

Supporting Information

Insight into the solvent effects on ethanol oxidation on Ir(100)

Ruitao Wu, Lichang Wang*

School of Chemical and Biomolecular Sciences and the Materials Technology Center,
Southern Illinois University, Carbondale, Illinois 62901, United States

Table of contents

1. Supplementary tables and figures	S2
2. Coordinates of transition states in this work	S17

1. Supplementary tables and figures

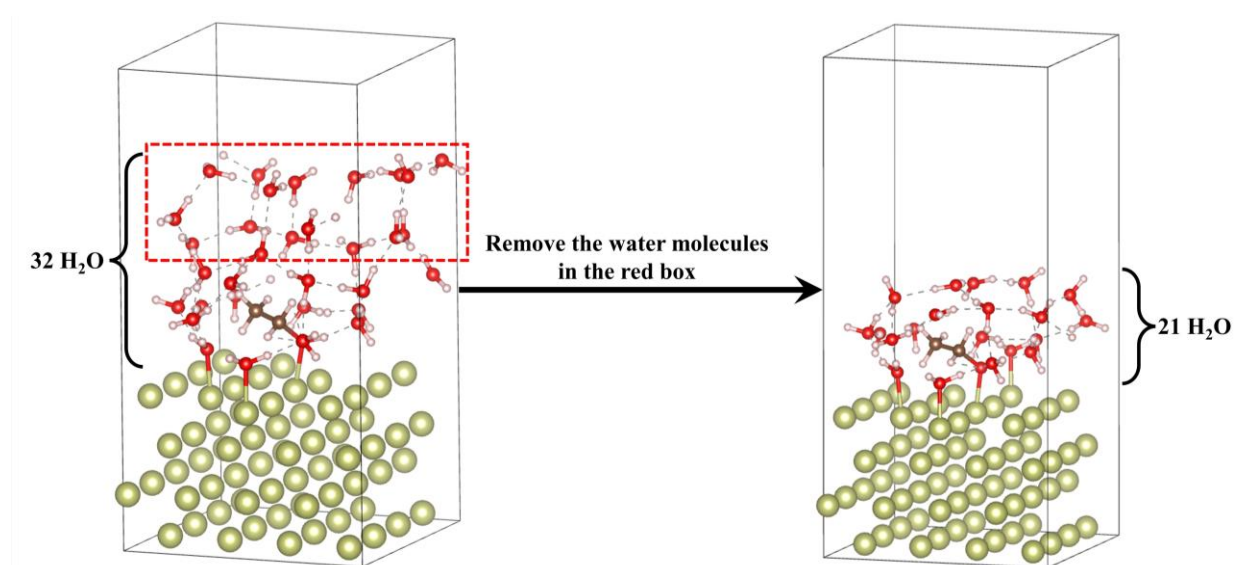


Fig. S1 The trans-ethanol adsorption configurations in the explicit solvation model with 32 (left) and 21 (right) water molecules, respectively.

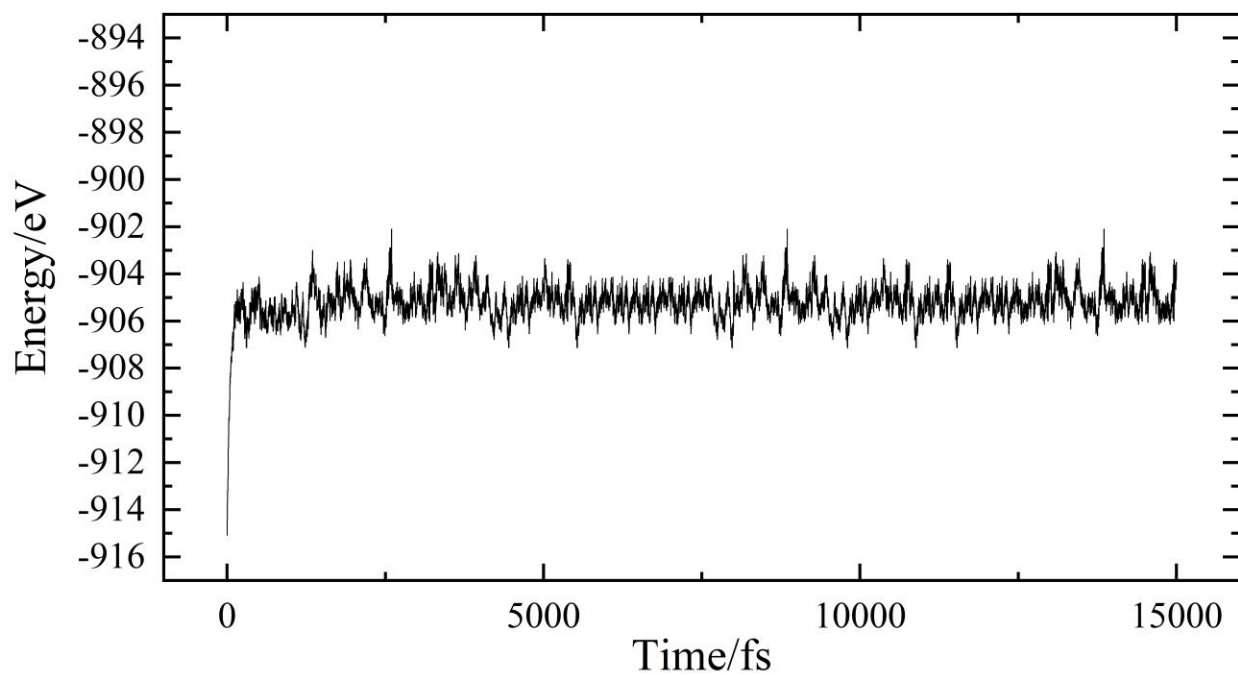
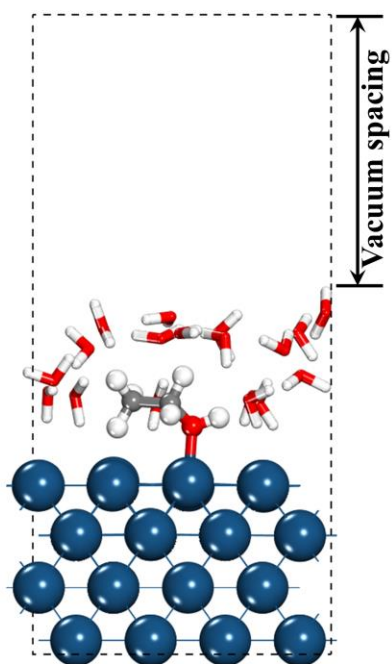


Fig. S2 The total energy fluctuation of an AIMD trajectory of the adsorbed trans-ethanol in the 21-H₂O-containing system at ~300 K.



Vacuum spacing/Å	DFT energy/eV
5	-1078.7187
6	-1078.9489
10	-1078.7551
11	-1078.7344
12	-1078.7232
15	-1078.7014

Fig. S3 The vacuum spacing in the explicit model and the system energies at various vacuum spacing

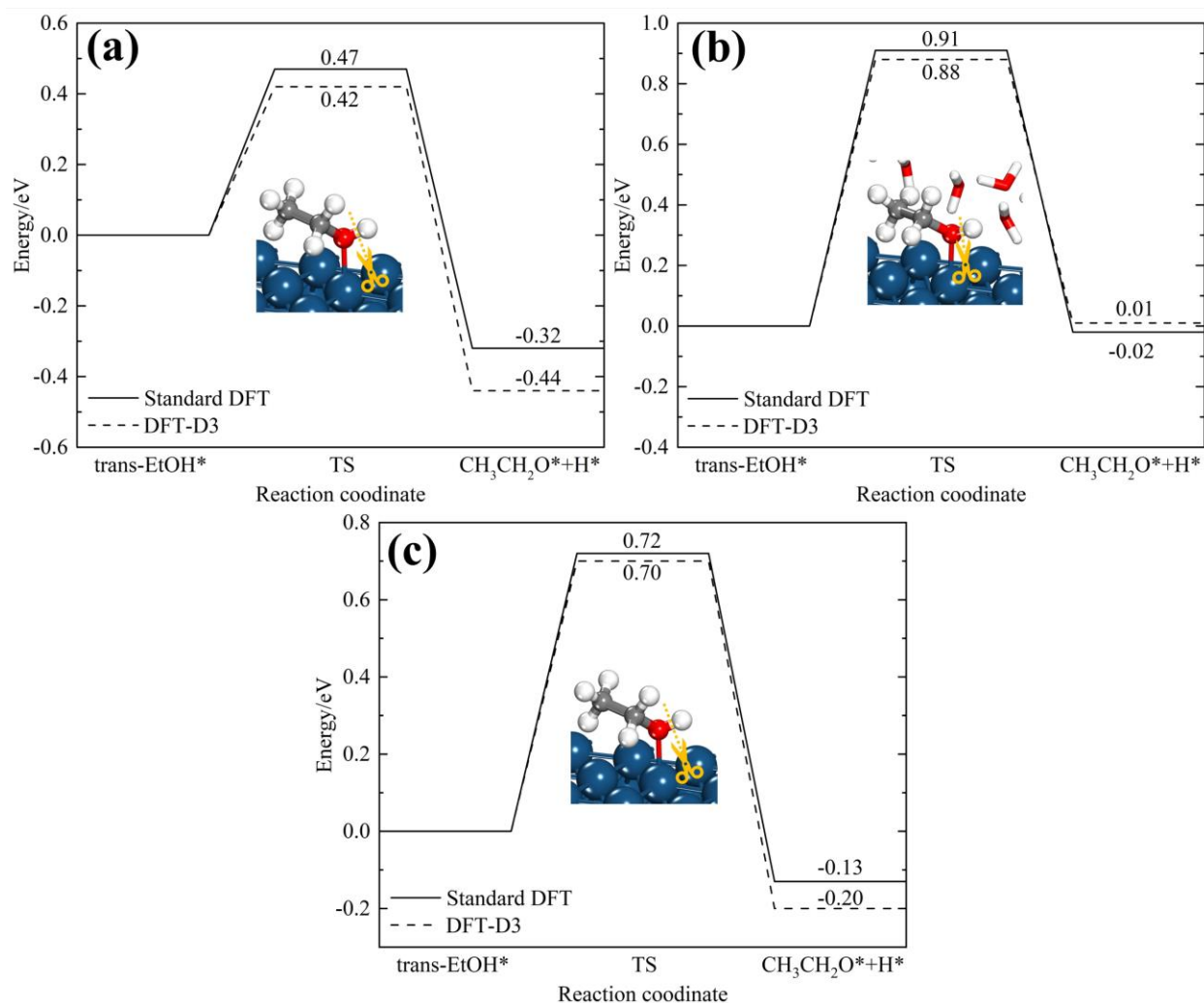


Fig. S4 Potential energy diagrams for the ethanol's O-H cleavage in the (a) gas-phase, (b) explicit, and (c) implicit (VASPsol) models using the standard DFT and DFT-D3 methods.

Table S1. A comparison of the calculation time of vibrational frequencies of two ethanol adsorption structures (gas-phase vs. explicit) using different DFT methods.

Studied model	DFT method	The number of calculated frequencies	Calculation time/h
Trans-EtOH+Ir(100)	Standard DFT	75	5.0
Trans-EtOH+Ir(100)	VASPsol	75	13.6
Trans-EtOH+Ir(100)	DFT-D3	75	5.2
Trans-EtOH+21H ₂ O+Ir(100)	Standard DFT	264	24.4
Trans-EtOH+21H ₂ O+Ir(100)	DFT-D3	264	24.7

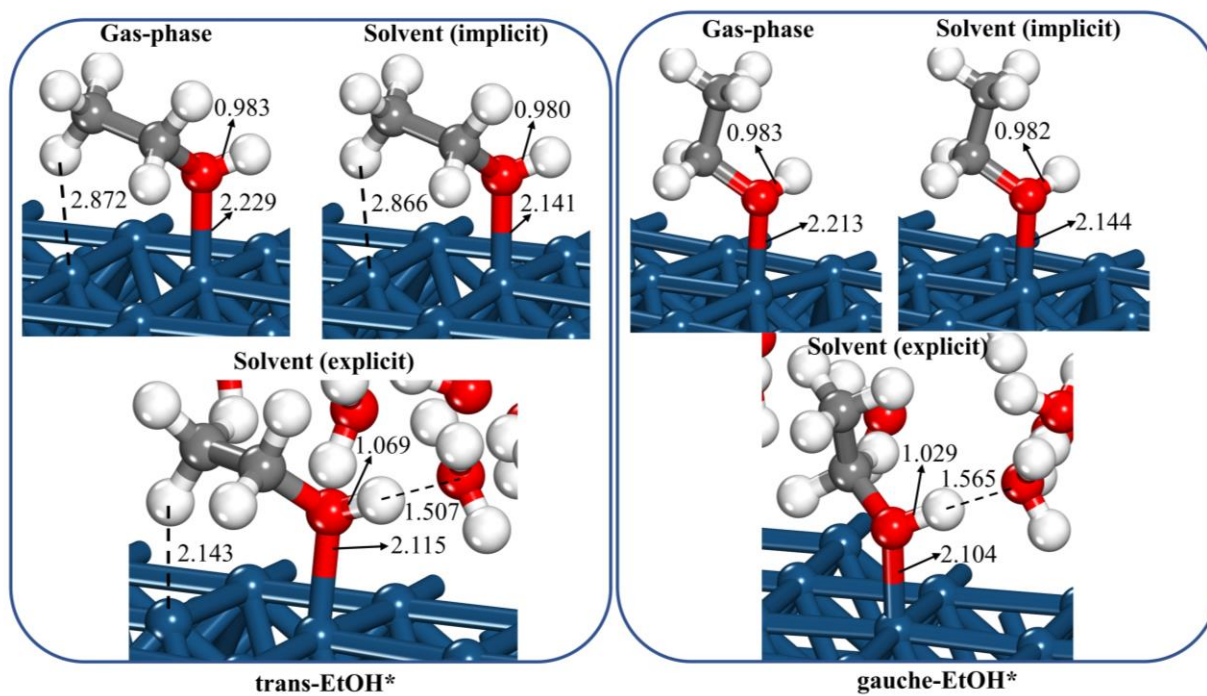


Fig. S5 The adsorption configurations of trans-ethanol (left) and gauche-ethanol (right) in the gas phase, implicit solvation, and explicit solvation models

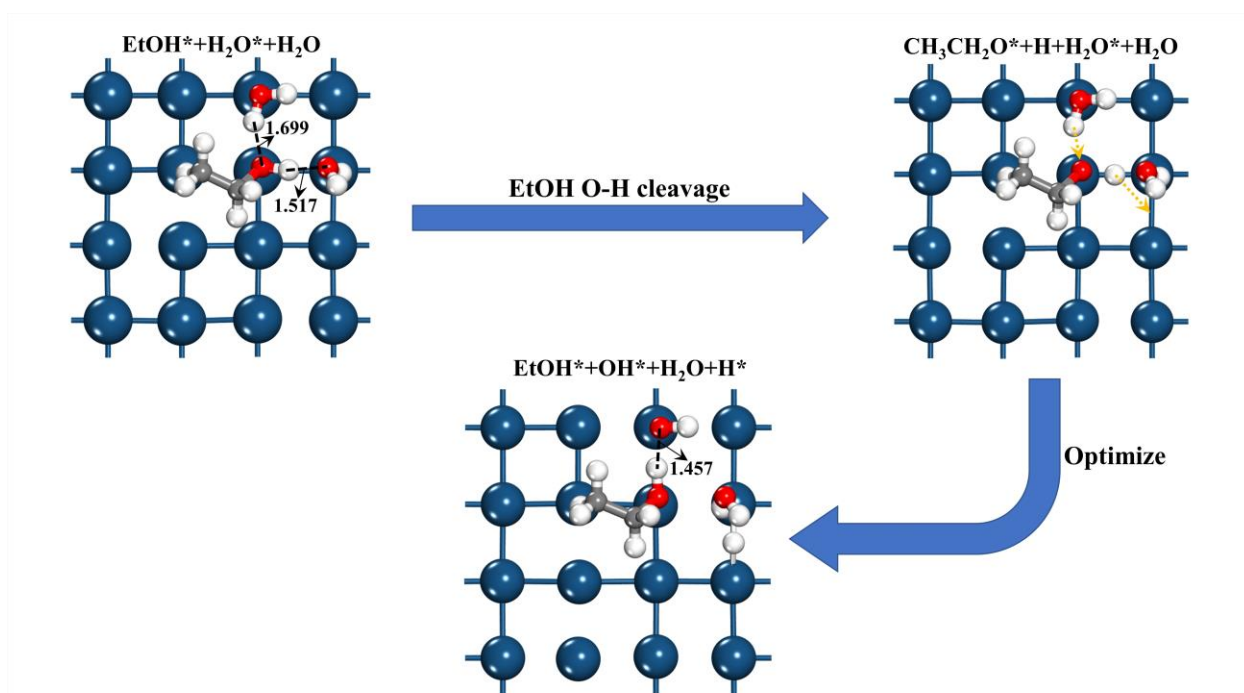


Fig. S6 Top view of the H-transfer process for the adsorbed trans-ethanol with two H-bonded (EW and WE) water molecules in the explicit model (the other 19 H_2O molecules were not displayed here).

