Supporting Information

Dynamics studies for the multi-well and multi-channel reaction of OH with C_2H_2 on a full-dimensional global potential energy surface

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Table S1. Comparison of the energies (kcal/mol) of different basis sets at stationary points for the C_2H_2+OH reaction. The geometries of stationary points were based on the geometry optimization results under the UCCSD(T)-F12b/cc-pVTZ-F12 method and the energies are relative to the corresponding reactant energies.

Basis set	R	P1	P2	P3	P4	P5	Int1a
cc-pVDZ-F12	0.000	13.800	13.229	−17.620	−20.791	−56.443	−35.504
cc-pVTZ-F12	0.000	13.808	13.070	−17.486	−20.664	−55.704	−35.617
cc-pVQZ-F12	0.000	13.670	12.911	−17.464	−20.660	−55.567	−35.731
aug-cc-pV5Z	0.000	13.633	12.875	−17.432	−20.651	−55.485	−35.778
Basis set	Int1b	Int1c	Int1d	Int2	Int3	Int4	TS1
cc-pVDZ-F12	−34.086	−33.061	−32.374	−62.910	−39.493	−70.044	0.747
cc-pVTZ-F12	−34.206	−33.159	−32.446	−62.974	−39.549	−69.980	0.631
cc-pVQZ-F12	−34.316	−33.268	−32.552	−63.003	−39.634	−69.981	0.580
aug-cc-pV5Z	−34.360	−33.321	−32.597	−63.034	−39.670	−69.997	0.588
Basis set	TS2	TS3	TS4a	TS4b	TS5a	TS5b	TS6
cc-pVDZ-F12	19.464	2.753	14.145	16.530	15.781	17.656	−1.671
cc-pVTZ-F12	19.234	2.485	13.815	16.160	15.459	17.328	−1.887
cc-pVQZ-F12	19.152	2.439	13.688	16.023	15.318	17.172	−1.947
aug-cc-pV5Z	19.118	2.423	13.633	15.964	15.279	17.130	−1.969
Basis set	TS7	TS8	TS9	TS10	TS11	TS12	TS13
cc-pVDZ-F12	−19.591	−14.688	15.042	37.898	15.935	−2.929	−18.096
cc-pVTZ-F12	−19.826	−14.721	14.946	37.728	15.630	−3.022	−18.146
cc-pVQZ-F12	−19.869	−14.713	14.915	37.682	15.488	−3.062	−18.166
aug-cc-pV5Z	−19.912	−14.714	14.900	37.656	15.451	−3.067	−18.171
Basis set	TS14	TS15	TS16	TS17	TS18	TS19	C1
cc-pVDZ-F12	−51.025	−5.232	−31.210	−30.162	−29.962	−28.905	−3.031
cc-pVTZ-F12	−50.570	−5.263	−31.423	−30.244	−30.027	−29.085	−3.061
cc-pVQZ-F12	−50.497	−5.249	−31.580	−30.339	−30.118	−29.233	−3.019
aug-cc-pV5Z	−50.450	−5.249	−31.630	−30.386	−30.161	−29.286	−3.032

Table S2. Harmonic vibrational frequencies (cm^{-1}) of the stationary points for the C_2H_2+OH reaction.

