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Supporting Information

for

P-Stereogenic Bisphosphines with a Hydrazine Backbone. From N–N Atropoisomerism to Double Nitrogen Inversion

Contribution by

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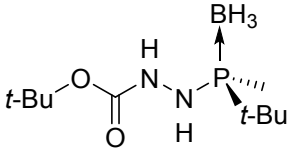
General Methods. All reactions were carried out under nitrogen atmosphere in dried solvents. THF, Et_2O and CH_2Cl_2 were dried in a PureSolv purification system from Innovative Technology, Inc. Toluene and deuterated solvents were purchased from Aldrich and used without further purification. Thin layer chromatography was carried out using TLC-aluminum sheets with silica gel (Merk 60 F_{254}). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 35-70 μm). NMR spectra were recorded at 23°C on a Varian Mercury 400 and on a Varian Unity 300 spectrometres. ^{1}H NMR and ^{13}C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. ^{31}P NMR spectra were referenced to phosphoric acid. Signal multiplicities in the ^{13}C spectra have been assigned by HSQC experiments. Optical rotations were recorded on a Perkin Elmer polarimeter at the sodium D line at room temperature (concentration in g/mL). Melting points were determined using a Büchi melting point apparatus and were not corrected. IR spectra were recorded in a FT-IR apparatus. HRMS were recorded using an electrospray ionization spectrometer. HPLC chromatography was performed on an Agilent Technologies Series 1100 chromatograph with UV detector. NaH as dispersion oil (60%w/w), DABCO, anhydrous triethylamine, pyrrolidine, methyl iodide, allyl bromide and 3-bromo-2-bromomethyl-1-propene were purchased from Aldrich and used without further purification. $[Rh(COD)_2][BF_4]$ and $NaBAr^F_4$ were purchased from STREM Chemicals and used without further purification. Phosphinous acid **1**[1] and $[Rh(COD)_2][BAr^F_4]$[2] prepared following the literature procedure.

Synthesis of new compounds

(*R*)-*tert*-butyl-2-(*tert*-butyl(methyl)phosphino)hydrazinecarboxylate-borane (2).



To a Schlenk tube containing 365 mg of methanesulfonic anhydride (2.10 mmol, 1.2 eq), a solution of 233 mg of **1** (1.75 mmol, 1.0 eq) in dichloromethane (10mL) was cannulated and the mixture was cooled at -20 ºC. 878 μL of triethylamine (6.30mmol, 3.0 eq) were added dropwise over 10 minutes and the mixture was allowed to react for 1 hour at -20 ºC. Then, a dichloromethane solution of 833 mg of *tert*-butyl carbazate (6.30 mmol, 3.0 eq) was cannulated and the mixture was stirred at -20 ºC overnight. After that time, the solution was allowed to warm at room

temperature, the organic phase was washed with 3x20 mL of HCl (aq) 1.0 M solution and 20 mL of brine, dried over anhydrous $MgSO_4$, filtrated and the solvent was removed under reduced pressure. The resulting solid was dissolved in 10 mL of dichloromethane and washed with 4x10 mL of NaOH (aq) 1.0 M solution, dried over anhydrous $MgSO_4$, filtrated and the solvent was removed under reduced pressure. Finally the product was eluted through a SiO_2 flash column with hexane:AcOEt (8:2) as eluting phase to yield 253 mg of a white solid. Yield: 58%.

TLC (hexane:AcOEt 8:2): Rf = 0.50

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.10 (brs, 1H, CO-NH), 4.19 (brd, $^2J_{PH}$ = 19.3 Hz, 1H, PNH),1.45 (s, 9H, $(CH_3)_3CO$), 1.45 (d, $^2J_{PH}$ = 8.9 Hz, 3H, PCH_3), 1.16 (d, $^3J_{PH}$ = 14.2 Hz, 9H, $PC(CH_3)_3$) and 0.41 ppm (q, $^1J_{BH}$ = 84.0 Hz, 3H, BH_3).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 156.8 (s, C=O), 81.5 (s, CO-NH), 30.8 (d, $^1J_{PC}$ = 39.0 Hz, $PC(CH_3)_3$), 28.2 (s, $(CH_3)_3CO$), 24.8 (d, $^2J_{PC}$ = 2.8 Hz, $PC(CH_3)_3$) and 6.5 ppm (d, $^1J_{PC}$ = 6.5 Hz, PCH_3).

^{31}P-NMR (202 MHz, $CDCl_3$) δ 81.2 ppm (brs).

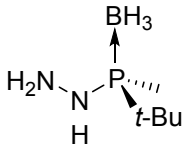
IR film, cm^{-1}ν: 3000.4, 2971.9, 2388.5, 1708.7, 1513.1, 1160.9.

MS (ESI, high res., positive mode). Calcd. for $[M+NH_4]^+$ 266.2163 , found 266.2169 . Calcd. for $[2M+NH_4]^+$ 514.3988, found 514.4003 . Calcd. for $[2M+Na]^+$ 519.3548 found, 519.3558. Calcd. for $[2M+K]^+$ 535.3287 found 535.3301.

$[\alpha]_D$ = +19.0º (1 g/100mL, $CHCl_3$).

MP (ºC) = 108-110.

(*R*)-(*tert*-butyl(methyl)phosphanyl)hydrazine-borane (3)



In a Schlenk, 960 mg of **2** (3.87 mmol, 1.0 eq) were dissolved in 19 mL of a 1.25 M anhydrous solution of HCl in methanol. The mixture was stirred overnight at room temperature and NaOH (aq) 1.0 M solution was added until pH = 10. The solvent was evaporated under reduced pressure and the aqueous phase was extracted 4x12 mL of dichloromethane. The combined organic phase was washed with 20 mL of brine, dried over $MgSO_4$, filtrated and the solvent was removed under

reduced pressure to yield 520 mg of crude. The crude was eluted through a SiO_2 flash column with hexane:AcOEt (8:2) to yield 413 mg of a white pure product. Yield: 72%.

TLC (hexane:AcOEt 8:2): Rf = 0.69

^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.55 (brd, $^2J_{PH}$ = 22.4 Hz, 1H, PNH), 3.37 (brs, 2H, NH_2), 1.40 (d, $^2J_{PH}$ = 8.9 Hz, 3H, PCH_3), 1.17 (d, $^3J_{PH}$ = 14.1 Hz, 9H, $PC(CH_3)_3$) and 0.38 ppm (qd, $^1J_{BH}$ = 96.0 Hz, $^2J_{PH}$ = 16.0 Hz, 3H, BH_3).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 31.1 (d, $^1J_{PC}$ = 39.0 Hz, P*C*$(CH_3)_3$), 25.2 (d, $^2J_{PC}$ = 2.7 Hz, $PC(CH_3)_3$) and 6.0 ppm (d, $^1J_{PC}$ = 39.9 Hz, PCH_3).

^{31}P-NMR (202 MHz, $CDCl_3$) δ 75.7 ppm (q, $^1J_{BC}$ = 66.7 Hz).

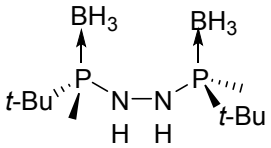
IR film, cm^{-1}ν: 3348, 3209, 2968, 2867, 2380, 2341, 1069, 889.

MS (ESI, high res., positive mode). Calcd. for $[M-H]^+$ 147.1228, found 147.1219. Calcd. for $[2M+H]^+$ 297.2674, found 297.2680.

$[\alpha]_D$ = +1.0º (1 g/100mL, $CHCl_3$).

MP (ºC) = 129-130.

1,2-bis((*R*)-*tert*-butyl(methyl)phosphanyl)hydrazine-bisborane (4)



Stepwise synthesis

In a Schlenk tube, 1.030 g of methanesulfonic anhydride (5.92 mmol, 1.2 eq) were dissolved in 15 mL of dichloromethane. A solution of 660 mg of **1** (4.93 mmol, 1.0 eq) in dichloromethane was cannulated over the methanesulfonic anhydride solution. The mixture was cooled at -20 ºC and 2.06 mL of triethylamine (14.79 mmol, 3.0 eq) were added dropwise during 10 min. The mixture was allowed to react for 1 hour at -20 ºC, and then, a solution of 413 mg of **3** (2.79 mmol, 0.57 eq) was cannulated. The mixture was stirred overnight at -20 ºC. The organic phase was washed with 3x15 mL of HCl (aq) 1.0 M solution, 10 mL of NaOH (aq) 1.0 M solution and 15 mL of brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude was purified by elution through a SiO_2 flash column with DCM:TEA (97.5:2.5) to yield 410 mg of a crystalline colorless solid. Yield: 56%.

One-Pot synthesis

In a Schlenk tube, 1.170 g of methanesulfonic anhydride 6.72 mmol, 1.2 eq) were dissolved in 20 mL of dichloromethane. A solution of 750 mg of **1** (5.60 mmol, 1.0 eq) in dichloromethane was cannulated over the methanesulfonic anhydride solution. The mixture was cooled at -20 ºC and 2.33 mL of triethylamine (16.75 mmol, 3.0 eq) were added dropwise during 10 min. The mixture was allowed to react for 1 hour at -20 ºC, and then, 2.25 mL of 1.0M solution of hydrazine in THF (2.25 mmol. 0.4 eq) were added dropwise. The resulting mixture was stirred for 60 hours at -20 ºC. The organic phase was washed with 2x25 mL of brine, dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The resulting of crude were purified by elution through SiO_2 flash column with hexane:AcOEt (95:5) to (80:20) as eluting phase to yield 488 mg of pure crystalline colorless crystalline solid. Yield: 82%.

TLC (DCM:MeOH 95:5): Rf = 0.49

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.77 (dbr, $^2J_{PH}$ =18.7 Hz, 2H, NH-NH), 1.43 (d, $^2J_{PH}$ = 8.8 Hz, 6H, PCH_3), 1.20 (d, $^3J_{PH}$ = 14.0 Hz, 18H, $PC(CH_3)_3$) and 0.85-0.04 ppm (m, 6H, BH_3).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 31.1 (d, $^1J_{PC}$ = 33.8 Hz, P*C*$(CH_3)_3$), 25.4 (d, ^2J = 2.8 Hz, PC(*C*$H_3)_3$) and 6.6 ppm (d, $^1J_{PC}$ = 39.0 Hz, PCH3).

^{31}P-NMR (202 MHz, $CDCl_3$): δ 81.7 ppm (q, $^1J_{PB}$ = 92.9 Hz).

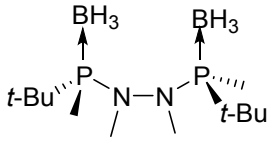
IR film, cm-1 ν: 3302, 2959, 2377, 2343, 1462, 129, 1069.

MS (ESI, high res., positive mode). Calcd. for $[M-H]^+$ 263.2143, found 263.2148. Calcd. for $[2M+H]^+$ 529.4526, found 529.4539. Calcd. for $[M-NH]^+$ 282.2565, found 282.2569.

$[\alpha]_D$ = -59.7 º (1 g/100mL, $CHCl_3$).

MP (ºC) = 159-160.

1,2-bis((*R*)-*tert*-butyl(methyl)phosphanyl)-1,2-dimethylhydrazinebisborane (5)



A solution of 75 mg of 1,2-bis((*R*)-*tert*-butyl(methyl)phosphanyl)-1-methylhydrazine-bisborane (0.27 mmol, 1.0 eq) in 2 mL of THF was cannulated over a suspension of 44 mg of 60% NaH (1.08 mmol, 4.0 eq) in THF. The mixture was stirred at 55 ºC for 45 min. Then, 134 µL of MeI (2.16 mmol, 8.0 eq) were added and the resulting mixture was stirred at 55 ºC for 4h. The reaction

was followed by silica TLC (hexane:AcOEt 8:2) until the monomethylated product disappeared. Finally, the mixture was allowed to cool at room temperature and 5 mL of Et_2O were added. The excess of hydride was destroyed by a very slow addition of 4 mL of water. The organic phase was washed with 2x5 mL of brine, dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield 75 mg of a pure colorless crystalline solid. During the TLC analysis two different spots were observed corresponding to two different atropoisomers undergoing rapid exchange. Yield: 95%.