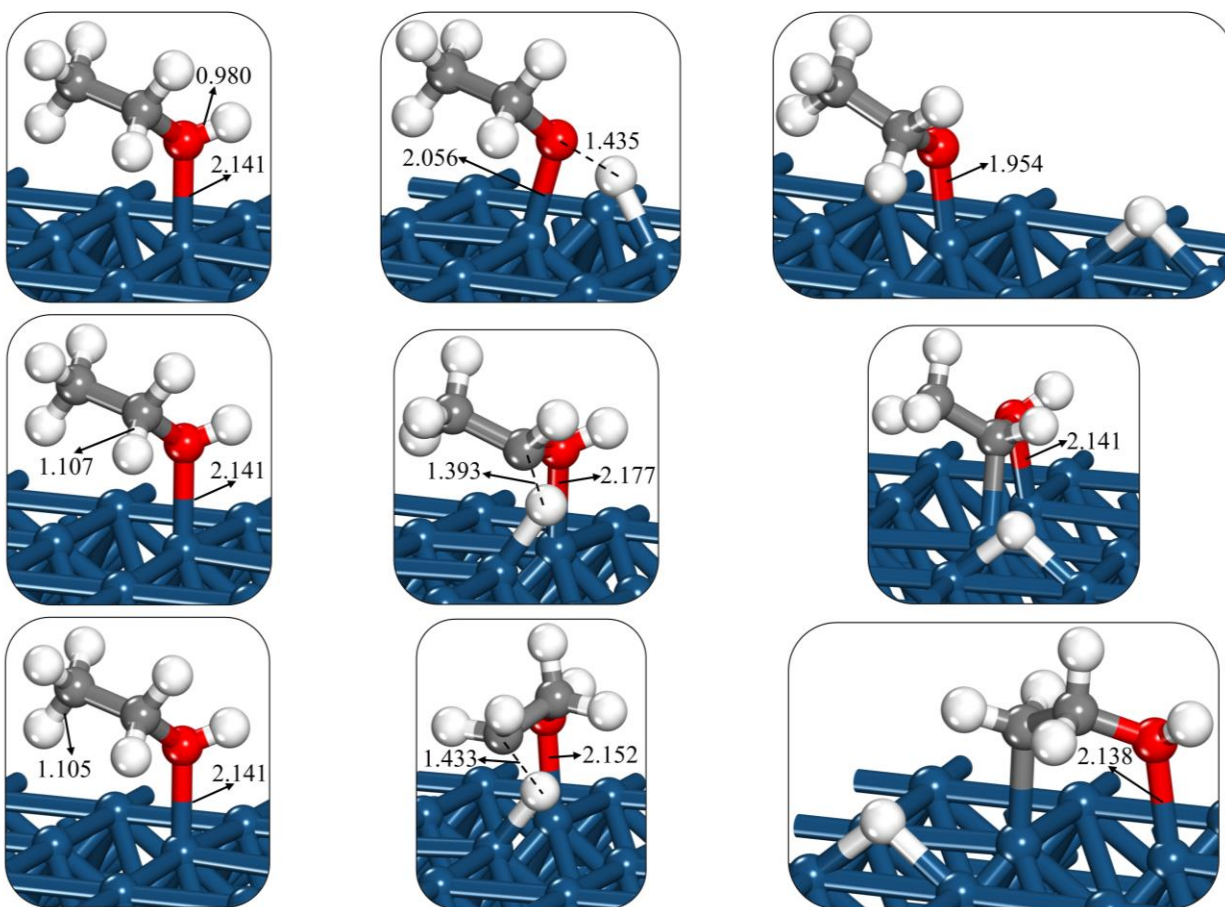


Fig. S7 The ISs (left), TSs (middle), and FSs (right) with distances in Å for R1, R2, and R3 (from top to bottom) in the implicit model, respectively.

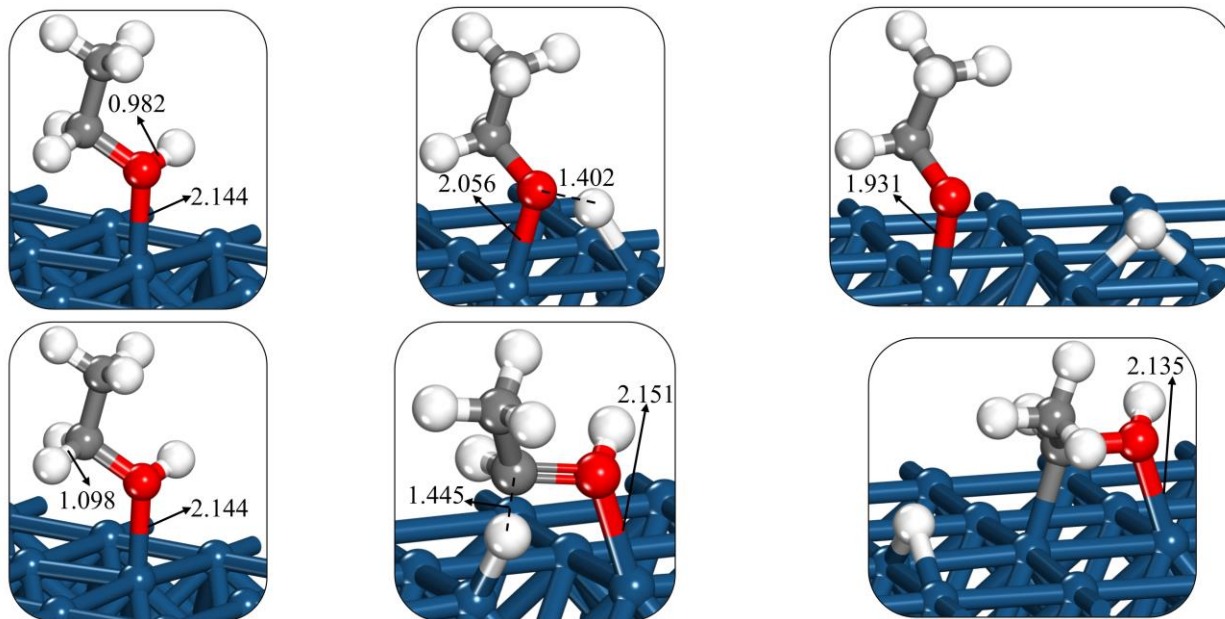


Fig. S8 The ISs (left), TSs (middle), and FSs (right) with distances in Å for R4 (top) and R5 (bottom) in the implicit model, respectively.

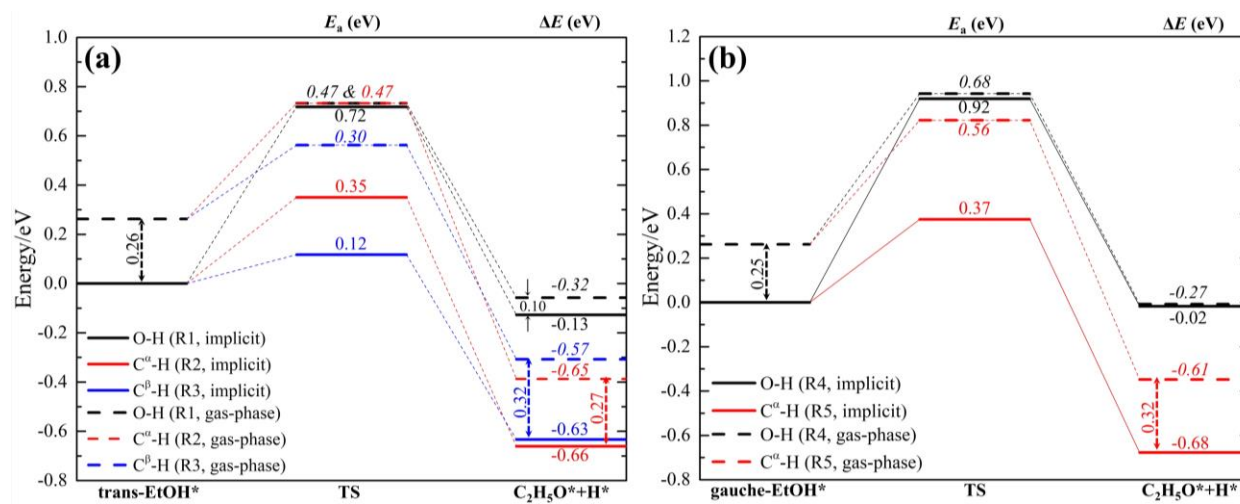


Fig. S9 Potential energy diagrams for the dehydrogenation reactions of (a) trans-ethanol and (b) gauche-ethanol adsorption structures in the gas-phase and implicit solvent models.

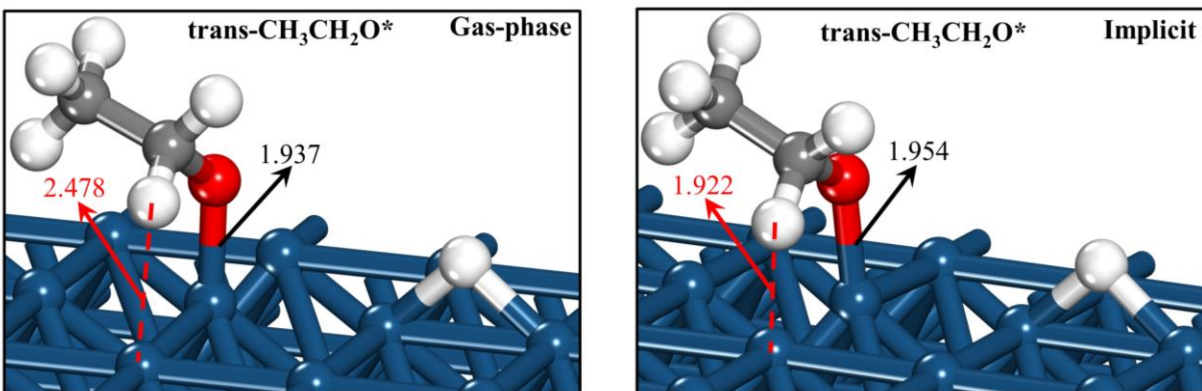


Fig. S10 The FS structures of trans-ethanol hydroxyl dehydrogenation in the gas-phase (left) and implicit (right) models.

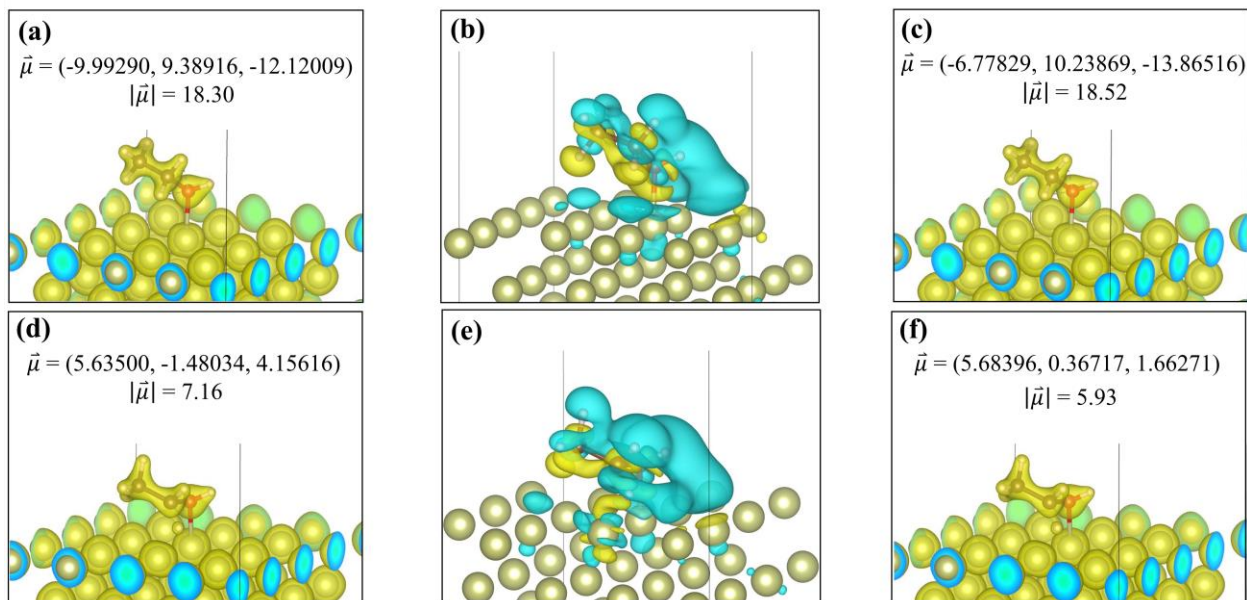


Fig. S11 The charge density contour of R3's IS (a and c) and TS (d and f) and the CCD isosurface for R3's IS (b) and TS (e) between standard DFT and VASPsol. Note: the contour (a) and (d) were calculated using the standard DFT, and the contour (c) and (f) were calculated using the VASPsol code. $\vec{\mu}$ and $|\vec{\mu}|$ denote the total electronic dipole moment of the system and its length, respectively.

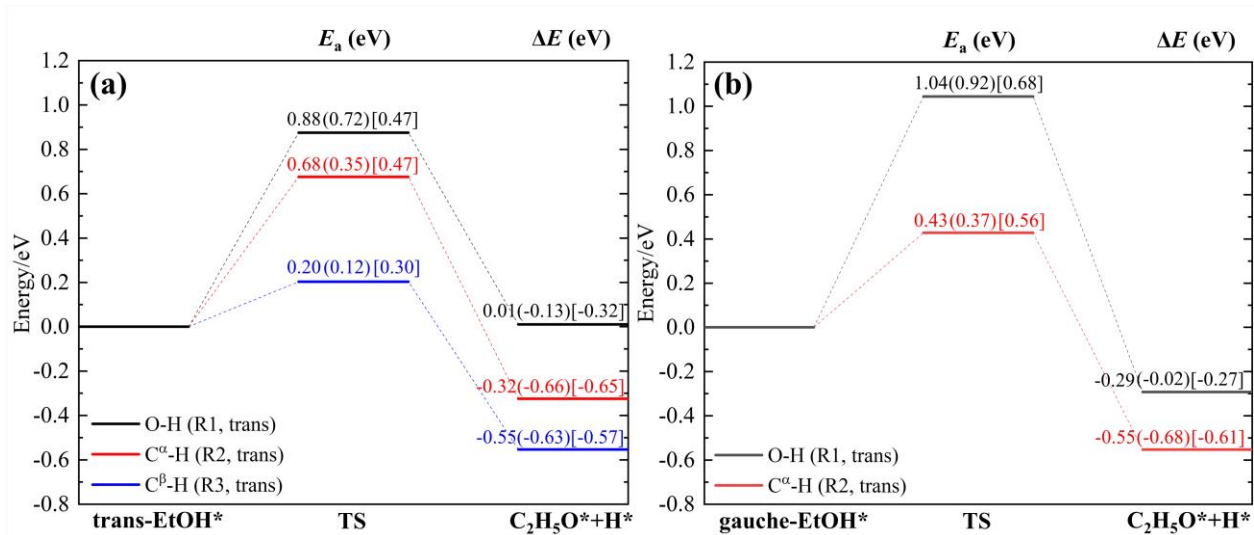


Fig. S12 Potential energy diagrams for the dehydrogenation reactions of (a) trans-ethanol and (b) gauche-ethanol adsorption structures in the explicit solvation model. The data in parentheses and square brackets denote the data (E_a and ΔE) from implicit and gas-phase models, respectively.

