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Supporting Information

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A New Phosphoramidite Ligand for Asymmetric Allylic Substitution.

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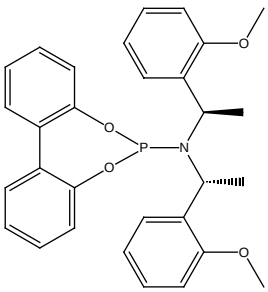
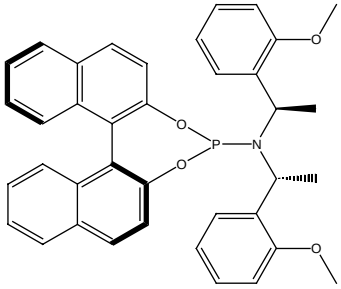
General Procedures. ^{1}H (400 MHz) ,^{13}C (100 MHz) and ^{31}P (162 MHz) NMR spectra were recorded in $CDCl_3$, and chemical shift (δ) are given in ppm relative to $CDCl_3$. Evolution of reaction was followed by GC-MS Hewlett Packard (EI mode) HP6890-5973. Optical rotations were measured at 22°C in a 10 cm cell in the stated solvent ; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1} (concentration c given as g/100 mL). Enantiomeric excesses were determined by chiral-GC (capillary column, 10 psi H_2) or chiral-SFC with the stated column. Temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C) ; retention time (R_T) are given in min. Flash chromatography were performed using silica gel 32-63 μm, 60 Å.

All reactions were conducted under a nitrogen atmosphere. CH_2Cl_2, was distilled from CaH_2 under nitrogen. THF was distilled from sodium-benzophenone ketyl under nitrogen. *para*Metylcinnamyl chloride (**4b**) was synthesized by the reaction of corresponding allylic alcohol with $SOCl_2$ in the presence of pyridine. Cinnamyl carbonate (**9**) was synthesized by the reaction of cinnamyl alcohol with methyl chloroformate in the presence of pyridine. Benzylamine (Fluka), allylamine (Fluka) and *n*-hexylamine (Fluka) were distilled on CaH_2 under reduced pressure. 3-butenylMgBr (**5b**) and 4-pentenylMgBr (**5c**) were synthesized in ether by addition of the corresponding bromide onto magnesium. (*E*)-cinnamyl chloride (**4a**) (Aldrich), (*E*)-cinnamyl alcohol (Acros), 4-bromo-1-butene (Aldrich), 5-bromo-1-pentene (Fluka) and Copperthiophene carboxylate (FrontierScientific) were purchased and used without further purification. In some cases the enantiomers of ligands **1b-3b** have been used.

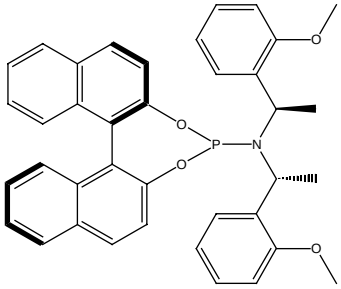
General procedure for phosphoramidite ligand synthesis. To a stirred mixture of Et_3N (6 eq) and PCl_3 (1eq) at 0°C, a solution of Bis-[(*R*)1-(2-methoxy-phenyl)-ethyl]-amine[1] (22.2 mmol) in THF (10 ml) was added and the reaction mixture was stirred at room temperature for nearly 3h until complete disappearance of PCl_3 (checked by ^{31}P NMR). Biphenol or binaphtol (1 eq) in THF (5ml) was slowly added to the reaction mixture at 0°C and the suspension was stirred at room temperature overnight. The suspension was filtered trough celite with toluene and concentrated under reduced pressure. Purification by flash chromatography on Silicagel using ether as eluent gave the ligand as white foam.



O,O'-1,1'-diphenyl-2,2'-diyl-N,N'-di-(*R*,*R*)-1-(2-methoxyphenyl)-ethyl phosphoramidite 1b ^{1}H NMR (400 MHz, $CDCl_3$) : 7.56-6.46 (m, 16H), 5.05 (quint, J = 7.52 Hz, 2H), 3.65 (s, 6H), 1.62 (d, J = 7.32 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) : 156.2, 152.4, 152.3, 151.9, 151.8, 132.2, 130.8, 130.8, 130.8, 130.7, 130.0, 129.0, 127.6, 127.6, 127.4, 124.0, 122.5, 119.5, 109.2, 54.7, 49.3, 49.2, 22.3, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) : 152.41. $[\alpha]_D^{22}$ = +34.1 (*c* 1, $CHCl_3$).



O,O'-(*S*)-1,1'-dinaphthyl-2,2'-diyl)-N,N'-di-(*R*,*R*)-1-(2-methoxyphenyl)-ethylphosphoramidite 2b ^{1}H NMR (400 MHz, $CDCl_3$) : 8.05-5.03 (m, 20H), 5.07 (dq, J_1 = 1.04 Hz, J_2 = 7.08 Hz, 2H), 3.52 (s, 6H), 1.61 (d, J = 7.08 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 150.7, 150.16, 133.0, 132.3, 131.4, 130.5, 129.5, 128.4, 128.2, 127.5, 127.4, 127.3, 127.2, 126.0, 125.8, 124.7, 124.4, 124.4, 124.3, 122.8, 122.5, 121.8, 119.4, 109.3, 65.9, 54.6, 48.3, 48.2, 22.2, 15.3. ^{31}P NMR (162 MHz, $CDCl_3$) : 152.15. $[\alpha]_D^{22}$ = +272.2 (*c* 1, $CHCl_3$).



O,O'-(*R*)-1,1'-dinaphthyl-2,2'-diyl)-N,N'-di-(*R*,*R*)-1-(2-methoxyphenyl)-ethylphosphoramidite 3b ^{1}H NMR (400 MHz, $CDCl_3$) : 8.04-6.52 (m, 20H), 4.99 (dq, J_1 = 1.24 Hz, J_2 = 7.08 Hz, 2H), 3.58 (s, 6H), 1.55 (d, J = 7.08 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) : 156.1, 149.9, 132.8, 132.5, 131.4, 130.3, 129.2, 128.3, 128.0, 127.7, 127.6, 127.4, 127.3, 125.9, 125.6, 124.7, 124.5, 124.2, 122.7, 1212.5, 119.6, 109.2, 54.6, 50.3, 50.2, 22.6, 22.5. ^{31}P NMR (162 MHz, $CDCl_3$) : 152.25. $[\alpha]_D^{22}$ = -144.3 (*c* 1.1, $CHCl_3$).

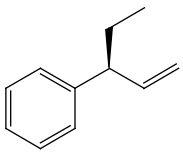
Typical procedure for enantioselective copper-catalyzed S_N2' substitution with Grignard reagent. A dried Schlenk tube was charged with copper salt (1 mol%) and the chiral ligand (1.1 mol%). Dichloromethane (2 mL) was added and the mixture was stirred at room temperature for 30 min. The allylic chloride (1 mmol) was introduced dropwise and the reaction mixture was stirred at room temperature for a further 5 min before being cooled to –78°C in an ethanol-dry ice cold bath. The Grignard (3 M in diethyl ether, 1.2 eq) in dichloromethane (0.6 mL) was added over 40 min *via* a syringe pump. Once the addition was complete the reaction mixture was left at –78°C for a further four hour at which point gas chromatography of an aliquot showed that all the starting material had been converted. The reaction was quenched by addition of aqueous hydrochloric acid (1N, 2 mL). Diethyl ether (10 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by flash column chromatography (eluent = pentane) to yield the product as a mixture of S_N2' and S_N2 regioisomers. Gas Chromatography or Supercritical Fluid Chromatography on a chiral stationary phase showed the enantiomeric excess of S_N2' product.

