Catalyst-Controlled Switch in Diastereoselectivities: Enantioselective Construction of Functionalized 3,4-Dihydro-2*H*-thiopyrano[2,3-*b*]quinoline with Three Contiguous Stereocenters

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Supporting Information

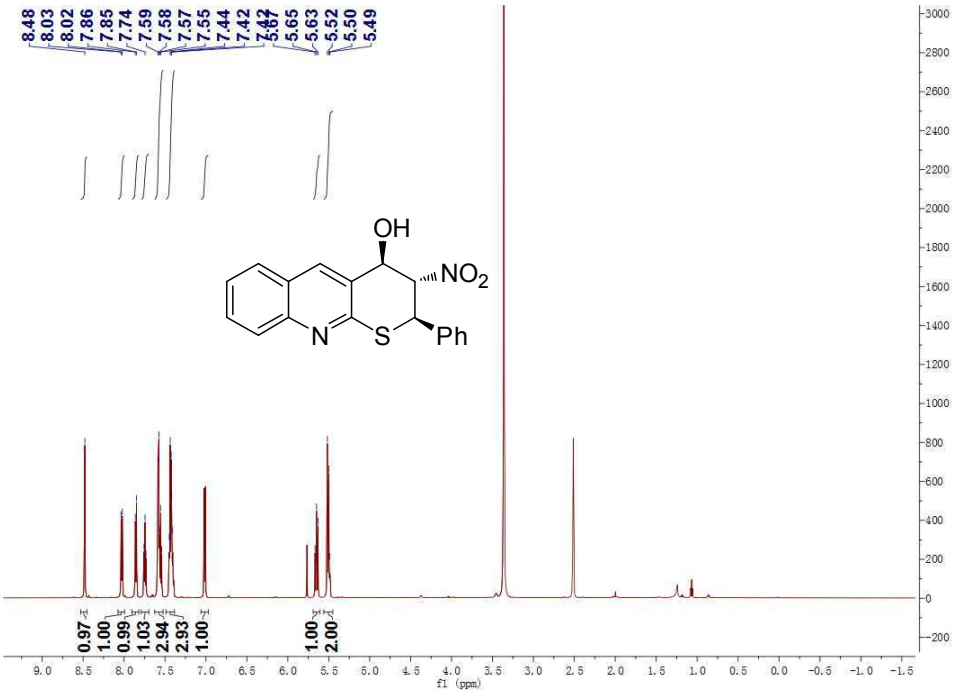
1.^{1}H NMR and ^{13}C NMR spectra. S2

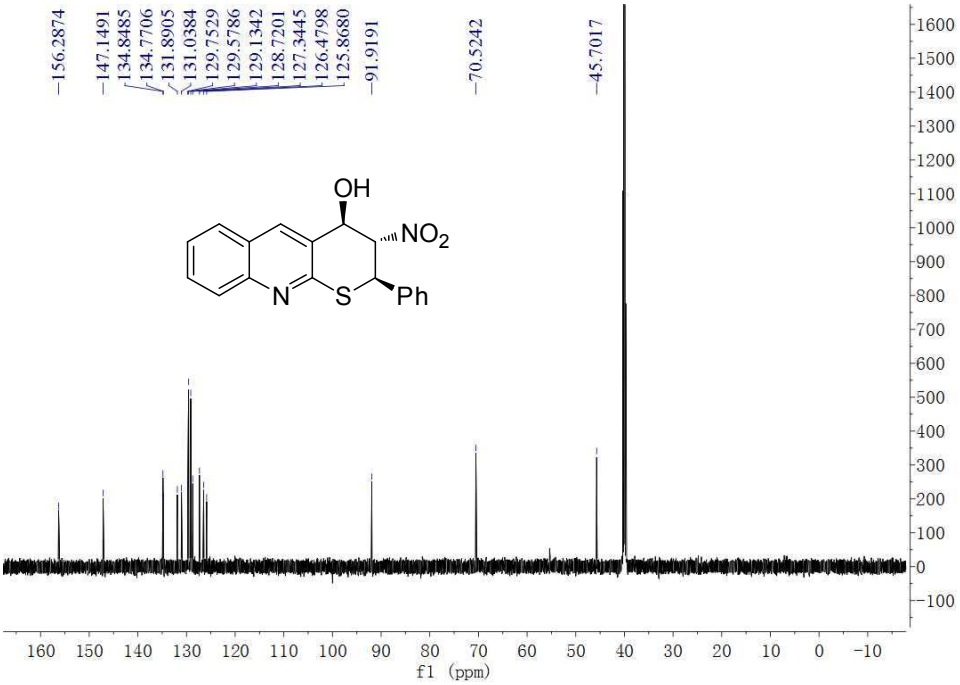
2.HPLC spectra. S16

3. X-ray data of enantiopure of 3ae and 3'ae S30

1. 1H NMR and 13C NMR spectra

3aa





