Supporting Information

Bimetallic oxidative addition in nickel-catalyzed alkyl-aryl Kumada coupling reactions

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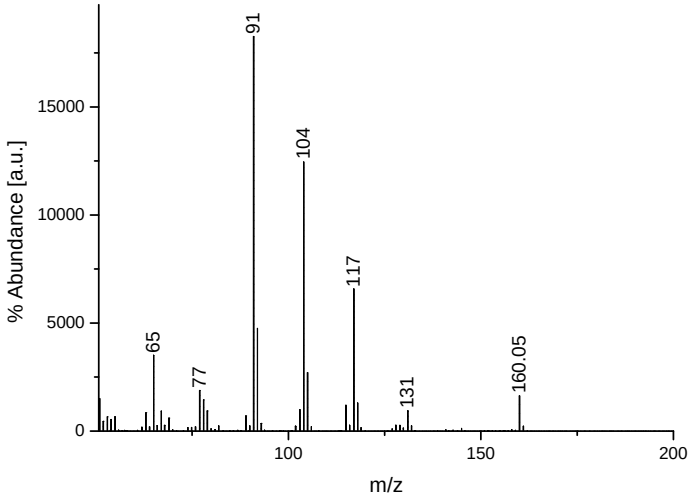


Figure S1. Mass spectrum of compound 8.

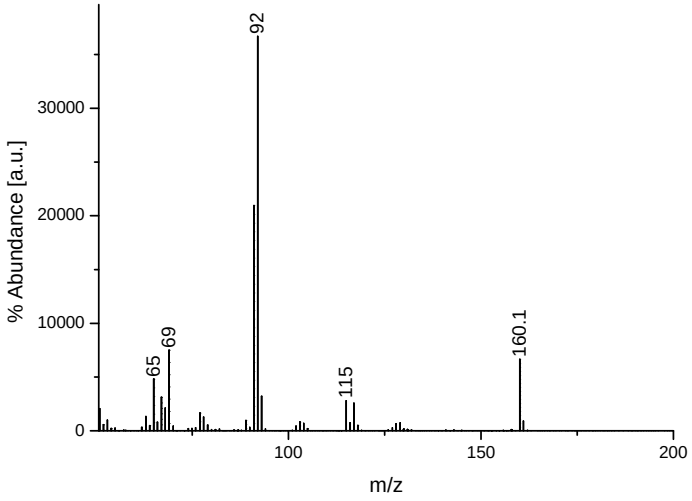


Figure S2. Mass spectrum of compound 9.

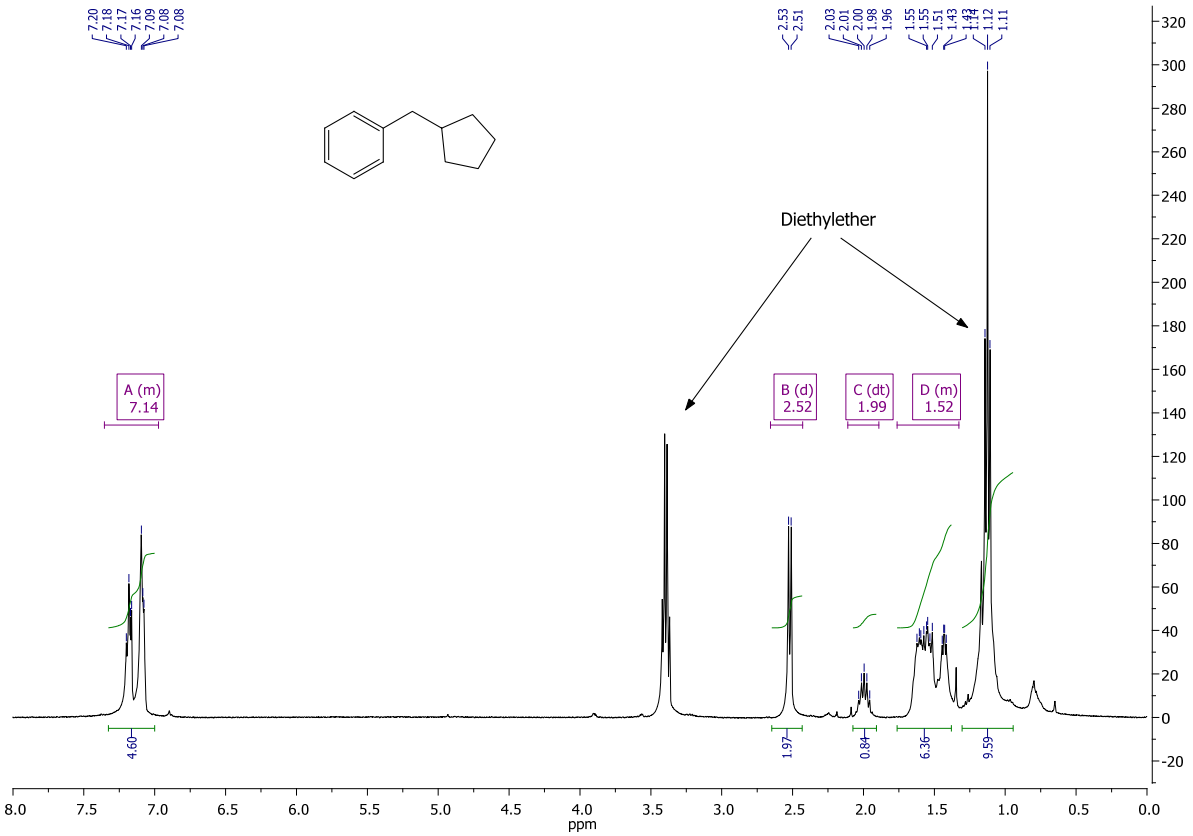


Figure S3: ^{1}H NMR ($CDCl_3$) of 9.

