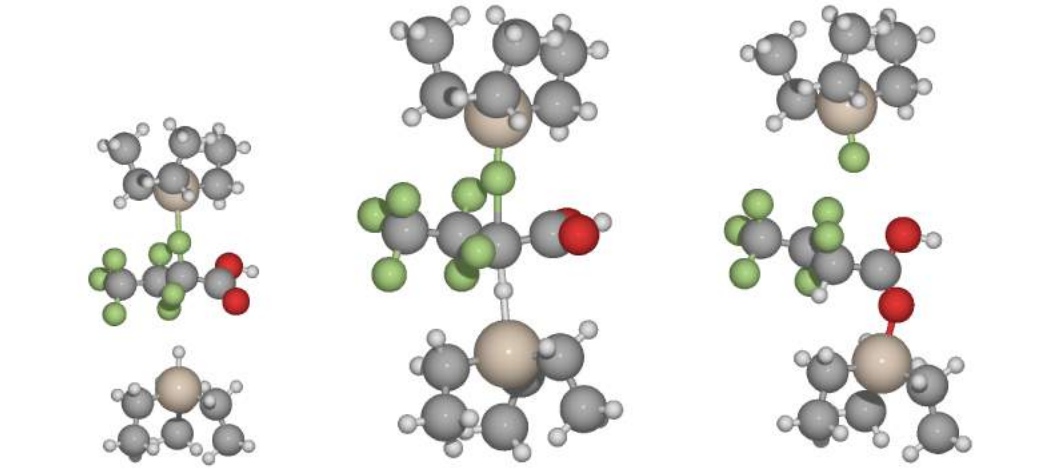
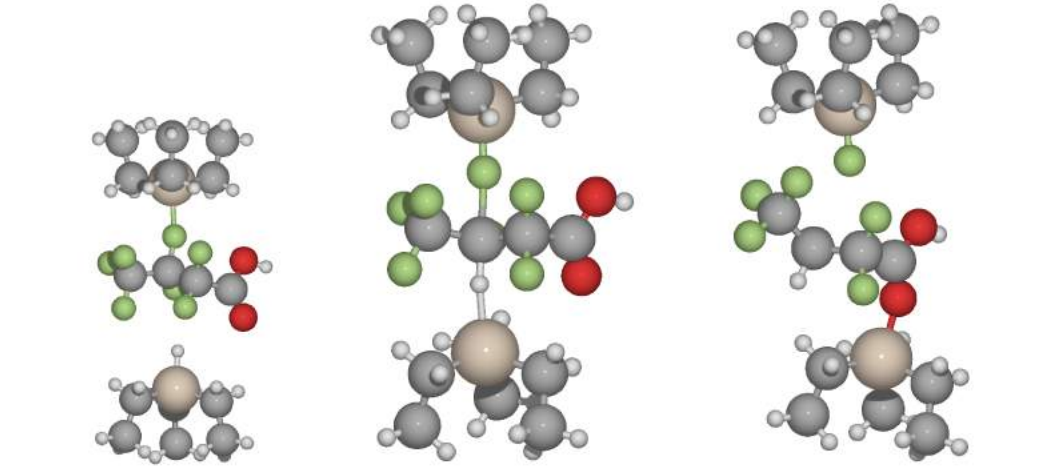


(c) C_ω

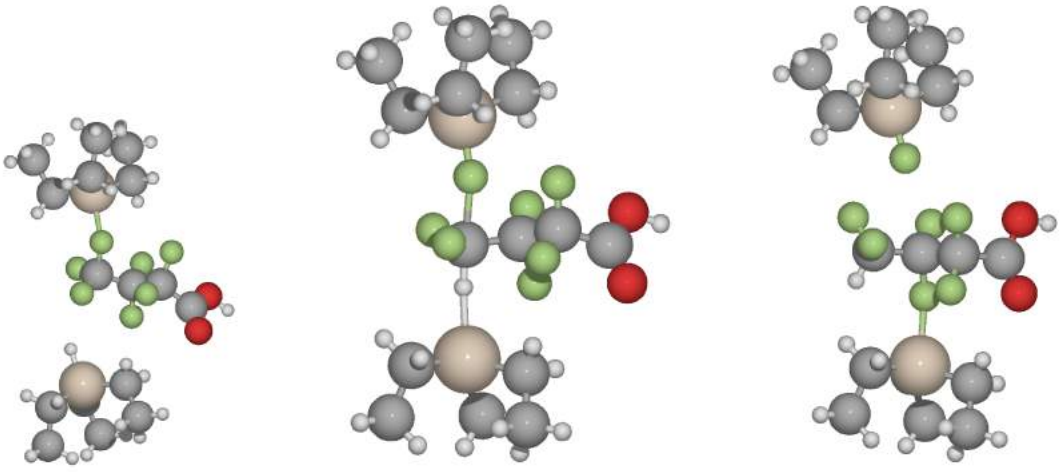
Figure S12: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for HFB.



(a) C_α

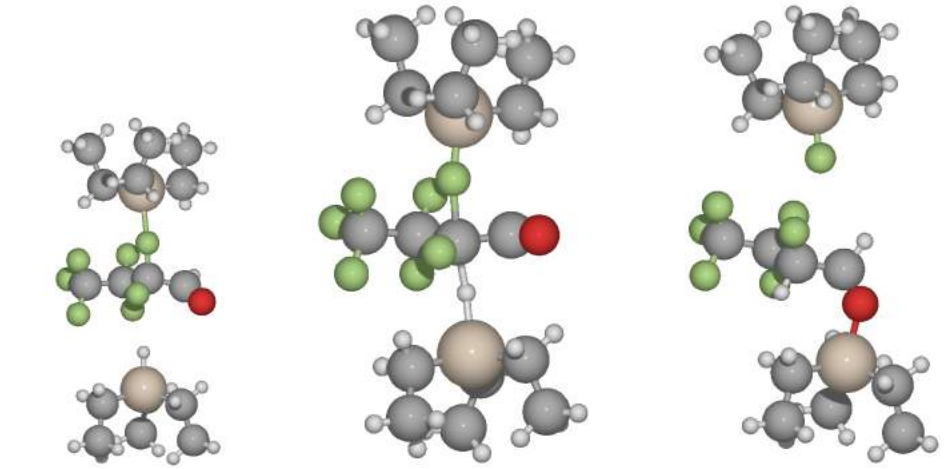


(b) C_β

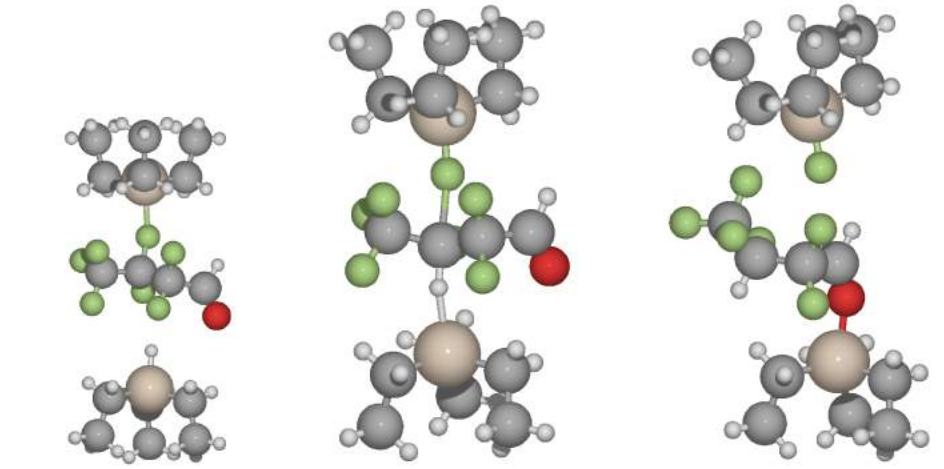


(c) C_ω

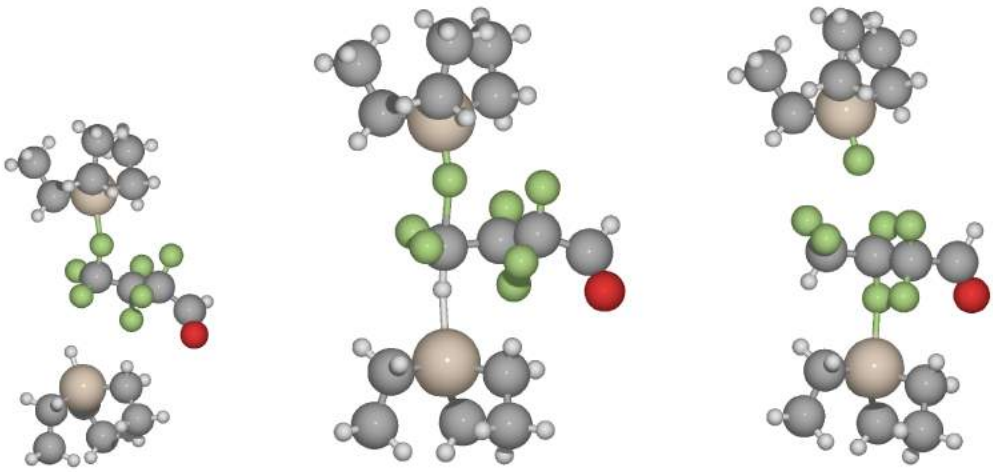
Figure S13: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFBA.



(a) C_α

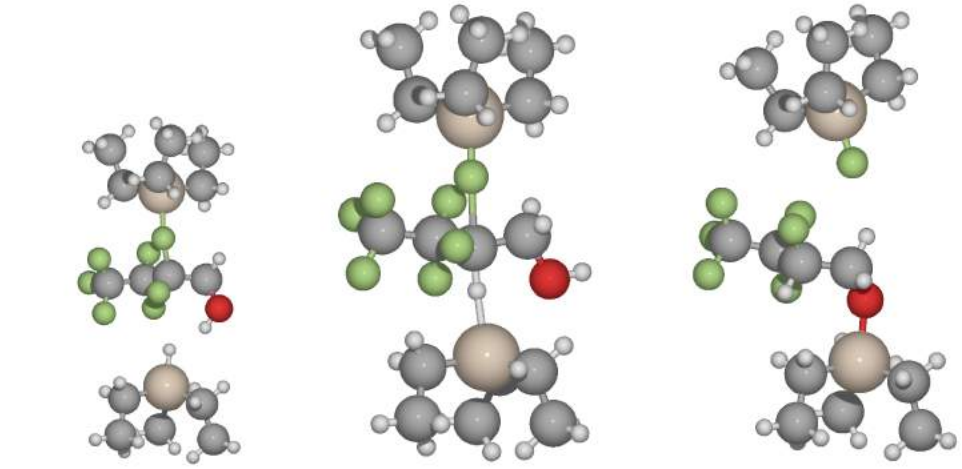


(b) C_β

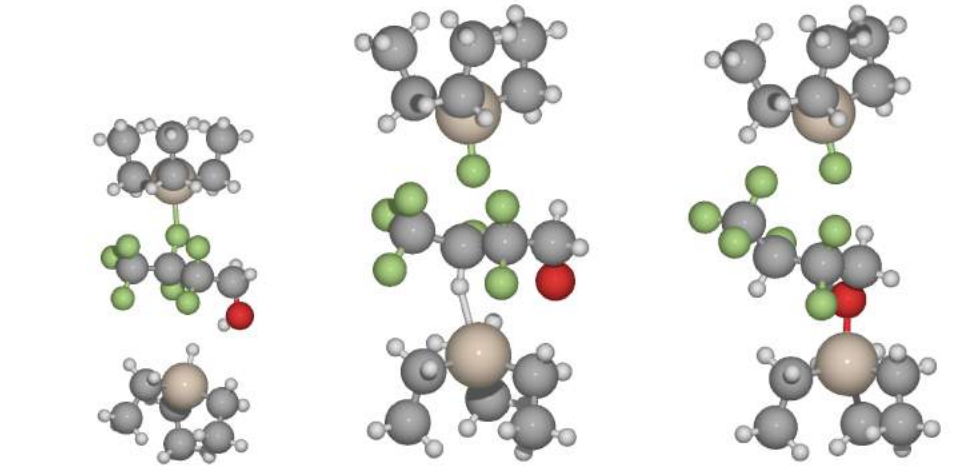


(c) C_ω

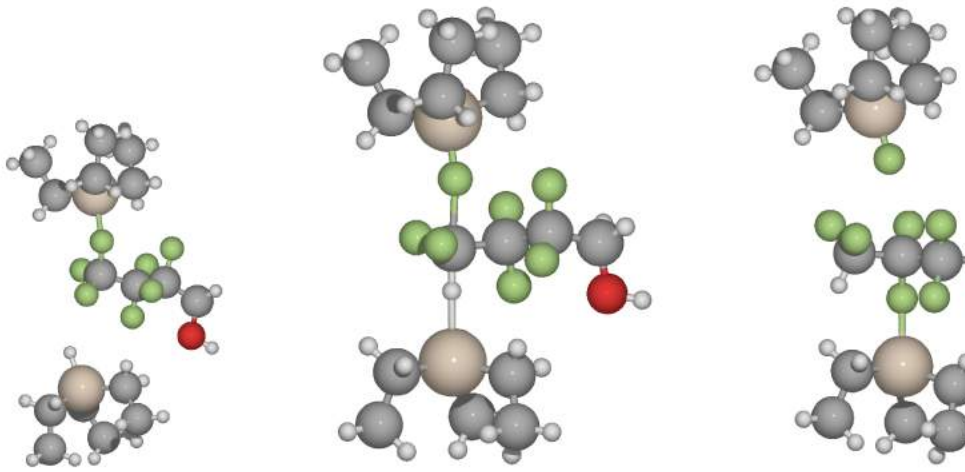
Figure S14: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFB.



