ELECTRONIC SUPPLEMENTARY INFORMATION (ESI):

NMR Spin-Spin Coupling Constants: Bond angle dependence of the sign and magnitude of the vicinal $^3J_{HF}$ coupling

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Figure S1. SSCC (Hz) in terms of NBO decomposition for compound **3**, in parentheses $-E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

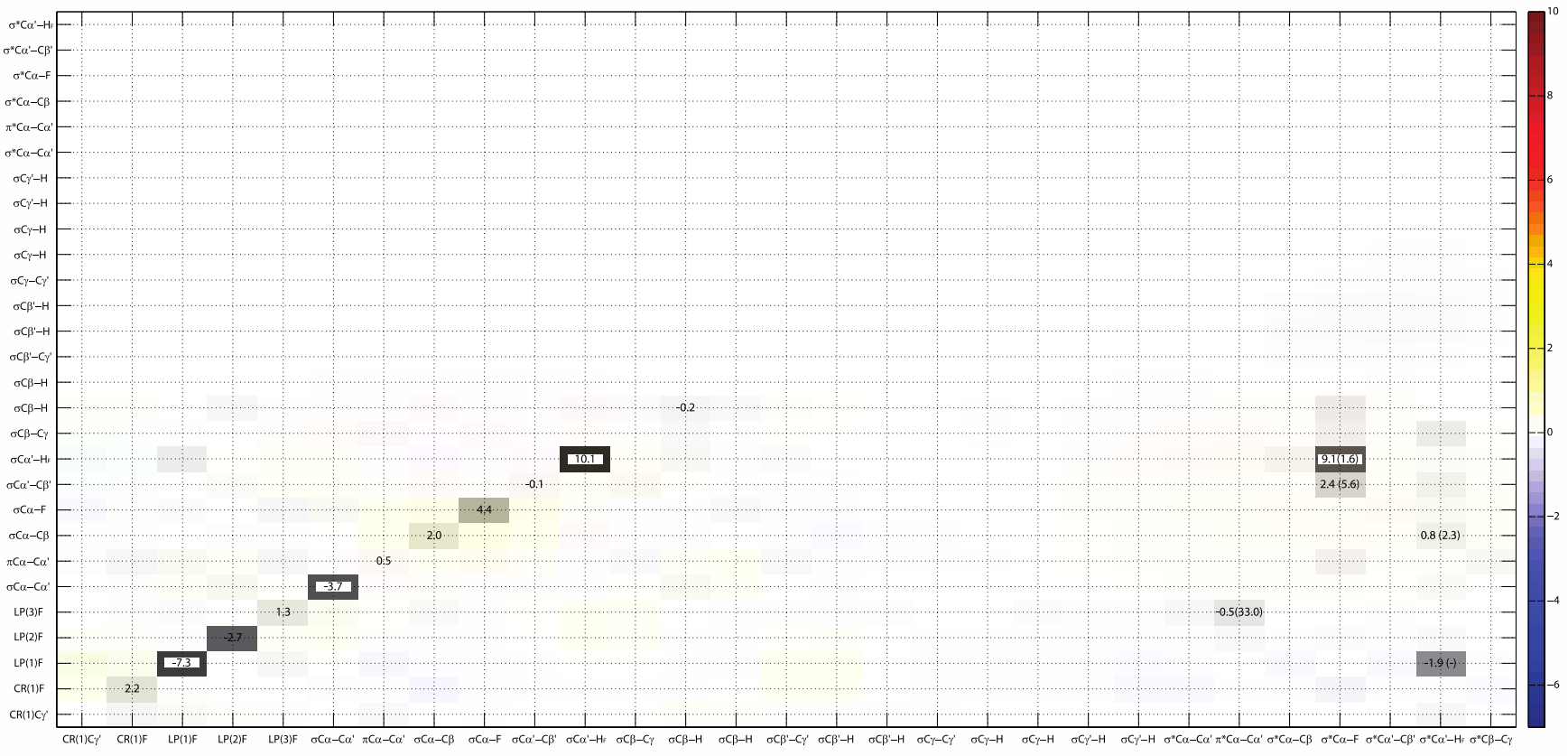


Figure S2. SSCC (Hz) in terms of NBO decomposition for compound **4**, in parentheses -$E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

