

Supporting Information

Density Functional Study of Nickel N-Heterocyclic Carbene Catalyzed C-O Bond Hydrogenolysis of Methyl Phenyl Ether: The Concerted β -H Transfer Mechanism

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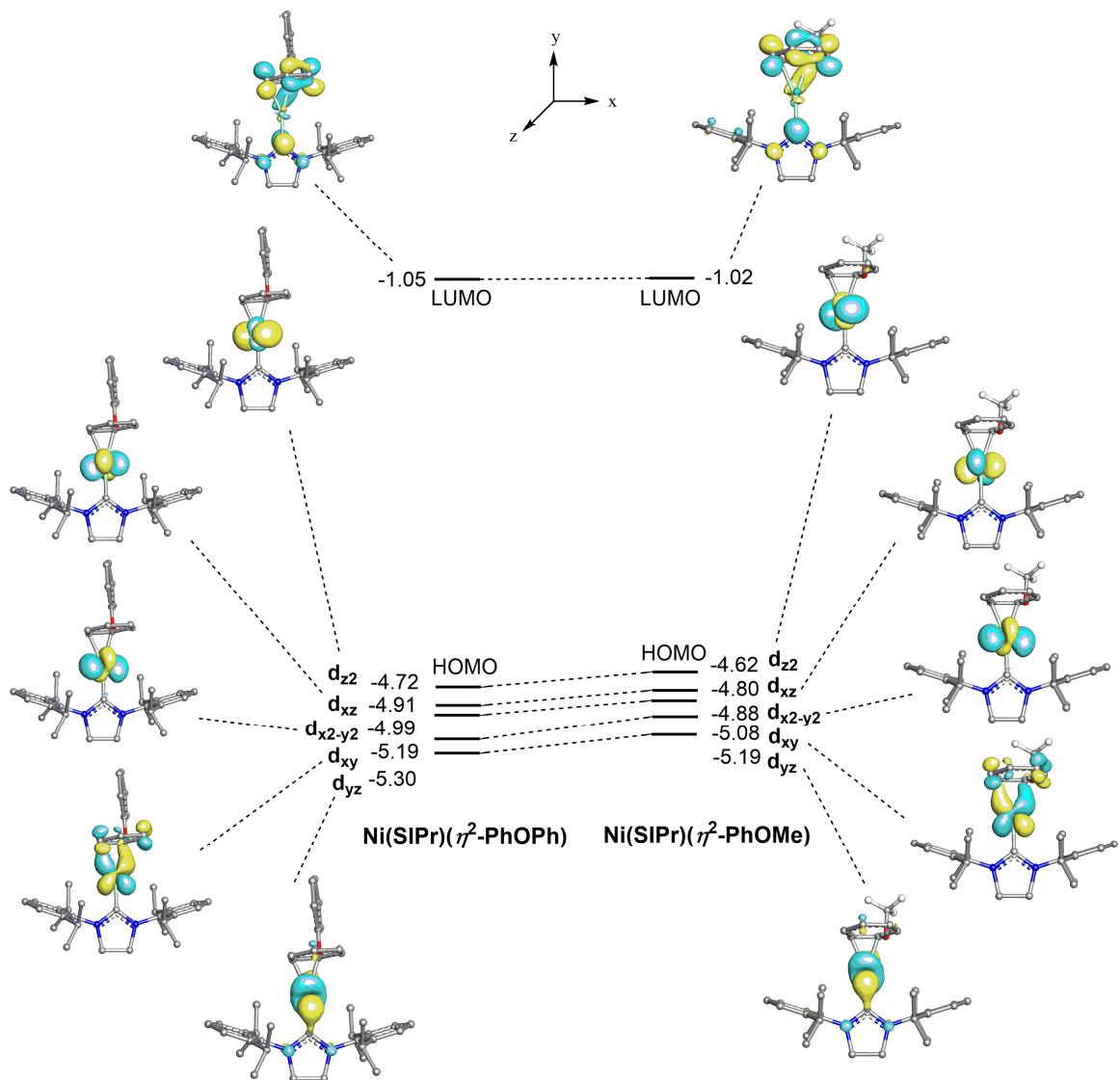


Figure S1. Selected molecular orbitals (MOs) and MO energies (in eV) of $\text{Ni}(\text{SIPr})(\eta^2\text{-PhOPh})$, **IN1_{Ph}**, and $\text{Ni}(\text{SIPr})(\eta^2\text{-PhOMe})$, **IN1**.