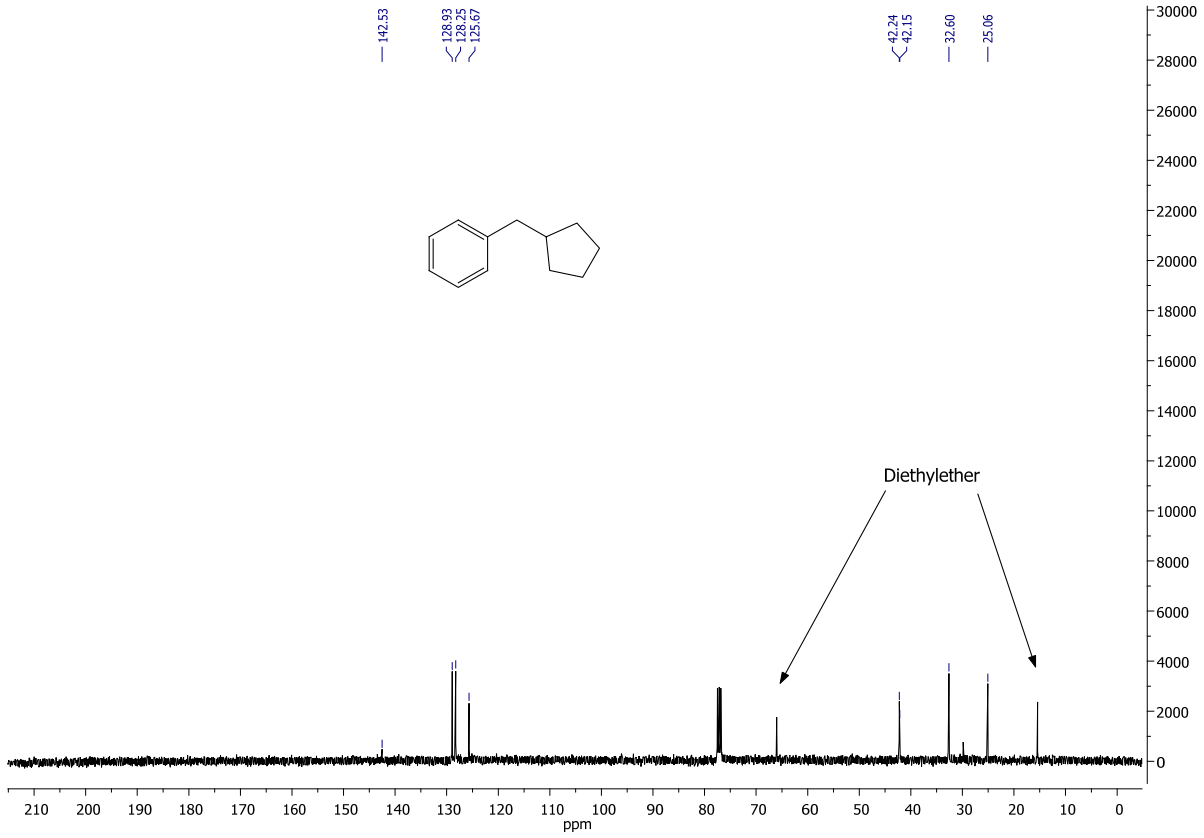


Figure S4. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of 9.