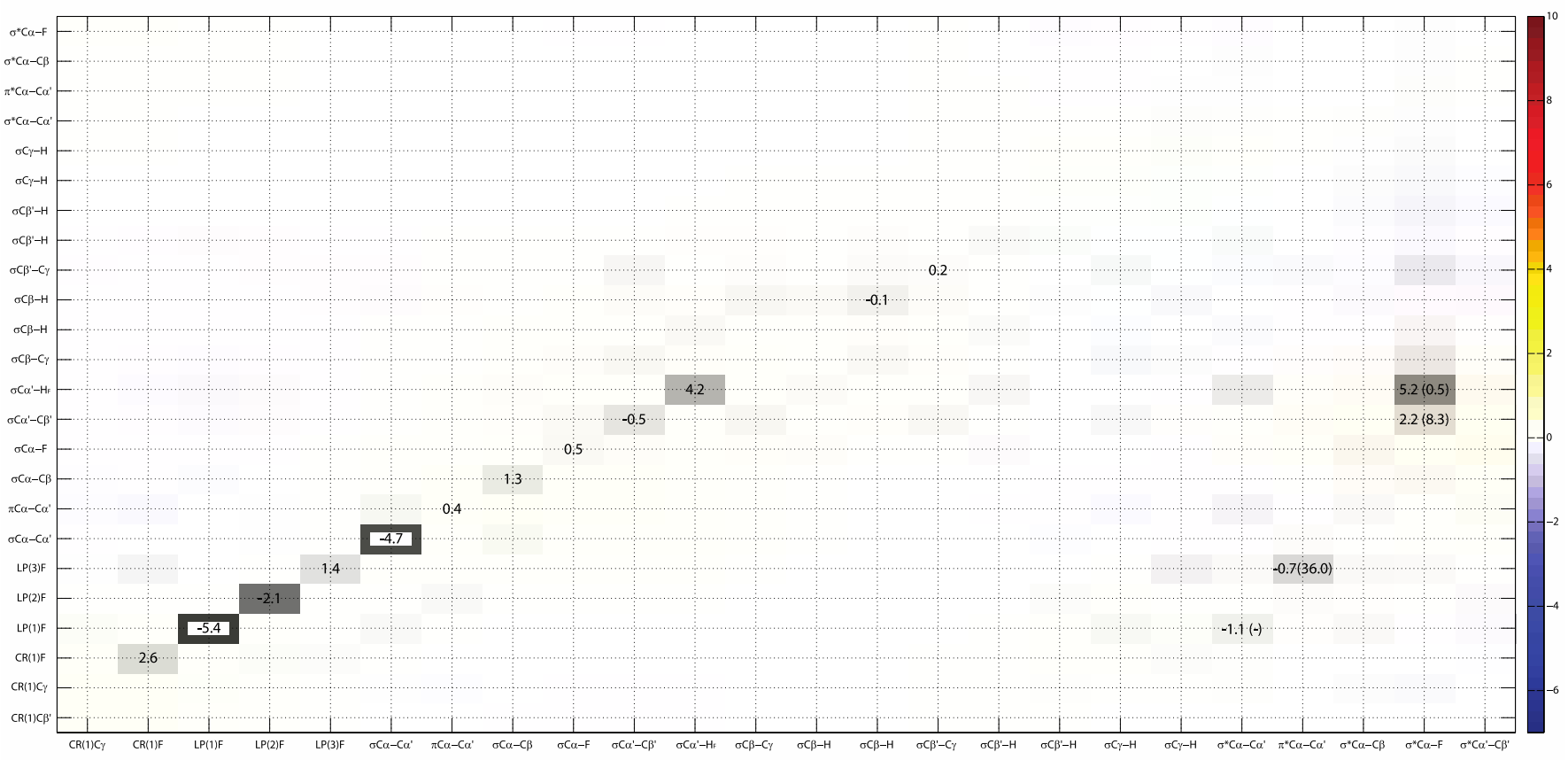


Figure S3. SSCC (Hz) in terms of NBO decomposition for compound **5**, in parentheses -$E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

