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Supporting Information

Enantioselective organocatalytic vinylogous aldol−cyclization cascade reaction of 3-alkylidene oxindoles with *o*-quinones

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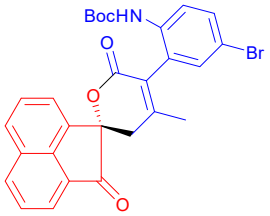
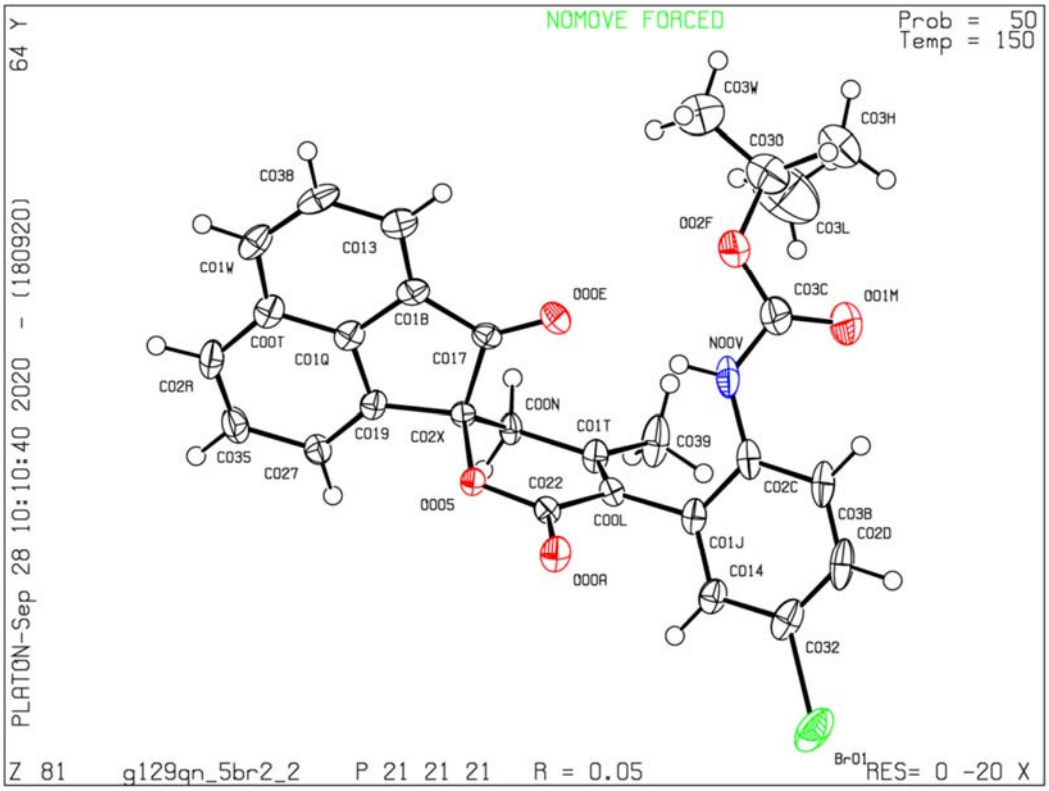
1. Absolute Configuration and X-Ray Analysis Data

Table 1. Crystal data and structure refinement for 5d.

Identification code	**5d**	
Empirical formula	C28 H25 Br N O5	
Formula weight	535.40	
Temperature	150.15 K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	P2**1**2**1**2**1**	
Unit cell dimensions	a = 7.2170(7) Å	a= 90°.
	b = 15.0680(14) Å	b= 90°.
	c = 23.762(2) Å	g = 90°.
Volume	2584.0(4) $Å^3$	
Z	4	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	1.628 mm^{-1}	
F(000)	1100	
Crystal size	0.49 x 0.32 x 0.24 mm^3	
Theta range for data collection	2.905 to 26.411°.	
Index ranges	-9<=h<=9, -18<=k<=18, -29<=l<=29	
Reflections collected	40741	
Independent reflections	5270 [R(int) = 0.0539]	
Completeness to theta = 25.243°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5270 / 0 / 320	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1421	
R indices (all data)	R1 = 0.0593, wR2 = 0.1477	
Absolute structure parameter	0.048(17)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.108 and -0.596 $e.Å^{-3}$	


BocHN
O
Br
O
O

5d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Temp = 150
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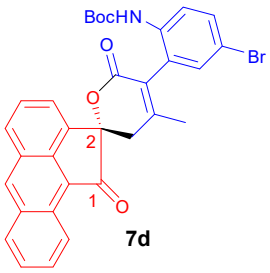
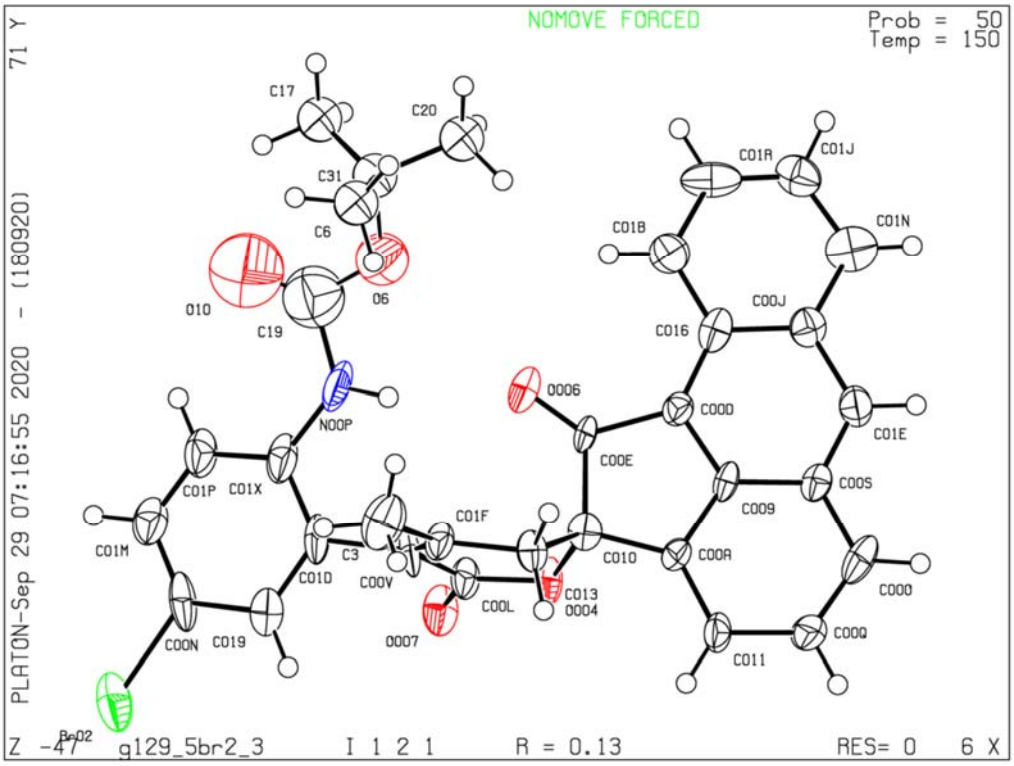
C038
C013
C03L
O02F
C01W
C03C
O01M
O00E
C01B
C00T
C01Q
C017
N00V
C02R
C00N
C01T
C039
C019
C02X
C035
C027
C02C
C022
O005
C03B
C02D
C00L
C01J
O00A
C014
C032
Br01
Z 81
g129qn_5br2_2
P 21 21 21
R = 0.05
RES= 0 -20 X

Table 1. Crystal data and structure refinement for 7d

Identification code	**7d**	
Empirical formula	C31 H24 Br N O5	
Formula weight	570.42	
Temperature	150.15 K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	I 1 2 1	
Unit cell dimensions	a = 7.179(2) Å	a= 90°.
	b = 15.131(6) Å	b= 92.737(16)°.
	c = 26.209(11) Å	g = 90°.
Volume	2843.7(18) $Å^3$	
Z	4	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	1.484 mm^{-1}	
F(000)	1168	
Crystal size	0.49 x 0.32 x 0.24 mm^3	
Theta range for data collection	2.909 to 26.550°.	
Index ranges	-8<=h<=8, -18<=k<=19, -32<=l<=32	
Reflections collected	22836	
Independent reflections	5867 [R(int) = 0.1031]	
Completeness to theta = 25.243°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5867 / 19 / 329	
Goodness-of-fit on F^2	1.409	
Final R indices [I>2sigma(I)]	R1 = 0.1349, wR2 = 0.3526	
R indices (all data)	R1 = 0.1777, wR2 = 0.3872	
Absolute structure parameter	0.09(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.213 and -1.513 e.$Å^{-3}$	


BocHN
O
Br
O
2
1
O

7d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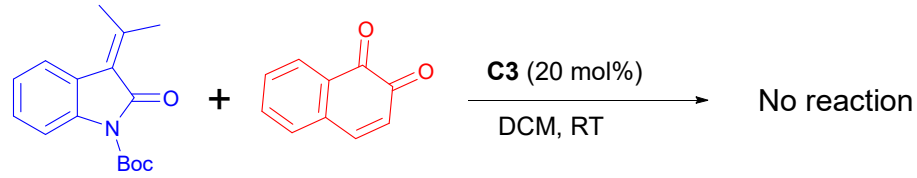
C20
C31
C6
O10
O6
C19
NOOP
C01P
C01X
C01M
C01D
C3
C01F
C00V
C00L
O007
C013
O004
C00N
C019
O006
C00D
C00E
C010
C00A
C009
C00S
C01E
C01R
C01J
C01B
C01N
C00J
C016
C00O
C00Q
C011
Z -47
g129_5br2_3
I 1 2 1
R = 0.13
RES= 0
6 X

2. Unsuccessful substrates



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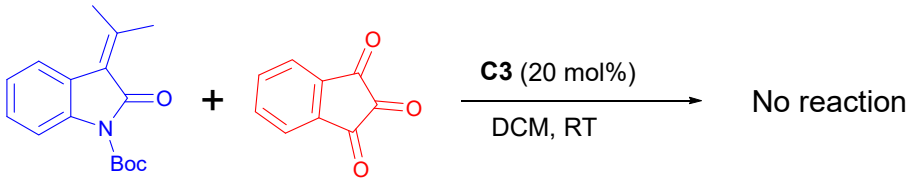
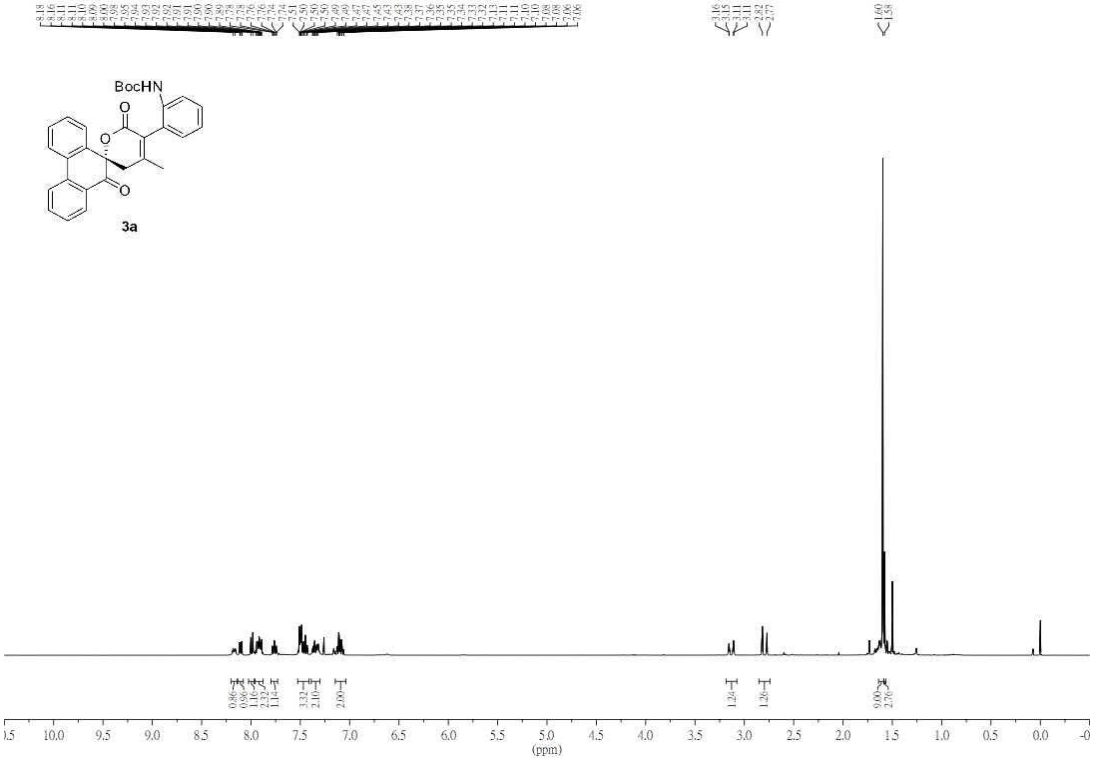
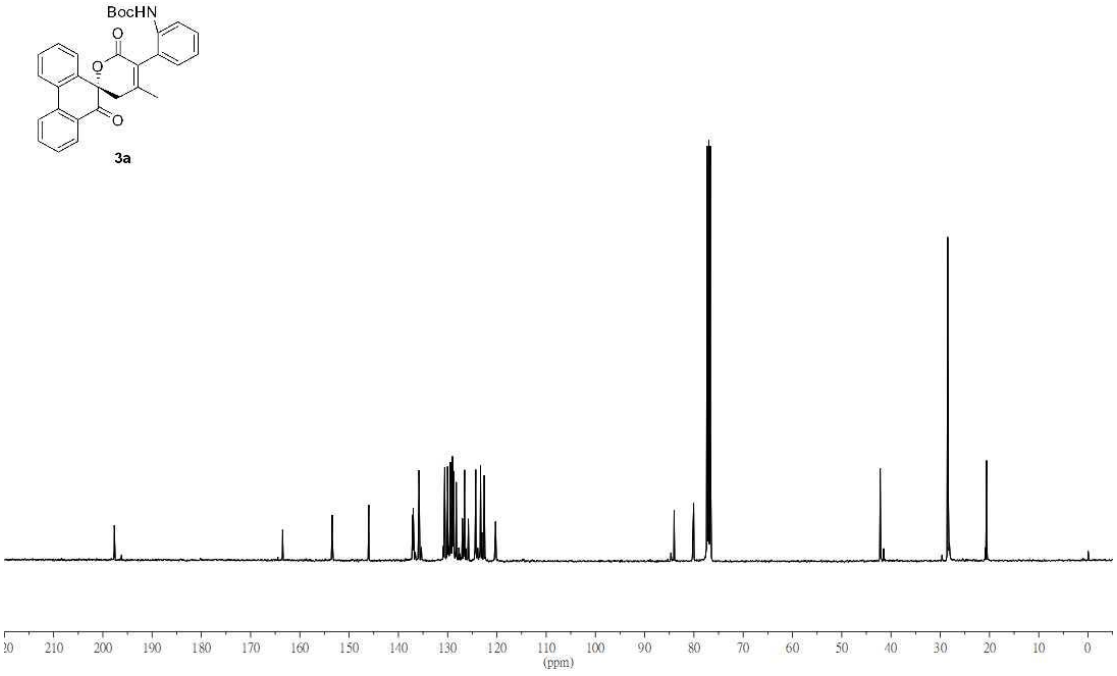
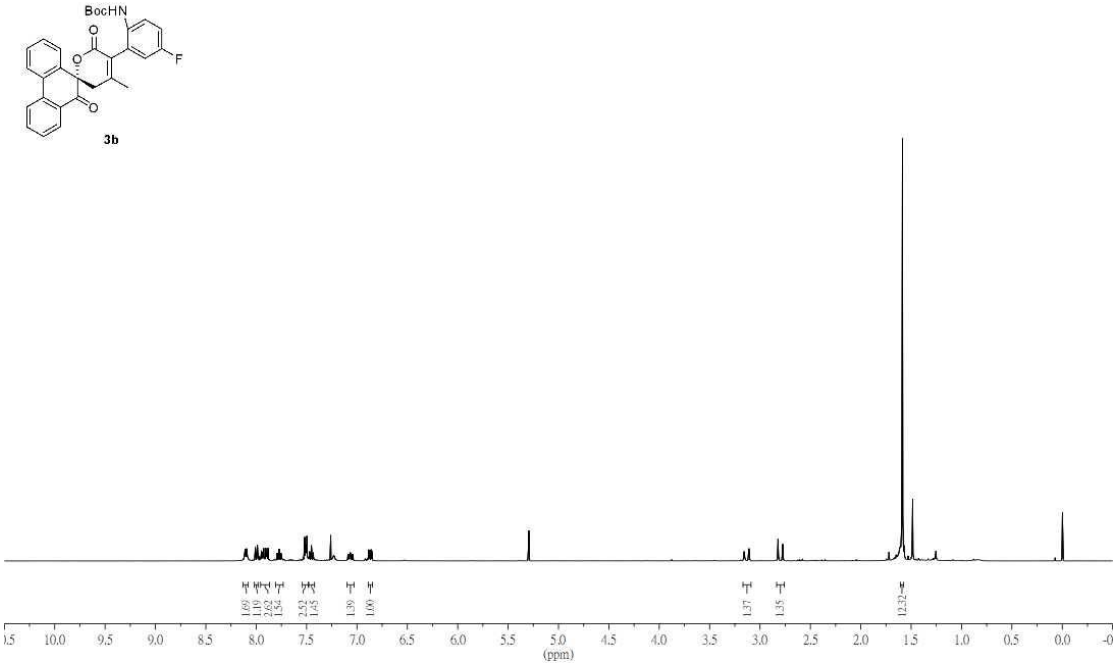


1a

3. Copies of NMR Spectra of Products 3, 5 and 7



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F
O
O
O
3b
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1.10
2.03
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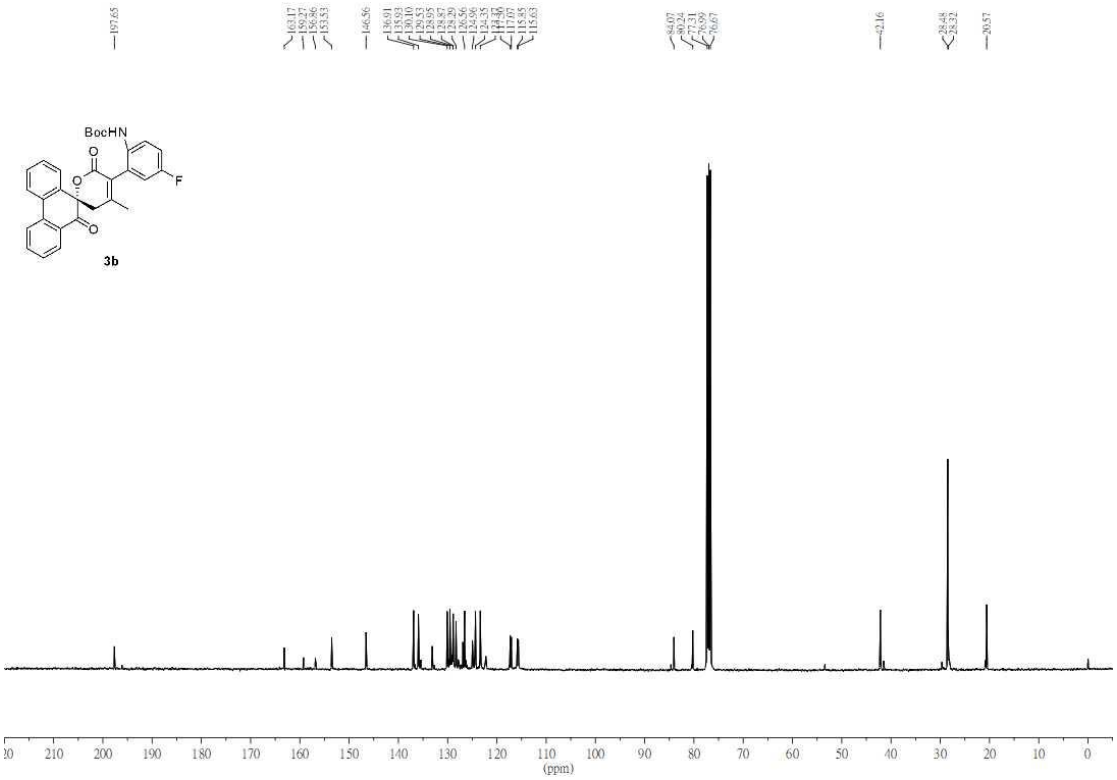
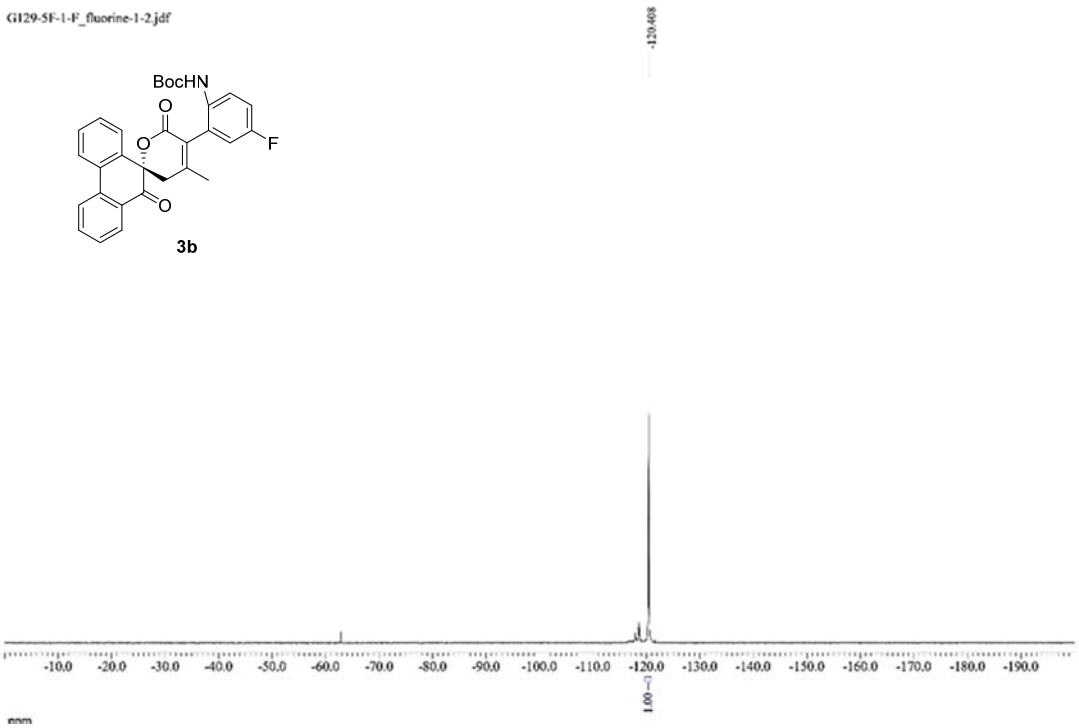
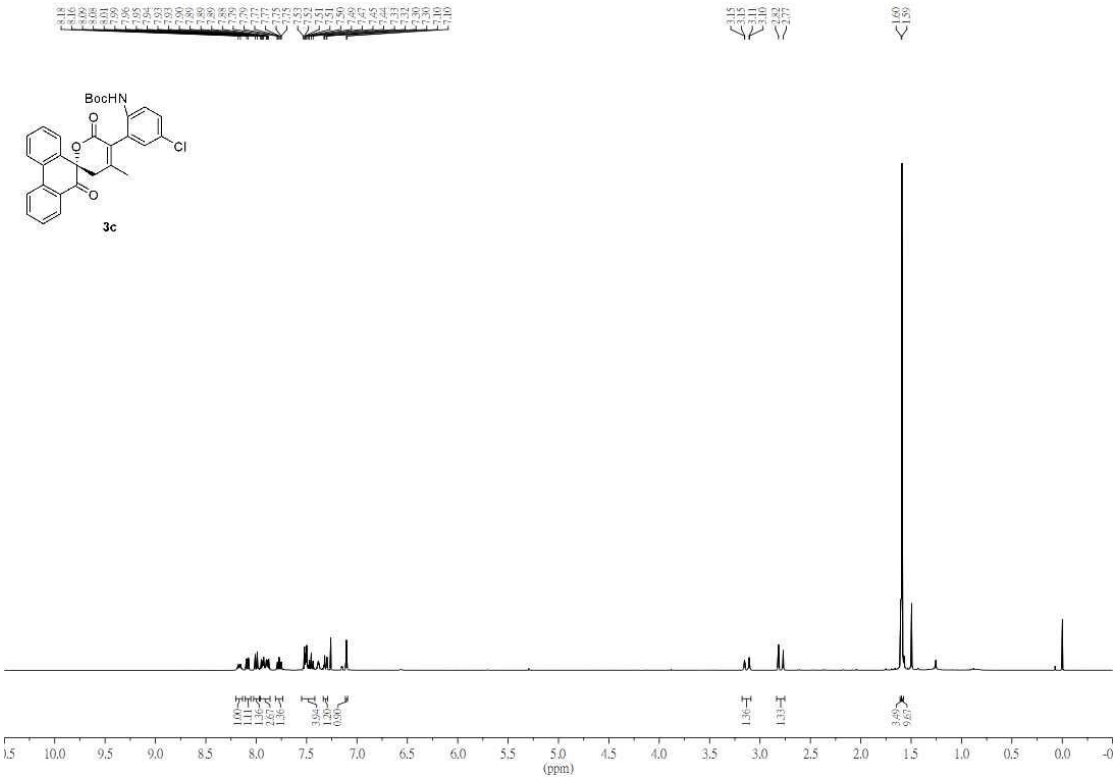
2.52
1.45
1.39
1.00
1.37
1.35
12.32
(ppm)


BocHN
F
O
O
O
3b
(ppm)

