Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Borohydride Intermediates Pave the Way for Magnesium-Catalyzed Enantioselective Ketone Reduction

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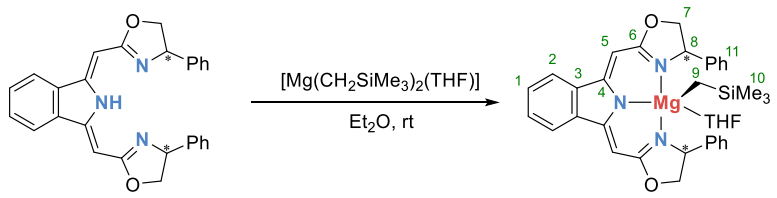
Contents

1 General Information

All manipulations, except those indicated, were carried out under exclusion of air and moisture using standard Schlenk and glovebox techniques. As inert gas, Argon 5.0, purchased from Messer Group GmbH, was used after drying over Granusic© phosphorus pentoxide granulate. Solvents were dried over activated alumina columns using a solvent purification system (M. Braun SPS 800) or according to standard literature-known methods and stored in glass ampules under an argon atmosphere.[1] Toluene was distilled from sodium, *n*–pentane from sodium/potassium alloy, and tetrahydrofuran, benzene and *n*-hexane from potassium. The same procedures were used to dry the deuterated solvents. Degassed solvents and liquid substrates were obtained by three successive freeze-pump-thaw-cycles. NMR spectra were recorded on Bruker Avance (400 MHz, 600 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual proton solvent signals or carbon resonances.[2,3] $BF_3{\cdot}OEt_2$ (^{11}B), CCl_3F (^{19}F) and $SiMe_4$ (^{29}Si) were used as external standards. Mass spectra were acquired on a JEOL JMS-700 magnetic sector (LIFDI) spectrometer at the mass spectrometry facility of the Institute of Organic Chemistry at the University of Heidelberg. Elemental analyses were carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department on a vario MICRO cube (Elementar). HPLC analyses were carried out on an Agilent 1200 Series chromatograph using chiral Daicel columns (AD-H, OD-H, OB-H, and OJ-H). For GC analyses a Finnigan Focus GC by Thermo Electron with astec Chiraldex columns (B-PM) was used. $[Mg(CH_2SiMe_3)_2THF]$,[4] and boxmi ligands were synthesized according to literature procedures. All substrates and other reagents were obtained from commercial suppliers and were used without further purification.

2 Synthetic Procedures and Analytical Data

2.1 Preparation of Precatalyst 1



1

To a room temperature ethereal solution of $[Mg(CH_2SiMe_3)_2THF]$ (249 mg, 922 µmol, 2.0 equiv. in 3 mL Et_2O) was added ^{H,Ph}boxmi-H ligand (200 mg, 461 µmol, 1.0 equiv.) as a solid in small portions, whereupon the solution turned dark brown. After stirring the mixture for 1 h, precipitation of an orange solid had occurred, and the reaction was added 10 mL of pentane. The solid precipitate was filtered and the residue was washed with pentane two more times (10 mL, respectively). The remaining golden-orange solid was dried *in vacuo* to give pure **1** (224 mg, 365 µmol, 79%). X-ray quality crystals of **1** were obtained by layering a THF solution with *n*-pentane and cooling to –40°C.

EA: calcd. C: 70.29 %, H: 6.55 %, N: 6.83 %; found: C: 69.84 %, H: 6.60 %, N: 7.45 %.[1]

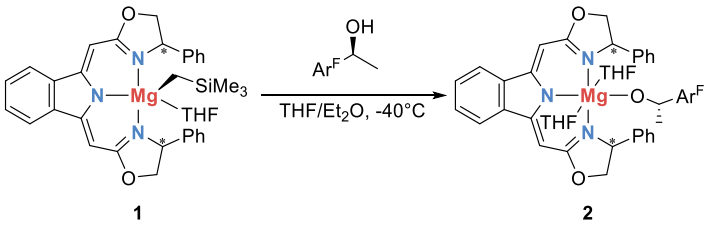
^{1}H-NMR (600.13 MHz, C_6D_6, 295 K): δ (ppm) = –2.06 (d, J = 11.3 Hz, 1 H, H-9), –1.68 (d, J= 11.3 Hz, 1 H, H9), 0.19 (s, 9 H, H-10), 1.32 (m, 4 H, H-THF), 3.49 (m, 4 H, H-THF), 3.74 (t, J = 8.3 Hz, 2 H, H-7/8), 3.99 (dd, J = 8.3 Hz, 9.8 Hz, 2 H, H-7/8), 4.77 (dd, J = 8.3 Hz, 9.5 Hz, 2 H, H-7/8), 5.76 (s, 2 H, H-5), 6.93-6.95 (m, 4 H, H-11), 6.96-6.99 (m, 2 H, H-1/2), 7.07-7.14 (m, 6 H, H-11), 7.24-7.26 (m, 2 H, H-1/2).

^{13}C{^{1}H}-NMR (150.90 MHz, C_6D_6, 295 K): δ (ppm) = 7.74 (1 C, C-9), 4.41 (3 C, C-10), 25.53 (2 C, C-THF), 67.98 (2 C, C-THF), 68.18 (2 C, C-8), 73.81 (2 C, C-7), 81.14 (2 C, C-5), 120.97 (2 C, C-2), 127.65 (4 C, C-Ph), 128.36 (2 C, C-Ph), 129.13 (4 C, C-Ph), 129.42 (2 C, C-1), 139.29 (2 C, C-3), 141.46 (2 C, C-Ph), 163.52 (2 C, C-4), 170.34 (2 C, C-6).

MS (LIFDI+) $[M–(CH_2SiMe_3,THF)]^+ = C_{28}H_{22}MgN_3O_2^+$, calcd.: 487.1, found: 487.3.

[1] Despite several attempts, high N values were obtained for elemental analysis of compound 1.

2.2 Preparation of Alkoxide 2



1 2

A solution of the magnesium precatalyst **1** (100 mg, 163 µmol, 1.0 equiv.) in 3 mL THF was cooled to –40 °C and was added neat (S)-1-(4-fluorophenyl)ethanol (22.9 mg, 163 µmol, 1.0 equiv.) in one portion. After stirring the mixture for 1 h at this temperature, the solution was layered with cold *n*-pentane, resulting in the formation of orange crystals after a week. Attempts to isolate and further characterize **2** in its pure state remained unsuccessful due to its pronounced thermal lability. Based on preliminary ^{19}F NMR studies at low temperatures, pronounced dynamic effects are hypothesized for the solution state, obstructing additional insights from such an analysis. No enhancement of the stability of the alkoxide could be achieved by variation of the alkoxide function.

^{1}H NMR (399.89 MHz, THF-D$_8$, 233 K): δ (ppm) = 1.03 (d, J = 5.4 Hz, 3 H, H-10), 3.36 (q, J = 5.4 Hz, 1 H, H-9), 4.17 (dd, J = 2.5 Hz, 8.4 Hz, 2 H, H-7), 4.35 (t, J = 8.4 Hz, 2 H, H-7), 5.54 (dd, J = 2.5 Hz, 8.4 Hz, 2 H, H-8), 5.58 (2 H, H-5), 6.85 (t, J = 8.5, 2 H, H-Ar), 7.12-7.26 (m, 12 H, H-Ar, H-Ph), 7.37-7.44 (m, 2 H, H-1), 7.73-7.81 (m, 2 H, H-2).[2]

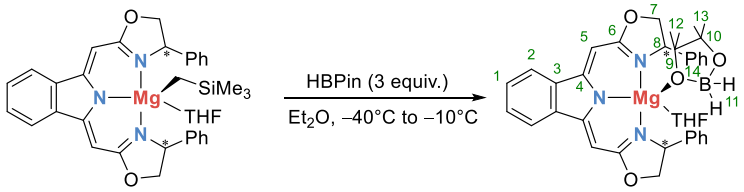
^{13}C{^{1}H} NMR (100.55 MHz, THF-D$_8$, 233 K): δ (ppm) = 31.19 (1 C, C-10), 65.53 (1 C, C-9), 68.53 (2 C, C-7), 74.95 (2 C, C-8), 80.29 (2 C, C-5), 114.27 (d, J = 20.5 Hz, 2 C, C-Ar) 120.87 (2 C, C-2), 127.42 (4 C, C-Ph), 127.53 (2 C, C-Ph), 127.90 (d, J = 7.5 Hz, 2 C, C-Ar), 128.76 (4 C, C-Ph), 129.33 (2 C, C-1), 140.69 (2 C, C-3), 145.41 (2 C, C-Ph), 152.08 (1 C, C-Ar), 161.55 (d, J = 239 Hz, 1 C, C-Ar), 163.16 (2 C, C-4) 169.84 (2 C, C-6).[2]

^{19}F{^{1}H} NMR (376.27 MHz, THF-D$_8$, 233 K): δ (ppm) = –120.57 (br s, 1 F-Ar).

MS (LIFDI+): [M–(2 THF)]$^+$ = $C_{36}H_{30}FMgN_3O_3^+$, calcd.: 595.2, found: 595.2.

[2] THF signals not listed due to overlap with NMR solvent.

