Supporting Information

A Computational Insight Into Hydroamination of an Activated Olefin as Catalyzed by a 1,2,4-Triazole Derived Nickel(II) N-heterocyclic Carbene Complex

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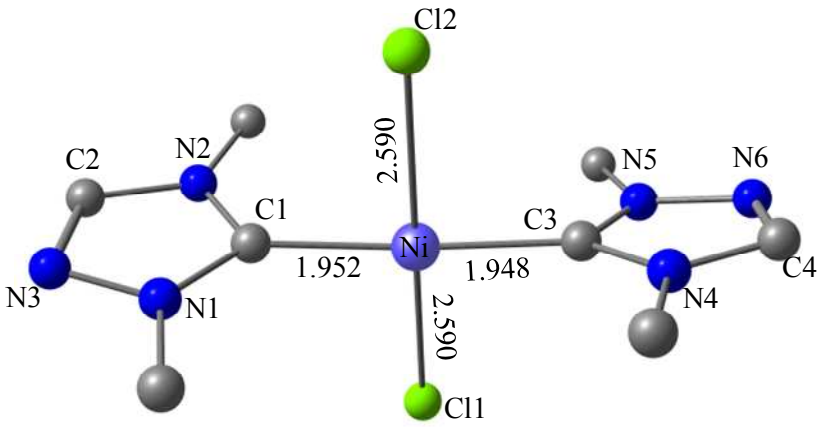


Figure S1. Computed structure of **A** with selected bond lengths in Å. Some important bond angles (°); Cl2−Ni−C1 86.4, Cl2−Ni−C3 86.4, Cl1−Ni−Cl2 180.0, C3−Ni−C1 172.8.

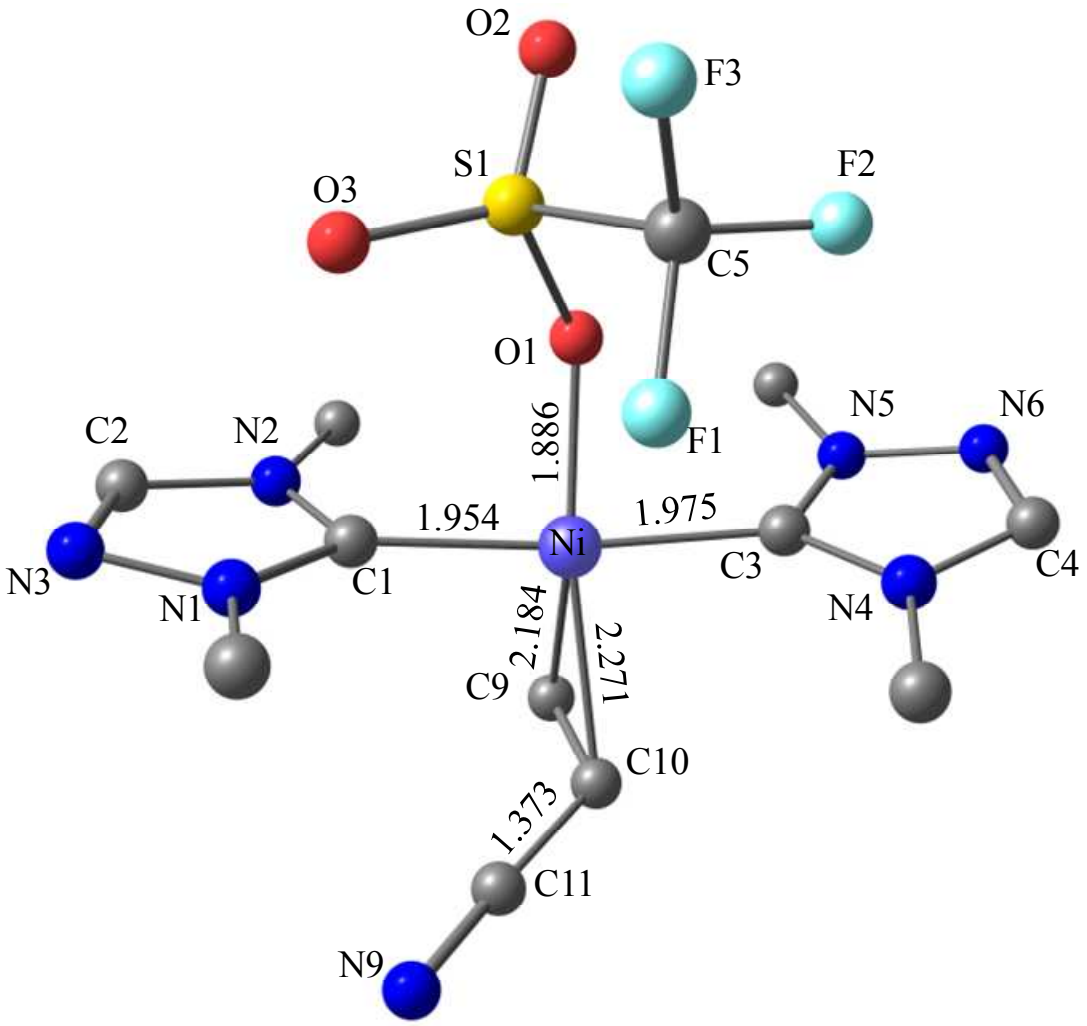


Figure S2. Computed structure of **C** (alkene coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 173.3, O1−Ni−C9 143.7, O1−Ni−C10 171.8, C1−Ni−O1 89.5, C1−Ni−C9 89.2, C3−Ni−O1 84.2, C3−Ni−C9 97.2.

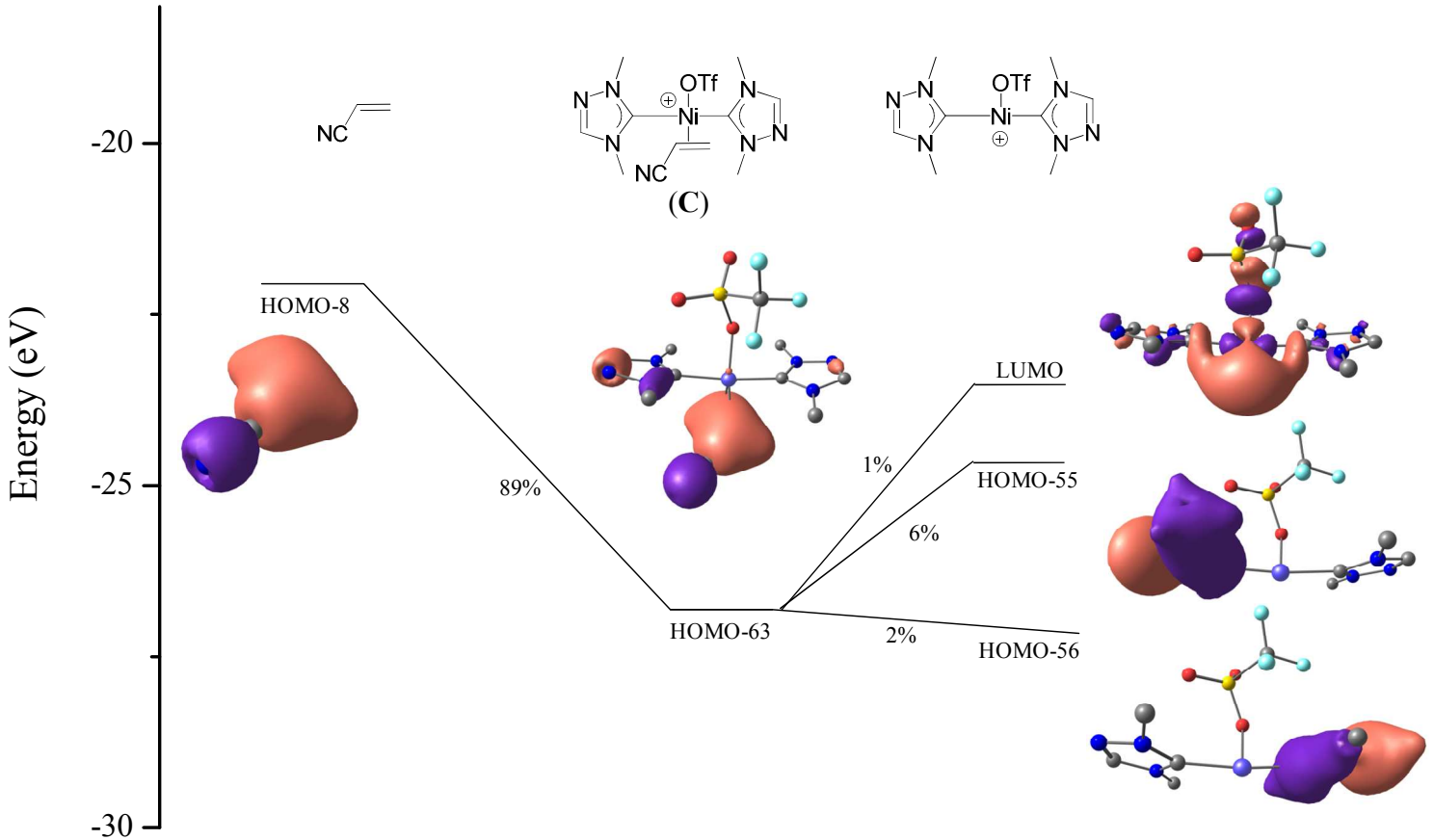


Figure S3. Simplified orbital interaction diagram showing major contribution of the $[(NHC)_2(OTf)Ni{-}(H_2C{=}CHCN)]^+$ bond in **C**.

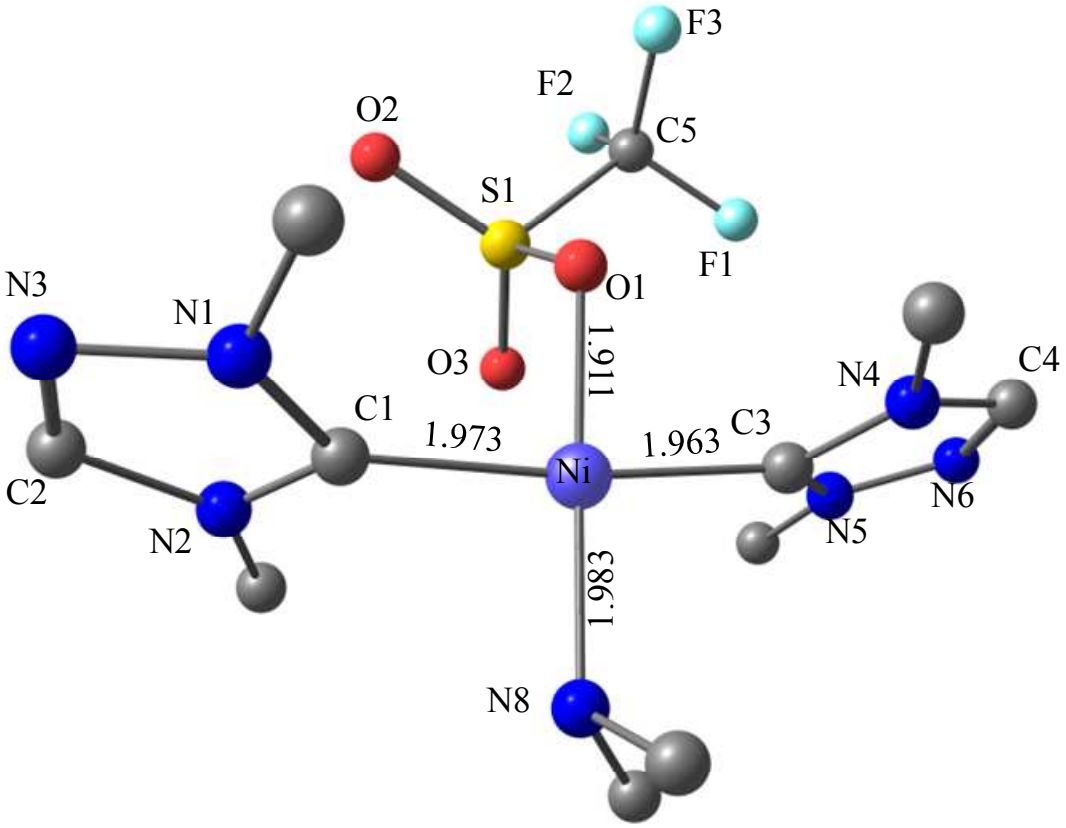


Figure S4. Computed structure of **C'** (amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 173.0, O1−Ni−N8 174.1, C1−Ni−O1 88.1, C1−Ni−N8 91.5, C3−Ni−O1 85.9, C3−Ni−N9 85.4.

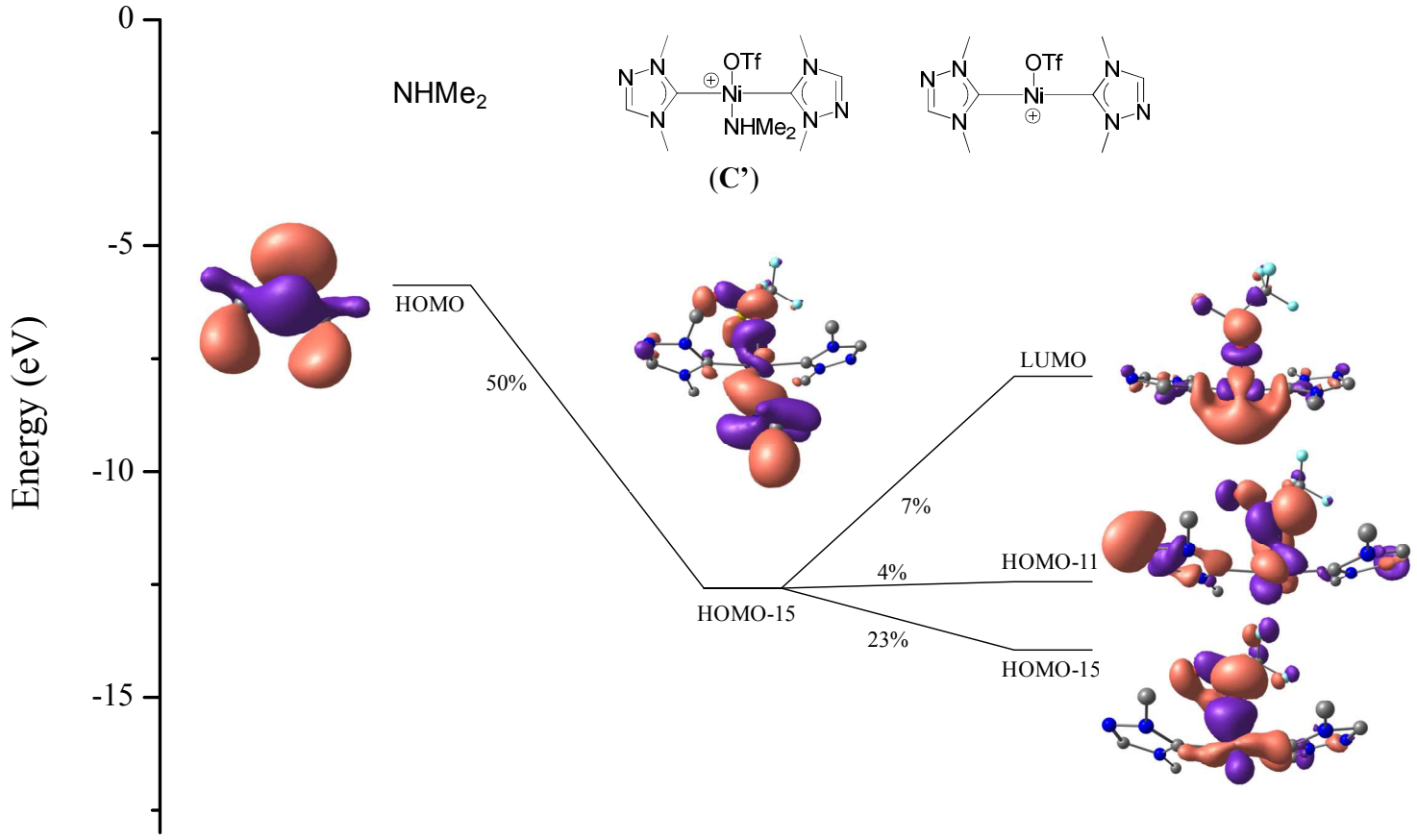


Figure S5. Simplified orbital interaction diagram showing major contribution of the $[(NHC)_2(OTf)Ni{-}(NHMe_2)]^+$ bond in **C'**.

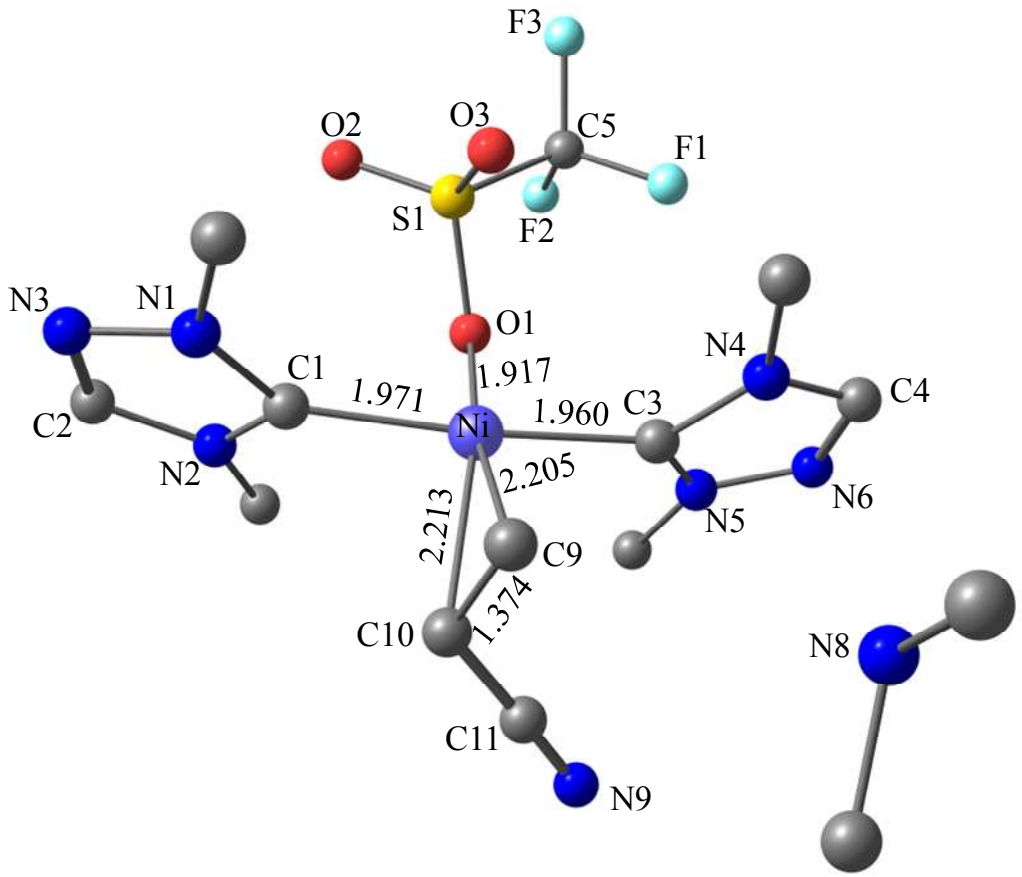


Figure S6. Computed structure of **C'' (**amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 172.3, O1−Ni−C9 168.4, O1−Ni−C10 155.2, C1−Ni−O1 89.0, C1−Ni−C10 87.5, C3−Ni−O1 85.3, C3−Ni−C10 99.8, C3−Ni−C9 89.9.

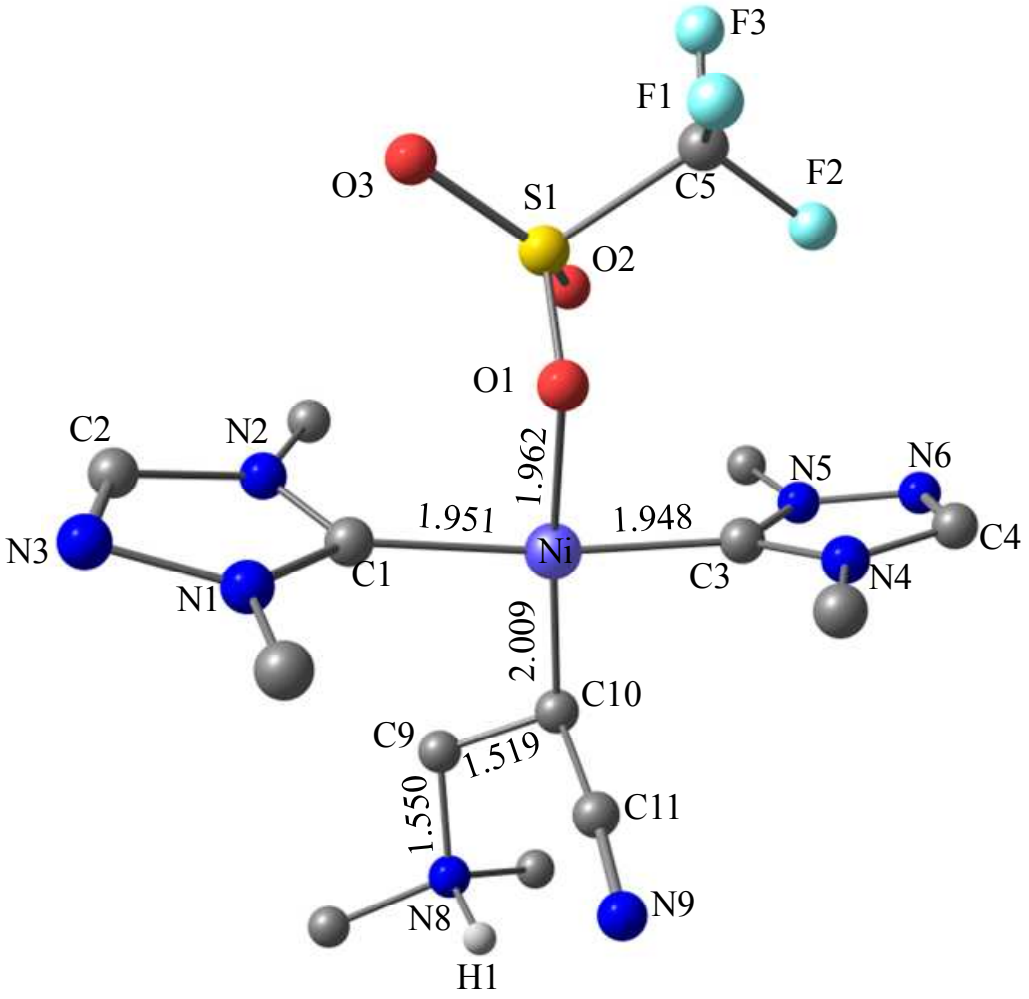


Figure S7. Computed structure of **D (**common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 172.8, O1−Ni−C10 170.2, C1−Ni−O1 86.4, C1−Ni−C10 96.9, C3−Ni−O1 86.5, C3−Ni−C10 90.3.

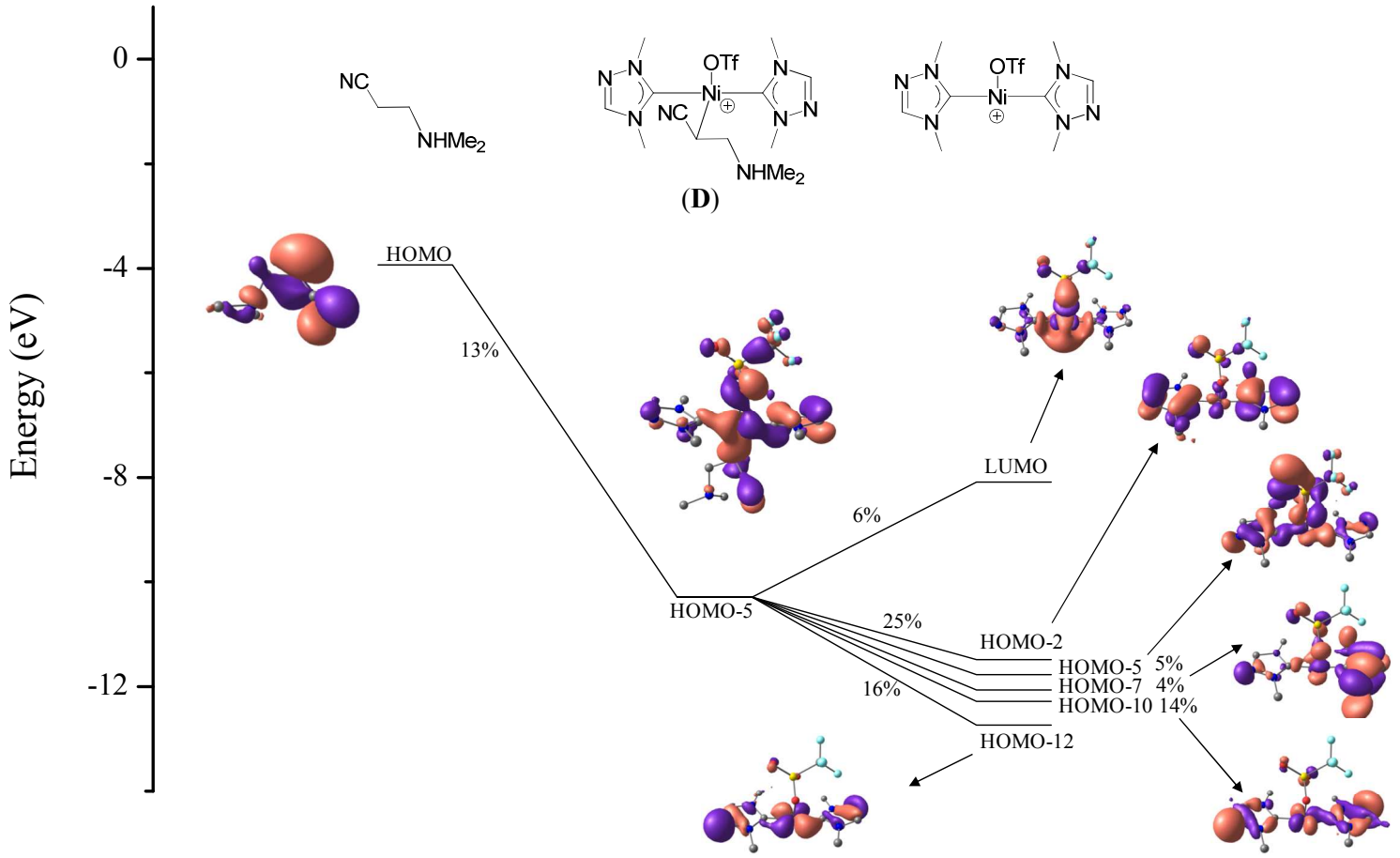


Figure S8. Simplified orbital interaction diagram showing major contribution of the $[(NHC)_2(OTf)Ni{-}CH(CN)(CH_2NHMe_2)]^+$ bond in **D**.