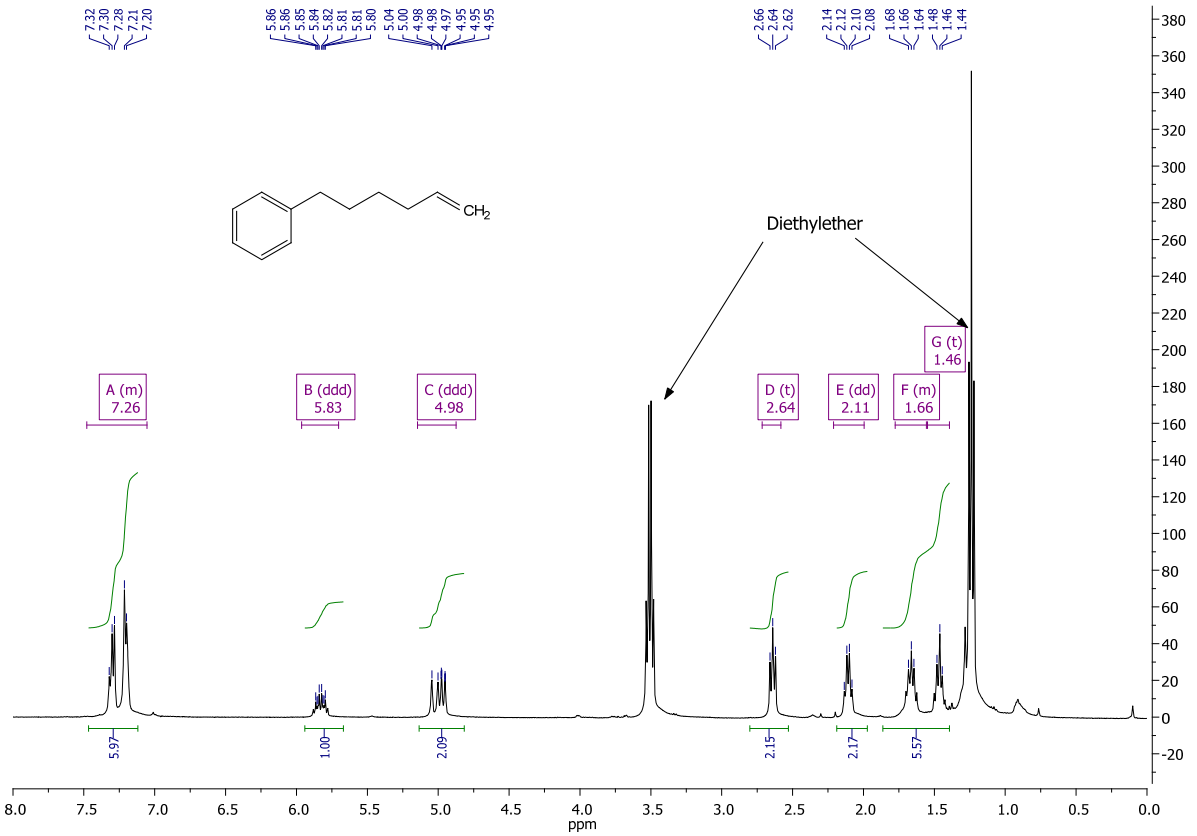


Figure S5. ^{1}H NMR ($CDCl_3$) of 8.

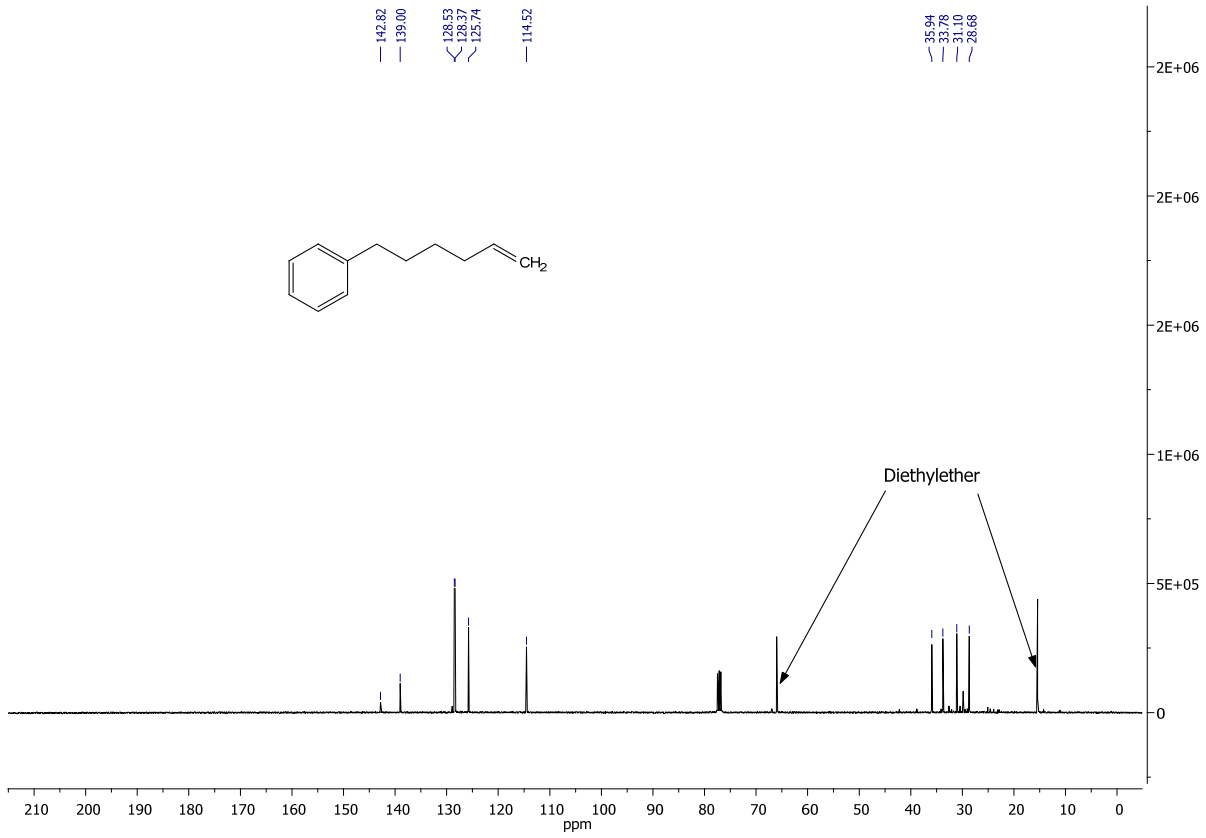


Figure S6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of 8.

