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Supporting Information

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Enantioselective Rhodium-Catalyzed Allylic C–H Activation for the Addition to Conjugated Dienes**

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Supporting Information

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1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, dioxane, dimethoxyethane, dibutyl ether, benzene and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane, acetonitrile, chlorobenzene and 1,2-dichloroethane were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) or Bruker AVANCE 600 (^{1}H at 600 MHz, ^{13}C at 150 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI). Optical rotations were measured on a Perkin-Elmer 341 LC spectrometer. The enatiomeric excesses (*ee*) of the products were determined by chiral HPLC analysis using Aglient HP 1100 instrument.

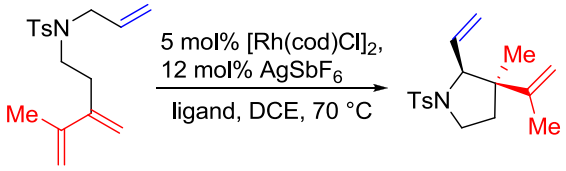
Abbreviations:
Bn = benzyl
cod = (1*Z*,5*Z*)-cycloocta-1,5-diene
coe = (*Z*)-cyclooctene
DCE = 1,2-dichloroethane
DEAD = diethyl azodicarboxylate
DME = dimethoxyethane
DMF = *N*,*N*-dimethylformamide
DMP = Dess-Martin periodinane
EA = ethyl acetate
PE = petroleum ether
TBAF = tetra-*n*-butylammonium fluoride
THF = tetrehydrofuran
TBS = *t*-butyldimethylsilyl

2. Experimental Procedures and Characterization Data

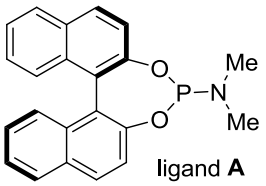
2.1 Screening of the Standard Reaction Conditions

2.1.1 Screening of the Amount of the Chiral Ligand A

Table S1



Entry	[Ag]	ligand	t (h)	yield	*ee*
1	$AgSbF_6$	PPh_3 (0.3 eq.)	12	86%	–
2	$AgSbF_6$	**A** (0.1 eq.)	12	61%	-59%
3	$AgSbF_6$	**A** (0.2 eq.)	12	95%	-57%
4	$AgSbF_6$	**A** (0.25 eq.)	20	95%	-58%
5	$AgSbF_6$	**A** (0.3 eq.)	20	85%	-59%
6	$AgSbF_6$	**A** (0.4 eq)	12	NR	–
7	AgOTf	**A** (0.3 eq.)	12	85%	-70%



As shown above, 0.2 eq. of the ligand gave the best yield, and 0.3 eq. of the ligand gave the best *ee*, while with a little decrease in yield. 0.4 eq. of the ligand completely inhibited the reaction. To make a balance between yield and *ee*, we used 0.25 eq. of the ligand in the further reactions. AgOTf gave higher *ee* than $AgSbF_6$, therefore we used AgOTf instead of $AgSbF_6$ in the following studies.

2.1.2 Screening of the Solvents

Table S2

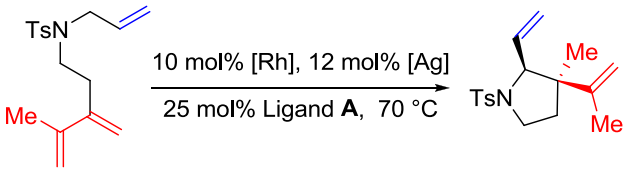
Entry	solvent	t (h)	yield	*ee*
1	DCE	12	85%	-70%
2	Chlorobenzene	11	85%	-75%
3	THF	35	90%	-77%
4	Benzene	40	86%	-80%
5	Dioxane	32	80%	-82%
6	toluene	70	50%	–
7	$(n\text{-Bu})_2O$	70	90%	-71%
8	**DME**	**11**	**87%**	**-80%**
9	CH_3CN	70	0%	–

In order to make a balance of the reaction time, yield and enantiomeric excess, DME was found to

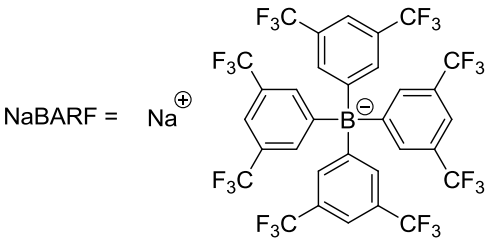
be the best choice among various solvents tested.

2.1.3 Screening of the Salt Additives

Table S3



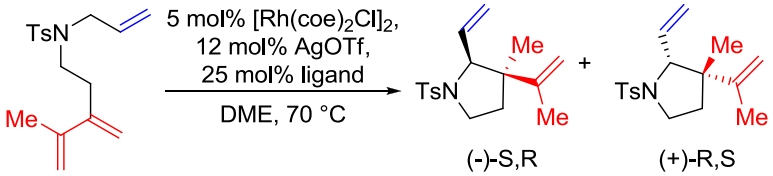
Entry	[Rh] (0.05 eq.)	[Ag]	Solvent	t (h)	yield	*ee*
1	$[Rh(cod)Cl]_2$	AgOAc	DME	20	N.R.	–
2	$[Rh(cod)Cl]_2$	AgO_2CCF_3	DME	20	N.R.	–
3	$[Rh(cod)Cl]_2$	$AgPF_6$	DME	20	N.R.	–
4	$[Rh(cod)Cl]_2$	$AgClO_4$	DME	20	69%	-77%
5	$[Rh(cod)Cl]_2$	$AgBF_4$	DME	11	92%	-73%
6	$[Rh(cod)Cl]_2$	$AgSbF_6$	DME	11	72%	-67%
7	$[Rh(cod)Cl]_2$	AgNO3	DME	11	N.R.	–
8	$[Rh(cod)Cl]_2$	AgOTs	DME	11	N.R.	–
9	$[Rh(cod)Cl]_2$	$AgO_2C_4F_7$	DME	11	N.R.	–
10	$[Rh(cod)Cl]_2$	$AgO_2C_{10}H_{17}$	DME	11	N.R.	–
11	**$[Rh(cod)Cl]_2$**	**AgOTf**	**DME**	**11**	**87%**	**-80%**
12	$[Rh(cod)Cl]_2$	NaBARF	DME	20	N.R.	–
13	$[Rh(cod)Cl]_2$	NaBARF	chlorobenzene	32	75%	-59%
14	**$[Rh(coe)_2Cl]_2$**	**AgOTf**	**DME**	**8**	**87%**	**-80%**



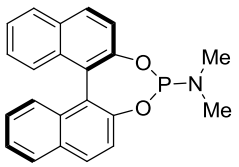
AgOTf was found to be the best choice among the various salts we screened. Besides, we also used $[Rh(coe)_2Cl]_2$ as the rhodium precursor, which took shorter time to give a complete transformation than $[Rh(cod)Cl]_2$.

2.1.4 Screening of the Chiral Ligands

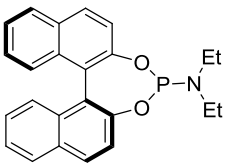
Table S4



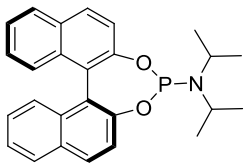
Entry	ligand	t (h)	yield	*ee*
1	**A**	8	87%	-80%
2	**B**	**11**	**90%**	**90%**
3	**C**	11	90%	89%
4	**D**	11	90%	87%
5	**E**	**11**	**90%**	**90%**
6	**F**	24	Mixture	-
7	**G**	24	Mixture	-
8	**H**	11	91%	87%
9	**I**	11	90%	70%
10	**J**	36	83%	14%
11	**K**	48	57%	-77%
12	**L**	11	90%	83%
13	**M**	11	N.R.	-
14	**N**	11	20%	91%
15	**O**	11	<50%	-



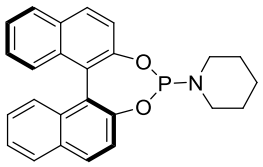
(*R*)-ligand **A**
11 h, 87% yield, -80% *ee*



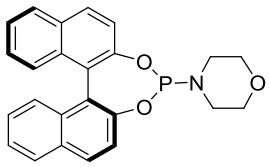
(*S*)-ligand **B**
11 h,90% yield, 90% *ee*



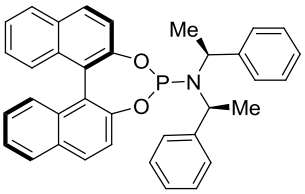
(*S*)-ligand **C**
11 h, 90% yield, 89% *ee*



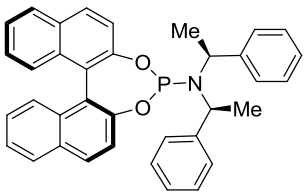
(*S*)-ligand **D**
11 h, 90% yield, 87% *ee*



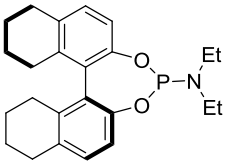
(*S*)-ligand **E**
11 h, 90% yield, 90% *ee*



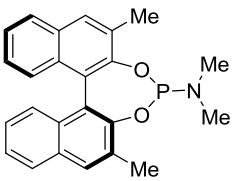
(*Ra*, *S*, *S*)-ligand **F**
24 h, Mixture



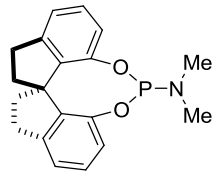
(*Sa*, *S*, *S*)-ligand **G**
24 h, Mixture



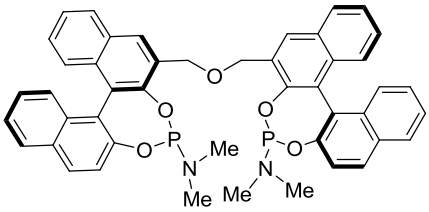
(*S*)-ligand **H**
11 h,91% yield, 87% *ee*



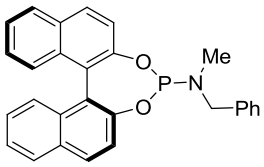
(*S*)-ligand **I**
11 h, 90% yield, 70% *ee*



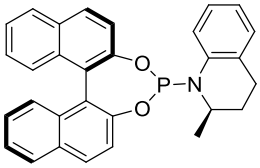
(*R*)-ligand **J**
36 h, 83% yield, 14% *ee*



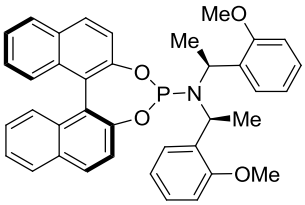
(*R*)-Ligand **K**
48 h, 57%, -77%ee



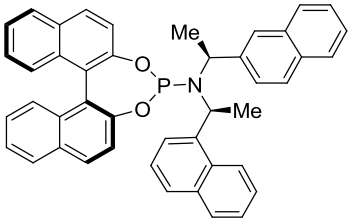
(*S*)-ligand **L**
11 h, 90% yield, 83% *ee*



(Ra, R)-ligand **M**
11 h, No Reaction



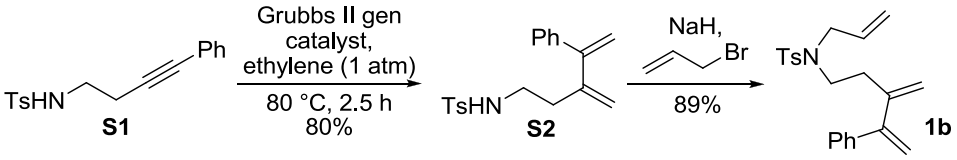
(Sa, S, S)-ligand **N**
11 h, 20% yield, 91% *ee*



(Sa, S, S)-ligand **O**
11 h, <50% yield

2.2 Syntheses of Substrates

***N*-allyl-4-methyl-*N*-(3-methylene-4-phenylpent-4-enyl)benzenesulfonamide**



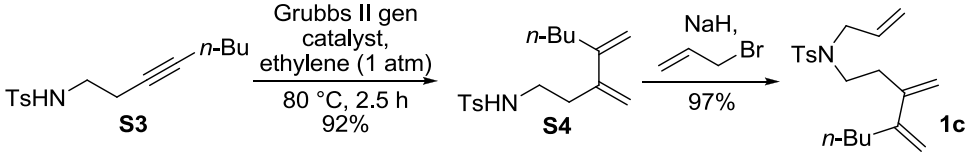
Sulfonamide **S1** [1] (409 mg, 1.37 mmol) and Grubbs II generation catalyst (58 mg, 0.068 mmol) were dissolved in toluene (20 mL) under ethylene atmosphere. Ethylene was then bubbled to the solution for 5 min, and the reaction mixture was stirred under 1 atm ethylene at 80 ℃ for 2.5 h. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluted with PE/EA = 10:1 to 3:1) to afford sulfonamide **S2** as a light brown oil (358 mg, 1.09 mmol, 80%).

NaH (138 mg, 50%, 2.88 mmol) was suspended in DMF (5 mL) under argon and cooled to 0 ℃. A DMF solution (10 mL) of **S2** (358 mg, 1.09 mmol) was added slowly to the above mixture. The reaction mixture was warmed to room temperature and stirred for 15 min. Then allyl bromide (310 mg, 2.56 mmol) was added dropwise to the above light yellow solution. The resulting mixture was stirred for 15 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford sulfonamide **1b** (358 mg, 0.97 mmol, 89%) as a pale oil.

Spectra data of **1b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.3 Hz, 2H), 7.35-7.22 (m, 7H), 5.61 (ddt, J = 17.3, 9.9 and 6.3 Hz, 1H), 5.30 (s, 1H), 5.18 (s, 1H), 5.11-5.05 (m, 3H), 5.01 (s, 1H), 3.77 (d, J = 6.3 Hz, 2H), 3.23 (t, J = 8.3 Hz, 2H), 2.49 (t, J = 8.3 Hz, 2H), 2.41 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.7, 145.4, 143.1, 140.7, 137.2, 133.1, 129.6, 128.12, 128.06, 127.4, 127.1, 118.8, 117.6, 114.3, 50.8, 46.6, 33.6, 21.5. IR (neat): υ 3088, 3036, 2935, 2879, 2265, 1456. $C_{22}H_{26}NO_2S$ $(M+H)^+$: 368.1679. Found: 368.1678.

***N*-allyl-*N*-(3,4-dimethyleneoctyl)-4-methylbenzenesulfonamide**



Sulfonamide **S4** was prepared by following the procedure for converting **S1** to **S2**. **S3** [2] (754 mg, 2.70 mmol) and Grubbs II generation catalyst (45 mg, 0.053 mmol) were used, and **S4** (765 mg, 2.49 mmol) was generated as a light brown in 92% yield.

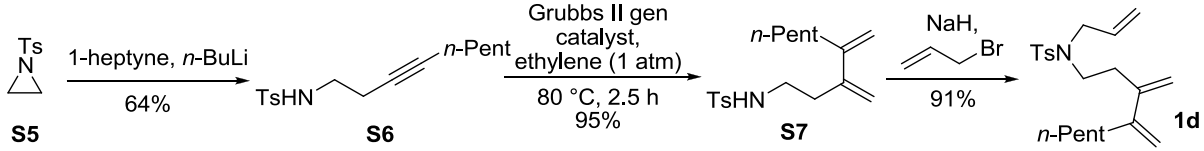
Sulfonamide **1c** was synthesized by following the procedure for converting **S2** to **1b**. NaH (238 mg, 50%, 4.96 mmol), **S4** (765 mg, 2.49 mmol), and allyl bromide (580 mg, 4.79 mmol) were used, and **1c** (836 mg, 2.41 mmol) was generated as a pale oil in 97% yield.

Spectra data of **1c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.68 (ddt, J = 16.7, 10.0

and 6.8 Hz, 1H), 5.19 (d, *J* = 16.7 Hz, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 5.11 (s, 1H), 5.08 (s, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 3.83 (d, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 7.9 Hz, 2H), 2.50 (t, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.19 (t, *J* = 7.4 Hz, 2H), 1.44-1.35 (m, 2H), 1.35-1.25 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 144.3, 137.2, 133.4, 129.6, 127.1, 118.7, 113.6, 113.1, 112.0, 51.0, 47.3, 33.9, 33.6, 30.8, 22.5, 21.4, 13.9. IR (neat): υ 3099, 2965, 2939, 2875, 1602, 1464. HRMS (ESI) calcd for $C_{20}H_{30}NO_2S$ $(M+H)^+$: 348.1992. Found: 348.1992.

***N*-allyl-*N*-(3,4-dimethylenenonyl)-4-methylbenzenesulfonamide**



To a cold solution (-78 ℃) of 1-heptyne (837mg, 8.70 mmol) in THF (5 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 4.0 mL, 6.4 mmol) over a period of 10 min, and the mixture was stirred at -78 ℃ for 15 min and at 0 ℃ for 15 min. After cooling to -78 ℃ and then addition of HMPA (0.8 mL, 4.60 mmol), a THF (10 mL) solution of **S5** [3] (793 mg, 4.02 mmol) was added dropwise over 10 min. The mixture was allowed to warm to room temperature and stirred for an additional 12 h. After that, saturated aqueous NH_4Cl and water were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate, and the combined extract was washed with water and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (eluted with PE/EA = 20:1 to 10:1) to afford **S6** (641 mg, 2.56 mmol, 64%) as a light yellow oil.

Spectra data of **S6**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.86-4.79 (br, 1H), 3.05 (q, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.30 (tt, *J* = 6.6 and 2.2 Hz, 2H), 2.10 (tt, *J* = 7.1 and 2.2 Hz, 2H), 1.49-1.40 (m, 2H), 1.34-1.25 (m 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 137.0, 129.7, 127.1, 83.2, 75.6, 42.1, 31.0, 28.5, 22.2, 21.5, 19.9, 18.6, 13.9. IR (neat): υ 3415-3181(br), 2965, 2958, 2875, 1605, 1438. HRMS (ESI) calcd for $C_{16}H_{23}NNaO_2S$ $(M+Na)^+$: 316.1342. Found: 316.1343.

Sulfonamide **S7** was prepared by following the procedure for converting **S1** to **S2**. **S6** (610 mg, 2.74 mmol) and Grubbs II generation catalyst (65 mg, 0.076 mmol) were used, and **S7** (836 mg, 2.60 mmol) was generated as a light brown in 95% yield.

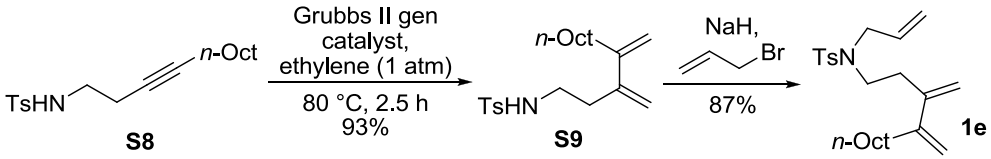
Sulfonamide **1d** was synthesized by following the procedure for converting **S2** to **1b**. NaH (238 mg, 50%, 4.96 mmol), **S7** (800 mg, 2.49 mmol), and allyl bromide (580 mg, 4.79 mmol) were used, and **1d** (821 mg, 2.27 mmol) was generated as a pale oil in 91% yield.

Spectra data of **1d**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.68 (ddt, *J* = 17.2, 10.4 and 6.4 Hz, 1H), 5.19 (dq, *J* = 17.2 and 1.5 Hz, 1H), 5.15 (dq, *J* = 10.4 and 1.5 Hz, 1H), 5.10 (s, 1H), 5.07 (s, 1H), 4.94 (s, 1H), 4.93 (s, 1H), 3.83 (d, *J* = 6.4 Hz, 2H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.49 (t, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.18 (t, *J* = 7.8 Hz, 2H), 1.45-1.36 (m, 2H), 1.35-1.21 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 144.3, 143.1, 137.2, 133.4, 129.6, 127.1, 118.7, 113.7, 112.1, 51.0, 47.3, 33.9, 31.7, 28.3, 22.5, 21.5, 14.0. IR (neat): υ 3091, 2961, 2939, 2879, 1684, 1605, 1501, 1464. HRMS (ESI) calcd for $C_{21}H_{31}NNaO_2S$ $(M+Na)^+$: 384.1968. Found: 384.1972.

_N_-allyl-_N_-(3,4-dimethylenedodecyl)-4-methylbenzenesulfonamide



Sulfonamide **S8** was prepared by following the procedure for converting **S5** to **S6**. **S5** (793 mg, 4.02 mmol) and 1-decyne (1.20 g, 8.70 mmol), and **S8** (835 mg, 2.49 mmol) was generated as a light yellow oil in 62% yield.

Spectra data of **S8**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.89-4.80 (br, 1H), 3.05 (q, J = 6.4 Hz, 2H), 2.43 (s, 3H), 2.29 (tt, J = 6.4 and 2.4 Hz, 2H), 2.09 (tt, J = 7.0 and 2.4 Hz, 2H), 1.48-1.39 (m, 2H), 1.37-1.20 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.4, 137.0, 129.7, 127.1, 83.2, 75.6, 42.1, 31.8, 29.14, 29.06, 28.9, 28.8, 22.6, 21.5, 19.9, 18.6, 14.0. IR (neat): υ 3486-3114(br), 2939, 2857, 1602, 1501, 1468, 1438. HRMS (ESI) calcd for $C_{19}H_{30}NO_2S$ $(M+H)^+$: 336.1992. Found: 336.1992.

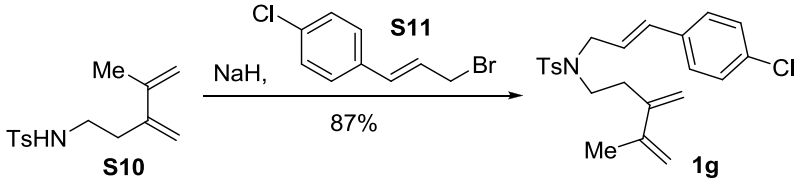
Sulfonamide **S9** was prepared by following the procedure for converting **S1** to **S2**. **S8** (800 mg, 2.38 mmol) and Grubbs II generation catalyst (61 mg, 0.072 mmol) were used, and **S9** (803 mg, 2.21 mmol) was generated as a light brown in 93% yield.

Sulfonamide **1e** was synthesized by following the procedure for converting **S2** to **1b**. NaH (238 mg, 50%, 4.96 mmol), **S9** (803 mg, 2.21 mmol), and allyl bromide (550 mg, 4.54 mmol) were used, and **1e** (775 mg, 1.92 mmol) was generated as a pale oil in 87% yield.

Spectra data of **1e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.68 (ddt, J = 17.2, 10.4 and 6.4 Hz, 1H), 5.18 (d, J = 17.2 Hz, 2H), 5.15 (d, J = 10.4 Hz, 2H), 5.10 (s, 1H), 5.07 (s, 1H), 3.83 (d, J = 6.4 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H), 2.50 (t, J = 8.4 Hz, 2H), 2.42 (s, 3H), 2.18 (t, J = 7.4 Hz, 2H), 1.45-1.35 (m, 2H), 1.34-1.20 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.8, 144.3, 143.1, 137.2, 133.4, 129.6, 127.1, 118.7, 113.7, 112.1, 51.0, 47.3, 33.93, 33.90, 31.9, 29.5, 29.4, 29.3, 28.6, 22.6, 21.4, 14.1. IR (neat): υ 3106, 2954, 2931, 2861, 1707, 1605, 1460. HRMS (ESI) calcd for $C_{24}H_{37}NNaO_2S$ $(M+Na)^+$: 426.2437. Found: 426.2438.

(_E_)-_N_-(3-(4-chlorophenyl)allyl)-4-methyl-_N_-(4-methyl-3-methylenepent-4-enyl)benzenesulfonamide



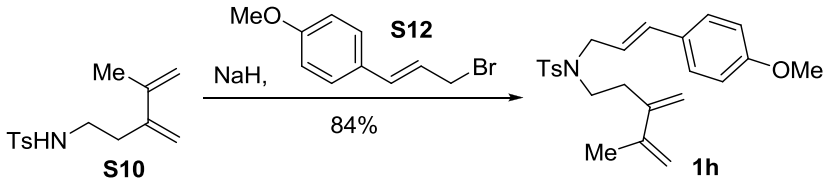
NaH (126 mg, 50%, 2.63 mmol) was suspended in DMF (5 mL) under argon and cooled to 0 ℃. A

DMF solution (10 mL) of **S10** [4] (276 mg, 1.04 mmol) was added slowly to the above mixture. The reaction mixture was warmed to room temperature and stirred for 15 min. Then a DMF solution (5 mL) of **S11** [5] (230 mg, 0.99 mmol) was added dropwise to the above light yellow solution. The resulting mixture was stirred for 15 min at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford sulfonamide **1g** (376 mg, 0.90 mmol, 87%) as a pale oil.

Spectra data of **1g**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.31-7.25 (m, 4H), 7.19 (d, J = 8.9 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 5.99 (dt, J = 16.0 and 7.0 Hz, 1H), 5.09 (s, 1H), 5.06 (s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 3.97 (dd, J = 7.0 and 1.0 Hz, 2H), 3.25 (t, J = 7.9 Hz, 2H), 2.56 (t, J = 7.9 Hz, 2H), 2.42 (s, 3H), 1.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5, 143.2, 141.8, 137.2, 134.7, 133.6, 132.4, 129.7, 128.7, 128.6, 127.2, 125.3, 114.5, 113.2, 50.5, 47.7, 33.8, 21.4, 20.9. IR (neat): υ 3103, 2961, 2939, 2883, 1602, 1497. HRMS (ESI) calcd for $C_{23}H_{27}ClNO_2S$ $(M+H)^+$: 416.1446. Found: 416.1446.

(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-4-methyl-*N*-(4-methyl-3-methylenepent-4-enyl)benzenesulfonamide

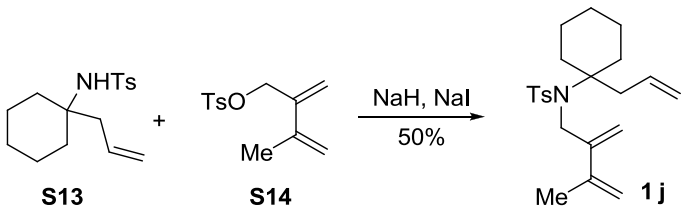


Sulfonamide **1h** was synthesized by following the procedure for converting **S10** to **1g**. NaH (98 mg, 50%, 2.04 mmol), **S10** (390 mg, 1.47 mmol), and **S12** [6] (500 mg, 2.07 mmol) were used, and **1h** (508 mg, 1.23 mmol) was generated as a colorless oil in 84% yield.

Spectra data of **1h**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.40 (d, J = 15.8 Hz, 1H), 5.85 (dt, J = 15.8 and 6.8 Hz, 1H), 5.083 (s, 1H), 5.078 (s, 1H), 4.95 (s, 1H), 4.94 (s, 1H), 3.96 (dd, J = 6.9 and 1.0 Hz, 2H), 3.80 (s, 3H), 3.24 (t, J = 8.1 Hz, 2H), 2.57 (t, J = 8.1 Hz, 2H), 2.42 (s, 3H), 1.84 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.5, 144.6, 141.8, 137.4, 133.3, 129.6, 129.0, 127.6, 127.2, 122.1, 116.1, 114.3, 114.0, 113.2, 55.3, 50.7, 47.5, 33.8, 21.5, 20.9. IR (neat): υ 3058, 2965, 2931, 2864, 1684, 1605, 1516, 1468. HRMS (ESI) calcd for $C_{24}H_{30}NO_3S$ $(M+H)^+$: 412.1941. Found: 412.1942.

***N*-(1-allylcyclohexyl)-4-methyl-*N*-(3-methyl-2-methylenebut-3-enyl)benzenesulfonamide**

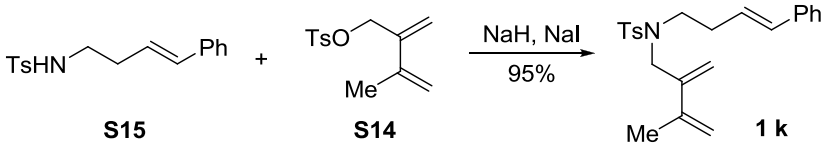


NaH (168 mg, 50%, 3.50 mmol) was suspended in DMF (5 mL) under argon and cooled to 0 ℃. A DMF solution (5 mL) of **S13** [7] (279 mg, 0.95 mmol) was added slowly to the above mixture. The reaction mixture was warmed to room temperature and stirred for 15 min. Then a DMF solution (5 mL) of **S14** [4] (693 mg, 2.75 mmol) was added dropwise to the above light yellow solution. After that, NaI (350 mg, 2.34 mmol) was added to the above solution. The resulting mixture was stirred for 1.5 h at room temperature. After that, saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with ether. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 50:1 to 30:1) to afford sulfonamide **1j** (179 mg, 0.48 mmol, 50%) as a pale oil.

Spectra data of **1j**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 5.83(ddt, J = 15.6, 11.7 and 7.4 Hz, 1H), 5.18 (s, 1H), 5.15 (s, 1H), 5.08 (d, J = 11.7 Hz, 1H), 5.07 (d, J = 15.6 Hz, 1H), 4.94 (s, 1H), 4.92 (s, 1H), 4.23 (s, 2H), 2.74 (d, J = 7.4 Hz, 2H), 2.40 (s, 3H), 2.22 (d, J = 12.5 Hz, 2H), 1.86 (s, 3H), 1.66 (td, J = 12.5 and 3.5 Hz, 2H), 1.61-1.52 (m, 3H), 1.42-1.29 (m, 2H), 1.13-1.06 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.1, 142.7, 141.5, 140.1, 134.3, 129.2, 127.8, 118.0, 113.7, 111.5, 66.8, 48.0, 38.4, 34.4, 25.0, 23.0, 21.7, 21.5. IR (neat): υ 2935, 2875, 1669, 1646, 1605, 1501, 1449. HRMS (ESI) calcd for $C_{22}H_{31}NNaO_2S$ $(M+Na)^+$: 396.1968. Found: 396.1972.

(*E*)-4-methyl-*N*-(3-methyl-2-methylenebut-3-enyl)-*N*-(4-phenylbut-3-enyl)benzenesulfonamide

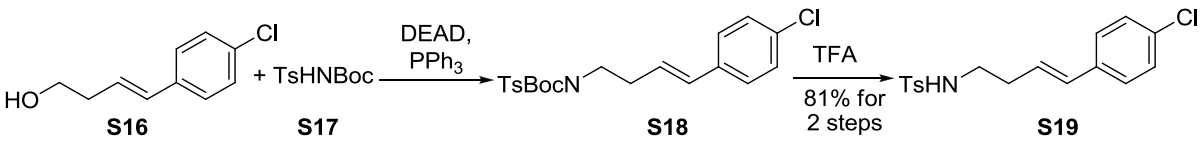


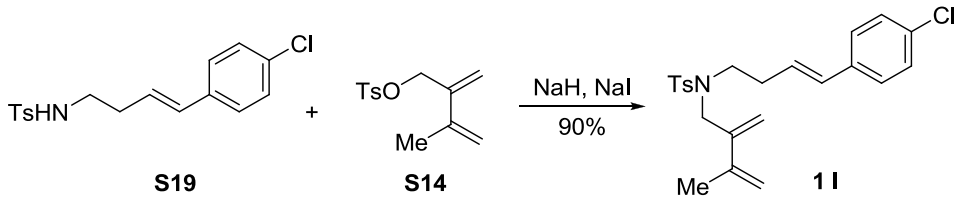
Sulfonamide **1k** was synthesized by following the procedure for converting **S13** to **1j**. NaH (198 mg, 50%, 4.13 mmol), **S15** [8] (660 mg, 2.19 mmol), **S14** (846 mg, 3.35 mmol) and NaI (423 mg, 2.82 mmol) were used, and **1k** (789 mg, 2.07 mmol) was generated as a pale oil in 95% yield.

Spectra data of **1k**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.28-7.26 (m, 4H), 7.22-7.18 (m, 1H), 6.30 (d, J = 16.1 Hz, 1H), 6.01 (dt, J = 16.1 and 7.1 Hz, 1H), 5.294 (s, 1H), 5.285 (s, 1H), 5.18 (s, 1H), 5.07 (s, 1H), 4.00 (s, 2H), 3.17 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 2.34 (q, J = 7.6 Hz, 2H), 1.92 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 143.2, 142.2, 140.4, 137.2, 136.4, 131.9, 129.7, 128.5, 127.3, 127.2, 126.5, 126.0, 116.0, 114.6, 51.6, 47.7, 32.4, 21.5, 21.3. IR (neat): υ 3095, 3036, 2980, 2931, 2879, 1605, 1501, 1456. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1835.

(*E*)-*N*-(4-(4-chlorophenyl)but-3-enyl)-4-methyl-*N*-(3-methyl-2-methylenebut-3-enyl)benzenesulfonamide





S19 **S14** **1 l**

S16 [9] (456 mg, 2.50 mmol), **S17** [10] (690 mg, 2.54 mmol) and PPh_3 (1.31 g, 4.99 mmol) were dissolved in 30 mL THF under Argon. Then DEAD was added dropwise to the above solution. After 3 h, the solvent was removed under reduced pressure. The resultant mixture was purified by flash column chromatography to give the crude product **S18**, which was used directly in the next step without further purification.

S18 was dissolved in 40 mL DCM under Argon. Then TFA (2.85 g, 25.0 mmol) was added dropwise to the above solution. The resultant mixture was stirred at room temperature overnight. After that, saturated aqueous $NaHCO_3$ was added slowly to quench the reaction. The aqueous layer was extracted with DCM for three times. The combined extract was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (eluted with PE/EA = 10:1 to 5:1) to afford sulfonamide **S19** (676 mg, 2.01 mmol, 81% for 2 steps) as a pale oil.

Spectra data of **S19**:

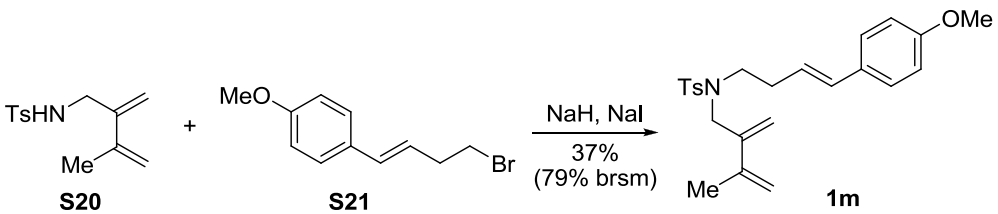
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 2H), 7.28-7.13 (m, 6H), 6.30 (d, J = 16.0 Hz, 1H), 5.96 (dt, J = 16.0 and 7.0 Hz, 1H), 4.79 (t, J = 6.2 Hz, 1H), 3.09 (q, J = 6.6 Hz, 2H), 2.39 (s, 3H), 2.35 (qd, J = 6.6 and 1.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 137.3, 135.6, 133.0, 131.8, 129.6, 128.6, 127.3, 127.1, 126.6, 42.6, 33.0, 21.4. IR (neat): υ 3412-3196(br), 3073, 3054, 2983, 2946, 2887, 1661, 1605, 1497, 1412. HRMS (ESI) calcd for $C_{17}H_{19}ClNO_2S$ $(M+H)^+$: 336.0820. Found: 336.0814.

Sulfonamide **1l** was synthesized by following the procedure for converting **S13** to **1j**. NaH (144 mg, 50%, 3.00 mmol), **S19** (559 mg, 1.66 mmol), **S14** (472 mg, 1.87 mmol) and NaI (305 mg, 2.03 mmol) were used, and **1l** (619 mg, 1.49 mmol) was generated as a pale oil in 90% yield.

Spectra data of **1l**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.27-7.17 (m, 4H), 6.26 (d, J = 15.8 Hz, 1H), 6.00 (dt, J = 15.8 and 7.3 Hz, 1H), 5.31 (s, 1H), 5.28 (s, 1H), 5.17 (s, 1H), 5.08 (s, 1H), 3.98 (s, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.42 (s, 3H), 2.34 (q, J = 7.3 Hz, 2H), 1.91 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 142.1, 140.3, 136.1, 135.7, 132.6, 130.6, 129.7, 128.5, 127.3, 127.23, 127.15, 116.1, 114.7, 51.7, 47.6, 32.4, 21.5, 21.3. IR (neat): υ 3062, 2965, 2935, 2872, 1724, 1687, 1605, 1497, 1460. HRMS (ESI) calcd for $C_{23}H_{27}ClNO_2S$ $(M+H)^+$: 416.1446. Found: 416.1445.

(*E*)-*N*-(4-(4-methoxyphenyl)but-3-enyl)-4-methyl-*N*-(3-methyl-2-methylenebut-3-enyl)benzenesulfonamide



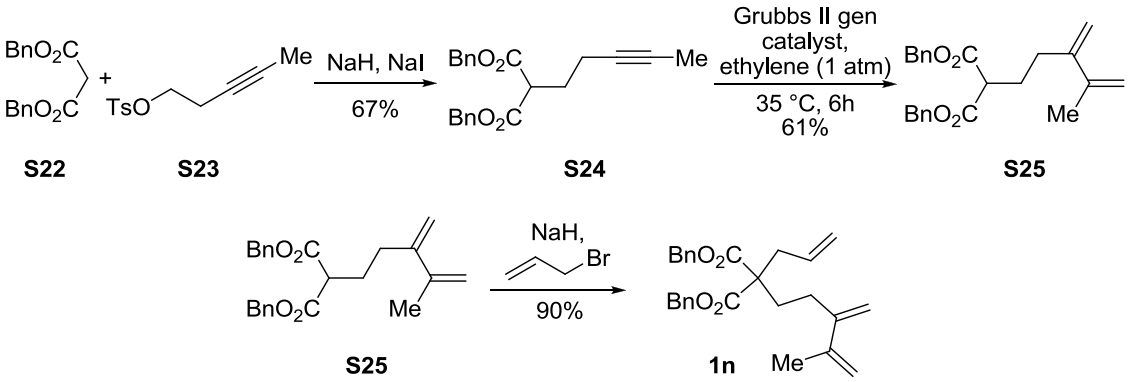
S20 **S21** **1m**

Sulfonamide **1m** was synthesized by following the procedure for converting **S13** to **1j**. NaH (180 mg, 50%, 5.83 mmol), **S20** [4] (400 mg, 1.59 mmol), **S21** [11] (612 mg, 2.54 mmol) and NaI (420 mg, 2.80 mmol) were used, and **1m** (242 mg, 0.59 mmol) was generated as a pale oil in 37% (79% brsm) yield.

Spectra data of **1m**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.24 (d, J = 15.9 Hz, 1H), 5.86 (dt, J = 15.9 and 7.5 Hz, 1H), 5.28 (s, 2H), 5.18 (s, 1H), 5.07 (s, 1H), 4.00 (s, 2H), 3.79 (s, 3H), 3.16 (t, J = 7.6 Hz, 2H), 2.42 (s, 3H), 2.31 (q, J = 7.5 Hz, 2H), 1.92 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.9, 143.2, 142.2, 140.5, 136.5, 131.3, 130.1, 129.6, 127.3, 127.1, 124.2, 115.8, 114.5, 113.9, 55.2, 51.5, 47.8, 32.3, 21.5, 21.3. IR (neat): υ 3106, 3039, 2942, 2946, 1609, 1516, 1453. HRMS (ESI) calcd for $C_{24}H_{30}NO_3S$ $(M+H)^+$: 412.1941. Found: 412.1941.

Dibenzyl 2-allyl-2-(4-methyl-3-methylenepent-4-enyl)malonate



Sulfonamide **S24** was synthesized by following the procedure for converting **S13** to **1j**, but a higher temperature and longer reaction time were needed (70 ℃ for 12 h). NaH (100 mg, 50%, 2.08 mmol), **S22** [12] (1.21 g, 4.26 mmol), **S23** [4] (402 mg, 1.69 mmol) and NaI (433 mg, 2.89 mmol) were used, and **S24** (398 mg, 1.14 mmol) was generated as a pale oil in 67% yield.

Spectra data of **S24**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 10H), 5.14 (s, 4H), 3.71 (t, J = 7.3 Hz, 1H), 2.25-2.18 (m, 2H), 2.11 (q, J = 7.1 Hz, 2H), 1.74 (t, J = 2.5 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.8, 135.3, 128.5, 128.2, 128.0, 77.1, 76.9, 67.1, 67.0, 50.6, 27.9, 16.6, 3.4. IR (neat): υ 2972. 2931, 2376, 2339, 1736. HRMS (ESI) calcd for $C_{22}H_{22}NaO_4$ $(M+Na)^+$: 373.1410. Found: 373.1414.

Sulfonamide **S24** (378 mg, 1.08 mmol) and Grubbs II generation catalyst (14 mg, 0.016 mmol) were dissolved in DCM (15 mL) under ethylene atmosphere. Ethylene was then bubbled to the solution for 5 min, and the reaction mixture was stirred under 1 atm ethylene at 35 ℃ for 5 h. The reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography (eluted with PE/EA = 10:1 to 3:1) to afford sulfonamide **S25** as a light brown oil (251 mg, 0.66 mmol, 61%).

Sulfonamide **1n** was synthesized by following the procedure for converting **S2** to **1b**. NaH (64 mg, 50%, 1.33 mmol), **S25** (251 mg, 0.66 mmol), and allyl bromide (91 mg, 0.73 mmol) were used, and **1n** (249 mg, 0.59 mmol) was generated as a pale oil in 90% yield.

Spectra data of **1n**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (m, 10H), 5.60 (ddt, J = 16.3, 11.3 and 7.4 Hz, 1H), 5.19 (s, 2H), 5.11 (s, 2H), 5.05 (d, J = 16.3 Hz, 1H), 5.04 (d, J = 11.3 Hz, 1H), 5.03 (s, 1H), 4.93 (s, 1H), 4.88 (s, 1H), 4.85 (s, 1H), 2.73 (d, J = 7.4 Hz, 2H), 2.16-2.03 (m, 4H), 1.85 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.8, 147.1, 142.0, 135.4, 132.1, 128.5, 128.3, 119.2, 112.8, 112.7, 67.0, 66.0, 57.6, 37.2, 32.2, 28.2, 21.1. IR (neat): υ 3103, 3043, 2961, 2935, 1739, 1605, 1505, 1460. HRMS (ESI) calcd for $C_{27}H_{30}NaO_4$ $(M+Na)^+$: 441.2036. Found: 441.2039.

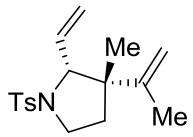
2.3 General Procedures for Rh(I)-Catalyzed Asymmetric C-H Activation/addition Reactions

General Procedures

General Procedures for the Asymmetric C-H Activation/addition Reactions: Anhydrous DME (1.0 mL) was added to a mixture of $[Rh(coe)_2Cl]_2$ (2.5 mg, 3.5 μmol) and AgOTf (2.1 mg, 8.2 μmol, 1.2 equiv. to Rh) under argon. The mixture was stirred at room temperature for 15 min. Then the mixture was transferred to another tube, which contained the chiral ligand **B** (6.8 mg, 17.6 μmol, 2.5 equiv. to Rh) under Argon. The resultant mixture was stirred at room temperature for another 15 min. To the resulting yellow suspension was added dropwise a DME (1.3 mL) solution of the substrate (70 μmol). The reaction tube was immersed into an oil bath (The temperature was indicated in each case). When TLC indicated the disappearance of the starting material or no further conversion of the substrate, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the corresponding product.

Experimental data for cycloadducts

(2*R*, 3*S*)-3-methyl-3-(prop-1-en-2-yl)-1-tosyl-2-vinylpyrrolidine



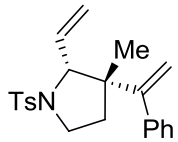
2a

Reaction time of 8 h at 70 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1a** (21.3 mg, 70 μmol) was converted to product **2a** (19.2 mg, 63 μmol) as a colorless oil in 90% yield and 90% *ee* as determined by HPLC analysis (Chiral OJ-H, hexane: *i*-PrOH = 93:7, 1.0 mL/min, 254 nm), t_r 11.0 min (major), 19.2 min (minor); $[\alpha]^{20}_D$ = +8.0 °(c = 1.05, $CDCl_3$).

Spectra data of **2a**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.55 (ddd, *J* = 16.8 Hz, 10.0 Hz and 6.8 Hz, 1H), 5.28 (dt, *J* = 16.8 Hz and 1.4 Hz, 1H), 5.11 (dt, *J* = 10.0 Hz and 1.4 Hz, 1H), 4.76 (t, *J* = 1.4 Hz, 1H), 4.65 (s, 1H), 3.99 (d, *J* = 6.8 Hz, 1H), 3.48 (t, *J* = 9.3 Hz, 1H), 3.29 (ddd, *J* = 10.9 Hz, 9.3 Hz and 6.8 Hz, 1H), 2.42 (s, 3H), 2.16 (q, *J* = 10.8 Hz, 1H), 1.70 (s, 3H), 1.55 (dd, *J* = 12.3 Hz and 6.8 Hz, 1H), 0.72 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.6, 143.1, 135.9, 135.5, 129.4, 127.4, 117.0, 111.5, 69.4, 50.6, 45.4, 32.8, 23.4, 21.5, 20.3. IR (neat): υ 3095, 2980, 2890, 1650, 1598, 1497, 1456, 1408. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1520.

(2*R*, 3*S*)-3-methyl-3-(1-phenylvinyl)-1-tosyl-2-vinylpyrrolidine



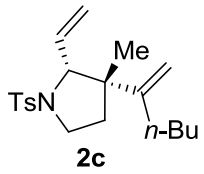
2b

Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1b** (25.6 mg, 70 μmol) was converted to product **2b** (19.2 mg, 53 μmol) as a colorless oil in 75% yield (recovered substrate: 2.4 mg, 6.5 μmol, 83% yield, brsm) and 77% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_r 18.9 min (major), 20.8 min (minor); $[\alpha]^{20}_D$ = +14.9 °(c = 0.68, $CDCl_3$).

Spectra data of **2b**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.32-7.17 (m, 7H), 5.75 (ddd, *J* = 16.7, 10.2 and 5.5 h Hz, 1H), 5.28 (d, *J* = 16.7 Hz, 1H), 5.161 (d, *J* = 10.2 Hz, 1H), 5.158 (s, 1H), 5.11 (s, 1H), 4.29 (d, *J* = 5.5 Hz, 1H), 3.46 (t, *J* = 9.1 Hz, 1H), 3.26 (ddd, *J* = 10.9, 9.1 and 7.4 Hz, 1H), 2.40 (s, 3H), 2.23 (q, *J* = 10.7 Hz, 1H), 1.59 (dd, *J* = 12.3 and 7.2 Hz, 1H), 0.79 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.8, 143.1, 142.2, 136.0, 129.4, 128.0, 127.8, 127.3, 127.1, 117.3, 116.6, 116.1, 69.7, 50.2, 44.7, 34.1, 25.4, 21.5. IR (neat): υ 3091, 3069, 2987, 2939, 2894, 2261, 1624, 1456, 1400. HRMS (ESI) calcd for $C_{22}H_{25}NNaO_2S$ $(M+Na)^+$: 390.1498. Found: 390.1494.

(2*R*, 3*S*)-3-(hex-1-en-2-yl)-3-methyl-1-tosyl-2-vinylpyrrolidine



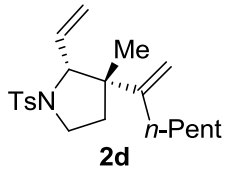
2c

Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1c** (24.2 mg, 70 μmol) was converted to product **2c** (21.8 mg, 63 μmol) as a colorless oil in 90% yield and 94% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_r 12.0 min (major), 13.5 min (minor); $[\alpha]^{20}_D$ = -5.8 °(c = 1.09, $CDCl_3$).

Spectra data of **2c**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.50 (ddd, *J* = 16.8, 9.9 and 6.5 Hz, 1H), 5.25 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 9.9 Hz, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 4.04 (d, *J* = 6.7 Hz, 1H), 3.48 (t, *J* = 9.2 Hz, 1H), 3.28 (ddd, *J* = 10.7, 9.0 amd 6.5 Hz, 1H), 2.42 (s, 3H), 2.17 (q, *J* = 10.7 Hz, 1H), 2.04-1.92 (m, 1H), 1.92-1.80 (m, 1H), 1.58-1.51 (m, 1H), 1.50-1.40 (m, 1H), 1.40-1.24 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.71 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.2, 143.1, 136.0, 135.8, 129.4, 127.4, 116.8, 109.3, 69.5, 51.3, 45.3, 32.8, 32.1, 30.6, 23.7, 22.8, 21.5, 14.0. IR (neat): υ 3099, 2965, 2939, 1646, 1605, 1497, 1471. HRMS (ESI) calcd for $C_{20}H_{30}NO_2S$ $(M+H)^+$: 348.1992. Found: 348.1990.