Species	Methods	Frequencies
C_2H_2	PES	3499.88, 3399.29, 2007.81, 744.10, 744.04, 604.65, 604.64
	Ab initio	3502.99, 3411.01, 2007.49, 748.88, 748.88, 616.29, 616.29
OH	PES	3748.13
	Ab initio	3740.38
C_2H	PES	3444.56, 1916.52, 351.20, 351.19
	Ab initio	3445.17, 2021.27, 351.02, 351.02
H_2O	PES	3966.77, 3841.25, 1659.33
	Ab initio	3943.31, 3833.31, 1651.18
HCCOH	PES	3816.54, 3472.86, 2233.24, 1277.49, 1066.46, 567.38, 561.88, 401.68, 376.86
	Ab initio	3818.91, 3478.61, 2242.20, 1272.66, 1069.28, 623.14, 538.72, 401.78, 368.48
HCCO	PES	3330.23, 2066.87, 1223.18, 557.09, 501.11, 499.99
	Ab initio	3325.18, 2061.97, 1226.78, 570.72, 515.73, 490.58
H_2	PES	4419.08
	Ab initio	4401.22
$OCCH_2$	PES	3293.57, 3192.14, 2187.64, 1416.00, 1150.85, 1017.39, 585.04, 512.07, 434.02
	Ab initio	3303.83, 3195.51, 2194.56, 1414.05, 1154.16, 991.11, 587.81, 518.70, 435.60
CH_3	PES	3296.18, 3296.13, 3121.74, 1427.62, 1427.60, 489.72
	Ab initio	3304.57, 3304.37, 3121.04, 1421.72, 1421.69, 508.79
CO	PES	2166.66
	Ab initio	2164.92
Int1a	PES	3810.09, 3308.99, 3134.69, 1666.59, 1378.33, 1253.34, 1104.21, 812.76, 807.07, 584.43, 476.18, 452.16
	Ab initio	3814.53, 3300.83, 3139.11, 1658.61, 1364.07, 1252.57, 1109.22, 825.96, 797.81, 587.43, 475.99, 452.88
Int1b	PES	3814.07, 3286.21, 3176.99, 1639.60, 1377.01, 1258.39, 1060.32, 887.98, 836.01, 575.23, 452.78, 431.15
	Ab initio	3822.31, 3279.77, 3198.19, 1641.33, 1363.01, 1254.50, 1065.14, 898.85, 814.50, 580.66, 444.83, 417.82
Int1c	PES	3884.02, 3298.47, 3095.31, 1695.28, 1332.91, 1301.09, 1109.14, 830.18, 764.85, 620.97, 484.07, 268.11
	Ab initio	3874.45, 3299.23, 3091.37, 1692.95, 1315.93, 1276.27, 1120.95, 796.15, 791.43, 617.22, 488.23, 259.48
Int1d	PES	3849.10, 3280.91, 3147.61, 1677.16, 1336.69, 1263.67, 1078.68, 852.89, 845.82, 614.84, 430.41, 246.08
	Ab initio	3862.23, 3291.90, 3153.76, 1675.52, 1328.74, 1258.71, 1082.57, 864.13, 831.65, 614.41, 439.85, 230.00

Int2	PES	3272.22, 3143.65, 2972.90, 1591.55, 1501.35, 1396.00, 1180.73, 987.62, 984.02, 691.51, 491.08, 420.58
	Ab initio	3276.58, 3155.51, 2983.46, 1576.88, 1475.67, 1401.30, 1162.29, 972.47, 965.32, 735.32, 500.13, 426.21
Int3	PES	3822.81, 3208.64, 3068.96, 1690.48, 1422.99, 1284.62, 1114.09, 933.37, 773.93, 712.52, 421.97, 107.97
	Ab initio	3823.94, 3250.27, 3116.13, 1697.19, 1409.49, 1244.39, 1131.33, 961.52, 814.58, 629.84, 443.04, 317.88
Int4	PES	3256.21, 3019.29, 3008.52, 1890.11, 1505.66, 1461.75, 1336.41, 1058.87, 870.52, 868.41, 417.51, 183.64
	Ab initio	3144.44, 3138.16, 3037.17, 1901.77, 1467.49, 1465.07, 1361.86, 1055.73, 959.24, 867.76, 469.02, 98.65
TS1	PES	3758.23, 3469.42, 3380.02, 1897.77, 789.24, 747.21, 704.29, 588.99, 557.83, 242.10, 91.56, 412.66i
	Ab initio	3754.36, 3476.45, 3398.34, 1908.13, 798.28, 738.15, 715.55, 603.52, 588.18, 237.79, 106.45, 402.72i
TS2	PES	3786.08, 3444.40, 1990.84, 1576.86, 1049.76, 570.30, 568.32, 423.30, 268.40, 120.42, 84.26, 1216.71i
	Ab initio	3783.18, 3437.62, 2028.71, 1627.14, 1166.53, 620.40, 596.44, 542.09, 327.86, 162.12, 112.35, 1330.53i
TS3	PES	3264.64, 3185.46, 1955.49, 1409.77, 1304.80, 1118.08, 989.86, 892.09, 845.53, 658.32, 272.38, 2366.74i
	Ab initio	3190.43, 3145.17, 2008.99, 1406.61, 1304.95, 1154.99, 1093.43, 1004.93, 892.37, 797.50, 315.62, 2165.96i
TS4a	PES	3854.60, 3220.37, 2280.82, 1717.16, 1249.86, 1006.69, 773.65, 569.38, 521.25, 369.05, 262.91, 1749.66i
	Ab initio	3829.47, 3180.40, 2313.63, 1786.67, 1259.74, 1012.72, 813.68, 602.26, 544.58, 464.69, 341.72, 1768.64i
TS4b	PES	3689.56, 3186.80, 2131.80, 1732.66, 1288.62, 978.75, 716.15, 515.01, 485.93, 293.64, 186.29, 2000.17i
	Ab initio	3709.56, 3173.30, 2324.33, 1777.08, 1283.77, 992.73, 789.86, 581.73, 514.34, 413.40, 307.24, 1830.44i
TS5a	PES	3799.66, 3436.90, 2115.63, 1272.26, 1058.37, 595.34, 559.28, 529.14, 466.17, 451.64, 215.28, 784.06i
	Ab initio	3783.63, 3462.34, 2147.53, 1280.27, 1062.79, 608.65, 543.94, 531.27, 449.24, 413.05, 246.45, 752.75i
TS5b	PES	3771.75, 3421.67, 2087.20, 1287.95, 1053.14, 599.25, 577.00, 537.49, 476.30, 441.95, 225.29, 937.04i
	Ab initio	3802.97, 3457.02, 2135.01, 1271.35, 1053.62, 595.81, 538.43, 516.69, 453.27, 417.38, 179.69, 880.49i
TS6	PES	3292.34, 3107.45, 2383.35, 1617.31, 1501.17, 1101.56, 986.23, 788.51, 598.90, 485.43, 362.64, 1832.00i
	Ab initio	3270.06, 3138.88, 2435.31, 1671.57, 1407.87, 1123.11, 955.37, 742.30, 558.16, 428.93, 389.46, 2026.53i

