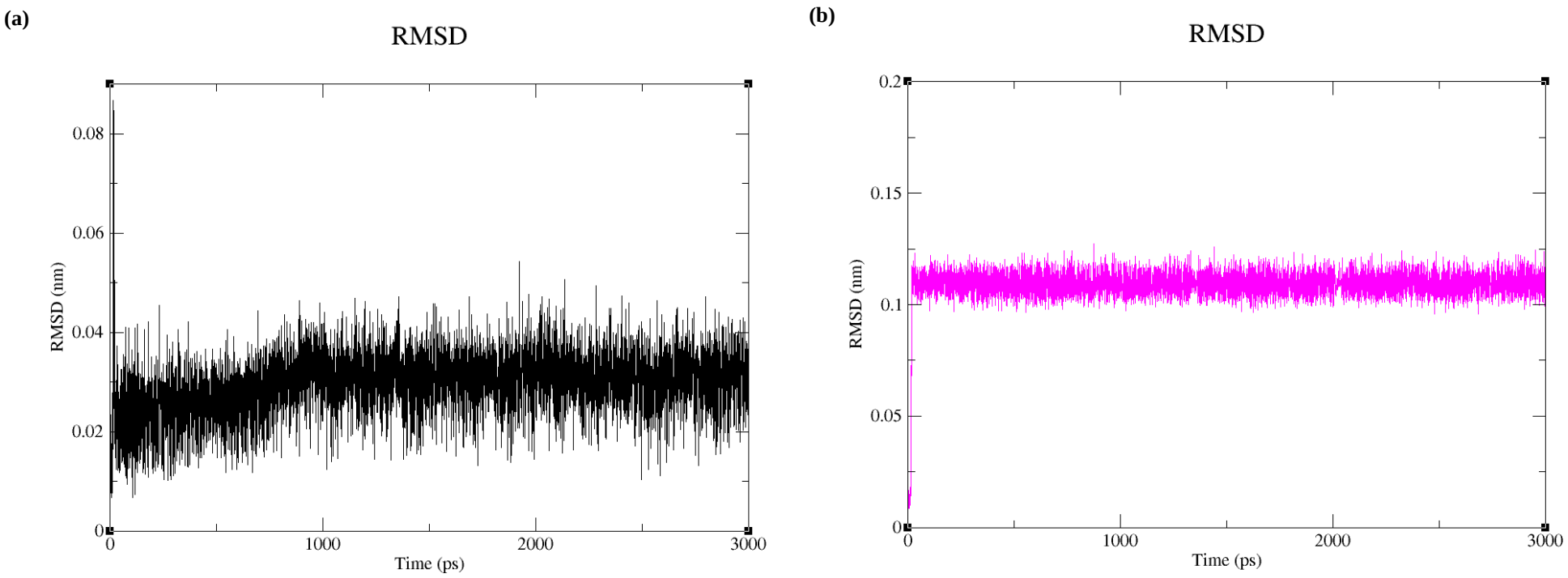
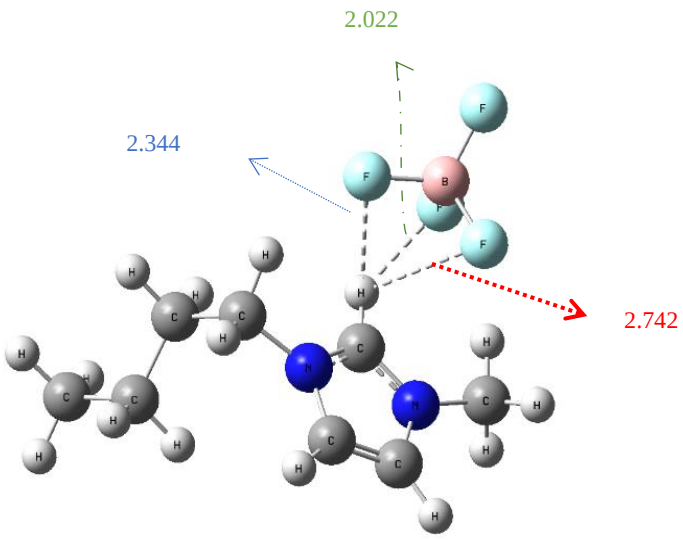
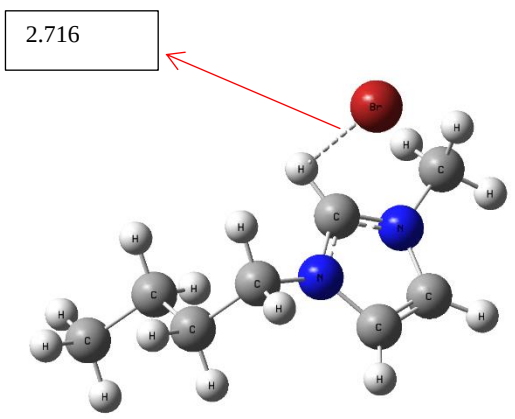


