Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Regioselective Hydrosilylation of Epoxides catalyzed by Nickel(II)Hydrido Complexes

Jan Wenz, Hubert Wadepohl and Lutz H. Gade*

Contents:

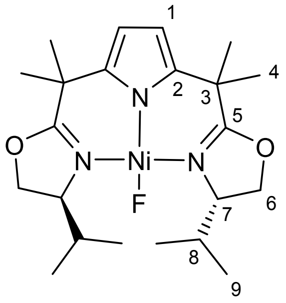
I. General Information

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were predried over activated 4 Å molecular sieves and were refluxed over magnesium (methanol), sodium (toluene), potassium (hexane), sodium-potassium alloy (tetrahydrofurane, diethyl ether) or calcium hydride (dichloromethane) under an argon atmosphere and collected by distillation. ^{1}H and ^{13}C[1] NMR spectra were recorded on a Bruker Avance III 600, Bruker Avance II 400 and Bruker DRX 200 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane.[2] ^{19}F NMR was measured at 376 MHz, and 1,4-bis(trifluoromethyl)benzene (−63.4 ppm) was used as an internal standard. All NMR spectra were recorded at room temperature (295 K). Mass spectra were recorded by the mass spectrometry service at the Organic Chemistry Laboratory of the University Heidelberg and the elemental analyses were measured by the analytical services of the University of Heidelberg Complexes [(S)$^{i\text{Pr}}$(PdmBox)NiCl], [(R)$^{\text{Ph}}$(PdmBox)NiCl], [(S)$^{i\text{Pr}}$(PdmBox)NiH] **2a** were synthesized according to the literature procedures.[3] $PhSiD_3$ was prepared according to literature procedure.[4] All other reagents were commercially available and used as received. Liquids were degassed by three freeze-pump-thaw cycles before use.

II. a) Preparation of precatalysts

1) [(S)$^{i\mathrm{Pr}}$(PdmBox)NiF] (1a)

To a solution of complex [(S)$^{i\mathrm{Pr}}$(PdmBox)NiCl] (1 g, 2.15 mmol) in 50 ml acetone an excess of CsF (1 g, 6.3 mmol) was added and stirred for 24 h. After removal of the solvents, the residue was treated with a toluene/pentane (1/10) mixture and filtrated. The solvents were removed in vacuo. The residue was treated with a toluene/pentane (1:3) mixture and the inorganic metal salts were filtered off. After the removal of the solvents, the product was recrystallized from a toluene/pentane mixture at room temperature to give the product in 90% yield.



^{1}H NMR (C_6D_6, 600 MHz, 295 K): δ (ppm) = 6.08 (s, 2 H, H^1), 3.90-3.84 (m, 2 H, H^7), 3.61-3.54 (m, 4 H, H$^{6/6'}$), 2.66-2.52 (m, 2 H, H^8), 2.46 (s, 6 H, H$^{4'}$), 1.53 (s, 6 H, H$^{4'}$), 0.93 (d, $^3J_{\mathrm{H,H}}$ = 6.8 Hz, 6 H, H^9), 0.90 (d, $^3J_{\mathrm{H,H}}$ = 7.0 Hz, 6 H, H$^{9'}$).

^{13}C NMR (C_6D_6, 150 MHz, 295 K): δ (ppm) = 176.71 (C^5), 137.9 (C^2), 103.8 (C^1), 70.2 (C^6), 65.1 (C^7), 38.6 (C^3), 35.2 (C^4), 31.3 (C^8), 22.7 (C$^{4'}$), 18.5 (C$^{9'}$), 16.1 (C^9).

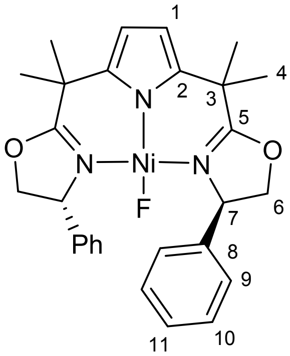
^{19}F NMR (C_6D_6, 376 MHz, 295 K): δ (ppm)= -448.6 (s).

HR-FAB$^+$: Anal. Calcd for $C_{22}H_{34}N_3NiO_2F$: m/z 430.2003 (M^+-F).

Elemental Anal. Calcd for $C_{22}H_{34}N_3O_2NiF$. C 58.69, H 7.61, N 9.33. Found C 58.77, H 7.44, N 9.36.

2) [(R)^{Ph}(PdmBox)NiF] (1b)

According to procedure mentioned above. Yield 76% after crystallization from toluene pentane mixture.



^{1}H NMR (C_6D_6, 600 MHz, 295 K): δ (ppm) = 7.30 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H^{11}), 7.17 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H^{10}), 7.11 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, H^{11}), 6.11 (s, 2 H, H^1), 4.83 (dd, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 10.7 Hz, 2 H, H^7), 3.69 - 3.63 (m, 2 H, H^6), 3.56-3.51 (m, 4 H, $H^{6'}$), 2.28 (s, 6 H, H^4), 1.54 (s, 6 H, $H^{4'}$).

^{13}C NMR (C_6D_6, 150 MHz, 295 K): δ (ppm) = 176.6 (C^5), 141.9 (C^8), 137.5 (C^2), 129.1 ($C^{9,10,11}$), 128.6 ($C^{9,10,11}$), 127.4 ($C^{9,10,11}$), 103.6 (C^1), 75.6 (d, $J_{C,F}$ = 2.7 Hz, C^6), 63.4 (C^7), 38.3 (C^3), 34.7 (C^4), 22.3 ($C^{4'}$).

^{19}F NMR (C_6D_6, 376 MHz, 295 K): δ (ppm)= -445.7 (s).

HR-FAB$^+$: Anal. Calcd for $C_{28}H_{30}N_3NiO_2F$: m/z 533.1355 (M^+).

Elemental Anal. Calcd for $C_{22}H_{34}N_3O_2NiF$. C, 64.89; H, 5.83; N, 8.11. Found: C 64.59; H 6.09; N 8.12.

II b) General Synthetic Procedure for stoichiometric epoxide activation.

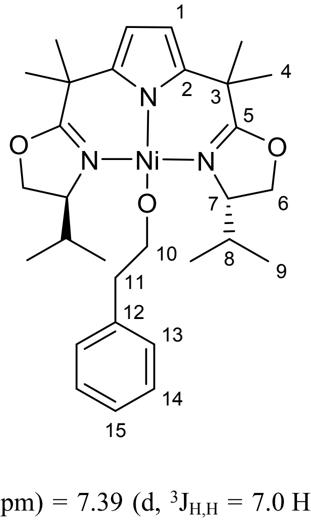
To a solution of [(S)$^{i\mathrm{Pr}}$(PdmBox)NiH] **2a** (120 mg, 0.28 mmol) in 0.5 ml d_6-benzene the corresponding epoxide (0.28 mmol, 1.01 equiv.) was added in 0.5 ml d_6-benzene. The reaction progress was monitored periodically using ^{1}H NMR spectroscopy. After complete conversion the solvent was removed in vacuo the crude was recrystallized from a pentane mixture at −40 °C to give a red crystalline solid.

1) [(S)$^{i\mathrm{Pr}}$(PdmBox)Ni(OC_8H_{10})] (3a)

a) Preparation of the 2-Phenylethanolate complex [(S)$^{\mathrm{iPr}}$(PdmBox)Ni(OC_8H_{10})] (**2a**). After 6 hours, ^{1}H NMR spectrum of the crude reaction mixture showed complete conversion. Yield 68%.

b) For identification purposes complex was also independently generated from the metathesis reaction between [(S)$^{\mathrm{iPr}}$(PdmBox)NiCl] and $PhCH_2CH_2ONa$.

To a stirring solution of 2-phenylethan-1-ol (40 mg, 0.321 mmol, 1.5 equiv.) in 10 mL of THF was added NaH (8 mg, 0.332 mmol, 1.55 equiv.) at room temperature over a period of 30 min. [((S)$^{i\mathrm{Pr}}$PdmBox)NiCl] (100 mg, 0.215 mmol, 1 equiv.) was then added and the reaction mixture was stirred for additional 2 h. The volatiles were removed under vacuum, the residue extracted with pentane and filtered through a pad of Celite. The red residue was washed two times with 1 ml of cold pentane. Yield (35 %). Single crystals of **3a** were grown by slow cooling a saturated pentan solution to -40°C.



