

Direct Chemical Dynamics Simulations of the $\text{CH}_3\text{O}^- + \text{CH}_3\text{I}$ System: Substitution vs Proton Transfer

Supporting Information

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Opacity Function

Variation of the opacity function with respect to impact parameter for the PBE0 (180 trajectories) and PM6 method (10000 trajectories) at collision energy of 1.6 eV is shown in the Figure below.

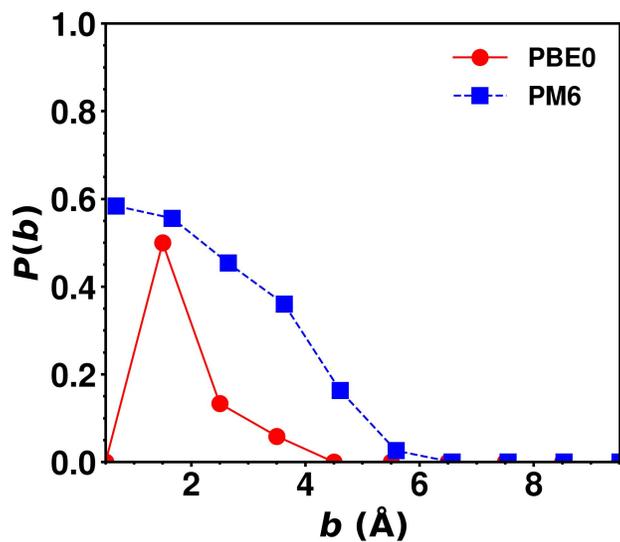


Figure S1: Variation of the opacity function with respect to the impact parameter computed using PBE0/aug-cc-pVDZ/ECP level of theory and PM6 method.

PES Scan

Potential energy scan plots as the reactants approach each other computed using the density functional PBE0/aug-cc-pVDZ/ECP and semi-empirical PM6 methods.

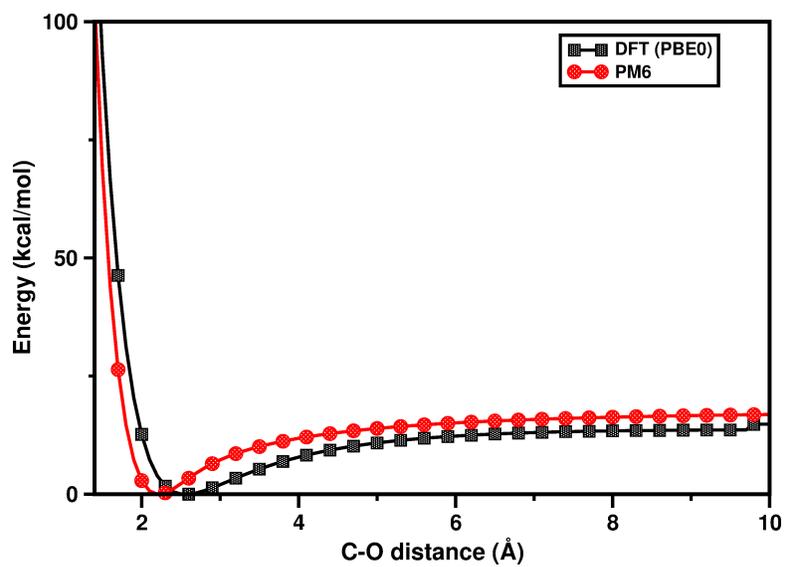


Figure S2: Potential energy scan as the reactants approach each other.

Comparison of Simulation and Experimental data

Product branching ratios, energies, and scattering angles computed in the present work are compared with experimental data in the Figures below. The experimental data are reproduced from *Faraday Discuss.* **2024**, 251, 573-586, with permission from the Royal Society of Chemistry.

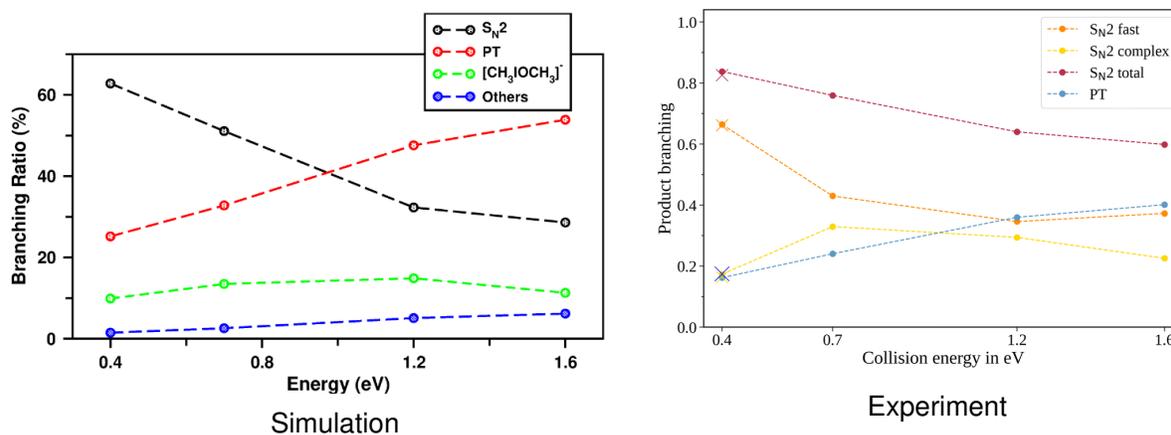


Figure S3: Experimental (right) and simulation (left) product branching ratios as a function of collision energy. Experimental data are reproduced from *Faraday Discuss.* **2024**, 251, 573-586, with permission from the Royal Society of Chemistry.

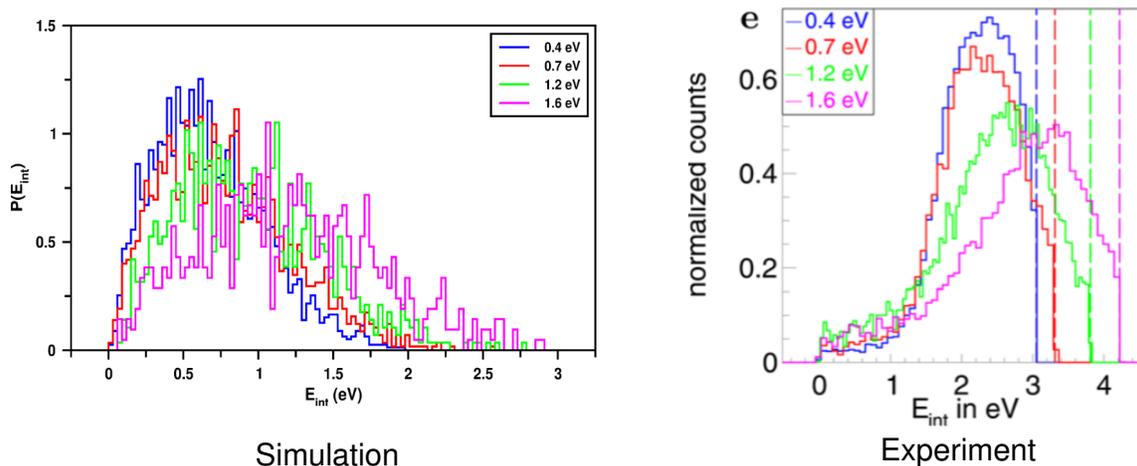


Figure S4: Experimental (right) and simulation (left) product energies at different collision energies. Experimental data are reproduced from *Faraday Discuss.* **2024**, 251, 573-586, with permission from the Royal Society of Chemistry.