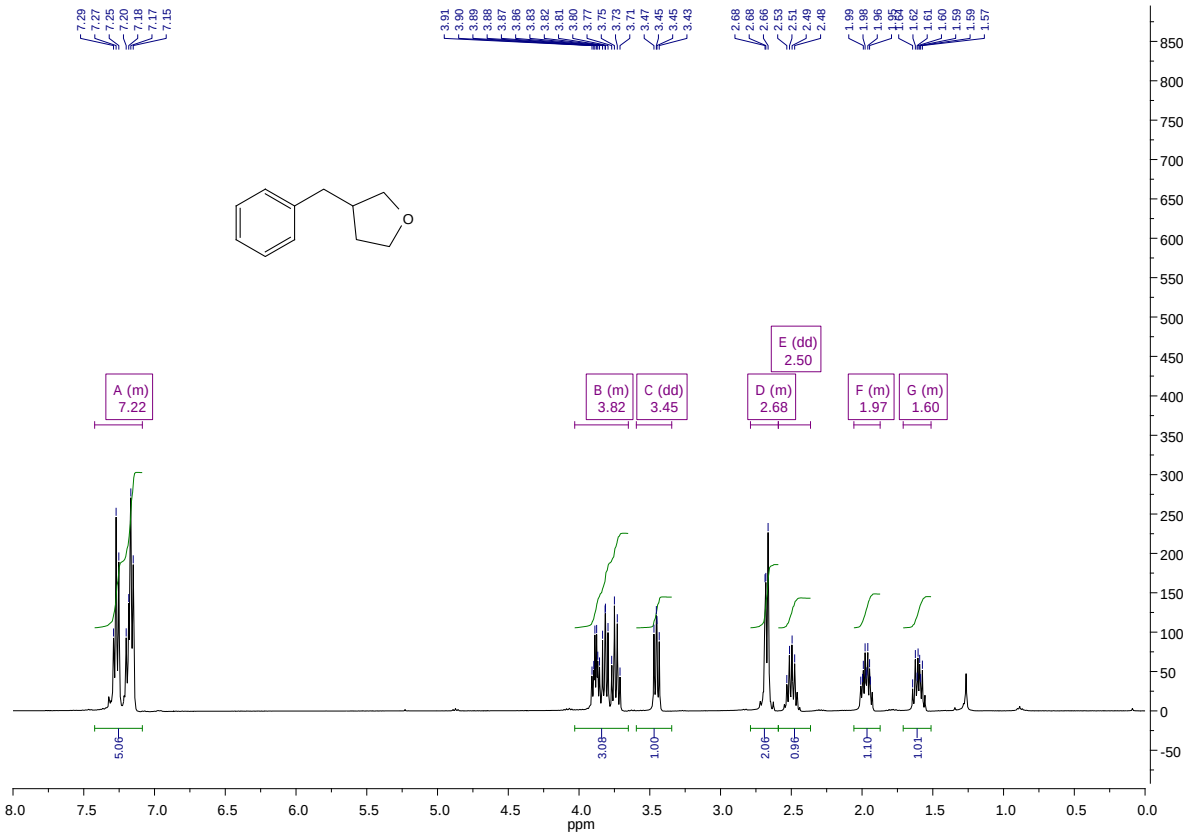


Figure S7. ^{1}H NMR ($CDCl_3$) of 3-benzyltetrahydrofuran.

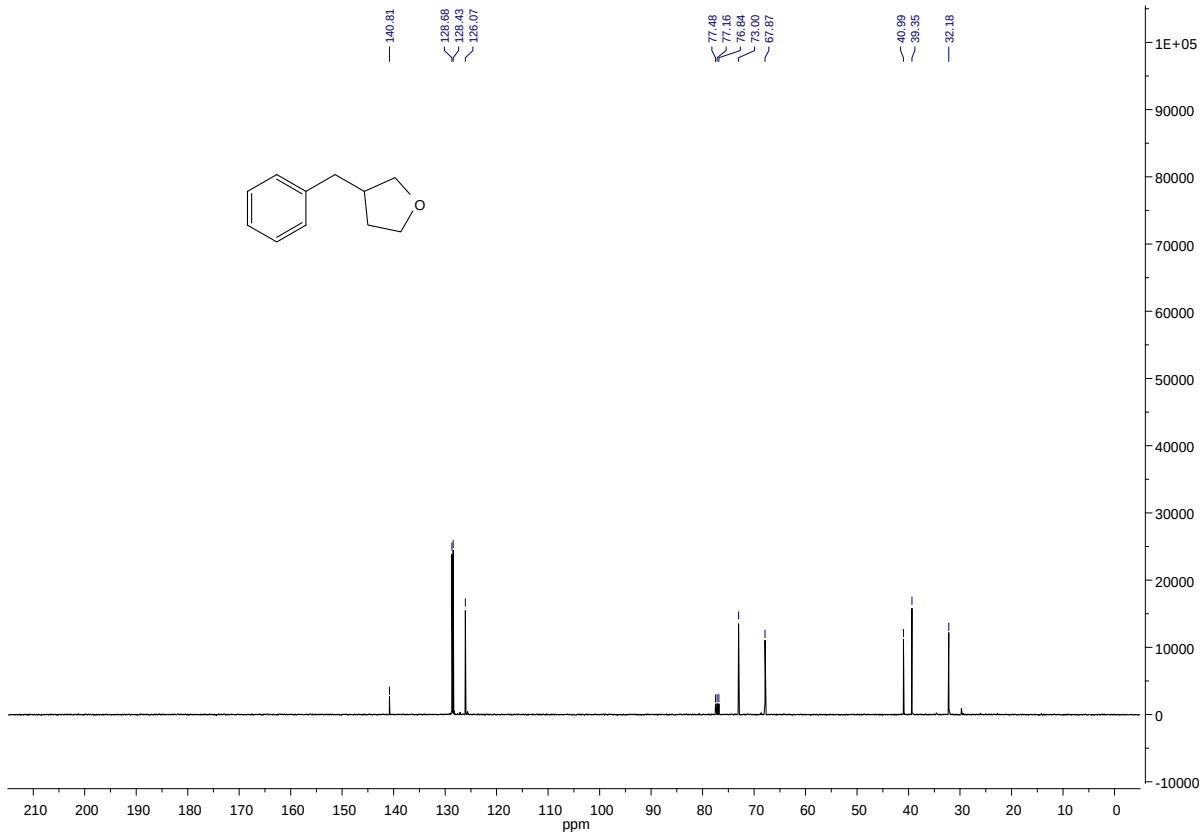


Figure S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of 3-benzyltetrahydrofuran.

