Catalytic Asymmetric Synthesis of Quaternary Carbons Bearing Two Aryl Substituents. Enantioselective Synthesis of 3-Alkyl-3-Aryl Oxindoles by Catalytic Asymmetric Intramolecular Heck Reactions

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Supporting Information

Experimental procedures for the preparation of **11a-k**, **18a-j**, hydroxyl ethyl derivatives **18a'**, **18b'**, **18d'**, **18g'**, **20-25**, **26a**, **27a**, **27b**, **28a**, **28b**, **30**; copies of ¹H and ¹³C NMR spectra for **11a-k**, **18a-j**, **18a'**, **18b'**, **18d'**, **18g'**, **20-25**, **26a**, **27a**, **27b**, **28a**, **28b**, **30**; HPLC traces used to determine the enantiopurity of **18a'**, **18b'**, **18c**, **18d'**, **18e**, **18f**, **18g'**, **18h**, **18i**, **18j**, **23**, **24**, and **30**; graphical data for the thermal equilibration of atropisomers **23** and **24**.

Part 2

Data File D:\DATA\ABD1\12130101.D

Sample Name: ABD-I-59

anisoyl system
70:30 Hex/IPA, 1 mL/min

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=====
Injection Date   : 12/13/01 1:31:53 PM      Seq. Line :    1
Sample Name      : ABD-I-59                 Location  : Vial 2
Acq. Operator    : abd                      Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\ABD1.M
Last changed     : 11/28/01 1:16:24 PM by abd
Analysis Method  : D:\METHODS\EJV\3.M
Last changed     : 9/1/02 12:38:56 PM by EJV
10% IPA-Hexanes
1 mL/min;
```

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

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.416	MM	1.8601	3.87436e4	347.14801	89.4511
2	38.181	MM	5.0868	4569.00928	14.97012	10.5489

Totals : 4.33126e4 362.11813

Results obtained with enhanced integrator!

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

H spectrum

Current Data Parameters
USER: croun
NAME: 2003-1-28
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20030128
Time: 14:40
INSTRUM: spect
PROBHD: 5 mm broadband
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 8
DS: 4
SWH: 8819.800 Hz
FIDRES: 0.120000 Hz
AQ: 4.399600 sec
RG: 382.5
RW: 302.5
DB: 55.400 usec
DE: 0.30 usec
TE: 300.2 K
D1: 0.2000000 sec

===== CHANNEL f1 =====
NUC1: 1H
P1: 13.00 usec
PL1: -1.00 dB
SFO1: 500.136051 MHz

F2 - Processing parameters
SI: 32768
SF: 500.136051 MHz
WDW: EM
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.00

1D NMR plot parameters
CY: 32.00 cm
F1P: 10.500 ppm
F1: 0.500 ppm
F2P: -0.200 ppm
F2: -0.000 ppm
NUC1: 1H
NUC2: 13C

Data File D:\DATA\ABD1\12070101.D

Sample Name: abd-i-50

pyridinyl product
85:15 Hexanes:IPA, OJ column, 1 mL/min

```
=====
Injection Date   : 12/7/01 1:08:24 PM      Seq. Line :    1
Sample Name      : abd-i-50                Location  : Vial 11
Acq. Operator    : abd                     Inj       :    1
                                           Inj Volume: 5 µl

Acq. Method      : D:\METHODS\ABD4.M
Last changed     : 12/3/01 8:42:58 AM by t
Analysis Method  : D:\METHODS\EJV\3.M
Last changed     : 9/1/02 12:38:56 PM by EJV
10% IPA-Hexanes
1 mL/min;
=====
```

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

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
```

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.021	MM	1.5109	3.58282e4	395.22009	95.8083
2	29.069	BB	1.6285	1567.49854	11.58521	4.1917

Totals : 3.73957e4 406.80531

Results obtained with enhanced integrator!