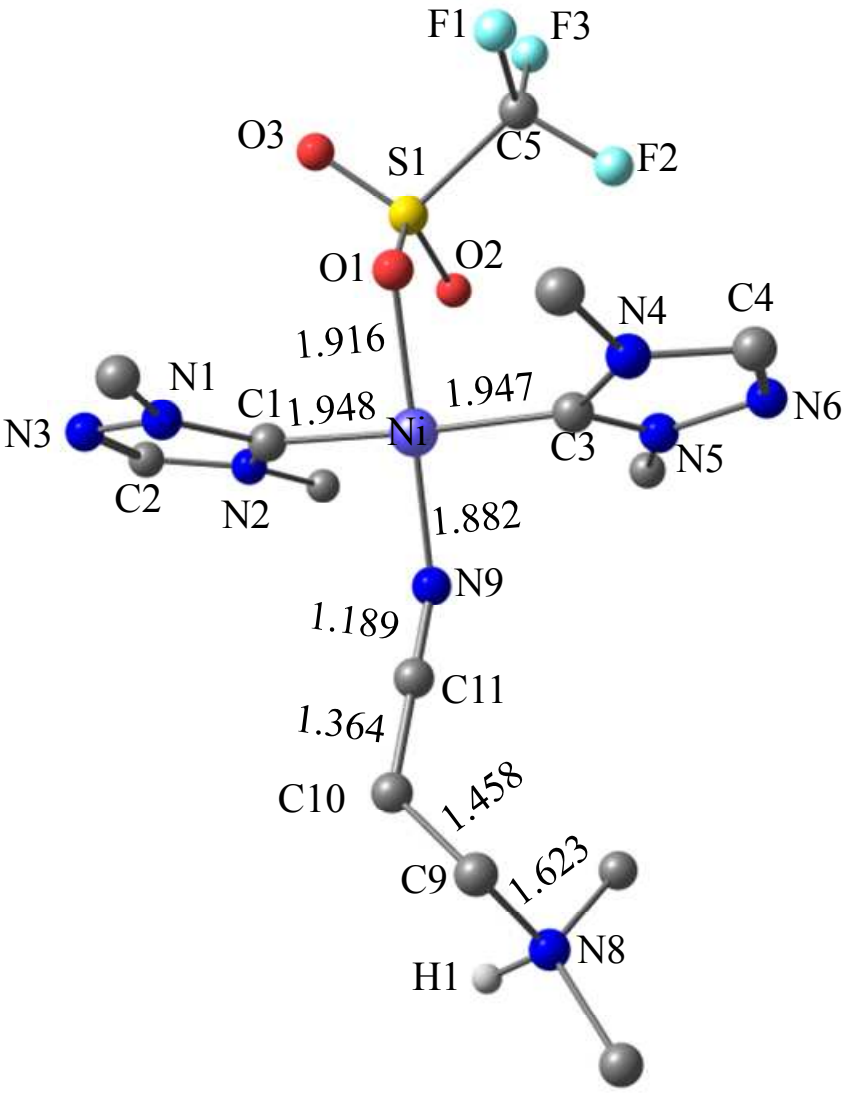


Figure S9. Computed structure of **E (**common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.4, O1−Ni−N9 177.8, C1−Ni−O1 89.3, C1−Ni−N9 90.7, C3−Ni−O1 87.8, C3−Ni−N9 92.3.

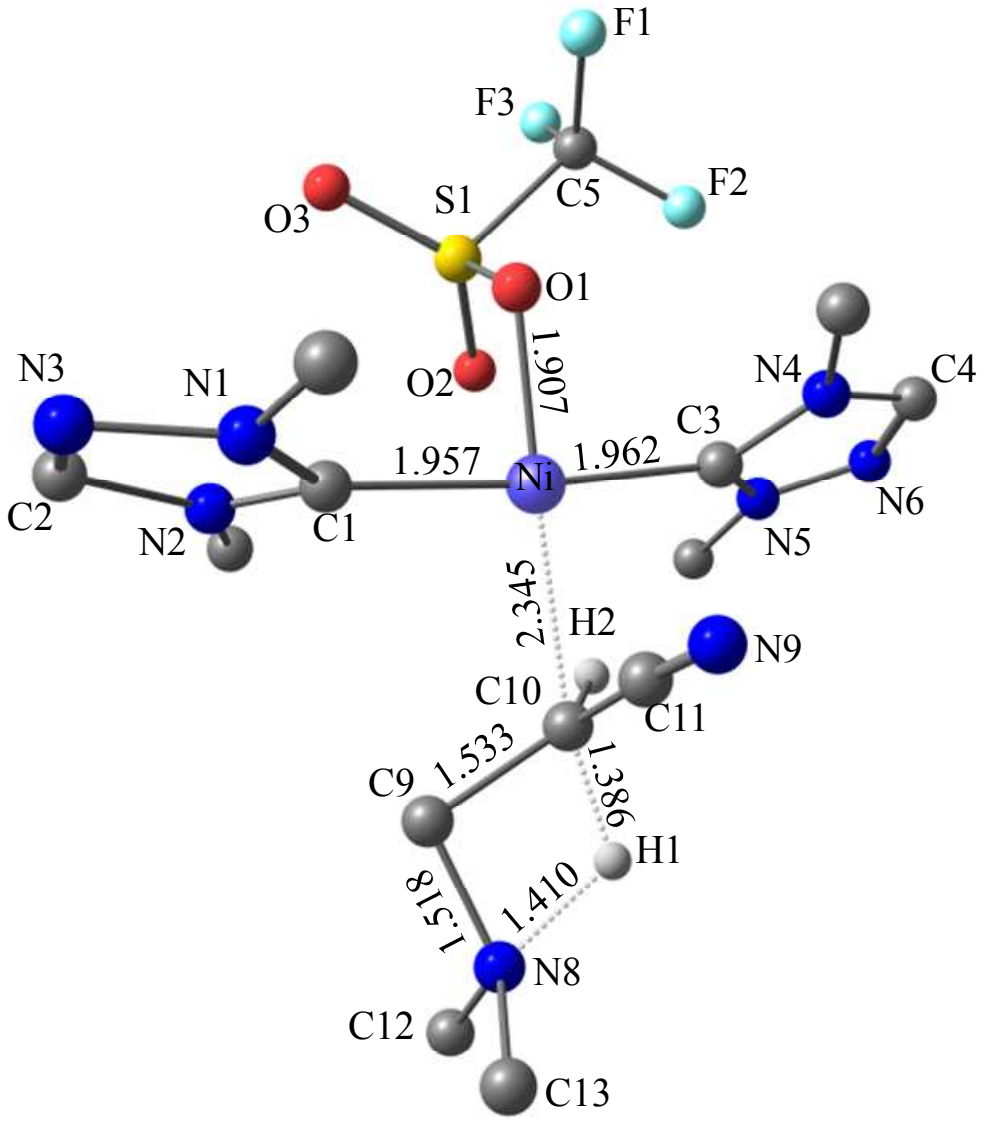


Figure S10. Computed structure of **TS3** (common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 174.7, O1−Ni−C10 172.0, C1−Ni−O1 87.5, C1−Ni−C10 92.1, C3−Ni−O1 87.3, C3−Ni−C10 93.1. Calculated imaginary frequency involving Ni•••C10, C10•••H1, H1•••N8 bonds is i1611 cm^{-1}.

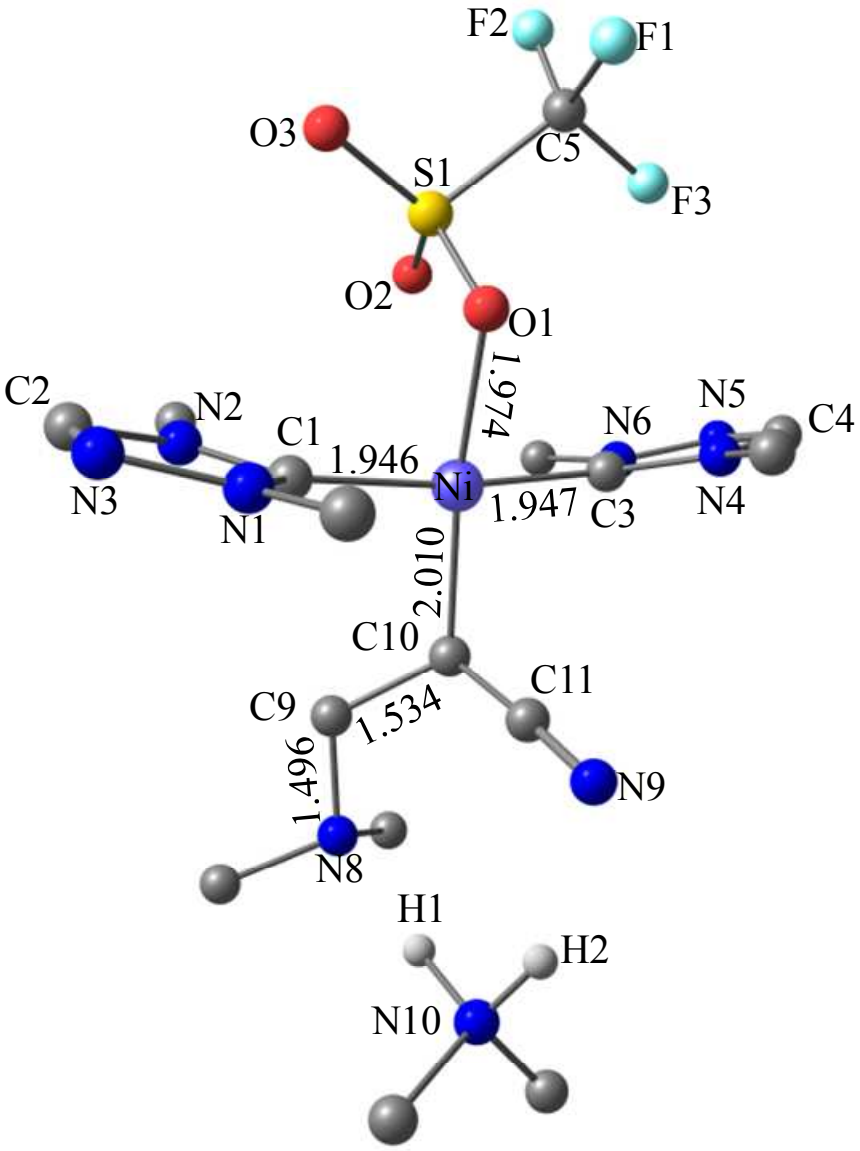


Figure S11. Computed structure of **D'** (common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 172.9, O1−Ni−C10 171.1, C1−Ni−O1 86.7, C1−Ni−C10 96.1, C3−Ni−O1 86.4, C3−Ni−C10 91.0.

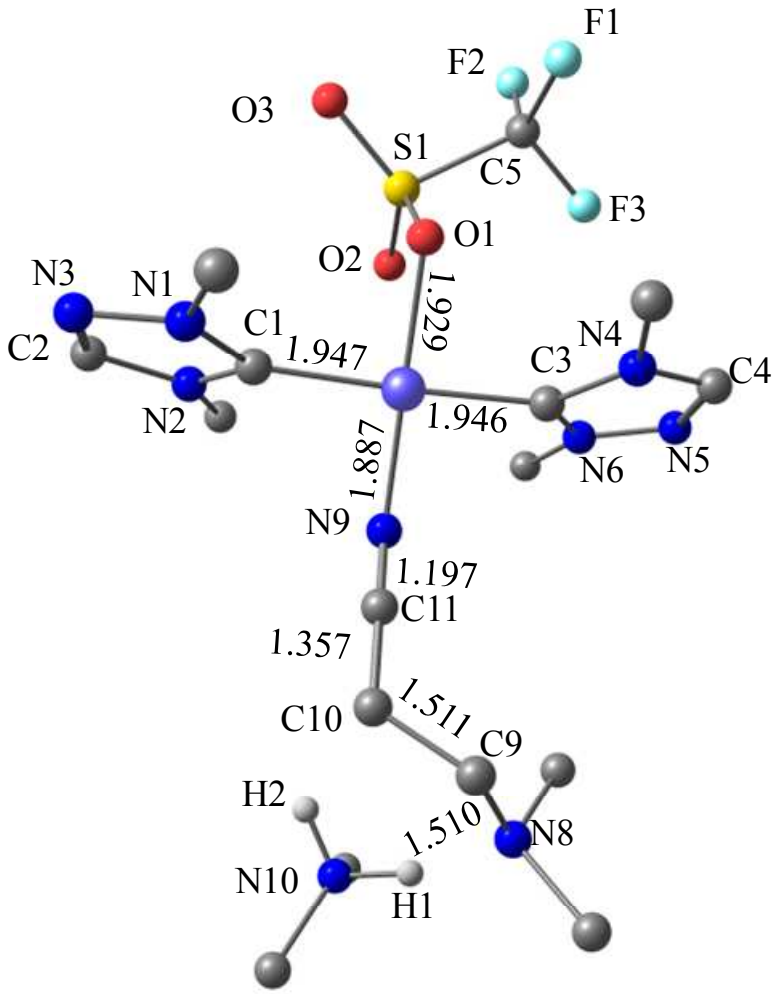


Figure S12. Computed structure of **E'** (common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.7, O1−Ni−C10 178.8, C1−Ni−O1 89.3, C1−Ni−N9 90.9, C3−Ni−O1 88.0, C3−Ni−N9 91.8.

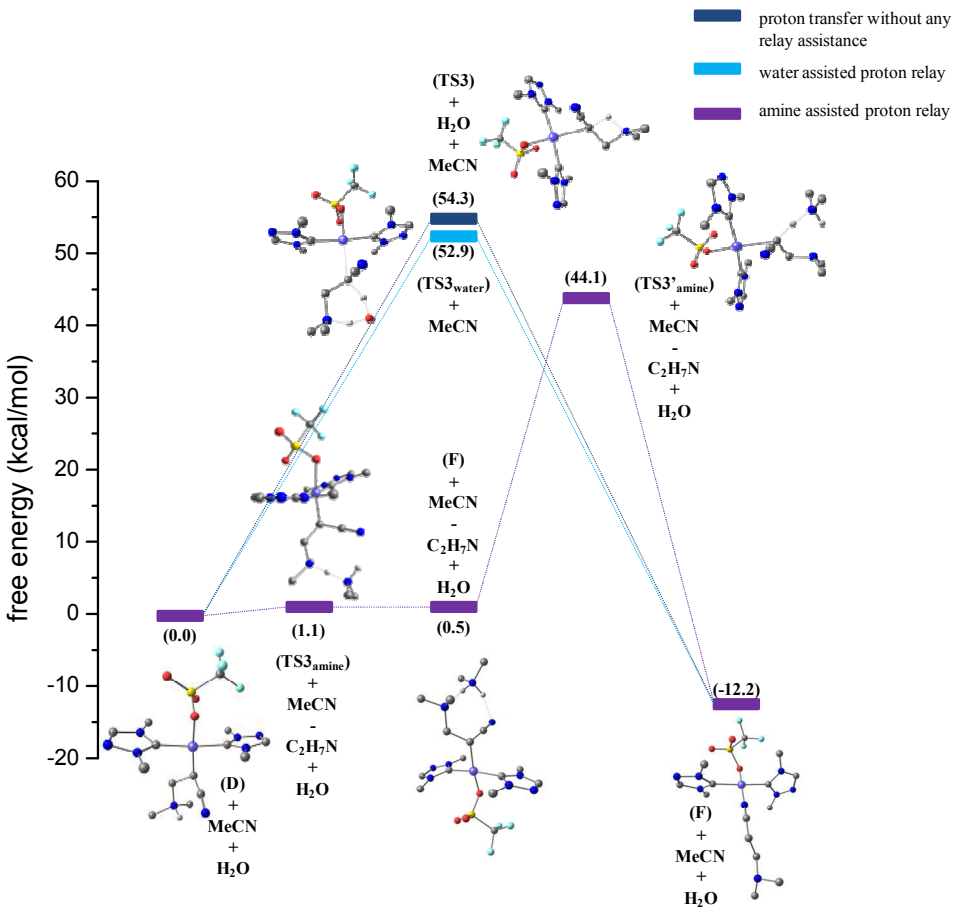


Figure S13. Overlay of the computed solvent (MeCN) phase free energies (ΔG) at the B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level of theory depicting a proton shuttle step (D→E) with amine (purple) and water (sky blue) and without any relay assistance (dark blue).

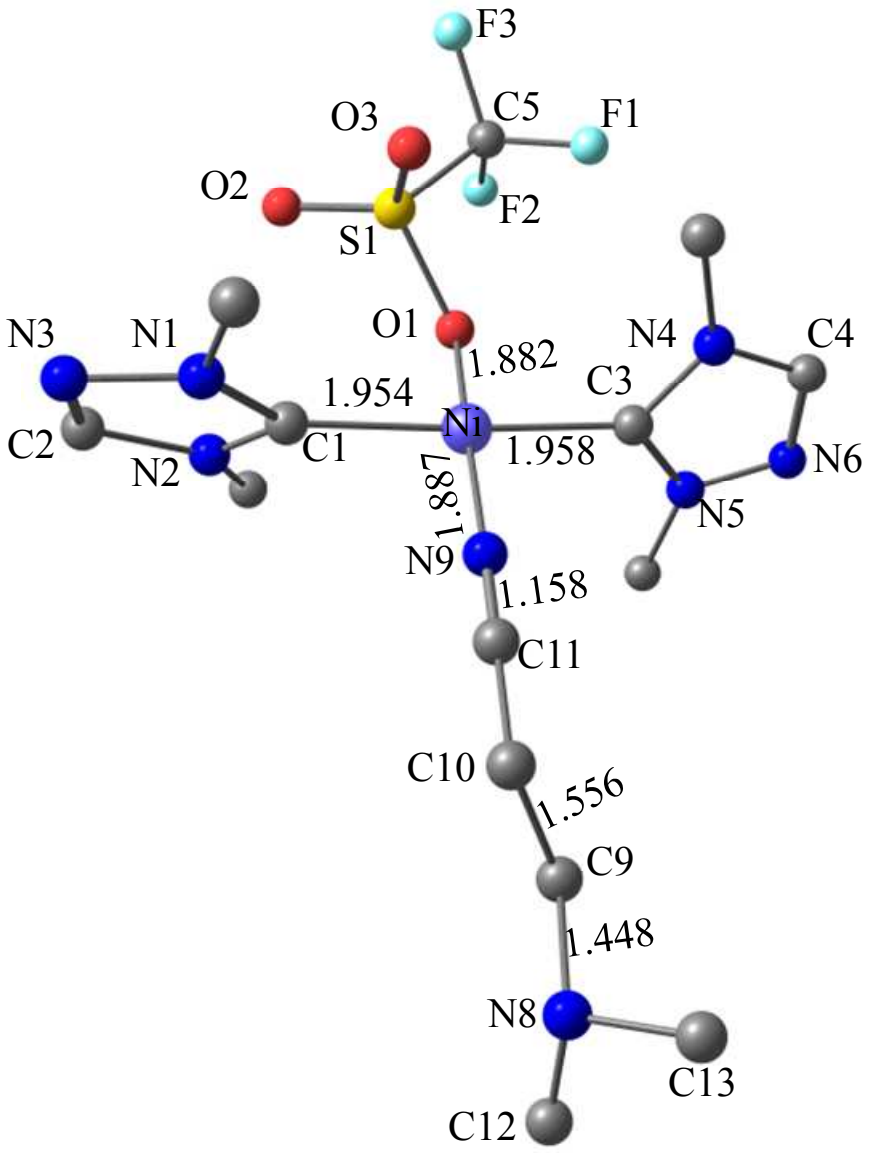


Figure S14. Computed structure of **F** (common for both alkene and amine coordination) with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.6, O1−Ni−N9 175.0, C1−Ni−O1 90.8, C1−Ni−N9 91.2, C3−Ni−O1 86.2, C3−Ni−N9 92.0.

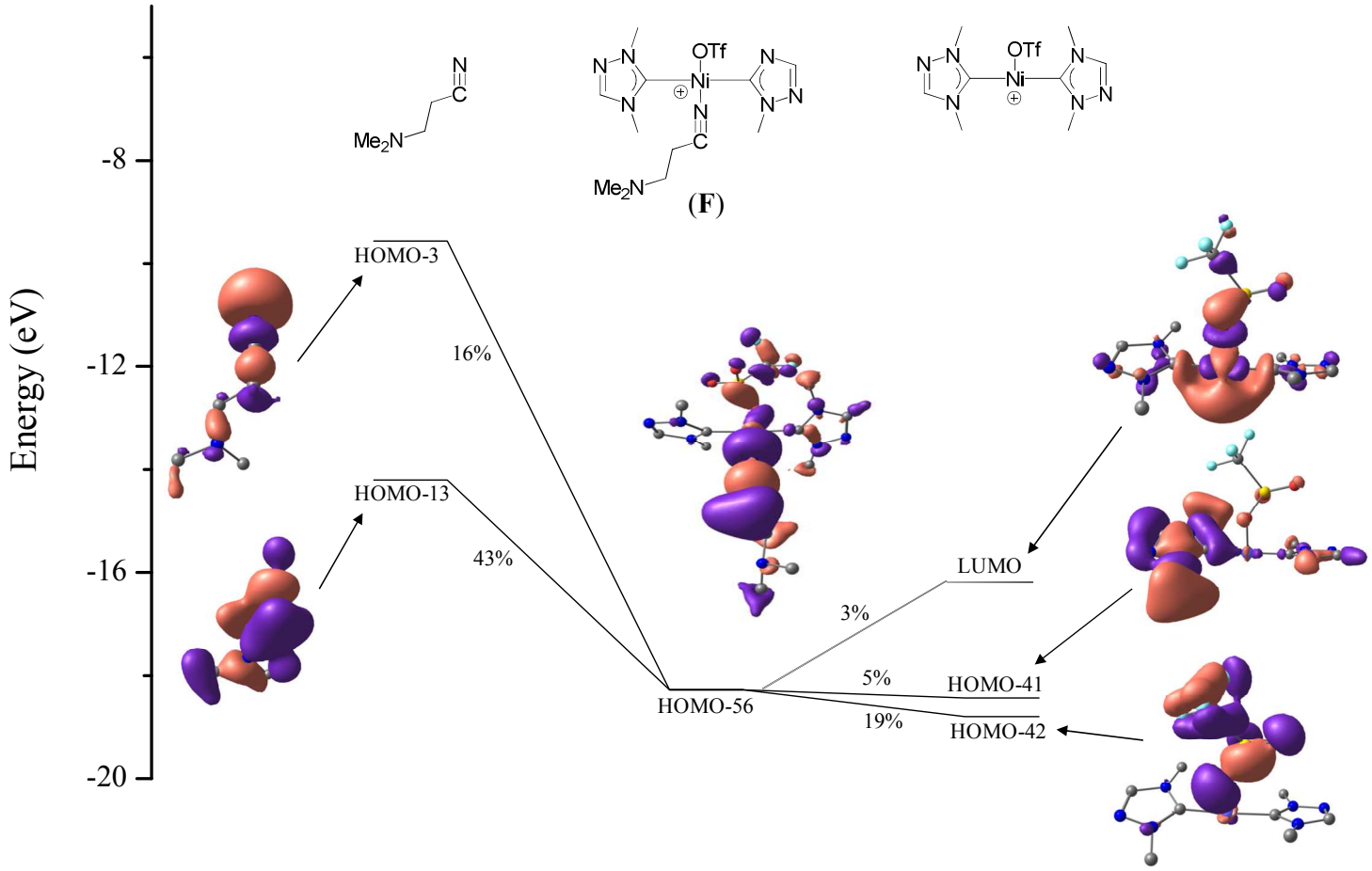


Figure S15. Simplified orbital interaction diagram showing major contribution of the $[(NHC)_2(OTf)Ni{-}NC(CH_2)_2NMe_2]^+$ bond in **F**.

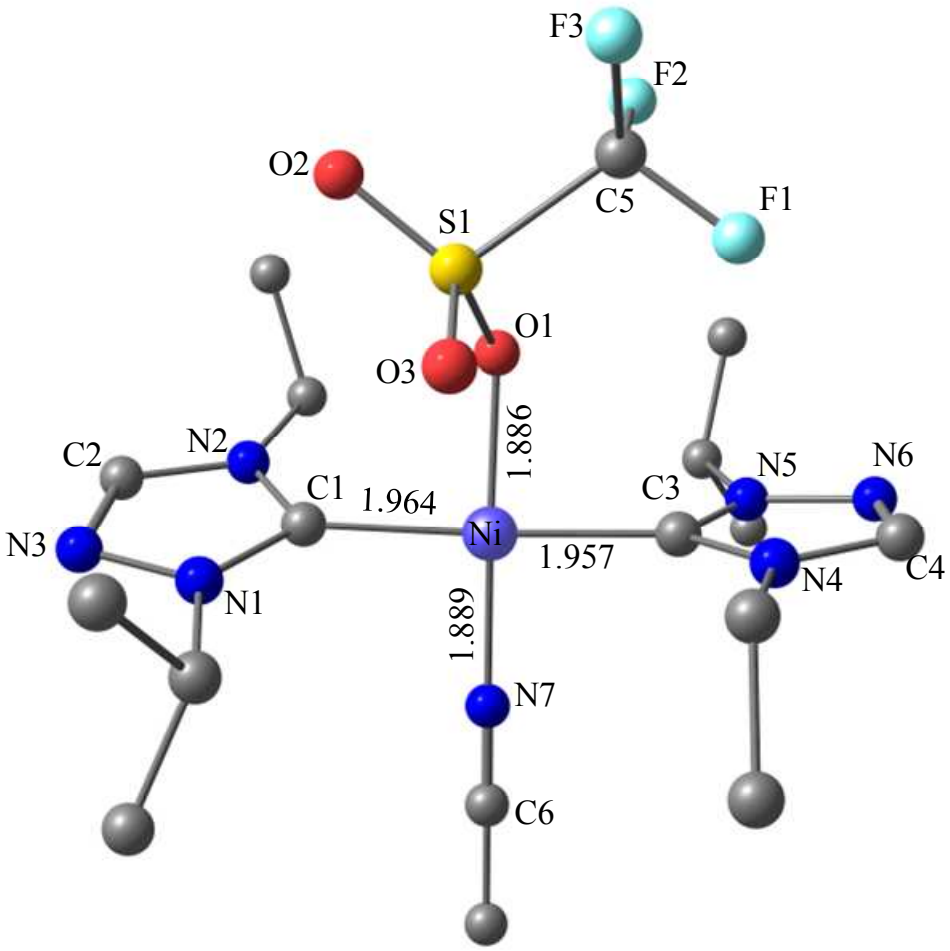


Figure S16. Computed structure of **B** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.9, O1−Ni−C10 172.5, C1−Ni−O1 89.7, C1−Ni−N7 91.3, C3−Ni−O1 87.5, C3−Ni−N7 91.7.

