Electronic Supplementary Information

Asymmetric 1,3-dipolar cycloaddition with a *P*-stereogenic dipolarophile: An efficient approach to novel *P*-stereogenic bidentate ligand systems

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General

All operations involving air-sensitive organophosphorus compounds were carried out in an argon or nitrogen atmosphere, using standard vacline and Schlenk techniques. All glassware was flame-dried at reduced pressure and filled with a protective gas (repeated 3 times). The following solvents were distilled before use under a slight positive pressure of nitrogen or argon. Diethyl ether (DEE), toluene, benzene, hexane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Methylene chloride (DCM) and triethylamine (Et_3N) were distilled from calcium hydride. Petroleum ether (PE) and *tert*-butyl methyl ether (TBME) were distilled from calcium chloride. PMHS (Acros) and $Ti(O\textit{i}Pr)_4$ (Acros) were used without further purification. (S_P,S_P)-**6** was prepared according to the published procedure.[1-3]

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured at 25 ºC with Bruker AM 400 (^{1}H: 400.1, ^{13}C: 100.1, ^{31}P NMR: 162 MHz), 500 (^{1}H: 500, ^{13}C: 125 MHz) or WP 200 SY (^{1}H: 200.1, ^{13}C: 50.3 MHz) spectrometers. The chemical shifts refer to δ_{TMS} = 0 ppm or to residual solvent signals as internal standard. For ^{31}P NMR a solution of H_3PO_4 30 % in water is used as external reference. The multiplicity of the peaks are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The deuterated solvents [D_6]-benzene, $CDCl_3$ and CD_2Cl_2 were distilled under argon and used immediately. Atom numbering is arbitrary and does not correspond to the IUPAC.

Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR 580 and 1710 spectrometers. Signal intensities are abbreviated s (strong), m (medium) or w (weak).

Mass spectra (MS) were measured on a Micromass LCT with Lock-Spray-unit (ESI). The injection was made in Loop-Modes in a HPLC-Alliance 2695 (Waters). All values are given in atomic units of mass per elemental charge (*m/z*). The intensity is given as a percentage of the base peak.

High resolution mass spectra (HRMS) were recorded with the peak-matching method in Micromass LCT with Lock-Spray-unit (ESI). All values are given in atomic units of mass per elemental charge (*m/z*).

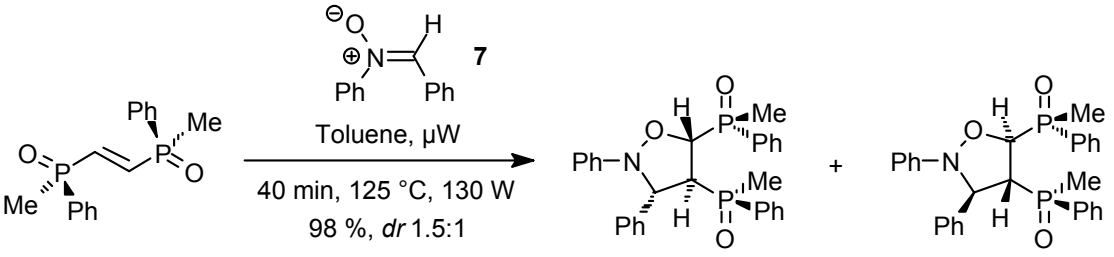
Optical rotations were determined with a Perkin Elmer PE-241 instrument at 20 °C with the light frequency of 589 nm (D-line of a sodium vapor lamp) in a cuvette (d =1 dm or d = 0.1 dm; concentration c is given in g/100 mL).

Melting points were determined with the Electrothermal IA 9200.

Microanalyses were conducted with a Elementar Vario EL instrument with acetamide as standard.

Microwave (μW) heating was carried out with a CEM Corporation Discover® LabMate™ single-mode microwave cavity.

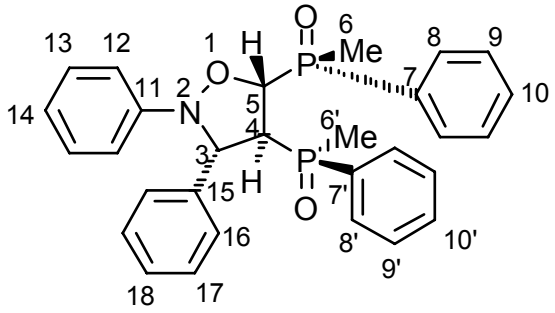
Synthesis of New *P*-stereogenic Diphosphine Dioxides



(S_P,S_P)-**6** (R_P,S$_P$)-**8a** (R_P,S$_P$)-**8b**

In a 80-mL microwave tube were placed (S_P,S_P)-**6** (500 mg, 1.6 mmol) and *C*,*N*-diphenylnitrone (730 mg, 3.7 mmol) in toluene (5 mL). The reaction mixture was heated for 40 min at 125 ºC (130 W). After the reaction, the toluene was removed at reduced pressure, and a black-brownish residue was separated by column chromatography (SiO_2, MeOH / CH_2Cl_2 (20:1) to give 501 mg (1.0 mmol, 62 %) of (R_P,S_P)-**8a** and 310 mg (0.6 mmol, 36 %) of (R_P,S_P)-**8b** as white viscous liquids, which crystallized as white solids after addition of petroleum ether. Ratio of diastereoisomers 1.5:1 (^{31}P NMR)

(4*S*$_P$,5*R*$_P$)-(+)-Bis-(4*S*,5*R*)-[methyl(phenyl)phosphinyl]-(*N*,3*S*)-diphenylisoxazolidine dioxide (8a)

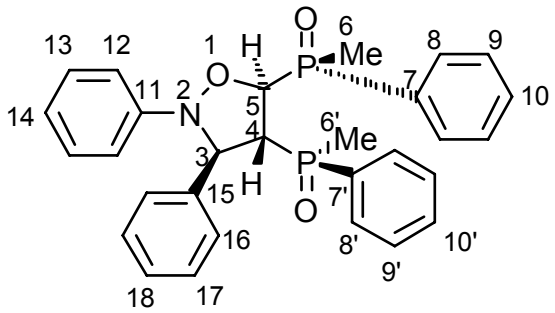


(R_P,S$_P$)-**8a**

(R_P,S_P)-**8a** (major): M. p. = 172 ºC. – $[\alpha]^{D}_{20}$ = +100.8 (c = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 3049 (w) cm^{-1}, 1593 (w), 1488 (w), 1437 (w), 1286 (w), 1190 (s, P=O), 1116 (s, C-N), 1045 (w), 874 (s), 784 (w), 757 (w), 735 (s), 689 (s). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 1.66 (d, $^2J_{PH}$ = 13.1 Hz, 3H, 6-H), 1.79 (d, $^2J_{PH}$ = 13.4 Hz, 3H, 6'-H), 4.04 (m, 1H, 4-H), 4.54 (dt, J =

5.8 Hz, $^{2}J_{PH}$ = 12.7 Hz, 1H, 5-H), 4.98 (dd, J_{HH} = 7.5 Hz, $^{2}J_{PH}$ = 14.3 Hz, 1H, 3-H), 7.2-7.8 (m, 20H$_{Ar}$) ppm. – ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, HH-COSY, NOE, $CDCl_3$): δ= 13.0 (d, $^{1}J_{PC}$ = 70.9 Hz, C-6), 16.4 (d, $^{1}J_{PC}$ = 70.6 Hz, C-6'), 54.8 (dd, $^{1}J_{PC}$ = 68.5 Hz, J = 2.8 Hz, C-4), 72.1 (C-3), 77.2 (d, $^{1}J_{PC}$ = 76.3 Hz, C-5), 118.8 (C-12, C-12'), 124.9 (C-14), 129.0 (C-18), 128.3 (C-10'), 128.42 (C-10), 128.45 (C-16), 128.5 (C-17), 128.6 (C-13), 129.9 (d, $^{3}J_{PC}$ = 9.4 Hz, C-9'), 130.4 (d, $^{3}J_{PC}$ = 9.2 Hz, C-9), 131.2 (d, $^{1}J_{PC}$ = 97.9 Hz, C-7'), 131.7 (d, $^{2}J_{PC}$ = 2.9 Hz, C-8'), 131.9 (d, $^{2}J_{PC}$ = 2.7 Hz, C-8), 132.9 (d, $^{1}J_{PC}$ = 93.2 Hz, C-7), 138.6 (d, $^{3}J_{PC}$ = 2.3 Hz, C-15), 147.9 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = + 38.0 (d, J = 20.3 Hz), + 39.8 (d, J = 19.8 Hz) ppm. – MS (EI) *m/z* (%): 502 [M^++H], 362 (19) [Ph-C-[CH-P(Ph)Me]$_2$], 334 (23) [CH-NH-O-[C-P(O)(Ph)Me]$_2$], 180 (57) [C-C-P(Ph)Me-O-NH], 165 (74) [C-O-C-P(O)(Ph)Me], 139 (66) [Ph(Me)P=O], 91 (62) [PhN]. – HR-MS (ESI) calcd for: $[M+H]^+$ ($C_{29}H_{29}NO_3P_2$): calcd. 502.1701, found 502.1708. – Anal ($C_{29}H_{29}NO_3P_2$): Calcd: C 69.45, H 5.83, N 2.79; found: C 68.93, H 6.05, N 2.87.

