

Supporting Information

Ligand-Controlled Chemodivergent Telomerization and Hydrofunctionalization of Isoprene with Hydrazones under Ni Catalysis

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9. Computational Studies

9.1 Computational methods

9.1.1 Conformational sampling

Conformational sampling was performed using Grimme's *CREST* program,^{10,11} which used metadynamics (MTD) with genetic z-matrix crossing (GC) performed at the GFN2-xTB¹²⁻¹⁴ extended semiempirical tight-binding level of theory with *opt=vtight* option. The isolated conformers were used for further density functional theory (DFT) calculations.

9.1.2 Density functional theory (DFT) calculations

Geometry optimizations were carried out using *Gaussian 16* rev. C.02 software¹⁵ in the gas phase using the global-hybrid meta-NGA (nonseparable gradient approximation) MN15 functional¹⁶ and the def2-SVP^{17,18} basis set for all atoms. Truhlar's MN15 functional was chosen to study the present system, as this functional has been employed in the studies of a range of organometallic systems with good accuracy.¹⁹⁻²² Minima and transition structures on the potential energy surface (PES) were confirmed as such by harmonic frequency analysis, showing respectively zero and one imaginary frequency. Where needed, intrinsic reaction coordinate (IRC)^{23,24} analysis were carried out to connect the appropriate reactant/product states passing through a given transition state. To improve on the accuracy of the corrected Gibbs free energy profile, single point (SP) calculations on the gas phase optimized geometries were performed at MN15 with def2-TZVP^{17,18} basis set for all atoms in the implicit SMD continuum model²⁵ for 2-Propanol solvent.

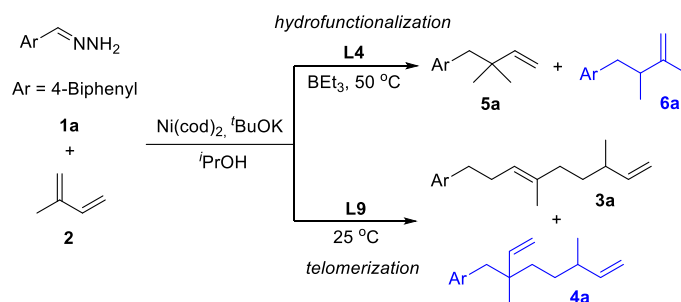
Gibbs free energies were evaluated at the reaction temperature of 323.15 K (50 °C) for hydrofunctionalization and 298.15 K (25 °C) for telomerization, using natural abundance weighted masses and a quasi-RRHO treatment of vibrational entropies and enthalpies.^{26,27} Vibrational entropies of frequencies below 100 cm⁻¹ were corrected according to a free rotor description, using Grimme's smooth damping function to interpolate between the two limiting descriptions.²⁶ For vibrational enthalpy, the quasi-RRHO correction proposed by Head-Gordon was adopted by

modifying the vibrational internal energy expression before deriving the enthalpy, a cutoff value of 100 cm⁻¹ was used.²⁷ These corrections were implemented using the thermochemistry analysis codes in *CHEMSMART* software.²⁸ The free energies reported in Gaussian from gas-phase optimization were further corrected using standard concentration of 1 mol/L,²⁹ which were used in solvation calculations, instead of the gas-phase 1 atm used by default in the Gaussian program.

Unless otherwise stated, the final corrected Gibbs free energy SMD(2-Propanol)-MN15/def2-TZVP//MN15/def2-SVP is used for discussion. *All Gibbs free energy values in the text and figures are quoted in kcal mol⁻¹.* All calculations were submitted and analyzed using *CHEMSMART* package. Non-covalent interactions (NCIs) were analyzed using *NCIPLOT*³⁰ calculations combined with *CHEMSMART* commands. The .wfn files for *NCIPLOT* were generated at MN15/DGDZVP^{31,32} level of theory. NCI indices calculated with *NCIPLOT* were visualized at a gradient isosurface value of $s = 0.5$ au. These are colored according to the sign of the second eigenvalue (λ_2) of the Laplacian of the density ($\nabla^2\rho$) over the range from -0.1 (blue = attractive) to +0.1 (red = repulsive). Molecular orbitals are visualized using an isosurface value of 0.05 au throughout. Optimized structures and molecular orbitals are prepared and visualized using *PyMOL* software,³³ with the corresponding .pse *PyMOL* session files were generated using *CHEMSMART* commands.

9.2 Model reaction

Scheme S1 shows the model reaction that we used for computational studies of the reaction mechanism for telomerization and hydrofunctionalization reaction.



Scheme S1. Model reaction used for DFT based mechanistic studies.

9.3 Gibbs free energy profiles for two pathways

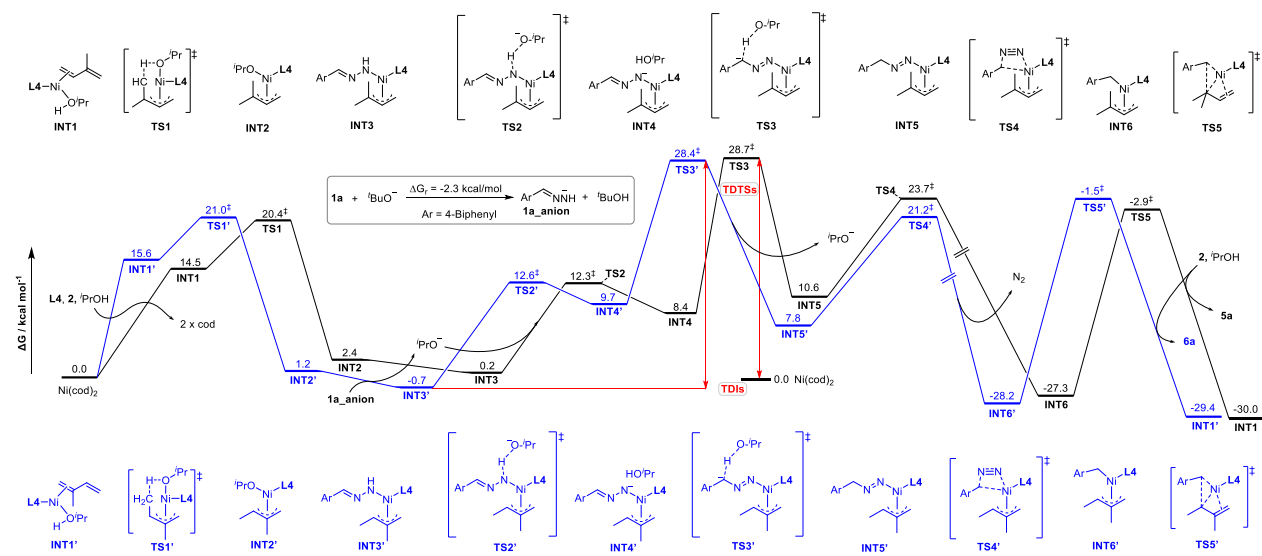


Figure S4. Gibbs free energy profile for hydrofunctionalization reaction in the absence of BET_3 . The Gibbs free energies are given in SMD(2-Propanol)-MN15/def2-TZVP//MN15/def2-SVP level of theories. The black line corresponds to the pathway leading to the major product **5a**, whereas the blue line represents the pathway leading to the minor product **6a**.