G129-5F-1-F_fluorine-1-2.jdf

3b

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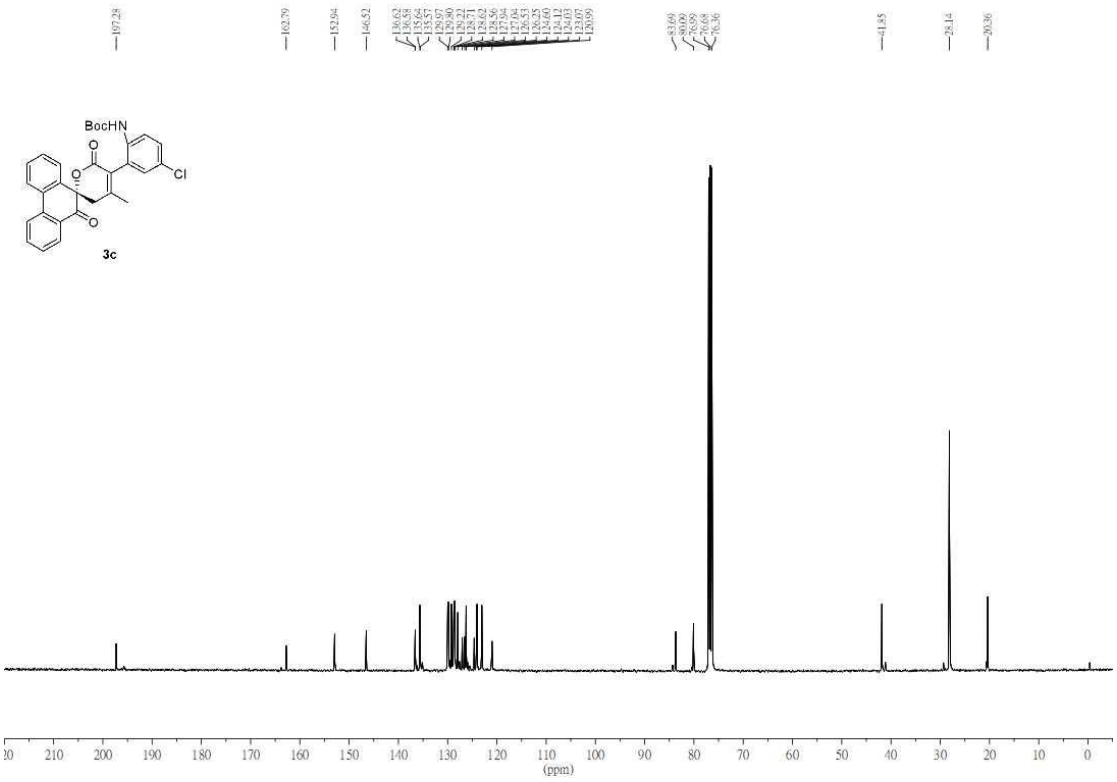
(ppm)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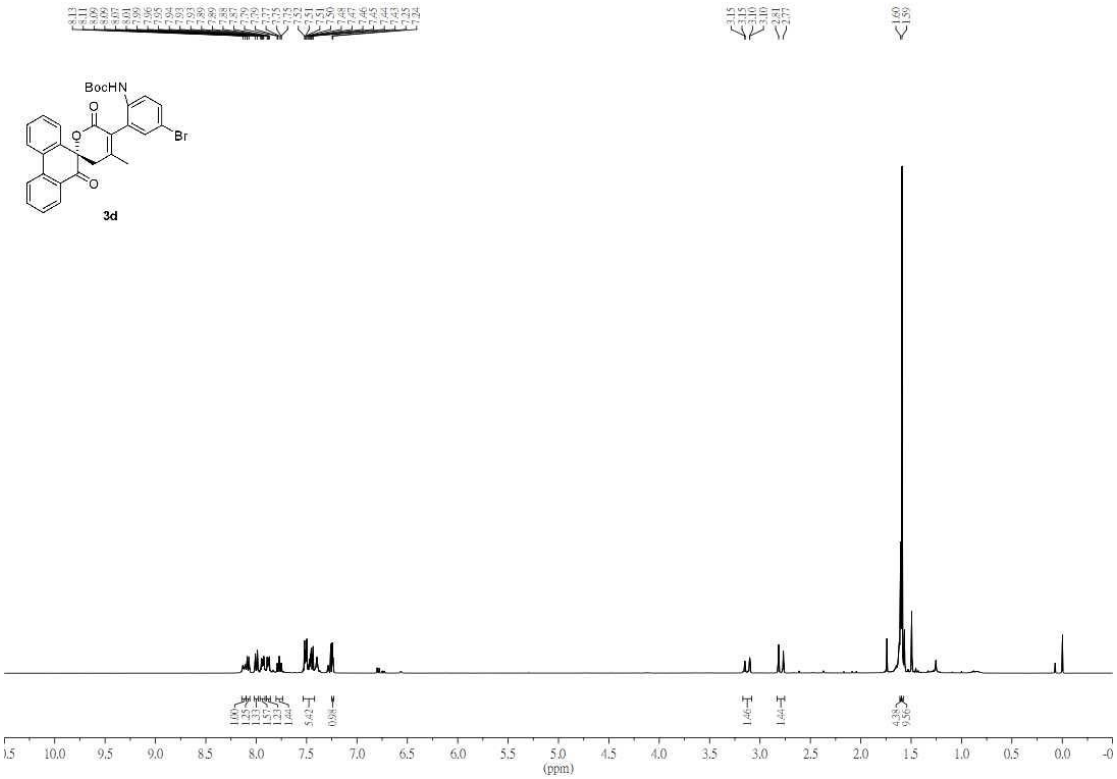
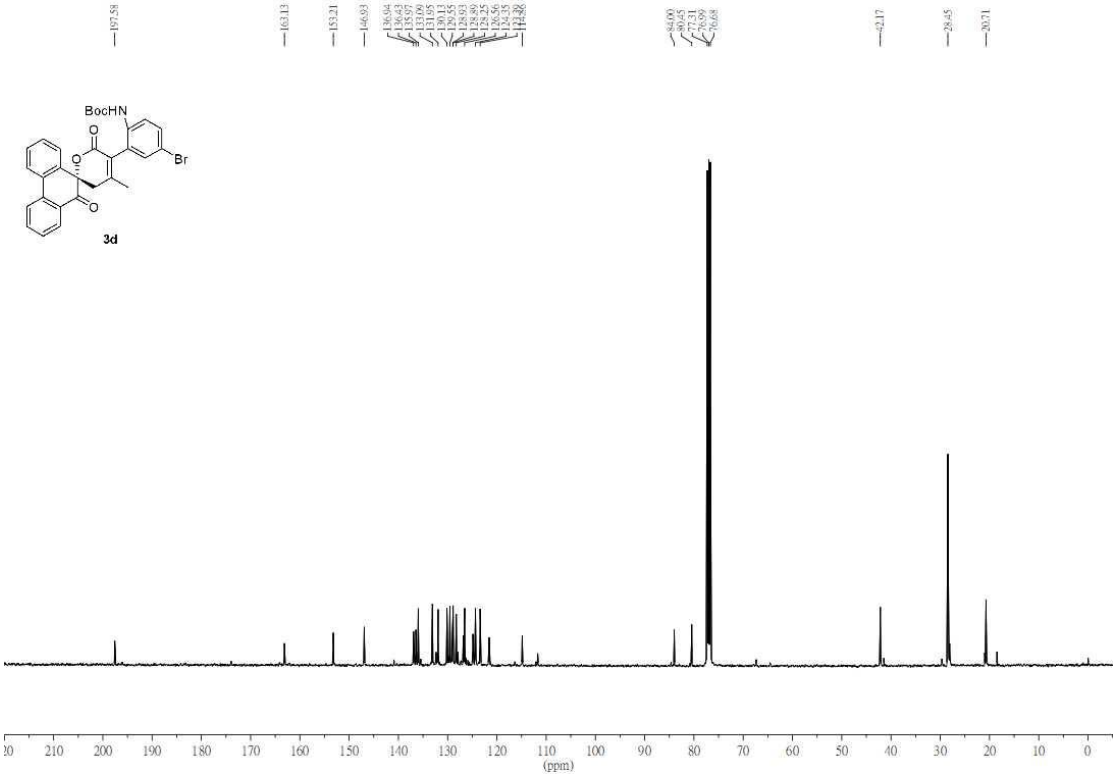
O
3c
(ppm)


BocHN
Br
3d
(ppm)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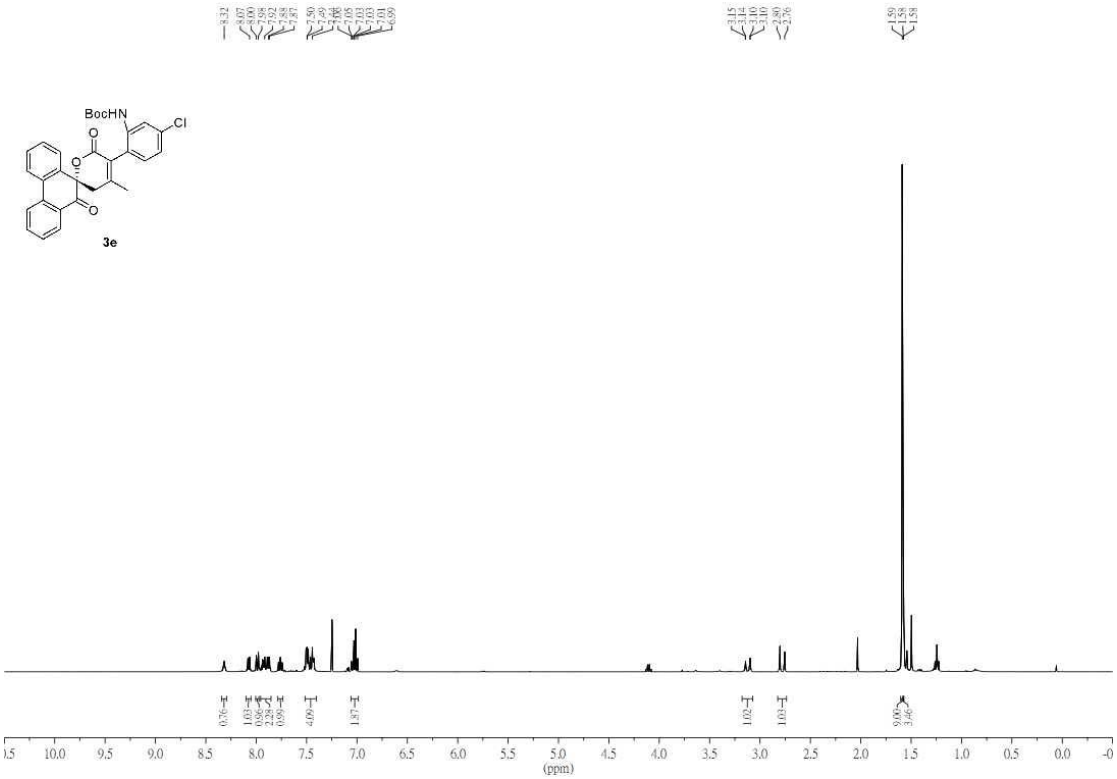
Br
3d
(ppm)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Cl
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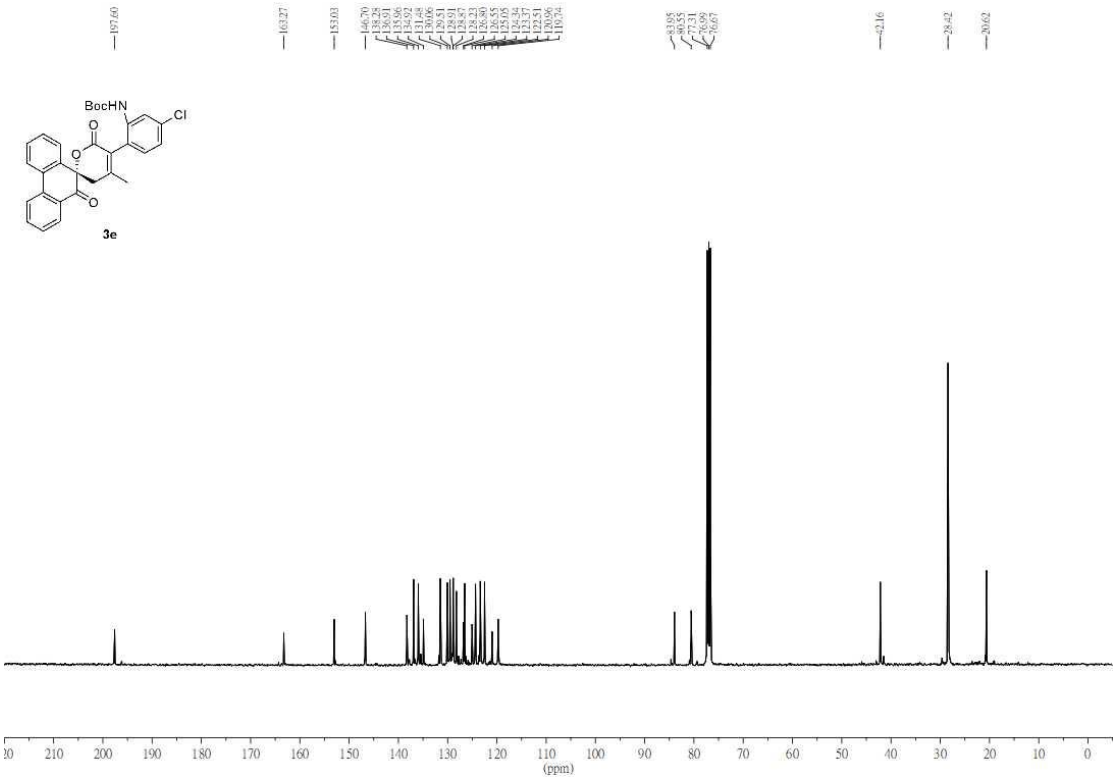
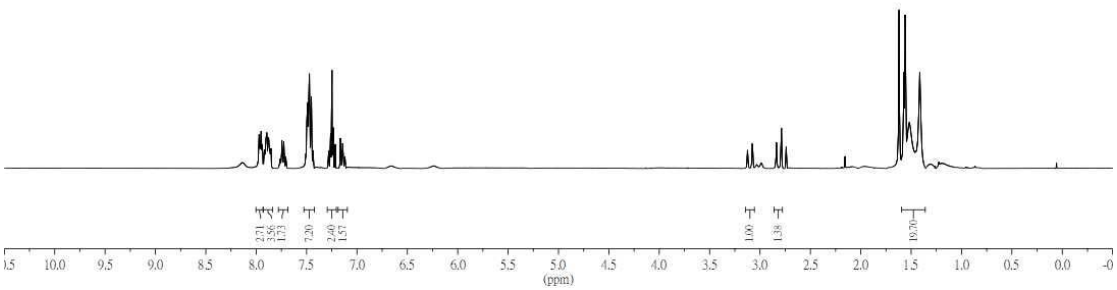
O
O
3e
(ppm)


BocHN
Cl
O
O
O
3e
(ppm)

BocHN
Cl
O
O
O
O

3f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1.57
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1.38
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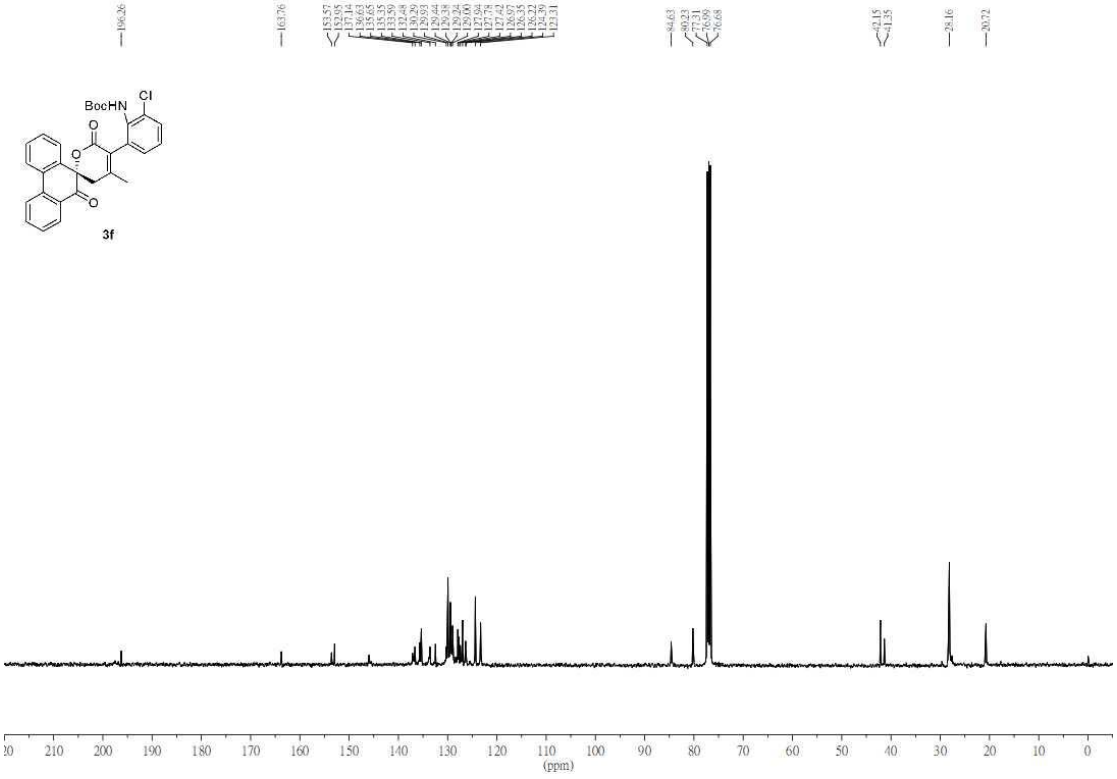
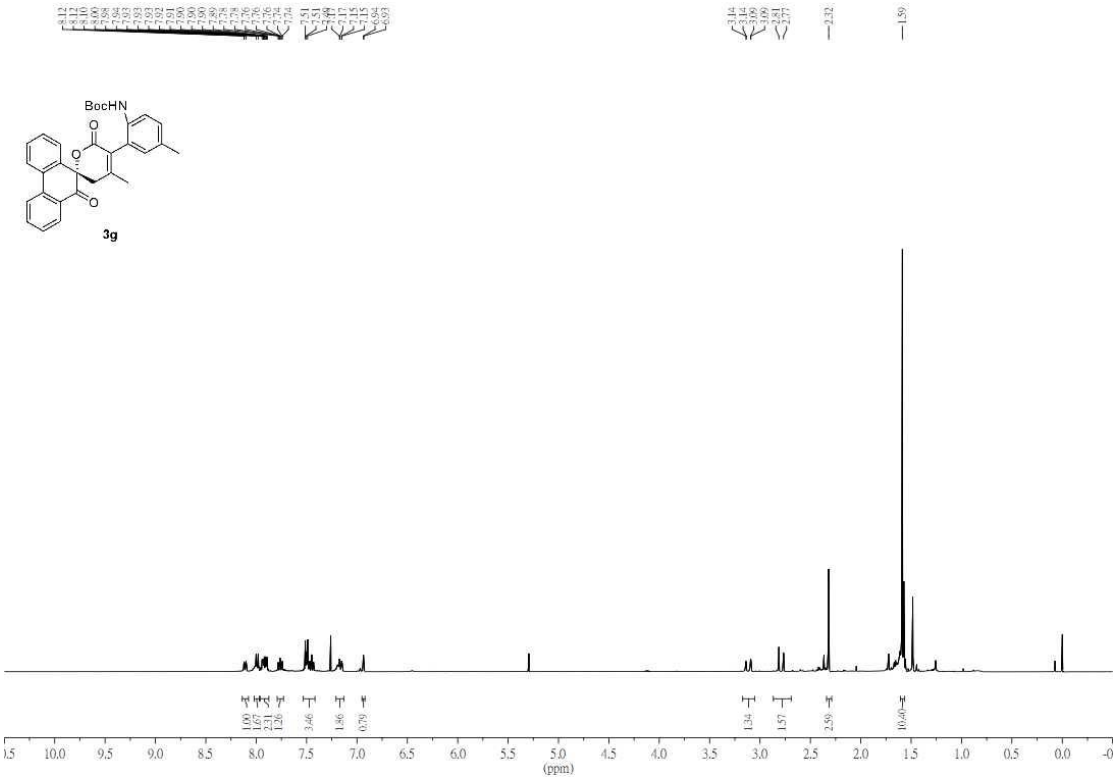
(ppm)



