

Mechanistic Investigations of the Hydrogenolysis of Diaryl Ethers Catalyzed by Nickel Complexes of *N*-Heterocyclic Carbene Ligands

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General Experimental Details

All reactions were conducted under inert atmosphere in a nitrogen-filled glovebox or with standard Schlenk techniques, unless otherwise specified. Vessels used in air-free reactions were oven-dried prior to use. Vials used as reaction vessels were sealed with Teflon-lined caps. Filtration in the glovebox was achieved either through the use of a sintered glass frit or a syringe filter. Toluene, THF, Et₂O, pentane, and dichloromethane were sparged with nitrogen and dried with an Innovative Pure-Solv solvent purification system. Benzene was degassed via 3 cycles of freeze-pump-thaw and dried over 4 Å molecular sieves before use. All solvents for air and moisture sensitive reactions were stored over 4 Å molecular sieves and frequently tested using a standard solution of sodium benzophenone ketyl in THF to confirm the absence of oxygen and moisture. C₆D₆, C₇D₈, CD₂Cl₂, and C₆D₁₂ were degassed via 3 cycles of freeze-pump-thaw and dried over 4 Å molecular sieves before use. NaO*t*-Bu was sublimed under vacuum prior to use. Pressures of H₂ were monitored by a Vacuum Research digital pressure gauge attached to the Schlenk line. All other commercial solvents or reagents were used as received.

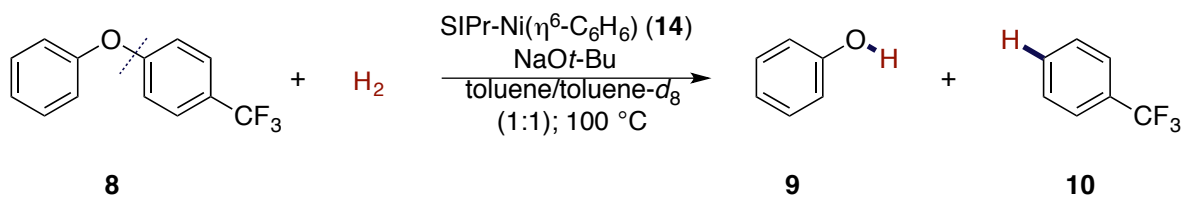
NMR spectra were acquired on Bruker AV-300, AVB-400, AVQ-400, DRX-500, AV-500 and AV-600 spectrometers at the University of California, Berkeley NMR facility. ¹H and ¹³C chemical shifts were reported relative to residual solvent peaks. Multiplicities are denoted as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Magnetic susceptibilities for paramagnetic compounds were determined via Evans method.¹ Elemental analysis data were obtained via the UC Berkeley Microanalytical Facility using a Perkin Elmer 2400 Series II combustion analyzer. High-resolution mass spectra were recorded at the UC Berkeley QB3/Chemistry Mass Spectrometry facility. UV-vis spectra were recorded on a Cary 400 UV-vis spectrophotometer at the UC Berkeley College of Chemistry Catalysis Center. GC yields were determined against dodecane as an internal standard with a 5 point calibration curve.

Silica-gel chromatography was performed with Silicycle SiliaFlash P60 silica gel or via the use of a Teledyne Isco Combiflash® Rf system with RediSep Gold™ columns. Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates pre-coated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with KMnO₄.

1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride (SIPr•HCl) was purchased from Sigma Aldrich, and Ni(DME)Cl₂ was purchased from Strem Chemicals. 1,3-Bis(2,6-di-*i*-

propylphenyl)imidazolidin-2-ylidene (SIPr)² and [SIPr–Ni(μ–Cl)]₂³ were prepared as previously reported in the literature. SIPr–Ni(η⁶–C₆H₆) (**14**) was prepared according to a modified literature procedure.⁴ NaOPh and phenoxide **17** were prepared by treatment of the corresponding phenol in THF with NaH (1.1 equiv.), filtration, and concentration. All other solvents and reagents were obtained from commercial sources and used without further purification.

General Procedure for Initial Rate Kinetics



Stock solutions of 4-(trifluoromethyl)diphenyl ether (**8**, 0.500 M), 1,3,5-trimethoxy-4-(trifluoromethyl)benzene (**S1**, internal standard, 0.500 M), and SIPr–Ni(η⁶–C₆H₆) (**14**, 0.100 M) were prepared in a 1:1 mixture of toluene and toluene-*d*₈. In a glovebox, the indicated amount of NaOt-Bu (± 0.2 mg) was measured onto a square of weighing paper and transferred to a J. Young NMR tube. In most cases, a static gun assisted in complete transfer of base into the NMR tube. The NMR tube was charged with the indicated amount of NaOt-Bu, followed by the indicated amounts of stock solutions and 1:1 toluene/toluene-*d*₈ (see Table S1). The NMR tube was sealed and transferred to a Schlenk line, where it was degassed via 3 cycles of freeze-pump-thaw. Care was taken that the contents of the NMR tube were fully frozen prior to exposure to vacuum to limit any possible evaporation of solvent. The atmosphere of the Schlenk line was exchanged for H₂ via three cycles of evacuation and backfilling. The NMR tube was then charged to ~1 atm of H₂ as measured by a pressure gauge attached to the Schlenk line.

Once charged, the NMR tube was shaken and transferred to a pre-heated NMR spectrometer, which had been previously locked and shimmed on a dummy sample. The reaction progress was monitored by ¹⁹F-NMR spectroscopy. Data collection typically began within 1 min of transferring the NMR tube to the spectrometer. The first 90 seconds of data were discarded, due to temperature equilibration. In all cases, data to 15% conversion were used to measure the initial rate. In the ¹⁹F-NMR spectra, the peak corresponding to diaryl ether starting material has appears at -62.72 ppm, the peak corresponding to internal standard at -54.79 ppm, and the peak corresponding to hydrogenolysis product (PhCF₃, **10**) at -63.72 ppm.

Table S1: Molarities and Volumes of Stock Solutions Used for Kinetic Experiments

	Ar₂O (8)	SIPr– Ni(η^6– C₆H₆) (14)	NaOt-Bu	Standard (S1)	1:1 Toluene/to luene-<i>d</i>₈	
	0.500 M	0.100 M		0.500 M	Neat	
Entry	Volume (μ L)	Volume (μ L)	Amount (mg)	Volume (μ L)	Volume (μ L)	Total volume (μ L)
1	200	50	12.1	100	250	600
2	100	50	12.1	100	350	600
3	50	50	12.1	100	400	600
4	25	50	12.1	100	425	600
5	100	100	12.1	100	300	600
6	100	75	12.1	100	325	600
7	100	50	12.1	100	350	600
8	100	25	12.1	100	375	600
9	100	50	14.5	100	350	600
10	100	50	9.7	100	350	600
11	100	50	4.8	100	350	600
12	100	50	2.4	100	350	600

The reagent being varied is shown in red

Table S2: Molarities of Each Reagent and Initial Rates for Each Kinetic Experiment

Entry	[8] (M)	[14] (M)	[NaOt-Bu] (M)	Temperature (K)	Initial (M/s)	Rate
1	0.1683	0.00833	0.210	373.15	6.86E-06	
2	0.084	0.00833	0.210	373.15	3.09E-06	
3	0.042	0.00833	0.210	373.15	1.71E-06	
4	0.021	0.00833	0.210	373.15	8.59E-07	
5	0.0833	0.0167	0.210	373.15	6.26E-06	
6	0.0833	0.0125	0.210	373.15	4.80E-06	
7	0.0833	0.00833	0.210	373.15	3.14E-06	
8	0.0833	0.00417	0.210	373.15	1.31E-06	
9	0.0833	0.00833	0.251	373.15	3.62E-06	
10	0.0833	0.00833	0.168	373.15	3.18E-06	
11	0.0833	0.00833	0.083	373.15	3.31E-06	
12	0.0833	0.00833	0.042	373.15	3.24E-06	

The reagent being varied is shown in red

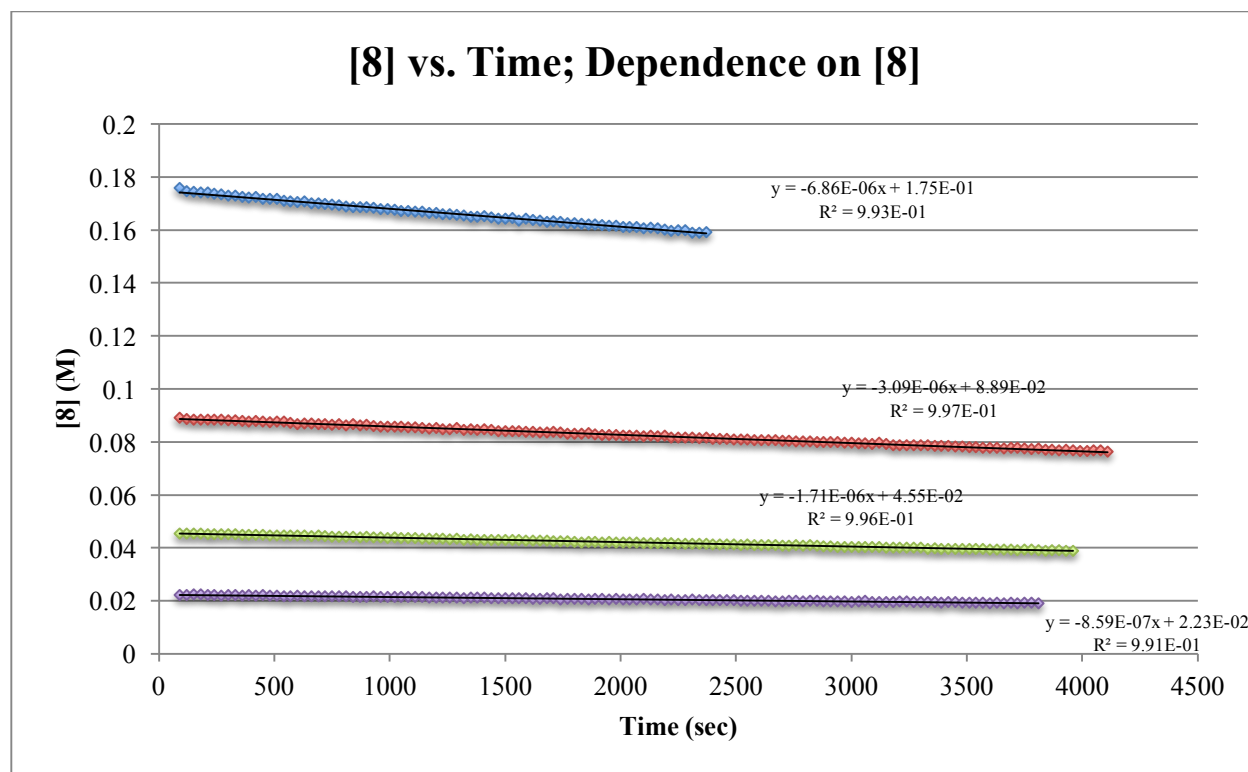


Figure S1: Plot of the concentration of **8** over time with four different initial concentrations of **8**.

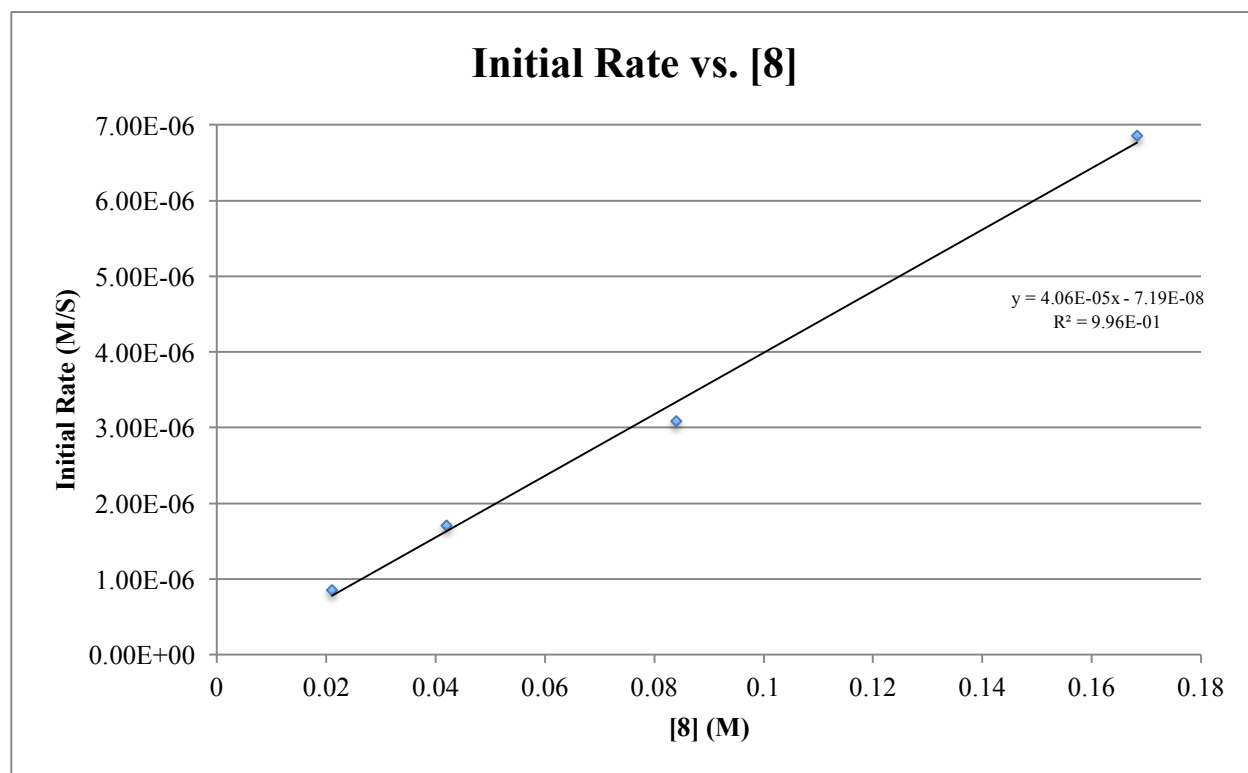


Figure S2: Plot of the initial rate of hydrogenolysis vs. the concentration of **8**.

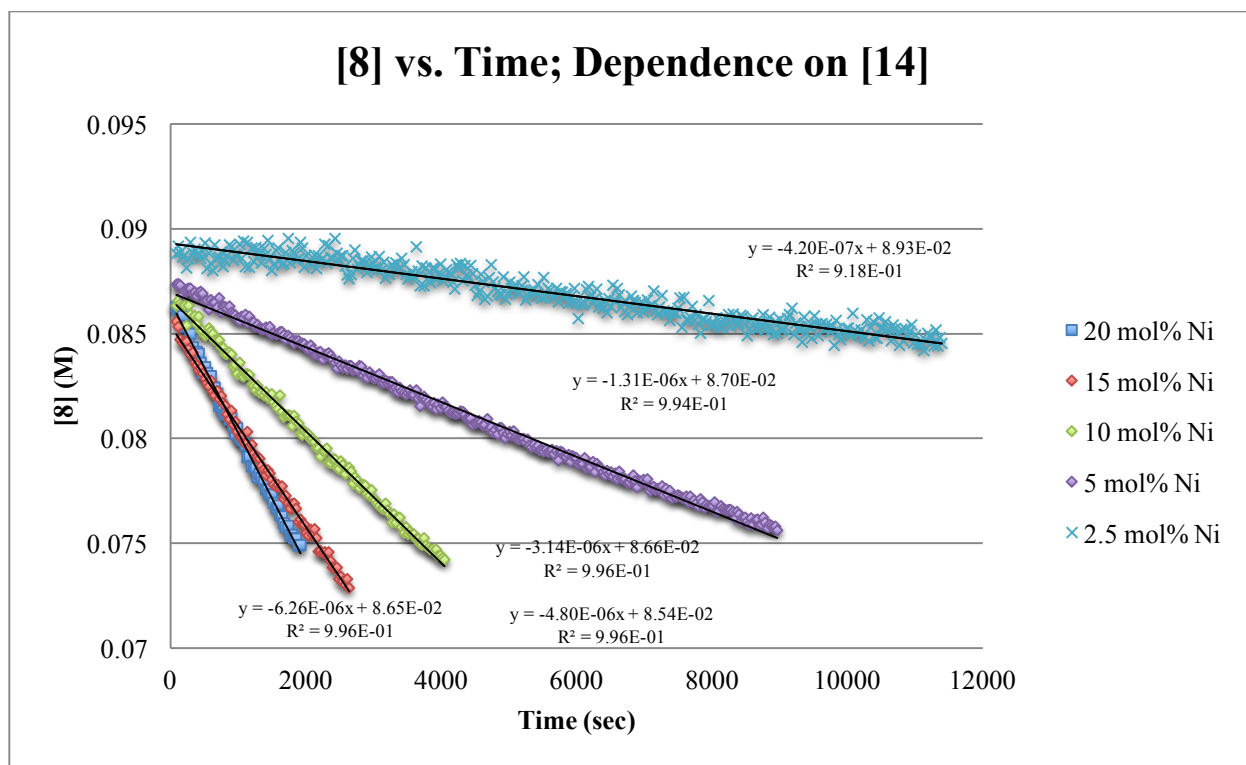


Figure S3: Plot of the concentration of **8** over time with four different initial concentrations of **14**.

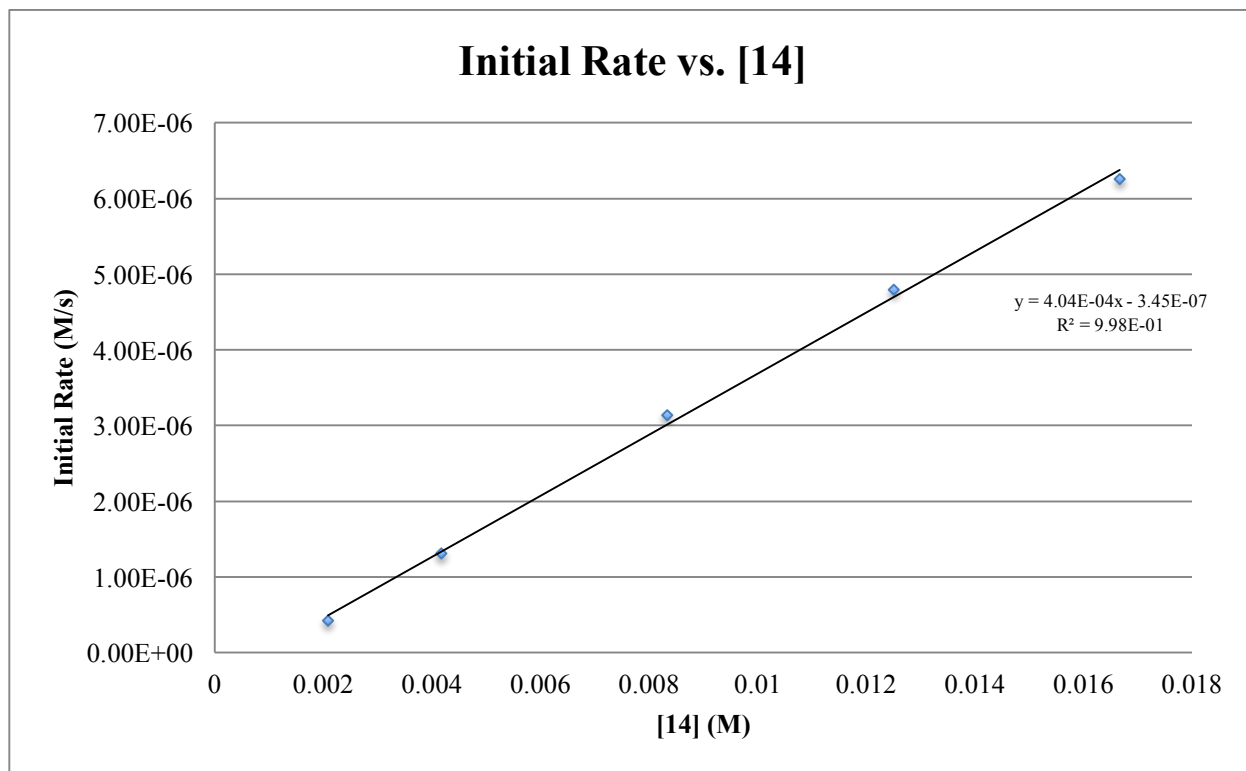


Figure S4: Plot of the initial rate of hydrogenolysis vs. the concentration of **14**.

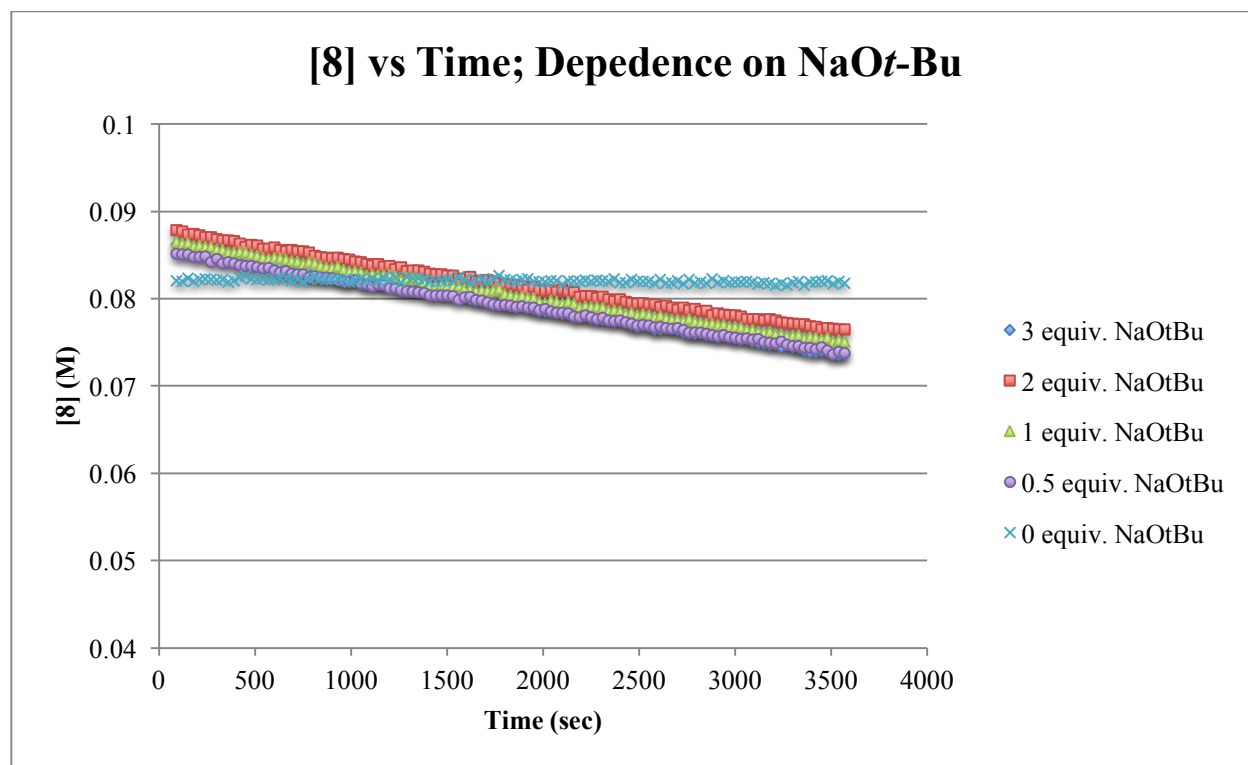


Figure S5: Plot of the concentration of **8** over time with five different initial concentrations of NaOt-Bu.