(a) C_α

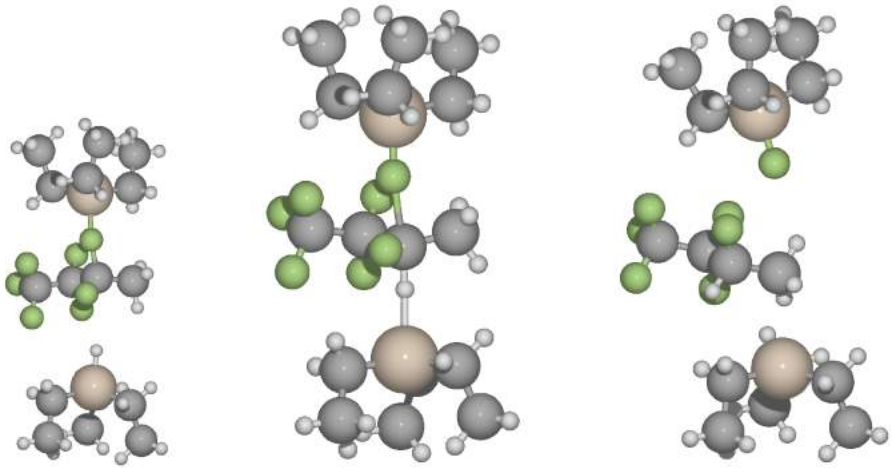


(b) C_β

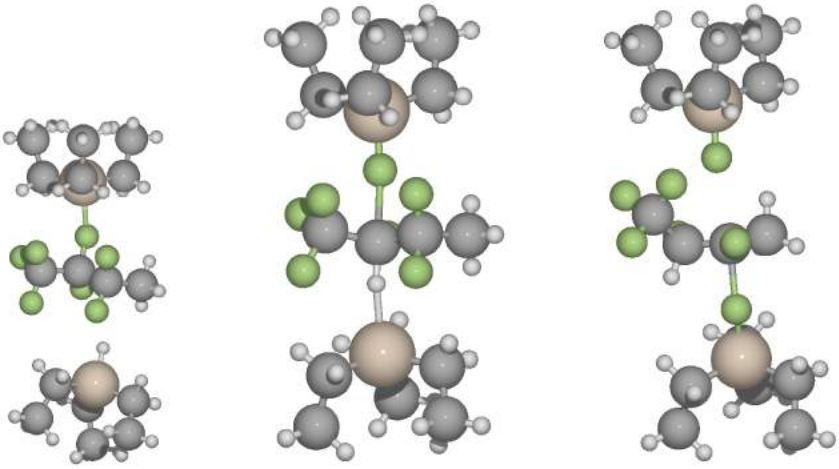


(c) C_ω

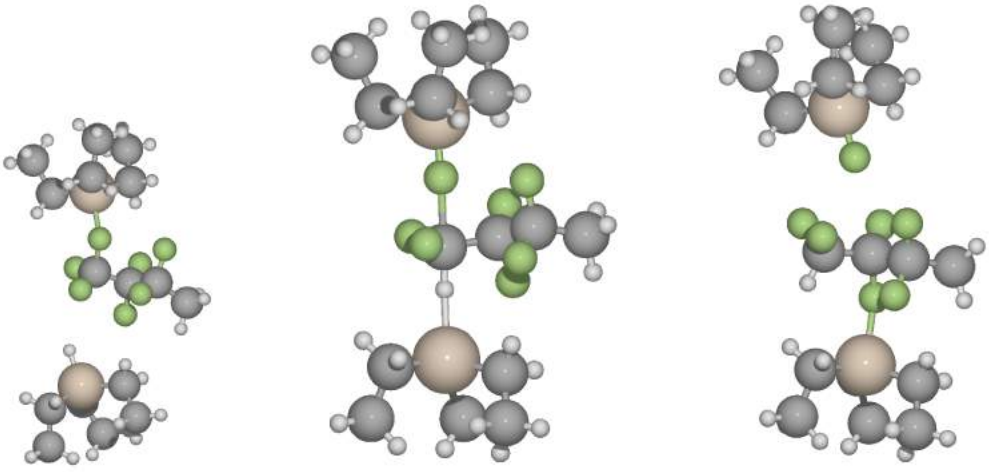
Figure S15: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFBO.



(a) C_α

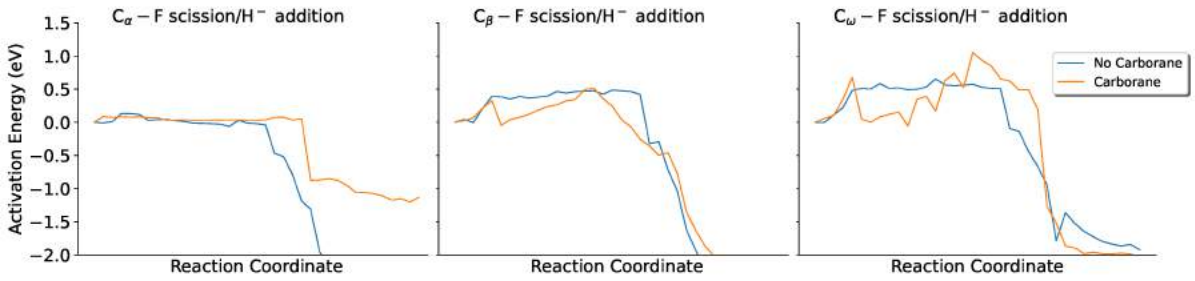


(b) C_β

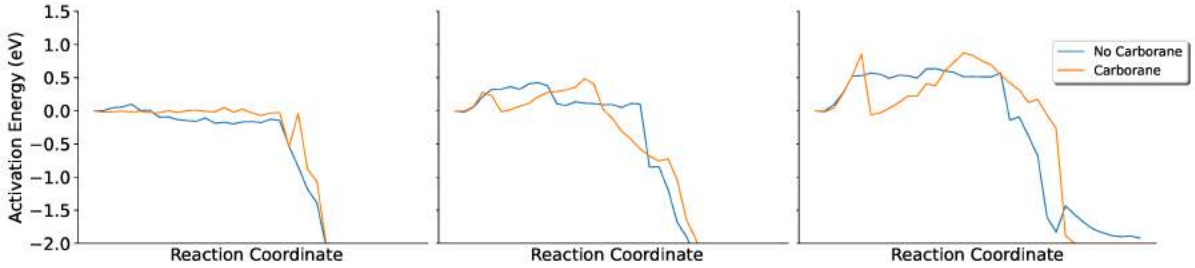


(c) C_ω

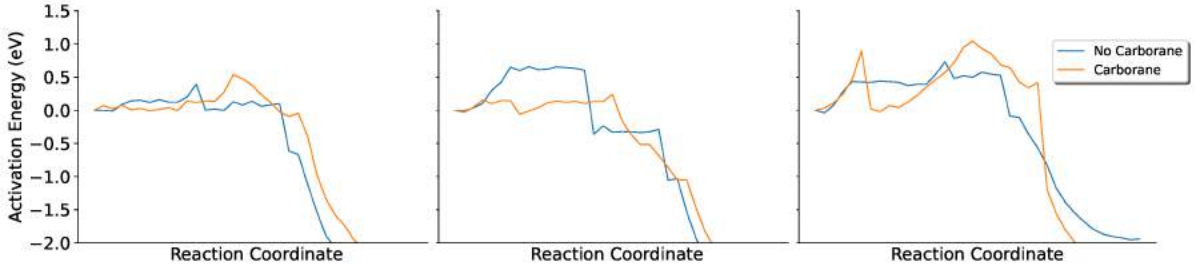
Figure S16: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFB.



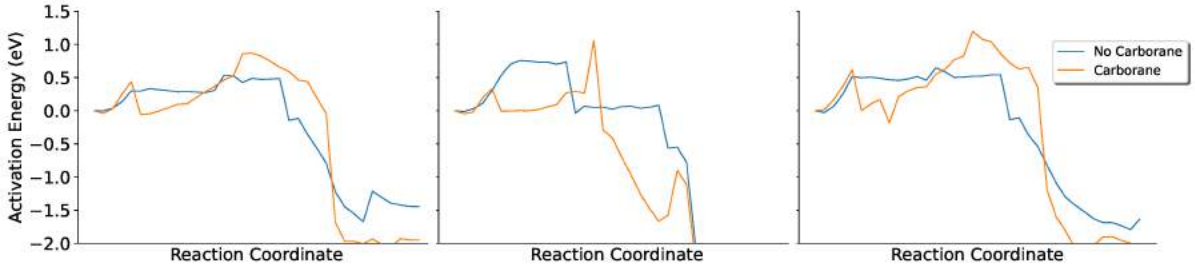
(a) PFBA



(b) PFB

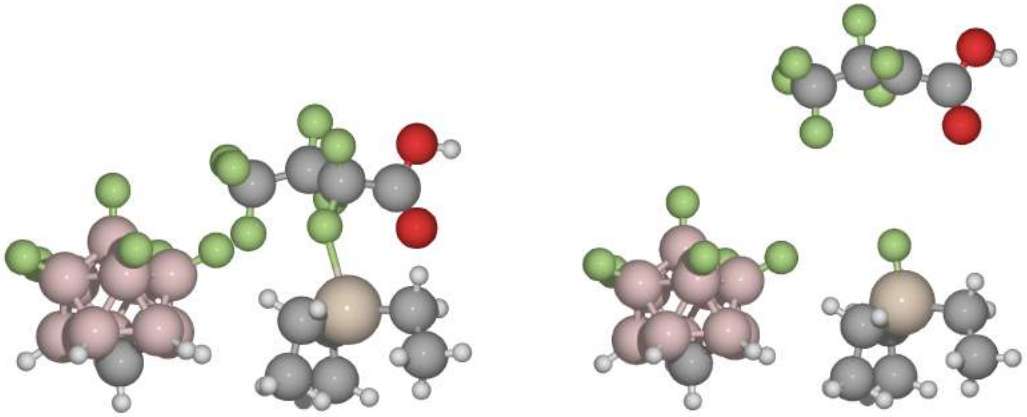


(c) HFBO

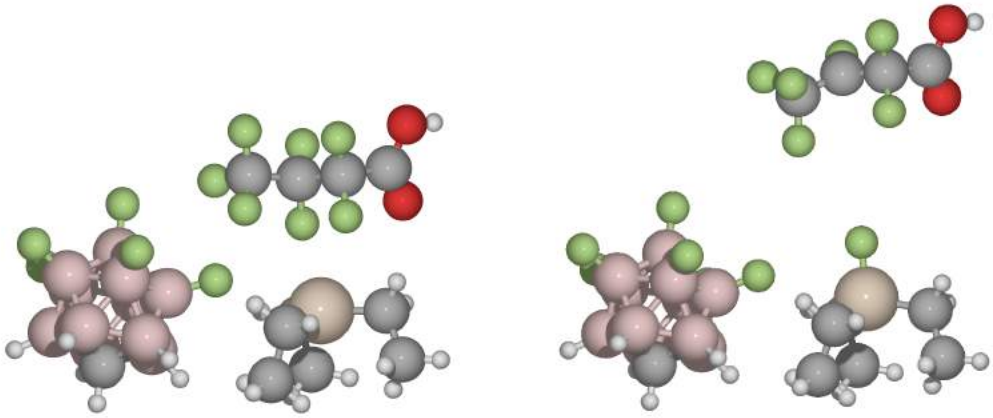


(d) HFB

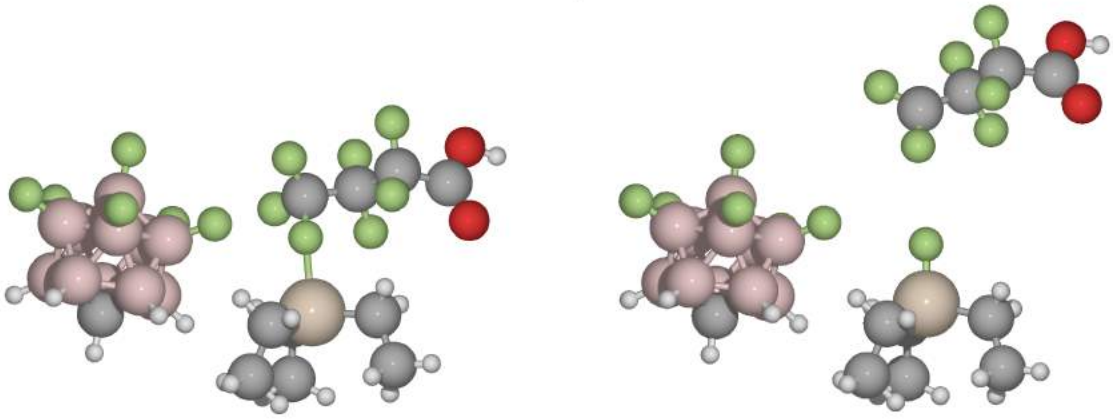
Figure S17: Reaction pathways for the four per-fluorinated molecules in the current study as a function of carbon position and in the presence/absence of carborane ($[HCB_{11}H_5F_6]^-$).



(a) C_α

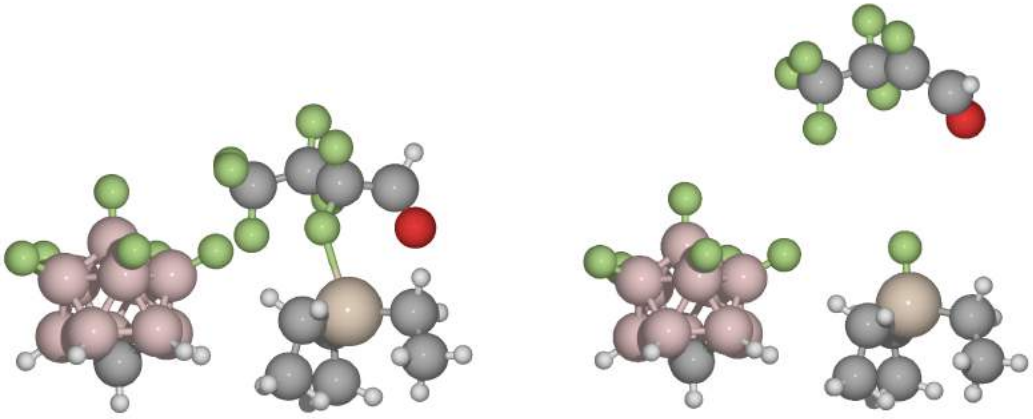


(b) C_β

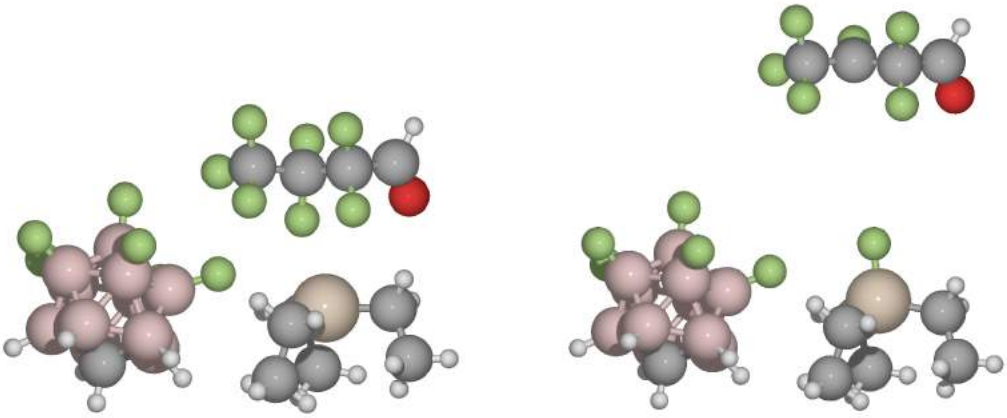


(c) C_ω

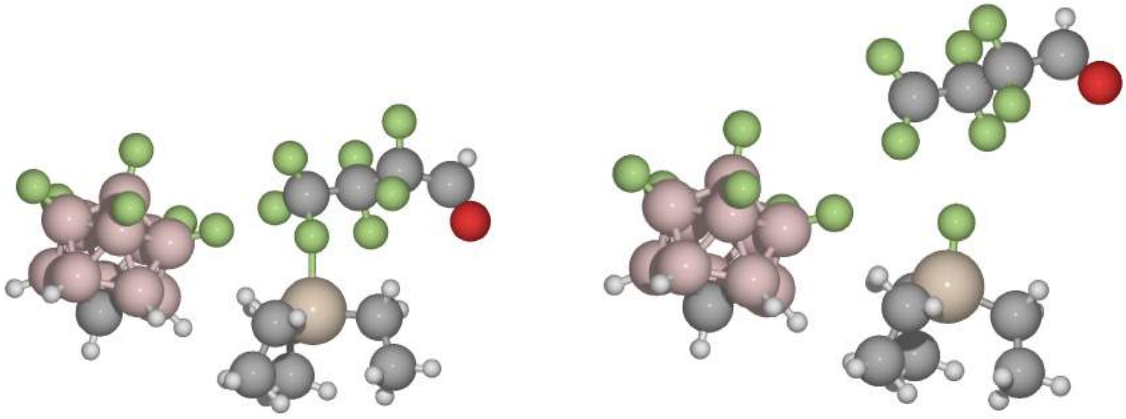
Figure S18: Initial and final states of carbocation formation/defluorination as a function of position for PFBA in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

