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Supporting Information

Rh-Catalyzed Enantioselective Conjugate Addition of Arylboronic Acids with a Dynamic Library of Chiral Tropos Phosphorus Ligands

Chiara Monti, Cesare Gennari,* Umberto Piarulli*

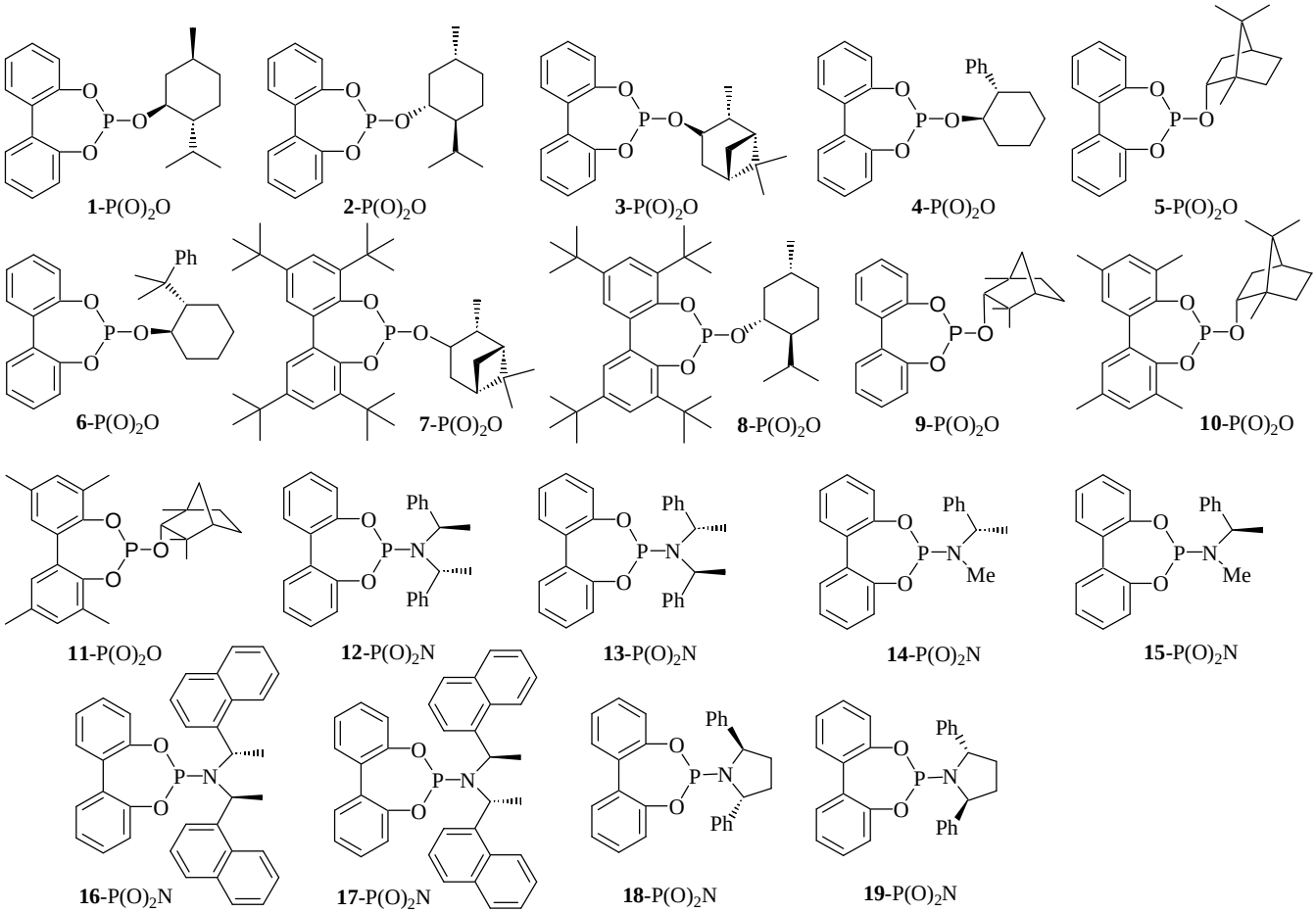
General Remarks: All reactions were carried out in flame-dried glassware with magnetic stirring under argon atmosphere. All commercially available reagents were used as received. The solvents were dried by distillation over the following drying agents and were transferred under nitrogen: CH_2Cl_2 (CaH_2), THF (Na), Et_2O (Na), toluene (Na), Et_3N (CaH_2), pyridine (CaH_2). Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F_{254} precoated glass plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with a ceric ammonium molybdate (CAM) solution. Flash column chromatography was performed using silica gel 60Å, particle size 40–64 μm, following the procedure by Still and co-workers.[1] Proton NMR spectra were recorded on a spectrometer operating at 400.13 MHz. Proton chemical shifts are reported in ppm (d) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$ d 7.26 ppm; C_6D_6, d 7.15 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of doublet. Carbon NMR spectra were recorded on a 400 spectrometer operating at 100.56 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (d) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, d 77.0). ^{31}P NMR spectra were recorded on a 400 spectrometer operating at 162 MHz, with complete proton decoupling. ^{31}P NMR chemical shifts are reported in ppm (d) relative to external 85% H_3PO_4 at 0 ppm (positive values downfield). Infrared spectra were recorded on a standard FT/IR; peaks are reported in cm^{-1}. Optical rotation values were measured on an automatic polarimeter with a 1 dm cell at the sodium D line. Gas chromatography was performed on a GC instrument equipped with a flame ionization detector, using a chiral capillary column. HPLC analyses were performed with a chiral stationary phase column. High resolution mass spectra (HRMS) were performed on a hybrid quadrupole time of flight mass spectrometer equipped with an ESI ion source. A Reserpine solution 100 pg/μl (about 100 count/s), 0.1% HCOOH/CH_3CN 1:1, was used as reference compound (Lock Mass).

General procedure for the synthesis of phosphites: PCl_3 (2 eq, 6 mmol, 525 μl) was added to a solution of the alcohol (1 eq, 3 mmol) in dichloromethane (17 ml), in a Schlenk tube, under argon, at room temperature. After stirring for 2 hours, the solvent and excess PCl_3 were removed under reduced pressure. The resulting residue was dissolved in tetrahydrofuran (7 ml), and a solution of the biphenol (1 eq, 3 mmol) and triethylamine (3 eq, 9 mmol, 1.25 ml) in THF (10 ml) was slowly added. Upon addition, the formation of a white precipitate was immediately observed. The reaction mixture was stirred overnight, and then filtered over a PTFE membrane filter. The solvent was removed and the crude product was purified either by crystallisation or by chromatography, to give the desired compound as a white foamy solid.

General procedure for the synthesis of phosphoramidites: a solution of the amine (1 eq, 3 mmol) and triethylamine (1.13 eq, 3.4 mmol, 472.5 μl) in dry toluene (2.6 ml) was added to a solution of PCl_3 (1 eq, 3 mmol, 262 μl) in toluene (38 ml), in a Schlenk tube, under argon. The reaction mixture was heated to 70°C for 6 hours, and then allowed to cool to room temperature. Triethylamine (2.26 eq, 6.78 mmol, 945 μl) was added, and the mixture was cooled to –78°C. A solution of biphenol (1 eq, 3 mmol) in a 4 : 1 toluene : THF mixture (7.5 ml) was slowly added. The reaction mixture was stirred overnight, while slowly warming to room temperature. The mixture was filtered over a pad of celite, and the solvent removed under reduced pressure. The crude product was purified either by crystallisation or by chromatography, to give the desired compound as a white powder.

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

Bis-[(*S*)-1-naphth-1-yl-ethyl]amine and bis-[(*R*)-1-naphth-1-yl-ethyl]amine were synthesised in two steps, as reported in the literature.[2] (*R*,*R*)-2,5-diphenylpyrrolidine and (*S*,*S*)-2,5-diphenylpyrrolidine were prepared following a literature procedure.[3] 3,3',5,5'-tetramethyl-biphenol[4] and 3,3',5,5'-tetra-*tert*-butyl-biphenol[5] were prepared following the reported procedures.



[2] A. Alexakis, S. Gille, F. Prian, S. Rosset, K. Ditrich, *Tetrahedron Lett.* **2004**, *45*, 1449-1451.
[3] D. J. Aldous, W. M. Dutton, P. G. Steel, *Tetrahedron: Asymmetry* **2000**, *11*, 2455-2462.
[4] A. Alexakis, D. Polet, S. Rosset, S. March, *J. Org. Chem.* **2004**, *69*, 5660-5667.
[5] D. H. R. Barton, S. Choi, B. Hu, J. A. Smith, *Tetrahedron* **1998**, *54*, 3367-3378.

1-$P(O)_2O$, **Biphenol / (1*S*, 2*R*, 5*S*)-(+)-menthol**: 97% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.37 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.30 (t, *J* = 7.5 Hz, 2H, Ar**H**), 7.22-7.20 (m, 2H, Ar**H**), 4.20-4.16 (m, 1H, C**H**), 2.32-2.27 (m, 1H, C**H**), 2.25-2.18 (m, 1H, C**H**), 1.73-1.69 (m, 2H, C**H**), 1.51-1.35 (m, 2H, C**H**), 1.08-1.04 (m, 3H, C**H**), 0.99 (d, *J* = 6.5 Hz, 3H, C$\mathbf{H}_3$), 0.96 (d, *J* = 7.0 Hz, 3H, C$\mathbf{H}_3$), 0.88 (d, *J* = 6.9 Hz, 3H, C$\mathbf{H}_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 156.0, 149.8, 131.8, 130.3, 129.4, 128.1, 125.4, 122.5, 120.3, 118.5, 76.7 (d, $J_{C,P}$ = 17.4 Hz), 48.9, 44.6, 34.5, 32.2, 25.7, 23.3, 22.5, 21.4, 16.0; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 152.8; m.p. = 98°C; IR (CCl_4): ν_{max} = 3068, 3030, 2958, 2871, 1943, 1910, 1600, 1570, 1556, 1545, 1499, 1476, 1438, 1386, 1370, 1271, 1249, 1210, 1187, 1097, 1013, 992, 900 cm^{-1}; $[\alpha]_D$ = + 17.4 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{27}NaO_3P]^+$: 393.1595 $[M+Na]^+$; found: 393.1579; $C_{22}H_{27}O_3P$ calcd. C 71.33, H 7.35; found: C 71.23, H 7.32.

2-$P(O)_2O$, **Biphenol / (1*R*, 2*S*, 5*R*)-(-)-menthol**: 88% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.37 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.30 (t, *J* = 7.5 Hz, 2H, Ar**H**), 7.22-7.20 (m, 2H, Ar**H**), 4.20-4.16 (m, 1H, C**H**), 2.32-2.27 (m, 1H, C**H**), 2.25-2.18 (m, 1H, C**H**), 1.73-1.69 (m, 2H, C**H**), 1.51-1.35 (m, 2H, C**H**), 1.08-1.04 (m, 3H, C**H**), 0.99 (d, *J* = 6.5 Hz, 3H, C$\mathbf{H}_3$), 0.96 (d, *J* = 7.0 Hz, 3H, C$\mathbf{H}_3$), 0.88 (d, *J* = 6.9 Hz, 3H, C$\mathbf{H}_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 156.0, 149.8, 131.8, 130.3, 129.4, 128.1, 125.4, 122.5, 120.3, 118.5, 76.7 (d, $J_{C,P}$ = 17.4 Hz), 48.9, 44.6, 34.5, 32.2, 25.7, 23.3, 22.5, 21.4, 16.0; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 152.8; m.p. = 98°C; IR (CCl_4): ν_{max} = 3068, 3030, 2958, 2871, 1943, 1910, 1600, 1570, 1556, 1545, 1499, 1476, 1438, 1386, 1370, 1271, 1249, 1210, 1187, 1097, 1013, 992, 900 cm^{-1}; $[\alpha]_D$ = - 17.4 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{27}NaO_3P]^+$: 393.1595 $[M+Na]^+$; found: 393.1579; $C_{22}H_{27}O_3P$ calcd. C 71.33, H 7.35; found: C 71.23, H 7.32.

3-$P(O)_2O$, **Biphenol / (1*R*, 2*R*, 3*R*, 5*S*)-(-)-isopinocampheol**: 76% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.38 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.29 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.21 (t, *J* = 7.6 Hz, 2H, Ar**H**), 4.77-4.69 (m, 1H, C**H**), 2.59-2.52 (m, 1H, C**H**), 2.41-2.36 (m, 1H, C**H**), 2.27-2.23 (m, 1H, C**H**), 2.10-2.03 (m, 1H, C**H**), 1.99-1.97 (m, 1H, C**H**), 1.87-1.84 (m, 1H, C**H**), 1.25 (s, 3H, C$\mathbf{H}_3$), 1.20 (d, *J* = 7.2 Hz, 3H, C$\mathbf{H}_3$), 1.15 (d, *J* = 10 Hz, 1H, C**H**), 0.91 (s, 3H, C$\mathbf{H}_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.0, 130.4, 129.4, 125.4, 122.6, 122.4, 76.1 (d, $J_{C,P}$ = 15 Hz), 48.2, 46.1, 42.0, 38.8, 38.2, 34.4, 28.0, 24.3, 20.4; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 147.7; m.p. = 106°C; IR (CCl_4): ν_{max} = 3069, 3029, 2959, 2910, 2872, 1943, 1911, 1601, 1567, 1553, 1499, 1476, 1437, 1386, 1370, 1260, 1249, 1210, 1187, 1097, 996, 942, 897, 857 cm^{-1}; $[\alpha]_D$ = - 17.0 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{27}NaO_4P]^+$: 409.1545 $[M+Na+H_2O]^+$; found: 409.1538; $C_{22}H_{25}O_3P$ calcd. C 71.72, H 6.84; found: C 71.80, H 6.86.

4-$P(O)_2O$, **Biphenol / (1*R*,2*S*)-(-)-*trans*-2-phenyl-1-cyclohexanol**: 63% yield;

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.46-6.90 (m, 12H, Ar**H**), 6.50-6.40 (m, 1H, Ar**H**), 4.50-4.38 (m, 1H, Cy**H**), 2.80-2.65 (m, 1H, Cy**H**), 2.35-2.20 (m, 1H, Cy**H**), 2.10-1.20 (m, 7H, Cy**H**); ^{13}C-NMR (100 MHz, C_6D_6): δ = 149.9, 143.9, 130.4, 130.1, 129.5, 129.4, 129.1, 129.0, 128.4, 127.3, 125.5, 125.4, 122.8, 122.7, 79.3 (d, $J_{C,P}$ = 17 Hz), 52.2, 36.0, 34.5, 26.3, 25.7; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 151.5; m.p. = 117°C; IR (CCl_4): ν_{max} = 3066, 3031, 2961, 2936, 2859, 1942, 1911, 1604, 1556, 1498, 1476, 1437, 1260, 1250, 1210, 1187, 1097, 1025, 901, 855, 831 cm^{-1}; $[\alpha]_D$ = - 53.6 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{24}H_{25}NaO_4P]^+$: 431.1388 $[M+Na+H_2O]^+$; found: 431.1370; $C_{24}H_{23}O_3P$ calcd. C 73.83, H 5.94; found: C 71.15, H 6.16.

5-P(O)$_2$O, **Biphenol / (-)-borneol**: 82% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.40-7.36 (m, 2H, Ar**H**), 7.30-7.26 (m, 2H, Ar**H**), 7.20 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.62-4.56 (m, 1H, C**H**), 2.26-2.18 (m, 1H, C**H**), 2.06-2.00 (m, 1H, C**H**), 1.87-1.62 (m, 2H, C**H**), 1.32-1.24 (m, 3H, C**H**), 0.94 (s, 3H, C**H**$_3$), 0.88 (s, 3H, C**H**$_3$), 0.77 (s, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.2, 131.6, 131.5, 130.3, 129.4, 129.3, 125.3, 122.5, 81.5, 50.2, 48.1, 45.4, 38.4, 28.5, 26.9, 20.4, 19.0, 13.8; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 145.4; m.p. = 88°C; IR (CCl_4): ν_{max} = 3069, 3030, 2961, 2881, 2453, 1943, 1601, 1499, 1476, 1438, 1264, 1210, 1188, 1097, 891, 858 cm^{-1}; $[\alpha]_D$ = - 5.5 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{25}NaO_3P]^+$: 391.1439 $[M+Na]^+$; found: 391.1427; $C_{22}H_{25}O_3P$ calcd. C 71.72, H 6.84; found: C 71.78, H 6.87.

6-P(O)$_2$O, **Biphenol / (1*R*,2*S*)-(-)-*trans*-(1-methyl-1-phenylethyl)cyclohexanol**: 79% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58-7.10 (m, 13H, Ar**H**), 4.32-4.24 (m, 1H, C**H**), 2.28-2.24 (m, 1H, C**H**), 1.99-1.92 (m, 1H, C**H**), 1.76-1.56 (m, 3H, C**H**), 1.50 (s, 3H, C**H**$_3$), 1.46 (s, 3H, C**H**$_3$), 1.38-1.19 (m, 1H, C**H**); 1.19-0.88 (m, 3H, C**H**); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.3, 149.6, 131.4, 129.9, 129.4, 129.0, 127.9, 126.0, 125.3, 124.9, 124.8, 122.2, 122.0, 121.0, 117.0, 77.5 (d, $J_{C,P}$ = 16 Hz), 52.6, 40.8, 36.8, 30.4, 27.6, 25.6, 24.8, 24.6; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 153.4; m.p. = 128°C; IR (CCl_4): ν_{max} = 3065, 3031, 2935, 2859, 1943, 1553, 1499, 1476, 1437, 1260, 1210, 1187, 1098, 1016, 900, 847, 830 cm^{-1}; $[\alpha]_D$ = - 12.6 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{27}H_{29}NaO_3P]^+$: 455.1752 $[M+Na]^+$; found: 455.1743; $C_{27}H_{29}O_3P$ calcd. C 74.98, H 6.76; found: C 72.39, H 6.90.

7-P(O)$_2$O, **3,3',5,5'-tetra-*tert*-butyl-biphenol / (1*R*, 2*R*, 3*R*, 5*S*)-(-)-isopinocampheol**: 87% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53-7.51 (m, 1H, Ar**H**), 7.45-7.43 (m, 1H, Ar**H**), 7.28-7.26 (m, 1H, Ar**H**), 7.19-7.17 (m, 1H, Ar**H**), 4.75-4.57 (m, 1H, C**H**), 2.59-2.52 (m, 1H, C**H**), 2.41-2.36 (m, 1H, C**H**), 2.27-2.23 (m, 1H, C**H**), 2.10-1.94 (m, 2H, C**H**), 1.87-1.84 (m, 1H, C**H**), 1.50 (s, 18H, *t*Bu), 1.45 (s, 3H, C**H**$_3$), 1.36 (s, 18H, *t*Bu), 1.20 (d, *J* = 7.2 Hz, 3H, C**H**$_3$), 1.06 (d, *J* = 10 Hz, 1H, C**H**), 0.89 (s, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 127.0, 126.9, 125.4, 124.5, 76.7, 48.2, 46.0, 45.7, 42.0, 38.2, 33.9, 31.9, 31.8, 31.6, 27.9, 24.3, 20.5; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 146.7; m.p. = 75°C; IR (CCl_4): ν_{max} = 2963, 2907, 2871, 2448, 1945, 1595, 1556, 1545, 1475, 1440, 1397, 1363, 1260, 1229, 1094, 1018, 937, 879 cm^{-1}; $[\alpha]_D$ = + 5.3 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{38}H_{57}NaO_3P]^+$: 615.3943 $[M+Na]^+$; found: 615.3935; $C_{38}H_{57}O_3P$ calcd. C 76.99, H 9.69; found: C 77.02, H 9.71.

8-P(O)$_2$O, **3,3',5,5'-tetra-*tert*-butyl-biphenol / (1*R*, 2*S*, 5*R*)-(-)-menthol**: 84% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1H, Ar**H**), 7.43 (s, 1H, Ar**H**), 7.19 (s, 1H, Ar**H**), 7.18 (s, 1H, Ar**H**), 4.11-4.06 (m, 1H, C**H**), 2.25-2.15 (m, 1H, C**H**), 2.10-1.80 (m, 2H, C**H**), 1.70-1.55 (m, 2H, C**H**), 1.50 (s, 18H, 2 x *t*Bu), 1.50-0.60 (m, 4H, C**H**), 1.36 (s, 18H, 2 x *t*Bu), 0.87-0.84 (m, 6H, 2 x C**H**$_3$), 0.73 (d, *J* = 6.9 Hz, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.0, 131.7, 130.3, 129.4, 125.4, 122.5, 79.1, 76.7, 76.6, 58.3, 48.9, 44.5, 34.5, 32.2, 25.7, 23.3, 22.5, 21.4, 16.0; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 147.0; m.p. = 140°C; IR (CCl_4): ν_{max} = 2962, 2870, 1595, 1558, 1547, 1456, 1413, 1396, 1362, 1093, 1017 cm^{-1}; $[\alpha]_D$ = - 17.3 (c 1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{38}H_{59}NaO_3P]^+$: 617.4099 $[M+Na]^+$; found: 617.4093; $C_{38}H_{59}O_3P$ calcd. C 76.73, H 10.00; found: C 76.69, H 9.97.

9-P(O)$_2$O, **Biphenol / (1*R*)-endo-(+)-fenchol**: 78% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.44-7.21 (m, 6H, Ar**H**), 3.96 (d, *J* = 11.6 Hz, 1H, C**H**), 1.85-1.67 (m, 4H, C**H**), 1.58-1.40 (m, 3H, C**H**), 1.24 (s, 3H, C**H**$_3$), 1.04 (s, 3H, C**H**$_3$), 0.96 (s, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 130.5, 129.6, 125.6, 125.5, 122.9, 89.2 (d, $J_{C,P}$ = 12.0 Hz), 50.1, 48.8, 41.8, 40.4, 30.6, 26.7, 26.5, 22.2, 20.2; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 148.6; m.p. = 104°C; IR (CCl_4): ν_{max} = 3069, 3030, 2962, 2873, 1944, 1911, 1602, 1569, 1556, 1499, 1476, 1437, 1260, 1210, 1187, 1098, 1015, 904, 857 cm^{-1}; $[\alpha]_D$ = + 9.8 (c

1.00, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{22}H_{25}NaO_3P]^+$: 391.1439 $[M+Na]^+$; found: 391.1423; $C_{22}H_{25}O_3P$ calcd. C 71.72, H 6.84; found: C 69.42, H 7.07.

10-$P(O)_2O$, **3,3',5,5'-tetramethyl-biphenol / (-)-borneol**: 76% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 2H, Ar**H**), 7.08 (s, 2H, Ar**H**), 4.65-4.60 (m, 1H, C**H**), 2.40 (s, 12H, 4 x C**H**$_3$), 2.27-2.20 (m, 1H, C**H**), 2.07-2.00 (m, 1H, C**H**), 1.76-1.67 (m, 2H, C**H**), 1.33-1.23 (m, 3H, C**H**), 0.96 (s, 3H, C**H**$_3$), 0.91 (s, 3H, C**H**$_3$), 0.86 (s, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 134.2, 131.6, 130.6, 128.6, 81.8 (d, $J_{C,P}$ = 12.0 Hz), 50.5, 48.4, 45.7, 38.5, 28.9, 27.3, 21.6, 20.8, 19.4, 17.5, 14.1; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 145.7; m.p. = 81°C; IR (CCl_4): ν_{max} = 2957, 2880, 1557, 1478, 1260, 1245, 1214, 1188, 1154, 1119, 1030, 866, 830 cm^{-1}; $[\alpha]_D$ = + 2.5 (c 1.01, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{26}H_{35}NaO_4P]^+$: 465.2171 $[M+Na+H_2O]^+$; found: 465.2141; $C_{26}H_{33}O_3P$ calcd. C 73.56, H 7.84; found: C 72.15, H 8.06.

11-$P(O)_2O$, **3,3',5,5'-tetramethyl-biphenol / (1*R*)-endo-(+)-fenchol**: 78% yield;

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.08 (s, 2H, Ar**H**), 3.94 (dd, J_1 = 12.0, J_2 = 1.6 Hz, 1H, C**H**), 2.41 (s, 6H, 2 x C**H**$_3$), 2.40 (s, 6H, 2 x C**H**$_3$), 1.84-1.69 (m, 4H, C**H**), 1.59-1.43 (m, 3H, C**H**), 1.21 (s, 3H, C**H**$_3$), 1.09 (s, 3H, C**H**$_3$), 0.90 (s, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 146.9, 146.4, 134.3, 132.0, 131.7, 131.5, 130.7, 128.6, 88.8 (d, $J_{C,P}$ = 15.0 Hz), 50.0, 48.7, 41.9, 40.4, 30.8, 26.9, 26.4, 22.4, 21.6, 20.1, 17.7, 17.5; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 149.7; m.p. = 91°C; IR (CCl_4) ν_{max} 2962, 2872, 1945, 1557, 1478, 1260, 1214, 1187, 1154, 1098, 1012, 871, 831 cm^{-1}; $[\alpha]_D$ = - 27.5 (c 1.01, $CHCl_3$); HRMS (ESI) *m/z* calcd for $[C_{26}H_{35}NaO_4P]^+$: 465.2171 $[M+Na+H_2O]^+$; found: 465.2153; $C_{26}H_{33}O_3P$ calcd. C 73.56, H 7.84; found: C 72.39, H 7.98.

12-$P(O)_2N$, **Biphenol / (*R,R*)-bis(**a**-methylbenzyl)amine**: 89% yield; $[\alpha]_D$ = + 238.0 (c 1.00, $CHCl_3$);

13-$P(O)_2N$, **Biphenol / (*S,S*)-bis(**a**-methylbenzyl)amine**: 80% yield; $[\alpha]_D$ = - 238.0 (c 1.00, $CHCl_3$);

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49-7.56 (m, 2H, Ar**H**), 7.22-7.41 (m, 6H, Ar**H**), 7.11-7.20 (m, 10H, Ar**H**), 4.58-4.66 (m, 2H, 2 x **H**-benzyl), 1.77 (d, *J* = 7.2 Hz, 6H, 2 x C**H**$_3$-benzyl); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.5, 143.4, 131.6, 130.4, 130.2, 129.5, 129.4, 128.3, 128.2, 127.0, 125.0, 124.4, 122.9, 122.4, 53.1, 53.0, 22.7; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 147.6; m.p. = 105°C; IR (CCl_4): ν_{max} = 3065, 3030, 2963, 2905, 1943, 1911, 1602, 1546, 1497, 1476, 1436, 1375, 1261, 1211, 1194, 1098, 1015, 889, 830 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{28}H_{26}NNaO_2P]^+$: 462.1599 $[M+Na]^+$; found: 462.1574; $C_{28}H_{26}NO_2P$ calcd. C 76.52, H 5.96, N 3.19; found: C 76.60, H 5.97, N 3.21.

14-$P(O)_2N$, **Biphenol / (*S*)-(-)-*N,*a-dimethylbenzylamine**: 55% yield; $[\alpha]_D$ = + 23.0 (c 1.00, $CHCl_3$);

15-$P(O)_2N$, **Biphenol / (*R*)-(+)-*N,*a-dimethylbenzylamine**: 40% yield; $[\alpha]_D$ = - 23.0 (c 1.00, $CHCl_3$);

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54-7.09 (m, 13H, Ar**H**), 4.92-4.84 (m, 1H, C**H**), 2.23 (d, *J* = 4.8 Hz, 3H, C**H**$_3$), 1.69 (d, *J* = 7.2 Hz, 3H, C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.3, 142.7, 131.6, 130.3, 129.8, 129.0, 128.0, 127.7, 125.1, 125.0, 122.6, 56.3, 55.9, 27.7, 19.2; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 149.6; m.p. = 109°C; IR (CCl_4): ν_{max} = 3067, 3030, 2963, 2905, 1603, 1564, 1556, 1498, 1476, 1436, 1260, 1208, 1194, 1098, 1013, 934 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{21}H_{20}NNaO_2P]^+$: 372.1129 $[M+Na]^+$; found: 372.1112; $C_{21}H_{20}NO_2P$ calcd. C 72.20, H 5.77, N 4.01; found: C 72.31, H 5.79, N 3.98.

16-$P(O)_2N$, **Biphenol / bis-[(*S*)-1-naphth-1-yl-ethyl]amine**: 60% yield; $[\alpha]_D$ = + 204.8 (c 0.53, $CHCl_3$);

17-$P(O)_2N$, **Biphenol / bis-[(*R*)-1-naphth-1-yl-ethyl]amine**: 71% yield; $[\alpha]_D$ = - 204.8 (c 0.53, $CHCl_3$);

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.62-7.22 (m, 18H, Ar**H**), 6.86 (t, *J* = 7.6 Hz, 2H, Ar**H**), 5.61-5.53 (m, 2H, 2 x C**H**), 1.83 (d, *J* = 7.2 Hz, 6H, 2 x C**H**$_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 139.1, 133.8, 131.5, 130.9, 130.8, 129.9, 129.8, 129.0, 127.6, 125.9, 125.5, 125.3, 125.2, 124.7, 123.9, 123.1, 123.0, 51.5, 51.4, 23.7, 23.6; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 150.1; m.p. not determined due to decomposition; IR (CCl_4): ν_{max} = 3053, 2964,

2905, 2876, 1943, 1912, 1600, 1566, 1499, 1476, 1435, 1396, 1373, 1262, 1212, 1194, 1175, 1142, 1098, 1016, 960, 891, 850 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{36}H_{30}NNaO_2P]^+$: 562.1912 $[M+Na]^+$; found: 562.1910; $C_{36}H_{30}NO_2P$ calcd. C 80.13, H 5.60, N 2.60; found: C 80.15, H 5.63, N 2.59.

18-$P(O)_2N$, **Biphenol / (*R*,*R*)-2,5-diphenylpyrrolidine**: 67% yield; $[\alpha]_D$ = + 111.4 (c 1.03, $CHCl_3$);

19-P(O)-N, **Biphenol / (*S*,*S*)-2,5-diphenylpyrrolidine**: 73% yield; $[\alpha]_D$ = - 111.4 (c 1.03, $CHCl_3$);

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50-6.96 (m, 18H, Ar**H**), 5.10 (d, *J* = 5.6 Hz, 2H, C**H**), 2.51-2.38 (m, 2H, C**H**), 1.89-1.78 (m, 2H, C**H**); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.1, 130.4, 129.9, 129.6, 129.2, 128.9, 127.5, 125.0, 124.4, 122.7, 122.2, 63.4, 63.1, 34.3, 33.0; ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 149.2; m.p. = 101°C; IR (CCl_4): ν_{max} = 3065, 3029, 2963, 2904, 1943, 1603, 1546, 1497, 1476, 1436, 1261, 1211, 1097, 1019, 829 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{28}H_{24}NNaO_2P]^+$: 460.1442 $[M+Na]^+$; found: 460.1431; $C_{28}H_{24}NO_2P$ calcd. C 76.87, H 5.53, N 3.20; found: C 76.70, H 6.00, N 3.21.

Standard procedure for the Rh-catalysed asymmetric 1,4-conjugate addition of arylboronic acid to enones. Isolation of the product and a_D determination: the reaction was performed using standard Schlenk techniques, under argon. The ligands $\mathbf{L^a}$ (0.03 eq, 0.015 mmol) and $\mathbf{L^b}$ (0.03 eq, 0.015 mmol) and $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.0075 mmol, 2.9 mg) were weighed and 1.0 ml of degassed dioxane was added. After 30 min. under stirring, a solution of the appropriate arylboronic acid (2 eq, 1 mmol) in 1.0 ml of dioxane was added, followed by KOH 2M solution in water (1 eq, 0.5 mmol, 250 μl). A solution of the substrate (1 eq, 0.5 mmol) in dioxane (0.5 ml) was added, and the reaction mixture was stirred overnight under argon, at the aprropriate temperature. The reaction mixture was quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo, to give the crude product, which was purified by flash chromatography.

(3*R*)-3-Phenylcyclohexan-1-one (**22Aa**):[6] yellow oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1; 0.48 mmol, 83.5 mg, 95% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.72-1.90 (m, 2H), 2.05-2.20 (m, 2H), 2.35-2.61 (m, 4H), 2.98-3.10 (m, 2H), 7.20-7.28 (m, 3H), 7.29-7.40 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.5, 32.7, 41.1, 44.7, 48.9, 126.5, 126.6, 128.6, 144.3, 211.0; $[\alpha]_D$ = + 20.5 (c 0.985, $CHCl_3$) (95% ee, L^a = **6**-$P(O)_2O$, L^b = **19**-$P(O)_2N$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm).

3-(1-naphthyl)cyclohexan-1-one (**22Ab**):[7] yellow oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 85 / 15; 0.45 mmol, 100.9 mg, 90% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.90-2.10 (m, 2H), 2.18-2.32 (m, 2H), 2.44-2.64 (m, 2H), 2.65-2.86 (m, 2H), 3.84-3.94 (m, 1H), 7.42 (d, 1H, *J* = 7.2 Hz), 7.46-7.59 (m, 3H), 7.78 (d, 1H, *J* = 8.0 Hz), 7.90 (d, 1H, *J* = 8.8 Hz), 8.06 (d, 1H, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.3, 33.0, 40.0, 42.1, 49.3, 123.1, 123.4, 126.2, 126.3, 126.9, 127.9, 129.7, 134.9, 141.3, 211.4; $[\alpha]_D$ = + 37.95 (c 1.5, $CHCl_3$) (82.5% ee, L^a = **6**-$P(O)_2O$, L^b = **19**-$P(O)_2N$). The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 95:5, flow rate 1 ml/min).

