Electronic Supplementary Information

Combination of a binaphthol-derived phosphite and a C_1-symmetric phosphinamine generates heteroleptic catalysts in Rh- and Pd-mediated reactions

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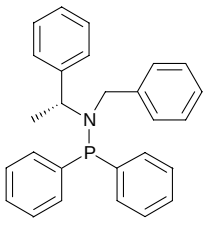
General Remarks. All reactions were carried out in flame-dried glassware with magnetic stirring under nitrogen atmosphere, unless otherwise stated. The solvents for reactions were dried by distillation over the following drying agents and transferred under nitrogen: CH_2Cl_2 (CaH_2), MeOH (CaH_2), THF (Na), benzene (Na), toluene (Na), hexane (Na), Et_3N (CaH_2). Dry Et_2O (over molecular sieves in bottles with crown cap) was purchased from Fluka and stored under nitrogen. The reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F_{254} pre-coated glass plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with a potassium permanganate alkaline solution. Flash column chromatography was performed using either neutral alumina (50-200 μm) or silica gel (60 Å, particle size 40-64 μm), following the procedure by Still and co-workers.[S1] Proton NMR spectra were recorded on a spectrometer operating at 400.13 MHz. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (Me_4Si) employed as the internal standard ($CDCl_3$ δ = 7.26 ppm; CD_2Cl_2 = 5.32 ppm; d_6-DMSO = 2.50 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-doublet, dq = doublet-quartet. ^{13}C-NMR spectra were recorded on a 400 MHz spectrometer operating at 100.56 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ = 77.23 ppm; CD_2Cl_2 = 54.00 ppm; d_6-DMSO = 39.51 ppm). ^{31}P NMR spectra were recorded on a 400 MHz spectrometer operating at 162 MHz, with complete proton decoupling. ^{31}P NMR chemical shifts are reported in ppm (δ) relative to external 85% H_3PO_4 at 0 ppm (positive values downfield). The

coupling constant values are given in Hz. Infrared spectra were recorded on a standard FT/IR spectrometer. Optical rotation values were measured on an automatic polarimeter with a 1 dm cell at the sodium D line (λ = 589 nm). Gas chromatography was performed on a GC instrument equipped with a flame ionization detector, using a chiral capillary column. High resolution mass spectra (HRMS) were performed on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer APEX II & Xmass software (Bruker Daltonics) – 4.7 T Magnet (Magnex) equipped with ESI source.

Materials. Commercially available reagents were used as received. While both enantiomers of 2,2'-dihydroxy-1,1'-binaphthalene (BINOL) are commercially available, (*R*)-3,3'-dimethyl-2,2'-dihydroxy-1,1'-binaphthalene (3,3'-Me-BINOL) was synthesized from BINOL according to known protocols.[S2] The preparation of the corresponding chlorophosphites (BINOL-PCl and 3,3'-Me-BINOL-PCl) was carried out on gram scale according to a literature procedure.[S3] Phosphinamines (*R*,*R*)- and (*S*,*S*)-**4a** were prepared according to literature procedures.[S4] Non-commercially available substrates for catalysis experiments [*N*-(1-phenylvinyl)acetamide and *rac*-1,3-diphenyl-3-acetoxyprop-1-ene] were prepared according to literature procedures.[S5]

General Procedure for the Synthesis of Phosphinamine Ligands 4b-4e. Chlorodiphenylphosphine (3.76 mmol, 1 equiv, 830 mg, 0.7 mL) was added dropwise into a stirred solution of the selected primary or secondary amine (4.70 mmol, 1.25 equiv) and Et_3N (0.68 mL, 4.89 mmol, 1.3 equiv) in benzene (5 mL). The mixture was stirred overnight and then dry hexane (5 mL) was added for favouring the precipitation of the ammonium salt. The obtained suspension was filtered under nitrogen on a short pad of celite. The filtrate was concentrated at rotavapor to give the crude product, which was purified by column chromatography using short pads of neutral alumina as stationary phase, and eluent mixtures containing 2-5% Et_3N (in order to prevent product degradation in the column).
Compounds **4b**,[S6] **4d**[S7] and **4e**[S7] have been previously reported in the literature. Their physical and spectroscopic data are superimposable with those reported in the literature.

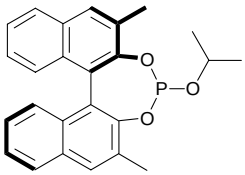


(*R*)-*N*-benzyl-1,1-diphenyl-*N*-(1-phenylethyl)phosphinamine 4c. The product was prepared according to the General Procedure and purified by column chromatography on neutral alumina (eluent: 90 : 10 : 5 hexane/CH_2Cl_2/Et_3N). A colourless oil was obtained, which crystallized on standing at 5 °C eventually giving a white solid (773 mg, 52%). mp 63-64 °C; $[\alpha]_D^{22}$ + 88.6 (*c* 1 in CH_2Cl_2); ν_{max}(film)/cm^{-1} 3051.8, 2974.7, 2925.5, 1240.0, 973.9 and 879.4; ^{1}H-NMR: δ_H (CD_2Cl_2; 400

MHz; Me_4Si) 7.58 (2 H, m), 7.42-7.22 (14 H, m), 7.12 (2 H, m), 6.97 (2 H, dd, *J* 2.1, 7.7), 4.20 (1 H, d, J_{AB} 15.1), 4.15 (1 H, dq, $J_{H,H}$ 7.1, $J_{H,P}$ 18.0), 4.06 (1 H, d, J_{AB} 15.1), 1.71 (3 H, d, *J* 7.1); δ_C (CD_2Cl_2; 100 MHz; Me_4Si) 144.9, 141.3, 141.1, 140.3, 133.8, 133.5, 132.7, 132.5, 129.3, 129.0, 128.9, 128.8, 128.7, 128.5, 128.5, 128.3, 128.3, 127.7, 127.5, 58.0 (d, $J_{C,P}$ 25.4), 54.1 (d, $J_{C,P}$ 9.2), 21.7 (d, $J_{C,P}$ 18.4); δ_P (CD_2Cl_2, 162 MHz; H_3PO_4) 44.8; *m*/*z* (ESI +) 396.18804 ($[M + H]^+$. $C_{27}H_{27}NP$ requires 396.18756).

General Procedure for the Synthesis of the Phosphites. BINOL-PCl or 3,3'-Me-BINOL-PCl (1.43 mmol, 1 equiv) was added to a stirred mixture of the selected alcohol (1.43 mmol, 1 equiv) and Et_3N (4.3 mmol, 3 equiv, 0.6 mL) in THF (10 mL). The obtained mixture was stirred overnight and then filtered through a pad of celite. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography on silica gel.

Compounds **2a**,[S8] **2b**[S9] and **2c**[S10] have been previously reported in the literature. Their physical and spectroscopic data are superimposable with those reported in the literature.



(11b*R*)-4-isopropoxy-2,6-dimethyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 2d. The product was prepared according to the General Procedure and purified by column chromatography on silica gel (eluent: CH_2Cl_2). A white solid was obtained (478 mg, 83%). mp = 65 °C (dec.); $[\alpha]_D^{22}$ -547.6 (*c* 1 in CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3057.6, 3025.8, 2967.0, 2924.5, 1492.6, 1454.1, 1433.8, 1091.5, 1071.3, 1026.0, 914.1 and 883.2. δ_H (CD_2Cl_2; 400 MHz; Me_4Si) 7.92-7.89 (3 H, m), 7.87 (1 H, s), 7.44 (2 H, m), 7.29-7.20 (4 H, m), 4.59 (1 H, m), 2.66 (3 H, d, *J* 0.6), 2.62 (3 H, d, *J* 0.6), 1.38 (3 H, d, *J* 6.1), 1.33 (3 H, d, *J* 6.2); δ_C (CD_2Cl_2; 100 MHz; Me_4Si) 148.8, 147.7, 132.3, 132.1, 131.7, 131.0, 130.4, 130.1, 128.3, 128.2, 127.4, 127.3, 125.9, 125.8, 125.6, 125.5, 124.9, 124.9, 123.4, 79.9 (d, $J_{C,P}$ 14.4), 25.2, 25.0, 18.3, 17.8; δ_P (CD_2Cl_2, 162 MHz; H_3PO_4) 148.2. *m*/*z* (ESI +) 425.12718 ($[M + Na]^+$. $C_{25}H_{23}O_3PNa$ requires 425.12770).

Complexation experiments

General procedure for complexation experiments with [Rh(acac)(C_2H_4)$_2$]. The complexation experiments were run in NMR tubes under nitrogen atmosphere and monitored by ^{1}H and ^{31}P NMR spectroscopy. The typical scale of the experiments was 0.0134 mmol (3.5 mg) of [Rh(acac)(C_2H_4)$_2$] in 0.75 mL of deuterated solvent (0.018 M concentration) and up to 0.0268 mmol of ligand or ligands (0.0134 mmol each). In all of the experiments CD_2Cl_2 was used as solvent.

Experiments with one ligand: CD_2Cl_2 was added to a 1:1 mixture of [Rh(acac)(C_2H_4)$_2$] and the ligand, then ^{1}H and ^{31}P-NMR spectra were recorded. The mono-ligated species [Rh(acac)(C_2H_4)L] was usually dominant at this stage; more ligand was added (always monitoring the experiment by NMR) until the doublet signal of the homocomplex [Rh(L)$_2$(acac)] appeared.

Ligand combinations: CD_2Cl_2 was added to a 1:1:1 mixture of ligand A, ligand B and [Rh(acac)(C_2H_4)$_2$], then ^{1}H and ^{31}P NMR spectra were recorded. It is important to remark that the formation of the heterocomplexes proved kinetically quite slow, and an equilibration time of the order of 1-2 h was necessary for observing the hetero/homocomplexes ratios reported below.

Positional screening of the phosphite/C_1-phosphinamine combinations. [Rh(acac)(C_2H_4)$_2$] was chosen as the rhodium source for the positional screening. The possible phosphite/C_1 phosphinamine combinations form a 4 × 4 matrix which would require 32 experiments to be covered, considering that two diastereoisomeric combinations are to be examined for each couple of ligands. In order to limit the number of complexation experiments, we opted for a positional screening covering one line and one column of the matrix (14 experiments in total): all the possible diastereoisomeric combinations of the phosphinamine ligands with phosphites (*R*)- and (*S*)-**2b** were analyzed first, then the aminophosphine giving the highest hetero/homocomplexes ratio (**4b**) was combined with all of the phosphites.

Table 1. Positional screening of phosphite/C_1 phosphinamine combination (detected percent of heterocomplex is printed in each cell).

Phosphites	**Phosphinamines**				
	(*R*)-**4b**	(*S*)-**4b**	(*S*)-**4c**	(*R*)-**4d**	(*S*)-**4e**
(*S*)-**2a**	**83%**	**> 99%**			
(*R*)-**2b**	**99%**	**96%**	**81%**	**74%**	**70%**
(*S*)-**2b**			**81%**	**81%**	**84%**
(*R*)-**2c**	**94%**	**81%**			
(*R*)-**2d**	**96%**	**> 90%**			

Table 2. ^{31}P-NMR data of the observed phosphite/C_1 phosphinamine heterocomplexes

