Supporting Information

In situ-Generated Chiral Co(I)-Catalyst for Asymmetric [2+2+2] Cycloadditions of Triynes

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General methods

All experiments were carried out under inert gas atmosphere (argon) in flame dried Schlenk tubes or glass reaction vials. The anhydrous solvents (tetrahydrofuran, toluene, dichloromethane and *n*-hexane) were dried in a solvent purification system MD-5 from Inert (former Innovative Technology). All NMR spectra were recorded on a Bruker AV 300, AV 400 or Fourier 300 NMR spectrometer. HPLC-analysis was performed on a Hewlett Packard HP 1100 with DAD, chiralyzer and RI-detector and chiral columns. HRMS (ESI-TOF) was performed at a Agilent 6210 Time-of-Flight LC/MS. Elemental analysis was performed at a Perkin Elmer AAS-Analyst 300 (Co), Leco Microanalysator-TruSpec CHNS (C, H), Radiometer Analytical SAS (Titrator) Titralab 870-TIM 870 (Br) and a Perkin Elmer UV/VIS-spectrometer Lambda 2 (P).

$CoBr_2$ (0.05 M) and ZnI_2 (0.25 M) were used as solutions in dry THF.

Commercially available chiral *P,P*- and *P,N*-ligands

(*aR*)-BINAP (**4**)   (*aS*)-QUINAP (**5**)   (*aR*)-QUINAP (**5**)   (*R*)-PHOX (**11**)

(*R,aR*)-*N*-PINAP (**6**)   (*R,aS*)-*N*-PINAP   (*S,aR*)-*N*-PINAP   (*R,aR*)-*O*-PINAP   (*R,aS*)-*O*-PINAP

(*aR,S*)-Ph-Bn-SIPHOX (**12**)   (*S,S*)-Et-DUPHOS (**10**)
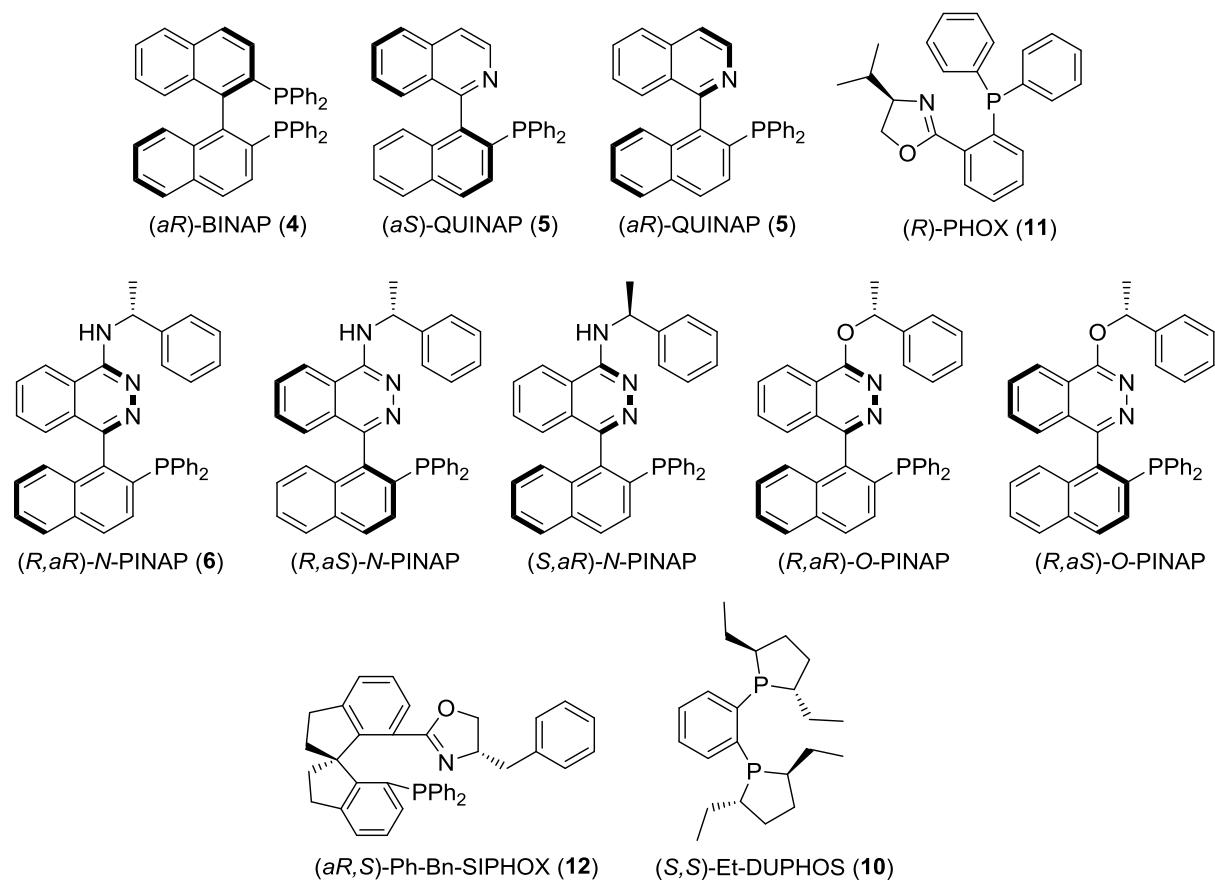
Scheme S1: Available chiral *P,P*- and *P,N*-ligands

## Ligand screening in glass reaction vial
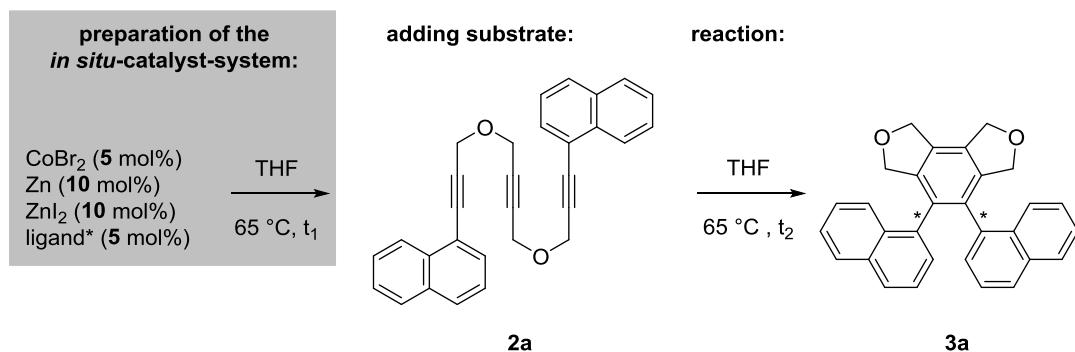
Table S1. Screening of chiral ligands in reaction glass vial under "semi-oxygen free" conditions

Entry	Chiral ligand	t_1 [h]	t_2 [h]	yield [%]	d/l: $meso$[a]	Sel. [b] [% ee]
1	no ligand	0.5	40	73[c]	1.4:1	--
2	(aR)-BINAP (**4**)	5 min	17	58	1.3:1	--
3	(aR)-QUINAP (**5**)	0.5	22	70	1.4:1	(+)6
4	(aS)-QUINAP (**5**)	2	21	>95	1.4:1	(-)57
5	(R)-PHOX (**11**)	2	26	77	1:1.2	(-)32
6	(R, aR)-N-PINAP (**6**)	0.5	16	66	1:1.2	(+)17
7	(R, aS)-N-PINAP	0.5	16	>95	1:1.3	(-)25
8	(S, aR)-N-PINAP	0.5	16	58	1:1	(+)11
9	(R, aR)-O-PINAP	0.5	16	51	1:1.4	--
10	(R, aS)-O-PINAP	0.5	16	63	1:1.5	--

[a] Determined by integration from the proton NMR spectra. [b] Determined by chiral HPLC. [c] Conditions: 10 mol% CoBr$_2$, 10 mol% ZnI$_2$, 30 mol% Zn.

Chiral ligand screening for catalytic reactions with CoBr$_2$ in a reaction glass vial

CoBr$_2$ (5 mol% in regard to the triyne), the respective chiral ligand (5 mol% in regard to the triyne) and Zn (10 mol% in regard to the triyne) were dissolved in THF (1 mL), ZnI$_2$ (10 mol% in regard to the triyne) was added and the solution stirred at 65 °C for 5 min-2 h.

After cooling to room temperature the triyne **2a** (0.25 mmol) was added and the mixture again heated to 65 °C for 16-40 h. At the end of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography (c-hexane/ethyl acetate 4:1, v/v) to yield the benzene derivative. The ee values were determined by chiral HPLC-analysis. (Cellulose 2, n-heptane/isopropanol 95:5, v/v, 1 mL/min).

Optimization of the catalytic reactions with CoBr$_2$ in a Schlenk tube

CoBr$_2$ (1-5 mol% in regard to the triyne), the respective chiral ligand (1-5 mol% in regard to the triyne), Zn (2-10 mol% in regard to the triyne) were dissolved in THF (1 mL), ZnI$_2$ (2-10 mol% in regard to the triyne) was added and the solution stirred at 0-65 °C for 1-2 h. After the triyne **2a** (0.25 mmol) was added the mixture was again stirred at 0-65 °C for 6-27 h. At the end of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography (*c*-hexane/ethyl acetate 4:1, v/v) to yield the benzene derivative. The *ee* values were determined by chiral HPLC-analysis. (Cellulose 2, *n*-heptane/isopropanol 95:5, v/v, 1 mL/min).

Screening of catalyst loading

2a   **3a**
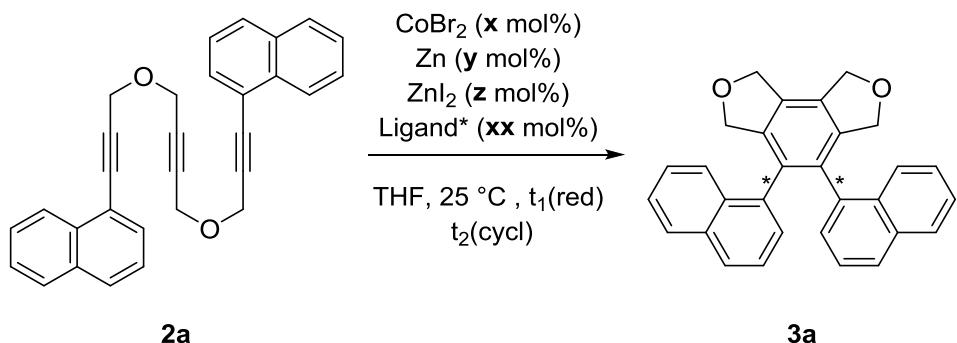
Table S2. Screening of the catalysts loading

#	x	y	z	ligand*	t$_1$	t$_2$	yield	d/l:	Sel.
	[mol%]			[mol%]	[h]	[h]	[%]	meso[a]	[% ee][b]
1	2.5	5	5	(*aR*)-QUINAP (**5**) [2.5]	1	4	73	1.3:1	(+)76
2	1	2	2	(*aR*)-QUINAP (**5**) [1]	1	21	70	1.3:1	(+)81

[a] determined out of the Integrals in the proton NMR spectra. [b] determined by chiral HPLC.

Synthesis of cobalt(II)-precursor complex 7

To a solution of (*R,aR*)-*N*-PINAP (**6**) (0.10 g, 0.18 mmol) in 8 mL THF a solution of CoBr$_2$ (3.55 mL, 0.18 mL, 0.05 M in THF) in THF was added and stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue washed twice with *n*-hexane and dried in vacuo. The resulting green solid was recrystallized under argon atmosphere from a dichloromethane/THF mixture, yielding green crystals.
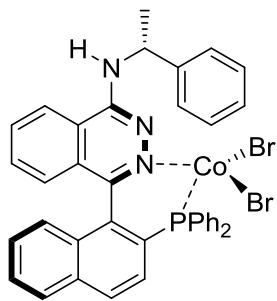
| EA:	calc.:	C 58.64	H 3.88	Br 20.53	Co 7.57	P 3.98
	found:	C 58.82	H 3.58	Br 18.81	Co 6.46	P 3.88

Crystal Structure data: CCDC 1418399 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oxidation of (*R,aR*)-*N*-PINAP (6) to SI-I

A suspension of (*R,aR*)-*N*-PINAP (**6**) (0.10 g, 0.18 mmol) in hydrogenperoxide (3.00 mL, 29.0 mmol, 30% in H_2O) was stirred at room temperature for 24 h. The reaction was stopped by adding water to the solution and was extracted thrice with dichloromethane. The combined organic phases were washed with brine, dried with sodium sulfate and the solvent was evaporated. The resulting product **SI-I** was isolated as colorless oil (92 mg, 89%) without further purification.
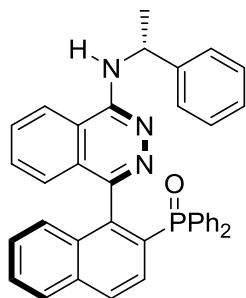
SI-I

^{1}H-NMR (CDCl$_3$, 300 MHz): δ = 1.72 (d, *J* = 6.8 Hz, 3H), 5.38 (s$_{br}$, 1H), 5.71 (p, *J* = 6.4 Hz, 1H), 6.26-6.34 (m, 2H), 6.65-6.72 (m, 1H), 6.83-6.87 (m, 1H), 6.87-6.91 (m, 1H), 6.95 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.10 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.25-7.29 (m, 1H), 7.29-7.32 (m, 1H), 7.34-7.42 (m, 4H), 7.42-7.49 (m, 2H), 7.50-7.58 (m, 3H), 7.59-7.64 (m, 2H), 7.88-7.92 (m, 1H), 7.94 (dt, *J* = 8.3, 1.5 Hz, 2H), 8.11 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.28 (dd, *J* = 10.9, 8.7 Hz, 1H) ppm. **^{13}C-NMR** (CDCl$_3$, 75 MHz): δ = 22.1, 50.2, 117.0, 119.9, 120.4, 126.6, 126.8, 126.9, 127.0, 127.1, 127.2, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6,

128.7, 129.1, 129.3, 129.7, 129.8, 130.5, 130.7, 130.9, 131.0, 131.1, 131.3, 131.4, 131.5, 131.6, 132.4, 132.6, 132.7, 144.2, 152.2 ppm. **^{31}P-NMR** (CDCl$_3$, 121 MHz): δ = 31.65 ppm. **HRMS** (ESI-TOF) C$_{38}$H$_{30}$N$_3$OP: calc.: 576.2199 [M+H]$^+$, 598.2019 [M+Na]$^+$ found: 576.2204 [M+H]$^+$, 598.2025 [M+Na]$^+$

Catalytic evaluation of ligand SI-I

CoBr$_2$ (0.0.6 mL, 0.05 M in THF, 2.5 mol% in regard to the triyne), ligand **SI-I** (1.8 mg, 2.5 mol% in regard to the triyne), Zn (0.41 mg, 5 mol% in regard to the triyne) were dissolved in THF (1 mL), ZnI$_2$ (0.03 mL, 0.25 M in THF, 5 mol% in regard to the triyne) was added and the solution stirred at 25 °C for 1 h. After the triyne **2a** (0.1 mL, 1.25 M in THF, 0.125 mmol) was added the mixture was again stirred at 25 °C for 4 d. At the end of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography (*c*-hexane/ethyl acetate 4:1, v/v) to yield the benzene derivative **3a** (48 mg, 93%) of a racemic mixture. The *ee* value was determined by chiral HPLC-analysis. (Cellulose 2, *n*-heptane/isopropanol 95:5, v/v, 1 mL/min).