(3*R*)-3-(2-methoxyphenyl)cyclohexan-1-one (**22Ac**):[8] clear oil; purified by flash chromatography (eluent: hexane / diethyl ether = 8 / 2; 0.45 mmol, 91.8 mg, 90% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.75-1.96 (m, 2H), 2.01-2.09 (m, 1H), 2.11-2.21 (m, 1H), 2.33-2.66 (m, 4H), 3.38-3.50 (m, 1H), 3.84 (s, 3H), 6.89 (d, 1H, *J* = 8.0 Hz), 6.96 (t, 1H, *J* = 7.4 Hz), 7.19-7.28 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.2, 31.7, 38.6, 42.1, 48.2, 55.9, 111.2, 121.3, 127.2, 128.2, 133.1, 157.2, 212.0; $[\alpha]_D$ = + 16.3 (c 1.0, $CHCl_3$) (41% ee, L^a = L^b = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (OD-H, 254 nm, hexane: 2-propanol = 97:3, flow rate 1 ml/min).

(3*R*)-3-(4-methoxyphenyl)cyclohexan-1-one (**22Ad**):[9] yellow oil; purified by flash chromatography (eluent: hexane / diethyl ether = 75 / 25; 0.44 mmol, 90.2 mg, 88% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.71-1.90 (m, 2H), 2.02-2.12 (m, 1H), 2.13-2.21 (m, 1H), 2.33-2.63 (m, 4H), 2.94-3.03 (m, 1H), 3.82 (s, 3H), 6.89 (dd, 2H, *J* = 11.6 Hz, 3.2 Hz), 7.16 (dd, 2H, *J* = 11.6 Hz, 3.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.5, 33.0, 41.2, 44.0, 49.3, 55.3, 114.0,

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[6] $[\alpha]_D$ = - 21 (c 0.96, $CHCl_3$) was reported for (3*S*)-3-phenylcyclohexan-1-one (97% ee), see: Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580.

[7] C. S. Cho, S. Motofusa, K. Ohe, S. Uemura, *J. Org. Chem.* **1995**, *60*, 883-888; $[\alpha]_D$ = + 45.8 (c 1.5, $CHCl_3$) was reported for 3-(1-naphthalene)cyclohexan-1-one (98% ee), see: M. Pucheault, S. Darses, J. Genet, *Eur.J. Org- Chem.* **2002**, 3552-3557.

[8] P. Jones, C. K. Reddy, P. Knochel, *Tetrahedron* **1998**, *54*, 1471-1490; $[\alpha]_D$ = - 36.3 (c 1.02, $CHCl_3$) was reported for (3*S*)-3-(2-methoxyphenyl)cyclohexan-1-one (94% ee), see: C. Defieber, J. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *21*, 3873-3876.

[9] C. S. Cho, S. Motofusa, K. Ohe, S. Uemura, *J. Org. Chem.* **1995**, *60*, 883-888; $[\alpha]_D$ = + 13.6 (c 1.15, $CHCl_3$) was reported for (3*R*)-3-(4-methoxyphenyl)cyclohexan-1-one (96% ee), see: C. Defieber, J. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *21*, 3873-3876.

127.5, 136.6, 158.3, 211.2; $[\alpha]_D$ = + 9.01 (c 1.02, $CHCl_3$) (64% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 98:2, flow rate 0.5 ml/min).

3-(4-chlorophenyl)cyclohexan-1-one (**22Ae**):[10] pale yellow oil; purified by flash chromatography (eluent: hexane / diethyl ether = 8 / 2; 0.39 mmol, 81.4 mg, 78% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.70-1.88 (m, 2H), 1.95-2.20 (m, 2H), 2.29-2.60 (m, 4H), 2.91-3.02 (m, 1H), 7.11-7.17 (m, 2H), 7.21-7.29 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.4, 32.6, 41.0, 44.0, 48.7, 128.0, 128.7, 132.3, 142.8, 210.5; $[\alpha]_D$ = + 5.28 (c 1.02, $CHCl_3$) (63% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 98:2, flow rate 1 ml/min).

3-(3-nitrophenyl)cyclohexan-1-one (**22Af**):[11] colourless oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1; 0.95 mmol, 165.4 mg, 95% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.75-1.99 (m, 2H), 2.11-2.25 (m, 2H), 2.38-2.68 (m, 4H), 3.12-3.19 (m, 1H), 7.50-7.62 (m, 2H), 8.24-8.26 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.3, 32.5, 41.0, 44.2, 48.4, 121.5, 121.9, 129.7, 133.1, 146.3, 148.6, 209.7. The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 90:10, flow rate 1 ml/min).

(3*R*)-3-(4-methylphenyl)cyclohexan-1-one (**22Ag**):[12] pale yellow oil; purified by flash chromatography (eluent: hexane / diethyl ether = 8 / 2; 0.48 mmol, 90 mg, 96% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.70-1.87 (m, 2H), 2.03-2.20 (m, 2H), 2.36 (s, 3H), 2.31-2.68 (m, 4H), 2.94-3.07 (m, 1H), 7.11 (d, 2H, *J* = 8.3 Hz), 7.14 (d, 2H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.7, 26.3, 33.6, 41.9, 45.1, 49.8, 127.1, 130.0, 136.9, 142.1, 211.9; $[\alpha]_D$ = + 14.8 (c 1.0, $CHCl_3$) (75% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 97:3, flow rate 1 ml/min).

(3*R*)-3-Phenylcyclopentan-1-one (**22Ba**):[13] yellow oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1; 0.48 mmol, 76.8 mg, 95% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.91-2.08 (m, 1H), 2.27-2.40 (m, 2H), 2.41-2.54 (m, 2H), 2.66-2.73 (m, 1H), 3.40-3.45 (m, 1H), 7.23-7.28 (m, 3H), 7.34 (t, 2H, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 31.1, 38.8, 42.1, 45.7, 126.7, 128.6, 143.0, 218.3; $[\alpha]_D$ = + 74.2 (c 0.81, $CHCl_3$) (73% ee, L^a = **6**-$P(O)_2O$, L^b = **19**-$P(O)_2N$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (Supelco γ-DEX 225, 25 m, film 0.25 μm).

(3*R*)-3-Phenylcycloheptan-1-one (**22Ca**):[14] yellow oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1; 0.49 mmol, 91.2 mg, 97% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.48-1.60 (m, 1H), 1.68-1.82 (m, 2H), 1.97-2.12 (m, 3H), 2.58-2.70 (m, 3H), 2.88-3.02 (m, 2H), 7.19-7.27 (m, 3H), 7.30-7.41 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.1, 29.2, 39.2, 42.7, 43.9, 51.2, 126.3, 126.4, 128.6, 146.9, 213.4; $[\alpha]_D$ = + 55.0 (c 0.75, $CHCl_3$) (90% ee, L^a = **6**-$P(O)_2O$, L^b = **19**-$P(O)_2N$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm).

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[10] R. T. Stemmler, C. Bolm, *J.Org.Chem.* **2005**, *70*, 9925-9931.

[11] F. Gini, B. Hessen, A. J. Minnard, *Org. Lett.* **2005**, *7*, 5309-5312; C. S. Cho, S. Motofusa, K. Ohe, S. Uemura, *J. Org. Chem.* **1995**, *60*, 883-888.

[12] Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580; $[\alpha]_D$ = - 17 (c 0.95, $CHCl_3$) was reported for (3*S*)-3-(4-methylphenyl)cyclohexan-1-one (99% ee), see: Y. Takaya, M. Ogasawara, T. Hayashi, *Tet.Lett.* **1999**, *40*, 6957-6961.

[13] $[\alpha]_D$ = - 92 (c 0.82, $CHCl_3$) was reported for (3*S*)-3-phenylcyclopentan-1-one (97% ee), see: Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580.

[14] Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580; $[\alpha]_D$ = + 116.8 (c 0.35, $CHCl_3$) was reported for (3*R*)-3-phenylcycloheptan-1-one (95% ee), see: C. Defieber, J. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *21*, 3873-3876.

(4*R*)-4-(phenyl)tetrahydro-2H-pyran-2-one (**22Da**):[15] clear oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 1 / 1; 0.38 mmol, 66.0 mg, 76% isolated yield); complete conversion at 80°C overnight. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.00-2.12 (m, 1H), 2.15-2.23 (m, 1H), 2.65 (dd, 1H, *J* = 17.6 Hz, 10.6 Hz), 2.95 (ddd, 1H, *J* = 17.6 Hz, 6.0 Hz, 1.6 Hz), 3.20-3.31 (m, 1H), 4.37-4.55 (m, 2H), 7.21 (d, 2H, *J* = 7.3 Hz), 7.27 (t, 1H, *J* = 7.4 Hz), 7.36 (t, 2H, *J* = 7.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.3, 37.4, 37.5, 68.6, 126.5, 127.2, 129.0, 142.8, 170.7; $[\alpha]_D$ = - 1.63 (c 2.70, $CHCl_3$) (40% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm; 150°C, 0.1°C/min).

(4*R*)-4-phenylpentan-2-one (**22Ea**):[16] pale yellow oil; purified by flash chromatography (eluent: hexane / dichloromethane = 7 / 3; 0.38 mmol, 61.0 mg, 75% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (d, 3H, *J* = 6.8 Hz), 2.09 (s, 3H), 2.65-2.81 (m, 2H), 3.29-3.37 (m, 1H), 7.19-7.38 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.7, 31.2, 36.1, 52.7, 127.0, 127.4, 129.2, 146.8, 208.5; $[\alpha]_D$ = - 33.94 (c 0.51, $CHCl_3$) (76% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm, 80°C, 1°C/min).

(4*S*)-5-methyl-4-phenyl-hexan-2-one (**22Fa**):[17] clear oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 6 / 1; 0.43 mmol, 81.8 mg, 86% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.77 (d, 3H, *J* = 6.8 Hz), 0.95 (d, 3H, *J* = 6.4 Hz), 1.81-1.90 (m, 1H), 2.00 (s, 3H), 2.80-2.85 (m, 2H), 2.91-2.97 (m, 1H), 7.15-7.31 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.0, 21.4, 31.3, 34.0, 48.4, 48.8, 126.9, 127.8, 128.8, 129.4, 143.9, 209.0; $[\alpha]_D$ = - 32.6 (c 0.51, $CHCl_3$) (93% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by GC equipped with a chiral capillary column (Supelco γ-DEX 225, 25 m, film 0.25 μm, 110°C, 0.5°C/min).

(4*S*)-4-(4-methoxyphenyl)-4-phenyl-butan-2-one (**22Gd**):[18] yellow oil; purified by flash chromatography (eluent: hexane / ethyl acetate = 1 / 5; 0.49 mmol, 124.5 mg, 98% isolated yield); complete conversion at 80°C overinght; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.17 (d, 2H, *J* = 7.6 Hz), 3.79 (s, 3H), 4.57 (t, 1H, *J* = 7.6 Hz), 6.83-6.86 (m, 2H), 7.15-7.34 (m, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 31.0, 45.7, 50.3, 55.6, 114.4, 126.8, 128.0, 129.0, 129.1, 136.4, 144.6, 158.5, 207.4; $[\alpha]_D$ = - 1.3 (c 2.0, $CHCl_3$) (80% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (OD-H, 254 nm, hexane: 2-propanol = 98:2, flow rate 1 ml/min).

4-phenyloctan-2-one (**22Ha**):[19] clear oil; purified by flash chromatography (eluent: hexane / diethyl ether = 10 / 1; 0.3 mmol, 61.8 mg, 60% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.81 (t, 3H, *J* = 7.2 Hz), 1.06-1.30 (m, 4H), 1.54-1.65 (m, 2H), 2.00 (s, 3H), 2.70 (d, 2H, *J* = 8.0 Hz), 3.05-3.15 (m, 1H), 7.15-7.30 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.9, 22.6, 29.5, 30.6, 36.2, 41.3, 50.9, 126.3, 127.4, 128.4, 144.6, 208.0; $[\alpha]_D$ = - 36.73 (c 1.19, toluene) (75% ee, $L^a = L^b$ = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (OD-H, 254 nm, hexane: 2-propanol = 95:5, flow rate 0.5 ml/min).

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[15] $[\alpha]_D$ = + 4.0 (c 2.70, $CHCl_3$) was reported for (4*S*)-4-(phenyl)tetrahydro-2H-pyran-2-one (98% ee), see: Y. Takaya, T. Senda, H. Kurushima, M. Ogasawara, T. Hayashi, *Tetrahedron: Asymmetry* **1999**, *10*, 4047-4056.

[16] $[\alpha]_D$ = + 40.0 (c 0.5, $CHCl_3$) was reported for (4*S*)-4-phenylpentan-2-one, see: L. F. Tietze, B. Weigand, L. Volkel, C. Wulff, C. Bittner, *Chem. Eur. J.* **2001**, *7*, 161-168.

[17] $[\alpha]_D$ = - 33.0 (c 1.12, $CHCl_3$) was reported for (5*S*)-5-methyl-4-phenyl-hexan-2-one (97% ee), see: Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580 and T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052-5058.

[18] S. Oi, M. Moro, H. Ito, Y. Honma, S. Miyano, Y. Inoue, *Tetrahedron* **2002**, *58*, 91-97; $[\alpha]_D$ = -0.6 (c 0.72, $CHCl_3$) was reported for (4*S*)-4-(4-methoxyphenyl)-4-phenyl-2-butanone (90% ee), see: C. Defieber, J. Paquin, S. Serna, E. M. Carreira, *Org. Lett.* **2004**, *21*, 3873-3876.

[19] E. L. Stangeland, T. Sammakia, *Tetrahedron* **1997**, *53*, 16503-16510.

(4*R*)-4-phenylnonan-2-one (**22Ia**):[20] clear oil; purified by flash chromatography (eluent: hexane / diethyl ether = 10 / 1; 0.44 mmol, 95 mg, 88% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.82 (t, 3H, *J* = 6.9 Hz), 1.15-1.33 (m, 6H), 1.53-1.68 (m, 2H), 2.03 (s, 3H), 2.73 (dd, 2H, *J* = 7.4 Hz, 2.9 Hz), 3.10-3.15 (m, 1H), 7.15-7.30 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 22.4, 27.0, 30.6, 31.7, 36.4, 41.2, 50.9, 126.2, 127.4, 128.4, 144.5, 207.9; $[\alpha]_D$ = - 17.15 (c 1.30, $CHCl_3$) (92% ee, L^a = L^b = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (OD-H, 210 nm, hexane: 2-propanol = 9:1, flow rate 0.2 ml/min).

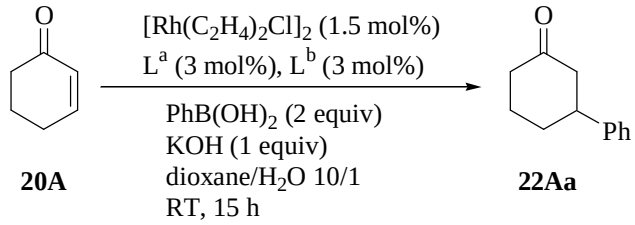
(3*S*)-*tert*-butyl-3-(4-methoxyphenyl)-3-phenylpropanoate (**22Jd**):[21] white solid; purified by flash chromatography (eluent: hexane / diethyl ether = 9 / 1; 0.45 mmol, 140.5 mg, 90% isolated yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.95 (d, 2H, *J* = 8.4 Hz), 3.79 (s, 3H), 4.45 (t, 1H, *J* = 8.4 Hz), 6.83-6.85 (m, 2H), 7.17-7.26 (m, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.9, 42.3, 46.7, 55.2, 80.5, 113.8, 126.3, 127.7, 128.4, 128.7, 135.8, 144.0, 158.1, 171.2; $[\alpha]_D$ = + 1.2 (c 1.0, MeOH) (79% ee, L^a = L^b = **6**-$P(O)_2O$). The enantiomeric excess was determined by chiral HPLC (AD-H, 254 nm, hexane: 2-propanol = 97:3, flow rate 0.35 ml/min).

General procedure for the ligand library screening: Rh-catalysed conjugate addition of arylboronic acid to enones: the reaction was performed using standard Schlenk techniques, under argon. A solution of the ligands (0.03 eq, 0.006 mmol of L^a + 0.03 eq, 0.006 mmol of L^b) and $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.003 mmol, 5.8 mg) in degassed dioxane (500 μl) was stirred for 30 min. A solution of the appropriate arylboronic acid (2 eq, 0.4 mmol) in degassed dioxane (300 μl) was added, followed by KOH solution 2M in water (1 eq, 0.2 mmol, 100 μl). A solution of the substrate (1 eq, 0.2 mmol) in dioxane (200 μl) was then added, and the reaction mixture was stirred overnight under argon, at the appropriate temperature. The reaction mixture was quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with either diethyl ether (for GC analysis) or hexane (for HPLC analysis). In the first case, the crude organic extracts were directly analyzed by GC, equipped with a chiral capillary column, using *n*-tridecane as internal standard: yields and ee's were determined by integration of the GC traces. In the latter case, the crude organic extracts were filtered through silica, dried and concentrated in vacuo, for ee's determination with a chiral HPLC. Yields were determined via NMR spectroscopy of the crude product.

[20] $[\alpha]_D$ = - 17.0 (c 1.26, $CHCl_3$) was reported for (3*R*)-3-phenyl-2nonanone (92% ee), see: Y. Takaya, M. Ogasawara, T. Hayashi, *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580 and T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052-5058.

[21] $[\alpha]_D$ = + 1.6 (c 0.96, MeOH) was reported for (3*S*)-*tert*-butyl-3-(4-methoxyphenyl)-3-phenylpropanoate (93% ee), see: J. Paquin, C. R. J. Stephenson, C. Defieber, E. M. Carreira, *Org. Lett.* **2005**, *7*, 3821-3824.

Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-phenylcyclohexan-1-one (22Aa).

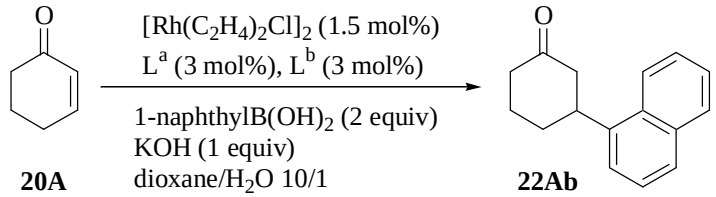


20A **22Aa**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**1**-$P(O)_2O$	**1**-$P(O)_2O$	100	8	*S*
2	**2**-$P(O)_2O$	**2**-$P(O)_2O$	100	8	*R*
3	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	28	*S*
4	**4**-$P(O)_2O$	**4**-$P(O)_2O$	100	41	*R*
5	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	19	*R*
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	70	*R*
7	**7**-$P(O)_2O$	**7**-$P(O)_2O$	60	rac	-
8	**8**-$P(O)_2O$	**8**-$P(O)_2O$	0	-	-
9	**9**-$P(O)_2O$	**9**-$P(O)_2O$	100	28	*R*
10	**10**-$P(O)_2O$	**10**-$P(O)_2O$	50	8	*S*
11	**11**-$P(O)_2O$	**11**-$P(O)_2O$	100	7	*R*
12	**12**-$P(O)_2N$	**12**-$P(O)_2N$	56	3	*S*
13	**13**-$P(O)_2N$	**13**-$P(O)_2N$	56	3	*R*
14	**14**-$P(O)_2N$	**14**-$P(O)_2N$	90	7	*R*
15	**15**-$P(O)_2N$	**15**-$P(O)_2N$	90	7	*S*
16	**16**-$P(O)_2N$	**16**-$P(O)_2N$	30	rac	-
17	**17**-$P(O)_2N$	**17**-$P(O)_2N$	30	rac	-
18	**18**-$P(O)_2N$	**18**-$P(O)_2N$	100	36	*S*
19	**19**-$P(O)_2N$	**19**-$P(O)_2N$	100	36	*R*
20	**2**-$P(O)_2O$	**18**-$P(O)_2N$	100	73	*S*
21	**2**-$P(O)_2O$	**19**-$P(O)_2N$	100	81	*R*
22	**3**-$P(O)_2O$	**12**-$P(O)_2N$	30	61	*S*
23	**3**-$P(O)_2O$	**13**-$P(O)_2N$	40	32	*S*
24	**3**-$P(O)_2O$	**14**-$P(O)_2N$	0	-	-
25	**3**-$P(O)_2O$	**15**-$P(O)_2N$	100	4	*S*
26	**3**-$P(O)_2O$	**16**-$P(O)_2N$	100	25	*S*
27	**3**-$P(O)_2O$	**17**-$P(O)_2N$	100	30	*S*
28	**3**-$P(O)_2O$	**18**-$P(O)_2N$	100	74	*S*
29	**3**-$P(O)_2O$	**19**-$P(O)_2N$	100	80	*R*
30	**4**-$P(O)_2O$	**12**-$P(O)_2N$	60	23	*R*
31	**4**-$P(O)_2O$	**13**-$P(O)_2N$	55	20	*R*

32	**4**-$P(O)_2O$	**14**-$P(O)_2N$	20	9	*R*
33	**4**-$P(O)_2O$	**15**-$P(O)_2N$	25	9	*R*
34	**4**-$P(O)_2O$	**16**-$P(O)_2N$	90	17	*R*
35	**4**-$P(O)_2O$	**17**-$P(O)_2N$	80	27	*R*
36	**4**-$P(O)_2O$	**18**-$P(O)_2N$	95	69	*S*
37	**4**-$P(O)_2O$	**19**-$P(O)_2N$	95	83	*R*
38	**5**-$P(O)_2O$	**12**-$P(O)_2N$	90	10	*R*
39	**5**-$P(O)_2O$	**13**-$P(O)_2N$	100	15	*R*
40	**5**-$P(O)_2O$	**14**-$P(O)_2N$	70	27	*R*
41	**5**-$P(O)_2O$	**15**-$P(O)_2N$	100	21	*R*
42	**5**-$P(O)_2O$	**18**-$P(O)_2N$	100	51	*S*
43	**5**-$P(O)_2O$	**19**-$P(O)_2N$	100	74	*R*
44	**6**-$P(O)_2O$	**12**-$P(O)_2N$	92	65	*R*
45	**6**-$P(O)_2O$	**13**-$P(O)_2N$	100	70	*R*
46	**6**-$P(O)_2O$	**14**-$P(O)_2N$	100	58	*R*
47	**6**-$P(O)_2O$	**15**-$P(O)_2N$	100	54	*R*
48	**6**-$P(O)_2O$	**16**-$P(O)_2N$	100	58	*R*
49	**6**-$P(O)_2O$	**17**-$P(O)_2N$	100	64	*R*
50	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	70	*S*
51	**6**-$P(O)_2O$	**19**-$P(O)_2N$	100	95	*R*
52	**7**-$P(O)_2O$	**18**-$P(O)_2N$	100	rac	-
53	**7**-$P(O)_2O$	**19**-$P(O)_2N$	90	rac	-
54	**9**-$P(O)_2O$	**12**-$P(O)_2N$	40	28	*R*
55	**9**-$P(O)_2O$	**13**-$P(O)_2N$	30	8	*R*
56	**9**-$P(O)_2O$	**14**-$P(O)_2N$	70	14	*R*
57	**9**-$P(O)_2O$	**15**-$P(O)_2N$	70	20	*R*
58	**9**-$P(O)_2O$	**18**-$P(O)_2N$	100	87	*S*
59	**9**-$P(O)_2O$	**19**-$P(O)_2N$	100	91	*R*
60	**10**-$P(O)_2O$	**18**-$P(O)_2N$	80	9	*S*
61	**10**-$P(O)_2O$	**19**-$P(O)_2N$	90	4	*R*
62	**11**-$P(O)_2O$	**18**-$P(O)_2N$	100	22	*R*
63	**11**-$P(O)_2O$	**19**-$P(O)_2N$	90	8	*R*

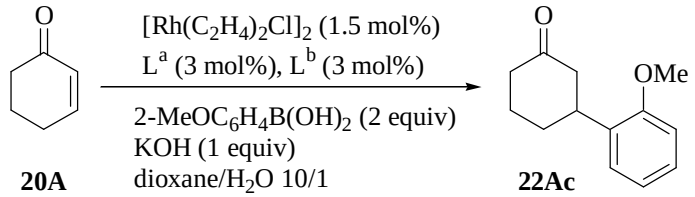
Rh-catalysed asymmetric 1,4-conjugate addition of 1-naphthylboronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(1-naphthyl)cyclohexan-1-one (22Ab).



20A **22Ab**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	90	3	(+)
2	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	12	(-)
3	**4**-$P(O)_2O$	**4**-$P(O)_2O$	100	12	(+)
4	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	6	(+)
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	42	(+)
6	**7**-$P(O)_2O$	**7**-$P(O)_2O$	0	-	-
7	**8**-$P(O)_2O$	**8**-$P(O)_2O$	0	-	-
8	**9**-$P(O)_2O$	**9**-$P(O)_2O$	100	23	(+)
9	**10**-$P(O)_2O$	**10**-$P(O)_2O$	20	rac	-
10	**11**-$P(O)_2O$	**11**-$P(O)_2O$	0	-	-
11	**12**-$P(O)_2N$	**12**-$P(O)_2N$	0	-	-
12	**14**-$P(O)_2N$	**14**-$P(O)_2N$	0	-	-
13	**18**-$P(O)_2N$	**18**-$P(O)_2N$	50	52	(-)
14	**19**-$P(O)_2N$	**19**-$P(O)_2N$	50	52	(+)
15	**3**-$P(O)_2O$	**18**-$P(O)_2N$	100	73	(-)
16	**3**-$P(O)_2O$	**19**-$P(O)_2N$	100	61	(+)
17	**4**-$P(O)_2O$	**18**-$P(O)_2N$	100	60	(-)
18	**4**-$P(O)_2O$	**19**-$P(O)_2N$	100	47	(+)
19	**5**-$P(O)_2O$	**18**-$P(O)_2N$	100	49	(-)
20	**5**-$P(O)_2O$	**19**-$P(O)_2N$	100	53	(+)
21	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	43	(-)
22	**6**-$P(O)_2O$	**19**-$P(O)_2N$	95	83	(+)
23	**9**-$P(O)_2O$	**18**-$P(O)_2N$	100	75	(-)
24	**9**-$P(O)_2O$	**19**-$P(O)_2N$	100	70	(+)

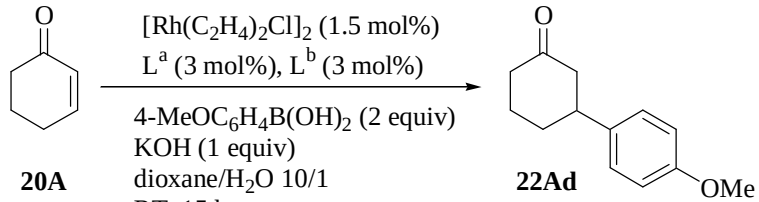
Rh-catalysed asymmetric 1,4-conjugate addition of (2-methoxyphenyl)boronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(2-methoxyphenyl)cyclohexan-1-one (22Ac).



20A **22Ac**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	22	*S*
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	95	4	*S*
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	92	4	*R*
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	41	*R*
5	**9**-$P(O)_2O$	**9**-$P(O)_2O$	95	rac	-
6	**10**-$P(O)_2O$	**10**-$P(O)_2O$	80	rac	-
7	**11**-$P(O)_2O$	**11**-$P(O)_2O$	100	3	*R*
8	**18**-$P(O)_2N$	**18**-$P(O)_2N$	100	42	*S*
9	**19**-$P(O)_2N$	**19**-$P(O)_2N$	100	42	*R*
10	**6**-$P(O)_2O$	**18**-$P(O)_2N$	73	25	*S*
11	**6**-$P(O)_2O$	**19**-$P(O)_2N$	80	40	*R*

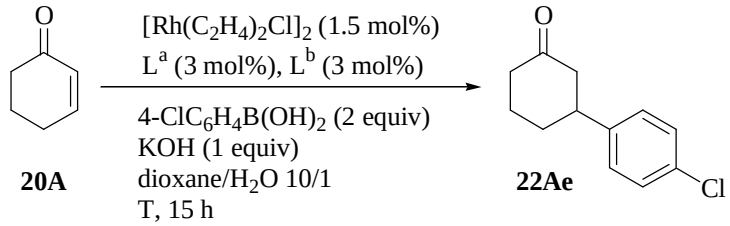
Rh-catalysed asymmetric 1,4-conjugate addition of (4-methoxyphenyl)boronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(4-methoxyphenyl)cyclohexan-1-one (22Ad).



20A **22Ad**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	25	*S*
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	100	32	*R*
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	15	*R*
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	64	*R*
5	**18**-$P(O)_2N$	**18**-$P(O)_2N$	50	6	*S*
6	**19**-$P(O)_2N$	**19**-$P(O)_2N$	50	6	*R*
7	**6**-$P(O)_2O$	**18**-$P(O)_2N$	95	60	*S*
8	**6**-$P(O)_2O$	**19**-$P(O)_2N$	97	92	*R*

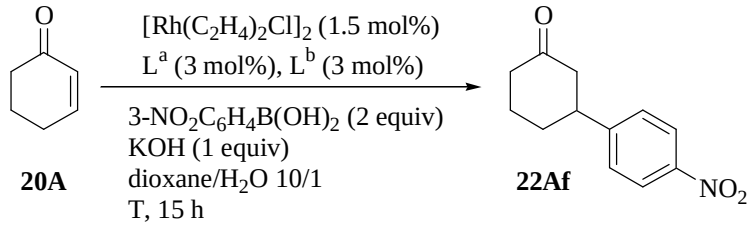
Rh-catalysed asymmetric 1,4-conjugate addition of (4-chlorophenyl)boronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(4-chlorophenyl)cyclohexan-1-one (22Ae).



20A **22Ae**

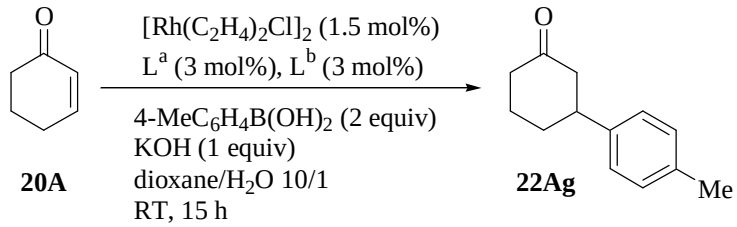
Entry	Ligand L^a	Ligand L^b	T (°C)	Catalyst mol %	Yield (%)	ee (%)	Abs. Config.
1	**3**-$P(O)_2O$	**3**-$P(O)_2O$	23	3	40	33	(-)
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	23	3	60	29	(+)
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	23	3	52	14	(+)
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	3	50	58	(+)
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	3	57	18	(+)
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	10	100	63	(+)
7	**9**-$P(O)_2O$	**9**-$P(O)_2O$	23	3	30	17	(+)
8	**12**-$P(O)_2N$	**12**-$P(O)_2N$	23	3	0	-	-
9	**14**-$P(O)_2N$	**14**-$P(O)_2N$	23	3	0	-	-
10	**18**-$P(O)_2N$	**18**-$P(O)_2N$	23	3	0	-	-
11	**19**-$P(O)_2N$	**19**-$P(O)_2N$	23	3	0	-	-
12	**19**-$P(O)_2N$	**19**-$P(O)_2N$	23	10	0	-	-
13	**6**-$P(O)_2O$	**18**-$P(O)_2N$	23	10	100	40	(-)
14	**6**-$P(O)_2O$	**19**-$P(O)_2N$	23	10	95	85	(+)
15	**9**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	90	63	(-)
16	**9**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	80	10	(-)

Rh-catalysed asymmetric 1,4-conjugate addition of (3-nitrophenyl)boronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(3-nitrophenyl)cyclohexan-1-one (22Af).



Entry	Ligand L^a	Ligand L^b	T (°C)	Catalyst mol %	Reaction time (h)	Yield (%)	ee (%)
1	**3**-$P(O)_2O$	**3**-$P(O)_2O$	23	3	15	0	-
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	23	3	15	0	-
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	23	3	15	0	-
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	3	15	0	-
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	3	48	0	-
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	3	72	0	-
7	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	3	15	0	-
8	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	10	15	0	-
9	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	10	15	0	-
10	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	10	48	0	-
11	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	10	72	0	-

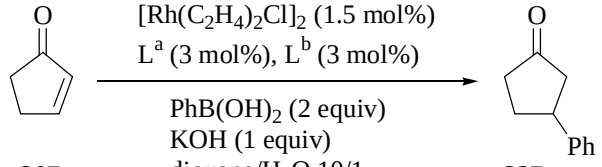
Rh-catalysed asymmetric 1,4-conjugate addition of (4-methylphenyl)boronic acid to 2-cyclohexen-1-one 20A. Synthesis of 3-(4-methylphenyl)cyclohexan-1-one (22Ag).



Entry	Ligand L^a	Ligand L^b	T (°C)	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	23	100	20	*R*
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	23	94	56	*R*
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	23	100	82	*R*
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	100	75	*R*
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	100	53	*R*
6	**18**-$P(O)_2N$	**18**-$P(O)_2N$	23	90	41	*S*
7	**19**-$P(O)_2N$	**19**-$P(O)_2N$	23	90	41	*R*
8	**5**-$P(O)_2O$	**18**-$P(O)_2N$	23	98	68	*S*
9	**5**-$P(O)_2O$	**19**-$P(O)_2N$	23	100	70	*R*

10	**6**-$P(O)_2O$	**18**-$P(O)_2N$	23	97	24	*R*
11	**6**-$P(O)_2O$	**19**-$P(O)_2N$	23	100	99	*R*

Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 2-cyclopenten-1-one (20B). Synthesis of 3-phenylcyclopentan-1-one (22Ba).