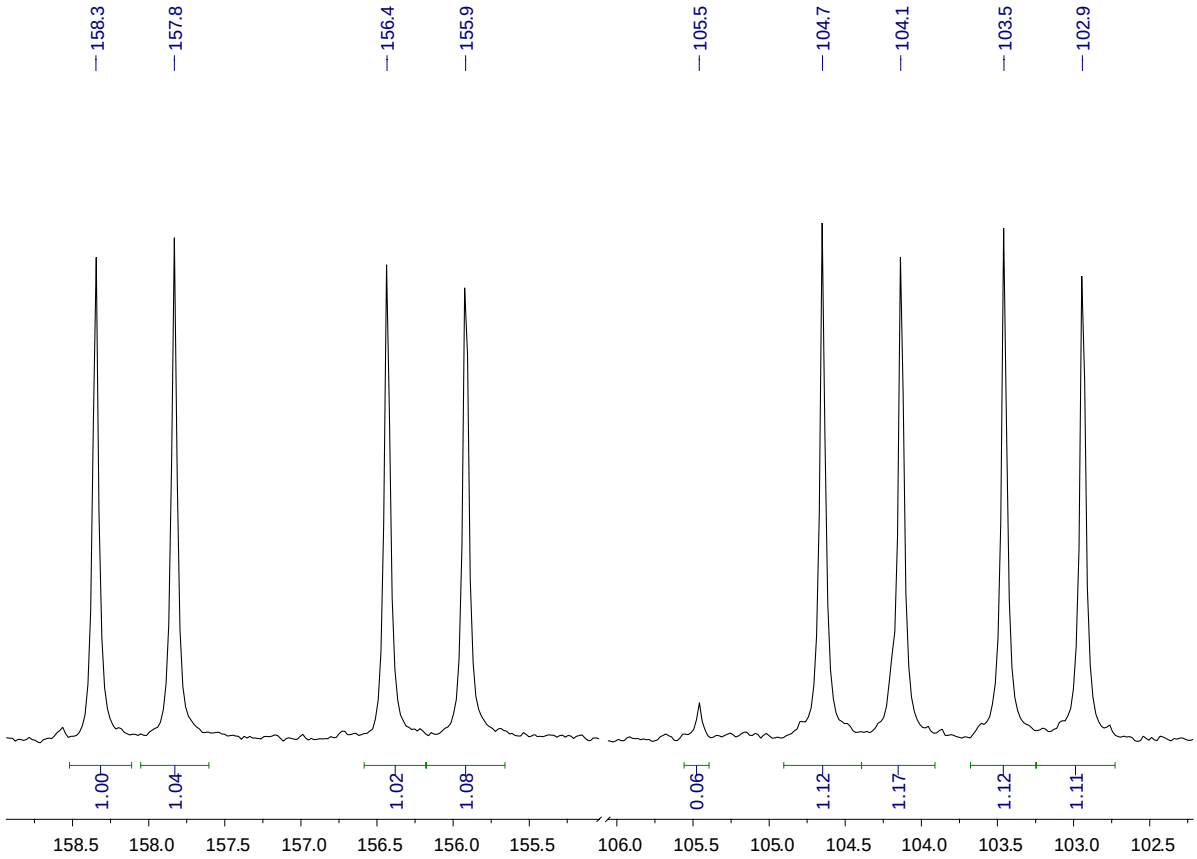
Entry	Heterocomplex	Phosphite		Phosphinamine		
		δ (ppm)	$^1J_{P,Rh}$ (Hz)	δ (ppm)	$^1J_{P,Rh}$ (Hz)	$^2J_{P,P}$ (Hz)
1	(*R*)-**2b**/(*R*)-**4b**	157.1	309.8	103.8	193.2	83.5
2	(*R*)-**2b**/(*S*)-**4b**	155.4	310.1	103.9	192.5	84.7
3	(*R*)-**2b**/(*R*)-**4c**	156.4	310.0	107.5	199.1	80.4
4	(*S*)-**2b**/(*R*)-**4c**	156.1	310.8	104.2	194.6	84.3
5	(*R*)-**2b**/(*R*)-**4d**	157.1	314.6	77.7	183.1	87.3
6	(*S*)-**2b**/(*R*)-**4d**	156.9	314.7	78.4	182.9	87.6
7	(*R*)-**2b**/(*S*)-**4e**	156.9	316.0	76.1	183.0	87.0
8	(*S*)-**2b**/(*S*)-**4e**	157.1	316.1	76.0	182.4	87.1
9	(*S*)-**2a**/(*R*)-**4b**	147.0	324.8	102.8	187.6	86.3
10	(*S*)-**2a**/(*S*)-**4b**	147.4	324.6	103.3	189.6	85.3
11	(*R*)-**2c**/(*R*)-**4b**	157.1	310.2	103.9	193.5	83.6
12	(*R*)-**2c**/(*S*)-**4b**	155.5	309.8	104.1	193.0	85.1
13	(*R*)-**2d**/(*R*)-**4b**	154.7	310.2	106.8	196.8	82.9
14	(*R*)-**2d**/(*S*)-**4b**	152.0	311.4	105.8	195.9	83.6

Table 3. ^{31}P-NMR data of the observed mono- and homocomplexes

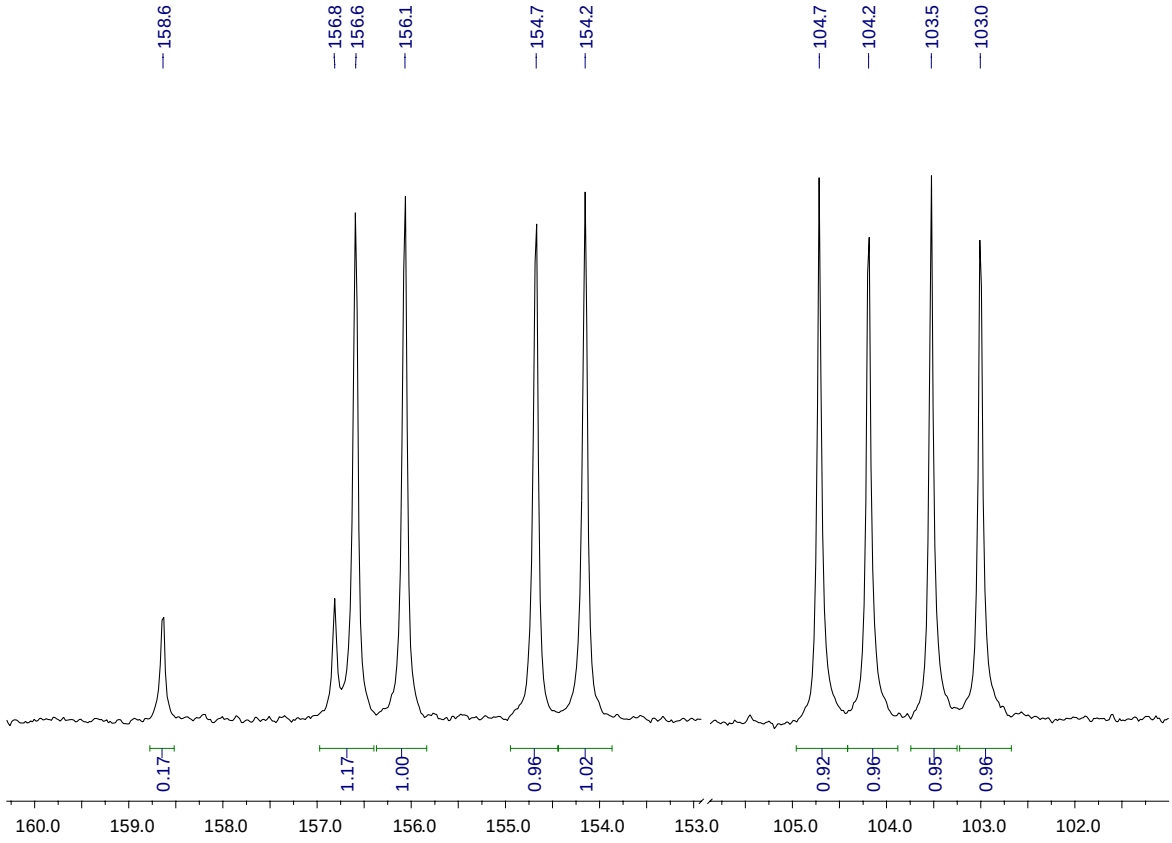
Entry	Ligand	Mono-complex		Homocomplex	
		δ (ppm)	$^1J_{P,Rh}$ (Hz)	δ (ppm)	$^1J_{P,Rh}$ (Hz)
1	(*S*)-**2a**	141.4	303.0	150.4	303.1
2	(*R*)- or (*S*)-**2b**	147.1	292.3	157.6	295.1
3	(*R*)-**2c**	146.6	293.4	158.9	295.8
4	(*R*)-**2d**	141.2	293.8	151.8	299.8
5	(*R*)- or (*S*)-**4b**	101.3	193.0	104.8	203.6
6	(*R*)-**4c**	105.5	193.0	107.2	205.4
7	(*R*)-**4d**	79.2	187.6	83.6	199.1
8	(*S*)-**4e**	77.9	187.2	81.9	198.7

^{31}P-NMR spectra of the heterocombinations

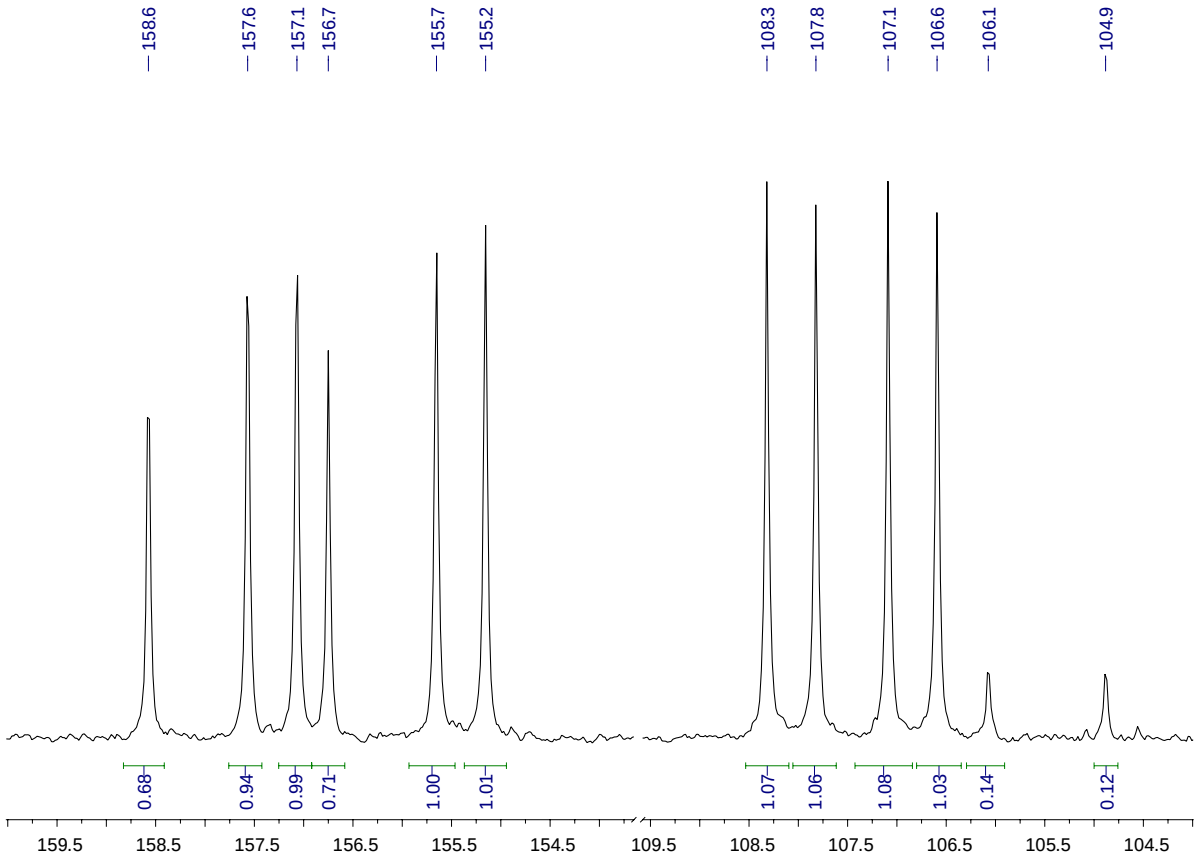
- (*R*)-**2b**/(*R*)-**4b**: Heterocomplex/Homo **4b** = 99 : 1



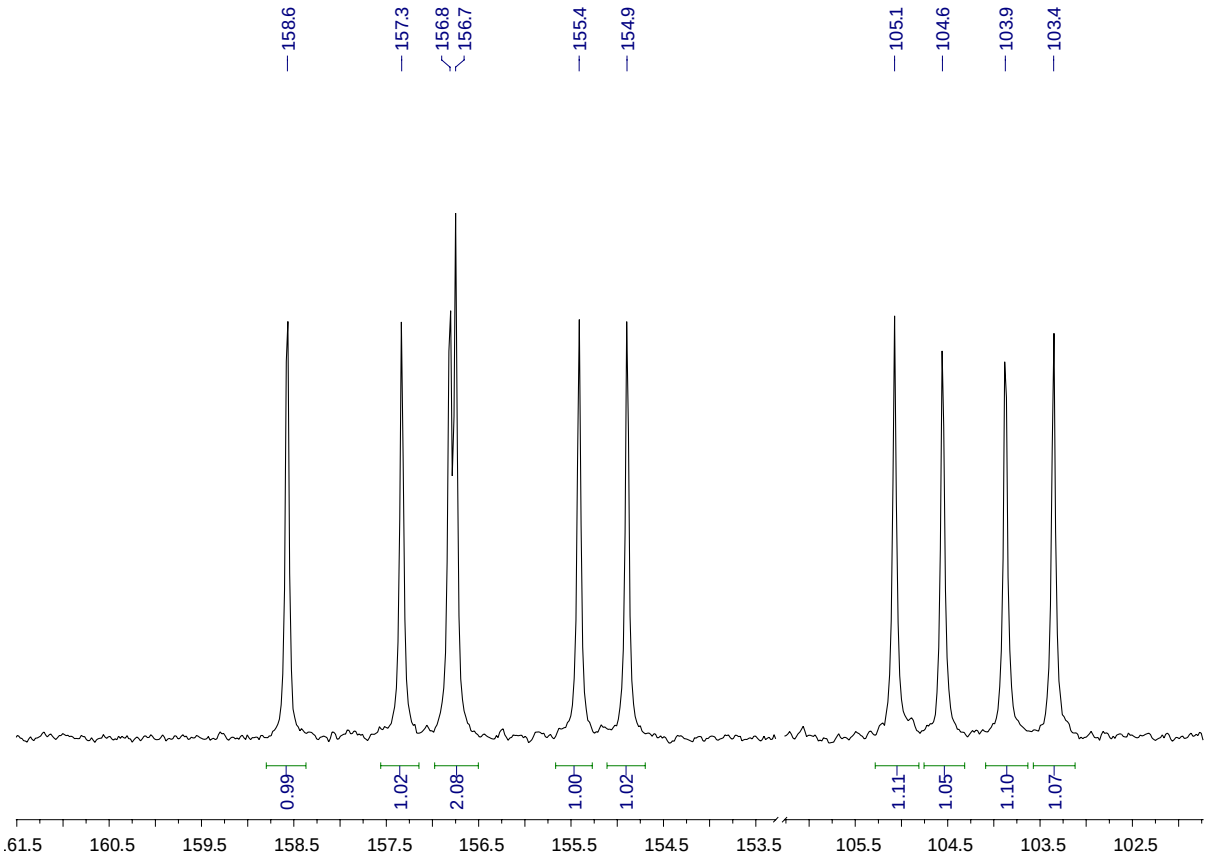
- (*R*)-**2b**/(*S*)-**4b**: Heterocomplex/Homo **2b** = 96 : 4