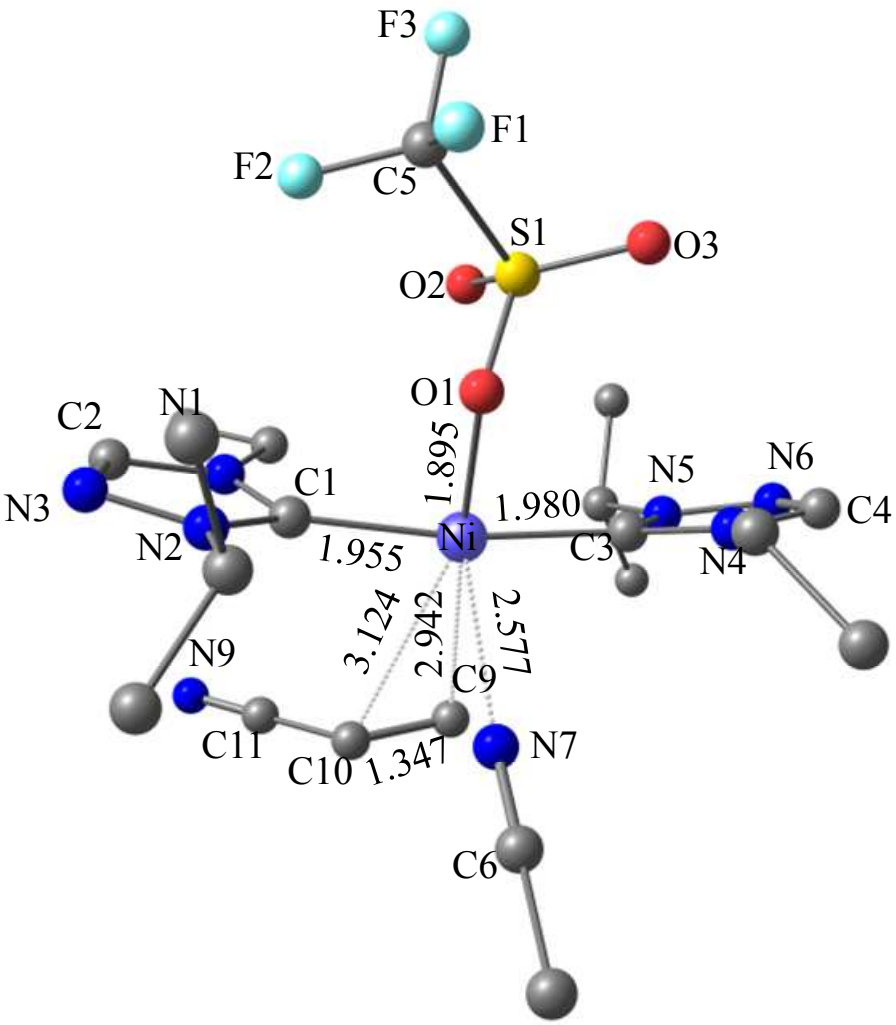


Figure S17. Computed structure of **TS1** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 171.1, O1−Ni−C9 175.0, O1−Ni−C10 159.2, C1−Ni−O1 89.9, C1−Ni−C10 110.7, C1−Ni−C9 85.9, C3−Ni−O1 86.2, C3−Ni−C10 73.8, C3−Ni−C9 97.5, C1−Ni−N7 90.8, C3−Ni−N7 99.0. Calculated imaginary frequency involving Ni•••C9•••C10, Ni•••N7, bonds is *i*77.5 cm^{-1}

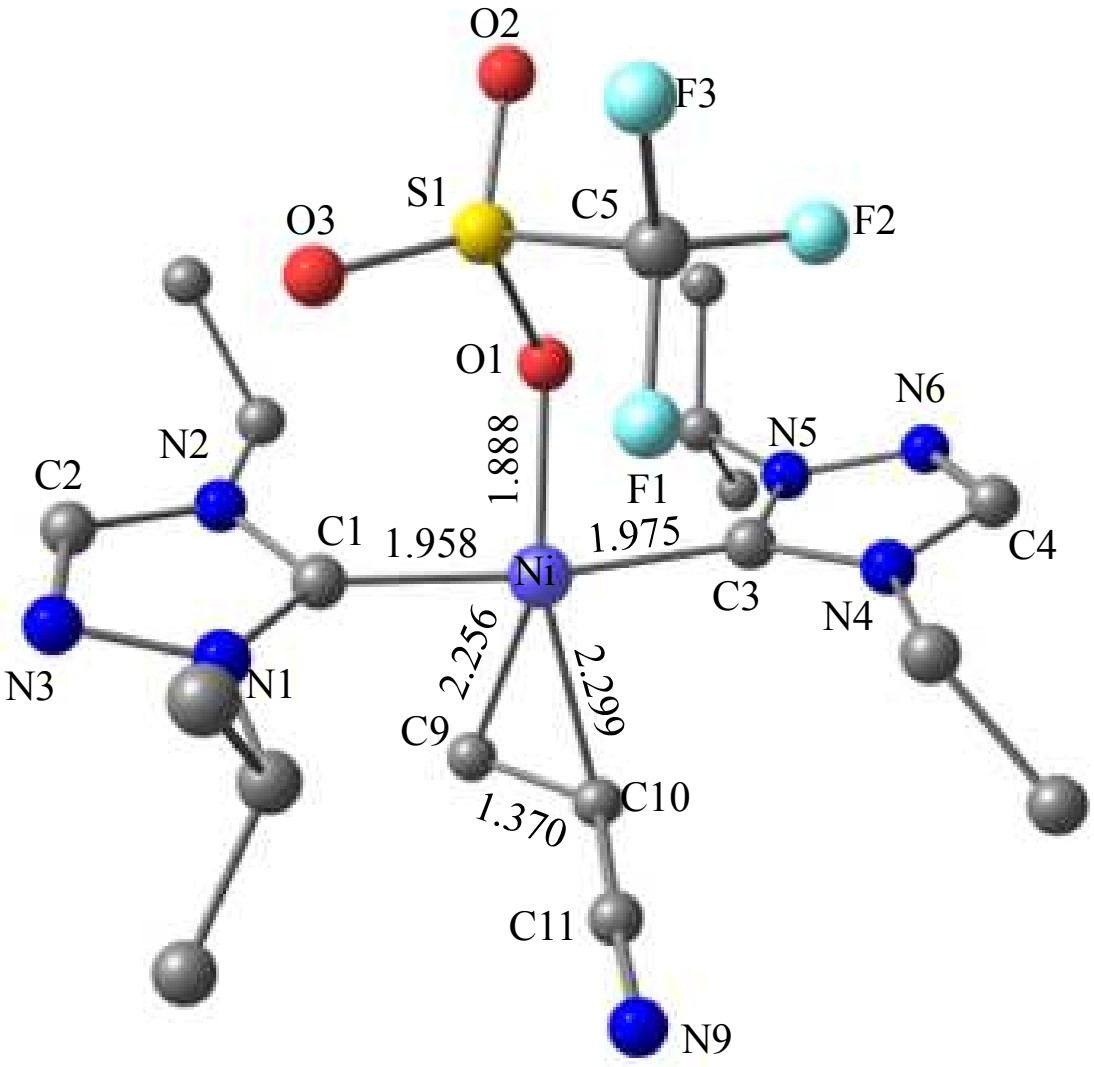


Figure S18. Computed structure of **C** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 172.2, O1−Ni−C9 151.6, O1−Ni−C10 163.5, C1−Ni−O1 90.1, C1−Ni−C10 106.0, C1−Ni−C9 79.7, C3−Ni−O1 82.2, C3−Ni−C10 81.7, C3−Ni−C9 107.8.

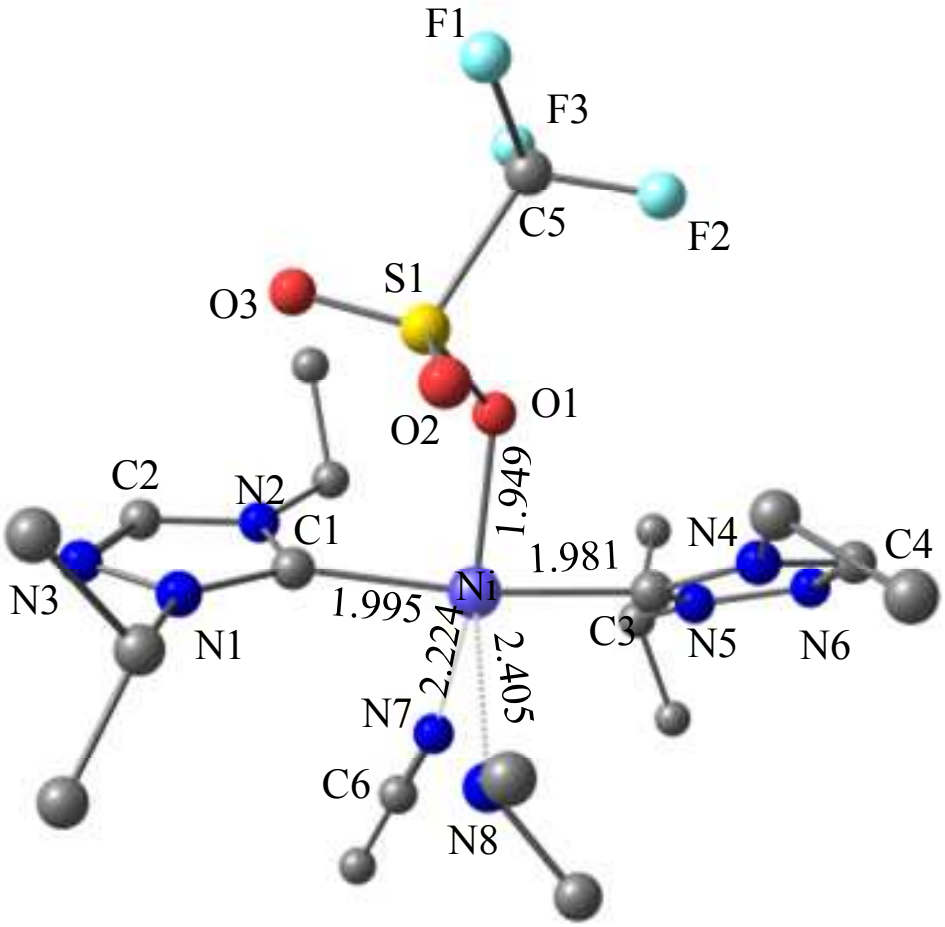


Figure S19. Computed structure of **TS1'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 167.6, O1−Ni−N7 145.9, O1−Ni−N8 134.3, C1−Ni−O1 88.9, C1−Ni−N7 82.5, C1−Ni−N8 99.6, C3−Ni−O1 84.6, C3−Ni−N7 97.1, C3−Ni−N8 92.5. Calculated imaginary frequency involving Ni•••N7, Ni•••N8, bonds is *i*113 cm^{-1}

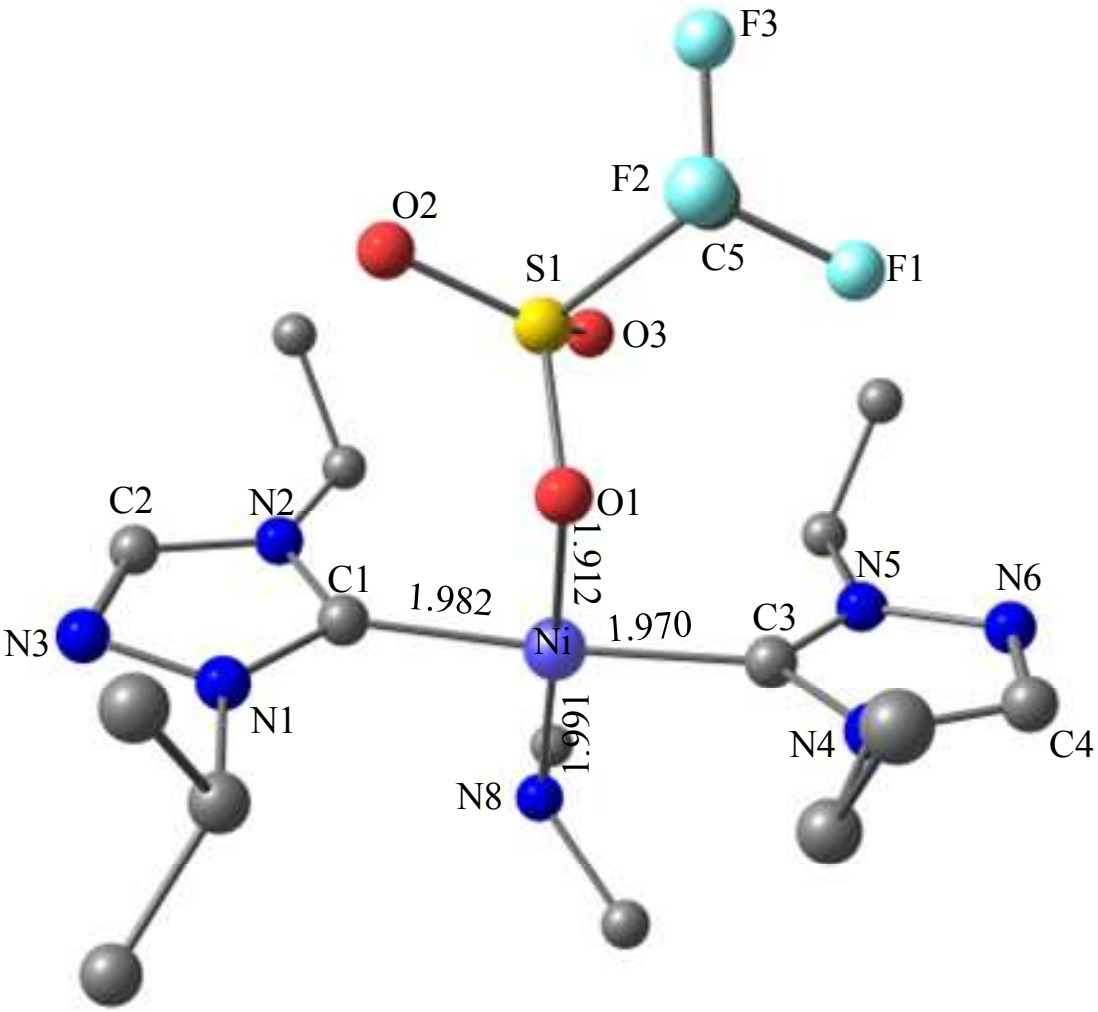


Figure S20. Computed structure of **C'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 174.3, O1−Ni−N8 171.1, C1−Ni−O1 88.7, C1−Ni−N8 90.1, C3−Ni−O1 85.7, C3−Ni−N8 95.5.

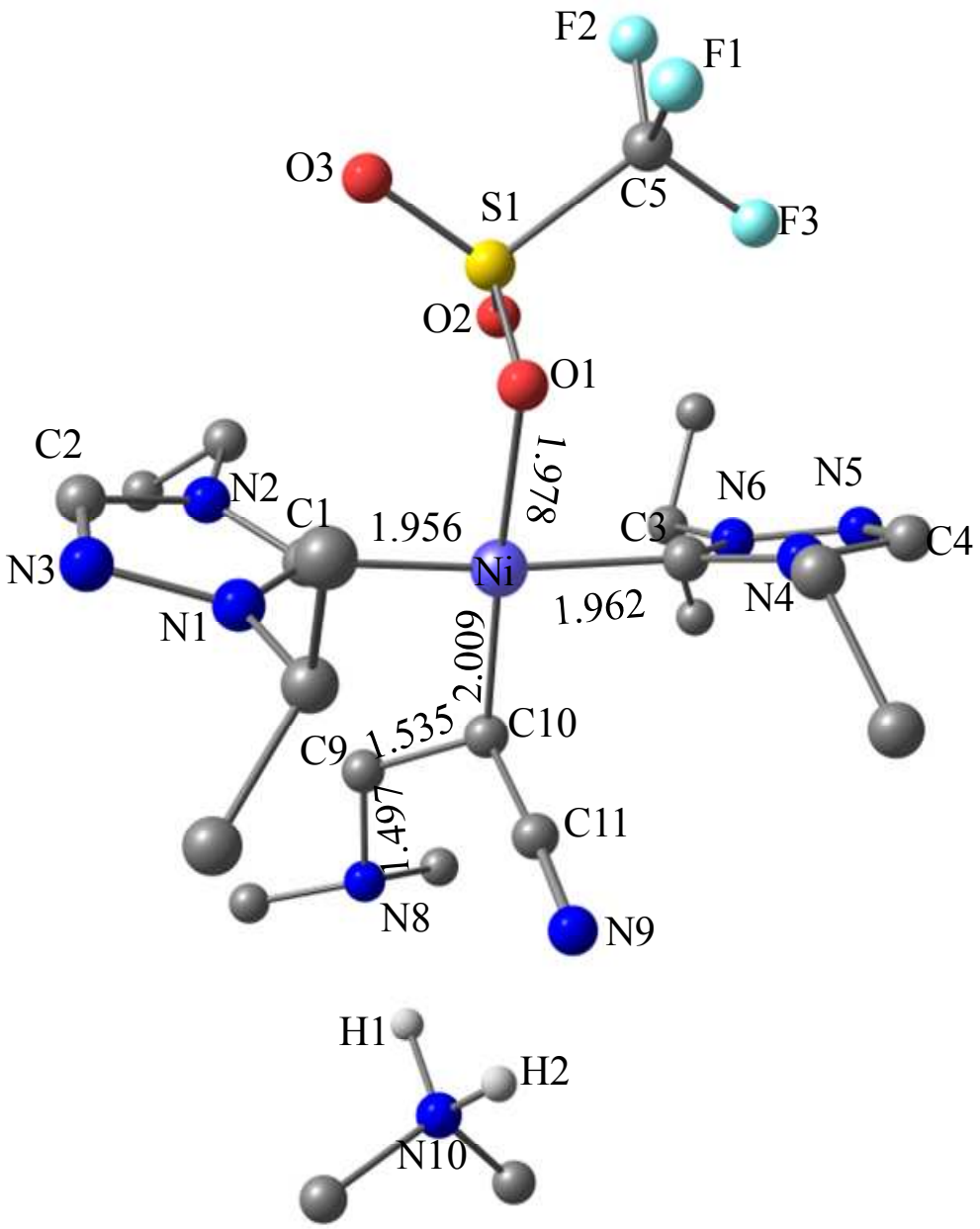


Figure S21. Computed structure of **D'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 172.6, O1−Ni−C10 175.5, C1−Ni−O1 86.3, C1−Ni−C10 95.4, C3−Ni−O1 86.8, C3−Ni−C10 91.3.

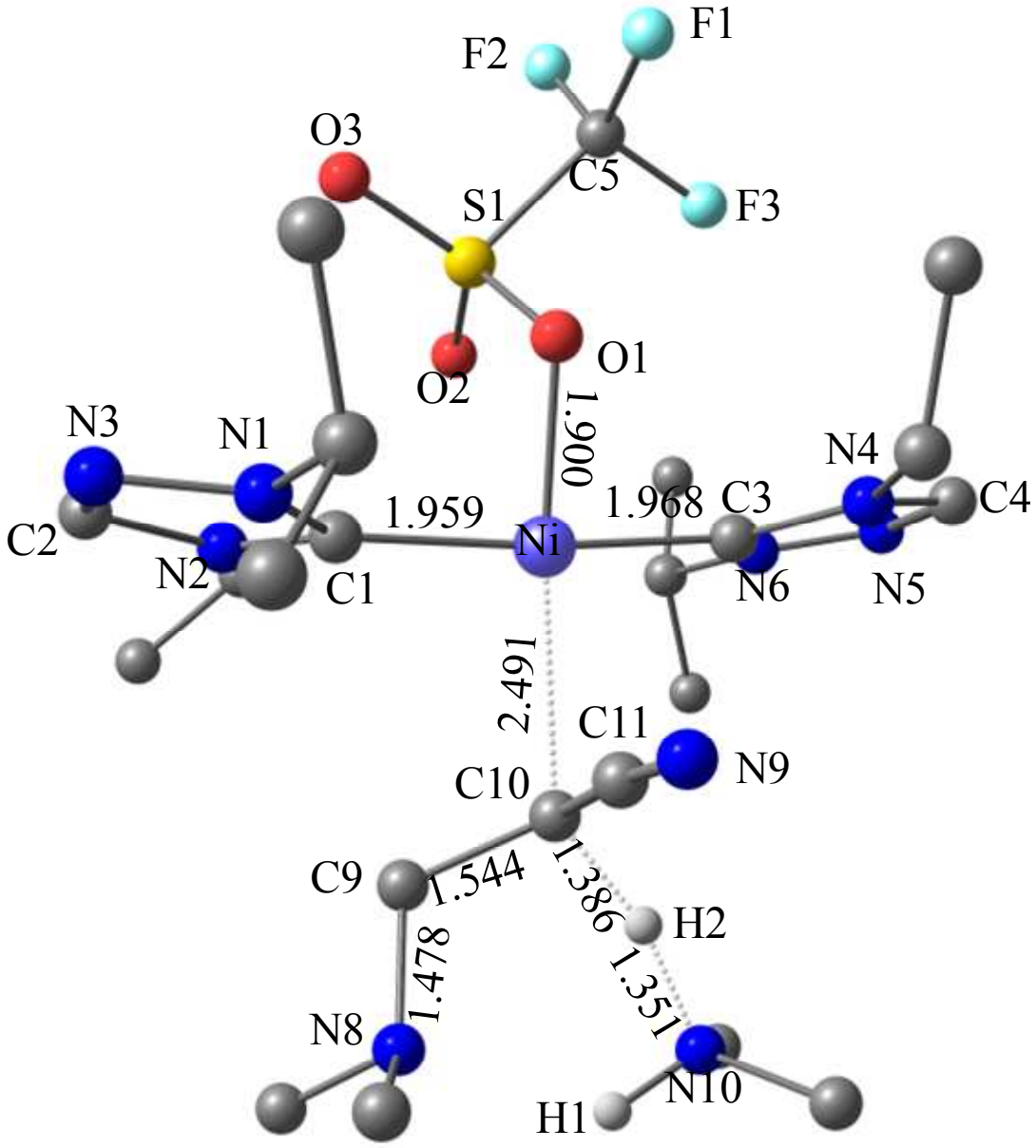


Figure S22. Computed structure of **TS3'$_{amine}$** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 174.3, O1−Ni−C10 168.9, C1−Ni−O1 89.1, C1−Ni−C10 93.0, C3−Ni−O1 86.5, C3−Ni−C10 92.0. Calculated imaginary frequency involving N10•••H2•••C10, Ni•••C10, bonds is i1177 cm^{-1}.

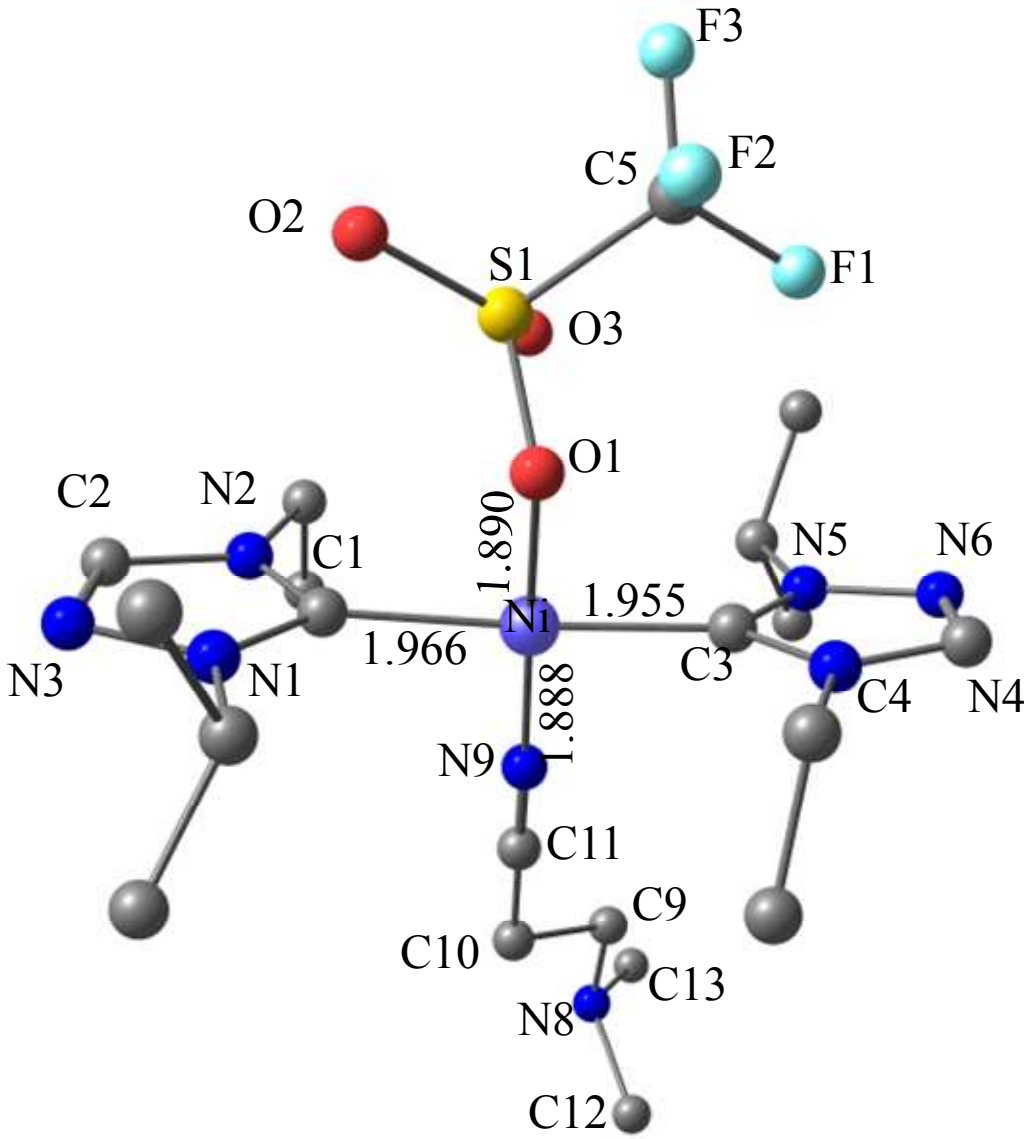


Figure S23. Computed structure of **F** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.3, O1−Ni−N9 173.2, C1−Ni−O1 89.3, C1−Ni−N9 91.4, C3−Ni−O1 87.2, C3−Ni−N9 92.2.