TLC (hexane:AcOEt 8:2): Rf = 0.3 and 0.5

^{1}H-NMR (500 MHz, $CDCl_3$): Atropoisomer-(R_PR_PSa) δ 2.93 (dd, $^3J_{PH}$ = 4.0 and $^4J_{PH}$ = 0.9 Hz, 6H, NCH_3), 1.55 (d, $^2J_{PH}$ = 8.7 Hz, 6H, PCH_3), 1.19 (d, $^3J_{PH}$ = 13.7 Hz, 18H, $PC(CH_3)_3$) and 0.95-0.25 ppm (m, 6H, BH_3). Atropoisomer-(R_PR_PRa) δ 2.90 (d, $^3J_{PH}$ = 5.3 Hz, 6H, NCH_3), 1.41 (d, $^2J_{PH}$ = 7.7 Hz, 6H, PCH_3), 1.23 (d, $^3J_{PH}$ = 14.2 Hz, 18H, $PC(CH_3)_3$) and 0.95-0.25 ppm (m, 6H, BH_3).

^{13}C-NMR (101 MHz, $CDCl_3$) Atropoisomer-(R_PR_PSa) δ 39.3 (dd, $^2J_{PC}$ = 5 and $^3J_{PC}$ = 1.2 Hz, NCH_3), 33.2 (d, $^1J_{PC}$ = 33.3 Hz, P*C*$(CH_3)_3$), 26.8 (d, $^2J_{PC}$ = 3.1 Hz, PC(*C*$H_3)_3$) and 7.7 ppm (d, $^1J_{PC}$ = 38.5 Hz, PCH_3). Atropoisomer-(R_PR_PRa) δ 37.3 (d, $^2J_{PC}$ = 1.9 Hz, NCH_3), 33.7 (d, $^1J_{PC}$ = 37.3 Hz, P*C*$(CH_3)_3$), 25.8 (d, $^2J_{PC}$ = 2.6 Hz, PC(*C*$H_3)_3$) and 8.67 ppm (d, $^1J_{PC}$ =36.0 Hz, PCH_3).

^{31}P-NMR (202 MHz, CDCl3) δ 94.2 (q, $^1J_{PB}$ = 60.6 Hz) and 92.8ppm (q, $^1J_{PB}$ = 72.7 Hz).

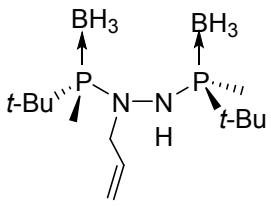
IR film, cm-1ν: 2958, 2870, 2390, 1294, 1072, 1054, 895.

MS (ESI, high res., positive mode). Calcd. for [M-H]+ 291.2456, found 291.2459.
Calcd. for [M+NH]+ 310.2878, found 310.2882 Calcd. for [2M+NH]+ 602.5418,
found 602.5423.

$[\alpha]_D$ = +34.1 º (1 g/100mL, CHCl3).

MP (ºC) = 171-172.

1,2-bis((R)-tert-butyl(methyl)phosphanyl)-1-allylhydrazine-bisborane (6)



A solution of 70 mg of **5** (0.27 mmol, 1.0 eq) in 2 mL of THF was cannulated over a suspension of 44 mg of 60% NaH (1.08 mmol, 4.0 eq) in THF. The mixture was stirred at 55 ºC for 30 min.

70 µL of allyl bromide (0.8 mmol, 3.0 eq) were added and the mixture was stirred for 3h. After that time, the reaction mixture was allowed to cool at room temperature and 5 mL of Et_2O were added. The excess of hydride was destroyed by a slow addition of 4 mL of water. The organic phase was washed with 2x5 mL of brine, dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield 40 mg of pure white solid. Yield: 49%.

TLC (hexane:AcOEt 8:2): Rf = 0.30

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.89 (dddd, $^2J_{HH}$ = 17.2, 10.3, 7.8, 5.2 Hz, 1H, CH), 5.30 (m, , 2H, CH_2), 4.28 (ddd, $^2J_{HH}$ = 16.5, 6.6, 5.2 Hz, 1H, NCH_2), 3.81 (ddd, $^2J_{HH}$ = 17.2, 11.3, 8.2 Hz, 1H, NCH_2), 3.75 (d, $^2J_{PH}$ = 5.0 Hz, 1H, NH), 1.57 (d, $^2J_{PH}$ = 8.7 Hz, 3H, PCH_3), 1.44 (d, $^2J_{PH}$ = 8.4 Hz, 3H, PCH_3), 1.22 (d, $^3J_{PH}$ = 13.8 Hz, 9H, $PC(CH_3)_3$), 1.18 (d, $^3J_{PH}$ = 13.8 Hz, 9H, $PC(CH_3)_3$), and 0.95-0.25 ppm (m, 6H, BH3).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 133.9 (s, CH), 120.2 (s, CH_2), 56.5 (d, $^2J_{PC}$ = 12.2 Hz, NCH_2), 33.1 (d, $^1J_{PC}$ = 33.1 Hz, P*C*$(CH_3)_3$), 31.0 (d, $^1J_{PC}$ = 41.8 Hz, P*C*$(CH_3)_3$), 26.6 (d, $^2J_{PC}$ = 2.9 Hz, PC(*C*$H_3)_3$), 24.9 (d, $^2J_{PC}$ = 2.4 Hz, PC(*C*$H_3)_3$), 12.7 (d, $^1J_{PC}$ = 27.8 Hz, PCH_3) and 8.6 ppm (d, $^1J_{PC}$ = 43.6 Hz, PCH_3).

31P-NMR (202 MHz, $CDCl_3$): δ 94.6 (q, $^1J_{PB}$ = 131.6 Hz) and 81.1 ppm (q, $^1J_{PB}$ = 122.7 Hz).

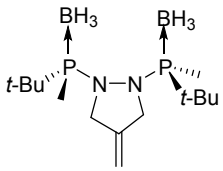
IR film, cm-1ν: 3256, 2979, 2930, 2904, 2868, 2382, 2350, 1474, 1416, 1071, 884.

MS (ESI, high res., positive mode). Calcd. for [M+H]+ 305.2500, found 305.25011.

$[\alpha]_D$ = -33.5 º (1 g/100mL, CHCl3).

MP (ºC) = 116-117.

1,2-bis(tert-butyl(methyl)phosphanyl)-4-methylenepyrazolidine (7)



A solution of 100 mg of **4** (0.38 mmol, 1.0 eq) in 15 mL of THF was cannulated over a suspension of 91 mg of 60% NaH (2.28 mmol, 6.0 eq) in THF. The mixture was stirred at 55 ºC for 1 h. Then, 130 µL (1.14 mmol, 3.0 eq) of 3-bromo-2-(bromomethyl)prop-1-ene were added and the resulting mixture was stirred at 55 ºC for 4h. The reaction was followed by silica TLC (hexane:AcOEt 8:2) until the substrate disappeared. Finally, the mixture was allowed to cool at room temperature and 5 mL of Et_2O were added. The excess of hydride was destroyed by a very slow addition of 4 mL

of water. The organic phase was washed with 2x5 mL of brine, dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude was crystallized in ether at -25ºC to yield 92 mg of a pure colorless crystalline solid (**8**-$R_PR_NR_NR_P$). During the TLC analysis two different spots were observed corresponding to two different N-inversion isomers undergoing rapid exchange. Yield: 77%.

TLC (hexane:AcOEt 8:2): Rf = 0.4 and 0.6

^{1}H-NMR (400 MHz, $CDCl_3$): Isomer-($R_PR_NR_NR_P$) δ 5.14 (quint., $^4J_{HH}$ = 2.3 Hz, 2H, CH_2), 3.96 (m, 2H, NCH_2), 3.86 (m, 2H, NCH_2), 1.42 (d, $^2J_{PH}$ = 7.7 Hz, 6H, PCH_3), 1.22 (d, $^3J_{PH}$ = 13.8 Hz, 18H, $PC(CH_3)_3$) and 0.88-0.22 ppm (m, 6H, BH_3). Isomer-($R_PS_NS_NR_P$) δ 5.12 (quint. $^4J_{HH}$ = 2.3 Hz, 2H, CH_2), 3.96 (m, 2H, NCH_2), 3.92 (m, 2H, NCH_2), 1.51 (d, $^2J_{PH}$ = 8.6 Hz, 6H, PCH_3), 1.21 (d, $^3J_{PH}$ = 13.3 Hz, 18H, $PC(CH_3)_3$) and 0.80-0.22 ppm (m, 6H, BH_3).

^{13}C-NMR (101 MHz, $CDCl_3$): Isomer-($R_PR_NR_NR_P$) δ 147.9 (s, *C*CH2), 105.3 (s, C*C*H_2), 56.2 (s, NCH_2), 32.6 (d, $^1J_{PC}$ = 35.3 Hz, P*C*$(CH_3)_3$), 25.6 (s, PC(*C*$H_3)_3$) and 8.5 ppm (d, $^1J_{PC}$ = 33.6 Hz, PCH_3). Isomer-($R_PS_NS_NR_P$) δ 147.8 (s, *C*CH2), 104.8 (s, C*C*H_2), 56.1 (d, $^2J_{PC}$ = 6.1 Hz, NCH_2), 32.3 (d, $^1J_{PC}$ = 30.1 Hz,P *C*$(CH_3)_3$), 25.9 (d, $^2J_{PC}$ = 2.3 Hz, PC(*C*$H_3)_3$) and 8.3 ppm (d, $^1J_{PC}$ = 33.6 Hz, PCH_3).

^{31}P-NMR (202 MHz, $CDCl_3$): Isomer-($R_PR_NR_NR_P$) δ 95.4 ppm (br q, $^1J_{PB}$ = 83.8 Hz). Isomer-($R_PS_NS_NR_P$) δ 101.7 ppm (br q, $^1J_{PB}$ = 70.9 Hz).

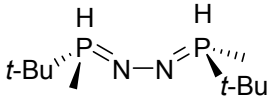
IR film, cm-1ν: 2950, 2927, 2870, 2378, 1470, 1394, 1293, 1069, 1054, 886.

MS ESI (high res., positive mode). Calcd. for [M-H]- 315.246, found 315.246. Calcd. for [M+Na]+ 339.244, found 339.244.

$[\alpha]_D$ = +6.5 º (1 g/100mL, $CHCl_3$).

MP (ºC) = 186-187.

1,2-bis((R)-tert-butyl(methyl)phosphino)hydrazine



In a Schlenk flask, 75 mg of **4** (0.28 mmol, 1.0 eq) were dissolved with 128 mg of DABCO (1.14 mmol, 4.0 eq) in 2 mL of toluene (or were dissolved in 2 mL of anhydrous pyrrolidine). The mixture was stirred for 6 h at 90 ºC. The solvent was removed under reduced pressure and the reaction crude was eluted with two eluting phases: hexane:AcOEt (75:25) and DCM:MeOH

(90:10) to yield 100 mg of a mixture DABCO·BH_3 (or pyrrolidine·BH_3) and the product in a (1:1) molar proportion.

TLC (hexane:AcOEt 8:2) Rf ~ 0.05

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (dq, $^1J_{PH}$ = 445.7, 3.8 Hz, 2H, PH), 1.40 (dd, $^2J_{PH}$ = 12.8, 3.8 Hz, 6H, PCH_3) and 1.08 ppm (d, $^2J_{PH}$ = 16.6 Hz, 18H, $PC(CH_3)_3$).

^{31}P NMR (162 MHz, $CDCl_3$) δ 45.45 ppm .