(4*S*$_P$,5*R*$_P$)-(–)-Bis-(4*R*,5*S*)-[methyl(phenyl)phosphinyl]-(*N*,3*R*)-diphenylisoxazolidine dioxide (8b)

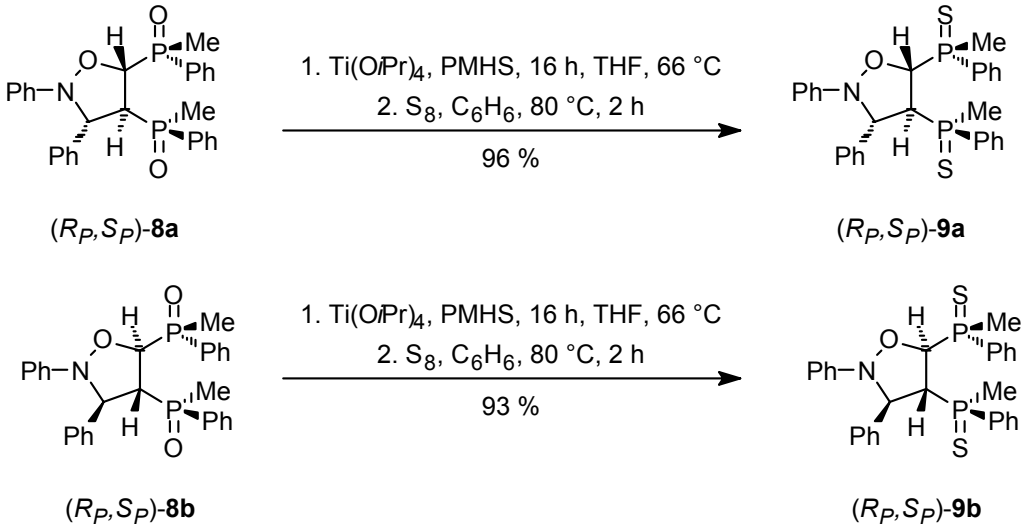


(R_P,S$_P$)-**8b**

(R_P,S_P)-**8b** (minor): M. p. = 69 ºC. – $[\alpha]^{D}_{20}$ = – 183.2 (c = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 3047 (w) cm^{-1}, 1597 (w), 1489 (w), 1438 (w), 1297 (w), 1178 (s, P=O), 1115 (s, C-N), 1027 (w), 889 (s), 742 (s), 693 (s). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ= 1.93 (d, $^{2}J_{PH}$ = 13.1 Hz, 3H, 6-H), 2.07 (d, $^{2}J_{PH}$ = 13.2 Hz, 3H, 6'-H), 3.2 (m, 1H, 4-H), 4.3 (dd, J = 8.8 Hz, $^{2}J_{PH}$ = 13.2 Hz, 1H, 3-H), 5.3 (dddd, $^{2}J_{PH}$ = 16.4 Hz, J = 9.2 Hz, J = 6.8 Hz, J = 2.1 Hz, 1H, 5-H), 5.94 (d, J = 7.1 Hz, 2H, 16-H), 6.64-7.66 (m, 14H$_{Ar}$), 7.95 (m, 4H, 8-H + 8H') ppm. – ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, HH-COSY, NOE, $CDCl_3$): δ= 14.5 (d, $^{1}J_{PC}$ = 69.9 Hz, C-6'), 16.8 (d, $^{1}J_{PC}$ = 71.5 Hz, C-6), 53.8 (dd, $^{1}J_{PC}$ = 70.0 Hz, $^{1}J_{PC}$ = 2.9 Hz, C-4), 71.8 (C-3), 75.4 (d, $^{1}J_{PC}$ = 81.3 Hz, C-5), 118.8 (C-12, C-12'), 124.9 (C-14), 129.0 (C-18), 128.3 (C-10'), 128.42

(C-10), 128.45 (C-16), 128.5 (C-17), 128.6 (C-13), 129.9 (d, $^1J_{PC}$ = 9.4 Hz, C-9'), 130.4 (d, $^1J_{PC}$ = 9.2 Hz, C-9), 131.2 (d, $^1J_{PC}$ = 97.9 Hz, C-7'), 131.7 (d, $^1J_{PC}$ = 2.9 Hz, C-8'), 131.9 (d, $^1J_{PC}$ = 2.7 Hz, C-8), 132.9 (d, $^1J_{PC}$ = 93.2 Hz, C-7), 138.6 (d, $^3J_{PC}$ = 2.3 Hz, C-15), 147.9 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = + 37.8 (d, J = 16.4 Hz); + 36.1 (d, J = 15.9 Hz) ppm. – MS (EI) *m/z* (%): 502 [M^++H], 362 (19) [Ph-C-[CH-P(Ph)Me]$_2$], 334 (23) [CH-NH-O-[C-P(O)(Ph)Me]$_2$], 180 (57) [C-C-P(Ph)Me-O-NH], 165 (74) [C-O-C-P(O)(Ph)Me], 139 (66) [Ph(Me)P=O], 91 (62) [PhN].– HR-MS (ESI) calcd for: $[M+H]^+$ ($C_{29}H_{29}NO_3P_2$): calcd. 502.1701, found 502.1708. – Anal ($C_{29}H_{29}NO_3P_2$): Calcd. C 69.45, H 5.83, N 2.79; found: C 68.96, H 5.91, N 2.80.

Reduction of New *P*-Chiral Diphosphine Dioxides. Synthesis of Disulfides, Diboranes and Diphosphines

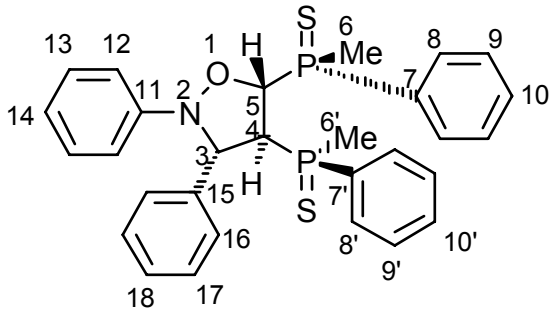


(R_P,S_P)-**8a** (R_P,S_P)-**9a**

(R_P,S_P)-**8b** (R_P,S_P)-**9b**

To the stirred diphosphine dioxide (R_P,S_P)-**8a** (100 mg, 0.2 mmol) in THF (4 mL) was added polymethylhydrosiloxane (PMHS) (0.4 mL), and the mixture was degassed two times. Ti(*i*-OPr)$_4$ (0.2 mL, 0.6 mmol) was added via syringe and the reaction mixture was heated at 66 ºC for 17 h. After cooling to 25 ºC, the THF was removed at reduced pressure, and to the residue was added freshly distilled benzene (3 mL). Sulfur (150 mg, 4.7 mmol) was added as a powder, and the reaction mixture was stirred for 2 h at 70 ºC. After completed reaction and solvent removal, the black residue was purified by column chromatography (SiO_2, 100x4 cm, toluene) to give diphosphine disulfide (R_P,S_P)-**9a** 102.2 mg (0.2 mmol, 96 %) as a colorless viscous oil, which crystallized on standing to give a colorless solid.

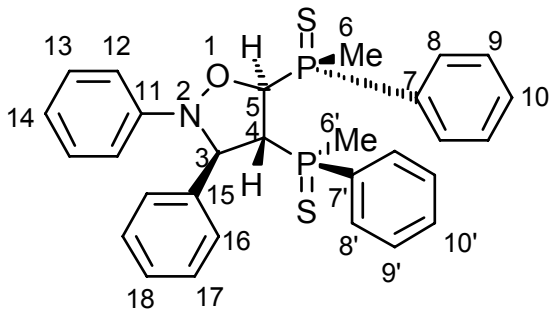
(4*S*$_P$,5*R*$_P$)-(–)-Bis-(4*S*,5*R*)-[methyl(phenyl)thiophosphinyl]-(*N*,3*S*)-(diphenyl)isoxazolidine (9a)



(*R*$_P$,S$_P$)-**9a**

(*R*$_P$,*S*$_P$)-**9a**: M. p. = 71 ºC.- $[\alpha]^{D}_{20}$ = + 91.0 (*c* = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 3055 (w) cm^{-1}, 1596 (s), 1487 (s), 1454 (w), 1435 (w), 1408 (w), 1310 (w), 1287 (w), 1158 (w), 1105 (s, C-N), 1044 (w), 999 (w), 886 (s), 742 (s), 690 (s, P=S). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 1.70 (d, $^2J_{PH}$ = 12.9 Hz, 3H, 6-H), 2.08 (d, $^2J_{PH}$ = 13.7 Hz, 3H, 6-H'), 4.61 (dddd, $^2J_{PH}$ = 20.1 Hz, *J* = 14.0 Hz, *J* = 9.5 Hz, *J* = 3.8 Hz, 1H, 5-H), 4.90 (m, 2H, 3-H, 4-H), 7.03-7.76 (m, 20H$_{Ar}$) ppm. – ^{13}C NMR ($CDCl_3$, BB, DEPT, HMQC, HMBC, HH-COSY, 100.6 MHz): δ = 17.7 (d, $^1J_{PC}$ = 57.1 Hz, C-6), 20.3 (d, $^1J_{PC}$ = 56.9 Hz, C-6), 54.3 (dd, $^1J_{PC}$ = 51.6 Hz, $^1J_{PC}$ = 7.7 Hz, C-4), 74.4 (d, $^2J_{PC}$ = 4.4 Hz, C-3), 79.9 (dd, $^1J_{PC}$ = 54.8, *J* = 1.9 Hz, C-5), 121.1 (C-12), 126.1 (C-13), 128.3 (d, $^2J_{PC}$ = 2.5 Hz, C-8'), 128.5 (d, $^2J_{PC}$ = 3.1 Hz, C-8), 128.6 (C-14), 128.9 (C-18), 129.0 (C-17), 129.2 (d, $^1J_{PC}$ = 79.7 Hz, C-7'), 129.6 (C-16), 130.2 (d, $^3J_{PC}$ = 10.4 Hz, C-9'), (d, $^4J_{PC}$ = 2.9 Hz, C-10'), 131.5 (d, $^3J_{PC}$ = 10.4 Hz, C-9), 131.8 (d, $^4J_{PC}$ = 2.9 Hz, C-10), 131.9 (d, $^1J_{PC}$ = 73.9 Hz, C-7), 136.9 (d, $^3J_{PC}$ = 1.9 Hz, C-15), 147.3 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = + 46.7 (d, *J* = 29.7 Hz); + 50.93 (d, *J* = 28.7 Hz) ppm. – MS (EI) *m/z* (%): 534 [M^++H], 378 (22) [O-N-C-[CH-P(S)(Ph)Me]$_2$], 336 (15) [[HC-P(S)(Ph)Me]$_2$], 238 (31) [N-C(Ph)-C-P(Ph)Me], 181 (45) [C-CH-P(Ph)Me-O-NH], 155 (100) [Ph(Me)P=S], 91 (32) [PhN]. – HR-MS (ESI) for $[M+H]^+$ ($C_{29}H_{30}NOP_2S_2$): Calcd. 534.1246, found 534.1244. – Anal ($C_{29}H_{29}NOS_2P_2$): Calcd C 65.27, H 5.48, N 2.62; found C 65.35, H 5.78, N 2.53.

