Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPORTING INFORMATION (ESI)

Enantioselective Conjugate Addition of Phenylboronic Acid to Enones Catalyzed by a Chiral Tropos/Atropos Rhodium Complex at the Coalescence Temperature

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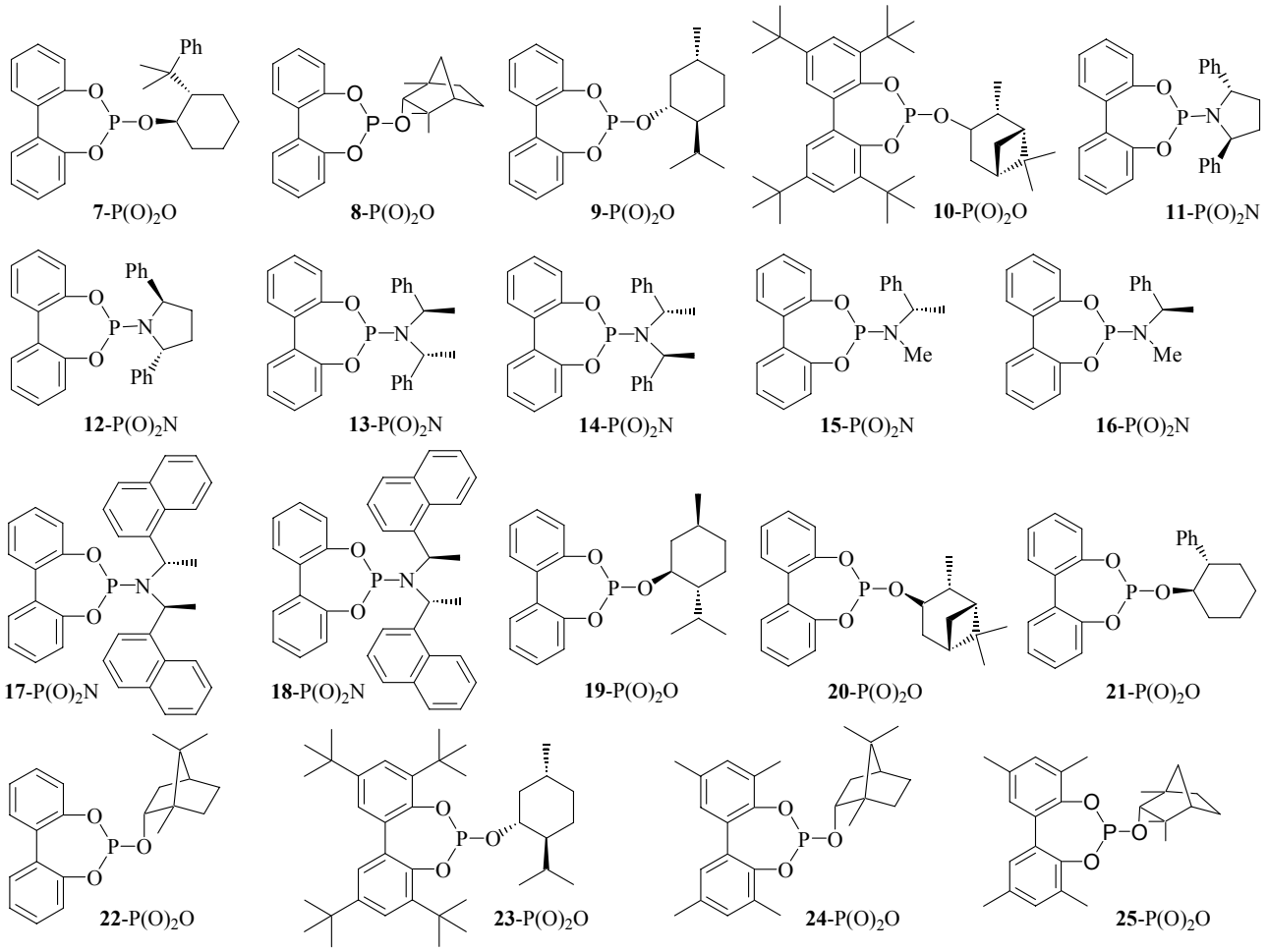
General procedure for the synthesis of phosphites: PCl_3 (2 eq, 6 mmol, 525 μl) was added to a solution of the alcohol (1 eq, 3 mmol) in dichloromethane (17 ml), in a Schlenk tube, under argon, at room temperature. After stirring for 2 hours, the solvent and excess PCl_3 were removed under reduced pressure. 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.

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.[1] (*R*,*R*)-2,5-diphenylpyrrolidine and (*S*,*S*)-2,5-diphenylpyrrolidine were prepared following a literature procedure.[2] 3,3',5,5'-tetramethyl-biphenol[3] and 3,3',5,5'-tetra-*tert*-butyl-biphenol[4] were prepared following the reported procedures.

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



7-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.

8-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.

9-$P(O)_2O$, 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.

10-$P(O)_2O$, 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$\mathbf{H}_3$), 1.36 (s, 18H, *t*Bu), 1.20 (d, *J* = 7.2 Hz, 3H, C$\mathbf{H}_3$), 1.06 (d, *J* = 10 Hz, 1H, C**H**), 0.89 (s, 3H, C$\mathbf{H}_3$); ^{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.

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

12-$P(O)_2N$, Biphenol / (*R*,*R*)-2,5-diphenylpyrrolidine: 67% 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.

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

14-$P(O)_2N$, Biphenol / (*S*,*S*)-bis(α-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$\mathbf{H}_3$-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.

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

16-$P(O)_2N$, Biphenol / (*R*)-(+)-*N*,α-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.

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

18-$P(O)_2N$, 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.

19-$P(O)_2O$, 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**H**$_3$), 0.96 (d, *J* = 7.0 Hz, 3H, C**H**$_3$), 0.88 (d, *J* = 6.9 Hz, 3H, C**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.

20-$P(O)_2O$, 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**H**$_3$), 1.20 (d, *J* = 7.2 Hz, 3H, C**H**$_3$), 1.15 (d, *J* = 10 Hz, 1H, C**H**), 0.91 (s, 3H, C**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.

21-$P(O)_2O$, 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.

22-$P(O)_2O$, 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.

23-$P(O)_2O$, 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.

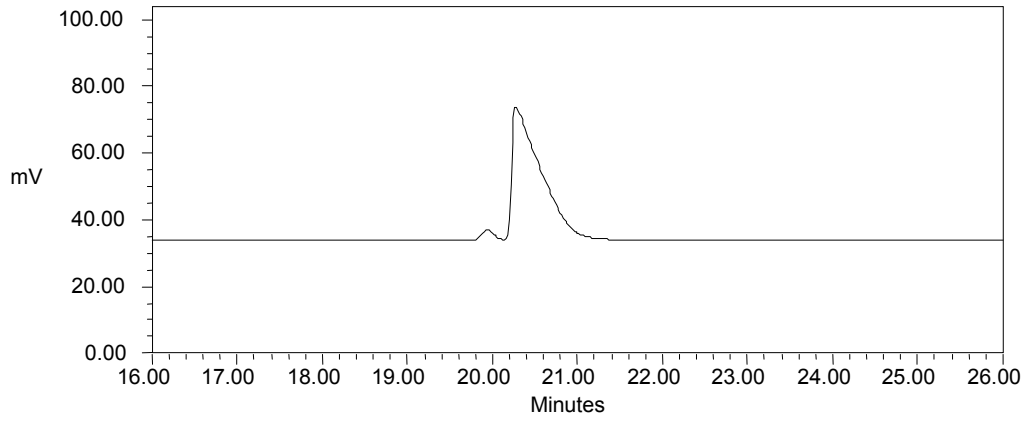
24-$P(O)_2O$, 3,3',5,5'-tetramethyl-biphenol / (-)-borneol: 76% yield;
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 2H, Ar**H**), 7.08 (s, 2H, Ar**H**), 4.65-4.60 (m, 1H, C**H**), 2.40 (s, 12H, 4 x C**H**$_3$), 2.27-2.20 (m, 1H, C**H**), 2.07-2.00 (m, 1H, C**H**), 1.76-1.67 (m, 2H, C**H**), 1.33-1.23 (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.

25-$P(O)_2O$, 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.

Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclohexen-1-one. Synthesis of 3-phenylcyclohexan-1-one: the reaction was performed using standard Schlenk techniques, under argon. The ligands **7**-$P(O)_2O$ (0.03 eq, 0.03 mmol, 12.9 mg) and **11**-$P(O)_2N$ (0.03 eq, 0.03 mmol, 13.1 mg) and $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.015 mmol, 5.8 mg) were weighed and 2.5 ml of degassed dioxane were added. After 30 min. under stirring, a solution of phenyl boronic acid (2 eq, 2 mmol, 243.8 mg) in 1.5 ml of dioxane was added, followed by 0.5 ml of a 2M solution of KOH (1 eq, 1 mmol) in water. A solution of 2-cyclohexen-1-one (1 eq, 1 mmol, 103 μl) in dioxane (1 ml) was added, and the reaction mixture was stirred overnight under argon, at room temperature. The reaction mixture was quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with diethyl ether. The combined organic extracts were dried and evaporated in vacuo, to give a yellow oil. The crude product was purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1) to yield 3-phenylcyclohexan-1-one as a yellow oil (0.95 mmol, 165.4 mg, isolated yield: 95%). 3-phenylcyclohexan-1-one: $[\alpha]_D$ = + 20.5 (c 0.985, $CHCl_3$);[5] 94.7% optical purity (*R*).

The enantiomeric excess of 3-phenylcyclohexan-1-one 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): 95% ee (*R*).



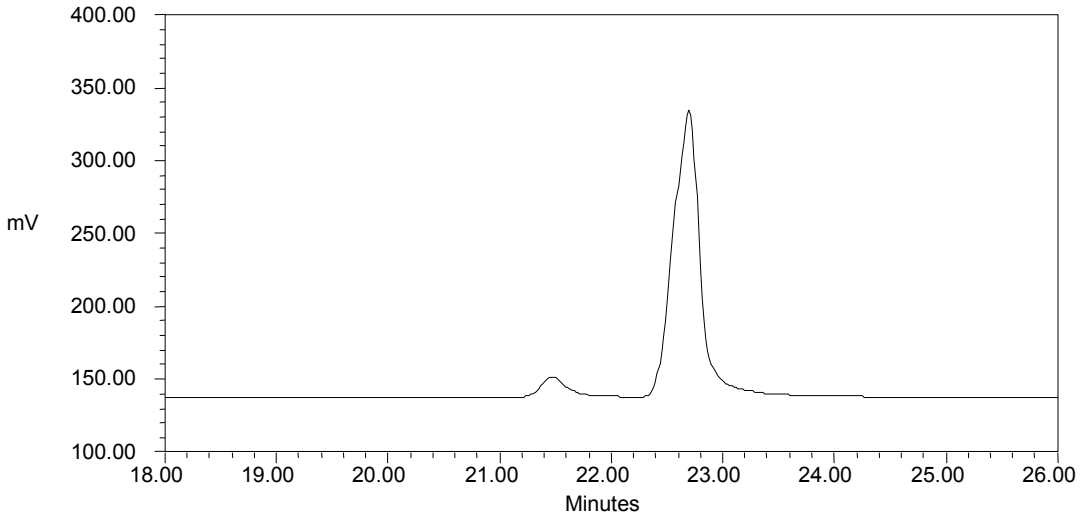
(*S*)-3-phenylcyclohexan-1-one: 19.9 min.

(*R*)-3-phenylcyclohexan-1-one: 20.3 min.

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

Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclohepten-1-one. Synthesis of 3-phenylcycloheptan-1-one: the reaction was performed using standard Schlenk techniques, under argon. The ligands **7**-$P(O)_2O$ (0.03 eq, 0.03 mmol, 12.9 mg) and **11**-$P(O)_2N$ (0.03 eq, 0.03 mmol, 13.1 mg) and $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.015 mmol, 5.8 mg) were weighed and 2.5 ml of degassed dioxane were added. After 30 min. under stirring, a solution of phenyl boronic acid (2 eq, 2 mmol, 243.8 mg) in 1.5 ml of dioxane was added, followed by 0.5 ml of a 2M solution of KOH (1 eq, 1 mmol) in water. A solution of 2-cyclohepten-1-one (1 eq, 1 mmol, 111.5 μl) in dioxane (1 ml) was added, and the reaction mixture was stirred overnight under argon, at room temperature. The reaction mixture was quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with diethyl ether. The combined organic extracts were dried and evaporated in vacuo, to give a yellow oil. The crude product was purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1) to yield 3-phenylcycloheptan-1-one as a yellow oil (0.97 mmol, 182.5 mg, isolated yield: 97%). 3-phenylcycloheptan-1-one: $[\alpha]_D$ = + 56.0 (c 0.75, $CHCl_3$);[6] 89.8% optical purity (*R*). The absolute configuration was tentatively assigned as (*R*) by analogy with the other cases.

The enantiomeric excess of 3-phenylcycloheptan-1-one 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): 90% ee (*R*).



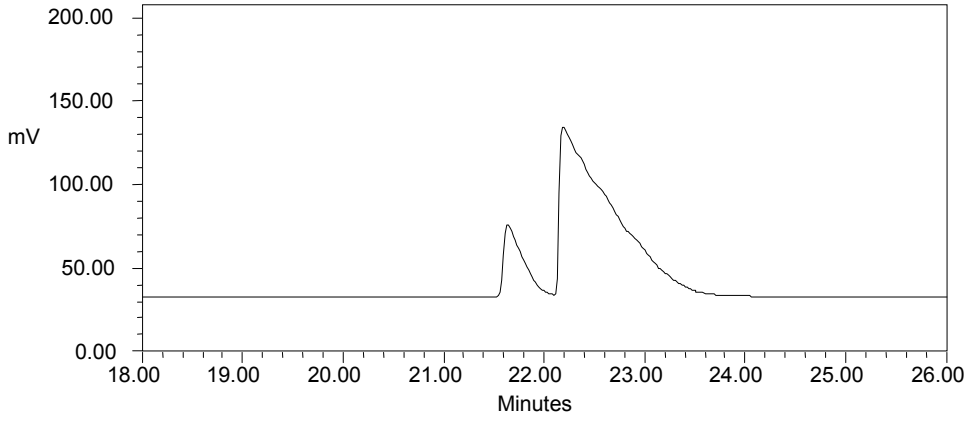
(*S*)-3-phenylcycloheptan-1-one: 21.5 min.

(*R*)-3-phenylcycloheptan-1-one: 22.7 min.

[6] $[\alpha]_D$ = - 58 (c 0.75, $CHCl_3$) was reported for 3-phenylcycloheptanone (93% ee), see: Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.* 1998, **120**, 5579, and references therein.

Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclopenten-1-one. Synthesis of 3-phenylcyclopentan-1-one: the reaction was performed using standard Schlenk techniques, under argon. The ligands **7**-$P(O)_2O$ (0.03 eq, 0.03 mmol, 12.9 mg) and **11**-$P(O)_2N$ (0.03 eq, 0.03 mmol, 13.1 mg) and $[Rh(eth)_2Cl]_2$ (0.015 eq, 0.015 mmol, 5.8 mg) were weighed and 2.5 ml of degassed dioxane were added. After 30 min. under stirring, a solution of phenyl boronic acid (2 eq, 2 mmol, 243.8 mg) in 1.5 ml of dioxane was added, followed by 0.5 ml of a 2M solution of KOH (1 eq, 1 mmol) in water. A solution of 2-cyclopenten-1-one (1 eq, 1 mmol, 83.7 μl) in dioxane (1 ml) was added, and the reaction mixture was stirred overnight under argon, at room temperature. The reaction mixture was quenched with a satd. aqueous $NaHCO_3$ solution, and extracted with diethyl ether. The combined organic extracts were dried and evaporated in vacuo, to give a yellow oil. The crude product was purified by flash chromatography (eluent: hexane / ethyl acetate = 10 / 1) to yield 3-phenylcyclopentan-1-one as a yellow oil (0.95 mmol, 165.4 mg, isolated yield: 95%). 3-phenyl cyclopentan-1-one: $[\alpha]_D$ = + 74.2 (c 0.81, $CHCl_3$);[7] 78.2% optical purity (*R*).

