catalysts

MDPI

Supporting Information

Enantioselective Mannich reaction promoted by chiral phosphinoyl aziridines

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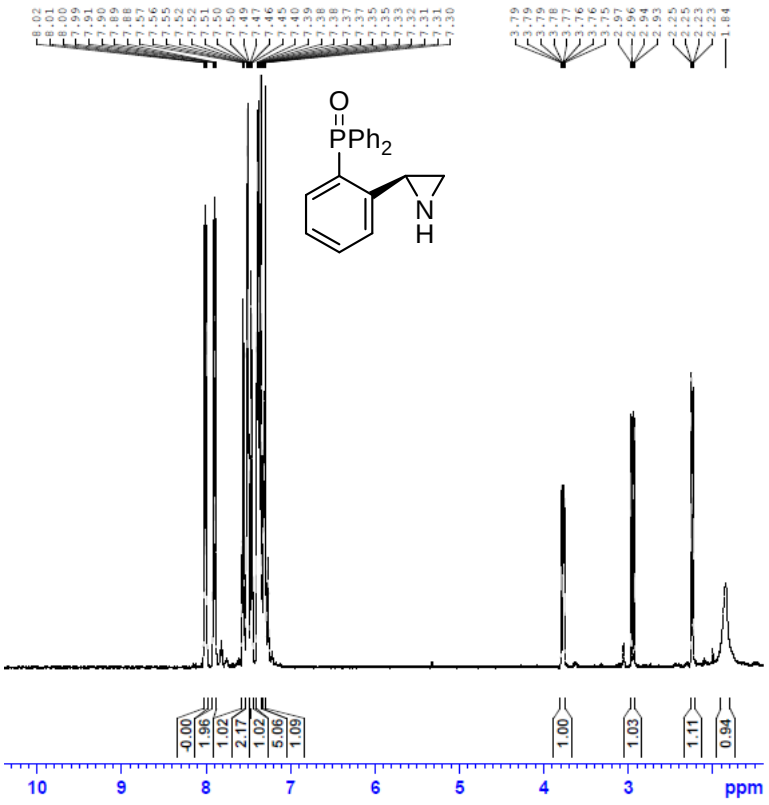
List of contents

1.Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra

The ^{1}H, ^{13}C and ^{31}P NMR of **9**

^{1}H NMR (600 MHz, $CDCl_3$):

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RG                          287
DW                       40.533 usec
DE                        8.50 usec
TE                       294.1 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                         9.40 usec
PL1                       -3.00 dB
PL1W               30.57242203 W
SFO1               600.2637069 MHz

F2 - Processing parameters
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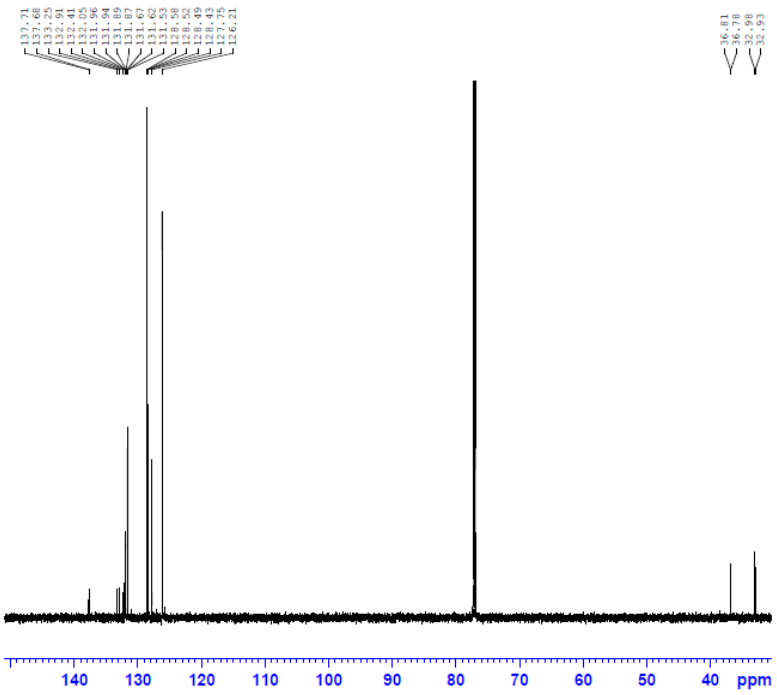
^{13}C NMR (150 MHz, $CDCl_3$):