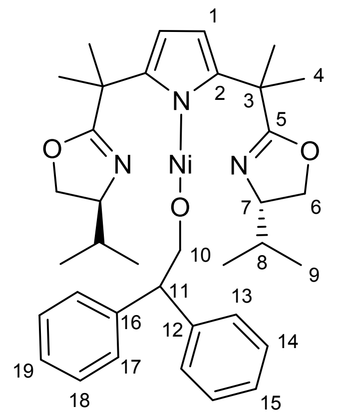
^{1}H NMR (C_6D_6, 600 MHz, 295 K): δ (ppm) = 7.39 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, H^{13}), 7.24 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, H^{14}), 7.08 (tt, $^3J_{H,H}$ = 7.3 Hz, 2.3 Hz, 1 H, H^{15}), 6.10 (s, 2 H, H^1), 4.16 (ddd, $^3J_{H,H}$ = 8.8 Hz, 7.1 Hz, 6.0 Hz, 1 H, H^{10}), 3.81 (dt, $^3J_{H,H}$ = 9.9 Hz, 4.0 Hz, 2 H, H^7), 3.72 (dd, $^3J_{H,H}$ = 9.1 Hz, 4.4 Hz, 2 H, H^6), 3.56 (dd, $^3J_{H,H}$ = 9.6 Hz, 9.3 Hz, 23.37 (dt, $^3J_{H,H}$ = 8.9 Hz, 6.9 Hz, 1 H, $H^{10'}$), 3.00- 2.85 (m, 4 H, H^8, H^{11}), 2.61 (s, 3 H, H^4), 1.60 (s, 3 H, $H^{4'}$), 0.73 (d, $^3J_{H,H}$ = 2.1 Hz, 6 H, H^9), 0.72 (d, $^3J_{H,H}$ = 1.4 Hz, 6 H, $H^{9'}$).

^{13}C NMR (C_6D_6, 150 MHz, 295 K): δ (ppm) = 175.0 (C^5), 141.4 (C^{12}), 136.7 (C^2), 128.4 ($C^{13,14,15}$), 127.5 ($C^{13,14,15}$), 124.5 ($C^{13,14,15}$), 101.6 (C^1), 68.3 (C^{10}), 67.9 (C^6), 64.3 (C^7), 42.3 (C^{11}), 37.4 (C^3), 33.8 (C^4), 30.3 (C^8), 21.2 ($C^{4'}$), 17.4 ($C^{9'}$), 13.6 (C^9).

Elemental Anal. Calcd. for $C_{30}H_{43}N_3NiO_3$: C 65.23, H 7.85, N 7.61. Found: C 65.46, H 7.97, N 7.50.

2) [(S)^{iPr}(PdmBox)Ni-(O$C_{14}H_{15}$)] (4a)

Preparation of the 2,2-Diphenylethanolate complex [(S)^{iPr}(PdmBox)Ni(O$C_{14}H_{15}$)] (**4a**). After 36 hours, ^{1}H NMR spectrum of the crude reaction mixture showed complete conversion. Red solid. Yield 74%.



^{1}H NMR (C_6D_6, 600 MHz, 295 K): δ (ppm) = 7.46-7.42 (m, 4 H, H^{15,18}), 7.20-7.13 (m, 4 H, H^{13,17}), 7.01-7.00 (m, 2 H, H^{15,19}), 6.05 (s, 2 H, H^1), 4.42 (dd, $^3J_{H,H}$ = 9.1 Hz, 5.6 Hz, 1 H, H^{10}), 4.09 (dd, $^3J_{H,H}$ = 6.3 Hz, 6.3 Hz, 1 H, H^{11}), 3.77 (dd, $^3J_{H,H}$ = 9.0 Hz, 7.6 Hz, 1 H, H$^{10'}$), 3.70-3.66 (m, 2 H, H^7), 3.61 (dd, $^3J_{H,H}$ = 9.0 Hz, 4.6 Hz, 23.44 (dd, $^3J_{H,H}$ = 9.4 Hz, 9.0 Hz, 2 H, H^6), 2.94 (ds, $^3J_{H,H}$ = 6.9 Hz, 3.7 Hz, 2 H, H^8), 2.58 (s, 6 H, H^4), 1.54 (s, 6 H, H$^{4'}$), 0.64 (d, $^3J_{H,H}$ = 2.1 Hz, 6 H, H^9), 0.63f (d, $^3J_{H,H}$ = 1.8 Hz, 6 H, H$^{9'}$).

^{13}C NMR (C_6D_6, 150 MHz, 295 K): δ (ppm) = 175.1 (C^5), 144.5 (C$^{12/16}$), 144.4 (C$^{12/16}$), 136.7 (C^2), 128.2 (C^{13,14,17,18}), 127.8 (C^{13,14,17,18}), 127.2 (C^{13,14,17,18}), 127.1 (C^{13,14,17,18}), 124.9 (C^{15,19}), 124.8 (C^{15,19}), 101.6 (C^1), 72.0 (C^{10}), 67.8 (C^6), 64.3 (C^7), 56.4 (C^{11}), 37.5 (C^3), 33.8 (C^4), 30.3 (C^8), 21.2 (C$^{4'}$), 17.3 (C$^{9'}$), 13.6 (C^9).

Elemental Anal. Calcd. for for $C_{36}H_{47}N_3NiO_3$: C 68.80, H 7.54, N 6.69. Found: C 69.13, H 7.41, N 6.45.

II. c) General Procedure for the Synthesis of Epoxides

All epoxides that were not commercially available were synthesized under standard Corey Chaykovsky conditions as follows. A oven-dried 100 ml flask was charged with a stir bar, trimethyl sulfonium iodide (9.8 g, 48 mmol, 2 equiv.), and sodium hydride (60% dispersion in oil, 1.9 g, 48 mmol, 2 equiv). The flask was evacuated and refilled 3x with argon, and anhydrous DMSO (30 ml) and THF (22 ml) were added and the reaction was stirred for 20 minutes at room temperature. The solution was then cooled to 0 °C and the aldehyde (24 mmol, 1 equiv.) in THF (10 ml) was added at 0 °C and allowed to stir until consumption of aldehyde by TLC. The reaction was diluted with water (40 ml) and extracted with Et_2O (30 ml x 4). The combined organic layers were washed with water (20 ml) and brine (20 ml x 2), dried over $NaSO_4$, and concentrated under reduced pressure. The crude product was either purified by vacuum distillation or column chromatography(Aluminum oxide). Epoxides were stored under Ar .

III. Catalytic Hydrosilylation of Epoxides

a) Screening of Silanes in the Hydrosilylation of Styrene oxide

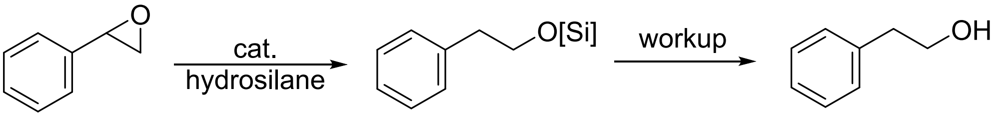


Table 1 Reaction conditions: Substrate (0.25 mmol) in 0.5 ml C_6D_6, [a]Conversion was determined by ^1H NMR analysis of crude reaction mixture using 1,4-dimethoxybenzene as the internal standard. [b]Isolated yield of purified product after column chromatography. [c]Isolated without workup as stable $PhCH_2CH_2OSiPh_3$. In case of this sterically demanding triphenylsilane the nickel alkoxido complex was identified as the resting state instead of the nickel hydrido complex.