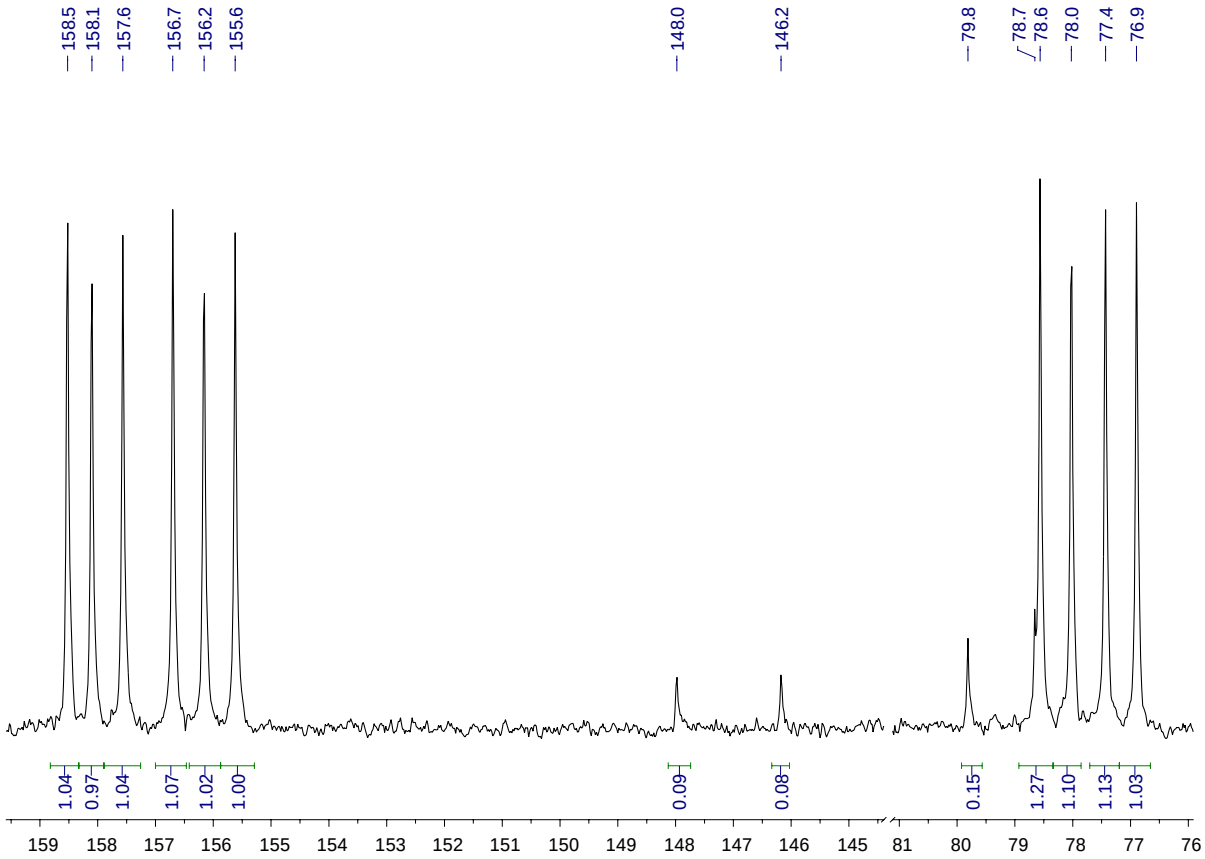
- (*R*)-**2b**/(*R*)-**4c**: Heterocomplex/Homo **2b**/Mono **4c** = 81 : 14 : 5



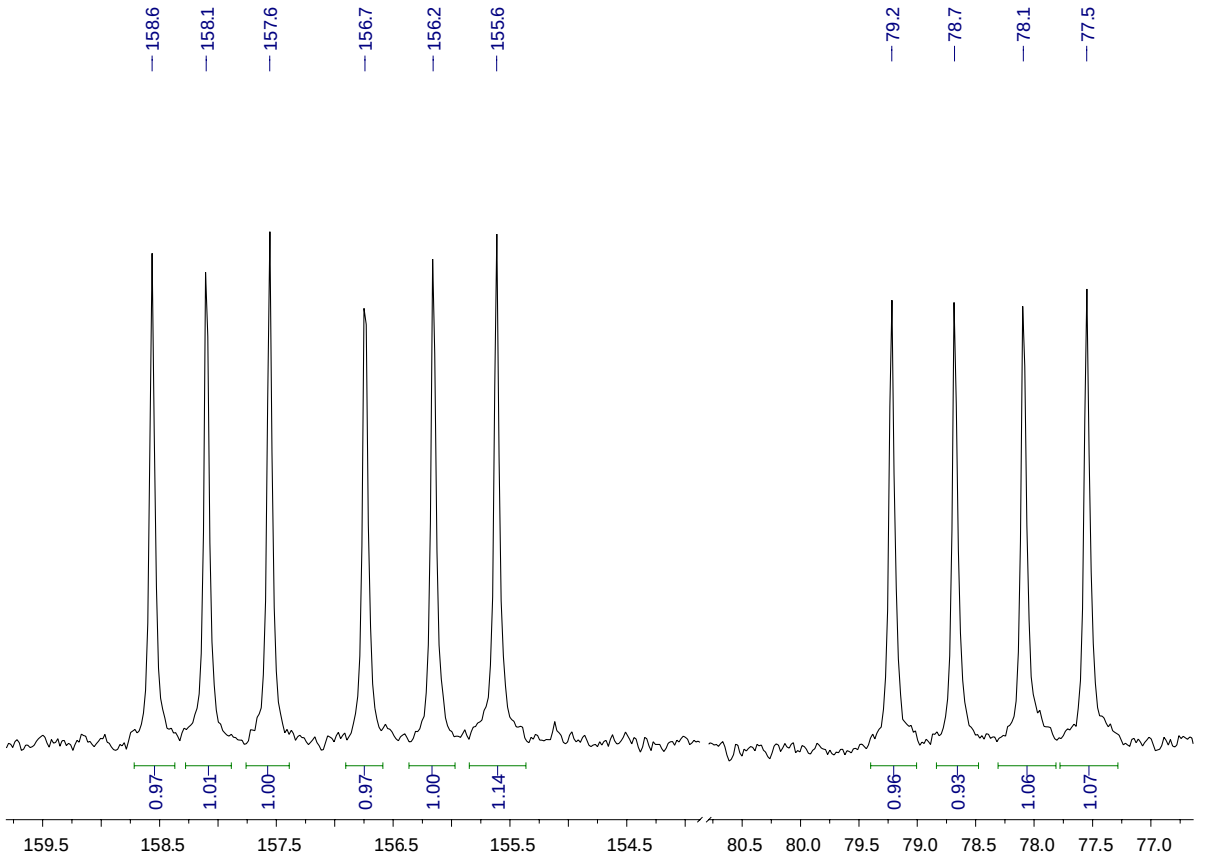
- (*S*)-**2b**/(*R*)-**4c**: Heterocomplex/Homo **2b**/ = 81 : 19



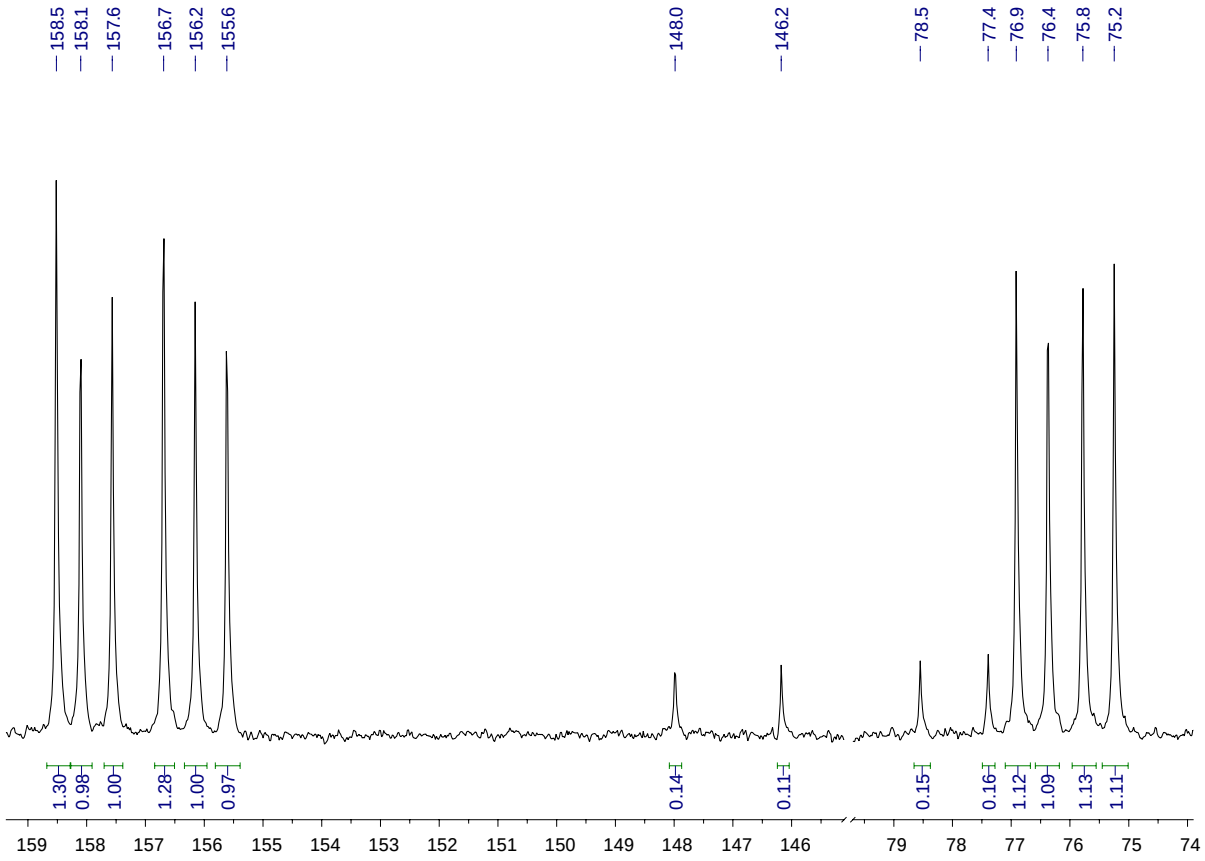
- (*R*)-**2b**/(*R*)-**4d**: Heterocomplex/Homo **2b**/Mono **2b**/Mono **4d** = 74 : 18 : 3 :5



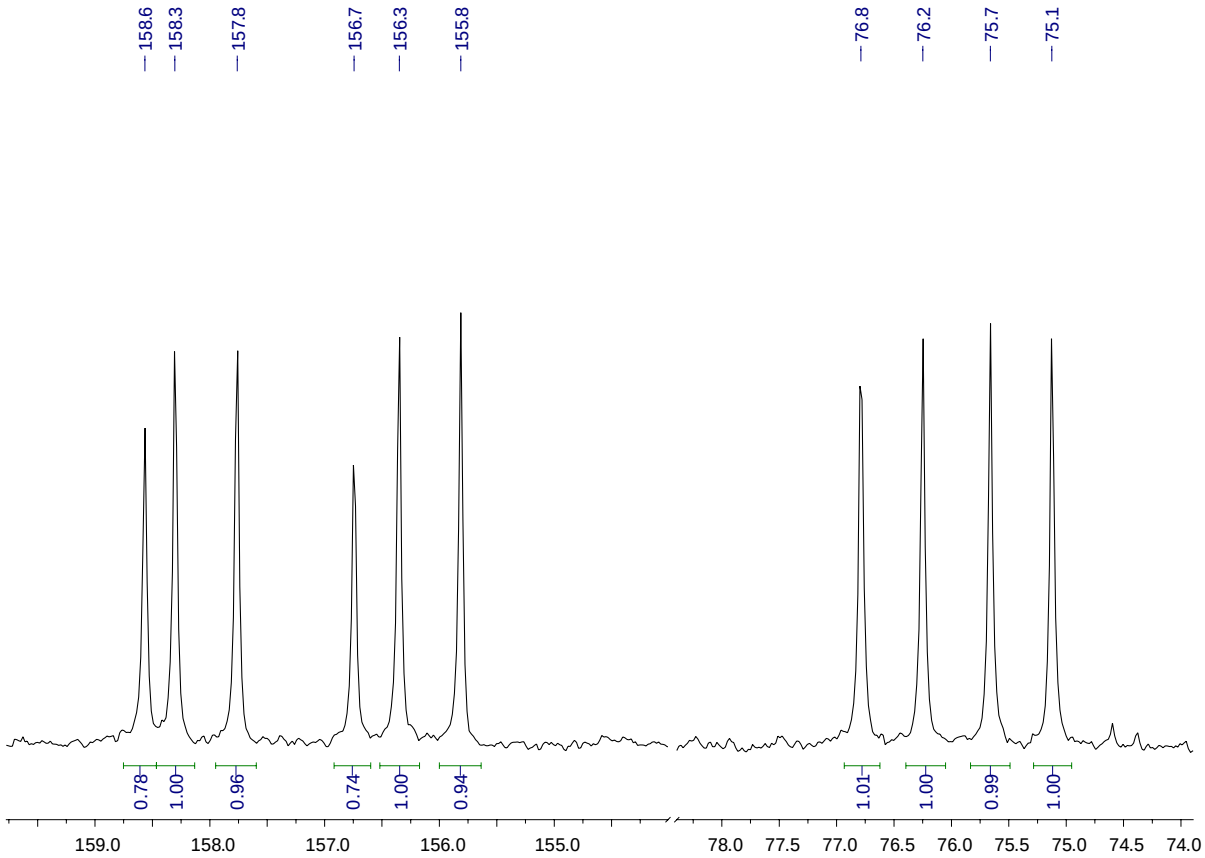
- (*S*)-**2b**/(*R*)-**4d**: Heterocomplex/Homo **4d** = 81 : 19