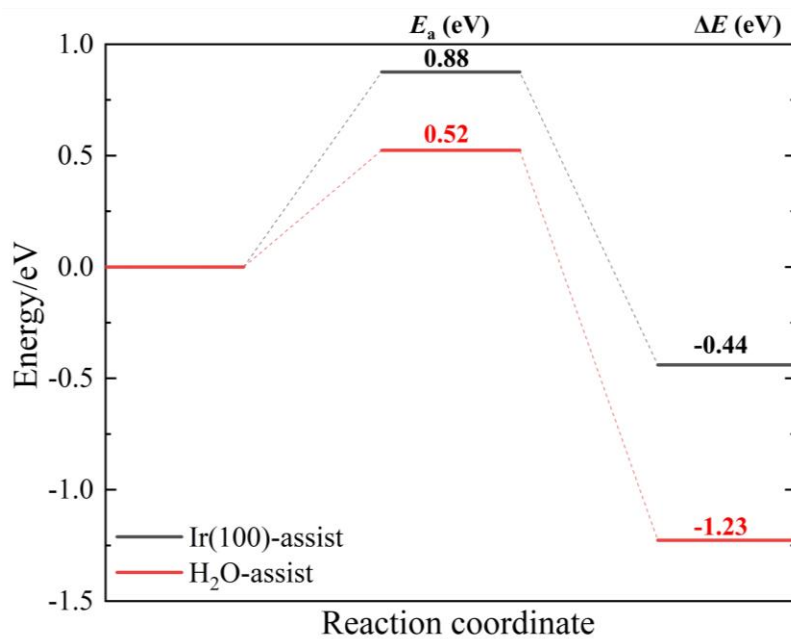


Fig. S13 Potential energy diagrams for the O-H dehydrogenations on Ir(100) in gas phase [Ir(100)-assist] and in solution [H₂O-assist] at a potential of 0.45 V (vs RHE).

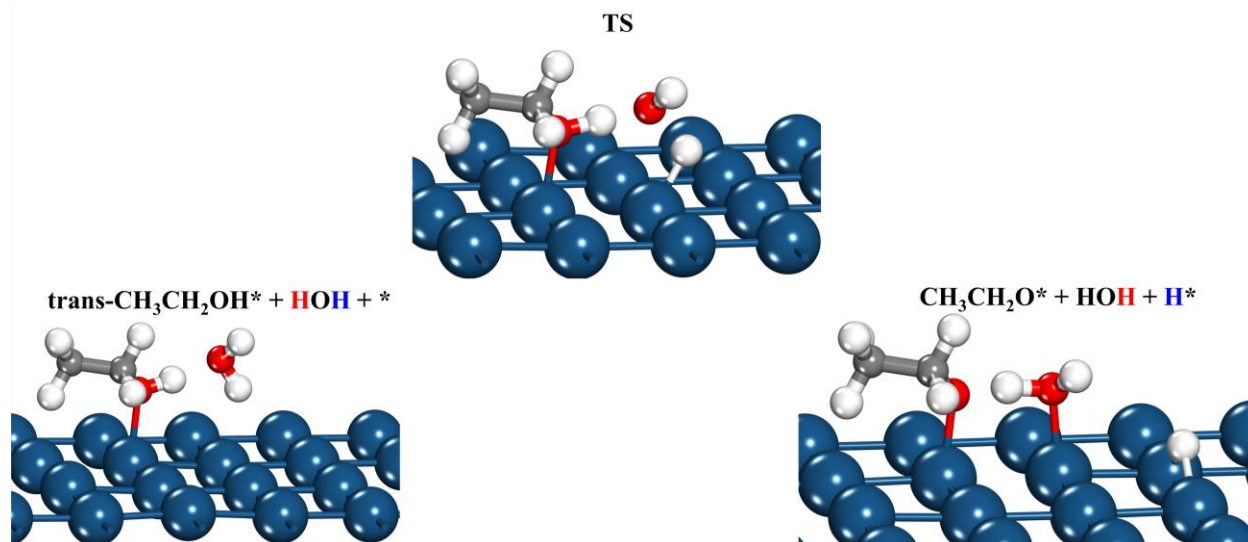


Fig. S14 IS (left), TS (middle), and FS (right) with distances in Å for the H₂O-assist O-H dehydrogenation of trans-ethanol in the explicit model (the other 20 water molecules were not visualized).

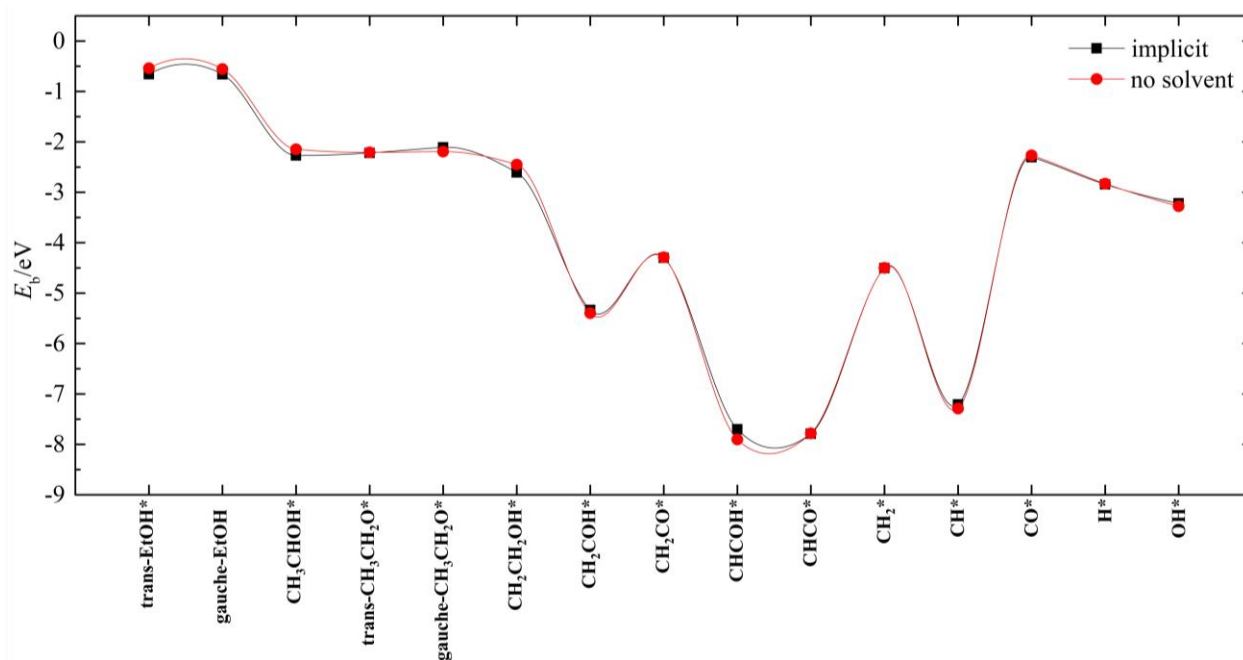


Fig. S15 Calculated binding energies of some relevant species in the gas phase and the implicit model.

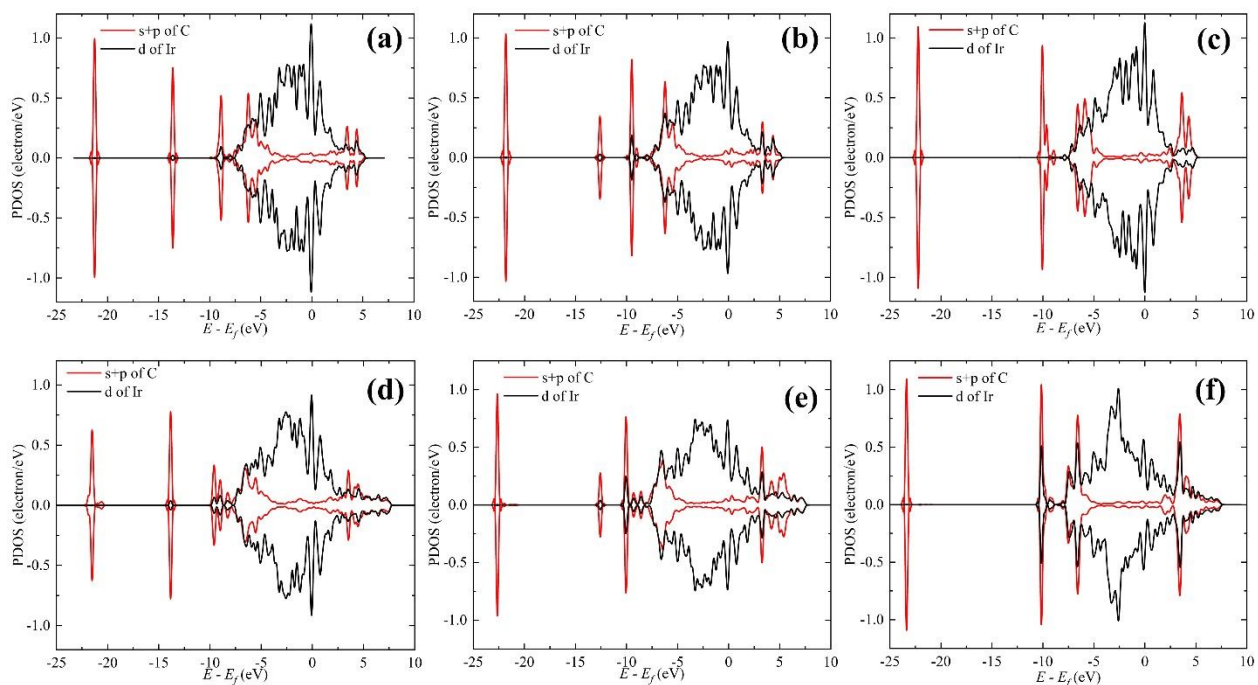


Fig. S16 (s+p)-projected density of state (PDOS) plots for the C in CO of CHCO and d-projected DOS plots for the C's nearest binding Ir. (a), (b), and (c) are the PDOS plots of the IS, TS, and FS of R7 in the gas phase, respectively; (d), (e), and (f) are the PDOS plots of the IS, TS, and FS of R7 in the explicit solvation, respectively.

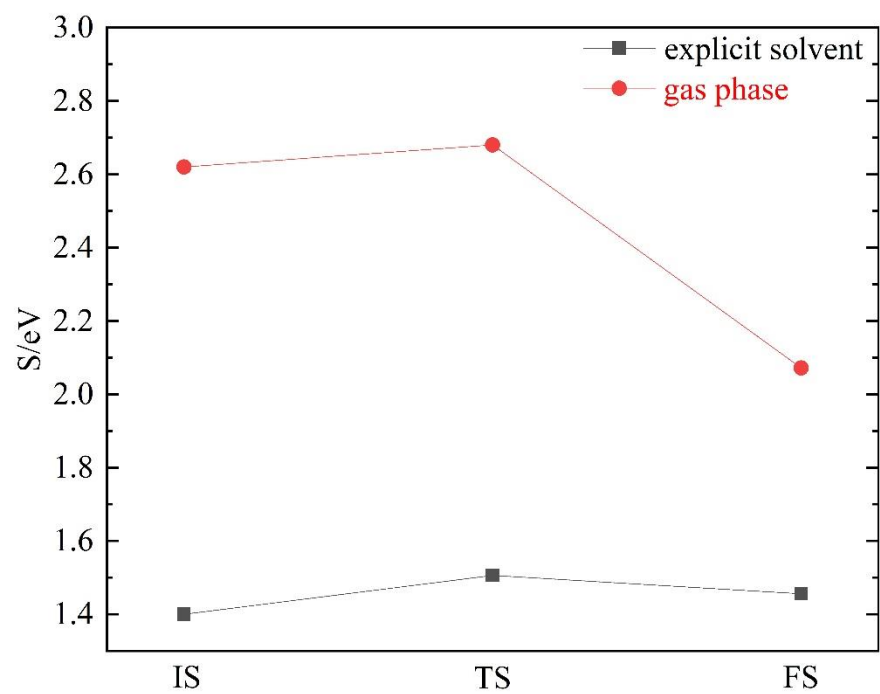


Fig. S17 The PDOS overlapping areas between C and Ir for IS, TS, and FS of R7 in the gas-phase and explicit models.

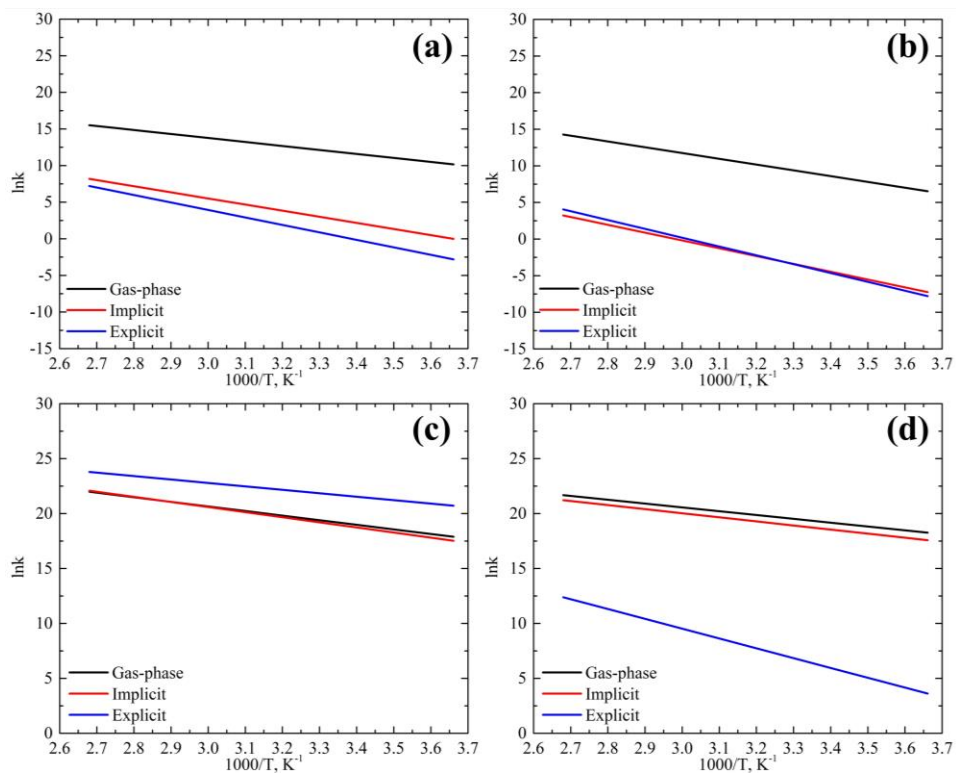


Fig. S18 Arrhenius plots of the reaction rate constants (k) for (a) R1, (b) R4, (c) R6, and (d) R7.

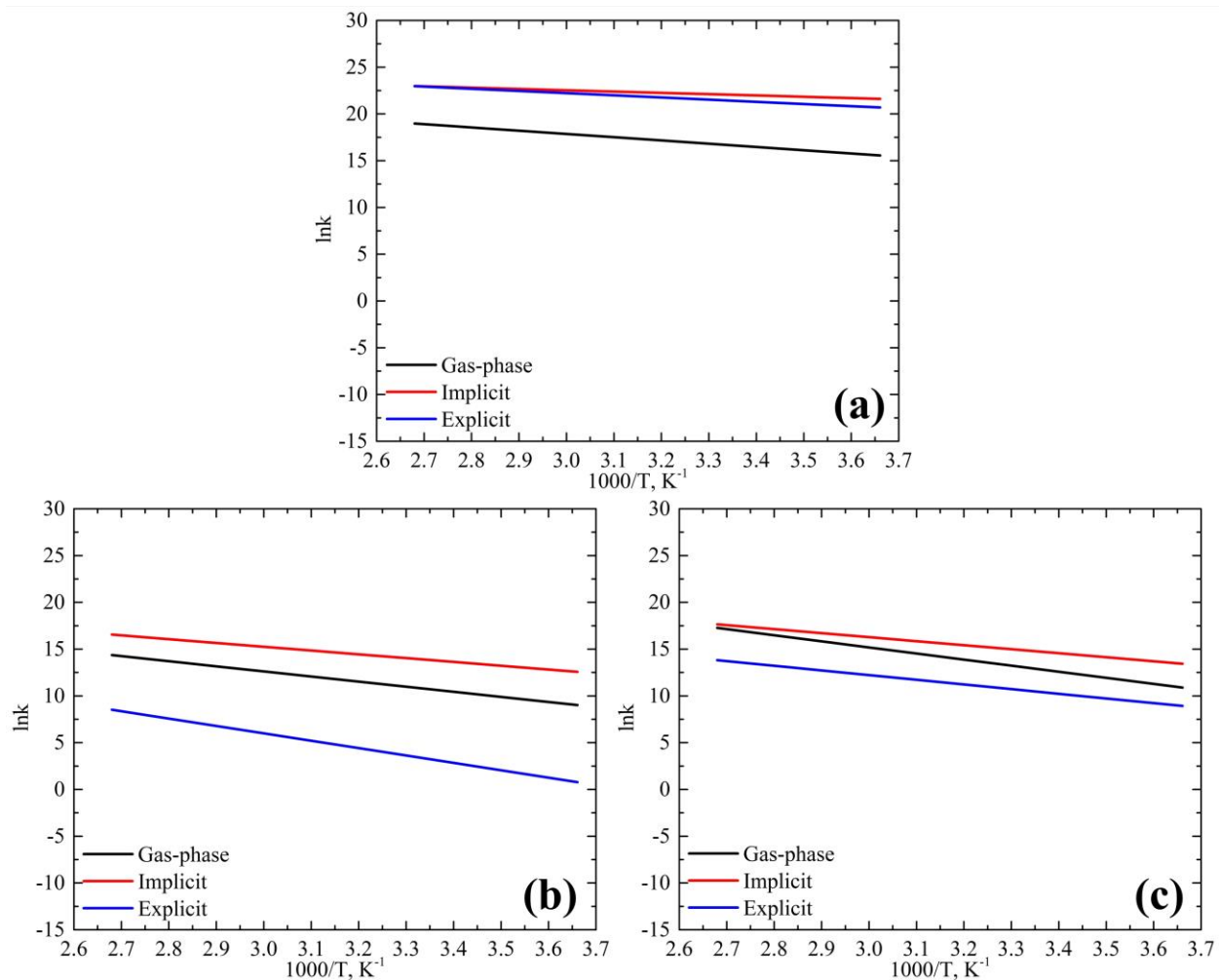


Fig. S19 Arrhenius plots of the reaction rate constants (k) for (a) R3, (b) R2, and (c) R5.