Initially, coordination of the **L4**-supported Ni species with one molecule of isoprene and one molecule of isopropanol gives rise to two distinct coordination arrangements, **INT1** and **INT1'**, which subsequently evolve into competing reaction pathways (Figure S4). The subsequent ligand-to-ligand hydrogen transfer (LLHT) proceeds through **TS1** and **TS1'**, with **TS1** being 0.6 kcal/mol lower in energy than **TS1'**. Next, the resulting intermediates **INT2** and **INT2'** undergo anion exchange to form the more stable intermediates **INT3** ($\Delta G = 0.2$ kcal/mol) and **INT3'** ($\Delta G = -0.7$ kcal/mol), respectively. These are followed by isopropoxide-assisted deprotonation of proximal *N* (*N* coordinated to Ni) of the azo-group via **TS2/TS2'** and then reprotonation at the α -C of the azo-group via **TS3/TS3'**, which are identified as the turnover-determining transition states (TDTs). These pathways give overall activation barriers of 28.7 kcal/mol (via **TS3**) and 29.1 kcal/mol (via **TS3'**), respectively. Thereafter, N_2 extrusion occurs to generate the corresponding thermodynamically stable Ni–C intermediates **INT6** (–27.3 kcal/mol) and **INT6'** (–28.2 kcal/mol). Finally, reductive elimination is followed by product dissociation and coordination of new

substrate molecules, thereby releasing the corresponding products **5a** and **6a** and regenerating the initial intermediates **INT1** and **INT1'** to continue the catalytic cycle. Overall, the catalytic cycle is both thermodynamically favorable and kinetically feasible.

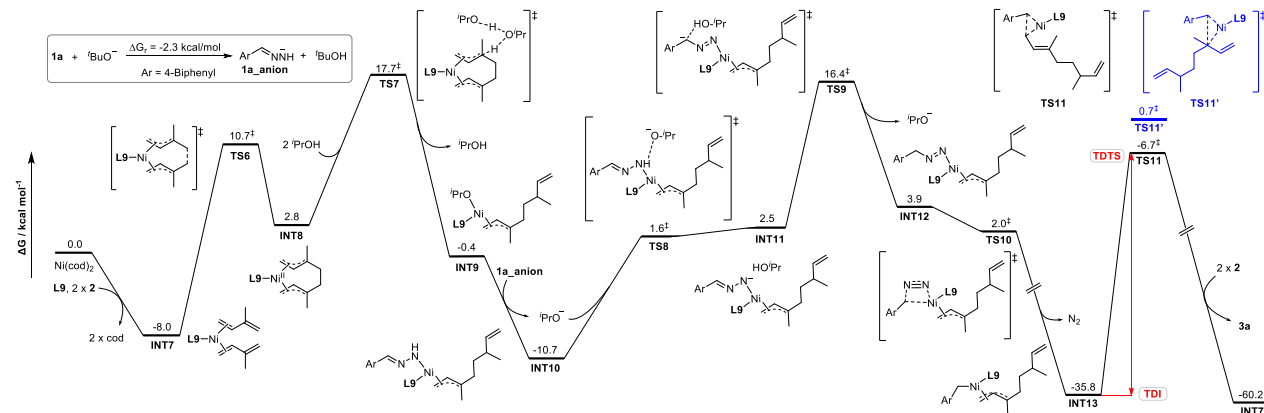


Figure S5. Gibbs free energy profile for telomerization reaction. The Gibbs free energies are given in SMD(2-Propanol)-MN15/def2-TZVP//MN15/def2-SVP level of theories.

Having established the hydrofunctionalization pathway for the **L4**-supported system (Figure S4), we also carried out a complete DFT investigation of the **L9**-controlled telomerization pathway (Figure S5) to further understand the similarities and differences between the two mechanisms. Based on our previous work,³⁴ the *head-to-head* arrangement of the two isoprene species was considered as the initial coordination mode for the subsequent mechanistic investigation. A notable difference is observed in the denitrogenation step. The intermediate **INT12** lies at 3.9 kcal/mol, whereas the subsequent N₂ extrusion transition state **TS10** is lower in energy at 2.0 kcal/mol. This result suggests that, within the more sterically congested and electron-rich environment created by ligand **L9**, N₂ extrusion appears to be effectively spontaneous and leads to the formation of the thermodynamically stable intermediate **INT13** (−35.8 kcal/mol). The overall process remains highly thermodynamically favorable. However, upon employing ligand **L9**, both the TDTS and turnover-determining intermediate (TDI) are altered. This change may originate from the sterically congested and electron-rich nature of ligand **L9**, which lowers the barrier of the proton-transfer step **TS9** while simultaneously increasing the barrier of the sterically sensitive reductive elimination step **TS11**. As a result, the overall activation barrier of the telomerization pathway is

determined by **TS11** and amounts to 29.1 kcal/mol (Although the computed activation barrier associated with **TS11** is higher than might be expected from the experimental reactivity, thorough conformational sampling and extensive transition-state searches were performed for **TS11**, and the reported structure corresponds to the lowest-energy transition state located at the present level of theory). In addition, this telomerization pathway also exhibits regioselectivity in this reductive elimination step. **TS11**, corresponding to reductive elimination at the terminal carbon to afford the major product **3a**, is 7.4 kcal/mol lower in energy than **TS11'**, indicating a strong kinetic preference for this pathway. As shown in Figure S6, no coordination interaction between the Ni center and the alkene is observed in this transition state. The observed regioselectivity is likely associated primarily with steric effects.