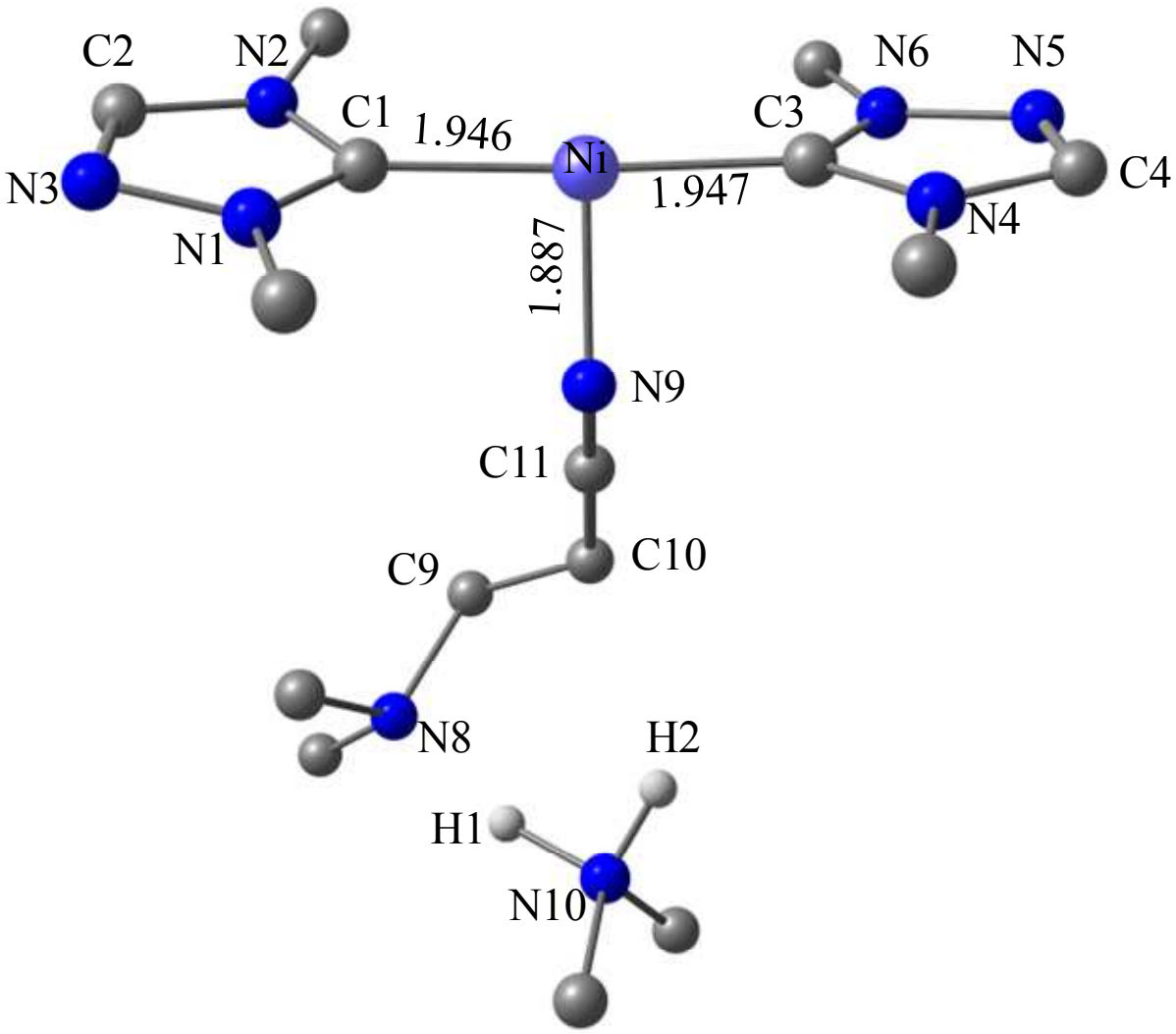


Figure S24. Computed structure of **E'** without OTf with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 176.7, C1−Ni−N9 91.8, C3−Ni−N9 90.9.

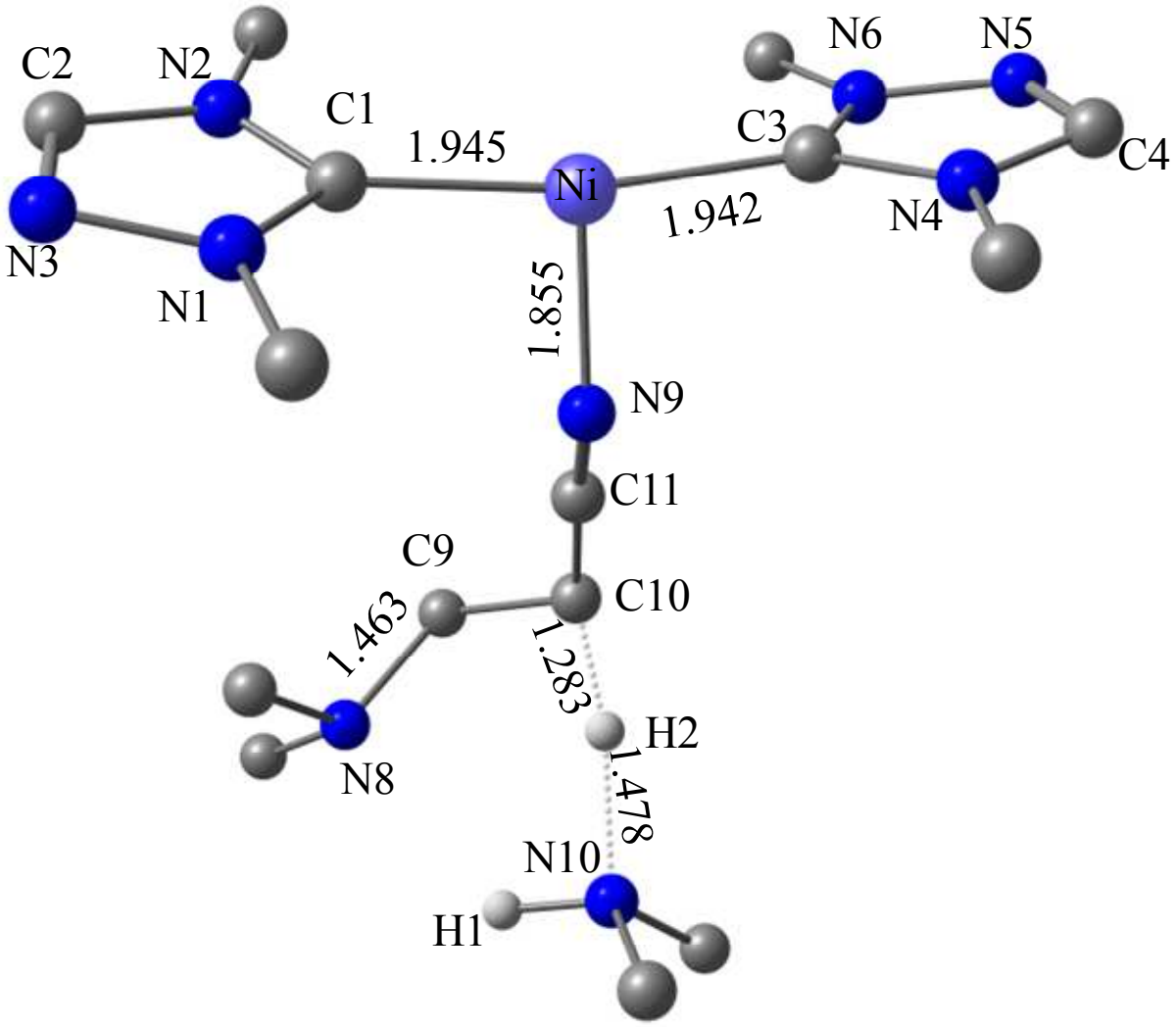


Figure S25. Computed structure of **TS3N'$_{amine}$** without OTf with selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 169.5, C1−Ni−N9 95.5, C3−Ni−C10 94.9. Calculated imaginary frequency involving N10•••H2•••C10, bond is i714 cm^{-1}.

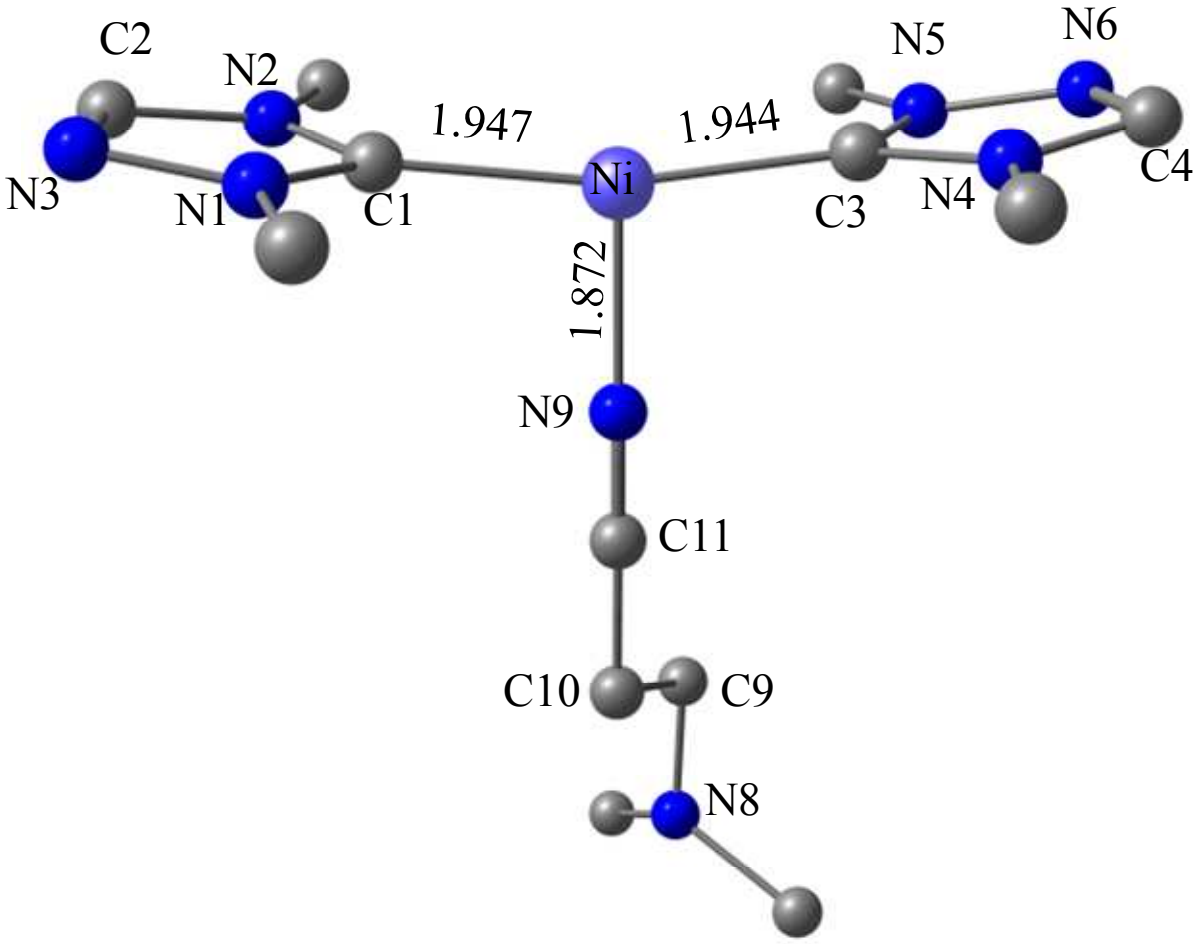


Figure S26. Computed structure of **F** without OTf selected bond lengths in Å. Some important bond angles (°); C1−Ni−C3 167.6, C1−Ni−N9 96.1, C3−Ni−O1 87.2, C3−Ni−N9 96.2.

The Density Functional Theory (DFT) computational studies on the reactant, product, transition state and the intermediate species, were carried out using GAUSSIAN 09 suite of quantum chemical programs.

Table S1. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **B**.

Ground state electronic energy (isolated gas phase) = -1905.0829475Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -1905.1588697Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3244.428533 Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3244.507654 Hartree/Particle. [B3LYP/TZVP]

Ni	-0.646308000	0.585196000	0.194797000
O	0.584382000	-0.728566000	0.757165000
N	-2.767752000	-1.236491000	-0.844068000
N	-2.477700000	-1.539165000	1.239622000
N	-3.602550000	-2.271193000	-0.515538000
N	1.612330000	2.225836000	-0.889562000
N	1.461641000	2.404361000	1.221636000
N	2.572921000	3.131431000	0.884536000
C	-2.060991000	-0.769992000	0.196422000
C	-3.404503000	-2.431832000	0.762138000
H	-3.902574000	-3.168981000	1.374749000
C	0.855584000	1.833785000	0.171778000
C	2.639255000	3.002812000	-0.409896000
H	3.401547000	3.445623000	-1.034430000
C	-2.629772000	-0.879348000	-2.254576000
H	-2.462267000	0.195064000	-2.339115000
H	-1.782954000	-1.418072000	-2.685353000
H	-3.555801000	-1.157474000	-2.757081000
C	1.399256000	1.853994000	-2.292363000
H	0.580736000	2.440806000	-2.718091000
H	2.314596000	2.064378000	-2.847942000
H	1.176773000	0.787392000	-2.352541000
C	-1.983834000	-1.470178000	2.616900000
H	-0.893806000	-1.485207000	2.602056000

H	-2.348472000	-0.562506000	3.105188000
H	-2.352099000	-2.341191000	3.160786000
C	1.123512000	2.270502000	2.633908000
H	0.166454000	1.754709000	2.713018000
H	1.898274000	1.690776000	3.140750000
H	1.056553000	3.263740000	3.081872000
S	0.953505000	-1.818798000	-0.293155000
O	0.524109000	-3.146584000	0.129270000
O	0.628574000	-1.349238000	-1.653505000
C	2.810065000	-1.748860000	-0.152125000
F	3.219972000	-0.509492000	-0.472513000
F	3.184303000	-2.024496000	1.093770000
F	3.351026000	-2.620620000	-0.994663000
C	-3.606109000	3.886426000	-0.589701000
H	-3.259658000	4.804379000	-0.104158000
H	-3.716239000	4.070668000	-1.663339000
H	-4.579232000	3.605583000	-0.174330000
C	-2.644336000	2.814584000	-0.367598000
N	-1.882359000	1.962478000	-0.190627000

Table S2. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **B0**.

Ground state electronic energy (isolated gas phase) = -1772.26276119Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3111.84942Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3111.928242Hartree/Particle. [B3LYP/TZVP]

Ni	-0.054149000	-1.158616000	0.036872000
O	0.113349000	0.501508000	-0.764340000
N	-2.794136000	-1.243402000	1.130103000
N	-2.868540000	-0.991120000	-0.982976000
N	-4.120703000	-1.203890000	0.825501000
N	2.777485000	-0.911744000	0.996621000
N	2.649187000	-2.011281000	-0.819684000
N	3.981380000	-1.955902000	-0.535537000
C	-1.995901000	-1.126438000	0.054139000
C	-4.137312000	-1.037885000	-0.470423000
H	-5.033918000	-0.948495000	-1.066341000
C	1.878213000	-1.391867000	0.091149000
C	4.030867000	-1.278332000	0.579323000

H	4.940110000	-1.032764000	1.109017000
C	-2.393466000	-1.386564000	2.529486000
H	-2.244171000	-2.440841000	2.778052000
H	-1.482609000	-0.808172000	2.692291000
H	-3.196337000	-0.978773000	3.143274000
C	2.477060000	-0.154420000	2.218714000
H	2.418359000	-0.833082000	3.073968000
H	3.274616000	0.571593000	2.386360000
H	1.533970000	0.377864000	2.092098000
C	-2.528265000	-0.693324000	-2.378901000
H	-2.331570000	0.375445000	-2.481344000
H	-1.644306000	-1.262391000	-2.667095000
H	-3.366801000	-0.987328000	-3.011980000
C	2.230877000	-2.689906000	-2.043083000
H	1.151151000	-2.577201000	-2.151234000
H	2.738225000	-2.233686000	-2.895140000
H	2.494062000	-3.748172000	-1.982340000
S	-0.536635000	1.686855000	0.048378000
O	-1.792888000	2.122089000	-0.552781000
O	-0.475939000	1.395527000	1.489894000
C	0.760800000	2.987439000	-0.304095000
F	1.931326000	2.564677000	0.186647000
F	0.864339000	3.175086000	-1.613539000
F	0.402716000	4.112872000	0.297528000

Table S3. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS0**.

Ground state electronic energy (isolated gas phase) = -1943.10352366Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3282.70508526Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3282.78848521Hartree/Particle. [B3LYP/TZVP]

Ni	-0.487319000	0.752397000	0.146936000
O	0.383087000	-0.792994000	0.770578000
N	-2.906439000	-0.627367000	-0.968775000
N	-2.777807000	-0.876552000	1.142321000
N	-3.934320000	-1.467401000	-0.641844000

N	2.079983000	1.782522000	-0.988502000
N	2.041573000	1.969459000	1.130072000
N	3.292854000	2.380024000	0.762907000
C	-2.176036000	-0.244996000	0.092527000
C	-3.829610000	-1.604559000	0.649633000
H	-4.485031000	-2.208282000	1.260294000
C	1.272952000	1.598037000	0.094182000
C	3.286474000	2.254327000	-0.534824000
H	4.120031000	2.491222000	-1.180039000
C	-2.657282000	-0.382101000	-2.392586000
H	-3.613888000	-0.463815000	-2.907804000
H	-2.242556000	0.615532000	-2.527079000
H	-1.958055000	-1.133022000	-2.766615000
C	1.756883000	1.479170000	-2.391216000
H	1.007055000	2.178816000	-2.764447000
H	2.671397000	1.577406000	-2.977823000
H	1.386862000	0.454933000	-2.458619000
C	-2.332285000	-0.862595000	2.537015000
H	-1.290131000	-1.180503000	2.583496000
H	-2.443664000	0.138565000	2.961705000
H	-2.951578000	-1.558273000	3.104787000
C	1.732623000	1.892281000	2.553731000
H	0.679676000	1.634853000	2.668238000
H	2.350401000	1.119992000	3.017326000
H	1.943906000	2.856685000	3.020011000
C	-2.375426000	2.809079000	1.286744000
C	-1.383372000	3.223974000	0.472300000
H	-3.255730000	2.300964000	0.908146000
H	-2.330004000	3.015850000	2.351665000
H	-0.536199000	3.788631000	0.851360000
S	0.495376000	-1.984689000	-0.246821000
O	-0.328541000	-3.112330000	0.171627000
O	0.405169000	-1.482823000	-1.627097000
C	2.284909000	-2.429897000	0.046480000
F	3.043400000	-1.362895000	-0.242756000
F	2.462934000	-2.767128000	1.319660000
F	2.616238000	-3.438928000	-0.747304000
C	-1.410496000	3.012677000	-0.946184000
N	-1.385909000	2.812414000	-2.093857000

Table S4. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS1**.

Ground state electronic energy (isolated gas phase) = -2075.8718081Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2075.9498658 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3415.230858 Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3415.312856 Hartree/Particle. [B3LYP/TZVP]

Ni	0.591106000	-0.047397000	0.079021000
O	-1.076321000	-0.258668000	-0.794679000
N	0.493173000	-2.696520000	1.574210000
N	0.632611000	-2.958998000	-0.530111000
N	0.450433000	-4.050774000	1.380484000
N	-0.359313000	2.751322000	0.482770000
N	0.628058000	2.565267000	-1.389832000
N	0.151852000	3.848901000	-1.365584000
C	0.613238000	-1.992671000	0.433965000
C	0.526213000	-4.178553000	0.087164000
H	0.503265000	-5.121075000	-0.440175000
C	0.342077000	1.864041000	-0.280063000
C	-0.440313000	3.933050000	-0.209090000
H	-0.933582000	4.816979000	0.168132000
C	0.312930000	-2.206996000	2.938607000
H	1.267223000	-2.196983000	3.472182000
H	-0.135814000	-1.216008000	2.897796000
H	-0.372863000	-2.888580000	3.441687000
C	-0.937926000	2.524784000	1.812107000
H	-0.215773000	2.799426000	2.584252000
H	-1.825821000	3.151804000	1.911263000
H	-1.240410000	1.481598000	1.901608000
C	0.543116000	-2.754418000	-1.977917000
H	-0.498938000	-2.580963000	-2.252827000
H	1.149669000	-1.896088000	-2.260276000
H	0.919630000	-3.648209000	-2.479391000
C	1.261637000	2.108456000	-2.620818000
H	1.701594000	1.129177000	-2.445729000
H	0.510770000	2.048806000	-3.412657000
H	2.032893000	2.826328000	-2.906956000

C	2.469367000	0.204189000	2.068728000
C	2.890868000	1.342298000	1.480486000
H	1.874064000	0.225122000	2.975053000
H	2.813327000	-0.756858000	1.703766000
H	3.527421000	1.313883000	0.601818000
S	-2.268238000	-0.850096000	0.023078000
O	-2.573081000	-2.218344000	-0.388594000
O	-2.127930000	-0.542649000	1.456618000
C	-3.623699000	0.257808000	-0.622548000
F	-3.305769000	1.531465000	-0.349103000
F	-3.746087000	0.105920000	-1.937543000
F	-4.763730000	-0.053362000	-0.018539000
C	2.575849000	2.642505000	1.985314000
N	2.314494000	3.706980000	2.374317000
C	5.185892000	-1.200372000	-2.232957000
H	5.860943000	-0.341974000	-2.307052000
H	5.673787000	-1.986162000	-1.647796000
H	4.985470000	-1.580089000	-3.239836000
C	3.936252000	-0.801002000	-1.591999000
N	2.941533000	-0.481765000	-1.085209000

Table S5. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **C**.

Ground state electronic energy (isolated gas phase) = -1943.1076033Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -1943.1969139Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3282.455333Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3282.548768Hartree/Particle. [B3LYP/TZVP]

Ni	3.432129000	0.314442000	7.466127000
O	4.953088000	-0.135203000	8.487905000
N	3.933261000	3.267482000	7.578906000
N	5.322326000	2.279471000	6.303718000
N	4.793250000	4.243584000	7.160871000
N	1.745391000	-1.793154000	8.870993000
N	3.375788000	-2.631605000	7.794101000
N	2.795561000	-3.688760000	8.440319000
C	4.224845000	2.058764000	7.082610000

C	5.629989000	3.615848000	6.387347000
H	6.461969000	4.076247000	5.874514000
C	2.771238000	-1.458621000	8.035162000
C	1.807182000	-3.149560000	9.092628000
H	1.115463000	-3.690308000	9.722613000
C	2.966164000	3.626493000	8.614122000
H	2.252944000	4.348447000	8.215017000
H	2.448305000	2.725941000	8.938559000
H	3.517487000	4.051057000	9.454161000
C	0.797555000	-0.889520000	9.530023000
H	-0.212812000	-1.295929000	9.447700000
H	1.067970000	-0.771731000	10.580713000
H	0.836010000	0.087005000	9.048864000
C	6.105232000	1.269105000	5.589489000
H	6.276126000	0.416071000	6.247798000
H	5.593569000	0.951990000	4.676225000
H	7.067708000	1.704734000	5.317281000
C	4.603116000	-2.884226000	7.041600000
H	5.440644000	-2.985720000	7.734876000
H	4.472859000	-3.804584000	6.471136000
H	4.789096000	-2.044581000	6.373021000
C	2.593895000	0.284723000	5.449739000
C	1.518579000	0.543776000	6.263947000
H	3.072848000	1.076903000	4.886642000
H	2.828575000	-0.740611000	5.180140000
H	0.906092000	-0.275183000	6.628390000
S	5.595311000	0.546427000	9.741762000
O	6.789377000	-0.199737000	10.103983000
O	5.613743000	2.005007000	9.646414000
C	4.299405000	0.163227000	11.024812000
F	3.142440000	0.785211000	10.677793000
F	4.053446000	-1.150910000	11.074034000
F	4.679239000	0.596944000	12.214055000
C	0.972193000	1.852239000	6.453839000
N	0.493718000	2.897195000	6.630606000

Table S6. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS2**.

Ground state electronic energy (isolated gas phase) = -2078.2912775Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2078.3701953Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -2078.8686883Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.687195Hartree/Particle. [B3LYP/TZVP]

Ni	-0.314068000	-0.105563000	0.263036000
O	1.470175000	0.540186000	0.580362000
N	-0.843196000	2.538900000	1.471994000
N	-1.052888000	2.695319000	-0.638830000
N	-1.008963000	3.876292000	1.228120000
N	1.158538000	-2.492387000	1.217922000
N	0.720297000	-2.677461000	-0.854383000
N	1.491526000	-3.770243000	-0.554441000
C	-0.853534000	1.786440000	0.360624000
C	-1.132170000	3.941600000	-0.065583000
H	-1.277984000	4.853292000	-0.626313000
C	0.506179000	-1.871452000	0.196340000
C	1.742291000	-3.629127000	0.716126000
H	2.325032000	-4.319073000	1.308916000
C	-0.529379000	2.124668000	2.839088000
H	-0.993499000	2.842230000	3.515401000
H	-0.932706000	1.129321000	3.022491000
H	0.554548000	2.129706000	2.978324000
C	1.277046000	-1.999348000	2.594190000
H	1.889540000	-2.702278000	3.160678000
H	1.758680000	-1.020284000	2.582049000
H	0.290041000	-1.929591000	3.055580000
C	-1.123025000	2.425612000	-2.077979000
H	-0.347385000	1.708573000	-2.350704000
H	-2.114525000	2.050780000	-2.349053000
H	-0.941266000	3.359747000	-2.611720000
C	0.347177000	-2.456025000	-2.250002000
H	1.081686000	-1.805155000	-2.727410000
H	0.313257000	-3.428105000	-2.741280000
H	-0.634857000	-1.981232000	-2.289862000
C	-2.784454000	-0.233221000	-0.390580000
C	-2.206423000	-1.167779000	0.452735000
H	-3.148474000	0.714334000	-0.022041000
H	-2.742526000	-0.371785000	-1.463597000
H	-2.008190000	-2.164261000	0.071843000
S	2.200776000	1.074551000	-0.683334000
O	1.580207000	0.516170000	-1.902438000
O	2.448231000	2.510212000	-0.613279000
C	3.837645000	0.204284000	-0.485724000
F	4.380390000	0.524838000	0.686342000

F	3.633163000	-1.122297000	-0.527990000
F	4.647690000	0.556761000	-1.475688000
C	-2.340508000	-1.075588000	1.878872000
N	-2.405286000	-1.009718000	3.039548000
N	-5.217769000	-0.741704000	-0.655938000
C	-5.394760000	-2.152852000	-1.010961000
H	-4.963424000	-2.334653000	-2.001178000
H	-4.876952000	-2.784066000	-0.282264000
H	-6.452516000	-2.453467000	-1.041532000
C	-5.894062000	0.182127000	-1.572920000
H	-5.451564000	0.092239000	-2.570878000
H	-6.971782000	-0.020885000	-1.661699000
H	-5.763352000	1.210975000	-1.224161000
H	-5.558322000	-0.588736000	0.292315000

Table S7. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **D**.