The enantiomeric excess of 3-phenylcyclopentan-1-one was determined by GC equipped with a chiral capillary column (Supelco γ-DEX 225, 25 m, film 0.25 μm): 73% ee (*R*).



(*S*)-3-phenylcyclopentan-1-one: 21.6 min.

(*R*)-3-phenylcyclopentan-1-one: 22.2 min.

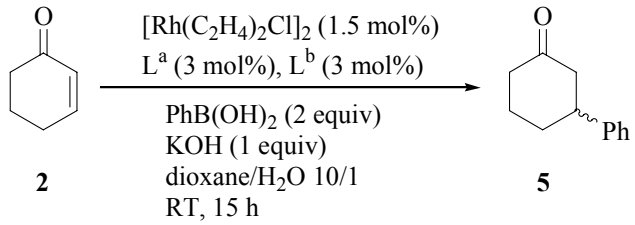
[7] $[\alpha]_D$ = - 92 (c 0.82, $CHCl_3$) was reported for (*S*)-3-phenylcyclopentanone (97% ee), see: Y. Takaya, M. Ogasawara and T. Hayashi, *J. Am. Chem. Soc.* 1998, **120**, 5579, and references therein.

General procedure for the ligand library 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 appropriate cyclic enone (1.6 mmol) 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 phenyl boronic 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 the cyclic enone (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, using *n*-tridecane as internal standard: yields and ee's were determined by integration of the GC traces.

3-phenylcyclohexan-1-one and 3-phenylcycloheptan-1-one: MEGADEX DACTBSβ, diacetyl-t-butylsilyl-β-cyclodextrin OV 1701, 25 m, film 0.25 μm.

3-phenylcyclopentan-1-one: Supelco γ-DEX 225, 25 m, film 0.25 μm.

Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclohexen-1-one: Ligand library screening.

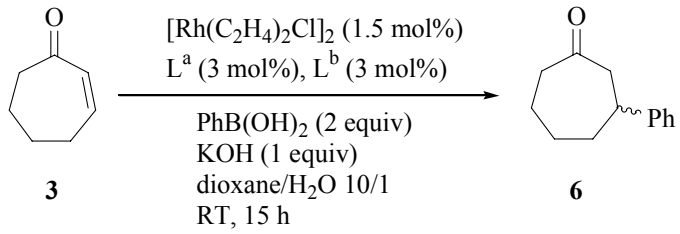


2 **5**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**7**-$P(O)_2O$	**7**-$P(O)_2O$	100	70	*R*
2	**8**-$P(O)_2O$	**8**-$P(O)_2O$	100	28	*R*
3	**9**-$P(O)_2O$	**9**-$P(O)_2O$	100	8	*R*
4	**10**-$P(O)_2O$	**10**-$P(O)_2O$	60	rac	-
5	**11**-$P(O)_2N$	**11**-$P(O)_2N$	100	36	*R*
6	**12**-$P(O)_2N$	**12**-$P(O)_2N$	100	36	*S*
7	**13**-$P(O)_2N$	**13**-$P(O)_2N$	56	3	*S*
8	**14**-$P(O)_2N$	**14**-$P(O)_2N$	56	3	*R*
9	**15**-$P(O)_2N$	**15**-$P(O)_2N$	90	7	*R*
10	**16**-$P(O)_2N$	**16**-$P(O)_2N$	90	7	*S*
11	**17**-$P(O)_2N$	**17**-$P(O)_2N$	30	rac	-
12	**18**-$P(O)_2N$	**18**-$P(O)_2N$	30	rac	-
13	**19**-$P(O)_2O$	**19**-$P(O)_2O$	100	8	*S*
14	**20**-$P(O)_2O$	**20**-$P(O)_2O$	100	28	*S*
15	**21**-$P(O)_2O$	**21**-$P(O)_2O$	100	41	*R*
16	**22**-$P(O)_2O$	**22**-$P(O)_2O$	100	19	*R*
17	**23**-$P(O)_2O$	**23**-$P(O)_2O$	0	-	-
18	**24**-$P(O)_2O$	**24**-$P(O)_2O$	50	8	*S*
19	**25**-$P(O)_2O$	**25**-$P(O)_2O$	100	7	*R*
20	**7**-$P(O)_2O$	**11**-$P(O)_2N$	100	95	*R*
21	**7**-$P(O)_2O$	**12**-$P(O)_2N$	100	70	*S*
22	**7**-$P(O)_2O$	**13**-$P(O)_2N$	92	65	*R*
23	**7**-$P(O)_2O$	**14**-$P(O)_2N$	100	70	*R*
24	**7**-$P(O)_2O$	**15**-$P(O)_2N$	100	58	*R*
25	**7**-$P(O)_2O$	**16**-$P(O)_2N$	100	54	*R*
26	**7**-$P(O)_2O$	**17**-$P(O)_2N$	100	58	*R*
27	**7**-$P(O)_2O$	**18**-$P(O)_2N$	100	64	*R*
28	**8**-$P(O)_2O$	**11**-$P(O)_2N$	100	91	*R*
29	**8**-$P(O)_2O$	**12**-$P(O)_2N$	100	87	*S*
30	**8**-$P(O)_2O$	**13**-$P(O)_2N$	40	28	*R*
31	**8**-$P(O)_2O$	**14**-$P(O)_2N$	30	8	*R*
32	**8**-$P(O)_2O$	**15**-$P(O)_2N$	70	14	*R*
33	**8**-$P(O)_2O$	**16**-$P(O)_2N$	70	20	*R*
34	**9**-$P(O)_2O$	**11**-$P(O)_2N$	100	81	*R*
35	**9**-$P(O)_2O$	**12**-$P(O)_2N$	100	73	*S*

36	**10**-$P(O)_2O$	**11**-$P(O)_2N$	90	rac	-
37	**10**-$P(O)_2O$	**12**-$P(O)_2N$	100	rac	-
38	**20**-$P(O)_2O$	**11**-$P(O)_2N$	100	80	*R*
39	**20**-$P(O)_2O$	**12**-$P(O)_2N$	100	74	*S*
40	**20**-$P(O)_2O$	**13**-$P(O)_2N$	30	61	*S*
41	**20**-$P(O)_2O$	**14**-$P(O)_2N$	40	32	*S*
42	**20**-$P(O)_2O$	**15**-$P(O)_2N$	0	-	-
43	**20**-$P(O)_2O$	**16**-$P(O)_2N$	100	4	*S*
44	**20**-$P(O)_2O$	**17**-$P(O)_2N$	100	25	*S*
45	**20**-$P(O)_2O$	**18**-$P(O)_2N$	100	30	*S*
46	**21**-$P(O)_2O$	**11**-$P(O)_2N$	95	83	*R*
47	**21**-$P(O)_2O$	**12**-$P(O)_2N$	95	69	*S*
48	**21**-$P(O)_2O$	**13**-$P(O)_2N$	60	23	*R*
49	**21**-$P(O)_2O$	**14**-$P(O)_2N$	55	20	*R*
50	**21**-$P(O)_2O$	**15**-$P(O)_2N$	20	9	*R*
51	**21**-$P(O)_2O$	**16**-$P(O)_2N$	25	9	*R*
52	**21**-$P(O)_2O$	**17**-$P(O)_2N$	90	17	*R*
53	**21**-$P(O)_2O$	**18**-$P(O)_2N$	80	27	*R*
54	**22**-$P(O)_2O$	**11**-$P(O)_2N$	100	74	*R*
55	**22**-$P(O)_2O$	**12**-$P(O)_2N$	100	51	*S*
56	**22**-$P(O)_2O$	**13**-$P(O)_2N$	90	10	*R*
57	**22**-$P(O)_2O$	**14**-$P(O)_2N$	100	15	*R*
58	**22**-$P(O)_2O$	**15**-$P(O)_2N$	70	27	*R*
59	**22**-$P(O)_2O$	**16**-$P(O)_2N$	100	21	*R*
60	**24**-$P(O)_2O$	**11**-$P(O)_2N$	90	4	*R*
61	**24**-$P(O)_2O$	**12**-$P(O)_2N$	80	9	*S*
62	**25**-$P(O)_2O$	**11**-$P(O)_2N$	90	8	*R*
63	**25**-$P(O)_2O$	**12**-$P(O)_2N$	100	22	*R*

Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclohepten-1-one: Ligand library screening.

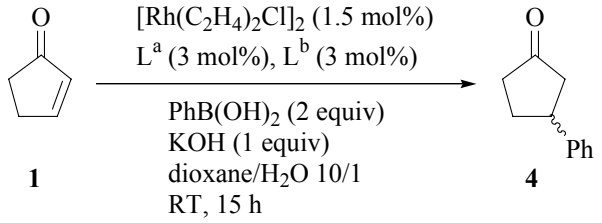


3 **6**

Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**7**-$P(O)_2O$	**7**-$P(O)_2O$	100	45	*R*
2	**8**-$P(O)_2O$	**8**-$P(O)_2O$	50	21	*R*
3	**9**-$P(O)_2O$	**9**-$P(O)_2O$	90	rac	-
4	**10**-$P(O)_2O$	**10**-$P(O)_2O$	30	6	*S*
5	**11**-$P(O)_2N$	**11**-$P(O)_2N$	40	45	*R*
6	**12**-$P(O)_2N$	**12**-$P(O)_2N$	40	45	*S*
7	**13**-$P(O)_2N$	**13**-$P(O)_2N$	0	-	-
8	**14**-$P(O)_2N$	**14**-$P(O)_2N$	0	-	-
9	**15**-$P(O)_2N$	**15**-$P(O)_2N$	5	21	*S*
10	**16**-$P(O)_2N$	**16**-$P(O)_2N$	5	21	*R*
11	**17**-$P(O)_2N$	**17**-$P(O)_2N$	0	-	-
12	**18**-$P(O)_2N$	**18**-$P(O)_2N$	0	-	-
13	**19**-$P(O)_2O$	**19**-$P(O)_2O$	90	rac	-
14	**20**-$P(O)_2O$	**20**-$P(O)_2O$	100	28	*S*
15	**21**-$P(O)_2O$	**21**-$P(O)_2O$	80	11	*R*
16	**22**-$P(O)_2O$	**22**-$P(O)_2O$	100	19	*R*
17	**23**-$P(O)_2O$	**23**-$P(O)_2O$	0	-	-
18	**24**-$P(O)_2O$	**24**-$P(O)_2O$	0	-	-
19	**25**-$P(O)_2O$	**25**-$P(O)_2O$	15	rac	-
20	**7**-$P(O)_2O$	**11**-$P(O)_2N$	100	90	*R*
21	**7**-$P(O)_2O$	**12**-$P(O)_2N$	100	35	*S*
22	**7**-$P(O)_2O$	**13**-$P(O)_2N$	40	38	*R*
23	**7**-$P(O)_2O$	**14**-$P(O)_2N$	30	41	*R*
24	**7**-$P(O)_2O$	**15**-$P(O)_2N$	70	18	*R*
25	**7**-$P(O)_2O$	**16**-$P(O)_2N$	90	19	*R*
26	**8**-$P(O)_2O$	**11**-$P(O)_2N$	100	90	*R*
27	**8**-$P(O)_2O$	**12**-$P(O)_2N$	100	80	*S*
28	**9**-$P(O)_2O$	**11**-$P(O)_2N$	100	80	*R*
29	**9**-$P(O)_2O$	**12**-$P(O)_2N$	80	83	*S*
30	**10**-$P(O)_2O$	**11**-$P(O)_2N$	30	5	*R*
31	**10**-$P(O)_2O$	**12**-$P(O)_2N$	20	25	*S*
32	**20**-$P(O)_2O$	**11**-$P(O)_2N$	100	64	*R*
33	**20**-$P(O)_2O$	**12**-$P(O)_2N$	100	62	*S*
34	**21**-$P(O)_2O$	**11**-$P(O)_2N$	100	81	*R*
35	**21**-$P(O)_2O$	**12**-$P(O)_2N$	100	75	*S*

36	**22**-$P(O)_2O$	**11**-$P(O)_2N$	100	86	*R*
37	**22**-$P(O)_2O$	**12**-$P(O)_2N$	100	71	*S*
38	**24**-$P(O)_2O$	**11**-$P(O)_2N$	40	30	*R*
39	**24**-$P(O)_2O$	**12**-$P(O)_2N$	50	rac	-
40	**25**-$P(O)_2O$	**11**-$P(O)_2N$	10	55	*R*
41	**25**-$P(O)_2O$	**12**-$P(O)_2N$	10	29	*S*

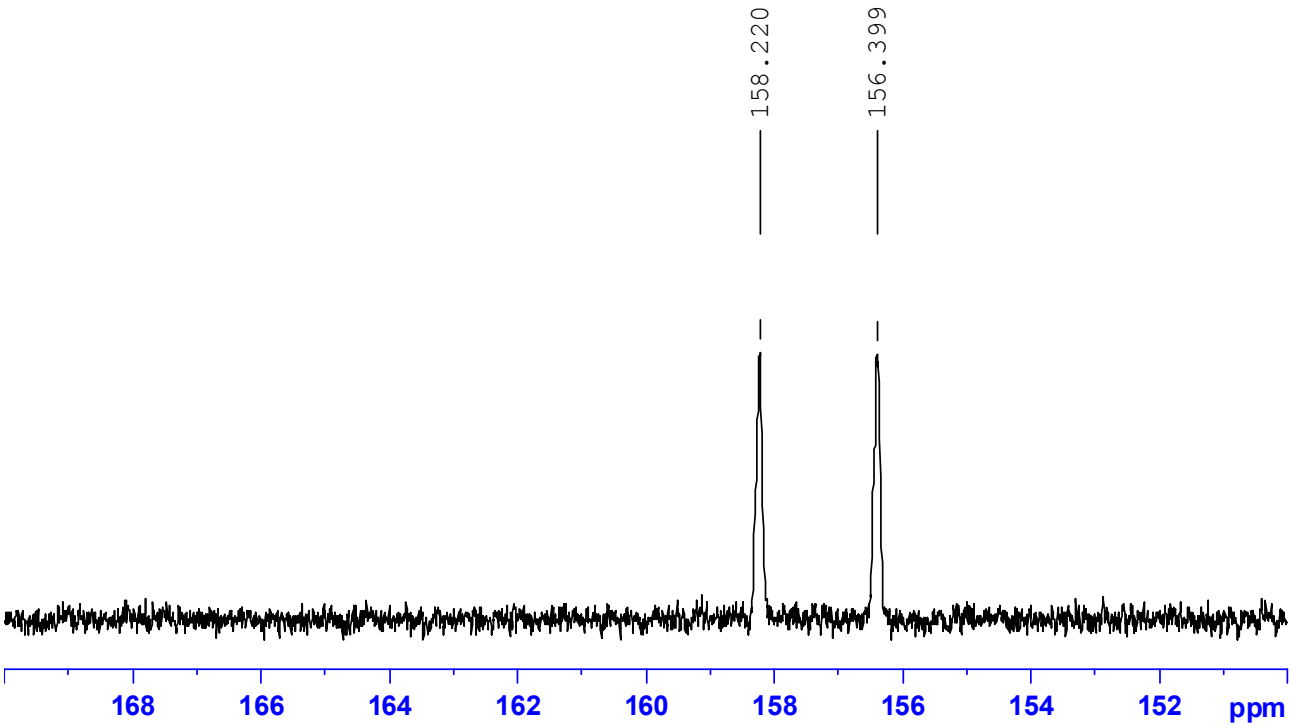
Rh-catalysed asymmetric 1,4-conjugate addition of phenyl boronic acid to 2-cyclopenten-1-one: Ligand library screening.



Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**7**-$P(O)_2O$	**7**-$P(O)_2O$	100	45	*R*
2	**8**-$P(O)_2O$	**8**-$P(O)_2O$	60	16	*R*
3	**9**-$P(O)_2O$	**9**-$P(O)_2O$	100	15	*R*
4	**10**-$P(O)_2O$	**10**-$P(O)_2O$	100	58	*S*
5	**11**-$P(O)_2N$	**11**-$P(O)_2N$	90	32	*R*
6	**12**-$P(O)_2N$	**12**-$P(O)_2N$	90	32	*S*
7	**13**-$P(O)_2N$	**13**-$P(O)_2N$	0	-	-
8	**14**-$P(O)_2N$	**14**-$P(O)_2N$	0	-	-
9	**15**-$P(O)_2N$	**15**-$P(O)_2N$	0	-	-
10	**16**-$P(O)_2N$	**16**-$P(O)_2N$	0	-	-
11	**17**-$P(O)_2N$	**17**-$P(O)_2N$	0	-	-
12	**18**-$P(O)_2N$	**18**-$P(O)_2N$	0	-	-
13	**19**-$P(O)_2O$	**19**-$P(O)_2O$	100	15	*S*
14	**20**-$P(O)_2O$	**20**-$P(O)_2O$	100	15	*S*
15	**21**-$P(O)_2O$	**21**-$P(O)_2O$	100	27	*R*
16	**22**-$P(O)_2O$	**22**-$P(O)_2O$	100	8	*R*
17	**23**-$P(O)_2O$	**23**-$P(O)_2O$	0	-	-
18	**24**-$P(O)_2O$	**24**-$P(O)_2O$	0	-	-
19	**25**-$P(O)_2O$	**25**-$P(O)_2O$	0	-	-
20	**7**-$P(O)_2O$	**11**-$P(O)_2N$	100	73	*R*
21	**7**-$P(O)_2O$	**12**-$P(O)_2N$	100	13	*R*
22	**7**-$P(O)_2O$	**13**-$P(O)_2N$	100	26	*R*
23	**7**-$P(O)_2O$	**14**-$P(O)_2N$	100	35	*R*
24	**7**-$P(O)_2O$	**15**-$P(O)_2N$	90	40	*R*
25	**7**-$P(O)_2O$	**16**-$P(O)_2N$	90	40	*R*
26	**8**-$P(O)_2O$	**11**-$P(O)_2N$	100	68	*R*
27	**8**-$P(O)_2O$	**12**-$P(O)_2N$	100	26	*S*
28	**9**-$P(O)_2O$	**11**-$P(O)_2N$	100	55	*R*
29	**9**-$P(O)_2O$	**12**-$P(O)_2N$	100	13	*S*
30	**10**-$P(O)_2O$	**11**-$P(O)_2N$	100	20	*S*
31	**10**-$P(O)_2O$	**12**-$P(O)_2N$	100	42	*S*
32	**20**-$P(O)_2O$	**11**-$P(O)_2N$	100	51	*R*
33	**20**-$P(O)_2O$	**12**-$P(O)_2N$	100	38	*S*
34	**21**-$P(O)_2O$	**11**-$P(O)_2N$	100	61	*R*
35	**21**-$P(O)_2O$	**12**-$P(O)_2N$	100	36	*S*

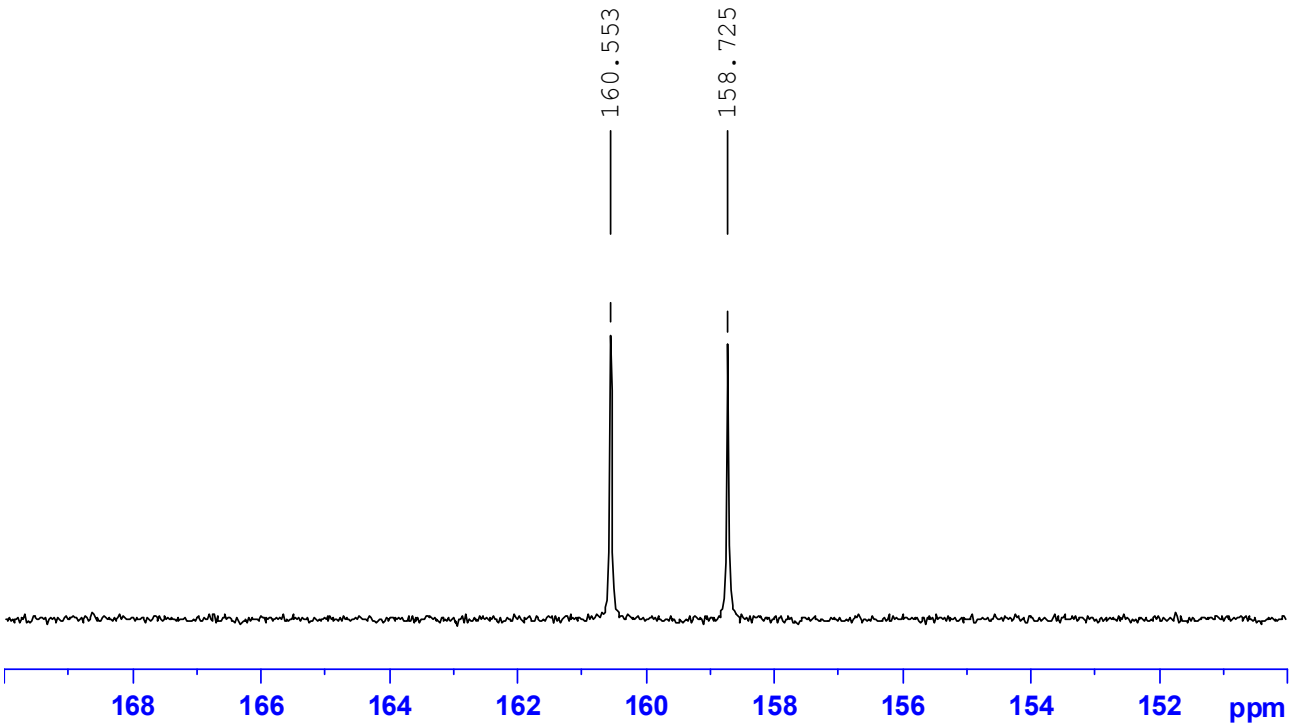
36	**22**-$P(O)_2O$	**11**-$P(O)_2N$	100	60	*R*
37	**22**-$P(O)_2O$	**12**-$P(O)_2N$	100	47	*S*
38	**24**-$P(O)_2O$	**11**-$P(O)_2N$	100	31	*R*
39	**24**-$P(O)_2O$	**12**-$P(O)_2N$	100	21	*S*
40	**25**-$P(O)_2O$	**11**-$P(O)_2N$	70	50	*R*
41	**25**-$P(O)_2O$	**12**-$P(O)_2N$	90	61	*R*

Figure A: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **7**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 380 K



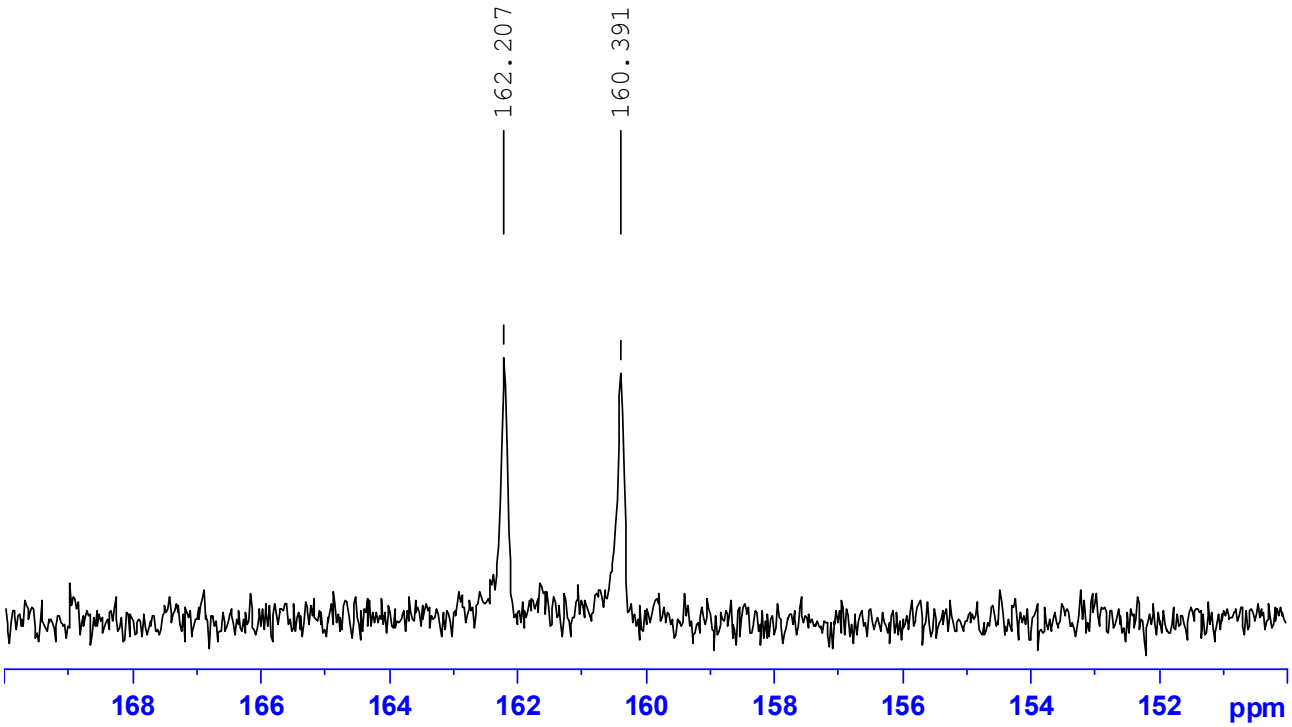
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 157.3 (d, $J_{P, Rh}$ = 295 Hz) ppm.

Figure B: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **7**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 300 K



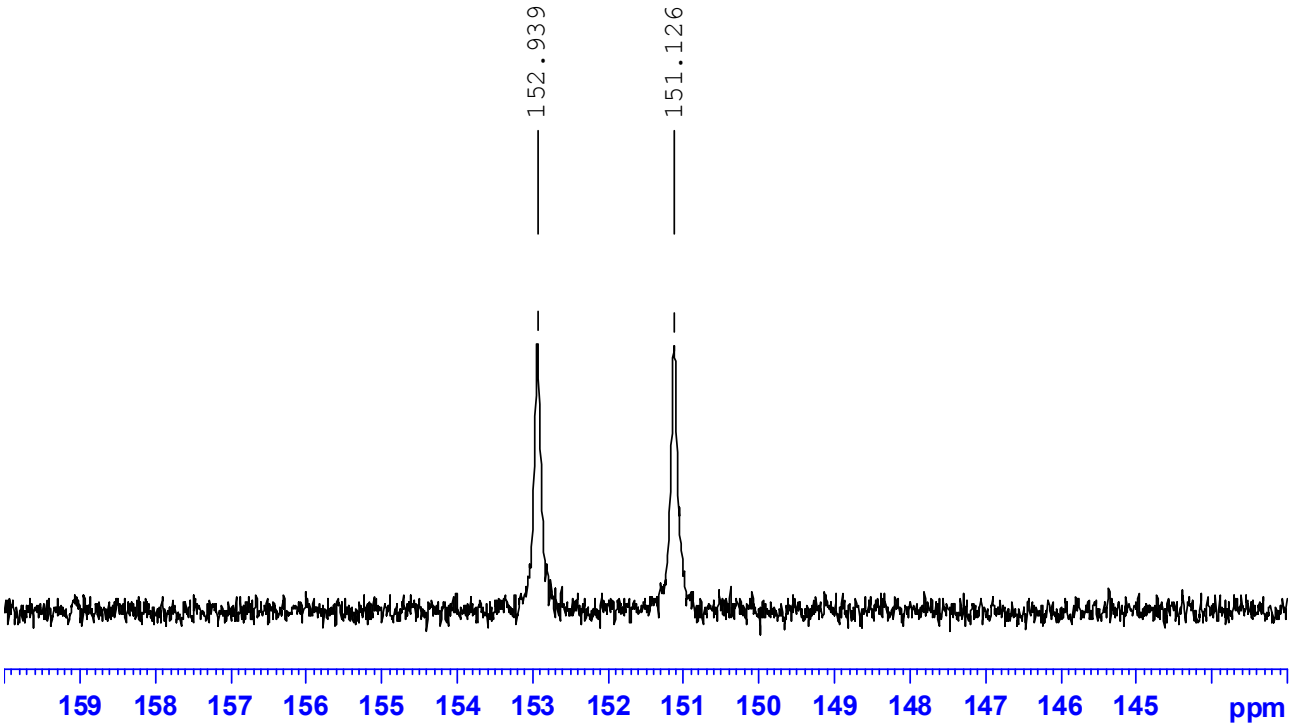
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 159.6 (d, $J_{P, Rh}$ = 296 Hz) ppm.

Figure C: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **7**-P(O)$_2$O (2.0 equiv) in toluene-d$_8$ at 230 K



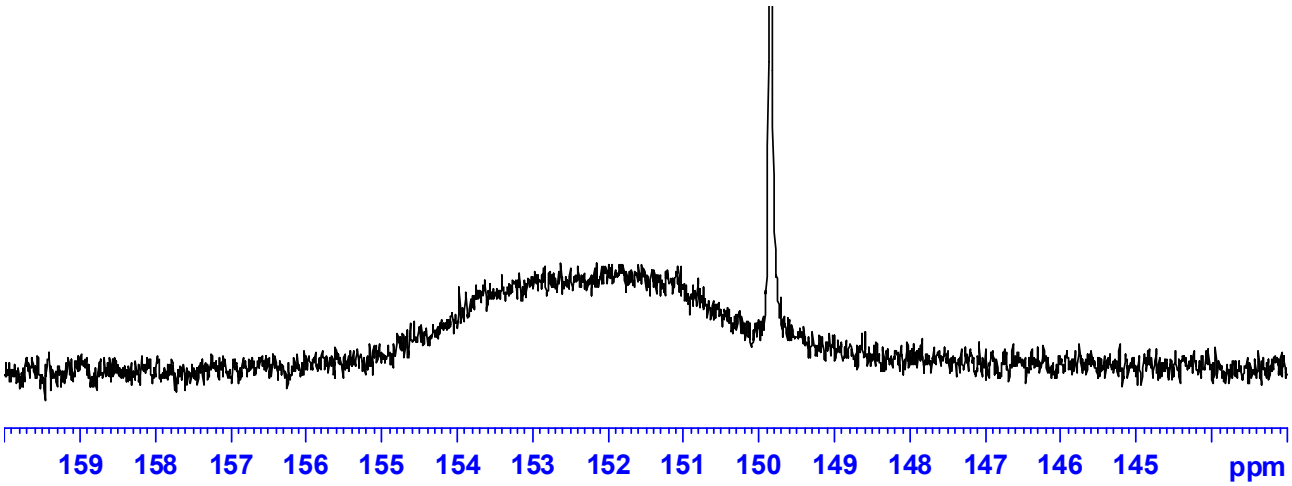
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 161.3 (d, $J_{P, Rh}$ = 294 Hz) ppm.

