Supporting Information for:

Air-Stable Secondary Phosphine Oxides as Diazaphospholene Precatalysts

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General Considerations

Reduction reactions were carried out in 4 dram oven dried scintillation vials with green Qorpak® PTFE lined caps, some of which were cooled to –35 °C in the glovebox freezer. Substrates, reagents and solvents were loaded into vials under dinitrogen inside an IT Glovebox (< 20 ppm H_20, O_2). ^{1}H, ^{13}C, ^{19}F, ^{11}B and ^{31}P NMR data were collected at 300K on a Bruker AV-500 NMR spectrometer. Standard NMR tubes and caps were used. Caps on sensitive samples were overwrapped with PTFE tape. Chemical shifts are reported in parts per million from phosphoric acid (for ^{31}P NMR). ^{1}H NMR spectra are referenced to residual non-deuterated NMR solvent ($CHCl_3$ = 7.26 ppm). ^{13}C NMR spectra are referenced to the central $CDCl_3$ peak (77.16 ppm). Mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University).

Solvents

Diethyl ether for the reduction reactions was purchased as anhydrous ACS reagent grade, >99.0% stabilized by BHT in 1L metal cans from Aldrich. The cans were taken into the glovebox through the antechamber with a nitrogen purge, and without evacuation. Under evacuation, the concavity at the bottom of the can may pop out, preventing storage in an upright position. The diethyl ether was used without further purification. Diethyl ether for extractions was purchased in drums from Fisher, dispensed into 500 mL glass bottles and used as received.

Dichloromethane (ACS grade) was purchased from Fisher. Dichloromethane for reactions was distilled from calcium hydride immediately before use, while no purification was carried out on dichloromethane used for extractive work-ups.

Deuterochloroform for NMR of complexes was stored over activated 3 Å molecular sieves, but otherwise used as received. Deuterochloroform for substrates and products was used as received.

Tetrahydrofuran was purchased from Aldrich in a Sure/seal® bottle (anhydrous, >99.9%, inhibitor free, catalogue number 401757). For reaction screenings in the glovebox, the bottle was brought into the glovebox through the antechamber with nitrogen purge, the septum was removed from the bottle, and activated 3 Å molecular sieves were added for long term storage.

Reagents

3 Å Molecular sieves were purchased from Aldrich and dried at 200 °C at 0.5 torr in a round-bottom flask with a heating mantle for 36 hours prior to use.

Silica was SiliaFlash Irregular Silica Gel M60 purchased from Silicycle and used as received.

Triethylamine was purchased from Aldrich in a Sure/Seal® bottle and used as received.

Tert-Butyldimethylsilyl triflate (TBSOTf) was purchased from Oakwood and used as received.

Pinacolborane was purchased from Oakwood Chemical stored at ambient temperature in the glovebox, and otherwise used as received. Distillation of pinacolborane gave no improvement on enantioselecivity.

Phosphorus (III) Bromide was purchased as the 99% purity grade from Aldrich in a Sure/Seal® bottle and used as received. The 97% purity grade can also be used with no detriment to yield or purity, however products may be darker in colour.

Substituted pyridines were purchased from Oakwood Chemical and used as received.

Diazaphospholene Bromides: The diazaphospholene bromides **3a**[1] and **3b**[2] were prepared following the procedures of our previous work.

Reduction Substrates: Imine substrates **5a**[1] and **5b**–**5c**[2] were prepared following the procedures of our previous work. Chalcone **6** was prepared following a literature procedure.[3]

HPLC Conditions:

Racemates were obtained by $NaBH_4$ reduction of the imine in ethanol. HPLC data was acquired on a Varian Prostar instrument, with detection at 254 nm, using a Chiralpak ADH column. A hexanes/isopropanol solvent mixture was used as the eluent, with 0.1 vol% cyclohexylamine present in the hexanes as an additive.[4] Use of this additive ensures clean peak shapes, and in some cases allows separation of otherwise inseparable enantiomer mixtures. Hexanes(+$CyNH_2$)/isopropanol ratios, flow rates, and columns used are specified for each compound. The columns were stored in the cyclohexylamine containing eluant system, however the injector loop and hexanes pump module were flushed with pure hexanes at the end of every day. Without this procedure, deposition of orange residues (presumably carbamates derived from the reaction of cyclohexylamine and CO_2 in air) inside the pump head necessitated frequent cleaning.

X-ray Crystallography

The crystal chosen was attached to the tip of a MicroLoop with Paratone-N oil. Measurements were made on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III CMOS detector using monochromated Cu Kα radiation (λ = 1.54178 Å) from an Incoatec micro-focus sealed tube at 100 K.[5] The initial orientation and unit cell were indexed using a least-squares analysis of the reflections collected from a complete 360° phi-scan, 2 seconds per frame and 1° per frame. For data collection, a strategy was calculated to maximize data completeness and multiplicity, in a reasonable amount of time, and then implemented using the Bruker Apex 3 software suite.[5] The crystal to detector distance was set to 4.0 cm. Cell refinement and data reduction were performed with the Bruker SAINT[6] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS[7]). The structure was solved using SHELXT-2014[8] and was refined using a full-matrix least-squares method on F^2 with SHELXL-2018.[8] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens. The carbon atoms of the ethyl acetate solvent molecules were restrained to have similar thermal parameters using a SIMU command during refinement. The occupancies of the non-hydrogen atoms in the solvent were first refined. However, this value came out to be very close to 50% so the occupancies were then set to 0.5 for each atom in the solvent. This gave a ratio of one molecule of ethyl acetate for every two molecules of the main product.

Four reflections were omitted from the final refinement because of poor agreements between F^2_{obs} and F^2_{calc}. These were (0 1 3, 2 0 10, 1 0 13 and 7 0 9).

The molecule was found to crystallize in the chiral space group $P2_12_12_1$, with R chirality at C3 and C15. The absolute structure of the molecule was reliably determined; although values did not refine completely to zero as expected, they are close enough to be taken as such. Using the program Platon[9] the refined structure was calculated to have a Flack parameter of 0.060(3), a Parsons parameter of 0.081(3) and a Hooft parameter of 0.050(1). These values agree with the Parson's value calculated by the program SHELXL, 0.060(3) from 2136 selected quotients.

Table S1. Crystal data and structure refinement for compound **2b**.

Identification code	**2b**	
Empirical formula	$C_{28}H_{29}N_2O_2P$	
Formula weight	456.50	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.1724(2) Å	a= 90°
	b = 11.6412(3) Å	b= 90°
	c = 22.2670(6) Å	g = 90°
Volume	2377.62(10) $Å^3$	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	1.240 mm^{-1}	
F(000)	968	
Crystal size	0.219 x 0.207 x 0.104 mm^3	
Theta range for data collection	3.970 to 79.580°	
Index ranges	-11<=h<=11, -14<=k<=14, -28<=l<=28	
Reflections collected	50273	
Independent reflections	5094 [R(int) = 0.0294]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7543 and 0.6726	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5094 / 12 / 333	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0955	
R indices (all data)	R1 = 0.0367, wR2 = 0.0955	
Absolute structure parameter	0.060(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.209 and -0.268 $e.Å^{-3}$	

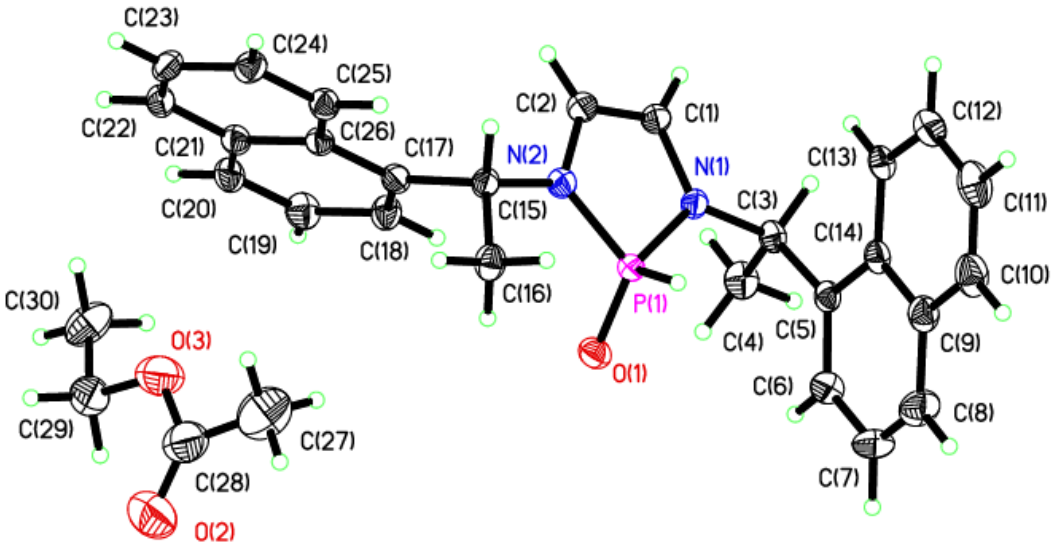


Figure S1. Structural diagram of compound **2b** including one part of the disordered ethyl acetate solvent molecule**.** Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have not been labelled.

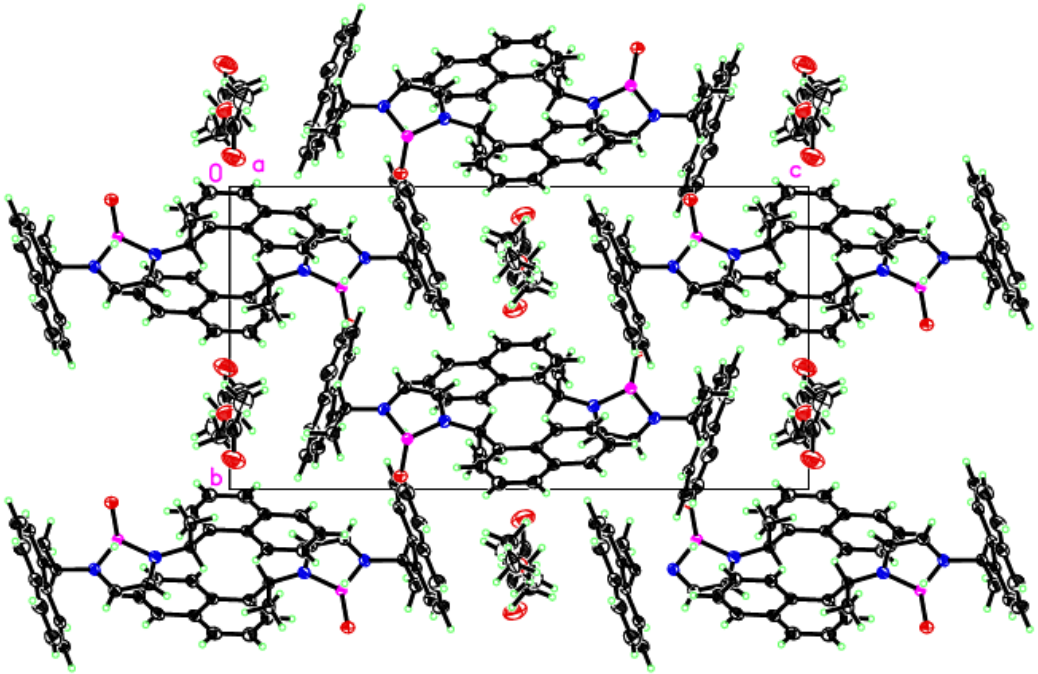
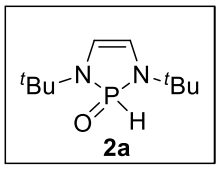


Figure S2. Packing diagram for compound **2b** viewed down the *X*–axis**.**

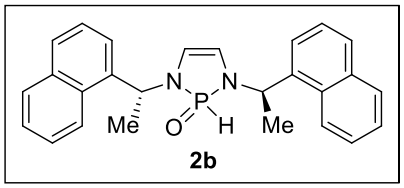
Synthesis of SPO Precatalysts:



2a

Oxide 2a: Bromide **3a** (1.0 g, 3.58 mmol, 1 equiv) was dissolved in 10 mL of dichloromethane in a 50 mL Schlenk flask. Triethylamine (0.50 ml, 3.58 mmol, 1 equiv) was added, and the dark solution was stirred for 5 minutes followed by the addition of excess water (10 mL). After 1 hour, the reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated in vacuo. Compound **2a** (702 mg, 92% yield) was obtained as beige solid without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (dt, *J*= 646.2, 1.7 Hz, 1H), 5.92 (dd, *J*= 16.0, 1.8 Hz, 2H), 1.40 (s, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 110.5 (d, *J*= 10.2), 53.5 (d, *J*= 4.7) 30.1 (d, J= 4.0).
^{31}P NMR (202 MHz, $CDCl_3$): δ 3.34 (dt, *J*= 646.2, 16.2 Hz).
HRMS(ESI): calculated $(M+Na)^+$ $[C_{10}H_{21}N_2OPNa]^+$ 239.1284, found 239.1282.

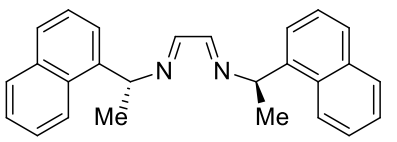


2b

Oxide 2b: Bromide **3b** (1.0 g, 2.10 mmol, 1 equiv) was dissolved in 10 mL of dichloromethane in a 50 mL Schlenk flask. Triethylamine (0.30 ml, 2.10 mmol, 1 equiv) was added, and the dark solution was stirred for 5 minutes followed by the addition of excess water (10 mL). After 1 hour, the reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated in vacuo resulting in a crude brown solid. Purification by flash chromatography (EtOAc/Hexanes 50:50 v/v) provided **2b** (582 mg, 67% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, *J*= 650.7 Hz, 1H), 8.16 (d, *J*= 8.5 Hz, 1H), 7.99 (d, *J*= 650.7 Hz, 1H), 7.90–7.87 (m, 2H), 7.83 (d, *J*= 8.2 Hz, 1H), 7.78 (d, *J*= 8.2 Hz, 1H), 7.70 (d, *J*= 7.1 Hz, 1H), 7.62–7.56 (m, 2H), 7.54–7.47 (m, 5H), 5.73 (dd, *J*= 16.3, 1.2 Hz, 2H), 5.56–5.50 (m, 2H), 1.90 (dd, *J*= 52.9, 6.9 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2 (d, *J*= 2.4 Hz), 135.8 (d, *J*= 4.3 Hz), 134.1, 134.0, 131.2, 130.5, 129.2, 129.1, 129.0, 128.3, 126.8, 126.4, 125.9, 125.8, 125.7, 125.4, 124.7, 124.2, 123.1, 122.5, 113.7 (d, *J*= 10.4 Hz), 112.5 (d, *J*= 10.4 Hz), 51.7 (d, *J*= 6.0 Hz), 51.1 (d, *J*= 6.0 Hz), 21.7 (d, *J*= 1.8 Hz), 21.4 (d, *J*= 4.1 Hz).
^{31}P NMR (202 MHz, $CDCl_3$): δ 6.68 (m).
HRMS(ESI): calculated $(M+Na)^+$ $[C_{26}H_{25}N_2OPNa]^+$ 435.1597, found 435.1608.

