Theoretical study on the reaction of Ti$^+$ with acetone and the role of intersystem crossing

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Table S1. Bond dissociation energies (ΔH at 298 K) of $Ti^+(H_2O)_n$, $Ti^+(NH_3)_n$ (n= 1 and 2), and (D_0 at 298 K) $Ti^+(C_2H_4)$ calculated by various DFT functionals with the aug-cc-pVTZ basis set.

DFT/aug-cc-pVTZ	B3LYP	B3P86	PBE0	B98	M05	Exp.
$Ti^+(H_2O) \rightarrow Ti^+ + H_2O$	37.4	38.0	37.5	35.3	33.7	37.7 ± 1.4[a]
$Ti^+(H_2O)_2 \rightarrow Ti^+(H_2O) + H_2O$	32.8	33.7	33.3	31.4	28.3	32.6 ± 1.2[a]
$Ti^+(NH_3) \rightarrow Ti^+ + NH_3$	46.7	47.7	47.3	44.6	42.4	47.1 ± 1.7[b]
$Ti^+(NH_3)_2 \rightarrow Ti^+(NH_3) + NH_3$	37.9	39.5	39.1	37.6	37.3	42.1 ± 4.1[b]
$Ti^+(C_2H_4) \rightarrow Ti^+ + C_2H_4$	30.5	35.1	34.6	34.0	34.7	34.9 ± 2.6[c]

a: reference[1]
b: reference[2]
c: reference[3]

Figure S1. Selective molecular orbitals of [4]IM1 and [2]IM2. Natural electron configurations of Ti, C(2), and O are summarized.

Ti
α 4s(0.66) 3d(2.33) 4p(0.02)
β 4s(0.01) 3d(0.06)
C(2)
α 2s(0.45) 2p(1.26) 3p(0.01)
β 2s(0.44) 2p(1.15)
O
α 2s(0.83) 2p(2.50)
β 2s(0.83) 2p(2.55)

Ti
α 4s(0.10) 3d(1.72) 4p(0.01)
β 4s(0.07) 3d(0.61) 4p(0.01)
C(2)
α 2s(0.50) 2p(1.43)
β 2s(0.51) 2p(1.51)
O
α 2s(0.88) 2p(2.38) 3d(0.01)
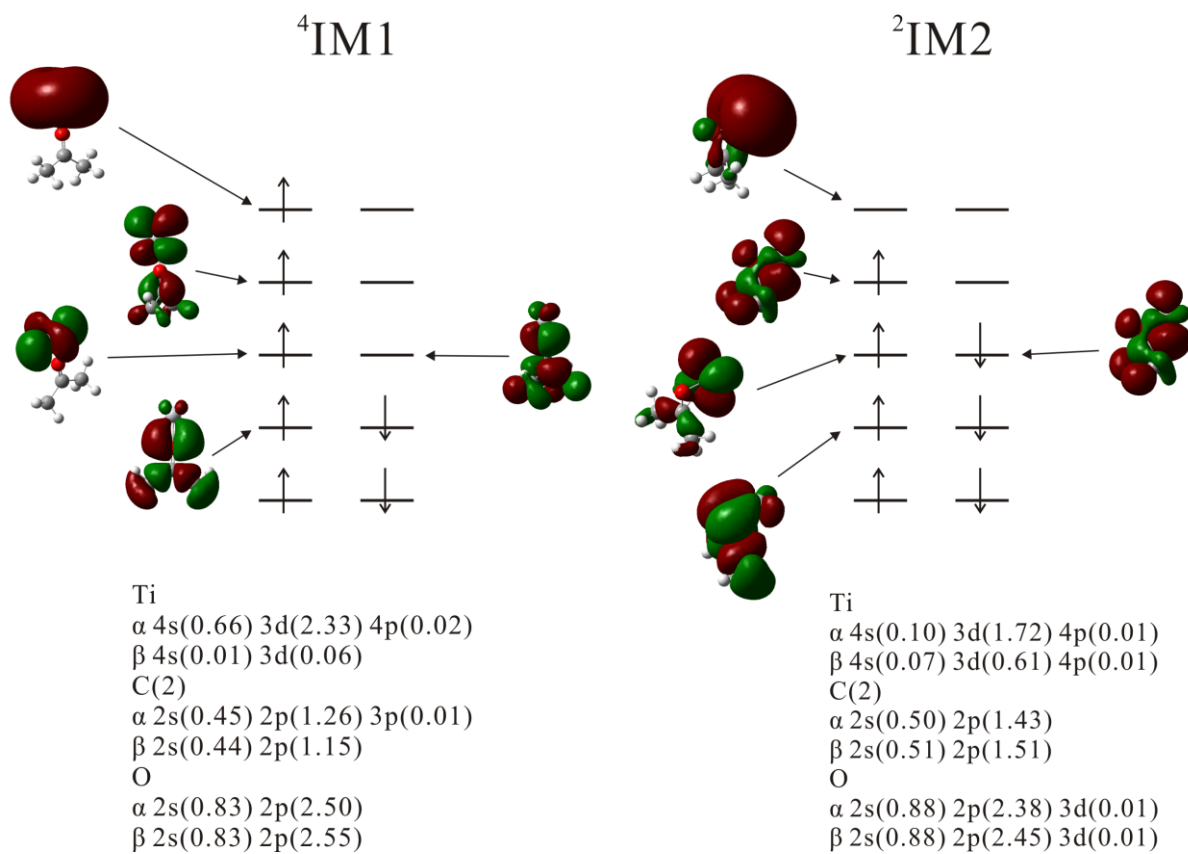β 2s(0.88) 2p(2.45) 3d(0.01)