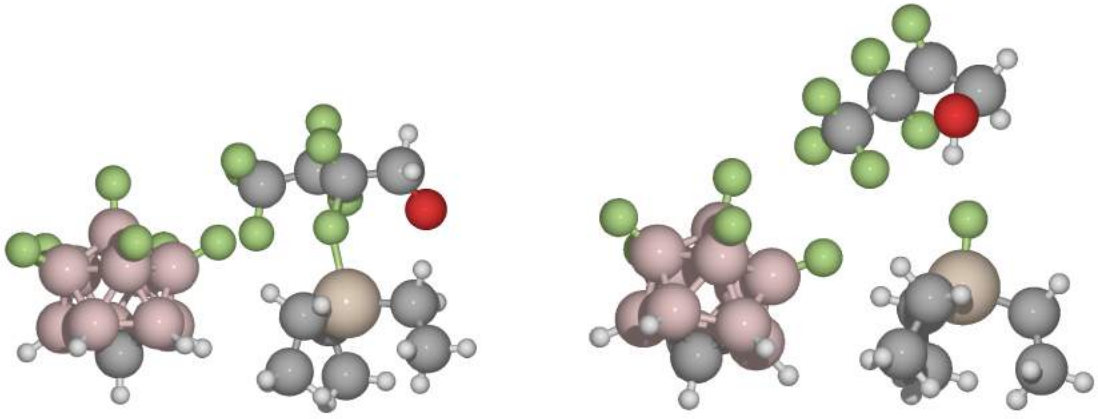


(b) C_β

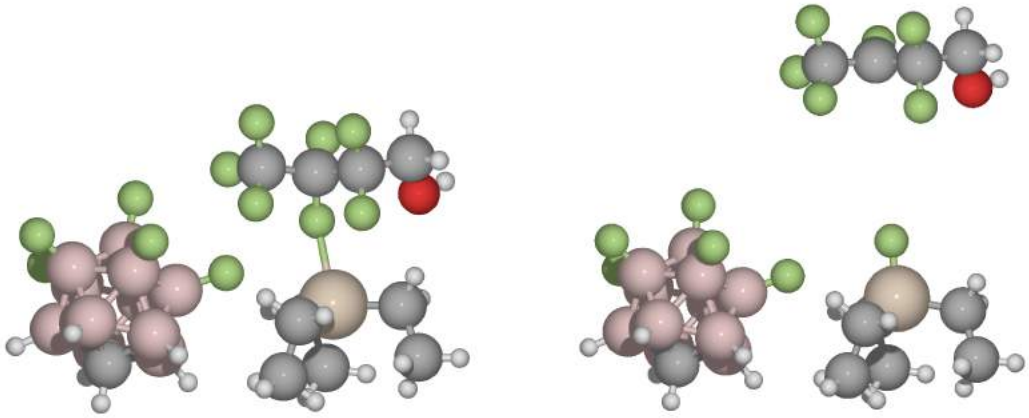


(c) C_ω

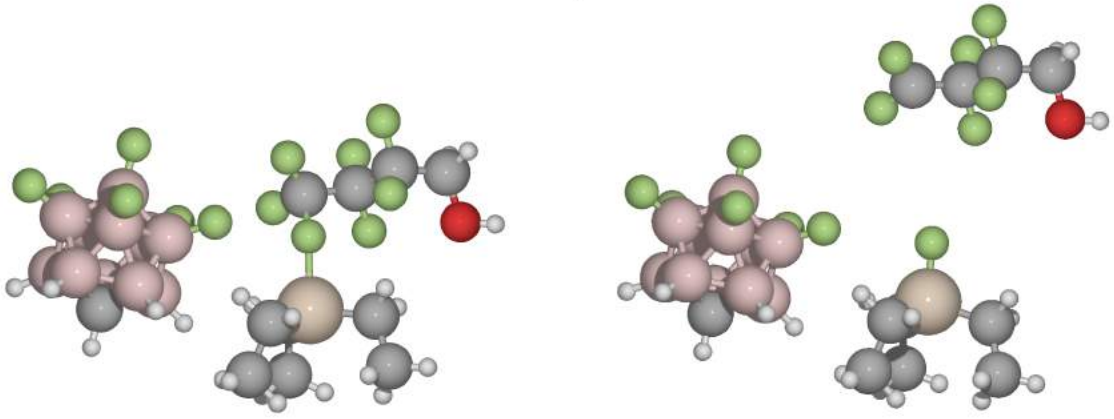
Figure S19: Initial and final states of carbocation formation/defluorination as a function of position for PFB in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

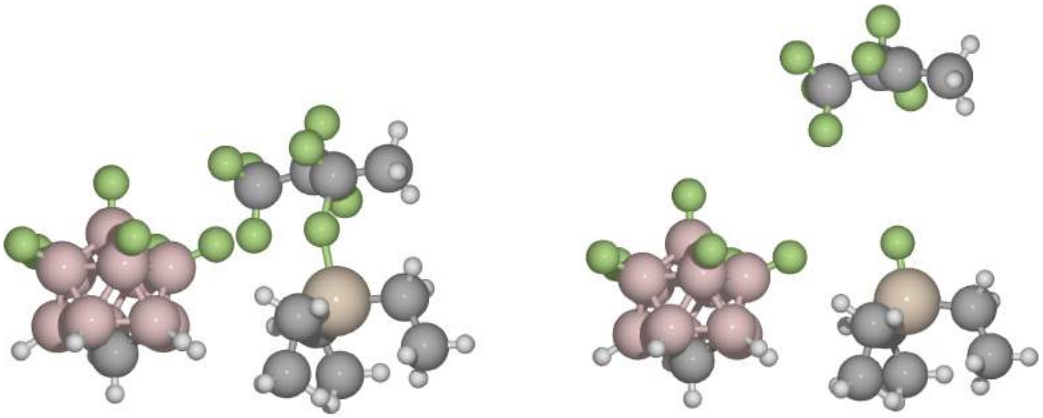


(b) C_β

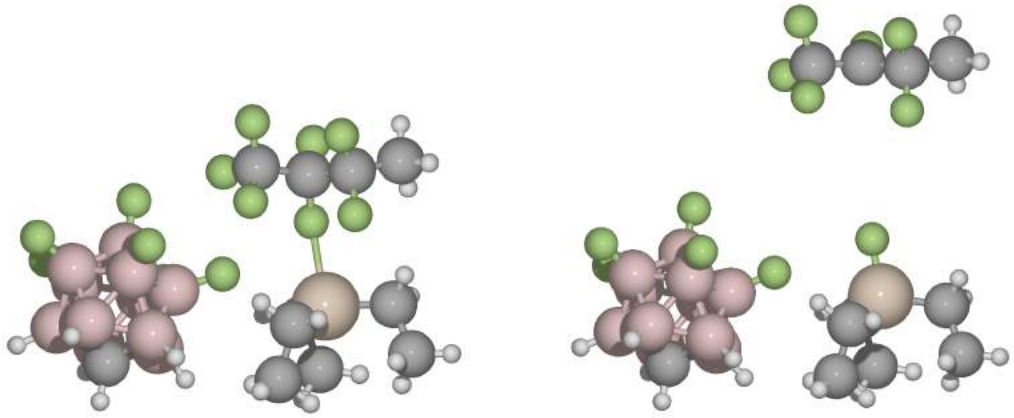


(c) C_ω

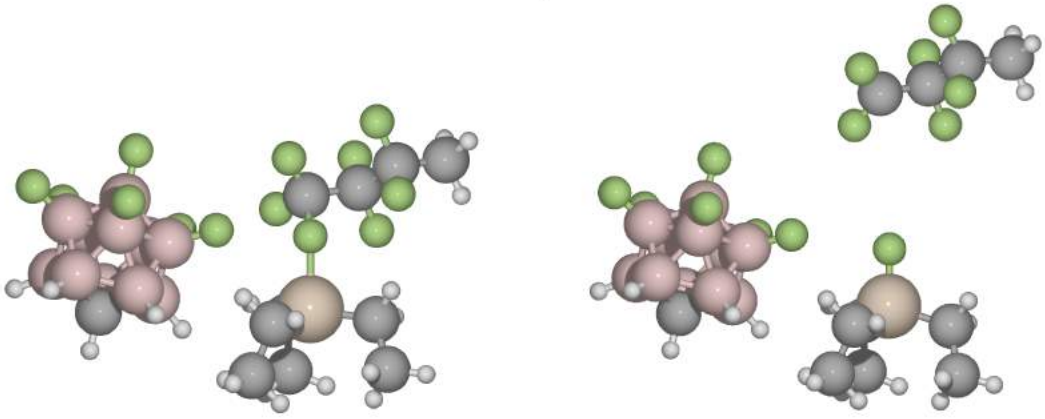
Figure S20: Initial and final states of carbocation formation/defluorination as a function of position for HFBO in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

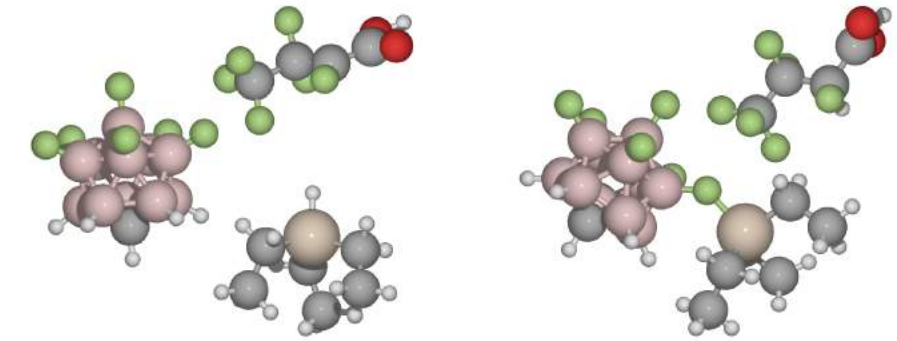


(b) C_β

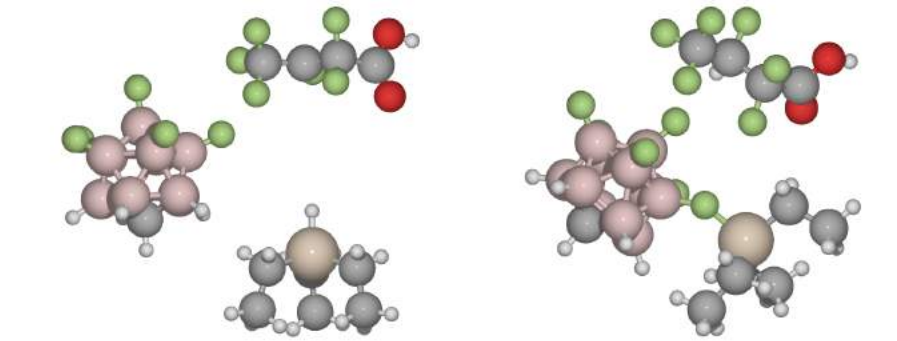


(c) C_ω

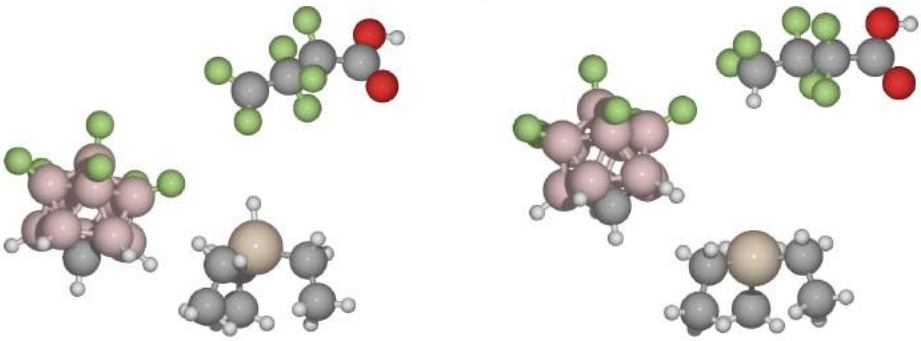
Figure S21: Initial and final states of carbocation formation/defluorination as a function of position for HFB in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

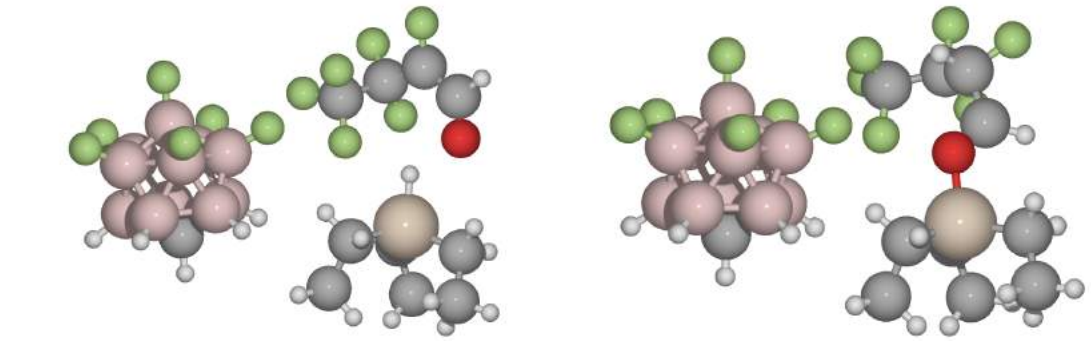


(b) C_β

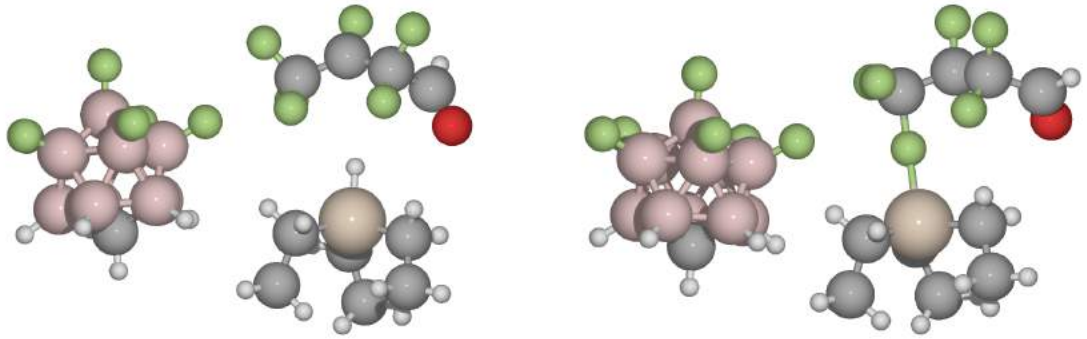


(c) C_ω

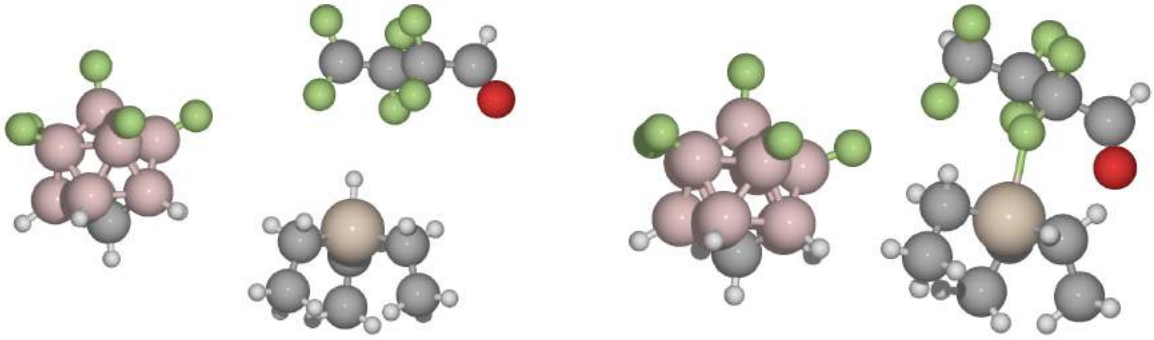
Figure S22: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for PFBA.



