Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Asymmetric metal free β-boration of α,β-unsaturated imines assisted by *(S)*-MeBoPhoz

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Supporting information for this article is given via a link at the end of the document.

Contents:

1.Instrumentation and chemical

All reactions and manipulations were carried out under Ar using Schlenk-type techniques or Radleys Carousel 12 reactions. Dry solvents were dried using a MBRAUN Solvent Purification System (MB-SPS). Bis(pinacolato)diboron was used as purchased from AllyChem. Phosphines were supplied by Johnson Matthey or Solvias and used without further purifications. Benzylamine and *n*-butylamine were distilled over KOH pellets and CaH_2 respectively. Molecular sieve (3 Å ,1-2 mm) beads were supplied by Alfa Aesar and stored at 100 °C prior to use, followed by cooling under Ar. Montmorillonite K 10 was provided by Sigma Aldrich and stored at 100 °C prior to use, followed by cooling under Ar. All other materials were purchased directly from standard chemical suppliers and used without further purification, unless stated otherwise.

High performance liquid chromatography (HPLC) was carried out using a Shimadzu Class VP model equipped with an autosampler and UV detector or a Hewlett-Packard HP 5989 MS at an ionizing voltage of 70 eV. Chiral HPLC was carried out on either a Chiralpak AD-H column (dimensions 250 × 4.6 mm) or Chiralpak OD-H column (dimensions 250 x 4.6 mm) in order to determine enantiomeric excesses (ees). Alternatively ESI-TOF was also used. NMR spectra were obtained using a Varian Mercury 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shift of residual solvent resonances. Coupling constants (J) are given in Hz and NMR peaks are described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Deuterated chloroform ($CDCl_3$) was used as solvent for routine NMR measurements.

2. General experimental procedure for organocatalytic β-boration of α,β-unsaturated ketimines generated *in situ* using bis(pinacolato)diboron.

Montmorillonite K 10 (140 mg) and ketone or aldehyde (0.5 mmol) were added under Ar into an oven-dried Schlenk tube with a stirring bar. THF (2 mL) and amine (0.5 mmol) were added and the resulting mixture was stirred for 6 h at rt. After addition of phosphine (10 mol%), Cs_2CO_3 (15 mol%), bis(pinacolato)diboron (1.1 eq), MeOH (2.5 eq), the reaction mixture was stirred overnight at 70 °C. The conversion and the enantiomeric excess (ee) were determined by NMR spectroscopy and HPLC-UV, respectively.

3 General experimental procedure for organocatalytic β-boration of α,β-unsaturated aldimines generated *in situ* with bis(pinacolato)diboron.

Molecular sieves 3Å (1g), aldehyde (1 mmol), THF (4 mL) were added under Ar to an oven-dried Schlenk tube with a stirring bar. Benzhydrylamine (1 mmol) was added and the resulting mixture stirred for 5 h at rt.

In another oven-dried Schlenk tube, phosphine (6 mol%), $NaOBu^t$ (9 mol%), bis(pinacolato)diboron (1.1 eq) were added under Ar. To this vessel, was decanted the above aldimine solution and the combined mixture was stirred at rt. After 5 mins, MeOH (1.25 mmol) was added and the reaction mixture was heated at 70 °C overnight.

4. Derivatization protocols

4.1 General procedure for the synthesis of γ-amino alcohols.[1]

A solution of $NaBH_4$ (1.5 mmol) in methanol (2 mL) was added to a solution of the β-borated ketimine/aldimine in THF and the mixture stirred for 3 h at rt. All solvent was removed under reduced pressure, and the mixture was redissolved in THF (4 mL), followed by the addition of aqueous NaOH (0.6 mL, 20% w/v solution), H_2O_2 (0.25 mL, 30% w/v solution). The resulting mixture was refluxed for 1 h, cooled to rt, and the mixture was partionated between EtOAc and saturated aqueous NaCl solution. The aqueous layer was re-extracted further with EtOAc (3 x). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield a crude yellow oil. Purification was achieved by silica gel chromatography using a mixture of petroleum ether and EtOAc.

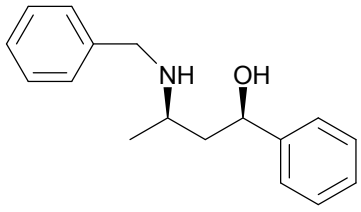
4.2 Synthesis of γ-amino alcohols O,N-diacetate derivatives.[2]

When aldehydes were used as substrates for the synthesis of γ-aminoalcohols, transformation into diacetate was required in order to determine the enantioselectivity.

The γ-amino alcohol (0.19 mmol), pyridine (0.5 mL, 6.2 mmol) and acetic anhydride (0.5 mL, 5.3 mmol) were combined in DCM (3.0 mL) and stirred overnight. The resulting solution was diluted with DCM (10.0 mL), washed with HCl (3 x 10 mL, w/v 20%) and water (3 x), and the organic layer was separated, dried over $MgSO_4$ and evaporated under reduced pressure to yield a dark yellow oil.

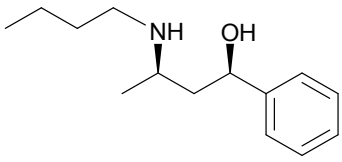
4.3. Characterization of γ-amino alcohols:

3-(Benzylamino)-1-phenylbutan-1-ol[1]



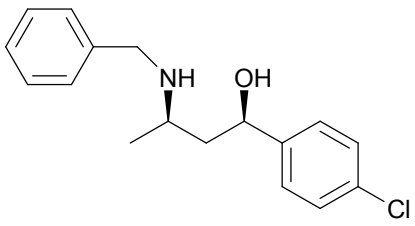
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33- 7.13 (m, 10H), 4.84 (dd, *J* 10.6, 2.0 Hz, 1H), 3.92 (d, *J* 12.5 Hz, 1H), 3.71 (d, *J* 12.5, 1H), 3.09 - 2.95 (m, 1H), 1.68 (dt, *J* 14.4, 2.3 Hz, 1H), 1.52 (dt, *J* 14.4, 10.8 Hz, 1H), 1.14 (d, *J* 6.3 Hz, 3H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 145.3, 139.3, 128.6, 128.4, 128.2, 1271.3, 127.0, 125.6, 75.4, 54.3, 50.9, 46.1, 21.1

3-(Butylamino)-1-phenylbutan-1-ol[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 5H), 4.95 (dd, *J* 11.2, 2 Hz, 1H), 3.07-3.02 (m, 1H), 2.86-2.82 (m, 1H), 2.59-2.55 (m, 1H), 1.71 (dt, *J* 14.4, 2 Hz, 1H), 1.57-1.48 (m, 3H), 1.43-1.38 (m, 2H), 1.17 (d, *J* 6.4Hz, 3H), 0.96 (t, *J* 6Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ 142.3, 128.4, 127.5, 125.7, 74.1, 55.2, 50.9, 44.4, 30.6, 20.7, 20.0, 14.0

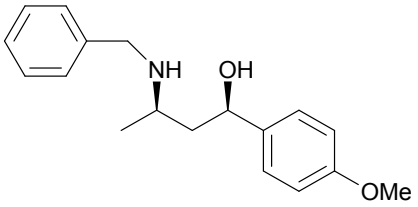
3-(Benzylamino)-1-(4-chlorophenyl)butan-1-ol[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 7.20 (d, *J* 8.4, 2H), 7.13 (d, *J* 8.4 Hz, 2H), 4.84

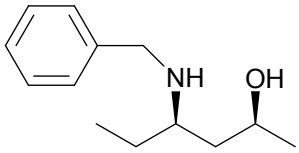
(dd, *J* 10.8, 2.4 Hz, 1H), 3.68 (d, *J* 10 Hz, 1H), 3.65 (d, *J* 10 Hz, 1H), 3.10-3.20 (m, 1H), 1.59 (dt, *J* 15.2, 10.8 Hz, 1H), 1.37 (dt, *J* 15.2, 2.4 Hz, 1H), 1.29 (d, *J* 6.8 Hz, 3H). **^{13}C NMR:** ($CDCl_3$, 100.6 MHz) δ 139.7, 138.4, 133.4, 131.6, 128.8, 127.9, 127.5, 116.8, 63.4, 55.2, 46.1, 27.4, 20.6

3-(Benzylamino)-1-(4-methoxyphenyl)butan-1-ol[1]



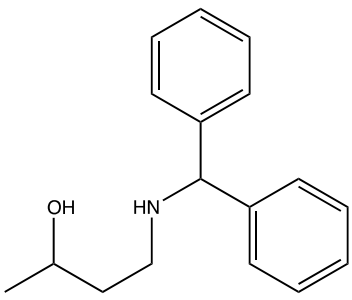
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5H), 7.13 (d, *J* 8.8 Hz, 2H), 6.77 (d, *J* 8.8 Hz, 2H), 4.81 (dd, *J* 11.2, 2.0 Hz, 1H), 3.71 (s, 3H), 3.11 (m, 5H), 1.62 (dd, *J* 15.2, 10.8 Hz, 1H), 1.36 (dt, *J* 15.2, 2.4 Hz,1H), 1.16 (d, *J* 6.8 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ 157.8, 136.2, 135.0, 130.2, 129.3, 128.6, 126.8, 113.8, 75.7, 57.0, 55.2, 54.6, 40.9, 19.2.

4-(Benzylamino)hexan-2-ol



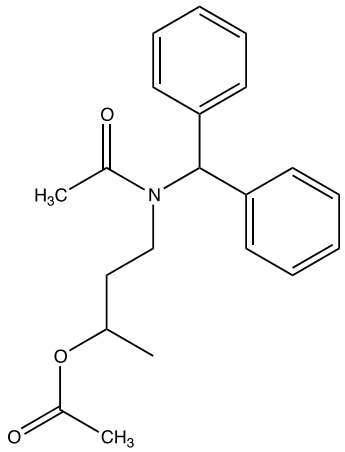
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.20 (m, 5H), 4.05 (m, 1H), 3.85 (d, *J* 12 Hz, 1H), 3.63 (d, *J* 12 Hz, 1H), 2.70-2.80 (m, 1H), 1.70-1.30 (m, 4H), 1.10 (d, *J* 6.8Hz, 3H); 0.89 (t, *J* 7.2 Hz 7.2, 3H).
^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 139.4, 128.5, 128.5, 127.2, 69.2, 59.4, 50.2, 41.1, 26.3, 23.9, 9.4

4-(Benzhydrylamino)butan-2-ol[2]