Figure S2. Singly occupied molecular orbital (SOMO) of the ^{2}IM4. It indicates that 3d orbital of Ti interacts with π* orbital of C=C.
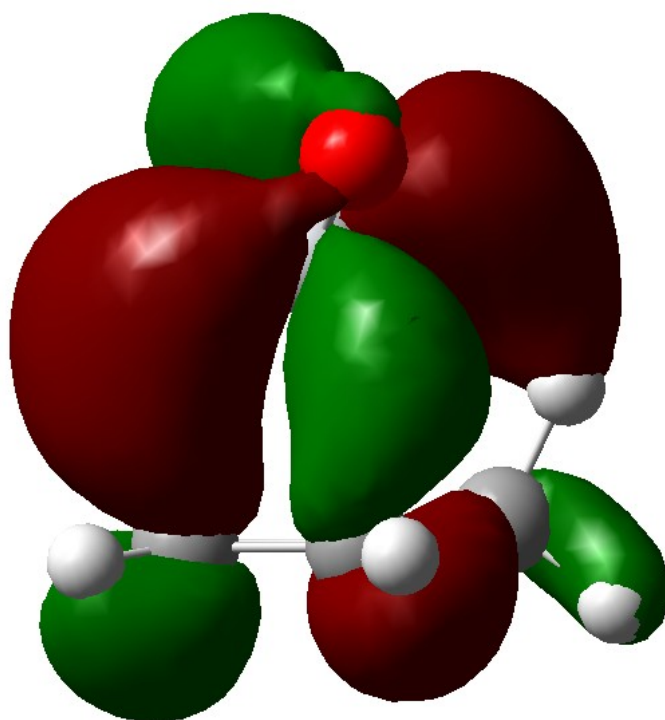
Figure S3. Selected parameters (bond lengths in Å and angles in degree) of optimized geometries calculated by the PBE0/aug-cc-pVTZ on reaction potential energy surfaces of the direct H shift pathway. The superscript denotes the spin multiplicity.
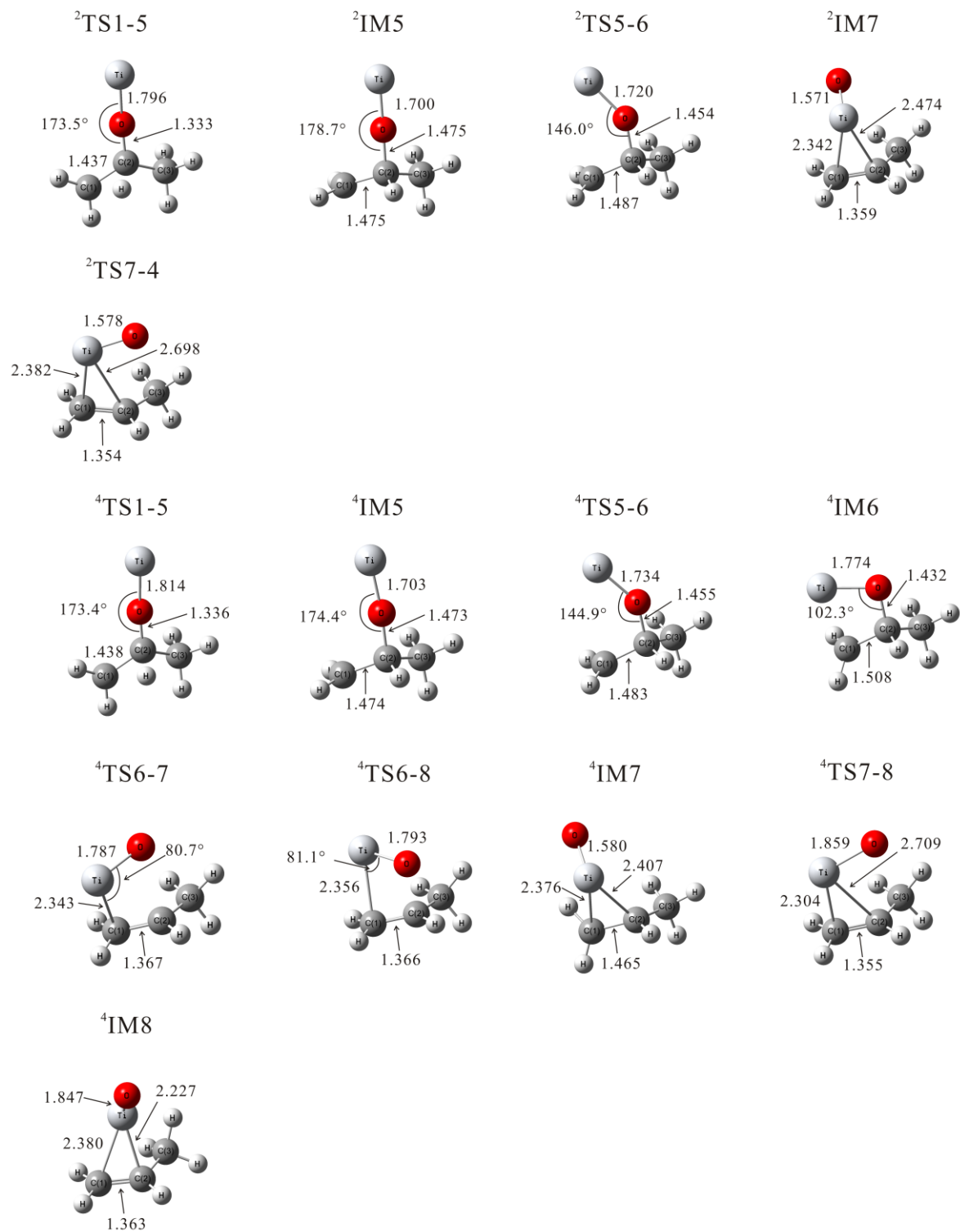