Table S1. Electronic energies, free energy corrections and solvation corrections for relevant structures.

Compound	M06/def2-SVP Electronic Energy (hartree)	M06/def2-SVP Free Energy Correction (hartree)	PBE0-dDsC/TZ2P Electronic Energy (hatree)	PBE0-dDsC/TZ2P Solvation Energy (kcal/mol)
Pr•	-118.273347	0.060490	-2.270501	-1.776
Alkyl-Aryl Product	-349.647201	0.149248	-5.541063	-5.671
PrBr	-2692.096364	0.063695	-2.441702	-4.418
B1	-2524.241194	0.370118	-14.236379	-14.482
B2	-2642.542537	0.456829	-16.532473	-17.036
$TS_{B2,B3}$	-2642.539524	0.456340	-16.526524	-17.123
B3	-2292.918795	0.284971	-11.017955	-13.226
E1	-5098.010154	0.366921	-14.359434	-16.805
$TS_{E1,E2}$	-5216.274880	0.453378	-16.619274	-19.424
E2	-5216.304288	0.453729	-16.645939	-21.730
$TS_{E2,E3}$	-5216.297697	0.452335	-16.634902	-22.158
E3	-4866.758159	0.287040	-11.207878	-14.150

Table S2. Reaction free energies including solvation corrections (in THF using the COSMO-RS solvation model) computed at the PBE0-dDsC/TZ2P//M06/def2-SVP level. Values in kcal/mol.

Reaction	PBE0-dDsC/TZ2P
B1 + Pr• → **B2**	-0.38
B2 → **$TS_{B2,B3}$**	3.34
$TS_{B2,B3}$ → **B3** + Alkyl-Aryl Prod	-36.05
E1 + Pr• → **TS-E1,E2**	22.14
$TS_{E1,E2}$ → **E2**	-18.82
E2 → **$TS_{E2,E3}$**	5.62
$TS_{E2,E3}$ → **E3**	-79.29
B1 + PrBr → **E1** + Pr•	26.51

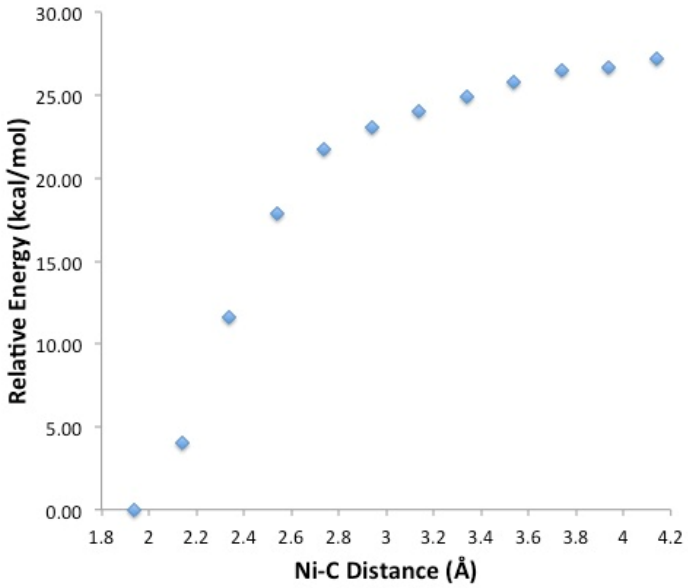


Figure S9. Potential energy surface scan (computed at the M06/def2-SVP level) of the propyl radical dissociation from **B2**. Despite having a small overall bond dissociation energy, removal of the propyl radical from **B2** to reform **B1** and a propyl radical requires a significant amount of energy.