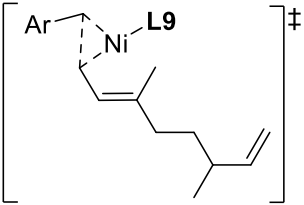
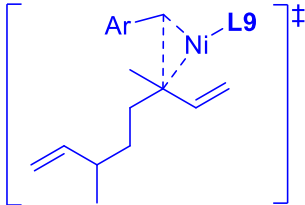
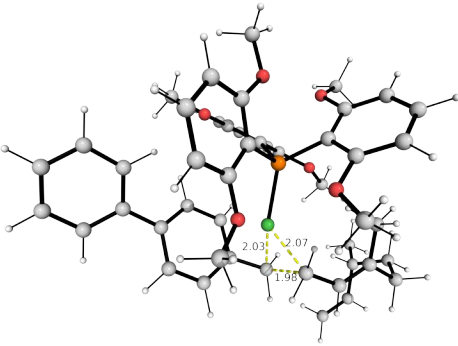
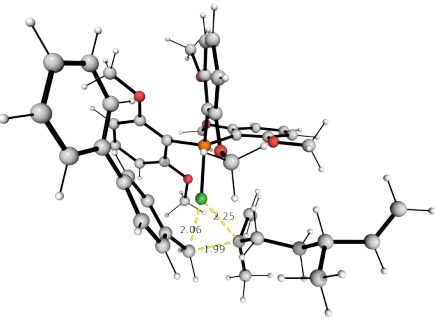
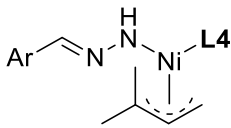
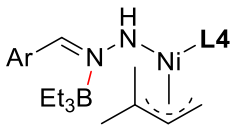
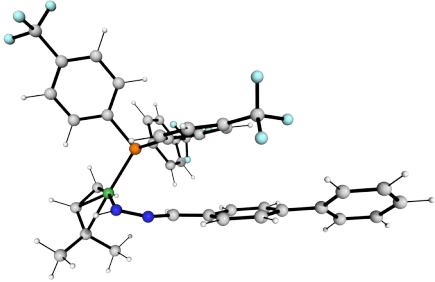
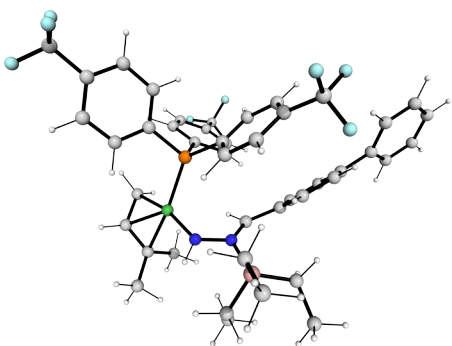
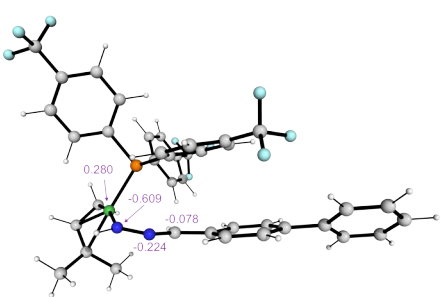
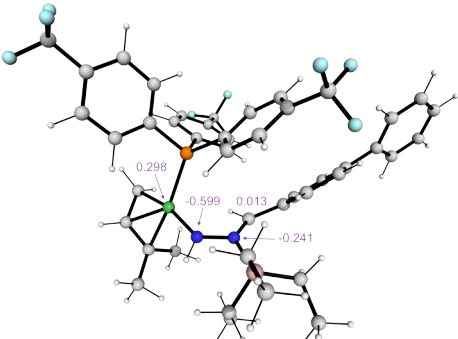
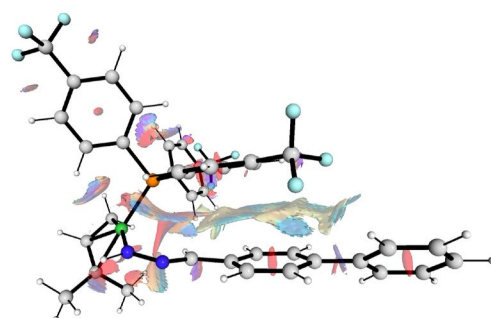
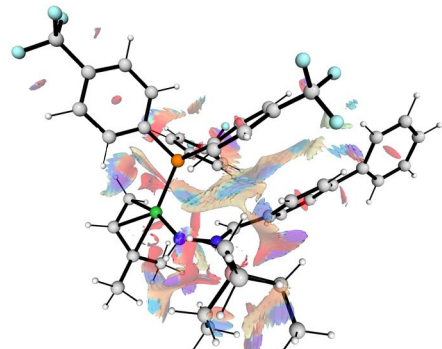
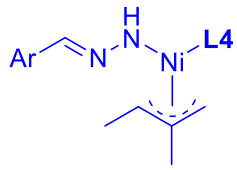
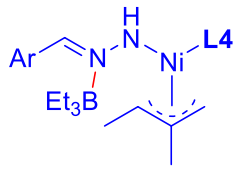
	TS11	TS11'
$\Delta\Delta G^\ddagger$	0.0 kcal/mol	7.4 kcal/mol
structure		
DFT optimized geometry		

Figure S6. DFT-optimized geometries of **TS11** and **TS11'** together with the corresponding Gibbs free energy difference.

9.4 Investigation of the role of BEt₃ in the hydrofunctionalization pathway

For the hydrofunctionalization pathway, we hypothesized that the additive BEt₃ exerts its effect after the association of **1a_{anion}** with the Ni complex, giving **INT3** and **INT3'**. As a Lewis acid, BEt₃ is proposed to coordinate to one of the nitrogen atoms of **1a_{anion}**, thereby modulating the steric environment and charge distribution of the key intermediates and transition states. To gain deeper insight into this effect, non-covalent interaction (NCI) analysis and NBO charge analysis were performed on **INT3** and **INT3'**, the TDIs of the two competing pathways, together with their corresponding BEt₃-bound adducts, **INT3_BEt₃** and **INT3'_BEt₃** (Figure S7). Upon coordination to **INT3/INT3'**, BEt₃ induces a redistribution of charge over the Ni–N–N=C fragment rather than acting only at the local coordination site. The increase in energy upon BEt₃ coordination is likely mainly attributable to a steric penalty. According to the NCI analysis of the four species, coordination of BEt₃ introduces steric congestion and repulsive interactions to **INT3** and **INT3'** structures.

	INT3	INT3_BEt₃
$\Delta\Delta G$	0.0 kcal/mol	4.9 kcal/mol
structure		
DFT optimized geometry		

NBO charge		
NCI plot		
		
	INT3'	INT3'_BEt₃
$\Delta\Delta G$	0.0 kcal/mol	8.1 kcal/mol
structure		

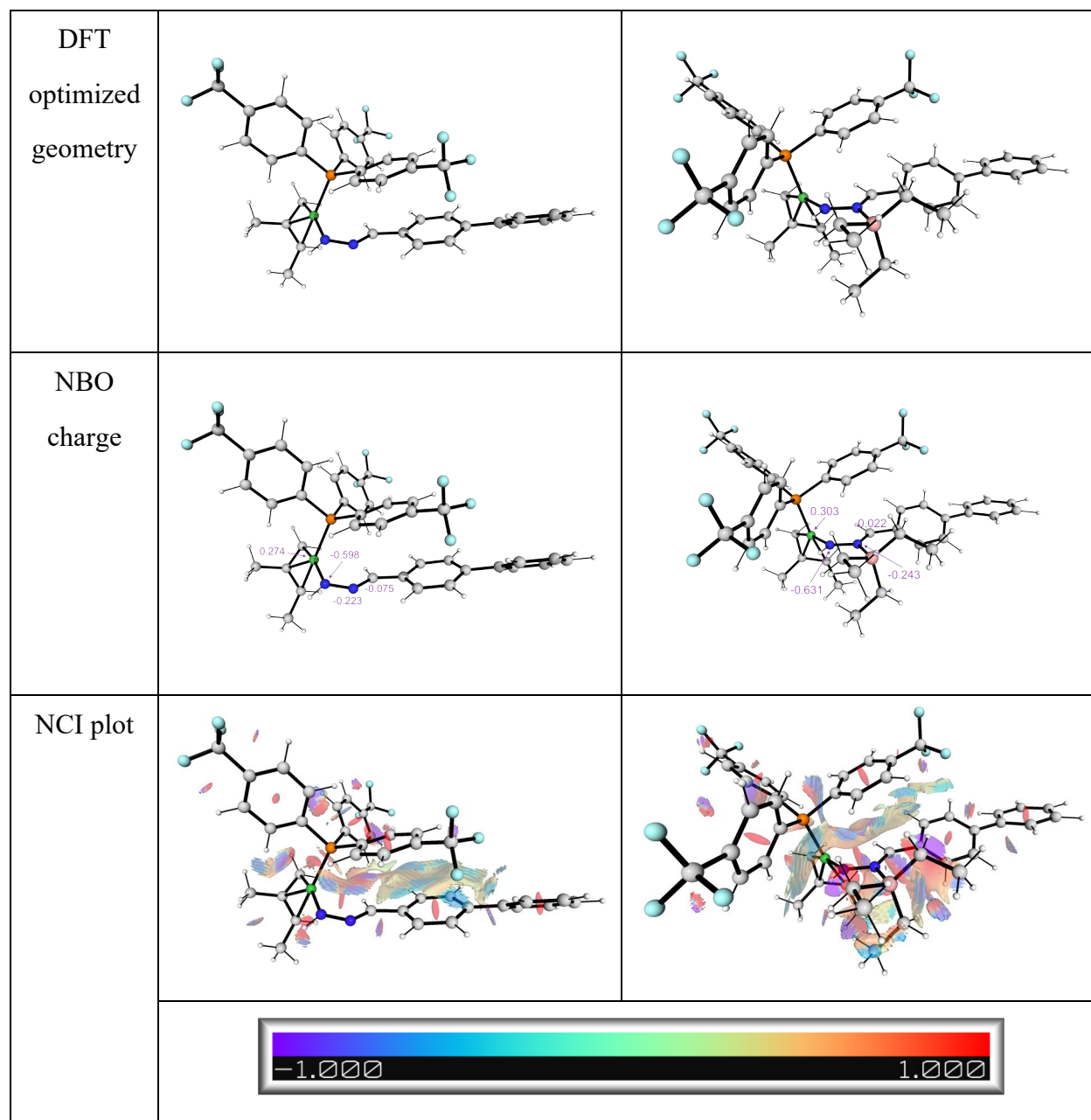
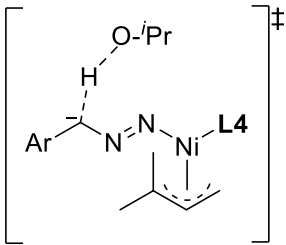
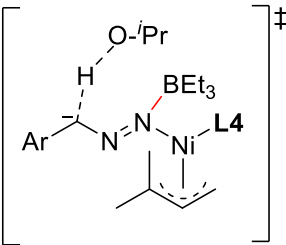