Typical procedure for tandem copper catalyzed enantioselective allylation-intermolecular metathesis. Same procedure as above until full conversion of the allylic chloride when gas chromatography of an aliquot showed that all the starting material had been converted. Enantiomeric excess of the S_N2' product was measured with this aliquot. At this point the reaction mixture was allowed to warm to room temperature and stirred for one hour. Grubbs' catalyst first generation[2] (5 mol%) as solid was added and the reaction mixture was stirred at room temperature for a further two hours at which point gas chromatography of an aliquot

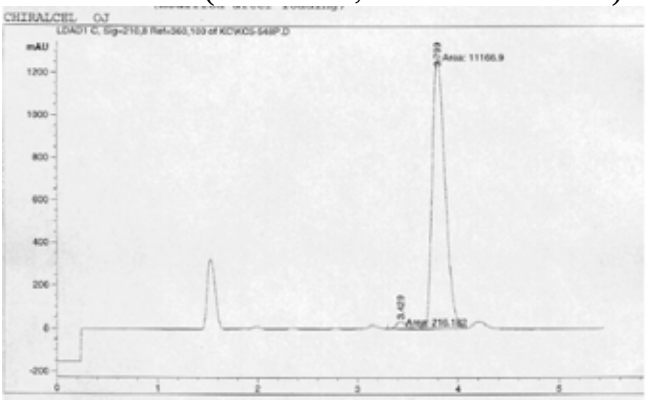
showed that all the S_N2' product had been converted. The reaction was quenched by addition of aqueous hydrochloric acid (1N, 2 mL). Diethyl ether (10 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by flash column chromatography (eluent = pentane) to yield the metathesis-product. Analysis by chiral GC or SFC showed the enantiomeric excess.

Typical procedure for tandem copper catalyzed enantioselective allylation-intramolecular metathesis. Same procedure as above until full conversion of the allylic chloride when gas chromatography of an aliquot showed that all the starting material had been converted. Enantiomeric excess of the S_N2' product was measured with this aliquot. At this point the reaction mixture was allowed to warm to room temperature and stirred for one hour. Ethyl acrylate (3 equivalents) and Grubbs' catalyst second generation[3] (5 mol%) as solid was added and the reaction mixture was stirred at 40°C overnight. The reaction was quenched by addition of aqueous hydrochloric acid (1N, 2 mL). Diethyl ether (10 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by flash column chromatography (eluent = pentane/ether:95/5) to yield the metathesis-product. Analysis by chiral SFC showed an enantiomeric excess of 96%.

Typical procedure for enantioselective copper-catalyzed S_N2' substitution with organozinc reagent. Under an argon atmosphere ligand **3b** (2 mol%) and CuTC (1 mol%) were dissolved in THF (2.5 mL) and stirred at room temperature for 10 min. To the cooled solution (-40°C) was added Et_2Zn (1 M in hexane, 1.1 eq). After 5 min, cinnamyl bromide (0.5 mmol) was added and the reaction was stirred at –40°C for 18h. The mixture was quenched by addition of aqueous sulfuric acid (1M, 1 mL). Diethyl ether (5 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by flash column chromatography (eluent = pentane) to yield the product as a mixture of S_N2' and S_N2 regioisomers. Supercritical Fluid Chromatography on a chiral stationary phase showed an enantiomeric excess of 91%.



(+)-3(*S*)-Phenyl-1-pentene ^{1}H NMR (400 MHz, $CDCl_3$): 7.32-7.20 (m, 5H), 5.98 (m, 1H), 5.08-5.03 (m, 2H), 3.16 (dt, J_1 = 7.58, J_2 = 7.32 Hz, 1H), 1.76 (dq, J_1 = 7.58, J_2 = 7.32 Hz, 2H), 0.90 (t, J = 7.32 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.7, 142.5, 128.6, 127.8, 126.3, 114.2, 51.9, 28.5, 12.3. $[\alpha]_D^{22}$ = +55.2 (*c* 1.1, $CHCl_3$) for 96% ee. Lit[4] $[\alpha]_D^{22}$ = +35.0 (*c* 6 , C_6H_6) (*S*) enantiomer. Ee was measured by chiral SFC with a Chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 3.43 (*R*), 3.80 (*S*).



Area Percent Report

Sorted by Signal
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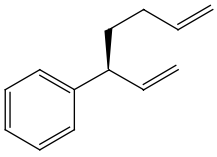
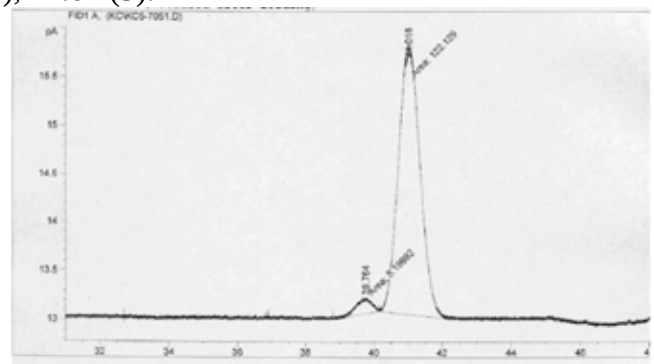


(+)-3(*S*)-Phenyl-1,6-heptadiene[5] ^{1}H NMR (400 MHz, $CDCl_3$): 7.37-7.22 (m, 5H), 5.98 (m, 1H), 5.85 (m, 1H), 5.10-4.99 (m, 4H), 3.32 (q, J = 7.32 Hz, 1H), 2.06 (m, 2H), 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 142.2, 138.5, 128.5, 127.6, 126.2, 114.7, 114.2, 49.2, 34.5, 31.6. $[\alpha]_D^{22}$ = +33.0 (*c* 1.0, $CHCl_3$) for 92% ee. Ee was measured by chiral GC with a Hydrodex B-3P column (program: 75-45-1-170) R_T: 39.76 (*R*), 41.02 (*S*).



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Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.764	MM	0.5124	5.19982	1.69133e-1	4.08378
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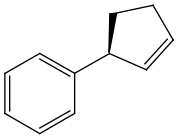
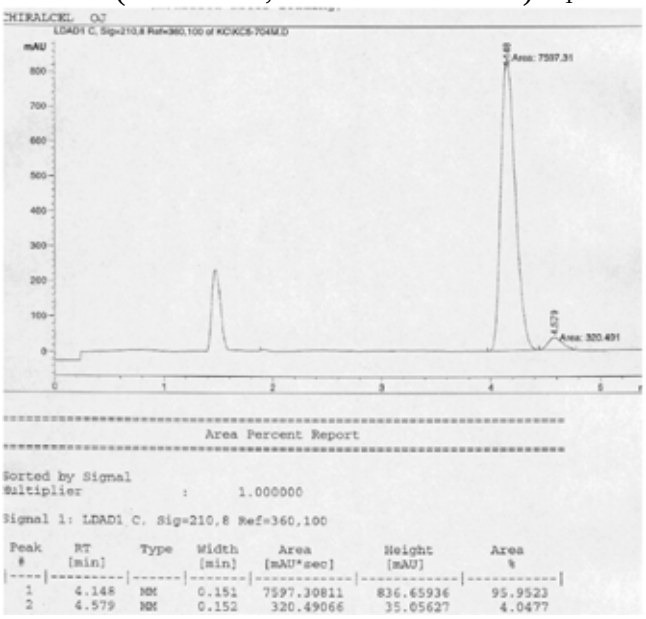


(-)-3(*S*)-Phenylcyclopentene[6] ^{1}H NMR (400 MHz, $CDCl_3$): 7.33-7.19 (m, 5H), 5.96 (m, 1H), 5.80 (m, 1H), 3.90 (m, 1H), 2.52-2.40 (m, 3H), 1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.6, 134.3, 131.9, 128.4, 127.2, 126.0, 51.3, 33.8, 32.5. $[\alpha]_D^{22}$ = - 163.4 (*c* 1.05, $CHCl_3$) for 92% ee. Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 4.15 (*S*), 4.58 (*R*).