2.3 Preparation of Hydridoborate 3



1 **3**

A suspension of **1** (100 mg, 163 µmol, 1.0 equiv.) in 2 mL diethyl ether was cooled to –40°C and was added neat HBPin (200 µL, 176 mg, 1.38 mmol, 8.45 equiv.). After stirring the mixture for several minutes and warming to –10°C, the residue dissolved producing a yellow solution which was cooled to –40°C and layered with cold *n*-pentane. After standing for 3 d quantitative precipitation had occurred. The supernatant was removed and the residue was dried *in vacuo*, furnishing borohydride **3** in a quantitative fashion as a yellow solid (106 mg, 162 µmol, >99%). X-ray quality crystals of **3** were obtained by layering a THF solution with *n*-pentane at –40°C.

EA: calcd. C: 66.88%, H: 5.79%, N: 7.31%; found: C: 67.21%, H: 6.02%, N: 7.61%.

^{1}H NMR (600.13 MHz, benzene-D$_6$, 295 K): δ (ppm) = 1.00 (s, 6 H, H-12/H-13), 1.11 (s, 6 H, H-12/H-13), 1.12-1.17 (m, 4 H, H-THF), 3.25-3.44 (m, 4 H, H-THF), 3.45-3.54 (m, 2 H, H-11), 3.81-3.90 (m, 2 H, H-8), 3.95-4.12 (m, 2 H, H-8), 5.53 (br s, 2 H, H-9), 5.81(s, 2 H, H-5), 7.01-7.05 (m, 2 H, H-1), 7.05-7.10 (m, 2 H, H-Ph), 7.10-7.16 (m, 4 H, H-Ph), 7.20-7.26 (m, 4 H, H-Ph), 7.29-7.33 (m, 2 H, H-2).[3]

^{13}C{^{1}H} NMR (150.90 MHz, benzene-D$_6$, 295 K): δ (ppm) = 25.35 (2 C, C-12/C-13), 25.90 (2 C, C-12/C-13), 26.00 (2 C, C-THF), 67.94 (br s, 4 C, C-8, C-THF), 75.05 (2 C, C-7), 78.64 (2 C, C-9/C-10), 81.11 (2 C, C-5), 120.80 (2 C, C-2), 127.43 (4 C, C-Ph), 127.80 (2 C, C-Ph), 128.85 (4 C, C-Ph), 129.45 (2 C, C-1), 139.53 (2 C, C-3), 143.27 (2 C, C-Ph), 162.95 (2 C, C-4), 170.86 (2 C, C-6).[2]

^{11}B{^{1}H} NMR (128.30 MHz, benzene-D$_6$, 295 K): δ (ppm) = 1.63 (br s, 1 B, B-Pin).[2]

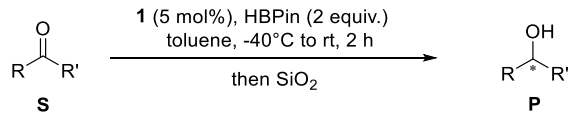
MS (LIFDI+): $[MO\text{-}(2H,THF)]^+ = C_{34}H_{34}BMgN_3O_5^+$, calcd.: 599.2, found: 599.2.

[3] Short acquisition times allowed the characterization of this mildly thermally labile compound at room temperature, giving significantly better resolved resonances compared to low temperature NMR studies.

2.3 NMR Analysis of the Reaction of Hydridoborate 3 with 4'-Fluoro-acetophenone

Exemplary Procedure: Under an inert gas atmosphere, borohydride complex **3** (20.7 mg, 31.5 μmol, 1.0 equiv.) was dissolved in 0.5 mL toluene-D_8, transferred to a Young NMR tube and cooled to −40°C in a cold bath. The solution was added neat 4'-fluoroacetophenone (4.88 mg, 4.29 μL, 31.5 mmol, 1.0 equiv.), the tube was sealed and immediately frozen in liquid nitrogen prior to any mixing events, after which the frozen sample was transferred to the NMR facility. Prior to loading the tube onto the pre-cooled NMR spectrometer (−80°C), the mixture was allowed to partially melt, the tube was shaken vigorously and was transferred to the machine, recording a sequence of ^{1}H, ^{11}B, and ^{19}F spectra at temperature increments of 10°C.

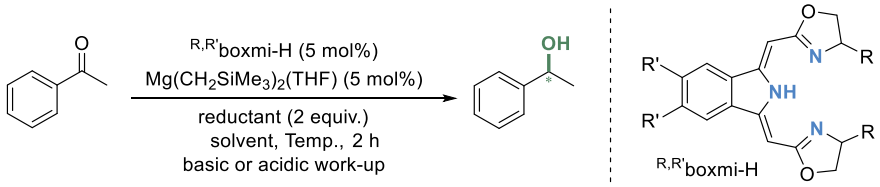
2.4 Catalytic Enantioselective Reduction



Exemplary Procedure: A solution of the precatalyst **1** (4.6 mg, 7.5 μmol, 5 mol%) in 0.5 mL toluene was cooled to –40 °C and was added neat HBPin (43.5 μL, 38.4 mg, 0.30 mmol, 2.0 equiv.) in one portion. The mixture was stirred for 5 min, after which the substrate (0.15 mmol, 1.0 equiv.) was added and the mixture was warmed to rt over a period of 2 h. The resulting boric ester was subjected to hydrolysis by addition onto a short silica column. The residue was eluted with ether and analyzed directly by HPLC (for methods see Section 3.1).

Spectral data for the synthesised compounds have been reported previously.[5]

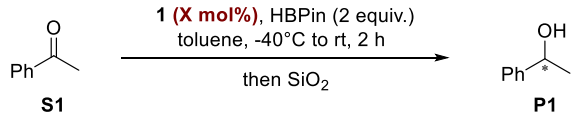
2.5 Complete List of Screening Results



#	R[a]	R'	reductant	solvent	%c.[b]	%ee[b]
1[c]	Ph	H	$(EtO)_2MeSiH$	toluene	36	33 (*R*)
2[c]	Ph	H	Ph_2SiH_2	toluene	0	nd
3[c]	Ph	H	HBPin	toluene	>99	89 (*S*)
4[c]	Ph	Me	HBPin	toluene	>99	87 (*S*)
5[c]	iPr	Me	HBPin	toluene	>99	5 (*S*)
6[c]	tBu	H	HBPin	toluene	>99	11 (*R*)
7[c]	Bn	Me	HBPin	toluene	>99	4 (*R*)
8[c,e]	Ph	H	HBPin	toluene	>99	92 (*S*)
9[d,e]	Ph	H	HBPin	toluene	>99	96 (*S*)
10[d,e]	Ph	H	HBPin	hexane	>99	89 (*S*)
11[d,e]	Ph	H	HBPin	DCM	>99	90 (*S*)
12[d,e]	Ph	H	HBPin	THF	>99	95 (*S*)
13[d,e]	Ph	H	HBPin	Et_2O	>99	95 (*S*)
14[d,e]	Ph	H	HBPin	MeCN	>99	70 (*S*)
15[d,e]	Ph	H	HBPin	TMEDA	>99	10 (*S*)

[a] (*S*)-enantiomers of all ligands were employed. [b] Determined by HPLC analysis. [c] Performed at rt. [d] Warmed from −40°C to rt over 2 h. [e] Isolated precatalyst **1** was used. Basic work-up (K_2CO_3/MeOH) for hydrosilylation, acidic work-up (SiO_2) for hydroboration

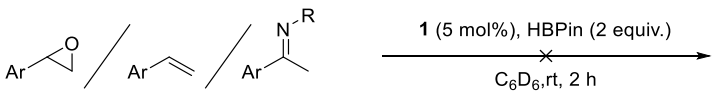
2.6 Catalyst Loadings



We applied our standard procedure for the reduction of acetophenone **S1** at different catalyst loadings (5 mol%, 2.5 mol%, 1 mol%, 0.5 mol%, 0.1 mol%): After activation of the catalyst at –40°C (*vide supra*), the catalyst/HBPin mixture was added varying amounts of acetophenone. After warming to rt over a period of 2 h, the resulting boric ester was subjected to hydrolysis by addition onto a short silica column. The residue was eluted with diethyl ether and analyzed by HPLC.

Catalyst loading (mol%)	%conv.	%ee
5	>99	95
2.5	>99	93
1	>99	92
0.5	>99	92
0.25	>99	90

2.7 Catalytic Reduction of Other Substrates



Exemplary Procedure: A solution of the precatalyst **1** (2.5 mg, 4.1 µmol, 5 mol%) in 0.5 mL C_6D_6 was added neat HBPin (23.6 µL, 20.7 mg, 0.16 mmol, 2.0 equiv.) in one portion. The mixture was stirred for 5 min, after which the substrate (0.08 mmol, 1.0 equiv.) was added. The mixture was transferred into a Young NMR tube and the reaction progress was monitored by NMR spectroscopy. No reaction was observed within 1 d at rt.