(2*R*, 3*S*)-3-(hept-1-en-2-yl)-3-methyl-1-tosyl-2-vinylpyrrolidine



2d

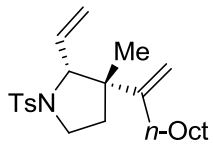
Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1d** (25.3 mg, 70 μmol) was converted to product **2d** (21.3 mg, 59 μmol) as a

colorless oil in 84% yield and 94% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 99:1, 0.8 mL/min, 254 nm), t_r 12.0 min (major), 12.9 min (minor); $[\alpha]^{20}_D$ = -8.5 °(c = 1.23, $CDCl_3$).

Spectra data of **2d**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.50 (ddd, *J* = 17.2, 10.4 and 6.9 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 4.03 (d, *J* = 7.2 Hz, 1H), 3.48 (t, *J* = 9.0 Hz, 1H), 3.28 (ddd, *J* = 11.0, 9.0 and 6.9 Hz, 1H), 2.42 (s, 3H), 2.21-2.11 (m, 1H), 2.02-1.91 (m, 1H), 1.89-1.78 (m, 1H), 1.58-1.22 (m, 7H), 0.89 (t, *J* = 13.9 Hz, 3H), 0.71 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 143.1, 135.9, 135.8, 129.4, 127.4, 116.8, 109.3, 69.5, 51.3, 45.3, 32.8, 32.3, 31.9, 28.0, 23.7, 22.6, 21.5, 14.0. IR (neat): υ 3103, 2965, 2942, 2875, 1646, 1605, 1501, 1471. HRMS (ESI) calcd for $C_{21}H_{32}NO_2S$ $(M+H)^+$: 362.2148. Found: 362.2151.

(2*R*, 3*S*)-3-(dec-1-en-2-yl)-3-methyl-1-tosyl-2-vinylpyrrolidine



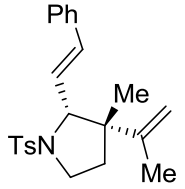
2e

Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1e** (28.3 mg, 70 μmol) was converted to product **2d** (25.8 mg, 64 μmol) as a colorless oil in 91% yield and 94% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 99:1, 0.7 mL/min, 254 nm), t_r 12.1 min (major), 13.1 min (minor); $[\alpha]^{20}_D$ = -7.4 °(c = 0.76, $CDCl_3$).

Spectra data of **2e**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.50 (ddd, *J* = 16.9, 10.3 and 6.9 Hz, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.09 (d, *J* = 10.3 Hz, 1H), 5.10 (s, 1H), 5.07 (s, 1H), 4.04 (d, *J* = 6.9 Hz, 1H), 3.48 (t, *J* = 8.9 Hz, 1H), 3.28 (ddd, *J* = 11.3, 9.3 and 6.9 Hz, 1H), 2.42 (s, 3H), 2.22-2.11 (m, 1H), 2.03-1.91 (m, 1H), 1.90-1.78 (m, 1H), 1.54 (dd, *J* = 12.2 and 6.8 Hz, 1H), 1.51-1.19 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.71 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 143.1, 135.8, 129.4, 127.4, 116.8, 109.3, 69.5, 51.3, 45.3, 32.8, 32.4, 31.9, 29.7, 29.5, 29.3, 28.3, 23.7, 22.6, 21.5, 14.1. IR (neat): υ 3099, 2935, 2861, 1650, 1605, 1497, 1471. HRMS (ESI) calcd for $C_{24}H_{37}NNaO_2S$ $(M+Na)^+$: 426.2437. Found: 426.2439.

(2*R*, 3*S*)-3-methyl-3-(prop-1-en-2-yl)-2-styryl-1-tosylpyrrolidine



2f

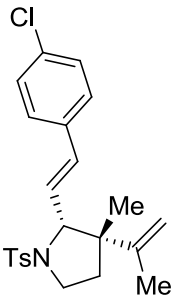
Reaction time of 11 h at 75 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1f** (26.6 mg, 70 μmol) was converted to product **2f** (15.7 mg, 41 μmol) as a colorless crystall (m.p.: 72-74 ℃ recrystallization from PE and EA) in 59% yield (recovered substrate: 5.2

mg, 14 μmol 74% yield, brsm) and 85% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 95:5, 1.0 mL/min, 250 nm), t_r 8.1 min (major), 11.9 min (minor); $[\alpha]^{20}_D$ = -67.5 °(c = 0.68, $CDCl_3$).

Spectra data of **2f**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.29-7.18 (m, 7H), 6.51 (d, *J* = 15.6 Hz, 1H), 5.73 (dd, *J* = 15.6 Hz and 7.9 Hz, 1H), 4.74 (t, *J* = 1.4 Hz, 1H), 4.67 (s, 1H), 4,19 (d, *J* = 7.9 Hz, 1H), 3.51 (t, *J* = 9.3 Hz, 1H), 3.42 (ddd, *J* = 10.8 Hz, 9.3 Hz and 6.7 Hz, 1H), 2.36 (s, 3H), 2.29-2.19 (m, 1H), 1.71 (s, 3H), 1.64 (dd, *J* = 12.2 Hz and 6.7 Hz, 1H), 0.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.7, 143.0, 136.8, 136.4, 132.2, 129.4, 128.3, 127.51, 127.47, 126.9, 126.6, 111.6, 69.2, 51.0, 45.4, 33.2, 23.7, 21.4, 20.2. IR (neat): υ 3069, 3039, 2976, 2935, 2890, 2861, 1650, 1456, 1373. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1832.

(2*R*, 3*S*)-2-(4-chlorostyryl)-3-methyl-3-(prop-1-en-2-yl)-1-tosylpyrrolidine



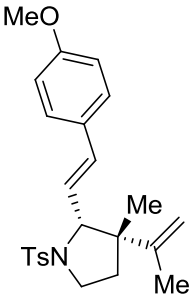
2g

Reaction time of 11 h at 75 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1g** (29.0 mg, 70 μmol) was converted to product **2g** (13.0 mg, 31 μmol) as a colorless oil in 45% yield (recovered substrate: 13.6 mg, 33 μmol, 85% yield, brsm) and 87% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_r 8.6 min (major), 10.0 min (minor); $[\alpha]^{20}_D$ = -67.1 °(c = 0.34, $CDCl_3$).

Spectra data of **2g**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.26-7.20 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 15.7 Hz, 1H), 5.73 (dd, *J* = 15.7 and 7.8 Hz, 1H), 4.75 (s, 1H), 4.67 (s, 1H), 4.16 (d, *J* = 7.8 Hz, 1H), 3.52 (t, *J* = 9.1 Hz, 1H), 3.40 (ddd, *J* = 10.8, 9.3 and 6.9 Hz, 1H), 2.37 (s, 3H), 2.23 (q, *J* = 10.8 Hz, 1H), 1.70 (s, 3H), 1.63 (q, *J* = 6.7 Hz, 1H), 0.86 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.5, 143.1, 136.2, 135.2, 133.1, 130.9, 129.4, 128.5, 127.8, 127.4, 116.1, 111.7, 69.0, 51.0, 45.4, 33.1, 23.6, 21.4, 20.2. IR (neat): υ 2961, 2935, 2879, 1650, 1602, 1497. HRMS (ESI) calcd for $C_{23}H_{27}ClNO_2S$ $(M+H)^+$: 416.1446. Found: 416.1449.

(2*R*, 3*S*)-2-(4-methoxystyryl)-3-methyl-3-(prop-1-en-2-yl)-1-tosylpyrrolidine



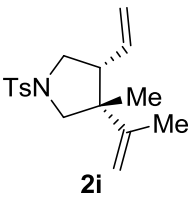
2h

Reaction time of 11 h at 75 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1h** (28.7 mg, 70 μmol) was converted to product **2h** (16.1 mg, 39 μmol) as a colorless oil in 56% yield (recovered substrate: 10.8 mg, 26 μmol, 90% yield, brsm) and 88% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_r 9.2 min (major), 12.0 min (minor); $[\alpha]^{20}_D$ = -56.1 °(c = 0.77, $CDCl_3$). The major enantiomer contains 0.45% epimer from the minor diastereoisomer as determined by NMR analysis.

Spectra data of **2h**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.59 (dd, *J* = 15.9 and 8.0 Hz, 1H), 4.73 (s, 1H), 4.66 (s, 1H), 4.17 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.49 (t, *J* = 9.2 Hz, 1H), 3.41 (ddd, *J* = 10.8, 9.5, and 6.9 Hz, 1H), 2.36 (s, 3H), 2.24 (q, *J* = 10.8 Hz, 1H), 1.70 (s, 3H), 1.63 (q, *J* = 6.9 Hz, 1H), 0.89 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.1, 146.8, 142.9, 136.3, 131.6, 129.5, 129.3, 127.7, 127.5, 124.7, 113.7, 111.5, 69.3, 55.2, 50.9, 45.3, 33.1, 23.6, 21.4, 20.2. IR (neat): υ 3054, 2983, 2942, 2846, 1646, 1613, 1516, 1468. HRMS (ESI) calcd for $C_{24}H_{30}NO_3S$ $(M+H)^+$: 412.1941. Found: 412.1943.

(3*R*, 4*R*)-3-methyl-3-(prop-1-en-2-yl)-1-tosyl-4-vinylpyrrolidine



2i

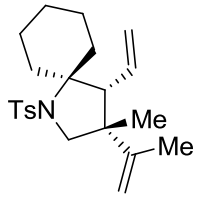
Reaction time of 11 h at 70 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1i** (21.3 mg, 70 μmol) was converted to product **2i** (16.0 mg, 53 μmol) as a colorless oil in 75% yield and 63% *ee* as determined by HPLC analysis (Chiral OJ-H, hexane: *i*-PrOH = 95:5, 0.8 mL/min, 250 nm), t_r 14.4 min (minor), 16.0 min (major); $[\alpha]^{20}_D$ = +27.7 °(c = 1.22, $CDCl_3$).

Spectra data of **2i**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.26 (ddd, *J* = 17.0 Hz, 10.0 Hz and 8.9 Hz, 1H), 4.90 (d, *J* = 17.0 Hz, 1H), 4.88 (d, *J* = 8.9 Hz, 1H), 4.75 (s, 1H), 4.56 (s, 1H), 3.58 (dd, *J* = 10.0 Hz and 6.7 Hz, 1H), 3.46 (d, *J* = 9.3 Hz, 1H), 3.25 (dd, *J* = 10.3 Hz and 3.4 Hz, 1H), 3.19 (d, *J* = 9.3 Hz, 1H), 2.44 (s, 3H), 2.42-2.38 (m, 1H), 1.64 (s, 3H), 1.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.6, 143.3, 136.3, 134.3, 129.6, 127.3, 116.1, 111.3, 56.3, 51.8, 51.1, 50.1, 24.5, 21.5, 20.4. IR

(neat): υ 3088, 2980, 2931, 2909, 2879, 1471, 1643, 1456. HRMS (ESI) calcd for $C_{17}H_{24}NO_2S$ $(M+H)^+$: 306.1522. Found: 306.1522.

(3*R*, 4*R*)-3-methyl-3-(prop-1-en-2-yl)-1-tosyl-4-vinyl-1-azaspiro[4.5]decane



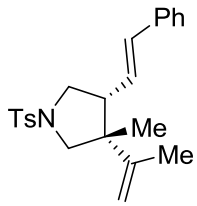
2j

Reaction time of 11 h at 70 ℃. Purification (SiO_2, PE:EA = 100:1 to 30:1). Following the general procedure, sulfonamide **1j** (26.0 mg, 70 μmol) was converted to product **2j** (22.9 mg, 61 μmol) as a colorless oil in 88% yield and 68% *ee* as determined by HPLC analysis of the dihydroboration-oxidation product **2jj** (Chiral AS-H, hexane: *i*-PrOH = 60:40, 0.5 mL/min, 254 nm), t_r 10.4 min (major), 12.8 min (minor); $[\alpha]^{20}_D$ = +23.7 °(c = 1.04, $CDCl_3$).

Spectra data of **2j**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.50 (dt, *J* = 16.9 and 10.6 Hz, 1H), 5.00 (dd, *J* = 10.6 and 1.8 Hz, 1H), 4.98 (dd, *J* = 16.9 and 1.8 Hz, 1H), 4.63 (s, 1H), 4.49 (s, 1H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.16 (d, *J* = 9.6 Hz, 1H), 2.56 (dd, *J* = 12.9 and 3.5 Hz, 1H), 2.49 (d, *J* = 10.8 Hz, 1H), 2.42 (s, 3H), 2.38-2.30 (m, 1H), 1.98-1.91 (m, 1H), 1.80-1.73 (m, 1H), 1.70-1.63 (m, 1H), 1.59 (s, 3H), 1.58-1.52 (m, 1H), 1.47-1.39 (m, 2H), 1.35-1.26 (m, 2H), 1.14 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.6, 142.6, 138.5, 135.2, 129.3, 127.3, 116.6, 109.6, 72.4, 59.1, 55.9, 48.4, 38.1, 33.0, 26.3, 25.0, 24.6, 23.2, 21.5, 20.0. IR (neat): υ 3091, 2946, 2879, 1646, 1605, 1497, 1456. HRMS (ESI) calcd for $C_{22}H_{32}NO_2S$ $(M+H)^+$: 374.2148. Found: 374.2148.

(3*R*, 4*R*)-3-methyl-3-(prop-1-en-2-yl)-4-styryl-1-tosylpyrrolidine



2k

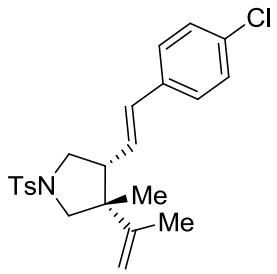
Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1k** (26.6 mg, 70 μmol) was converted to product **2k** (22.6 mg, 59 μmol) as a colorless oil in 85% yield and 84% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 95:5, 1.0 mL/min, 250 nm), t_r 12.9 min (minor), 14.9 min (major); $[\alpha]^{20}_D$ = -38.6 °(c = 0.81, $CDCl_3$).

Spectra data of **2k**:

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.45 (dd, *J* = 15.9 and 9.3 Hz, 1H), 4.74 (s, 1H), 4.59 (s, 1H), 3.69 (dd, *J* = 10.5 and 6.7 Hz, 1H), 3.51 (d, *J* = 9.3 Hz, 1H), 3.31 (dd, *J* = 10.5

and 3.3 Hz, 1H), 3.28 (d, *J* = 10.0 Hz, 1H), 2.55 (ddd, *J* = 10.0, 6.7 and 3.3 Hz, 1H), 2.40 (s, 3H), 1.64 (s, 3H), 1.11 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 146.6, 143.4, 136.8, 134.0, 131.1, 129.7, 128.4, 127.9, 127.40, 127.37, 126.1, 111.4, 56.4, 52.4, 50.5, 50.4, 24.7, 21.5, 20.4. IR (neat): υ 3095, 3069, 3036, 2983, 2946, 2890, 1646, 1605, 1497, 1449. HRMS (ESI) calcd for $C_{23}H_{28}NO_2S$ $(M+H)^+$: 382.1835. Found: 382.1834.

(3*R*, 4*R*)-4-(4-chlorostyryl)-3-methyl-3-(prop-1-en-2-yl)-1-tosylpyrrolidine



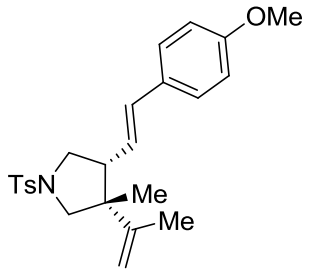
2l

Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1l** (29.0 mg, 70 μmol) was converted to product **2l** (23.2 mg, 56 μmol) as a colorless oil in 80% yield (recovered substrate: 2.6 mg, 6.3 μmol, 88% yield, brsm) and 84% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 97:3, 1.0 mL/min, 254 nm), t_r 20.2 min (major), 24.1 min (minor); $[\alpha]^{20}_D$ = -28.6 °(c = 0.81, $CDCl_3$).

Spectra data of **2l**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.16 (d, *J* = 16.0Hz, 1H), 5.43 (dd, *J* = 16.0 and 9.5 Hz, 1H), 4.74 (s, 1H), 4.59 (s, 1H), 3.68 (dd, *J* = 10.5 and 6.6 Hz, 1H), 3.51 (d, *J* = 9.5 Hz, 1H), 3.30 (dd, *J* = 10.5 and 3.3 Hz, 1H), 3.27 (d, *J* = 9.5 Hz, 1H), 2.54 (ddd, *J* = 9.5, 6.8 and 3.3 Hz, 1H), 2.41 (s, 3H), 1.63 (s, 3H), 1.09 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.4, 143.5, 135.2, 133.8, 133.0, 129.9, 129.7, 128.6, 128.5, 127.4, 127.2, 111.5, 56.3, 52.3, 50.4, 50.2, 24.6, 21.5, 20.3. IR (neat): υ 3054, 2976, 2935, 2864, 1650, 1602, 1497, 1453. HRMS (ESI) calcd for $C_{23}H_{27}ClNO_2S$ $(M+H)^+$: 416.1446. Found: 416.1446.

(3*R*, 4*R*)-4-(4-methoxystyryl)-3-methyl-3-(prop-1-en-2-yl)-1-tosylpyrrolidine



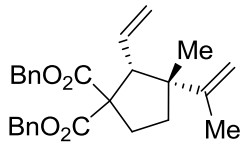
2m

Reaction time of 11 h at 80 ℃. Purification (SiO_2, PE:EA = 100:1 to 20:1). Following the general procedure, sulfonamide **1m** (28.7 mg, 70 μmol) was converted to product **2m** (22.9 mg, 56 μmol) as a colorless oil in 80% yield and 84% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 95:5, 1.0 mL/min, 254 nm), t_r 16.5 min (major), 18.9 min (minor); $[\alpha]^{20}_D$ = -43.5 °(c = 1.12, $CDCl_3$).

Spectra data of **2m**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.15 (d, *J* = 15.6 Hz, 1H), 5.31 (dd, *J* = 15.6 and 9.2 Hz, 1H), 4.73 (s, 1H), 4.58 (s, 1 H), 3.79 (s, 3H), 3.67 (dd, *J* = 10.4 and 6.3 Hz, 1H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.29 (dd, *J* = 10.5 and 3.6 Hz, 1H), 3.26 (d, *J* = 9.6 Hz, 1H), 2.52 (ddd, *J* = 9.5, 6.3 and 3.6 Hz, 1H), 2.42 (s, 3H), 1.64 (s, 3H), 1.09 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.0, 146.7, 143.4, 134.1, 130.5, 129.6, 127.4, 127.2, 125.6, 113.9, 111.3, 110.6, 56.6, 55.3, 52.5, 50.5, 50.4, 24.6, 21.5, 20.4. IR (neat): υ 3091, 2976, 2924, 2887, 1613, 1516, 1468. HRMS (ESI) calcd for $C_{24}H_{30}NO_3S$ $(M+H)^+$: 412.1941. Found: 412.1944.

(2*R*, 3*R*)-dibenzyl 3-methyl-3-(prop-1-en-2-yl)-2-vinylcyclopentane-1,1-dicarboxylate



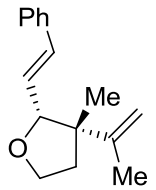
2n

Reaction time of 11 h at 75 ℃. Purification (SiO_2, PE:EA = 100:1 to 50:1). Following the general procedure, substrate **1n** (29.2 mg, 70 μmol) was converted to product **2n** (21.6 mg, 52 μmol) as a colorless oil in 74% yield and 81% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 99:1, 1.0 mL/min, 254 nm), t_r 6.1 min (minor), 6.7 min (major); $[\alpha]^{20}_D$ = -19.4 °(c = 1.11, $CDCl_3$).

Spectra data of **2n**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30-7.23 (m, 8H), 7.19-7.17 (m, 2H), 5.43 (dt, *J* = 16.8 and 10.2 Hz, 1H), 5.11 (d, *J* = 5.5 Hz, 2H), 5.00 (d, *J* = 10.2 Hz, 1H), 4.96 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.84 (dd, *J* = 10.2 and 2.5 Hz, 1H), 4.68 (s, 2H), 3.39 (d, *J* = 10.4 Hz, 1H), 2.84-2.75 (m, 1H), 2.23-2.13 (m, 2H), 1.66 (s, 3H), 1.59-1.49 (m, 1H), 1.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.2, 170.3, 149.5, 135.9, 135.5, 135.3, 128.45, 128.37, 128.2, 128.14, 128.05, 117.2, 113.4, 110.0, 67.3, 67.1, 65.2, 56.9, 52.5, 35.1, 31.3, 25.1, 20.1. IR (neat): υ 3091, 3043, 2969, 2935, 1739, 1646, 1505, 1464. HRMS (ESI) calcd for $C_{27}H_{30}NaO_4$ $(M+Na)^+$: 441.2036. Found: 441.2042.

(2*R*, 3*S*)-3-methyl-3-(prop-1-en-2-yl)-2-styryltetrahydrofuran



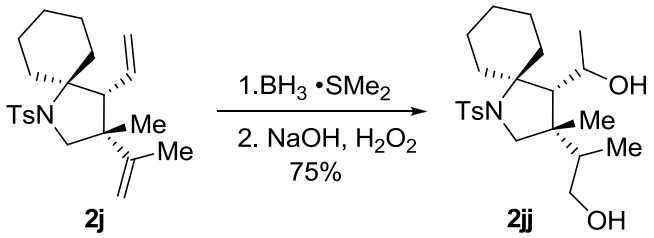
2o

Reaction time of 11 h at 60 ℃. Purification (SiO_2, PE:EA = 100:1). Following the general procedure, substrate **1o** (15.9 mg, 70 μmol) was converted to product **2o** (10.2 mg, 45 μmol) as a colorless oil in 64% yield (recovered substrate: 4.0 mg, 18 μmol, 86% yield, brsm) and 64% *ee* as determined by HPLC analysis (Chiral OD-H, hexane: *i*-PrOH = 97:3, 1.0 mL/min, 254 nm), t_r 5.0 min (minor), 6.0 min (major); $[\alpha]^{20}_D$ = +49.0 °(c = 0.51, $CDCl_3$).

Spectra data of **2o**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.20 (m, 5H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.8 and 6.9 Hz, 1H), 4.82 (s, 1H), 4.78 (s, 1H), 4.21 (d, *J* = 6.9 Hz, 1H), 4.12 (td, *J* = 8.4 and 3.0 Hz, 1H), 4.00 (q, *J* = 8.2 Hz, 1H), 2.29 (dt, *J* = 12.3 and 8.6 Hz, 1H), 1.78 (s, 3H), 1.74 (ddd, *J* = 12.3, 7.4 and 3.0 Hz, 1H), 1.27 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 137.1, 131.3, 128.4, 128.0, 127.4, 126.5, 111.2, 87.1, 66.6, 51.3, 36.0, 24.6, 21.1. IR (neat): υ 3091, 3039, 2976, 2950, 2890, 2253, 1646, 1456. HRMS (ESI) calcd for $C_{16}H_{20}NaO$ $(M+Na)^+$: 251.1406. Found: 251.1405.

2.4 The Derivatization Reaction of 2j to 2jj



2j **2jj**

2j was dissolved in 1.8 mL THF under Argon, and then a THF solution of $BH_3 \cdot SMe_2$ (2M, 0.3 mL) was added dropwise to the above solution at 0 ℃. The reaction mixture was stirred at room temperature for 1.5 h. Then 0.7 mL 1N NaOH (aq.) and 0.7 mL 30% H_2O_2 (aq.) were added to the reaction system at 0 ℃ sequentially. The resultant mixture was allowed to warm to room temperature spontaneously. After 30 min, 10 mL Et_2O was added to the reaction. The aqueous layer was extracted by Et_2O three times. The combined extract was dried by $MgSO_4$. The crude product was purified by column chromatography (eluted with PE/EA = 10:1 to 1:1) to afford **2jj** as a pale oil.

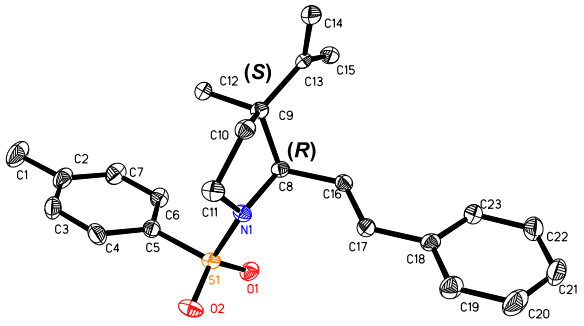
Spectra data of **2jj**:

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.56 (q, *J* = 7.3 Hz, 1H), 3.79 (d, *J* = 10.3 and 2.4 Hz, 1H), 3.49 (d, *J* = 8.8 Hz, 1H), 3.33 (t, *J* = 9.6 Hz, 1H), 3.00 (d, *J* = 8.8 Hz, 1H), 2.64-2.54 (m, 2H), 2.47 (td, *J* = 13.3 and 3.3 Hz, 1H), 2.40 (s, 3H), 2.04 (d, *J* = 13.6 Hz, 2H), 1.88 (s, 1H), 1.82-1.71 (m, 2H), 1.70-1.55 (m, 3H), 1.44 (d, *J* = 7.4 Hz, 3H), 1.37-1.24 (m, 2H), 1.21-1.12 (m, 1H), 0.94 (s, 3H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.3, 139.3, 129.2, 127.2, 73.6, 66.8, 66.4, 59.12, 59.07, 45.2, 38.8, 37.5, 33.5, 25.8, 25.1, 24.9, 24.4, 22.1, 21.4, 12.8. IR (neat): υ 3576-3196 (br), 2961, 2935, 2861, 1739, 1672, 1605, 1460. HRMS (ESI) calcd for $C_{22}H_{36}NO_4S$ $(M+H)^+$: 410.2360. Found: 410.2358.

2.5 Absolute Configuration Determination

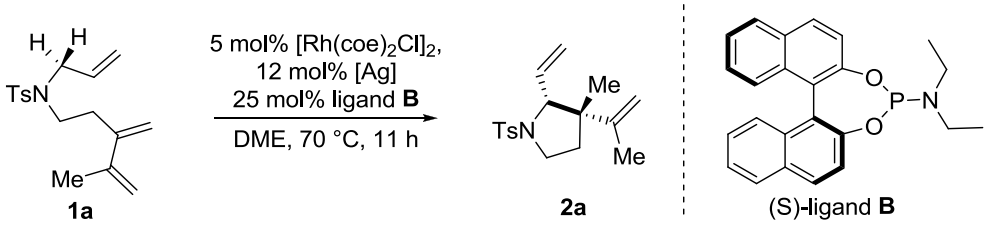
X-ray structure of 2f:

CCDC Number: CCDC 789812



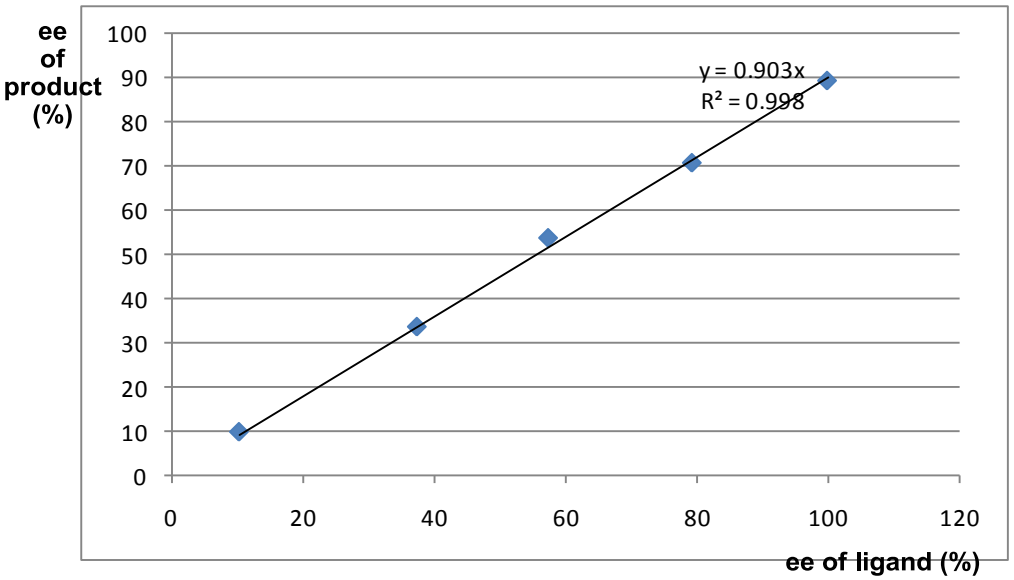
2.6 Nonliner Effect Study of the standard Substrate

The reactions were done following the same procedures as stated above by using the phosphoramidite ligands in different ees, which were determined by HPLC. After the completion of the reaction, the product was separated and purified by column chromatography, and the ees of these products were also determined by HPLC analysis. The ees of the phosphoramidite ligands and corresponding products were shown in the table below.



Ee of the ligand	10.4%	37.5%	57.5%	79.4%	100.0%
Ee of the product	10.1%	33.9%	54.0%	71.0%	89.6%

These date showd there was no nonliner effect in this asymmetric allylic C-H activation/addition:



2.7 References

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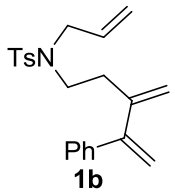
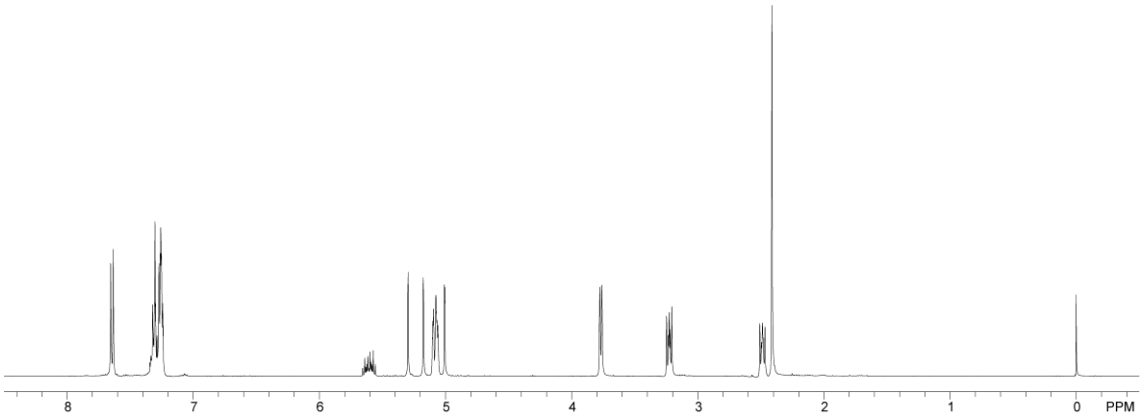
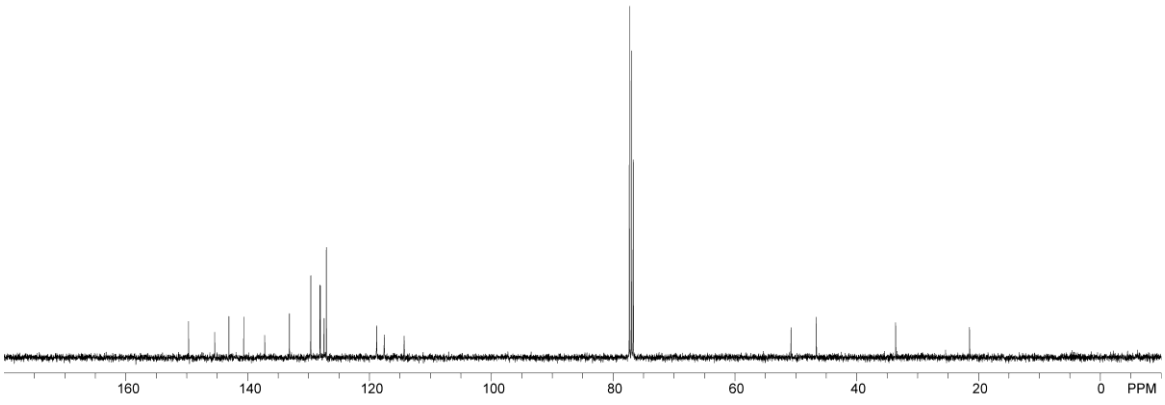
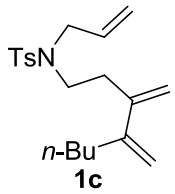
3 ^{1}H and ^{13}C-NMR Spectra for New Compounds



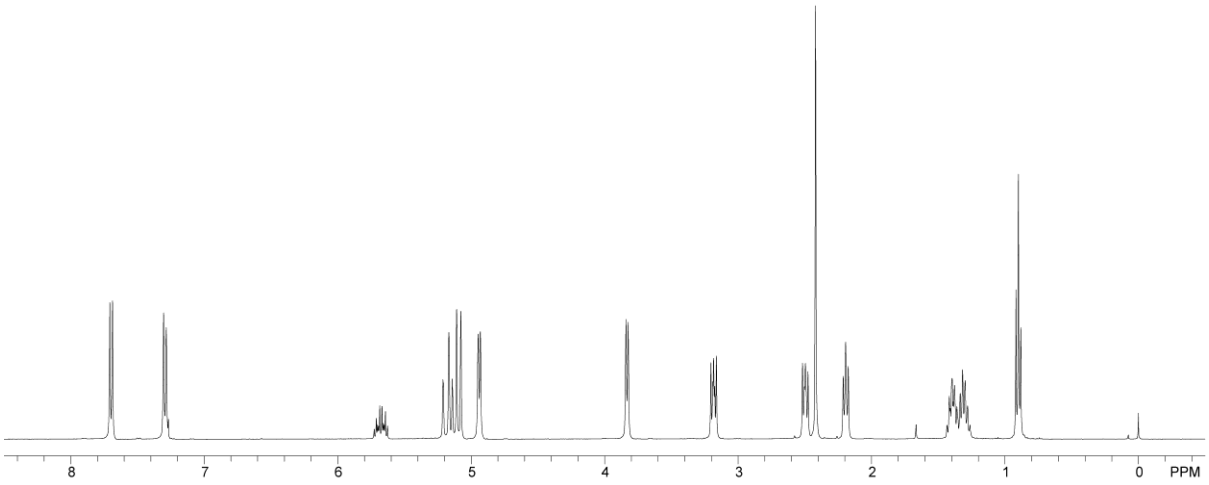
1b

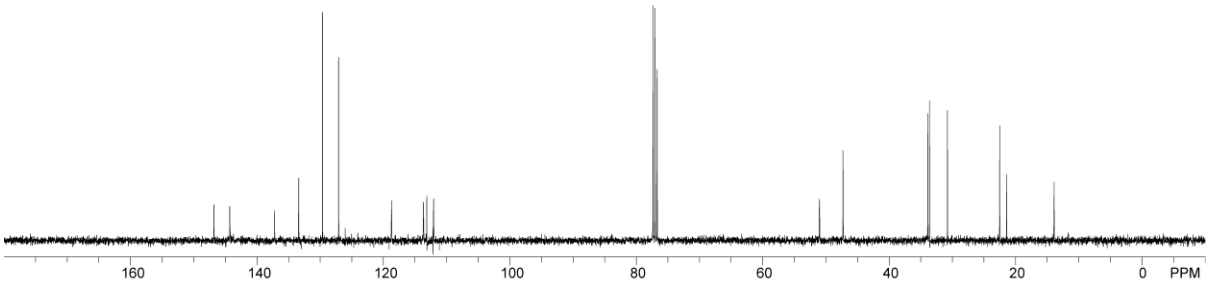


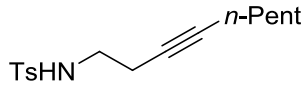




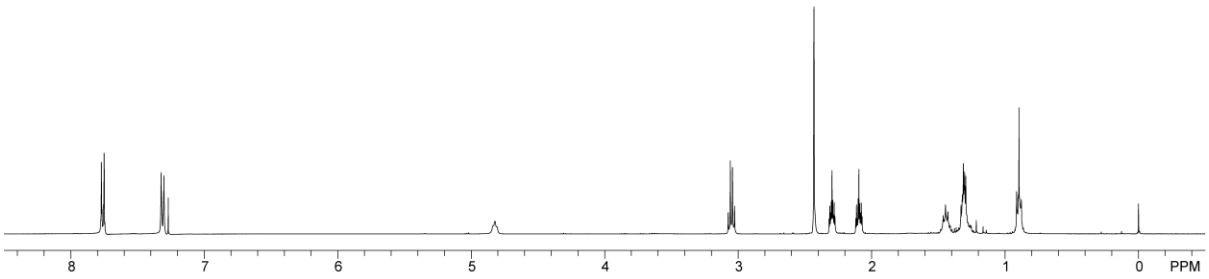
1c

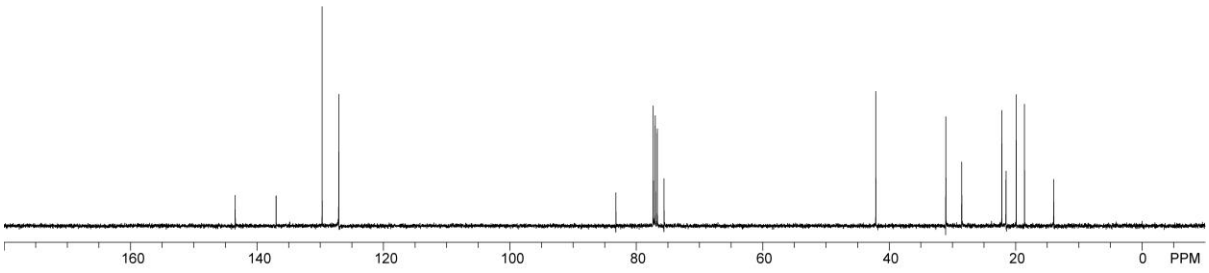


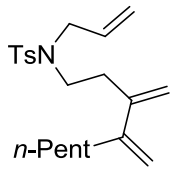




S6







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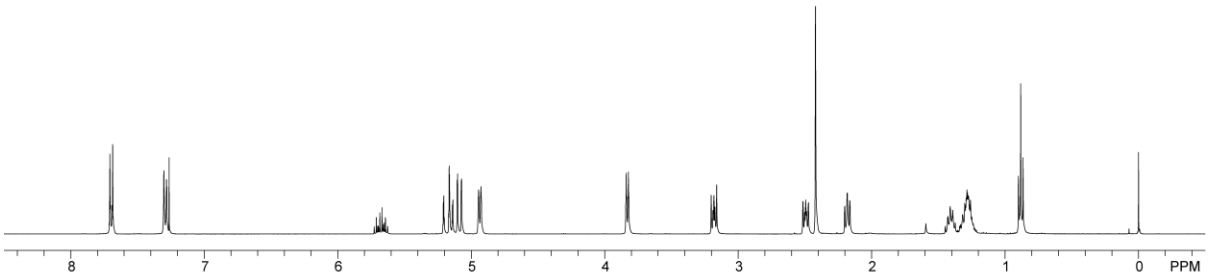

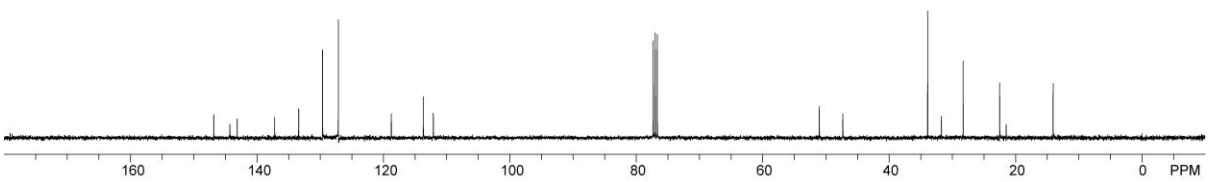

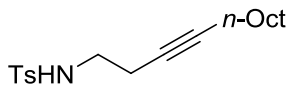

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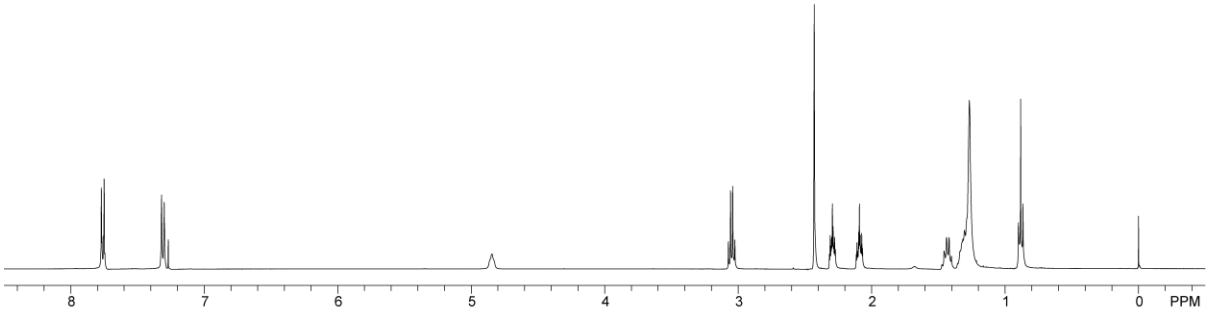

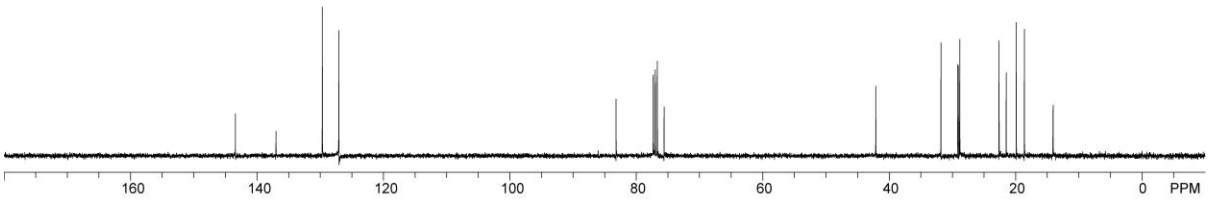

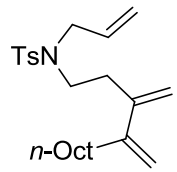

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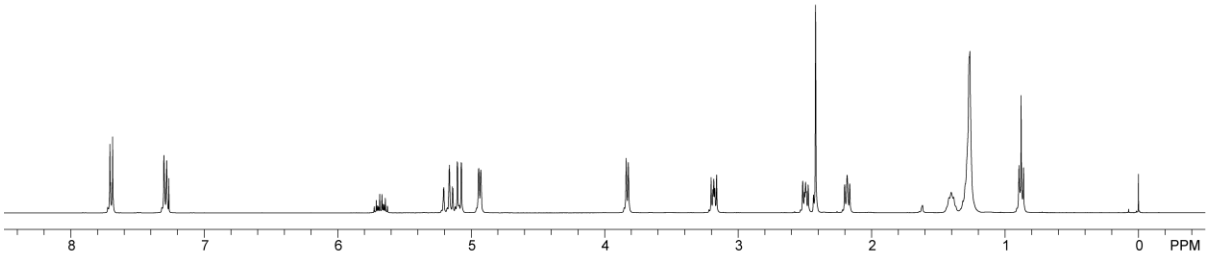

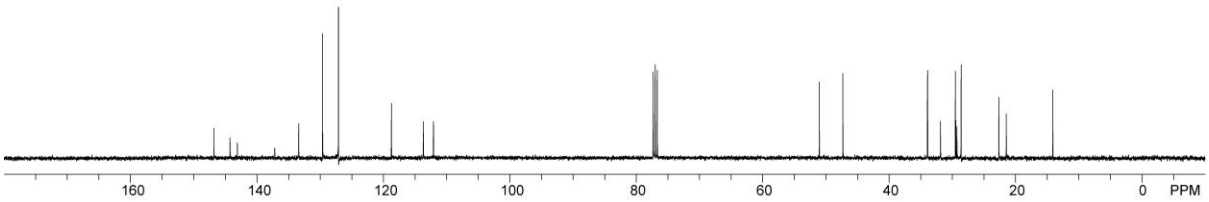

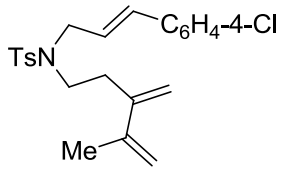

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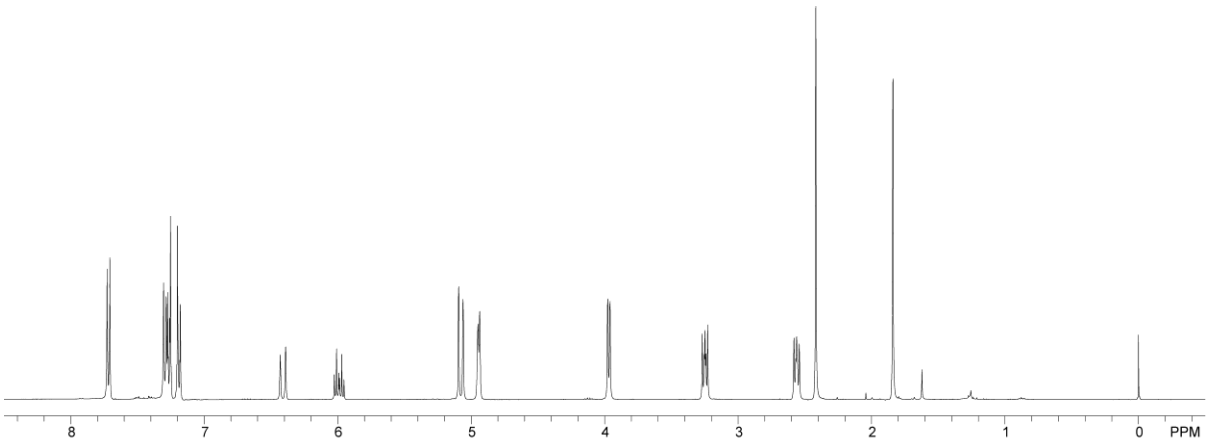