General procedure to Rh(I) complexes. In a Schlenk flask, 0.16 mmol of **5** or **7** were dissolved in 2 mL of anhydrous pyrrolidine and the mixture was stirred at 80 ºC for 2 h. Pyrrolidine was evaporated under reduced pressure and 2mL of dichloromethane were added. The deprotected diphosphine was cannulated over a solution of 167 mg $[Rh(COD)_2]BArF_4$ (0.15 mmol, 0.95 eq.) in dichloromethane under N_2 atmosphere at -20ºC. The crude was eluted through SiO_2 under nitrogen positive pressure with degassed solvent dcm:hexane (1:1). The solvent was removed under reduced pressure and the orange solid was washed with hexane.

[Rh(5)(COD)]BAr^F_4 (8)

Yield: 82%

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (br, 8H, CH_{ArF}), 7.53 (br, 4H, CH_{ArF}), 5.52 (m, 2H, CH_{COD}), 5.07 (m, 2H, CH_{COD}), 2.72 (m, 6H, NCH_3), 2.59-2.53 (m, 2H, $CH_{2\ COD}$), 2.43-2.33 (m, 2H, $CH_{2\ COD}$), 2.26-2.09 (m, 4H, $CH_{2\ COD}$), 1.50 (d, $^2J_{PH}$ = 6.3 Hz, 6H, PCH_3) and 1.12 ppm (d, $^3J_{PH}$ = 14.9 Hz, 18H, $PC(CH_3)_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.7 (q, $^1J_{BC}$ = 40 Hz, CB_{BArF4}), 134.7 (s, CH_{BArF4}), 128.8 (qq, $^2J_{FC}$ = 31.5 Hz, $^3J_{BC}$ = 2.7 Hz, C_{BArF4}), 124.5 (q, $^1J_{FC}$ = 272 Hz, CF_{BArF4}), 117.4 (m, CH_{BArF4}), 103.2 (dt, $^1J_{RhC}$ = 7 Hz, $^2J_{PC}$ = 3.6 Hz, CH_{COD}), 96.0 (m, CH_{COD}), 39.0 (m, P*C*$(CH_3)_3$, 37.1 (m, NCH_3), 32.6 (s, $CH_{2\ COD}$), 27.3 (s, $CH_{2\ COD}$), 27.2 (m, PC(*C*$H_3)_3$) and 9.6 ppm (m, PCH_3).

^{31}P-NMR (202MHz, CDCl3) δ 136.0 ppm (d, $^1J_{RhP}$ = 164 Hz)

MS ESI (high res., positive mode). Calcd. for [M-BF_4]+ 475.192, found 475.193.

[Rh(7)(COD)]BAr^F_4 (9)

Yield: 75%

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.71 (br, 8H, CH_{ArF}), δ 7.53 (br, 4H, CH_{ArF}), 5.63 (m, 2H, CH_{COD}), 5.07 (m, 2H, CH_2), 4.96 (m, 2H, CH_{COD}), 3.73 (m, 4H, PCH_2), 2.61-2.55 (m, 2H, $CH_{2\ COD}$), 2.47-

2.36 (m, 2H, $CH_{2\ COD}$), 2.14-2.10 (m, 4H, $CH_{2\ COD}$), 1.52 (d, $^{2}J_{PH}$ = 6.3 Hz, 6H, PCH_3) and 1.20 ppm (d, $^{3}J_{PH}$ = 14.7 Hz, 18H, $C(CH_3)_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 161.7 (q, $^{1}J_{BC}$ = 40 Hz, CB_{BArF4}), 134.7 (s, CH_{BArF4}), 128.8 (qq, $^{2}J_{FC}$ = 31.5 Hz, $^{3}J_{BC}$ = 2.7 Hz, C_{BArF4}), 124.5 (q, $^{1}J_{FC}$ = 272 Hz, CF_{BArF4}), 119.4 (s, CCH_2), 116.4 (m, CH_{BArF4}), 105.8 (s, CCH_2), 101.9 (dt, $^{1}J_{RhC}$ = 6.8 Hz, $^{2}J_{PC}$ = 3.1 Hz, CH_{COD}), 93.3 (m, CH_{COD}), 52.3 (s, NCH_2), 38.6 (m, $C(CH_3)_3$, 33.9 (s, $CH_{2\ COD}$), 27.3 (d, $^{2}J_{PC}$ = 2.7 Hz, $C(CH_3)_3$), 26.5 (s, $CH_{2\ COD}$), and 9.9 (d, $^{1}J_{PC}$ = 23.7 Hz, PCH_3).

^{31}P-NMR (202MHz, CDCl3) δ 128.7 (d, $^{1}J_{RhP}$ = 164 Hz)

MS ESI (high res., positive mode). Calcd. for [M-Bar^{F}_{4}]+ 499.192, found 499.190

Kinetic studies

15 mg of pure crystals of **5** and **7** were dissolved in deuterated chloroform in a NMR tube and successive ^{1}H-NMR spectra were collected at controlled times.

Table 1. Kinetics data for the equilibrium **5**-($R_PR_PS_a$)/**5**-($R_PR_PR_a$)

Entry	time (min)	Molar fraction **5**-($R_PR_PS_a$)	Molar Fraction **5**-($R_PR_PR_a$)	ln ([Sa]-[Sa]eq)
0	0	1	0	-0,693147181
1	3	0,781	0,219	-1,26940061
2	9	0,592	0,408	-2,385966702
3	15	0,535	0,465	-3,352407217
4	20	0,518	0,482	-4,017383521
5	25	0,505	0,495	-5,298317367
6	30	0,505	0,495	-5,298317367
7	35	0,503	0,497	-5,80914299
8	40	0,503	0,497	-5,80914299
9	45	0,5	0,5	

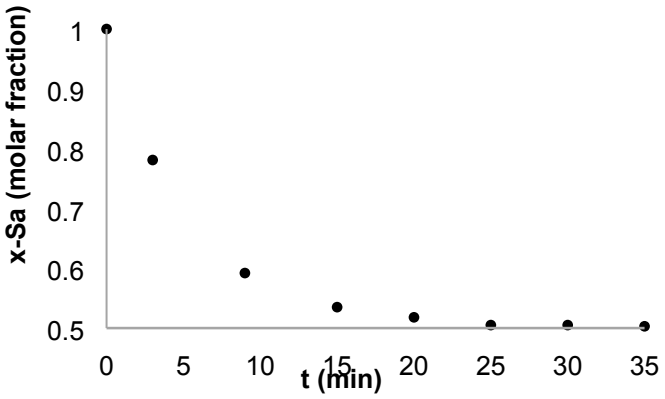


Figure 1. Reaction profile for the equilibrium **5**-($R_PR_PS_a$)/**5**-($R_PR_PR_a$) starting from **5**-($R_PR_PS_a$) in $CDCl_3$.

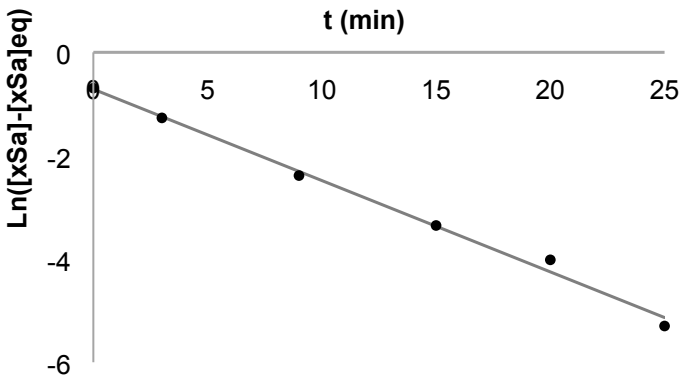


Figure 2. First order plot of Ln([**5**-($R_PR_PS_a$)]-[**5**-($R_PR_PS_a$)]eq) during time reaction (until concentration are equal).

$k = 1.47 \cdot 10^{-3}\ s^{-1}$

$\Delta G^{\ddagger} = 21\ Kcal \cdot mol^{-1} = 88\ KJ \cdot mol^{-1}$

Table 2. Kinetics data for the equilibrium **7**-($R_PR_NR_NR_P$)/**7**-($R_PS_NS_NR_P$)

Entry	time (h)	Molar fraction **7**-($R_PR_NR_NR_P$)	Molar Fraction **7**-($R_PS_NS_NR_P$)	ln ([R_NR_N]-[R_NR_N]eq)
1	0	1	0	-0,693147181
2	0,05	0,98	0,02	-0,733969175
3	0,35	0,96	0,04	-0,776528789
4	1,63	0,92	0,08	-0,867500568
5	2,5	0,893	0,107	-0,933945667
6	4,13	0,847	0,153	-1,058430499
7	6,61	0,787	0,213	-1,248273063
8	7,85	0,763	0,237	-1,335601247
9	12	0,699	0,301	-1,614450454
10	13,3	0,675	0,325	-1,742969305
11	24	0,58	0,42	-2,525728644

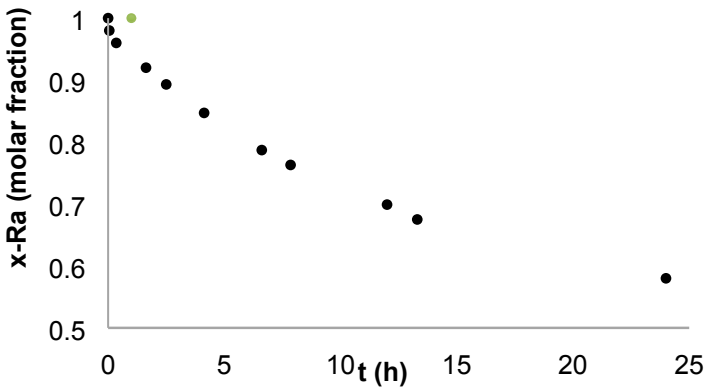


Figure 3. Reaction profile for the equilibrium **7**-($R_PR_NR_NR_P$)/**8**-($R_PS_NS_NR_P$) starting from **7**-($R_PR_NR_NR_P$) in $CDCl_3$.

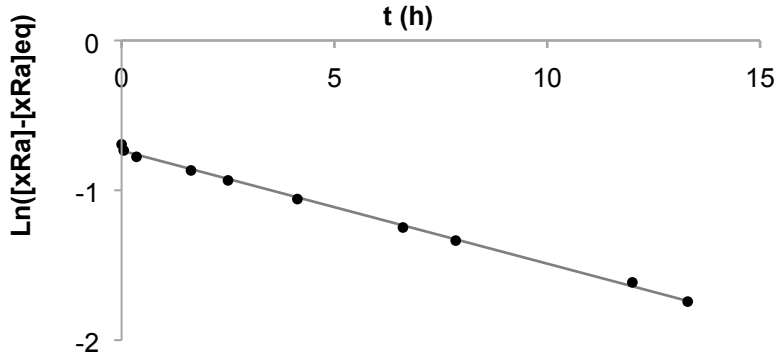
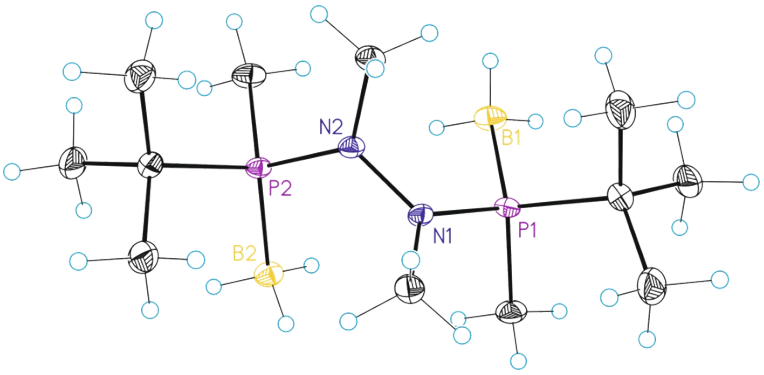


Figure 4. First order plot of Ln([**7**-($R_PR_NR_NR_P$)]-[**7**-($R_PR_NR_NR_P$)]eq) during time reaction (until concentration are equal).

