

## NMR Spectra and HPLC Profiles for

# Chiral squaramide catalyzed asymmetric synthesis of pyranones and pyranonaphthaquinones via cascade reactions of 1,3-dicarbonyls with Morita-Baylis-Hillman acetates of nitroalkenes

Divya K. Nair,<sup>a</sup> Rubem F. S. Menna-Barreto,<sup>b</sup> Eufrânio N. da Silva Júnior,<sup>\*c</sup> S. M. Mobin,<sup>d</sup> Irishi N. N. Namboothiri<sup>\*a</sup>

<sup>a</sup>Department of Chemistry and <sup>d</sup>National Single-Crystal X-Ray Diffraction Facility, Indian Institute of Technology Bombay, Mumbai 400 076, India, <sup>b</sup> Oswaldo Cruz Institute, FIOCRUZ, Rio de Janeiro, RJ, 21045-900, Brazil. <sup>c</sup> Institute of Exact Sciences, Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, MG, 31270-901, Brazil.

*irishi@iitb.ac.in, eufranio@ufmg.br*

1	Figure S1. <sup>1</sup> H NMR Spectrum of <b>4a</b>	5
2	Figure S2. <sup>13</sup> C NMR Spectrum of <b>4a</b>	6
3	Figure S3. HPLC profile of racemic <b>4a</b>	7
4	Figure S4. HPLC profile of enantioenriched <b>4a</b>	8
5	Figure S5. <sup>1</sup> H NMR Spectrum of <b>4b</b>	9
6	Figure S6. <sup>13</sup> C NMR Spectrum of <b>4b</b>	10
7	Figure S7. HPLC profile of racemic <b>4b</b>	11
8	Figure S8. HPLC profile of enantioenriched <b>4b</b>	12
9	Figure S9. <sup>1</sup> H NMR Spectrum of <b>4c</b>	13
10	Figure S10. <sup>13</sup> C NMR Spectrum of <b>4c</b>	14
11	Figure S11. HPLC profile of racemic <b>4c</b>	15
12	Figure S12. HPLC profile of enantioenriched <b>4c</b>	16

13	Figure S13. $^1\text{H}$ NMR Spectrum of <b>5a</b>	17
14	Figure S14. $^{13}\text{C}$ NMR Spectrum of <b>5a</b>	18
15	Figure S15. HPLC profile of racemic <b>5a</b>	19
16	Figure S16. HPLC profile of enantioenriched <b>5a</b>	20
17	Figure S17. $^1\text{H}$ NMR Spectrum of <b>5b</b>	21
18	Figure S18. $^{13}\text{C}$ NMR Spectrum of <b>5b</b>	22
19	Figure S19. HPLC profile of racemic <b>5b</b>	23
20	Figure S20. HPLC profile of enantioenriched <b>5b</b>	24
21	Figure S21. $^1\text{H}$ NMR Spectrum of <b>5c</b>	25
22	Figure S22. $^{13}\text{C}$ NMR Spectrum of <b>5c</b>	26
23	Figure S23. HPLC profile of racemic <b>5c</b>	27
24	Figure S24. HPLC profile of enantioenriched <b>5c</b>	28
25	Figure S25. $^1\text{H}$ NMR Spectrum of <b>5d</b>	29
26	Figure S26. $^{13}\text{C}$ NMR Spectrum of <b>5d</b>	30
27	Figure S27. COSY spectrum of <b>5d</b>	31
28	Figure S28. HSQC Spectrum of <b>5d</b>	32
29	Figure S29. HPLC profile of racemic <b>5d</b>	33
30	Figure S30. HPLC profile of enantioenriched <b>5d</b>	34
31	Figure S31. $^1\text{H}$ NMR Spectrum of <b>5e</b>	35

32	Figure S32. $^{13}\text{C}$ NMR Spectrum of <b>5e</b>	36
33	Figure S33. HPLC profile of racemic <b>5e</b>	37
34	Figure S34. HPLC profile of enantioenriched <b>5e</b>	38
35	Figure S35. $^1\text{H}$ NMR Spectrum of <b>5f</b>	39
36	Figure S36. $^{13}\text{C}$ NMR Spectrum of <b>5f</b>	40
37	Figure S37. HPLC profile of racemic <b>5f</b>	41
38	Figure S38. HPLC profile of enantioenriched <b>5f</b>	42
39	Figure S39. $^1\text{H}$ NMR Spectrum of <b>5g</b>	43
40	Figure S40. $^{13}\text{C}$ NMR Spectrum of <b>5g</b>	44
41	Figure S41. HPLC profile of racemic <b>5g</b>	45
42	Figure S42. HPLC profile of enantioenriched <b>5g</b>	46
43	Figure S43. $^1\text{H}$ NMR Spectrum of <b>5h</b>	47
44	Figure S44. $^{13}\text{C}$ NMR Spectrum of <b>5h</b>	48
45	Figure S45. HPLC profile of racemic <b>5h</b>	49
46	Figure S46. HPLC profile of enantioenriched <b>5h</b>	50
47	Figure S47. $^1\text{H}$ NMR Spectrum of <b>5i</b>	51
48	Figure S48. $^{13}\text{C}$ NMR Spectrum of <b>5i</b>	52
49	Figure S49. HPLC profile of racemic <b>5i</b>	53
50	Figure S50. HPLC profile of enantioenriched <b>5i</b>	54
51	Figure S51. $^1\text{H}$ NMR Spectrum of <b>5j</b>	55
52	Figure S52. $^{13}\text{C}$ NMR Spectrum of <b>5j</b>	56
53	Figure S53. HPLC profile of racemic <b>5j</b>	57

54	Figure S54. HPLC profile of enantioenriched <b>5j</b>	58
55	Figure S55. <sup>1</sup> H NMR Spectrum of <b>5k</b>	59
56	Figure S56. <sup>13</sup> C NMR Spectrum of <b>5k</b>	60
57	Figure S57. HPLC profile of racemic <b>5k</b>	61
58	Figure S58. HPLC profile of enantioenriched <b>5k</b>	62
59	Figure S59. <sup>1</sup> H NMR Spectrum of <b>5l</b>	63
60	Figure S60. <sup>13</sup> C NMR Spectrum of <b>5l</b>	64
61	Figure S61. HPLC profile of racemic <b>5l</b>	65
62	Figure S62. HPLC profile of enantioenriched <b>5l</b>	66
63	Figure S63. <sup>1</sup> H NMR Spectrum of <b>6f</b>	67
64	Figure S64. <sup>13</sup> C NMR Spectrum of <b>6f</b>	68
65	Figure S65. HPLC profile of racemic <b>6f</b>	69
66	Figure S66. HPLC profile of enantioenriched <b>6f</b>	70
67	Figure S67. <sup>1</sup> H NMR Spectrum of <b>8c</b>	71
68	Figure S68. <sup>13</sup> C NMR Spectrum of <b>8c</b>	72
69	Figure S69. HPLC profile of racemic <b>8c</b>	73
70	Figure S70. HPLC profile of enantioenriched <b>8c</b>	74
71	Figure S71. <sup>1</sup> H NMR Spectrum of <b>10c</b>	75
72	Figure S72. <sup>13</sup> C NMR Spectrum of <b>10c</b>	76
73	Figure S73. HPLC profile of racemic <b>10c</b>	77
74	Figure S74. HPLC profile of enantioenriched <b>10c</b>	78

Current Data Parameters  
NAME INN-DKN-112-1H  
EXPNO 13  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140113  
Time 10.33  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.152588 Hz  
AQ 3.2767999 sec  
RG 53.37  
DW 50.000 usec  
DE 6.50 usec  
TE 293.3 K  
D1 1.00000000 sec  
TD0 1

----- CHANNEL f1 -----  
SFO1 500.1330885 MHz  
NUC1 1H  
P1 13.00 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SF 500.1300123 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

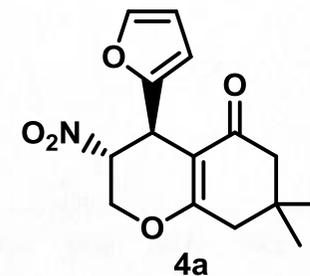
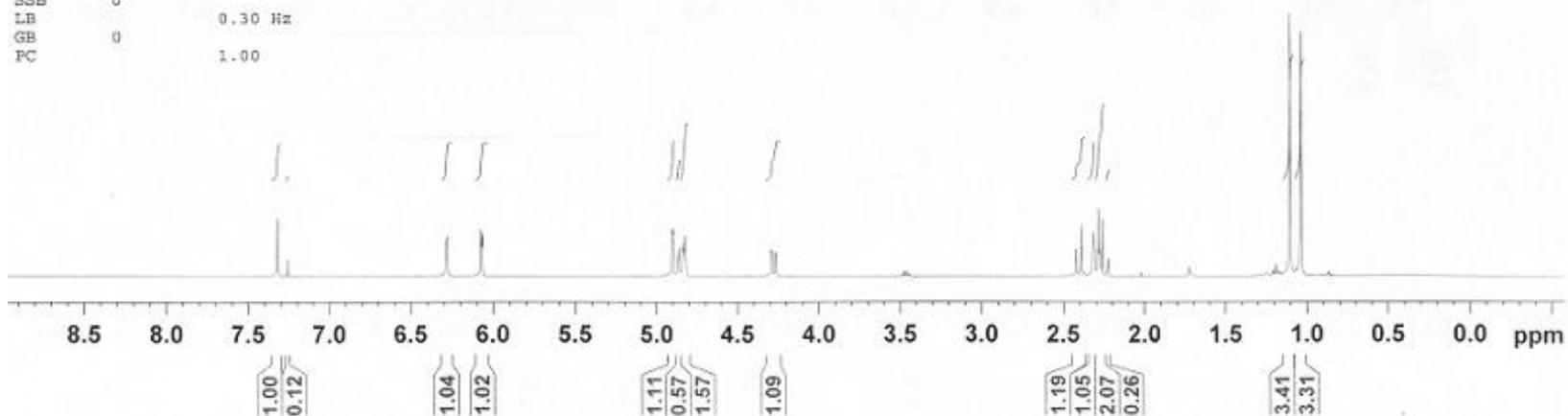


Figure S1. <sup>1</sup>H NMR Spectrum of 4a

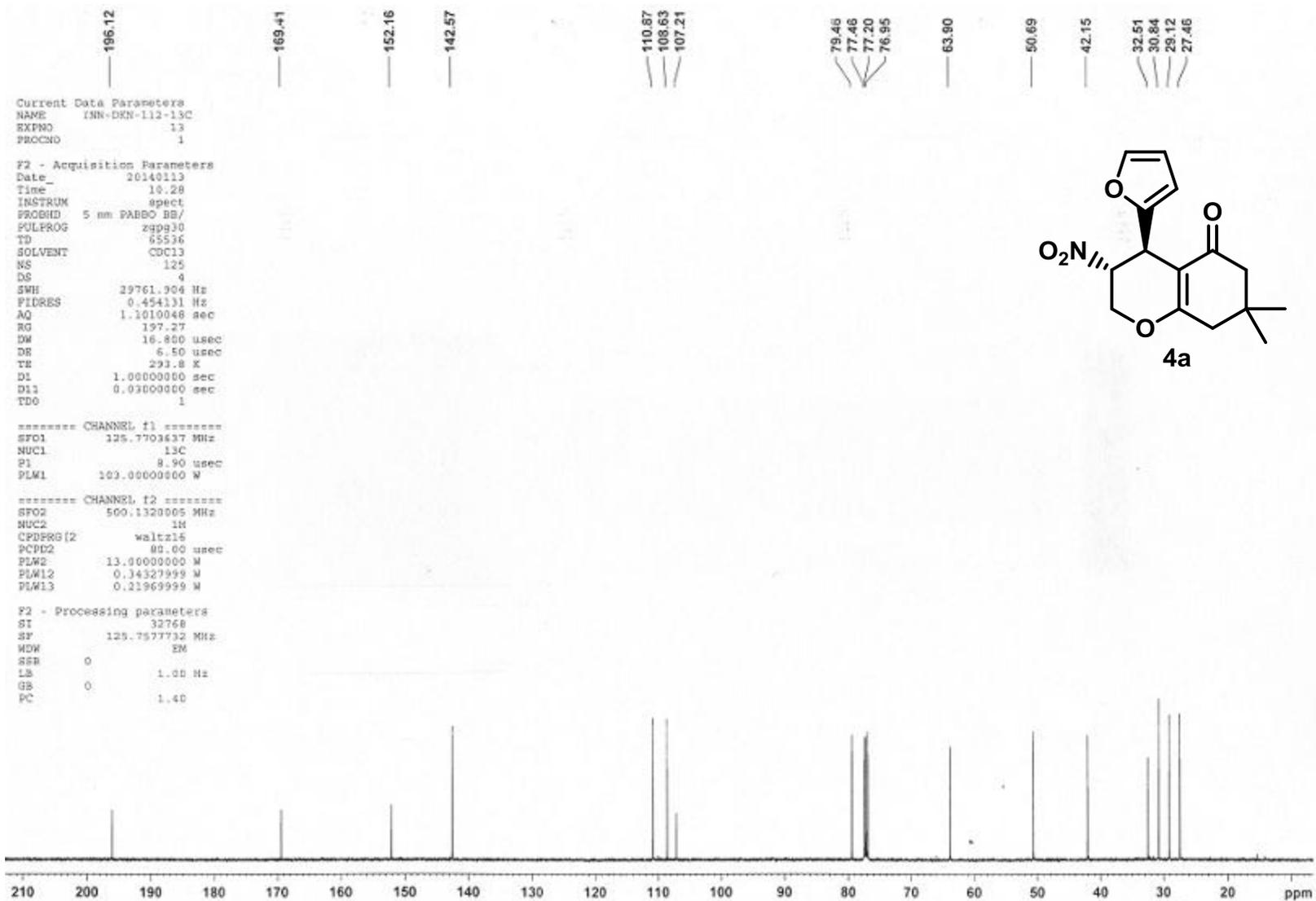
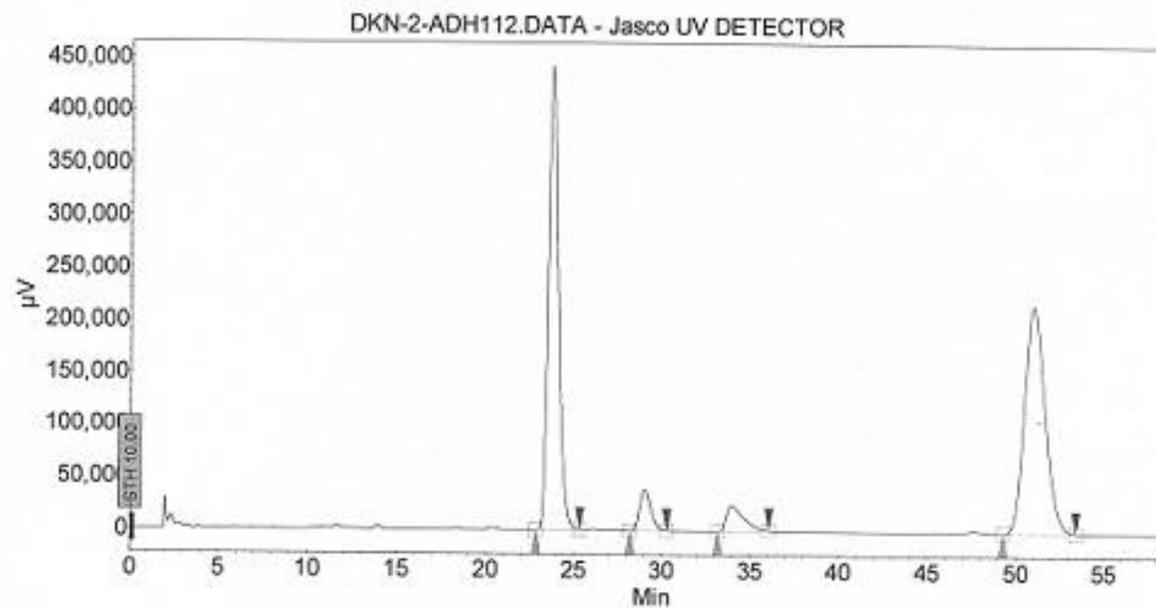
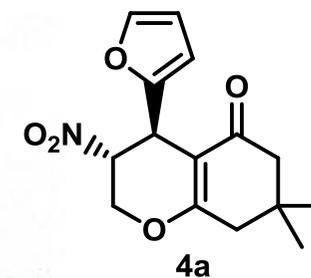


Figure S2. <sup>13</sup>C NMR Spectrum of 4a

## Chromatogram : DKN-2-ADH112\_channel2

System : JASCO HPLC  
Method : ksb-2%-1fr  
User : User1

Acquired : 10/20/2010 6:32:57 PM  
Processed : 10/20/2010 7:32:14 PM  
Printed : 3/16/2012 5:20:01 PM



### Peak results :

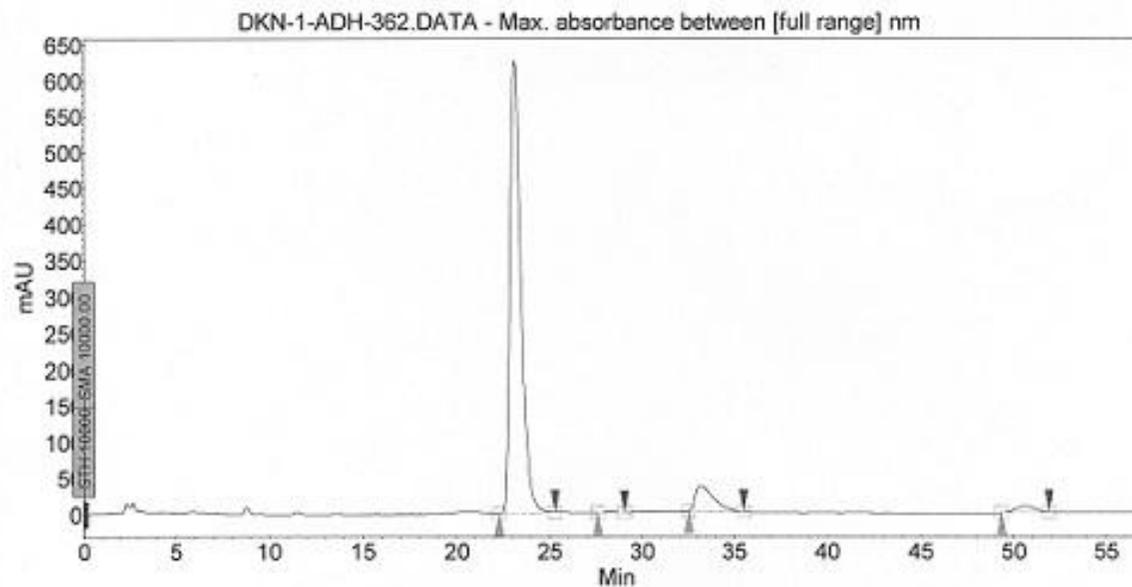
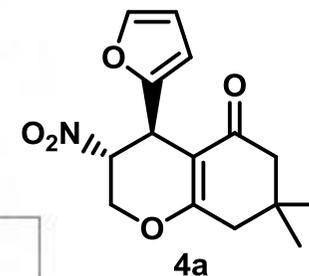
Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	23.683	45.60	443334.0	293665.3	45.600
2	UNKNOWN	29.033	4.52	38872.0	29115.8	4.521
3	UNKNOWN	33.975	4.26	24204.2	27441.8	4.261
4	UNKNOWN	50.925	45.62	217618.3	293777.3	45.618
Total			100.00	724228.5	644000.3	100.000

Figure S3. HPLC profile of racemic 4a

## Chromatogram : DKN-1-ADH-362\_channel5

System : JASCO HPLC  
 Method : ksb-2%-1f-230nm  
 User : User1

Acquired : 11/25/2011 11:24:06 AM  
 Processed : 3/16/2012 5:38:10 PM  
 Printed : 3/16/2012 5:38:37 PM



### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	23.105	89.28	626.4	425.5	89.280
1	UNKNOWN	28.305	0.20	1.5	1.0	0.203
3	UNKNOWN	33.198	6.36	35.4	39.8	8.359
4	UNKNOWN	50.596	2.16	8.4	10.3	2.158
Total			100.00	671.6	476.6	100.000

Figure S4. HPLC profile of enantioenriched 4a

Current Data Parameters  
NAME INN-DEK-CYCLOHEX-1H  
EXPNO 13  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140113  
Time\_ 10.37  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.152588 Hz  
AQ 3.2767999 sec  
RG 53.37  
DW 50.000 usec  
DE 6.50 usec  
TE 293.2 K  
D1 1.00000000 sec  
TDO 1

----- CHANNEL f1 -----  
SFO1 500.1330885 MHz  
NUC1 1H  
P1 13.00 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SF 500.1300122 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

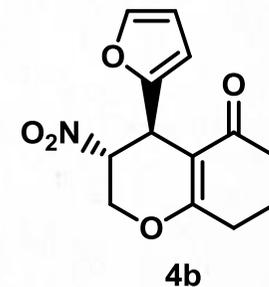
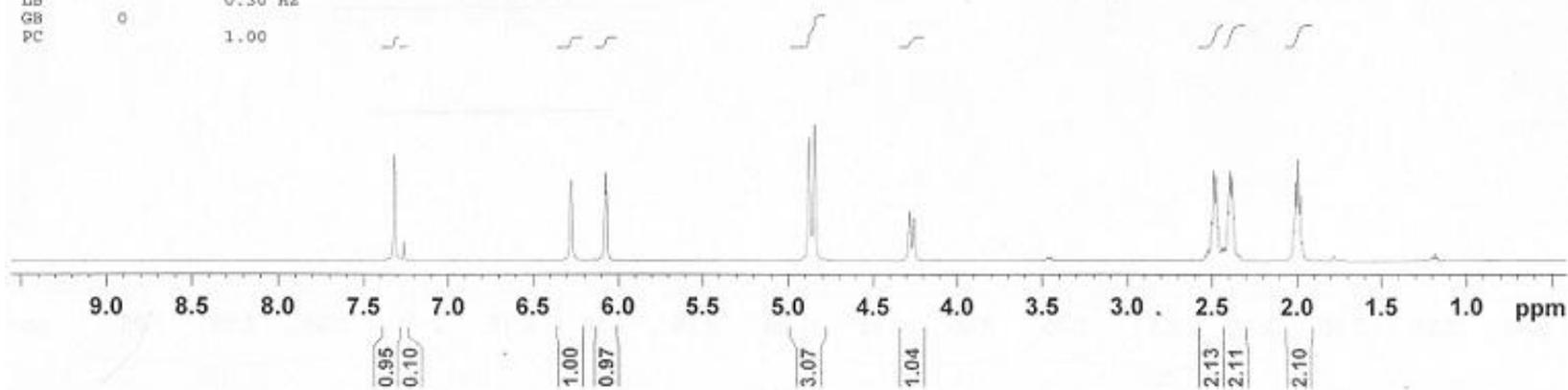


Figure S5. <sup>1</sup>H NMR Spectrum of 4b

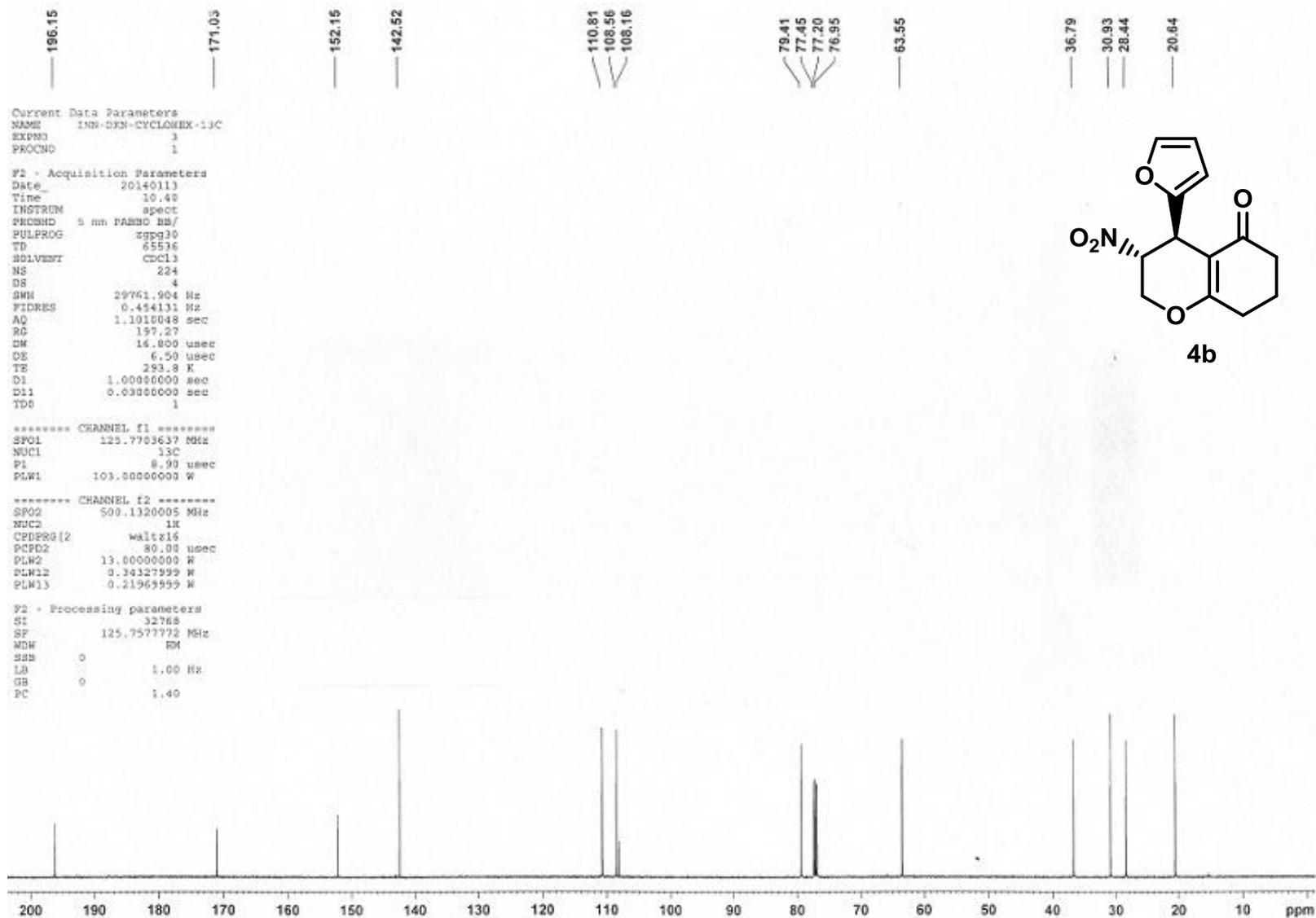
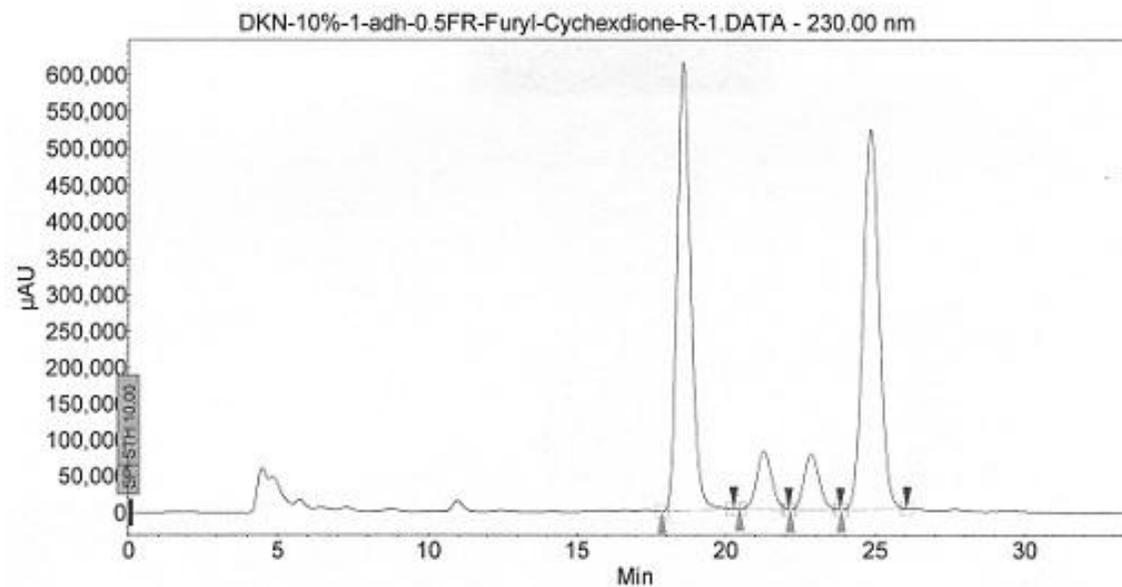
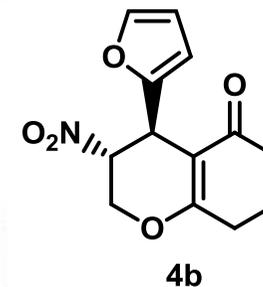


Figure S6. <sup>13</sup>C NMR Spectrum of 4b

## Chromatogram : DKN-10%-1-adh-0.5FR-Furyl-Cychexdione-R-1\_channel4

System : Jasco HPLC  
 Method : DKN-10%-05FR-230nm  
 User : User1

Acquired : 10/3/2012 4:33:02 PM  
 Processed : 10/3/2012 5:13:39 PM  
 Printed : 10/3/2012 5:13:57 PM



### Peak results :

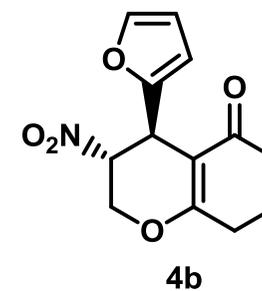
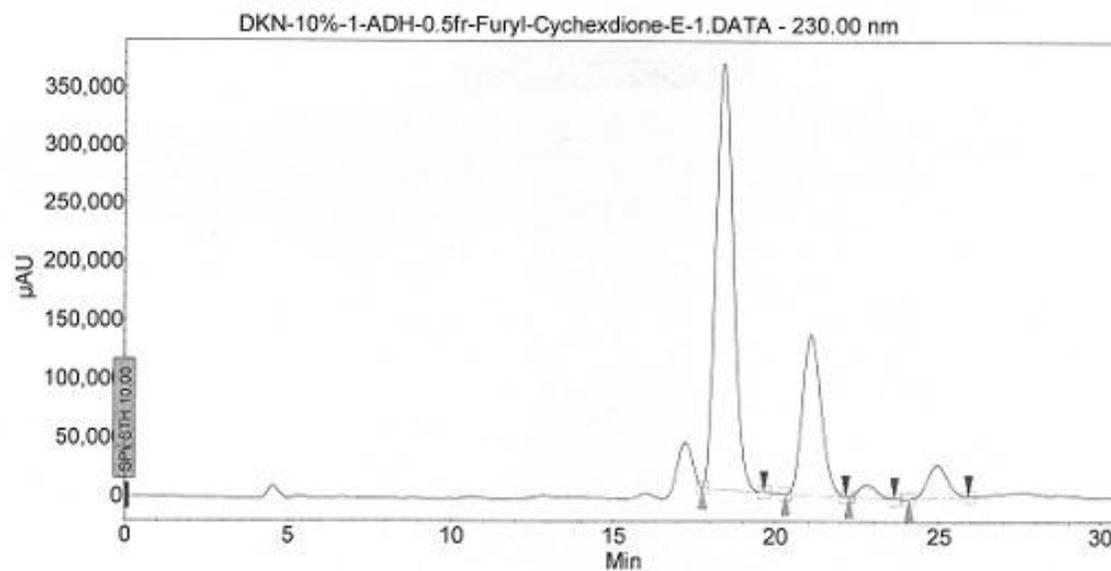
Index	Name	Time [Min]	Quantity [% Area]	Height [pAU]	Area [pAU.Min]	Area % [%]
4	UNKNOWN	18.572	43.93	615376.0	325814.3	43.931
2	UNKNOWN	21.278	6.18	79350.7	45855.9	6.183
3	UNKNOWN	22.865	5.95	76615.3	44101.8	5.946
1	UNKNOWN	24.852	43.94	521571.6	325877.0	43.940
Total						
			100.00	1292913.6	741649.1	100.000

