Electronic Supplementary Material (ESI) for Organdic and Biomolecular Chemistry

Supplementary Information for:

Convenient, Enantioselective Hydrosilylation of Imines in Protic Media Catalyzed by a Zn-Trianglamine Complex

Jadwiga Gajewy, Jacek Gawronski and Marcin Kwit*

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
Fax: (+48)-61-829-1505; e-mail: Marcin.Kwit@amu.edu.pl

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Experimental details

NMR spectra were recorded on a Bruker BioSpin 400 (400 MHz) or Varian MR 300 (300 MHz) instruments at 25 °C using $CDCl_3$, DMSO or D_2O as solvents, purchased from Sigma-Aldrich. Chemical shifts are reported in ppm relative to the TMS or D_2O peaks. Spectral assignments were obtained by analysis of chemical shifts and comparison with literature data (see Table B for details). Mass spectra were recorded on AMD-402 spectrometer.

Imines **4a-7** were prepared according to the literature procedures (see Table B for details). Imine **6** was prepared according to the procedure described by Krzyzanowska and Stec (*Synthesis*, 1978, 521).

Table 2 (full version). Effect of ligand, silane and solvent on the conversion, yield and enantioselectivity of the [Zn-diamine]-catalyzed hydrosilylation of imine **4d**.

Entry	Ligand	Silane	Solvent	Conversion[a] [%]	Yield[b] [%]	Ee[a] [%]
1	**1**	Ph_2SiH_2	Toluene	>99	82	92
2	**1**	Ph_2SiH_2	THF	98	71	84
3	**1**	Ph_2SiH_2	Toluene/MeOH[c]	>99	62	92
4	**1**	$(EtO)_3SiH$	Toluene	90	14	96
5	**1**	PMHS	Toluene	89	28	99
6	**2**	Ph_2SiH_2	Toluene	98	82	90
7	**2**	Ph_2SiH_2	THF	98	70	86
8	**2**	Ph_2SiH_2	Toluene/MeOH[c]	>99	74	87
9	**2**	$(EtO)_3SiH$	Toluene	90	16	98
10	**2**	PMHS	Toluene	94	16	94
11	**3**	Ph_2SiH_2	Toluene	99	66	>99
12	**3**	Ph_2SiH_2	THF	95	85	92
13	**3**	Ph_2SiH_2	CH_2Cl_2	96	64	94
14	**3**	Ph_2SiH_2	Toluene/MeOH[c]	>99	58	97
15	**3**	Ph_2SiH_2	MeOH	97	54	>99
16	**3**	$(EtO)_3SiH$	Toluene	93	6	97
17	**3**	$(EtO)_3SiH$	Toluene/MeOH[c]	97	52	96

18	**3**	PMHS	Toluene	90	56	96
19	**3**	PMHS	Toluene/MeOH[c]	>99	72	96

Reaction conditions: ligand 5 mol%; silane 1.2 eq, room temperature; reaction time 24 h. [a] Determined by HPLC using a CHIRALPAK IA column; [b] Isolated yields, average of two runs; [c] Solvents ratio 4:1 (v/v).

Table A. References

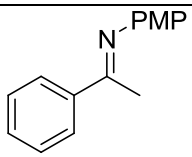
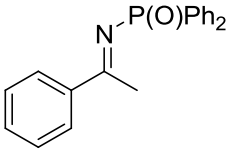
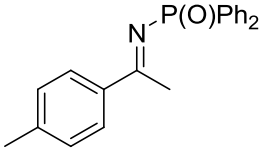
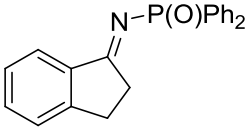
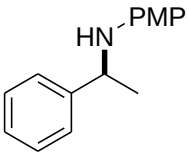
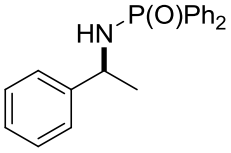
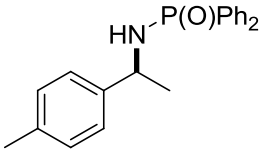
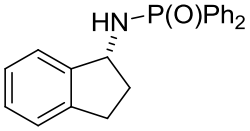
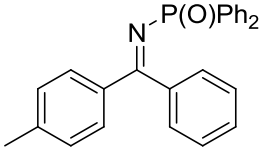
Product	Reference
	Mariappan Periasamy, Gadthula Srinivas, Pandi Bharathi *J. Org. Chem.*, **1999**, *64*, 4204
	You-Qing Wang, Sheng-Mei Lu, Yong-Gui Zhou *J. Org. Chem.*, **2007**, *72*, 3729
	Yi-Jing Chen, Chinpiao Chen Tetrahedron: *Asymmetry*, **2008**, *19*, 2201
	Tohru Yamada, Takushi Nagata, Kiyoaki D. Sugi, Kiyotaka Yorozu, Taketo Ikeno, Yuhki Ohtsuka, Daichi Miyazaki, Teruaki Mukaiyama *Chem. Eur. J.*, **2003**, *9*, 4485
	Yongxiang Chi, Yong-Gui Zhou, Xumu Zhang *J. Org. Chem.*, **2003**, *68*, 4120 You-Qing Wang, Sheng-Mei Lu, Yong-Gui Zhou *J. Org. Chem.*, **2006**, *71*, 7035
	You-Qing Wang, Sheng-Mei Lu, Yong-Gui Zhou *J. Org. Chem.*, **2006**, *71*, 7035
	You-Qing Wang, Sheng-Mei Lu, Yong-Gui Zhou *J. Org. Chem.*, **2006**, *71*, 7035
	Bu-Mahn Park, Soungyun Mun, Jaesook Yun *Adv. Synth. Catal*., **2006**, *348*, 1029

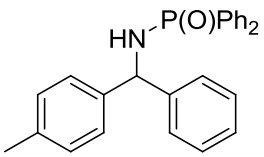
Table B. Retention times for HPLC separation of enantiomers of ArCH(NHX)R amines using a Chiralpak IA column.

Entry	Substrate	Flow [ml min^{-1}]	Hexane [%]	2-Propanol [%]	Ethanol [%]	Retention time [min]	
						Minor	Major
1	**4c**	0.500	95	5	0	16.77	15.93
2	**4d**	0.550	90	10	0	26.15	30.57
3	**5**	0.500	90	0	10	33.53	26.92
4	**6**	0.550	98	0	2	107.99	103.16
5	**7**	0.550	90	0	10	22.11	20.87

Spectral data for imine **6**, and for product of its reduction

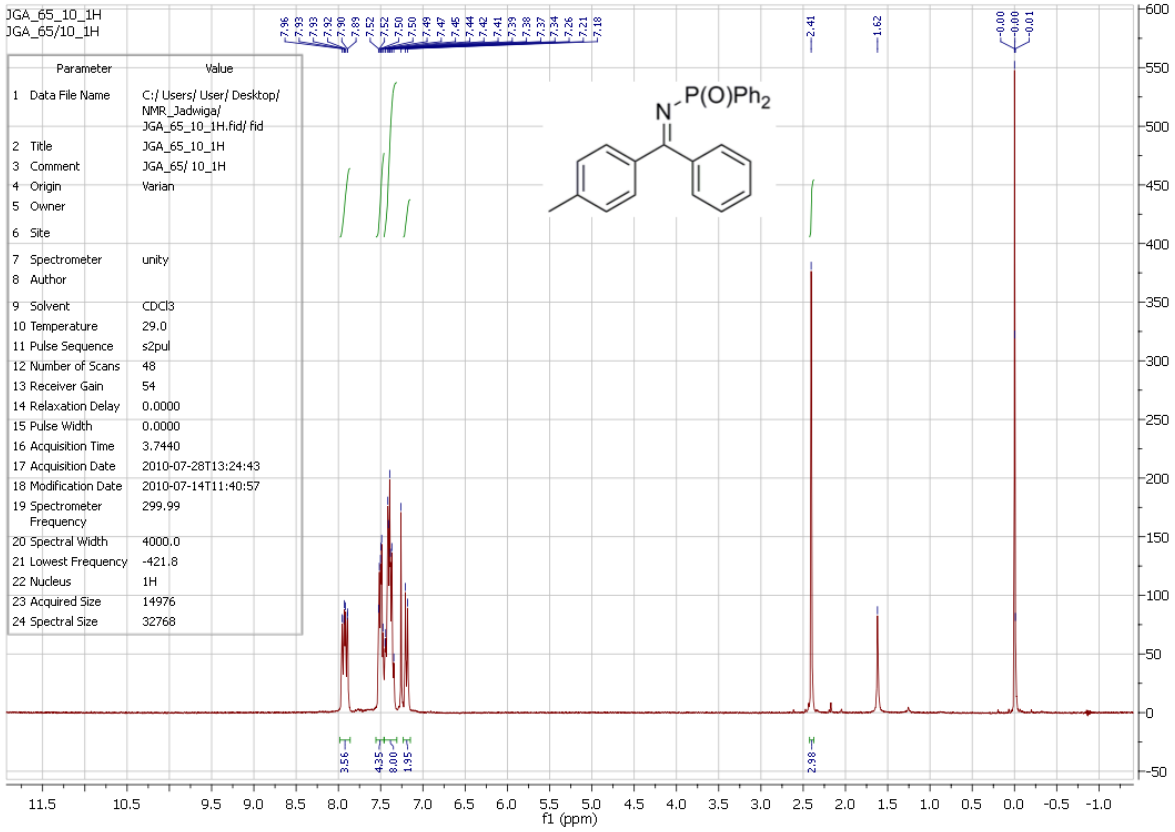


m.p. 142-145 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.96–7.89 (m, 4H), 7.52–7.47 (m, 4H), 7.45–7.34 (m, 9H), 7.19 (d, *J* = 7.9 Hz, 3H), 2.41 (s, 3H); (400 MHz, DMSO, δ): 7.83–7.79 (m, 4H), 7.54–7.39 (m, 13H), 7.26 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75.44 MHz, DMSO, δ): 180.7, 141.5, 137.9, 137.7, 135.5, 135.3, 135.1, 133.8, 130.8, 130.7, 130.6, 130.5, 129.0, 128.5, 128.2, 128.1, 127.9, 127.4, 20.6; ^{31}P NMR (121.45 MHz, DMSO, δ): 14.9; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{26}H_{22}NOP$, 395.14389; found 395.14595.