(a) C_α

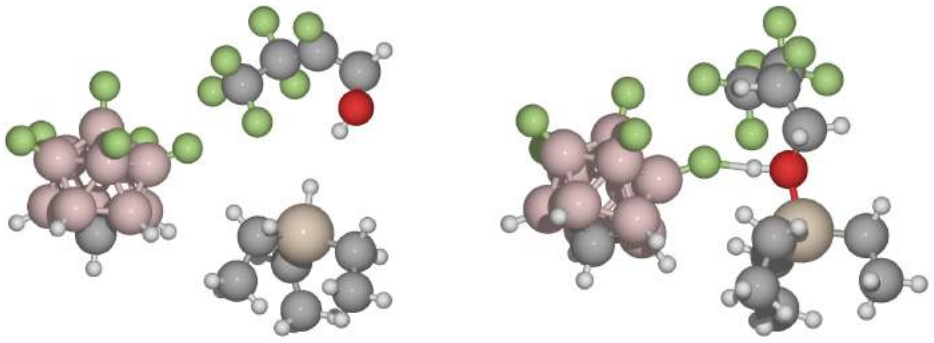


(b) C_β

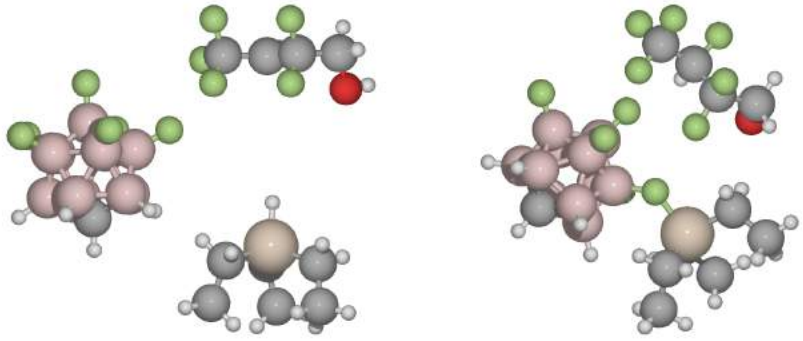


(c) C_ω

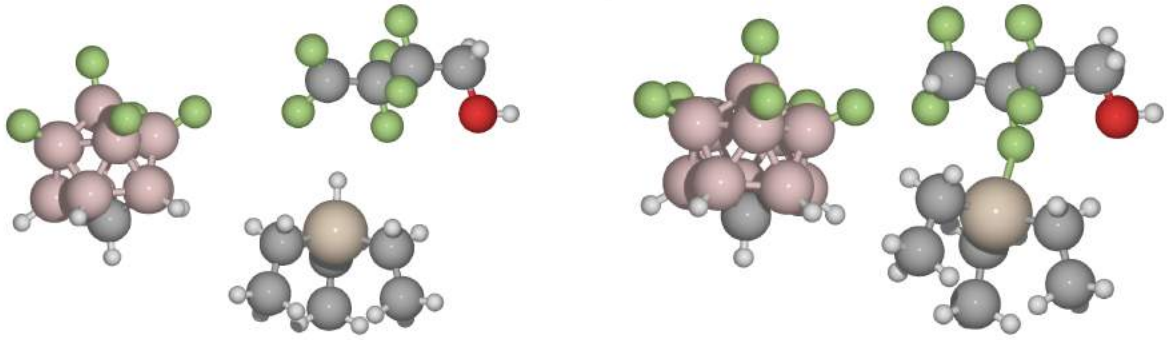
Figure S23: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for PFB.



(a) C_α

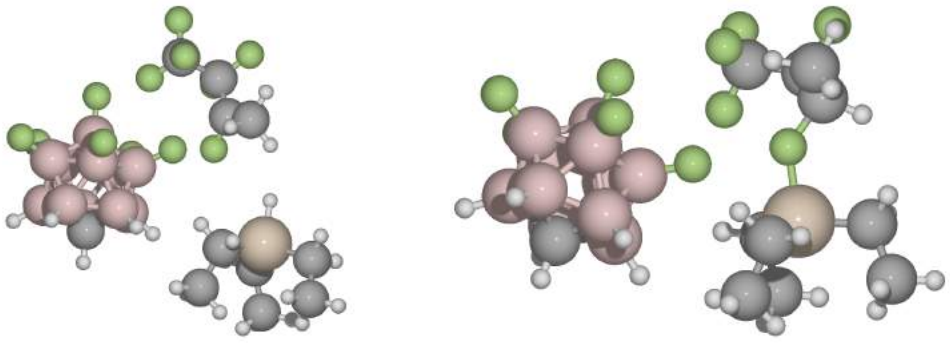


(b) C_β

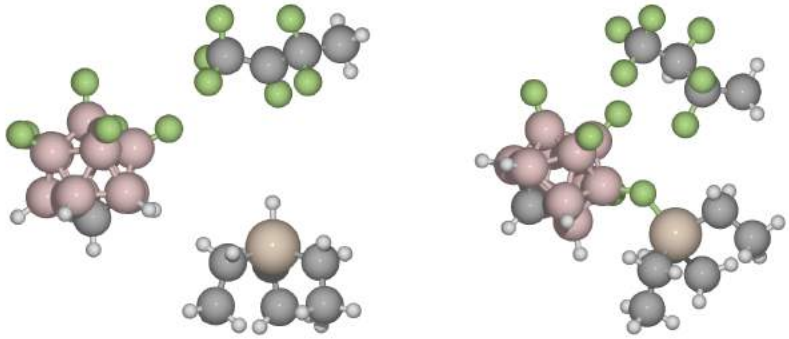


(c) C_ω

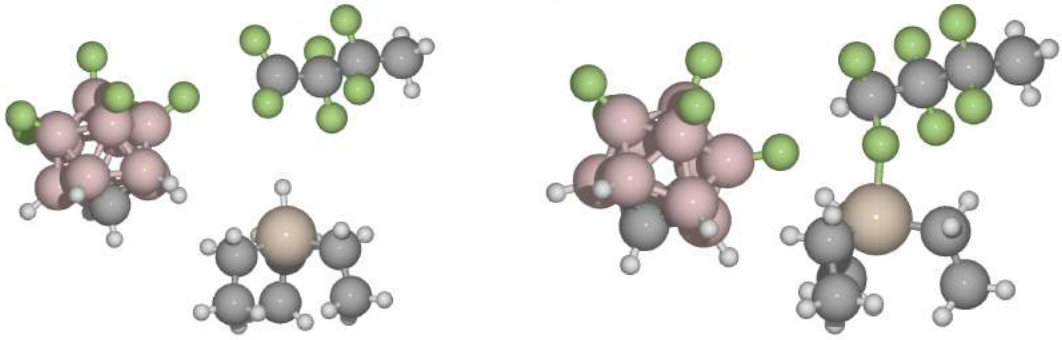
Figure S24: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for HFBO.



(a) C_α

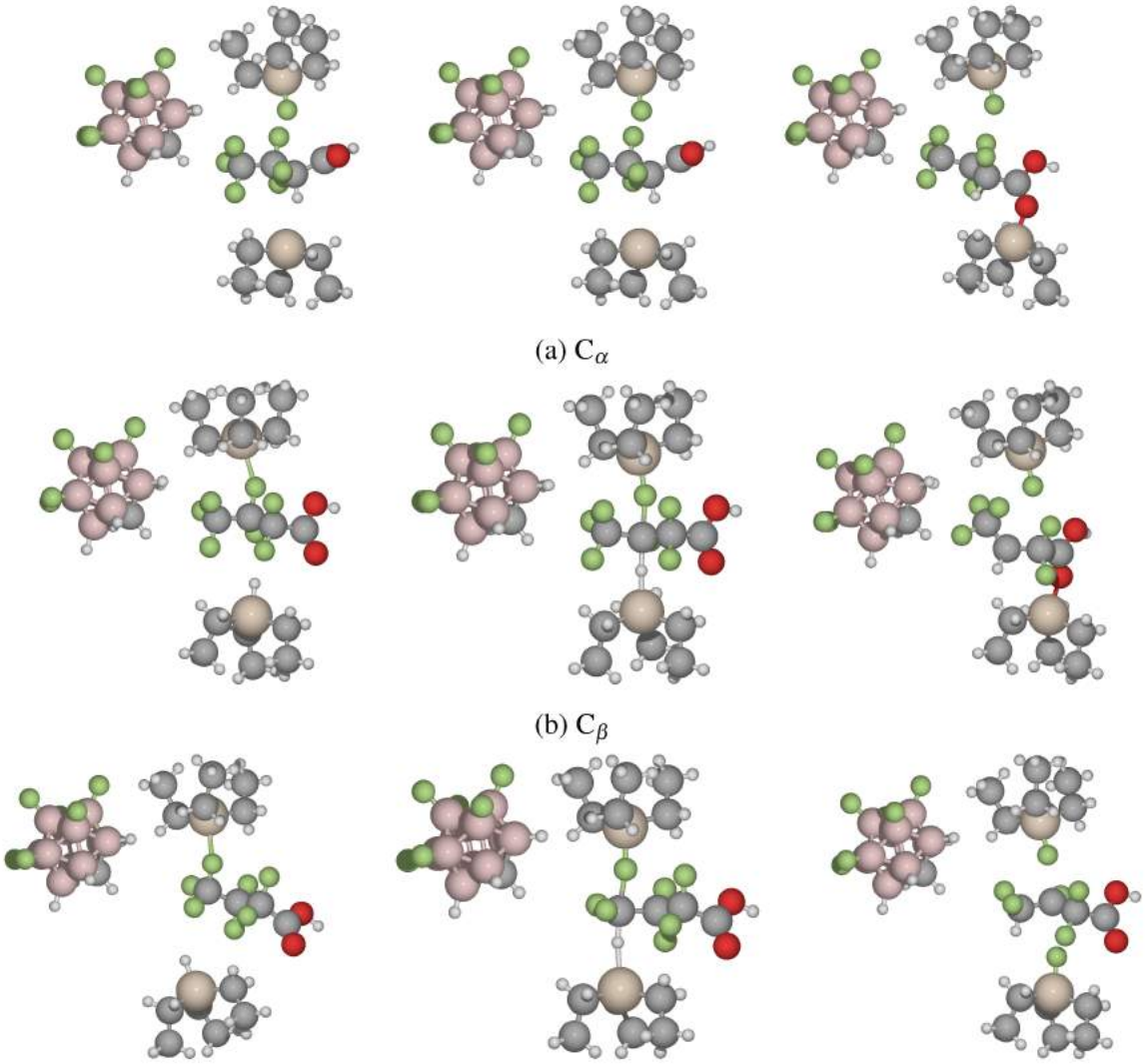


(b) C_β



(c) C_ω

Figure S25: Initial and final states of the hydride addtion reaction of the carbocation as a function of position for HFB.

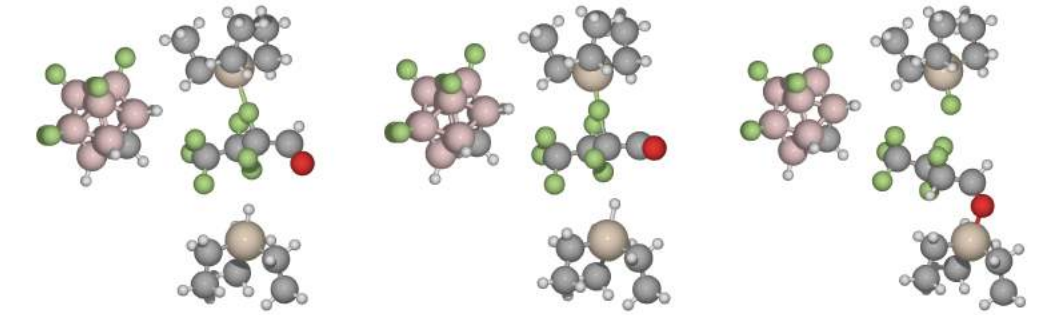


(a) C_α

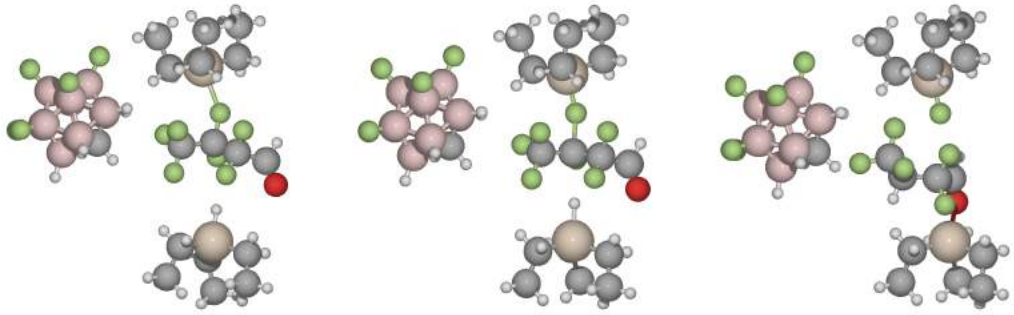
(b) C_β

(c) C_ω

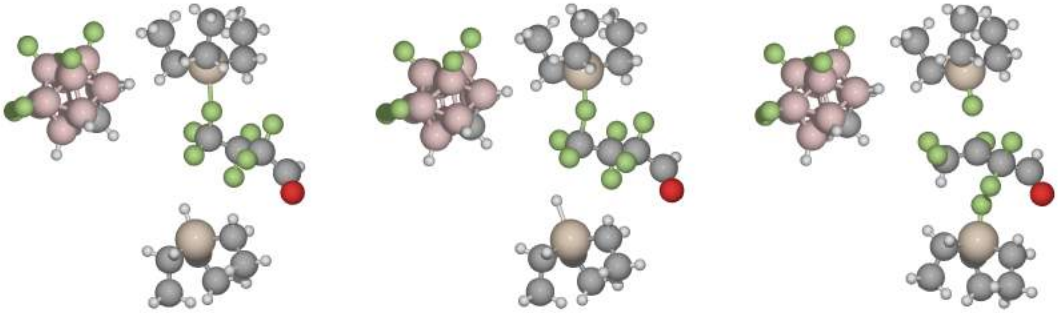
Figure S26: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFBA in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