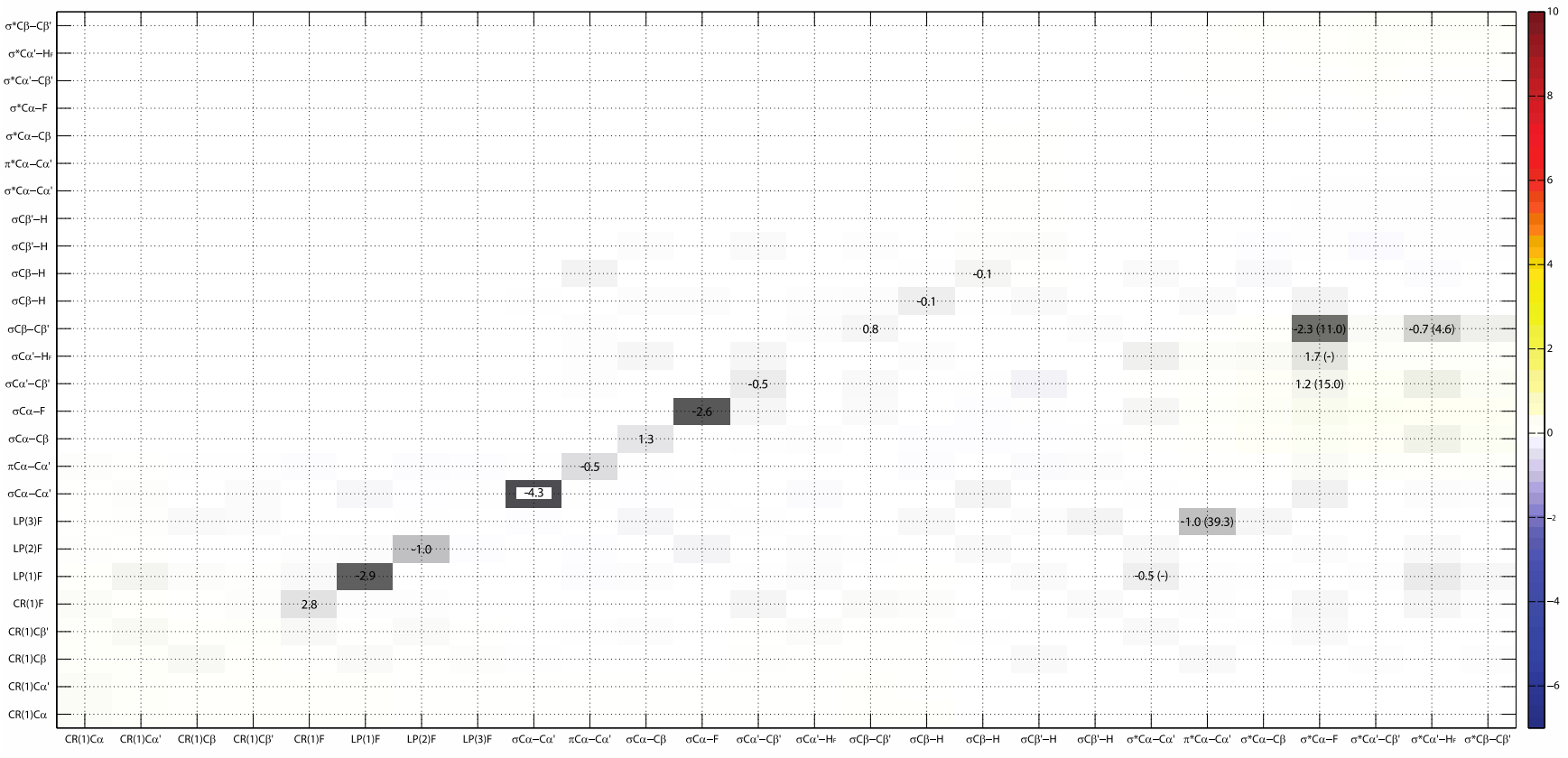


Figure S4. SSCC (Hz) in terms of NBO decomposition for compound **6**, in parentheses $-E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

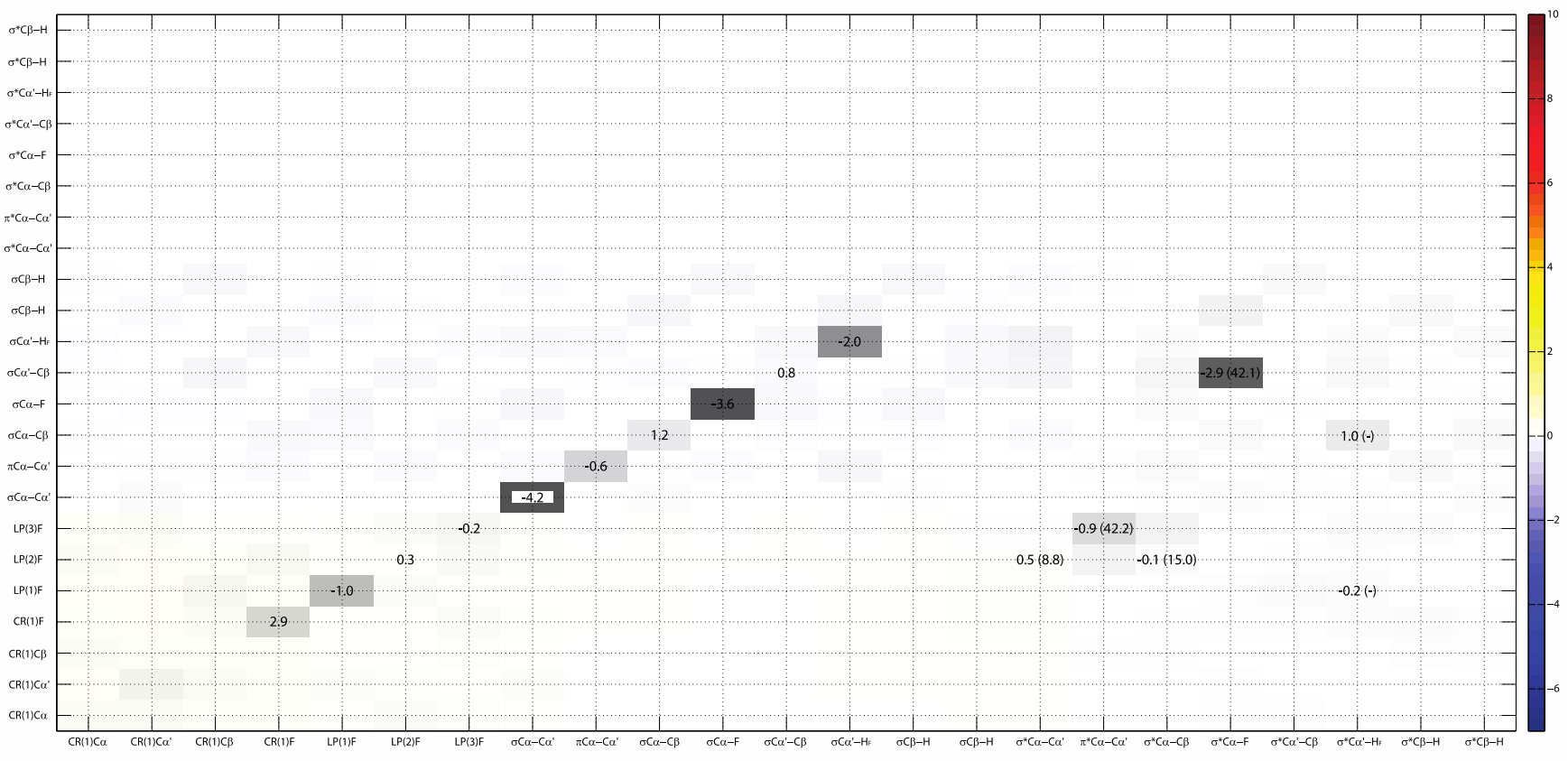
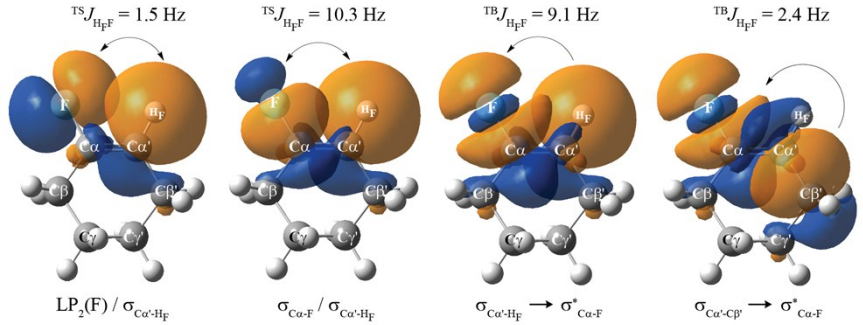
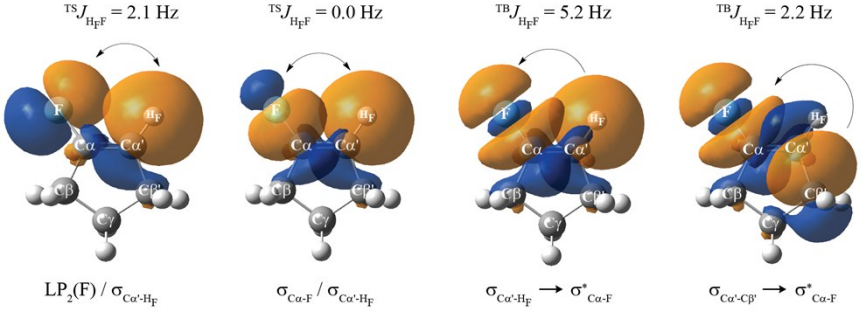