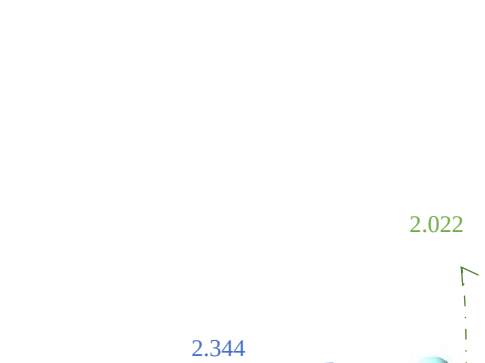
Figure S21. (a) RMSD values of BMIM (during 3ns of MD simulation) with respect to the Optimized geometry of (BMIM) (ß-OH-Pen) which was calculated at B3LYP/6-311++G (d, p) level. (b) RMSD values of (ß-OH-Pen) (during 3ns of MD simulation) with respect to the Optimized geometry of (BMIM) (ß-OH-Pen) which was calculated at B3LYP/6-311++G (d, p).



(a) (BMIM)(BF_4)

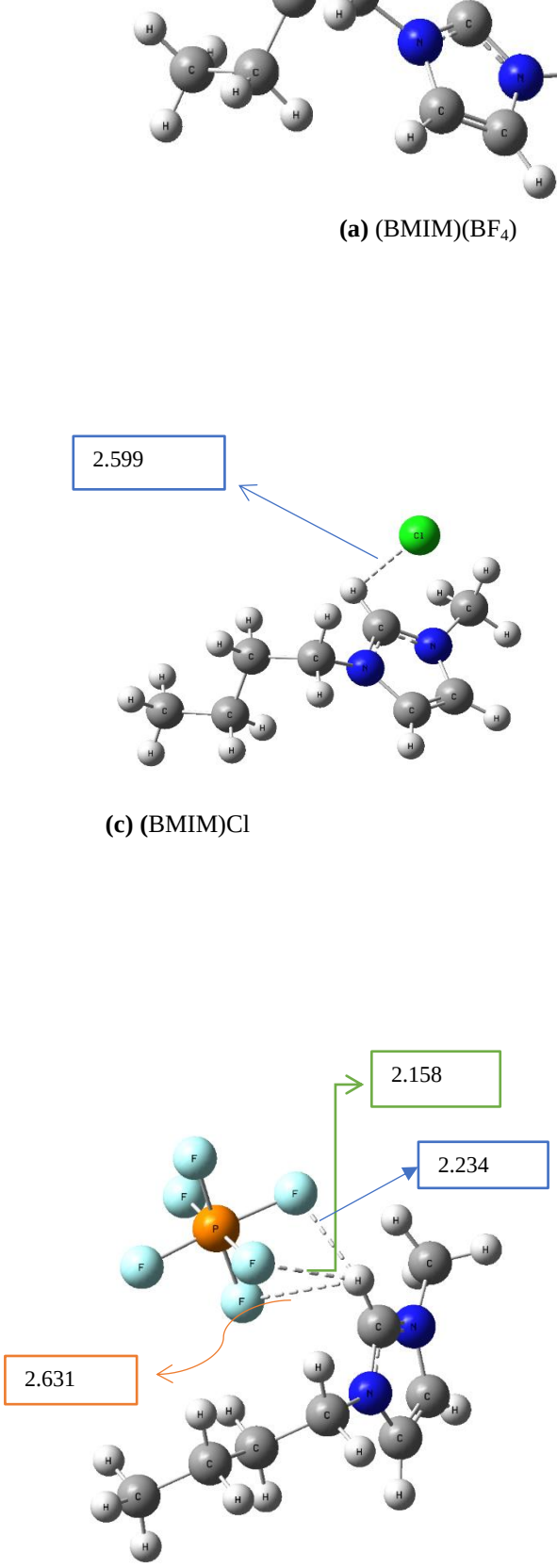


(b) (BMIM) Br



(c) (BMIM)Cl

(d) (BMIM)(TFSI)



(e) (BMIM)(PF_6)

Figure S22. Optimized geometries of the lowest energy conformers of the known ILs including: (a) (BMIM)(BF_4), (b) (BMIM)Br, (c) (BMIM)Cl, (d) (BMIM)(TFSI), and (e) (BMIM)(PF_6)

Table S1. ΔE_{int} and ΔE_{CEC} (kcal/mol) values of the known ILs including: (a) (BMIM)(BF_4), (b) (BMIM)Br, (c) (BMIM)Cl, (d) (BMIM)(TFSI), and (e) (BMIM)(PF_6) calculated at B3LYP/6- 311++ G (d, p) level alongside with their experimental melting points ºC.