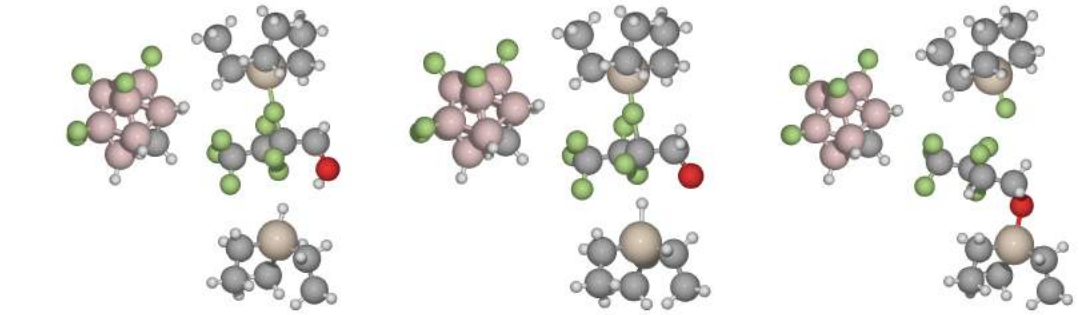


(b) C_β

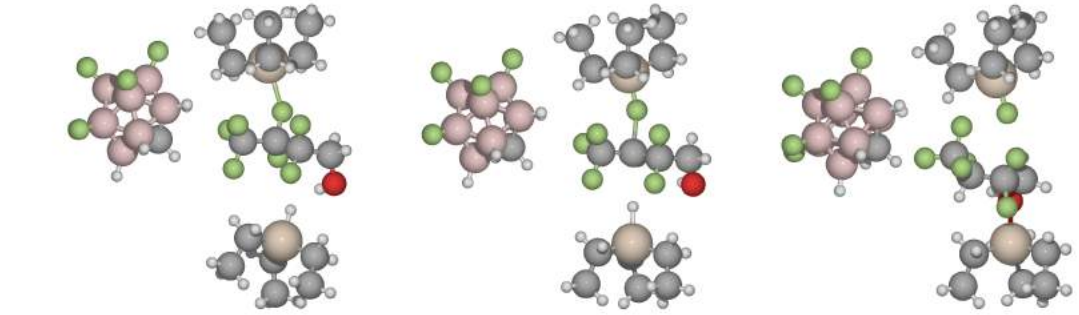


(c) C_ω

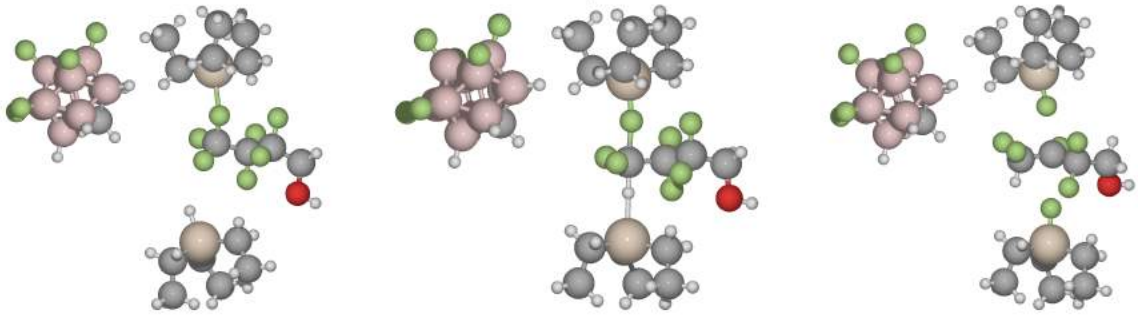
Figure S27: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFB in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

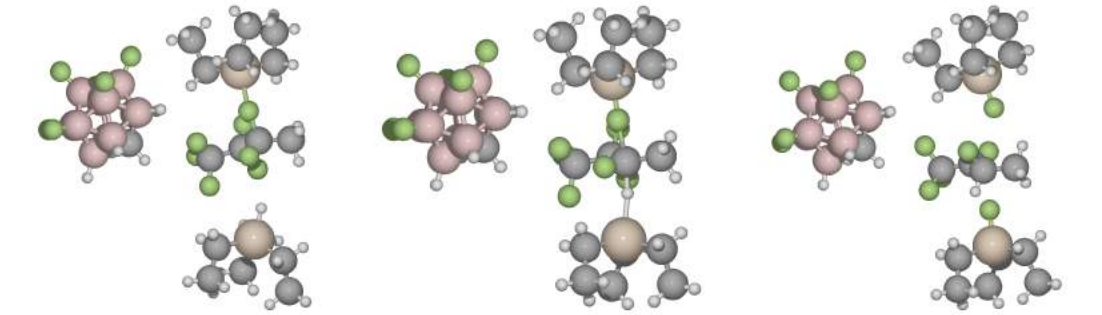


(b) C_β

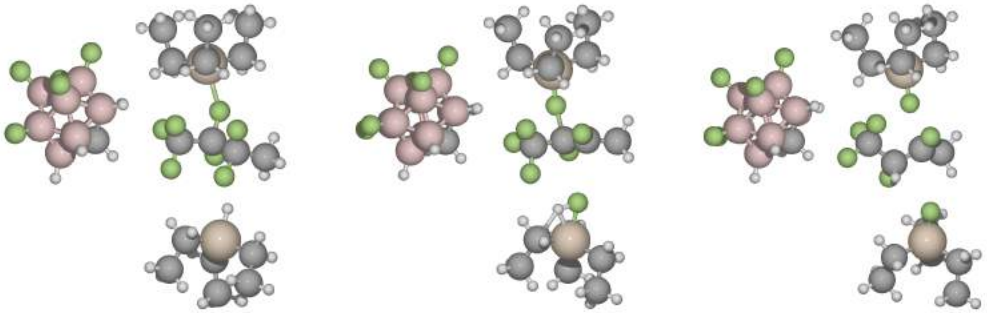


(c) C_ω

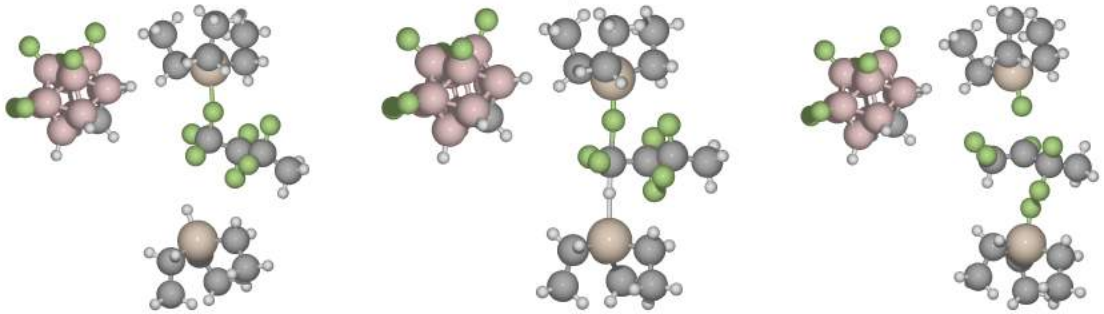
Figure S28: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFBO in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

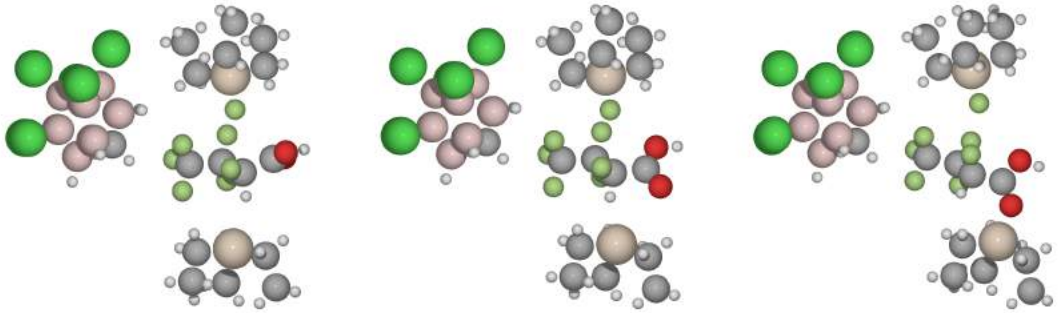


(b) C_β

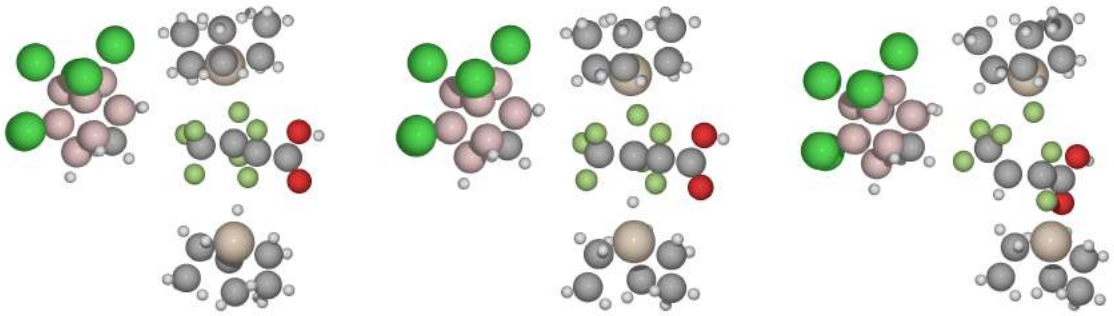


(c) C_ω

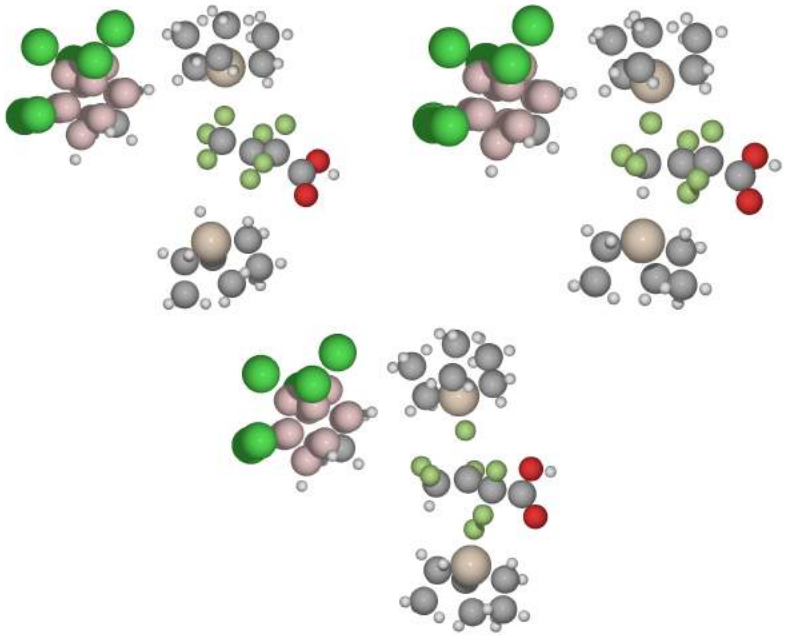
Figure S29: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFB in the presence of a carborane anion $\left([HCB_{11}H_5F_6]^-\right)$.



(a) C_α

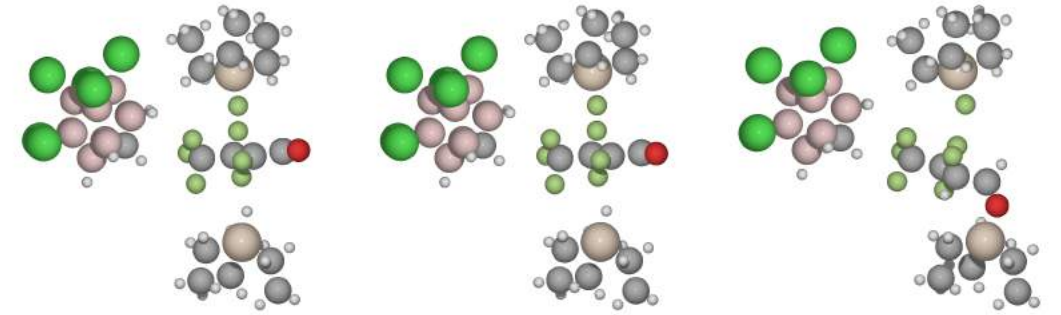


(b) C_β

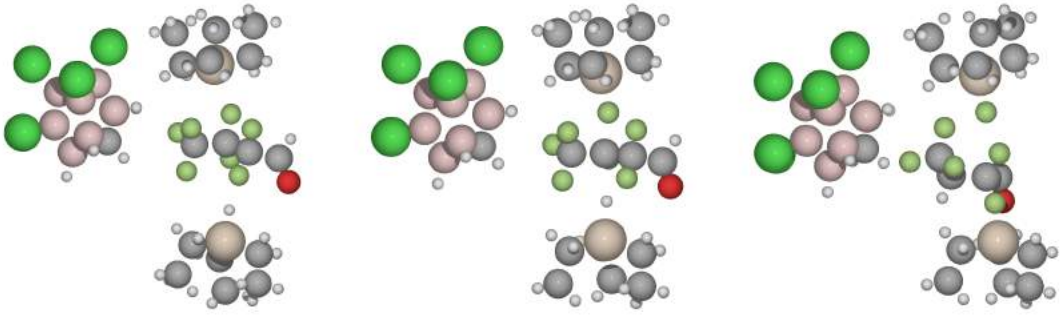


(c) C_ω

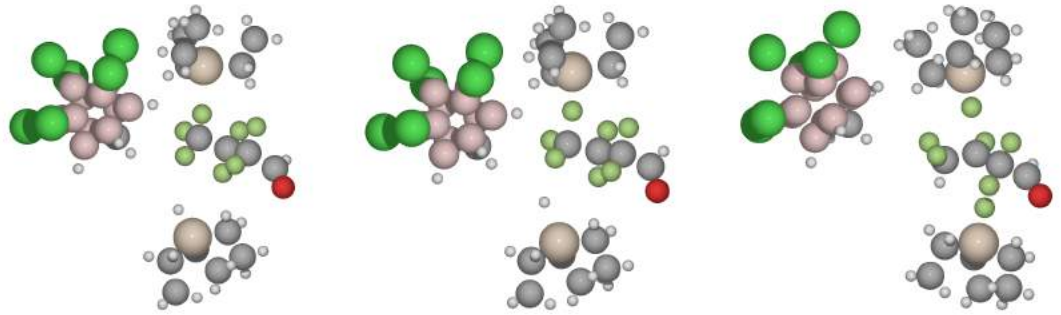
Figure S30: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFBA in the presence of a carborane anion $\left([HCB_{11}H_5Cl_6]^-\right)$.