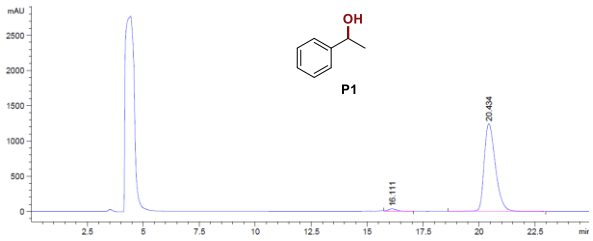
3 Chromatographic Data

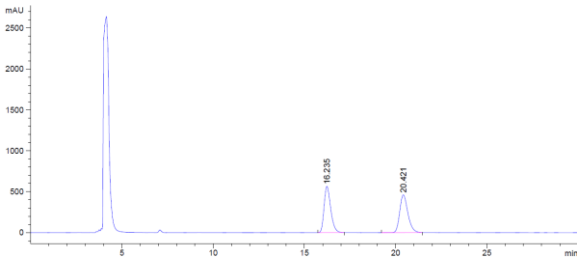
3.1 Overview of HPLC Methods

#	HPLC Column	Hexane/*i*PrOH	λ [nm]	v [mL/min]	T [°C]	t_{R1} [min]	t_{R2} [min]
P1	Chiralcel OD-H	98/2	210	1.0	20	15.2	19.9
P2	Chiralpak AD-H	95/5	230	0.8	20	16.1	17.6
P3	Chiralpak AD-H	95/5	215	1.0	20	17.2	18.4
P4	Chiralcel OD-H	98/2	210	1.0	10	25.1	26.8
P5	Chiralpak AD-H	98/2	210	1.0	20	14.2	16.4
P6	Chiralcel OD-H	99/1	210	0.8	20	21.9	25.5
P7	Chiralcel OD-H	95/5	210	0.8	20	19.5	28.0
P8	Chiralcel OD-H	95/5	210	1.0	20	16.5	17.8
P9	Chiralcel OD-H	99/1	210	1.0	20	20.0	23.1
P10	Chiralcel OD-H	99/1	210	1.0	20	24.9	28.0
P11	Chiralcel OD-H	98/2	230	0.5	25	34.4	36.4
P12	Chiralcel OD-H	85/15	230	1.0	20	6.3	12.3

3.2 HPLC Data

P1: The major isomer is (*S*)-configured.

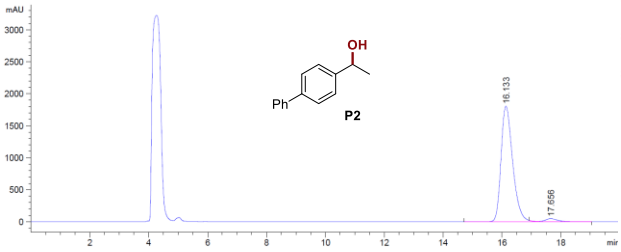


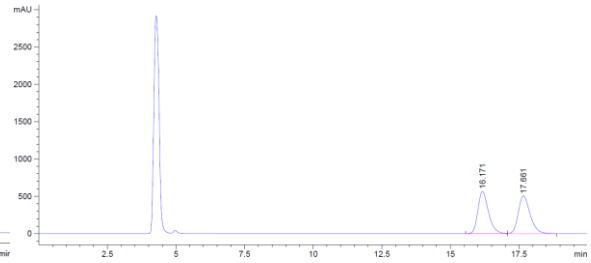


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.111	VB	0.4038	993.55780	36.93750	2.2394
2	20.434	BB	0.5412	4.33728e4	1242.56873	97.7606
Totals :				4.43664e4	1279.50622	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.235	BB	0.3855	1.41906e4	564.13531	49.8150
2	20.421	BB	0.4754	1.42960e4	461.44659	50.1850
Totals :				2.84865e4	1025.58191	

P2: The major isomer is (*S*)-configured.

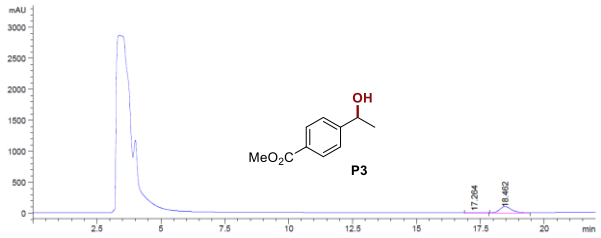


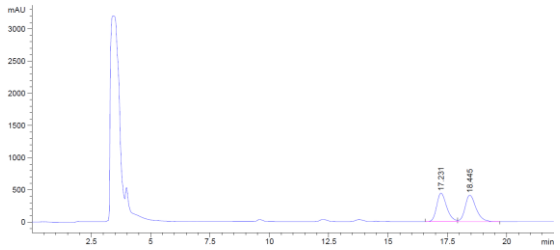


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.133	BV R	0.4196	4.94592e4	1805.54785	97.2993
2	17.656	VB E	0.4418	1372.84338	46.85808	2.7007
Totals :				5.08320e4	1852.40593	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.171	BV	0.4061	1.51945e4	568.00879	49.9848
2	17.661	VB	0.4602	1.52037e4	506.53748	50.0152
Totals :				3.03982e4	1074.54626	

P3

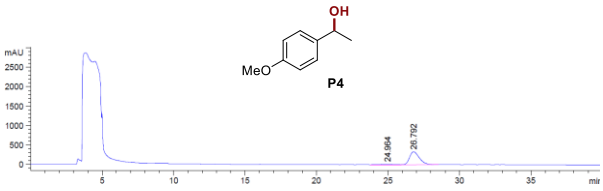


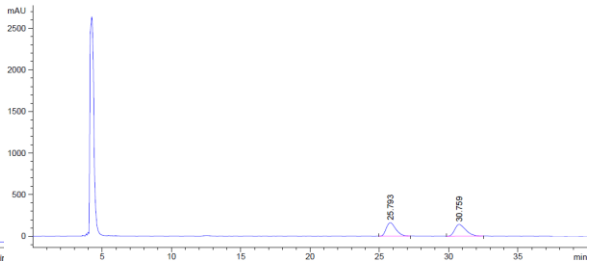


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.264	BB	0.3786	49.52815	1.90954	1.4285
2	18.462	BB	0.4630	3417.65967	112.32547	98.5715
Totals :				3.46719e3	114.23501	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.231	BV	0.4472	1.29377e4	442.44095	49.6298
2	18.445	VB	0.4872	1.31307e4	410.49481	50.3702
Totals :				2.60684e4	852.93576	

P4: The major isomer is (*S*)-configured.

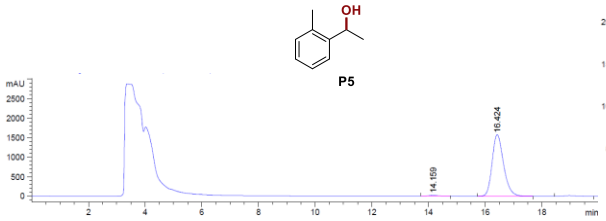


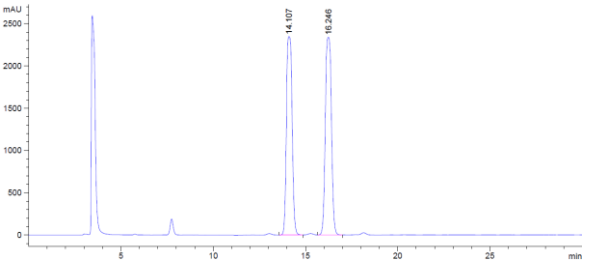


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.964	BV	0.7074	618.70477	13.73740	3.1812
2	26.792	VB	0.7365	1.88276e4	398.97708	96.8187
Totals :				1.94463e4	412.71448	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.793	BB	0.7417	7765.30859	161.27690	49.8027
2	30.759	BB	0.8659	7826.82031	142.26196	50.1973
Totals :				1.55921e4	303.53886	

P5

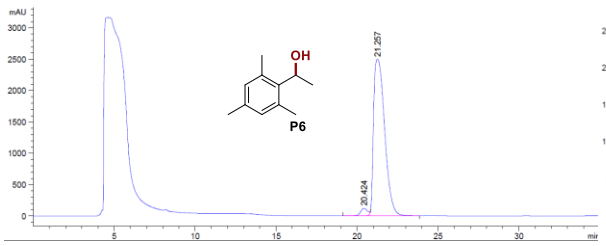


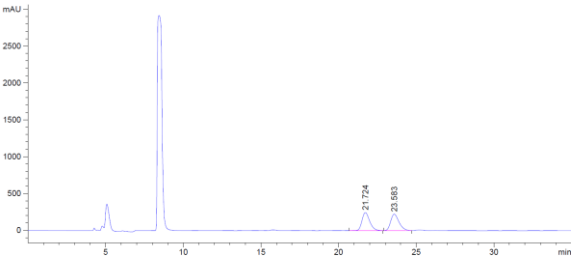


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.159	BB	0.3545	492.18301	21.38494	1.1019
2	16.424	BB	0.4292	4.41742e4	1575.23828	98.8981
Totals :				4.46664e4	1596.62322	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.107	VB	0.3408	5.04860e4	2348.27759	48.4725
2	16.246	VB	0.3657	5.36680e4	2338.56616	51.5275
Totals :				1.04154e5	4686.84375	

P6

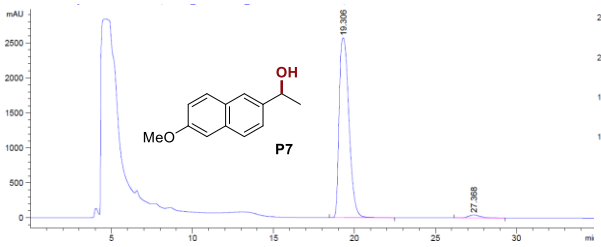




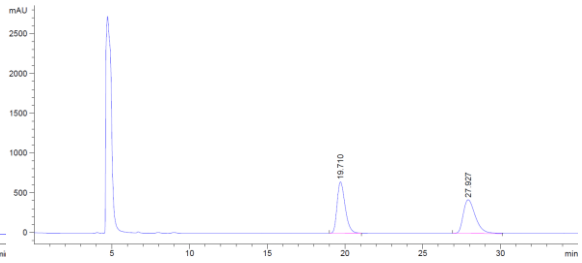
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.424	BV E	0.4480	3432.36182	117.76168	2.8153
2	21.257	VB R	0.7517	1.18487e5	2496.75806	97.1847
Totals :				1.21920e5	2614.51974	