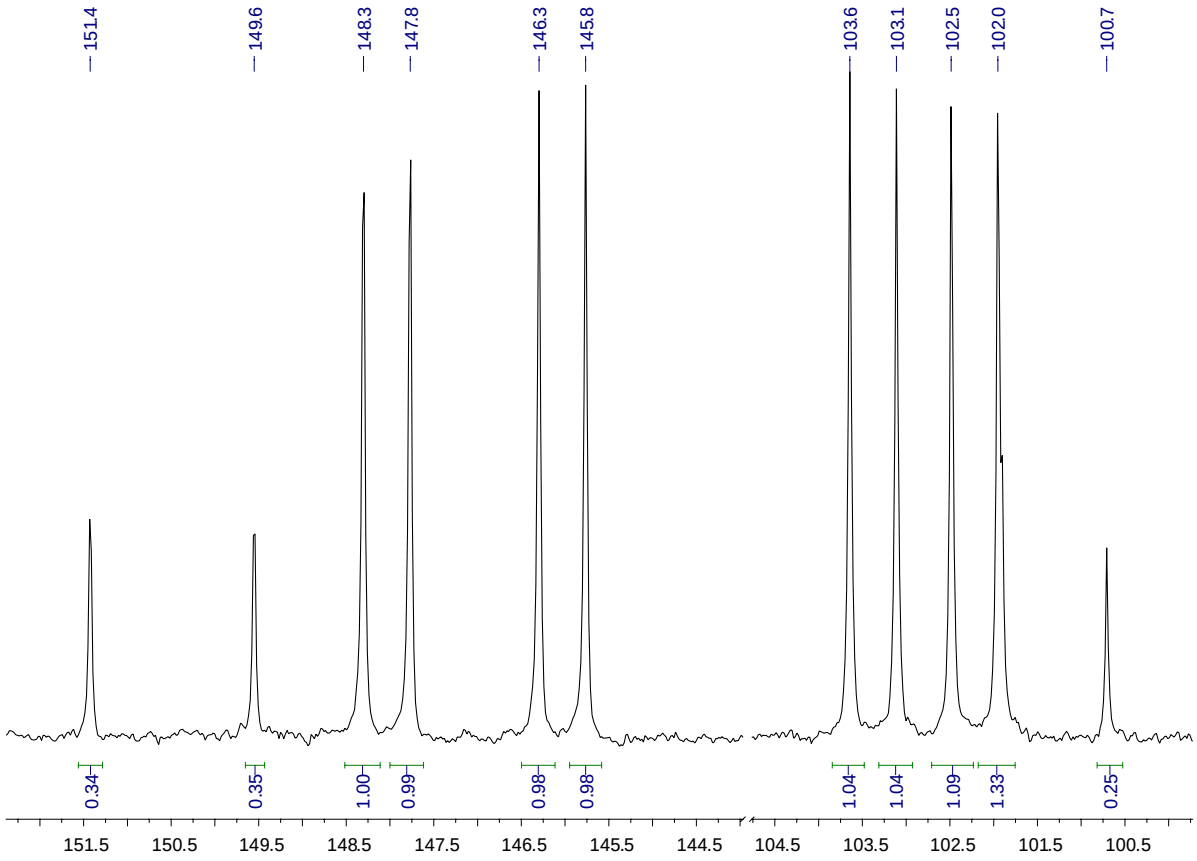
- (*R*)-**2b**/(*S*)-**4e**: Heterocomplex/Homo **2b**/Mono **2b**/Mono **4e** = 70 : 21 : 4 :5



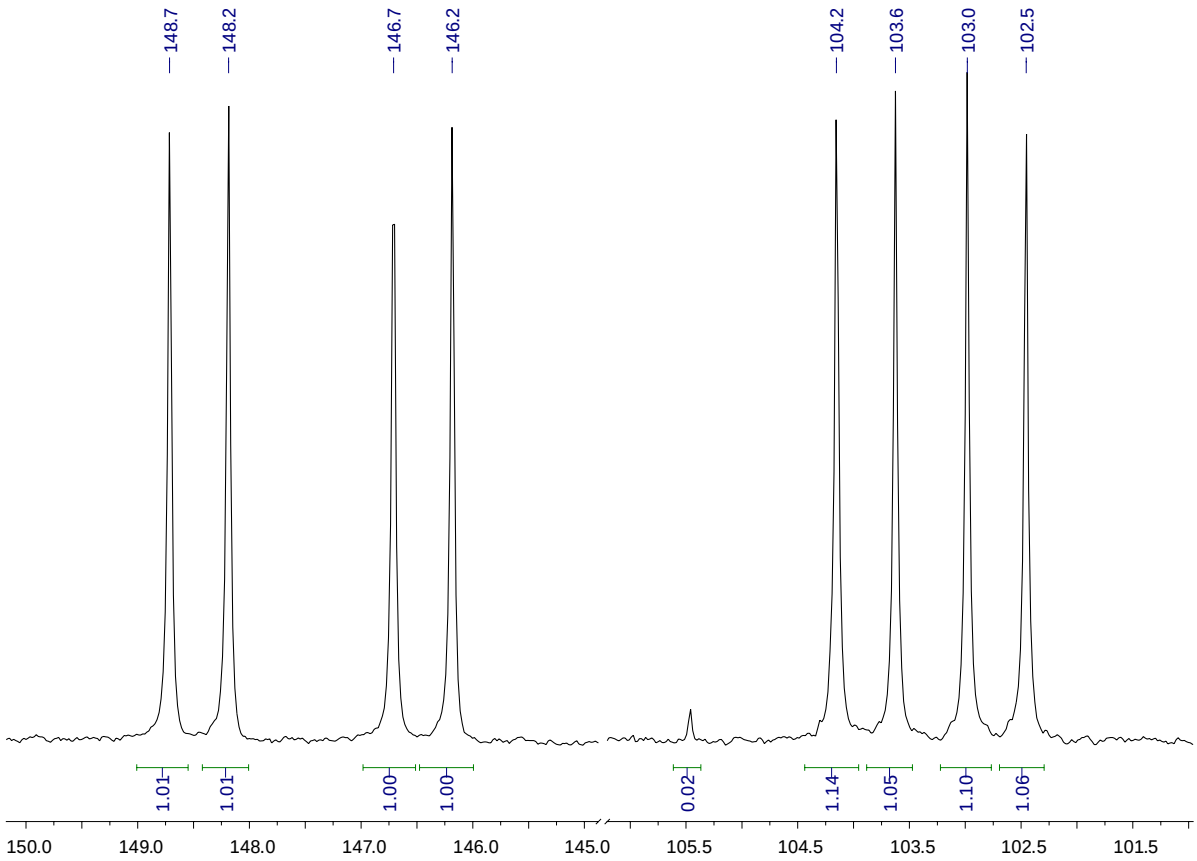
- (*S*)-**2b**/(*S*)-**4e**: Heterocomplex/Homo **2b** = 84 : 16



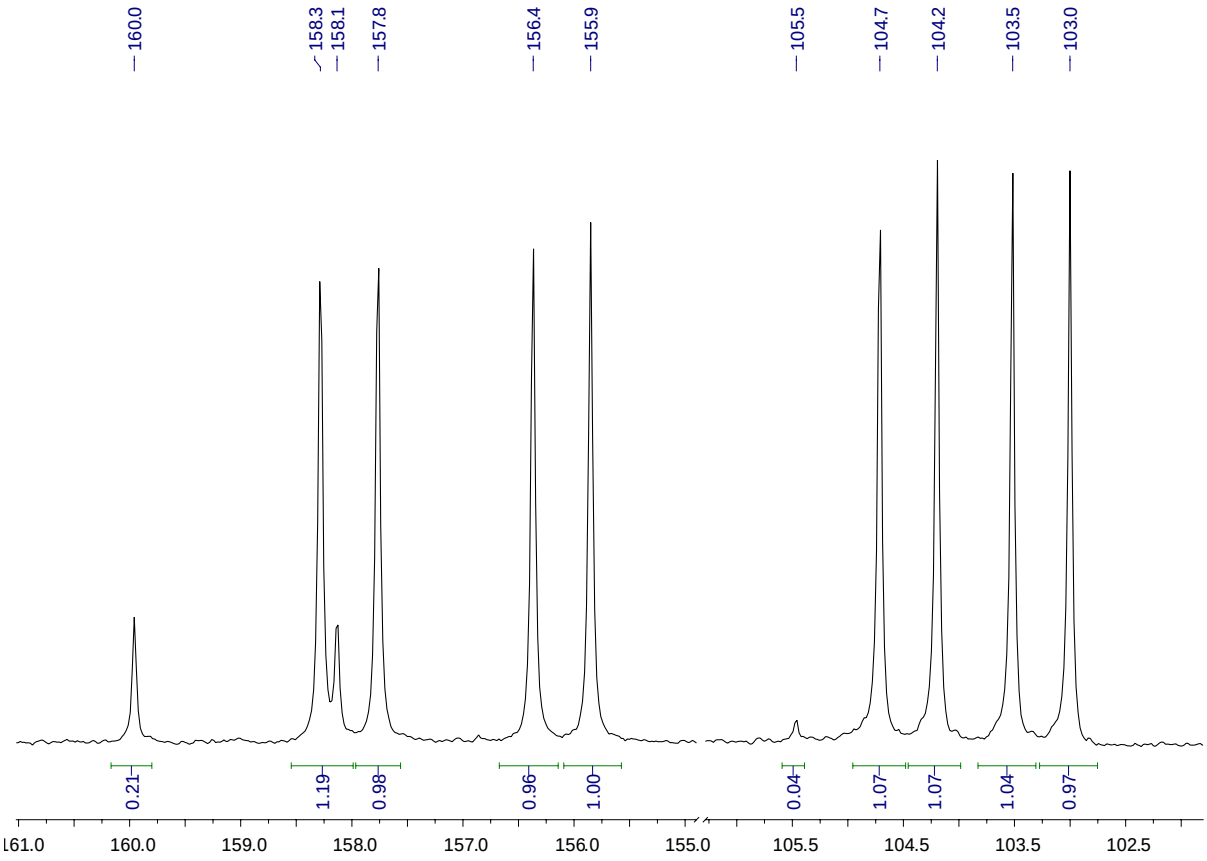
- (*S*)-**2a**/(*R*)-**4b**: Heterocomplex/Homo **2a**/Mono **4b** = 83 : 7 : 10



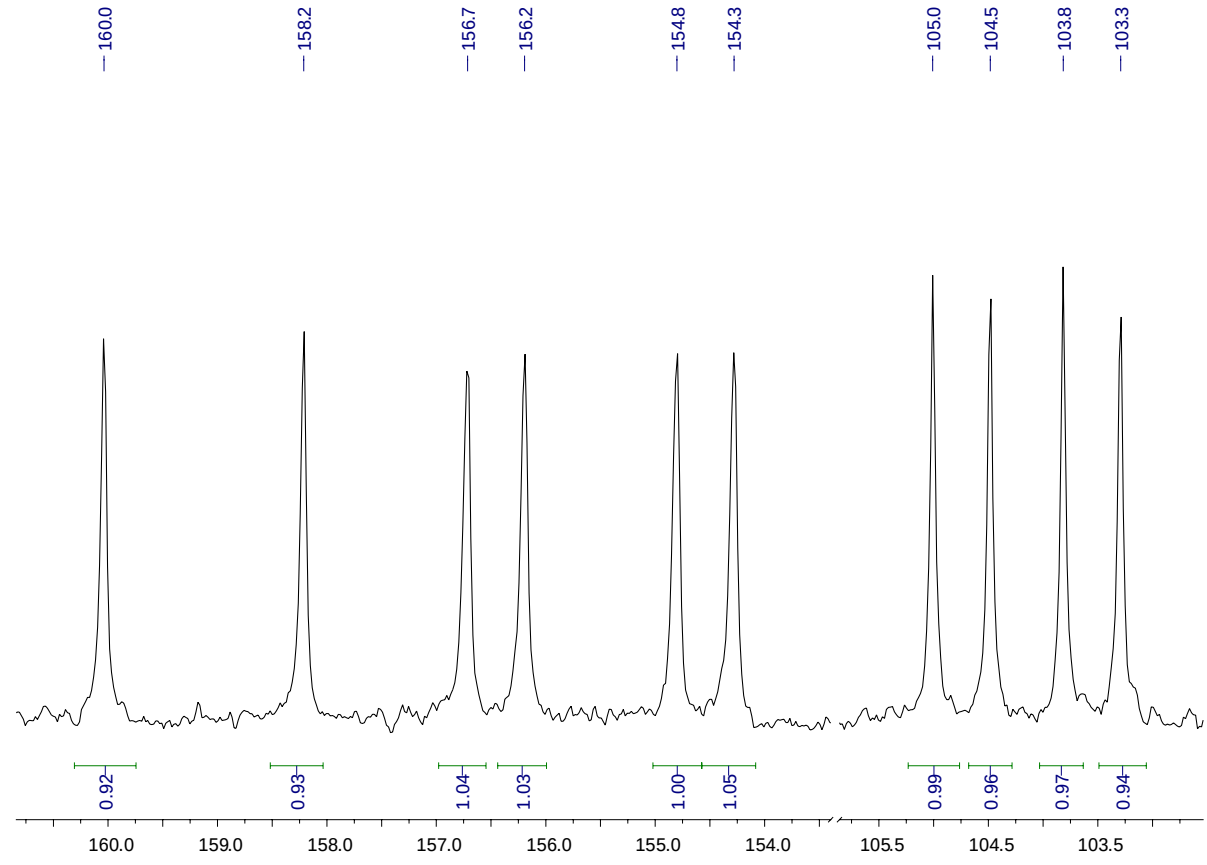
- (*S*)-**2a**/(*S*)-**4b**: Heterocomplex/Homo **4b** > 99 : 1