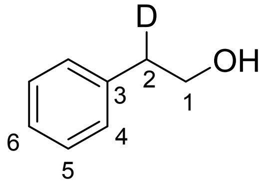
entry	Cat.	Silane (equiv)	Time (h)	Temp (°C)	Conv. [%][a]	workup	Yield[b]
1	2a 5 mol%	$PhSiH_3$ (1)	16 h	50	100	-	-
2	2a 5 mol%	$(EtO)_3SiH$ (2)	24 h	50	80	-	-
3	2a 5mol%	Ph_2MeSiH (2)	16 h	50	0	-	-
4	2a 5mol%	Ph_2SiH_2 (1)	16 h	50	100	-	-
5	2a 5mol%	PMHS (5)	16 h	50	0	-	-
6	2a 5mol%	$(EtO)_2MeSiH$ (2)	16 h	50	<10	-	-
7	2a 5mol%	$(TMS)_3SiH$ (2)	16 h	50	0	-	-
8	2a 5mol%	Ph_3SiH	120 h	50	100	HCl[5]	90[c]
9	2a 5mol%	Et_3SiH (2)	16 h	50	0	-	-
10	2a 5mol%	$PhMe_2SiH$	16 h	50	0		
	2a 5mol%	Ph_2SiH_2	24 h	30	100		
12	2a 5mol%	$PhSiH_3$ (1)	24 h	30	100	K_2CO_3, MeOH[6]	50
						TBAF, H_2O	60
						NaOH (5%), H_2O[7]	95
13	1b 5mol%	$PhSiH_3$ (1)	24 h	30	100	-	-
14	-	All above	120	80	-		

General Procedure for the Catalytic Hydrosilylation of Epoxides

A *J*-Young NMR tube was charged with the precatalyst **1a** or **1b** (5 mol%), epoxide (0.25 mmol), hydrosilane (1 equiv.) and 1,4-dimethoxybenzene as internal standard in 0.5 ml benzene-d_6. The conversion and the NMR yield of the corresponding silylether were determined directly from ^{1}H NMR Spectra of the reaction mixture after the reaction. After complete conversion 1 ml of MeOH was added followed by 1 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 2 ml). The combined organic layers were washed with brine dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by flash column chromatography on silica gel.

The reaction products were identified by comparison to authentic, commercially available samples. If the alcohols were not commercially available, they were synthesized using $LiAlH_4$ or $NaBH_4$ to reduce the corresponding aldehyde or ketone.

1) 2-phenylethan-2-d-1-ol



^{1}H NMR (CDCl$_3$, 600 MHz, 295 K): δ (ppm) = 7.35-7.30 (m, 2 H, H^4), 7.25-7.21 (m, 3 H, H^5, H^6), 3.85 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, H^1), 2.84 (m, 1 H, H^2).

^{2}H NMR **(CDCl$_3$, 600 MHz, 295 K):** δ (ppm) = 2.88 (bs).

^{13}C NMR (CDCl$_3$, 150 MHz, 295 K): δ (ppm) = 138.5 (C^6), 129.17 (C^5), 128.7 (C^4), 126.6 (C^3), 63.6 (C^1). 38.9 (t, $^1J_{C,D}$ = 19.4 Hz, C^2).

HR-EI$^+$: for C_8H_9DO m/z: 123.08024 (M^+), 92.06156 (M^+-CH_3O).

Solvent free conditions

A *J*-Young NMR tube was charged with the precatalyst **1a** (19 mg, 42.2 μmol, 1 mol%), styrene oxide (500 mg, 4.22 mmol) and phenylsilane (205 mg, 1.9 mmol, 0.45 equiv.). After 4 hours ^{1}H NMR spectra of the reaction mixture showed complete conversion. 5 ml of MeOH was added followed by 5 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 10 ml). The combined organic layers were washed with brine dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by vacuum distillation to give 2-phenylethan-1-ol in 95% yield.

Solvent free ball milling conditions:

A ball milling vessel (Achat, 20 ml) was charged with the precatalyst 1a (20 mg, 44.42 μmol, 3 mol%), 2-(4-Biphenylyl)oxirane (290 mg, 1.48 mmol), phenylsilane (81 mg, 0.74 mmol, 0.5 equiv.) and 10 grinding balls (Achat, diameter: 0.5 cm). The ball milling vessel was then transferred to a mixer mill and milled at 8 Hz for 90 min.The crude reaction mixture was isolated by washing the vessel and the ball with Et_2O (5 x 10 ml). The reaction mixture was concentrated to approx. 5 ml, then 5 ml of MeOH was added followed by 5 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 10 ml). The combined organic layers were washed with brine dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. 2-(4-Biphenylyl)ethanol was then isolated by flash column chromatography in 89% Yield.

Mechanistic studies

Determination of the ^{1}H-^{2}H Kinetic Isotope Effect using Competition Experiments

A J-Young NMR tube was charged with Nickel complex **1a** or **1b** (5 mol%) and styrene oxide (1 eq) in 0.4 ml benzene-d_6. A preformed 1:1 mixture of 1 equiv. $PhSiD_3$ and 1 equiv. $PhSiH_3$ was added in 0.1 ml benzene-d_6. The reaction was monitored by ^{1}H NMR spectoscopy. After 16 h at room temperature the reaction showed complete conversion and 1 ml of MeOH was added followed by 1 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 2 ml). The combined organic layers were washed with brine dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by flash column chromatography on silica gel. The ratio of deuterated to normal product was determined by ^{13}C NMR spectroscopy and averaged over two independent runs.

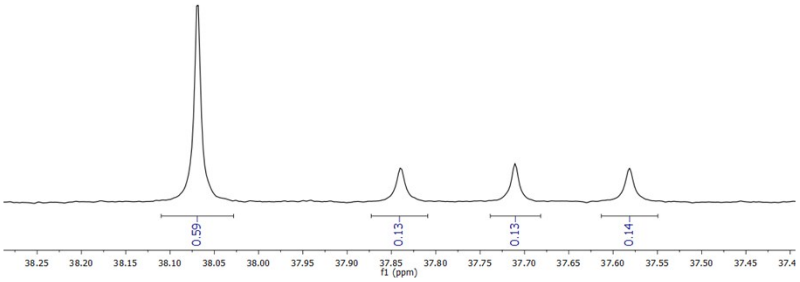


Figure S1 Exemplary ^{13}C-NMR spectrum of the competition hydrosilylation of styrene oxide with hydrosilane and deuterosilane.

Catalyst	Epoxide	Silane	k_H/k_D
1a	Styrene oxide	Ph_2SiD_2/Ph_2SiH_2	1.56
1a	Styrene oxide	$PhSiD_3/PhSiH_3$	1.58
1b	Styrene oxide	$PhSiD_3/PhSiH_3$	1.47

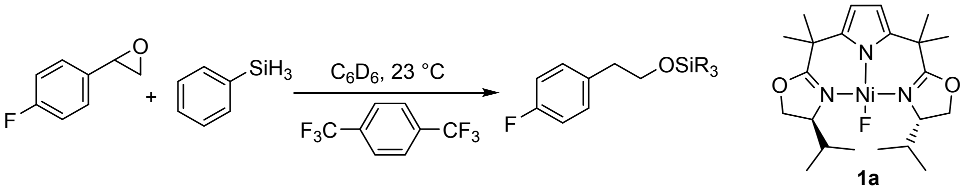
Stoichiometric reaction between [(S)(^{iPr}PdmBox)NiH] 2a, styrene oxide and Ph_2SiD_2.

A J-Young NMR tube was charged with [(S)(^{iPr}PdmBox)NiH] **2a** (20 mg, 46 µmol, 1 equiv.) and Ph_2SiD_2 (8.5 mg, 45.5 µmol, 1 equiv.) in 0.4 ml C_6D_6. No H/D exchange was observed at room temperature after 24 h. Then styrene oxide (5.5 mg, 45.8 µmol, 1 equiv.) dissolved in 0.1 ml C_6D_6 was added. After additional 24 h ^{1}H NMR indicated that Nickel hydrido complex **2a** was fully converted to the nickel-deuteride compound accompanied by the formation of silylether products of the epoxide. After alkaline hydrolysis no deuterium incorporation of the product alcohol could be monitored by NMR.