Substrate screening for catalytic reactions

Co-precursor **7** (2.5-10 mol% in regard to the triyne) or CoBr$_2$ (2.5-10 mol% in regard to the triyne) and (*aR*)-/(*aS*)-QUINAP (**5**) (2.5-10 mol% in regard to the triyne) and Zn (5-20 mol% in regard to the triyne) were dissolved in THF/toluene (1 mL) and ZnI$_2$ (5-20 mol% in regard to the triyne) was added and the solution stirred at 25-95 °C for a specific time. After cooling to room temperature the triyne **2a** (0.1-0.5 mmol) was added and the mixture again was stirred at the described temperature for a specific time. At the end of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography to yield the benzene derivative. The *ee* values were determined by chiral HPLC-analysis.

For every compound the specific reaction conditions are written in parentheses: (amount of substrate, catalyst loading, solvent, reaction temperature, time, eluent for column chromatography, yield, *d/l*:*meso* ratio, aggregation state)

Synthesis of cyclisation substrates

Compounds 2a, **2b**:

Synthesis according to the published procedure by Shibata et al. The analytical data were in accordance with the reported data.[1]

All other triynes have been synthesized by literature-known procedures we have published in preceding work and the analytical data were in accordance with the reported data.[2]

Characterization of cyclization products

Compound 3a:
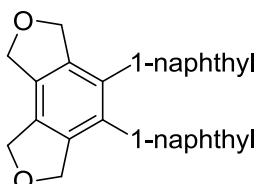
The compound was identified by NMR and MS and comparison with reported data.[1]

Optical rotation: $[\alpha]_D^{22}$ = 224.83 (c 1.0052, CHCl$_3$, 85% *ee*) obtained by the reaction described in Table 2, Entry 2.

Compound 3b:

9-phenanthrenyl:

(0.125 mmol, 2.5 mol% **7**, THF, 25 °C, 23 h, *c*-hex/EE (4:1, v/v), 43 mg (75%), (+)30% *ee*, 1.8:1 (*d/l:meso*, HPLC area), colorless solid)

NMR data were in accordance with published data.[1]

Conditions of the HPLC-analysis: Reprosil, *n*-heptane/EtOH 90:10 (v/v), 0.5 mL/min.

Compound 3c:

4-Me-1-naphthyl

(0.125 mmol, 2.5 mol% **7**, THF, 25 °C, 16 h, *c*-hex/EE (10:1, v/v), 51 mg (92%), (+)19% *ee*, 1.4:1 (*d/l:meso*, HPLC area), colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/Isopropanol 98:2 (v/v), 0.8 mL/min.

Compound 3d:
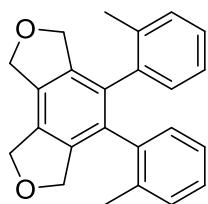
(0.25 mmol, 5 mol% **7**, THF, 65 °C, 18 h, *c*-hex/EE (4:1, v/v), 77 mg (90%), (+)15% *ee*, 1.4:1 (*d/l:meso*, HPLC area), colorless solid)

NMR data were in accordance with published data.[2]

Conditions of the HPLC-analysis: Cellulose 1, *n*-heptane/EtOH 99:1 (v/v), 0.4 mL/min.

Compound 3e:
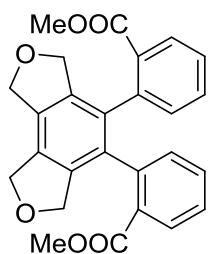
(0.125 mmol, 2.5 mol% **7**, THF, 25 °C, 17 h, *c*-hex/EE (4:1, v/v), 23 mg (42%), (+)24% *ee*, 2.7:1 (*d/l:meso*), colorless solid)

(0.25 mmol, 5 mol% (*aS*)-**5** + CoBr$_2$, THF, 65 °C, 17 h, *c*-hex/EE (4:1, v/v), 94 mg (87%), rac, 1:1.3 (*d/l:meso*), colorless solid)

NMR data were in accordance with published data.[2]

Conditions of the HPLC-analysis: Reprosil, *n*-heptane/EtOH 95:5 (v/v), 1 mL/min.

Compound 3f:

4-quinolinyl

(0.125 mmol, 10 mol% **7**, THF, 25-65 °C, 7 d, *n*-hex/THF (1:2, v/v + 0.5% NEt$_3$), 42 mg (81%), (+)46% *ee*, 1.2:1 (*d/l:meso*), yellow solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Eurocel, *n*-heptane/EtOH 90:10 (v/v), 0.5 mL/min.

Compound 3g:

4-isoquinolinyl

(0.125 mmol, 10 mol% **7**, THF, 25-65 °C, 6 d, *n*-hex/THF (1:2, v/v + 0.5% NEt$_3$), 45 mg (86%), (-)66% *ee*, 1.2:1 (*d/l:meso*), yellow solid)

8

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 1, *n*-heptane/EtOH 90:10 (v/v), 1 mL/min.

Compound 3h:
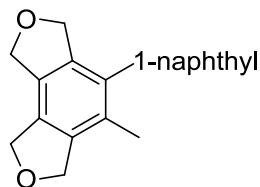
(0.25 mmol, 2.5 mol% **7**, THF, 25 °C, 17 h, *c*-hex/EE (4:1, v/v), 74 mg (>95%), (+)78% *ee*, colorless solid)

(0.25 mmol, 5 mol% (*aR*)-**5** + CoBr$_2$, THF, 25 °C, 17 h, *c*-hex/EE (4:1, v/v), 75 mg (>95%), (+)7% *ee*, colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/isopropanol 95:5 (v/v); 0.5 mL/min.

Compound 3i
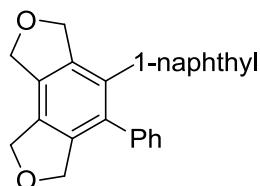
(0.25 mmol, 2.5 mol% **7**, THF, 25 °C, 19 h, *c*-hex/EE (4:1, v/v), 67 mg (74%), (-)55% *ee*, colorless solid)

(0.25 mmol, 2.5 mol-% (*aR*)-**5** + CoBr$_2$, THF, 25 °C, 17 h, *c*-hex/EE (4:1, v/v), 86 mg (94%), (-)18% *ee*, colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Eurocel, *n*-heptane/isopropanol 95:5 (v/v), 0.5 mL/min.

Compound 3k:
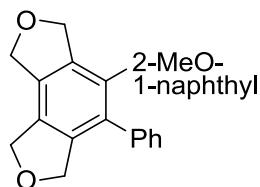
(0.25 mmol, 2.5 mol% **7**, THF, 25 °C, 19 h, *c*-hex/EE (4:1, v/v), 69 mg (70%), (+)12% *ee*, colorless solid)

9

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/isopropanol 95:5 (v/v), 0.5 mL/min.

Compound 3l:
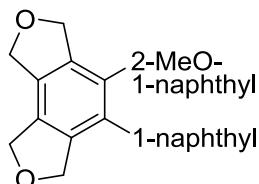
(0.125 mmol, 2.5 mol% **7**, THF, 25 °C, 15 h, *c*-hex/EE (6:1, v/v), F1: 15 mg (27%); F2: 19 mg (34%), F1: (+)39% *ee*; F2: (+)32% *ee*, colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/EtOH 95:5 (v/v), 1 mL/min.

Compound 9a:
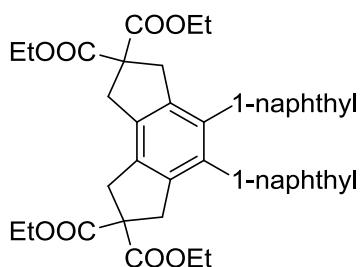
(0.125 mmol, 2.5 mol% **7**, THF, 25-65 °C, 43 h, *c*-hex/EE (4:1, v/v), 47 mg (53%), (-)78% *ee*, 2.2:1 (*d/l:meso*, HPLC area), colorless solid)

(0.125 mmol, 2.5 mol% **7**, toluene, 25-90 °C, 41 h, pentane/EE (6:1, v/v), 84 mg (>95%), (-)67% *ee*, 1.9:1 (*d/l:meso*, HPLC area), colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Eurocel, *n*-heptane/EtOH 99:1 (v/v), 0.5 mL/min.

Compound 9b:
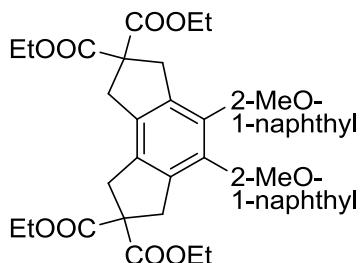
(0.125 mmol, 2.5 mol% **7**, THF, 25-65 °C, 41 h, *c*-hex/EE (4:1, v/v), 30 mg (32%), (-)13% *ee*, no *meso*-form detected), colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/EtOH 95:5 (v/v), 0.5 mL/min.

Compound 9c:
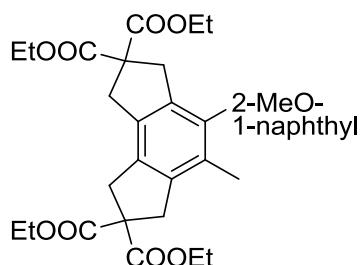
(0.25 mmol, 2.5 mol% (*aR*)-**5** + CoBr$_2$, THF, 25-65 °C, 44 h, *c*-hex /EE (10:1, v/v), 141 mg (91%), (-)17% *ee*, yellow oil)
NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/isopropanol 95:5 (v/v), 1 mL/min.

Compound 9d:
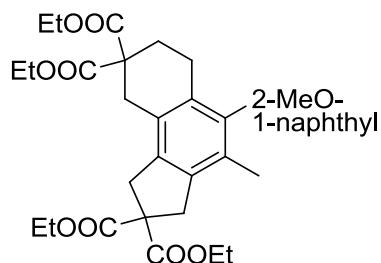
(0.15 mmol, 10 mol% **7**, toluene, 25-95 °C, 17 h, *c*-hex/EE (4:1, v/v), 60 mg (63%), (+)60% *ee*, colorless solid)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Reprosil, *n*-heptane/isopropanol 95:5 (v/v), 1 mL/min.

Compound 9e:
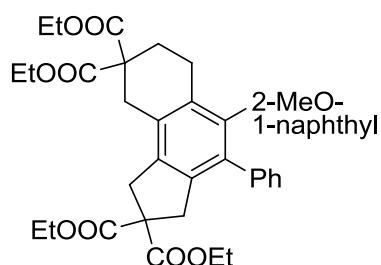
(0.15 mmol, 10 mol% **7**, toluene, 25-95 °C, 17 h, *c*-hex/EE (4:1, v/v), 90 mg (87%),

(-)11% *ee*, colorless sirup)

NMR data were in accordance with published data. [2]

Conditions of the HPLC-analysis: Cellulose 2, *n*-heptane/isopropanol 95:5 (v/v), 1 mL/min.