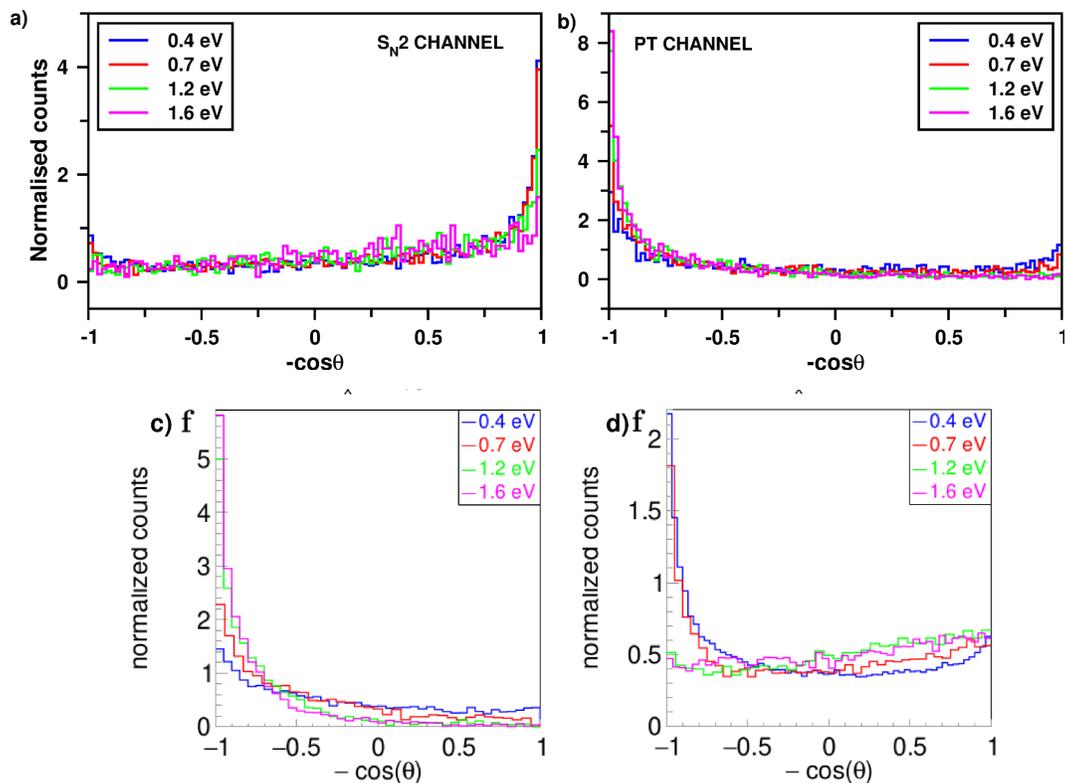
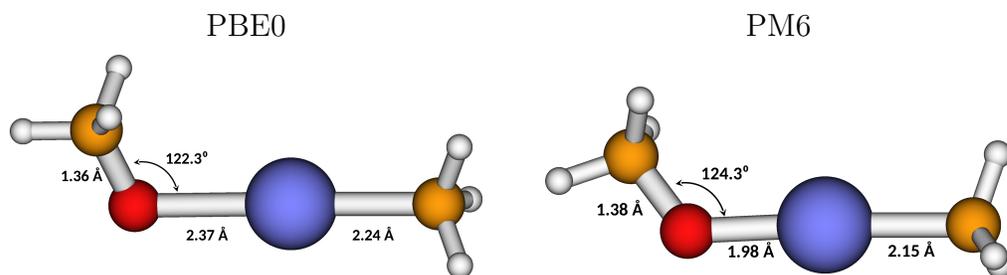


Figure S5: Experimental (bottom) and simulation (top) product scattering angle distributions at different collision energies. Experimental data are reproduced from *Faraday Discuss.* **2024**, 251, 573-586, with permission from the Royal Society of Chemistry.

Optimized Structure of $[\text{CH}_3\text{IOCH}_3]^-$

The structure of $[\text{CH}_3\text{IOCH}_3]^-$ intermediate optimized by PBE0/aug-cc-pVDZ/ECP and PM6 methods is presented below.



PES of Minor channels

The energies of the stationary points associated with several minor channels were calculated and shown in Figure below.

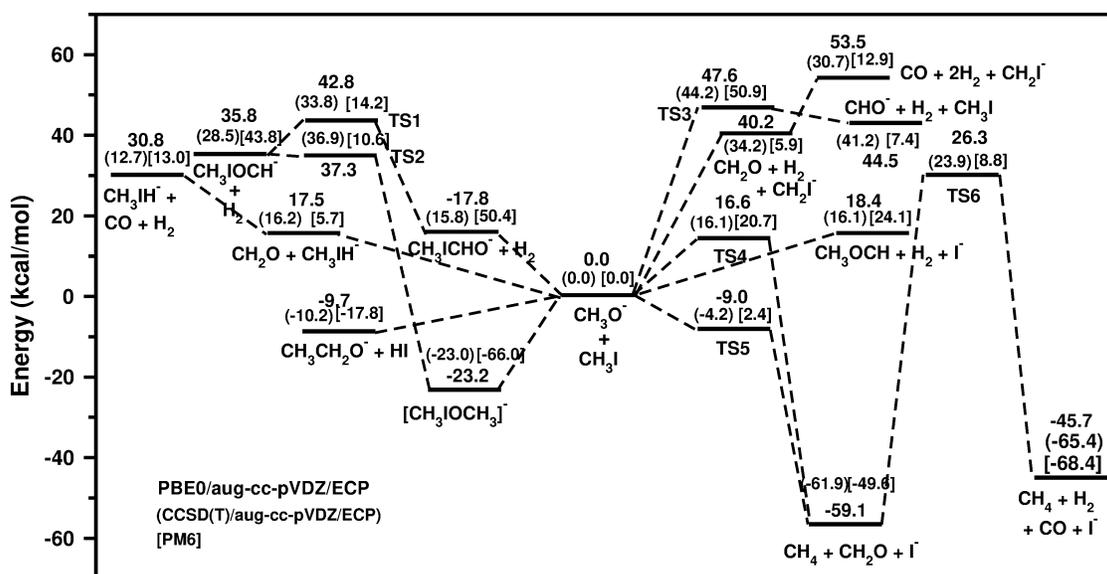


Figure S6: Potential energy diagram for minor channels computed using PBE0/aug-cc-pVDZ/ECP level of theory. CCSD(T) single point energies are given in brackets and PM6 energies are given in parentheses. All values are in kcal/mol relative to reactant energy and not zero point energy corrected.