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PROCNO                         1

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FIDRES                0.550197 Hz
AQ                    0.9087659 sec
RG                         2050
DW                       13.867 usec
DE                        8.50 usec
TE                       294.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                        10.50 usec
PL1                0 dB
PL1W               91.93504333 W
SFO1               150.9505906 MHz

======== CHANNEL f2 ========
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NUC2                         1H
PCPD2                     90.00 usec
PL2                       -3.00 dB
PL12                      16.26 dB
PL13                      18.00 dB
PL2W               30.57242203 W
PL12W               0.36251819 W
PL13W               0.24284527 W
SFO2               600.2624010 MHz

F2 - Processing parameters
SI                           32768
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PC                           1.40
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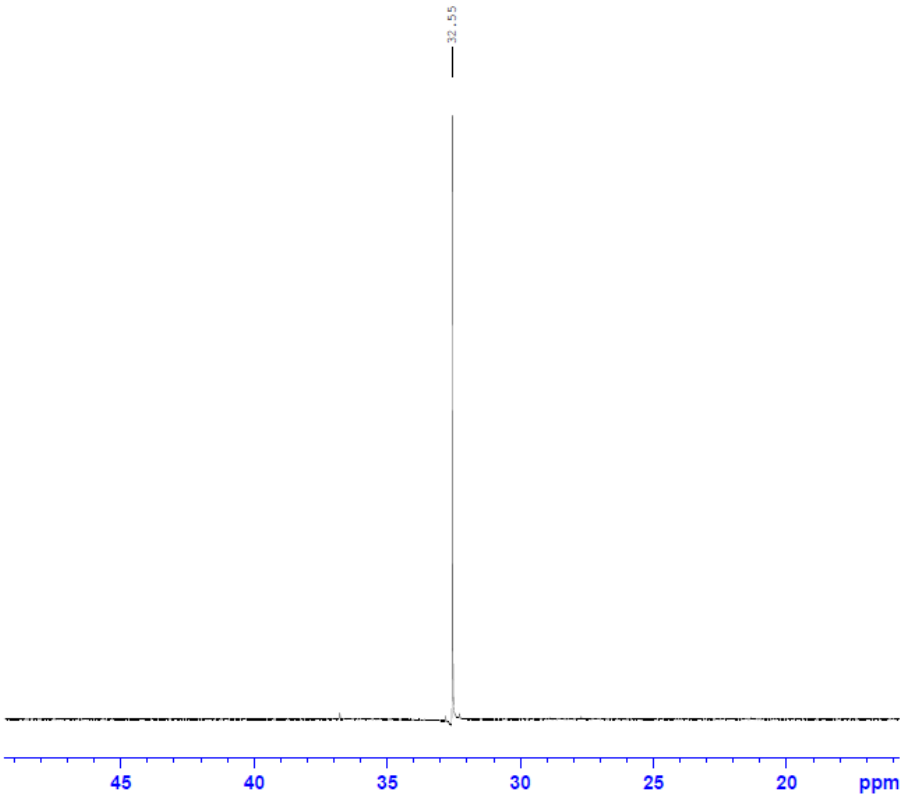
^{31}P NMR (243 MHz, $CDCl_3$):

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PROCNO                        1

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PULPROG             zgpg30
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SOLVENT                CDCl3
NS                       128
DS                         4
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FIDRES              1.467191 Hz
AQ                  0.3407872 sec
RG                       2050
DW                    5.200 usec
DE                    8.50 usec
TE                    299.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                           1