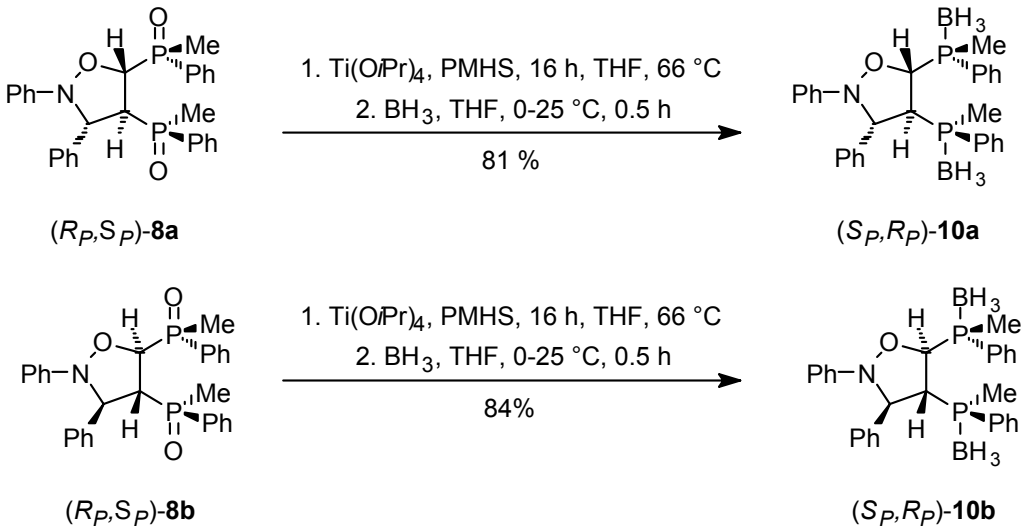
(4*S*$_P$,5*R*$_P$)-(–)-Bis-(4*R*,5*S*)-[methyl(phenyl)thiophosphinyl]-(*N*,3*R*)-(diphenyl)isoxazolidine (9b)



(R_P,S$_P$)-**9b**

(R_P,S_P)-**9b** was obtained by the procedure described above for (R_P,S_P)-**9a** as a white powder (98.9 mg, 0.2 mmol, 93 %). M. p. = 142 ºC. Column chromatography (SiO_2, 100x4 cm, hexane / EtOAc 7:3).

(R_P,S_P)-**9b**: $[\alpha]^D_{20}$ = –205.0 (c = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 3055 (w) cm^{-1}, 1596 (s), 1488 (s), 1454 (w), 1436 (s), 1406 (w), 1310 (w), 1289 (w), 1175 (w), 1157 (w), 1103 (s, C-N), 1072 (w), 1026 (w), 1000 (w), 884 (s), 741 (s), 689 (s, P=S). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 2.25 (d, $^2J_{PH}$ = 13.3 Hz, 3H, 6-H), 2.3 (d, $^2J_{PH}$ = 12.9 Hz, 3H, 6-H'), 3.73 (m, 1H, 4-H), 4.15 (dd, J = 8.5 Hz, $^2J_{PH}$ = 17.8 Hz, 1H, 3-H), 5.31 (dddd, $^2J_{PH}$ = 20.4 Hz, J = 12.3 Hz, J = 7.9 Hz, J = 4.4 Hz, 1H, 5-H), 5.74 (d, J = 7.2 Hz, 2H, 16-H), 6.58-7.64 (m, 16H$_{Ar}$), 8.19 (m, 2H, 9'-H) ppm. – ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, HMBC, HH-COSY, $CDCl_3$): δ = 18.6 (d, $^1J_{PC}$ = 58.6 Hz, C-6), 22.8 (d, $^1J_{PC}$ = 58.1 Hz, C-6), 53.2 (dd, $^1J_{PC}$ = 51.7 Hz, $^1J_{PC}$ = 7.3 Hz, C-4), 73.7 (d, $^2J_{PC}$ = 4.9 Hz, C-3), 80.5 (dd, $^1J_{PC}$ = 59.2 Hz, $^1J_{PC}$ = 1.0 Hz, C-5), 121.4 (C-12), 125.9 (C-14), 127.2 (C-13), 127.6 (C-17), 127.9 (C-10), 128.0 (C-18), 128.1 (d, $^4J_{PC}$ = 0.8 Hz, C-10'), 128.2 (C-16), 129.0 (dd, $^1J_{PC}$ = 78.4 Hz, J = 0.7 Hz, C-7), 129.2 (d, $^1J_{PC}$ = 72.5 Hz, C-7'), 131.2 (d, $^3J_{PC}$ = 10.4 Hz, C-9') 131.5 (d, $^2J_{PC}$ = 2.9 Hz, C-8'), 132.2 (d, $^2J_{PC}$ = 3.1 Hz, C-8), 133.8 (d, $^3J_{PC}$ = 10.2 Hz, C-9), 136.1 (d, $^3J_{PC}$ = 1.5 Hz, C-15), 147.1 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = + 43.3 (d, J = 27.2 Hz), + 46.8 (d, J = 27.2 Hz) ppm. – MS (EI) *m/z* (%):534 [M$^+$+H], 378 (22) [O-N-C-[CH-P(S)(Ph)Me]$_2$], 336 (15) [[HC-P(S)(Ph)Me]$_2$], 238 (31) [N-C(Ph)-C-P(Ph)Me], 181 (45) [C-CH-P(Ph)Me-O-NH], 155 (100) [Ph(Me)P=S], 91 (32) [PhN]. – HR-MS (ESI) for [M+H]$^+$ ($C_{29}H_{30}NOP_2S_2$): Calcd. 534.1246, found 534.1244. – Anal ($C_{29}H_{29}NOS_2P_2$): Calcd. C 65.27, H 5.48, N 2.62; found: C 65.38, H 5.84, N 2.58.

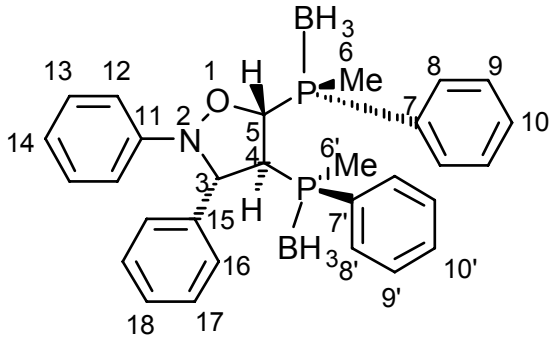


(R_P,S_P)-**8a** (S_P,R_P)-**10a**

(R_P,S_P)-**8b** (S_P,R_P)-**10b**

(4R_P,5S_P)-(+)-Bis-(4*S*,5*R*)-boranato[methyl(phenyl)phosphino]-(*N*,3*S*)-(diphenyl) isoxazolidine (10a)

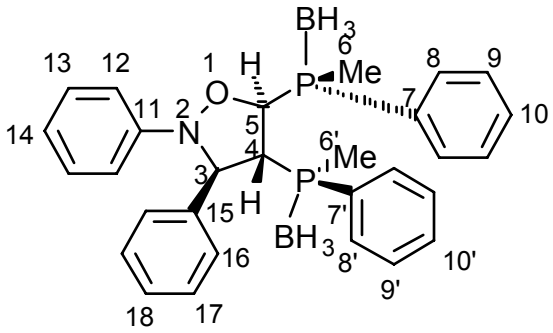
Polymethylhydrosiloxane (PMHS, 0.8 mL, excess) was added to the stirred diphosphine dioxide (S_P,R_P)-**8a** (200 mg, 0.4 mmol) in THF (7 mL), and the mixture was degassed two times. Ti(*i*-OPr)$_4$ (3 equiv., 0.35 mL, 1.2 mmol) was added via syringe, and the reaction mixture was heated at 66 ºC for 17 h. After cooling to 25 ºC, the reaction mixture was filtered trough silica gel under argon with THF (60 mL), which was thereafter evaporated. THF (10 mL) was again added to the residue, and the mixture was cooled to 0 ºC. Borane-THF complex (1.0 M in THF) (0.172 g, 2 mL, 2.0 mmol) was added dropwise over 3 min, and the reaction mixture was allowed to warm to 25 ºC. After 0.5 h 15 mL of water was carefully added and carefully extracted with EtOAc (4x20 mL). The collected extracts were dried over $MgSO_4$. Column chromatography (SiO_2, 4x50 cm, hexane / EtOAc 9:1) gave the desired diphosphine borane (S_P,R_P)-**10a** as a white solid (160.7 mg, 0.3 mmol, 81%).



(S_P,R_P)-**10a**

(S_P,R_P)-**10a**: M.p. = 74 ºC. - $[\alpha]^{D}_{20}$ = + 125.8 (c = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 2991 (w) cm^{-1}, 2375 (br, B-H), 2169 (w), 1596 (w), 1488 (s), 1454 (w), 1436 (w), 1412 (w), 1260 (w), 1180 (w), 1111 (w), 1060 (s, C-N), 888 (s), 742 (s), 690 (s). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.5-1.2 (br, 6H, BH_3), 1.42 (d, $^2J_{PH}$ = 10.2 Hz, 3H, 6-H'), 1.67 (d, $^2J_{PH}$ = 10.2 Hz, 3H, 6-H), 3.95-4.03 (m, 1H, 5-H), 4.64 (dddd, $^2J_{PH}$ = 16.6 Hz, J = 8.3 Hz, J = 4.8 Hz, J = 3.4 Hz, 1H, 4-H), 4.72 (dd, $^3J_{PH}$ = 14.7 Hz, J = 7.8 Hz; 1H, 3-H), 6.95-7.57 (m, 20H_{Ar}) ppm. – ^{13}C NMR (100.6 MHz, BB, DEPT, $CDCl_3$,): δ = 7.8 (d, $^1J_{PC}$ = 39.1 Hz, C-6'), 10.2 (d, $^1J_{PC}$ = 38.7 Hz, C-6), 51.5 (dd, $^1J_{PC}$ = 31.3 Hz, $^1J_{PC}$ = 10.2 Hz, C-4), 74.3 (d, $^2J_{PC}$ = 7.3 Hz, C-3), 76.5 (d, $^1J_{PC}$ = 32.8, $^1J_{PC}$ = 3.3 Hz, C-5), 120.2 (C-12), 125.3 (C-14), 125.7 (C-13), 126.3 (d, $^1J_{PC}$ = 54.3 Hz, C-7), 128.2 (C-16), 128.7 (C-17), 128.75 (C-10'), 128.8 (d, $^1J_{PC}$ = 53.1 Hz, C-7'), 128.9 (C-10), 131.3 (d, $^4J_{PC}$ = 2.5 Hz, C-10'), 131.6 (d, $^2J_{PC}$ = 8.8 Hz, C-8'), 131.9 (d, $^4J_{PC}$ = 2.5 Hz, C-10), 132.4 (d, $^2J_{PC}$ = 9.0 Hz, C-8), 137.1 (d, $^3J_{PC}$ = 2.3 Hz, C-15), 147.3 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = + 17.7 (d, J = 41.6 Hz), +24.6 (d, J = 45.5 Hz). – MS (EI) *m/z* (%):358 (23) [C-O-N(Ph)-C-C-P(BH_3)(Ph)Me], 346 (43) [O-N(Ph)-CH-C-CH-P(Ph)Me], 246 (41) [N-C(Ph)-C-P(B)C-Ph], 180 (46) [C-CH-P(Ph)Me-O-N], 123 (97) [P(Ph)Me], 91 (80) [PhN]. – Anal ($C_{29}H_{35}NOB_2P_2$): Calcd. C 70.06, H 7.10, N 2.82; found C 69.57, H 7.16, N 2.76.