Figure D: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (2.0 equiv) in toluene-d$_8$ at 380 K



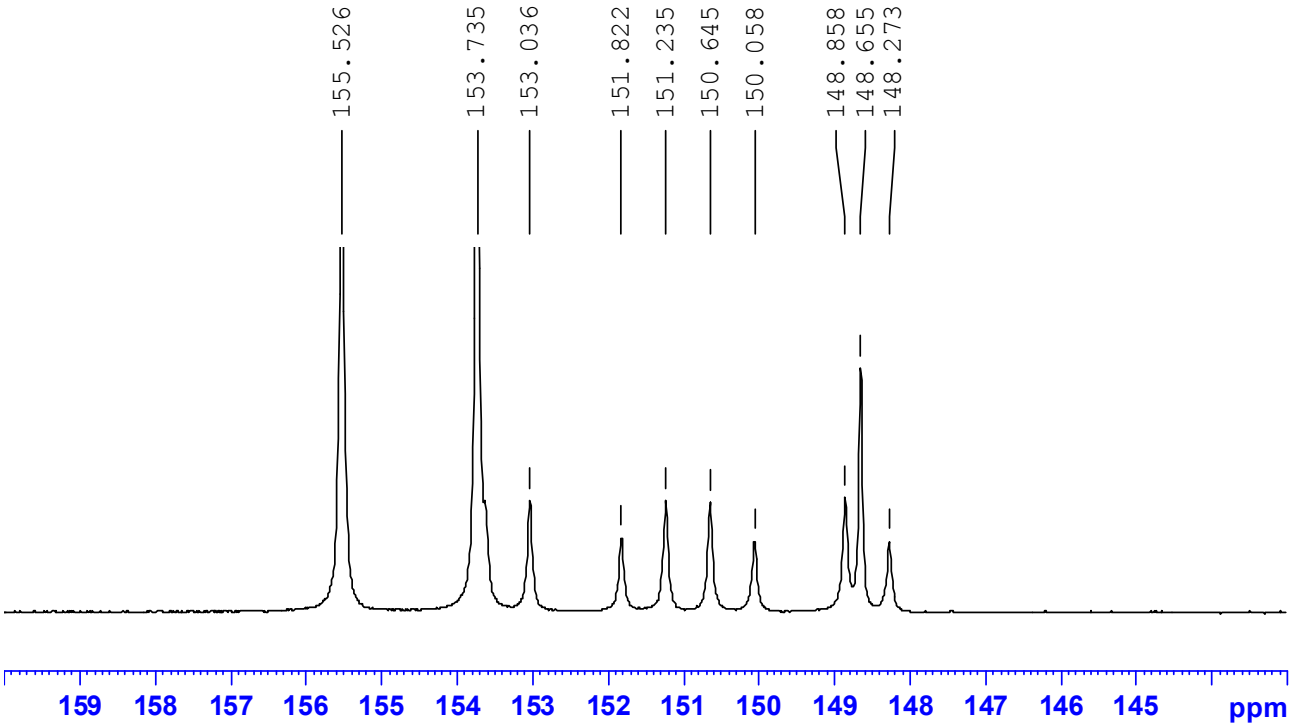
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 152.0 (d, $J_{P,\,Rh}$ = 294 Hz) ppm.

Figure E: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 320 K

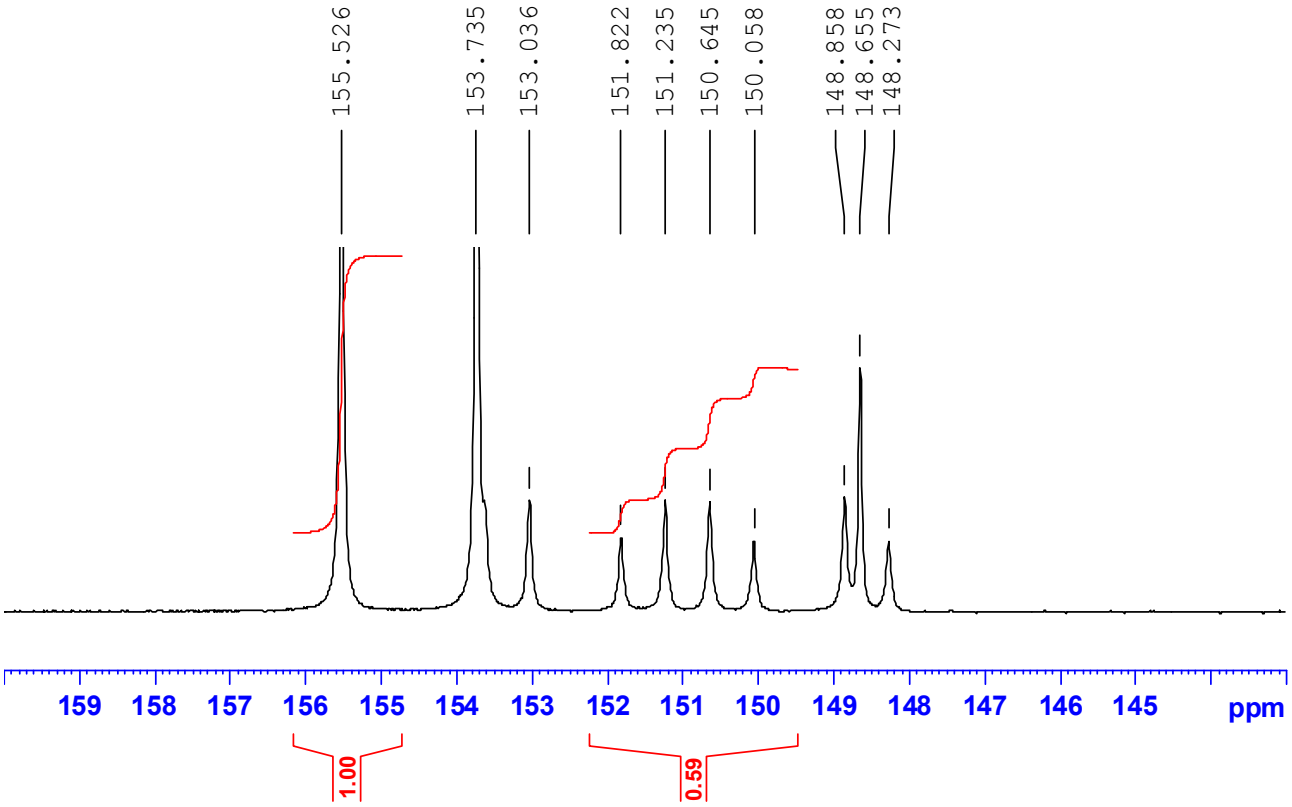


^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 151.9 (broad), 149.9 (s, excess ligand) ppm.

Figure F: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 230 K



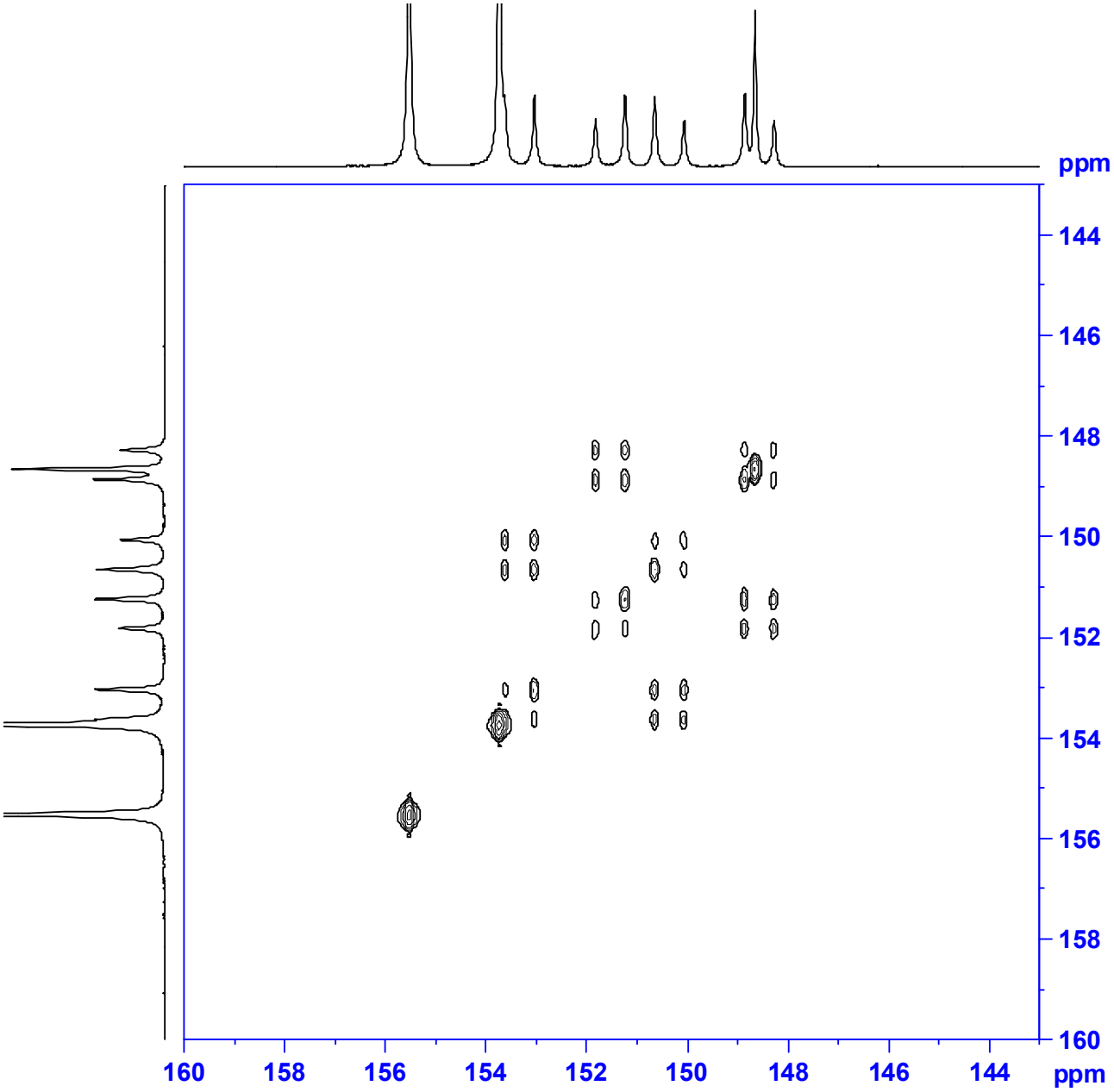
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 154.6 (d, $J_{P,\,Rh}$ = 290 Hz), 152.4 (dd, $J_{P,\,Rh}$ = 291.8 Hz, $J_{P,\,P}$ = 95 Hz), 149.5 (dd, $J_{P,\,Rh}$ = 289.5 Hz, $J_{P,\,P}$ = 95 Hz), 148.7 (s, excess ligand) ppm.



{Rh[(a*S*)-**11**]$_2$ + Rh[(a*R*)-**11**]$_2$} : Rh[(a*S*)-**11**][(a*R*)-**11**] = 1 : 0.59.

Rh[(a*S*)-**11**]$_2$ + Rh[(a*R*)-**11**]$_2$ = 62.9%; Rh[(a*S*)-**11**][(a*R*)-**11**] = 37.1%.

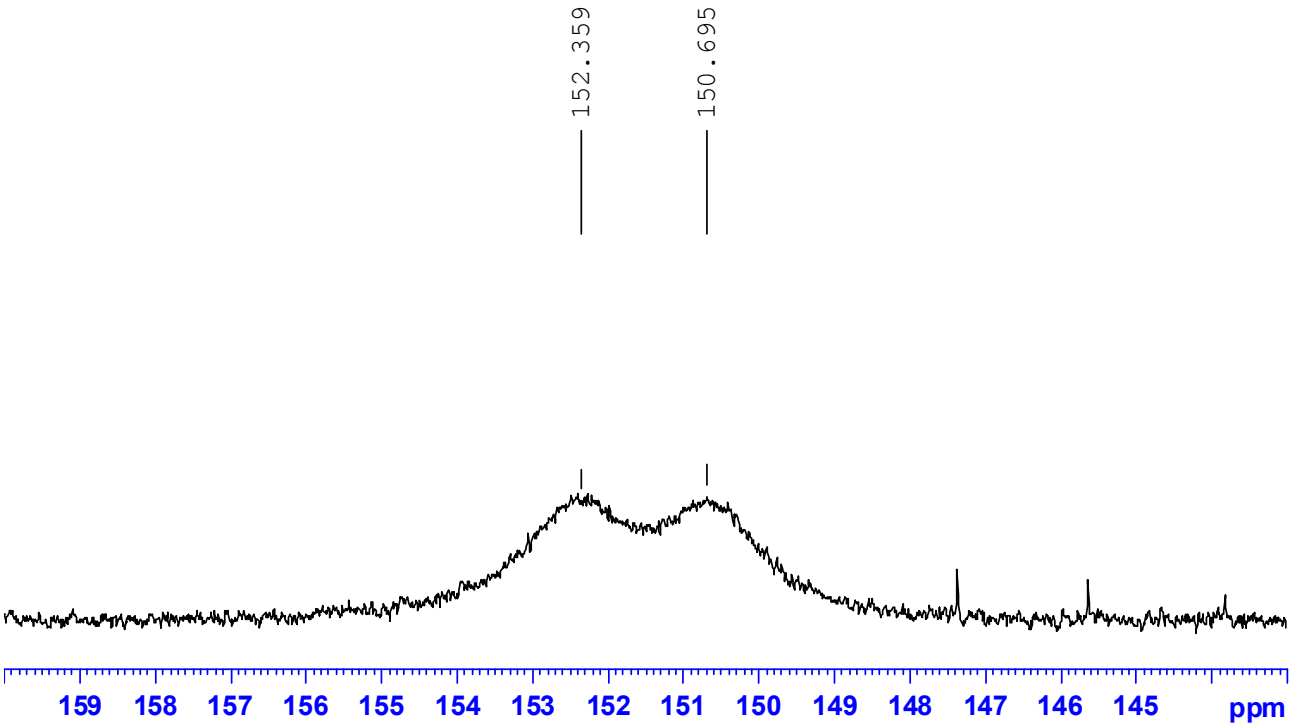
Figure G: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (3.0 equiv) in toluene-d$_8$ at 230 K



Considering the complex Rh[(a*S*)-**11**][(a*R*)-**11**], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**11**] ⇆ [(a*R*)-**11**] in toluene-d$_8$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**11**][(a*R*)-**11**] 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 $\Delta G^{\neq} = RT_c\,[23 + \ln (T_c / \Delta\nu)] = 14.38$ kcal / mol.[8]