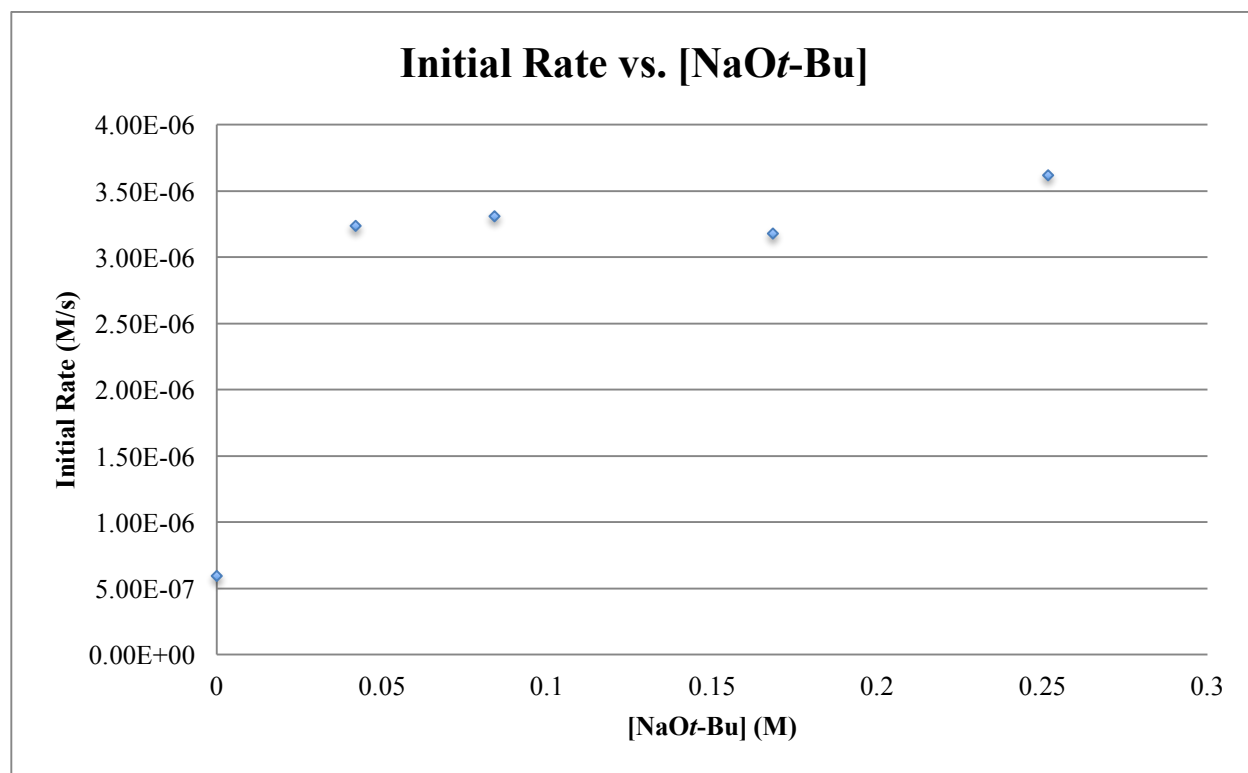


Figure S6: Plot of the initial rate of hydrogenolysis vs. the concentration of NaOt-Bu.

Procedure for the Dependence of the Initial Rate on H₂

The general procedure for initial rates was followed to prepare four J. Young NMR tubes as described above (Entry 7, Table S2), however, each NMR tube was charged to the pressure of H₂ indicated in Table S3. The initial rate was found to have a zeroth order dependence on the pressure of H₂.

Table S3: Molarities of Each Reagent and Initial Rates For Different Pressures of H₂

Entry	[8] (M)	[14] (M)	[NaOt-Bu] (M)	Pressure of H ₂ (Torr)	Initial Rate (M/s)
1	0.0833	8.33E-03	0.210	385	2.59E-06
2	0.0833	8.33E-03	0.210	766	3.08E-06
3	0.0833	8.33E-03	0.210	1129	3.29E-06
4	0.0833	8.33E-03	0.210	1486	3.10E-06

The parameter being varied is shown in red

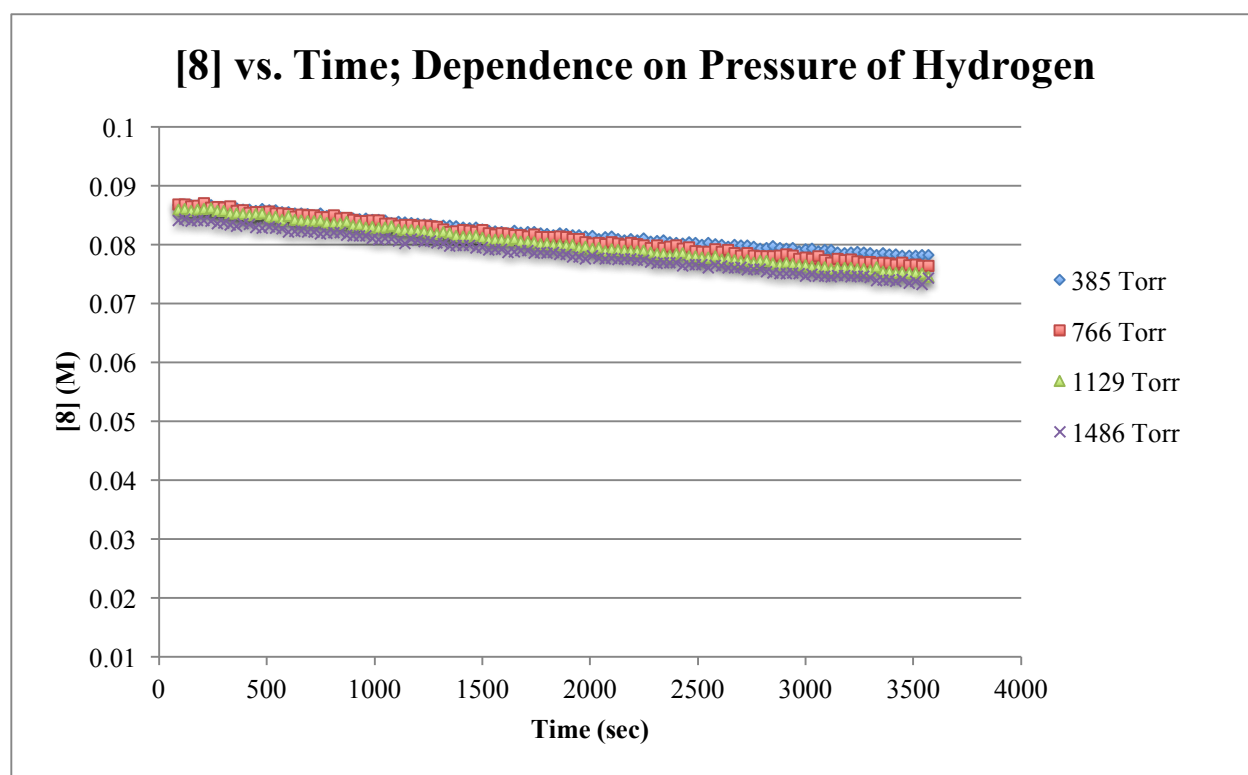
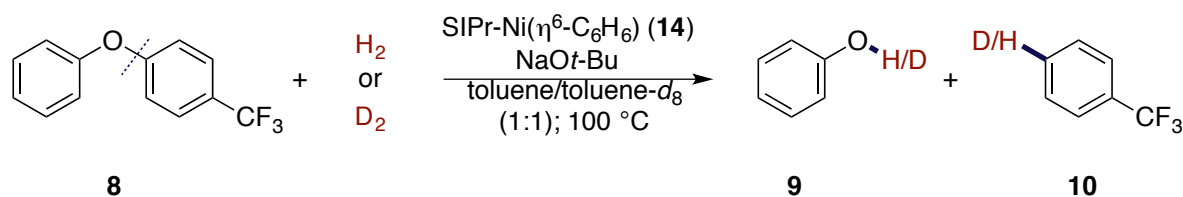


Figure S7: Plot of the concentration of **8** over time with 4 different initial pressures of H₂.

Procedure for determining the Kinetic Isotope Effect



The general procedure for initial rates was followed to prepare two J. Young NMR tubes as described above (Run #7 in Table S2), however, one NMR tube was charged with D_2 , rather than H_2 . The kinetic isotope experiment was repeated in triplicate (Table S4). The average kinetic isotope effect was calculated to be 1.04 ± 0.09 . A representative graph of the data is shown below.

Table S4: Initial Rates For Kinetic Isotope Effect Experiments

Entry	k_{H} (M/s)	k_{D} (M/s)	KIE	Average KIE	Std. Dev. For KIE
1	2.84E-06	2.65E-06	1.07		
2	2.68E-06	2.43E-06	1.10	1.04	0.09
3	2.38E-06	2.55E-06	0.93		

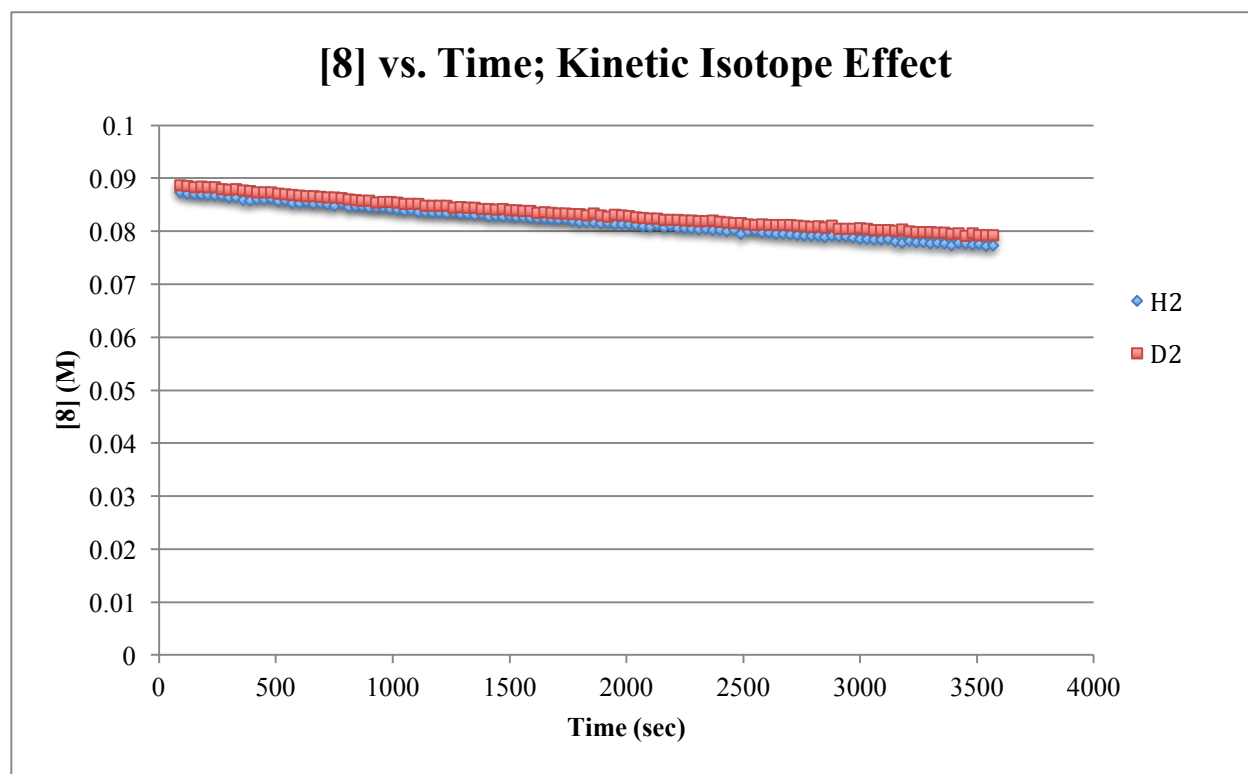


Figure S8: Plot of the concentration of **8** over time with 1 atm of H_2 (blue) and 1 atm of D_2 (red) for Table S4, Entry 1.

Procedure for H₂ Pressure Dependence on Conversion (Schlenk Tubes)

To confirm the zeroth order dependence of rate on H₂ pressure that was observed by NMR kinetics, a series of experiments were run in Schlenk tubes with vigorous stirring, such that gas diffusion in an NMR tube is not a variable. The similar conversions of starting material seen at all pressures of H₂ (Table S5) indicate that limited gas transfer in a J. Young NMR tube is not the explanation for the zeroth order dependence of rate on the pressure of H₂.

A stock solution of 4-(trifluoromethyl)diphenylether (**8**, 58.6 mg, 0.246 mmol), 1,3,5-trimethoxy-4-(trifluoromethyl)benzene (**S1**, internal standard, 59.4 mg, 0.248 mmol), and SiPr–Ni(η^6 -C₆H₆) (**14**, 14.4 mg, 0.0273 mmol) was prepared in 3.0 mL of a 4:1 mixture of toluene and toluene-*d*₈.

In a glovebox, five 15 mL Schlenk tubes equipped with a Teflon stopcock were charged with NaOt-Bu (12.0 mg, 0.125 mmol) and a magnetic stir bar. To each Schlenk tube was added 0.6 mL of the stock solution, and the reaction mixtures were removed from the glovebox. Each Schlenk tube was degassed via 3 cycles of freeze-pump-thaw, the atmosphere of the Schlenk line was exchanged via three cycles of evacuation and backfilling with H₂, and the tubes were pressurized to the indicated pressure of H₂ (Table S5). The Schlenk tubes were placed into an oil bath preheated to 100 °C and were allowed to stir for 90 min before being removed and cooled in an ice bath. The reaction mixtures were filtered over a 1 cm plug of Celite[®] directly into NMR tubes to measure the yield by ¹⁹F-NMR spectroscopy (Table S5). Similar conversions of starting material were observed over a range of different pressures of H₂ (\pm 6%).

Table S5: Molarities of Each Reagent and % Conversions For Different Pressures of H₂

Entry	[8] (M)	[14] (M)	[NaOtBu] (M)	Pressure of H ₂ (Torr)	[8] After Reaction (M)	Conversion (%)
1	0.0820	9.10E-03	0.208	397	0.0618	21
2	0.0820	9.10E-03	0.208	762	0.0582	27
3	0.0820	9.10E-03	0.208	1146	0.0622	23
4	0.0820	9.10E-03	0.208	1332	0.0596	25
5	0.0820	9.10E-03	0.208	1483	0.0586	26
The parameter being varied is shown in red						

Initial Rate Reproducibility

The general procedure for initial rates was followed to prepare four J. Young NMR tubes as described above (Entry 7, Table S2). The data collected are shown in Table S6. The average initial rate over 4 trials was 2.79×10^{-6} M/s, with a standard deviation of 0.14×10^{-6} M/s. The error bars on the graph below represent 1 standard deviation.

Table S6: Molarities of Each Reagent and Initial Rates For Reproducibility of Initial Rate Measurements

Entry	[8] (M)	[14] (M)	[NaOtBu] (M)	Initial Rate (M/s)	Average Initial Rate
1	0.0833	8.33E-03	0.210	2.59E-06	2.79E-06
2	0.0833	8.33E-03	0.210	2.83E-06	
3	0.0833	8.33E-03	0.210	2.82E-06	
4	0.0833	8.33E-03	0.210	2.91E-06	

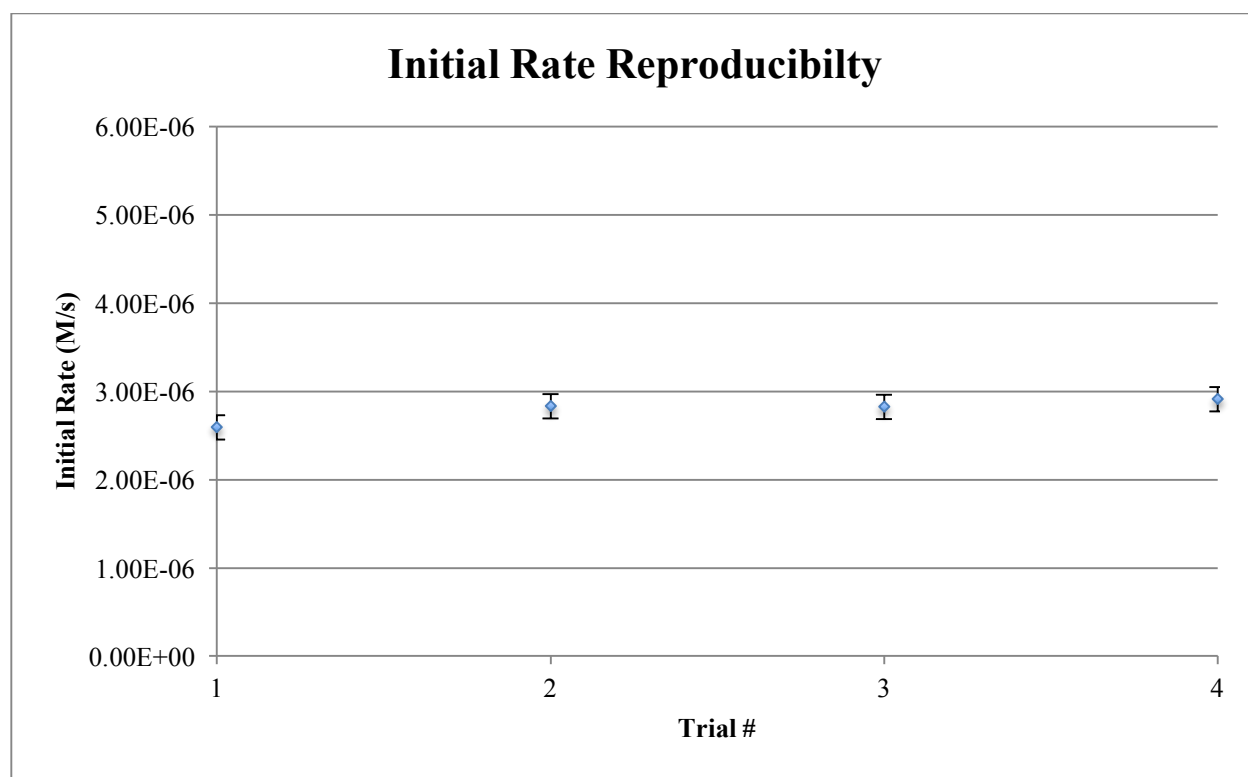


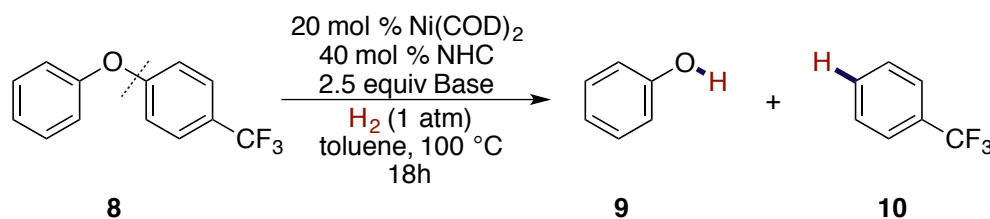
Figure S9: Plot of the initial rate of hydrogenolysis vs. the trial number.

General Procedure for the Hydrogenolysis of Diaryl Ethers

In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with Ni(COD)₂ (8.3 mg, 0.030 mmol) and SIPr•HCl or SIPr (0.060 mmol). Alternatively, a preformed Ni complex, such as **11**, **14**, **16** or **18**, (0.030 mmol) was added to the Schlenk tube. If applicable, the Schlenk tube was also charged with NaOt-Bu (36.0 mg, 0.375 mmol) or NaOPh (43.5 mg, 0.375 mmol).

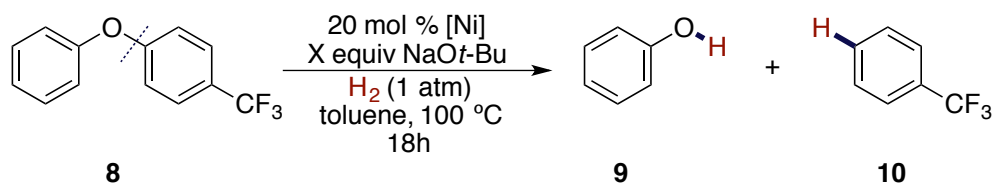
To the Schlenk tube was added a stock solution of diaryl ether (**8**, 0.150 mmol) and internal standard **S1** (0.150 mmol) in a 4:1 mixture of toluene and toluene-*d*₈ (0.8 mL). The reaction mixture was sealed, removed from the glovebox, and transferred to a Schlenk line. The reaction mixture was degassed via 3 cycles of freeze-pump-thaw, the atmosphere of the Schlenk line was exchanged via three cycles of evacuation and backfilling with H₂, and the reaction was pressurized to ~1 atm of H₂. The Schlenk tube was placed into a preheated oil bath and allowed to stir at the stated temperature for the stated period of time.

Determination of the Yield of Hydrogenolysis by ¹⁹F-NMR: The reaction mixture was cooled and then filtered over a 1 cm plug of Celite[®] directly into NMR tubes to measure the yield by ¹⁹F-NMR spectroscopy (1 scan).

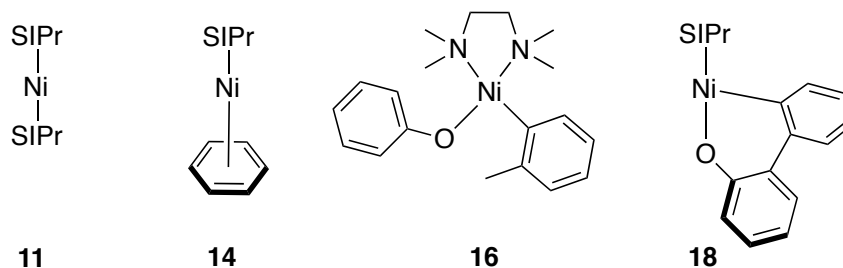


Entry	NHC Precursor	Base	Conversion (%)	Yield of 10 (%)
1	SIPr•HCl	NaOt-Bu	100	81
2	SIPr	–	19	19
3	SIPr	NaOt-Bu	100	82
4	SIPr	NaOPh	28	25

The reactions above were prepared following the general procedure for the hydrogenolysis of diaryl ether **8**. The NHC precursor or NHC and base added in each reaction are indicated.