TS7	PES	3378.96, 3125.76, 2008.97, 1852.76, 1491.52, 1224.39, 1120.71, 1069.18, 857.55, 617.39, 469.70, 1517.37i
	Ab initio	3256.09, 3075.76, 1925.88, 1822.21, 1449.78, 1211.19, 1110.63, 1034.10, 829.03, 630.85, 439.10, 1596.02i
TS8	PES	3301.73, 3163.02, 2064.33, 1432.63, 1140.47, 964.43, 637.24, 612.34, 542.58, 521.66, 233.20, 991.57i
	Ab initio	3303.74, 3178.27, 2097.96, 1416.95, 1129.77, 1008.71, 639.70, 615.06, 533.19, 502.28, 316.99, 1017.16i
TS9	PES	3269.36, 3107.54, 1737.95, 1439.38, 1365.43, 1133.36, 1008.86, 952.13, 746.89, 592.82, 349.62, 2484.85i
	Ab initio	3236.47, 3113.06, 1773.10, 1456.31, 1416.82, 1120.87, 1007.07, 976.78, 773.95, 578.88, 324.41, 2495.55i
TS10	PES	3809.29, 3326.13, 1774.42, 1608.02, 1216.07, 1036.78, 843.97, 669.60, 637.52, 521.01, 476.75, 1904.01i
	Ab initio	3758.35, 3302.46, 1765.49, 1599.33, 1209.83, 1028.16, 845.51, 701.11, 646.17, 513.84, 469.25, 1895.38i
TS11	PES	3780.94, 3458.99, 2190.71, 1275.35, 1081.31, 730.38, 576.00, 540.64, 437.14, 267.83, 68.55, 778.30i
	Ab initio	3810.04, 3439.89, 2166.21, 1264.56, 1070.82, 704.61, 611.74, 482.70, 377.99, 248.76, 82.71, 713.89i
TS12	PES	3258.24, 3122.54, 1995.14, 1399.90, 1142.83, 974.46, 746.76, 700.35, 635.91, 357.87, 183.81, 1839.78i
	Ab initio	3263.90, 3138.50, 2005.60, 1411.03, 1131.41, 1000.94, 751.08, 654.74, 520.79, 349.30, 260.92, 1942.88i
TS13	PES	3286.24, 3216.89, 2167.60, 1438.54, 1118.53, 940.70, 777.54, 596.41, 497.46, 425.18, 285.43, 733.76i
	Ab initio	3283.75, 3180.65, 2172.13, 1406.60, 1120.01, 1014.67, 759.21, 565.91, 528.75, 416.81, 288.97, 707.43i
TS14	PES	3285.32, 3240.26, 3091.52, 2033.82, 1430.57, 1399.93, 841.93, 525.83, 509.06, 248.71, 82.19, 408.17i
	Ab initio	3279.46, 3264.68, 3100.10, 2036.95, 1430.93, 1424.09, 853.17, 555.07, 505.07, 255.76, 32.09, 403.78i
TS15	PES	3279.62, 2154.28, 1775.03, 1240.48, 1042.74, 806.80, 630.15, 564.85, 529.86, 335.47, 264.03, 1373.64i
	Ab initio	3312.43, 2158.84, 1790.16, 1230.50, 1063.48, 849.27, 672.81, 568.74, 546.55, 313.55, 267.15, 1357.11i
TS16	PES	3794.54, 3399.80, 3131.46, 1639.79, 1378.89, 1233.07, 1047.76, 845.22, 519.39, 474.10, 434.51, 655.15i
	Ab initio	3813.51, 3423.61, 3145.01, 1649.07, 1369.75, 1235.29, 1051.79, 859.96, 524.75, 471.49, 434.33, 627.52i
TS17	PES	3848.73, 3275.05, 3075.48, 1648.60, 1322.62, 1231.65, 1095.77, 838.09, 774.93, 671.94, 468.98, 392.06i
	Ab initio	3845.37, 3278.49, 3079.86, 1645.42, 1298.05, 1245.77, 1104.54, 805.30, 789.34, 669.03, 472.13, 381.04i