Table S2. The reaction rate constant (k) at 20 °C of each studied elementary reaction in the gas-phase, implicit, and explicit models over Ir(100)

Reaction label	k/s^{-1}		
	Gas-phase	Implicit	Explicit
R1	1.01×10^5	7.94×10^0	7.70×10^{-1}
R2	3.20×10^4	7.92×10^5	1.56×10^1
R3	1.36×10^7	3.45×10^9	1.73×10^9
R4	4.95×10^3	1.02×10^{-2}	8.44×10^{-3}
R5	2.71×10^5	2.01×10^6	2.60×10^4
R6	1.66×10^8	1.30×10^8	2.16×10^9
R7	2.03×10^8	1.08×10^8	3.45×10^2

2. Coordinates of transition states in this work

Table S3. The Cartesian coordinates (in Å) of the R1's TS[trans-CH₃CH₂O···H][‡] in the implicit model

Element	x	y	z
Ir	9.3768206	9.6062374	0.4156915
Ir	9.3787937	6.8652959	0.4236015
Ir	6.6365366	9.6067858	0.4300544
Ir	9.3814268	4.1252308	0.4323442
Ir	6.6384006	6.8654051	0.4362991
Ir	9.3813162	1.3842887	0.4373400
Ir	6.6412520	4.1259980	0.4417113
Ir	3.8976779	9.6093082	0.4442092
Ir	6.6419101	1.3851660	0.4448336
Ir	3.8998711	6.8679276	0.4454581
Ir	3.9017353	4.1269851	0.4469152
Ir	3.9025030	1.3864820	0.4475397
Ir	1.1610128	1.3874688	0.4498294
Ir	1.1612321	4.1285205	0.4508702
Ir	1.1598065	6.8691339	0.4519110
Ir	1.1581615	9.6096373	0.4521192
Ir	8.0133677	8.2407017	2.3642585
Ir	8.0157804	5.4989915	2.3723767
Ir	8.0165482	2.7582691	2.3786216
Ir	5.2741804	8.2392759	2.3792458
Ir	8.0172062	0.0177656	2.3825765
Ir	5.2762642	5.4987726	2.3838253
Ir	5.2761545	2.7583785	2.3854907
Ir	5.2760448	0.0167786	2.3859069
Ir	2.5345545	0.0162303	2.3869479
Ir	2.5355413	2.7579401	2.3884048
Ir	10.7589159	0.0167786	2.3888211
Ir	2.5357609	8.2396050	2.3888211
Ir	2.5364187	5.4987726	2.3892374
Ir	10.7601223	2.7583785	2.3900702
Ir	10.7611094	5.4994302	2.3923597
Ir	10.7609997	8.2401533	2.3946495
Ir	6.6475029	9.6094179	4.3155317
Ir	3.8975685	1.3930618	4.3188620
Ir	6.6492572	1.3947067	4.3207355
Ir	3.8997617	9.6044836	4.3196945

Ir	9.3932695	6.8827319	4.3205276
Ir	9.3839483	9.6083212	4.3213601
Ir	9.3950253	4.1147027	4.3207355
Ir	1.1572843	1.3833017	4.3273969
Ir	9.3828516	1.3876883	4.3269806
Ir	1.1577230	9.6125984	4.3294783
Ir	1.1637543	4.1243534	4.3301029
Ir	1.1672636	6.8715467	4.3313513
Ir	6.6515608	6.8730812	4.3452983
Ir	3.9171982	4.1377325	4.3546653
Ir	6.6418004	4.1424479	4.3565388
Ir	3.9276164	6.8554258	4.3619509
Ir	5.2739611	0.0194105	6.1516933
Ir	8.0120516	0.0152433	6.1604357
Ir	5.2700133	2.7221894	6.1675134
Ir	5.2731938	8.2803993	6.1600194
Ir	2.5378442	0.0153530	6.1639743
Ir	10.7523365	0.0146950	6.1631417
Ir	2.5278649	2.7479608	6.1675134
Ir	10.7607803	2.7534437	6.1641827
Ir	2.5002296	5.5001984	6.1691785
Ir	10.7612190	8.2428942	6.1637664
Ir	10.7440014	5.4987726	6.1637664
Ir	2.5322516	8.2447596	6.1675134
Ir	8.0218124	8.2541904	6.1656399
Ir	8.0227995	2.7490573	6.1681376
Ir	8.0197287	5.4997597	6.1879129
Ir	5.2343726	5.4851742	6.2726336
C	3.9804742	4.6938386	9.5686064
C	5.4415278	4.5945926	9.1866369
O	5.8159208	5.6219254	8.2395182
H	3.7371297	5.6941938	9.9507847
H	3.7552245	3.9527292	10.3489914
H	3.3317020	4.4782391	8.7005873
H	5.6779633	3.5979664	8.7551250
H	6.0928221	4.7534957	10.0611086
H	7.1411009	5.5307941	7.6974745

Table S4. The Cartesian coordinates (in Å) of the R2's TS[trans-CH₃CHOH···H][#] in the implicit model

Element	x	y	z
Ir	1.5098540	1.3772701	0.6554896
Ir	4.2499189	4.1201863	0.6544487
Ir	1.5087574	4.1196380	0.6546569
Ir	4.2510152	1.3782572	0.6559058
Ir	6.9911900	1.3782572	0.6569467
Ir	9.7316933	4.1211734	0.6521590
Ir	6.9911900	4.1208444	0.6544487
Ir	9.7309256	1.3788054	0.6550732
Ir	1.5079896	6.8625536	0.6550732
Ir	4.2503576	9.6052504	0.6561140
Ir	1.5083187	9.6048117	0.6577792
Ir	4.2500281	6.8628831	0.6538243
Ir	6.9921770	6.8636503	0.6529916
Ir	9.7359695	9.6057987	0.6573630
Ir	6.9931636	9.6060181	0.6556977
Ir	9.7343254	6.8635406	0.6536161
Ir	0.1400409	0.0053735	2.5944812
Ir	2.8802154	2.7489474	2.5934405
Ir	0.1382863	2.7479608	2.5928159
Ir	2.8812022	0.0073475	2.5946894
Ir	5.6224737	0.0097601	2.5967710
Ir	8.3622093	2.7497151	2.5936487
Ir	5.6217055	2.7500441	2.5946894
Ir	8.3616610	0.0094311	2.5976036
Ir	0.1378476	5.4902182	2.5928159
Ir	2.8797767	8.2324762	2.5938568
Ir	0.1376283	8.2322578	2.5951056
Ir	2.8797767	5.4906573	2.5926077
Ir	5.6210480	5.4915347	2.5926077
Ir	8.3626480	8.2345600	2.5928159
Ir	5.6212668	8.2333536	2.5932324
Ir	8.3624287	5.4925218	2.5909426
Ir	1.5214784	1.3766123	4.5307670
Ir	4.2544150	4.1235862	4.5594931
Ir	1.5125957	4.1202960	4.5278525
Ir	4.2718515	1.4049056	4.5728149
Ir	6.9968920	1.3846177	4.5565786
Ir	9.7297192	4.1185412	4.5220246

Ir	6.9866934	4.1188703	4.5667782
Ir	9.7297192	1.3709097	4.5286851
Ir	1.5197237	6.8688045	4.5257711
Ir	4.2479448	9.6100760	4.5386772
Ir	1.5107312	9.6066761	4.5376363
Ir	4.2717419	6.8373313	4.5671945
Ir	6.9876804	6.8448982	4.5565786
Ir	9.7365179	9.6050310	4.5343056
Ir	6.9959054	9.6042633	4.5359712
Ir	9.7333384	6.8729720	4.5224409
Ir	0.1428922	0.0116244	6.3685937
Ir	2.8423812	2.7524569	6.3794184
Ir	0.1346674	2.7479608	6.3617249
Ir	2.8761578	0.0039479	6.3785858
Ir	5.6265306	10.9543371	6.3806672
Ir	8.4056358	2.7526760	6.3769202
Ir	5.6004305	2.7129776	6.5122228
Ir	8.3726273	10.9643164	6.3804588
Ir	0.1423439	5.4939475	6.3604755
Ir	2.8801055	8.2359858	6.3752551
Ir	0.1430019	8.2314892	6.3692183
Ir	2.8453422	5.4996500	6.3721328
Ir	5.6173191	5.5442829	6.4664278
Ir	8.3704338	8.2359858	6.3735900
Ir	5.6251054	8.2561646	6.3729653
Ir	8.4129839	5.4960303	6.3596430
C	4.4056416	3.1998861	9.3800154
C	5.7448583	3.5251493	8.7680311
O	5.8730555	4.9360862	8.5415554
H	4.3783355	3.6556494	10.3837538
H	4.2713032	2.1172829	9.4805555
H	3.5744982	3.6197894	8.7888470
H	6.5466123	2.7690160	7.9154158
H	6.5456252	3.2282889	9.4659853
H	6.6964126	5.2851467	8.9547491

Table S5. The Cartesian coordinates (in Å) of the R3's TS[trans-CH₂CHOH⋯H][‡] in the implicit model

Element	x	y	z
Ir	1.3790249	1.3782572	20.7943592
Ir	4.1177735	4.1162381	20.8008118
Ir	1.3763930	4.1170058	20.8037262
Ir	4.1207342	1.3760638	20.7943592
Ir	6.8620052	1.3736513	20.7947750
Ir	9.6009741	4.1152511	20.7970657
Ir	6.8591542	4.1150322	20.7972736
Ir	9.6041536	1.3732126	20.7985229
Ir	1.3745286	6.8547673	20.8074741
Ir	4.1142645	9.5965872	20.8076820
Ir	1.3734319	9.5950518	20.8116379
Ir	4.1154704	6.8554258	20.8043518
Ir	6.8561931	6.8563027	20.7997723
Ir	9.5975742	9.5993290	20.8014374
Ir	6.8554258	9.5979033	20.8033104
Ir	9.5987797	6.8575096	20.7976894
Ir	0.0080055	0.0024126	1.9104741
Ir	2.7499344	2.7431355	1.9225472
Ir	0.0087731	2.7432449	1.9240044
Ir	2.7500441	0.0008773	1.9113067
Ir	5.4924121	10.9661808	1.9142209
Ir	8.2306128	2.7422578	1.9194249
Ir	5.4906573	2.7422578	1.9212983
Ir	8.2315998	0.0003290	1.9183841
Ir	0.0072378	5.4810066	1.9319143
Ir	2.7462060	8.2211819	1.9317062
Ir	0.0051542	8.2200851	1.9333715
Ir	2.7475219	5.4825420	1.9300410
Ir	5.4876966	5.4829807	1.9258778
Ir	8.2271032	8.2253485	1.9229636
Ir	5.4865999	8.2226067	1.9279593
Ir	8.2287483	5.4836388	1.9202574
Ir	1.3711289	1.3765026	3.8569593
Ir	4.1191993	4.1191993	3.9079583
Ir	1.3838501	4.1111937	3.8888078
Ir	4.1190896	1.3790249	3.8515475
Ir	6.8672690	1.3778186	3.8552945
Ir	9.5986710	4.1077943	3.8604982

Ir	6.8408403	4.1249018	3.8890159
Ir	9.6020708	1.3669618	3.8607063
Ir	1.3960227	6.8414984	3.9023380
Ir	4.1168962	9.5919819	3.8575840
Ir	1.3740900	9.5931873	3.8604982
Ir	4.1209536	6.8354673	3.9160764
Ir	6.8423758	6.8475294	3.8888078
Ir	9.6056890	9.6017408	3.8609145
Ir	6.8636503	9.5931873	3.8552945
Ir	9.6039352	6.8616767	3.8634124
Ir	0.0065798	0.0005483	5.6979089
Ir	2.7419291	2.6955411	5.7151861
Ir	10.9588337	2.7360070	5.7062349
Ir	2.7471931	0.0064702	5.6927047
Ir	5.4899993	0.0030706	5.6899986
Ir	8.2335730	2.7371037	5.7020721
Ir	5.4972372	2.6992698	5.7024884
Ir	8.2285290	10.9647551	5.6983252
Ir	10.9419451	5.4817743	5.7022800
Ir	2.7480702	8.2668018	5.7064433
Ir	0.0000000	8.2342310	5.7058187
Ir	2.7136357	5.5075450	5.8434110
Ir	5.5460372	5.4796910	5.8063588
Ir	8.2346697	8.2306128	5.7029047
Ir	5.4953728	8.2696524	5.7029047
Ir	8.2561646	5.4829807	5.6931210
C	2.9727716	5.3656402	8.1231575
C	4.2869854	4.8215971	8.6104555
O	5.3877921	5.5182924	7.9518437
H	2.9143207	6.4587708	8.2082939
H	2.1541300	4.9529743	8.7307711
H	2.5771041	4.4071770	7.1344070
H	4.3825026	3.7399809	8.4197826
H	4.3973069	5.0143867	9.6878815
H	6.2319856	5.2424874	8.3729477

Table S6. The Cartesian coordinates (in Å) of the R4's TS[gauche-CH₃CH₂O···H][#] in the implicit model

Element	x	y	z
Ir	1.7976123	1.3669618	0.7937065
Ir	4.5363607	4.1052718	0.7805925
Ir	1.7945418	4.1063685	0.7837149
Ir	4.5385542	1.3649879	0.7943309
Ir	7.2785096	1.3625753	0.7932901
Ir	10.0181351	4.0998983	0.7697682
Ir	7.2768641	4.1022010	0.7762212
Ir	10.0190125	1.3596143	0.7887106
Ir	1.7909229	6.8463235	0.7691438
Ir	4.5306587	9.5857306	0.7433322
Ir	1.7889489	9.5869370	0.7516585
Ir	4.5326324	6.8444595	0.7620664
Ir	7.2741227	6.8409500	0.7537401
Ir	10.0127621	9.5796986	0.7116922
Ir	7.2724781	9.5816727	0.7302183
Ir	10.0159426	6.8390856	0.7427077
Ir	0.4277993	0.0032899	2.7362368
Ir	3.1691799	2.7463155	2.7266617
Ir	0.4271413	2.7452190	2.7279108
Ir	3.1693993	0.0040576	2.7385266
Ir	5.9107804	0.0042769	2.7404001
Ir	8.6516123	2.7460961	2.7218740
Ir	5.9102321	2.7467544	2.7260373
Ir	8.6521606	0.0037286	2.7393594
Ir	0.4252770	5.4868188	2.7181270
Ir	3.1656709	8.2271032	2.6950216
Ir	0.4238513	8.2278709	2.7035561
Ir	3.1675351	5.4875865	2.7133393
Ir	5.9088063	5.4875865	2.7089684
Ir	8.6518316	8.2253485	2.6731648
Ir	5.9083676	8.2267742	2.6854465
Ir	8.6504059	5.4857225	2.7012663
Ir	1.7934451	1.3650975	4.6652370
Ir	4.5488625	4.1259980	4.6848040
Ir	1.8029858	4.1074653	4.6527476
Ir	4.5355935	1.3693744	4.6681514
Ir	7.2834444	1.3735416	4.6658616
Ir	10.0133104	4.1103168	4.6527476