Figure S7. HPLC profile of racemic 4b

### Chromatogram : DKN-10%-1-ADH-0.5fr-Furyl-Cyhexdione-E-1\_channel4

System : Jasco HPLC  
Method : DKN-10%-05FR-230nm  
User : User1

Acquired : 10/3/2012 10:37:54 PM  
Processed : 10/3/2012 11:10:30 PM  
Printed : 10/3/2012 11:10:41 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
3	UNKNOWN	18.385	65.82	365050.8	225402.5	65.824
1	UNKNOWN	21.078	26.41	136356.5	90451.4	26.414
2	UNKNOWN	22.798	1.98	10945.8	6815.9	1.990
4	UNKNOWN	24.932	5.77	28027.2	19762.0	5.771
Total			100.00	540380.2	342431.8	100.000

Figure S8. HPLC profile of enantioenriched 4b

```

NAME      INN-DKN-407-1H
EXPNO     1
PROCNO    1
Date_     20121025
Time      18.58
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         0
SWH        8223.605 Hz
FIDRES     0.125493 Hz
AQ         3.9846387 sec
RG         32
DW         60.800 usec
DE         6.50 usec
TE         300.0 K
OI         1.00000000 sec
TDO        1

```

```

----- CHANNEL f1 -----
NUC1       1H
P1         13.50 usec
PL1        -1.00 dB
PL1W       10.56200695 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300095 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

```

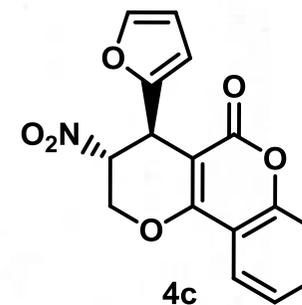
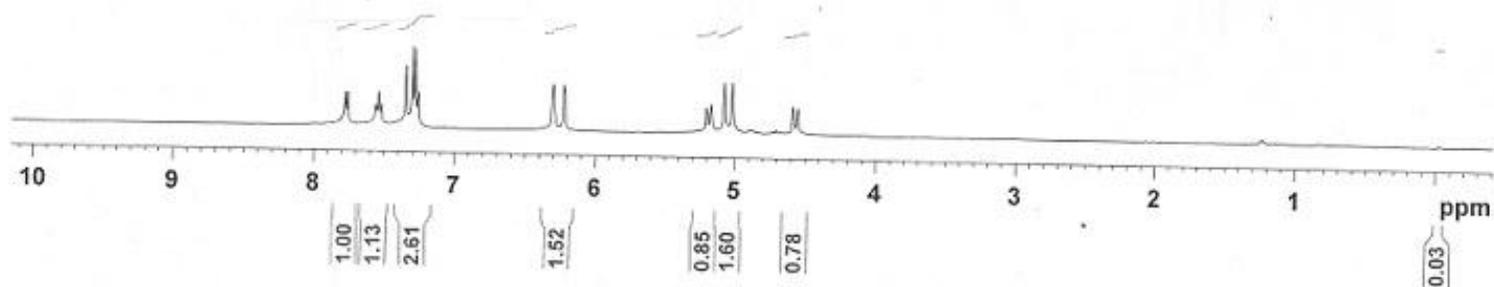


Figure S9. <sup>1</sup>H NMR Spectrum of 4c

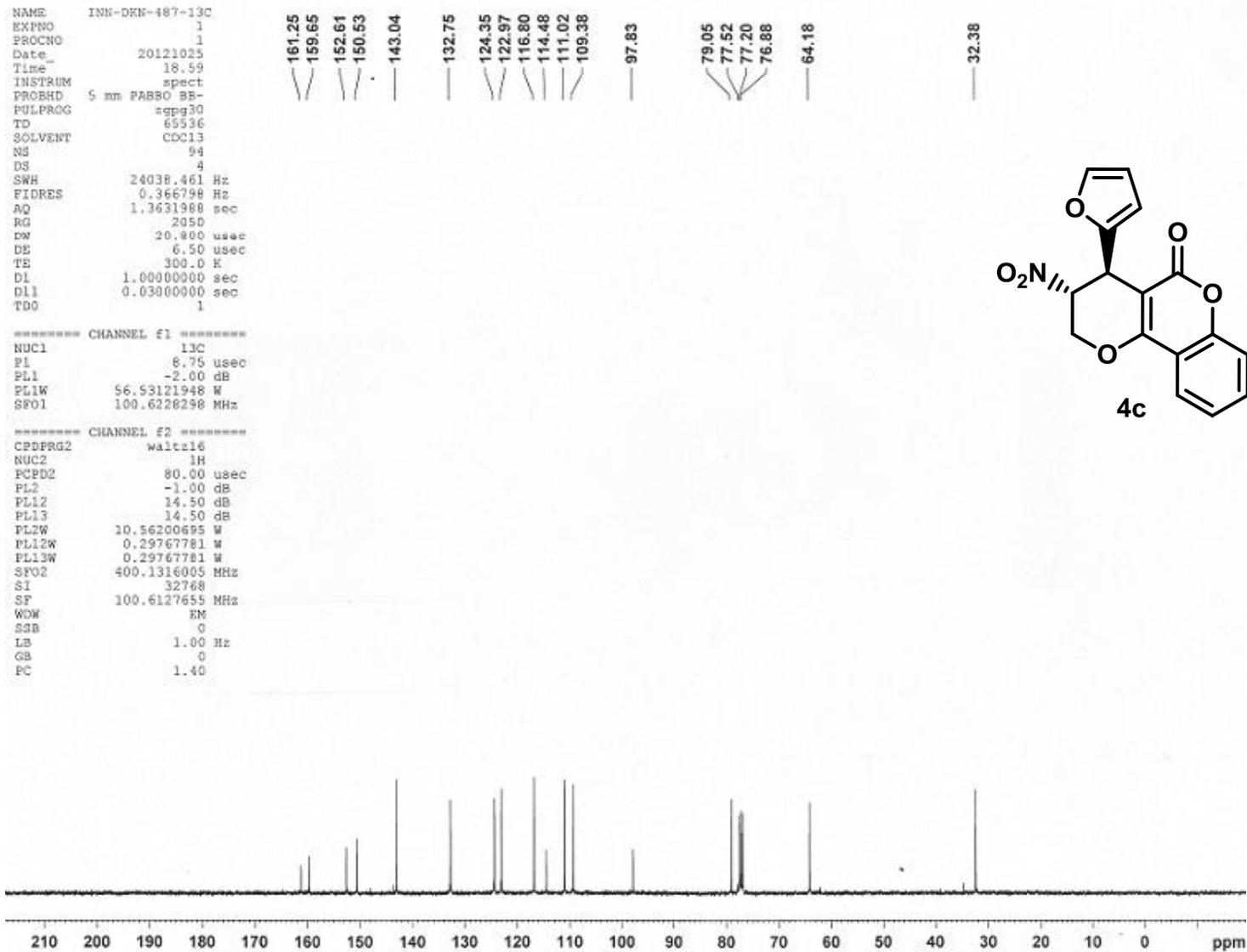
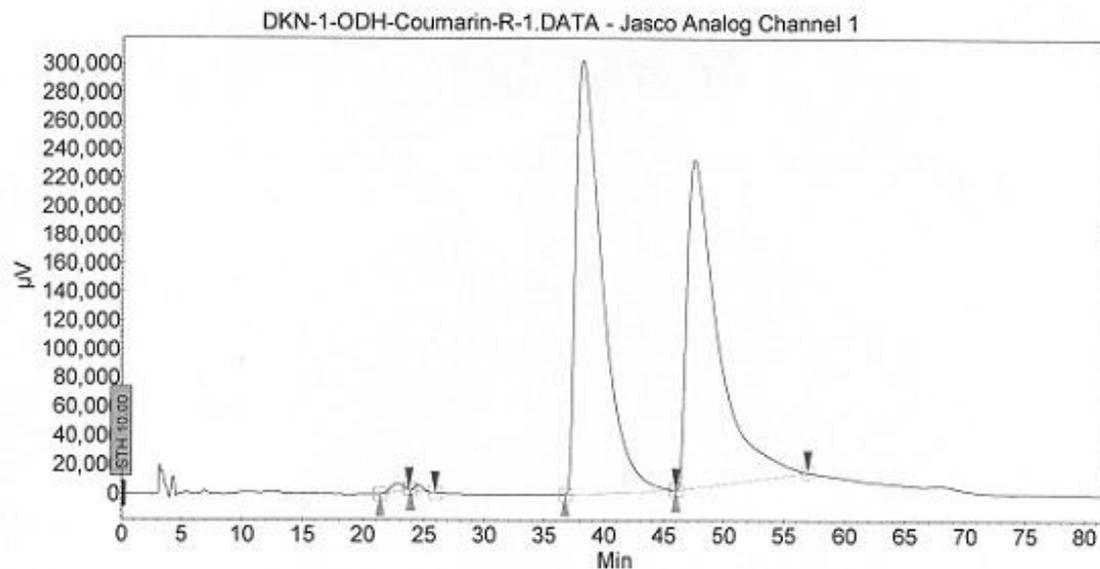
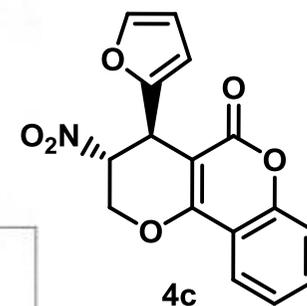


Figure S10 <sup>13</sup>C NMR Spectrum of 4c

## Chromatogram : DKN-1-ODH-Coumarin-R-1\_channel2

System : Jasco HPLC  
Method : DKN-10%-1FR-230nm  
User : User1

Acquired : 8/13/2012 4:30:55 PM  
Processed : 8/17/2012 5:52:40 PM  
Printed : 8/17/2012 5:53:37 PM



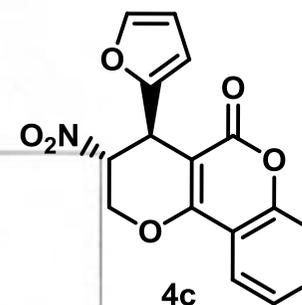
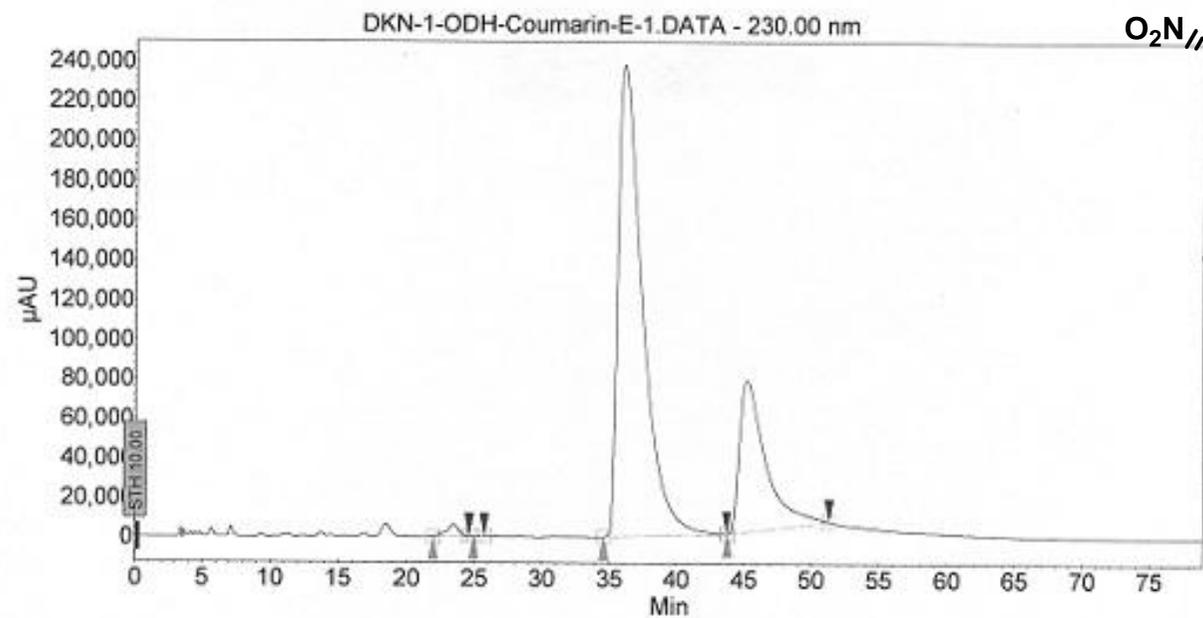
### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
3	UNKNOWN	22.742	0.38	4950.5	5508.2	0.378
4	UNKNOWN	24.608	0.19	3697.5	2783.6	0.189
1	UNKNOWN	38.117	52.79	302402.3	770200.8	52.790
2	UNKNOWN	47.475	46.64	228700.5	680510.6	46.643
Total			100.00	539750.8	1458983.1	100.000

Figure S11. HPLC profile of racemic 4c

System : Jasco HPLC  
Method : DKN-10%-1FR-230nm  
User : User1

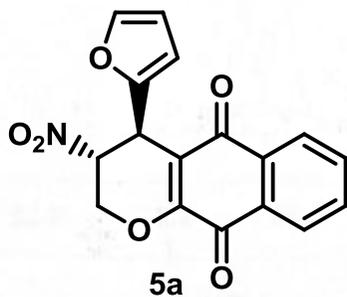
Acquired : 8/17/2012 4:16:28 PM  
Processed : 8/17/2012 5:55:21 PM  
Printed : 8/17/2012 5:55:39 PM



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
3	UNKNOWN	23.458	0.86	5857.7	5841.8	0.859
4	UNKNOWN	25.324	0.02	261.0	119.7	0.018
1	UNKNOWN	36.040	73.78	237748.6	501863.1	73.777
2	UNKNOWN	45.210	25.35	76713.5	172423.1	25.347
Total			100.00	320580.8	680247.7	100.000

Figure S12. HPLC profile of enantioenriched 4c



```

Current Data Parameters
NAME      INN-DMN-FURYL-1H
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20131101
Time      18.06
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10000.000 Hz
FIDRES     0.152588 Hz
AQ         3.2767999 sec
RG         134.65
EW         50.000 usec
DE         6.50 usec
TE         296.3 K
D1         1.0000000 sec
TD0        1

***** CHANNEL f1 *****
SFO1      500.1330885 MHz
NUC1       1H
P1         13.00 usec
PLW1      13.0000000 W

F2 - Processing parameters
SI         65536
SF         500.1300121 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```

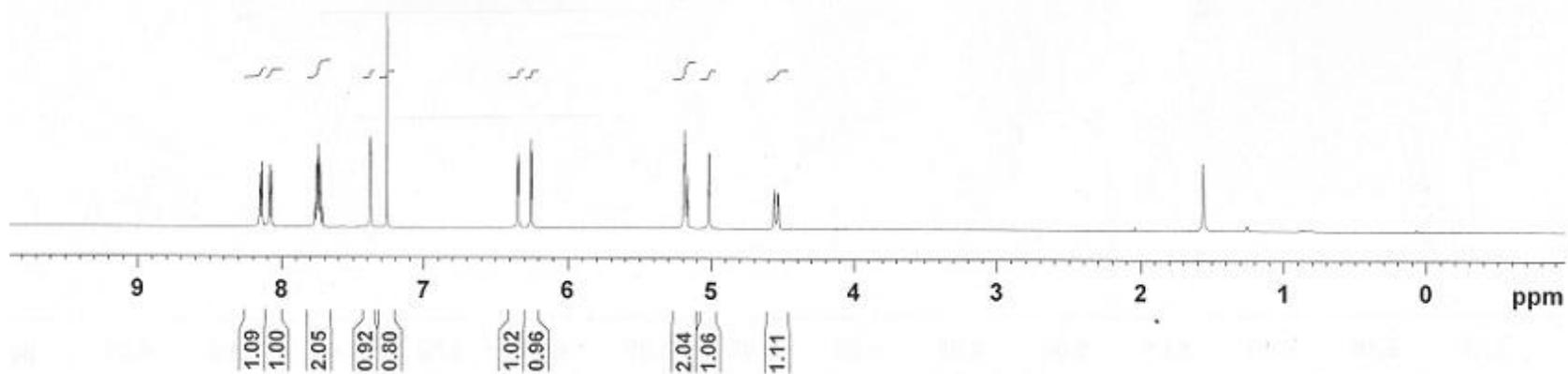


Figure S13.  $^1\text{H}$  NMR Spectrum of 5a

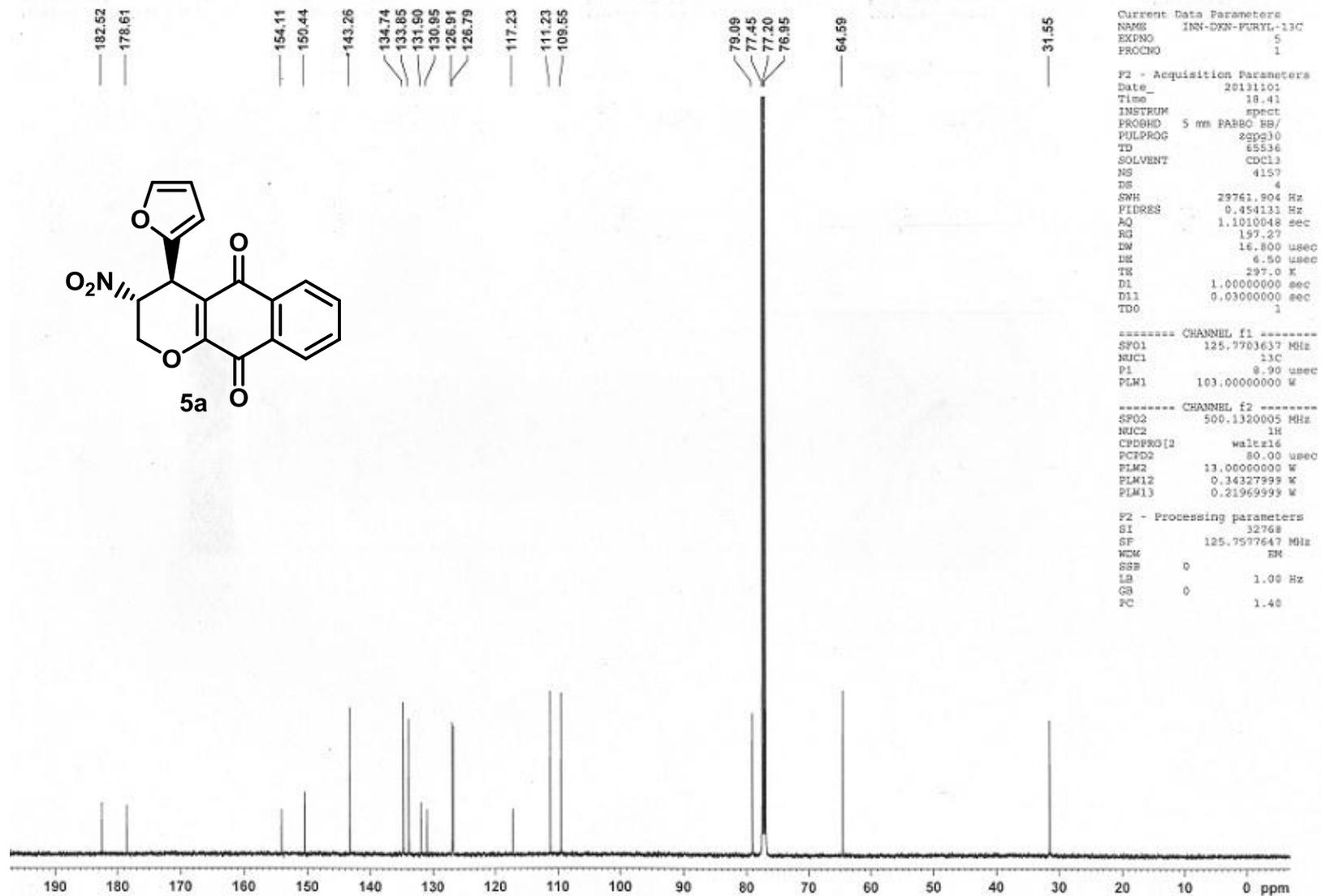
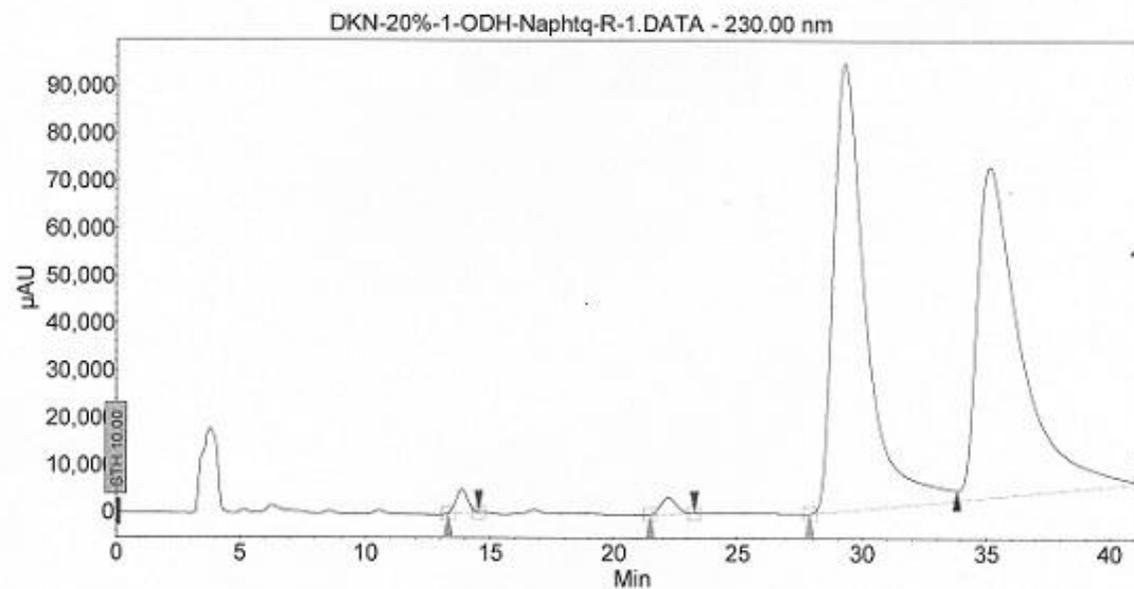
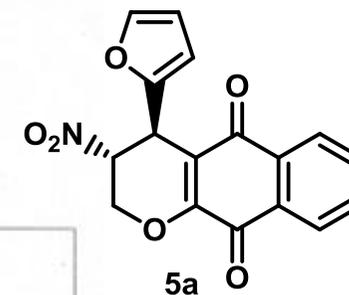


Figure S14. <sup>13</sup>C NMR Spectrum of 5a

# Chromatogram : DKN-20%-1-ODH-Naphtq-R-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 8/21/2012 4:21:12 PM  
Processed : 8/21/2012 5:05:56 PM  
Printed : 8/21/2012 6:09:42 PM



## Peak results :

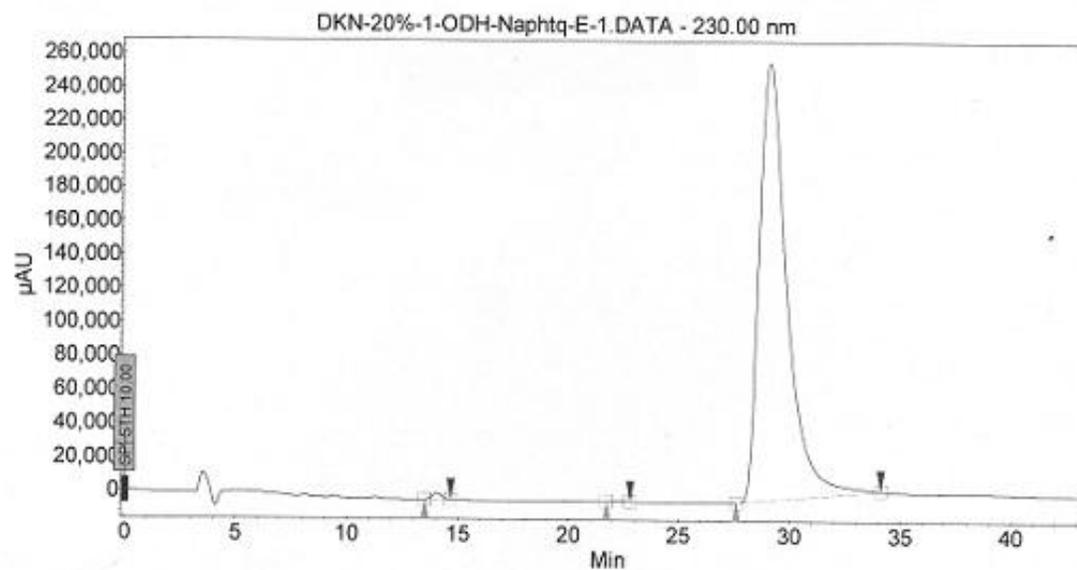
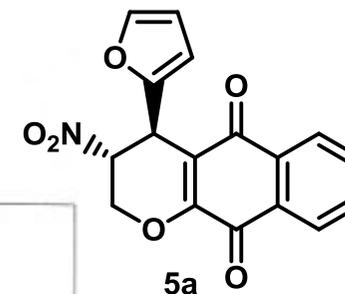
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
4	UNKNOWN	13.866	0.95	5030.6	2762.3	0.950
3	UNKNOWN	22.212	0.89	3569.8	2595.1	0.892
1	UNKNOWN	29.278	48.84	94698.8	142059.8	48.837
2	UNKNOWN	35.104	49.32	69953.0	143465.8	49.321
Total			100.00	173252.2	290883.0	100.000

Figure S15. HPLC profile of racemic 5a

# Chromatogram : DKN-20%-1-ODH-Naphtq-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 8/21/2012 5:04:01 PM  
Processed : 3/26/2013 6:19:43 PM  
Printed : 3/26/2013 6:20:04 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [ $\mu$ AU]	Area [ $\mu$ AU.Min]	Area % [%]
1	UNKNOWN	14.052	0.50	3822.8	1885.1	0.501
3	UNKNOWN	22.238	0.11	710.2	407.8	0.108
2	UNKNOWN	29.011	99.39	260056.1	374095.6	99.391
Total			100.00	264589.1	376388.5	100.000

Figure S16. HPLC profile of enantioenriched 5a

```

NAME      INN-DKN-491-1H
EXPNO     15
PROCNO    1
Date_     20120208
Time      22.31
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        16
DS        0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        32
DW        60.800 usec
DE        6.50 usec
TE        293.2 K
D1        1.00000000 sec
TD0       1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300095 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

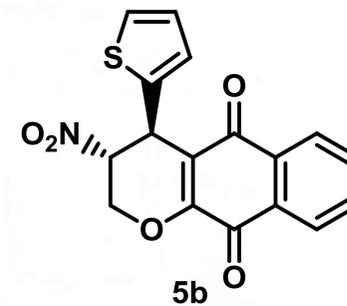
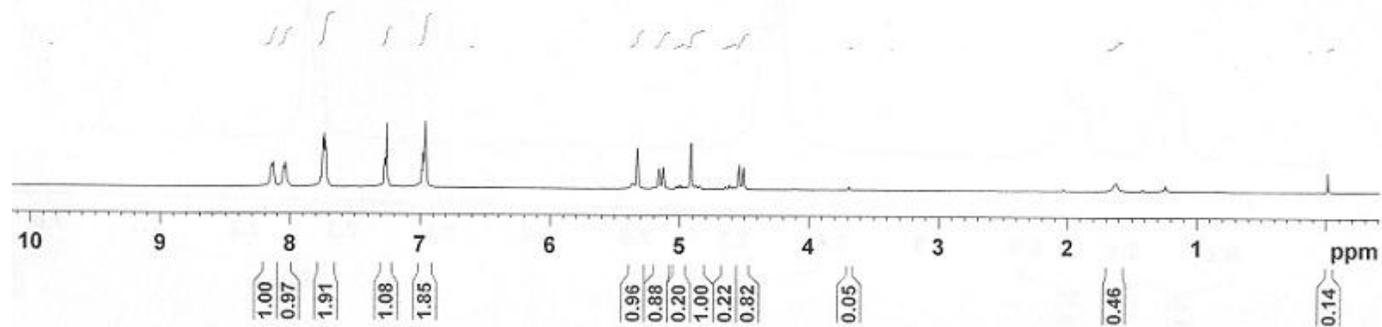