Area Percent Report

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Signal 1: LDAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
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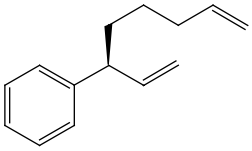
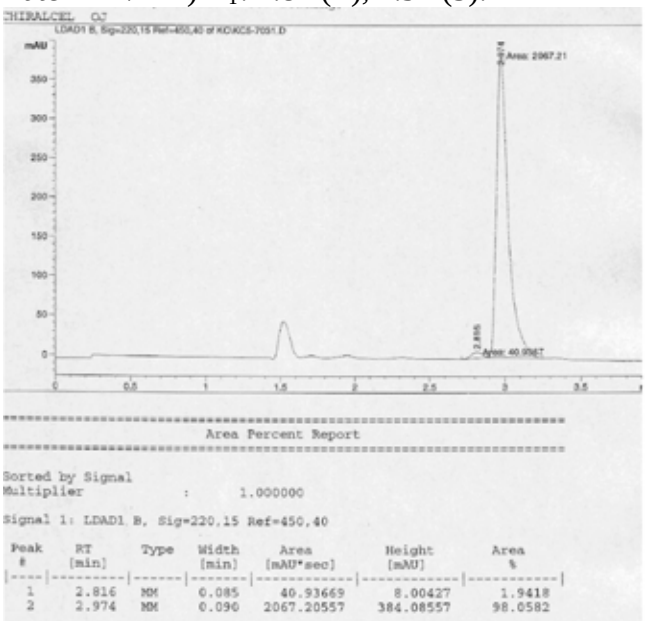
2	4.579	MM	0.152	320.49066	35.05627	4.0477



(+)-3(*S*)-Phenyl-1,7-octadiene[5] ^{1}H NMR (400 MHz, $CDCl_3$): 7.32-7.20 (m, 5H), 5.95 (m, 1H), 5.80 (m, 1H), 5.08-4.96 (m, 4H), 3.26 (q, *J* = 7.53 Hz, 1H), 2.10-1.32 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.5, 142.4, 138.8, 128.5, 127.6, 126.2, 114.6, 114.0, 49.9, 34.9, 33.8, 26.9. $[\alpha]_D^{22}$ = + 36.8 (*c* 1.07, $CHCl_3$) for 96% ee. Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, 10°C, flow rate 2mL/min) R_T: 2.82 (*R*), 2.97 (*S*).



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Sorted by Signal
Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

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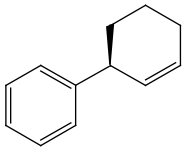
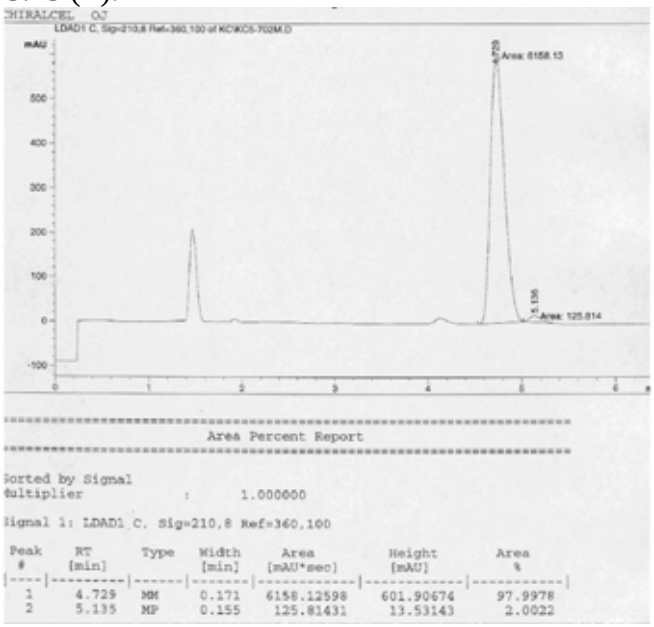
2	2.974	MM	0.090	2067.20557	384.08557	98.0582



(-)-3(*S*)-Phenylcyclohexene ^{1}H NMR (400 MHz, $CDCl_3$): 7.36-7.23 (m, 5H), 5.93 (m, 1H), 5.75 (m, 1H), 3.44 (m, 1H), 2.14-1.55 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.7, 130.2, 128.4, 128.3, 127.8, 126.0, 41.9, 32.7, 25.1, 21.2. $[\alpha]_D^{22}$ = -121.9 (*c* 1, $CHCl_3$) for 96% ee. Lit[7] $[\alpha]_D^{29}$ = +149.70 (*c* 6 , C_6H_6) (*R*) enantiomer. Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 4.73 (*S*), 5.15 (*R*).



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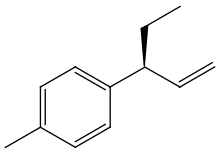
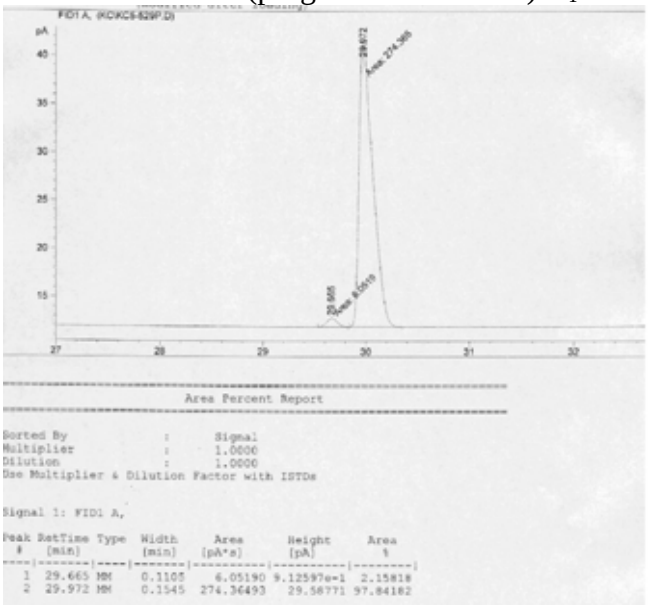
Signal 1: LDAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.729	MM	0.171	6158.12598	601.90674	97.9978
2	5.135	MP	0.155	125.81431	13.53143	2.0022



(+)-3(*S*)-(4-Methylphenyl)-1-pentene ^{1}H NMR (400 MHz, $CDCl_3$): 7.15 (d, *J* = 8.08 Hz, 2H), 7.11 (d, *J* = 8.08 Hz, 2H), 5.95 (m, 1H), 5.05 (m, 2H), 3.13 (q, *J* = 7.49 Hz, 1H), 2.35 (s, 3H), 1.75 (m, 2H), 0.90 (t, *J* = 7.32 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.5, 141.5, 135.6, 129.1, 127.5, 113.8, 51.4, 28.4, 21.1, 12.2. $[\alpha]_D^{22}$ = +55.9 (*c* 1.26, $CHCl_3$) for 96% ee. Ee was measured by chiral GC with a Chirasil-Dex CB column (program: 70-0-1-170) R_T: 29.66 (*R*), 29.97 (*S*).



Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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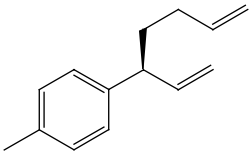
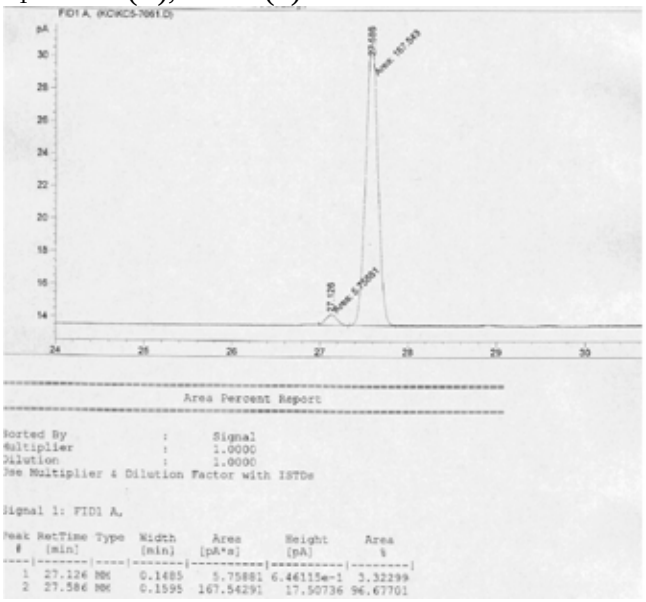


(+)-3(*S*)-(4-Methylphenyl)-1,6-heptadiene ^{1}H NMR (400 MHz, $CDCl_3$): 7.18 (d, *J* = 8.08 Hz, 2H), 7.14 (d, *J* = 8.08 Hz, 2H), 5.99 (m, 1H), 5.87 (m, 1H), 5.11-5.00 (m, 4H), 3.30 (q, *J* = 7.48 Hz, 1H), 2.38 (s, 3H), 2.08 (m, 2H), 1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 141.3, 138.6, 135.7, 129.2, 127.5, 114.7, 114.0, 48.8, 34.5, 31.6, 21.1. $[\alpha]_D^{22}$ = +35.5 (*c* 1.22, $CHCl_3$) for 93% ee. Ee was measured by chiral GC with a Hydrodex B-3P column (program: 80-0-1-170) R_T: 27.13 (*R*), 27.59 (*S*).



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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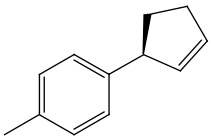
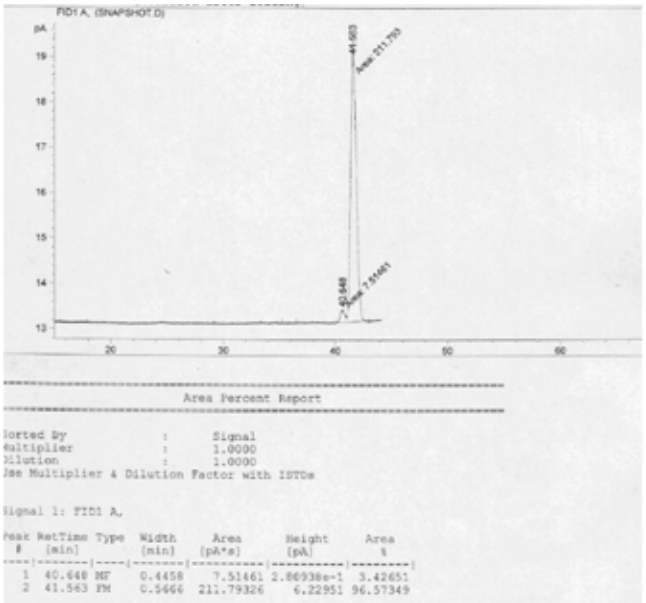
2	27.586	MM	0.1595	167.54291	17.50736	96.67701



(-)-3(*S*)-(4-Methylphenyl)cyclopentene[8] ^{1}H NMR (400 MHz, $CDCl_3$): 7.12 (s, 4H), 5.94 (m, 1H), 5.79 (m, 1H), 3.88 (m, 1H), 2.52-2.39 (m, 3H), 2.35 (s, 3H), 1.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 135.5, 134.5, 131.7, 129.1, 127.1, 50.9, 33.9, 32.5, 21.0. $[\alpha]_D^{22}$ = -171.9 (*c* 1.15, $CHCl_3$) for 93% ee. Ee was measured by chiral GC with a Chiraldex B-TA column (program: 70-45-1-170) R_T: 40.65 (*R*), 41.56 (*S*).

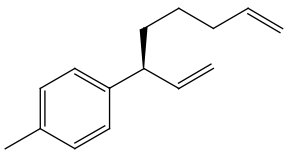


Area Percent Report

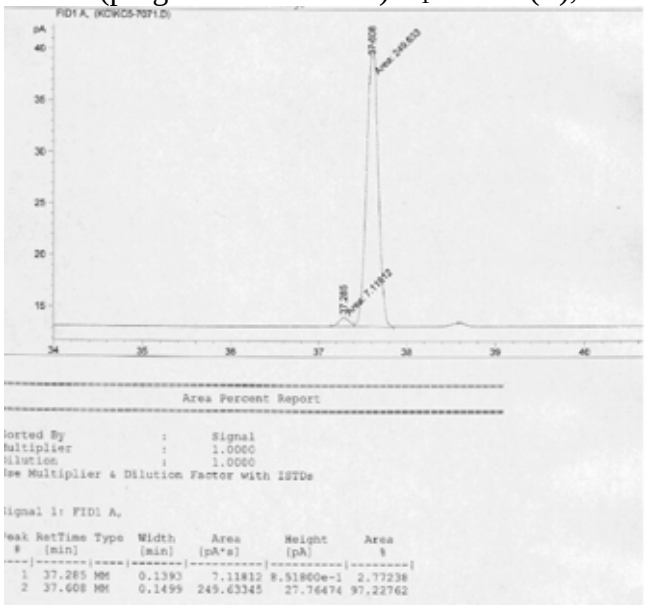
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

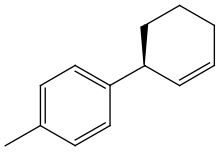
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.648	MF	0.4458	7.51461	2.80938e-1	3.42651
2	41.563	FM	0.5466	211.79326	6.22951	96.57349

