Transfer Hydrocyanation by the Nickel(0)/Lewis Acid Cooperative Catalysis, Mechanism Investigation and Computational Prediction of Shuttle Catalysts

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Table S1. The ΔE_{gas}, ΔG_{gas},and,ΔE_{sol} of the species involved in Figure 1, 2, and 3.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
Ni(COD)$_2$	0.0	0.0	0.0
Cplx1	-16.2	-12.0	-0.6
1	-7.9	-7.2	-0.3
TS1-2	27.6	29.0	37.9
2	8.6	9.5	15.3
TS2-3	24.4	22.0	32.4
3	23.6	21.0	30.1
4	29.4	11.1	8.7
5	15.8	13.1	21.0
TS5-6	22.6	20.4	29.3
6	15.2	14.6	23.2
7	11.0	10.5	19.1
TS7-8	28.8	28.4	35.3
8	-11.8	-10.8	0.14
9	19.2	15.1	24.7
TS9-10	23.3	21.5	31.0
10	11.4	9.6	12.2
11	10.2	9.4	16.4
TS11-12	26.7	28.3	33.8
12	-11.0	-8.0	2.6
13	-7.6	8.5	5.5
TS13-14	42.5	56.1	49.0
14	-8.6	5.0	6.5
15	-1.8	12.3	9.6
TS15-16	55.5	69.0	59.7
16	-1.5	10.0	10.8

Table S2. The ΔE_{gas}, ΔG_{gas},and, ΔE_{sol} of the species involved in Figure 5.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
Ni(COD)$_2$	0.0	0.0	0.0
LA^N-1	-52.2	-33.8	-37.0
LA^N-TS1-2	-18.5	-3.4	-5.7
LA^N-2	-36.4	-23.3	-23.1
LA^N-TS2-3	-19.1	-6.7	-3.8
LA^N-3	-23.7	-13.0	-10.9
LA^N-4	-15.1	-17.9	-9.3
LA^N-5	-32.4	-18.3	-16.1
LA^N-TS5-6	-27.8	-14.2	-8.6
LA^N-6	-33.6	-18.5	-16.4
LA^N-7	-41.2	-23.6	-24.9
LA^N-TS7-8	-24.3	-8.8	-8.8
LA^N-8	-53.3	-35.4	-35.9

Table S3. The ΔE_{gas}, ΔG_{gas},and, ΔE_{sol} of the species involved in Figure 7.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
$Ni(COD)_2$	0.0	0.0	0.0
LA^O-1	-30.3	-10.5	-8.1
LA^O-TS1-2	4.9	21.0	25.1
LA^O-2	-10.6	8.2	9.1
LA^O-TS2-3	17.6	32.7	34.6
LA^O-3	8.4	23.6	23.8
LA^O-4	19.9	19.2	27.9
LA^O-5	4.3	20.6	23.8
LA^O-TS5-6	10.8	27.0	32.5
LA^O-6	2.3	21.0	22.8
LA^O-7	-3.2	15.1	14.9
LA^O-TS7-8	9.4	26.9	30.3
LA^O-8	-23.1	-5.8	-0.7

Table S4. The ΔE_{gas}, ΔG_{gas},and, ΔE_{sol} of the species involved in Figure 8.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
Ni(COD)$_2$	0.0	0.0	0.0
2LA-1	-71.5	-35.1	-41.8
2LA-TS1-2	-43.4	-9.7	-14.5
2LA-2	-53.1	-18.7	-26.1
2LA-TS2-3	-34.3	-2.6	-5.8
2LA-3	-34.9	-4.7	-8.4
2LA-4	-29.9	-15.3	-11.9
2LA-5	-45.0	-13.7	-16.5
2LA-TS5-6	-39.9	-5.9	-7.9
2LA-6	-47.5	-12.5	-17.1
2LA-7	-55.2	-19.2	-26.5
2LA-TS7-8	-44.6	-8.4	-14.0
2LA-8	-70.2	-31.8	-37.9

Table S5. The ΔE_{gas}, ΔG_{gas},and, ΔE_{sol} of the species involved in Figure 10.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
$Ni(COD)_2$	0.0	0.0	0.0
L1-LA^{N}-1	-54.9	-39.8	-39.3
L1-LA^{N}-TS1-2	-15.8	-3.0	-3.3
L1-LA^{N}-2	-29.7	-17.7	-17.0
L1-LA^{N}-TS2-3	-22.1	-11.0	-6.5
L1-LA^{N}-3	-26.7	-16.0	-15.5
L1-LA^{N}-4	-7.6	-14.1	-3.3
L1-LA^{N}-5	-31.6	-20.6	-14.7
L1-LA^{N}-TS5-6	-22.6	-12.1	-6.5
L1-LA^{N}-6	-40.9	-28.9	-23.4
L1-LA^{N}-7	-46.1	-31.6	-26.1
L1-LA^{N}-TS7-8	-29.2	-15.7	-10.9
L1-LA^{N}-8	-59.0	-43.8	-37.9
L2-LA^{N}-1	-52.1	-33.0	-36.5
L2-LA^{N}-TS1-2	-20.4	-4.6	-7.2
L2-LA^{N}-2	-35.4	-21.3	-21.5
L2-LA^{N}-TS2-3	-16.8	-5.2	-1.2
L2-LA^{N}-3	-22.4	-12.2	-8.9
L2-LA^{N}-4	-7.3	-12.8	-1.6
L2-LA^{N}-5	-31.0	-18.0	-13.6
L2-LA^{N}-TS5-6	-27.0	-14.1	-6.8
L2-LA^{N}-6	-37.6	-22.7	-19.2
L2-LA^{N}-7	-39.3	-22.6	-22.6
L2-LA^{N}-TS7-8	-22.5	-7.9	-6.7
L2-LA^{N}-8	-53.4	-34.6	-34.6
L3-LA^{N}-1	-49.2	-32.5	-20.6
L3-LA^{N}-TS1-2	-21.4	-7.0	-10.9
L3-LA^{N}-2	-36.9	-23.4	-27.7
L3-LA^{N}-TS2-3	-23.3	-13.5	-12.1
L3-LA^{N}-3	-24.6	-15.8	-16.0
L3-LA^{N}-4	-14.7	-18.6	-13.4
L3-LA^{N}-5	-33.0	-20.5	-22.9
L3-LA^{N}-TS5-6	-25.7	-13.8	-13.9
L3-LA^{N}-6	-31.8	-18.8	-21.0
L3-LA^{N}-7	-40.7	-24.5	-28.8
L3-LA^{N}-TS7-8	-21.1	-7.3	-10.2
L3-LA^{N}-8	-72.6	-43.9	-57.4

Table S6. The ΔE_{gas}, ΔG_{gas},and,ΔE_{sol} of the species involved in Figure S1.

Species	ΔE_{gas}	ΔG_{gas}	ΔE_{sol}
9	19.2	15.1	24.7
TS9-10	23.3	21.5	31.0
10	11.4	9.6	12.2
11	10.2	9.4	16.4
TS11-12	26.7	28.3	33.8
12	-11.0	-8.0	2.6
LA^{N}-9	-29.8	-16.9	-14.0
LA^{N}-TS9-10	-25.3	-11.2	-8.0
LA^{N}-10	-34.8	-22.6	-24.6
LA^{N}-11	-37.4	-22.1	-22.4
LA^{N}-TS11-12	-22.6	-6.5	-7.9
LA^{N}-12	-52.7	-32.2	-32.7
LA^{O}-9	-0.3	13.1	18.3
LA^{O}-TS9-10	8.4	23.2	27.7
LA^{O}-10	0.9	17.7	17.2
LA^{O}-11	-10.7	8.5	11.8
LA^{O}-TS11-12	4.4	21.9	29.8
LA^{O}-12	-32.9	-13.7	-7.6
2LA-9	-51.4	-20.4	-23.5
2LA-TS9-10	-39.5	-10.3	-11.2
2LA-10	-45.5	-14.7	-21.0
2LA-11	-53.3	-17.9	-24.3
2LA-TS11-12	-36.9	-0.5	-8.1
2LA-12	-69.4	-31.5	-35.1

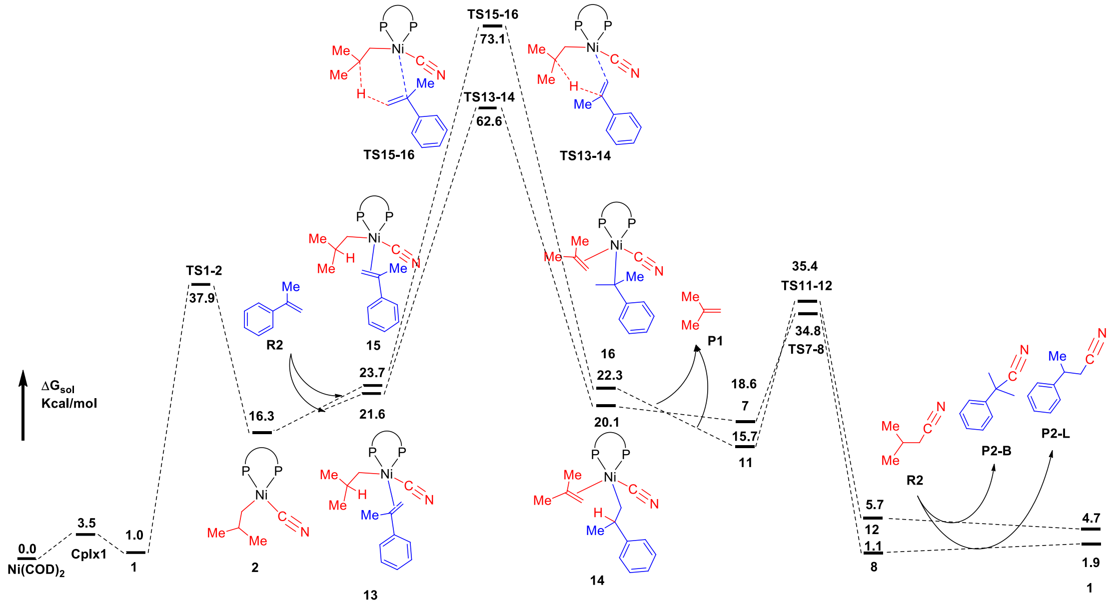


Figure S1. Free energy profiles of the mechanism of the direct H-transfer from substrate**R1** to**R2**.

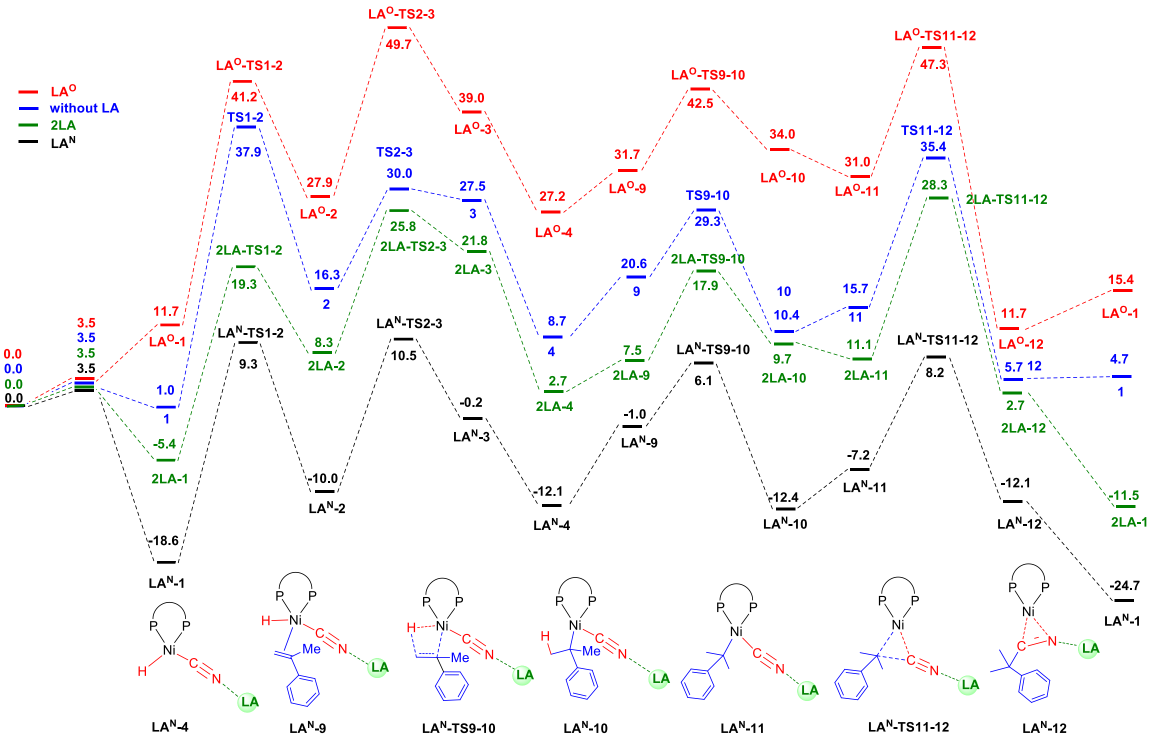


Figure S2.Free energy profile of the mechanism of transfer hydrocyanation leading to the branched Markovnikov **P2-B**.