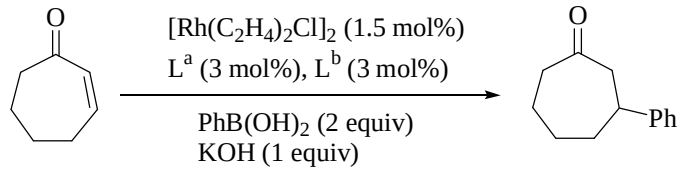


20B **22Ba**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**1**-$P(O)_2O$	**1**-$P(O)_2O$	100	15	*S*
2	**2**-$P(O)_2O$	**2**-$P(O)_2O$	100	15	*R*
3	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	15	*S*
4	**4**-$P(O)_2O$	**4**-$P(O)_2O$	100	27	*R*
5	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	8	*R*
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	45	*R*
7	**7**-$P(O)_2O$	**7**-$P(O)_2O$	100	58	*S*
8	**8**-$P(O)_2O$	**8**-$P(O)_2O$	0	-	-
9	**9**-$P(O)_2O$	**9**-$P(O)_2O$	60	16	*R*
10	**10**-$P(O)_2O$	**10**-$P(O)_2O$	0	-	-
11	**11**-$P(O)_2O$	**11**-$P(O)_2O$	0	-	-
12	**12**-$P(O)_2N$	**12**-$P(O)_2N$	0	-	-
13	**13**-$P(O)_2N$	**13**-$P(O)_2N$	0	-	-
14	**14**-$P(O)_2N$	**14**-$P(O)_2N$	0	-	-
15	**15**-$P(O)_2N$	**15**-$P(O)_2N$	0	-	-
16	**16**-$P(O)_2N$	**16**-$P(O)_2N$	0	-	-
17	**17**-$P(O)_2N$	**17**-$P(O)_2N$	0	-	-
18	**18**-$P(O)_2N$	**18**-$P(O)_2N$	90	32	*S*
19	**19**-$P(O)_2N$	**19**-$P(O)_2N$	90	32	*R*
20	**2**-$P(O)_2O$	**18**-$P(O)_2N$	100	13	*S*
21	**2**-$P(O)_2O$	**19**-$P(O)_2N$	100	55	*R*
22	**3**-$P(O)_2O$	**18**-$P(O)_2N$	100	38	*S*
23	**3**-$P(O)_2O$	**19**-$P(O)_2N$	100	51	*R*
24	**4**-$P(O)_2O$	**18**-$P(O)_2N$	100	36	*S*
25	**4**-$P(O)_2O$	**19**-$P(O)_2N$	100	61	*R*
26	**5**-$P(O)_2O$	**18**-$P(O)_2N$	100	47	*S*
27	**5**-$P(O)_2O$	**19**-$P(O)_2N$	100	60	*R*
28	**6**-$P(O)_2O$	**12**-$P(O)_2N$	100	26	*R*
29	**6**-$P(O)_2O$	**13**-$P(O)_2N$	100	35	*R*
30	**6**-$P(O)_2O$	**14**-$P(O)_2N$	90	40	*R*
31	**6**-$P(O)_2O$	**15**-$P(O)_2N$	90	40	*R*

32	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	13	*R*
33	**6**-$P(O)_2O$	**19**-$P(O)_2N$	100	73	*R*
34	**7**-$P(O)_2O$	**18**-$P(O)_2N$	100	42	*S*
35	**7**-$P(O)_2O$	**19**-$P(O)_2N$	100	20	*S*
36	**9**-$P(O)_2O$	**18**-$P(O)_2N$	100	26	*S*
37	**9**-$P(O)_2O$	**19**-$P(O)_2N$	100	68	*R*
38	**10**-$P(O)_2O$	**18**-$P(O)_2N$	100	21	*S*
39	**10**-$P(O)_2O$	**19**-$P(O)_2N$	100	31	*R*
40	**11**-$P(O)_2O$	**18**-$P(O)_2N$	90	61	*R*
41	**11**-$P(O)_2O$	**19**-$P(O)_2N$	70	50	*R*

Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 2-cyclohepten-1-one (20C). Synthesis of 3-phenylcycloheptan-1-one (22Ca).

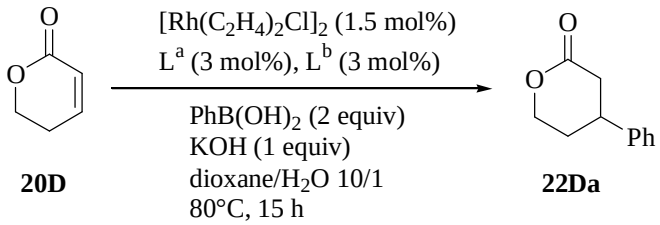


20C **22Ca**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**1**-$P(O)_2O$	**1**-$P(O)_2O$	90	rac	-
2	**2**-$P(O)_2O$	**2**-$P(O)_2O$	90	rac	-
3	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	28	*S*
4	**4**-$P(O)_2O$	**4**-$P(O)_2O$	80	11	*R*
5	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	19	*R*
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	45	*R*
7	**7**-$P(O)_2O$	**7**-$P(O)_2O$	30	6	*S*
8	**8**-$P(O)_2O$	**8**-$P(O)_2O$	0	-	-
9	**9**-$P(O)_2O$	**9**-$P(O)_2O$	50	21	*R*
10	**10**-$P(O)_2O$	**10**-$P(O)_2O$	0	-	-
11	**11**-$P(O)_2O$	**11**-$P(O)_2O$	15	rac	-
12	**12**-$P(O)_2N$	**12**-$P(O)_2N$	0	-	-
13	**13**-$P(O)_2N$	**13**-$P(O)_2N$	0	-	-
14	**14**-$P(O)_2N$	**14**-$P(O)_2N$	5	21	*S*
15	**15**-$P(O)_2N$	**15**-$P(O)_2N$	5	21	*R*
16	**16**-$P(O)_2N$	**16**-$P(O)_2N$	0	-	-
17	**17**-$P(O)_2N$	**17**-$P(O)_2N$	0	-	-
18	**18**-$P(O)_2N$	**18**-$P(O)_2N$	40	45	*S*
19	**19**-$P(O)_2N$	**19**-$P(O)_2N$	40	45	*R*
20	**2**-$P(O)_2O$	**18**-$P(O)_2N$	80	83	*S*
21	**2**-$P(O)_2O$	**19**-$P(O)_2N$	100	80	*R*
22	**3**-$P(O)_2O$	**18**-$P(O)_2N$	100	62	*S*
23	**3**-$P(O)_2O$	**19**-$P(O)_2N$	100	64	*R*
24	**4**-$P(O)_2O$	**18**-$P(O)_2N$	100	75	*S*
25	**4**-$P(O)_2O$	**19**-$P(O)_2N$	100	81	*R*
26	**5**-$P(O)_2O$	**18**-$P(O)_2N$	100	71	*S*
27	**5**-$P(O)_2O$	**19**-$P(O)_2N$	100	86	*R*
28	**6**-$P(O)_2O$	**12**-$P(O)_2N$	40	38	*R*
29	**6**-$P(O)_2O$	**13**-$P(O)_2N$	30	41	*R*
30	**6**-$P(O)_2O$	**14**-$P(O)_2N$	70	18	*R*
31	**6**-$P(O)_2O$	**15**-$P(O)_2N$	90	19	*R*

32	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	35	*S*
33	**6**-$P(O)_2O$	**19**-$P(O)_2N$	100	90	*R*
34	**7**-$P(O)_2O$	**18**-$P(O)_2N$	20	25	*S*
35	**7**-$P(O)_2O$	**19**-$P(O)_2N$	30	5	*R*
36	**9**-$P(O)_2O$	**18**-$P(O)_2N$	100	80	*S*
37	**9**-$P(O)_2O$	**19**-$P(O)_2N$	100	90	*R*
38	**10**-$P(O)_2O$	**18**-$P(O)_2N$	50	rac	-
39	**10**-$P(O)_2O$	**19**-$P(O)_2N$	40	30	*R*
40	**11**-$P(O)_2O$	**18**-$P(O)_2N$	10	29	*S*
41	**11**-$P(O)_2O$	**19**-$P(O)_2N$	10	55	*R*

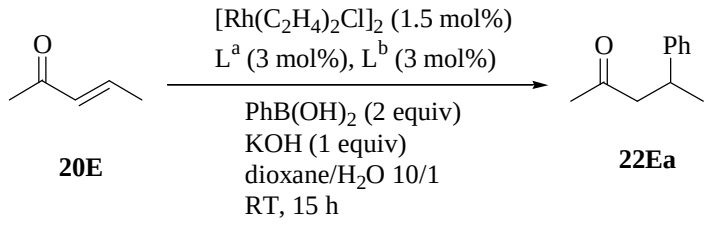
Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 5,6-dihydro-2H-pyran-2-one (20D). Synthesis of 4-(phenyl)tetrahydro-2H-pyran-2-one (22Da).



20D **22Da**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	70	30	*S*
2	**3**-$P(O)_2O$	**3**-$P(O)_2O$	80	rac	-
3	**4**-$P(O)_2O$	**4**-$P(O)_2O$	95	21	*R*
4	**5**-$P(O)_2O$	**5**-$P(O)_2O$	90	rac	-
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	40	*R*
6	**7**-$P(O)_2O$	**7**-$P(O)_2O$	0	-	-
7	**8**-$P(O)_2O$	**8**-$P(O)_2O$	0	-	-
8	**9**-$P(O)_2O$	**9**-$P(O)_2O$	40	10	*S*
9	**10**-$P(O)_2O$	**10**-$P(O)_2O$	20	rac	-
10	**11**-$P(O)_2O$	**11**-$P(O)_2O$	60	5	*R*
11	**12**-$P(O)_2N$	**12**-$P(O)_2N$	0	-	-
12	**14**-$P(O)_2N$	**14**-$P(O)_2N$	0	-	-
13	**17**-$P(O)_2N$	**17**-$P(O)_2N$	60	rac	-
14	**18**-$P(O)_2N$	**18**-$P(O)_2N$	80	50	*S*
15	**19**-$P(O)_2N$	**19**-$P(O)_2N$	80	50	*R*
16	**6**-$P(O)_2O$	**19**-$P(O)_2N$	65	48	*R*

Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 3-penten-2-one (20E). Synthesis of 4-phenylpentan-2-one (22Ea).

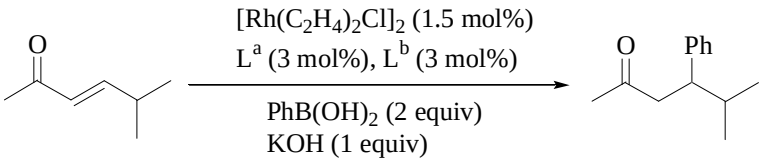


20E **22Ea**

Entry	Ligand L^a	Ligand L^b	T (°C)	Catalyst mol %	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	23	3	55	24	*R*
2	**3**-$P(O)_2O$	**3**-$P(O)_2O$	23	3	55	rac	
3	**4**-$P(O)_2O$	**4**-$P(O)_2O$	23	3	50	63	*R*
4	**5**-$P(O)_2O$	**5**-$P(O)_2O$	23	3	55	rac	
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	3	45	76	*R*
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	40	3	80	67	*R*
7	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	5	75	76	*R*
8	**7**-$P(O)_2O$	**7**-$P(O)_2O$	23	3	60	4	*R*
9	**8**-$P(O)_2O$	**8**-$P(O)_2O$	23	3	0	-	-
10	**9**-$P(O)_2O$	**9**-$P(O)_2O$	23	3	45	15	*R*
11	**10**-$P(O)_2O$	**10**-$P(O)_2O$	23	3	50	4	*R*
12	**11**-$P(O)_2O$	**11**-$P(O)_2O$	23	3	0	-	-
13	**12**-$P(O)_2N$	**12**-$P(O)_2N$	23	3	20	20	*S*
14	**13**-$P(O)_2N$	**13**-$P(O)_2N$	23	3	20	20	*R*
15	**14**-$P(O)_2N$	**14**-$P(O)_2N$	23	3	30	rac	-
16	**15**-$P(O)_2N$	**15**-$P(O)_2N$	23	3	30	rac	-
17	**18**-$P(O)_2N$	**18**-$P(O)_2N$	23	3	20	19	*S*
18	**19**-$P(O)_2N$	**19**-$P(O)_2N$	23	3	20	19	*R*
19	**2**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	30	9	*R*
20	**2**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	50	17	*R*
21	**3**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	55	19	*S*
22	**3**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	55	25	*R*
23	**4**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	60	30	*R*
24	**4**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	60	37	*R*
25	**6**-$P(O)_2O$	**12**-$P(O)_2N$	23	3	10	66	*R*
26	**6**-$P(O)_2O$	**13**-$P(O)_2N$	23	3	30	60	*R*
27	**6**-$P(O)_2O$	**14**-$P(O)_2N$	23	3	50	42	*R*
28	**6**-$P(O)_2O$	**15**-$P(O)_2N$	23	3	0	-	-
29	**6**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	60	57	*R*
30	**6**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	60	64	*R*

31	**9**-$P(O)_2O$	**18**-$P(O)_2N$	23	3	25	12	*R*
32	**9**-$P(O)_2O$	**19**-$P(O)_2N$	23	3	25	rac	-

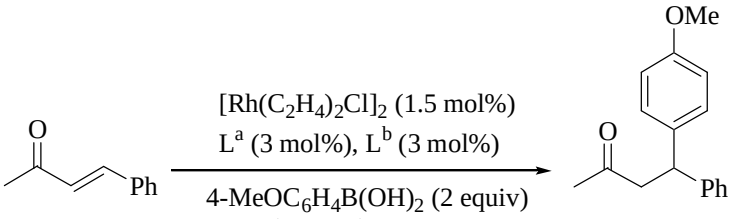
Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 5-methyl-3-hexen-2-one (20F). Synthesis of 5-methyl-4-phenyl-hexan-2-one (22Fa).



20F **22Fa**

Entry	Ligand L^a	Ligand L^b	T (°C)	Yield (%)	ee (%)	Abs. Config.
1	**1**-$P(O)_2O$	**1**-$P(O)_2O$	23	10	20	*R*
2	**2**-$P(O)_2O$	**2**-$P(O)_2O$	23	10	20	*S*
3	**3**-$P(O)_2O$	**3**-$P(O)_2O$	23	20	9	*R*
4	**4**-$P(O)_2O$	**4**-$P(O)_2O$	23	10	52	*S*
5	**5**-$P(O)_2O$	**5**-$P(O)_2O$	23	90	26	*R*
6	**6**-$P(O)_2O$	**6**-$P(O)_2O$	23	90	93	*S*
7	**6**-$P(O)_2O$	**6**-$P(O)_2O$	80	90	80	*S*
8	**7**-$P(O)_2O$	**7**-$P(O)_2O$	23	0	-	-
9	**8**-$P(O)_2O$	**8**-$P(O)_2O$	23	0	-	-
10	**9**-$P(O)_2O$	**9**-$P(O)_2O$	23	60	17	*S*
11	**10**-$P(O)_2O$	**10**-$P(O)_2O$	23	25	14	*S*
12	**11**-$P(O)_2O$	**11**-$P(O)_2O$	23	0	-	-
13	**12**-$P(O)_2N$	**12**-$P(O)_2N$	23	0	-	-
14	**14**-$P(O)_2N$	**14**-$P(O)_2N$	23	0	-	-
15	**18**-$P(O)_2N$	**18**-$P(O)_2N$	23	5	48	*R*
16	**19**-$P(O)_2N$	**19**-$P(O)_2N$	23	5	48	*S*
17	**4**-$P(O)_2O$	**14**-$P(O)_2N$	23	10	21	*S*
18	**4**-$P(O)_2O$	**15**-$P(O)_2N$	23	5	4	*R*
19	**6**-$P(O)_2O$	**12**-$P(O)_2N$	23	20	89	*S*
20	**6**-$P(O)_2O$	**13**-$P(O)_2N$	23	20	90	*S*
21	**6**-$P(O)_2O$	**14**-$P(O)_2N$	23	0	-	-
22	**6**-$P(O)_2O$	**15**-$P(O)_2N$	23	10	26	*S*
23	**6**-$P(O)_2O$	**18**-$P(O)_2N$	23	5	35	*S*
24	**6**-$P(O)_2O$	**19**-$P(O)_2N$	23	85	81	*S*

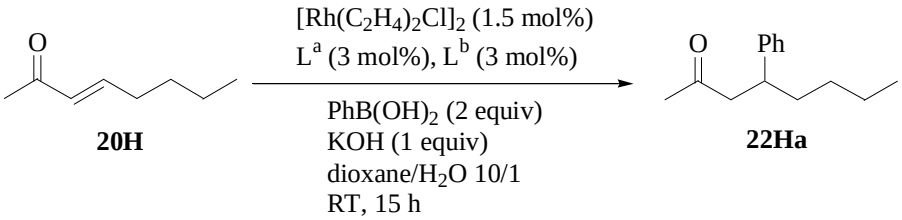
Rh-catalysed asymmetric 1,4-conjugate addition of (4-methoxyphenyl)boronic acid to 4-phenyl-3-buten-2-one (20G). Synthesis of 4-(4-methoxyphenyl)-4-phenyl-butan-2-one (22Gd).



20G **22Gd**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**3**-$P(O)_2O$	**3**-$P(O)_2O$	100	22	*R*
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	90	31	*S*
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	rac	-
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	80	*S*
5	**9**-$P(O)_2O$	**9**-$P(O)_2O$	50	8	*S*
6	**10**-$P(O)_2O$	**10**-$P(O)_2O$	85	67	*S*
7	**18**-$P(O)_2N$	**18**-$P(O)_2N$	90	42	*R*
8	**19**-$P(O)_2N$	**19**-$P(O)_2N$	90	42	*S*
9	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	50	*S*
10	**6**-$P(O)_2O$	**19**-$P(O)_2N$	100	82	*S*

Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 3-octen-2-one (20H). Synthesis of 4-phenyloctan-2-one (22Ha).

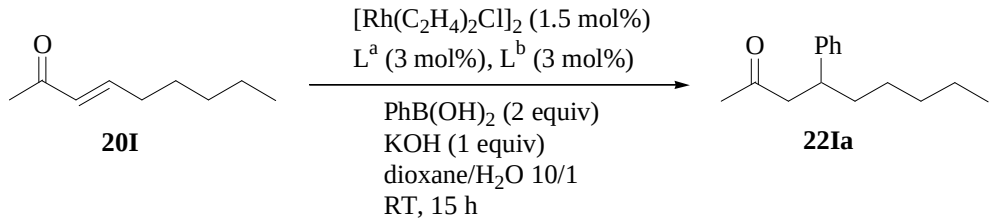


20H **22Ha**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**1**-$P(O)_2O$	**1**-$P(O)_2O$	50	20	(+)
2	**3**-$P(O)_2O$	**3**-$P(O)_2O$	40	8	(-)
3	**4**-$P(O)_2O$	**4**-$P(O)_2O$	80	60	(-)
4	**5**-$P(O)_2O$	**5**-$P(O)_2O$	80	rac	-
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	72	75	(-)
6	**18**-$P(O)_2N$	**18**-$P(O)_2N$	40	54	(+)
7	**19**-$P(O)_2N$	**19**-$P(O)_2N$	40	54	(-)
8	**6**-$P(O)_2O$	**18**-$P(O)_2N$	30	44	(-)

9	**6**-$P(O)_2O$	**19**-$P(O)_2N$	50	63	(-)

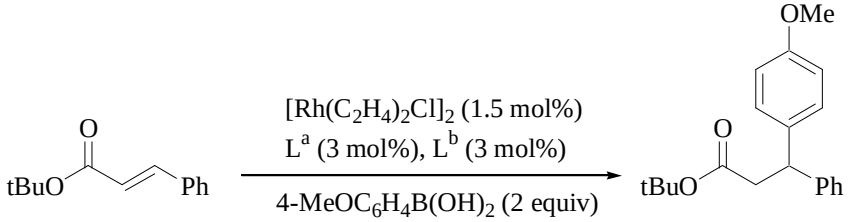
Rh-catalysed asymmetric 1,4-conjugate addition of phenylboronic acid to 3-nonen-2-one (20I). Synthesis of 4-phenylnonan-2-one (22Ia).



20I **22Ia**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	100	29	*R*
2	**4**-$P(O)_2O$	**4**-$P(O)_2O$	92	70	*R*
3	**5**-$P(O)_2O$	**5**-$P(O)_2O$	100	rac	-
4	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	92	*R*
5	**9**-$P(O)_2O$	**9**-$P(O)_2O$	23	20	*R*
6	**18**-$P(O)_2N$	**18**-$P(O)_2N$	5	61	*S*
7	**19**-$P(O)_2N$	**19**-$P(O)_2N$	5	61	*R*
8	**6**-$P(O)_2O$	**18**-$P(O)_2N$	20	8	*R*
9	**6**-$P(O)_2O$	**19**-$P(O)_2N$	97	80	*R*

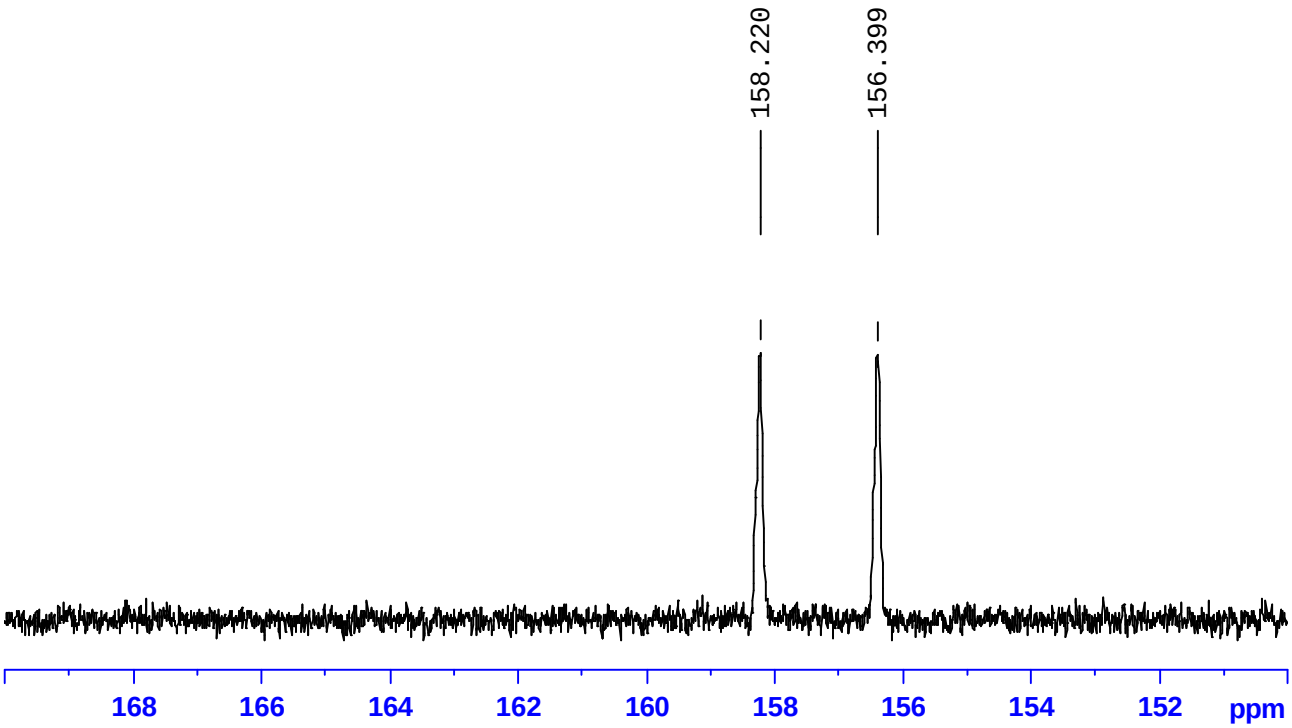
Rh-catalysed asymmetric 1,4-conjugate addition of (4-methoxyphenyl)boronic acid to *t*Bu-cinnamate (20J). Synthesis of *tert*-butyl-3-(4-methoxyphenyl)-3-phenylpropanoate (22Jd).



20J **22Jd**

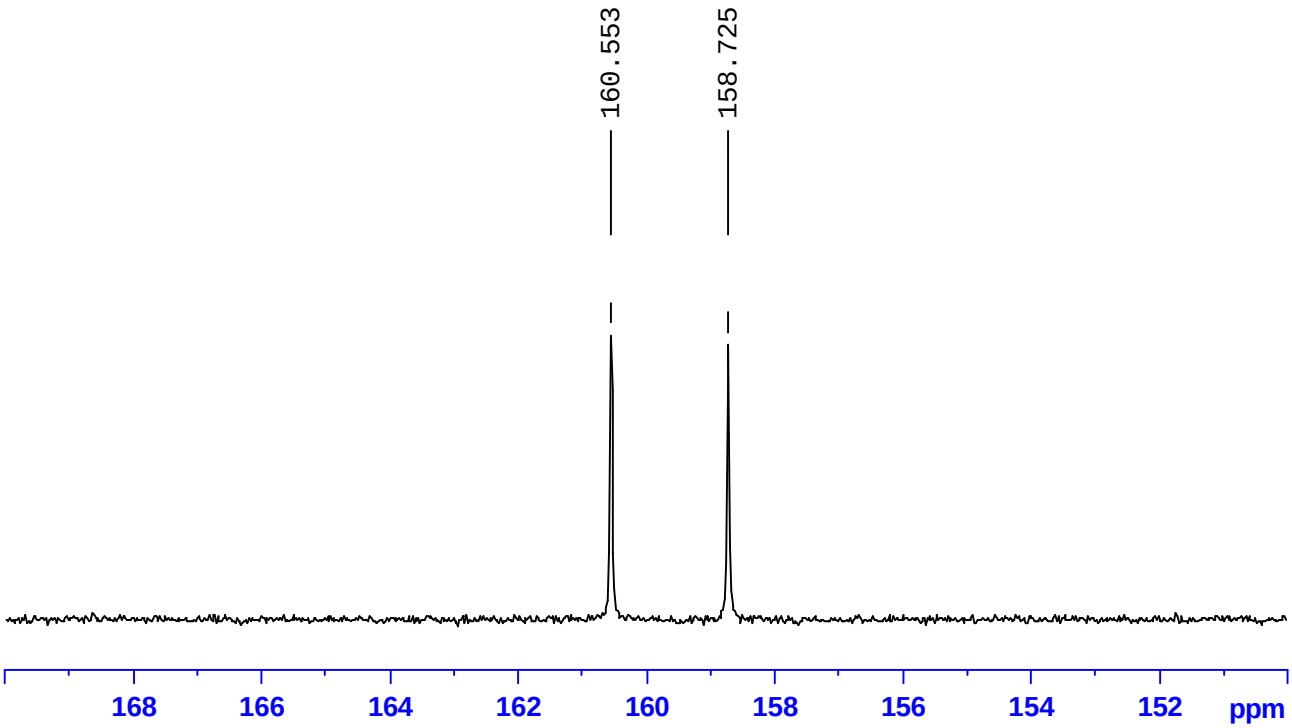
Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**2**-$P(O)_2O$	**2**-$P(O)_2O$	42	5	*S*
2	**3**-$P(O)_2O$	**3**-$P(O)_2O$	94	6	*S*
3	**4**-$P(O)_2O$	**4**-$P(O)_2O$	0	-	-
4	**5**-$P(O)_2O$	**5**-$P(O)_2O$	91	33	*S*
5	**6**-$P(O)_2O$	**6**-$P(O)_2O$	95	79	*S*
6	**9**-$P(O)_2O$	**9**-$P(O)_2O$	15	6	*S*
7	**18**-$P(O)_2N$	**18**-$P(O)_2N$	5	30	*S*
8	**19**-$P(O)_2N$	**19**-$P(O)_2N$	5	30	*R*
9	**6**-$P(O)_2O$	**18**-$P(O)_2N$	100	71	*S*
10	**6**-$P(O)_2O$	**19**-$P(O)_2N$	72	52	*S*

Figure A: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **6**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 380 K



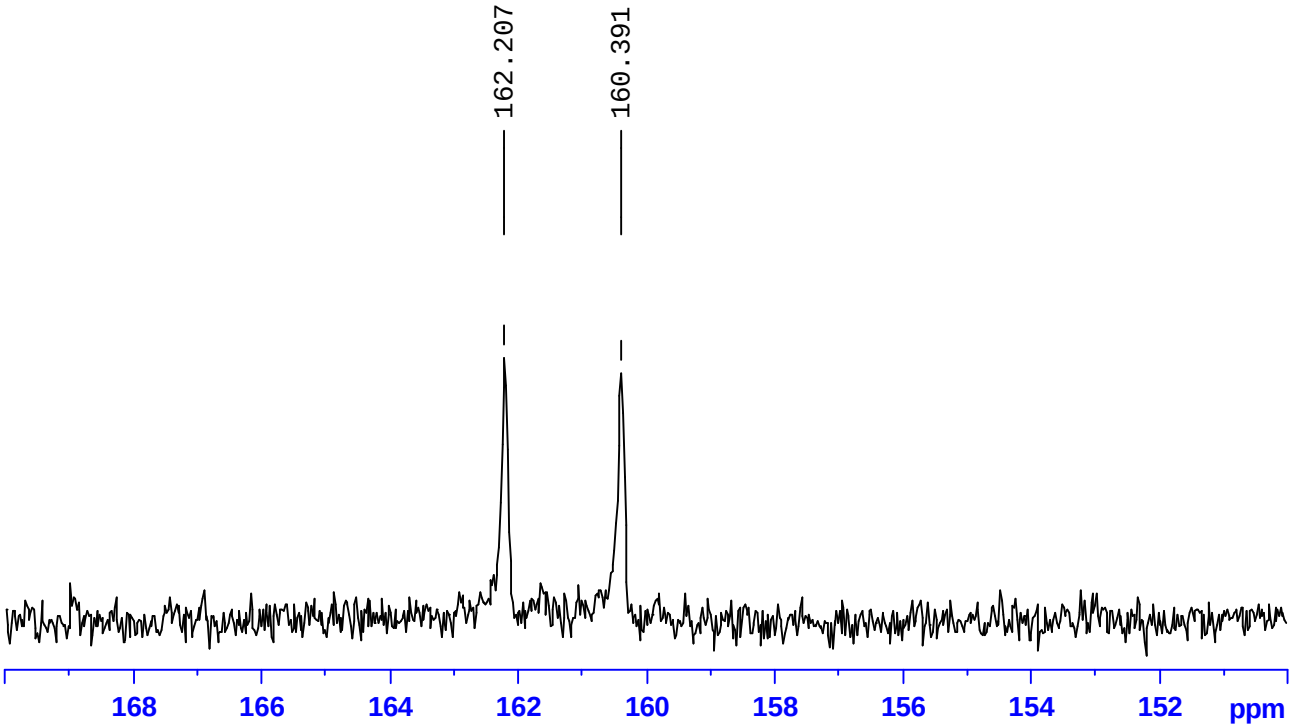
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 157.3 (d, $J_{P, Rh}$ = 295 Hz) ppm.

Figure B: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **6**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 300 K



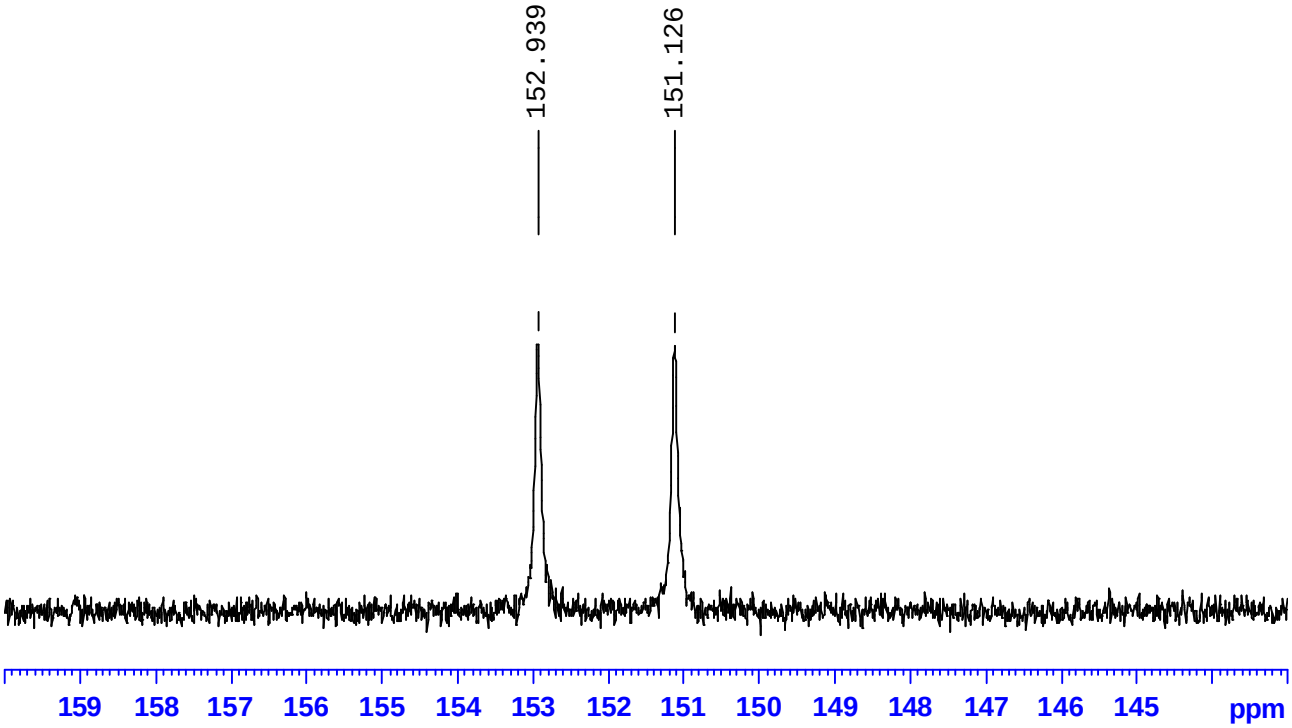
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 159.6 (d, $J_{P, Rh}$ = 296 Hz) ppm.