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.724	BB	0.5333	8574.23926	246.83929	50.4017
2	23.583	BB	0.5754	8437.55762	224.03615	49.5983
Totals :				1.70118e4	470.87544	

P7

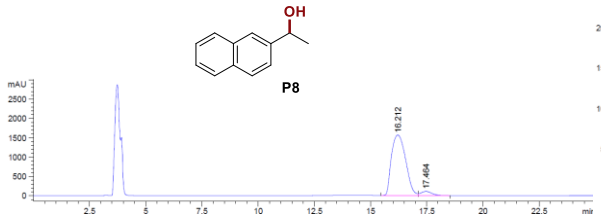


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.306	BB	0.6651	1.07591e5	2566.47412	98.0466
2	27.368	BB	0.7773	2143.57471	41.72945	1.9534
Totals :				1.09735e5	2608.20357	

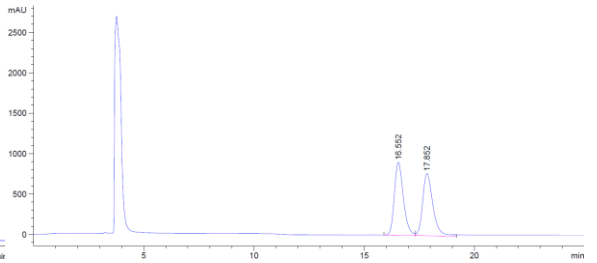


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.710	BB	0.5546	2.31084e4	644.08221	50.1815
2	27.927	MM	0.9048	2.29412e4	422.57077	49.8185
Totals :				4.60496e4	1066.65298	

P8

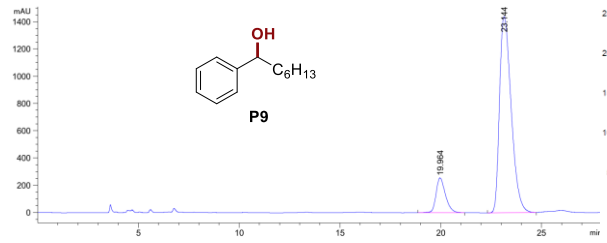


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.212	VV	0.7452	6.90233e4	1569.17786	94.8033
2	17.464	VB	0.5192	3783.53442	109.48335	5.1967
Totals :				7.28060e5	6089.01359	



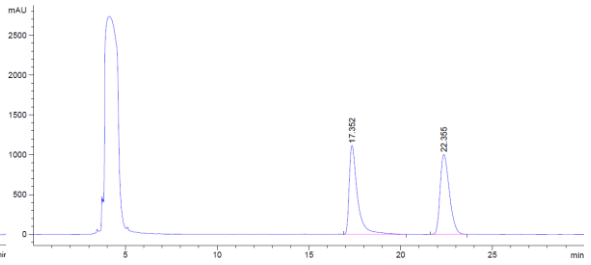
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.552	MF	0.4751	2.57487e4	903.32465	50.7427
2	17.852	FM	0.5411	2.49950e4	769.85748	49.2573
Totals :				5.07437e4	1673.18213	

P9



Signal 2: DAD1 C, Sig=210,4 Ref=off

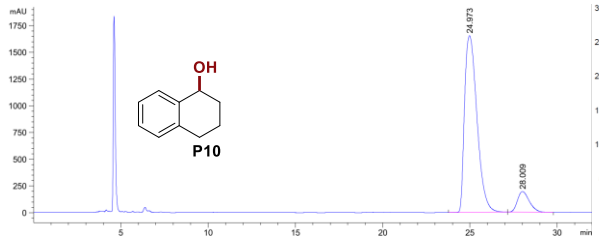
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.964	BB	0.4900	8279.73730	255.53160	12.5176
2	23.144	BB	0.6266	5.78651e4	1440.64343	87.4824



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

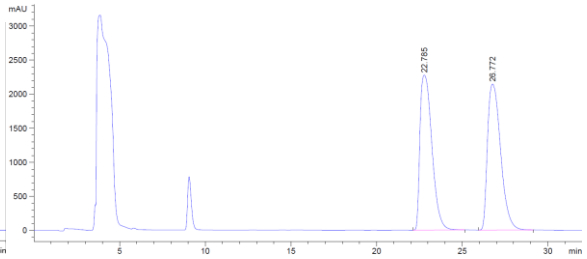
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.352	VB	0.4614	3.49421e4	1115.57532	49.9325
2	22.355	BB	0.5395	3.50366e4	1003.04236	50.0675

P10



Signal 2: DAD1 C, Sig=210,4 Ref=off

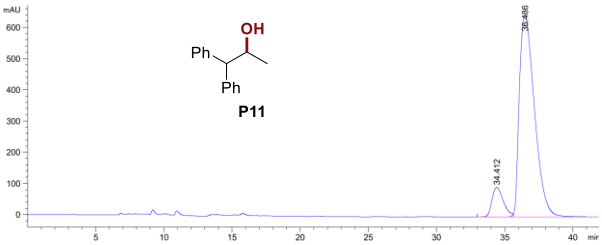
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.973	BB	0.7804	8.17277e4	1654.27820	89.9189
2	28.009	BB	0.7262	9162.76758	193.57646	10.0811
Totals :				9.08905e4	1847.85466	



Signal 2: DAD1 D, Sig=215,8 Ref=360,100

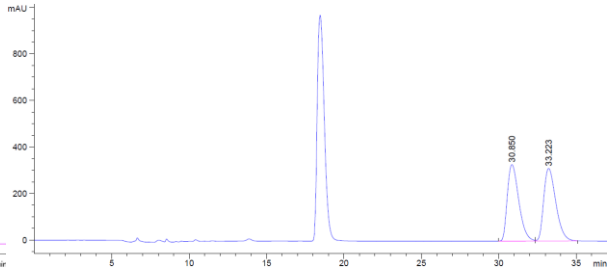
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.785	BB	0.7643	1.10023e5	2274.66260	49.1366
2	26.772	BB	0.8443	1.13890e5	2142.21973	50.8634
Totals :				2.23912e5	4416.88232	

P11



Signal 3: DAD1 D, Sig=230,4 Ref=off

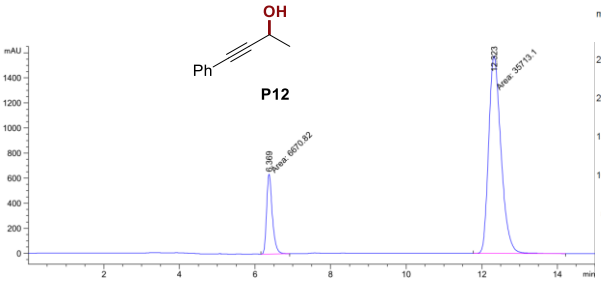
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.412	BV E	0.8758	5413.89355	94.30280	9.7879
2	36.486	VBAR	1.1910	4.98985e4	646.10663	90.2121
Totals :				5.53124e4	740.40942	



Signal 1: DAD1 B, Sig=230,16 Ref=360,100

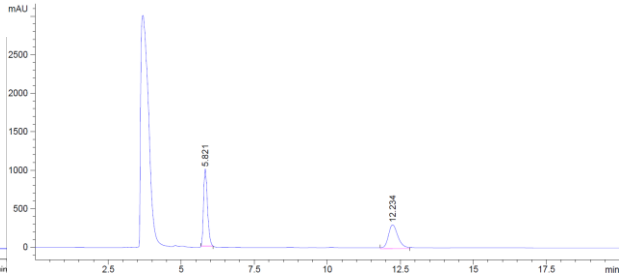
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.850	BV	0.8033	1.68864e4	328.70493	49.9015
2	33.223	VB	0.8481	1.69530e4	311.89572	50.0985
Totals :				3.38393e4	640.60065	

P12



Signal 3: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.369	MM	0.1747	6670.81689	636.57764	15.7390
2	12.323	MM	0.3774	3.57131e4	1576.97229	84.2610
Totals :				4.23840e4	2213.54993	