## NMR spectra of compound SI-I:

¹H-NMR:
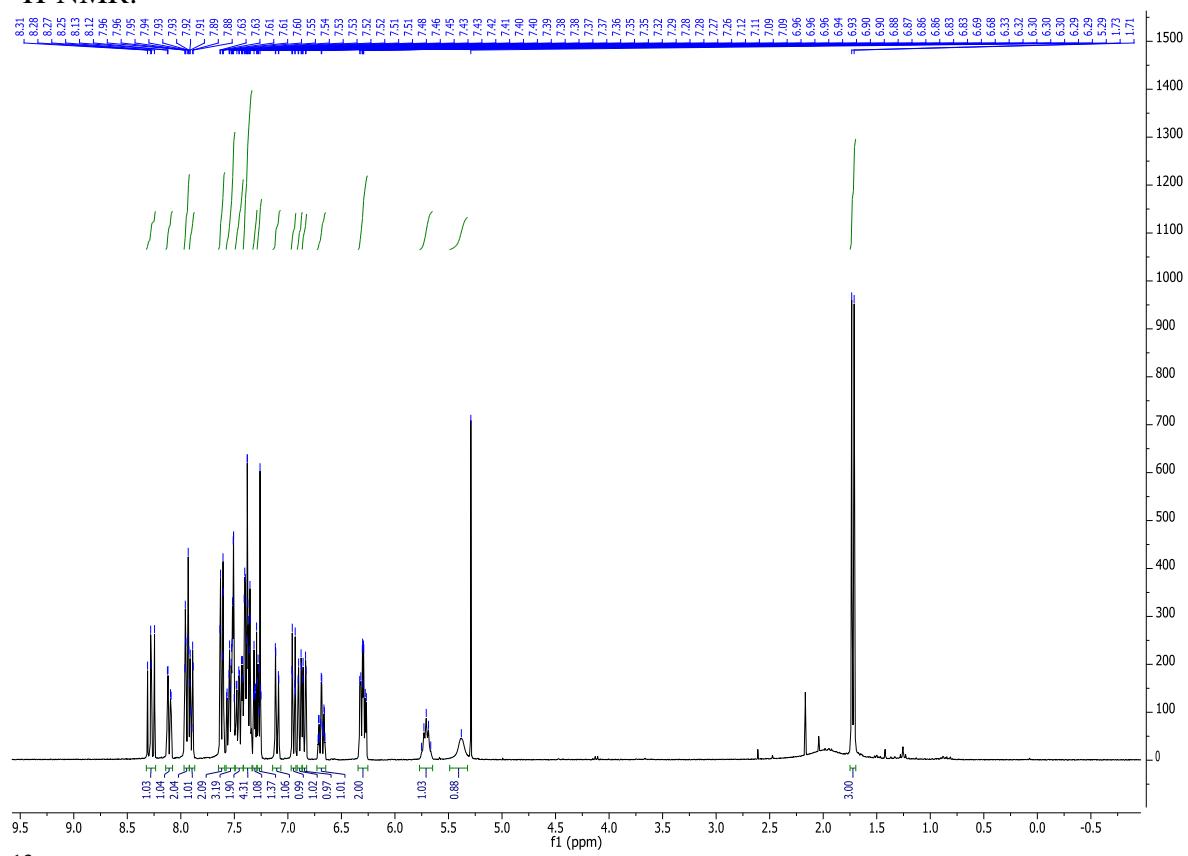
¹³C-NMR:
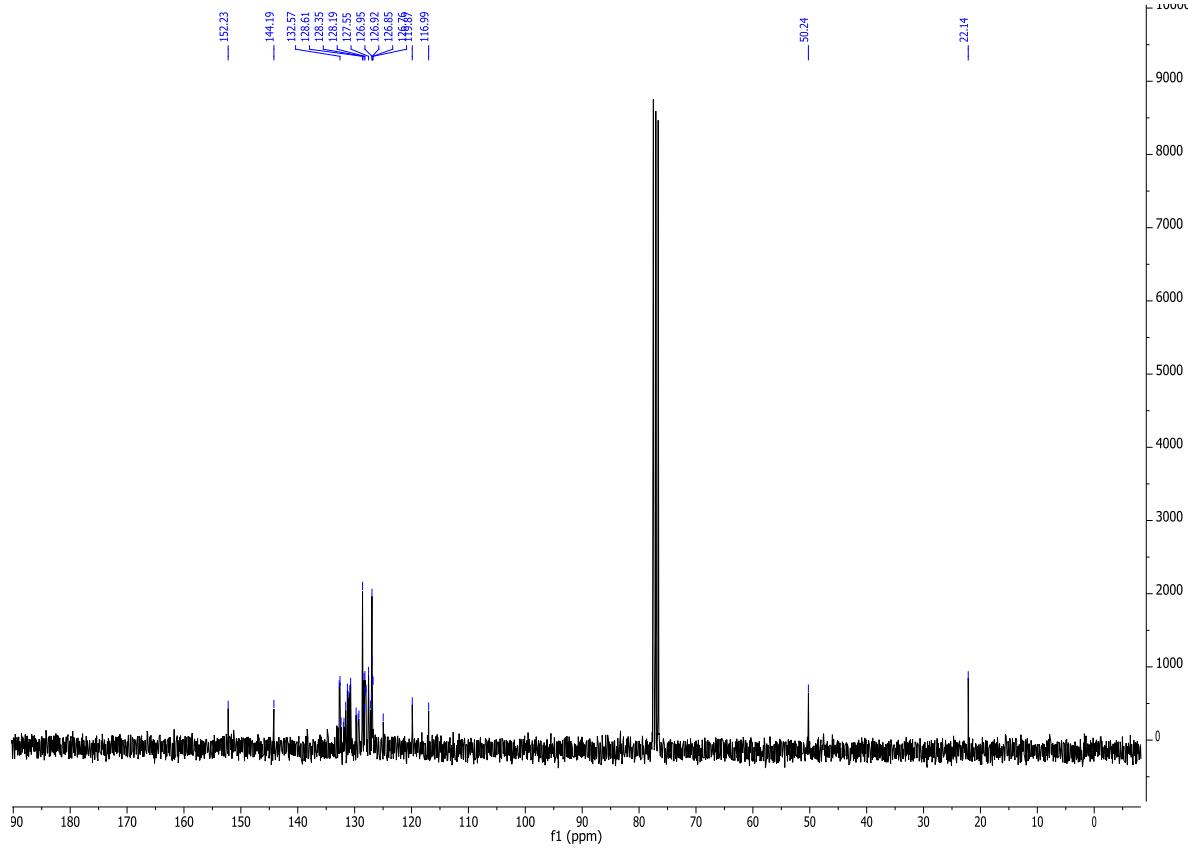
³¹P-NMR:
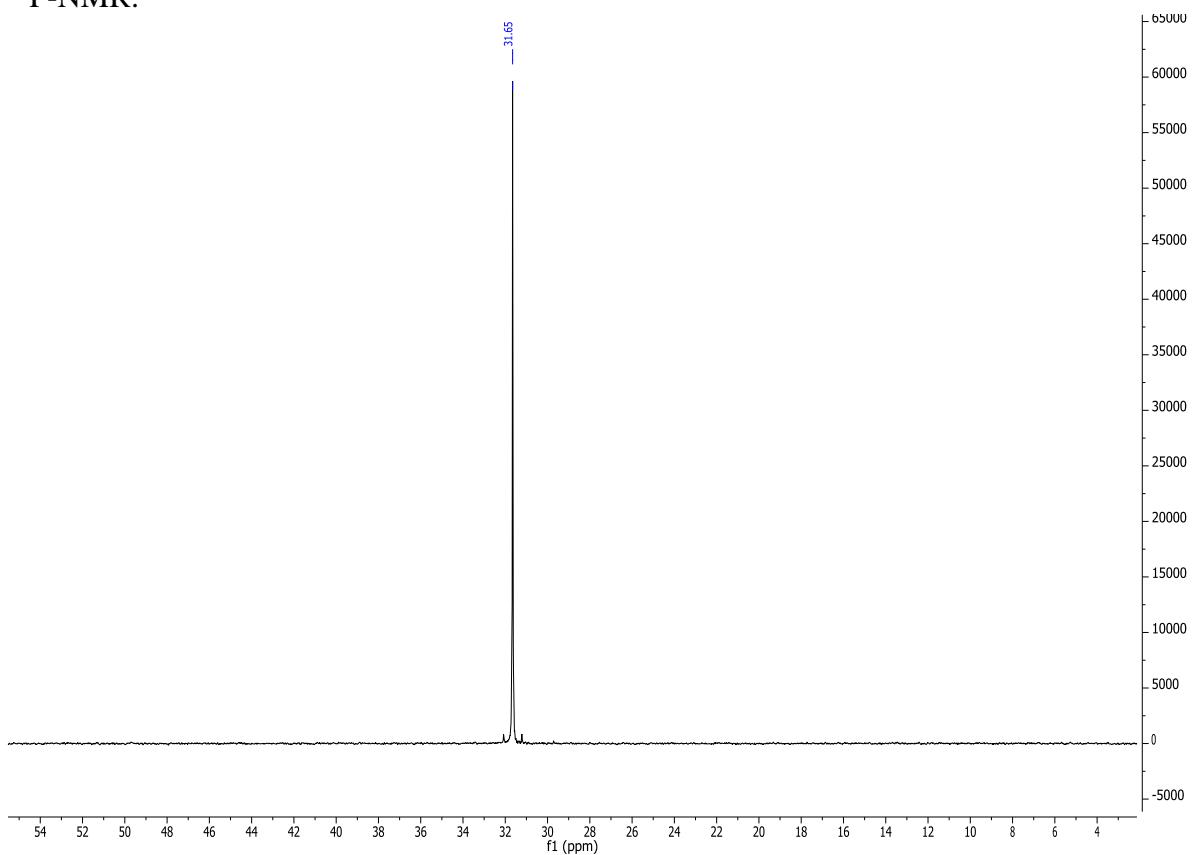
HPLC analysis:

Table 1, entry 1:

```
================================================================
Acq. Operator    :                         Seq. Line :    5
Acq. Instrument : LC 3                      Location : Vial 12
Injection Date  : 5/6/2014 4:44:56 PM            Inj :    1
                                          Inj Volume : 1.0 µl
Different Inj Volume from Sequence !   Actual Inj Volume : 0.2 µl
Acq. Method      : D:\HPCHEM\1\METHODS\FISCHER2.M
Last changed     : 5/6/2014 3:51:35 PM
                   (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 9/2/2015 2:38:40 PM
                   (modified after loading)
Additional Info : Peak(s) manually integrated
```
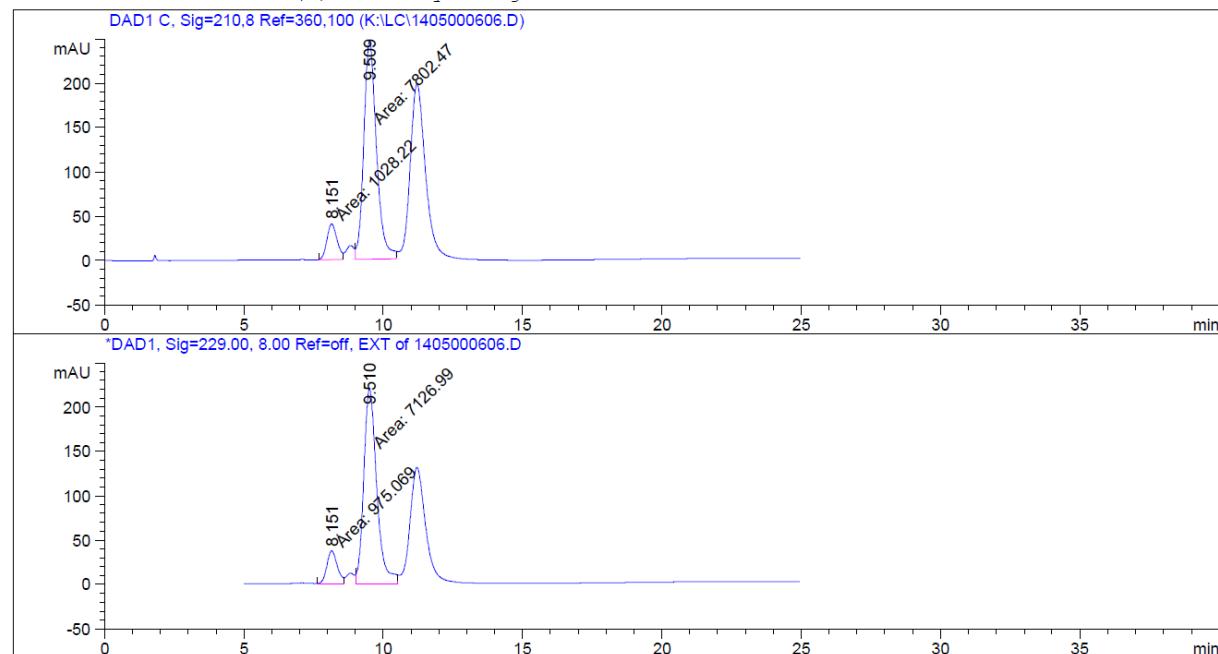


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================================================================
                   Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area        Height      Area
 #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.151 MF   0.4252 1028.22241   40.30477  11.6437
   2   9.509 FM   0.5300 7802.47461  245.36790  88.3563

Totals :                 8830.69702  285.67267
```

```
Signal 2: DAD1, Sig=229.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.151 MF    0.4363  975.06885   37.25163  12.0348
   2   9.510 MF    0.5392 7126.98779  220.29738  87.9652

Totals :                  8102.05664  257.54901
```

```
Signal 2: DAD1, Sig=229.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.151 MF    0.4363  975.06885   37.25163  12.0348
```

Table 1, entry 2:

```
==================================================================
Acq. Operator    :                        Seq. Line :    2
Acq. Instrument : LC 2                     Location : Vial 12
Injection Date  : 5/15/2014 1:30:40 PM         Inj :    1
                                         Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 5/15/2014 11:46:45 AM
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
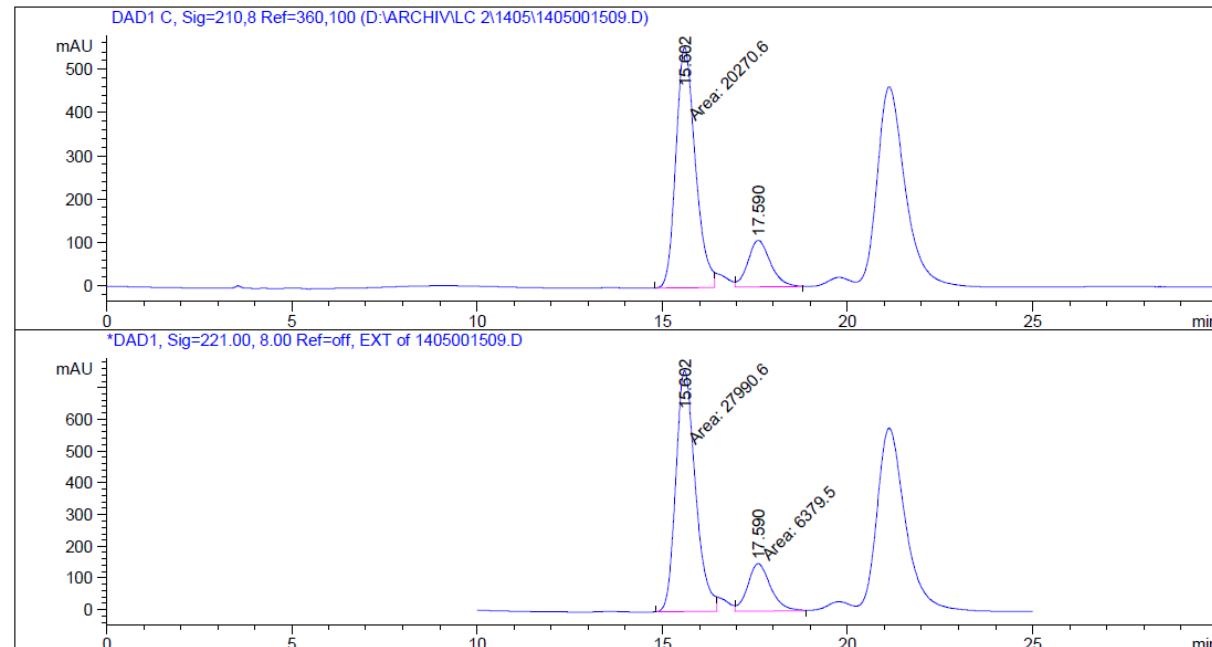


```
==================================================================
                      Area Percent Report
==================================================================

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


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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1  15.602 MF    0.6093 2.02706e4   554.45905   81.6528
  2  17.590 VB    0.6398 4554.75391  107.61131   18.3472

Totals :                  2.48253e4   662.07035
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1  15.602 MF    0.6151 2.79906e4   758.38672   81.4388
  2  17.590 FM    0.7128 6379.50195  149.16548   18.5612

Totals :                  3.43701e4   907.55220
```

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Table 1, entry 3:

Additional Info : Peak(s) manually integrated
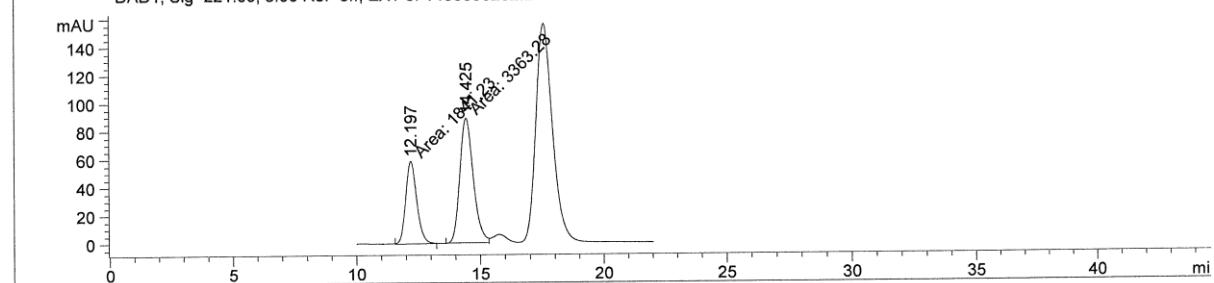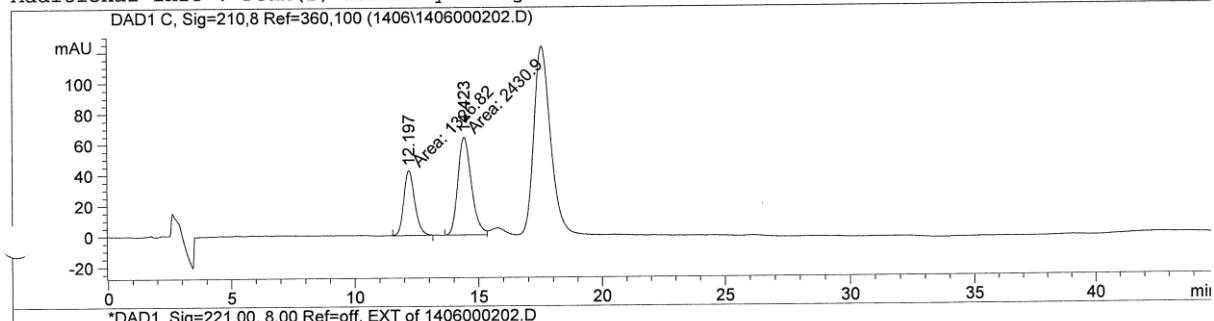

```
=====================================================================
                      Area Percent Report
=====================================================================

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


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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]    [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.197 MM   0.5215 1326.81787    42.40629  35.3091   35.0183
   2  14.423 MM   0.6341 2430.90137    63.89017  64.6909   64.9817

Totals :                   3757.71924  106.29646
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]    [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.197 MM   0.5217 1841.22791    58.82172  35.3776   35.0345
   2  14.425 MM   0.6314 3363.28052    88.77180  64.6224   64.9655

Totals :                   5204.50842  147.59353
```
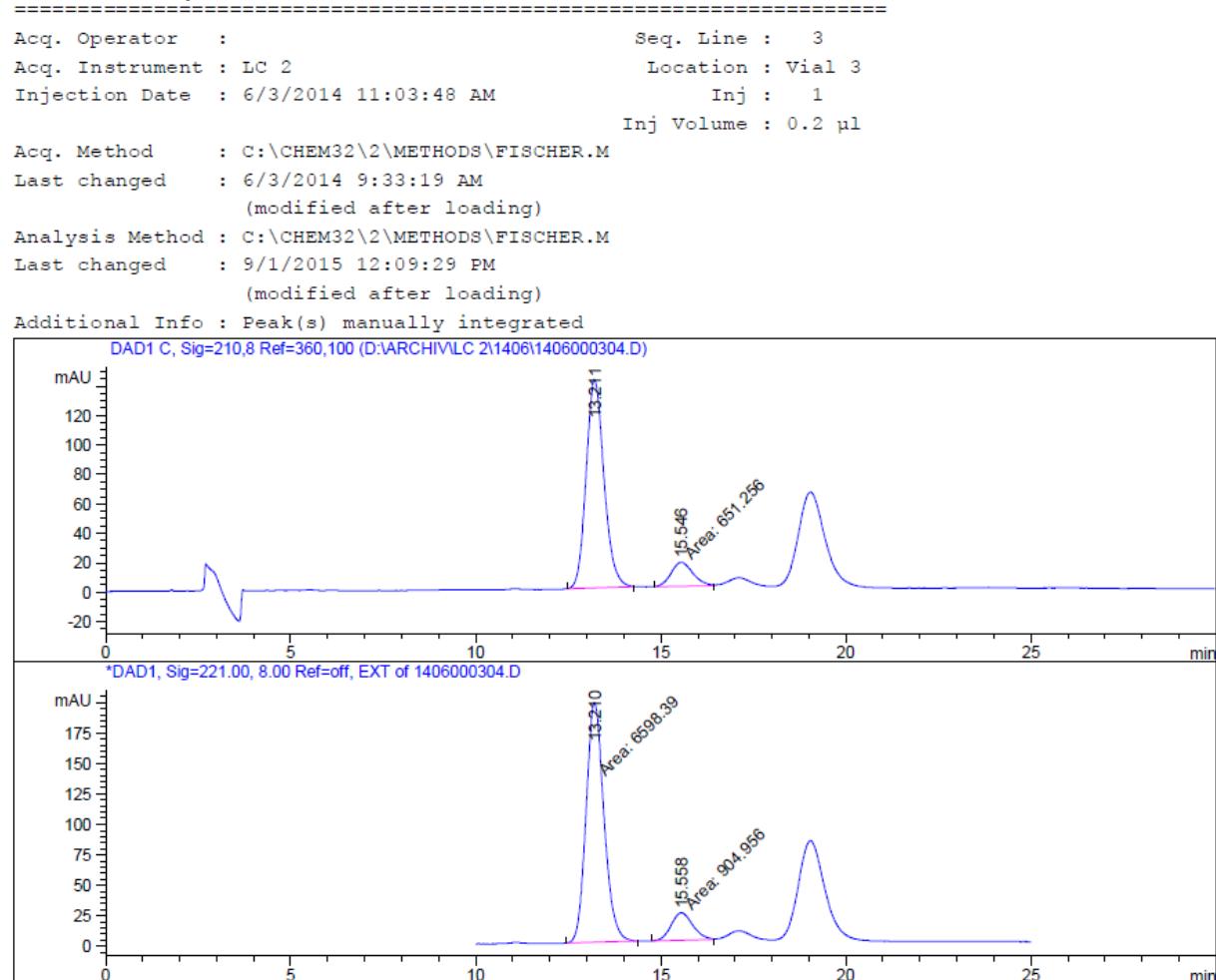
18

Table 1, entry 4:

```
======================================================================
Acq. Operator   :                              Seq. Line :    3
Acq. Instrument : LC 2                          Location : Vial 3
Injection Date  : 6/3/2014 11:03:48 AM              Inj :    1
                                             Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 6/3/2014 9:33:19 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```



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


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



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

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.211 BB   0.5181  4754.74268  141.47903   87.9531
  2  15.546 MM   0.6724   651.25568   16.14193   12.0469

Totals :                 5405.99835  157.62096
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.210 MM   0.5593  6598.39209  196.61552   87.9393
  2  15.558 MM   0.6709   904.95636   22.48225   12.0607

Totals :                 7503.34845  219.09777
```

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Table 1, entry 5:

```
================================================================
Acq. Operator   :                           Seq. Line :    4
Acq. Instrument : LC 2                       Location : Vial 4
Injection Date  : 6/3/2014 12:05:58 PM           Inj :    1
                                          Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 6/3/2014 9:33:19 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
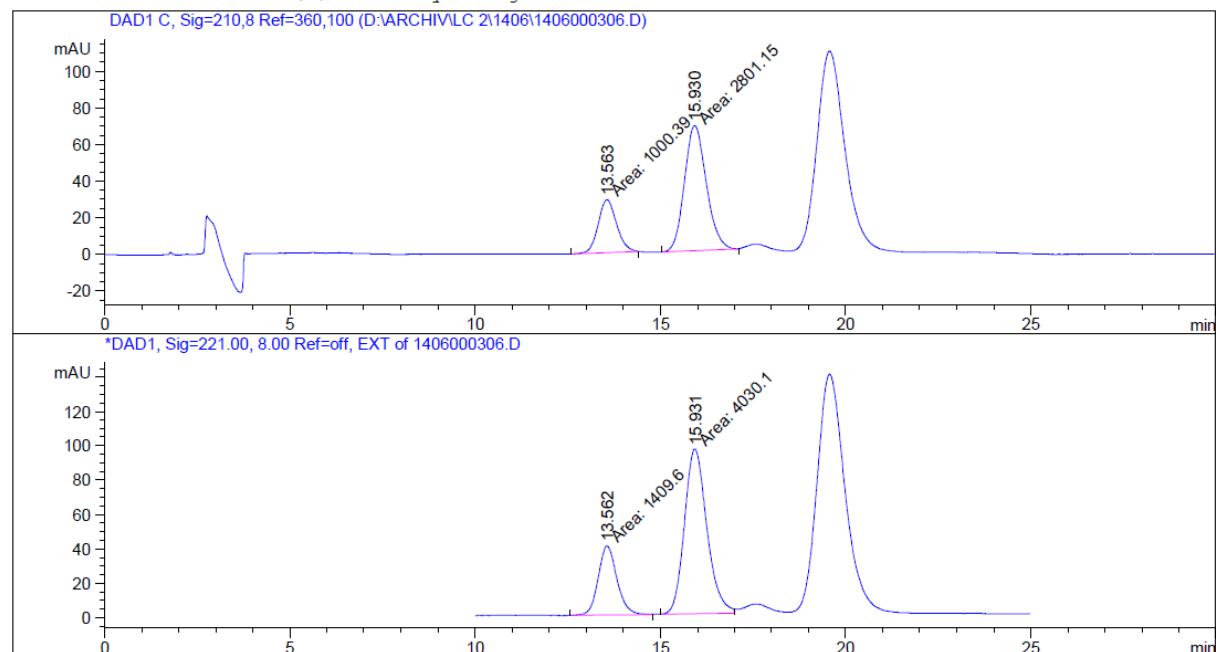


```
================================================================
                    Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  13.563 MM   0.5763  1000.38519   28.93310  26.3153
  2  15.930 MM   0.6847  2801.14600   68.18134  73.6847

Totals :               3801.53119   97.11443
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  13.562 MM   0.5861  1409.60083   40.08610  25.9132
  2  15.931 MM   0.7005  4030.09644   95.88995  74.0868

Totals :               5439.69727  135.97605
```

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Table 1, entry 6:

```
================================================================
Acq. Operator   :                           Seq. Line :    5
Acq. Instrument : LC 2                       Location : Vial 5
Injection Date  : 6/3/2014 1:08:09 PM            Inj :    1
                                          Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 6/3/2014 9:33:19 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
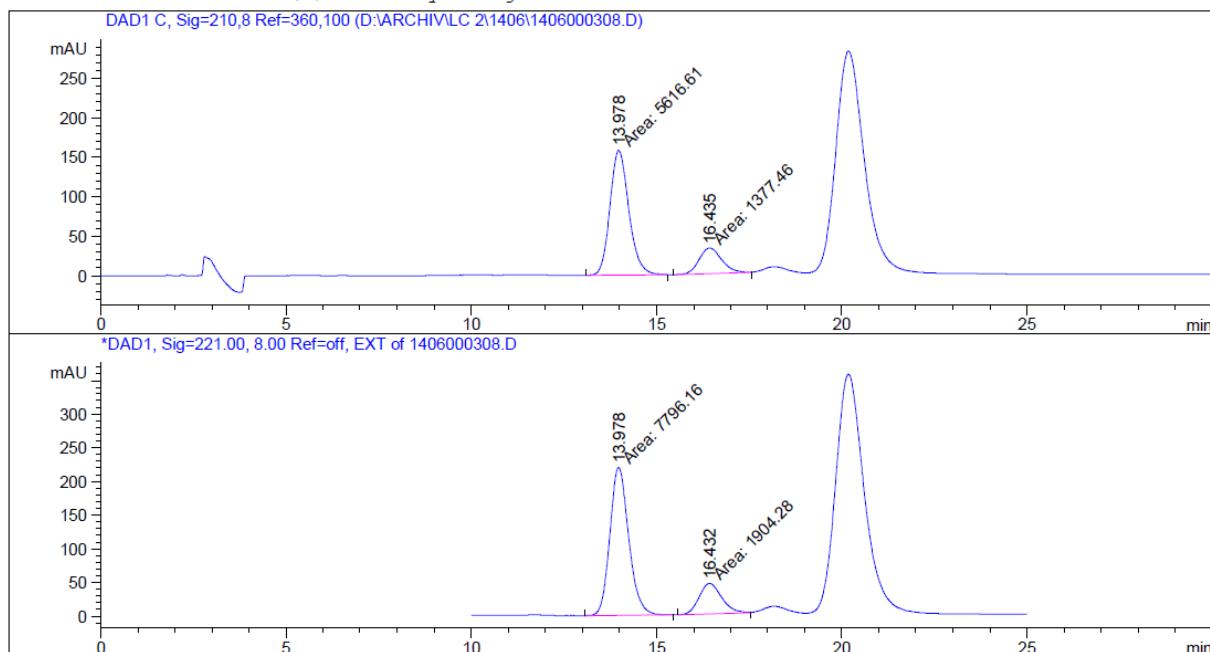


```
================================================================
                    Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.978 MM   0.5916  5616.60547  158.23508   80.3053
  2  16.435 MM   0.7045  1377.46033   32.58535   19.6947

Totals :                 6994.06580  190.82043
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.978 MM   0.5914  7796.16260  219.71109   80.3691
  2  16.432 MM   0.7040  1904.28052   45.08112   19.6309

Totals :                 9700.44312  264.79221
```

Table 1, entry 7:

```
========================================================================
Acq. Operator   :                           Seq. Line :    6
Acq. Instrument : LC 2                       Location : Vial 6
Injection Date  : 6/3/2014 2:10:21 PM            Inj :    1
                                          Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 6/3/2014 9:33:19 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
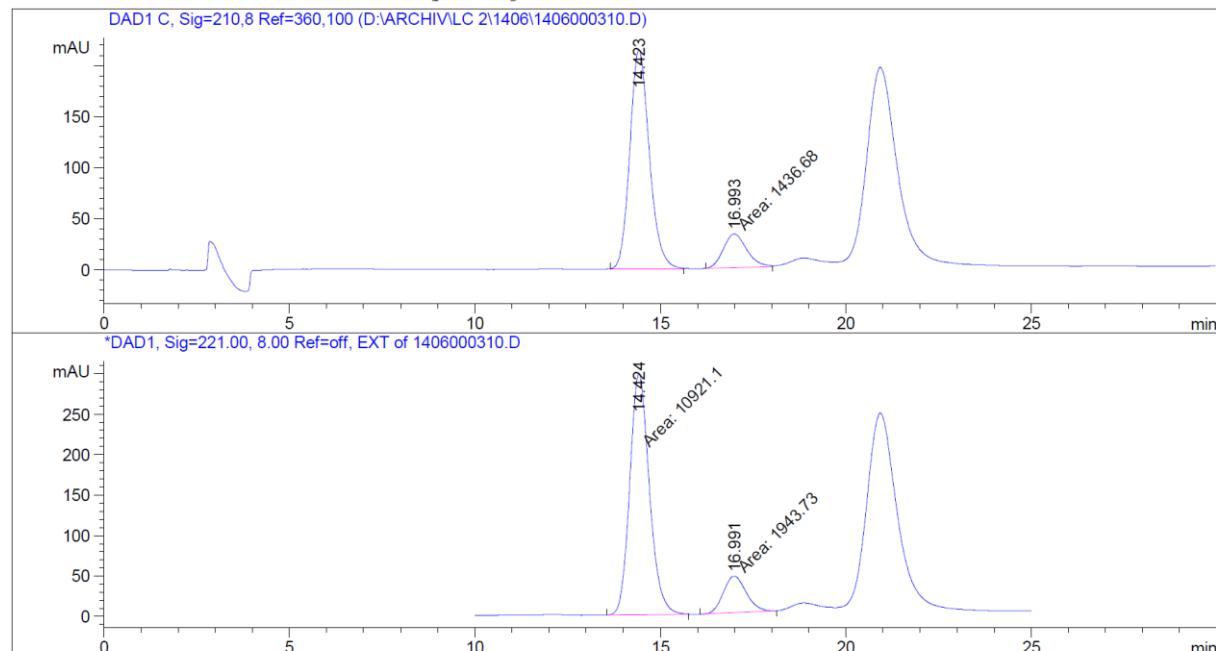