Ir	7.2663364	4.1375132	4.6908407
Ir	10.0218639	1.3663038	4.6664858
Ir	1.8023279	6.8617864	4.6435885
Ir	4.5302200	9.5917616	4.6579514
Ir	1.7988186	9.5869370	4.6583681
Ir	4.5520430	6.8532329	4.6768942
Ir	7.2816896	6.8661728	4.6644044
Ir	10.0170383	9.5879240	4.6514988
Ir	7.2911210	9.5947227	4.6508741
Ir	10.0157232	6.8601413	4.6383848
Ir	0.4242900	10.9566402	6.4982767
Ir	3.1626003	2.7379811	6.5020227
Ir	0.4254963	2.7482896	6.4980683
Ir	3.1646838	10.9636583	6.4984846
Ir	5.9114380	10.9461126	6.4978600
Ir	8.6524897	2.7420387	6.5016065
Ir	5.9100122	2.7125392	6.4995255
Ir	8.6508446	10.9638777	6.4978600
Ir	0.4290056	5.4876966	6.4812074
Ir	3.1571169	8.2230453	6.5005665
Ir	0.4229741	8.2177820	6.4916153
Ir	3.1281657	5.4850645	6.4905744
Ir	5.9061742	5.4452562	6.5825801
Ir	8.6600571	8.2276516	6.4976521
Ir	5.9025555	8.2069244	6.5347042
Ir	8.6928463	5.4884639	6.4878683
C	5.5269561	5.5630355	10.9116430
C	5.0997052	5.3301091	9.4784746
O	6.0438023	5.9589229	8.5684080
H	6.5440898	5.1831594	11.0798340
H	4.8426528	5.0112062	11.5731688
H	5.4881353	6.6264477	11.1805820
H	4.0868483	5.7274222	9.2746878
H	5.0930157	4.2538667	9.2390928
H	5.8538647	7.2450624	8.0448904

Table S7. The Cartesian coordinates (in Å) of the R5's TS[gauche-CH₃CHOH···H][‡] in the implicit model

Element	x	y	z
Ir	1.4829863	1.3720063	0.5280969
Ir	4.2209673	4.1130581	0.5216439
Ir	1.4792578	4.1129484	0.5164400
Ir	4.2239285	1.3711289	0.5376721
Ir	6.9634452	1.3708000	0.5412108
Ir	9.7026329	4.1140451	0.5235174
Ir	6.9621286	4.1132774	0.5233092
Ir	9.7041674	1.3711289	0.5401700
Ir	1.4766258	6.8531227	0.5024934
Ir	4.2168002	9.5951614	0.4895876
Ir	1.4753097	9.5943937	0.4852163
Ir	4.2184448	6.8535614	0.5060321
Ir	6.9597158	6.8546581	0.5076973
Ir	9.6999998	9.5981226	0.4902121
Ir	6.9584002	9.5961485	0.4908366
Ir	9.7007685	6.8563027	0.5070729
Ir	0.1077997	0.0095408	2.4662559
Ir	2.8484128	2.7527859	2.4641745
Ir	0.1065934	2.7513599	2.4566805
Ir	2.8500576	0.0115147	2.4785373
Ir	5.5912194	0.0132693	2.4895697
Ir	8.3329287	2.7539923	2.4704192
Ir	5.5904512	2.7535534	2.4691701
Ir	8.3321610	0.0135983	2.4883206
Ir	0.1056064	5.4921923	2.4475217
Ir	2.8438067	8.2346697	2.4348242
Ir	0.1028648	8.2326965	2.4306610
Ir	2.8466580	5.4938374	2.4508522
Ir	5.5886970	5.4948244	2.4531419
Ir	8.3291998	8.2386179	2.4381545
Ir	5.5865035	8.2363148	2.4371140
Ir	8.3317223	5.4967985	2.4537666
Ir	1.4825476	1.3762832	4.3981705
Ir	4.2186642	4.1301656	4.4229412
Ir	1.4749808	4.1250114	4.3900518
Ir	4.2352238	1.4074279	4.4412589
Ir	6.9608126	1.3890042	4.4323082
Ir	9.6949558	4.1255598	4.3954644

Ir	6.9550004	4.1233664	4.4306431
Ir	9.6919947	1.3763930	4.4037905
Ir	1.4802446	6.8767009	4.3736076
Ir	4.2110977	9.6053600	4.3987947
Ir	1.4750904	9.6034966	4.3940072
Ir	4.2260118	6.8488460	4.4114923
Ir	6.9439244	6.8429241	4.4198189
Ir	9.7038383	9.6003151	4.3965049
Ir	6.9622383	9.5957098	4.4006681
Ir	9.6938591	6.8752751	4.3804770
Ir	0.1074707	0.0070185	6.2328753
Ir	2.8055341	2.7607911	6.2364135
Ir	0.1013295	2.7519083	6.2301683
Ir	2.8392007	0.0018643	6.2414093
Ir	5.5881486	10.9495115	6.2468214
Ir	8.3671436	2.7619975	6.2576456
Ir	5.5641322	2.7112231	6.3804588
Ir	8.3365479	10.9594908	6.2470298
Ir	0.1075804	5.5040364	6.2208018
Ir	2.8408461	8.2351084	6.2368298
Ir	0.1090060	8.2298450	6.2299609
Ir	2.8034506	5.5051327	6.2253814
Ir	5.5693960	5.5672026	6.3223829
Ir	8.3356705	8.2337923	6.2380786
Ir	5.5851874	8.2559443	6.2355814
Ir	8.3692274	5.5071068	6.2314181
C	6.1370173	3.0170760	9.8027849
C	5.4709177	3.5131960	8.5361433
O	5.6684222	4.9402537	8.3773184
H	7.2207165	3.1939640	9.8040333
H	5.9411573	1.9434655	9.9199772
H	5.6867366	3.5471919	10.6558161
H	4.3950043	3.2867398	8.5446777
H	6.5434313	2.9814351	7.7266169
H	5.0613227	5.4410892	8.9741077

Table S8. The Cartesian coordinates (in Å) of the R6's TS[CH₂···CO][#] in the implicit model

Element	x	y	z
Ir	1.3721160	1.3671811	0.3203552
Ir	4.1150322	4.1093297	0.3166083
Ir	1.3727740	4.1093297	0.3176491
Ir	4.1148129	1.3675101	0.3184817
Ir	6.8590450	1.3675101	0.3199388
Ir	9.6010838	4.1104259	0.3222286
Ir	6.8591542	4.1097679	0.3184817
Ir	9.6019611	1.3675101	0.3247265
Ir	1.3734319	6.8523550	0.3151512
Ir	4.1156898	9.5952711	0.3143186
Ir	1.3732126	9.5949421	0.3151512
Ir	4.1156898	6.8531227	0.3145267
Ir	6.8597026	6.8538904	0.3170246
Ir	9.6026182	9.5973549	0.3226449
Ir	6.8599219	9.5966969	0.3178573
Ir	9.6017408	6.8538904	0.3207715
Ir	0.0013160	10.9655228	2.2618446
Ir	2.7428064	2.7394068	2.2549756
Ir	0.0010966	2.7401745	2.2574735
Ir	2.7433548	10.9658518	2.2593470
Ir	5.4859414	0.0013160	2.2587225
Ir	8.2277613	2.7402840	2.2589307
Ir	5.4861612	2.7396259	2.2545593
Ir	8.2280903	0.0023029	2.2608039
Ir	0.0021933	5.4821033	2.2560163
Ir	2.7443419	8.2251291	2.2512288
Ir	0.0020836	8.2235937	2.2528942
Ir	2.7434642	5.4826517	2.2524776
Ir	5.4863801	5.4829807	2.2522695
Ir	8.2283096	8.2250195	2.2564328
Ir	5.4869285	8.2258968	2.2520614
Ir	8.2268839	5.4828711	2.2570572
Ir	1.3680584	1.3676198	4.1954246
Ir	4.1120710	4.1058202	4.2035427
Ir	1.3619173	4.1103168	4.2010446
Ir	4.1061492	1.3724449	4.1856408
Ir	6.8579483	1.3767219	4.1943836
Ir	9.5796986	4.1122904	4.2183218

Ir	6.8453364	4.1130581	4.2351823
Ir	9.6005354	1.3747479	4.1927180
Ir	1.3620269	6.8545485	4.2000036
Ir	4.1074653	9.5892391	4.1854329
Ir	1.3680584	9.5945034	4.1950078
Ir	4.1108646	6.8598123	4.2022934
Ir	6.8439112	6.8514776	4.2333093
Ir	9.5992184	9.5867167	4.1925101
Ir	6.8582768	9.5851822	4.1945915
Ir	9.5775061	6.8500519	4.2185297
Ir	10.9612465	10.9639874	6.0376229
Ir	2.7327173	2.7320592	6.0334597
Ir	0.0049349	2.7317302	6.0374141
Ir	2.7421484	10.9640970	6.0301290
Ir	5.4791427	10.9633293	6.0243006
Ir	8.2289667	2.7026694	6.0426183
Ir	5.4676280	2.7034369	6.0320024
Ir	8.2233744	10.9637680	6.0234680
Ir	10.9615746	5.4824324	6.0397038
Ir	2.7332656	8.2314892	6.0336680
Ir	0.0036189	8.2312708	6.0367904
Ir	2.7179127	5.4827614	6.0263824
Ir	5.4066544	5.4792519	6.1335835
Ir	8.2273226	8.2551775	6.0436592
Ir	5.4682856	8.2545185	6.0342922
Ir	8.2555056	5.4782653	6.2530661
C	5.9259133	5.4197044	8.0405188
C	7.8319836	5.4080801	8.1331491
O	8.1949711	5.3599377	9.2657366
H	5.7496834	6.3213625	8.6441774
H	5.7568121	4.4821868	8.5900555

Table S9. The Cartesian coordinates (in Å) of the R7's TS[CH \cdots CO] ‡ in the implicit model

Element	x	y	z
Ir	1.4018350	1.4080857	0.3784312
Ir	4.1503439	4.1519885	0.3944594
Ir	1.4038090	4.1545110	0.3803047
Ir	4.1564851	1.4081954	0.3819699
Ir	6.8783450	1.4094017	0.3859249
Ir	9.6134758	4.1534147	0.3873820
Ir	6.8772492	4.1476021	0.3948757
Ir	9.6162167	1.4056731	0.3821781
Ir	1.4132400	6.8779068	0.3782231
Ir	4.1479311	9.6268539	0.3836352
Ir	1.4060020	9.6198359	0.3782231
Ir	4.1514406	6.8788939	0.3919615
Ir	6.8827319	6.8806486	0.3884228
Ir	9.6207132	9.6249905	0.3786394
Ir	6.8775778	9.6297054	0.3842597
Ir	9.6222487	6.8862414	0.3794720
Ir	0.0279643	0.0326799	2.1954424
Ir	2.7649584	2.7698932	2.2025199
Ir	0.0318026	2.7732928	2.1964831
Ir	2.7673712	0.0404660	2.1919038
Ir	5.5221305	0.0364084	2.2287476
Ir	8.2456360	2.7780085	2.2231274
Ir	5.5170865	2.7764730	2.2343678
Ir	8.2467327	0.0345442	2.2127194
Ir	0.0266484	5.5257502	2.2156336
Ir	2.7723057	8.2519960	2.2150092
Ir	0.0304866	8.2464037	2.2145929
Ir	2.7753766	5.5132484	2.2322865
Ir	5.5193892	5.5179639	2.2445676
Ir	8.2614279	8.2623053	2.2114706
Ir	5.5207052	8.2582483	2.2229192
Ir	8.2538614	5.5197182	2.2297885
Ir	1.3975581	1.4030412	4.1904287
Ir	4.1308236	4.1298366	4.1798124
Ir	1.4022735	4.1411324	4.1804371
Ir	4.1434350	1.4034798	4.2033343
Ir	6.8839383	1.4036993	4.2195706
Ir	9.6419878	4.1308236	4.1694045

Ir	6.8859124	4.1478214	4.2060404
Ir	9.6223583	1.4038090	4.1893878
Ir	1.4035896	6.8881054	4.1862655
Ir	4.1301656	9.6435232	4.1698213
Ir	1.4047958	9.6333246	4.1752329
Ir	4.1382804	6.8898597	4.1833510
Ir	6.8854737	6.8912864	4.2022934
Ir	9.6405630	9.6428652	4.1662822
Ir	6.8856931	9.6268539	4.2000036
Ir	9.6249905	6.8883252	4.1975060
Ir	0.0299383	0.0259904	6.0093131
Ir	2.7692354	2.7793243	6.0170150
Ir	0.0288416	2.7795436	6.0120192
Ir	2.7703321	0.0263194	6.0134764
Ir	5.5033784	0.0114051	6.0168071
Ir	8.2651567	2.7830532	6.0174313
Ir	5.5046940	2.7932518	6.0213866
Ir	8.2651567	0.0228101	6.0141006
Ir	0.0428786	5.5077648	6.0107703
Ir	2.7610104	8.2649374	6.0082722
Ir	0.0427690	8.2693233	6.0091047
Ir	2.7610104	5.5128088	6.0105619
Ir	5.4838581	5.5057907	6.1394119
Ir	8.2731619	8.2658148	6.0986128
Ir	5.4818840	8.2718458	6.1362896
Ir	8.2732716	5.5097389	6.0977802
C	5.9271202	6.8916149	7.4943123
C	7.7687078	6.8854737	7.6269093
O	8.1482544	6.8832803	8.7819777
H	5.6291628	6.8943563	8.5527954

Table S10. The Cartesian coordinates (in Å) of the R1's TS[trans-CH₃CH₂O···H][#] in the explicit model

Element	x	y	z
Ir	1.5819033	1.3708000	0.5127700
Ir	4.3235035	4.1124001	0.5127700
Ir	1.5819033	4.1124001	0.5127700
Ir	4.3235035	1.3708000	0.5127700
Ir	7.0651031	1.3708000	0.5127700
Ir	9.8067026	4.1124001	0.5127700
Ir	7.0651031	4.1124001	0.5127700
Ir	9.8067026	1.3708000	0.5127700
Ir	1.5819033	6.8540001	0.5127700
Ir	4.3235035	9.5956001	0.5127700
Ir	1.5819033	9.5956001	0.5127700
Ir	4.3235035	6.8540001	0.5127700
Ir	7.0651031	6.8540001	0.5127700
Ir	9.8067026	9.5956001	0.5127700
Ir	7.0651031	9.5956001	0.5127700
Ir	9.8067026	6.8540001	0.5127700
Ir	0.2111032	0.0000000	2.4512849
Ir	2.9527032	2.7416000	2.4512849
Ir	0.2111032	2.7416000	2.4512849
Ir	2.9527032	0.0000000	2.4512849
Ir	5.6943030	0.0000000	2.4512849
Ir	8.4359026	2.7416000	2.4512849
Ir	5.6943030	2.7416000	2.4512849
Ir	8.4359026	0.0000000	2.4512849
Ir	0.2111032	5.4832001	2.4512849
Ir	2.9527032	8.2248001	2.4512849
Ir	0.2111032	8.2248001	2.4512849
Ir	2.9527032	5.4832001	2.4512849
Ir	5.6943030	5.4832001	2.4512849
Ir	8.4359026	8.2248001	2.4512849
Ir	5.6943030	8.2248001	2.4512849
Ir	8.4359026	5.4832001	2.4512849
Ir	1.5868381	1.3891139	4.3919153
Ir	4.2862177	4.0882740	4.4067202
Ir	1.5732398	4.1058202	4.3902702
Ir	4.3216391	1.3647685	4.4074249
Ir	7.0580850	1.3713483	4.3775802
Ir	9.8073616	4.1132774	4.3613648

Ir	7.0459118	4.1301656	4.3771100
Ir	9.8018780	1.3727740	4.3634801
Ir	1.5657827	6.8473105	4.3695898
Ir	4.3255868	9.6084309	4.3764052
Ir	1.5631506	9.5982323	4.3608952
Ir	4.3203230	6.8498330	4.3677096
Ir	7.0717931	6.8715467	4.3679452
Ir	9.7965050	9.5834274	4.3674750
Ir	7.0521626	9.6195068	4.3855700
Ir	9.8025360	6.8590450	4.3778148
Ir	0.2026591	10.9639874	6.2023549
Ir	2.9498520	2.7036562	6.3078704
Ir	0.1662506	2.7428064	6.2002397
Ir	2.9146500	10.9271412	6.1936598
Ir	5.6916714	0.0081151	6.3010550
Ir	8.4293232	2.7406130	6.2035298
Ir	5.7123981	2.7494957	6.1934252
Ir	8.4648542	0.0038382	6.1929545
Ir	0.1742561	5.4896708	6.2117548
Ir	2.9484265	8.2314892	6.1974201
Ir	0.2097873	8.2228260	6.2108150
Ir	2.8975422	5.5200467	6.2089348
Ir	5.6503282	5.4776073	6.1950698
Ir	8.4196730	8.2365341	6.2119904
Ir	5.6790600	8.2392759	6.1807351
Ir	8.3931341	5.4817743	6.2425399
O	7.9806881	1.1687989	9.3426600
O	5.4169631	0.4159556	11.6926603
O	4.6136742	8.9490213	9.2787399
O	5.1546469	4.4654083	12.3034248
O	2.6992698	3.0421891	11.9246054
O	7.0894489	2.6688929	11.6278000
O	2.7818468	2.7207639	8.4113550
O	9.8828096	6.5393744	12.0341158
O	0.8534053	3.7351561	10.0377903
O	4.6893425	7.2516418	11.5267496
O	9.8054972	10.2005062	10.2114544
O	8.0644712	8.1731482	9.6620255
O	9.5358334	3.8949366	11.5239296
O	5.7189775	0.1392733	8.4061852
O	0.5447011	6.4119444	9.7022104