$k = 1.045 \cdot 10^{-5}\ s^{-1}$

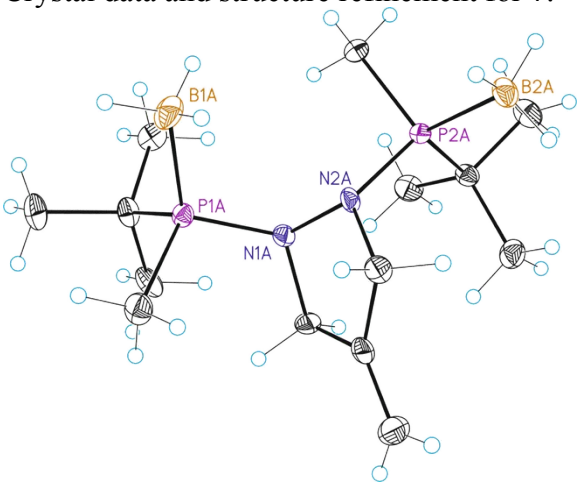
$\Delta G^{\ddagger} = 24\ Kcal \cdot mol^{-1} = 100.4\ KJ \cdot mol^{-1}$

Crystal data and structure refinement parameters
Crystal data and structure refinement for **5**.



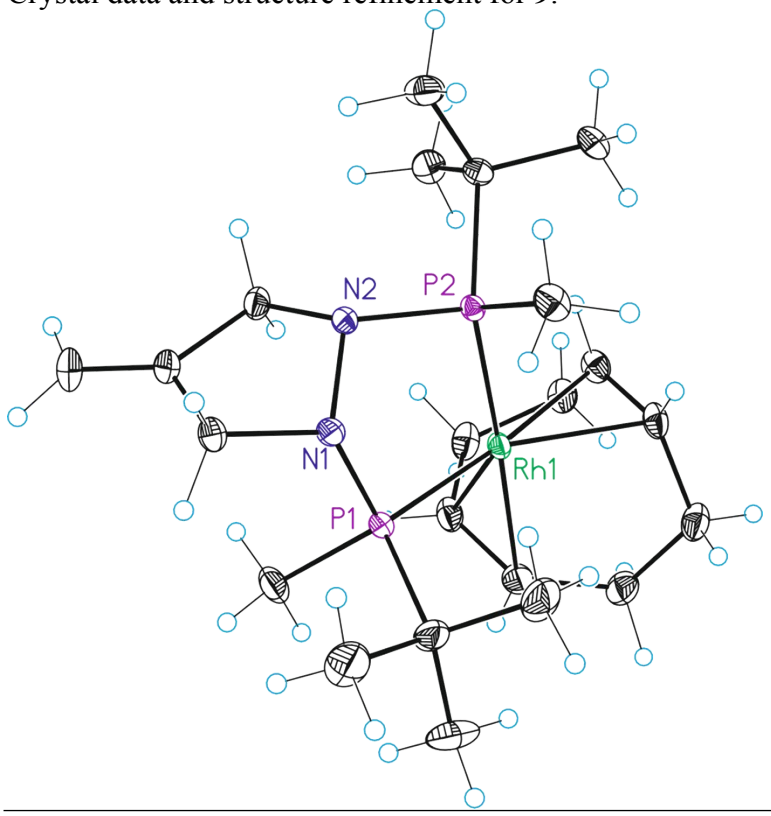
Empirical formula	C12 H36 B2 N2 P2
Formula weight	291.99
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 6.7712(4)Å α= 90° b = 21.3766(14)Å β = 114.0523(16)° c = 6.9819(4)Å γ = 90°
Volume	922.85(10) $Å^3$
Z	2
Density (calculated)	1.051 Mg/m^3
Absorption coefficient	0.224 mm^{-1}
F(000)	324
Crystal size	0.55 x 0.30 x 0.10 mm^3
Theta range for data collection	1.905 to 32.566°.
Index ranges	-10<=h<=7,-31<=k<=31,-5<=l<=10
Reflections collected	10290
Independent reflections	5570[R(int) = 0.0257]
Completeness to theta =32.566°	90.4%
Absorption correction	Empirical
Max. and min. transmission	0.978 and 0.899
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5570/ 1/ 175
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0856
R indices (all data)	R1 = 0.0389, wR2 = 0.0881
Flack parameter	x =-0.01(4)
Largest diff. peak and hole	0.405 and -0.331 $e.Å^{-3}$

Crystal data and structure refinement for **7**.



Empirical formula	C14 H36 B2 N2 P2	
Formula weight	316.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4260(10)Å	α= 90°.
	b = 13.8793(12)Å	β = 90°.
	c = 27.409(2)Å	γ = 90°.
Volume	3966.2(6) $Å^3$	
Z	8	
Density (calculated)	1.058 Mg/m^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	1392	
Crystal size	0.25 x 0.25 x 0.06 mm^3	
Theta range for data collection	1.486 to 25.565°.	
Index ranges	-12<=h<=12,-15<=k<=16,-33<=l<=24	
Reflections collected	25315	
Independent reflections	7282[R(int) = 0.0541]	
Completeness to theta =25.565°	97.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.987 and 0.833	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7282/ 180/ 429	
Goodness-of-fit on F^2	0.810	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.1032	
R indices (all data)	R1 = 0.0441, wR2 = 0.1112	
Flack parameter	x =0.06(4)	
Largest diff. peak and hole	0.328 and -0.234 $e.Å^{-3}$	

Crystal data and structure refinement for **9**.



Empirical formula	C54 H54 B F24 N2 P2 Rh
Formula weight	1362.65
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 12.92590(14)Å α= 90°. b = 12.42237(13)Å β = 107.0548(12)°. c = 18.1785(2)Å γ = 90°.
Volume	2790.56(6) $Å^3$
Z	2
Density (calculated)	1.622 Mg/m^3
Absorption coefficient	0.484 mm^{-1}
F(000)	1376
Crystal size	0.15 x 0.15 x 0.1 mm^3
Theta range for data collection	2.015 to 35.492°.
Index ranges	-21<=h<=20,-20<=k<=20,-28<=l<=29
Reflections collected	84093
Independent reflections	23935[R(int) = 0.0177]
Completeness to theta =35.492°	96.100006%
Absorption correction	Multi-scan
Max. and min. transmission	0.953 and 0.733

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23935/ 85/ 819
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0198, wR2 = 0.0529
R indices (all data)	R1 = 0.0204, wR2 = 0.0531
Flack parameter	x =-0.022(2)
Largest diff. peak and hole	0.574 and -0.305 e.$Å^{-3}$

General Procedure for the Rh-Catalysed Asymmetric Hydrogenations

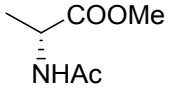
Substrates (0.37, 3.7 or 18.5 mmol), and catalyst (0.0037 mmol) were weighed and placed into a pressure vessel. Anhydrous MeOH (1 or 2.5 mL) was added to the reaction mixture. The pressure vessel was pressure with 3 or 5 bar of H_2, the reaction mixtures were stirred overnight at room temperature. The autoclave was depressurized; the reaction mixture was filtered through a short pad of SiO_2 and subsequently eluted with EtOAc. The resulting solution was concentrated under vacuum. The conversion was determined by ^1H NMR and the enantiomeric excess was determined by GC or HPLC analysis on chiral stationary phases.

Pressure vessels for hydrogenations: Ace® glass pressure tube with Teflon screw-cap equipped with pressure gauge and valve.

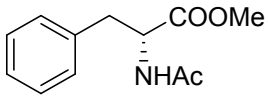
Hydrogenation substrates

Methyl 2-acetamidoacrylate and dimethyl itaconate were commercially available (Sigma-Aldrich®). (*Z*)-Methyl 2-acetamido-3-phenylacrylate,[3] and *N*-(1-Phenylvinyl)acetamide[4] were prepared according to the cited literature procedures.

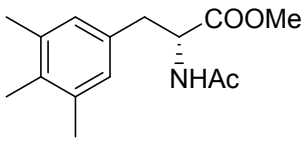
Hydrogenation products:



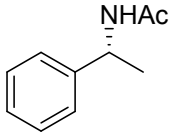
(*R*)-Methyl 2-acetamidopropanoate (MAA):[5] GC conditions: Supelco Beta DEX™ 120 (30 m x 0.25 mm x 0.25 µm), isothermal 90 ºC, 15 psi He, $t_R(S)$ = 63.4 min, $t_R(R)$ =65.2 min (major peak).



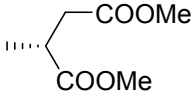
(*R*)-Methyl 2-acetamido-3-phenylpropanoate (Z-MAC):[5] HPLC conditions: Chiralpak® ADH (250 x 4.6 mm), 5µ (COL-HP-51), 90:10 *n*-heptane/2-propanol, 1.0 mL/min, 210 nm, $t_R(R)$ = 10.0 min (major peak) and $t_R(S)$ = 13.8 min.



(*R*)-Methyl 2-acetamido-3-(3,4,5-trimethylphenyl)propanoate:[4] HPLC conditions: Chiralpak® IA (250 x 4.6 mm), 5µ (COL-HP-90) 95:5 heptane/2-propanol, 1 mL/min, 254 nm, $t_R(R)$ =15.9 min (major peak), $t_R(S)$ =20.4 min



(*R*)-*N*-(1-Phenylethyl)acetamide (PVA):[6] Chiralpak® ADH (250 x 4.6 mm), 5μ (COL-HP-51), 95:5 *n*-heptane/2-propanol, 1.0 mL/min, 216 nm, t_R(*R*) = 11.9 min (major peak), t_R(*S*) = 15.4 min.



(*S*)-Dimethyl 2-methylsuccinate (DMI):[7] GC conditions: Chiraldex B-DM (30 m x 0.25 mm), isothermal 80 ºC, 15 psi He, t_R(*S*) = 22.5 min (major peak), t_R(*R*) = 22.7 min.

1 S. Orgué, A. Flores, M. Biosca, O. Pamies, M. Diéguez, A. Riera and X. Verdaguer, *Chem. Commun.*, 2015, **51**, 17548–17551.

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5 M. J. Burk, J. E. Feaster, W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1993, **115**, 10125–10138.