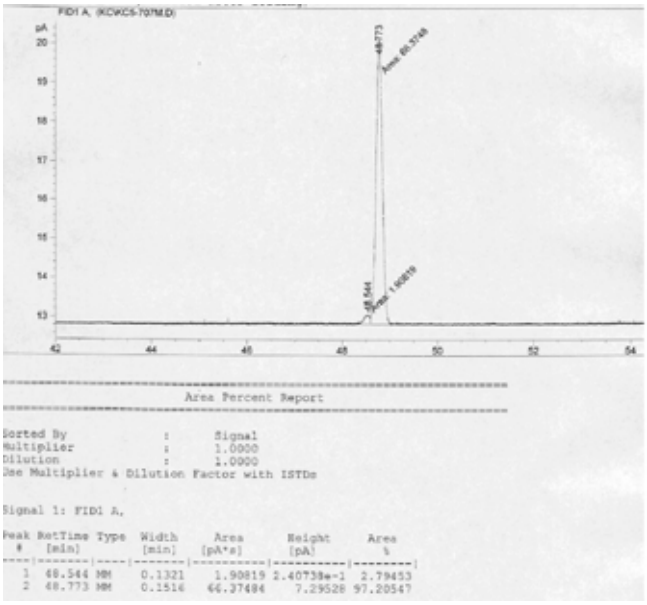


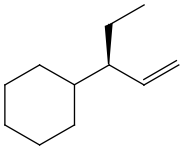
(+)-3(*S*)-(4-Methylphenyl)-1,7-octadiene ^{1}H NMR (400 MHz, $CDCl_3$): 7.13 (d, *J* = 8.08 Hz, 2H), 7.09 (d, *J* = 8.08 Hz, 2H), 5.97 (m, 1H), 5.80 (m, 1H), 5.05-4.92 (m, 4H), 3.22 (q, *J* = 7.56 Hz, 1H), 2.34 (s, 3H), 2.07 (m, 2H), 1.71 (m, 2H), 1.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.6, 141.5, 138.8, 135.6, 129.2, 127.4, 114.5, 113.8, 49.4, 34.9, 33.7, 26.9, 21.0. $[\alpha]_D^{22}$ = +39.5 (*c* 0.9, $CHCl_3$) for 94% ee. Ee was measured by chiral GC with a Hydrodex B-3P column (program: 80-0-1-170) R_T: 37.28 (*R*), 37.61 (*S*).





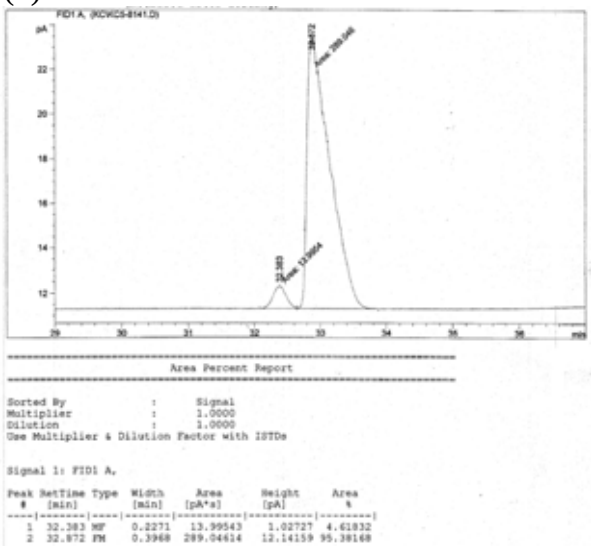
(-)-3(*S*)-(4-Methylphenyl)cyclohexene[9] ^{1}H NMR (400 MHz, $CDCl_3$): 7.15 (s, 4H), 5.91 (m, 1H), 5.74 (m, 1H) 3.41 (m, 1H), 2.37 (s, 3H), 2.14-1.56 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 135.5, 130.5, 129.0, 128.2, 127.7, 41.5, 32.7, 25.1, 21.3, 21.0. $[\alpha]_D^{22}$ = -129.3 (*c* 1.1, $CHCl_3$) for 94% ee. Ee was measured by chiral GC with a Hydrodex B-3P column (program: 75-0-1-170) R_T: 48.52 (*R*), 48.77 (*S*).





(+)-3(*S*)- Cyclohexyl-1-pentene ^{1}H NMR (400 MHz, $CDCl_3$): 5.55 (dt, J_1 = 17.20 Hz, J_2 = 10.24 Hz, 1H), 4.99 (dd, J_1 = 10.24 Hz, J_2 = 2.28 Hz, 1H), 4.91 (ddd, J_1 = 17.20 Hz, J_2 = 2.28 Hz, J_3 = 0.72 Hz, 1H), 1.74-0.87 (m, 14H), 0.83 (t, J = 7.32 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 141.5, 115.0, 52.0, 41.5, 31.2, 29.7, 26.8, 26.8, 26.7, 24.4, 12.1. $[\alpha]_D^{22}$ = +9.9 (c = 1.22, $CHCl_3$) for 91% ee.

Ee was measured by chiral GC with a Chirasil-Dex CB column, Helium flow (program: 75-35-1-170) R_T: 32.38 (*R*), 32.87 (*S*).

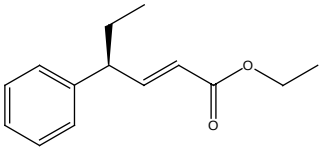


Area Percent Report

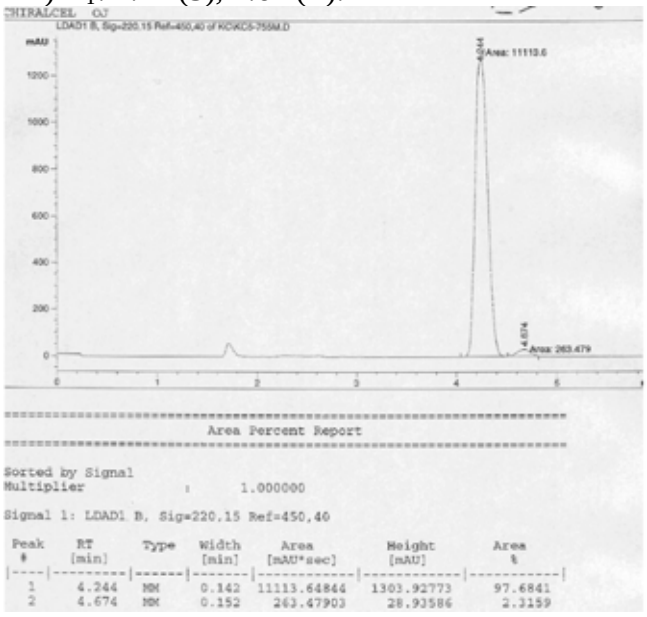
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.383	MF	0.2271	13.99543	1.02727	4.61832
2	32.872	FM	0.3968	289.04614	12.14159	95.38168



(*S*,*E*)-ethyl-4-phenylhex-2-enoate 8[5] ^{1}H NMR (400 MHz, $CDCl_3$): 7.32-7.18 (m, 5H), 7.08 (dd, J_1 = 15.68, J_2 = 7.84 Hz, 1H), 5.80 (dd, J_1 = 15.68, J_2 = 1.28 Hz, 1H), 4.18 (q, J = 7.08 Hz, 2H), 3.30 (q, J = 7.56 Hz, 1H, 1.81 (dq, J_1 = 7.56, J_2 = 7.32 Hz, 2H), 1.28 (t, J = 7.08 Hz, 3H), 0.89 (t, J = 7.32 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.73, 151.74, 142.17, 128.68, 127.81, 126.74, 120.83, 60.28, 50.28, 27.94, 14.26, 12.14. $[\alpha]_D^{22}$ = +1.95 (c 1, $CHCl_3$) for 96% ee. Ee was measured by chiral SFC with a chiralcel OD-H column (1% MeOH, flow rate 2mL/min) R_T: 4.24 (*S*), 4.67 (*R*).



