

Supplementary Information for
Photocatalytic C–F alkylation of trifluoromethyls using *o*-
Phosphinophenolate: Mechanistic insights and substrate
prediction

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Computational details

The Gaussian 09 suite of ab initio programs¹ was employed to perform the ground state and excited state geometry optimizations, vibrational frequency calculations, and intrinsic reaction coordinate (IRC) at the B3LYP functional with Grimme's GD3 dispersion correction, referring to the benchmark calculations in previous studies,²⁻⁵ and def2TZVP basis set.⁶⁻⁷ The triplet excited states were optimized by using time-dependent density functional theory (TDDFT) at the same level. The accuracy of numerical integrations is at the ultrafine grid (99,590) level. The solvent effect of N,N-dimethylacetamide ($\epsilon = 37.78$) was considered by using the integral equation formalism polarizable continuum (IEFPCM)⁸ solvation model with the SMD radii.⁹ The Multiwfn program was used to perform spin population and natural population analysis.¹⁰

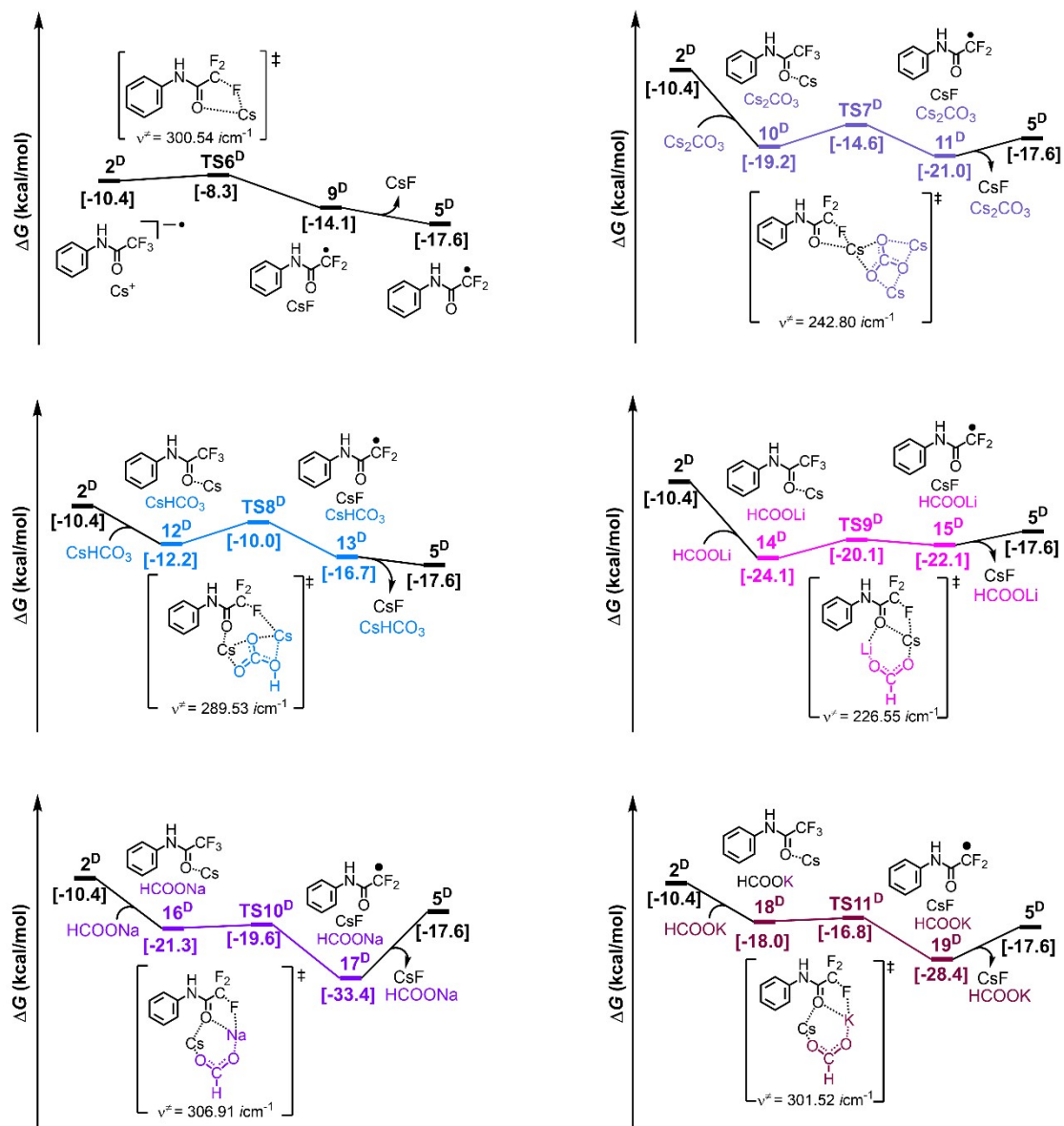


Figure S1 Different paths of N-phenyl-2,2,2-trifluoroacetamide defluorination.

Table S1 The calculated free energy difference using B3LYP-D3 and MP2 between two double-bonded carbons coupling with carbon radical in **5^D**.

	$\Delta\Delta G$ (kcal/mol)
B3LYP-D3	3.3
MP2	3.0

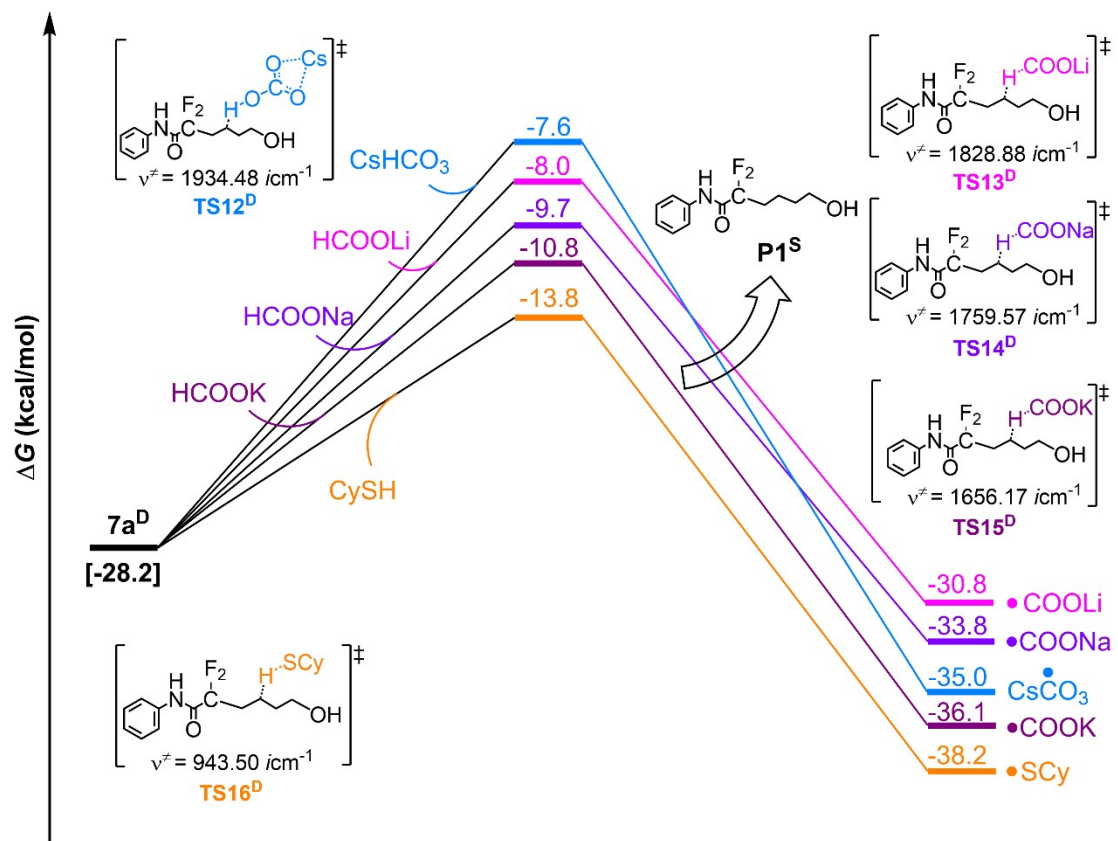


Figure S2 Different paths of hydrogen atom transfer from different additives.