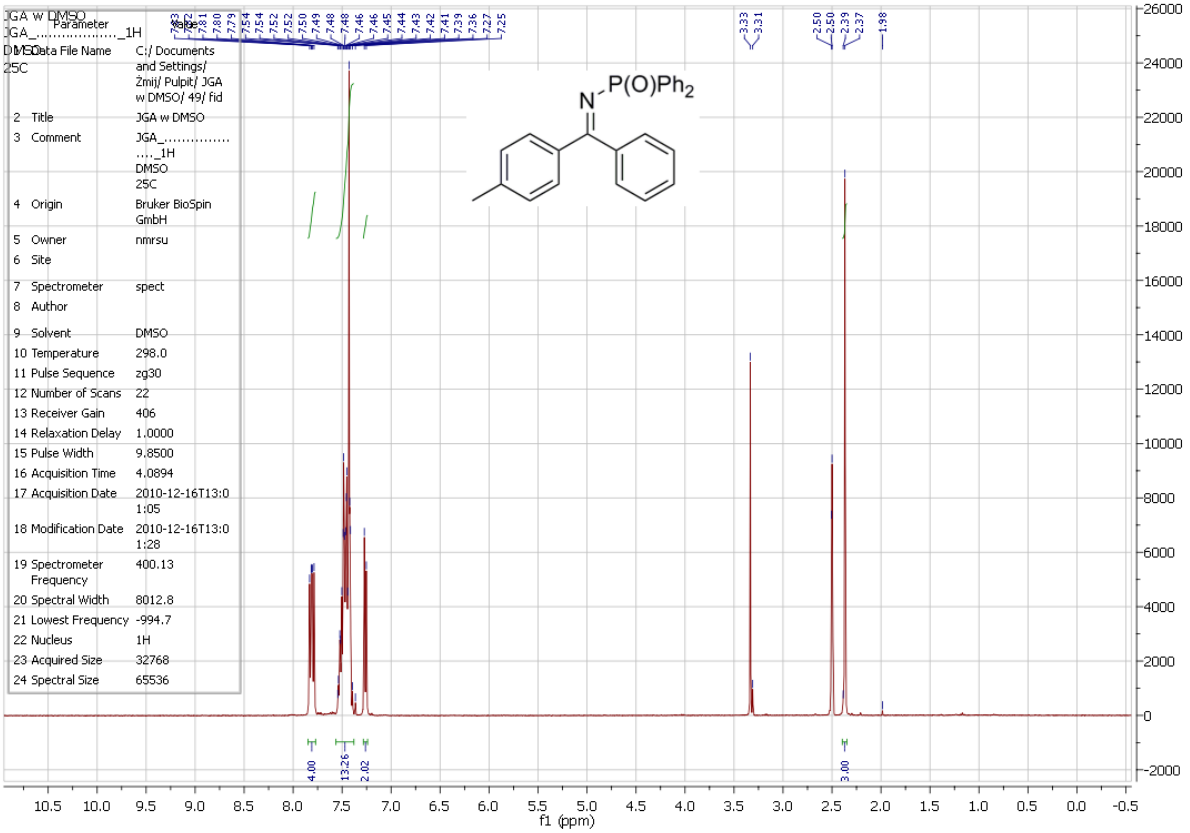


177-179 ºC; $[\alpha]_D$ = -2.8 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.93–7.80 (m, 4H), 7.52–7.47 (m, 2H), 7.44–7.35 (m, 4H), 7.32–7.25 (m, 5H), 7.16(q, *J* = 8.2 Hz, 4H), 5.45 (t, *J* = 10.7 Hz, 1H), 3.63 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$, δ): 143.53, 143.49, 140.50, 140.46, 136.71, 133.03, 133.01, 132.30, 132.20, 132.16, 131.77, 131.74, 131.68, 131.58, 129.10, 128.60, 128.47, 128.37, 128.26, 128.25, 127.51, 127.48, 127.03, 58.27, 51.45, 21.03; ^{31}P NMR (121.45 MHz, $CDCl_3$, δ): 22.9; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{26}H_{24}NOP$, 397.15955;

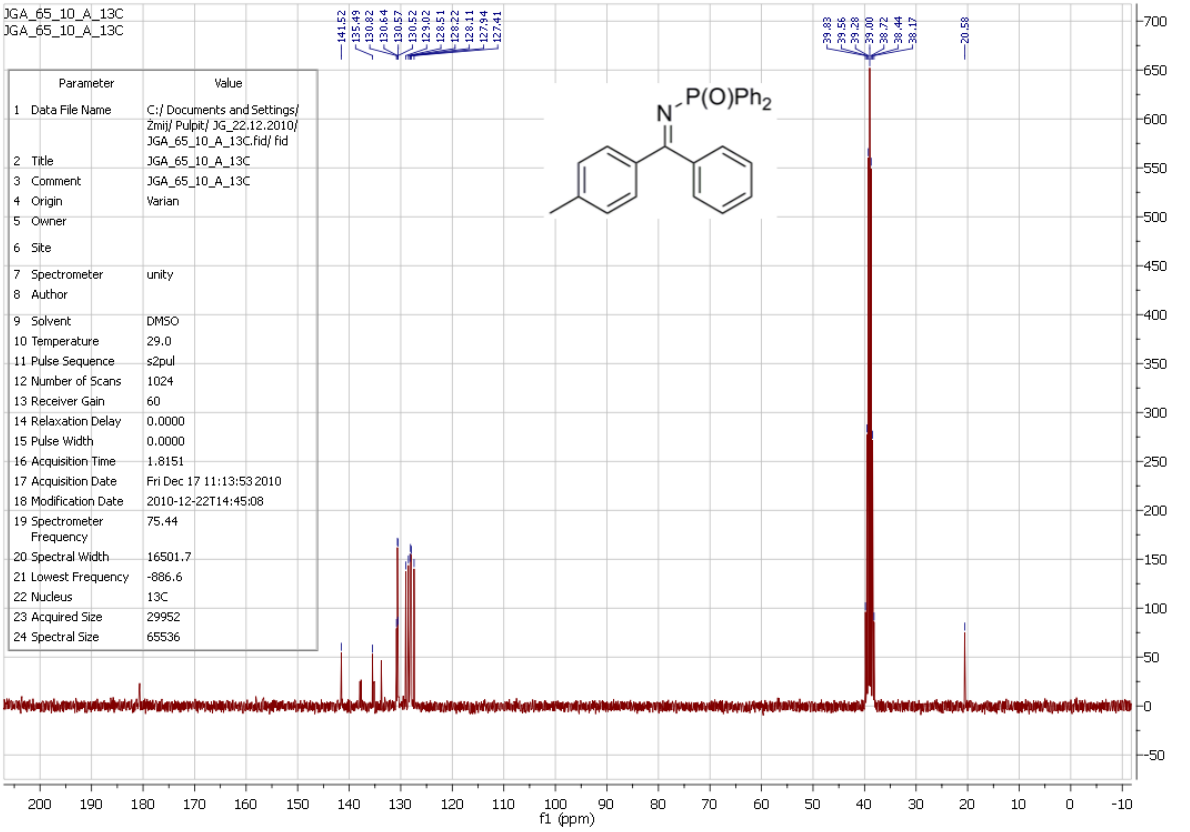
found 397.15824.