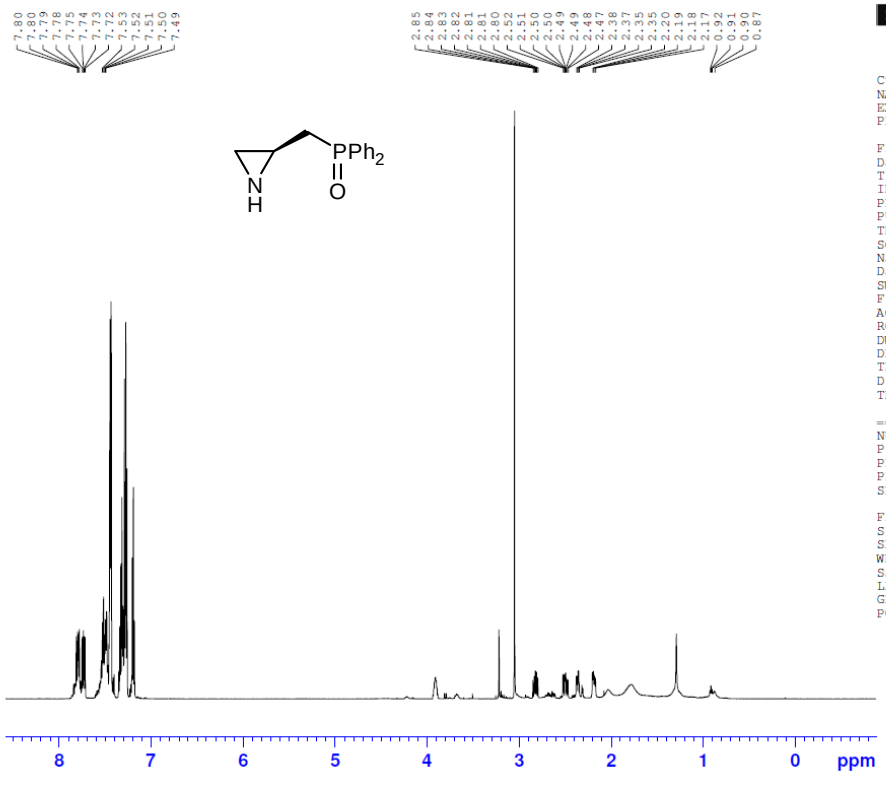
======== CHANNEL f1 ========
NUC1                       31P
P1                       13.70 usec
PL1                       0.40 dB
PL1W              69.18420410 W
SFO1             242.9775524 MHz

======== CHANNEL f2 ========
CPDPRG[2               waltz16
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -3.00 dB
PL12                    16.26 dB
PL13                    18.00 dB
PL2W              30.57242203 W
PL12W              0.36251819 W
PL13W              0.24284537 W
SFO2             600.2624010 MHz

F2 - Processing parameters
SI                        32768
SF                242.9897020 MHz
WDW                          no
SSB                0
LB                 0 Hz
GB                 0
PC                        1.40
```

The ^{1}H, ^{13}C and ^{31}P NMR of **14**

^{1}H NMR (600 MHz, $CDCl_3$):

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PROCNO                       1

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TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12335.526 Hz
FIDRES              0.188225 Hz
AQ                  2.6563926 sec
RG                       256
DW                   40.533 usec
DE                    8.50 usec
TE                    294.1 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.40 usec
PL1                     -3.00 dB
PL1W              30.57242203 W
SFO1             600.2637069 MHz

F2 - Processing parameters
SI                        32768
SF                600.2600000 MHz
WDW                          EM
SSB                0
LB                        0.30 Hz
GB                 0
PC                        1.00
```
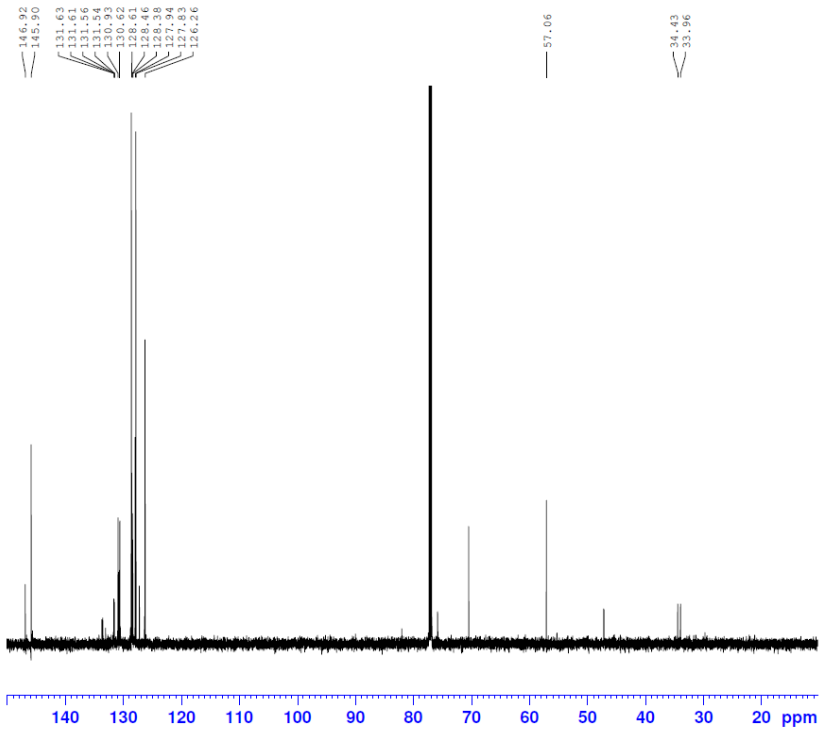

