SUPPORTING INFORMATION

**DOI:**

**Title:** Diastereoselective desymmetrization of diarylphosphinous acid-borane amides under Birch reduction

**Authors:** Marek Stankevič

Copies of NMR spectras
$^1$H NMR spectra of diphenylphosphinous acid-borane (S)-α-methylbenzylamide (10a) (500 MHz, CDCl$_3$).

$^{13}$C NMR spectra of diphenylphosphinous acid-borane (S)-α-methylbenzylamide (10a) (126 MHz, CDCl$_3$).
$^3$P NMR spectra of diphenylphosphinous acid-borane (S)-α-methylbenzylamide (10a) (126 MHz, CDCl$_3$).

$^1$H NMR spectra of diphenylphosphinic acid (S)-α-methylbenzylamide (11a) (500 MHz, CDCl$_3$).
$^{13}$C NMR spectra of diphenylphosphinic acid (S)-α-methylbenzylamide (11a) (126 MHz, CDCl$_3$).

$^{31}$P NMR spectra of diphenylphosphinic acid (S)-α-methylbenzylamide (11a) (202 MHz, CDCl$_3$).
$^1$H NMR spectra of diphenylphosphinous acid-borane N-methyl-(S)-$\alpha$-methylbenzylamide (10b) (400 MHz, CDCl$_3$).

$^{13}$C NMR spectra of diphenylphosphinous acid-borane N-methyl-(S)-$\alpha$-methylbenzylamide (10b) (75 MHz, CDCl$_3$).
$^{31}$P NMR spectra of diphenylphosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (10b) (162 MHz, CDCl$_3$).

$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-ethyl-(S)-$\alpha$-methylbenzylamide (10c) (500 MHz, CDCl$_3$).
$^{13}$C NMR spectra of diphenylphosphinous acid-borane $N$-ethyl-(S)-$\alpha$-methylbenzylamide (10c) (126 MHz, CDCl$_3$).

$^{31}$P NMR spectra of diphenylphosphinous acid-borane $N$-ethyl-(S)-$\alpha$-methylbenzylamide (10c) (202 MHz, CDCl$_3$).
$^1$H NMR spectra of diphenylphosphinic acid $N$-methyl-($S$)-$\alpha$-methylbenzylamide (11b) (500 MHz, CDCl$_3$).

$^{13}$C NMR spectra of diphenylphosphinic acid $N$-methyl-($S$)-$\alpha$-methylbenzylamide (11b) (126 MHz, CDCl$_3$).
$^{31}$P NMR spectra of diphenylphosphinic acid $N$-methyl-($S$)-$\alpha$-methylbenzylamide (11b) (202 MHz, CDCl$_3$).

$^1$H NMR spectra of diphenylphosphinic acid $N$-ethyl-($S$)-$\alpha$-methylbenzylamide (11c) (500 MHz, CDCl$_3$).
$^{13}$C NMR spectra of diphenylphosphinic acid $N$-ethyl-($S$)-$\alpha$-methylbenzylamide (11b) (126 MHz, CDCl$_3$).

$^{31}$P NMR spectra of diphenylphosphinic acid $N$-ethyl-($S$)-$\alpha$-methylbenzylamide (11b) (202 MHz, CDCl$_3$).
$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (10d) (500 MHz, CDCl$_3$).

$^{13}$C NMR spectra of diphenylphosphinous acid-borane $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (10d) (126 MHz, CDCl$_3$).
$^{31}P$ NMR spectra of diphenylphosphinous acid-borane $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (10d) (202 MHz, CDCl$_3$).

$^1$H NMR spectra of diphenylphosphinic acid $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (11d) (500 MHz, CDCl$_3$).
$^{13}$C NMR spectra of diphenylphosphinic acid N-isopropyl-(S)-α-methylbenzylamide (11d) (126 MHz, CDCl$_3$).