(4R_P,5S_P)-(–)-Bis-(4*R*,5*S*)-boranato[methyl(phenyl)phosphino]-(*N*,3*R*)-(diphenyl)isoxazolidine (10b)



(R_P,S$_P$)-**10b**

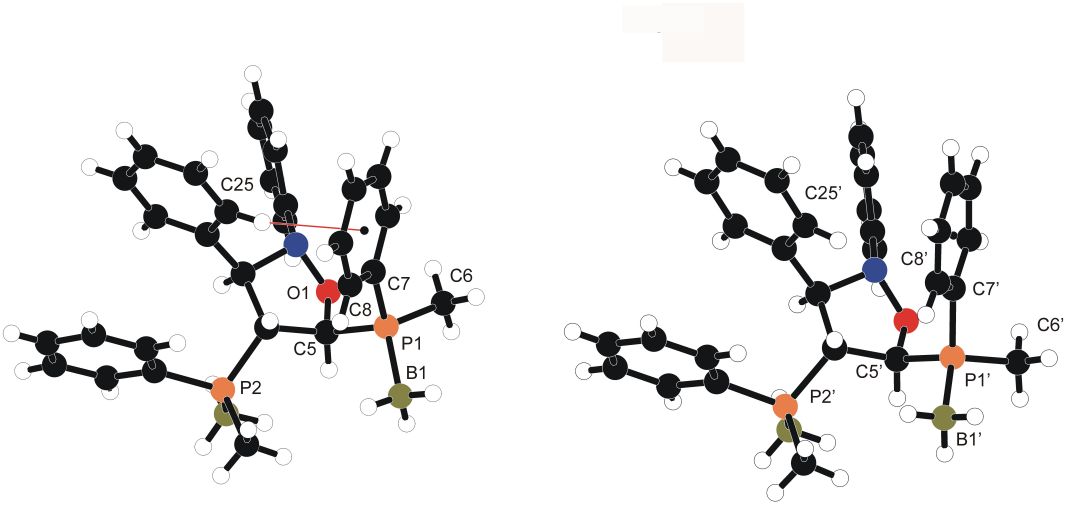
(S_P,R_P)-**10b** was obtained by the procedure described above for (S_P,R_P)-**10a** as a white powder (166.7 mg, 0.3 mmol, 84 %). M. p. = 115-116 ºC. Column chromatography (SiO_2, 4x50 cm, toluene).

(*S*$_P$,*R*$_P$)-**10b**: $[\alpha]^{D}_{20}$ = –269.0 (*c* = 0.5, $CHCl_3$). – IR (ATR): $\tilde{\nu}$ = 2924 (w) cm^{-1}, 2363 (br, B-H), 1593 (w), 1485 (s), 1454 (w), 1436 (w), 1412 (w), 1293 (w), 1260 (s), 1224 (w), 1188 (w), 1063 (s, C-N), 1023 (s), 891 (s), 794 (s), 743 (s), 691 (s). – ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 0.5-1.2 (br, 6H, B*H*$_3$), 1.81 (d, $^2J_{PH}$ = 9.9 Hz, 3H, 6-H), 1.92 (d, $^2J_{PH}$ = 9.9 Hz, 3H, 6'-H), 3.41-3.51 (m, 1H, 5-H), 4.07 (dd, $^3J_{PH}$ = 15.4 Hz, *J* = 8.5 Hz, 1H, 3-H), 5.02 (dddd, $^2J_{PH}$ = 16.1 Hz, *J* = 10.9 Hz, *J* = 6.5 Hz, *J* = 4.4 Hz, 1H, 4-H), 5.76 (d, *J* = 7.2 Hz, 2H, 16-H), 6.95-7.57 (m, 18H$_{Ar}$) ppm. – ^{13}C NMR (100.6 MHz, BB, DEPT, HMQC, $CDCl_3$): δ = 9.2 (d, $^1J_{PC}$ = 42.9 Hz, C-6'), 13.2 (d, $^1J_{PC}$ = 38.7 Hz, C-6), 49.7 (dd, $^1J_{PC}$ = 32.9 Hz, $^1J_{PC}$ = 8.05 Hz, C-4), 74.4 (d, $^2J_{PC}$ = 8.2 Hz, C-3), 77.1 (d, $^1J_{PC}$ = 30.5, $^1J_{PC}$ = 5.2 Hz, C-5), 121.0 (C-12), 125.2 (C-14), 125.8 (C-13), 126.0 (d, $^1J_{PC}$ = 51.4 Hz, C-7'), 126.4 (dd, $^1J_{PC}$ = 53.7 Hz, $^1J_{PC}$ = 0.8 Hz, C-7'), 127.7 (C-17), 128.2 (d, $^3J_{PC}$ = 10.2 Hz, C-9'), 128.3 (d, $^3J_{PC}$ = 10.2 Hz, C-9), 128.4 (C-18), 128.9 (C-16), 131.6 (d, $^4J_{PC}$ = 2.5 Hz, C-10'), 132.1 (d, $^2J_{PC}$ = 9.4 Hz, C-8'), 132.2 (d, $^4J_{PC}$ = 2.5 Hz, C-10), 134.7 (d, $^2J_{PC}$ = 9.4 Hz, C-8), 135.9 (d, $^3J_{PC}$ = 1.3 Hz, C-15), 147.1 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = +17.1 (d, *J* = 45.7 Hz), + 19.7 (d, *J* = 44.6 Hz) ppm. – MS (EI) *m/z* (%): 494 [M^+-3H], 358 (23) [C-O-N(Ph)-C-C-P(BH_3)(Ph)Me], 346 (43) [O-N(Ph)-CH-C-CH-P(Ph)Me], 246 (41) [N-C(Ph)-C-P(B)C-Ph], 180 (46) [C-CH-P(Ph)Me-O-N], 123 (97) [P(Ph)Me], 91 (80) [PhN]. – Anal ($C_{29}H_{35}NOB_2P_2$): Calcd C 70.06, H 7.10, N 2.82; found C 69.49, H 7.37, N 2.70.

Crystal Structure Analysis of (*Sp,Rp*)-10b:

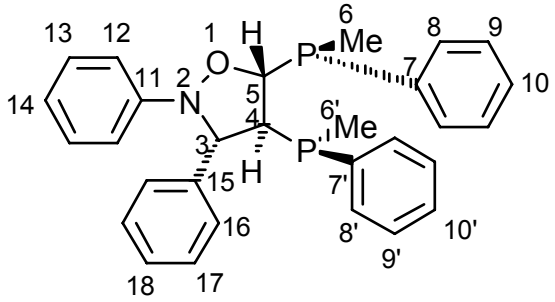
Crystals were obtained by slow evaporation from toluene at 20 ºC. Empirical formula $C_{29}H_{35}B_2NOP_2$, formula weight 497.14 g/mol, crystal system monoclinic, space group $P2_1$, *Z* = 4, unit cell dimensions *a* = 16.370(6), *b* = 11.336(7), *c* = 17.169(6) Å, β = 112.33(4)º, *V* = 2947 (3) Å^3, *T* = 294 K, $d_{calc.}$ = 1.120 g/cm^3, μ = 0.169 mm^{-1}, $Mo_{K\alpha}$ radiation (λ= 0.71073 Å), crystal size 0.37 x 0.29 x 0.17 mm^3, STOE IPDS one-axis diffractometer with imaging plate detector, θ-range 2.21 to 25.06º, empirical absorption correction, T_{min} = 0.9108, T_{max} = 0.9741, reflections collected / unique 38592 / 10351 [*R*(int) = 0.0977], direct methods, full-matrix least-squares refinement on F^2, R_1 = 0.0422 ($I > 2\sigma_I$), wR_2 = 0.0940, goodness-of-fit on F^2 = 0.768, final difference electron density 0.20 and –0.15 eÅ^{-3}, completeness of data 98.7%, Flack parameter -0.01(5).

In the cystal structure, two crystallographically independent molecules exist (see Figure below). Both molecules possess the same absolute configuration but differ slightly in their conformation caused by packing forces in the crystal.



The different conformations mainly concern the substituents at the C5/C5' atoms of the isoxazolidine ring as seen by the following torsion angles (°): O1-C5-P1-C7, 81.5(3); O1'-C5'-P1'-C7', 63.6(2); O1-C5-P1-C6, -32.8(3); O1'-C5'-P1'-C6', -49.1(3); O1-C5-P1-B1, -153.3(3); O1'-C5'-P1'-B1', -169.8(2); B1-P1-C7-C8, -29.1(4); B1'-P1'-C7'C8', -12.2(3). For one molecule (left-hand side in the Figure), there appear to exist edge-to-face π···π interactions between two phenyl rings, as indicated by the orientation of the C25-H25 bond with respect to the phenyl ring attached at the P1 atom and the following contact distances (Å) and angles (°) [M = centroid of the phenyl ring]: C25···M, 3.584(11); H25···M, 2.67; C25-H25···M, 168.