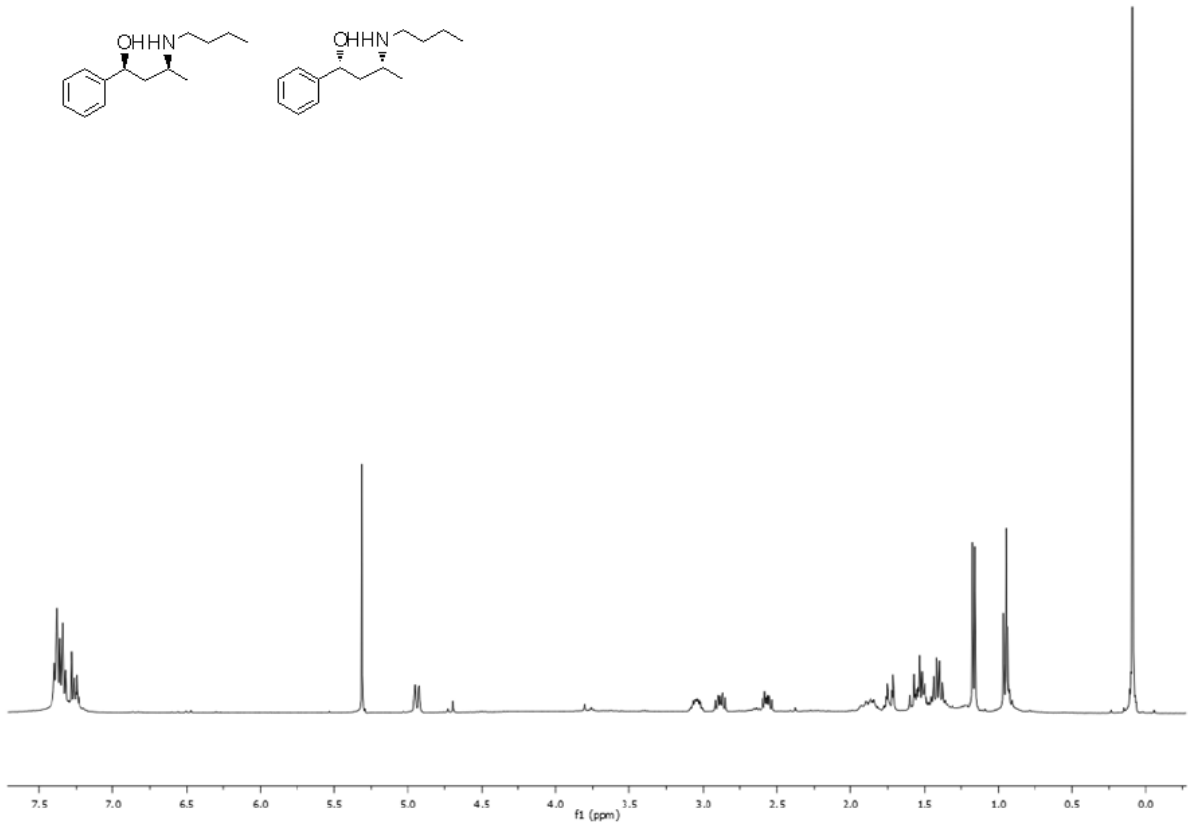
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.17 (m, 10H), 4.78 (s, 1H), 4.02-3.94 (m, 1H), 2.95 (ddd, *J* 11.9, 3.6, 1.4 Hz, 1H), 2.71 (dt, *J* 10.6, 3.4 Hz, 1H), 1.69-1.47 (m, 2H), 1.17 (d, *J* 6.2 Hz, 1H). **^{13}C NMR**: (100.6 MHz, $CDCl_3$) δ 143.3, 142.8, 128.6, 128.6, 128.4, 127.2, 127.1, 126.9, 69.5, 67.9, 47.1, 37.5, 23.4.

4-(*N*-Benzhydrylacetamido)butan-2-yl acetate [2]

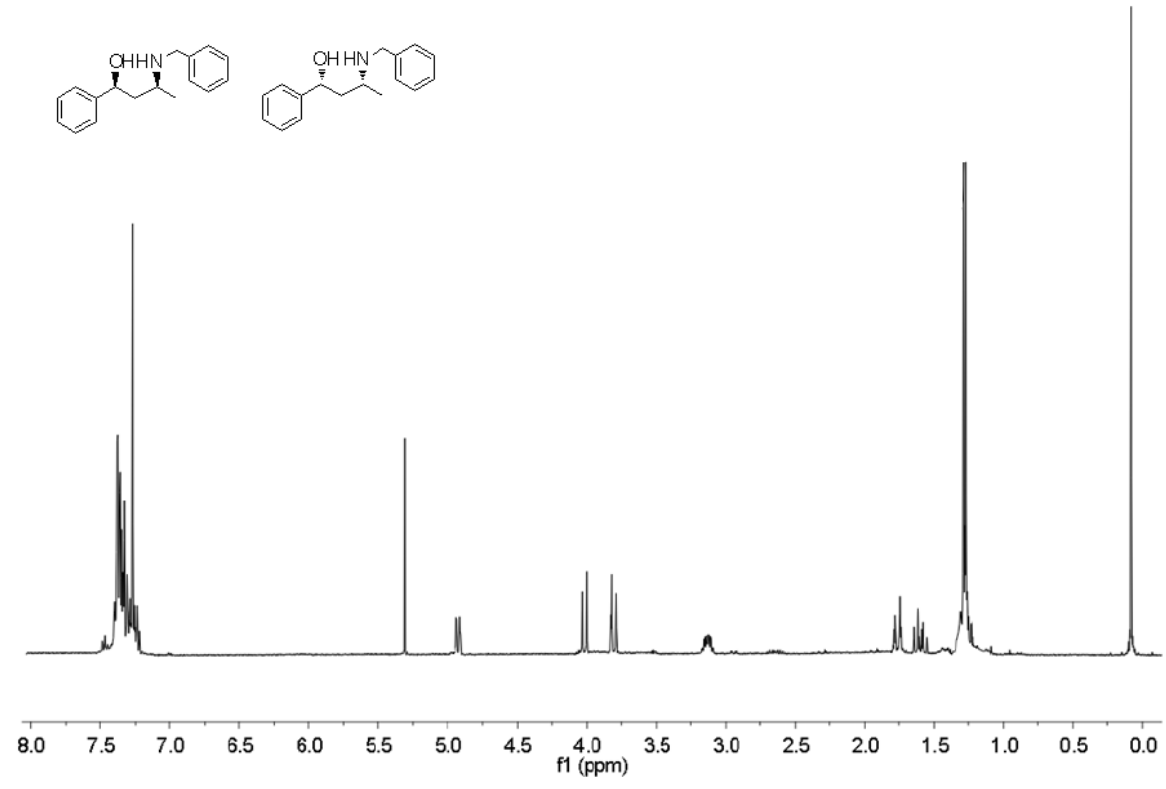


^{1}H NMR (400 MHz, $CDCl_3$) observed as a mixture of rotamers, major rotamer: δ 7.32-7.04 (m, 10H), 6.15 (s, 1H), 4.53-4.41 (m, 1H), 3.36-3.15 (m, 2H), 2.10 (s, 3H), 1.83 (s, 3H), 1.21-1.10 (m, 2H), 0.85 (t, *J* 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 170.4, 139.6, 139.1, 129.2, 129.1, 128.7, 128.7, 128.5, 128.0, 69.2, 66.0, 56.97, 41.4, 33.9, 21.7, 21.3.

