A PART OF THE MANUSCRIPT # 70 0486 847

PART II – PAGES S-7 – S101 of the Supporting Information for
**Regio- and Diastereoselective Insertion of Allenes into Stable
Oxapalladacycles with a Metal-Bonded Stereogenic Carbon.
Preparation of Contiguously Substituted 3,4-Dihydro-2H-1-
Benzopyrans**

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Sample ID: C159_C138
Method: C:\EZStart\Projects\Default\Methods\helena02.met
Data File: C:\EZStart\Projects\Lu\C159_C138
Column: CHIRALPAK AD
Eluent: 4/96 i-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

Sample ID: C221_C149
Method: C:\EZStart\Projects\Default\Methods\helena02.met
Data File: C:\EZStart\Projects\Lu\C221_C149
Column: CHIRALPAK AD
Eluent: 4/96 *i*-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

Sample ID: B73_C125
Method: C:\EZStart\Projects\Default\Methods\helena02.met
Data File: C:\EZStart\Projects\Lu\B73_C125
Column: CHIRALPAK AD
Eluent: 1/99 *i*-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

Sample ID: B183_C124
Method: C:\EZStart\Projects\Default\Methods\helen02.met
Data File: C:\EZStart\Projects\Lu\B183_C124
Column: CHIRALPAK AD
Eluent: 1/99 *i*-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

Sample ID: C27a_C136
Method: C:\EZStart\Projects\Default\Methods\helena02.met
Data File: C:\EZStart\Projects\Lu\C27a_C136
Column: CHIRALPAK AD
Eluent: 1/99 *i*-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

Sample ID: C217a_C144
Method: C:\EZStart\Projects\Default\Methods\helena02.met
Data File: C:\EZStart\Projects\Lu\C217a_C144
Column: CHIRALPAK AD
Eluent: 1/99 *i*-PrOH/Hexane
Flow rate: 1 mL/min; Detection: 245 nm

1b

¹H NMR (400 MHz, CDCl₃)

1b

¹³C NMR (100 MHz, CDCl₃)

1c
¹H NMR (400 MHz, CDCl₃)

1c
¹³C NMR (125 MHz, CDCl₃)

2b

¹³C NMR (125 MHz, CDCl₃)

2c

^{13}C NMR (125 MHz, CDCl_3)

3b

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

0 M

¹³C NMR (100 MHz, CDCl₃)

5a

¹H NMR (500 MHz, CDCl₃)

5a

¹³C NMR (125 MHz, CDCl₃)

5a

NOE ^1H NMR(500 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

5c
¹³C NMR (100 MHz, CDCl₃)

6
¹H NMR (500 MHz, CDCl₃)

¹³C NMR (125 MHz, CDCl₃)

6
NOE ^1H NMR (500 MHz, CDCl_3)

7

^1H NMR (500 MHz, CDCl_3)

7

^{13}C NMR (125 MHz, CDCl_3)

8a : 8b

96 : 4

¹H NMR (500 MHz, CDCl₃)

8a : 8b

96 : 4

^{13}C NMR (125 MHz, CDCl_3)

¹H NMR and ¹³C NMR Chemical Shift Assignments for Benzopyran **8a**

Measured at 500 MHz in CDCl₃

Long range (mostly three bond) connectivities observed in the 500 MHz HMBC spectrum of benzopyran **8a** in CDCl₃.

Proton (ppm)	Assignment	Correlation (carbon)
5.07	H2	C3, C4, C9, C13
4.24	H3	C10, C11, C12
3.35	H11	C3
5.69/5.12	H12	C3, C4, C10
7.47	H5	C4, C7, C9
6.93	H6	C8, C10
7.23	H7	C5, C9
6.98	H8	C6, C9, C10

8a
HMBC 2D NMR
(500 MHz, CDCl₃)

8a
HMBC 2D NMR
(500 MHz, CDCl₃)

8a
NOE ^1H NMR (500 MHz, CDCl_3)