TS18	PES	3837.53, 3283.73, 3146.66, 1625.63, 1313.49, 1222.14, 1044.43, 893.93, 862.19, 651.71, 415.09, 339.75i
	Ab initio	3840.68, 3272.82, 3160.40, 1623.53, 1311.53, 1234.72, 1049.82, 873.41, 859.67, 668.09, 430.04, 339.22i
TS19	PES	3843.21, 3406.74, 3081.13, 1672.27, 1336.92, 1253.20, 1052.21, 801.18, 520.25, 481.58, 282.23, 669.68i
	Ab initio	3853.21, 3430.66, 3086.71, 1684.16, 1333.61, 1254.61, 1060.30, 820.27, 530.31, 475.74, 274.44, 637.37i
C1	PES	3711.28, 3496.55, 3391.01, 2007.36, 763.47, 751.85, 622.89, 616.60, 333.45, 228.34, 128.24, 72.71
	Ab initio	3686.49, 3494.36, 3401.84, 2003.57, 764.77, 750.87, 636.72, 611.56, 391.62, 235.91, 118.86, 69.10

Table S3. Geometry parameters used to identify Int1 (Int1a-d), Int2, Int3, and Int4. Distances and angles are in units of angstrom and degree, respectively.

	Int1a-d			Int2	
	Equilibrium geometry	Value range		Equilibrium geometry	Value range
$r_{C_1C_2}$	1.32	0.99-1.65	$r_{C_1C_2}$	1.43	1.07-1.79
r_{C_1O}	1.37	1.02-1.71	r_{C_1O}	1.23	0.92-1.54
$r_{C_1H_1}$	1.09	0.81-1.36	$r_{C_1H_1}$	1.10	0.83-1.38
$r_{C_2H_2}$	1.07	0.81-1.35	$r_{C_2H_2}$	1.08	0.81-1.35
r_{OH_3}	0.96	0.72-1.20 and $r_{OH_3} = \min(r_{C_1H_3}, r_{C_2H_3}, r_{H_1H_3}, r_{H_2H_3}, r_{OH_3})$	$r_{C_2H_3}$	1.08	0.81-1.35
$\theta_{OC_1C_2}$	125.0	90.0-165.0	$\theta_{OC_1C_2}$	123.0	90.0-165.0
$\theta_{H_1C_1C_2}$	121.0	90.0-165.0	$\theta_{H_1C_1C_2}$	117.0	90.0-165.0
$\theta_{C_1C_2H_2}$	137.0	90.0-180.0	$\theta_{C_1C_2H_2}$	121.0	90.0-165.0
			$\theta_{C_1C_2H_3}$	119.0	90.0-165.0

	Int3			Int4	
	Equilibrium geometry	Value range		Equilibrium geometry	Value range
$r_{C_1C_2}$	1.32	0.99-1.65	$r_{C_1C_2}$	1.51	1.14-1.89
r_{C_1O}	1.34	1.00-1.67	r_{C_1O}	1.18	0.89-1.48
$r_{C_2H_1}$	1.08	0.81-1.36	$r_{C_2H_1}$	1.08	0.81-1.37
$r_{C_2H_2}$	1.09	0.81-1.36	$r_{C_2H_2}$	1.10	0.81-1.37
r_{OH_3}	0.96	0.72-1.20 and	$r_{C_2H_3}$	1.10	0.81-1.37

		$r_{OH_3} = \min(r_{C_1H_3},$ $r_{C_2H_3}, r_{H_1H_3}, r_{H_2H_3}, r_{OH_3})$			
$\theta_{OC_1C_2}$	131.0	90.0-165.0	$\theta_{OC_1C_2}$	129.0	90.0-165.0
$\theta_{C_1C_2H_1}$	120.0	90.0-165.0	$\theta_{C_1C_2H_1}$	110.0	90.0-165.0
$\theta_{C_1C_2H_2}$	120.0	90.0-165.0	$\theta_{C_1C_2H_2}$	108.0	90.0-165.0
			$\theta_{C_1C_2H_3}$	108.0	90.0-165.0