Ground state electronic energy (isolated gas phase) = -2078.3245515Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2078.4156152Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.628673Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.723146Hartree/Particle. [B3LYP/TZVP]

Ni	3.743790000	0.293486000	7.714597000
O	4.188019000	0.817148000	9.552515000
N	4.121207000	3.179889000	7.293873000
N	5.925873000	2.176634000	6.799543000
N	5.029064000	4.181403000	7.058694000
N	1.867274000	-1.352778000	9.332021000
N	3.381101000	-2.571078000	8.478439000
N	2.653790000	-3.417093000	9.276568000
C	4.629586000	1.942377000	7.162118000
C	6.120104000	3.537134000	6.761044000
H	7.063407000	4.003369000	6.516448000
C	2.940099000	-1.302707000	8.491755000
C	1.737353000	-2.642430000	9.782888000
H	0.964729000	-2.967295000	10.464432000

C	2.806465000	3.543563000	7.816648000
H	2.543887000	4.523424000	7.417095000
H	2.073180000	2.799470000	7.502757000
H	2.847465000	3.587215000	8.907975000
C	1.042703000	-0.211693000	9.736870000
H	0.324595000	-0.552133000	10.484757000
H	1.686469000	0.554630000	10.172032000
H	0.504472000	0.187216000	8.874564000
C	6.959702000	1.167794000	6.549955000
H	6.881179000	0.376484000	7.297067000
H	6.857445000	0.756575000	5.540535000
H	7.936962000	1.645122000	6.639818000
C	4.592151000	-3.092662000	7.853988000
H	5.395014000	-3.133199000	8.592294000
H	4.379227000	-4.090102000	7.466586000
H	4.890224000	-2.419248000	7.050715000
C	3.542733000	0.493506000	4.685489000
C	2.966191000	-0.174868000	5.922258000
H	3.624610000	1.573582000	4.811529000
H	4.519090000	0.087665000	4.410339000
H	3.026774000	-1.263389000	5.854665000
S	5.598995000	0.433784000	10.037685000
O	6.171542000	-0.637043000	9.192563000
O	6.428680000	1.598523000	10.336128000
C	5.182545000	-0.380911000	11.658741000
F	4.514559000	0.467351000	12.440394000
F	4.410797000	-1.457459000	11.426249000
F	6.299053000	-0.769635000	12.266407000
C	1.590113000	0.239763000	6.086514000
N	0.496137000	0.645402000	6.143301000
N	2.642328000	0.321089000	3.435637000
C	2.593509000	-1.093522000	2.937607000
H	3.591688000	-1.375750000	2.597463000
H	2.270092000	-1.746267000	3.747623000
H	1.885442000	-1.153385000	2.109491000
C	3.012546000	1.277704000	2.340659000
H	4.033088000	1.062271000	2.018859000
H	2.323467000	1.148654000	1.504239000
H	2.946975000	2.297434000	2.722877000
H	1.694948000	0.563249000	3.760908000

Table S8. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **E**.

Ground state electronic energy (isolated gas phase) = -2078.32966603Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3418.06894546Hartree/Particle. [B3LYP/TZVP]

Ni	0.043524000	0.360131000	0.166720000
N	-0.342199000	-2.399663000	-0.835516000
N	0.138590000	-2.438340000	1.230909000
N	-0.241837000	-3.731376000	-0.520845000
N	0.316603000	3.086405000	-1.009611000
N	0.589759000	3.136289000	1.094776000
N	0.766264000	4.432529000	0.685095000
C	-0.109083000	-1.580744000	0.200756000
C	0.055363000	-3.720711000	0.747678000
H	0.206514000	-4.603705000	1.351410000
C	0.310880000	2.288349000	0.094485000
C	0.600567000	4.367555000	-0.605642000
H	0.685037000	5.207275000	-1.279774000
C	-5.066307000	0.119888000	0.939935000
C	-4.111834000	1.123362000	0.485050000
H	-4.629725000	-0.848834000	1.196627000
H	-5.708064000	0.463103000	1.756461000
H	-4.368795000	2.175219000	0.568399000
C	-2.847231000	0.812331000	0.080780000
N	-1.759347000	0.568280000	-0.332257000
N	-6.162710000	-0.275754000	-0.190095000
C	-7.316640000	-1.031921000	0.382055000
H	-6.943897000	-1.969287000	0.799914000
H	-7.778128000	-0.435241000	1.171084000
H	-8.048490000	-1.243046000	-0.400344000
C	-5.528511000	-0.982027000	-1.341538000
H	-5.189646000	-1.962998000	-1.001444000
H	-6.256121000	-1.098969000	-2.147144000
H	-4.679259000	-0.385743000	-1.676653000
F	2.891281000	-2.434135000	-0.380874000
F	4.099973000	-1.557870000	1.202830000
F	4.828138000	-1.557199000	-0.851578000
C	3.750874000	-1.442101000	-0.083677000
S	2.927949000	0.204194000	-0.373328000
O	3.937768000	1.226883000	-0.127214000
O	2.299391000	0.110478000	-1.704568000
O	1.858459000	0.153682000	0.745600000
C	-0.528854000	-2.018712000	-2.233092000
H	-1.108156000	-1.096018000	-2.268985000
H	0.445462000	-1.860543000	-2.701997000
H	-1.058958000	-2.830006000	-2.732449000
C	0.556147000	-2.057895000	2.581079000
H	1.596722000	-1.728976000	2.563333000
H	-0.077225000	-1.246203000	2.942546000

H	0.445646000	-2.921603000	3.239381000
C	0.145486000	2.632239000	-2.391856000
H	-0.849486000	2.199742000	-2.514493000
H	0.255672000	3.492386000	-3.054472000
H	0.909158000	1.885925000	-2.620337000
C	0.744215000	2.817198000	2.509442000
H	1.497825000	3.487631000	2.923296000
H	-0.202640000	2.959730000	3.038409000
H	1.083004000	1.784873000	2.592541000
H	-6.498056000	0.629550000	-0.534111000

Table S9. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3**.

Ground state electronic energy (isolated gas phase) = -2078.2443569Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3417.554633Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.636685Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -2078.9001725Hartree/Particle. [B3LYP/TZVP]

Ni	-0.276332000	-0.104253000	0.179048000
O	1.428916000	0.600587000	0.663107000
N	-1.187316000	2.393132000	1.439154000
N	-1.140130000	2.675130000	-0.667956000
N	-1.477080000	3.718124000	1.251488000
N	1.157365000	-2.526548000	1.150888000
N	0.862496000	-2.644751000	-0.950977000
N	1.586999000	-3.761621000	-0.631374000
C	-0.968426000	1.723288000	0.296126000
C	-1.440050000	3.860986000	-0.041819000
H	-1.618540000	4.789090000	-0.565134000
C	0.577655000	-1.869476000	0.108042000
C	1.753908000	-3.658575000	0.657073000
H	2.294076000	-4.368627000	1.266045000
C	-1.007284000	1.915384000	2.809737000
H	-1.712350000	2.450119000	3.446667000
H	-1.205238000	0.844562000	2.849808000
H	0.015279000	2.124277000	3.134185000
C	1.202605000	-2.078717000	2.547382000

H	1.828759000	-2.773883000	3.108646000
H	1.641058000	-1.080235000	2.586504000
H	0.195590000	-2.069293000	2.967923000
C	-0.991057000	2.505137000	-2.116539000
H	-0.160669000	1.827423000	-2.317094000
H	-1.917906000	2.124153000	-2.556431000
H	-0.764705000	3.477655000	-2.556733000
C	0.529026000	-2.407432000	-2.353739000
H	1.247987000	-2.961528000	-2.956874000
H	-0.478246000	-2.774782000	-2.574978000
H	0.621299000	-1.341105000	-2.561872000
C	-3.533138000	0.003393000	-0.469856000
C	-2.429401000	-0.992748000	-0.096212000
H	-3.827493000	0.688664000	0.326972000
H	-3.293161000	0.572934000	-1.368168000
H	-1.666945000	-1.249274000	-0.843428000
S	2.235952000	1.184050000	-0.533175000
O	1.714390000	0.645799000	-1.807067000
O	2.442307000	2.622180000	-0.409163000
C	3.878041000	0.347053000	-0.246810000
F	4.343590000	0.667492000	0.957574000
F	3.709080000	-0.982145000	-0.315232000
F	4.734098000	0.731895000	-1.185020000
C	-2.222555000	-1.312720000	1.284499000
N	-2.136517000	-1.570821000	2.420648000
N	-4.625442000	-1.003830000	-0.781591000
C	-5.207972000	-0.909629000	-2.132562000
H	-5.798154000	0.008808000	-2.246902000
H	-4.408503000	-0.920422000	-2.878482000
H	-5.857614000	-1.771412000	-2.300476000
C	-5.647298000	-1.125746000	0.280137000
H	-6.283824000	-0.232668000	0.315526000
H	-6.268213000	-2.000592000	0.075698000
H	-5.155469000	-1.259247000	1.246665000
H	-3.477717000	-1.786914000	-0.536233000

Table S10. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3$_{water}$**.

Ground state electronic energy (isolated gas phase) = -2154.686674 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2154.766724 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3494.019794Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3494.103587Hartree/Particle. [B3LYP/TZVP]

Ni	-0.103693000	-0.053710000	0.161013000
O	1.608970000	0.595863000	0.668803000
N	-0.924934000	2.505068000	1.363475000
N	-0.884675000	2.722672000	-0.751749000
N	-1.180387000	3.830889000	1.137408000
N	1.243338000	-2.521818000	1.150963000
N	0.962623000	-2.625710000	-0.953809000
N	1.644071000	-3.768258000	-0.630493000
C	-0.733370000	1.796373000	0.239649000
C	-1.147916000	3.934189000	-0.160163000
H	-1.304952000	4.850765000	-0.709955000
C	0.695870000	-1.843577000	0.104804000
C	1.803473000	-3.673323000	0.659658000
H	2.311993000	-4.403667000	1.271830000
C	-0.751895000	2.060558000	2.746612000
H	-1.420192000	2.651938000	3.372837000
H	-1.005149000	1.003237000	2.822061000
H	0.284268000	2.226449000	3.051946000
C	1.298816000	-2.076350000	2.548074000
H	1.851091000	-2.822093000	3.121769000
H	1.819233000	-1.118272000	2.596798000
H	0.287669000	-1.980094000	2.946619000
C	-0.750340000	2.500149000	-2.194449000
H	-0.598880000	3.465944000	-2.679112000
H	0.117818000	1.867483000	-2.383566000
H	-1.657957000	2.040025000	-2.595865000
C	0.654796000	-2.369825000	-2.358963000
H	-0.378983000	-2.652489000	-2.581863000
H	0.833587000	-1.315711000	-2.573892000
H	1.327212000	-2.986391000	-2.954948000
C	-3.372672000	0.111762000	-0.536960000
C	-2.332721000	-0.957043000	-0.153527000
H	-3.341765000	0.996160000	0.108649000
H	-3.166440000	0.434695000	-1.560696000
H	-1.487084000	-1.086625000	-0.852822000
S	2.460815000	1.156547000	-0.509546000

O	1.948239000	0.642920000	-1.796625000
O	2.714972000	2.585340000	-0.370680000
C	4.065254000	0.259673000	-0.191392000
F	4.513367000	0.554580000	1.026042000
F	3.850732000	-1.062054000	-0.274321000
F	4.955698000	0.620660000	-1.106549000
C	-2.078319000	-1.159134000	1.244634000
N	-1.963122000	-1.334435000	2.394788000
N	-4.776881000	-0.436875000	-0.532237000
C	-5.649857000	0.298593000	-1.474103000
H	-5.713847000	1.361733000	-1.209760000
H	-5.257890000	0.202955000	-2.490399000
H	-6.652909000	-0.132919000	-1.441683000
C	-5.360606000	-0.445788000	0.834468000
H	-5.464476000	0.576475000	1.219135000
H	-6.344573000	-0.918382000	0.795719000
H	-4.722775000	-1.021909000	1.506809000
H	-4.590362000	-1.732865000	-0.853632000
O	-4.021535000	-2.760719000	-0.861013000
H	-3.006842000	-2.115487000	-0.553678000
H	-3.954082000	-3.135979000	-1.756845000

Table S11. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3N$_{water}$**.

Ground state electronic energy (isolated gas phase) = -2154.74190080Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3494.52294123Hartree/Particle. [B3LYP/TZVP]

Ni	0.279373000	0.368387000	0.363509000
N	-0.262479000	-2.373012000	-0.628626000
N	0.323713000	-2.429011000	1.410932000
N	-0.195097000	-3.707153000	-0.315752000
N	0.537207000	3.118955000	-0.793886000
N	1.062317000	3.090809000	1.263810000
N	1.248554000	4.389339000	0.869262000
C	0.055421000	-1.565777000	0.393036000
C	0.165405000	-3.707944000	0.936348000
H	0.314951000	-4.595759000	1.533392000
C	0.627801000	2.288732000	0.282168000
C	0.926024000	4.373833000	-0.392693000
H	0.967888000	5.230360000	-1.049510000

C	-5.072010000	0.346279000	0.923124000
C	-4.074215000	1.274210000	0.209235000
H	-4.642524000	-0.232136000	1.749370000
H	-5.875911000	0.962321000	1.329986000
H	-4.210373000	2.318558000	0.500634000
C	-2.706605000	0.931219000	0.254807000
N	-1.567928000	0.667812000	0.204788000
N	-5.730411000	-0.629365000	-0.034838000
C	-7.097359000	-1.002641000	0.403467000
H	-7.074031000	-1.470693000	1.393921000
H	-7.718599000	-0.105083000	0.435924000
H	-7.524925000	-1.704008000	-0.316540000
C	-4.884511000	-1.824539000	-0.264336000
H	-4.783202000	-2.407829000	0.657577000
H	-5.341490000	-2.447776000	-1.036803000
H	-3.894753000	-1.507415000	-0.601316000
H	-4.597918000	1.251885000	-1.087263000
F	2.983760000	-2.495395000	-0.542649000
F	4.492174000	-1.599741000	0.747865000
F	4.785556000	-1.632870000	-1.410759000
C	3.890521000	-1.507256000	-0.438253000
S	3.025898000	0.136049000	-0.587932000
O	4.045593000	1.172243000	-0.488445000
O	2.198316000	0.046352000	-1.807004000
O	2.128902000	0.069970000	0.680394000
C	-0.504905000	-1.987378000	-2.017242000
H	-1.111654000	-1.080958000	-2.033822000
H	0.448001000	-1.795276000	-2.515025000
H	-1.029793000	-2.810194000	-2.502284000
C	0.782713000	-2.053509000	2.749454000
H	1.712430000	-1.488664000	2.663704000
H	0.022475000	-1.450156000	3.251157000
H	0.956270000	-2.962953000	3.326950000
C	0.168128000	2.725884000	-2.156142000
H	-0.895545000	2.479354000	-2.199058000
H	0.370676000	3.564330000	-2.824498000
H	0.771414000	1.866415000	-2.453989000
C	1.367809000	2.724813000	2.642712000
H	2.205881000	3.338496000	2.973776000
H	0.502168000	2.908950000	3.285343000
H	1.650277000	1.672745000	2.664257000
H	-5.753522000	0.005209000	-1.081134000
O	-5.468433000	0.948287000	-1.913539000
H	-5.069863000	0.631709000	-2.741386000

Table S12. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **$TS3_{amine}$**.

Ground state electronic energy (isolated gas phase) = -2213.51743452Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2213.598199Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3553.22264855Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3553.30654143Hartree/Particle. [B3LYP/TZVP]

Ni	-0.198987000	-0.007215000	-0.025650000
O	-1.965342000	0.456060000	-0.767655000
N	0.508286000	2.543726000	-1.305443000
N	0.095081000	2.899809000	0.745522000
N	0.543234000	3.909107000	-1.170591000
N	-1.211615000	-2.626865000	-1.006522000
N	-1.209053000	-2.575189000	1.114568000
N	-1.793515000	-3.773476000	0.790609000
C	0.225787000	1.889904000	-0.165280000
C	0.286372000	4.093804000	0.091837000
H	0.225890000	5.059013000	0.573156000
C	-0.848244000	-1.842459000	0.048402000
C	-1.779851000	-3.773791000	-0.511720000
H	-2.158176000	-4.574231000	-1.130689000
C	0.592440000	1.978274000	-2.648587000
H	1.247945000	2.614673000	-3.244136000
H	0.997314000	0.967389000	-2.589373000
H	-0.403913000	1.952359000	-3.097458000
C	-1.083693000	-2.267814000	-2.420375000
H	-1.546477000	-3.053311000	-3.020358000
H	-1.601417000	-1.322800000	-2.593608000
H	-0.029325000	-2.178671000	-2.690278000
C	-0.248324000	2.759730000	2.163307000
H	-1.002878000	1.979907000	2.276817000
H	0.643744000	2.522424000	2.751388000
H	-0.663774000	3.706262000	2.513494000
C	-1.182855000	-2.183129000	2.519269000
H	-2.175172000	-1.844014000	2.822138000

H	-0.876280000	-3.044305000	3.115195000
H	-0.480646000	-1.358516000	2.636938000
C	2.621754000	0.408926000	1.042386000
C	1.655141000	-0.617712000	0.457597000
H	2.729956000	1.265071000	0.372268000
H	2.227020000	0.777047000	1.997137000
H	1.498567000	-1.450537000	1.145838000
S	-3.007219000	0.950176000	0.251040000
O	-2.641629000	0.537166000	1.623776000
O	-3.400692000	2.340225000	0.030160000
C	-4.457891000	-0.116844000	-0.218649000
F	-4.777884000	0.079665000	-1.498236000
F	-4.129093000	-1.409723000	-0.048023000
F	-5.500794000	0.170938000	0.554709000
C	2.102755000	-1.117056000	-0.817283000
N	2.489358000	-1.464297000	-1.865147000
N	4.033663000	-0.081618000	1.307296000
C	4.064489000	-1.255552000	2.216446000
H	3.564720000	-1.023243000	3.164221000
H	3.567817000	-2.104607000	1.744704000
H	5.103988000	-1.522170000	2.421885000
C	4.841330000	1.027327000	1.879177000
H	4.446856000	1.332051000	2.855220000
H	5.876233000	0.698341000	2.004013000
H	4.816139000	1.883709000	1.200900000
H	4.628948000	-0.419801000	0.212104000
H	4.569869000	-1.246824000	-1.463565000
N	5.289837000	-0.765795000	-0.911855000
C	5.717025000	0.434844000	-1.668813000
H	6.426381000	1.012290000	-1.069536000
H	6.198038000	0.156179000	-2.612453000
H	4.841138000	1.050417000	-1.888219000
C	6.405225000	-1.703390000	-0.642864000
H	6.897685000	-2.008594000	-1.572362000
H	7.143852000	-1.217312000	0.000897000
H	6.018685000	-2.592721000	-0.139143000

Table S13. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **$TS3_{amine}$**.

Ground state electronic energy (isolated gas phase) = -2213.50839444Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3553.29312976Hartree/Particle. [B3LYP/TZVP]

Ni	0.601896000	0.337339000	0.208090000
N	0.326989000	-2.367039000	-0.970478000
N	0.908278000	-2.516332000	1.064172000
N	0.516496000	-3.708865000	-0.754855000
N	0.661947000	3.148992000	-0.774973000
N	1.006040000	3.073640000	1.317386000
N	1.087522000	4.403873000	0.994323000
C	0.563451000	-1.606311000	0.109005000
C	0.873347000	-3.765899000	0.496878000
H	1.102048000	-4.677066000	1.030235000
C	0.744514000	2.278024000	0.269853000
C	0.881280000	4.415319000	-0.292206000
H	0.891366000	5.302242000	-0.908624000
C	-4.185377000	-0.582227000	1.505833000
C	-3.470371000	0.616525000	0.928313000
H	-3.483061000	-1.334625000	1.898169000
H	-4.800015000	-0.252571000	2.349572000
H	-3.767399000	1.601482000	1.283315000
C	-2.249571000	0.530645000	0.342442000
N	-1.220840000	0.453487000	-0.265253000
C	-6.076497000	-2.137401000	1.294982000
H	-5.561767000	-2.900296000	1.898038000
H	-6.681941000	-1.518043000	1.963438000
H	-6.740593000	-2.646968000	0.590524000
C	-4.357897000	-2.101761000	-0.408606000
H	-3.802266000	-2.907021000	0.095895000
H	-5.038241000	-2.555691000	-1.136047000
H	-3.639598000	-1.467094000	-0.934357000
F	3.570259000	-2.218847000	-0.650071000
F	4.801865000	-1.424919000	0.959298000
F	5.442302000	-1.207925000	-1.112796000
C	4.392991000	-1.213422000	-0.297877000
S	3.482033000	0.407315000	-0.408578000
O	4.452039000	1.452116000	-0.099197000
O	2.821779000	0.401353000	-1.727916000
O	2.454255000	0.203473000	0.727938000
C	0.047084000	-1.905019000	-2.327049000
H	-0.587256000	-1.020599000	-2.268722000
H	0.985221000	-1.655696000	-2.829431000
H	-0.458358000	-2.712806000	-2.856892000
C	1.371066000	-2.204708000	2.416850000
H	2.406535000	-1.861405000	2.380740000
H	0.743288000	-1.420235000	2.841650000
H	1.292517000	-3.103224000	3.031965000

C	0.480007000	2.776427000	-2.179697000
H	-0.460412000	2.233586000	-2.291384000
H	0.454600000	3.688165000	-2.779356000
H	1.313105000	2.144142000	-2.494014000
C	1.233183000	2.667313000	2.699464000
H	1.933980000	3.374218000	3.144132000
H	0.294488000	2.679566000	3.261205000
H	1.668580000	1.668321000	2.695130000
N	-5.122870000	-1.289568000	0.556029000
H	-5.633296000	-0.353621000	-0.115586000
N	-5.924685000	0.778066000	-0.811271000
H	-5.007000000	1.229036000	-0.661942000
C	-6.155052000	0.523648000	-2.258514000
C	-6.994674000	1.576532000	-0.154949000
H	-7.073482000	-0.055230000	-2.376219000
H	-6.249841000	1.470395000	-2.795740000
H	-5.311375000	-0.042528000	-2.657182000
H	-7.102473000	2.543061000	-0.652865000
H	-7.936486000	1.027287000	-0.215783000
H	-6.727914000	1.730484000	0.892495000

Table S14. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **D'**.

Ground state electronic energy (isolated gas phase) = -2213.52336850Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2213.604056Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3553.22861356Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3553.31214459Hartree/Particle. [B3LYP/TZVP]

Ni	-0.197232000	0.027844000	-0.006689000
O	-1.972843000	0.382713000	-0.793134000
N	0.403455000	2.585297000	-1.335398000
N	-0.045852000	2.952902000	0.705471000
N	0.376576000	3.952885000	-1.221518000
N	-1.103957000	-2.671422000	-0.879318000
N	-1.099218000	-2.526352000	1.237227000
N	-1.640452000	-3.758230000	0.968147000
C	0.139881000	1.936806000	-0.188067000

C	0.099214000	4.144111000	0.035727000
H	-0.007736000	5.112522000	0.502189000
C	-0.767546000	-1.828019000	0.138808000
C	-1.630309000	-3.814922000	-0.332883000
H	-1.980782000	-4.654899000	-0.914722000
C	0.527542000	2.003285000	-2.667346000
H	1.163231000	2.656957000	-3.265793000
H	0.973517000	1.011341000	-2.585804000
H	-0.460896000	1.926994000	-3.127917000
C	-1.005645000	-2.364428000	-2.307116000
H	-1.334752000	-3.237569000	-2.873383000
H	-1.649481000	-1.513049000	-2.535588000
H	0.029821000	-2.135385000	-2.566473000
C	-0.398477000	2.816580000	2.121423000
H	-1.154802000	2.037931000	2.232575000
H	0.489489000	2.577176000	2.713801000
H	-0.812723000	3.765574000	2.466299000
C	-1.084316000	-2.071844000	2.623499000
H	-2.079714000	-1.721853000	2.903071000
H	-0.780123000	-2.905787000	3.257798000
H	-0.382812000	-1.242732000	2.711643000
C	2.612011000	0.611484000	1.071323000
C	1.678104000	-0.470715000	0.515603000
H	2.671006000	1.446488000	0.367996000
H	2.179605000	1.001457000	2.006381000
H	1.554668000	-1.292329000	1.224328000
S	-3.060021000	0.860392000	0.183540000
O	-2.722627000	0.491910000	1.575439000
O	-3.499367000	2.229109000	-0.080915000
C	-4.453761000	-0.270625000	-0.307037000
F	-4.742021000	-0.109813000	-1.599793000
F	-4.081184000	-1.547154000	-0.103703000
F	-5.531160000	-0.011302000	0.428231000
C	2.170008000	-0.987402000	-0.730996000
N	2.607302000	-1.341443000	-1.758574000
N	4.018917000	0.176103000	1.333008000
C	4.079932000	-0.851498000	2.389213000
H	3.624759000	-0.500609000	3.329490000
H	3.561051000	-1.758729000	2.070240000
H	5.124734000	-1.105339000	2.593010000
C	4.814537000	1.349374000	1.743419000
H	4.430523000	1.805757000	2.669463000
H	5.853137000	1.051529000	1.919506000
H	4.794569000	2.107279000	0.954012000
H	4.889351000	-0.495316000	-0.130686000
H	4.512957000	-1.222592000	-1.558724000

N	5.340313000	-0.909817000	-1.012515000
C	6.064187000	0.152986000	-1.768473000
H	6.885681000	0.532424000	-1.157972000
H	6.456567000	-0.266124000	-2.697016000
H	5.364573000	0.958860000	-1.996236000
C	6.182541000	-2.088929000	-0.658628000
H	6.581768000	-2.535783000	-1.571153000
H	7.003778000	-1.764992000	-0.016507000
H	5.562828000	-2.817509000	-0.133455000

Table S15. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **E'**.

Ground state electronic energy (isolated gas phase) = -2213.50940711Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3553.29613762Hartree/Particle. [B3LYP/TZVP]

Ni	0.603762000	0.330955000	0.210949000
N	0.343714000	-2.370599000	-0.976599000
N	0.935076000	-2.523701000	1.054845000
N	0.543712000	-3.711862000	-0.767146000
N	0.640260000	3.147589000	-0.759212000
N	0.991493000	3.065008000	1.331693000
N	1.062762000	4.397244000	1.014504000
C	0.579571000	-1.612425000	0.104835000
C	0.906453000	-3.771265000	0.482789000
H	1.143956000	-4.682856000	1.011550000
C	0.732183000	2.272433000	0.281319000
C	0.852449000	4.413170000	-0.271317000
H	0.854463000	5.302968000	-0.883655000
C	-4.173452000	-0.627281000	1.519804000
C	-3.468126000	0.579613000	0.947484000
H	-3.464740000	-1.378531000	1.902655000
H	-4.785408000	-0.307495000	2.369276000
H	-3.770734000	1.560539000	1.308870000
C	-2.248735000	0.505127000	0.357180000
N	-1.221507000	0.437985000	-0.254189000
N	-5.111885000	-1.332902000	0.569621000
C	-6.057597000	-2.190802000	1.307154000
H	-5.536184000	-2.956028000	1.901462000
H	-6.662180000	-1.579435000	1.983700000
H	-6.723256000	-2.697918000	0.602387000
C	-4.347016000	-2.134679000	-0.403856000
H	-3.785171000	-2.940546000	0.092728000
H	-5.028173000	-2.587114000	-1.131461000

H	-3.634226000	-1.492752000	-0.928306000
F	3.589733000	-2.196768000	-0.665196000
F	4.819659000	-1.399252000	0.943688000
F	5.452599000	-1.169662000	-1.129361000
C	4.405657000	-1.186284000	-0.311554000
S	3.481786000	0.427656000	-0.413646000
O	4.444398000	1.478821000	-0.102702000
O	2.818126000	0.421638000	-1.731250000
O	2.458710000	0.211489000	0.724836000
C	0.054202000	-1.905164000	-2.329972000
H	-0.587029000	-1.026161000	-2.265200000
H	0.988085000	-1.646150000	-2.835382000
H	-0.446988000	-2.714791000	-2.861038000
C	1.401170000	-2.214212000	2.406892000
H	2.433270000	-1.861255000	2.367762000
H	0.768165000	-1.437592000	2.838328000
H	1.333698000	-3.116346000	3.018008000
C	0.456720000	2.780265000	-2.165103000
H	-0.477779000	2.227059000	-2.275455000
H	0.417967000	3.694746000	-2.759856000
H	1.295618000	2.159223000	-2.486337000
C	1.225603000	2.653918000	2.711203000
H	1.921077000	3.364949000	3.157632000
H	0.288210000	2.654961000	3.275250000
H	1.669947000	1.658916000	2.700922000
H	-5.766259000	-0.149792000	-0.267525000
N	-5.960814000	0.807071000	-0.826159000
H	-5.044289000	1.261226000	-0.679286000
C	-6.198540000	0.560926000	-2.273679000
C	-7.030422000	1.596704000	-0.158562000
H	-7.114836000	-0.021650000	-2.389726000
H	-6.301114000	1.510710000	-2.804054000
H	-5.354506000	0.001532000	-2.681055000
H	-7.145588000	2.565661000	-0.650050000
H	-7.970089000	1.043537000	-0.216980000
H	-6.757985000	1.745607000	0.888145000

Table S16. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3'$_{amine}$**.