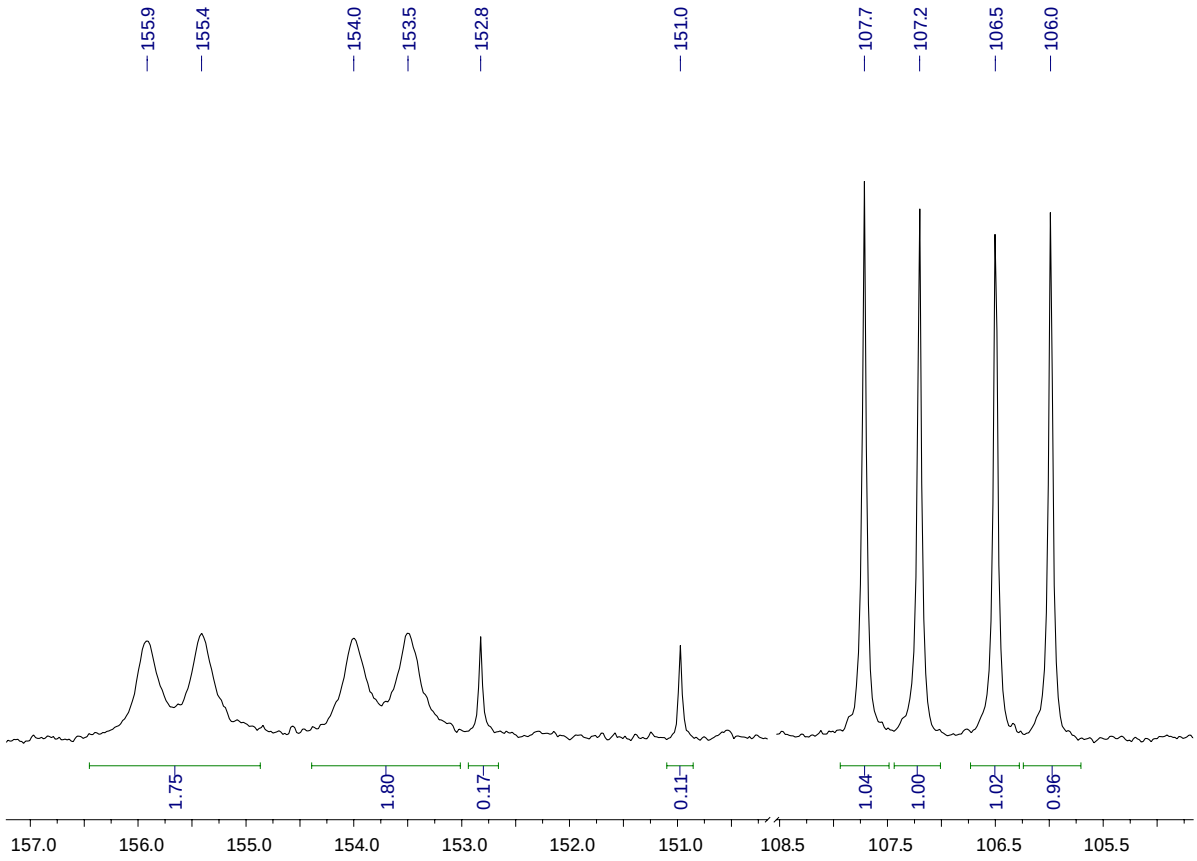
- (*R*)-**2c**/(*R*)-**4b**: Heterocomplex/Homo **2c**/Homo **4b** = 94 : 5 :1



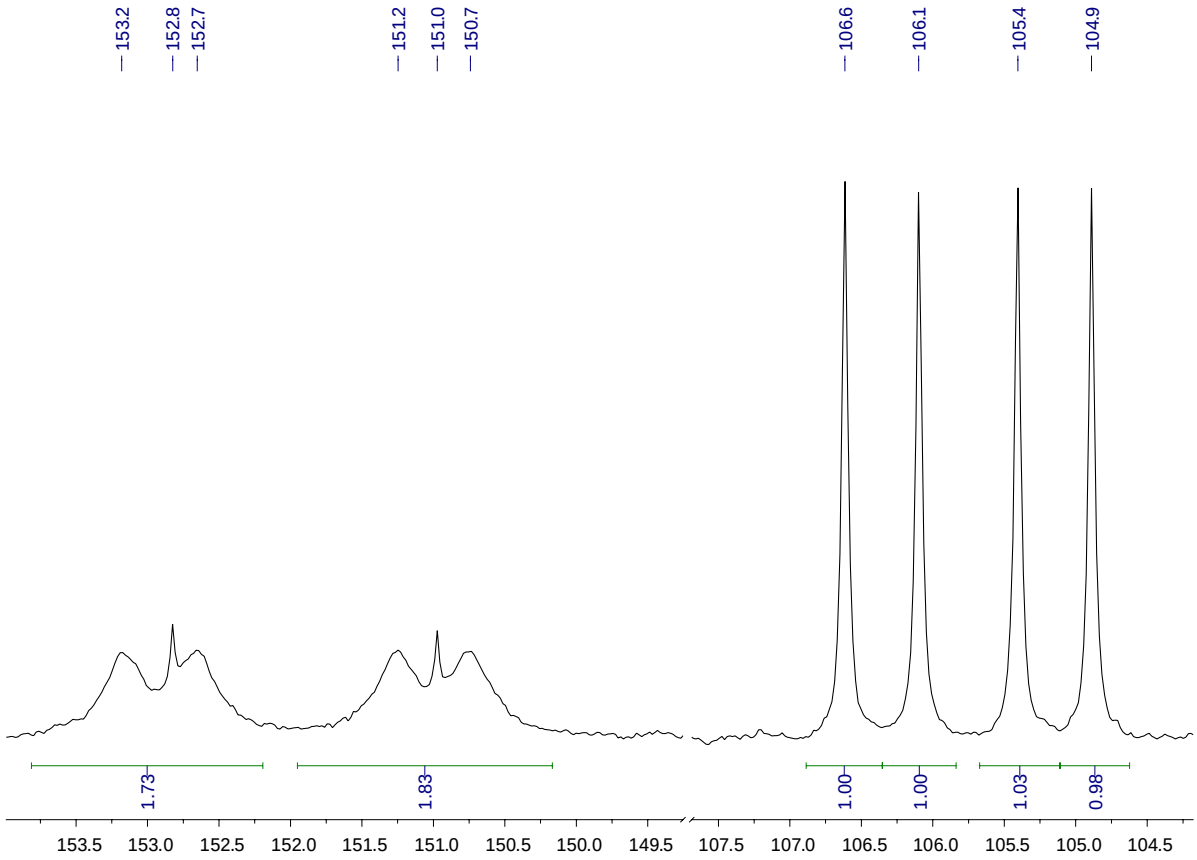
- (*R*)-**2c**/(*S*)-**4b**: Heterocomplex/Homo **2c** = 81 : 19



- (*R*)-**2d**/(*R*)-**4b**: Heterocomplex/Homo **2d** = 96 : 4



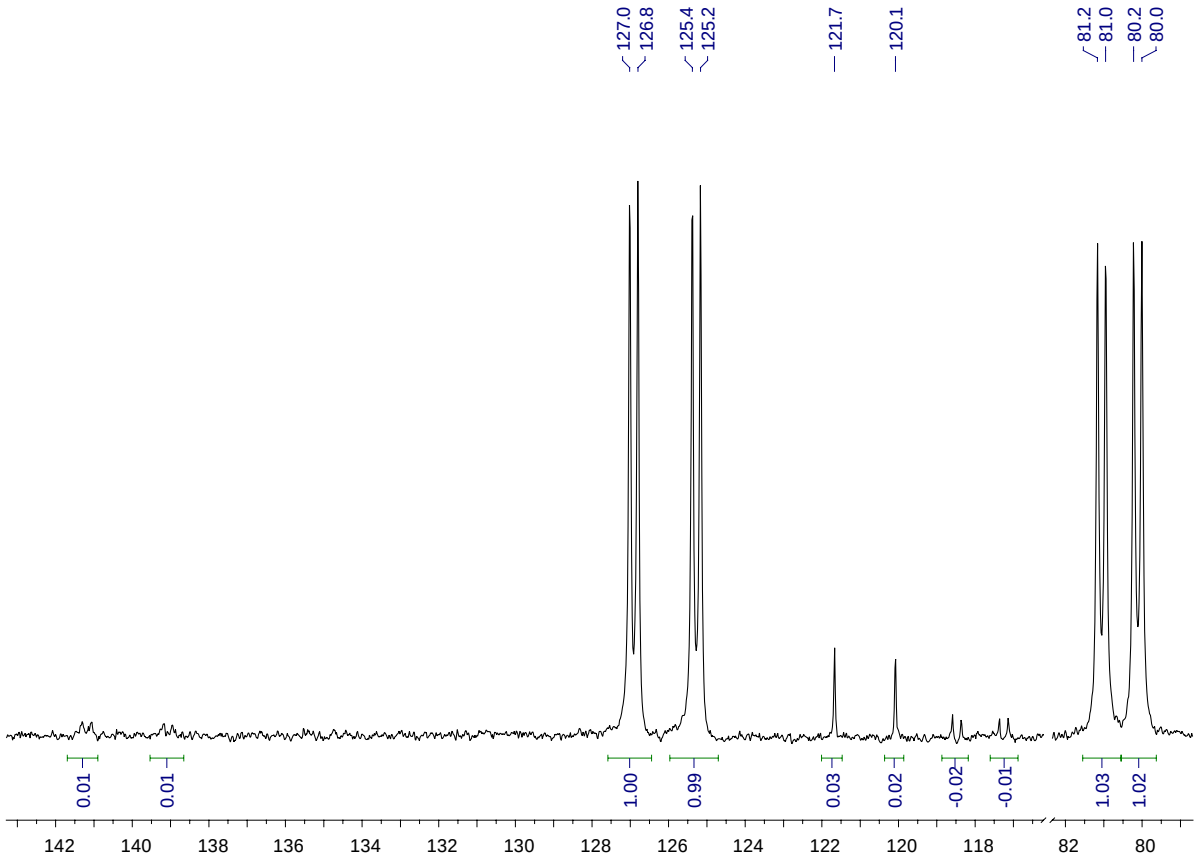
- (*R*)-**2d**/(*S*)-**4b**: Heterocomplex/Homo **2d** > 9 :1 (an exact assessment was not possible in this case)



Complexation of the combination (*R*)-2b/(*R*)-4b with [Rh(COD)$_2$BF$_4$]

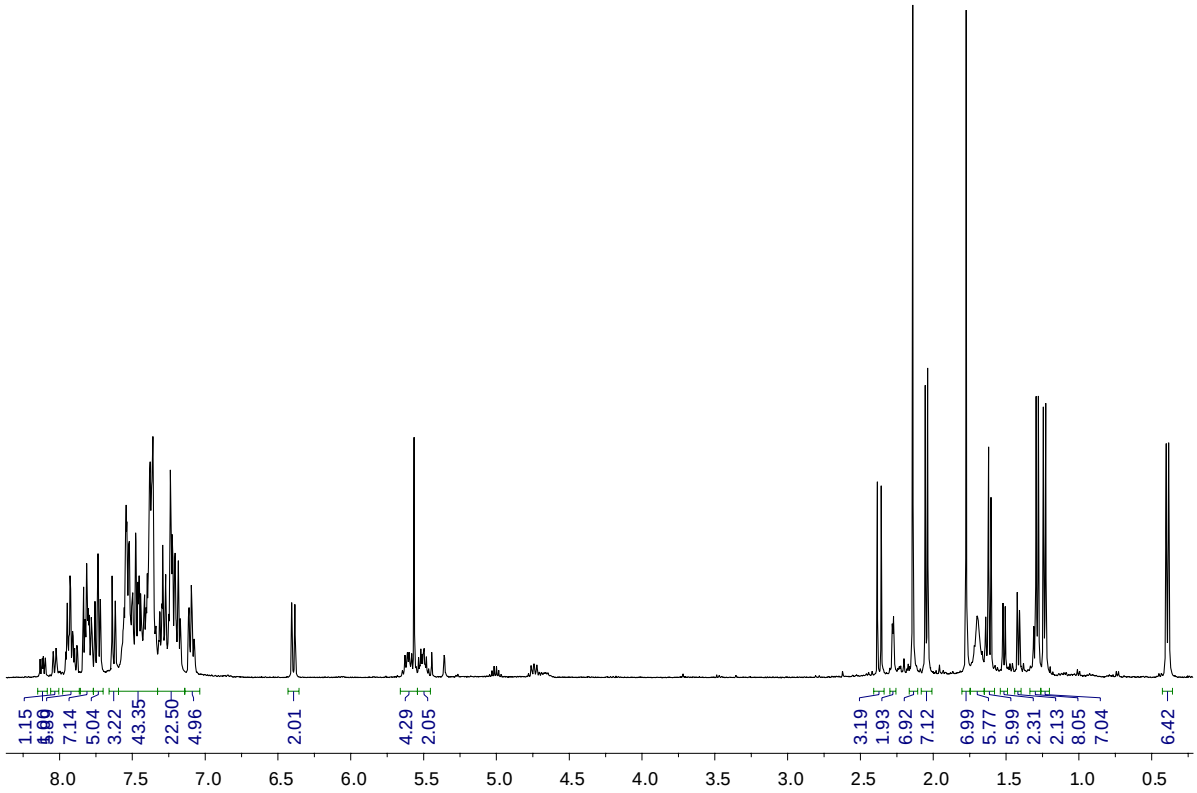
The above-described General Procedure was followed using the appropriate quantity of [Rh(COD)$_2$BF$_4$] (0.0134 mmol, 5.4 mg).