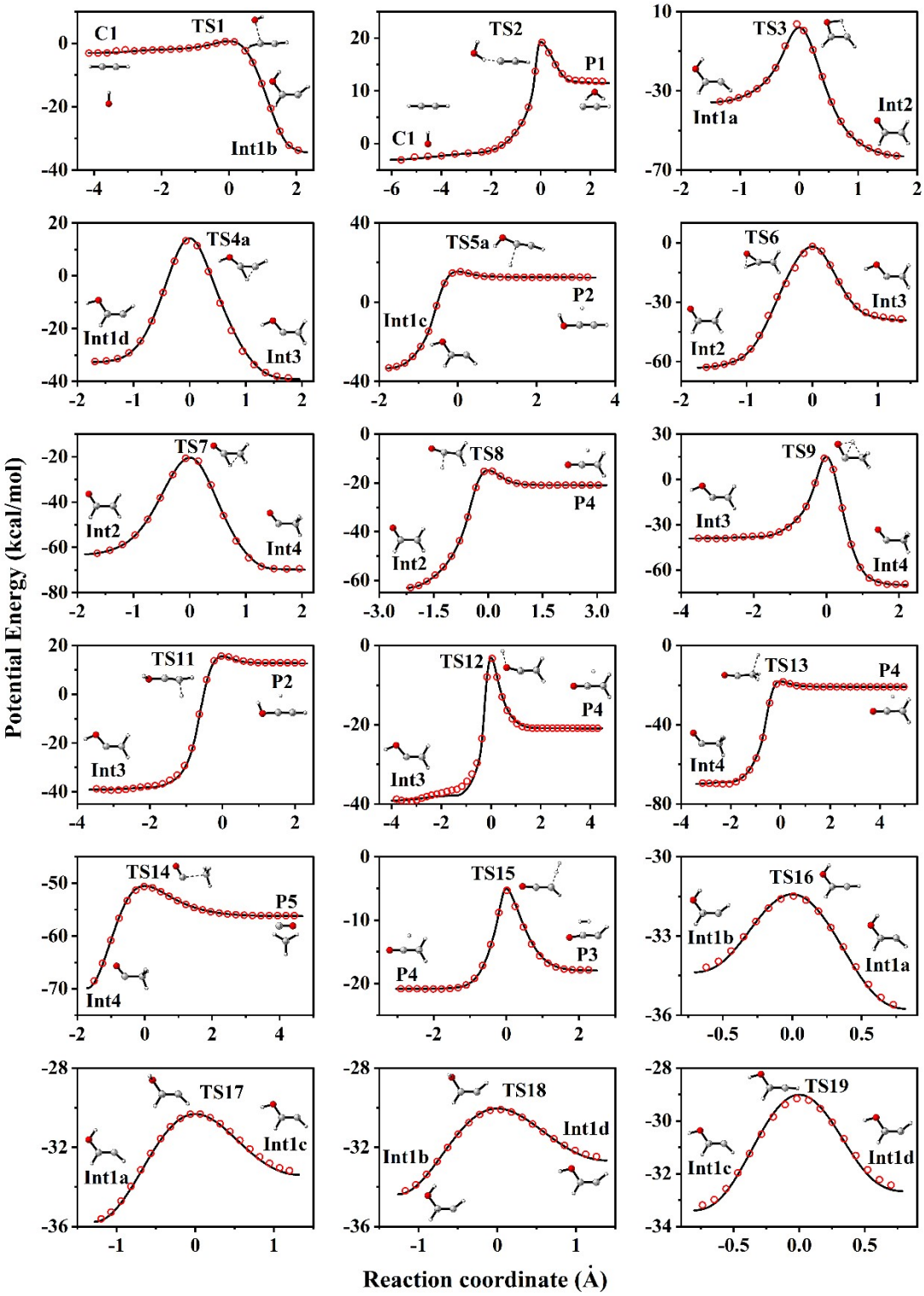
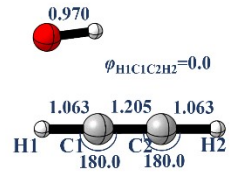
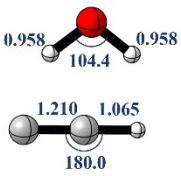


Figure S1. Comparison of the potential energies along the reaction paths on the PES (solid line) and the corresponding *ab initio* energies (red circle). The reaction path is defined as the steepest descent path through the mass-scaled coordinates from the saddle point to the minimum.