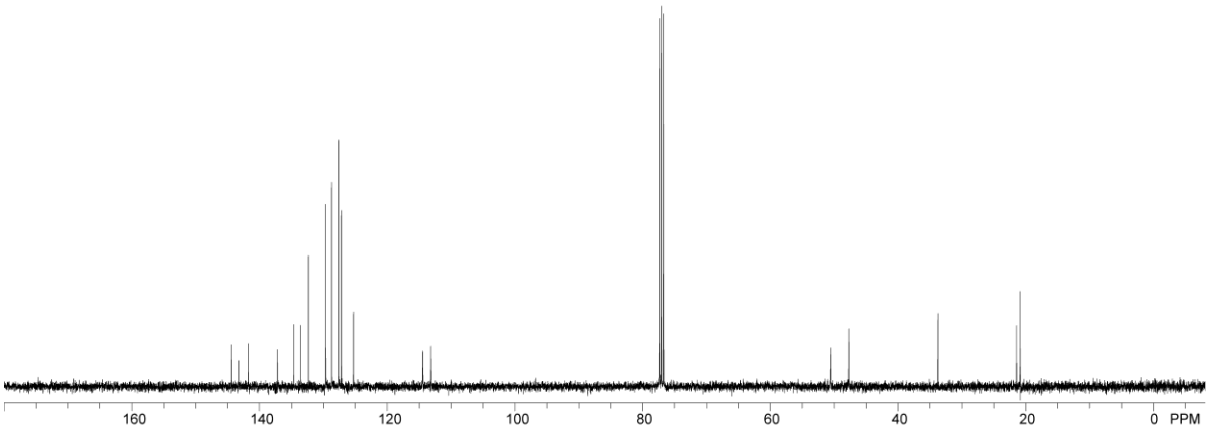

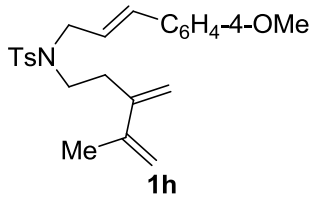

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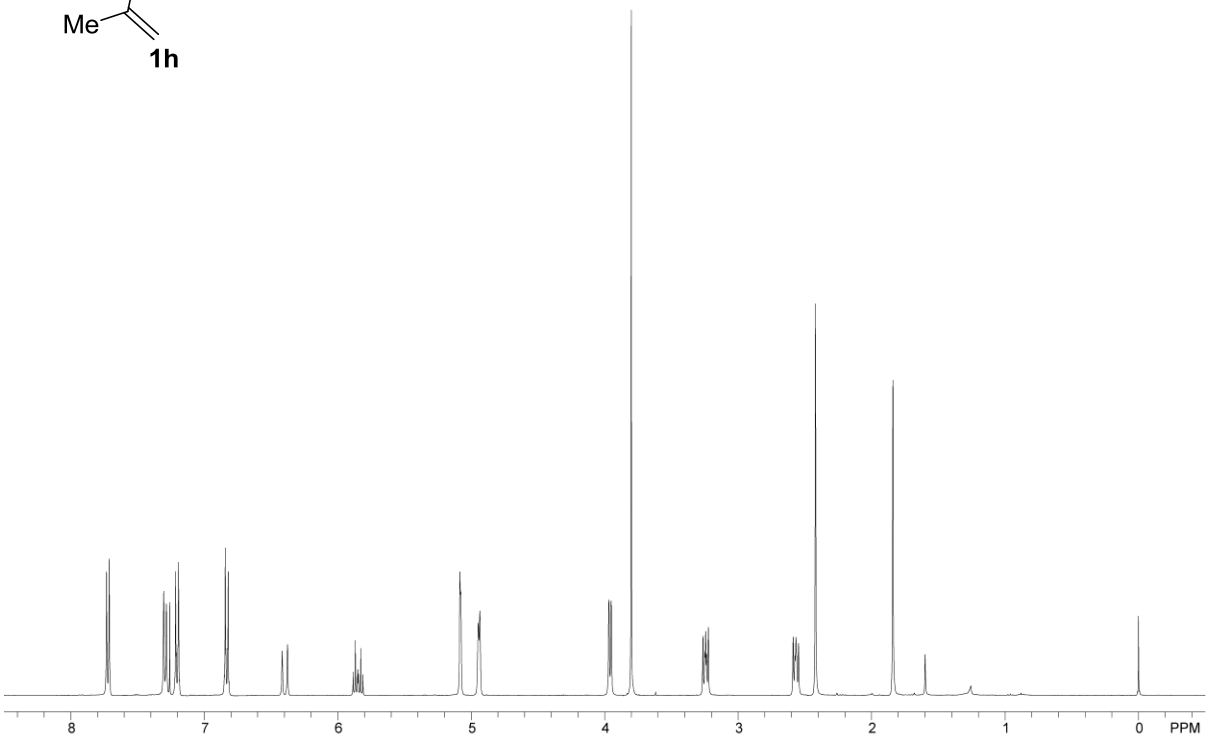

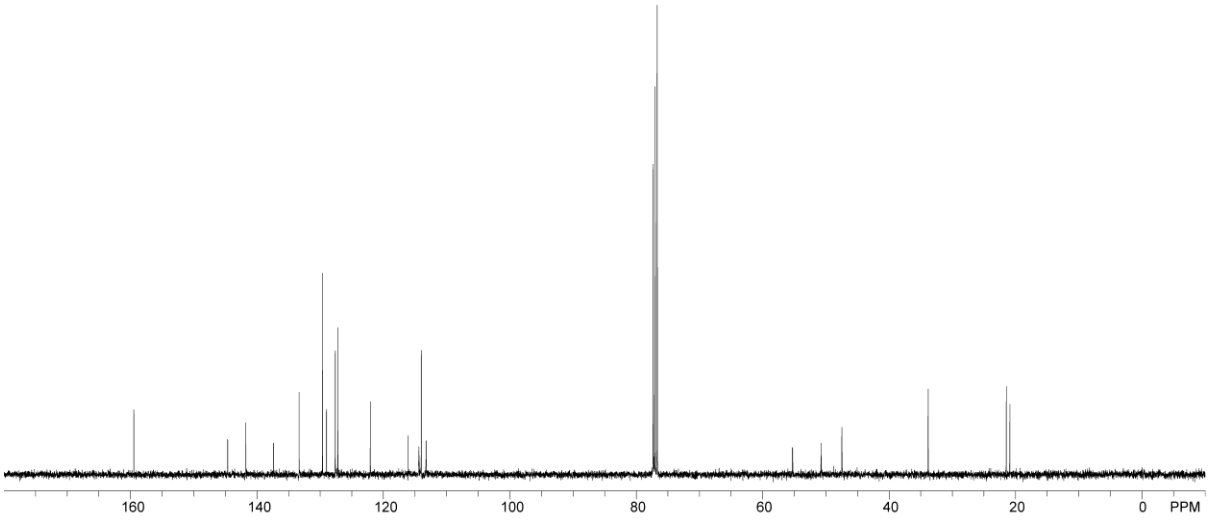

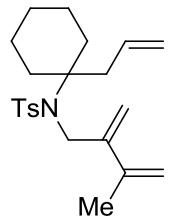

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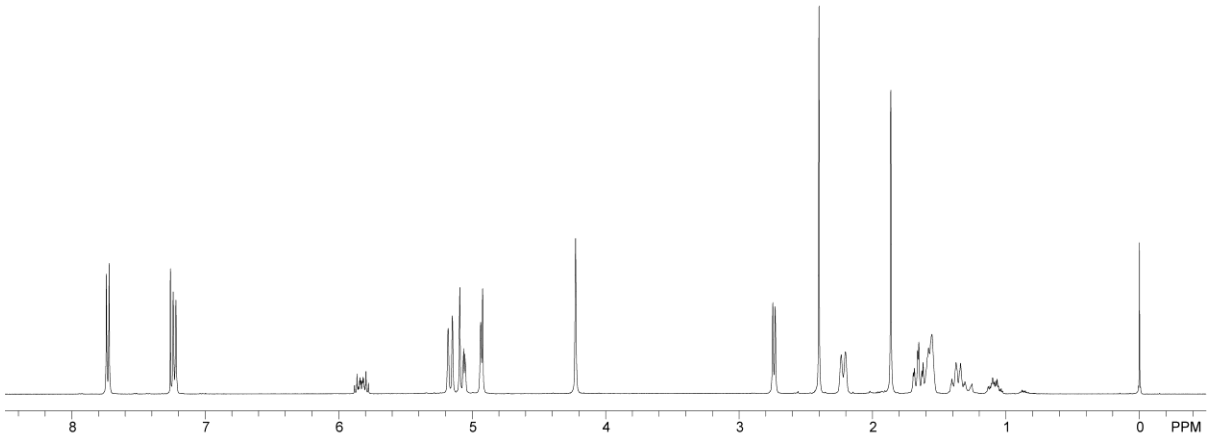

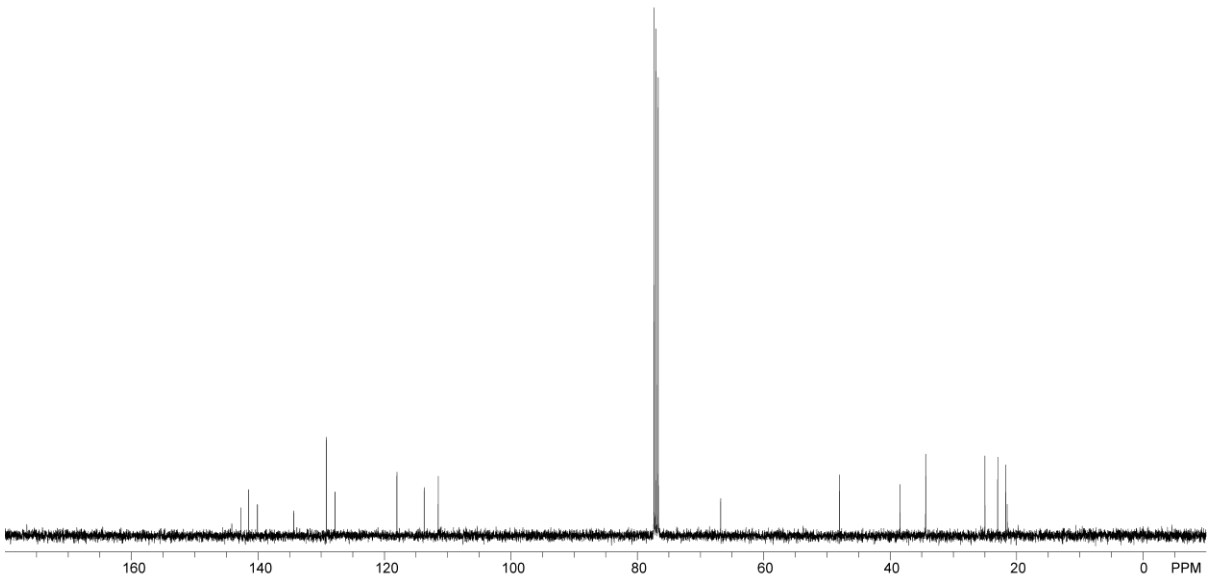

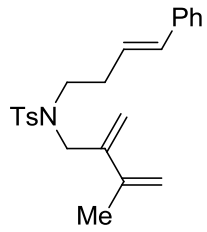

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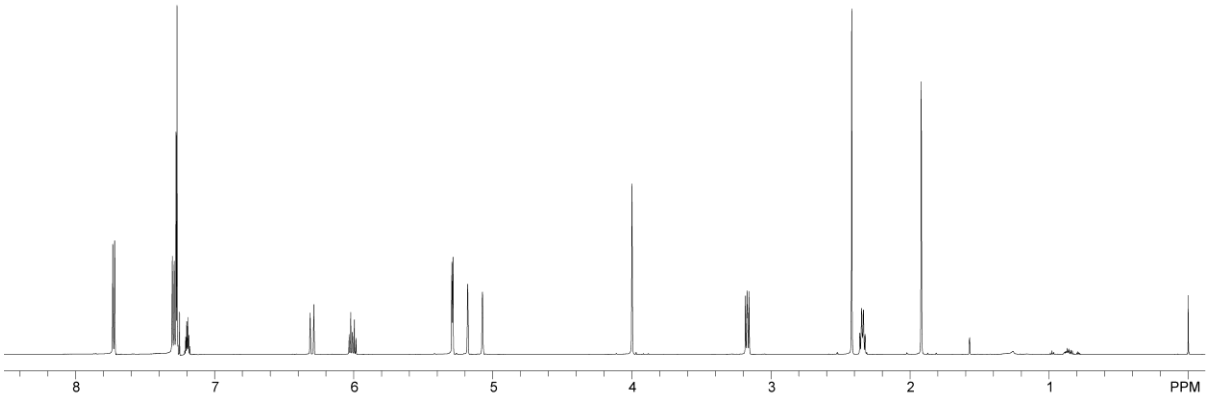

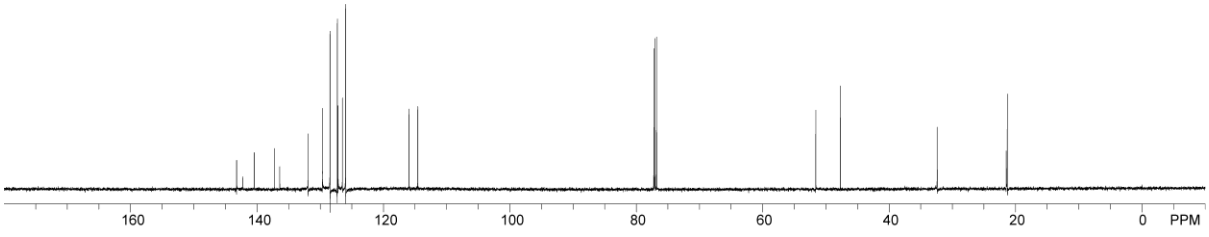

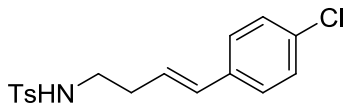

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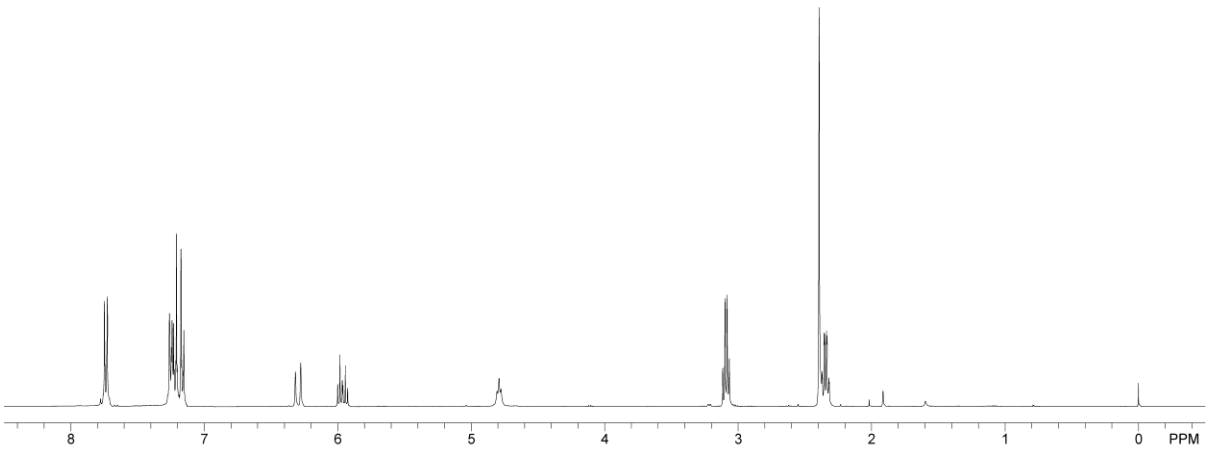

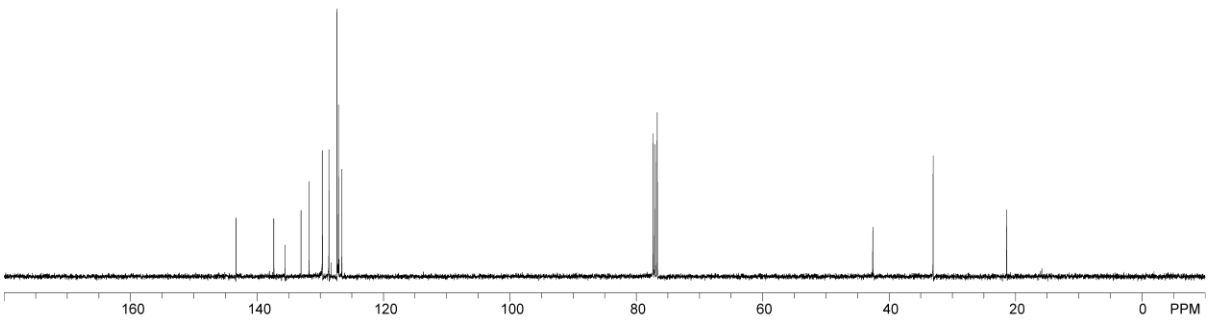

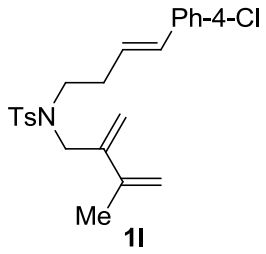

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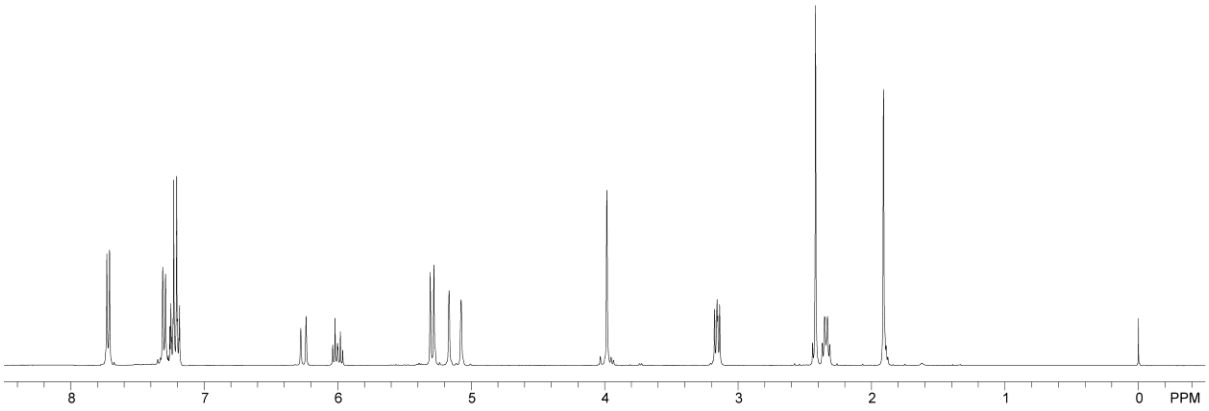

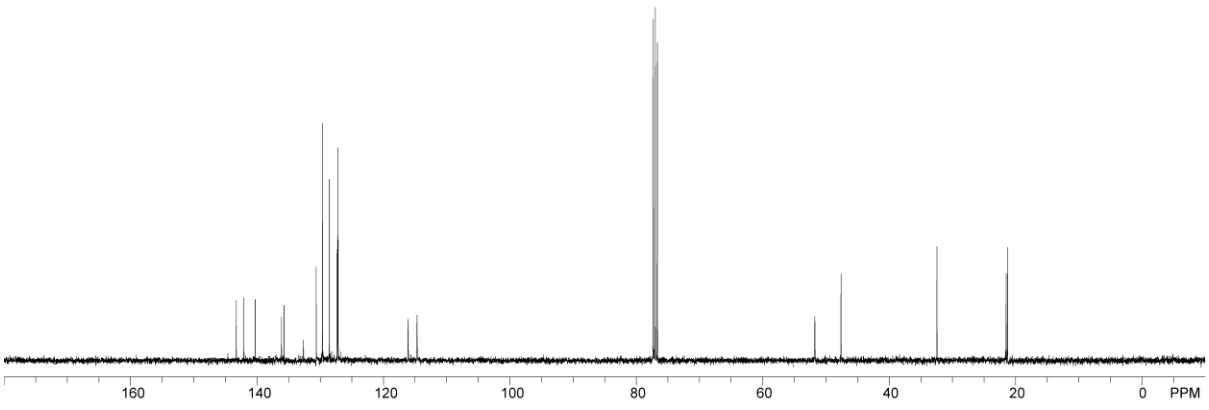

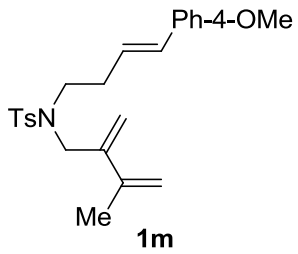

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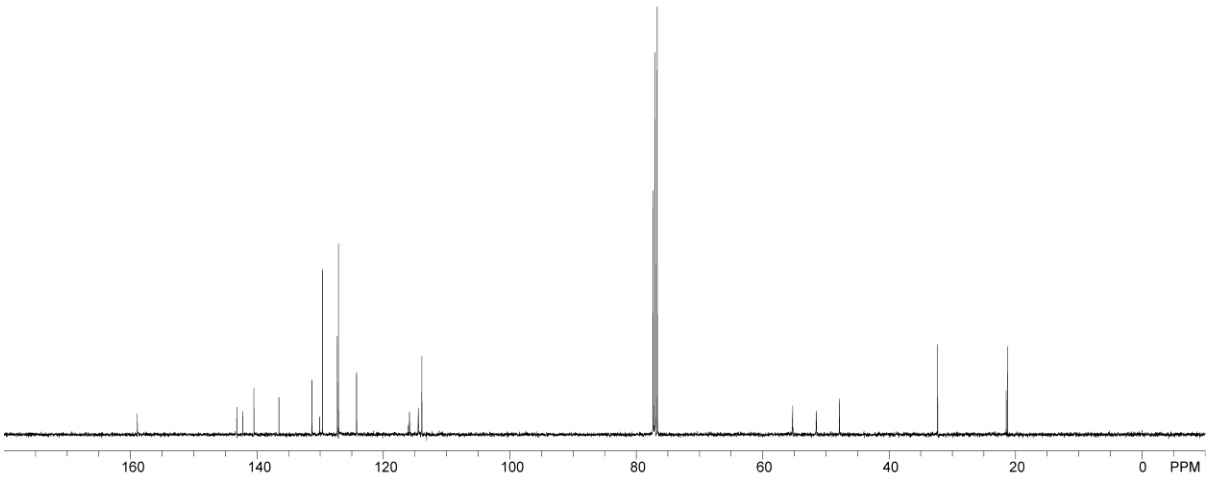

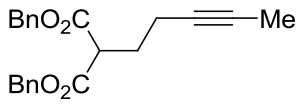

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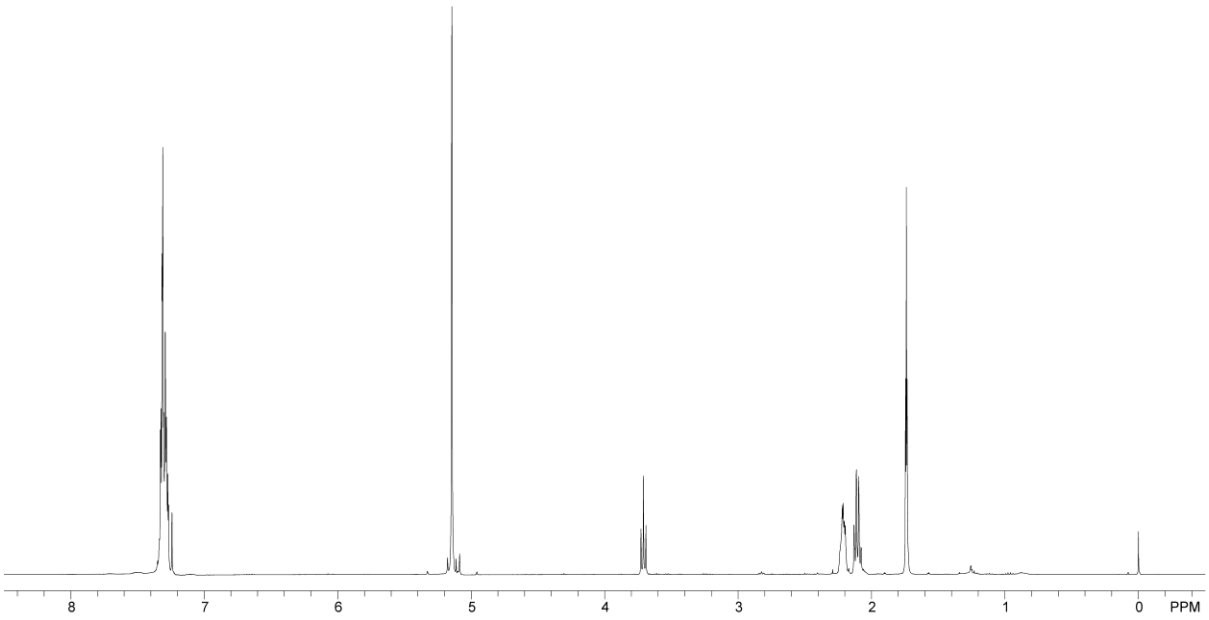

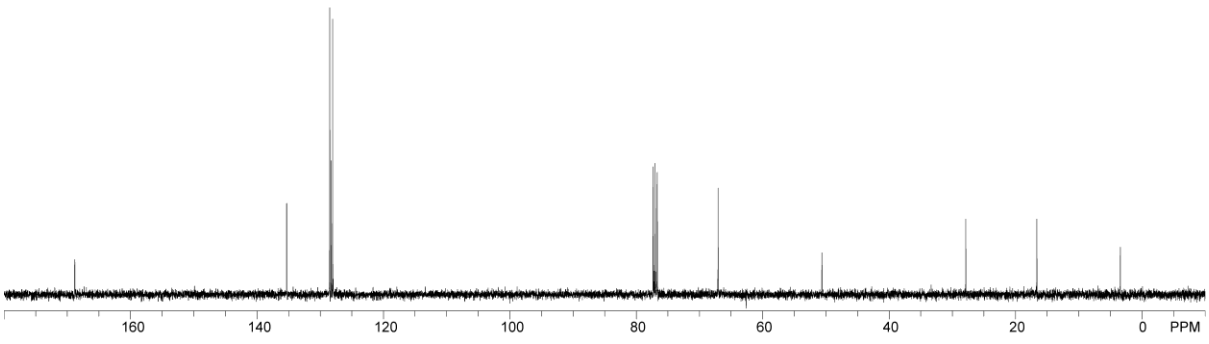

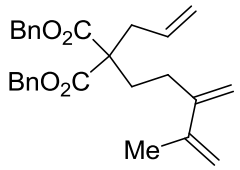

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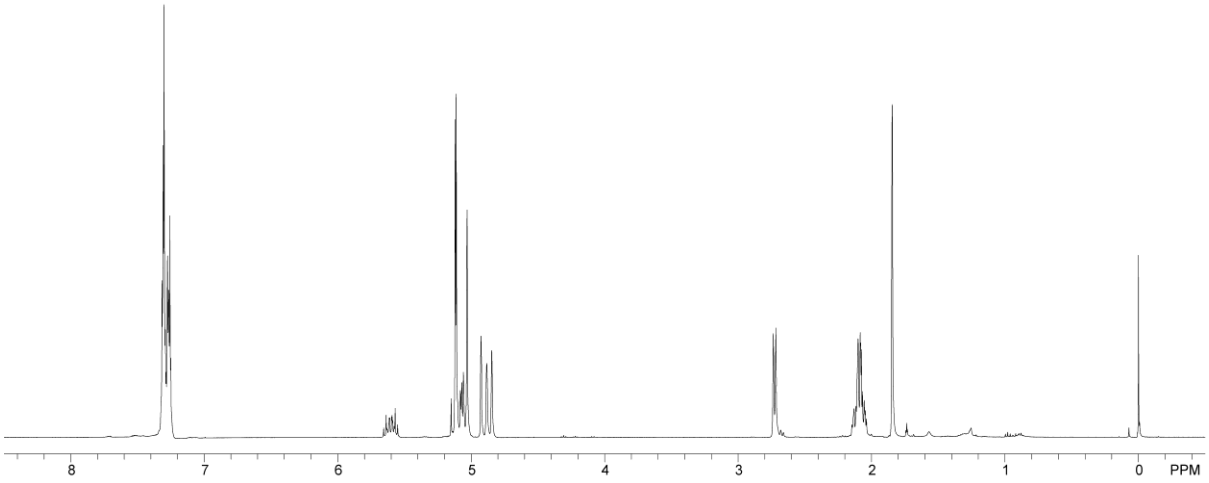

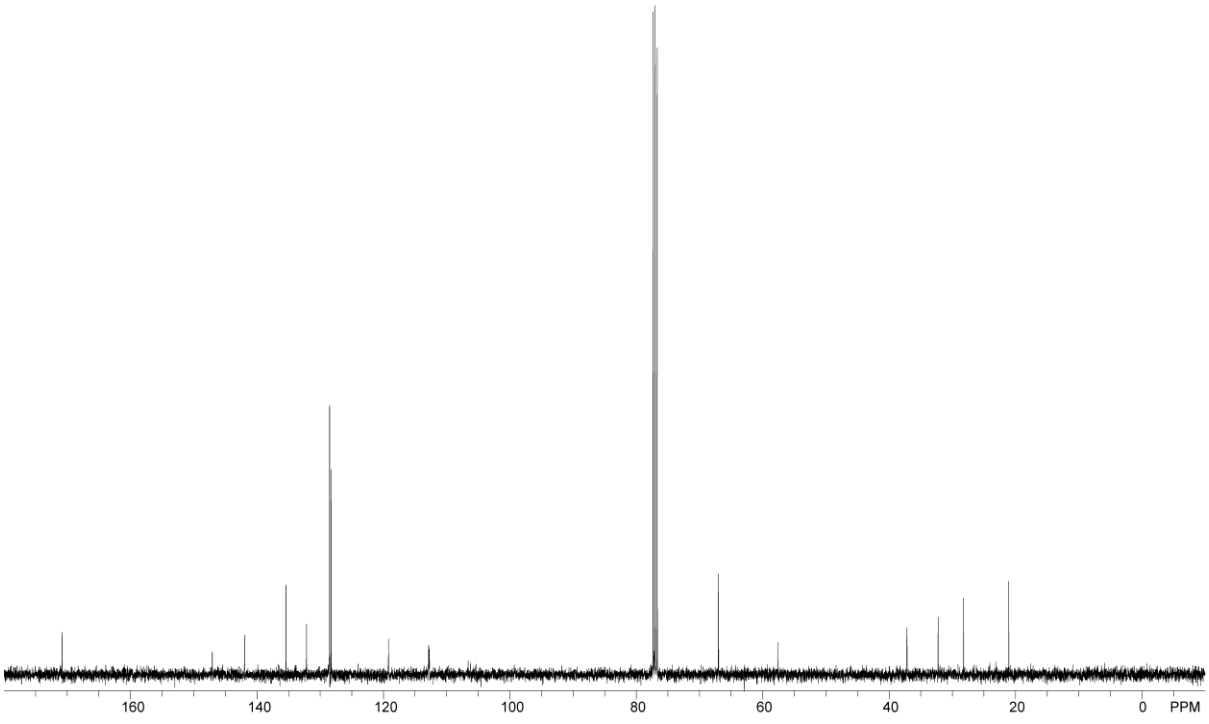

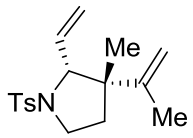

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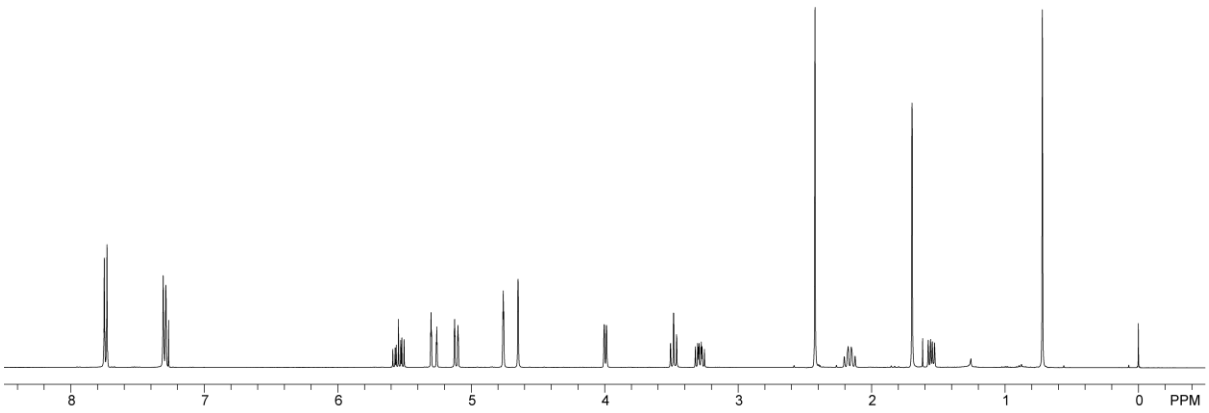

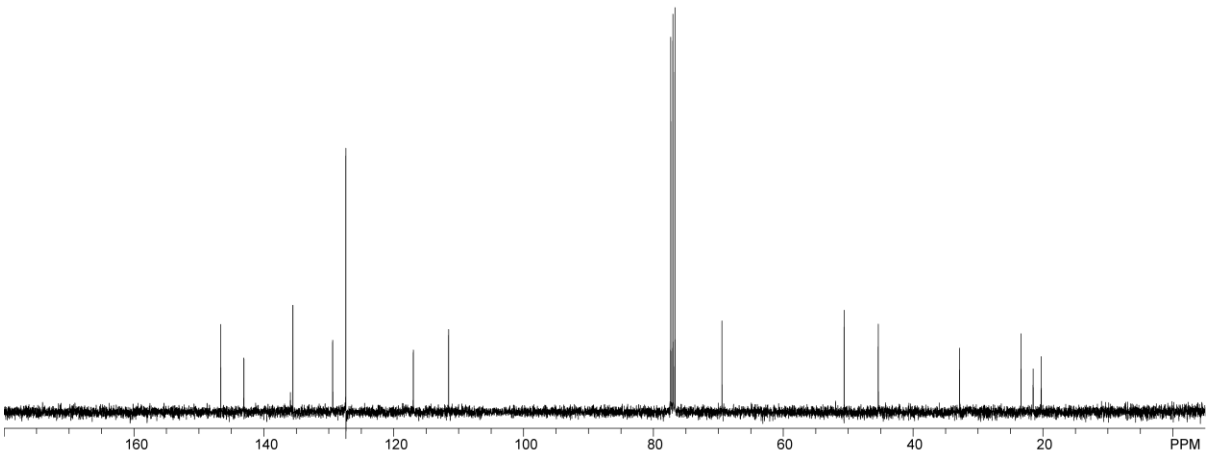

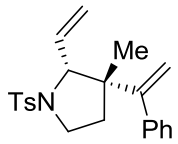

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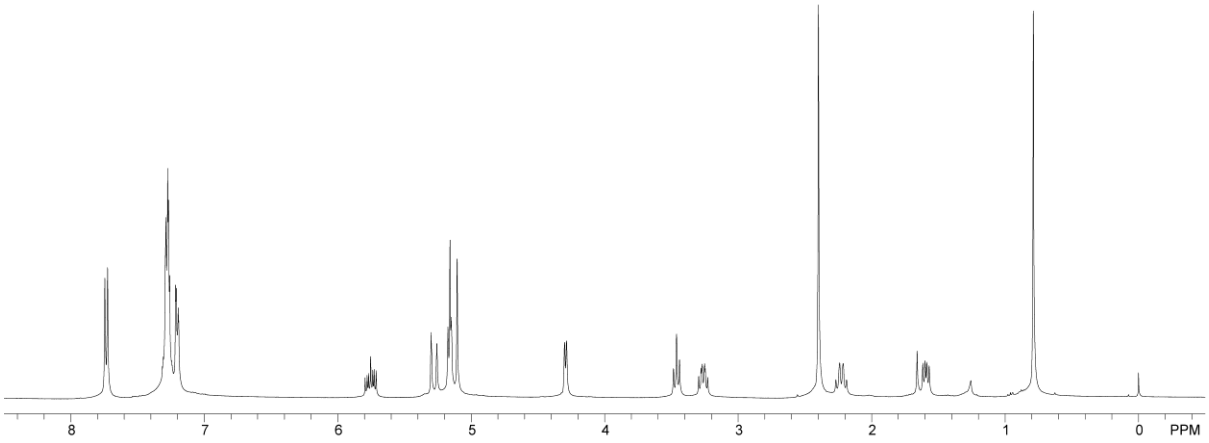

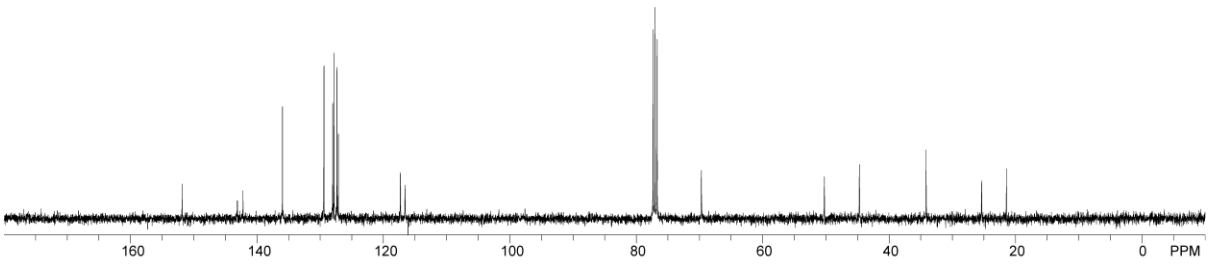

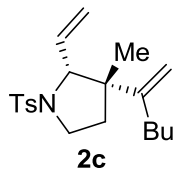

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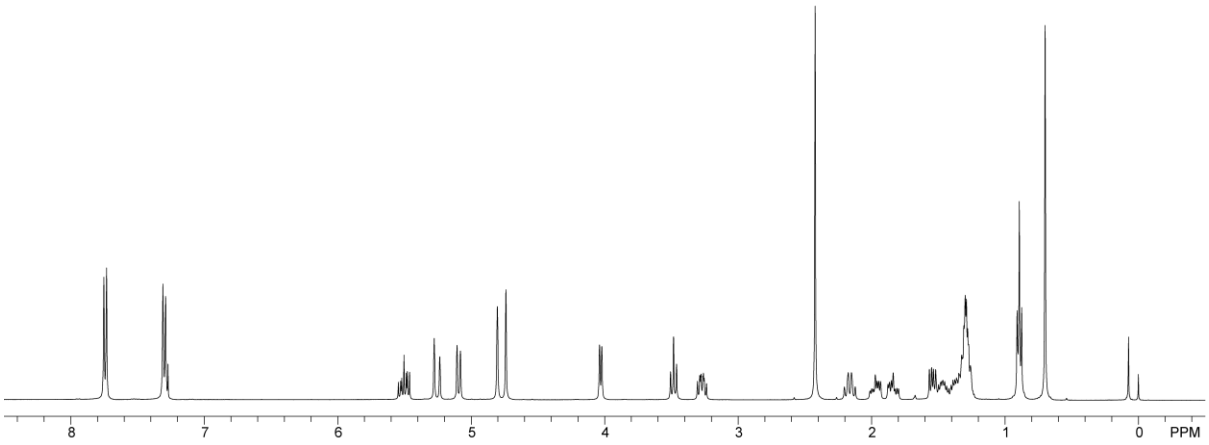

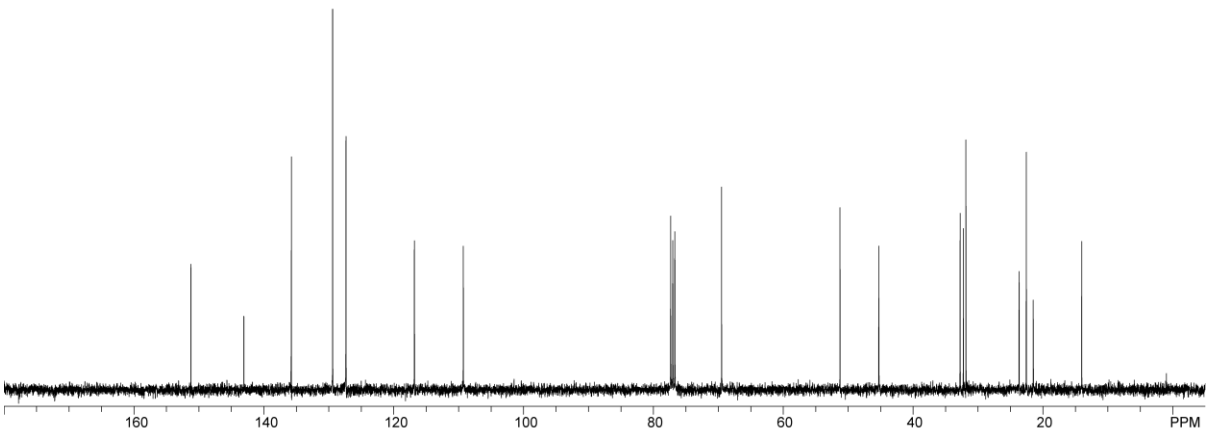

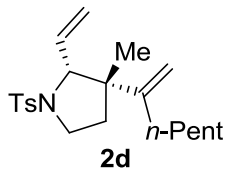

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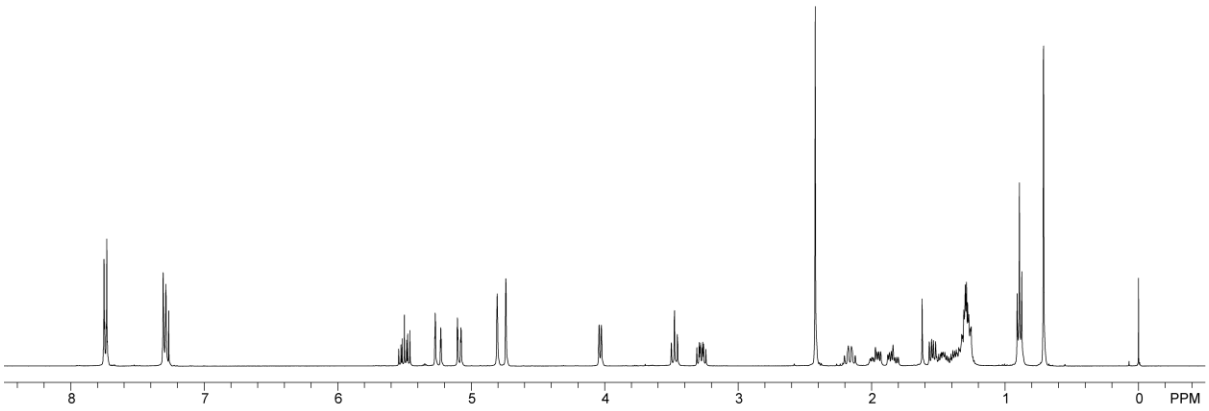

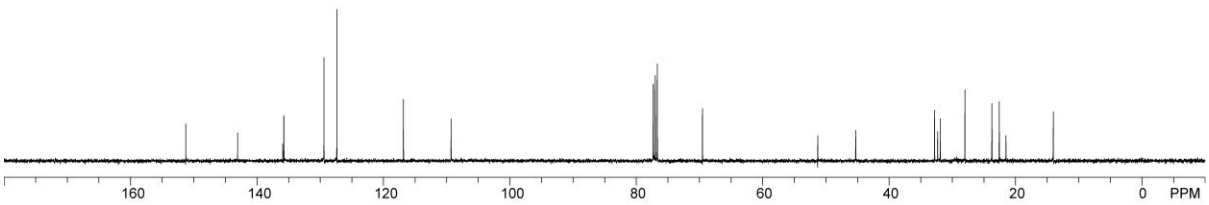

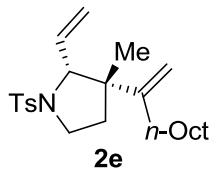

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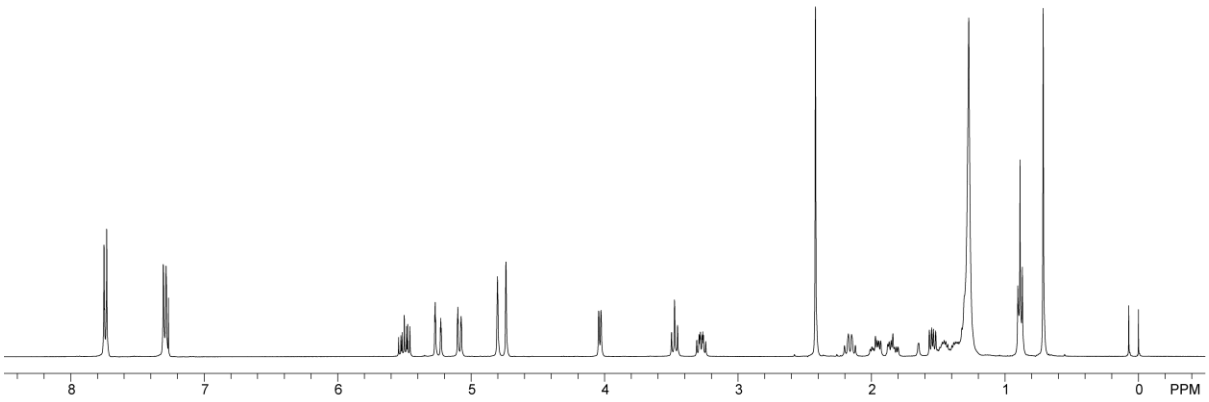

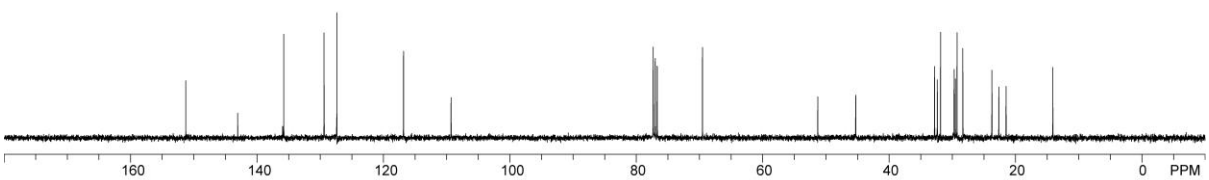

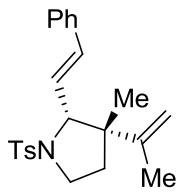

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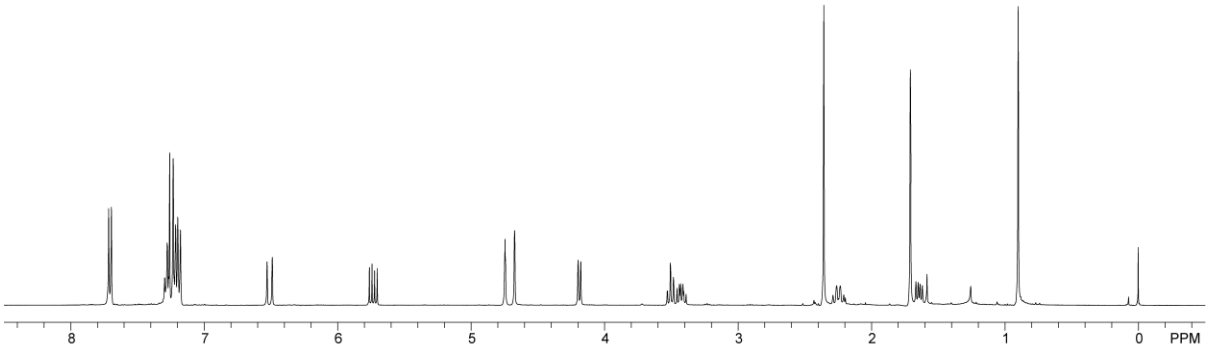

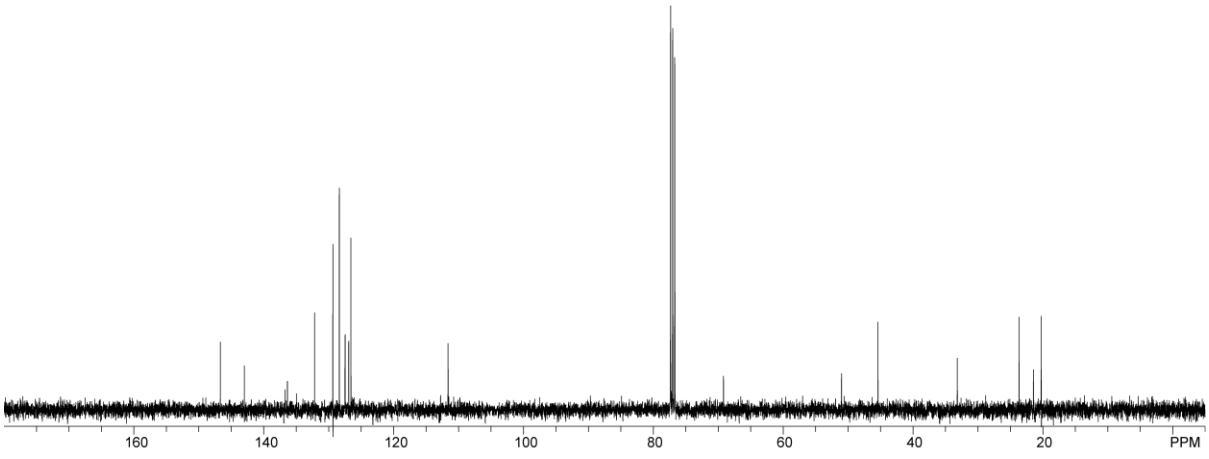

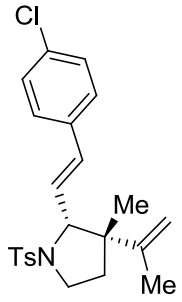

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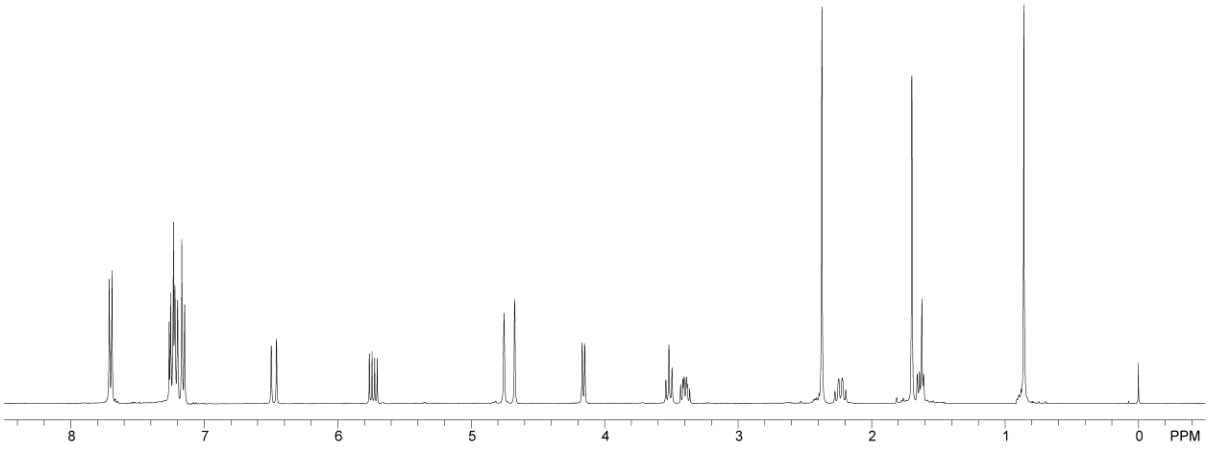
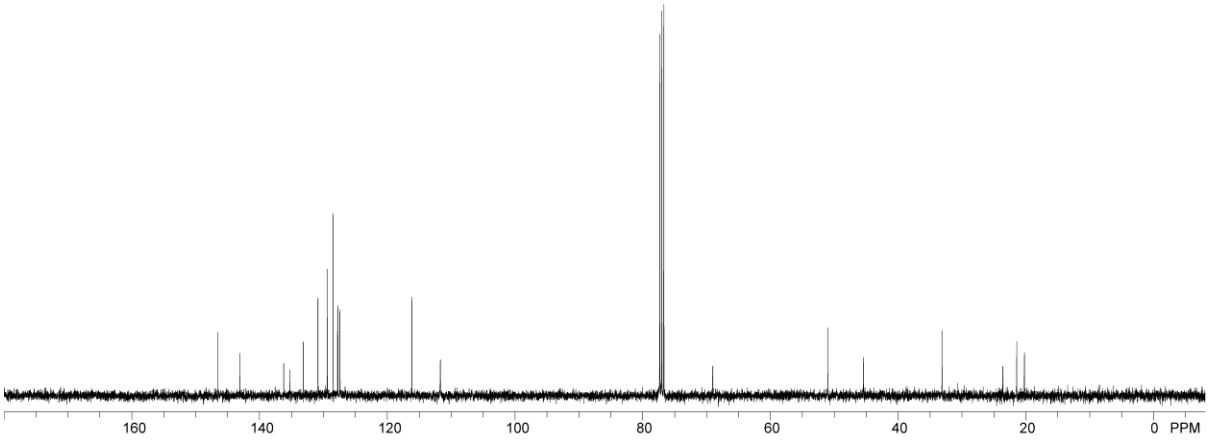
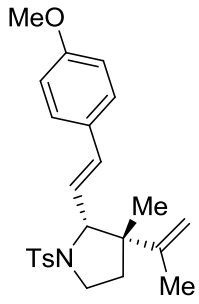
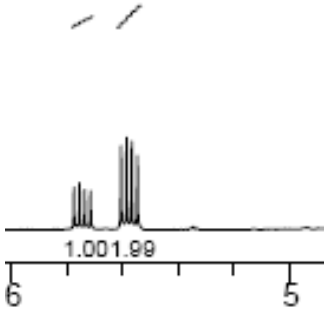


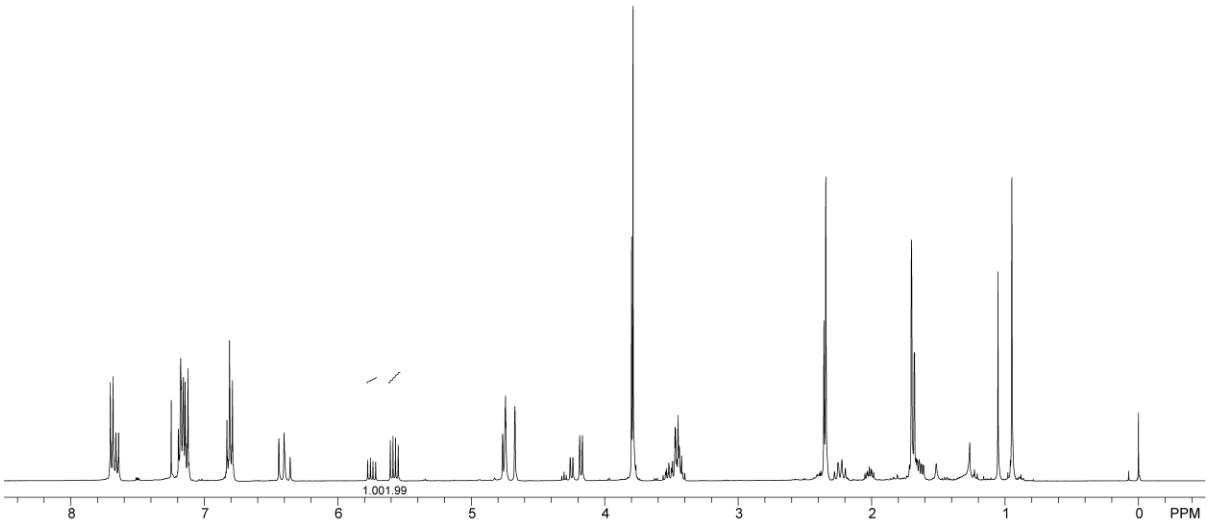




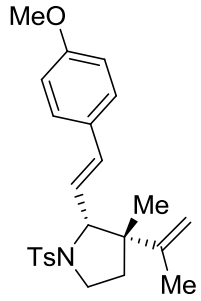
racemic 2h

The ratio of the major and minor diastereoisomers is 2:1.