$\text{CH}_4 + \text{CH}_2\text{O} + \text{I}^-$ Channel

Stationary point energies for the hydride transfer channel, computed using various methods, forming $\text{CH}_4 + \text{CH}_2\text{O} + \text{I}^-$ products are given below.

Table S1: Stationary point energies for the hydride transfer channel, computed using various methods, forming $\text{CH}_4 + \text{CH}_2\text{O} + \text{I}^-$ products are given below. Given energies are in kcal/mol and relative to that of the reactants.

Species	B3LYP	B3LYP-D3	PBE0	PBE0-D3	ω -B97	ω -B97-D3	MPW1K	M06-2X	MP2	CCSD(T)	PM6
$\text{CH}_3\text{O}^- + \text{CH}_3\text{I}$	0	0	0	0	0	0	0	0	0	0	0
TS4	15.3	12.5	16.6	14.9	27.1	23.8	24.5	21.6	23.8	16.1	20.7
TS5	-9.1	-7.6	-9.0	-10.1	-2.1	-4.7	-4.6	-5.4	-2.7	-4.2	2.4
$\text{CH}_4 + \text{CH}_2\text{O} + \text{I}^-$	-61.9	-60.9	-59.1	-58.6	-62.6	-61.6	-62.3	-62.0	-62.3	-61.9	-49.6

Internal Energy Distribution of Proton Transfer Channel

Internal energy distribution of proton transfer (PT) products, computed without zero-point energy constraint, is presented in Figure S7(a). Soft ZPE constraint was applied, wherein trajectories with a total vibrational energy of CH_3OH and CH_2I^- less than the corresponding sum of zero-point energies were excluded. This action significantly diminished the number of trajectories under evaluation. The plot is illustrated in Figure S7(b).

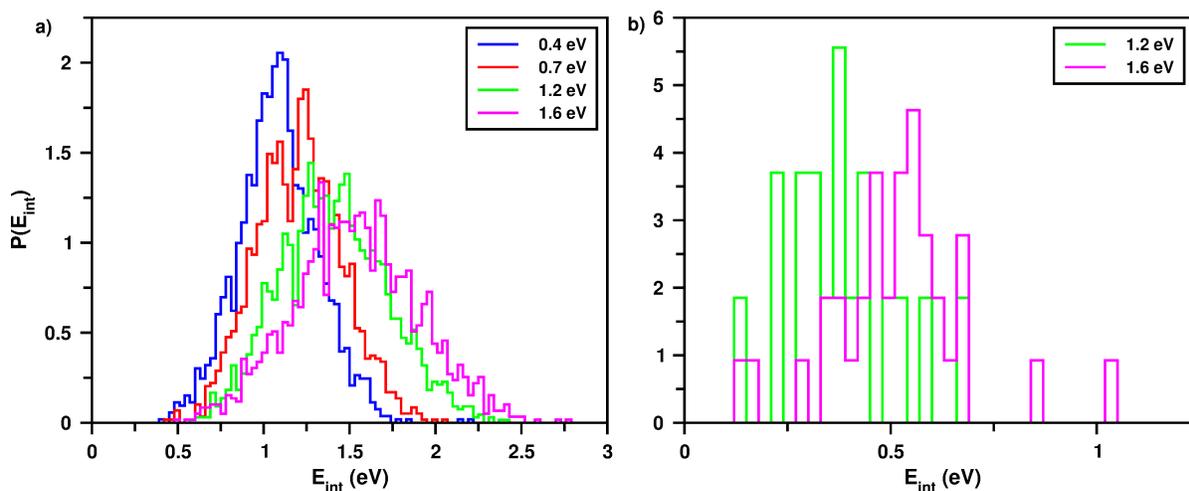
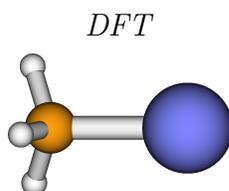


Figure S7: Internal energy distribution of PT channel (a) without ZPE and (b) with ZPE constraint.

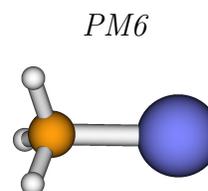
Cartesian Coordinates of Relevant structures

The optimized geometries of the stationary points obtained using PBE0/aug-cc-pVDZ/ECP theory and PM6 method are presented below. The Cartesian coordinates are given in Angstroms unit.

1. CH₃I

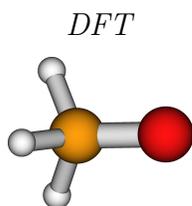


C 0.00000000 0.00000000 -1.72626259
I 0.00000000 0.00000000 0.41460864
H -0.80946134 0.65429164 -2.05886457
H 0.97136385 0.37386826 -2.05886457
H -0.16190251 -1.02815990 -2.05886457

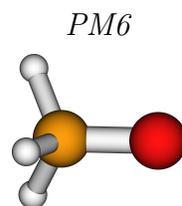


C 0.000180783 0.000280654 -1.708321376
I 0.000003440 0.000016612 0.423193145
H -0.801761834 0.645969975 -2.066179421
H 0.961631258 0.368945185 -2.065977866
H -0.160532101 -1.016070405 -2.066889153

2. CH₃O⁻

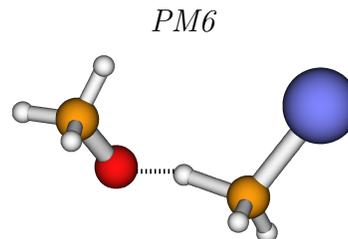
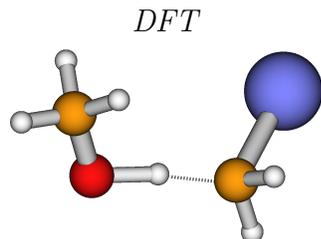


C -0.02212569 -0.50998572 0.07334371
H -0.45639029 -1.21466826 -0.71559835
H 0.99637054 -0.98172414 0.29260976
H -0.62593279 -0.78051907 1.00607459
O -0.00441462 0.78232400 -0.25084939



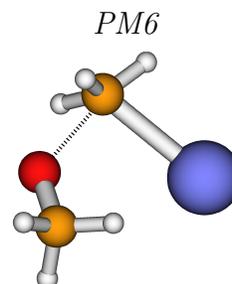
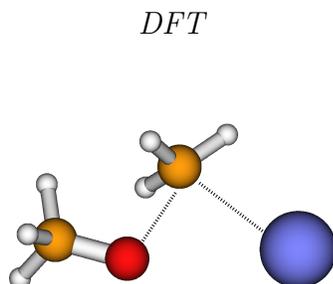
C -0.022565831 -0.534365054 0.079771328
H -0.457837946 -1.164498771 -0.725112228
H 0.995811785 -0.932779261 0.274468182
H -0.619688628 -0.734648370 0.994179671
O -0.006807252 0.768796662 -0.244597809