Ground state electronic energy (isolated gas phase) = -2213.45608936Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2213.529932Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3553.15887238Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3553.23629332Hartree/Particle. [B3LYP/TZVP]

Ni	0.138007000	0.157114000	0.192697000
O	1.969582000	0.433838000	0.636322000
N	-0.044231000	2.906005000	1.224292000
N	-0.052025000	2.964464000	-0.901408000
N	-0.015164000	4.236676000	0.905193000
N	0.946220000	-2.490011000	1.303655000
N	0.585503000	-2.641021000	-0.785749000
N	1.019658000	-3.885015000	-0.410197000
C	-0.064346000	2.098140000	0.152977000
C	-0.020151000	4.241422000	-0.396911000
H	-0.000742000	5.130301000	-1.010403000
C	0.523805000	-1.765101000	0.230711000
C	1.235689000	-3.758127000	0.869152000
H	1.597502000	-4.546568000	1.512748000
C	0.082753000	2.528746000	2.631350000
H	-0.404460000	3.300251000	3.227860000
H	-0.403811000	1.567181000	2.793366000
H	1.141582000	2.469379000	2.895634000
C	1.151158000	-1.987964000	2.667548000
H	1.508874000	-2.813273000	3.285106000
H	1.899989000	-1.194195000	2.645612000
H	0.209387000	-1.609239000	3.067519000
C	-0.042961000	2.618539000	-2.325426000
H	0.294964000	3.489707000	-2.889075000
H	0.654096000	1.796401000	-2.492764000
H	-1.049073000	2.347739000	-2.657491000
C	0.324903000	-2.386103000	-2.201476000
H	-0.751942000	-2.343084000	-2.392466000
H	0.810586000	-1.452255000	-2.487780000
H	0.754557000	-3.216105000	-2.761584000
C	-3.051018000	1.009817000	-0.484337000
C	-2.275416000	-0.239507000	-0.010121000
H	-2.698877000	1.927902000	0.014187000
H	-2.840304000	1.121865000	-1.552772000
H	-1.483818000	-0.596092000	-0.698369000
S	2.899386000	0.733955000	-0.575854000

O	2.267308000	0.280936000	-1.831765000
O	3.467062000	2.075228000	-0.514789000
C	4.269927000	-0.479612000	-0.219519000
F	4.790634000	-0.234897000	0.980645000
F	3.766906000	-1.724332000	-0.234796000
F	5.206274000	-0.372197000	-1.153859000
C	-2.001518000	-0.380878000	1.393667000
N	-1.871604000	-0.520050000	2.548146000
N	-4.514485000	0.878698000	-0.341041000
C	-5.205172000	1.789609000	-1.263274000
H	-4.962743000	2.850422000	-1.075837000
H	-4.938364000	1.549920000	-2.297811000
H	-6.286335000	1.666375000	-1.152254000
C	-4.949093000	1.138012000	1.039813000
H	-4.708770000	2.165347000	1.366234000
H	-6.032200000	1.001742000	1.111372000
H	-4.469934000	0.442460000	1.733153000
H	-4.872273000	-1.259955000	-0.621988000
H	-3.146922000	-1.277015000	-0.274346000
N	-4.220278000	-2.053017000	-0.550819000
C	-4.581923000	-2.936931000	0.575102000
H	-5.538435000	-3.441047000	0.394779000
H	-3.803152000	-3.693818000	0.703623000
H	-4.652851000	-2.345076000	1.490325000
C	-4.101357000	-2.745631000	-1.845993000
H	-3.310961000	-3.499475000	-1.782731000
H	-5.037551000	-3.243788000	-2.123166000
H	-3.845157000	-2.019383000	-2.622660000

Table S17. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3N'$_{amine}$**.

Ground state electronic energy (isolated gas phase) = -2213.50742219Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3553.28676659Hartree/Particle. [B3LYP/TZVP]

Ni	0.577884000	0.339661000	0.358816000
N	0.135745000	-2.314917000	-0.874832000
N	0.791064000	-2.542614000	1.130579000
N	0.270085000	-3.668693000	-0.698419000
N	0.697673000	3.185889000	-0.548077000
N	1.201672000	3.010892000	1.506543000

N	1.323901000	4.346647000	1.225642000
C	0.451596000	-1.596835000	0.211783000
C	0.672382000	-3.774808000	0.536353000
H	0.878699000	-4.708824000	1.038255000
C	0.819926000	2.272617000	0.455333000
C	1.016956000	4.420667000	-0.038156000
H	1.021707000	5.330478000	-0.620347000
C	-4.481762000	-0.312751000	1.562283000
C	-3.762907000	0.820712000	0.804537000
H	-3.813264000	-0.822321000	2.280305000
H	-5.276822000	0.150181000	2.155072000
H	-3.958481000	1.806577000	1.234598000
C	-2.405464000	0.667101000	0.523889000
N	-1.281715000	0.535721000	0.199143000
N	-5.133245000	-1.324810000	0.690902000
C	-6.097890000	-2.119281000	1.463251000
H	-5.624075000	-2.664641000	2.297595000
H	-6.872680000	-1.465757000	1.876141000
H	-6.578174000	-2.851422000	0.807082000
C	-4.137627000	-2.206719000	0.072498000
H	-3.555665000	-2.770724000	0.823649000
H	-4.636797000	-2.927195000	-0.583043000
H	-3.434938000	-1.621561000	-0.528568000
H	-5.835144000	-0.166388000	-0.839157000
H	-4.651920000	0.926538000	-0.495588000
N	-5.552754000	0.744794000	-1.251674000
C	-5.090913000	0.585177000	-2.647060000
H	-5.914623000	0.271696000	-3.295230000
H	-4.694038000	1.538082000	-3.006380000
H	-4.300897000	-0.168623000	-2.675676000
C	-6.615415000	1.758623000	-1.069583000
H	-6.242493000	2.734226000	-1.391196000
H	-7.502020000	1.499595000	-1.655469000
H	-6.882082000	1.806583000	-0.011281000
F	3.420531000	-2.315496000	-0.728772000
F	4.867278000	-1.455710000	0.652259000
F	5.197665000	-1.317915000	-1.497127000
C	4.280798000	-1.299323000	-0.536538000
S	3.348729000	0.312508000	-0.579800000
O	4.326053000	1.378098000	-0.392753000
O	2.543364000	0.279063000	-1.816344000
O	2.445997000	0.116213000	0.666595000
C	-0.179011000	-1.803741000	-2.206275000
H	-0.841944000	-0.943378000	-2.105888000
H	0.742466000	-1.499371000	-2.707954000
H	-0.667856000	-2.604808000	-2.760473000

C	1.295561000	-2.280774000	2.479188000
H	2.268683000	-1.790764000	2.413508000
H	0.593898000	-1.641195000	3.018588000
H	1.392312000	-3.230982000	3.007120000
C	0.373794000	2.885030000	-1.944293000
H	-0.638111000	2.478713000	-2.008251000
H	0.431600000	3.810530000	-2.519745000
H	1.093500000	2.161719000	-2.333049000
C	1.509296000	2.543382000	2.853590000
H	2.308283000	3.169565000	3.251282000
H	0.626822000	2.623217000	3.494833000
H	1.848143000	1.509861000	2.788528000

Table S18. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **F**.

Ground state electronic energy (isolated gas phase) = -2078.3551706 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2078.4280766 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.666194Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.742589Hartree/Particle. [B3LYP/TZVP]

Ni	3.381548000	0.742649000	7.588816000
O	5.081519000	0.578102000	8.380266000
N	2.361664000	3.096384000	9.105972000
N	4.046884000	3.641613000	7.930868000
N	2.588323000	4.414032000	9.400032000
N	3.356563000	-2.244005000	7.767632000
N	4.140470000	-1.588747000	5.905571000
N	4.262423000	-2.953815000	5.878527000
C	3.235734000	2.588988000	8.224098000
C	3.624905000	4.717140000	8.671113000
H	4.092648000	5.690283000	8.640673000
C	3.600231000	-1.120059000	7.039482000
C	3.772960000	-3.324249000	7.027295000
H	3.701934000	-4.348130000	7.364819000
C	1.341347000	2.382080000	9.869482000
H	0.569568000	3.099622000	10.147526000
H	0.917798000	1.591577000	9.249230000

H	1.796644000	1.945002000	10.761094000
C	2.749705000	-2.307851000	9.102162000
H	3.067063000	-1.445018000	9.689109000
H	1.659477000	-2.331245000	9.018920000
H	3.092222000	-3.219018000	9.595739000
C	5.258739000	3.602040000	7.109489000
H	6.087950000	3.219194000	7.707387000
H	5.092384000	2.952897000	6.249253000
H	5.479159000	4.612146000	6.759752000
C	4.665052000	-0.826393000	4.779198000
H	5.755208000	-0.898194000	4.762471000
H	4.258577000	-1.234790000	3.852013000
H	4.364575000	0.215145000	4.895947000
C	-0.222276000	1.084810000	3.758103000
C	-0.469434000	1.166013000	5.292966000
H	0.497245000	1.864230000	3.488480000
H	0.241822000	0.109513000	3.515502000
H	-0.915736000	2.137332000	5.535304000
S	5.212664000	0.839461000	9.908282000
O	5.813827000	2.141174000	10.193007000
O	3.977998000	0.450559000	10.613299000
C	6.479373000	-0.466951000	10.309472000
F	5.984986000	-1.668328000	9.975157000
F	7.597482000	-0.244727000	9.624146000
F	6.731994000	-0.441325000	11.613024000
C	0.760051000	1.008532000	6.062252000
N	1.752497000	0.895568000	6.648300000
N	-1.460598000	1.329016000	3.047295000
C	-2.342194000	0.163650000	3.014339000
H	-1.904023000	-0.690625000	2.465686000
H	-2.586538000	-0.170084000	4.028539000
H	-3.283020000	0.437028000	2.528766000
C	-1.233970000	1.865509000	1.704435000
H	-0.715495000	1.156670000	1.033734000
H	-2.198145000	2.115819000	1.252716000
H	-0.641765000	2.784083000	1.765652000
H	-1.172222000	0.390774000	5.618617000

Table S19. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS4**.

Ground state electronic energy (isolated gas phase) = -2211.1019458Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2211.7255748Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3550.420974Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3550.496229Hartree/Particle. [B3LYP/TZVP]

Ni	0.205480000	-0.091464000	0.205378000
O	1.658131000	0.284431000	-1.018993000
N	-0.032602000	2.813989000	1.080009000
N	-0.682837000	2.482242000	-0.914809000
N	-0.391272000	4.051187000	0.609091000
N	1.670519000	-2.665626000	0.770653000
N	0.452151000	-2.813644000	-0.961269000
N	1.108192000	-4.015429000	-0.887908000
C	-0.201241000	1.829860000	0.182780000
C	-0.777437000	3.816341000	-0.611306000
H	-1.119867000	4.570427000	-1.304742000
C	0.764492000	-1.962961000	0.030864000
C	1.842842000	-3.892893000	0.178843000
H	2.511473000	-4.652844000	0.556427000
C	0.548654000	2.739999000	2.418316000
H	-0.232992000	2.559343000	3.160628000
H	1.295601000	1.948253000	2.431743000
H	1.023210000	3.701224000	2.614642000
C	2.403034000	-2.206342000	1.954380000
H	2.576725000	-1.133514000	1.876954000
H	1.840623000	-2.440201000	2.861475000
H	3.365262000	-2.721222000	1.982167000
C	-0.938150000	1.885017000	-2.225052000
H	-0.062821000	1.307339000	-2.525670000
H	-1.820859000	1.242657000	-2.183242000
H	-1.108999000	2.687277000	-2.944794000
C	-0.384945000	-2.577557000	-2.130208000
H	0.235816000	-2.617191000	-3.028247000
H	-1.153331000	-3.351936000	-2.186454000
H	-0.843251000	-1.595730000	-2.037306000
C	-5.302871000	0.007208000	-0.609445000
C	-4.473296000	-1.096807000	0.099366000
H	-5.100309000	0.958797000	-0.107450000
H	-4.955394000	0.109669000	-1.656332000
H	-4.808658000	-1.185920000	1.138928000
S	2.866850000	1.074364000	-0.454581000

O	2.953910000	2.422442000	-1.008907000
O	2.984084000	0.895265000	1.006036000
C	4.250858000	0.072412000	-1.195720000
F	4.171455000	-1.189268000	-0.738253000
F	4.151261000	0.060296000	-2.523182000
F	5.419261000	0.593710000	-0.834777000
C	-3.039705000	-0.810578000	0.087900000
N	-1.907858000	-0.561276000	0.073713000
N	-6.720841000	-0.279346000	-0.501721000
C	-7.166824000	-1.313391000	-1.433130000
H	-7.040407000	-1.020950000	-2.492412000
H	-6.621411000	-2.248606000	-1.269086000
H	-8.226218000	-1.522240000	-1.259827000
C	-7.536601000	0.929175000	-0.622900000
H	-7.460324000	1.409555000	-1.615594000
H	-8.585936000	0.671853000	-0.451583000
H	-7.238780000	1.657049000	0.138663000
H	-4.626840000	-2.072337000	-0.375356000
C	-0.824989000	-0.732020000	4.938879000
H	-1.696052000	-0.128967000	5.213591000
H	-1.051369000	-1.785970000	5.127907000
H	0.022500000	-0.433731000	5.564180000
C	-0.500202000	-0.531772000	3.529419000
N	-0.233868000	-0.365643000	2.414584000

Table S20. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **E**.

Ground state electronic energy (isolated gas phase) = -2154.766724 Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2155.3062733Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.666194Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.742589Hartree/Particle. [B3LYP/TZVP]

Ni	-0.103693000	-0.053710000	0.161013000
O	1.608970000	0.595863000	0.668803000
N	-0.924934000	2.505068000	1.363475000

N	-0.884675000	2.722672000	-0.751749000
N	-1.180387000	3.830889000	1.137408000
N	1.243338000	-2.521818000	1.150963000
N	0.962623000	-2.625710000	-0.953809000
N	1.644071000	-3.768258000	-0.630493000
C	-0.733370000	1.796373000	0.239649000
C	-1.147916000	3.934189000	-0.160163000
C	0.695870000	-1.843577000	0.104804000
C	1.803473000	-3.673323000	0.659658000
C	-0.751895000	2.060558000	2.746612000
C	1.298816000	-2.076350000	2.548074000
C	-0.750340000	2.500149000	-2.194449000
C	0.654796000	-2.369825000	-2.358963000
C	-3.372672000	0.111762000	-0.536960000
C	-2.332721000	-0.957043000	-0.153527000
S	2.460815000	1.156547000	-0.509546000
O	1.948239000	0.642920000	-1.796625000
O	2.714972000	2.585340000	-0.370680000
C	4.065254000	0.259673000	-0.191392000
F	4.513367000	0.554580000	1.026042000
F	3.850732000	-1.062054000	-0.274321000
F	4.955698000	0.620660000	-1.106549000
C	-2.078319000	-1.159134000	1.244634000
N	-1.963122000	-1.334435000	2.394788000
N	-4.776881000	-0.436875000	-0.532237000
C	-5.649857000	0.298593000	-1.474103000
C	-5.360606000	-0.445788000	0.834468000
H	-4.590362000	-1.732865000	-0.853632000
O	-4.021535000	-2.760719000	-0.861013000
H	-3.006842000	-2.115487000	-0.553678000
H	-3.954082000	-3.135979000	-1.756845000

Table S21. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS1'**.

Ground state electronic energy (isolated gas phase) = -2040.2336346Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2040.3079357Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3379.535989Hartee/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3379.613474Hartree/Particle. [B3LYP/TZVP]

Ni	0.705117000	0.074405000	0.003479000
O	-1.121625000	0.158994000	-0.682276000
N	0.491517000	-2.919165000	0.830616000
N	0.589569000	-2.542415000	-1.256875000
N	0.411718000	-4.153494000	0.237597000
N	-0.048151000	2.964816000	0.354386000
N	1.350254000	2.737128000	-1.225807000
N	1.055052000	4.076716000	-1.203644000
C	0.592671000	-1.906389000	-0.047536000
C	0.467058000	-3.888716000	-1.034647000
H	0.419753000	-4.628941000	-1.819835000
C	0.705234000	2.021305000	-0.283631000
C	0.198233000	4.181748000	-0.230979000
H	-0.273185000	5.103836000	0.077298000
C	0.296840000	-2.865141000	2.278149000
H	1.185915000	-2.471368000	2.776326000
H	-0.578067000	-2.253122000	2.501614000
H	0.128634000	-3.889284000	2.608196000
C	-1.041574000	2.763109000	1.413238000
H	-0.720242000	3.276420000	2.323259000
H	-1.999739000	3.169395000	1.085191000
H	-1.163842000	1.699754000	1.601717000
C	0.568223000	-1.901967000	-2.571901000
H	-0.188934000	-1.117156000	-2.571438000
H	1.549643000	-1.483698000	-2.809360000
H	0.309372000	-2.654417000	-3.318584000
C	2.258504000	2.282095000	-2.272101000
H	2.041781000	1.242161000	-2.507493000
H	2.088626000	2.907188000	-3.149102000
H	3.297756000	2.386438000	-1.948800000
N	1.647606000	0.352695000	2.204517000
H	2.087438000	-0.565641000	2.234146000
S	-2.216619000	-0.649536000	0.058585000
O	-2.379139000	-2.005554000	-0.468234000
O	-2.110872000	-0.473564000	1.520059000
C	-3.717869000	0.308786000	-0.494913000
F	-3.615696000	1.586924000	-0.102773000
F	-3.813346000	0.265768000	-1.822261000
F	-4.799542000	-0.233081000	0.054170000
C	5.237542000	-1.054147000	-0.967742000
H	5.526817000	-0.783589000	-1.988279000
H	5.934286000	-0.584255000	-0.266320000
H	5.301440000	-2.141259000	-0.856873000
C	3.876046000	-0.603453000	-0.696925000
N	2.796498000	-0.240743000	-0.482446000
C	2.721027000	1.356800000	2.333913000

H	3.245124000	1.284849000	3.298015000
H	3.445330000	1.235218000	1.526611000
H	2.287009000	2.357622000	2.256359000
C	0.716639000	0.442679000	3.351407000
H	-0.165472000	-0.172611000	3.174856000
H	1.196341000	0.148936000	4.295964000
H	0.387324000	1.478225000	3.456762000

Table S22. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **C'**.

Ground state electronic energy (isolated gas phase) = -1907.4971466Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -1907.5766291Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3246.788341Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3246.871632Hartree/Particle. [B3LYP/TZVP]

Ni	-1.525193000	-0.592508000	-0.032858000
O	0.269036000	-0.075435000	0.377367000
N	-1.969328000	1.998480000	1.359234000
N	-2.447159000	2.223400000	-0.697851000
N	-2.264323000	3.325304000	1.208625000
N	-0.319174000	-3.189201000	0.765251000
N	-0.382318000	-3.048335000	-1.352986000
N	0.284425000	-4.218647000	-1.092291000
C	-2.057871000	1.290893000	0.222013000
C	-2.548050000	3.434710000	-0.057339000
H	-2.829394000	4.354659000	-0.548826000
C	-0.771135000	-2.392257000	-0.247569000
C	0.312154000	-4.274706000	0.207166000
H	0.772221000	-5.066526000	0.780546000
C	-1.471333000	1.552798000	2.656784000
H	-2.090670000	1.995817000	3.437822000
H	-1.524199000	0.465309000	2.698583000
H	-0.433760000	1.873663000	2.773653000
C	-0.362793000	-2.870831000	2.193221000
H	0.174628000	-3.647335000	2.739897000
H	0.123876000	-1.908355000	2.363101000

H	-1.395312000	-2.841142000	2.548941000
C	-2.619053000	2.009043000	-2.138250000
H	-1.719426000	1.537494000	-2.537474000
H	-3.501211000	1.391819000	-2.331820000
H	-2.763270000	2.979315000	-2.615766000
C	-0.503922000	-2.630430000	-2.749340000
H	-0.613469000	-1.547215000	-2.783439000
H	0.417102000	-2.914388000	-3.258950000
H	-1.348513000	-3.135966000	-3.225128000
S	0.960370000	0.772350000	-0.725318000
O	0.308959000	0.540790000	-2.031586000
O	1.205290000	2.144824000	-0.294528000
C	2.601608000	-0.106253000	-0.803823000
F	3.197069000	-0.058007000	0.385395000
F	2.390673000	-1.388855000	-1.139514000
F	3.368613000	0.469165000	-1.721658000
N	-3.414744000	-1.152110000	-0.257026000
C	-3.914046000	-1.895103000	0.931014000
H	-3.388721000	-2.849318000	1.002248000
H	-3.728418000	-1.307298000	1.832636000
H	-4.989698000	-2.088166000	0.842612000
C	-3.736512000	-1.873242000	-1.516489000
H	-3.245120000	-2.846757000	-1.506593000
H	-4.818923000	-2.020900000	-1.608409000
H	-3.374554000	-1.297365000	-2.370223000
H	-3.925573000	-0.270316000	-0.281602000

Table S23. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS1''**.

Ground state electronic energy (isolated gas phase) = -2078.2689761Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2078.3482753Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.584263Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.667466Hartree/Particle. [B3LYP/TZVP]

Ni	0.375671000	0.245805000	0.096748000
O	-1.024781000	-0.624200000	-0.814192000

N	1.770632000	-2.269218000	0.841508000
N	1.882489000	-1.956253000	-1.257516000
N	2.417206000	-3.368720000	0.352715000
N	-1.385392000	2.162192000	1.607314000
N	-1.515644000	2.466574000	-0.491182000
N	-2.435310000	3.323776000	0.047968000
C	1.443223000	-1.375130000	-0.106817000
C	2.470599000	-3.151600000	-0.930285000
H	2.910606000	-3.825152000	-1.650944000
C	-0.850748000	1.741462000	0.422996000
C	-2.334954000	3.114661000	1.329246000
H	-2.916893000	3.623258000	2.084193000
C	1.490589000	-2.218035000	2.273504000
H	0.593429000	-1.621544000	2.436926000
H	1.313200000	-3.239388000	2.610581000
H	2.346589000	-1.801902000	2.810994000
C	-1.131333000	1.593525000	2.935051000
H	-1.767671000	2.108069000	3.656611000
H	-1.378651000	0.530805000	2.918911000
H	-0.088164000	1.737716000	3.220939000
C	1.688275000	-1.450278000	-2.615902000
H	2.454264000	-0.712076000	-2.863963000
H	1.759916000	-2.286923000	-3.312807000
H	0.691061000	-1.015078000	-2.687707000
C	-1.498633000	2.321980000	-1.943201000
H	-2.396132000	1.784163000	-2.256762000
H	-1.483344000	3.313747000	-2.397300000
H	-0.617041000	1.751559000	-2.228020000
C	2.383385000	1.661287000	1.620880000
C	3.369190000	0.871083000	2.084765000
H	2.186020000	1.759801000	0.549012000
H	1.841658000	2.308110000	2.302666000
H	3.628030000	0.847141000	3.141335000
S	-1.863619000	-1.627461000	0.052779000
O	-1.676923000	-3.003477000	-0.385855000
O	-1.736462000	-1.289888000	1.481111000
C	-3.569929000	-1.083359000	-0.474634000
F	-3.734563000	0.207574000	-0.143665000
F	-3.695608000	-1.214078000	-1.792538000
F	-4.478642000	-1.819563000	0.149171000
C	4.155984000	0.042468000	1.224320000
N	4.779702000	-0.640810000	0.518851000
N	2.213236000	2.191494000	-1.658979000
H	1.718743000	1.871367000	-2.490650000
C	1.956341000	3.632742000	-1.502653000
H	2.350343000	4.232112000	-2.337520000

H	0.882695000	3.817076000	-1.414477000
H	2.438164000	3.986312000	-0.584452000
C	3.650250000	1.933577000	-1.860846000
H	3.830251000	0.863811000	-1.991893000
H	4.062457000	2.475383000	-2.725619000
H	4.202350000	2.254049000	-0.971965000

Table S24. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **C''**.

Ground state electronic energy (isolated gas phase) = -2078.2924425Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2078.3699412Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -3417.608998Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -3417.690281Hartree/Particle. [B3LYP/TZVP]

Ni	-0.612017000	-0.265479000	0.068839000
O	1.056405000	-1.208500000	0.020099000
N	-1.958895000	-2.189167000	-1.847283000
N	-1.496515000	-3.097945000	0.019821000
N	-2.333617000	-3.499152000	-1.983555000
N	0.877776000	2.347598000	0.070977000
N	1.081866000	1.313508000	1.918882000
N	1.889545000	2.410896000	2.034946000
C	-1.443701000	-1.906559000	-0.640193000
C	-2.034860000	-4.029514000	-0.832519000
H	-2.183546000	-5.068144000	-0.575230000
C	0.444856000	1.242425000	0.740523000
C	1.748622000	3.019705000	0.892559000
H	2.257588000	3.930691000	0.612950000
C	-2.106041000	-1.310508000	-3.008054000
H	-1.320275000	-0.556352000	-2.981084000
H	-1.983081000	-1.926362000	-3.898895000
H	-3.102789000	-0.859618000	-3.019652000
C	0.542409000	2.736132000	-1.303136000
H	1.287455000	3.456560000	-1.645490000
H	0.582393000	1.854029000	-1.942769000
H	-0.446174000	3.200771000	-1.325205000

C	-0.967961000	-3.367163000	1.359764000
H	-1.511921000	-2.783310000	2.106784000
H	-1.099397000	-4.427846000	1.577730000
H	0.093690000	-3.116888000	1.380979000
C	1.046234000	0.367551000	3.032194000
H	0.722912000	-0.602005000	2.654548000
H	2.057031000	0.286486000	3.432872000
H	0.362307000	0.723134000	3.805199000
C	-2.347046000	1.069931000	-0.193902000
C	-2.596264000	0.266222000	0.893139000
H	-2.042299000	2.113640000	-0.075712000
H	-2.701464000	0.753136000	-1.170248000
H	-3.162961000	-0.654934000	0.790262000
S	1.613313000	-1.380420000	-1.425852000
O	1.629293000	-2.776125000	-1.845883000
O	1.003760000	-0.366618000	-2.312526000
C	3.377975000	-0.843784000	-1.145088000
F	3.380579000	0.431075000	-0.726246000
F	3.938862000	-1.613444000	-0.218361000
F	4.048766000	-0.935109000	-2.286104000
C	-2.376012000	0.694119000	2.243582000
N	-2.207556000	1.008334000	3.350459000
N	-2.360081000	4.340008000	0.226878000
H	-1.559648000	4.837872000	0.615751000
C	-2.824550000	5.080852000	-0.954987000
H	-3.199447000	6.089427000	-0.718437000
H	-2.009555000	5.177351000	-1.679791000
H	-3.639616000	4.526160000	-1.432913000
C	-3.395858000	4.282679000	1.269589000
H	-2.996417000	3.793971000	2.163385000
H	-3.779963000	5.274665000	1.555802000
H	-4.244292000	3.692317000	0.904693000

Table S25. B3LYP/TZVP//B3LYP/6-31G(d) level optimized coordinates of dimethylamine (**C_2H_7N**).