Figure C: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **6**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 230 K



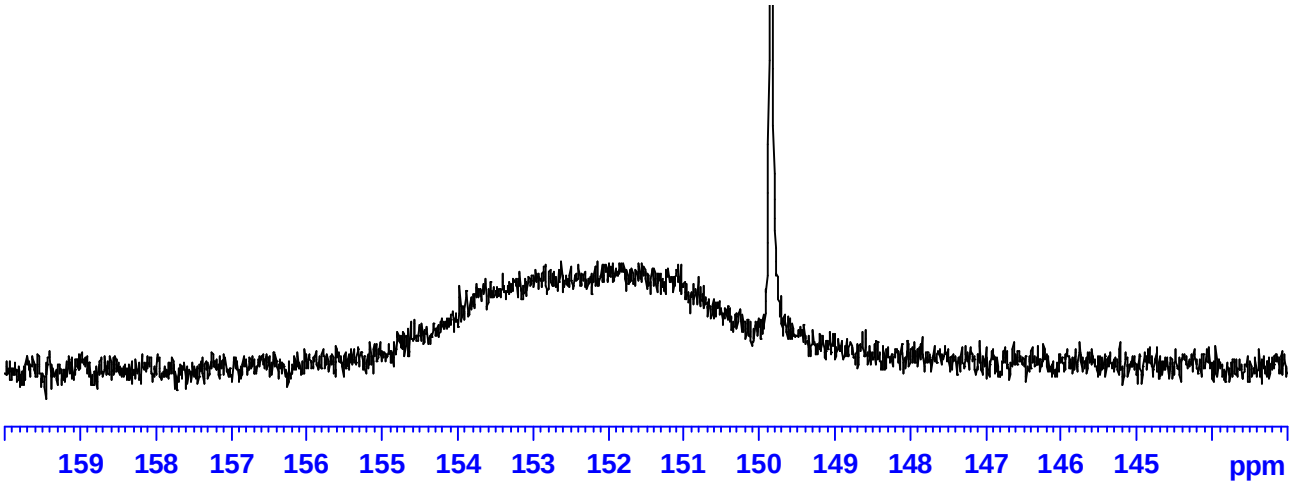
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 161.3 (d, $J_{P, Rh}$ = 294 Hz) ppm.

Figure D: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (2.0 equiv) in toluene-d$_8$ at 380 K



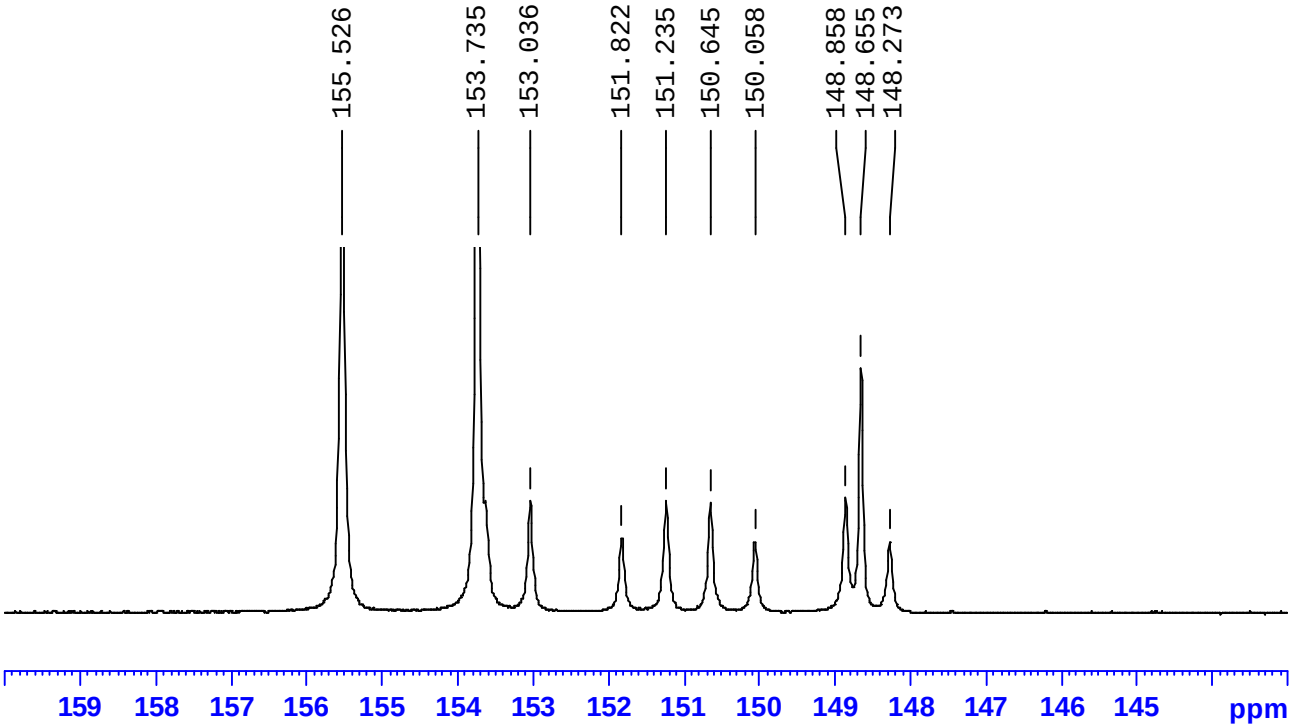
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 152.0 (d, $J_{P, Rh}$ = 294 Hz) ppm.

Figure E: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 320 K

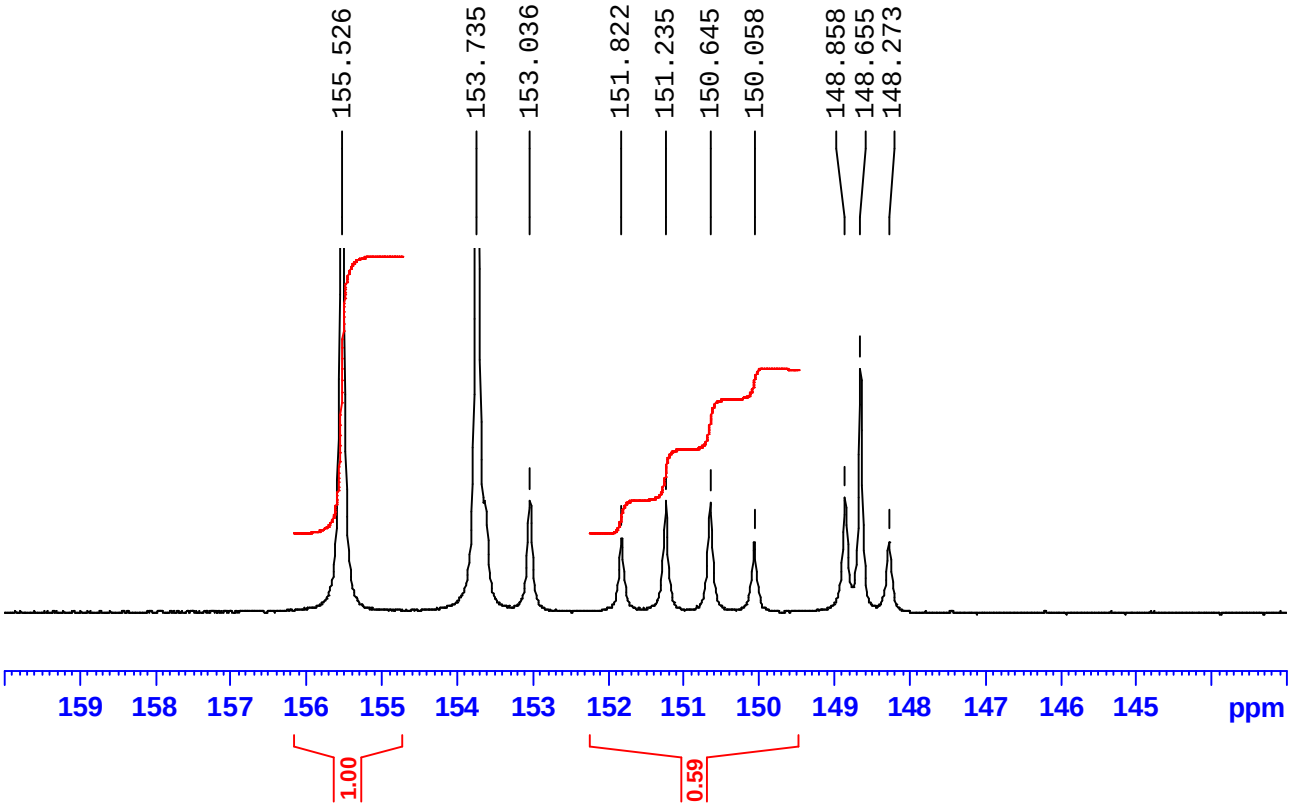


^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 151.9 (broad), 149.9 (s, excess ligand) ppm.

Figure F: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 230 K



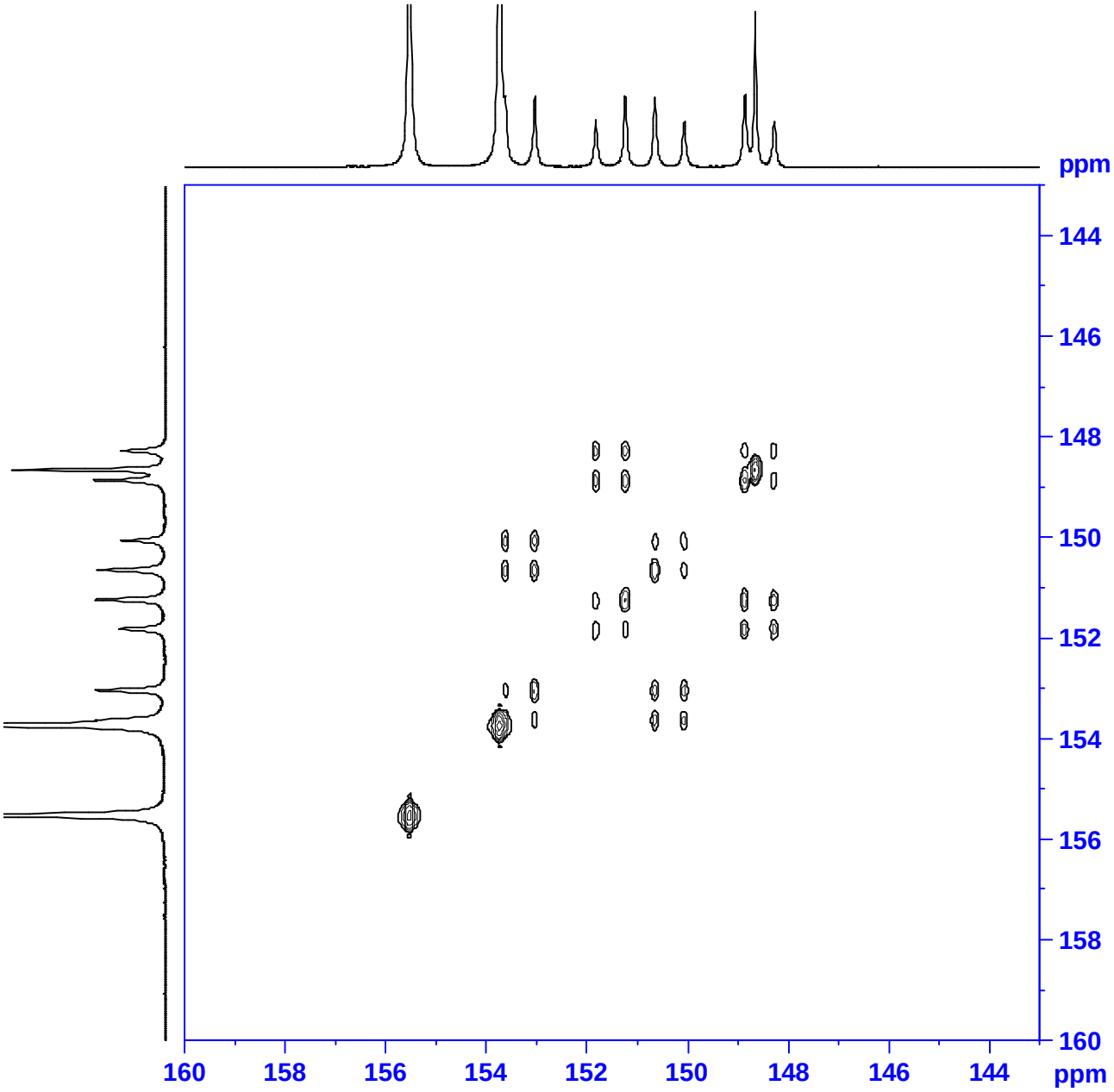
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 154.6 (d, $J_{P,\,Rh}$ = 290 Hz), 152.4 (dd, $J_{P,\,Rh}$ = 291.8 Hz, $J_{P,\,P}$ = 95 Hz), 149.5 (dd, $J_{P,\,Rh}$ = 289.5 Hz, $J_{P,\,P}$ = 95 Hz), 148.7 (s, excess ligand) ppm.



{Rh[(a*S*)-**19**]$_2$ + Rh[(a*R*)-**19**]$_2$} : Rh[(a*S*)-**19**][(a*R*)-**19**] = 1 : 0.59.

Rh[(a*S*)-**19**]$_2$ + Rh[(a*R*)-**19**]$_2$ = 62.9%; Rh[(a*S*)-**19**][(a*R*)-**19**] = 37.1%.

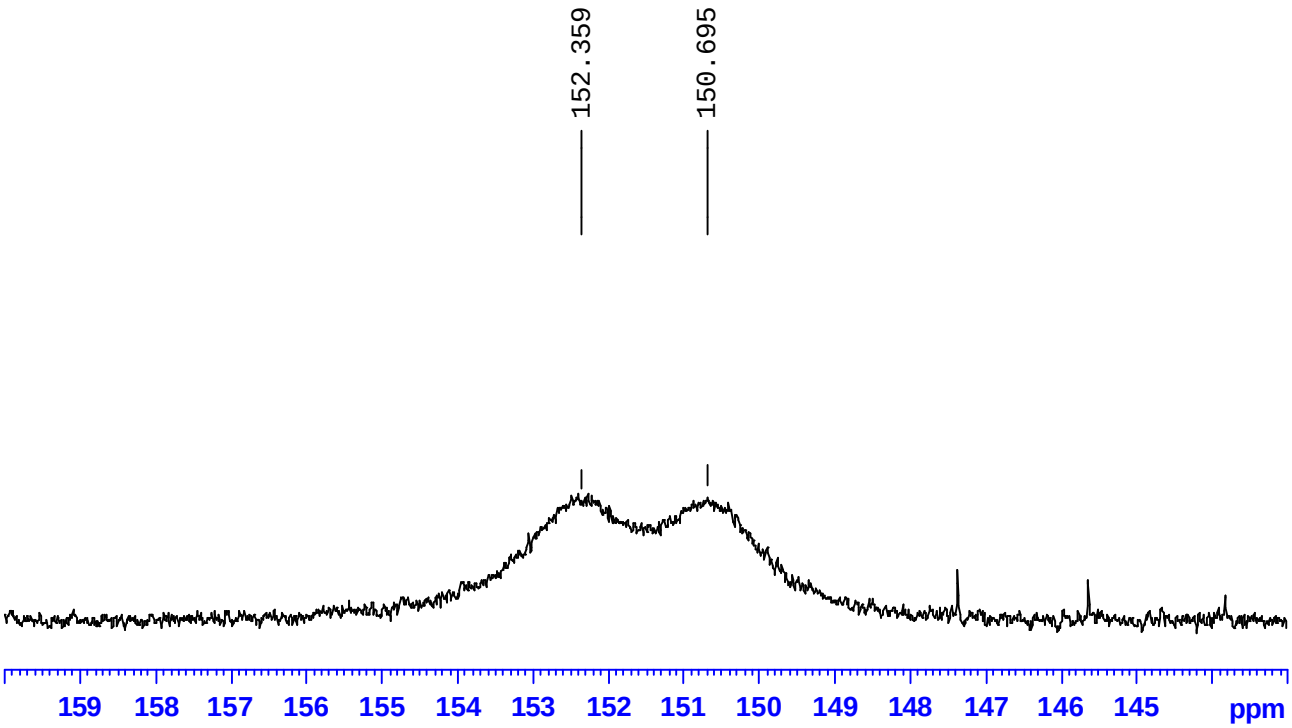
Figure G: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 230 K



Considering the complex Rh[(a*S*)-**19**][(a*R*)-**19**], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**19**] ? [(a*R*)-**19**] in toluene-d$_8$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**19**][(a*R*)-**19**] complex are = 152.4 ppm (dd, $J_{P,\ Rh}$ = 291.8 Hz, $J_{P,\ P}$ = 95 Hz) and = 149.5 ppm (dd, $J_{P,\ Rh}$ = 289.5 Hz, $J_{P,\ P}$ = 95 Hz), respectively; this gives a frequency separation (Δν) of 469.8 Hz. On warming, the lines broaden and coalesce: the coalescence temperature (T_c) is 320 K. From these data, the free energy of activation was calculated $\Delta G^{?} = RT_c [23 + \ln (T_c / \Delta\nu)] = 14.38$ kcal / mol.[22]

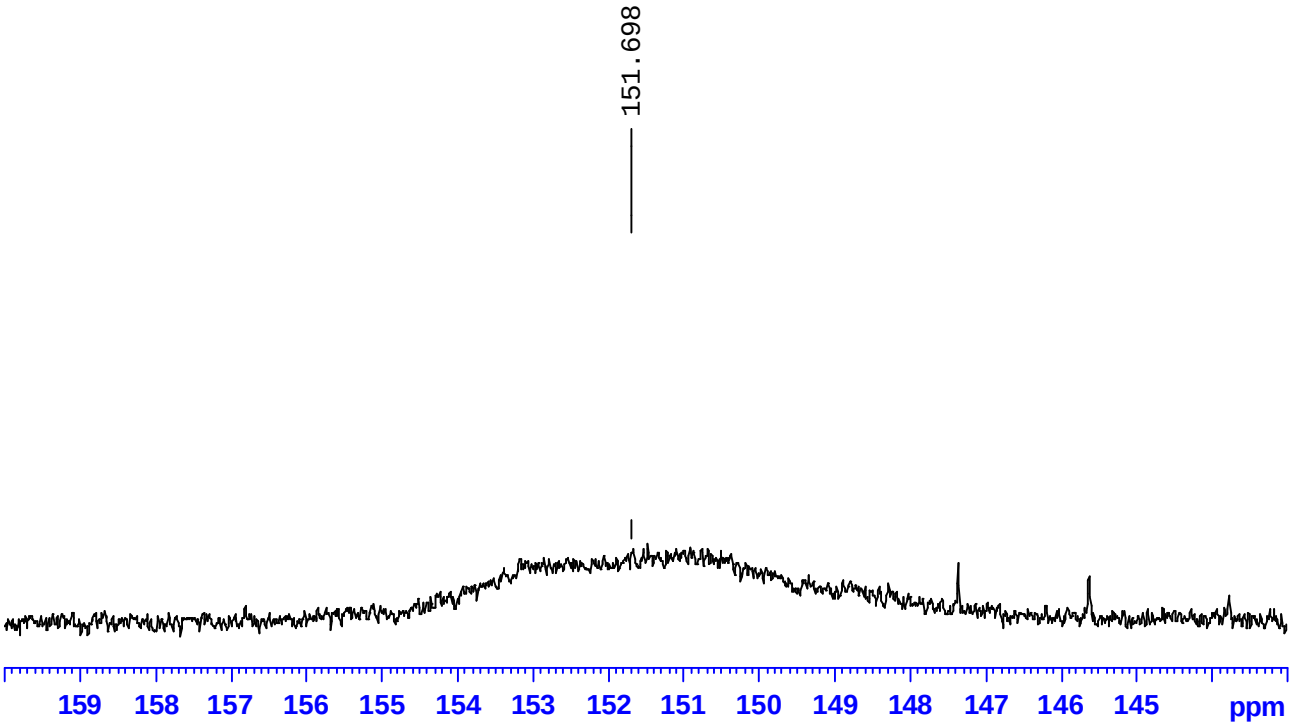
[22] M. Oki, in *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH: Weinheim, 1985.

Figure H: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 310 K



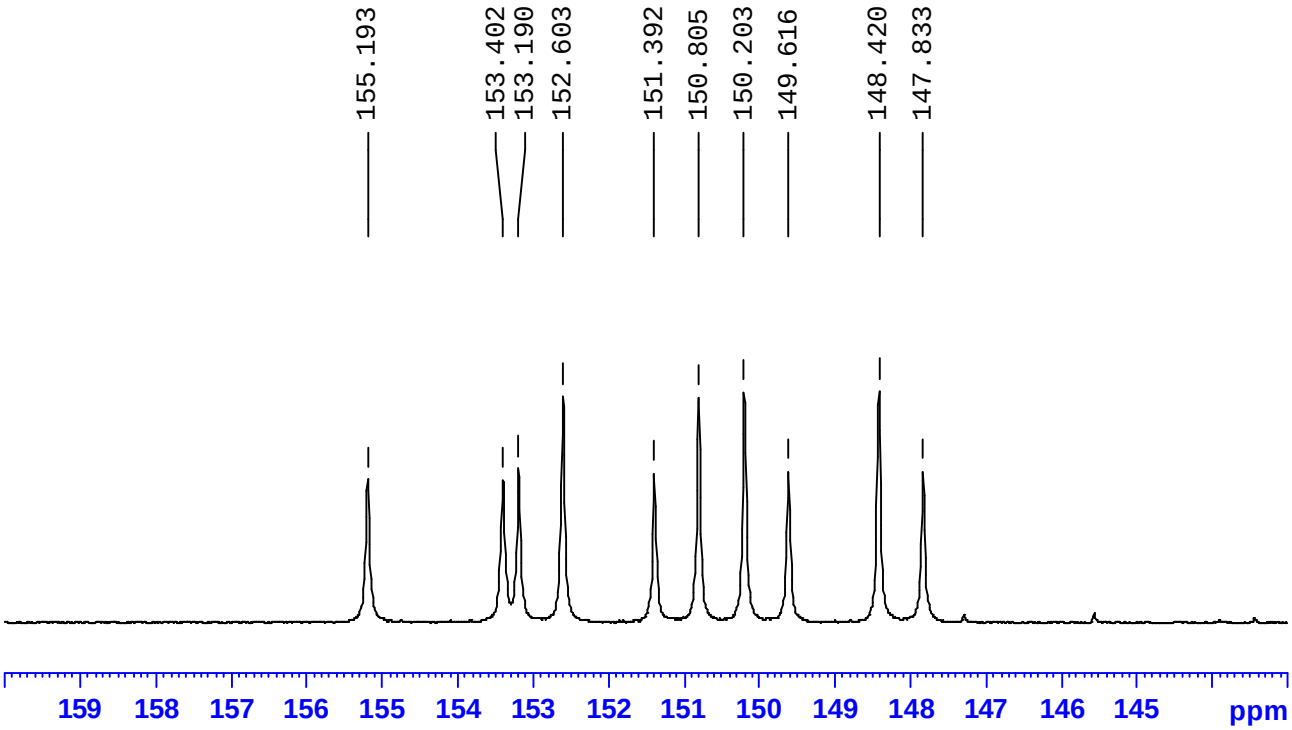
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 151.5 (d, $J_{P, Rh}$ = 270 Hz) ppm.

Figure I: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 290 K

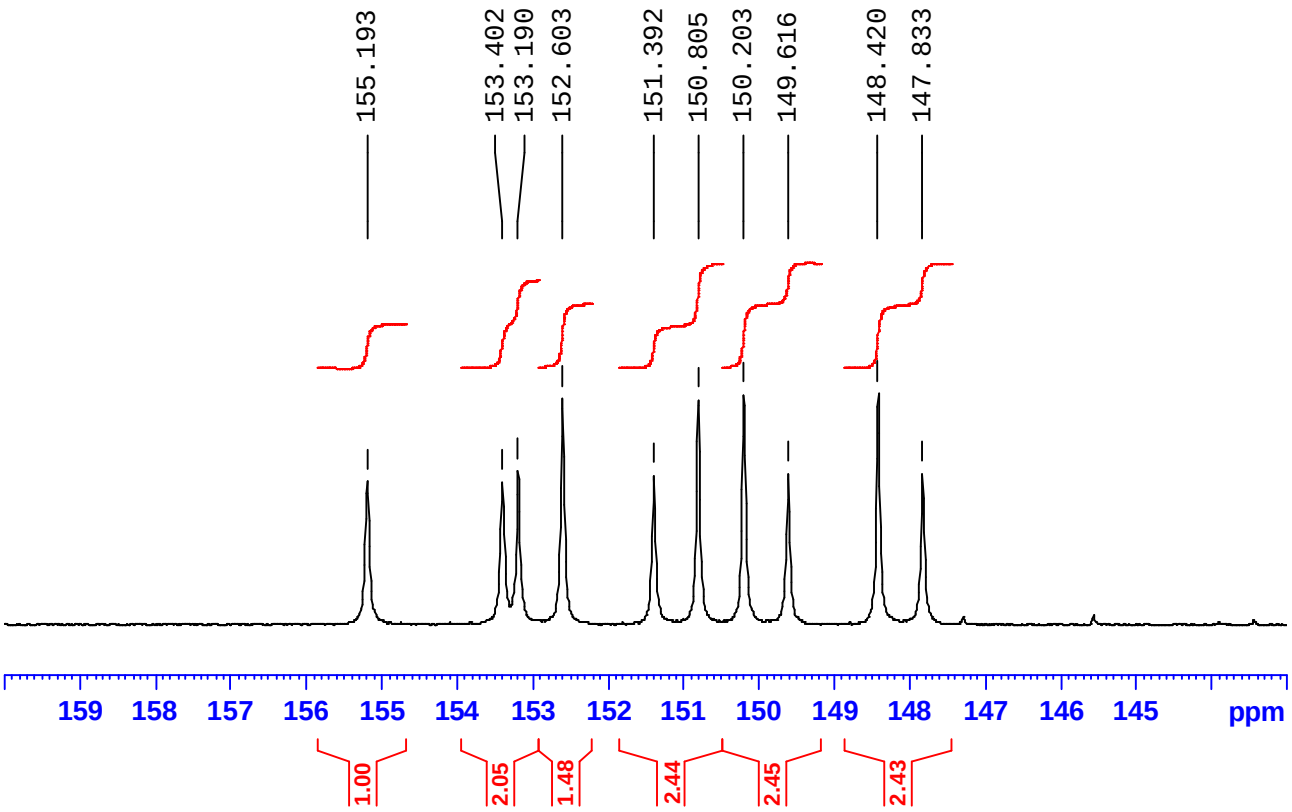


^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 151.7 ppm (broad).

Figure J: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 230 K



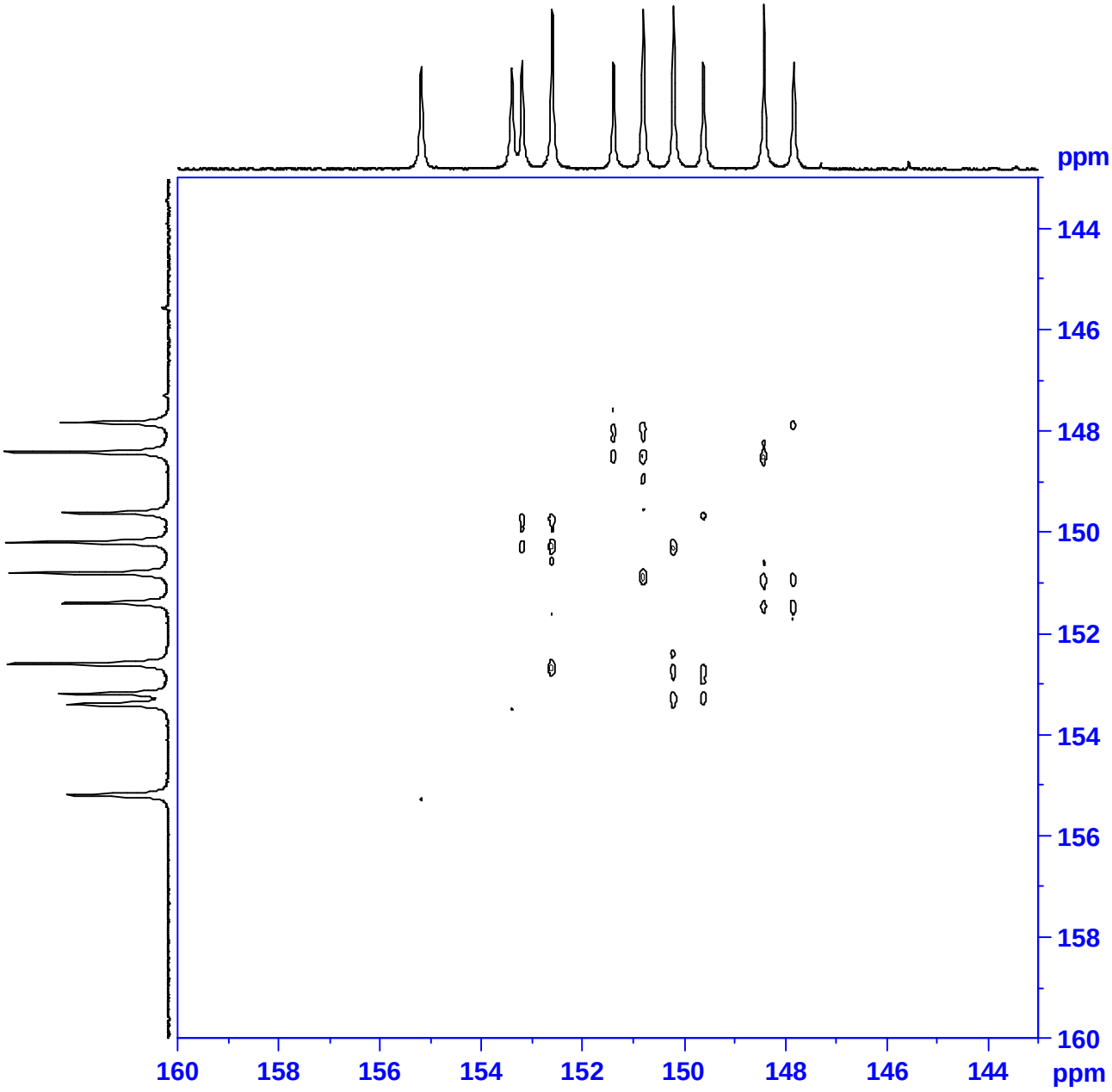
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 154.3 (d, $J_{P,\,Rh}$ = 290.1 Hz), 152.0 (dd, $J_{P,\,Rh}$ = 291.3 Hz, $J_{P,\,P}$ = 95 Hz), 149.0 (dd, $J_{P,\,Rh}$ = 288.8 Hz, $J_{P,\,P}$ = 95 Hz) ppm.



{Rh[(a*S*)-**19**]$_2$ + Rh[(a*R*)-**19**]$_2$} : Rh[(a*S*)-**19**][(a*R*)-**19**] = 2 : 9.85.

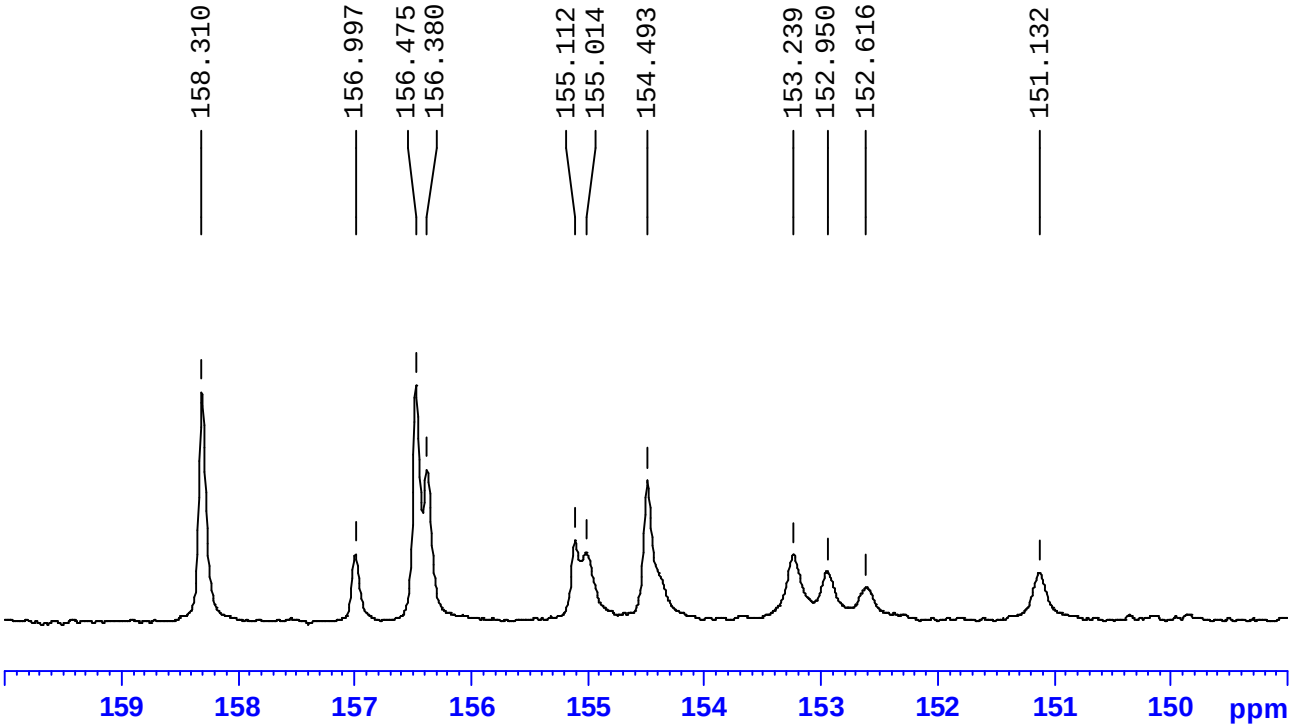
Rh[(a*S*)-**19**]$_2$ + Rh[(a*R*)-**19**]$_2$ = 16.9%; Rh[(a*S*)-**19**][(a*R*)-**19**] = 83.1%.