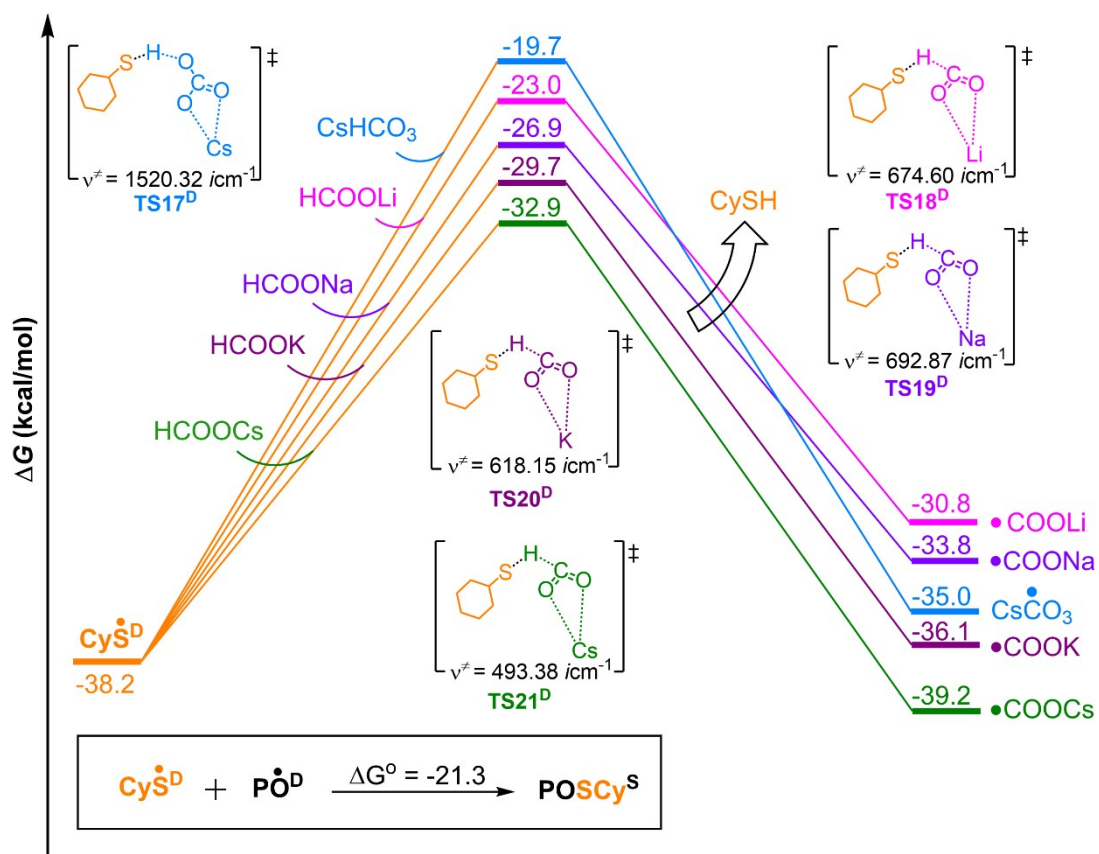


Figure S3 Different paths of hydrogen atom transfer to regenerate CySH.