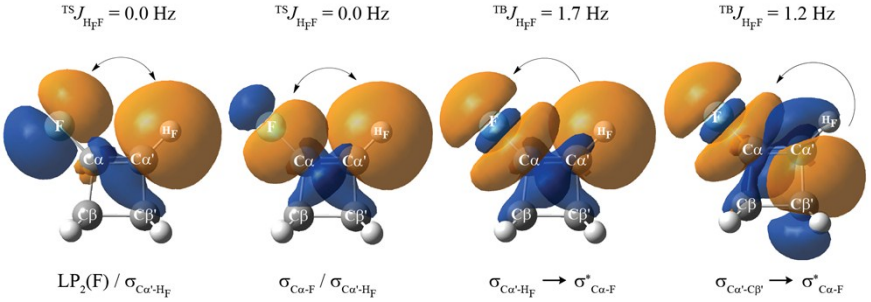
Figure S5. Main $^{3}J_{H_FF}$ through-space ($^{TS}J_{H_FF}$) and through-bond ($^{TB}J_{H_FF}$) transmission mechanisms for compounds **3**-**6**.



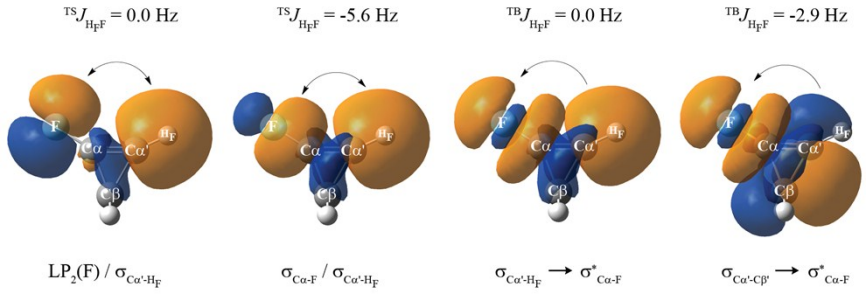
Compound **3**



Compound **4**



Compound **5**



Compound **6**

Table S1. Experimental (J_{exp})[a] and theoretical $^{3}J_{H_FF}$ ($^{total}J$)[a] coupling constants at the PBE0 and SOPPA(CCSD) levels of theory using TZ2P and aug-cc-pTVZ-J basis sets for fluoro-ethylene series from 20° to 120° angle between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors (θ). Distances $r_{F\text{—}H_F}$, $r_{C\text{-}H_F}$, and $r_{C\text{-}F}$ (Angstrom) and bond angles were calculated at the MP2/aug-cc-pVTZ level.