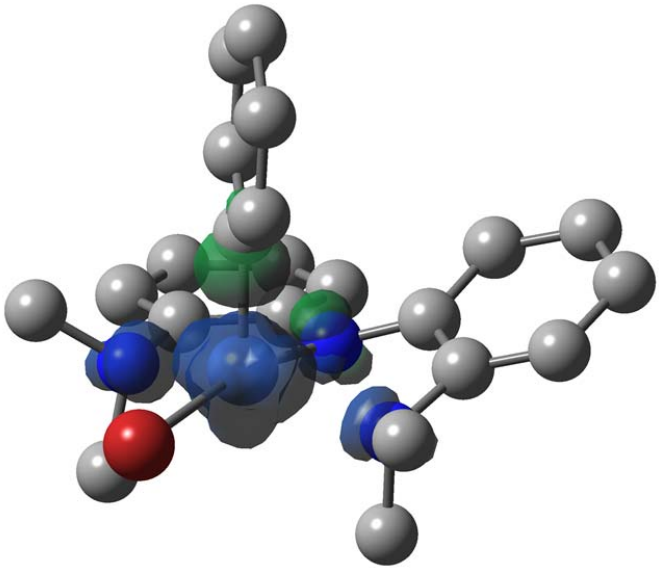
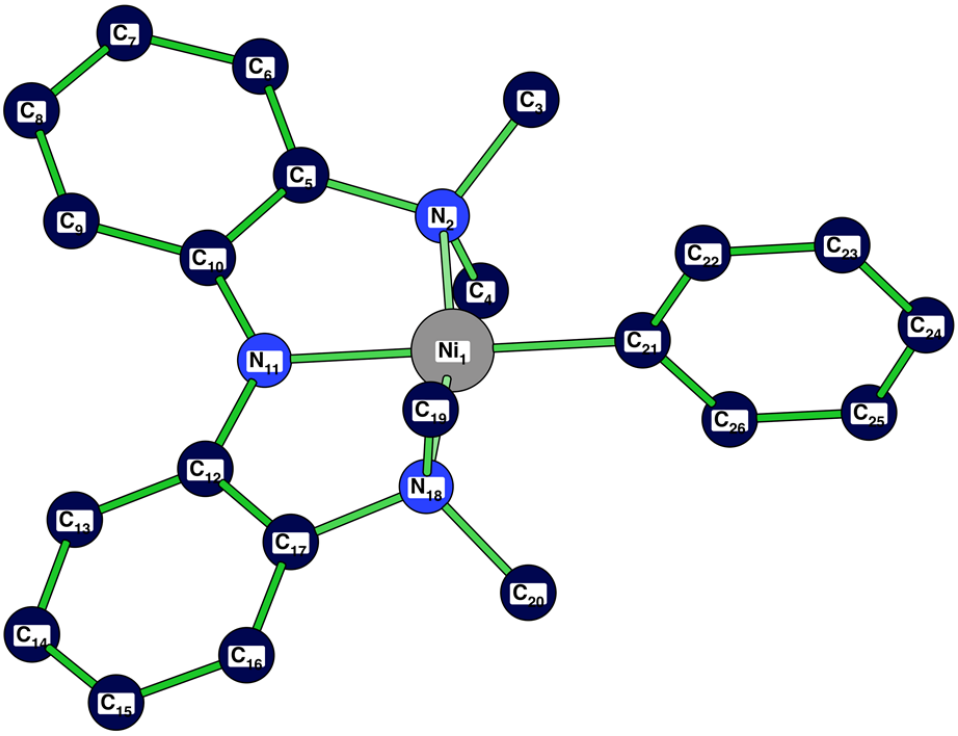


Figure S10. Spin density plot of **E1** computed at the M06/def2-SVP level. The large amount of spin density on the nickel center identifies the compound as being a Ni(III) halide species over a Ni(II) ligand cation complex. The later would be identified from virtually no spin density on the nickel with a majority being the nitrogen atom.

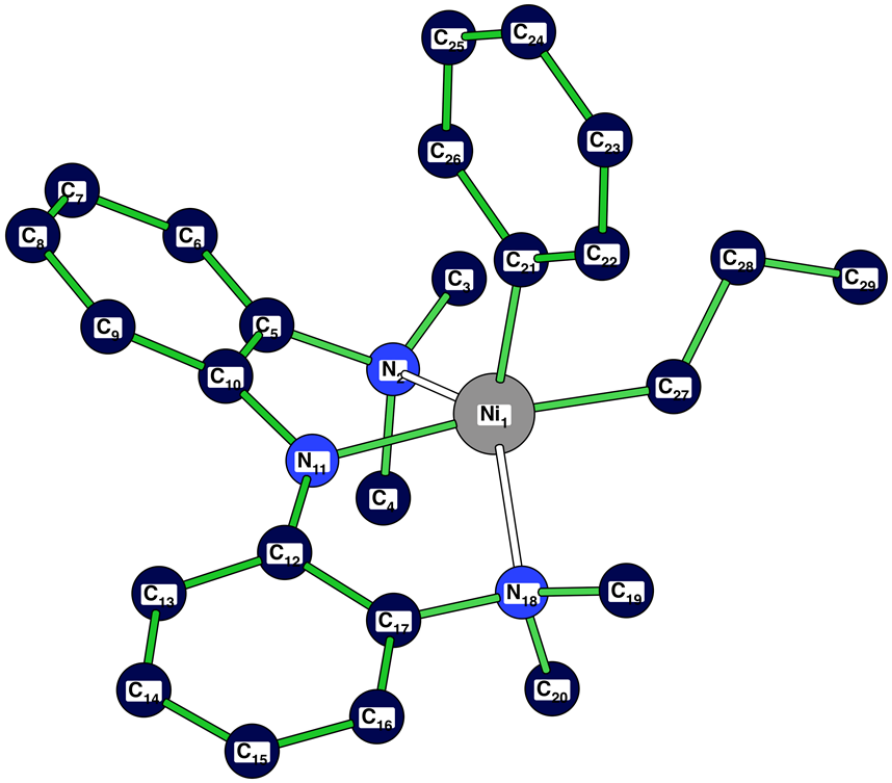
Key bonding parameters

B1



Ni1-N2:	1.991 Å
Ni1-N11:	1.890 Å
Ni1-N18:	1.991 Å
Ni-C21:	1.908 Å
N2-Ni1-N11:	84.6801°
N2-Ni1-N18:	169.3615°
N2-Ni1-C21:	95.3176°
N11-Ni1-N18:	84.6814°
N11-Ni1-C21:	179.9940°
N18-Ni1-C21:	95.3208°