^{13}C NMR (150 MHz, $CDCl_3$):

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PROCNO                   1

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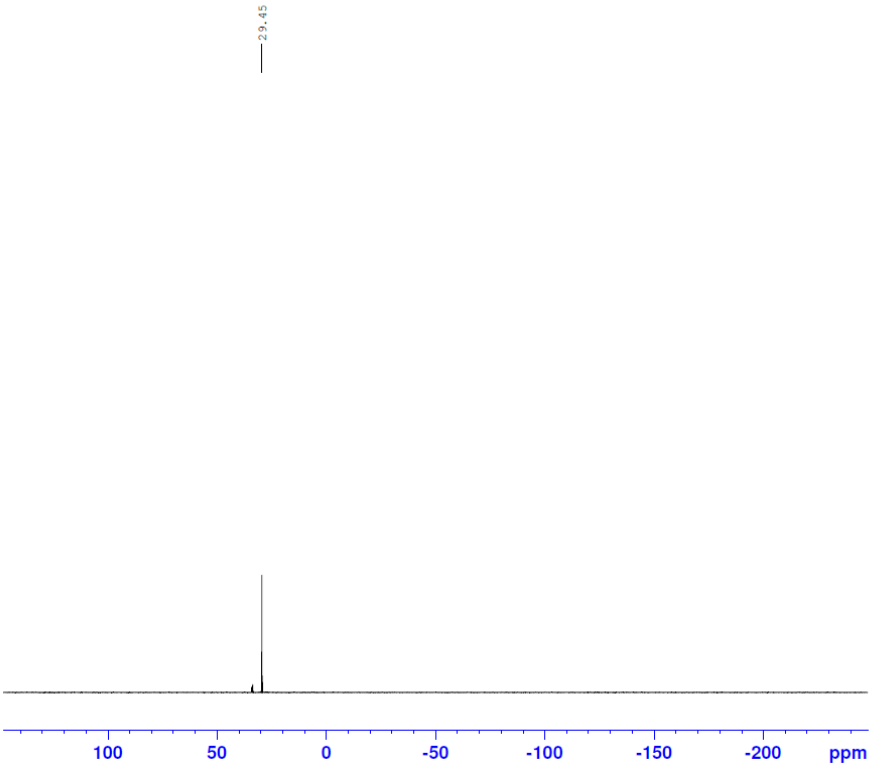
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                 2050
DW               13.867 usec
DE                8.50 usec
TE               294.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.50 usec
PL1       0 dB
PL1W        91.93504333 W
SFO1       150.9505906 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              16.26 dB
PL13              18.00 dB
PL2W        30.57242203 W
PL12W        0.36251819 W
PL13W        0.24284537 W
SFO2       600.2624010 MHz

F2 - Processing parameters
SI                32768
SF          150.9354970 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                1.40
```

^{31}P NMR (243 MHz, $CDCl_3$):

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Current Data Parameters
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EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190726
Time              22.52
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           96153.844 Hz
FIDRES         1.467191 Hz
AQ            0.3407872 sec
RG                 2050
DW                5.200 usec
DE                8.50 usec
TE               294.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 31P
P1                13.70 usec
PL1               0.40 dB
PL1W        69.18420410 W
SFO1       242.9775524 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              16.26 dB
PL13              18.00 dB
PL2W        30.57242203 W
PL12W        0.36251819 W
PL13W        0.24284537 W
SFO2       600.2624010 MHz

F2 - Processing parameters
SI                32768
SF          242.9897020 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                1.40
```
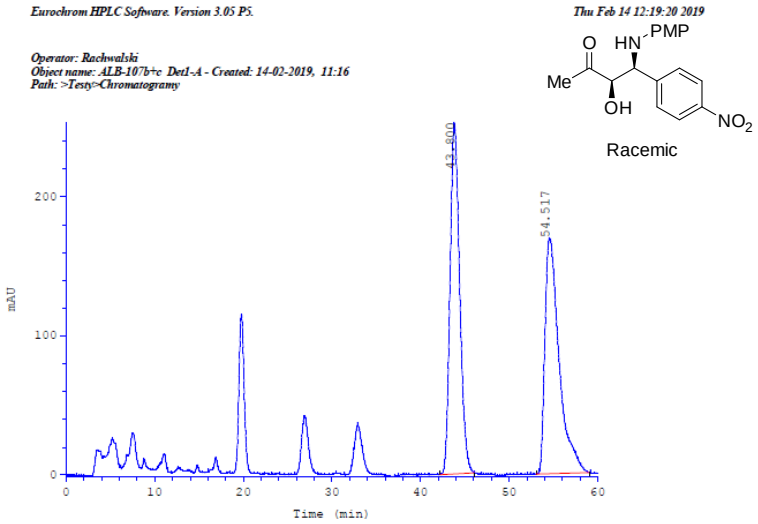