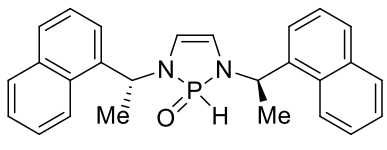
One Pot Synthesis of Oxide 2b:



10

1.) PBr_3, Cyclohexene, CH_2Cl_2
2.) NEt_3, H_2O

72%



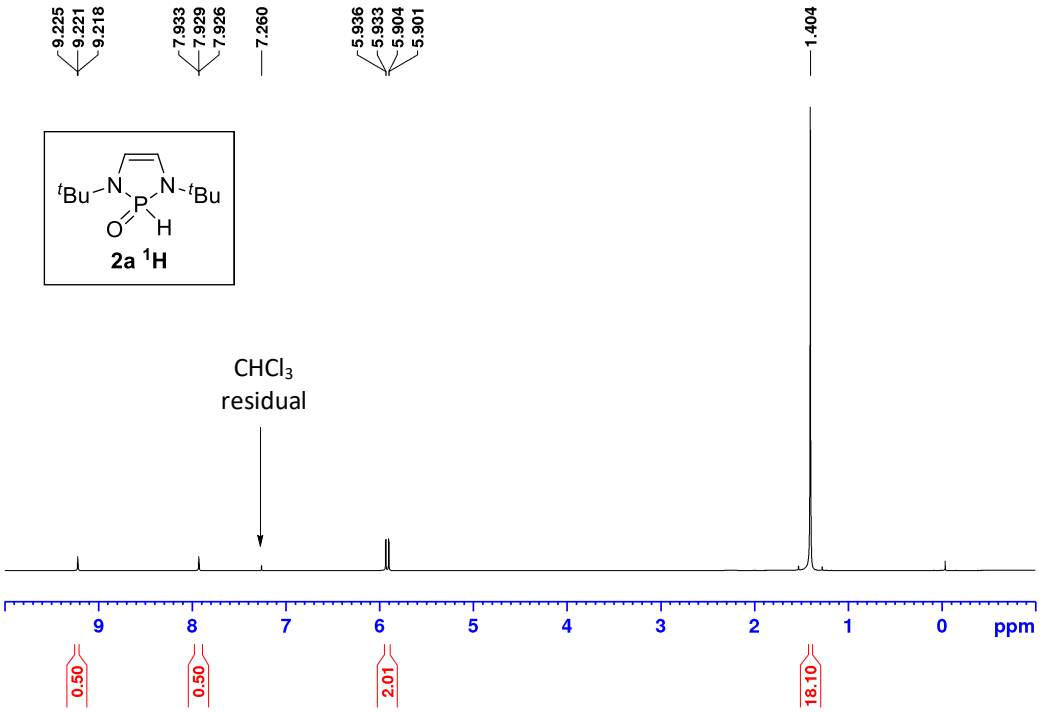
2b

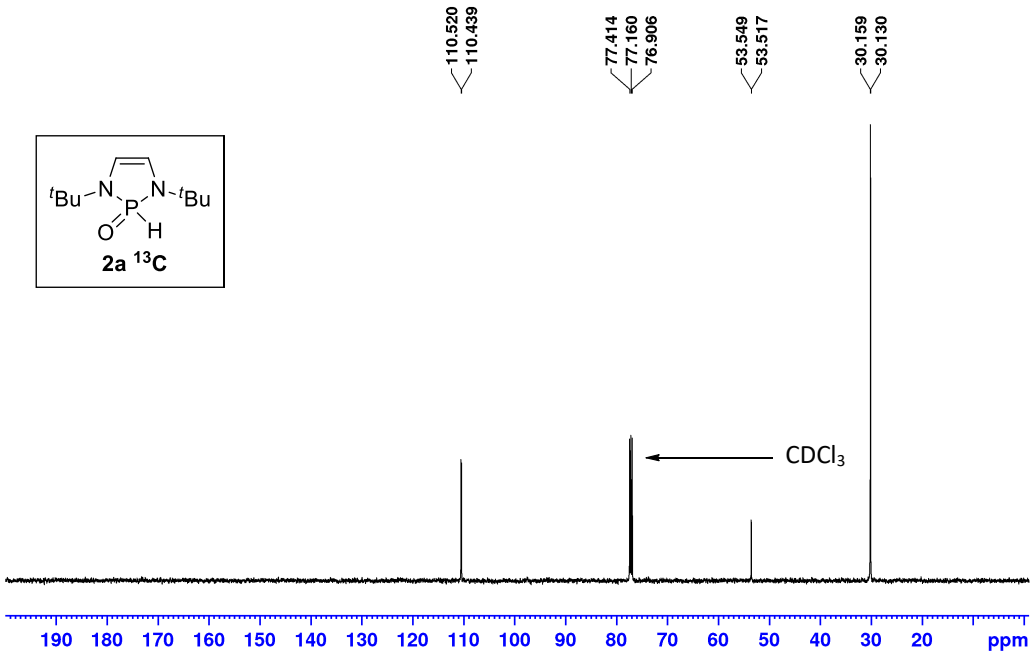
One pot synthesis of precatalyst 2b: In a Schlenk flask, 0.26 mL (2.74 mmol, 1 equiv) of PBr_3 and 1.39 mL (13.7 mmol, 5 equiv) cyclohexene were dissolved in 3 mL of dichloromethane.

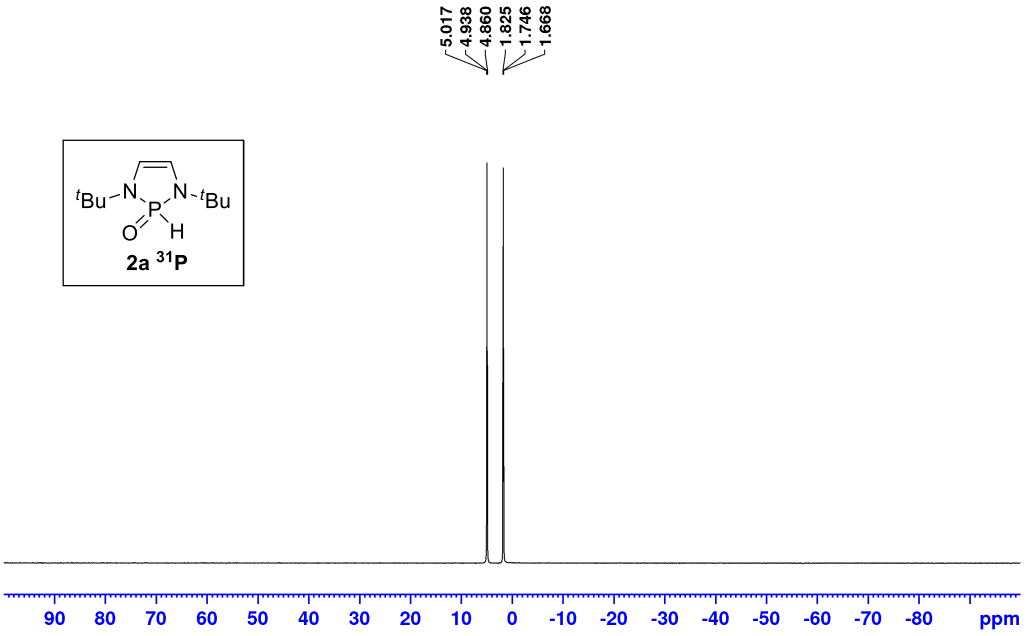
Diimine **10** (1.00 g, 2.74 mmol, 1 equiv) dissolved in 10 mL of dichloromethane was added over 5 minutes with 2 mL dichloromethane used to rinse and complete the transfer. After 1.5 hours, triethylamine (0.40 mL, 2.74 mmol, 1 equiv) was added to the dark brown reaction mixture and stirred for 5 minutes, following by the addition of excess water (10 mL). After 1 hour, the reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated in vacuo resulting in a crude brown solid. Purification by flash chromatography (EtOAc/Hexanes 50:50 v/v) provided **2b** (817 mg, 72% yield) as a white solid.

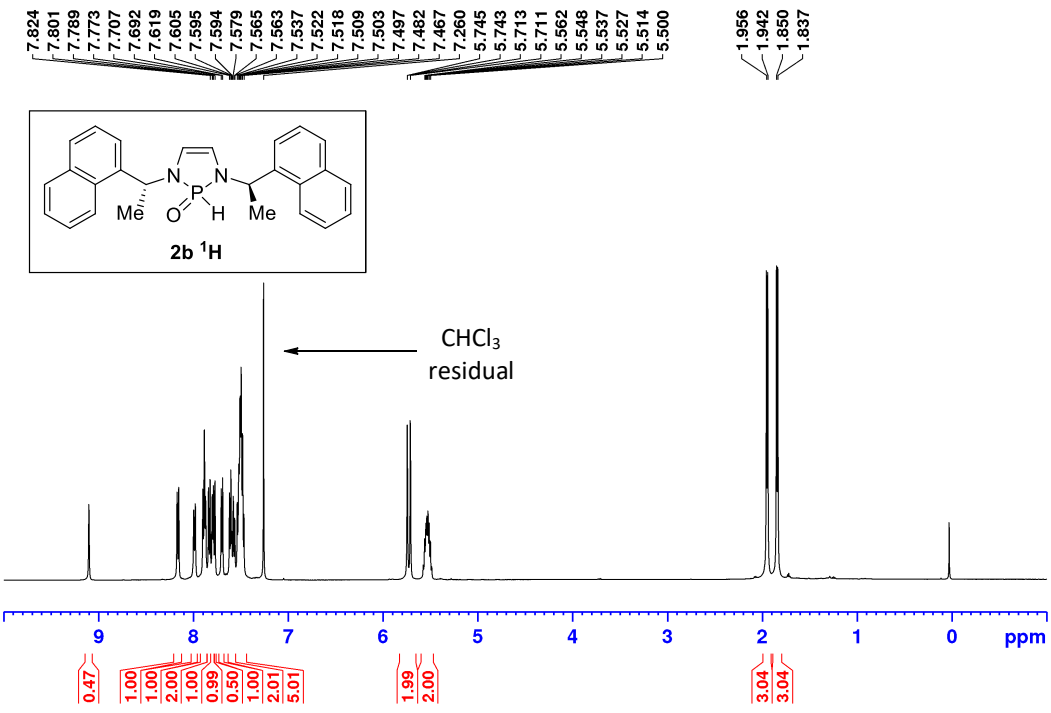
NMR data were in agreement with material prepared via the two-step route shown above.

NMR Spectra of Precatalysts:






5.017
4.938
4.860
1.825
1.746
1.668
tBu
N
P
O
H
tBu
2a 31P
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm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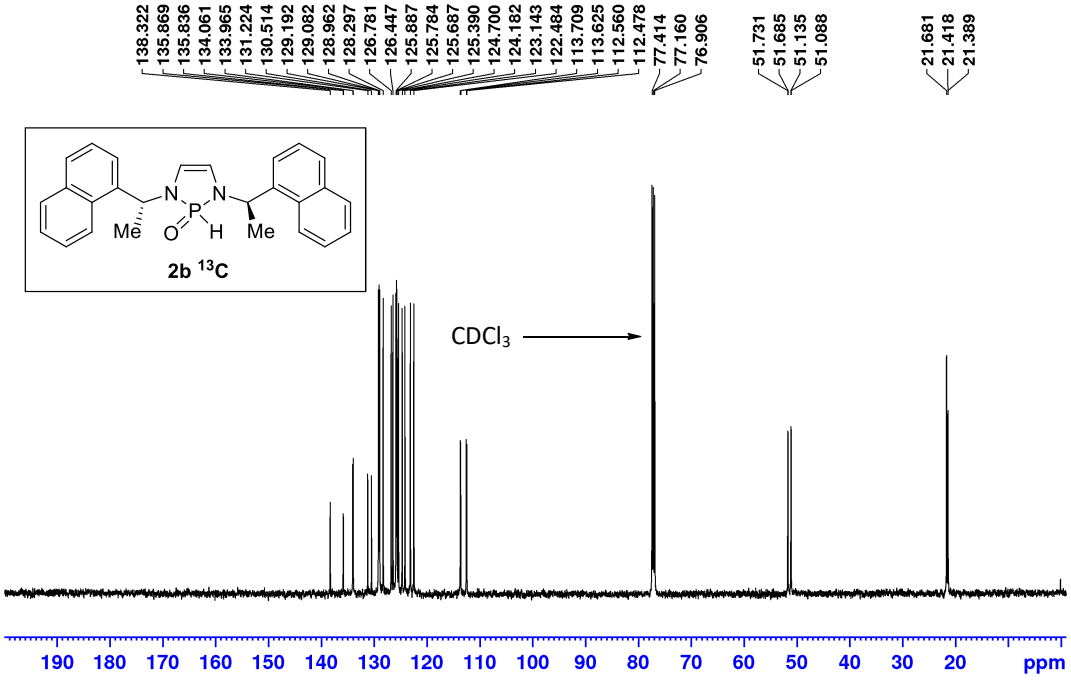
7.801
7.789
7.773
7.707
7.692
7.619
7.605
7.595
7.594
7.579
7.565
7.563
7.537
7.522
7.518
7.509
7.503
7.497
7.482
7.467
7.260
5.745
5.743
5.713
5.711
5.562
5.548
5.537
5.527
5.514
5.500
1.956
1.942
1.850
1.837
Me
N
P
O
H
N
Me
2b 1H
CHCl3
residual
9 8 7 6 5 4 3 2 1 0 ppm
0.47
1.00
1.00
2.00
1.00
0.99
0.50
1.00
2.01
5.01
1.99
2.00
3.04
3.04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133.965
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130.514
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126.447
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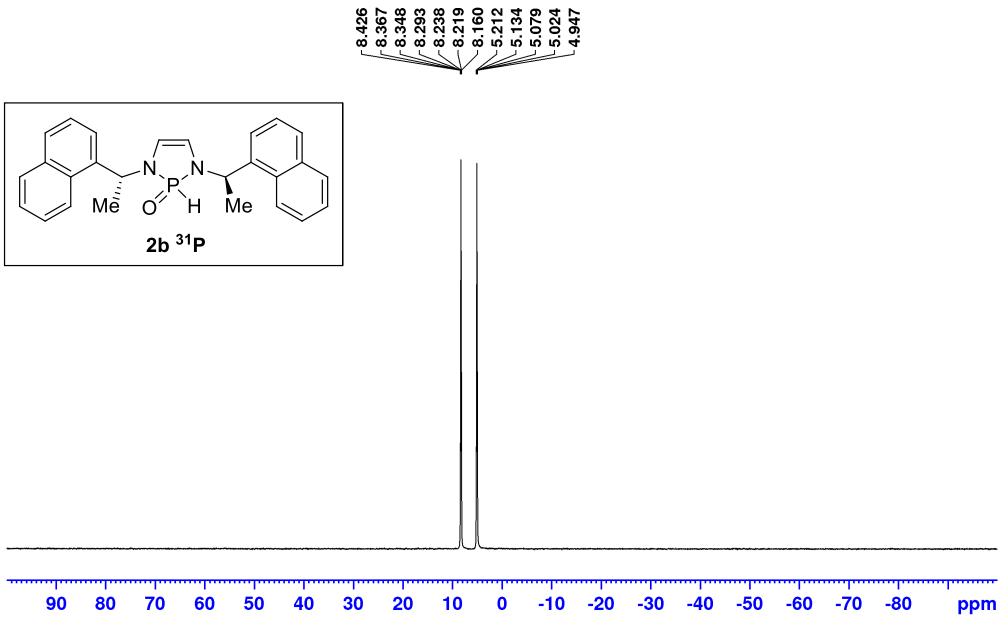
125.784
125.687
125.390
124.700
124.182
123.143
122.484
113.709
113.625
112.560
112.478
77.414
77.160
76.906
51.731
51.685
51.135
51.088
21.681
21.418
21.389
Me
O
H
Me
2b ^{13}C
CDCl$_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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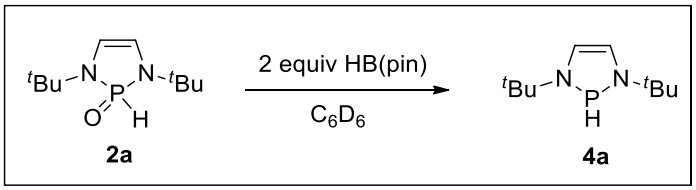
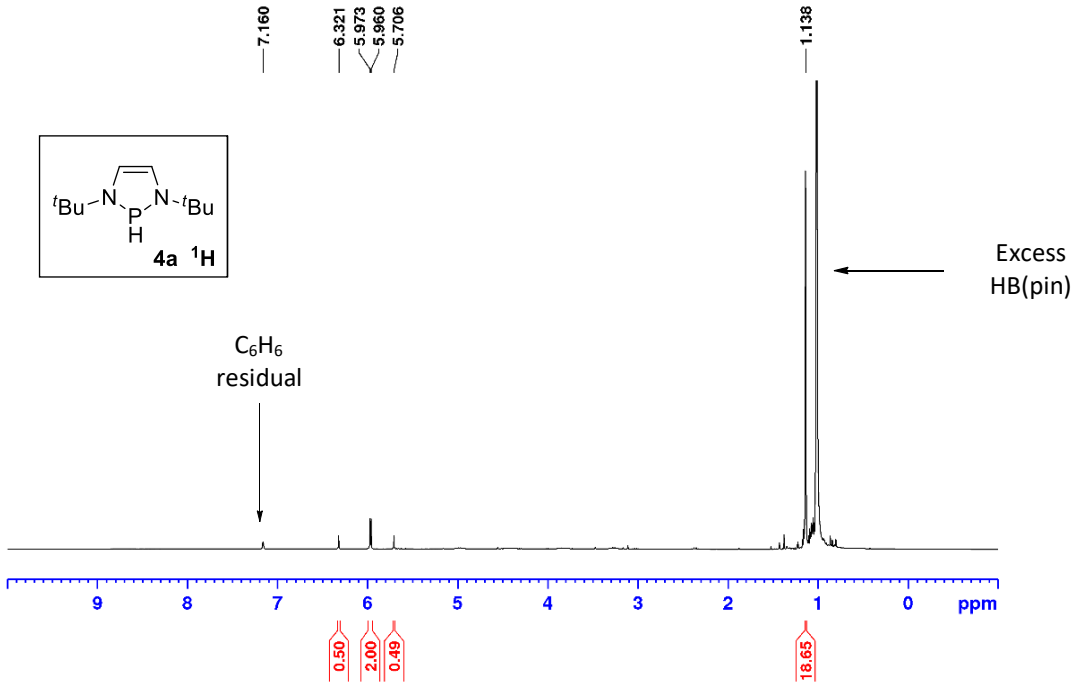
8.367
8.348
8.293
8.238
8.219
8.160
5.212
5.134
5.079
5.024
4.947
Me
O
H
Me
2b ^{31}P
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