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

¹H spectrum

Data File D:\DATA\ABD1\01150203.D

Sample Name: abd-I-9

acetamide enol ether
75:25 Hex/IPA, AS column, 1 ml/min

=====
Injection Date : 1/15/02 5:31:06 PM   Seq. Line : 1
Sample Name : abd-I-98   Location : Vial 1
Acq. Operator : abd   Inj : 1
Inj Volume : 5 µl

Acq. Method : D:\METHODS\ABD1.M
Last changed : 1/15/02 5:29:28 PM by abd
Analysis Method : D:\METHODS\EJV\3.M
Last changed : 9/1/02 12:38:56 PM by EJV
10% IPA-Hexanes
1 mL/min;

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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.341	MM	4.0077	2.12742e4	88.47134	86.5868
2	34.033	MM	8.4249	3295.60034	6.51954	13.4132

Totals :   2.45698e4   94.99087

Results obtained with enhanced integrator!

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*** End of Report ***

OD-H, 85:15 Hex/IPA 1 mL/min

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=====
Injection Date : 12/22/01 11:12:25 AM      Seq. Line : 1
Sample Name    : abd-I-74                  Location  : Vial 1
Acq. Operator  : abd                      Inj      : 1
                                           Inj Volume: 5 µl

Acq. Method    : D:\METHODS\ABD6.M
Last changed   : 12/21/01 9:28:30 AM by abd
Analysis Method: D:\METHODS\EJV\3.M
Last changed   : 9/1/02 12:38:56 PM by EJV
10% IPA-Hexanes
1 mL/min;
=====
```

Area Percent Report

```
=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
=====
```

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.333	BB	1.7627	5.01476e4	428.09079	96.6709
2	58.274	MM	4.4195	1726.97705	6.51265	3.3291

Totals : 5.18746e4 434.60344

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\ABD1\01020203.D

Sample Name: abd-I-79

=====

Injection Date	: 1/2/02 5:16:12 PM	Seq. Line	: 2
Sample Name	: abd-I-79	Location	: Vial 3
Acq. Operator	: abd	Inj	: 1
		Inj Volume	: 5 µl
Acq. Method	: D:\METHODS\ABDNO2.M		
Last changed	: 1/2/02 3:52:31 PM by abd		
Analysis Method	: D:\METHODS\EJV\3.M		
Last changed	: 9/1/02 12:38:56 PM by EJV		
10% IPA-Hexanes			
1 mL/min;			

DAD1 B, Sig=254,100 Ref=360,100 (ABD1\01020203.D)

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Area Percent Report
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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	61.009	MM	2.0421	3095.29834	25.26272	6.0785
2	62.959	MM	3.8617	4.78269e4	206.41309	93.9215

Totals : 5.09222e4 231.67580

Results obtained with enhanced integrator!

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*** End of Report ***

Data File D:\HPCHEM\1\DATA\OESTI\20000031.D

Sample Name: MO-II-29

Heck product with ortho-nitro substituent

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=====
Injection Date   : 5/11/01 1:34:32 PM
Sample Name      : MO-II-29
Acq. Operator    : Martin Oestreich
Location         : Vial 81
Inj Volume       : 2.5 µl
Method           : D:\HPCHEM\1\METHODS\OESTIA.M
Last changed     : 5/11/01 1:33:03 PM by Martin Oestreich
                  (modified after loading)
=====

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Area Percent Report
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```

Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000