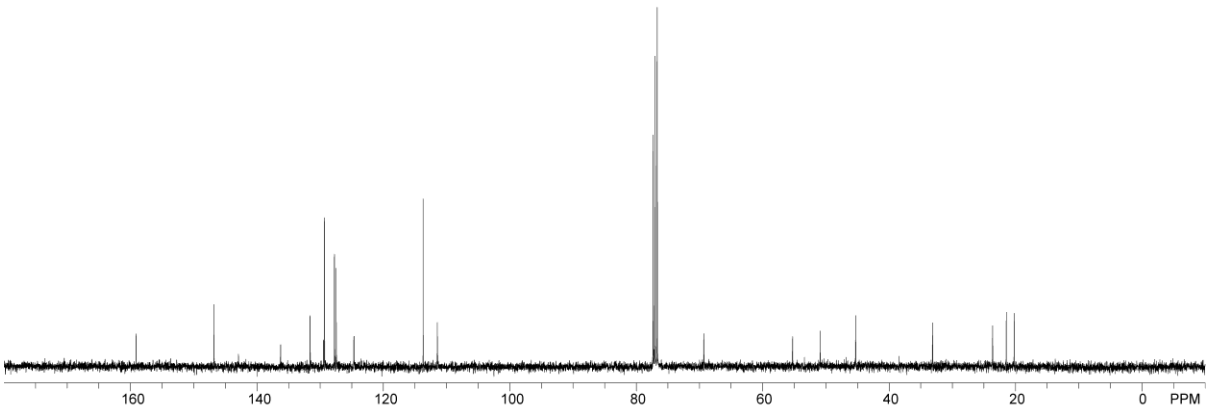


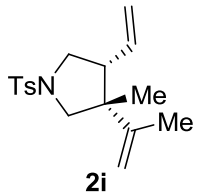


The ratio of the major and minor diastereoisomers is 52.6:1 according to the NMR spectra.

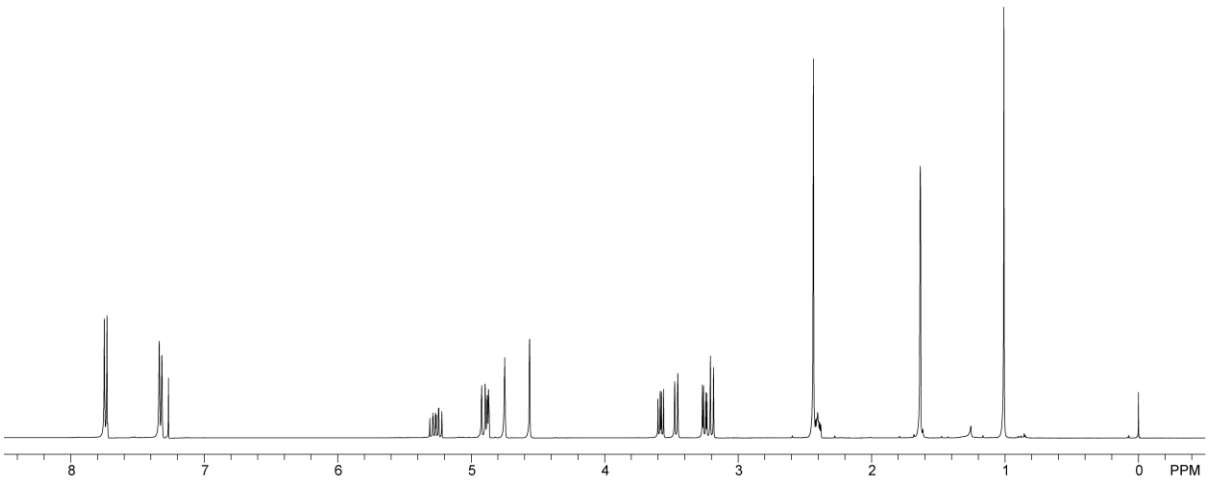


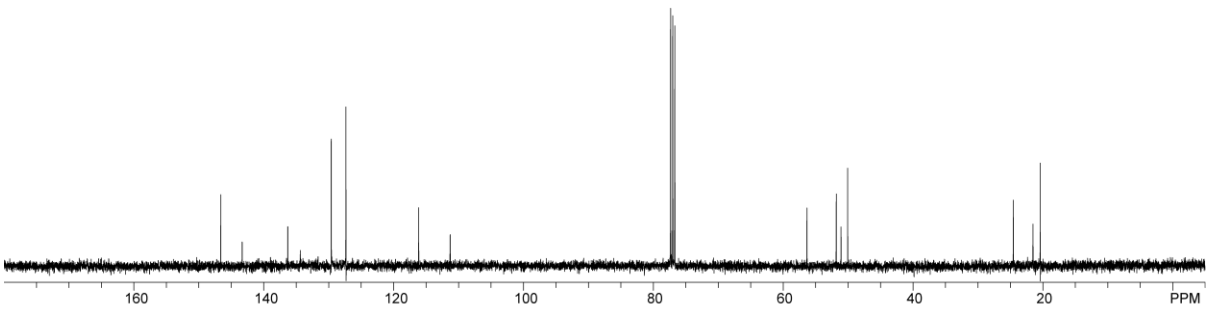
2h

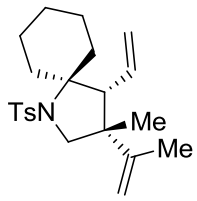




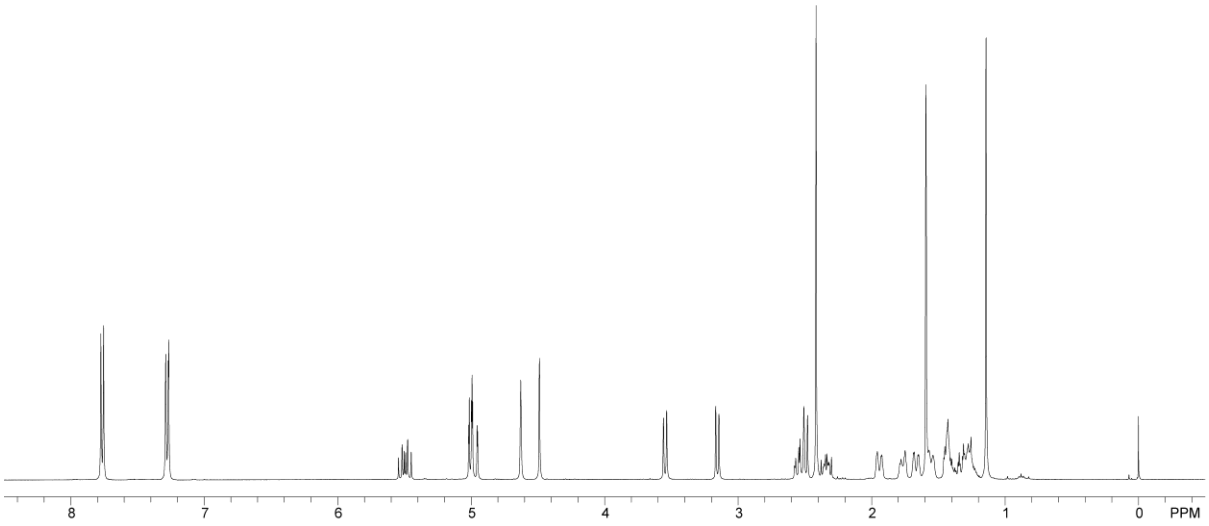
2i

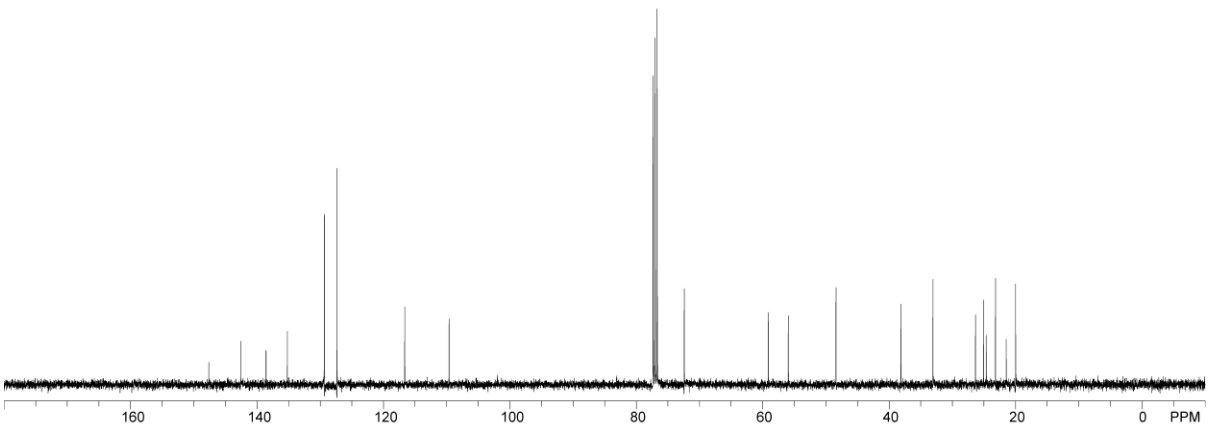


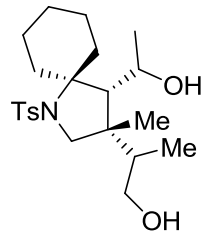




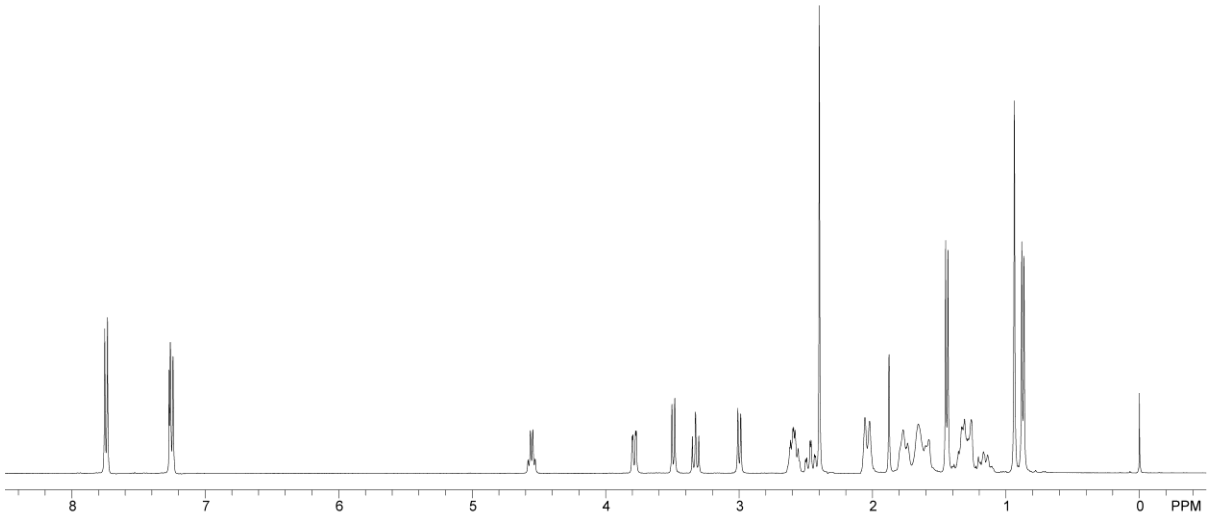
2j

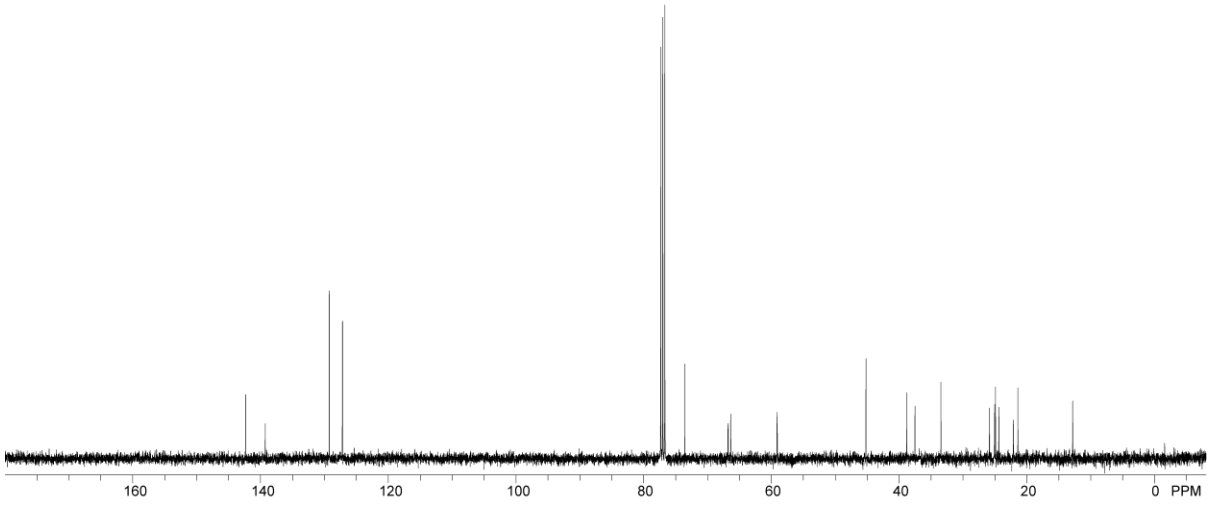


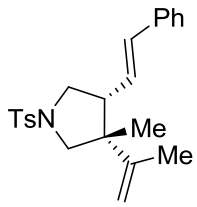




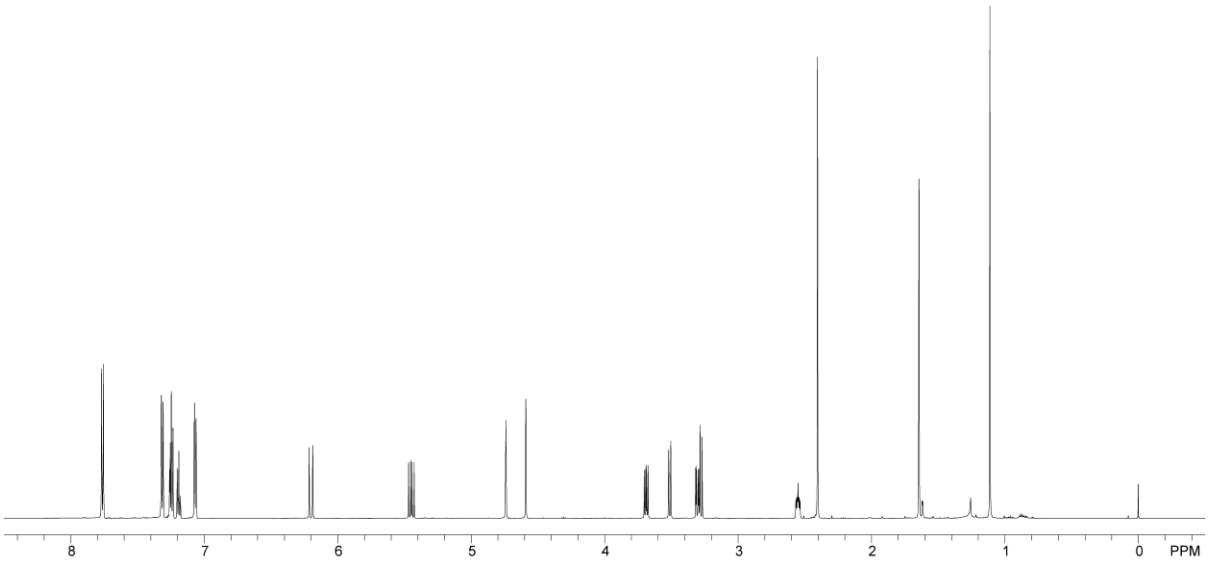
2ij

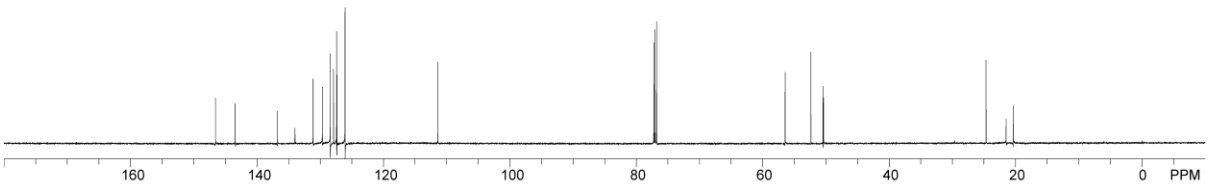


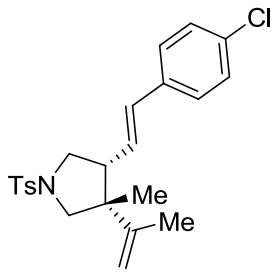




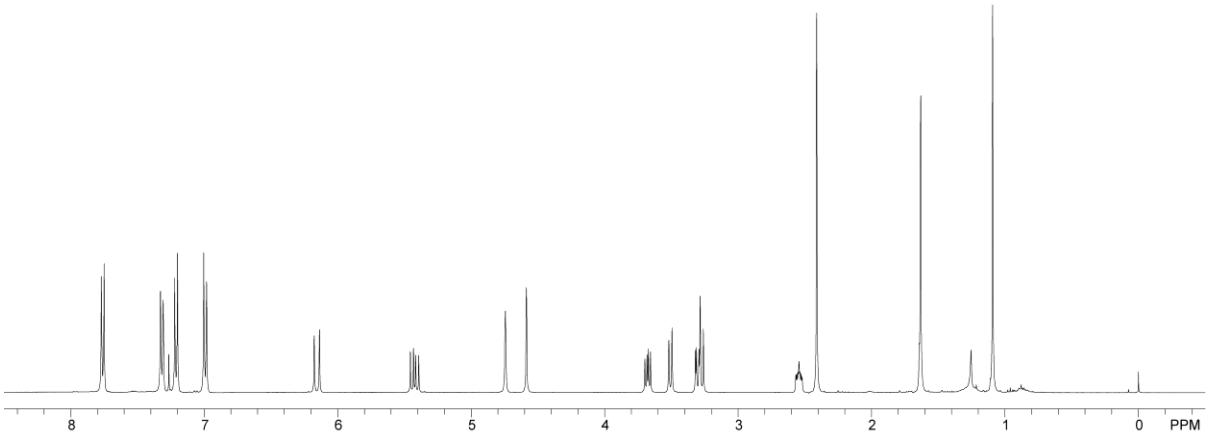
2k

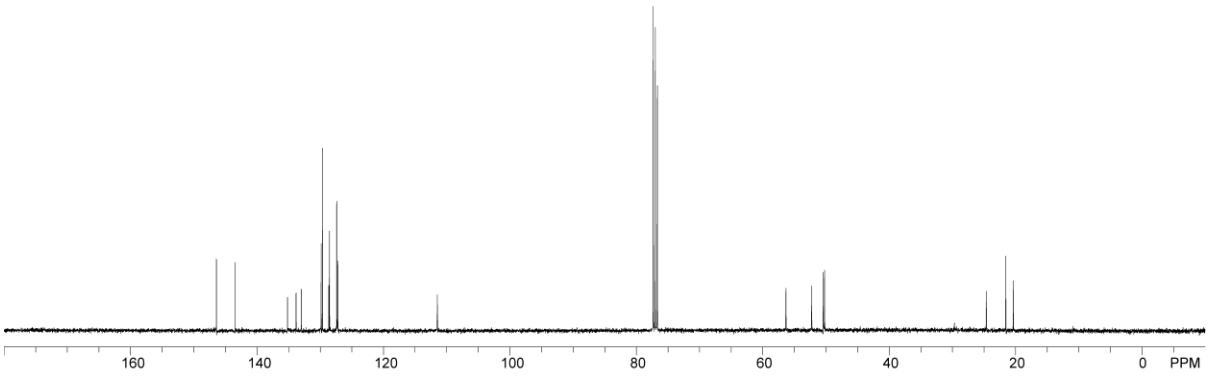


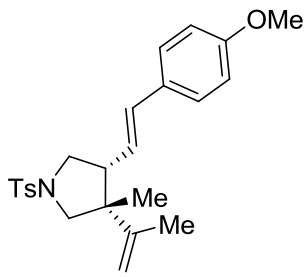




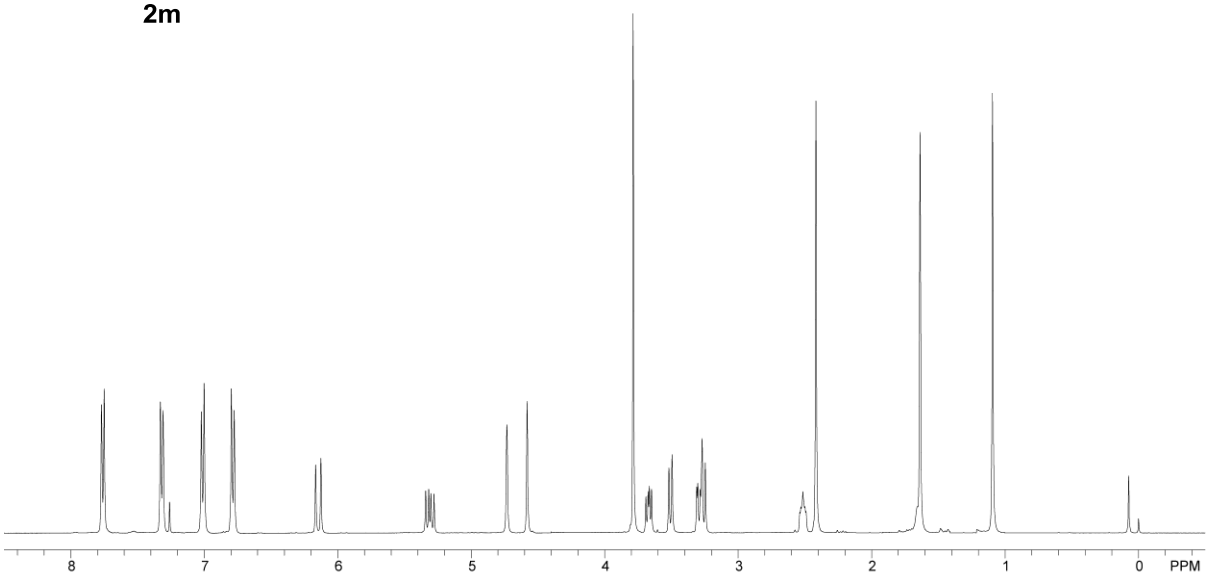
2l

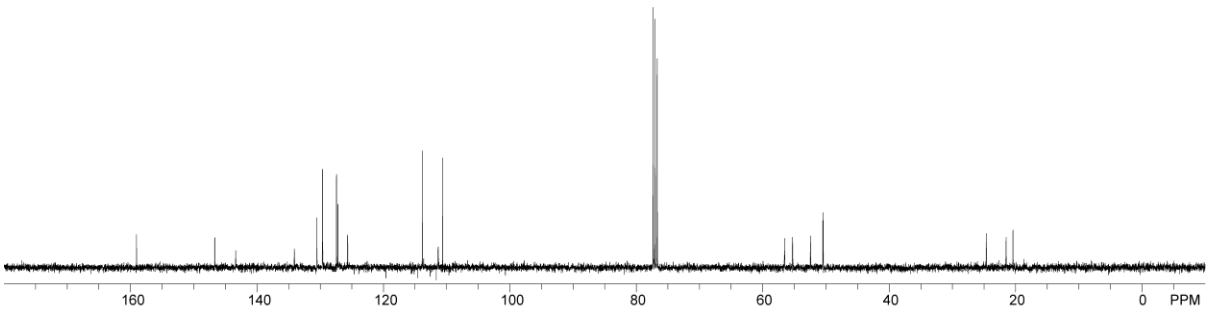


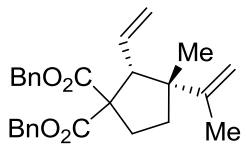




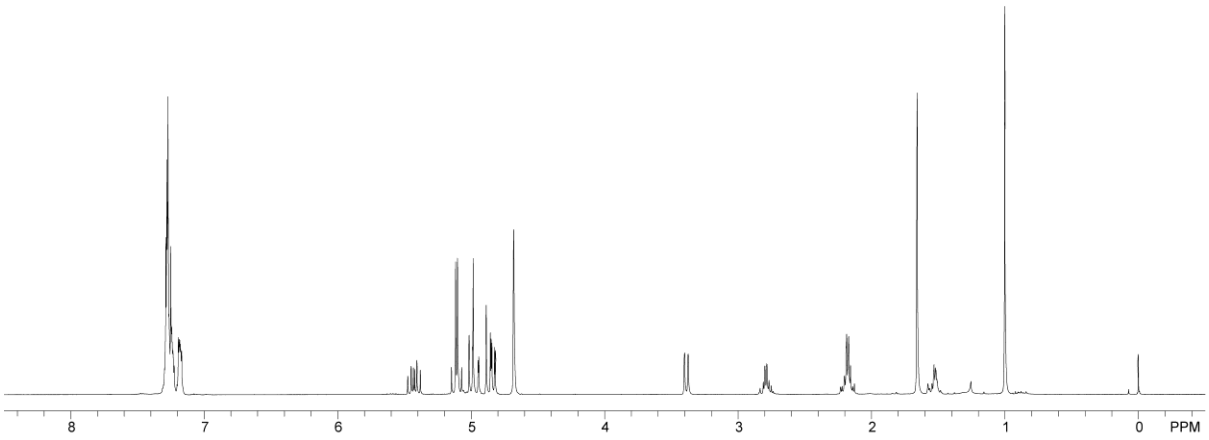
2m

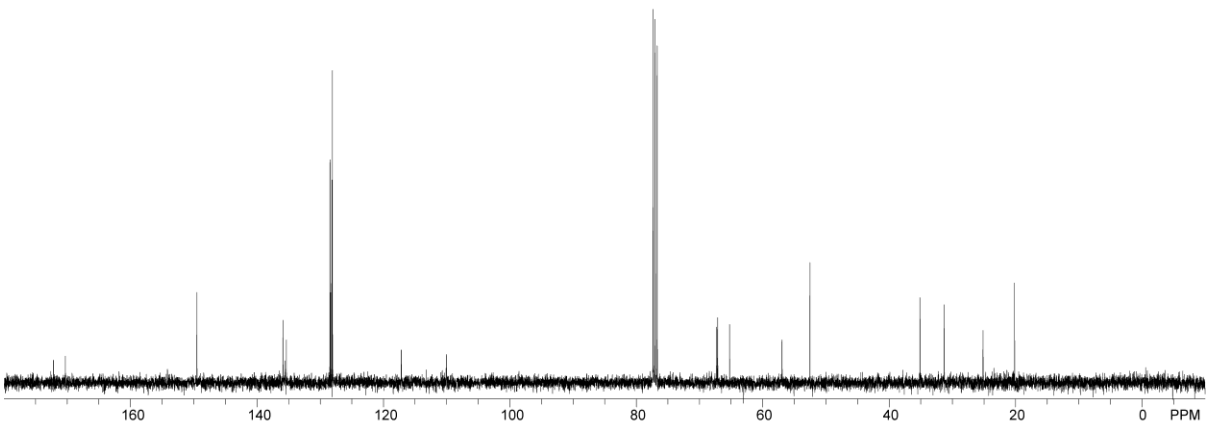


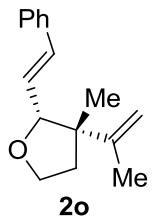



Me
BnO2C
BnO2C
Me

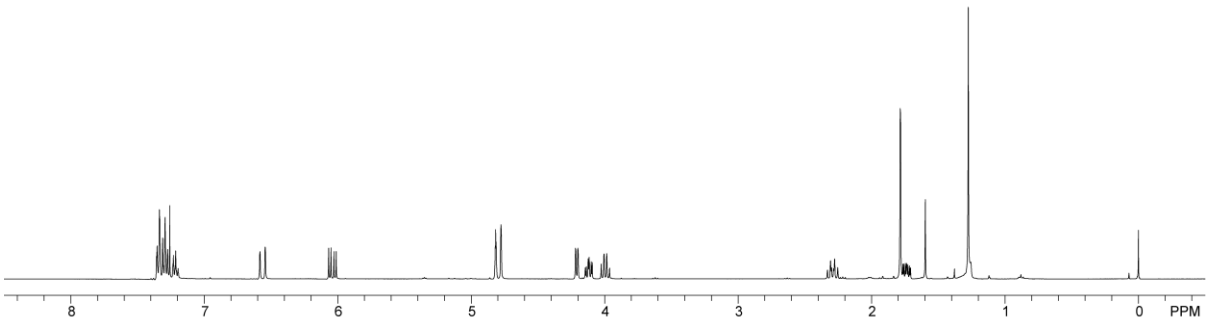
2n

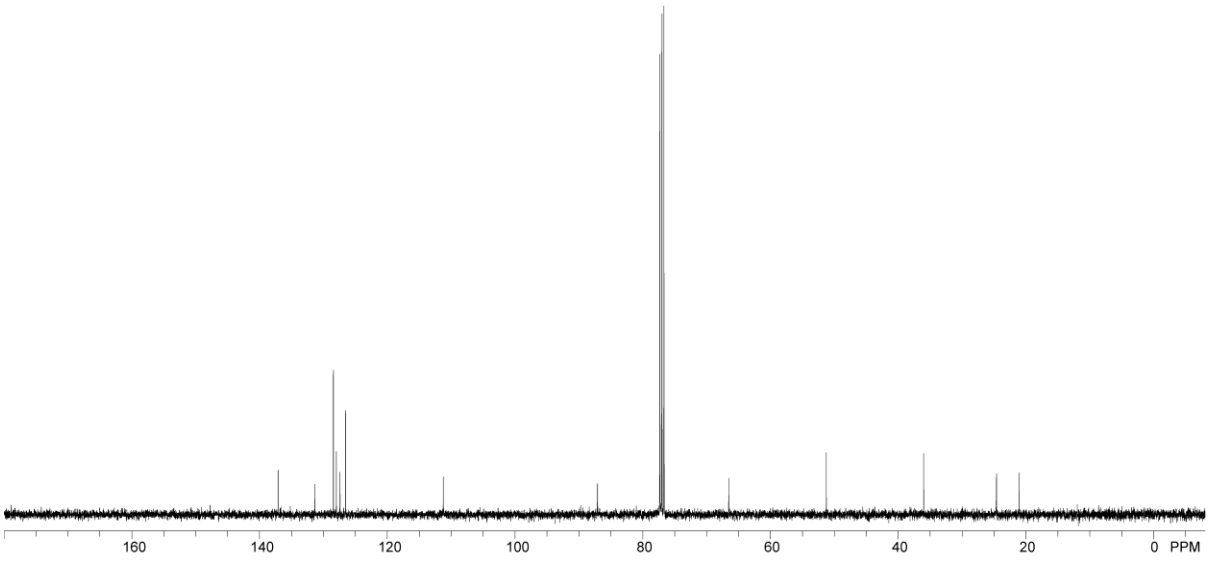

8
7
6
5
4
3
2
1
0
PPM


160
140
120
100
80
60
40
20
0
PPM



2o





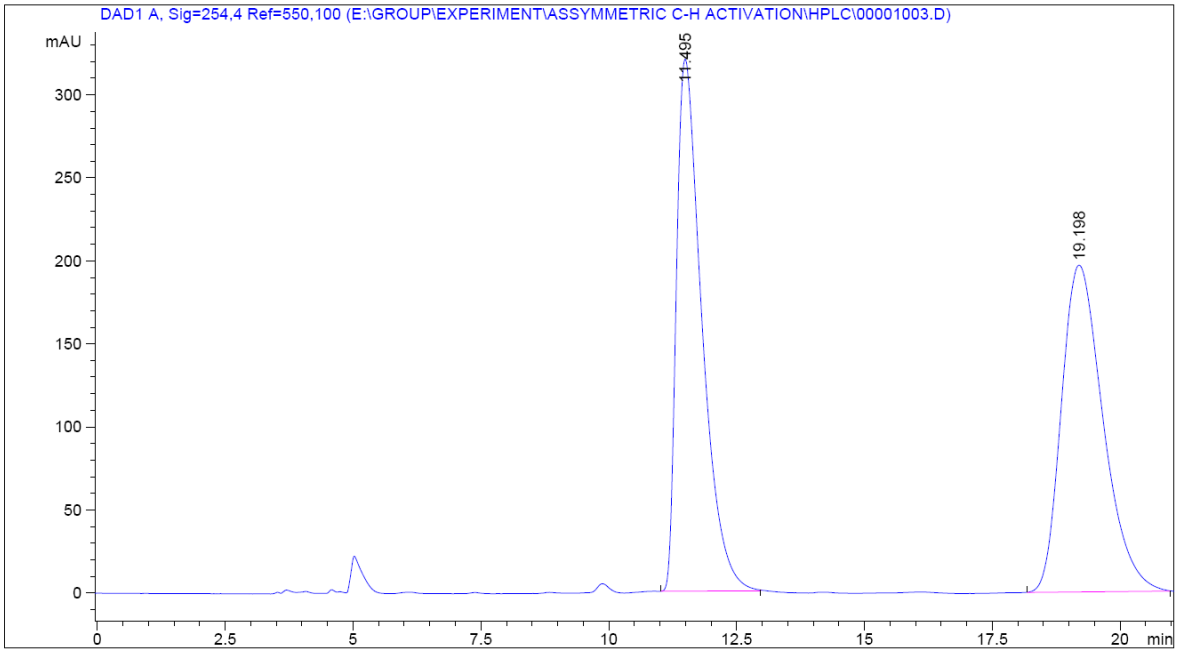
4 HPLC Diagrams for Enantiomeric Purity Determination

Enantiomeric excess was determined by HPLC, conditions: Daicel Chiralcel OJ-H, OD-H or OB-H column, column temperature 30 ℃, eluted with hexanes/ *i*-PrOH using the indicated ratio, at the indicated flow rate, DAD detector, detecting at the indicated wavelength.

4.1 Data for Table S1

The diagram for racemic **2a**:

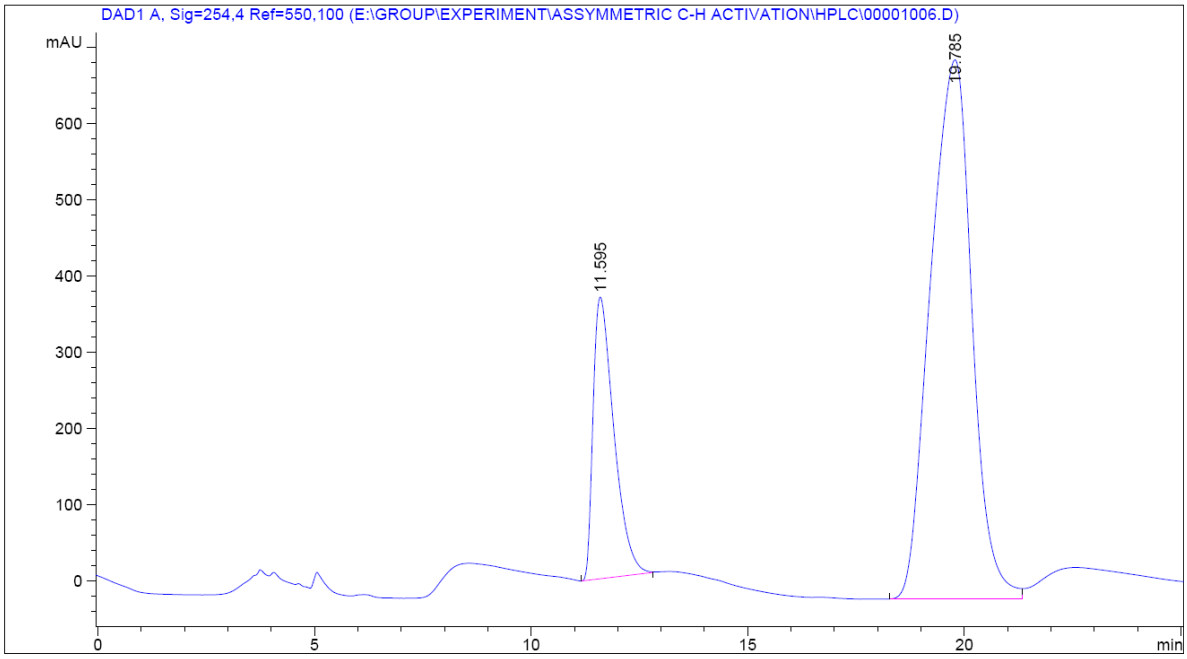
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-25 2:41:22
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-25 2:29:27  by Lyf
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.495 BB    0.5254 1.10778e4   320.41080  49.8185
   2  19.198 BB    0.8693 1.11585e4   196.85855  50.1815

Totals :                  2.22362e4   517.26935

=====================================================================
                         *** End of Report ***
```

1. 1.0 eq. Ligand **A** to Rh ($AgSbF_6$)

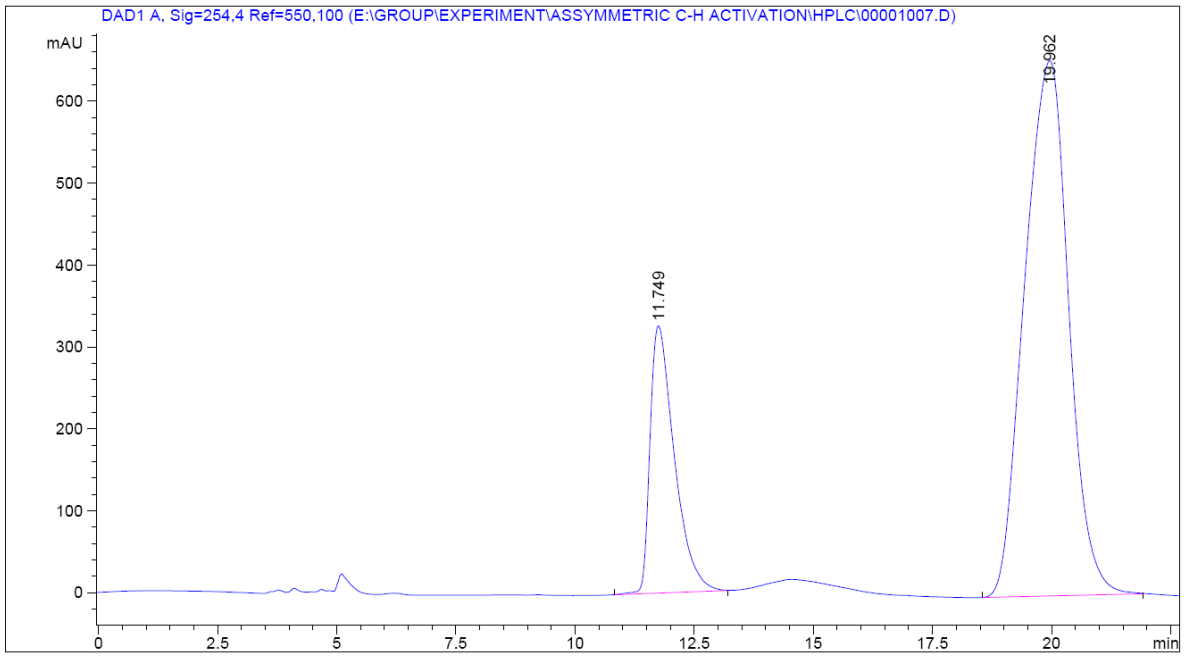
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-23 13:18:00
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-23 13:14:53  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.595 VB    0.5110 1.23283e4   369.77393  20.7425
   2  19.785 BV    1.0882 4.71067e4   708.03076  79.2575

Totals :                  5.94350e4  1077.80469

================================================================================
                          *** End of Report ***
```

2. 2.0 eq. Ligand **A** to Rh ($AgSbF_6$)

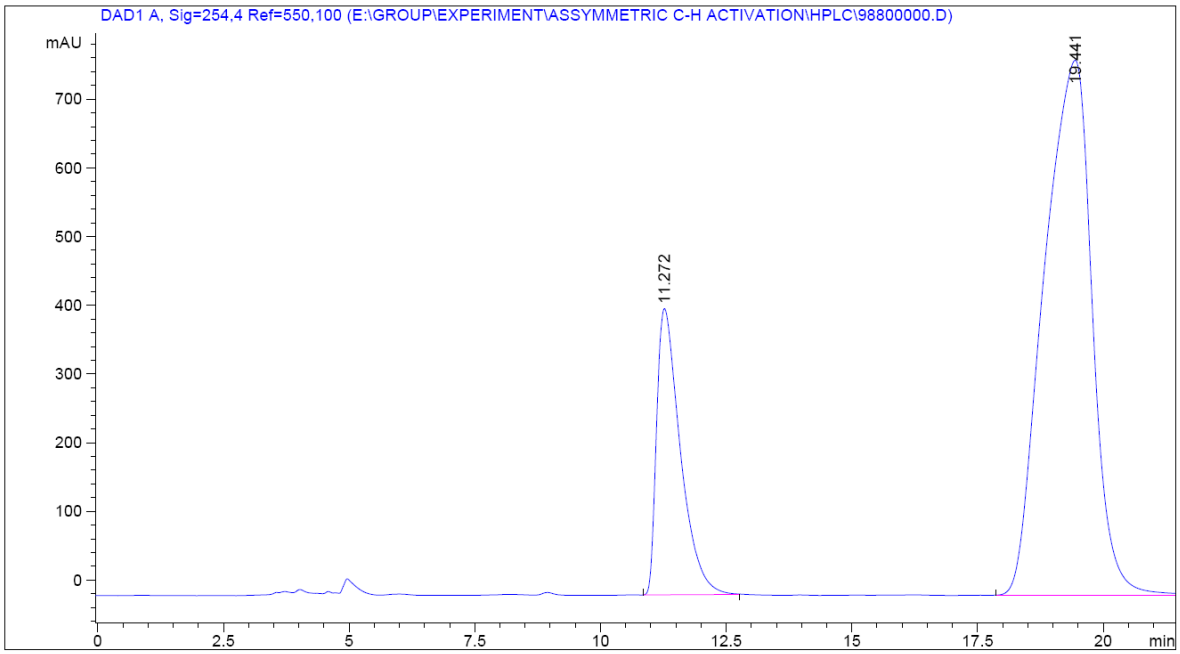
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-23 13:47:20
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-23 13:14:53  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.749 BB    0.5334 1.15584e4   326.18115  21.5918
   2  19.962 BB    1.0413 4.19730e4   653.48022  78.4082