Figure K: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **19**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 230 K

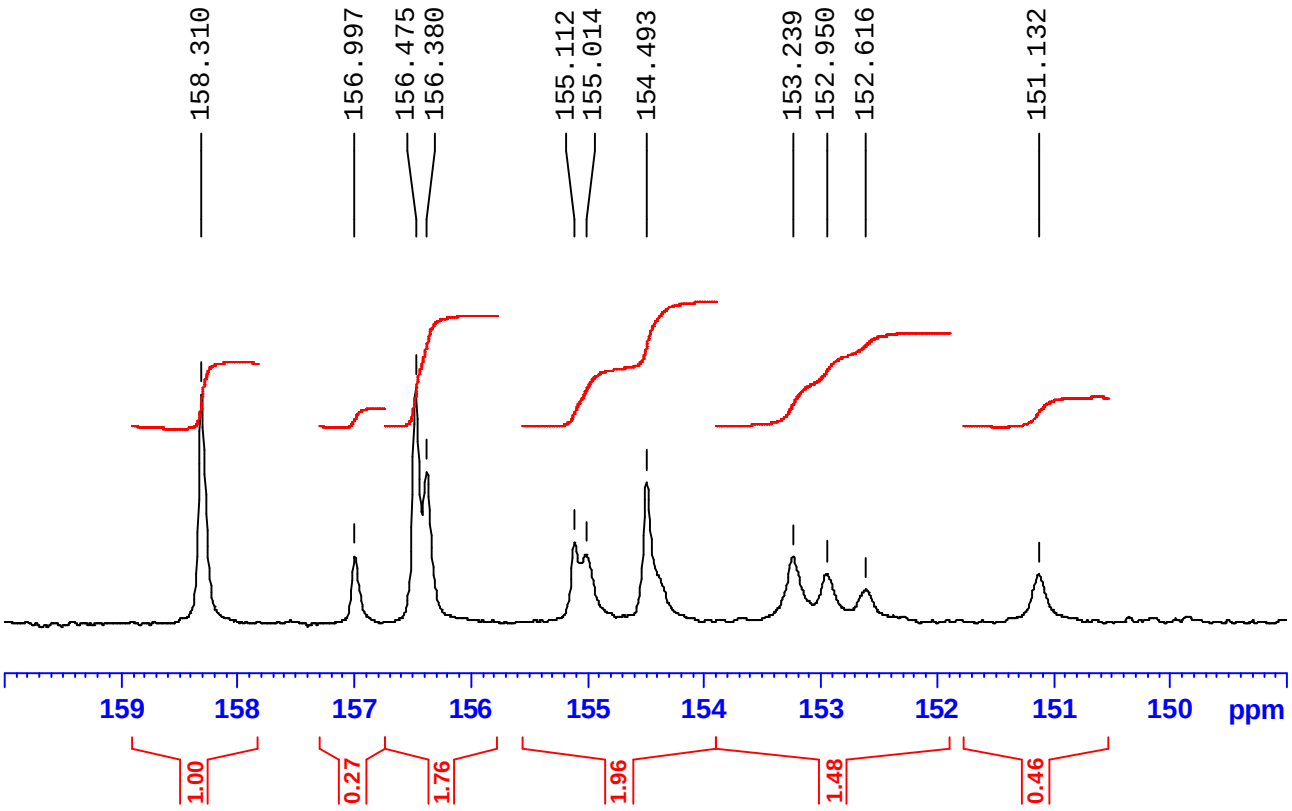


Considering the complex Rh[(a*S*)-**19**][(a*R*)-**19**], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**19**] ? [(a*R*)-**19**] in dichloromethane-d$_2$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**19**][(a*R*)-**19**] complex are = 152.0 ppm (dd, $J_{P, Rh}$ = 291.3 Hz, $J_{P, P}$ = 95 Hz) and = 149.0 ppm (dd, $J_{P, Rh}$ = 288.8 Hz, $J_{P, P}$ = 95 Hz), respectively; this gives a frequency separation (Δν) of 486.0 Hz. On warming, the lines broaden and coalesce: the coalescence temperature (T_c) is 290 K. From these data, the free energy of activation was calculated $\Delta G^? = RT_c [23 + \ln (T_c / \Delta\nu)]$ = 12.95 kcal / mol.[22]

Figure L: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 375 K



^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 157.4 (d, $J_{P,\,Rh}$ = 297.3 Hz, Rh[**6**-P(O)$_2$O]$_2$), 155.7 (dd, $J_{P,\,Rh}$ = 305.4 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N]), 153.8 (dd, $J_{P,\,Rh}$ = 287.5 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N]), 152.0 (d, $J_{P,\,Rh}$ = 294.5 Hz, Rh[**19**-P(O)$_2$N]$_2$) ppm.



Rh[**6**-P(O)$_2$O]$_2$ = 28%; Rh[**19**-P(O)$_2$N]$_2$ = 14%; Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N] = 58%.

Figure M: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 375 K

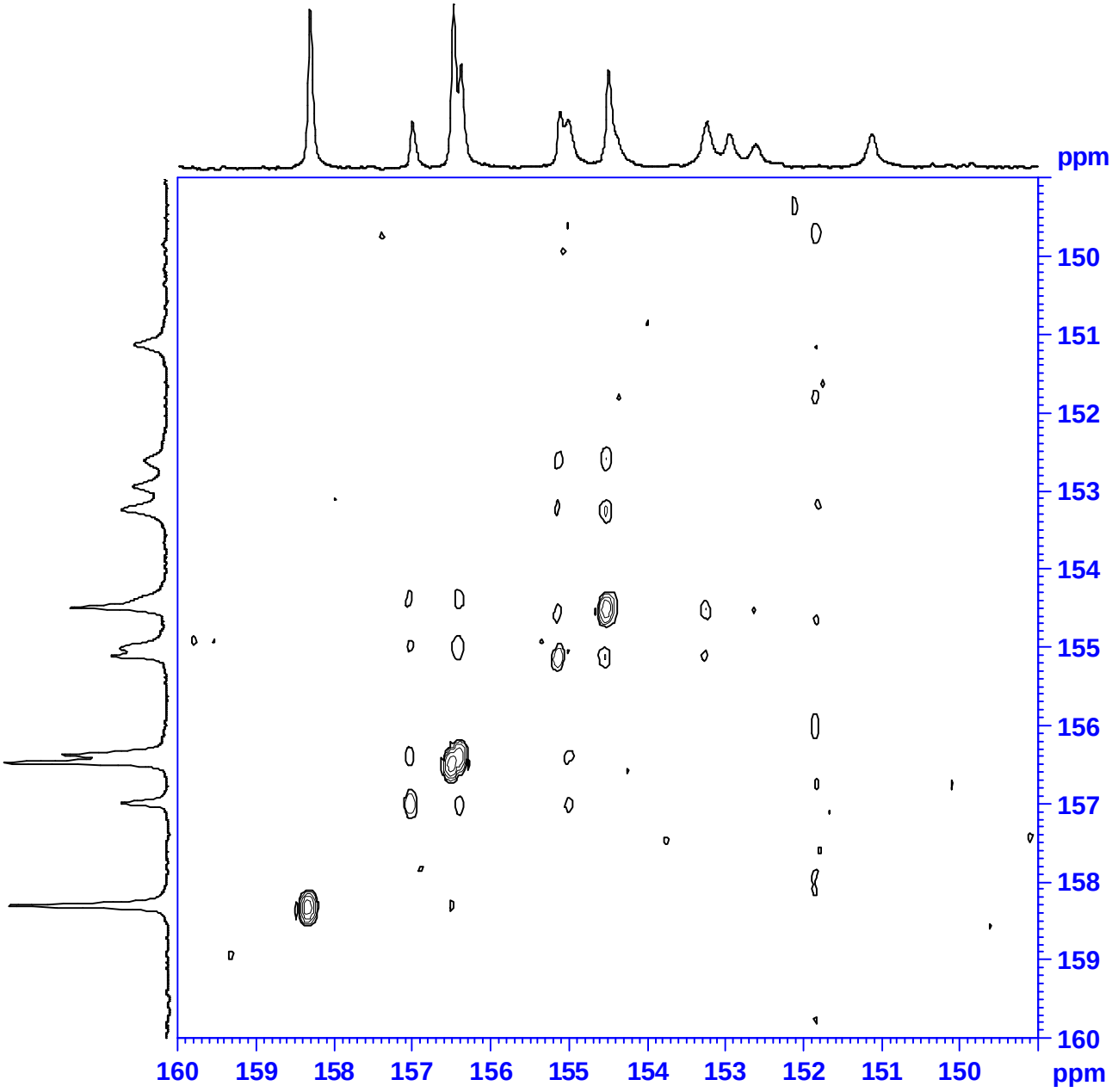
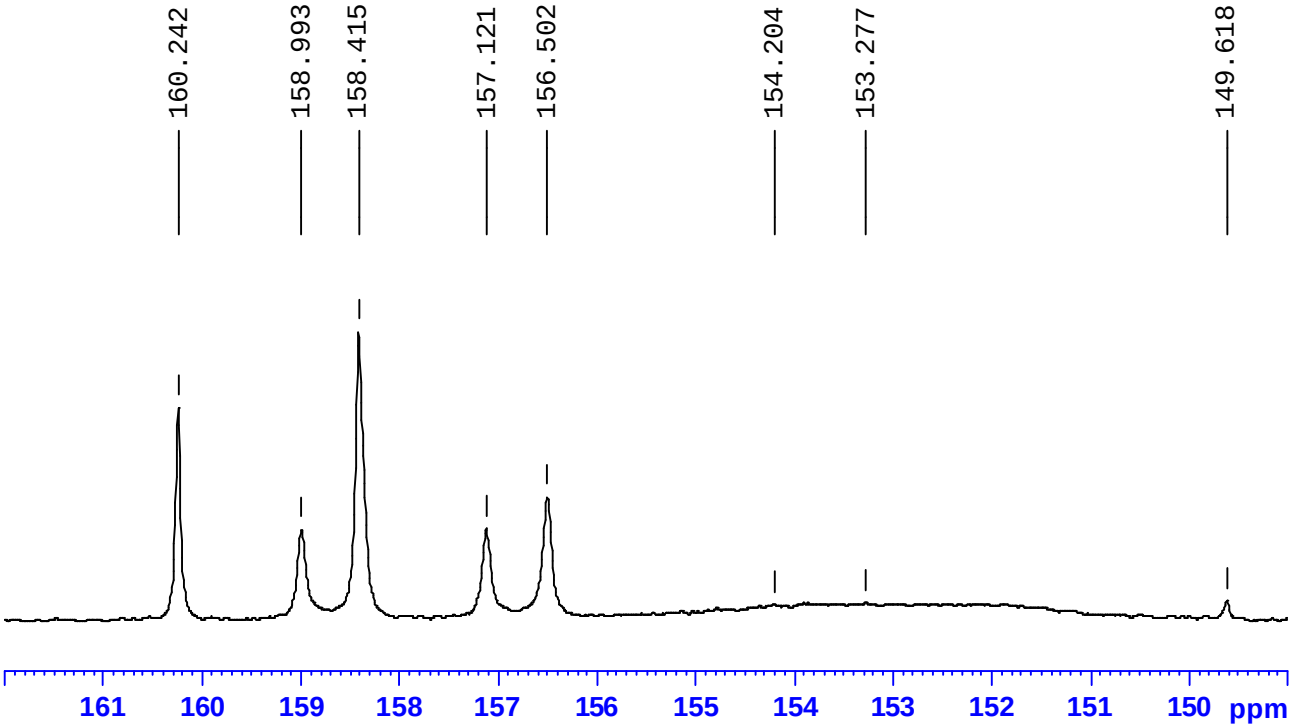
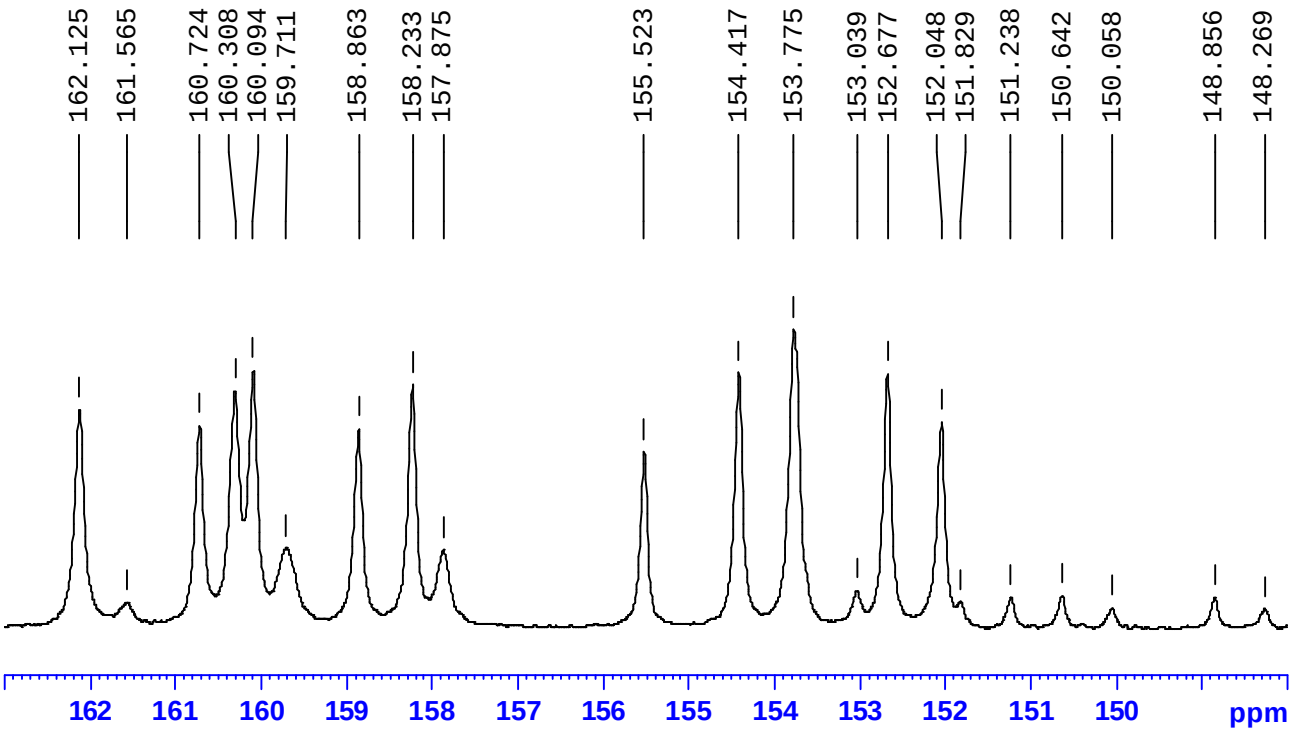


Figure N: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 310 K



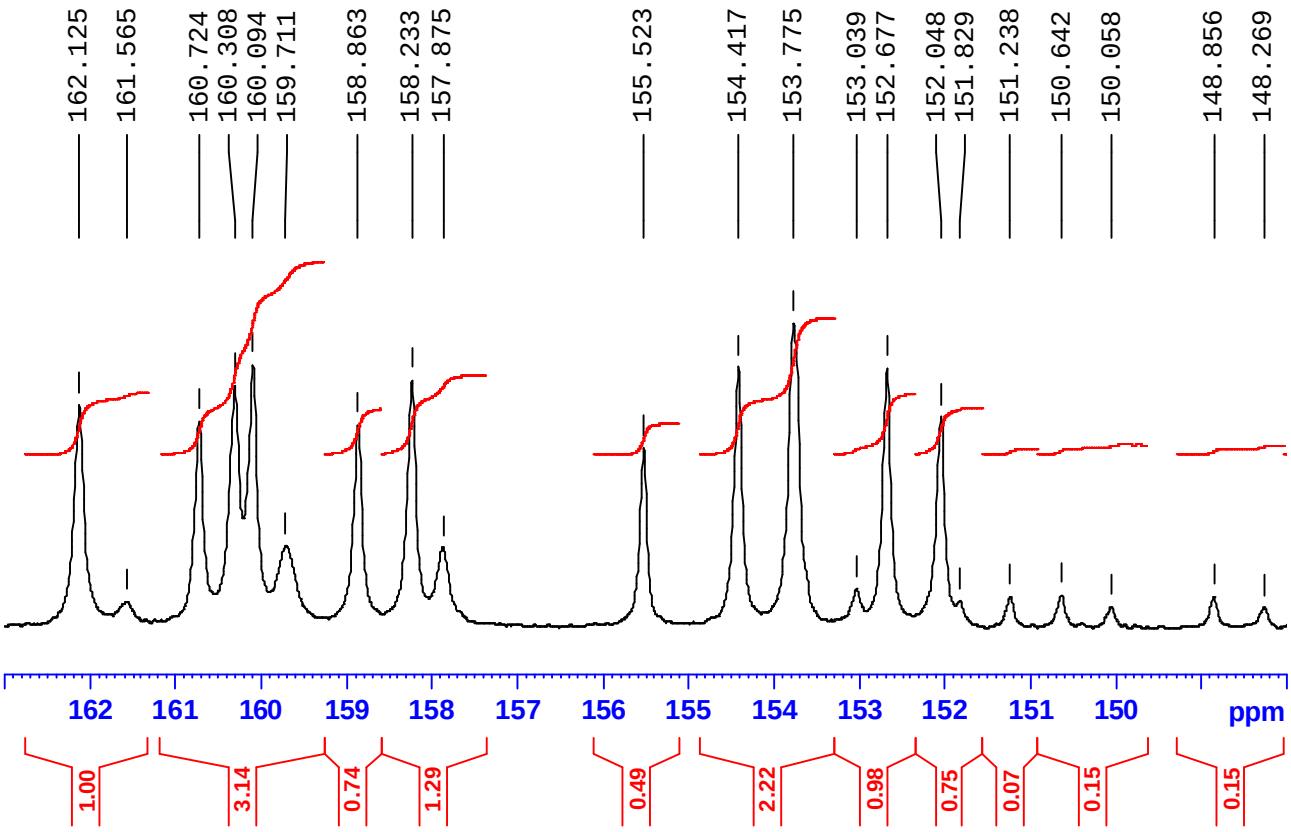
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 159.3 (d, $J_{P,\ Rh}$ = 296.0 Hz, Rh[**6**-P(O)$_2$O]$_2$), 157.7 (dd, $J_{P,\ Rh}$ = 303.2 Hz, $J_{P,\ P}$ = 100.3 Hz, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N]), 155.5-150.5 (broad signal, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N] and Rh[**19**-P(O)$_2$N]$_2$), 149.6 (s, excess ligand) ppm.

Figure O: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 161.2 (d, $J_{P,\,Rh}$ = 294.3 Hz, Rh[**6**-P(O)$_2$O]$_2$), 159.5 (dd, $J_{P,\,Rh}$ = 301.5 Hz, $J_{P,\,P}$ = 102.0 Hz, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N]), 158.8 (d, $J_{P,\,Rh}$ = 297.4 Hz, unknown species), 154.6 (d, $J_{P,\,Rh}$ = 283.2 Hz, Rh[**19**-P(O)$_2$N]$_2$), 153.2 (dd, $J_{P,\,Rh}$ = 281.9 Hz, $J_{P,\,P}$ = 101.9 Hz, Rh[**6**-P(O)$_2$O][**19**-P(O)$_2$N]), 152.4 (dd, $J_{P,\,Rh}$ = 291.7 Hz, $J_{P,\,P}$ = 95.7 Hz, Rh[**19**-P(O)$_2$N]$_2$), 149.4 (dd, $J_{P,\,Rh}$ = 290.0 Hz, $J_{P,\,P}$ = 95.0 Hz, Rh[**19**-P(O)$_2$N]$_2$) ppm.

Figure P: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



Rh[**7**-P(O)$_2$O]$_2$ = 20.9%; Rh[**19**-P(O)$_2$N]$_2$ = 16.4%; Rh[**7**-P(O)$_2$O][**19**-P(O)$_2$N] = 62.7%.

Figure Q: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **19**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K

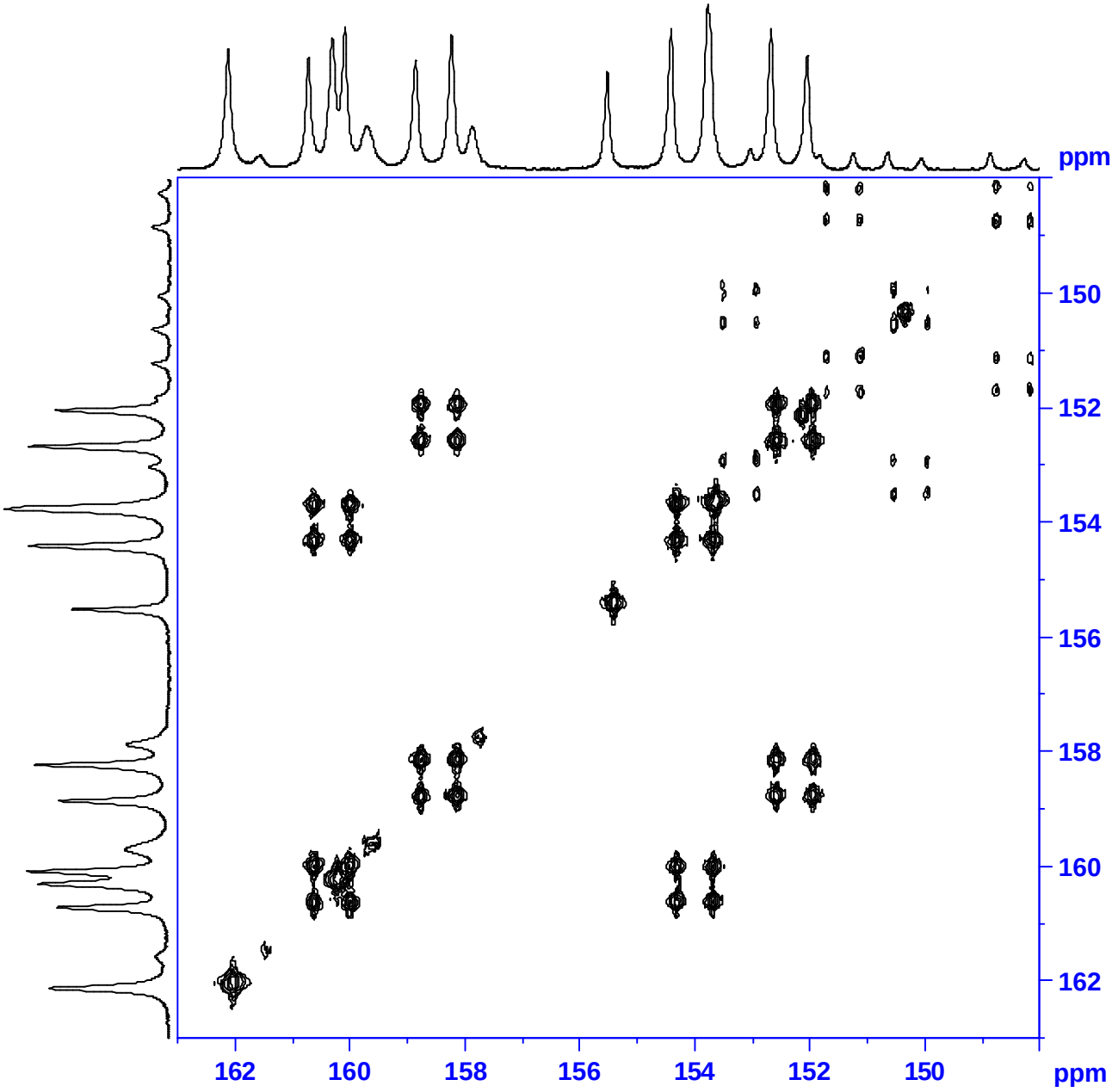
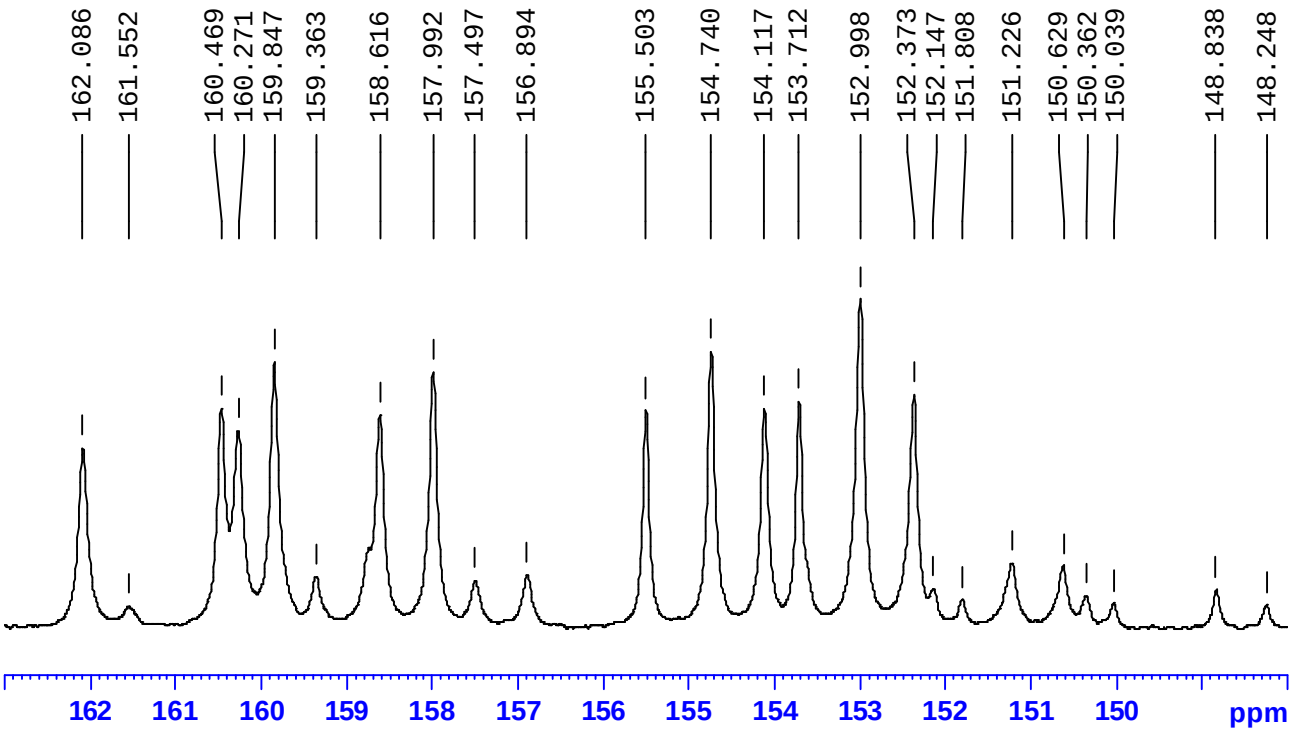
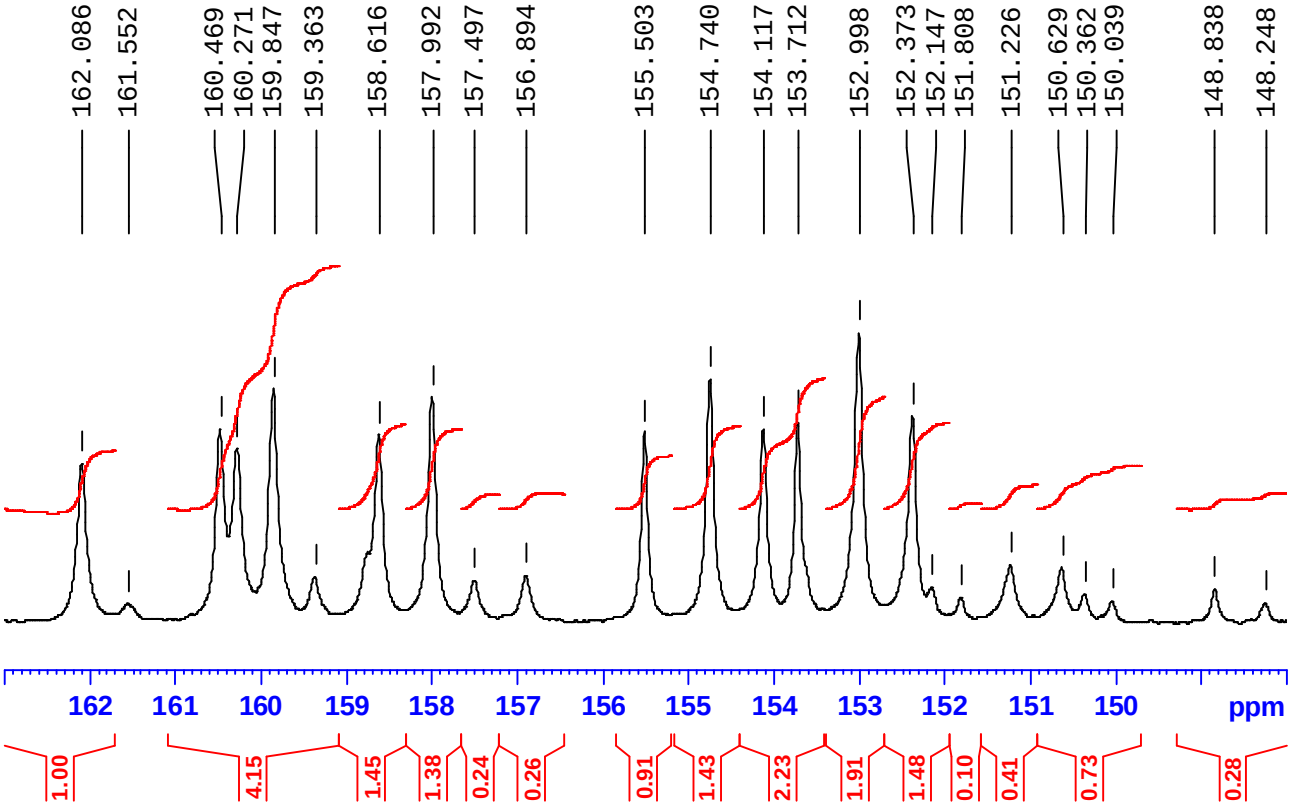


Figure R: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **18**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 161.2 (d, $J_{P,\,Rh}$ = 294.0 Hz, Rh[**6**-P(O)$_2$O]$_2$), 159.2 (dd, $J_{P,\,Rh}$ = 300.5 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], major), 158.1 (dd, $J_{P,\,Rh}$ = 302.3 Hz, $J_{P,\,P}$ = 97.7 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], minor), 154.6 (d, $J_{P,\,Rh}$ = 290.1Hz, Rh[**18**-P(O)$_2$N]$_2$), 153.5 (dd, $J_{P,\,Rh}$ = 282.2 Hz, $J_{P,\,P}$ = 101.0 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], major), 152.4 (dd, $J_{P,\,Rh}$ = 290.1 Hz, $J_{P,\,P}$ = 95.6 Hz, Rh[**18**-P(O)$_2$N]$_2$), 151.8 (dd, $J_{P,\,Rh}$ = 282.5 Hz, $J_{P,\,P}$ = 97.2 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], minor), 149.3 (dd, $J_{P,\,Rh}$ = 290.1Hz, $J_{P,\,P}$ = 95.6 Hz, Rh[**18**-P(O)$_2$N]$_2$) ppm.