2. HPLC chromatograms of Mannich products

(*3R*,*4S*)-3-Hydroxy-4-(methoxyphenylamino)-4-(4-nitrophenyl)butan-2-one 15

ee (96%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15, flow = 1.0 mL/min, retention times (min): 43.46 (major), 54.45 (minor).



Operator: Rachwalski
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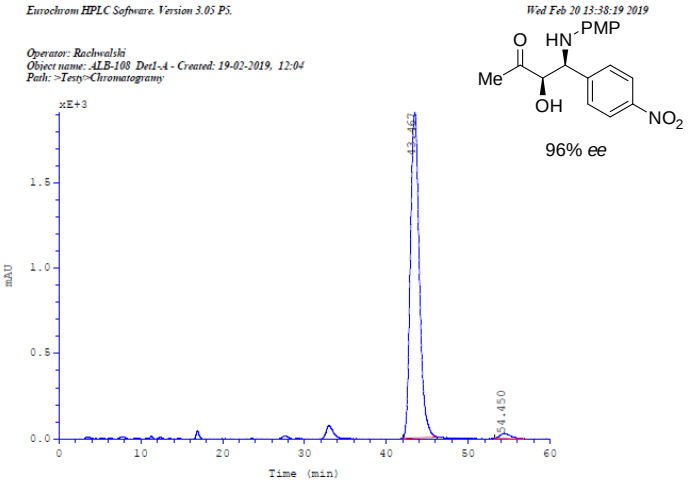
Path: >Testy>Chromatogramy

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	43.800	42.23	46.08		0		315.858	252.972	50.0404	1.153	BB
2	54.517	53.05	59.05		0		315.348	169.96	49.9596	1.621	BB



Operator: Rachwalski
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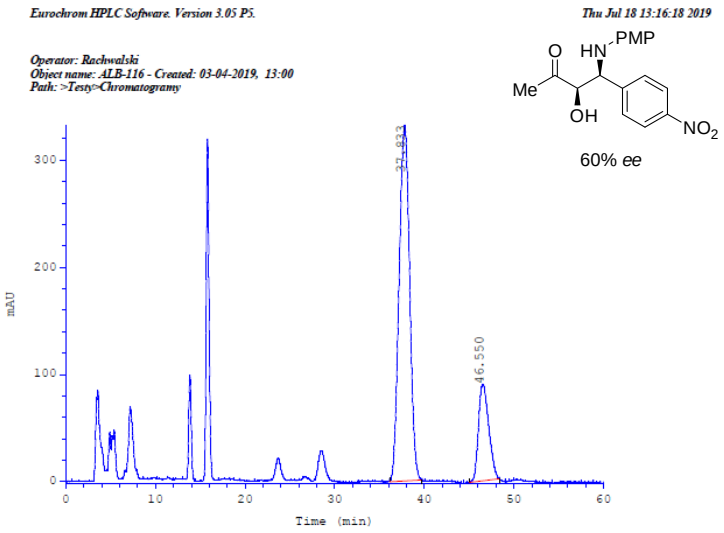
Path: >Testy>Chromatogramy

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	43.467	41.98	46.19		-1		2419.07	1906.8	98.2108	1.168	BB+
2	54.450	53.20	56.89		-1		44.0693	30.5524	1.7891	1.352	BB+

ee (60%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15, flow = 1.0 mL/min, retention times (min): 37.83 (major), 46.55 (minor).