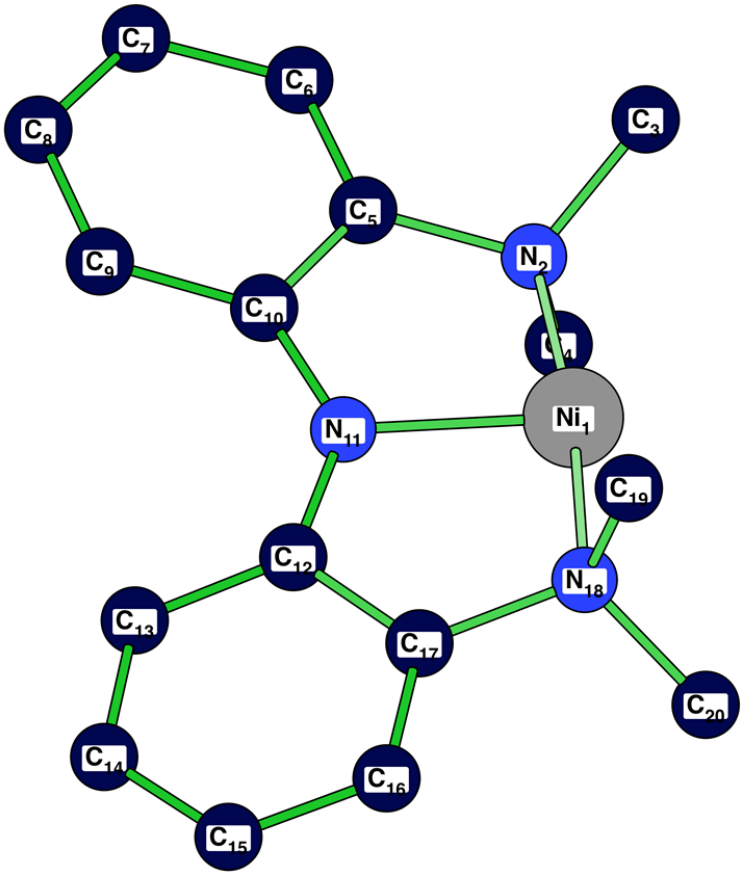
B2



Ni1-N2:	2.328 Å
Ni1-N11:	1.940 Å
Ni1-N18:	2.229 Å
Ni1-C21:	1.900 Å
Ni1-C27:	1.938 Å
N2-Ni1-N11:	76.3223°
N2-Ni1-N18:	135.0338°
N2-Ni1-C21:	112.2318°
N2-Ni1-C27:	97.4380°
N11-Ni1-N18:	80.2638°
N11-Ni1-C21:	104.8943°
N11-Ni1-C27:	170.0435°

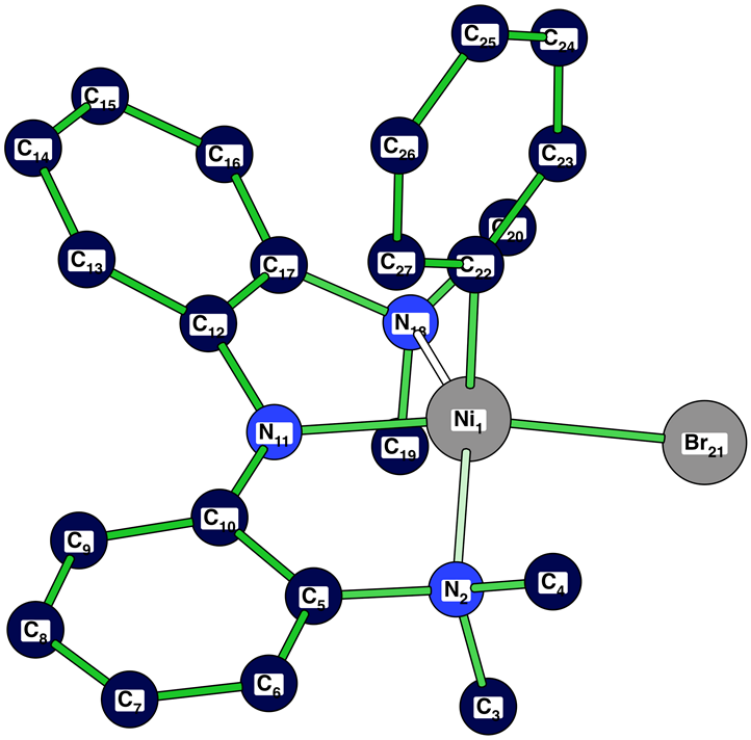
N18-Ni1-C21:	110.6279°
N18-Ni1-C27:	99.4706°

B3



Ni1-N2:	1.994 Å
Ni1-N11:	1.909 Å
Ni1-N18:	1.994 Å
N2-Ni1-N11:	86.6730°
N2-Ni1-N18:	173.3481°
N11-Ni1-N18:	86.6751°