(4*R*$_P$,5*S*$_P$)-(–)-Bis-(4*S*,5*R*)-[methyl(phenyl)phosphinyl]-(*N*,3*S*)-(diphenyl) isoxazolidine (11a)

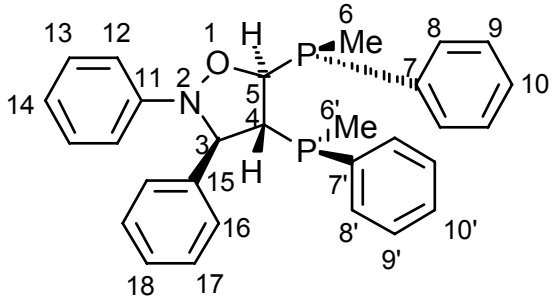


(*S*$_P$,R$_P$)-**11a**

Diphosphine borane (*S*$_P$,*R*$_P$)-**10a** (50.0 mg, 0.1 mmol) and DABCO (38.6 mg, 0.3 mmol) in toluene (2 mL) were placed in a Schlenk flask. The reaction mixture was stirred at 70 ºC over 3 h. After filtration through silica gel with toluene (50 mL) as eluent and evaporation in high vacuum, pure diphosphine (*S*$_P$,*R*$_P$)-**11a** was obtained as an air-sensitive viscous white solid 43.2 mg (0.1 mmol, 87 %). To avoid oxidation, (*S*$_P$,*R*$_P$)-**11** was stored in a Schlenk flask under argon at –25 ºC.

(*S*$_P$,*R*$_P$)-**11a**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 1.20 (d, $^2J_{PH}$ = 4.3 Hz, 3H, 6-H), 1.44 (d, $^2J_{PH}$ = 4.3 Hz, 3H, 6'-H), 2.71 (m, 1H, 4-H), 4.13 (dd, J = 9.3 Hz, $^2J_{PH}$ = 18.7 Hz, 1H, 5-H), 4.5 (dd, J = 5.7 Hz, $^3J_{PH}$ = 10.7 Hz, 1H, 3-H), 6.66 – 7.54 (m, 20H$_{Ar}$) ppm. – ^{13}C NMR (100.6 MHz BB, DEPT, $CDCl_3$): δ = 7.1 (d, $^1J_{PC}$ = 15.0 Hz, C-6'), 10.2 (dd, $^1J_{PC}$ = 15.9 Hz, $^1J_{PC}$ = 3.5 Hz, C-6), 49.7 (dd, $^1J_{PC}$ = 32.9 Hz, $^1J_{PC}$ = 8.1 Hz, C-4), 74.4 (d, $^2J_{PC}$ = 8.2 Hz, C-3), 77.08 (d, $^1J_{PC}$ = 30.5, $^1J_{PC}$ = 5.2 Hz, C-5), 114.6 (C-12), 121.7 (C-14), 126.8 (C-13), 127.2 (C-17), 128.3 (d, $^3J_{PC}$ = 7.1 Hz, C-9), 128.4 (d, $^3J_{PC}$ = 6.7 Hz, C-9'), 128.6 (C-16), 128.8 (C-18), 129.0 (C-10), 129.1 (C-10'), 132.1 (d, $^1J_{PC}$ = 18.6 Hz, C-7'), 132.1 (d, $^1J_{PC}$ = 19.2 Hz, C-7), 135.7 (d, $^2J_{PC}$ = 15.0 Hz, C-8'), 136.4 (d, $^2J_{PC}$ = 11.9 Hz, C-8), 142.6 (d, $^3J_{PC}$ = 2.5 Hz, C-15), 150.6 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = – 28.8 (d, J = 10.9 Hz), – 30.6 (d, J = 10.9 Hz) ppm.

(4*Rp*,5*Sp*)-(–)-Bis-(4*R*,5*S*)-[methyl(phenyl)phosphinyl]-(*N*,3*R*)-(diphenyl)isoxazolidine (11b)



(R_P,S$_P$)-**11b**

(S_P,R_P)-**11b** was obtained by the procedure described above for (S_P,R_P)-**11a** as an air-sensitive viscous white solid 43.7 mg (0.1 mmol, 88 %). To avoid oxidation, (S_P,R_P)-**11b** was stored in a Schlenk flask under argon at – 25 ºC.

(S_P,R_P)-**11b**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 1.44 (d, $^2J_{PH}$ = 4.3 Hz, 3H, 6-H), 1.62 (d, $^2J_{PH}$ = 4.3 Hz, 3H, 6'-H), 2.52 (dddd, J = 5.2 Hz, J = 9.3 Hz, J = 12.6 Hz, $^2J_{PH}$ = 27.3 Hz, 1H, 4-H), 4.31 (dd, J = 5.7 Hz, $^3J_{PH}$ = 12.2 Hz, 1H, 3-H), 4.42 (ddd, J = 9.4 Hz, J = 14.2 Hz, $^2J_{PH}$ = 23.6 Hz, 1H, 5-H), 6.53 – 7.74 (m, 20H$_{Ar}$) ppm. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 7.1 (d, $^1J_{PC}$ = 11.1 Hz, C-6'), 10.2 (dd, $^1J_{PC}$ = 7.7 Hz, $^1J_{PC}$ = 14.3 Hz, C-6), 56.5 (dd, $^1J_{PC}$ = 27.6 Hz, $^1J_{PC}$ = 9.8 Hz, C-4), 74.9 (dd, $^2J_{PC}$ = 19.4 Hz, $^2J_{PC}$ = 4.2 Hz, C-3), 77.1 (dd, $^1J_{PC}$ = 49.3 Hz, $^1J_{PC}$ = 23.2 Hz, C-5), 114.3 (C-12), 121.5 (C-14), 126.5 (C-13), 126.6 (C-17), 128.0 (d, $^3J_{PC}$ = 7.7 Hz, C-9), 128.2 (C-10), 128.4 (d, $^3J_{PC}$ = 7.5 Hz, C-9'), 128.8 (C-16), 129.0 (C-10'), 129.5 (C-18), 129.6 (C-18), 132.7 (d, $^1J_{PC}$ = 20.0 Hz, C-7'), 134.5 (d, $^1J_{PC}$ = 20.1 Hz, C-7), 136.5 (d, $^2J_{PC}$ = 13.6 Hz, C-8'), 142.6 (d, $^3J_{PC}$ = 3.3 Hz, C-15), 150.8 (C-11) ppm. – ^{31}P NMR ($CDCl_3$, 162 MHz): δ = –27.5 (d, J = 7.6 Hz), –30.2 (d, J = 7.6 Hz) ppm.

(1) Demchuk, O. M.; Pietrusiewicz, K. M.; Michrowska, A.; Grela, K., *Org. Lett.* 2003, **5**, 3217-3220.
(2) Vinokurov, N.; Michrowska, A.; Szmigielska, A.; Drzazga, Z.; Wojciuk, G.; Demchuk, O. M.; Grela, K.; Pietrusiewicz, K. M.; Butenschön, H., *Adv. Synth. Catal.* 2006, **348**, 931-938.
(3) Vinokurov, N.; Garabatos Perera, J. R.; Zhao-Karger, Z.; Wiebcke, M.; Butenschön, H., *Organometallics* 2008, **27**,1878-1886.

^{1}HNMR

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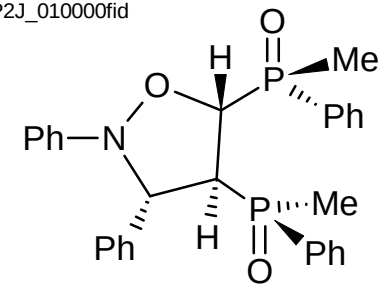

(R*p*, S*p*)-**8a**

^{13}CNMR

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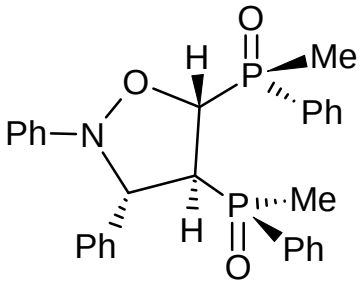

(R*p*, S*p*)-**8a**

^{31}PNMR

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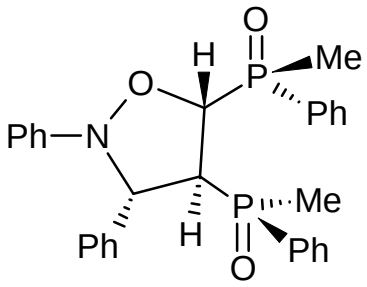
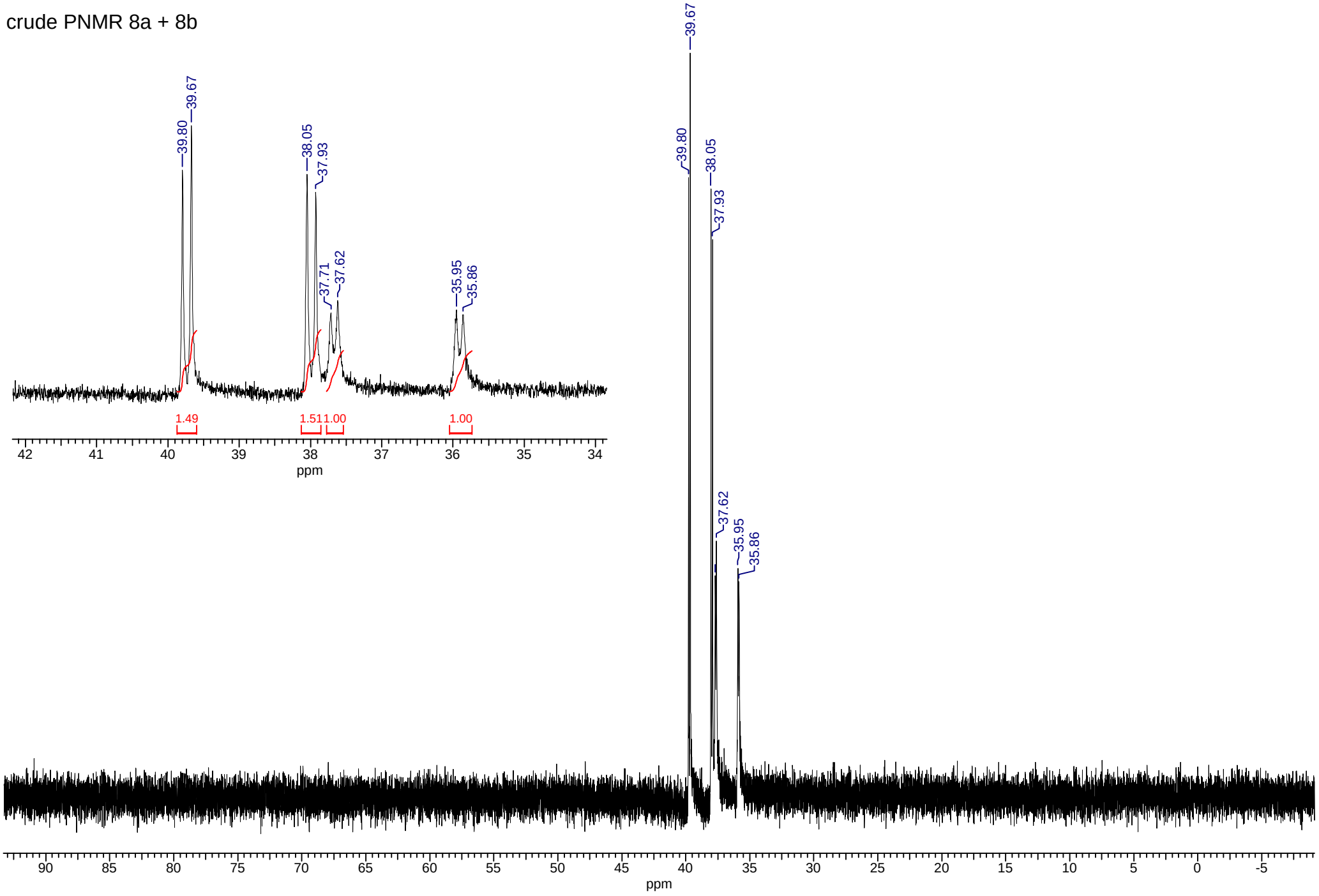