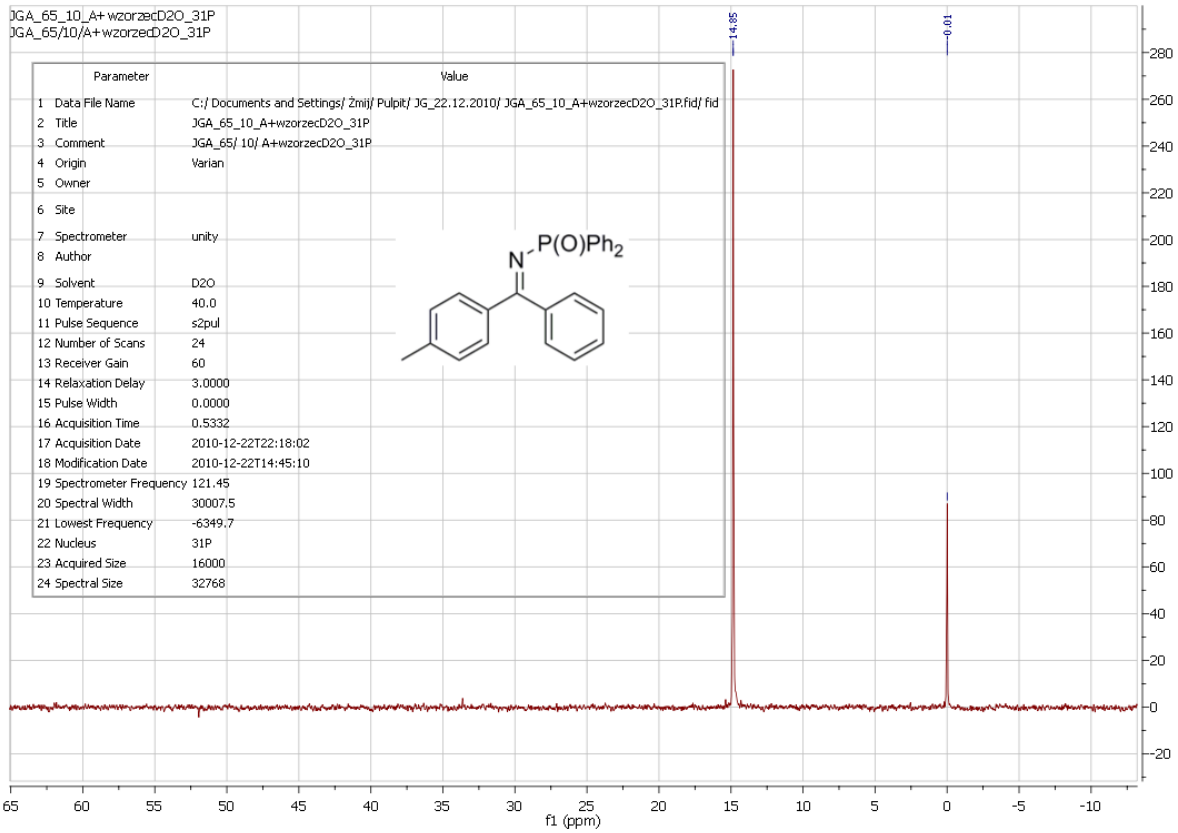
^{1}H NMR spectrum of imine **6** measured in $CDCl_3$



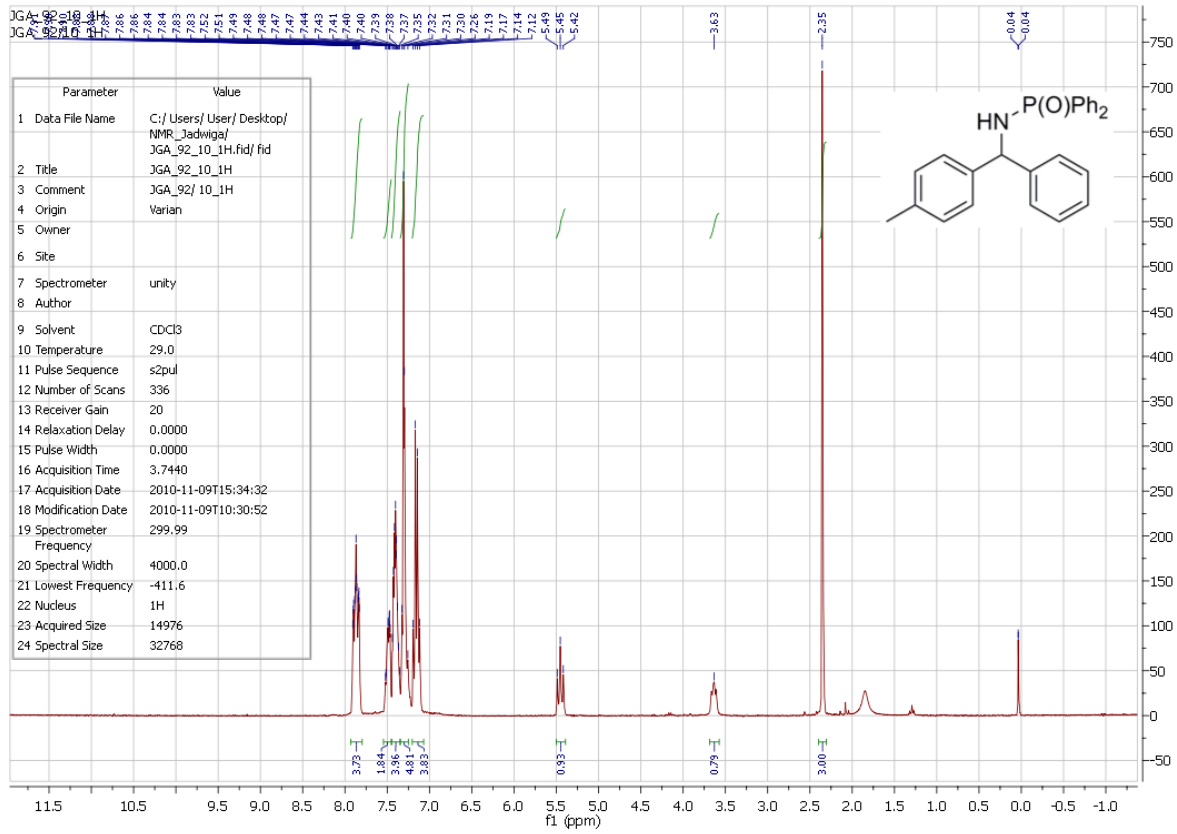
^{1}H NMR spectrum of imine **6** measured in DMSO



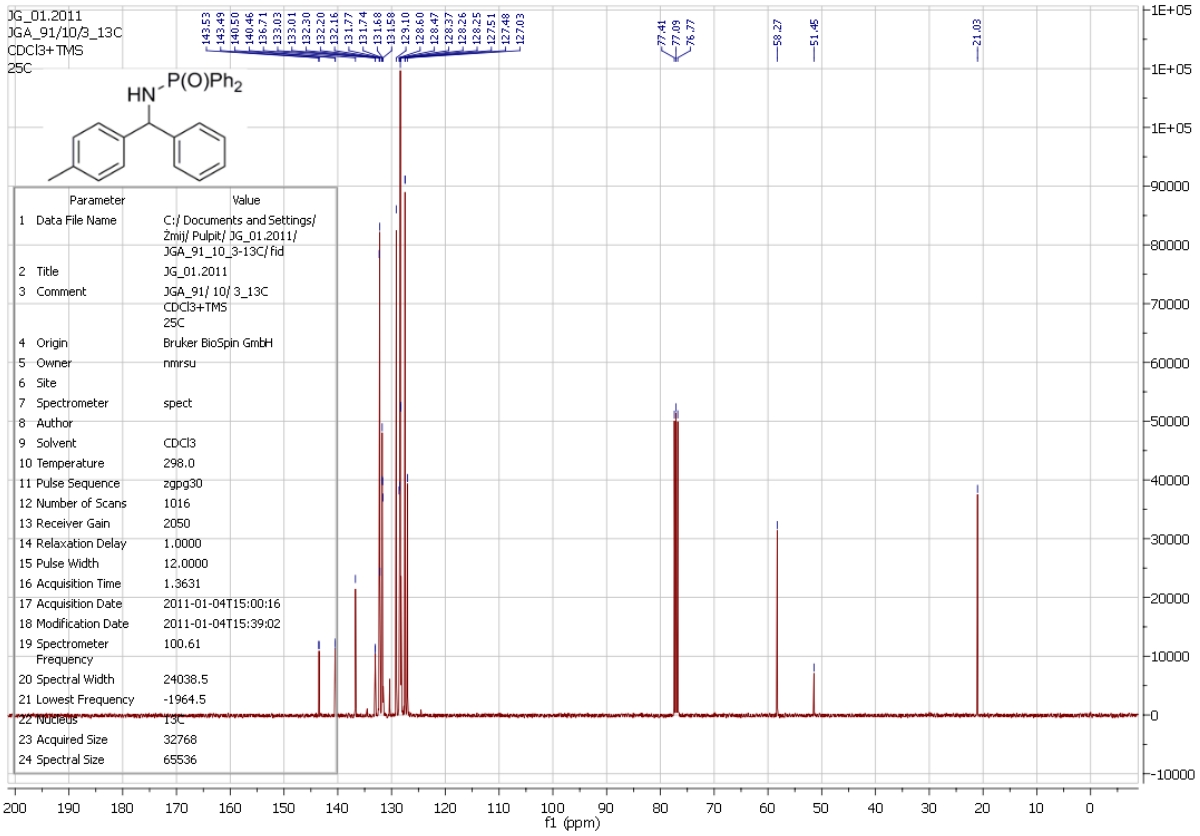
^{13}C NMR spectrum of imine **6** measured in DMSO