Figure S4. The reaction potential energy surfaces of the direct H shift pathway at the PBE0/aug-cc-pVTZ level. The related optimized structures are depicted in Figure S3 and their energies are summarized in Table S2.
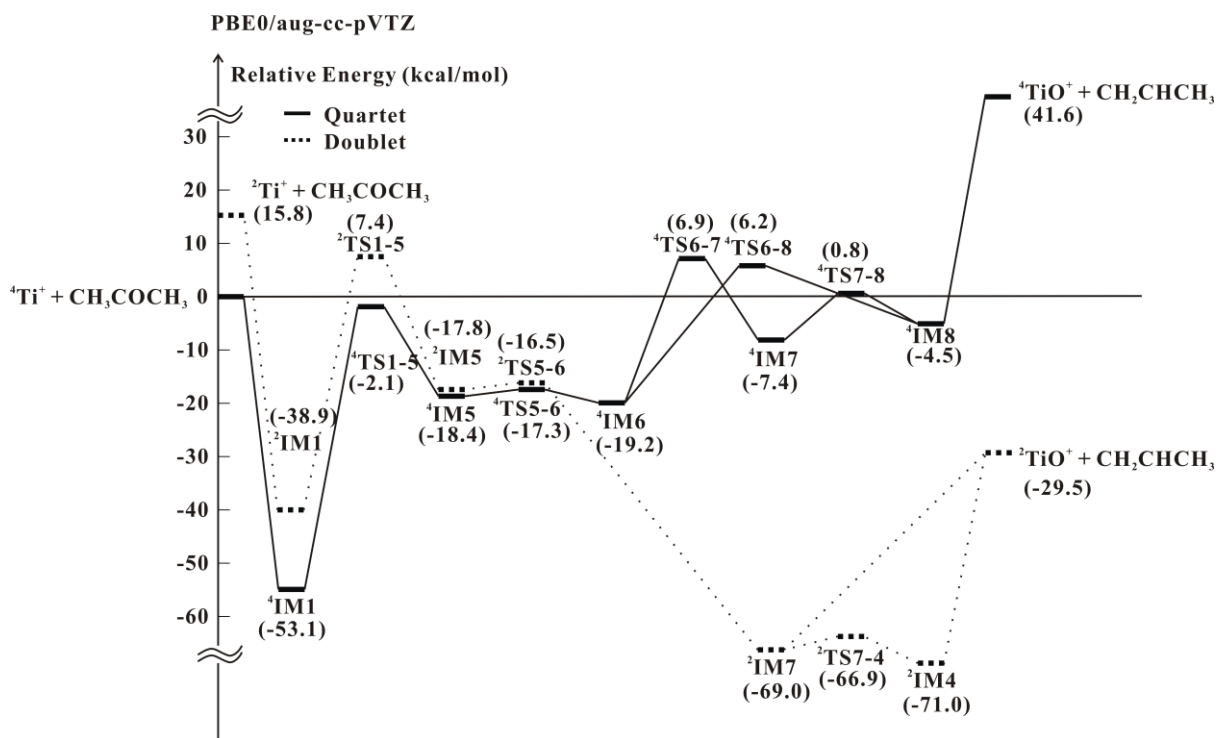
Table S2. Relative energies (ΔE, kcal/mol) calculated by the PBE0/aug-cc-pVTZ, single point relative energies ($\Delta E_{CCSD(T)}$, kcal/mol) calculated by the CCSD(T)/cc-pVTZ, atomic charges (NPA), and $<S^2>$ values for all species involved in the direct H shift pathway.[a]