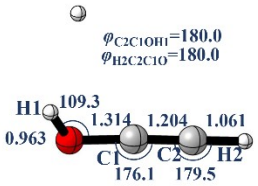
r-PES



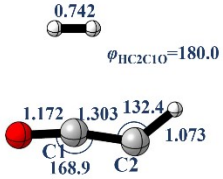
P1-PES



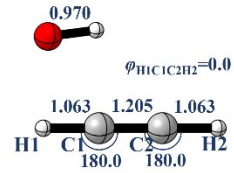
P2-PES



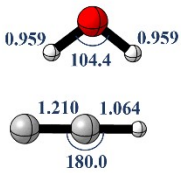
P3-PES



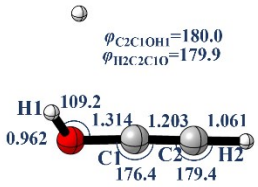
r-*ab initio*



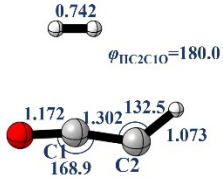
P1-*ab initio*



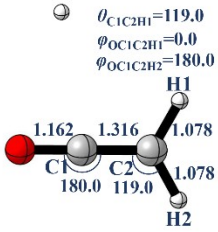
P2-*ab initio*



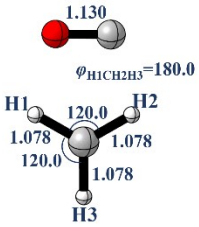
P3-*ab initio*



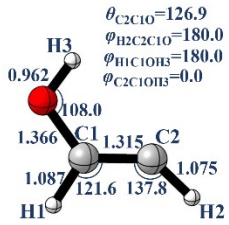
P4-PES



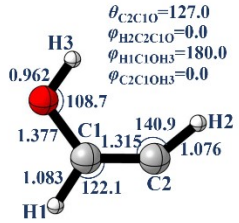
P5-PES



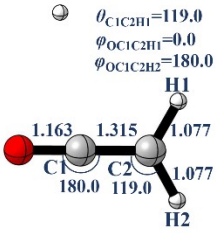
Int1a-PES



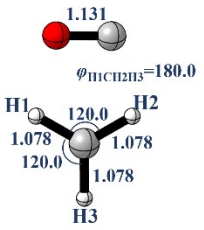
Int1b-PES



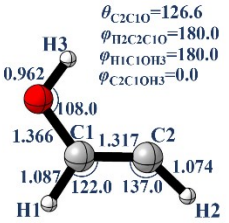
P4-*ab initio*



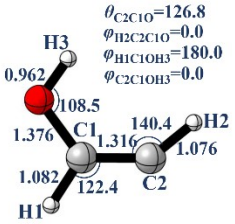
P5-*ab initio*



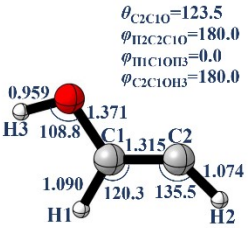
Int1a-*ab initio*



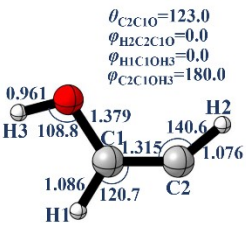
Int1b-*ab initio*



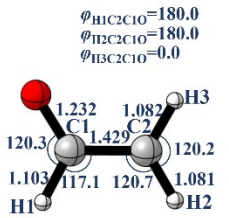
Int1c-PES