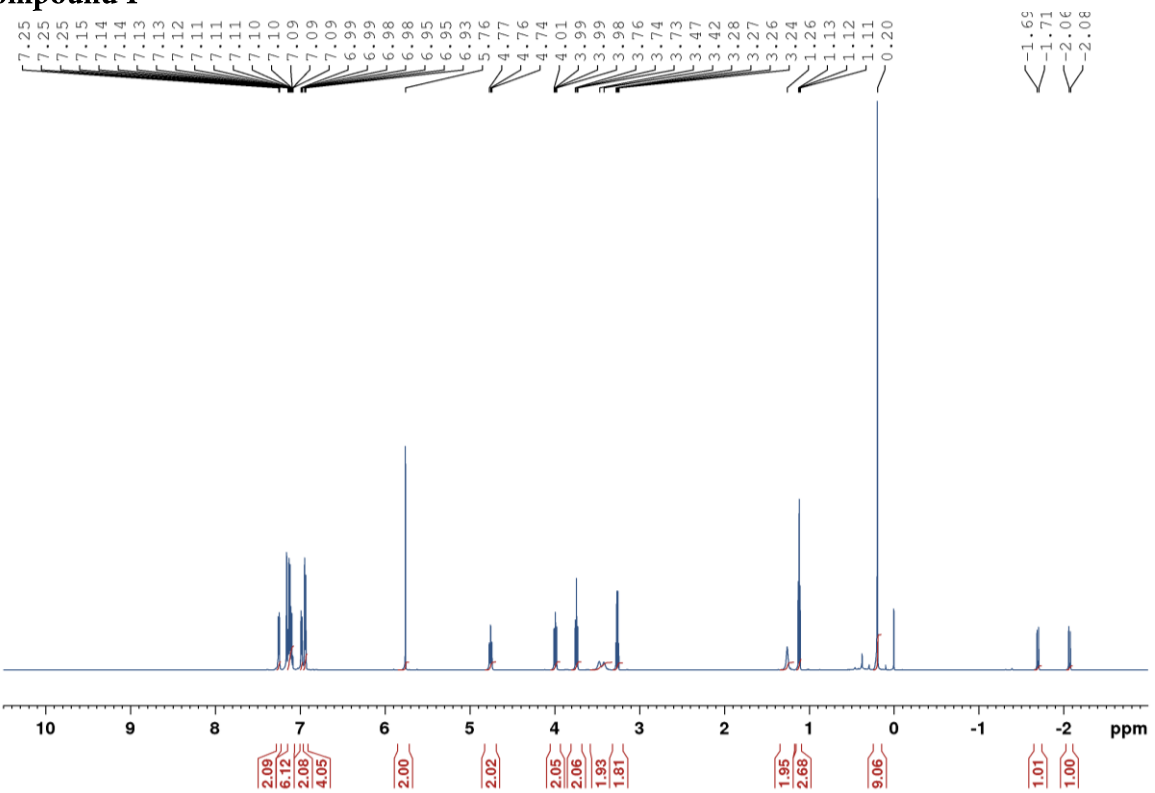


Signal 2: DAD1 D, Sig=215,8 Ref=360,100

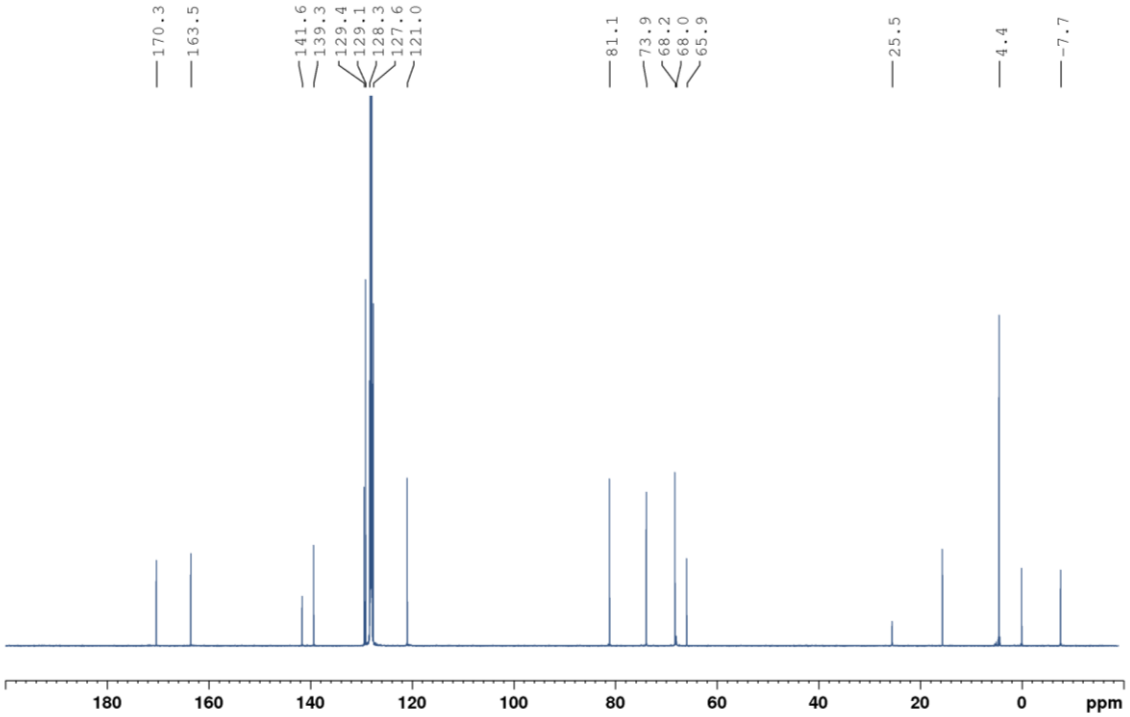
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.821	MM	0.1550	9297.17578	999.97711	56.2973
2	12.234	MM	0.3873	7217.25879	310.59656	43.7027
Totals :				1.65144e4	1310.57367	

4 NMR Spectra

Compound 1

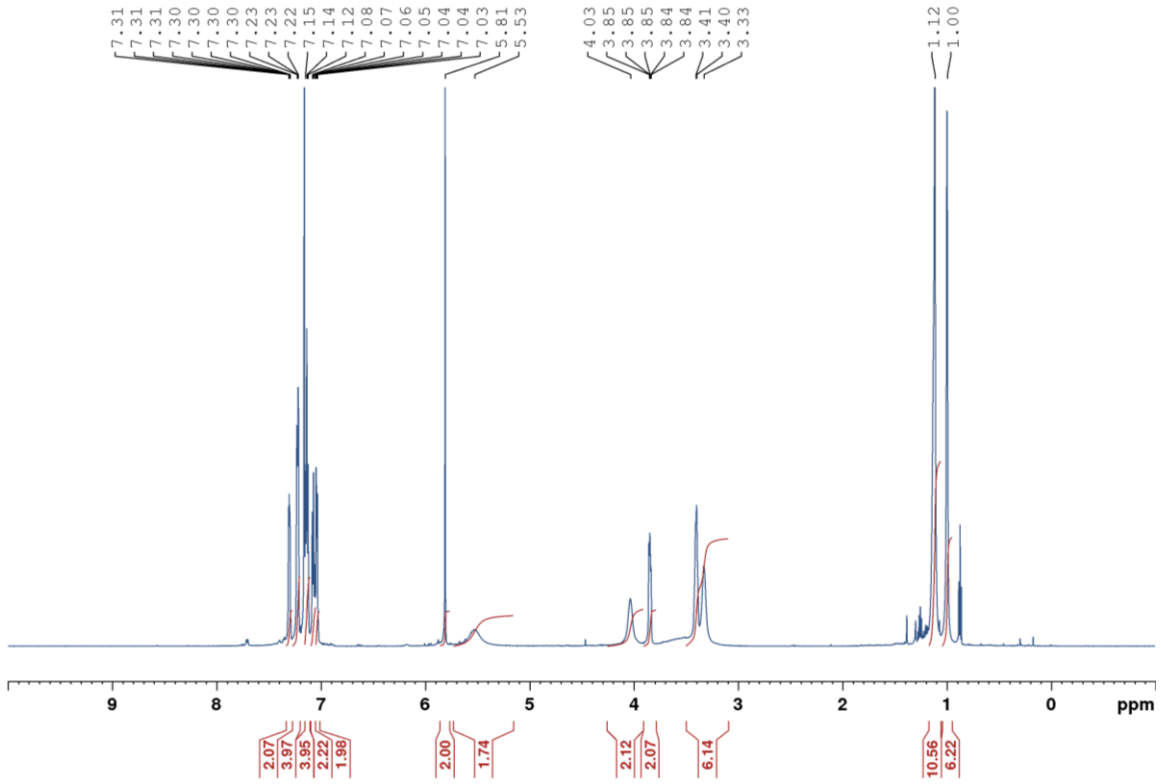


^{1}H NMR spectrum of ^{Ph}boxmiMg(CH_2SiMe_3)(THF)$_{0.5}$(Et_2O)$_{0.5}$ (600.13 MHz, C_6D_6, 295 K).