Totals :                  5.35314e4   979.66138

=====================================================================
                      *** End of Report ***
```

3. 2.5 eq. Ligand **A** to Rh ($AgSbF_6$)

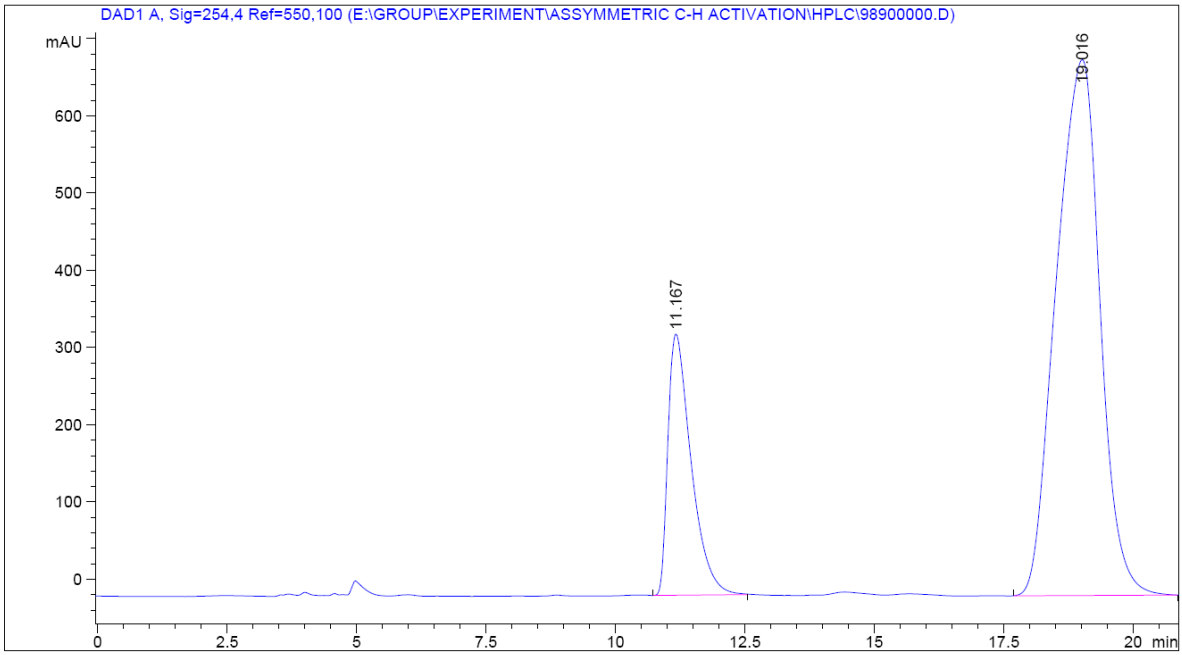
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-28 6:57:32
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-28 6:32:04  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.272 BB    0.4944 1.36539e4   416.53555  20.9010
   2  19.441 BBA   1.1062 5.16724e4   778.68970  79.0990

Totals :                  6.53263e4  1195.22525


================================================================================
                          *** End of Report ***
```

4. 3.0 eq. ligand **A** to Rh ($AgSbF_6$)

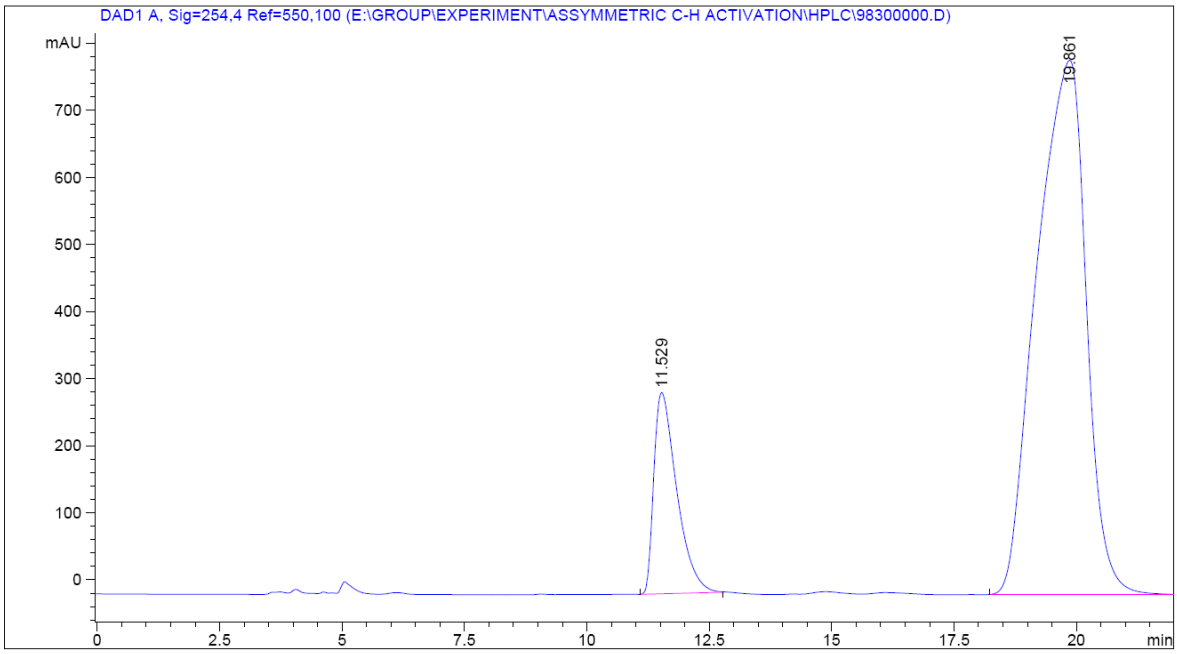
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-28 7:20:34
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-28 6:32:04  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.167 BB    0.4723 1.05613e4   338.17764  20.6000
   2  19.016 BB    0.9604 4.07070e4   693.86444  79.4000

Totals :                  5.12682e4  1032.04208


================================================================================
                          *** End of Report ***
```

5. 3.0 eq. ligand **A** to Rh (AgOTf)

```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-28 6:33:01
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-28 6:32:04  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```

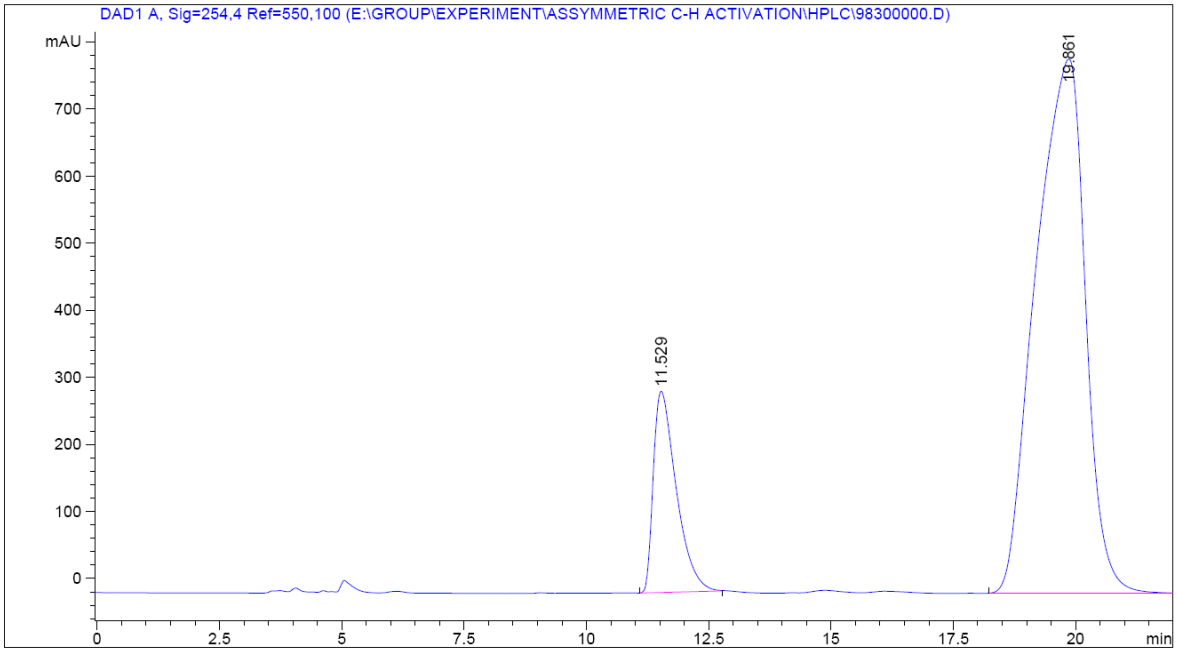



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.529 BB    0.4939 9768.87305  299.96158  14.8603
   2  19.861 BBA   1.1852 5.59690e4   797.05615  85.1397

Totals :                  6.57379e4  1097.01773


=====================================================================
                      *** End of Report ***
```

4.2 Data for Table S2

1. DCE as solvent

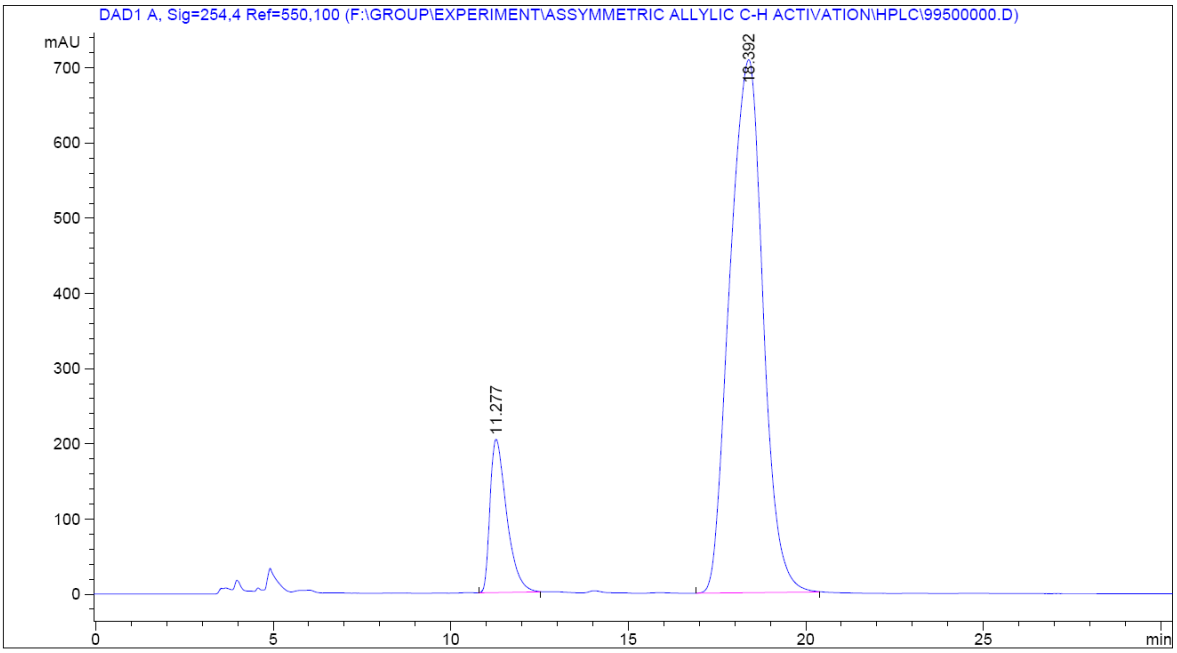
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-3-28 6:33:01
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-3-28 6:32:04  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.529 BB    0.4939 9768.87305  299.96158  14.8603
   2  19.861 BBA   1.1852 5.59690e4   797.05615  85.1397

Totals :                  6.57379e4  1097.01773


=====================================================================
                      *** End of Report ***
```

2. Chlorobenzene as solvent

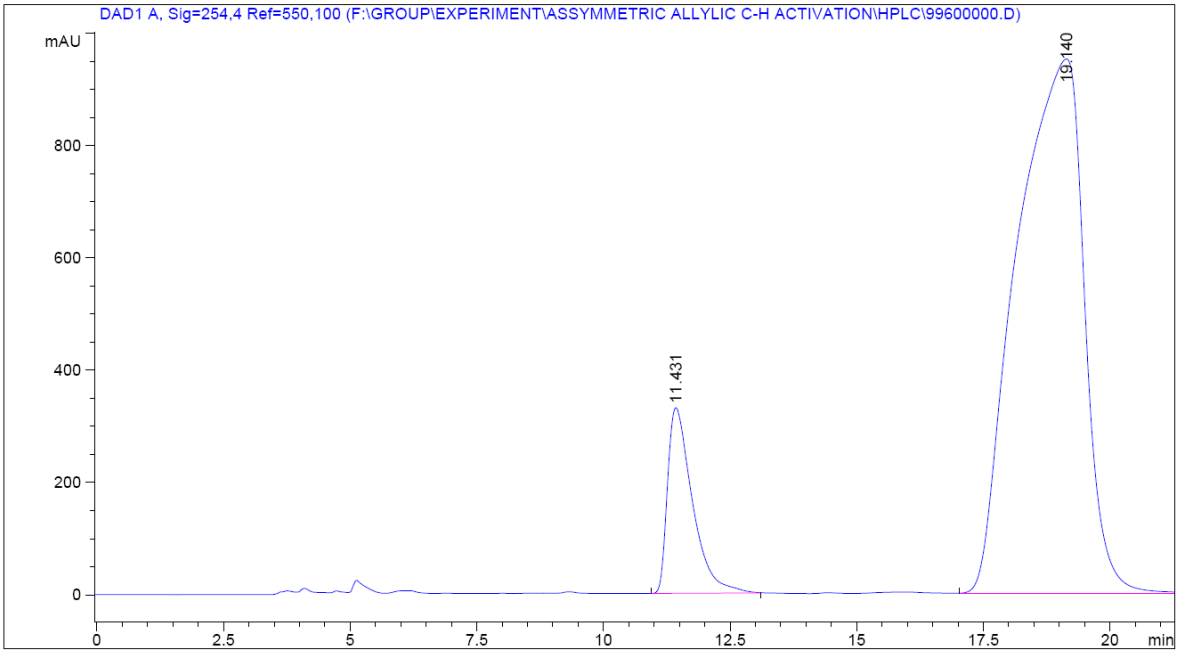
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-1 12:48:42
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-1 12:27:55  by lyf
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.277 BB    0.4925 6648.46924  203.84474  12.5977
   2  18.392 BB    1.0532 4.61267e4   708.87482  87.4023

Totals :                  5.27752e4   912.71956


=====================================================================
                        *** End of Report ***
```

3. THF as solvent

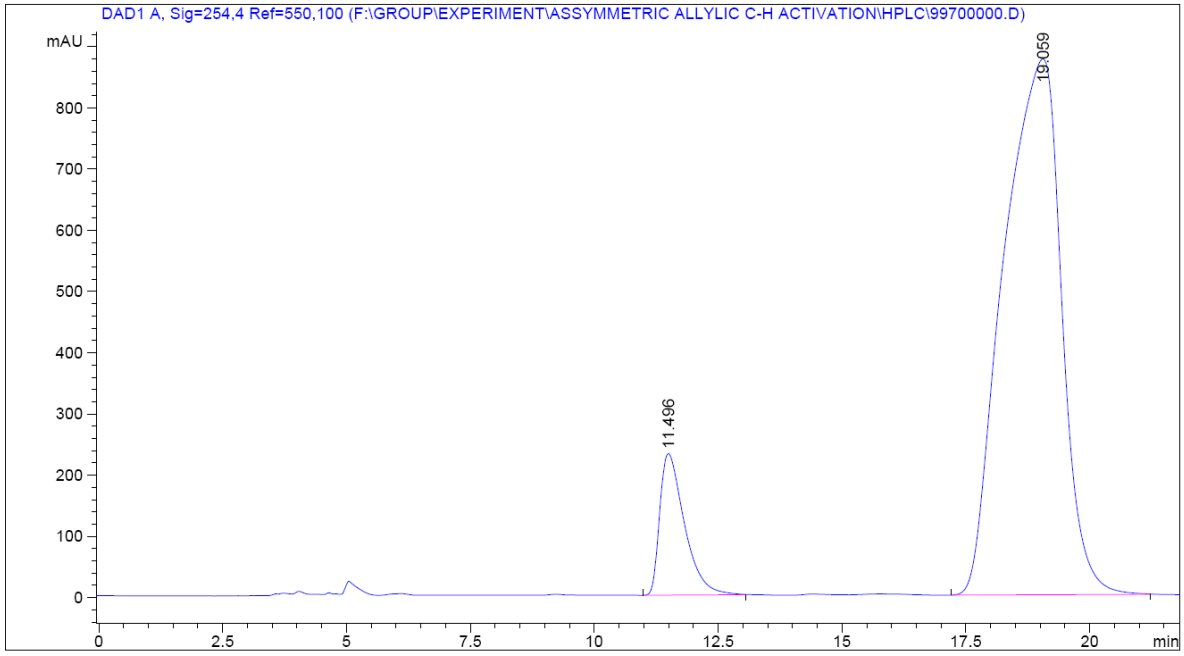
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-2 10:25:05
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-2 10:23:36  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.431 BB    0.5138 1.13360e4   330.77939  11.4272
   2  19.140 BBA   1.1869 8.78659e4   951.89410  88.5728

Totals :                  9.92019e4  1282.67349


================================================================================
                          *** End of Report ***
```

4. Benzene as solvent

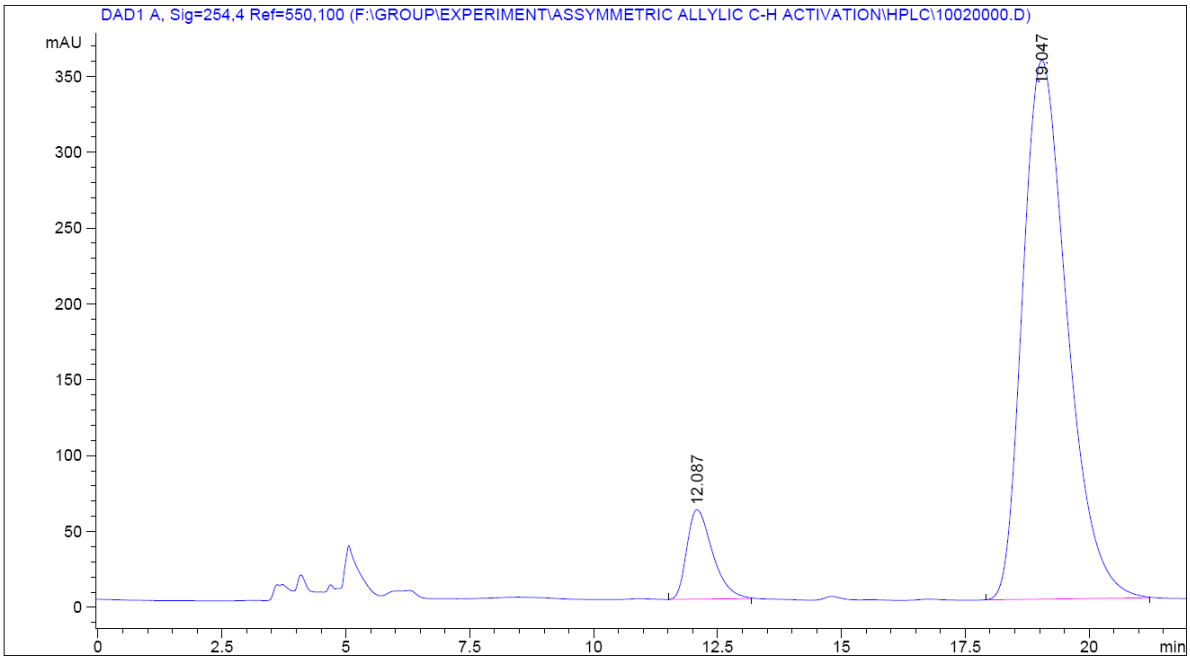
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-2 10:48:23
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-2 10:23:36  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.496 BB    0.5247 8021.51123  231.26636  10.1429
   2  19.059 BB    1.1028 7.10638e4   875.64703  89.8571

Totals :                  7.90853e4  1106.91339

================================================================================
                          *** End of Report ***
```

5. Dioxane as solvent

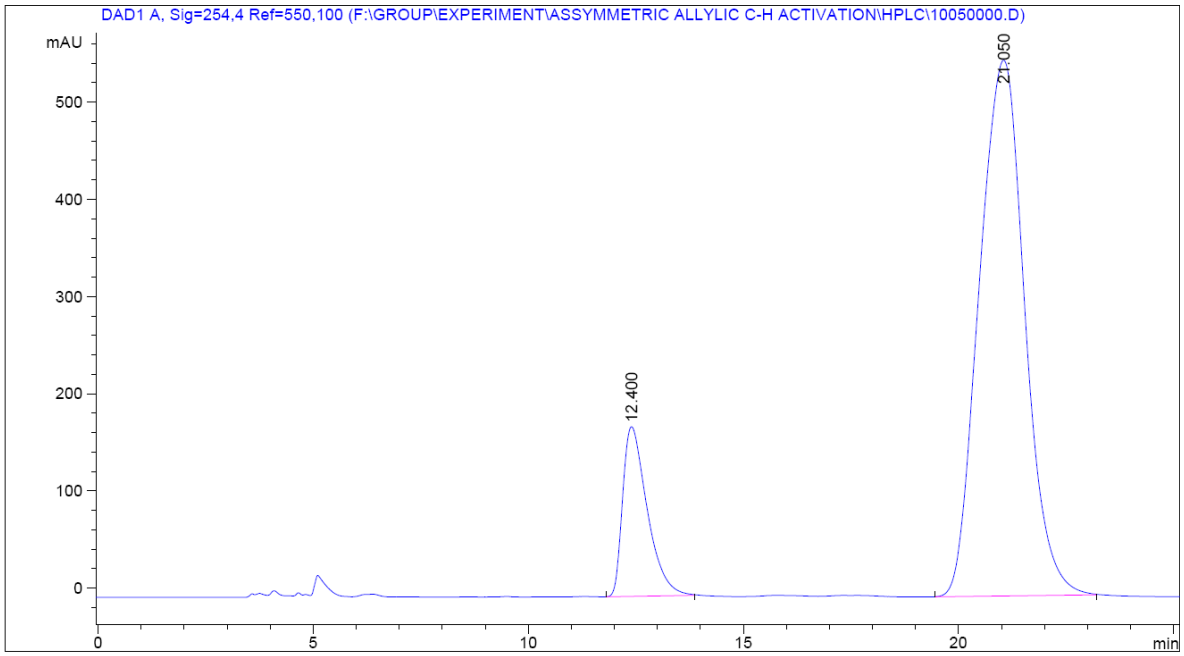
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-2 11:34:51
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-2 10:23:36  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hxane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.087 BB    0.5369 2126.46338   58.94907   8.7545
   2  19.047 BB    0.9499 2.21635e4   355.24719  91.2455

Totals :                  2.42899e4   414.19626

=====================================================================
                        *** End of Report ***
```

6. *n*-Bu_2O as solvent

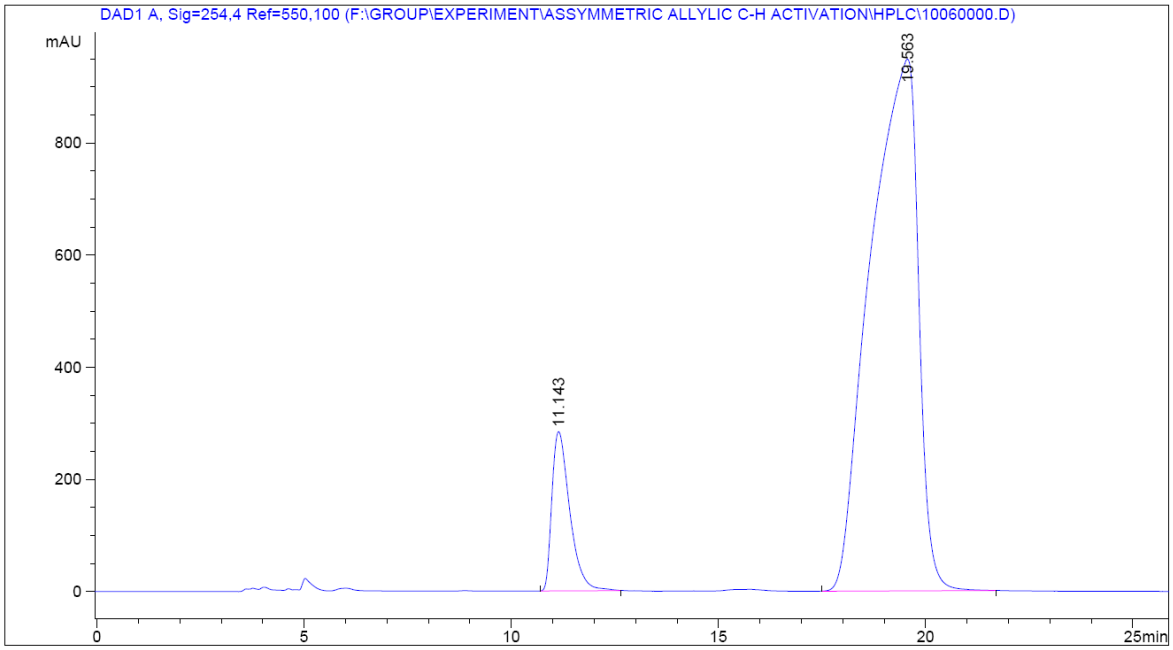
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-14 11:16:14
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-14 11:07:33  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.400 BB    0.6043 6913.33740  174.47380  14.5898
   2  21.050 BB    1.1588 4.04715e4   551.11365  85.4102

Totals :                  4.73849e4   725.58745

======================================================================
                        *** End of Report ***
```

7. DME as solvent

```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-8 10:44:38
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-8 10:40:18  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```

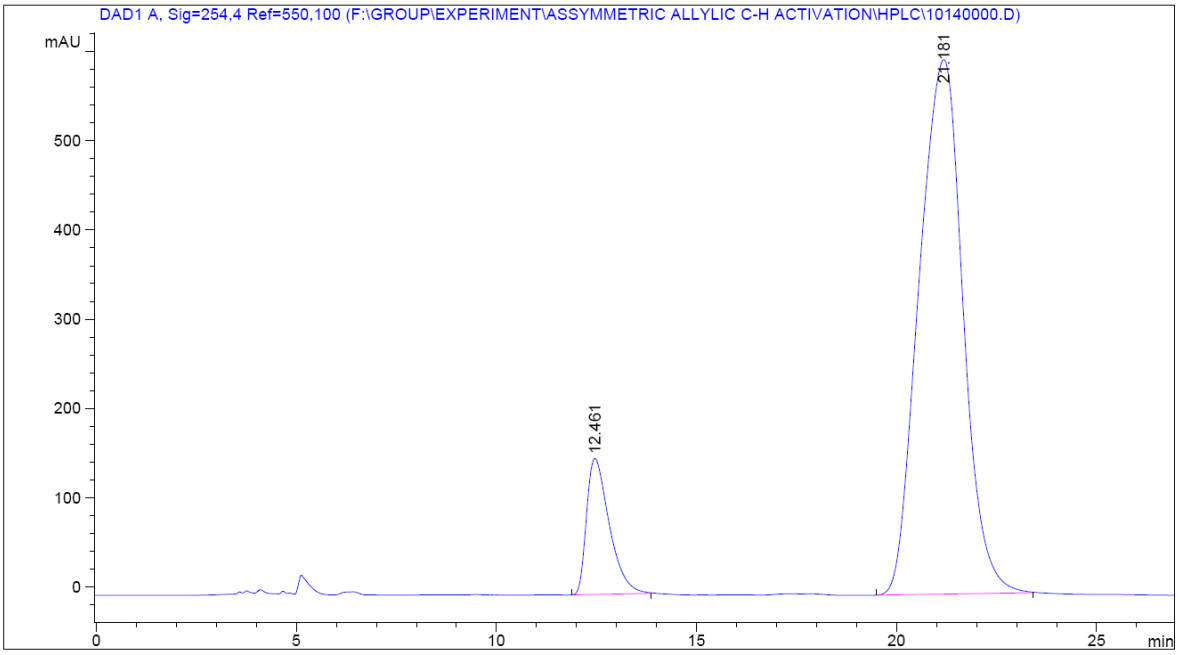



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.143 BB    0.4597 8515.43652  284.09116  10.0778
   2  19.563 BB    1.0665 7.59812e4   948.59113  89.9222

Totals :                  8.44967e4  1232.68228

=====================================================================
                        *** End of Report ***
```

4.3 Data for Table S3

1. $AgClO_4$ as salt

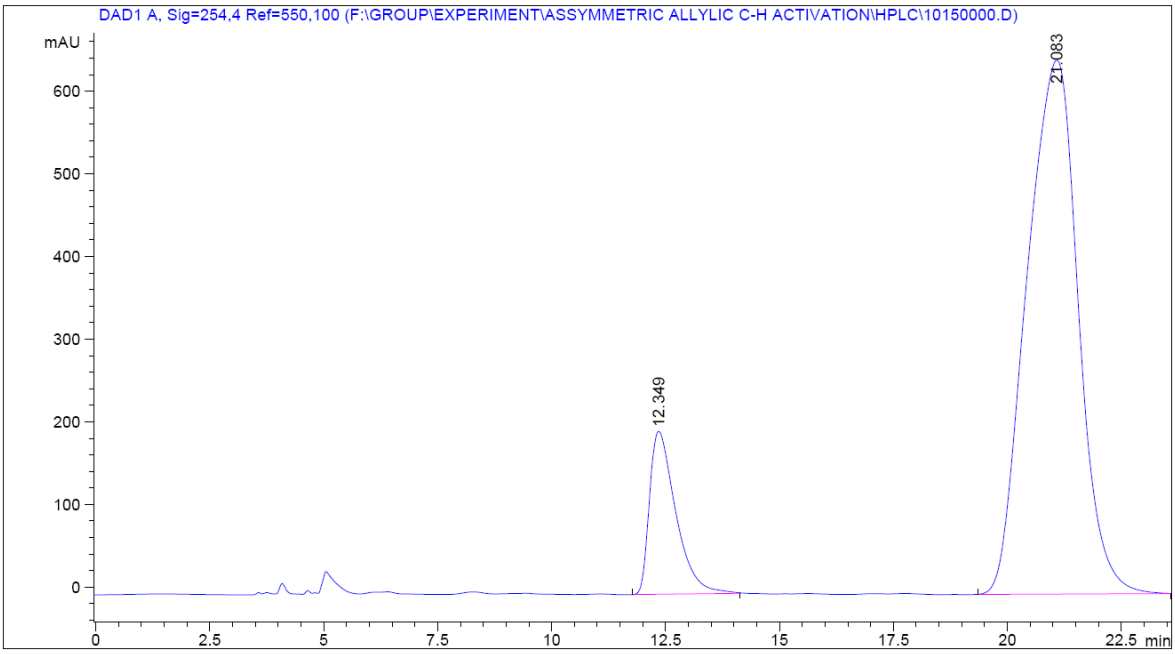
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-14 11:43:51
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-14 11:07:33  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H AgClO4 hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.461 BB    0.6046 6011.54297  152.26437  11.6446
   2  21.181 BB    1.2231 4.56136e4   598.54871  88.3554

Totals :                  5.16251e4   750.81308

=====================================================================
                        *** End of Report ***
```

2. $AgBF_4$ as salt

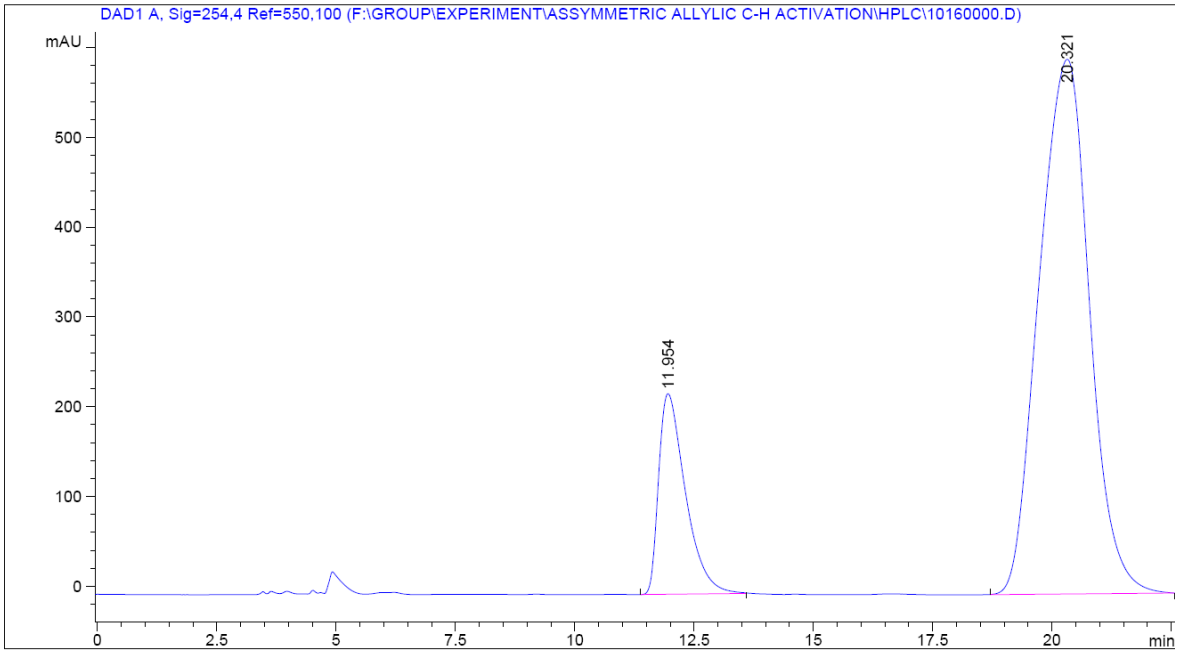
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-14 12:13:45
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-14 11:07:33  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H AgBF4 hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.349 BB    0.6091 7926.64258  197.15764  13.5553
   2  21.083 BB    1.2869 5.05498e4   645.99414  86.4447

Totals :                  5.84764e4   843.15178

=====================================================================
                        *** End of Report ***
```

3. $AgSbF_6$ as salt

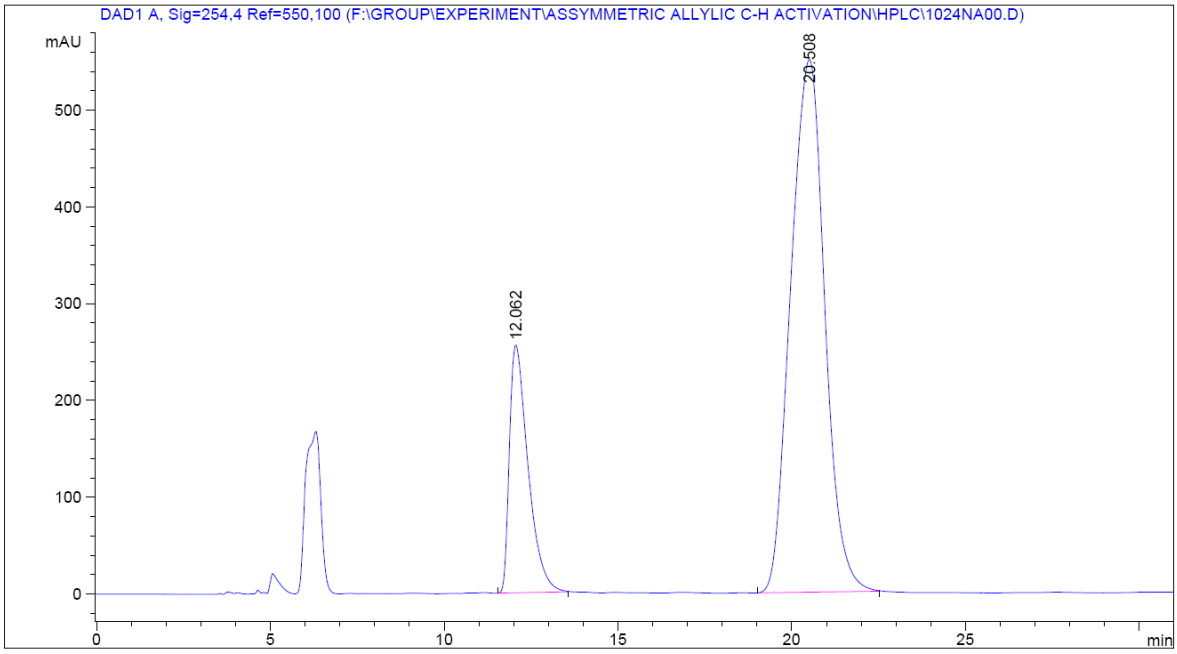
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-14 12:39:05
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-14 11:07:33  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H AgSbF4 hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.954 BB    0.5892 8720.15820  223.51950  16.6370
   2  20.321 BB    1.1917 4.36942e4   595.72333  83.3630

Totals :                  5.24144e4   819.24283


=====================================================================
                      *** End of Report ***
```

4. NaBARF as salt

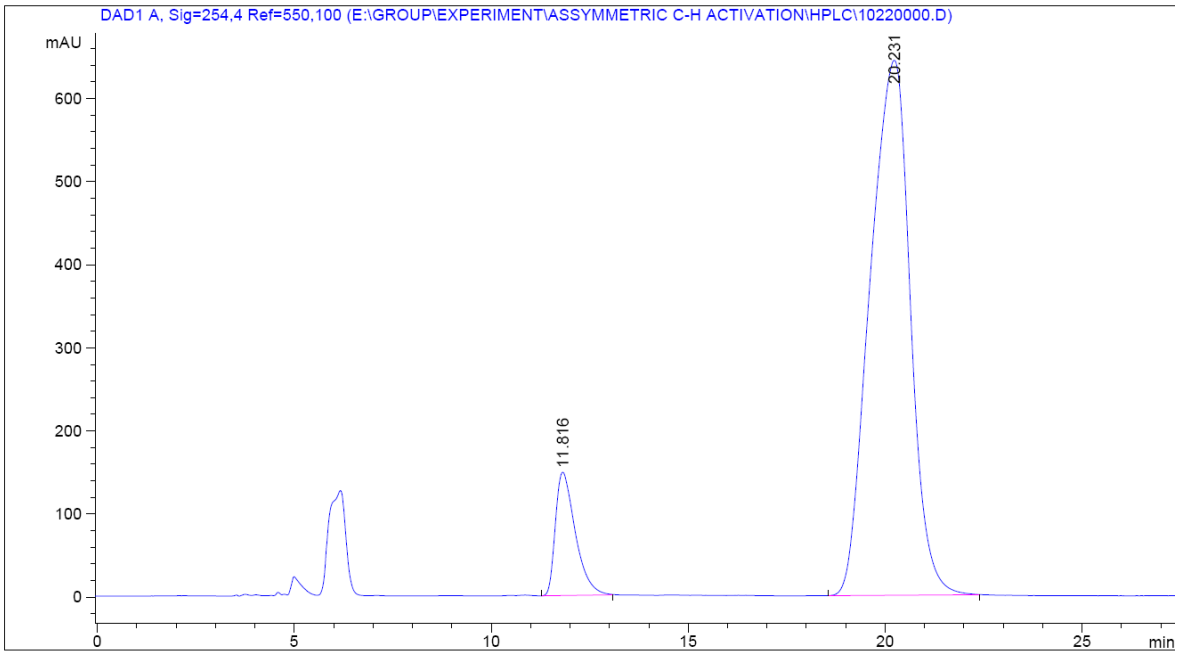
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-18 10:46:43
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-15 13:17:15  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H NaBPh4 hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.062 BB    0.5581 9532.38477  256.19003  20.2901
   2  20.508 BB    1.0775 3.74480e4   550.59723  79.7099

Totals :                  4.69804e4   806.78726


=====================================================================
                         *** End of Report ***
```

5. $[Rh(coe)_2Cl]_2$ as Rh precursor, AgOTf as salt

```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-18 11:19:34
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-15 13:17:15  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```

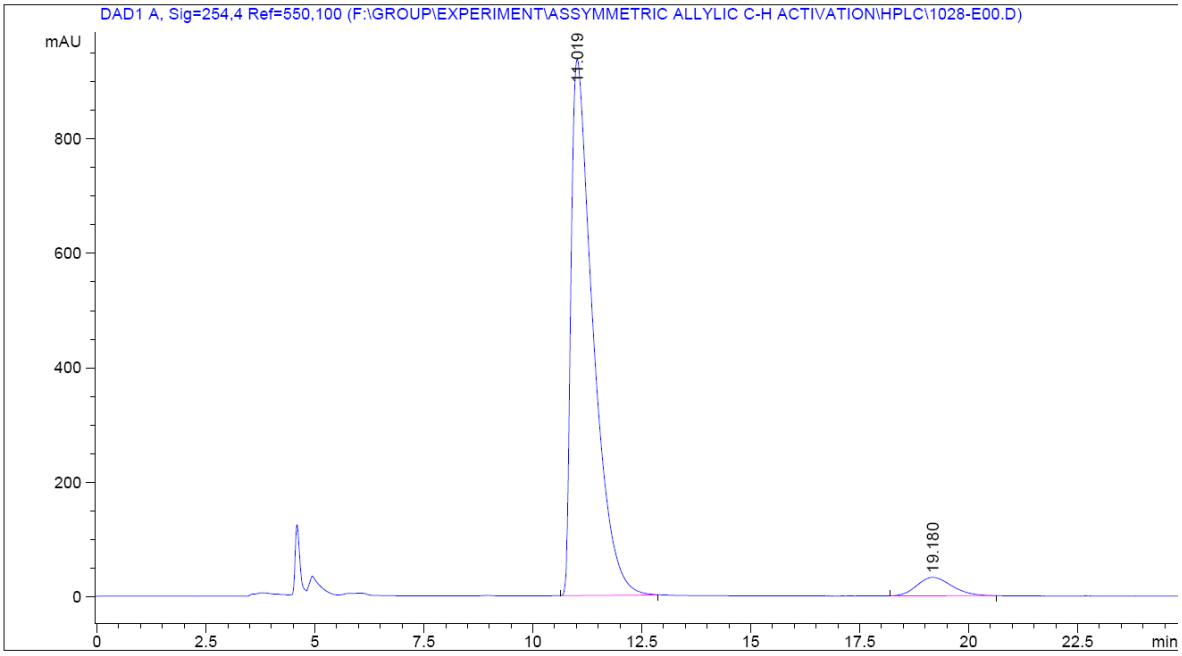



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.816 BB    0.5336 5209.11084  148.36922  10.2423
   2  20.231 BB    1.1513 4.56499e4   643.78436  89.7577

Totals :                  5.08590e4   792.15358

================================================================================
                          *** End of Report ***
```

4.4 Data for Table S4

1. Ligand **B**

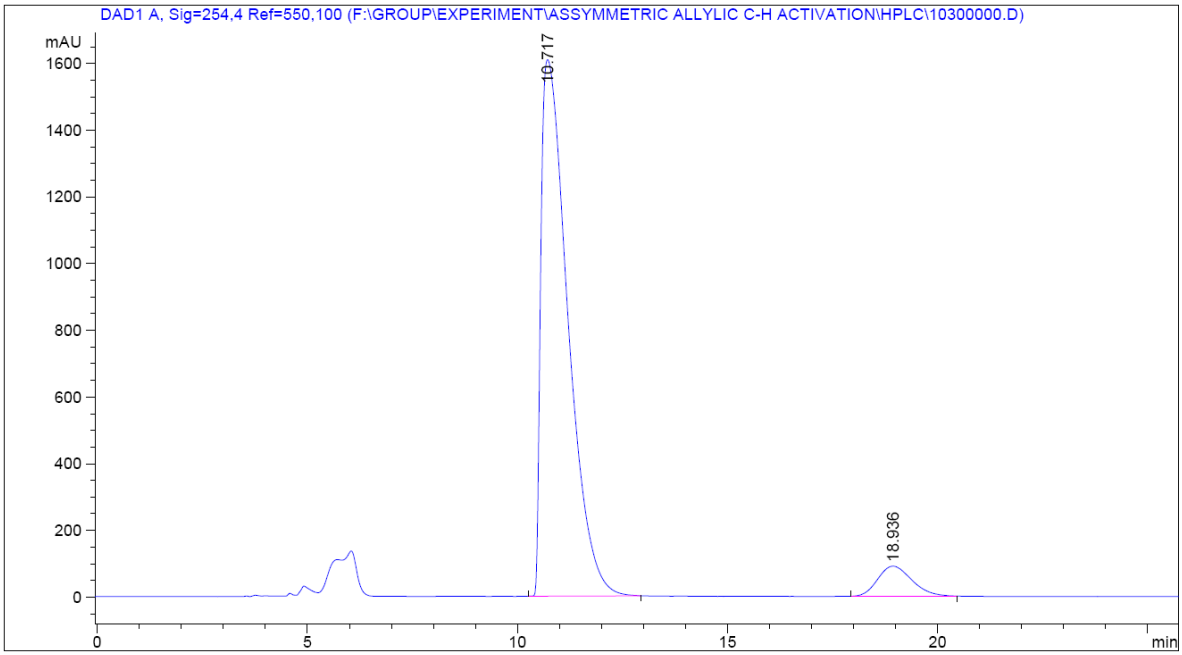
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 6:10:24
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.019 BB    0.5133 3.26917e4   936.31732  94.7910
   2  19.180 BB    0.8236 1796.50220   32.26457   5.2090

Totals :                  3.44882e4   968.58189


=====================================================================
                      *** End of Report ***
```

2. Ligand **D**

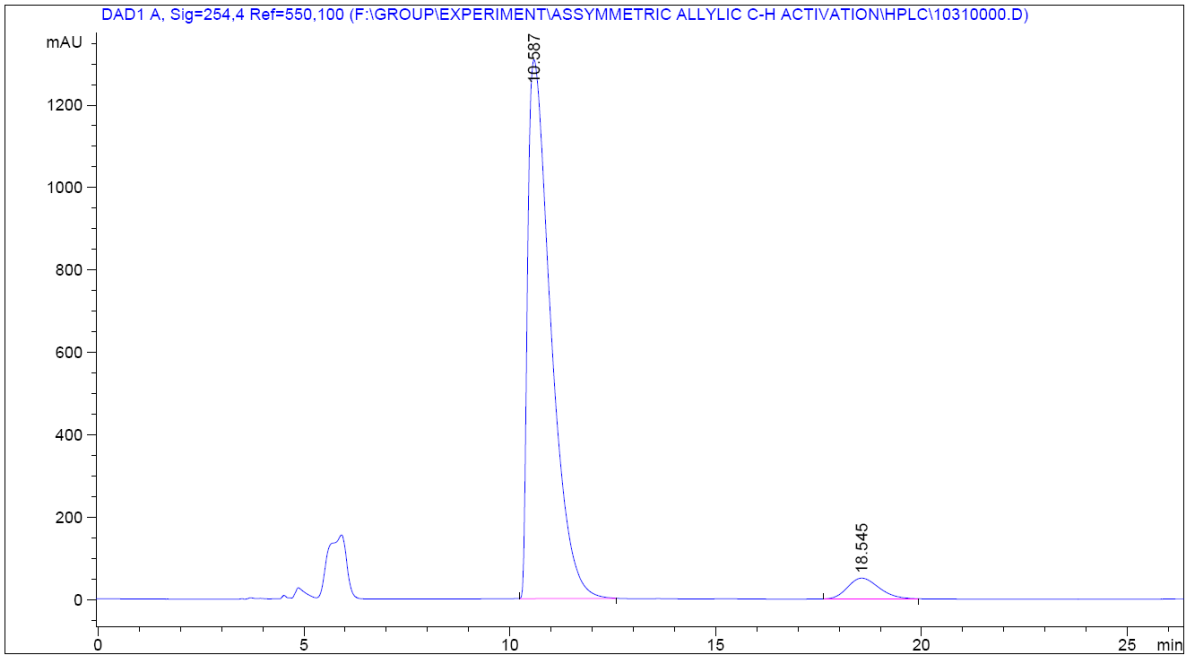
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 6:37:04
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                           Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.717 BB    0.6811 7.15855e4  1608.85852  93.3362
   2  18.936 BB    0.8588 5110.86719   90.23969   6.6638