Doublet		^{2}TS1-5	^{2}IM5	^{2}TS5-6	-	-	-	^{2}IM7	^{2}TS7-4	^{2}IM4
ΔE		7.4(7.6)	-17.8(-17.4)	-16.5(-16.3)				-69.0(-68.5)	-66.9(-66.5)	-71.0(-70.5)
$\Delta E_{CCSD(T)}$		16.8	-13.6	-10.4				-70.5	-70.2	-71.7
[b]Atomic Charges	Ti	1.102	1.352	1.367				1.571	1.557	1.365
	O	-0.821	-0.782	-0.776	-	-	-	-0.645	-0.677	-0.545
	C(1)	-0.298	-0.233	-0.273				-0.554	-0.660	-0.455
	C(2)	0.136	0.011	0.018				-0.180	-0.019	-0.218
	C(3)	-0.633	-0.622	-0.621				-0.666	-0.678	-0.685
$<S^2>$		1.737	1.763	1.732				0.758	0.759	0.758

Quartet		^{4}TS1-5	^{4}IM5	^{4}TS5-6	^{4}IM6	^{4}TS6-7	^{4}TS6-8	^{4}IM7	^{4}TS7-8	^{4}IM8
ΔE		-2.1(-1.9)	-18.4(-18.0)	-17.3(-17.1)	-19.2(-18.9)	6.9(7.5)	6.2(6.8)	-7.4(-6.9)	0.8(1.4)	-4.5(-3.9)
$\Delta E_{CCSD(T)}$		12.9	-14.1	-11.1	-12.1	13.5	13.0	-3.1	5.0	-0.5
[b]Atomic Charges	Ti	1.097	1.340	1.386	1.311	1.259	1.276	1.434	1.342	1.328
	O	-0.833	-0.784	-0.801	-0.728	-0.523	-0.521	-0.671	-0.482	-0.425
	C(1)	-0.221	-0.222	-0.253	-0.343	-0.548	-0.533	-0.379	-0.675	-0.463
	C(2)	0.091	0.011	0.010	-0.004	0.003	-0.044	-0.221	-0.009	-0.293
	C(3)	-0.626	-0.622	-0.621	-0.601	-0.670	-0.684	-0.670	-0.682	-0.660
$<S^2>$		3.796	3.767	3.766	3.763	3.769	3.770	3.765	3.756	3.756

a: values in parenthesis are calculated by the aug-cc-pVQZ.
b: the related figures are depicted in Figure S3.