(R*p*, S*p*)-**8a**

crude PNMR 8a + 8b



1HNMR

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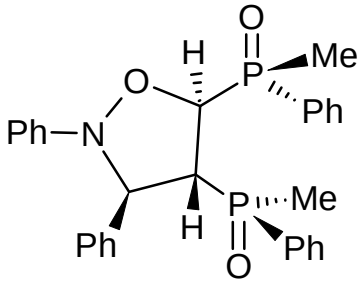
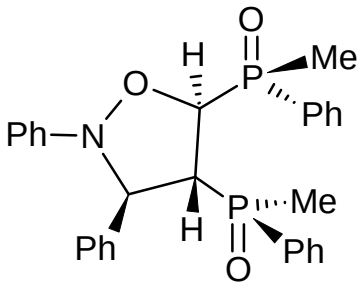


(R*p*, S*p*)-**8b**

^{13}CNMR

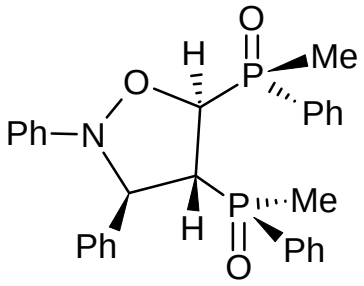
NVCLCP4J_010000fid



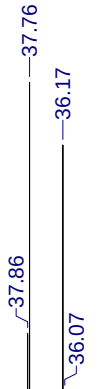
(R*p*, S*p*)-**8b**

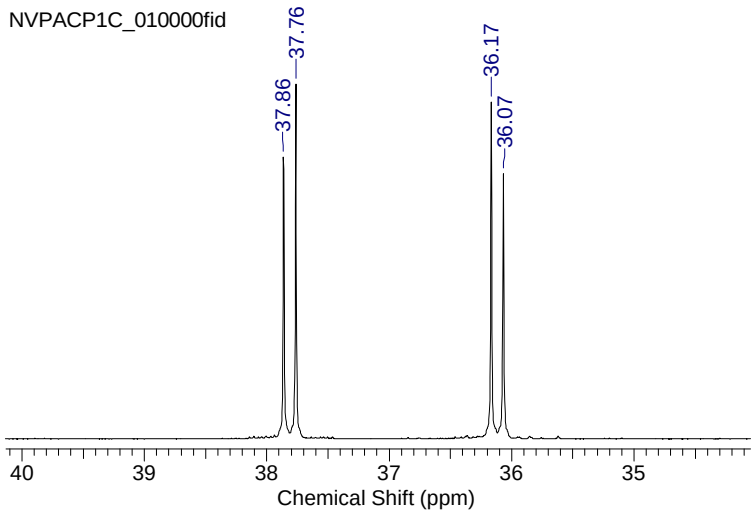
^{31}PNMR

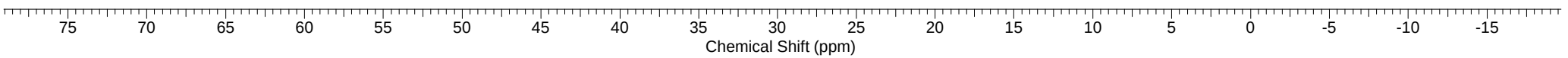
NVPACP1C_010000fid



(R*p*, S*p*)-**8b**







^{1}HNMR

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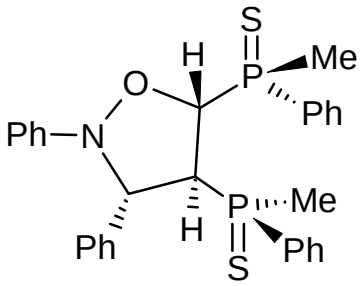
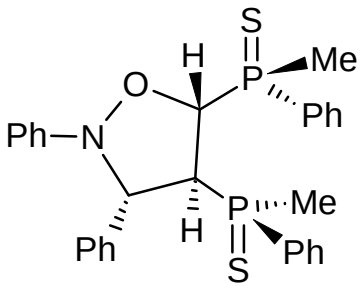


(R*p*, S*p*)-**9a**

^{13}CNMR

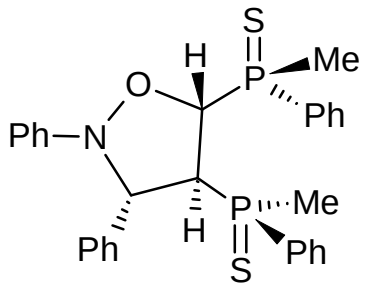
CNMR 9a.esp



(R*p*, S*p*)-**9a**

^{31}PNMR

NVPATI5C_010000fid



(R*p*, S*p*)-**9a**

^{1}HNMR

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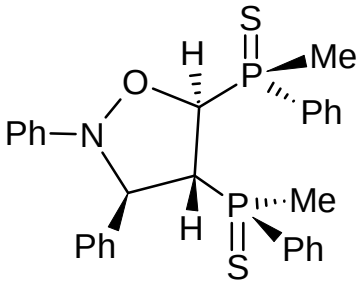

(R*p*, S*p*)-**9b**

^{13}CNMR

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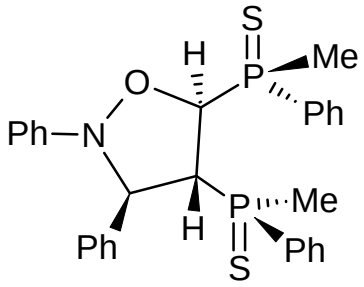

(R*p*, S*p*)-**9b**

^{31}PNMR

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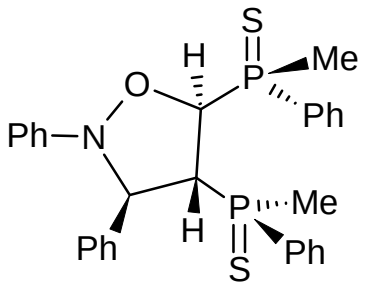

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^{1}HNMR

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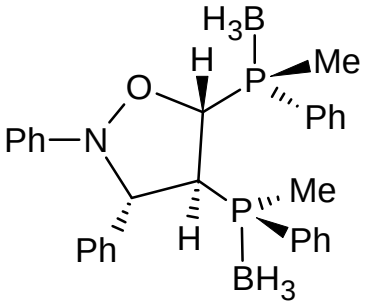
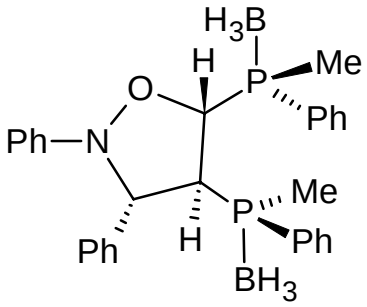


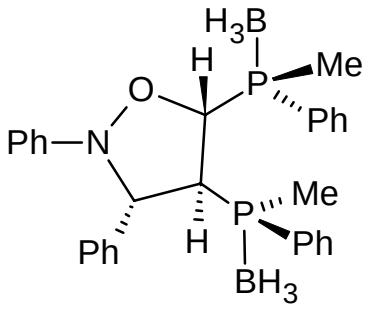
(R*p*, S*p*)-**10a**

^{13}CNMR



(S*p*, R*p*)-**10a**

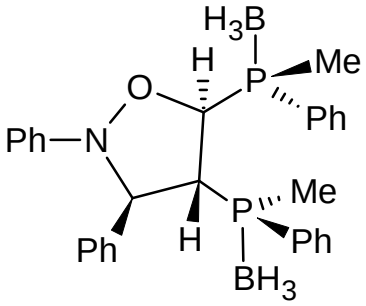
^{31}PNMR



(*Sp*, R*p*)-**10a**

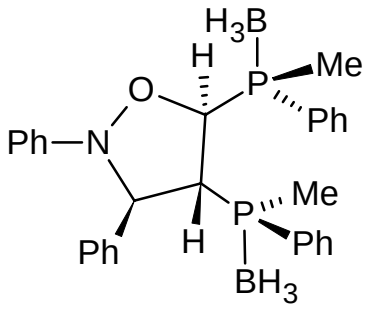
^{1}HNMR

NVHA530J_010000fid



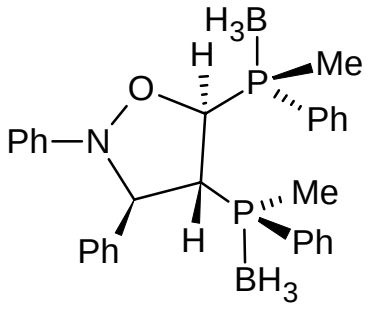
(R*p*, S*p*)-**10b**

^{13}CNMR



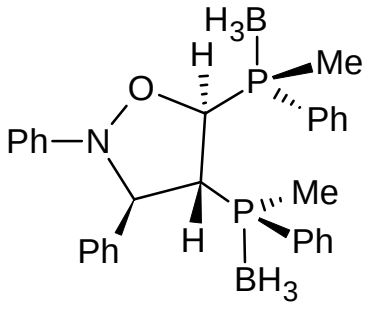
(S*p*, R*p*)-**10b**

^{13}CNMR (DEPT 90)