```

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.217	VV	0.1610	19.03525	1.55255	0.3189
2	11.940	VP	0.2615	20.89854	1.23422	0.3502
3	14.221	BV	0.3676	76.16884	3.20114	1.2763
4	15.710	VV	0.6052	5349.29004	135.90143	89.6304
5	17.230	VV	0.7247	296.09927	6.13944	4.9613
6	25.663	VV	0.8628	92.08887	1.29311	1.5430
7	28.337	VP	0.9461	114.58689	1.49851	1.9200

```
Totals :                5968.16770  150.82040
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Results obtained with enhanced integrator!

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*** End of Report ***
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=====
Injection Date   : 11/1/00 9:11:40 AM
Sample Name      : jjk-iii-17
Acq. Operator    : jkodan
Vial             : 21
Inj Volume       : 20 ul
Acq. Method      : D:\HPCHEM\1\METHODS\JJKIND.M
Last changed     : 11/1/00 9:09:53 AM by lebsack
                  (modified after loading)
Analysis Method  : D:\HPCHEM\1\METHODS\TPRODH2.M
Last changed     : 12/10/00 10:39:03 PM by TPR
=====
    
```

Area Percent Report

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=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
    
```

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.530	MM	2.1648	4.44275e4	342.03894	98.0691
2	20.143	MM	2.6704	874.73718	5.45939	1.9309

Totals : 4.53022e4 347.49833

Results obtained with enhanced integrator!

*** End of Report ***

18h

18h

S Injection Date : 1/26/02 4:35:29 PM Seq. Line : 1
Sample Name : abd-I-118 Location : Vial 5
Acq. Operator : amy Inj : 1
Inj Volume : 5 µl
Acq. Method : D:\METHODS\ABD1.M
Last changed : 1/24/02 9:51:15 PM by ABD
Analysis Method : D:\METHODS\EJV\3.M
Last changed : 9/1/02 12:38:56 PM by EJV
10% IPA-Hexanes
1 mL/min;

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.499	VP	0.2809	3682.41333	199.93222	6.5327
2	10.359	VB	0.6728	5.26868e4	1203.45642	93.4673

Totals : 5.63692e4 1403.38864

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\DATA\WEISS\MW192-4.D

Sample Name: MMW-1-192-4

5%IPA/Hexane; ODH; .85 ML/MIN;
E enol ether; R BINAP
Boc protected aniline

Injection Date : 2/13/02 10:19:18 PM
Sample Name : MMW-1-192-4
Acq. Operator : abd

Location : Vial 61

Inj Volume : 10 µl

Method : D:\METHODS\MMW2.M
Last changed : 2/13/02 9:18:54 PM by abd
(modified after loading)

5% IPA; .85 mL/min; ODH

DAD1 B, Sig=254,16 Ref=360,100 (WEISS\MW192-4.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.457	BP	0.2006	199.66243	13.65712	2.6378
2	14.506	BB	1.0230	7369.50244	108.41526	97.3622

Totals : 7569.16487 122.07238

Results obtained with enhanced integrator!

*** End of Report ***

¹H spectrum

¹³C spectrum with ¹H decoupling

Data File D:\DATA\WEISS\MW192-3.D

Sample Name: MMW-1-192-3

5%IPA/Hexane; ODH; .85 ML/MIN;
Z enol ether; R BINAP
Boc protected aniline

=====
Injection Date : 2/14/02 12:48:33 PM
Sample Name : MMW-1-192-3 Location : Vial 65
Acq. Operator : mmw Inj Volume : 10 µl
Method : D:\METHODS\MMW2.M
Last changed : 2/14/02 12:15:42 PM by ike
(modified after loading)

5% IPA; .85 mL/min; ODH
DAD1 B, Sig=254,16 Ref=360,100 (WEISS\MW192-3.D)

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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.430	PB	0.1951	16.56817	1.17046	0.1306
2	7.474	BP	0.1499	46.66462	4.25524	0.3679