BocHN
Cl
O
O
O
O

3f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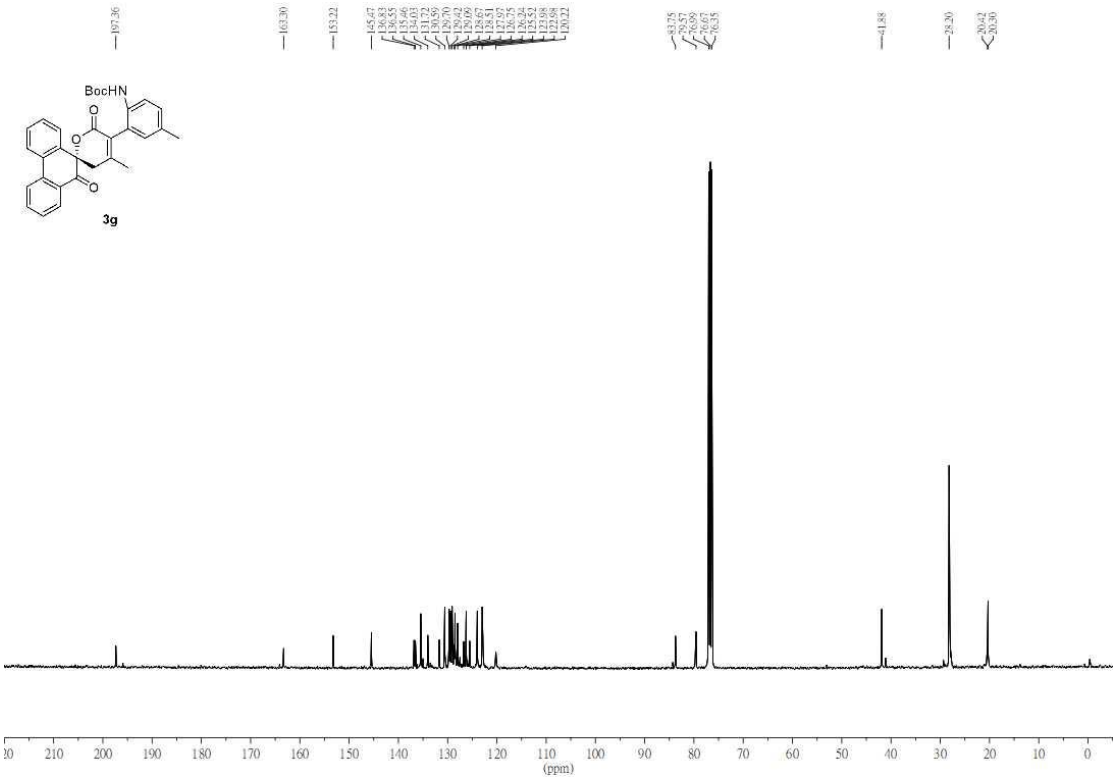
3g
(ppm)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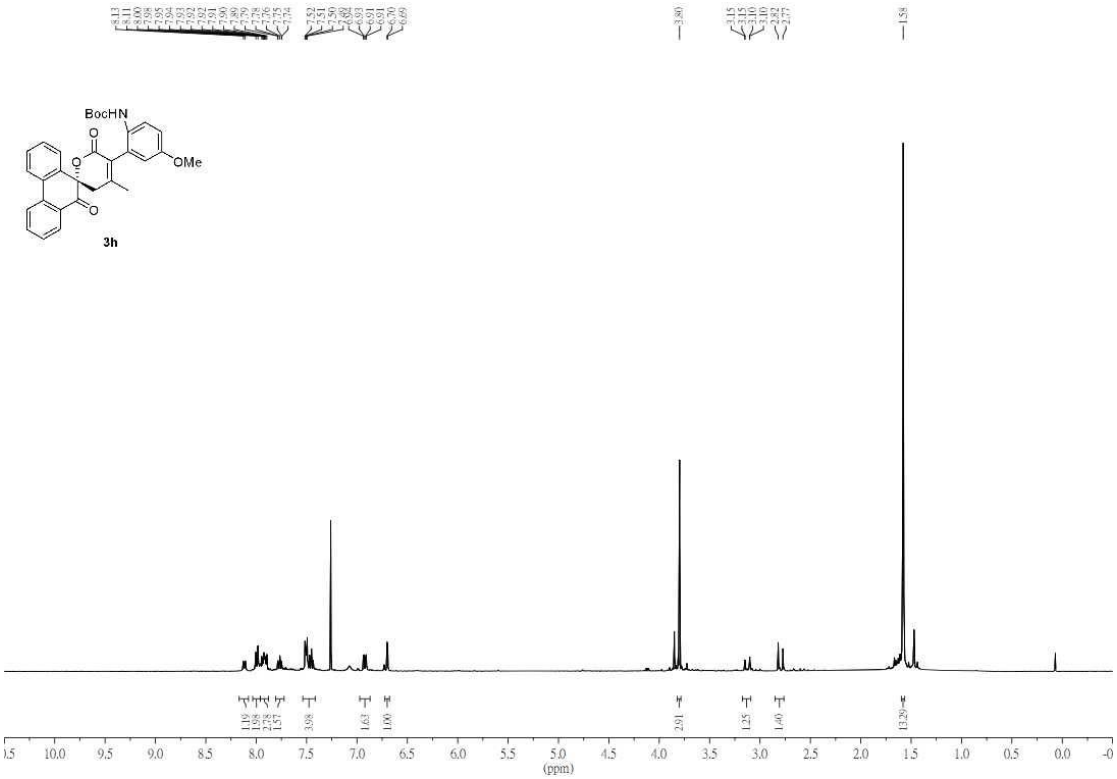
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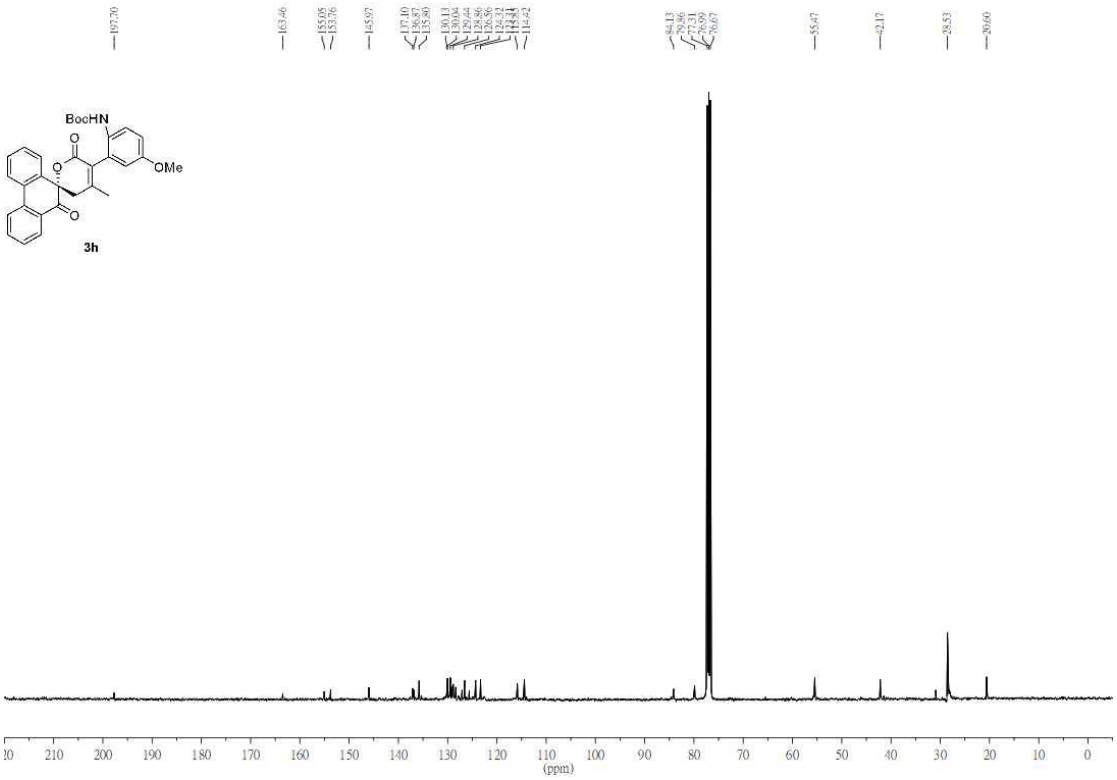
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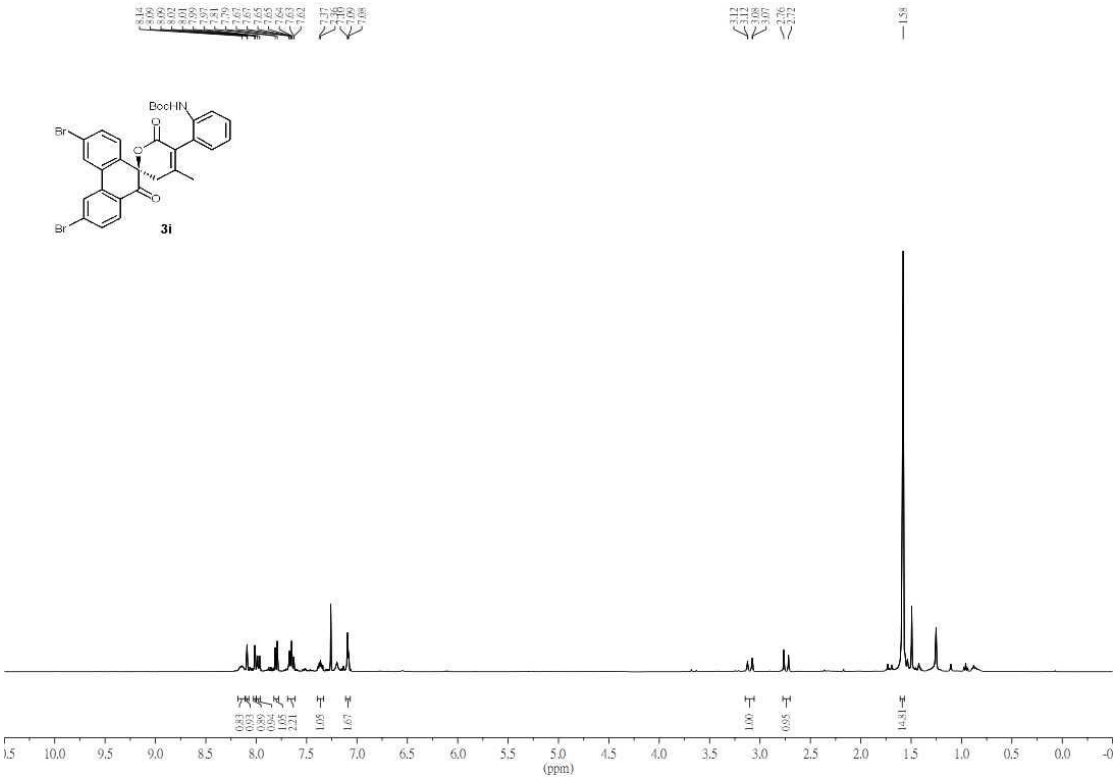
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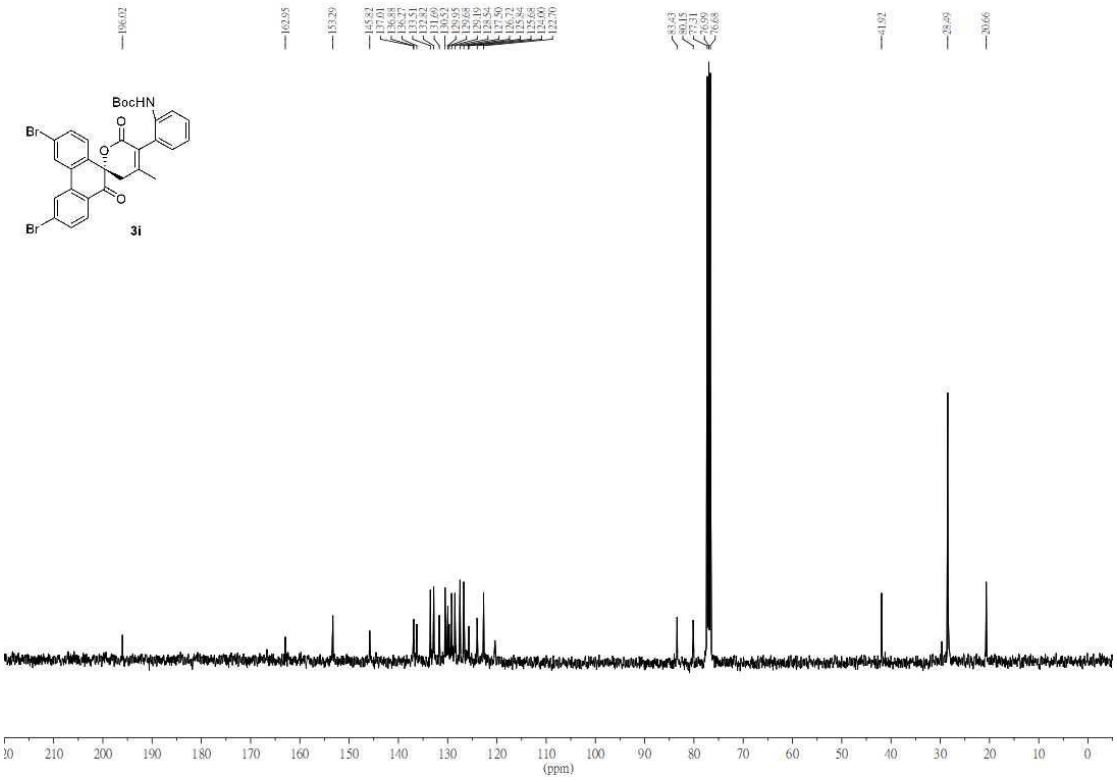
Br
O
O
3i
(ppm)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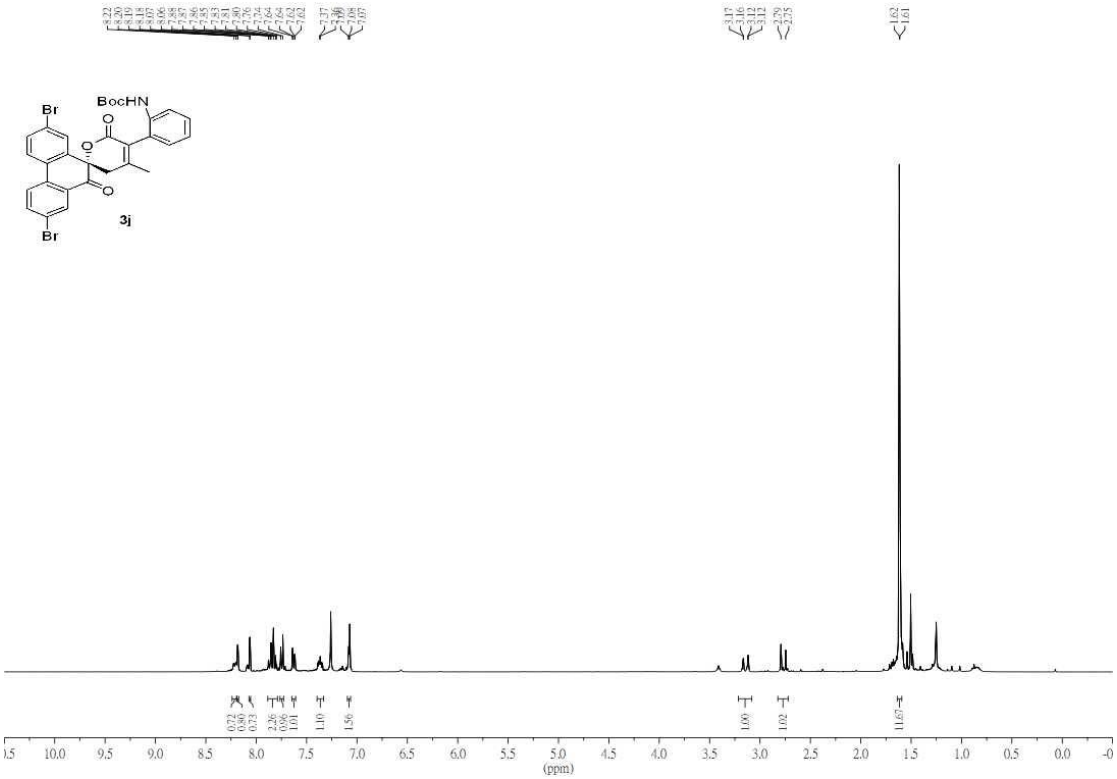
(ppm)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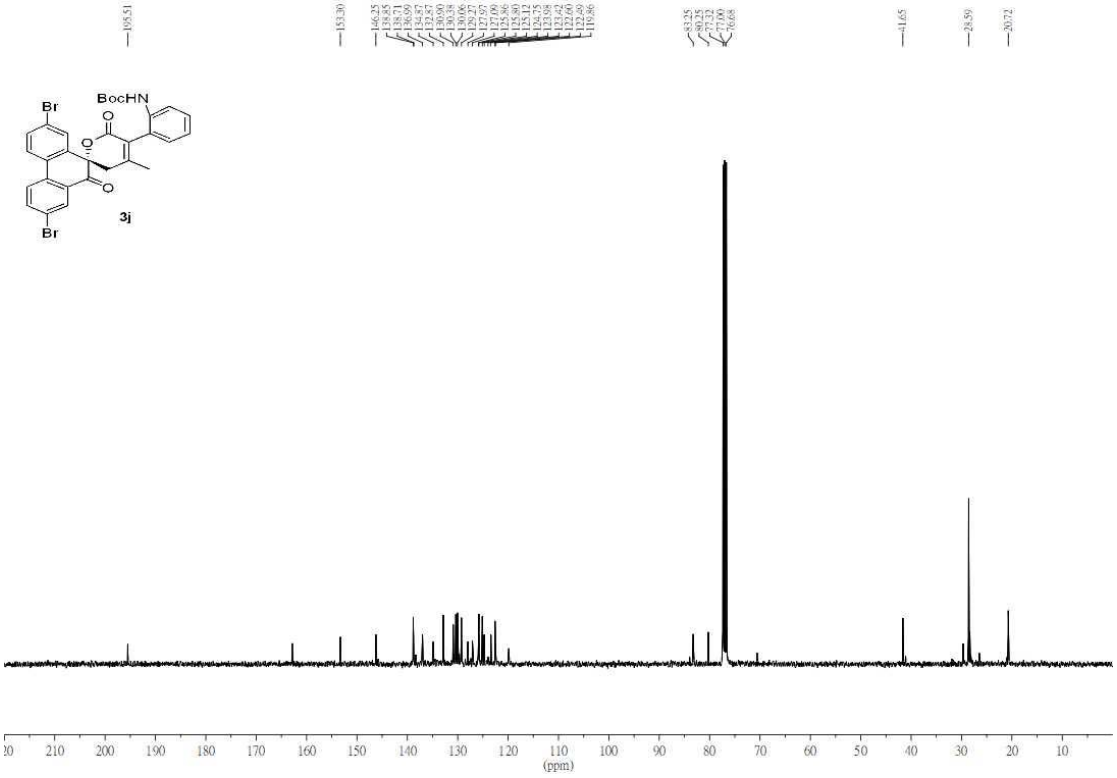
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Br
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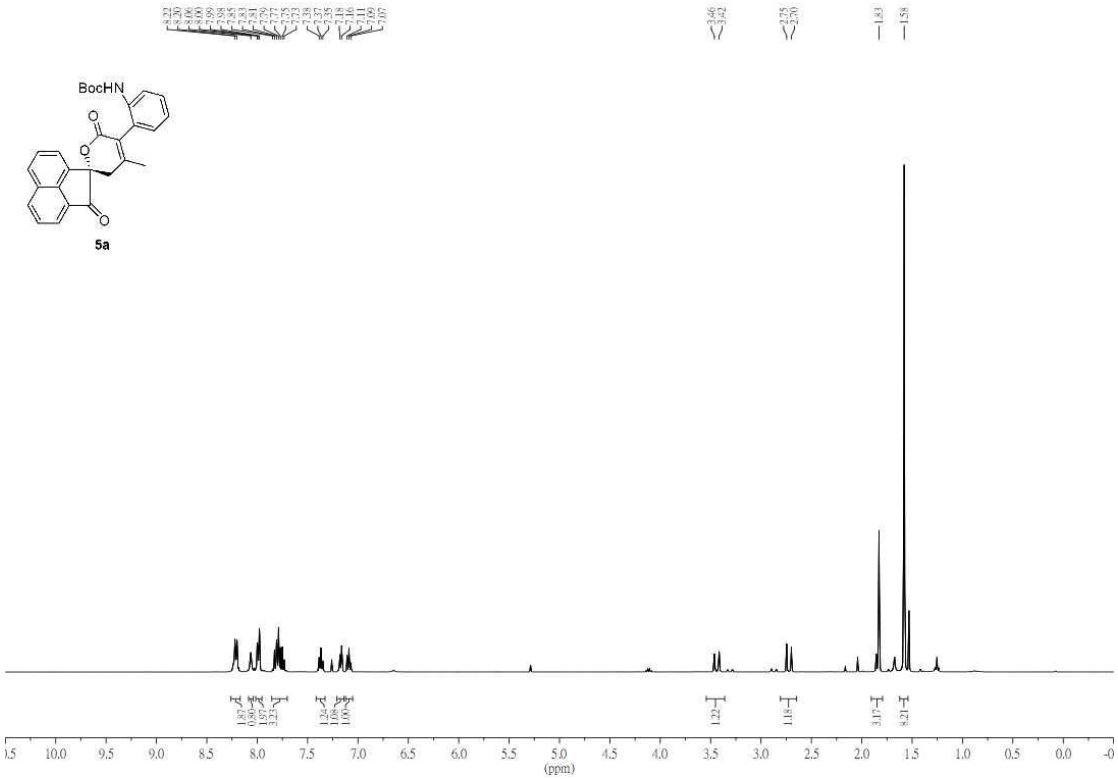
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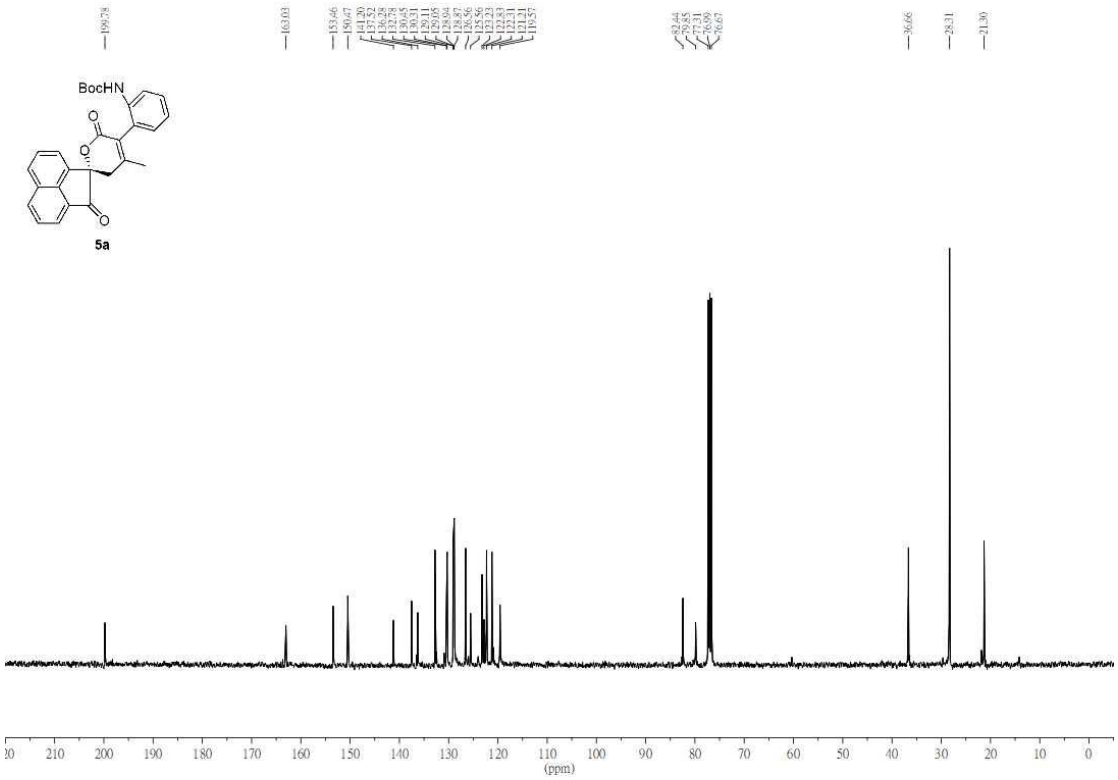
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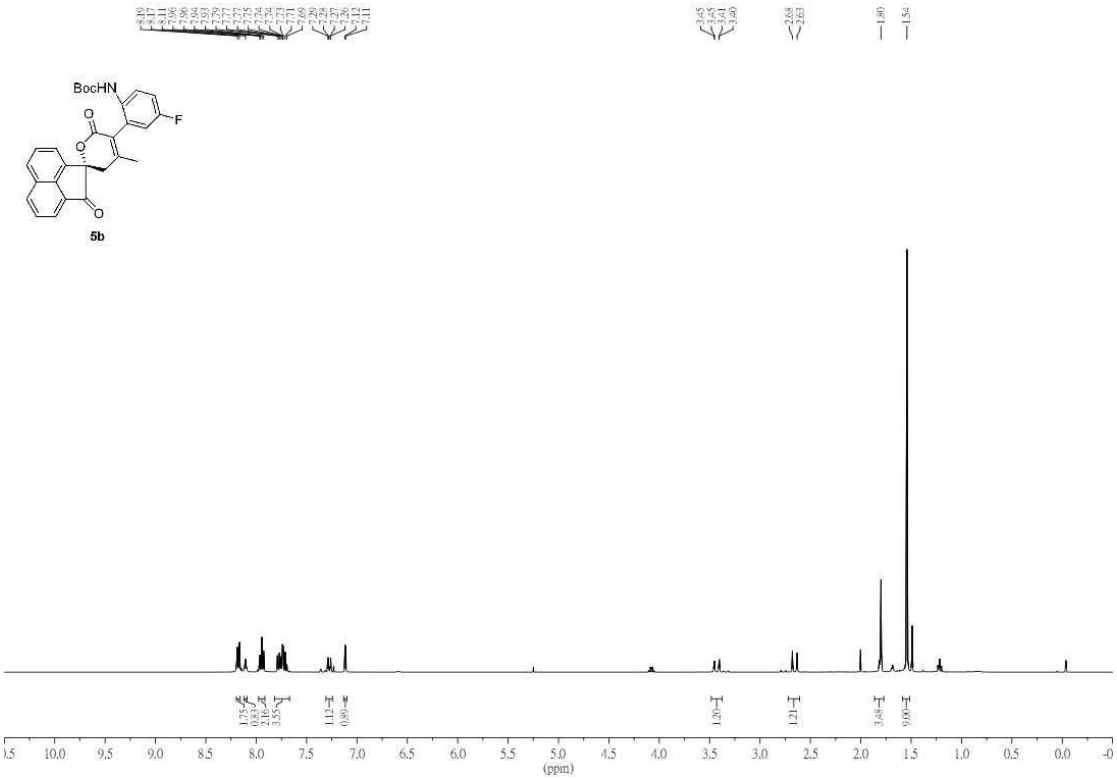
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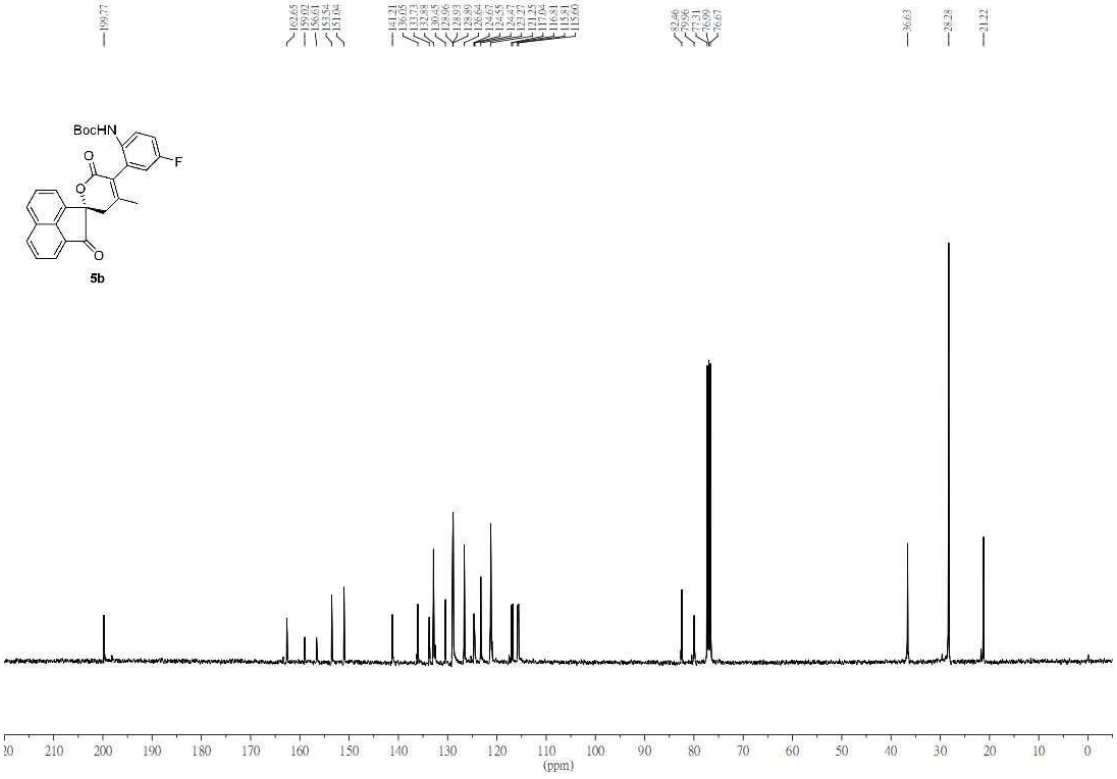
O
O
O
5b
(ppm)


BocHN
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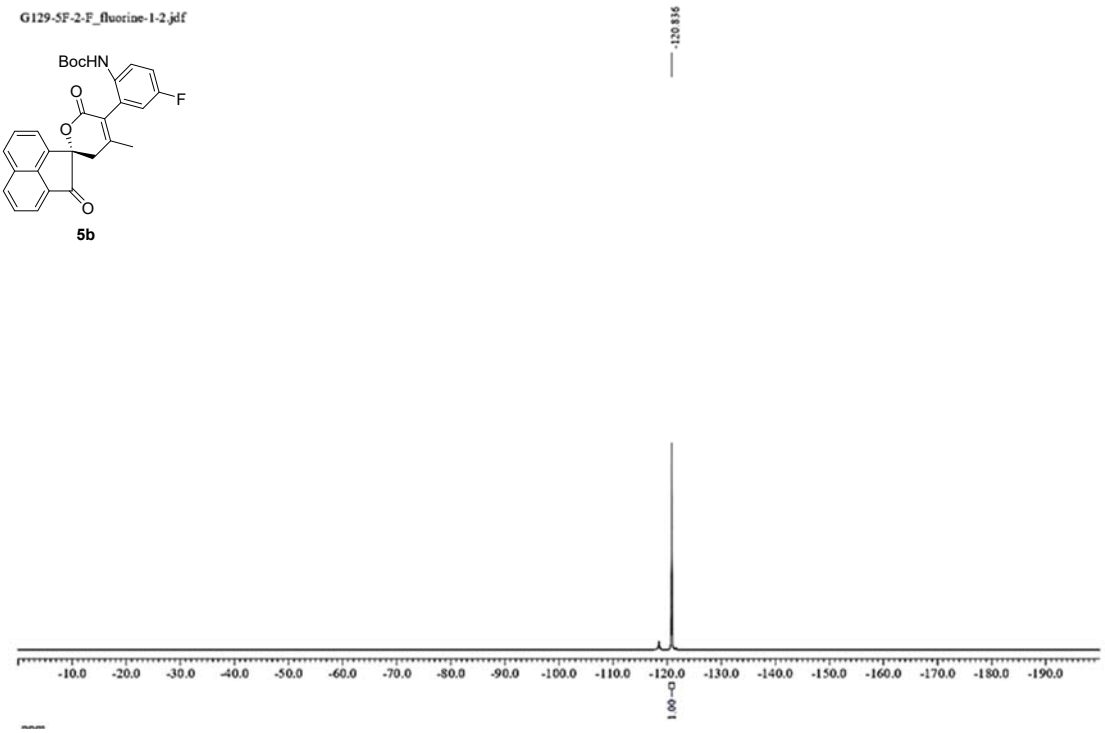
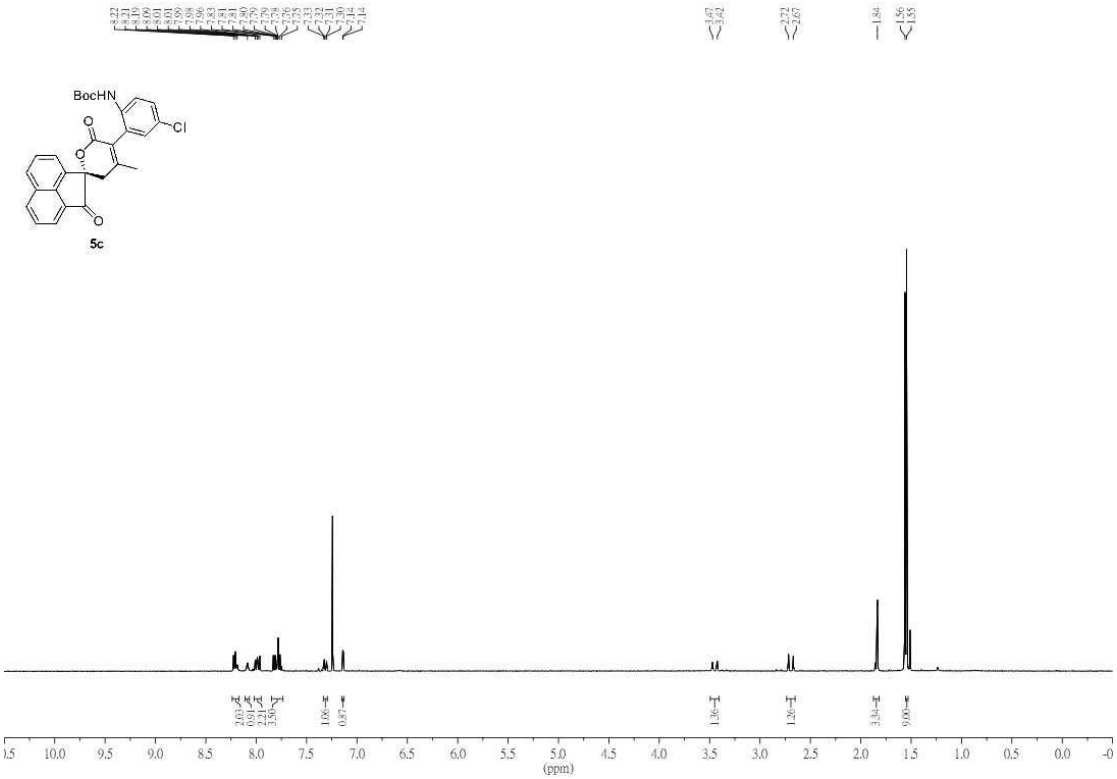
5b
(ppm)