Figure S: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **18**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



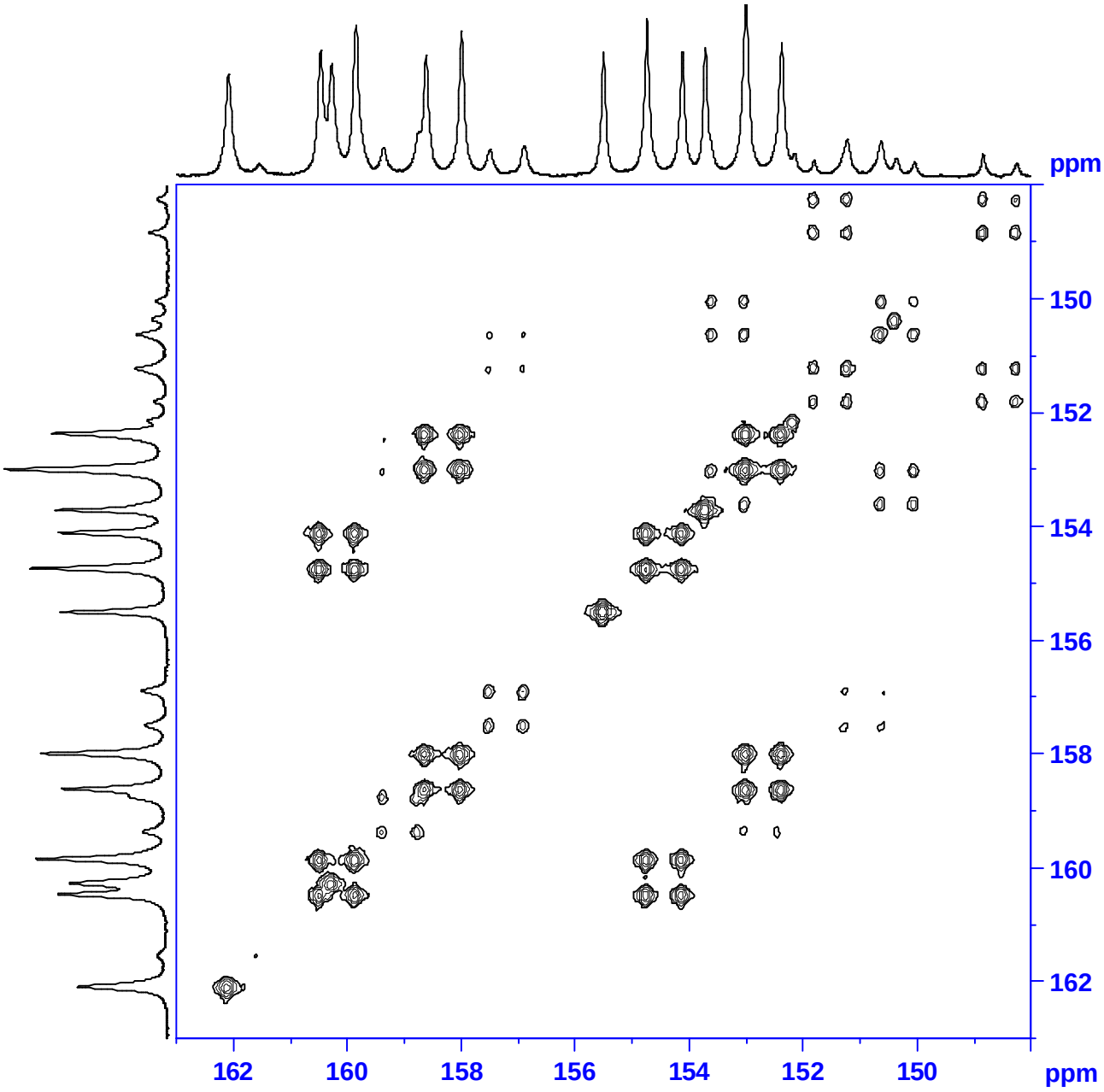
{Rh[(a*S*)-**18**]$_2$ + Rh[(a*R*)-**18**]$_2$ + Rh[(a*S*)-**18**][(a*R*)-**18**]} = 16.4%;

Rh[**6**-P(O)$_2$O]$_2$ = 11.1%;

{Rh[(a*S*)-**18**][**6**-P(O)$_2$O] + Rh[(a*R*)-**18**][**6**-P(O)$_2$O]} = 72.5%;

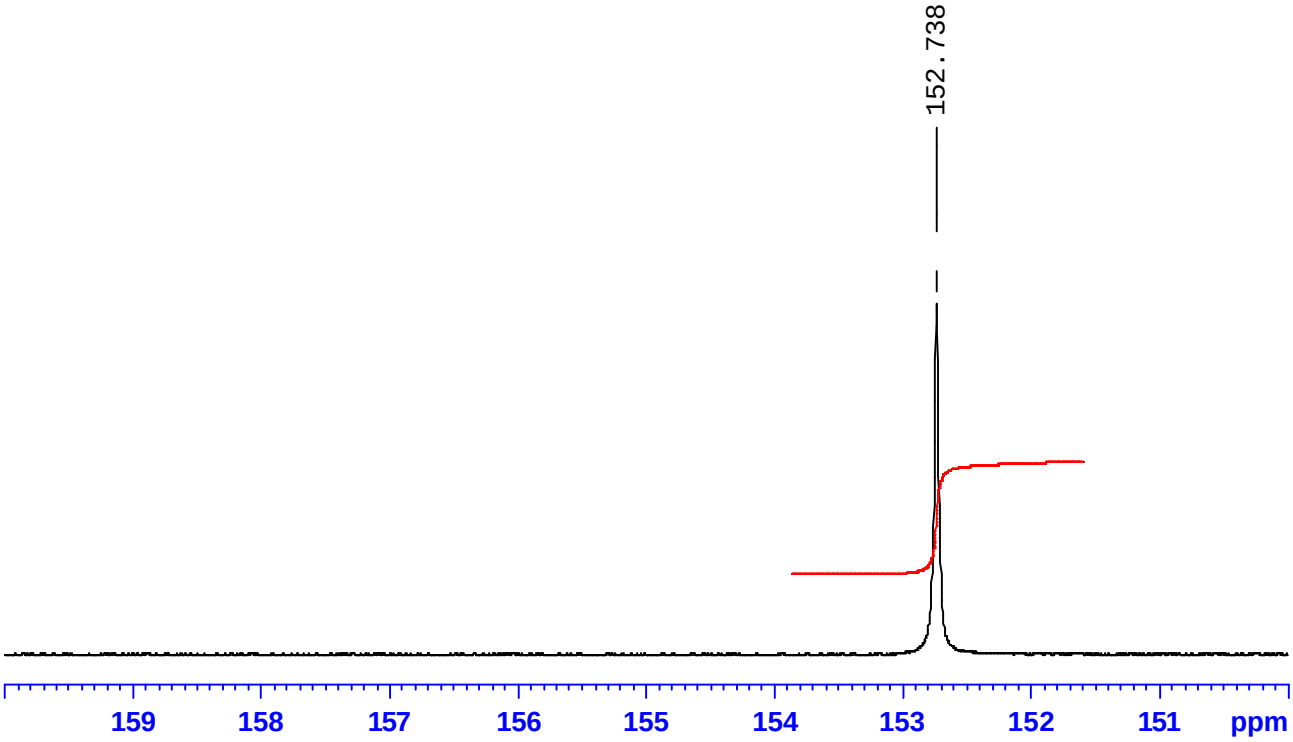
Rh[(a*S*)-**18**][**6**-P(O)$_2$O] : Rh[(a*R*)-**18**][**6**-P(O)$_2$O] = 85:15 or 15:85.

Figure T: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **6**-P(O)$_2$O (1.0 equiv) and **18**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



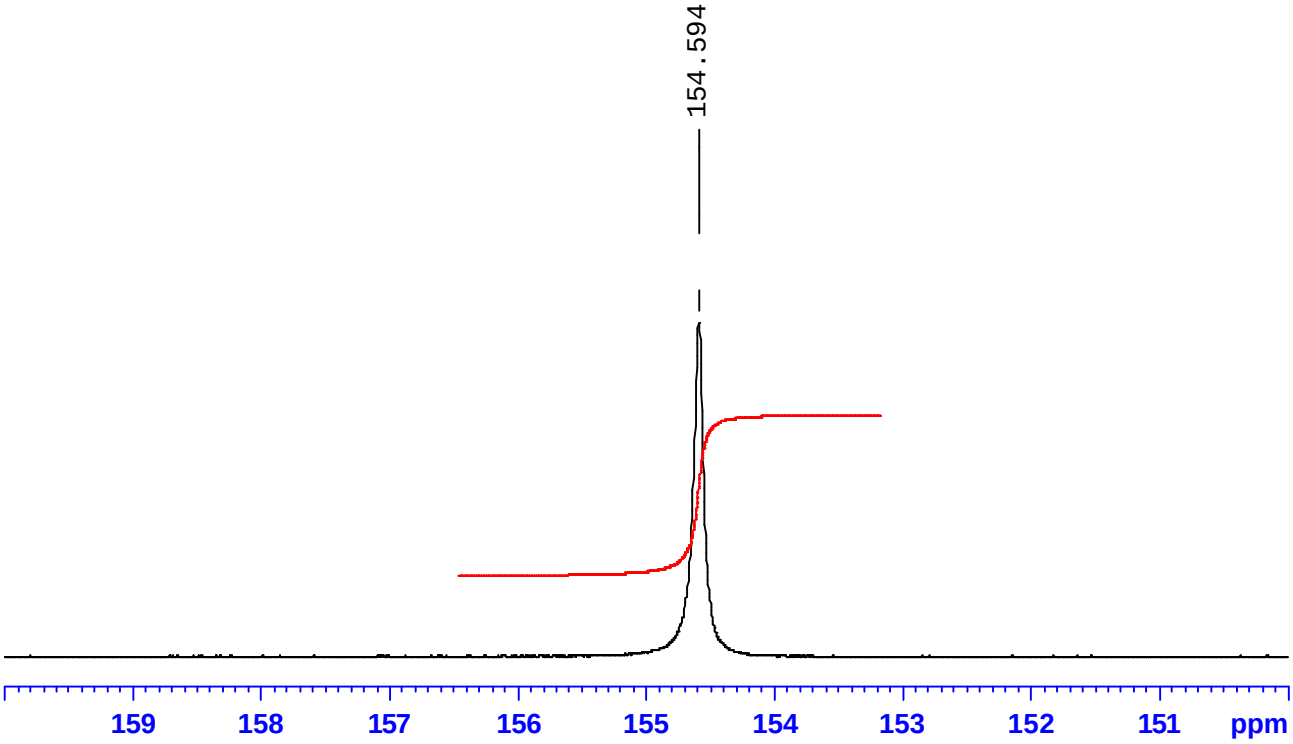
Considering the complexes Rh[(a*S*)-**18**][**6**-P(O)$_2$O] and Rh[(a*R*)-**18**][**6**-P(O)$_2$O], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**18**] ? [(a*R*)-**18**] in toluene-d$_8$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**18**][**6**-P(O)$_2$O] and Rh[(a*R*)-**18**][**6**-P(O)$_2$O] complexes are = 159.2 ppm (dd, $J_{P,\ Rh}$ = 300.5 Hz, $J_{P,\ P}$ = 101.0 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], major) and = 158.1 ppm (dd, $J_{P,\ Rh}$ = 302.3 Hz, $J_{P,\ P}$ = 97.7 Hz, Rh[**6**-P(O)$_2$O][**18**-P(O)$_2$N], minor); this gives a frequency separation (Δν) of 178.2 Hz. On warming, the lines broaden and coalesce: the coalescence temperature (T_c) is 310 K. From these data, the free energy of activation was calculated $\Delta G^{?} = RT_c\ [23 + \ln (T_c / \Delta\nu)] = 14.51$ kcal / mol.[22]

Figure U: ^{31}P-NMR of **4**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 253 K.



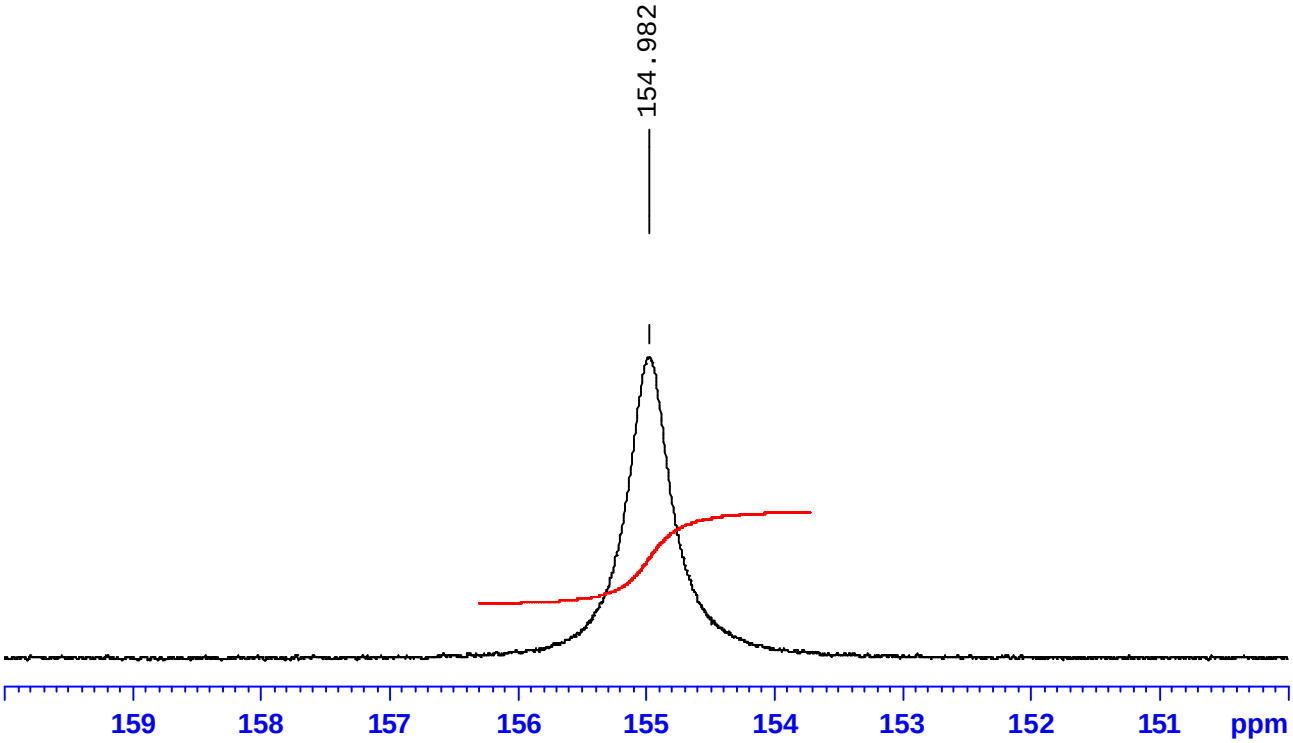
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 152.7 ppm (s, **4**-P(O)$_2$O).

Figure V: ^{31}P-NMR of **4**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 203 K.



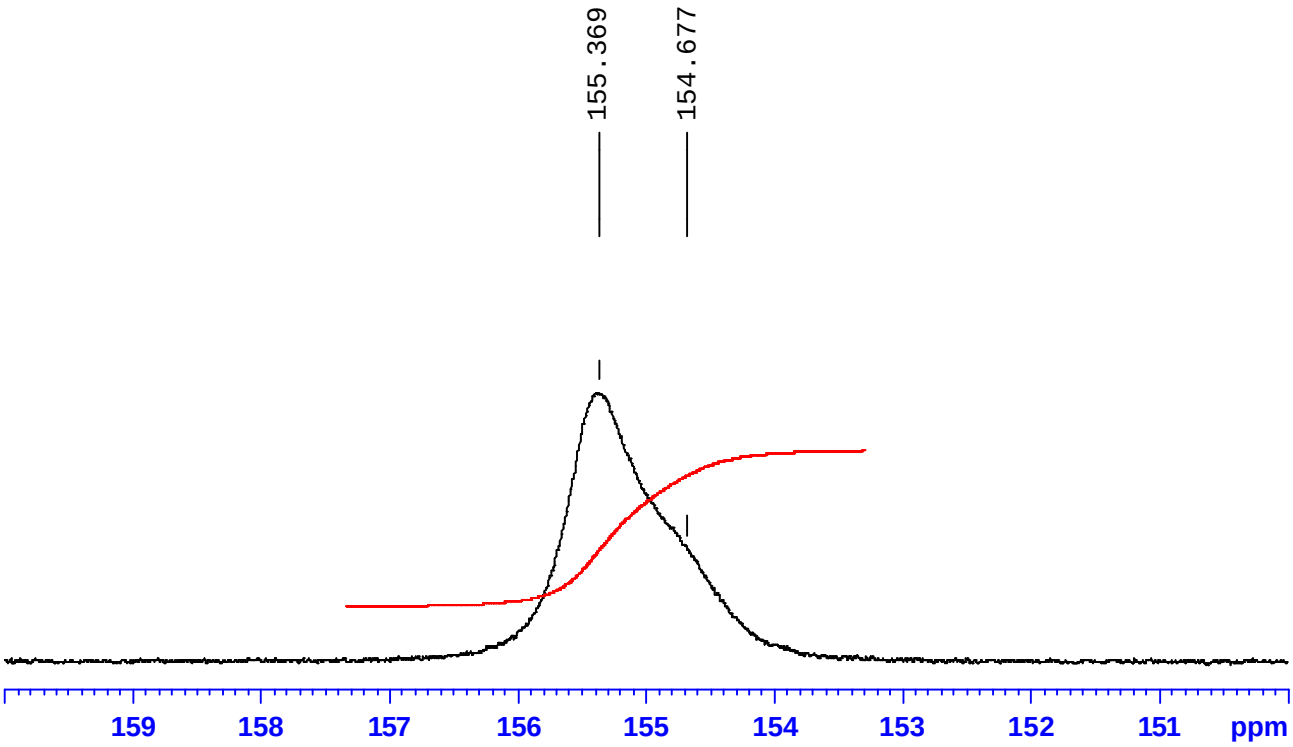
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 154.6 ppm (s, **4**-P(O)$_2$O).

Figure W: ^{31}P-NMR of **4**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 193 K.



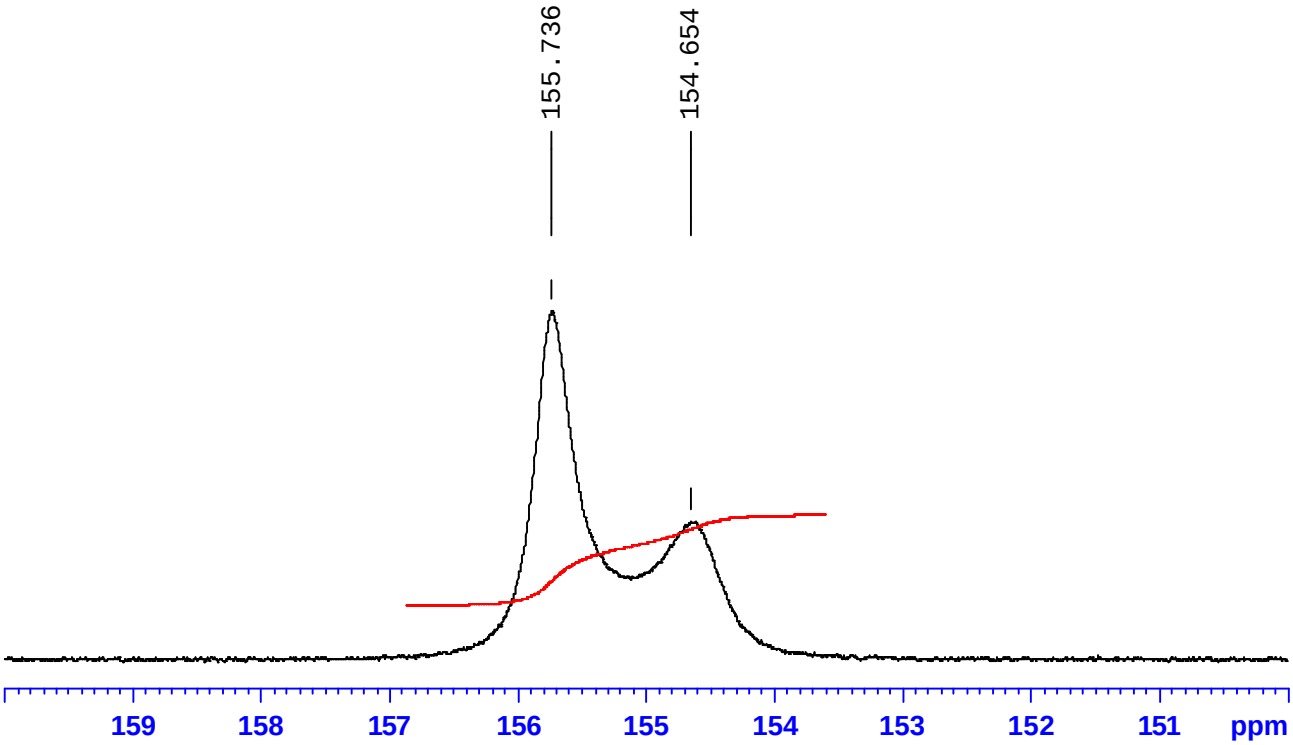
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 155.0 ppm (s, **4**-P(O)$_2$O).

Figure X: ^{31}P-NMR of **4**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 188 K.



^{31}P-NMR (162 MHz, THF-d$_8$): δ = 155.3 ppm (broad s, **4**-P(O)$_2$O).

Figure Y: ^{31}P-NMR of **4**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 183 K.

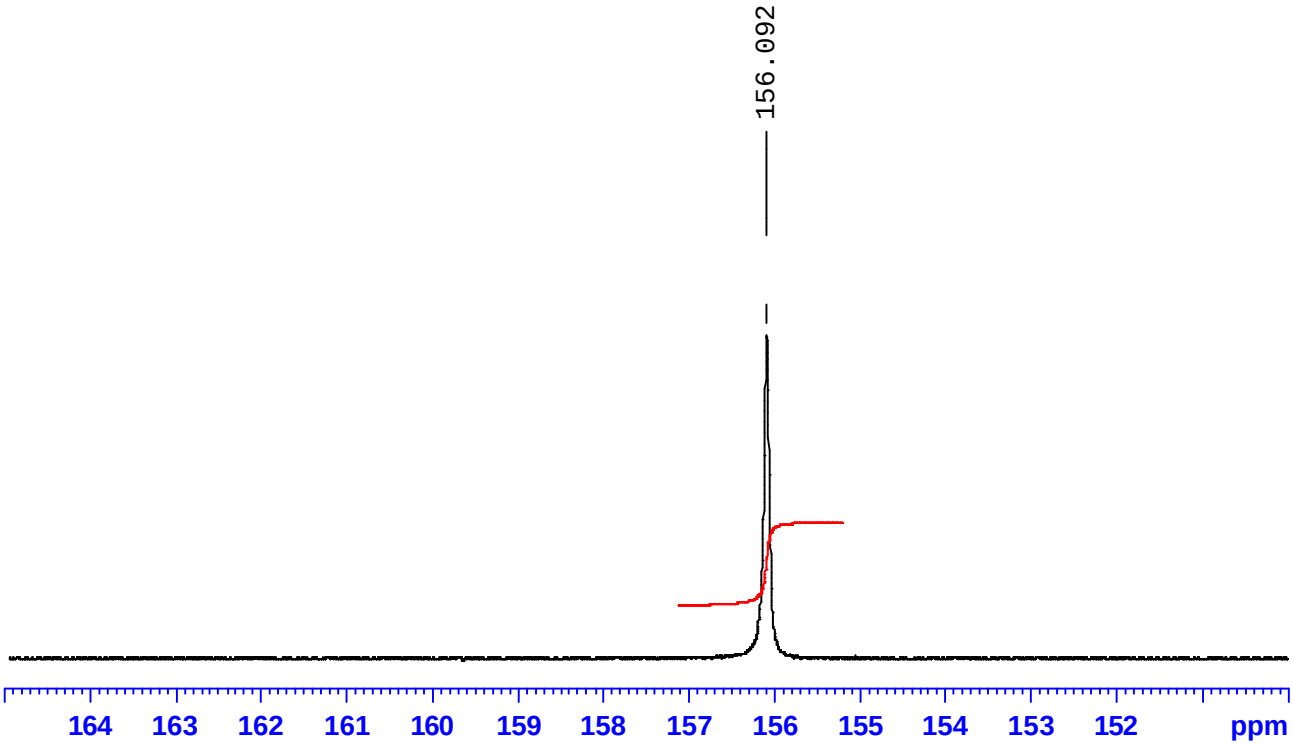


^{31}P-NMR (162 MHz, THF-d$_8$): δ = 155.7 [s, (a*R*)-**4**-P(O)$_2$O], 154.6 [s, (a*S*)-**4**-P(O)$_2$O] ppm **or**

δ = 155.7 [s, (a*S*)-**4**-P(O)$_2$O], 154.6 [s, (a*R*)-**4**-P(O)$_2$O] ppm.

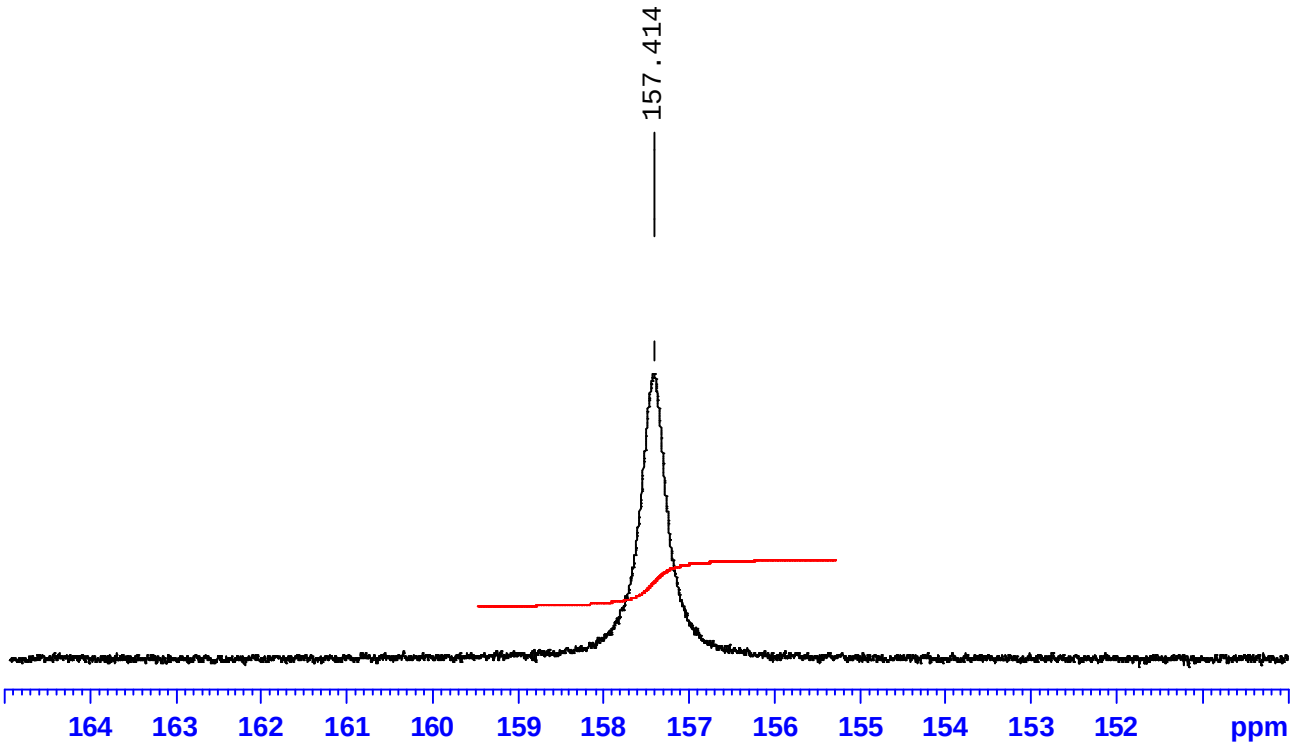
Considering the ligand **4**-P(O)$_2$O, a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**4**-P(O)$_2$O] ? [(a*R*)-**4**-P(O)$_2$O] in THF-d$_8$ was performed. At 183 K, the chemical shifts of the two P atoms of [(a*S*)-**4**-P(O)$_2$O] and [(a*R*)-**4**-P(O)$_2$O] are 155.7 ppm and 154.6 ppm; this gives a frequency separation (Δν) of 291.6 Hz. On warming, the lines broaden and coalesce: the coalescence temperature (T_c) is 190 K. From these data, the free energy of activation was calculated $\Delta G^? = RT_c [23 + \ln (T_c / \Delta\nu)] = 8.5$ kcal / mol.

Figure Z: ^{31}P-NMR of **6**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 253 K.



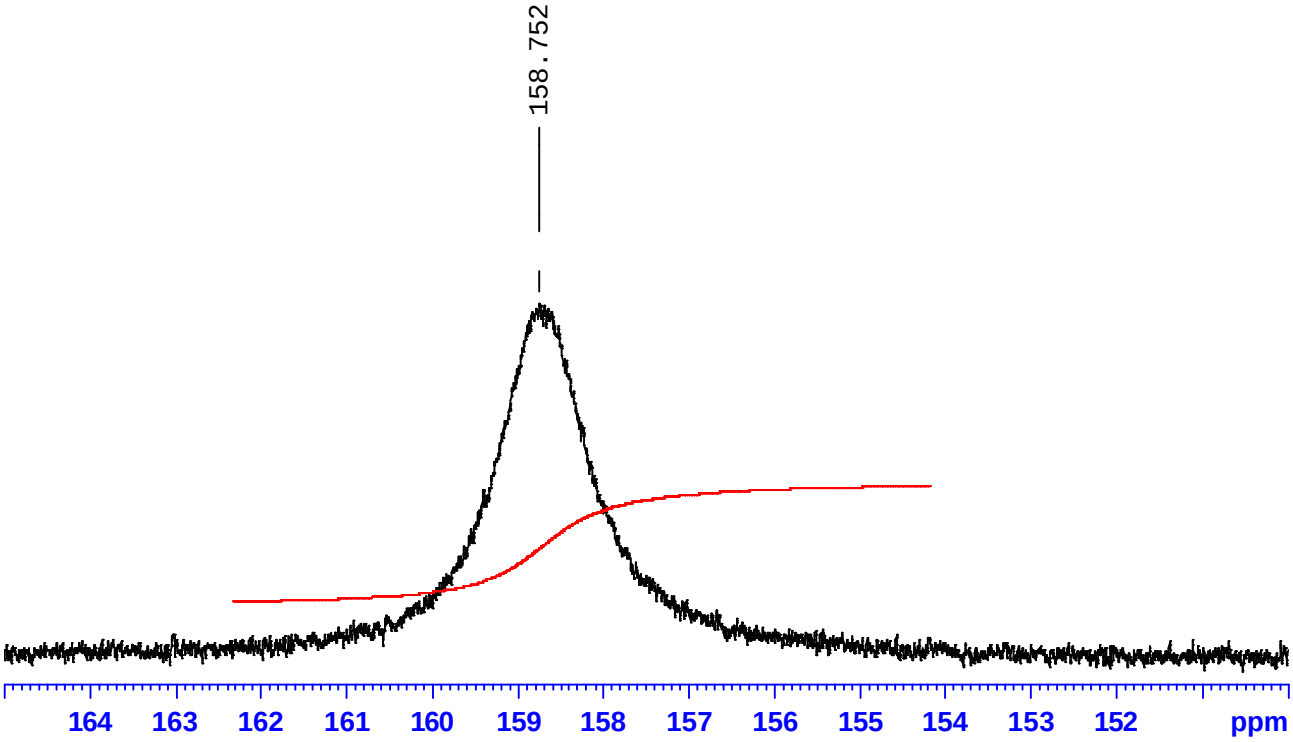
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 156.1 ppm (s, **6**-P(O)$_2$O).

Figure AA: ^{31}P-NMR of **6**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 223 K.



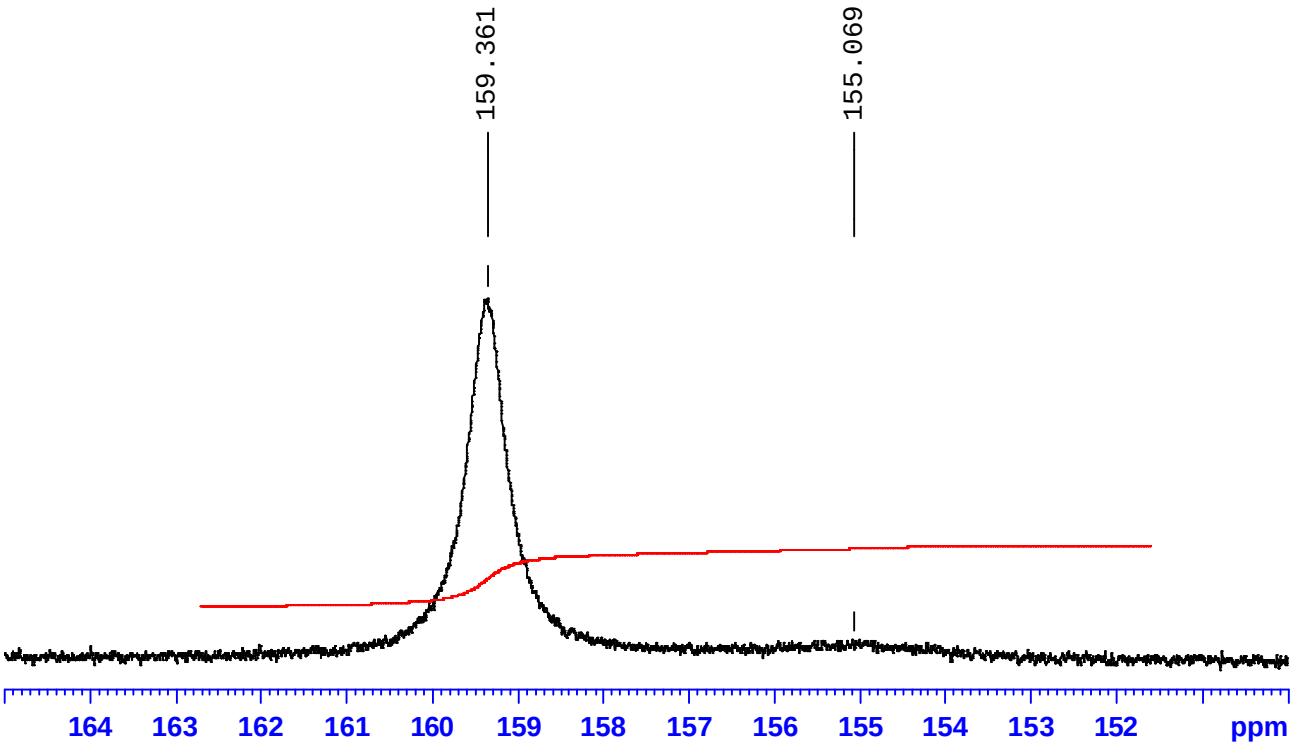
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 157.4 ppm (s, **6**-P(O)$_2$O).

Figure AB: ^{31}P-NMR of **6**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 203 K.