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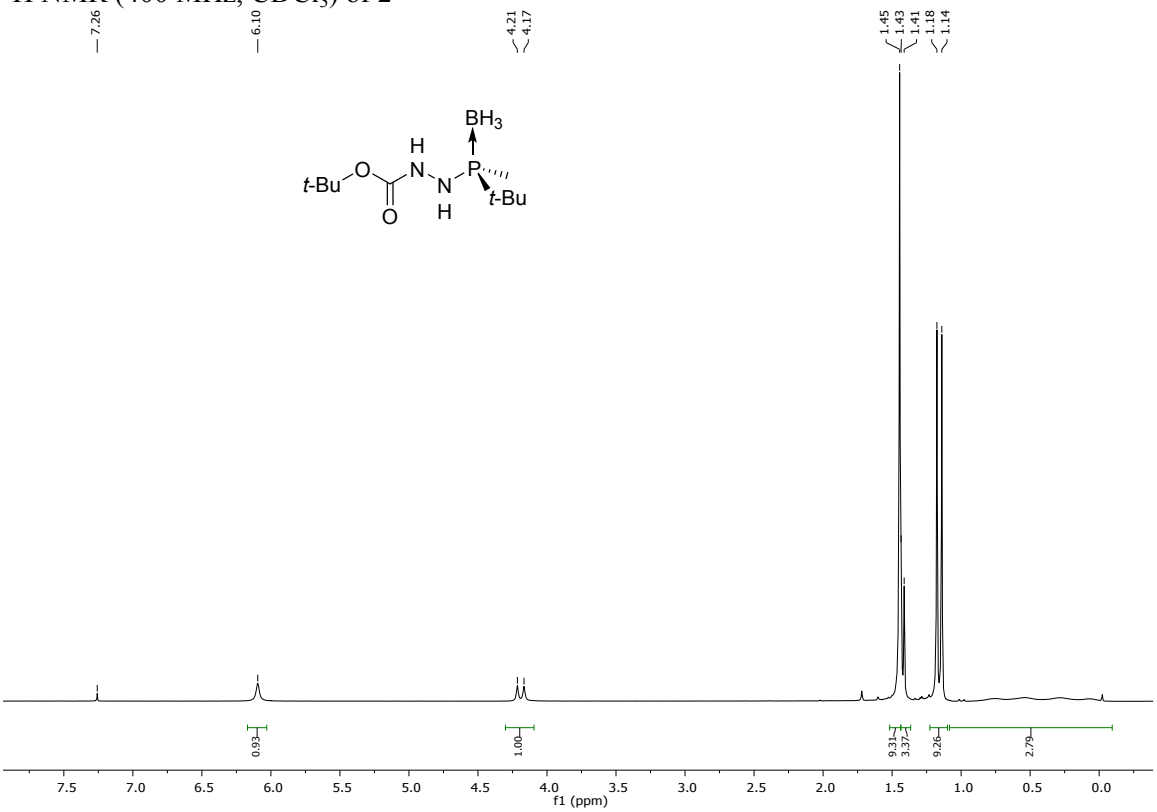
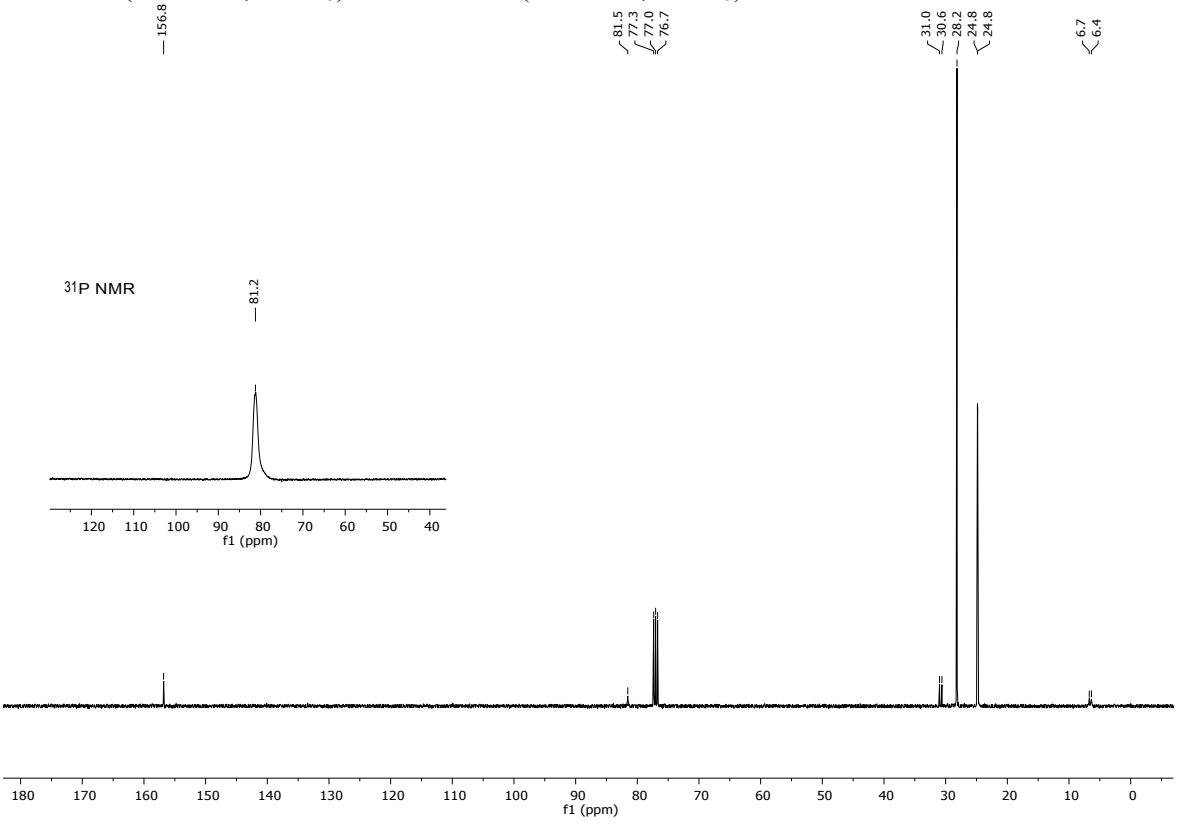
(*R*)-*tert*-butyl 2-(*tert*-butyl(methyl)phosphino)hydrazinecarboxylate-borane