- (*R*)-**2b**/(*R*)-**4b**: Heterocomplex/Homo **4b** = 99 : 1
  $^1J_{\text{Rh-phosphite}}$ = 264.6 Hz; $^1J_{\text{Rh-phosphinamine}}$ = 153.0 Hz; $^2J_{\text{P-P}}$ = 34.7 Hz.

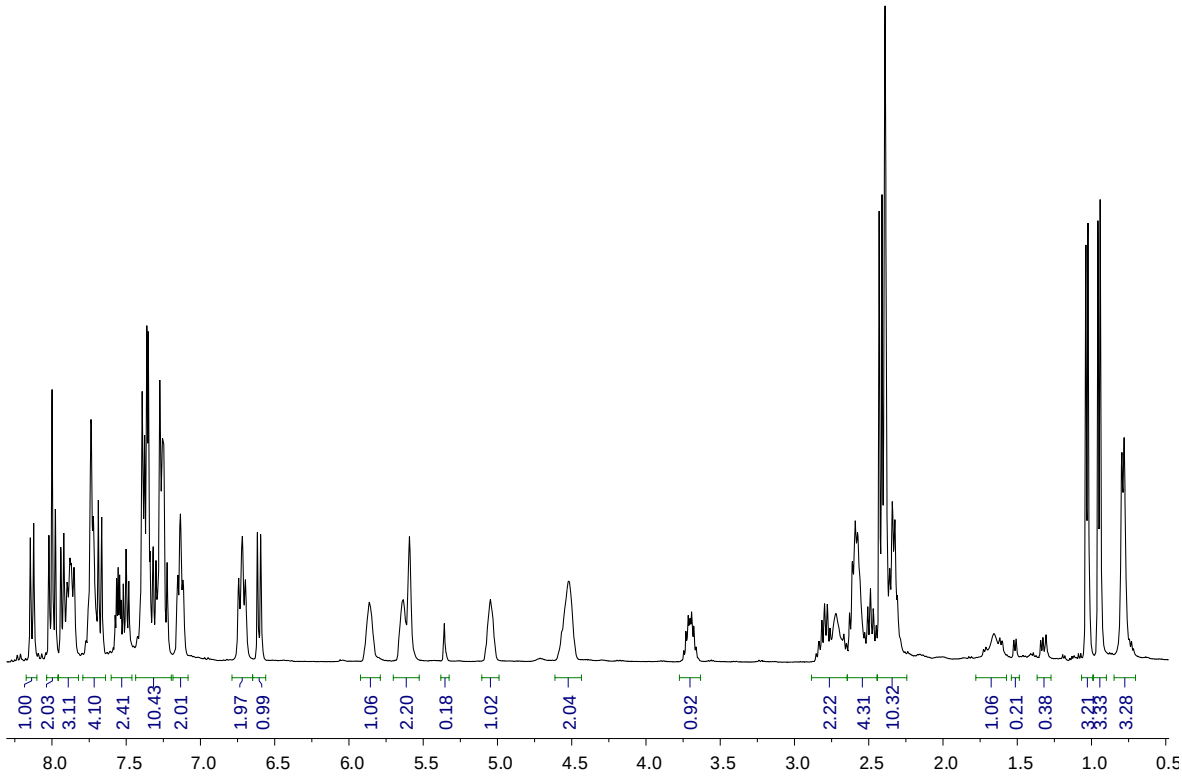


*^{1}H-NMR of the experiments involving the combination (R)-**2b**/(R)-**4b***

- (*R*)-**2b**/(*R*)-**4b**/[Rh(acac)(C_2H_4)$_2$]



- (*R*)-**2b**/(*R*)-**4b**/[Rh (COD)$_2$$BF_4$]



Screening of the ligands in rhodium-catalysed asymmetric hydrogenations

General procedure for asymmetric hydrogenation of methyl 2-acetamidoacrylate. The reactions were performed using standard Schlenk techniques. Seven oven-dried glass test tubes with stirring bars were employed: in each one the ligand (0.022 equiv., 0.00922 mmol) or the mixture of ligands (0.011 equiv., 0.00461 mmol each) was weighted, then the test tubes were placed in a Schlenk and subjected to three vacuum/nitrogen cycles. A 1.048 mM CH_2Cl_2 stock solution of $[Rh(COD)_2BF_4]$ (4 mL, 0.01 equiv, 0.00419 mmol) was added and the mixtures were stirred for 30 min under nitrogen. A solution of the substrate (0.419 mmol) in CH_2Cl_2 (4 mL) was finally added. The reaction mixtures were subjected to three vacuum/hydrogen cycles and then left stirring overnight at room temperature under ambient H_2 pressure. Samples were taken for chiral GC analysis. GC conditions: capillary column: MEGADEX DACTBSβ, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 μm; diameter = 0.25 mm; length = 25 m; carrier: hydrogen; flow: 1 mL/min; oven temperature: 140 °C for 6 min, then a 8 °C/min gradient is applied): $t_{substrate}$ = 3.7 min; t_R = 4.6 min; t_S = 5.2 min.[S11]

General procedure for asymmetric hydrogenation of *N*-(1-phenylvinyl)acetamide. A Parr multireactor was employed, allowing six reactions in parallel under hydrogen pressure. L^a (0.011 equiv., 0.00407 mmol) and L^b (0.011 equiv., 0.00407 mmol) [or, alternatively, 0.022 mmol, 0.00814 mmol of a single ligand] were weighted in special glass vessels. The vessels were purged with nitrogen and a 0.462 mM CH_2Cl_2 stock solution of $[Rh(COD)_2BF_4]$ (8 mL, 0.01 equiv, 0.00370 mmol) was added in each one. After 30 min *N*-(1-phenylvinyl)acetamide (60 mg, 0.370 mmol, 1 equiv.) was added and the vessels were placed in the respective autoclaves and purged one time with argon and three times with H_2 (5 bar). The reactions were stirred overnight under pressure of hydrogen and then analysed by chiral GC for conversion and e.e. determination. GC conditions: capillary column: MEGADEX DACTBSβ, diacetyl-*tert*-butylsilyl-β-cyclodextrin, 0.25 μm; diameter = 0.25 mm; length = 25 m; carrier: hydrogen; flow: 1.3 mL/min; oven temperature: 160 °C for 8 min, then a 8 °C/min gradient is applied; t_R = 6.7 min; t_S = 6.9 min; $t_{substrate}$ = 8.6 min.[S12]

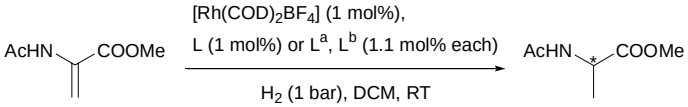


Table 4. Ligand screening in Rh-catalysed asymmetric hydrogenation of methyl 2-acetamidoacrylate

Entry	Ligands	After 20 h (1 bar H_2)	
		Conv. [%]	**e.e. [%] (abs. conf.)**
Homocombinations			
1	(*S*)-**2a**	100	80 (*R*)
2	(*R*)-**2b**	100	96 (*S*)
3	(*S*)-**2b**	100	96 (*R*)
4	(*R*)-**2c**	100	97 (*S*)
5	(*R*)-**2d**	100	42 (S)
6	(*R*,*R*)-**4a**	0	-
7	(*R*)-**4b**	52	12 (*S*)
8	(*S*)-**4b**	57	12 (*R*)
9	(*R*)-**4c**	3	10 (*R*)
10	(*R*)-**4d**	100	6 (*R*)
11	(*S*)-**4e**	100	6 (*R*)
Heterocombinations			
12	(*R*,*R*)-**4a**/(*R*)-**2b**	78	91 (*S*)
13	(*R*,*R*)-**4a**/(*R*)-**2c**	100	95 (*S*)
14	(*S*,*S*)-**4a**/(*R*)-**2c**	96	92 (*S*)
15	(*R*)-**4b**/(*S*)-**2a**	9	4 (*R*)
16	(*R*)-**4b**/(*R*)-**2b**	87	60 (*R*)
17	(*R*)-**4b**/(*R*)-**2c**	85	46 (*R*)
18	(*R*)-**4b**/(*R*)-**2d**	34	13 (*R*)
19	(*S*)-**4b**/(*S*)-**2a**	13	6 (*S*)
20	(*S*)-**4b**/(*R*)-**2b**	48	40 (*R*)
21	(*S*)-**4b**/(*R*)-**2c**	42	56 (*R*)
22	(*S*)-**4b**/(*R*)-**2d**	13	16 (*R*)
23	(*R*)-**4c**/(*S*)-**2a**	5	14 (*R*)
24	(*R*)-**4c**/(*R*)-**2b**	11	55 (*S*)
25	(*R*)-**4c**/(*S*)-**2b**	25	57 (*R*)
26	(*R*)-**4c**/(*R*)-**2c**	73	78 (*S*)
27	(*R*)-**4c**/(*R*)-**2d**	9	12 (*S*)
28	(*R*)-**4d**/(*S*)-**2a**	100	44 (*R*)
29	(*R*)-**4d**/(*R*)-**2b**	100	rac.
30	(*R*)-**4d**/(*S*)-**2b**	100	6 (*R*)
31	(*R*)-**4d**/(*R*)-**2c**	100	9 (*S*)
32	(*R*)-**4d**/(*R*)-**2d**	100	23 (*R*)
33	(*S*)-**4e**/(*S*)-**2a**	100	22 (*R*)
34	(*S*)-**4e**/(*R*)-**2b**	100	6 (*R*)
35	(*S*)-**4e**/(*S*)-**2b**	100	40 (*S*)
36	(*S*)-**4e**/(*R*)-**2c**	100	9 (*S*)
37	(*S*)-**4e**/(*R*)-**2d**	100	20 (*R*)

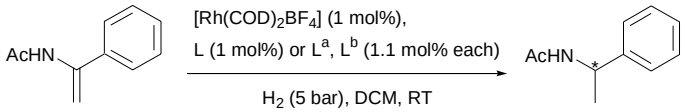


Table 5. Ligand screening in Rh-catalysed asymmetric hydrogenation of *N*-(1-phenylvinyl)acetamide

Entry	Ligands	After 20 h (5 bar H_2)	
		Conv. [%]	**e.e. [%] (abs. conf.)**
Homocombinations			
1	(*S*)-**2a**	100	86 (*R*)
2	(*R*)-**2b**	100	92 (*S*)
3	(*S*)-**2b**	100	92 (*R*)
4	(*R*)-**2c**	100	90 (*S*)
5	(*R*)-**2d**	100	6 (*S*)
6	(*R*,*R*)-**4a**	30	29 (*R*)
7	(*R*)-**4b**	83	7 (*R*)
8	(*S*)-**4b**	74	7 (*S*)
9	(*R*)-**4c**	53	4 (*S*)
10	(*R*)-**4d**	100	12 (*R*)
11	(*S*)-**4e**	100	4 (*R*)
Heterocombinations			
12	(*R*)-**4b**/(*S*)-**2a**	15	rac.
13	(*R*)-**4b**/(*R*)-**2b**	99	57 (*R*)
14	(*R*)-**4b**/(*R*)-**2c**	80	56 (*R*)
15	(*R*)-**4b**/(*R*)-**2d**	95	29 (*R*)
16	(*S*)-**4b**/(*S*)-**2a**	49	17 (*S*)
17	(*S*)-**4b**/(*R*)-**2b**	96	38 (*R*)
18	(*S*)-**4b**/(*R*)-**2c**	92	31 (*R*)
19	(*R*)-**4c**/(*S*)-**2a**	78	9 (*S*)
20	(*R*)-**4c**/(*R*)-**2b**	60	6 (*S*)
21	(*R*)-**4c**/(*S*)-**2b**	99	44 (*R*)
22	(*R*)-**4c**/(*R*)-**2c**	70	12 (*R*)
23	(*R*)-**4d**/(*S*)-**2a**	60	8 (*R*)
24	(*R*)-**4d**/(*R*)-**2b**	100	60 (*S*)
25	(*R*)-**4d**/(*S*)-**2b**	100	4 (*R*)
26	(*R*)-**4d**/(*R*)-**2c**	100	rac.
27	(*S*)-**4e**/(*S*)-**2a**	100	36 (*S*)
28	(*S*)-**4e**/(*R*)-**2b**	100	6 (*S*)
29	(*S*)-**4e**/(*S*)-**2b**	100	43 (*S*)
30	(*S*)-**4e**/(*R*)-**2c**	100	rac.