G129-5F-2-F_fluorine-1-2.jdf

5b

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Cl
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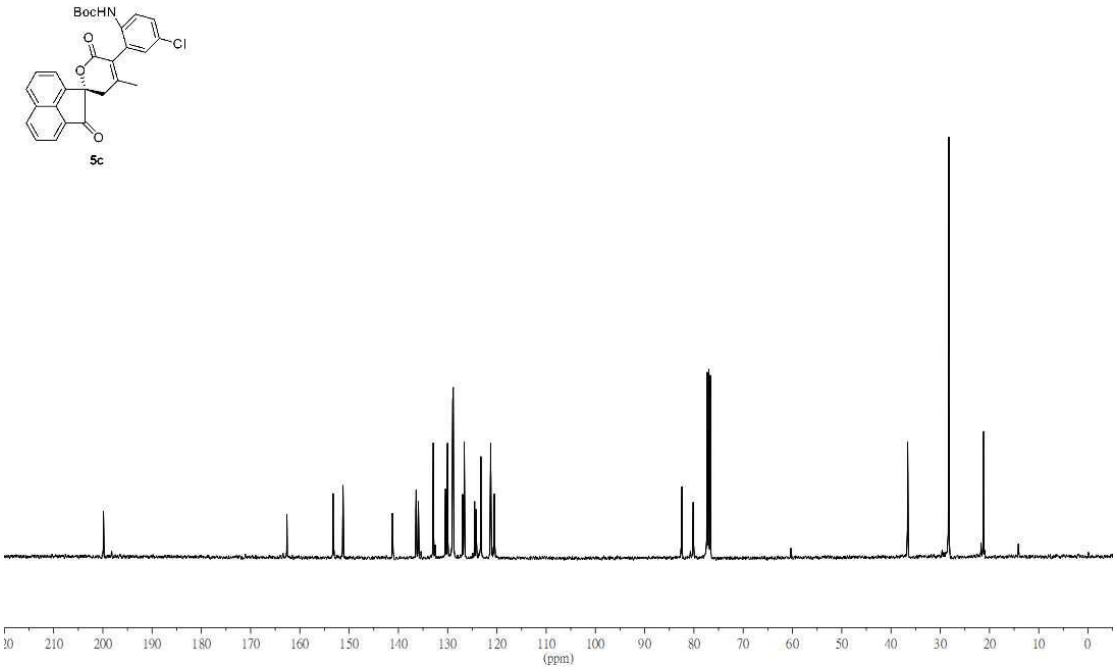
O
O
5c
(ppm)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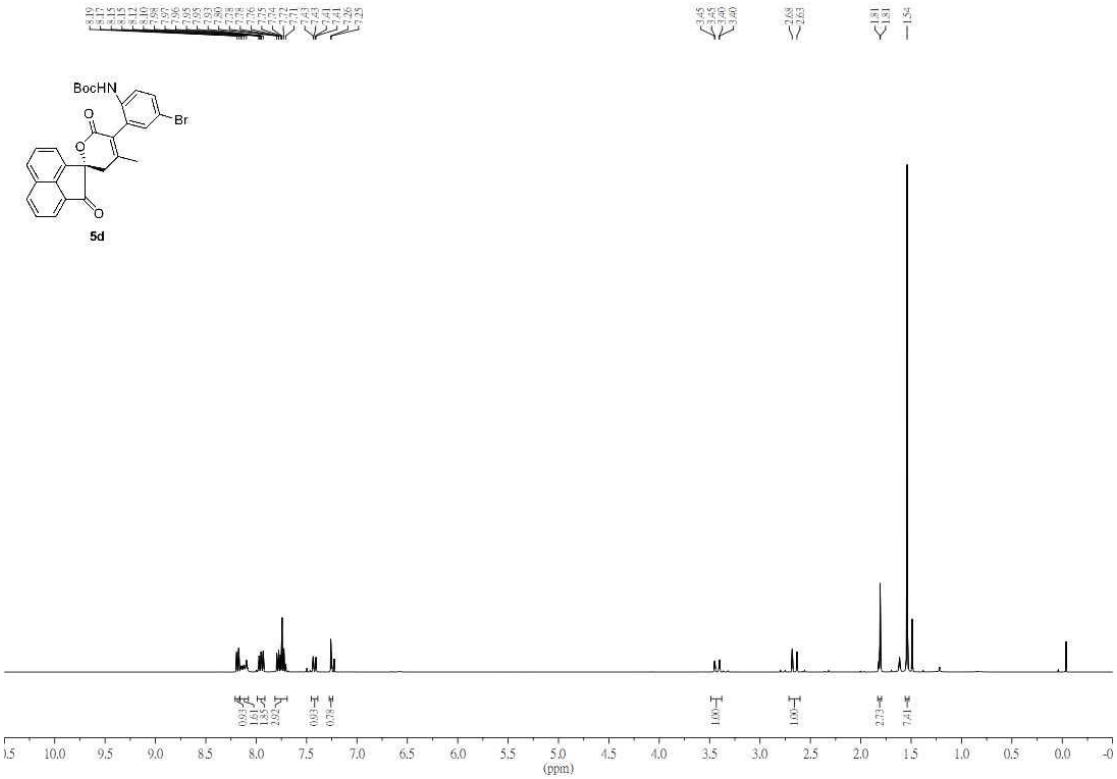
O
O
5c
(ppm)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Br
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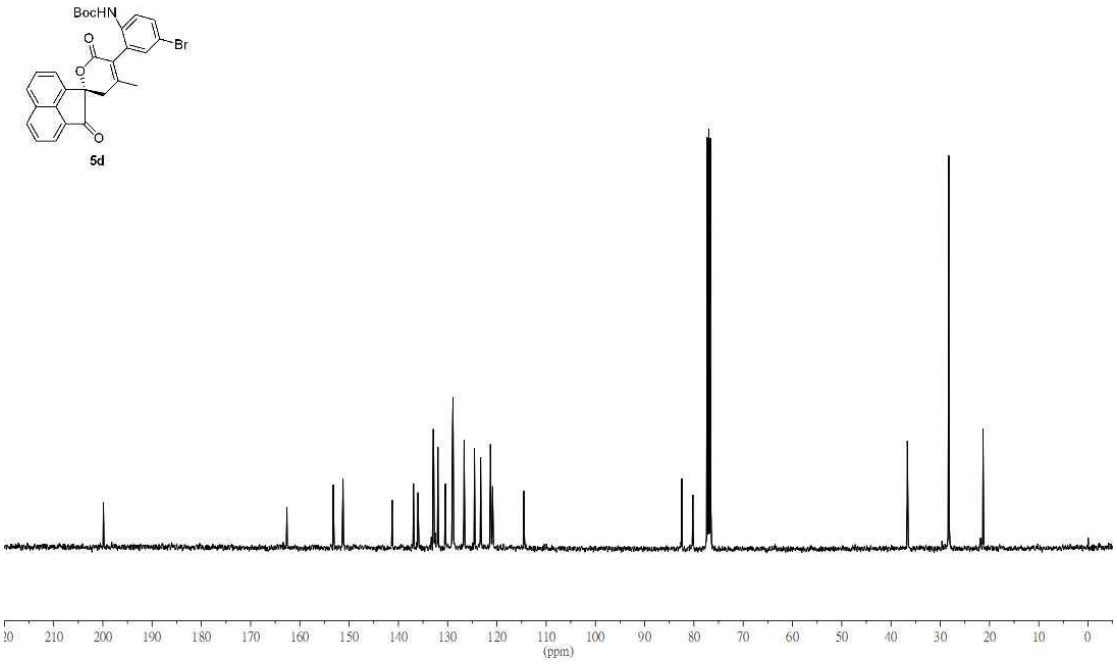
O
O
5d
(ppm)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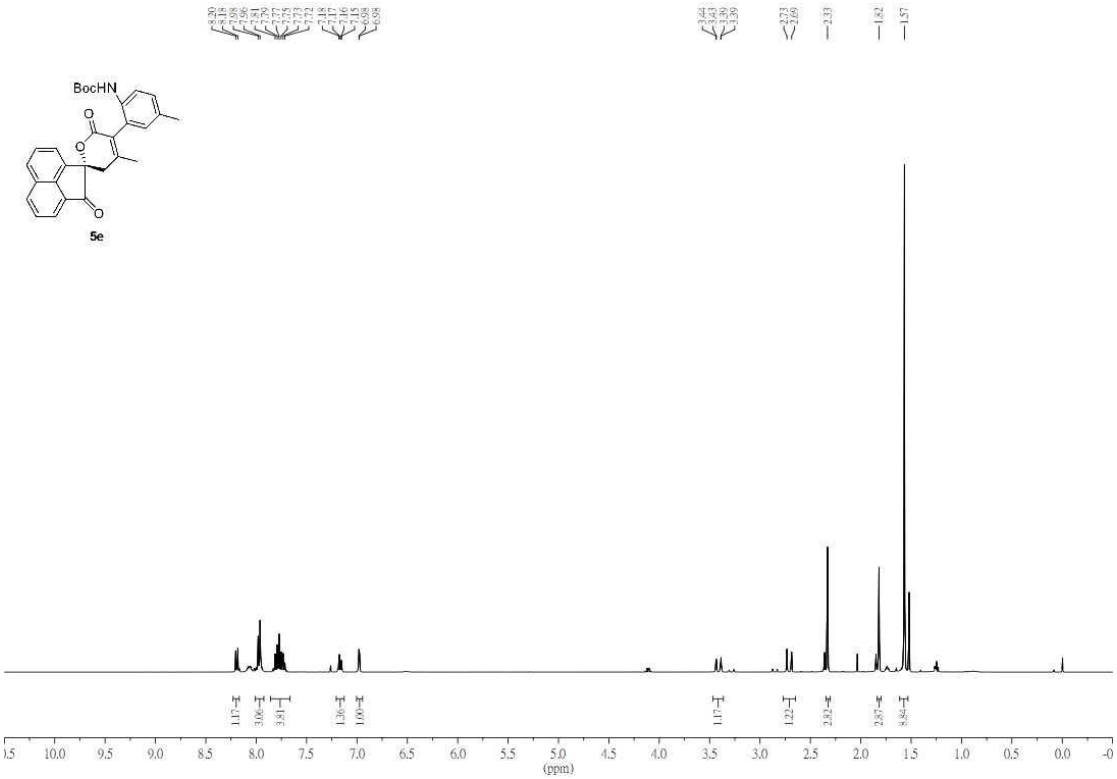
5d
(ppm)


BocHN
O
O
O
5e
8.30
8.18
7.98
7.96
7.79
7.77
7.75
7.73
7.72
7.18
7.17
7.16
7.15
6.98
6.98
3.46
3.43
3.40
3.39
2.73
2.69
2.33
1.82
1.57
1.17
3.06
3.81
1.38
1.09
1.17
1.22
2.83
2.87
8.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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1.0
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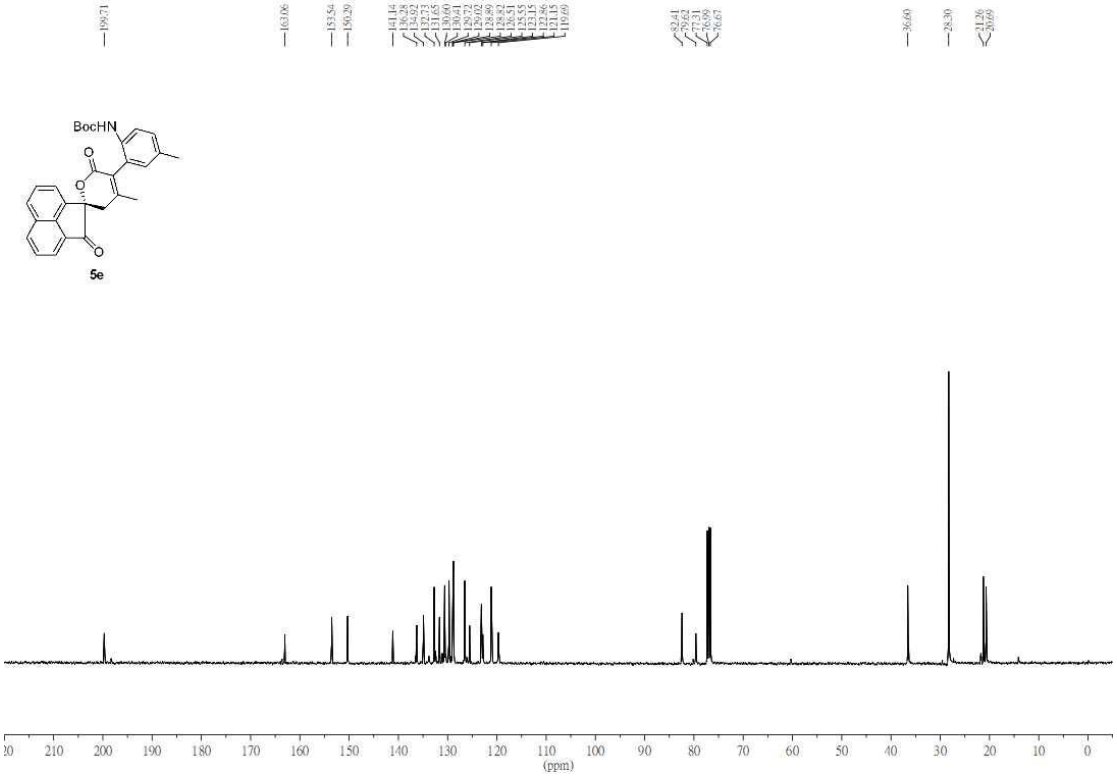
0.0
(ppm)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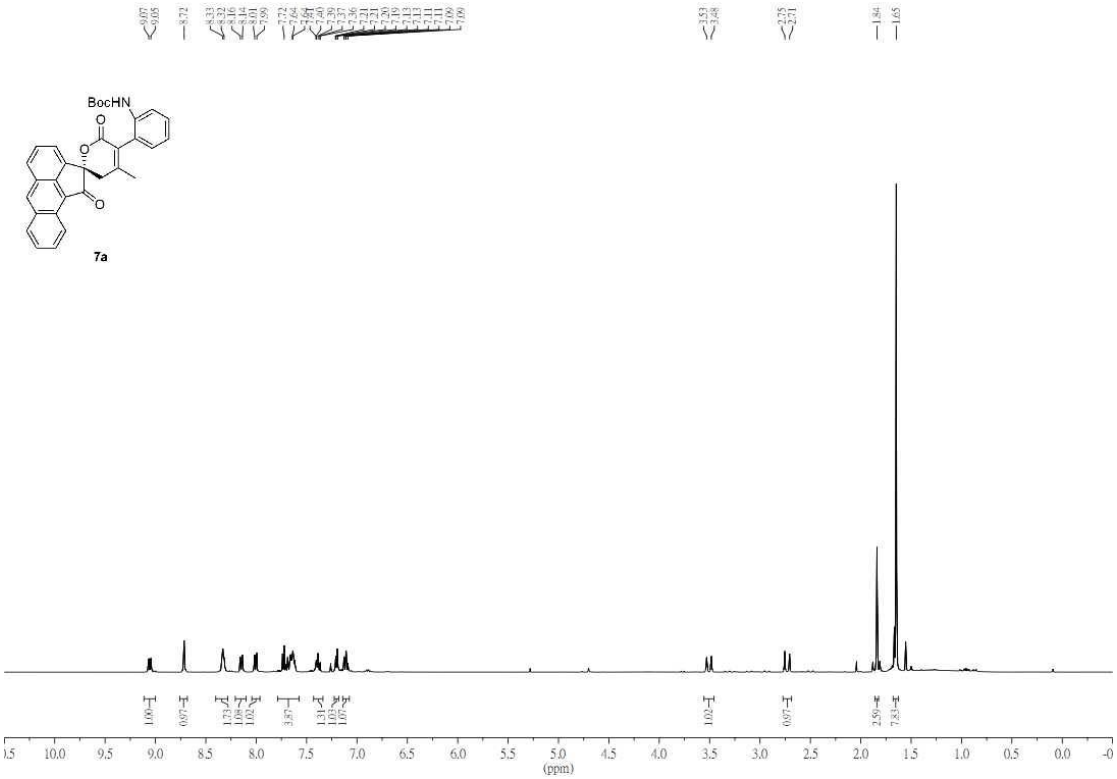
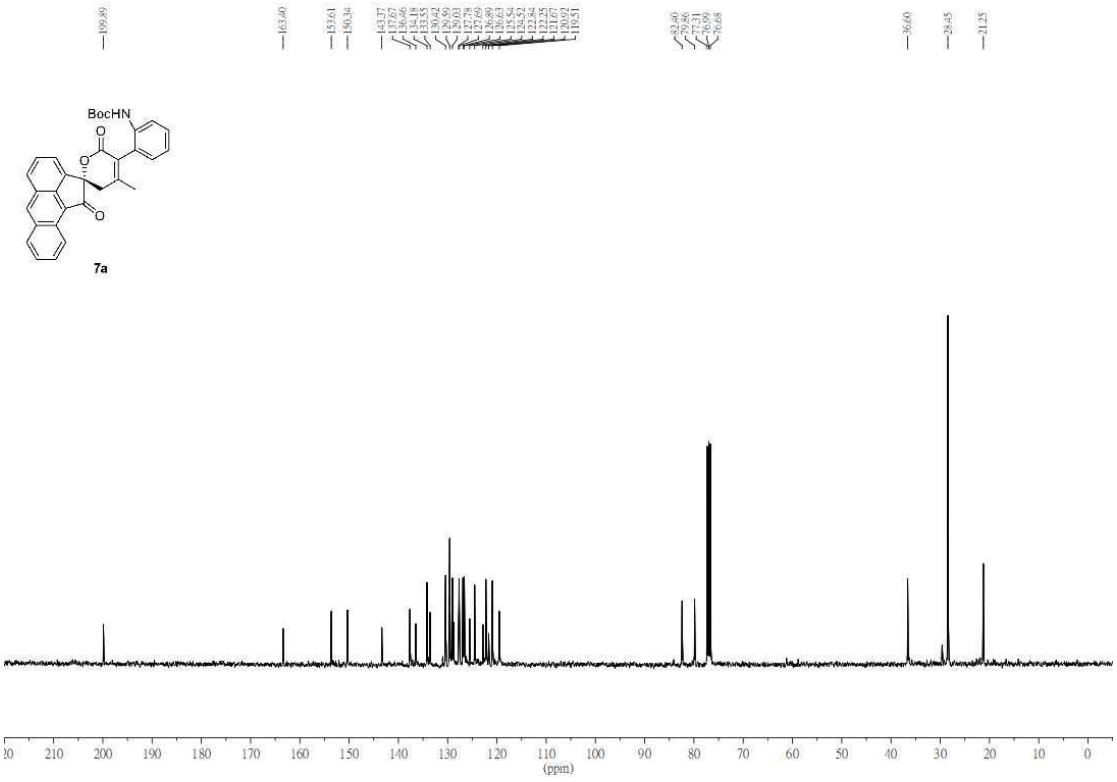
163.06
153.54
150.29
141.14
136.28
134.92
132.73
131.65
130.60
130.41
129.72
129.02
128.98
128.82
126.51
125.15
123.15
122.86
121.13
119.69
82.41
79.62
77.31
16.99
16.67
36.60
28.39
21.26
20.69
BocHN
O
O
O
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


BocHN
O
O
O
7a
(ppm)


BocHN
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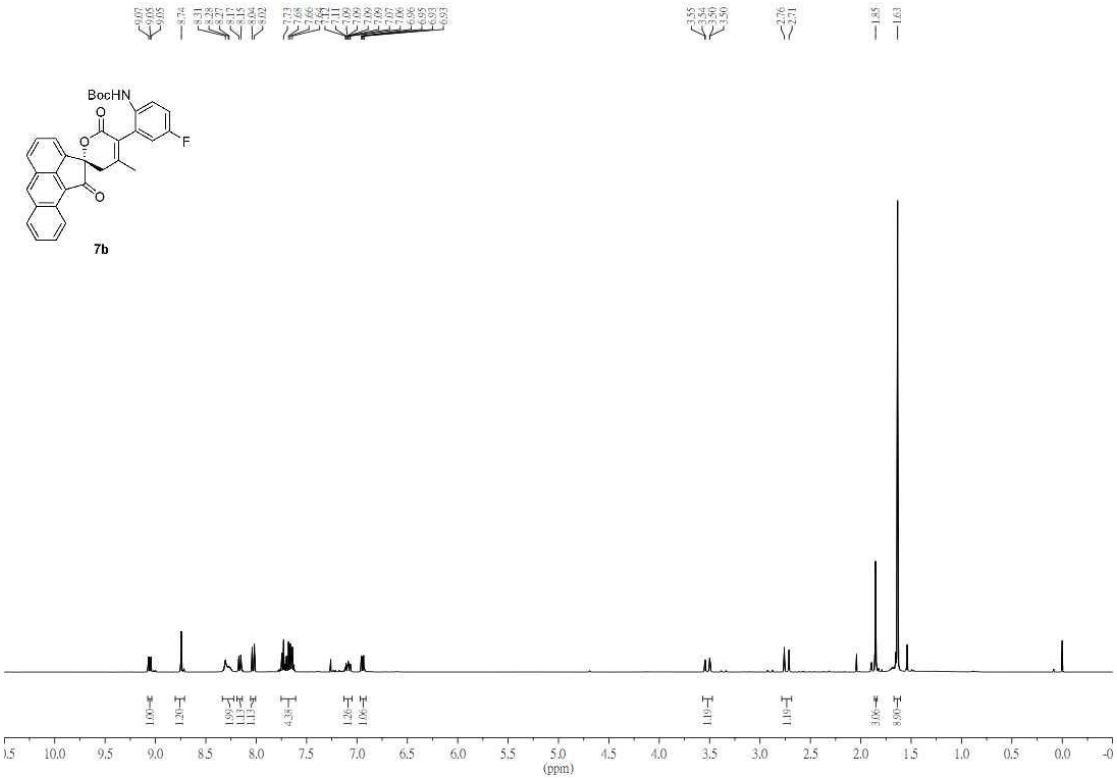
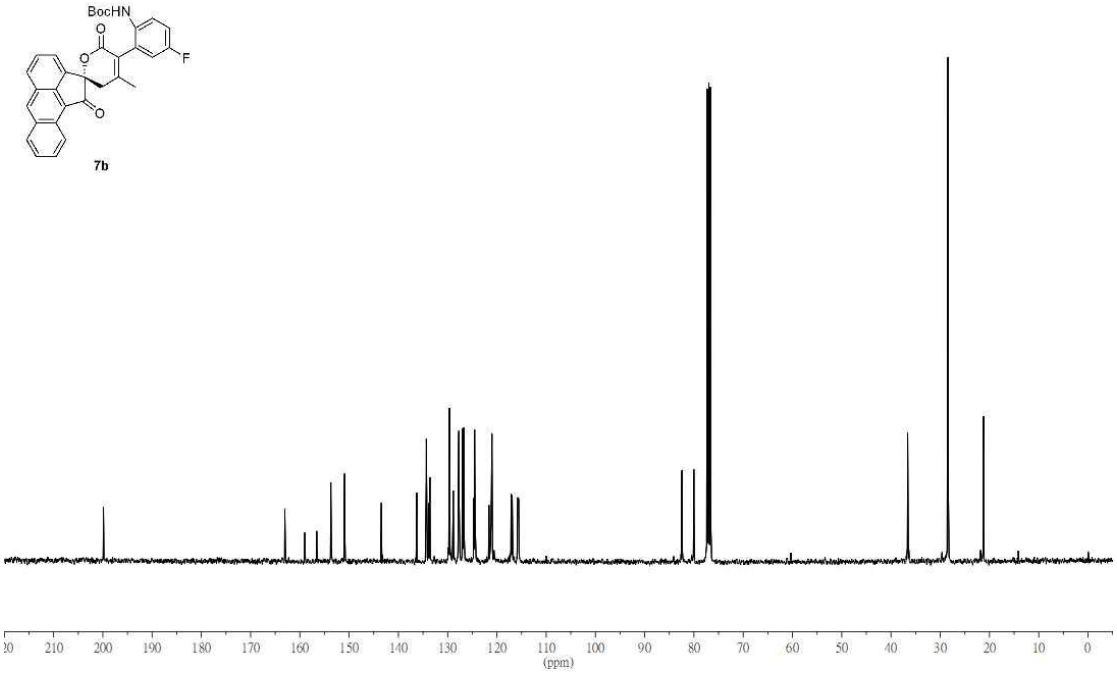
O
O
7a
(ppm)


BocHN
F
O
O
O
7b
(ppm)