Entry	[Ni]	X	Conversion (%)	Yield of 10 (%)
1 ^a	11	2.5	100	69
2	11	0	14	12
3	14	2.5	98	79
4	14	0	16	16
5	16	2.5	< 5	0
6 ^b	16	2.5	91	62
7 ^c	18	2.5	94	63
8	18	0	8	0



The reactions above were prepared following the general procedure for the hydrogenolysis of diaryl ether **8**. The preformed Ni catalyst and the equivalents of NaOt-Bu added in each reaction are indicated. The following alterations to the general procedure were made:

- ^aEntry 1: The reaction mixture was heated for 6 h
- ^bEntry 6: SIPr•HCl (**1**, 40 mol%) was added as ligand
- ^cEntry 7: The reaction mixture was allowed to stir at room temperature for 10 min prior to heating

Identification of the Resting State of the Catalyst (NMR):

Thermolysis of Ni(SIPr)₂ (11): An NMR sample of Ni(SIPr)₂ (**11**, 10 mg) in C₆D₆ (0.6 mL) was heated in an aluminum block at 100 °C for 1 h. The ¹H-NMR spectrum of this sample was recorded and is reproduced below, along with spectra of Ni(SIPr)₂ (**11**), SIPr-Ni(η⁶-C₆D₆) (**12**), and of SIPr (**13**) in C₆D₆ for comparison.

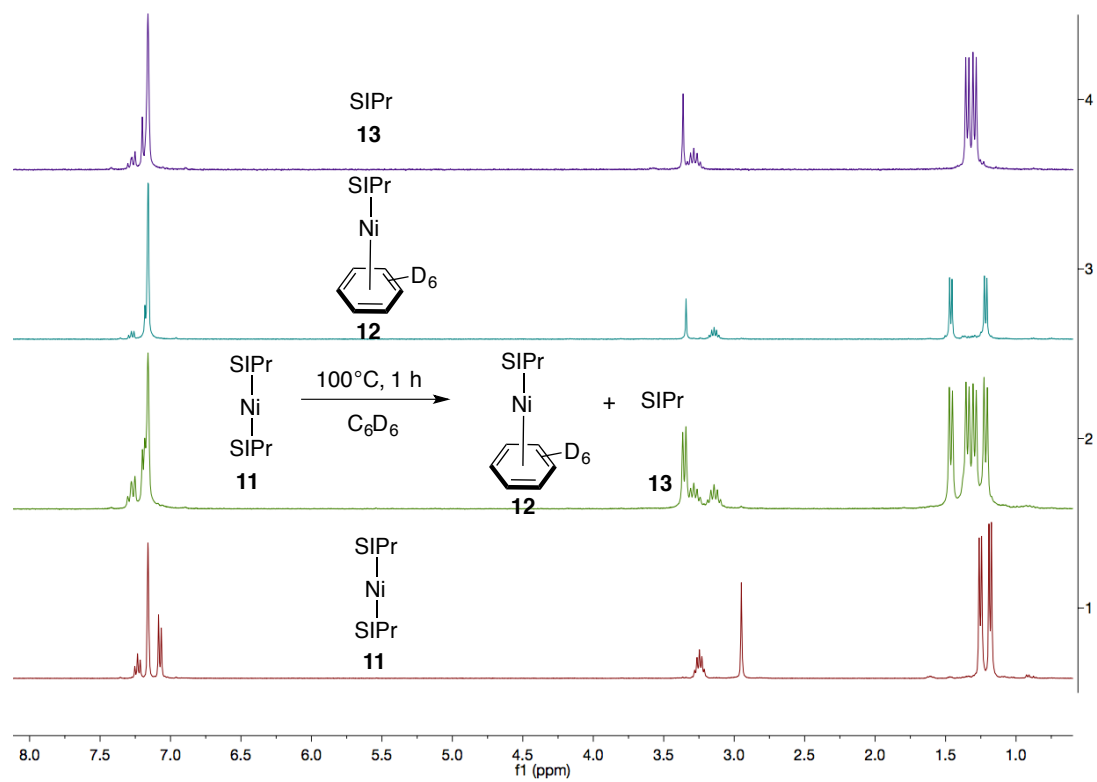


Figure S10: ^1H -NMR spectrum (500 MHz, C_6D_6) for the thermolysis of $\text{Ni}(\text{SIPr})_2$ (**11**).

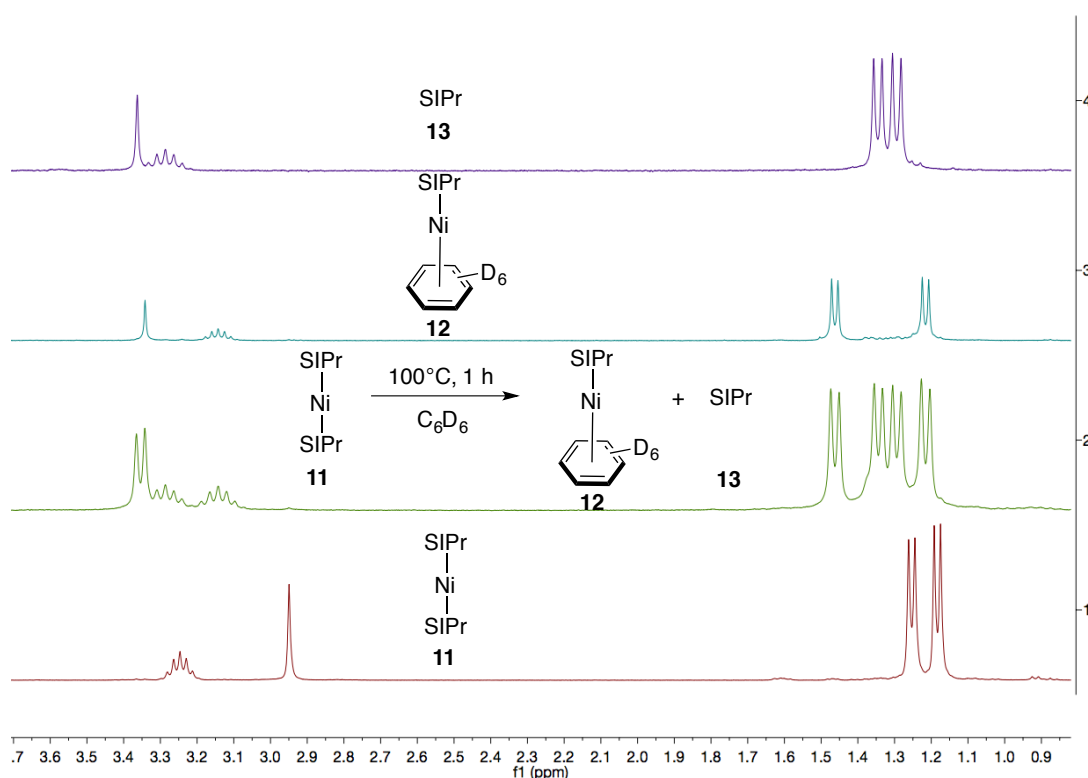


Figure S11: Expansion of the ^1H -NMR spectrum (500 MHz, C_6D_6) for the thermolysis of $\text{Ni}(\text{SIPr})_2$ (**11**).

Monitoring the resting state of the catalyst by NMR spectroscopy: In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with $\text{Ni}(\text{COD})_2$ (9.0 mg, 0.033 mmol), $\text{SIPr}\cdot\text{HCl}$ (**1**, 24.6 mg, 0.060 mmol), and NaOt-Bu (36.0 mg, 0.375 mmol). To the Schlenk tube was added a stock solution of Ph_2O (25.5 mg, 0.150 mmol) in C_6D_6 (0.8 mL), and the reaction mixture was pressurized to ~ 1 atm of H_2 following the general procedure for hydrogenolysis of diaryl ethers. The reaction mixture was allowed to stir vigorously for 1 h, the Schlenk tube was brought back into the glovebox, and an aliquot was removed and filtered for NMR analysis. The remaining reaction mixture was removed from the glovebox, pressurized to ~ 1 atm of H_2 following the general procedure for hydrogenolysis of diaryl ethers, and heated at 100°C for 1 h. The reaction mixture was brought back into the glovebox, and a final aliquot was removed and filtered for NMR analysis.

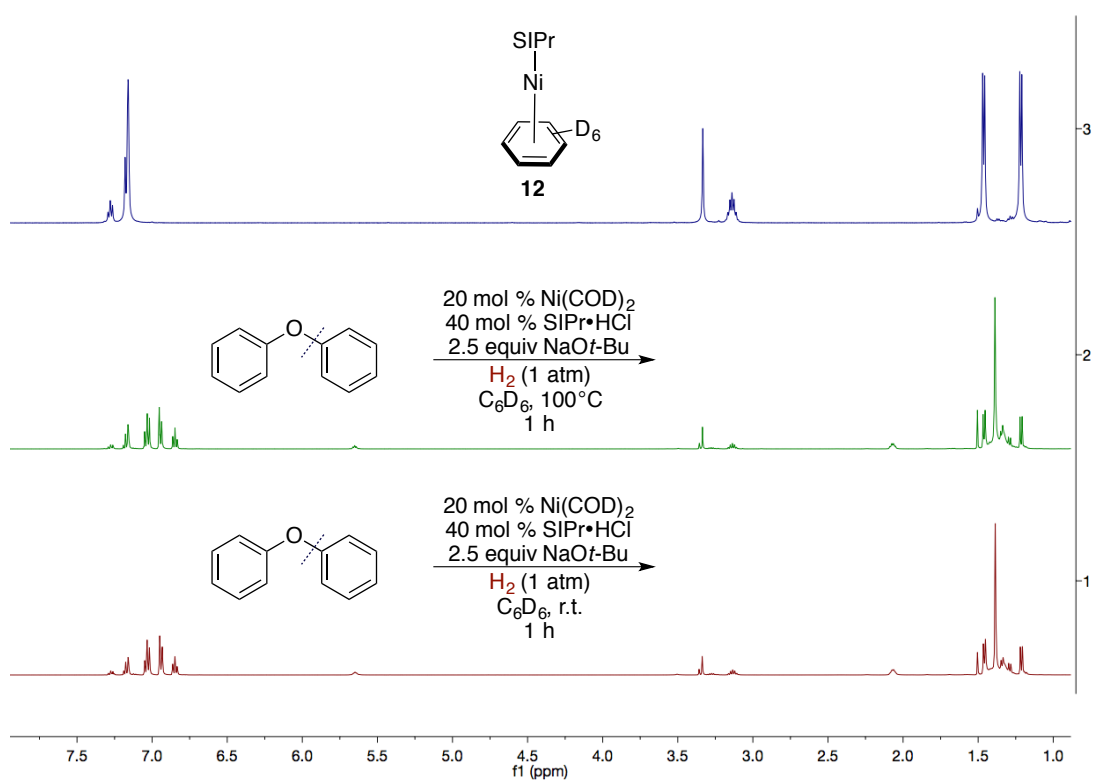


Figure S12: ^1H -NMR spectrum (500 MHz, C_6D_6) for the hydrogenolysis of Ph_2O with H_2 catalyzed by the combination of $\text{Ni}(\text{COD})_2$, $\text{SiPr}\cdot\text{HCl}$ with added NaOt-Bu .

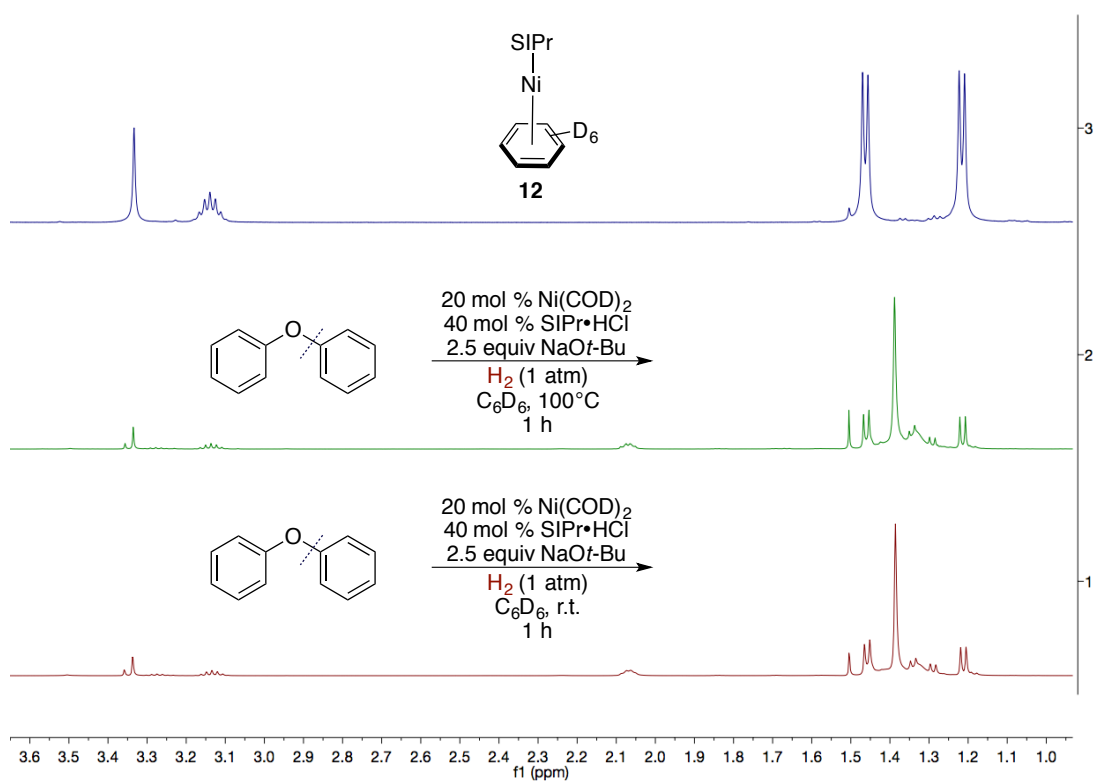


Figure S13: Expansion of the ^1H -NMR spectrum (500 MHz, C_6D_6) for the hydrogenolysis of Ph_2O with H_2 catalyzed by the combination of $\text{Ni}(\text{COD})_2$, $\text{SIPr}\cdot\text{HCl}$ with added NaOt-Bu .

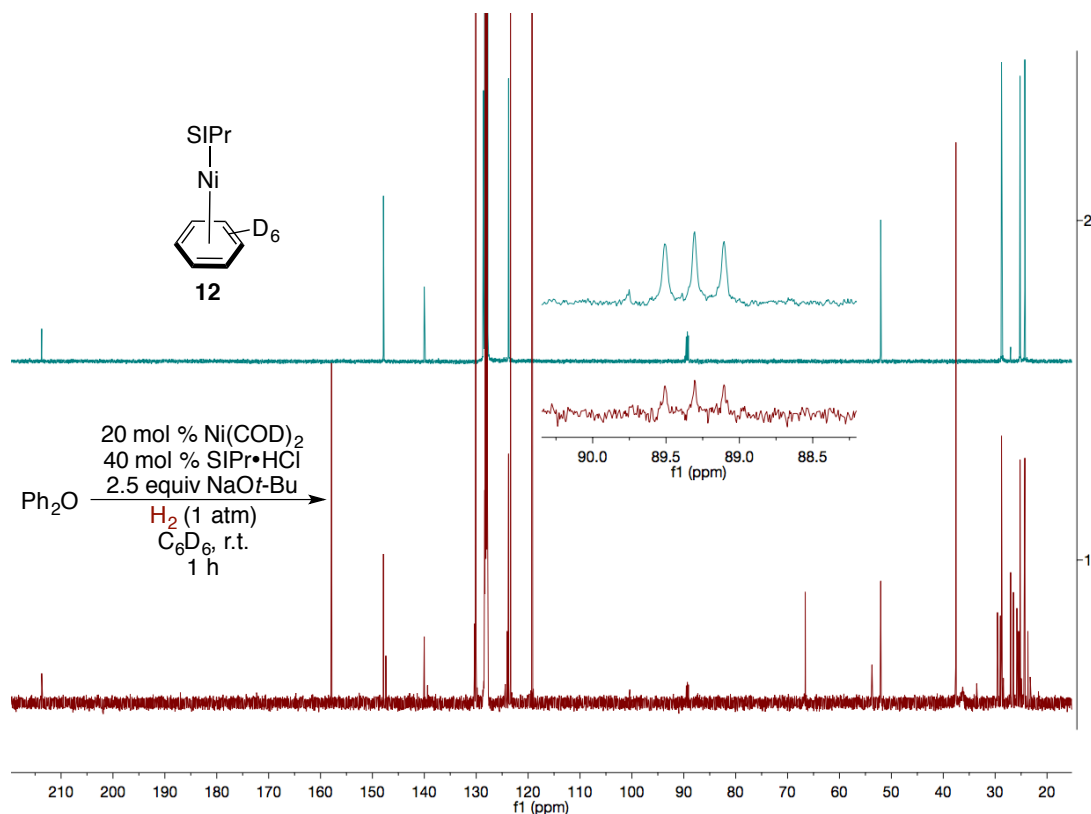


Figure S14: ^{13}C -NMR spectrum (126 MHz, C_6D_6) for the hydrogenolysis of Ph_2O with H_2 catalyzed by the combination of $\text{Ni}(\text{COD})_2$, $\text{SIPr}\cdot\text{HCl}$ with added NaOt-Bu .

Identification of the Resting State of the Catalyst (UV-Vis):

Cuvettes containing solutions for analysis were prepared in the glovebox, sealed with Teflon tape and parafilm, removed from the glovebox, and analyzed immediately. A UV-Vis spectrum of the following solutions were recorded at ambient temperature:

Ni(SIPr)₂ (11): A sample of $\text{Ni}(\text{SIPr})_2$ (**11**, 2.2 mg) was dissolved in toluene (20 mL, 0.13 μM).

Catalytic Conditions: In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.030 mmol), $\text{SIPr}\cdot\text{HCl}$ (**1**, 24.6 mg, 0.060 mmol), and NaOt-Bu (36.0 mg, 0.375 mmol). To the Schlenk tube was added a stock solution of Ph_2O (25.5 mg, 0.150 mmol) in toluene (0.8 mL), and the reaction mixture pressurized to ~ 1 atm of H_2 following the general procedure for hydrogenolysis of diaryl ethers. The reaction mixture was allowed to stir for 5 min, brought back into the glovebox, and an aliquot of 88 μL was withdrawn and diluted with toluene (20 mL total volume, $[\text{Ni}] = 0.17 \mu\text{M}$).

SIPr-Ni(η^6 -C₆H₆) (**14**): A sample of *SIPr*-Ni(η^6 -C₆H₆) (**14**, 1.8 mg) was dissolved in toluene (20 mL, 0.17 μ M).

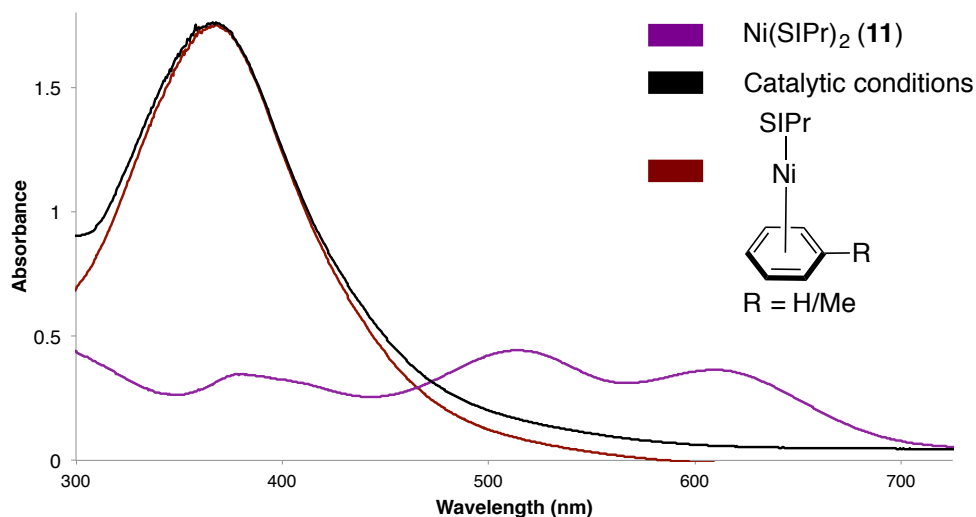


Figure S15: UV-Vis spectrum (toluene, 298K) of Ni(*SIPr*)₂ (**11**, 0.13 μ M, purple trace), an aliquot from a typical hydrogenolysis reaction mixture under H₂ prior to heating ([Ni] = 0.17 μ M, black trace), and of *SIPr*-Ni(η^6 -C₆H₆) (**14**, 0.17 μ M, red trace).

Reaction Profile

Combination of Ni(COD)₂, SIPr•HCl, and NaOt-Bu (blue line): The general procedure for the hydrogenolysis of diaryl ethers was followed with five Schlenk tubes, each charged with Ni(COD)₂ (8.3 mg, 0.030 mmol), *SIPr*•HCl (25.6 mg, 0.060 mmol), and NaOt-Bu (36.0 mg, 0.375 mmol). To each tube was added a stock solution of diaryl ether (**8**, 0.150 mmol) and internal standard **S1** (0.150 mmol) in a 4:1 mixture of toluene and toluene-*d*₈ (0.8 mL). The reaction mixtures were pressurized and heated as described in the general procedure. At the specified time point, one of the reaction mixtures was removed from the oil bath and cooled in an ice bath. Conversion was determined by ¹⁹F-NMR as described in the general procedure (Figure S16).

SIPr-Ni(η^6 -C₆H₆) (**14**) and NaOt-Bu (red line): The general procedure for the hydrogenolysis of diaryl ethers was followed with five Schlenk tubes, each charged with NaOt-Bu (36.0 mg, 0.375 mmol). To each tube was added a stock solution of diaryl ether (**8**, 0.150

mmol), internal standard **S1** (0.150 mmol), and preformed SIPr–Ni(η^6 –C₆H₆) (**14**, 15.9 mg, 0.030 mmol) in a 4:1 mixture of toluene and toluene-*d*₈ (0.8 mL). The reaction mixtures were pressurized and heated as described in the general procedure. At the specified time point, one of the reaction mixtures was removed from the oil bath and cooled in an ice bath. Conversion was determined by ¹⁹F-NMR as described in the general procedure (Figure S16).