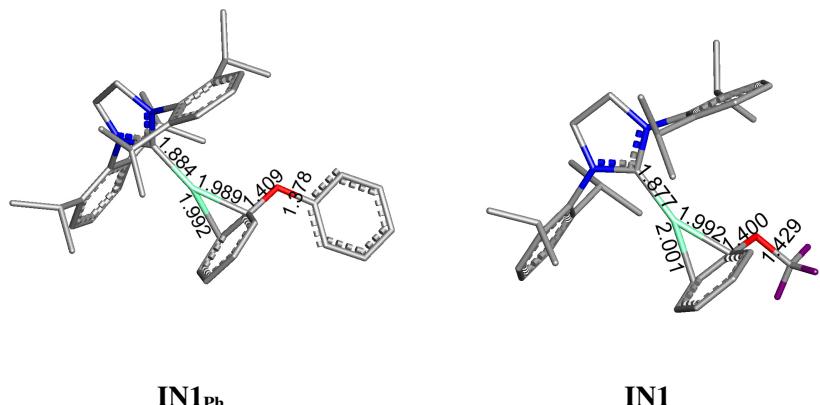


Figure S2. Optimized geometries of $\text{Ni}(\text{SIPr})(\eta^2\text{-PhOPh})$, **IN1_{Ph}**, and $\text{Ni}(\text{SIPr})(\eta^2\text{-PhOMe})$, **IN1**. Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those from methoxy. Ni atoms are shown in green, C atoms in gray, O atoms in red, N atoms in blue, and H atoms in purple.

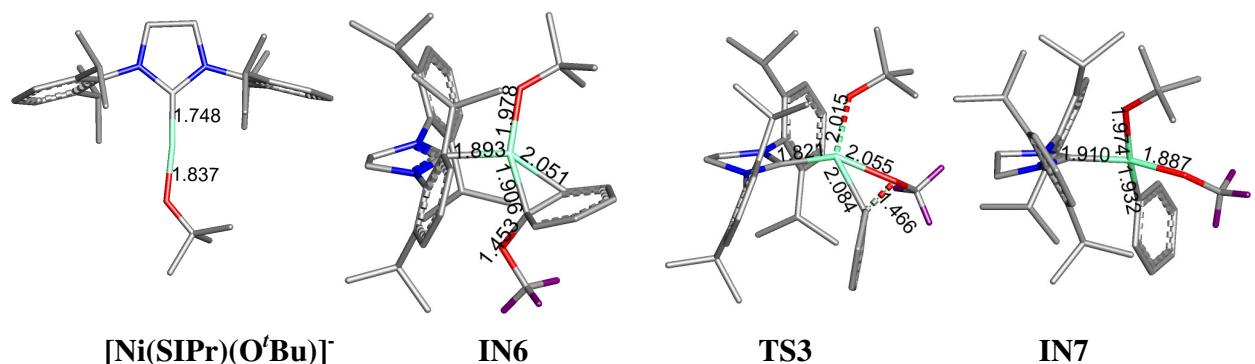


Figure S3. Optimized geometries of the intermediates ($[\text{Ni}(\text{SIPr})(\text{O}'\text{Bu})]^-$, **IN6** and **IN7**) and the transition state (**TS3**) in the formation of **IN1** and the C-O bond oxidative addition involving *tert*-butoxide base. Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those from methoxy. Ni atoms are shown in green, C atoms in gray, O atoms in red, N atoms in blue, and H atoms in purple.

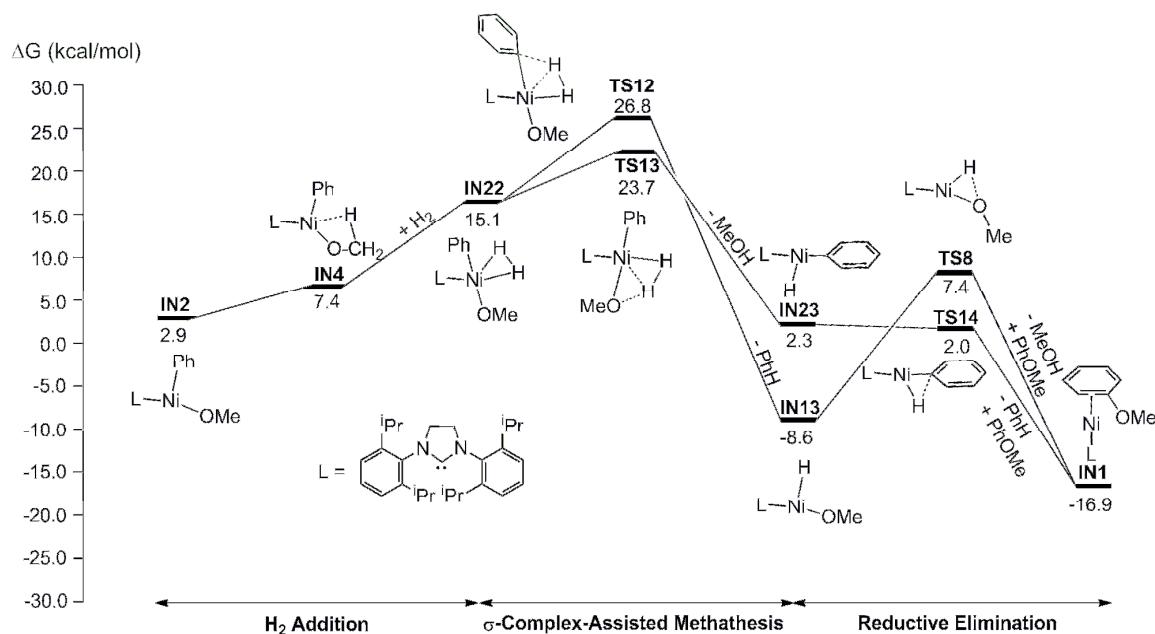


Figure S4. Relative free energy profiles for (i) H₂ addition to **IN4** to form Ni(SIPr)(Ph)(OMe)(H₂), **IN22**, (ii) σ-complex assisted metathesis of **IN22** to generate benzene (or methanol), and (iii) reductive elimination of methanol (or benzene). Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