Figure S5. Selected parameters (bond lengths in Å and angles in degree) of optimized geometries calculated by the PBE0/aug-cc-pVTZ on reaction potential energy surfaces of the metal-mediated H migration pathway. The superscript denotes the spin multiplicity.
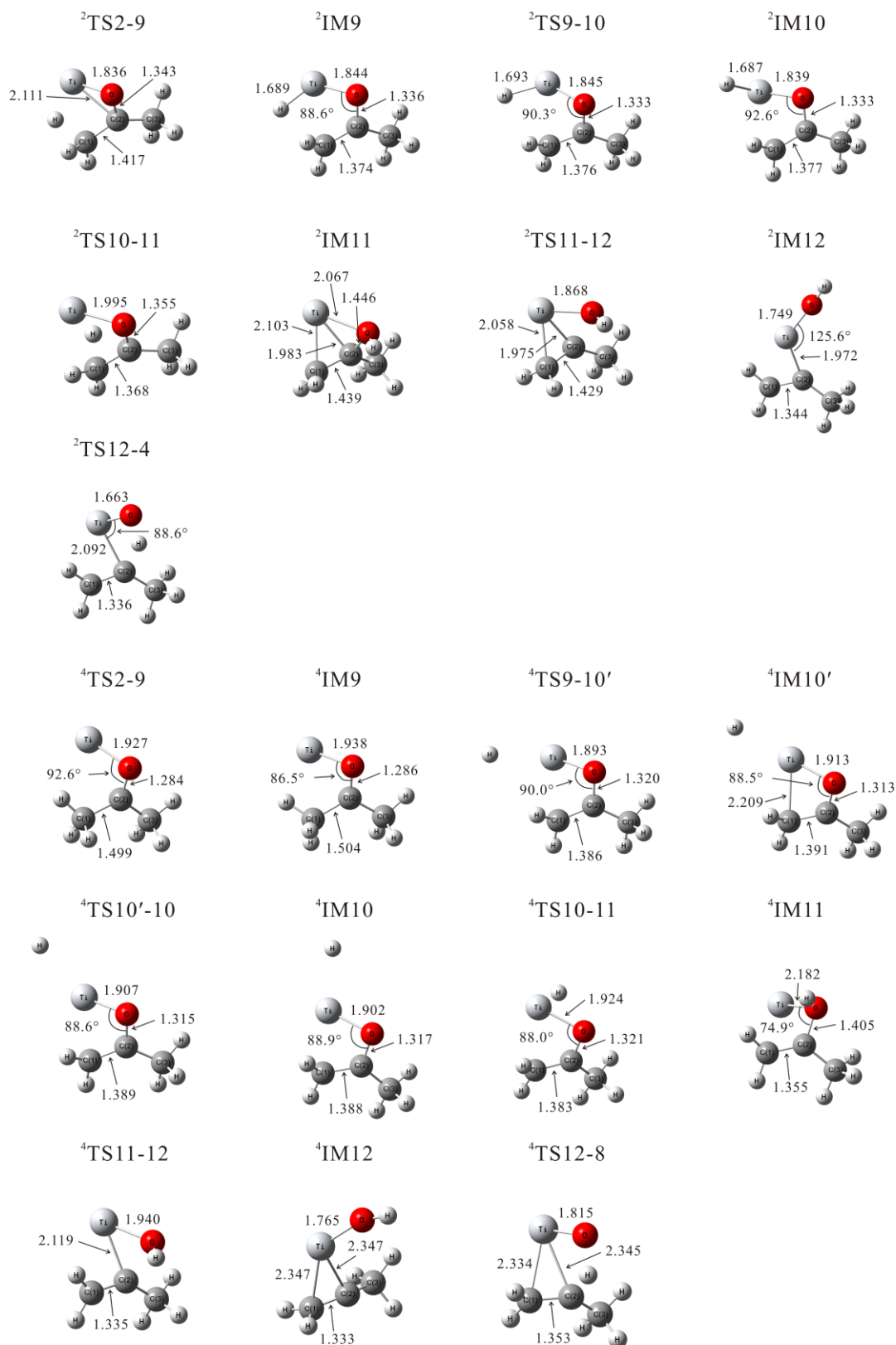
Figure S6. The reaction potential energy surfaces of the metal-mediated H migration pathway at the PBE0/aug-cc-pVTZ level. The related optimized structures are depicted in Figure S5 and their energies are summarized in Table S3.
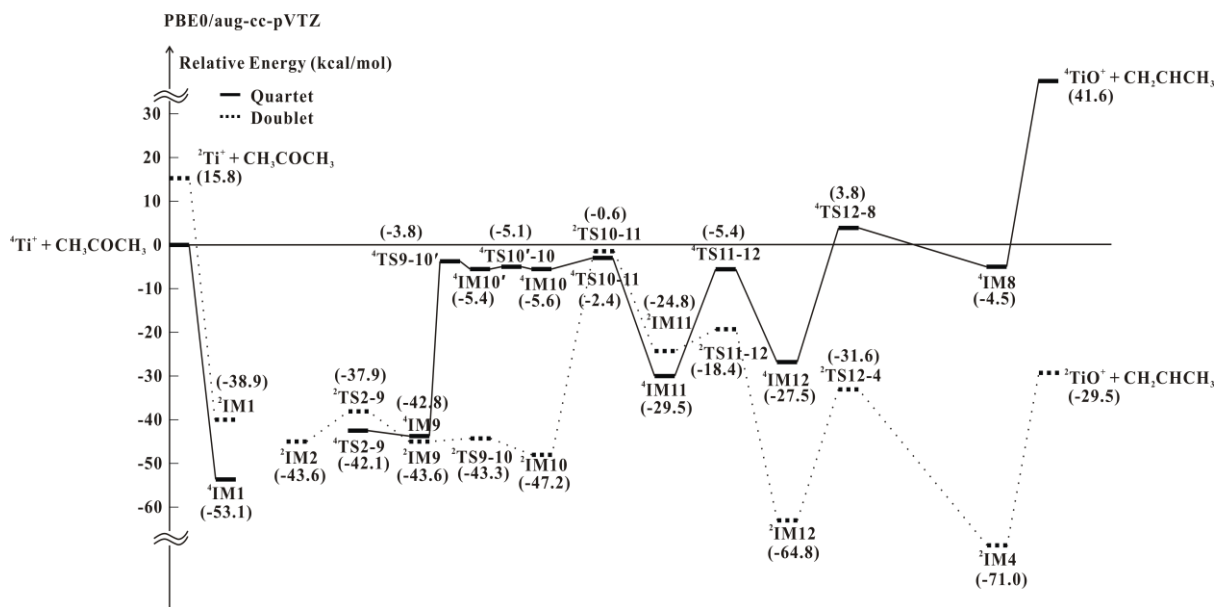
Table S3. Relative energies (ΔE, kcal/mol) calculated by the PBE0/aug-cc-pVTZ, single point relative energies ($\Delta E_{CCSD(T)}$, kcal/mol) calculated by the CCSD(T)/cc-pVTZ, atomic charges (NPA), and $<S^2>$ values for all species involved in the metal-mediated H migration pathway.[a]