3. TS_{PT}



C 1.24422223 -0.62968114 0.05867540	C 0.000000000 0.000000000 0.000000000
I 0.11779415 1.18265539 -0.52731998	I 2.150172273 0.000000000 0.000000000
O 0.25092871 -2.92672235 -0.66258768	O -1.172521579 2.386896799 0.000000000
C -0.91788967 -3.17415472 0.01978602	C -0.854513112 3.175157598 -1.091057323
H -0.90272013 -2.79342824 1.06996854	H 0.221343527 3.404598946 -1.110773134
H -1.82028362 -2.71482790 -0.45230027	H -1.122597260 2.672816459 -2.032650249
H 0.64606700 -1.83916582 -0.34623060	H -0.462690382 1.245019720 -0.028292410
H 2.22349729 -0.44418658 -0.41700070	H -0.366698019 -0.455792912 -0.889056514
H 1.38255904 -0.46243903 1.14179039	H -0.372938708 -0.389063365 0.918433444
H -1.13002616 -4.26409735 0.09303159	H -1.417792230 4.115449666 -1.018643860

4. TS_f

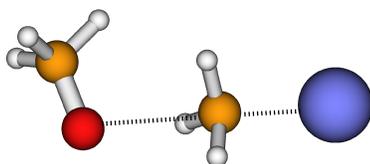


C -1.35451423 -1.05662833 -0.24056245	C 0.000000000 0.000000000 0.000000000
O 0.69943917 -1.52878059 0.05281644	O 1.995241034 0.000000000 0.000000000
C 0.78195584 -2.78423845 -0.43643001	C 2.839433551 1.083786559 0.000000000
I -0.51213457 1.22020175 0.90862901	I -0.041688179 1.929885783 1.545979467
H -1.40782233 -1.94464135 0.38581023	H 0.315589069 0.187421863 -1.017652357

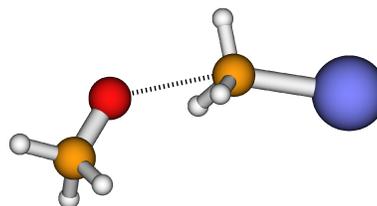
H -2.24201772 -0.42794006 -0.16636951	H 0.353085165 -0.920056622 0.453318680
H -1.01947947 -1.21029769 -1.26416213	H -1.049227748 0.194535158 0.171276556
H -0.21855398 -3.15416185 -0.82232347	H 3.456938495 1.078177426 -0.910988620
H 1.08934836 -3.55582048 0.31538136	H 3.497301826 1.056580873 0.880493413
H 1.47182281 -2.89605382 -1.31197671	H 2.263341577 2.026739684 0.029064202

5. TS_b

DFT



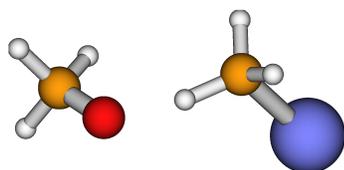
PM6



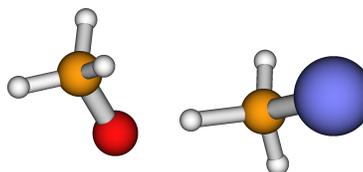
C 0.63923712 0.82792492 -0.16900447	C 0.000000000 0.000000000 0.000000000
O 0.58978202 3.23850300 0.87660649	I 2.198630166 0.000000000 0.000000000
C -0.34618005 3.92823646 0.19246904	O -2.101163430 1.250648467 0.000000000
I -0.02732589 -1.29352842 -0.29282630	C -2.639545518 1.726871968 -1.156874489
H 0.16551954 1.37035078 0.66214616	H -0.331351763 -0.504048069 -0.892867442
H 1.72002934 0.76768972 -0.03216020	H -0.340291086 -0.474001190 0.906544300
H 0.37065590 1.26017249 -1.13436004	H -0.458603300 1.053543896 -0.012887819
H -1.11823402 3.28714983 -0.33556761	H -2.510586426 2.820891378 -1.238146971
H 0.05763619 4.59255438 -0.62913685	H -3.720979631 1.510626019 -1.198753230
H -0.97180585 4.62411068 0.82523200	H -2.170633854 1.267069025 -2.045080788

6. $\text{CH}_3\text{O}^- \dots \text{HCH}_2\text{I}$

DFT



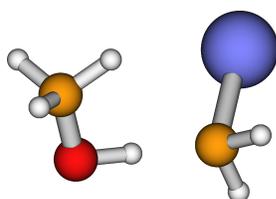
PM6



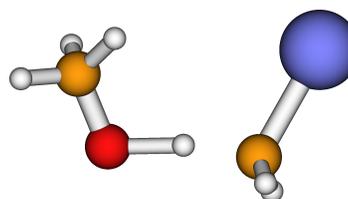
C 1.08738084 -0.59538438 0.30797250	C 0.000000000 0.000000000 0.000000000
I -0.05850057 1.22222638 -0.07122001	I 2.150170000 0.000000000 0.000000000
O 0.19908549 -3.02022092 -0.60491966	O -1.172520026 2.386889917 0.000000000
C -0.63092083 -3.53800170 0.33000241	C -0.854510135 3.175159529 -1.091059584
H -0.81576323 -2.85920696 1.21610607	H 0.221349740 3.404599504 -1.110779616
H -1.66675869 -3.77911318 -0.04532642	H -1.122600018 2.672809653 -2.032649173
H 0.58701264 -1.53672429 -0.14874303	H -0.462689996 1.245019878 -0.028300001
H 2.06768646 -0.39612275 -0.14063242	H -0.366700005 -0.455789932 -0.889059884
H 1.17885630 -0.63850958 1.39953663	H -0.372940034 -0.389070083 0.918430115
H -0.27205088 -4.50186133 0.79458454	H -1.417790335 4.115449863 -1.018649687

7. $\text{CH}_3\text{OH} \dots \text{CH}_2\text{I}^-$

DFT



PM6

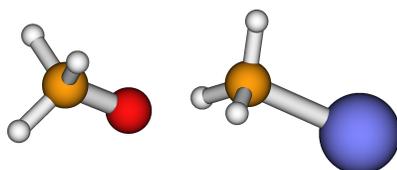


C 1.24802070 -0.61781413 0.30173831	C 0.000000000 0.000000000 0.000000000
I -0.14088198 1.10969519 0.02528037	I 2.148676304 0.000000000 0.000000000
O 0.31774612 -3.00859804 -0.49727978	O -1.128078917 2.406913945 0.000000000
C -0.79662412 -3.25312958 0.29273255	C -0.286689206 3.452541494 0.344252024
H -0.91779939 -2.47980382 1.07793045	H 0.546062883 3.108572091 0.973145379
H -1.73995925 -3.26257597 -0.29508085	H 0.127996450 3.918746300 -0.561903106