Mercury Test[8]

To a solution of [(S)(^{iPr}PdmBox)NiH] **2a** (5.0 mg, 11.6 µmol) and styrene oxide (30 ml, 250 µmol) in 0.5 ml C_6D_6, Hg(0) (350 mg, 1.75 mmol). After 15 minutes $PhSiH_3$ (27 mg, 250 µmol) was added. The reaction was monitored periodically by NMR yielded the same conversion and selectivity as a sample without addition of Hg(0).

Details for Kinetic Experiments



1a

catalyst:

	Reaction conditions	Standard conditions
[Catalyst]	0.011 - 0.034 M	5 mg, 5 mol% (0.02 M)
[[Epoxide]	0.21 - 0.65 M	30 mg (0.44 M)
[Silane]	0.1 - 0.74 M	30 mg 1.2 equiv. (0.55 M)

[(S)^{iPr}(PdmBox)NiF] (1a), 4'-fluorostyrene oxide, $PhSiH_3$, and 1,4- bis(trifluoromethyl)benzene as internal standard were dissolved in 0.5 ml benzene-d_6 in a J. Young NMR tube. The sample was measured at ambient conditions (23 °C) and ^{19}F NMR spectra were recorded until at least 50 % conversion were observed. For analysis of the spectra, the integral of the internal standard was set to 1 in each spectrum and the values for the starting material as well as the products were used without further manipulation.

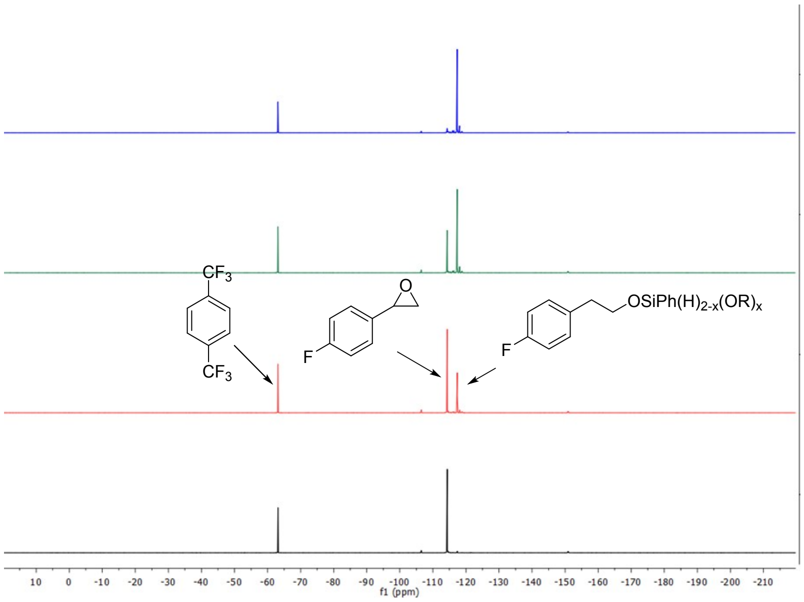


Figure S2 Typical $^{19}F\{^1H\}$ NMR spectra recorded during a kinetic measurement run.

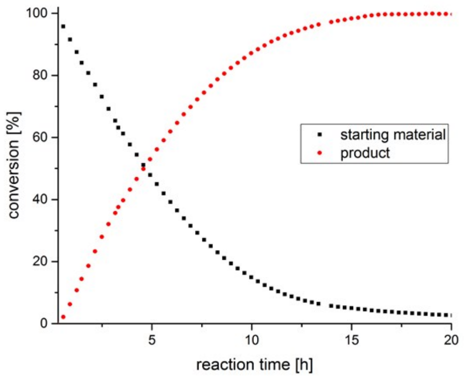


Figure S3 Typical reaction profile for the catalytic hydrosilylation using **1a** as catalyst.

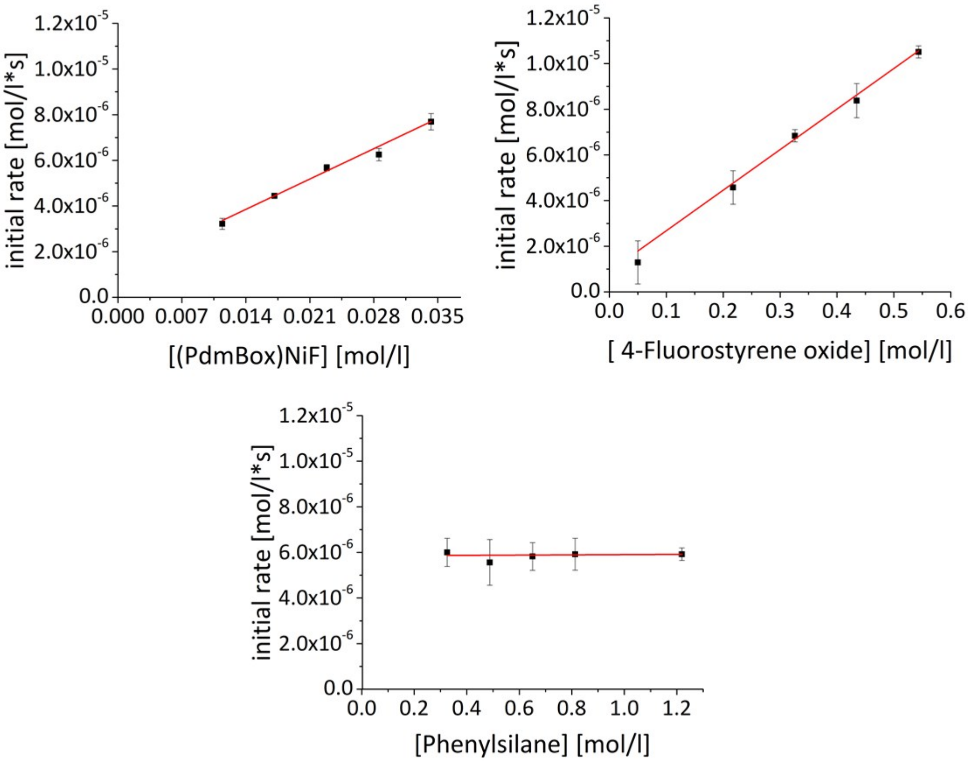


Figure S4 Determining the rate law for the catalytic hydrosilylation.

X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-Ka radiation, microfocus X-ray tubes, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 0.4...1°) were integrated by profile fitting.[#1] Data were corrected for air and detector absorption, Lorentz and polarization effects[#2] and scaled essentially by application of appropriate spherical harmonic functions.[#2,#3,#4] Absorption by the crystal was treated numerically (Gaussian grid).[#4,#5] An illumination correction was performed as part of the numerical absorption correction.[#4] The structures were solved by direct methods with dual-space recycling (VLD-procedure, compound **1b**)[#6] or by the charge flip procedure (compound **3a**·$Ph(CH_2)_2OH$)[#7] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[#8] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. The position of the hydroxyl hydrogen in **3a**·$Ph(CH_2)_2OH$ was taken from a difference Fourier synthesis and refined.

CCDC 1532348 and 1532349 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

References

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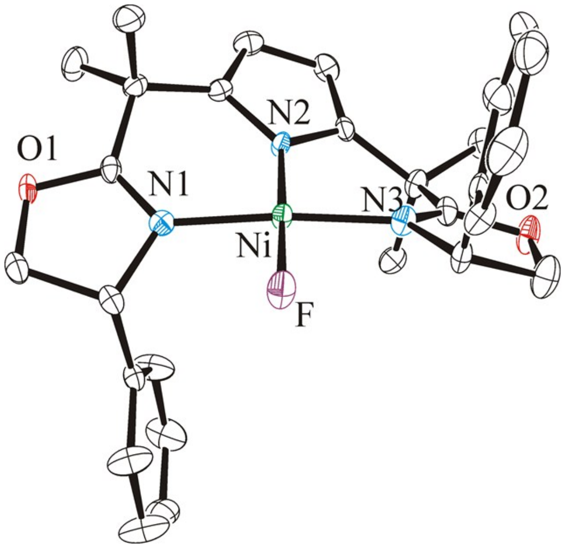