(*Sp*, R*p*)-**10b**

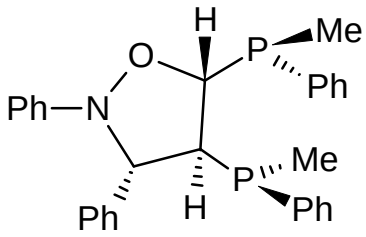
^{31}PNMR



(S*p*, R*p*)-**10b**

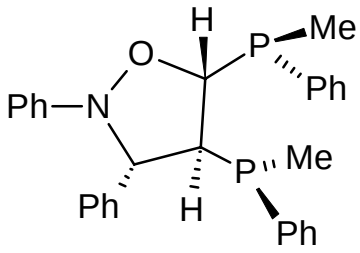
^{1}HNMR

NVHAT11C_010000fid



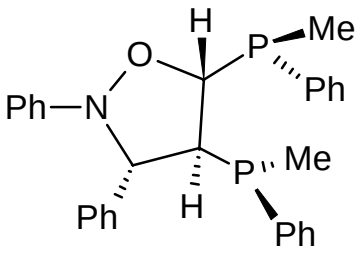
(R*p*, S*p*)-**11a**

^{13}CNMR

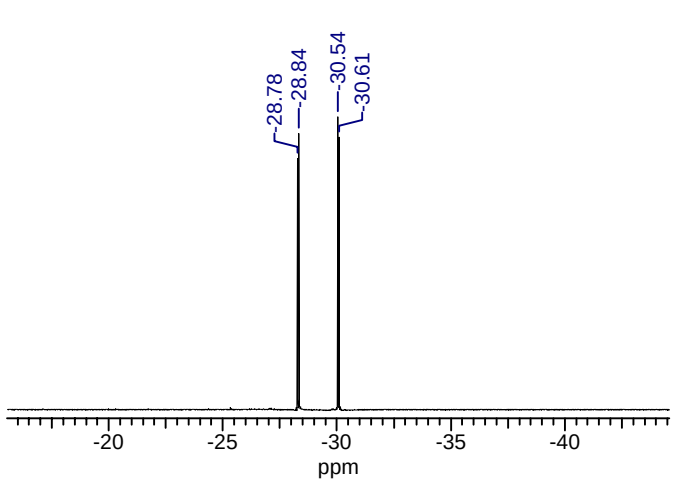


(S*p*, R*p*)-**11a**

^{31}PNMR

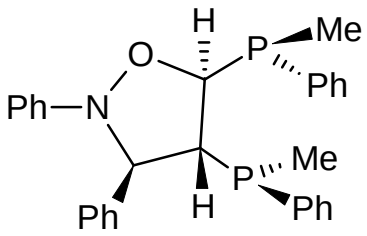


(S*p*, R*p*)-**11a**



^{1}HNMR

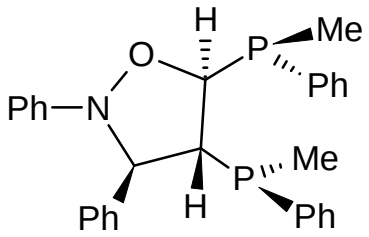
NVHATB3C_010000fid



(R*p*, S*p*)-**11b**

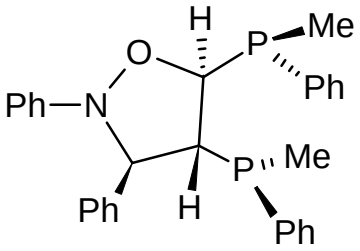
^{13}CNMR

NVCLTB3C_010000fid

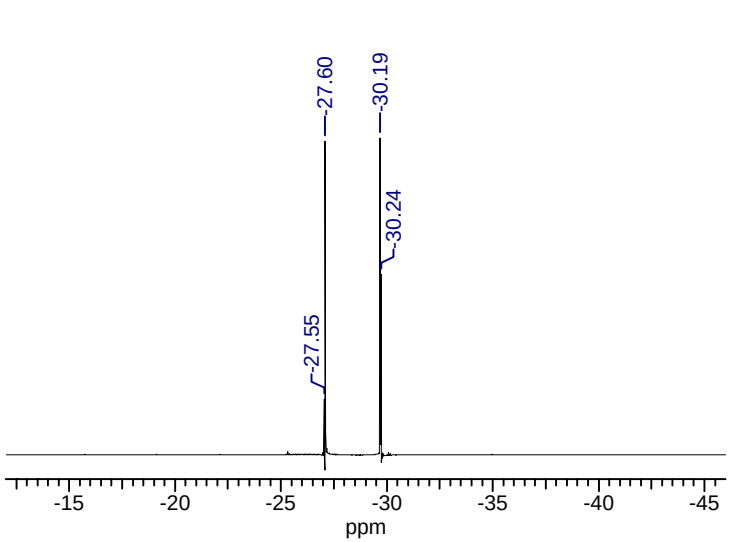


(R*p*, S*p*)-**11b**

^{31}PNMR

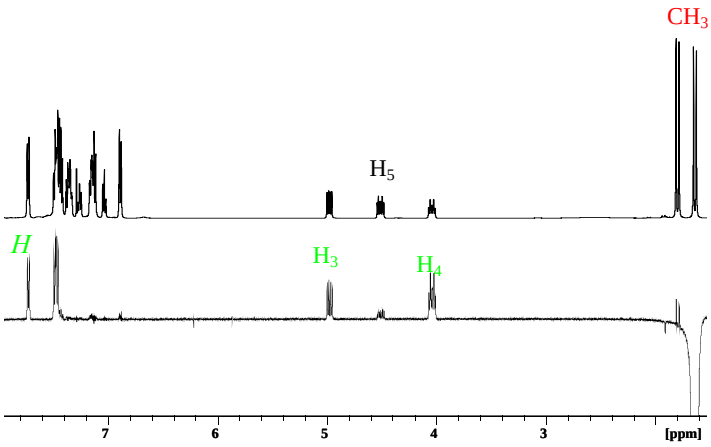


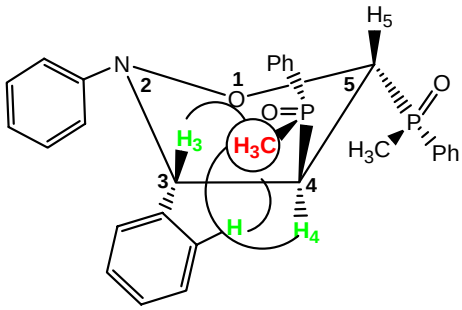
(*Sp*, R*p*)-**11b**



NOE of Diphosphine Dioxides (8a) and (8b)

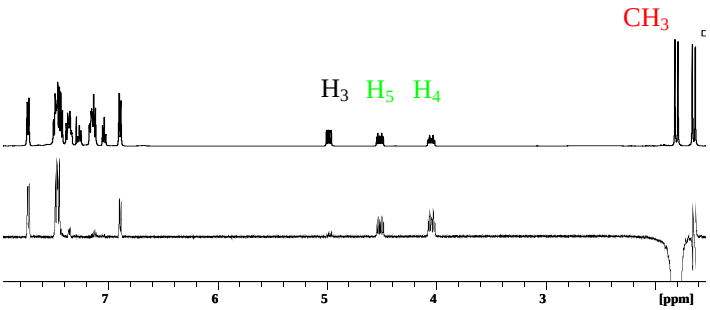
($4S_P$,$5R_P$)-(+)-Bis-(4*S*,5*R*)-[methyl(phenyl)phosphinyl]-(*N*,3*S*)-diphenylisoxazolidine dioxide (8a)

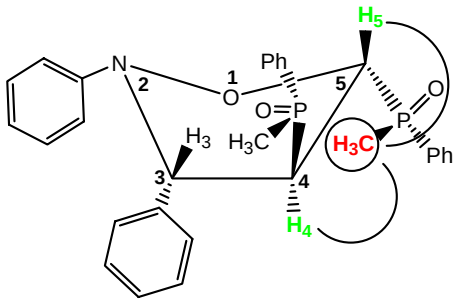




(*Rp,Sp*)-**8a**

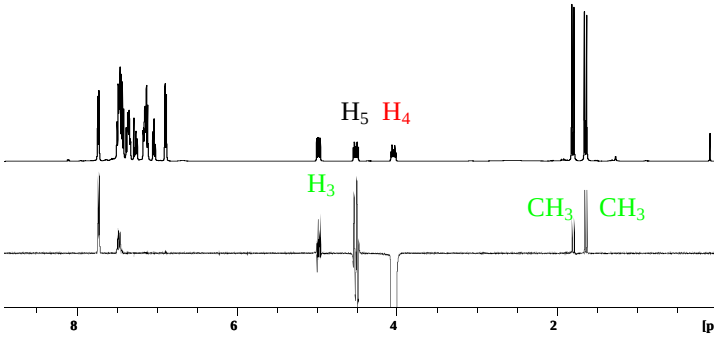
Fig. 1 Irradiation (NOE) of CH_3 at δ = 1.62 ppm