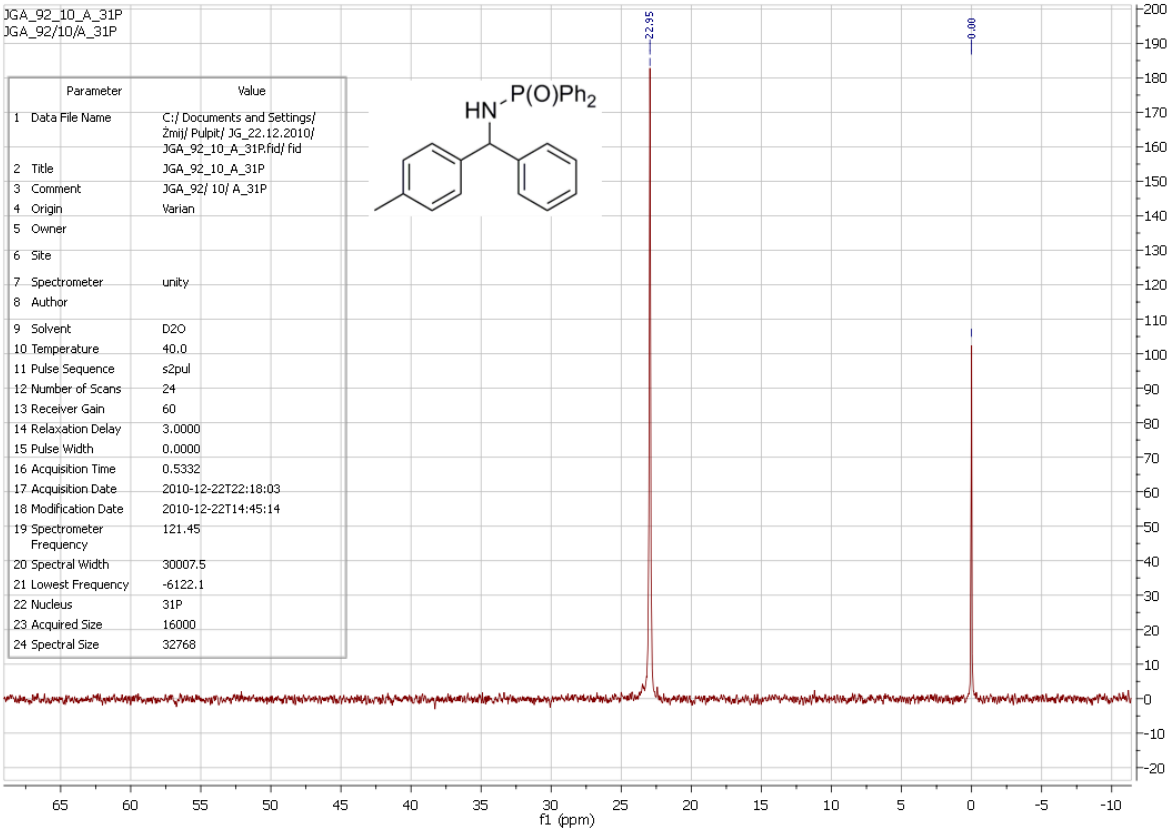
^{31}P NMR spectrum of imine **6** measured in D_2O



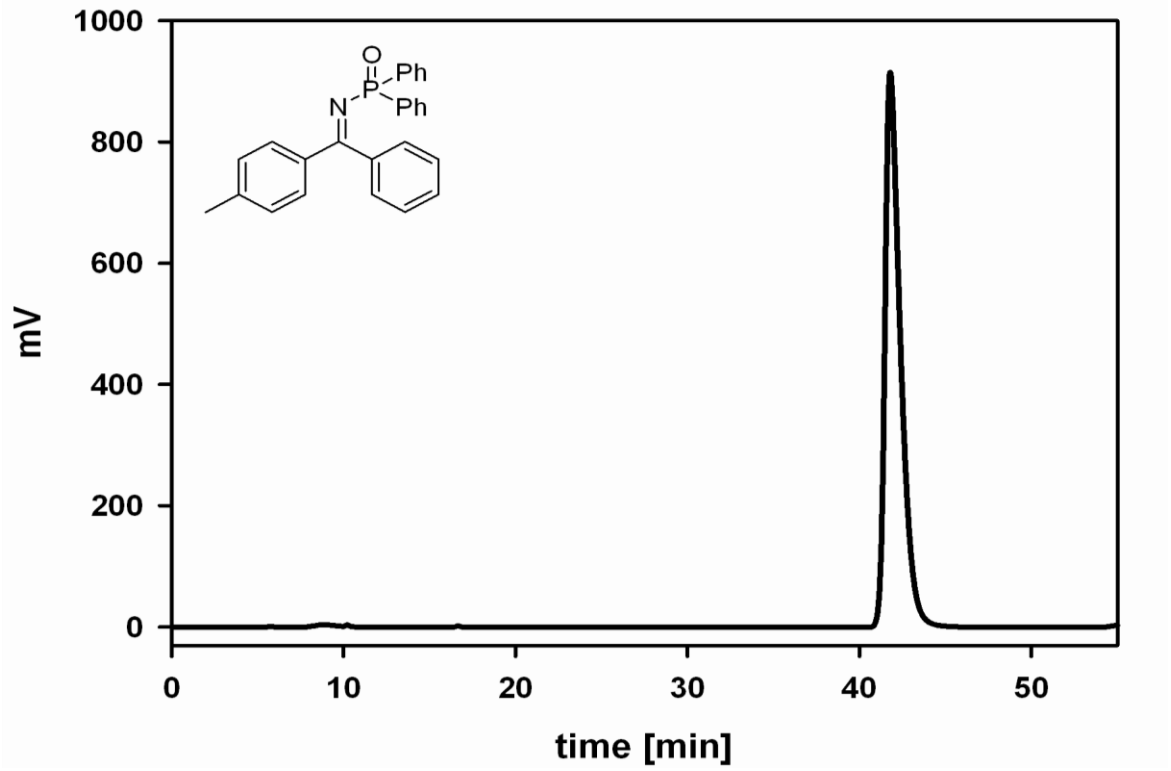
^{1}H NMR spectrum of the product of imine **6** reduction measured in $CDCl_3$



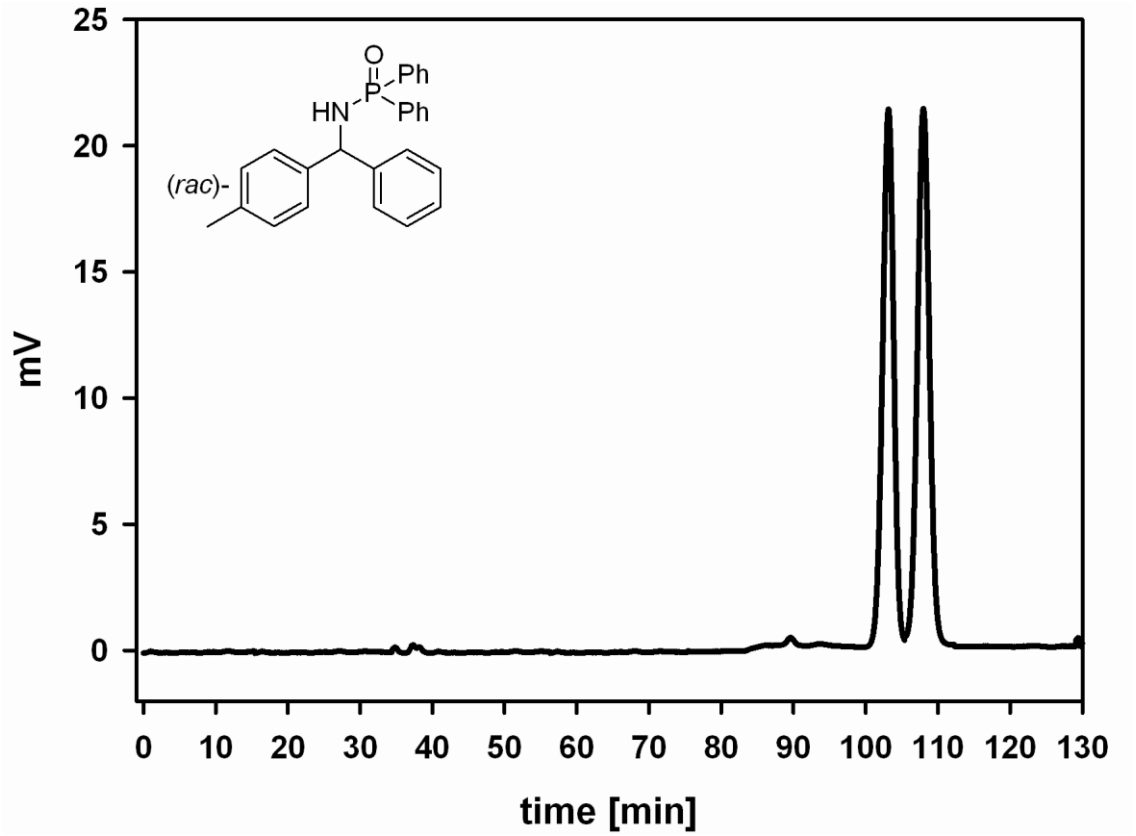
^{13}C NMR spectrum of the product of imine **6** reduction measured in $CDCl_3$



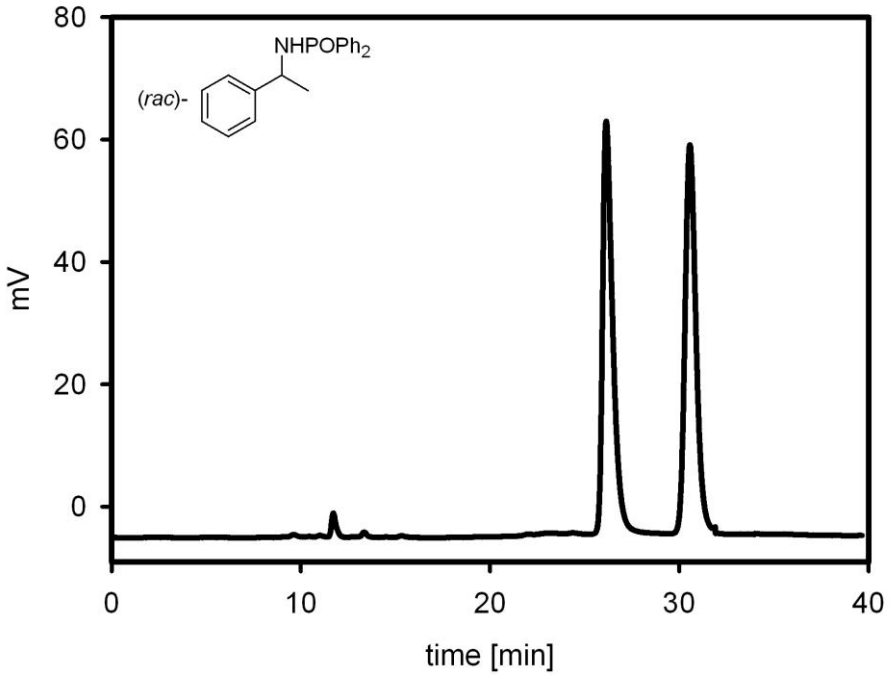
^{31}P NMR spectrum of the product of imine **6** reduction measured in D_2O