Figure S17. <sup>1</sup>H NMR Spectrum of 5b

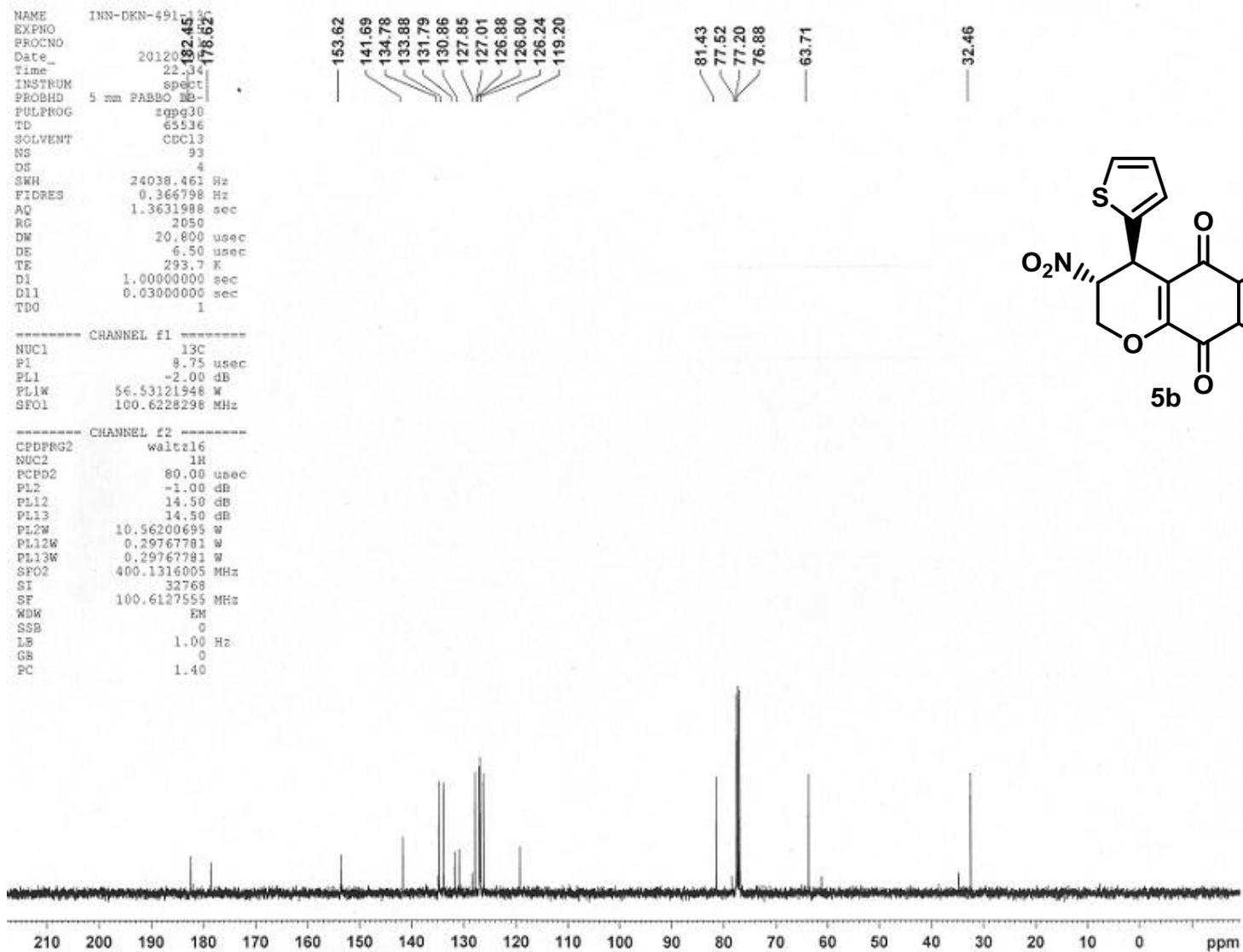
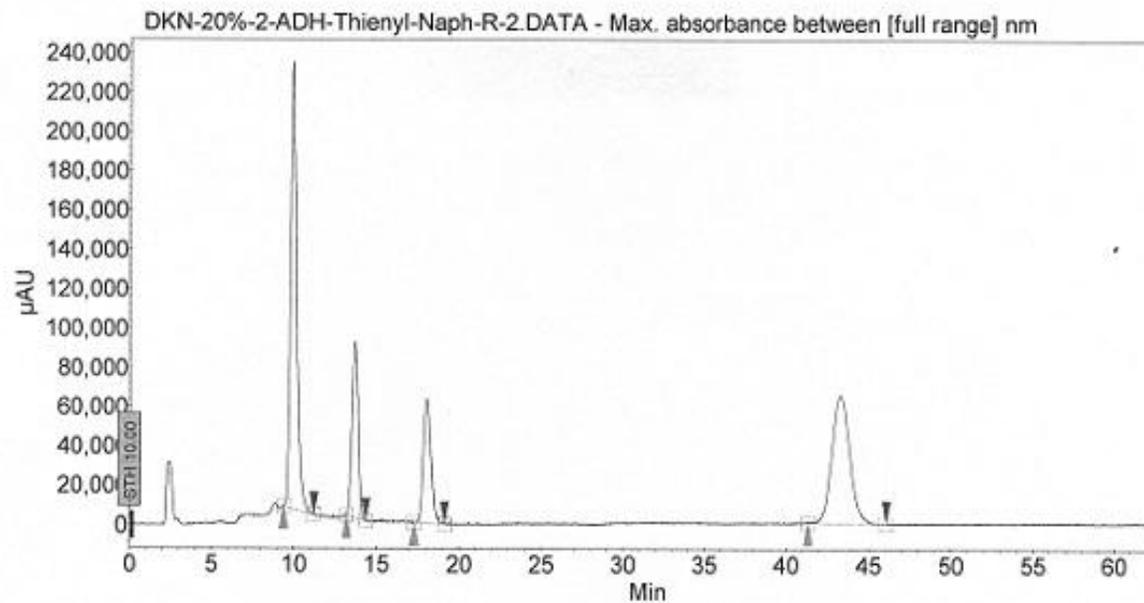
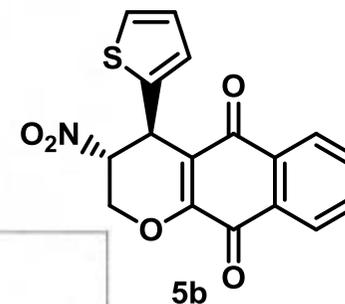


Figure S18. <sup>13</sup>C NMR Spectrum of 5b

## Chromatogram : DKN-20%-2-ADH-Thienyl-Naph-R-2\_channel5

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 9/5/2012 6:11:14 PM  
 Processed : 9/5/2012 7:20:23 PM  
 Printed : 9/5/2012 7:20:54 PM



### Peak results :

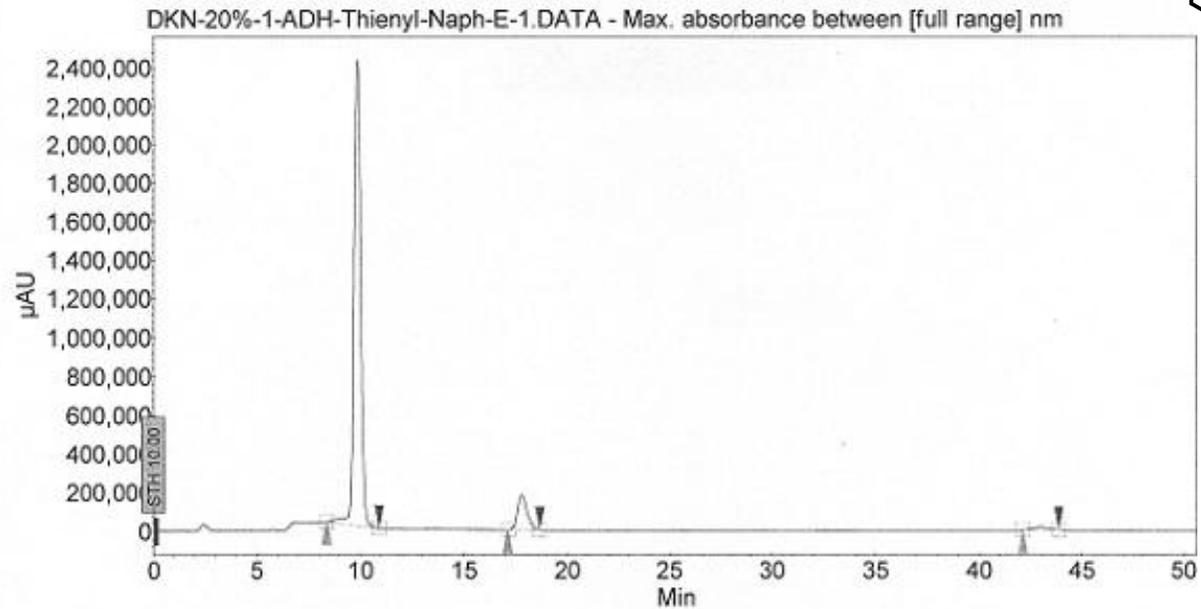
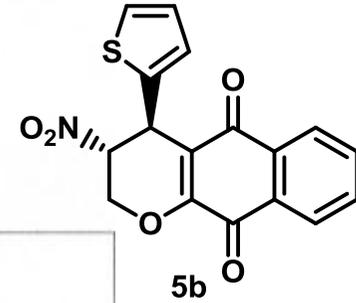
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
2	UNKNOWN	9.906	38.45	227019.1	94797.3	38.453
1	UNKNOWN	13.879	14.88	89803.1	36684.8	14.881
3	UNKNOWN	18.025	13.94	63380.7	34382.9	13.939
4	UNKNOWN	43.264	32.73	64705.4	80680.8	32.727
Total			100.00	444808.4	246525.9	100.000

Figure S19. HPLC profile of racemic 5b

# Chromatogram : DKN-20%-1-ADH-Thienyl-Naph-E-1\_channel5

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 7:19:42 PM  
Processed : 9/8/2012 8:14:42 PM  
Printed : 9/8/2012 8:14:50 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [ $\mu\text{AU}$ ]	Area [ $\mu\text{AU}\cdot\text{Min}$ ]	Area % [%]
2	UNKNOWN	9.853	89.27	2411494.3	917112.2	89.272
1	UNKNOWN	17.772	9.40	180018.6	96517.5	9.395
3	UNKNOWN	42.970	1.33	14113.5	13696.8	1.333
Total			100.00	2605626.4	1027326.4	100.000

Figure S20. HPLC profile of enantioenriched 5b

```

NAME      INN-DKN-496-1H
EXPNO     1
PROCNO    1
Date_     20120211
Time      18.47
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDC13
NS         7
DS         0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG         32
DW        60.800 usec
DE        6.50 usec
TE        293.0 K
D1        1.0000000 sec
TDO       1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1     400.1324710 MHz
SI        32768
SF        400.1300095 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

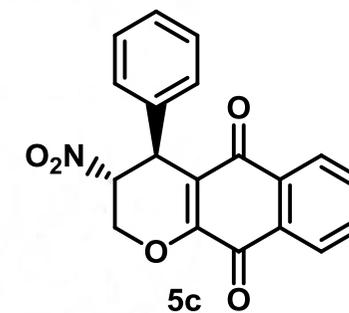
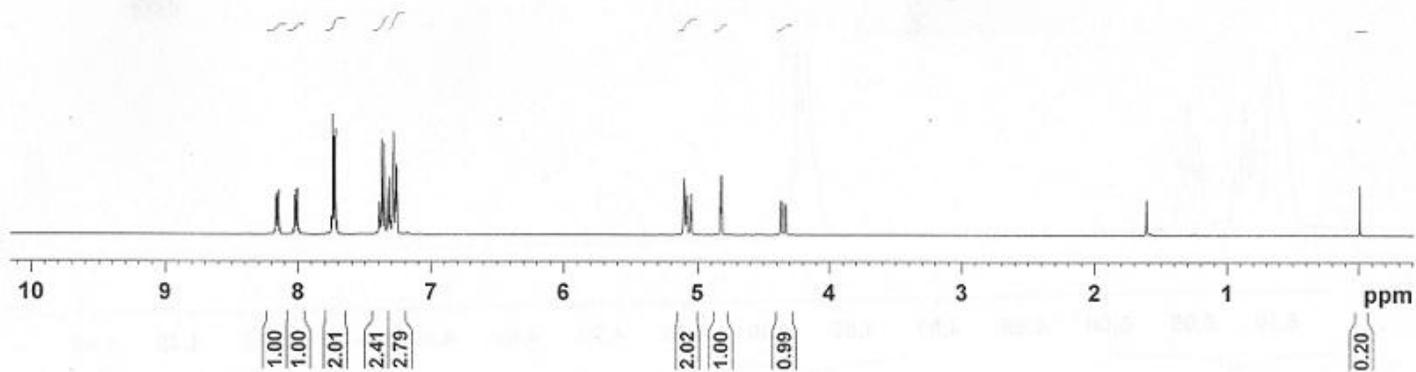


Figure S21. <sup>1</sup>H NMR Spectrum of 5c

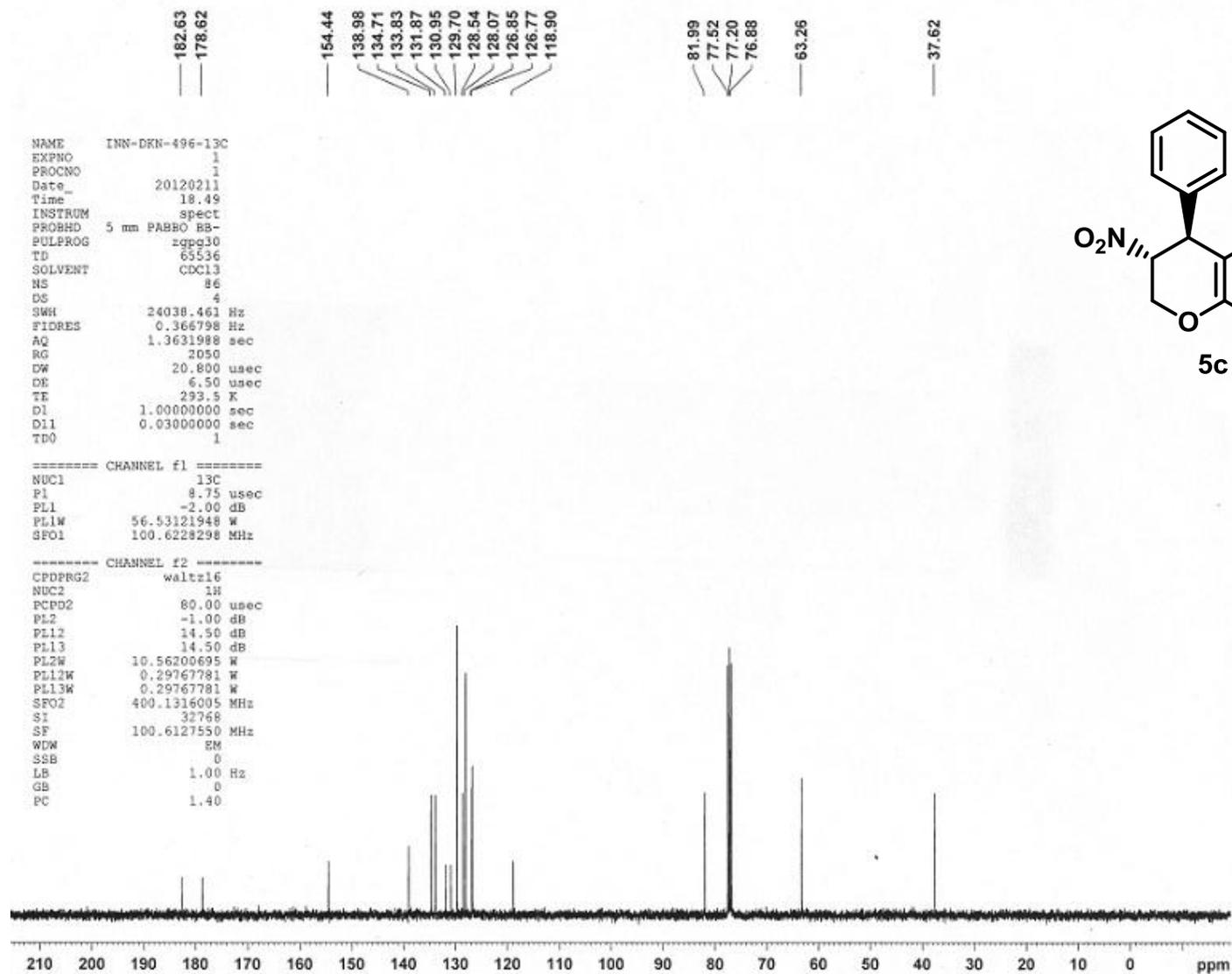
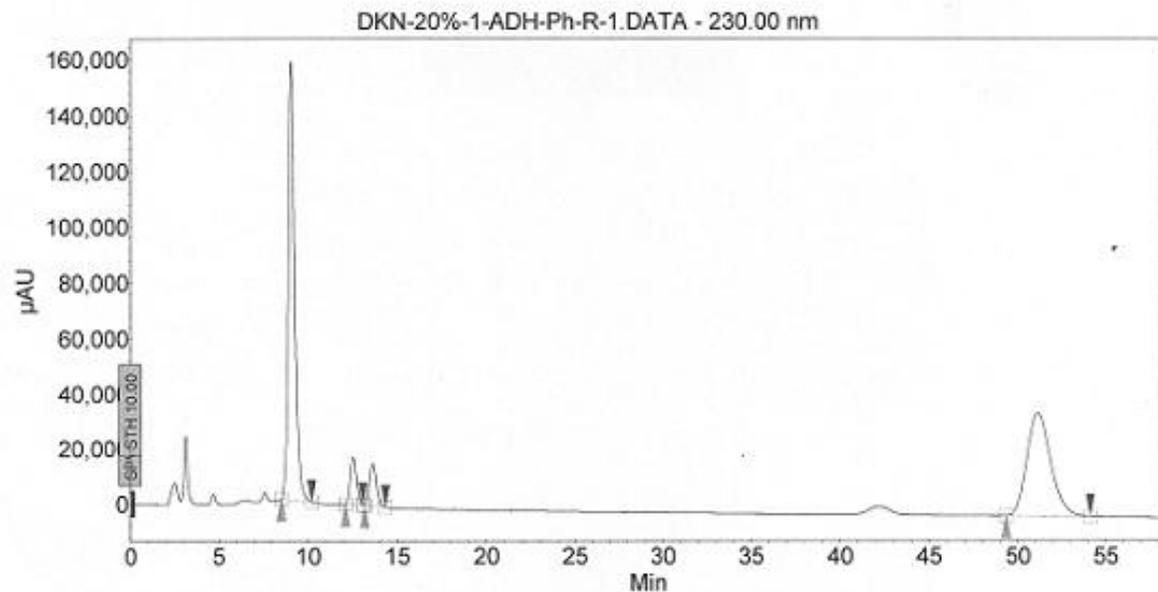
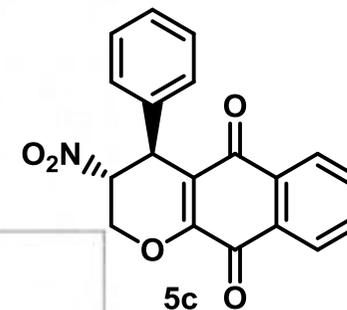


Figure S22. <sup>13</sup>C NMR Spectrum of 5c

### Chromatogram : DKN-20%-1-ADH-Ph-R-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 1:23:32 PM  
Processed : 12/11/2012 6:40:18 PM  
Printed : 12/11/2012 6:40:45 PM



#### Peak results :

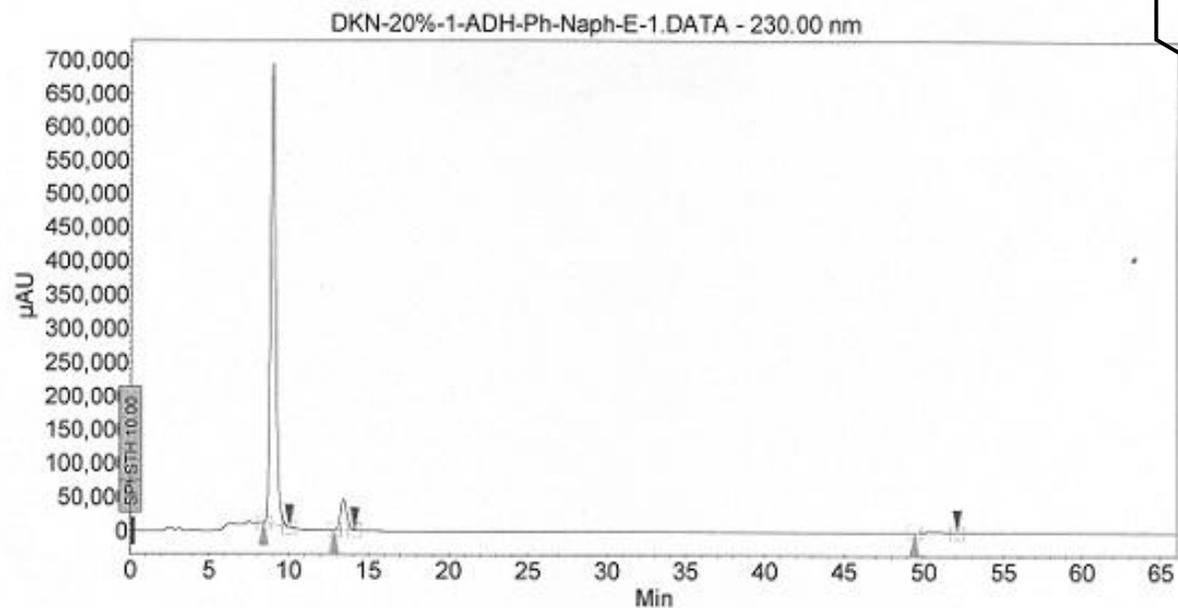
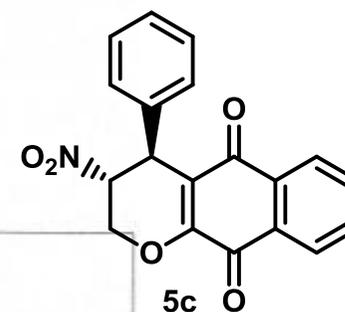
Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU.Min]	Area % [%]
1	UNKNOWN	9.093	47.55	157631.6	64434.9	47.549
3	UNKNOWN	12.546	4.90	16891.4	6642.2	4.902
4	UNKNOWN	13.626	4.89	15263.0	6628.9	4.892
2	UNKNOWN	51.116	42.66	36899.5	57805.2	42.657
Total			100.00	227085.7	135511.2	100.000

Figure S23. HPLC profile of racemic 5c

# Chromatogram : DKN-20%-1-ADH-Ph-Naph-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 10:41:56 PM  
Processed : 9/8/2012 7:09:22 PM  
Printed : 12/11/2012 7:06:30 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.957	92.38	686708.4	258533.1	92.379
3	UNKNOWN	13.422	6.95	45034.6	19449.2	6.950
2	UNKNOWN	50.635	0.67	1387.2	1880.0	0.672
Total			100.00	732130.2	279862.3	100.000

Figure S24. HPLC profile of enantioenriched 5c

```

NAME      inn-dkn-naph-e-1h
EXPNO     4
PROCNO    1
Date_     20120927
Time      19.36
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         6
DS         0
SWH        9223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         32
RW         60.800 usec
DE         6.50 usec
TE         300.0 K
D1         1.00000000 sec
TDO        1

```

```

----- CHANNEL f1 -----
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz
SI         32768
SF        400.1300095 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```

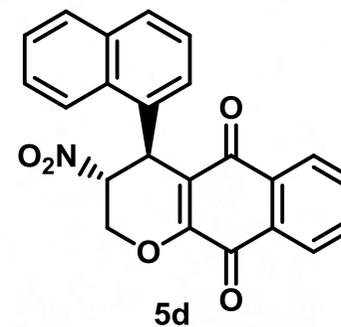
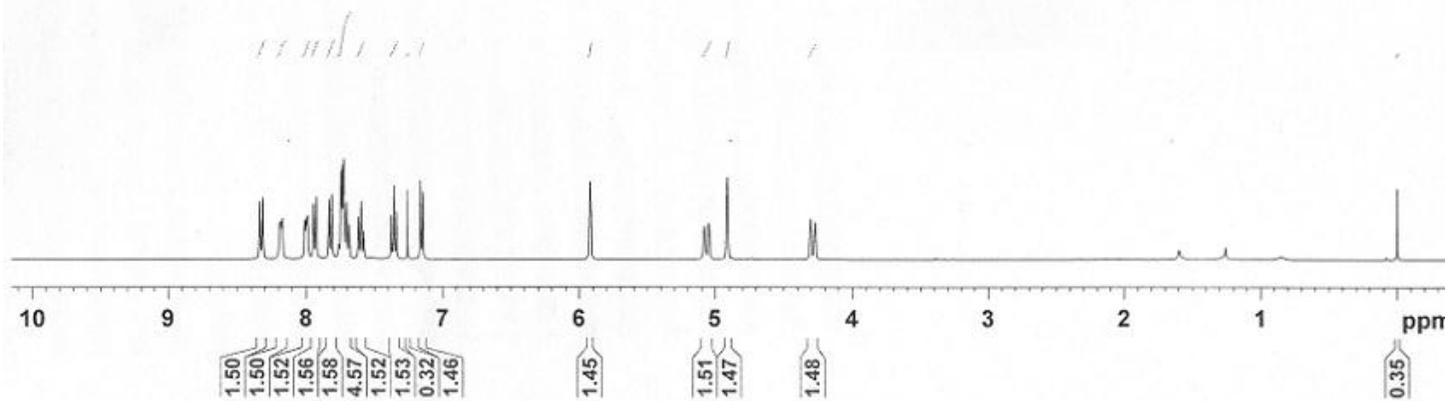
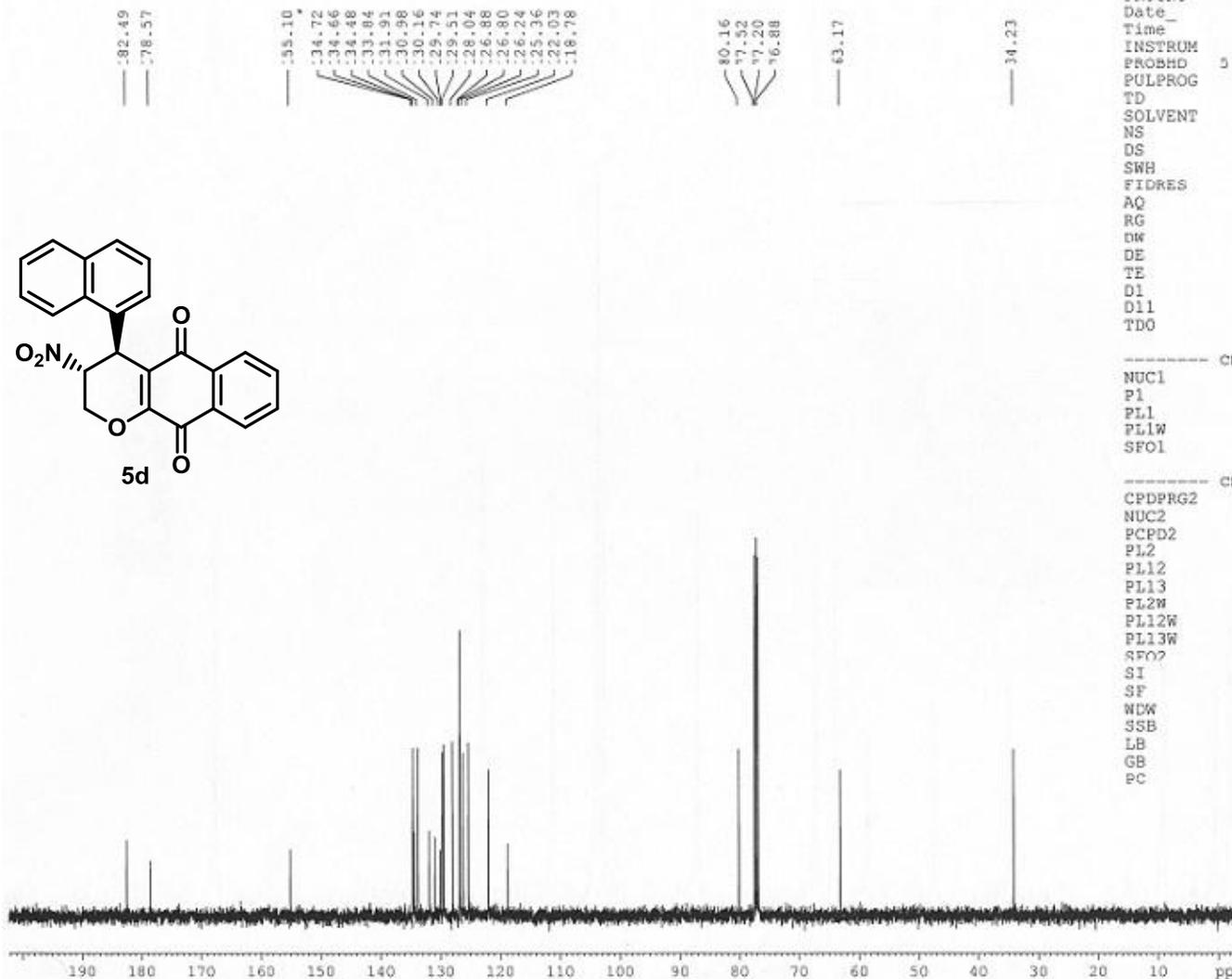


Figure S25. <sup>1</sup>H NMR Spectrum of 5d

INN-DKN-Naph-E-C13



```

NAME      INN-DKN-Naph-E-C13
EXPNO     21
PROCNO    1
Date_     20120928
Time      13.00
INSTRUM   spect
PROBHD    5 mm PABBO B5-
PULPROG   zgpg30
TD         65536
SOLVENT   CDC13
NS         47
DS         2
SWH        27777.777 Hz
FIDRES     0.423855 Hz
AQ         1.1796980 sec
RG         912
DW         18.000 usec
DE         6.50 usec
TE         300.0 K
D1         1.00000000 sec
D11        0.03000000 sec
TDO        1
  
```

```

----- CHANNEL f1 -----
NUC1       13C
P1         8.75 usec
PL1        -2.00 dB
PL1W       56.53121948 W
SFO1       100.6244401 MHz
  
```

```

----- CHANNEL f2 -----
CPDPRG2    waltz16
NUC2        1H
PCPD2       80.00 usec
PL2         -1.00 dB
PL12        14.50 dB
PL13        14.50 dB
PL2W        10.56200695 W
PL12W       0.29767781 W
PL13W       0.29767781 W
SFO2        400.1316005 MHz
SI          32768
SF          100.6127566 MHz
WDW         EM
SSB         U
LB          1.00 Hz
GB          0
PC          1.40
  