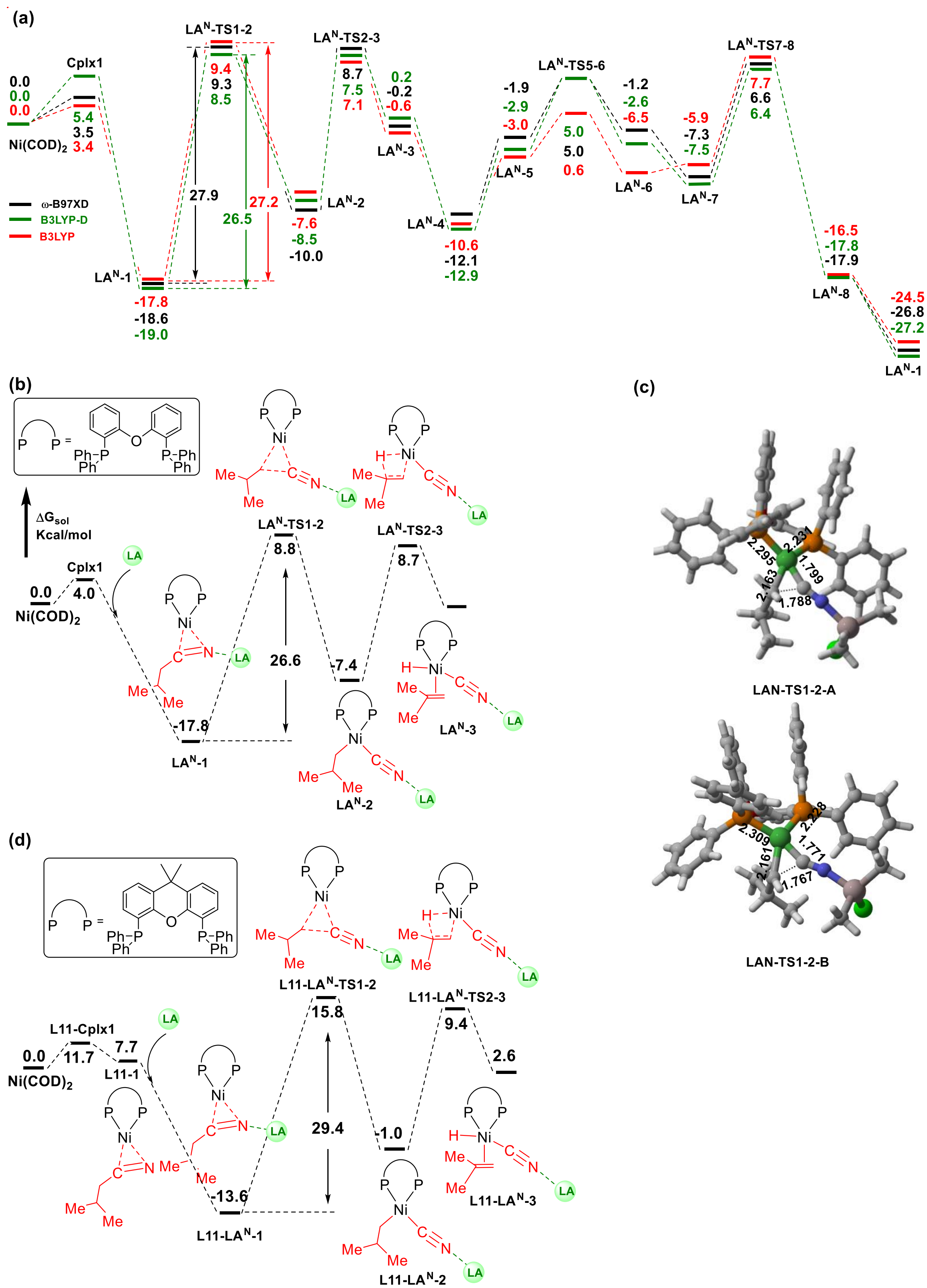

(a)
Cplx1
0.0
0.0
0.0
Ni(COD)2
5.4
3.5
3.4
ω-B97XD
B3LYP-D
B3LYP
LAN-1
-17.8
-18.6
-19.0
LAN-TS1-2
9.4
9.3
8.5
27.9
26.5
27.2
-7.6
-8.5
-10.0
LAN-2
LAN-TS2-3
8.7
7.5
7.1
0.2
-0.2
-0.6
LAN-3
LAN-4
-10.6
-12.1
-12.9
-1.9
-2.9
-3.0
LAN-5
LAN-TS5-6
5.0
5.0
0.6
-1.2
-2.6
-6.5
LAN-6
-5.9
-7.3
-7.5
LAN-7
LAN-TS7-8
7.7
6.6
6.4
-16.5
-17.8
-17.9
LAN-8
-24.5
-26.8
-27.2
LAN-1
(b)
P P =
Ph-P
Ph
O
P-Ph
Ph
ΔGsol
Kcal/mol
0.0
Ni(COD)2
Cplx1
4.0
LA
-17.8
LAN-1
LAN-TS1-2
8.8
26.6
-7.4
LAN-2
LAN-TS2-3
8.7
LAN-3
Me
Ni
C
N
H
(c)
2.295
2.231
1.799
2.163
1.788
LAN-TS1-2-A
2.309
2.228
1.771
2.161
1.767
LAN-TS1-2-B
(d)
P P =
Ph-P
Ph
O
P-Ph
Ph
L11-LAN-TS1-2
L11-LAN-TS2-3
L11-Cplx1
0.0
11.7
7.7
Ni(COD)2
L11-1
15.8
9.4
2.6
29.4
-1.0
-13.6
L11-LAN-1
L11-LAN-2
L11-LAN-3

Figure S3.(a)Free energy profile for the test of the ω-B97XD functional by the other two functional with empirical dispersion correction; (b) Free energy profile for the test of the basis set(LanL2DZ were exployed for Ni and the all-electron 6-31+G* basis set was used in describing all other main-group atoms including P and Cl); (c) Structure papameters of the transition state LAN-TS1-2. (LAN-TS1-2-A:LanL2DZ were exployed for Ni, P, Clandthe all-electron 6-31G* basis set was used in describing all other main-group atoms;LAN-TS1-2-B:LanL2DZ were exployed for Ni and the all-electron 6-31+G* basis set was used in describing all other main-group atoms including P and Cl); (d)Free energy profile when ligand L11 is used in the calculation withω-B97XD functional(LanL2DZ were exployed for Ni, P, Clandthe all-electron 6-31G* basis set was used in describing all other main-group atoms).

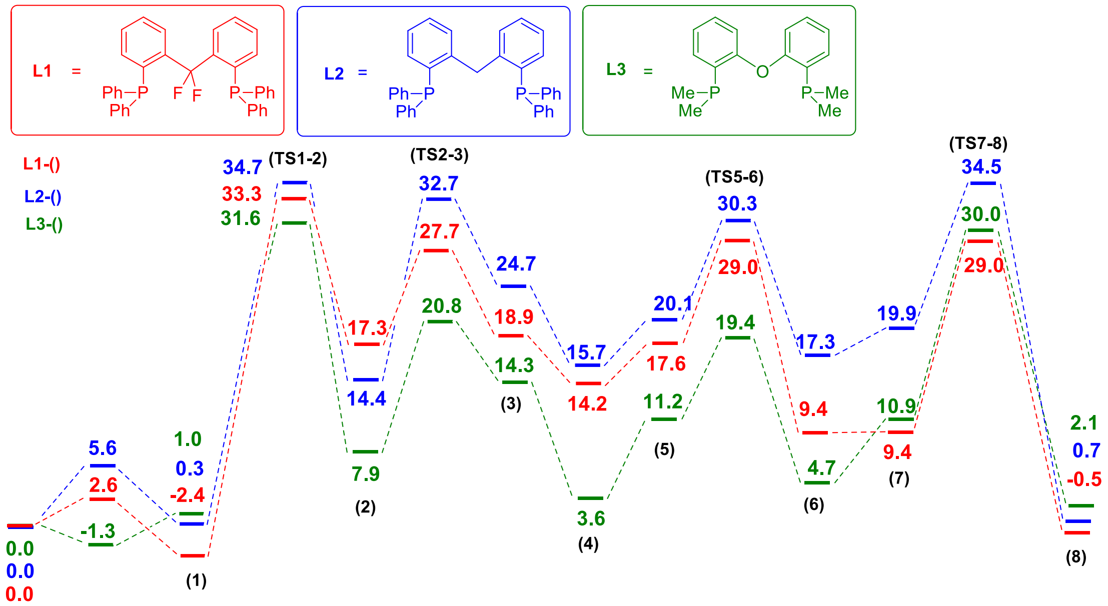
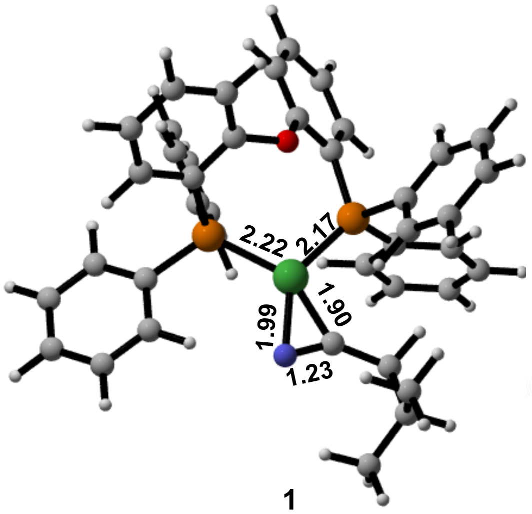
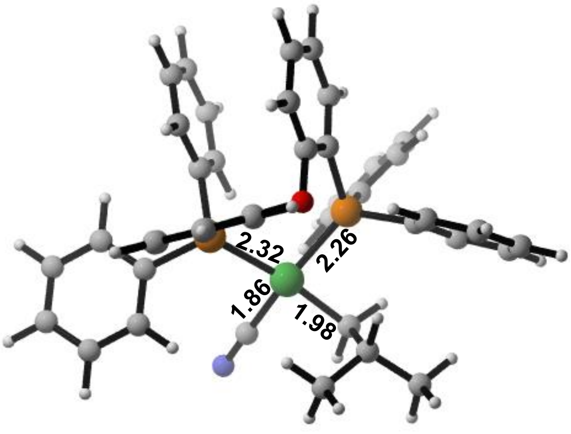


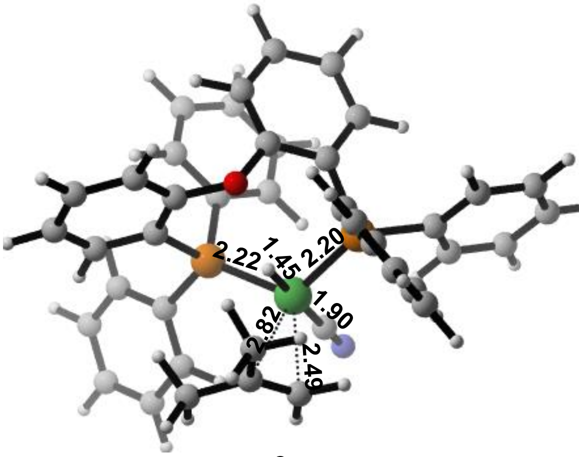
Figure S4.Free energy profile for three new catalysts with ligand L1, L2, and L3 catalyzed transfer hydrocynation.


2.22
2.17
1.99
1.90
1.23

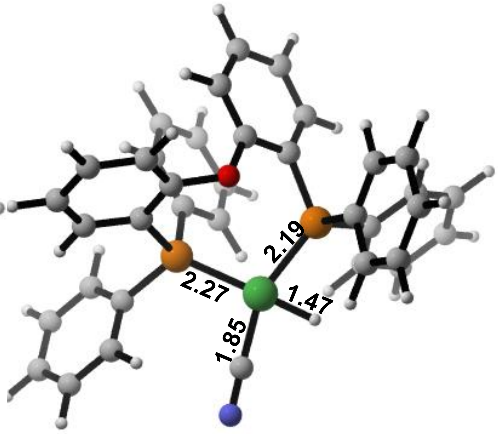
1


2.32
2.26
1.86
1.98

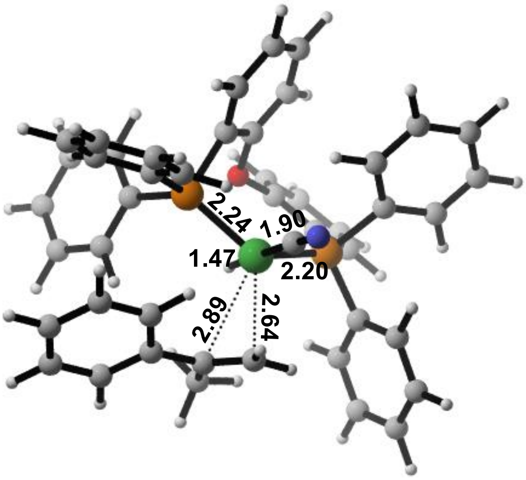
2


2.22
1.45
2.20
1.90
2.82
2.49

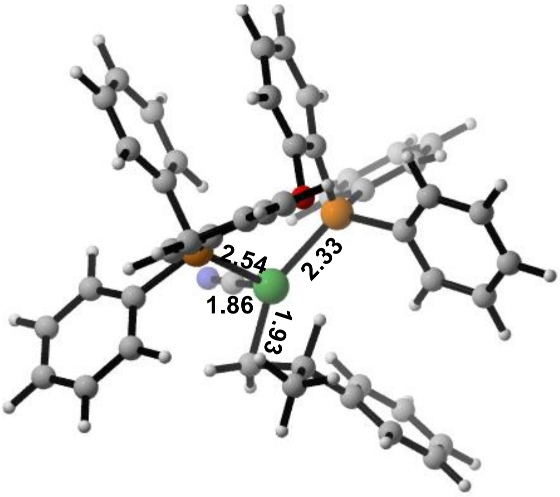
3


2.19
2.27
1.47
1.85

4

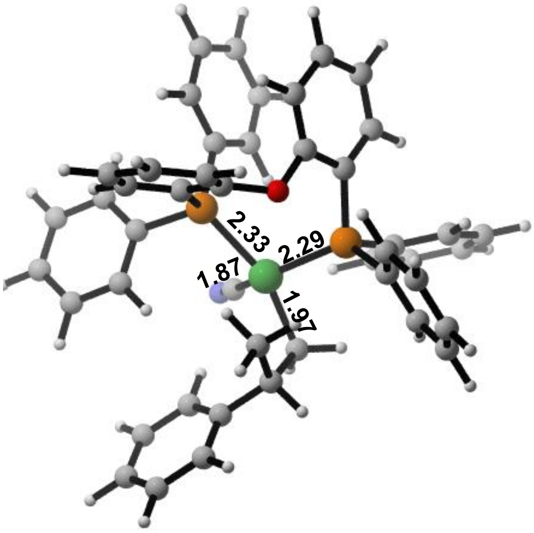

2.24
1.90
1.47
2.20
2.89
2.64

5


2.54
2.33
1.86
1.93

6

Figure S5 continued



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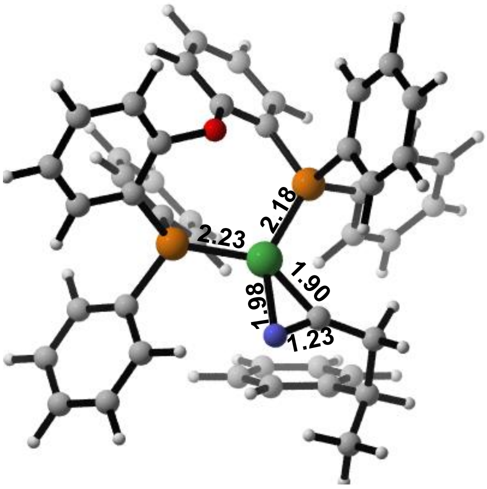

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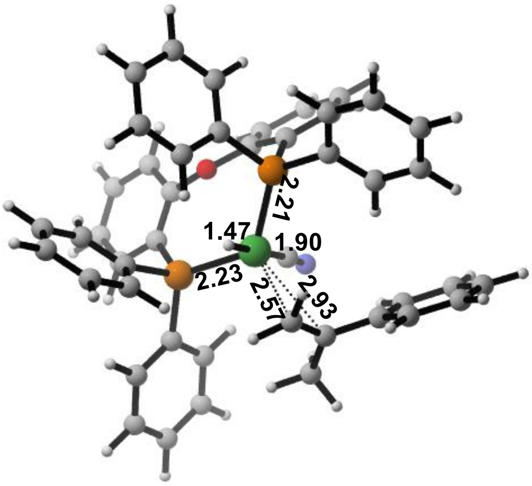

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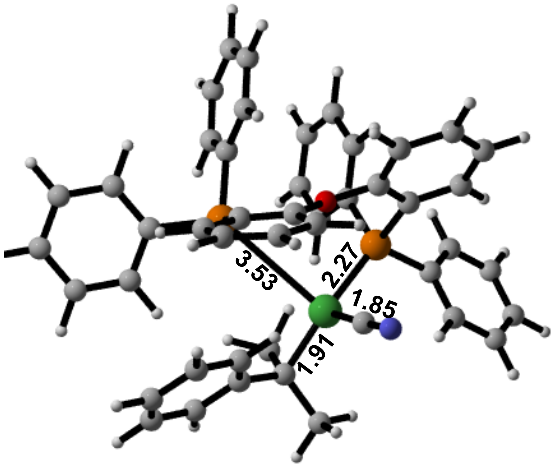