θ	**20**		**40**		**60**		**Equilibrium (63.2)**		**80**		**100**		**120**	
Methods	PBE0	CCSD	PBE0	CCSD	PBE0	CCSD	PBE0	CCSD	PBE0	CCSD	PBE0	CCSD	PBE0	CCSD
^{FC}J	51.5	46.0	42.1	27.7	23.2	15.7	24.1	16.0	14.4	9.8	11.8	5.7	11.0	5.4
^{SD}J	-0.4	-0.9	-1.3	-1.0	-0.7	-0.7	-0.6	-0.7	-0.1	-0.3	0.4	0.2	0.5	0.3
^{PSO}J	-7.7	-3.6	-4.3	-3.0	-4.3	-3.0	-4.5	-3.5	-4.5	-3.1	-4.3	-3.1	-3.6	-2.7
^{DSO}J	1.4	0.3	0.3	-0.1	-0.5	-0.5	-0.6	-0.6	-1.0	-0.9	-1.4	-1.5	-1.7	-1.7
$^{total}J$[b]	44.8	41.8	36.8	23.6	17.7	11.5	18.4	11.2	8.8	5.5	6.5	1.3	6.2	1.3
J_{exp}							19.63[c]							
$r_{F\text{—}H_F}$	1.838		2.213		2.580		2.606		2.919		3.221		3.477	
$r_{C\text{-}H_F}$	1.089		1.091		1.091		1.078		1.090		1.090		1.091	
$r_{C\text{-}F}$	1.426		1.386		1.368		1.346		1.359		1.358		1.365	
$\angle_{F\text{-}C=C}$	100		110		120		122		130		140		150	
$\angle_{H_F\text{-}C=C}$	100		110		120		121		130		140		150	
θ[d]	20		40		60		63		80		100		120	

[a] in Hz. [b] $^{total}J = {}^{FC}J + {}^{SD}J + {}^{PSO}J + {}^{DSO}J$. [c] V. S. Watts, J. H. Goldstein, *J. Chem. Phys.*, 1965, **42**, 228-233. [d] Angle between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors.

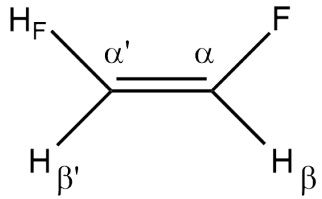


Table S2. NLMO contributions[a] for $^3J_{H_FF}$ (in Hz) at PBE0/TZ2P varying the angle between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors of fluoro-ethylene from 60° to 120°.

Parent NBO	60			80			100			120		
	$J^{(L)}$	$J^{(NL)}$	$J^{(L+NL)}$	$J^{(L)}$	$J^{(NL)}$	$J^{(L+NL)}$	$J^{(L)}$	$J^{(NL)}$	$J^{(L+NL)}$	$J^{(L)}$	$J^{(NL)}$	$J^{(L+NL)}$
CR (F)	3.23	0.01	3.24	2.93	-0.01	2.92	3.00	-0.02	2.98	3.08	0.03	3.11
$LP_1(F)$	-12.03	0.08	-11.94	-11.57	-0.43	-12.00	-11.12	-0.61	-11.73	-10.42	-0.44	-10.86
$LP_2(F)$	-2.92	-0.08	-3.01	0.60	0.13	0.73	4.18	0.38	4.56	6.80	0.66	7.46
$LP_3(F)$	1.60	-0.68	0.92	0.66	-1.00	-0.35	-0.03	-1.12	-1.15	-0.28	-1.01	-1.29
$\sigma_{C\alpha\text{-}C\alpha'}$	0.41	0.01	0.42	-0.06	0.05	-0.01	-0.48	0.07	-0.41	-0.72	0.09	-0.63
$\pi_{C\alpha=C\alpha'}$	-4.52	0.23	-4.29	-4.39	0.40	-3.99	-3.82	0.53	-3.29	-3.33	0.70	-2.63
$\sigma_{C\alpha\text{-}H\beta}$	2.49	0.64	3.13	2.68	1.27	3.94	2.36	1.93	4.29	1.85	2.58	4.43
$\sigma_{C\alpha'\text{-}H\beta'}$	-0.21	3.05	2.84	-0.73	3.18	2.45	-0.88	2.77	1.89	-0.65	1.98	1.33
$\sigma_{C\alpha'\text{-}H_F}$	14.18	5.76	19.94	9.58	2.72	12.31	7.54	0.83	8.37	6.62	-0.61	6.01
$\sigma_{C\alpha\text{-}F}$	6.71	-0.08	6.63	3.38	0.06	3.45	1.62	0.11	1.73	0.29	0.07	0.36
Sum	9.05	9.02	18.07	3.42	6.45	9.87	2.89	4.96	7.85	3.86	4.12	7.98

[a] $J^{(L)}$ – Lewis, $J^{(NL)}$ – Non-Lewis, $J^{(L+NL)} = J^{(L)} + J^{(NL)}$.