Name of structures	Abbreviation	E_{SCF}(Hartree/Particle)	ΔE_{int} (kcal/mol)	ΔE_{CEC} (kcal/mol)	Melting point, ºC
tetrafluoroborate	($BF4^-$)	-424.6616			
1-butyl-3-methylimidazolium	(BMIM)	-423.05161			
chloride	Cl	-460.30231			
1-butyl-3-methylimidazolium chloride	(BMIM) Cl	-883.49464	-88.3	88.3	89
1-butyl-3-methylimidazolium tetrafluoroborate	(BMIM) (BF4)	-847.84118	-80.3	80.3	-82
bromide	Br	-423.05161			
1-butyl-3-methylimidazolium bromide	(BMIM) Br	-2997.42117	-83.6	83.6	60
hexafluorophosphate	(PF_6)	-940.87213			
1-butyl-3-methylimidazolium hexafluorophosphate	(BMIM) (PF_6)	-1364.04423	-75.6	75.6	10
trifluoromethyl sulfonate	(TF)	-961.69669			
1-butyl-3-methylimidazolium trifluoromethyl sulfonate	(BMIM)(TF)	-1384.87053	-76.7	76.7	-15
bis (trifluoromethyl sulfonyl) amide	TFSI	-1827.54373			
1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) amide	(BMIM)(TFSI)	-2250.70975	-71.8	71.8	-8