```

Figure S26. <sup>13</sup>C NMR Spectrum of 5d

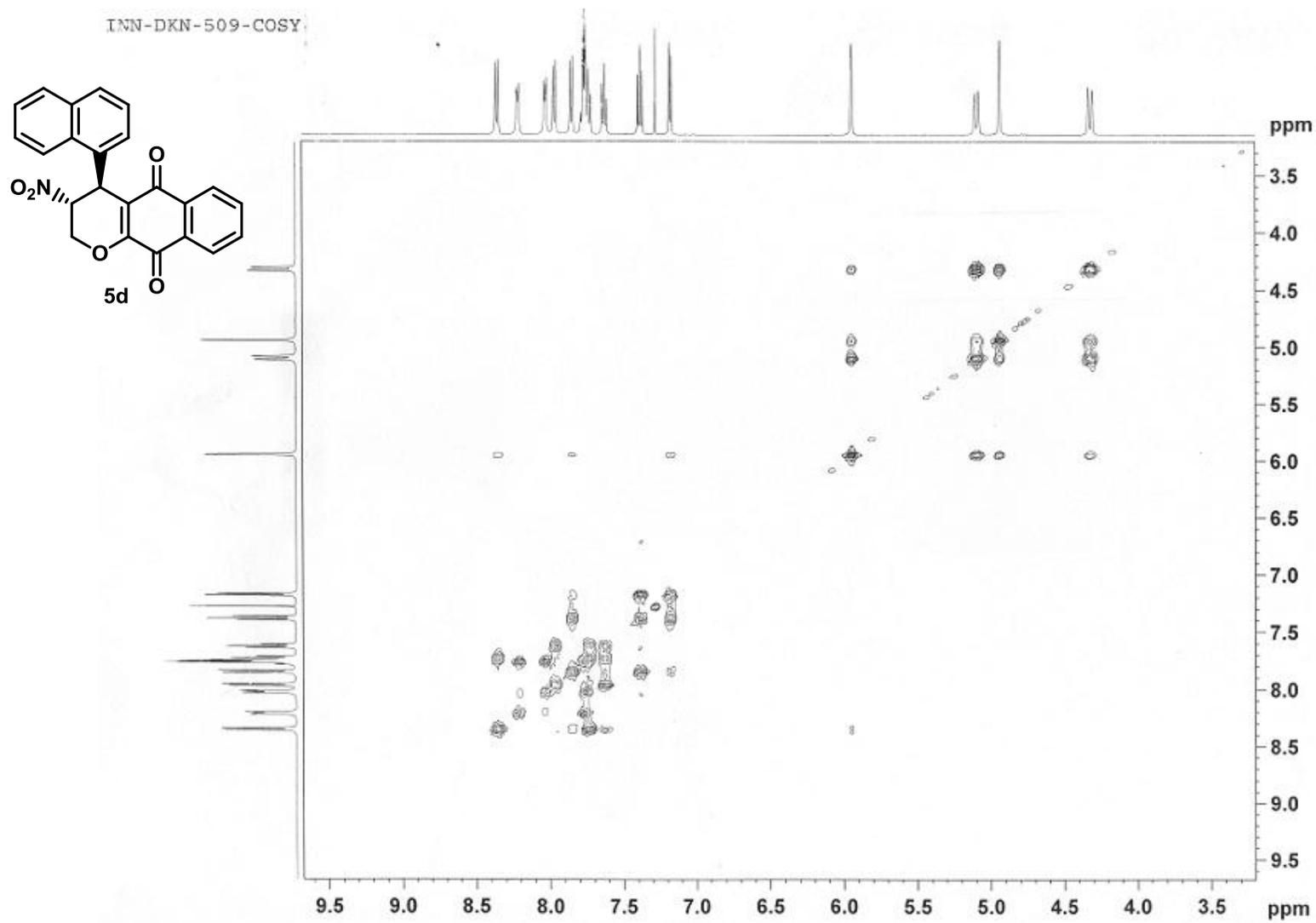
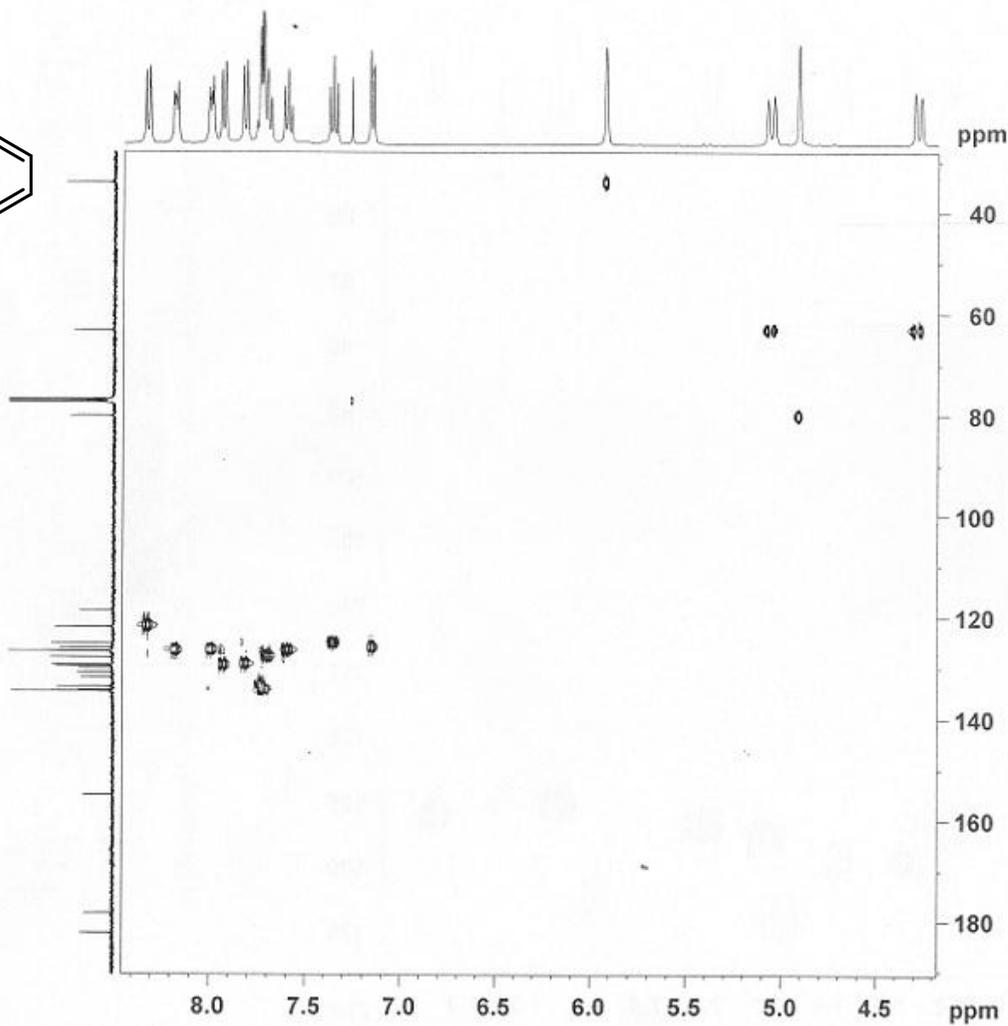
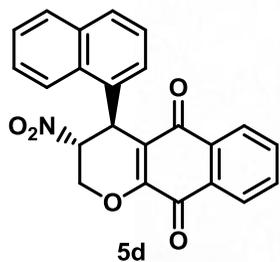


Figure S27. COSY Spectrum of 5d

INN-DKN-509-HSQC



```

NAME      INN-DKN-509-HSQC
EXPNO     3
PROCNO    1
Date_     20140107
Time      10.48
INSTRUM   spect
PROBHD    5 mm SEI 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         16
SWH        2000.000 Hz
FIDRES     0.974563 Hz
AQ         0.5320500 sec
RG         2050
LW         250.000 usec
TE         300.2
TE        296.2 K
CNS2      145.000000
D0         0.0000000 sec
D1         1.0000000 sec
D2         0.00172414 sec
D3         0.03000000 sec
D4         0.0000440 sec
D5         0.00020000 sec
D6         0.0000445 sec
SFOFINS

----- CHANNEL f1 -----
NUC1      13C
P1         6.75 usec
P2         13.50 usec
P3         1000.00 usec
PL1        -3.00 dB
PL12       16.73802424 dB
SFO1      400.1325362 MHz

----- CHANNEL f2 -----
CPDPRG2   gddp
NUC2      13C
P1         13.00 usec
P2         26.00 usec
P3         90.00 usec
PL1        -3.00 dB
PL12       12.50 dB
PL13       71.16858673 dB
PL14       2.00580325 dB
SFO2      100.6219303 MHz

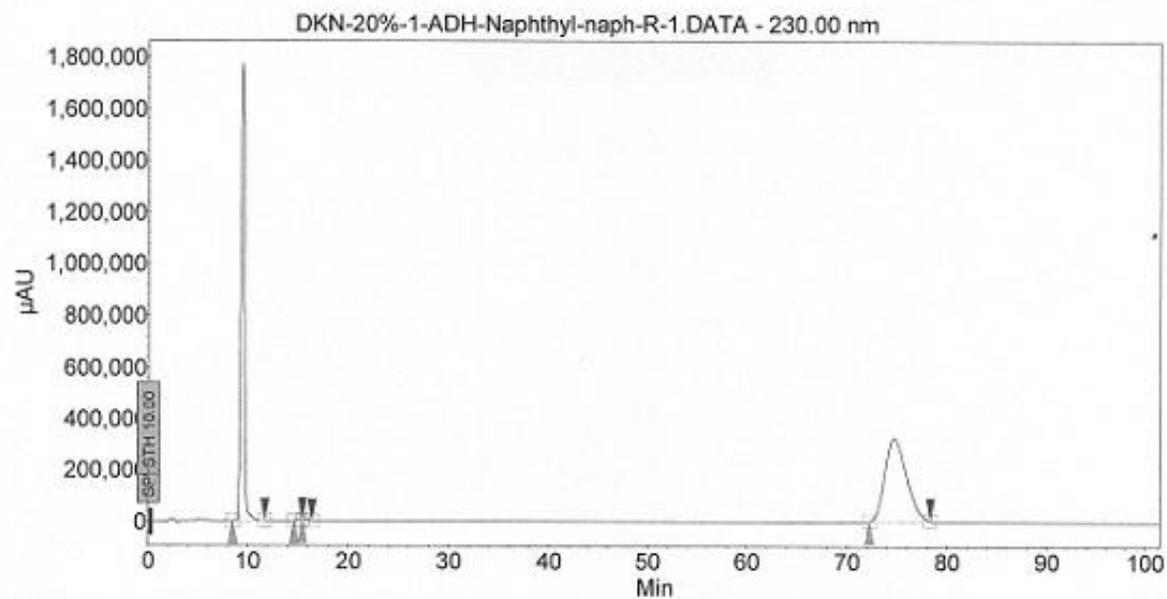
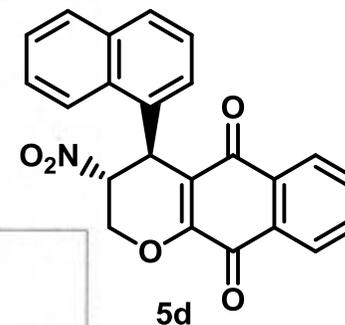
----- GRADIENT CHANNEL -----
GPNAM1    SINE.100
GPNAM2    SINE.100
GPZ1      80.00 Hz
GPZ2      20.16 Hz
P16       1000.00 usec
MDO       2
TD         150
SFO1      100.6228 MHz
FIDRES     134.143773 Hz
SW         200.000 ppm
TKMODE    Echo-Antiecho
SI         2048
SF         400.1300104 MHz
WDW        QSINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
WC2       echo-antiecho
SF         100.6127650 MHz
WDW        QSINE
SSB        2
LB         0.00 Hz
GB         0
    
```

Figure S28. HSQC Spectrum of 5d

## Chromatogram : DKN-20%-1-ADH-Naphthyl-naph-R-1\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 9/18/2012 12:38:01 PM  
 Processed : 9/26/2012 9:10:38 AM  
 Printed : 12/11/2012 8:03:05 PM



### Peak results :

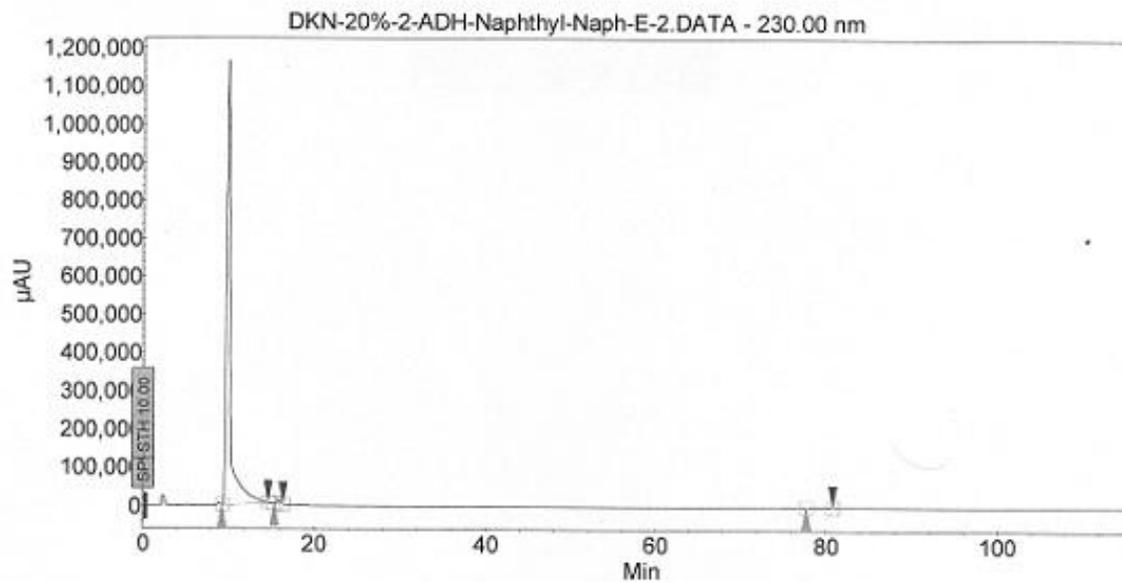
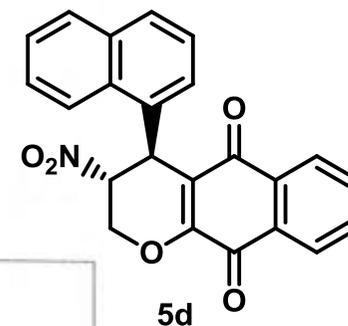
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
2	UNKNOWN	9.423	46.96	1773634.7	716012.6	46.958
3	UNKNOWN	15.048	0.20	7485.2	3074.0	0.202
4	UNKNOWN	15.848	0.22	7713.1	3417.3	0.224
1	UNKNOWN	74.680	52.82	322244.4	802304.9	52.617
Total			100.00	2111077.5	1524808.8	100.000

Figure S29. HPLC profile of racemic 5d

### Chromatogram : DKN-20%-2-ADH-Naphthyl-Naph-E-2\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/26/2012 11:19:00 AM  
Processed : 12/11/2012 8:05:28 PM  
Printed : 12/11/2012 8:06:01 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [ $\mu\text{AU}$ ]	Area [ $\mu\text{AU}\cdot\text{Min}$ ]	Area % [%]
2	UNKNOWN	9.903	98.92	1164851.8	597213.2	98.917
3	UNKNOWN	15.868	0.62	7831.5	3768.9	0.624
1	UNKNOWN	79.132	0.46	1540.1	2768.8	0.459
Total			100.00	1174223.4	603750.9	100.000

Figure S30. HPLC profile of enantioenriched 5d

```

NAME      INN-DKN-490-1H
EXPNO     15
PROCNO    1
Date_     20120208
Time      22.39
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        16
DS        0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        32
DW        60.800 usec
DE        6.50 usec
TE        293.2 K
Dl        1.00000000 sec
TDO       1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300095 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

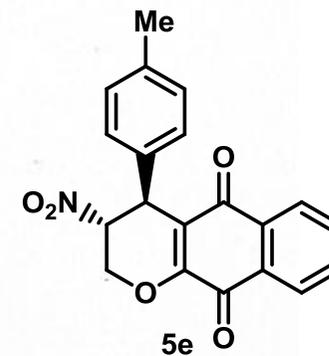
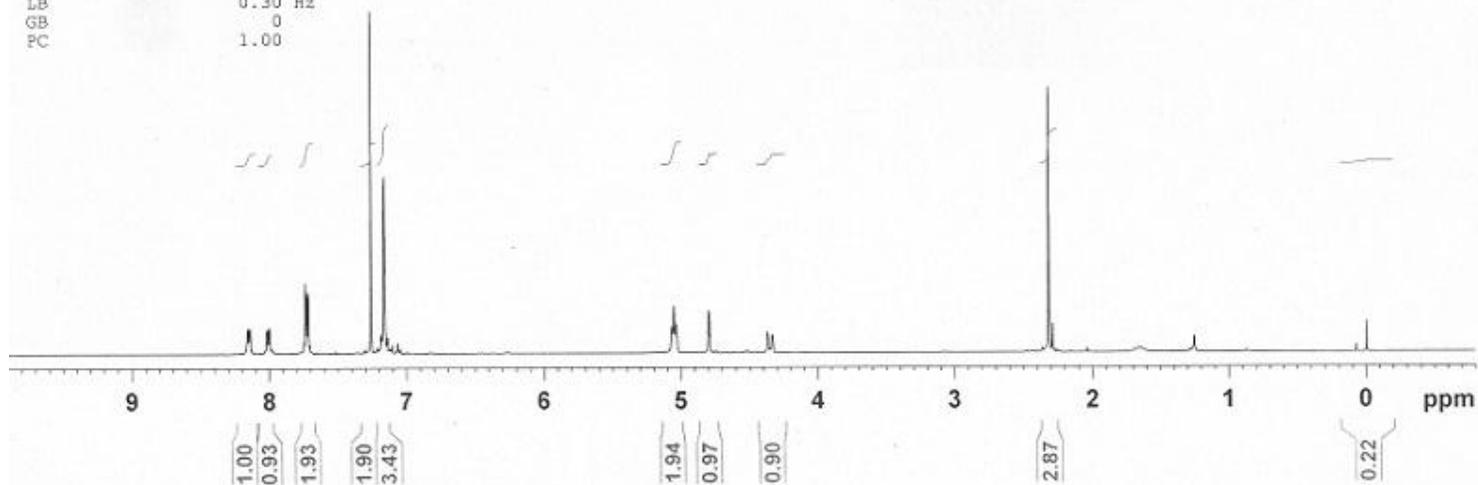


Figure S31. <sup>1</sup>H NMR Spectrum of 5e

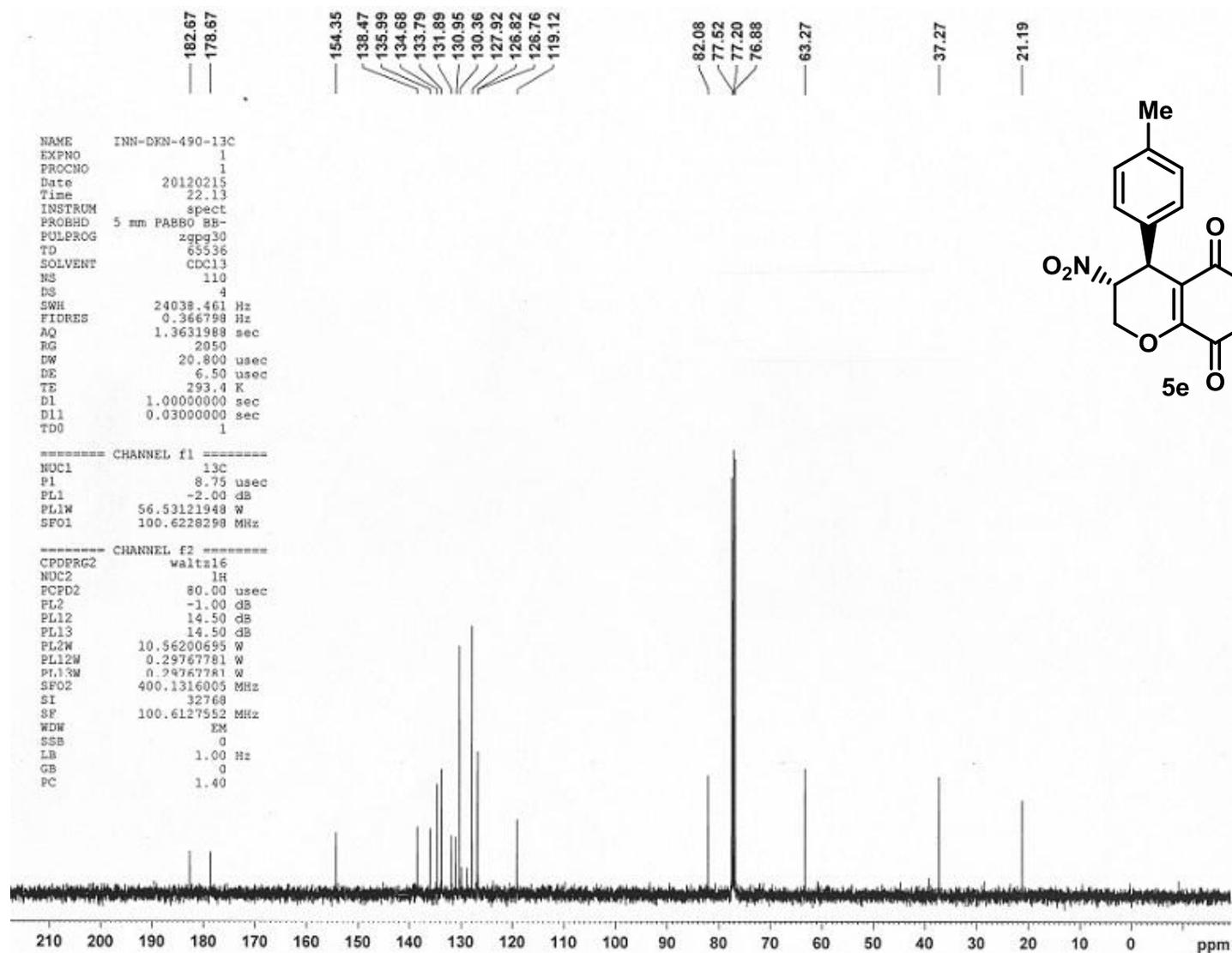
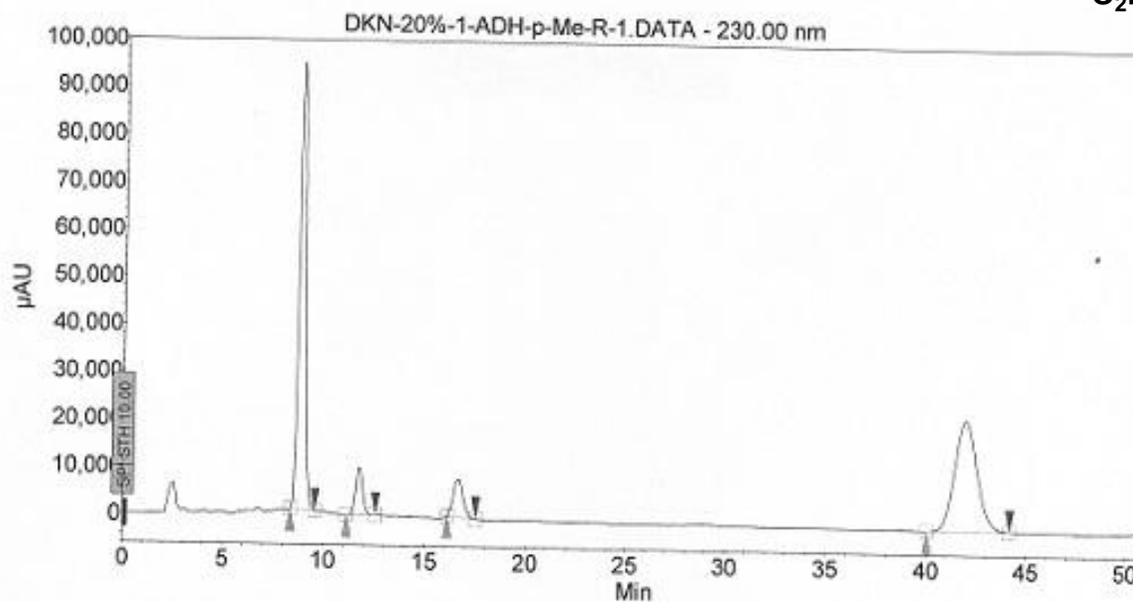
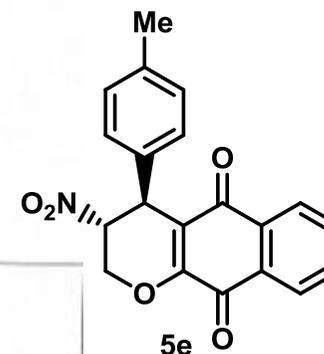


Figure S32. <sup>13</sup>C NMR Spectrum of 5e

# Chromatogram : DKN-20%-1-ADH-p-Me-R-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 2:28:47 PM  
Processed : 12/11/2012 8:07:58 PM  
Printed : 12/11/2012 8:08:09 PM



## Peak results :

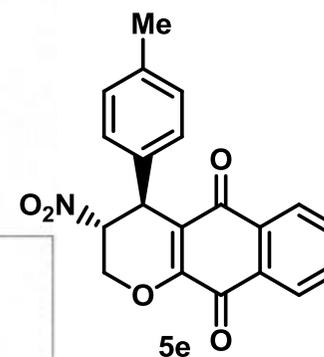
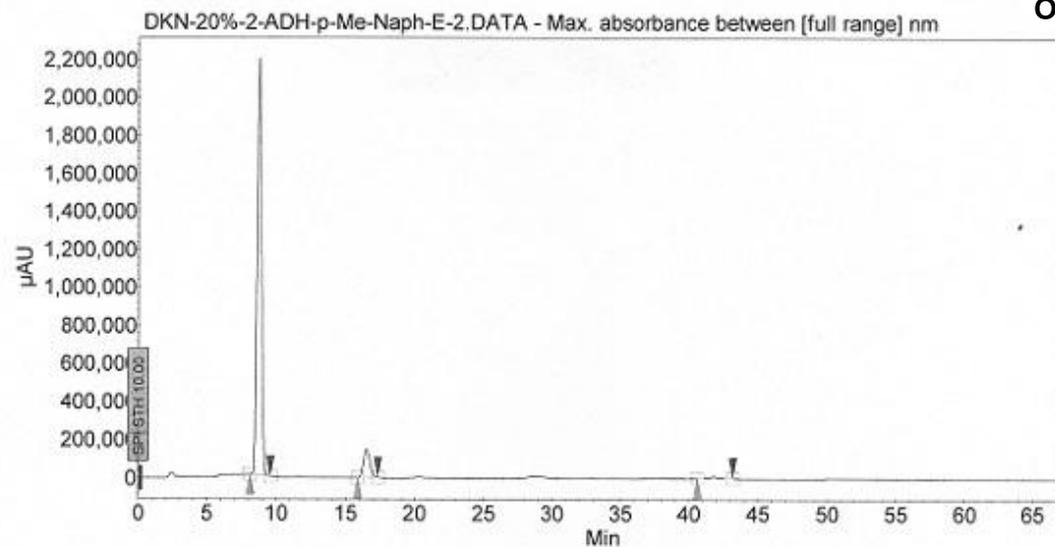
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.799	46.48	94117.1	33129.7	46.479
2	UNKNOWN	11.746	5.39	9856.7	3840.7	5.388
3	UNKNOWN	16.639	6.13	7906.4	4369.9	6.131
4	UNKNOWN	41.904	42.00	23256.6	29939.3	42.003
Total			100.00	135136.8	71279.6	100.000

Figure S33. HPLC profile of racemic 5e

### Chromatogram : DKN-20%-2-ADH-p-Me-Naph-E-2\_channel5

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 4:09:16 PM  
Processed : 12/11/2012 8:09:39 PM  
Printed : 12/11/2012 8:09:49 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU.Min]	Area % [%]
2	UNKNOWN	8.744	90.14	2191269.2	802454.4	90.140
3	UNKNOWN	16.527	8.76	148212.6	78001.0	8.762
1	UNKNOWN	41.825	1.10	8003.4	9778.2	1.098
Total			100.00	2345485.2	890233.5	100.000

Figure S34. HPLC profile of enantioenriched 5e

```

NAME      INN-DKN-490-1H      5f
EXPNO     3
PROCNO    2
Date_     20121011
Time      18.49
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         7
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         32
DW         60.800 usec
DE         6.50 usec
TE         294.2 K
D1         1.00000000 sec
TD0        1

```