Totals :                  7.66964e4  1699.09821

================================================================================
                           *** End of Report ***
```

3. Ligand **E**

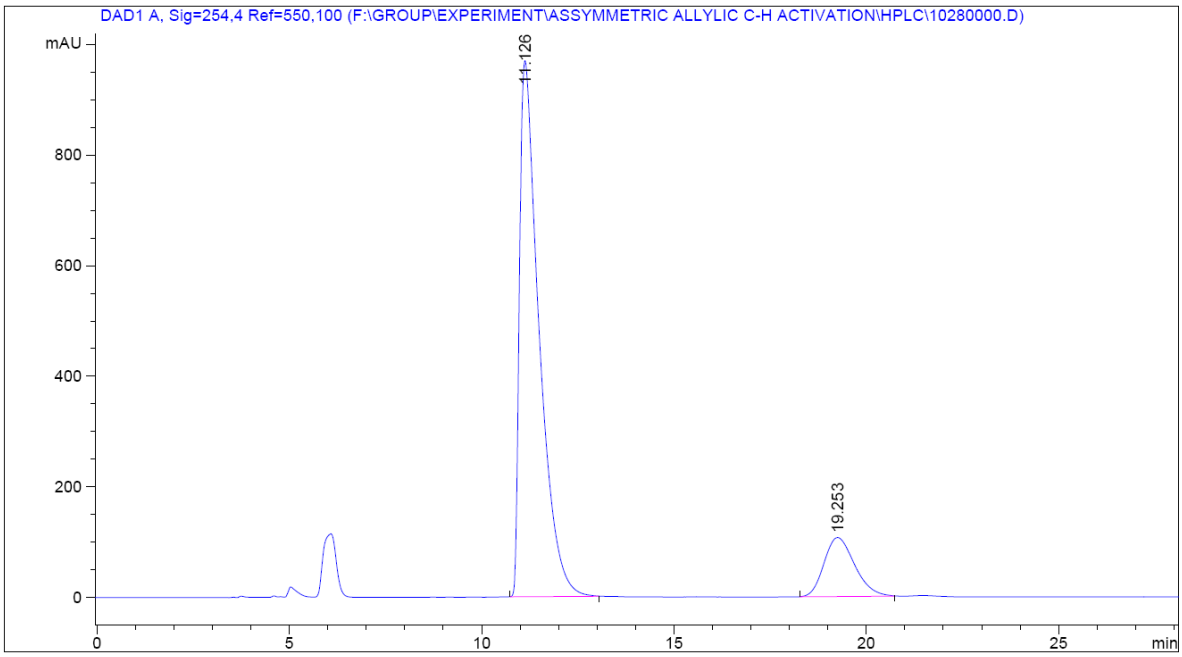
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 7:04:25
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.587 BB    0.5910 5.07526e4  1307.00378  94.9696
   2  18.545 BB    0.7728 2688.28345   50.51720   5.0304

Totals :                  5.34408e4  1357.52098

=====================================================================
                        *** End of Report ***
```

4. Ligand **I**

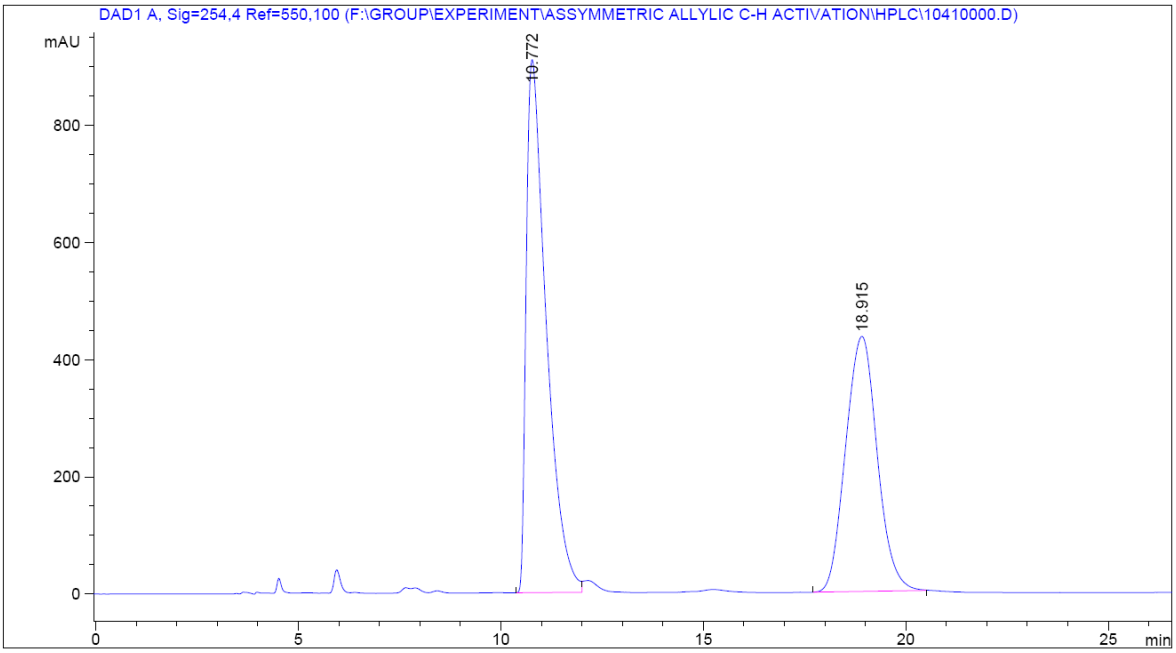
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 5:39:30
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.126 BB    0.5191 3.41570e4   969.25879  85.2299
   2  19.253 BB    0.8414 5919.33203  106.67091  14.7701

Totals :                  4.00763e4  1075.92970


=====================================================================
                        *** End of Report ***
```

5. Ligand **J**

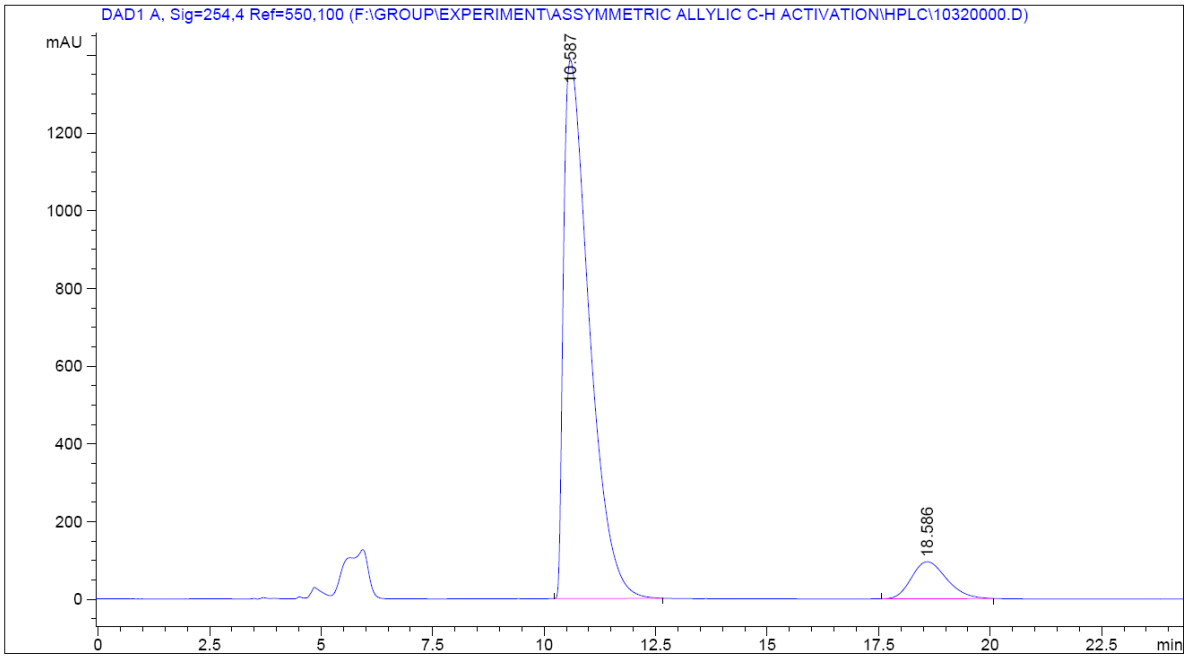
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-24 4:07:57
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 7:59:25  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.772 BV    0.5106 3.12488e4   910.03754  56.9467
   2  18.915 BB    0.8629 2.36250e4   435.51160  43.0533

Totals :                  5.48738e4  1345.54913

=====================================================================
                        *** End of Report ***
```

6. Ligand **L**

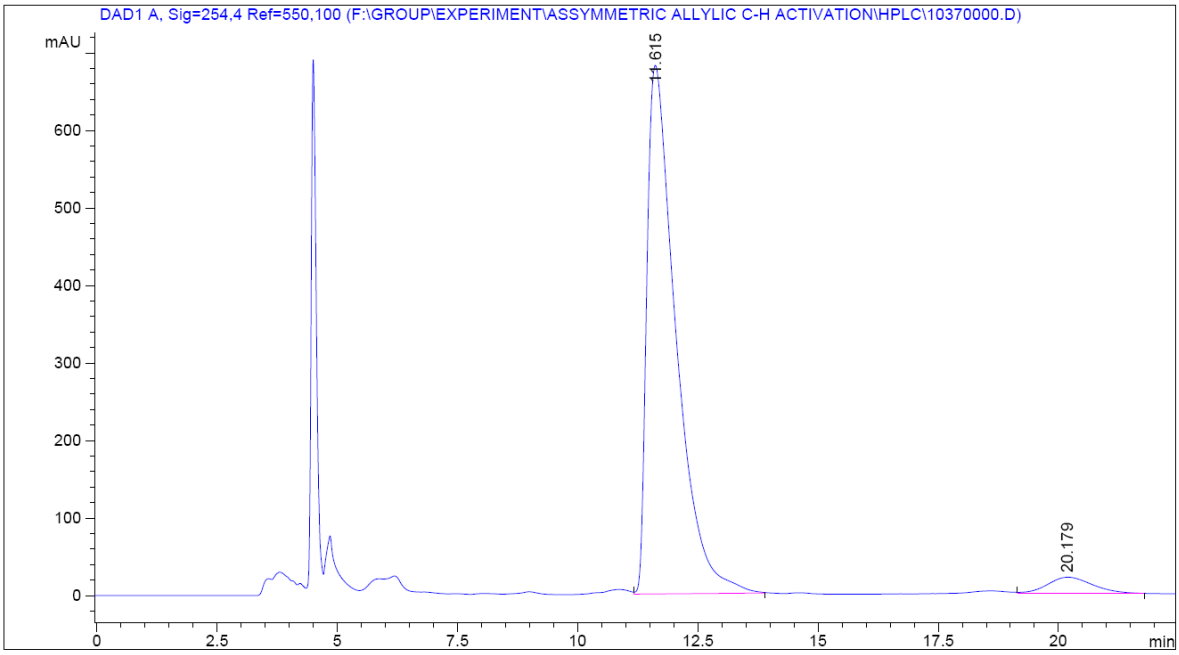
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 7:32:40
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.587 BB    0.6008 5.54579e4  1386.02063  91.3506
   2  18.586 BB    0.8441 5250.95410   95.40913   8.6494

Totals :                  6.07088e4  1481.42976

================================================================================
                          *** End of Report ***
```

7. Ligand **N**

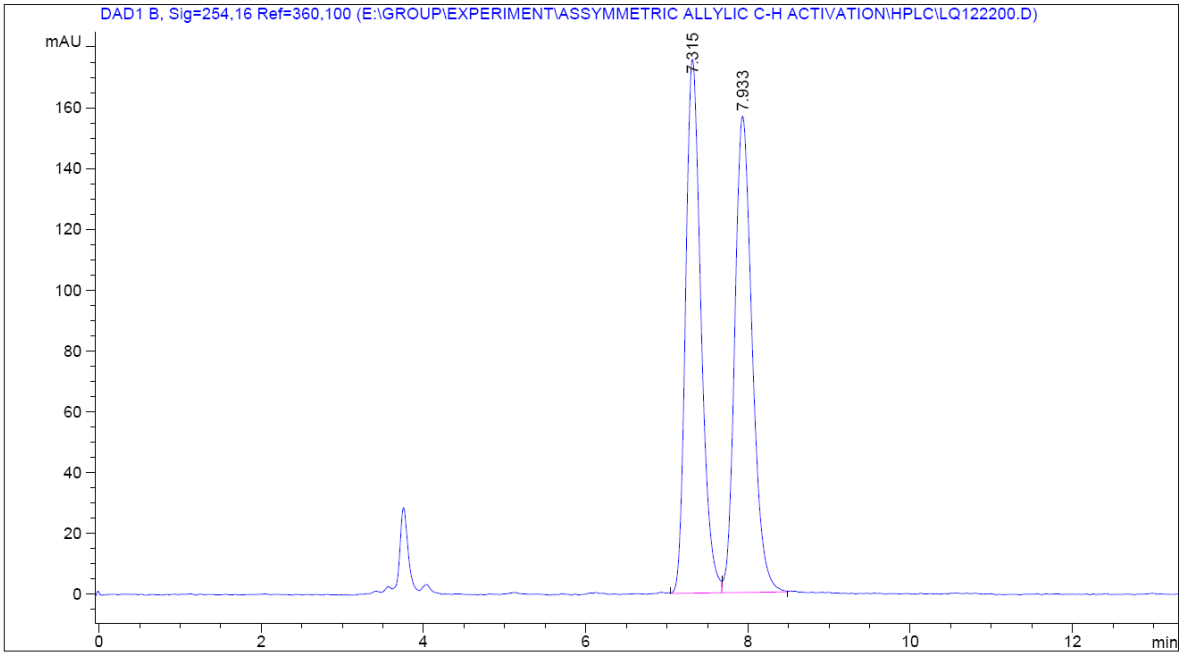
```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-22 4:24:24
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 7:59:25  by LQ-Yu
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.615 VB    0.6184 2.85451e4   681.80402  95.4872
   2  20.179 VB    0.7717 1349.07153   20.77251   4.5128

Totals :                  2.98942e4   702.57652

=====================================================================
                      *** End of Report ***
```

8. Racemic **2a** separated by OD-H

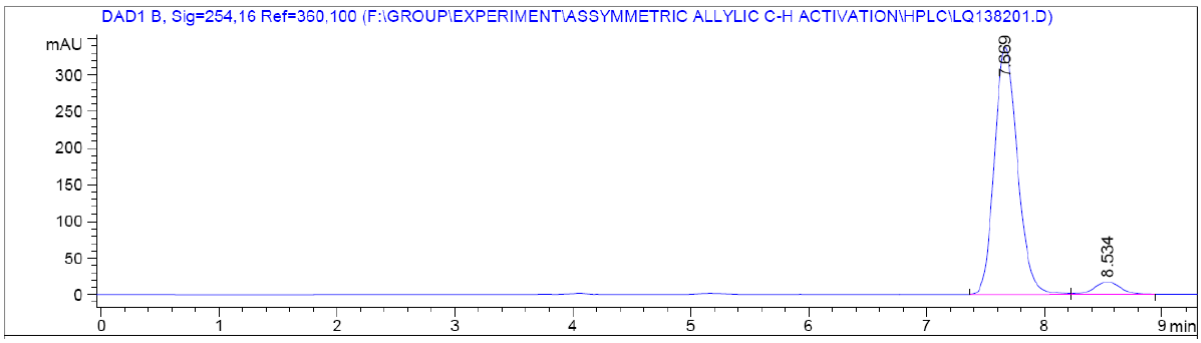
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 1:15:02
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-20 23:37:31  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.315 VV    0.2040 2317.79248  175.62682  49.8331
   2   7.933 VB    0.2297 2333.31885  156.69621  50.1669

Totals :                  4651.11133  332.32303


=====================================================================
                        *** End of Report ***
```

9. Ligand **C**

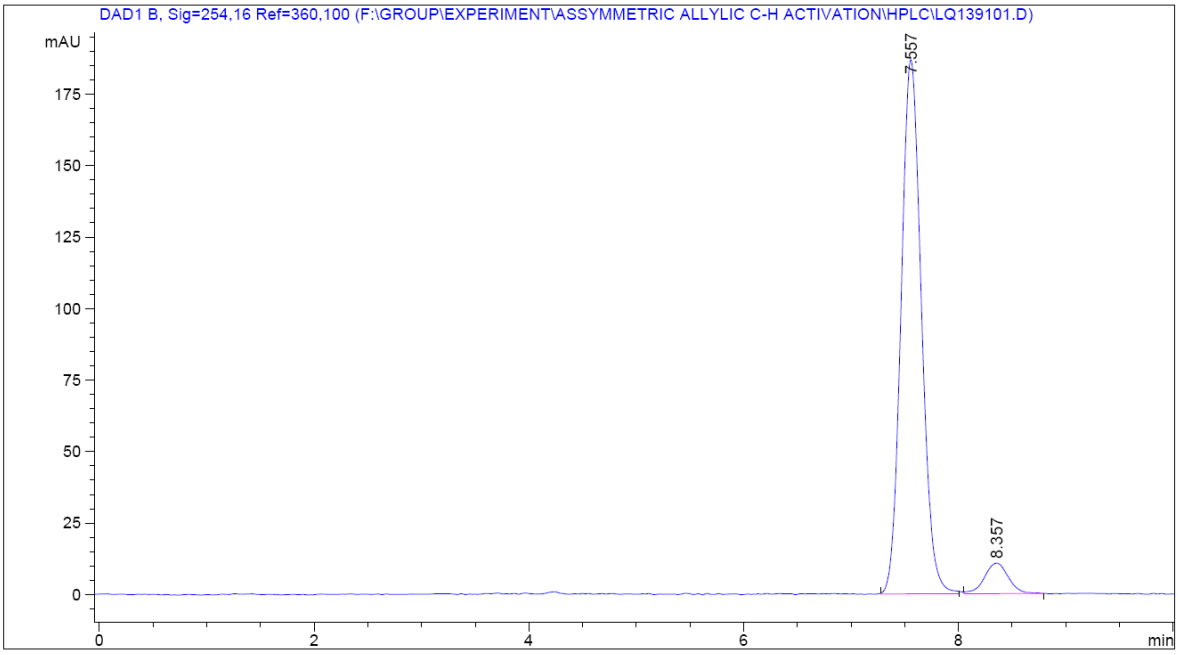
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-12 4:52:10
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-12 4:33:02  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.669 BV    0.2114 4611.42773  337.53702  94.4236
   2   8.534 VB    0.2404  272.34030   17.04273   5.5764

Totals :                  4883.76804  354.57975


================================================================================
                          *** End of Report ***
```

10. Ligand **H**

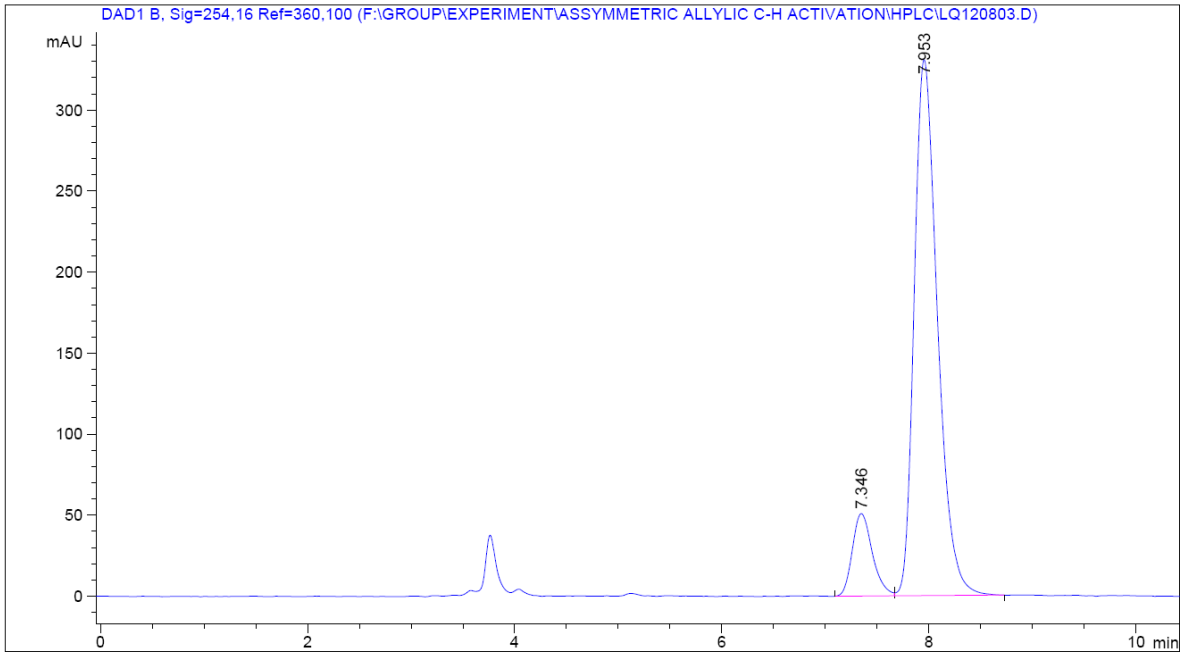
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-17 4:59:32
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-17 4:08:31  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2010-11-16 15:06:01
                  (modified after loading)
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.557 BB    0.2028 2446.76855  186.86728  93.6189
   2   8.357 BB    0.2401  166.77374   10.68530   6.3811

Totals :                  2613.54230  197.55257


=====================================================================
                      *** End of Report ***
```

11. Ligand **K**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 1:31:14
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-20 23:37:31  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```

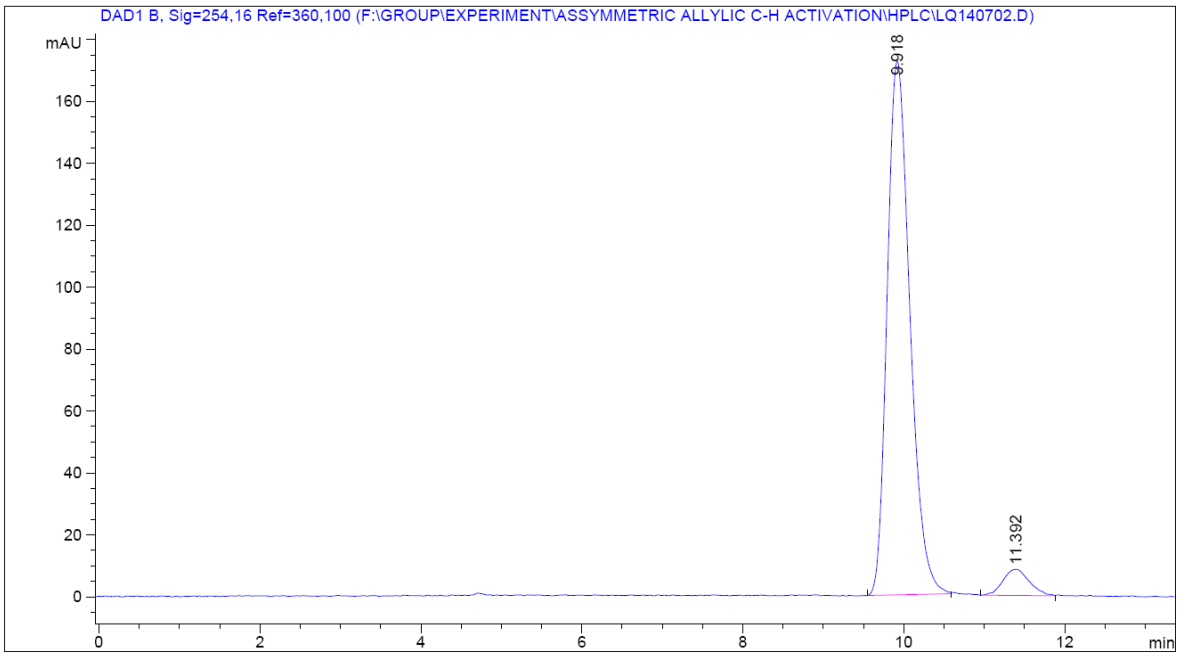



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.346 BV    0.2029  684.90796   50.91212  11.7248
   2   7.953 VB    0.2378 5156.63770  330.90814  88.2752

Totals :                   5841.54565  381.82026

=====================================================================
                        *** End of Report ***
```

4.5 HPLC data of 2a using lower rhodium loadings

1. 1.5 mol% $[Rh(coe)_2Cl]_2$

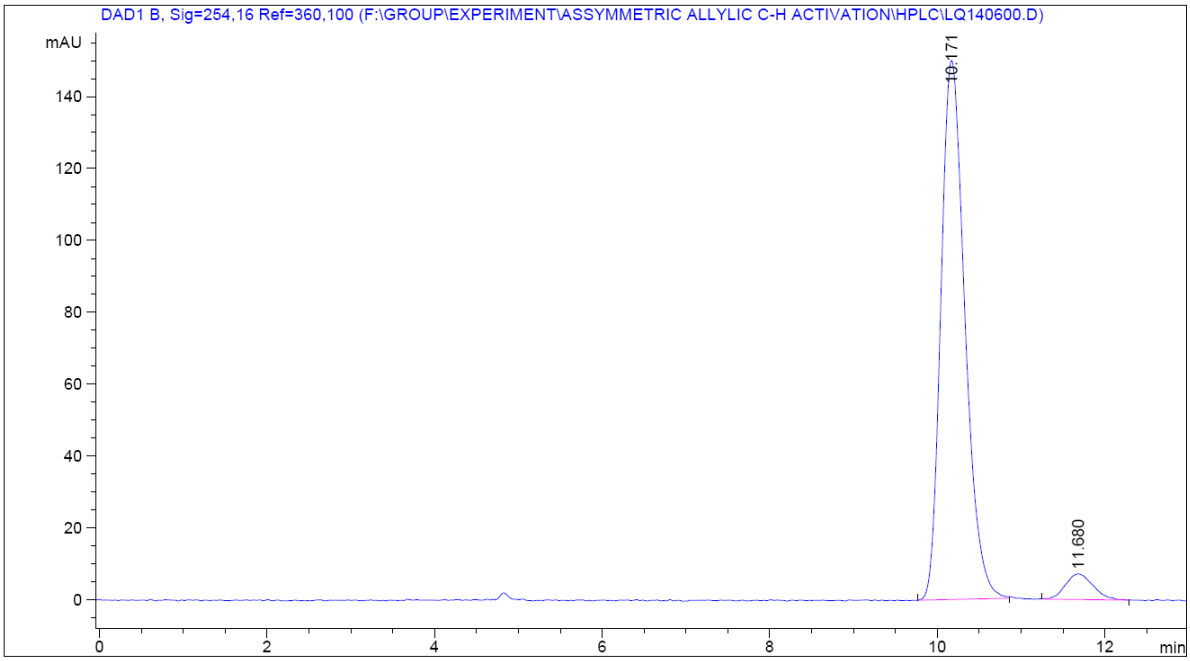
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-24 11:34:41
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-24 9:59:54  by WY
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.918 BB    0.3007 3380.08228  172.46413  94.6272
   2  11.392 BV    0.2706  191.91599    8.39708   5.3728

Totals :                  3571.99826  180.86121

=====================================================================
                      *** End of Report ***
```

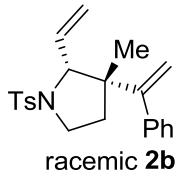
2. 1.0 mol% $[Rh(coe)_2Cl]_2$

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-24 10:50:41
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-24 9:59:54  by WY
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```



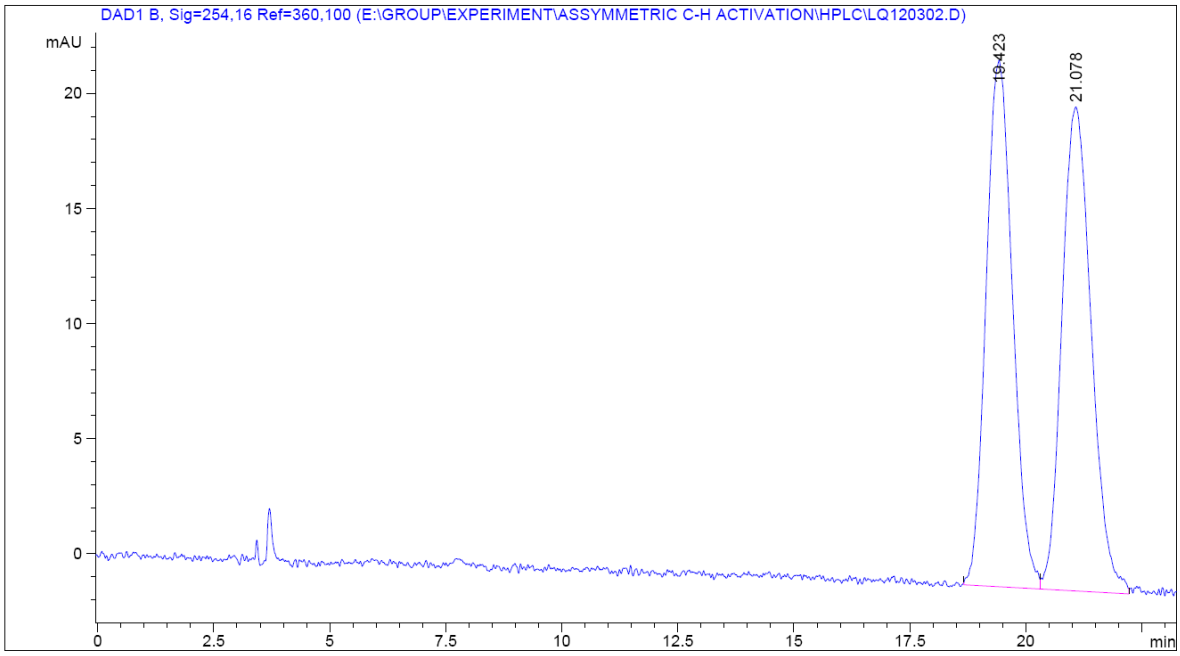

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.171 BB    0.3056 2976.89038  149.93988  94.7991
   2  11.680 BB    0.2788  163.31894    7.14227   5.2009

Totals :                  3140.20932  157.08215

================================================================================
                          *** End of Report ***
```

4.6 HPLC data for other products



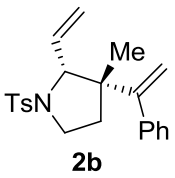
racemic **2b**

```
Acq. Operator    : LQ
Acq. Instrument  : Instrument 1                    Location :   -
Injection Date   : 2010-7-13 5:42:05
Acq. Method      : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed     : 2010-7-13 5:34:52  by LQ
                   (modified after loading)
Analysis Method  : C:\Chem32\1\METHODS\DEF_LC.M
Last changed     : 2004-4-7 0:10:12
Sample Info      : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```

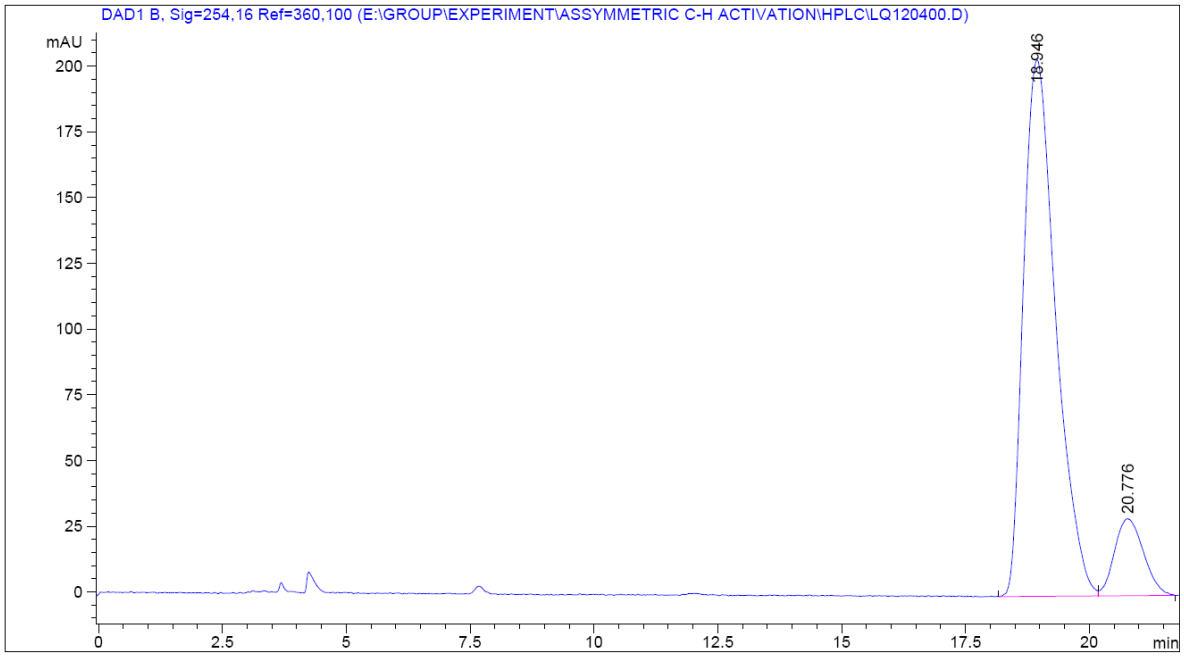



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.423 BV    0.4746  907.59473   22.88716  49.5015
   2  21.078 VB    0.5317  925.87439   21.02586  50.4985

Totals :                  1833.46912   43.91303

=====================================================================
                      *** End of Report ***
```

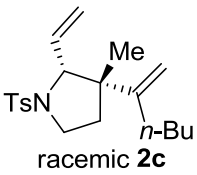
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-13 6:13:03
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-13 5:34:52  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```



2b

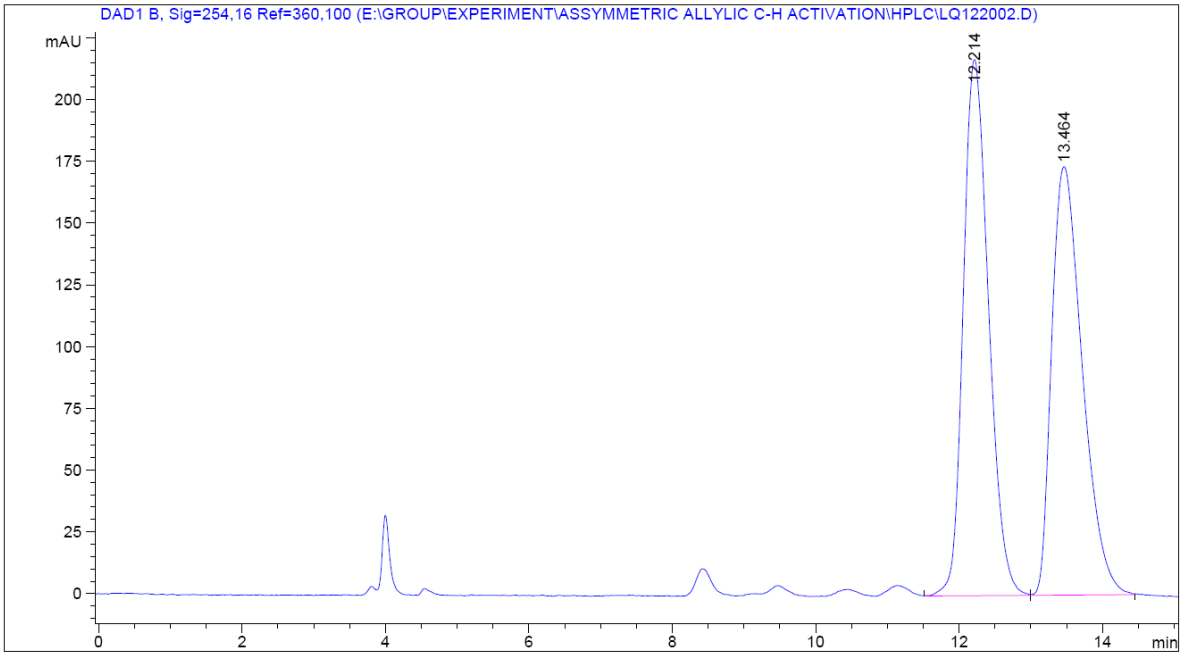



```
==================================================================
                    Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.946 BV    0.6929 9249.44434  204.00868  88.5347
   2  20.776 VBA   0.5252 1197.81055   29.28618  11.4653

Totals :                  1.04473e4   233.29486


==================================================================
                    *** End of Report ***
```

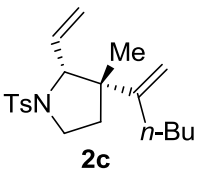


racemic **2c**

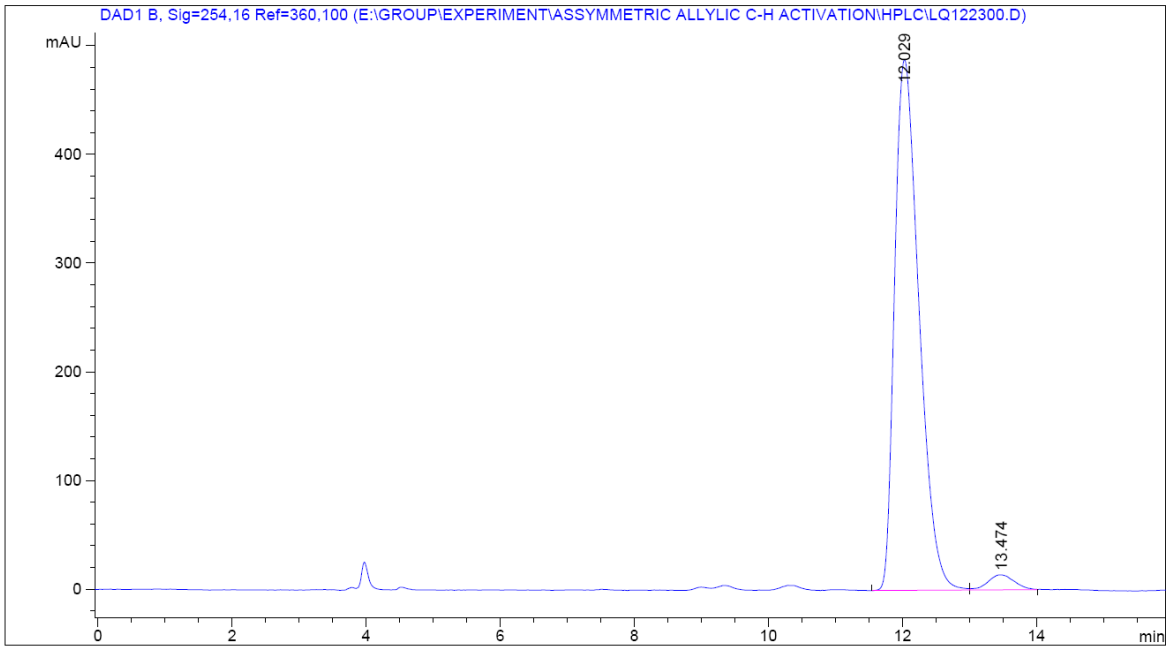
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 4:08:20
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-21 3:50:17  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```



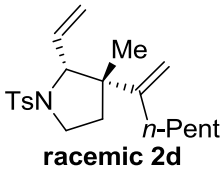

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.214 VV    0.3822 5326.40820  217.11043  50.8715
   2  13.464 VB    0.4679 5143.90576  173.51320  49.1285

Totals :                  1.04703e4   390.62363

=====================================================================
                        *** End of Report ***
```




```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 4:24:59
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-21 3:50:17  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```

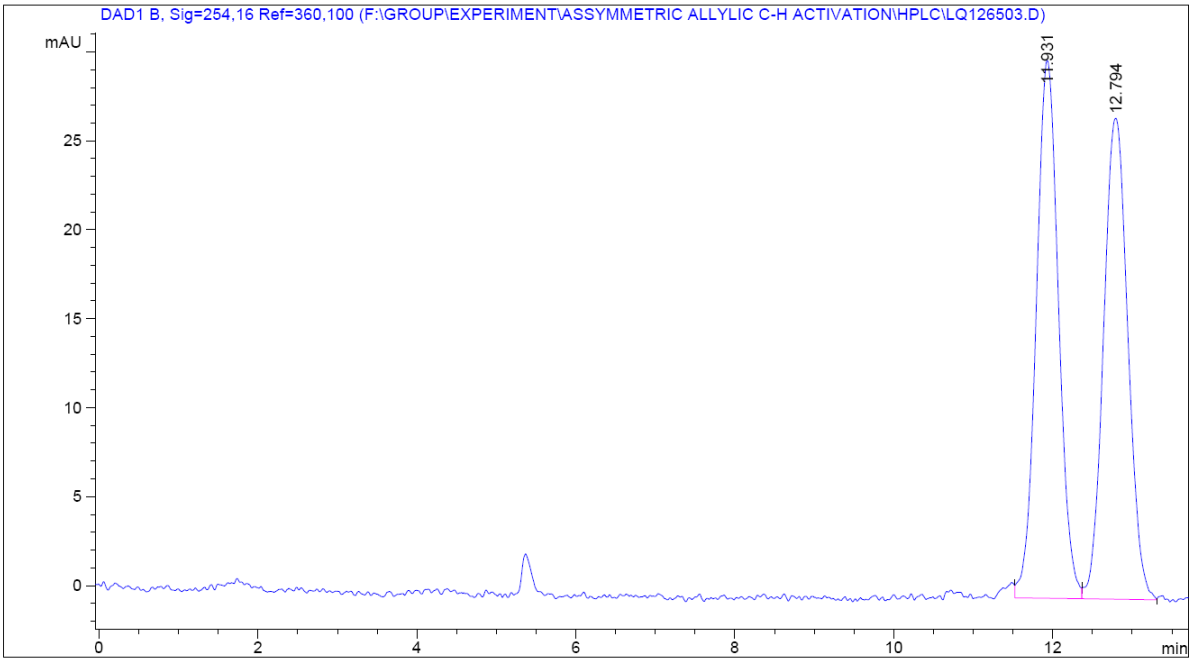



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.029 BB    0.3918 1.22926e4   488.12122  97.0157
   2  13.474 BV    0.3326  378.12607   13.84810   2.9843

Totals :                  1.26707e4   501.96931

=====================================================================
                        *** End of Report ***
```

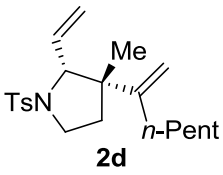


racemic 2d

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-8-31 6:18:24
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-8-31 5:25:39  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.8 ml/min, Hexane:iPrOH = 99:1
```

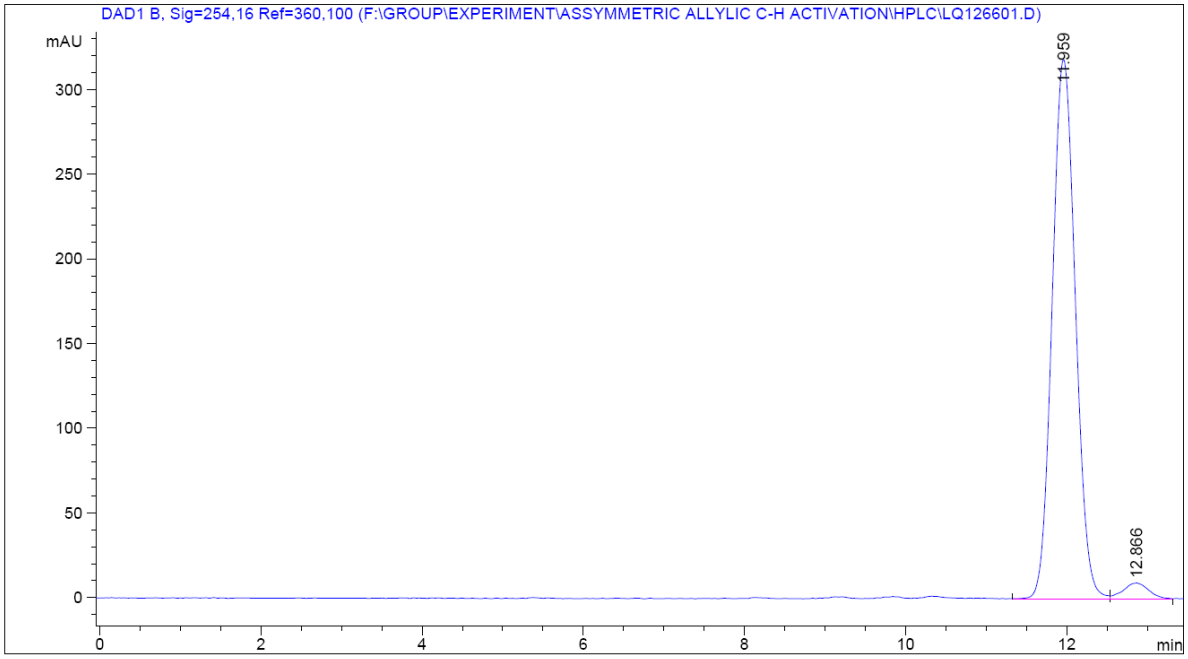



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.931 VV    0.2957  590.11157   30.23633  50.6784
   2  12.794 VV    0.3219  574.31268   27.03195  49.3216

Totals :                  1164.42426   57.26828

=====================================================================
                        *** End of Report ***
```

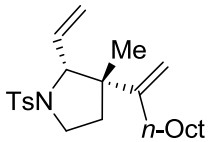


2d

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-8-31 6:03:34
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-8-31 5:25:39  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.8 ml/min, Hexane:iPrOH = 99:1
```

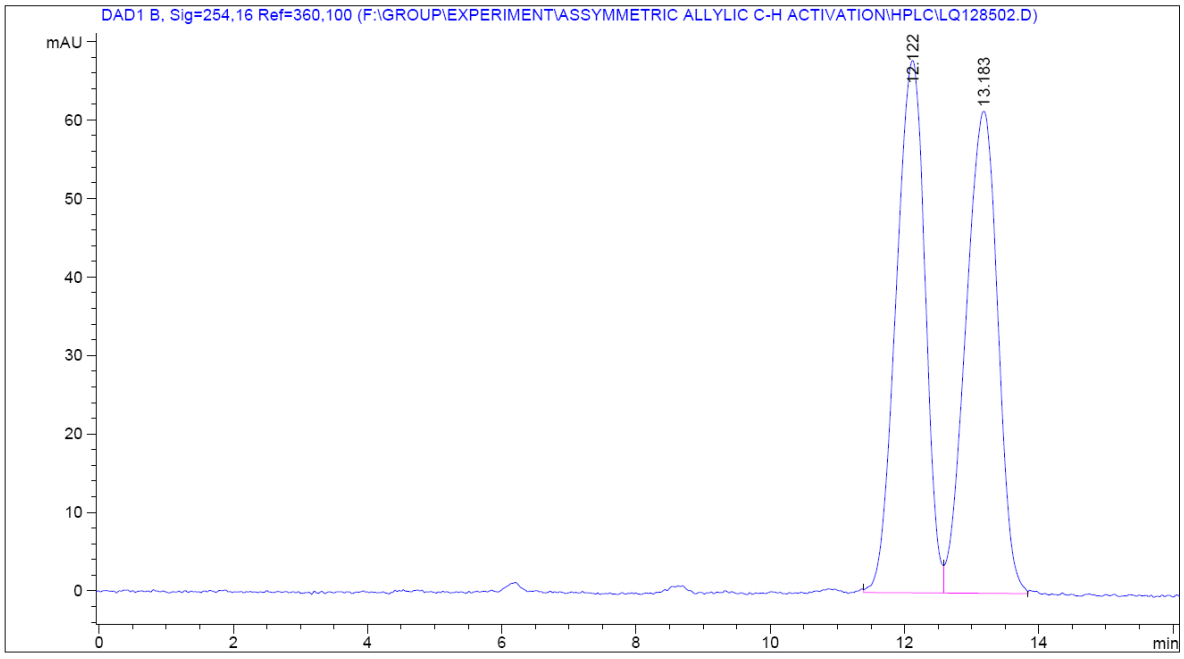



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.959 VV    0.3168 6355.61621  318.55103  96.8828
   2  12.866 VV    0.2681  204.49222    9.38722   3.1172

Totals :                  6560.10843  327.93825

=====================================================================
                        *** End of Report ***
```