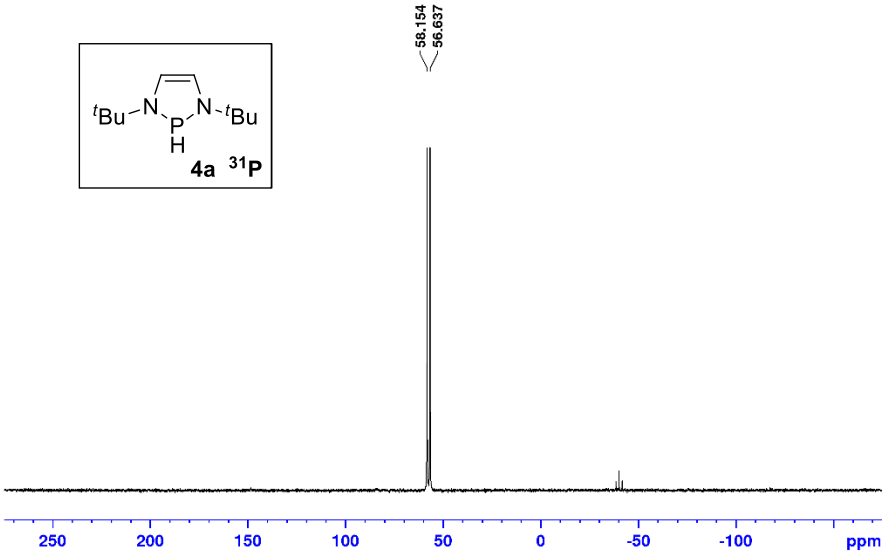
In Situ Formation of Diazaphospholene Hydride and Phosphenium Triflates

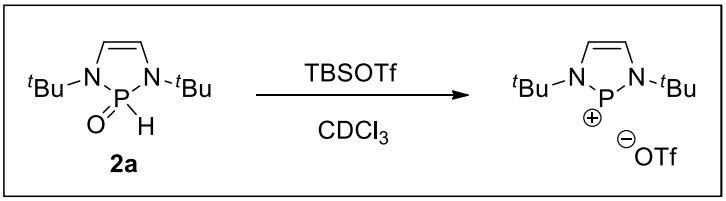


Precatalyst **2a** (50 mg, 0.23 mmol, 1 equiv) was dissolved in 1 mL of C_6D_6 in a 1 dram vial and HB(pin) (0.07 ml, 0.46 mmol, 2 equiv) was added. The reaction mixture was stirred overnight and then analyzed by ^{31}P NMR to show complete conversion to the diazaphospholene hydride **4a**.

NMR data were in agreement with literature values for this compound.[10]

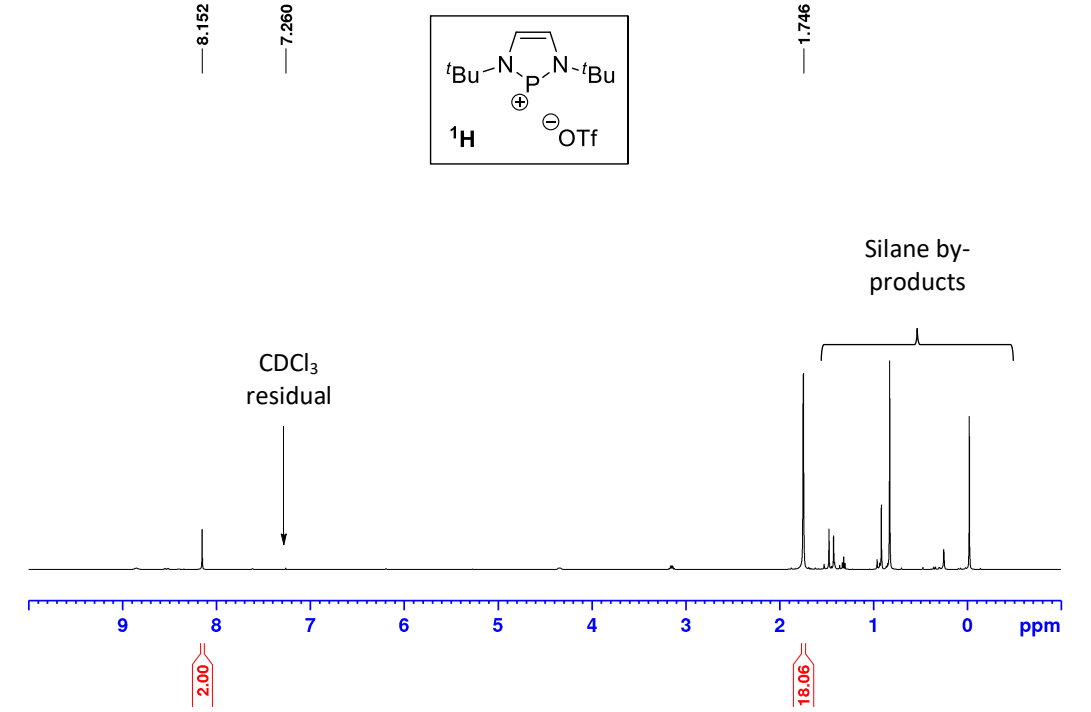






Precatalyst **2a** (30 mg, 0.14 mmol, 1 equiv) was dissolved in 1 mL of $CDCl_3$ in a 1 dram vial and TBSOTf (0.03 ml, 0.14 mmol, 1 equiv) was added. The reaction mixture was immediately analyzed by ^{31}P NMR to show high conversion to the phosphenium triflate.

NMR data were in agreement with literature values for this compound.[11]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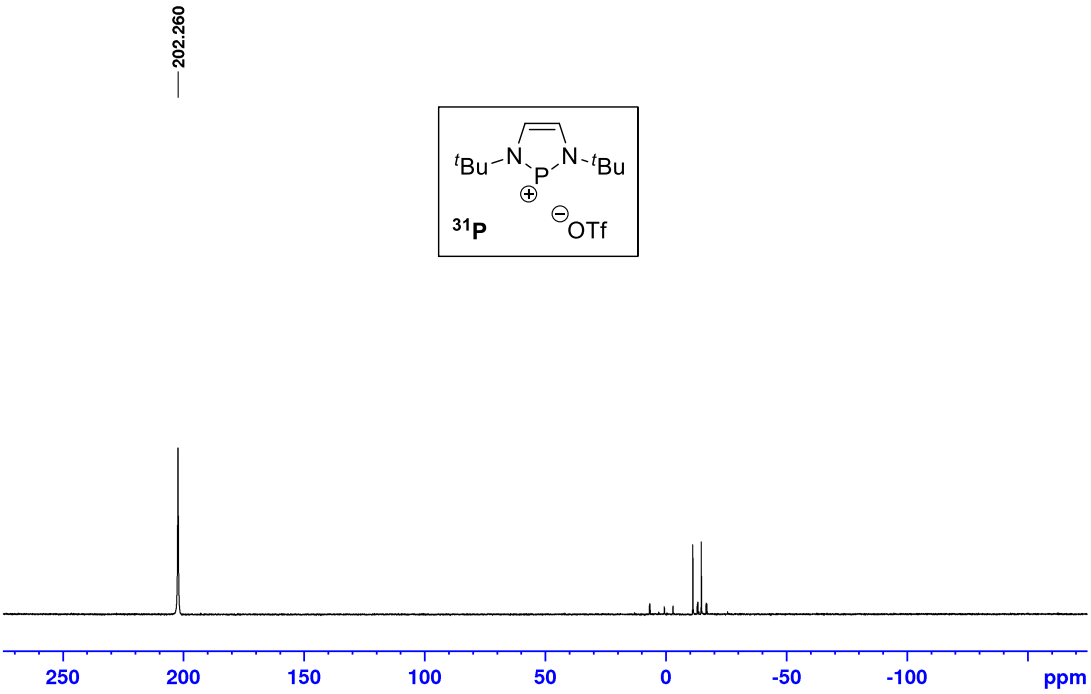
1.746
tBu
N
P
N
tBu
1H
OTf
Silane by-products
CDCl3 residual
9
8
7
6
5
4
3
2
1
0
ppm
2.00
18.06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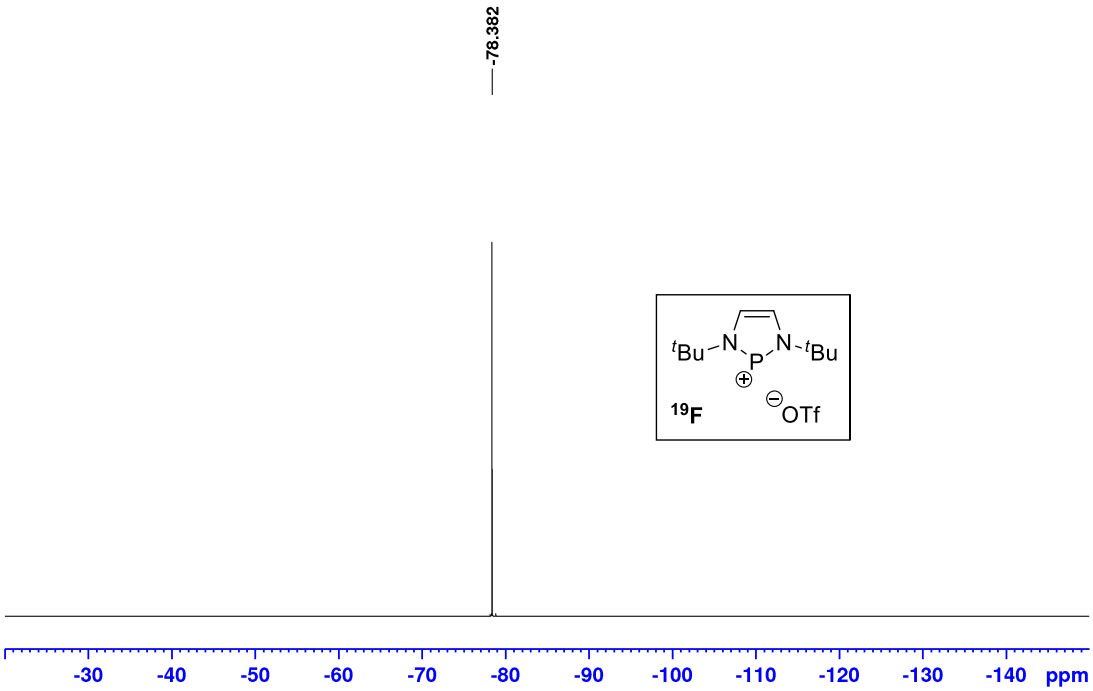
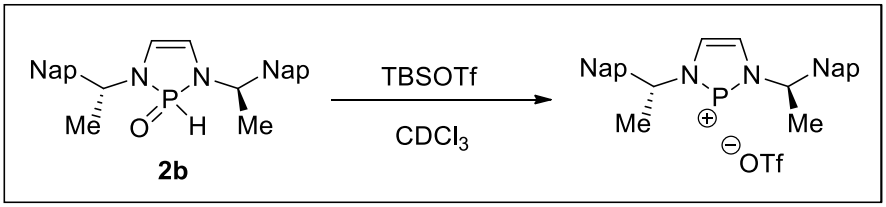
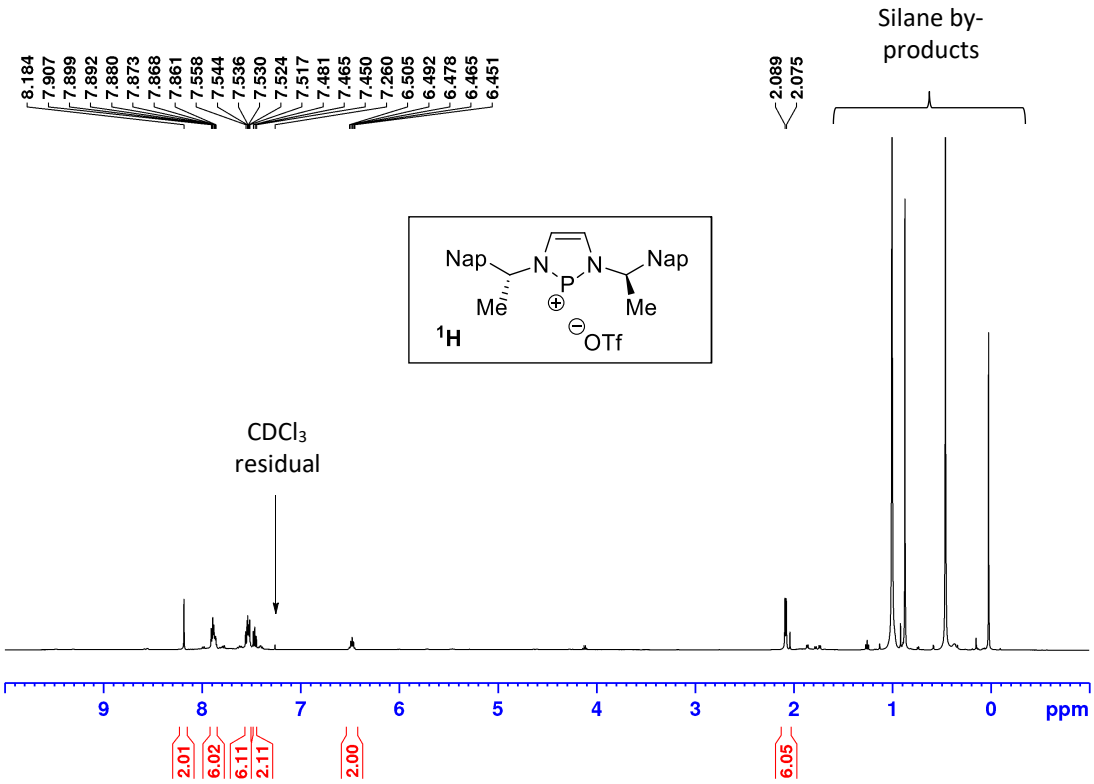
N
P
N
tBu
31P
OTf
250
200
150
100
50
0
-50
-100
ppm





Precatalyst **2b** (30 mg, 0.073 mmol, 1 equiv) was dissolved in 1 mL $CDCl_3$ in a 1 dram vial and TBSOTf (0.02 ml, 0.073 mmol, 1 equiv) was added. The reaction mixture was immediately analyzed by ^{31}P NMR to show almost complete conversion to the phosphenium triflate.