```
========================================================================
                    Area Percent Report
========================================================================

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


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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  14.423 BB    0.5615 7831.39160  214.72615  84.4987
  2  16.993 MM    0.7283 1436.67542   32.87614  15.5013

Totals :                  9268.06702  247.60229
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  14.424 MM    0.6100 1.09211e4   298.38892  84.8912
  2  16.991 MM    0.7155 1943.72559   45.27864  15.1088

Totals :                  1.28649e4   343.66755
```

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Table 1, entry 8:

```
================================================================
Acq. Operator    :                          Seq. Line :   7
Acq. Instrument : LC 2                       Location : Vial 7
Injection Date  : 6/3/2014 3:12:33 PM           Inj :    1
                                         Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 6/3/2014 9:33:19 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/1/2015 12:09:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
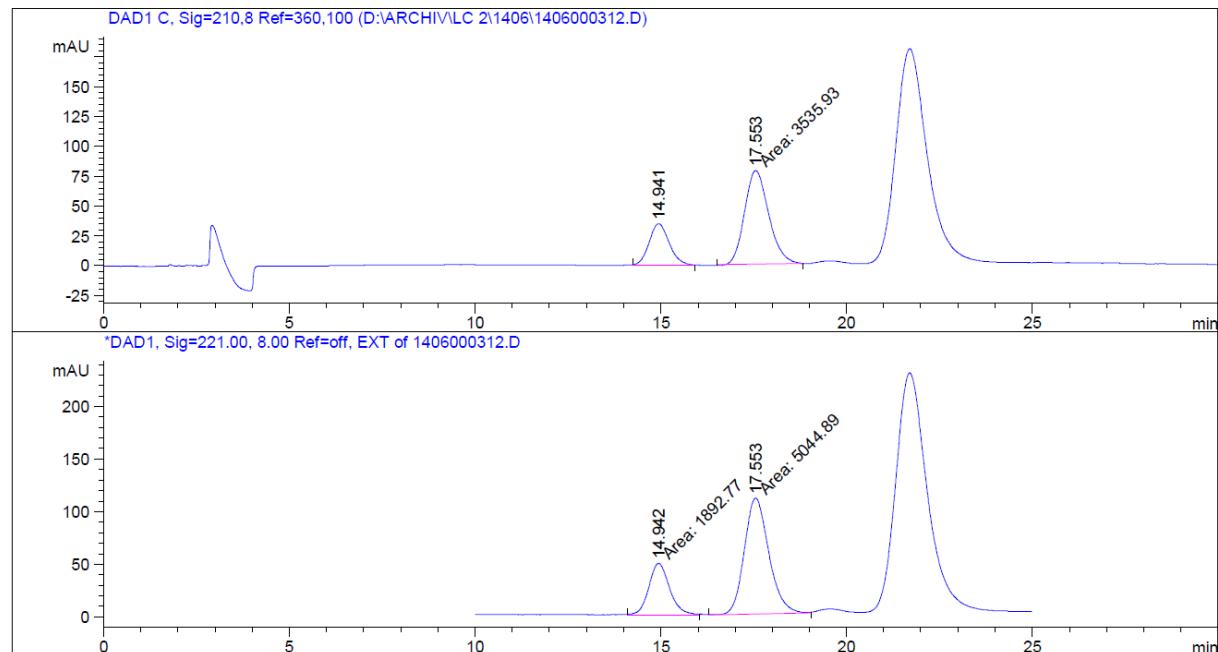


```
================================================================
                   Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.941 BB   0.5638  1304.23267   34.75591   26.9460
  2  17.553 MM   0.7528  3535.93408   78.28011   73.0540

Totals :                 4840.16675  113.03602
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.942 MM   0.6453  1892.77344   48.88490   27.2826
  2  17.553 MM   0.7646  5044.89404  109.96222   72.7174

Totals :                 6937.66748  158.84712
```

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Table 2, entry 1:

```
================================================================
Acq. Operator    :                        Seq. Line :    2
Acq. Instrument  : LC 2                    Location  : Vial 2
Injection Date   : 12/18/2014 11:11:30 AM      Inj  :    1
                                         Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 12/18/2014 9:37:12 AM
Analysis Method  : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed     : 8/26/2015 1:42:29 PM
                   (modified after loading)
Additional Info : Peak(s) manually integrated
```
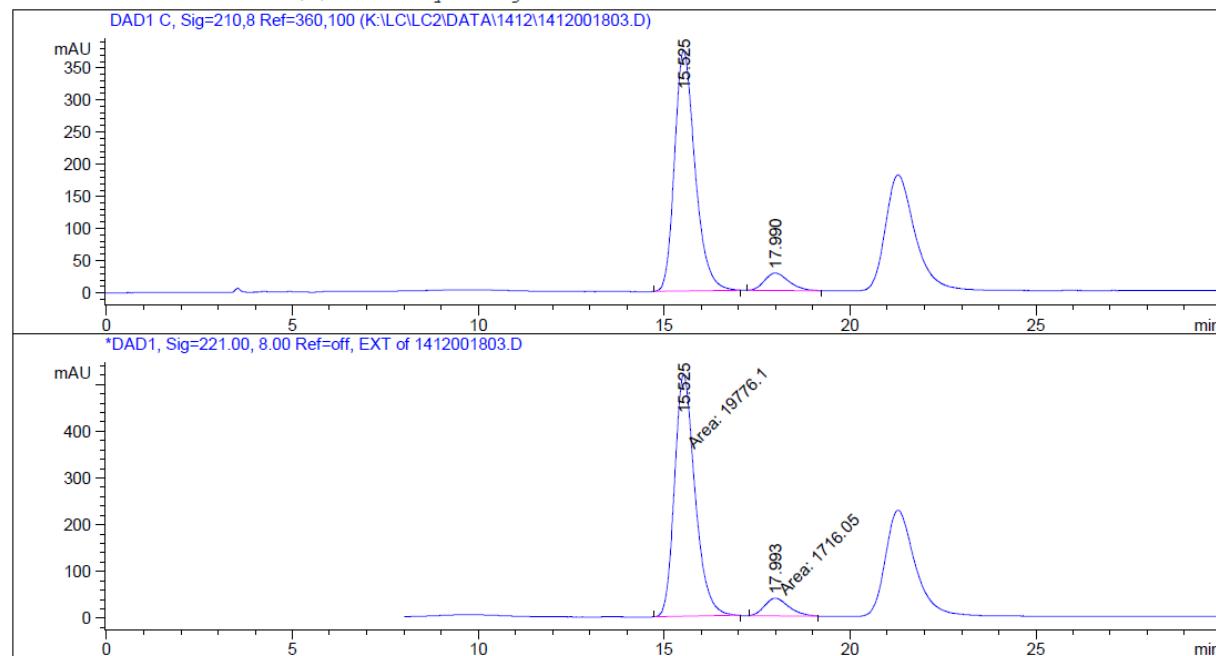


```
================================================================
                  Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1  15.525 BB    0.5862  1.43760e4   374.22119   92.0729
  2  17.990 BB    0.6101  1237.71704   27.13681    7.9271

Totals :                  1.56137e4   401.35800
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1  15.525 MM    0.6396  1.97761e4   515.30829   92.0155
  2  17.993 MM    0.7633  1716.04749   37.47045    7.9845

Totals :                  2.14921e4   552.77874
```

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Table 2, entry 2:

```
================================================================
Acq. Operator    :                        Seq. Line :    1
Acq. Instrument  : LC 2                    Location  : Vial 2
Injection Date   : 1/9/2015 2:33:46 PM          Inj :    2
                                         Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 1/9/2015 9:46:40 AM
Analysis Method  : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed     : 8/26/2015 1:42:29 PM
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
```
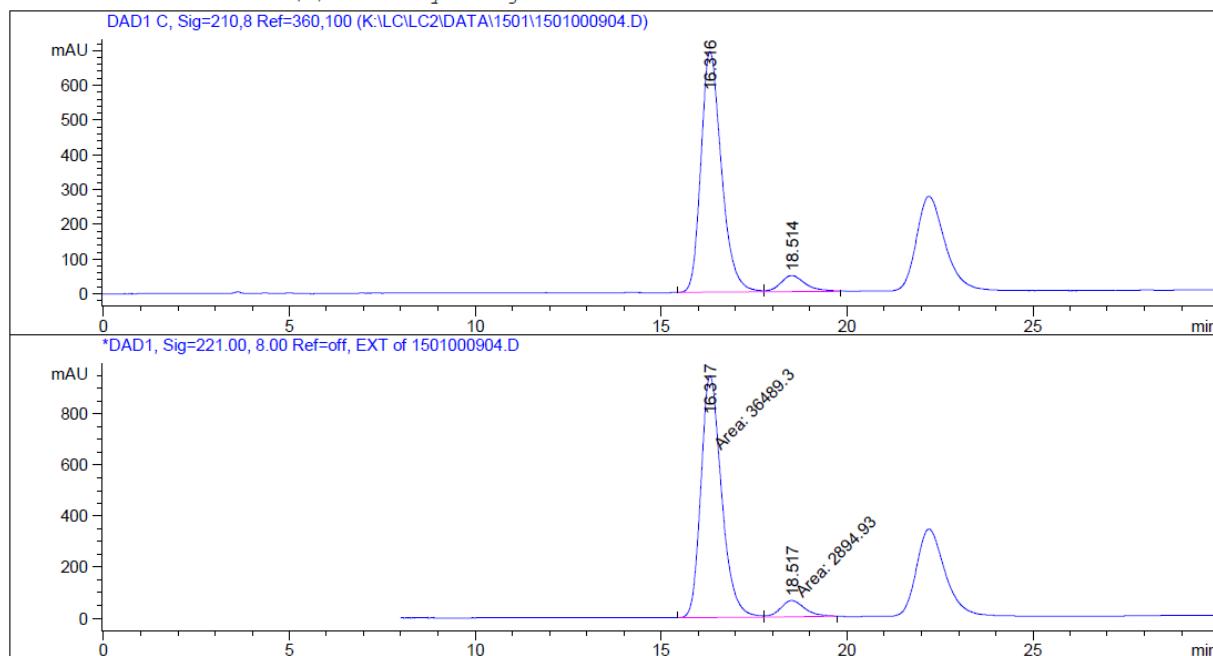


```
================================================================
                    Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.316 BB    0.5829 2.65403e4    692.89911   92.6167
  2  18.514 BB    0.6419 2115.77148    45.88992    7.3833

Totals :                  2.86561e4    738.78903
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.317 MF    0.6425 3.64893e4    946.61737   92.6495
  2  18.517 FM    0.7591 2894.92773    63.55793    7.3505

Totals :                  3.93842e4   1010.17530
```

Table 3, entry 1:
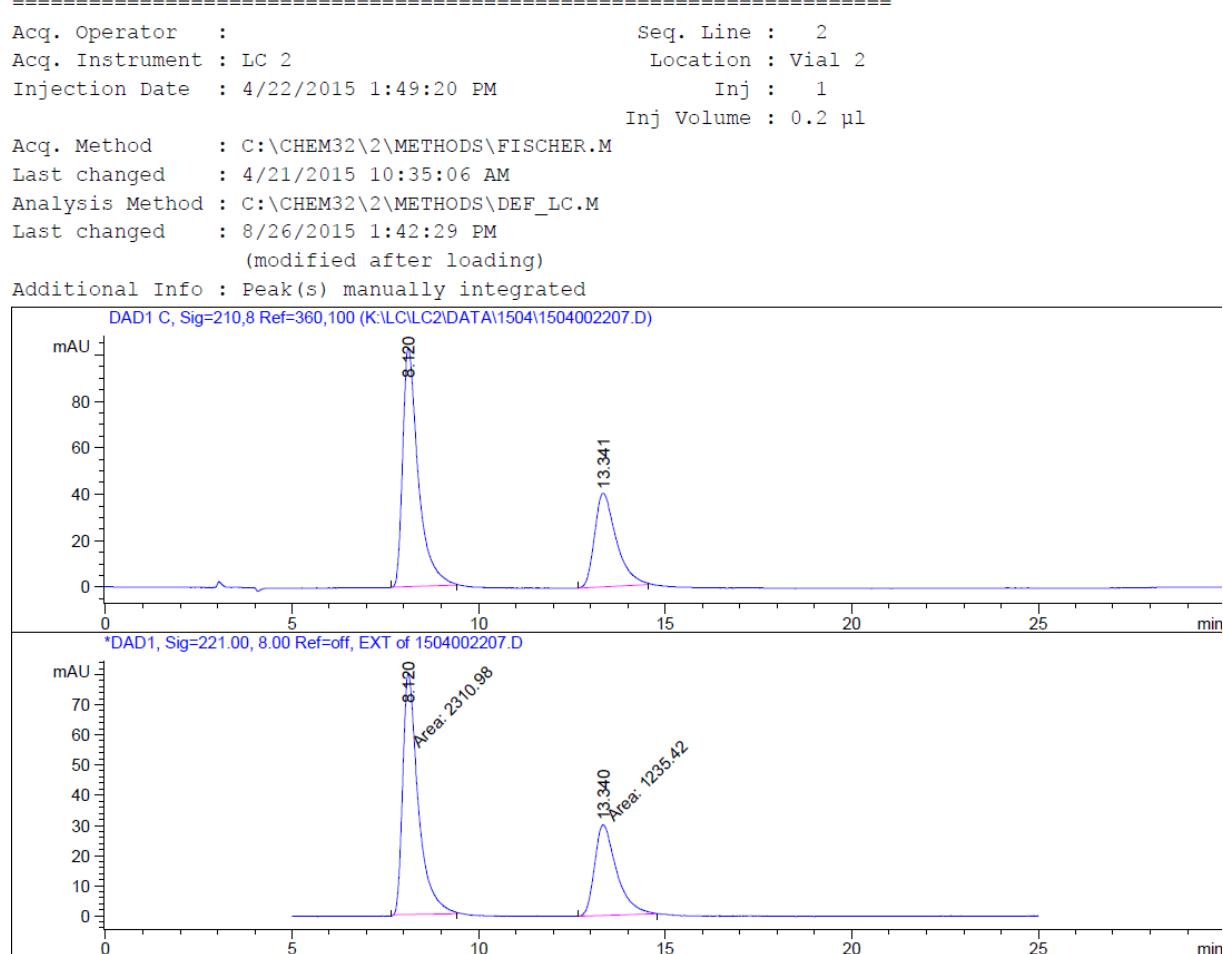
```
================================================================
Acq. Operator    :                          Seq. Line :    2
Acq. Instrument : LC 2                       Location : Vial 2
Injection Date  : 4/22/2015 1:49:20 PM            Inj :    1
                                           Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 4/21/2015 10:35:06 AM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed     : 8/26/2015 1:42:29 PM
                   (modified after loading)
Additional Info : Peak(s) manually integrated
```