O	3.2809277	1.0448786	10.3023996
O	6.7977424	8.9560394	11.8978157
O	8.3383026	5.5409932	9.6815300
O	1.5101830	10.1337214	9.4883595
O	5.9600191	5.8811708	8.1916304
O	2.0330608	8.0928745	11.1965752
O	10.7537622	9.1923656	12.5356045
H	8.6858273	0.5364763	9.6674299
H	8.3293104	1.5318964	8.4860849
H	5.9458728	10.5509930	11.7669201
H	6.0521369	1.1705536	11.7941799
H	4.4132085	8.4908447	8.4242802
H	4.7812409	8.2512293	9.9665852
H	5.0089035	5.4192662	12.0919247
H	4.2775540	4.0258751	12.1986151
H	2.8975422	2.1872485	11.4141846
H	2.3696196	2.7754862	12.8002157
H	6.4086542	3.3982680	11.7361355
H	7.2112856	2.4611890	10.6734648
H	1.9065087	3.0205853	8.7878246
H	3.1190636	1.9621084	9.0054350
H	10.3005199	6.5963993	11.1408796
H	10.1566410	7.3640471	12.4897804
H	10.9146395	3.5821745	10.4217806
H	1.4651110	3.5741689	10.8116455
H	3.7710161	7.5942321	11.6726847
H	5.3392110	7.8751912	11.9391756
H	9.3083906	9.4011660	9.8730555
H	10.6972847	10.2119122	9.7626057
H	7.6355753	8.2983847	8.7828894
H	8.2336836	7.1719155	9.7247696
H	9.6298151	4.7147846	12.0717144
H	8.6823177	3.4344573	11.7619848
H	6.6073656	0.4396430	8.7908802
H	5.3906436	10.2448111	8.8444595
H	0.7163253	5.4243107	9.7275906
H	0.3852496	6.6371942	8.7551603
H	4.1446414	0.6843033	10.6925001
H	2.6676865	0.2860037	10.0699854
H	7.2512031	8.6546831	11.0480547
H	7.4548492	8.8259783	12.6037550

H	8.5810986	5.2754965	8.7626801
H	8.8212624	4.9279714	10.2974653
H	1.8229446	9.3230848	9.9947844
H	1.7040689	9.9745989	8.5314398
H	3.6945801	6.5194149	9.3678045
H	3.2882750	4.9045033	10.0013657
H	3.2341013	5.1953321	8.2578993
H	5.3184848	3.9666567	8.7549248
H	5.7519870	5.1131935	10.0650501
H	7.1589756	5.5911098	7.6652303
H	1.3553374	8.4305296	11.8338957
H	1.5598608	7.3866377	10.6643000
H	10.7941179	9.8318167	13.2664557
H	10.3485537	9.6694040	11.7441244
C	3.8019412	5.4460239	9.1981344
C	5.2446809	5.0180054	9.0970850

Table S11. The Cartesian coordinates (in Å) of the R2's TS[trans-CH₃CHOH···H][‡] in the explicit model

Element	x	y	z
Ir	1.5819033	1.3708000	0.5127700
Ir	4.3235035	4.1124001	0.5127700
Ir	1.5819033	4.1124001	0.5127700
Ir	4.3235035	1.3708000	0.5127700
Ir	7.0651031	1.3708000	0.5127700
Ir	9.8067026	4.1124001	0.5127700
Ir	7.0651031	4.1124001	0.5127700
Ir	9.8067026	1.3708000	0.5127700
Ir	1.5819033	6.8540001	0.5127700
Ir	4.3235035	9.5956001	0.5127700
Ir	1.5819033	9.5956001	0.5127700
Ir	4.3235035	6.8540001	0.5127700
Ir	7.0651031	6.8540001	0.5127700
Ir	9.8067026	9.5956001	0.5127700
Ir	7.0651031	9.5956001	0.5127700
Ir	9.8067026	6.8540001	0.5127700
Ir	0.2111032	0.0000000	2.4512849
Ir	2.9527032	2.7416000	2.4512849
Ir	0.2111032	2.7416000	2.4512849
Ir	2.9527032	0.0000000	2.4512849
Ir	5.6943030	0.0000000	2.4512849
Ir	8.4359026	2.7416000	2.4512849
Ir	5.6943030	2.7416000	2.4512849
Ir	8.4359026	0.0000000	2.4512849
Ir	0.2111032	5.4832001	2.4512849
Ir	2.9527032	8.2248001	2.4512849
Ir	0.2111032	8.2248001	2.4512849
Ir	2.9527032	5.4832001	2.4512849
Ir	5.6943030	5.4832001	2.4512849
Ir	8.4359026	8.2248001	2.4512849
Ir	5.6943030	8.2248001	2.4512849
Ir	8.4359026	5.4832001	2.4512849
Ir	1.5948435	1.3724449	4.3808699
Ir	4.2863269	4.0922217	4.4241099
Ir	1.5776263	4.1057105	4.3827500
Ir	4.3412690	1.3785862	4.4473753
Ir	7.0594006	1.3681681	4.4046049
Ir	9.8080196	4.1142645	4.3402147

Ir	7.0466800	4.1102066	4.3855700
Ir	9.7980394	1.3513895	4.3437400
Ir	1.5800389	6.8497233	4.3590150
Ir	4.3297544	9.6042633	4.3808699
Ir	1.5787230	9.5960388	4.3615999
Ir	4.3364434	6.8234043	4.3858051
Ir	7.0625811	6.8465428	4.3740549
Ir	9.7984781	9.5834274	4.3557248
Ir	7.0530400	9.6146812	4.3912101
Ir	9.8125153	6.8682561	4.3484402
Ir	0.2086906	10.9569693	6.1875501
Ir	2.9235327	2.7429161	6.3008199
Ir	0.1420149	2.7389681	6.1753302
Ir	2.9169526	10.9195738	6.1981249
Ir	5.6961679	10.9464407	6.3109250
Ir	8.4752731	2.7422578	6.2047052
Ir	5.6798272	2.7527859	6.3003497
Ir	8.4761505	10.9569693	6.2032948
Ir	0.2025494	5.4924121	6.2004752
Ir	2.9466717	8.2183294	6.1995354
Ir	0.2121998	8.2210712	6.2025900
Ir	2.9115794	5.5073261	6.2155151
Ir	5.6798272	5.5408831	6.2690949
Ir	8.4281178	8.2265549	6.1988301
Ir	5.6978126	8.2136145	6.1875501
Ir	8.4873362	5.4850645	6.1567655
O	8.0062399	1.0143920	9.4075203
O	5.2452292	0.2630839	11.6842003
O	4.5443664	8.7364922	9.2056551
O	5.1807470	4.2931261	12.3776846
O	2.5966244	2.9233134	12.0305901
O	7.1903396	2.5111959	11.7756147
O	2.1154187	2.3843148	8.2933855
O	9.7144756	6.6559467	11.7619848
O	0.8642620	3.8511803	10.1397800
O	4.6822143	6.8839383	11.3232403
O	9.8459635	10.1115694	10.3082752
O	7.9886937	8.3291998	9.5099802
O	9.2959976	4.1110840	11.1573296
O	5.6991282	10.9412870	8.4447250
O	0.5589574	6.4539456	9.6112652

O	2.9760618	0.8952969	10.3674955
O	6.6221704	8.7917633	11.7688007
O	8.3520107	5.6684222	9.2404346
O	1.4483325	9.8816042	9.4422998
O	6.0639806	5.0551815	8.3333349
O	2.1218886	7.9139028	11.2090302
O	10.8628769	9.0516663	12.5701504
H	8.7236624	0.4117883	9.7651901
H	8.3620996	1.3260571	8.5319099
H	5.7391558	10.3741055	11.7363701
H	5.8965235	0.9643852	11.9058046
H	4.2747030	8.3603449	8.3255796
H	4.6994314	7.9635806	9.8096056
H	5.0273266	5.2100272	12.0254202
H	4.2956486	3.8614891	12.3635845
H	2.7021210	2.0656312	11.5009003
H	2.2331977	2.6656029	12.8956242
H	6.4435277	3.1760890	11.8618603
H	7.2338762	2.1540203	10.8586445
H	1.5894700	3.0458081	8.8350601
H	2.6021073	1.7926774	8.9410448
H	10.2483206	6.7009091	10.9293795
H	10.0864563	7.3690920	12.3297453
H	10.8967638	3.7217767	10.4614944
H	1.4551317	3.6246147	10.9145746
H	3.7675068	7.2366176	11.4922047
H	5.3192525	7.5376458	11.7107553
H	9.2797680	9.3738594	9.9350948
H	10.7189980	10.0727482	9.8194752
H	7.6978645	8.5167255	8.5760899
H	8.2060480	7.3525324	9.5055151
H	9.4183826	4.9163466	11.7333145
H	8.5830727	3.5207627	11.5464907
H	6.5904770	0.2248112	8.8376446
H	5.3601570	10.0582724	8.8235455
H	0.7669900	5.4759622	9.6911650
H	0.5592864	6.6652684	8.6433001
H	3.8545799	0.5473331	10.7026052
H	2.4103050	0.1127346	10.0890198
H	7.0964670	8.6305571	10.8957748
H	7.2932048	8.6385622	12.4571142

H	8.9325724	5.5758657	8.4278049
H	8.6910915	5.0090127	9.9386196
H	1.8414779	9.1106663	9.9470797
H	1.6354193	9.7403564	8.4795055
H	4.8889308	3.6149642	10.3068647
H	4.7571149	2.1331842	9.3083506
H	3.9509747	3.6483018	8.7939348
H	6.7694492	2.9851637	7.6151752
H	6.9648705	3.4237103	9.1591253
H	6.9820876	5.4053388	8.6682100
H	1.4801350	8.2683373	11.8712597
H	1.5923213	7.2788382	10.6389198
H	10.8538847	9.6407814	13.3428307
H	10.4367228	9.5512962	11.8024044
C	4.8332214	3.2242315	9.2801495
C	6.0657353	3.6529078	8.5558805

Table S12. The Cartesian coordinates (in Å) of the R3's TS[trans-CH₂CH₂OH···H][‡] in the explicit model

Element	x	y	z
Ir	1.5819033	1.3708000	0.5127700
Ir	4.3235035	4.1124001	0.5127700
Ir	1.5819033	4.1124001	0.5127700
Ir	4.3235035	1.3708000	0.5127700
Ir	7.0651031	1.3708000	0.5127700
Ir	9.8067026	4.1124001	0.5127700
Ir	7.0651031	4.1124001	0.5127700
Ir	9.8067026	1.3708000	0.5127700
Ir	1.5819033	6.8540001	0.5127700
Ir	4.3235035	9.5956001	0.5127700
Ir	1.5819033	9.5956001	0.5127700
Ir	4.3235035	6.8540001	0.5127700
Ir	7.0651031	6.8540001	0.5127700
Ir	9.8067026	9.5956001	0.5127700
Ir	7.0651031	9.5956001	0.5127700
Ir	9.8067026	6.8540001	0.5127700
Ir	0.2111032	0.0000000	2.4512849
Ir	2.9527032	2.7416000	2.4512849
Ir	0.2111032	2.7416000	2.4512849
Ir	2.9527032	0.0000000	2.4512849
Ir	5.6943030	0.0000000	2.4512849
Ir	8.4359026	2.7416000	2.4512849
Ir	5.6943030	2.7416000	2.4512849
Ir	8.4359026	0.0000000	2.4512849
Ir	0.2111032	5.4832001	2.4512849
Ir	2.9527032	8.2248001	2.4512849
Ir	0.2111032	8.2248001	2.4512849
Ir	2.9527032	5.4832001	2.4512849
Ir	5.6943030	5.4832001	2.4512849
Ir	8.4359026	8.2248001	2.4512849
Ir	5.6943030	8.2248001	2.4512849
Ir	8.4359026	5.4832001	2.4512849
Ir	1.5913343	1.3913072	4.3818102
Ir	4.2981710	4.1012139	4.4288101
Ir	1.5923213	4.1090002	4.4154148
Ir	4.3316183	1.3718966	4.4050751
Ir	7.0665288	1.3705807	4.3745251
Ir	9.8238106	4.1142645	4.3529053

Ir	7.0449247	4.1225991	4.3731151
Ir	9.8119669	1.3619173	4.3564301
Ir	1.5973659	6.8340411	4.3975549
Ir	4.3379788	9.6006451	4.3733501
Ir	1.5776263	9.5861692	4.3585448
Ir	4.3334827	6.8404016	4.3886247
Ir	7.0655417	6.8633218	4.3641849
Ir	9.8071413	9.5906649	4.3620701
Ir	7.0625811	9.6135855	4.3811049
Ir	9.8334618	6.8614573	4.3641849
Ir	0.2189990	10.9610262	6.1955395
Ir	2.9686046	2.6693316	6.3104553
Ir	0.1658120	2.7327173	6.2009449
Ir	2.9236424	10.9285660	6.1835551
Ir	5.6956196	0.0048252	6.2951798
Ir	8.4410582	2.7421484	6.1936598
Ir	5.7319179	2.7431355	6.1953049
Ir	8.4713249	10.9653034	6.1934252
Ir	0.1912540	5.4876966	6.2185702
Ir	2.9653144	8.2471724	6.1995354
Ir	0.2134061	8.2284184	6.2159853
Ir	2.9757326	5.5174155	6.3492298
Ir	5.7569213	5.4938374	6.2399549
Ir	8.4326134	8.2271032	6.1960101
Ir	5.7054887	8.2382889	6.1856704
Ir	8.4718733	5.4818840	6.1555901
O	7.9659934	1.2065233	9.3356104
O	5.3917403	0.3459899	11.7467098
O	4.5241885	8.9520922	9.2246904
O	5.0759077	4.4107957	12.2087193
O	2.6034234	3.0288103	11.9269543
O	7.0320945	2.6356645	11.5730448
O	2.6740470	2.6329229	8.4369698
O	9.5404396	6.7504773	11.8806591
O	0.7192862	3.7667391	10.0751553
O	4.6018305	7.1037049	11.3624849
O	9.8216171	10.2621374	10.2015848
O	8.0242252	8.3252525	9.4665051
O	9.2299805	4.1400352	11.2463951
O	5.7057085	0.1412472	8.4134703
O	0.3116651	6.4469275	9.6871700

O	3.2502217	1.0138437	10.3681993
O	6.7037601	8.8319006	11.7523508
O	8.1116266	5.5712605	9.2902555
O	1.5021775	10.1456747	9.4643898
O	5.7154679	5.6473670	8.3424997
O	1.9799834	8.0358496	11.1303053
O	10.7759142	9.2040997	12.4996500
H	8.6952591	0.5982171	9.6502752
H	8.2816057	1.5722529	8.4642296
H	5.9086962	10.4712677	11.7800798
H	6.0374417	1.0902796	11.8350706
H	4.3373208	8.5944777	8.3138304
H	4.7017345	8.1778641	9.8166552
H	4.9292874	5.3720007	12.0200148
H	4.1865330	3.9836545	12.1565504
H	2.8239577	2.1722245	11.4233494
H	2.3179681	2.7596946	12.8171349
H	6.3082023	3.3259995	11.6503601
H	7.1531630	2.3514156	10.6346903
H	1.7681127	2.8632176	8.7687902
H	3.0465758	1.9045347	9.0413895
H	10.0446739	6.7512445	11.0285501
H	9.9527760	7.4799619	12.3957806
H	10.7671404	3.6652999	10.4443398
H	1.3300051	3.5806394	10.8426647
H	3.6921675	7.4727249	11.5086546
H	5.2673812	7.7409625	11.7319050
H	9.3106928	9.4910898	9.8258200
H	10.7134056	10.2692661	9.7494450
H	7.7137661	8.5184803	8.5391951
H	8.1670074	7.3358636	9.4707356
H	9.3197956	4.9361959	11.8327198
H	8.4719820	3.5660539	11.5702257
H	6.5948639	0.4326245	8.7936993
H	5.3740845	10.2481003	8.8423452
H	0.4972166	5.4637895	9.7445097
H	0.2067166	6.6511221	8.7231998
H	4.1122904	0.6485529	10.7547750
H	2.6453149	0.2556268	10.1089954
H	7.1451578	8.6593981	10.8645201
H	7.3668985	8.5542307	12.4098797