NMR data were in agreement with literature values for this compound.[2]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7.880
7.873
7.868
7.861
7.558
7.544
7.536
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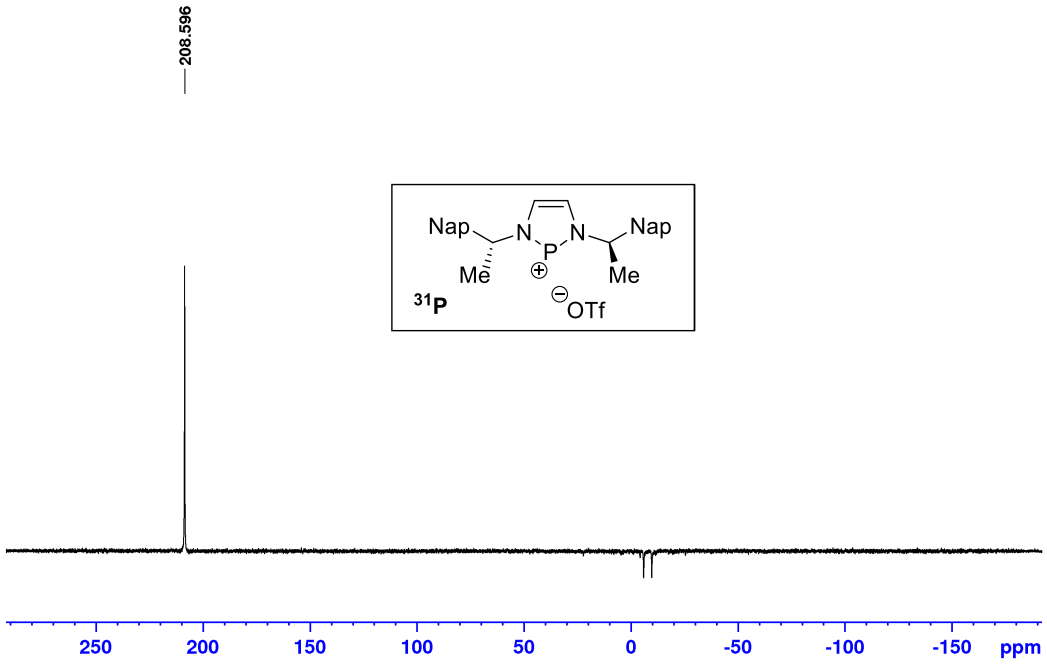
7.517
7.481
7.465
7.450
7.260
6.505
6.492
6.478
6.465
6.451
2.089
2.075
Silane by-products
Nap
N
P
N
Nap
Me
Me
OTf
1H
CDCl3 residual
9
8
7
6
5
4
3
2
1
0
ppm
2.01
6.02
6.11
2.11
2.00
6.05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N
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Me
Me
OTf
31P
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150
100
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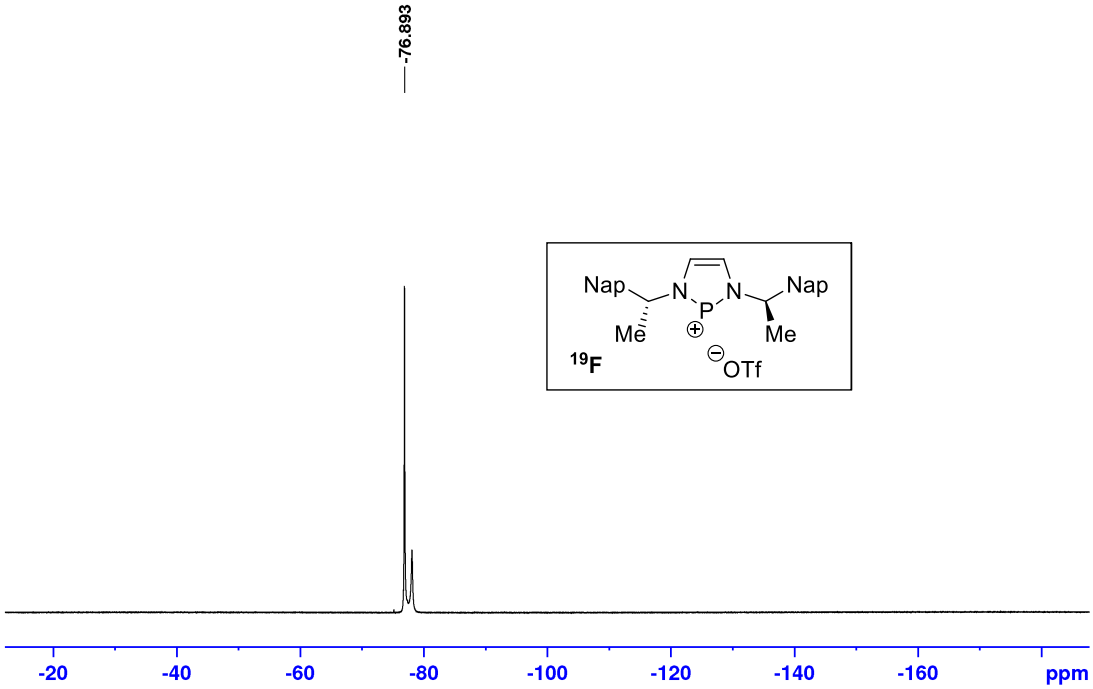
-150
ppm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P
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Me
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OTf
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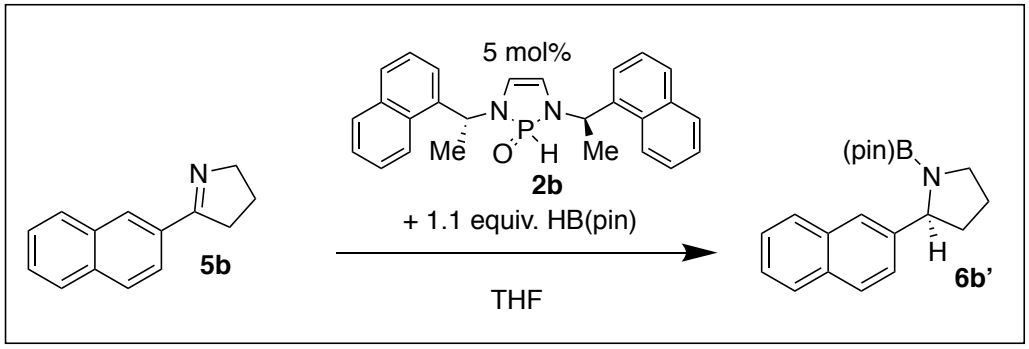
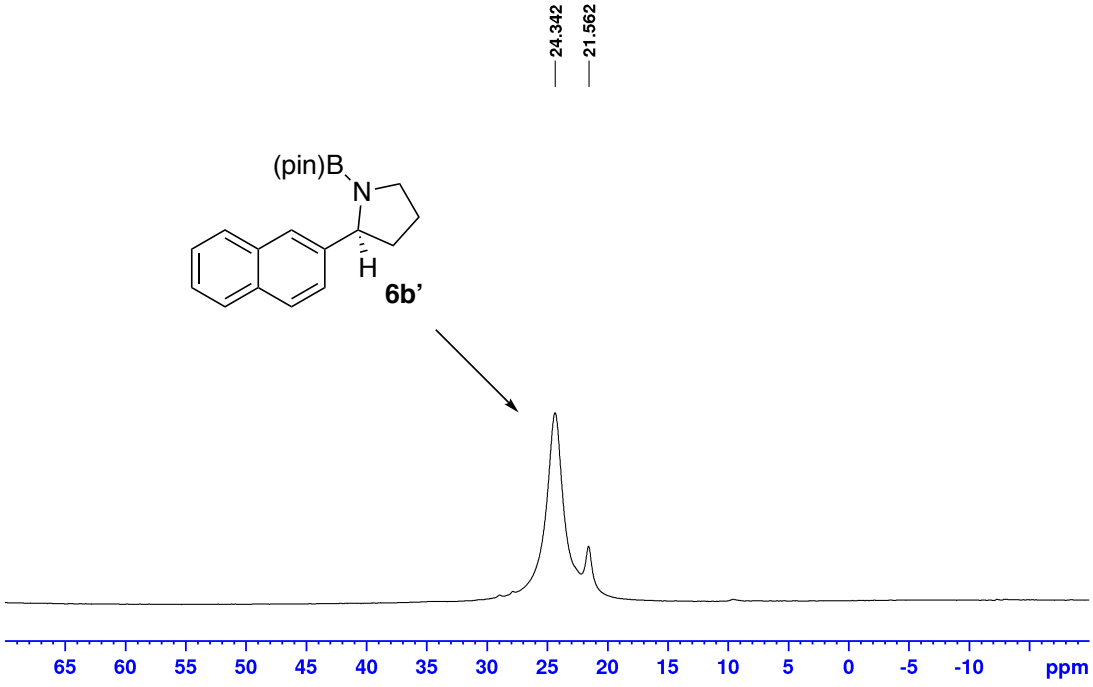
-80
-100
-120
-140
-160
ppm

In Situ Asymmetric Reduction Reactions in NMR Tubes

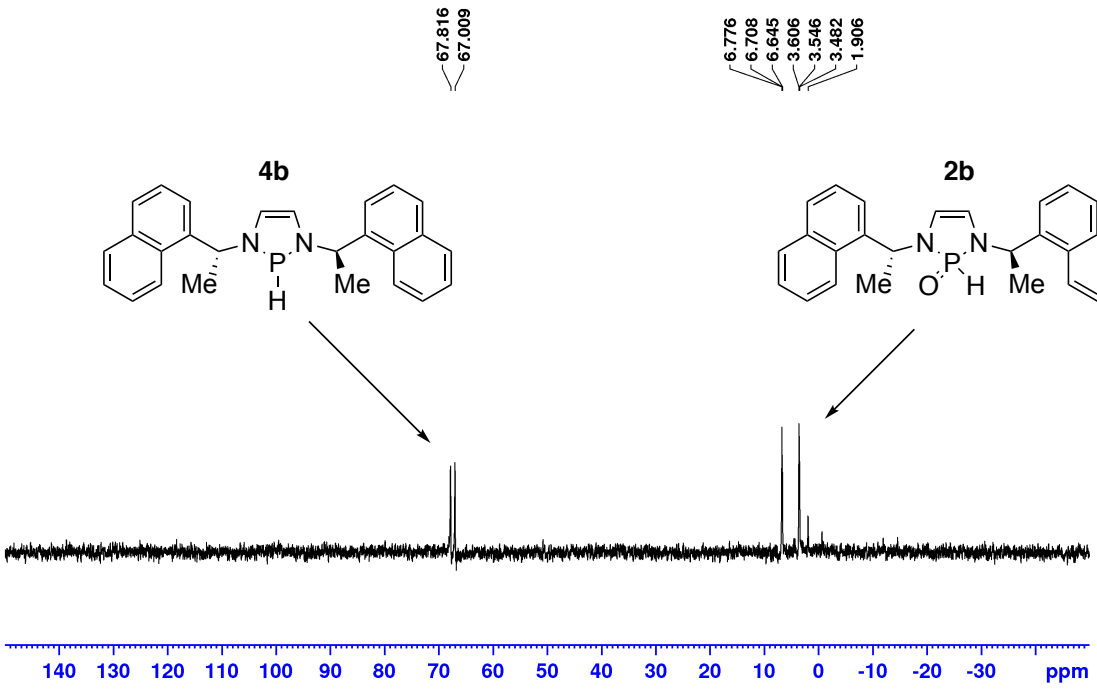


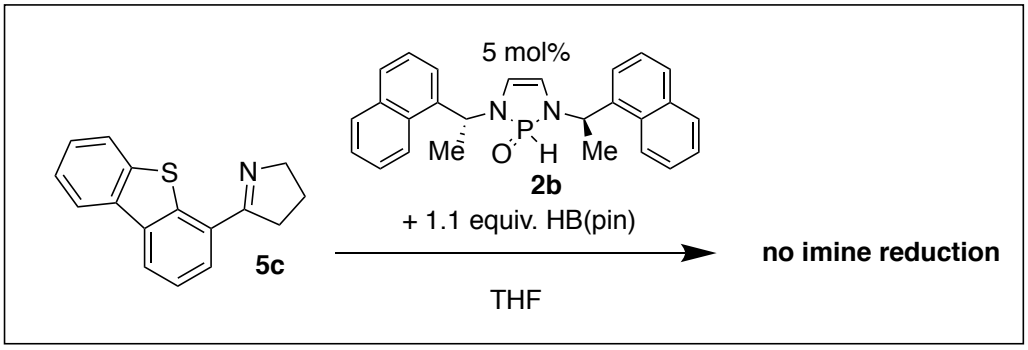
In a glovebox, the imine **5b** (50 mg, 0.25 mmol, 1 equiv) and precatalyst **2b** (5 mol%) were mixed in THF (1 mL) at room temperature. HB(pin) (0.04 mL, 0.28 mmol, 1.1 equiv) was added and the reaction was swirled to mix components. The mixture was placed in an NMR tube with a C_6D_6 capillary so that automated locking/shimming could be conducted, overwapped with Teflon tape, and removed from the glovebox. The ^{11}B spectrum was acquired approximately 5 minutes after the mixing, while the ^{31}P spectrum was acquired approximately 9 minutes after the mixing.

^{11}B Spectrum:



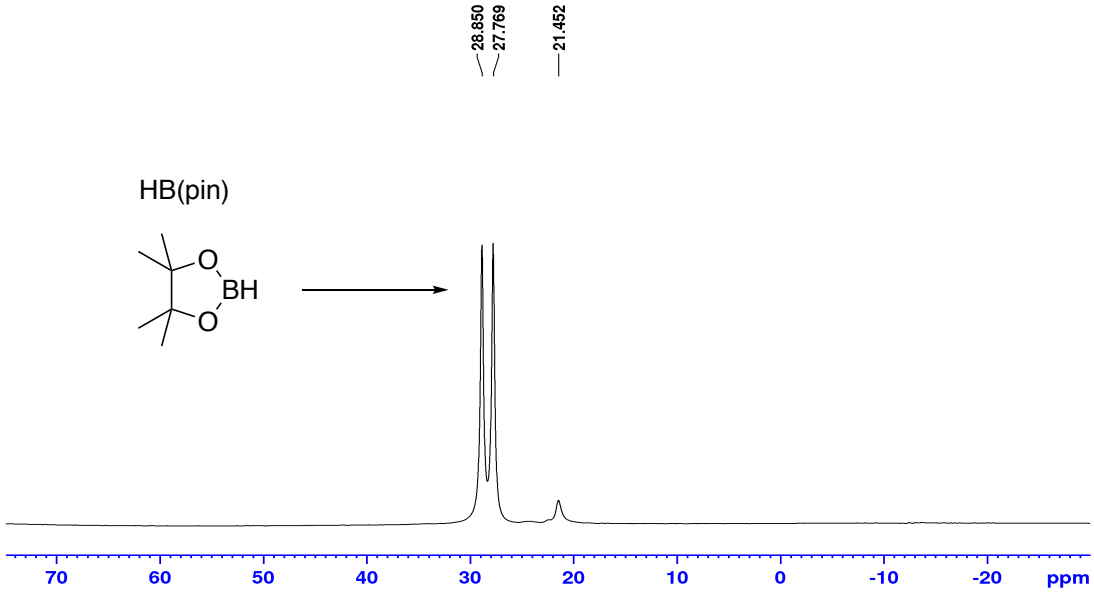
^{31}P Spectrum:



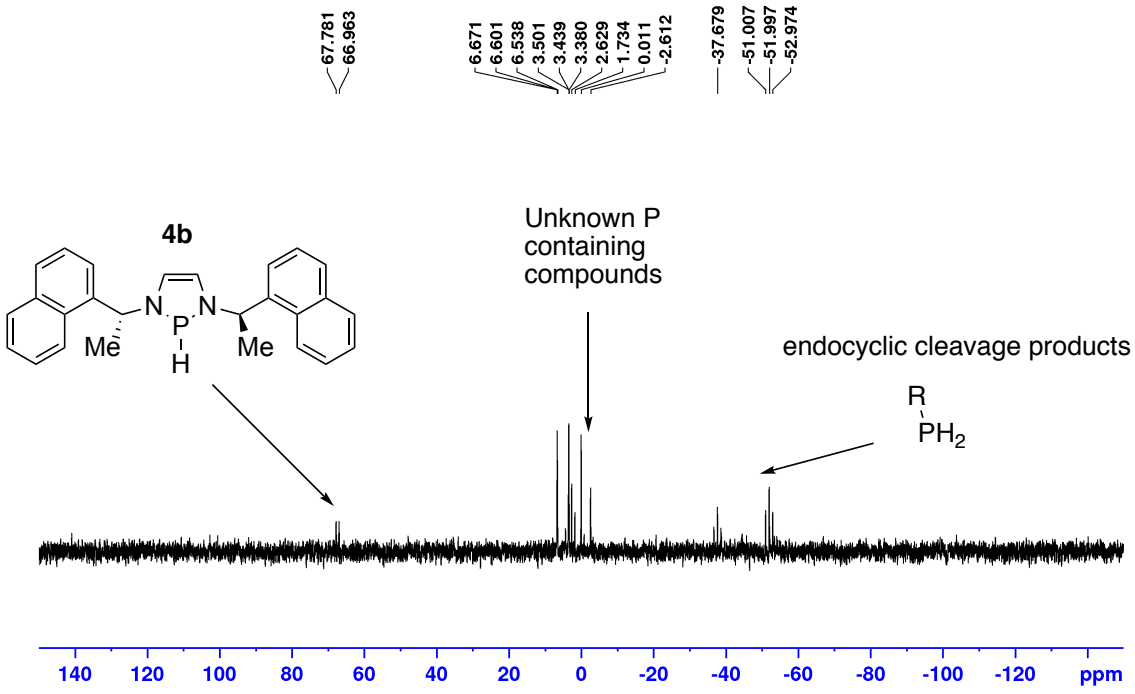


The imine **5c** (50 mg, 0.20 mmol, 1 equiv) and precatalyst **2b** (5 mol%) were mixed in THF (1 mL) at room temperature, followed by the addition of HB(pin) (0.03 mL, 0.22 mmol, 1.1 equiv). The reaction was swirled to mix components The mixture was placed in an NMR tube with a C_6D_6 capillary so that automated locking/shimming could be conducted, overwapped with Teflon tape, and removed from the glovebox. The ^{11}B spectrum was acquired approximately 5 minutes after the mixing, while the ^{31}P spectrum was acquired approximately 9 minutes after the mixing. Further ^{11}B and ^{31}P spectra were acquired 2 hours after mixing.