^{1}H NMR (400 MHz, $CDCl_3$) of **2**

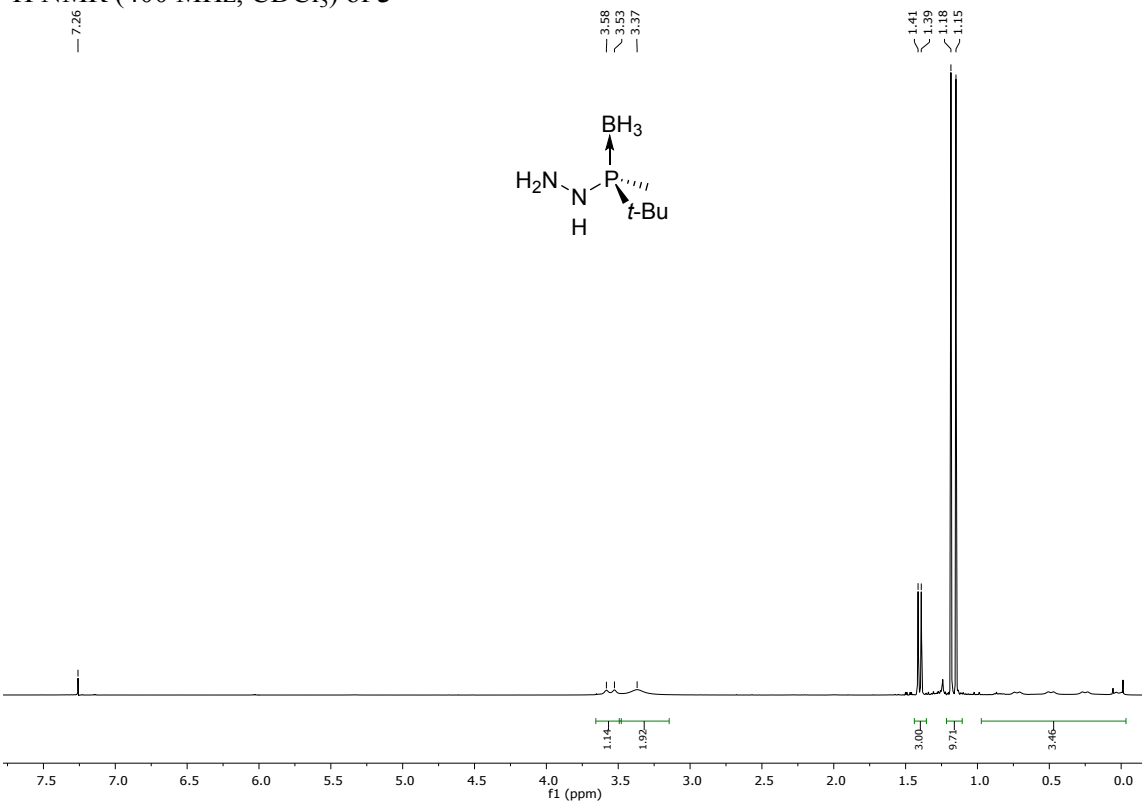


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **2**

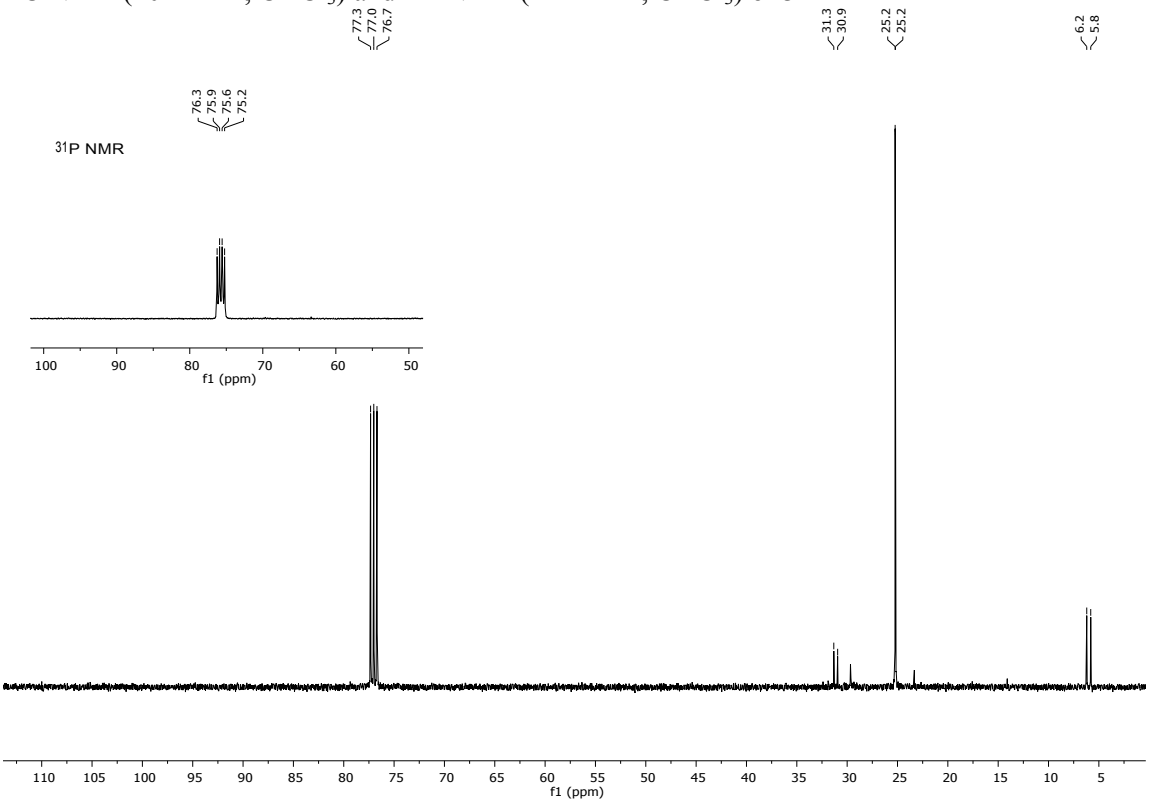


(*R*)-(*tert*-butyl(methyl)phosphanyl)hydrazine-borane

^{1}H NMR (400 MHz, $CDCl_3$) of **3**

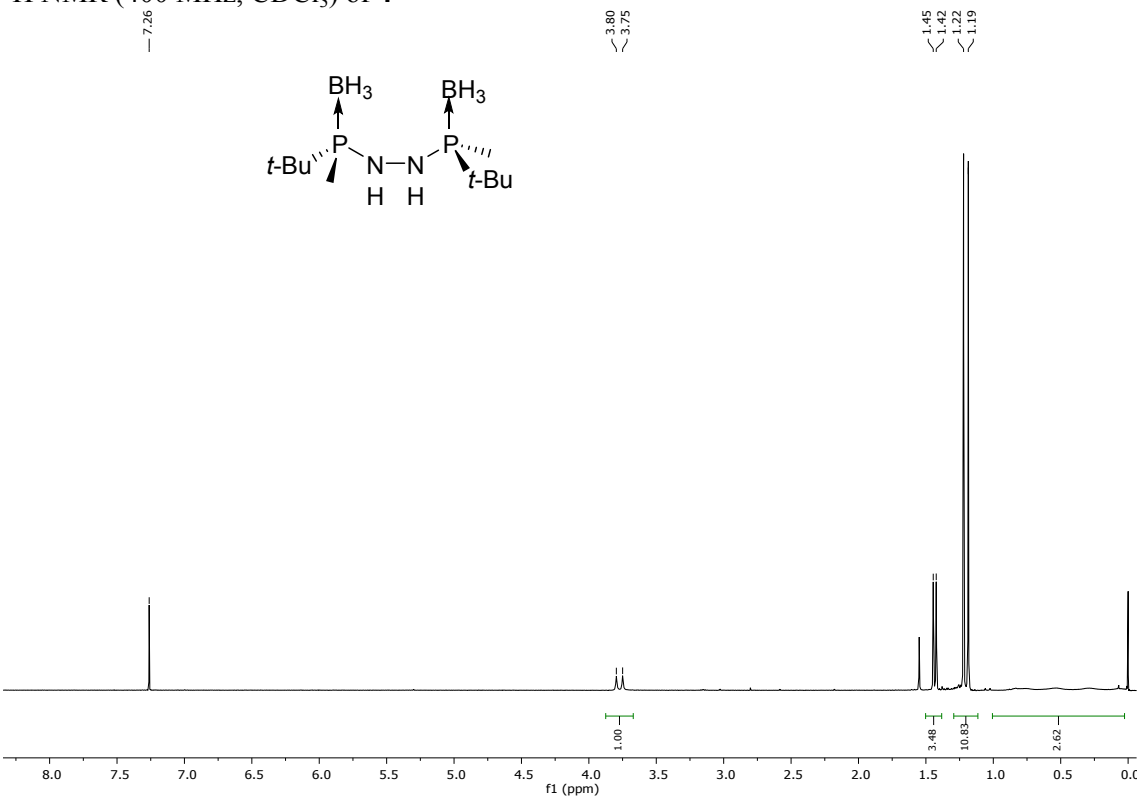


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **3**

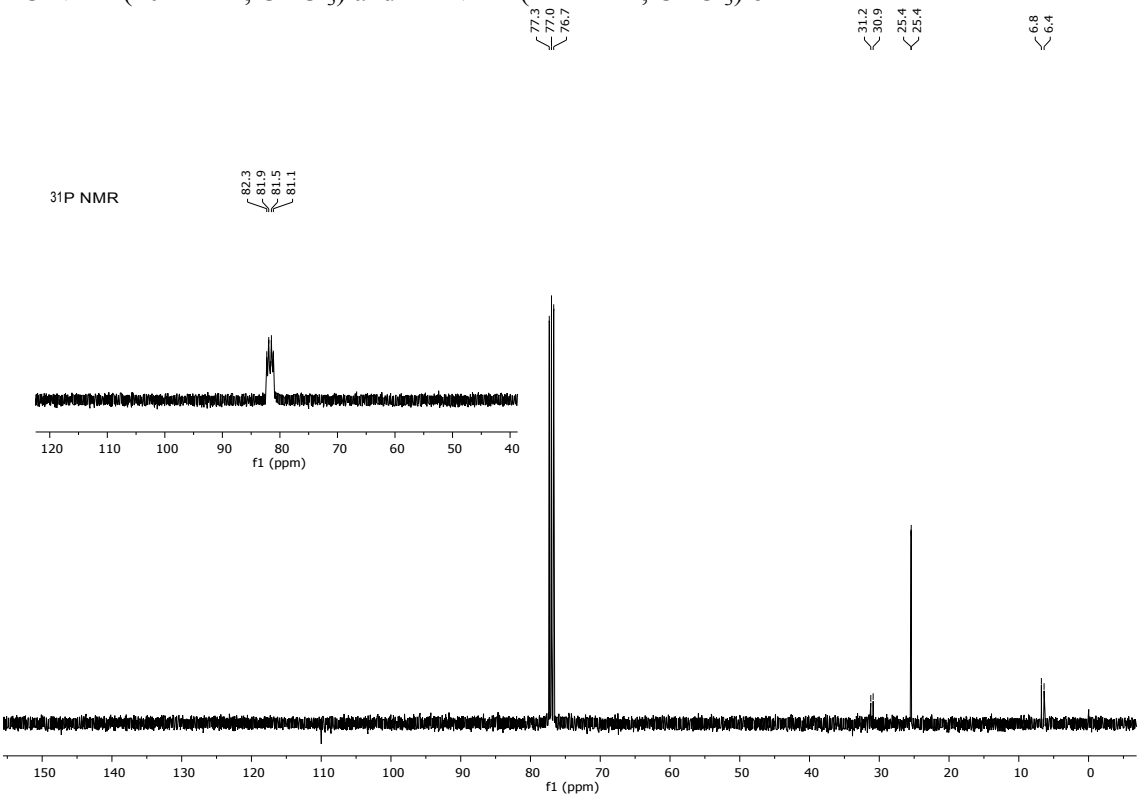


1,2-bis((R)-tert-butyl(methyl)phosphanyl)hydrazine-bisborane

^{1}H NMR (400 MHz, $CDCl_3$) of **4**

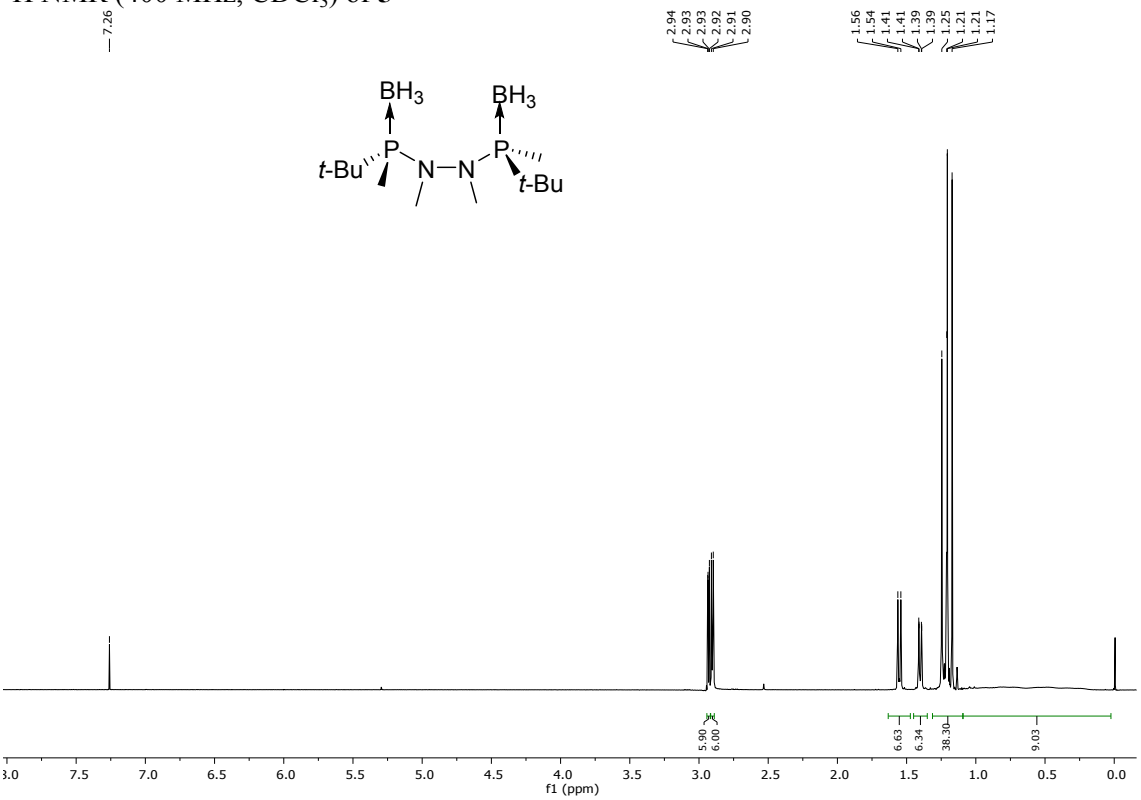


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **4**