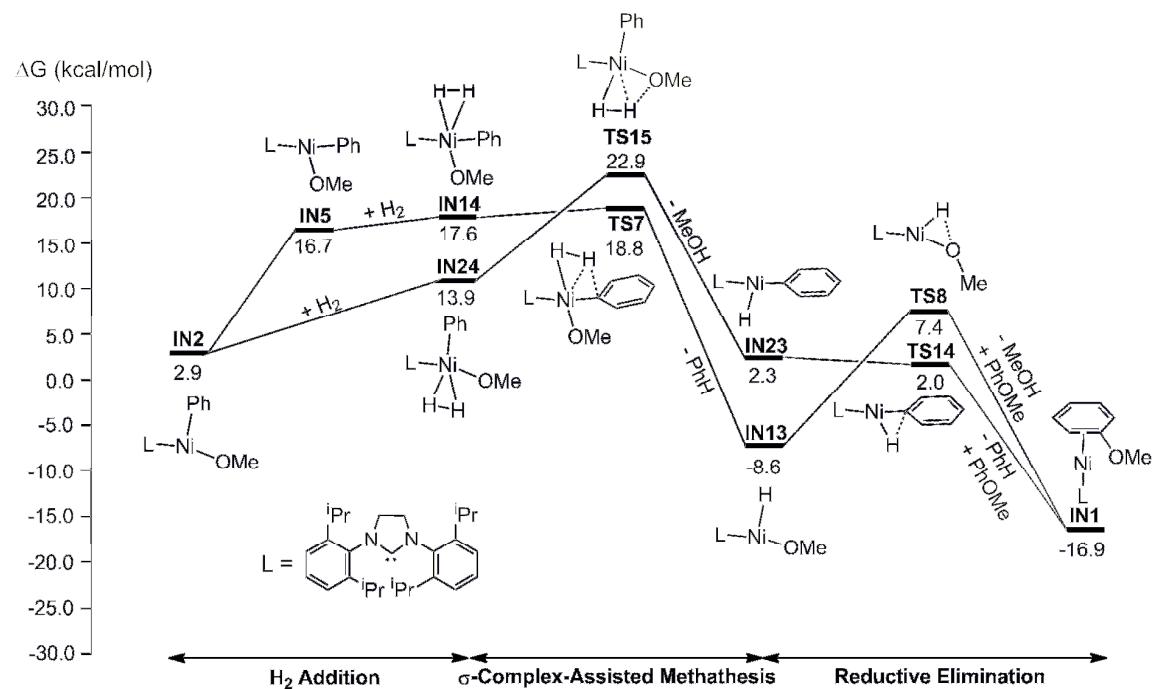


Figure S5. Relative free energy profiles for (i) H₂ addition to **IN2** (and **IN5**) to form Ni(SIPr)(Ph)(OMe)(H₂), **IN24** (and **IN14**), (ii) σ-complex assisted metathesis of **IN24** (and **IN14**) to generate methanol (and benzene), and (iii) reductive elimination of benzene (and methanol). Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