Screening of the ligands in the palladium-catalysed asymmetric allylic substitution of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene with dimethyl malonate

General procedure. $[Pd(\eta^3C_3H_5)Cl]_2$ (2.81 mg, 0.0077 mmol) and the ligand (0.0311 mmol) or mixture of ligands (0.0155 mmol each) were dissolved under nitrogen in degassed CH_2Cl_2 (1.0 mL). The resulting clear solution was stirred for 20 min at R.T., then a solution of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (129 mg, 0.51 mmol) in degassed CH_2Cl_2 (1.0 mL), dimethyl malonate (170 μL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)-acetamide (BSA, 370 μL, 1.5 mmol), and a pinch of AcOK were added. The reaction mixture was stirred at room temperature. After 1h the solution was diluted with Et_2O (5 mL) and saturated aqueous NH_4Cl (25 mL) was added. The phases were separated and the aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Conversion was determined by ^1H NMR analysis of the crude reaction mixture. An aliquot of the crude was passed through a pad of silica using 5:1 hexane/EtOAc as the eluent. The solvents were removed under vacuum and the residue was directly analyzed by HPLC for the determination of the enantiomeric excess. HPLC conditions: column: CHIRALCEL OD-H; eluent: 99:1 hexane/isopropanol; flow: 0.3 mL/min; $\lambda = 250$ nm; $t_R = 24$ min, $t_S = 26$ min.[S13]

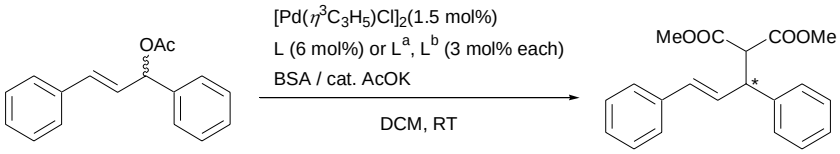


Table 6. Ligand screening in Pd-catalysed allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene

Entry	Ligands	After 1 h (R.T.)	
		Conv. [%]	**e.e. [%] (abs. conf.)**
Homocombinations			
1	(*S*)-**2a**	41	25 (*S*)
2	(*R*)-**2b**	100	58 (*S*)
3	(*R*)-**2c**	100	40 (*S*)
4	(*R*)-**2d**	60	73 (*R*)
5	(*R*,*R*)-**4a**	96	72 (*R*)
6	(*R*)-**4b**	100	68 (*R*)
7	(*S*)-**4b**	100	68 (*S*)
8	(*R*)-**4c**	100	rac.
9	(*R*)-**4d**	94	7 (*S*)
10	(*S*)-**4e**	100	15 (*R*)
Heterocombinations			
11	(*R*,*R*)-**4a**/(*R*)-**2b**	100	74 (*R*)
12	(*R*)-**4b**/(*S*)-**2a**	100	20 (*S*)
13	(*R*)-**4b**/(*R*)-**2b**	100	69 (*S*)
14	(*R*)-**4b**/(*R*)-**2c**	100	16 (*S*)
15	(*R*)-**4b**/(*R*)-**2d**	100	56 (*R*)
16	(*S*)-**4b**/(*S*)-**2a**	100	60 (*S*)
17	(*S*)-**4b**/(*R*)-**2b**	100	69 (*S*)
18	(*S*)-**4b**/(*R*)-**2c**	100	39 (*S*)
19	(*S*)-**4b**/(*R*)-**2d**	100	31 (*R*)
20	(*R*)-**4c**/(*R*)-**2b**	76	44 (*S*)
21	(*R*)-**4c**/(*S*)-**2b**	100	31 (*R*)
22	(*R*)-**4d**/(*R*)-**2b**	100	14 (*S*)
23	(*R*)-**4d**/(*S*)-**2b**	100	18 (*R*)
24	(*S*)-**4e**/(*R*)-**2b**	100	rac.
25	(*S*)-**4e**/(*S*)-**2b**	100	6 (*R*)

Calculations

Methods. The structures of the ligands were pre-optimised using the semi-empirical PM6 Hamiltonian,[S14] within the Mopac2009 programme.[S15] Rhodium was considered as a +1 cation in square planar geometry, bearing the anionic acac ligand, $(CH_3COCHCOCH_3)^-$, and bound in a bidentate fashion through the oxygen atoms. The whole complex is a closed-shell neutral molecule. After pre-optimisation using PM6,[S14] calculations were performed at the B3LYP/SDD level of theory[S16] in the Gaussian03 programme suite.[S17] The employed basis set consists of SDD effective core potential[S18] for rhodium and Dunning-Hay valence double-ζ basis D95V set for the remaining atoms. All degrees of freedom were free to optimise with default convergence criteria. The nature of the obtained stationary points was confirmed by frequency calculation within the same level of theory. Free energies of isodesmic reactions were calculated in order to minimise the error resulting from inadequate treatment of electron correlation.

Results and discussion. In the Equation 1 of the article, the hypothetical reaction could be described as ligand exchange between two homocomplexes, $[Rh(P[OPh]_3)_2(acac)]$ and $[Rh(PPh_3)_2(acac)]$, forming the heterocomplex $[Rh(PPh_3)(P[OPh]_3)(acac)]$. Calculated energies in kcal/mol, at temperature T = 298 K, are shown in Table 7. From the results it can be concluded that the heterocomplex formation is favoured. The calculated quantities are as following: E = electronic energy, G = Gibbs free energy, H = enthalpy, TS = temperature (298 K) times entropy.

Table 7

	E	G	H	TS
phosphite	-1869661.80	-1869289.38	-1869196.66	92.67
phosphine	-1586441.70	-1586074.30	-1585994.36	79.90
heterocomplex	-1728055.28	-1727684.39	-1727599.01	85.34
reaction	-7.06	-5.11	-7.00	-1.89

In the Equation 2 of the article, the hypothetical reaction could be described as ligand exchange between two homocomplexes, $[Rh(P[OPh]_3)_2(acac)]$ and $[Rh(PPh_2NMe_2)_2(acac)]$, forming the heterocomplex $[Rh(PPh_2NMe_2)(P[OPh]_3)(acac)]$). Calculated energies in kcal/mol, at temperature T = 298 K, are shown in Table 8. Again, the heterocomplex formation is significantly favoured.

Table 8

	E	G	H	TS
phosphite	-1869661.80	-1869289.38	-1869196.66	92.67
phosphinamine	-1464618.28	-1464258.05	-1464181.99	76.02
heterocomplex	-1667143.61	-1666779.35	-1666692.96	86.35
reaction	-7.15	-11.29	-7.27	4.02

Optimized geometries as XYZ coordinates for all 5 structures (two phosphite complexes are identical), distances in Ångstroms:

$[Rh(P[OPh]_3)_2(acac)]$

```
  89
scf: -2979.497982
Rh    -0.275792    -1.234429     0.098781
 H    -3.287161    -5.167736    -1.419462
 C    -3.251852    -4.076613    -1.352398
 C    -1.930415    -3.586031    -0.797230
 H    -4.072873    -3.720629    -0.719070
 H    -3.413584    -3.652023    -2.351877
 O    -1.863385    -2.287251    -0.617288
 C    -0.887744    -4.497791    -0.523886
 C     0.391057    -4.162024    -0.019281
 H    -1.081734    -5.545582    -0.720786
 C     1.424062    -5.242992     0.225777
 O     0.792563    -2.951846     0.274500
 H     1.670685    -5.278076     1.294943
 H     1.070644    -6.228127    -0.091784
 H     2.347785    -4.994602    -0.310568
 O     3.116909    -0.921044     0.716179
 P     1.587478    -0.101742     0.746580
 O     1.908411     1.298481    -0.179944
 O     1.833479     0.543219     2.331051
 O    -2.035624     1.293014    -1.577465
 P    -1.594314     0.609197    -0.031340
 O    -3.206026     0.580127     0.591228
 O    -1.067080     1.962001     0.861707
 C     1.207603     0.030862     3.496484
 C     1.838551    -0.999326     4.213931
 C     0.015724     0.624161     3.944815
 C     1.258276    -1.442690     5.416985
 H     2.759647    -1.429850     3.831958
 C    -0.552012     0.172067     5.150631
 H    -0.442221     1.412728     3.355461
 C     0.065004    -0.858594     5.888262
 H     1.737362    -2.237826     5.983321
 H    -1.473013     0.624266     5.510483
 H    -0.378402    -1.202313     6.819603
 C     3.022616     2.172082    -0.193603
 C     3.208502     2.874808    -1.397950
 C     3.867316     2.372247     0.913247
 C     4.265855     3.796429    -1.496789
 H     2.531535     2.689405    -2.226694
 C     4.924461     3.294341     0.793413
 H     3.695258     1.829566     1.835245
```

C	5.129490	4.008491	-0.403058
H	4.415447	4.342223	-2.425359
H	5.584982	3.454355	1.642292
H	5.948608	4.718663	-0.482739
C	3.647872	-1.659489	-0.359887
C	4.628547	-2.608905	-0.022592
C	3.274396	-1.444503	-1.699905
C	5.242223	-3.357584	-1.041836
H	4.894447	-2.741268	1.021635
C	3.892070	-2.207015	-2.708865
H	2.525464	-0.701187	-1.956401
C	4.874727	-3.163595	-2.389551
H	6.005940	-4.087731	-0.783977
H	3.606086	-2.044612	-3.745444
H	5.351338	-3.742977	-3.176136
C	-1.499334	3.311595	0.782029
C	-2.831570	3.674466	1.047356
C	-0.510945	4.271253	0.505282
C	-3.174552	5.039671	1.024499
H	-3.566169	2.905372	1.258459
C	-0.868848	5.632133	0.495170
H	0.506626	3.944989	0.314689
C	-2.199851	6.019957	0.750963
H	-4.201847	5.334357	1.225146
H	-0.110300	6.383514	0.289737
H	-2.472665	7.072300	0.741104
C	-1.228089	1.252506	-2.738801
C	-0.782376	2.476148	-3.266985
C	-0.954239	0.031535	-3.381560
C	-0.050822	2.476041	-4.469089
H	-1.016831	3.397755	-2.742373
C	-0.215342	0.045639	-4.579361
H	-1.315367	-0.898154	-2.952797
C	0.237046	1.262608	-5.127023
H	0.289361	3.419293	-4.889980
H	0.000748	-0.893061	-5.084182
H	0.802571	1.266495	-6.055494
C	-4.299621	-0.210189	0.169056
C	-4.834807	-1.119936	1.096889
C	-4.890990	-0.012667	-1.091897
C	-5.988916	-1.847799	0.754217
H	-4.350646	-1.239561	2.061643
C	-6.039709	-0.754625	-1.424806
H	-4.455642	0.703581	-1.780754
C	-6.593230	-1.670449	-0.507455
H	-6.414972	-2.546631	1.470279
H	-6.505888	-0.608301	-2.396405
H	-7.486856	-2.232100	-0.768437

[Rh(PPh$_3$)$_2$(acac)]

83

scf: -2528.15767805

C	-1.211722	-2.967171	0.825890
C	-1.605488	-2.121621	-0.234652
C	-1.826766	-2.684850	-1.508237
C	-1.681759	-4.069808	-1.712532
C	-1.307495	-4.909573	-0.647310
C	-1.068470	-4.351240	0.623283
P	-1.777973	-0.262661	0.047480
Rh	0.039795	1.254192	0.055591
O	1.448004	2.743843	0.018458
C	1.230785	4.030910	-0.036338
C	-0.042321	4.651988	-0.044223

C	-1.285882	3.982940	0.010443
C	-2.578800	4.779524	0.000319
C	-3.015954	0.211357	-1.301484
C	-4.373969	-0.165150	-1.259318
C	-5.245190	0.193938	-2.305119
C	-4.765198	0.930685	-3.405871
C	-3.410652	1.312708	-3.449468
C	-2.542384	0.958744	-2.399708
C	-2.807361	-0.214161	1.635868
C	-2.656101	0.894351	2.496616
C	-3.413355	0.986349	3.679607
C	-4.329107	-0.028344	4.017923
C	-4.482353	-1.138222	3.164422
C	-3.727727	-1.229196	1.979872
O	-1.443163	2.684787	0.071720
P	1.814032	-0.281003	0.001417
C	3.531859	0.482140	-0.228918
C	4.303043	0.298166	-1.392287
C	5.575867	0.894227	-1.506630
C	6.087727	1.679518	-0.458357
C	5.315667	1.870518	0.705946
C	4.045213	1.281363	0.816414
C	1.751178	-1.526343	-1.412343
C	1.391792	-1.014919	-2.680359
C	1.363551	-1.853223	-3.808427
C	1.678627	-3.220732	-3.679146
C	2.010468	-3.739564	-2.414268
C	2.048504	-2.896478	-1.286277
C	2.135886	-1.272027	1.576015
C	3.283018	-2.080851	1.735251
C	3.511915	-2.760600	2.945419
C	2.603009	-2.627947	4.014933
C	1.471478	-1.803425	3.869420
C	1.241481	-1.128245	2.655176
C	2.484609	4.885868	-0.102870
H	-3.032633	1.890801	-4.289812
H	-1.502398	1.275179	-2.413180
H	-5.439201	1.207901	-4.213496
H	-6.291811	-0.098470	-2.258269
H	-4.764788	-0.725133	-0.415271
H	-2.121165	-2.052923	-2.340843
H	-1.031113	-2.557640	1.815049
H	-1.952992	1.678081	2.233361
H	-3.843968	-2.102935	1.344329
H	-1.858474	-4.485912	-2.701561
H	-0.772980	-4.986613	1.455006
H	-3.285472	1.846300	4.333251
H	-5.183688	-1.930041	3.417911
H	-1.202091	-5.980729	-0.804472
H	-4.911852	0.041935	4.933744
H	0.776624	-1.676559	4.696455
H	0.385544	-0.466461	2.547615
H	2.784397	-3.148423	4.952717
H	4.399051	-3.379842	3.057094
H	4.013080	-2.156513	0.933413
H	1.127124	0.036191	-2.774813
H	2.290182	-3.319859	-0.316982
H	3.931235	-0.312377	-2.209342
H	3.451398	1.448228	1.710824
H	1.091565	-1.443286	-4.778437
H	2.234301	-4.797672	-2.299565
H	6.161421	0.738590	-2.410065
H	5.700061	2.478264	1.522140