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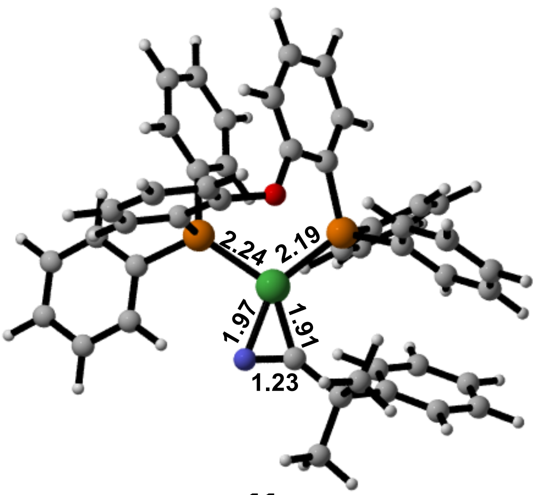

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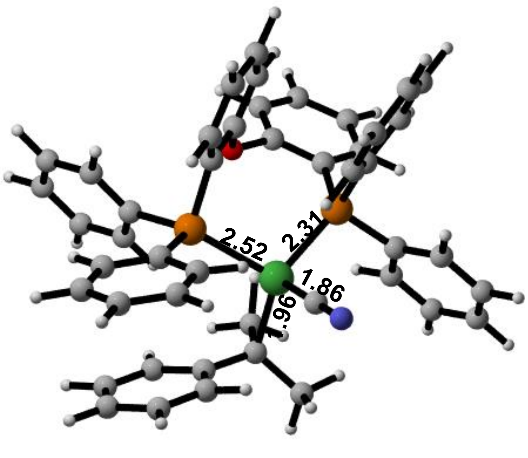
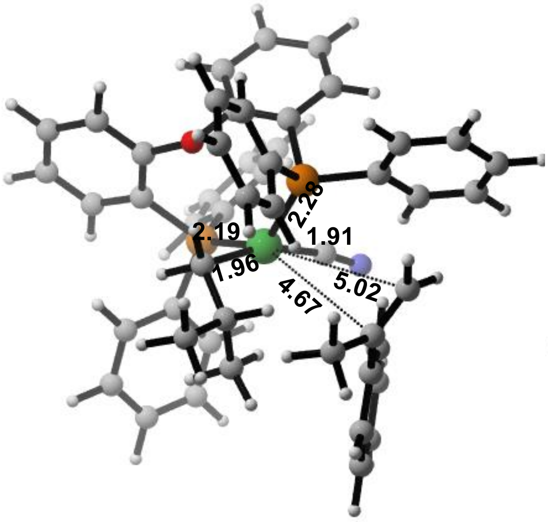


12

Figure S5 continued



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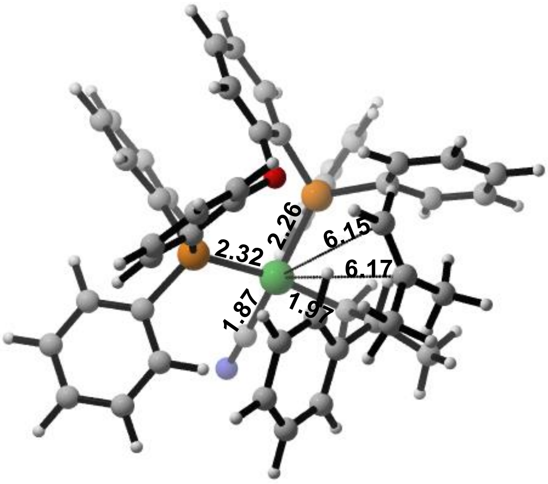

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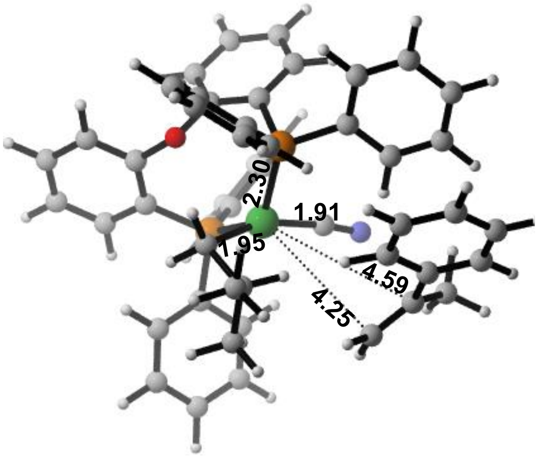

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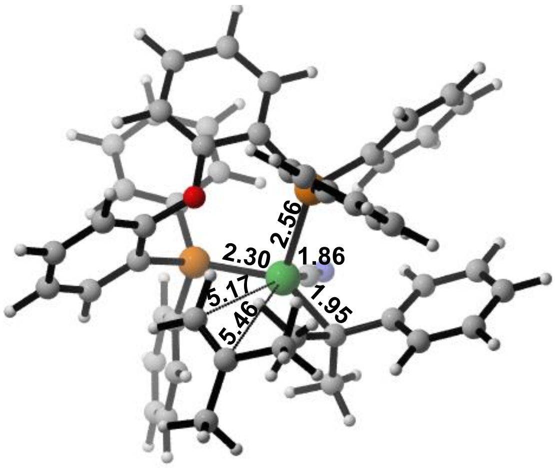

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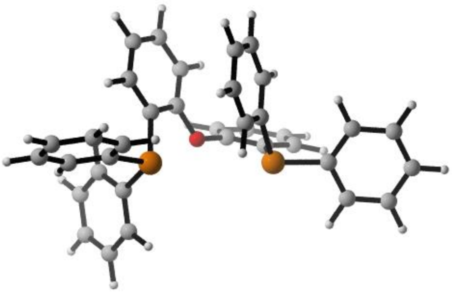

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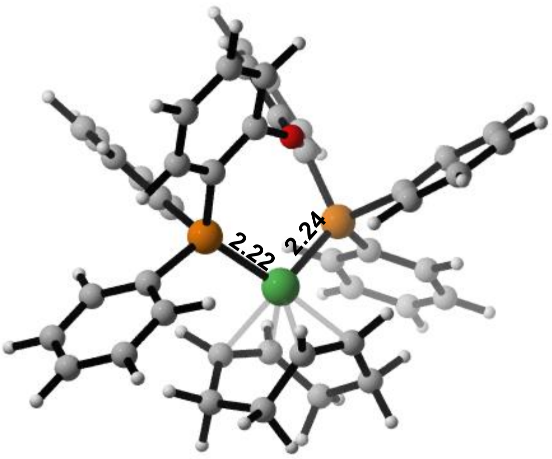
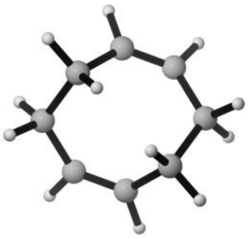
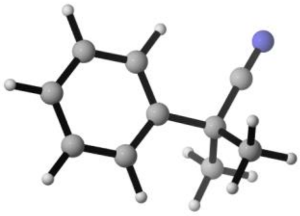


Cplx1

Figure S5 continued



COD



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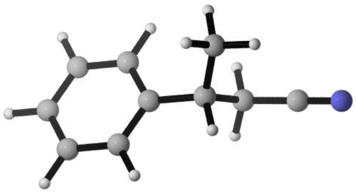
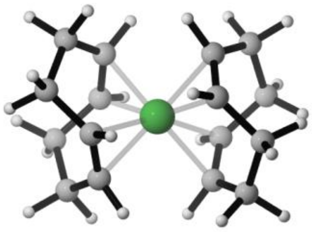
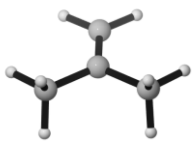


P2-B



Ni(COD)2



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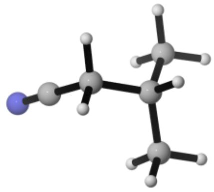

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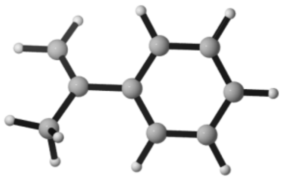

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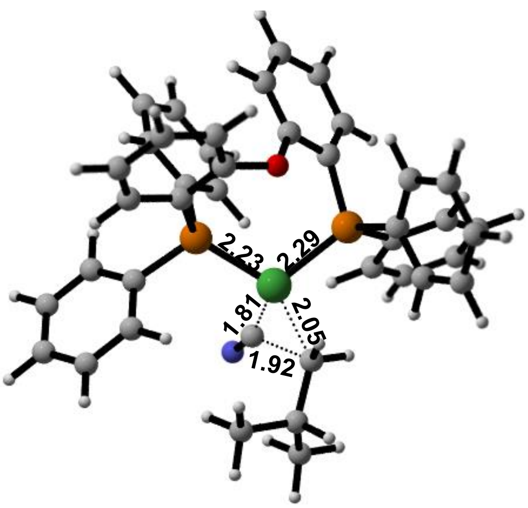

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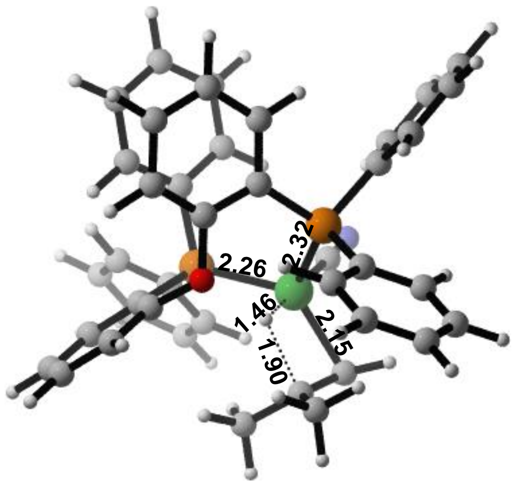
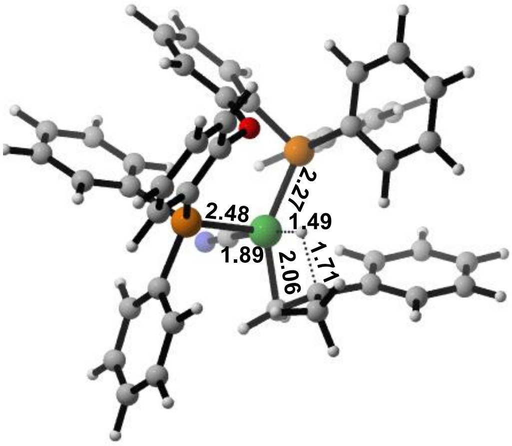


TS2-3

Figure S5 continued



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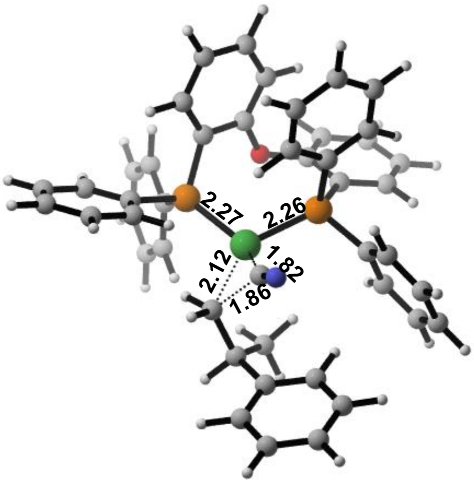
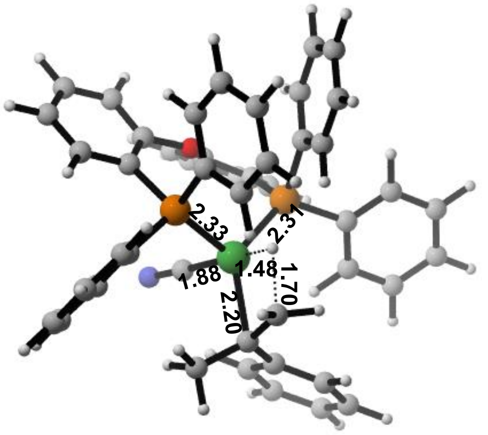
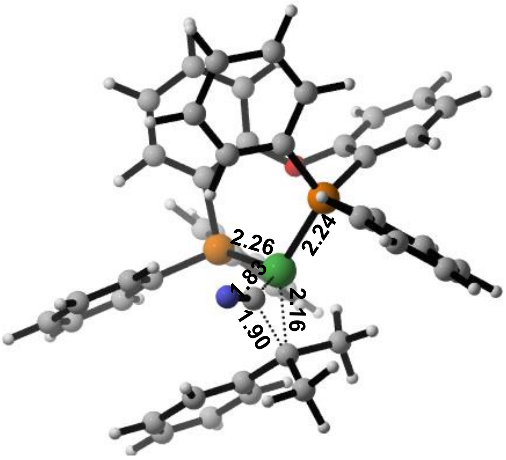