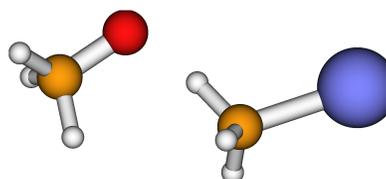
H 0.67670798 -2.03574127 -0.22273584	H -0.465803944 1.254935940 0.031674961
H 2.13201748 -0.24272219 -0.25115886	H -0.377563229 -0.371232721 -0.922481640
H 1.50394771 -0.48998491 1.37252961	H -0.374368514 -0.453104220 0.885591382
H -0.72918113 -4.23542677 0.80645317	H -0.864023114 4.206319987 0.897198367

8. $[\text{CH}_3\text{O}^- \dots \text{CH}_3\text{I}]_f$

DFT



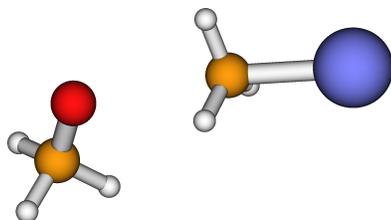
PM6



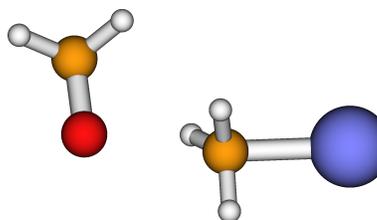
C -0.92797927 0.66856146 0.04016373	C 0.000000000 0.000000000 0.000000000
O 0.73644539 2.87283548 0.04481349	I 2.149250354 0.000000000 0.000000000
C -0.12721994 3.90668917 -0.04749275	O -1.220684645 2.366281823 0.000000000
I 0.09164950 -1.24866782 -0.00305838	C -2.565357962 2.083515686 -0.124121053
H -1.57146553 0.65858368 -0.84716806	H -0.365923245 -0.427560259 -0.905001512
H -1.54158861 0.63391378 0.94786617	H -0.366763505 -0.427335016 0.904850471
H -0.14456032 1.52532480 0.04062201	H -0.463530107 1.230076752 0.001163701
H -1.21919987 3.60393489 -0.10977613	H -2.751321317 1.001335480 -0.196753988
H 0.01825857 4.56591234 -0.95293170	H -2.964420010 2.568596107 -1.028860766
H -0.09996265 4.62598901 0.82294407	H -3.109057032 2.474139181 0.750495989

9. $[\text{CH}_3\text{O}^- \dots \text{CH}_3\text{I}]_b$

DFT



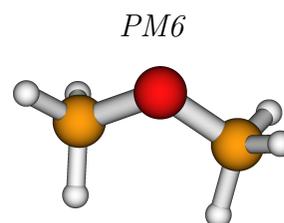
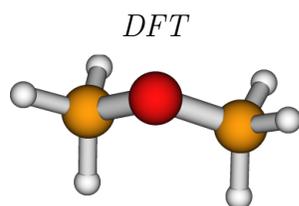
PM6



C 1.06419779 0.62402022 -0.27052688	C 0.000000000 0.000000000 0.000000000
O 0.18543291 3.06047809 0.62085365	I 2.147849289 0.000000000 0.000000000

C -0.55109922 3.62532192 -0.36388958	O -1.127632787 2.409358019 0.000000000
I -0.16227972 -1.16153316 -0.00966239	C -0.652665425 3.159331928 1.063321857
H 0.55937300 1.57415560 0.16243871	H -0.070203539 2.539973708 1.759889837
H 2.00061619 0.38777352 0.24831218	H -0.009146010 3.969638885 0.690227476
H 1.24032978 0.67918027 -1.35111938	H -0.470805684 1.250886610 -0.083557919
H -0.70774224 2.96223444 -1.26708360	H -0.373733057 -0.491011814 -0.866068027
H -0.11371786 4.57300546 -0.79326921	H -0.371571786 -0.343232193 0.936354795
H -1.59704843 3.91565004 -0.05801466	H -1.504000167 3.599574335 1.600101232

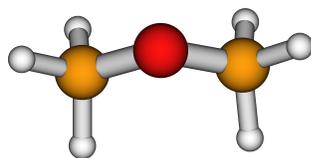
10. $[\text{CH}_3\text{OCH}_3\cdots\text{I}^-]_{f/b}$



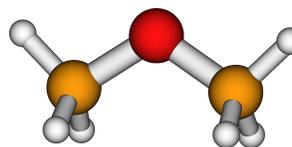
C 1.09708713 -2.50311419 0.11003924	C 0.000000000 0.000000000 0.000000000
O 0.40189395 -3.67206527 -0.26821543	O 1.443900803 0.000000000 0.000000000
C -0.97254782 -3.56542807 0.03580535	C 2.001683930 1.331190845 0.000000000
I -1.74214914 0.53649601 -0.82579625	I -0.970025007 3.377457163 1.325408053
H 0.64262356 -1.60025933 -0.33146391	H -0.409111418 0.893659340 0.529150062
H 2.13240447 -2.61367403 -0.23902891	H -0.265277422 -0.914325274 0.530745442
H 1.10064794 -2.38241537 1.21032258	H -0.347716244 -0.011547318 -1.033355184
H -1.41612964 -2.65713037 -0.40563237	H 1.439205399 1.992904510 0.690490867
H -1.13500094 -3.52966898 1.13011708	H 1.961486787 1.738924798 -1.011761081
H -1.46482651 -4.46022645 -0.36785939	H 3.026601958 1.179235673 0.338386742

11. CH_3OCH_3

DFT



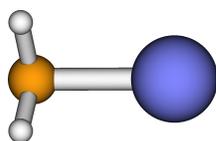
PM6



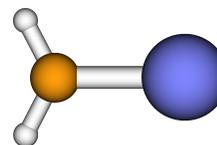
C 1.16501528 0.00000000 0.19920963	C 1.203738809 0.000018929 0.217675959
H 1.21791770 -0.89645772 0.84363873	H 1.264170497 -0.902047674 0.832620504
H 2.02253240 0.00000000 -0.48357698	H 1.989098630 0.000055197 -0.549079559
H 1.21791770 0.89645772 0.84363873	H 1.264049203 0.902108640 0.832701641
O 0.00000000 0.00000000 -0.58577300	O 0.000081650 -0.000087209 -0.570300997
C -1.16501528 0.00000000 0.19920963	C -1.203858254 0.000026519 0.217601516
H -1.21791770 0.89645772 0.84363873	H -1.264032245 0.901931329 0.832399546
H -1.21791770 -0.89645772 0.84363873	H -1.264141273 -0.901952872 0.832261771
H -2.02253240 0.00000000 -0.48357698	H -1.989057788 0.000095951 -0.548384093