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

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


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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   8.120 BB   0.4282 2979.22900  102.77245  64.7460
  2  13.341 BB   0.5885 1622.18018   40.22208  35.2540

Totals :                 4601.40918  142.99452
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   8.120 MM   0.4811 2310.97998   80.05103  65.1642
  2  13.340 MM   0.6852 1235.41675   30.05008  34.8358

Totals :                 3546.39673  110.10111
```

Table 3, entry 2:

```
================================================================
Acq. Operator   :                          Seq. Line :    3
Acq. Instrument : LC 2                      Location : Vial 3
Injection Date  : 5/11/2015 5:32:43 PM          Inj :    1
                                         Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 5/11/2015 2:19:18 PM
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/2/2015 11:47:09 AM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
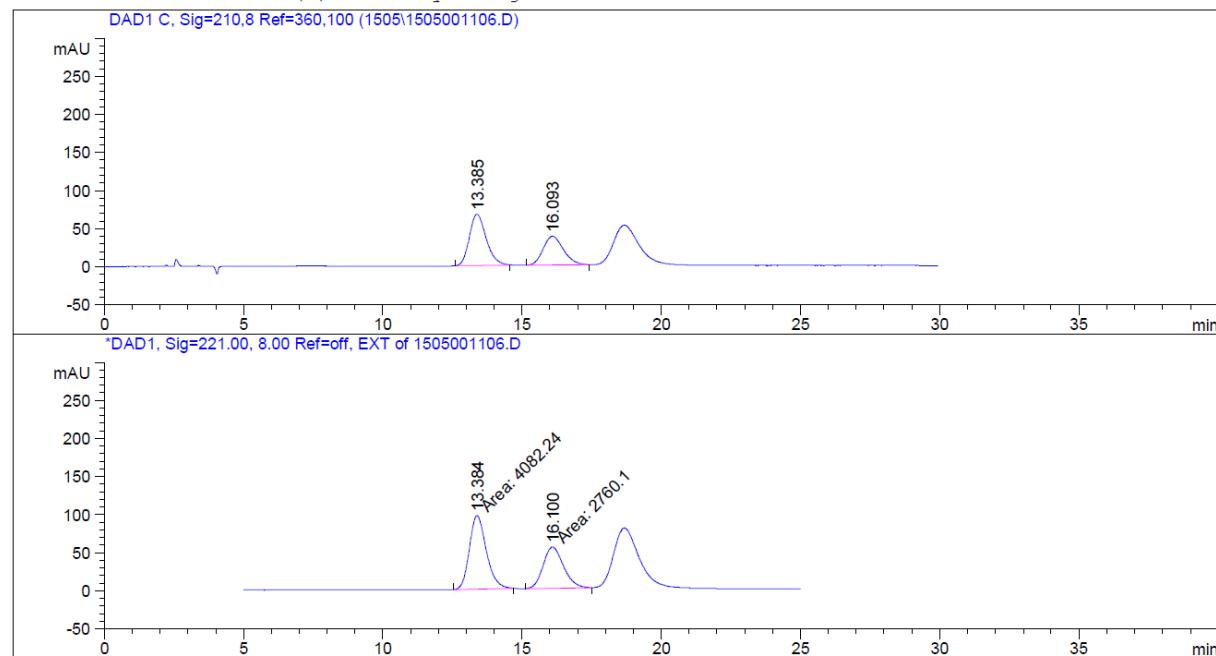


```
================================================================
                    Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.385 BB    0.6407 2841.62915   67.56503  59.6591
  2  16.093 BB    0.7700 1921.48242   37.86501  40.3409

Totals :                   4763.11157  105.43003
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  13.384 MM    0.7037 4082.24390   96.68655  59.6615
  2  16.100 MM    0.8484 2760.09644   54.22163  40.3385

Totals :                   6842.34033  150.90818
```

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Table 3, entry 4:

```
======================================================================
Acq. Operator    :                        Seq. Line :    2
Acq. Instrument : LC 2                     Location : Vial 53
Injection Date  : 9/11/2015 10:00:32 AM        Inj :    1
                                        Inj Volume : 1.0 μl
Different Inj Volume from Sequence !    Actual Inj Volume : 0.2 μl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/10/2015 4:09:16 PM
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/11/2015 10:52:41 AM
                  (modified after loading)
Method Info     : Reprosil,  Heptan/EtOH 95:5, Fluß: 1ml/min


Additional Info : Peak(s) manually integrated
```
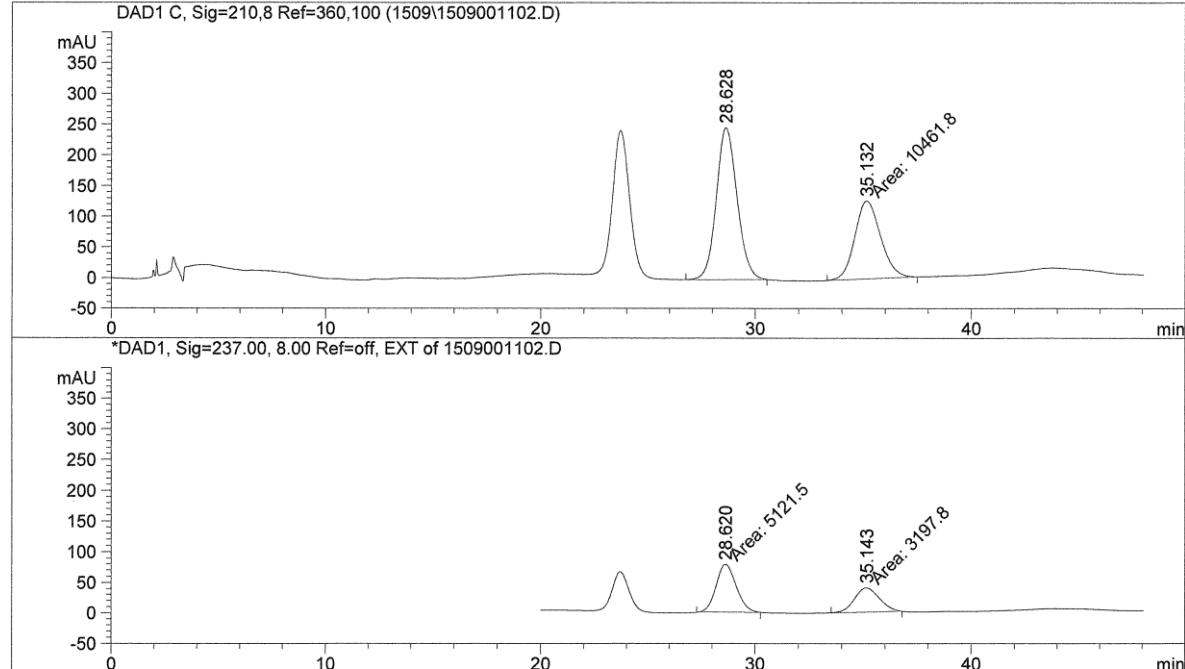


```
======================================================================
                     Area Percent Report
======================================================================


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


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


Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]    [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.628 VB   0.9427  1.66227e4   247.13280  61.3735      61.76
   2  35.132 MM   1.3742  1.04618e4   126.87939  38.6265      38.24

Totals :                  2.70846e4   374.01218
```
Signal 2: DAD1, Sig=237.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

```
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]    [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.620 MM   1.0881  5121.49854   78.44955  61.5616      61.40
   2  35.143 MM   1.3271  3197.80444   40.16091  38.4384      38.60

Totals :                  8319.30298  118.61047
```

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Table 3, entry 6:

```
================================================================
Acq. Operator   :                        Seq. Line :    2
Acq. Instrument : LC 2                    Location : Vial 2
Injection Date  : 4/17/2015 4:46:33 PM        Inj :    2
                                          Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 4/17/2015 12:41:22 PM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 8/26/2015 1:42:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
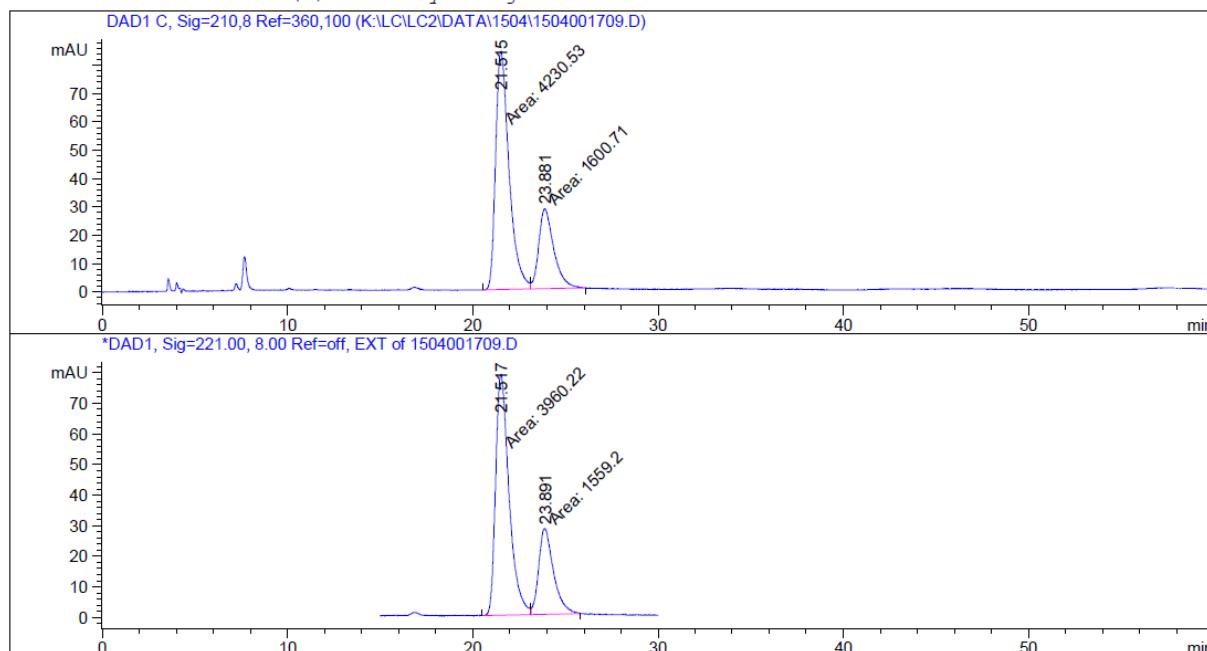


```
================================================================
                  Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  21.515 MF    0.8394 4230.52930   83.99963   72.5494
  2  23.881 FM    0.9464 1600.71033   28.18929   27.4506

Totals :                 5831.23962  112.18892
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  21.517 MF    0.8418 3960.22412   78.40485   71.7507
  2  23.891 FM    0.9286 1559.19873   27.98620   28.2493

Totals :                 5519.42285  106.39105
```

29

Table 3, entry 7:

```
================================================================
Acq. Operator   :                        Seq. Line :    2
Acq. Instrument : LC 2                    Location : Vial 2
Injection Date  : 4/21/2015 12:08:26 PM       Inj :    1
                                         Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 4/21/2015 11:01:55 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 8/26/2015 1:42:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
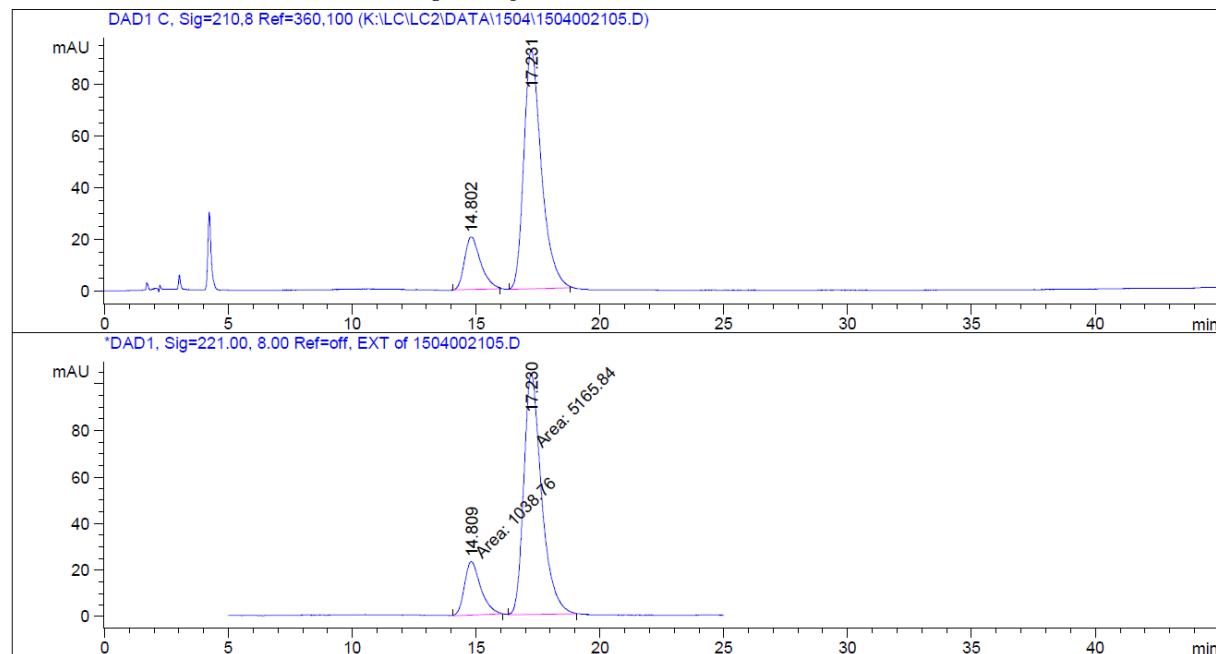


```
================================================================
                    Area Percent Report
================================================================

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


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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.802 BB    0.6313  922.25848   20.40525   16.7797
  2  17.231 BB    0.7421 4574.00781   92.30441   83.2203

Totals :                 5496.26630  112.70966
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.809 MM    0.7546 1038.75818   22.94155   16.7418
  2  17.230 MM    0.8327 5165.83838  103.39096   83.2582


Totals :                 6204.59656  126.33251
```