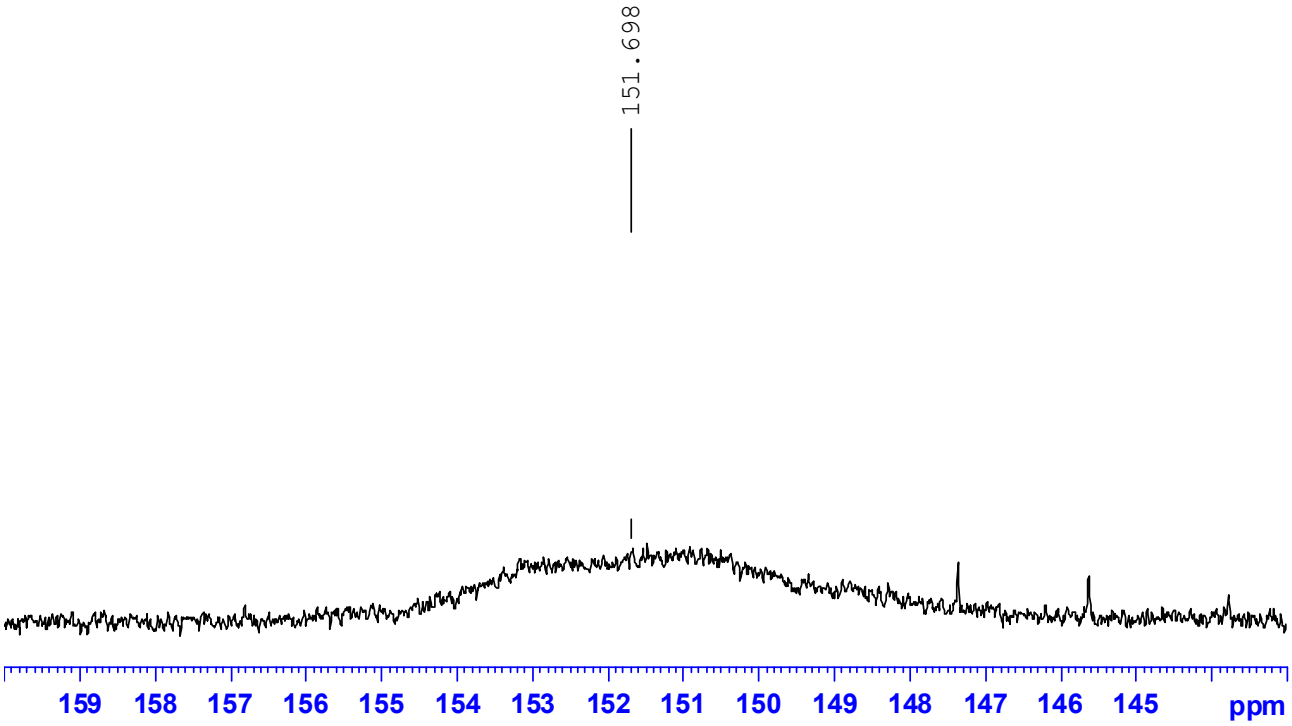
[8] M. Oki, in *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH: Weinheim, 1985.

Figure H: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 310 K



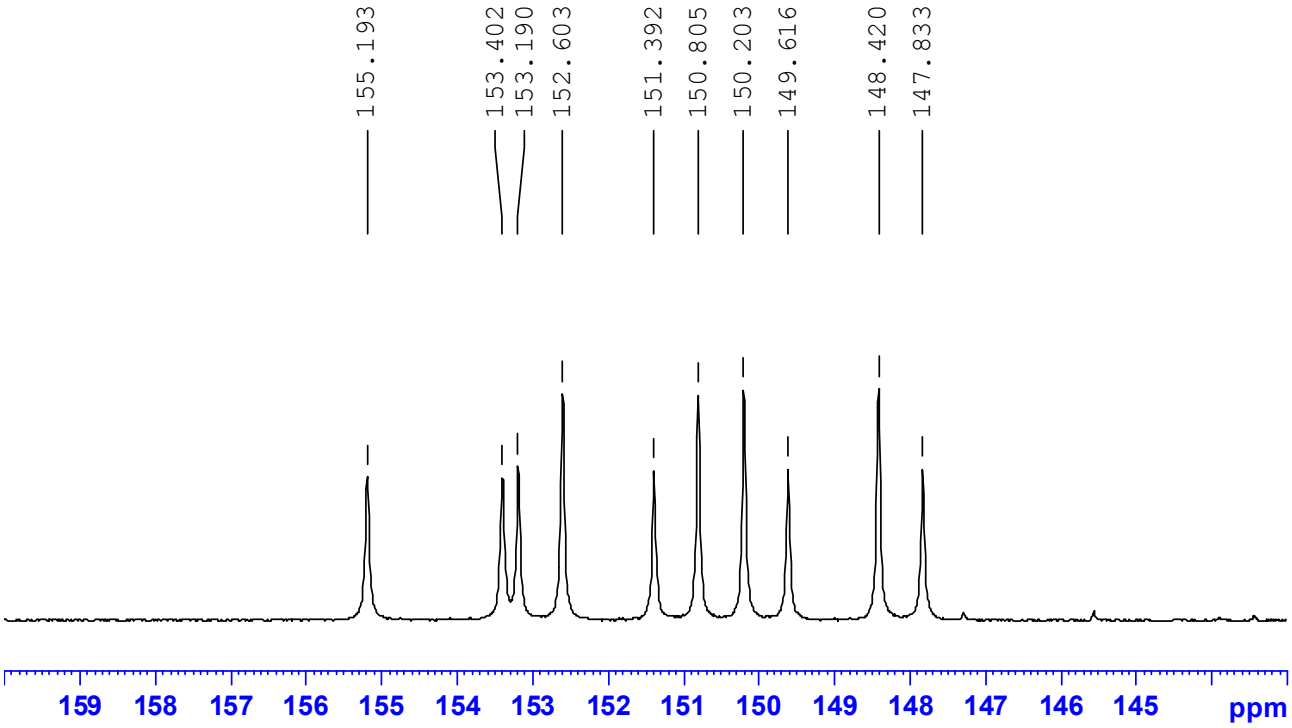
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 151.5 (d, $J_{P,\,Rh}$ = 270 Hz) ppm.

Figure I: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 290 K

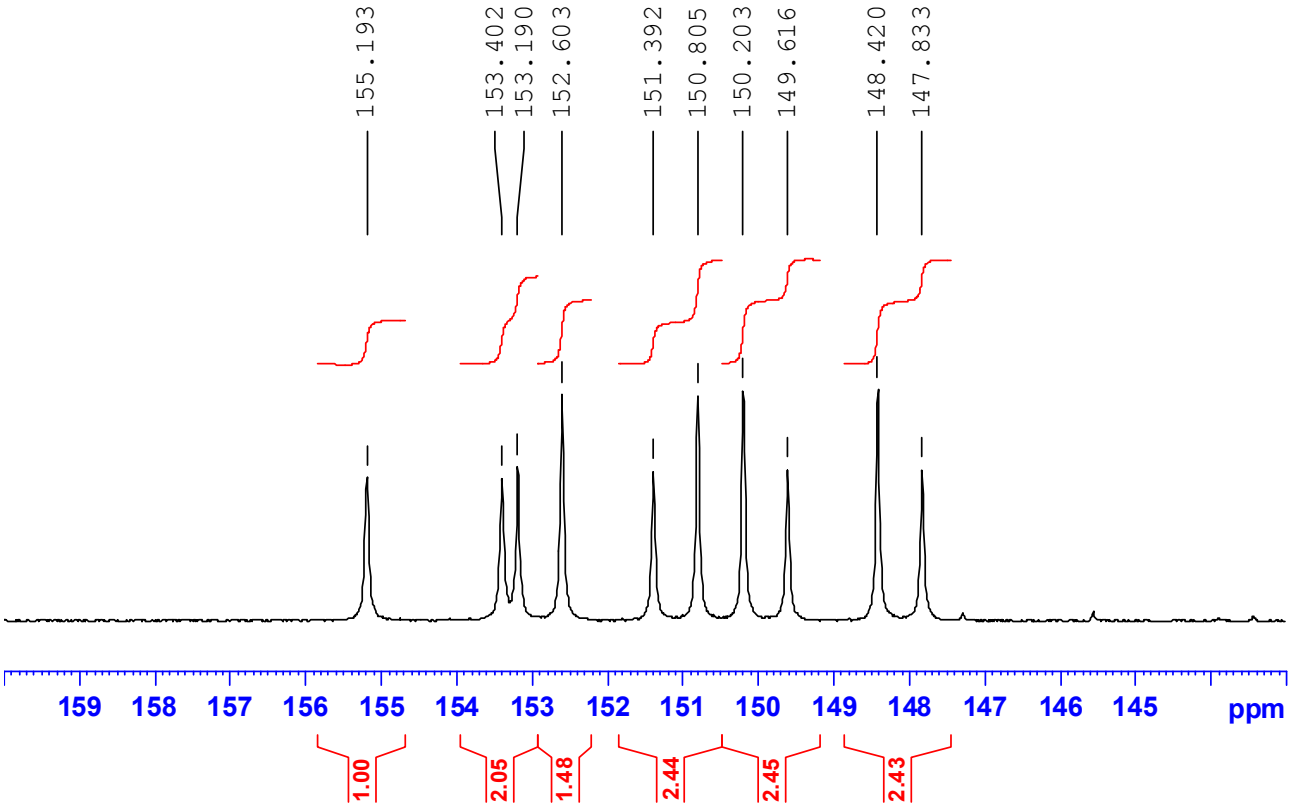


^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 151.7 ppm (broad).

Figure J: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 230 K



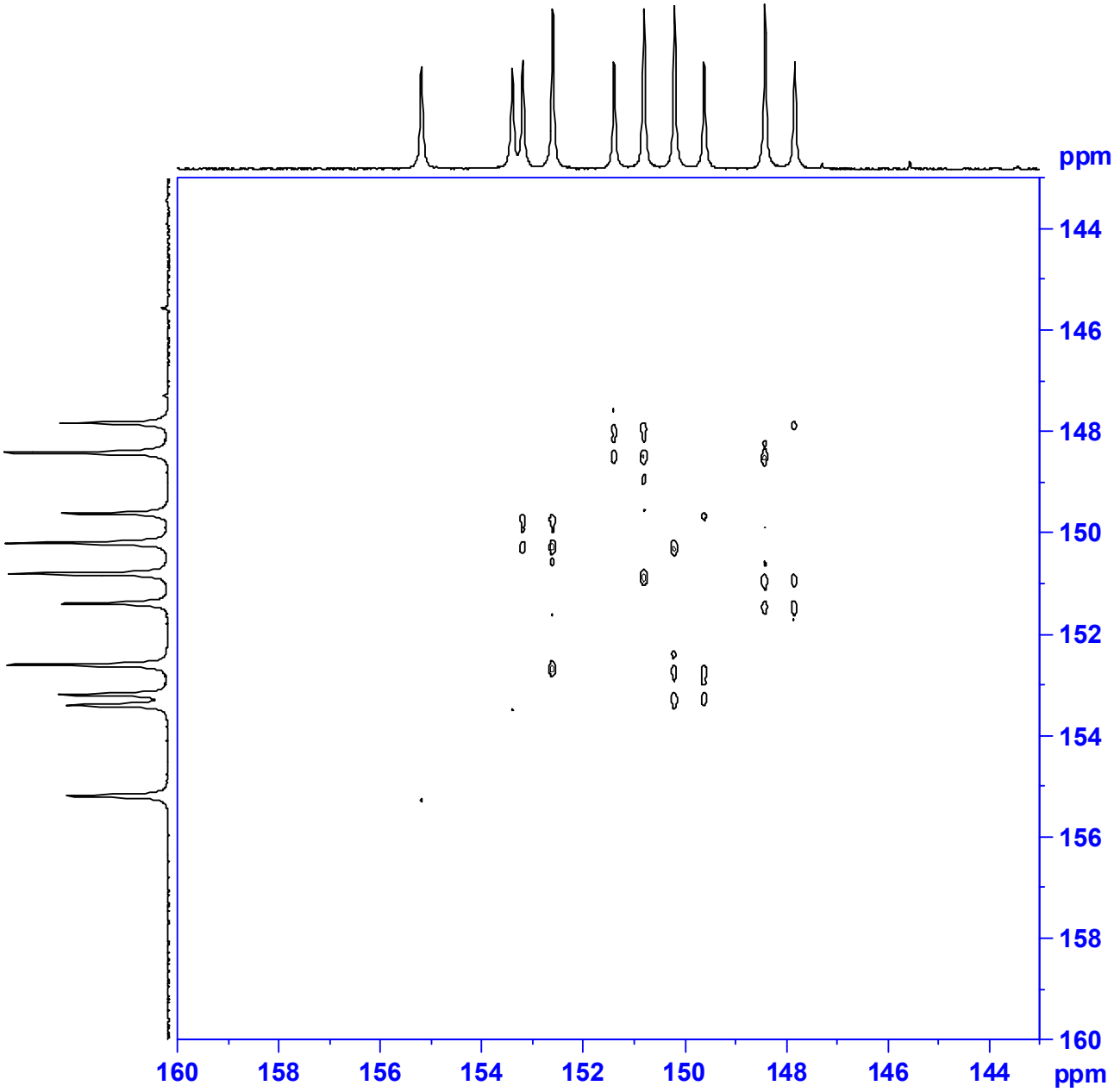
^{31}P-NMR (162 MHz, Dichloromethane-d$_2$): δ = 154.3 (d, $J_{P,\,Rh}$ = 290.1 Hz), 152.0 (dd, $J_{P,\,Rh}$ = 291.3 Hz, $J_{P,\,P}$ = 95 Hz), 149.0 (dd, $J_{P,\,Rh}$ = 288.8 Hz, $J_{P,\,P}$ = 95 Hz) ppm.



{Rh[(a*S*)-**11**]$_2$ + Rh[(a*R*)-**11**]$_2$} : Rh[(a*S*)-**11**][(a*R*)-**11**] = 2 : 9.85.

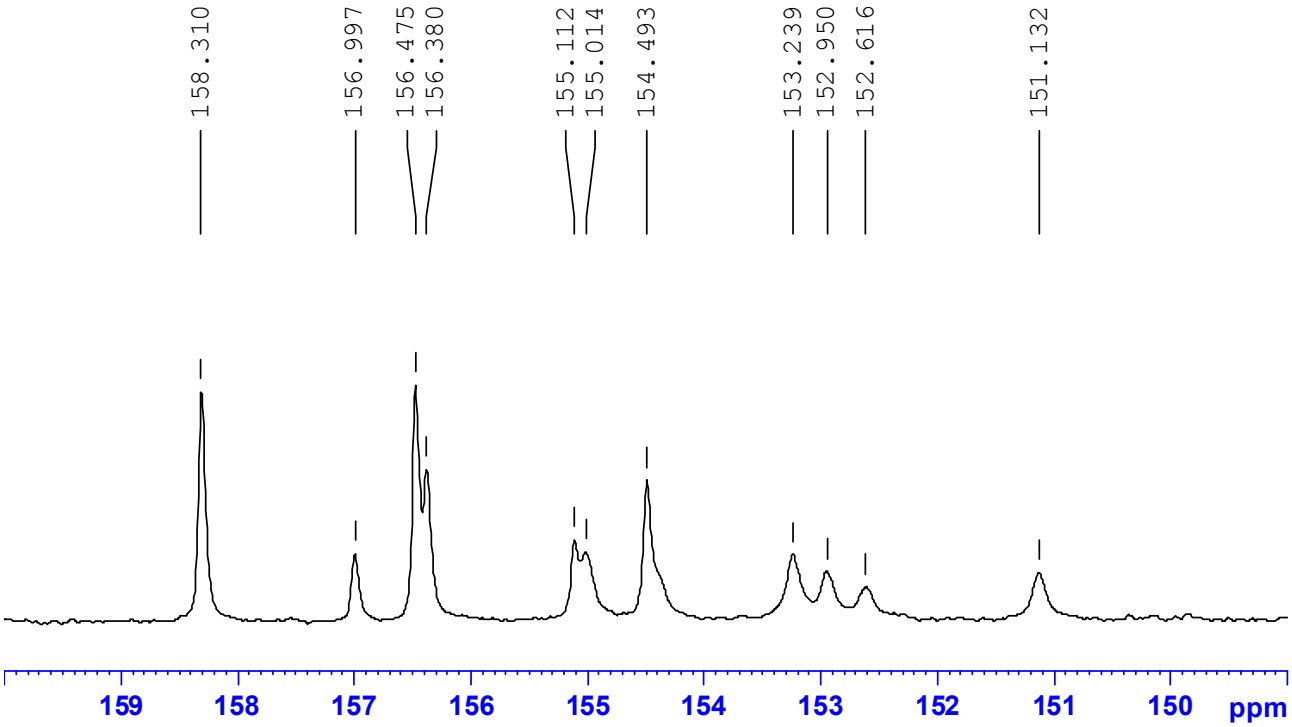
Rh[(a*S*)-**11**]$_2$ + Rh[(a*R*)-**11**]$_2$ = 16.9%; Rh[(a*S*)-**11**][(a*R*)-**11**] = 83.1%.