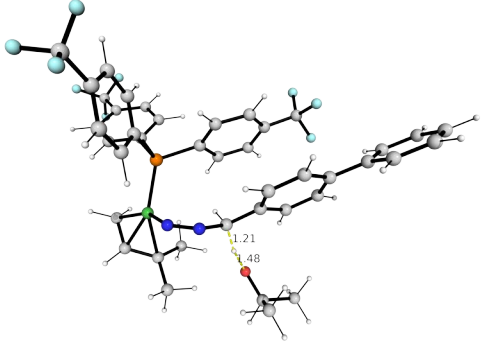
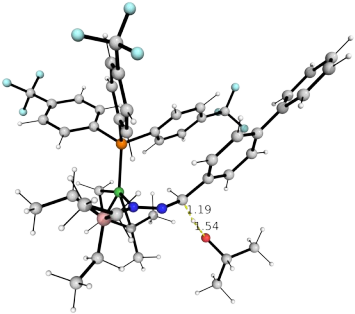
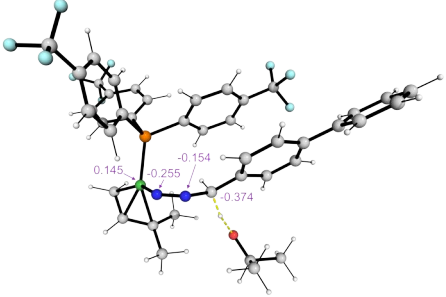
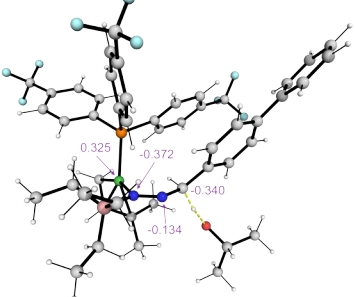
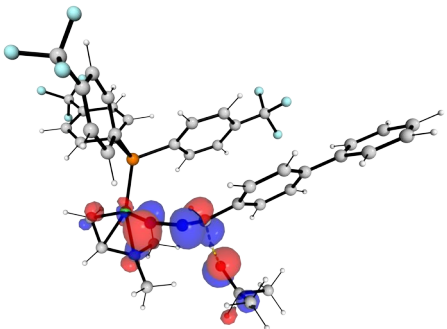
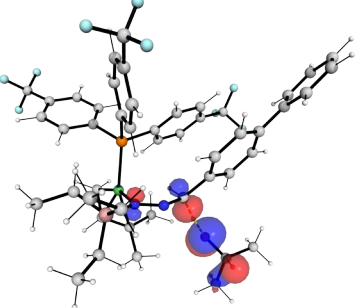
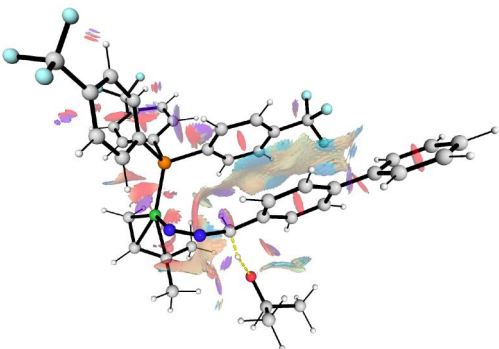
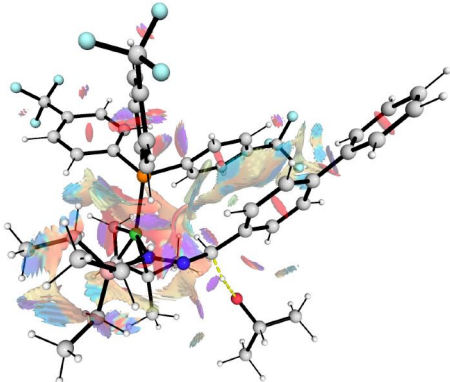
Figure S7. DFT-optimized geometries, NBO charge analysis and noncovalent interaction (NCI) plots of **INT3**, **INT3_BEt₃**, **INT3'** and **INT3'_BEt₃** together with the corresponding Gibbs free energy difference.

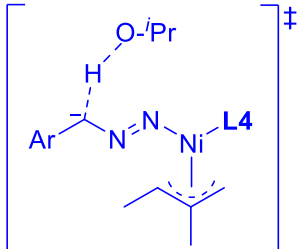
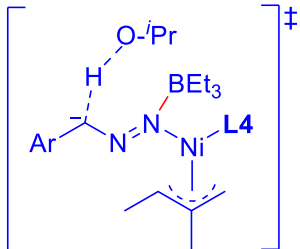
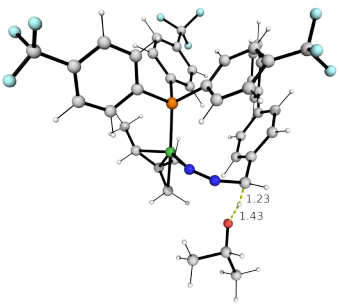
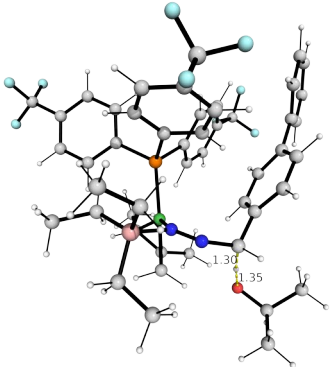
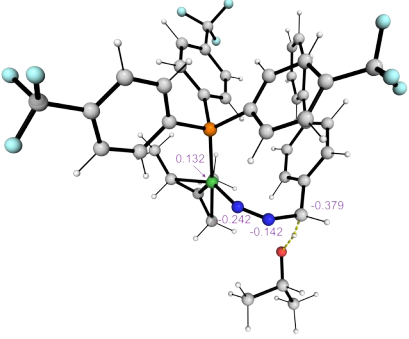
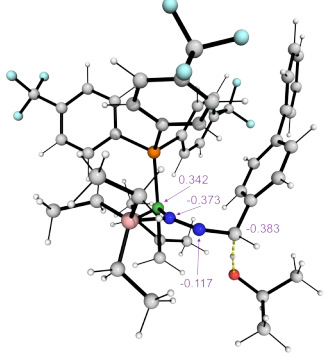
Next, we turned to the analysis of the TDTs for the two competing pathways, **TS3** and **TS3'**, together with their corresponding BEt₃-bound adducts **TS3_BEt₃** and **TS3'_BEt₃** (Figure S8). In contrast to the TDIs, coordination of BEt₃ at the TDTs effectively lowers the reaction barriers by 8.9 and 6.0 kcal/mol, respectively. In the transition states, BEt₃ exerts a more pronounced influence

on the charge distribution at the coordinated nitrogen atom and the Ni center. For example, in **TS3**, the borane-bound α -nitrogen becomes more negative (from -0.255 to -0.372), whereas the directly connected Ni center becomes more positive (from 0.145 to 0.325). By contrast, the distal nitrogen atom and the carbon atom directly involved in the reaction exhibit only minor changes in NBO charge. Notably, frontier molecular orbital (FMO) analysis suggests that, for both **TS3** and **TS3'**, introduction of BEt_3 changes the orientation of the highest occupied molecular orbital (HOMO) at the carbon center involved in proton transfer from isopropanol, such that the orbital is directed more toward the transferring proton. This more favorable alignment may facilitate orbital overlap and thereby lower the activation barrier.