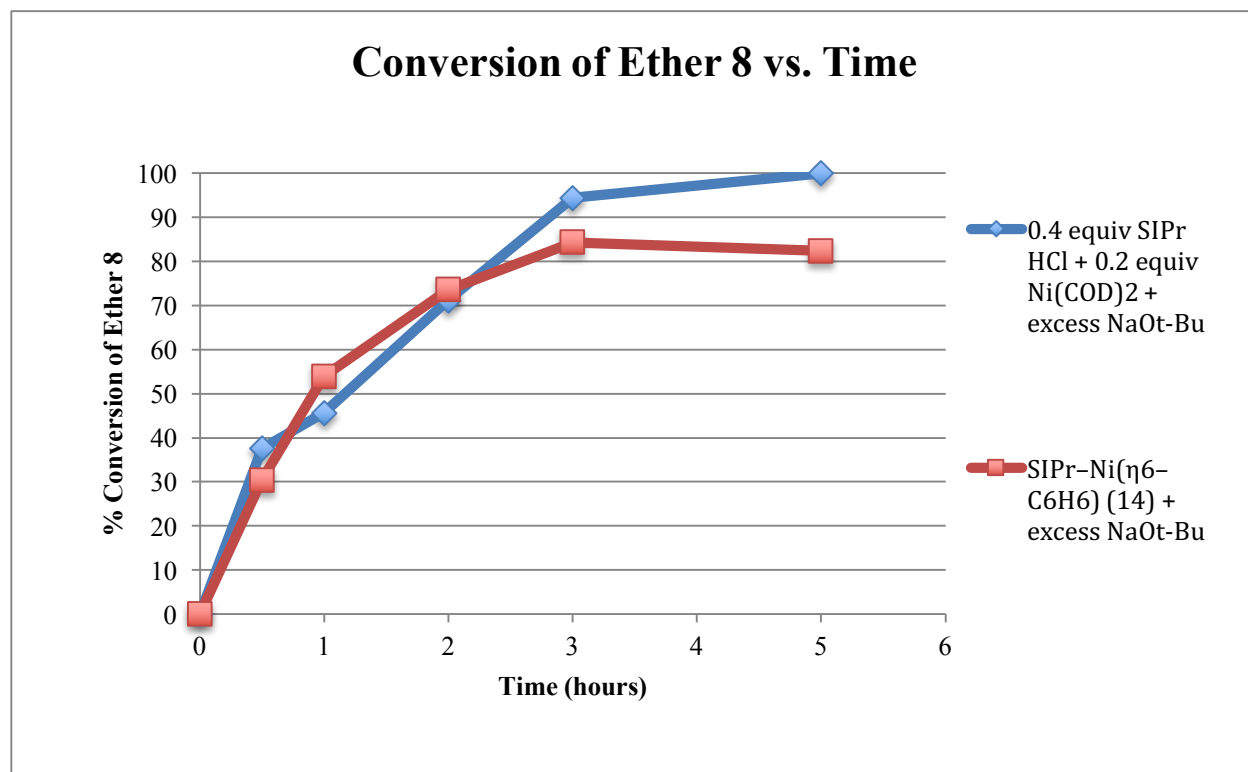
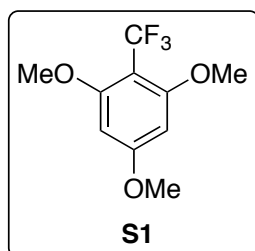


Figure S16: Plot of % conversion of ether **8** vs. time for the hydrogenolysis catalyzed by the combination of Ni(COD)₂ and SIPr•HCl with added NaOt-Bu (blue line) and for the hydrogenolysis catalyzed by SIPr–Ni(η^6 –C₆H₆) (**14**) with added NaOt-Bu (red line).

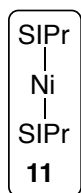
Synthesis, Characterization, and Other Mechanistic Experiments

1,3,5-Trimethoxy-4-(trifluoromethyl)benzene (S1)



This compound was prepared as previously reported in the literature.⁵ To a 20 mL vial was added trimethoxybenzene (0.856 g, 5.09 mmol), (diacetoxyiodo)benzene (3.28 g, 10.2 mmol), and AgF (0.154 g, 1.21 mmol). DMSO (15 mL) was added, and the reaction mixture was stirred briefly before TMSF₃ (0.890 mL, 6.02 mmol) was added. The reaction mixture turned purple and was allowed to stir at room temperature for 12 h. Water (75 mL) was added, and the reaction mixture was extracted with Et₂O (50 mL x 3). The combined organic extracts were dried over Na₂SO₄ and concentrated *in vacuo* to give a yellow oil. The crude product was purified via automated column chromatography (Combiflash[®] 40 g cartridge, 0-25% EtOAc/Hex) to give 1,3,5-trimethoxy-4-(trifluoromethyl)benzene (**S1**) as a white crystalline solid (0.990 g, 82%). The ¹H-NMR and ¹⁹F-NMR spectral data were identical to those previously reported.⁵

Ni(SIPr)₂ (**11**):



Ni(SIPr)₂ has been previously reported⁶ but was prepared by an alternative procedure. A 20 mL vial was charged with SIPr-Ni(η⁶-C₆H₆) (**14**, 0.060 g; 0.114 mmol), SIPr (**13**, 0.044 g; 0.114 mmol) and pentane (3 mL). Over the course of stirring for 2 h, the brown/red solution had turned deep purple. The solution was filtered, and the filtrate was concentrated to give Ni(SIPr)₂ as a purple powder (**11**, 0.080 g, 83%). The ¹H-NMR spectral data were identical those was previously reported.⁶

¹H-NMR (400 MHz, C₆D₆) δ 7.23 (t, *J* = 7.7 Hz, 4H), 7.08 (d, *J* = 7.7 Hz, 8H), 3.25 (hept, *J* = 6.9 Hz, 8H), 2.95 (s, 8H), 1.25 (d, *J* = 6.8 Hz, 24H), 1.18 (d, *J* = 6.9 Hz, 24H).

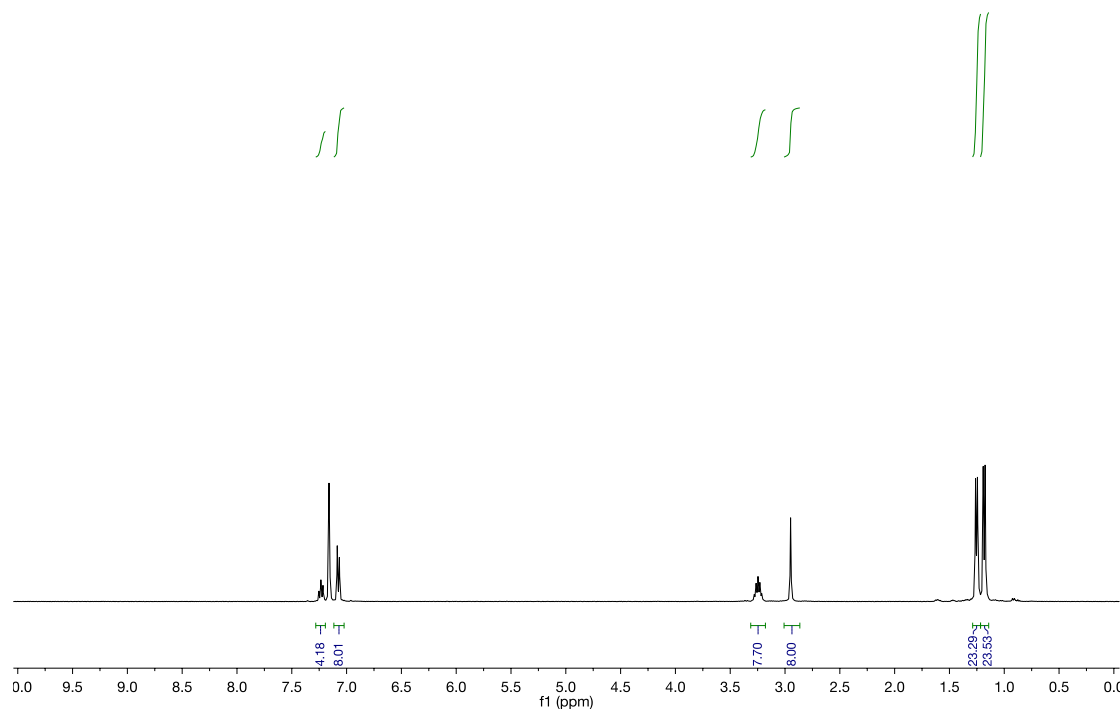
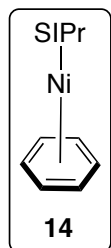


Figure S17: ^1H -NMR spectrum (400 MHz, C_6D_6) of $\text{Ni}(\text{SIPr})_2$ (**11**)

$\text{SIPr-Ni}(\eta^6\text{-C}_6\text{D}_6)$ (12**) / $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**)**



$\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**) was prepared according to a modified literature procedure.⁷ A stainless steel Parr reactor was brought into the glovebox and charged with SIPr (**13**, 0.823 g, 2.11 mmol), $\text{Ni}(\text{COD})_2$ (0.580 g, 2.11 mmol), and a stir bar. Benzene (10 mL, well dried and rigorously degassed) was added, and the reaction mixture was allowed to briefly stir for 3 min until a red-brown homogenous solution was obtained. The reactor was sealed, removed from the glovebox, and pressurized to 700 psi of H_2 . The reaction mixture was allowed to stir for 3 h, the reactor was partially vented, and brought back into the glovebox. The deep red reaction solution was filtered to remove trace amounts of Ni black and lyophilized to provide $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ as a red solid (**14**, 1.08 g, 97%). In some cases, trace amounts of cyclooctane can be observed in the product by ^1H -NMR spectroscopy. Trace cyclooctane can be removed by dissolving the product in benzene and repeatedly removing the solvent. If the product is not pure by NMR, most likely the SIPr was not pure (it should be a white solid and can be recrystallized prior to use from pentane/ Et_2O if necessary), or the solvent was not sufficiently degassed and dried. Although $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**) is highly

soluble in most solvents including pentane, it can be recrystallized from HMDSO if necessary, albeit with low recovery. The ^1H -NMR spectral data for $\text{SiPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**) in C_6D_{12} were identical to those previously reported. In addition, the ^1H and ^{13}C NMR spectral data in C_6D_6 are provided below. When dissolved in C_6D_6 , the compound in solution is $\text{SiPr-Ni}(\eta^6\text{-C}_6\text{D}_6)$ (**12**).

^1H -NMR (500 MHz, C_6D_6) δ 7.28 (t, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 7.6$ Hz, 4H), 3.33 (s, 4H), 3.14 (hept, $J = 6.9$ Hz, 4H), 1.46 (d, $J = 6.8$ Hz, 12H), 1.22 (d, $J = 7.0$ Hz, 12H).

^{13}C -NMR (126 MHz, C_6D_6) δ 213.7, 147.9, 140.0, 128.6, 123.8, 89.3 (t, $J_{\text{C-D}} = 25.4$ Hz), 52.1, 28.8, 25.2, 24.3.

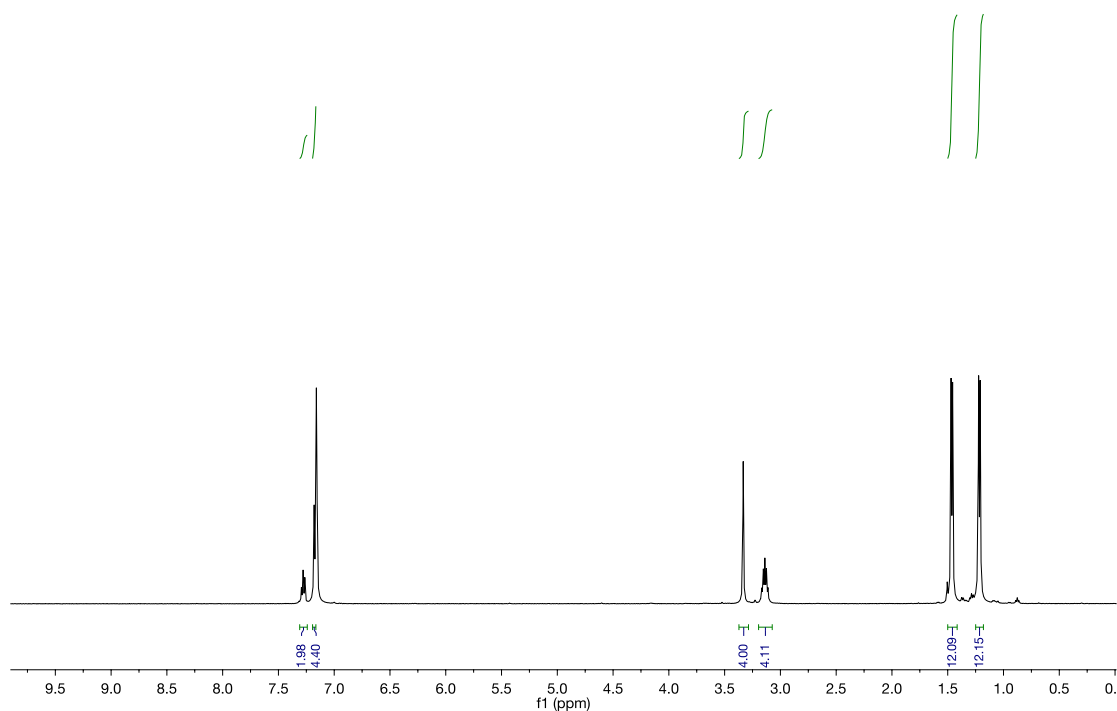


Figure S18: ^1H -NMR spectrum (500 MHz, C_6D_6) of $\text{SiPr-Ni}(\eta^6\text{-C}_6\text{D}_6)$ (**12**).

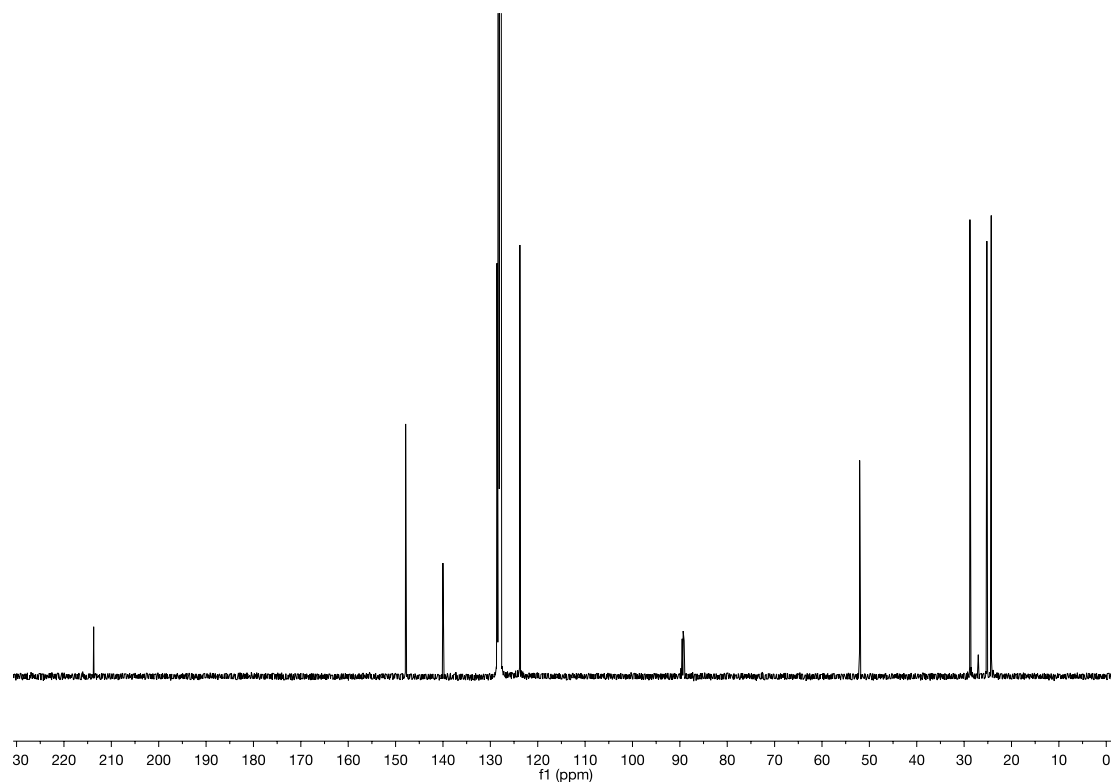
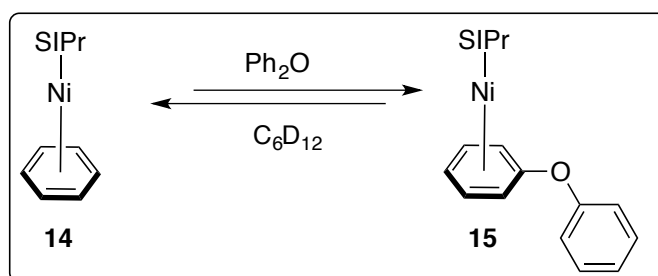


Figure S19: ^{13}C -NMR spectrum (126 MHz, C_6D_6) of $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{D}_6)$ (**12**).

Preparation of $\text{SIPr-Ni}(\eta^6\text{-Ph-OPh})$ (15**) *in situ***



In a glovebox, to a J. Young NMR tube was added a solution of $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**, 0.023 g, 0.038 mmol) in C_6D_{12} (0.6 mL). To the NMR tube was added Ph_2O (6 μL , 0.038 mmol). The NMR tube was sealed and a ^1H -NMR spectrum was collected. The NMR tube was brought back into the glovebox and an additional equivalent of Ph_2O was added. This procedure was repeated to obtain the spectra below.

Mixture of Ph₂O, SIPr-Ni(C₆H₆) (**14**) and **15** formed *in situ* (1 equiv of Ph₂O)

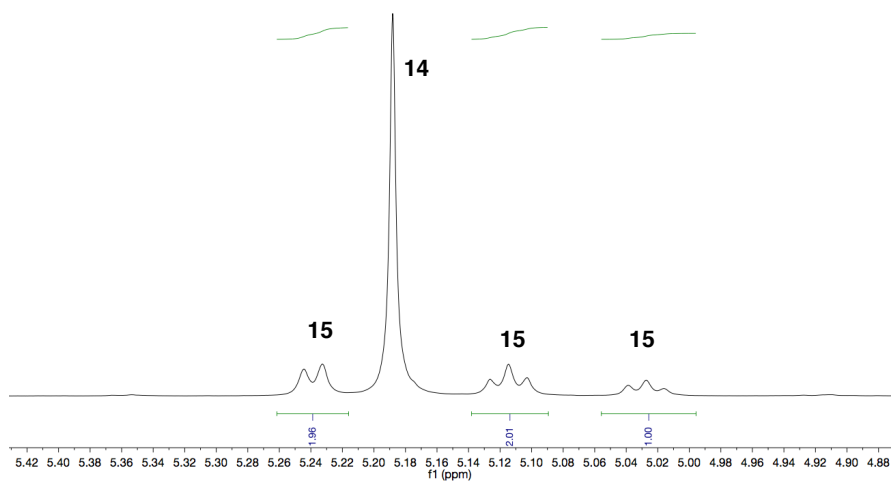


Figure S20: Expansion of the ¹H-NMR spectrum (500 MHz, C₆D₁₂) of the mixture of **15**, 1 equiv of Ph₂O, and starting material **14** generated *in situ*.

Mixture of Ph₂O, SIPr-Ni(C₆H₆) (**14**) and **15** formed *in situ* (1 equiv of Ph₂O)

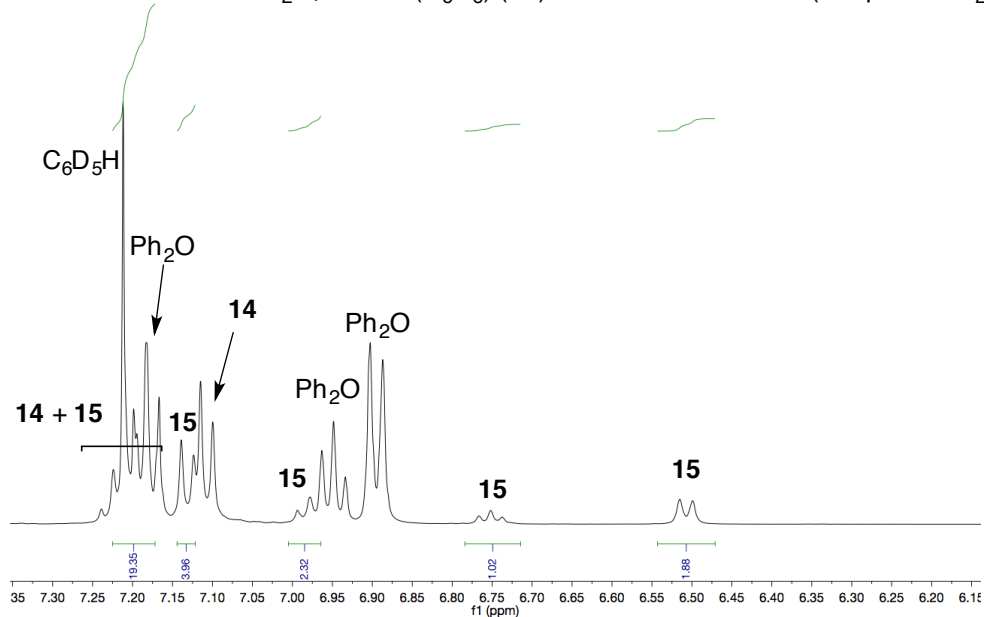


Figure S21: Expansion of the ¹H-NMR spectrum (500 MHz, C₆D₁₂) of the mixture of **15**, 1 equiv of Ph₂O, and starting material **14** generated *in situ*.

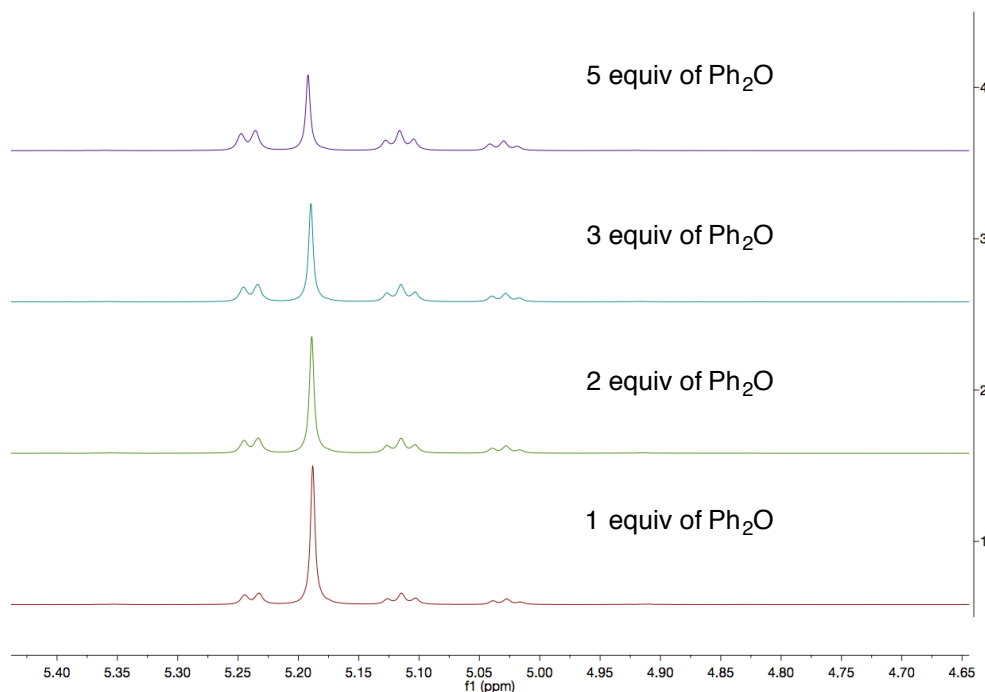
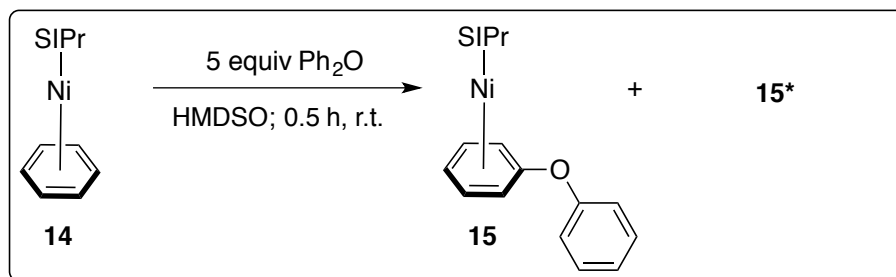
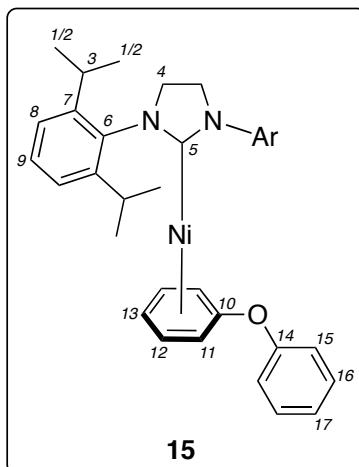


Figure S22: Layered expansion of the ^1H -NMR spectrum (500 MHz, C_6D_{12}) of the mixture of **15**, varying equiv of Ph_2O , and starting material **14** generated *in situ*.