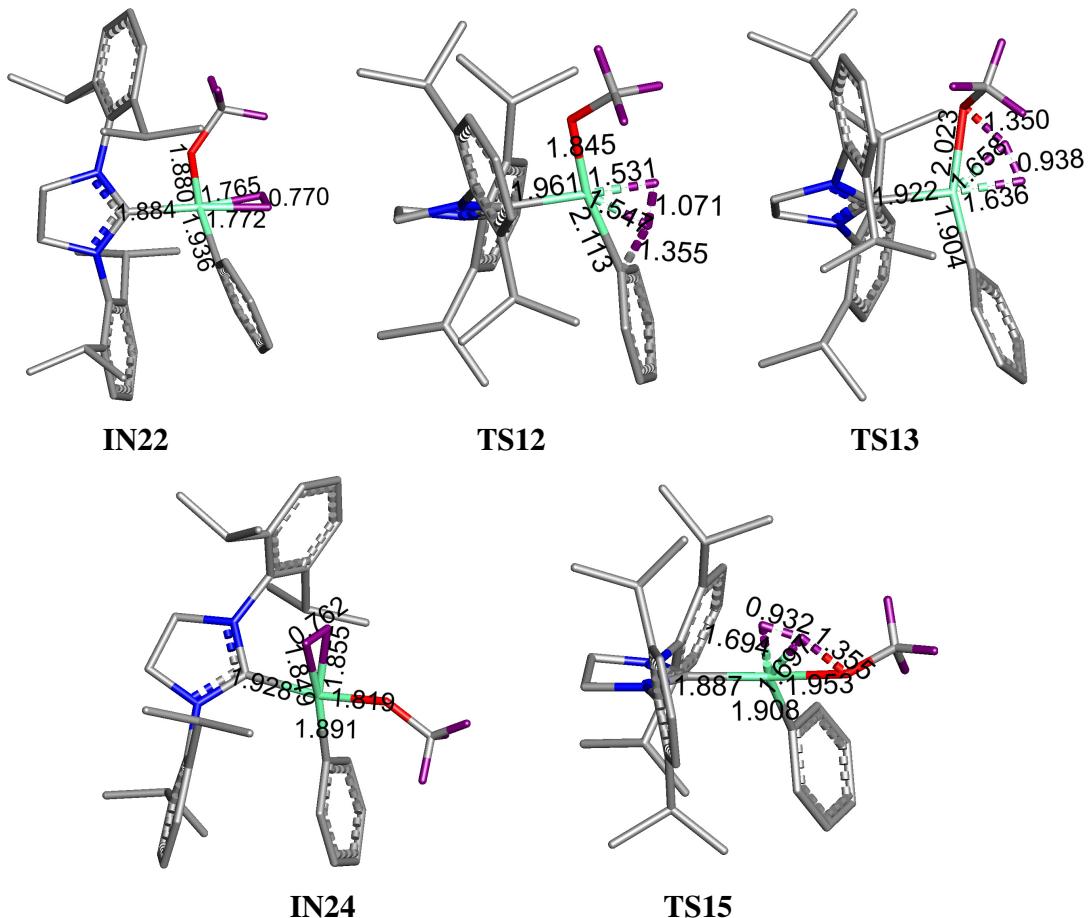


Figure S6. Optimized geometries of the H₂ addition intermediates (**IN22** and **IN24**) and σ-complex assisted metathesis transition states (**TS12**, **TS13** and **TS15**). Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those from methoxy and those on nickel. Ni atoms are shown in green, C atoms in gray, O atoms in red, N atoms in blue, and H atoms in purple.

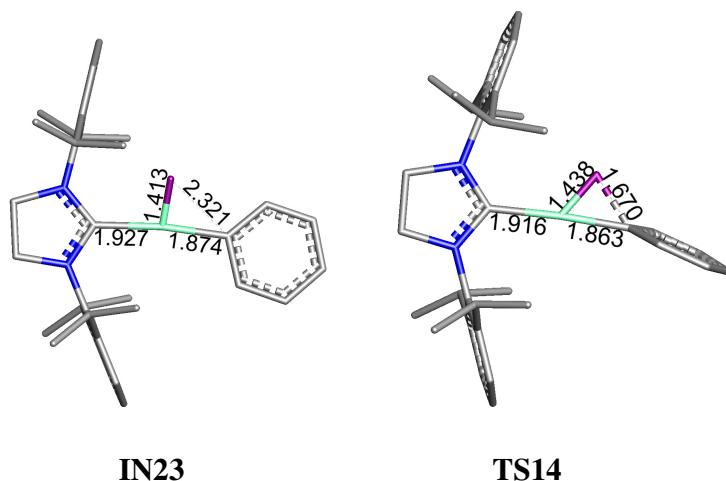


Figure S7. Optimized geometries of **IN23** and the C-H bond reductive elimination transition state **TS14**. Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those on nickel. Ni atoms are shown in green, C atoms in gray, N atoms in blue, H atoms in purple.

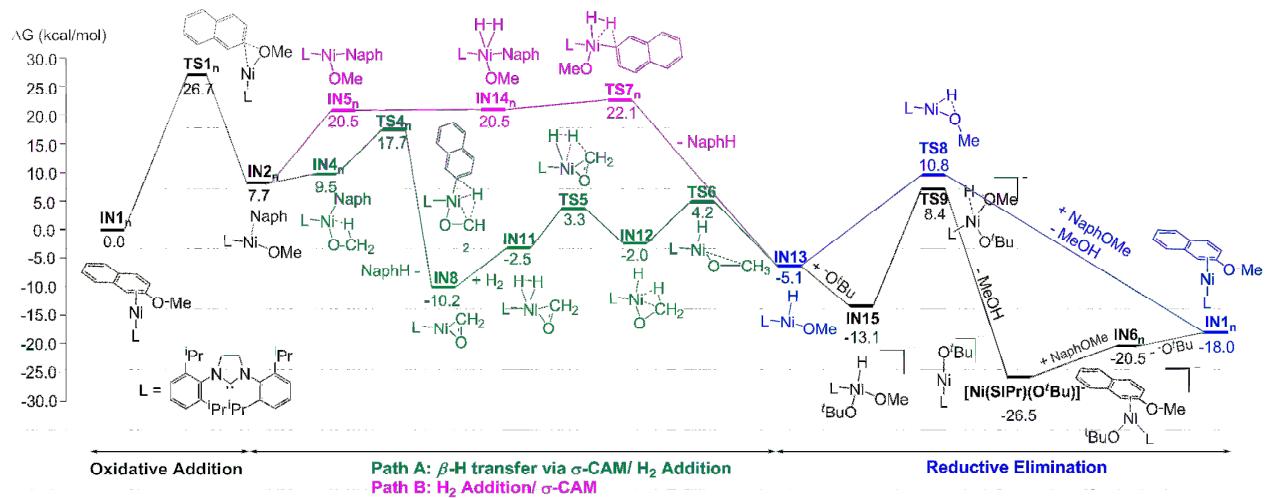


Figure S8. Relative free energy profiles for the C-O bond hydrogenolysis of 2-methoxynaphthalene by Ni-SiPr catalyst. Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