30

Table 3, entry 8:

```
================================================================
Acq. Operator    :                        Seq. Line :    2
Acq. Instrument  : LC 2                    Location : Vial 2
Injection Date   : 3/13/2015 9:49:47 AM       Inj :    1
                                          Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 3/13/2015 8:25:45 AM
Analysis Method  : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed     : 8/26/2015 1:42:29 PM
                   (modified after loading)
Additional Info : Peak(s) manually integrated
```
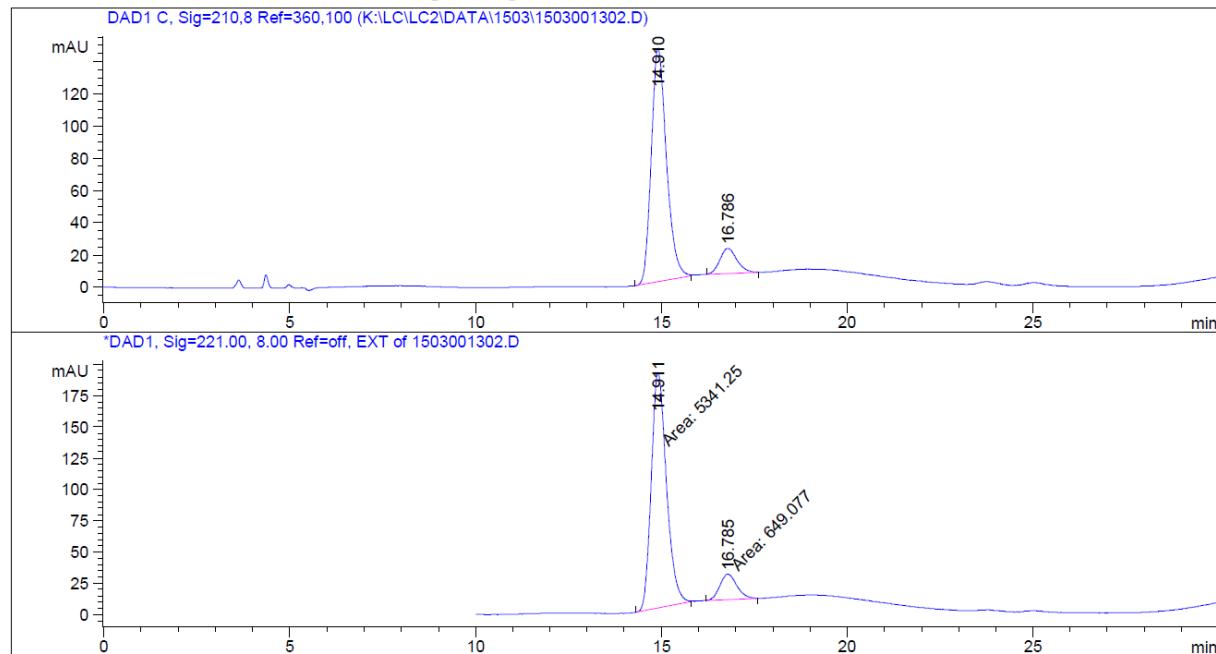


```
================================================================
                     Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area        Height     Area
 #   [min]         [min]   [mAU*s]       [mAU]       %
---|-------|----|-------|----------|----------|--------|
 1  14.910 BB    0.4318 4113.48535  144.63231  89.1668
 2  16.786 BB    0.4208  499.76450   15.63947  10.8332

Totals :                 4613.24985  160.27178
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height     Area
 #   [min]         [min]   [mAU*s]       [mAU]       %
---|-------|----|-------|----------|----------|--------|
 1  14.911 MM    0.4729 5341.25195  188.23424  89.1646
 2  16.785 MM    0.5308  649.07733   20.38070  10.8354

Totals :                 5990.32928  208.61494
```

Table 3, entry 9:

```
================================================================
Acq. Operator     :                          Seq. Line :    3
Acq. Instrument : LC 2                        Location : Vial 3
Injection Date  : 3/13/2015 10:52:02 AM           Inj :    1
                                            Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 3/13/2015 8:25:45 AM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 8/26/2015 1:42:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
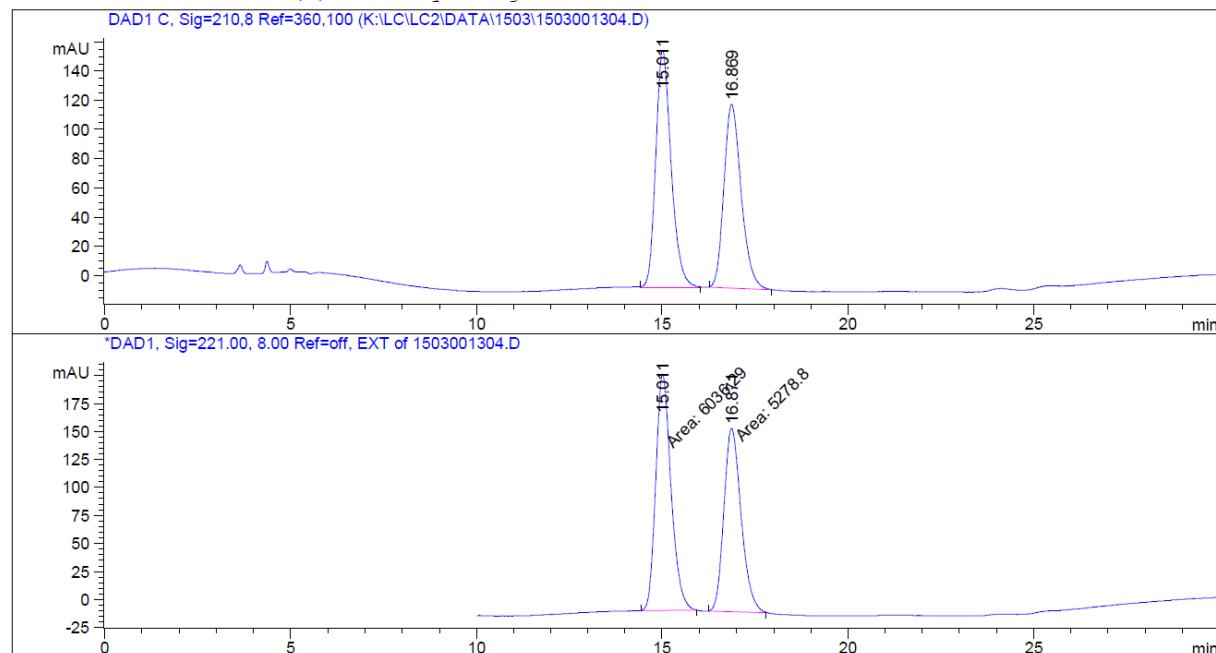


```
================================================================
                     Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  15.011 BB    0.4439 4671.35059  162.26993  53.3722
   2  16.869 BB    0.4960 4081.04785  125.95349  46.6278

Totals :                   8752.39844  288.22342
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  15.011 MM    0.4770 6036.29199  210.89539  53.3473
   2  16.871 MM    0.5366 5278.80078  163.95473  46.6527

Totals :                   1.13151e4   374.85011
```

Table 3, entry 10:
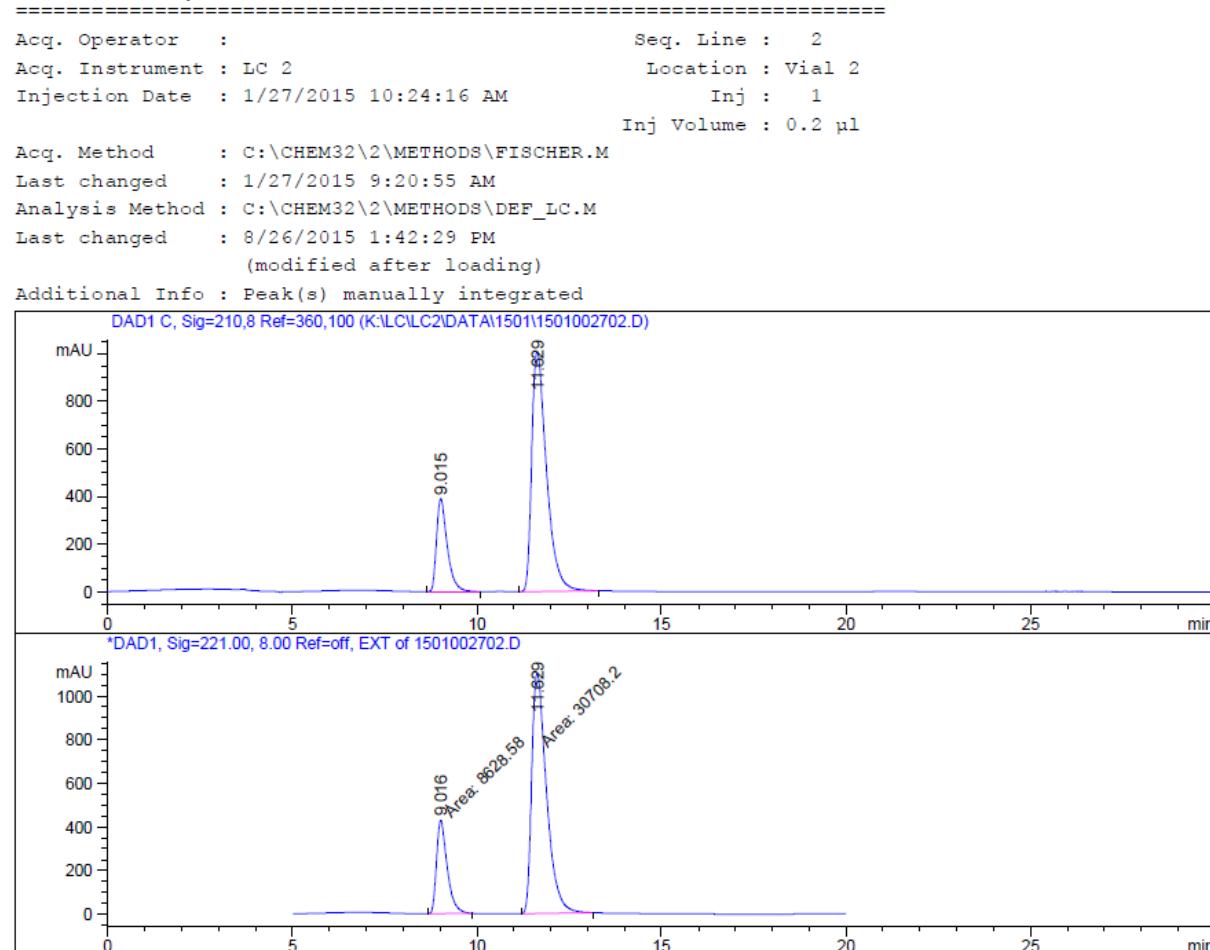
```
=================================================================
Acq. Operator   :                          Seq. Line :    2
Acq. Instrument : LC 2                      Location : Vial 2
Injection Date  : 1/27/2015 10:24:16 AM        Inj :    1
                                        Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 1/27/2015 9:20:55 AM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 8/26/2015 1:42:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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


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



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

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.015 BB   0.3066 7904.02979   389.77368   21.9532
   2  11.629 BB   0.4258 2.81000e4   1006.09882   78.0468

Totals :                  3.60040e4   1395.87250
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.016 MM   0.3357 8628.58008   428.33780   21.9352
   2  11.629 MM   0.4650 3.07082e4   1100.62622   78.0648

Totals :                  3.93368e4   1528.96402
```

Table 3, entry 11:

```
================================================================
Acq. Operator   :                        Seq. Line :    3
Acq. Instrument : LC 2                    Location : Vial 3
Injection Date  : 1/27/2015 11:26:26 AM       Inj :    1
                                       Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 1/27/2015 9:20:55 AM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 8/26/2015 1:42:29 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
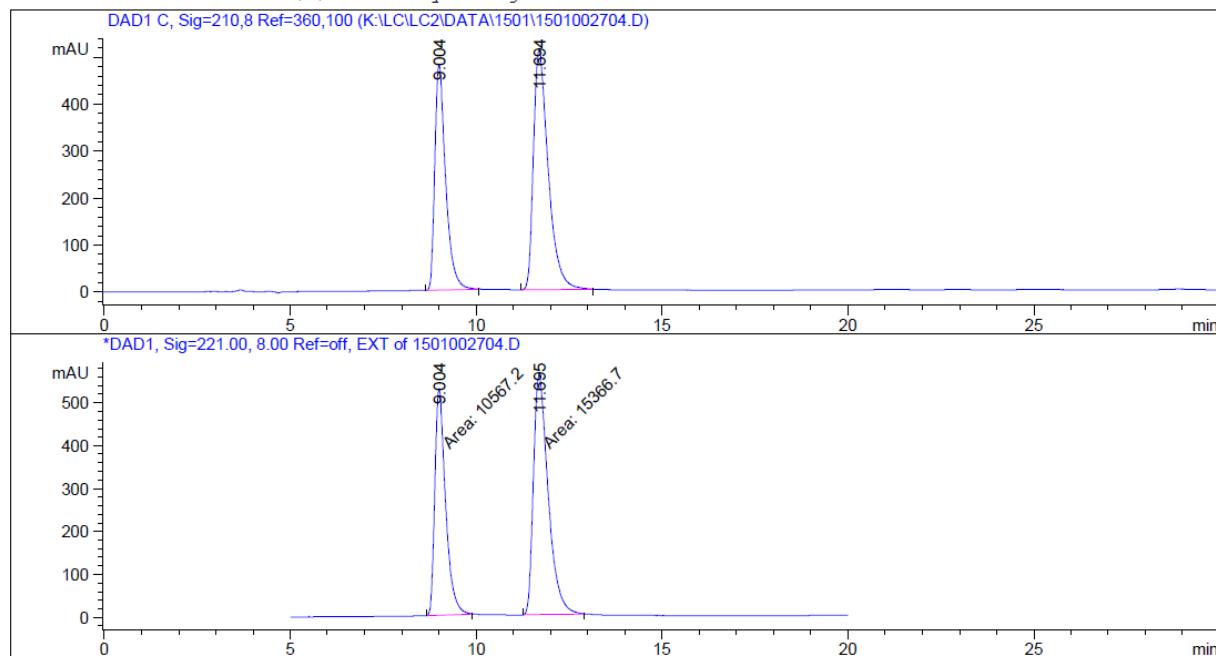


```
================================================================
                    Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.004 BB    0.3033  9685.88672  480.34552  40.7177
  2  11.694 BB    0.4171  1.41020e4   509.23453  59.2823

Totals :                  2.37879e4   989.58005
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.004 MM    0.3342  1.05672e4   526.97723  40.7466
  2  11.695 MM    0.4584  1.53667e4   558.66986  59.2534

Totals :                  2.59338e4   1085.64709
```