Doublet		²TS2-9	²IM9	²TS9-10	-	-	²IM10	²TS10-11	²IM11	²TS11-12	²IM12	²TS12-4
ΔE		-37.9	-43.6	-43.3			-47.2	-0.6	-24.8	-18.4	-64.8	-31.6
		(-37.6)	(-43.3)	(-43.0)			(-47.0)	(-0.3)	(-24.6)	(-18.0)	(-64.5)	(-31.2)
$\Delta E_{CCSD(T)}$		-30.9	-39.1	-39.2			-42.1	5.3	-19.4	-9.8	-61.5	-28.4
[b]Atomic Charges	Ti	1.324	1.416	1.575			1.560	1.108	1.349	1.389	1.631	1.456
	O	-0.602	-0.620	-0,660	-	-	-0.645	-0.656	-0.746	-0.853	-0.971	-0.708
	C(1)	-0.557	-0.513	-0.548			-0.651	-0.654	-0.756	-0.814	-0.472	-0.663
	C(2)	0.232	0.323	0.341			0.407	0.380	0.103	0.160	-0.243	-0.236
	C(3)	-0.670	-0.676	-0.682			-0.683	-0.674	-0.658	-0.704	-0.673	-0.438
$<S^2>$		0.784	0.765	0.763			0.760	1.398	0.812	0.769	0.756	0.757