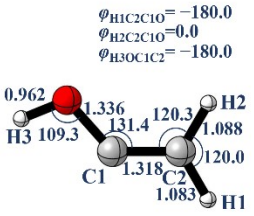
Int1d-PES



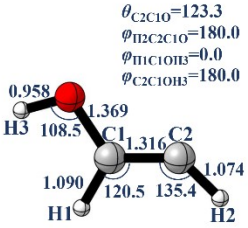
Int2-PES



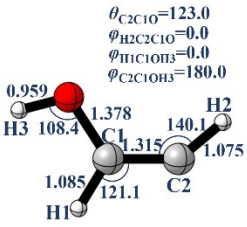
Int3-PES



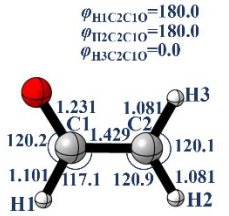
Int1c-*ab initio*



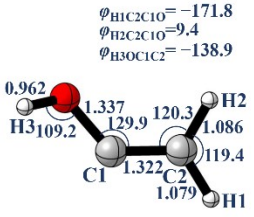
Int1d-*ab initio*



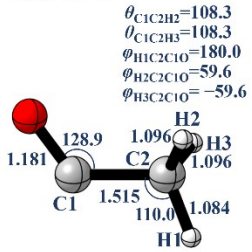
Int2-*ab initio*



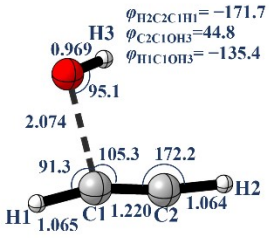
Int3-*ab initio*



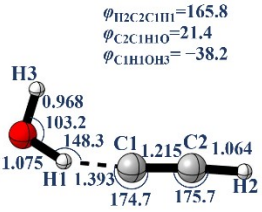
Int4-PES



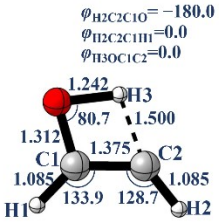
TS1-PES



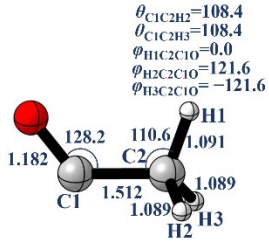
TS2-PES



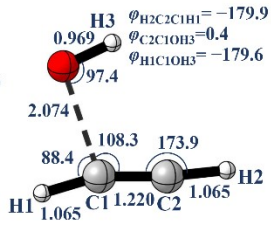
TS3-PES



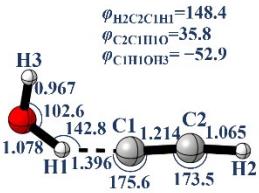
Int4-*ab initio*



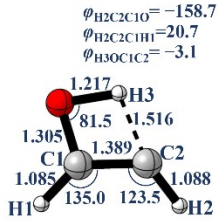
TS1-*ab initio*



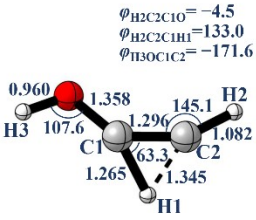
TS2-*ab initio*



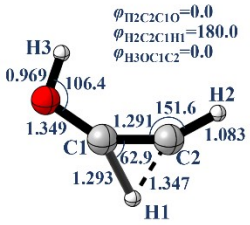
TS3-*ab initio*



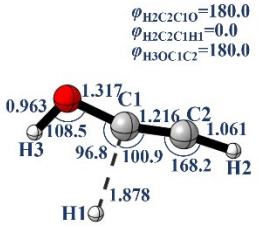
TS4a-PES



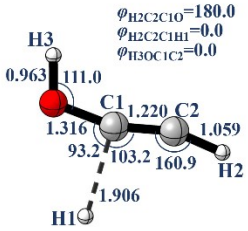
TS4b-PES