Table 3, entry 13, fraction 2:

```
================================================================
Acq. Operator    :                            Seq. Line :   1
Acq. Instrument  : LC 2                        Location  : Vial 1
Injection Date   : 2/24/2015 12:06:10 PM          Inj   :   1
                                               Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 2/24/2015 9:04:36 AM
Analysis Method  : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed     : 8/26/2015 1:42:29 PM
                   (modified after loading)
Additional Info : Peak(s) manually integrated
```
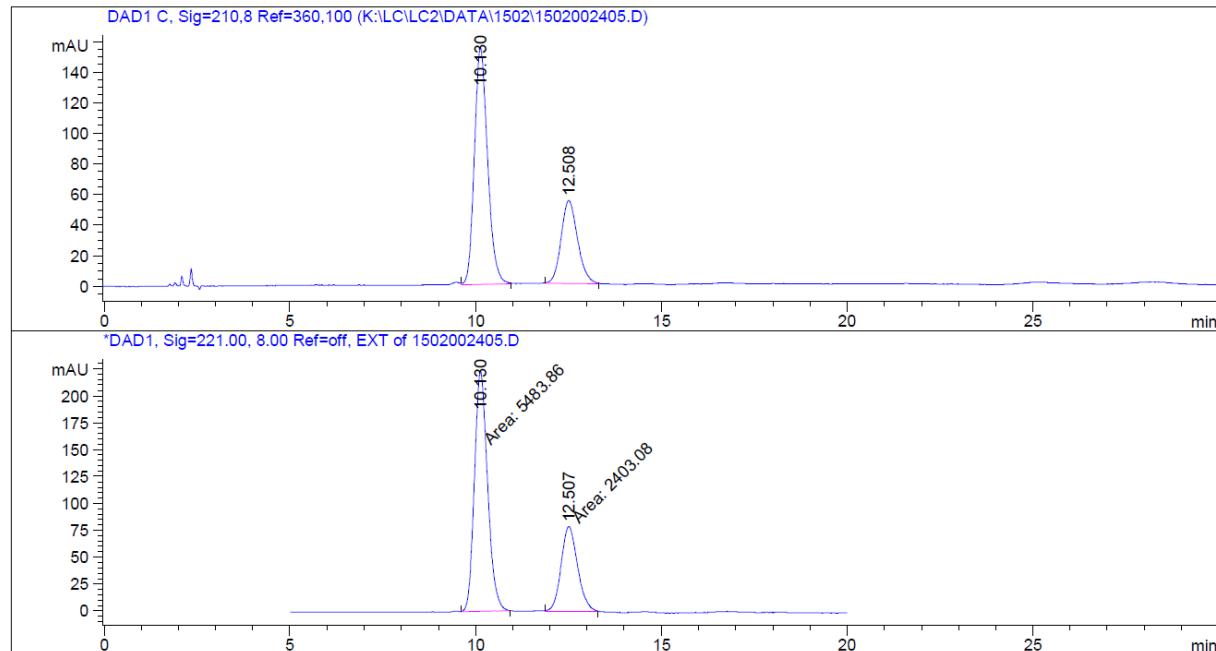


```
================================================================
                  Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.130 VB    0.3757 3817.41235  154.79221  69.5629
  2  12.508 BB    0.4711 1670.29871   54.26474  30.4371

Totals :                 5487.71106  209.05695
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.130 MM    0.4095 5483.85547  223.20137  69.5309
  2  12.507 MM    0.5099 2403.07959   78.54385  30.4691

Totals :                 7886.93506  301.74522
```

Table 4, entry 1:

```
=================================================================
Acq. Operator    :                        Seq. Line :    2
Acq. Instrument : LC 2                     Location : Vial 2
Injection Date  : 1/15/2015 12:12:30 PM        Inj :    1
                                        Inj Volume : 0.2 µl
Acq. Method     : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 1/15/2015 9:35:55 AM
Analysis Method : C:\CHEM32\2\METHODS\FISCHER.M
Last changed    : 9/2/2015 2:38:40 PM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```
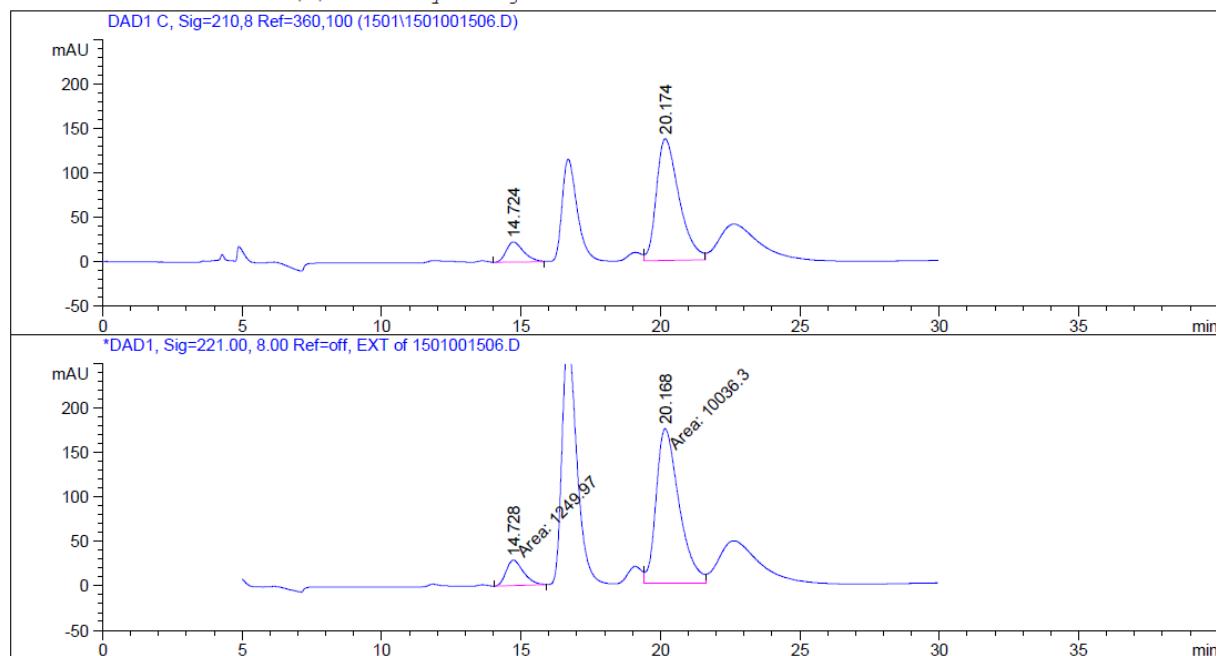


```
=================================================================
                    Area Percent Report
=================================================================


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



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

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.724 VB    0.6075  971.99133   22.61041   11.1065
  2  20.174 VV    0.8427 7779.53174  136.96205   88.8935

Totals :                 8751.52307  159.57246
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  14.728 MM    0.7234 1249.96912   28.79745   11.0751
  2  20.168 FM    0.9578 1.00363e4   174.64882   88.9249

Totals :                 1.12863e4   203.44627
```

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Table 4, entry 2:

```
================================================================
Acq. Operator    :                          Seq. Line :    2
Acq. Instrument  : LC 2                      Location  : Vial 2
Injection Date   : 3/18/2015 11:51:02 AM        Inj    :    1
                                             Inj Volume : 0.2 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 3/18/2015 10:27:46 AM
Analysis Method  : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 9/2/2015 11:47:09 AM
                   (modified after loading)
Additional Info  : Peak(s) manually integrated
```
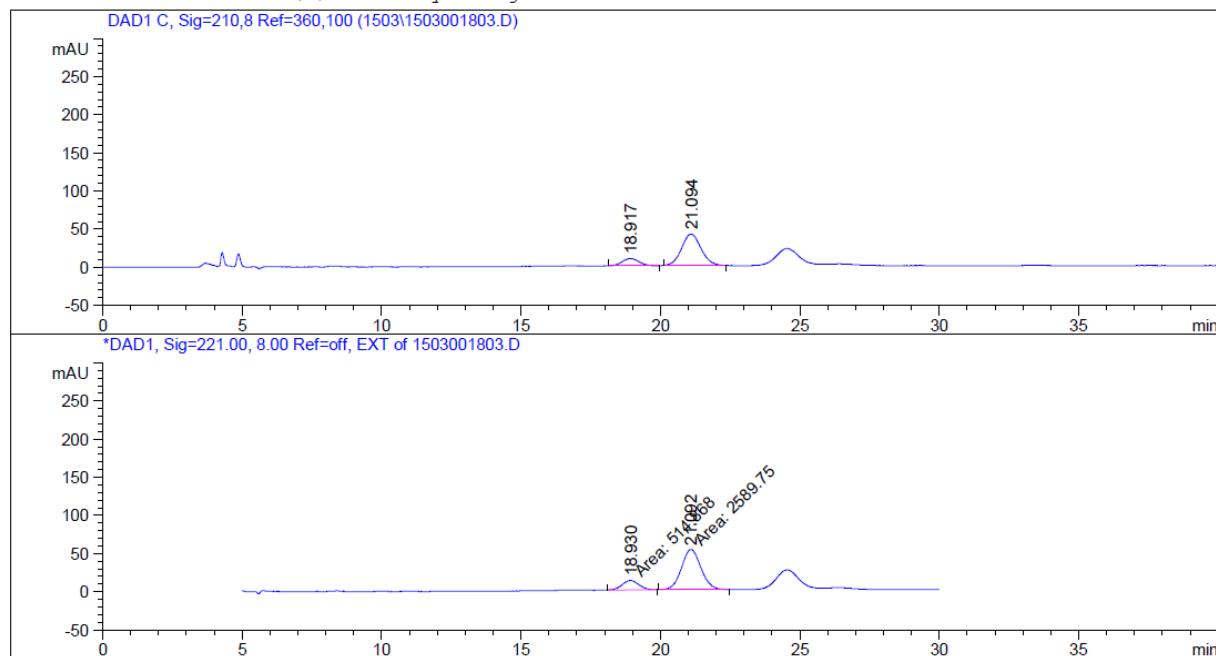


```
================================================================
                    Area Percent Report
================================================================


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



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

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  18.917 BB   0.4976  401.98444    9.65834   16.5819
  2  21.094 BB   0.6839 2022.25647   41.54563   83.4181

Totals :                2424.24091   51.20397
Signal 2: DAD1, Sig=221.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  18.930 MM   0.6909  514.86804   12.42091   16.5840
  2  21.092 MM   0.8152 2589.74683   52.94692   83.4160

Totals :                3104.61487   65.36782
```

Table 4, entry 5:

```
Acq. Operator    :                        Seq. Line :   3
Acq. Instrument : LC 2                      Location : Vial 32
Injection Date  : 10/7/2015 4:48:24 PM          Inj :   1
                                         Inj Volume : 0.4 µl
Different Inj Volume from Sequence !   Actual Inj Volume : 0.1 µl
Acq. Method      : C:\CHEM32\2\METHODS\FISCHER.M
Last changed     : 10/7/2015 4:17:08 PM
                   (modified after loading)
Analysis Method  : C:\CHEM32\2\METHODS\JUNGK.M
Last changed     : 10/8/2015 9:21:55 AM
                   (modified after loading)
Method Info      : Cellulose2, Heptan/IEtOH 98:2, Fluß: 0.8 ml/min

Additional Info : Peak(s) manually integrated
```
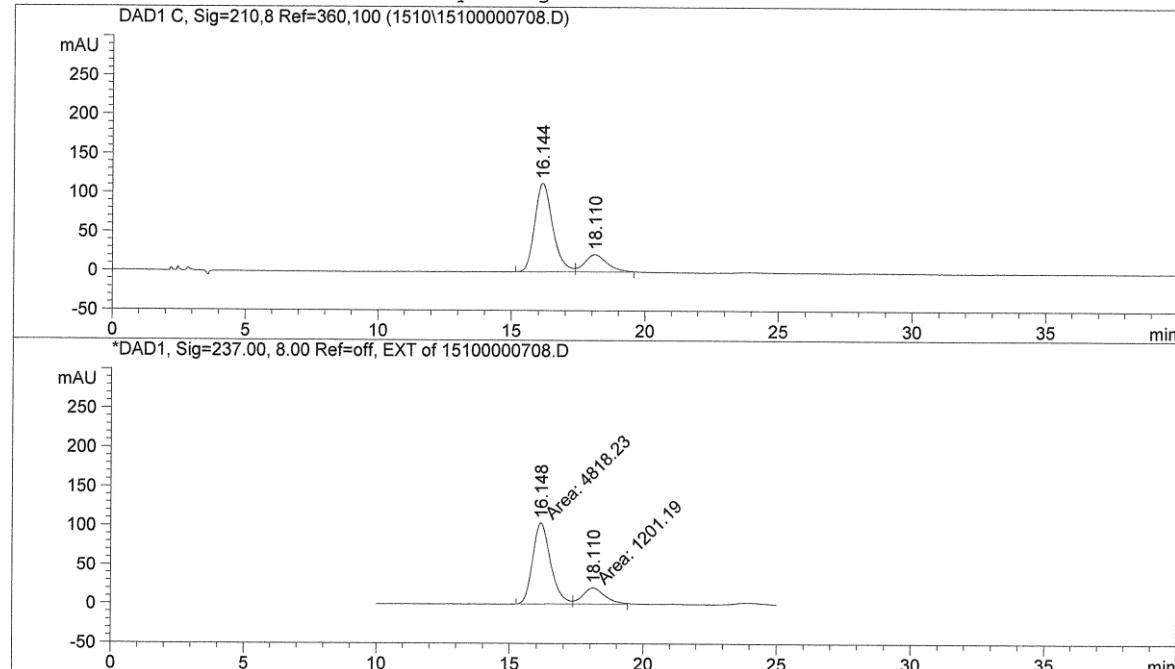


```
=====================================================================
                      Area Percent Report
=====================================================================

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


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

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.144 VB   0.6774  5278.08447  113.31342  80.0891    80.21
  2  18.110 BB   0.6871  1312.17957   22.67734  19.9109    19.79

Totals :                6590.26404  135.99076
Signal 2: DAD1, Sig=237.00, 8.00 Ref=off, EXT
 Signal has been modified after loading from rawdata file!

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  16.148 MF   0.7729  4818.23145  103.90434  80.0447    80.41
  2  18.110 FM   0.9599  1201.19116   20.85699  19.9553    19.59

Totals :                6019.42261  124.76133
```

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References:

[1]   Shibata,T.; Tsuchikama, K.; Otsuka, M. *Tetrahedron: Asymmetry* **2006**, *17*, 614-619.

[2]   Jungk, P.; Fischer, F.; Thiel, I.; Hapke, M. *J. Org. Chem.* **2015**, *80*, 9781-9793.

[3]   Knöpfel, T. F.; Aschwanden, P.; Ichikawa, T.; Watanabe, T.; Carreira, E. M. *Angew. Chem.* **2004**, *116*, 6097-6099; *Angew. Chem. Int. Ed.* **2004**, *43*, 5971-5973.