Figure S6. SSCC (Hz) in terms of NBO decomposition for fluoro-ethylene with 60° angle value between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors, in parentheses $-E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

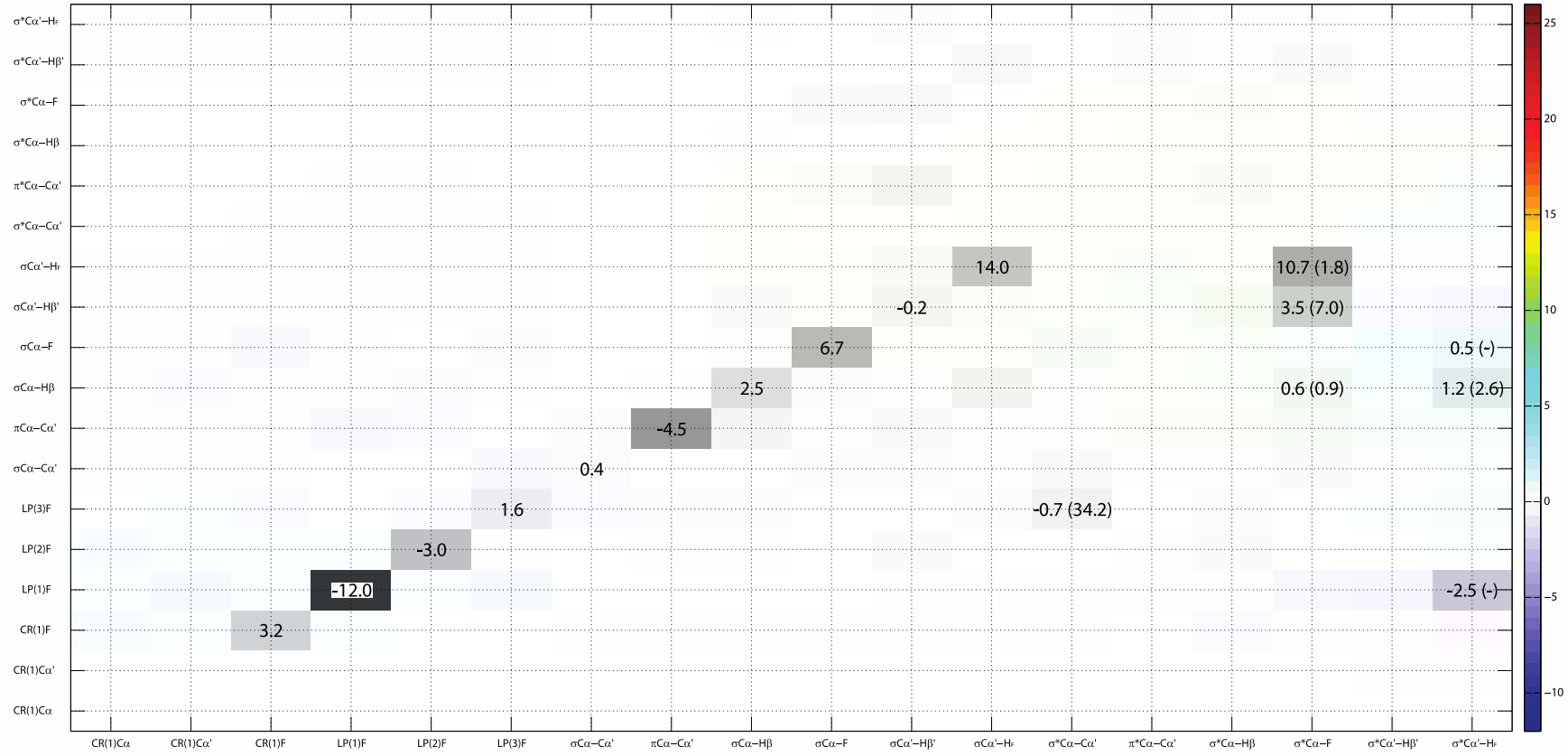


Figure S7. SSCC (Hz) in terms of NBO decomposition for fluoro-ethylene with 80° angle value between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors, in parentheses $-E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