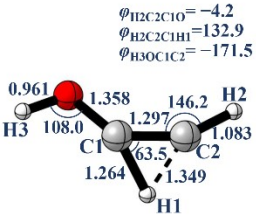
TS5a-PES



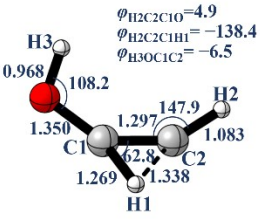
TS5b-PES



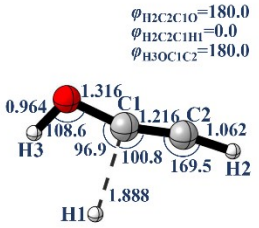
TS4a-*ab initio*



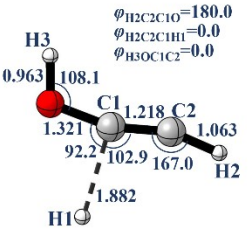
TS4b-*ab initio*



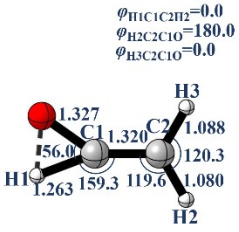
TS5a-*ab initio*



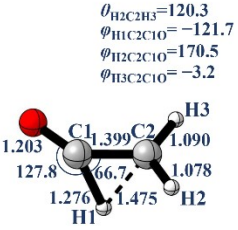
TS5b-*ab initio*



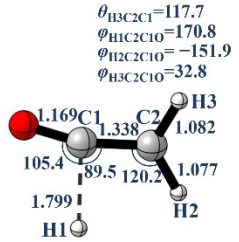
TS6-PES



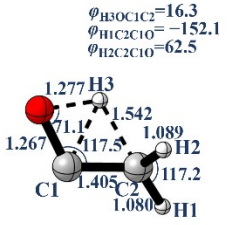
TS7-PES



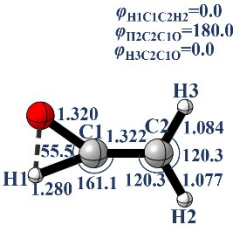
TS8-PES



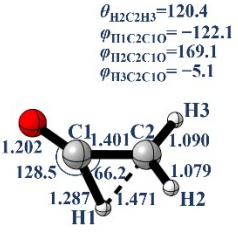
TS9-PES



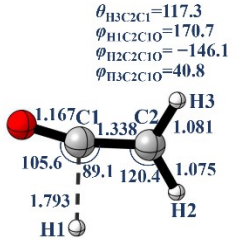
TS6-*ab initio*



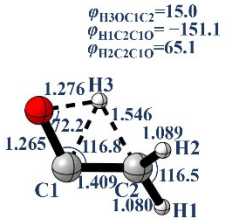
TS7-*ab initio*



TS8-*ab initio*



TS9-*ab initio*



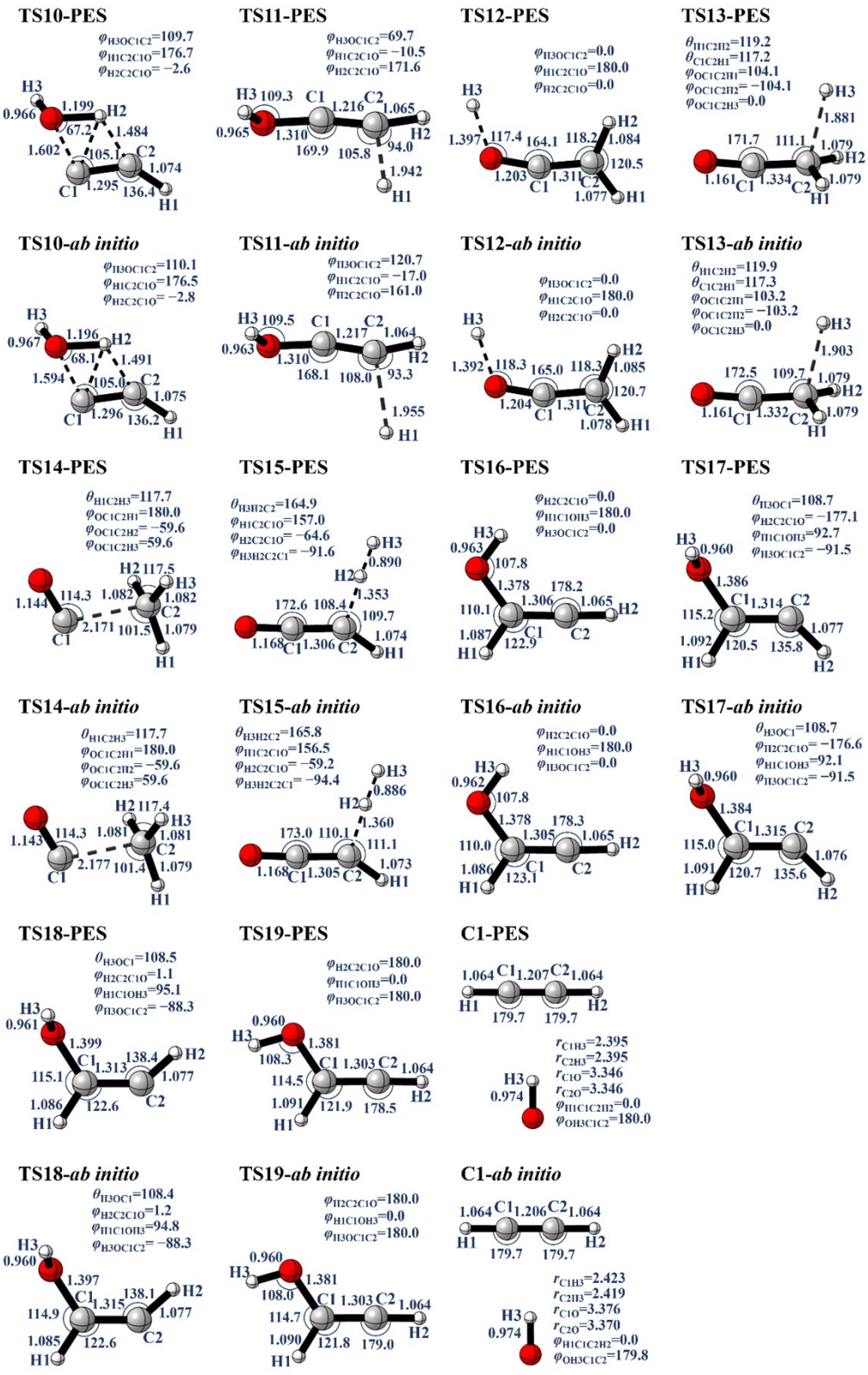


Figure S2. The geometry parameters of the stationary points. The geometric values of the PIP-NN PES and *ab initio* calculations are shown in the figure. All distances are in angstrom and angles are in degree.