Isolation of $\text{SiPr-Ni}(\eta^6\text{-Ph-OPh})$ (**15**) and **15***



To a solution of $\text{SiPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**, 0.110 g, 0.209 mmol) in HMDSO (3 mL) was added Ph_2O (0.177 g, 1.04 mmol). The deep red reaction mixture was allowed to stir for 30 min, filtered, and concentrated to ~ 1.5 mL. During concentration, a black/red crystalline solid formed. The crystals were filtered, washed with cold HMDSO (2 x 2 mL), and dried to give a mixture of η^6 -bound **15** and **15*** (0.044 g). η^6 -bound **15** and **15*** are in a ratio of 3.17:1 by ^1H -NMR spectroscopy; residual **14** represents approximately 1% of the total mixture. Crystals of η^6 -bound **15** suitable for single crystal X-ray diffraction were grown by slow evaporation from a concentrated solution of the reaction mixture in pentane at 0°C .



Characterization data for $\text{SiPr-Ni}(\eta^6\text{-Ph-OPh})$ (**15**):

$^1\text{H-NMR}$ (500 MHz, C_6D_{12}) δ 7.20 – 7.16 (m, 2H, H_9), 7.13 (d, $J = 7.7$ Hz, 4H, H_8), 6.98 (td, $J = 7.7, 0.8$ Hz, 2H, H_{16}), 6.75 (tt, $J = 7.7, 0.8$ Hz, 1H, H_{17}), 6.51 (dd, $J = 7.7, 0.8$ Hz, 2H, H_{15}), 5.24 (d, $J = 6.0$ Hz, 2H, H_{11}), 5.11 (t, $J = 6.0$ Hz, 2H, H_{12}), 5.03 (t, $J = 6.0$ Hz, 1H, H_{13}), 3.68 (s, 4H, H_4), 3.04 (hept, $J = 6.8$ Hz, 1H, H_3), 1.40 (d, $J = 7.0$ Hz, 12H, $H_{1/2}$), 1.20 (d, $J = 7.0$ Hz, 13H, $H_{1/2}$).

$^{13}\text{C-NMR}$ (126 MHz, C_6D_{12}) δ 214.73 (C_5), 159.41 (C_{14}), 148.25 (C_6), 140.20 (C_7), 130.64 (C_{10}), 129.36 (C_{16}), 128.16 (C_9), 124.05 (C_8), 122.03 (C_{17}), 118.02 (C_{15}), 88.96 (C_{13}), 87.37 (C_{12}), 84.51 (C_{11}), 52.66 (C_4), 29.32 (C_3), 25.40 ($C_{1/2}$), 24.42 ($C_{1/2}$).

Characterization data for minor species **15***:

The characterization data that was assigned to the minor species in solution **15*** is consistent with a Ni complex ligated by a molecule of diphenyl ether and a SIPr ligand.

$^1\text{H-NMR}$ (500 MHz, C_6D_{12}) δ 7.26 – 7.18 (m, 4H, $H_9^* + H_{16}^*$), 7.08 (d, $J = 7.6$ Hz, 4H, H_8^*), 6.97 – 6.92 (m, 1H, H_{17}^*), 6.91 – 6.88 (m, 2H, H_{15}^*), 4.95 – 4.87 (m, 4H, $H_{11,12}^*$), 4.82 (t, $J = 5.5$ Hz, 1H, H_{13}^*), 3.60 (s, 4H, H_4^*), 3.05 (hept, $J = 6.9$ Hz, 4H, H_3^*), 1.29 (d, $J = 6.9$ Hz, 12H, $H_{1/2}^*$), 1.16 (d, $J = 6.9$ Hz, 12H, $H_{1/2}^*$).

$^{13}\text{C-NMR}$ (126 MHz, C_6D_{12}) δ 214.24 (C_5^*), 158.40 (C_{14}^*), 148.10 (C_6^*), 140.30 (C_7^*), 134.21 (C_{10}^*), 129.95 (C_{16}^*), 128.03 (C_9^*), 123.97 (C_8^*), 123.38 (C_{17}^*), 119.47 (C_{15}^*), 88.64 (C_{13}^*), 83.59 (2C, $C_{11/12}^*$), 86.59 (2C, $C_{11/12}^*$), 52.60 (C_4^*), 29.24 (C_3^*), 25.32 ($C_{1/2}^*$), 24.67 ($C_{1/2}^*$).

HSQC correlations were observed between the H_{13}^* triplet (4.82 ppm) and C_{13}^* (88.64 ppm). Additional correlations were observed between the H_{11} - H_{12}^* multiplet (4.95 – 4.87 ppm,

4H) and 2 peaks in the ^{13}C -NMR spectrum at 83.59 and 86.59 ppm. Complete labeled spectra are represented below.

Minor resonances corresponding to $\text{SiPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**) were present in both the ^1H and ^{13}C -NMR spectra, although some resonances were obscured or not well resolved from the major products **15** and **15***. Full characterization data for **14** are included in Ogoshi's original report.⁴

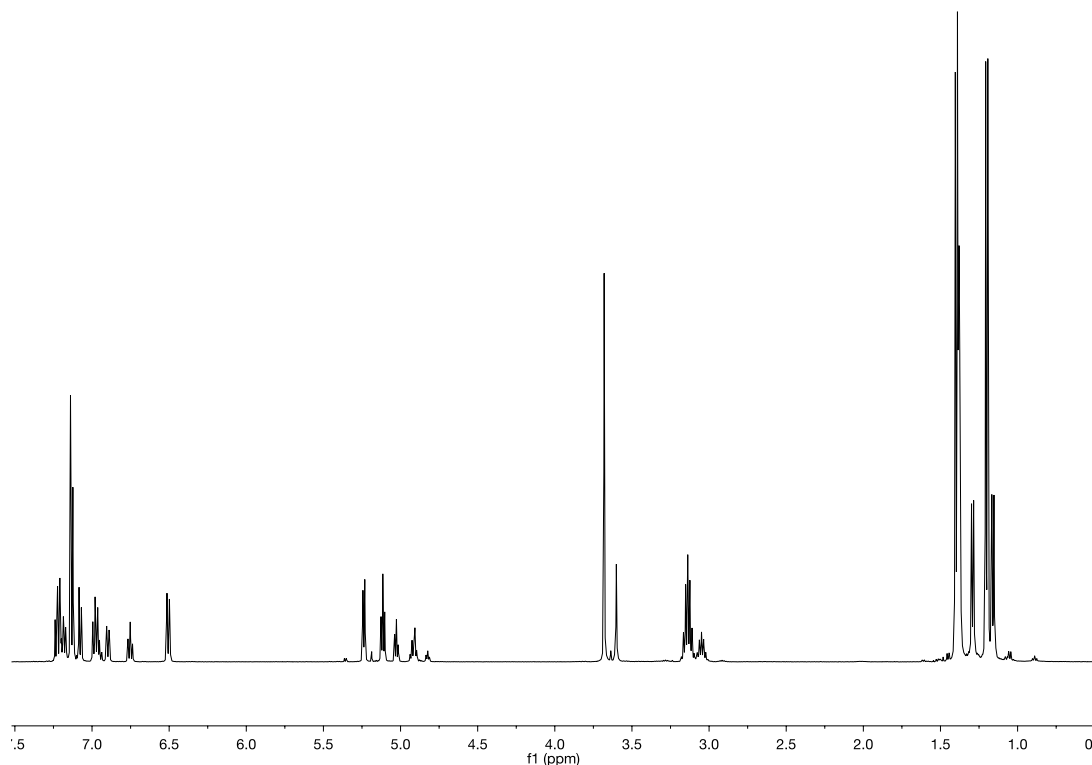


Figure S23: ^1H -NMR spectrum (500 MHz, C_6D_{12}) of the mixture of **15**, **15***, and starting material **14**

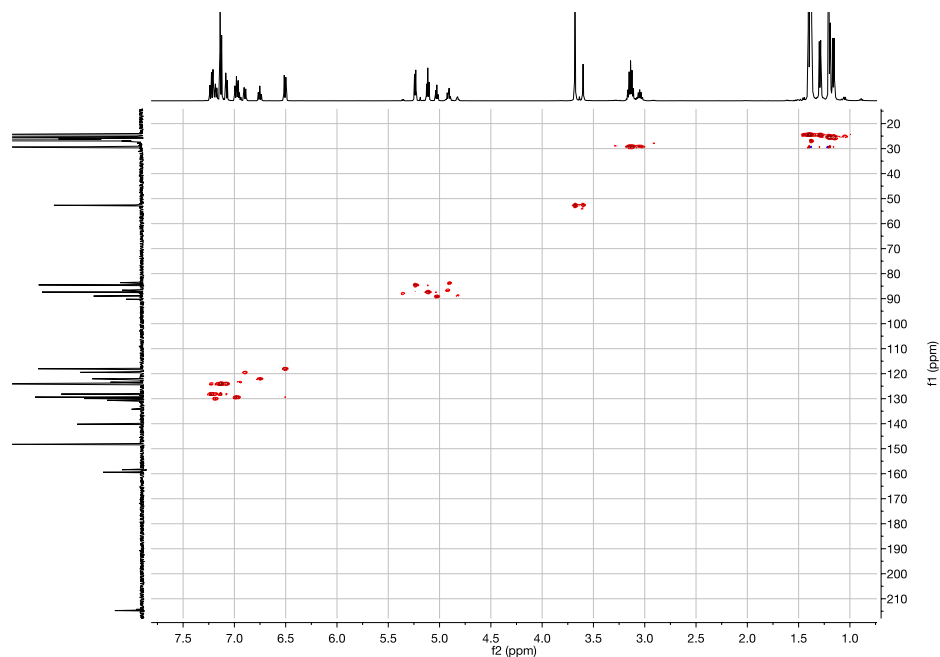


Figure S24: ^1H - ^{13}C HSQC of the mixture of **15**, **15***, and starting material **14**

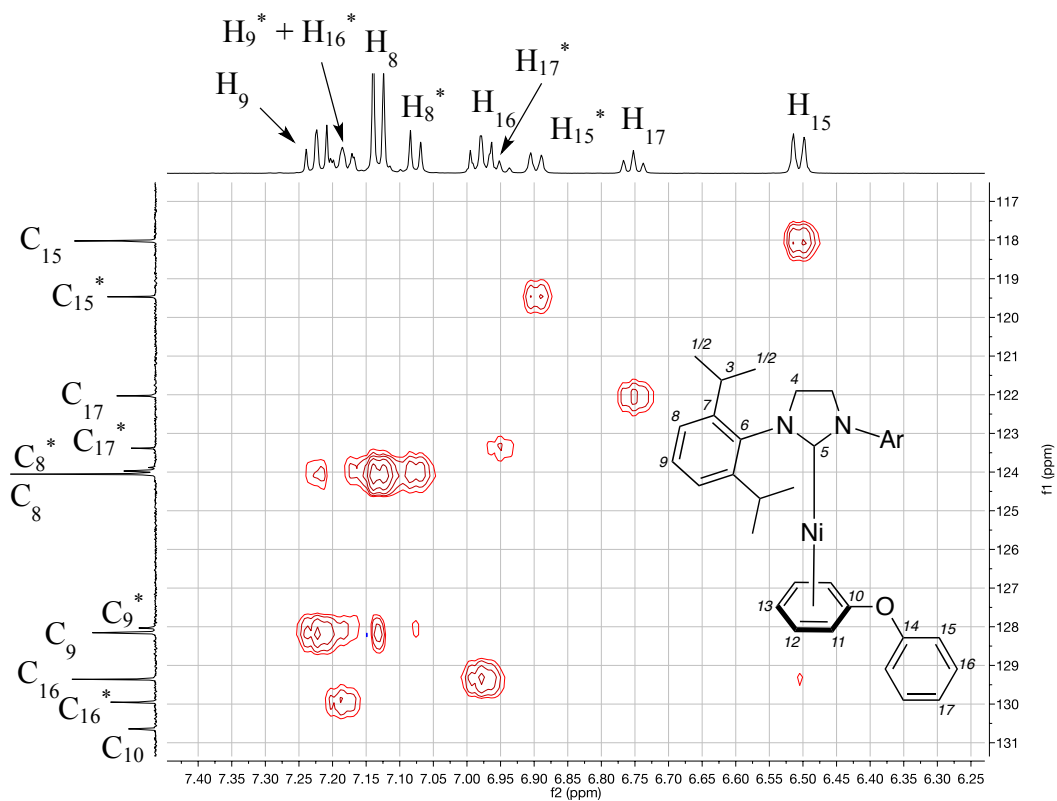


Figure S25: Expansion of the ^1H - ^{13}C HSQC spectrum of the mixture of **15**, **15***, and starting material **14**. Asterisks indicate peaks assigned to **15***.

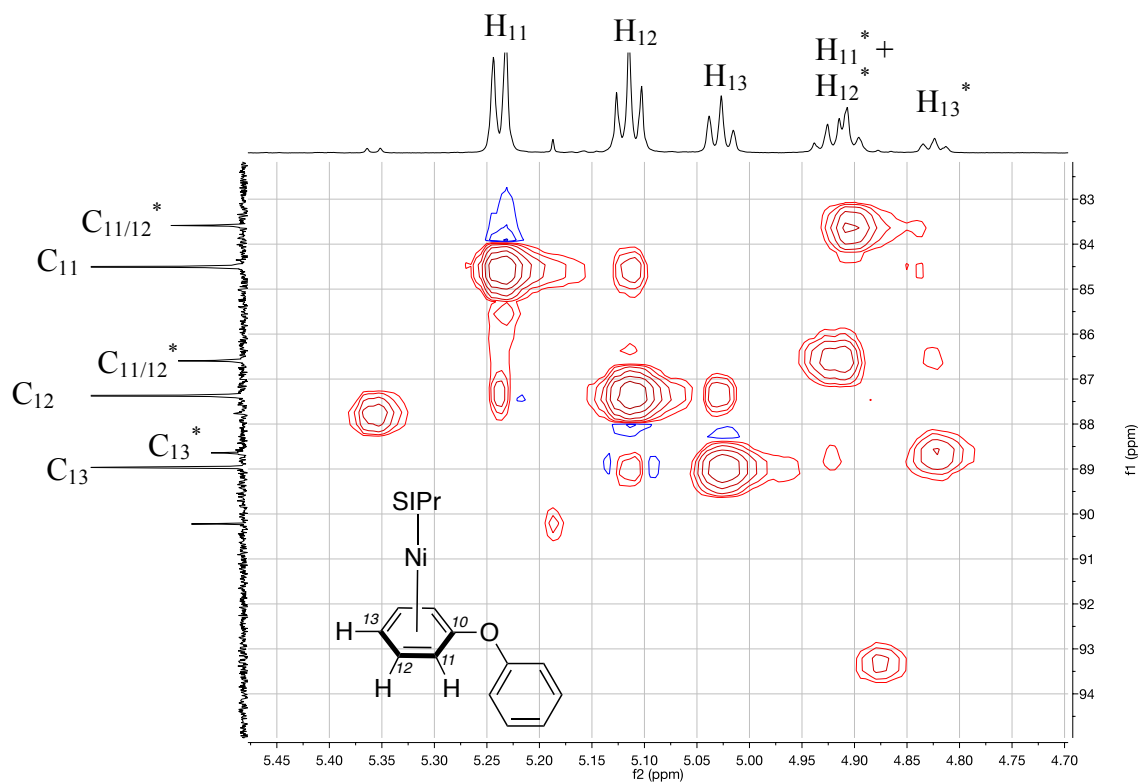


Figure S26: Expansion of the ^1H - ^{13}C HSQC spectrum of the mixture of **15**, **15***, and starting material **14**. Asterisks indicate peaks assigned to **15***.

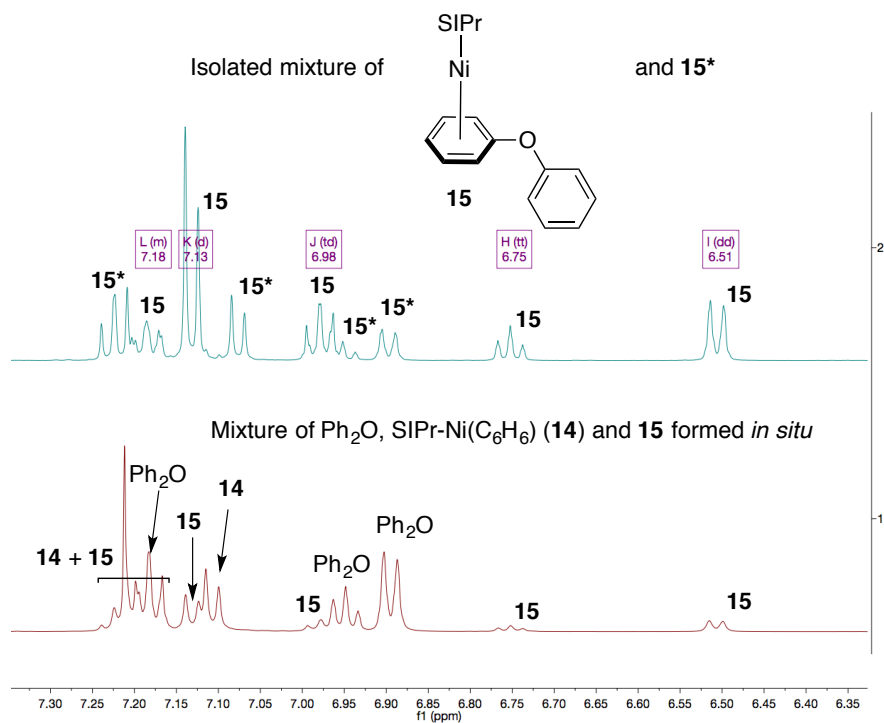


Figure S27: Comparison of ^1H -NMR spectrum of the isolated mixture of **15** and **15*** (top) with the ^1H -NMR spectrum of **15*** generated *in situ* in the presence of excess Ph_2O (bottom).

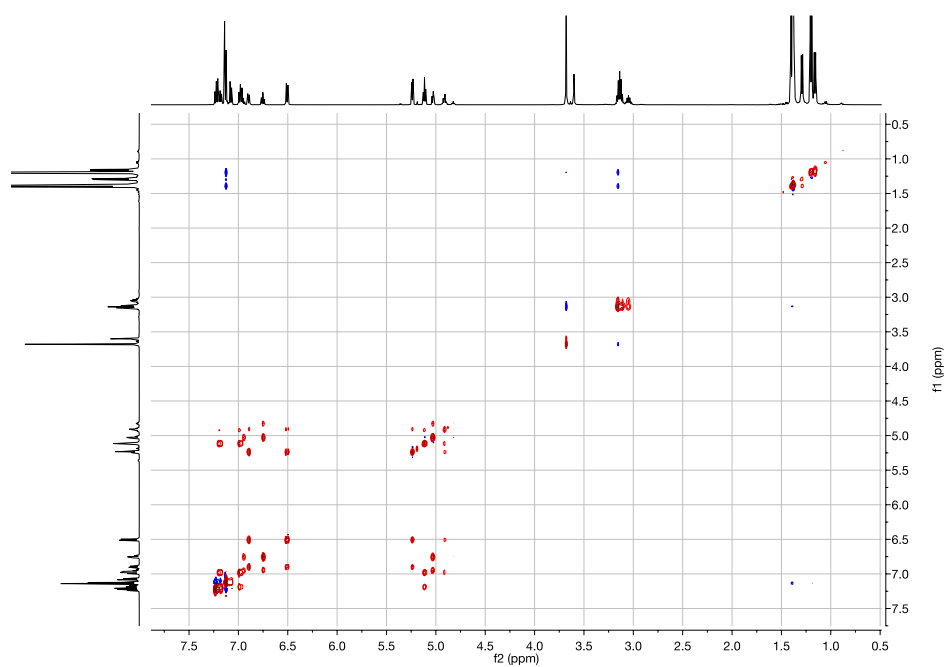


Figure S28: ^1H - ^1H EXSY spectrum of the mixture of η^6 -bound **15**, **15***, and starting material **14** (red crosspeaks correspond to EXSY interactions).