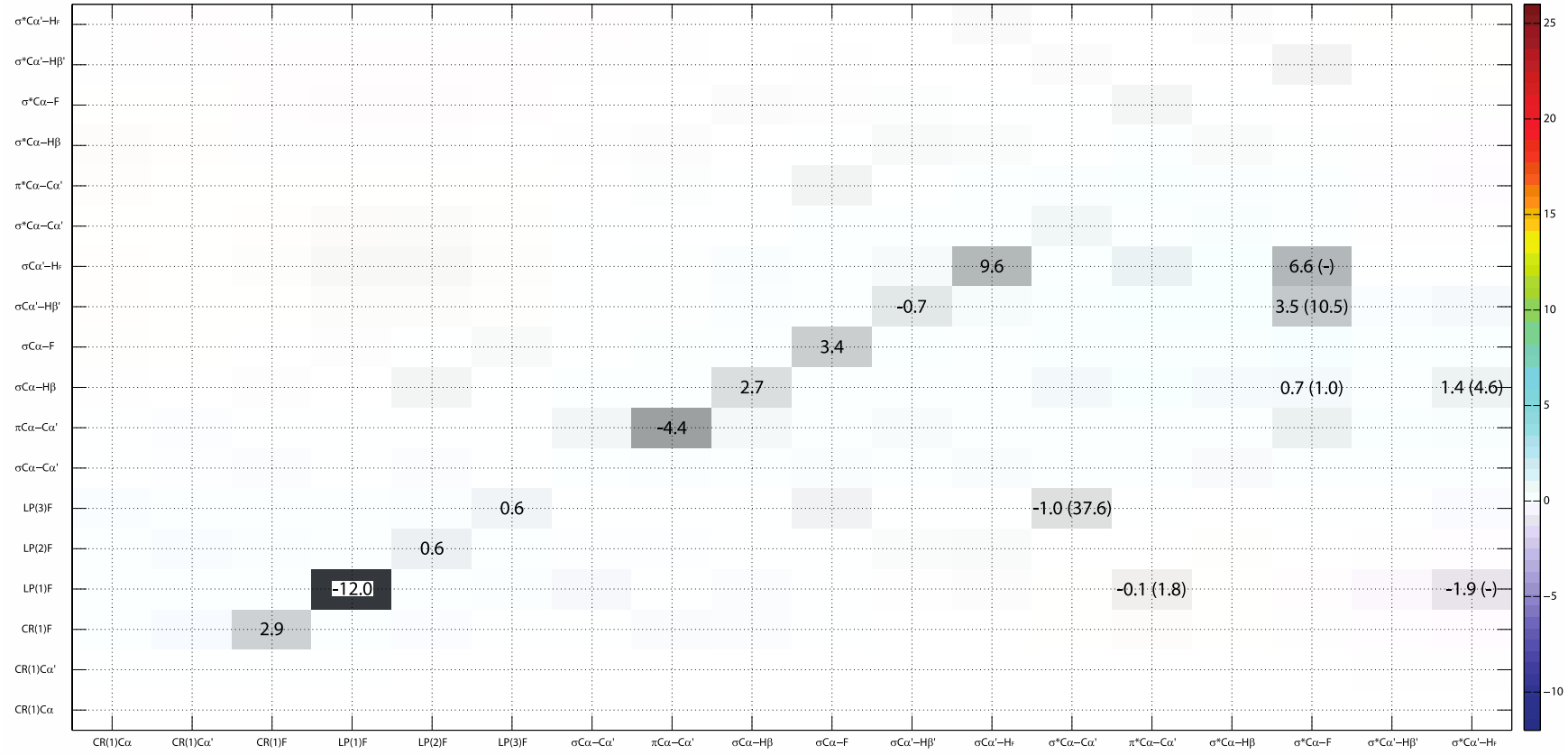


Figure S8. SSCC (Hz) in terms of NBO decomposition for fluoro-ethylene with 100° angle value between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors, in parentheses $-E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