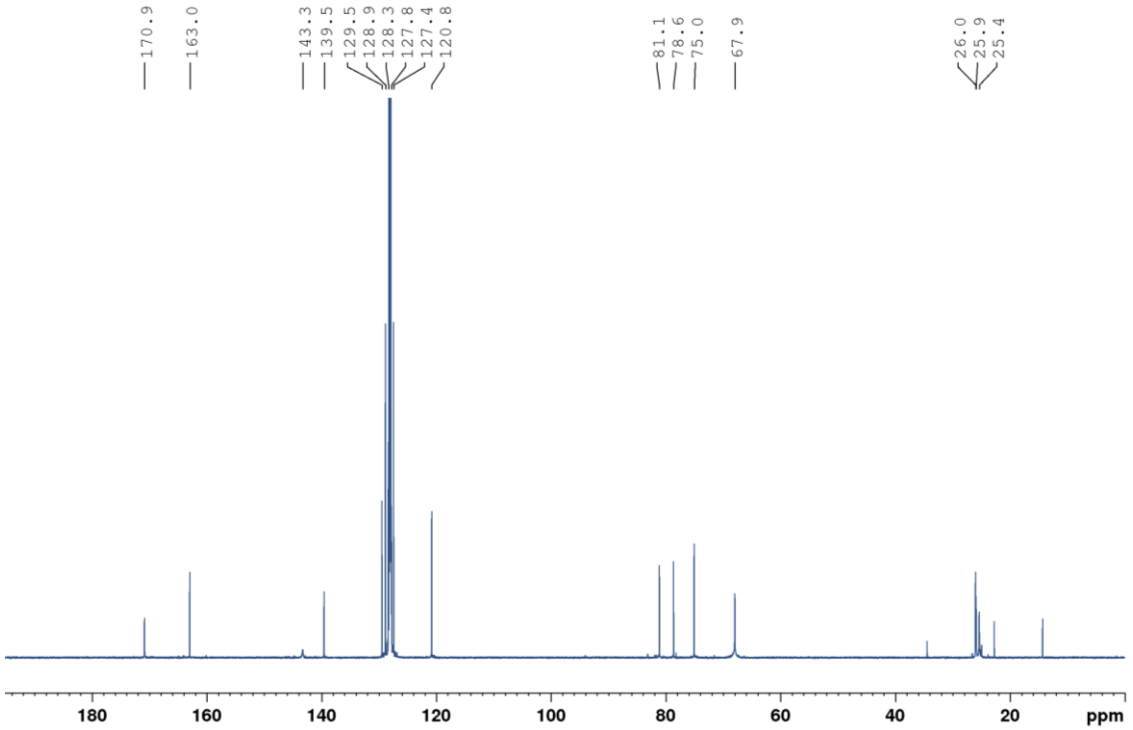


^{13}C NMR spectrum of ^{Ph}boxmiMg(CH_2SiMe_3)(THF)$_{0.5}$(Et_2O)$_{0.5}$ (150.90 MHz, C_6D_6, 295 K).

Compound 3



^{1}H NMR spectrum of compound 3 (600.13 MHz, C_6D_6, 295 K).



^{13}C NMR spectrum of compound 3 (150.90 MHz, C_6D_6, 295 K).

5 X-Ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-K_α radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 0.4...1°) were integrated by profile fitting[6,7] Data were corrected for air and detector absorption, Lorentz and polarization effects[7] and scaled essentially by application of appropriate spherical harmonic functions.[7-9] Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling process), and augmented by a spherical correction[7-9] or numerically (Gaussian grid).[7,8,10] An illumination correction was performed as part of the numerical absorption correction.[8]

The structures were solved by the charge flip procedure[11] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[12] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.[13] In complex **3** the positions of hydrogen atoms on boron were taken from difference Fourier syntheses and fully refined. Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry[13] and adp restraints[14] were applied.

Crystals of complex **1**·0.5OEt_2 were found twinned; the structure was solved using only reflections with small overlap factors (typically < 0.4). Final refinement was carried out against all single and composite reflections involving both domains (refined twin fractions 0.66:0.34).

CCDC 1961879 – 1961881 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via https://www.ccdc.cam.ac.uk/structures/?.

Table S1. Details of the crystal structure determinations of complexes **1, 2** and **3**.

	1·0.5OEt_2	**2**	**3**
formula	$C_{38}H_{46}MgN_3O_{3.50}Si$	$C_{44}H_{46}FMgN_3O_5$	$C_{38}H_{44}BMgN_3O_5$
crystal system	triclinic	triclinic	orthorhombic
space group	*P* 1	*P* 1	$P\,2_12_12_1$
a /Å	9.7605(2)	9.5675(4)	10.60635(16)
b /Å	10.6398(3)	9.7347(4)	16.6805(3)
c /Å	17.7151(4)	11.4970(3)	19.3703(2)
α /°	94.6517(18)	65.663(3)	
β /°	98.1677(18)	88.065(3)	
γ /°	90.4055(18)	84.019(3)	
V /Å^3	1814.72(7)	970.28(7)	3426.98(9)
Z	2	1	4
M_r	653.18	740.15	657.88
F_{000}	698	392	1400
d_c /Mg·m^{-3}	1.195	1.267	1.275
m /mm^{-1}	1.059	0.838	0.100
max., min. transmission factors	1.000, 0.507 [a]	1.000, 0.941[b]	1.000, 0.744[b]
X-radiation, *l* /Å	Cu-*K*a, 1.54184	Cu-*K*a, 1.54184	Mo-*K*a, 0.71073
data collect. temperat. /K	120(1)	120(1)	120(1)
q range /°	4.2 to 70.7	4.2 to 71.0	2.2 to 32.5
index ranges *h*, *k*, *l*	±11, ±12, ±21	±11, ±11, ±14	±15, -24 ... 25, ±29
reflections measured	60236	23936	145176
unique [R_{int}]	18074 [0.0325]	6787 [0.0271]	12099 [0.0726]
observed [$I \geq 2s(I)$]	15882	6573	9996
data / restraints /parameters	18074 / 28 / 857	6787 / 121 / 534	12099 / 85 / 473
GooF on F^2	1.013	1.035	1.025
R indices [$F>4s(F)$] $R(F)$, $wR(F^2)$	0.0395, 0.0982	0.0256, 0.0618	0.0496, 0.1127
R indices (all data) $R(F)$, $wR(F^2)$	0.0453, 0.1009	0.0271, 0.0631	0.0670, 0.1207
absolute structure parameter	–0.028(17)	–0.019(17)	–0.01(7)
largest residual peaks /e·Å^{-3}	0.360, –0.231	0.116, –0.149	0.320, –0.254
CCDC deposition number	1961879	1961880	1961881

[a] semi-empirical absorption correction. [b] numerical absorption correction.

6 Computational Details

6.1 DFT Setup

All calculations were performed with the software suite Gaussian 09 Revision D.01 at the DFT level of theory.[15] All geometry optimizations were carried out with Ahlrichs' def2 basis set family,[16,17] employing def2TZVP basis functions for Mg, N, B and def2SVP for the remaining elements along with the BP86 functional and no structural simplifications.[18,19] Tight convergence criteria and an ultrafine integration grid have been used throughout all calculations. Gibbs free enthalpy corrections were calculated using the harmonic approximation at 233 K at the level of theory of the geometry optimization. The presence of a single imaginary frequency for transition states and their absence in the case of stationary points was confirmed by frequency calculations. The connection of two stationary points by the proposed transition state was confirmed by an optimization run in each direction of the vibration associated with the imaginary frequency or by calculation of the intrinsic reaction coordinate as implemented for the IRC keyword in Gaussian. Single point energies of the optimized structures were calculated with PBE0/def2QZVPP as the computational tool, accounting for solvation effects of toluene with the SMD model.[20–22] Dispersion effects were included with Grimme's recent dispersion correction GD3 as implemented in Gaussian.[23,24] The functionals and basis sets applied herein have been shown to produce reliable results for geometrical parameters and thermochemical data for comparable systems. An overview of Gibbs corrections and SCF energies is shown in Section 6.2.

6.2 Geometries, Energies and Gibbs Corrections

B-1

δG_{corr} 0.569041

E_{SCF} -2006.24142214

G_{rel} 2.5 kcal/mol

79

MgH-OBH XYZ

O	-0.24082	-1.78716	-3.71185
O	-0.82268	3.50677	2.42788
N	-1.94790	0.55845	-0.53566
N	0.34807	-0.75401	-1.77333
N	0.04069	1.84359	1.15186
C	-2.63903	-0.11705	-1.50803
C	-4.05777	0.30226	-1.47399
C	-4.14961	1.30161	-0.46912
C	-2.78746	1.45273	0.08988
C	-5.18626	-0.07801	-2.21592
H	-5.12146	-0.84875	-3.00003
C	-6.41398	0.54948	-1.93122
H	-7.31590	0.26238	-2.49456
C	-6.50526	1.54400	-0.93377
H	-7.47737	2.02065	-0.73111
C	-5.37165	1.93443	-0.19568
H	-5.45059	2.71484	0.57751
C	-2.04970	-0.99603	-2.41211
H	-2.67188	-1.49240	-3.16844
C	-0.63424	-1.16813	-2.56001
C	1.60216	-0.87535	-2.57846
H	1.74664	0.10417	-3.09270
C	1.19453	-1.93573	-3.62156
H	1.42990	-2.96675	-3.27323
H	1.63037	-1.77684	-4.62605
C	2.88792	-1.19657	-1.84170
C	4.06182	-0.48134	-2.16264
H	4.01195	0.34188	-2.89499
C	5.28835	-0.80260	-1.55630
H	6.19501	-0.23522	-1.82077
C	5.35250	-1.83858	-0.60847
H	6.31029	-2.08707	-0.12379
C	4.18556	-2.54756	-0.27218
H	4.21381	-3.34158	0.48979
C	2.96398	-2.23432	-0.88961
H	2.05988	-2.78561	-0.59466
C	-2.38341	2.35986	1.05858
H	-3.12204	3.03453	1.51084
C	-1.02763	2.52122	1.51118
C	1.21509	2.41199	1.85719
H	1.72263	1.59434	2.41072
C	0.55921	3.41916	2.84963
H	1.00201	4.43394	2.80734
H	0.57882	3.05436	3.89837
C	2.21409	3.03902	0.89160
C	3.57796	2.68852	0.95191
H	3.90950	1.92886	1.67861
C	4.51173	3.29107	0.08975
H	5.57376	3.00457	0.14870
C	4.08979	4.24960	-0.84700
H	4.81981	4.72235	-1.52336
C	2.72844	4.59959	-0.92103
H	2.38965	5.34607	-1.65732
C	1.79785	3.99769	-0.05889
H	0.73211	4.27060	-0.12864
H	1.58244	-0.74030	1.02855
H	1.42155	-0.74844	3.04519
Mg	-0.08119	-0.02170	0.17855
C	-1.07945	-2.40133	2.28141
C	0.02899	-3.49789	1.95908
O	1.26070	-2.77921	2.06417
O	-0.45758	-1.20547	1.76261
C	0.05425	-4.66692	2.95769
H	-0.91386	-5.21141	2.97670
H	0.84465	-5.38756	2.66330
H	0.28787	-4.31671	3.98089
C	-0.11353	-4.06337	0.52861
H	-0.18384	-3.25127	-0.22382
H	0.78618	-4.66857	0.29548
H	-1.00259	-4.71807	0.41506
C	-2.42841	-2.61256	1.58819
H	-2.88431	-3.57478	1.90140
H	-3.13014	-1.79970	1.86613
H	-2.33354	-2.61699	0.48484
C	-1.29027	-2.19913	3.79376
H	-1.90620	-1.29082	3.95272
H	-1.81567	-3.05942	4.25533
H	-0.32389	-2.05250	4.31508
B	1.03924	-1.34331	2.03223