From a geometric perspective, BEt_3 still introduces an unfavorable steric effect, which appears to be the primary origin of the enhanced regioselectivity. Conformational sampling analysis shows that the lowest-energy conformation of **TS3'** differs from that of **INT3'** in the geometry of the Ni coordination sphere. In particular, the isoprene substrate reorients its coordination mode to accommodate the approach of isopropanol, and the introduction of BEt_3 may further aggravate steric congestion in this region. Consistent with this interpretation, the NCI plots show that **TS3** $_{\text{BEt}_3}$ exhibits less steric congestion than **TS3'** $_{\text{BEt}_3}$. Therefore, although coordination of BEt_3 lowers the barriers of both transition states, the different steric environments increase the $\Delta\Delta G^\ddagger$ value from 0.4 to 3.3 kcal/mol, thereby further favoring the **TS3** $_{\text{BEt}_3}$ pathway.

	TS3	TS3 $_{\text{BEt}_3}$
$\Delta\Delta G^\ddagger$	0.0 kcal/mol	-8.9 kcal/mol
structure		

DFT optimized geometry		
NBO charge		
HOMO		
NCI plot		

		
	TS3'	TS3'_BEt ₃
$\Delta\Delta G^\ddagger$	0.0 kcal/mol	-6.0 kcal/mol
structure		
DFT optimized geometry		
NBO charge		

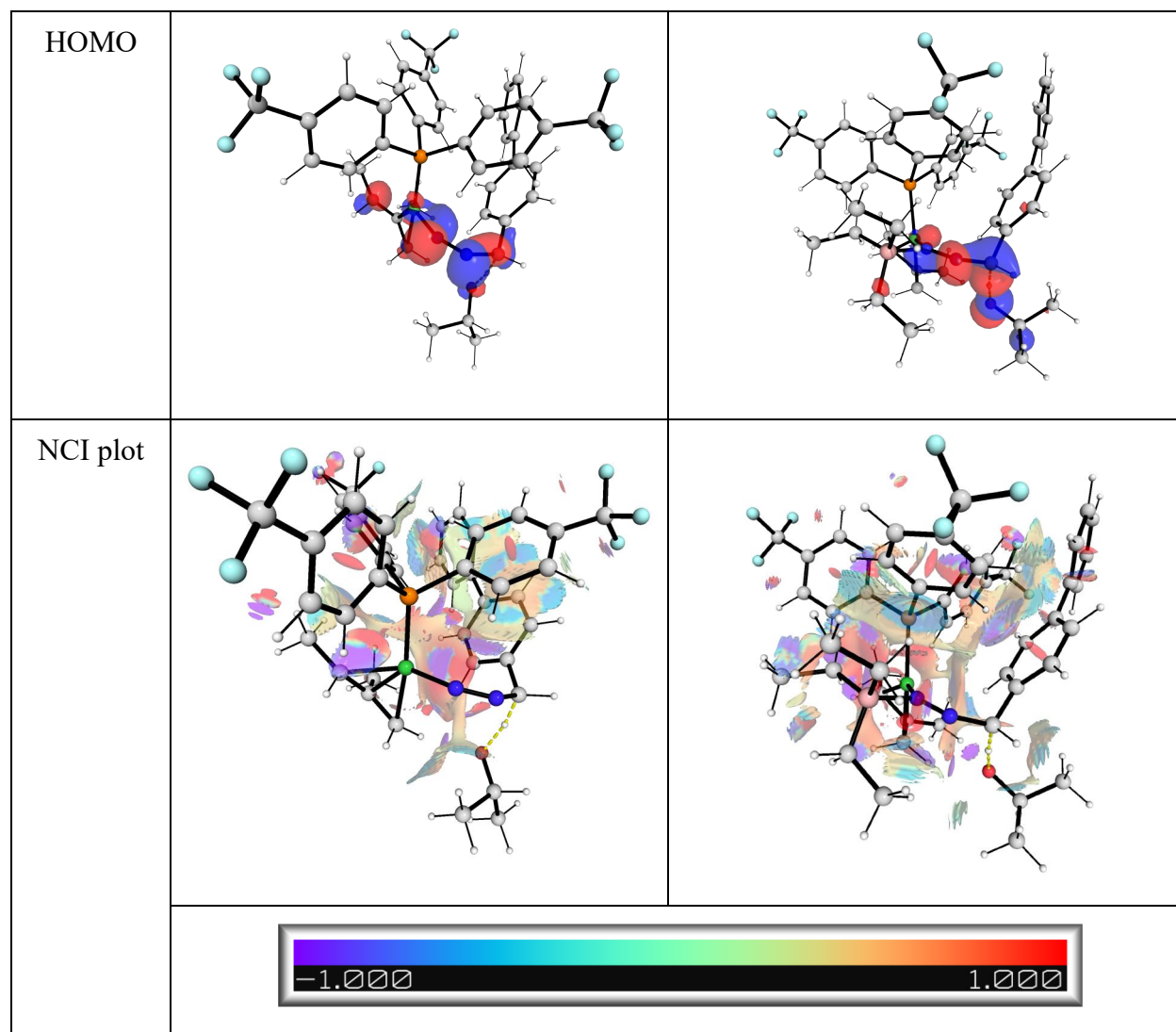


Figure S8. DFT-optimized geometries, NBO charge analysis, frontier molecular orbitals (HOMO) and noncovalent interaction (NCI) plots of **TS3**, **TS3_BEt₃**, **TS3'** and **TS3'_BEt₃** together with the corresponding Gibbs free energy difference.

As shown in Figure S9, in addition to coordination of BEt₃ to the proximal *N* of **1a_{anion}** (*N* coordinated to Ni), coordination to the distal *N* was also considered (**TS3_BEt₃_a**). However, owing to the greater steric hindrance associated with this arrangement, its energy is 6.2 kcal/mol higher than that of **TS3_BEt₃**. According to the calculations shown by the pink line, if BEt₃ remains coordinated to nitrogen or continues to interact with nitrogen atom during the subsequent denitrogenation step, the following process becomes kinetically highly unfavorable, with an overall activation barrier of 30.9 kcal/mol. In contrast, after proton transfer from isopropanol, BEt₃

may coordinate to the resulting oxyanion and dissociate from the Ni-containing reacting species (black line), thereby facilitating the subsequent N₂ extrusion step, which proceeds through the same transition state, **TS4**, as in the absence of BEt₃.