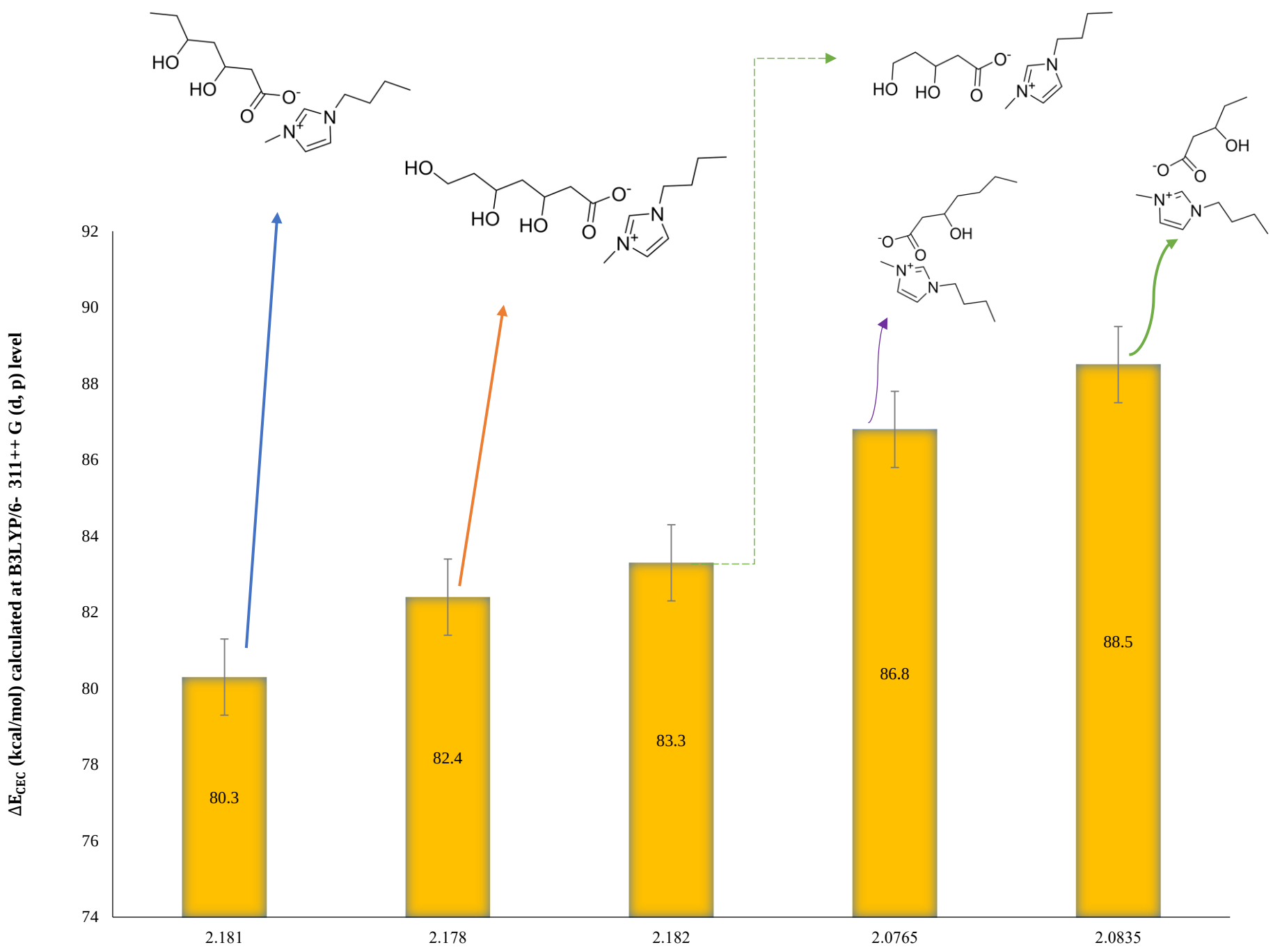


Figure S23. ΔE_{CEC} (kcal/mol) calculated at B3LYP/6-311++ G (d, p) level and average length of intermolecular bond distances (Å) in the ionic liquids including (BMIM) (ß-OH-Pen), (BMIM) (ß, δ -DI-OH-Pen), (BMIM)(ß-OH-Hep), (BMIM) (ß, δ -DI-OH-Hep) and (BMIM) (ß, δ, σ-Tri-OH-Hep).