H	1.654769	-3.872674	-4.549542
H	7.071514	2.135687	-0.544693
H	-0.063853	5.734989	-0.094201
H	-3.154136	4.565082	0.910390
H	-2.397788	5.856791	-0.062939
H	-3.196425	4.466010	-0.850939
H	3.132986	4.659946	0.752735
H	3.052569	4.636481	-1.008473
H	2.252862	5.955269	-0.107668

[Rh(PPh$_3$)(P[OPh]$_3$)(acac)]

86
scf: -2753.833454

Rh	-0.317372	-1.246075	0.027370
H	2.021742	-5.823282	0.839647
C	2.219137	-4.751075	0.748928
C	0.946022	-3.954077	0.540279
H	2.901382	-4.575076	-0.091737
H	2.731253	-4.402955	1.655505
O	1.125813	-2.666187	0.388584
C	-0.309610	-4.603635	0.527108
C	-1.562009	-3.972467	0.345120
H	-0.313468	-5.677654	0.673766
C	-2.833967	-4.799921	0.362708
O	-1.748651	-2.691622	0.146685
H	-3.301670	-4.776425	-0.630542
H	-2.642806	-5.840891	0.639338
H	-3.550156	-4.358705	1.065850
P	-2.063043	0.334376	-0.241731
O	2.635436	0.467320	0.915708
P	1.377292	0.195313	-0.279724
O	2.503963	-0.142564	-1.564440
O	1.001779	1.790916	-0.776769
C	1.857675	2.907498	-0.935558
C	2.916450	2.901889	-1.862216
C	1.546507	4.053832	-0.183352
C	3.678893	4.073926	-2.025556
H	3.131257	1.999896	-2.423616
C	2.313515	5.219638	-0.363509
H	0.713860	4.020979	0.512477
C	3.382988	5.233562	-1.281673
H	4.501590	4.078764	-2.736800
H	2.075209	6.112106	0.210529
H	3.974866	6.135436	-1.417445
C	2.440619	0.507189	2.312134
C	2.797264	1.691452	2.982094
C	1.982980	-0.622323	3.016909
C	2.696197	1.744301	4.384392
H	3.150296	2.540083	2.403469
C	1.876135	-0.551154	4.418725
H	1.727488	-1.525962	2.472953
C	2.231500	0.626142	5.107232
H	2.980461	2.653860	4.908573
H	1.521400	-1.418617	4.970694
H	2.154698	0.669417	6.190928
C	3.369774	-1.253598	-1.662543
C	3.086823	-2.231544	-2.632060
C	4.532638	-1.321056	-0.873247
C	3.988287	-3.296018	-2.816638
H	2.178903	-2.147479	-3.222289
C	5.423636	-2.393136	-1.064335
H	4.715908	-0.551085	-0.131285
C	5.157910	-3.381593	-2.034027

H	3.778280	-4.052607	-3.569199
H	6.325753	-2.452168	-0.459744
H	5.854638	-4.203198	-2.181974
C	-1.901582	1.860589	0.848462
C	-2.390724	3.127859	0.475080
C	-1.273382	1.703192	2.102799
C	-2.262483	4.223500	1.350537
H	-2.850250	3.275301	-0.497160
C	-1.147984	2.796664	2.979550
H	-0.869752	0.733650	2.385593
C	-1.645840	4.060498	2.606681
H	-2.639253	5.198208	1.049351
H	-0.654308	2.660116	3.938268
H	-1.548242	4.907637	3.281831
C	-2.415055	0.990347	-1.970708
C	-3.670285	1.545770	-2.305933
C	-1.405865	0.926832	-2.952537
C	-3.909042	2.034044	-3.603560
H	-4.467617	1.578892	-1.568196
C	-1.643997	1.417571	-4.249896
H	-0.440313	0.497270	-2.707969
C	-2.894307	1.974062	-4.579119
H	-4.880597	2.455955	-3.850054
H	-0.855337	1.364347	-4.996348
H	-3.078382	2.351413	-5.582438
C	-3.746928	-0.347251	0.261293
C	-4.391861	-1.270434	-0.590441
C	-4.354408	0.000397	1.483773
C	-5.634933	-1.819804	-0.233517
H	-3.923225	-1.564355	-1.525450
C	-5.597520	-0.556082	1.845560
H	-3.875086	0.707420	2.154295
C	-6.243443	-1.464866	0.987582
H	-6.123983	-2.524129	-0.902661
H	-6.056103	-0.274876	2.790752
H	-7.205508	-1.890481	1.264015

[Rh(PPh$_2$NMe$_2$)$_2$(acac)]

79

scf: -2334.019559

Rh	-0.141441	-1.117071	0.094583
H	2.476463	-4.368992	2.218472
C	2.013393	-4.753826	1.300240
C	0.835000	-3.877041	0.913408
H	1.716098	-5.794250	1.461968
H	2.776792	-4.714121	0.513092
O	1.140078	-2.630913	0.655840
C	-0.466054	-4.425275	0.862366
C	-1.641010	-3.719891	0.509418
H	-0.574168	-5.473627	1.117061
C	-2.978874	-4.440192	0.509934
O	-1.694937	-2.461082	0.162370
H	-3.389019	-4.465934	-0.508344
H	-2.892587	-5.465414	0.882448
H	-3.694367	-3.887253	1.130777
P	-1.692795	0.557982	-0.442597
N	-1.504067	1.359845	-2.030333
C	-2.545174	2.292280	-2.504573
C	-0.935523	0.542924	-3.119659
H	-2.921577	2.908538	-1.683228
H	-2.109726	2.961838	-3.259908
H	-3.404058	1.769251	-2.961245
H	-0.430931	1.196058	-3.847482

H	-0.209247	-0.166899	-2.709323
H	-1.708043	-0.031504	-3.663924
H	2.312911	-1.694597	2.872047
C	3.043057	-0.915702	2.596631
H	3.763683	-1.354437	1.903078
H	3.580348	-0.599835	3.502527
N	2.401233	0.276825	2.000928
P	1.827932	0.179386	0.286393
C	1.391388	0.857139	2.920077
H	1.887226	1.122747	3.863745
H	0.952422	1.765500	2.496371
H	0.570145	0.152459	3.136639
C	-3.524338	0.061133	-0.508719
C	-4.560468	0.825942	0.066041
C	-3.861992	-1.066289	-1.291860
C	-5.909049	0.464911	-0.124165
H	-4.329528	1.706208	0.658338
C	-5.208114	-1.420725	-1.491792
H	-3.073400	-1.675615	-1.720182
C	-6.237947	-0.658564	-0.905058
H	-6.695170	1.064297	0.329721
H	-5.451616	-2.291325	-2.096930
H	-7.279134	-0.935532	-1.055341
C	-1.695135	2.004187	0.756421
C	-1.186939	3.270149	0.407246
C	-2.137768	1.778465	2.079532
C	-1.141969	4.305635	1.361291
H	-0.810278	3.438475	-0.595999
C	-2.095717	2.812176	3.031222
H	-2.502403	0.795731	2.370402
C	-1.600417	4.083139	2.673117
H	-0.739885	5.275694	1.079107
H	-2.442444	2.625840	4.045066
H	-1.565531	4.883412	3.408891
C	2.101214	1.984934	-0.214576
C	1.709769	2.406083	-1.501094
C	2.774512	2.889047	0.631047
C	1.983439	3.716062	-1.935908
H	1.193668	1.722909	-2.165123
C	3.036398	4.204163	0.202918
H	3.104089	2.550361	1.608548
C	2.643147	4.622654	-1.082957
H	1.685067	4.024970	-2.935337
H	3.553789	4.893496	0.866702
H	2.854162	5.635851	-1.418431
C	3.323587	-0.573983	-0.579810
C	4.622003	-0.070592	-0.350113
C	3.133836	-1.604787	-1.520028
C	5.721467	-0.603768	-1.046399
H	4.774216	0.730192	0.368860
C	4.233358	-2.130455	-2.226213
H	2.134230	-1.995876	-1.685830
C	5.529086	-1.633795	-1.990023
H	6.719522	-0.213148	-0.860992
H	4.077080	-2.924624	-2.952947
H	6.378696	-2.040747	-2.534117

[Rh(PPh$_2$NMe$_2$)(P[OPh]$_3$)(acac)]

84

scf: -2656.766044

Rh	-0.510204	-1.114235	-0.033342
H	-3.625475	-4.322460	-1.346402
C	-3.289632	-4.477116	-0.312421

C	-1.972514	-3.757260	-0.092962
H	-3.208319	-5.551373	-0.123453
H	-4.057111	-4.048042	0.343147
O	-2.042709	-2.452703	-0.201555
C	-0.802646	-4.492523	0.196296
C	0.481504	-3.943391	0.426966
H	-0.896057	-5.571010	0.249814
C	1.652972	-4.856866	0.732653
O	0.770541	-2.668422	0.401674
H	1.360283	-5.910746	0.741906
H	2.439015	-4.705513	-0.017629
H	2.082962	-4.596424	1.708465
H	-2.520691	-1.457180	-3.016276
C	-3.237397	-0.632659	-2.859200
H	-4.029086	-0.991226	-2.197368
H	-3.684654	-0.369121	-3.827060
N	-2.591860	0.579177	-2.298907
P	-2.145342	0.496839	-0.555857
C	-1.514262	1.070032	-3.192857
H	-1.962009	1.367779	-4.150224
H	-1.009207	1.936149	-2.758916
H	-0.750338	0.297520	-3.391076
O	2.838937	-0.455969	-0.286733
P	1.272480	0.246602	0.035171
O	1.259695	1.615275	-0.991664
O	1.831291	1.094406	1.439357
C	3.162303	-1.394177	-1.281342
C	4.277658	-2.210265	-1.017771
C	2.466946	-1.489589	-2.501658
C	4.702086	-3.133324	-1.989465
H	4.790510	-2.105592	-0.066298
C	2.897420	-2.424147	-3.461866
H	1.611530	-0.850689	-2.699352
C	4.012705	-3.247613	-3.214587
H	5.569011	-3.759359	-1.790763
H	2.361411	-2.502352	-4.404952
H	4.342792	-3.961994	-3.964445
C	2.148694	2.718707	-1.050090
C	1.561814	3.955791	-1.365378
C	3.538537	2.589370	-0.873266
C	2.385129	5.086080	-1.517946
H	0.484158	4.018321	-1.477377
C	4.347051	3.731635	-1.022098
H	3.969140	1.628019	-0.617711
C	3.779837	4.979561	-1.347317
H	1.935966	6.045478	-1.763760
H	5.422160	3.641404	-0.885504
H	4.413901	5.854913	-1.464145
C	2.183026	0.550488	2.688479
C	2.533229	1.491288	3.674377
C	2.195337	-0.831072	2.960953
C	2.899577	1.042633	4.955191
H	2.519156	2.546982	3.420943
C	2.561974	-1.261879	4.250228
H	1.932763	-1.552442	2.193114
C	2.914528	-0.335874	5.250509
H	3.173311	1.767762	5.718075
H	2.571837	-2.327331	4.469041
H	3.197746	-0.680742	6.241685
C	-1.968008	2.323901	-0.142642
C	-1.272318	2.692699	1.024798
C	-2.600623	3.314223	-0.921456
C	-1.208044	4.043730	1.412741

H	-0.778398	1.939436	1.632421
C	-2.527135	4.666088	-0.538279
H	-3.144539	3.024503	-1.816187
C	-1.833905	5.034257	0.632220
H	-0.665537	4.318166	2.313696
H	-3.014874	5.425550	-1.145238
H	-1.780986	6.078825	0.930532
C	-3.814015	0.156390	0.244734
C	-4.998630	0.702828	-0.290996
C	-3.862142	-0.572874	1.448245
C	-6.226151	0.507762	0.367511
H	-4.960271	1.269151	-1.217859
C	-5.089232	-0.756055	2.113462
H	-2.949977	-0.999172	1.855798
C	-6.273913	-0.219309	1.573985
H	-7.137112	0.927383	-0.053123
H	-5.118294	-1.316019	3.045335
H	-7.222191	-0.363369	2.087067

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