(a) C_α

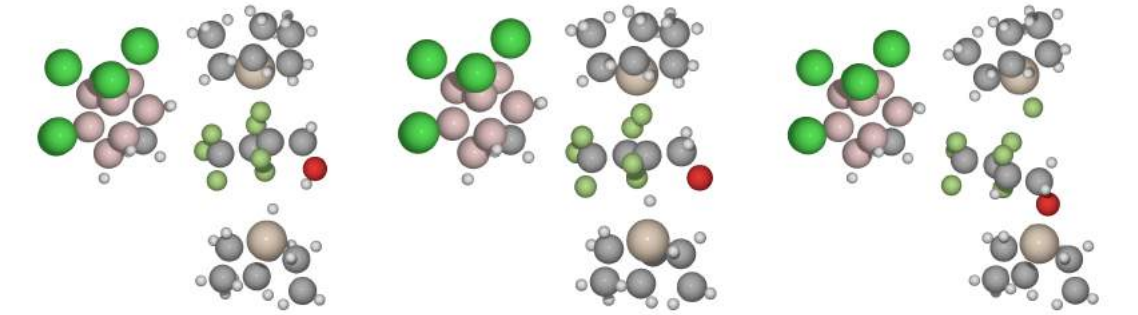


(b) C_β

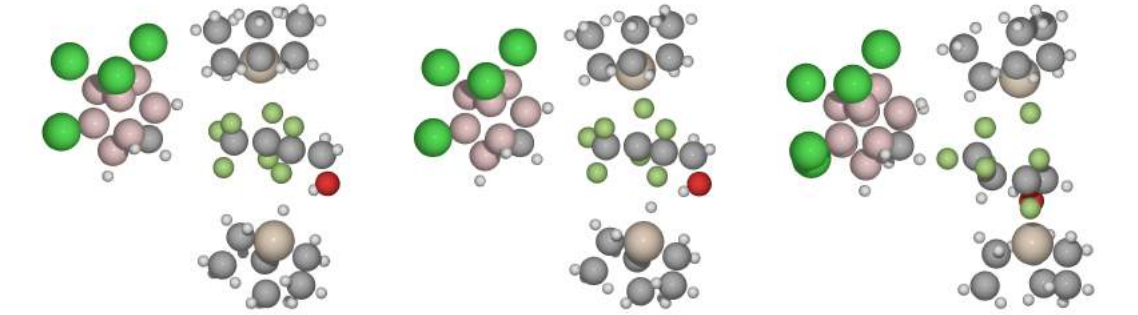


(c) C_ω

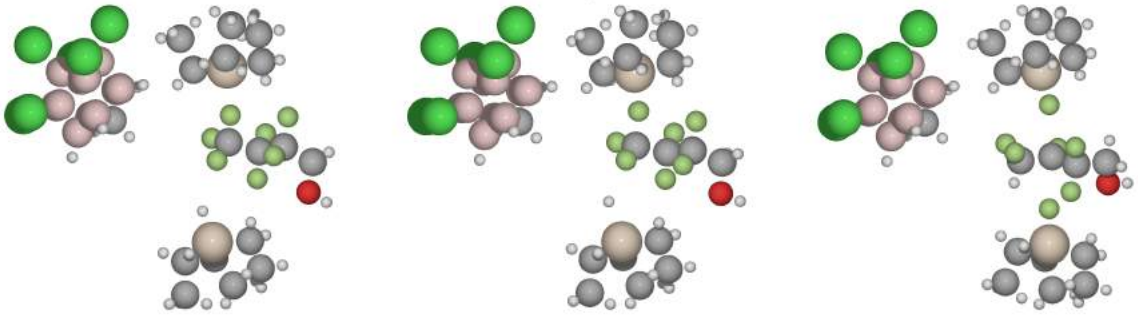
Figure S31: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFB in the presence of a carborane anion $\left([HCB_{11}H_5Cl_6]^-\right)$.



(a) C_α

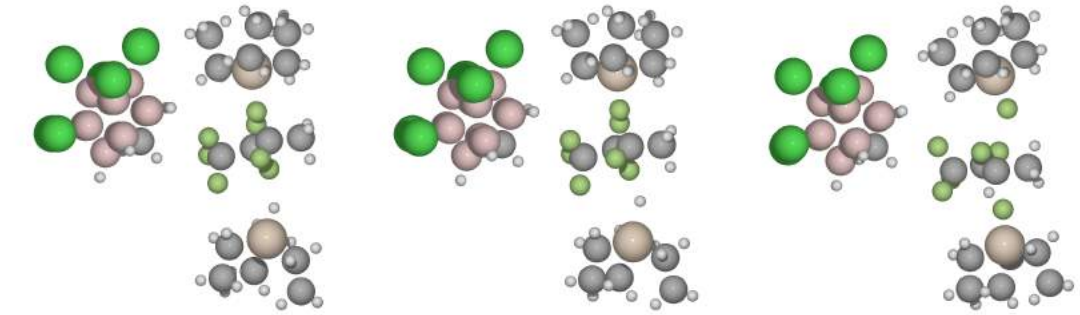


(b) C_β

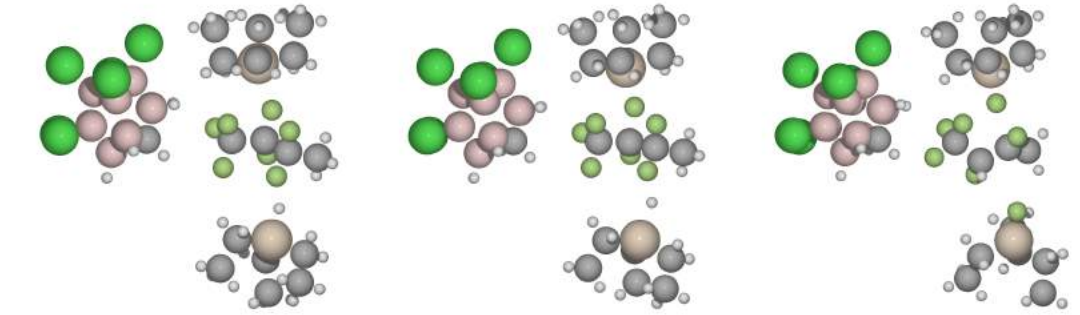


(c) C_ω

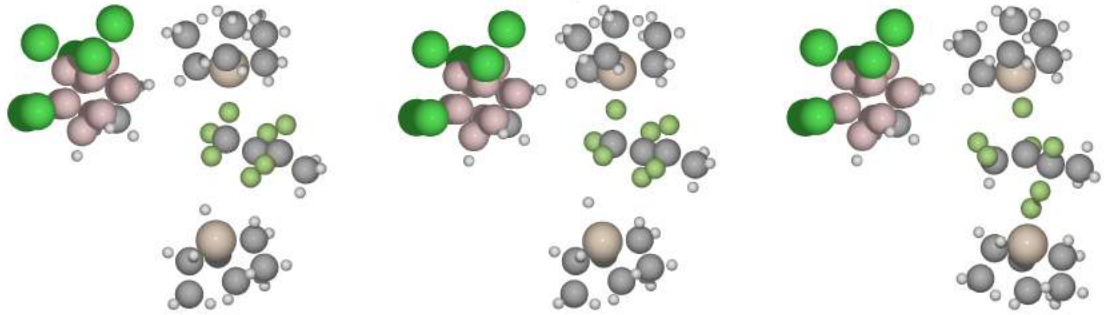
Figure S32: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFBO in the presence of a carborane anion $\left([HCB_{11}H_5Cl_6]^-\right)$.



(a) C_α

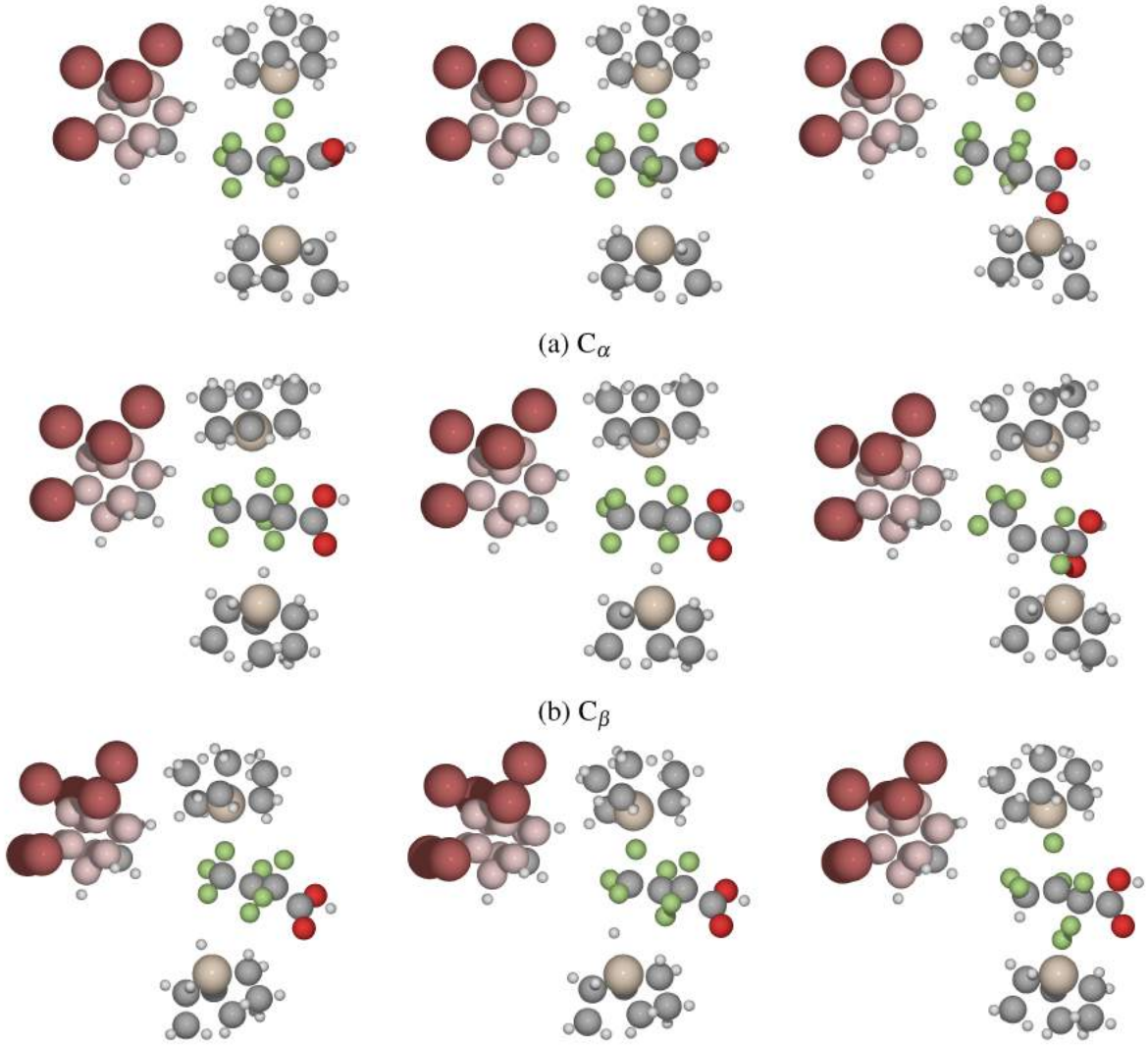


(b) C_β



(c) C_ω

Figure S33: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFB in the presence of a carborane anion $\left([HCB_{11}H_5Cl_6]^-\right)$.

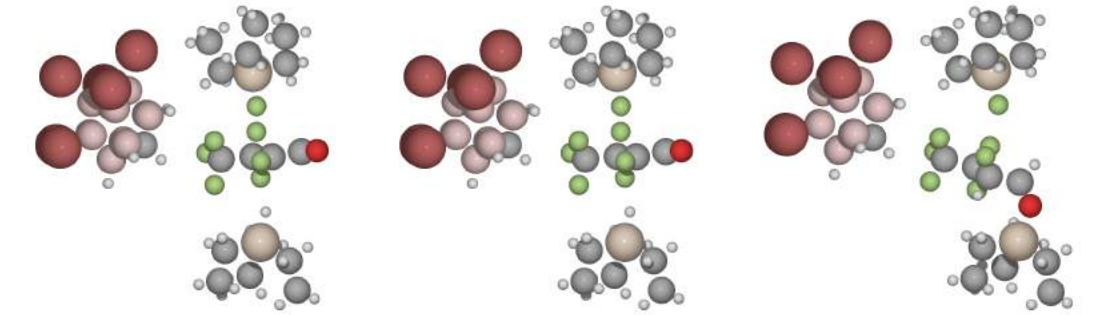


(a) C_α

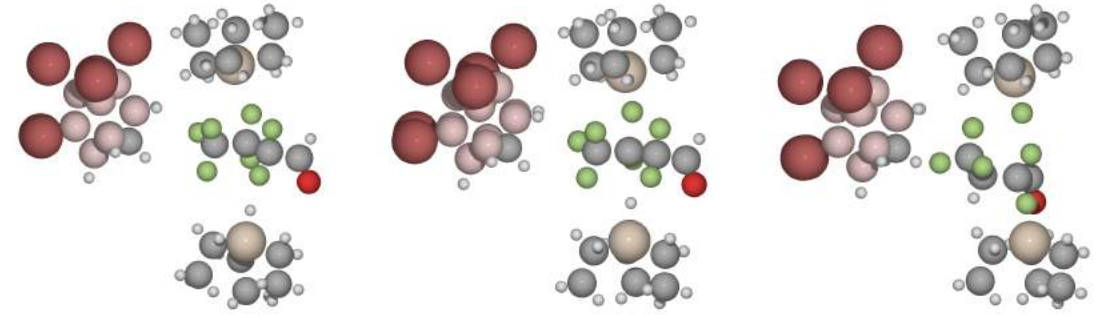
(b) C_β

(c) C_ω

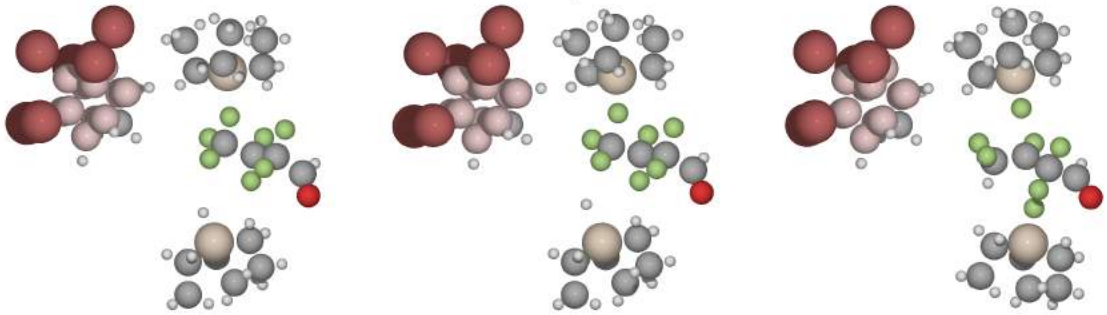
Figure S34: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFBA in the presence of a carborane anion $\left([HCB_{11}H_5Br_6]^-\right)$.