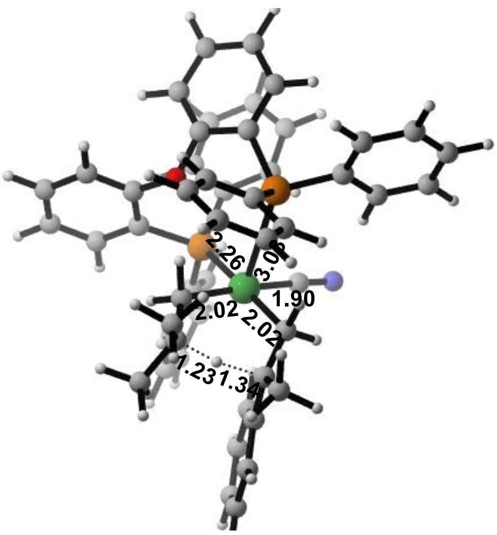
TS7-8



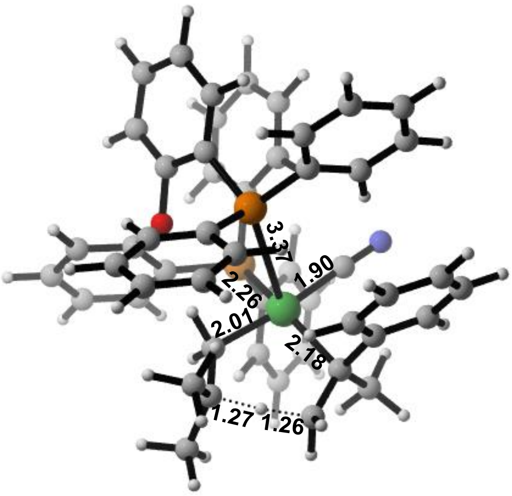
TS9-10



TS11-12

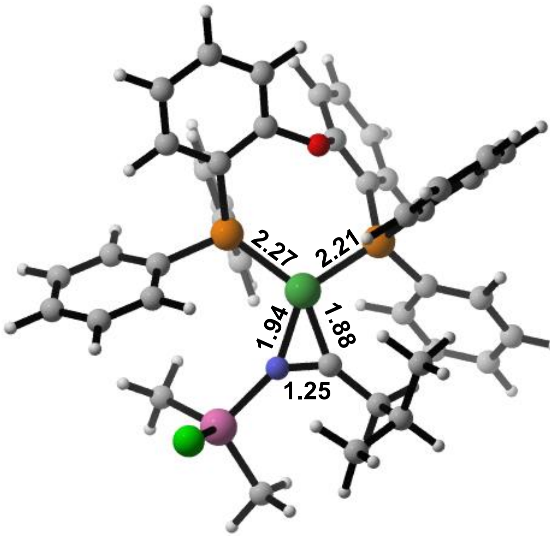


TS13-14

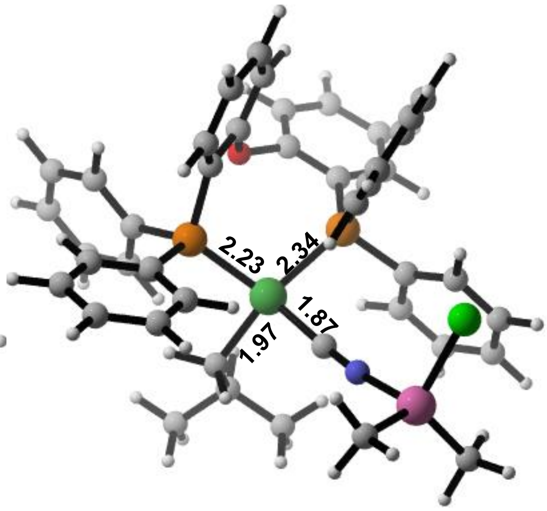


TS-15-16

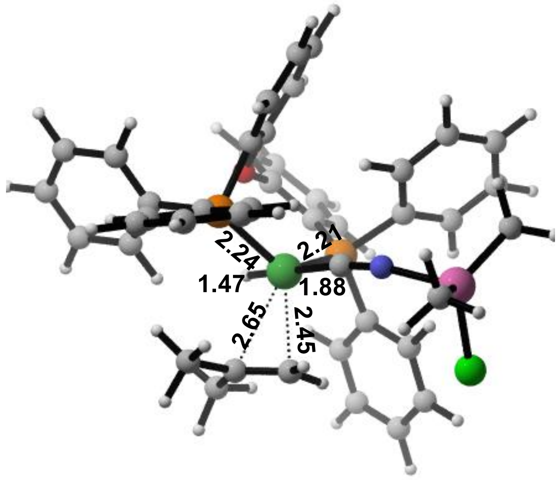
Figure S5. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the reactions without Lewis acid.