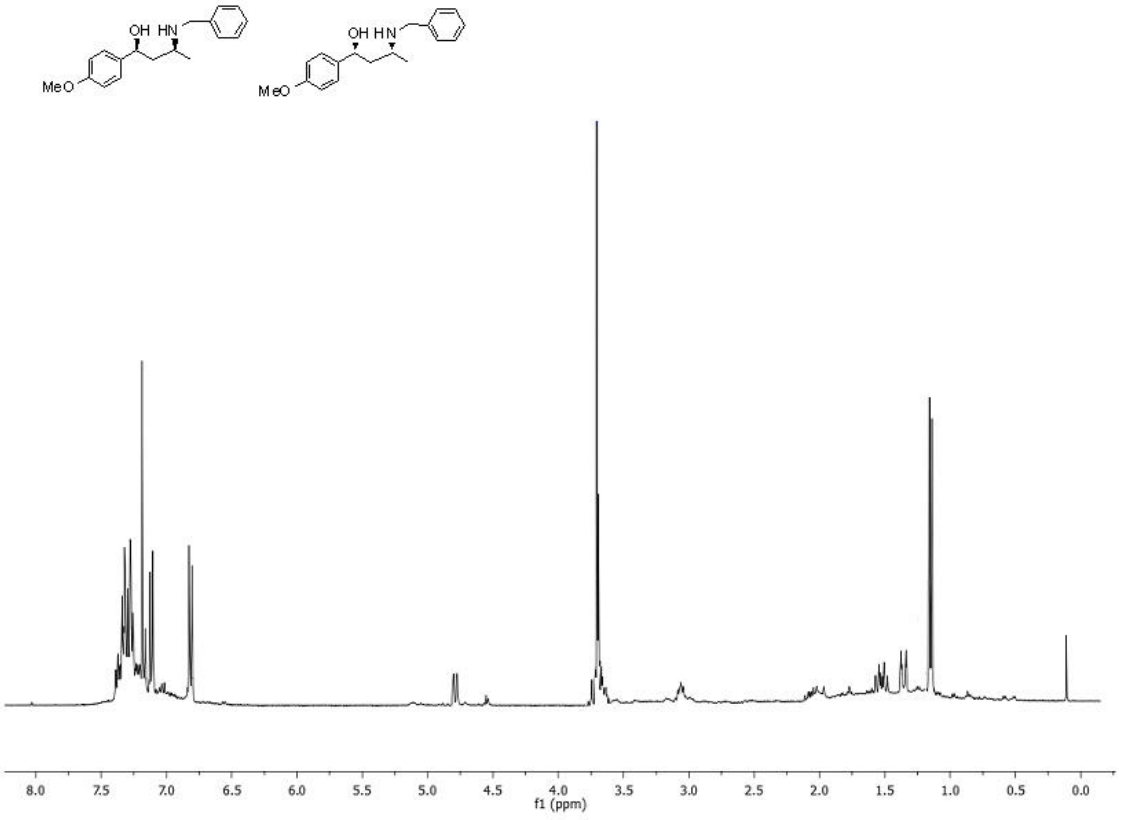
^{1}H NMR


OHHN
OHHN
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

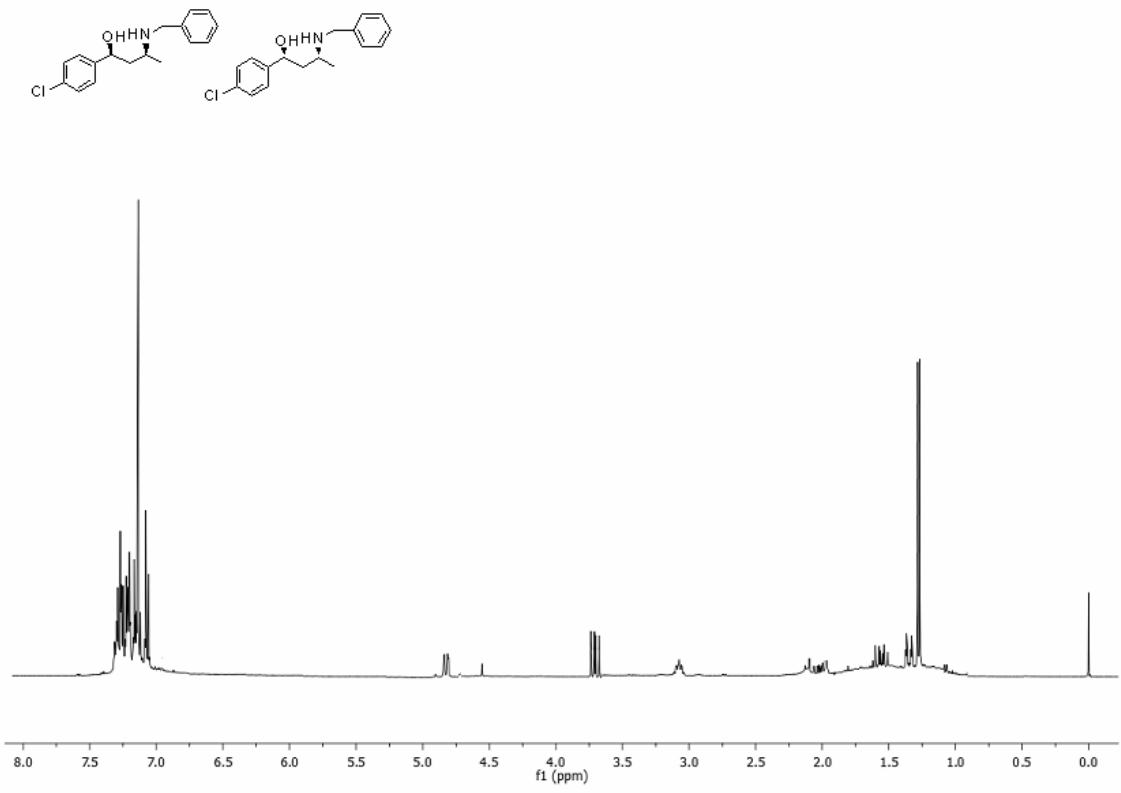
^{1}H NMR


OHHN
OHHN
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

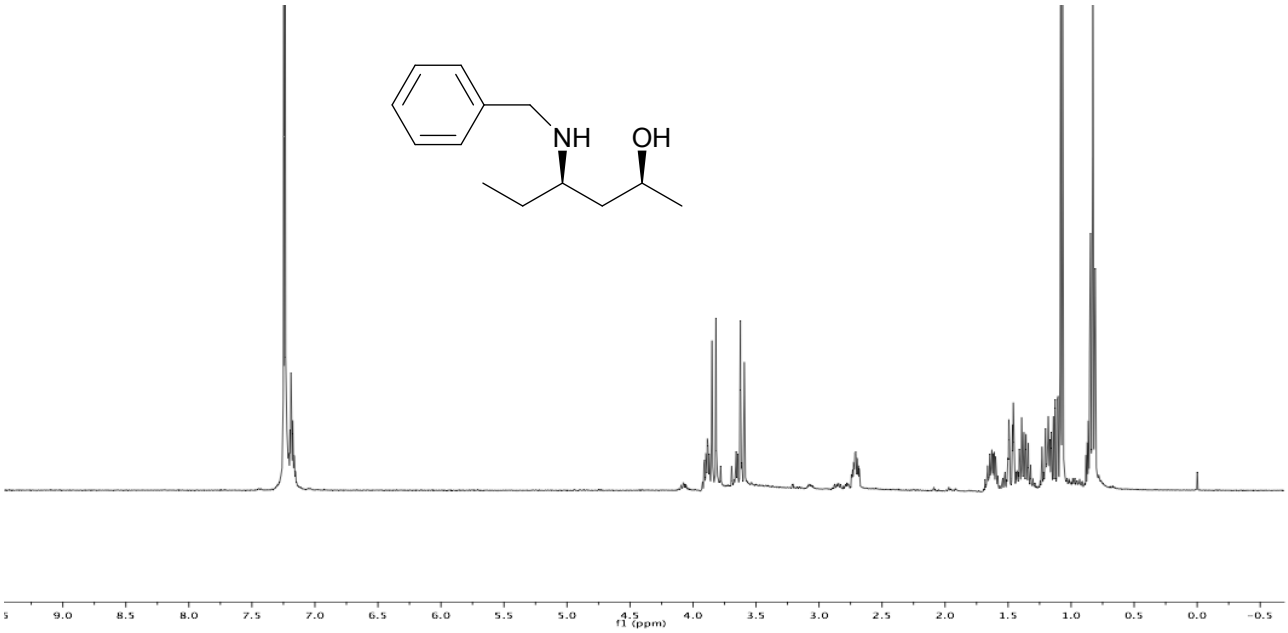
^{1}H NMR


OH HN
MeO
OH HN
MeO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

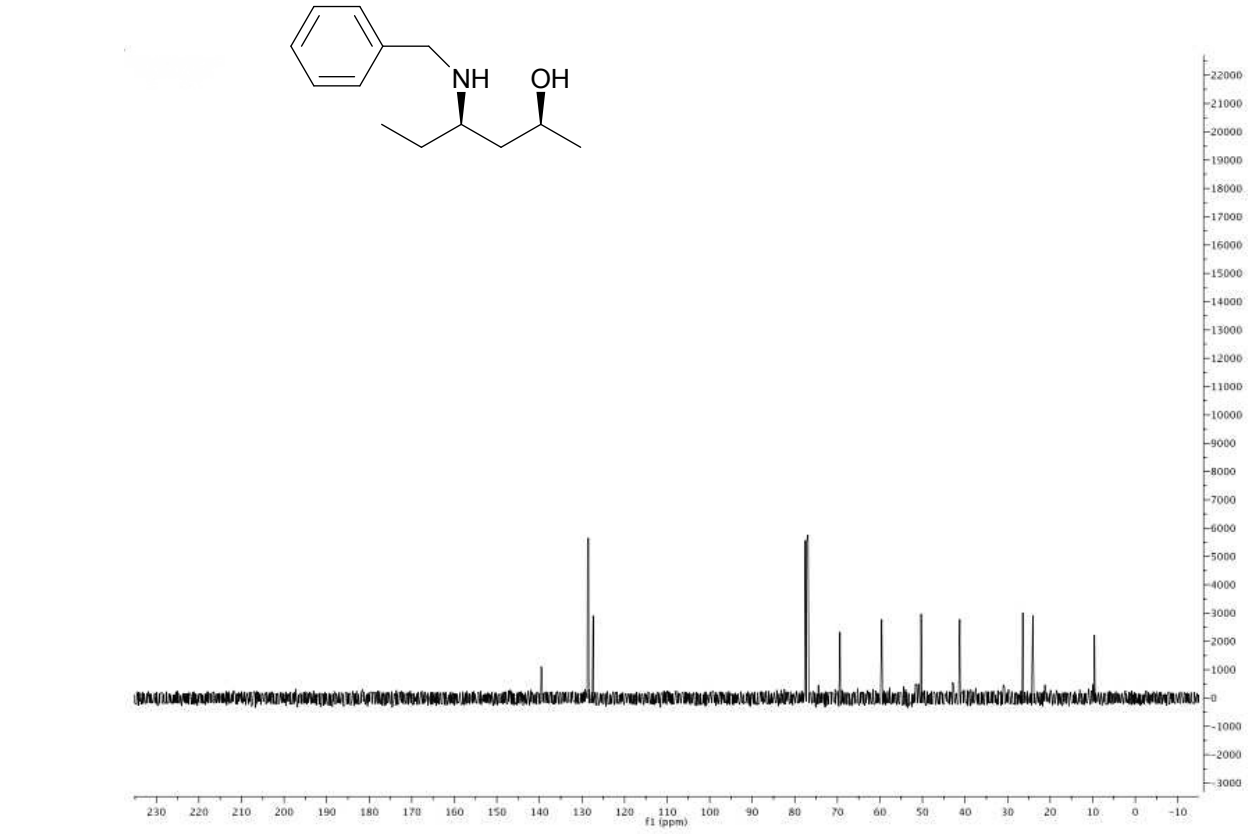
^{1}H NMR


OHHN
Cl
OHHN
Cl
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{1}H NMR



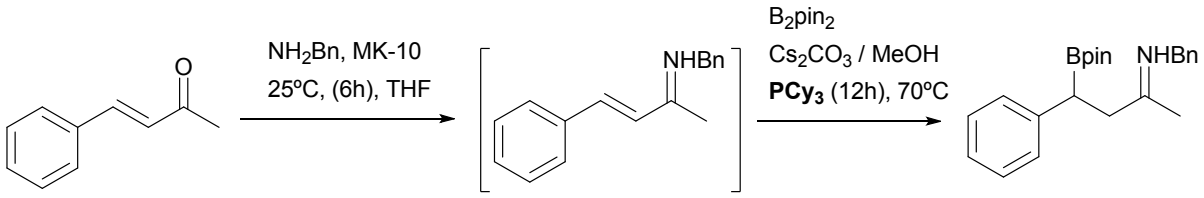
^{13}C NMR



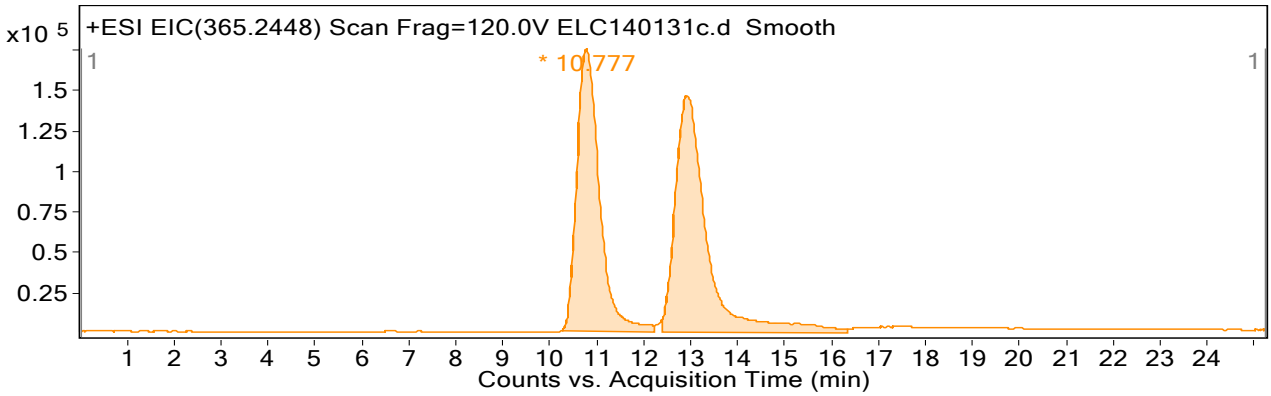
5. Analysis of the enantiomeric excesses (ees) by HPLC

5.1 Analysis of 5.1 Analysis of 1-phenyl-N-(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2- ylidene)methanamine

The enantiomeric excess (ee) was obtained by chiral HPLC-MS analysis using a OD-H column (heptane:2-propanol, 99:1, flowrate 1mL/min, 25 °C). The evaluation was carried using an aliquot of β-borated imine.

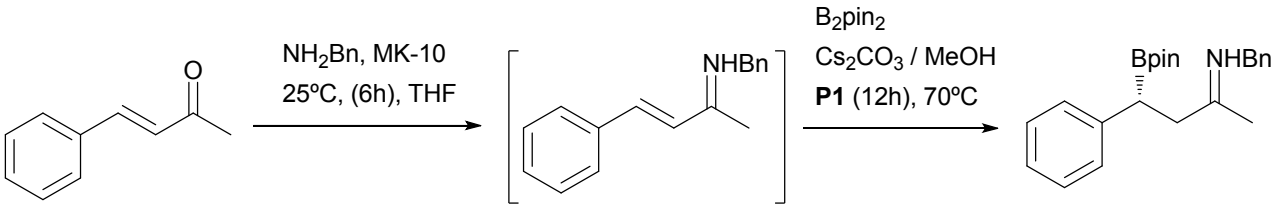


Racemic mixture with PCy_3

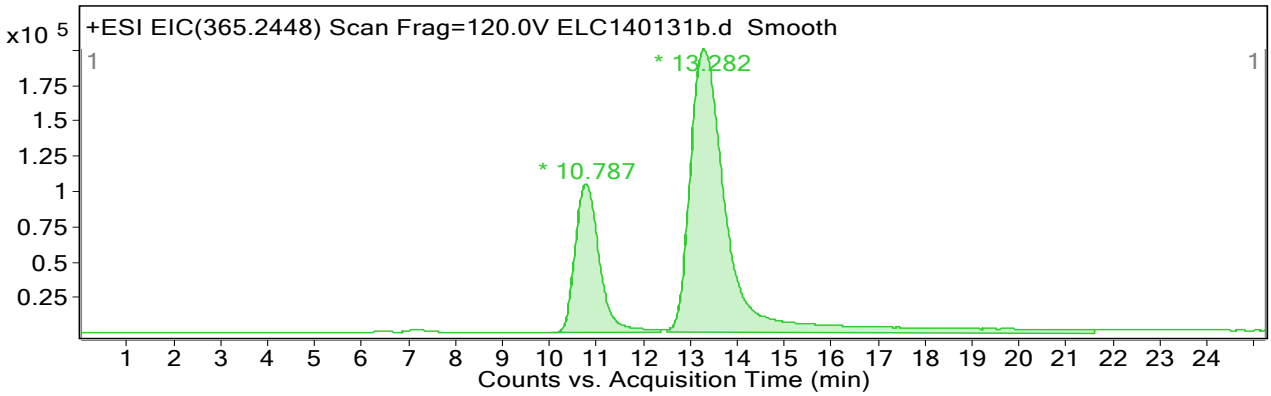


t_r (*S*)-enantiomer: 10.77 min,

t_r (*R*)-enantiomer: 13.28 min



54% ee in the presence of 10 mol% (*S*)-MeBoPhoz (**P1**)

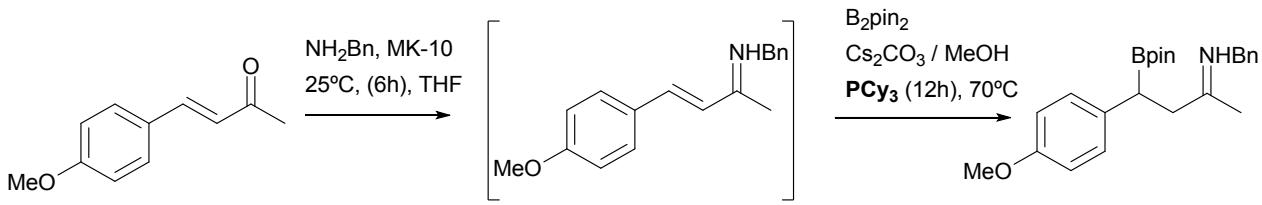


t_r (*S*)-enantiomer: 10.77 min,

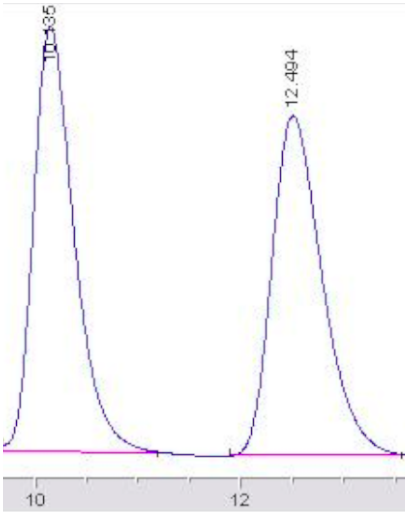
t_r (*R*)-enantiomer: 13.28 min

5.2 Analysis of N-(4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2- yl)butan-2-ylidene)-1-phenylmethanamine

The ee was obtained by HPLC-UV analysis using a OD-H column (hexane:2-propanol, 98:2, flowrate 1mL/min, 25 °C). The wavelength used for the analysis was 210 nm. The evaluation was carried using an aliquot of β-borated imine.