BocHN
F
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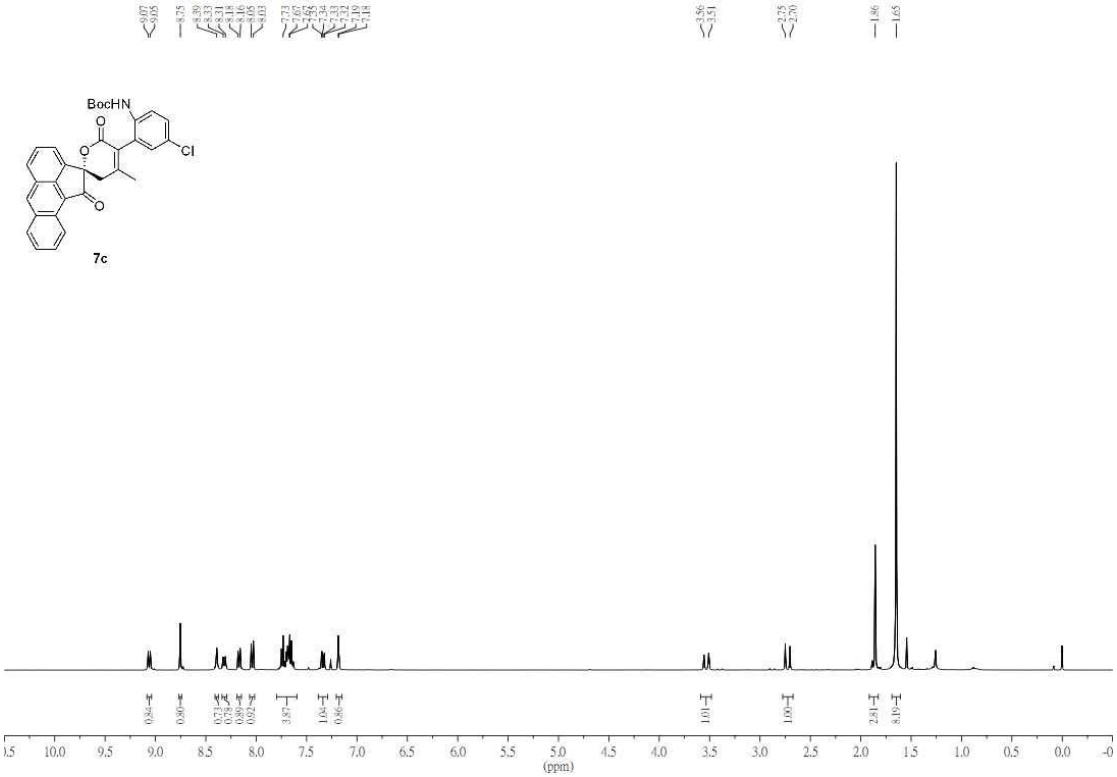
O
O
7b
(ppm)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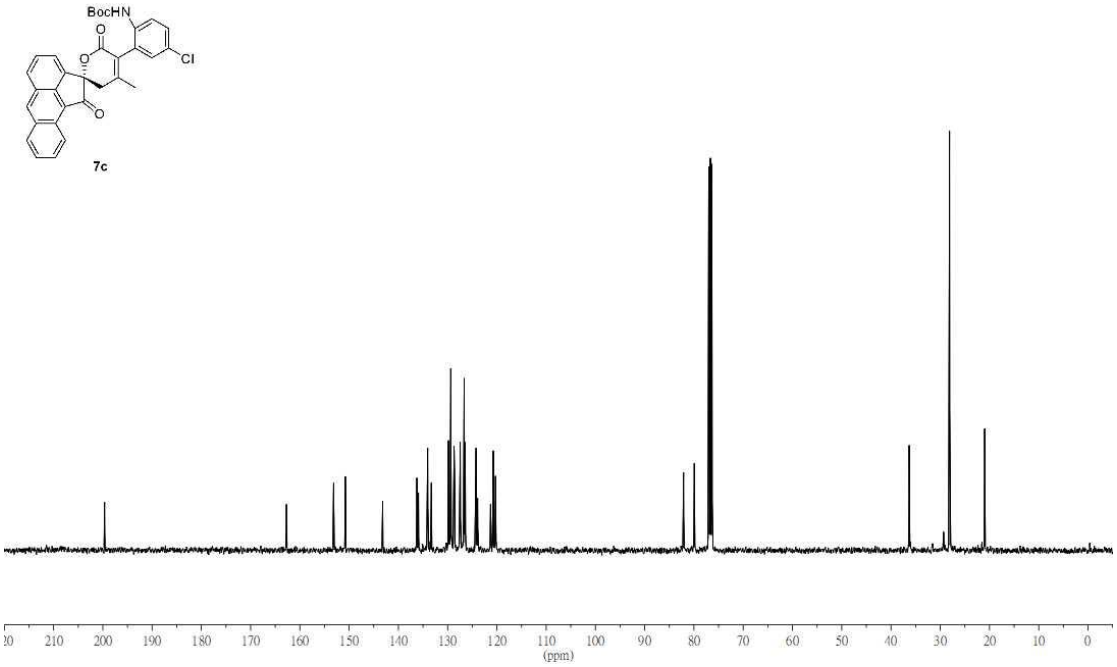
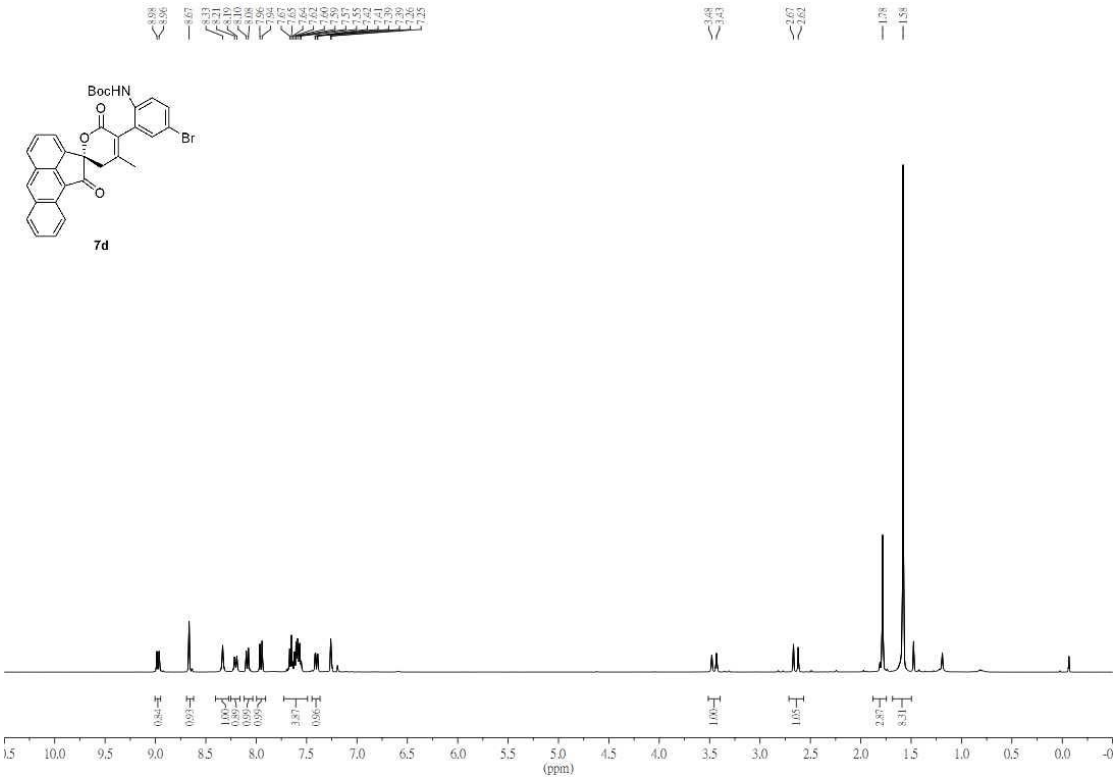
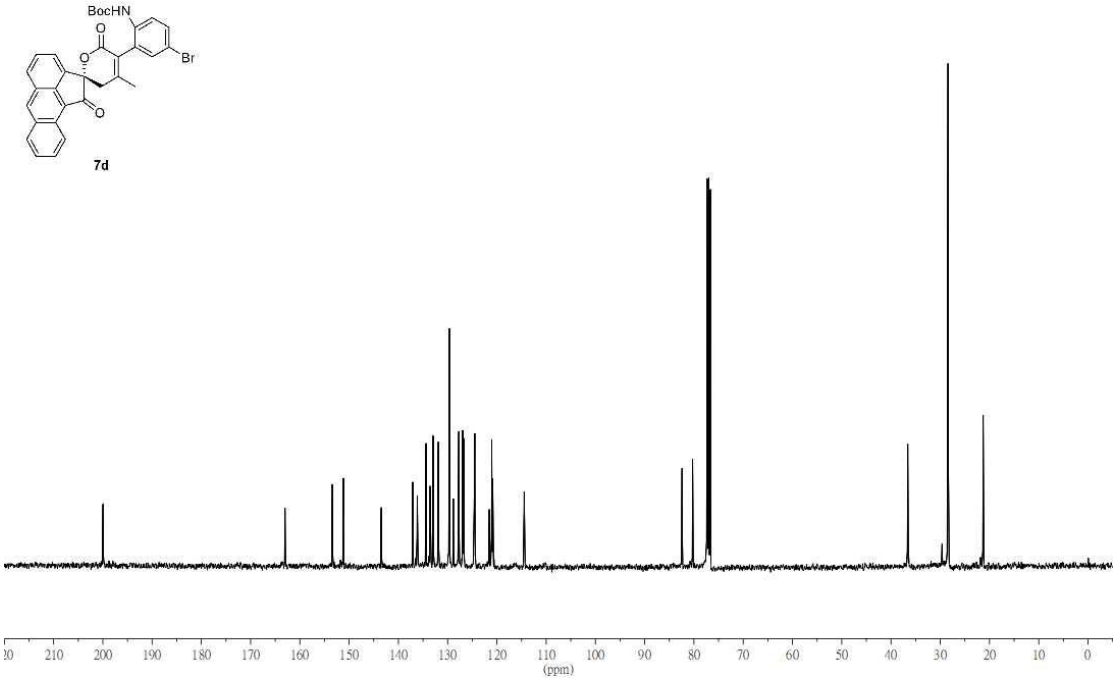
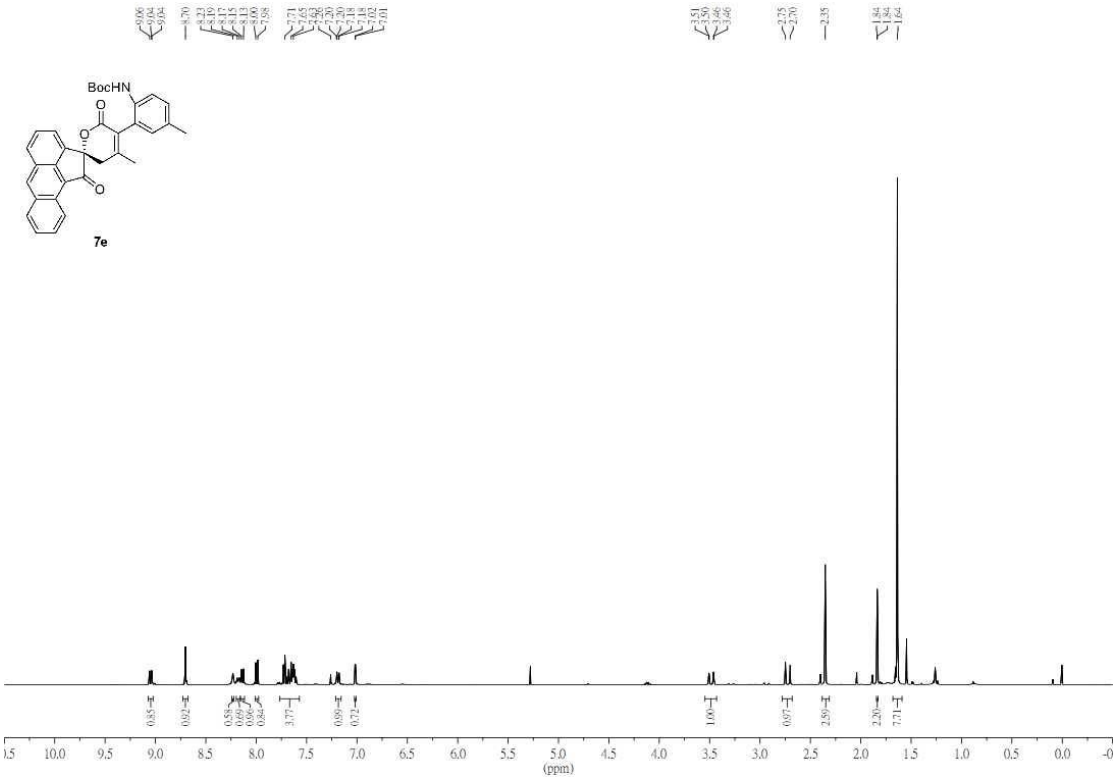
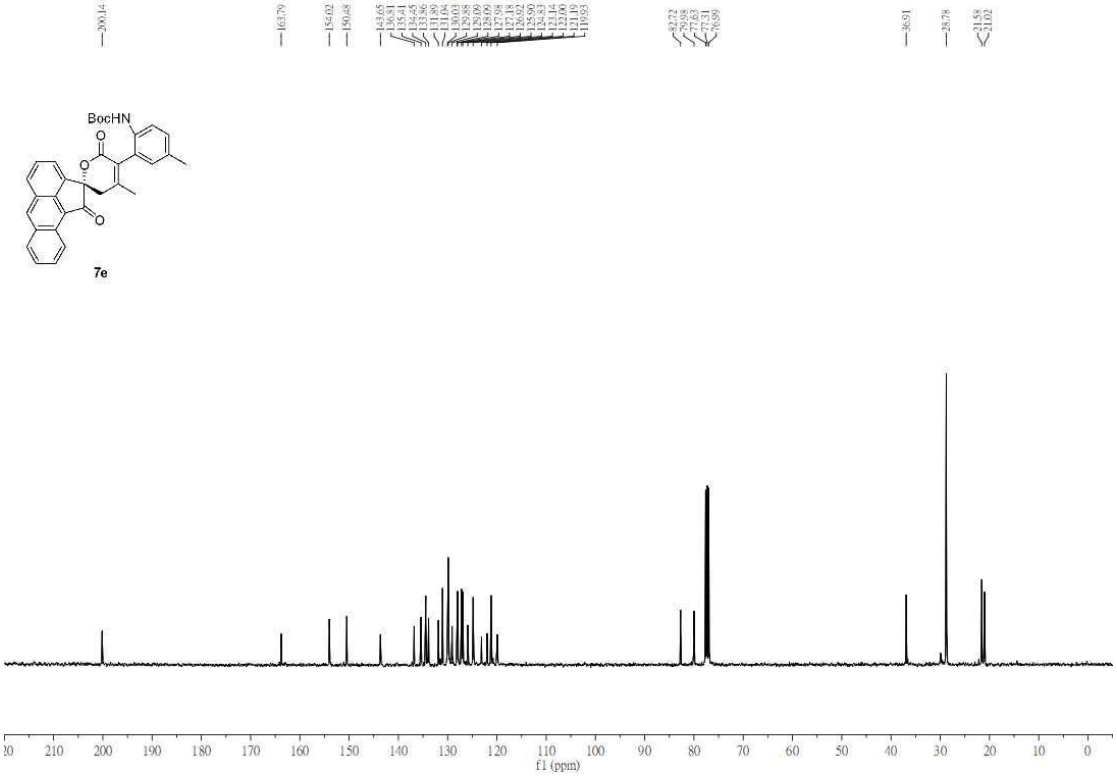
Cl
O
O
O
7c
(ppm)

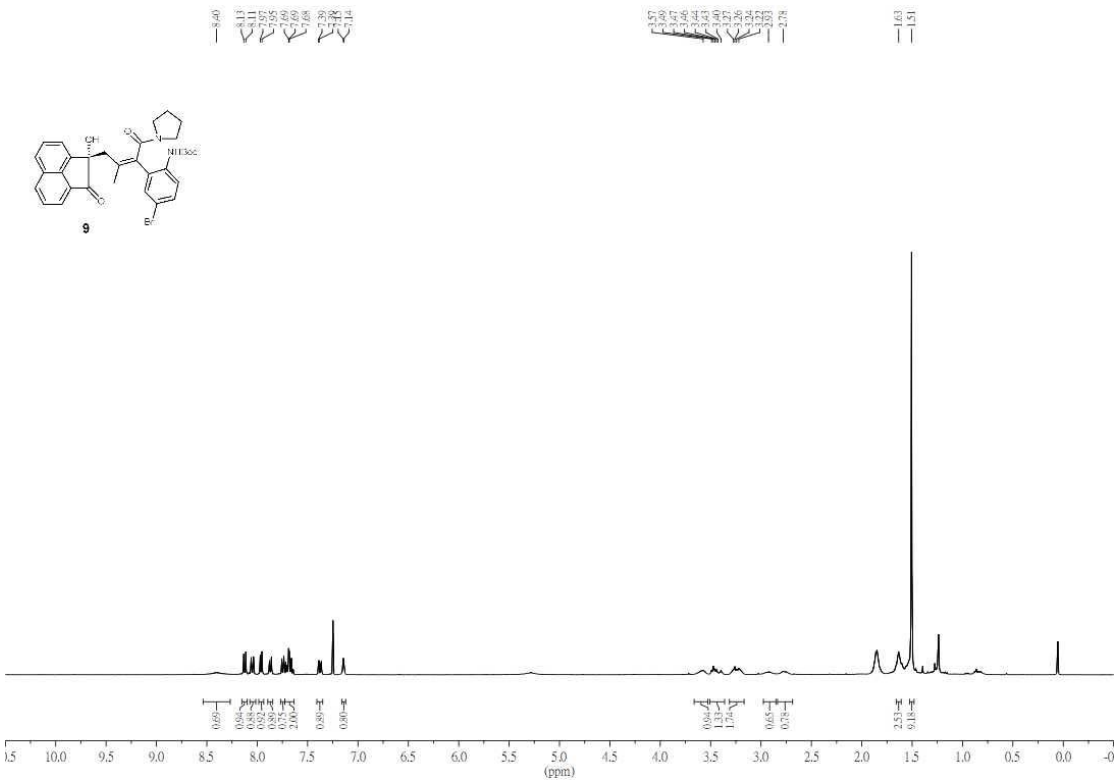

BocHN
Cl
O
O
O
7c
(ppm)


BocHN
Br
O
O
O
7d
(ppm)


BocHN
Br
O
O
O
7d
(ppm)


BocHN
7e
(ppm)


BocHN
7e
f1 (ppm)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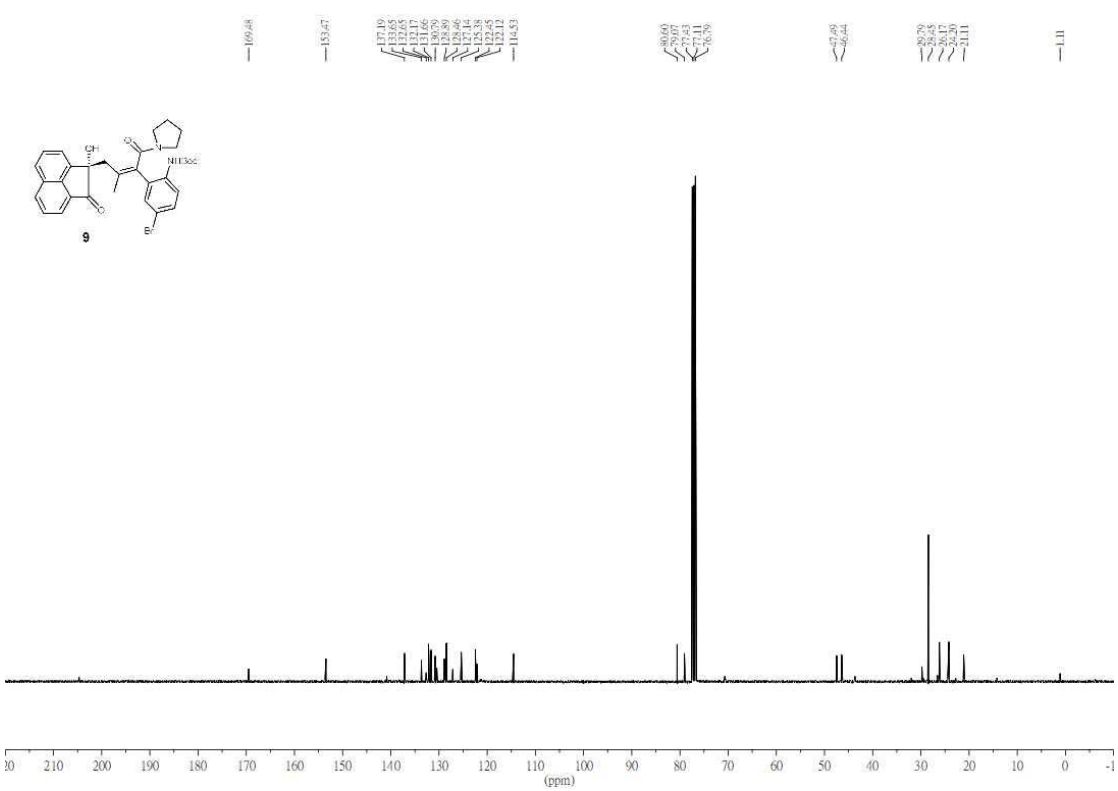
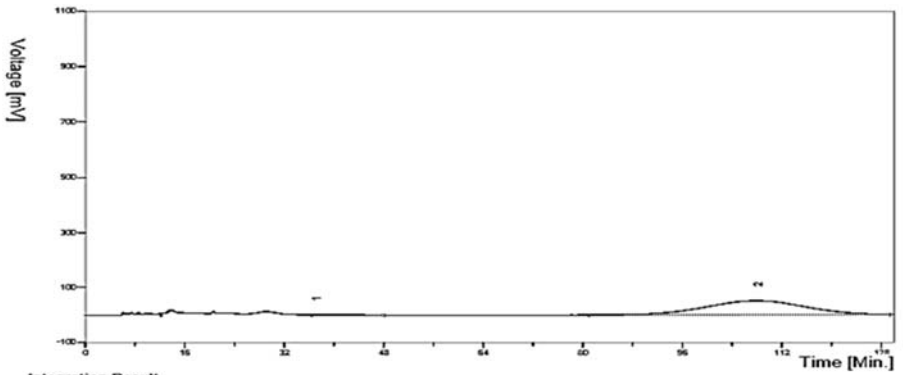
8.13
8.11
7.97
7.95
7.69
7.69
7.68
7.39
7.38
7.38
7.14
3.57
3.49
3.47
3.46
3.43
3.40
3.27
3.26
3.24
3.22
3.03
2.78
1.63
1.51
9
(ppm)


169.68
153.47
137.10
133.65
132.65
132.17
131.66
130.70
128.80
128.66
127.14
125.58
122.45
122.12
114.53
80.69
79.07
77.83
77.11
76.79
47.69
46.64
29.79
28.65
26.17
24.30
21.11
1.11
9
(ppm)

4. Copies of HPLC Spectra of Products 3, 5, 7, and 9

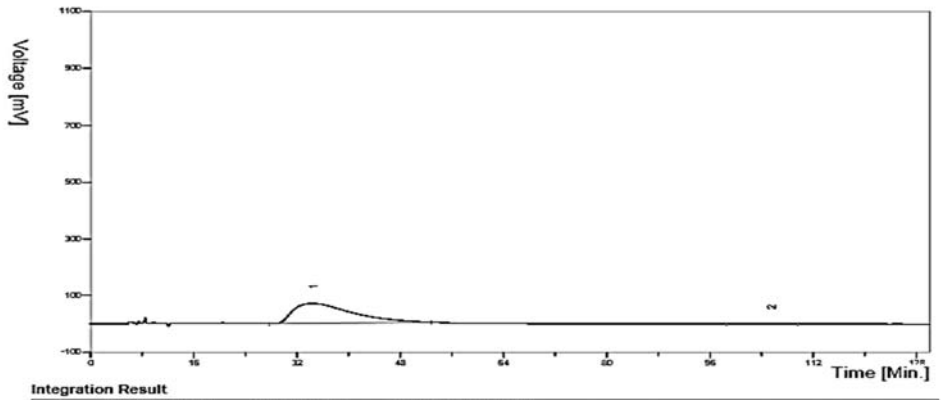
3a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	36.88	82.65	0.1443
2	107.90	57190.39	99.8557
Total		57273.05	100

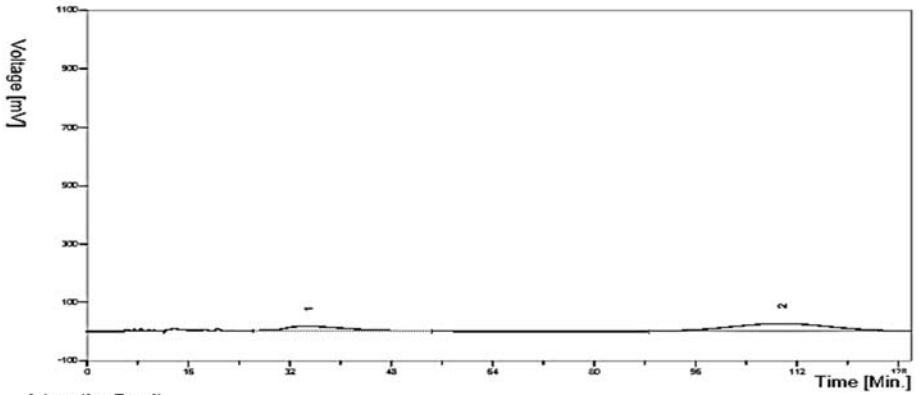
ent-3a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	34.26	43993.67	99.8794
2	105.28	53.11	0.1206
Total		44046.78	100

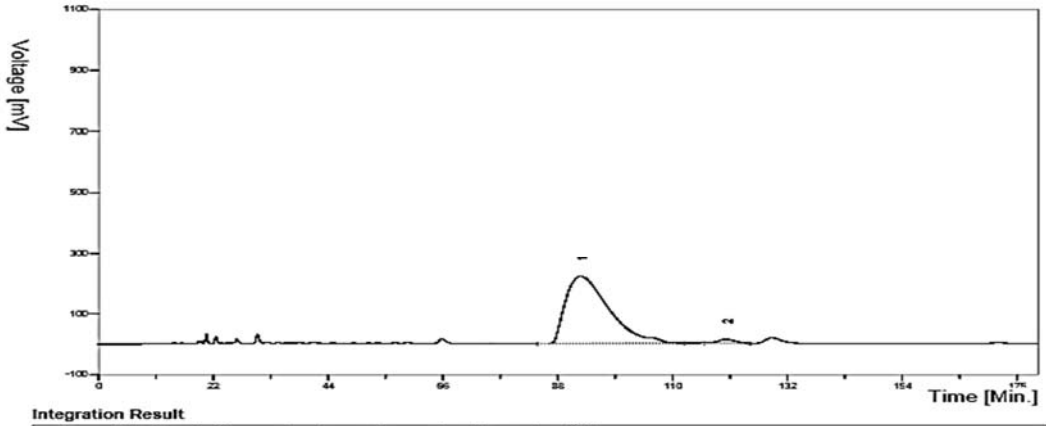
3a + *ent*-3a as *rac*-3a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	34.63	10853.03	27.1155
2	109.43	29172.14	72.8845
Total		40025.18	100

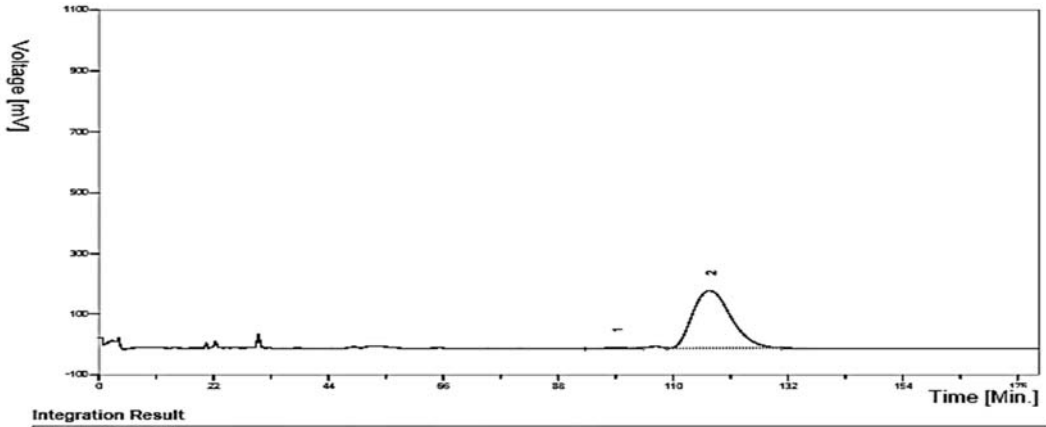
3b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	92.39	126399.06	97.9389
2	120.21	2659.99	2.0611
Total		129059.05	100

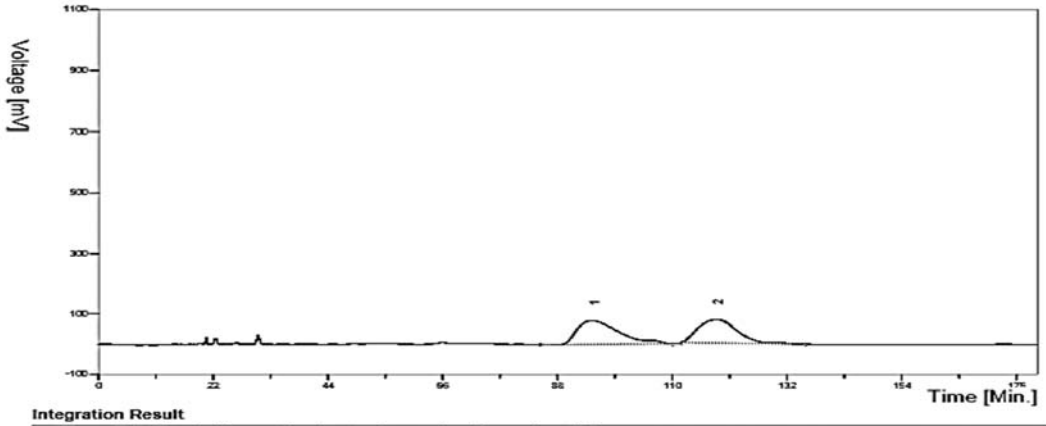
***ent*-3b**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	98.93	281.73	0.2939
2	116.97	95573.77	99.7061
Total		95855.50	100

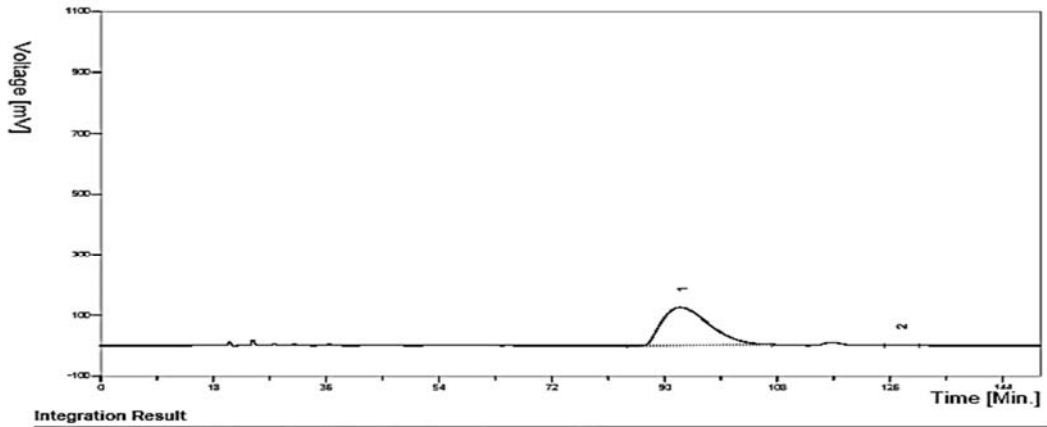
3b + *ent*-3b as *rac*-3b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	94.71	42958.30	51.3889
2	118.41	40636.21	48.6111
Total		83594.52	100

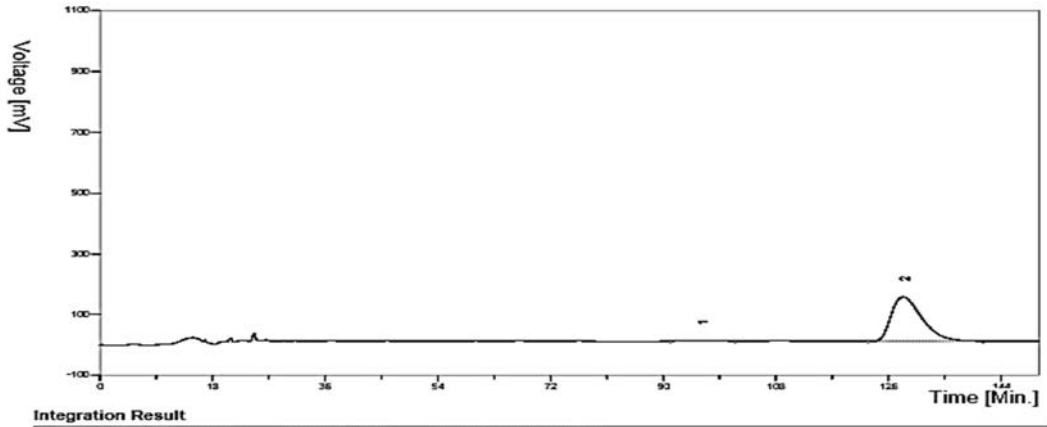
3c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	92.56	64827.06	99.4966
2	127.56	328.01	0.5034
Total		65155.07	100

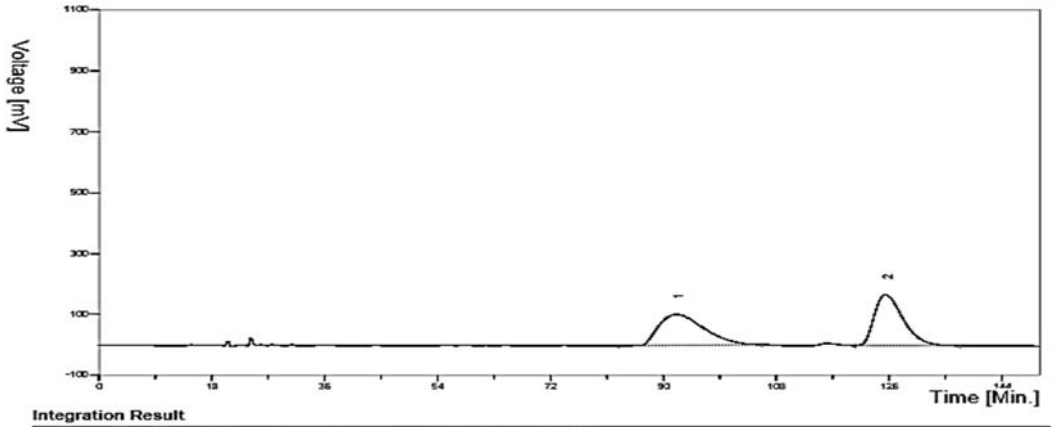
***ent*-3c**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	96.06	671.71	1.3389
2	128.32	49497.97	98.6611
Total		50169.68	100