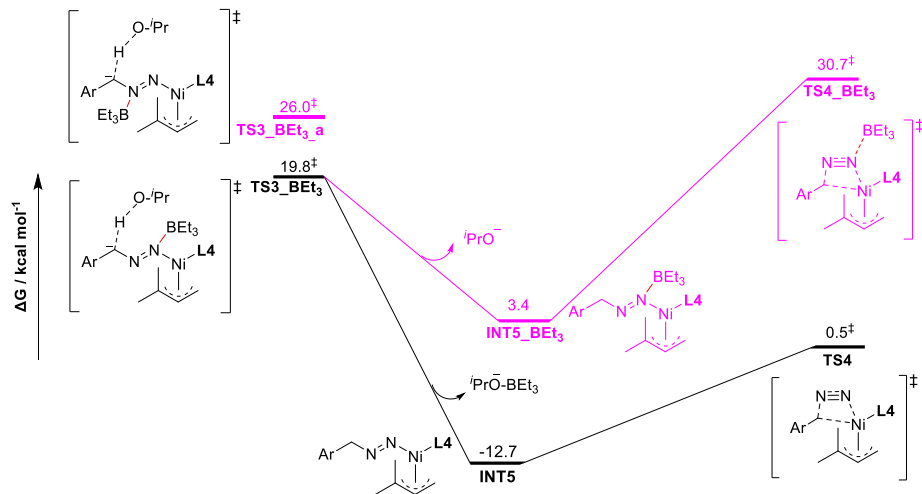


Figure S9. The Gibbs free energy profile for the additional BEt₃-involved pathway from protonation to denitrogenation. Gibbs free energies are given in SMD(2-Propanol)-MN15/def2-TZVP//MN15/def2-SVP level of theories. Relative Gibbs free energies are given in kcal/mol with respect to the same starting materials Ni(cod)₂, as in Figure S4.

Overall, the BEt₃ additive does not change the TDIs and TDTs of the original reaction, but it significantly modulates both the electronic and steric features of the TDTs. Electronically, coordination of BEt₃ lowers the activation barriers for both competing pathways. Sterically, the additional congestion introduced by BEt₃ imposes unequal penalties on the two pathways, thereby increasing $\Delta\Delta G^\ddagger$ and ultimately enhancing the regioselectivity while simultaneously facilitating the overall reaction.

9.5 Analysis of key transition states in the chemodivergence-determining step

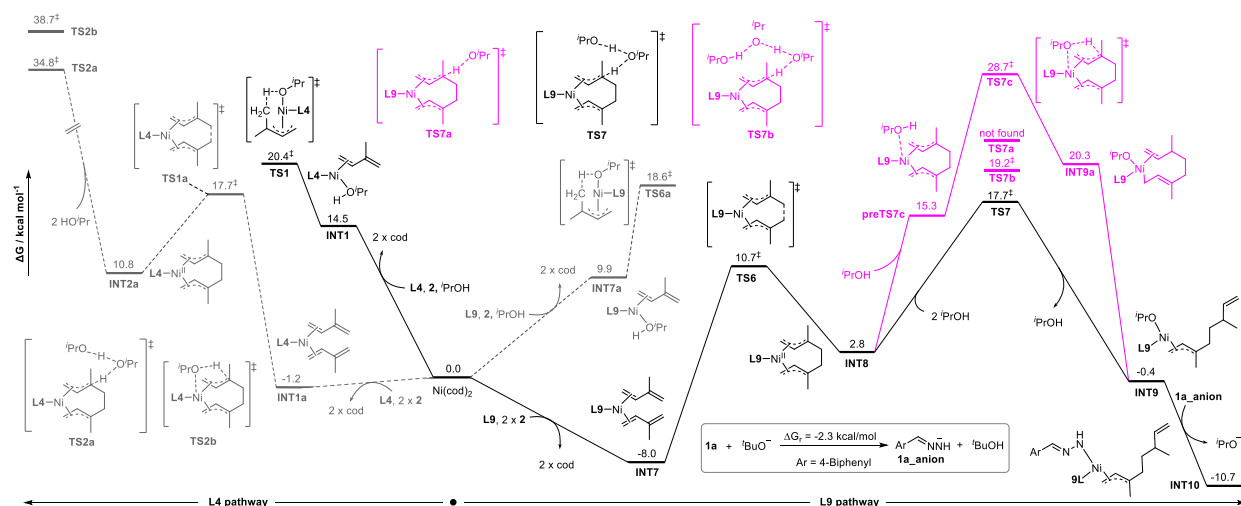
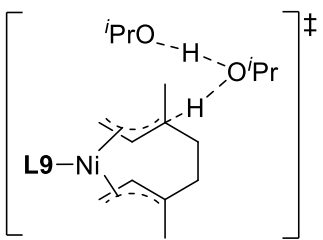
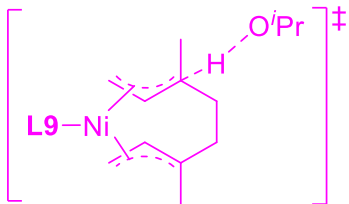
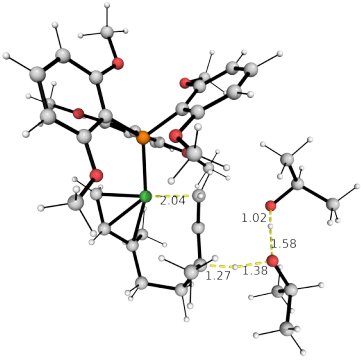


Figure S10. The Gibbs free energy profiles for the possible reaction pathways with ligands **L4** and **L9**. Gibbs free energies are given in SMD(2-Propanol)-MN15/def2-TZVP//MN15/def2-SVP level of theories. Relative Gibbs free energies for four pathways are given in kcal/mol with respect to the same starting materials $\text{Ni}(\text{cod})_2$. The thermochemical corrections for the **L4**-related pathways (left) were evaluated at 323.15 K (50 °C), whereas those for the **L9**-related pathways (right) were evaluated at 298.15 K (25 °C).

According to the analysis of Figure 6B, the ligand-controlled chemodivergence between **L4** and **L9** mainly originates from the barrier difference between the protonation pathways following oxidative cyclometallation (**TS2a** and **TS7**) and the competing LLHT pathways (**TS1** and **TS6a**). Therefore, we next turned to a more detailed analysis of the key protonation transition states **TS2a** and **TS7** (see Figure S11). We first examined **TS7** in the **L9** pathway by considering whether isopropanol enters the Ni coordination sphere. For the outer-sphere mode, no transition state corresponding to **TS7a** could be located with only one isopropanol molecule, presumably because unactivated isopropanol is insufficiently acidic to deliver the proton directly. We therefore considered the participation of two or three isopropanol molecules to enable proton-bridge-assisted transfer for the protonation process. The results show that, when two isopropanol molecules are involved, proton-transfer relay enables the reaction to proceed with an activation barrier of 25.7 kcal/mol (**TS7**). When three isopropanol molecules are used, the third isopropanol does not directly participate in proton transfer, but instead forms a hydrogen-bonding interaction with the oxygen atom of the second isopropanol. As a result, the corresponding transition state **TS7b** is 1.5

kcal/mol higher in energy than that of **TS7**. Consequently, the inner-sphere pathway was also examined. In this case, isopropanol cannot effectively enter the Ni coordination sphere, with an O $\cdots$ Ni distance of 3.19 Å, indicating only a weak interaction with the metal center. The O–H bond of isopropanol is therefore not effectively activated, resulting in an activation barrier that is 11.0 kcal/mol higher than **TS7**.