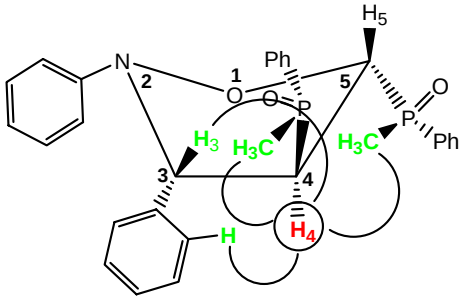




(*Rp,Sp*)-**8a**

Fig. 2 Irradiation (NOE) of CH_3 at δ = 1.78 ppm





(*Rp,Sp*)-**8a**

Fig. 3 Irradiation (NOE) of H_4 at δ = 4.01 ppm

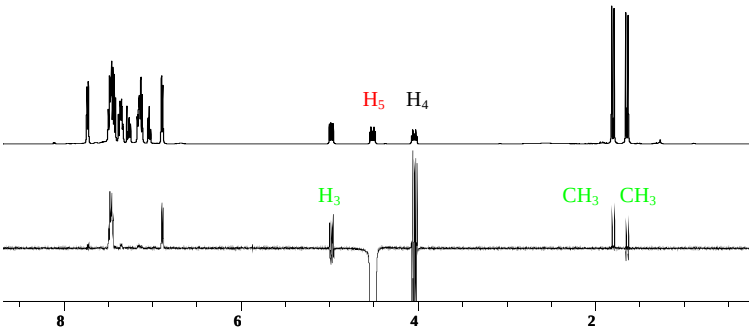
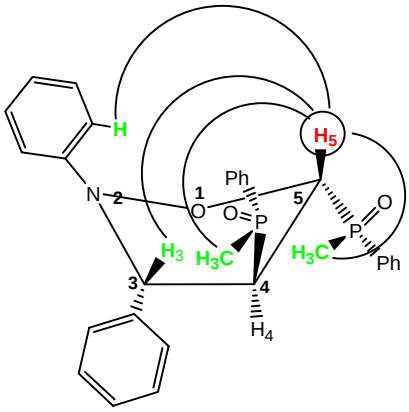
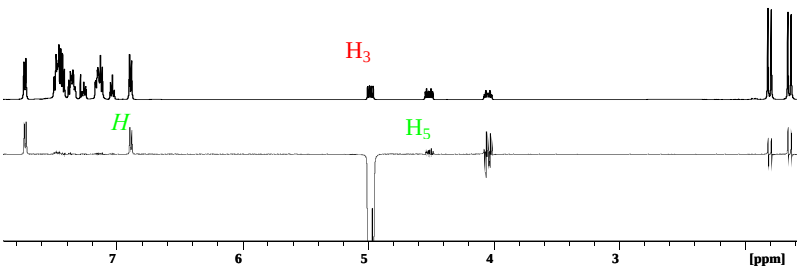
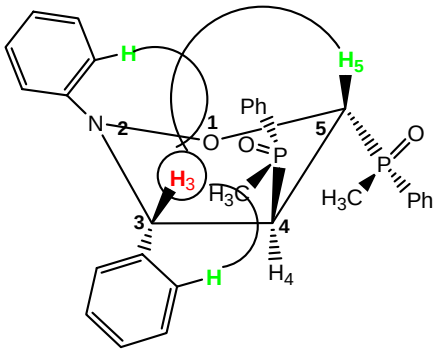


Fig. 4 Irradiation (NOE) of H_5 at 4.47



(*Rp,Sp*)-**8a**

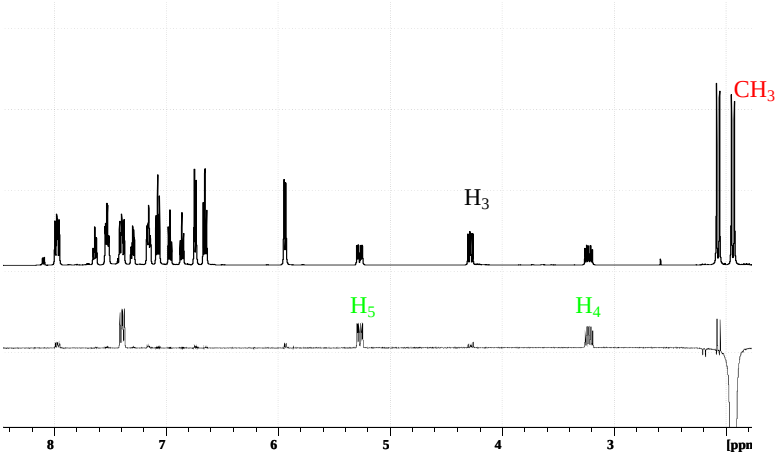


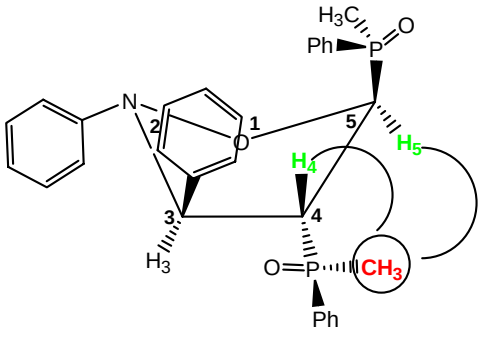


(*Rp,Sp*)-**8a**

Fig. 5 Irradiation (NOE) of H_3 at 4.96 ppm

(4*S*$_P$,5*R*$_P$)-(–)-Bis-(4*R*,5*S*)-([methyl(phenyl)phosphinyl]-(*N*,3*R*)-diphenylisoxazolidine dioxide (8b)





(*Rp,Sp*)-**8b**

Fig. 6 Irradiation (NOE) of CH_3 at 1.92 ppm

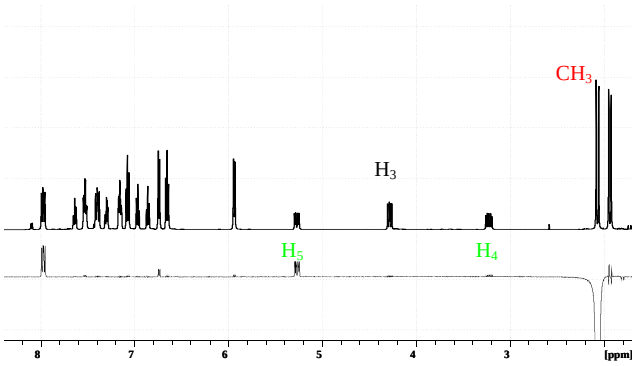
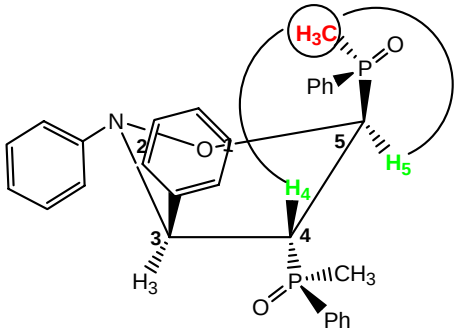


Fig. 7 Irradiation (NOE) of CH_3 at 2.06 ppm



(*Rp,Sp*)-**8b**

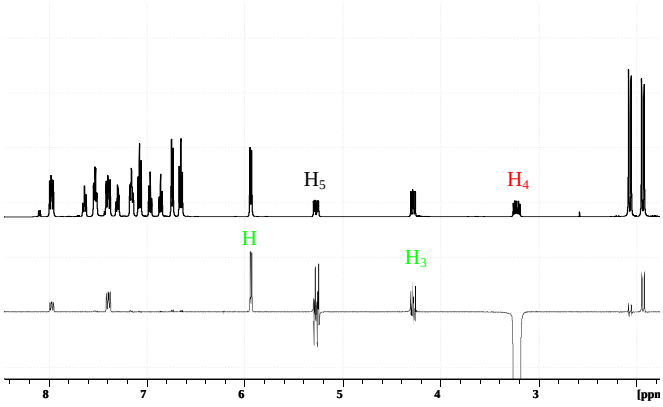
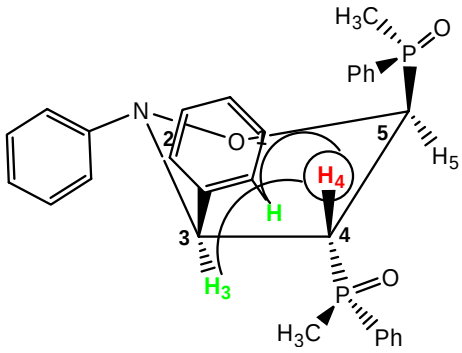


Fig. 8 Irradiation of H_4 at 3.19 ppm



(*Rp,Sp*)-**8b**

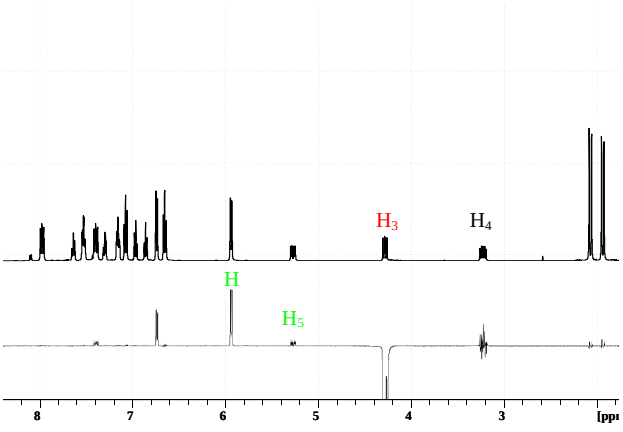
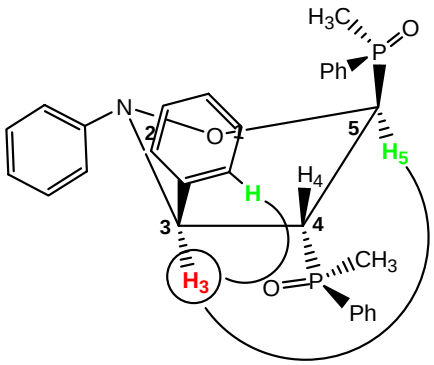


Fig. 9 Irradiation (NOE) of H_3 at 4.26 ppm



(*Rp,Sp*)-**8b**

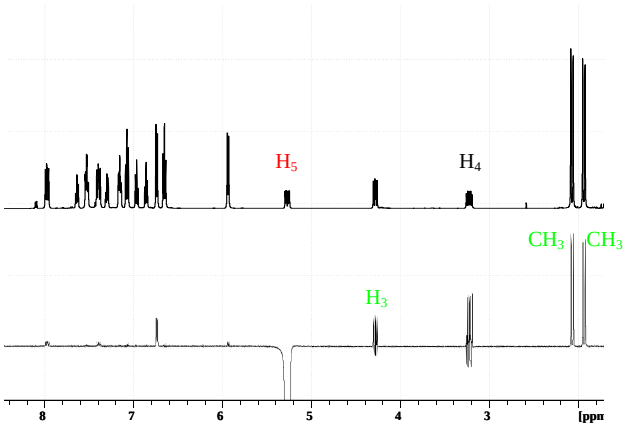
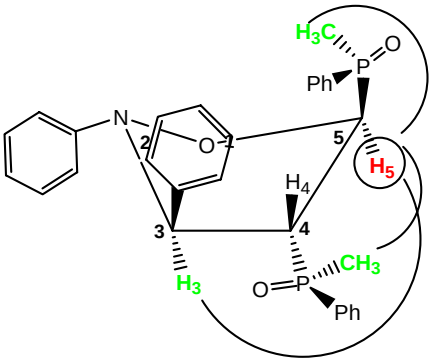


Fig. 10 Irradiation (NOE) of H_5 at 5.23 ppm



(*Rp,Sp*)-**8b**