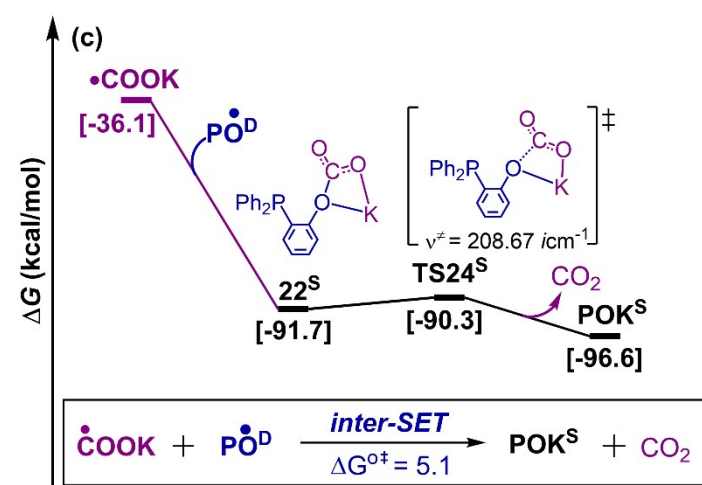
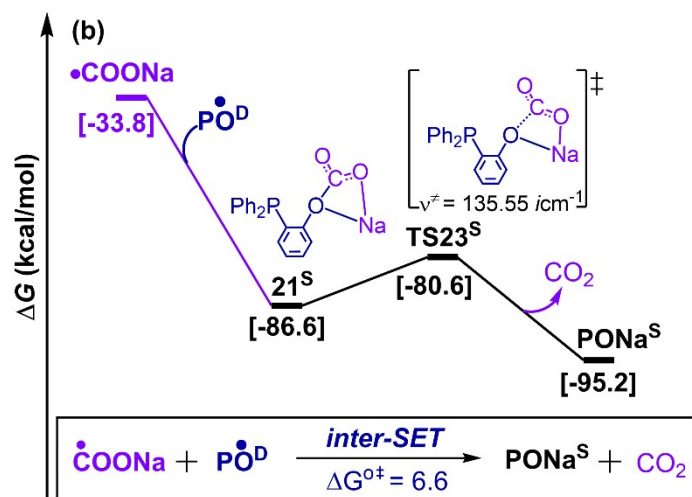
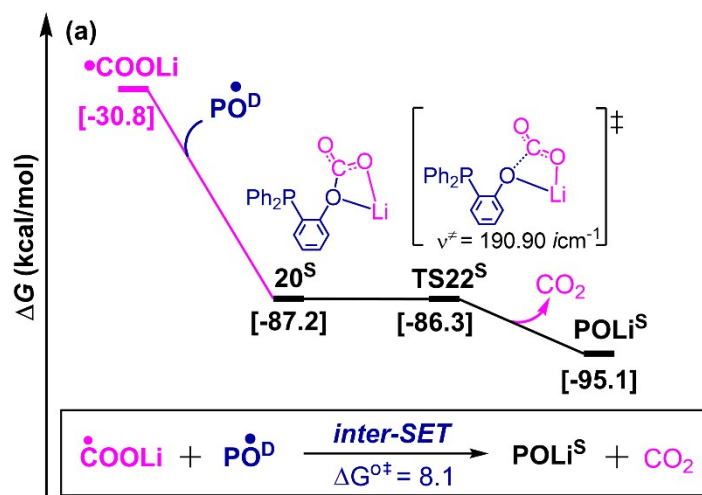


Figure S4 Different paths of photocatalyst regeneration assisted by formate radical.