B-2

δG_{corr} 0.697542

E_{SCF} -2390.87758153

G_{rel} 2.8 kcal/mol

96

MgHOBH-Ketone-bottom XYZ

O	1.23782	2.12126	-3.58944
O	1.02122	-3.14860	3.06027
N	1.96595	-1.09919	-0.70348
N	0.41511	1.36029	-1.60200
N	0.21388	-1.49911	1.71975
C	2.71270	-0.71526	-1.79257
C	3.80221	-1.69027	-2.01699
C	3.66322	-2.67460	-1.00930
C	2.51007	-2.25724	-0.18160
C	4.82502	-1.77824	-2.97451
H	4.94037	-1.01501	-3.76025
C	5.70771	-2.87210	-2.90801
H	6.51920	-2.96356	-3.64733
C	5.56710	-3.85605	-1.90484
H	6.27021	-4.70354	-1.87442
C	4.54275	-3.76678	-0.94409
H	4.44062	-4.53795	-0.16422
C	2.49649	0.40721	-2.58247
H	3.18166	0.59829	-3.41921
C	1.37176	1.28688	-2.50892
C	-0.67982	2.14012	-2.25540
H	-1.31456	1.39797	-2.79849
C	0.10487	2.96212	-3.29668
H	0.46181	3.92585	-2.86678
H	-0.44770	3.15720	-4.23562
C	-1.61128	2.99342	-1.41662
C	-2.92779	3.19746	-1.89281
H	-3.26006	2.67679	-2.80761
C	-3.81706	4.05075	-1.21802
H	-4.83653	4.20128	-1.60885
C	-3.40356	4.70601	-0.04350
H	-4.09902	5.37041	0.49428
C	-2.09934	4.50354	0.43923
H	-1.76071	4.99651	1.36400
C	-1.20371	3.66155	-0.24489
H	-0.19680	3.51891	0.17503
C	2.10899	-2.90781	0.97401
H	2.67563	-3.78906	1.30320
C	1.08018	-2.47064	1.87430
C	-0.63144	-1.45799	2.93661
H	-0.64485	-0.41691	3.32542
C	0.14363	-2.38687	3.91675
H	-0.50237	-3.09082	4.47675
H	0.76769	-1.80679	4.63124
C	-2.06540	-1.92658	2.70979
C	-3.09810	-1.41928	3.52854
H	-2.86531	-0.63665	4.26994
C	-4.41520	-1.89490	3.40398
H	-5.20820	-1.48783	4.05195
C	-4.72022	-2.88360	2.45043
H	-5.75148	-3.25806	2.34982
C	-3.69894	-3.39094	1.62656
H	-3.92971	-4.16350	0.87570
C	-2.38115	-2.91795	1.75736
H	-1.58544	-3.31092	1.10538
H	-0.46494	1.54033	1.44335
O	-1.43031	-0.48866	-0.52794
C	-2.66806	-0.37897	-0.54574
C	-3.38982	0.47787	0.46049
H	-4.04475	-0.15728	1.09469
H	-4.02995	1.22953	-0.04588
H	-2.65539	1.00071	1.10024
H	0.21891	1.46688	3.34680
Mg	0.47883	0.10189	0.22895
C	-3.44331	-1.11505	-1.59413
C	-4.85506	-1.05003	-1.66839
C	-2.73842	-1.89583	-2.54239
C	-5.54526	-1.74997	-2.67001
H	-5.42072	-0.45239	-0.93845
C	-3.42955	-2.59273	-3.54191
H	-1.64085	-1.93898	-2.47170
C	-4.83468	-2.52094	-3.60784
H	-6.64406	-1.69443	-2.71999
H	-2.87306	-3.19682	-4.27572
H	-5.37823	-3.06890	-4.39410
C	2.86941	1.82928	1.94243
C	2.33950	3.33271	1.83697
O	0.93954	3.23162	2.12796
O	1.68597	1.07640	1.60436
C	2.98774	4.29149	2.85128
H	4.08868	4.35247	2.71465
H	2.57093	5.31031	2.71241
H	2.77446	3.98398	3.89260
C	2.51436	3.91494	0.41833
H	2.10001	3.23102	-0.34879
H	1.96264	4.87521	0.35647
H	3.57782	4.11591	0.17171
C	3.99775	1.47109	0.97104

H	4.89181	2.10151	1.15875
H	4.29494	0.41166	1.11080
H	3.69426	1.60116	-0.08505
C	3.28060	1.44087	3.37686
H	3.45875	0.34678	3.41343
H	4.21182	1.95296	3.69283
H	2.48019	1.68192	4.10348
B	0.52287	1.83417	2.19974

B-3

δG_{corr} 0.697633

E_{SCF} -2390.88215240

G_{rel} 0.0 kcal/mol

96

MgHOBH-Ketone-front XYZ

O	0.76121	2.05542	-3.85414
O	1.44265	-3.31243	2.60948
N	2.22310	-0.80890	-0.89214
N	0.20903	1.26394	-1.78608
N	0.47709	-1.70765	1.32073
C	2.85612	-0.31476	-2.01425
C	4.12464	-1.04059	-2.23484
C	4.20660	-2.01058	-1.20863
C	2.99003	-1.84549	-0.38625
C	5.13373	-0.92911	-3.20466
H	5.07621	-0.17715	-4.00740
C	6.23173	-1.80512	-3.12579
H	7.03938	-1.73527	-3.87155
C	6.31309	-2.77468	-2.10188
H	7.18322	-3.44894	-2.06197
C	5.29904	-2.88945	-1.13348
H	5.36898	-3.64950	-0.33943
C	2.38283	0.68777	-2.84578
H	2.98283	0.97361	-3.71975
C	1.10601	1.32345	-2.75063
C	-1.02568	1.89541	-2.33197
H	-1.68400	1.07329	-2.70173
C	-0.48052	2.70662	-3.53394
H	-0.27335	3.76278	-3.24899
H	-1.13503	2.69107	-4.42697
C	-1.85366	2.77595	-1.41509
C	-3.21123	2.99992	-1.74350
H	-3.66155	2.46051	-2.59400
C	-3.99003	3.90284	-1.00097
H	-5.04413	4.07154	-1.27448
C	-3.42275	4.58647	0.09121
H	-4.03058	5.29224	0.67959
C	-2.08032	4.35307	0.43496
H	-1.63429	4.85709	1.30602
C	-1.29748	3.45789	-0.31601
H	-0.25460	3.25914	-0.02412
C	2.69708	-2.61227	0.72837
H	3.41933	-3.37039	1.05822
C	1.51045	-2.49443	1.52148
C	-0.54431	-2.07243	2.33358
H	-0.93130	-1.14141	2.80006
C	0.29390	-2.86704	3.36855
H	-0.21769	-3.75557	3.78536
H	0.65233	-2.21339	4.19371
C	-1.69956	-2.89000	1.76260
C	-2.95109	-2.86982	2.41752
H	-3.09070	-2.21844	3.29707
C	-4.01232	-3.67554	1.97008
H	-4.98110	-3.64708	2.49447
C	-3.83802	-4.51493	0.85553
H	-4.66805	-5.14699	0.50207
C	-2.59765	-4.53872	0.19412
H	-2.45259	-5.19360	-0.68023
C	-1.53700	-3.73217	0.64316
H	-0.57015	-3.74881	0.11644
H	-0.76102	2.41054	2.33310
O	-1.54788	-0.14193	-0.03063
C	-2.75726	0.03252	0.20830
C	-3.20335	0.84999	1.38879
H	-3.85609	0.24390	2.05140
H	-3.80348	1.71773	1.04005
H	-2.32523	1.22917	1.94869
H	-0.23614	0.62789	3.15699
Mg	0.52948	0.09505	0.08524
C	-3.76978	-0.57828	-0.70715
C	-5.15808	-0.36046	-0.53682
C	-3.32746	-1.38567	-1.78308
C	-6.08030	-0.93008	-1.42718
H	-5.52183	0.26404	0.29218
C	-4.25016	-1.95396	-2.67110
H	-2.24729	-1.55935	-1.89873
C	-5.62841	-1.72597	-2.49582
H	-7.15826	-0.75230	-1.28836
H	-3.89654	-2.58181	-3.50399
H	-6.35417	-2.17239	-3.19432
C	2.43155	1.99064	1.77839
C	2.10926	3.01462	2.94862
O	1.08433	2.34819	3.66615
O	1.10730	1.46945	1.46058