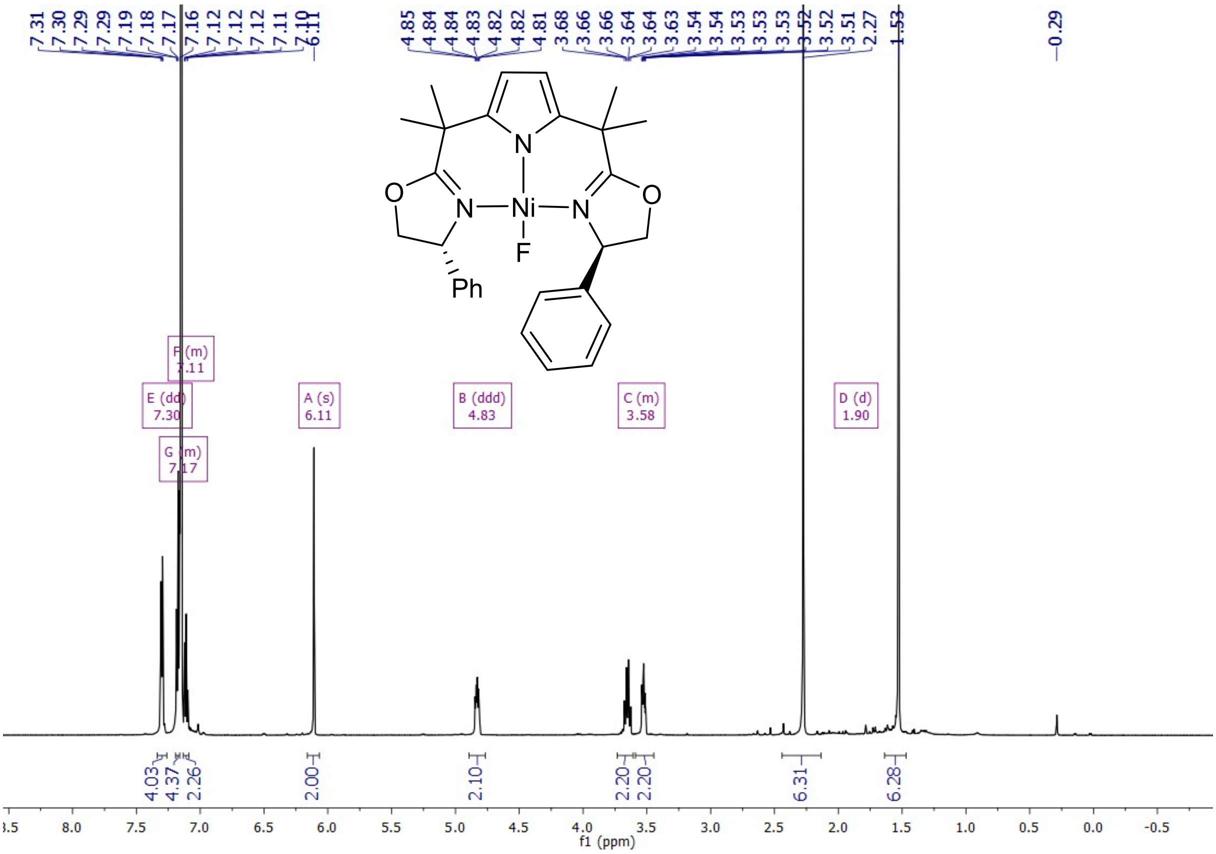
Figure S5 Molecular structure of 1b. Hydrogen atoms are omitted for clarity; thermal ellipsoids displayed at 50% probability. Only one of the three independent molecules is shown. Selected bond lengths [Å] and angles [°]: Ni–F 1.814(3) ... 1.828(3), Ni–N1 1.875(4) ... 1.894(4), Ni–N2 1.860(4) ... 1.867(4), Ni–N3 1.892(4) ... 1.892(5), N(1)–Ni–N(2) 90.21(18) ... 91.42(18), N(1)–Ni–F 88.58(16) ... 88.96(16) .

Table S1 Details of the crystal structure determinations of **1b** and **3a**·$C_8H_{10}O$.

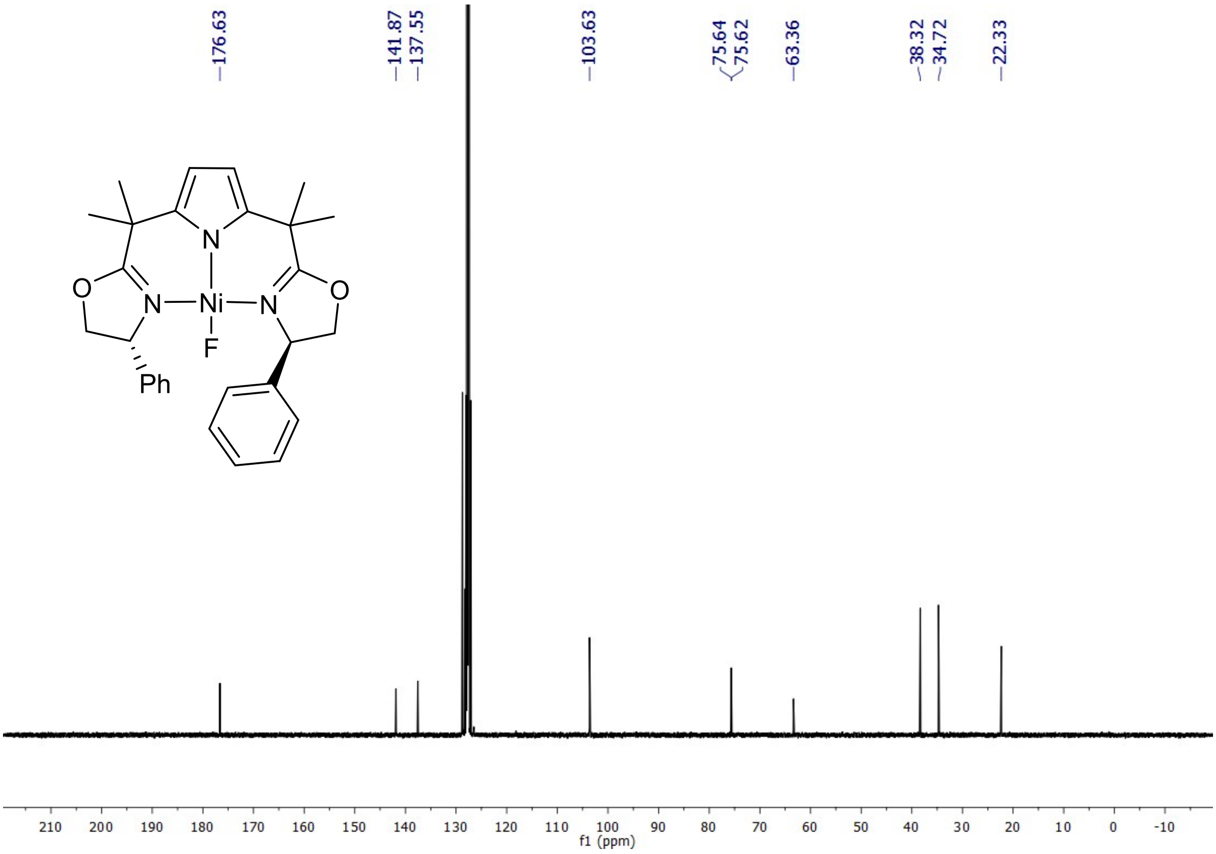
	[1b]	**[3a]·$C_8H_{10}O$**
formula	$C_{28}H_{30}N_3NiO_2F$	$C_{38}H_{53}N_3NiO_4$
M_r	518.26	674.54
crystal system	tetragonal	orthorhombic
space group	$P\,4_1$	$P\,2_12_12_1$
a /Å	11.68973(13)	9.93003(15)
b /Å	11.68973(13)	10.15945(19)
c /Å	54.0604(8)	35.2869(6)
V /Å^3	7387.3(2)	3559.88(11)
Z	12	4
F_{000}	3264	1448
d_c /Mg·m^{-3}	1.398	1.259
X-radiation, λ /Å	Mo-$K\alpha$, 0.71073	Cu-$K\alpha$, 1.54184
μ /mm^{-1}	0.826	1.118
max., min. transmission factors	0.979, 0.899	0.974, 0.901
data collect. temperat. /K	120(1)	120(1)
θ range /°	2.9 to 25.4	4.5 to 71.0
index ranges h,k,l	-14 ... 14, -14 ... 14, -65 ... 65	-12 ... 12, -12 ... 12, -43 ... 40
reflections measured	110399	122869
unique [R_{int}]	13494 [0.1099]	6862 [0.0845]
observed [$I \geq 2\sigma(I)$]	11850	6225