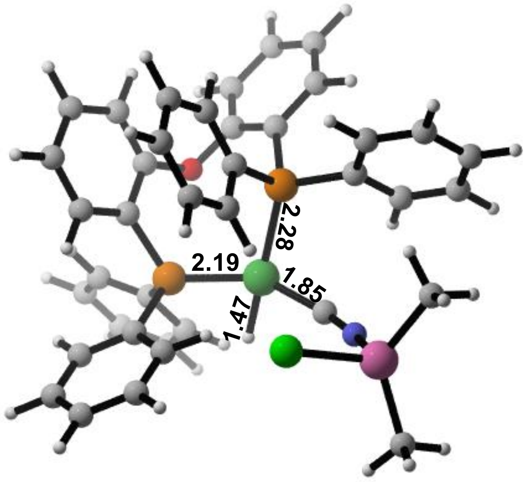
LA^{N}-1



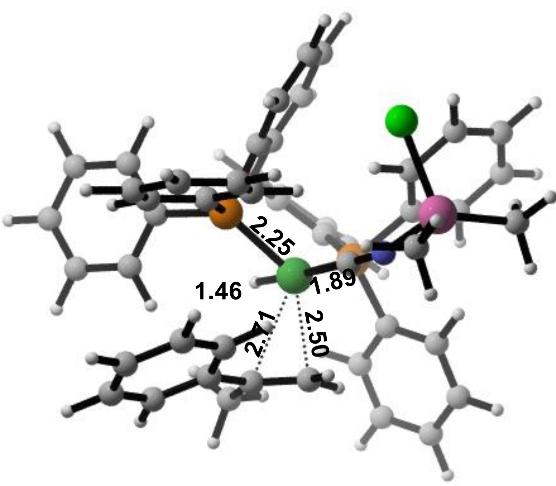
LA^{N}-2



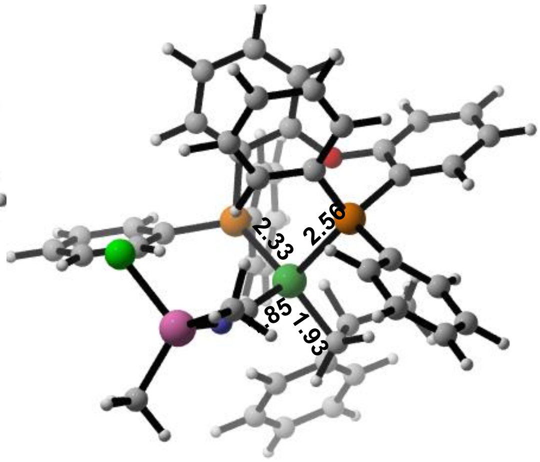
LA^{N}-3



LA^{N}-4

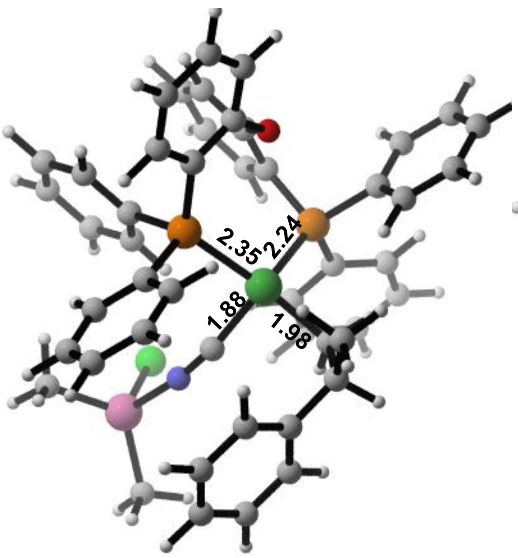


LA^{N}-5

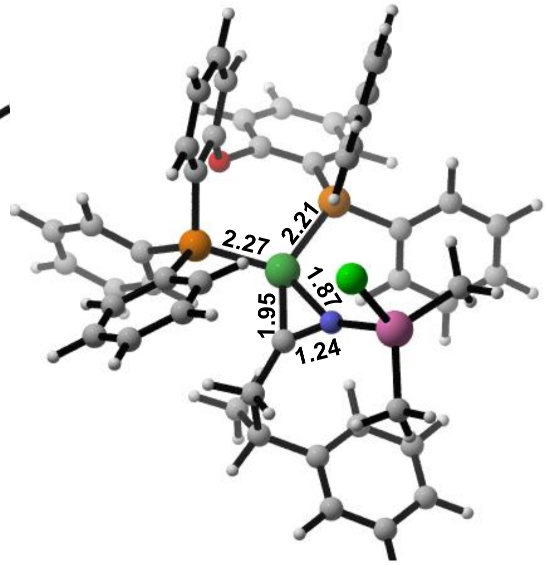


LA^{N}-6

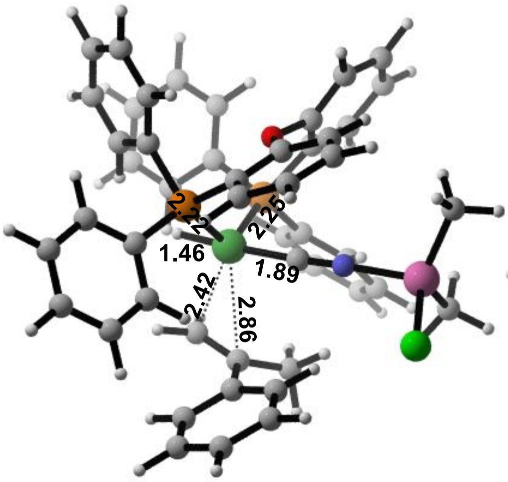
Figure S6 continued



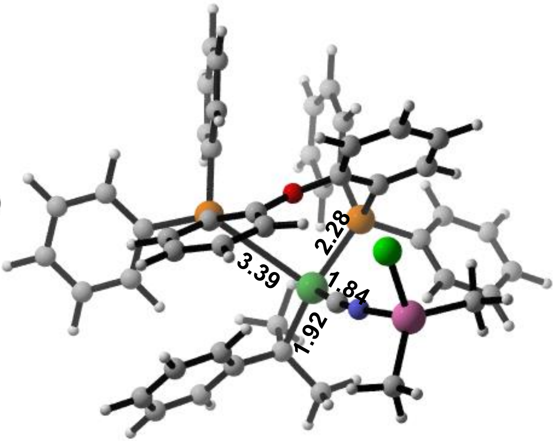
LA^{N}-7



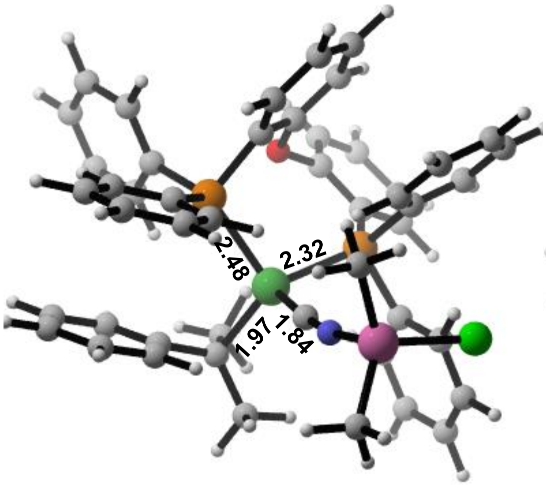
LA^{N}-8



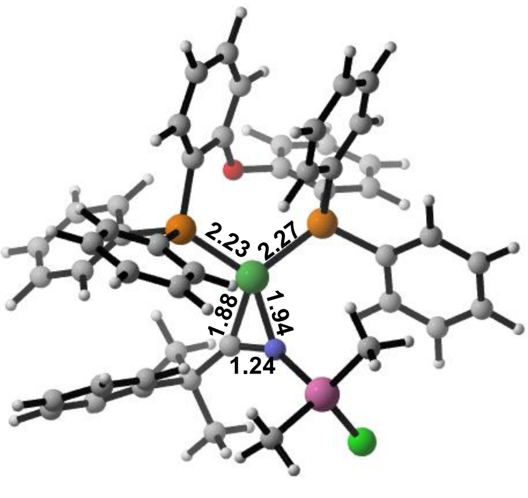
LA^{N}-9



LA^{N}-10

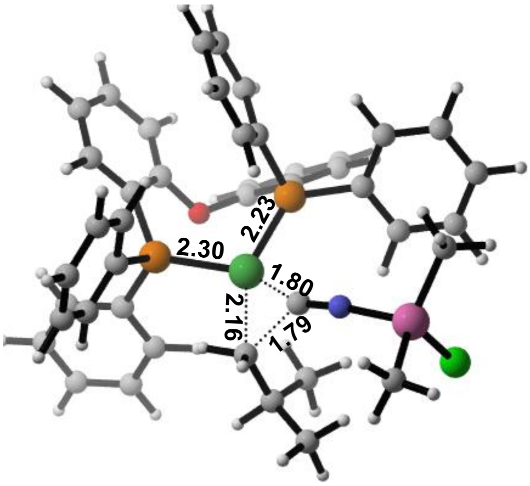


LA^{N}-11

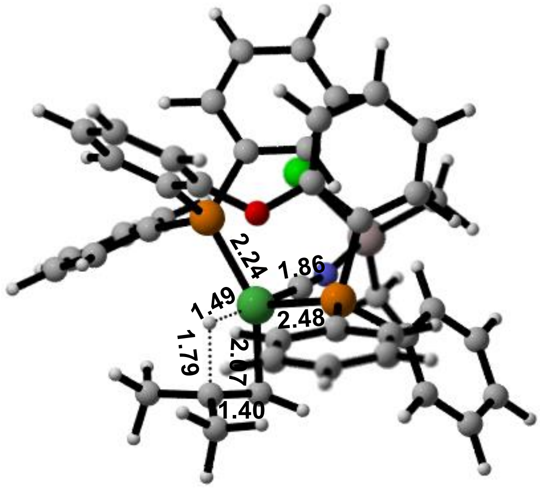


LA^{N}-12

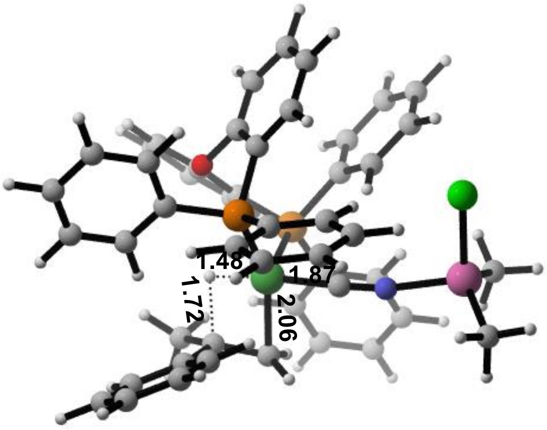
Figure S6 continued



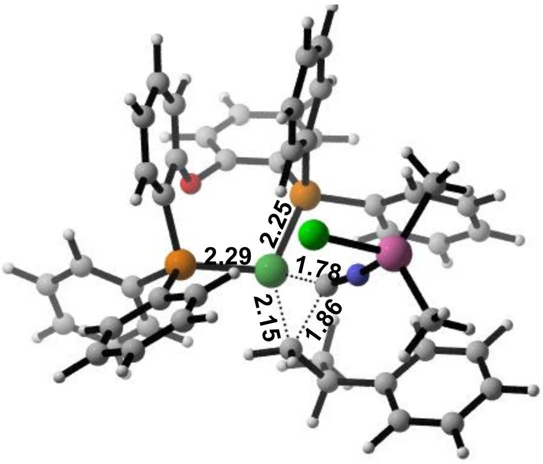
LA^{N}-TS1-2



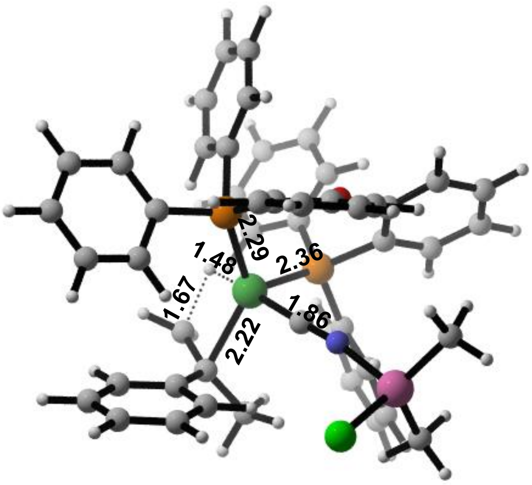
LA^{N}-TS2-3



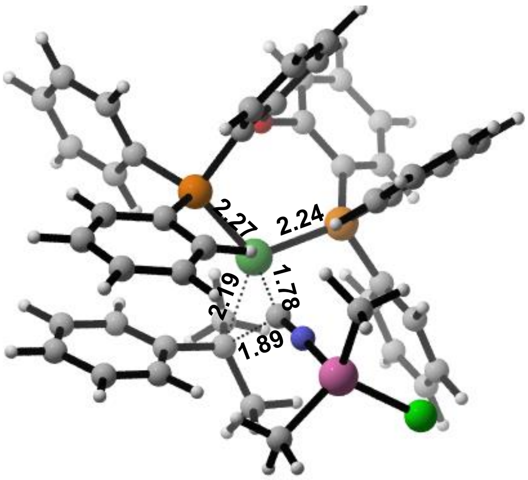
LA^{N}-TS5-6



LA^{N}-TS7-8

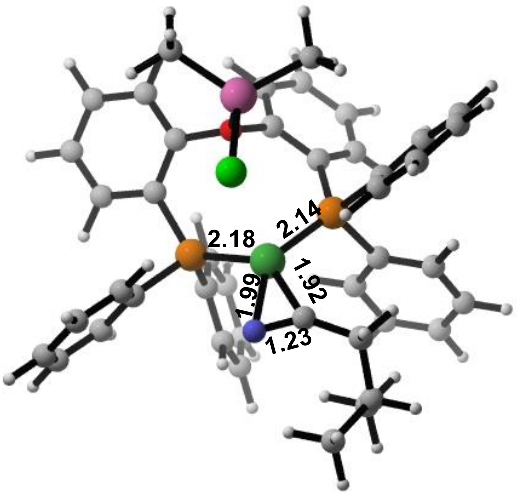


LA^{N}-TS9-10

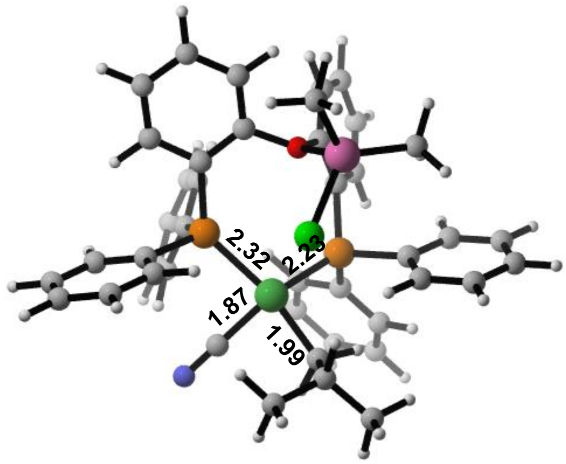


LA^{N}-TS11-12

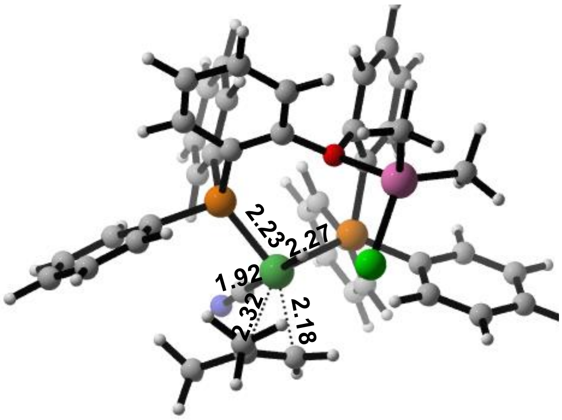
Figure S6. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the reactions with one Lewis acid bind to the N atom of nitrile.