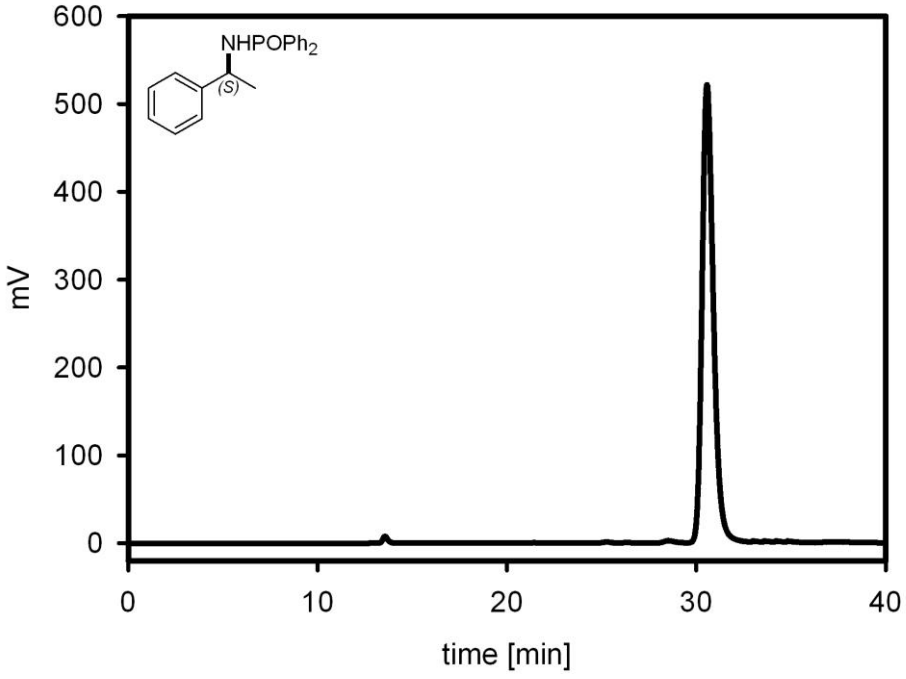


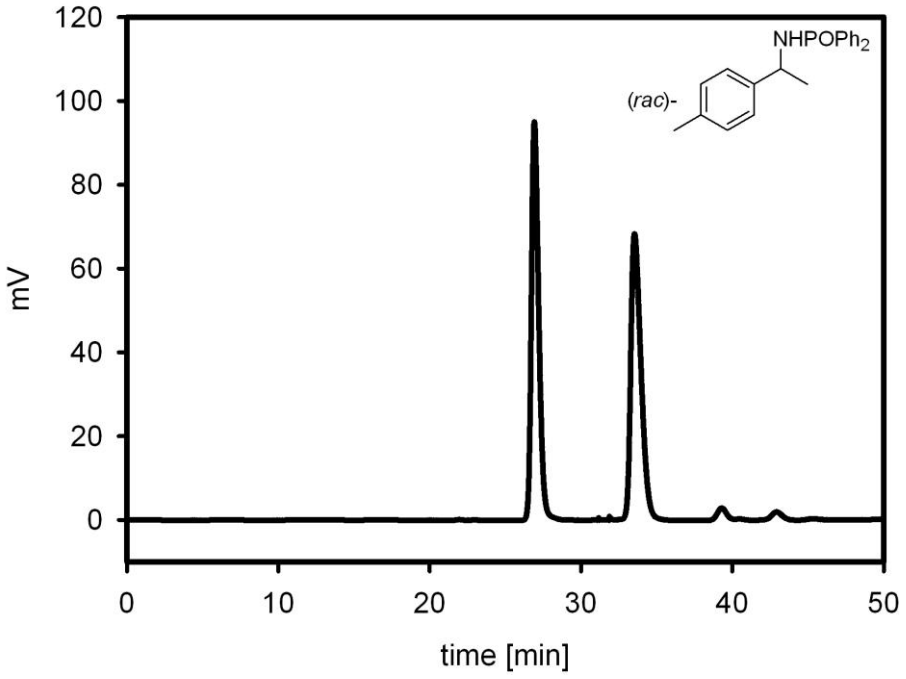
Chromatogram of imine **6**

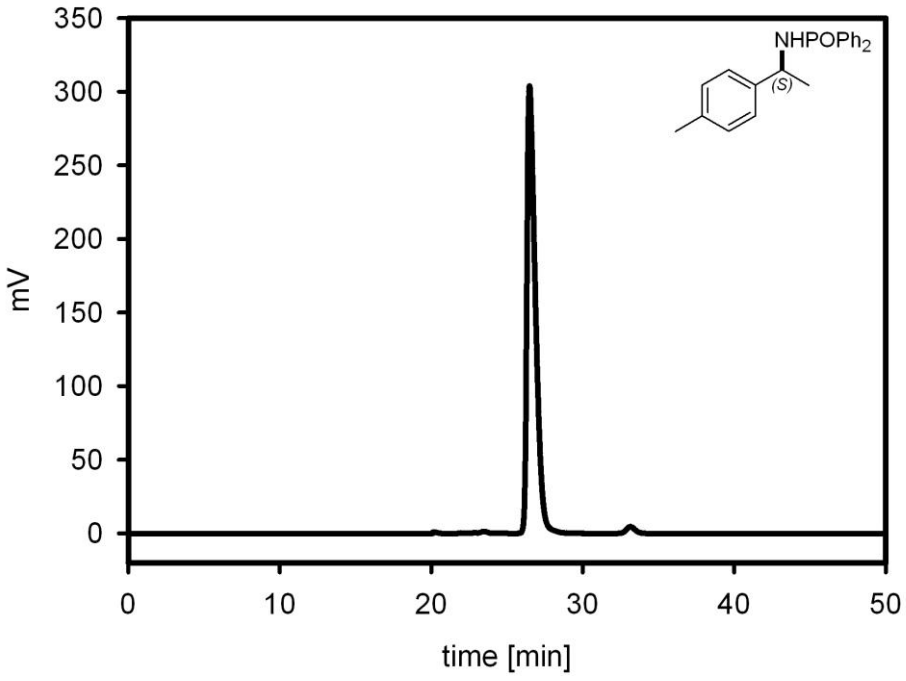


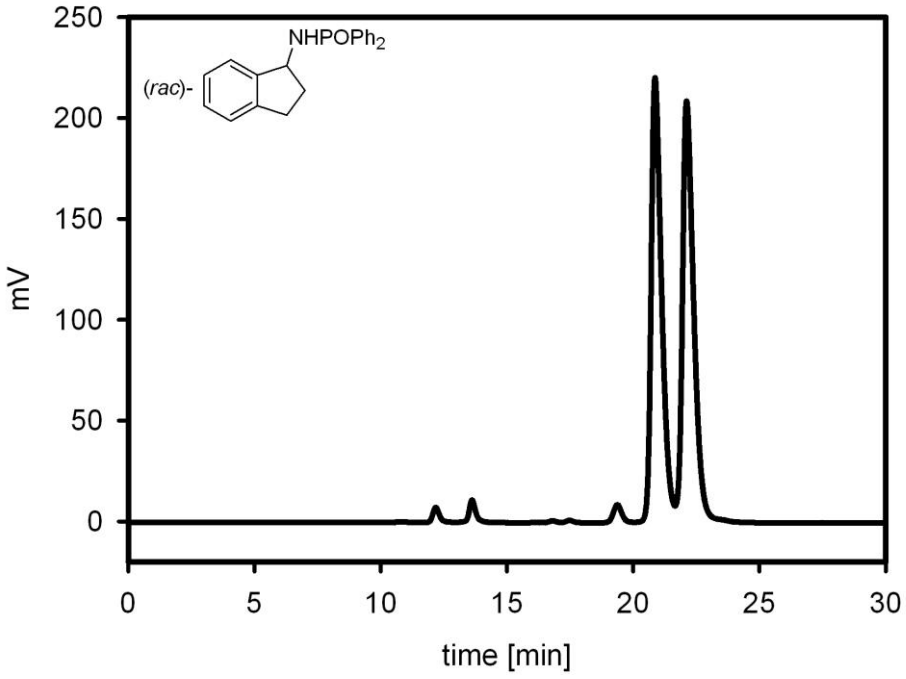
Chromatogram of the racemic product of imine **6** reduction.