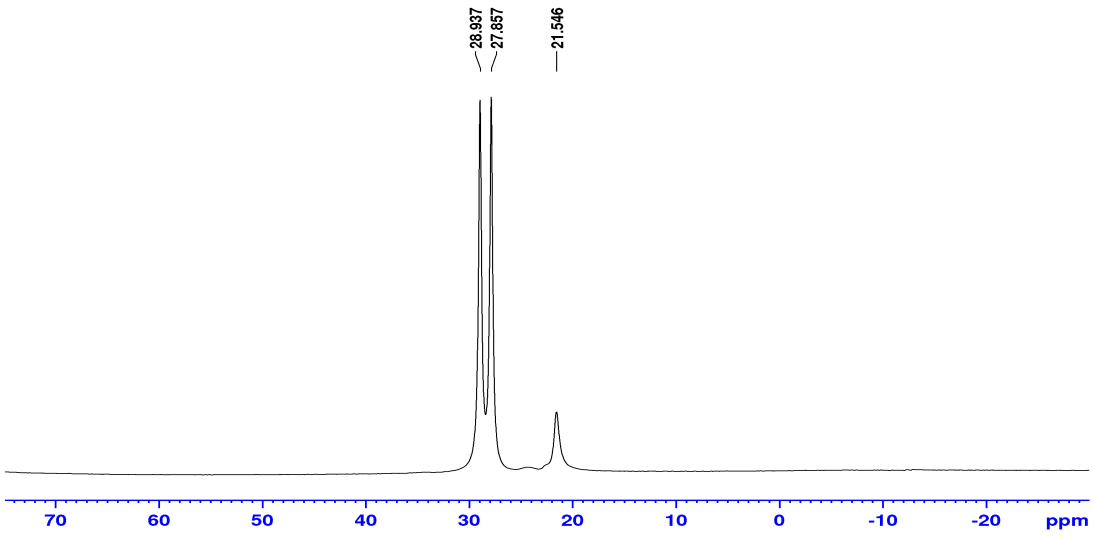
^{11}B Spectrum after 5 minutes:



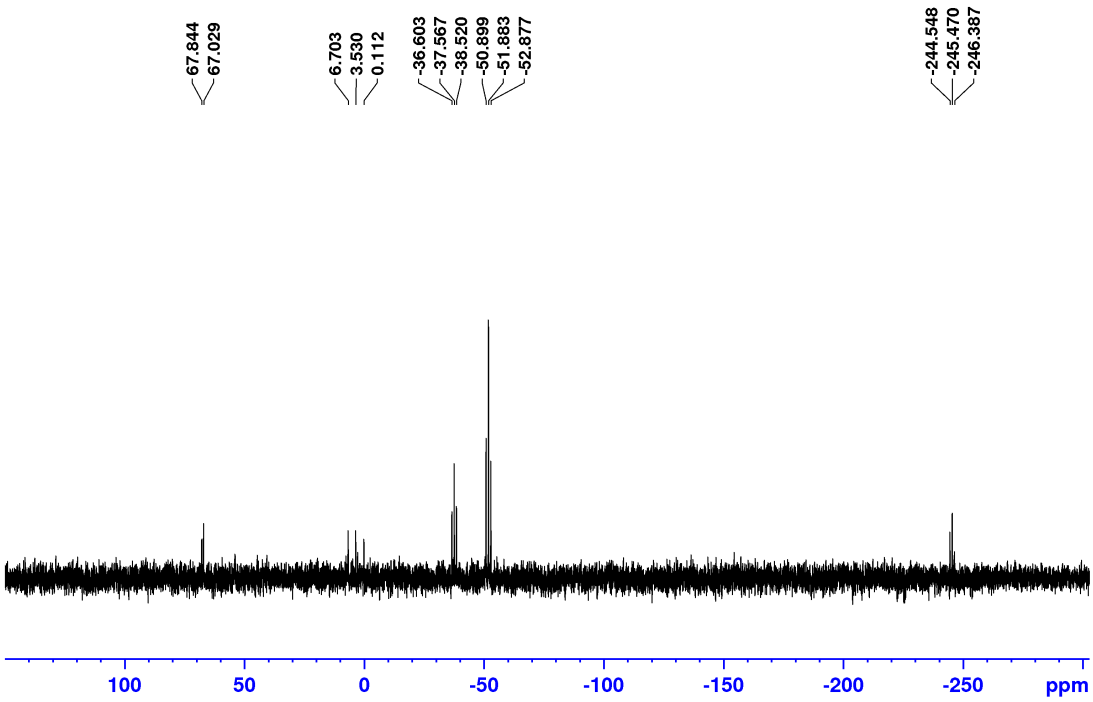
^{31}P Spectrum after 9 minutes:



^{11}B Spectrum after 2 hours:

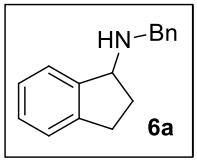


^{31}P Spectrum after 2 hours:



Tabulated Data for Reduction Products:

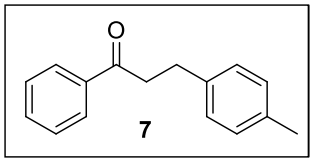
_N_-benzyl-2,3-dihydro-1_H_-inden-1-amine (6a)



The imine **5a** (100 mg, 0.45 mmol, 1 equiv) and precatalyst **2a** (1 mol%) were mixed in THF (2 mL) at room temperature, followed by the addition of HB(pin) (0.07 mL, 0.50 mmol, 1.1 equiv). The reaction was swirled to mix components and was left for 16 hours without stirring. Several drops of 1M HCl were added until the bubbling stopped, then 2M NaOH was added until the reaction mixture was basic to pH paper. The reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. Purification by flash chromatography (EtOAc/MeOH/iPrNH$_2$ 90:9:1 v/v) provided **6a** (91 mg, 90% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.39 (m, 3H), 7.35 (t, J= 7.6 Hz, 2H), 7.28–7.21 (m, 4H), 4.32 (t, J= 6.6 Hz, 1H), 3.93 (q, J= 11.4 Hz, 2H), 3.07–3.01 (m, 1H), 2.86–2.80 (m, 1H), 2.48–2.42 (m, 1H), 1.94–1.87 (m, 1H), 1.57 (brs, 1H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5, 143.8, 140.9, 128.5, 128.3, 127.5, 127.0, 126.4, 124.9, 124.3, 62.9, 51.6, 33.8, 30.6.

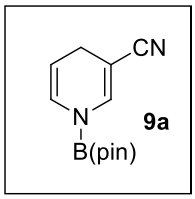
1-phenyl-3-(_p_-tolyl)propan-1-one (7)



The chalcone **6** (100 mg, 0.48 mmol, 1 equiv) and precatalyst **2a** (1 mol%) were mixed in Et_2O (2 mL) at room temperature, followed by the addition of HB(pin) (0.08 mL, 0.53 mmol, 1.1 equiv). The reaction was swirled to mix components and was left for 16 hours without stirring. The reaction mixture was washed with 1M HCl, extracted with Et_2O, dried over Na_2SO_4 and concentrated. Purification by flash chromatography (Hexanes/EtOAc 95:5 v/v) provided **7** (93 mg, 92% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–8.00 (m, 2H), 7.61–7.58 (m, 1H), 7.50 (t, J= 7.7 Hz, 2H), 7.20 (d, J= 8.0 Hz, 2H), 7.16 (d, J= 8.0 Hz, 2H), 3.35–3.31 (m, 2H), 3.08 (t, J= 7.7 Hz, 2H), 2.37 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 138.3, 137.1, 135.7, 133.1, 129.3, 128.7, 128.4, 128.2, 40.7, 29.9, 21.1.

1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine-3-carbonitrile (9a)

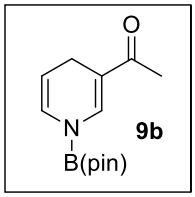


3-cyanopyridine **8a** (200 mg, 1.92 mmol, 1 equiv) and precatalyst **2a** (1 mol%) were mixed in Et_2O (1 mL) at room temperature, followed by the addition of HB(pin) (0.31 mL, 2.11 mmol, 1.1 equiv). The reaction was swirled to mix components and left for 16 hours without stirring. The reaction mixture was then concentrated in vacuo to remove solvent and unreacted HB(pin). Compound **9a** (373 mg, 84% yield) was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91 (s, 1H), 6.12 (dd, J= 8.3, 1.2 Hz, 1H), 4.77 (dt, J= 8.2, 3.5 Hz, 1H), 3.01 (t, J= 1.4 Hz, 2H), 1.25 (s, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0, 125.4, 120.5, 103.6, 85.5, 84.8, 24.7, 23.4.

^{11}B NMR (160 MHz, $CDCl_3$): δ 23.6 (s).

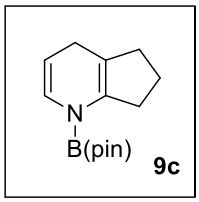
1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridin-3-yl)ethanone (9b)



3-acetylpyridine **8b** (200 mg, 1.65 mmol, 1 equiv) and precatalyst **2a** (1 mol%) were mixed in Et_2O (1 mL) at room temperature, followed by the addition of HB(pin) (0.26 mL, 1.82 mmol, 1.1 equiv). The reaction was swirled to mix components and left for 16 hours without stirring. The reaction mixture was then concentrated in vacuo to remove solvent and unreacted HB(pin). Compound **9b** (352 mg, 86% yield) was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (s, 1H), 6.19 (d, *J*= 8.0 Hz, 1H), 4.97 (dt, *J*= 7.8, 3.7 Hz, 1H), 2.97 (brs, 2H), 2.26 (s, 3H), 1.28 (s, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 140.0, 124.9, 115.3, 107.3, 84.6, 24.7, 24.6, 21.3.
^{11}B NMR (160 MHz, $CDCl_3$): δ 23.9 (s).

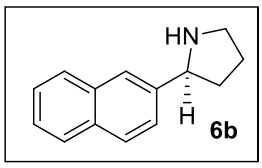
1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,5,6,7-tetrahydro-1*H*-cyclopenta[*b*]pyridine (9c)



2,3-cyclopentenopyridine **8c** (200 mg, 1.68 mmol, 1 equiv) and precatalyst **2a** (5 mol%) were mixed in Et_2O (1 mL) at room temperature, followed by the addition of TBSOTf (5 mol%). Subsequently, HB(pin) (0.27 mL, 1.85 mmol, 1.1 equiv) was added, the reaction mixture was swirled to mix components and left for 16 hours without stirring. The reaction mixture was then concentrated in vacuo to remove the volatile components. Compound **9c** (372 mg, 90% yield) was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.35 (d, *J*= 8.1 Hz, 1H), 4.69 (dt, *J*= 8.1, 3.3 Hz, 1H), 2.82 (brs, 2H), 2.60–2.56 (m, 2H), 2.13 (t, *J*= 7.1 Hz, 2H), 1.82 (quintet, *J*= 7.5 Hz, 2H), 1.21 (s, 12H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 134.8, 128.5, 112.8, 102.2, 82.9, 33.6, 32.8, 25.4, 24.6, 20.6.
^{11}B NMR (160 MHz, $CDCl_3$): δ 23.8 (s).

(*S*)-2-(naphthalen-2-yl)pyrrolidine (6b)



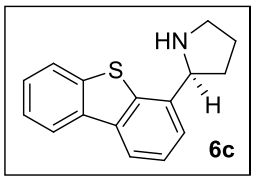
The imine **5b** (100 mg, 0.51 mmol, 1 equiv) and precatalyst **2b** (5 mol%) were mixed in THF (2 mL) at room temperature and then cooled to –35 °C for 30 minutes in the glovebox freezer. Pre-cooled HB(pin) (0.08 mL, 0.56 mmol, 1.1 equiv) was added and the reaction was swirled to mix components. The reaction was held at –35 °C for 16 hours without stirring. The reaction was then removed from the freezer and glovebox. Several drops of 1M HCl was added until the bubbling stops, then 2M NaOH is added until the reaction mixture is basic to pH paper. The reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. Purification by flash chromatography (EtOAc/MeOH/*i*$PrNH_2$ 90:9:1 v/v) provided **6b** (85 mg, 84% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.80 (m, 4H), 7.51–7.43 (m, 3H), 4.30 (t, *J*= 7.7 Hz, 1H), 3.29–3.25 (m, 1H), 3.11–3.06 (m, 1H), 2.28–2.26 (m, 1H), 2.00–1.90 (m, 3H), 1.79–1.76 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 133.6, 132.8, 128.2, 127.9, 127.7, 126.1, 125.5, 125.4, 124.7, 62.8, 47.3, 34.5, 25.8.

The enantiomeric excess was determined by HPLC on a Chiralpak AD-H column with a 95:5 Hexane:iPrOH mobile phase at a 0.9 mL/min flow rate. t_{major}= 13.980 min, t_{min}= 11.941 min. Enantiomeric ratio= 92:8.

(*S*)-2-(dibenzo[*b*,*d*]thiophen-4-yl)pyrrolidine (6c)



Method A: The imine **5c** (100 mg, 0.40 mmol, 1 equiv) and precatalyst **2b** (5 mol%) were mixed in THF (2 mL) at room temperature, followed by the addition of HB(pin) (0.06 mL, 0.44 mmol, 1.1 equiv). The reaction was swirled to mix components and was left for 16 hours without stirring. Several drops of 1M HCl was added until the bubbling stops, then 2M NaOH is added until the reaction mixture is basic to pH paper. The reaction mixture was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. Purification by flash chromatography (EtOAc/MeOH/*i*$PrNH_2$ 90:9:1 v/v) provided **6c** (25 mg, 24% yield) as a yellow oil.

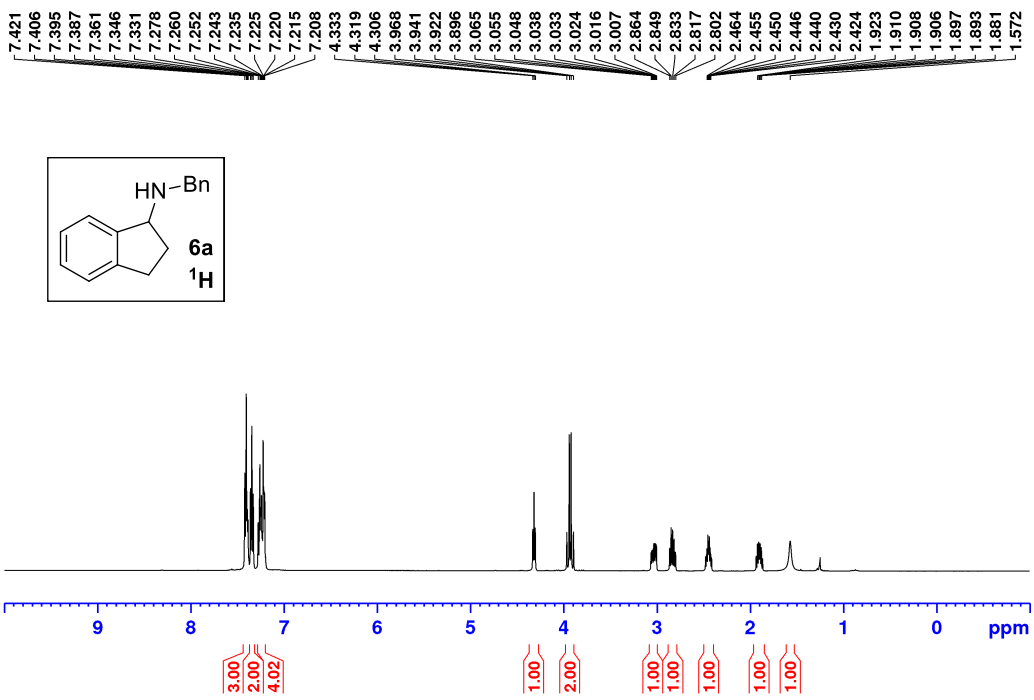
The enantiomeric excess was determined by HPLC on a Chiralpak AD-H column with a 95:5 Hexane:iPrOH mobile phase at a 0.9 mL/min flow rate. t_{major}= 10.477 min, t_{min}= 11.755 min. Enantiomeric ratio= 52:48.

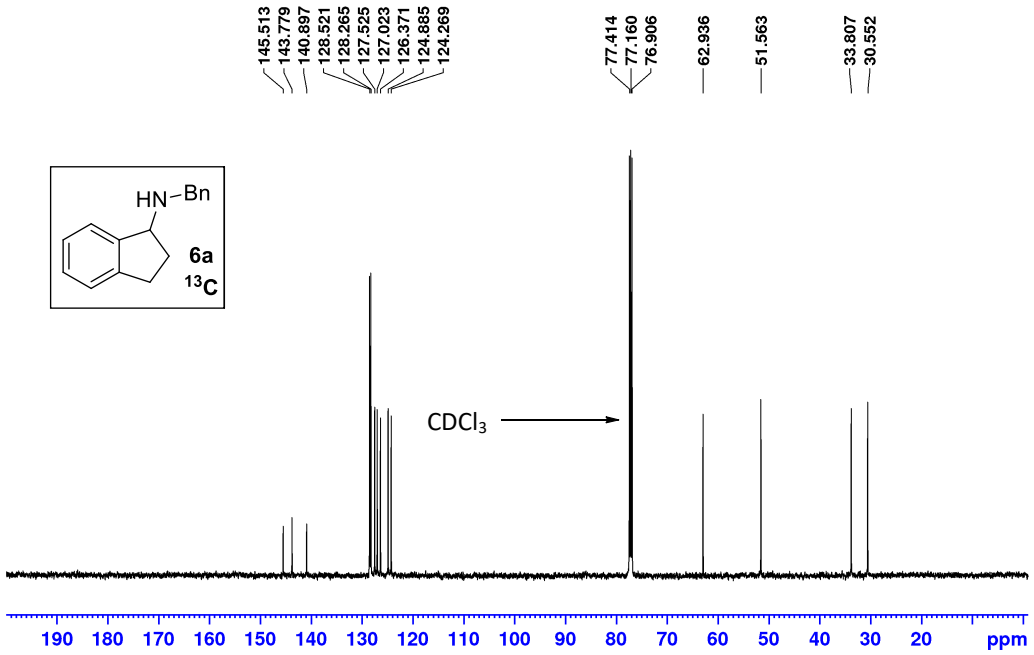
Method B: The imine **5c** and precatalyst **2b** were mixed as in Method A along with the addition of TBSOTf (5 mol%) prior to addition of HB(pin). Reaction times and work-up procedures were identical to Method A. Purification by flash chromatography (EtOAc/MeOH/*i*$PrNH_2$ 90:9:1 v/v) provided **6c** (95 mg, 94% yield) as a yellow oil.