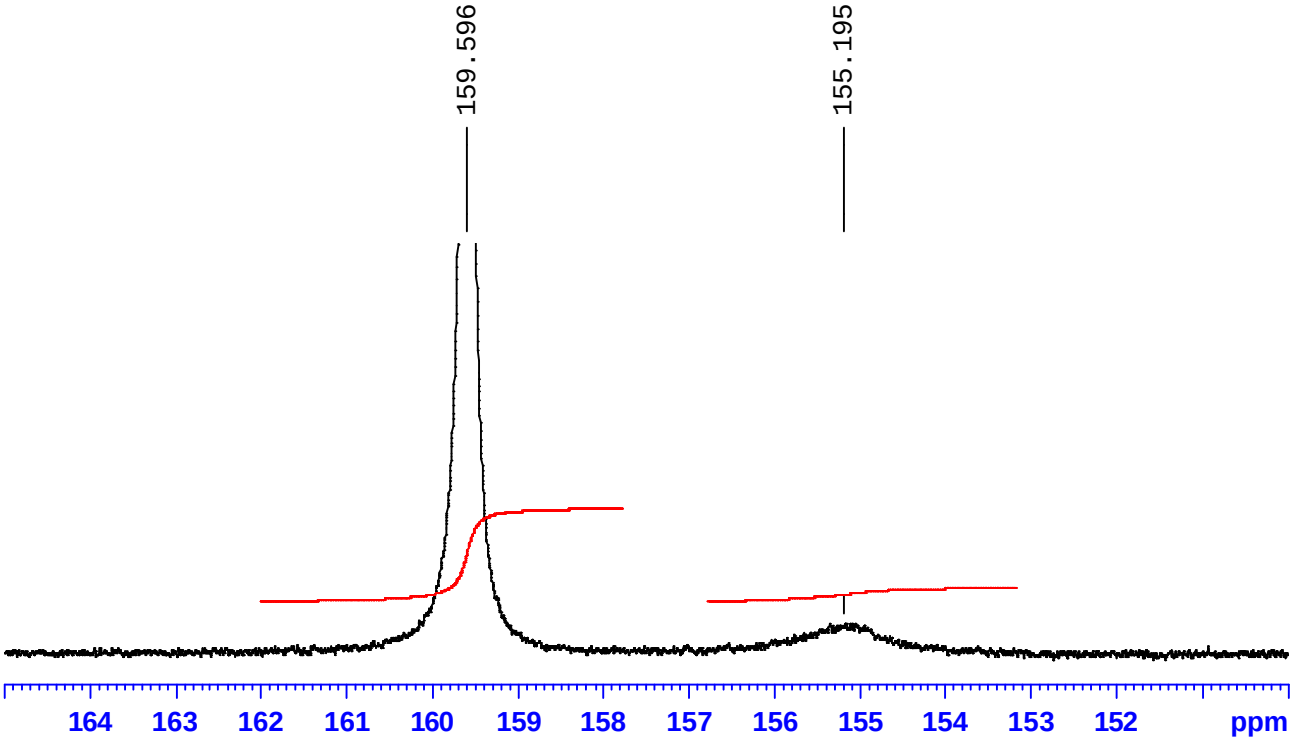
^{31}P-NMR (162 MHz, THF-d$_8$): δ = 158.7 ppm (bs, **6**-P(O)$_2$O).

Figure AC: ^{31}P-NMR of **6**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 193 K.



^{31}P-NMR (162 MHz, THF-d$_8$): δ = 159.4 ppm (broad s, **6**-P(O)$_2$O).

Figure AD: ^{31}P-NMR of **6**-P(O)$_2$O in tetrahydrofurane-d$_8$ at 183 K.

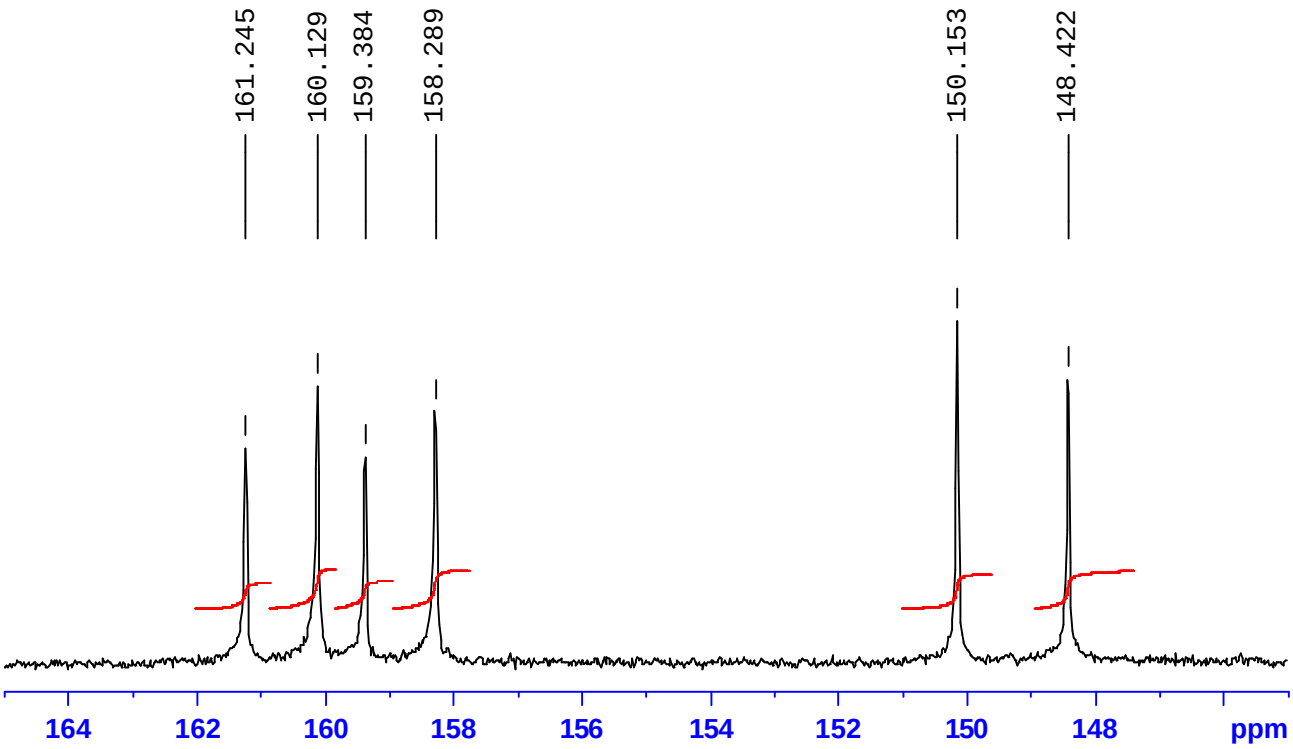


^{31}P-NMR (162 MHz, THF-d$_8$): δ = 159.6 [s, (a*R*)-**6**-P(O)$_2$O], 155.2 [s, (a*S*)-**6**-P(O)$_2$O] ppm **or**

δ = 159.6 [s, (a*S*)-**6**-P(O)$_2$O], 155.2 [s, (a*R*)-**6**-P(O)$_2$O] ppm.

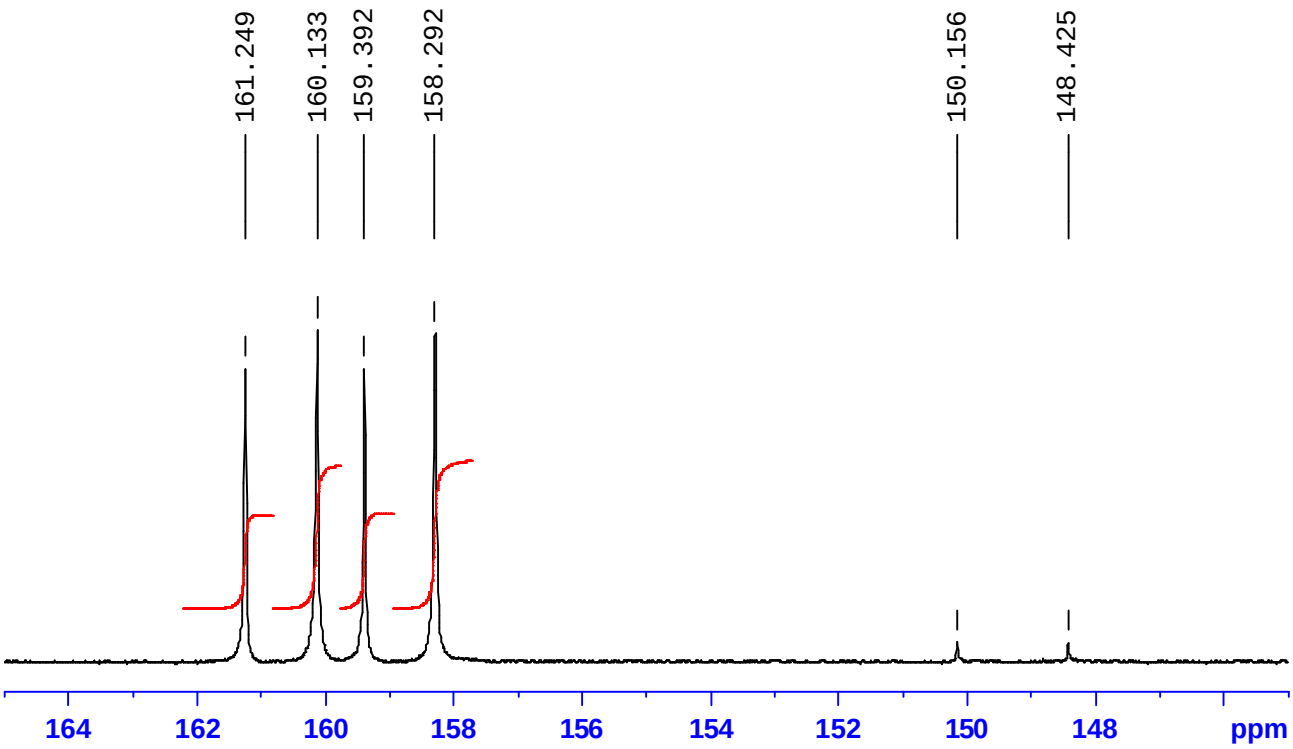
Considering the ligand **6**-P(O)$_2$O, a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**6**-P(O)$_2$O] ? [(a*R*)-**6**-P(O)$_2$O] in THF-d$_8$ was performed. At 183 K, the chemical shifts of the two P atoms of [(a*S*)-**6**-P(O)$_2$O] and [(a*R*)-**6**-P(O)$_2$O] are 159.6 ppm and 155.2 ppm; this gives a frequency separation (Δν) of 729 Hz. On warming, the lines broaden and coalesce: the coalescence temperature (T_c) is 197 K. From these data, the free energy of activation was calculated $\Delta G^? = RT_c [23 + \ln (T_c / \Delta\nu)] = 8.5$ kcal / mol.

Figure AE: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **13**-P(O)$_2$N (1.0 equiv) in dichloromethane-d$_2$.



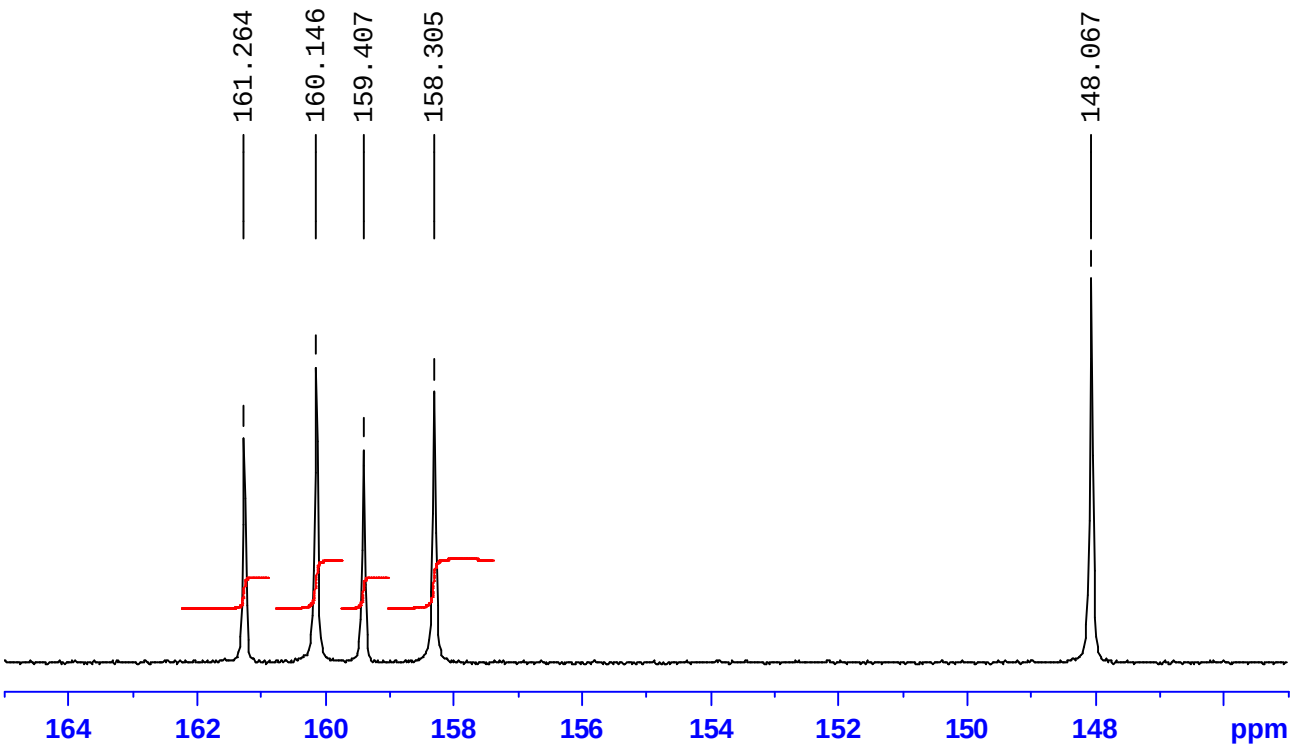
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 160.3 (d, $J_{P, Rh}$ = 301 Hz, Rh[**13**-P(O)$_2$N]$_2$), 159.2 (d, $J_{P, Rh}$ = 298 Hz, Rh[**13**-P(O)$_2$N]$_2$), 149.2 (d, $J_{P, Rh}$ = 280 Hz, Rh**13**-P(O)$_2$N) ppm.

Figure AF: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **13**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$.

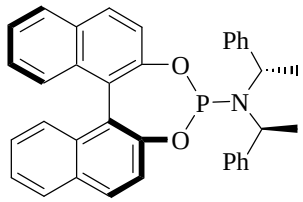


^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 160.3 (d, $J_{P, Rh}$ = 301 Hz, Rh[**13**-P(O)$_2$N]$_2$), 159.2 (d, $J_{P, Rh}$ = 298 Hz, Rh[**13**-P(O)$_2$N]$_2$), 149.2 (d, $J_{P, Rh}$ = 280 Hz, Rh**13**-P(O)$_2$N) ppm.

Figure AG: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **13**-P(O)$_2$N (3.0 equiv) in dichloromethane-d$_2$.



^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 160.3 (d, $J_{P,\ Rh}$ = 301 Hz, Rh[**13**-P(O)$_2$N]$_2$), 159.2 (d, $J_{P,\ Rh}$ = 298 Hz, Rh[**13**-P(O)$_2$N]$_2$), 148.0 (s, excess ligand **13**-P(O)$_2$N) ppm.

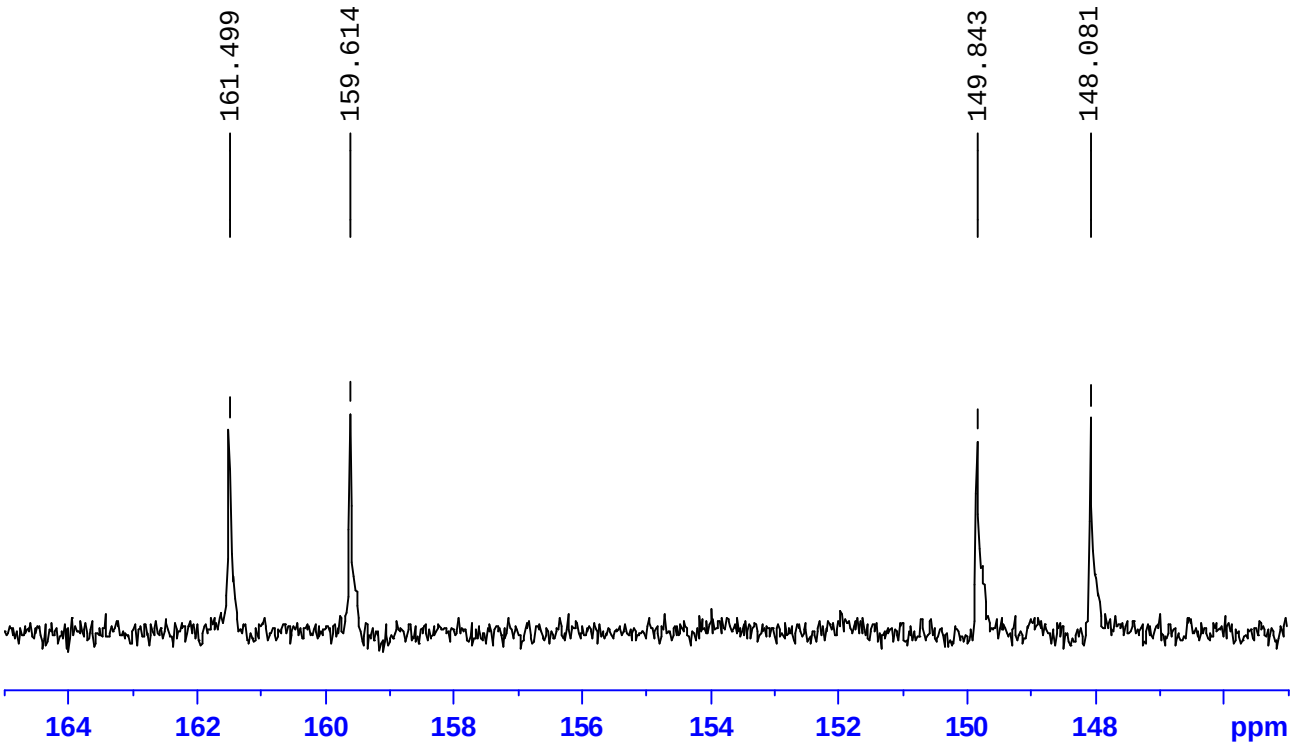


(*S*)-Binaphthol / (*S*,*S*)-bis(a-methylbenzyl)amine

23-$P(O)_2N$

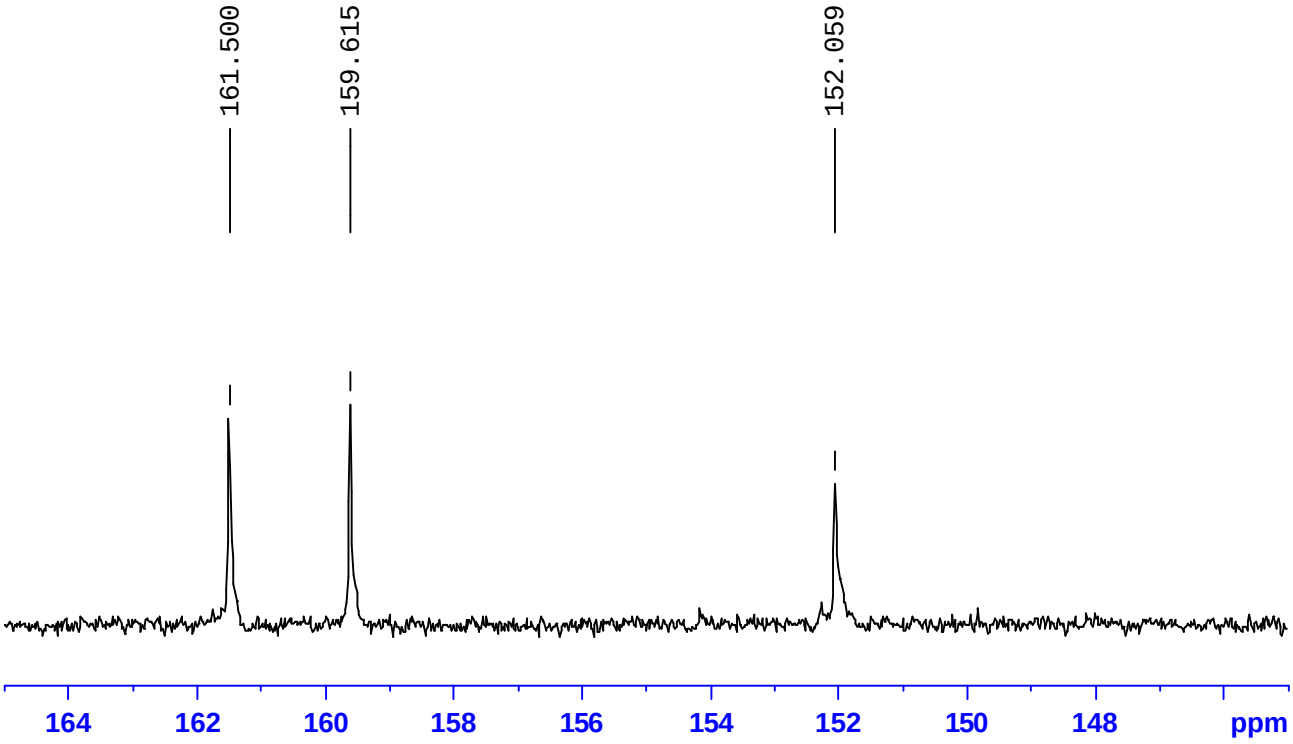
23-P(O)-N, (*S*)-binaphthol / (*S*,*S*)-bis(α-methylbenzyl)amine: 89% yield. ^{31}P-NMR (162 MHz, Dichloromethane-d_2): δ = 152.1 ppm.

Figure AH: ^{31}P-NMR of the complex between Rh(acac)$(eth)_2$ (1.0 equiv) and **23**-$P(O)_2N$ (1.0 equiv) in dichloromethane-d_2.



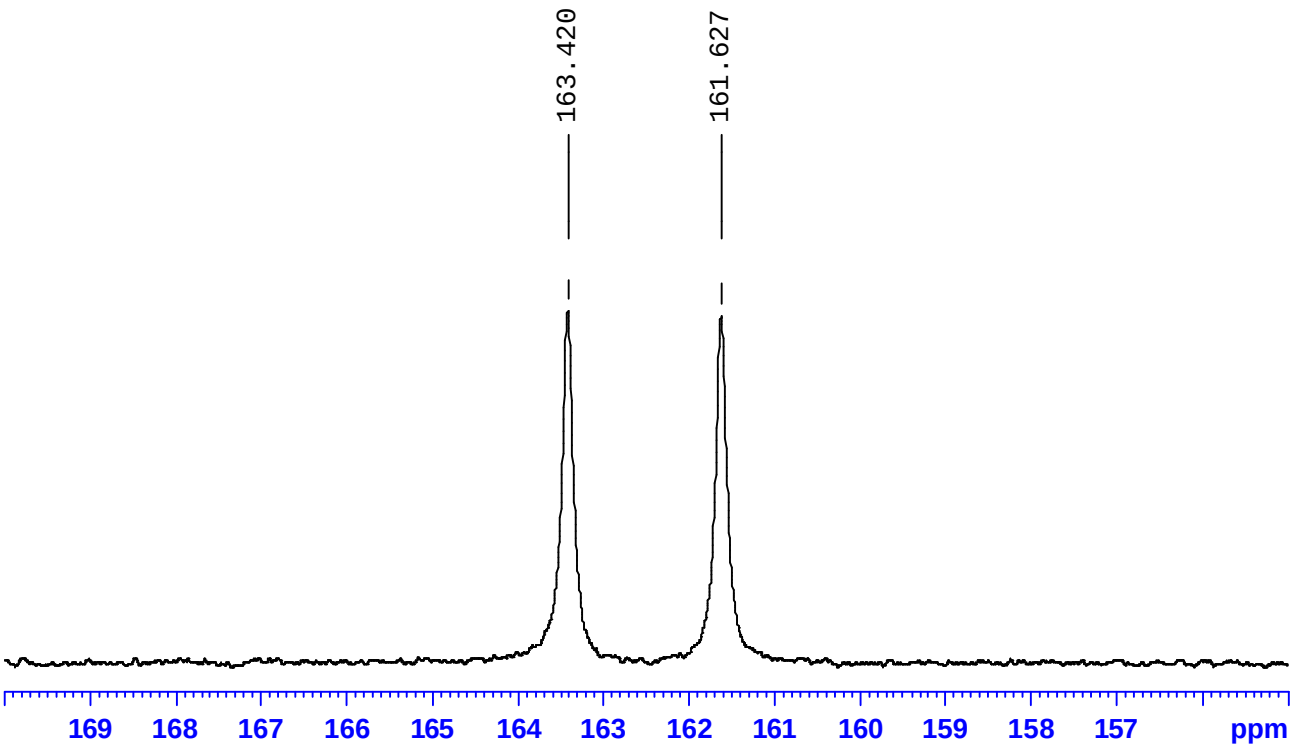
^{31}P-NMR (162 MHz, Dichloromethane-d_2): δ = 160.5 (d, $J_{P, Rh}$ = 307.8 Hz, Rh[**23**-$P(O)_2N]_2$), 149.0 (d, $J_{P, Rh}$ = 275.4 Hz, Rh**23**-$P(O)_2N$) ppm.

Figure AI: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **23**-P(O)$_2$N (2.2 equiv) in dichloromethane-d$_2$.



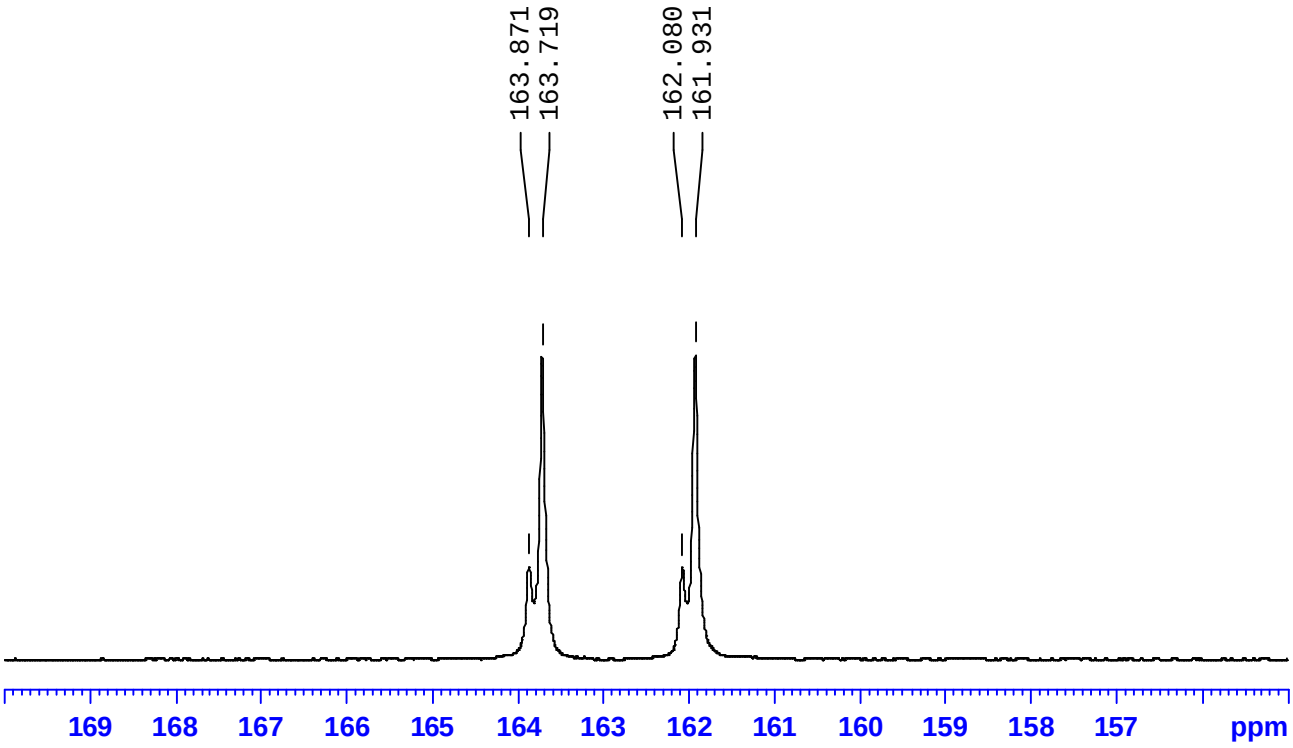
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 160.5 (d, $J_{P, Rh}$ = 307.8 Hz, Rh[**23**-P(O)$_2$N]$_2$), 152.1 (s, excess ligand **23**-P(O)$_2$N) ppm.

Figure AJ: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **14**-P(O)$_2$N (2.2 equiv) in toluene-d$_8$ at 295K.



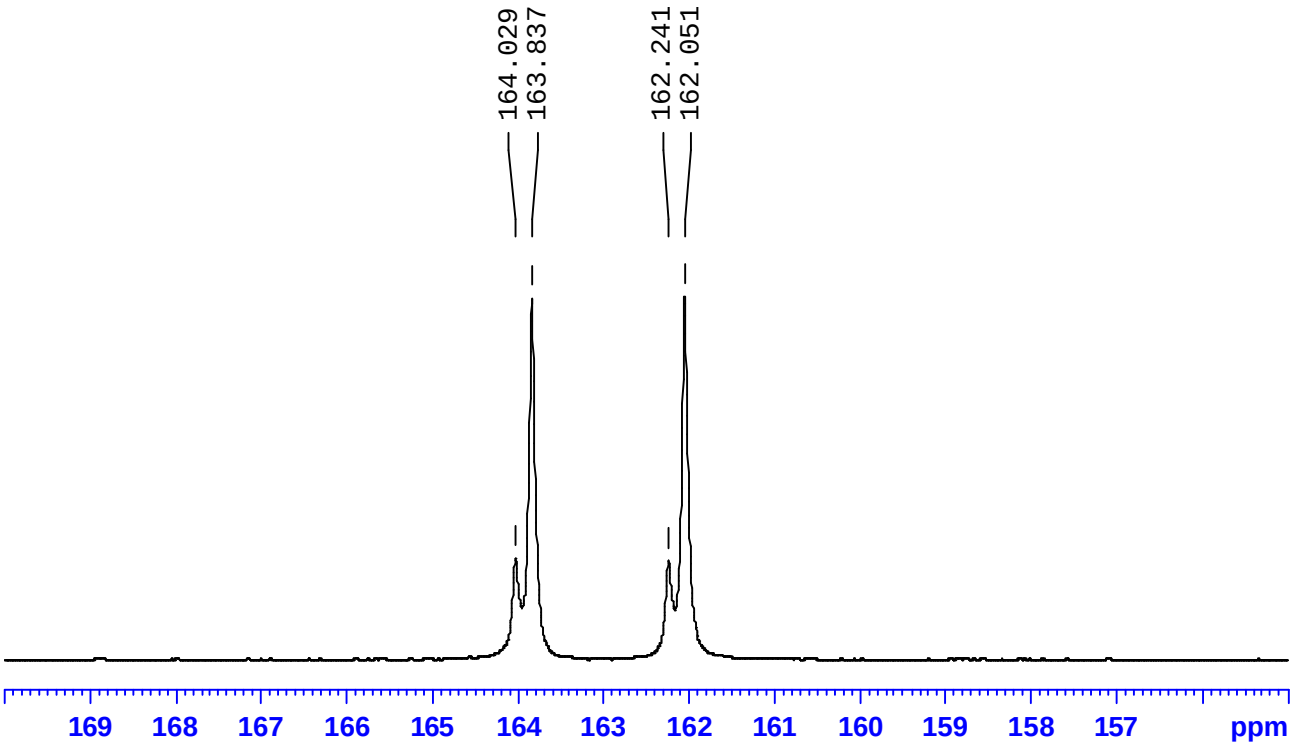
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 162.5 ppm (d, $J_{P, Rh}$ = 290.3 Hz, Rh[**14**-P(O)$_2$N]$_2$).

Figure AK: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **14**-P(O)$_2$N (2.2 equiv) in toluene-d$_8$ at 253K.



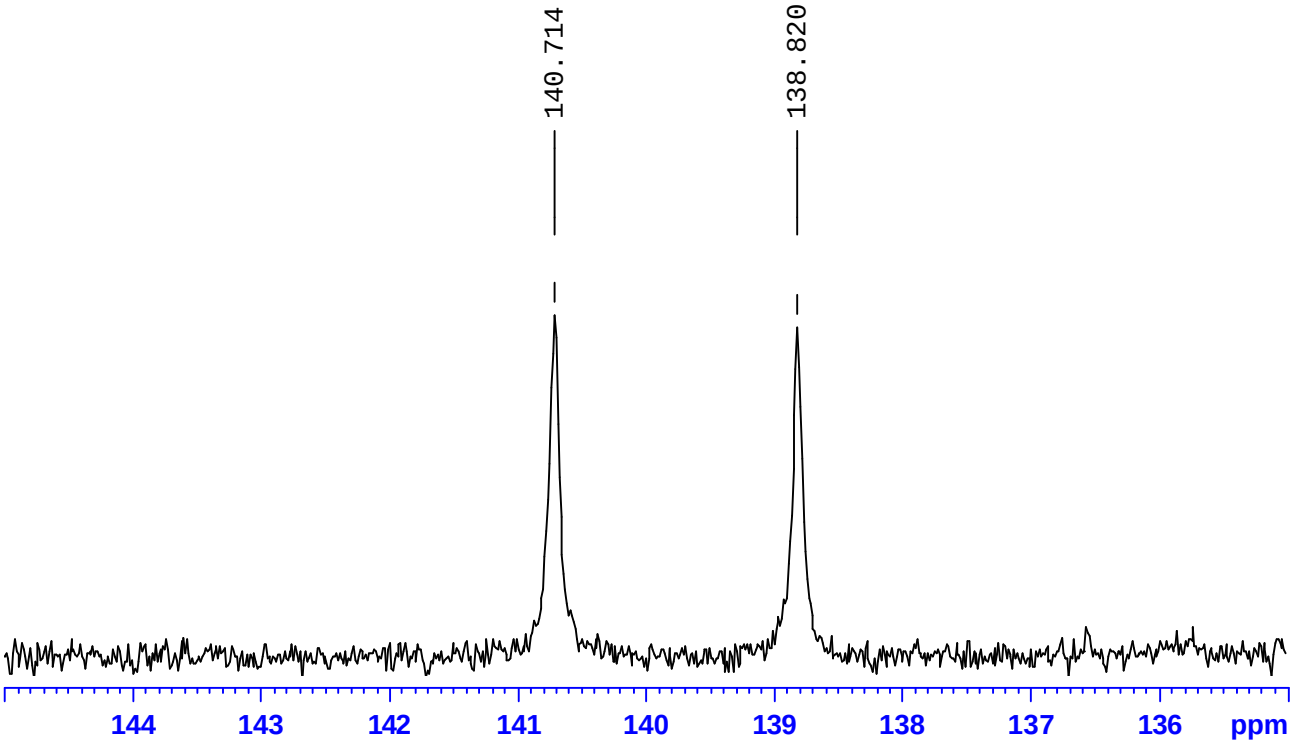
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 163.0 (d, $J_{P,\ Rh}$ = 290.1 Hz, Rh[**14**-P(O)$_2$N]$_2$), 162.8 (d, $J_{P,\ Rh}$ = 289.6 Hz, Rh[**14**-P(O)$_2$N]$_2$) ppm.