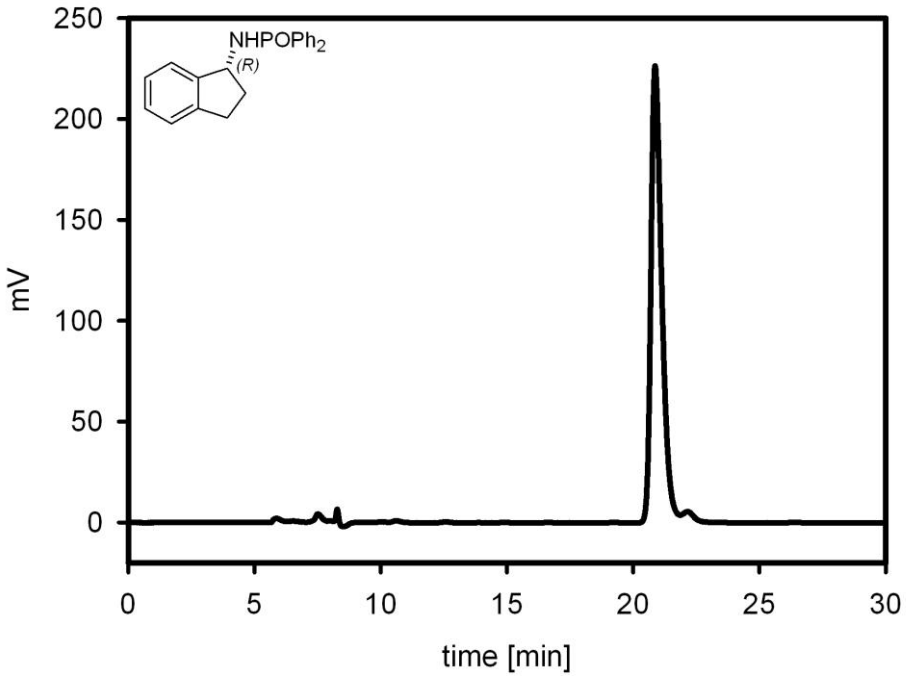












Copies of HPLC chromatograms of racemic and non-racemic product obtained from imines **4d**-**7** (only the best results are shown).

Computational details:

Preliminary calculations were performed with the use of split valence double-ξ basis set 6-31G(d) and PBE0 density functional. The next step involved re-optimization of all structures with the use enhanced 6-311G(d,p) basis set and above-mentioned PBE0 functional. No symmetry or internal coordinate constrains were applied during optimizations. All reported ground state structures were confirmed as being true minima by the vibrational analysis. Transition state (TS) structures were located with the use of Berny algorithm and were verified by the presence only one imaginary eigenvalue in the Hessian matrix. The identities of all transition states were confirmed by animating the negative eigenvector coordinate with the use of either GaussView or MOLDEN software and by intrinsic reaction coordinate (IRC) calculation. For all stationary points the Gibbs free energies (ΔG) and enthalpies (ΔH) were calculated at 298 K.

Additionally, single-point calculations with the use of PBE0/def2-TZVPP or COSMO/PBE0/def2-TZVPP methods were also performed to get more accurate energies. The same calculations were performed employing the Conductor-like Screening Model (COSMO) of methanol solution, as implemented in Turbomole software.[1]

Results obtained with the use of both methods show the same trend. Relative energies (in kcal mol^{-1}) reported in the main text are referred to computed total energy difference (ΔE) and unless stated otherwise are given relative to the starting materials in each step of reaction. Binding energies (E_b), activation bariers (E_a) and reaction energies (E_r) were calculated based on respective values of total energies whenever possible and defined according to Sakaki et al. work.[2] Binding energy is defined accordingly to these authors [2] as the energy difference between the precursor complex and the sum of the reactants energies, the activation energy is the energy difference between the respective transition state and the precursor complex and the reaction energy is the energy difference between the product and the sum of the reactants, where negative value of E_r indicates that the reaction is exothermic.

In the case of compounds characterizing by multiple conformational minima, the energetic relationships were calculated and discussed here by taking into account the lowest-energy conformers. Unless stated otherwise for all calculated structures and transition states descriptor “a” is related to the formation of the final amine of (*S*) absolute configuration, whereas ”b” is related to the (*R*) absolute configuration of amine.

All calculations were carried out with the use of Gaussian 03 or Turbomole 6.0 packages.[1,3]

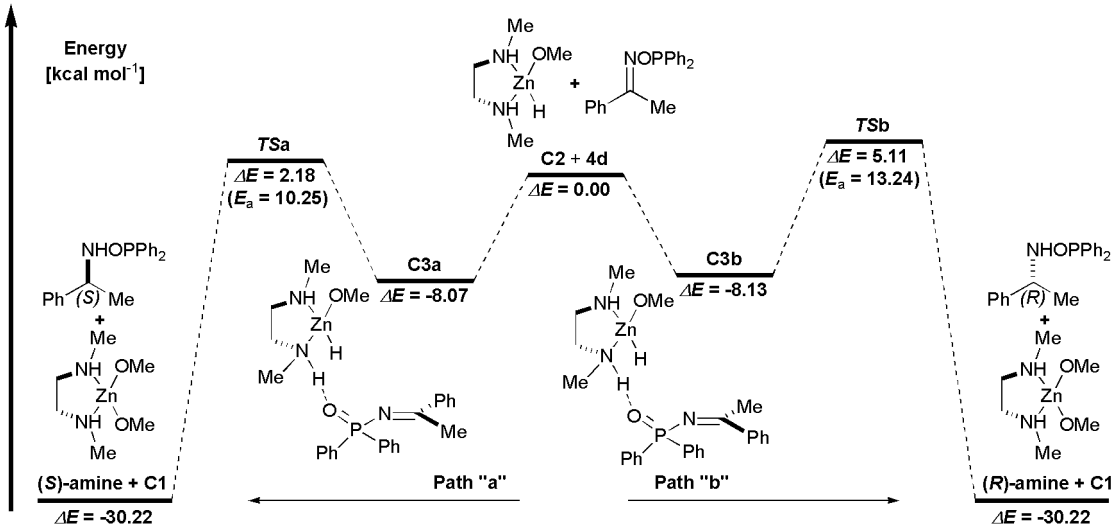
[1] R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel *Chem. Phys. Lett*. **1989**, *162*, 165 (see also www.turbomole-gmbh.com for an overview of the TURBOMOLE program).

[2] S. Sakaki, M. Sumimoto, M. Fukuhara, M. Sugimoto, H. Fujimoto, S. Matsuzaki *Organometallics* **2002**, *21*, 3788.

[3] M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford CT, 2004.

Table C. Single-point energies [in Hartree] calculated at the PBE0/def2-TZVPP level for all stationary points found at the PBE/6-311G(d,p) level.

Structure	E_{tot}	E_{tot} **(COSMO)**
C1	-2278.21045167256	-2278.2326840268
C2	-2163.73700713041	-2163.7496474570
C3a	-3407.24540015746	-3407.2651609675
C3b	-3407.24549943596	-3407.2648171379
***TS*a**	-3407.22905634912	-3407.2478210310
***TS*b**	-3407.22437230356	-3407.2442749263
4d	-1243.49552961571	-1243.5136517047
product	-1244.70995404206	-1244.7284065218
MeOH	-115.63970298059	-115.6476986850



Scheme A. Energy profile for the reduction of ketimine **4d** calculated at the PBE0/def2-TZVPP//PBE0/6-311G(d,p) level.

Cartesian coordinates for all structures optimized at the COSMO/PBE0/def2-TZVPP//PBE0/6-311G(d,p) level.

C1

C	0.00000000	0.00000000	0.00000000
C	1.51840056	0.00000000	0.00000000
H	-0.36782113	1.03289032	0.00000000
N	-0.48666957	-0.64460256	1.22737806
N	2.01415133	0.74110588	1.17055821
H	1.88215971	-1.03116716	0.07992436
H	-0.30774351	-1.65242177	1.15497858
H	1.94034509	1.74413907	0.96818840
C	-1.91517444	-0.41852412	1.45830707
C	3.40383770	0.41798529	1.50360524
H	-2.52836081	-0.68709945	0.58975314
H	-2.05996061	0.63563435	1.70481522
H	-2.23514498	-1.01489764	2.31523607
H	4.07132489	0.49077168	0.63656792
H	3.43710139	-0.59323433	1.91449334
H	3.75289701	1.10575990	2.27629344

H	1.90384073	0.41585965	-0.93898954
H	-0.38557553	-0.49245866	-0.90191564
Zn	0.68429761	0.24357731	2.73211366
O	1.51258071	-1.06589729	3.78346666
C	2.19239927	-0.59846935	4.89954256
H	2.68486728	-1.42308637	5.44429453
H	2.99524952	0.12838306	4.66144345
C	-0.95948808	1.75466382	4.39701194
H	1.54061181	-0.09084270	5.63761271
H	-0.33419034	1.56029184	5.29034565
O	-0.23751549	1.80774974	3.21305172
H	-1.74348457	0.97058951	4.40620293
H	-1.48284374	2.70706769	4.59282931

C2

C	0.00000000	0.00000000	0.00000000
C	1.52016559	0.00000000	0.00000000
H	-0.38027397	1.03023667	0.00000000
N	-0.48750430	-0.66301366	1.20449474
N	2.01421238	0.66154964	1.20877935
H	1.87321833	-1.03439024	0.05432655
H	-0.15313223	-1.63064535	1.20498155
H	1.80526040	1.65339704	1.16516468
C	-1.92985827	-0.60273757	1.36529712
C	3.44470464	0.46903937	1.42760827
H	-2.47630186	-0.99172514	0.49377450
H	-2.23954240	0.43323869	1.53104273
H	-2.22164533	-1.18215539	2.24362600
H	4.06179696	0.81070091	0.58576850
H	3.61367310	-0.59699934	1.59486210
H	3.74450133	1.00930848	2.32862972
H	1.90563770	0.46067741	-0.92067138
H	-0.37059282	-0.47609361	-0.92072545

Zn	0.95305580	-0.31714161	2.82884574
O	1.55838917	-2.02311900	2.28425504
C	2.14708268	-3.00542556	3.05908671
H	2.33962687	-3.91701234	2.46852689
H	3.12423804	-2.70300530	3.48501611
H	0.64509026	0.65926805	3.98592670
H	1.52680458	-3.32104542	3.92026168