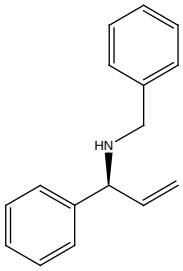
Area Percent Report

Sorted by Signal
Multiplier : 1.000000

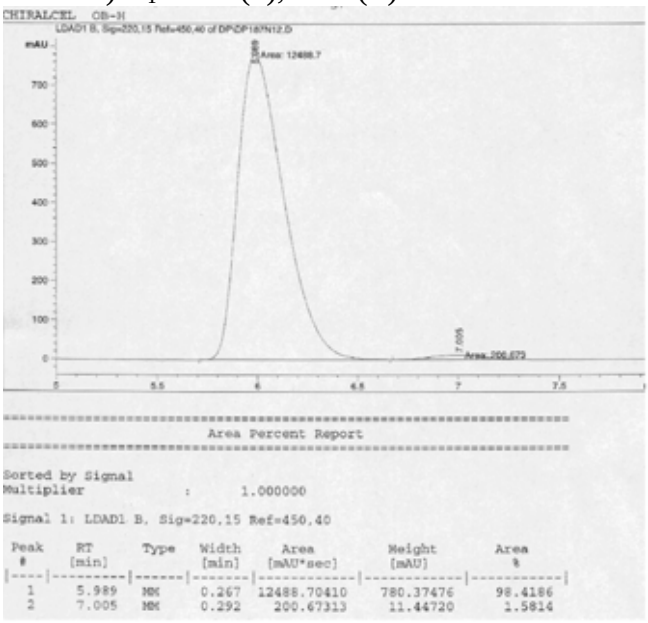
Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

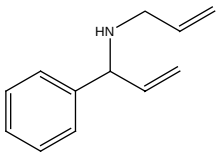
Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.244	MM	0.142	11113.64844	1303.92773	97.6841
2	4.674	MM	0.152	263.47903	28.93586	2.3159

General Procedure for the Iridium Catalyzed Enantioselective Allylic Amination: $[Ir(cod)Cl]_2$ (0.01 mmol) and ligand (0.02 mmol) were dissolved in 0.5 mL of THF in a 3 mL-test tube under argon. A small magnetic stirbar was added, the test tube was capped with a septum and the mixture was stirred for 10 minutes. Amine (**10**, 1.3 mmol) and cinnamyl methycarbonate (**9**, 0.98 mmol) were added to the reaction mixture by syringe. The reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated *in vacuo*. ^{1}H-NMR analysis of the residual crude mixture indicated the ratio of regioisomers **11**/**12**. The mixture was then purified by flash column chromatography on silica gel (cyclohexane : ethyl acetate 8:2) to give the secondary amine as a white oil. A small amount of the product was derivatized into the corresponding acetamide by treatment with acetic anhydride in diethylether over 5 minutes. The acetamide was washed with water and filtered on silicagel. Chiral SFC analysis indicated the enantiomeric excess.

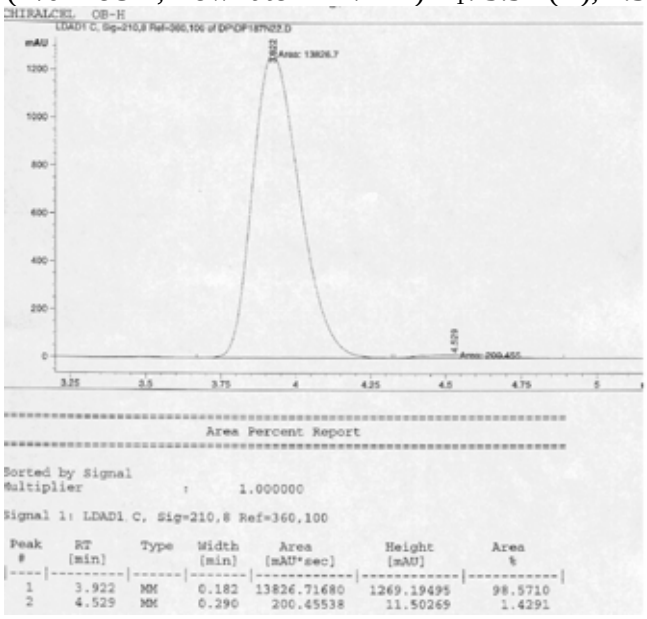


(*S*)-*N*-(1-Phenyl-2-propenyl)benzylamine 11a[10] ^{1}H NMR (400.13 MHz, $CDCl_3$) : 7.30–7.22 (m, 10H), 5.99 (ddd, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.26 (d, *J* = 17.1, 1H), 5.17 (d, *J* = 10.2, 1H), 4.27 (d, *J* = 7.2 Hz, 1H), 3.81 (d of AB pattern, *J* = 13.4 Hz, 1H), 3.75 (d of AB pattern, *J* = 13.4 Hz, 1H), 1.72 (brs, 1H). ^{13}C NMR (100.59 MHz, $CDCl_3$) 142.84, 141.02, 140.50, 128.59, 128.42, 128.20, 127.37, 127.26, 126.94, 115.20, 65.17, 51.33. The absolute configuration was determined by comparison of the optical rotation with literature data.[10] Ee was measured by chiral SFC analysis of the acetamide with a chiralcel OB-H column (2% MeOH, flow rate 2mL/min) R_T: 5.99 (*S*), 7.00 (*R*).





(+)-*N*-(1-Phenyl-2-propenyl)allylamine 11b[10] ^{1}H NMR (400.13 MHz, $CDCl_3$) 7.45–7.26 (m,5H), 5.91–6.02 (m, 2H), 5.29-5.13 (m, 4H), 4.27 (d, J = 7.1 Hz, 1H), 3.29-3.19 (m, 2H), 1.50-1.30 (brs, 1H). ^{13}C NMR (100.59 MHz, $CDCl_3$) 142.74, 140.88, 136.78, 128.61, 127.33, 127.25, 115.97, 115.16, 65.24, 49.92. Ee was measured by chiral SFC analysis of the acetamide with a chiralcel OB-H column (1% MeOH, flow rate 2mL/min) R_T: 3.92 (+), 4.53 (-).



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Signal 1: LDAD1 C, Sig=210,8 Ref=360,100

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
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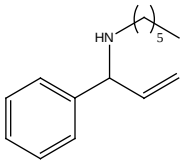
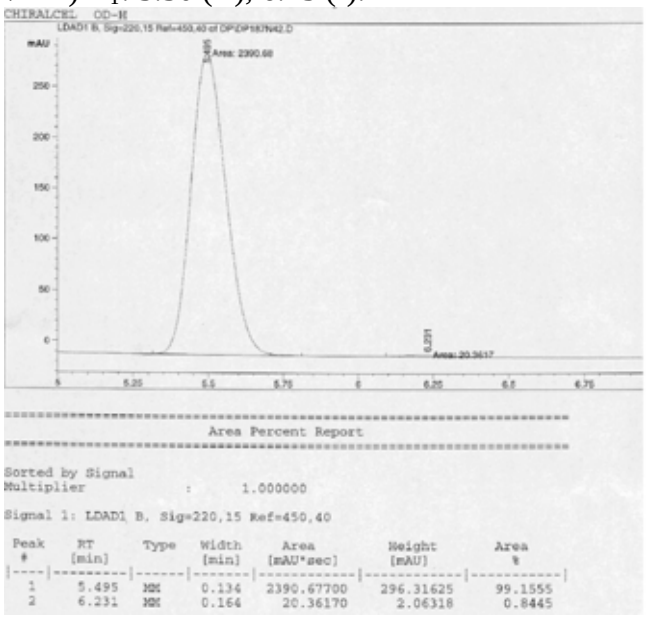
2	4.529	MM	0.290	200.45538	11.50269	1.4291



(+)-*N*-(1-Phenyl-2-propenyl)-*n*-hexylamine 11c[10] ^{1}H NMR (400.13 MHz, $CDCl_3$) 7.40–7.26 (m, 5H), 5.98 (ddd, J = 17.2, 8.6, 7.0 Hz, 1H), 5.25 (dt, J = 17.2, 1.3 Hz, 1H), 5.14 (dt, J = 10.4, 1.6, 1.3Hz, 1H), 4.21 (d, J = 7.0 Hz, 1H), 2.65-2.50 (m, 2H), 1.55–1.28 (m, 9H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.59 MHz, $CDCl_3$) 143.14, 141.30, 128.51, 127.27, 127.13, 114.81, 66.32, 47.76, 31.82, 30.20, 27.09, 22.66, 14.08.