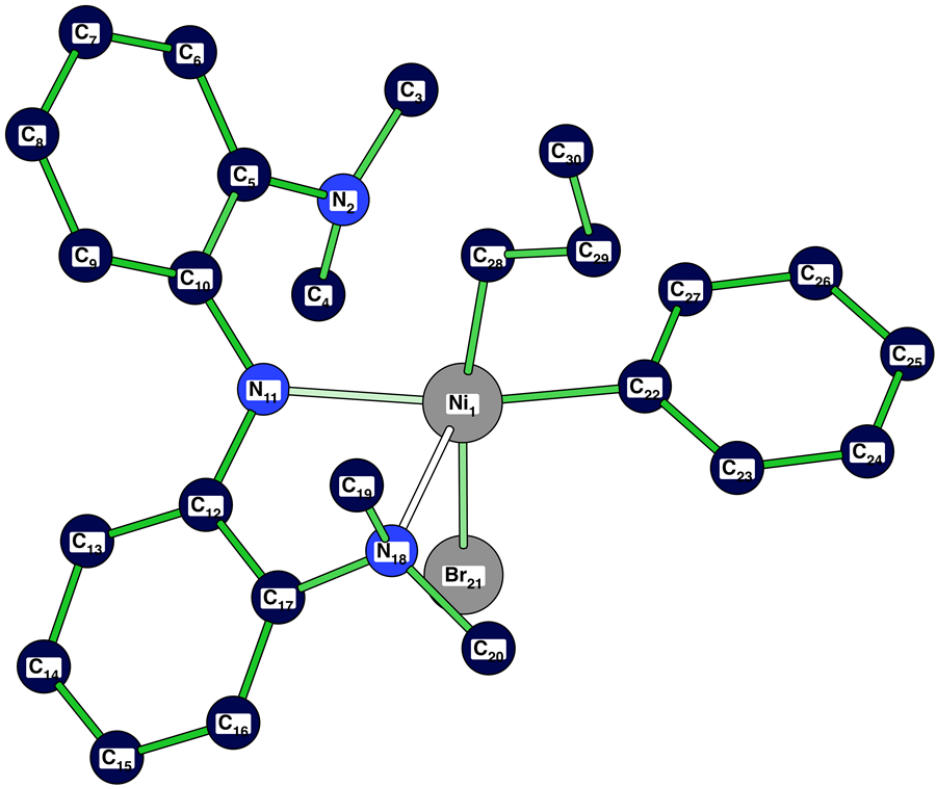
E1



Ni1-N2:	2.167 Å
Ni1-N11:	1.903 Å
Ni1-N18:	2.264 Å
Ni1-Br21:	2.363 Å
Ni1-C22:	1.922 Å
N2-Ni1-N11:	82.8767°
N2-Ni1-N18:	149.7876°
N2-Ni1-Br21:	96.2488°
N2-Ni1-C22:	102.1306°
N11-Ni1-N18:	78.5206°
N11-Ni1-Br21:	166.0978°
N11-Ni1-C22:	94.0955°
N18-Ni1-Br21:	96.2114°

N18-Ni1-C22:	102.7509°
Br21-Ni1-C22:	99.6366°

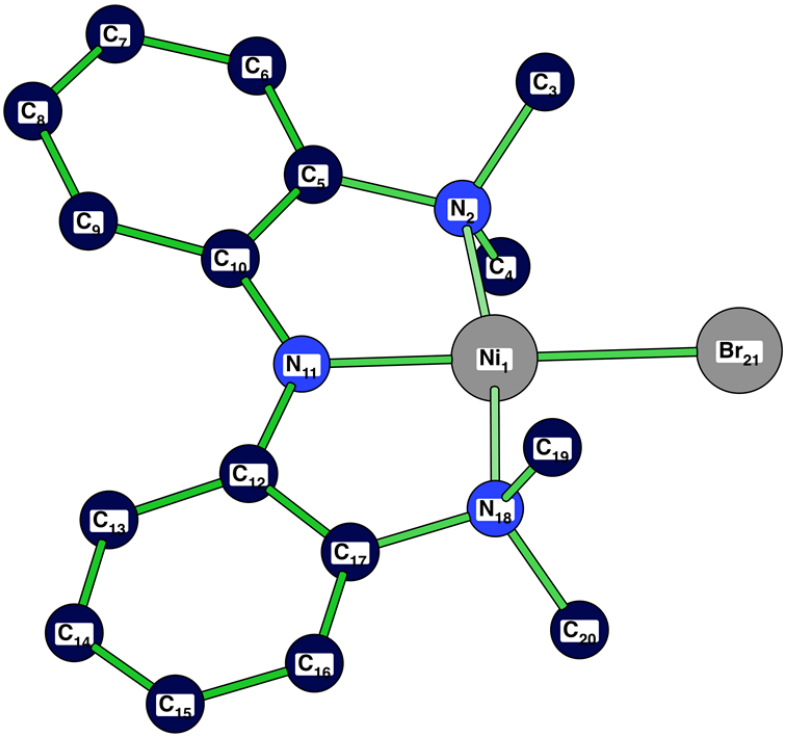
E2



Ni1-N2:	3.036 Å
Ni1-N11:	2.078 Å
Ni1-N18:	2.340 Å
Ni1-Br21:	2.440 Å
Ni1-C22:	1.917 Å
Ni1-C28:	1.971 Å
N2-Ni1-N11:	62.8140°
N2-Ni1-N18:	137.0434°
N2-Ni1-Br21:	96.4761°

N2-Ni1-C22:	105.3921°
N2-Ni1-C28:	82.6577°
N11-Ni1-N18:	74.3912°
N11-Ni1-Br21:	93.1138°
N11-Ni1-C22:	168.1978°
N11-Ni1-C28:	94.6474°
N18-Ni1-Br21:	89.0626°
N18-Ni1-C22:	117.3394°
N18-Ni1-C28:	97.8576°
Br21-Ni1-C22:	88.5677°
Br21-Ni1-C28:	170.7542°
C22-Ni1-C28:	82.8177°

E3



Ni1-N2:	1.985 Å
Ni1-N11:	1.853 Å
Ni1-N18:	1.985 Å
Ni1-Br21:	2.353 Å
N2-Ni1-N11:	85.6892°
N2-Ni1-N18:	171.3749°
N2-Ni1-Br21:	94.3121°
N11-Ni1-N18:	85.6857°
N11-Ni1-Br21:	179.9845°
N18-Ni1-Br21:	94.3130°