4d

C	1.72518900	-0.03868200	1.02564800
C	3.00674200	-0.00797200	0.26738200
C	2.98950900	0.19077700	-1.11707800
C	4.23971300	-0.17268500	0.90410000
C	4.16793000	0.22239000	-1.84304800
H	2.02976100	0.32646100	-1.60148500
C	5.42229500	-0.14601500	0.17568300
H	4.28473600	-0.32815900	1.97560500
C	5.39003200	0.05203600	-1.19826900
H	4.13795800	0.38273300	-2.91572500
H	6.37096900	-0.27960800	0.68460400
H	6.31411800	0.07620100	-1.76647700
C	1.80526200	-0.09737000	2.52578300
H	2.29089900	-1.03017900	2.83098700
H	2.41993200	0.72608600	2.90138900
H	0.81308500	-0.05090400	2.97169300
N	0.64138800	-0.01544700	0.34640100
P	-0.94890800	-0.01383700	0.89843800
O	-1.28103500	-0.01225000	2.35575900
C	-1.61131900	1.46408300	0.07563700
C	-1.33153600	1.78722800	-1.25295900
C	-2.44548000	2.28849400	0.82950100
C	-1.88452400	2.92651900	-1.82072900
H	-0.67801000	1.14996500	-1.83834100

C	-2.99643600	3.42889200	0.25696000
H	-2.64324900	2.02537800	1.86352200
C	-2.71748700	3.74717000	-1.06634900
H	-1.66457300	3.17756200	-2.85323200
H	-3.64328800	4.07040800	0.84637900
H	-3.14818300	4.63766100	-1.51278100
C	-1.62679700	-1.47246200	0.05654600
C	-2.69794900	-2.11562800	0.67768600
C	-1.13279400	-1.95947000	-1.15455400
C	-3.27850300	-3.22905200	0.08422700
H	-3.05287000	-1.74237600	1.63274100
C	-1.71445300	-3.07556600	-1.74173300
H	-0.28316100	-1.47435500	-1.62164900
C	-2.78921400	-3.70753000	-1.12573500
H	-4.11019800	-3.72819400	0.57048500
H	-1.32496600	-3.45671500	-2.68010700
H	-3.24185800	-4.57923900	-1.58724300

The product

C	-1.63991700	0.80035000	0.74358900
C	-2.95199400	0.19098700	0.26904600
C	-3.02436900	-0.34941900	-1.01943000
C	-4.08888500	0.15122500	1.07359200
C	-4.20629000	-0.90781100	-1.48392200
H	-2.14193000	-0.33746100	-1.65526600
C	-5.27329800	-0.41278300	0.60742600
H	-4.06413100	0.56338900	2.07607300
C	-5.33651300	-0.94290300	-0.67254200
H	-4.24457200	-1.31880500	-2.48765600
H	-6.14696700	-0.43460800	1.25102800
H	-6.25944500	-1.38135600	-1.03800900
C	-1.69612400	1.42578700	2.13027400
H	-2.46489200	2.20125000	2.18713100

H	-1.90577200	0.67242300	2.89598500
H	-0.73197100	1.88267800	2.35921900
N	-0.54642300	-0.18738400	0.69039900
P	0.58639600	-0.17211300	-0.54734400
O	0.14494500	-0.33013700	-1.96656800
C	1.42354800	1.42576100	-0.33087100
C	1.86725800	1.89120600	0.90843600
C	1.64199400	2.19272600	-1.47516800
C	2.52110300	3.11225800	1.00014100
H	1.69749500	1.29892900	1.80127200
C	2.29324900	3.41688400	-1.37919400
H	1.28813600	1.81442000	-2.42867000
C	2.73311400	3.87574600	-0.14381100
H	2.86499800	3.47111000	1.96467900
H	2.45712900	4.01278000	-2.27095600
H	3.24303500	4.83082000	-0.06965100
C	1.70039000	-1.50856000	-0.03347000
C	2.23373300	-2.30743800	-1.04555000
C	2.03949300	-1.75984100	1.29792700
C	3.10378800	-3.34298000	-0.72887900
H	1.94364000	-2.11110900	-2.07264300
C	2.90771400	-2.79773400	1.60976700
H	1.61380400	-1.15216400	2.08928600
C	3.44216500	-3.58698600	0.59687800
H	3.51422100	-3.96376100	-1.51835100
H	3.16644000	-2.99309100	2.64524800
H	4.12079700	-4.39710800	0.84338700
H	-1.37712400	1.59499500	0.03390900
H	-0.84438600	-1.11771000	0.95845300

C3a

C	2.06303800	-1.48818800	1.40132700

C	2.32443300	-2.42790500	0.23605800
H	1.03556400	-1.10976200	1.35778400
N	2.97645200	-0.34863000	1.32292800
N	2.16834100	-1.69916400	-1.02851600
H	3.36331800	-2.76915200	0.27965400
H	3.93532900	-0.69911600	1.40902300
H	1.16784300	-1.52407400	-1.16038400
C	2.70743700	0.68296300	2.31107300
C	2.66547200	-2.46477800	-2.17043000
H	2.72307300	0.30016500	3.34187700
H	1.72366000	1.12478300	2.12785700
H	3.45399000	1.47546900	2.22434400
H	2.17648400	-3.44278100	-2.26825300
H	3.74191000	-2.60528400	-2.04626700
H	2.49186500	-1.89588900	-3.08712400
H	1.65202000	-3.29443500	0.29007600
H	2.16351900	-2.03385900	2.35140000
Zn	3.45697900	-0.01933200	-0.77612400
O	4.96200200	-1.09291300	-0.33062800
C	6.23199200	-1.04901400	-0.87097100
H	6.92646200	-1.70262800	-0.31524300
H	6.27320700	-1.38705300	-1.92599200
H	3.23677100	1.33016800	-1.52318500
C	-0.58451000	1.70708500	-0.63213800
C	-0.38227700	3.07641800	-0.09637300
C	-1.35500000	3.66167100	0.71898600
C	0.79176500	3.78359900	-0.37300300
C	-1.16722300	4.93368400	1.23423700
H	-2.25995600	3.10203200	0.92647100
C	0.98621300	5.05022100	0.16284700
H	1.57002900	3.33371000	-0.98120700
C	0.00670800	5.62998700	0.95942300
H	-1.93551400	5.38679100	1.85201500

H	1.90704800	5.58463400	-0.04474700
H	0.15646100	6.62454200	1.36679800
C	0.19298600	1.34108500	-1.85643900
H	-0.17334500	0.42230600	-2.30780000
H	0.16656600	2.15992400	-2.57883400
H	1.25025100	1.19472800	-1.59146900
H	6.68525700	-0.03819100	-0.86098700
N	-1.39493900	0.94000900	0.00370500
P	-1.74271600	-0.66482600	-0.34036000
O	-0.79413300	-1.49450400	-1.16078300
C	-3.38413700	-0.59406000	-1.10815000
C	-3.58773300	-1.33420700	-2.27188000
C	-4.42596700	0.16597600	-0.57319600
C	-4.82848200	-1.31219700	-2.89821500
H	-2.76562100	-1.91730700	-2.67390800
C	-5.66221600	0.18414100	-1.20272900
H	-4.26961400	0.74081800	0.33348500
C	-5.86366700	-0.55468900	-2.36482600
H	-4.98588100	-1.88778800	-3.80432300
H	-6.47161600	0.77533700	-0.78744100
H	-6.83194800	-0.53883400	-2.85438100
C	-1.93896700	-1.36375600	1.32067600
C	-1.80151200	-2.74723000	1.45263700
C	-2.21665900	-0.58431100	2.44427000
C	-1.95107800	-3.34523100	2.69655200
H	-1.56126200	-3.34255600	0.57762400
C	-2.36236700	-1.18797400	3.68743800
H	-2.29311700	0.49187100	2.33860600
C	-2.23353000	-2.56631800	3.81366000
H	-1.84246100	-4.42015500	2.79602400
H	-2.57142100	-0.57952200	4.56119000
H	-2.34775800	-3.03454000	4.78591500

C3b

C	-3.07549600	-1.80830000	-1.98762600
C	-2.88852900	-2.46791000	-0.63156100
H	-2.09812200	-1.53972200	-2.40601400
N	-3.86103000	-0.58468500	-1.82890500
N	-2.23344700	-1.52343600	0.27818600
H	-3.87039200	-2.69582000	-0.20508600
H	-4.77637300	-0.83560900	-1.43984400
H	-1.26317900	-1.41846800	-0.03382700
C	-4.01088600	0.17670400	-3.05683500
C	-2.23946800	-1.98626200	1.66362400
H	-4.45763500	-0.41087900	-3.87218700
H	-3.03352700	0.53460900	-3.39428000
H	-4.64402600	1.04740200	-2.87197600
H	-1.76915900	-2.97119300	1.78429100
H	-3.27593400	-2.03383600	2.00657400
H	-1.69972400	-1.26670200	2.28411800
H	-2.31253300	-3.39689700	-0.73853500
H	-3.54950800	-2.51434100	-2.68611400
Zn	-3.45392200	0.21406900	0.16447700
O	-5.05811800	-0.72767400	0.55965700
C	-6.01954700	-0.43215200	1.50633900
H	-6.87001800	-1.13272100	1.44404700
H	-5.64555300	-0.49615400	2.54748700
H	-2.85899100	1.62116500	0.47688100
C	0.72982900	1.73736500	-0.42231500
C	0.80894900	3.15026100	0.02097200
C	2.03379200	3.69534400	0.41399300
C	-0.34343400	3.93789900	0.08423700
C	2.10988400	5.01089700	0.84187900
H	2.91884500	3.07096500	0.36498500
C	-0.26736400	5.24830100	0.53736100
H	-1.30657900	3.51057500	-0.17524900