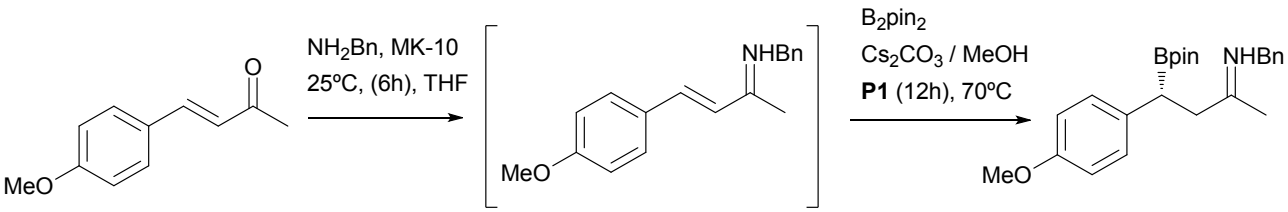


Racemic mixture with PCy_3

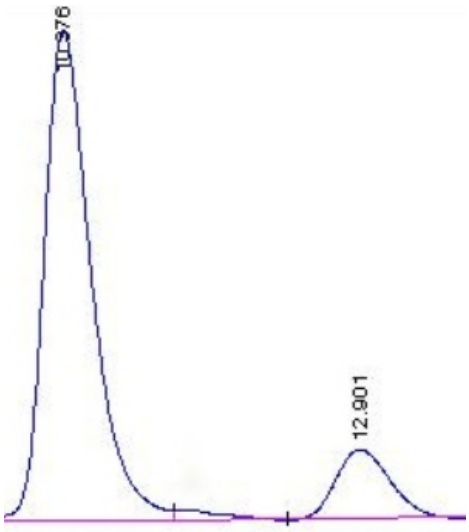


t_r (*R*)-enatiomer: 10.13 min,

t_r (*S*)-enantiomer: 12.49 min



70 % ee in the presence of 10 mol% (*S*)-MeBoPhoz (**P1**)

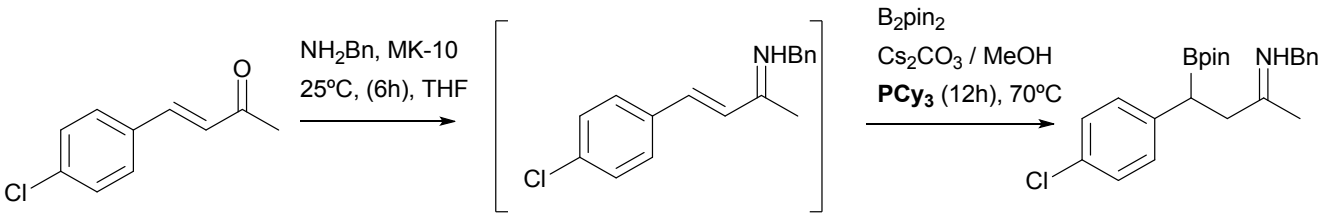


t_r (*S*)-enantiomer 12.90 min

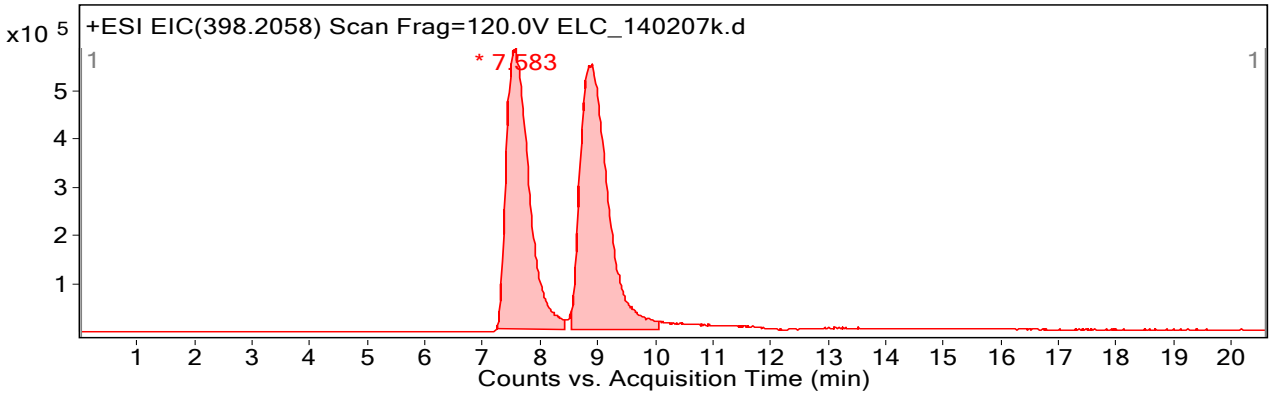
t_r (*R*)-enantiomer 10.37 min

5.3 Analysis of N-(4-(4-chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ylidene)-1-phenylmethanamine

The enantiomeric excess was obtained by chiral HPLC-MS analysis using a OD-H column (hexane/2-propanol, 98:2, flowrate 1mL/min, 25 °C). The evaluation was carried using an aliquot of β-borated imine.

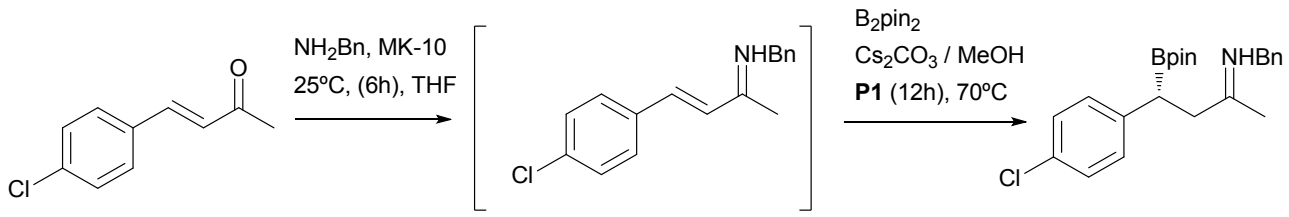


Racemic mixture with PCy_3

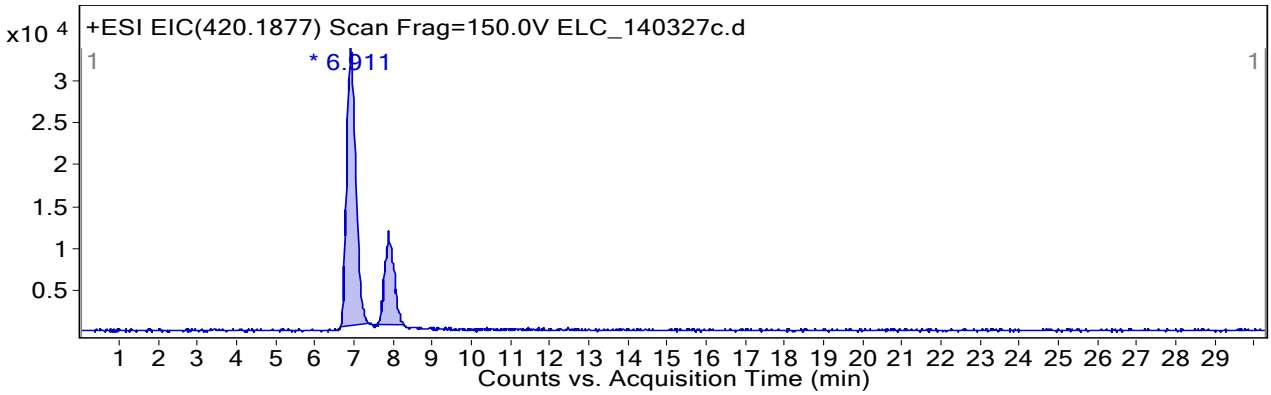


t_r (*R*)-enantiomer: 7.58 min

t_r (*S*)-enantiomer: 8.91 min



50 % ee in the presence of 10 mol% (*S*)-MeBoPhoz (**P1**)

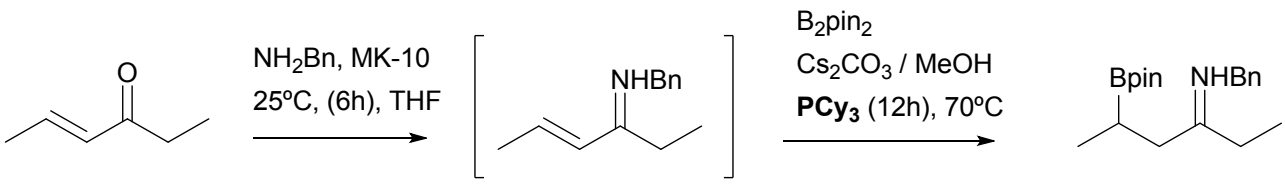


t_r (*R*)-enantiomer: 6.91 min

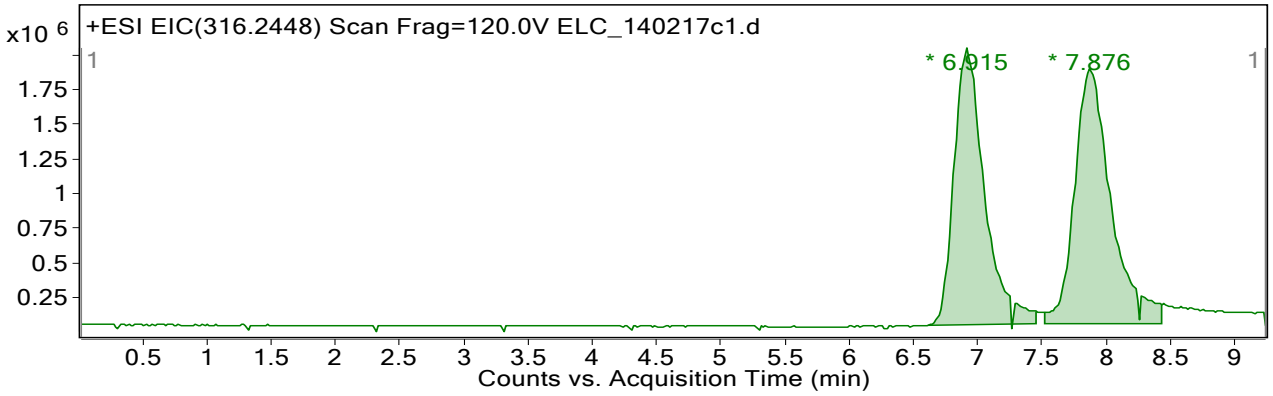
t_r (*S*)-enantiomer: 7.89 min

5.4 Analysis of 1-phenyl-N-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-ylidene)methanamine

The ee was obtained by chiral HPLC-MS analysis using a OD-H column (hexane:2-propanol, 99:1, flowrate 1mL/min, 25 °C). The evaluation was carried using an aliquot of β-borated imine.