Figure K: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **11**-P(O)$_2$N (2.0 equiv) in dichloromethane-d$_2$ at 230 K

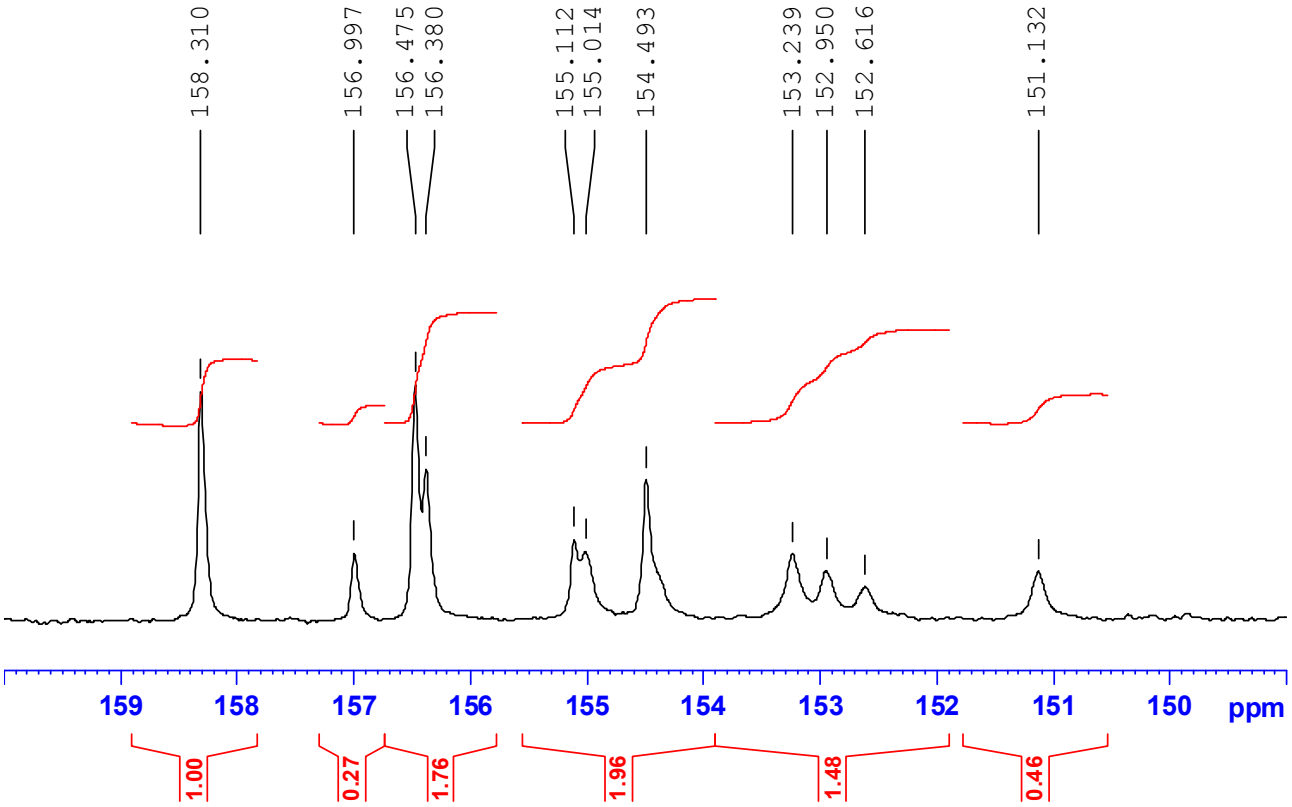


Considering the complex Rh[(a*S*)-**11**][(a*R*)-**11**], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**11**] ⇆ [(a*R*)-**11**] in dichloromethane-d$_2$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**11**][(a*R*)-**11**] 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 ($\Delta\nu$) 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 $\Delta G^{\neq} = RT_c [23 + \ln (T_c / \Delta\nu)] = 12.95$ kcal / mol.[8]

Figure L: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-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[**7**-P(O)$_2$O]$_2$), 155.7 (dd, $J_{P,\,Rh}$ = 305.4 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N]), 153.8 (dd, $J_{P,\,Rh}$ = 287.5 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N]), 152.0 (d, $J_{P,\,Rh}$ = 294.5 Hz, Rh[**11**-P(O)$_2$N]$_2$) ppm.



Rh[**7**-P(O)$_2$O]$_2$ = 28%; Rh[**11**-P(O)$_2$N]$_2$ = 14%; Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N] = 58%.

Figure M: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 375 K

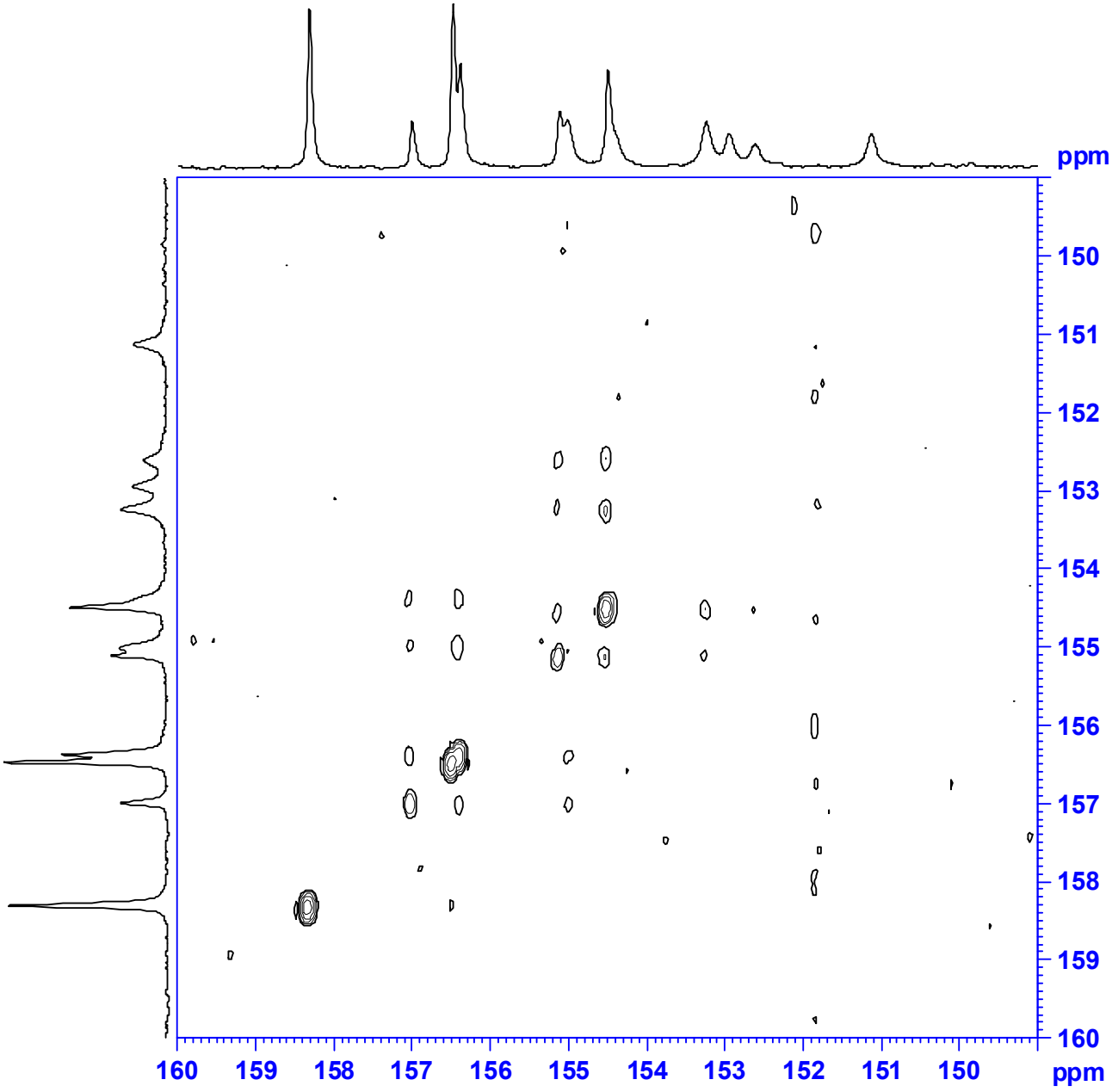
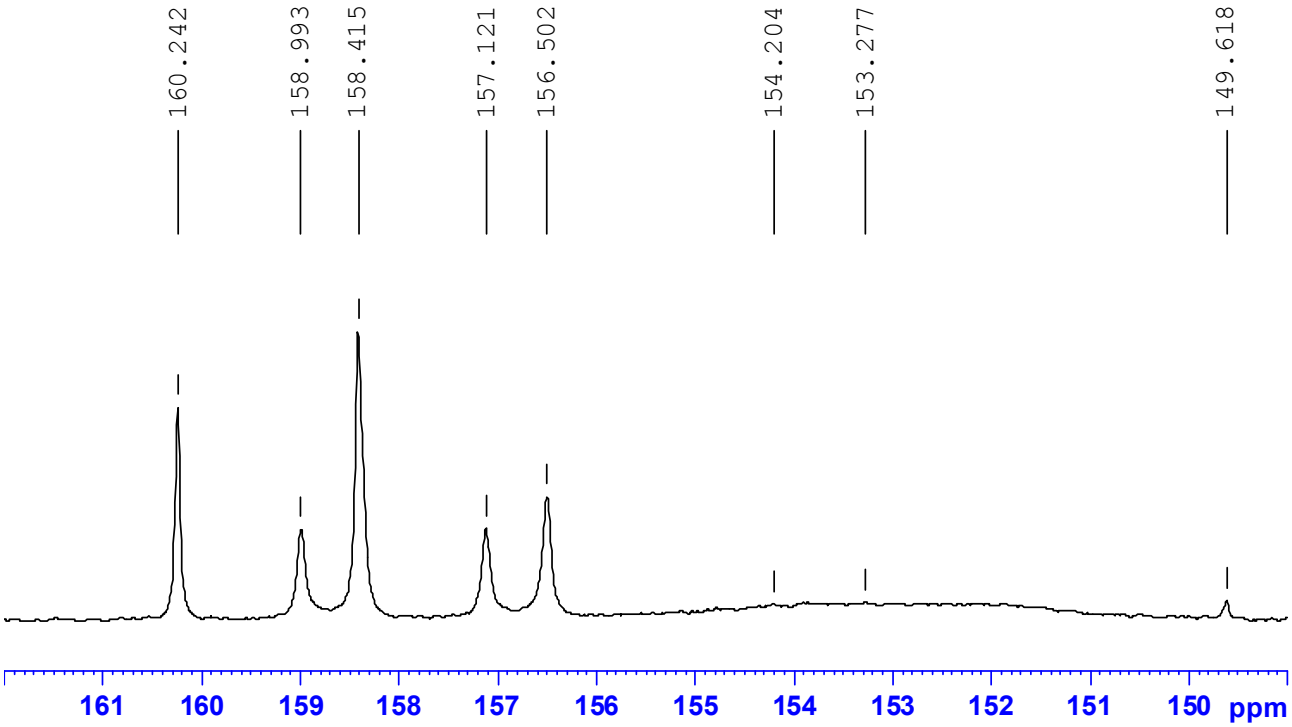
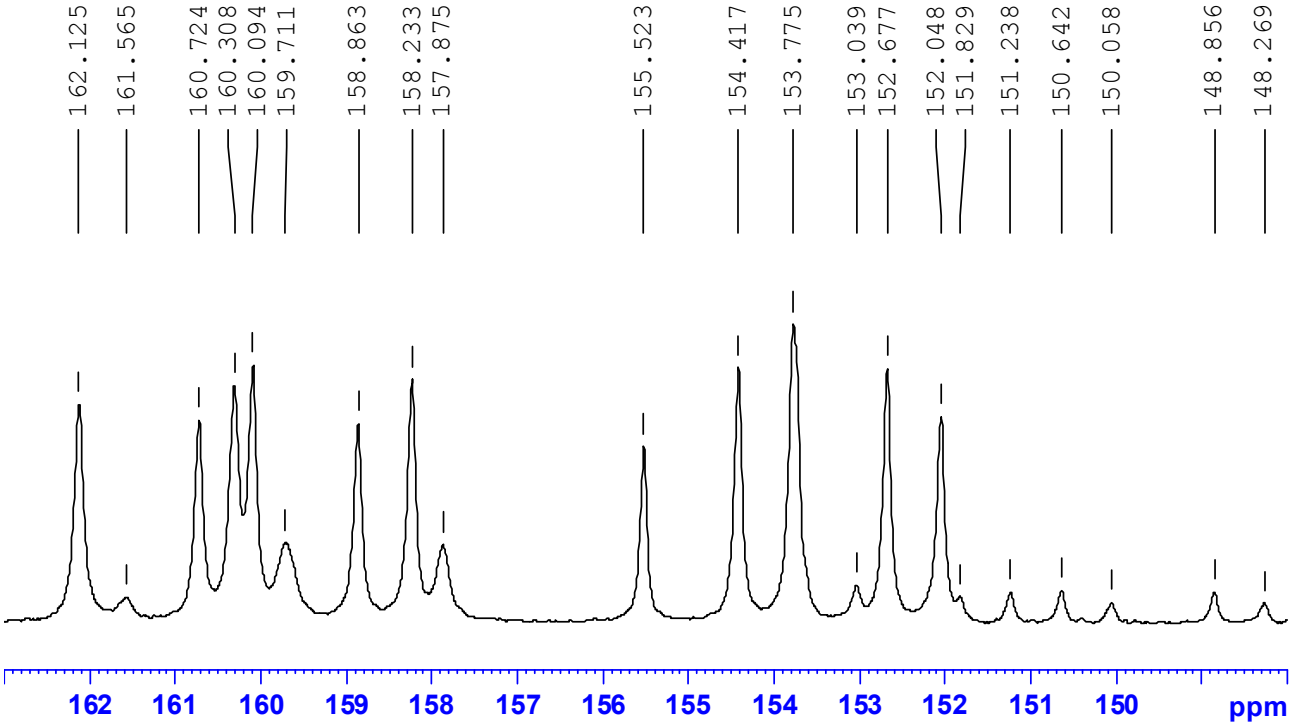