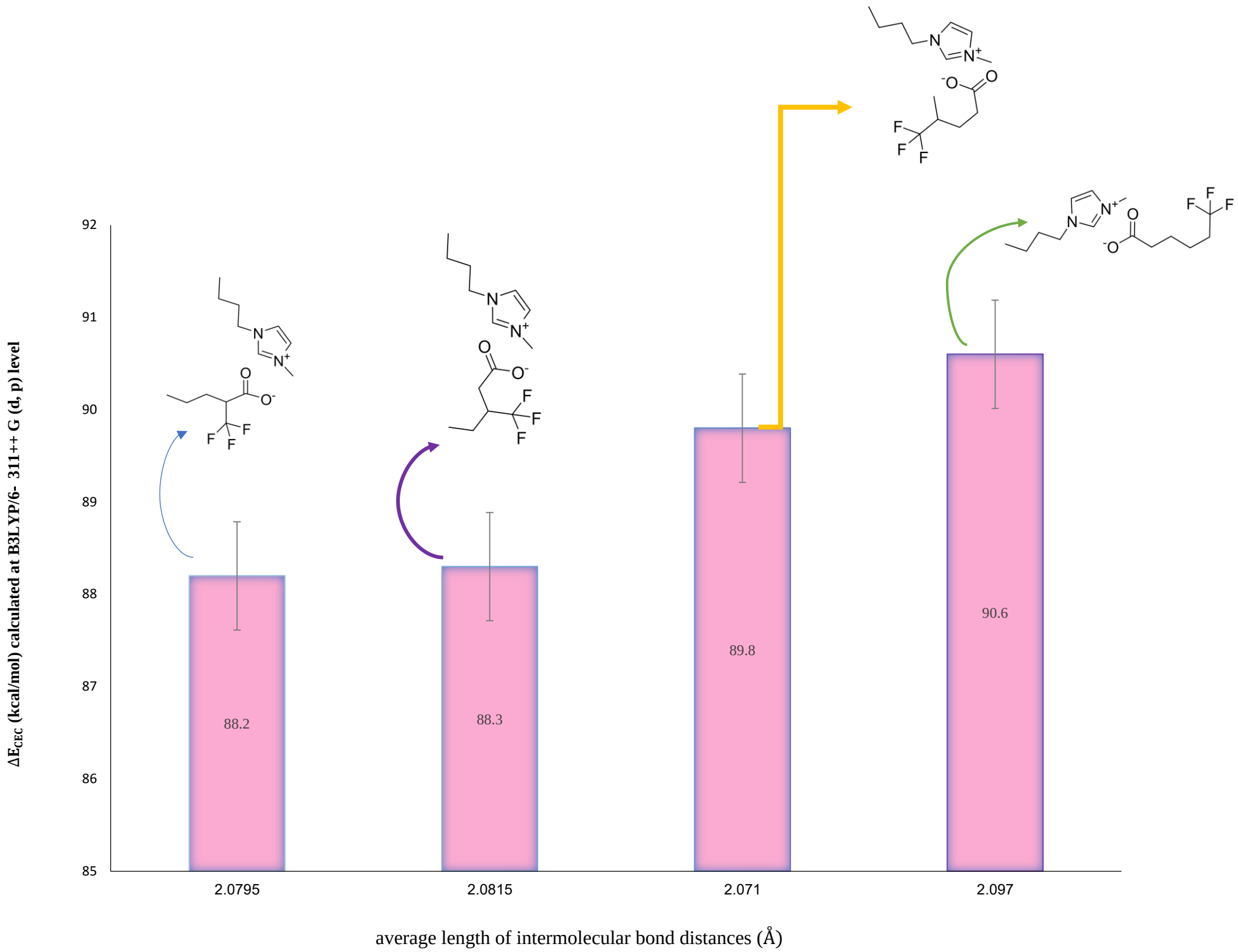


Figure S24. ΔE_{CEC} (kcal/mol) calculated at B3LYP/6-311++ G (d, p) level and average length of intermolecular bond distances (Å) in CF_3-contatining carboxylate-based ILs including: (BMIM)(α−CF_3-Pen), (BMIM)(ß−CF_3-Pen), (BMIM), (BMIM) (γ−CF_3-Pen) and (BMIM) (δ- CF_3-Pen) at B3LYP/6- 311++ G (d, p).