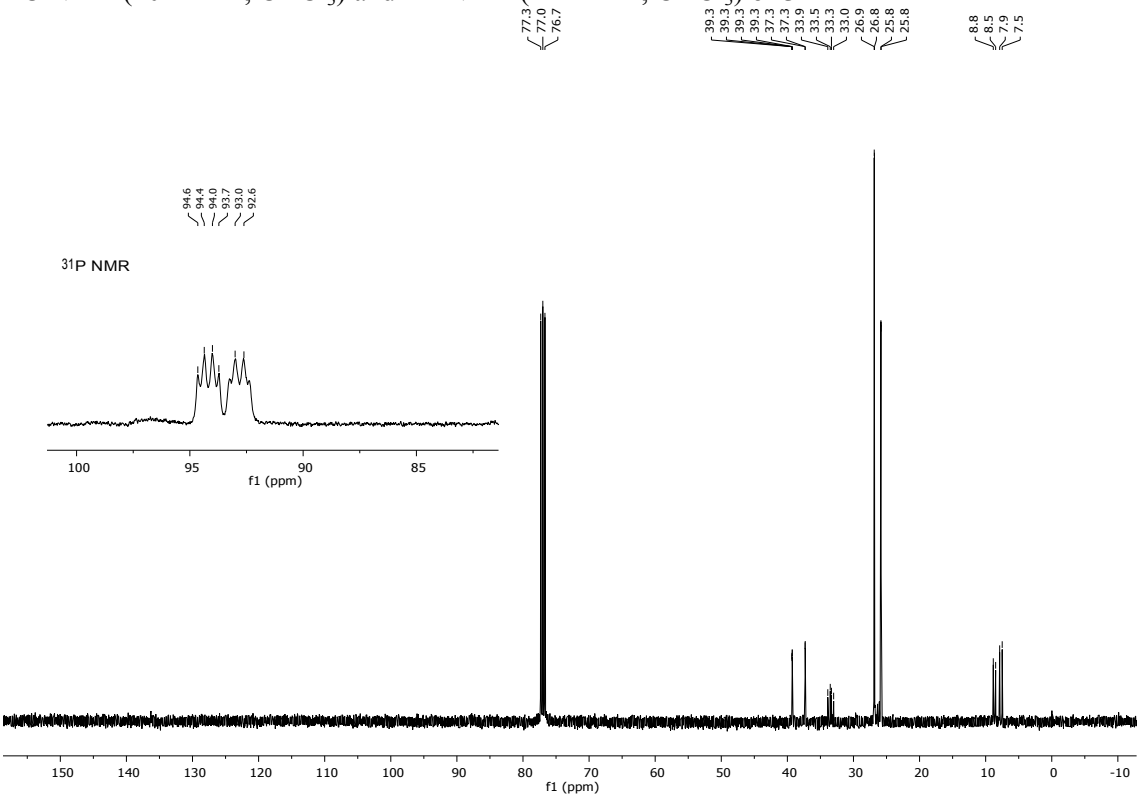


1,2-bis((*R*)-*tert*-butyl(methyl)phosphanyl)-1,2-dimethylhydrazinebisborane

^{1}H NMR (400 MHz, $CDCl_3$) of **5**

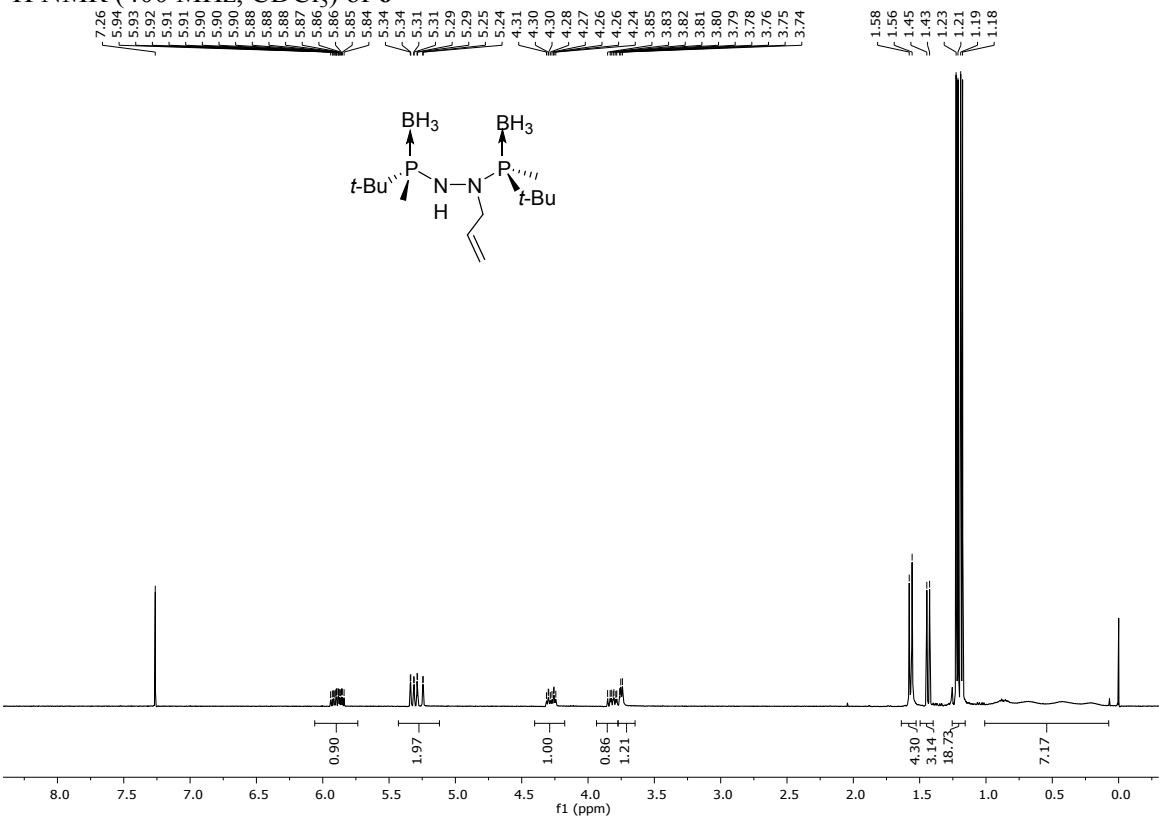


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **5**

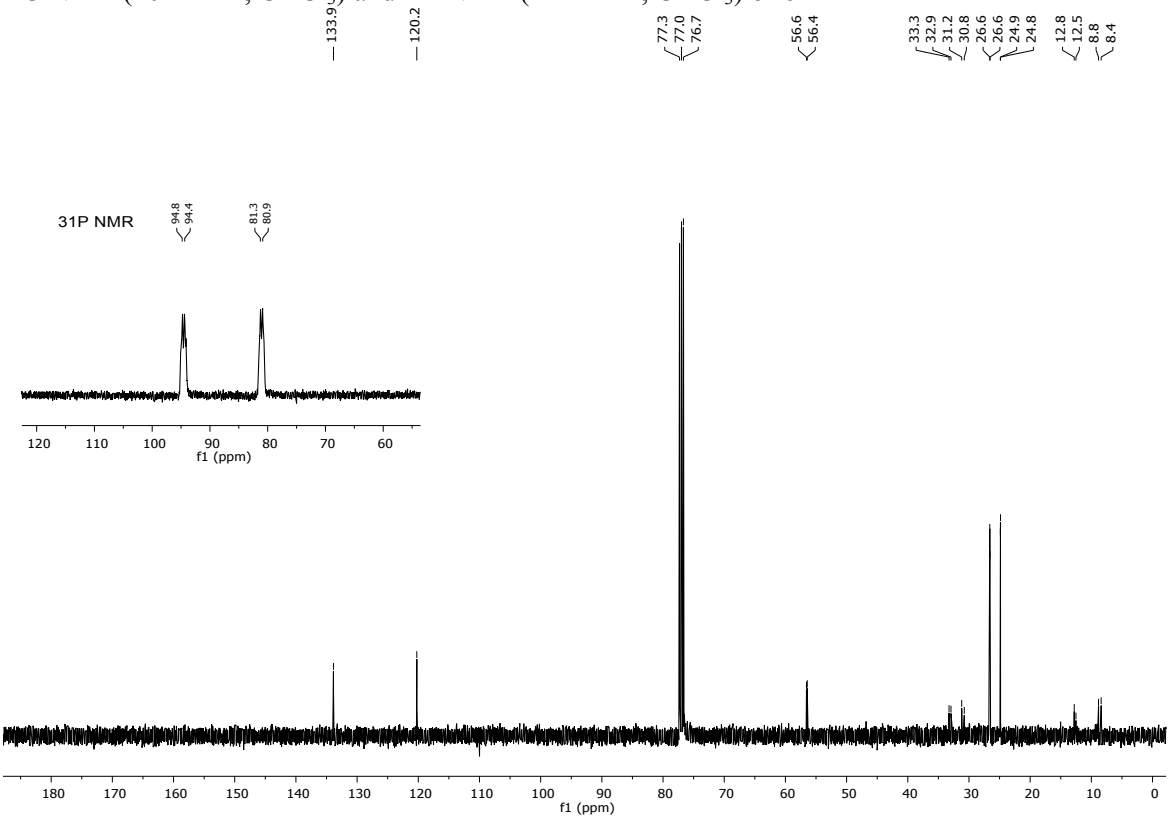


1,2-bis((*R*)-*tert*-butyl(methyl)phosphanyl)-1-allylhydrazine-bisborane

^{1}H NMR (400 MHz, $CDCl_3$) of **6**

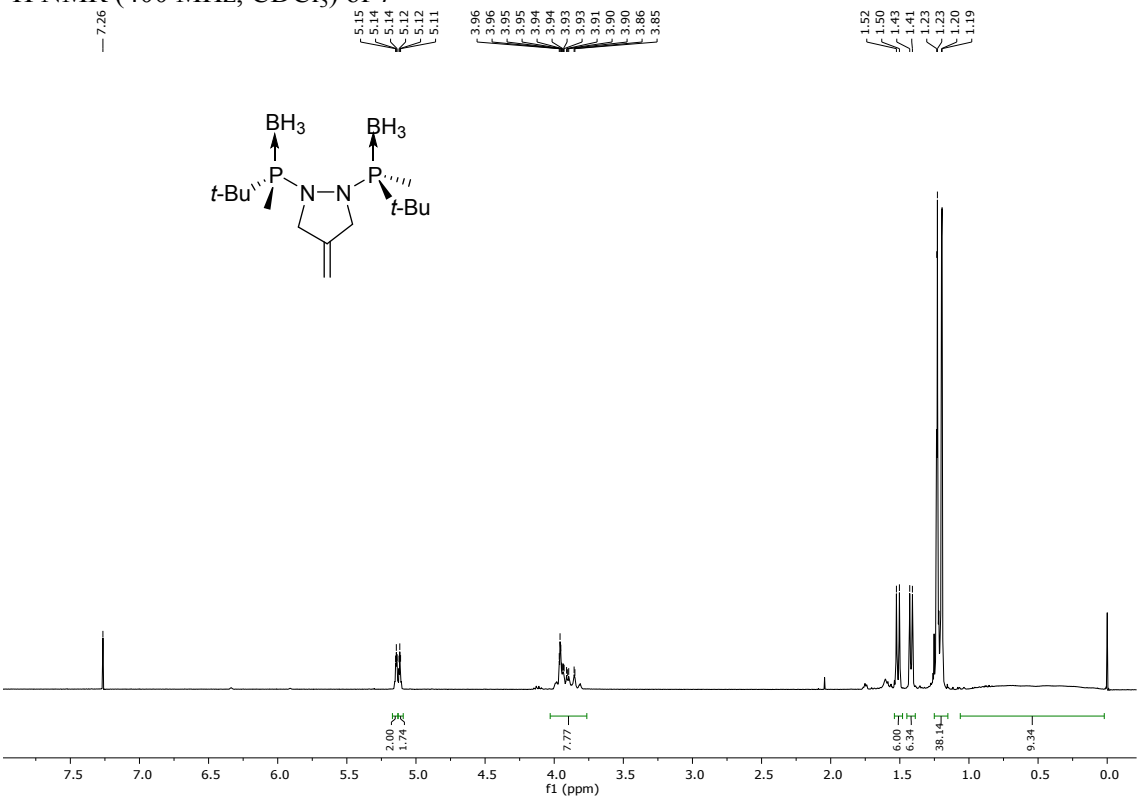


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **6**

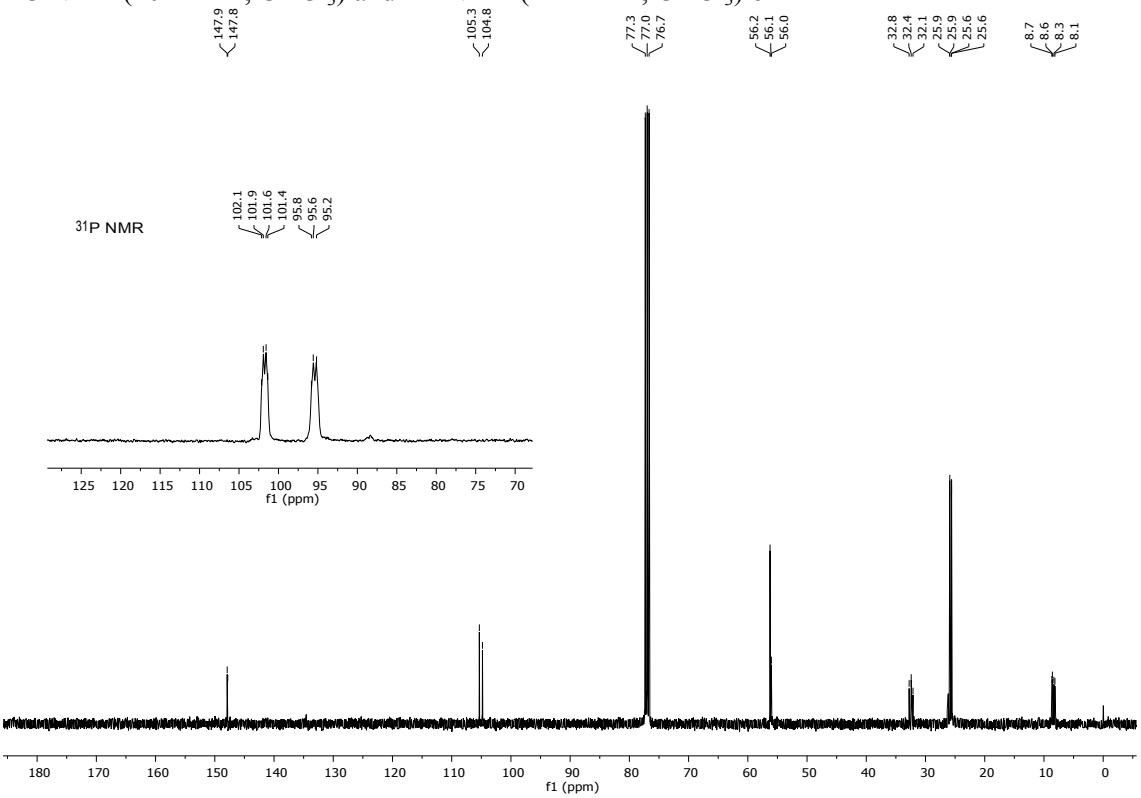


1,2-bis(tert-butyl(methyl)phosphanyl)-4-methylenepyrazolidine