Operator: Rachwalski
Object name: ALB-131c_Det1-B - Created: 03-04-2019, 14:00
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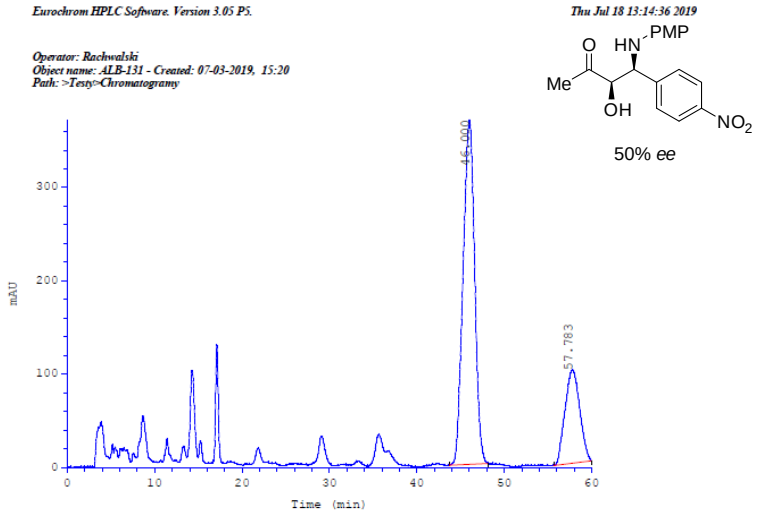
	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	37.833	36.17	39.72		0		451.241	332.312	79.0016	1.301	BB
2	46.550	45.08	48.38		0		119.938	90.3126	20.9984	1.255	BB

ee (50%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15, flow = 1.0 mL/min, retention times (min): 46.00 (major), 57.78 (minor).



Operator: Rachwalski
Object name: ALB-116cc_Det1-B - Created: 07-03-2019, 16:21
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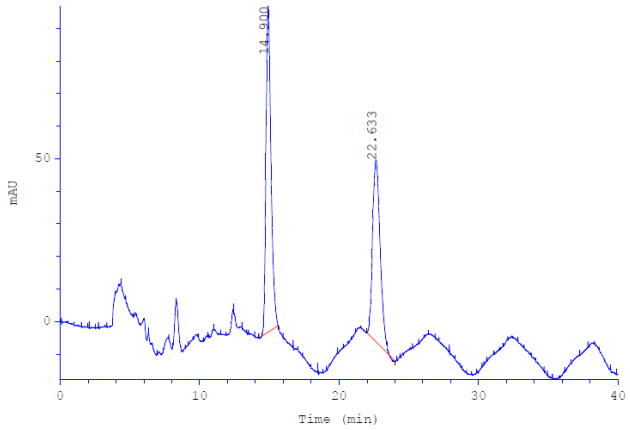
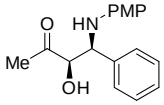
	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	46.000	43.70	48.13		0		565.415	369.136	74.2524	1.448	BB
2	57.783	55.67	59.97		0		196.062	100.406	25.7476	1.913	BB

(*3R*,4*S*)-3-Hydroxy-4-(methoxyphenylamino)-4-phenyl-butan-2-one 16

ee (89%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15, flow = 1.0 mL/min, retention times (min): 13.13 (major), 18.98 (minor).

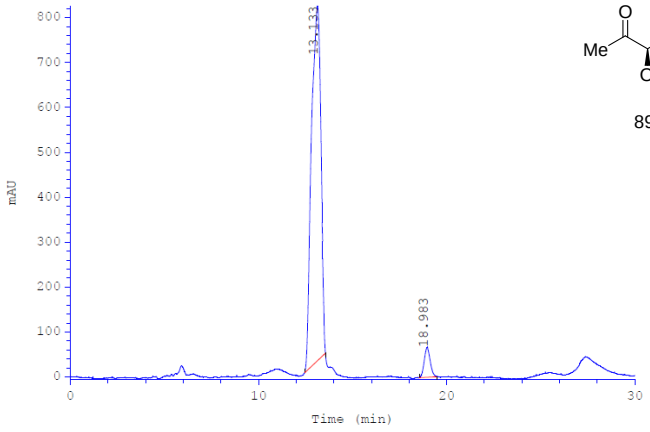


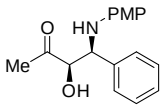


Racemic

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	14.900	14.44	15.62		-1		41.7946	100.097	54.4290	0.378	BB+
2	22.633	21.99	24.01		-1		34.9928	55.6887	45.5710	0.593	BB+