(a) C_α

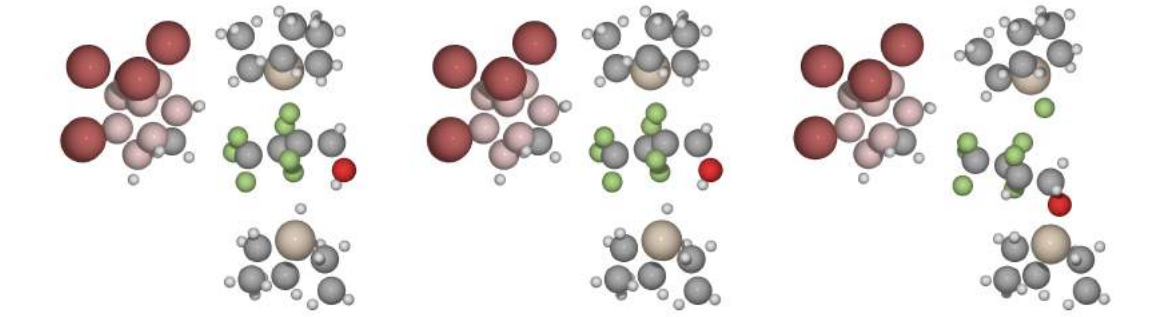


(b) C_β

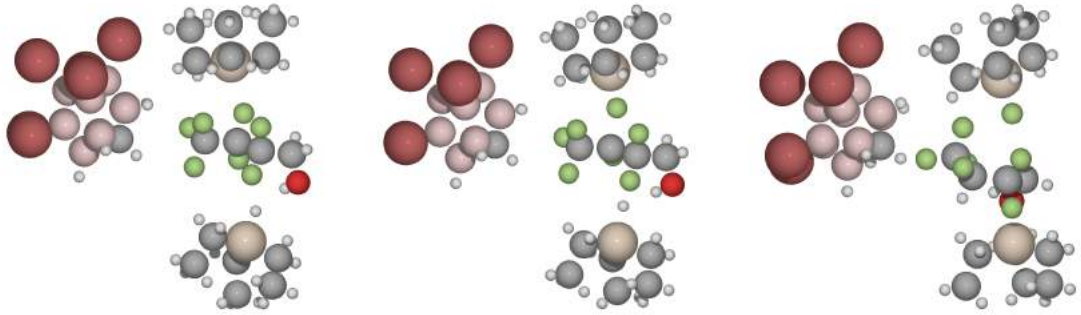


(c) C_ω

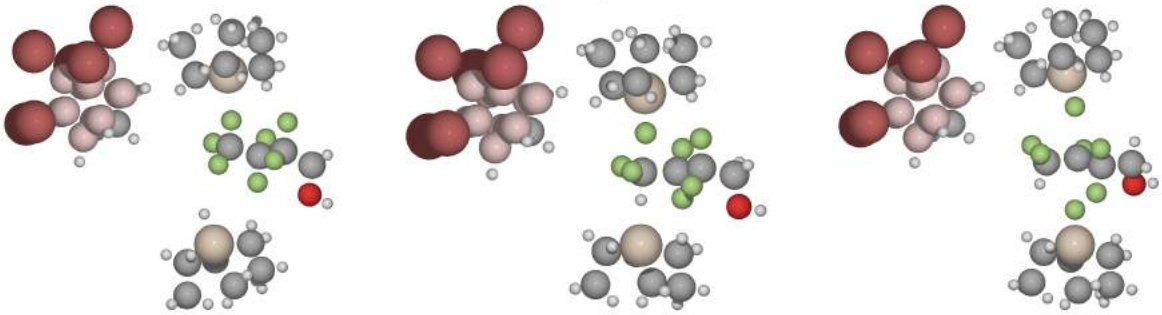
Figure S35: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFB in the presence of a carborane anion $\left([HCB_{11}H_5Br_6]^-\right)$.



(a) C_α

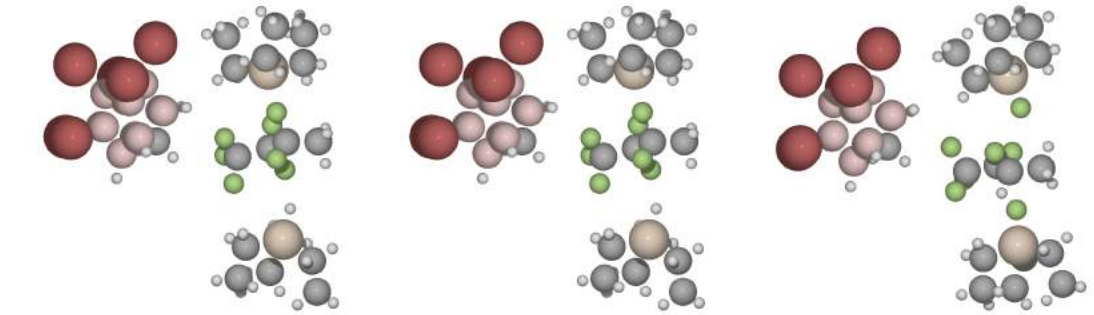


(b) C_β

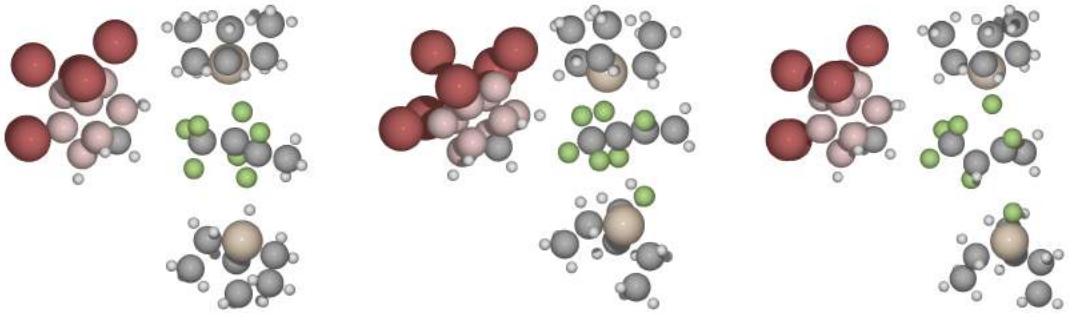


(c) C_ω

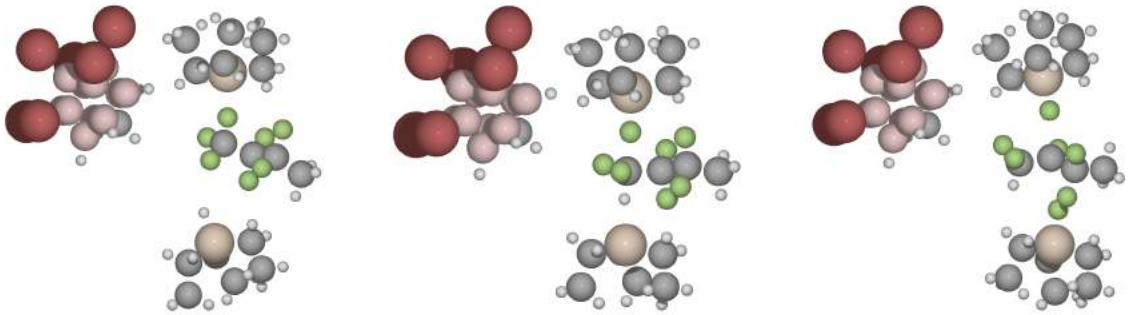
Figure S36: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFBO in the presence of a carborane anion $\left([HCB_{11}H_5Br_6]^-\right)$.



(a) C_α

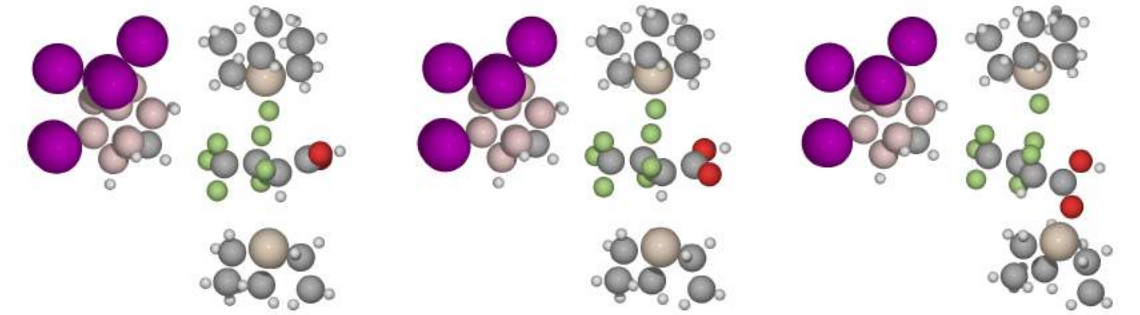


(b) C_β

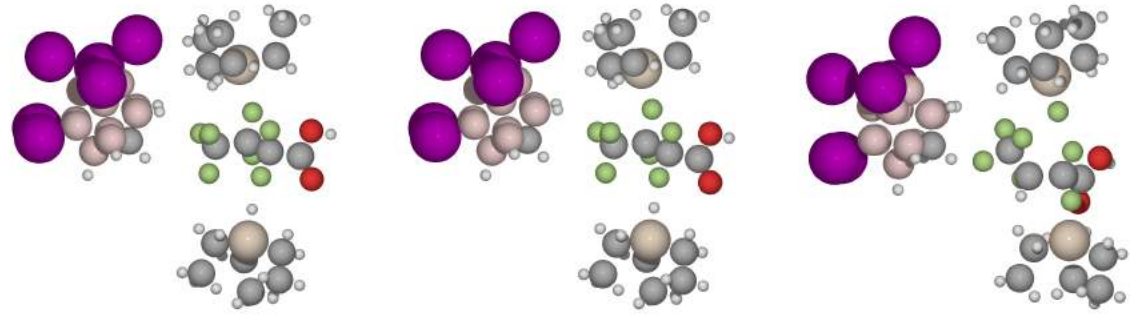


(c) C_ω

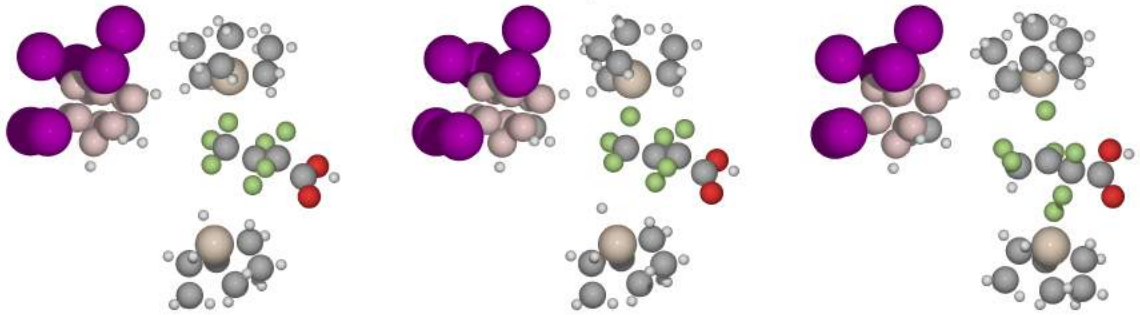
Figure S37: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFB in the presence of a carborane anion $\left([HCB_{11}H_5Br_6]^-\right)$.



(a) C_α

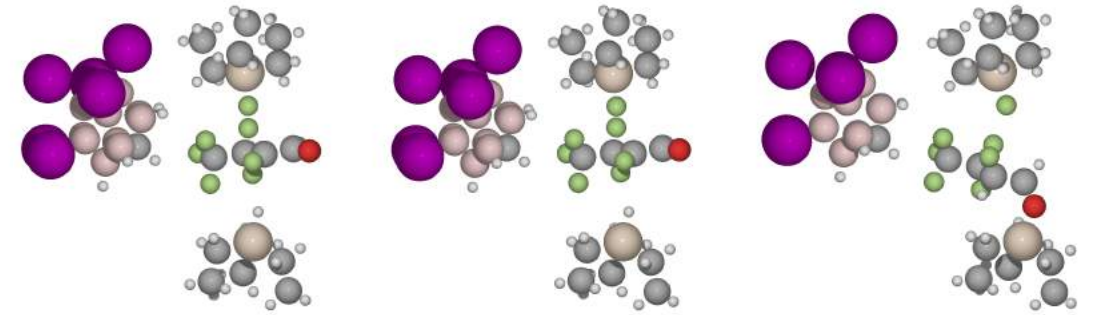


(b) C_β

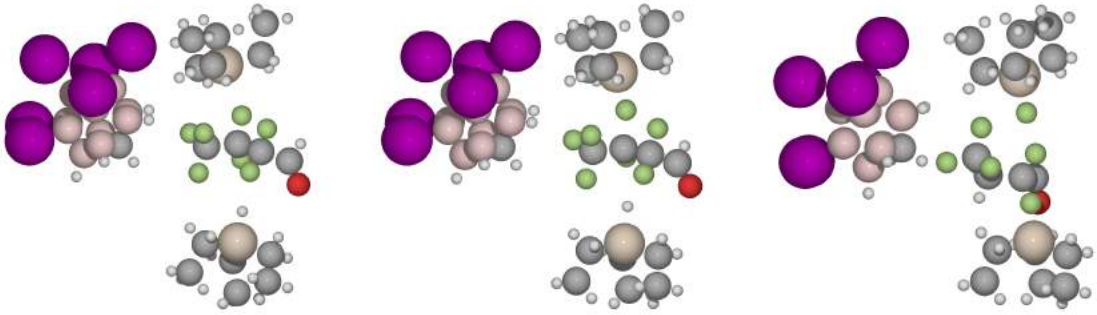


(c) C_ω

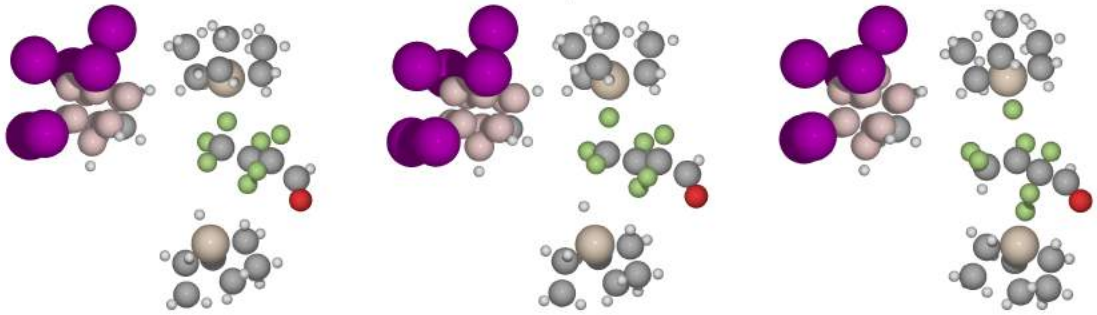
Figure S38: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFBA in the presence of a carborane anion $\left([HCB_{11}H_5I_6]^-\right)$.