$^{31}$P NMR spectra of diphenylphosphinic acid N-isopropyl-(S)-α-methylbenzylamide (11d) (202 MHz, CDCl$_3$).
$^1$H NMR spectra of Diphenylphosphinous acid-borane (2S)-2-(hydroxymethyl)pyrolidinamide (16a) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of Diphenylphosphinous acid-borane (2S)-2-(hydroxymethyl)pyrolidinamide (16a) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of Diphenylphosphinous acid-borane (2S)-2-(hydroxymethyl)pyridinamide (16a) (202 MHz, CDCl$_3$)

$^1$H NMR spectra of diphenylphosphinous acid-borane (2S)-2-(methoxymethyl)pyridinamide (16b) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of diphenylphosphinous acid-borane (2S)-2-(methoxymethyl)pyrrolidinamide (16b) (126 MHz, CDCl$_3$)

$^{31}$P NMR spectra of diphenylphosphinous acid-borane (2S)-2-(methoxymethyl)pyrrolidinamide (16b) (202 MHz, CDCl$_3$)
$^1$H NMR spectra of diphenylphosphinous acid-borane (2S)-2-(trimethylsiloxy)methyl)pyrrolidinamide (16c) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of diphenylphosphinous acid-borane (2S)-2-(trimethylsiloxy)methyl)pyrrolidinamide (16c) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of diphenylphosphinous acid-borane (2S)-2-(trimethylsililoxymethyl)pyrolidinamide (16c) (201 MHz, CDCl$_3$)

$^1$H NMR spectra of N-neomethyl methyl carbamate (23a) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of $N$-neomenthyl methyl carbamate (23a) (500 MHz, CDCl$_3$)

$^1$H NMR spectra of 9-((methoxycarbonyl)amino)-9-epi-quinine (23b) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of 9-((methoxycarbonyl)amino)-9-\textit{epi}-quinine (23b) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of 9-((methoxycarbonyl)amino)-9-\textit{epi}-quinidine (23c) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of 9-((methoxycarbonyl)amino)-9-\textit{epi}-quinidine (23b) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of $N$-bornyl methyl carbamate (23d) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of $N$-bornyl methyl carbamate (23d) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of $N$-($R$)-1-(1-naphthyl)ethyl methyl carbamate (23e) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of $N$-(R)-1-(1-naphthyl)ethyl methyl carbamate (23e) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of $N$-(S)-1-(2-naphthyl)ethyl methyl carbamate (23f) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of $N$-(S)-1-(2-naphthyl)ethyl methyl carbamate (23f) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of $N$-methylneomenthylamine (24a) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of N-methylneomenthylamine (24a) (126 MHz, CDCl$_3$)

$^1$H NMR spectra of 9-(methylamino)-9-\textit{epi}-quinine (24b) (500 MHz, CDCl$_3$)
$^1$H NMR spectra of 9-(methylamino)-9-\textit{epi}-quinidine (24c) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 9-(methylamino)-9-\textit{epi}-quinidine (24c) (126 MHz, CDCl$_3$)
$^1$H NMR spectra of N-methyl-(R)-1-(1-naphthyl)ethylamine (24e) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of N-methyl-(R)-1-(1-naphthyl)ethylamine (24e) (126 MHz, CDCl$_3$)
$^1$H NMR spectra of $N$-methyl-($S$)-1-(2-naphthyl)ethylamine (24f) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of $N$-methyl-($S$)-1-(2-naphthyl)ethylamine (24f) (126 MHz, CDCl$_3$)
$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-methylneomenthylamide (25a) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of diphenylphosphinous acid-borane $N$-methylneomenthylamide (25a) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of diphenylphosphinous acid-borane $N$-methylneomenthylamide (25a) (202 MHz, CDCl$_3$)

$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-methyl-bornylamide (25d) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of diphenylphosphinous acid-borane N-methyl-bornylamide (25d) (126 MHz, CDCl$_3$)

$^{31}$P NMR spectra of diphenylphosphinous acid-borane N-methyl-bornylamide (25d) (202 MHz, CDCl$_3$)
$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-methyl-($R$)-1-(1-naphthyl)ethylamide (25e) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of diphenylphosphinous acid-borane $N$-methyl-($R$)-1-(1-naphthyl)ethylamide (25e) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of diphenylphosphinous acid-borane $N$-methyl-$(R)$-1-(1-naphthyl)ethylamide (25e) (202 MHz, CDCl$_3$)

$^1$H NMR spectra of diphenylphosphinous acid-borane $N$-methyl-$(S)$-1-(2-naphthyl)ethylamide (25f) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of diphenylphosphinous acid-borane N-methyl-(S)-1-(2-naphthyl)ethylamide (25f) (126 MHz, CDCl$_3$)