Figure N: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 310 K



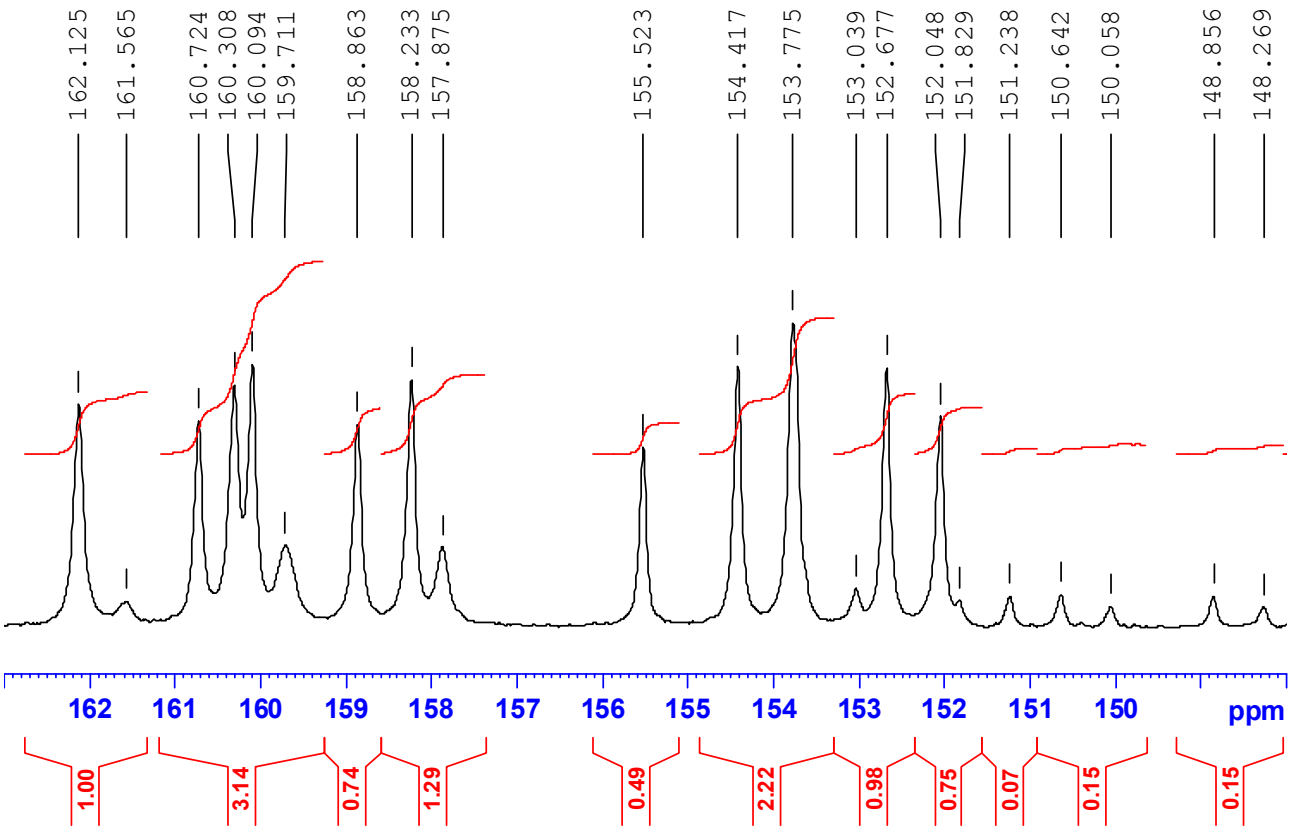
^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 159.3 (d, $J_{P,\,Rh}$ = 296.0 Hz, Rh[**7**-P(O)$_2$O]$_2$), 157.7 (dd, $J_{P,\,Rh}$ = 303.2 Hz, $J_{P,\,P}$ = 100.3 Hz, Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N]), 155.5-150.5 (broad signal, Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N] and Rh[**11**-P(O)$_2$N]$_2$), 149.6 (s, excess ligand) ppm.

Figure O: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-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[**7**-P(O)$_2$O]$_2$), 159.5 (dd, $J_{P,\,Rh}$ = 301.5 Hz, $J_{P,\,P}$ = 102.0 Hz, Rh[**7**-P(O)$_2$O][**11**-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[**11**-P(O)$_2$N]$_2$), 153.2 (dd, $J_{P,\,Rh}$ = 281.9 Hz, $J_{P,\,P}$ = 101.9 Hz, Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N]), 152.4 (dd, $J_{P,\,Rh}$ = 291.7 Hz, $J_{P,\,P}$ = 95.7 Hz, Rh[**11**-P(O)$_2$N]$_2$), 149.4 (dd, $J_{P,\,Rh}$ = 290.0 Hz, $J_{P,\,P}$ = 95.0 Hz, Rh[**11**-P(O)$_2$N]$_2$) ppm.

Figure P: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



Rh[**7**-P(O)$_2$O]$_2$ = 20.9%; Rh[**11**-P(O)$_2$N]$_2$ = 16.4%; Rh[**7**-P(O)$_2$O][**11**-P(O)$_2$N] = 62.7%.

Figure Q: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **11**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K

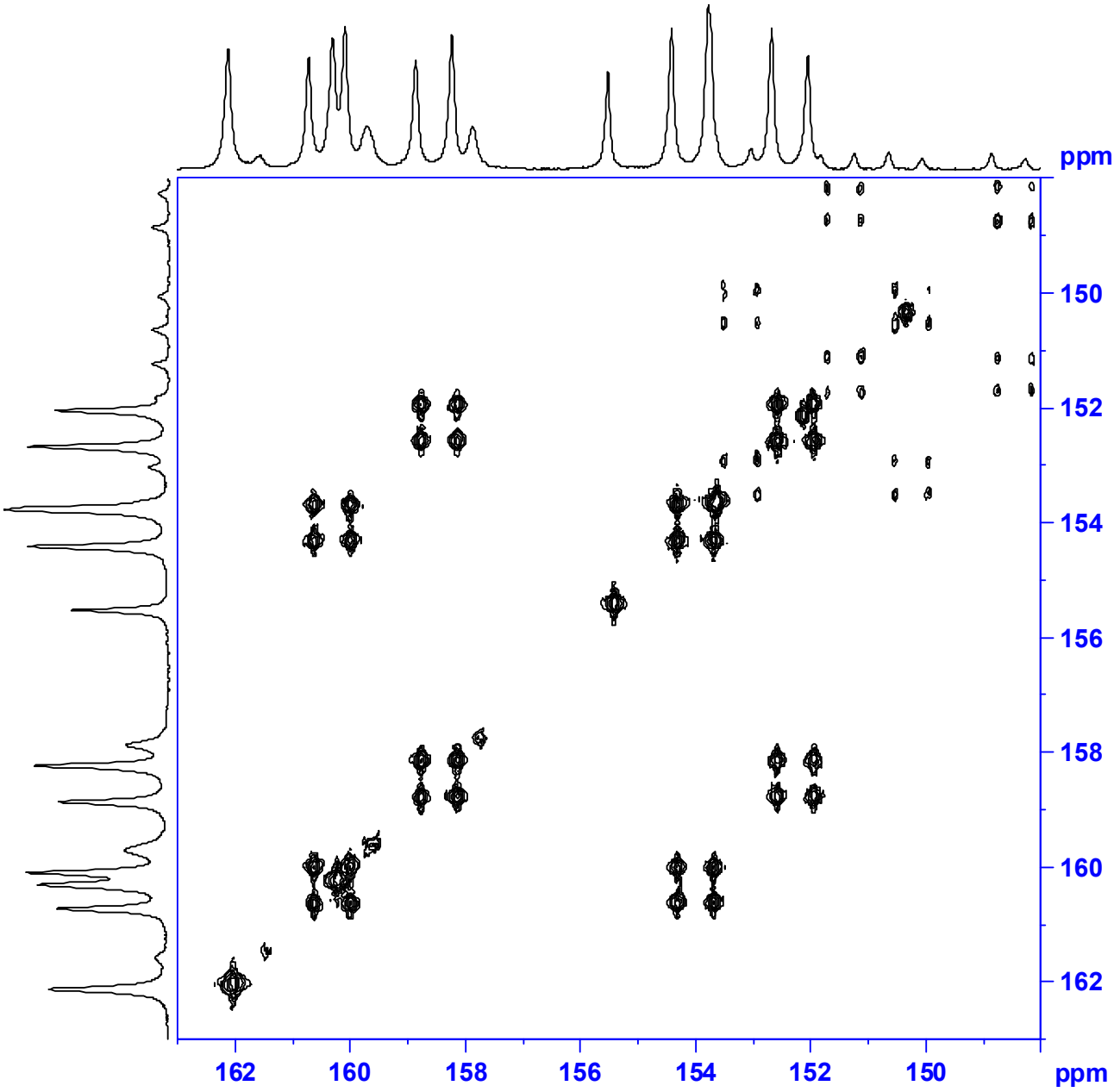
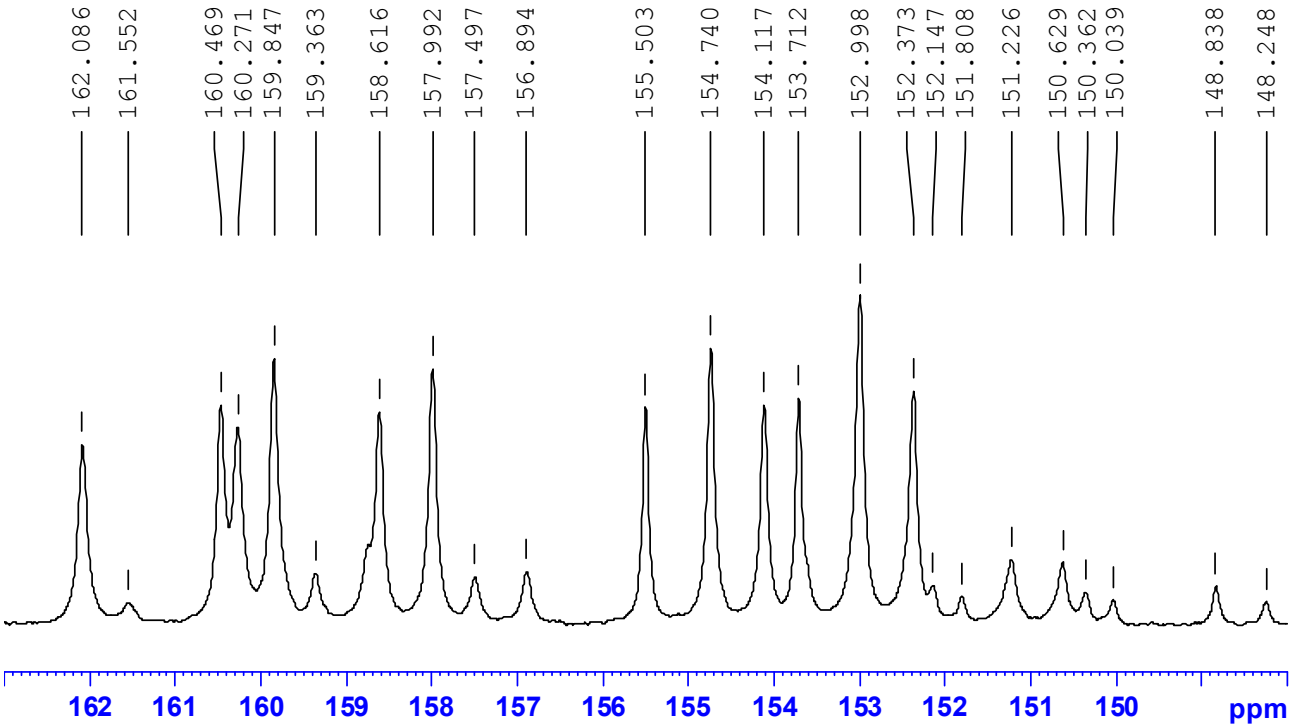
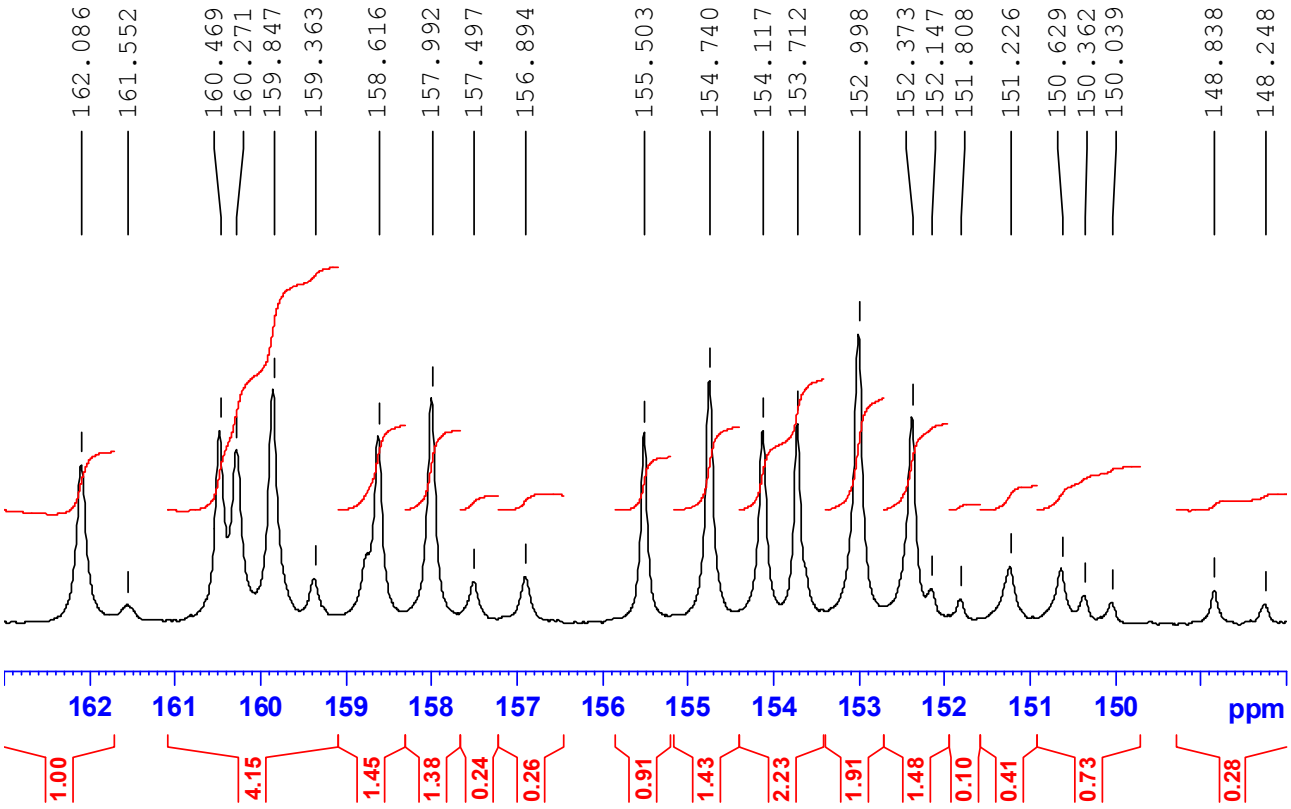


Figure R: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **12**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



^{31}P-NMR (162 MHz, Toluene-d$_8$): δ = 161.2 (d, $J_{P,\,Rh}$ = 294.0 Hz, Rh[**7**-P(O)$_2$O]$_2$), 159.2 (dd, $J_{P,\,Rh}$ = 300.5 Hz, $J_{P,\,P}$ = 101 Hz, Rh[**7**-P(O)$_2$O][**12**-P(O)$_2$N], major), 158.1 (dd, $J_{P,\,Rh}$ = 302.3 Hz, $J_{P,\,P}$ = 97.7 Hz, Rh[**7**-P(O)$_2$O][**12**-P(O)$_2$N], minor), 154.6 (d, $J_{P,\,Rh}$ = 290.1Hz, Rh[**12**-P(O)$_2$N]$_2$), 153.5 (dd, $J_{P,\,Rh}$ = 282.2 Hz, $J_{P,\,P}$ = 101.0 Hz, Rh[**7**-P(O)$_2$O][**12**-P(O)$_2$N], major), 152.4 (dd, $J_{P,\,Rh}$ = 290.1 Hz, $J_{P,\,P}$ = 95.6 Hz, Rh[**12**-P(O)$_2$N]$_2$), 151.8 (dd, $J_{P,\,Rh}$ = 282.5 Hz, $J_{P,\,P}$ = 97.2 Hz, Rh[**7**-P(O)$_2$O][**12**-P(O)$_2$N], minor), 149.3 (dd, $J_{P,\,Rh}$ = 290.1Hz, $J_{P,\,P}$ = 95.6 Hz, Rh[**12**-P(O)$_2$N]$_2$) ppm.