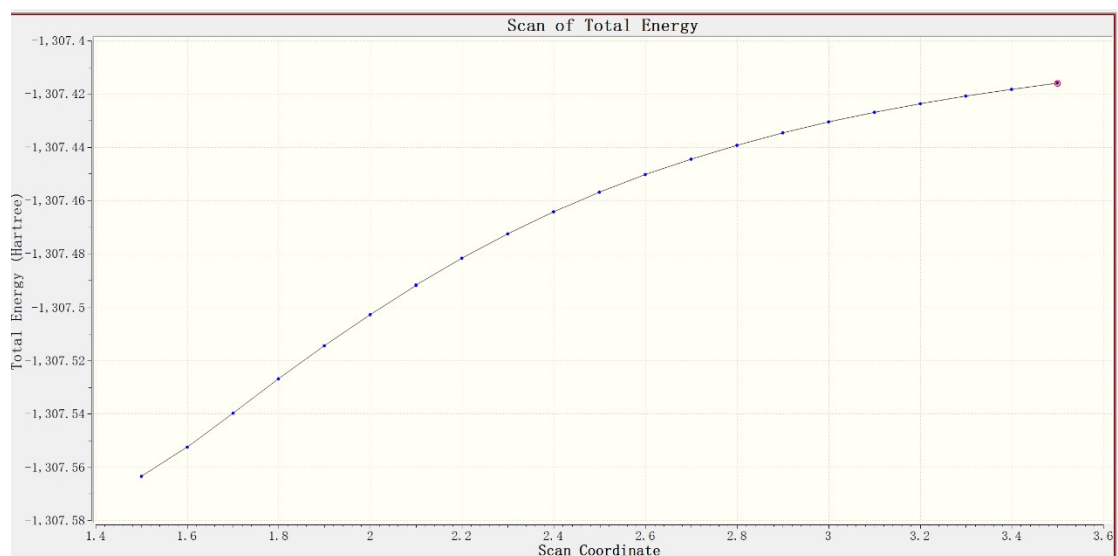


Figure S5 The scanning results of potential energy surface for coupling process between lithium formate radical and PO^\bullet radical.

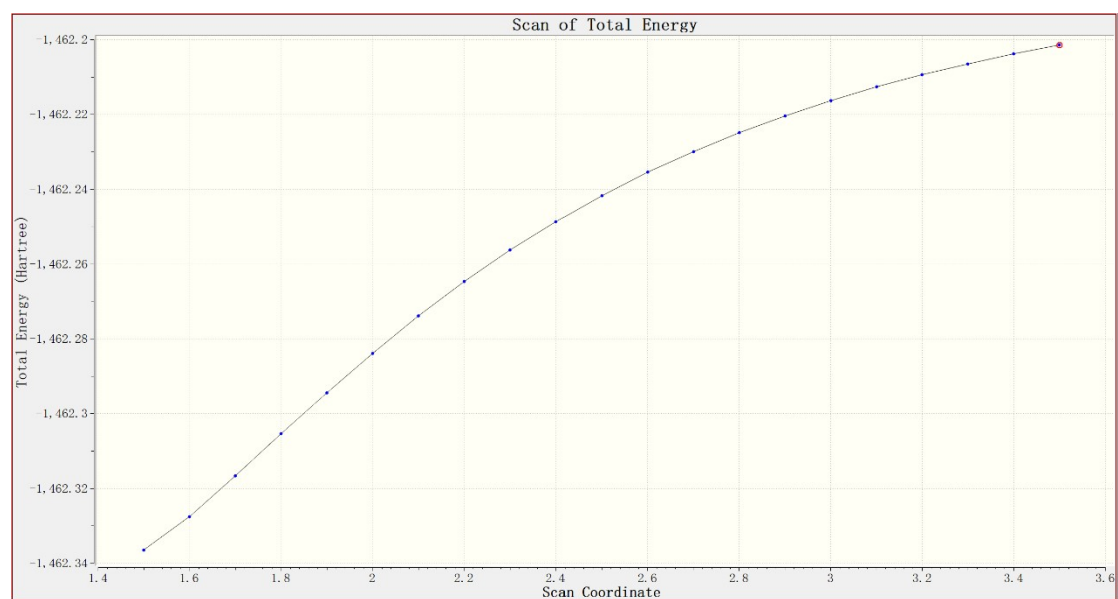


Figure S6 The scanning results of potential energy surface for coupling process between sodium formate radical and PO^\bullet radical.