Quartet		⁴TS2-9	⁴IM9	⁴TS9-10′	⁴IM10′	⁴TS10′-10	⁴IM10	⁴TS10-11	⁴IM11	⁴TS11-12	⁴IM12	⁴TS12-8
ΔE		-42.1	-42.8	-3.8	-5.4	-5.1	-5.6	-2.4	-29.5	-5.4	-27.5	3.8
		(-42.0)	(-42.6)	(-3.5)	(-5.1)	(-4.9)	(-5.4)	(-2.2)	(-29.3)	(-5.0)	(-27.2)	(4.4)
$\Delta E_{CCSD(T)}$		-30.6	-30.7	1.9	0.5	1.2	0.5	4.0	-21.1	4.5	-18.9	13.7
[b]Atomic Charges	Ti	1.143	1.131	1.246	1.246	1.257	1.231	1.249	0.954	1.232	1.385	1.430
	O	-0.679	-0.646	-0.681	-0.678	-0.678	-0.674	-0.676	-0.728	-0.886	-0.986	-0.714
	C(1)	-0.718	-0.697	-0.709	-0.713	-0.705	-0.698	-0.683	-0.563	-0.536	-0.677	-0.598
	C(2)	0.437	0.403	0.394	0.411	0.404	0.405	0.385	0.231	0.096	0.142	-0.053
	C(3)	-0.704	-0.695	-0.684	-0.682	-0.681	-0.681	-0.679	-0.671	-0.693	-0.732	-0.680
$<S^2>$		3.756	3.756	3.758	3.758	3.758	3.756	3.758	3.754	3.759	3.762	3.763

a: values in parenthesis are calculated by the aug-cc-pVQZ.
b: the related figures are depicted in Figure S5.