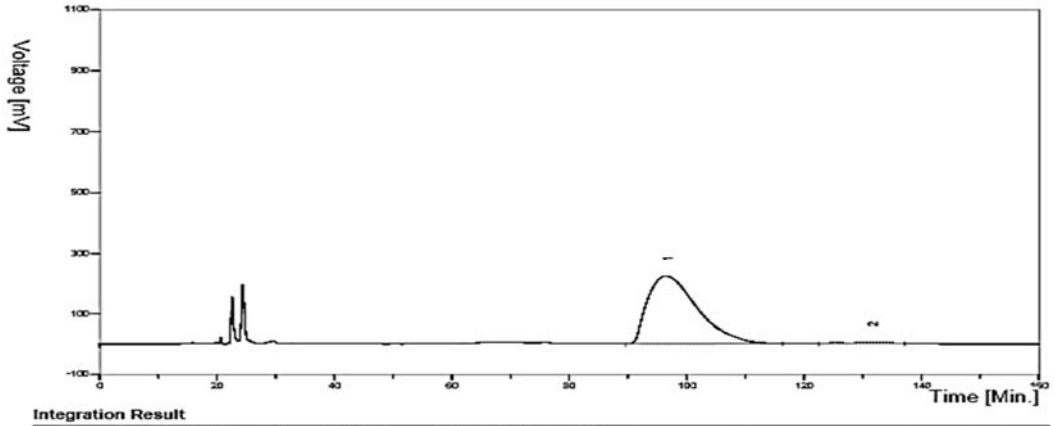
3c + *ent*-3c as *rac*-3c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	92.09	50682.83	48.8436
2	125.49	53082.78	51.1564
Total		103765.61	100

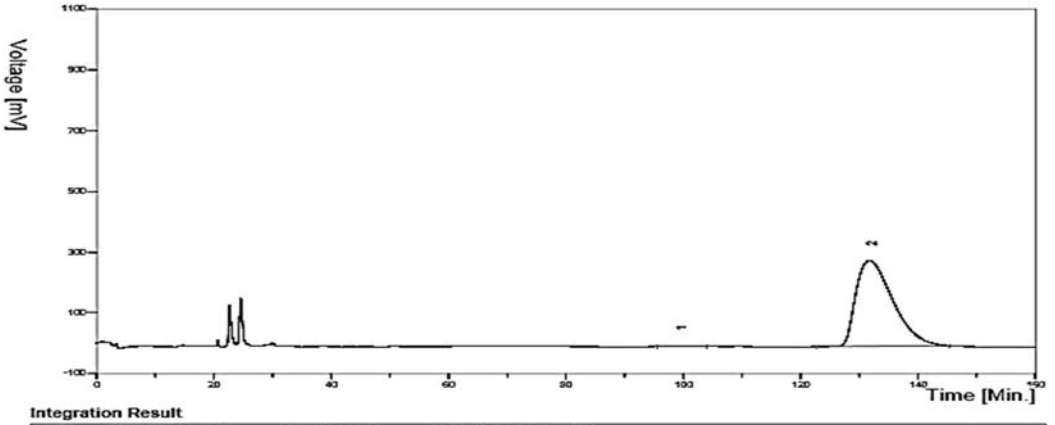
3d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	96.44	131181.99	98.3963
2	131.44	2138.09	1.6037
Total		133320.08	100

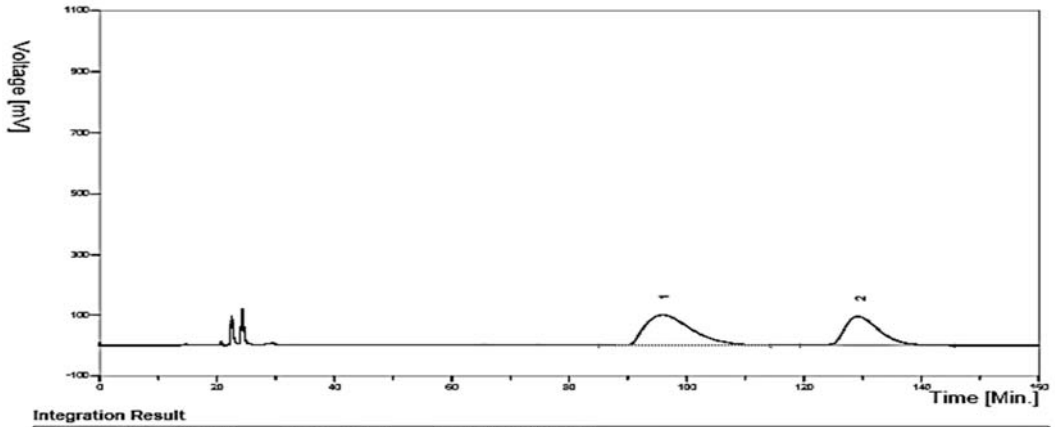
***ent*-3d**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	99.34	420.62	0.3409
2	131.77	122978.65	99.6591
Total		123399.26	100

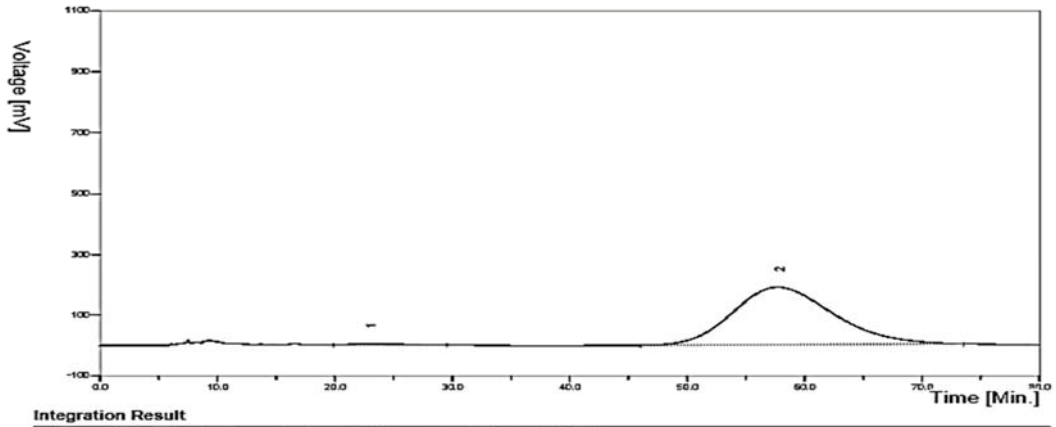
3d + *ent*-3d as *rac*-3d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	95.85	54609.33	58.6591
2	129.26	38486.79	41.3409
Total		93096.13	100

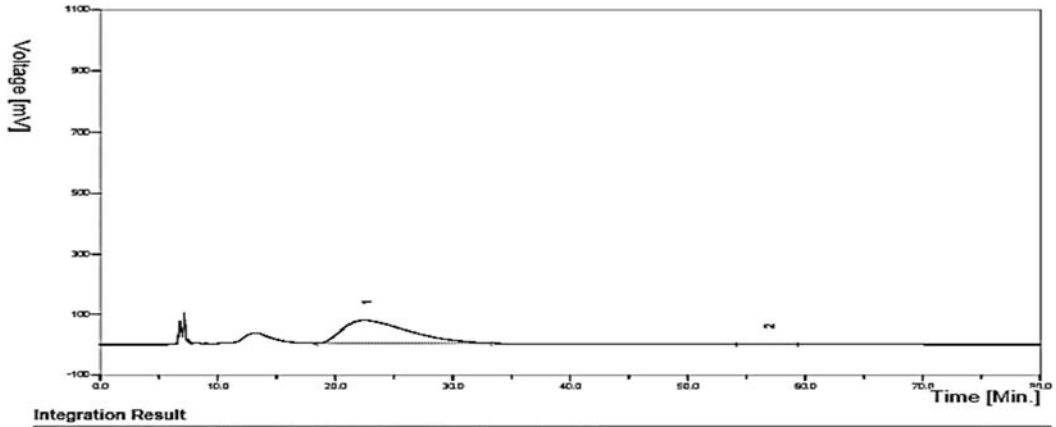
3e



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	22.91	1006.99	0.8903
2	57.70	112099.25	99.1097
Total		113106.24	100

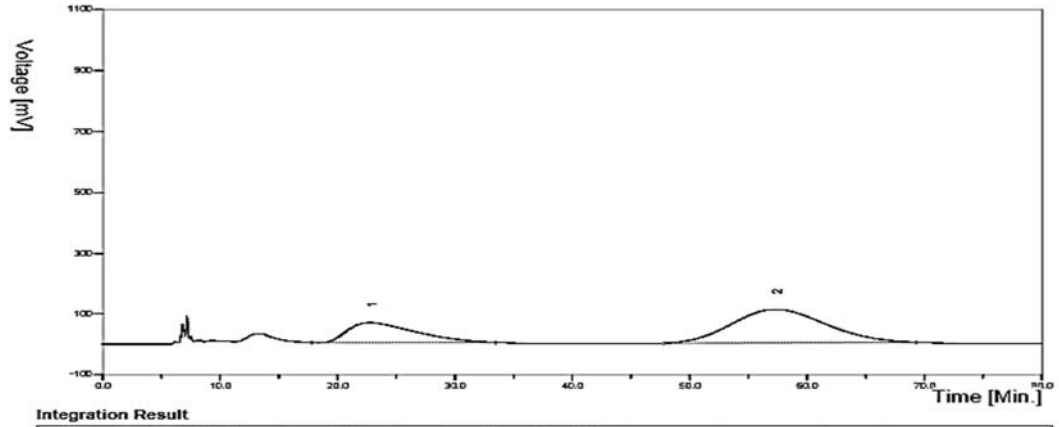
***ent*-3e**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	22.53	29180.28	99.7736
2	56.79	66.21	0.2264
Total		29246.48	100

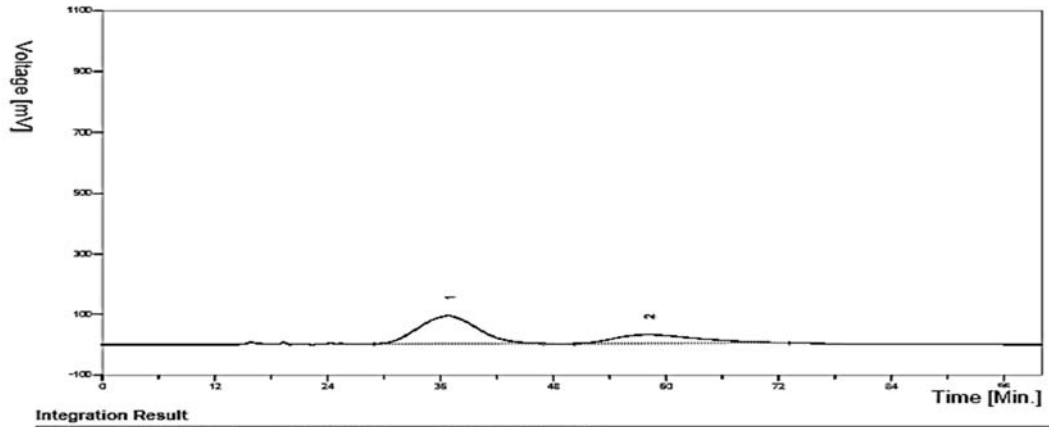
3e + *ent*-3e as *rac*-3e



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	22.79	25920.35	29.8296
2	57.29	60974.30	70.1704
Total		86894.65	100

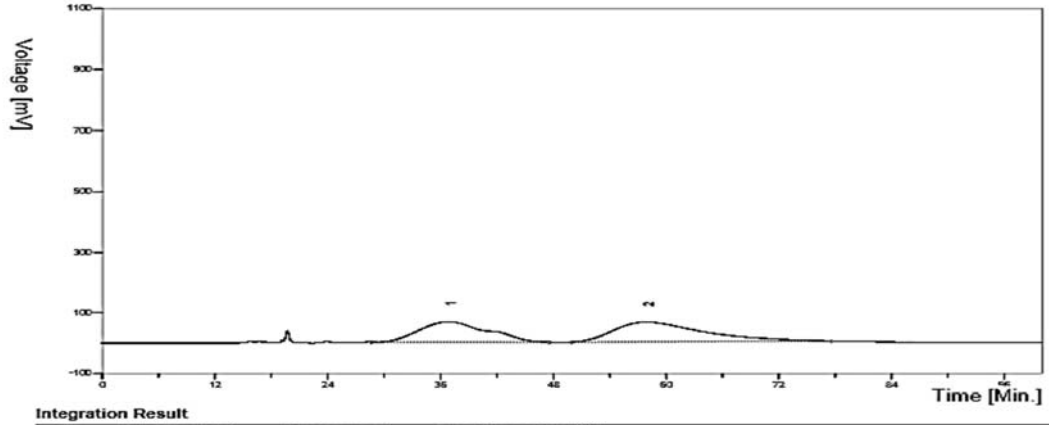
3f



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	36.86	39447.07	69.1205
2	58.08	17622.89	30.8795
Total		57069.96	100

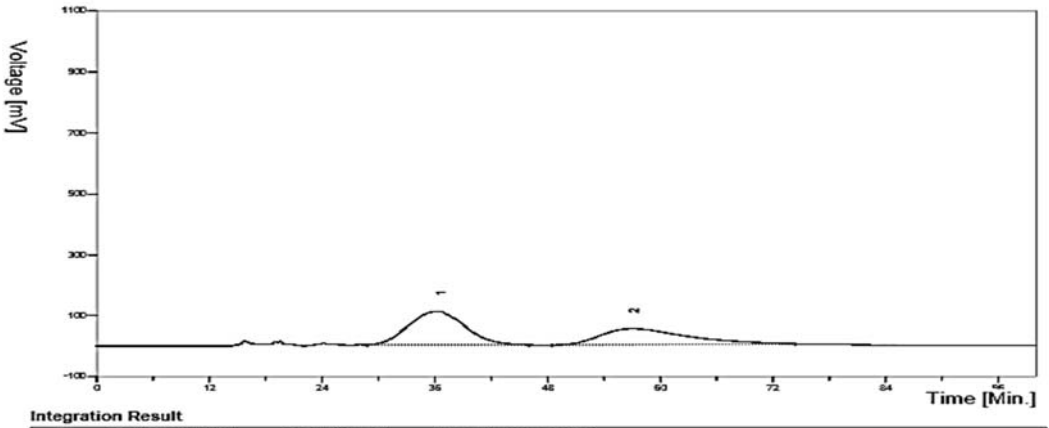
***ent*-3f**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	36.87	33265.73	43.8011
2	57.94	42681.53	56.1989
Total		75947.26	100

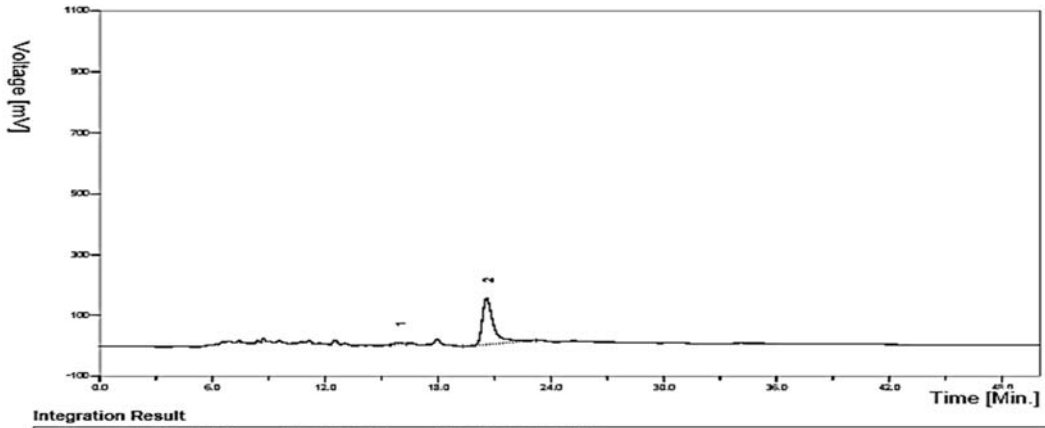
3f + *ent*-3f as *rac*-3f



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	36.46	45222.75	57.7838
2	57.00	33039.24	42.2162
Total		78261.99	100

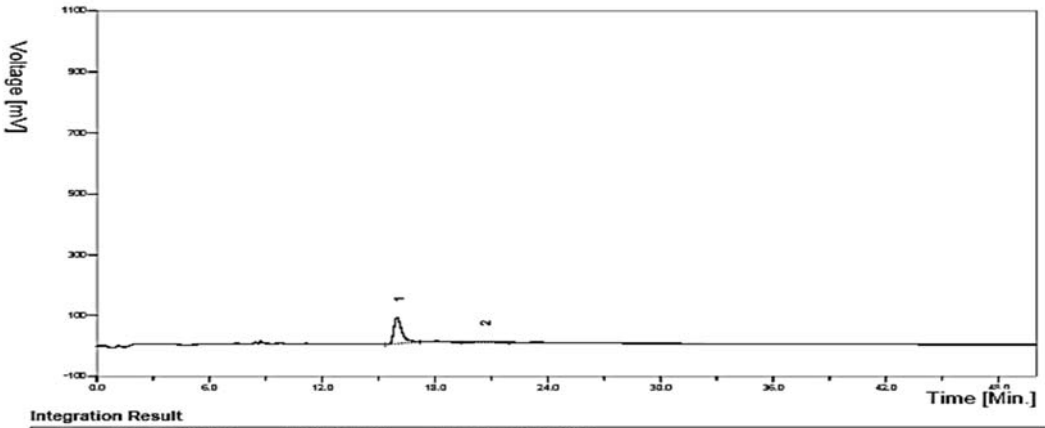
3g



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	15.92	151.26	2.4643
2	20.58	5986.88	97.5357
Total		6138.14	100

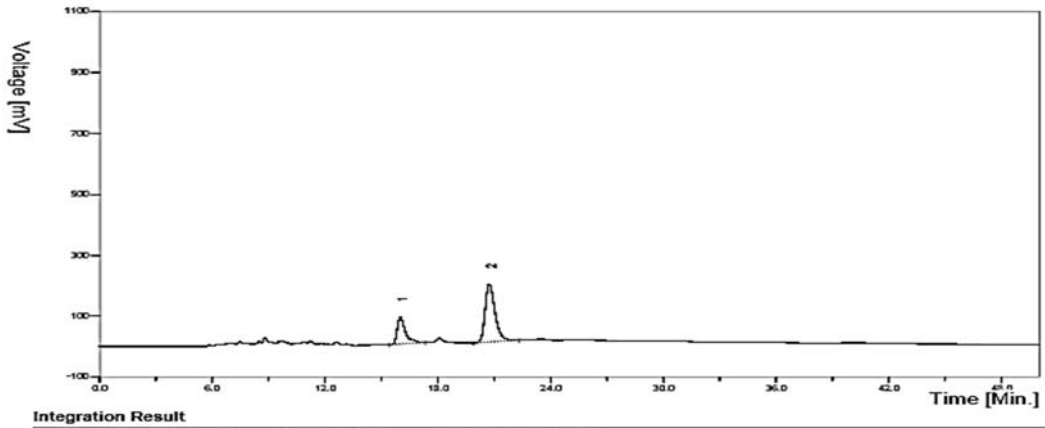
***ent*-3g**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	15.98	2486.66	93.8358
2	20.59	163.35	6.1642
Total		2650.01	100

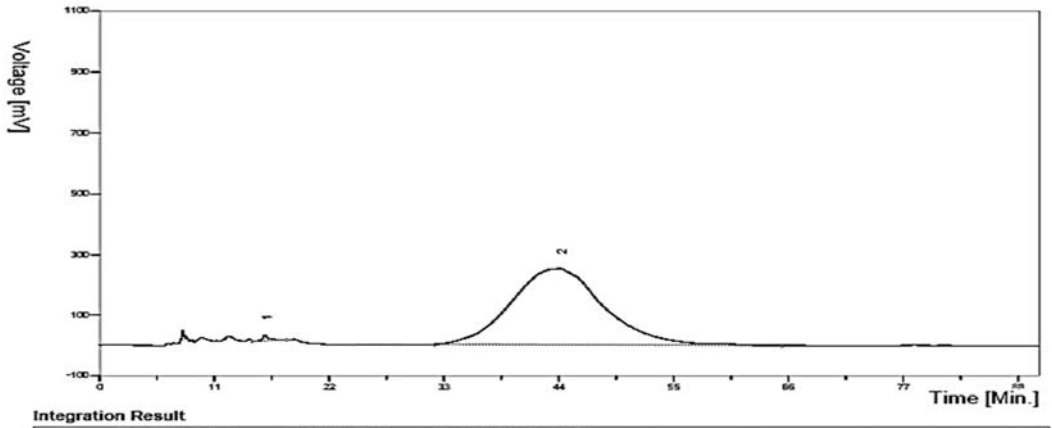
3g + *ent*-3g as *rac*-3g



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	16.01	2644.06	27.6505
2	20.74	6918.35	72.3495
Total		9562.40	100

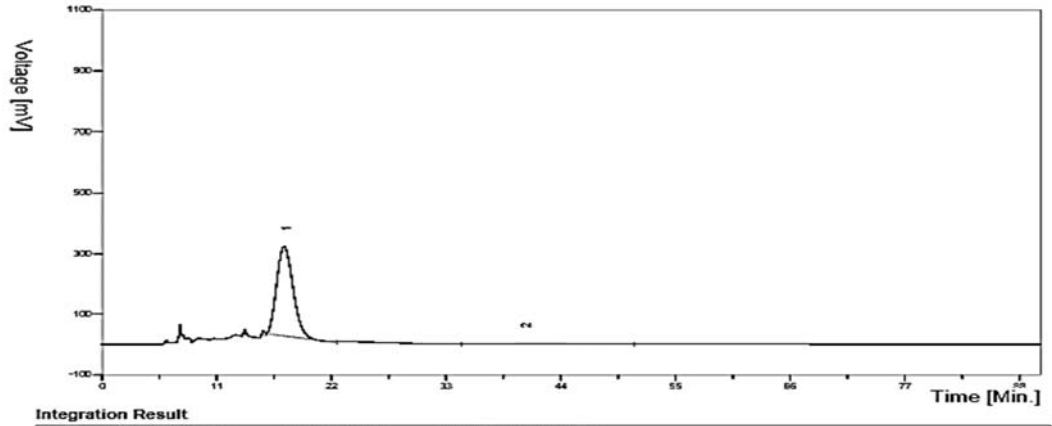
3h



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	15.85	611.00	0.3952
2	44.11	153989.31	99.6048
Total		154600.31	100

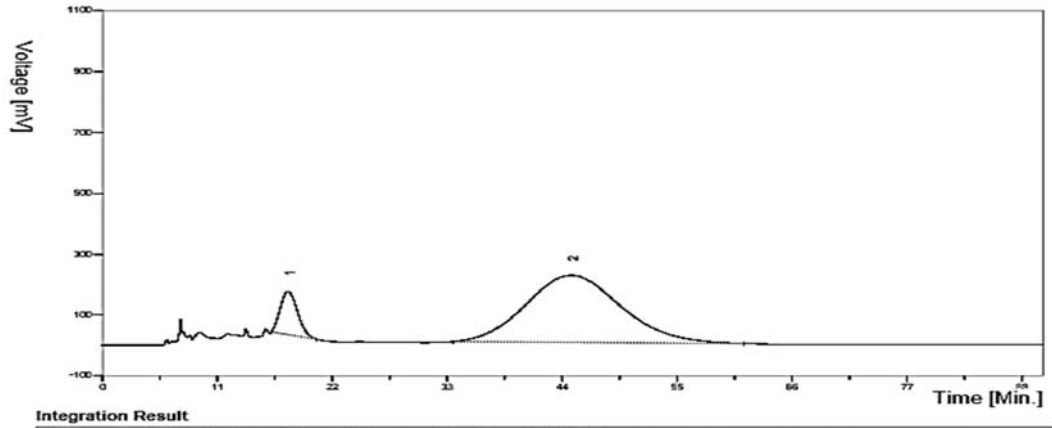
***ent*-3h**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	17.46	31751.05	97.4607
2	40.50	827.28	2.5393
Total		32578.32	100

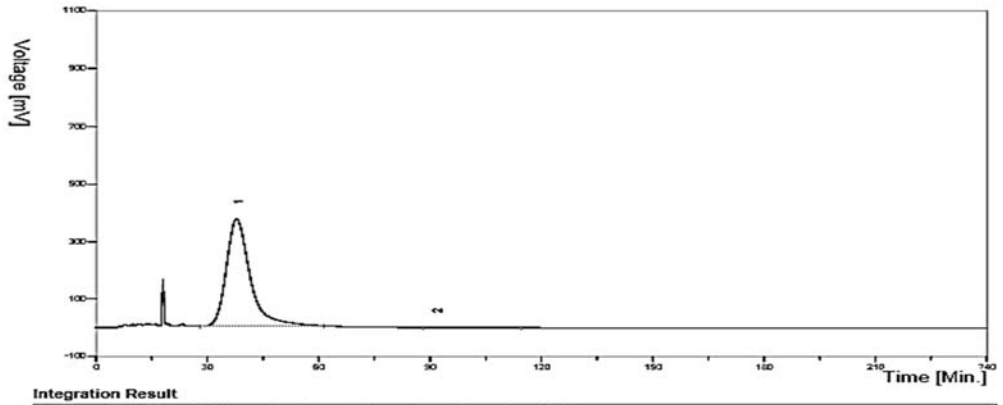
3h + *ent*-3h as *rac*-3h



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	17.76	16231.58	10.4396
2	44.87	139248.85	89.5604
Total		155480.44	100

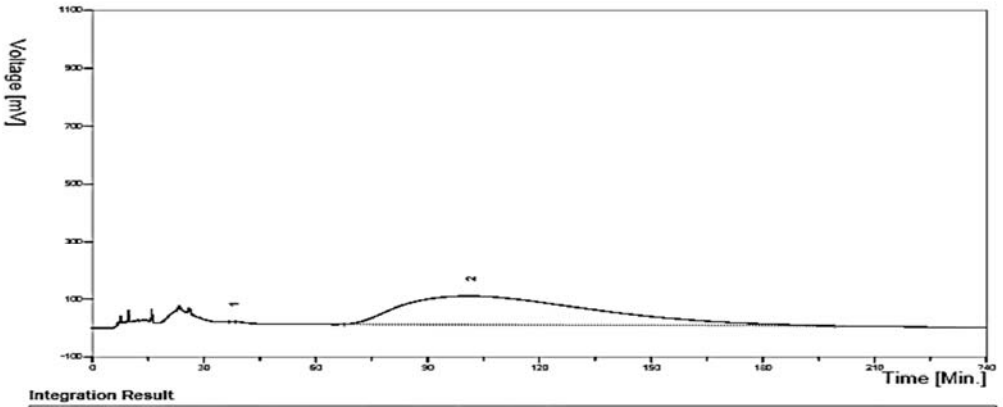
3i



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	37.89	165632.71	99.9481
2	91.47	85.98	0.0519
Total		165718.69	100

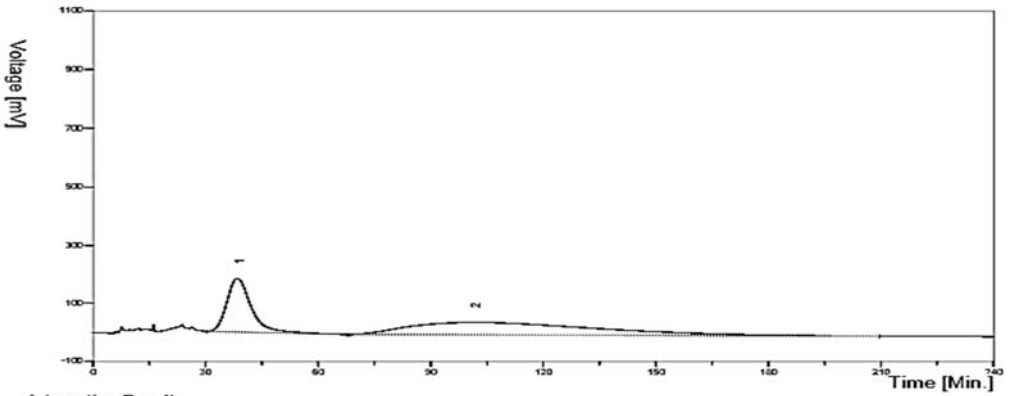
***ent*-3i**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	37.60	27.41	0.0078
2	101.21	352075.26	99.9922
Total		352102.67	100