```

----- CHANNEL f1 -----
NUC1       1H
P1         13.50 usec
PL1        -1.00 dB
PL1W       10.56200695 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300095 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         -1.00

```

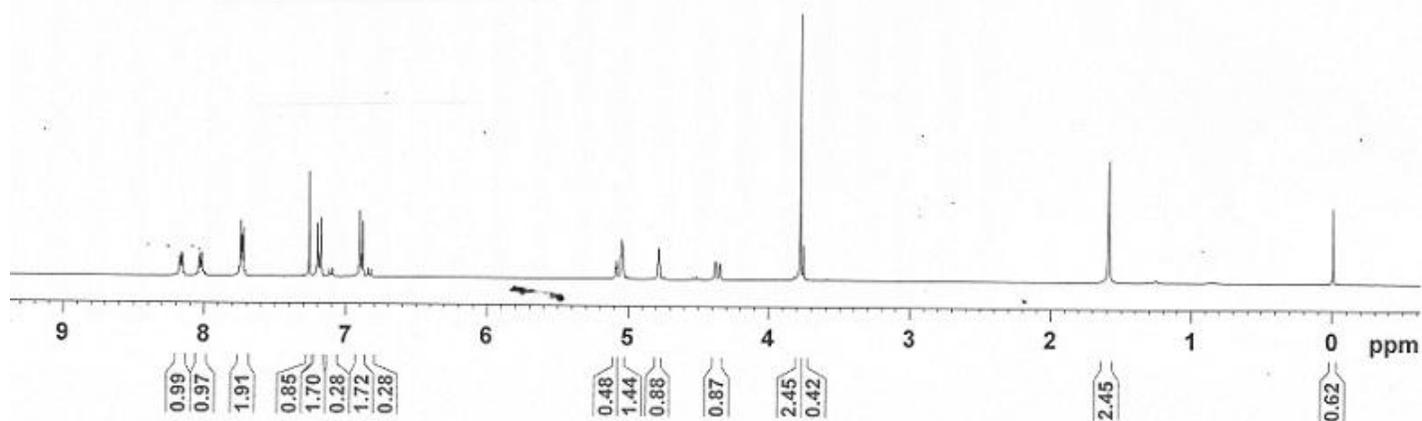
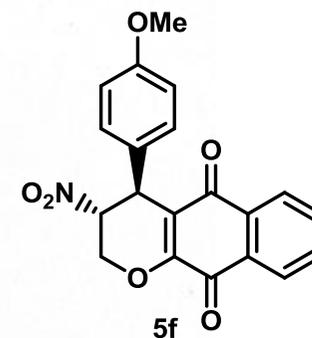


Figure S35. <sup>1</sup>H NMR Spectrum of 5f

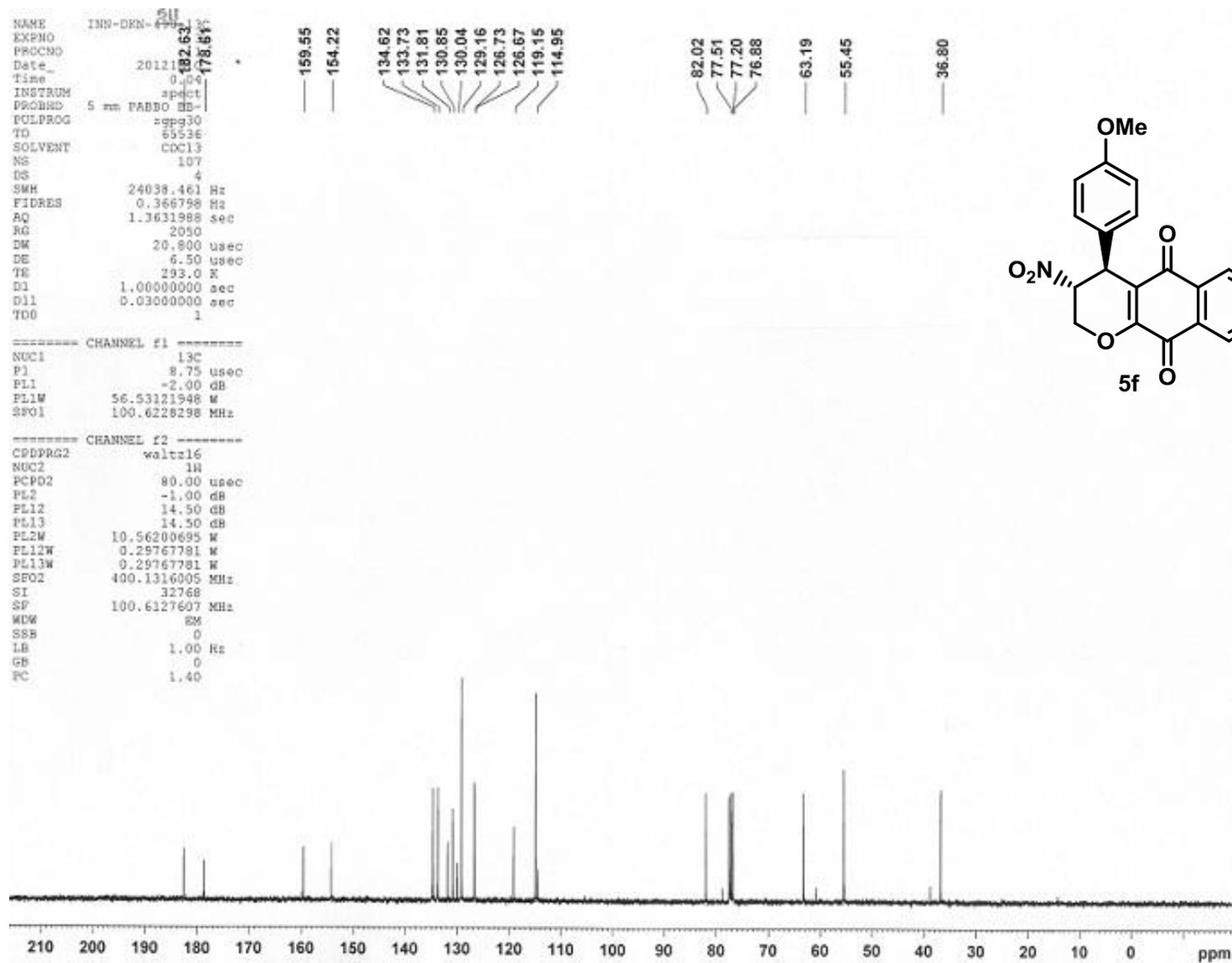
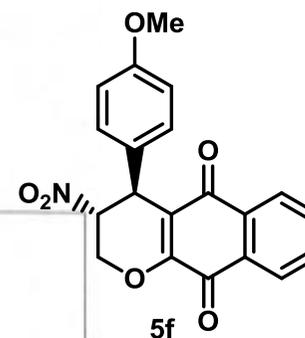
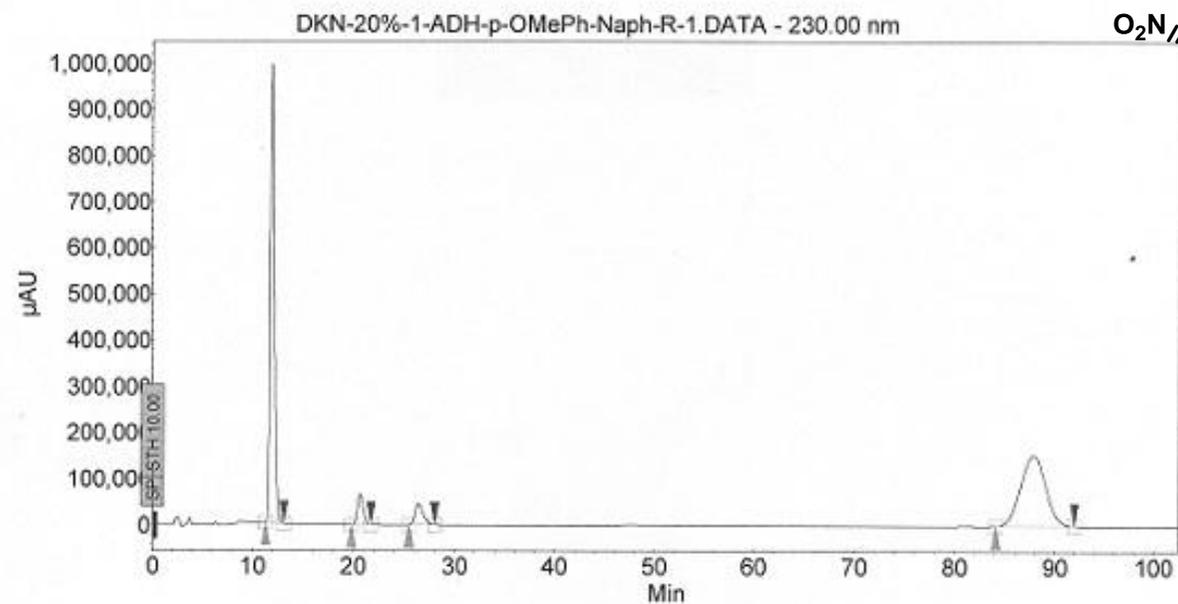


Figure S36. <sup>13</sup>C NMR Spectrum of 5f

### Chromatogram : DKN-20%-1-ADH-p-OMePh-Naph-R-1\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 9/18/2012 3:48:48 PM  
 Processed : 12/11/2012 6:59:31 PM  
 Printed : 12/11/2012 7:00:32 PM



#### Peak results :

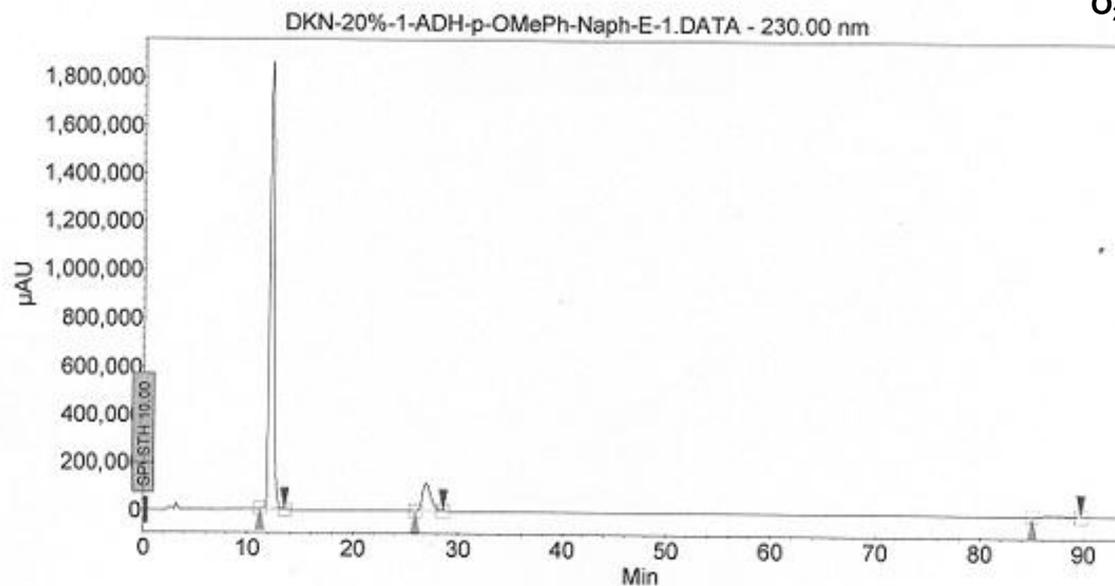
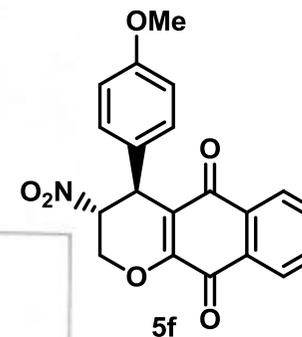
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	11.902	45.71	992470.7	446506.0	45.710
4	UNKNOWN	20.673	4.63	65921.2	45180.4	4.625
3	UNKNOWN	26.431	4.32	44894.3	42223.2	4.322
2	UNKNOWN	87.875	45.34	153332.6	442913.2	45.342
Total			100.00	1256608.7	976822.7	100.000

Figure S37. HPLC profile of racemic 5f

# Chromatogram : DKN-20%-1-ADH-p-OMePh-Naph-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/25/2012 2:46:09 PM  
Processed : 9/25/2012 4:56:38 PM  
Printed : 12/11/2012 7:01:34 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU Min]	Area % [%]
1	UNKNOWN	12.182	87.87	1858567.8	834204.2	87.871
2	UNKNOWN	26.950	11.12	115759.6	105543.4	11.117
3	UNKNOWN	87.195	1.01	3927.6	9599.5	1.011
Total			100.00	1978245.0	949347.2	100.000

Figure S38. HPLC profile of enantioenriched 5f

```

NAME      INN-DJN.-512-1H
EXPNO     10
PROCNO    1
Date_     20121113
Time      19.51
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         13
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         181
DW         60.800 usec
DE         6.50 usec
TE         293.6 K
D1         2.00000000 sec
TDO        1

```

```

----- CHANNEL f1 -----
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300095 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```

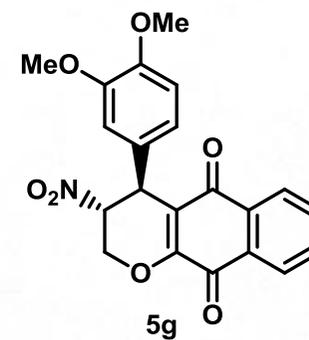
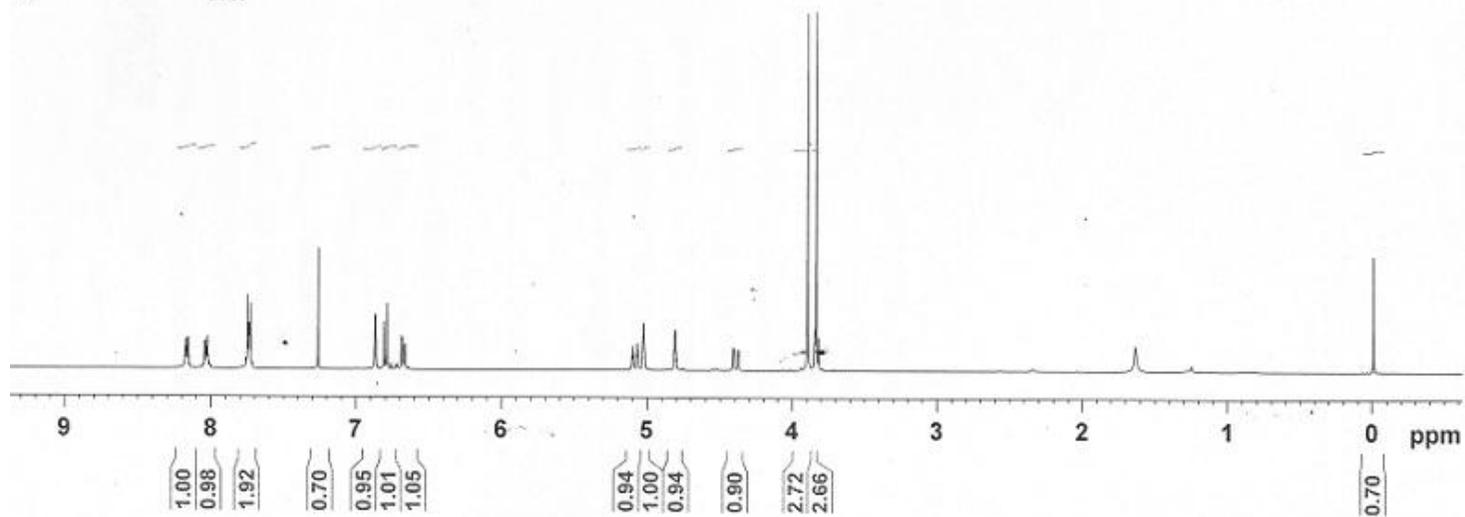


Figure S39. <sup>1</sup>H NMR Spectrum of 5g

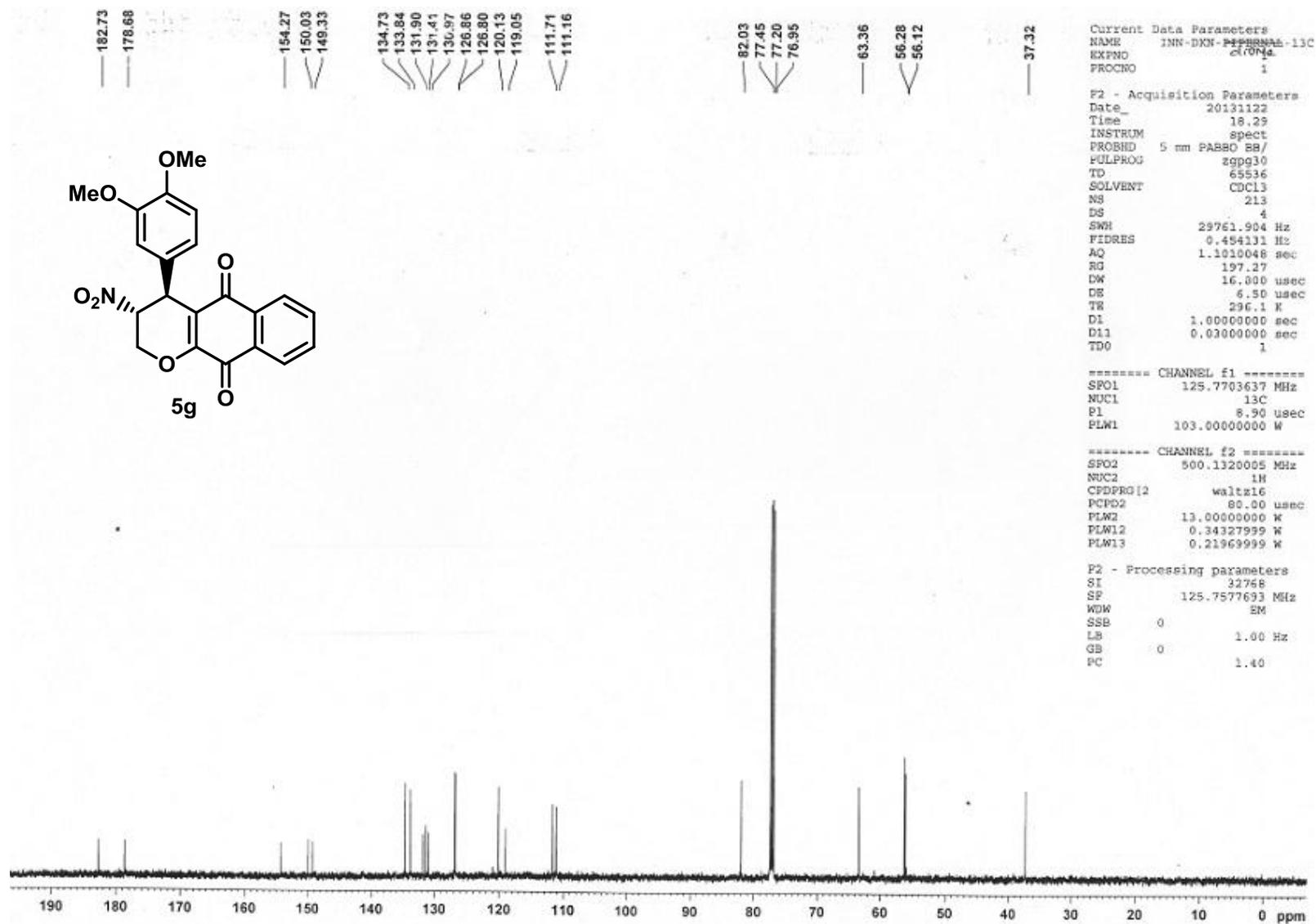
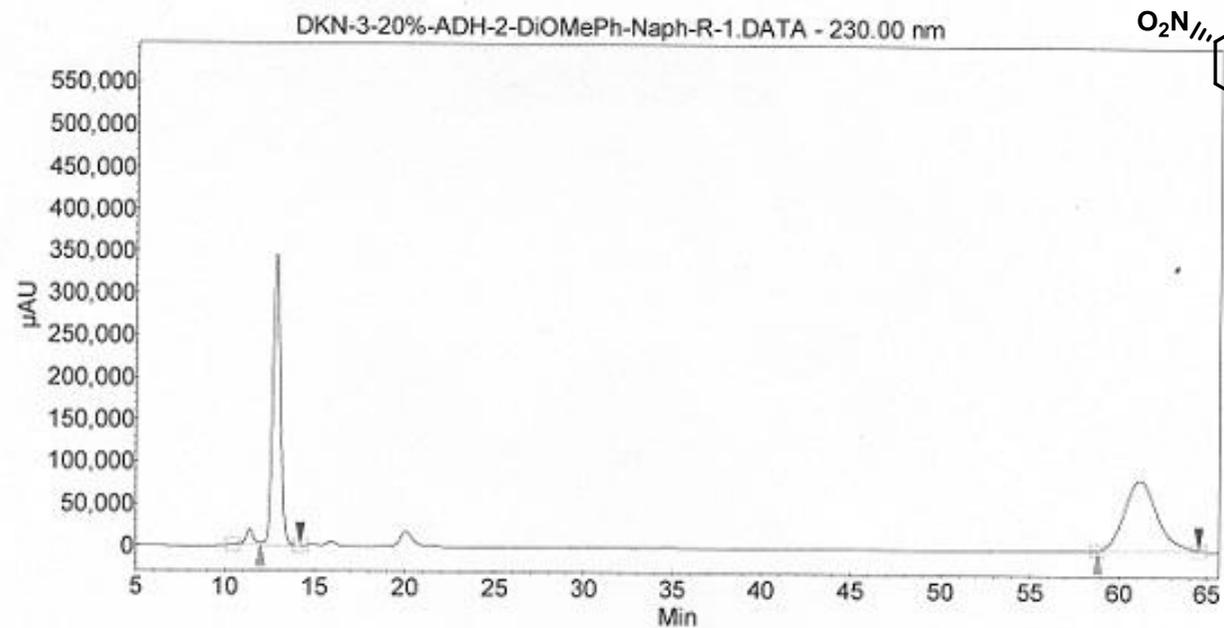
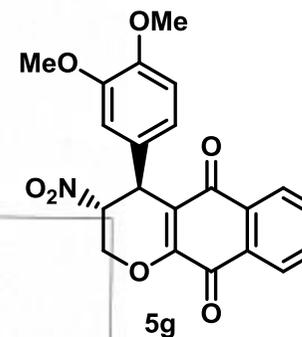


Figure S40.  $^{13}\text{C}$  NMR Spectrum of 5g

# Chromatogram : DKN-3-20%-ADH-2-DiOMePh-Naph-R-1\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 3/15/2013 10:55:06 AM  
 Processed : 3/15/2013 1:07:36 PM  
 Printed : 3/15/2013 1:25:50 PM



## Peak results :

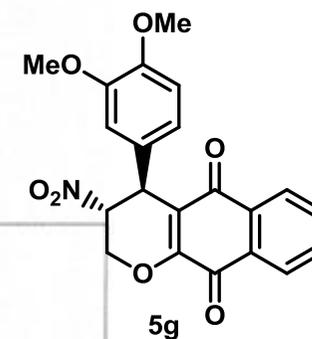
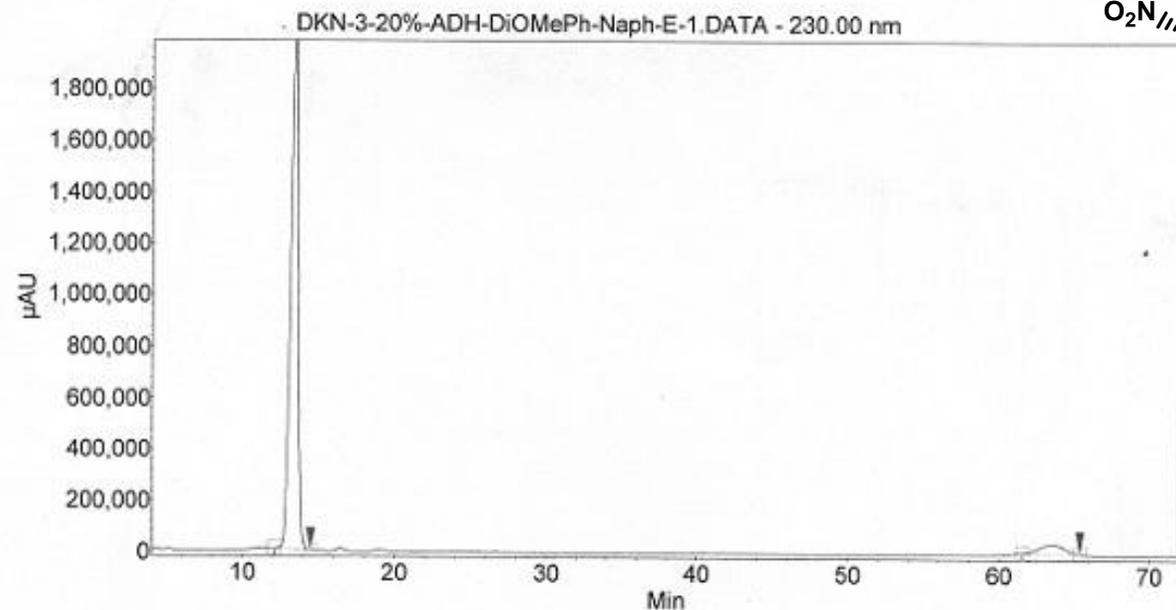
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	12.862	49.48	345326.2	172356.2	49.483
2	UNKNOWN	61.191	50.52	82605.8	175959.2	50.517
Total			100.00	427932.0	348315.3	100.000

Figure S41. HPLC profile of racemic 5g

# Chromatogram : DKN-3-20%-ADH-DiOMePh-Naph-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 3/15/2013 12:04:22 PM  
Processed : 3/15/2013 1:22:56 PM  
Printed : 3/15/2013 1:30:25 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
2	UNKNOWN	13.422	94.35	1996989.4	1137023.6	94.347
1	UNKNOWN	63.511	5.65	36867.6	68127.7	5.653
Total			100.00	2033857.0	1205151.3	100.000

Figure S42. HPLC profile of enantioenriched 5g

```

NAME      INN-DKN-497-1H
EXPNO    1
PROCNO   1
Date_    20120916
Time     16.31
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       0
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.9846387 sec
RG       50.8
DW       60.800 usec
DE       6.50 usec
TE       293.3 K
D1       1.00000000 sec
TD0      1

```

```

===== CHANNEL f1 =====
NUC1     1H
P1       13.50 usec
PL1      -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz
SI       32768
SF       400.1300095 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00

```

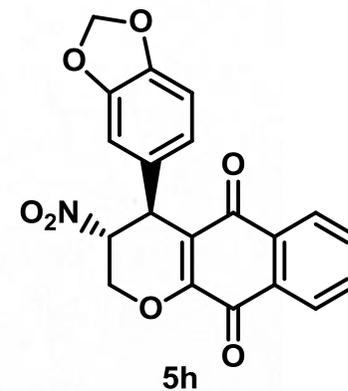
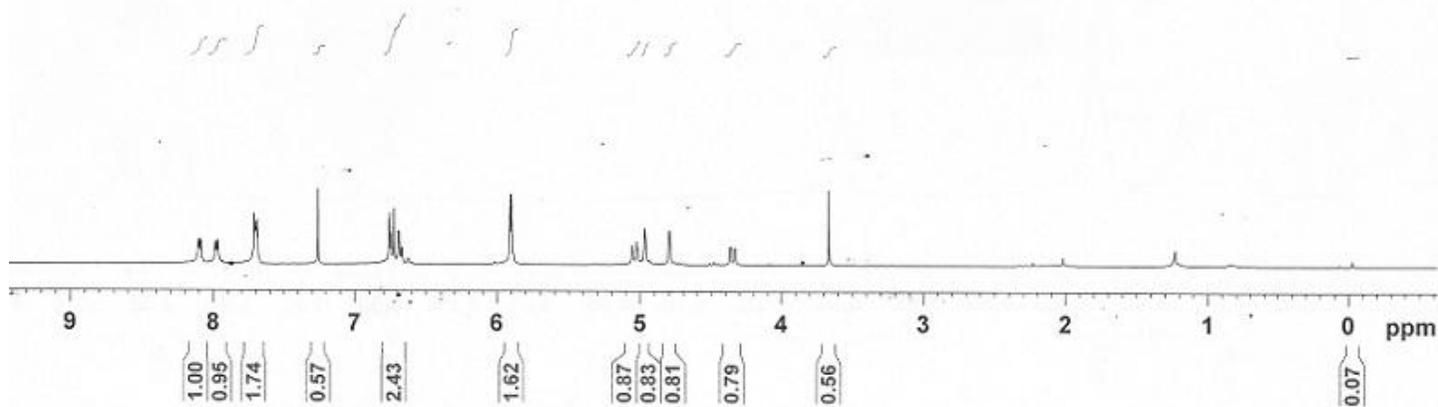


Figure S43. <sup>1</sup>H NMR Spectrum of 5h

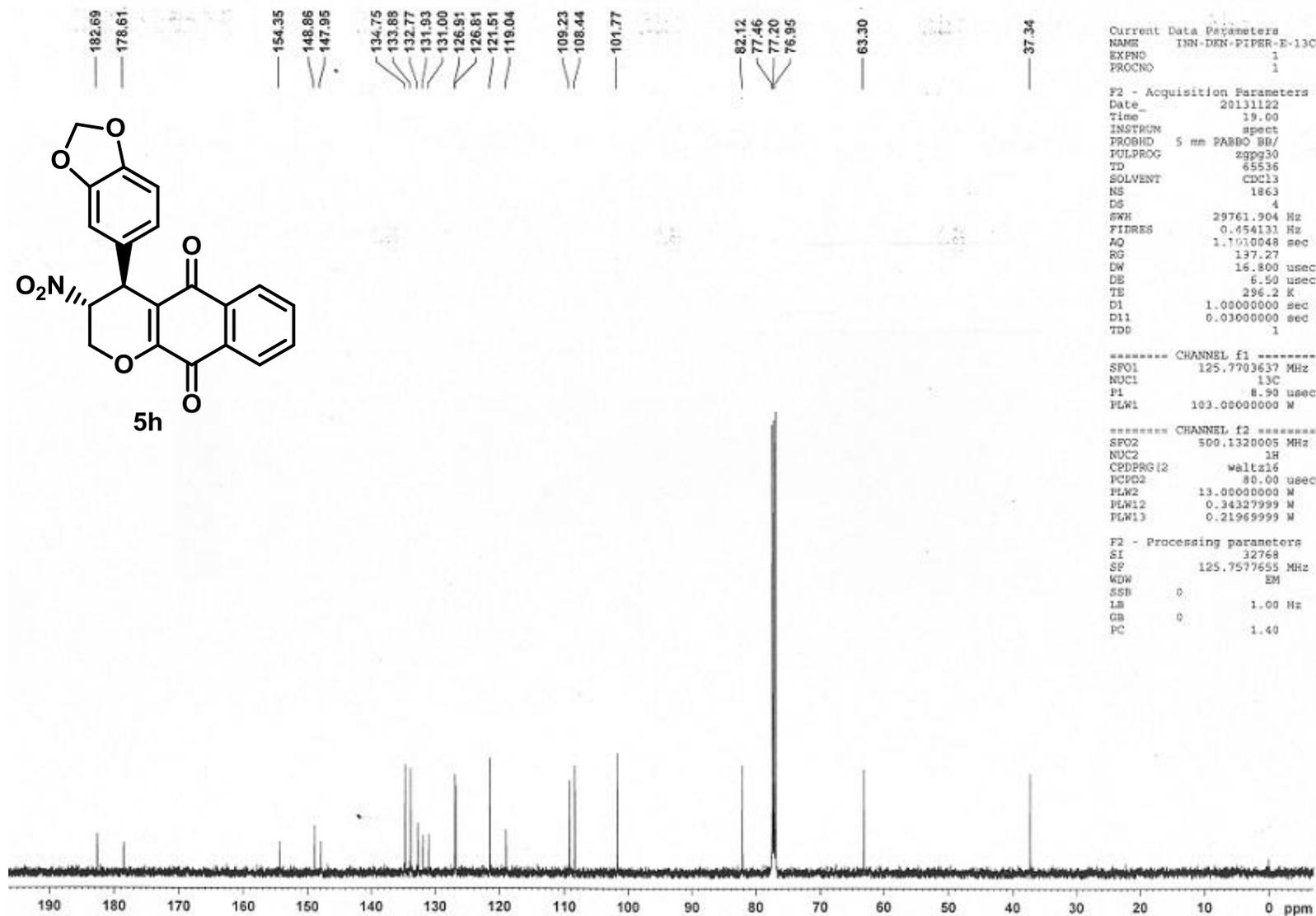
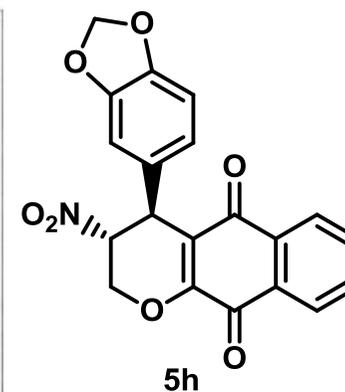
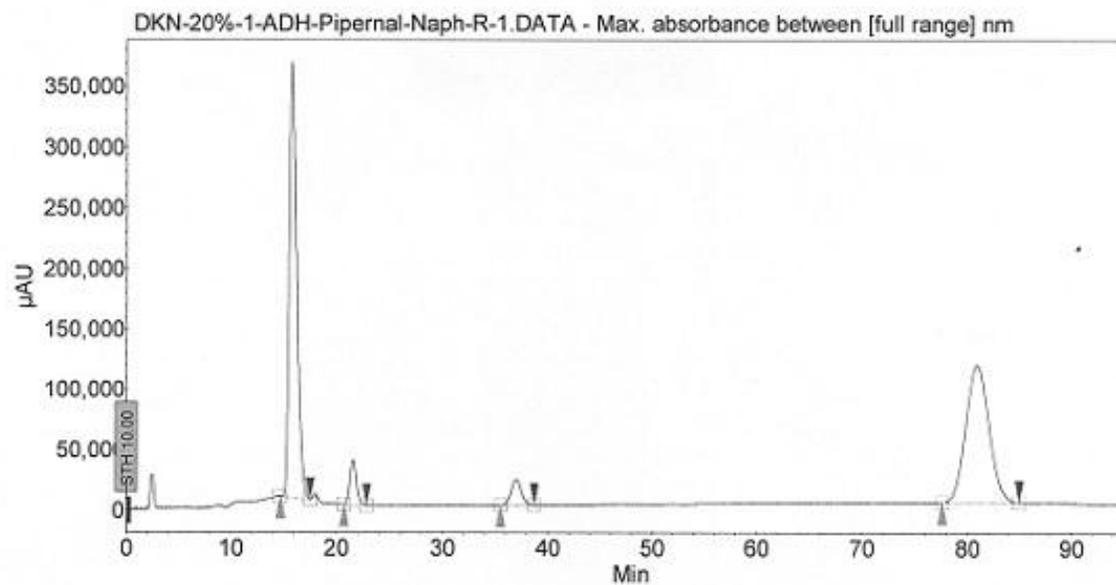


Figure S44. <sup>13</sup>C NMR Spectrum of 5h

## Chromatogram : DKN-20%-1-ADH-Pipernal-Naph-R-1\_channel5

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/6/2012 3:37:55 PM  
Processed : 9/6/2012 5:16:25 PM  
Printed : 9/6/2012 5:17:53 PM