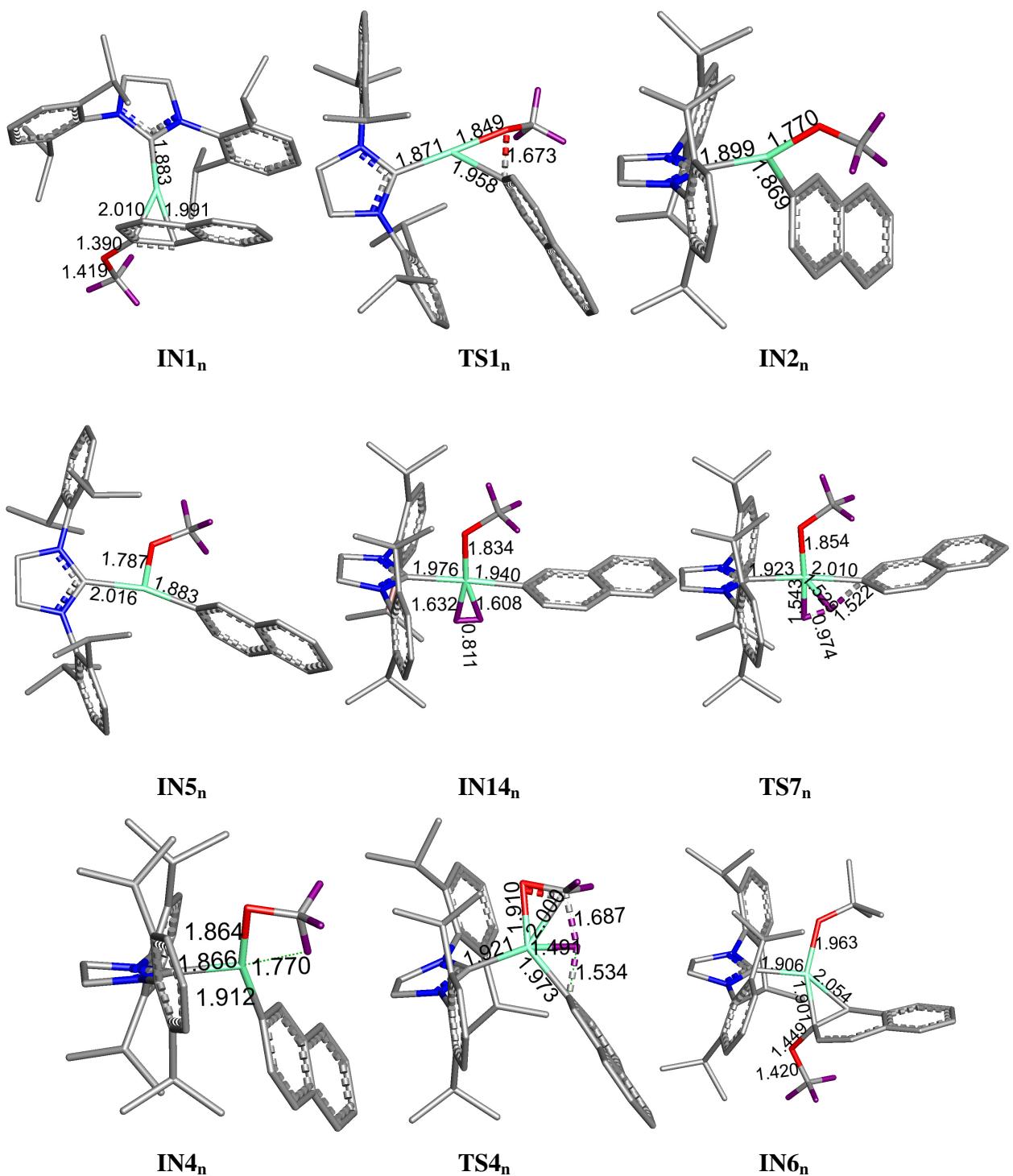


Figure S9. Optimized geometries of the transition states and intermediates for the C-O bond hydrogenolysis of 2-methoxynaphthalene by Ni-SiPr catalyst. Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those from the methoxy. Ni atoms are shown in green, C atoms in gray, O atoms in red, N atoms in blue, and H atoms in purple.