Figure S: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **12**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



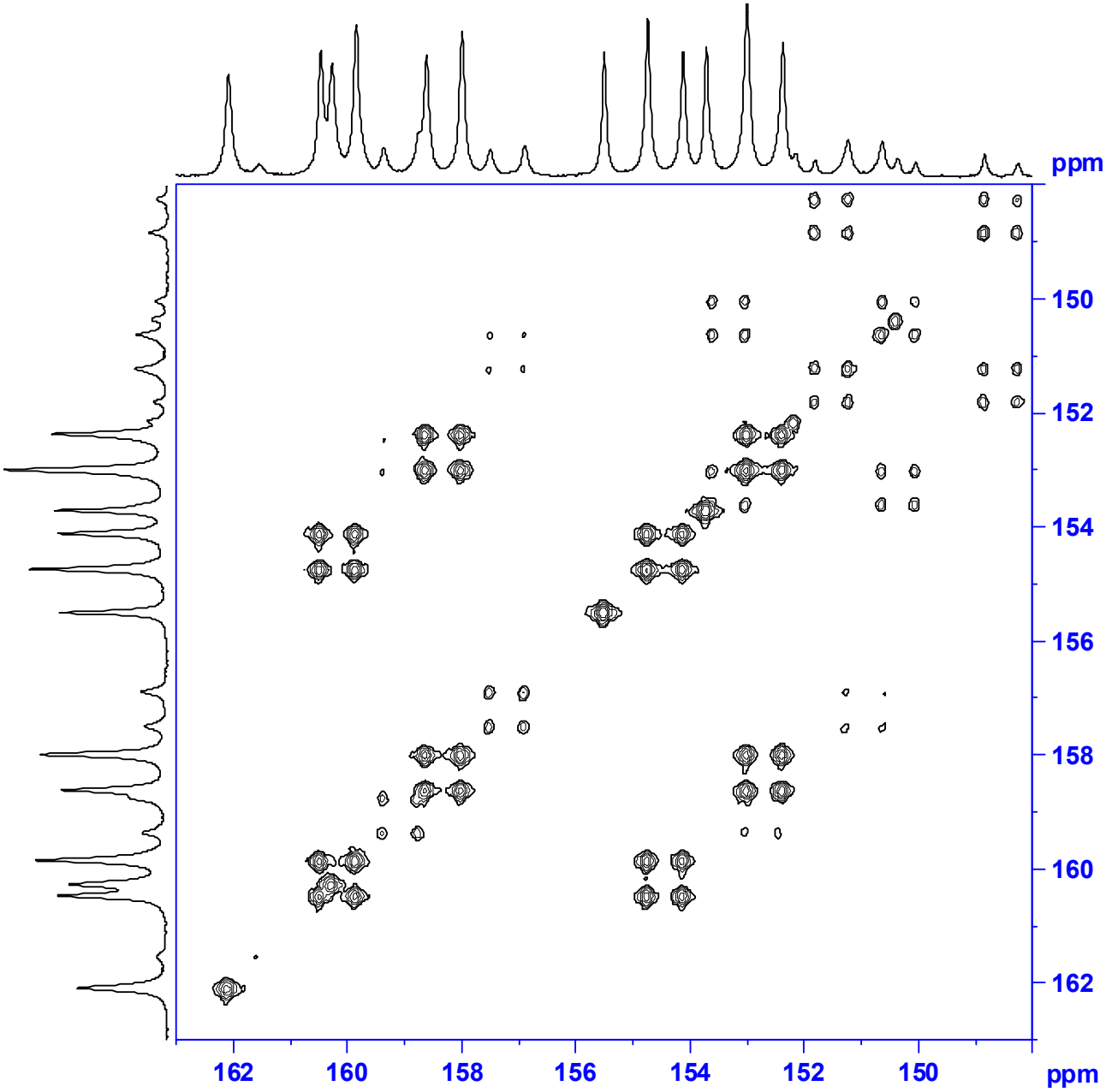
{Rh[(a*S*)-**12**]$_2$ + Rh[(a*R*)-**12**]$_2$ + Rh[(a*S*)-**12**][(a*R*)-**12**]} = 16.4%;

Rh[**7**-P(O)$_2$O]$_2$ = 11.1%;

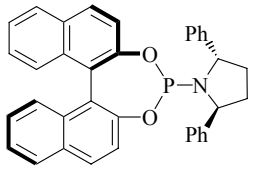
{Rh[(a*S*)-**12**][**7**-P(O)$_2$O] + Rh[(a*R*)-**12**][**7**-P(O)$_2$O]} = 72.5%;

Rh[(a*S*)-**12**][**7**-P(O)$_2$O] : Rh[(a*R*)-**12**][**7**-P(O)$_2$O] = 85:15 or 15:85.

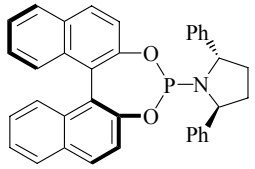
Figure T: ^{31}P-COSY of the complex between Rh(acac)(eth)$_2$ (1.0 equiv), **7**-P(O)$_2$O (1.0 equiv) and **12**-P(O)$_2$N (1.0 equiv) in toluene-d$_8$ at 230 K



Considering the complexes Rh[(a*S*)-**12**][**7**-P(O)$_2$O] and Rh[(a*R*)-**12**][**7**-P(O)$_2$O], a calculation of the free energy of activation for the rotation around the biphenol stereogenic axis [(a*S*)-**12**] ⇆ [(a*R*)-**12**] in toluene-d$_8$ was performed. At 230 K, the chemical shifts of the two P atoms of the Rh[(a*S*)-**12**][**7**-P(O)$_2$O] and Rh[(a*R*)-**12**][**7**-P(O)$_2$O] complexes are = 159.2 ppm (dd, $J_{P,\,Rh}$ = 300.5 Hz, $J_{P,\,P}$ = 101.0 Hz, Rh[**7**-P(O)$_2$O][**12**-P(O)$_2$N], major) and = 158.1 ppm (dd, $J_{P,\,Rh}$ = 302.3 Hz, $J_{P,\,P}$ = 97.7 Hz, Rh[**7**-P(O)$_2$O][**12**-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 $\Delta G^{\neq} = RT_c\,[23 + \ln (T_c / \Delta\nu)] = 14.51$ kcal / mol.[8]



(*R*)-Binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine
26-$P(O)_2N$



(*S*)-Binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine
27-$P(O)_2N$

26-P(O)-N, (*R*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine:[9] 70% yield. ^{31}P-NMR (162 MHz, Toluene-d_8): δ = 153.7 ppm.

27-P(O)-N, (*S*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine:[9] 60% yield. ^{31}P-NMR (162 MHz, Toluene-d_8): δ = 146.5 ppm.

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

Figure U: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **27**-P(O)-N [(*S*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine] (2.0 equiv) in toluene-d$_8$ at 300 K

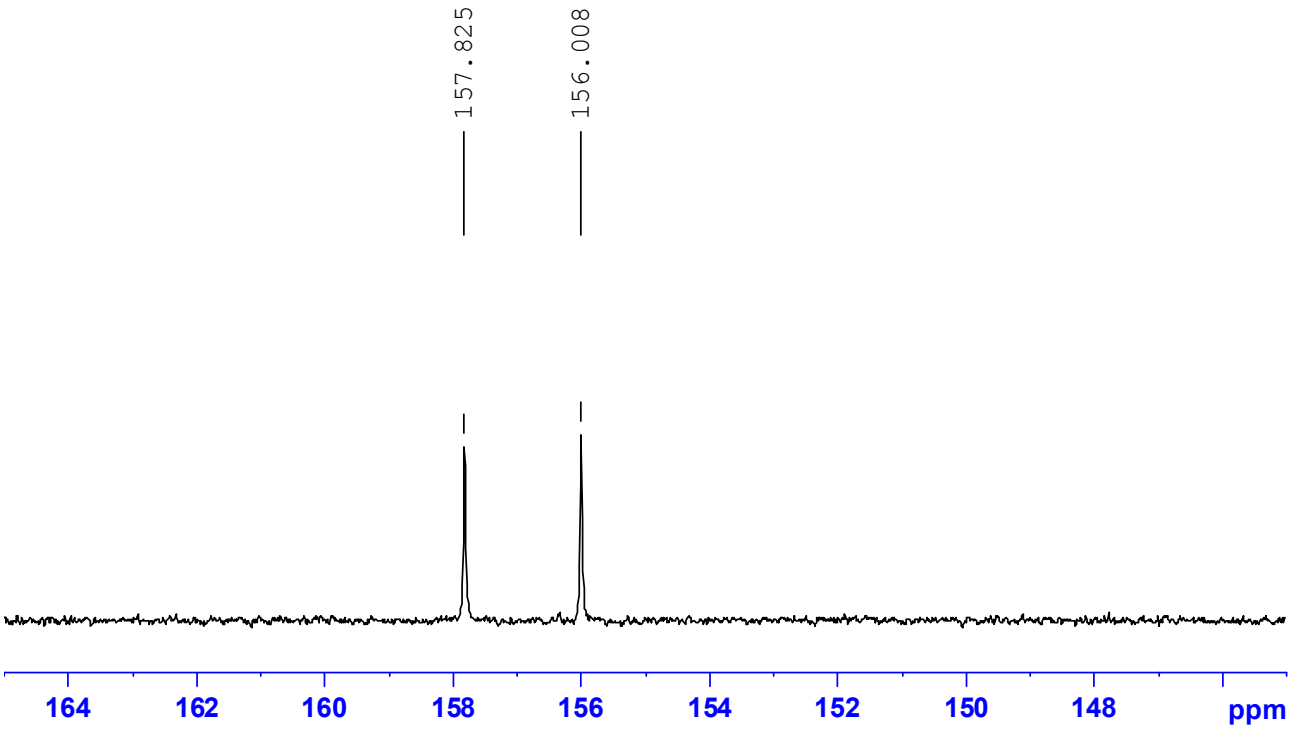
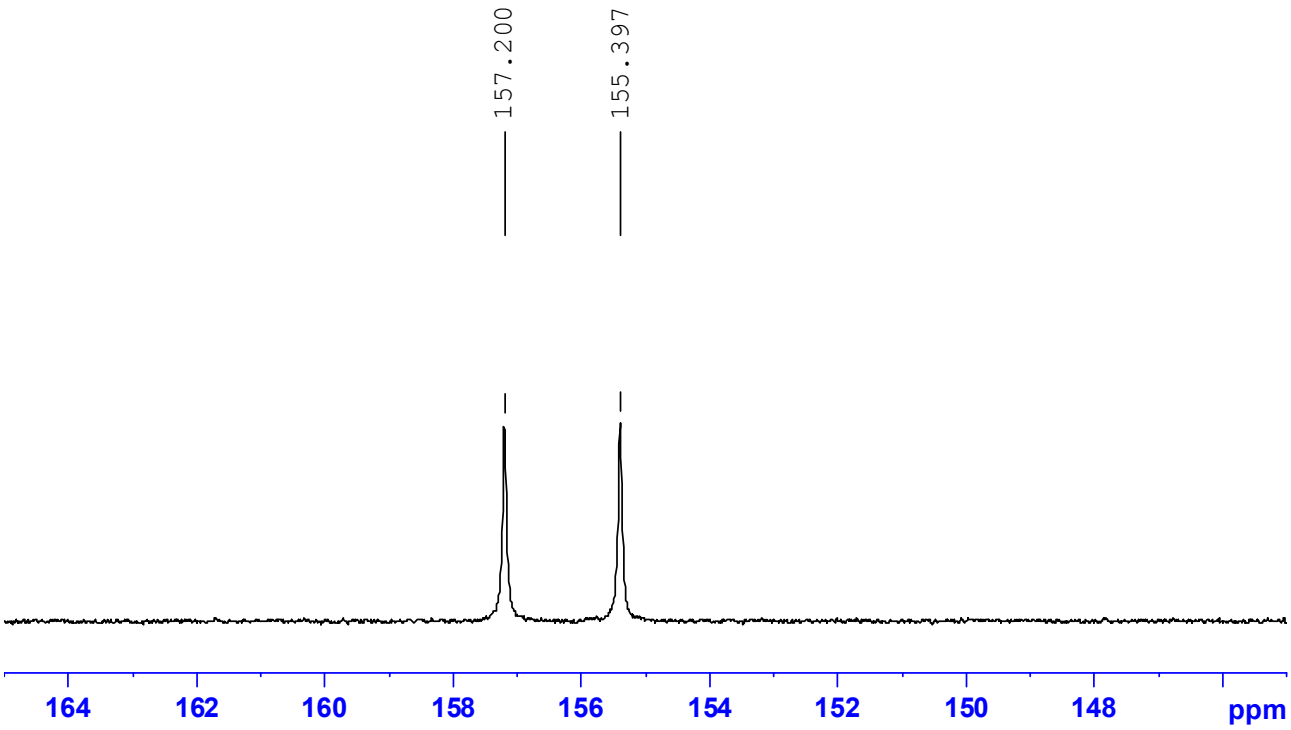
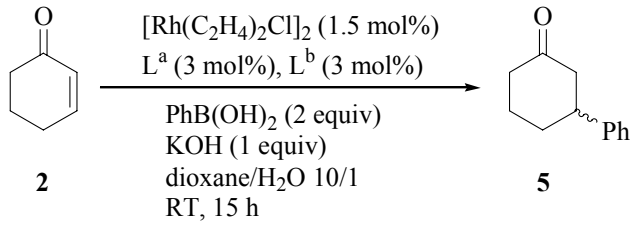


Figure V: ^{31}P-NMR of the complex between Rh(acac)(eth)$_2$ (1.0 equiv) and **27**-P(O)-N [(*S*)-binaphthol / (*S*,*S*)-2,5-diphenylpyrrolidine] (2.0 equiv) in toluene-d$_8$ at 230 K



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 phenyl boronic 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.



Entry	Ligand L^a	Ligand L^b	Yield (%)	ee (%)	Abs. Config.
1	**7**-$P(O)_2O$	**7**-$P(O)_2O$	100	70	*R*
2	**26**-$P(O)_2N$	**26**-$P(O)_2N$	40	40	*R*
3	**27**-$P(O)_2N$	**27**-$P(O)_2N$	50	28	*R*
4	**7**-$P(O)_2O$	**26**-$P(O)_2N$	70	72	*R*
5	**7**-$P(O)_2O$	**27**-$P(O)_2N$	50	46	*R*