### Peak results :

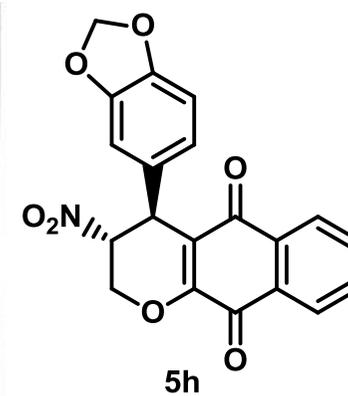
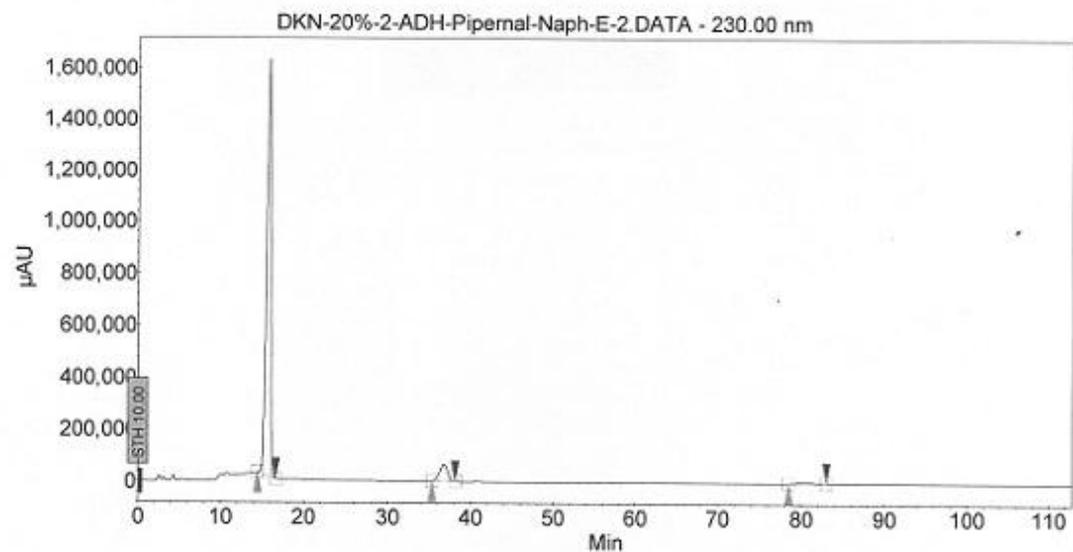
Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU.Min]	Area % [%]
1	UNKNOWN	15.781	46.04	359269.7	290511.2	46.043
2	UNKNOWN	21.539	3.99	36524.9	25172.6	3.990
3	UNKNOWN	37.000	3.77	21212.7	23795.9	3.771
4	UNKNOWN	80.878	46.20	113065.8	291475.9	46.196
Total			100.00	530973.2	630955.6	100.000

Figure S45. HPLC profile of racemic 5h

## Chromatogram : DKN-20%-2-ADH-Pipernal-Naph-E-2\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/8/2012 5:17:23 PM  
Processed : 9/8/2012 8:21:55 PM  
Printed : 9/8/2012 8:22:05 PM



### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	15.728	91.97	1615816.1	909811.0	91.974
3	UNKNOWN	38.800	7.11	64578.5	70333.9	7.110
2	UNKNOWN	80.438	0.92	4060.1	9058.8	0.916
Total			100.00	1684454.7	989203.6	100.000

Figure S46. HPLC profile of enantioenriched 5h

```

NAME      INN-DKN-633-1H
EXPNO     1
PROCNO    1
Date_     20130907
Time      11.34
INSTRUM   spect
PROBHD    5 mm SEI 1H/D-
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        16
DS        0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        114
DW        60.800 usec
DE        6.50 usec
TE        295.1 K
D1        1.00000000 sec
TDO       1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        6.75 usec
PL1       -3.00 dB
PL1W      16.73965454 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300104 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

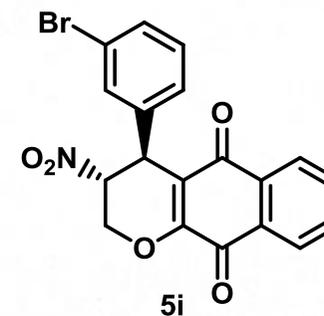
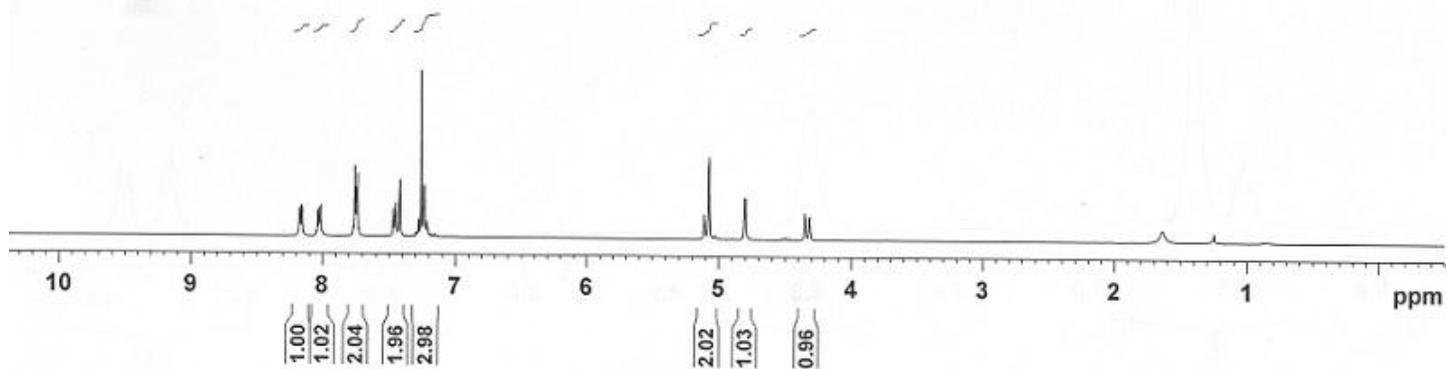


Figure S47. <sup>1</sup>H NMR Spectrum of 5i

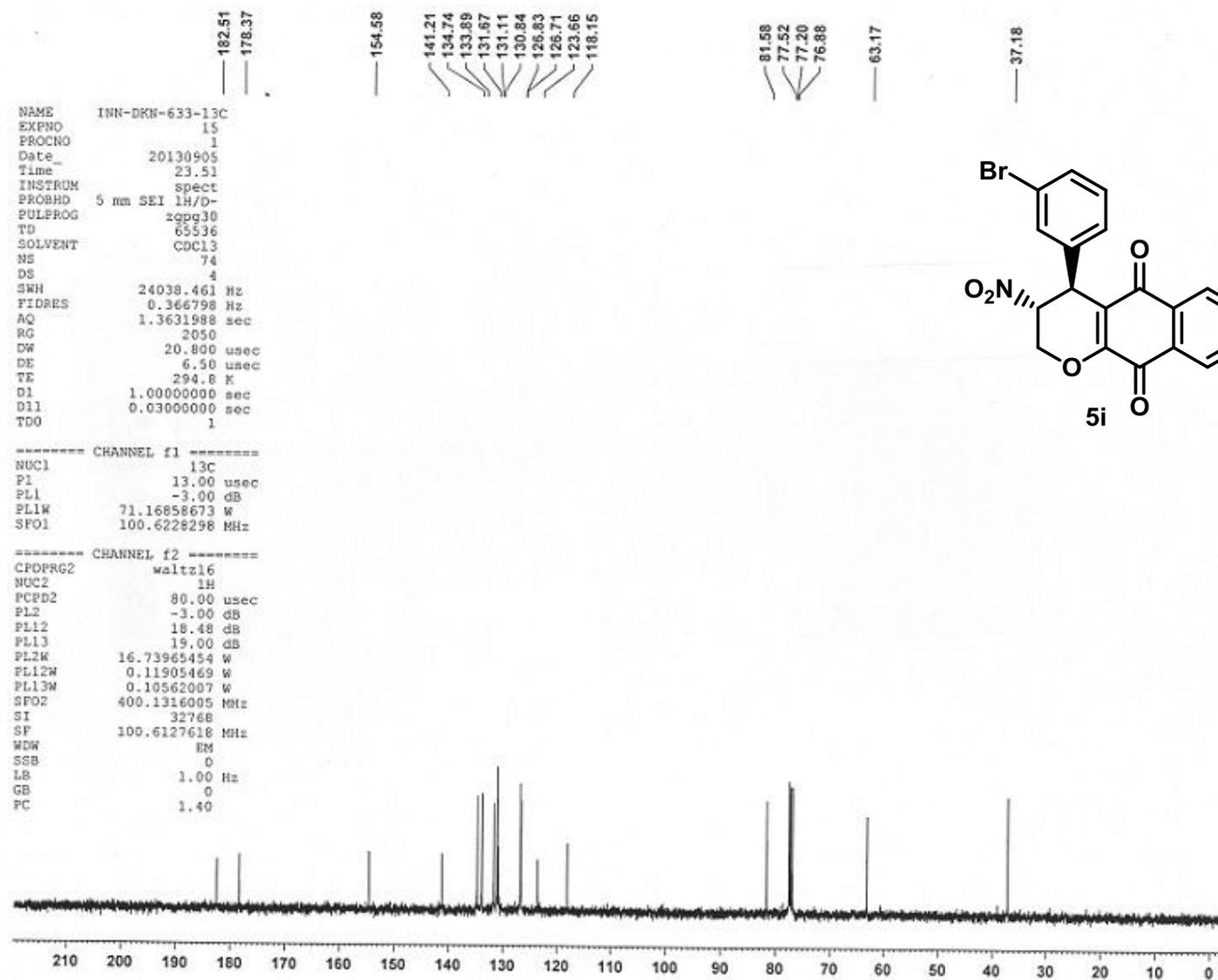
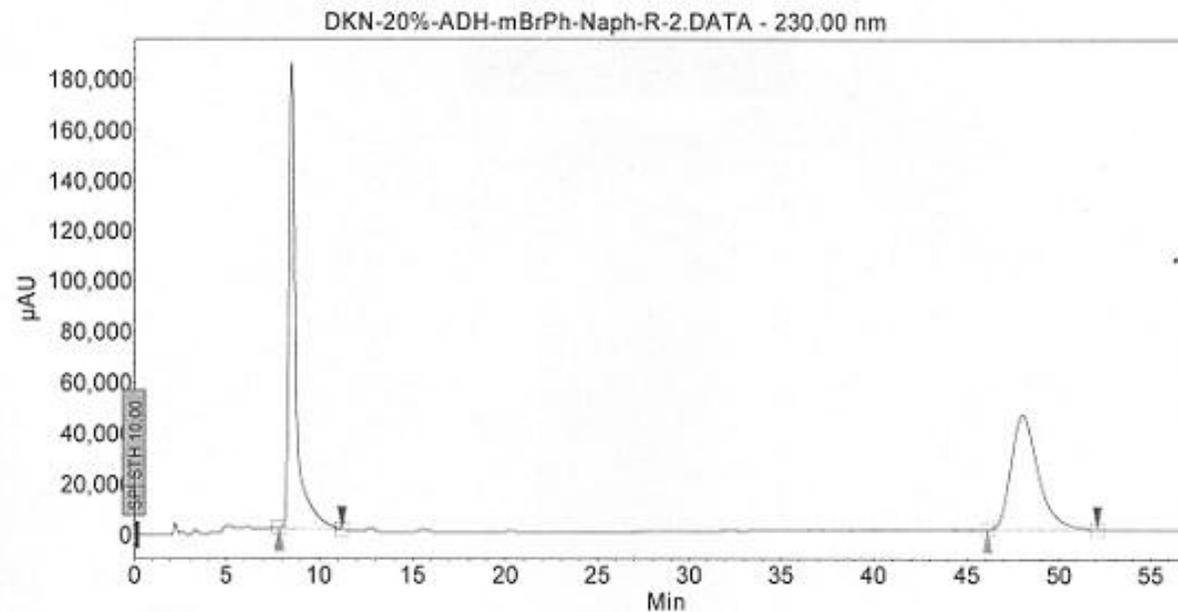
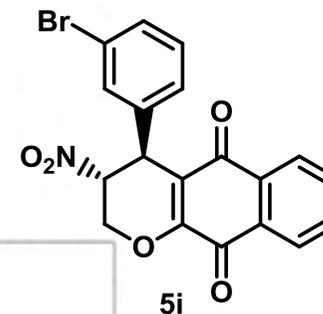


Figure S48. <sup>13</sup>C NMR Spectrum of 5i

# Chromatogram : DKN-20%-ADH-mBrPh-Naph-R-2\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 7/27/2013 2:26:58 PM  
Processed : 7/27/2013 3:26:35 PM  
Printed : 7/27/2013 3:26:48 PM



## Peak results :

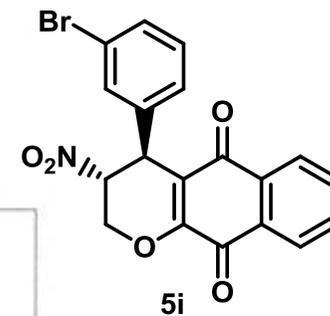
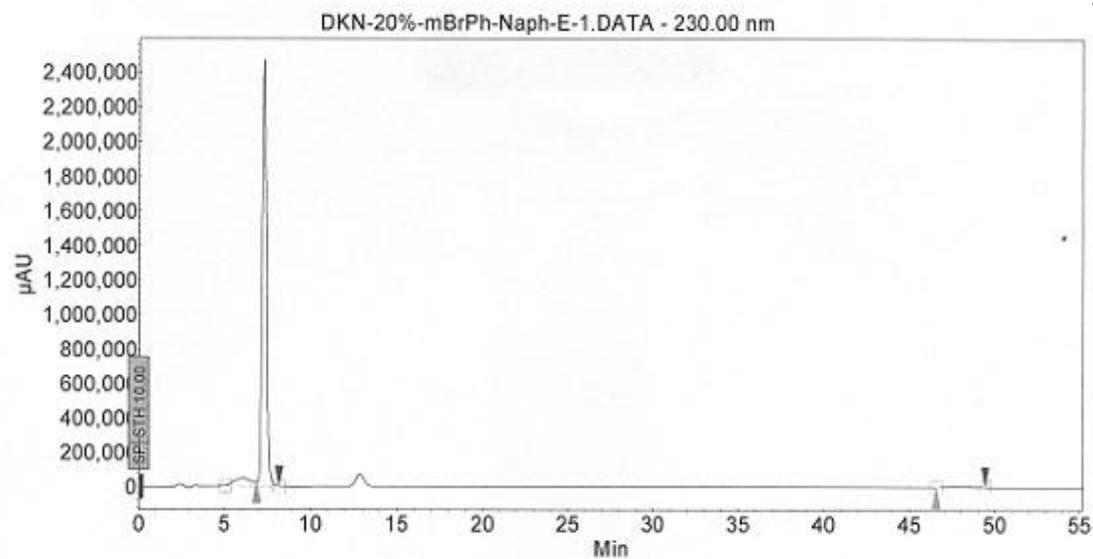
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.506	50.69	183933.1	79274.3	50.688
2	UNKNOWN	48.037	49.31	45114.5	77120.8	49.312
Total			100.00	229047.5	156395.1	100.000

Figure S49. HPLC profile of racemic 5i

### Chromatogram : DKN-20%-mBrPh-Naph-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 7/29/2013 10:53:21 AM  
Processed : 7/29/2013 2:34:52 PM  
Printed : 7/29/2013 2:35:27 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	7.293	98.70	2468155.6	705861.9	98.700
2	UNKNOWN	47.823	1.30	6128.3	9296.1	1.300
Total			100.00	2474284.0	715257.9	100.000

Figure S50. HPLC profile of enantioenriched 5i

```

NAME inn-dkn-498-1h
EXPNO 1
PROCNO 1
Date_ 20120211
Time_ 19.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 293.2 K
D1 1.00000000 sec
TDO 1

```

```

----- CHANNEL f1 -----
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

```

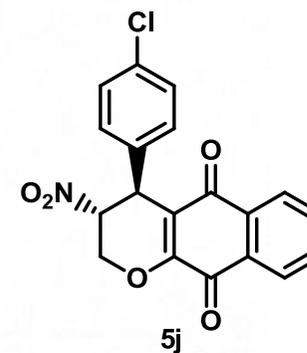
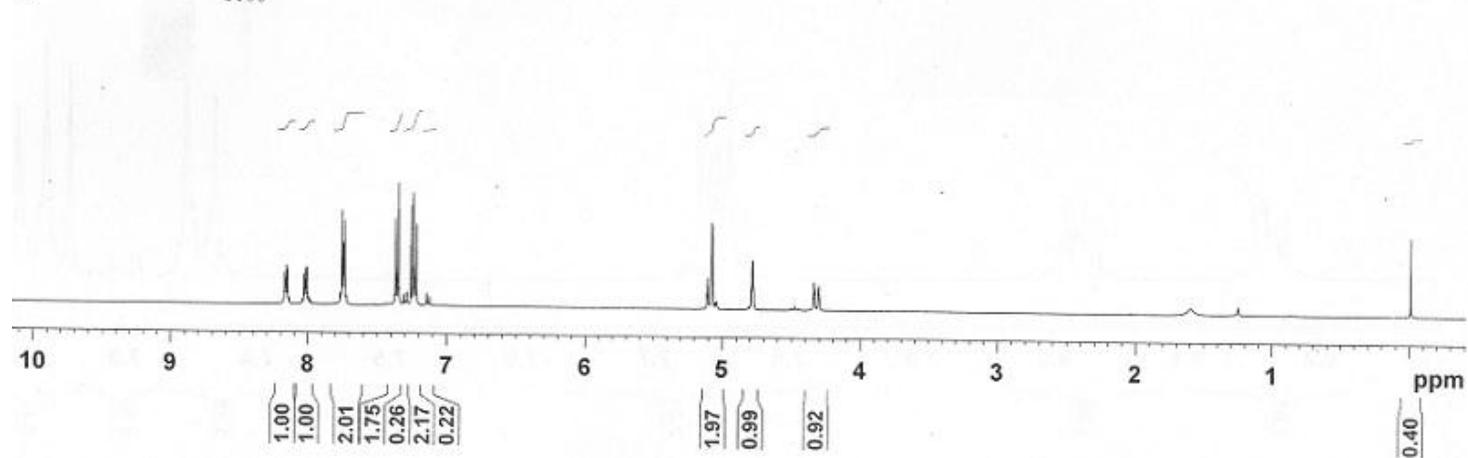


Figure S51. <sup>1</sup>H NMR Spectrum of 5j

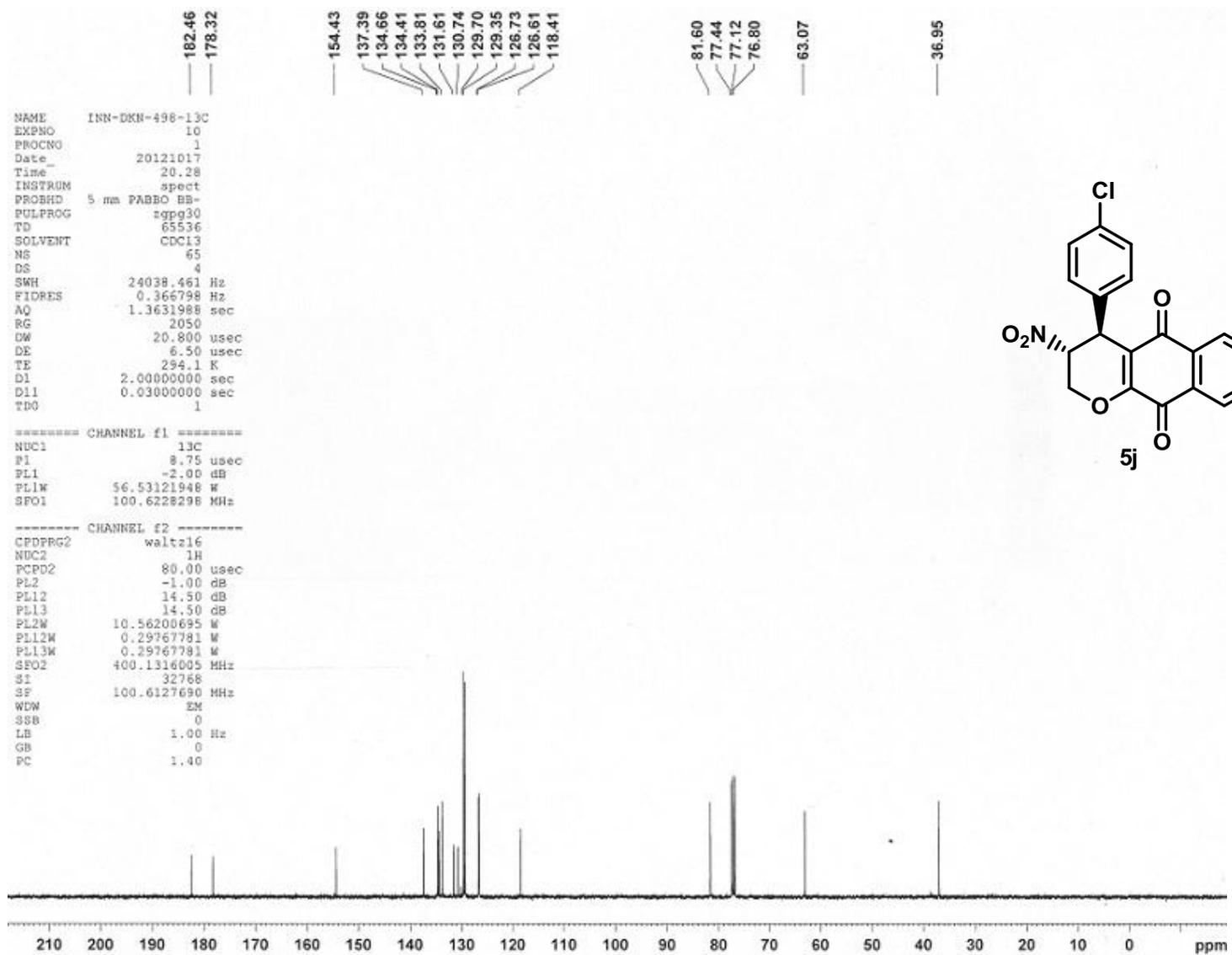
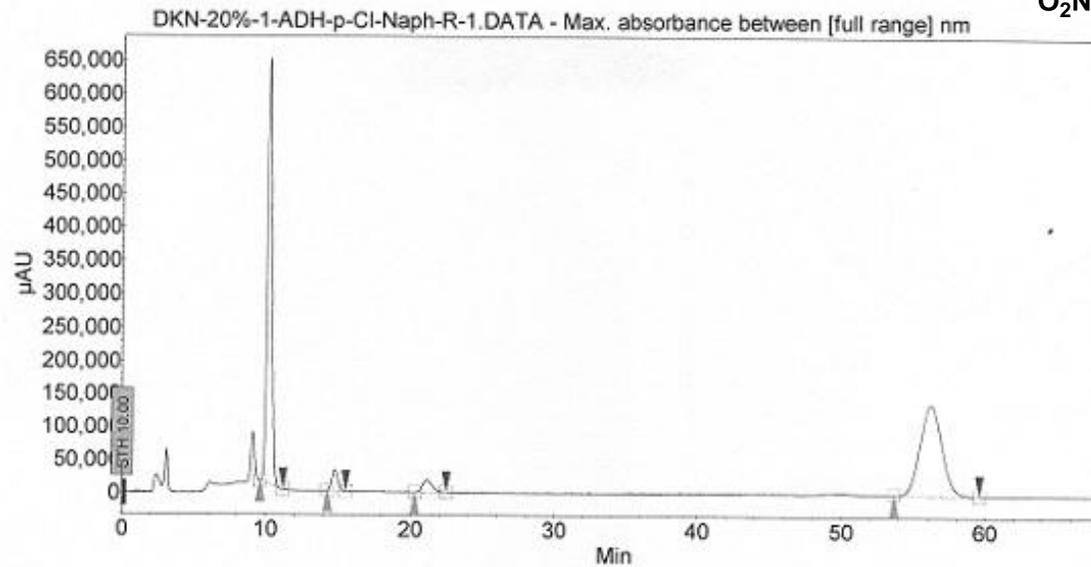
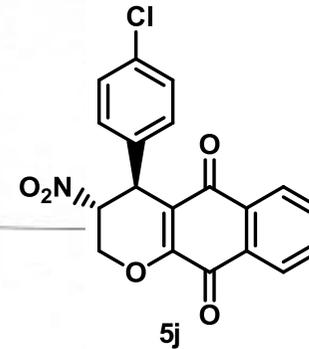


Figure S52. <sup>13</sup>C NMR Spectrum of 5j

# Chromatogram : DKN-20%-1-ADH-p-Cl-Naph-R-1\_channel5

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 9/5/2012 8:18:15 PM  
 Processed : 9/5/2012 9:34:29 PM  
 Printed : 9/5/2012 9:34:44 PM



## Peak results :

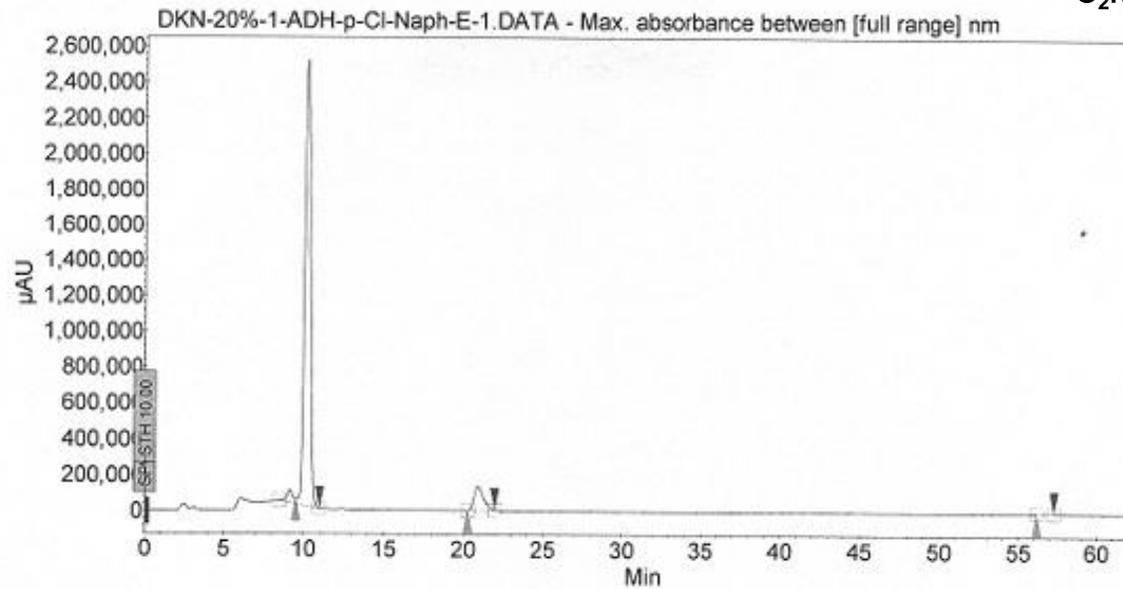
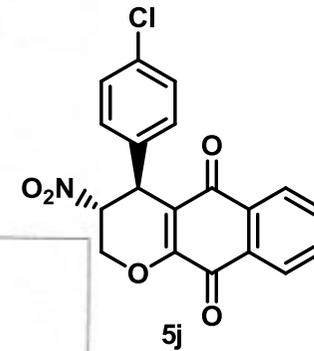
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	10.183	47.46	640568.9	242452.5	47.458
2	UNKNOWN	14.781	2.90	31551.7	14805.9	2.898
3	UNKNOWN	21.139	2.74	18246.4	13977.5	2.736
4	UNKNOWN	56.193	46.91	137053.2	239643.1	46.908
Total			100.00	827420.3	510879.0	100.000

Figure S53. HPLC profile of racemic 5j

# Chromatogram : DKN-20%-1-ADH-p-Cl-Naph-E-1\_channel5

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/5/2012 9:31:42 PM  
Processed : 12/11/2012 7:52:49 PM  
Printed : 12/11/2012 7:53:01 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	10.159	92.12	2486392.6	1069827.5	92.120
3	UNKNOWN	20.905	7.83	131796.0	90970.7	7.833
2	UNKNOWN	56.703	0.05	1149.5	543.0	0.047
Total			100.00	2629328.1	1161341.2	100.000

Figure S54. HPLC profile of enantioenriched 5j

```

NAME      INN-DKN-508-1H
EXPNO     9
PROCNO    1
Date_     20120929
Time      22.28
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        4
DS        0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        32
DW        60.800 usec
DE        6.50 usec
TE        300.0 K
D1        1.00000000 sec
TD0       1

```

```

----- CHANNEL f1 -----
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SF01     400.1324710 MHz
SI        32768
SF        400.1300095 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

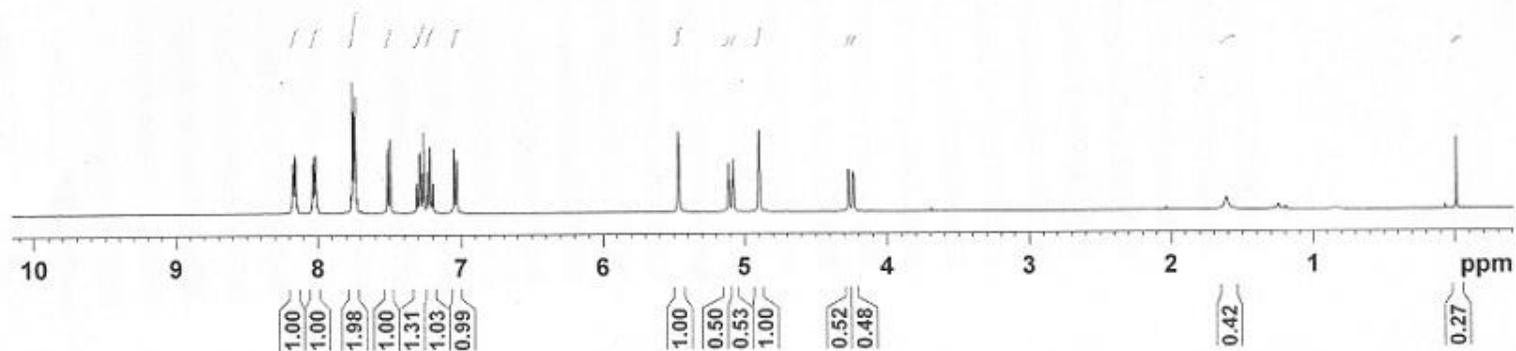
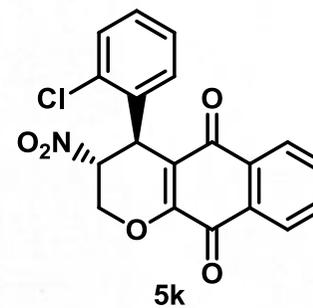