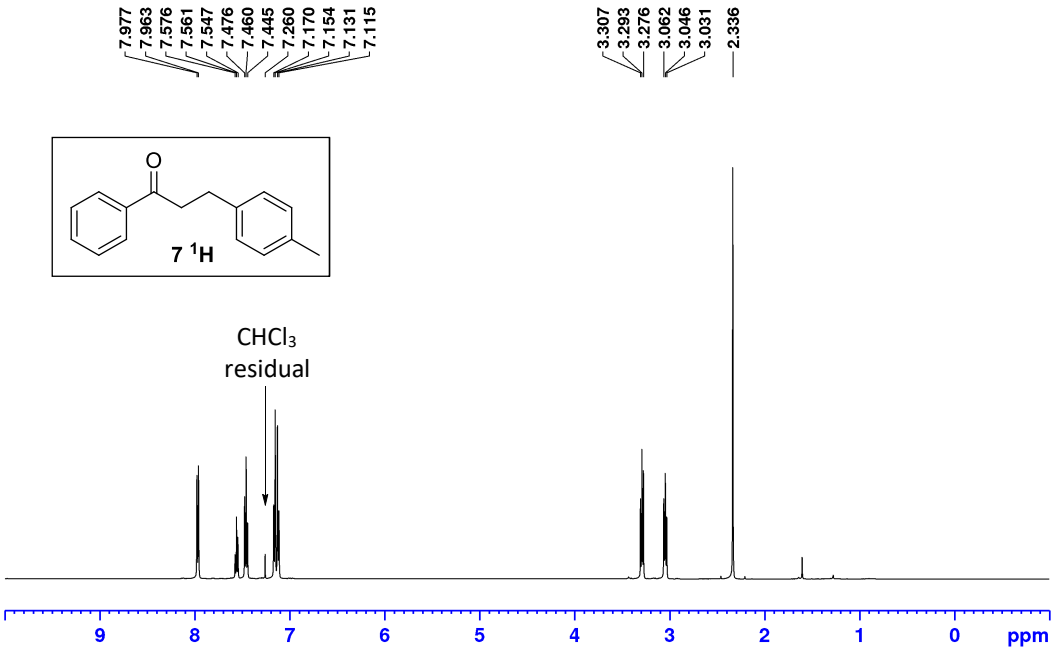
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16–8.14 (m, 1H), 8.05 (dd, *J*= 7.8, 1.0 Hz, 1H), 7.88–7.85 (m, 1H), 7.51 (d, *J*= 7.1 Hz, 1H), 7.46–7.42 (m, 3H), 4.52 (t, *J*= 7.6 Hz, 1H), 3.35–3.31 (m, 1H), 3.17–3.12 (m, 1H), 2.37–2.31 (m, 1H), 2.05–1.82 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 139.8, 137.4, 136.3, 135.8, 126.7, 124.7, 124.3, 124.0, 122.7, 121.6, 120.1, 61.9, 47.1, 32.9, 25.8.

The enantiomeric excess was determined by HPLC on a Chiralpak AD-H column with a 95:5 Hexane:iPrOH mobile phase at a 0.9 mL/min flow rate. t_{major}= 10.535 min, t_{min}= 11.723 min. Enantiomeric ratio= 93:7.

NMR Spectra of Reduction Products:



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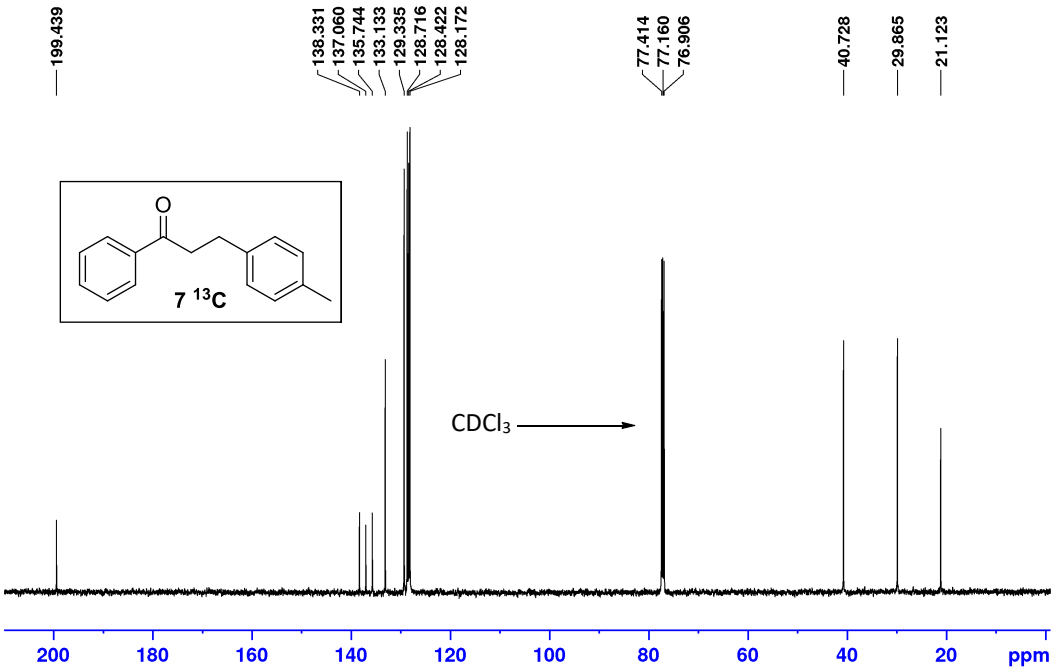
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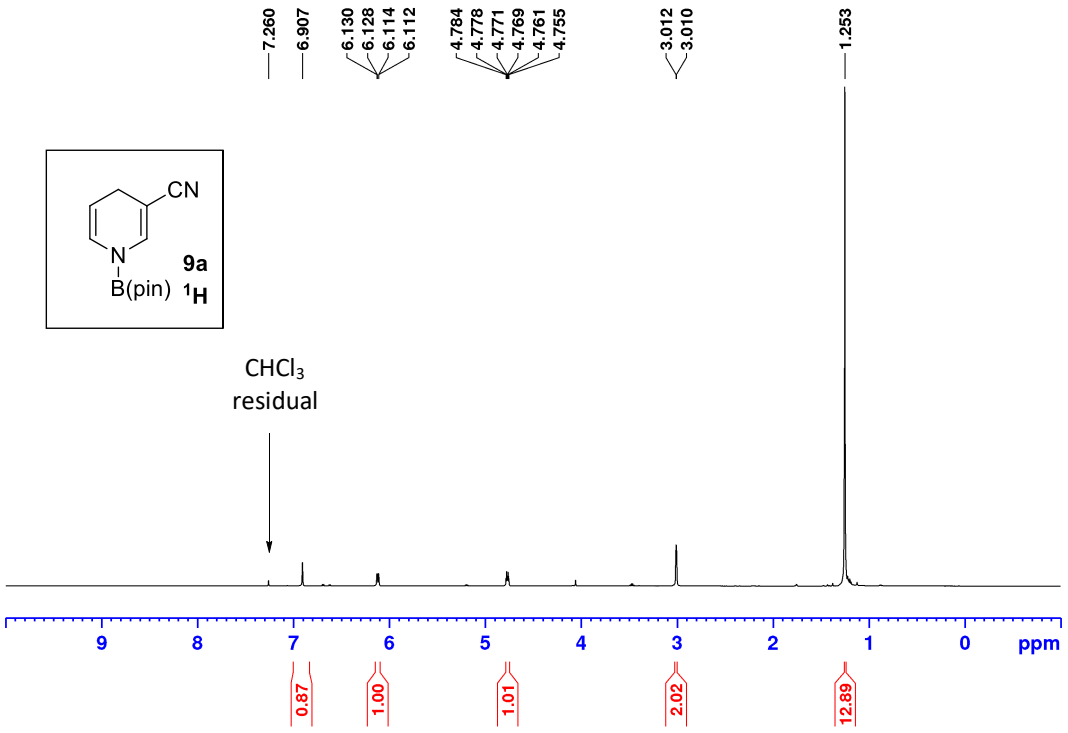
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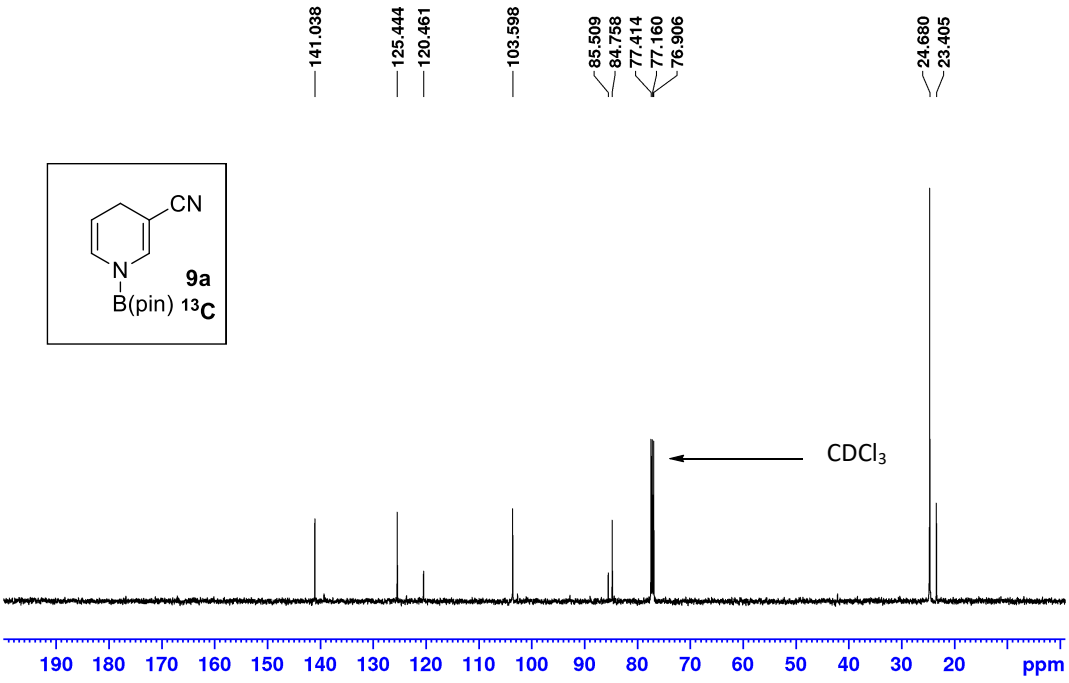
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13C
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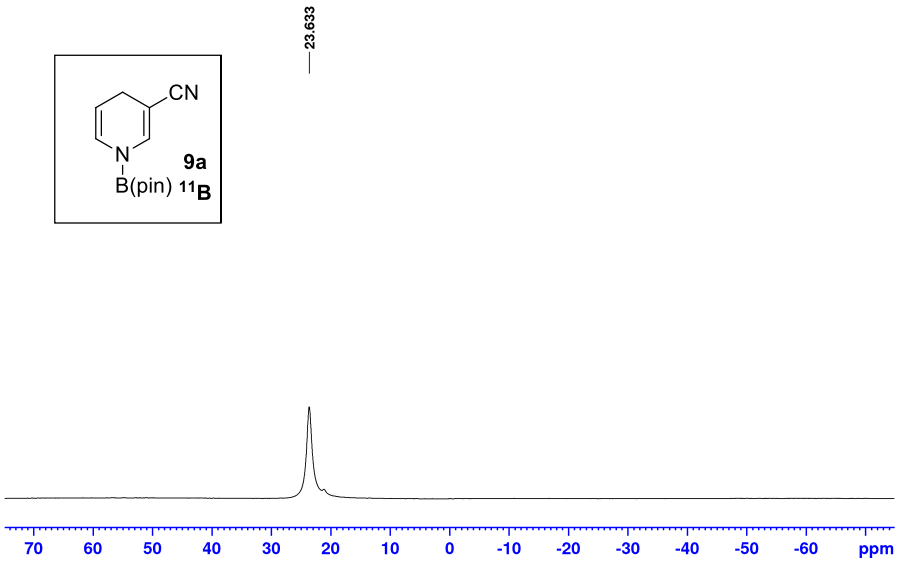
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N
B(pin)
9a
11B
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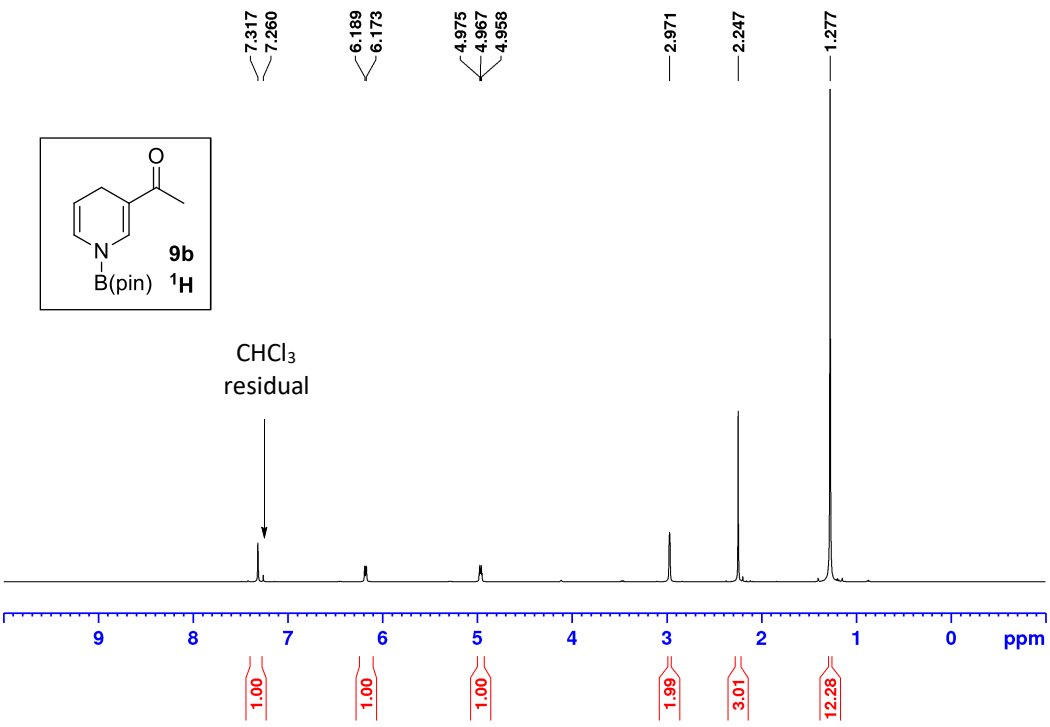
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B(pin)
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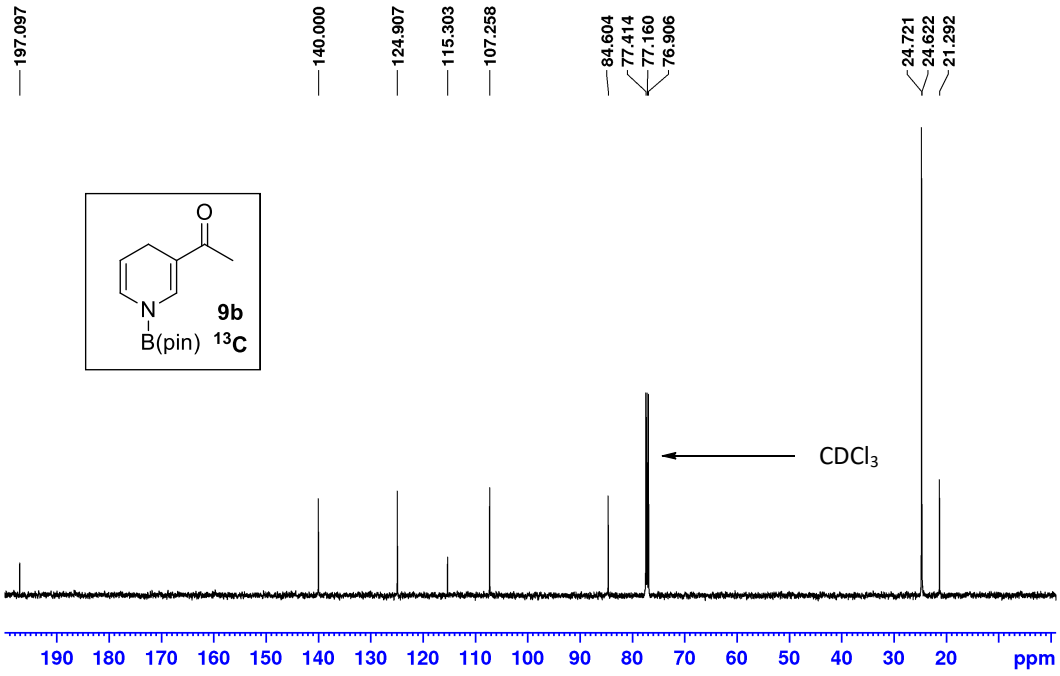
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84.604
77.414
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24.622
21.292
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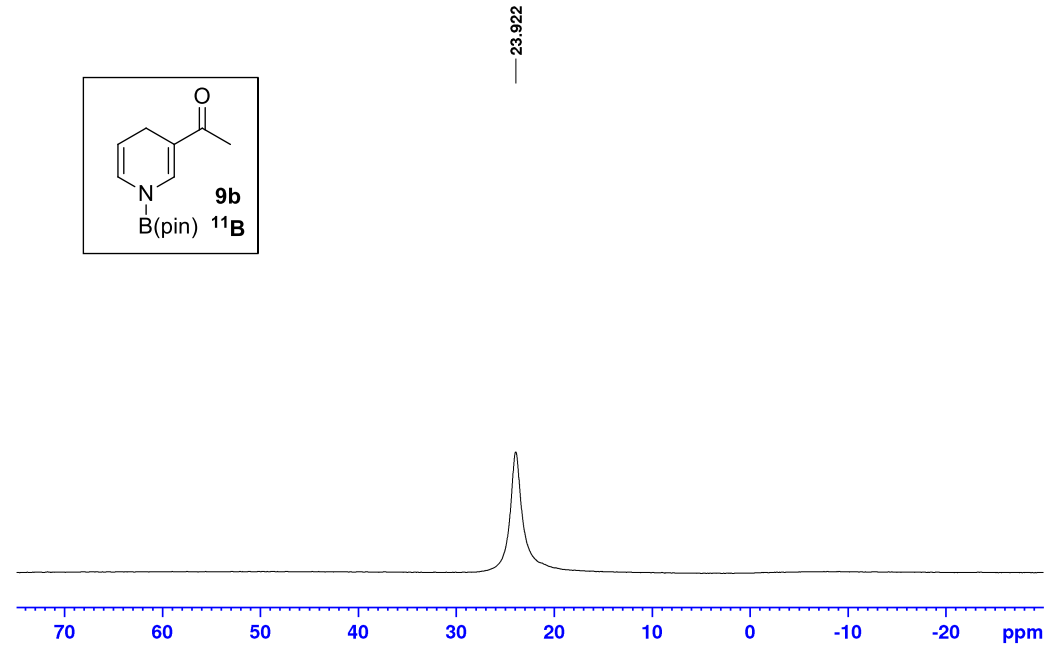
N
B(pin)
9b
13C
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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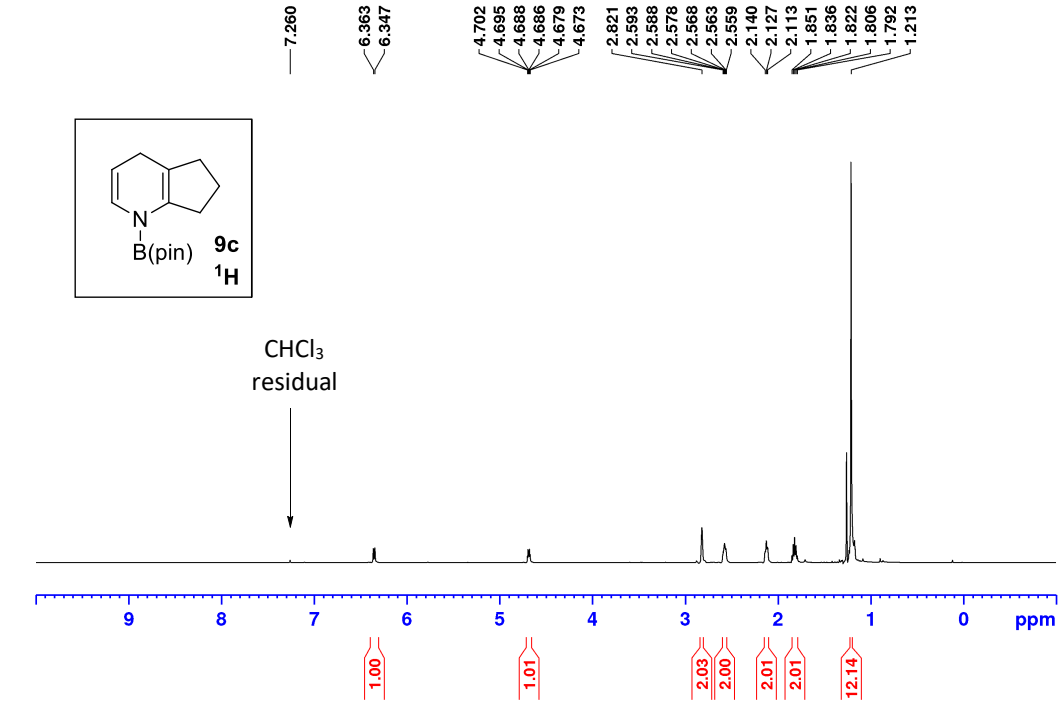
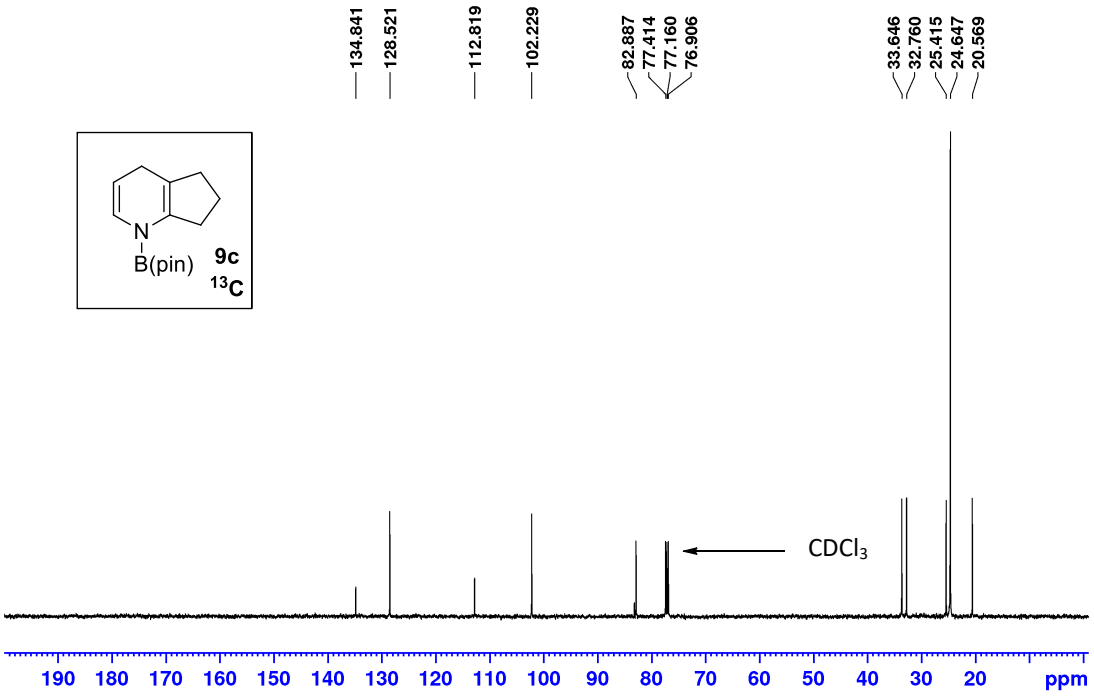
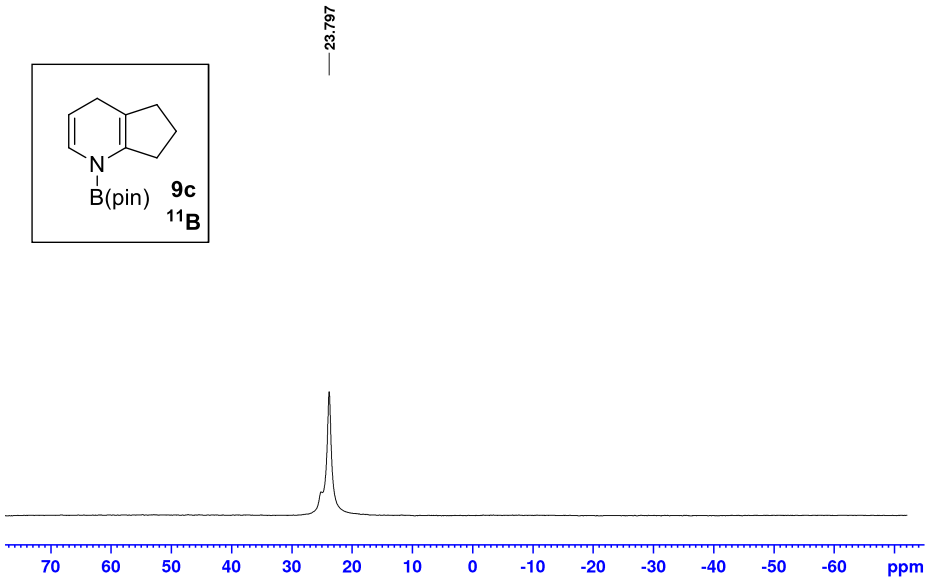
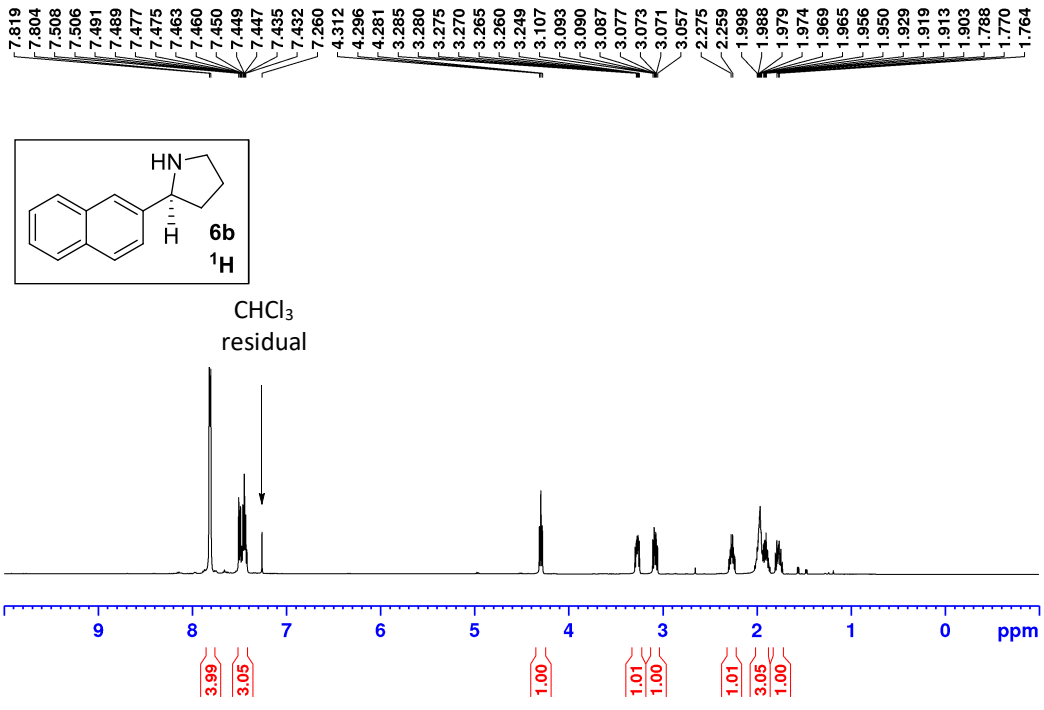
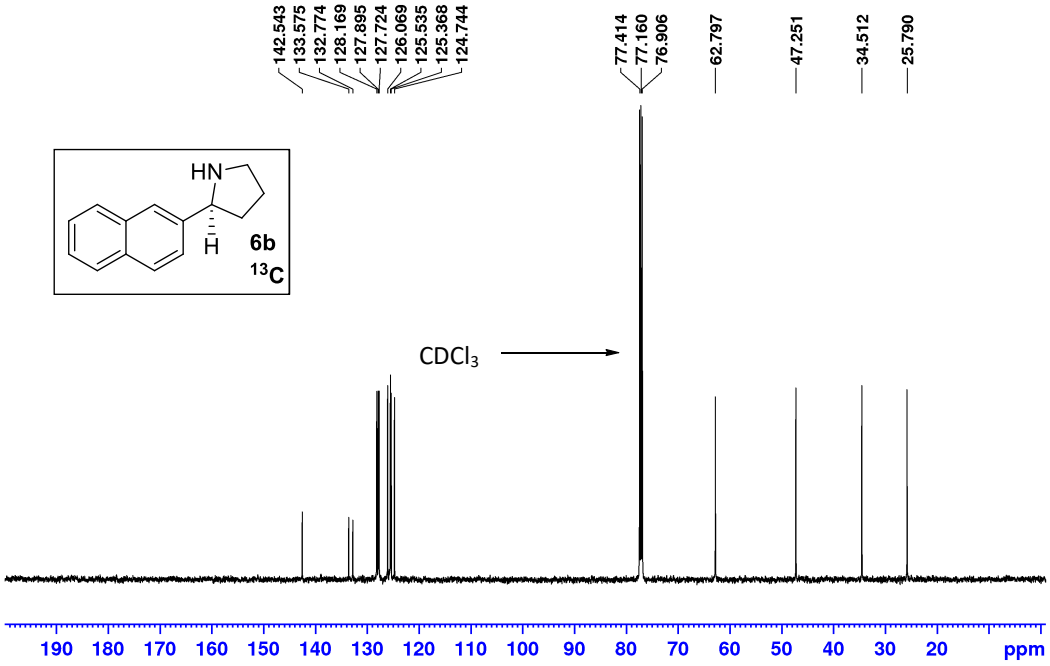
B(pin)
9b
11B
70 60 50 40 30 20 10 0 -10 -20 ppm

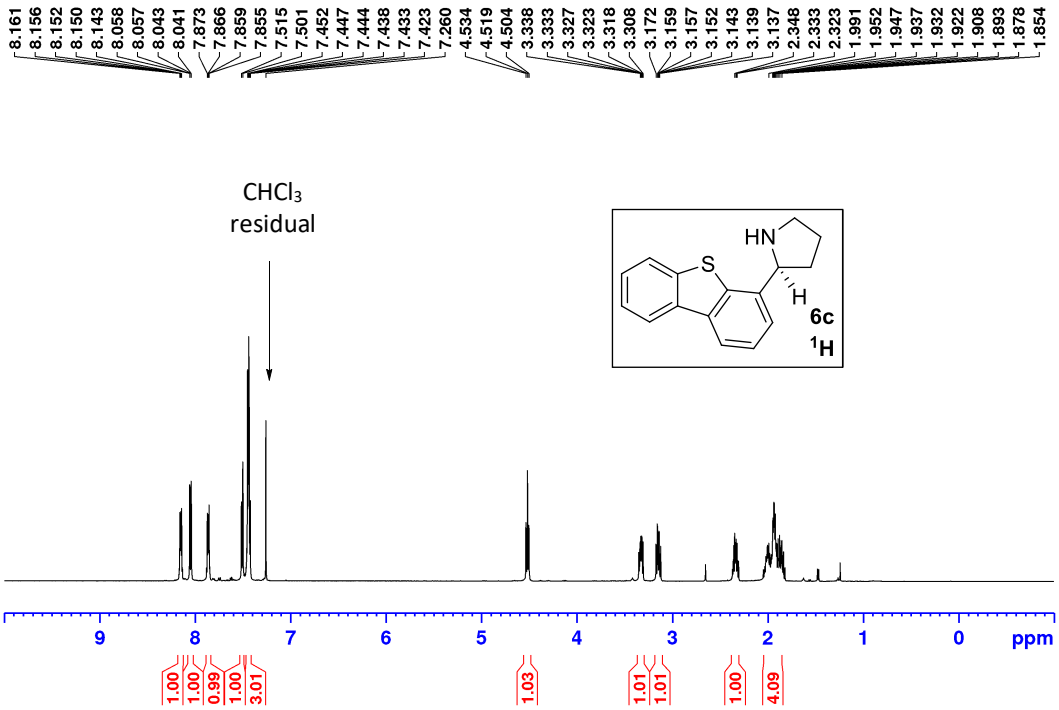

7.260
6.363
6.347
4.702
4.695
4.688
4.686
4.679
4.673
2.821
2.593
2.588
2.578
2.568
2.563
2.559
2.140
2.127
2.113
1.851
1.836
1.822
1.806
1.792
1.213
N
B(pin)
9c
1H
CHCl3
residual
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.03
2.00
2.01
2.01
12.14