H	8.6197004	5.4067645	8.4421396
H	8.5184803	4.9673409	9.9947844
H	1.8102237	9.3112412	9.9259300
H	1.6882774	10.0312958	8.4968948
H	3.3409140	6.5973864	8.7685547
H	2.6035330	5.1115489	9.3379602
H	2.2747605	5.0548525	7.7735653
H	4.7173066	3.8329761	8.6082850
H	4.8184166	4.9202948	10.0340300
H	6.6317115	5.4789233	8.7737246
H	1.3451387	8.4179182	11.7873650
H	1.4385724	7.3745747	10.6100149
H	10.8008080	9.8208504	13.2504749
H	10.3668671	9.6984644	11.7196856
C	3.3290701	5.5150027	8.6136904
C	4.6546888	4.8797193	8.9478607

Table S13. The Cartesian coordinates (in Å) of the R4's TS[gauche-CH₃CH₂O···H][#] in the explicit model

Element	x	y	z
Ir	1.5819033	1.3708000	0.5127700
Ir	4.3235035	4.1124001	0.5127700
Ir	1.5819033	4.1124001	0.5127700
Ir	4.3235035	1.3708000	0.5127700
Ir	7.0651031	1.3708000	0.5127700
Ir	9.8067026	4.1124001	0.5127700
Ir	7.0651031	4.1124001	0.5127700
Ir	9.8067026	1.3708000	0.5127700
Ir	1.5819033	6.8540001	0.5127700
Ir	4.3235035	9.5956001	0.5127700
Ir	1.5819033	9.5956001	0.5127700
Ir	4.3235035	6.8540001	0.5127700
Ir	7.0651031	6.8540001	0.5127700
Ir	9.8067026	9.5956001	0.5127700
Ir	7.0651031	9.5956001	0.5127700
Ir	9.8067026	6.8540001	0.5127700
Ir	0.2111032	0.0000000	2.4512849
Ir	2.9527032	2.7416000	2.4512849
Ir	0.2111032	2.7416000	2.4512849
Ir	2.9527032	0.0000000	2.4512849
Ir	5.6943030	0.0000000	2.4512849
Ir	8.4359026	2.7416000	2.4512849
Ir	5.6943030	2.7416000	2.4512849
Ir	8.4359026	0.0000000	2.4512849
Ir	0.2111032	5.4832001	2.4512849
Ir	2.9527032	8.2248001	2.4512849
Ir	0.2111032	8.2248001	2.4512849
Ir	2.9527032	5.4832001	2.4512849
Ir	5.6943030	5.4832001	2.4512849
Ir	8.4359026	8.2248001	2.4512849
Ir	5.6943030	8.2248001	2.4512849
Ir	8.4359026	5.4832001	2.4512849
Ir	1.5894700	1.3963518	4.3977900
Ir	4.2938938	4.0984726	4.4020200
Ir	1.5732398	4.1098776	4.3916802
Ir	4.3148398	1.3714581	4.4111853
Ir	7.0516143	1.3645492	4.3747602
Ir	9.8046198	4.1211734	4.3681803

Ir	7.0524921	4.1084518	4.3634801
Ir	9.8083487	1.3716774	4.3594847
Ir	1.5668792	6.8498330	4.3583102
Ir	4.3215294	9.6075535	4.3841600
Ir	1.5707176	9.6019611	4.3620701
Ir	4.3206520	6.8461041	4.3731151
Ir	7.0544662	6.8495035	4.3825150
Ir	9.7900343	9.5857306	4.3670049
Ir	7.0470085	9.6138039	4.3933249
Ir	9.7948599	6.8641992	4.3707652
Ir	0.2005755	10.9598207	6.1945996
Ir	2.9463427	2.7285500	6.3149199
Ir	0.1662506	2.7465348	6.2021203
Ir	2.9054379	10.9363518	6.2030602
Ir	5.6927681	10.9462223	6.3024650
Ir	8.4327230	2.7333751	6.1943650
Ir	5.7183199	2.7329366	6.1896653
Ir	8.4616747	0.0054832	6.1976547
Ir	0.1811649	5.4965792	6.2032948
Ir	2.9445882	8.2306128	6.1997700
Ir	0.2085809	8.2216206	6.1997700
Ir	2.9058766	5.5298071	6.1948352
Ir	5.6566887	5.5110545	6.2289100
Ir	8.4218664	8.2333536	6.2115197
Ir	5.6838851	8.2290773	6.1971850
Ir	8.3996048	5.4716854	6.2188048
O	7.7011547	1.3971193	9.3774405
O	5.3529191	0.3688000	11.6489496
O	4.3659430	9.1306248	9.3088207
O	5.1362233	3.7891104	13.2427206
O	2.5567067	3.0912087	12.2171803
O	7.2221422	2.5909216	11.8900595
O	2.8865759	2.9858217	8.4231052
O	9.8044004	6.8020191	11.6705704
O	0.9821508	3.9840932	10.1155748
O	4.1175542	7.4105449	12.7024555
O	9.5390139	10.4544888	10.1395454
O	7.8574257	8.4220858	9.4705000
O	9.4016047	4.1669030	11.1970444
O	5.5651193	0.2696638	8.3826847
O	0.7122676	6.6013341	9.5334797

O	3.2475896	1.3154197	10.3954601
O	6.4506559	8.8134766	11.7424803
O	8.3368769	5.8507938	9.3504152
O	1.2411771	10.7288685	9.3882504
O	2.0392020	8.5203447	10.7728701
O	10.8164892	9.3768206	12.2731104
O	5.7587852	4.9295068	8.2092552
H	8.4231825	0.7633711	9.6679001
H	8.0362883	1.8237123	8.5471849
H	5.7558250	10.4287176	11.7119303
H	6.0564137	1.0129664	11.8949947
H	4.0347581	8.8172045	8.4271002
H	3.6140869	9.0062656	9.9379148
H	5.1043110	4.7591982	13.3456497
H	4.2351141	3.5572810	12.9069042
H	2.7862334	2.3100722	11.6127596
H	2.0506070	2.7277825	12.9649496
H	6.4565778	3.1225729	12.2538404
H	7.1162066	2.4670014	10.9190397
H	2.0314159	3.3222709	8.8160248
H	3.2002149	2.2480023	9.0458555
H	10.2868128	6.8215394	10.8097649
H	10.1548862	7.5756993	12.1638355
H	0.0357505	3.8418589	10.3916998
H	1.5135825	3.7952518	10.9385443
H	3.3892758	7.7370143	12.1351652
H	4.9150310	7.8653216	12.3461952
H	9.0592337	9.6593151	9.7616653
H	10.3971348	10.5704041	9.6488647
H	7.4266653	8.5486374	8.5894852
H	8.1094341	7.4367542	9.4935293
H	9.5200415	4.9960728	11.7300253
H	8.6836348	3.6097004	11.6101751
H	6.4145765	0.6160924	8.8277750
H	5.1345782	10.4573402	8.8745403
H	0.9102112	5.6298208	9.6951599
H	0.6234398	6.7099013	8.5532951
H	4.0676570	0.8503347	10.7702856
H	2.5560486	0.6521719	10.1122856
H	6.8765907	8.6324215	10.8511248
H	7.1597433	8.6585217	12.3913145

H	8.8083229	5.6760988	8.4992447
H	8.6530380	5.1536598	9.9912596
H	1.5362830	9.8250170	9.6963348
H	1.3788054	10.7442207	8.4000750
H	1.3772701	8.8277330	11.4477901
H	1.6080033	7.7330670	10.3080397
H	10.8311844	9.9253597	13.0756350
H	10.2695951	9.8669090	11.5831499
H	4.6069846	3.9881506	10.3630295
H	4.1153612	5.5559072	11.0734348
H	5.8359890	5.1680260	10.9101105
H	5.1612267	6.7421427	9.0900354
H	3.8500838	5.6425419	8.5946550
H	6.9633350	5.3555512	7.6525397
C	4.8543868	5.0551815	10.4314156
C	4.8617339	5.6821308	9.0637150

Table S13. Cartesian coordinates (in Å) of the R5's TS[gauche-CH₃CHOH···H][‡] in the explicit model

Element	x	y	z
Ir	1.5819033	1.3708000	0.5127700
Ir	4.3235035	4.1124001	0.5127700
Ir	1.5819033	4.1124001	0.5127700
Ir	4.3235035	1.3708000	0.5127700
Ir	7.0651031	1.3708000	0.5127700
Ir	9.8067026	4.1124001	0.5127700
Ir	7.0651031	4.1124001	0.5127700
Ir	9.8067026	1.3708000	0.5127700
Ir	1.5819033	6.8540001	0.5127700
Ir	4.3235035	9.5956001	0.5127700
Ir	1.5819033	9.5956001	0.5127700
Ir	4.3235035	6.8540001	0.5127700
Ir	7.0651031	6.8540001	0.5127700
Ir	9.8067026	9.5956001	0.5127700
Ir	7.0651031	9.5956001	0.5127700
Ir	9.8067026	6.8540001	0.5127700
Ir	0.2111032	0.0000000	2.4512849
Ir	2.9527032	2.7416000	2.4512849
Ir	0.2111032	2.7416000	2.4512849
Ir	2.9527032	0.0000000	2.4512849
Ir	5.6943030	0.0000000	2.4512849
Ir	8.4359026	2.7416000	2.4512849
Ir	5.6943030	2.7416000	2.4512849
Ir	8.4359026	0.0000000	2.4512849
Ir	0.2111032	5.4832001	2.4512849
Ir	2.9527032	8.2248001	2.4512849
Ir	0.2111032	8.2248001	2.4512849
Ir	2.9527032	5.4832001	2.4512849
Ir	5.6943030	5.4832001	2.4512849
Ir	8.4359026	8.2248001	2.4512849
Ir	5.6943030	8.2248001	2.4512849
Ir	8.4359026	5.4832001	2.4512849
Ir	1.5762007	1.3903203	4.3787551
Ir	4.2862177	4.0889320	4.4182353
Ir	1.5832193	4.1048331	4.4017849
Ir	4.3194456	1.3751867	4.4083653
Ir	7.0623617	1.3743093	4.3771100
Ir	9.8158054	4.1162381	4.3484402

Ir	7.0369196	4.1298366	4.3766398
Ir	9.7984781	1.3688260	4.3538451
Ir	1.6062486	6.8261456	4.4050751
Ir	4.3356757	9.6161070	4.3686500
Ir	1.5726914	9.5845242	4.3566647
Ir	4.3262448	6.8545485	4.3733501
Ir	7.0625811	6.8633218	4.3648901
Ir	9.7997942	9.5844145	4.3608952
Ir	7.0572076	9.6207132	4.3818102
Ir	9.8300619	6.8654051	4.3653603
Ir	0.2091292	10.9606981	6.1821446
Ir	2.9850540	2.6895096	6.3285503
Ir	0.1399313	2.7440126	6.1920147
Ir	2.9127855	10.9383259	6.1788549
Ir	5.7009931	0.0037286	6.2984700
Ir	8.4306393	2.7439029	6.1981249
Ir	5.7263250	2.7530053	6.2000051
Ir	8.4674864	0.0016450	6.1962447
Ir	0.1939956	5.4868188	6.2108150
Ir	2.9705787	8.2559443	6.1931901
Ir	0.2109935	8.2272129	6.2096400
Ir	2.9347186	5.5411029	6.3407702
Ir	5.7764416	5.4908767	6.2220950
Ir	8.4300909	8.2255678	6.1995354
Ir	5.7018704	8.2532034	6.1793251
Ir	8.4594812	5.4822130	6.1715698
O	7.7738619	1.2799982	9.3706255
O	5.2023506	0.3397391	11.7690353
O	4.4102473	9.0241413	9.2794456
O	4.9130569	4.1681094	12.6187954
O	2.2622588	3.0067675	12.1130753
O	6.9060907	2.6024365	11.7227402
O	2.2766247	2.3775156	8.3516655
O	9.5396709	6.8050904	11.6017151
O	0.5190397	3.7363625	10.0833797
O	4.4411726	6.8547673	12.0428095
O	9.5841951	10.2939405	10.1813755
O	7.7631145	8.3923664	9.3929501
O	8.9548330	4.2426810	11.0724955
O	5.5595260	0.2404931	8.4045401
O	0.4358048	6.4018550	9.5386505

O	3.0701535	1.1083741	10.4840555
O	6.4076676	8.8122702	11.6724501
O	7.4879680	5.6251054	9.3170452
O	1.2392032	10.3946123	9.3710947
O	2.0760491	8.1348753	10.7404404
O	10.9218769	9.1815090	12.2662945
O	5.2209935	5.8814993	8.2130146
H	8.4827299	0.6463596	9.6841154
H	8.1088858	1.6536236	8.5124054
H	5.6716032	10.4327755	11.7608109
H	5.8818288	1.0457560	11.9048653
H	4.1223798	8.7529421	8.3641195
H	3.6396384	8.8434153	9.8645954
H	4.7985678	5.1466413	12.4951859
H	4.0096450	3.7936070	12.5045843
H	2.5468369	2.1865904	11.5871449
H	1.9332668	2.6888516	12.9715309
H	6.1429386	3.2339914	11.9123859
H	6.9509435	2.3789413	10.7644100
H	1.5394632	2.8961167	8.7687902
H	2.7921553	1.9014641	9.0780497
H	10.0925970	6.7615533	10.7803898
H	9.9841394	7.4937801	12.1440954
H	10.5246735	3.7125649	10.3494005
H	1.0285387	3.5286586	10.9152803
H	3.6071780	7.2294898	11.6863146
H	5.1307402	7.5515728	11.9027500
H	9.0732708	9.5278282	9.7950354
H	10.4401226	10.3703756	9.6744804
H	7.4186602	8.5946960	8.4827948
H	7.8091741	7.3947535	9.4190350
H	9.1366568	5.0526590	11.6205149
H	8.2932310	3.6495082	11.5363846
H	6.4326706	0.5297868	8.8324747
H	5.1440091	10.4085398	8.8689003
H	0.5439335	5.4121375	9.6688404
H	0.3163807	6.5368519	8.5601101
H	3.9296997	0.7226858	10.8729801
H	2.4491262	0.3781215	10.2069902
H	6.8115602	8.6825380	10.7608852
H	7.1333146	8.6164103	12.2919102

H	7.8886795	5.4300132	8.4193449
H	7.9957118	5.0416927	9.9701099
H	1.5378183	9.4803429	9.6194897
H	1.3716774	10.4713764	8.3843298
H	1.4642339	8.5066366	11.4289894
H	1.5356250	7.4172344	10.2824249
H	0.0209458	9.7416725	13.0580101
H	10.3713627	9.6864014	11.5892601
H	4.2752509	3.6272466	9.3870754
H	2.7907295	4.4353604	9.9773951
H	4.3744969	5.0523300	10.4680748
H	3.3050537	6.4763174	8.6914749
H	3.3665752	4.4989657	7.5874448
H	5.9562907	5.5983477	8.8757143
C	3.8171847	4.5930576	9.6406403
C	3.8615985	5.5553589	8.4856148

Table S14. Cartesian coordinates (in Å) of the R6's TS[CH₂⋯CO][‡] in the explicit model