In the same manner, **TS2a** and **TS2b** in the **L4** pathway was also investigated. Although the steric congestion around the **L4**-supported Ni species is smaller than that of the **L9**-supported system, isopropanol still cannot be effectively activated through coordination to the Ni center. The corresponding O $\cdots$ Ni distance in **TS2b** is 2.45 Å, suggesting only a weak interaction between isopropanol and the metal center and leading to a high activation barrier of 39.9 kcal/mol. The activation barrier of **TS2a** also remains prohibitively high (36.0 kcal/mol).

	TS7	TS7a
$\Delta G^\ddagger$	17.7 kcal/mol	\
structure		
DFT optimized geometry		Not located
	TS7b	TS7c
$\Delta G^\ddagger$	19.2 kcal/mol	28.7 kcal/mol

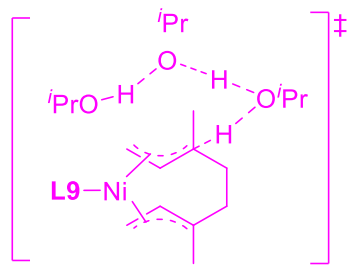
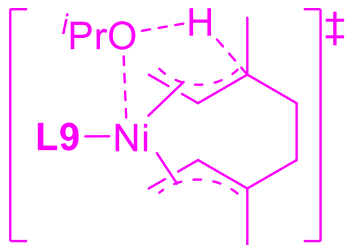
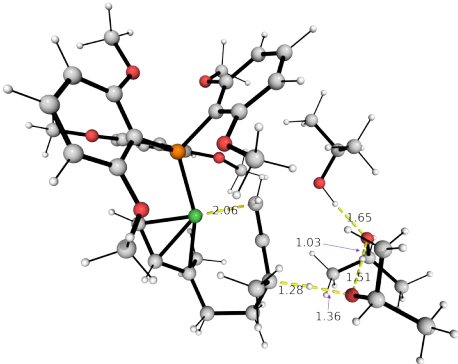
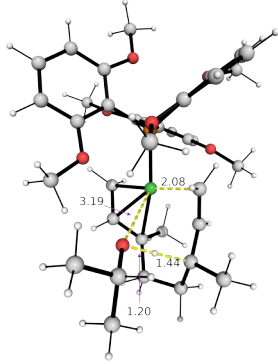
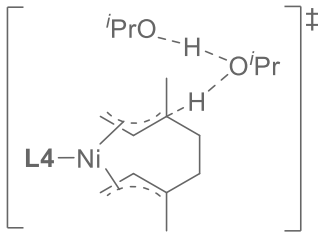
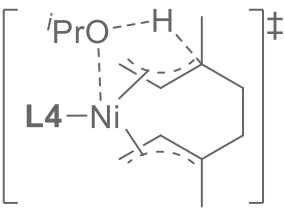
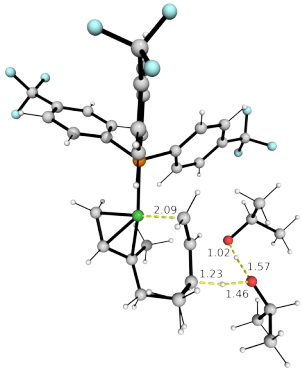
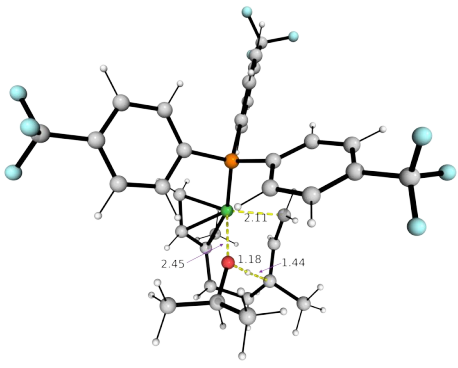
structure		
DFT optimized geometry		
	TS2a	TS2b
$\Delta G^\ddagger$	34.8 kcal/mol	38.7 kcal/mol
structure		
DFT optimized geometry		

Figure S11. The relative Gibbs free energies and DFT-optimized geometries of key protonation transition states.

Following the proton transfer, the resulting isopropoxide preferentially coordinates to the Ni center. We further examined whether the generated alkene remains coordinated to the metal center. Our calculations show that retention of alkene coordination would require disruption of the stabilizing η^3 -allyl coordination at the Ni center (shown in Figure S12). The large energy difference between the two coordination modes (20.7 kcal/mol) indicates that, after proton transfer, the intermediate strongly favors alkene dissociation in order to preserve the stable η^3 -allyl coordination and relieve steric congestion around the coordination sphere.

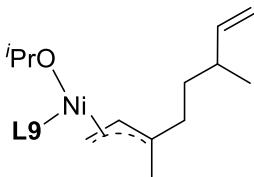
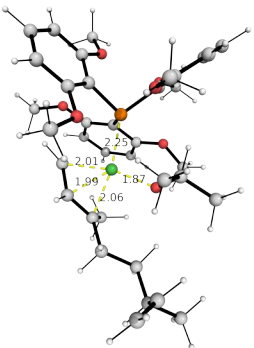
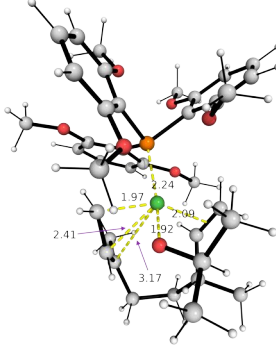
	INT9	INT9a
$\Delta\Delta G$	0.0 kcal/mol	20.7 kcal/mol
structure		
DFT optimized geometry		

Figure S12. DFT-optimized geometries of INT9 and INT9a together with the corresponding Gibbs free energy difference.

9.6 Optimized structures and absolute energies

Geometries of all optimized structures (in .xyz format with their associated energy in Hartrees) are included in a separate folder named *DFT_optimized_structures* with an associated readme.txt file. All these data have been deposited and uploaded to zenodo.org (DOI: [10.5281/zenodo.20430792](https://doi.org/10.5281/zenodo.20430792)).

Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 323.15 K/50 °C) for optimized structures for hydrofunctionalization pathway are given below. Single point corrections in SMD(2-Propanol) using MN15/def2-TZVP level of theory are also included.

Structure	E/au	ZPE/au	H/au	TS/au	qh-G/au	SP
Ni(cod) ₂	-2131.111086	0.364726	-2130.726158	0.063143	-2130.789878	-2132.113481
L4	-2044.11407	0.291231	-2043.790902	0.1062	-2043.890237	-2046.36737
cod	-311.347189	0.180485	-311.156884	0.041529	-311.19854	-311.735491
1a	-610.808612	0.221281	-610.571849	0.055931	-610.627871	-611.557371
1a_anion	-610.223908	0.20729	-610.001633	0.054927	-610.056594	-611.042429
^t BuOH	-233.176779	0.13533	-233.032622	0.03756	-233.070272	-233.486713
^t BuO ₋ anion	-232.544719	0.119193	-232.416937	0.037128	-232.454153	-232.965661
2	-194.872887	0.113608	-194.751541	0.035786	-194.787425	-195.119969
ⁱ PrOH	-193.946025	0.108058	-193.830684	0.034172	-193.864916	-194.206541
ⁱ PrO ₋ anion	-193.312189	0.091679	-193.21363	0.033396	-193.247073	-193.685474
N ₂	-109.305532	0.005743	-109.296207	0.020507	-109.316713	-109.442412
INT1	-3941.33825	0.517569	-3940.77164	0.138775	-3940.905305	-3944.331868
INT1'	-3941.33772	0.517467	-3940.771046	0.139159	-3940.905042	-3944.329882
INT1a	-3942.286618	0.523632	-3941.713884	0.139466	-3941.847617	-3945.271988
TS1	-3941.332286	0.511883	-3940.772047	0.138002	-3940.904734	-3944.317121
TS1'	-3941.333059	0.512305	-3940.77264	0.136392	-3940.904033	-3944.317695
TS1a	-3942.257467	0.522758	-3941.686479	0.137565	-3941.818397	-3945.242015