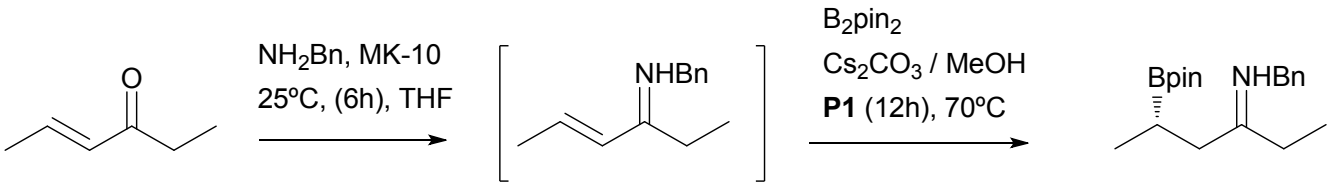


Racemic mixture with PCy_3

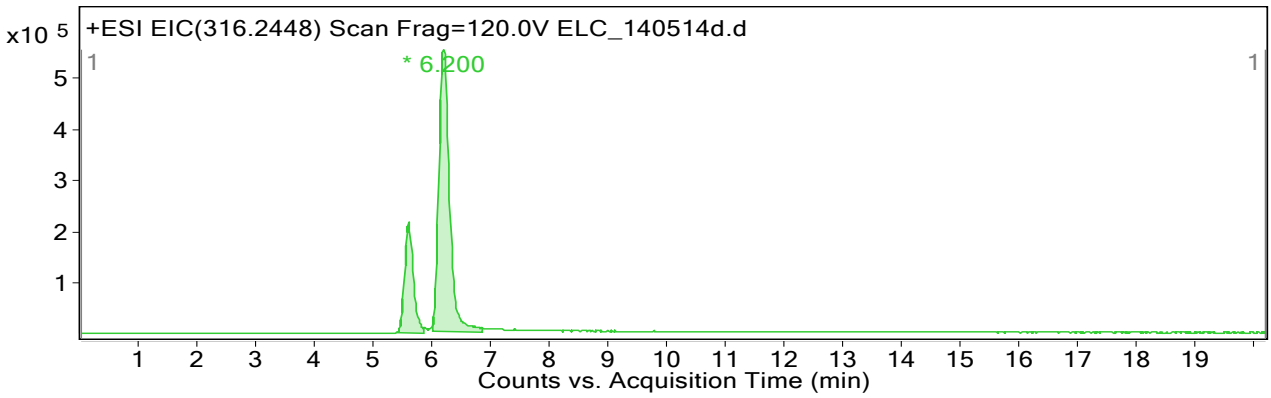


t_r (*S*)-enantiomer: 6.91min

t_r (*R*)-enantiomer: 7.78 min

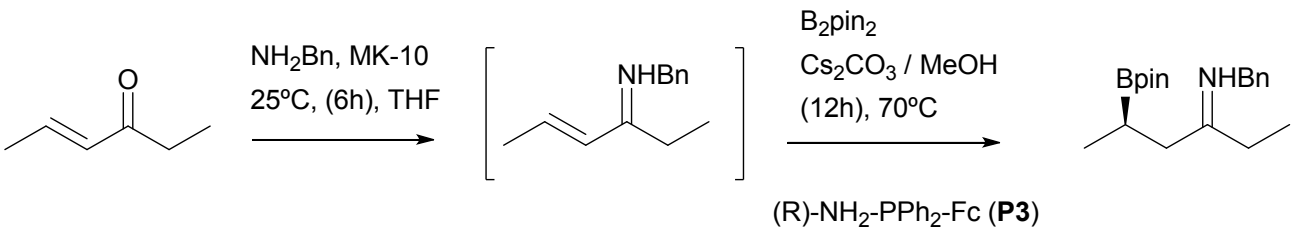


51% ee in the presence of 10 mol% (*S*)-MeBoPhoz (**P1**)

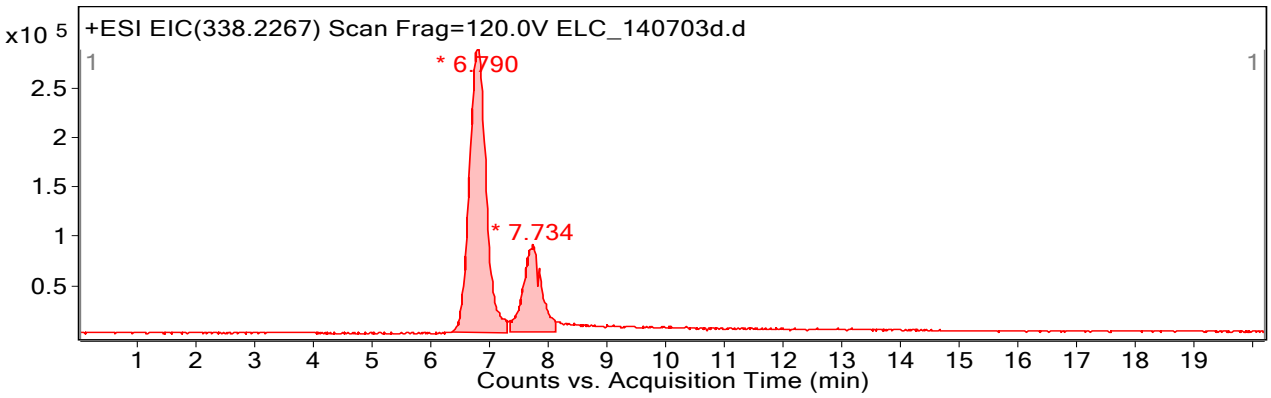


t_r (*S*)-enantiomer: 5.61min

t_r (*R*)-enantiomer: 6.20 min

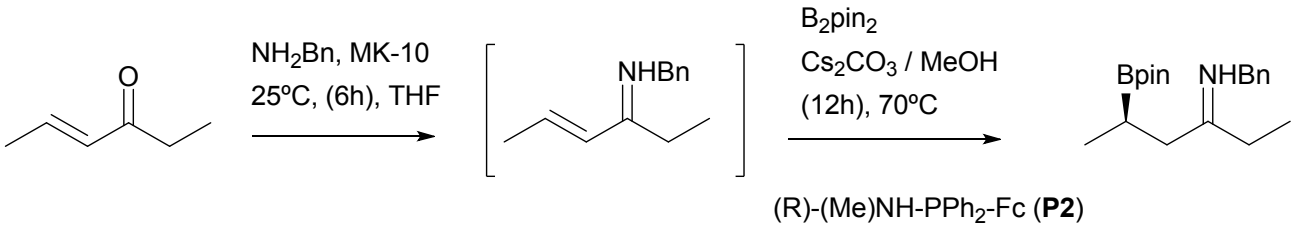


50% ee in the presence of 10 mol% (*R*)-NH_2-PPh_2-Fc (**P3**)

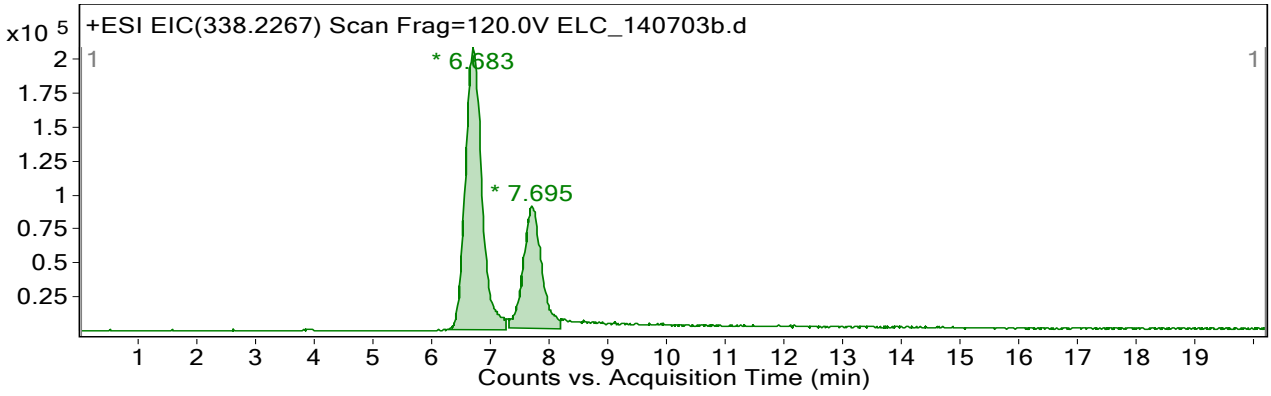


t_r (*S*)-enantiomer: 6.79min

t_r (*R*)-enantiomer: 7.73 min



35% ee in the presence of 10 mol% (*R*)-MeNH-PPh_2-Fc (**P2**)

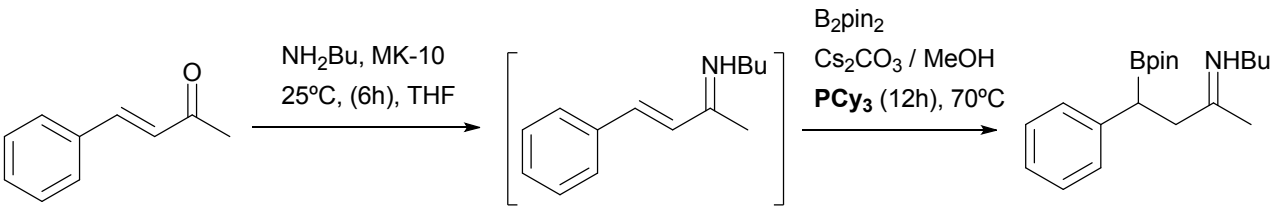


t_r (*S*)-enantiomer: 6.68min

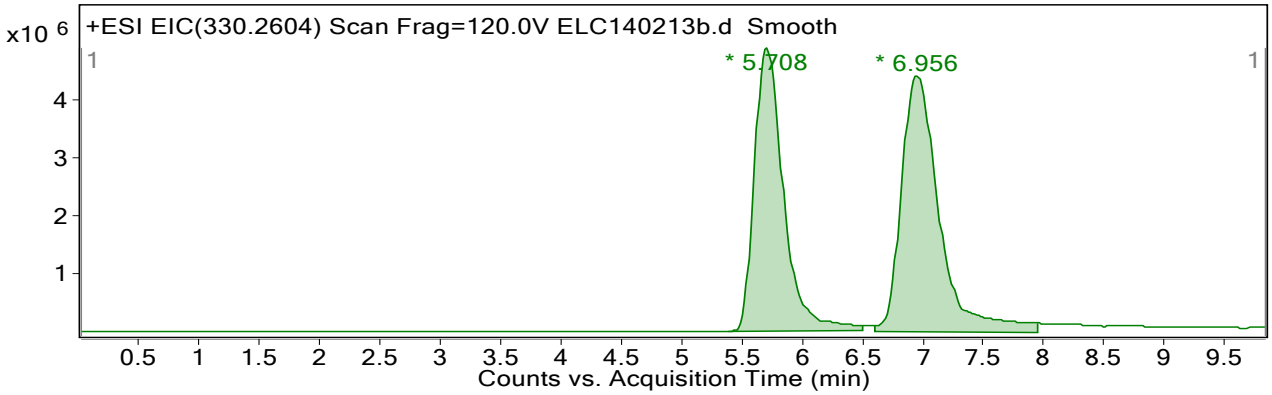
t_r (*R*)-enantiomer: 7.69 min

5.5 Analysis of *N*-(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ylidene)butan-1-amine

The optimization of racemic mixture was obtained by chiral HPLC-MS analysis using a OD-H column (hexane:2-propanol, 98:2, fllowrate 1mL/min, 25 °C). The evaluation was carried using an aliquot of β-borated imine.