Ground state electronic energy (isolated gas phase) = -135.1603979Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (MeCN) = -135.1634037Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (isolated gas phase) = -135.2166524Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -135.2200935Hartree/Particle. [B3LYP,TZVP]

N	-2.307301000	0.113693000	-2.636613000
H	-3.202961000	0.587129000	-2.540236000
C	-2.536157000	-1.317584000	-2.785479000
H	-1.585844000	-1.814360000	-3.017128000
H	-2.955979000	-1.809831000	-1.886612000
H	-3.217401000	-1.496289000	-3.624287000
C	-1.470299000	0.434919000	-1.488110000
H	-1.838688000	0.029457000	-0.525588000
H	-0.463249000	0.030852000	-1.649621000
H	-1.380215000	1.522126000	-1.390441000

Table S26. B3LYP/TZVP//B3LYP/6-31G(d)level optimized coordinates of acrylonitrile(**C_3H_3N**).

Ground state electronic energy (isolated gas phase) = -170.8272052 Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (MeCN) = -170.8340707 Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (isolated gas phase) = -170.8943704Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -170.9018568Hartree/Particle. [B3LYP/TZVP]

C	-1.846523000	-0.056190000	-2.489103000
C	-1.950176000	-0.219771000	-1.164157000
H	-2.582008000	-0.987901000	-0.729402000
C	-2.552050000	-0.870824000	-3.430782000
N	-3.117435000	-1.519716000	-4.213647000
H	-1.209683000	0.716603000	-2.913080000
H	-1.398719000	0.420299000	-0.482838000

Table S27. B3LYP/TZVP//B3LYP/6-31G(d)level optimized coordinates of water (**H_2O**).

Ground state electronic energy (isolated gas phase) = -76.4070235 Hartree/Particle. [B3LYP, 6-31G(d)]

Ground state electronic energy (MeCN) = -76.414143 Hartree/Particle. [B3LYP, 6-31G(d)]

Ground state electronic energy (isolated gas phase) = -76.4605386Hartree/Particle. [B3LYP, TZVP]

Ground state electronic energy (MeCN) = -76.4682669Hartree/Particle. [B3LYP, TZVP]

O	-3.267727000	0.000000000	-1.917082000
H	-3.267727000	0.762631000	-1.319836000
H	-3.267727000	-0.762631000	-1.319836000

Table S28. B3LYP/TZVP//B3LYP/6-31G(d) level optimized coordinates of 3-(dimethylamino)propanenitrile(**$C_5H_{10}N_2$**).

Ground state electronic energy (isolated gas phase) = -306.0200684Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (MeCN) = -306.0279947Hartree/Particle. [B3LYP/6-31G(d)]

Ground state electronic energy (isolated gas phase) = -306.1343331Hartree/Particle. [B3LYP/TZVP]

Ground state electronic energy (MeCN) = -306.1433221Hartree/Particle. [B3LYP/TZVP]

C	5.351633000	-0.042002000	-0.275592000
C	4.361016000	-0.241029000	-1.444557000
H	5.153527000	0.936962000	0.172711000
H	5.153600000	-0.799331000	0.507070000
H	4.565493000	0.508447000	-2.217685000
C	2.968315000	-0.119351000	-1.007111000
N	1.871530000	-0.016990000	-0.641005000
N	6.734945000	-0.059135000	-0.736858000
C	7.202811000	-1.398917000	-1.074998000
H	7.198017000	-2.090207000	-0.209373000
H	6.584268000	-1.838624000	-1.863482000
H	8.227042000	-1.339705000	-1.457263000
C	7.628486000	0.574135000	0.227622000
H	7.674731000	0.042555000	1.197926000
H	8.642293000	0.609640000	-0.185201000
H	7.303139000	1.602511000	0.416418000
H	4.489283000	-1.225521000	-1.908354000

Table S29. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **B** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2140.98542576Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3480.73213747Hartree/Particle. [B3LYP/TZVP]

Ni	-0.256330000	0.594267000	0.310801000
O	0.451322000	-1.147791000	0.456860000
N	-3.147147000	-0.064550000	-0.060997000
N	-2.443735000	-0.808219000	1.806865000
N	-4.224666000	-0.693357000	0.502308000
N	2.104106000	1.477150000	-1.334272000
N	2.577437000	1.333160000	0.735812000
N	3.756014000	1.669957000	0.123875000
C	-2.045681000	-0.112498000	0.704489000
C	-3.765756000	-1.137231000	1.637957000
H	-4.348690000	-1.692125000	2.357982000
C	1.553772000	1.201693000	-0.118662000
C	3.435843000	1.750104000	-1.135907000
H	4.125352000	1.992757000	-1.931656000
C	-3.297653000	0.512976000	-1.417830000
H	-2.313790000	0.933643000	-1.643876000
C	1.429117000	1.433624000	-2.645194000
H	2.169155000	1.074354000	-3.365982000
H	0.651279000	0.670798000	-2.578942000
C	-1.607299000	-1.200146000	2.958952000
H	-0.620563000	-0.774345000	2.776711000
H	-2.027361000	-0.726101000	3.852566000
C	2.582029000	1.054554000	2.190614000
H	1.531282000	0.858326000	2.428034000
S	0.206695000	-2.125230000	-0.725685000
O	-0.509705000	-3.322558000	-0.298339000
O	-0.248666000	-1.392528000	-1.920203000
C	1.966765000	-2.636178000	-1.066784000
F	2.664030000	-1.564994000	-1.483477000
F	2.527616000	-3.109188000	0.047173000
F	1.986555000	-3.565990000	-2.013579000
C	-1.730194000	4.830540000	0.685167000
H	-0.899689000	5.529329000	0.543574000
H	-2.510039000	5.046001000	-0.052330000
H	-2.144300000	4.965097000	1.689688000

C	-1.262001000	3.459901000	0.524887000
N	-0.891398000	2.371612000	0.398385000
C	0.875337000	2.792905000	-3.068330000
H	0.411142000	2.706111000	-4.055902000
H	0.115215000	3.146004000	-2.363598000
H	1.665611000	3.548415000	-3.131139000
C	-3.616872000	-0.594464000	-2.425778000
H	-2.822660000	-1.345103000	-2.440072000
H	-4.567288000	-1.077100000	-2.180440000
H	-3.699871000	-0.158462000	-3.426614000
C	-4.351739000	1.623281000	-1.393822000
H	-4.424606000	2.082146000	-2.384800000
H	-5.333044000	1.218851000	-1.130046000
H	-4.096113000	2.403353000	-0.667232000
C	3.413307000	-0.200707000	2.472878000
H	3.361086000	-0.441618000	3.539480000
H	3.038205000	-1.055612000	1.902976000
H	4.462103000	-0.033333000	2.210019000
C	3.064988000	2.284750000	2.961929000
H	2.438427000	3.158841000	2.753107000
H	3.024425000	2.081341000	4.036449000
H	4.097861000	2.526901000	2.696489000
C	-1.514367000	-2.716798000	3.119149000
H	-2.489401000	-3.162286000	3.342786000
H	-1.115639000	-3.177935000	2.211714000
H	-0.847228000	-2.947583000	3.955853000

Table S30. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS1** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2311.77110906Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3651.58010816Hartree/Particle. [B3LYP/TZVP]

Ni	-0.146595000	-0.531875000	0.025548000
O	-0.034388000	1.170245000	-0.798692000
N	-3.016672000	-0.402411000	0.931844000
N	-2.882673000	-0.225255000	-1.185273000
N	-4.295777000	-0.166173000	0.511115000
N	2.357218000	-0.042764000	1.537260000
N	2.794753000	-0.339883000	-0.528085000

N	3.995413000	-0.038775000	0.053512000
C	-2.121974000	-0.447378000	-0.073138000
C	-4.181156000	-0.053718000	-0.780996000
H	-5.002985000	0.152210000	-1.450282000
C	1.775076000	-0.361725000	0.342914000
C	3.697851000	0.139171000	1.310377000
H	4.416636000	0.386276000	2.075010000
C	-2.779625000	-0.482530000	2.393499000
H	-1.704461000	-0.668295000	2.483274000
C	1.637442000	0.179306000	2.814177000
H	1.033893000	1.081434000	2.688793000
H	0.961430000	-0.668985000	2.947742000
C	-2.406830000	-0.030435000	-2.567154000
H	-2.561428000	1.023595000	-2.815686000
H	-1.333328000	-0.206010000	-2.552774000
C	2.750282000	-0.500052000	-1.999355000
H	1.699815000	-0.699391000	-2.218140000
C	-0.538770000	-3.094065000	1.416266000
C	0.783146000	-3.264803000	1.219722000
H	-0.948354000	-2.936868000	2.408301000
H	-1.233572000	-3.193644000	0.590200000
H	1.178171000	-3.468754000	0.229658000
S	-0.607969000	2.421523000	-0.066887000
O	-1.901647000	2.822583000	-0.616635000
O	-0.451674000	2.306652000	1.390468000
C	0.659536000	3.664684000	-0.639826000
F	1.865406000	3.299327000	-0.186951000
F	0.688001000	3.702399000	-1.973334000
F	0.346871000	4.861593000	-0.159264000
C	1.738823000	-3.231826000	2.283761000
N	2.534500000	-3.187926000	3.130982000
C	-0.112309000	-4.172295000	-3.673496000
H	-0.567864000	-5.111787000	-3.345148000
H	-0.683982000	-3.778202000	-4.519443000
H	0.913108000	-4.370849000	-4.000498000
C	-0.109545000	-3.206800000	-2.578028000
N	-0.103340000	-2.437912000	-1.708506000
C	2.569615000	0.288557000	4.014960000
H	1.958866000	0.412335000	4.914135000
H	3.173187000	-0.615488000	4.140799000
H	3.225502000	1.162660000	3.948600000
C	3.176803000	0.807050000	-2.675213000
H	3.085963000	0.700208000	-3.761083000
H	2.544842000	1.639792000	-2.355928000
H	4.218229000	1.043514000	-2.438970000
C	3.609691000	-1.695427000	-2.419555000

H	3.267998000	-2.620816000	-1.942393000
H	3.555434000	-1.823281000	-3.505573000
H	4.656530000	-1.534496000	-2.146961000
C	-3.116070000	0.858098000	3.053435000
H	-2.513145000	1.664783000	2.629796000
H	-4.176078000	1.093135000	2.922140000
H	-2.908985000	0.792253000	4.126633000
C	-3.575780000	-1.648053000	2.988237000
H	-3.342483000	-1.746542000	4.053080000
H	-4.649183000	-1.464212000	2.889452000
H	-3.347682000	-2.598069000	2.492808000
C	-3.109405000	-0.952394000	-3.561261000
H	-2.960641000	-2.005278000	-3.298618000
H	-4.186518000	-0.763741000	-3.612328000
H	-2.702356000	-0.779568000	-4.562805000

Table S31. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **C** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2179.00957889Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3518.77776691Hartree/Particle. [B3LYP/TZVP]

Ni	-0.089252000	0.234696000	-0.783454000
O	-0.253152000	-1.218897000	0.409398000
N	2.881671000	0.598828000	-0.598473000
N	2.370612000	-1.279263000	-1.475496000
N	4.072870000	-0.034945000	-0.815782000
N	-2.658992000	1.256450000	0.484789000
N	-2.966653000	-0.421839000	-0.793095000
N	-4.182013000	-0.189570000	-0.209145000
C	1.824260000	-0.133799000	-0.976763000
C	3.732856000	-1.174155000	-1.346676000
H	4.432333000	-1.938168000	-1.649726000
C	-2.013709000	0.430494000	-0.387325000
C	-3.965274000	0.834042000	0.565198000
H	-4.712299000	1.295339000	1.194013000
C	2.908204000	1.915930000	0.088256000
H	1.856414000	2.204613000	0.169203000
C	-2.082175000	2.365965000	1.273483000
H	-2.133796000	2.078733000	2.326976000
H	-1.027234000	2.424259000	1.005535000

C	1.645645000	-2.453218000	-2.004470000
H	0.596482000	-2.302002000	-1.748917000
H	1.743430000	-2.450461000	-3.096059000
C	-2.833457000	-1.580725000	-1.709477000
H	-1.791555000	-1.538482000	-2.045161000
C	0.279853000	1.079918000	-2.842673000
C	-0.547571000	1.973873000	-2.214921000
H	1.337508000	1.276536000	-2.959642000
H	-0.145388000	0.273046000	-3.432763000
H	-1.622864000	1.901781000	-2.334151000
S	0.524719000	-1.696669000	1.674866000
O	0.009690000	-3.005320000	2.052549000
O	1.966566000	-1.461338000	1.590338000
C	-0.093480000	-0.476739000	2.938739000
F	0.316163000	0.762884000	2.584260000
F	-1.431656000	-0.474302000	2.976121000
F	0.389586000	-0.767228000	4.135722000
C	-0.075781000	3.177057000	-1.596961000
N	0.269944000	4.153942000	-1.068844000
C	2.145136000	-3.770697000	-1.412339000
H	2.078444000	-3.762537000	-0.321156000
H	1.523294000	-4.587070000	-1.792137000
H	3.178542000	-3.985921000	-1.701253000
C	3.504626000	1.759466000	1.489869000
H	3.459633000	2.723253000	2.006737000
H	2.952809000	1.018580000	2.072269000
H	4.551273000	1.448561000	1.429257000
C	3.660802000	2.935909000	-0.769281000
H	3.214487000	3.040450000	-1.764018000
H	3.625892000	3.914642000	-0.282318000
H	4.707829000	2.642072000	-0.885288000
C	-3.067812000	-2.884314000	-0.941359000
H	-4.089200000	-2.920080000	-0.551443000
H	-2.931085000	-3.733082000	-1.619085000
H	-2.364974000	-2.983779000	-0.109648000
C	-3.771277000	-1.408087000	-2.907413000
H	-3.634629000	-2.242239000	-3.602392000
H	-4.815177000	-1.401135000	-2.581785000
H	-3.572011000	-0.475199000	-3.447290000
C	-2.786194000	3.697116000	1.021734000
H	-2.726069000	3.991424000	-0.030409000
H	-3.840193000	3.665398000	1.315572000
H	-2.300001000	4.475476000	1.617348000

Table S32. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS1'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2276.13129877Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3615.92461777Hartree/Particle. [B3LYP/TZVP]

Ni	0.289925000	-0.480186000	0.160052000
O	-0.204857000	1.194965000	-0.704231000
N	-2.613424000	-1.641073000	0.198373000
N	-1.677446000	-1.529937000	-1.708265000
N	-3.518438000	-2.177454000	-0.679931000
N	2.486357000	1.415475000	1.022808000
N	3.184463000	0.059267000	-0.459849000
N	4.239536000	0.900813000	-0.218909000
C	-1.472749000	-1.237097000	-0.386580000
C	-2.922514000	-2.088101000	-1.832600000
H	-3.351137000	-2.413196000	-2.769021000
C	2.092202000	0.334087000	0.282264000
C	3.781131000	1.716546000	0.683784000
H	4.345163000	2.531565000	1.111793000
C	-3.055137000	-1.470863000	1.600661000
H	-2.254687000	-0.901148000	2.068499000
C	1.657072000	2.254119000	1.910990000
H	1.472737000	3.196934000	1.390660000
H	0.693108000	1.761082000	2.007716000
C	-0.789116000	-1.205033000	-2.839144000
H	0.104335000	-0.753214000	-2.408951000
H	-0.499758000	-2.145141000	-3.322814000
C	3.360041000	-0.929737000	-1.546317000
H	2.399842000	-1.439963000	-1.614455000
N	0.361006000	-1.233984000	2.442811000
H	-0.307192000	-1.992630000	2.316348000
S	-1.505821000	1.890914000	-0.237399000
O	-2.691164000	1.457895000	-0.984397000
O	-1.594016000	1.947892000	1.231777000
C	-1.140741000	3.616992000	-0.842612000
F	-0.019931000	4.084371000	-0.273260000
F	-0.980587000	3.601243000	-2.165951000
F	-2.156795000	4.411306000	-0.521181000
C	1.275332000	-5.147153000	-0.552159000

H	1.807673000	-5.596290000	0.292277000
H	0.302031000	-5.636291000	-0.659030000
H	1.857808000	-5.311145000	-1.464229000
C	1.094650000	-3.716707000	-0.324893000
N	0.956983000	-2.580496000	-0.141885000
C	1.629906000	-1.835569000	2.897114000
H	1.530998000	-2.323234000	3.877903000
H	1.975848000	-2.570271000	2.168941000
H	2.388659000	-1.052489000	2.978655000
C	-0.176806000	-0.330318000	3.486106000
H	-0.989710000	0.279167000	3.087861000
H	-0.522983000	-0.883610000	4.370468000
H	0.617568000	0.344110000	3.810432000
C	2.314031000	2.504337000	3.267145000
H	1.625924000	3.077994000	3.895861000
H	2.553413000	1.568870000	3.783787000
H	3.236454000	3.087799000	3.180231000
C	3.645158000	-0.203616000	-2.865505000
H	3.713634000	-0.934552000	-3.677878000
H	2.846756000	0.506760000	-3.105048000
H	4.590365000	0.343223000	-2.812904000
C	4.454822000	-1.932012000	-1.170821000
H	4.214771000	-2.448618000	-0.235201000
H	4.562319000	-2.678593000	-1.964734000
H	5.416045000	-1.424955000	-1.047624000
C	-1.440614000	-0.245504000	-3.834467000
H	-2.317782000	-0.690731000	-4.315413000
H	-1.747187000	0.675645000	-3.333732000
H	-0.719977000	-0.001294000	-4.621649000
C	-3.210222000	-2.838317000	2.272763000
H	-3.506601000	-2.705992000	3.318000000
H	-3.983054000	-3.427402000	1.770109000
H	-2.275296000	-3.412771000	2.250455000
C	-4.337179000	-0.633558000	1.645202000
H	-4.191387000	0.320852000	1.133124000
H	-5.166885000	-1.167248000	1.173944000
H	-4.599322000	-0.434181000	2.689229000

Table S33. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **C'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2143.39895850Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3483.14692600Hartree/Particle. [B3LYP/TZVP]

Ni	-0.263527000	-0.867649000	-0.027364000
O	-0.060590000	0.897862000	0.678295000
N	-3.152971000	-0.408826000	0.454128000
N	-2.750274000	-0.023126000	-1.600142000
N	-4.347063000	0.003873000	-0.069882000
N	2.127930000	-1.161880000	1.710526000
N	2.741693000	-1.130031000	-0.326967000
N	3.903344000	-1.196683000	0.398596000
C	-2.152211000	-0.434633000	-0.442796000
C	-4.070925000	0.233085000	-1.321906000
H	-4.787538000	0.580083000	-2.050713000
C	1.635393000	-1.111239000	0.436356000
C	3.498033000	-1.211165000	1.634850000
H	4.151467000	-1.261638000	2.493661000
C	-3.067859000	-0.646506000	1.913583000
H	-2.045903000	-1.010866000	2.065198000
C	1.354646000	-1.083188000	2.962555000
H	0.304063000	-1.180389000	2.682157000
H	1.621361000	-1.950951000	3.575497000
C	-2.103286000	0.182601000	-2.914975000
H	-1.030735000	0.084500000	-2.746437000
H	-2.436602000	-0.618247000	-3.585165000
C	2.857506000	-1.016750000	-1.802813000
H	1.825520000	-0.913656000	-2.148898000
S	0.025580000	2.060959000	-0.339982000
O	0.570772000	1.592293000	-1.627030000
O	-1.182165000	2.884863000	-0.347739000
C	1.370256000	3.062856000	0.471858000
F	1.022845000	3.353691000	1.728336000
F	2.503965000	2.344100000	0.492053000
F	1.569188000	4.182667000	-0.211813000
N	-0.595534000	-2.776152000	-0.487168000
C	0.029482000	-3.779258000	0.415866000
H	1.112082000	-3.759050000	0.286313000
H	-0.210590000	-3.536385000	1.452823000
H	-0.341491000	-4.784693000	0.184736000
C	-0.340697000	-3.108787000	-1.914048000
H	0.727519000	-3.034106000	-2.116832000
H	-0.673208000	-4.129864000	-2.135629000
H	-0.876961000	-2.408114000	-2.555237000
H	-1.603361000	-2.848884000	-0.348589000
C	-4.072081000	-1.721945000	2.334436000
H	-3.906858000	-2.662668000	1.796354000

H	-3.971129000	-1.917872000	3.406334000
H	-5.095919000	-1.390909000	2.140502000
C	-3.249337000	0.677786000	2.661032000
H	-3.120127000	0.513181000	3.735685000
H	-2.515028000	1.415577000	2.325487000
H	-4.253436000	1.077903000	2.492690000
C	3.634807000	0.250071000	-2.171056000
H	3.155750000	1.135725000	-1.750689000
H	4.665437000	0.188067000	-1.810208000
H	3.655104000	0.353909000	-3.260496000
C	3.504867000	-2.282317000	-2.373520000
H	3.534535000	-2.218642000	-3.465629000
H	4.530903000	-2.384468000	-2.008653000
H	2.956079000	-3.189818000	-2.096610000
C	-2.406289000	1.558907000	-3.505134000
H	-2.101987000	2.348127000	-2.813334000
H	-1.840916000	1.674964000	-4.434737000
H	-3.467014000	1.680664000	-3.747461000
C	1.592776000	0.222787000	3.719836000
H	0.986084000	0.227381000	4.631156000
H	2.640709000	0.327305000	4.019458000
H	1.313184000	1.084313000	3.109399000

Table S34. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **D'** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2449.42130731Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3789.28595580Hartree/Particle. [B3LYP/TZVP]

Ni	0.213237000	0.059273000	0.042416000
O	1.964979000	0.762113000	0.634036000
N	-0.736069000	2.752660000	0.767239000
N	-0.124191000	2.768518000	-1.268583000
N	-0.808301000	4.068558000	0.385215000
N	1.317797000	-2.164214000	1.678775000
N	1.243632000	-2.749421000	-0.363032000
N	1.826869000	-3.805615000	0.290912000
C	-0.308836000	1.928060000	-0.206406000
C	-0.424587000	4.044811000	-0.858172000
H	-0.346545000	4.917223000	-1.489663000
C	0.917267000	-1.726252000	0.447088000

C	1.860113000	-3.416039000	1.532038000
H	2.265265000	-3.998446000	2.346721000
C	-0.981814000	2.415694000	2.185695000
H	-0.977782000	1.322356000	2.212247000
C	1.259281000	-1.416541000	2.945922000
H	2.268543000	-1.417528000	3.369842000
H	1.024397000	-0.384877000	2.684849000
C	0.424272000	2.417441000	-2.593038000
H	0.590089000	1.340391000	-2.585186000
H	1.410769000	2.882624000	-2.672642000
C	1.144091000	-2.816241000	-1.838656000
H	0.761105000	-1.834648000	-2.128476000
C	-2.514953000	0.119540000	-1.318608000
C	-1.589353000	-0.702820000	-0.411447000
H	-2.696045000	1.100597000	-0.872308000
H	-2.004004000	0.287916000	-2.279877000
H	-1.351526000	-1.666487000	-0.865106000
S	2.992063000	1.005259000	-0.482644000
O	2.670697000	0.218272000	-1.689743000
O	3.321875000	2.421150000	-0.653152000
C	4.485810000	0.184251000	0.263724000
F	4.766741000	0.722590000	1.451719000
F	4.230947000	-1.126592000	0.432615000
F	5.532257000	0.319025000	-0.547012000
C	-2.191188000	-0.927069000	0.872102000
N	-2.730552000	-1.055393000	1.903643000
N	-3.860321000	-0.479925000	-1.583784000
C	-3.752815000	-1.743474000	-2.336472000
H	-3.224861000	-1.606836000	-3.293939000
H	-3.216724000	-2.493170000	-1.749699000
H	-4.754551000	-2.127154000	-2.553927000
C	-4.669139000	0.482290000	-2.356592000
H	-4.213993000	0.714817000	-3.332485000
H	-5.665984000	0.068187000	-2.539782000
H	-4.773495000	1.416334000	-1.795745000
H	-4.846159000	-0.820623000	-0.090970000
H	-4.597903000	-1.146767000	1.503241000
N	-5.374250000	-1.034699000	0.820362000
C	-6.217507000	0.130897000	1.212472000
H	-6.975186000	0.301744000	0.445385000
H	-6.700457000	-0.076356000	2.169364000
H	-5.577232000	1.009472000	1.307887000
C	-6.124870000	-2.317076000	0.695137000
H	-6.602891000	-2.552052000	1.648107000
H	-6.883946000	-2.215708000	-0.082928000
H	-5.423206000	-3.109821000	0.430713000

C	-2.356571000	2.927083000	2.621358000
H	-3.150694000	2.503345000	1.995375000
H	-2.543932000	2.633066000	3.658706000
H	-2.406607000	4.017279000	2.553797000
C	0.162029000	2.957342000	3.049639000
H	0.012784000	2.656198000	4.091990000
H	1.124041000	2.568330000	2.702559000
H	0.191746000	4.050414000	3.007949000
C	0.167674000	-3.923712000	-2.247286000
H	0.535096000	-4.899769000	-1.916605000
H	-0.827651000	-3.769858000	-1.813206000
H	0.068792000	-3.945596000	-3.337331000
C	2.536342000	-3.007606000	-2.447266000
H	3.204174000	-2.204742000	-2.129035000
H	2.957928000	-3.972111000	-2.150284000
H	2.460241000	-2.982418000	-3.539194000
C	-0.489938000	2.841666000	-3.740430000
H	-0.036408000	2.541016000	-4.690119000
H	-1.475734000	2.369470000	-3.665791000
H	-0.633221000	3.926820000	-3.775445000
C	0.246600000	-1.999022000	3.930702000
H	0.267854000	-1.417269000	4.858247000
H	-0.767519000	-1.961676000	3.522361000
H	0.484144000	-3.037570000	4.185773000

Table S35. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3'$_{amine}$** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2449.35450288Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3789.20893301Hartree/Particle. [B3LYP/TZVP]