Element	x	y	z
Ir	1.3675101	1.3687165	0.3201470
Ir	4.1085620	4.1110840	0.3126533
Ir	1.3676198	4.1103168	0.3166083
Ir	4.1093297	1.3697034	0.3155675
Ir	6.8513680	1.3713483	0.3122370
Ir	9.5901165	4.1148129	0.3080738
Ir	6.8499422	4.1126194	0.3101554
Ir	9.5936260	1.3723353	0.3136941
Ir	1.3669618	6.8527942	0.3132778
Ir	4.1060395	9.5968065	0.3082820
Ir	1.3652072	9.5952711	0.3128615
Ir	4.1075749	6.8543291	0.3091146
Ir	6.8489552	6.8568511	0.3068249
Ir	9.5906649	9.6031666	0.3089065
Ir	6.8479691	9.5999870	0.3066167
Ir	9.5892391	6.8590450	0.3041188
Ir	10.9623423	10.9651937	2.2614286
Ir	2.7406130	2.7408323	2.2547674
Ir	10.9654131	2.7410517	2.2587225
Ir	2.7369940	0.0001097	2.2568491
Ir	5.4769492	0.0027416	2.2528942
Ir	8.2215099	2.7424772	2.2497716
Ir	5.4815550	2.7413807	2.2514367
Ir	8.2165756	0.0066895	2.2495635
Ir	10.9653034	5.4826517	2.2564328
Ir	2.7390778	8.2256775	2.2487309
Ir	10.9638777	8.2237034	2.2528942
Ir	2.7397356	5.4836388	2.2508125
Ir	5.4805679	5.4851742	2.2470655
Ir	8.2194262	8.2314892	2.2435269
Ir	5.4791427	8.2285290	2.2451921
Ir	8.2203035	5.4873672	2.2443595
Ir	1.3763930	1.3903203	4.1781473
Ir	4.0850935	4.1043944	4.2120771
Ir	1.3824244	4.1065879	4.2016692
Ir	4.1054912	1.3786957	4.2000036
Ir	6.8493943	1.3665231	4.1529598
Ir	9.5900078	4.1193089	4.1710701

Ir	6.8459949	4.1161289	4.1635761
Ir	9.6064568	1.3682778	4.1390138
Ir	1.3701420	6.8245001	4.1741920
Ir	4.1281915	9.5985613	4.1898041
Ir	1.3598336	9.5940647	4.1517115
Ir	4.1153612	6.8711076	4.1864738
Ir	6.8277903	6.8944659	4.1827269
Ir	9.5862789	9.5833178	4.1523356
Ir	6.8328347	9.6031666	4.1916776
Ir	9.5753126	6.8431435	4.1879306
Ir	10.9624519	10.9660711	5.9926605
Ir	2.7345815	2.6740470	6.1006947
Ir	10.9260435	2.7357879	5.9932852
Ir	2.7131970	10.9297724	5.9909954
Ir	5.4818840	0.0605345	6.0734262
Ir	8.2199745	2.6828201	5.9839182
Ir	5.5039268	2.7473025	5.9810038
Ir	8.2635117	0.0006580	5.9749670
Ir	0.0103080	5.4850645	5.9959912
Ir	2.6869874	8.2516680	5.9789224
Ir	10.9592724	8.2285290	6.0043173
Ir	2.7403936	5.5459280	6.0728016
Ir	5.4785943	5.4791427	6.0272150
Ir	8.2324762	8.2562742	5.9995294
Ir	5.5147829	8.2072535	6.0757160
Ir	8.2782068	5.4855027	6.1623092
O	6.6162486	5.4006228	7.7805300
O	8.2060480	4.7621593	7.9016771
O	8.6417427	4.2967453	8.9258146
O	7.9290361	1.1783397	9.0540400
O	5.1946740	0.5963528	11.4399471
O	4.8582249	8.5914068	8.2624159
O	4.9144826	4.4360185	10.6433258
O	2.6388450	3.1431894	11.6820345
O	6.9687090	2.6754727	11.1347876
O	2.5242460	2.8670557	8.2724075
O	8.9480343	6.4714923	10.5721359
O	0.5786969	3.6962252	9.9699354
O	4.5376773	7.2179751	10.4272585
O	9.8581362	10.5176544	10.0409174
O	8.0622787	8.6179457	9.4020805

O	9.5108299	3.6583912	11.7650890
O	5.6640358	0.1119669	8.2068367
O	0.3572853	6.2724519	9.3602400
O	3.1415446	1.1685796	10.0026159
O	6.3401146	8.9997959	11.3862419
O	3.0361576	5.4092865	8.2420158
O	1.4812316	10.2398758	9.1443806
H	1.9889760	7.9948349	10.5350847
H	0.1432212	9.1960945	12.1227055
H	6.6131778	6.3137951	8.3866863
H	6.1853786	4.5342774	8.3088350
H	8.7081995	0.6511848	9.4166517
H	8.2530937	1.5867286	8.2053804
H	5.6567979	10.6909237	11.4455671
H	5.8926854	1.3102654	11.4243345
H	3.9273970	8.8174248	7.9772391
H	4.7721386	7.9207020	9.0438404
H	4.8296027	5.4184985	10.7111864
H	4.1311526	4.0596514	11.1166773
H	2.7704415	2.2631359	11.2076435
H	2.5008874	2.9467812	12.6245747
H	6.3105054	3.3989263	10.9362049
H	7.2934237	2.3182969	10.2657280
H	1.5846448	2.9784744	8.5987988
H	2.9402015	2.1239724	8.8927183
H	8.5622358	5.6612945	10.1678934
H	9.8715153	6.4633770	10.1699753
H	10.6711845	3.5546491	10.4464092
H	1.2557625	3.5862319	10.6924524
H	3.5818458	7.4895034	10.6162663
H	5.1318364	7.8145471	10.9668036
H	9.3117895	9.7443047	9.7134848
H	10.7215204	10.4947357	9.5427952
H	7.9699411	8.5537920	8.4102077
H	8.4007015	7.7197971	9.7542839
H	9.3785753	4.6188283	11.8858213
H	8.5936003	3.2990222	11.6162567
H	6.5742469	0.4308698	8.5301065
H	5.5159898	10.1284580	8.4753609
H	0.5123503	5.2827344	9.5173998
H	0.3194512	6.3946171	8.3752375

H	4.0236821	0.8509927	10.4183083
H	2.5630672	0.3856883	9.7449160
H	6.9705729	8.9139290	10.6008625
H	6.8734107	8.7947235	12.1751614
H	2.9637794	4.4123311	8.4110403
H	3.9845316	5.6189642	8.3771105
H	1.7077974	9.3396444	9.5350933
H	1.5656730	10.1615763	8.1550064
H	1.4200392	8.3630867	11.2721720
H	1.4276060	7.2819090	10.0910835
C	0.2617680	9.7017546	12.9436798
C	10.6024256	9.7829065	11.4946918

Table S15. Cartesian coordinates (in Å) of the R7's TS[CH \cdots CO] ‡ in the explicit model

Element	x	y	z
Ir	1.4007382	1.4064409	0.3773905
Ir	4.1495762	4.1497955	0.3892555
Ir	1.4036993	4.1527562	0.3780149
Ir	4.1550593	1.4054538	0.3786394
Ir	6.8764811	1.4054538	0.3815536
Ir	9.6115017	4.1478214	0.3773905
Ir	6.8754940	4.1434350	0.3873820
Ir	9.6140242	1.4000803	0.3771823
Ir	1.4125820	6.8750553	0.3748926
Ir	4.1446414	9.6229067	0.3713539
Ir	1.4028219	9.6166554	0.3734354
Ir	4.1497955	6.8758235	0.3848841
Ir	6.8791132	6.8750553	0.3761415
Ir	9.6156683	9.6172037	0.3505381
Ir	6.8733010	9.6225777	0.3632357
Ir	9.6175327	6.8792229	0.3605296
Ir	0.0279643	0.0330089	2.1960669
Ir	2.7659454	2.7691259	2.2000220
Ir	0.0330089	2.7729640	2.1966913
Ir	2.7667131	0.0396984	2.1914873
Ir	5.5205951	0.0354215	2.2272906
Ir	8.2451983	2.7753766	2.2172990
Ir	5.5169768	2.7750475	2.2302048
Ir	8.2445393	0.0325702	2.2102215
Ir	0.0294996	5.5244336	2.2152174
Ir	2.7730734	8.2515583	2.2091808
Ir	0.0323509	8.2437725	2.2131360
Ir	2.7777894	5.5125899	2.2289557
Ir	5.5201569	5.5171957	2.2383230
Ir	8.2613182	8.2603312	2.1906548
Ir	5.5202665	8.2585764	2.2110543
Ir	8.2538614	5.5165381	2.2187562
Ir	1.4119240	1.4279349	4.1789799
Ir	4.1074653	4.1164575	4.1764817
Ir	1.4169685	4.1323590	4.1652417
Ir	4.1459575	1.3998609	4.2045832
Ir	6.8852544	1.3906492	4.1977143
Ir	9.6389170	4.1568136	4.1360993

Ir	6.8804293	4.1578007	4.1523356
Ir	9.6224680	1.3887850	4.1571231
Ir	1.3898815	6.8694630	4.1400542
Ir	4.1523175	9.6402330	4.1589966
Ir	1.3918555	9.6357374	4.1302710
Ir	4.1398158	6.8836088	4.1483808
Ir	6.9012656	6.8994012	4.1604538
Ir	9.6135855	9.6388073	4.1681557
Ir	6.8852544	9.6633720	4.1952162
Ir	9.6318989	6.8910666	4.1515031
Ir	0.0610828	0.0330089	5.9672651
Ir	2.7638617	2.7653971	6.0956988
Ir	10.9575167	2.7791052	5.9760079
Ir	2.7429161	10.9575167	5.9601884
Ir	5.4675179	0.0275257	6.0534425
Ir	8.2621956	2.8046567	5.9541516
Ir	5.5409932	2.8177068	5.9755917
Ir	8.3056221	0.0357505	6.0546918
Ir	0.0460589	5.5204864	5.9778814
Ir	2.7480702	8.2567129	5.9574814
Ir	0.0489101	8.2561646	5.9768405
Ir	2.7557466	5.5452700	5.9785056
Ir	5.5017328	5.4827614	6.0738425
Ir	8.2821541	8.2483778	6.0359578
Ir	5.4760718	8.2528744	6.0775895
Ir	8.2959719	5.4755235	6.0057745
O	5.8212943	6.8327250	7.4426889
O	7.6124363	7.5803046	7.7184982
O	7.8191533	7.6529021	8.9168644
O	8.2227163	0.3502668	8.2291107
O	5.3478746	10.7284288	11.0762949
O	4.0836678	9.2043190	8.9133253
O	5.1193347	3.3675621	12.1443539
O	2.3594210	2.4893727	11.8995600
O	7.0535884	1.8589146	11.0257130
O	2.7632039	2.7432449	8.2476358
O	8.6669655	5.3541255	10.8017349
O	0.8557082	3.4614346	9.8379631
O	4.0791717	7.0155349	10.4566088
O	9.5515156	9.7185335	9.5877571
O	7.0392222	3.8553476	9.1191940

O	9.6806993	2.8263705	11.1841202
O	5.5624871	0.1456338	8.1502180
O	0.1057161	6.0141935	9.3999987
O	3.0357189	0.7562430	9.9786787
O	6.5004435	7.5948901	11.4705467
O	4.4981980	4.4746203	9.6701880
O	1.1489497	9.8357639	9.1616583
H	1.5374893	7.7682686	10.8011112
H	10.4418774	8.9371777	12.1483088
H	5.5334263	6.7621017	8.4982586
H	8.8423185	10.6545153	8.8109121
H	8.5414000	1.2710058	8.3467197
H	5.7375112	9.8777657	11.3504391
H	6.0777984	0.4447972	11.0558958
H	3.8306735	8.8645802	8.0140829
H	4.1786370	8.3890772	9.4886742
H	4.8530707	3.7940454	11.2896576
H	4.2804055	2.9483166	12.4330683
H	2.5655894	1.7127323	11.2931957
H	1.7014370	2.1740887	12.5442257
H	6.4139180	2.3711550	11.6143827
H	7.0288048	2.4047122	10.1947460
H	1.8708678	2.9937174	8.6843519
H	3.0225594	1.8807375	8.7186975
H	8.0731344	4.9403634	10.1214743
H	9.4036884	5.7507801	10.2775927
H	10.9373388	3.0632443	10.1364613
H	1.4307861	3.2971580	10.6433258
H	3.2039435	7.2541642	10.8729248
H	4.8462715	7.1692843	11.0762949
H	9.1608915	8.8517485	9.3117399
H	10.5398073	9.7414532	9.3150702
H	6.0830622	4.1535239	9.1824741
H	7.2498870	3.8420782	8.1527166
H	9.3451271	3.7691517	11.2113905
H	8.8440723	2.2965834	11.2130556
H	6.5239115	0.1771074	8.4085426
H	5.0835843	10.2986555	8.5823536
H	0.4411783	5.0729470	9.5136538
H	0.1002329	6.1791277	8.4226971
H	3.8754163	0.2990537	10.2750950

H	2.4062476	0.0377244	9.6955833
H	7.0016074	7.4976182	10.6281309
H	6.9639926	6.9798942	12.0708742
H	3.8571024	4.0316873	9.0659056
H	4.2021050	5.4097252	9.8589878
H	1.4404366	9.0246897	9.6953754
H	1.3880173	9.6667719	8.2157879
H	0.9137204	8.1217155	11.4901123
H	1.0157080	7.0644455	10.3009062
C	10.2428370	9.4297876	12.9609585
C	9.9610004	9.3832903	11.4118462

Table S16. Cartesian coordinates (in Å) of the R6's TS[CH₂···CO][#] in the gas-phase model

Element	x	y	z
Ir	1.3721160	1.3671811	0.3203552
Ir	4.1150322	4.1093297	0.3166083
Ir	1.3727740	4.1093297	0.3176491
Ir	4.1148129	1.3675101	0.3184817
Ir	6.8590450	1.3675101	0.3199388
Ir	9.6010838	4.1104259	0.3222286
Ir	6.8591542	4.1097679	0.3184817
Ir	9.6019611	1.3675101	0.3247265
Ir	1.3734319	6.8523550	0.3151512
Ir	4.1156898	9.5952711	0.3143186
Ir	1.3732126	9.5949421	0.3151512
Ir	4.1156898	6.8531227	0.3145267
Ir	6.8597026	6.8538904	0.3170246
Ir	9.6026182	9.5973549	0.3226449
Ir	6.8599219	9.5966969	0.3178573
Ir	9.6017408	6.8538904	0.3207715
Ir	0.0013160	10.9655228	2.2618446
Ir	2.7428064	2.7394068	2.2549756
Ir	0.0010966	2.7401745	2.2574735
Ir	2.7433548	10.9658518	2.2593470
Ir	5.4859414	0.0013160	2.2587225
Ir	8.2277613	2.7402840	2.2589307
Ir	5.4861612	2.7396259	2.2545593
Ir	8.2280903	0.0023029	2.2608039
Ir	0.0021933	5.4821033	2.2560163
Ir	2.7443419	8.2251291	2.2512288
Ir	0.0020836	8.2235937	2.2528942
Ir	2.7434642	5.4826517	2.2524776
Ir	5.4863801	5.4829807	2.2522695
Ir	8.2283096	8.2250195	2.2564328
Ir	5.4869285	8.2258968	2.2520614
Ir	8.2268839	5.4828711	2.2570572
Ir	1.3688260	1.3665231	4.1837678
Ir	4.1121807	4.1137161	4.2110362
Ir	1.3652072	4.1116323	4.2052078
Ir	4.0954022	1.3704710	4.1700292
Ir	6.8588252	1.3769412	4.1906371
Ir	9.5904465	4.1144834	4.2176971

Ir	6.8472009	4.1054912	4.2287297
Ir	9.6106243	1.3748575	4.1793962
Ir	1.3650975	6.8578382	4.2091627
Ir	4.1272044	9.5863886	4.2045832
Ir	1.3690454	9.6009741	4.1912613
Ir	4.1336751	6.8637605	4.2358069
Ir	6.8456655	6.8468719	4.2293544
Ir	9.5810146	9.5818920	4.2099957
Ir	6.8579483	9.5909948	4.2072897
Ir	9.5679646	6.8579483	4.2428846
Ir	0.0018643	0.0058122	6.0440755
Ir	2.7341428	2.7128682	6.0415773
Ir	0.0078958	2.7145131	6.0455327
Ir	2.7377617	0.0063605	6.0392876
Ir	5.4800196	0.0322412	6.0284638
Ir	8.2341213	2.6988311	6.0438671
Ir	5.4668603	2.7001469	6.0324187
Ir	8.2260065	0.0270870	6.0295048
Ir	10.9521437	5.4783750	6.0802956
Ir	2.7207639	8.2522163	6.0459490
Ir	0.0180946	8.2503519	6.0494876
Ir	2.7160482	5.4799104	6.0715528
Ir	5.4276004	5.4531522	6.1398282
Ir	8.2909279	8.2612085	6.1317101
Ir	5.4127960	8.2647181	6.1219263
Ir	8.2254581	5.4462433	6.2116427
C	5.7769904	5.3928366	8.0823584
C	7.6858015	5.3842831	8.0921421
O	8.0540533	5.3486423	9.2211914
H	5.5880389	6.2970166	8.6766500
H	5.6078882	4.4604735	8.6385565