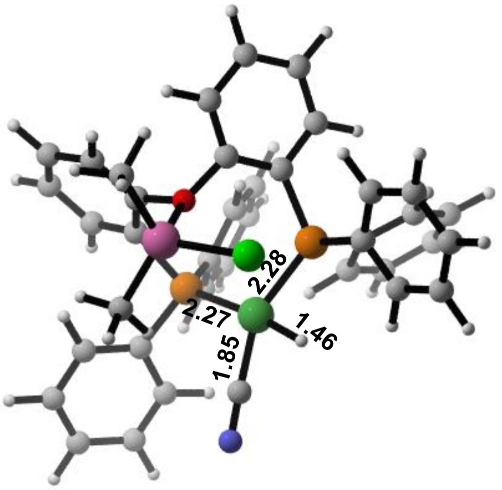
LA^{O}-1



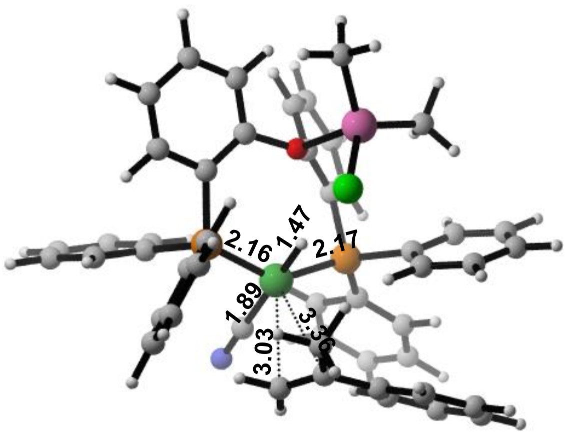
LA^{O}-2



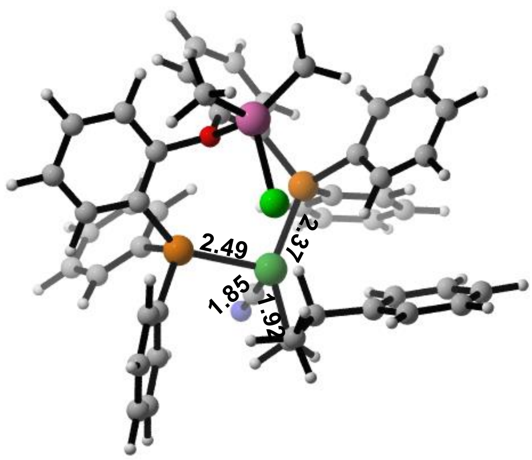
LA^{O}-3



LA^{O}-4

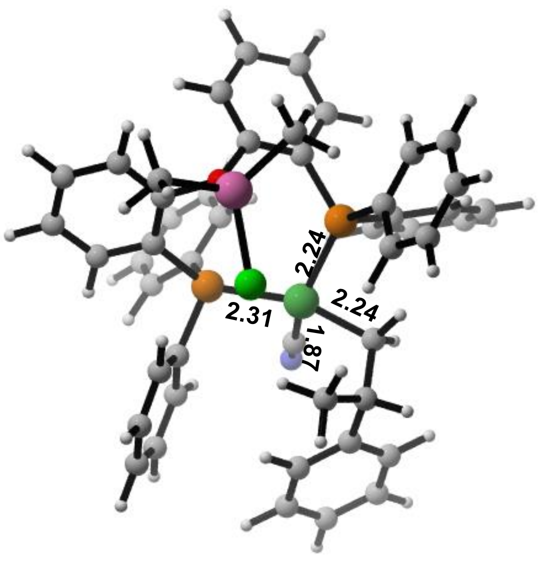


LA^{O}-5

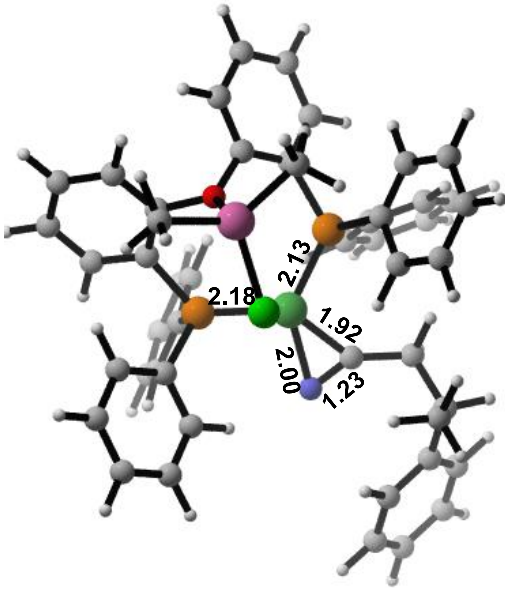


LA^{O}-6

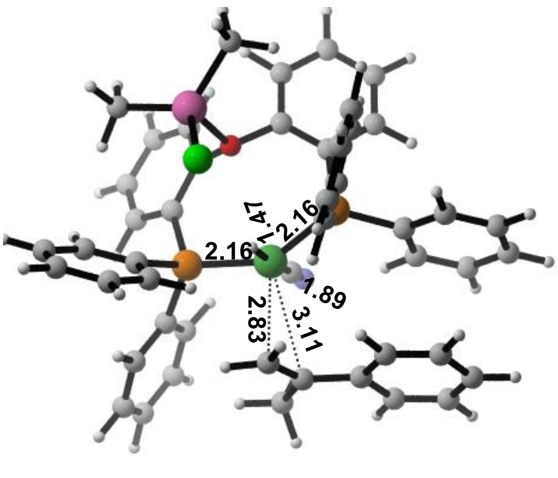
Figure S7 continued



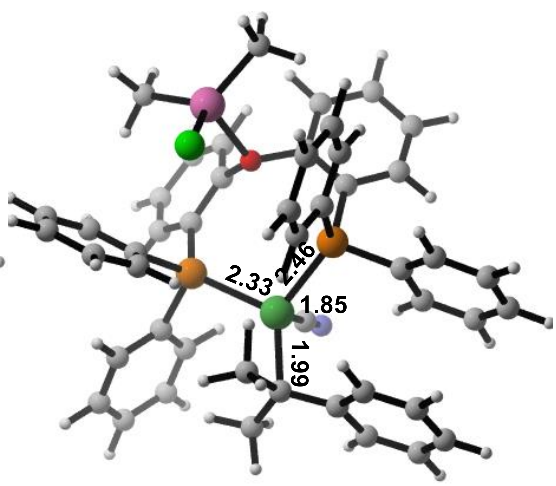
LA^{O}-7



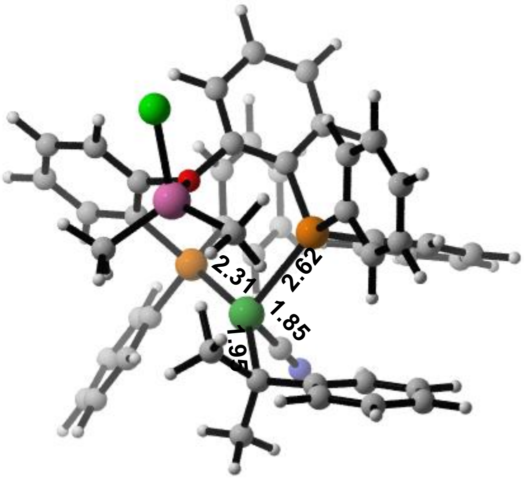
LA^{O}-8



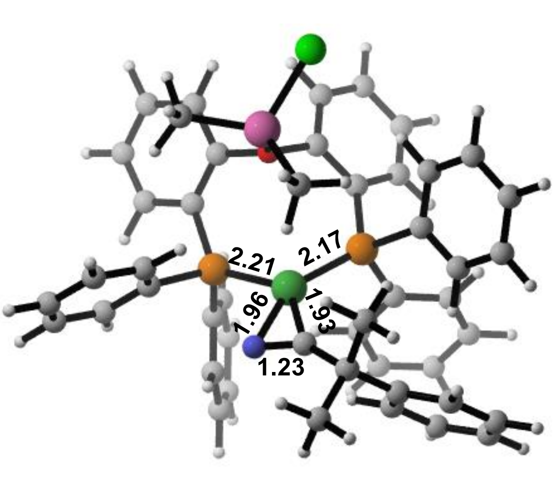
LA^{O}-9



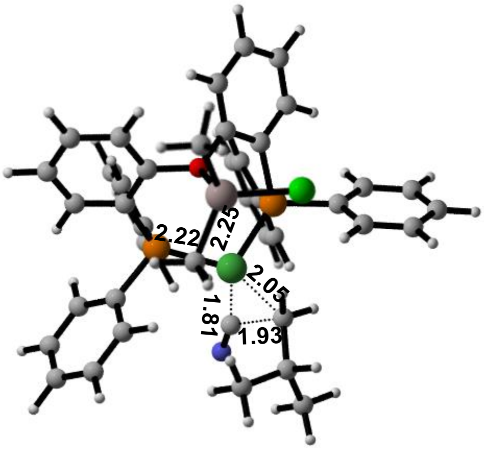
LA^{O}-10



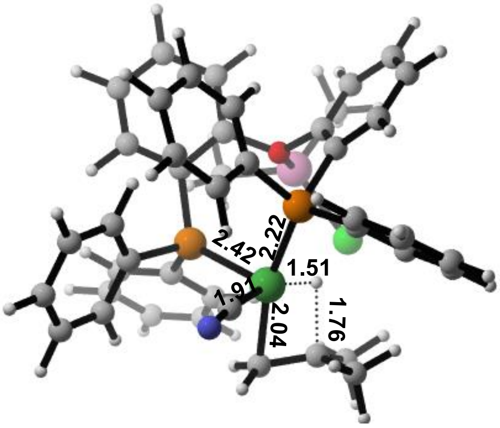
LA^{O}-11



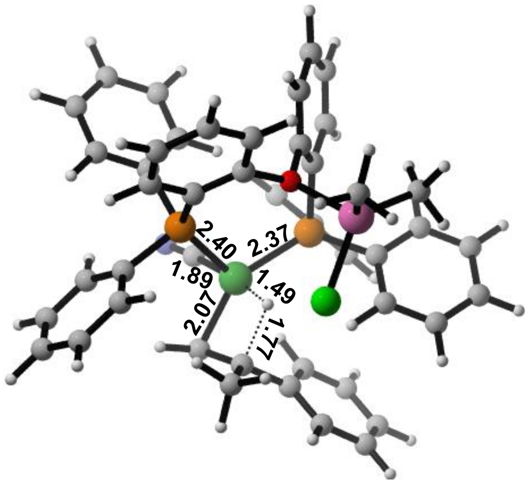
LA^{O}-12



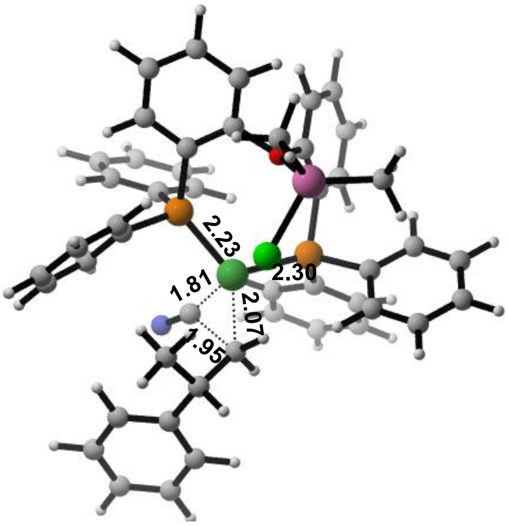
LA^{O}-TS1-2



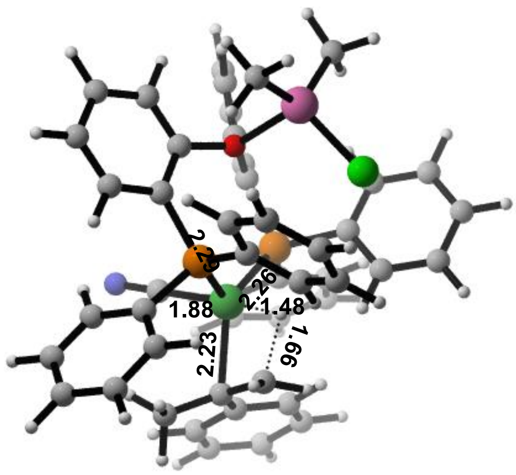
LA^{O}-TS2-3



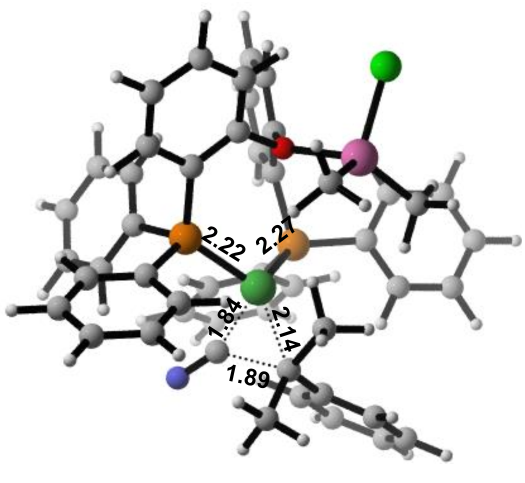
LA^{O}-TS5-6



LA^{O}-TA7-8

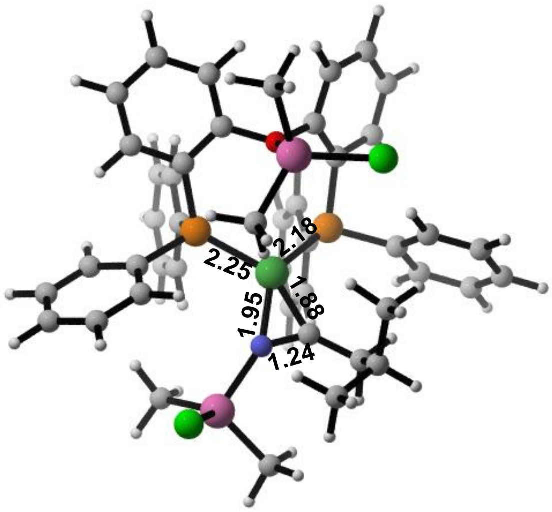


LA^{O}-TS9-10

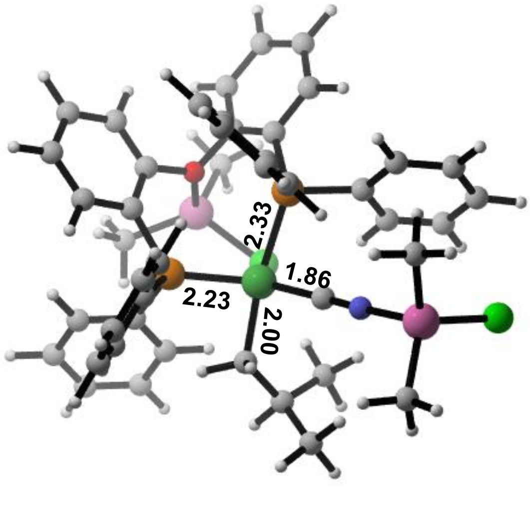


LA^{O}-TS11-12

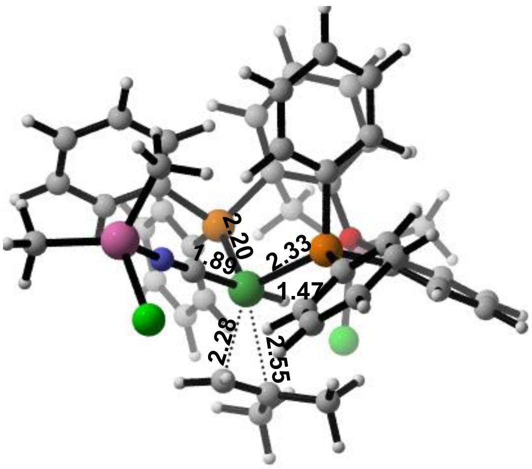
Figure S7. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the reactions withone Lewis acid bind to the O atom of the ligand.