Figure S55. <sup>1</sup>H NMR Spectrum of 5k

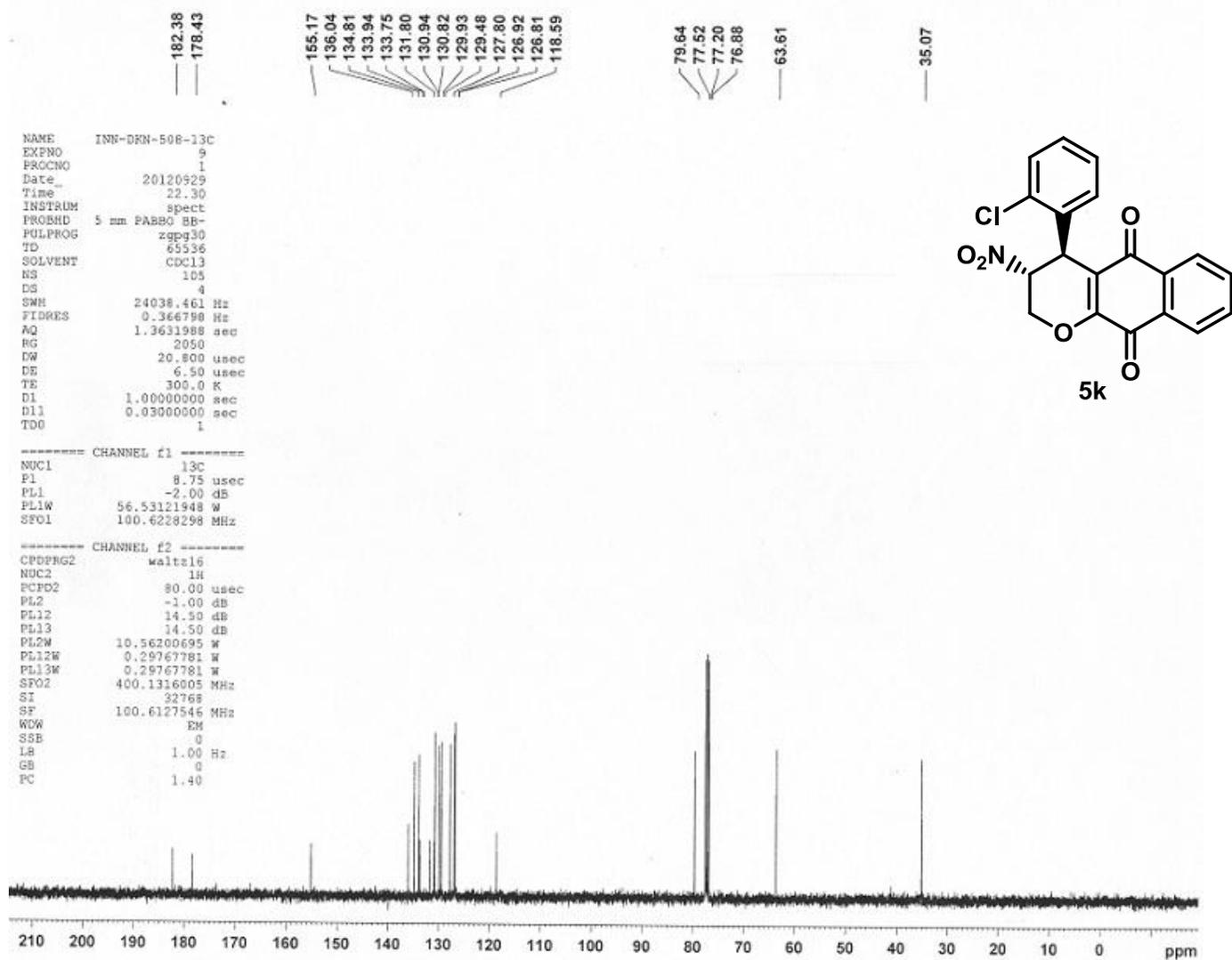
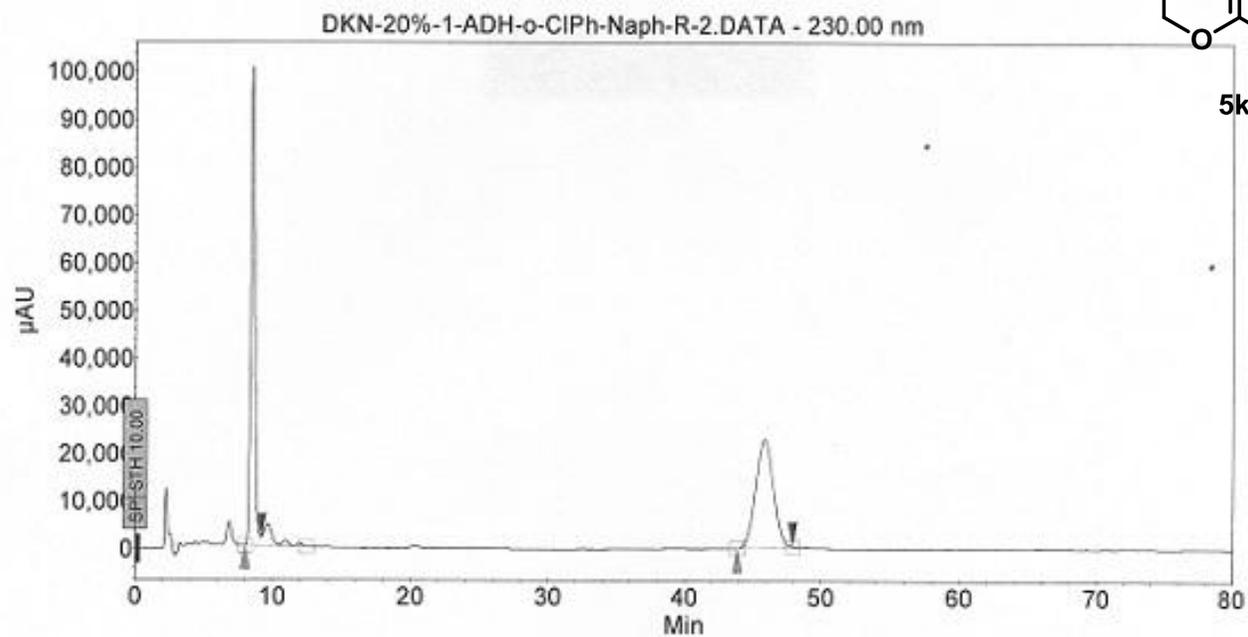
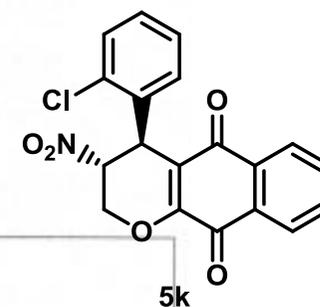


Figure S56.  $^{13}\text{C}$  NMR Spectrum of 5k

# Chromatogram : DKN-20%-1-ADH-o-CIPh-Naph-R-2\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 10/24/2013 12:42:25 PM  
Processed : 10/24/2013 2:02:45 PM  
Printed : 10/24/2013 3:47:19 PM



## Peak results :

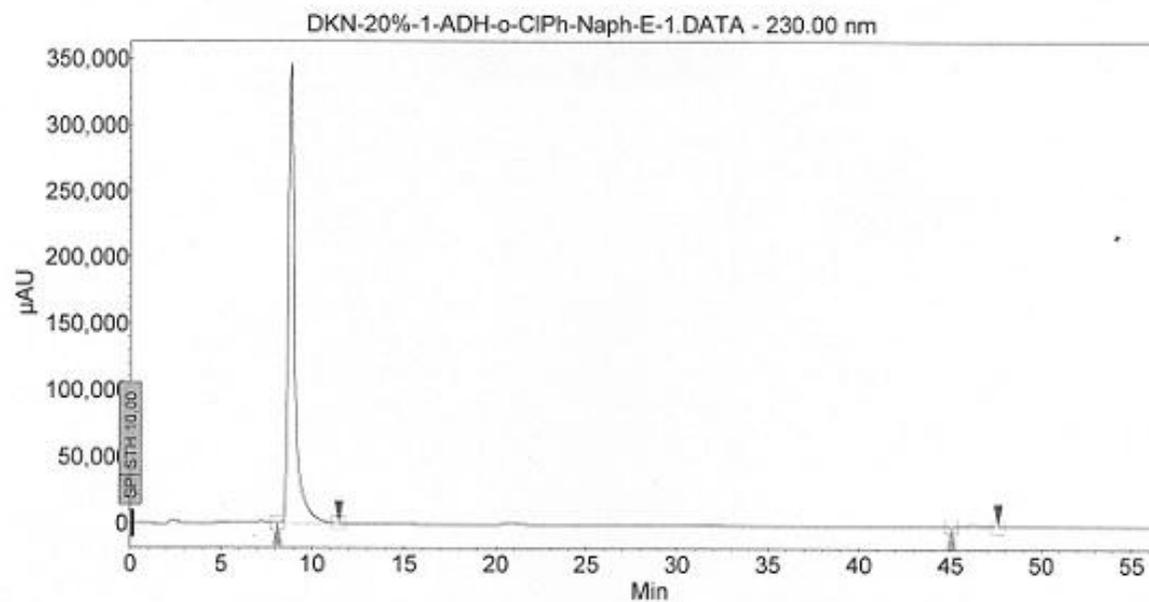
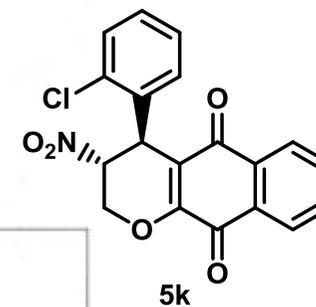
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.517	50.25	100265.4	34128.0	50.253
2	UNKNOWN	45.850	49.75	22748.5	33784.5	49.747
Total			100.00	123011.9	67912.5	100.000

Figure S57. HPLC profile of racemic 5k

# Chromatogram : DKN-20%-1-ADH-o-CIPh-Naph-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 9/25/2012 8:32:09 PM  
Processed : 9/25/2012 9:35:21 PM  
Printed : 9/25/2012 9:35:29 PM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.813	99.52	345552.8	139834.6	99.518
2	UNKNOWN	46.237	0.48	500.0	676.7	0.482
Total			100.00	346052.7	140511.4	100.000

Figure S58. HPLC profile of enantioenriched 5k

```

NAME      INN-DKN-492-1H
EXPNO     2
PROCNO    1
Date_     20121018
Time      18.53
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        65536
SOLVENT   CDC13
NS        12
DS        0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846387 sec
RG        32
DW        60.800 usec
DE        6.50 usec
TE        293.7 K
D1        1.00000000 sec
TD0       1

```

```

===== CHANNEL f1 =====
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFOL      400.1324710 MHz
SI        32768
SF        400.1300095 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

```

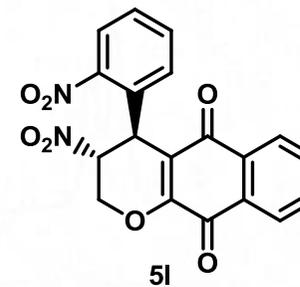
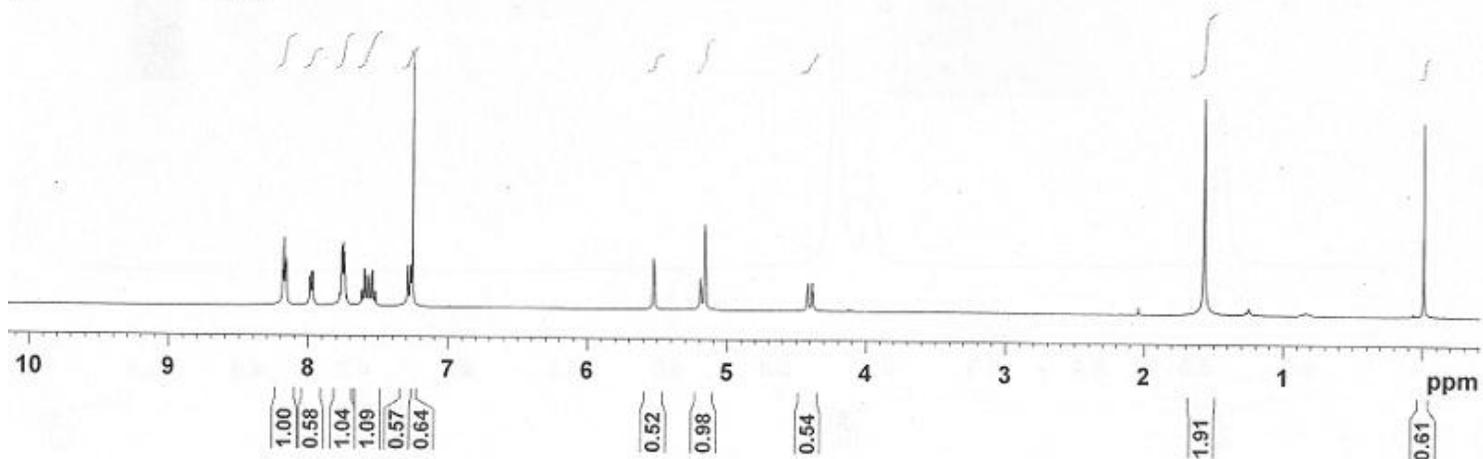


Figure S59. <sup>1</sup>H NMR Spectrum of 5l

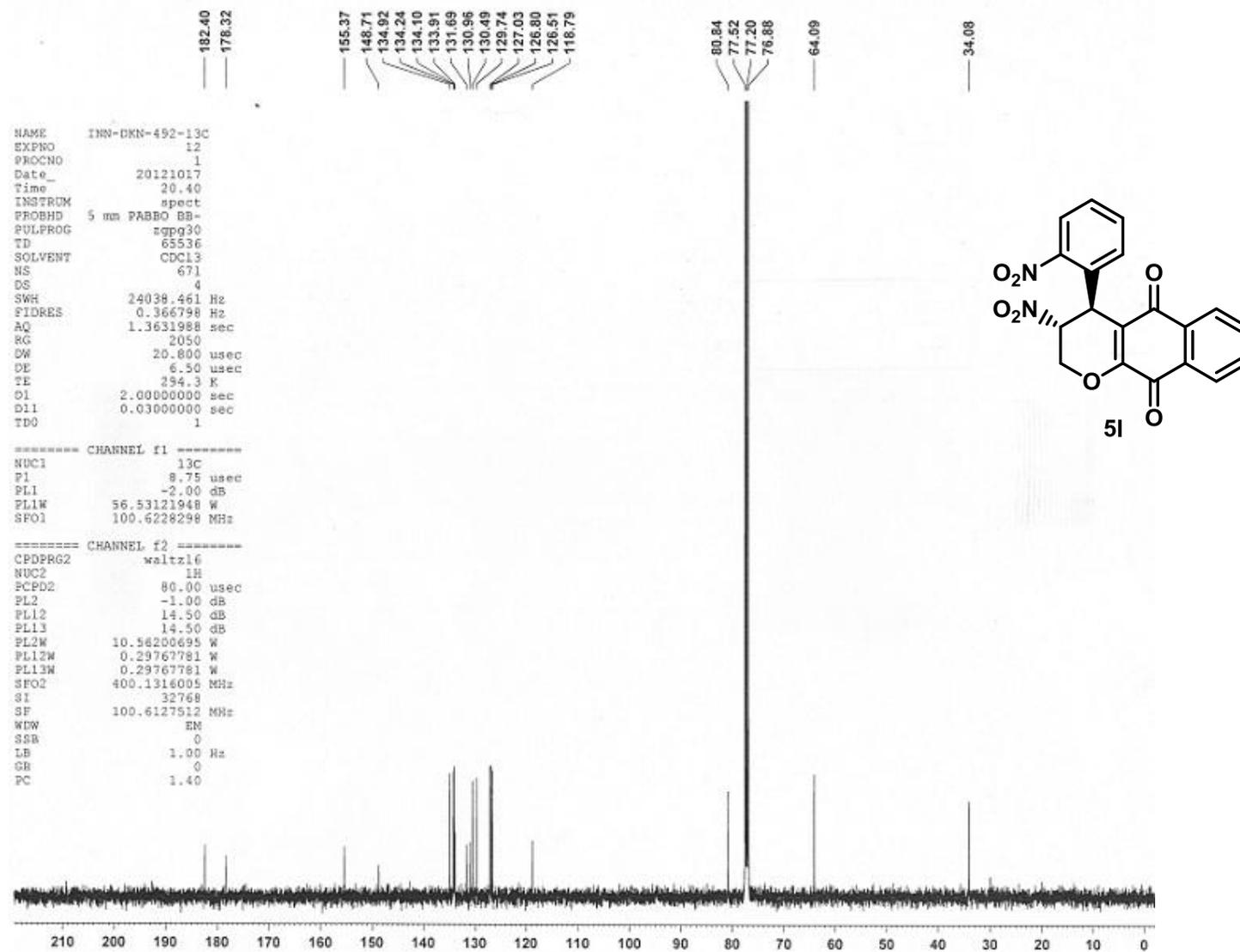
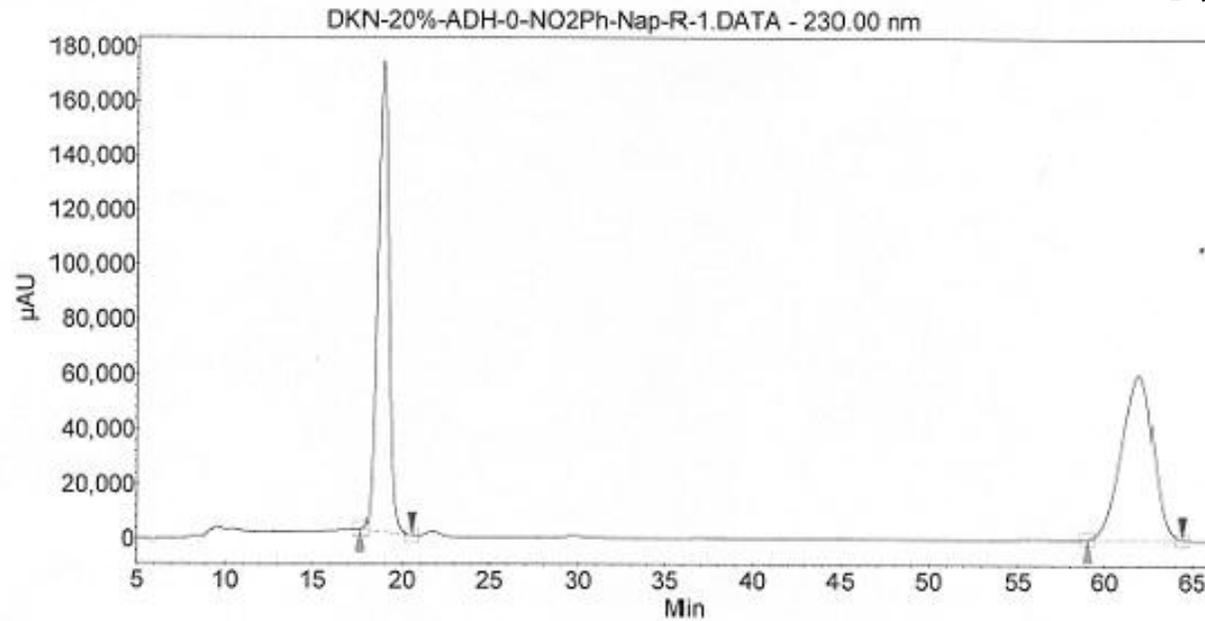
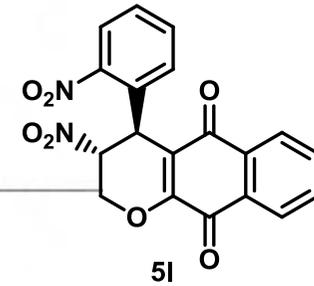


Figure S60.  $^{13}\text{C}$  NMR Spectrum of 5I

# Chromatogram : DKN-20%-ADH-0-NO2Ph-Nap-R-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 4/3/2013 3:23:08 PM  
Processed : 4/3/2013 4:30:48 PM  
Printed : 4/3/2013 4:47:00 PM



## Peak results :

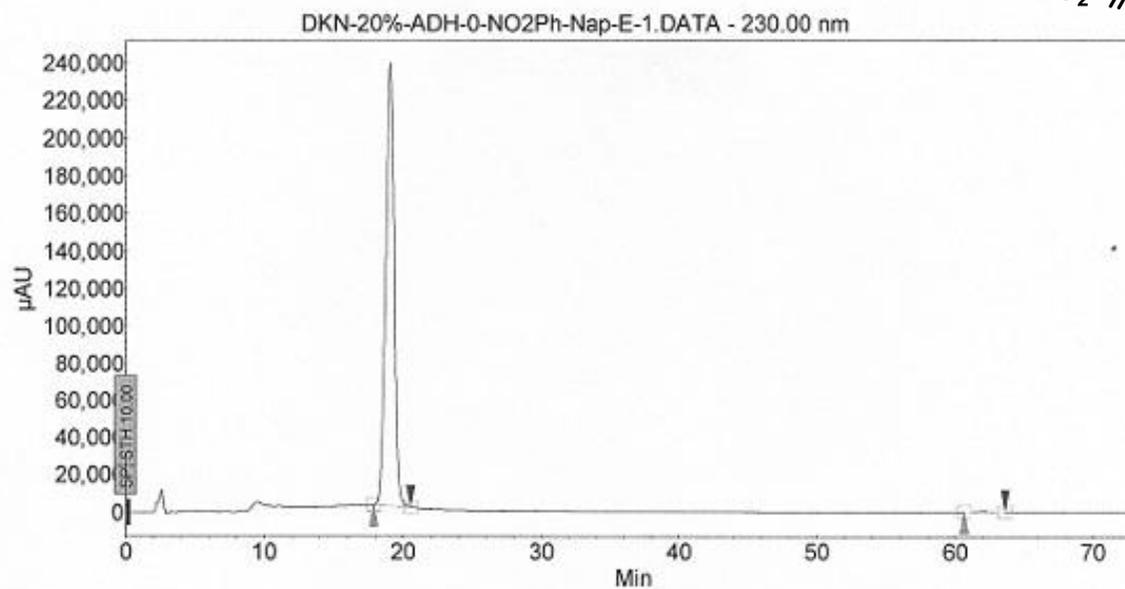
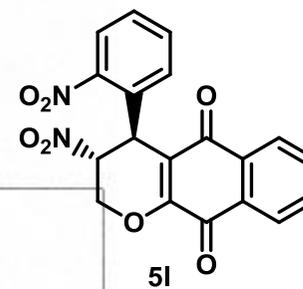
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	18.913	50.23	172162.1	125255.2	50.233
2	UNKNOWN	61.978	49.77	59920.5	124094.4	49.767
Total			100.00	232082.6	249349.6	100.000

Figure S61. HPLC profile of racemic 5I

# Chromatogram : DKN-20%-ADH-0-NO2Ph-Nap-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 4/3/2013 4:44:42 PM  
Processed : 4/3/2013 6:04:17 PM  
Printed : 4/3/2013 6:04:43 PM



### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	19.060	99.39	236570.0	165264.5	99.390
2	UNKNOWN	62.031	0.61	620.5	1014.9	0.610
Total			100.00	237190.5	166279.4	100.000

Figure S62. HPLC profile of enantioenriched 51

```

NAME      INN-DKN-625-1H
EXPNO     11
PROCNO    1
Date_     20130608
Time      20.09
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         11
DS         0
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ         3.9846387 sec
RG         144
DW         60.800 usec
DE         6.50 usec
TE         294.1 K
D1         1.00000000 sec
TD0        1

```

```

***** CHANNEL f1 *****
NUC1      1H
P1         13.50 usec
PL1        -1.00 dB
PLLW      10.56200695 W
SFO1      400.1324710 MHz
SI         32768
SF         400.1300091 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

```

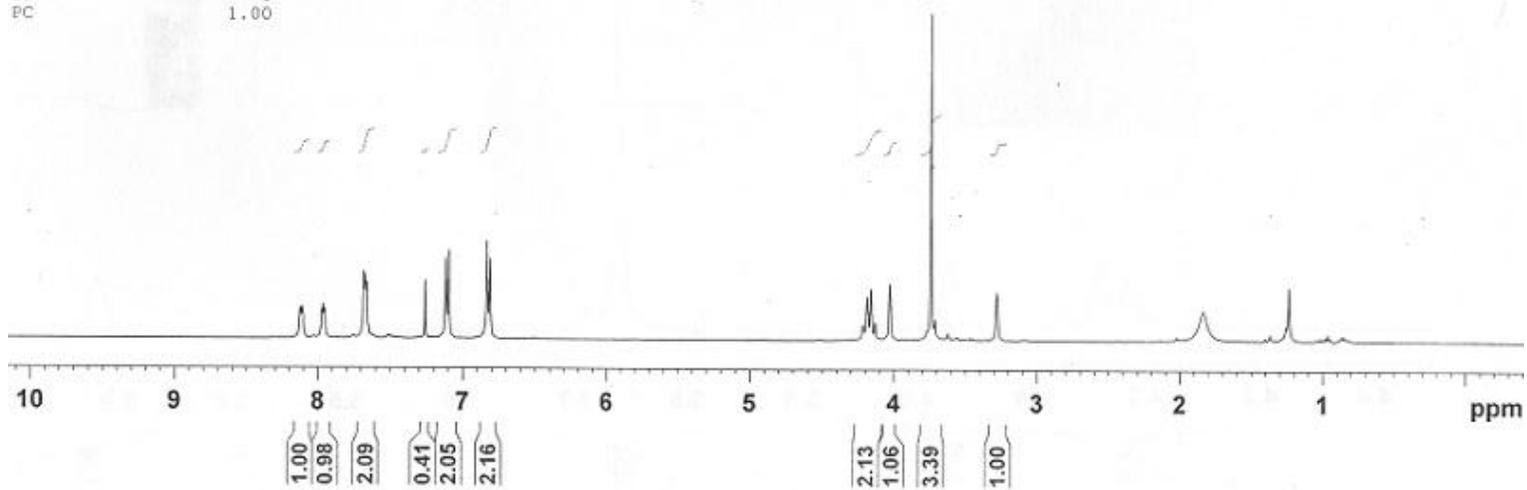
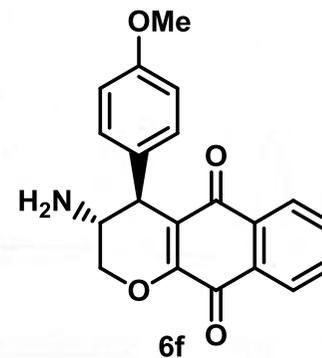


Figure S63. <sup>1</sup>H NMR Spectrum of 6f

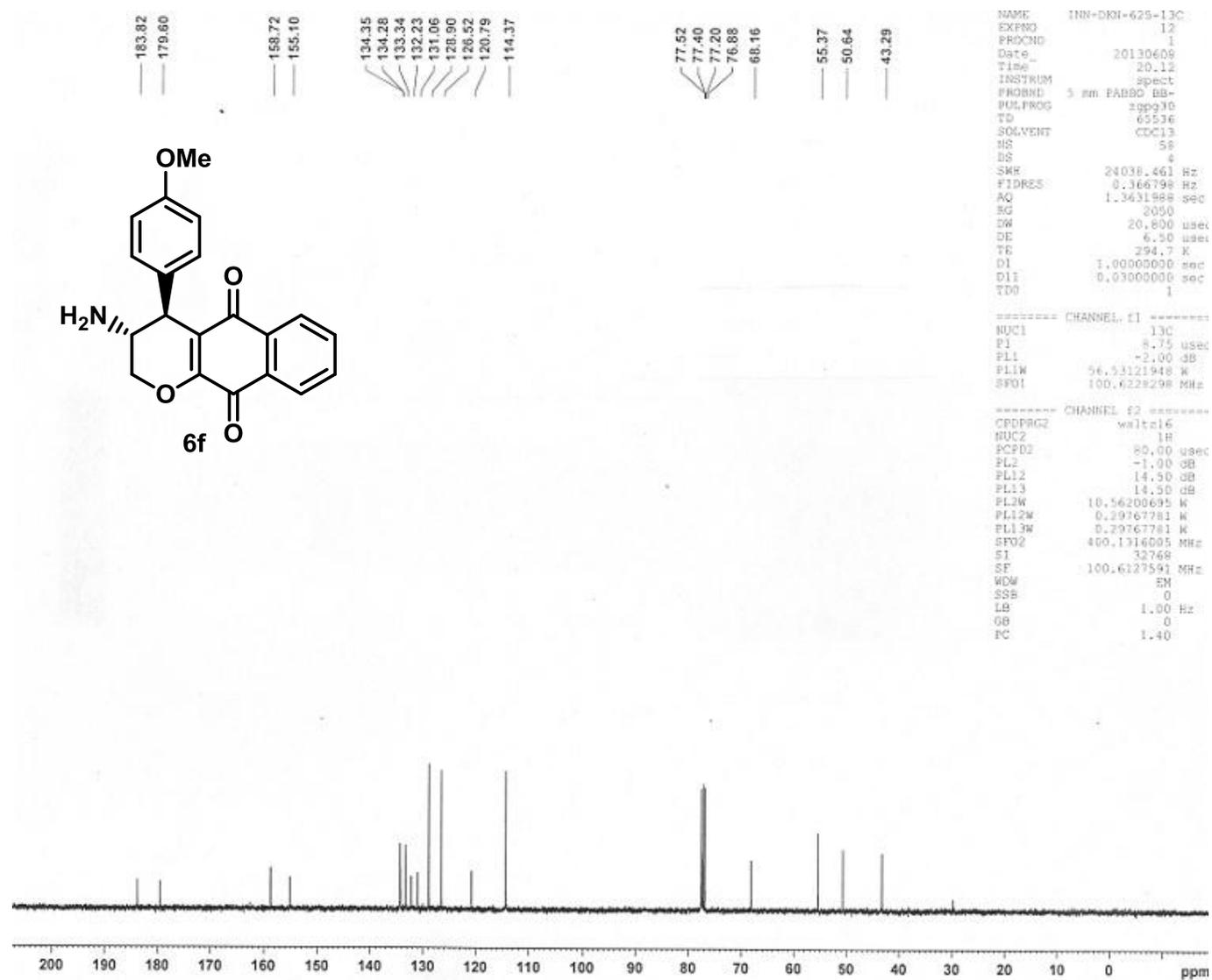
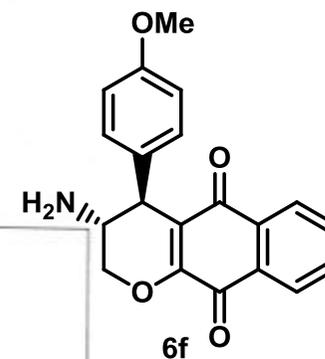
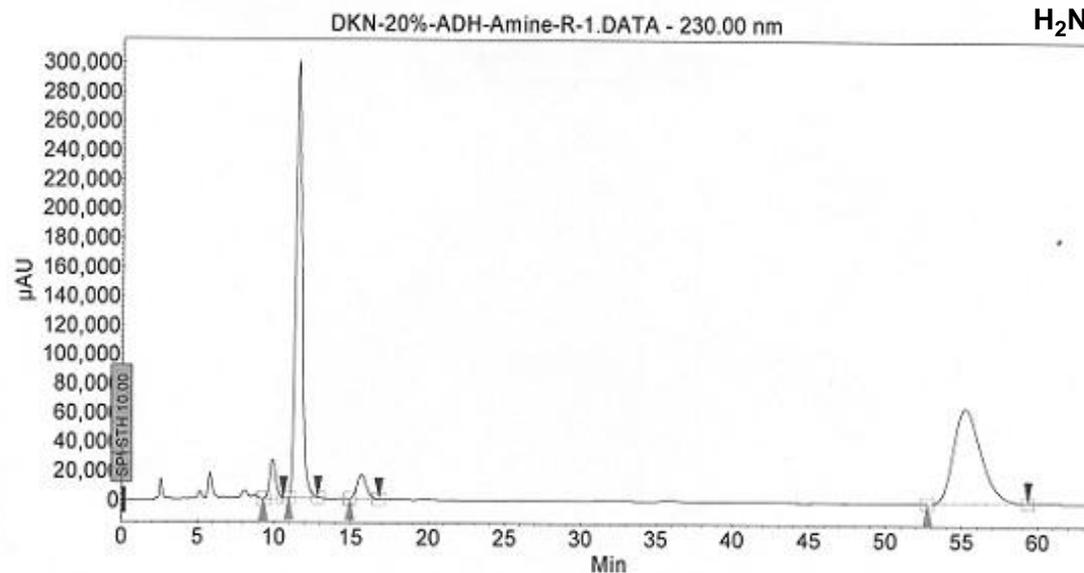


Figure S64.  $^{13}\text{C}$  NMR Spectrum of **6f**

### Chromatogram : DKN-20%-ADH-Amine-R-1\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 6/13/2013 1:58:31 PM  
 Processed : 6/13/2013 3:05:22 PM  
 Printed : 6/13/2013 3:05:43 PM