NMR Spectra of New Compounds

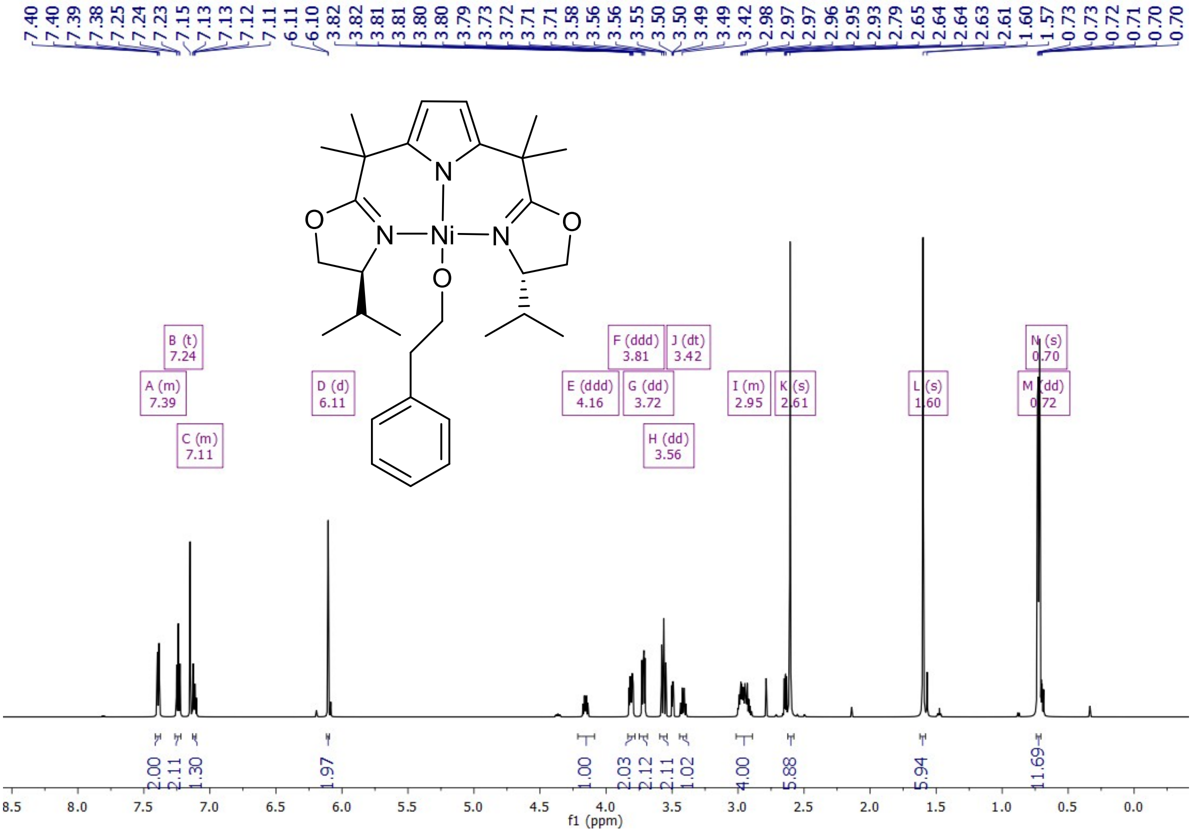
^{1}H NMR (C_6D_6, 600 MHz, 295 K):



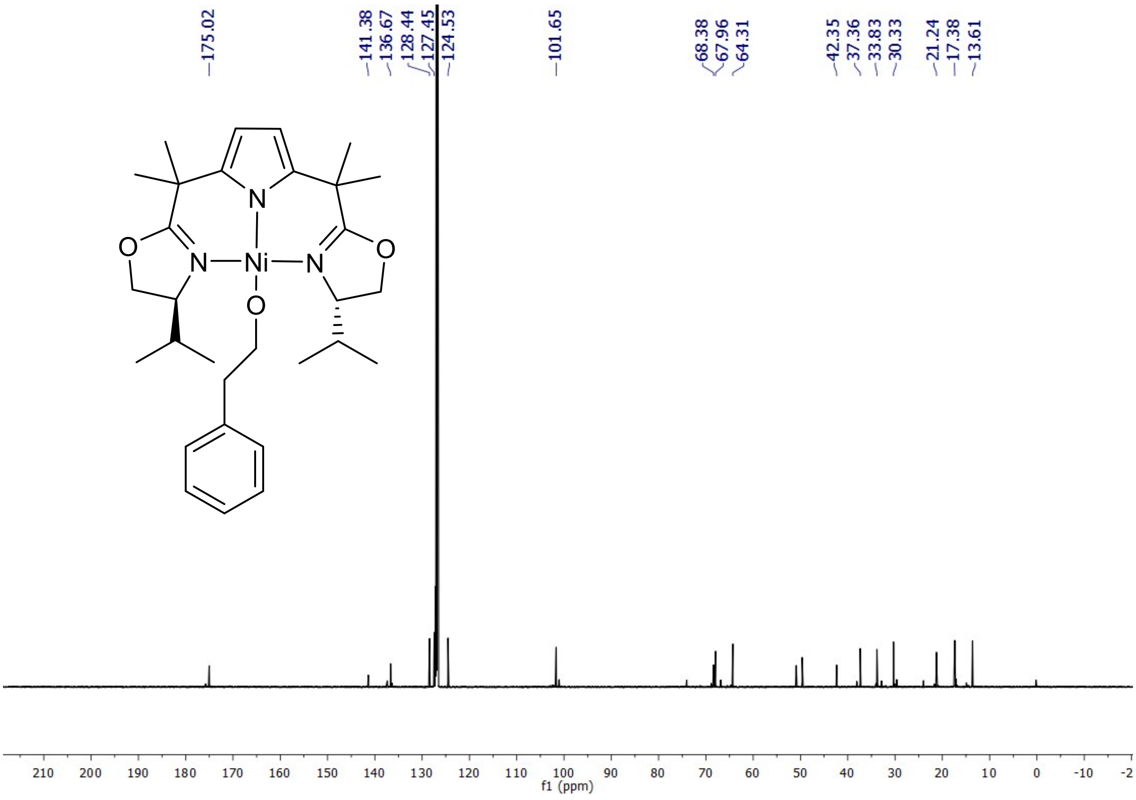
^{13}C NMR (C_6D_6, 150 MHz, 295 K):