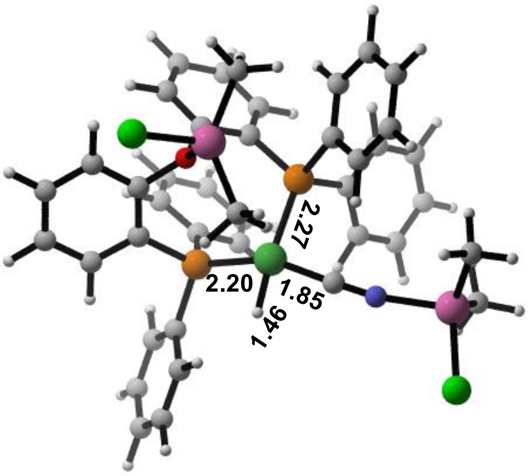
2LA-1



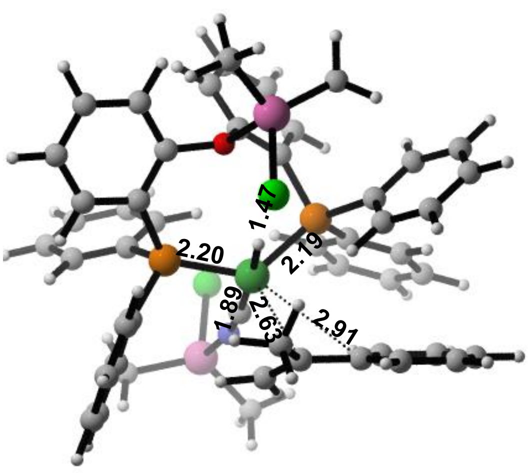
2LA-2



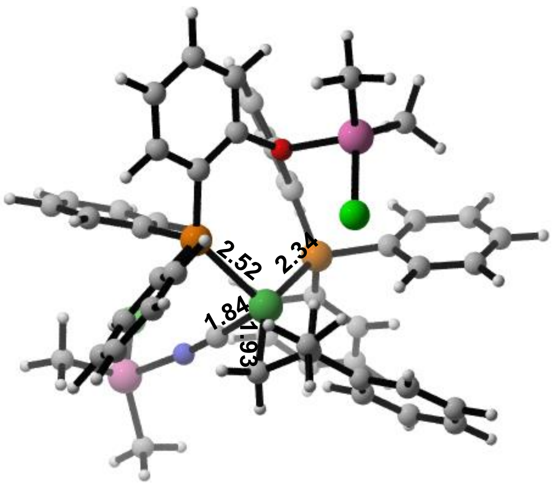
2LA-3



2LA-4

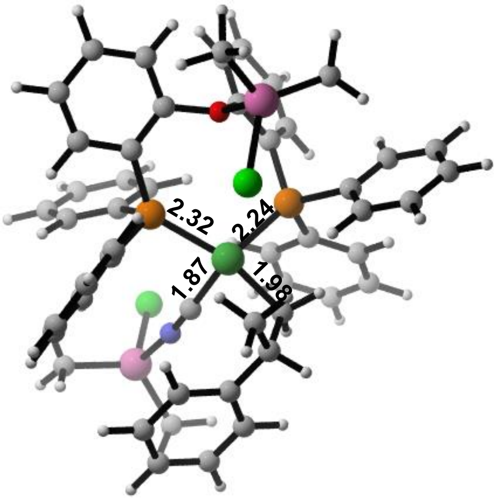


2LA-5

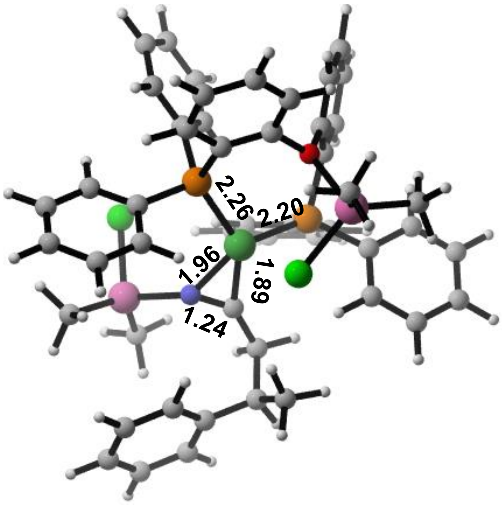


2LA-6

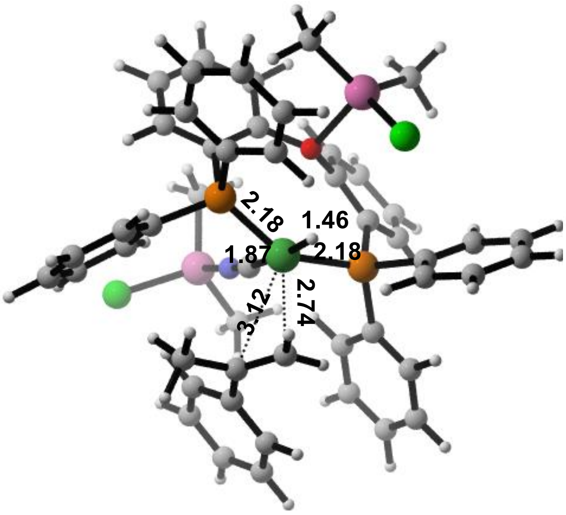
Figure S8 continued



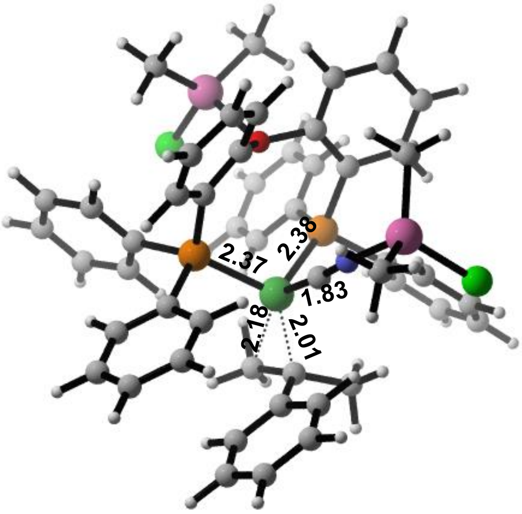
2LA-7



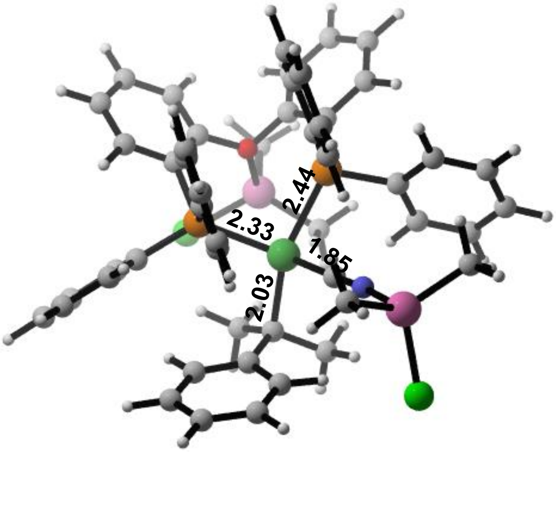
2LA-8



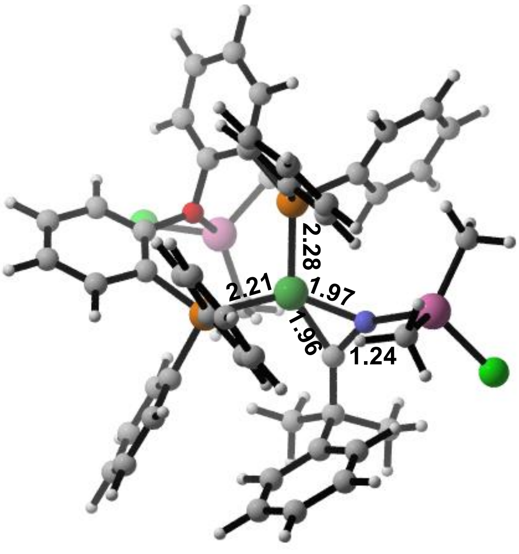
2LA-9



2LA-10

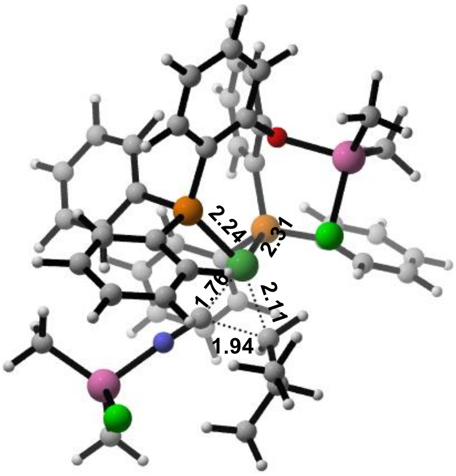


2LA-11

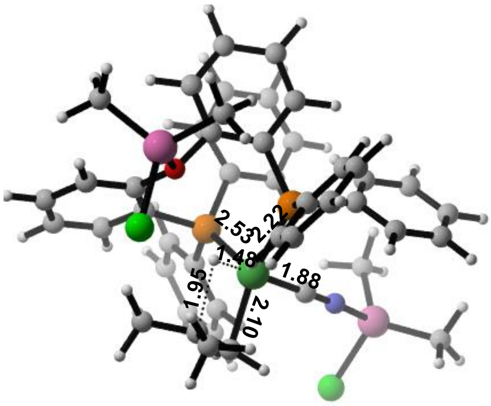


2LA-12

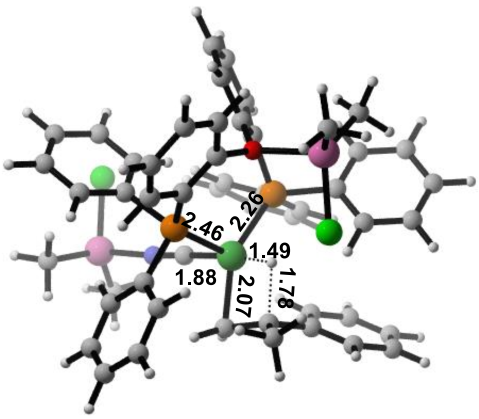
Figure S8 continued



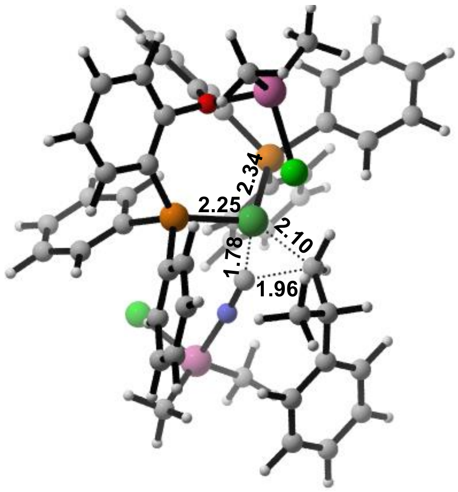
2LA-TS1-2



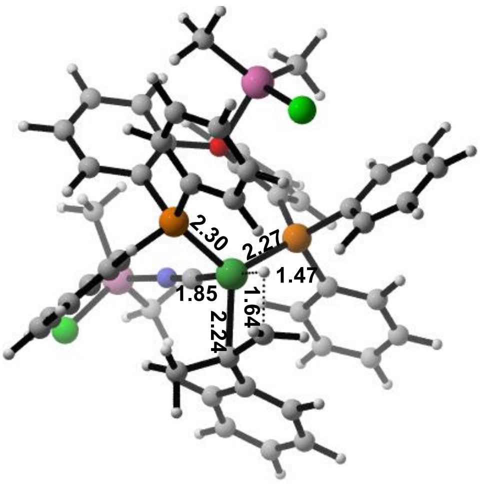
2LA-TS2-3



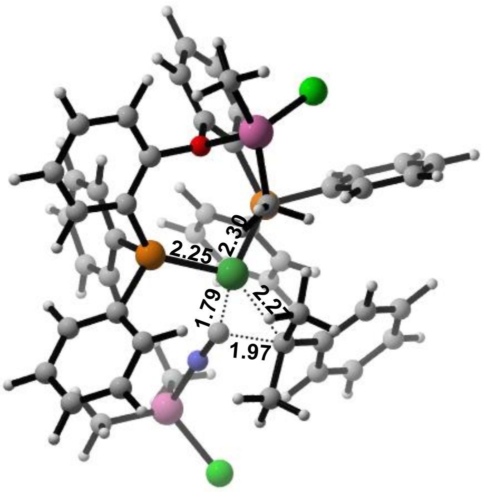
2LA-TS5-6



2LA-TS7-8

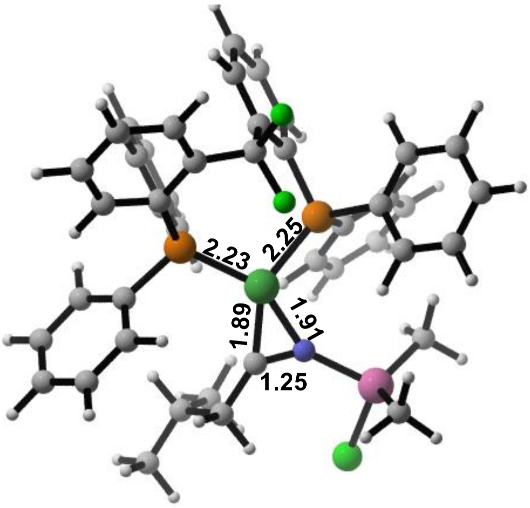


2LA-TS9-10

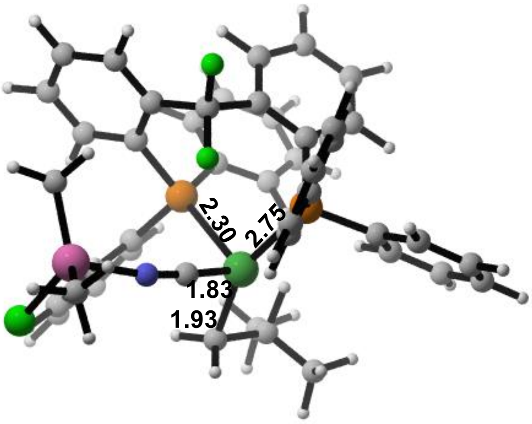


2LA-TS11-12

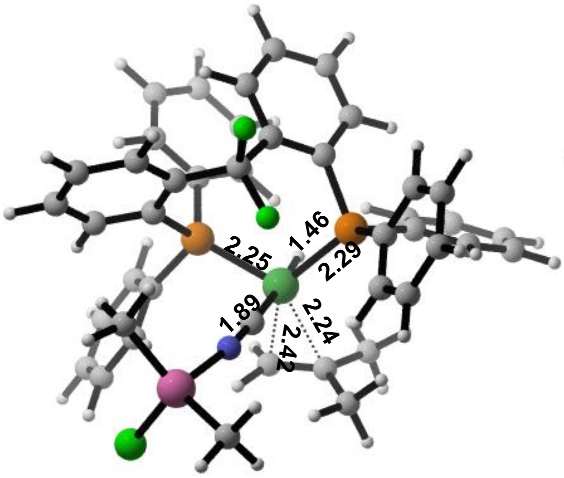
Figure S8. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the reactions with two molecular of Lewis acids bind to the N atom of the nitrile and the O atom of the ligand.



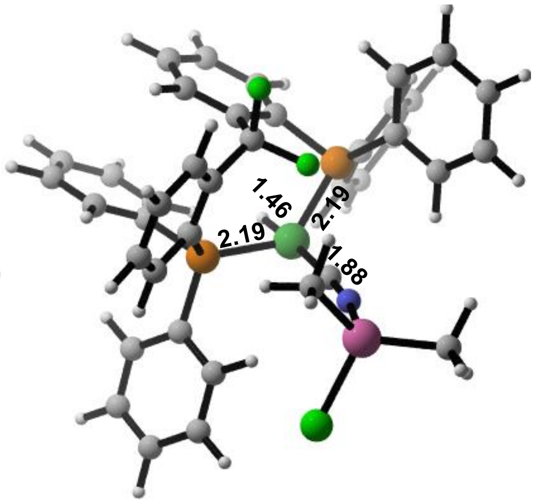
L1-LA^{N}-1



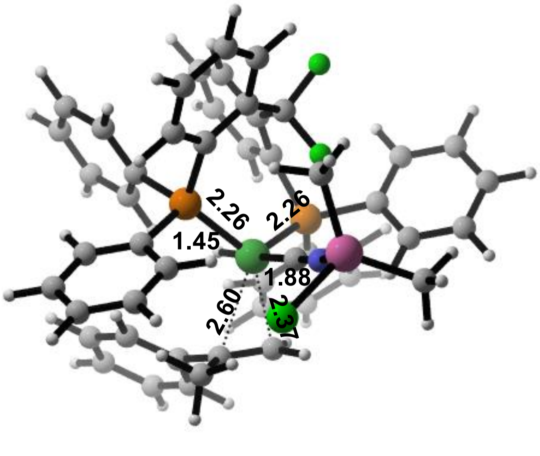
L1-LA^{N}-2



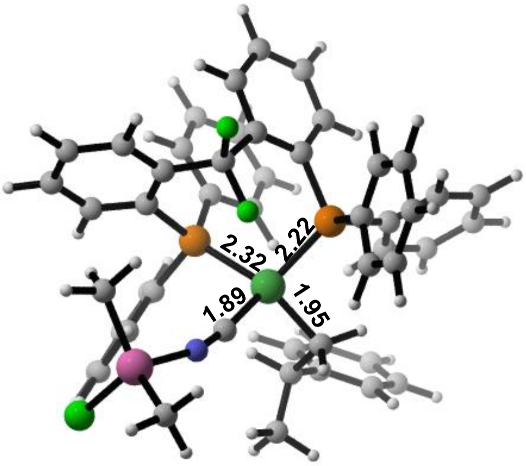
L1-LA^{N}-3



L1-LA^{N}-4

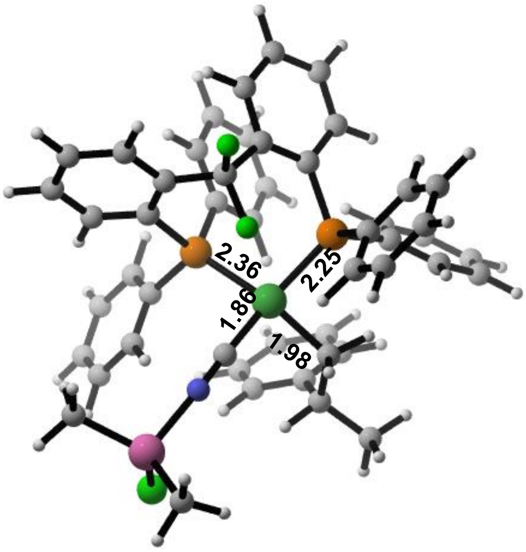


L1-LA^{N}-5

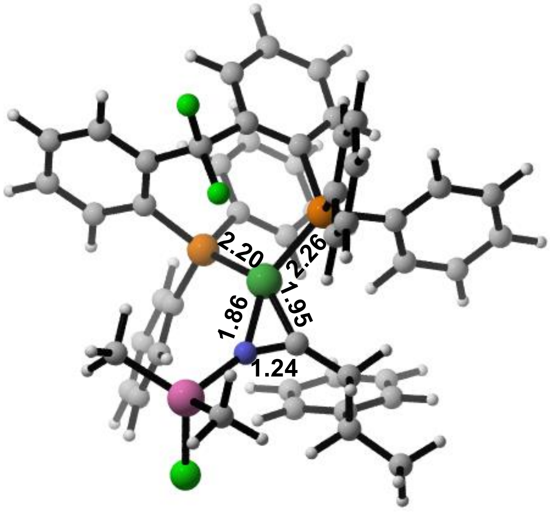


L1-LA^{N}-6

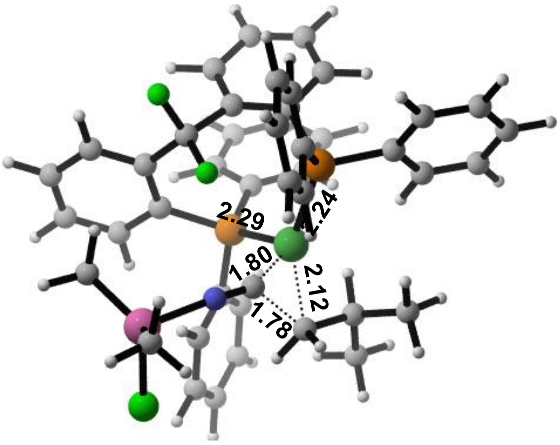
Figure S9 continued



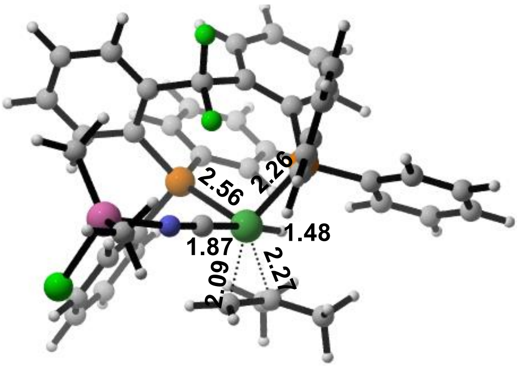
L1-LA^{N}-7



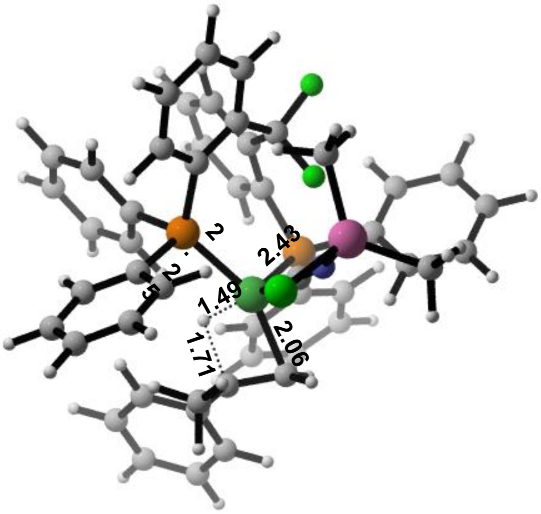
L1-LA^{N}-8



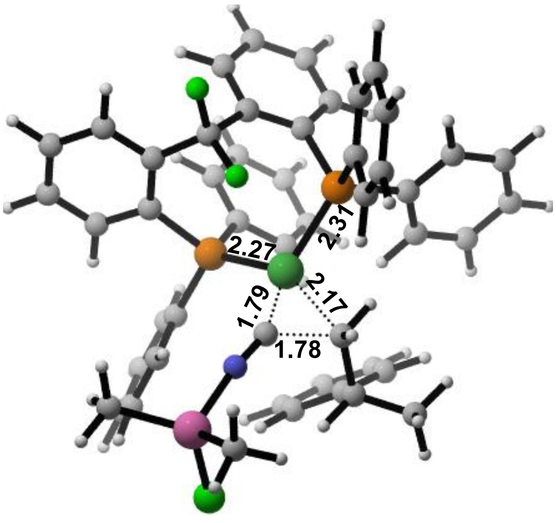
L1-LA^{N}-TS1-2



L1-LA^{N}-TS2-3

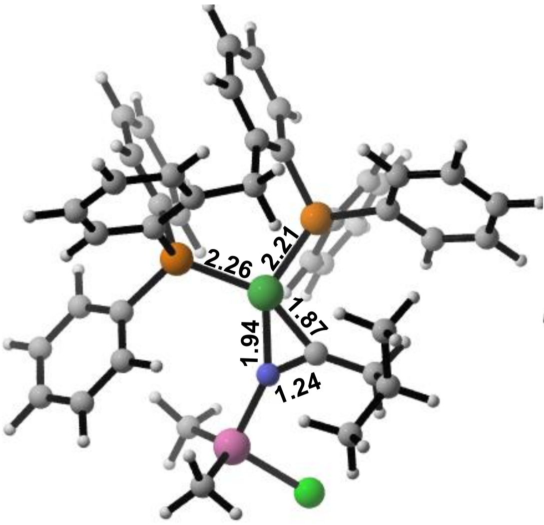


L1-LA^{N}-TS5-6

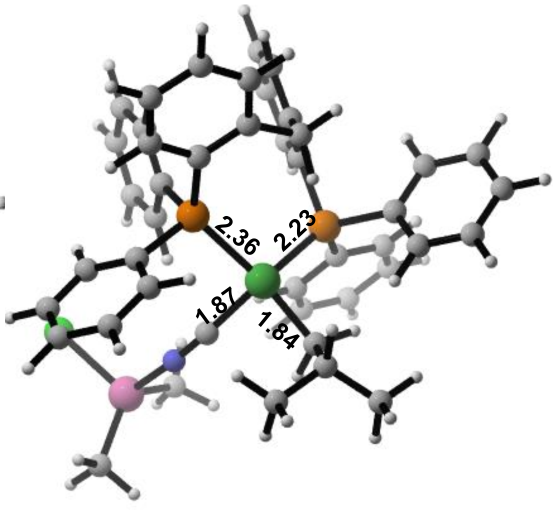


L1-LA^{N}-TS7-8

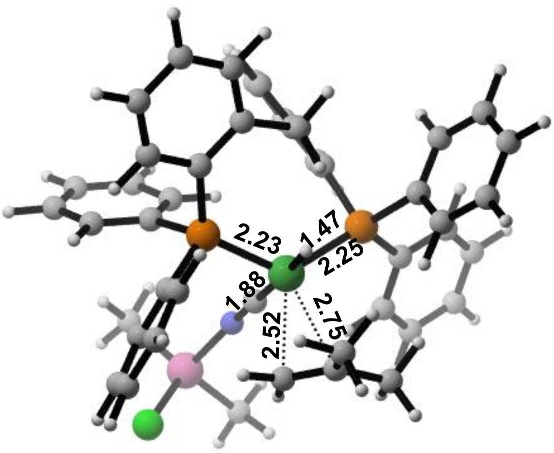
Figure S9. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the L1 catalyzed reactions.