^{1}H NMR (400 MHz, $CDCl_3$) of **7**

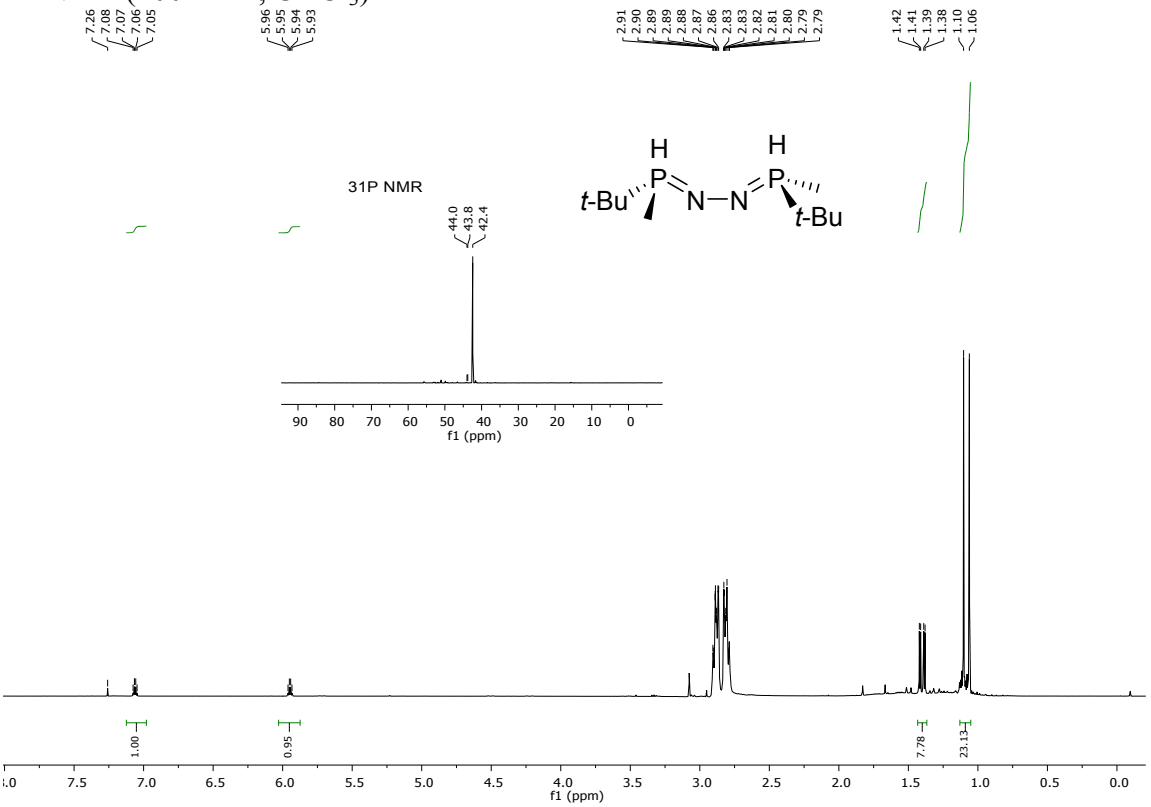


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **7**



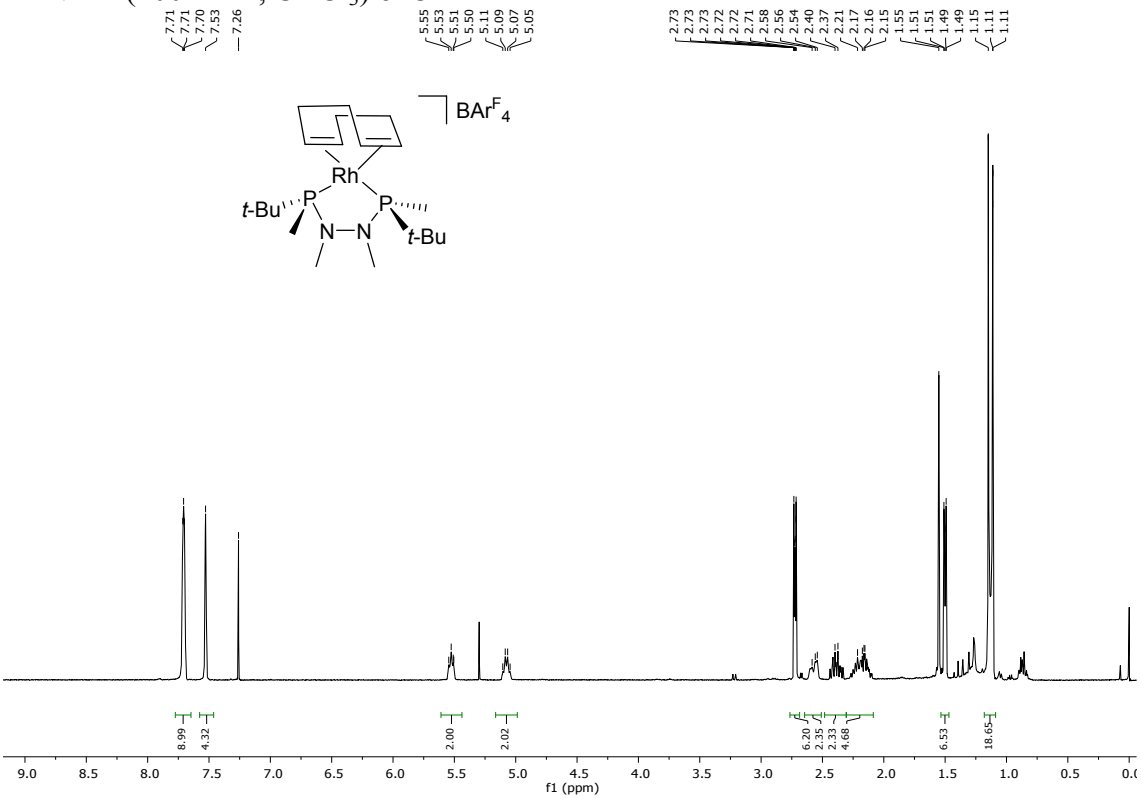
1,2-bis((R)-tert-butyl(methyl)phosphino)hydrazine + DABCO-BH_3

^{1}H NMR (400 MHz, $CDCl_3$)

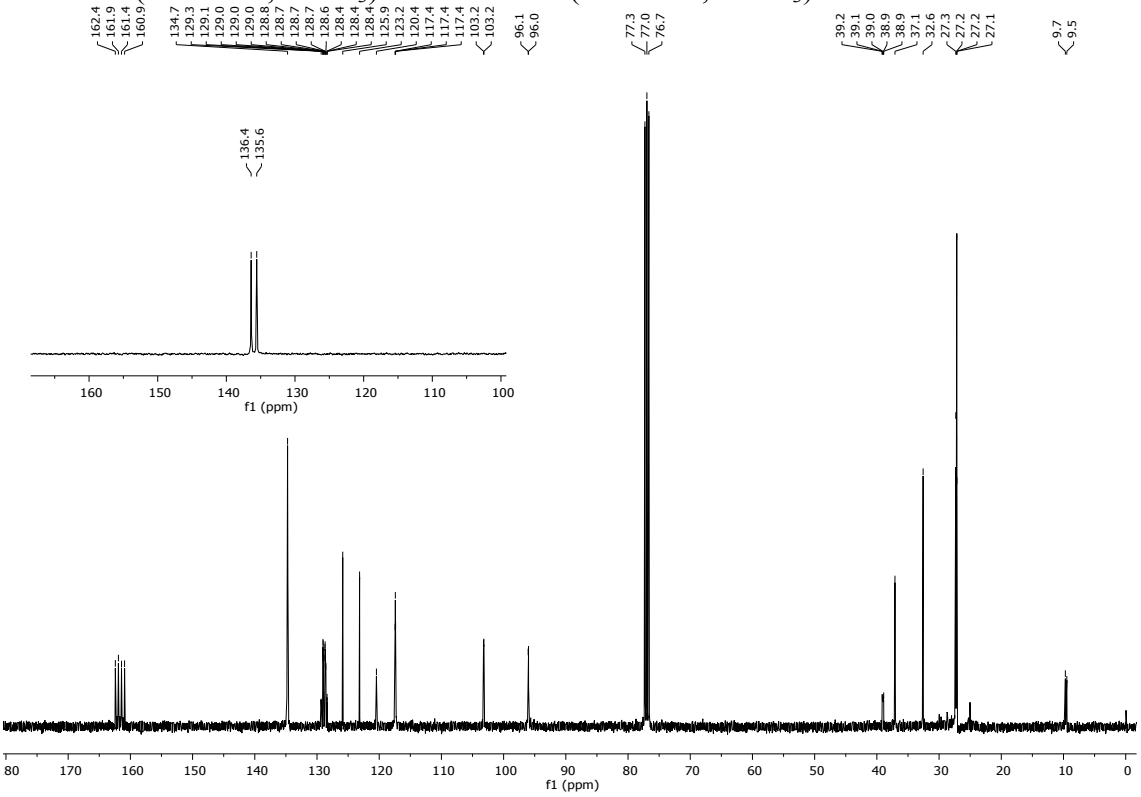


[Rh(5)(COD)]BAr$^F_4$

^{1}H NMR (400 MHz, $CDCl_3$) of **8**

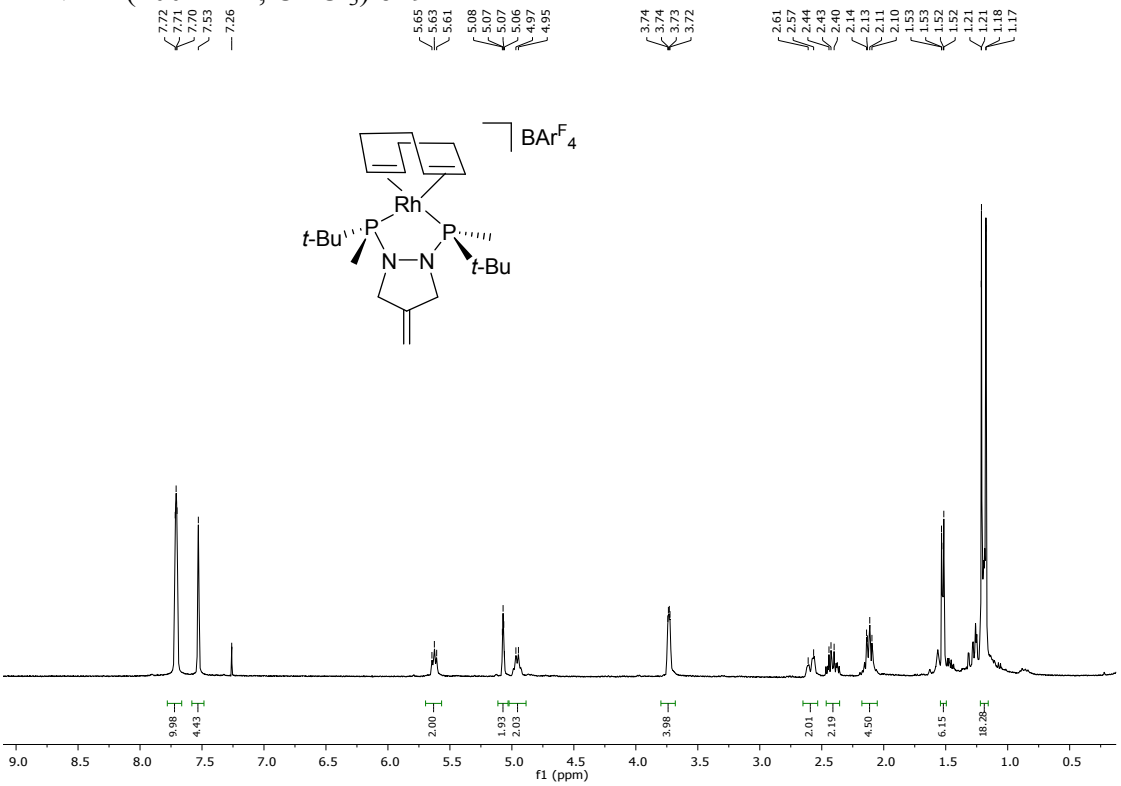


^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **8**



[Rh(7)(COD)]BAr$^F_4$

^{1}H NMR (400 MHz, $CDCl_3$) of **9**



^{13}C NMR (101 MHz, $CDCl_3$) and ^{31}P NMR (121 MHz, $CDCl_3$) of **9**