12. CH_2I^-

DFT



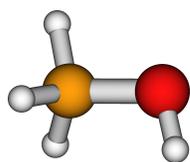
PM6



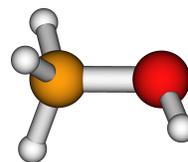
C -0.21085670 1.96061292 0.00000000	C 0.062213652 1.791170973 0.000064078
H 0.45745780 2.17651793 -0.86992152	H 0.081462098 2.263410169 -0.918072079
H 0.45745780 2.17651793 0.86992152	H 0.081494808 2.263645908 0.917973594
I 0.03342869 -0.31064990 0.00000000	I 0.014428790 -0.303683755 -0.000010936

13. CH_3OH

DFT



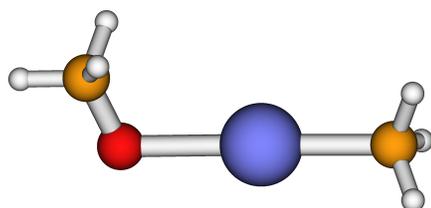
PM6



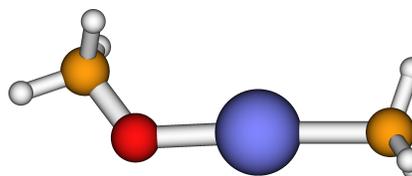
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H 0.51116909 1.04772532 -0.89735178	H 0.511558080 1.031437414 -0.905014745
H -1.02821649 1.03903350 0.00000000	H -1.043656311 1.008140617 -0.000148160
H 0.51116909 1.04772532 0.89735178	H 0.511563513 1.031456162 0.904537577
O -0.08304035 -0.75194208 0.00000000	O -0.084073804 -0.748864008 -0.000066988
H 0.80739664 -1.11254593 0.00000000	H 0.813017036 -1.136337482 0.000083320

14. $[\text{CH}_3\text{IOCH}_3]^-$

DFT



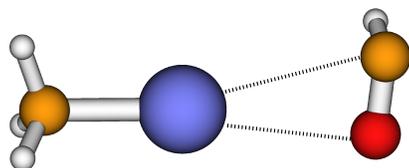
PM6



C 0.35240152 -2.61965106 -0.00023613	C 0.262327784 -2.440616538 -0.002112286
I -0.06074210 -0.41613401 -0.00189747	I -0.034917855 -0.313248572 -0.003163575
H -0.22315149 -3.10134961 0.80228907	H -0.336273874 -2.868249815 0.782151624
H 1.42429326 -2.79413374 0.16583379	H 1.303754009 -2.644569582 0.168812821
H 0.05916787 -3.05090100 -0.96736930	H -0.043196230 -2.828410524 -0.957330369
C 0.61496799 2.66452510 0.00029353	C 0.585011861 2.615967749 -0.002553248
H 1.27559867 2.49639426 0.89254300	H 1.213688850 2.533064685 0.896461681
H 0.39144640 3.76065675 -0.00015633	H 0.081336808 3.592553728 -0.004845050
H 1.28115804 2.49677845 -0.88786342	H 1.219560547 2.532323001 -0.897345334
O -0.52334819 1.91059500 -0.00340405	O -0.395287808 1.642930333 -0.004843454

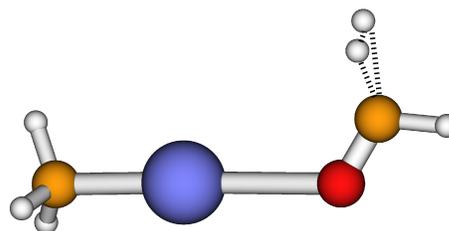
The optimized geometries of the stationary points associated with minor channel in Figure S6, obtained using PBE0/aug-cc-pVDZ/ECP theory, are presented below. The cartesian coordinates are given in Angstroms unit.

TS1



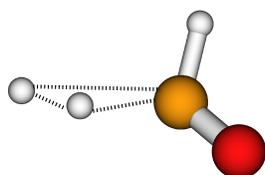
C -0.03973898 -2.53925840 -0.09062399
H 0.65160494 -2.96909434 0.64209835
H -1.06152290 -2.88099633 0.10490054
H 0.26397474 -2.81305153 -1.10679978
I 0.01199650 -0.37701682 0.08503259
C -0.69005971 2.87170336 0.05450258
H -1.17009013 2.82014558 -1.05485647
O 0.52786030 2.67429174 0.01184391

TS2



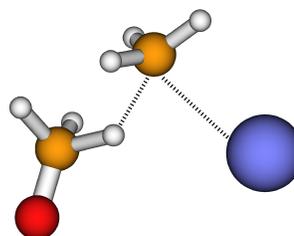
C -0.34666991 -2.55912943 -0.13290401
H -0.11242395 -2.97732094 0.85223015
H -1.40322093 -2.72809800 -0.36896969
H 0.28678102 -3.02540635 -0.89554054
I 0.03240231 -0.41954466 -0.09890275
C -0.37474561 2.99640743 -0.28920867
H -0.04108172 4.10082512 -0.32058366
O 0.54850176 2.19959568 -0.06818503
H -2.09810669 3.41432798 1.12443878
H -1.58298399 3.02427296 0.31357712

TS3



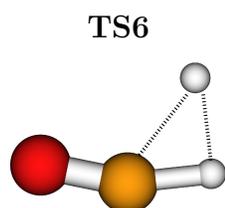
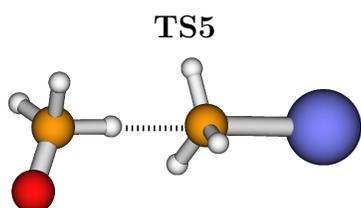
C -0.24034873 -0.33840103 -0.09277581
H -1.19464240 -0.63568987 0.54977946
H 1.11034046 -2.30941228 0.25193854
H 0.63042757 -1.55069442 -0.11031734

TS4

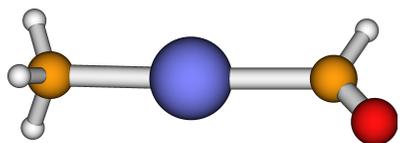


C -1.76923972 -0.68779305 0.05304752
H -2.30812012 0.25292210 -0.04332814
H -1.86967920 -1.13754184 1.04288256
H -1.95344862 -1.36593315 -0.78642820

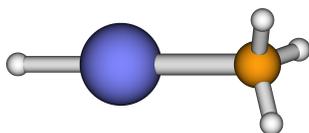
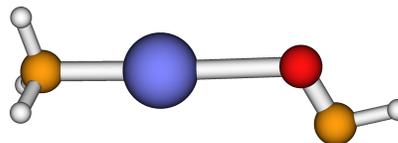
O 0.08540055 0.83977218 0.00014645 I 0.20290579 1.13674613 -0.08245858
 C -0.14460778 -2.85814849 -0.10256694
 H -0.34066575 -1.68429646 0.03684887
 H -1.04295464 -3.21588062 0.49572308
 H -0.40254455 -2.94451438 -1.20286498
 O 1.01844564 -3.27554313 0.26843153