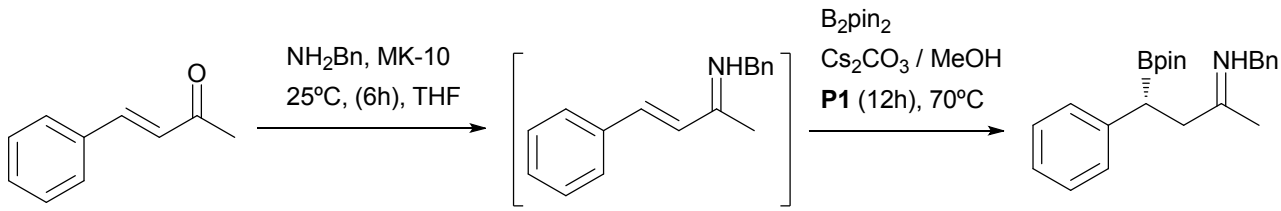
Racemic mixture with PCy_3



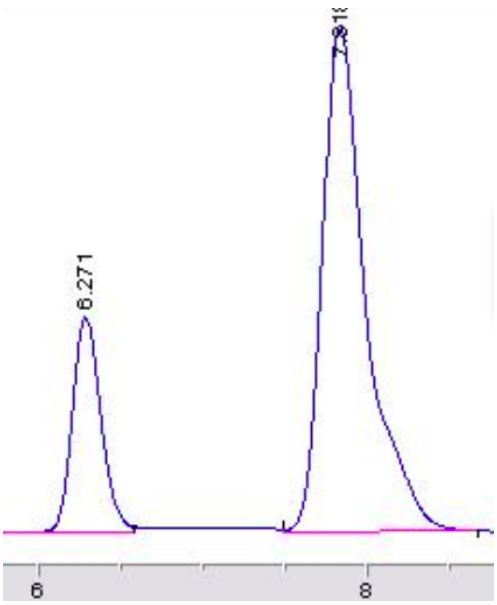
t_r (*S*)-enantiomer: 5.71 min

t_r (*R*)-enantiomer: 6.95 min

In this particular case, the ee analysis was run by HPLC-UV (wavelength at 210 nm) using a ODH chiral column (hexane;2-propanol, 98:2, flowrate 1mL/min, 25 °C). The evaluation was carried out using an aliquot of β-borated imine.



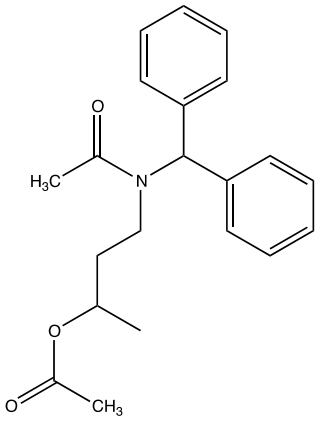
53 % ee in the presence of 10 mol% (*S*)-MeBoPhoz



t_r (*S*)-enantiomer: 6.27min

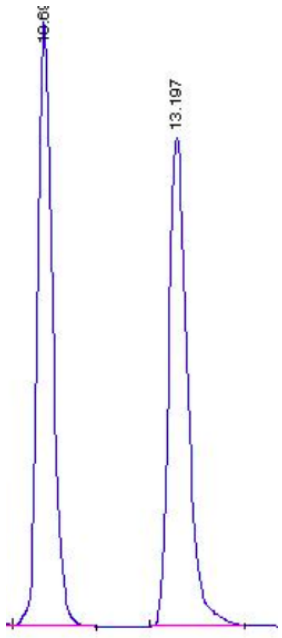
t_r (*R*)-enantiomer: 7.81 min

5.6 Anaylsis of 4-(*N*-benzhydrylacetamido)butan-2-yl acetate



The enantiomeric excess was obtained by HPLC-UV analysis using an AD-H column (hexane:2-propanol, 90:10, flowrate 1mL/min, 25 °C). The wavelength used for the analysis was 210 nm.

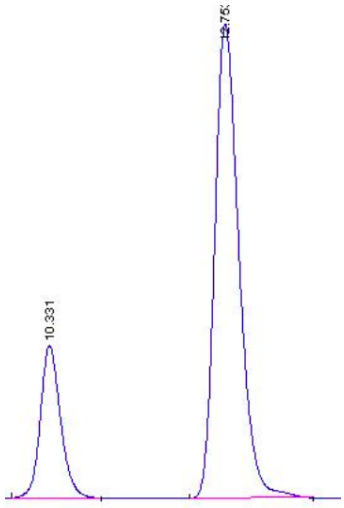
Racemic mixture with PCy_3



t_r (*S*)-enantiomer: 10.69 min

t_r (*R*)-enantiomer: 13.21 min

ee of 57% with (*S*)-MeBoPhoz



t_r (*S*)-enantiomer: 10.33 min

t_r (*R*)-enantiomer: 12.75 min

6. Computational details

Molecular structures for all species were optimized without constraints by using DFT-based methods as implemented in the Amsterdam Density Functional (ADF v2009.01) package.[3] A triple-ξ plus polarization Slater basis set was used on all atoms. Relativistic corrections were introduced by scalar-relativistic zero-order regular approximation (ZORA).[4] For geometry optimizations we used the local VWN correlation potential[5] together with the Becke exchange[6] and the Perdew correlation [7,8] (BP86) generalized gradient corrections. Stationary points in the potential energy hypersurface were characterized either as minima or transition states by means of harmonic vibrational frequency calculations. Standard corrections to Gibbs free energy at 298 K were evaluated, too. Solvent effects were introduced by using the continuous solvent model COSMO[9] and tetrahydrofuran as solvent.

Computed relative energies (in kcal·mol^{-1}) for the considered species

	ΔE	ΔG	ΔG_{sol}
R	**0.0**	**0.0**	**0.0**
TS	**13.5**	**32.3**	**55.3**
I	**-18.8**	**-51.7**	**-42.4**

Optimized Structures of the involved species

Model imine (trans)

C	-1.028226840	-2.184917209	4.719714171
C	-1.789448688	-3.352714560	4.282161801
C	-1.605529785	-4.635646105	4.673835984
H	-0.814157130	-4.859121064	5.394363912
C	0.103805642	-2.319151275	5.716024884
H	1.050645556	-1.993811905	5.258388077
H	-0.072707807	-1.663843126	6.582010348
H	0.236783486	-3.341377782	6.082737348
H	-2.571218103	-3.100518773	3.562742742
C	-2.363617625	-5.807350559	4.234192555
C	-3.424418072	-5.743551902	3.305799313
C	-2.022599568	-7.070488563	4.760419682

C	-4.109294946	-6.894412130	2.924890401
H	-3.715275976	-4.783454386	2.878294791
C	-2.708464762	-8.223677260	4.379276612
H	-1.204094089	-7.139713275	5.480335934
C	-3.756324299	-8.140910732	3.458459325
H	-4.926358189	-6.822186477	2.205685760
H	-2.424617874	-9.188457497	4.801595912
H	-4.295694524	-9.039642037	3.156309756
N	-1.386437186	-1.053213959	4.196624308
C	-0.669900880	0.149145449	4.579070896
H	-0.741757187	0.309491745	5.672796140
H	0.412654080	0.041404371	4.373423149
C	-1.170716574	1.401900803	3.877695551
C	-0.516735559	2.621465117	4.111770820
C	-2.267878885	1.380223413	3.010208071
C	-0.949544330	3.795904857	3.493544183
H	0.343572414	2.652084750	4.786187565
C	-2.703639936	2.556444717	2.389296721
H	-2.769224489	0.429762577	2.829493626
C	-2.048435900	3.767097506	2.627416603
H	-0.428054095	4.734900651	3.686223617
H	-3.560868817	2.524222983	1.714401576
H	-2.388684649	4.683104316	2.141671476

Bispin·OMe$^-$

B	-0.825545990	-0.435192997	-0.198587711
O	-1.964707449	-1.172534160	0.186215897
O	-1.222522098	0.865904340	-0.571661586
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C	-3.084722418	-0.256073243	0.333961099
C	-3.136410996	0.148028752	1.815168202
C	-4.370960027	-0.985755453	-0.052418588
C	-3.093672286	0.705320909	-2.071401112
C	-3.118309556	2.315534641	-0.147849350
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C	2.589998899	-0.233291352	1.333795794
C	1.992729478	1.984637077	0.142694610
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C	2.824543231	0.597035392	2.602426781
H	-2.584437766	1.452379177	-2.696620712
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H	-3.218719659	-0.764498610	2.422208797
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H	4.713812253	1.272046113	0.045116882
H	4.454123634	-0.245529528	-0.872389593
H	3.820342073	1.072726478	2.596625310
H	2.764265156	-0.059771913	3.484901816

H	3.350963939	-2.064321524	2.182694494
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H	-2.782648398	-0.290734907	-2.414232997
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H	-4.542602081	-1.815560510	0.648954501
H	-2.209917847	0.660774693	2.106696988
H	0.999480143	1.898714385	0.601044143
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H	2.058689590	1.377470858	2.708199276
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TS

C	-2.346592220	-1.114985927	3.523287573
C	-1.715440265	-2.388169548	3.382284163
C	-2.358399497	-3.637750605	3.233198718
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H	-0.624480110	-2.362477380	3.444121630
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C	-1.535751552	-6.480416231	0.860782234
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B	-4.194372962	-5.406438607	4.682471479
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I

C	-0.655011822	-1.268406291	1.860724100
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C	-2.427697658	-1.066833694	-1.152734425
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H	-2.341315774	-0.300409835	-4.485178867
N	-0.762940948	-0.754917961	3.098528070
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H	1.168945588	0.120382320	3.419922974
H	-0.021959075	1.227304403	2.747967039
C	-0.206788033	0.897303996	4.835051770
C	0.522762137	1.990160426	5.330617138
C	-1.192813811	0.327637816	5.649958446
C	0.277310186	2.506035189	6.606702828
H	1.295221597	2.443223164	4.700564373
C	-1.442676262	0.839724710	6.930833262
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C	-0.712082959	1.929139251	7.415833629
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C	1.851104208	-4.636966205	0.811416559
O	-0.425490220	-5.255033753	1.011551875
O	1.024939305	-3.742713165	0.009717817
B	-0.307836294	-3.996854953	0.377803526
C	2.184444624	-3.907322871	2.118584883
H	2.814879430	-4.519723998	2.781444851
H	2.729362649	-2.984241174	1.876124284
H	1.265290652	-3.620485222	2.649654670
C	3.130147296	-4.939026940	0.031741620
H	3.708297441	-4.011316023	-0.088285435
H	3.758131998	-5.665010226	0.572284047
H	2.910691506	-5.335269521	-0.968197229
C	1.070816237	-6.606883338	2.348177527
H	0.344820315	-7.431272435	2.409726566
H	2.083188065	-7.034538539	2.429220351
H	0.898403164	-5.935895867	3.198479771
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H	1.871295969	-7.432374875	-0.174660188
H	0.095445220	-7.568180816	-0.037271907
H	0.808193603	-6.335081910	-1.104716638

MeOBpin

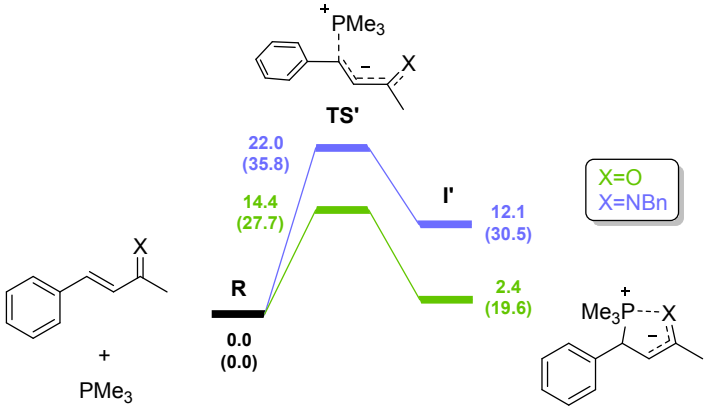
C	0.065731	0.180742	-0.317030
C	1.625812	0.155126	-0.562509
B	0.826565	2.270216	-0.836548
O	-0.316711	1.483894	-0.883772
O	1.978291	1.578202	-0.502474