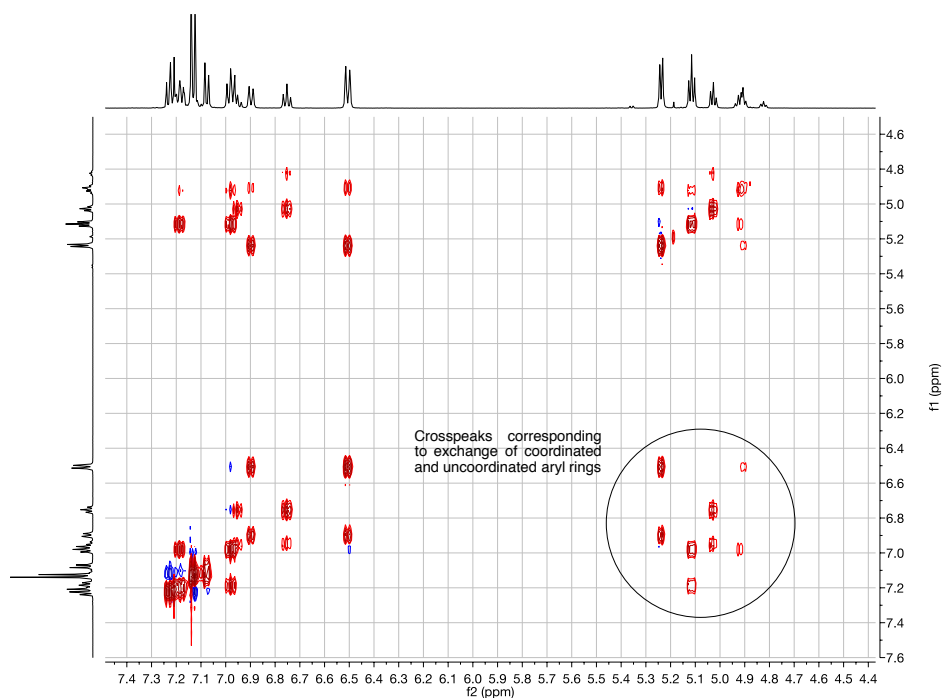


Figure S29: Expansion of ^1H - ^1H EXSY spectrum highlighting exchange of coordinated and uncoordinated aryl rings

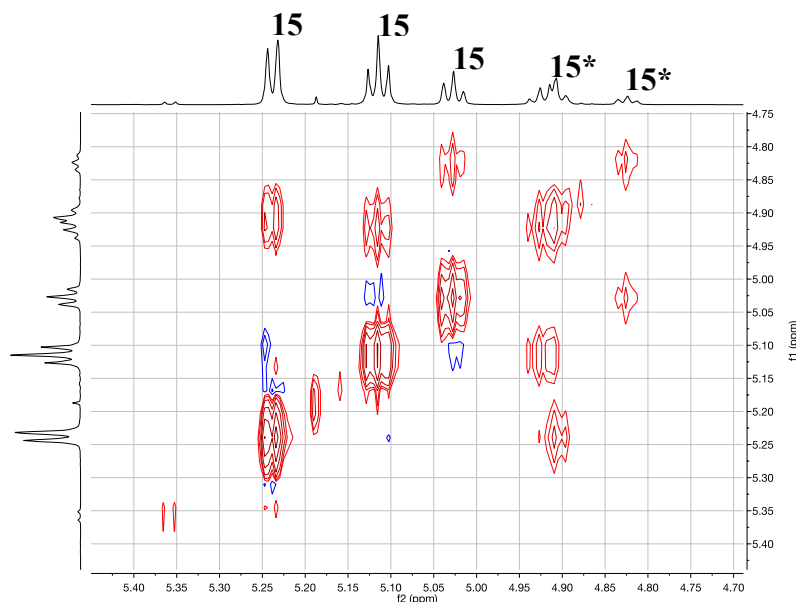
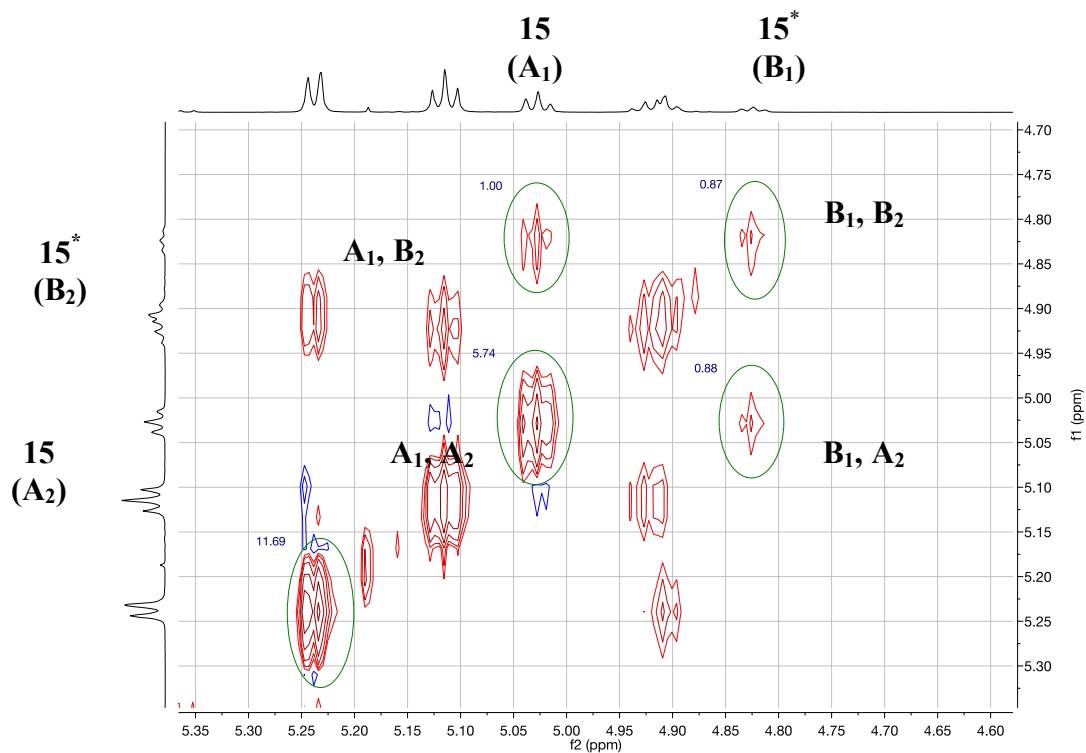


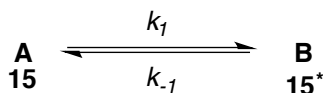
Figure S30: Expansion of ^1H - ^1H EXSY spectrum highlighting the isomerization between η^6 -bound **15** and **15***

^1H - ^1H EXSY Experiments

2D ^1H - ^1H EXSY experiments were recorded at 300 K with a 2 second mixing time. Integrations of relevant peaks in the EXSY spectrum, in addition to integrations from a reference ^1H -NMR spectrum with a 0 second mixing time, were used to calculate rate constants for chemical exchange. The raw values for integrations were introduced into EXSYCalc (Mestrelab), and rate exchange matrices and equilibrium constants for exchange were calculated. An example exchange matrix with the raw integration values for the exchange between η^6 -bound **15** and **15*** are included below.

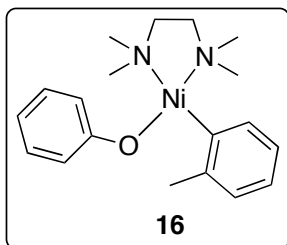


2 second mixing time			0 second mixing time		
	A ₁	B ₁			
A ₂	5.74	0.88	A	1.00	A ₂
B ₂	1.00	0.87	B	0.31	B ₂



For the exchange matrices above, the rate constant k_1 was calculated to be 0.11 s^{-1} . The half life for this exchange was calculated to be 6.1 s.

TMEDA-Ni(*o*-Tolyl)(OPh) (**16**)



To a mixture of TMEDA-Ni(*o*-Tolyl)Cl (0.500 g, 1.66 mmol) and NaOPh (0.228, 1.96 mmol) was added THF (15 mL). After 4 h, the deep red reaction mixture was filtered and concentrated. The orange residue was dissolved in benzene (40 mL) and filtered to remove NaCl and excess NaOPh. The filtrate was lyophilized to provide TMEDA-Ni(*o*-Tolyl)(OPh) as a fluffy orange solid (**16**, 0.424 g, 71%). Crystals suitable for single crystal

X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of **16** in THF at 0 °C.

¹H-NMR (500 MHz, C₆D₆) δ 7.75 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 2H), 6.83 (t, *J* = 7.0 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 2.26 (s, 3H), 1.82 (d, *J* = 4.4 Hz, 6H), 1.39 (td, *J* = 11.5, 3.3 Hz, 1H), 1.24 (td, *J* = 11.5, 3.8 Hz, 1H), 1.08 (s, 3H), 0.96 (dt, *J* = 12.9, 3.1 Hz, 1H), 0.74 (dt, *J* = 12.7, 3.4 Hz, 1H).

¹³C-NMR (151 MHz, CD₂Cl₂) δ 169.1, 150.9, 144.3, 136.8, 128.9, 126.2, 122.2, 121.8, 121.1, 112.4, 61.6, 56.6, 50.7, 48.5, 47.5, 45.6, 25.8.

Elemental Analysis: *Anal.* Calc. for C₁₉H₂₈N₂ONi: C, 63.54; H, 7.86; N, 7.80. Found: C, 63.79; H, 7.70; N, 7.67.

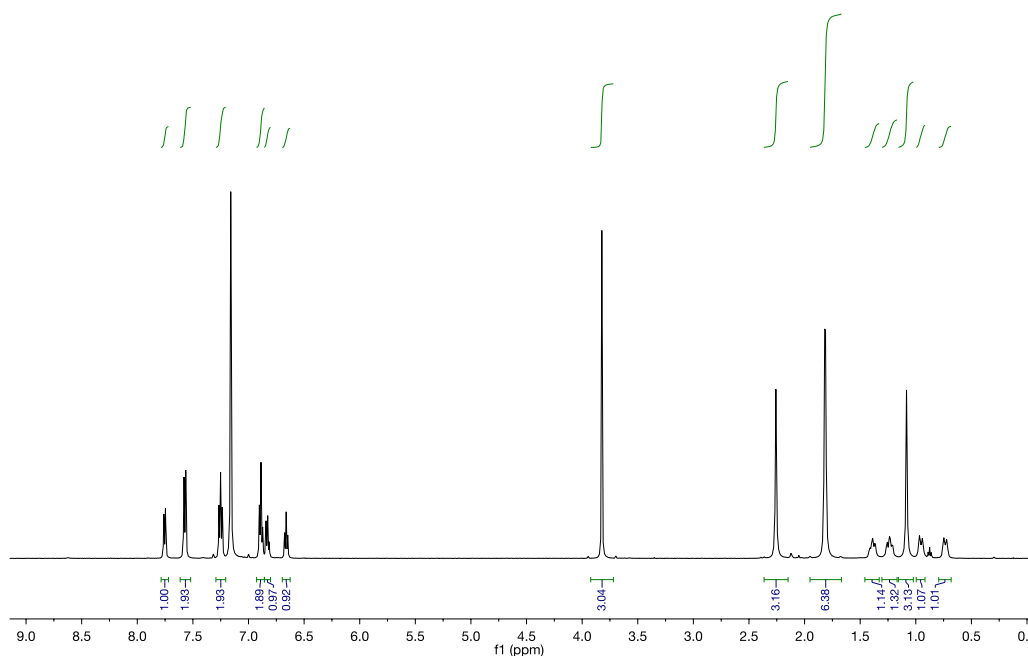


Figure S31: ¹H-NMR spectrum (500 MHz, C₆D₆) of TMEDA-Ni(*o*-Tolyl)(OPh) (**16**)

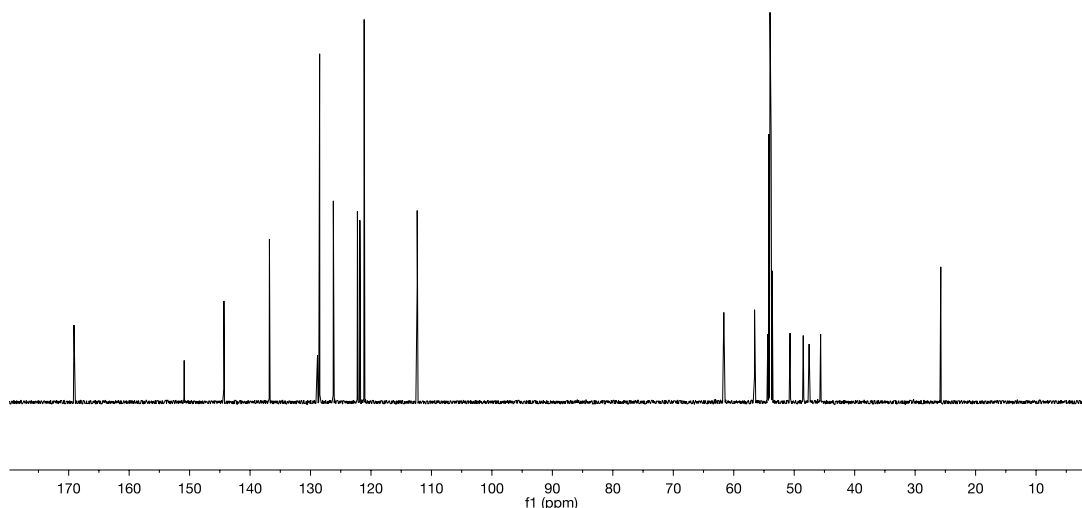
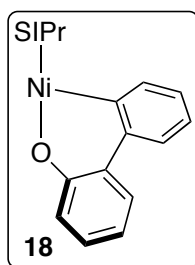


Figure S32: ^{13}C -NMR spectrum (151 MHz, CD_2Cl_2) of TMEDA-Ni(*o*-Tolyl)(OPh) (**16**)

Metallacycle **18**



A solution of SIPr-Ni($\eta^6\text{-C}_6\text{H}_6$) (**14**, 0.211 g, 0.396 mmol) in benzene (7 mL) and a solution of phenoxide **17** (0.107 g, 0.396 mmol) in benzene (3 mL) were frozen in a liquid nitrogen cooled cold well in the glovebox. The vial containing phenoxide **17** was withdrawn from the cold well, the solution was allowed to thaw, and the solution was layered onto the frozen solution of SIPr-Ni($\eta^6\text{-C}_6\text{H}_6$). The reaction mixture was allowed to warm to room temperature with stirring. During warming, the color transitioned from red to light orange to purple. After 1.5 h of stirring the reaction mixture was filtered to remove NaBr, the residue washed with benzene (5×10 mL), and the combined filtrate was lyophilized to give a brown/purple solid (Note: The desired product is only minimally soluble in benzene. The residue must be extracted with benzene well until the color of the resulting filtrate is no longer purple). The solids were washed with pentane (3×5 mL) and dried to provide metallacycle **18** as a purple powder (0.192 g, 79%).

Crystals suitable for single crystal X-ray diffraction were grown by vapor diffusion of pentane into a concentrated solution of **18** in THF at 0 °C.

¹H-NMR (600 MHz, C₆D₆): δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.15 – 7.08 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 4H), 6.87 (td, *J* = 7.0, 0.8 Hz, 1H), 6.73 (td, *J* = 6.5, 1.4 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.43 (td, *J* = 7.5, 1.0 Hz, 1H), 3.29 (s, 4H, *H_d*), 3.13 (hept, *J* = 6.8 Hz, 4H), 1.48 (d, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.8 Hz, 12H).

¹³C-NMR (151 MHz, C₆D₆): δ 207.6, 160.7, 146.9, 141.1, 138.9, 134.5, 132.4, 130.0, 128.14, 127.98, 126.2, 125.2, 125.1, 124.2, 122.0, 117.8, 115.3, 53.8, 29.6, 25.9, 24.1.

Elemental Analysis: Elemental analyses gave variable but consistently low values for C. A representative result is included. *Anal.* Calc. for C₃₉H₄₆N₂ONi: C, 75.86; H, 7.51; N, 4.54. Found: C, 74.80; H, 7.42; N, 4.20.

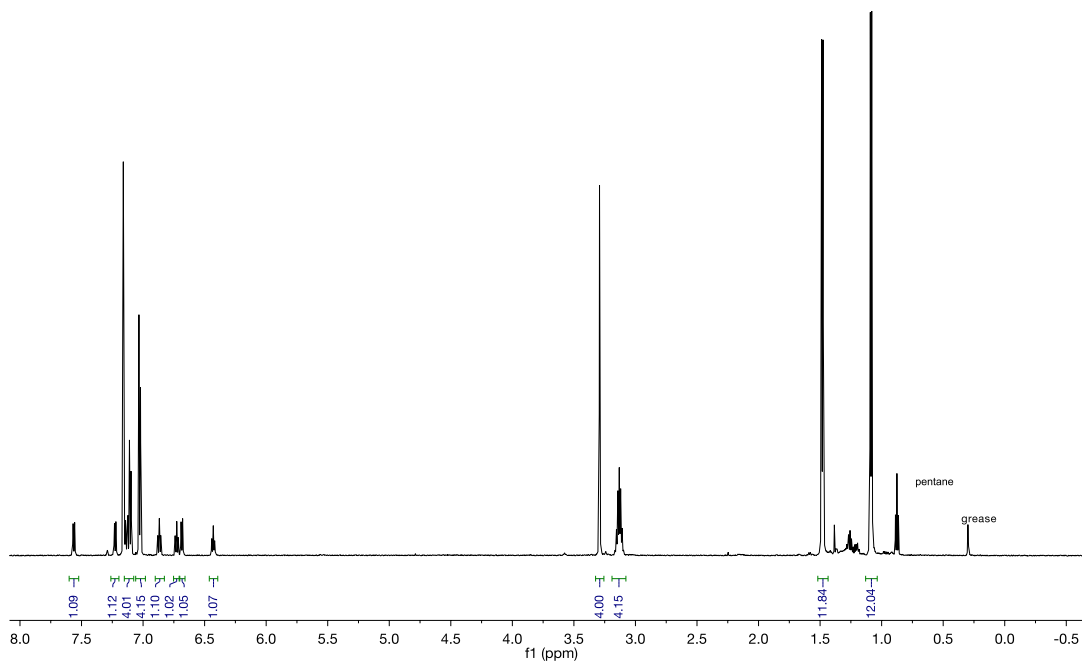


Figure S33: ¹H-NMR spectrum (500 MHz, C₆D₆) of metallacycle **18**. Residual pentane and grease impurities are labeled.

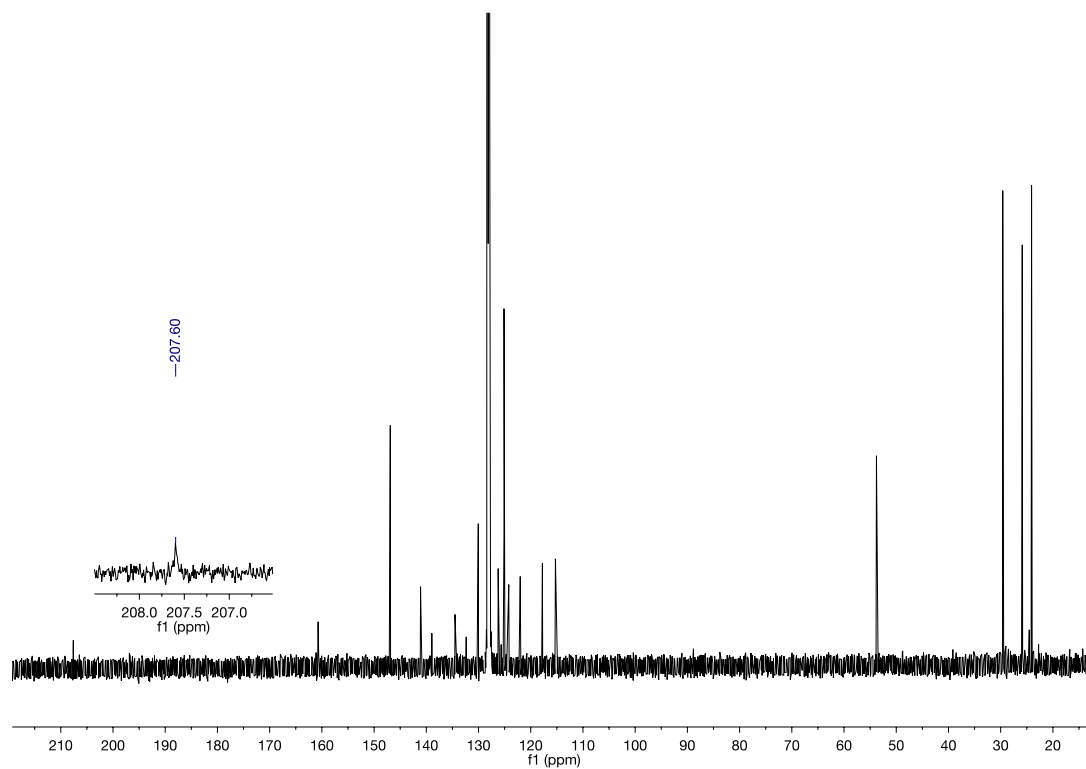


Figure S34: ^{13}C -NMR spectrum (151 MHz, C_6D_6) of metallacycle **18**.

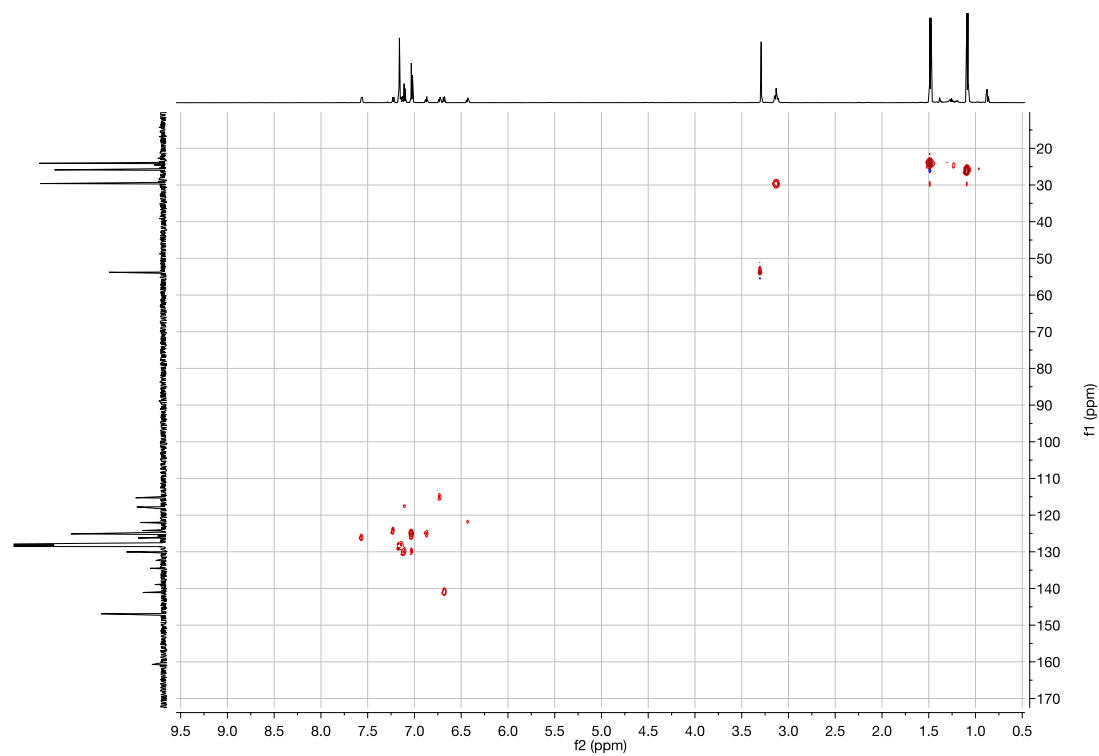


Figure S35: ^1H - ^{13}C HSQC of metallacycle **18**.