44





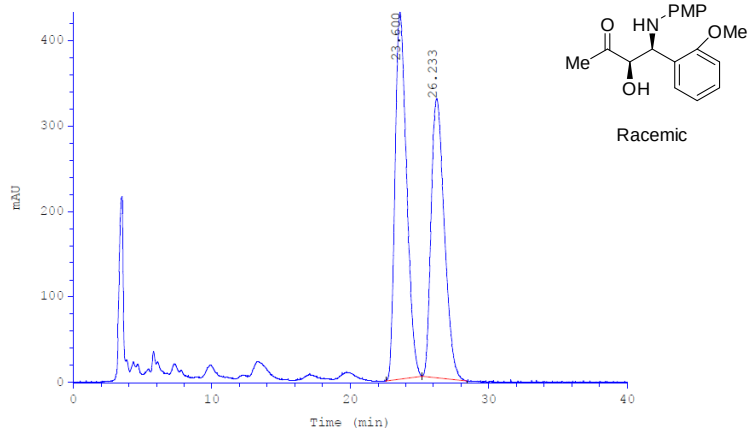
89% *ee*

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	13.133	12.46	13.56		-1		455.756	787.756	95.0205	0.600	BB+
2	18.983	18.53	19.47		0		23.8836	68.2054	4.9795	0.330	BB

45

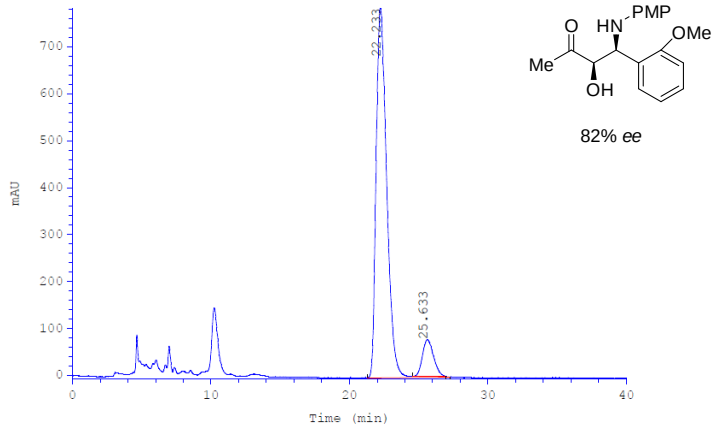
46 **(*3R*,*4S*)-3-Hydroxy-4-(methoxyphenylamino)-4-(2-methoxyphenyl)-butan-2-one 17**

47 *ee* (82%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15,
48 flow = 1.0 mL/min, retention times (min): 22.23 (major), 25.63 (minor).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	23.600	22.58	25.20		0		415.167	429.576	53.4616	0.912	BB
2	26.233	25.20	28.42		0		361.404	326.803	46.5384	1.037	BB

49

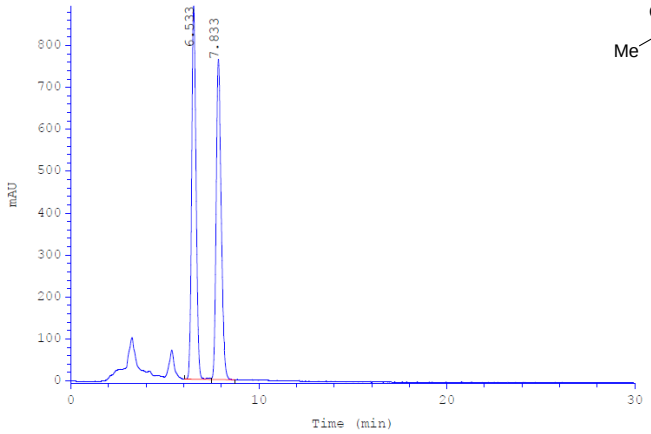


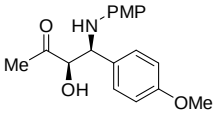
	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	22.233	21.28	27.30		0		698.487	787.516	90.5857	0.814	BB
2	25.633	24.58	26.97		0		72.5916	78.5601	9.4143	0.865	SS

50

51 **(*3R*,4*S*)-3-Hydroxy-4-(methoxyphenylamino)-4-(4-methoxyphenyl)-butan-2-one 18**

52 *ee* (90%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15,
53 flow = 1.0 mL/min, retention times (min): 6.73 (minor), 8.67 (major).