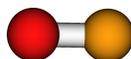
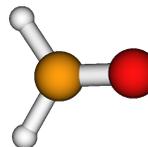
C -0.23435054 -0.89295956 0.00000000 C 0.21045849 0.44303911 0.00000000
 H 0.27213748 -1.17039786 -0.92032975 H 0.09075327 1.54342523 0.00000000
 H 0.27213748 -1.17039786 0.92032975 H -1.16654631 1.33634693 0.00000000
 H -1.31732522 -0.97746043 0.00000000 O -0.02208818 -0.70002159 0.00000000
 C -0.49696914 -3.99184007 0.00000000
 H -0.40101150 -2.81879618 0.00000000
 H -1.16559750 -4.14697824 -0.90273936
 H -1.16559750 -4.14697824 0.90273936
 O 0.64996440 -4.62646505 0.00000000
 I 0.02719854 1.46028530 0.00000000



C 0.22527850 -2.65819618 -0.00596871	H -0.71014744 -3.10377195 0.09772852
H 0.93852107 -2.94875595 0.78157477	C 0.29704954 -2.67066790 0.08052601
H -0.75130577 -3.13170845 0.18181467	H 0.85631111 -3.06233402 -0.77777484
H 0.60925217 -2.97412726 -0.98891346	H 0.82405525 -2.91772899 1.01005272
I -0.03721947 -0.27150961 0.00131628	I 0.14338093 -0.49052472 -0.10035561
C -0.37645587 2.12571828 -0.00350962	O -0.09428967 2.08245982 -0.33471111
H -1.48777581 2.44684189 -0.01576215	C 0.93670077 2.78239435 -0.29780708
O 0.44341984 3.02343643 -0.00098706	H 0.60371190 3.91549799 -0.42703194

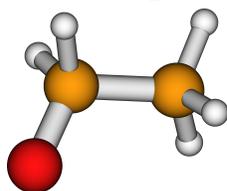


C 0.00000000 0.00000000 -1.98335300	H 0.00000000 -0.94630475 1.10283266
H -0.92078736 0.48541947 -2.34866365	C 0.00000000 0.00000000 0.51515900
H 0.04000809 -1.04013498 -2.34866365	H 0.00000000 0.94630475 1.10283266
H 0.88077927 0.55471551 -2.34866365	O 0.00000000 0.00000000 -0.68806231
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H 0.00000000 -0.00000000 2.37905901	

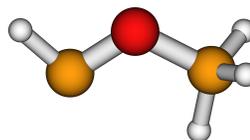
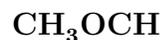


C -0.64592327 -0.02109310 0.00000000	H -0.37744888 -0.01479075 -0.04588249
O 0.48484899 0.01583310 0.00000000	H 0.37744888 0.01479075 0.04588249

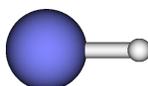




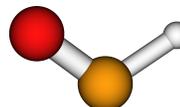
C 0.13564649 1.04062346 0.21222173
H 0.92378028 1.28337881 -0.52037488
H -0.64553377 1.82740493 0.17571165
C -0.44205078 -0.36559348 -0.09216518
H 0.59880826 1.04131839 1.21335774
H -0.98198226 -0.24484396 -1.09257194
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O 0.45695207 -1.34702065 -0.06063300



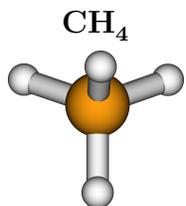
C -0.09056784 -1.14302597 0.15821313
H -1.16877708 -1.10302785 -0.03364554
H 0.43548038 -1.72333577 -0.60826567
O 0.43331656 0.19825790 0.11834087
H 0.12848183 -1.55133308 1.15134688
C -0.42338661 1.14182307 -0.11963313
H 0.22426669 2.06056094 -0.09738380