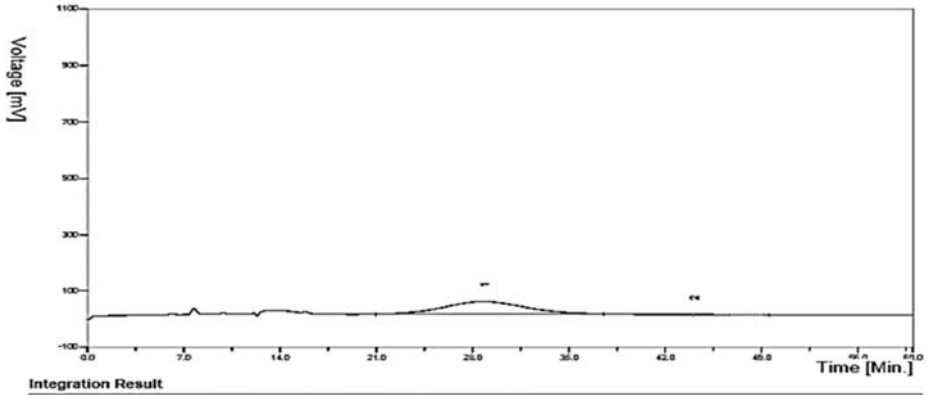
3i + *ent*-3i as *rac*-3i



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	38.47	82861.28	35.9673
2	101.47	147518.00	64.0327
Total		230379.28	100

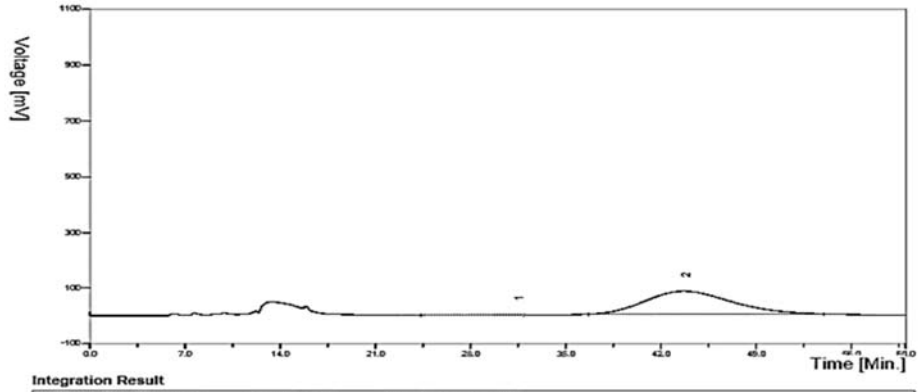
3j



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	28.77	17911.99	99.8672
2	44.00	23.82	0.1328
Total		17935.80	100

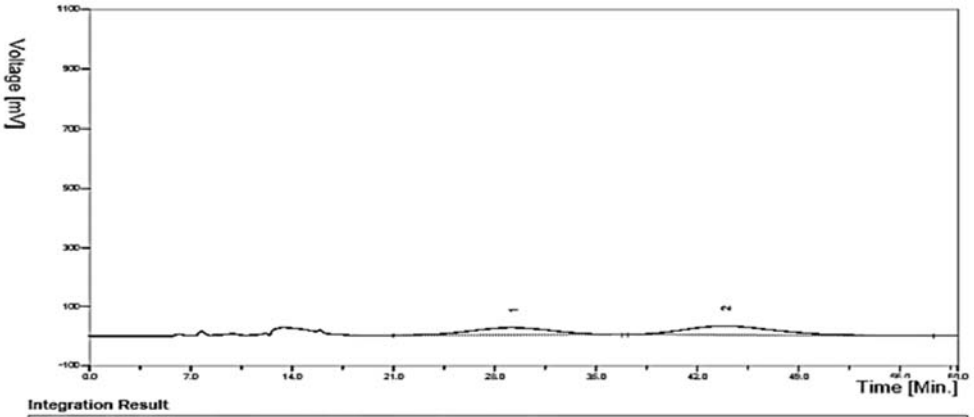
***ent*-3j**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	31.45	41.51	0.1147
2	43.73	36165.48	99.8853
Total		36206.99	100

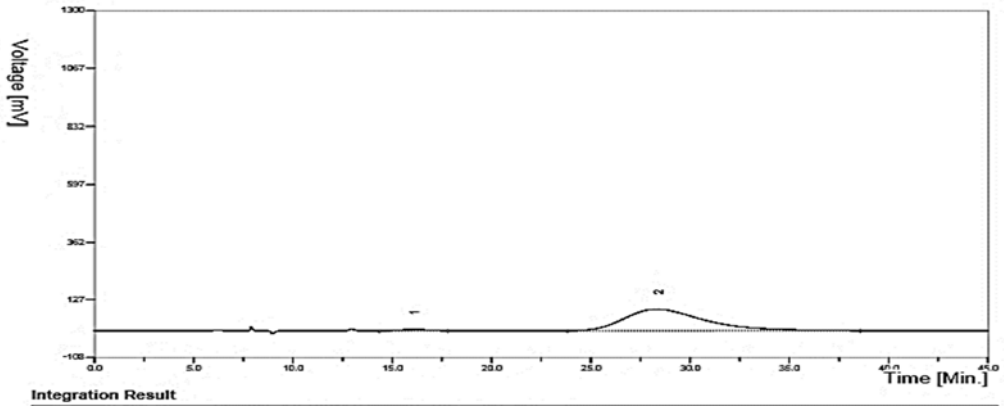
3j + *ent*-3j as *rac*-3j



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	29.15	9661.43	42.5645
2	43.85	13036.88	57.4355
Total		22698.30	100

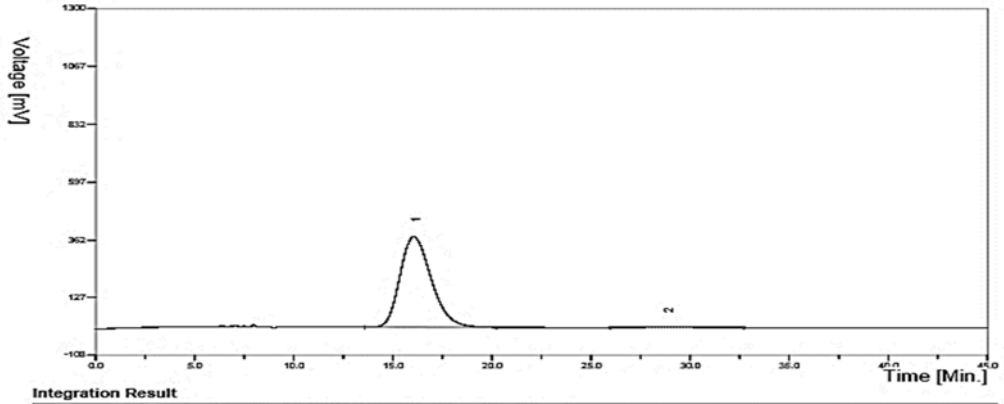
5a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	16.02	493.55	1.9862
2	28.33	24355.58	98.0138
Total		24849.13	100

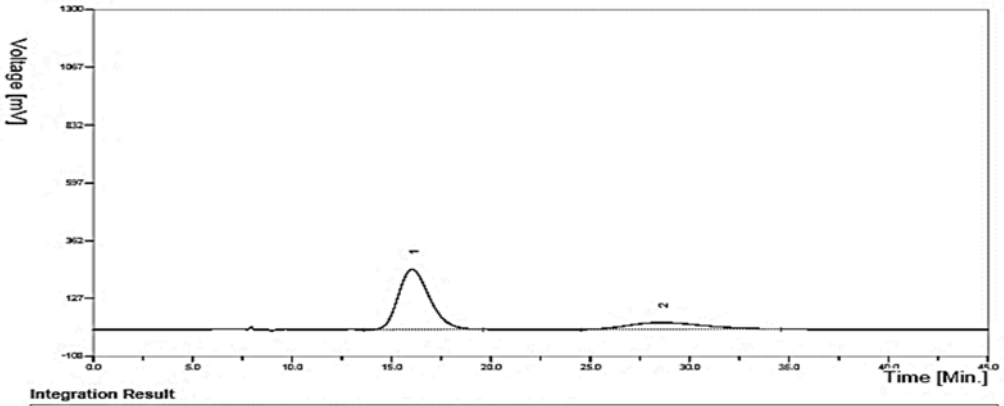
***ent*-5a**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	16.05	40481.63	98.9440
2	28.82	432.03	1.0560
Total		40913.66	100

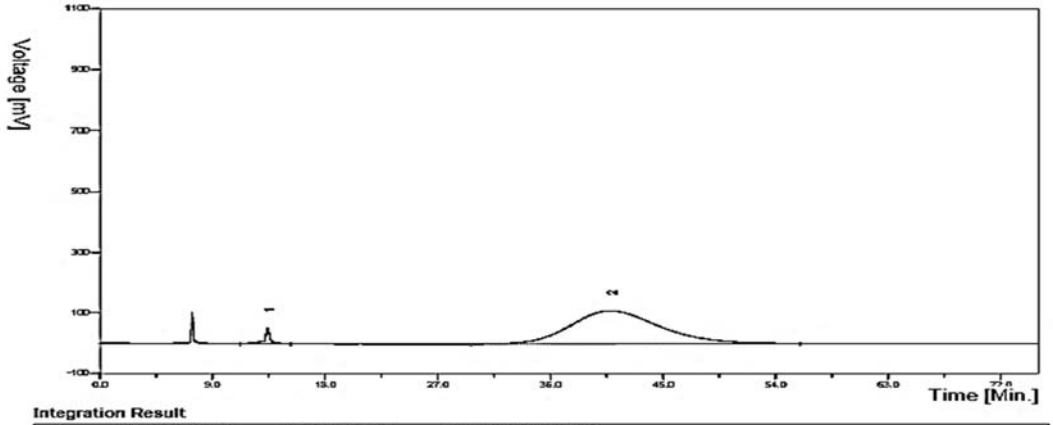
5a + *ent*-5a as *rac*-5a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	16.03	26311.67	78.5148
2	28.57	7200.05	21.4852
Total		33511.72	100

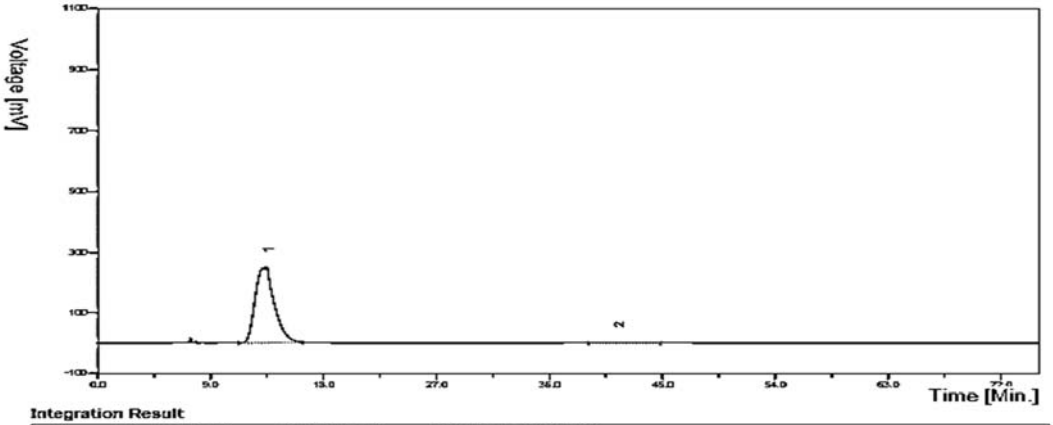
5b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.41	1574.23	2.8151
2	40.80	54347.03	97.1849
Total		55921.26	100

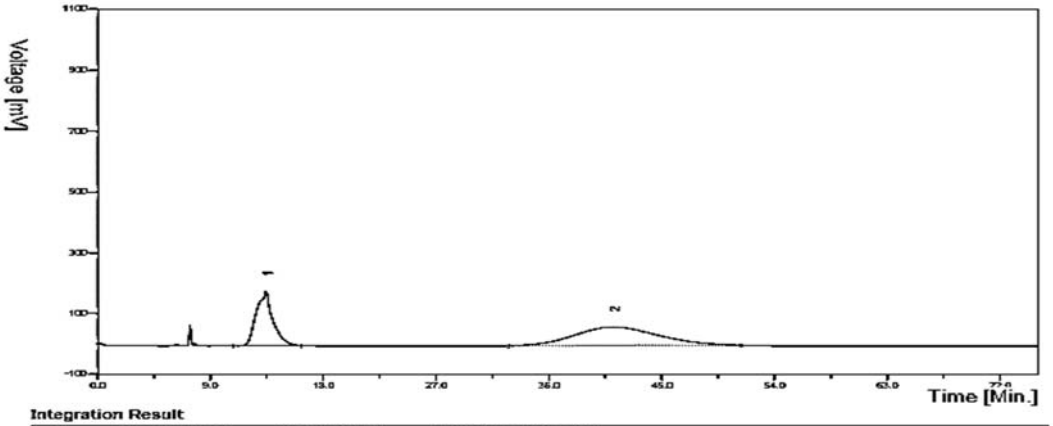
***ent*-5b**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.45	26219.41	99.7747
2	41.39	59.19	0.2253
Total		26278.61	100

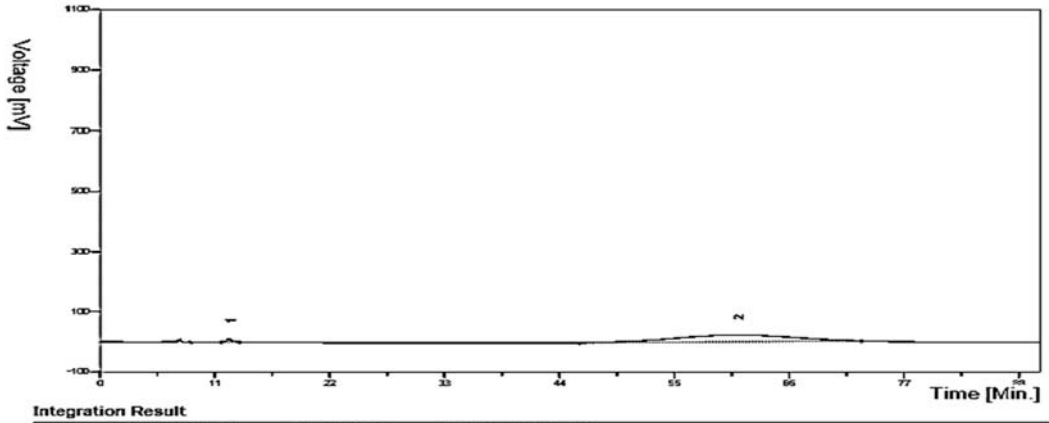
5b + *ent*-5b as *rac*-5b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.45	16282.21	36.4311
2	41.12	28410.89	63.5689
Total		44693.10	100

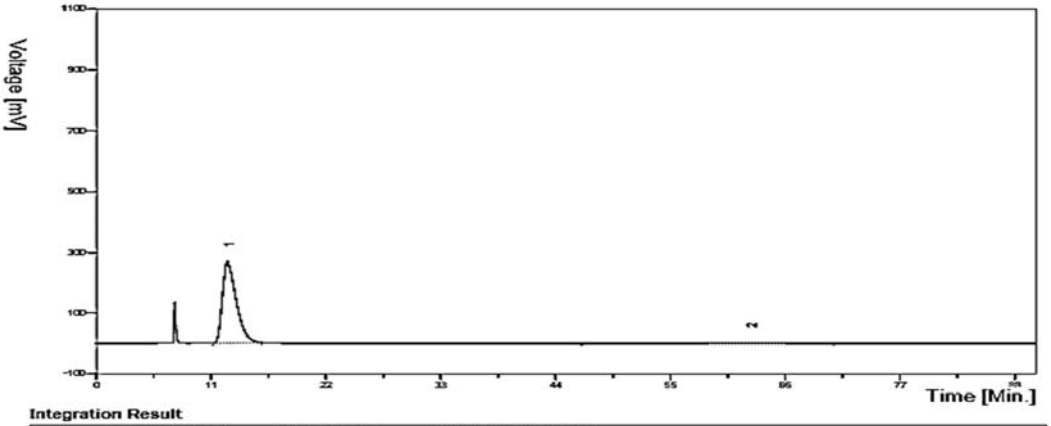
5c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.35	347.30	1.9427
2	60.99	17530.08	98.0573
Total		17877.38	100

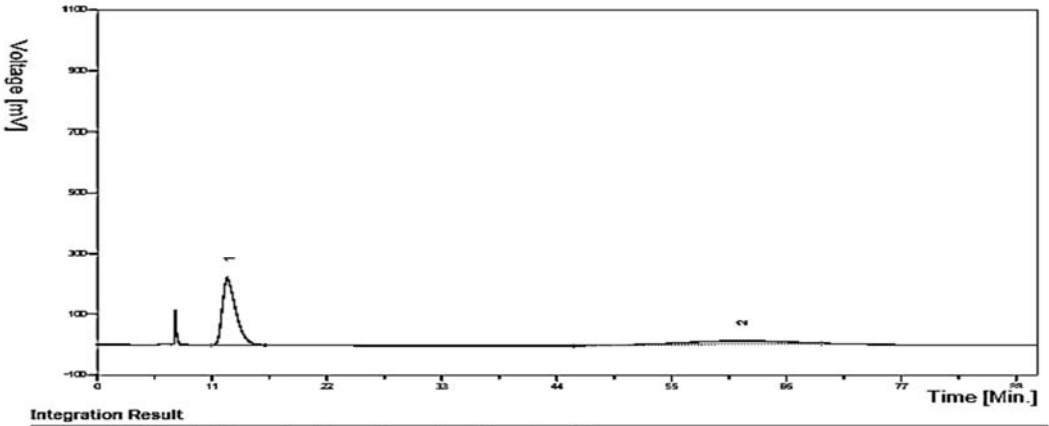
***ent*-5c**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.54	24456.01	98.9726
2	62.59	253.86	1.0274
Total		24709.88	100

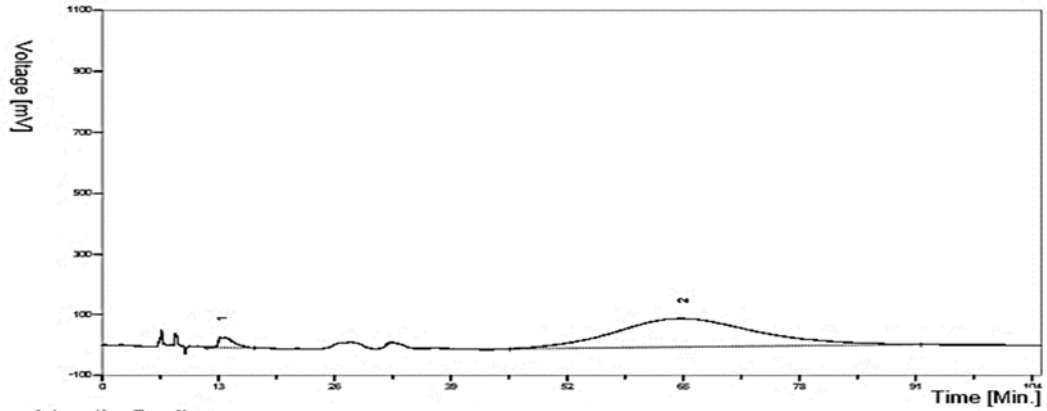
5c + *ent*-5c as *rac*-5c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.44	19422.09	74.8564
2	61.57	6523.71	25.1436
Total		25945.79	100

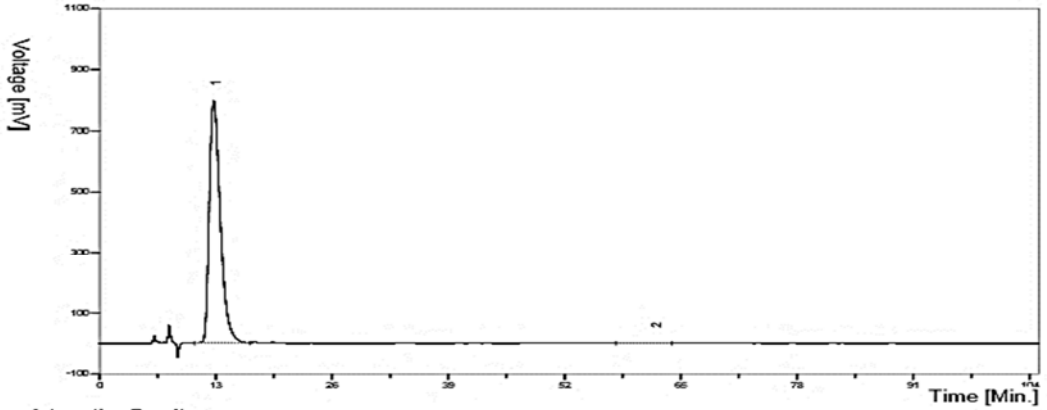
5d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	13.18	3855.33	3.6185
2	64.72	102689.15	96.3815
Total		106544.48	100

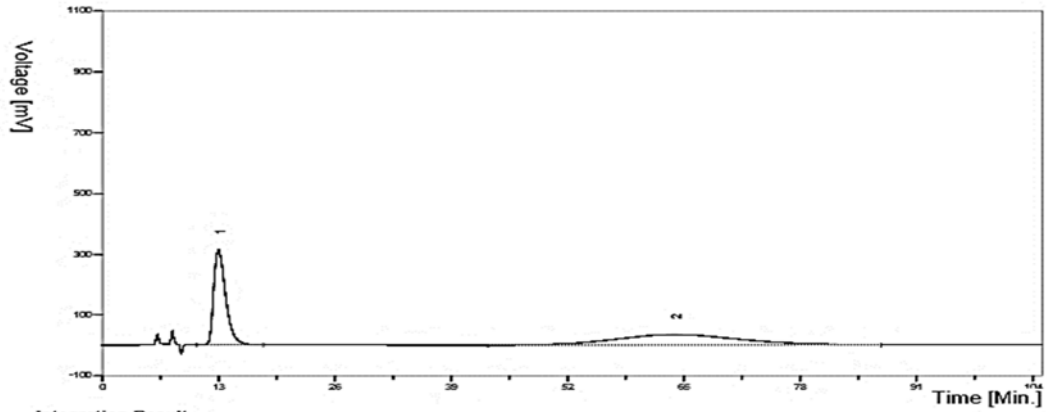
***ent*-5d**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.77	68411.24	99.9047
2	62.06	65.27	0.0953
Total		68476.52	100

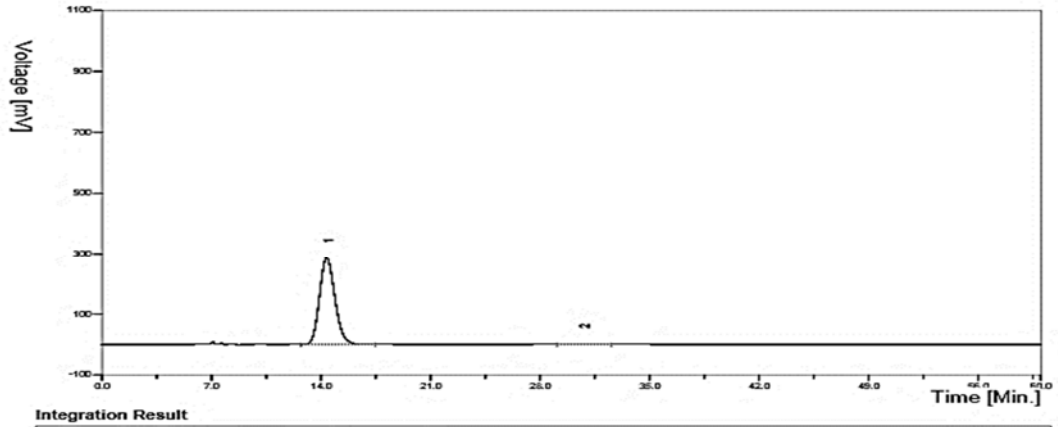
5d + *ent*-5d as *rac*-5d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	12.97	29037.86	46.4210
2	63.92	33515.38	53.5790
Total		62553.24	100

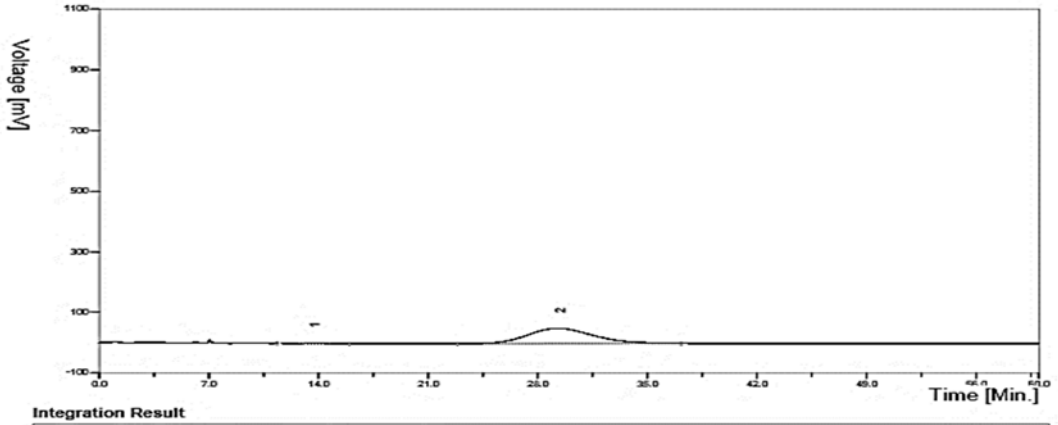
5e



Integration Result

#	Ret. Time(min)	Area Percentage(%)
1	14.37	99.8378
2	30.72	0.1622
Total		100

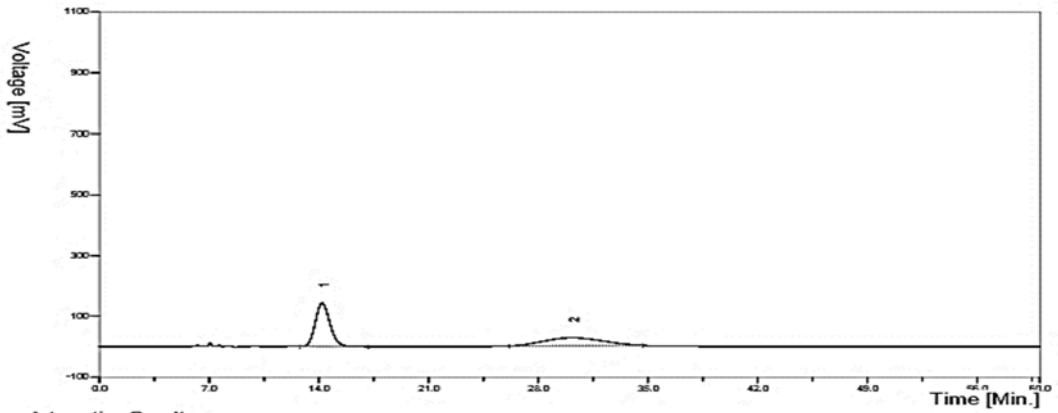
***ent*-5e**



Integration Result

#	Ret. Time(min)	Area Percentage(%)
1	13.63	0.4790
2	29.31	99.5210
Total		100

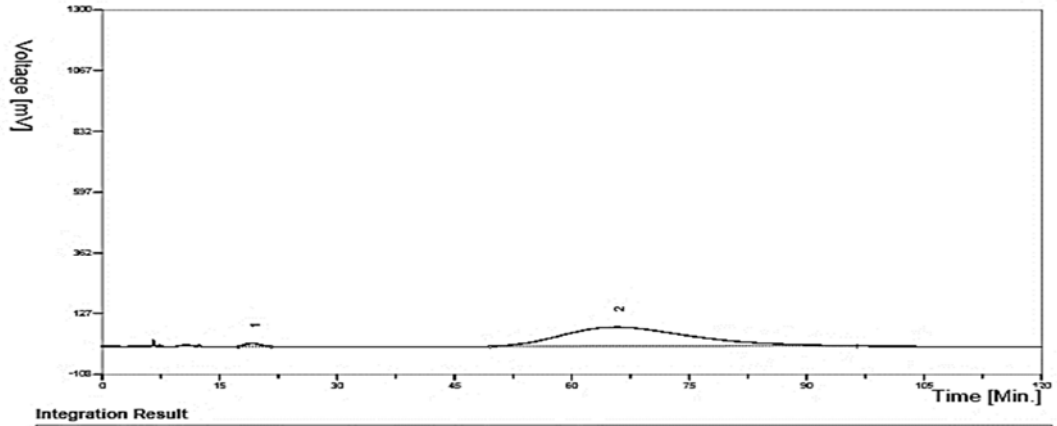
5e + *ent*-5e as *rac*-5e



Integration Result

#	Ret. Time(min)	Area Percentage(%)
1	14.21	57.7961
2	30.15	42.2039
Total		100

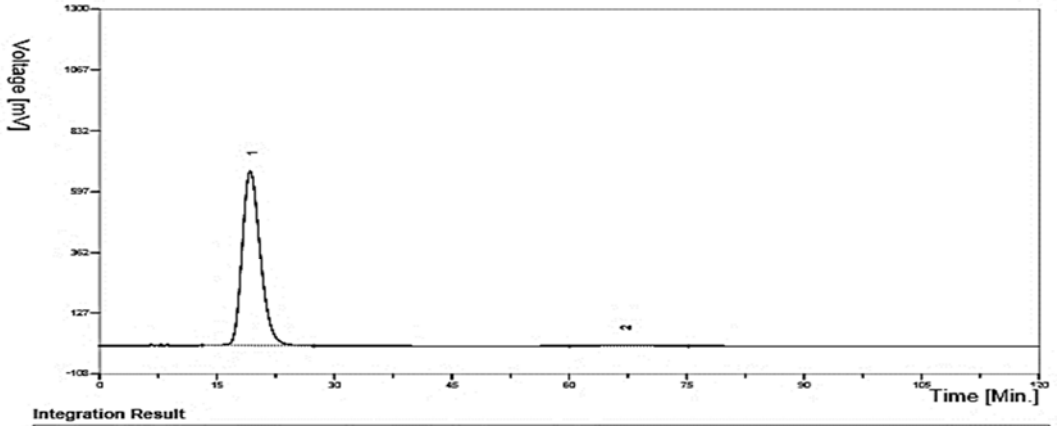
7a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	19.32	1610.73	1.8863
2	65.84	83780.18	98.1137
Total		85390.91	100