$^{31}$P NMR spectra of diphenylphosphinous acid-borane N-methyl-(S)-1-(2-naphthyl)ethylamide (25f) (202 MHz, CDCl$_3$)
$^1$H NMR spectra of di(o-tolyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33a) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of di(o-tolyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33a) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of di(o-toly)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33a) (202 MHz, CDCl$_3$)

$^1$H NMR spectra of di(p-toly)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33b) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of di(p-toly)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33b) (126 MHz, CDCl$_3$)

$^{31}$P NMR spectra of di(p-toly)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33b) (202 MHz, CDCl$_3$)
$^1$H NMR spectra of di(p-anisyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33c) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of di(p-anisyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33c) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of di(p-anisyl)phosphinous acid-borane N-methyl-(S)-$\alpha$-methylbenzylamide (33c) (202 MHz, CDCl$_3$)

$^1$H NMR spectra of di(3,5-dimethylphenyl)phosphinous acid-borane N-methyl-(S)-$\alpha$-methylbenzylamide (33d) (500 MHz, CDCl$_3$)
$^{13}$C NMR spectra of di(3,5-dimethylphenyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33d) (126 MHz, CDCl$_3$)

$^{31}$P NMR spectra of di(3,5-dimethylphenyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33d) (202 MHz, CDCl$_3$)
$^1$H NMR spectra of di(3,5-dimethoxyphenyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33e) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of di(3,5-dimethoxyphenyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33e) (126 MHz, CDCl$_3$)
$^{31}$P NMR spectra of di(3,5-dimethoxylphenyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (33e) (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (13b) (2 diastereomers) along with starting material 10b (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane $N$-ethyl-(S)-α-methylbenzylamide (13c) (2 diastereomers) along with starting material 10c (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane $N$-isopropyl-(S)-α-methylbenzylamide (13d) along with starting material 10d (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinic acid $N$-methyl-(S)-$\alpha$-methylbenzylamide (14b) along with bis(1,4-cyclohexadien-3-yl)phosphinic acid $N$-methyl-(S)-$\alpha$-methylbenzylamide (15b) and starting material 11b (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinic acid $N$-ethyl-(S)-$\alpha$-methylbenzylamide (14c) along with bis(1,4-cyclohexadien-3-yl)phosphinic acid $N$-ethyl-(S)-$\alpha$-methylbenzylamide (15c) and starting material 11c (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinic acid $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (14d) along with bis(1,4-cyclohexadien-3-yl)phosphinic acid $N$-isopropyl-(S)-$\alpha$-methylbenzylamide (15d) and starting material 11d (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane (2S)-2-(methoxymethyl)pyrolidinamide (26a) along with starting material 16b (202 MHz, CDCl$_3$)
$^3$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane (2S)-2-(trimethylsilyloxymethyl)pyrolidinamide (26b) along with starting material 16b (202 MHz, CDCl$_3$)

$^3$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane N-methyleneomenthylamide (26c) along with phenylphosphinous acid-borane N-methyleneomenthylamide (28) and starting material 16b (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)phenylphosphinous acid-borane N-methylbornylamide (26d) along with phenylphosphinous acid-borane N-methylbornylamide (29) (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (4-methyl-1,4-cyclohexadien-3-yl)(o-tolyl)phosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (34a) along with substrate (32a) (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (6-methyl-1,4-cyclohexadien-3-yl)(p-tolyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (34b) (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,4-cyclohexadien-3-yl)(p-anisyl)phosphinous acid-borane $N$-methyl-(S)-$\alpha$-methylbenzylamide (34c) along with substrate 32c (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (1,5-dimethyl-1,4-cyclohexadien-3-yl)(m-xylyl)phosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (34d) along with m-xylylphosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (35a) and substrate 32c (202 MHz, CDCl$_3$)

$^{31}$P NMR spectra of (1,5-dimethoxy-1,4-cyclohexadien-3-yl)(3,5-dimethoxyphenyl)phosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (34e) along with 3,5-dimethoxyphenylphosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (35b) (202 MHz, CDCl$_3$)
$^{31}$P NMR spectra of (p-anisyl)phenylphosphinous acid-borane N-methyl-(S)-α-methylbenzylamide (36) (202 MHz, CDCl$_3$)