C	-0.307565	0.220676	1.167921
H	-1.378143	0.450322	1.258404
H	-0.117218	-0.744678	1.658779
H	0.258098	0.999852	1.697483
C	-0.722010	-0.907954	-1.037571
H	-0.413835	-1.904985	-0.687697
H	-1.793760	-0.789887	-0.824322
H	-0.580407	-0.857324	-2.124111
C	2.433585	-0.585126	0.498641
H	2.149766	-1.648113	0.532976
H	3.502726	-0.526088	0.251845
H	2.288245	-0.148085	1.494095
C	2.004403	-0.337445	-1.963266
H	3.068901	-0.127872	-2.134217
H	1.840395	-1.419485	-2.071395
H	1.424888	0.183737	-2.738007
O	0.855704	3.611430	-1.094519
C	-0.386720	4.280955	-1.365803
H	-1.061333	4.228790	-0.499562
H	-0.149124	5.329745	-1.576635
H	-0.894398	3.841147	-2.235644

Computed relative energies (in kcal·mol^{-1}) for the considered species

	ΔE	ΔG	ΔG_{sol}
R	**0.0**	**0.0**	**0.0**
TS	**13.5**	**32.3**	**55.3**
I	**-18.8**	**-51.7**	**-42.4**

Substrate activation by PMe_3



Optimized Structures of the involved species

Model imine (trans)

C	-1.028226840	-2.184917209	4.719714171
C	-1.789448688	-3.352714560	4.282161801
C	-1.605529785	-4.635646105	4.673835984
H	-0.814157130	-4.859121064	5.394363912
C	0.103805642	-2.319151275	5.716024884
H	1.050645556	-1.993811905	5.258388077
H	-0.072707807	-1.663843126	6.582010348
H	0.236783486	-3.341377782	6.082737348
H	-2.571218103	-3.100518773	3.562742742
C	-2.363617625	-5.807350559	4.234192555
C	-3.424418072	-5.743551902	3.305799313
C	-2.022599568	-7.070488563	4.760419682
C	-4.109294946	-6.894412130	2.924890401
H	-3.715275976	-4.783454386	2.878294791
C	-2.708464762	-8.223677260	4.379276612
H	-1.204094089	-7.139713275	5.480335934
C	-3.756324299	-8.140910732	3.458459325
H	-4.926358189	-6.822186477	2.205685760
H	-2.424617874	-9.188457497	4.801595912
H	-4.295694524	-9.039642037	3.156309756
N	-1.386437186	-1.053213959	4.196624308
C	-0.669900880	0.149145449	4.579070896
H	-0.741757187	0.309491745	5.672796140
H	0.412654080	0.041404371	4.373423149
C	-1.170716574	1.401900803	3.877695551
C	-0.516735559	2.621465117	4.111770820
C	-2.267878885	1.380223413	3.010208071
C	-0.949544330	3.795904857	3.493544183
H	0.343572414	2.652084750	4.786187565
C	-2.703639936	2.556444717	2.389296721
H	-2.769224489	0.429762577	2.829493626
C	-2.048435900	3.767097506	2.627416603
H	-0.428054095	4.734900651	3.686223617
H	-3.560868817	2.524222983	1.714401576
H	-2.388684649	4.683104316	2.141671476

Model imine (cis)

C	-1.212000	-2.144000	4.677000
C	-1.889000	-3.353000	4.157000
C	-2.669000	-3.377000	3.056000
H	-2.800000	-2.437000	2.520000
C	-0.283000	-2.344000	5.861000
H	0.738000	-2.028000	5.612000
H	-0.603000	-1.734000	6.716000
H	-0.249000	-3.388000	6.181000
H	-1.714000	-4.265000	4.724000
C	-3.368000	-4.532000	2.483000
C	-3.317000	-5.828000	3.038000
C	-4.135000	-4.343000	1.315000
C	-4.003000	-6.887000	2.446000
H	-2.736000	-6.012000	3.938000
C	-4.824000	-5.403000	0.722000

H	-4.188000	-3.351000	0.872000
C	-4.761000	-6.680000	1.285000
H	-3.949000	-7.877000	2.891000
H	-5.408000	-5.231000	-0.178000
H	-5.295000	-7.509000	0.827000
N	-1.430000	-1.004000	4.119000
C	-0.741000	0.176000	4.629000
H	-0.941000	0.298000	5.708000
H	0.350000	0.058000	4.539000
C	-1.161000	1.445000	3.911000
C	-0.203000	2.385000	3.508000
C	-2.516000	1.725000	3.677000
C	-0.585000	3.581000	2.889000
H	0.852000	2.180000	3.676000
C	-2.902000	2.917000	3.058000
H	-3.268000	1.000000	3.976000
C	-1.937000	3.851000	2.661000
H	0.174000	4.295000	2.579000
H	-3.957000	3.117000	2.883000
H	-2.238000	4.777000	2.178000

Bispin·OMe$^-$

B	-0.825545990	-0.435192997	-0.198587711
O	-1.964707449	-1.172534160	0.186215897
O	-1.222522098	0.865904340	-0.571661586
C	-2.674909643	0.927135108	-0.609900028
C	-3.084722418	-0.256073243	0.333961099
C	-3.136410996	0.148028752	1.815168202
C	-4.370960027	-0.985755453	-0.052418588
C	-3.093672286	0.705320909	-2.071401112
C	-3.118309556	2.315534641	-0.147849350
B	0.833642540	-0.989708392	-0.059431743
O	1.820676761	-0.194581598	-0.886919418
O	1.252147897	-0.732987918	1.356201239
C	2.627682566	0.585352094	-0.014876160
C	2.589998899	-0.233291352	1.333795794
C	1.992729478	1.984637077	0.142694610
C	4.025758585	0.736627622	-0.632035996
C	3.569063549	-1.426435368	1.312955146
C	2.824543231	0.597035392	2.602426781
H	-2.584437766	1.452379177	-2.696620712
H	-4.181450880	0.810420352	-2.212281703
H	-2.710227383	2.554884337	0.842204379
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H	-4.303603392	-1.406012597	-1.063915110
H	-5.241362340	-0.310448825	-0.004682189
H	-3.218719659	-0.764498610	2.422208797
H	-3.996631908	0.799521609	2.038203226
H	2.615311176	2.670227568	0.743355894
H	1.860460746	2.416410624	-0.860632953
H	4.713812253	1.272046113	0.045116882
H	4.454123634	-0.245529528	-0.872389593
H	3.820342073	1.072726478	2.596625310
H	2.764265156	-0.059771913	3.484901816

H	3.350963939	-2.064321524	2.182694494
H	3.399250256	-2.024731879	0.409104888
H	-2.782648398	-0.290734907	-2.414232997
H	-2.750006950	3.070873550	-0.857888889
H	-4.542602081	-1.815560510	0.648954501
H	-2.209917847	0.660774693	2.106696988
H	0.999480143	1.898714385	0.601044143
H	3.949821461	1.312897843	-1.567956805
H	2.058689590	1.377470858	2.708199276
H	4.625642028	-1.110027821	1.363745361
O	0.978856577	-2.446013924	-0.362713714
C	0.652276591	-2.803928473	-1.679389485
H	0.682249786	-3.904739224	-1.777811366
H	1.352967770	-2.373688463	-2.425544962
H	-0.371611702	-2.470435765	-1.966667170

TS

C	-2.346592220	-1.114985927	3.523287573
C	-1.715440265	-2.388169548	3.382284163
C	-2.358399497	-3.637750605	3.233198718
C	-3.850844675	-1.001967248	3.355521703
H	-4.098043679	-0.271440258	2.568796879
H	-4.317102001	-1.957196410	3.100546130
H	-4.313981733	-0.646407353	4.288969468
H	-0.624480110	-2.362477380	3.444121630
C	-1.602733457	-4.748769313	2.583207227
C	-0.266615009	-5.056975788	2.895086448
C	-2.224759366	-5.490880502	1.563698068
C	0.423366148	-6.054581461	2.203056190
H	0.223601424	-4.524531190	3.710110017
C	-1.535751552	-6.480416231	0.860782234
H	-3.271987872	-5.290291865	1.333299183
C	-0.204074232	-6.769698457	1.175087418
H	1.457582759	-6.282481793	2.471162854
H	-2.047358956	-7.036628329	0.072037783
H	0.336702969	-7.548712410	0.632695303
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C	-2.248899424	1.230848103	3.801117877
H	-2.608683365	1.521990312	2.789498027
H	-3.162459208	1.230804712	4.431974886
C	-1.366722333	2.362662980	4.303602301
C	-1.882516053	3.668584758	4.350345238
C	-0.055296000	2.145982984	4.741121248
C	-1.113102920	4.732737410	4.824689625
H	-2.907074830	3.849995092	4.011564612
C	0.720413467	3.210512205	5.218044446
H	0.330248526	1.126856483	4.696605849
C	0.197751623	4.506346272	5.263411270
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H	-3.408221323	-3.626352885	2.939294271
B	-2.706020987	-4.161500757	5.213671516
B	-4.194372962	-5.406438607	4.682471479
O	-3.232123756	-3.098124536	5.983749280
O	-1.543592542	-4.666781437	5.829327127

O	-5.207180172	-4.628424431	3.996304442
O	-3.817457005	-6.561732408	3.903319760
O	-4.501461458	-5.868007720	6.043473736
C	-2.527845364	-3.027695720	7.255089814
C	-1.197183963	-3.837811034	6.978061906
C	-6.036933568	-3.771960597	4.766596053
C	-3.649469203	-7.685882066	4.783487357
C	-4.584387666	-7.309724067	5.997494561
C	-3.437782416	-3.686830180	8.301855842
C	-2.313884161	-1.553372014	7.606205904
C	-0.014750568	-2.953151758	6.563177929
C	-0.766011273	-4.773032296	8.111483813
H	-5.507838437	-2.855641664	5.074549272
H	-6.904609405	-3.494267976	4.146086779
H	-6.395096103	-4.274237013	5.680729106
C	-2.169808163	-7.813273933	5.180826153
C	-4.074375646	-8.950319853	4.025528208
C	-4.144639701	-7.869514629	7.352040426
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H	-3.686257990	-4.711487908	7.999702818
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H	-0.283833231	-2.301452477	5.722026117
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H	0.135129043	-5.324055266	7.803388960
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H	-1.829077707	-6.921791403	5.720079882
H	-1.989242971	-8.710991525	5.795322457
H	-3.374140030	-9.120818202	3.194664482
H	-5.083482584	-8.847401950	3.605657627
H	-4.047347708	-9.835295432	4.683098064
H	-3.133806003	-7.527225269	7.607873013
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H	-6.234216933	-8.754622778	5.740276799

I

C	-0.655011822	-1.268406291	1.860724100
C	-1.456020550	-2.360366367	1.479347849
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C	0.323700406	-0.656895859	0.862834687
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H	0.407581503	-1.233268160	-0.063503244
H	0.018902534	0.371052369	0.601130916
H	-2.115355952	-2.746016679	2.261090023
C	-1.720301643	-2.282281789	-1.149812152