Figure S7. Selected parameters (bond length in Å and angle in degree) of optimized geometries of intermediates calculated by the PBE0/aug-cc-pVTZ on the C-H activation reaction coordinate.
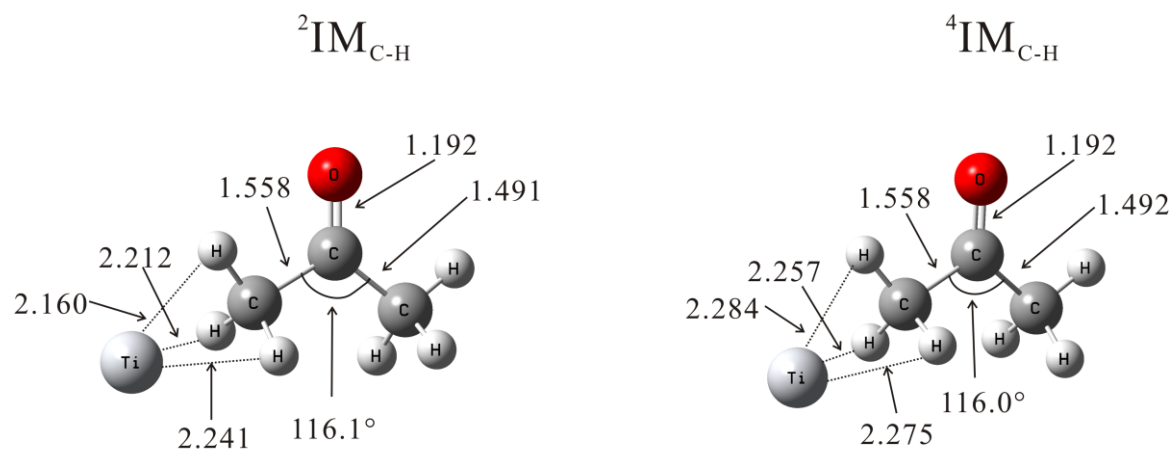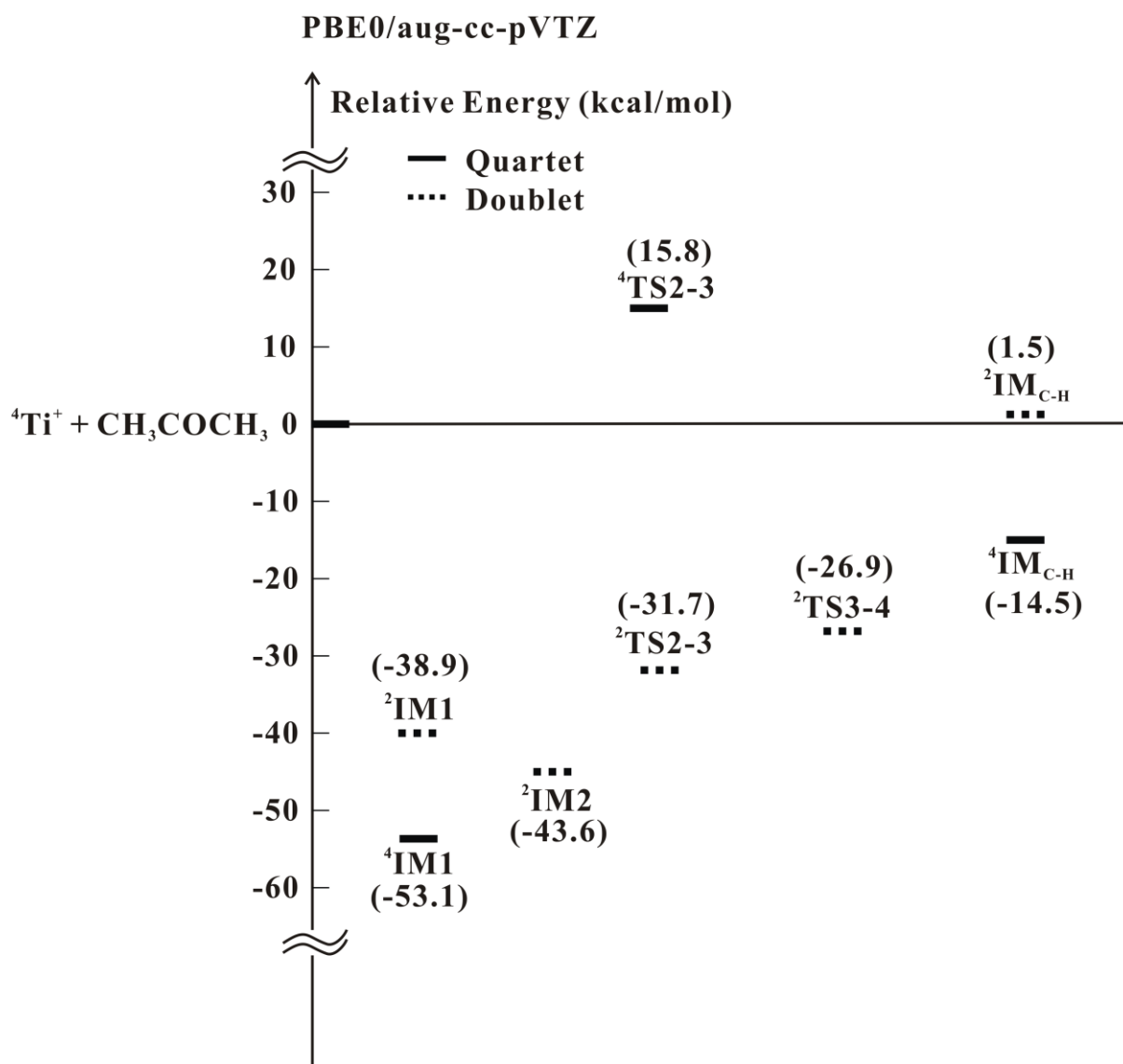
Figure S8. The relative energies of intermediates on the C-H activation reaction coordinate at the PBE0/aug-cc-pVTZ level. The related optimized structures are depicted in Figure S7.

PBE0/aug-cc-pVTZ

Relative Energy (kcal/mol)

— Quartet
···· Doublet

30

20   (15.8)
      ^{4}TS2-3

10   (1.5)
                                                         ^{2}IM$_{C-H}$

^{4}Ti$^+$ + CH$_3$COCH$_3$ 0   ····

-10

-20   (-31.7)   (-26.9) ^{4}IM$_{C-H}$
            ^{2}TS2-3 ^{2}TS3-4   (-14.5)

-30 (-38.9)   ····
     ^{2}IM1

-40 ····
                 ····
            ^{2}IM2
-50   (-43.6)
     ^{4}IM1
-60 (-53.1)

References

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(3)   Lide, D. R. *CRC Handbook of Chemistry and Physics*, 88th ed.; CRC Press: Boca Raton, FL, 2008.