C	3.28952	3.26806	3.89951
H	4.17226	3.67551	3.36237
H	2.98739	4.00737	4.66940
H	3.58587	2.34134	4.42679
C	1.59496	4.37214	2.41351
H	0.76635	4.22940	1.69278
H	1.19972	4.95763	3.26845
H	2.39215	4.96874	1.92330
C	3.04585	2.62811	0.52702
H	3.99996	3.13836	0.77653
H	3.27362	1.85763	-0.23791
H	2.36471	3.37086	0.06949
C	3.31237	0.83074	2.27469
H	3.36519	0.03937	1.50143
H	4.35060	1.16100	2.48359
H	2.88634	0.39081	3.19771
B	0.18988	1.70600	2.71355

B-ts (*S*)

δG_{corr}

E_{SCF}

G_{rel}

Atome

XYZ

H-1

δG_{corr} 0.388378

E_{SCF} -1594.61958877

G_{rel} 16.8 kcal/mol

57

MgH XYZ

Mg	0.08121	-0.14086	-0.99810
O	0.34771	-3.85197	1.15844
O	1.02553	4.01561	-0.88304
N	2.05315	-0.14895	-0.28127
N	-0.26631	-1.86292	0.24630
N	0.08838	1.96617	-0.60677
C	2.73925	-1.27748	0.09676
C	-2.84716	2.55351	2.56325
H	-2.58140	2.49023	3.63077
C	4.18515	-0.96856	0.15570
C	4.30610	0.41402	-0.14222
C	2.93120	0.90692	-0.38016
C	5.56155	1.04060	-0.14889
H	5.66322	2.11413	-0.37321
C	6.69832	0.25970	0.13368
H	7.69582	0.72684	0.12458
C	6.57799	-1.11542	0.42900
H	7.48309	-1.70423	0.64679
C	5.31789	-1.74276	0.44947
H	5.23145	-2.81491	0.68638
C	2.13671	-2.48183	0.43961
H	2.76273	-3.33291	0.73810
C	0.72157	-2.67544	0.57346
C	-1.51780	-2.45473	0.78612
H	-1.74661	-1.94088	1.74954
C	-1.09132	-3.91887	1.06208
H	-1.36269	-4.59041	0.21684
H	-1.49154	-4.33796	2.00528
C	2.55405	2.22365	-0.60513
H	3.32348	3.00354	-0.67502
C	1.19312	2.67630	-0.68976
C	-1.06076	2.87201	-0.82491
H	-1.49938	2.63620	-1.82126
C	-0.39344	4.28125	-0.83478
H	-0.61363	4.85572	0.09097
H	-0.66641	4.89730	-1.71453
C	-2.74202	-2.34161	-0.10550
C	-2.65440	-2.52313	-1.50258
H	-1.67089	-2.66283	-1.97699
C	-3.81252	-2.48382	-2.29716
H	-3.72563	-2.60973	-3.38785
C	-5.07158	-2.27206	-1.70819
H	-5.97766	-2.24230	-2.33439
C	-5.16769	-2.08661	-0.31794
H	-6.14878	-1.91056	0.15150
C	-4.00822	-2.11618	0.47544
H	-4.08513	-1.95790	1.56438
C	-2.15427	2.72143	0.22305
C	-3.51096	2.69967	-0.15956
H	-3.77237	2.74241	-1.22988
C	-4.52813	2.61430	0.80752
H	-5.58325	2.59649	0.49131
C	-4.19881	2.54302	2.17175
H	-4.99435	2.47370	2.93075
C	-1.83263	2.64298	1.59617
H	-0.77469	2.64090	1.90552
H	-0.53961	-0.31673	-2.63120

(H-1)$_2$

δG_{corr} 0.798154

E_{SCF} -3189.28888322

G_{rel} 7.9 kcal/mol

114

Dimer-XYZ

Mg	-1.10194	-0.91309	0.14623
O	-3.15015	-2.60727	3.59939
O	-1.29520	-1.70181	-4.08210
N	-3.19970	-0.84750	-0.30198
N	-1.72424	-1.82713	2.00956
N	-0.94713	-1.76483	-1.83695
C	-4.22449	-0.78958	0.61060
C	-5.44915	-0.29399	-0.05798
C	-5.10752	-0.12143	-1.42441
C	-3.69150	-0.53801	-1.54709
C	-6.74616	-0.01701	0.39949
H	-7.02052	-0.15579	1.45731
C	-7.69617	0.45111	-0.52865
H	-8.71859	0.68460	-0.19148
C	-7.35609	0.62425	-1.88747
H	-8.11704	0.99177	-2.59421
C	-6.05886	0.33166	-2.35079
H	-5.80385	0.46211	-3.41448
C	-4.13223	-1.24307	1.92069
H	-5.03367	-1.27726	2.54689
C	-2.95853	-1.86290	2.46512
C	-0.87461	-2.58938	2.97352
H	-0.21133	-3.26991	2.40324
C	-1.93810	-3.37737	3.77538
H	-1.72478	-3.45853	4.85826
H	-2.10826	-4.39370	3.35567
C	-0.00400	-1.68438	3.84226
C	1.39244	-1.64816	3.65581
H	1.84312	-2.23812	2.84225
C	2.20728	-0.86049	4.48785
H	3.29620	-0.84644	4.32678
C	1.63530	-0.09104	5.51547
H	2.27514	0.52394	6.16806
C	0.24085	-0.11137	5.70432
H	-0.21795	0.48856	6.50662
C	-0.57150	-0.90168	4.87393
H	-1.66204	-0.91390	5.03434
C	-2.99282	-0.71321	-2.73720
H	-3.47971	-0.47066	-3.69100
C	-1.72667	-1.38607	-2.82153
C	0.18346	-2.53270	-2.39953
H	1.13322	-2.04315	-2.09740
C	-0.03675	-2.40798	-3.94101
H	-0.13233	-3.39031	-4.44695
H	0.75480	-1.81320	-4.44191
C	0.21756	-3.96927	-1.89008
C	1.42964	-4.53649	-1.44599
H	2.34129	-3.91694	-1.43232
C	1.48081	-5.87392	-1.01403
H	2.43594	-6.30145	-0.66878
C	0.31572	-6.66002	-1.01573
H	0.35317	-7.70736	-0.67561
C	-0.90074	-6.09998	-1.44836
H	-1.81987	-6.70788	-1.44564
C	-0.94918	-4.76454	-1.88106
H	-1.90780	-4.32753	-2.20479
Mg	1.19478	0.78384	-0.06524
O	3.05258	2.71487	3.33007
O	1.76563	0.61419	-4.34645
N	3.30124	0.44674	-0.31661
N	1.77709	2.08894	1.55389
N	1.25212	1.14642	-2.19735
C	4.19534	0.41226	0.72458
C	5.41224	-0.31843	0.30200
C	5.21060	-0.65869	-1.06114
C	3.87688	-0.12555	-1.42338
C	6.60184	-0.66407	0.96050
H	6.76875	-0.39738	2.01619
C	7.58506	-1.36810	0.23872
H	8.52382	-1.65801	0.73695
C	7.38503	-1.70577	-1.11692
H	8.17008	-2.25517	-1.66044
C	6.19694	-1.34776	-1.78300
H	6.05197	-1.60820	-2.84351
C	3.99820	1.04485	1.94530
H	4.78758	1.00613	2.70770
C	2.89310	1.91540	2.23195
C	1.11702	3.30098	2.11833
H	1.40665	4.16115	1.47053
C	1.80753	3.42856	3.49624
H	1.21762	2.93361	4.29964
H	2.03354	4.47052	3.79407
C	-0.39785	3.26963	2.18983
C	-1.14779	4.32672	1.63656
H	-0.62554	5.14439	1.11254
C	-2.55030	4.34182	1.73443
H	-3.12159	5.17411	1.29296
C	-3.21946	3.29288	2.38603
H	-4.31878	3.29615	2.45741
C	-2.47859	2.23124	2.93705
H	-2.99839	1.39675	3.43343
C	-1.07860	2.22009	2.84186
H	-0.51123	1.37577	3.26417
C	3.30726	-0.13160	-2.69277

H	3.84939	-0.58990	-3.53031
C	2.08931	0.55541	-3.01799
C	0.20820	1.81900	-2.99955
H	-0.78726	1.47765	-2.64581
C	0.49292	1.30324	-4.44482
H	0.59687	2.11741	-5.18958
H	-0.26958	0.57626	-4.79504
C	0.26170	3.33728	-2.86330
C	-0.93049	4.07762	-2.72620
H	-1.89290	3.54390	-2.66317
C	-0.89967	5.48174	-2.65651
H	-1.84061	6.04500	-2.54896
C	0.32809	6.16382	-2.71539
H	0.35460	7.26388	-2.65878
C	1.52409	5.43294	-2.84018
H	2.49119	5.95979	-2.87887
C	1.49082	4.03036	-2.91286
H	2.43194	3.46331	-2.99675
H	-0.71075	0.94221	-0.07441
H	0.80042	-1.05832	0.41457

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