(a) C_α

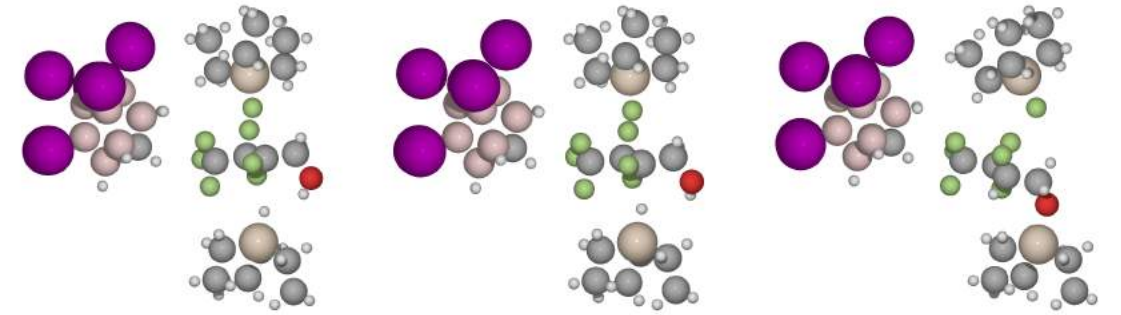


(b) C_β

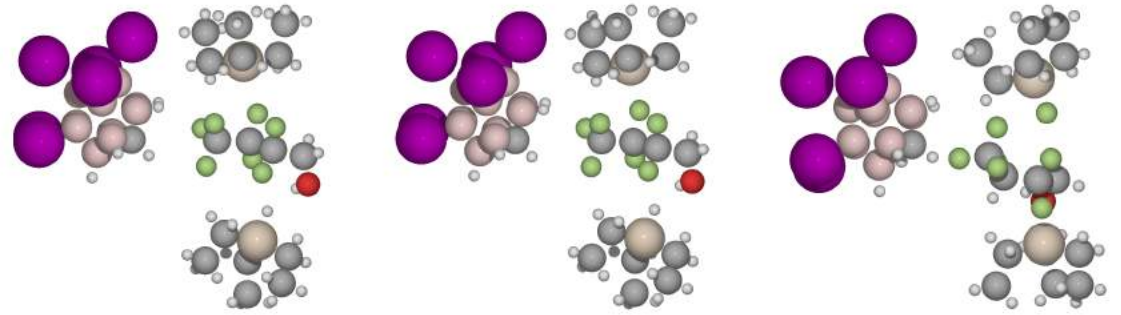


(c) C_ω

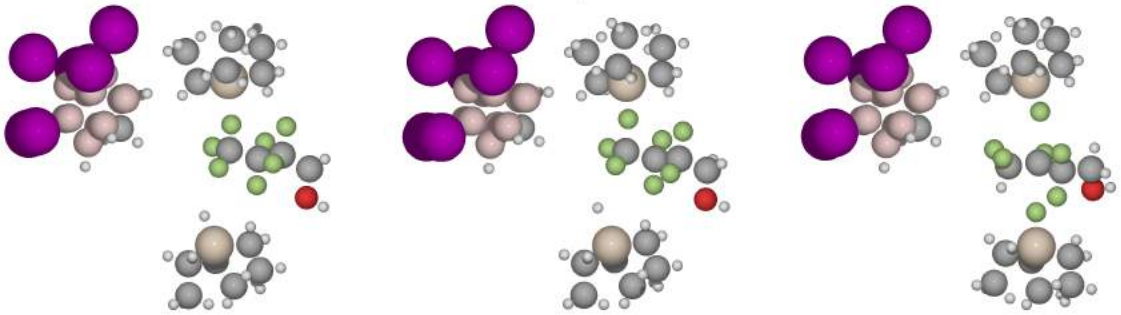
Figure S39: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for PFB in the presence of a carborane anion $\left([HCB_{11}H_5I_6]^-\right)$.



(a) C_α

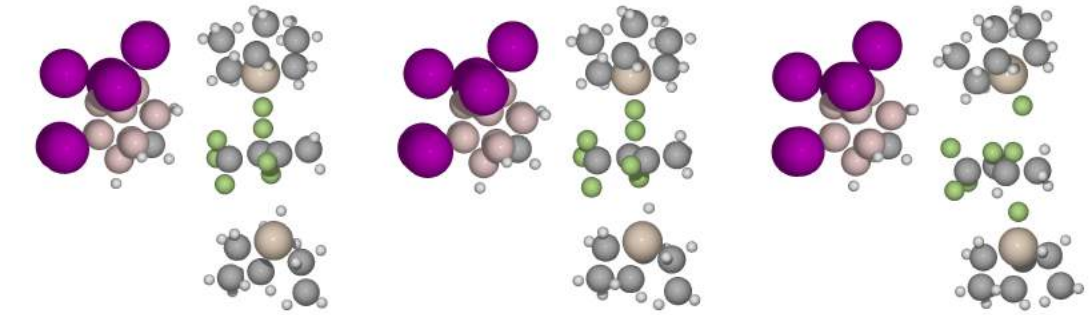


(b) C_β

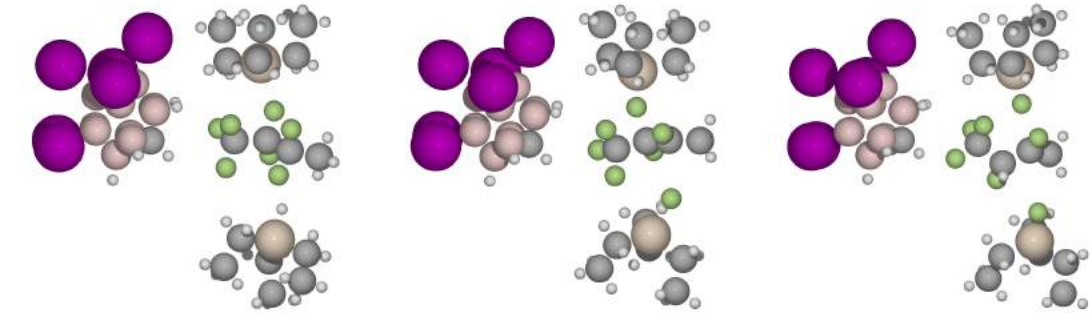


(c) C_ω

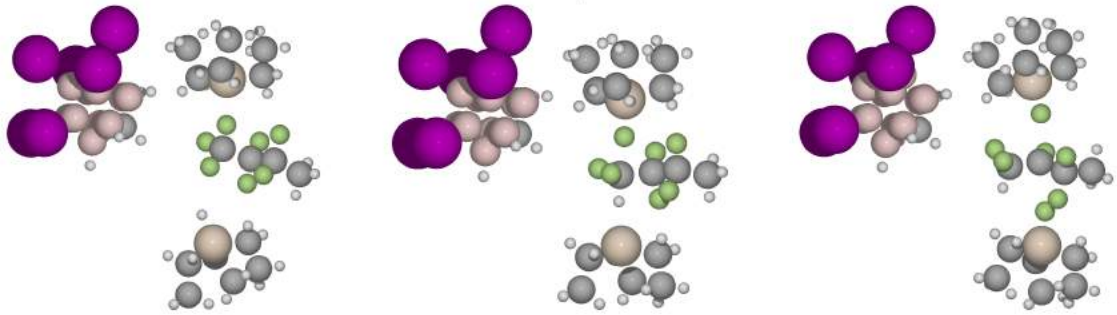
Figure S40: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFBO in the presence of a carborane anion $\left([HCB_{11}H_5I_6]^-\right)$.



(a) C_α

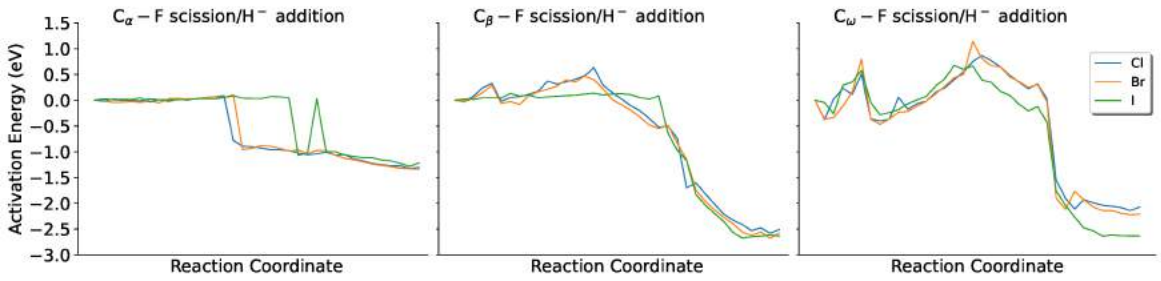


(b) C_β

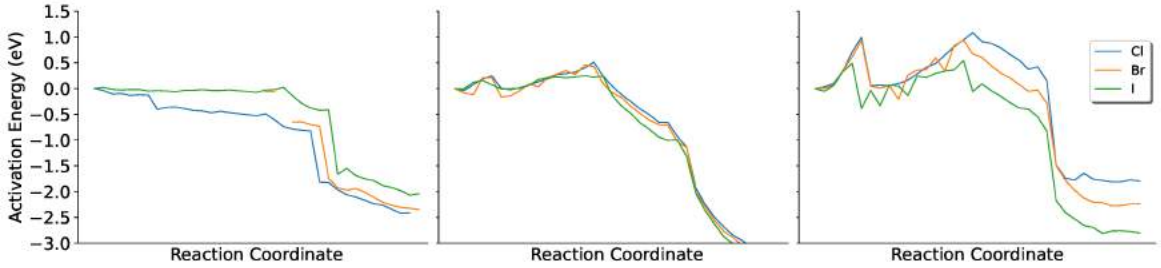


(c) C_ω

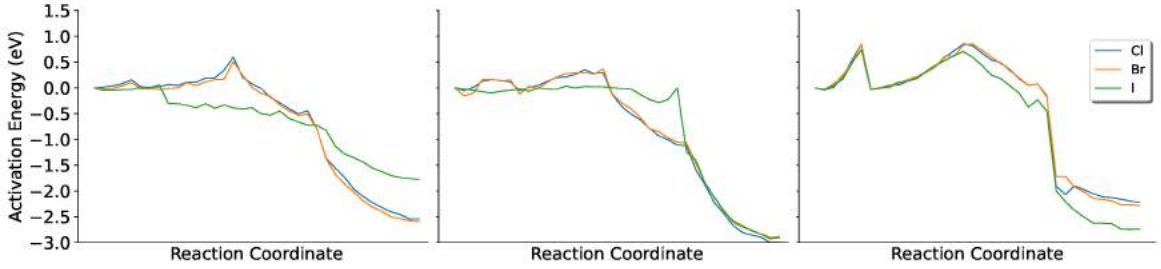
Figure S41: Initial, transition, and final states of the concerted defluorination/hydride addition reaction as a function of position for HFB in the presence of a carborane anion $\left([HCB_{11}H_5I_6]^-\right)$.



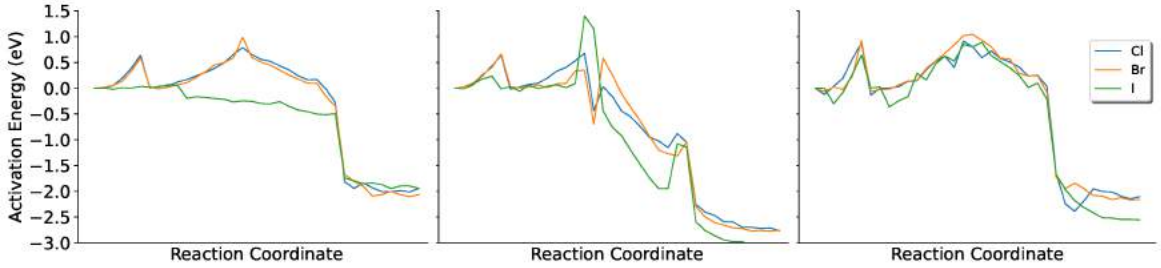
(a) PFBA



(b) PFB

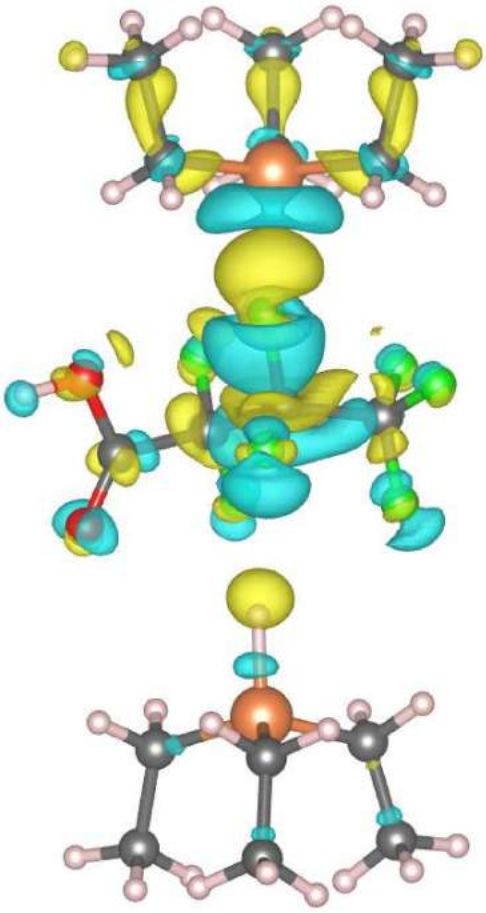


(c) HFBO

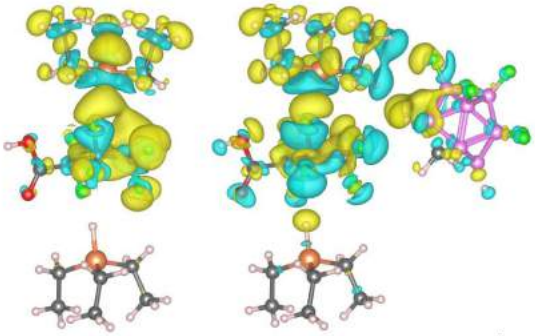


(d) HFB

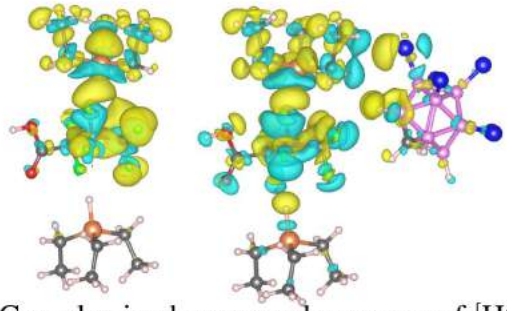
Figure S42: Reaction pathways for the four per-fluorinated molecules in the current study as a function of carbon position and in the presence of carborane $[HCB_{11}H_5X_6]^-$ where X={Cl, Br, I}.



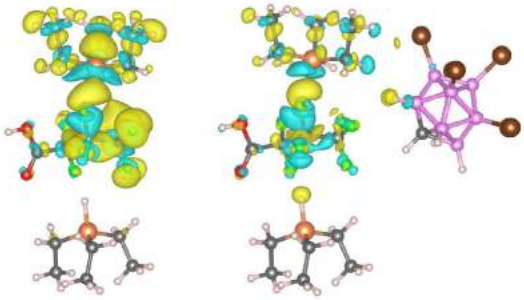
(a) Isolated PFBA/Et_3Si^+/Et_3SiH



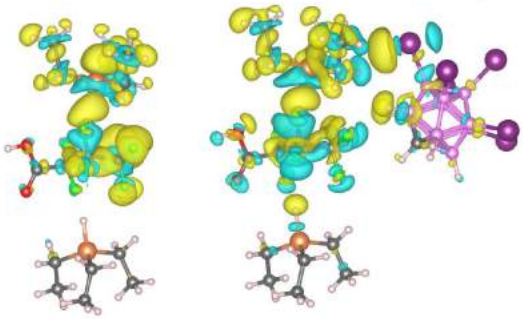
(b) Complex in absence and presence of $[HCB_{11}H_5F_6]^-$



(c) Complex in absence and presence of $[HCB_{11}H_5Cl_6]^-$



(d) Complex in absence and presence of $[HCB_{11}H_5Br_6]^-$



(e) Complex in absence and presence of $[HCB_{11}H_5I_6]^-$

Figure S43: PFBA charge differences across different carboranes. Isosurfaces without the carborane are at 0.01 e^- Å^{-3} and those with carborane are at 0.005 e^- Å^{-3}. The difference in isosurfaces is due to clarity; charge differences without the carborane showed little change between 0.01 e^- Å^{-3} and 0.005 e^- Å^{-3}. Blue regions denote areas of charge depletion, whilst yellow denotes areas of charge accumulation.