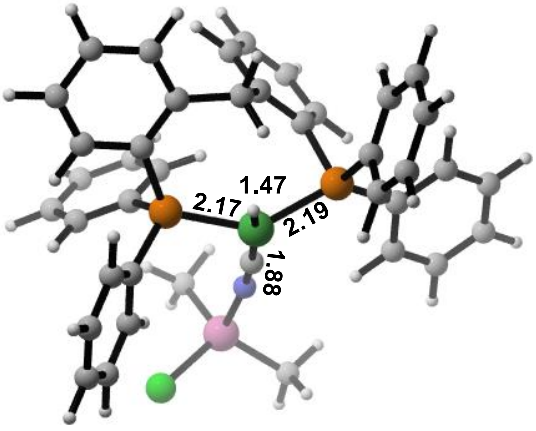
L2-LA^{N}-1



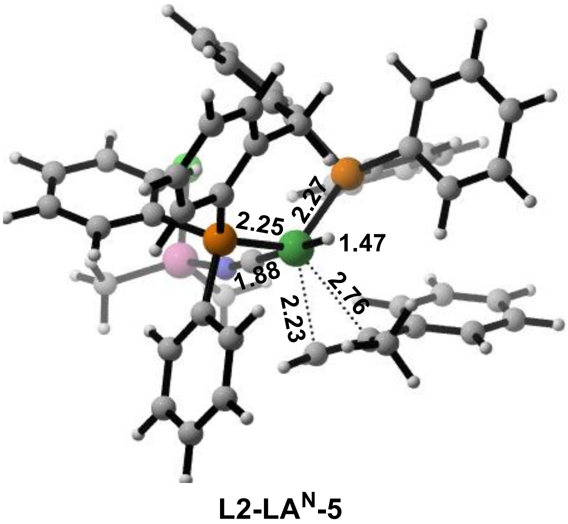
L2-LA^{N}-2



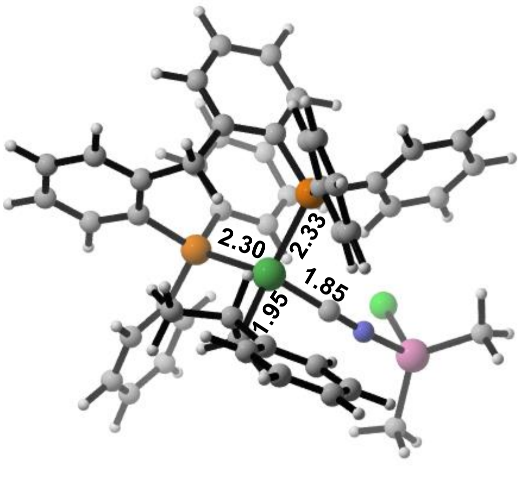
L2-LA^{N}-3



L2-LA^{N}-4

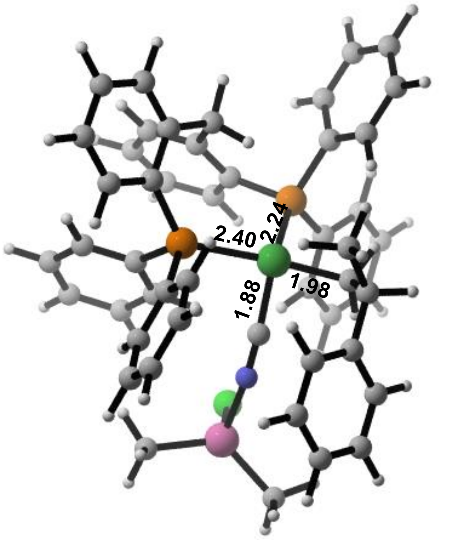


L2-LA^{N}-5

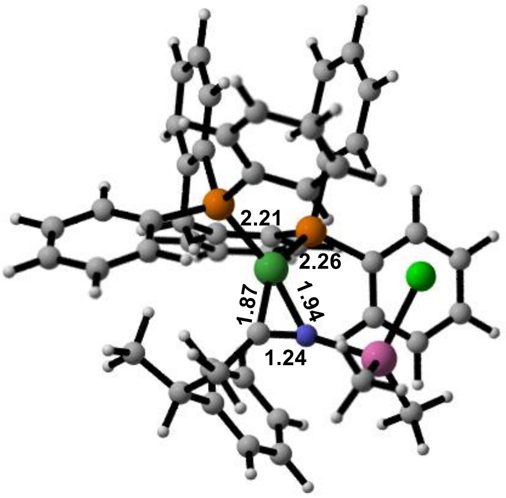


L2-LA^{N}-6

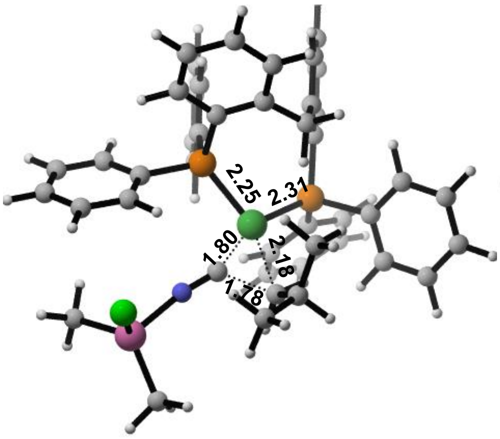
Figure S10 continued



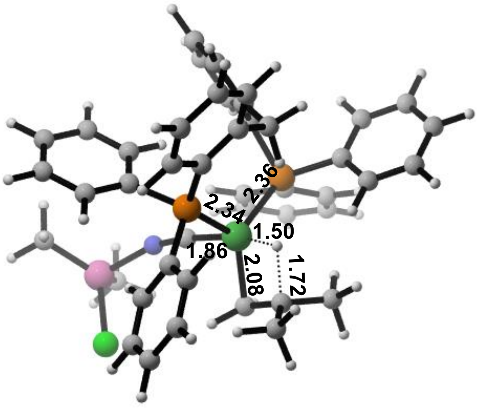
L2-LA^{N}-7



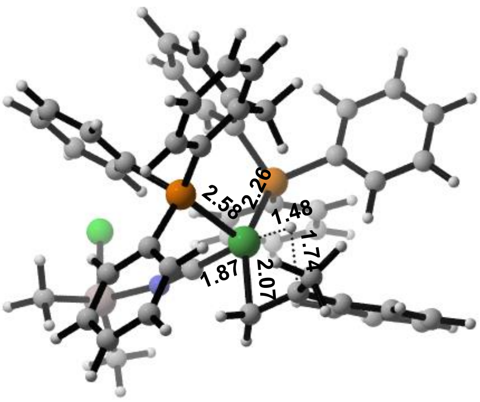
L2-LA^{N}-8



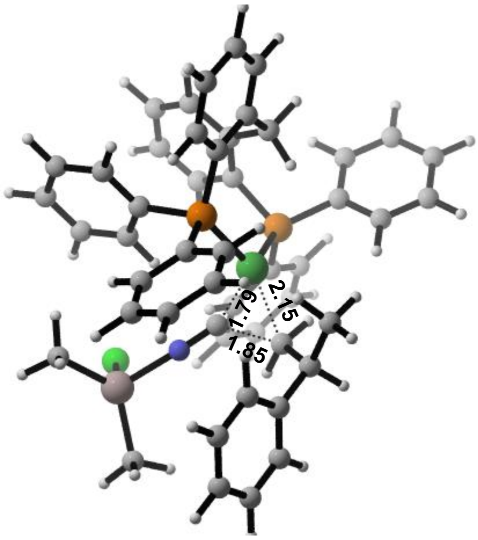
L2-LA^{N}-TS1-2



L2-LA^{N}-TS2-3

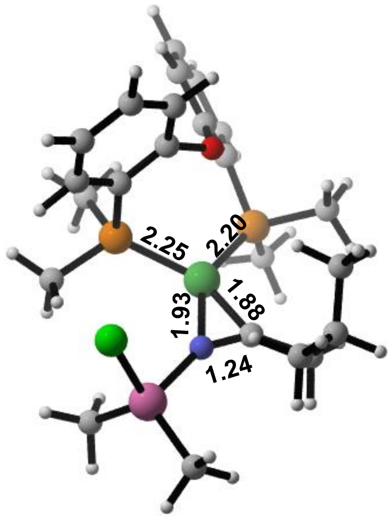


L2-LA^{N}-TS5-6

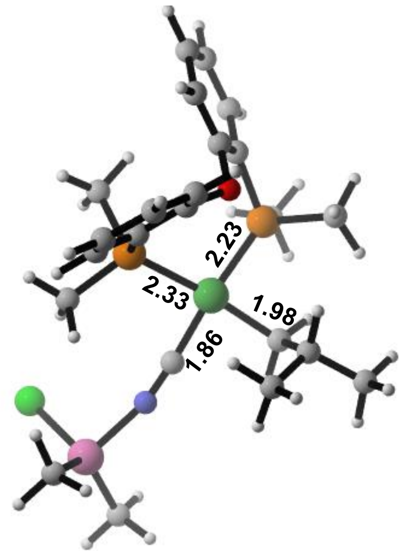


L2-LA^{N}-TS7-8

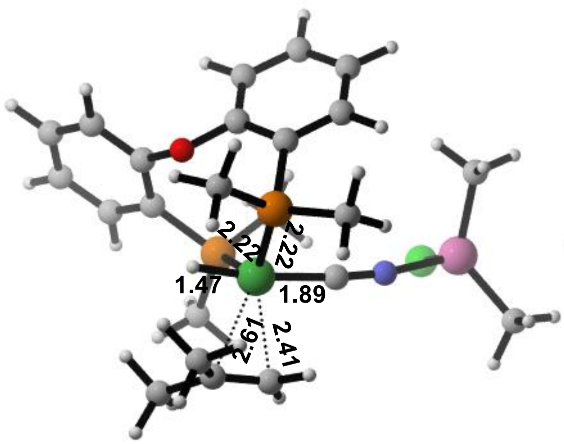
Figure S10. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the L2 catalyzed reactions.



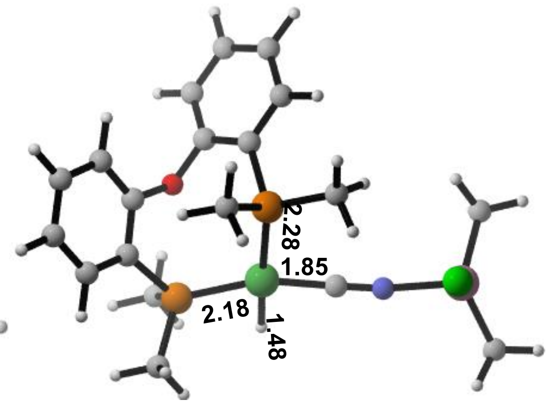
L3-LA^{N}-1



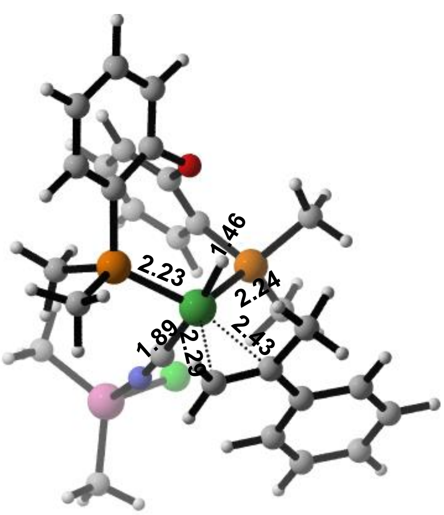
L3-LA^{N}-2



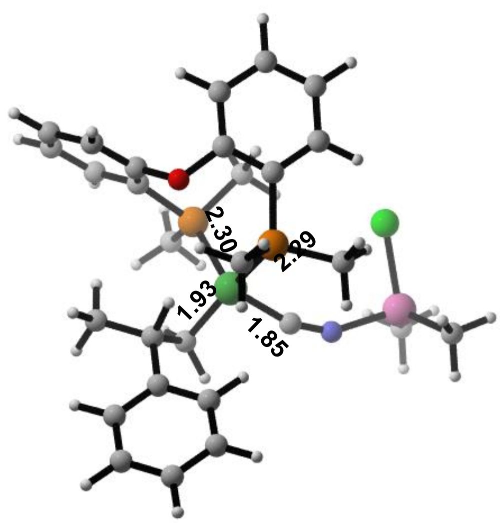
L3-LA^{N}-3



L3-LA^{N}-4

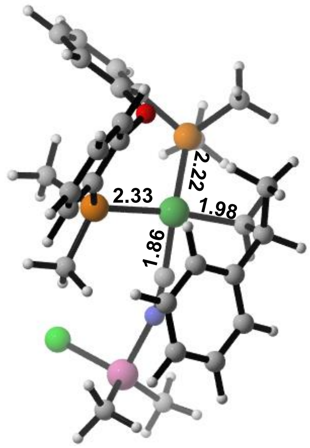


L3-LA^{N}-5

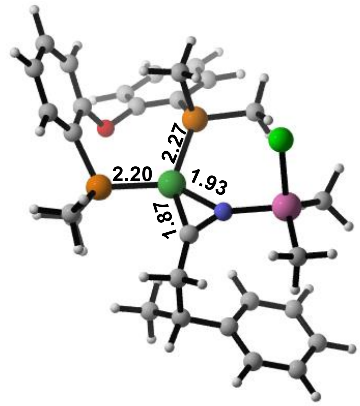


L3-LA^{N}-6

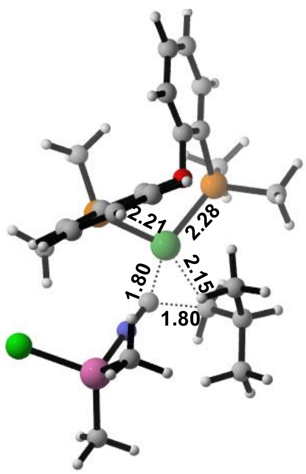
Figure S11 continued



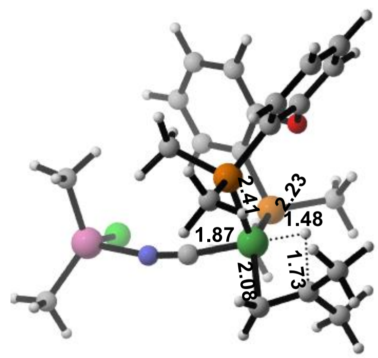
L3-LA^{N}-7



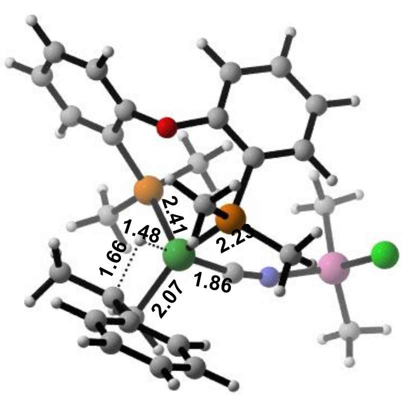
L3-LA^{N}-8



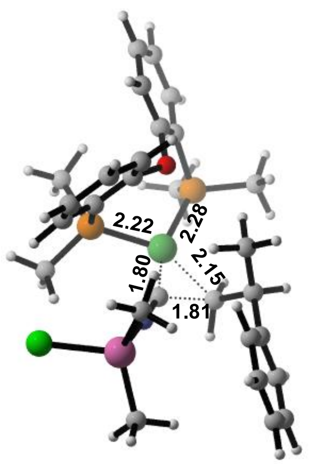
L3-LA^{N}-TS1-2



L3-LA^{N}-TS2-3



L3-LA^{N}-TS5-6



L3-LA^{N}-TS7-8

Figure S11. Optimized geometries with selected structural parameters (distances in Å) for the species involved in the L3 catalyzed reactions.