C	-2.427697658	-1.066833694	-1.152734425
C	-1.232456275	-2.756673981	-2.381500789
C	-2.660008974	-0.366340831	-2.338112612
H	-2.778739903	-0.681049201	-0.191968516
C	-1.455303072	-2.056205820	-3.571268625
H	-0.656984539	-3.685709925	-2.397137746
C	-2.173884617	-0.855289458	-3.558984148
H	-3.218689521	0.572820570	-2.311674522
H	-1.058725892	-2.445938889	-4.512442672
H	-2.341315774	-0.300409835	-4.485178867
N	-0.762940948	-0.754917961	3.098528070
C	0.073580835	0.354826412	3.441015705
H	1.168945588	0.120382320	3.419922974
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C	-0.206788033	0.897303996	4.835051770
C	0.522762137	1.990160426	5.330617138
C	-1.192813811	0.327637816	5.649958446
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H	1.295221597	2.443223164	4.700564373
C	-1.442676262	0.839724710	6.930833262
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C	-0.712082959	1.929139251	7.415833629
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H	-2.215960491	0.384202978	7.555289434
H	-0.909121714	2.328626869	8.413789698
H	-2.426742957	-3.735346527	0.199847466
C	0.889664115	-5.867557760	1.022532264
C	1.851104208	-4.636966205	0.811416559
O	-0.425490220	-5.255033753	1.011551875
O	1.024939305	-3.742713165	0.009717817
B	-0.307836294	-3.996854953	0.377803526
C	2.184444624	-3.907322871	2.118584883
H	2.814879430	-4.519723998	2.781444851
H	2.729362649	-2.984241174	1.876124284
H	1.265290652	-3.620485222	2.649654670
C	3.130147296	-4.939026940	0.031741620
H	3.708297441	-4.011316023	-0.088285435
H	3.758131998	-5.665010226	0.572284047
H	2.910691506	-5.335269521	-0.968197229
C	1.070816237	-6.606883338	2.348177527
H	0.344820315	-7.431272435	2.409726566
H	2.083188065	-7.034538539	2.429220351
H	0.898403164	-5.935895867	3.198479771
C	0.930145091	-6.861481970	-0.148159124
H	1.871295969	-7.432374875	-0.174660188
H	0.095445220	-7.568180816	-0.037271907
H	0.808193603	-6.335081910	-1.104716638

MeOBpin

C	0.065731	0.180742	-0.317030
C	1.625812	0.155126	-0.562509
B	0.826565	2.270216	-0.836548
O	-0.316711	1.483894	-0.883772
O	1.978291	1.578202	-0.502474
C	-0.307565	0.220676	1.167921
H	-1.378143	0.450322	1.258404
H	-0.117218	-0.744678	1.658779
H	0.258098	0.999852	1.697483
C	-0.722010	-0.907954	-1.037571
H	-0.413835	-1.904985	-0.687697
H	-1.793760	-0.789887	-0.824322
H	-0.580407	-0.857324	-2.124111
C	2.433585	-0.585126	0.498641
H	2.149766	-1.648113	0.532976
H	3.502726	-0.526088	0.251845
H	2.288245	-0.148085	1.494095
C	2.004403	-0.337445	-1.963266
H	3.068901	-0.127872	-2.134217
H	1.840395	-1.419485	-2.071395
H	1.424888	0.183737	-2.738007
O	0.855704	3.611430	-1.094519
C	-0.386720	4.280955	-1.365803
H	-1.061333	4.228790	-0.499562
H	-0.149124	5.329745	-1.576635
H	-0.894398	3.841147	-2.235644

PMe_3

C	-1.353000000	0.749000000	0.000000000
P	-0.747000000	-0.967000000	0.000000000
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C	-1.353000000	-1.825000000	1.486000000
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H	-0.997000000	1.254000000	-0.874000000
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H	-0.998000000	-1.319000000	-2.360000000
H	-0.995000000	-2.833000000	-1.487000000
H	-2.423000000	-1.826000000	-1.485000000
H	-0.997000000	-2.833000000	1.486000000
H	-0.996000000	-1.320000000	2.360000000
H	-2.423000000	-1.824000000	1.486000000

TS’ ketone (cis)

P	1.480000000	-0.133000000	-0.045000000
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C	-0.657663285	1.545523873	-0.902631909
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C	2.400266661	-1.738034971	-0.010391857
C	2.737550895	1.148539720	-0.399281814
C	0.916638610	0.155021573	1.666907681
C	0.456725153	0.069169334	-2.685837249

C	0.872780628	1.140945868	-3.492989964
C	0.549185692	-1.230951070	-3.214095725
C	1.372084104	0.919655725	-4.779929921
C	1.041069841	-1.455738383	-4.502369480
C	1.460300799	-0.378815437	-5.290125849
C	-2.488888374	2.854843527	0.251240777
O	-2.100878761	0.520578485	0.667850313
H	-0.343346332	2.470427022	-1.383317134
H	-0.769028949	-0.539218471	-0.994290413
H	2.788542936	-1.957340698	-1.015026958
H	2.225195334	2.119987677	-0.453287306
H	1.777684307	0.230587720	2.346842101
H	0.782623955	2.161405072	-3.121376599
H	0.205933233	-2.075806422	-2.611460277
H	1.681891579	1.768379254	-5.391801749
H	1.086399314	-2.472151487	-4.896376491
H	1.840704986	-0.549403416	-6.298474227
H	1.708807504	-2.539321420	0.287128152
H	3.235538808	-1.701135217	0.705786425
H	0.334633034	1.087201172	1.674809757
H	0.249312681	-0.659389963	1.975578946
H	3.215343246	0.937649471	-1.366042032
H	3.498578926	1.180291227	0.392389139
H	-3.526482310	2.715924297	-0.086528823
H	-2.529973088	3.084966216	1.325633742
H	-2.054132872	3.707352908	-0.289440863

I’ ketone

P	0.886778849	-0.357378580	0.125506973
C	2.284488087	-1.551346565	-0.334086108
C	0.266996132	-1.295435019	1.587534356
C	1.988748118	1.080624199	0.452836319
C	-0.087642114	-0.595449070	-1.498872984
C	-1.500723583	-0.175790654	-1.226148453
C	-1.665311306	0.632109579	-0.146744846
C	0.595333487	0.129319885	-2.655833118
C	1.381190600	-0.571981451	-3.584591666
C	0.431389177	1.514925822	-2.831852097
C	1.992901069	0.088148543	-4.655117367
C	1.049108180	2.177938117	-3.894767000
C	1.833130327	1.467676879	-4.811471907
C	-2.972857490	1.217877382	0.308306257
O	-0.591830253	0.938421297	0.586798616
H	2.837659112	-1.190988630	-1.213242510
H	2.990652390	-1.645646799	0.504253780
H	1.885300876	-2.551313333	-0.559608581
H	0.250035330	-0.625720090	2.455392063
H	-0.769518149	-1.592801871	1.372649131
H	0.879907072	-2.182610202	1.791275238
H	2.179728542	1.566136646	-0.516787026
H	1.496424646	1.796916242	1.117343619
H	2.945614266	0.733735885	0.863967760
H	-2.316311949	-0.477758881	-1.881805415
H	1.502839652	-1.652523165	-3.476723394
H	-0.201482334	2.063295395	-2.130729642

H	2.589091329	-0.478733121	-5.372022113
H	0.910922572	3.253973527	-4.013952611
H	2.307526917	1.985085571	-5.647004278
H	-2.913220878	2.316858463	0.314720191
H	-3.797999768	0.911909406	-0.347338383
H	-3.195449651	0.903695278	1.339210969
H	-0.005644843	-1.678127149	-1.686512034

TS’ imine (cis)

P	1.462122522	-0.053670653	0.001080600
C	0.007661972	0.324257001	-1.243676788
C	-0.529765623	1.634472588	-0.892707542
C	-1.709179181	1.707427525	-0.104461263
C	2.302073919	-1.705151551	0.051066071
C	2.787582252	1.142894413	-0.401979633
C	0.917661323	0.291531805	1.705524612
C	0.547595453	0.065047800	-2.634359440
C	0.930668707	1.111502718	-3.488335061
C	0.656683070	-1.253195801	-3.110032109
C	1.415894448	0.848445120	-4.773379983
C	1.129878372	-1.521273006	-4.398394333
C	1.517387577	-0.468454909	-5.233697276
N	-2.216031375	0.612626093	0.441146914
C	-3.509765425	0.673043124	1.110091426
C	-3.407274377	0.416218800	2.606005854
C	-3.095537431	-0.863052081	3.094774504
C	-3.629062564	1.443177752	3.534420304
C	-3.008607126	-1.107967408	4.468216746
C	-3.543562366	1.207140210	4.911405896
C	-3.232434922	-0.071461552	5.383424138
C	-2.341200219	3.091616354	0.019326302
H	-0.088735499	2.545423715	-1.291493918
H	-0.744597939	-0.434046628	-0.958005776
H	2.713975822	-1.932083512	-0.942174069
H	3.000777976	1.092416852	-1.480192271
H	1.782760626	0.553901674	2.332552391
H	0.816098603	2.142348990	-3.153628102
H	0.337705839	-2.079767419	-2.469810365
H	1.702307176	1.676755367	-5.422218671
H	1.183502263	-2.550627329	-4.754026239
H	1.882589469	-0.672166458	-6.241095299
H	-4.052871841	1.623190181	0.965498561
H	-4.153175066	-0.115943509	0.678167145
H	-2.929989206	-1.674780630	2.382567438
H	-3.885153481	2.442317349	3.172188269
H	-2.778882870	-2.111772322	4.828957204
H	-3.728767246	2.020156944	5.614839768
H	-3.174442840	-0.262463658	6.456049201
H	1.557226569	-2.471193782	0.312230611
H	3.110334332	-1.720024103	0.798832802
H	0.202570958	1.126469677	1.659921112
H	0.403523285	-0.585823358	2.120004336
H	3.698531395	0.902735027	0.163485363
H	2.448639139	2.155552628	-0.148017413
H	-3.316108555	3.129885723	-0.490464714
H	-2.509893457	3.370548124	1.070314152

H	-1.698300217	3.853319268	-0.439710215

I’imine

P	0.882001943	-0.696000738	0.148884047
C	2.304824802	-1.794026239	-0.527219237
C	0.404872667	-1.897339374	1.477497381
C	2.032364681	0.692250195	0.546064571
C	-0.125789479	-0.771496099	-1.477279953
C	-1.565929605	-0.623605116	-1.096618197
C	-1.804169349	0.036607414	0.072521536
C	0.410867616	0.253561751	-2.475595852
C	1.349917284	-0.118075011	-3.452665902
C	-0.043197310	1.584458531	-2.464557534
C	1.835818868	0.810928120	-4.378986296
C	0.447259575	2.516286657	-3.381897779
C	1.392152905	2.135369289	-4.342468446
N	-0.679414661	0.461389324	0.753644517
C	-0.803047396	0.938975040	2.118341729
C	-1.186177598	2.410579670	2.278467786
C	-1.757265282	2.857295728	3.479401302
C	-0.938333536	3.344391965	1.264709635
C	-2.068855142	4.206345484	3.667728810
C	-1.247679447	4.695877478	1.449359285
C	-1.813240572	5.132929897	2.651163945
C	-3.195093905	0.282509689	0.598250495
H	2.809733282	-1.317538071	-1.378777419
H	3.053953099	-1.975728039	0.257899033
H	1.915628080	-2.768837124	-0.856435552
H	0.410399351	-1.401867537	2.456375126
H	-0.625874247	-2.213422273	1.257750807
H	1.066953022	-2.771822509	1.501787217
H	2.334596892	1.111632103	-0.426230935
H	1.572311609	1.487091074	1.140016181
H	2.930426592	0.298275377	1.040775472
H	-2.360482390	-0.992767545	-1.742871504
H	1.690933722	-1.154900420	-3.502673273
H	-0.804246932	1.869579453	-1.736004499
H	2.555151245	0.494695358	-5.136163433
H	0.082508589	3.544755802	-3.353889117
H	1.767765267	2.862011728	-5.064973909
H	-1.502498374	0.335544907	2.729101967
H	0.178193889	0.812596368	2.609392150
H	-1.966912663	2.137799986	4.276147885
H	-0.507383087	2.991056793	0.327028813
H	-2.518390435	4.534240031	4.606664258
H	-1.049023689	5.411133490	0.649156140
H	-2.059344130	6.186520375	2.793245777
H	-3.374457372	1.354536656	0.770552071
H	-3.939711481	-0.087668223	-0.117234486
H	-3.364709109	-0.228301610	1.559168182
H	0.091696173	-1.772274420	-1.879498354

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