INT2	-3941.364592	0.517334	-3940.798611	0.137501	-3940.930947	-3944.351924
INT2'	-3941.363867	0.516952	-3940.798116	0.137443	-3940.930806	-3944.353163
INT2a	-3942.27251	0.52504	-3941.699188	0.137914	-3941.831418	-3945.25508
TS2	-4551.634455	0.721076	-4550.849605	0.171008	-4551.014209	-4555.397843
TS2'	-4551.628535	0.720717	-4550.844032	0.170109	-4551.008288	-4555.397281
TS2a	-4330.181743	0.742663	-4329.377713	0.162674	-4329.53559	-4333.67268
TS2b	-4136.214995	0.631172	-4135.529242	0.148096	-4135.672703	-4139.437245
INT3	-4358.236395	0.630883	-4357.548696	0.154615	-4357.697844	-4361.715013
INT3'	-4358.235623	0.63026	-4357.548259	0.15598	-4357.698535	-4361.715032
INT4	-4551.640811	0.725312	-4550.851063	0.173559	-4551.017724	-4555.406822
INT4'	-4551.63694	0.725157	-4550.847403	0.171214	-4551.012871	-4555.405745
TS3	-4551.593004	0.721586	-4550.807924	0.170348	-4550.972002	-4555.372471
TS3'	-4551.590154	0.721732	-4550.80524	0.16579	-4550.96657	-4555.375574
INT5	-4358.215726	0.630322	-4357.528558	0.155639	-4357.678366	-4361.69726
INT5'	-4358.217698	0.629507	-4357.530957	0.157318	-4357.682422	-4361.699657
TS4	-4358.184584	0.626812	-4357.500335	0.15625	-4357.651082	-4361.672488
TS4'	-4358.187415	0.626312	-4357.503441	0.157316	-4357.655179	-4361.675246
INT6	-4248.949803	0.619697	-4248.275082	0.153185	-4248.421621	-4252.294916
INT6'	-4248.954745	0.619571	-4248.280345	0.150737	-4248.425559	-4252.297374
TS5	-4248.915179	0.619108	-4248.242211	0.148165	-4248.384895	-4252.258104
TS5'	-4248.910271	0.618572	-4248.237198	0.152404	-4248.382803	-4252.25305

5a	-696.461695	0.328179	-696.113194	0.06688	-696.179698	-697.314099
6a	-696.464224	0.328705	-696.115305	0.066727	-696.181713	-697.3152885
BEt ₃	-261.93814	0.198577	-261.726233	0.051286	-261.776741	-262.270937
^t PrO _{-anion} _BEt ₃	-455.37087	0.296819	-455.055316	0.060623	-455.116536	-456.0213152
INT3_BEt₃	-4620.204719	0.835959	-4619.300168	0.178259	-4619.472793	-4624.010818
INT3'_BEt₃	-4620.20066	0.836048	-4619.29592	0.178259	-4619.468837	-4624.006462
TS3_BEt₃	-4813.59445	0.927031	-4812.592366	0.191869	-4812.778412	-4817.691255
TS3'_BEt₃	-4813.594315	0.925782	-4812.593775	0.186978	-4812.777241	-4817.688021
TS3_BEt₃_a	-4813.573845	0.925415	-4812.572889	0.194322	-4812.76065	-4817.678491
INT5_BEt₃	-4620.20752	0.835125	-4619.30397	0.176362	-4619.475492	-4624.013007
TS4_BEt₃	-4620.139032	0.828021	-4619.239914	0.186028	-4619.419797	-4623.956606

For telomerization pathway, analogous data are provided below. The only difference is that thermodynamic corrections were evaluated at 298.15 K (25 °C).

Structure	E/au	ZPE/au	H/au	TS/au	qh-G/au	SP
Ni(cod) ₂	-2131.111086	0.364726	-2130.729091	0.055519	-2130.785238	-2132.113481
L9	-1720.43598	0.471467	-1719.932299	0.091184	-1720.023597	-1722.282167
cod	-311.347189	0.180485	-311.158209	0.03712	-311.195482	-311.735491
1a	-610.808612	0.221281	-610.573974	0.049642	-610.623822	-611.557371
1a_{-anion}	-610.223908	0.20729	-610.003695	0.048775	-610.052616	-611.042429
^t BuOH	-233.176779	0.13533	-233.033741	0.033656	-233.067486	-233.486713
^t BuO _{-anion}	-232.544719	0.119193	-232.418024	0.033288	-232.4514	-232.965661

2	-194.872887	0.113608	-194.752501	0.032172	-194.784771	-195.119969
<i>i</i> PrOH	-193.946025	0.108058	-193.831553	0.030771	-193.862383	-194.206541
<i>i</i> PrO ₋ anion	-193.312189	0.091679	-193.214449	0.030102	-193.244597	-193.685474
N ₂	-109.305532	0.005743	-109.296484	0.01873	-109.315214	-109.442412
INT7	-3618.626956	0.704689	-3617.875923	0.119535	-3617.995895	-3621.197337
INT7a	-3617.66807	0.696935	-3616.923898	0.123846	-3617.047568	-3620.249398
TS6	-3618.597213	0.703927	-3617.847599	0.118108	-3617.966133	-3621.167635
TS6a	-3617.663064	0.693837	-3616.923722	0.117646	-3617.041889	-3620.236154
INT8	-3618.616015	0.707156	-3617.863578	0.117085	-3617.980917	-3621.184109
TS7	-4006.534071	0.922452	-4005.553909	0.145047	-4005.698634	-4009.606529
TS7b	-4200.513326	1.032887	-4199.41653	0.158148	-4199.574413	-4203.830636
preTS7c	-3812.56874	0.816462	-3811.700057	0.132023	-3811.832322	-3815.388479
TS7c	-3812.553433	0.812437	-3811.68987	0.128373	-3811.819084	-3815.365004
INT9	-3812.601082	0.817069	-3811.731864	0.131843	-3811.863995	-3815.414133
INT9a	-3812.573531	0.818111	-3811.7042	0.127394	-3811.83283	-3815.384837
INT10	-4229.48188	0.930938	-4228.49164	0.150926	-4228.640713	-4232.787935
TS8	-4422.865205	1.021321	-4421.779422	0.159111	-4421.938006	-4426.472275
INT11	-4422.868719	1.025636	-4421.778133	0.160253	-4421.93788	-4426.474417
TS9	-4422.831674	1.020622	-4421.746149	0.162234	-4421.90677	-4426.446377
INT12	-4229.461093	0.930277	-4228.471704	0.148074	-4228.61926	-4232.765384
TS10	-4229.435459	0.926298	-4228.449044	0.152996	-4228.600085	-4232.761878

INT13	-4120.197367	0.918879	-4119.221016	0.145017	-4119.365239	-4123.366722
TS11	-4120.151651	0.918416	-4119.176463	0.142024	-4119.31855	-4123.321454
TS11'	-4120.138489	0.91847	-4119.163299	0.141973	-4119.305012	-4123.310018
3a	-891.374245	0.446746	-890.903648	0.07494	-890.977718	-892.4681875