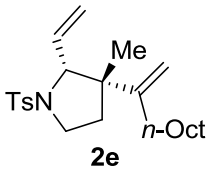


racemic 2e

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-9-10 0:43:14
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-9-10 0:37:36  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.7 ml/min, Hexane:iPrOH = 99:1
```

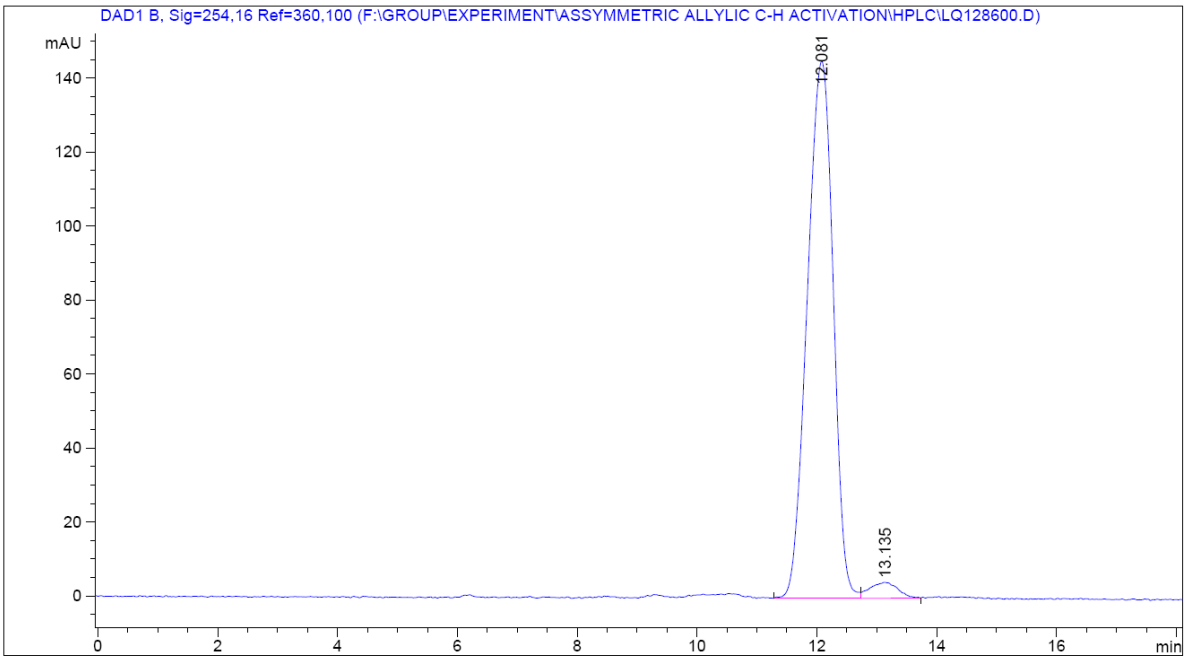



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.122 VV    0.4210 2040.36572   67.82430  50.1141
   2  13.183 VV    0.4579 2031.07336   61.40402  49.8859

Totals :                  4071.43909  129.22832

================================================================================
                          *** End of Report ***
```

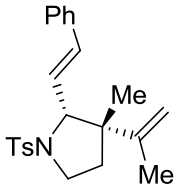


2e

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-9-10 1:12:46
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-9-10 0:37:36  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.7 ml/min, Hexane:iPrOH = 99:1
```

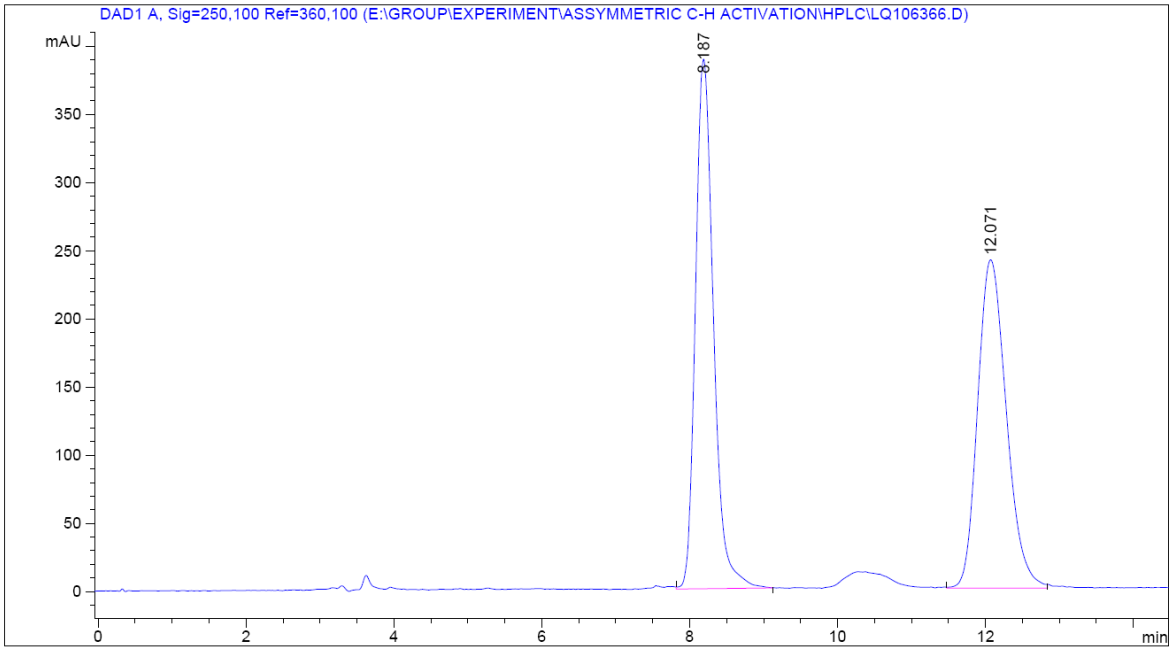



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.081 BV    0.4654 4347.47949  145.15578  96.8884
   2  13.135 VV    0.3981  139.61862    4.28535   3.1116

Totals :                  4487.09811  149.44113

======================================================================
                        *** End of Report ***
```

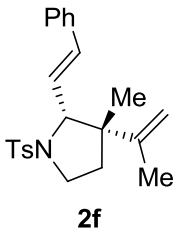


racemic **2f**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-5-18 0:37:28
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-5-18 0:27:04  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H,1.0ml/min,hexane:iPrOH=95:5
```

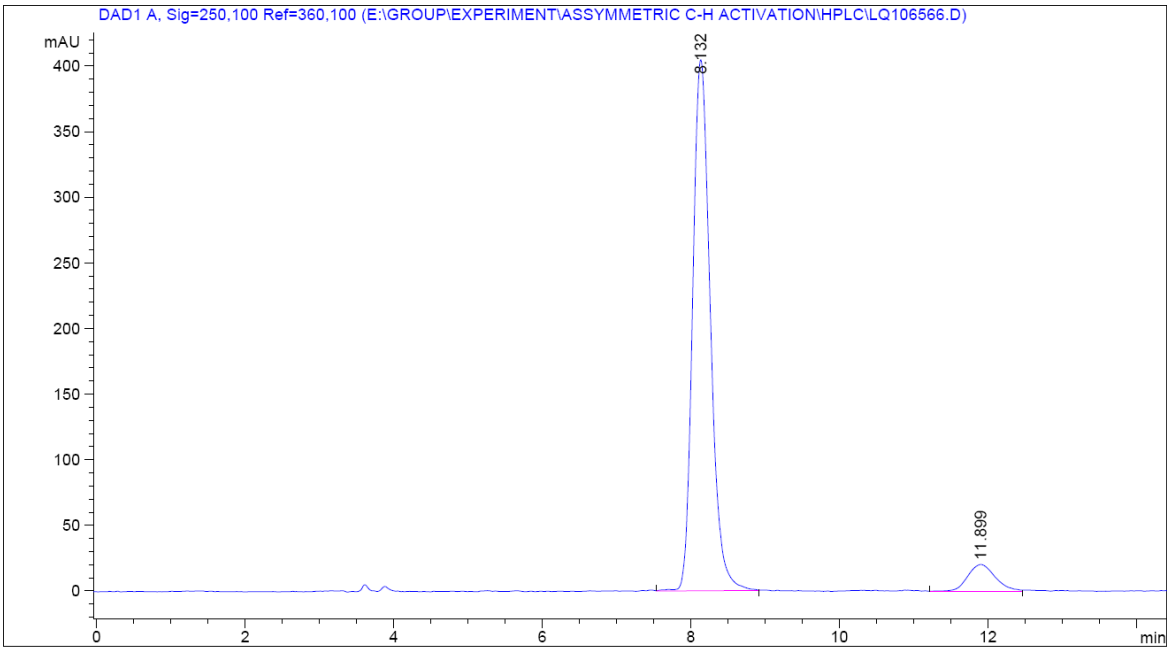



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.187 VB    0.2636 6580.10693  388.56491  50.3428
   2  12.071 VB    0.4224 6490.48535  240.83354  49.6572

Totals :                  1.30706e4   629.39845

=====================================================================
                      *** End of Report ***
```



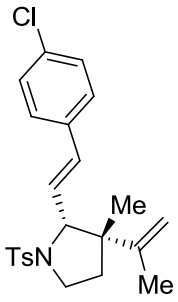
2f

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-5-18 1:13:17
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-5-18 0:27:04  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H,1.0ml/min,hexane:iPrOH=95:5
```

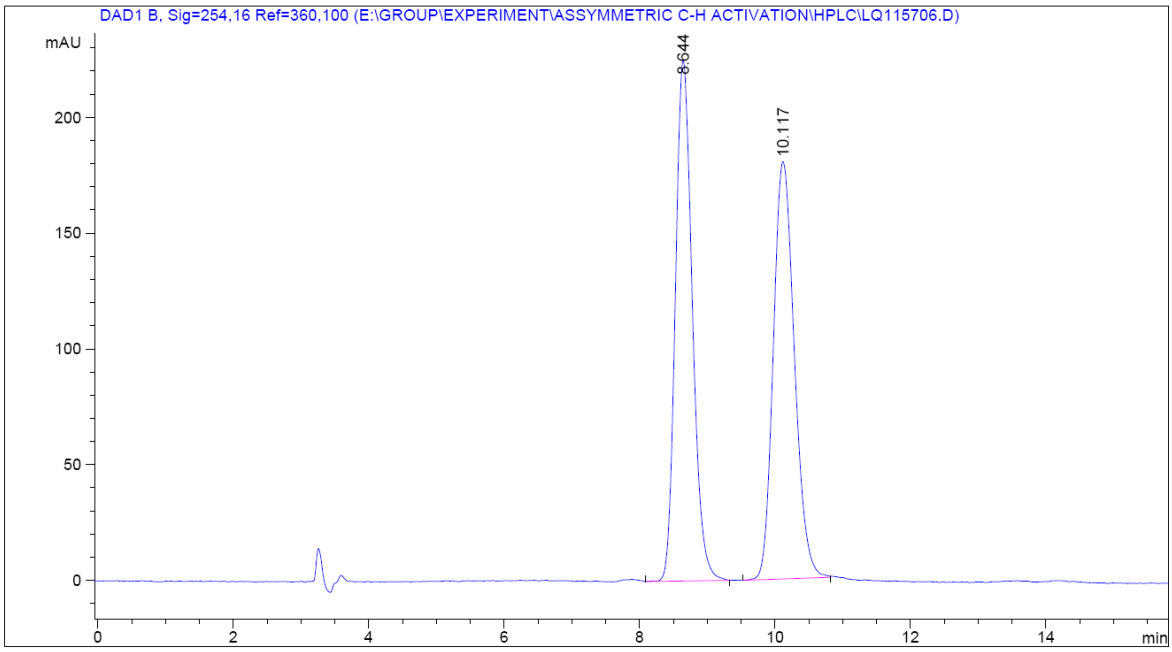



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.132 VB    0.2559 6658.53516  404.73236  92.5509
   2  11.899 VV    0.3464  535.92249   20.53922   7.4491

Totals :                  7194.45764  425.27159

=====================================================================
                        *** End of Report ***
```

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-2 5:32:41
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-2 4:46:13  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```

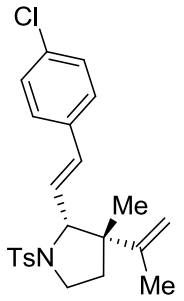


racemic **2g**

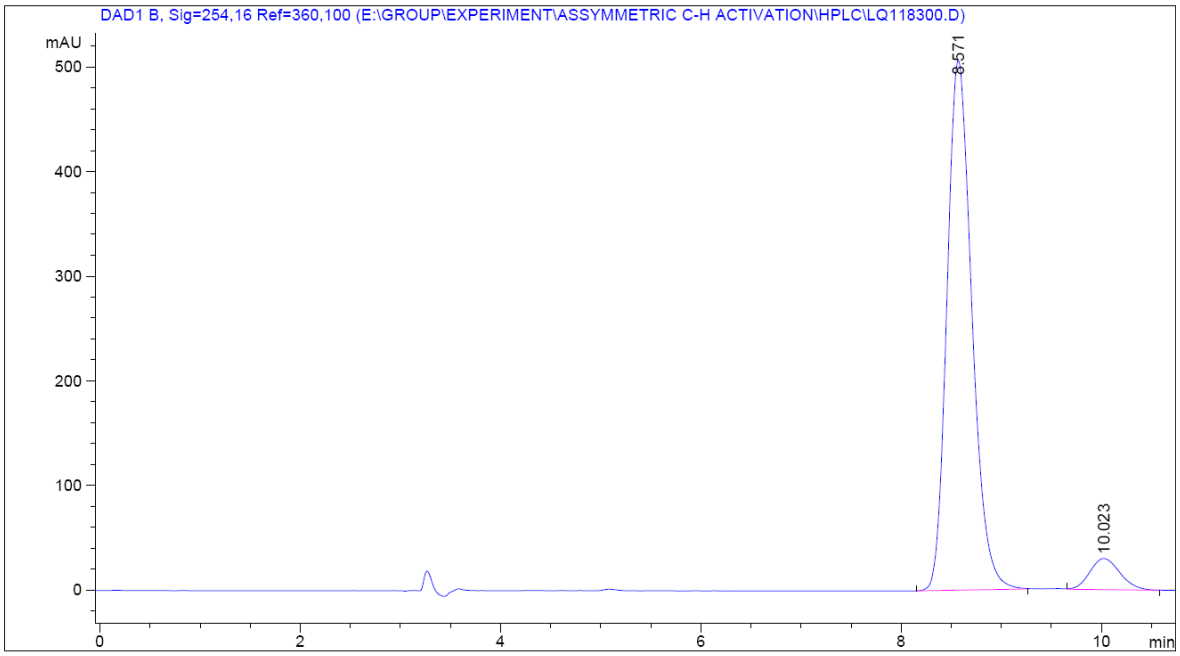



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.644 VB    0.2690 3913.35889  224.90189  50.1467
   2  10.117 BB    0.3398 3890.46387  180.25862  49.8533

Totals :                  7803.82275  405.16051

=====================================================================
                      *** End of Report ***
```

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-2 5:15:00
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-2 4:46:13  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```



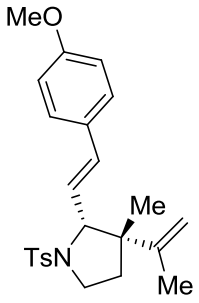
2g



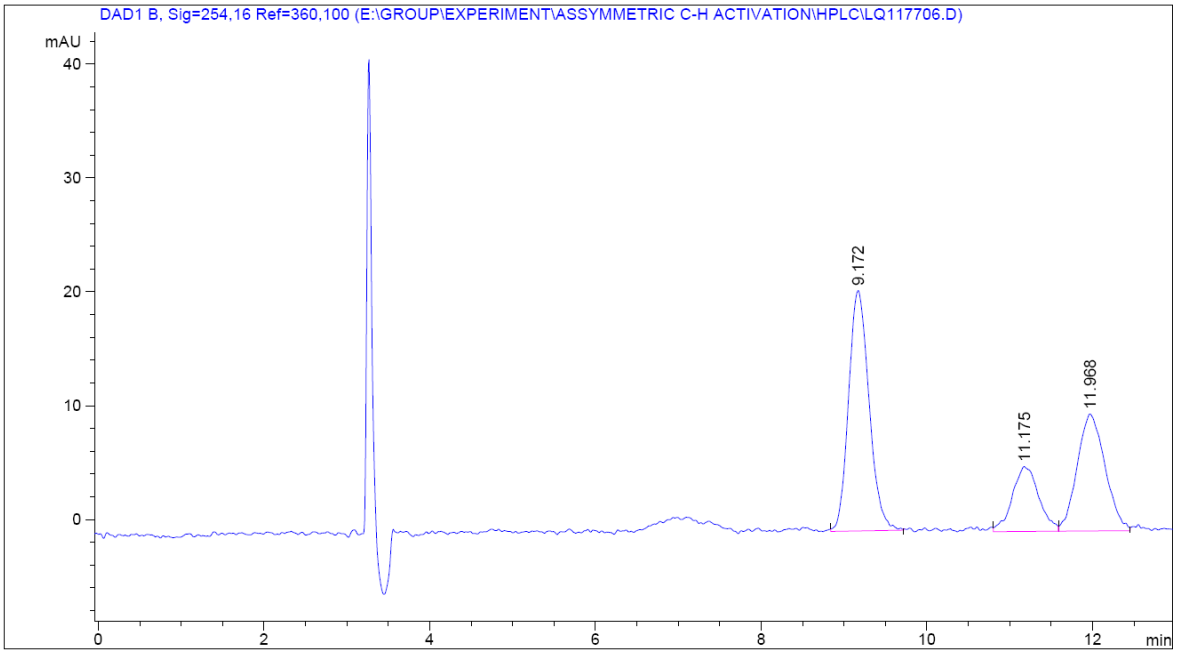

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.571 BB    0.2656 8749.85254  506.28903  93.3821
   2  10.023 BB    0.3150  620.09546   29.77006   6.6179

Totals :                  9369.94800  536.05910

=====================================================================
                        *** End of Report ***
```

The ratio of the major and minor diastereoisomers in racemic **2h** obtained by using PPh_3 as ligand is 2:1 as determined by the NMR spectra. So the first peak in the HPLC analysis is a mixture of the two epimers.

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-7 7:38:57
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-7 6:52:28  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```



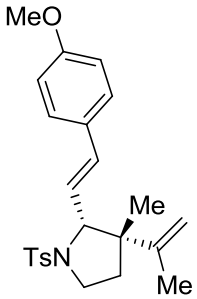
racemic **2h**



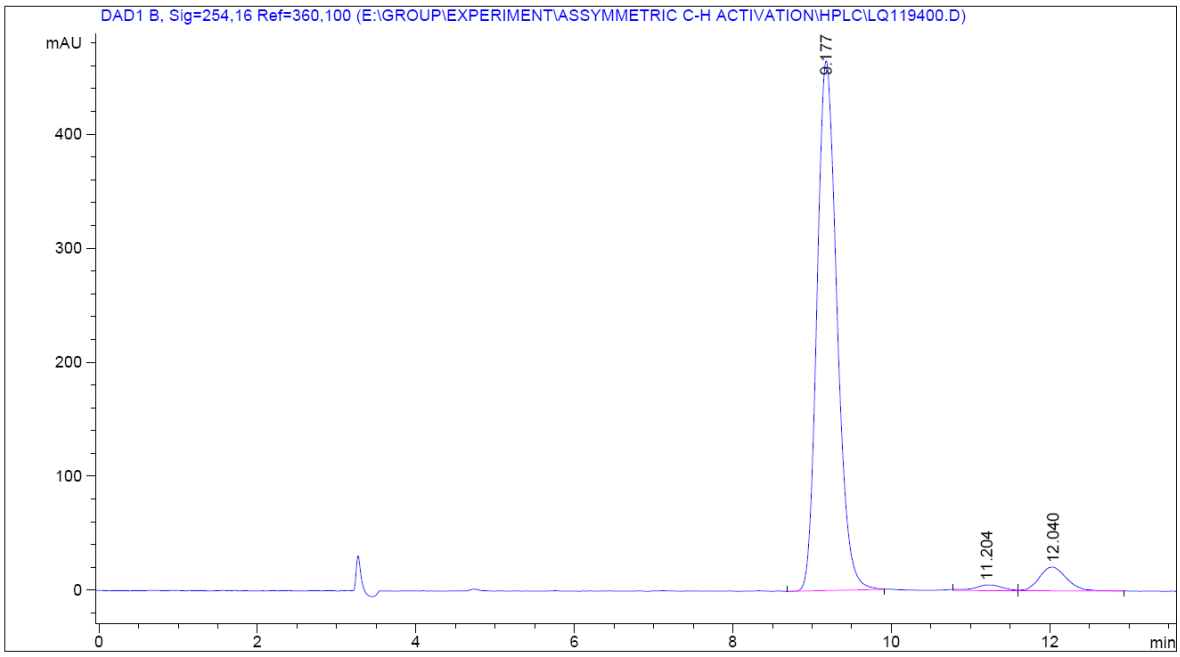

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.172 BB    0.2366  363.18170   21.11995  49.7779
   2  11.175 BV    0.2727  126.33853    5.69704  17.3160
   3  11.968 VV    0.2862  240.08371   10.29087  32.9060

Totals :                   729.60394   37.10785

=====================================================================
                        *** End of Report ***
```

The ratio of the major and minor diastereoisomers is 52.6:1 in **2h**. So the first peak in HPLC contains 0.45% epimer of the minor diastereoisomer.

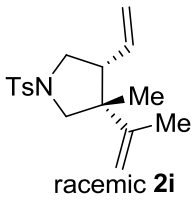
```
Acq. Operator    : LQ
Acq. Instrument  : Instrument 1                    Location :   -
Injection Date   : 2010-7-7 7:23:35
Acq. Method      : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed     : 2010-7-7 6:52:28  by LQ
                   (modified after loading)
Analysis Method  : C:\Chem32\1\METHODS\DEF_LC.M
Last changed     : 2004-4-7 0:10:12
Sample Info      : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```



2h

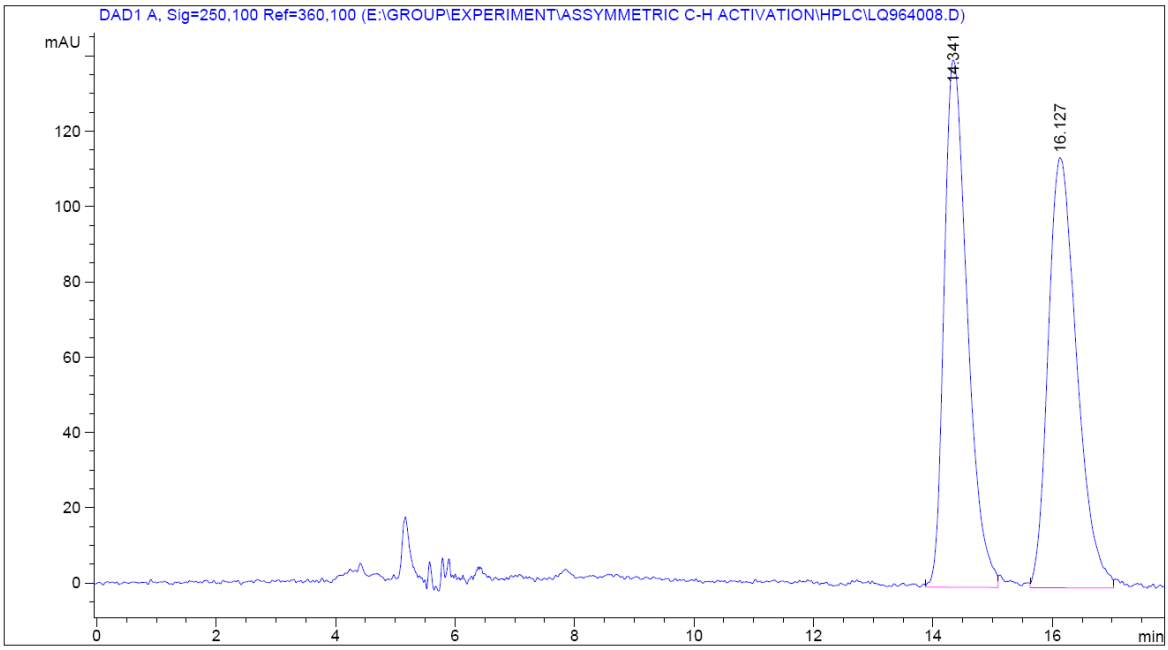



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.177 VB    0.2716 8109.30518  464.78992  92.8696
   2  11.204 VV    0.3019  123.29426    5.03184   1.4120
   3  12.040 VB    0.3295  499.33035   20.83930   5.7184

Totals :                  8731.92979  490.66106


=====================================================================
                      *** End of Report ***
```

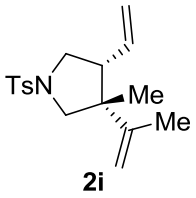


racemic **2i**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-6-2 5:21:04
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-6-2 5:19:45  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H,0.8 ml/min,hexane:iPrOH=95:5
```

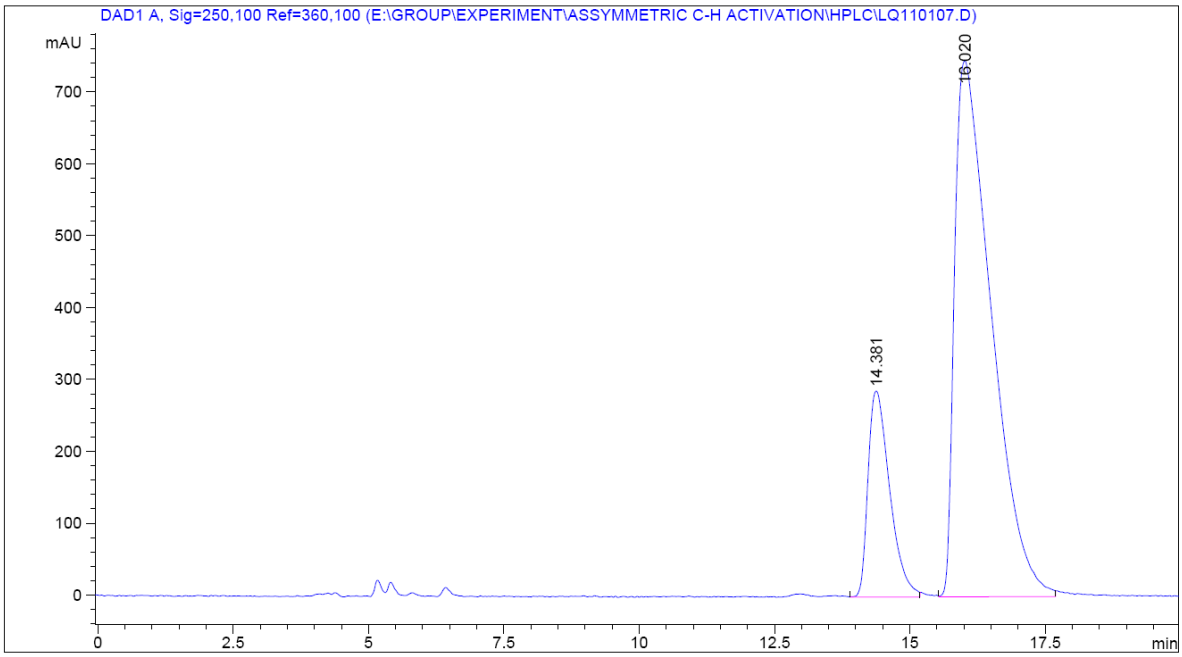



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.341 VV    0.3952 3784.21240  140.08578  49.8149
   2  16.127 VV    0.4050 3812.33960  114.34026  50.1851

Totals :                  7596.55200  254.42605

=====================================================================
                      *** End of Report ***
```

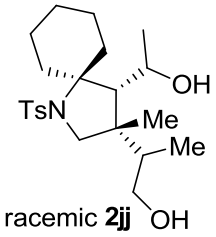


2i

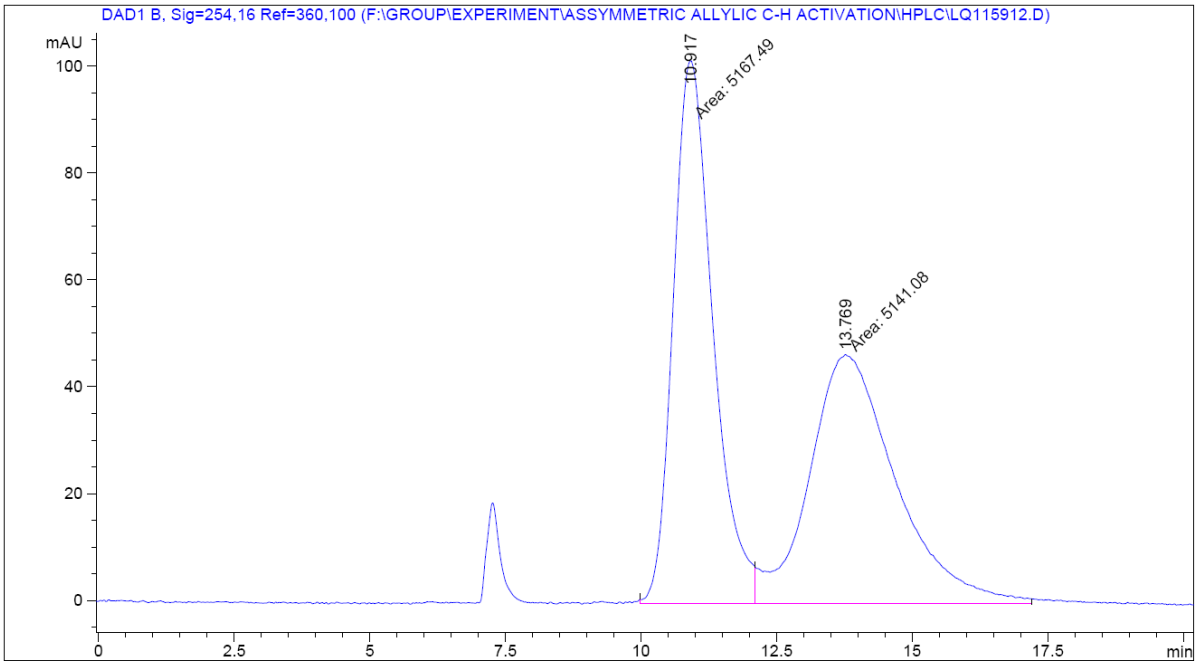
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-6-2 6:44:16
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-6-2 5:19:45  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H,0.8 ml/min,hexane:iPrOH=95:5
```



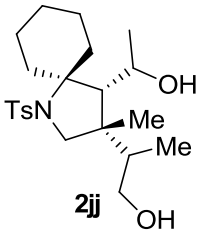

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.381 VV    0.4212 7985.34082  286.46823  18.5509
   2  16.020 VV    0.6444 3.50603e4   745.89636  81.4491

Totals :                  4.30456e4  1032.36459

=====================================================================
                        *** End of Report ***
```



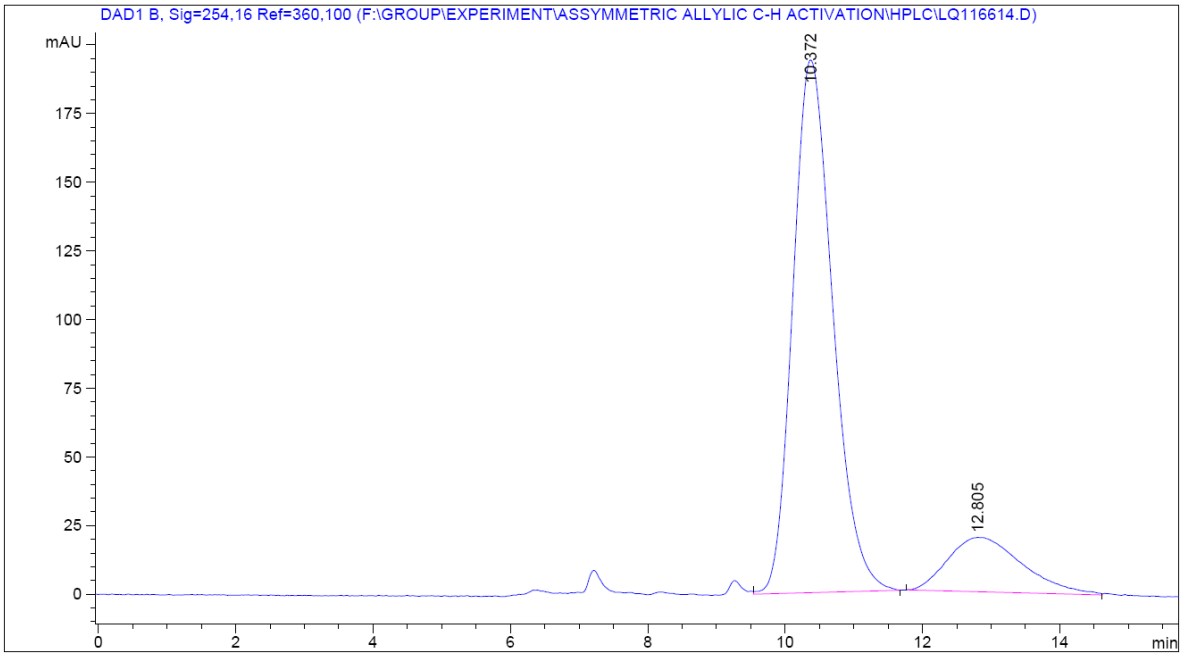

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-20 11:04:20
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-20 10:40:36  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : AS-H, 0.5 ml/min, Hexane:iPrOH = 60:40
```



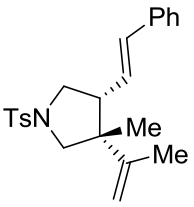

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.917 MM    0.8481 5167.49414  101.55460  50.1281
   2  13.769 MM    1.8402 5141.08447   46.56324  49.8719

Totals :                  1.03086e4   148.11784

=====================================================================
                        *** End of Report ***
```




```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-22 10:10:09
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-22 9:43:11  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : AS-H, 0.5 ml/min, Hexane:iPrOH = 60:40
```

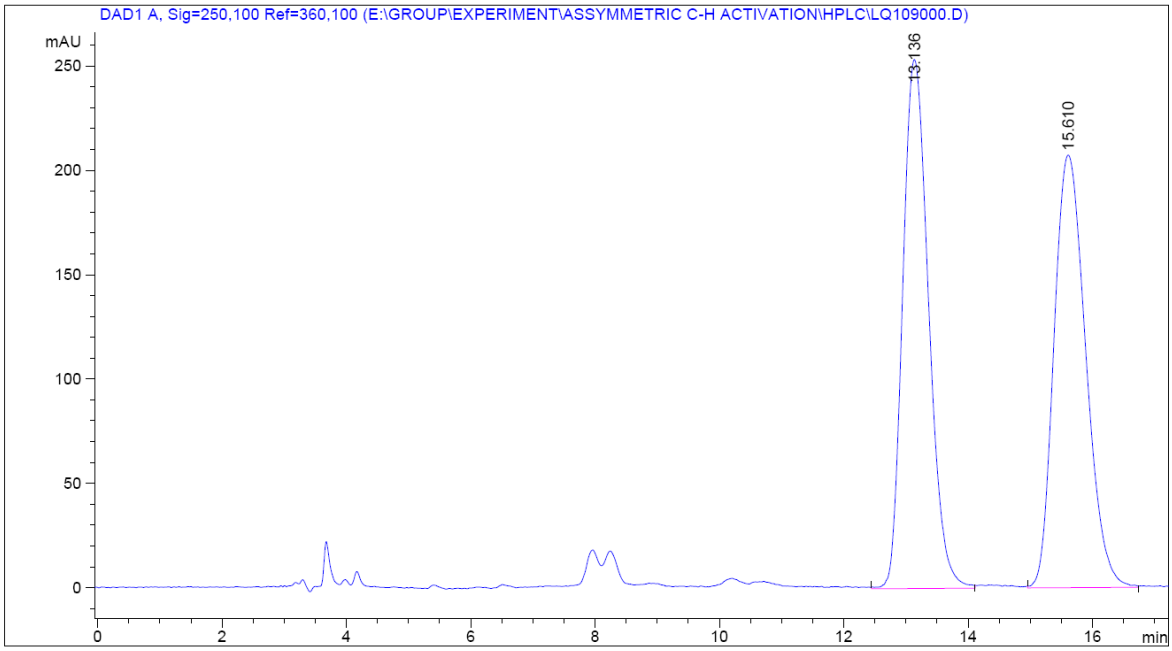



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.372 VB    0.6181 7848.47314  193.96117  84.0372
   2  12.805 BV    0.8856 1490.81567   19.77423  15.9628

Totals :                  9339.28882  213.73540

=====================================================================
                        *** End of Report ***
```

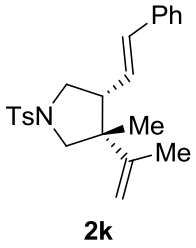


racemic **2k**

```
Acq. Operator    : LQ
Acq. Instrument  : Instrument 1                    Location :   -
Injection Date   : 2010-5-17 7:34:13
Acq. Method      : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed     : 2010-5-17 7:21:14  by Yuye-Li
                   (modified after loading)
Analysis Method  : C:\Chem32\1\METHODS\DEF_LC.M
Last changed     : 2004-4-7 0:10:12
Sample Info      : OD-H,1.0ml/min,hexane:iPrOH=95:5
```

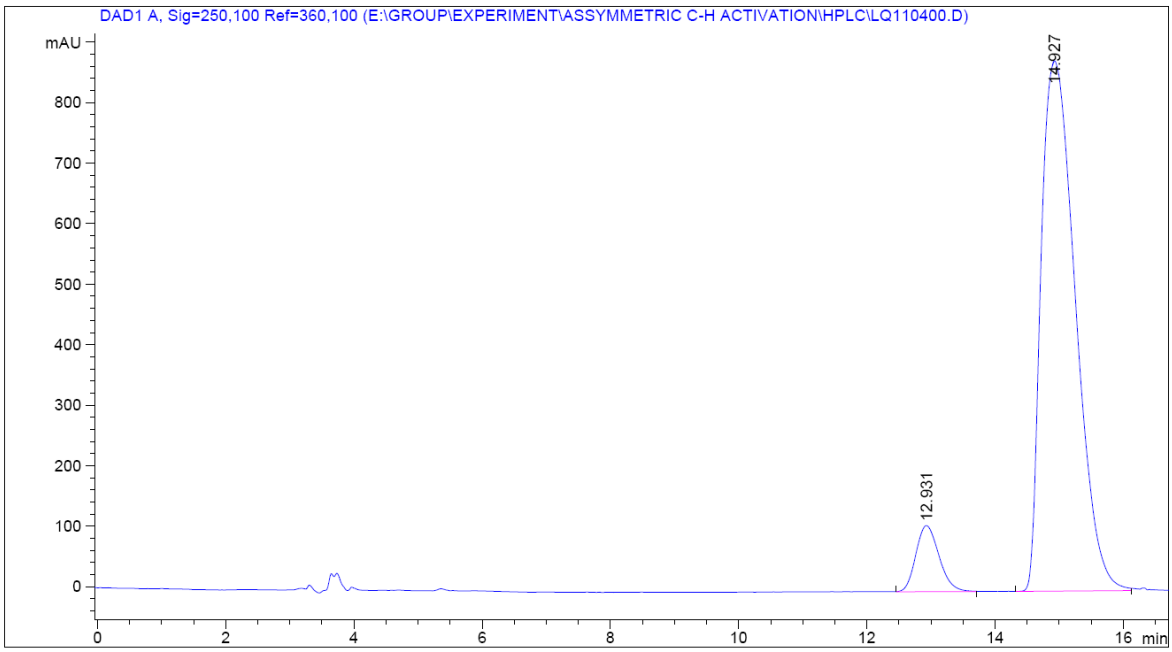



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.136 BB    0.4527 7316.83398  253.50702  49.8913
   2  15.610 BV    0.5516 7348.71875  207.30995  50.1087

Totals :                  1.46656e4   460.81697

=====================================================================
                        *** End of Report ***
```

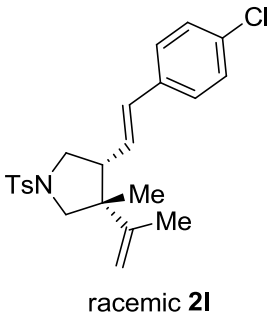


2k

```
Acq. Operator    : LQ
Acq. Instrument  : Instrument 1                    Location :   -
Injection Date   : 2010-5-25 0:46:01
Acq. Method      : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed     : 2010-5-25 0:27:32  by LQ
                   (modified after loading)
Analysis Method  : C:\Chem32\1\METHODS\DEF_LC.M
Last changed     : 2004-4-7 0:10:12
Sample Info      : OD-H,1.0 ml/min,hexane:iPrOH=95:5
```

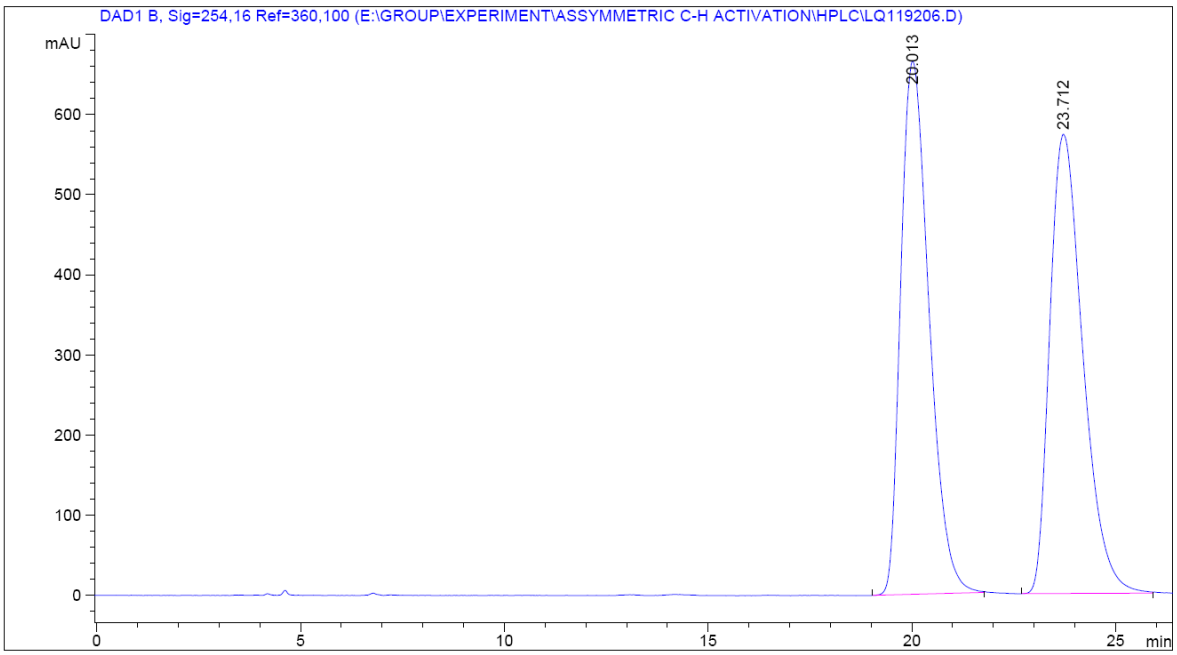



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.931 VB    0.3892 2747.05054  109.30888   7.7918
   2  14.927 VV    0.5846 3.25084e4   876.64301  92.2082

Totals :                  3.52555e4   985.95188

================================================================================
                          *** End of Report ***
```



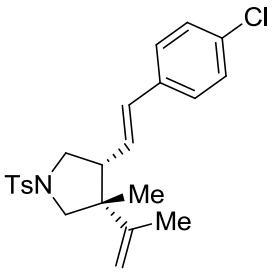
racemic **2l**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-16 4:22:27
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-16 3:10:36  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 97:3
```

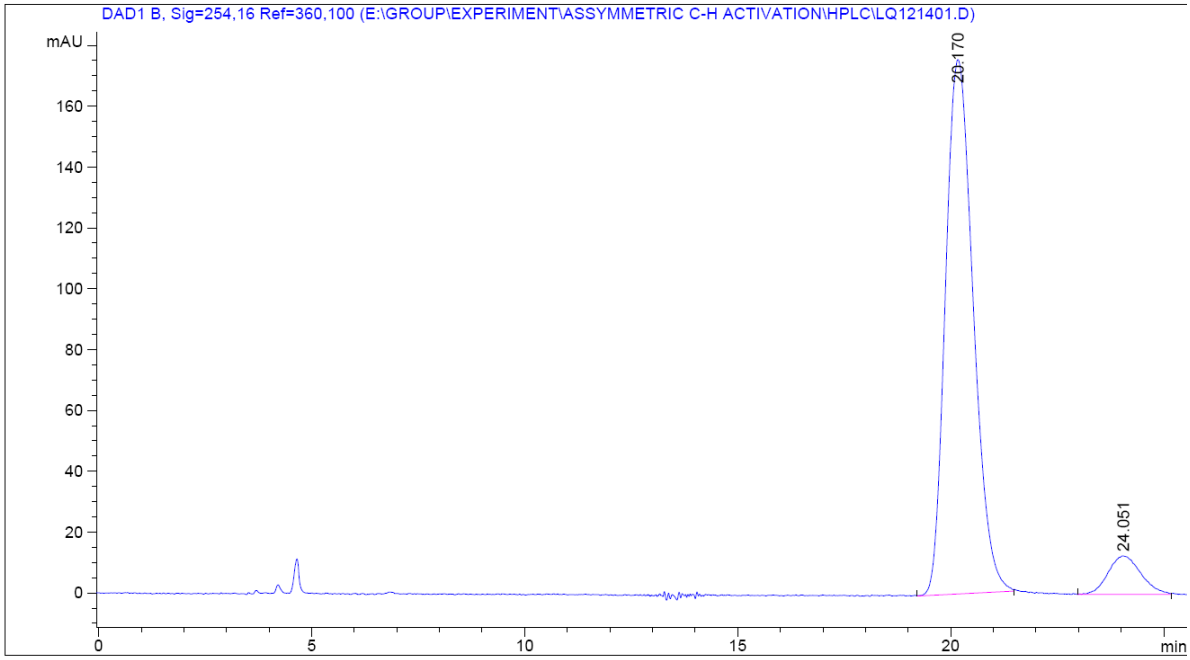



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.013 BB    0.7360 3.21847e4   665.74298  49.8494
   2  23.712 BB    0.8026 3.23792e4   573.57495  50.1506

Totals :                  6.45639e4  1239.31793

=====================================================================
                      *** End of Report ***
```