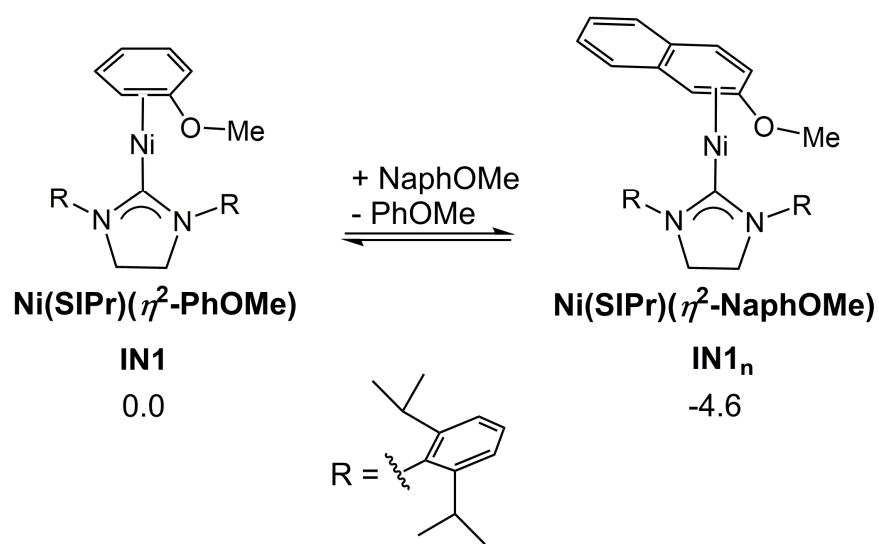


Figure S10. Relative free energy for $\text{Ni}(\text{SIPr})(\eta^2\text{-PhOMe})$ (**IN1**) and $\text{Ni}(\text{SIPr})(\eta^2\text{-NaphOMe})$ (**IN1_n**). Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

Table S1. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) in the formation of the active species for Ni-SIPr catalyzed methyl phenyl ether. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$ (kcal/mol)	$\Delta H_{298.15}$ (kcal/mol)	$\Delta S_{298.15}$ (cal/mol)	$\Delta G_{298.15}$ gas (kcal/mol)	$\Delta G_{298.15}$ (1 atm) (kcal/mol)	$\Delta G_{393.15}$ (1 atm) (kcal/mol)	$\Delta G_{298.15}$ (1 M) (kcal/mol)	$\Delta G_{393.15}$ (1 M) (kcal/mol)
Ni(COD) ₂ +2SIPr+PhOMe +PhOPh+O'Bu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni(COD)+COD+PhOMe +2SIPr+PhOPh+O'Bu	2.44	-0.05	47.99	-14.36	23.18	18.65	25.08	20.55
Ni(SIPr)(COD)+COD +PhOMe+SIPr+PhOPh +O'Bu	-3.41	-2.73	3.67	-3.82	-0.29	-0.64	-0.29	-0.64
Ni(SIPr) ₂ +2COD+PhOMe +PhOPh+O'Bu	-9.07	-7.11	-15.68	-2.44	-9.63	-8.14	-9.63	-8.14
Ni(SIPr)+2COD+PhOMe +SIPr+PhOPh+O'Bu	25.41	25.55	51.77	10.12	25.80	20.92	25.80	20.92
Ni(SIPr)(η^2 -PhOPh) +2COD+SIPr+PhOMe +O'Bu	2.05	2.49	5.36	0.89	4.58	4.06	4.58	4.06
Ni(SIPr)(η^2 -PhOMe) +2COD+SIPr+PhOPh +O'Bu	5.53	5.72	11.34	2.34	7.24	6.14	7.24	6.14
[Ni(SIPr)(O'Bu)] ⁺ +2COD +PhOMe+SIPr+PhOPh	-27.13	-25.74	4.56	-27.10	-6.51	-6.94	-6.51	-6.94
[Ni(SIPr)(η^2 -PhOMe) (O'Bu)] ⁺ +2COD+SIPr +PhOPh	-14.26	-12.65	-50.81	2.50	6.03	10.80	4.13	8.91

Table S2. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the C-O bond oxidative addition of methyl phenyl ether. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
IN1+H ₂ +PhOMe +O'Bu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TS1+H ₂ +PhOMe +O'Bu	16.45	15.57	-8.80	18.20	24.73	25.59	24.73	25.59
TS2+H ₂ +PhOMe +O'Bu	21.99	20.58	-3.30	21.57	30.01	30.33	30.01	30.33
IN2+H ₂ +PhOMe +O'Bu	-10.40	-10.12	-4.51	-8.77	2.44	2.87	2.44	2.87
IN3+H ₂ +PhOMe +O'Bu	-25.97	-26.47	-4.48	-25.13	-12.76	-12.35	-12.76	-12.35
IN4+H ₂ +PhOMe +O'Bu	-5.95	-6.15	-16.25	-1.31	5.84	7.39	5.84	7.39
IN5+H ₂ +PhOMe +O'Bu	2.89	2.83	1.77	2.30	16.89	16.72	16.89	16.72

Table S3. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the C-O bond oxidative addition of methyl phenyl ether in the presence of $\text{O}'\text{Bu}$ base. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
				(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
IN1+ $\text{O}'\text{Bu}+\text{PhOMe}$ +H ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
IN6+PhOMe+H ₂	-19.79	-18.36	-62.15	0.17	-1.21	4.66	-3.11	2.76
TS3+PhOMe+H ₂	-0.27	0.38	-62.22	18.93	24.66	30.55	22.76	28.65
IN7+PhOMe+H ₂	-33.45	-31.63	-62.53	-12.99	-5.80	0.10	-7.70	-1.79