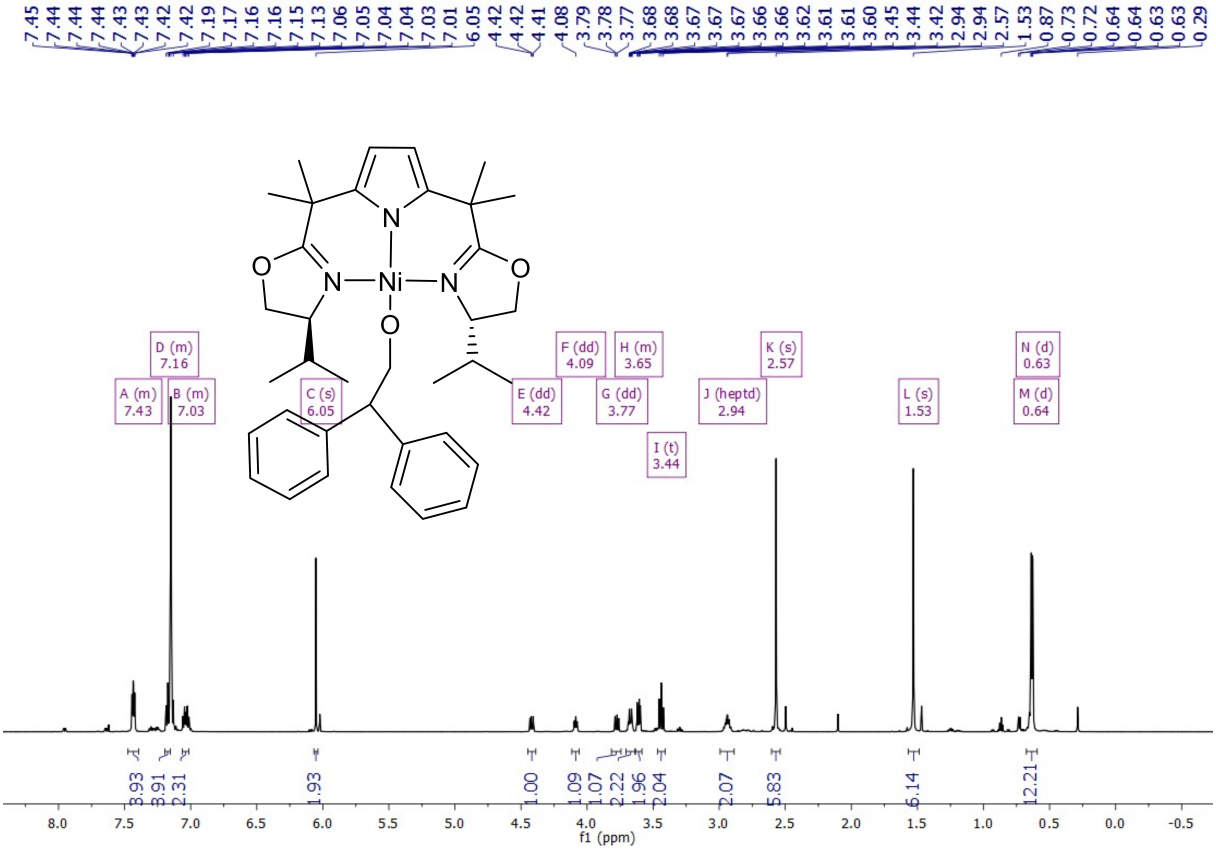
^{1}H NMR (C_6D_6, 600 MHz, 295 K):



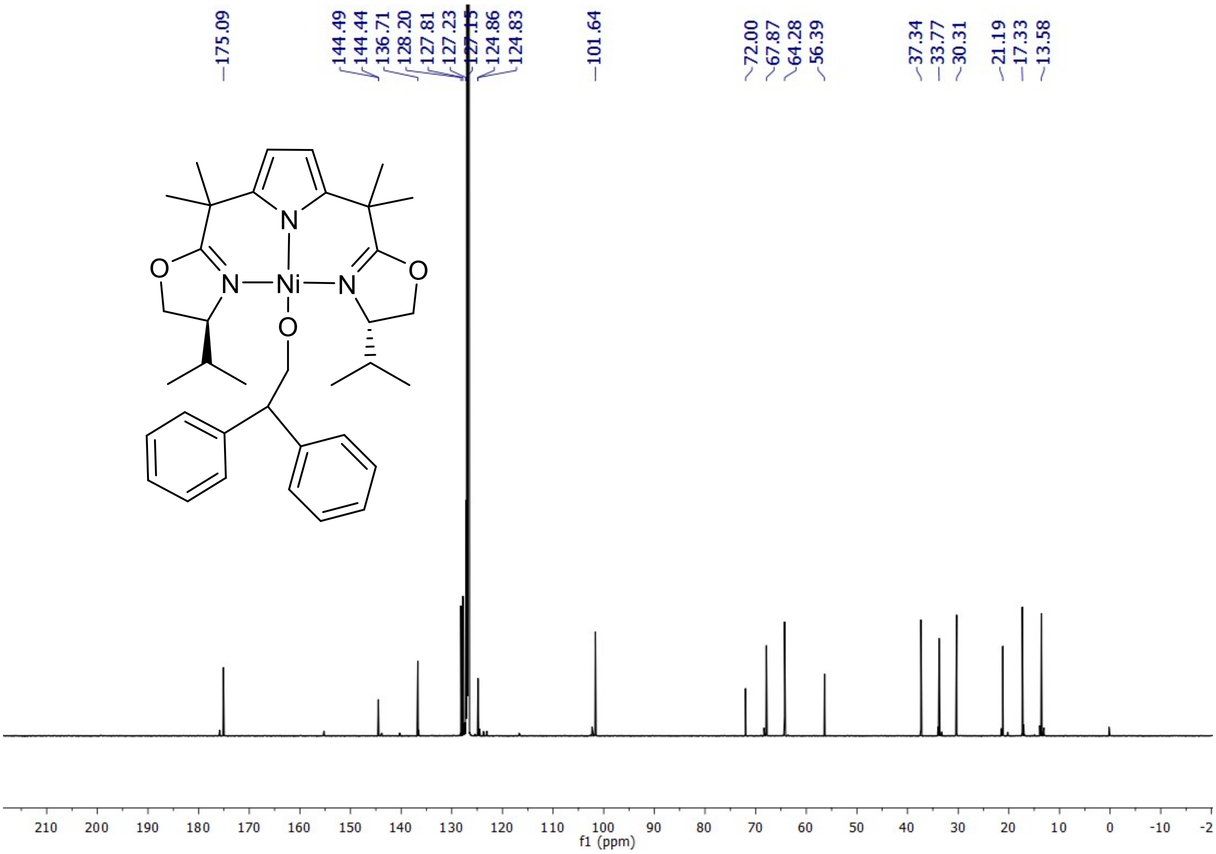
^{13}C NMR (C_6D_6, 150 MHz, 295 K):



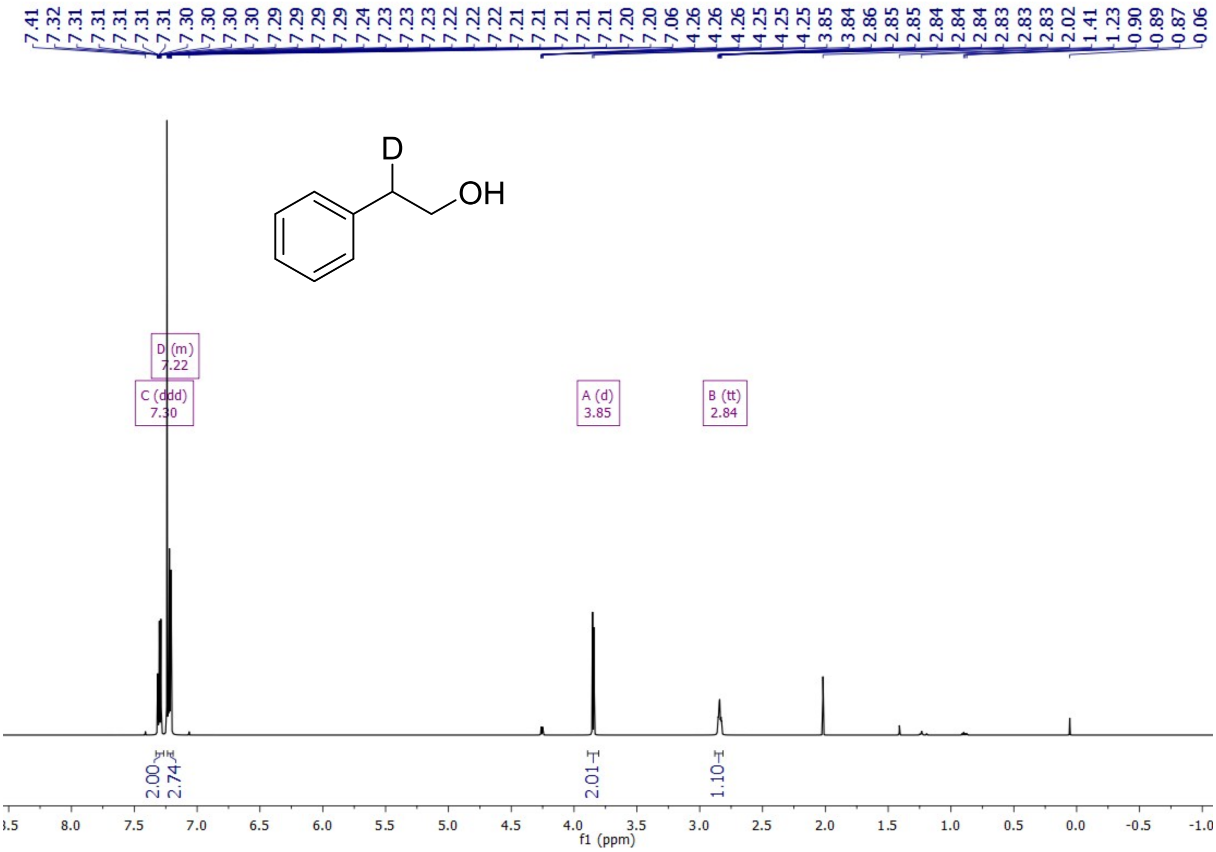
^{1}H NMR (C_6D_6, 600 MHz, 295 K):