9a : 9b
95 : 5

¹H NMR (400 MHz, CDCl₃)

9a : **9b**

95 : 5

^{13}C NMR (100 MHz, CDCl_3)

9a

NOE ^1H NMR (500 MHz, CDCl_3)

91 : 9

¹H NMR (500 MHz, CDCl₃)

10 : 11

91 : 9

¹³C NMR (125 MHz, CDCl₃)

¹H NMR and ¹³C NMR Chemical Shift Assignments for Benzopyrans **10**

Measured at 500 MHz in CDCl₃

Long range (mostly three bond) connectivities observed in the 500 MHz HMBC spectrum of benzopyran **10** in CDCl₃.

Proton (ppm)	Assignment	Correlation (carbon)
4.78	H2	C3, C4, C9, C11
2.83	H3	C4, C13
7.45	H5	C4, C7, C9,
6.91	H6	C8, C10
7.21	H7	C5, C9
6.93	H8	C6, C10
5.47 4.87	H13	C3, C4, C10,

10
NOE 1H NMR (500 MHz, $CDCl_3$)

12

¹H NMR (500 MHz, CDCl₃)

12

¹³C NMR (125 MHz, CDCl₃)

12

NOE ^1H NMR(500 MHz, CDCl_3)

13
 ^1H NMR (400 MHz, CDCl_3)

13

¹³C NMR (100 MHz, CDCl₃)

13

NOE ^1H NMR (500 MHz, CDCl_3)

14 : 15
92 : 8
¹H NMR (500 MHz, CDCl₃)

92 : 8

¹³C NMR (125 MHz, CDCl₃)

14
NOE 1H NMR (500 MHz, $CDCl_3$)

15

NOE ^1H NMR (500 MHz, CDCl_3)

16

¹H NMR (400 MHz, CDCl₃)

16

¹³C NMR (100 MHz, CDCl₃)

16
NOE ¹H NMR (500 MHz, CDCl₃)

17

^1H NMR (400 MHz, CDCl_3)

17

^{13}C NMR (125 MHz, CDCl_3)

18 : 19

90 : 10

¹H NMR (500 MHz, CDCl₃)

18 : 19
90 : 10
¹³C NMR (125 MHz, CDCl₃)

18

NOE ^1H NMR (500 MHz, CDCl_3)

19
NOE ^1H NMR (500 MHz, CDCl_3)

20
¹H NMR (400 MHz, CDCl₃)

20

¹³C NMR (125 MHz, CDCl₃)

20

NOE ^1H NMR (500 MHz, CDCl_3)

21
¹H NMR (400 MHz, CDCl₃)

21

^{13}C NMR (125 MHz, CDCl_3)

21
NOE ^1H NMR (500 MHz, CDCl_3)

22

¹H NMR (500 MHz, CDCl₃)

22

^{13}C NMR (125 MHz, CDCl_3)

22

NOE ^1H NMR (500 MHz, CDCl_3)

23

¹H NMR (500 MHz, CDCl₃)

23
 ^{13}C NMR (125 MHz, CDCl_3)

23

NOE ^1H NMR (500 MHz, CDCl_3)

24 : 25

22 : 78

¹H NMR (500 MHz, CDCl₃)

24 : 25

22 : 78

^{13}C NMR (125 MHz, CDCl_3)

24

NOE ^1H NMR (500 MHz, CDCl_3)

25
NOE ¹H NMR (500 MHz, CDCl₃)

26

¹H NMR (500 MHz, CDCl₃)

26

¹³C NMR (125 MHz, CDCl₃)

¹H NMR (500 MHz, CDCl₃)

27 : 28

28 : 72

¹³C NMR (125 MHz, CDCl₃)

(+)-**29c**
¹³C NMR (125 MHz, CDCl₃)

(-)-30c
 ^1H NMR (400 MHz, CDCl_3)
 50% *de*

(-)-30c
 ^{13}C NMR (125 MHz, CDCl_3)
 50% *de*