Table S4. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the conversion of methyl phenyl ether in the presence of H₂ (path A: β -H elimination/H₂ addition). The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
TS4+H ₂ +PhOMe +O'Bu	8.28	5.24	-14.67	9.62	14.24	15.65	14.24	15.65
IN8+PhH+H ₂ +PhOMe+O'Bu	-14.05	-15.36	37.07	-26.41	-12.09	-15.56	-10.19	-13.66
IN9+H ₂ +PhOMe +O'Bu	-3.26	-3.83	-11.70	-0.34	2.32	3.43	2.32	3.43
IN10+H ₂ +PhOMe +O'Bu	23.08	20.51	-11.97	24.08	30.06	31.19	30.06	31.19
IN11+PhH+PhOMe +O'Bu	-18.31	-17.15	2.92	-18.02	-5.75	-5.94	-5.75	-5.94
TS5+PhH+PhOMe +O'Bu	-12.37	-12.97	2.77	-13.80	-0.03	-0.19	-0.03	-0.19
IN12+PhH+PhOMe +O'Bu	-23.06	-20.67	1.68	-21.17	-5.38	-5.43	-5.38	-5.43
TS6+PhH+PhOMe +O'Bu	-17.01	-14.95	2.32	-15.65	0.84	0.74	0.84	0.74
IN13+PhH+PhOMe +O'Bu	-26.11	-23.19	12.63	-26.95	-7.48	-8.59	-7.48	-8.59

Table S5. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the conversion of methyl phenyl ether in the presence of H₂ (path B: H₂ addition/ σ-CAM). The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	ΔE _{298.15}	ΔH _{298.15}	ΔS _{298.15}	ΔG _{298.15}	ΔG _{298.15}	ΔG _{393.15}	ΔG _{298.15}	ΔG _{393.15}
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
IN14+PhOMe+·O'Bu	-4.69	-1.68	-33.97	8.45	16.26	19.51	14.36	17.62
TS7+PhOMe+·O'Bu	-2.96	-1.60	-36.68	9.34	17.12	20.67	15.23	18.78
IN13+PhH+PhOMe +·O'Bu	-26.11	-23.19	12.63	-26.95	-7.48	-8.59	-7.48	-8.59
IN22+PhOMe+·O'Bu	-3.73	-1.10	-40.40	10.94	13.12	16.97	11.22	15.08
TS12+PhOMe+·O'Bu	6.64	7.94	-42.44	20.60	24.59	28.69	22.70	26.80
TS13+PhOMe+·O'Bu	3.18	4.84	-43.79	17.89	21.41	25.63	19.51	23.74
IN23+MeOH+PhOMe +·O'Bu	-6.61	-3.71	12.50	-7.44	3.43	2.31	3.43	2.31
TS14+MeOH+PhOMe +·O'Bu	-4.12	-2.31	10.66	-5.49	2.92	2.00	2.92	2.00
IN24+PhOMe+·O'Bu	-4.09	-1.60	-38.45	9.87	12.14	15.81	10.25	13.91
TS15+PhOMe+·O'Bu	2.19	3.53	-41.75	15.98	20.80	24.84	18.91	22.94
IN1+MeOH+PhH +·O'Bu	-16.86	-12.42	11.55	-15.87	-15.86	-16.89	-15.86	-16.89

Table S6. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the reductive elimination in the presence and in the absence of $\text{O}'\text{Bu}$ base. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
IN13+PhH+PhOMe + $\text{O}'\text{Bu}$	-26.11	-23.19	12.63	-26.95	-7.48	-8.59	-7.48	-8.59
TS8+PhH+PhOMe + $\text{O}'\text{Bu}$	-5.63	-3.95	12.42	-7.65	8.42	7.35	8.42	7.35
IN15+PhH+PhOMe	-55.05	-50.75	-44.19	-37.57	-18.97	-14.70	-20.87	-16.60
TS9+PhH+PhOMe	-29.82	-27.19	-37.00	-16.16	3.22	6.81	1.33	4.92
$[\text{Ni}(\text{SIPr})(\text{O}'\text{Bu})]^-$ +PhOMe+PhH +MeOH	-49.52	-43.88	4.77	-45.30	-29.61	-29.96	-29.61	-29.96
IN6+PhH+MeOH	-36.66	-30.79	-50.60	-15.70	-17.07	-12.23	-18.97	-14.12
IN1+ $\text{O}'\text{Bu}$ +PhH +MeOH	-16.86	-12.42	11.55	-15.87	-15.86	-16.89	-15.86	-16.89