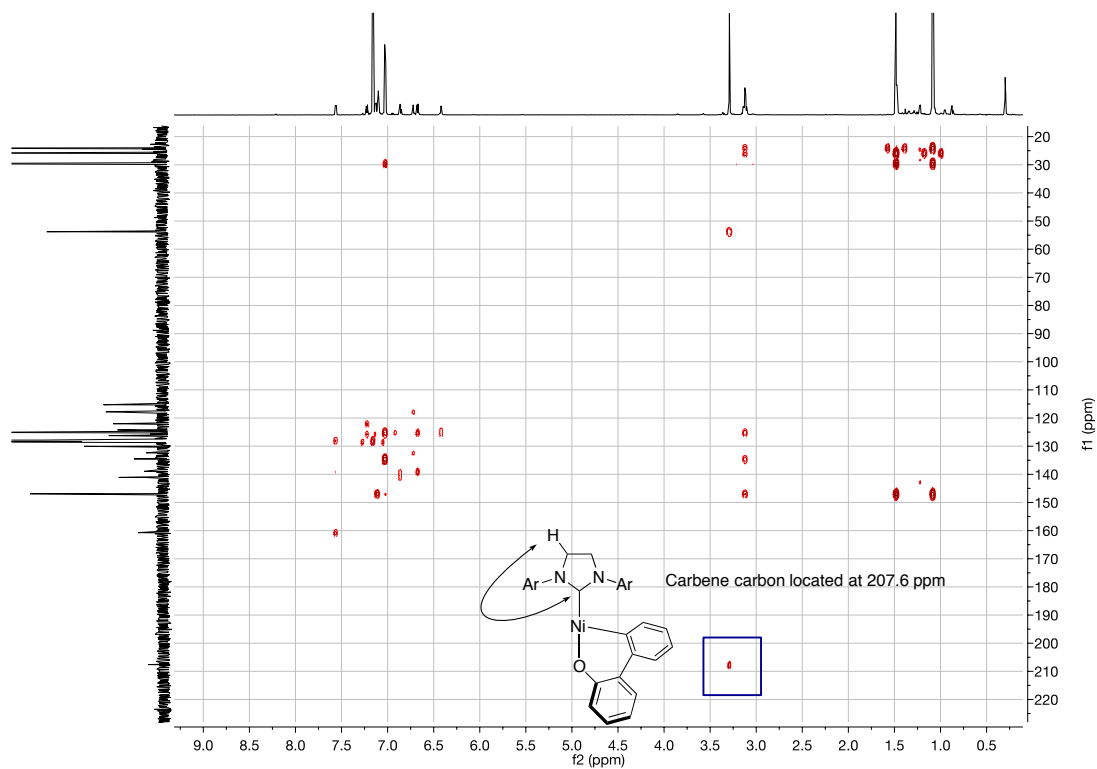
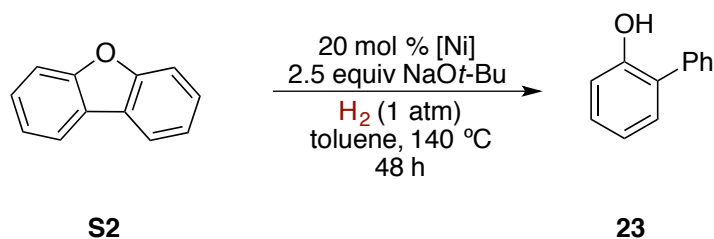
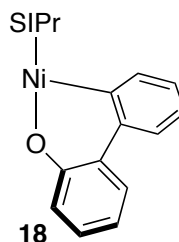
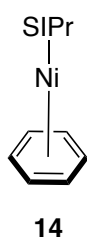


Figure S36: ^1H - ^{13}C HMBC of metallacycle 18. The signal indicating the location of the carbene carbon is highlighted.

Hydrogenolysis of Dibenzofuran

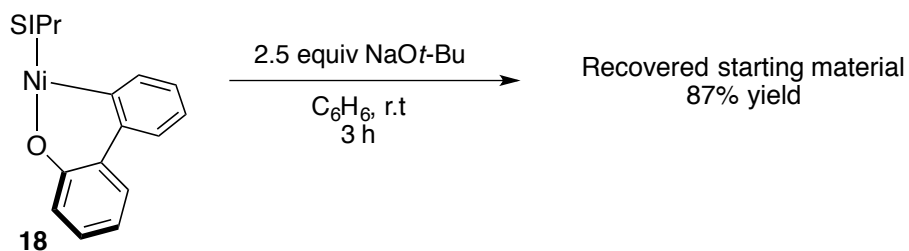


Entry	[Ni]	Conversion (%)	Yield of 23 (%)
1	14	88	87
2	18	49	49



The general procedure for the hydrogenolysis of diaryl ethers was followed with Ni complex **14** or **18** (0.030 mmol) and NaOt-Bu (36.0 mg, 0.375 mmol). Dibenzofuran (**S2**, 0.150 mmol) and dodecane (0.150 mmol) were added as a stock solution in toluene (0.8 mL). The reaction was pressurized as in the general procedure and heated at 140 °C for 48 h. The reaction mixture was allowed to cool to room temperature, diluted with Et₂O (1 mL), and quenched by the addition of 1.5 M HCl (1 mL). The reaction mixture was allowed to stir for 10 min, the organic layer was removed, and the aqueous layer was extracted with an additional portion of Et₂O (1 mL). The combined organic layers were filtered over a 1 cm plug of Celite[®] and analyzed by GC and GC/MS.

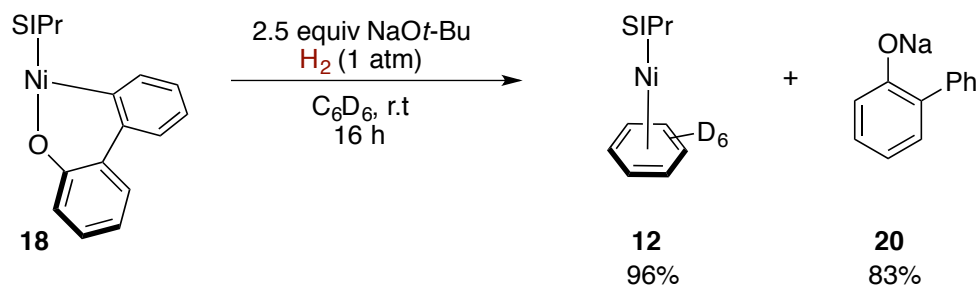
Reaction of metallacycle **18** with NaOt-Bu



To a 4 mL vial charged with metallacycle **18** (0.062 g, 0.100 mmol) and NaOt-Bu (0.024 g, 0.250 mmol) was added benzene (3 mL). The reaction mixture was allowed to stir vigorously

for 3 h, filtered, and layered with pentane (10 mL) to crystallize overnight. The yellow filtrate was decanted, and the purple crystalline solids were washed with pentane (1 mL) and dried (0.054 g, 87% yield). ^1H -NMR analysis in C_6D_6 indicated recovered starting material.

Reaction of metallacycle **18** with H_2 and NaOt-Bu

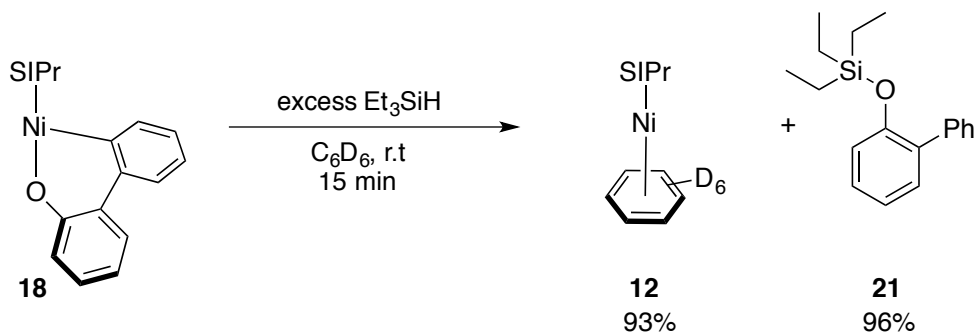


*Yield of **12**:* In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with NaOt-Bu (4.8 mg, 0.050 mmol). To the Schlenk tube was added a stock solution of metallacycle **18** (12.4 mg, 0.020 mmol) and trimethoxybenzene (1.7 mg, 0.0101 mmol) in C_6D_6 (0.8 mL). The reaction mixture was sealed, removed from the glovebox, and transferred to a Schlenk line. The reaction mixture was degassed via 3 cycles of freeze-pump-thaw, the atmosphere of the Schlenk line was exchanged via three cycles of evacuation and backfilling with H_2 , and the reaction was pressurized to ~ 1 atm of H_2 . The Schlenk tube was allowed to stir at room temperature for 16 h. The reaction mixture filtered over a 1 cm plug of Celite[®] directly into an NMR tube to quantify a yield of 96% of **12** by ^1H -NMR spectroscopy.

*Yield of **20**:* The yield of phenoxide **20** was determined by neutralization of the reaction mixture and quantification of 2-phenylphenol by GC. In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with NaOt-Bu (4.8 mg, 0.050 mmol). To the Schlenk tube was added a stock solution of metallacycle **18** (13.9 mg, 0.0225 mmol) and dodecane (3.8 mg, 0.0223 mmol) in C_6D_6 (0.8 mL). The reaction mixture was sealed, removed from the glovebox, and transferred to a Schlenk line. The reaction mixture was degassed via 3 cycles of freeze-pump-thaw, the atmosphere of the Schlenk line was exchanged via three cycles of evacuation and backfilling with H_2 , and the reaction was pressurized to ~ 1 atm of H_2 . The Schlenk tube was allowed to stir at room temperature for 16 h, diluted with Et_2O (1 mL), and quenched by the addition of 1.5 M HCl (1 mL). The reaction mixture was allowed to stir for 10 min, the organic layer was removed, and the aqueous layer was extracted with an

additional portion of Et₂O (1 mL). The combined organic layers were filtered over a 1 cm plug of Celite[®] and analyzed by GC to quantify a calibrated yield of 83% of 2-phenylphenol.

Reaction of metallacycle **18** with Et₃SiH



To a 4 mL vial charged with metallacycle **18** (20.9 mg, 0.034 mmol) and trimethoxybenzene (1.6 mg, 0.001 mmol) was added benzene (0.5 mL). Et₃SiH (22.0 mg, 0.189 mmol) was added, and the reaction mixture immediately turned to deep red color. The reaction mixture was allowed to stir vigorously for 15 min and concentrated completely to remove excess silane. The residue was suspended in C₆D₆, and filtered directly into an NMR tube to quantify a yield of 93% and 96% yield of **12** and **21** respectively by ¹H-NMR spectroscopy. An aliquot of this sample showed the major product to be silyl ether **21** by GC/MS (*m/z* = 284).

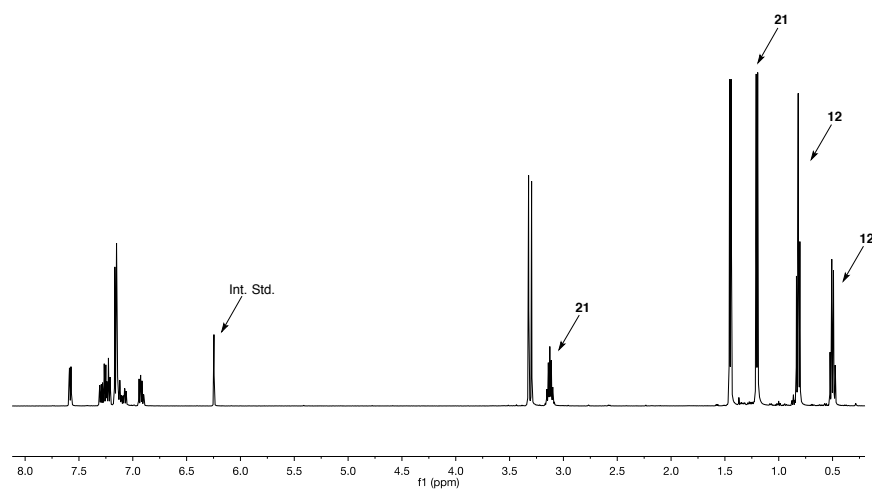
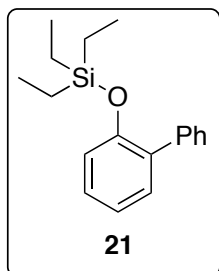


Figure S37: ¹H-NMR spectrum of the reaction between metallacycle **18** and Et₃SiH.

Authentic synthesis of silyl ether **21**



To a stirring solution of 2-phenylphenol (**22**, 0.500 g, 2.94 mmol) and NEt₃ (0.620 mL, 4.45 mmol) in THF (10 mL) under N₂ was added chlorotriethylsilane (1M in THF, 3.40 mL, 3.40 mmol) dropwise. The reaction mixture was allowed to stir for 6 h, was filtered over a plug of Celite, and was then concentrated to a yellow oil. The product was purified

by column chromatography (40 g cartridge, 0-10% EtOAc in Hexanes) to provide silyl ether **21** as a clear oil (0.751 g, 90%).

¹H-NMR (500 MHz, C₆D₆) δ 7.60 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.32 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.24 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.16 – 7.11 (m, 3H), 7.09 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1H), 6.93 (ddd, *J* = 14.1, 8.2, 1.5 Hz, 1H), 0.83 (t, *J* = 8.0 Hz, 9H), 0.51 (q, *J* = 8.0 Hz, 6H).

¹³C-NMR (126 MHz, C₆D₆) δ 153.1, 139.7, 133.8, 131.3, 130.1, 128.7, 128.2, 127.1, 122.2, 120.5, 6.8, 5.4.

HRMS (EI): *m/z* for C₁₈H₂₄OSi [M]⁺ calc'd: 284.1596; found: 284.1601.

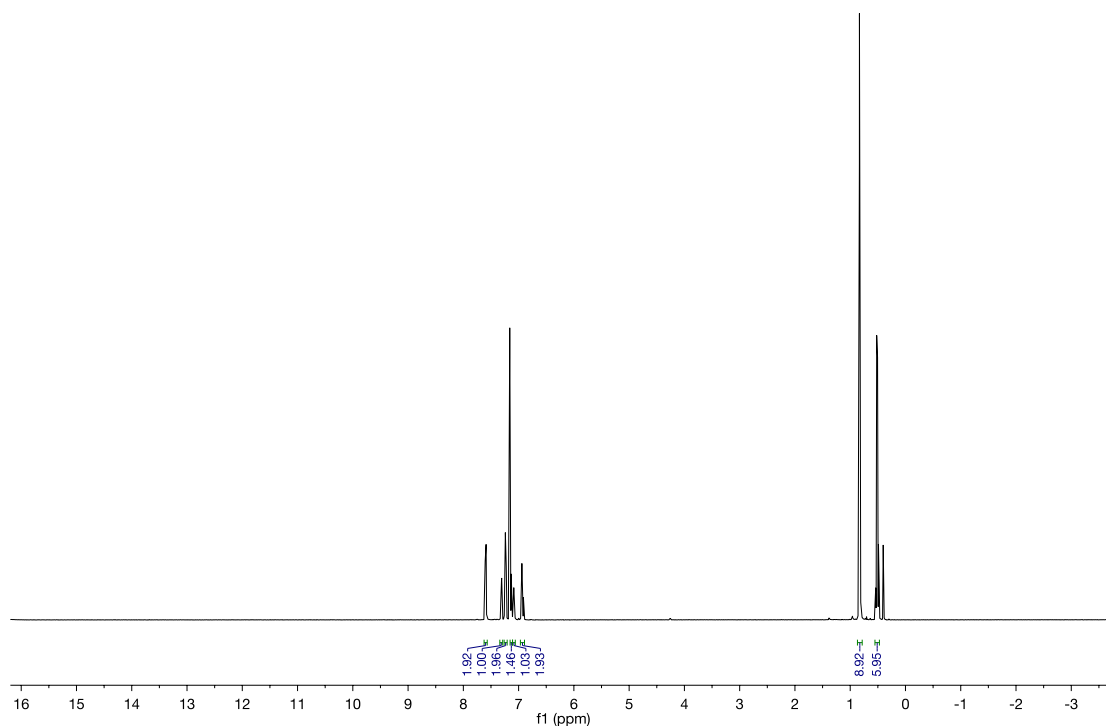


Figure S38: ¹H-NMR spectrum (500 MHz, C₆D₆) of silyl ether **21**.

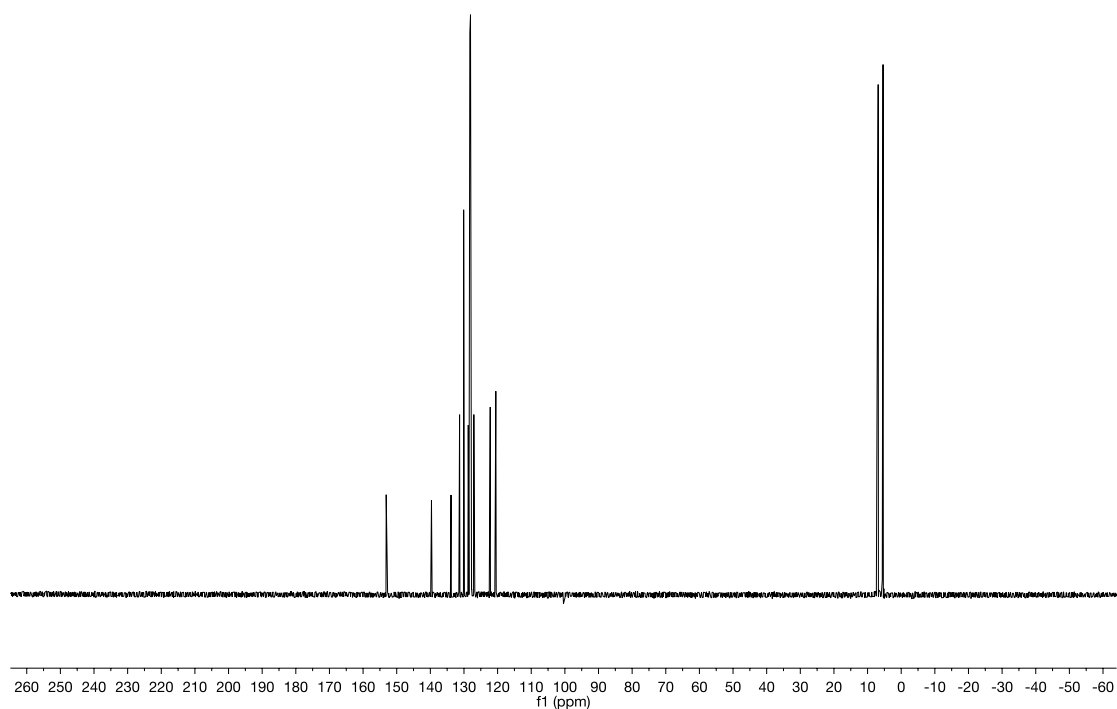
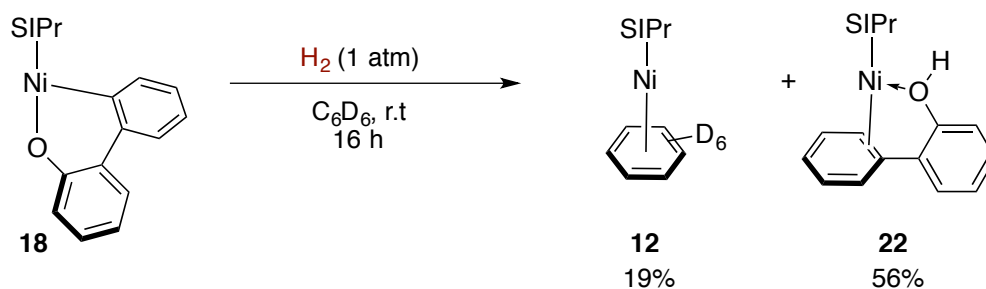


Figure S39: ^{13}C -NMR spectrum (126 MHz, C_6D_6) of silyl ether **21**.

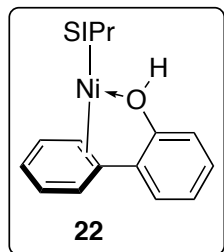
Reaction of metallacycle **18** with H_2



In a glovebox, a 15 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stir bar was charged with a stock solution of metallacycle **18** (12.4 mg, 0.020 mmol) and trimethoxybenzene (1.7 mg, 0.0101 mmol) in C_6D_6 (0.8 mL). The reaction mixture was sealed, removed from the glovebox, and transferred to a Schlenk line. The reaction mixture was degassed via 3 cycles of freeze-pump-thaw, the atmosphere of the Schlenk line was exchanged via three cycles of evacuation and backfilling with H_2 , and the reaction was pressurized to ~ 1 atm of H_2 . The purple reaction mixture turned to a red color as it was allowed to stir vigorously at room temperature for 16 h. The reaction mixture was filtered over a 1 cm plug of Celite[®]

directly into an NMR tube to quantify a yield of 19% of **12** along with the formation of Ni species **22** in 56% yield by ^1H -NMR spectroscopy.

Phenol-bound **22**



To a mixture of $\text{SIPr-Ni}(\eta^6\text{-C}_6\text{H}_6)$ (**14**, 0.300 g, 0.569 mmol) and 2-phenylphenol (**23**, 0.108 g, 0.635 mmol) was added pentane (10 mL). The reaction mixture was allowed to stir for 2 and then concentrated completely to a red foam. The crude product was washed with HMDSO (4 mL) and dried to give crude **22** as a red powder (0.310 g, 88%). The product was further purified by recrystallization from pentane/HMDSO to give **22** (0.157 g, 45%). Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation from a concentrated solution of **22** in pentane at 0 °C.

^1H -NMR: (500 MHz, C_6D_{12}) δ 7.59 (d, $J = 7.9$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.14 – 6.96 (m, 7H), 6.87 (broad s, 1H), 6.54 (dd, $J = 7.6, 1.8$ Hz, 1H), 6.41 (t, $J = 7.9$ Hz, 1H), 6.23 (t, $J = 7.6$ Hz, 1H), 3.15 (s, 8H), 2.12 (broad s, OH, 1H, integration is significantly higher than 1H due to broadening from hydrogen bonding), 1.08 (d, $J = 6.9$ Hz, 24H).

When degassed D_2O (5 μL) was added to an NMR sample of **22** in C_6D_{12} , the broad signal at 2.12 ppm was not present.

^{13}C -NMR: (126 MHz, C_6D_{12}) δ 213.1, 162.2, 147.0, 141.3, 137.1, 132.2, 130.3, 128.4, 128.1, 127.5, 127.4, 125.9, 125.2, 124.5, 116.2, 53.5, 29.5, 27.0, 26.8.

Elemental Analysis: We were not able to obtain satisfactory elemental analysis for this compound. A representative result is included. *Anal.* Calc. for $\text{C}_{39}\text{H}_{46}\text{N}_2\text{ONi}$: C, 75.61; H, 7.81; N, 4.52. Found: C, 74.07; H, 7.33; N, 4.22.