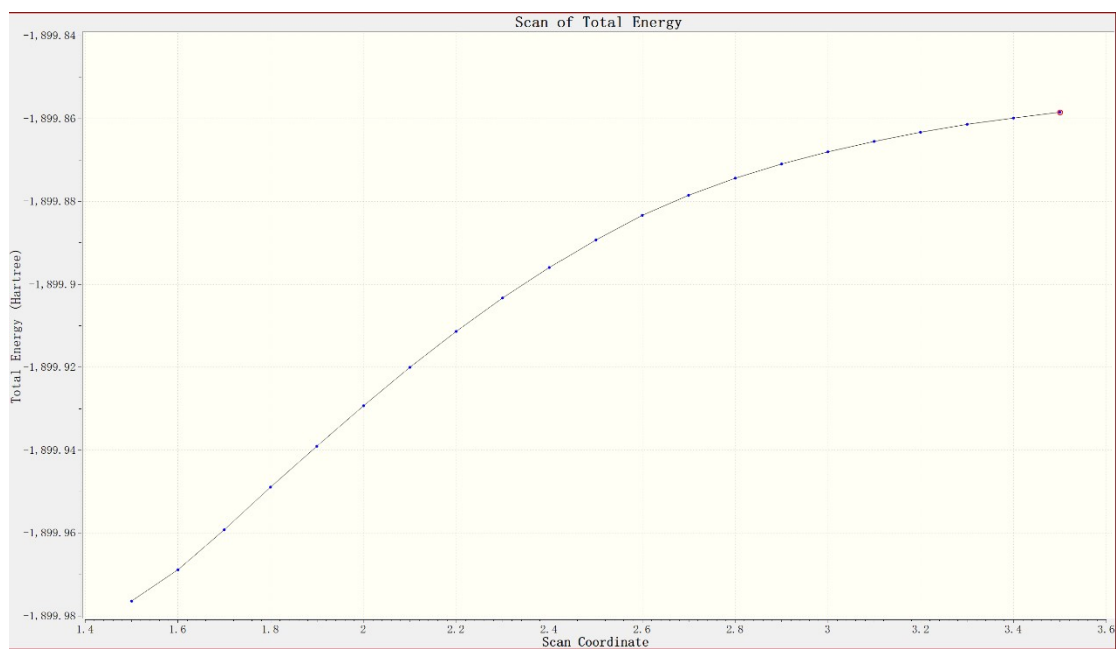


Figure S7 The scanning results of potential energy surface for coupling process between potassium formate radical and PO^{\bullet} radical.