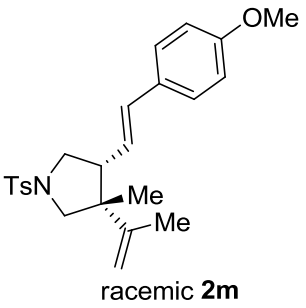
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-16 3:54:55
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-16 3:10:36  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 97:3
```



2l

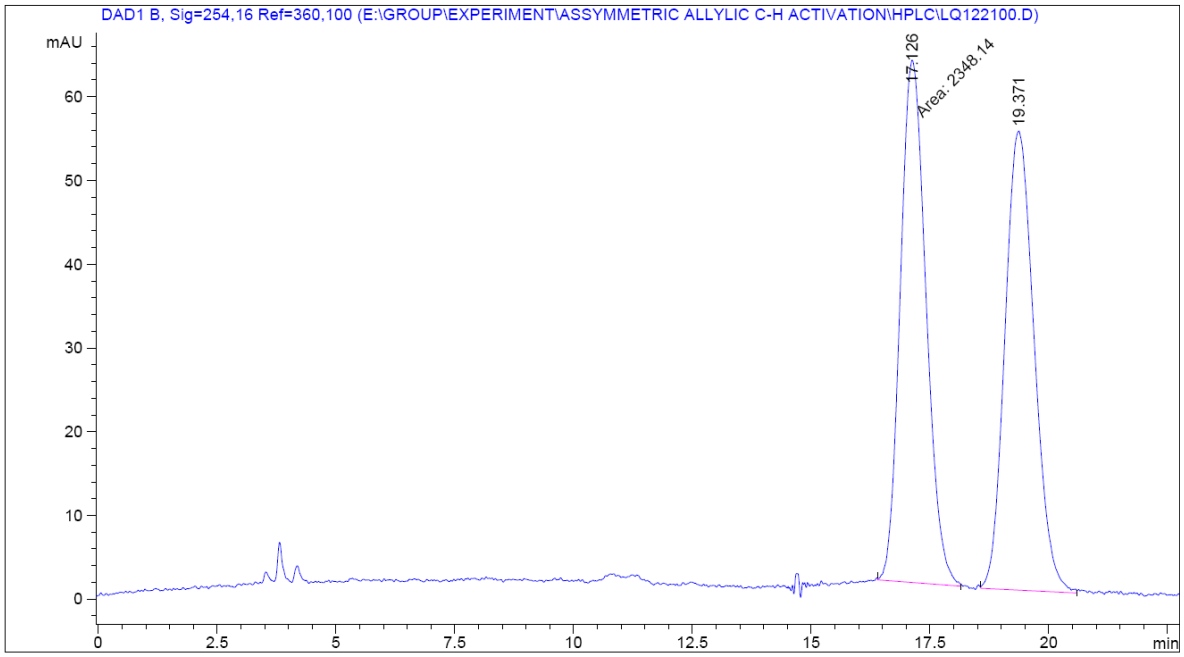



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.170 VB    0.6584 7957.73389  175.71146  92.1624
   2  24.051 VV    0.6478  676.73895   12.65764   7.8376

Totals :                  8634.47284  188.36910

=====================================================================
                        *** End of Report ***
```



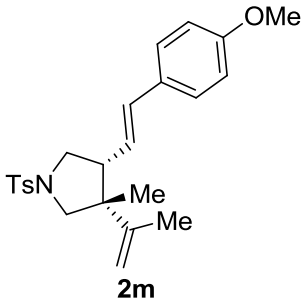
racemic **2m**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 0:15:19
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-20 23:37:31  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```

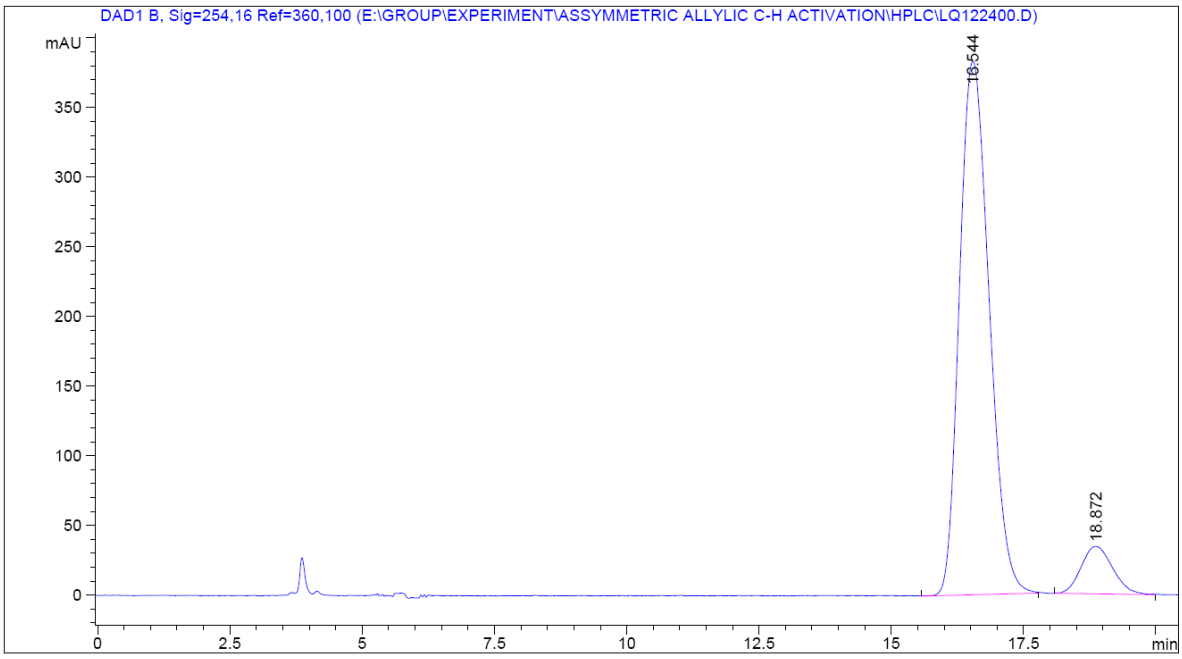



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.126 MM    0.6273 2348.13599   62.38484  50.0948
   2  19.371 VB    0.5416 2339.25293   54.85041  49.9052

Totals :                  4687.38892  117.23525

================================================================================
                          *** End of Report ***
```

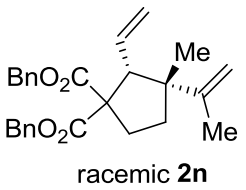
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-7-21 0:45:42
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-7-20 23:37:31  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 95:5
```



2m

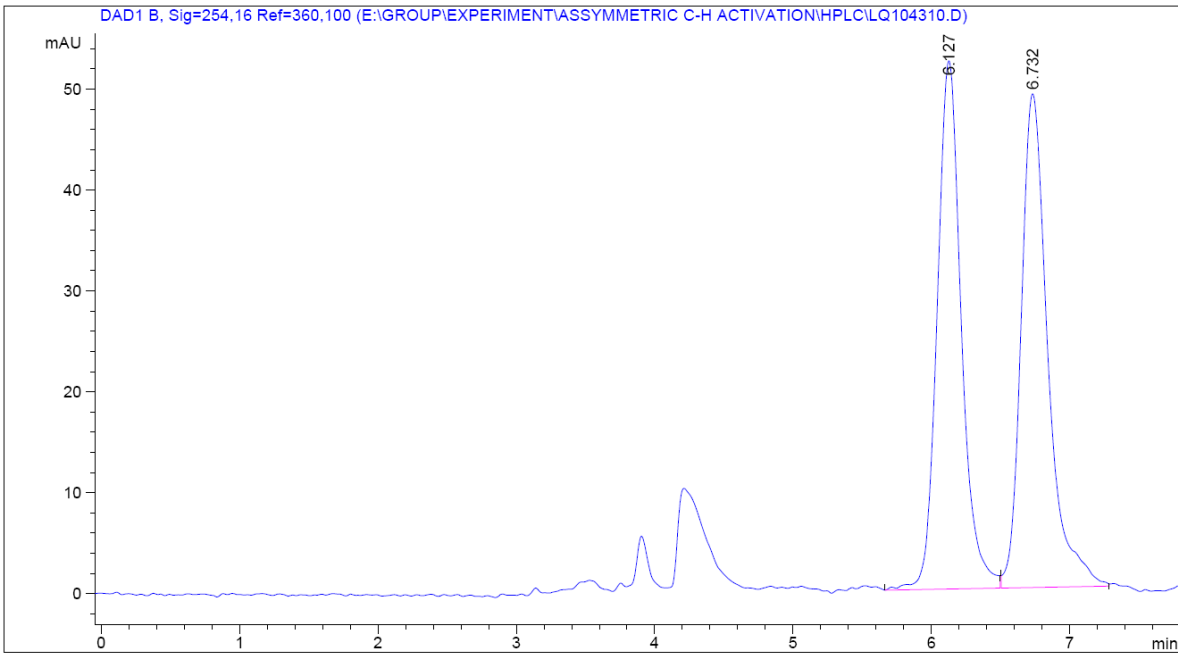



```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.544 VB    0.5908 1.49393e4   383.22903  91.3693
   2  18.872 BV    0.5089 1411.16113   34.09003   8.6307

Totals :                  1.63504e4   417.31907

=====================================================================
                    *** End of Report ***
```

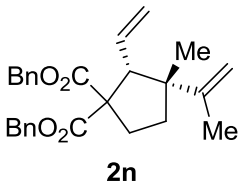


racemic **2n**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-6-10 3:16:27
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-6-10 3:02:03  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```

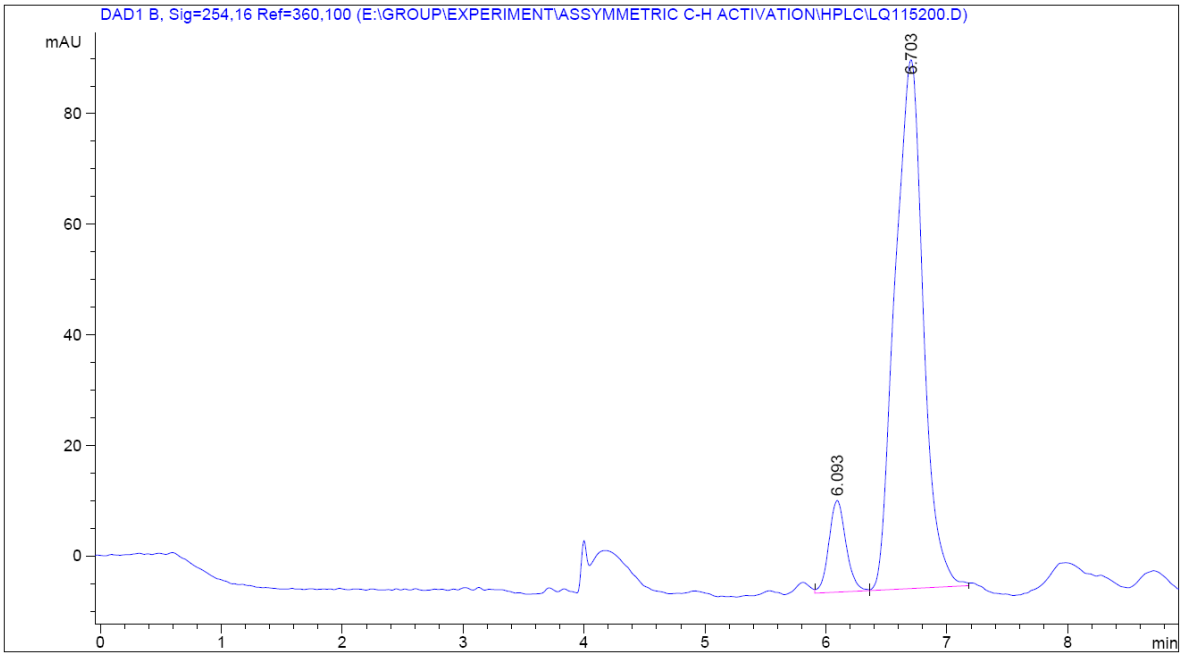



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.127 VB    0.1836  635.87244   52.38219  49.3179
   2   6.732 BB    0.1998  653.46161   48.93320  50.6821

Totals :                  1289.33405  101.31539


=====================================================================
                      *** End of Report ***
```

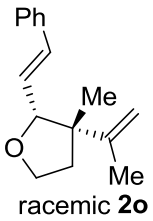


2n

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-6-10 3:03:18
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-6-10 3:02:03  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 99:1
```

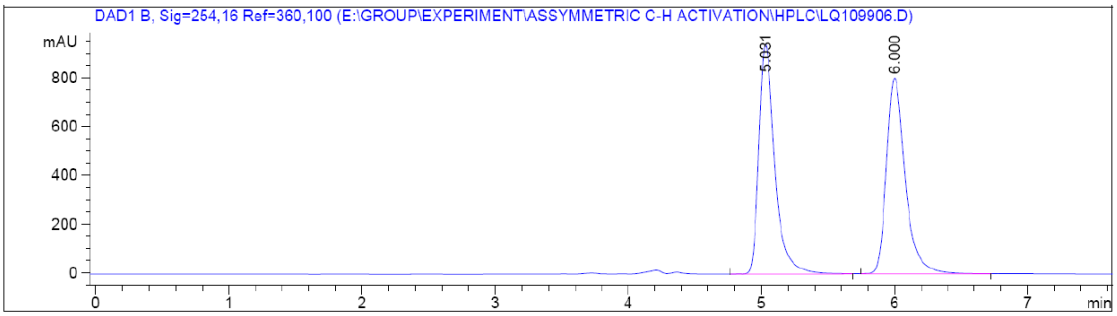



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.093 VV    0.1489  163.38475   16.58979   9.5235
   2   6.703 VB    0.2313 1552.21045   95.65040  90.4765

Totals :                   1715.59520  112.24018

=====================================================================
                        *** End of Report ***
```

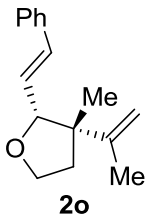


racemic **2o**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-6-4 12:09:13
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-6-4 12:07:15  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 mL/min, Hexane:iPrOH = 97:3
```

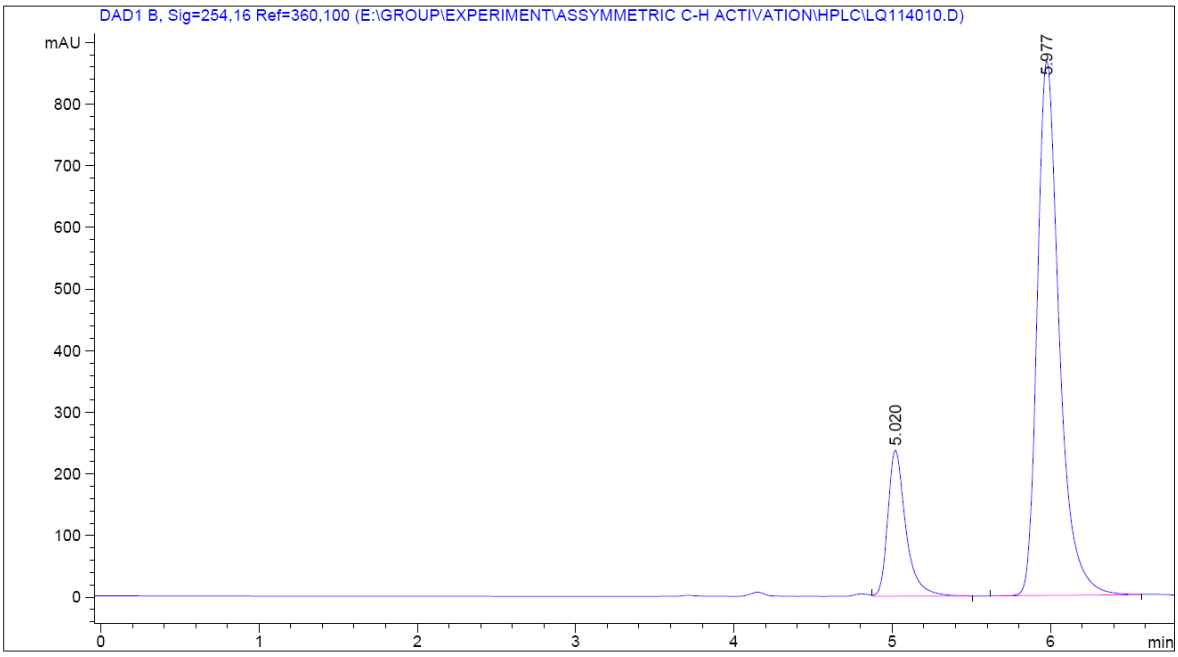



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


 Signal 2: DAD1 B, Sig=254,16 Ref=360,100

 Peak RetTime Type  Width     Area      Height     Area
   #   [min]        [min]   [mAU*s]     [mAU]       %
 ----|-------|----|-------|----------|----------|--------|
    1   5.031 BB    0.1248 7815.78906  941.58856  49.7998
    2   6.000 BB    0.1485 7878.62598  802.85468  50.2002

 Totals :                  1.56944e4  1744.44324


 ================================================================================
                          *** End of Report ***
```



2o

```
Acq. Operator    : LQ
Acq. Instrument  : Instrument 1                    Location :   -
Injection Date   : 2010-6-4 13:01:01
Acq. Method      : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed     : 2010-6-4 12:20:21  by LQ
                   (modified after loading)
Analysis Method  : C:\Chem32\1\METHODS\DEF_LC.M
Last changed     : 2004-4-7 0:10:12
Sample Info      : OD-H, 1.0 mL/min, Hexane:iPrOH = 97:3
```

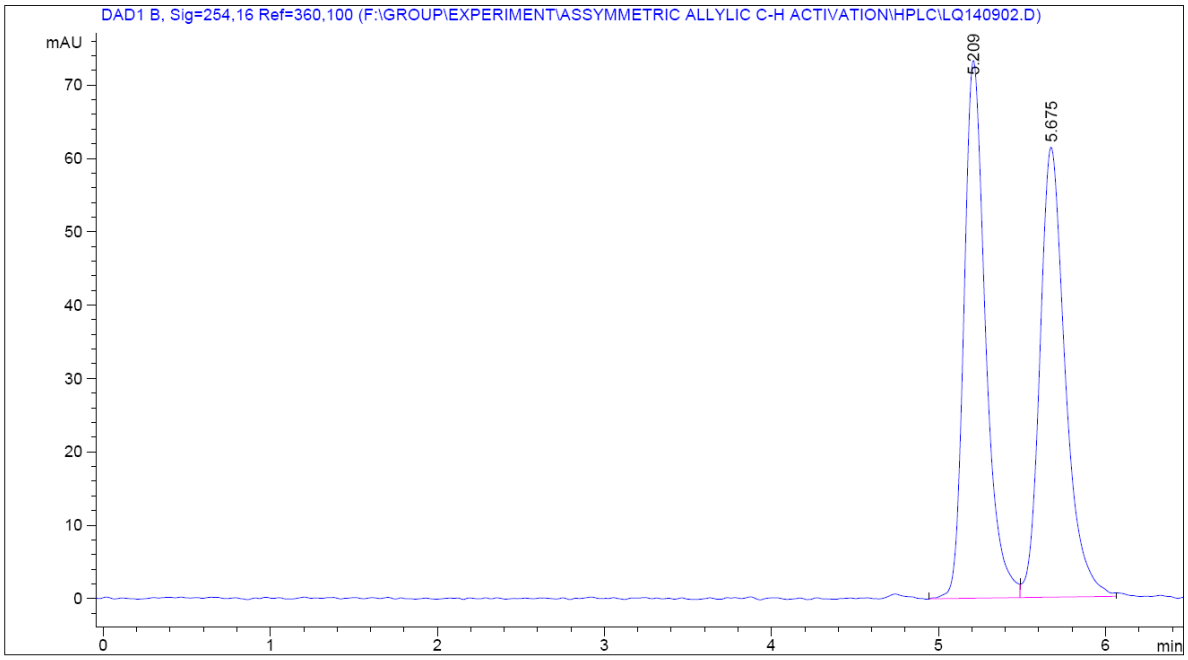



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.020 VB    0.1201 1869.56165  236.78214  18.2427
   2   5.977 BB    0.1467 8378.72266  867.52002  81.7573

Totals :                  1.02483e4  1104.30215

=====================================================================
                      *** End of Report ***
```

4.7 HPLC for the nonlinear effect study

Racemic ligand **B**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:07:35
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```

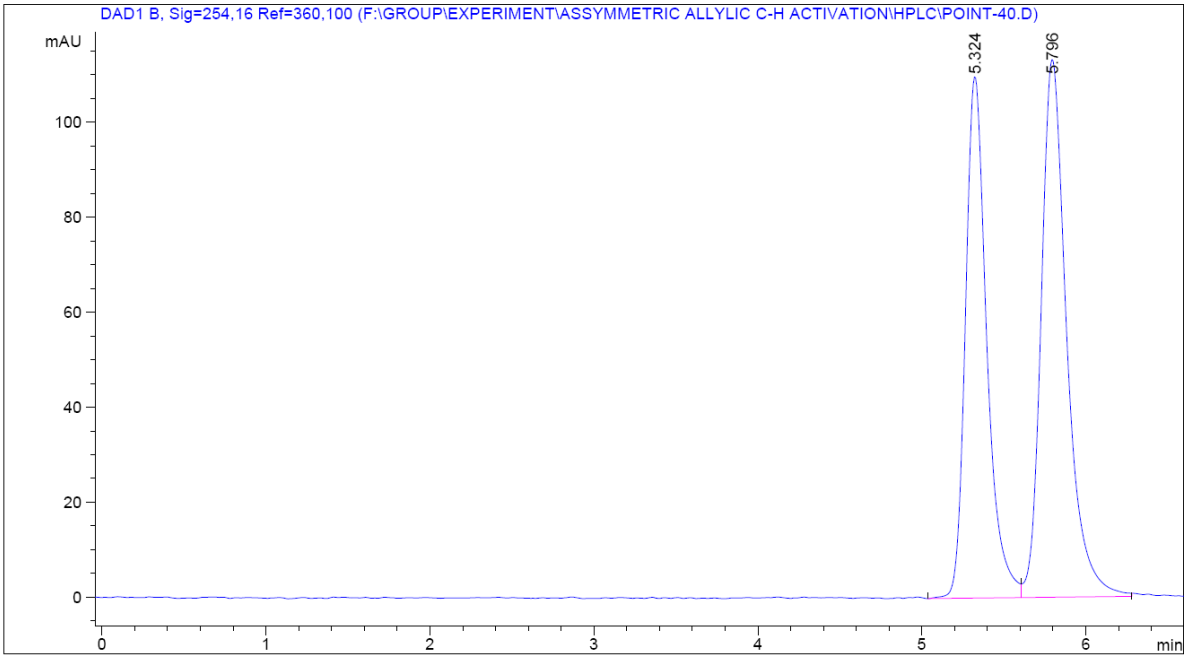



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.209 BV    0.1363  655.92078   73.37894  50.2269
   2   5.675 VB    0.1615  649.99390   61.38054  49.7731

Totals :                  1305.91467  134.75948

=====================================================================
                        *** End of Report ***
```

1. The first spot

(1) ee of ligand **B**

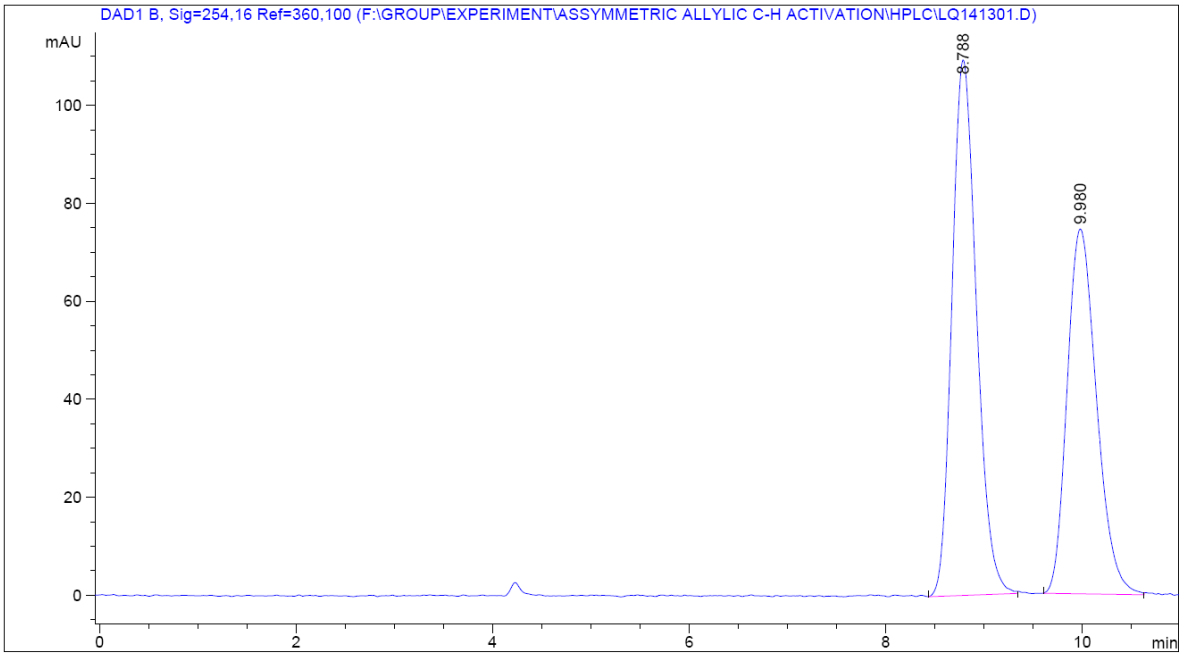
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:45:25
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.324 VV    0.1356  993.81427  109.81264  44.7828
   2   5.796 VB    0.1643 1225.37427  113.22057  55.2172

Totals :                   2219.18854  223.03321


=====================================================================
                        *** End of Report ***
```

(2) ee of the corresponding product **2a**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-26 10:56:40
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-26 8:54:04  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```

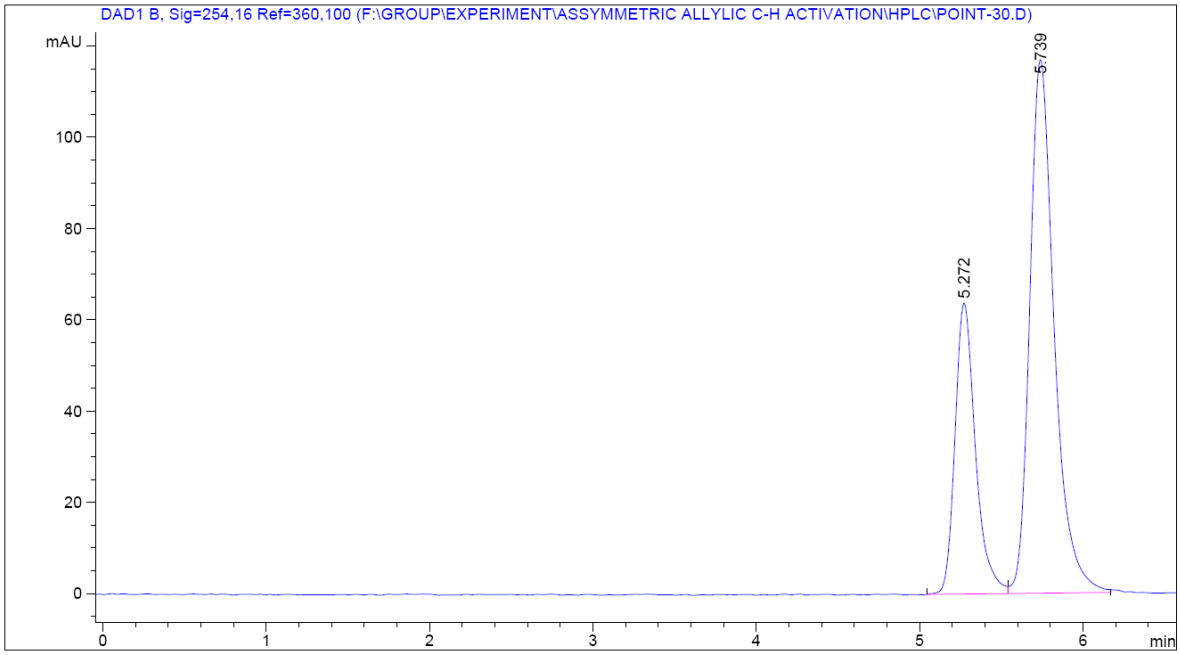



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.788 VB    0.2663 1895.12634  109.27471  55.0367
   2   9.980 BB    0.3187 1548.26001   74.43362  44.9633

Totals :                  3443.38635  183.70834

=====================================================================
                        *** End of Report ***
```

2 The second spot

(1) ee of the ligand **B**

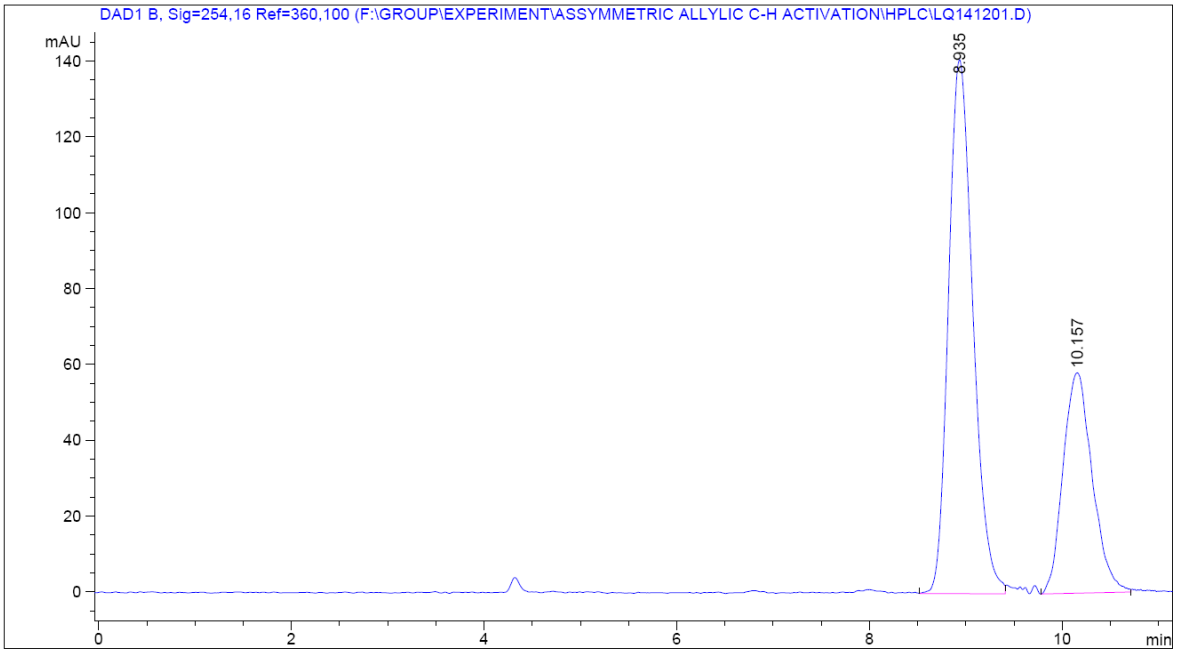
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:38:10
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.272 BV    0.1314  554.82123   63.81714  31.2468
   2   5.739 VB    0.1597 1220.78625  116.99271  68.7532

Totals :                  1775.60748  180.80984


=====================================================================
                        *** End of Report ***
```

(2) ee of the corresponding product **2a**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-26 10:30:45
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-26 8:54:04  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```

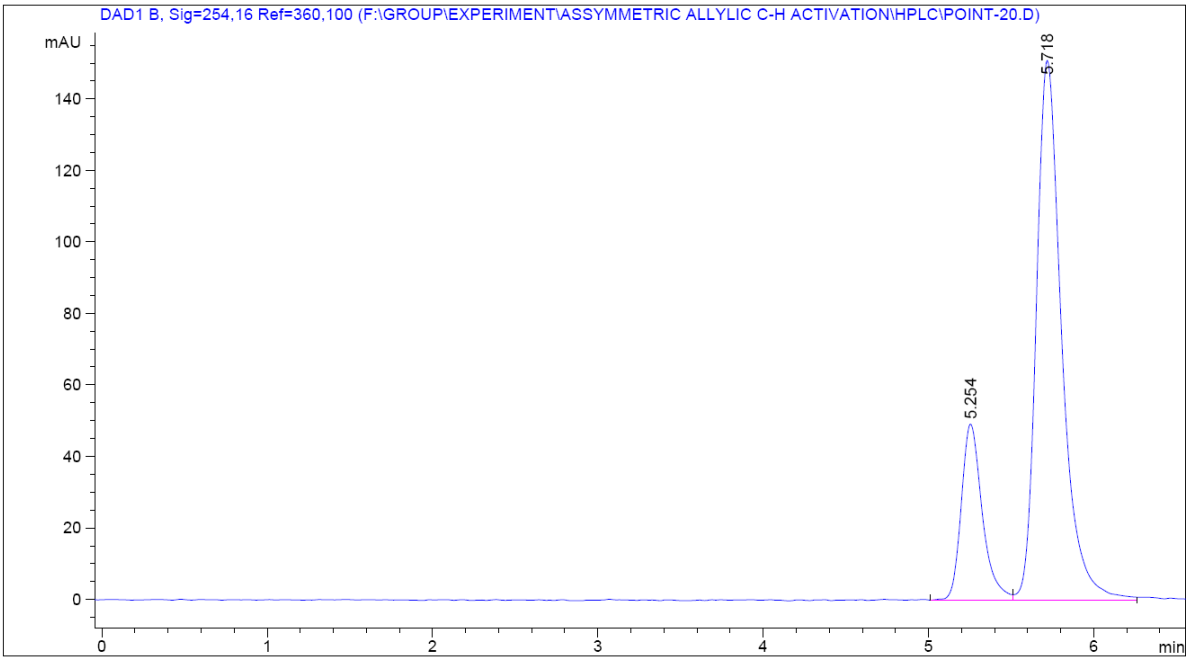



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.935 VV    0.2632 2478.08887  140.90225  66.9347
   2  10.157 VV    0.2896 1224.16162   58.14331  33.0653

Totals :                  3702.25049  199.04556

=====================================================================
                        *** End of Report ***
```

3 The third spot

(1) ee of the ligand **B**

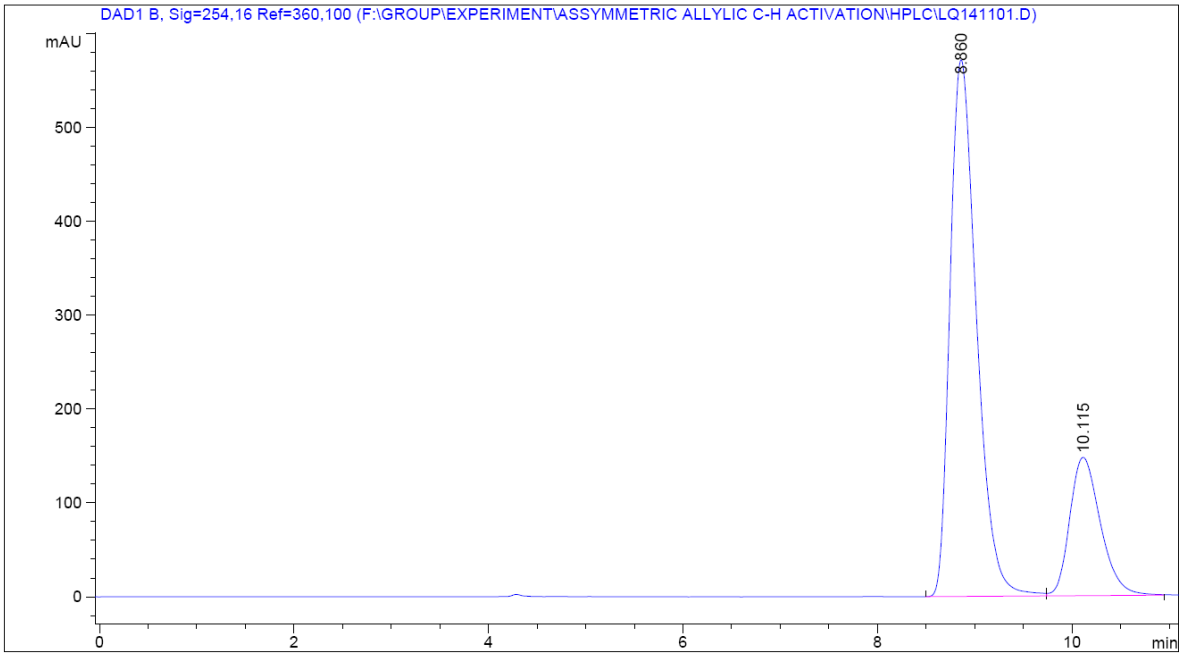
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:30:55
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.254 VV    0.1331  435.63586   49.29656  21.2710
   2   5.718 VB    0.1606 1612.38940  151.02728  78.7290

Totals :                  2048.02527  200.32384


=====================================================================
                        *** End of Report ***
```

(2) ee of the corresponding product **2a**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-26 11:46:12
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-26 11:21:23  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```

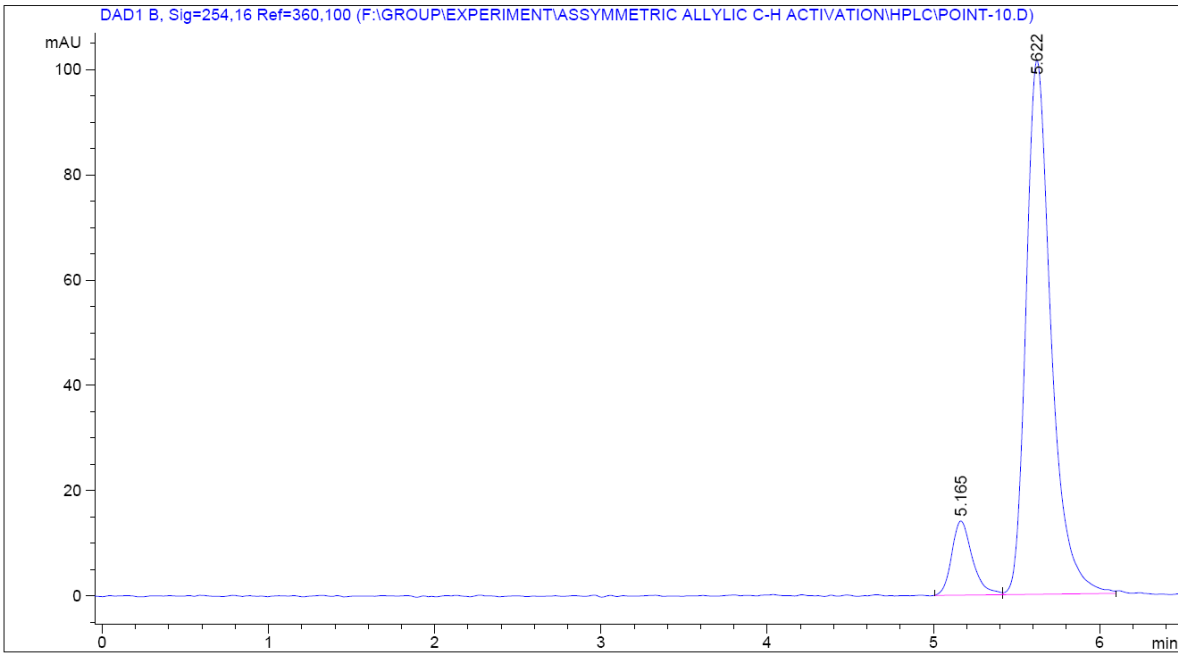



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.860 BV    0.2907 1.08150e4   571.59924  77.0029
   2  10.115 VB    0.3379 3229.93799  147.24707  22.9971

Totals :                  1.40450e4   718.84631

=====================================================================
                        *** End of Report ***
```

4 The forth spot

(1) ee of the ligand **B**

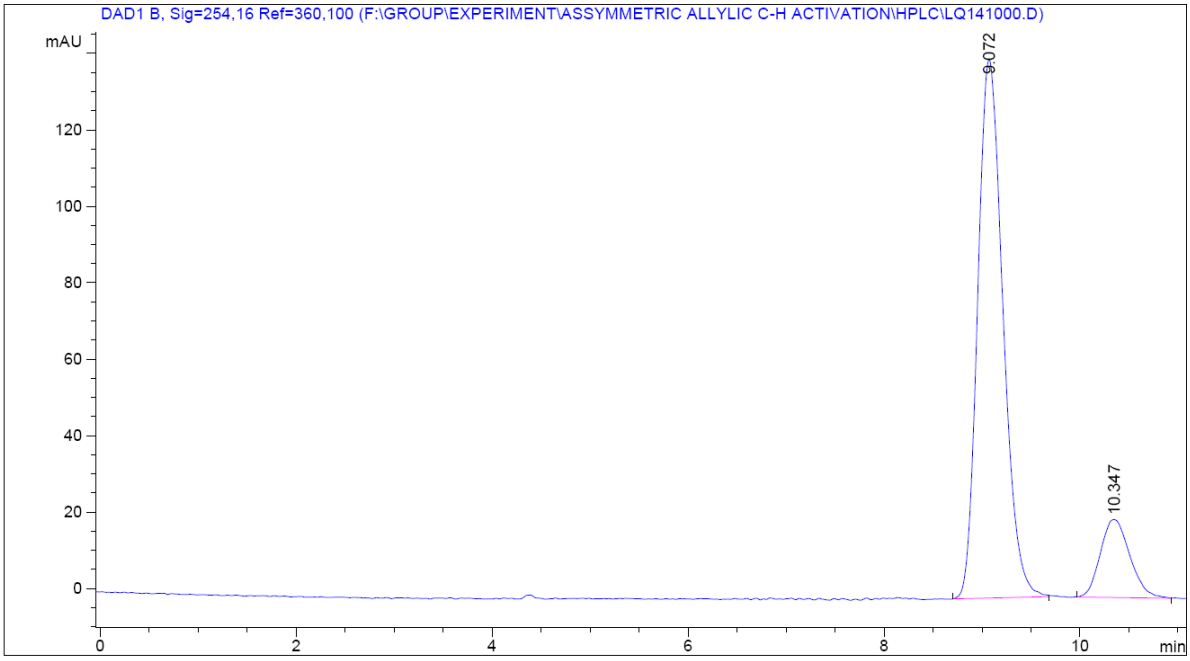
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:23:33
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.165 BV    0.1307  121.58602   14.08877  10.2797
   2   5.622 VB    0.1579 1061.18945  101.56117  89.7203

Totals :                  1182.77547  115.64994

=====================================================================
                      *** End of Report ***
```

(2) ee of the corresponding product **2a**

```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-26 9:51:55
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-26 8:54:04  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 1.0 ml/min, Hexane:iPrOH = 95:5
```

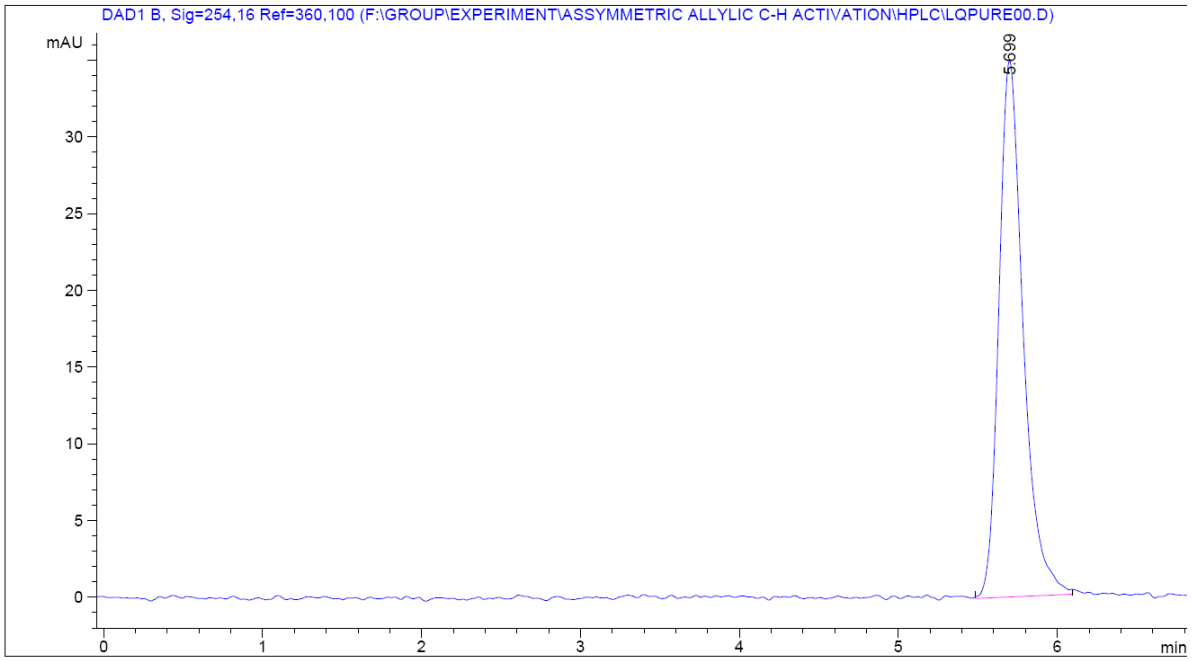



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.072 BB    0.2786 2519.34277  140.89529  85.5186
   2  10.347 BB    0.3022  426.61734   20.38385  14.4814

Totals :                  2945.96011  161.27915

=====================================================================
                      *** End of Report ***
```

5 The fifth spot

(1) ee of the ligand **B**

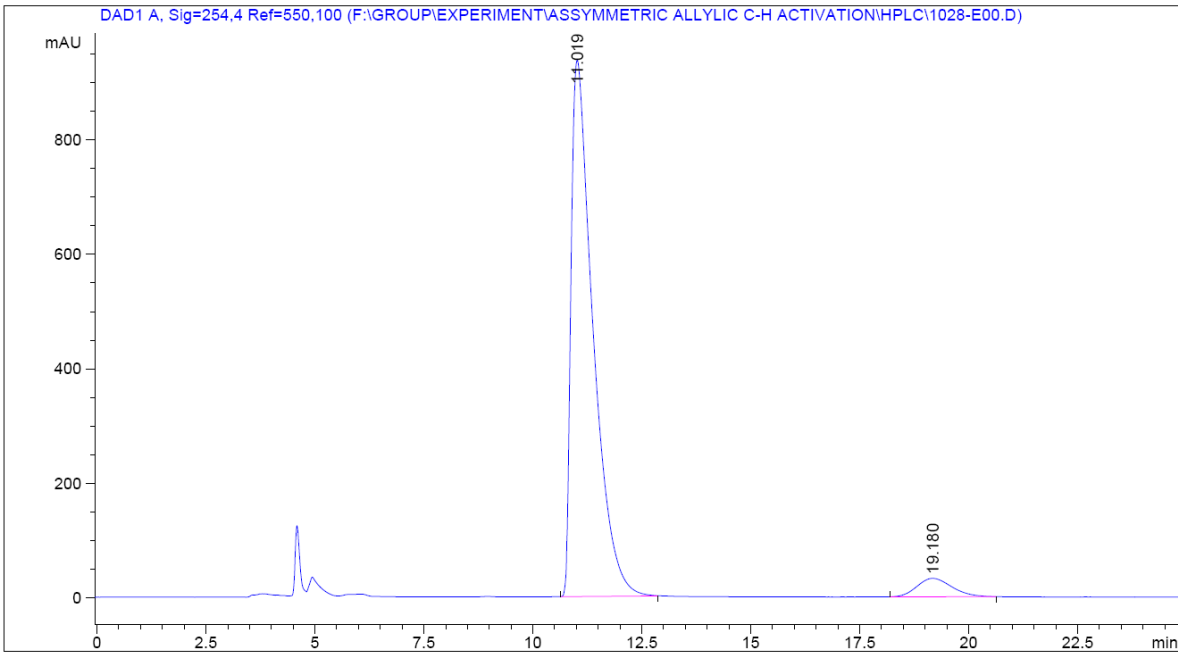
```
Acq. Operator   : LQ
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-11-25 5:15:15
Acq. Method     : C:\HPCHEM\1\METHODS\DEF_LC.M
Last changed    : 2010-11-25 4:58:06  by LQ
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OD-H, 0.9 ml/min, Hexane:iPrOH = 95:5
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.699 BB    0.1623  372.72647   34.98166 100.0000

Totals :                   372.72647   34.98166


=====================================================================
                        *** End of Report ***
```

(2) ee of the corresponding product **2a**

```
Acq. Operator   : LQ-Yu
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 2010-4-20 6:10:24
Acq. Method     : C:\HPCHEM\1\METHODS\BATCH.M
Last changed    : 2010-4-20 5:36:58  by LQ-Yu
                  (modified after loading)
Analysis Method : C:\Chem32\1\METHODS\DEF_LC.M
Last changed    : 2004-4-7 0:10:12
Sample Info     : OJ-H hexane:iPr = 93:7 1.0 ml/min
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.019 BB    0.5133 3.26917e4   936.31732  94.7910
   2  19.180 BB    0.8236 1796.50220   32.26457   5.2090

Totals :                  3.44882e4   968.58189

=====================================================================
                      *** End of Report ***
```