#### Peak results :

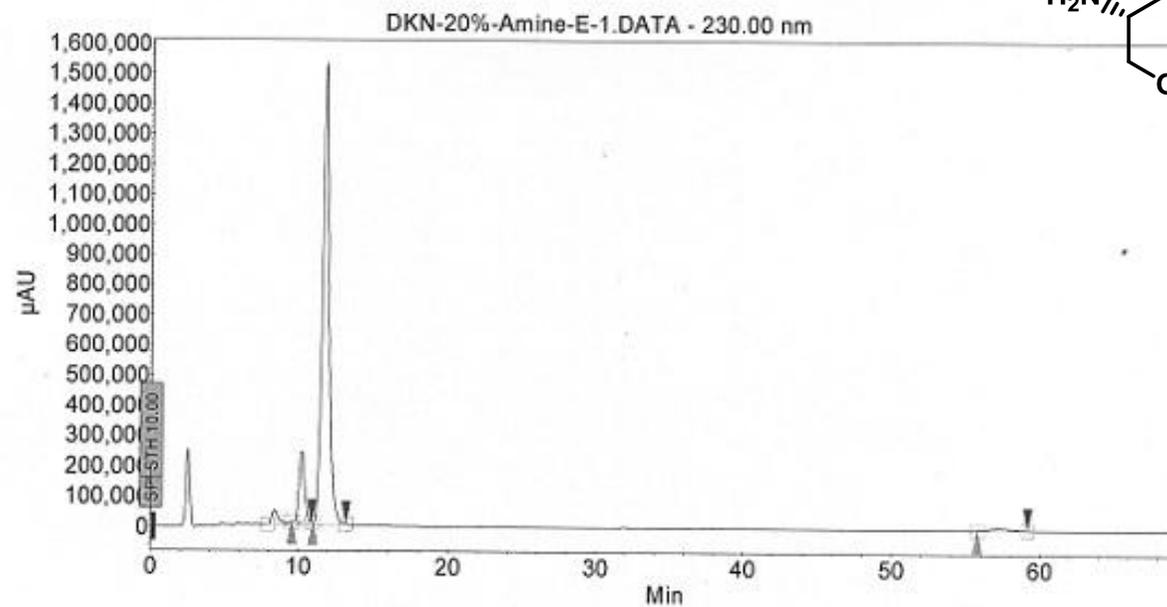
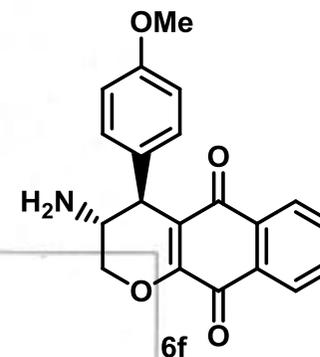
Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU.Min]	Area % [%]
1	UNKNOWN	9.893	4.10	26696.7	12263.8	4.097
3	UNKNOWN	11.506	46.62	299076.0	139560.2	46.620
2	UNKNOWN	15.666	3.88	16591.8	11622.7	3.883
4	UNKNOWN	55.183	45.40	64853.2	135912.5	45.401
Total			100.00	407217.7	299359.2	100.000

Figure S65. HPLC profile of racemic 6f

### Chromatogram : DKN-20%-Amine-E-1\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 6/13/2013 5:58:55 PM  
 Processed : 10/24/2013 12:30:37 PM  
 Printed : 12/17/2013 12:06:07 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU Min]	Area % [%]
3	UNKNOWN	10.183	11.11	230983.1	101657.7	11.107
1	UNKNOWN	11.716	87.35	1529094.6	799453.1	87.351
2	UNKNOWN	57.193	1.54	7818.2	14106.9	1.541
Total			100.00	1767895.9	915217.7	100.000

Figure S66. HPLC profile of enantioenriched 6f

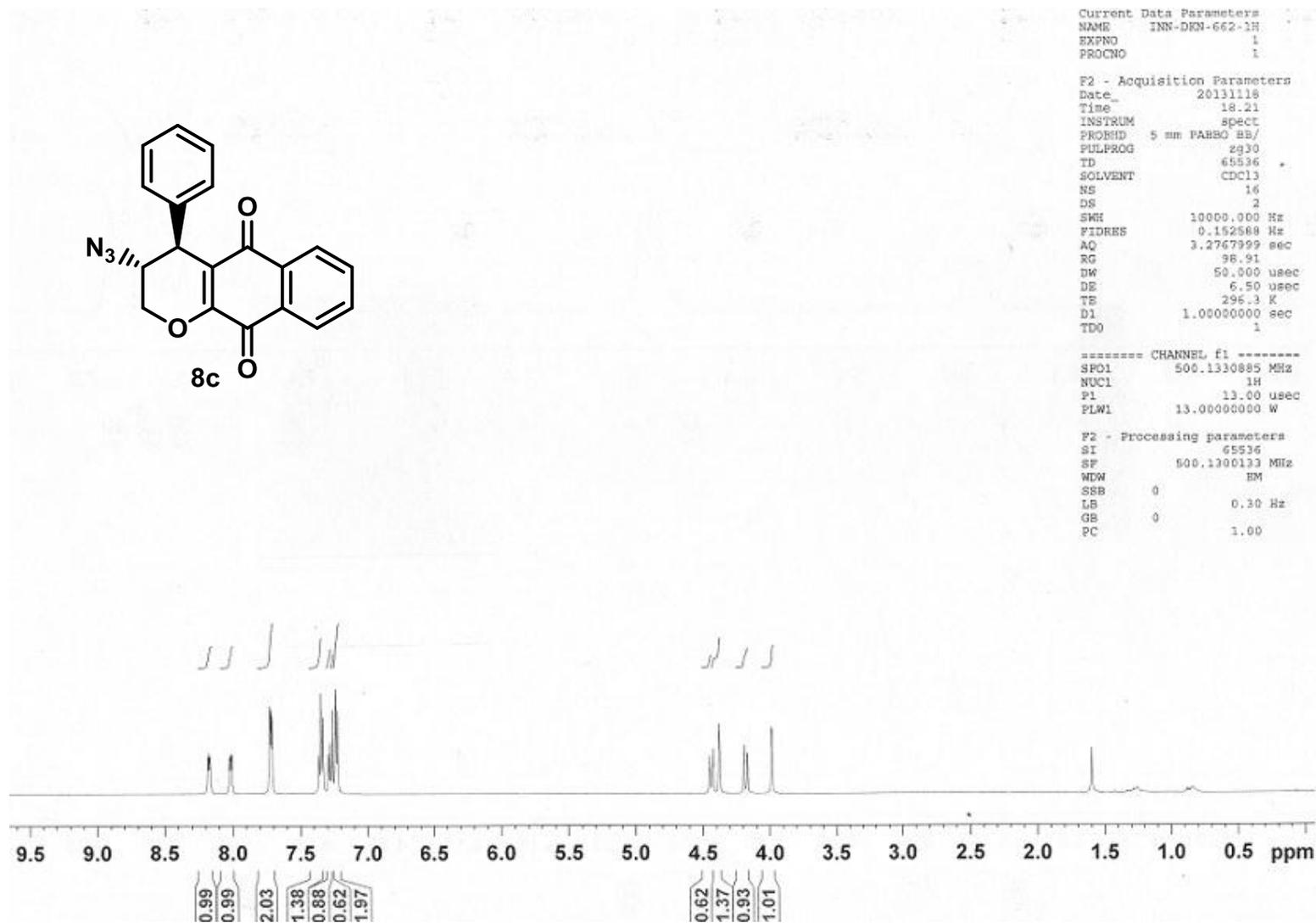


Figure S67.  $^1\text{H}$  NMR Spectrum of 8c

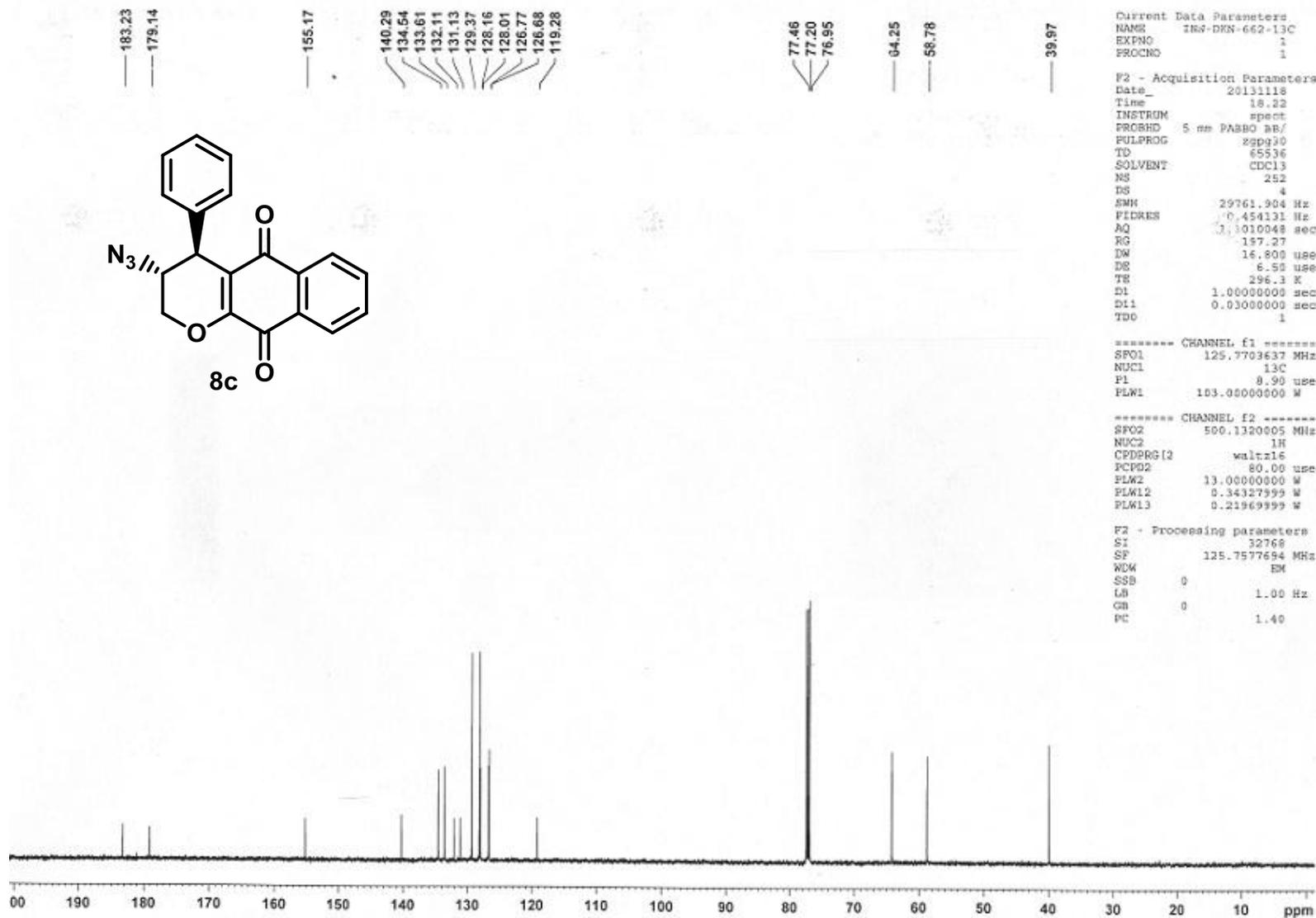
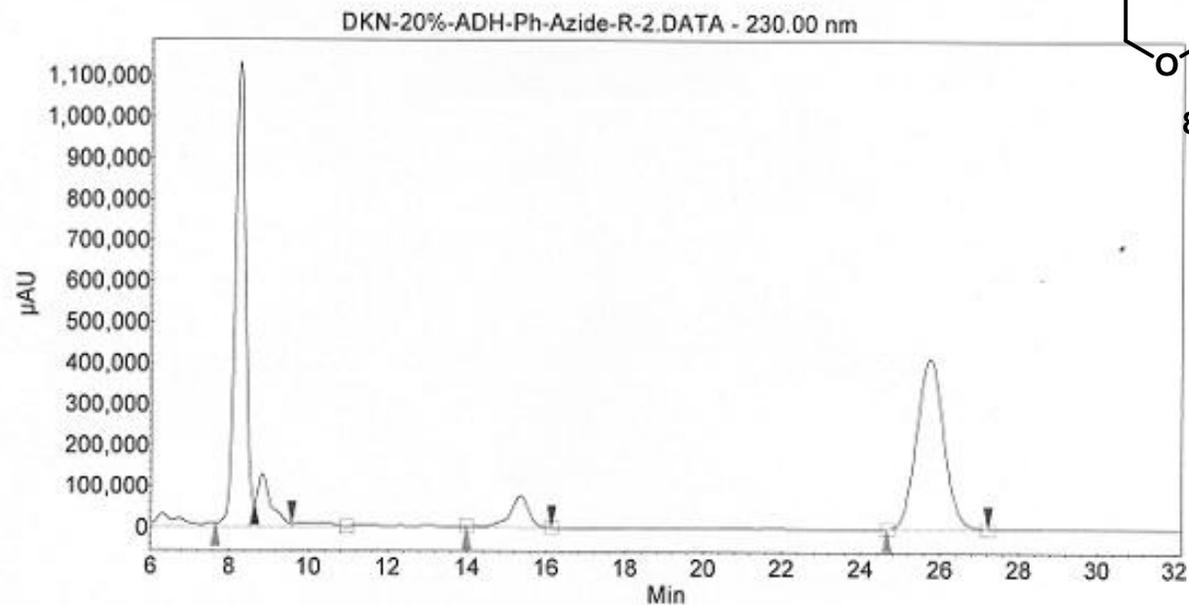
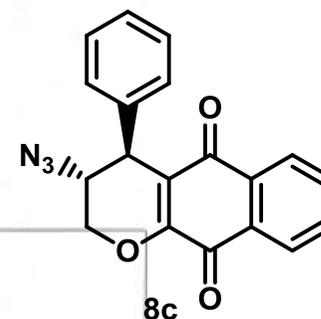


Figure S68. <sup>13</sup>C NMR Spectrum of 8c

### Chromatogram : DKN-20%-ADH-Ph-Azide-R-2\_channel4

System : Jasco HPLC  
 Method : DKN-20%-1FR-230nm  
 User : User1

Acquired : 12/17/2013 9:35:31 AM  
 Processed : 12/17/2013 10:10:15 AM  
 Printed : 12/17/2013 10:13:11 AM



#### Peak results :

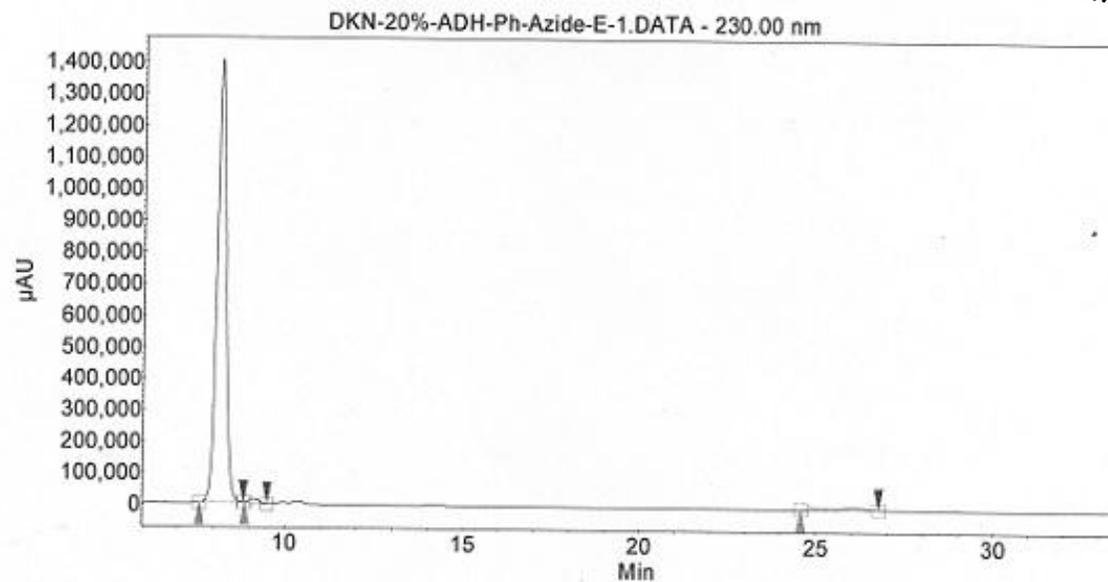
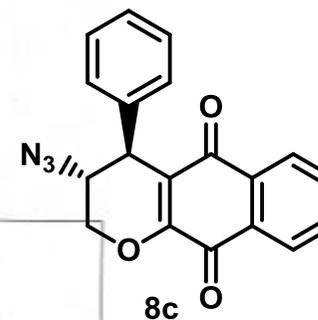
Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	8.239	44.89	1130478.8	344688.0	44.891
2	UNKNOWN	8.839	6.60	127121.7	50711.9	6.605
4	UNKNOWN	15.346	5.45	76039.3	41831.0	5.448
3	UNKNOWN	25.745	43.06	415169.0	330597.1	43.058
Total			100.00	1748808.8	767828.0	100.000

Figure S69. HPLC profile of racemic 8c

# Chromatogram : DKN-20%-ADH-Ph-Azide-E-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 12/16/2013 2:57:42 PM  
Processed : 12/17/2013 9:59:02 AM  
Printed : 12/17/2013 10:14:54 AM



## Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
2	UNKNOWN	8.173	97.51	1403387.8	408047.1	97.515
3	UNKNOWN	9.146	0.86	12744.2	3615.5	0.864
1	UNKNOWN	26.051	1.62	6216.0	6784.2	1.621
Total			100.00	1422348.0	418446.8	100.000

Figure S70. HPLC profile of enantioenriched 8c

Current Data Parameters  
NAME INN-DKN-666-1H  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20140110  
Time\_ 19.40  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10000.000 Hz  
FIDRES 0.152588 Hz  
AQ 3.2767999 sec  
RG 197.27  
DW 50.000 usec  
DE 6.50 usec  
TE 297.5 K  
D1 1.00000000 sec  
TDO 1

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
SFO1 500.1330885 MHz  
NUC1 1H  
P1 13.00 usec  
PLW1 13.00000000 W

F2 - Processing parameters  
SI 65536  
SP 500.1300119 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

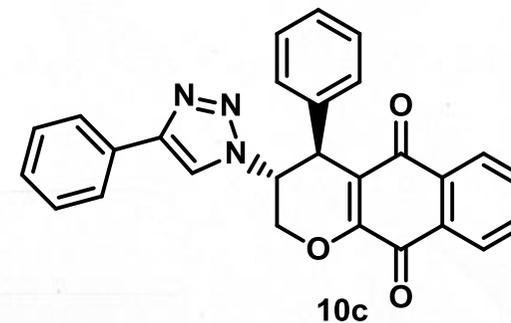
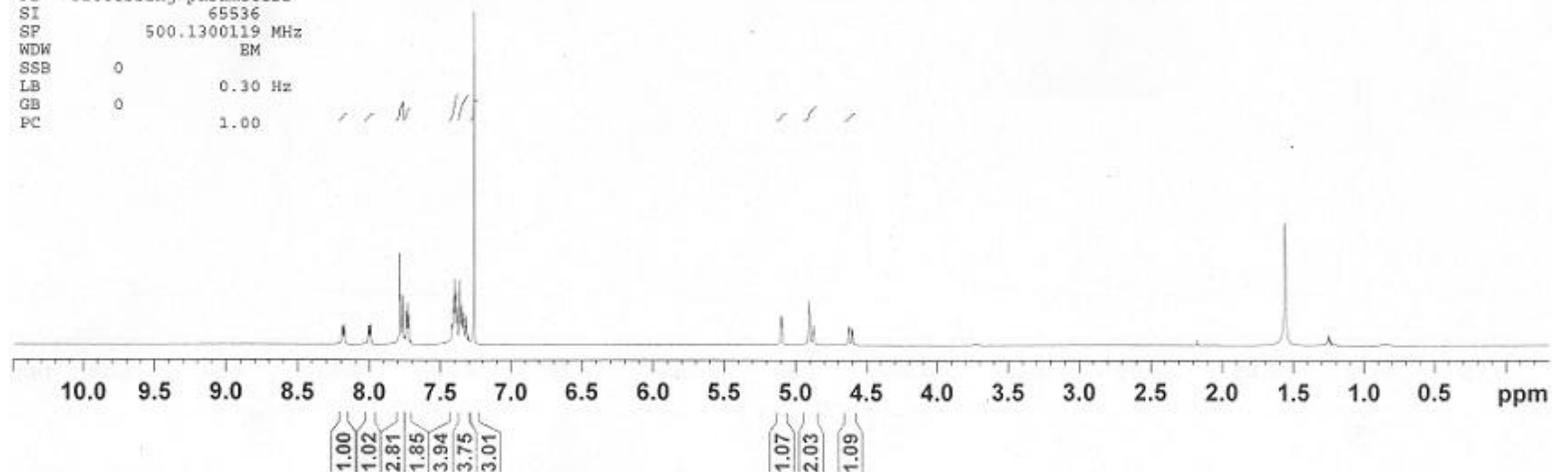


Figure S71. <sup>1</sup>H NMR Spectrum of 10c

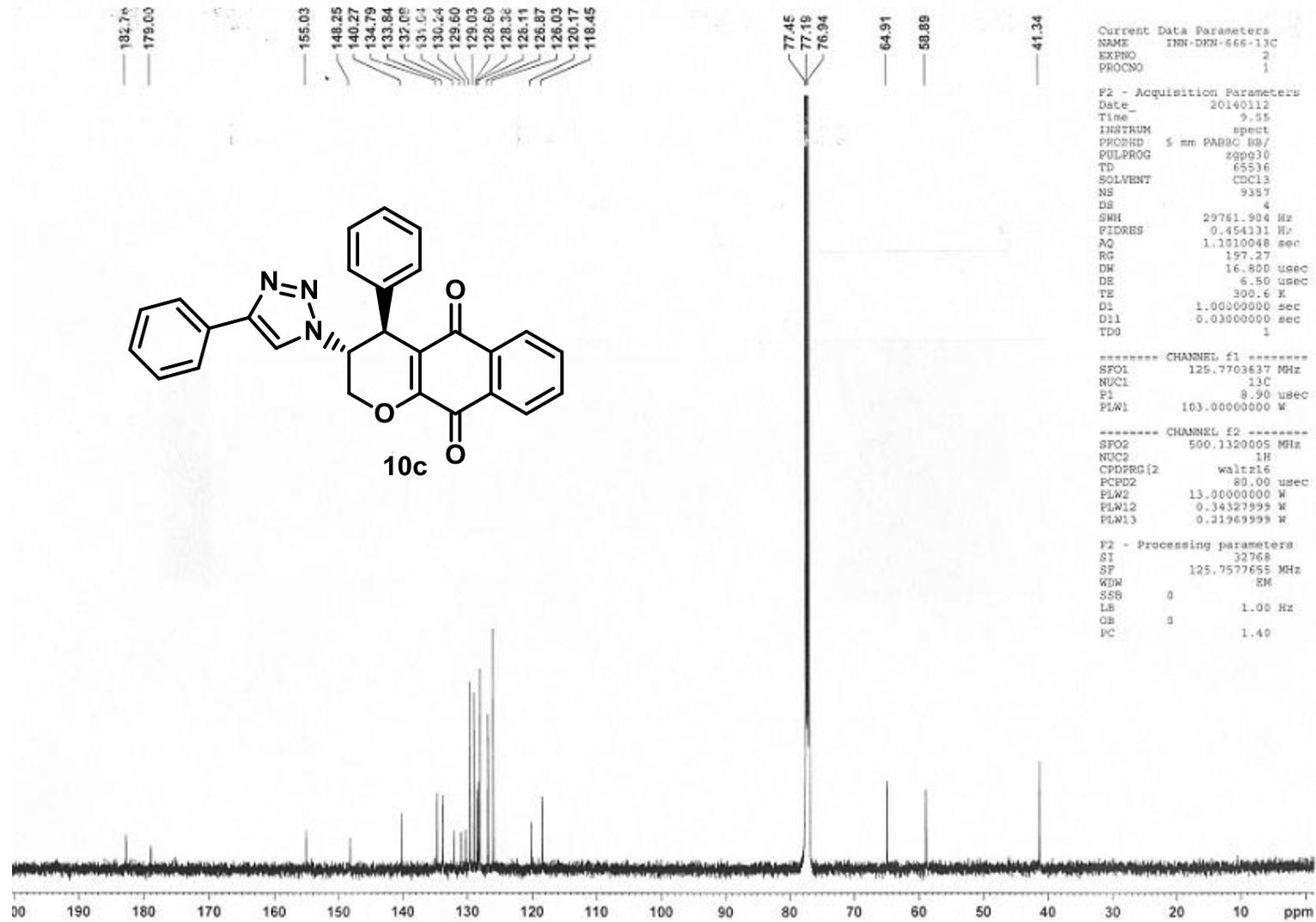
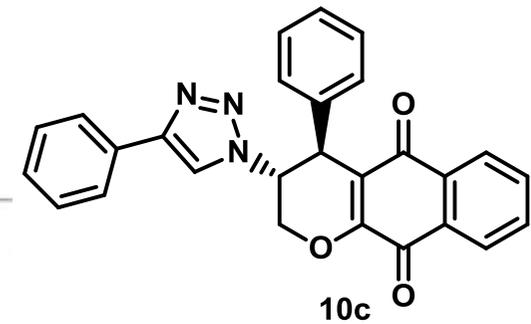
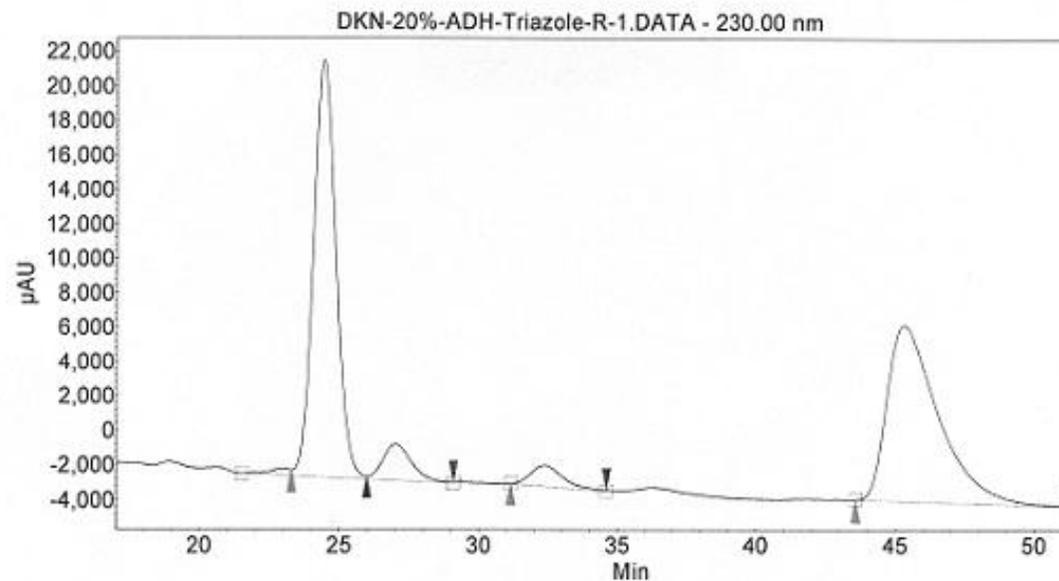


Figure S72.  $^{13}\text{C}$  NMR Spectrum of 10c

### Chromatogram : DKN-20%-ADH-Triazole-R-1\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 12/27/2013 4:45:30 PM  
Processed : 12/27/2013 5:40:06 PM  
Printed : 12/27/2013 5:44:27 PM



#### Peak results :

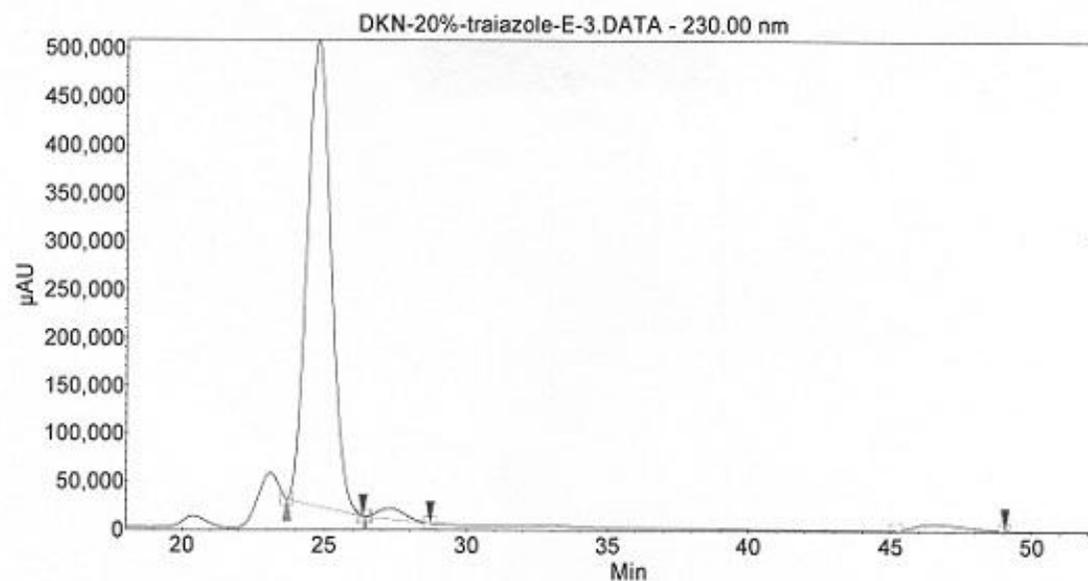
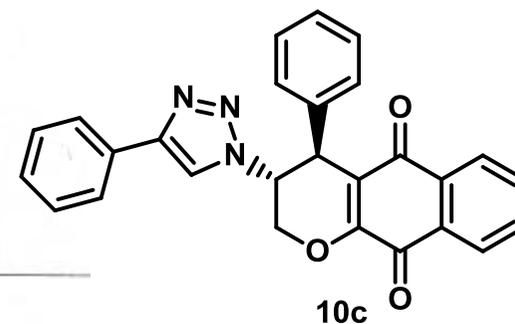
Index	Name	Time [Min]	Quantity [% Area]	Height [µAU]	Area [µAU.Min]	Area % [%]
1	UNKNOWN	24.438	46.74	24180.3	22404.1	46.735
2	UNKNOWN	27.011	4.66	2078.3	2379.7	4.964
3	UNKNOWN	32.398	3.28	1172.0	1573.5	3.282
4	UNKNOWN	45.317	45.02	10196.9	21581.2	45.019
Total			100.00	37627.4	47938.4	100.000

Figure S73. HPLC profile of racemic 10c

### Chromatogram : DKN-20%-traiazole-E-3\_channel4

System : Jasco HPLC  
Method : DKN-20%-1FR-230nm  
User : User1

Acquired : 1/15/2014 11:10:17 AM  
Processed : 1/15/2014 12:08:26 PM  
Printed : 1/15/2014 12:08:44 PM



#### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [μAU]	Area [μAU.Min]	Area % [%]
1	UNKNOWN	24.758	95.15	484062.7	468622.6	95.151
3	UNKNOWN	27.318	2.31	10956.3	11386.7	2.312
2	UNKNOWN	46.503	2.54	6647.9	12492.4	2.537
Total			100.00	501666.9	492503.7	100.000

Figure S74. HPLC profile of enantioenriched 10c