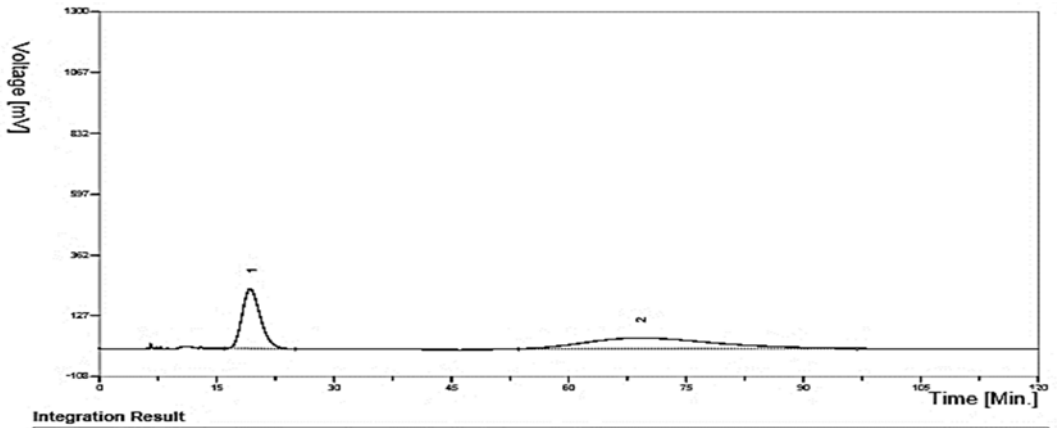
***ent*-7a**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	19.26	108276.60	99.4288
2	66.97	622.08	0.5712
Total		108898.68	100

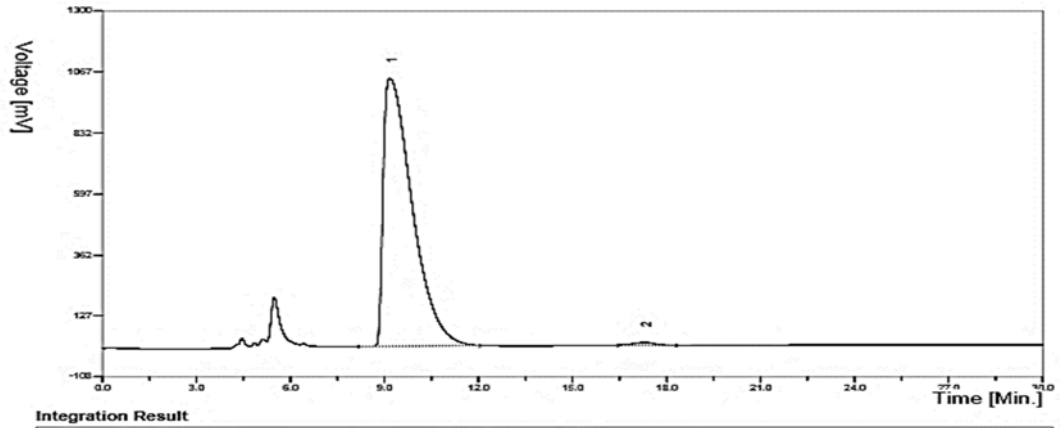
7a + *ent*-7a as *rac*-7a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	19.28	36962.67	43.8680
2	69.02	47296.26	56.1320
Total		84258.93	100

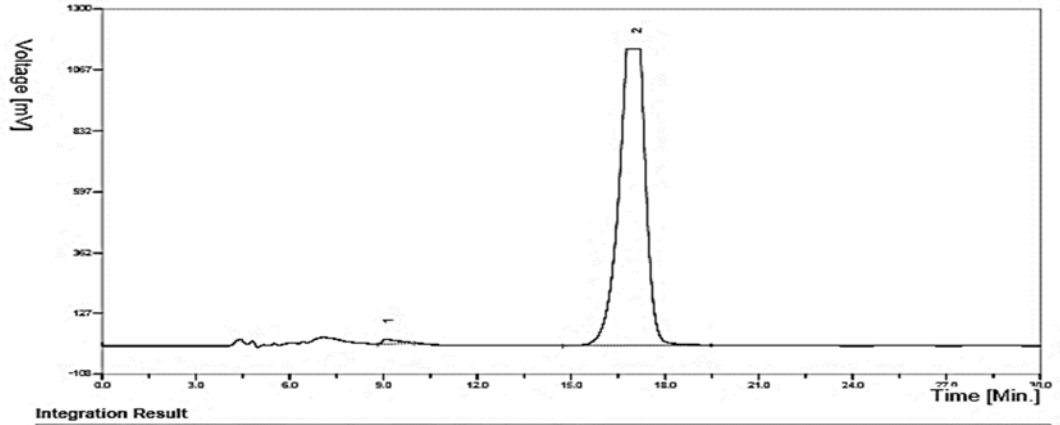
7b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.17	66292.44	99.2548
2	17.29	497.72	0.7452
Total		66790.16	100

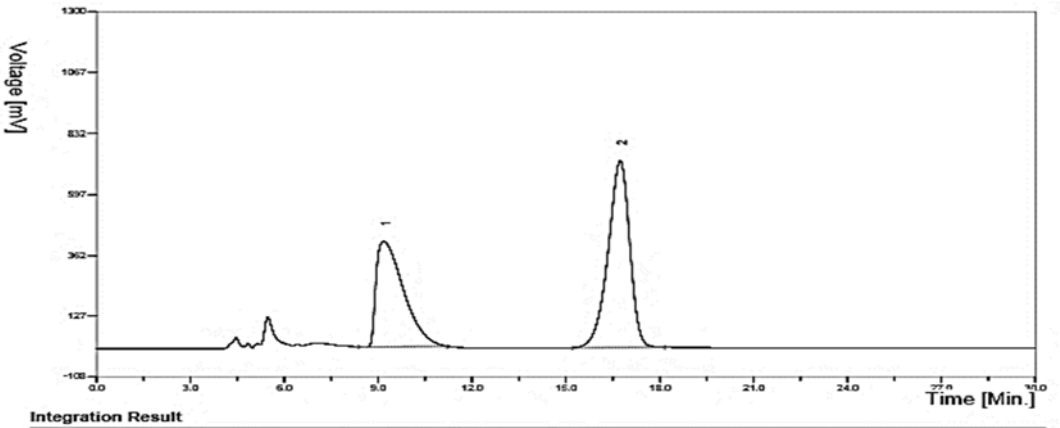
***ent*-7b**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.08	629.06	0.9080
2	17.04	68652.85	99.0920
Total		69281.91	100

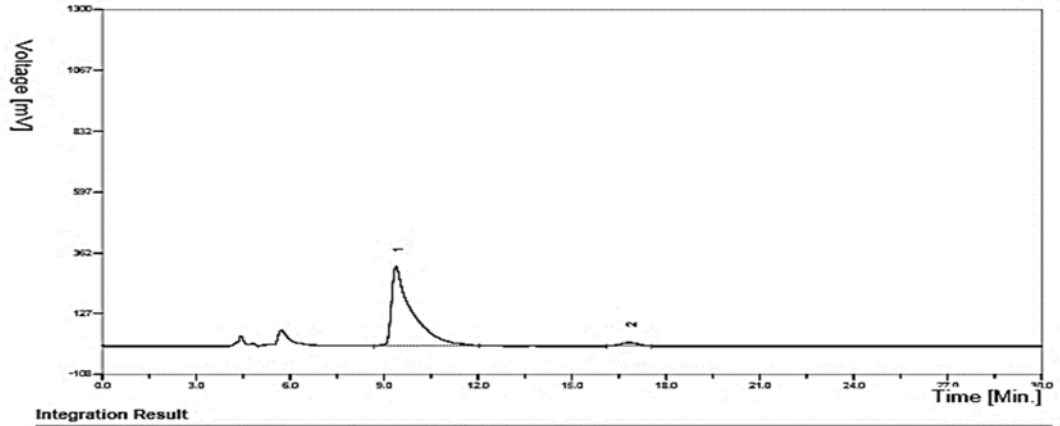
7b + *ent*-7b as *rac*-7b



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.18	24684.83	41.5671
2	16.74	34700.69	58.4329
Total		59385.52	100

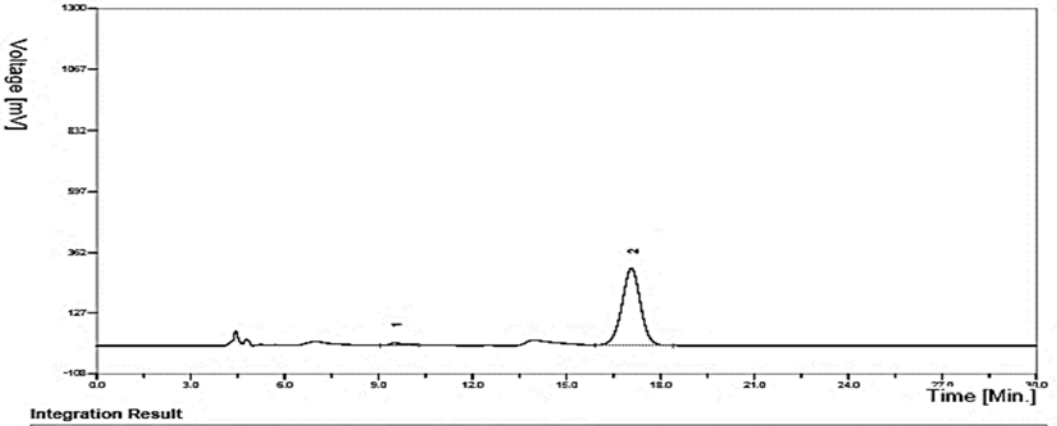
7c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.38	13708.73	96.4471
2	16.84	504.99	3.5529
Total		14213.73	100

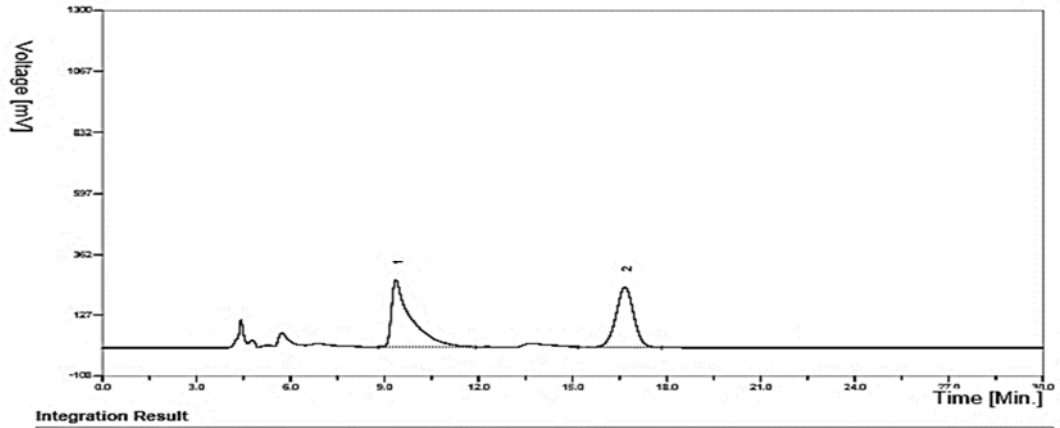
***ent*-7c**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.51	229.36	1.8576
2	17.07	12118.10	98.1424
Total		12347.47	100

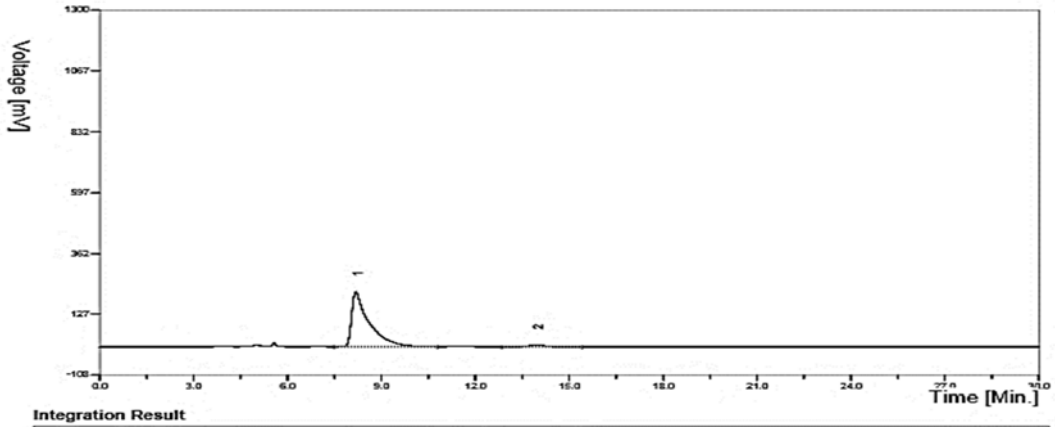
7c + *ent*-7c as *rac*-7c



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	9.36	11110.53	55.1772
2	16.67	9025.58	44.8228
Total		20136.11	100

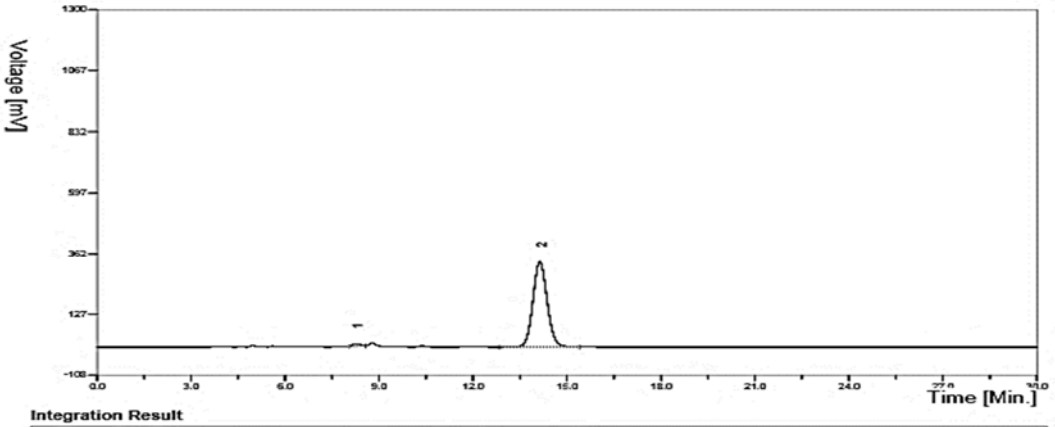
7d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.18	8134.36	97.4310
2	13.95	214.48	2.5690
Total		8348.84	100

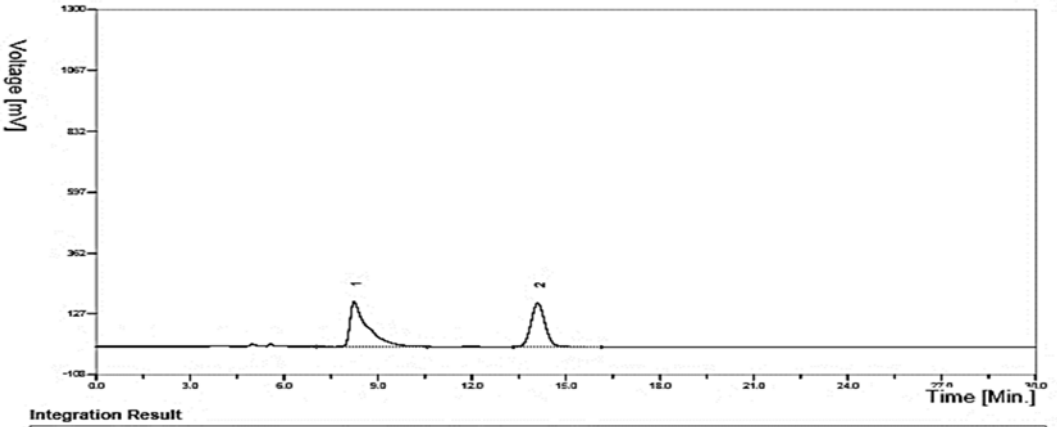
***ent*-7d**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.26	125.36	1.1982
2	14.13	10337.57	98.8018
Total		10462.93	100

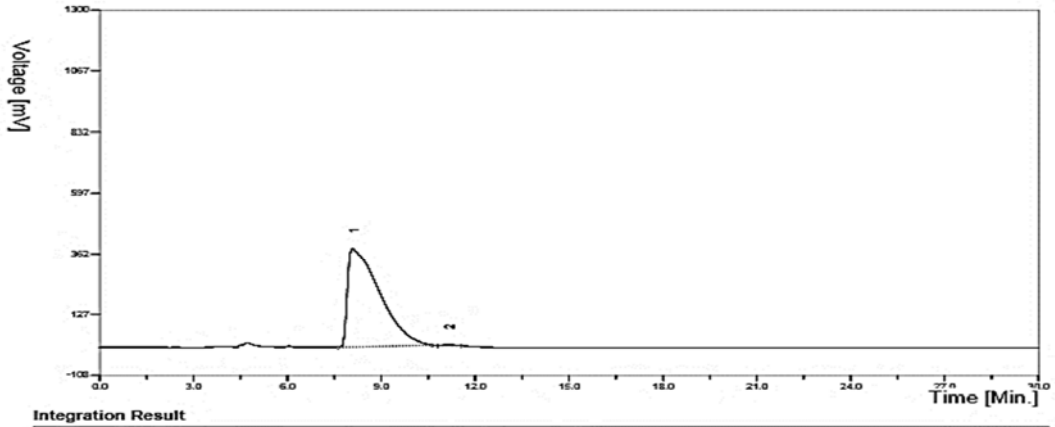
7d + *ent*-7d as *rac*-7d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.24	6564.77	55.8234
2	14.10	5195.11	44.1766
Total		11759.89	100

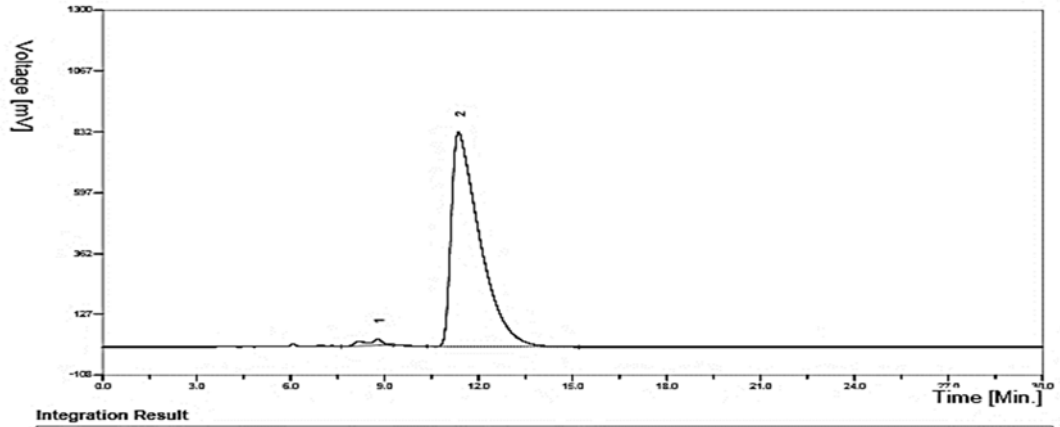
7e



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.08	27079.76	99.6597
2	11.12	92.47	0.3403
Total		27172.23	100

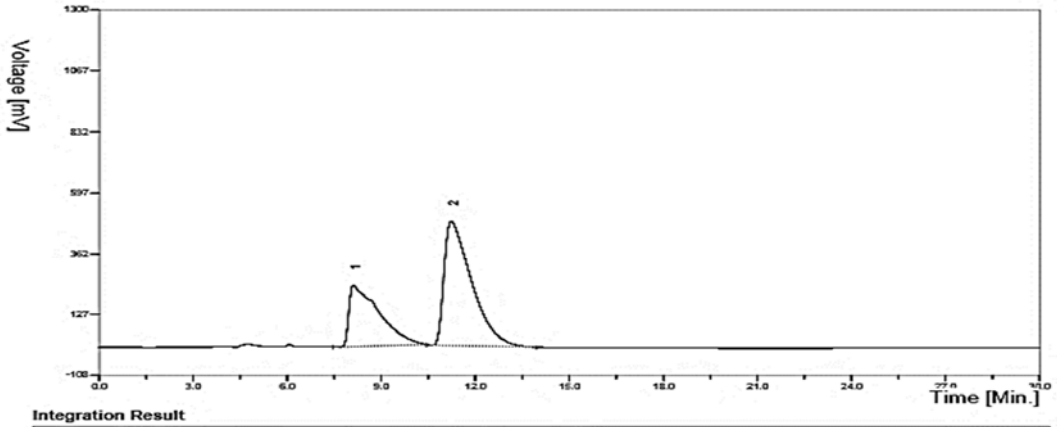
***ent*-7e**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.77	904.47	1.7097
2	11.36	51999.11	98.2903
Total		52903.58	100

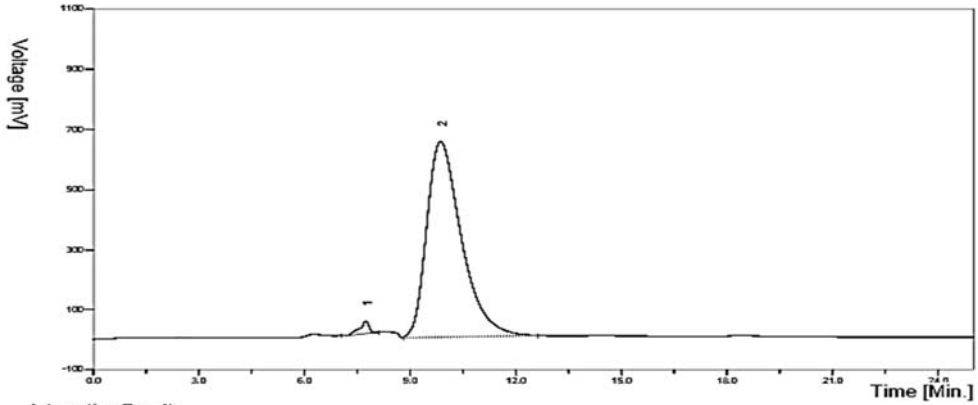
7e + *ent*-7e as *rac*-7d



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	8.11	15498.42	34.7082
2	11.24	29155.11	65.2918
Total		44653.53	100

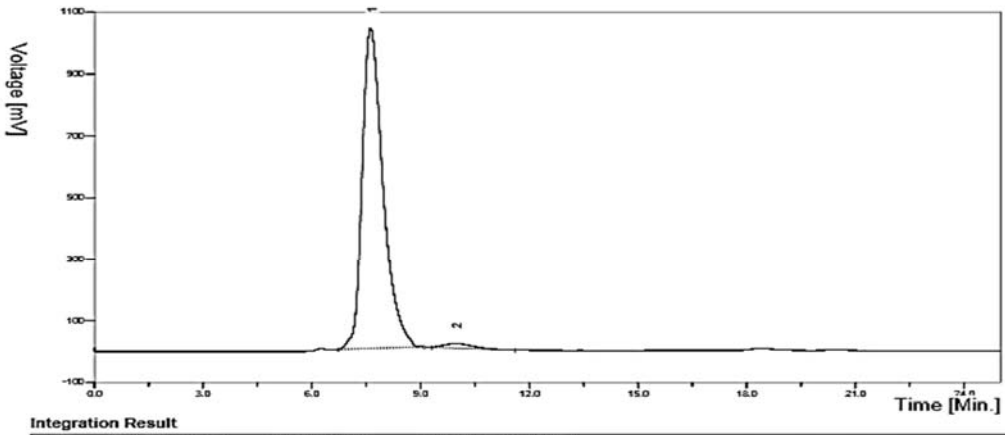
9



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	7.74	694.35	1.5290
2	9.86	44718.91	98.4710
Total		45413.27	100

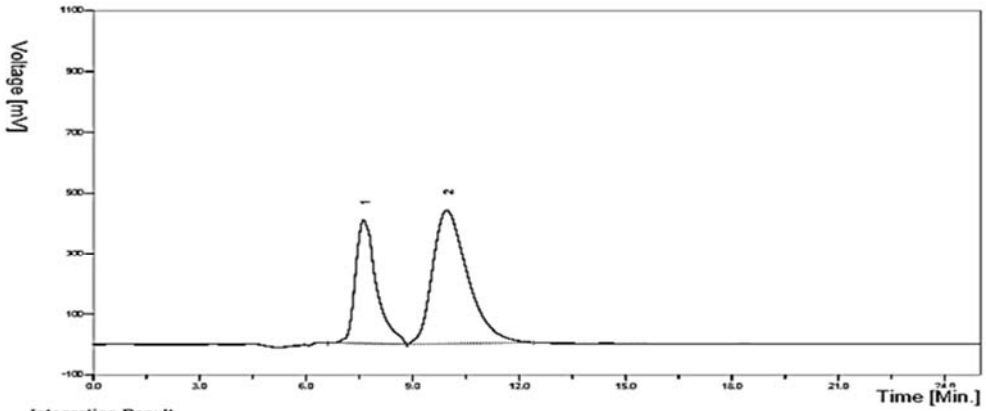
***ent*-9**



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	7.62	41705.21	98.1779
2	9.96	773.99	1.8221
Total		42479.21	100

9+ *ent*-9 as *rac*-9a



Integration Result

#	Ret. Time(min)	Area(mv.sec)	Area Percentage(%)
1	7.62	16739.03	35.6317
2	9.96	30238.94	64.3683
Total		46977.97	100