Ee was measured by chiral SFC analysis of the acetamide with a chiralcel OD-H column (3% MeOH, flow rate 1.8mL/min) R_T: 5.50 (+), 6.23 (-).



Area Percent Report

Sorted by Signal
Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.495	MM	0.134	2390.67700	296.31625	99.1555
2	6.231	MM	0.164	20.36170	2.06318	0.8445

References

(1) Saudan, L. A.; Bernardinelli, G.; Kündig, E. P. *Synlett* **2000**, 483.
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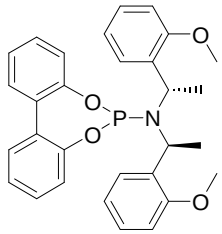
(10) Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc*. **2002**, *124*, 15164.

P31CPD

152.4089



260 220 180 140 100 60 20 -20 -60 -100 -140

(ppm)

1H Spectrum

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7.5141
7.5103
7.4946
7.4914
7.4131
7.4112
7.4093
7.3948
7.3910
7.3279
7.3235
7.3178
7.2995
7.2938
7.2906
7.2723
7.2710
7.2540
7.0349
7.0185
7.0160
7.0002
6.9958
6.8019
6.7994
6.7830
6.7811
6.7647
6.7622
6.4806
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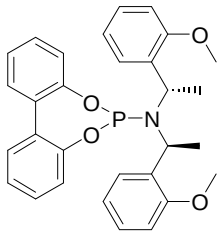
5.0935
5.0752
5.0556
5.0366
5.0183
3.6489
1.6367
1.6184



Integral

2.0451
1.9684
1.0863
5.1967
1.9917
2.0432
1.9439
2.0000
5.9657
6.0341

9.5 9.0 8.5 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

(ppm)

13C CPD-Spectrum

156.1817
152.4150
152.3573
151.8957
151.8298
132.1554
130.8366
130.8036
130.7707
130.7377
129.9629
129.0233
127.6056
127.5562
127.3666
124.0614
122.5201
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49.2871
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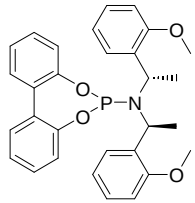
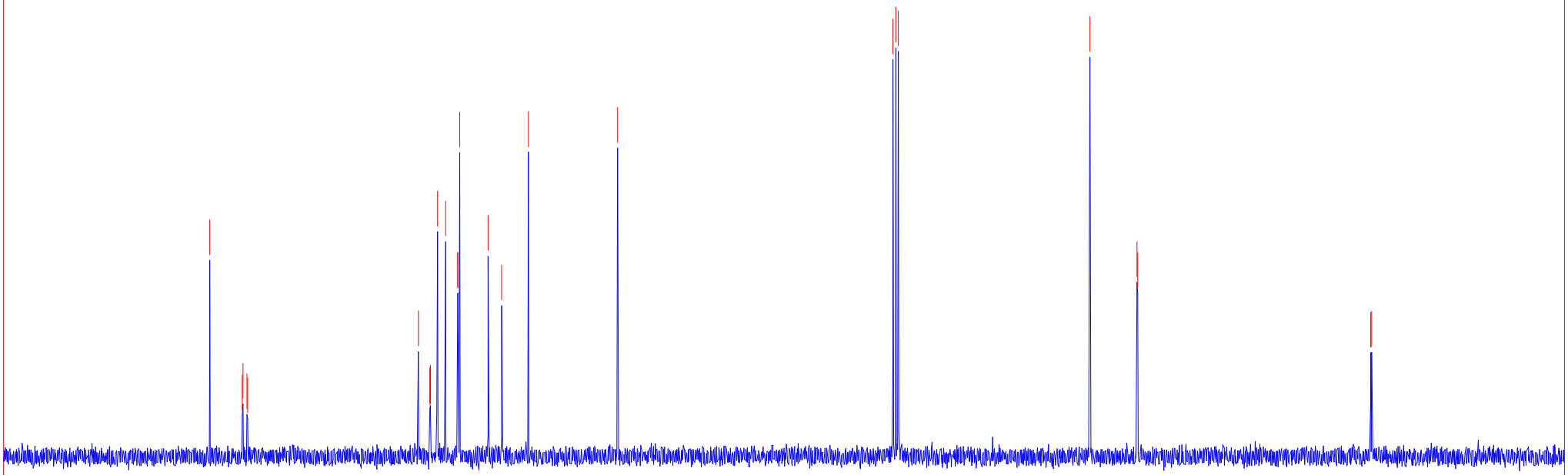
22.3595
22.1947



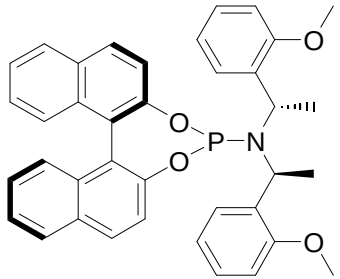


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

(ppm)

P31CPD

152.1476



260 220 180 140 100 60 20 -20 -60 -100 -140

(ppm)

1H Spectrum

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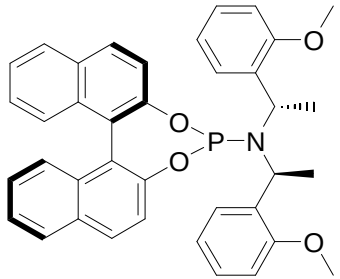
6.9983 6.9800 6.9604 6.7300 6.7117 6.6933 6.4686 6.4484

5.1156 5.0973 5.0770 5.0581 5.0398

3.5485

1.6298 1.6121



Integral

1.0290 3.0027 2.0194 8.7873 1.9663 2.0390 1.9655 2.0000 6.0062 5.9949

9.5 9.0 8.5 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

(ppm)

13C CPD-Spectrum

155.9427
150.7088
150.1566
133.0373
132.2790
131.4136
130.4987
130.2926
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128.3557
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127.4490
127.2759
127.2430
126.0231
125.8253
124.7290
124.4323
124.3746
124.2675
122.8416
122.5036
121.7618
119.4457
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65.9284