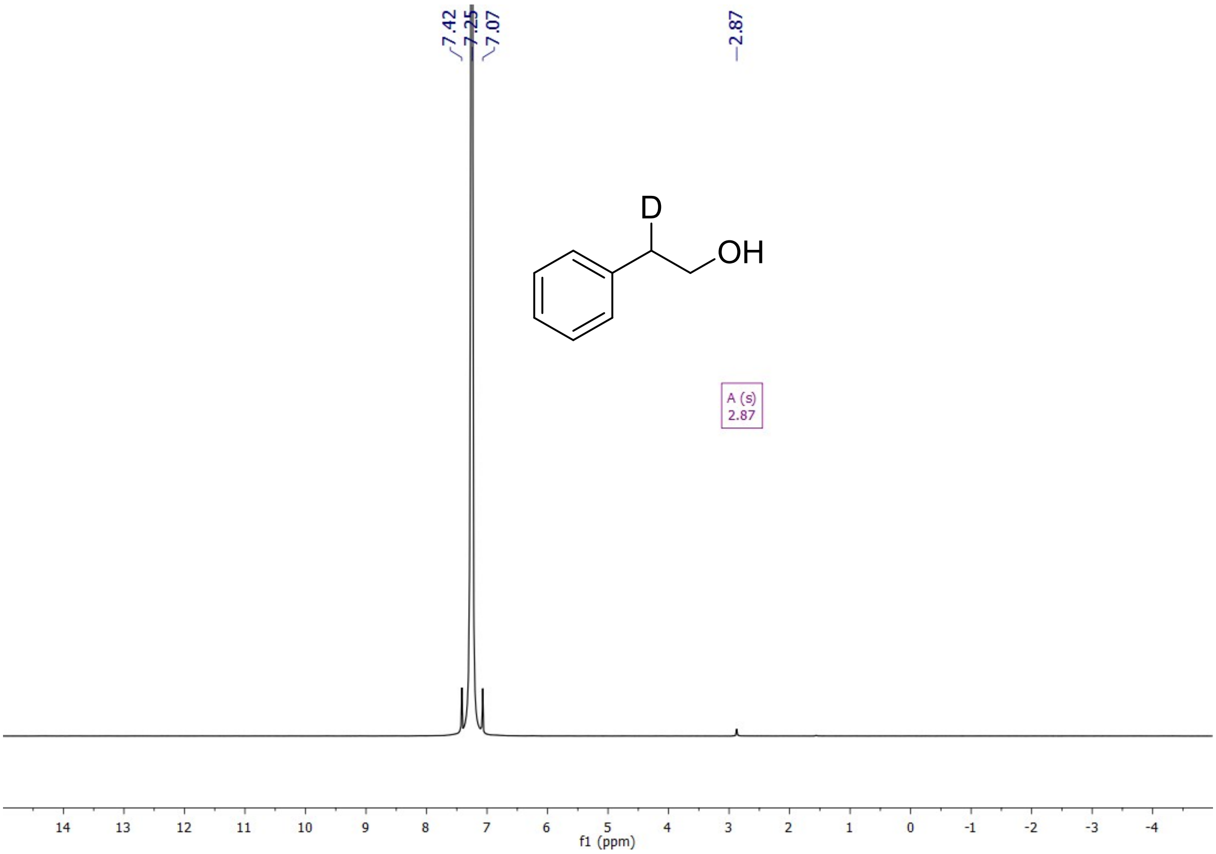
^{13}C NMR (C_6D_6, 150 MHz, 295 K):



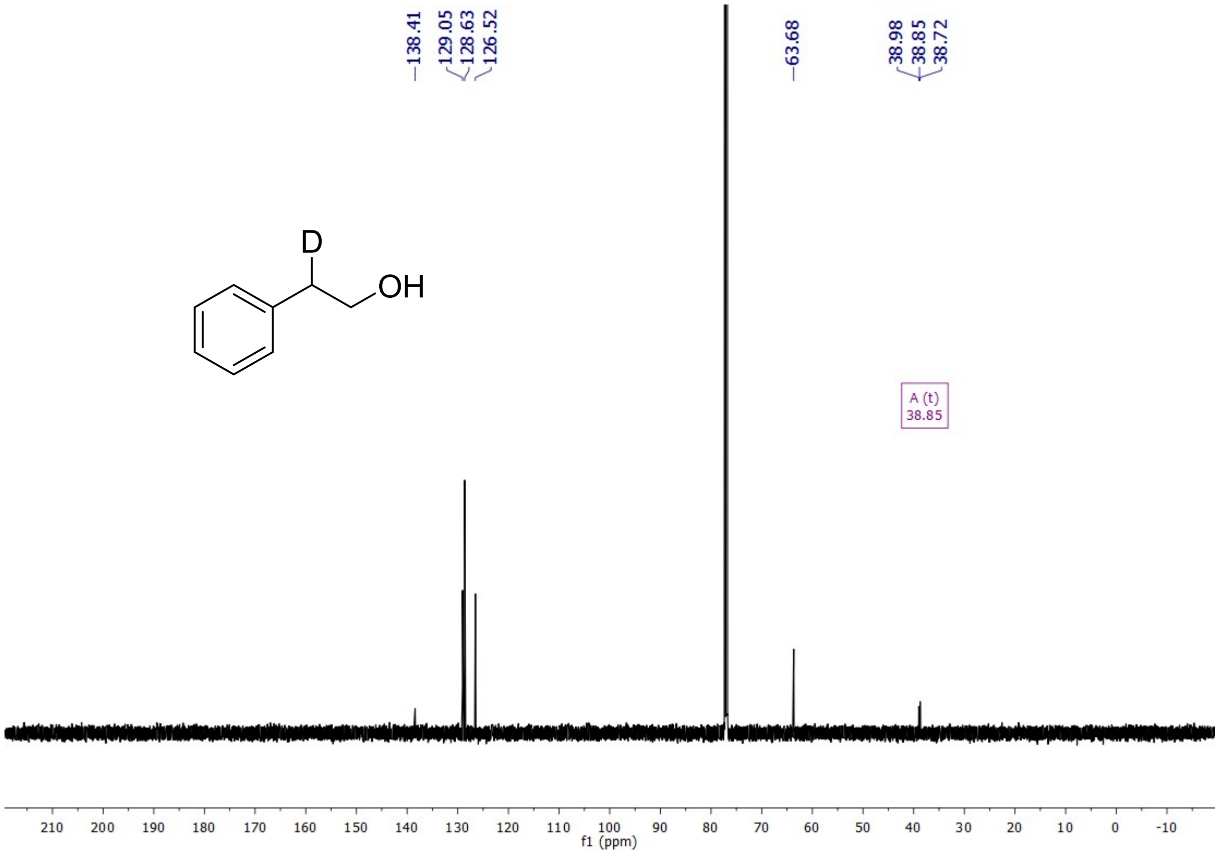
^{1}H NMR (CDCl$_3$, 600 MHz, 295 K):



^{2}H NMR (CDCl$_3$, 92 MHz, 295 K):



^{13}C NMR (CDCl$_3$, 150 MHz, 295 K):


138.41
129.05
128.63
126.52
63.68
38.98
38.85
38.72
D
OH
A (t)
38.85
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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