C	0.95770200	5.78957500	0.90721900
H	3.06767000	5.43284000	1.12804400
H	-1.17006400	5.84594900	0.60490300
H	1.01591900	6.81753600	1.24991600
C	-0.36455800	1.39236300	-1.38666000
H	-0.18579300	0.43109300	-1.86338400
H	-1.31905000	1.33527500	-0.84449800
H	-0.46407700	2.18176000	-2.13512000
H	-6.44824800	0.58395600	1.40167000
N	1.59809500	0.92272200	0.05437600
P	1.69642200	-0.73020200	-0.19577100
O	0.53173600	-1.49450300	-0.76486000
C	2.12205700	-1.33116400	1.45956100
C	1.90175300	-2.68376500	1.72871800
C	2.65519700	-0.50460000	2.44922100
C	2.22440600	-3.20597500	2.97364700
H	1.46490900	-3.31523000	0.96191400
C	2.97243600	-1.03234200	3.69484400
H	2.79523400	0.55010400	2.24148400
C	2.76201200	-2.38118300	3.95603800
H	2.05119100	-4.25691200	3.18020900
H	3.37926400	-0.38642400	4.46588300
H	3.01090000	-2.78998300	4.92993200
C	3.16477900	-0.91059000	-1.24522700
C	3.07310100	-1.75394500	-2.35138200
C	4.35982200	-0.24096100	-0.97606600
C	4.17175600	-1.92486700	-3.18561300
H	2.13554900	-2.26461400	-2.54549000
C	5.45318900	-0.41483100	-1.81246000
H	4.43284500	0.41290600	-0.11350500
C	5.35955800	-1.25633400	-2.91695300
H	4.09905700	-2.58108500	-4.04660800
H	6.38167600	0.10614100	-1.60354500

H	6.21683600	-1.39065600	-3.56852500

***TS*a**

C	1.54450100	-2.72405900	0.96427100
C	1.86952400	-3.23911300	-0.43085500
H	0.47380700	-2.50902700	1.04674700
N	2.27374300	-1.47792500	1.21348000
N	1.56600800	-2.21045100	-1.42586200
H	2.94343400	-3.44599900	-0.49698400
H	3.27700600	-1.67370700	1.21063700
H	0.55141600	-2.04363600	-1.47021600
C	1.88857800	-0.81330500	2.45297700
C	2.08471100	-2.52770700	-2.75098600
H	1.98071800	-1.47226600	3.32757100
H	0.85555700	-0.47023700	2.36759800
H	2.52360300	0.06192500	2.60497100
H	1.73382200	-3.49999000	-3.12168600
H	3.17724700	-2.52842500	-2.71207400
H	1.76331500	-1.75469000	-3.45263800
H	1.32304500	-4.17284900	-0.62301300
H	1.78317400	-3.49379100	1.71208100
Zn	2.46800000	-0.49508100	-0.66472700
O	4.25716000	-1.06955000	-0.63724000
C	5.38900600	-0.54892600	-1.23275500
H	5.31018400	-0.46064600	-2.33462700
H	5.65974000	0.46004500	-0.86449300
H	1.60614900	0.79499900	-1.02139700
C	0.23298100	1.56250900	-0.40469200
C	1.01573100	2.54696200	0.42202200
C	0.61907000	2.80290400	1.73321400
C	2.09688600	3.26032900	-0.09956500
C	1.28410000	3.74787300	2.50618900
H	-0.22221100	2.24763900	2.13035300

C	2.76345600	4.20177100	0.66904500
H	2.44525700	3.04446000	-1.10421500
C	2.35771500	4.45114100	1.97708500
H	0.95935500	3.93567300	3.52464500
H	3.60925800	4.73716700	0.25047000
H	2.88049600	5.18688600	2.57938400
C	-0.11793700	2.00861800	-1.80855400
H	-0.40535700	1.15451600	-2.42314700
H	-0.97341200	2.69157000	-1.73952700
H	0.70462700	2.53404800	-2.29203000
H	6.26581200	-1.19007400	-1.04015800
N	-0.52847600	0.73436500	0.28019900
P	-1.59996300	-0.32620900	-0.38615100
O	-1.10448100	-1.32107300	-1.40931300
C	-3.02180000	0.58324800	-1.07448500
C	-3.57391200	0.13463000	-2.27327900
C	-3.56921200	1.69637800	-0.43432600
C	-4.66282300	0.79581100	-2.82933500
H	-3.13000700	-0.72647400	-2.76238000
C	-4.65722400	2.35430400	-0.99209300
H	-3.13864300	2.05133100	0.49699800
C	-5.20458300	1.90415600	-2.18974700
H	-5.08806100	0.44617000	-3.76457500
H	-5.07893300	3.22108900	-0.49367100
H	-6.05432200	2.42069900	-2.62431000
C	-2.26294200	-1.19597200	1.06352800
C	-2.86518500	-2.43822700	0.85543800
C	-2.21258400	-0.66367000	2.35158600
C	-3.40965500	-3.13827600	1.92402500
H	-2.88678900	-2.85551500	-0.14621100
C	-2.76017100	-1.36534900	3.41901200
H	-1.72686500	0.29321800	2.50761800
C	-3.35984700	-2.60142000	3.20597200

H	-3.87274300	-4.10540100	1.75728400
H	-2.71489400	-0.94887100	4.42014100
H	-3.78601200	-3.14887400	4.04048100

***TS*b**

C	-1.20693800	-3.08738500	-0.39580600
C	-1.84616800	-2.62839300	0.90609900
H	-0.15096200	-2.80188900	-0.43314700
N	-1.87227500	-2.43717600	-1.52687800
N	-1.81247700	-1.16717900	1.01324500
H	-2.90269000	-2.91781000	0.90914700
H	-2.84360900	-2.74511800	-1.56905600
H	-0.86316600	-0.83744000	1.18863300
C	-1.20416800	-2.67776700	-2.80444400
C	-2.72324300	-0.65312100	2.03512500
H	-1.11825300	-3.74963400	-3.03042300
H	-0.20816700	-2.23192400	-2.76499300
H	-1.77616000	-2.19997000	-3.60301600
H	-2.56158800	-1.11911100	3.01618100
H	-3.74564300	-0.84140500	1.69914900
H	-2.58308100	0.42535900	2.12896600
H	-1.35694500	-3.11448000	1.76068300
H	-1.25675600	-4.18378100	-0.46423200
Zn	-2.38353700	-0.47954400	-0.89235000
O	-4.18462000	-0.98454700	-0.83237800
C	-5.33287700	-0.23135700	-0.97354700
H	-6.23261700	-0.86291600	-0.88003700
H	-5.43702700	0.56709000	-0.21136600
H	-1.43309300	0.70379400	-1.35356500
C	-2.82427500	3.91745600	2.00798800
C	-1.61935600	3.44010400	2.50620500
C	-0.79534200	2.65533100	1.70689500
C	-1.16222200	2.34049500	0.39907100

C	-2.37178800	2.83178000	-0.09417300
C	-3.19744200	3.61042200	0.70256000
H	-3.47289600	4.52342800	2.63199000
H	-1.31730500	3.67765500	3.52119600
H	0.14734800	2.27514100	2.08323900
H	-2.67786200	2.56872400	-1.10098800
H	-4.14212700	3.96922300	0.30764600
C	-0.21224300	1.53168400	-0.44321100
C	0.23206000	2.17154600	-1.73887300
H	1.02259200	2.89450000	-1.50061200
H	0.63471300	1.42069500	-2.41981300
H	-0.58566400	2.70164800	-2.22693200
H	-5.41587900	0.27318900	-1.95671800
N	0.53139400	0.68024100	0.22755400
P	1.72578900	-0.24303200	-0.46181300
O	1.39321000	-1.06034800	-1.67759100
C	2.21820900	-1.31216900	0.92462200
C	1.93951400	-1.00172800	2.25631100
C	2.91038000	-2.48713600	0.62349800
C	2.34925900	-1.85609700	3.27382800
H	1.38700300	-0.09594900	2.48224500
C	3.31870600	-3.33816600	1.64175800
H	3.10960700	-2.73331800	-0.41468200
C	3.03985500	-3.02288100	2.96759000
H	2.12702800	-1.61148800	4.30760400
H	3.85355500	-4.25124800	1.40143500
H	3.35929000	-3.68915200	3.76243500
C	3.17326100	0.81777100	-0.78182800
C	3.82008300	0.69448700	-2.01028800
C	3.63852800	1.74150000	0.15557500
C	4.92220700	1.49074200	-2.30020100
H	3.44070900	-0.02488500	-2.72921400
C	4.73952500	2.53491400	-0.13648000

H	3.13877400	1.83941700	1.11440100
C	5.38148100	2.41014800	-1.36496100
H	5.42247200	1.39381100	-3.25835300
H	5.09878900	3.25262000	0.59390300
H	6.24161100	3.03189000	-1.59160700

MeOH

O	-0.74543800	0.12373300	0.00000000
C	0.66005600	-0.02019000	-0.00002200
H	1.09016600	0.98402000	-0.00149500
H	1.02931500	-0.54520800	0.89159500
H	1.02903500	-0.54787800	-0.89006400
H	-1.14534800	-0.75966000	0.00009600