54.6364

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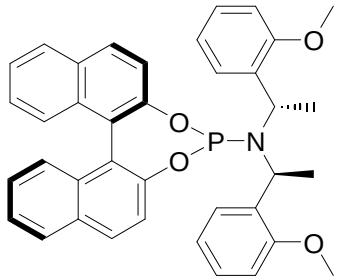
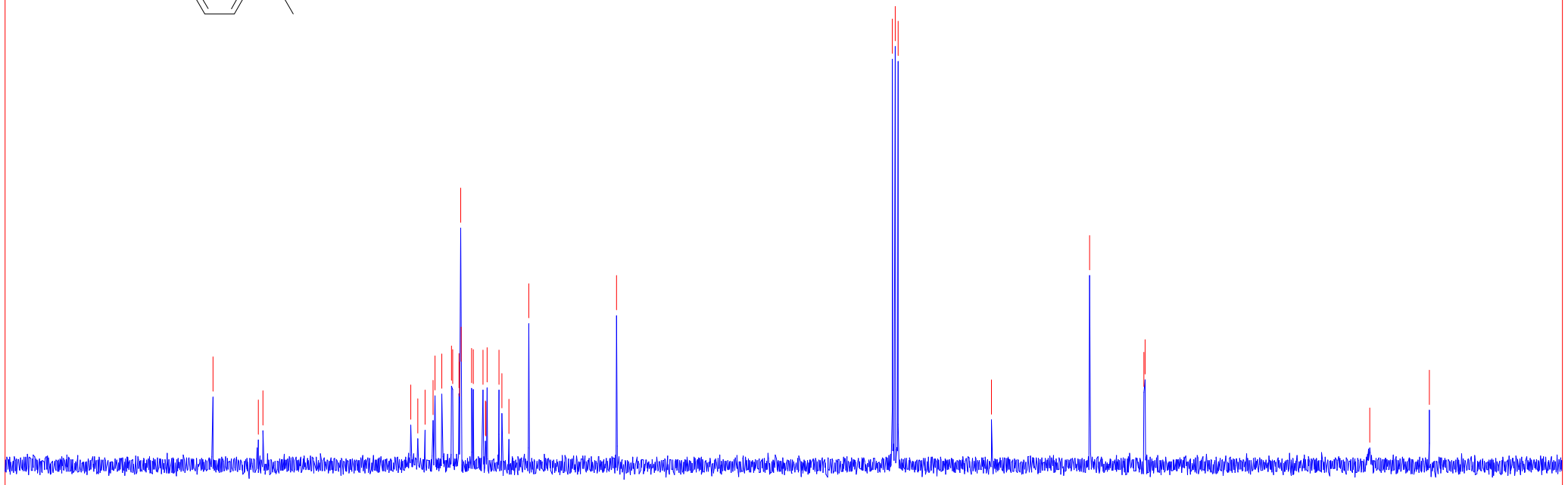
22.2441

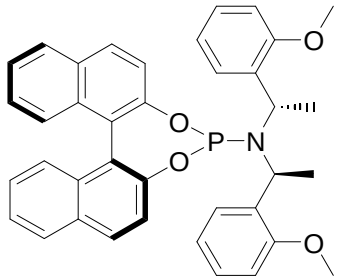
15.3535





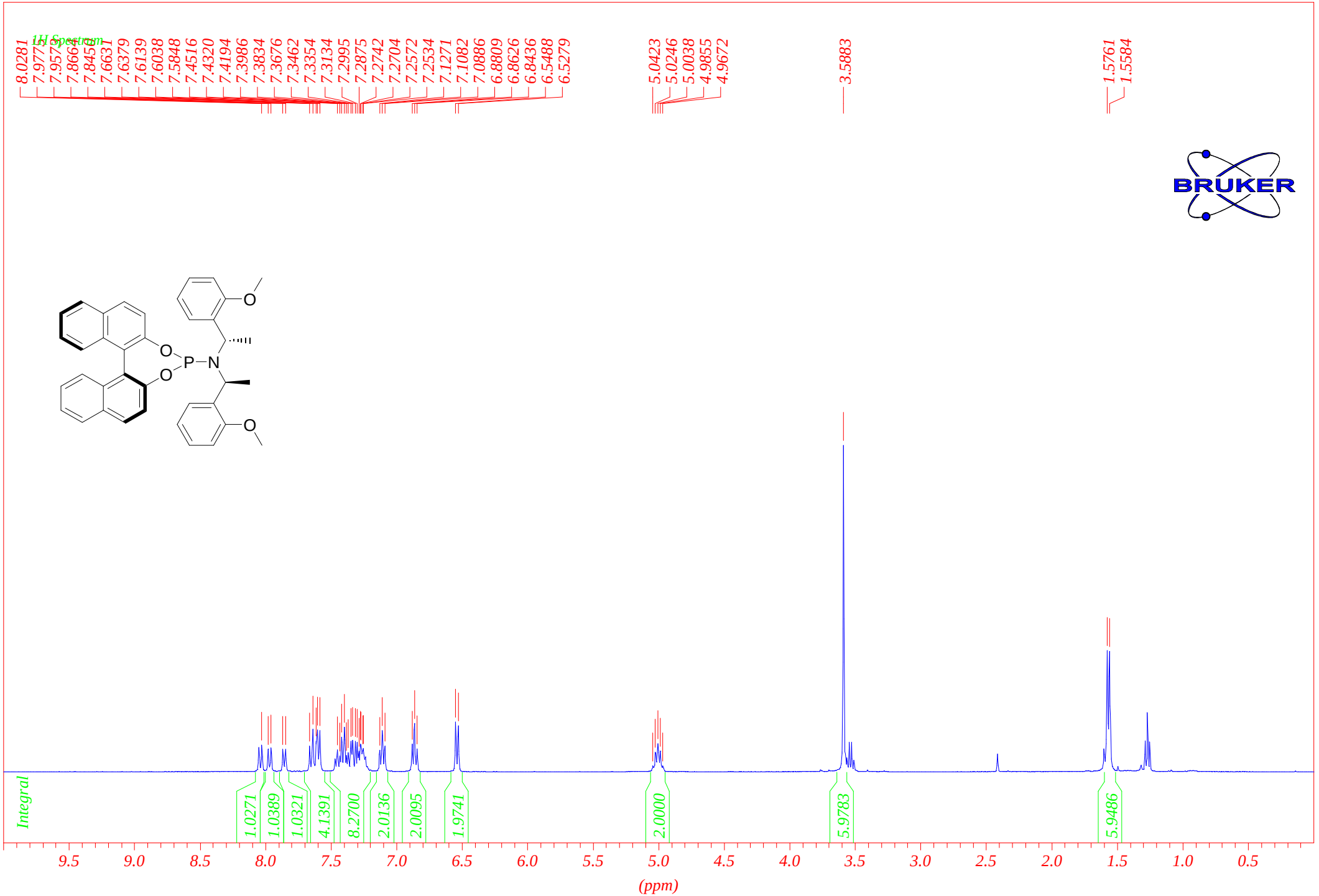
P31CPD

155.2557



260 220 180 140 100 60 20 -20 -60 -100 -140

(ppm)


1H Spectrum
8.0281
7.9774
7.9574
7.8664
7.8456
7.6631
7.6379
7.6139
7.6038
7.5848
7.4516
7.4320
7.4194
7.3986
7.3834
7.3676
7.3462
7.3354
7.3134
7.2995
7.2875
7.2742
7.2704
7.2572
7.2534
7.1271
7.1082
7.0886
6.8809
6.8626
6.8436
6.5488
6.5279
5.0423
5.0246
5.0038
4.9855
4.9672
3.5883
1.5761
1.5584
BRUKER
O
O
P
N
O
O
Integral
1.0271
1.0389
1.0321
4.1391
8.2700
2.0136
2.0095
1.9741
2.0000
5.9783
5.9486
9.5
9.0
8.5
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
(ppm)

13C CPD-Spectrum

156.1075
149.8846
132.7653
132.4768
131.3559
130.2926
129.2376
128.3227
128.0177
127.7045
127.6468
127.4325
127.2677
125.9489
125.6357
124.6796
124.5065
124.1686
122.6602
121.4981
119.6435
109.2170
77.4017
77.0885
76.7670
54.5952
50.2762
50.1691
22.6150
22.4667