IR (KBr solution cell, pentane): ν 3572 cm^{-1}

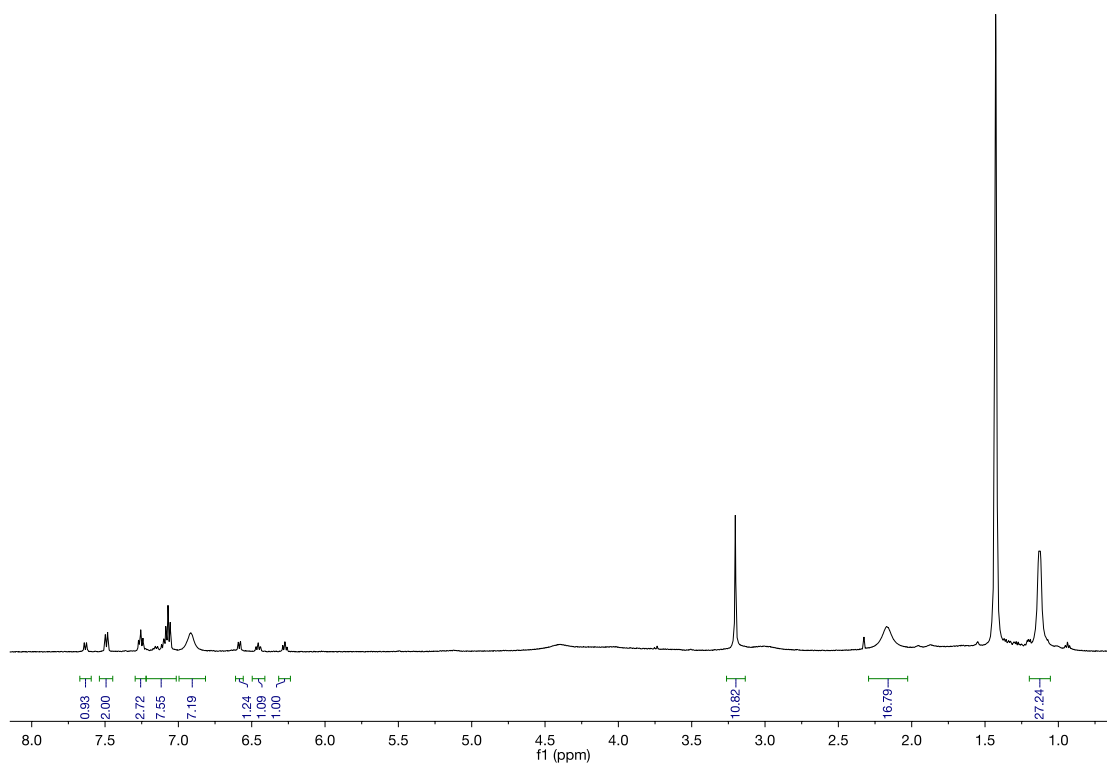


Figure S40: ¹H-NMR spectrum (500 MHz, C₆D₁₂) of phenol bound **22**.

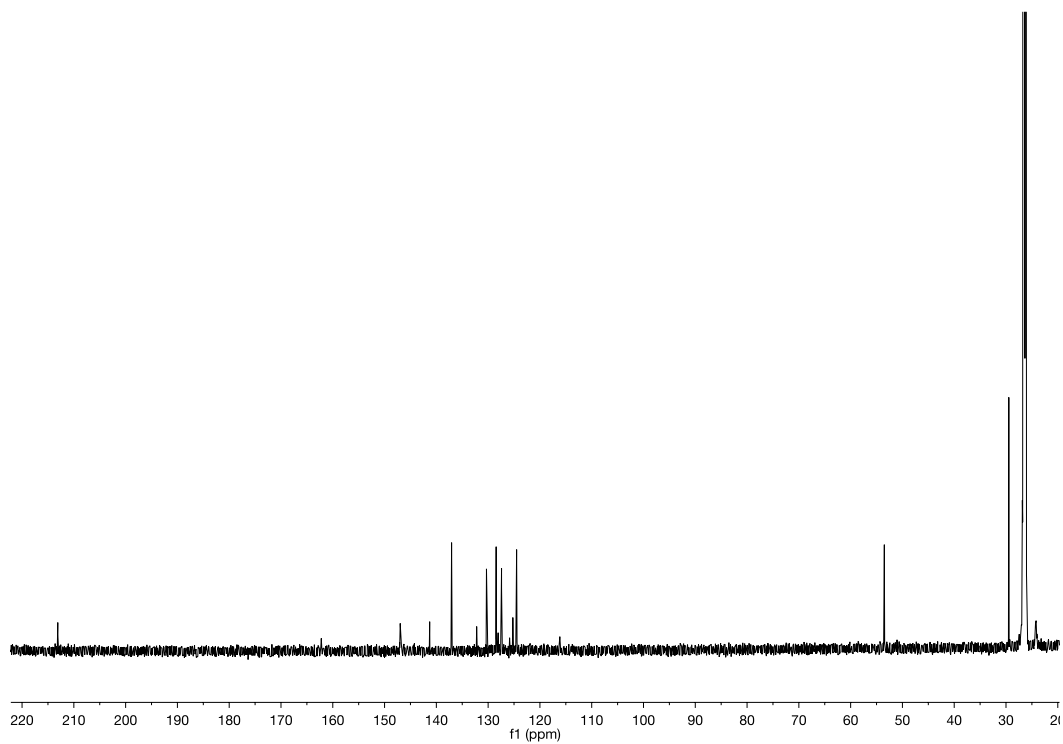


Figure S41: ¹³C-NMR spectrum (126 MHz, C₆D₁₂) of phenol bound **22**.

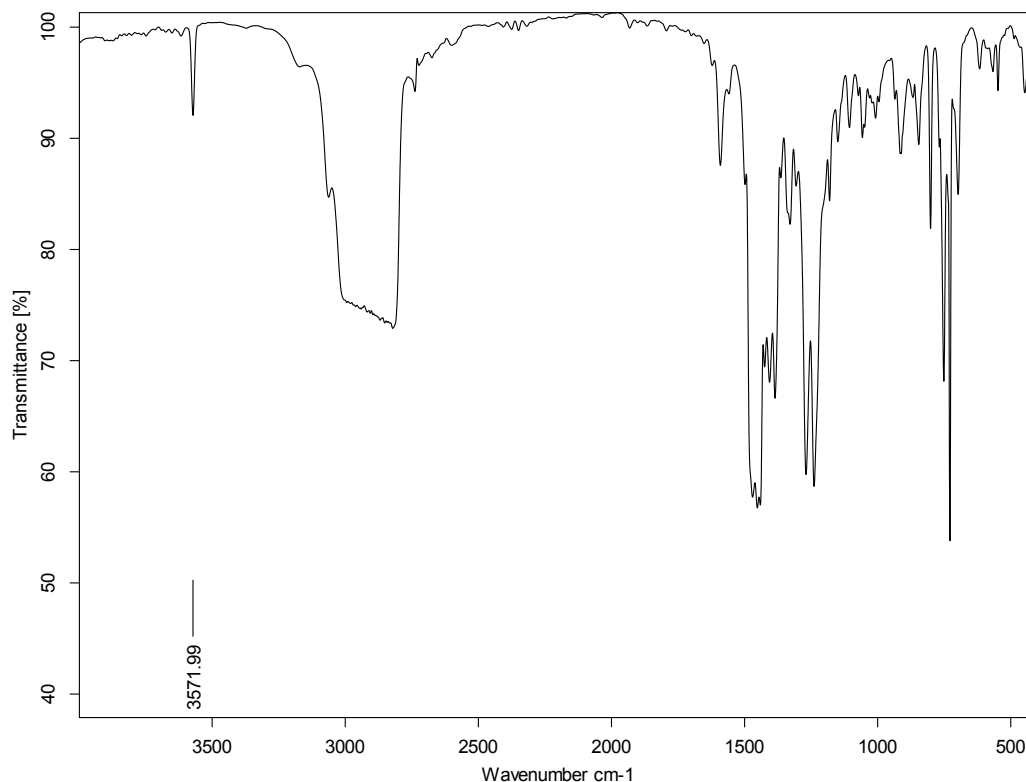
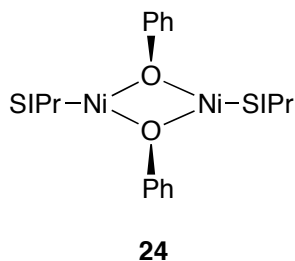


Figure S42: Solution cell IR spectra of phenol bound **22**.

[SIPr–Ni(μ–OPh)]₂ (24**)**



Method A: To a mixture of SIPr–Ni(η^6 –C₆H₆) (**14**, 0.200 g, 0.375 mmol) and PhOH (0.043 g, 0.452 mmol) was added pentane (5 mL). After four hours of stirring, an orange solid had precipitated from the reaction mixture. The reaction mixture was filtered, the solids were washed with pentane (3 × 3 mL), and were dried to give dimer **24** as an

orange solid (0.168 g, 82%).

Method B: To a solution of [SIPr–Ni(μ–Cl)]₂ (0.200 g, 0.206 mmol) in THF (8 mL) was added a solution of NaOPh (0.053 g, 0.454 mmol) in THF (2 mL). The reaction mixture was allowed to stir for 16 h. The dark orange reaction mixture was filtered, concentrated to dryness, and the residue was dissolved in benzene (5 mL). The benzene solution was filtered to removed excess NaOPh, the filtrate was lyophilized, and the resulting orange powder was washed with cold pentane (5 mL) to provide Ni dimer **24** as an orange solid (0.136 g, 61%). Analytically pure material as well crystals suitable for single crystal X-ray diffraction were obtained by layered

diffusion of pentane into a concentrated solution of dimer **24** in THF at 0 °C to provide orange blocks of Ni dimer **24** (0.049 g, 22%).

¹H-NMR (500 MHz, C₆D₆): δ 11.50 (Δv_{1/2} = 30.9 Hz, 4H), 8.21 (Δv_{1/2} = 79.5 Hz, 24H, Ar-CH(CH₃)₂), 7.44 (Δv_{1/2} = 22.6 Hz, 8H), 6.50 (Δv_{1/2} = 0.6 Hz, 8H), 5.75 (Δv_{1/2} = 21.6 Hz, 4H), 2.50 (Δv_{1/2} = 16.6 Hz, 24H, Ar-CH(CH₃)₂), -5.35 (Δv_{1/2} = 28.2 Hz, 2H), -7.21 (Δv_{1/2} = 30.2 Hz, 8H), -9.93 (Δv_{1/2} = 0.3 Hz, 4H).

Evans Method (298 K, C₆D₆): 2.89 μB.

Elemental Analysis: *Anal.* Calc. for C₆₆H₈₇N₄O₂Ni₂: C, 73.07; H, 7.99; N, 5.16. Found: C, 72.99; H, 7.85; N, 4.90.

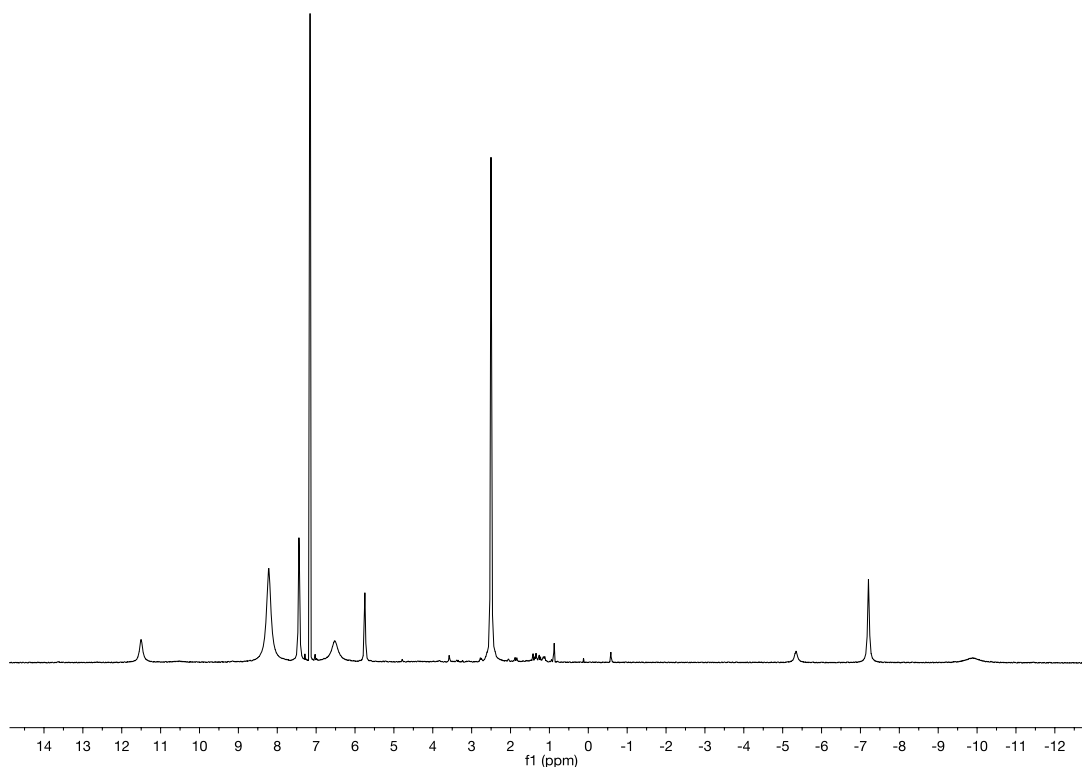
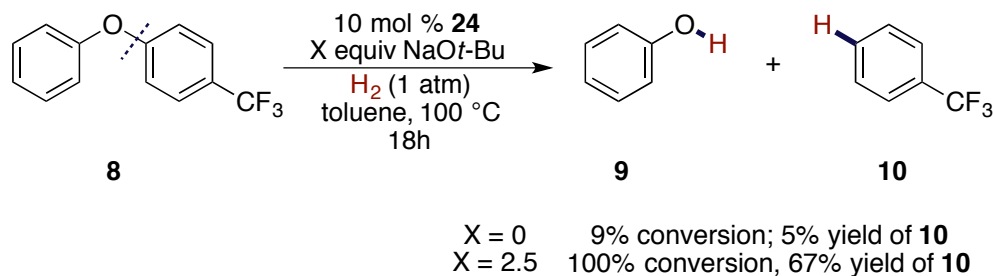


Figure S43: ¹H-NMR spectrum (500 MHz, C₆D₆) of dimer **24**.

Catalytic Reactivity of Dimer 24



The general procedure for the catalytic hydrogenolysis of diaryl ether **8** was followed with 10 mol % of dimer **24** (20 mol% Ni total) with and without NaOt-Bu.

Initial Rate Kinetics of Dimer 24

The general procedure for initial rates was followed to prepare two J. Young NMR tubes as described above (Entry 7, Table S2), except one J. Young NMR tubes was charged with a stock solution of dimer **24** (5 mol%, 0.0144 M solution, 174 μ L, 0.0025 mmol) instead of complex **14**. The data collected are shown below.

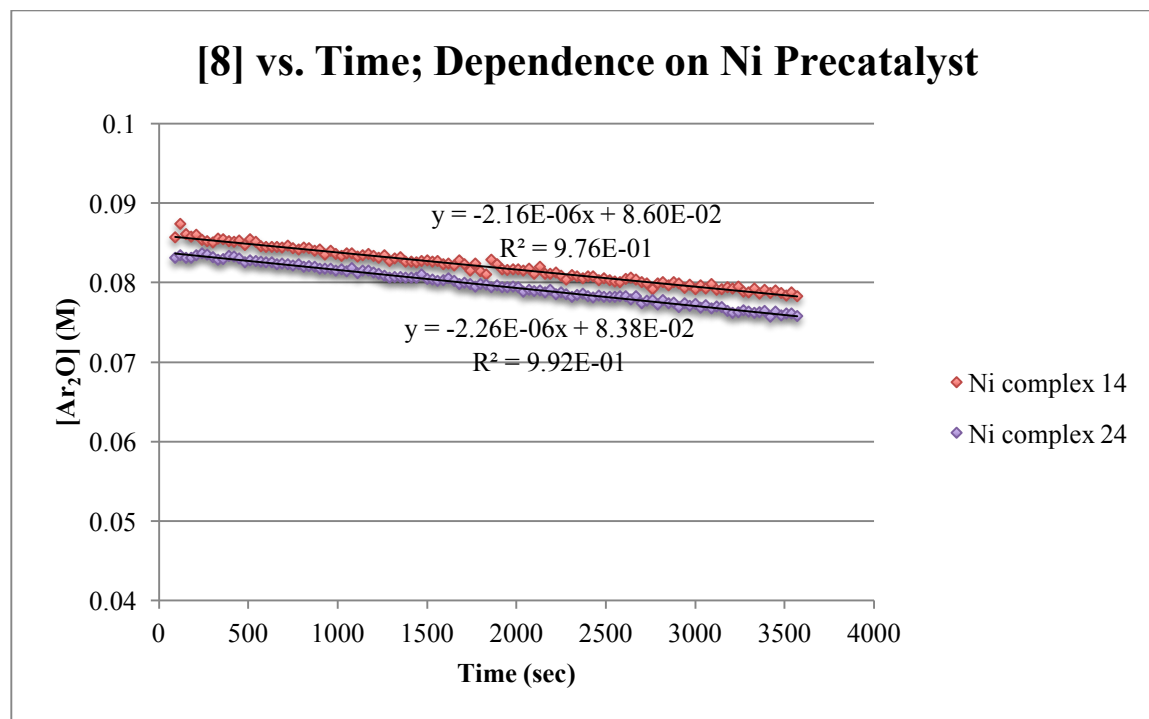


Figure S44: Plot of the concentration of **8** over time with Ni complex **14** or **24** as catalyst.

X-ray Data

A single crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

SIPr-Ni(η^6 -Ph-OPh) **15** (Yellow plate): Crystal-to-detector distance was 60 mm and exposure time was 30 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 25.000° in θ . A total of 45124 reflections were collected covering the indices, $-25 \leq h \leq 23$, $-20 \leq k \leq 20$, $-11 \leq l \leq 9$. 3259 reflections were found to be symmetry independent, with an R_{int} of 0.2026. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be $Pnma$ (No. 62).

TMEDA-Ni(*o*-Tolyl)(OPh) (**16**, orange prism): Crystal-to-detector distance was 40 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 99.9% complete to 25.000° in θ . A total of 23695 reflections were collected covering the indices, $-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$. 3346 reflections were found to be symmetry independent, with an R_{int} of 0.0283. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$ (No. 14).

Metallacycle **18**: Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 25.000° in θ . A total of 203027 reflections were collected covering the indices, $-14 \leq h \leq 14$, $-19 \leq k \leq 19$, $41 \leq l \leq 41$. 12257 reflections were found to be symmetry independent, with an R_{int} of 0.0468. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$ (No. 14).

Phenol-Bound Ni **22**: Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.4% complete to 23.254° in θ . A total of 64676 reflections were collected covering the indices, $-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$. 6048 reflections were found to be symmetry independent, with an R_{int} of 0.1498.

Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2).

[SIPr-Ni(μ -OPh)]₂ (**24**, yellow plate): Crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 100.0% complete to 25.000° in θ . A total of 76389 reflections were collected covering the indices, $-27 \leq h \leq 27$, $-12 \leq k \leq 12$, $-31 \leq l \leq 30$. 5360 reflections were found to be symmetry independent, with an R_{int} of 0.0351. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be C 2/c (No. 15).

Table S7: Crystal Structure Data

	SIPr-Ni(η^6 -Ph-OPh) 15	TMEDA-Ni(<i>o</i> -Tolyl)(OPh) (16)	Metallacycle 18	Phenol Bound Ni 22 • 2-phenylphenol 23	[SIPr-Ni(μ -OPh)] ₂ (24)
Empirical formula	C ₃₉ H ₄₈ N ₂ NiO	C ₁₉ H ₂₈ N ₂ NiO	C ₃₉ H ₄₆ N ₂ NiO	C ₅₁ H ₅₈ N ₂ NiO ₂	C ₆₆ H ₈₆ N ₄ Ni ₂ O ₂
Formula weight	619.50	359.14	617.49	789.70	1084.80
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P nma	P 2 ₁ /c	P 2 ₁ /c	P -1	C 2/c
Unit cell lengths (Å)	a = 21.429(4) b = 16.960(3) c = 9.3624(14)	a = 10.0969(9) b = 12.1670(10) c = 15.4244(13)	a = 12.060(3) b = 16.300(5) c = 34.014(9)	a = 9.7801(16) b = 13.485(2) c = 16.354(3)	a = 22.8854(18) b = 10.4415(9) c = 25.777(2)
Unit cell angles (°)	α = 90 β = 90 γ = 90	α = 90 β = 105.488(3) γ = 90	α = 90 β = 94.684(6) γ = 90	α = 95.574(4) β = 96.943(4) γ = 93.555(4)	α = 90 β = 108.919(4) γ = 90
Volume (Å ³)	3402.7(10)	1826.1(3)	6664(3)	2125.0(6)	5826.8(9)
Z	4	4	8	2	4
Density (calculated, mg/m ³)	1.209	1.306	1.231	1.234	1.237
Absorption coefficient (mm ⁻¹)	0.602	1.068	0.615	0.499	0.693
F(000)	1328	768	2640	844	2328
Crystal size (mm ³)	0.040 x 0.040 x 0.020	0.120 x 0.100 x 0.100	0.100 x 0.100 x 0.060	0.050 x 0.030 x 0.030	0.060 x 0.060 x 0.020
Theta range for data collection	1.901 to 25.544°	2.093 to 25.345°	1.201 to 25.386°	1.261 to 23.254°	1.670 to 25.373°

Index ranges	-25<= h<=23, -20<=k<=20, -11<=l<=9	-12<=h<=12, -14<=k<=14, -18<=l<=18	-14<=h<=14, -19<=k<=19, -41<=l<=41	-10<=h<=10, -14<=k<=14, -18<=l<=18	-27<=h<=27, -12<=k<=12, -31<=l<=30
Reflections collected	45124	23695	203027	64676	76389
Independent reflections	3259 [R(int) = 0.2026]	3346 [R(int) = 0.0283]	12257 [R(int) = 0.0468]	6048 [R(int) = 0.1498]	5360 [R(int) = 0.0351]
Completeness to theta = 25.000°	100.0 %	99.9 %	100.0 %	99.4%	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Analytical	Semi-empirical from equivalents
Max and min transmission	0.929 and 0.698	0.928 and 0.848	0.745 and 0.686	0.7452 and 0.6402	0.928 and 0.837
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	3259 / 0 / 212	3346 / 0 / 213	12257 / 0 / 775	6048 / 0 / 500	5360 / 0 / 342
Goodness-of-fit on F ²	1.030	1.097	1.047	1.043	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0801, wR2 = 0.1825	R1 = 0.0297, wR2 = 0.0699	R1 = 0.0340, wR2 = 0.0884	R1 = 0.0522, wR2 = 0.1012	R1 = 0.0355, wR2 = 0.0844
R indices (all data)	R1 = 0.1875, wR2 = 0.2491	R1 = 0.0363, wR2 = 0.0736	R1 = 0.0381, wR2 = 0.0919	R1 = 0.0880, wR2 = 0.1158	R1 = 0.0432, wR2 = 0.0888
Extinction coefficient	0.0011(6)	n/a	n/a	n/a	n/a
Largest diff. peak and hole	0.756 and -0.858 e.Å ⁻³	0.575 and -0.298 e.Å ⁻³	0.537 and -0.303 e.Å ⁻³	0.391 and -0.334 e.Å ⁻³	0.436 and -0.328 e.Å ⁻³

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