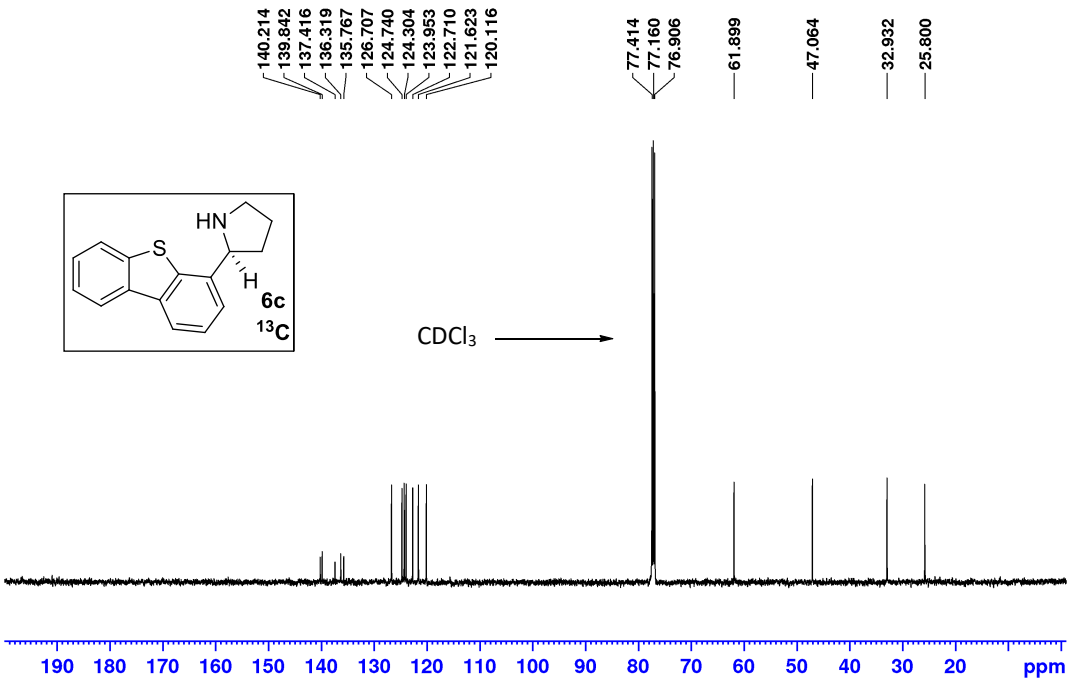

134.841
128.521
112.819
102.229
82.887
77.414
77.160
76.906
33.646
32.760
25.415
24.647
20.569
N
B(pin)
9c
13C
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


23.797
N
B(pin)
9c
11B
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm


7.819 7.804 7.508 7.506 7.491 7.489 7.477 7.475 7.463 7.460 7.450 7.449 7.447 7.435 7.432 7.260
4.312 4.296 4.281 3.285 3.280 3.275 3.270 3.265 3.260 3.249 3.107 3.093 3.090 3.087 3.077 3.073 3.071 3.057
2.275 2.259 1.998 1.988 1.979 1.974 1.969 1.965 1.956 1.950 1.929 1.919 1.913 1.903 1.788 1.770 1.764
HN
H
6b
1H
CHCl3
residual
9 8 7 6 5 4 3 2 1 0 ppm
3.99 3.05 1.00 1.01 1.00 1.01 3.05 1.00

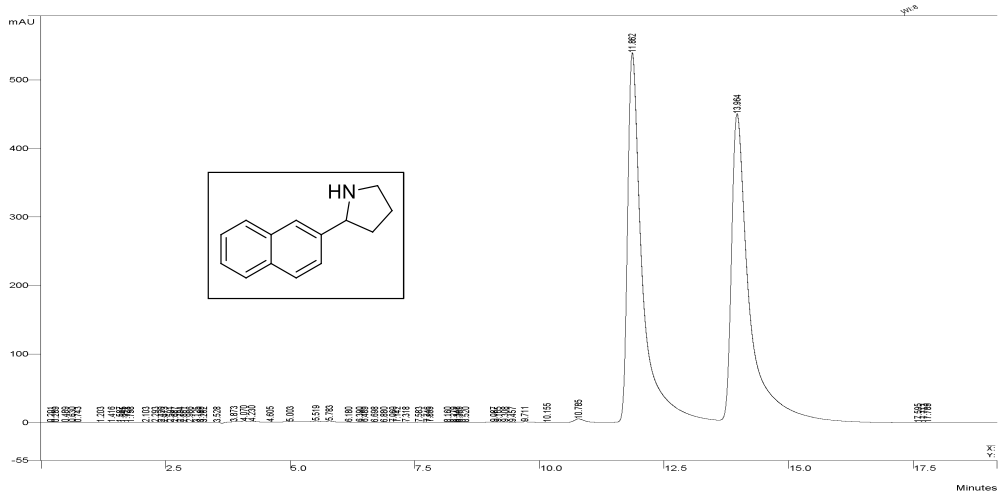

142.543
133.575
132.774
128.169
127.895
127.724
126.069
125.535
125.368
124.744
77.414
77.160
76.906
62.797
47.251
34.512
25.790
HN
H
6b
13C
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.161
8.156
8.152
8.150
8.143
8.058
8.057
8.043
8.041
7.873
7.866
7.859
7.855
7.515
7.501
7.452
7.447
7.444
7.438
7.433
7.423
7.260
4.534
4.519
4.504
3.338
3.333
3.327
3.323
3.318
3.308
3.172
3.159
3.157
3.152
3.143
3.139
3.137
2.348
2.333
2.323
1.991
1.952
1.947
1.937
1.932
1.922
1.908
1.893
1.878
1.854
CHCl3
residual
HN
S
H
6c
1H
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.00
0.99
1.00
3.01
1.03
1.01
1.01
1.00
4.09


140.214
139.842
137.416
136.319
135.767
126.707
124.740
124.304
123.953
122.710
121.623
120.116
77.414
77.160
76.906
61.899
47.064
32.932
25.800
HN
S
H
6c
13C
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

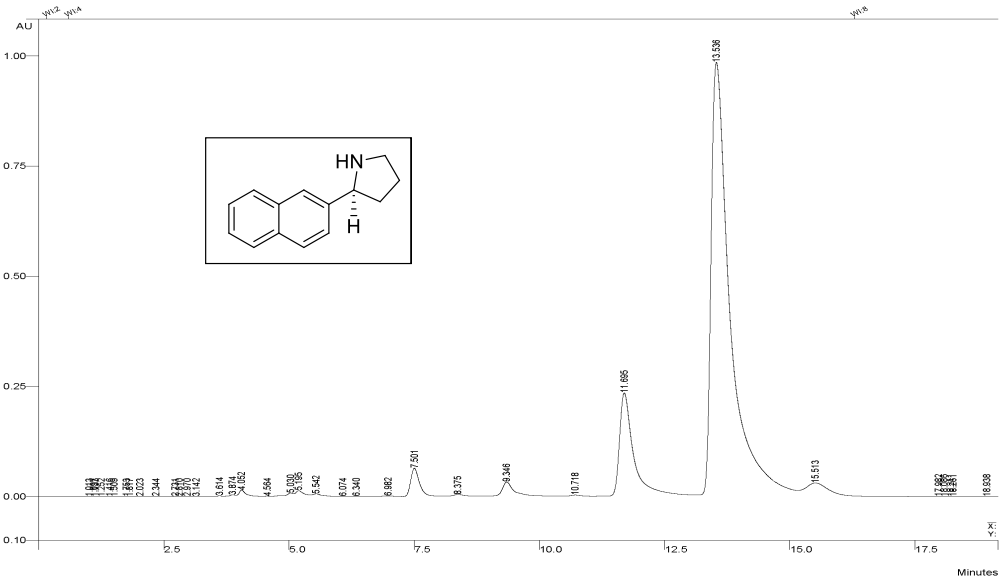
HPLC Traces of Racemates and Asymmetric Reductions:

Racemate of 6b:



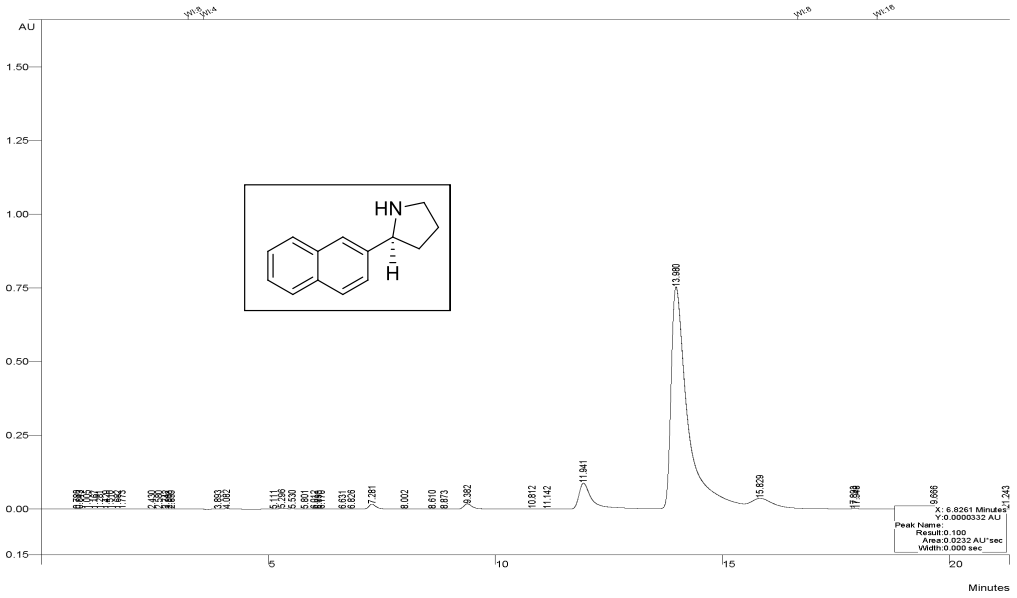
Peak Number	Retention Time	Area Number	Area Percent
1	11.862	113084120	49.7
2	13.964	114297432	50.3
Total			100

Asymmetric Product 6b: Reduced at Room Temperature



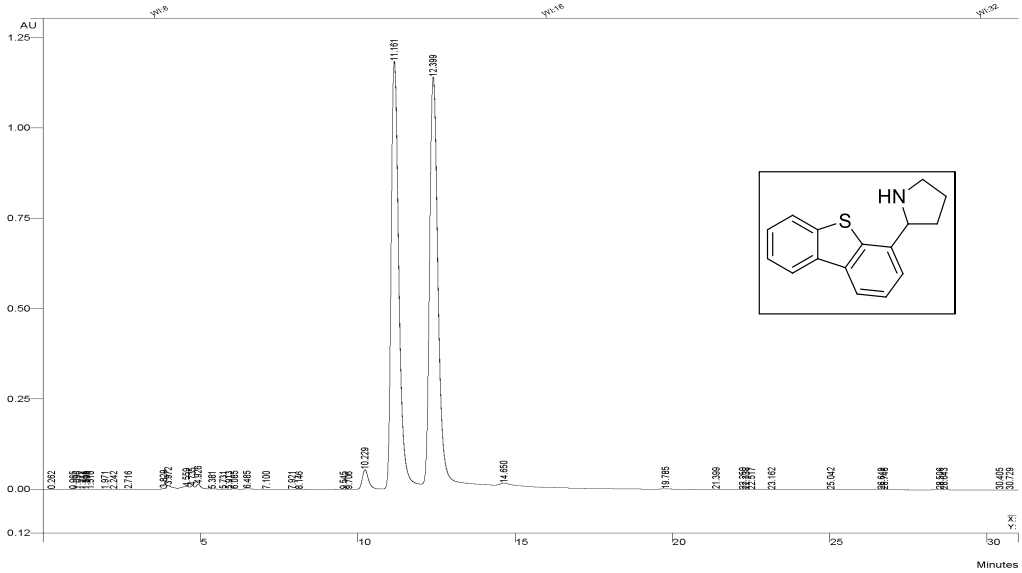
Peak Number	Retention Time	Area Number	Area Percent
1	11.695	46686236	15.0
2	13.536	265581648	85.0
Total			100

Asymmetric Product 6b: Reduced at –35 °C



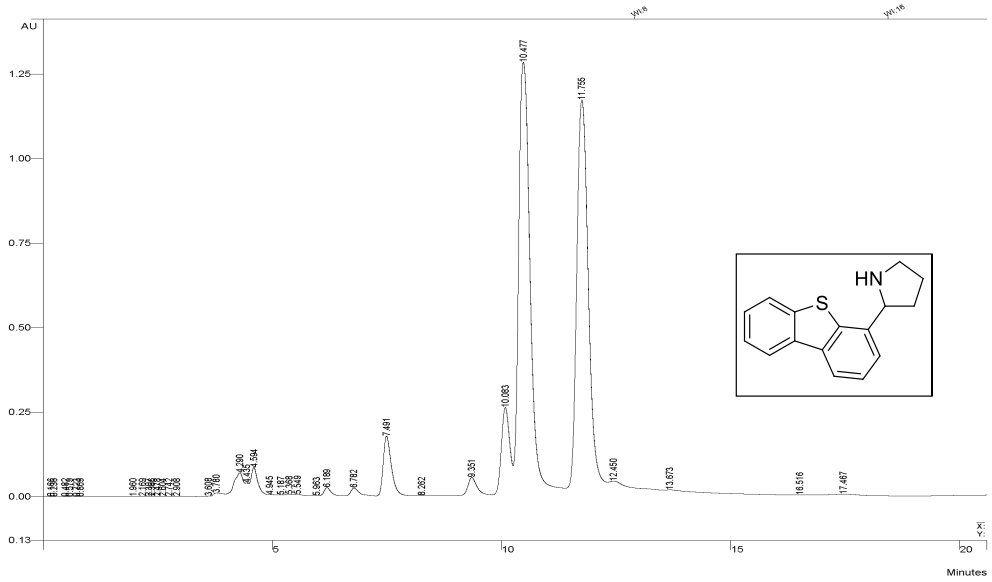
Peak Number	Retention Time	Area Number	Area Percent
1	11.941	17703020	8.4
2	13.980	198168352	91.6
Total			100

Racemate of 6c:



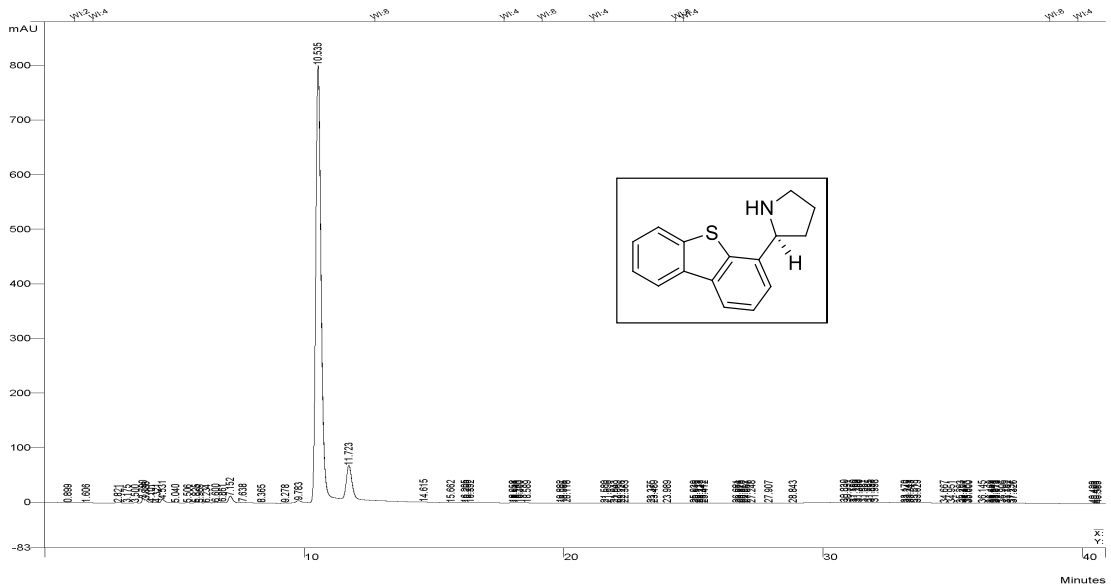
Peak Number	Retention Time	Area Number	Area Percent
1	11.161	212876592	48.5
2	12.399	226230000	51.5
Total			100

Asymmetric Product 6c: Reduced with Method A (without TBSOTf)



Peak Number	Retention Time	Area Number	Area Percent
1	10.477	219664560	51.6
2	11.755	206325264	48.4
Total			100

Asymmetric Product 6c: Reduced with Method B (with TBSOTf)



Peak Number	Retention Time	Area Number	Area Percent
1	10.535	166736448	93.3
2	11.723	11907766	6.7
Total			100

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[6] SAINT (Bruker, 2016) Bruker AXS Inc., Madison, Wisconsin, USA.
[7] SADABS (Bruker, 2016) Bruker AXS Inc., Madison, Wisconsin, USA.
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