Table S7. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the conversion of methyl phenyl ether in the absence of H₂. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
IN16+PhH+H ₂ +PhOMe+O'Bu	5.44	2.33	38.03	-9.01	2.56	-1.00	4.46	0.89
TS10+PhH+H ₂ +PhOMe+O'Bu	6.40	1.66	37.12	-9.40	3.15	-0.33	5.04	1.57
IN17+PhH+H ₂ +PhOMe+O'Bu	5.66	1.58	36.61	-9.34	4.44	0.99	6.33	2.88
TS11+PhH+H ₂ +PhOMe+O'Bu	10.90	5.27	37.62	-5.95	8.14	4.61	10.04	6.51
IN18+PhH+H ₂ +PhOMe+O'Bu	-12.98	-18.41	33.28	-28.33	-11.70	-14.84	-9.81	-12.94
IN19+PhH+H ₂ +PhOMe	-18.51	-23.25	-5.29	-21.68	-7.27	-6.78	-7.27	-6.78
IN20+PhH+PhOMe +2H ₂	-41.42	-47.04	19.87	-52.97	-31.50	-33.44	-29.61	-31.55
IN21+PhH+2H ₂ +PhOMe+O'Bu	-12.76	-19.53	69.31	-40.20	-25.12	-31.71	-21.33	-27.93
IN1+CO+PhH+2H ₂ +O'Bu	20.87	12.56	64.15	-6.56	-0.55	-6.70	3.24	-2.91

Table S8. Relative electronic energies, enthalpies, entropies, gas-phase free energies, free energies with solvent correction at 1 atm (at 298.15 K and 393.15 K), and free energies with solvent correction at 1 M (at 298.15 K and 393.15 K) (in kcal/mol) for the C-O bond hydrogenolysis of 2-methoxynaphthalene. The gas phase geometry structures were optimized by B3LYP/BS1. The solvent correction free energies were calculated by M06/BS2 in *m*-xylene.

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$	$\Delta H_{298.15}$	$\Delta S_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$	$\Delta G_{298.15}$	$\Delta G_{393.15}$
	(kcal/mol)	(kcal/mol)	(cal/mol)	gas	(1 atm)	(1 atm)	(1 M)	(1 M)
IN1 _n +H ₂ +NaphOMe +O'Bu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TS1 _n +H ₂ +NaphOMe +O'Bu	19.77	18.36	1.65	17.87	26.81	26.67	26.81	26.67
IN2 _n +H ₂ +NaphOMe +O'Bu	-5.72	-5.92	1.31	-6.31	7.83	7.70	7.83	7.70
IN4 _n +H ₂ +NaphOMe +O'Bu	-1.34	-2.24	-5.36	-0.64	8.96	9.47	8.96	9.47
TS4 _n +H ₂ +NaphOMe +O'Bu	12.82	9.16	-4.12	10.38	17.31	17.71	17.31	17.71
IN8+NapH+H ₂ +NaphOMe+O'Bu	-8.79	-10.60	47.83	-24.86	-7.60	-12.09	-5.70	-10.20
IN11+NapH +NaphOMe+O'Bu	-13.05	-12.39	13.68	-16.47	-1.26	-2.47	-1.26	-2.47
TS5+NapH +NaphOMe+O'Bu	-7.11	-8.21	13.54	-12.24	4.46	3.27	4.46	3.27
IN12+NapH +NaphOMe+O'Bu	-17.80	-15.91	12.45	-19.62	-0.89	-1.97	-0.89	-1.97
TS6+NapH +NaphOMe+O'Bu	-11.75	-10.19	13.09	-14.09	5.33	4.21	5.33	4.21

Reactions	B3LYP/BS1				M06/BS2//B3LYP/BS1			
	$\Delta E_{298.15}$ (kcal/mol)	$\Delta H_{298.15}$ (kcal/mol)	$\Delta S_{298.15}$ (cal/mol)	$\Delta G_{298.15}$ gas (kcal/mol)	$\Delta G_{298.15}$ (1 atm) (kcal/mol)	$\Delta G_{393.15}$ (1 atm) (kcal/mol)	$\Delta G_{298.15}$ (1 M) (kcal/mol)	$\Delta G_{393.15}$ (1 M) (kcal/mol)
IN13+NapH +NaphOMe+ $\text{O}'\text{Bu}$	-20.85	-18.42	23.39	-25.39	-2.99	-5.12	-2.99	-5.12
TS8+NapH +NaphOMe+ $\text{O}'\text{Bu}$	-0.37	0.82	23.19	-6.09	12.91	10.81	12.91	10.81
IN5 _n +H ₂ +NaphOMe + $\text{O}'\text{Bu}$	7.55	6.94	12.29	3.28	21.68	20.50	21.68	20.50
IN14 _n +NaphOMe + $\text{O}'\text{Bu}$	-0.04	2.27	-22.31	8.92	20.20	22.34	18.30	20.45
TS7 _n +NaphOMe + $\text{O}'\text{Bu}$	1.87	2.70	-26.52	10.60	21.38	23.96	19.49	22.07
IN15+NapH +NaphOMe	-49.79	-45.98	-33.43	-36.01	-14.49	-6.25	-16.38	-13.14
TS9+NapH +NaphOMe	-24.56	-22.42	-26.23	-14.60	7.71	15.27	5.82	8.38
[Ni(SIPr)(O' Bu)] ⁻ +NaphOMe+NaphH +MeOH	-44.26	-39.11	15.54	-43.75	-25.12	-21.51	-25.12	-26.50
IN6 _n +NaphH+MeOH	-40.93	-35.30	-39.32	-23.57	-22.38	-13.61	-24.27	-20.50
IN1 _n +NapH+MeOH + $\text{O}'\text{Bu}$	17.76	-13.25	12.39	16.94	-16.92	-13.03	-16.92	-18.02