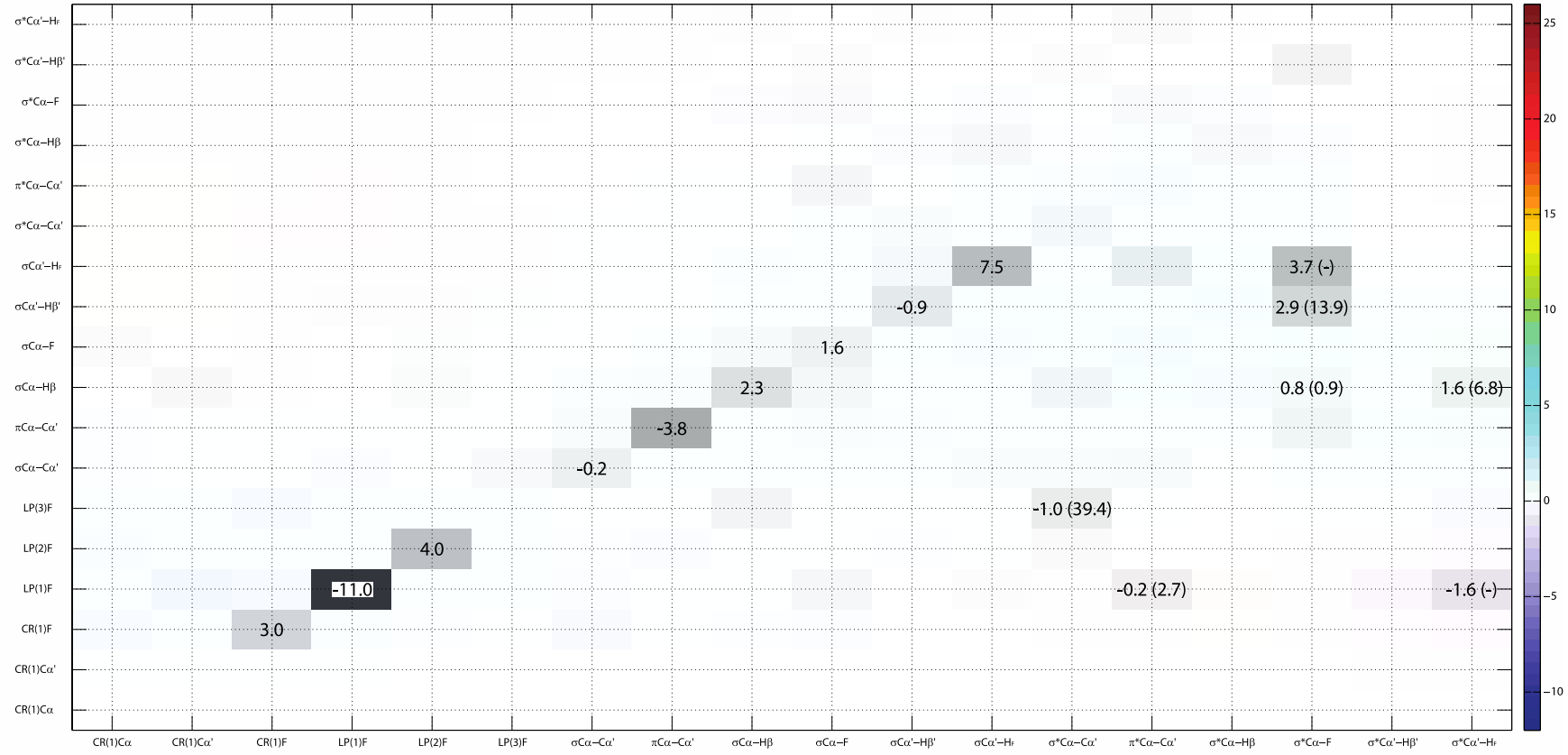


Figure S9. SSCC (Hz) in terms of NBO decomposition for fluoro-ethylene with 120° angle value between the $\sigma_{C\alpha\text{-}F}$ and $\sigma_{C\alpha'\text{-}H_F}$ vectors, in parentheses -$E^{(2)}$ (kcal mol^{-1}) delocalization associated with off-diagonal SSCC contribution.

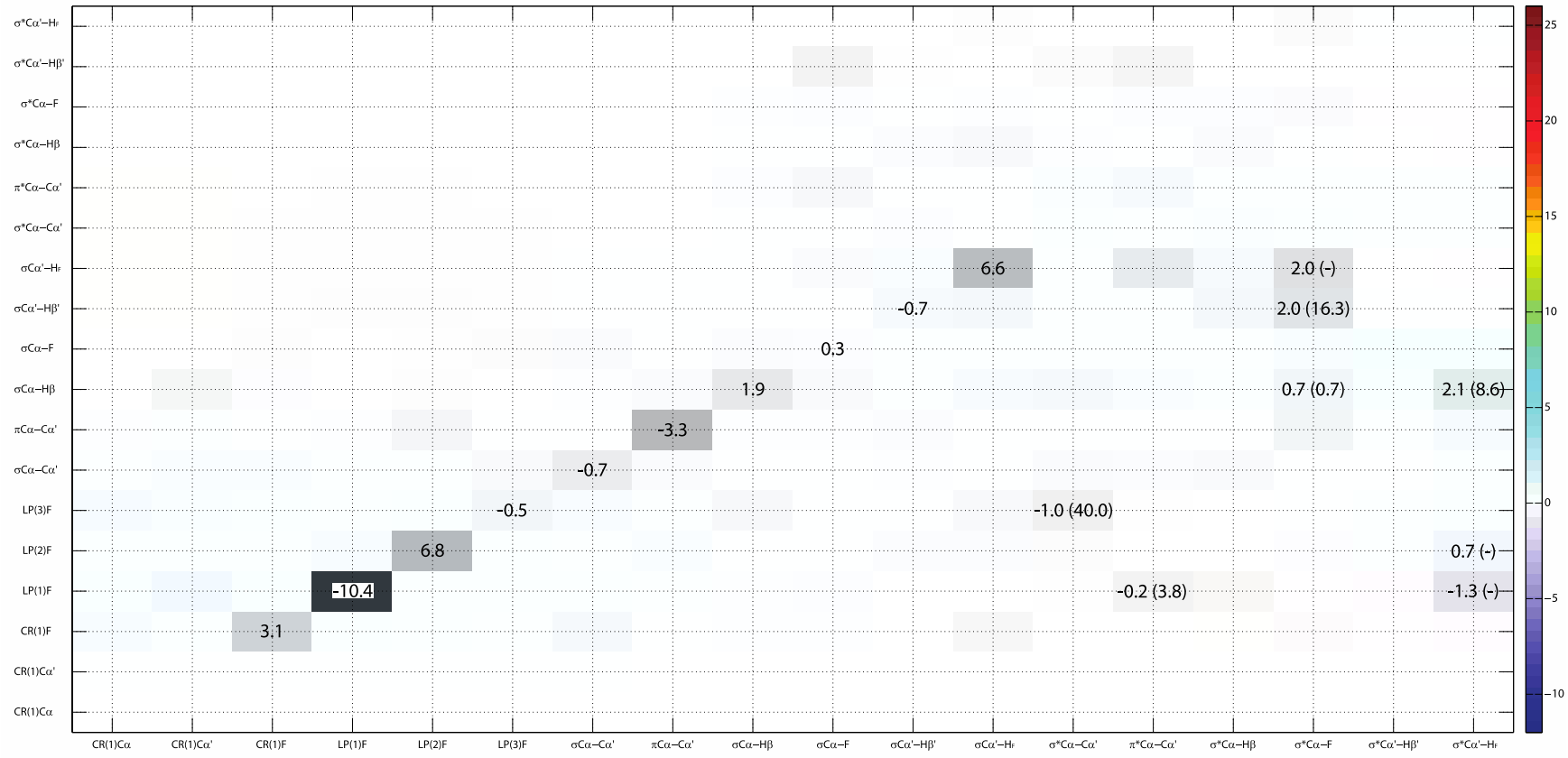


Figure S10. Main $^{3}J_{H_FF}$ through-space ($^{TS}J_{H_FF}$) and through-bond ($^{TB}J_{H_FF}$) transmission mechanisms for fluoroethylene.