Figure AL: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **14**-P(O)$_2$N (2.2 equiv) in toluene-d$_8$ at 233K.



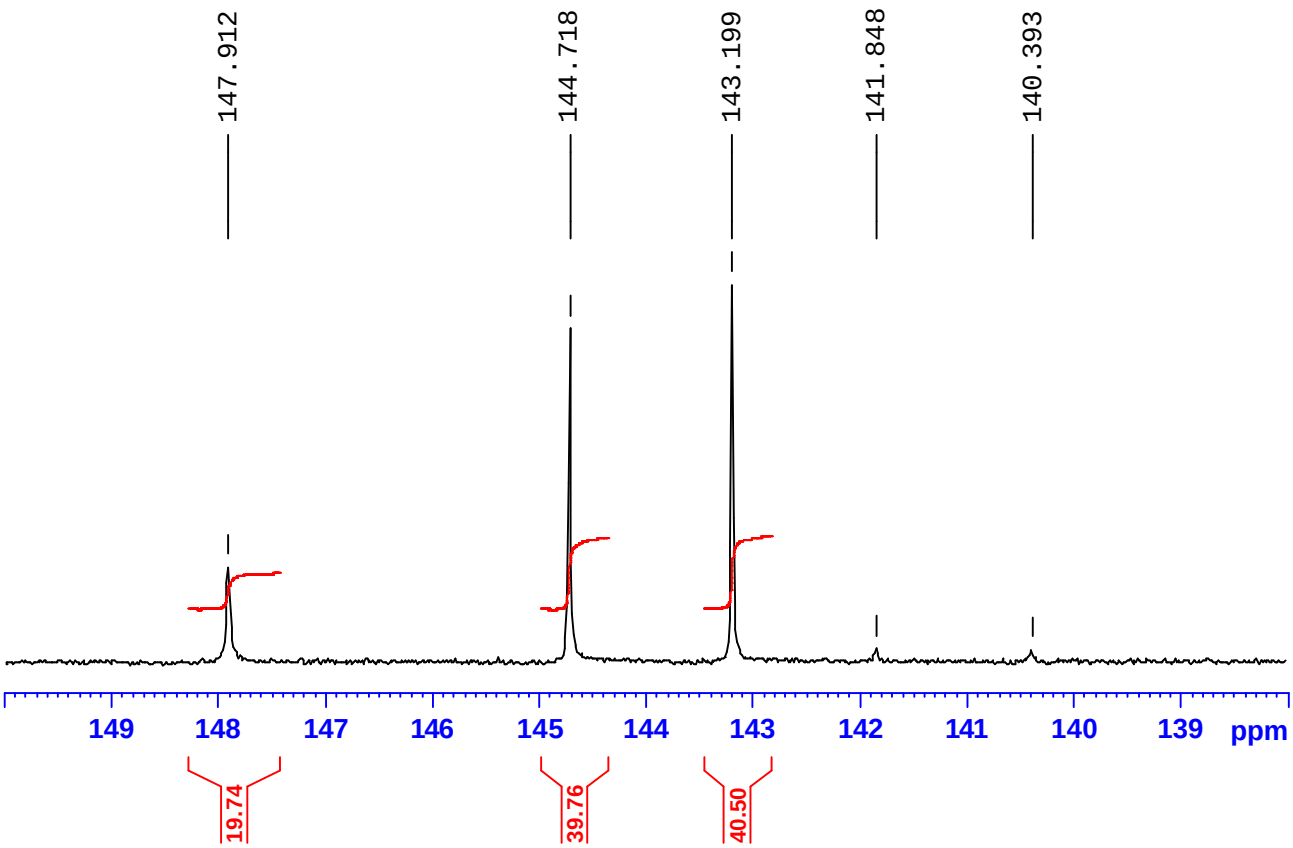
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 163.1 (d, $J_{P,\ Rh}$ = 289.6 Hz, Rh[**14**-P(O)$_2$N]$_2$), 162.9 (d, $J_{P,\ Rh}$ = 289.3 Hz, Rh[**14**-P(O)$_2$N]$_2$) ppm.

Figure AM: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **16**-P(O)$_2$N (2.2 equiv) in benzene-d$_6$ at 295 K.



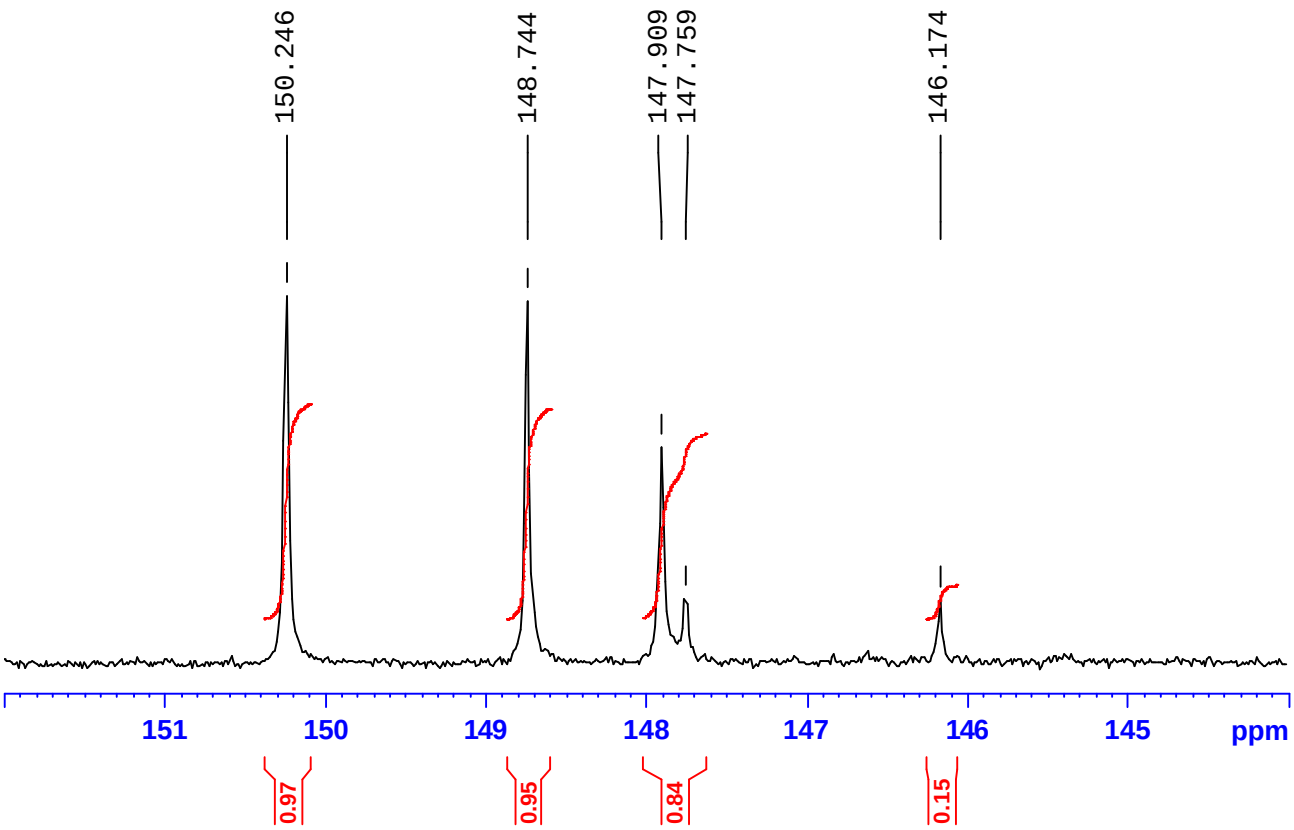
^{31}P-NMR (162 MHz, Benzene-d$_6$): δ = 139.7 ppm (d, $J_{P, Rh}$ = 306.8 Hz, Rh[**16**-P(O)$_2$N]$_2$).

Figure AN: ^{31}P-NMR of the complex between $Rh(COD)_2BF_4$ (1.0 equiv) and **13**-$P(O)_2N$ (2.2 equiv) in dichloromethane-d_2.

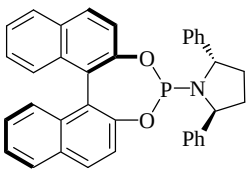


^{31}P-NMR (162 MHz, dichloromethane-d_2): δ = 147.9 (s, excess ligand), 144.0 (d, $J_{P,\,Rh}$ = 246.0 Hz, Rh[**13**-$P(O)_2N]_2$), 141.1 (d, $J_{P,\,Rh}$ = 235.7 Hz, Rh[**13**-$P(O)_2N$]) ppm.

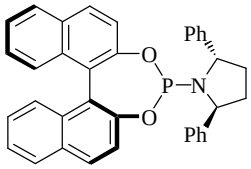
Figure AO: ^{31}P-NMR of the complex between $Rh(NBD)_2BF_4$ (1.0 equiv) and **13**-$P(O)_2N$ (2.2 equiv) in dichloromethane-d_2.



^{31}P-NMR (162 MHz, dichloromethane-d_2): δ = 149.5 (d, $J_{P,\,Rh}$ = 243.3 Hz, Rh[**13**-$P(O)_2N]_2$), 147.9 (s, excess ligand), 147.0 (d, $J_{P,\,Rh}$ = 256.8 Hz, Rh[**13**-$P(O)_2N$]) ppm.



(*R*)-Binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine
24-P(O)$_2$N

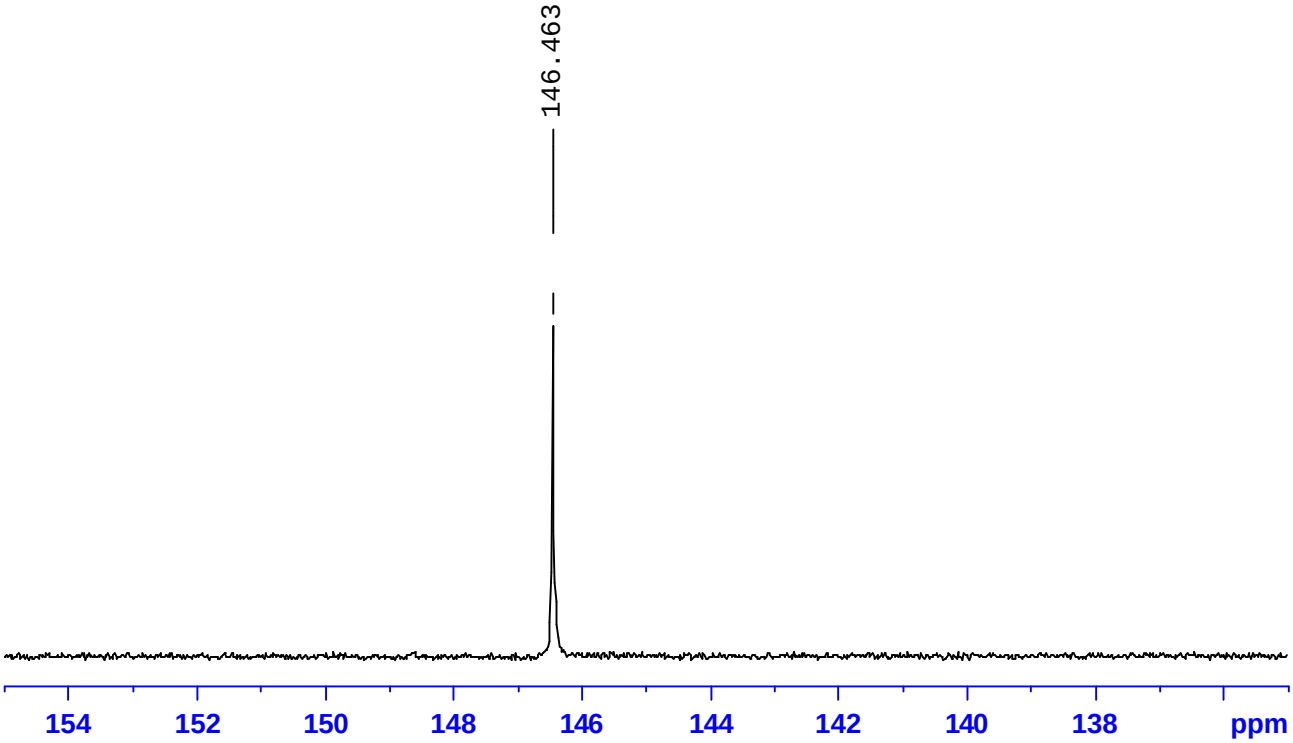


(*S*)-Binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine
25-P(O)$_2$N

24-P(O)-N, (*R*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine:[23] 70% yield. ^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 153.7 ppm.

25-P(O)-N, (*S*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine:[23] 60% yield. ^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 146.5 ppm.

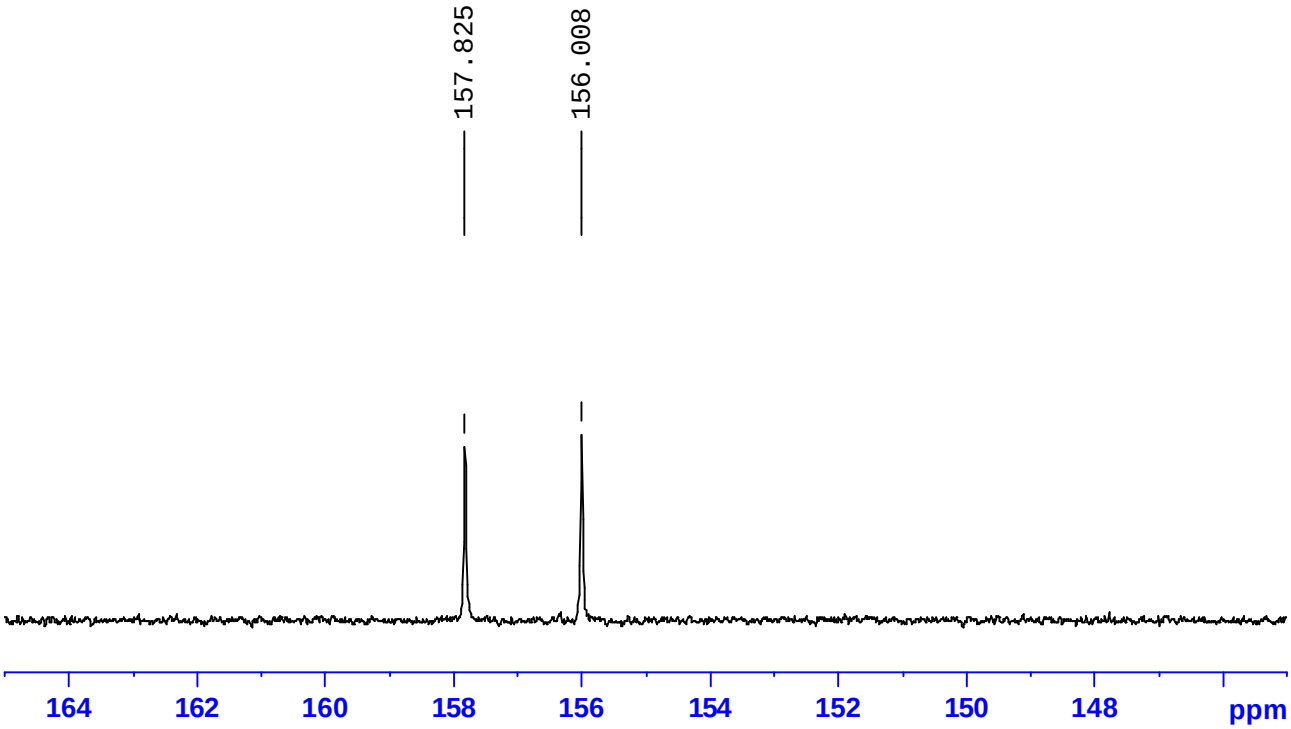
Figure AP: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **25**-P(O)$_2$N (2.2 equiv) in toluene-d$_8$.



^{31}P-NMR (162 MHz, toluene-d$_8$): δ = 146.5 ppm (s, ligand).

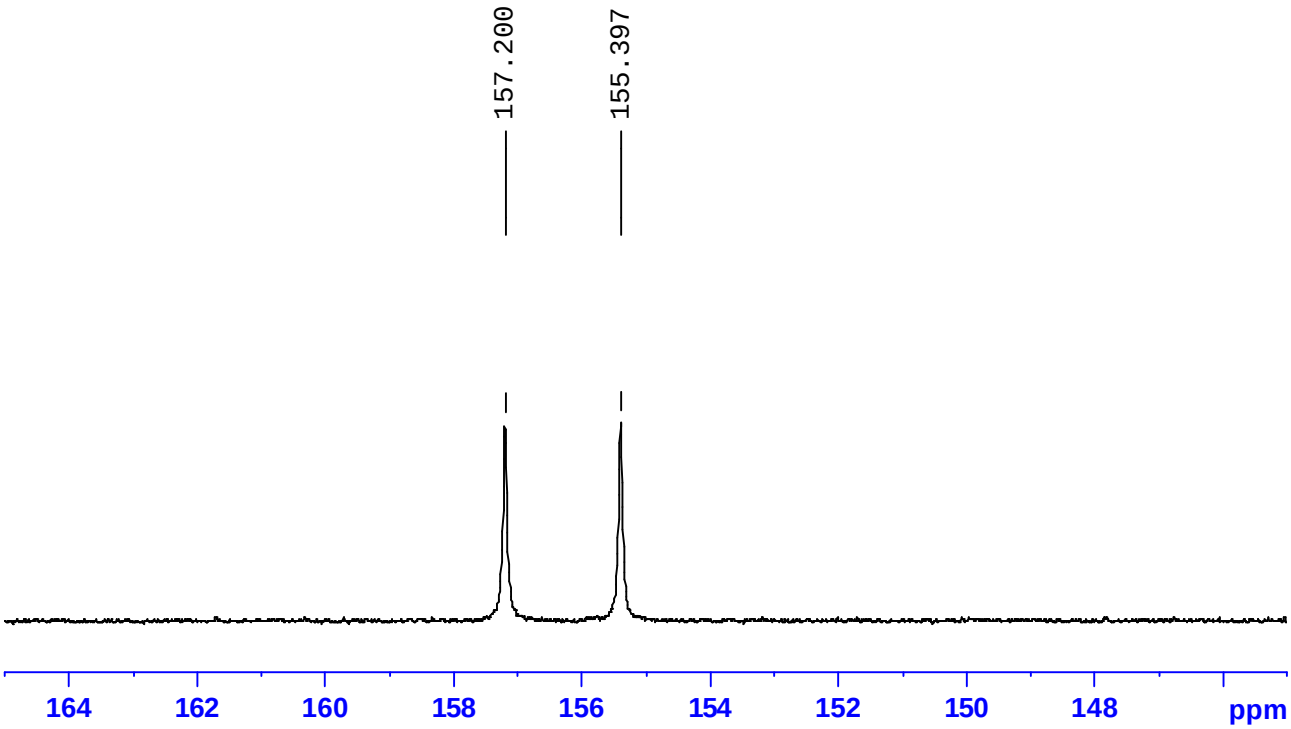
[23] Y. H. Choi, J. Y. Choi, H. Y. Yang and Y. H. Kim, *Tetrahedron: Asymmetry* 2002, **13**, 801-804.

Figure AQ: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **25**-P(O)-N (2.0 equiv) in toluene-d$_8$ at 300 K



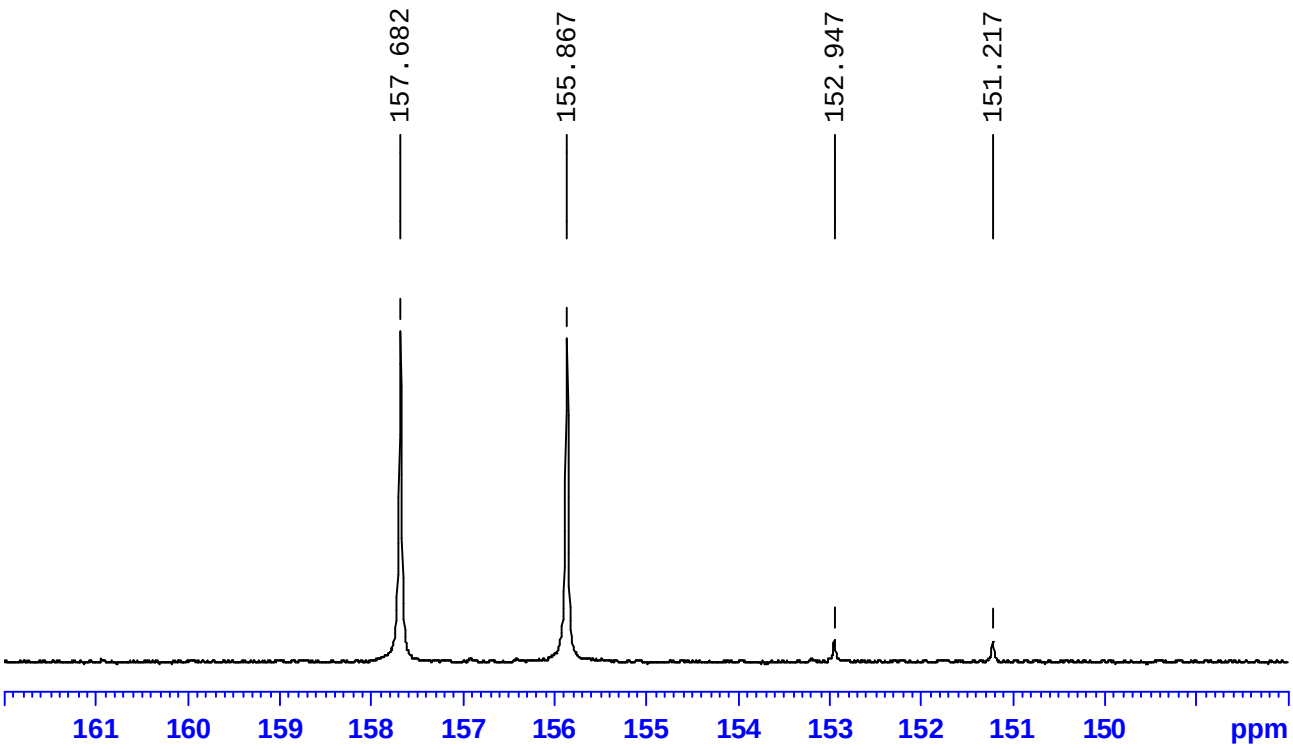
^{31}P-NMR (162 MHz, toluene-d$_8$): δ = 156.9 ppm (d, $J_{P, Rh}$ = 294.3 Hz, Rh[**25**-P(O)$_2$N]$_2$).

Figure AR: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **25**-P(O)-N (2.0 equiv) in toluene-d$_8$ at 230 K



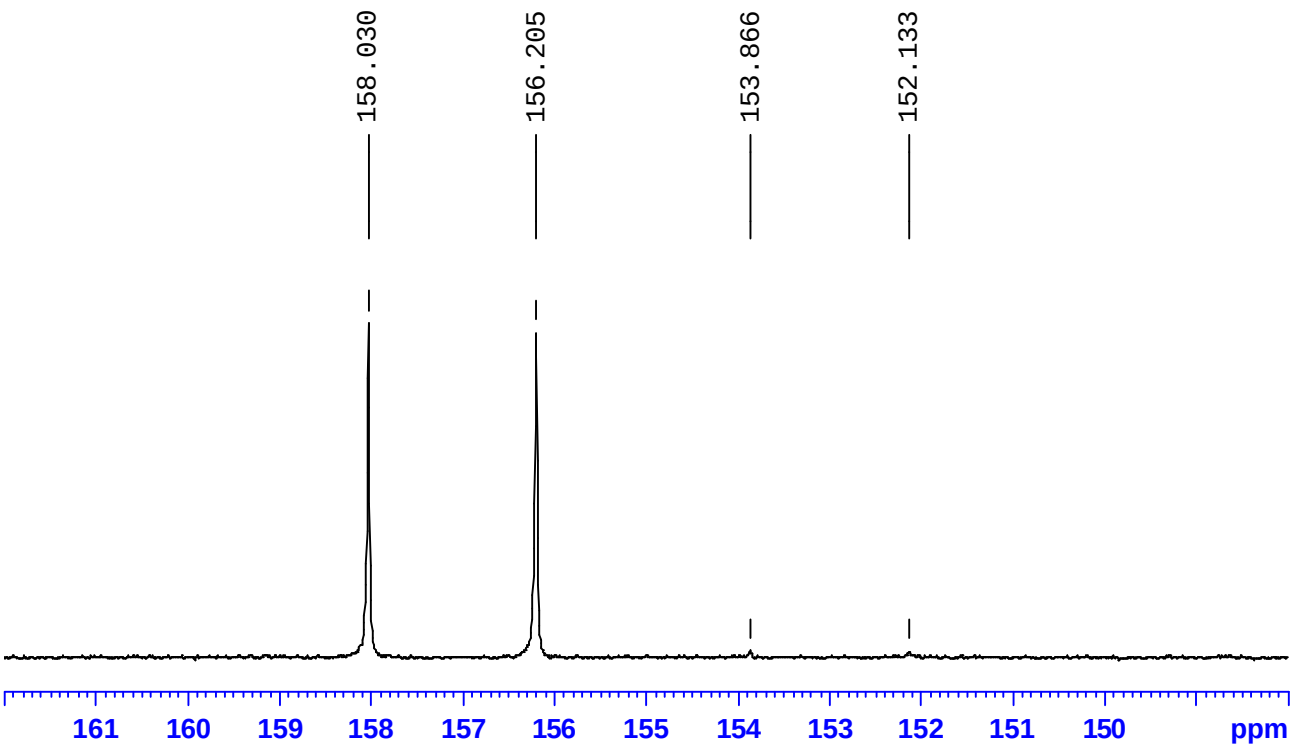
^{31}P-NMR (162 MHz, toluene-d$_8$): δ = 156.3 ppm (d, $J_{P, Rh}$ = 292.0 Hz, Rh[**25**-P(O)$_2$N]$_2$).

Figure AS: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **25**-P(O)-N (2.0 equiv) in toluene-d$_8$ at 295 K



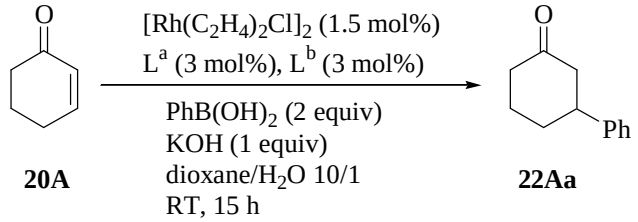
^{31}P-NMR (162 MHz, toluene-d$_8$): δ = 156.8 (d, $J_{P, Rh}$ = 294.0 Hz, Rh[**25**-P(O)$_2$N]$_2$), 152.0 (d, $J_{P, Rh}$ = 280.3 Hz, Rh[**25**-P(O)$_2$N]) ppm.

Figure AT: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **25**-P(O)-N (2.0 equiv) in toluene-d$_8$ at 360 K



^{31}P-NMR (162 MHz, toluene-d$_8$): δ = 157.1 (d, $J_{P, Rh}$ = 295.6 Hz, Rh[**25**-P(O)$_2$N]$_2$), 153.0 (d, $J_{P, Rh}$ = 280.7 Hz, Rh[**25**-P(O)$_2$N]) ppm.

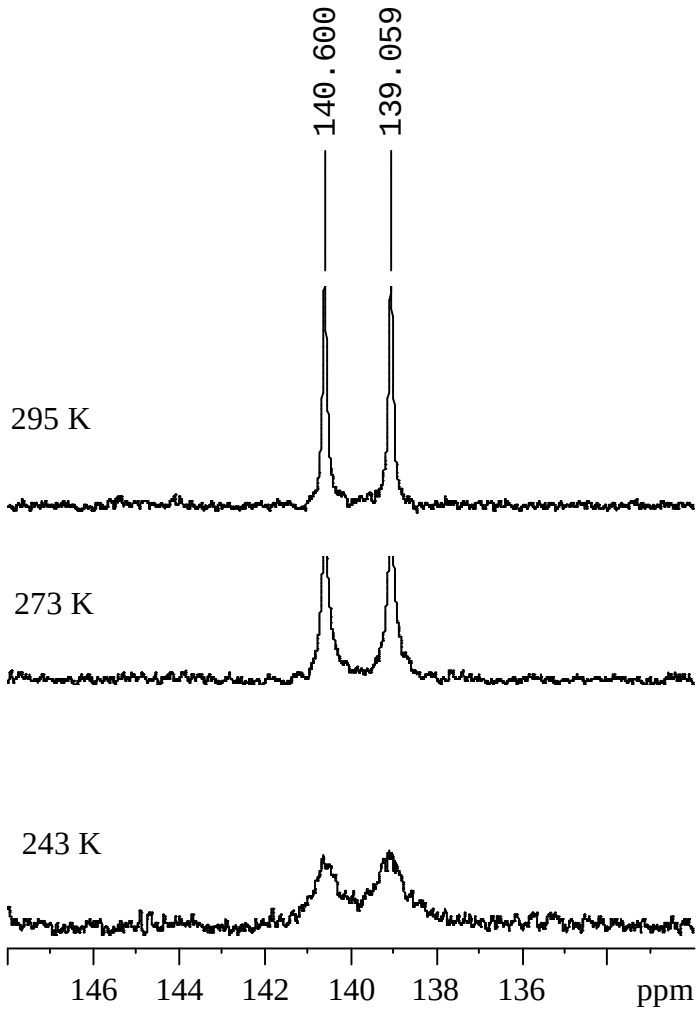
Procedure for the screening: in flame-dried flasks, stock solutions were freshly prepared: a 0.006M solution of $[Rh(eth)_2Cl]_2$ (0.024 mmol, 9.33 mg) in degassed dioxane (4 ml); a 1.33M solution of phenyl boronic acid (3.2 mmol, 390.4 mg) in dioxane (2.4 ml); a solution of the 2-cyclohexen-1-one (1.6 mmol, 165.4 μl) in dioxane (1.6 ml). The reactions were performed using standard Schlenk techniques. Seven flame-dried glass test tubes with stirring bars were placed in a Schlenk, under argon. In each test tube, the ligands (0.06 eq, 0.006 mmol of L^a and 0.006 mmol of L^b) were weighed and 0.5 ml of the stock solution of $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.003 mmol) were added, under argon. After 30 min. under stirring, 0.3 ml of the stock solution of phenylboronic acid (2 eq, 0.4 mmol) were added, followed by 0.1 ml of a 2M solution of KOH (1 eq, 0.2 mmol) in water and 0.2 ml of the stock solution of 2-cyclohexen-1-one (1 eq, 0.2 mmol). The reaction mixtures were stirred overnight under argon, at room temperature. *n*-Tridecane (0.04 mmol) was added to each test tube, and the reaction mixtures were quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with diethyl ether. The crude mixtures in diethyl ether were directly analyzed by GC equipped with a chiral capillary column (MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm), using *n*-tridecane as internal standard: yields and ee's were determined by integration of the GC traces.



20A **22Aa**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**6**-$P(O)_2O$	**6**-$P(O)_2O$	100	70	*R*
2	**19**-$P(O)_2N$	**19**-$P(O)_2N$	100	36	*R*
3	**24**-$P(O)_2N$	**24**-$P(O)_2N$	40	40	*R*
4	**25**-$P(O)_2N$	**25**-$P(O)_2N$	50	28	*R*
5	**6**-$P(O)_2O$	**24**-$P(O)_2N$	70	72	*R*
6	**6**-$P(O)_2O$	**25**-$P(O)_2N$	50	46	*R*
7	**6**-$P(O)_2O$	**19**-$P(O)_2N$	100	95	*R*

Figure AU: variable-temperature ^{31}P-NMR spectra of the complex between $Rh(NBD)_2BF_4$ (1.0 equiv) and **26**-$P(O)_2N$ [(*S*)-MonoPhos, 2.2 equiv] in chloroform-d_1.



^{31}P-NMR (162 MHz, Chloroform-d_1): δ = 139.8 ppm (d, $J_{P, Rh}$ = 249.6 Hz, Rh[**26**-$P(O)_2N]_2$).

Figure AV: variable-temperature ^{31}P-NMR spectra of the complex between $Rh(COD)_2BF_4$ (1.0 equiv) and **26**-$P(O)_2N$ [(*S*)-MonoPhos, 2.2 equiv] in chloroform-d_1.