Ni	-0.071842000	-0.058021000	0.139648000
O	-1.899660000	-0.422742000	0.510826000
N	0.133550000	-2.988130000	0.576526000
N	0.286735000	-2.550336000	-1.503967000
N	0.187371000	-4.204984000	-0.043482000
N	-0.848030000	2.429932000	1.647985000
N	-0.664502000	2.811537000	-0.439726000
N	-1.071382000	4.000023000	0.105550000
C	0.188859000	-1.954695000	-0.276952000
C	0.270897000	-3.909069000	-1.309209000
H	0.324028000	-4.638850000	-2.102259000

C	-0.506972000	1.832961000	0.469284000
C	-1.179608000	3.733456000	1.376087000
H	-1.486462000	4.445744000	2.128285000
C	-0.058485000	-2.954535000	2.048395000
H	-0.065784000	-1.891755000	2.298220000
C	-0.965132000	1.799009000	2.979186000
H	-0.395961000	0.871555000	2.943870000
H	-0.461582000	2.458943000	3.692642000
C	0.294149000	-1.864867000	-2.811077000
H	0.559802000	-0.825697000	-2.606979000
H	-0.728721000	-1.858597000	-3.195856000
C	-0.521261000	2.724331000	-1.913366000
H	-0.337003000	1.663292000	-2.104515000
S	-2.807702000	-0.798442000	-0.694418000
O	-2.286969000	-0.223708000	-1.946694000
O	-3.201912000	-2.204381000	-0.669567000
C	-4.310858000	0.206819000	-0.241868000
F	-4.742593000	-0.138403000	0.972333000
F	-3.984836000	1.509391000	-0.233379000
F	-5.267987000	-0.001201000	-1.138067000
C	1.123674000	-3.631960000	2.744338000
H	2.066731000	-3.134319000	2.497792000
H	0.984872000	-3.574829000	3.828179000
H	1.190512000	-4.685935000	2.459018000
C	-1.408782000	-3.584798000	2.400562000
H	-1.586771000	-3.476956000	3.475405000
H	-2.222479000	-3.097380000	1.856899000
H	-1.413953000	-4.651099000	2.156052000
C	0.667240000	3.570985000	-2.376149000
H	0.503672000	4.626187000	-2.136946000
H	1.600627000	3.248546000	-1.900555000
H	0.785213000	3.480340000	-3.460526000
C	-1.833886000	3.124838000	-2.591176000
H	-2.657106000	2.502476000	-2.235454000
H	-2.065976000	4.175789000	-2.397258000
H	-1.737879000	2.982945000	-3.672125000
C	1.268394000	-2.492224000	-3.804928000
H	1.271483000	-1.897020000	-4.723351000
H	2.288940000	-2.521256000	-3.408882000
H	0.976404000	-3.509536000	-4.083565000
C	-2.419980000	1.557402000	3.379492000
H	-2.444488000	1.089918000	4.369226000
H	-2.983693000	2.494663000	3.439198000
H	-2.918134000	0.893091000	2.669574000
C	3.177471000	-0.654413000	-0.642175000
C	2.374386000	0.414473000	0.130245000

H	2.785065000	-1.669332000	-0.473869000
H	3.047569000	-0.432498000	-1.706420000
H	1.616266000	0.964824000	-0.455643000
C	2.041652000	0.167703000	1.506259000
N	1.869452000	-0.000233000	2.651367000
N	4.628366000	-0.618799000	-0.360435000
C	5.385721000	-1.186374000	-1.483153000
H	5.126355000	-2.241297000	-1.682675000
H	5.200986000	-0.605350000	-2.392622000
H	6.455608000	-1.139930000	-1.259941000
C	4.955616000	-1.338627000	0.879942000
H	4.692334000	-2.409668000	0.820196000
H	6.029837000	-1.261912000	1.072730000
H	4.423174000	-0.905379000	1.729995000
H	5.016951000	1.454976000	0.096541000
H	3.269640000	1.468692000	0.226704000
N	4.378517000	2.235718000	0.304255000
C	4.596458000	2.752991000	1.669974000
H	5.581100000	3.225621000	1.763964000
H	3.826357000	3.494377000	1.900717000
H	4.518752000	1.930641000	2.384377000
C	4.464458000	3.263212000	-0.748233000
H	3.688444000	4.016450000	-0.585802000
H	5.441884000	3.759730000	-0.743304000
H	4.310635000	2.795237000	-1.724366000

Table S36. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **F** with ethyl and isopropyl substituent at the 1,4 position of NHC ligand.

Ground state electronic energy (isolated gas phase) = -2314.25622725Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -3654.06250927Hartree/Particle. [B3LYP/TZVP]

Ni	0.194198000	0.266185000	0.200568000
O	2.050354000	0.009544000	0.444017000
N	0.996627000	3.113937000	0.327186000
N	0.505788000	2.615263000	-1.683063000
N	1.238745000	4.253687000	-0.391429000
N	0.277532000	-2.092358000	2.025161000
N	-0.454300000	-2.645244000	0.105055000
N	-0.411089000	-3.813000000	0.821553000
C	0.553889000	2.095256000	-0.423049000
C	0.932882000	3.918999000	-1.611894000

H	1.012397000	4.574033000	-2.467467000
C	-0.043057000	-1.578131000	0.803833000
C	0.038127000	-3.443676000	1.986710000
H	0.208497000	-4.109665000	2.820379000
C	1.333966000	3.098259000	1.769385000
H	1.050618000	2.093900000	2.098825000
C	0.803561000	-1.342567000	3.178373000
H	1.331733000	-2.064403000	3.807481000
H	1.545244000	-0.641180000	2.790874000
C	0.113730000	1.920958000	-2.923148000
H	0.309292000	0.859471000	-2.767339000
H	0.802638000	2.256369000	-3.703728000
C	-0.857163000	-2.702776000	-1.320598000
H	-0.756960000	-1.671434000	-1.669734000
S	2.879831000	-0.197492000	-0.855269000
O	2.003424000	-0.621044000	-1.962469000
O	3.836228000	0.883678000	-1.067923000
C	3.850079000	-1.708180000	-0.356450000
F	4.546977000	-1.457307000	0.750778000
F	2.996944000	-2.718659000	-0.115654000
F	4.671482000	-2.053799000	-1.340837000
C	0.501094000	4.144595000	2.513571000
H	-0.572458000	3.969010000	2.381662000
H	0.728690000	4.100895000	3.583242000
H	0.734679000	5.150766000	2.154114000
C	2.843405000	3.285501000	1.945648000
H	3.101233000	3.194625000	3.005824000
H	3.397036000	2.529854000	1.381366000
H	3.150435000	4.277126000	1.600552000
C	-2.313321000	-3.161184000	-1.430619000
H	-2.429241000	-4.177773000	-1.043493000
H	-2.984323000	-2.499811000	-0.871051000
H	-2.620032000	-3.157814000	-2.481344000
C	0.112137000	-3.594454000	-2.100853000
H	1.136849000	-3.229510000	-2.002682000
H	0.060827000	-4.626810000	-1.742914000
H	-0.158757000	-3.581502000	-3.161264000
C	-1.335123000	2.198916000	-3.319758000
H	-1.564208000	1.677289000	-4.254629000
H	-2.030163000	1.846185000	-2.550772000
H	-1.511656000	3.267922000	-3.478633000
C	-0.294735000	-0.633489000	3.969557000
H	0.148101000	-0.103376000	4.818902000
H	-0.819503000	0.097727000	3.345352000
H	-1.029169000	-1.346303000	4.358719000
C	-5.107141000	-0.102580000	-0.150001000

C	-4.229754000	1.103640000	0.289620000
H	-4.831931000	-0.367879000	-1.175509000
H	-4.873088000	-0.975815000	0.488983000
H	-4.441118000	1.961380000	-0.359266000
C	-2.800164000	0.814195000	0.235054000
N	-1.668768000	0.574363000	0.175562000
N	-6.506913000	0.272074000	-0.125135000
C	-7.079682000	0.254995000	1.219385000
H	-7.081167000	-0.753746000	1.672469000
H	-6.530959000	0.928619000	1.886375000
H	-8.111812000	0.613464000	1.176063000
C	-7.310747000	-0.519134000	-1.057873000
H	-7.348139000	-1.592816000	-0.799267000
H	-8.335051000	-0.135432000	-1.060970000
H	-6.910302000	-0.418950000	-2.071719000
H	-4.466998000	1.406836000	1.315843000

Table S37. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **E'** without OTf.

Ground state electronic energy (isolated gas phase) = -1251.77444851Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2591.44156589Hartree/Particle. [B3LYP/TZVP]

Ni	0.603762000	0.330955000	0.210949000
N	0.343714000	-2.370599000	-0.976599000
N	0.935076000	-2.523701000	1.054845000
N	0.543712000	-3.711862000	-0.767146000
N	0.640260000	3.147589000	-0.759212000
N	0.991493000	3.065008000	1.331693000
N	1.062762000	4.397244000	1.014504000
C	0.579571000	-1.612425000	0.104835000
C	0.906453000	-3.771265000	0.482789000
H	1.143956000	-4.682856000	1.011550000
C	0.732183000	2.272433000	0.281319000
C	0.852449000	4.413170000	-0.271317000
H	0.854463000	5.302968000	-0.883655000
C	-4.173452000	-0.627281000	1.519804000
C	-3.468126000	0.579613000	0.947484000
H	-3.464740000	-1.378531000	1.902655000
H	-4.785408000	-0.307495000	2.369276000
H	-3.770734000	1.560539000	1.308870000
C	-2.248735000	0.505127000	0.357180000

N	-1.221507000	0.437985000	-0.254189000
N	-5.111885000	-1.332902000	0.569621000
C	-6.057597000	-2.190802000	1.307154000
H	-5.536184000	-2.956028000	1.901462000
H	-6.662180000	-1.579435000	1.983700000
H	-6.723256000	-2.697918000	0.602387000
C	-4.347016000	-2.134679000	-0.403856000
H	-3.785171000	-2.940546000	0.092728000
H	-5.028173000	-2.587114000	-1.131461000
H	-3.634226000	-1.492752000	-0.928306000
C	0.054202000	-1.905164000	-2.329972000
H	-0.587029000	-1.026161000	-2.265200000
H	0.988085000	-1.646150000	-2.835382000
H	-0.446988000	-2.714791000	-2.861038000
C	1.401170000	-2.214212000	2.406892000
H	2.433270000	-1.861255000	2.367762000
H	0.768165000	-1.437592000	2.838328000
H	1.333698000	-3.116346000	3.018008000
C	0.456720000	2.780265000	-2.165103000
H	-0.477779000	2.227059000	-2.275455000
H	0.417967000	3.694746000	-2.759856000
H	1.295618000	2.159223000	-2.486337000
C	1.225603000	2.653918000	2.711203000
H	1.921077000	3.364949000	3.157632000
H	0.288210000	2.654961000	3.275250000
H	1.669947000	1.658916000	2.700922000
H	-5.766259000	-0.149792000	-0.267525000
N	-5.960814000	0.807071000	-0.826159000
H	-5.044289000	1.261226000	-0.679286000
C	-6.198540000	0.560926000	-2.273679000
C	-7.030422000	1.596704000	-0.158562000
H	-7.114836000	-0.021650000	-2.389726000
H	-6.301114000	1.510710000	-2.804054000
H	-5.354506000	0.001532000	-2.681055000
H	-7.145588000	2.565661000	-0.650050000
H	-7.970089000	1.043537000	-0.216980000
H	-6.757985000	1.745607000	0.888145000

Table S38. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **TS3N'$_{amine}$** without OTf.

Ground state electronic energy (isolated gas phase) = -1251.72837760Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2591.39994637Hartree/Particle. [B3LYP/TZVP]

Ni	1.757193000	0.294460000	0.102314000
N	0.849007000	2.760734000	1.474407000
N	1.395278000	3.198678000	-0.536510000
N	0.689454000	4.107160000	1.348258000
N	2.841809000	-2.392639000	0.816301000
N	3.030796000	-2.011025000	-1.269974000
N	3.604806000	-3.230307000	-1.079493000
C	1.288151000	2.165271000	0.351364000
C	1.031011000	4.351317000	0.112018000
H	1.027501000	5.330809000	-0.345589000
C	2.561011000	-1.456748000	-0.137215000
C	3.477645000	-3.441426000	0.203189000
H	3.826856000	-4.325445000	0.718210000
C	-3.016765000	-0.098704000	-1.712406000
C	-2.134170000	-1.120080000	-0.931123000
H	-2.379602000	0.619647000	-2.260500000
H	-3.554464000	-0.680373000	-2.465839000
H	-1.927813000	-2.020616000	-1.521812000
C	-0.934635000	-0.666038000	-0.361756000
N	0.022108000	-0.345981000	0.250144000
N	-4.011151000	0.579797000	-0.881067000
C	-5.080184000	1.158663000	-1.710510000
H	-4.710020000	1.931144000	-2.405500000
H	-5.565602000	0.371223000	-2.294530000
H	-5.831955000	1.615412000	-1.061259000
C	-3.410728000	1.602215000	-0.023405000
H	-2.906578000	2.398316000	-0.602691000
H	-4.187292000	2.069766000	0.588205000
H	-2.678048000	1.150266000	0.654743000
H	-4.655551000	-1.133687000	0.486700000
H	-2.921430000	-1.576468000	-0.027182000
N	-4.115484000	-1.964048000	0.752618000
C	-3.873882000	-1.994722000	2.203320000
H	-4.805749000	-2.141814000	2.763673000
H	-3.193728000	-2.817809000	2.441265000
H	-3.421160000	-1.050422000	2.518344000
C	-4.738953000	-3.186847000	0.216310000
H	-4.078262000	-4.040374000	0.392737000
H	-5.704838000	-3.387208000	0.695973000
H	-4.898022000	-3.074201000	-0.859369000
C	3.021261000	-1.464506000	-2.626525000
H	4.044653000	-1.241405000	-2.936676000
H	2.590683000	-2.205231000	-3.302405000
H	2.417967000	-0.555345000	-2.633804000

C	2.563906000	-2.286156000	2.253503000
H	1.586410000	-1.823361000	2.396161000
H	2.549052000	-3.288722000	2.683634000
H	3.339382000	-1.695339000	2.747689000
C	0.575754000	2.157005000	2.778955000
H	-0.349937000	2.583870000	3.166879000
H	0.469793000	1.079898000	2.651568000
H	1.393870000	2.384238000	3.466889000
C	1.874240000	3.121567000	-1.921367000
H	2.962715000	3.217377000	-1.954641000
H	1.567106000	2.168672000	-2.355775000
H	1.424332000	3.930832000	-2.498820000

Table S39. B3LYP/TZVP//B3LYP/6-31G(d)-LANL2DZ level optimized coordinates of **F** without OTf.

Ground state electronic energy (isolated gas phase) = -1116.55601732Hartree/Particle. [B3LYP/LANL2DZ, 6-31G(d)]

Ground state electronic energy (MeCN) = -2456.19051163Hartree/Particle. [B3LYP/TZVP]

Ni	1.319934000	0.265988000	0.039919000
N	2.620298000	-2.184437000	-1.002240000
N	2.395020000	-2.323815000	1.111391000
N	3.195269000	-3.369055000	-0.661792000
N	0.907809000	3.079357000	-0.897771000
N	0.596056000	2.896191000	1.201534000
N	0.433621000	4.219812000	0.933366000
C	2.129663000	-1.504626000	0.050417000
C	3.046542000	-3.432249000	0.634396000
H	3.390591000	-4.248842000	1.253934000
C	0.899894000	2.162730000	0.114853000
C	0.629702000	4.307720000	-0.355216000
H	0.581377000	5.226347000	-0.923358000
C	2.633971000	-1.799168000	-2.413751000
H	2.232997000	-2.623141000	-3.006201000
H	2.016106000	-0.909526000	-2.540904000
H	3.661050000	-1.594356000	-2.724275000
C	1.222396000	2.825788000	-2.309313000
H	2.304743000	2.807689000	-2.460365000
H	0.782107000	1.874662000	-2.612897000
H	0.789550000	3.623112000	-2.915352000
C	2.103887000	-2.054911000	2.524579000
H	2.891850000	-1.438894000	2.965562000

H	1.139374000	-1.550599000	2.605929000
H	2.048767000	-3.003895000	3.060151000
C	0.460409000	2.458301000	2.590776000
H	1.269088000	2.887289000	3.186734000
H	-0.499262000	2.804336000	2.978365000
H	0.507535000	1.368651000	2.621412000
C	-3.866871000	-0.624519000	0.238851000
C	-2.855277000	-1.100219000	-0.872025000
H	-3.543326000	-1.028476000	1.201970000
H	-3.829679000	0.473860000	0.303115000
H	-2.857728000	-2.194942000	-0.927198000
C	-1.484255000	-0.653940000	-0.644266000
N	-0.393402000	-0.302368000	-0.455767000
N	-5.176197000	-1.112734000	-0.085486000
C	-6.003279000	-0.246520000	-0.914491000
H	-6.401413000	0.612736000	-0.348135000
H	-5.426485000	0.139413000	-1.761603000
H	-6.847013000	-0.815805000	-1.312855000
C	-5.885972000	-1.873492000	0.936418000
H	-6.289541000	-1.228751000	1.735314000
H	-6.722166000	-2.405645000	0.474886000
H	-5.217719000	-2.612031000	1.388574000
H	-3.173116000	-0.720882000	-1.850540000

Table S40. % of electron contribution and natural charge distribution in all intermediates species (**B−F, C'−C''**) and transition states (**TS1−TS3, TS1'−TS1''**) are shown.

Compound	% of electron contribution in (NHC)−Ni and Ni−X_{donar} bond								Natural Charge								
	Ni−C1	Ni−C3	Ni−O1	Ni−N7	Ni−N8	Ni−N9	Ni−C9	Ni−C10	Ni	Ccarbene		Xdonar					O1
										C1	C3	C9	C10	N7	N8	N9	
B	21.2 (Ni) 78.7 (C1)	21.0 (Ni) 78.9 (C3)	12.9 (Ni) 87.0 (O1)		13.0 (Ni) 86.9 (N8)				0.407	0.221	0.242				-0.359		-0.897
TS1	19.0 (Ni) 80.9 (C1)	19.6 (Ni) 80.3 (C3)	14.1 (Ni) 85.8 (O1)						0.528	0.164	0.189	-0.396	-0.293	-0.257	-0.412		-0.894
C	23.3 (Ni) 76.6 (C1)	21.8 (Ni) 78.1 (C3)	15.2 (Ni) 84.7 (O1)						0.401	0.226	0.261	-0.367	-0.341	-0.222			-0.898
TS2	22.4 (Ni) 77.5 (C1)	23.4 (Ni) 76.5 (C3)							0.412	0.198	0.223	-0.249	-0.487	-0.285		-0.642	-0.897
D	20.1 (Ni) 79.8 (C1)	20.6 (Ni) 79.3 (C3)						24.0 (Ni) 75.9 (C10)	0.338	0.21	0.23	-0.239	-0.612	-0.351		-0.456	-0.922
TS3	20.7 (Ni) 79.2 (C1)	20.9 (Ni) 79.0 (C3)	14.7 (Ni) 85.2 (O1)						0.451	0.195	0.201	-0.237	-0.715	-0.331		-0.505	-0.887
$TS3_{water}$	20.7 (Ni) 79.2 (C1)	20.9 (Ni) 79.0 (C3)	14.9 (Ni) 85.1 (O1)						0.463	0.192	0.203	-0.245	-0.701	-0.343		-0.528	-0.883
F	21.2 (Ni) 78.7 (C1)	20.9 (Ni) 79.0 (C3)	12.9 (Ni) 87.0 (O1)	13.2 (Ni) 86.7 (N7)					0.408	0.218	0.247	-0.236	-0.584	-0.37		-0.508	-0.896
TS4	22.1 (Ni) 77.8 (C1)	21.8 (Ni) 78.1 (C3)	13.2 (Ni) 86.7 (O1)						0.365	0.245	0.263	-0.238	-0.578	-0.377	-0.361	-0.507	-0.901
TS1'	21.0 (Ni) 78.9 (C1)	21.1 (Ni) 78.8 (C3)	12.6 (Ni) 87.3 (O1)						0.429	0.213	0.247				-0.382	-0.67	-0.915
C'	18.8 (Ni) 81.1 (C1)	18.7 (Ni) 81.2 (C3)	14.3 (Ni) 85.6 (O1)						0.544	0.17	0.173					-0.654	-0.906
TS1"	18.7 (Ni) 81.2 (C1)	17.7 (Ni) 82.2 (C3)	14.5 (Ni) 85.4 (O1)						0.581	0.157	0.158	-0.396	-0.292			-0.694	-0.9
C"	21.5 (Ni) 78.4 (C1)	20.7 (Ni) 79.2 (C3)	13.8 (Ni) 86.1 (O1)						0.421	0.212	0.221	-0.511	-0.188			-0.697	-0.899

Table S41. Charge decomposition analysis (CDA) of **B−F**and **C'−C''** structures showing the (donor)→$[NHC]_2$(OTf)Ni(II) (acceptor) σ-donation (*d*), thedonor←$[NHC]_2$(OTf)Ni(II) (acceptor) π-back donation (*b*), the *d*/*b* ratio and the donor ↔$[NHC]_2$(OTf)Ni(II) (acceptor) repulsive polarization (*r*) [donor fragment MeCN (**B**),C_2H_3CN (**C**),Me_2HN-C_2H_3CN (**D**), $Me_2N(CH_2)CN$ (**F**), $NHMe_2$ (**C'**), $NHMe_2$ and C_2H_3CN (**C''**)].

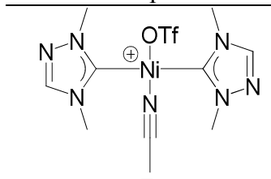
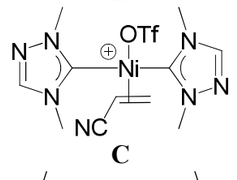
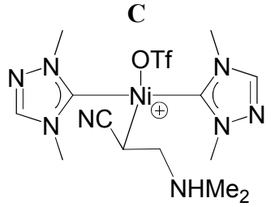
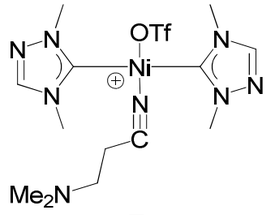
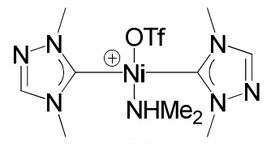
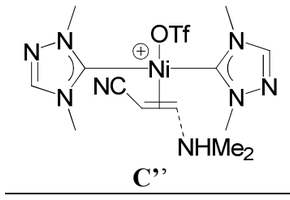
complex	donor→$[NHC]_2$(OTf)Ni(II) (acceptor)(*d*)	donor←$[NHC]_2$(OTf)Ni(II) (acceptor)(*b*)	*d*/*b* ratio	repulsive polarization (*r*)
 **B**	0.182	0.030	6.066	-0.098
 **C**	0.240	0.059	4.067	-0.133
 **D**	0.293	0.042	6.976	-0.117
 **F**	0.191	0.028	6.821	-0.101
 **C'**	0.200	0.024	8.333	-0.110
 **C''**	0.273	0.062	4.403	-0.132

Table S42. Bond distance and bond energy of $[NHC]_2(OTf)Ni(II)$−(donor fragment) bonds in **B–E** and **C'–C''**[donor fragment = MeCN (**B**),C_2H_3CN (**C**),Me_2HN-C_2H_3CN (**D**), $Me_2N(CH_2)CN$ (**F**), $NHMe_2$ (**C'**), $NHMe_2$ and C_2H_3CN (**C''**)].

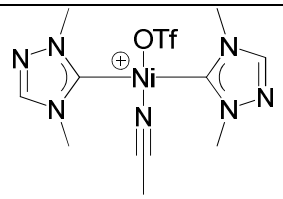
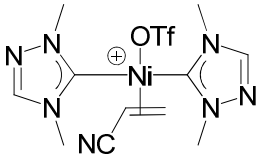
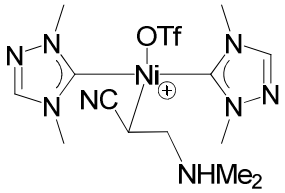
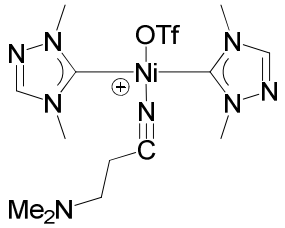
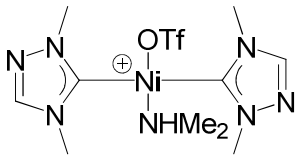
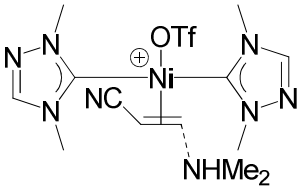
compound	*d*/$[NHC]_2(OTf)Ni(II)$ (Å)	D_e /$[NHC]_2(OTf)Ni(II)$–(donor) (kcal/mol)
 **B**	1.959 (Ni−C1) 1.953 (Ni−C3) 1.885 (Ni−O1) 1.890 (Ni−N8)	44.9
 **C**	1.954 (Ni−C1) 1.975 (Ni−C3) 1.886 (Ni−O1) 1.183 (Ni−C9) 2.271 (Ni−C10)	20.8
 **D**	1.959 (Ni−C1) 1.948 (Ni−C3) 1.962 (Ni−O1) 2.009 (Ni−C10)	81.6
 **F**	1.954 (Ni−C1) 1.958 (Ni−C3) 1.882 (Ni−O1) 1.887 (Ni−N7)	47.5
 **C'**	1.973 (Ni−C1) 1.963 (Ni−C3) 1.911 (Ni−O1) 1.983 (Ni−N9)	51.5
 **C''**	1.971 (Ni−C1) 1.960 (Ni−C3) 1.917 (Ni−O1) 2.205 (Ni−C9) 2.213 (Ni−C10)	28.9

Table 43. Comparison of the energies (kcal/mol) computed using B3LYP/LanL2DZ(Ni), 6-31G(d) rest (method 1) vs. B3LYP/ 6-31G(d) (method 2) for all. After the optimization, single point calculations were performed using TZVP basis set for all atoms and the tuoted energies are free energies incorporating solvation effects.

Compound	**Method 1**	**Method 2**
B1	0.0	0.0
TS1'	31.1	29.3
C'	-2.5	-1.9

Table 44. Computed energetics for replacing the model NHC to real NHC*. Here * represent substitution at the 1, 4 position with ethyl and isopropyl substituent (See Figure S16-S23 for details)

Compound	**Model System Energy(kcal/mol)**	**Real System Energy (kcal/mol)**
B	0.0	0.0
TS1	44.9	45.0
C	27.7	28.5
TS1'	29.3	32.3
C'	-1.9	-0.9
D'	14.5	15.9
TS3'$_{amine}$	58.0	59.0
F	1.8	1.3

Table 45. Computed pathway where dissociation of OTf is considered (see Figure S24-26) for E' to F conversion in comparison to the presence of OTf molecule throughout.

Compound	**With OTf Energy (kcal/mol)**	**Without OTf Energy (kcal/mol)**
E'	0.0	0.0
TS3N'$_{amine}$	3.8	20.1
F	-20.3	-18.7