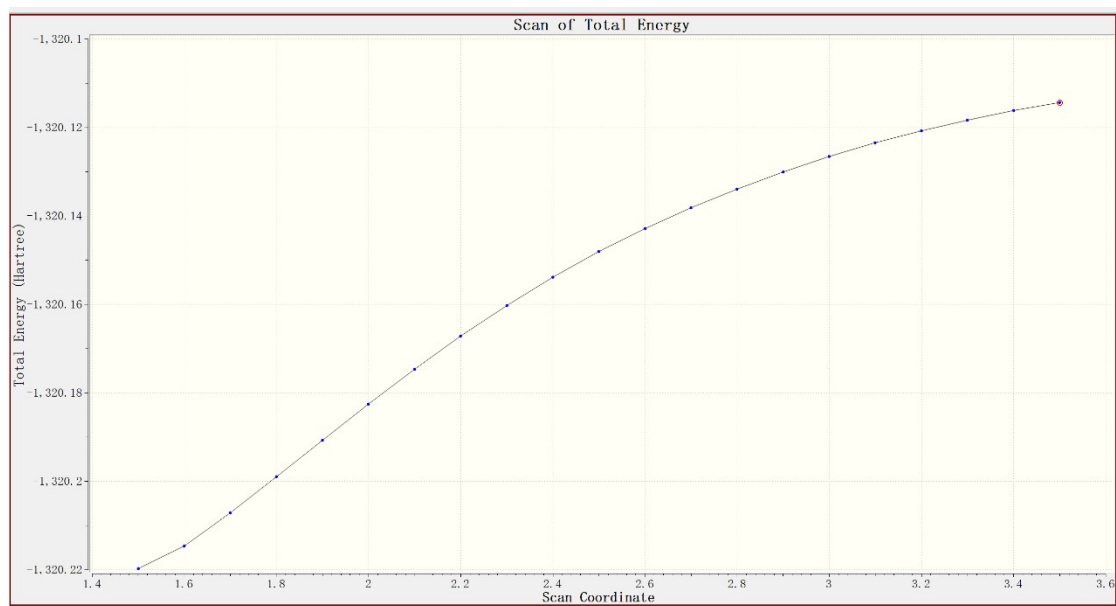


Figure S8 The scanning results of potential energy surface for coupling process between lithium formate radical and PO^{\bullet} radical.

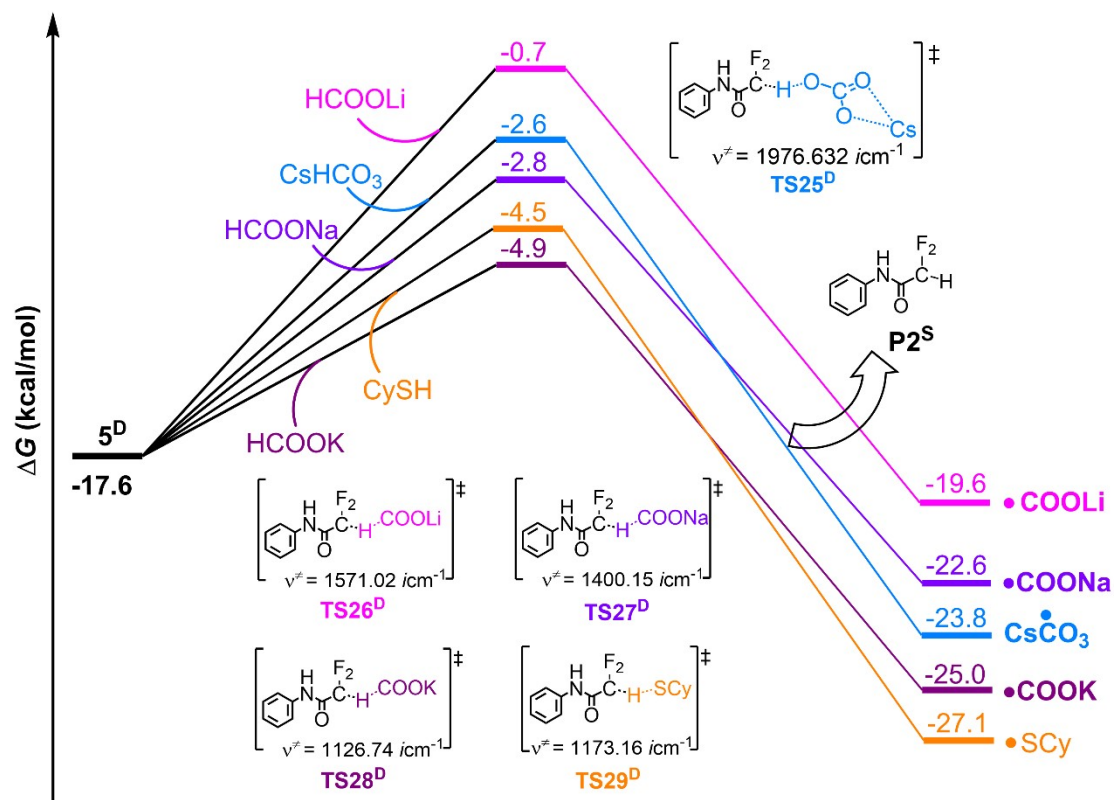


Figure S9 Different paths of N-phenyl-2,2,2-difluoromethylacetamide radical 5^D hydrodefluorination.

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