3	10.874	BB	0.8054	1.18401e4	216.71307	93.3420
4	14.079	BP	0.7796	781.31079	15.15219	6.1595

Totals : 1.26846e4 237.29095

Results obtained with enhanced integrator!

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*** End of Report ***

Data File D:\DATA\MWEISS\MW186-6C.D

Sample Name: MMW-1-186-6c

10%IPA/HX; ODH: .85 mL/min
E enol ether; R BINAP

=====
Injection Date : 2/16/02 3:42:06 PM
Sample Name : MMW-1-186-6c
Acq. Operator : abd
Location : Vial 61
Inj Volume : 10 µl
Method : D:\METHODS\MMW2.M
Last changed : 2/16/02 3:36:04 PM by abd
(modified after loading)

10% IPA; .85 mL/min; ODH

DAD1 B, Sig=254,16 Ref=360,100 (MWEISS\MW186-6C.D)

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

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.466	BB	0.3020	51.00165	2.10998	0.7220
2	6.011	PB	0.1070	76.92011	9.65169	1.0889
3	9.641	PB	0.3958	212.45720	8.15966	3.0076
4	11.951	BV	0.5186	200.32639	5.53038	2.8358
5	13.286	VB	0.6224	3292.91650	80.98792	46.6148
6	17.802	BB	0.9237	3230.47925	54.33356	45.7309

Totals : 7064.10110 160.77318

Results obtained with enhanced integrator!

*** End of Report ***

Chiral 2/16/02 4:08:24 PM abd

Page 1 of 1

Kh-I-80-0911

Data File D:\DATA\MWEISS\MW147-2.D

Sample Name: MMW-1-147-2

10% IPA/hex; BINAP; .85 mL/min
low Rf; ODH

Injection Date : 1/9/02 12:04:25 PM
Sample Name : MMW-1-147-2
Acq. Operator : abd

Location : Vial 32

Inj Volume : 10 µl

Method : D:\METHODS\WEISS.M
Last changed : 1/9/02 11:28:30 AM by abd
(modified after loading)

10% IPA-Hexanes
.85 mL/min;

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.019	PB	0.0778	40.69810	7.44352	0.9805
2	10.412	BB	0.6289	4110.19629	97.29494	99.0195

Totals : 4150.89439 104.73846

Results obtained with enhanced integrator!

*** End of Report ***

MMW-1-138B-1

188-5

Sample Name: MMW-1-138B-1

5% IPA/hex; racemic; 1 mL/min
high rf; racemic; ODH

952-ee

Injection Date : 12/14/01 2:40:26 PM

Sample Name : MMW-1-138B-1

Location : Vial 2

Acq. Operator : mmw

Inj Volume : 10 µl

Method : D:\METHODS\WEISS.M

Last changed : 10/24/01 10:42:18 PM by weiss

10% IPA-Hexanes

.85mL/min;

DAD1 B, Sig=254,16 Ref=360,100 (MWEISS\MMW138-2.D)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.342	BB	0.2399	33.94003	1.86829	0.3762
2	6.186	PB	0.2196	271.95898	15.43544	3.0148
3	10.787	BV	0.5927	210.47023	5.08749	2.3332
4	12.215	VB	0.9573	8297.23145	131.64890	91.9792
5	16.059	BB	0.6929	207.17273	4.17521	2.2966

Totals : 9020.77342 158.21531

Results obtained with enhanced integrator!

*** End of Report ***

Proton

13C spectrum with 1H decoupling

Injection Date : 2/11/02 7:34:25 PM
 Sample Name : jkk-iv-114 ~~XX~~
 Operator : jkogan Location : Vial 31

Injection Volume : 5 µl
 Method : C:\HPCHEM\1\METHODS\JKODAN.M\JKODAN.M
 Date changed : 2/11/02 6:40:13 PM by jkogan
 (modified after loading)

Area Percent Report

Integrated By : Signal
 Multiplier : 1.0000
 Integration : 1.0000

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

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
3.773	VB	0.1220	16.53969	2.05203	0.2351
13.895	BB	1.0294	5624.75928	75.82483	79.9538
20.318	BB	1.2606	1393.70874	12.98128	19.8110

Sum : 7035.00771 90.85814

Results obtained with enhanced integrator!

*** End of Report ***

2/11/02 8:13:48 PM jkogan

60% ee