H 0.00000000 0.00000000 -1.60104691
I 0.00000000 0.00000000 0.01215802



H -0.82603838 1.25592138 0.00000000
C 0.23036800 0.59153640 0.00000000
O -0.03180018 -0.61093428 0.00000000



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C 0.00000007 0.00000049 0.00000002
H 1.09596396 -0.00000355 0.00000145
H -0.36531327 1.02094614 0.15922588
H -0.36531893 -0.64836557 0.80454871
H -0.36532183 -0.37257252 -0.96377606

```

Comparison of single point energies

Single point energies for various stationary and non-stationary points were computed using the CCSD(T)/aug-cc-pVDZ/ECP method and compared with the PM6 energies of the same points in Figure S8. Good agreement was found between the PM6 approach and the benchmark CCSD(T) level.

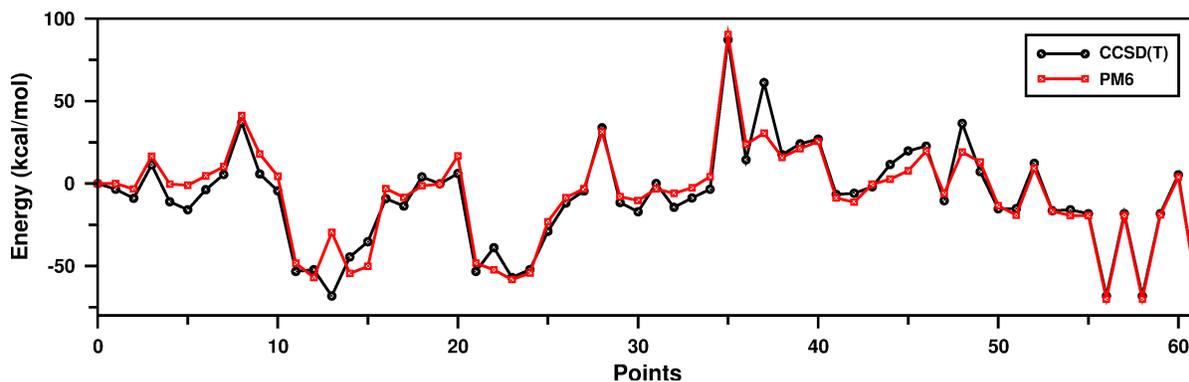
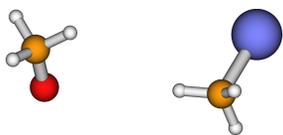
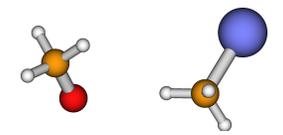
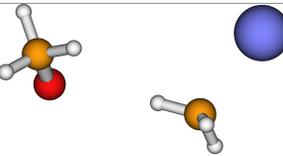
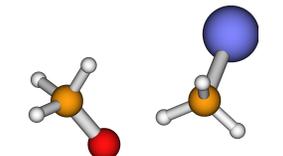
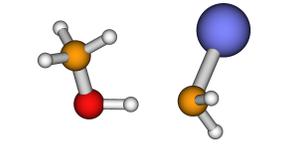
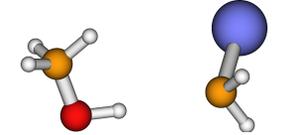
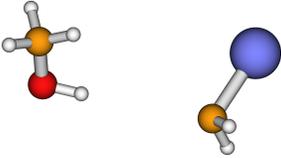
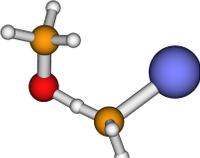
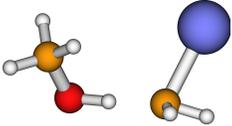
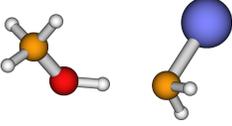
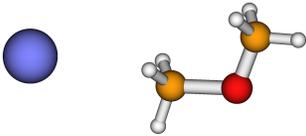
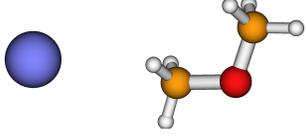
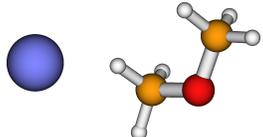


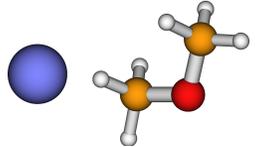
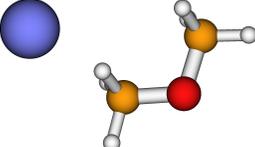
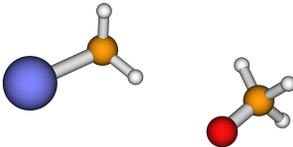
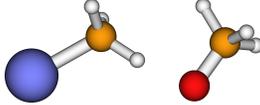
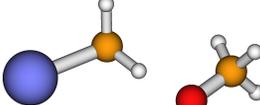
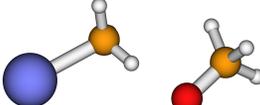
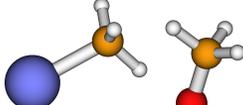
Figure S8: Comparison of single point energy of several stationary and non-stationary points using CCSD(T)/aug-cc-pVDZ/ECP level and PM6 method.

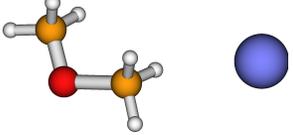
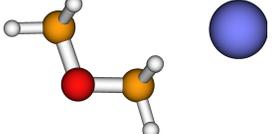
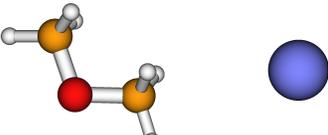
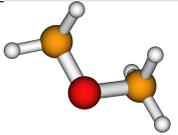
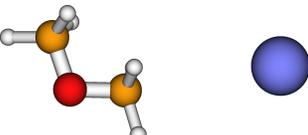
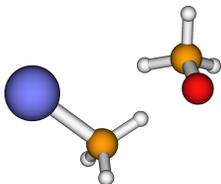
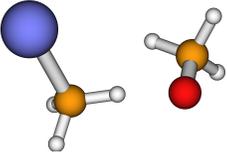
Figure above presents a comparison of single point energy of several stationary and non-stationary points using CCSD(T)/aug-cc-pVDZ/ECP level and PM6 method. The non-stationary points were generated by systematically perturbing relevant bond distances and bond angles from the equilibrium geometries, thereby sampling representative regions of the

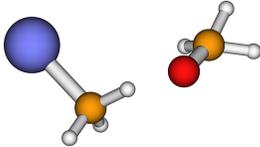
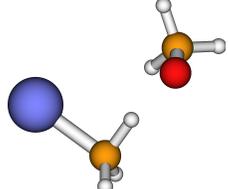
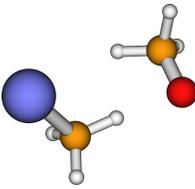
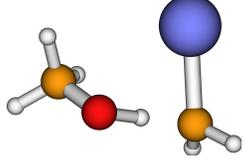
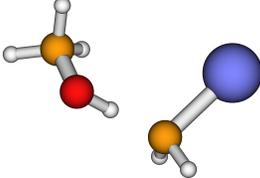
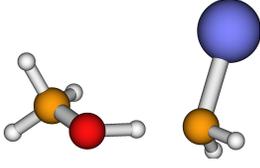
potential energy surface. The structures used here, along with their PM6 and CCSD(T) energies relative to the reactant energy, are provided below.

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	-0.02	-3.46
	-3.29	-8.91
	16.54	11.33
	-0.29	-10.96
	-1.03	-15.85
	4.58	-3.68

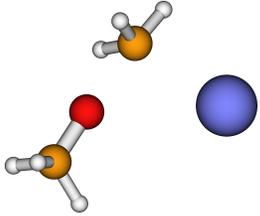
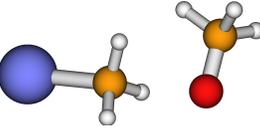
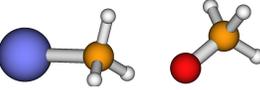
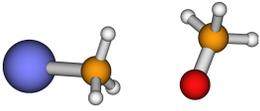
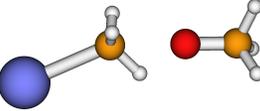
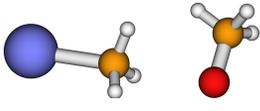
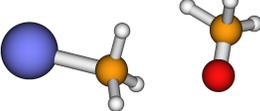
Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	10.20	5.50
	41.26	37.03
	17.98	5.85
	4.42	-4.38
	-48.26	-53.28
	-56.94	-52.21
	-29.57	-68.14

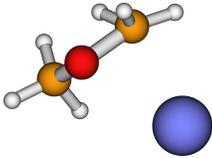
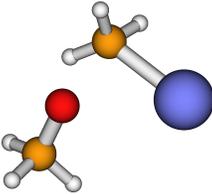
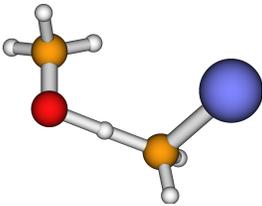
Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	-54.43	-44.50
	-50.21	-35.28
	-3.05	-9.13
	-8.30	-13.63
	-1.36	4.07
	-0.34	-0.13
	16.80	6.09

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	-48.27	-53.28
	-52.29	-38.82
	-58.22	-56.92
	-54.32	-52.13
	-23.07	-28.94
	-8.52	-11.78
	-3.12	-4.51

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	31.27	33.85
	-7.91	-11.51
	-10.30	-17.08
	-3.14	-0.01
	-5.94	-14.45
	-2.58	-8.76

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	4.15	-3.46
	90.32	87.21
	23.88	14.43
	30.52	61.12
	15.93	17.45
	21.15	24.10

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	25.53	26.94
	-8.71	-6.58
	-11.28	-5.89
	-0.43	-1.99
	2.66	11.62
	7.72	19.82
	19.65	22.72

Structure	PM6 Energy kcal/mol	CCSD(T) Energy kcal/mol
	-6.07	-10.37
	19.12	36.48
	13.02	7.20
	-13.38	-15.28