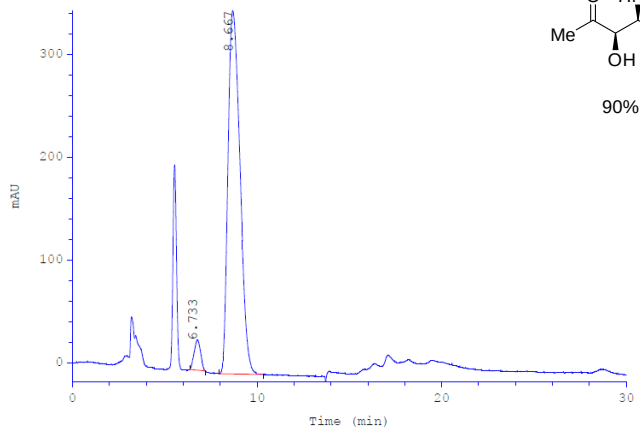


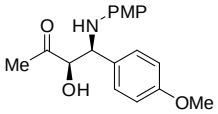


Racemic

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.533	6.07	7.47		0		237.376	890.573	50.2607	0.245	BP
2	7.833	7.47	8.73		0		234.913	763.802	49.7393	0.282	PB

54





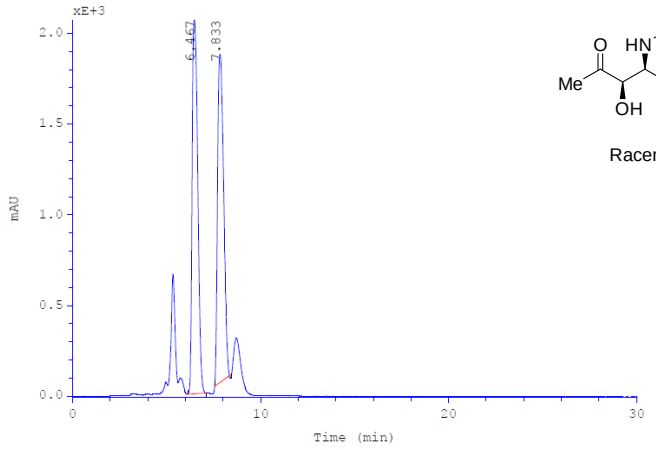
90% *ee*

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.733	6.35	7.19		-1		11.9145	29.5668	4.3190	0.395	BB+
2	8.667	7.93	10.33		0		263.949	353.769	95.6810	0.721	BB

55

56 **(*3R*,4*S*)-3-Hydroxy-4-(methoxyphenylamino)-4-(4-bromophenyl)-butan-2-one 19**

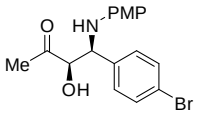
57 *ee* (91%) determined by HPLC analysis: Chiralcel AD-H column, Hexane : ^{i}PrOH = 85:15,
58 flow = 1.0 mL/min, retention times (min): 7.82 (minor), 11.52 (major).



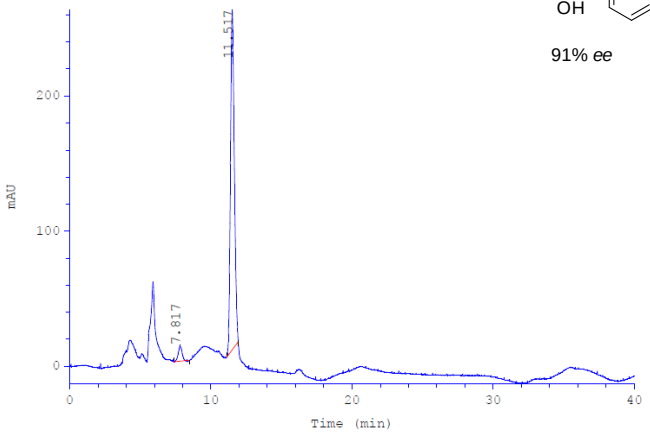
Racemic

	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.467	6.12	7.09		-1		702.718	2061.62	50.8393	0.326	BB+
2	7.833	7.55	8.46		-1		679.516	1816.84	49.1607	0.362	BB+

59



91% *ee*



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	7.817	7.40	8.52		-1		3.41694	12.0787	4.1079	0.274	BB+
2	11.517	11.14	11.94		-1		79.7627	251.261	95.8921	0.299	BB+

60