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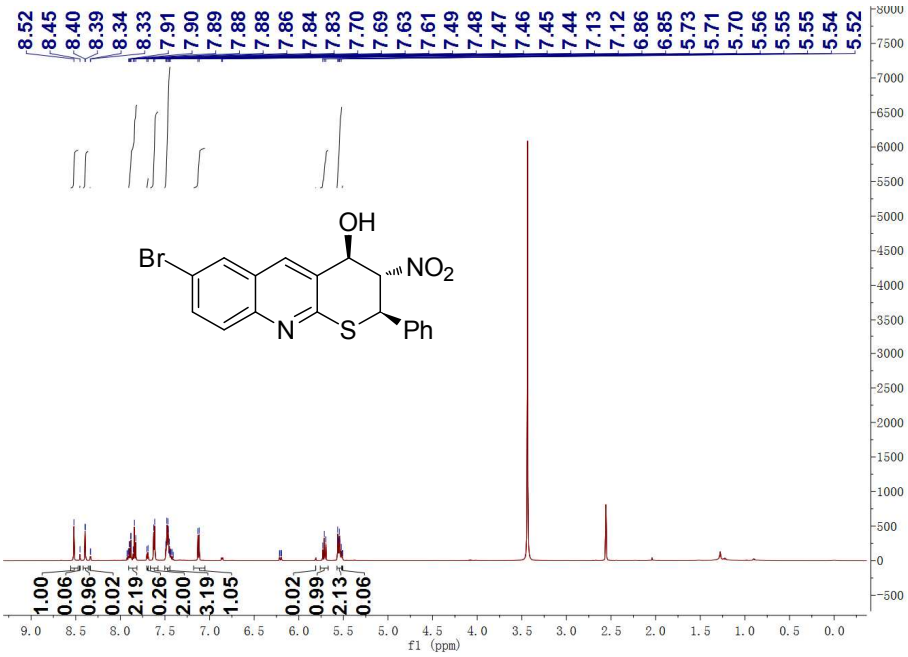
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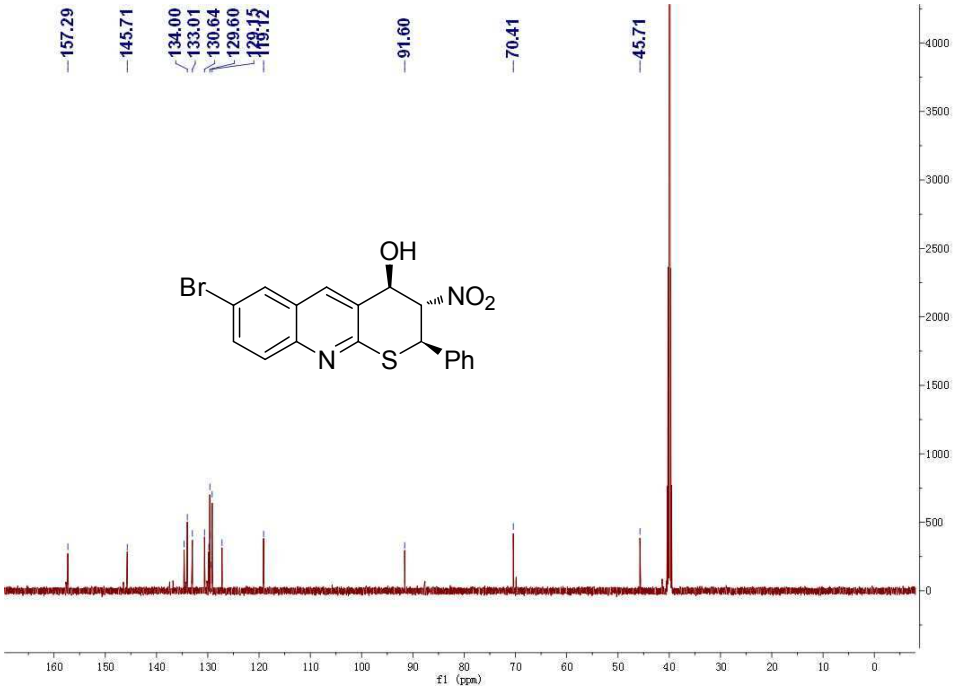
7.84
7.83
7.70
7.69
7.63
7.61
7.49
7.48
7.47
7.46
7.45
7.44
7.13
7.12
6.86
6.85
5.73
5.71
5.70
5.56
5.55
5.55
5.54
5.52
OH
Br
NO2
N
S
Ph
1.00
0.06
0.96
0.02
2.19
0.26
2.00
3.19
1.05
0.02
0.99
2.13
0.06
f1 (ppm)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91.60
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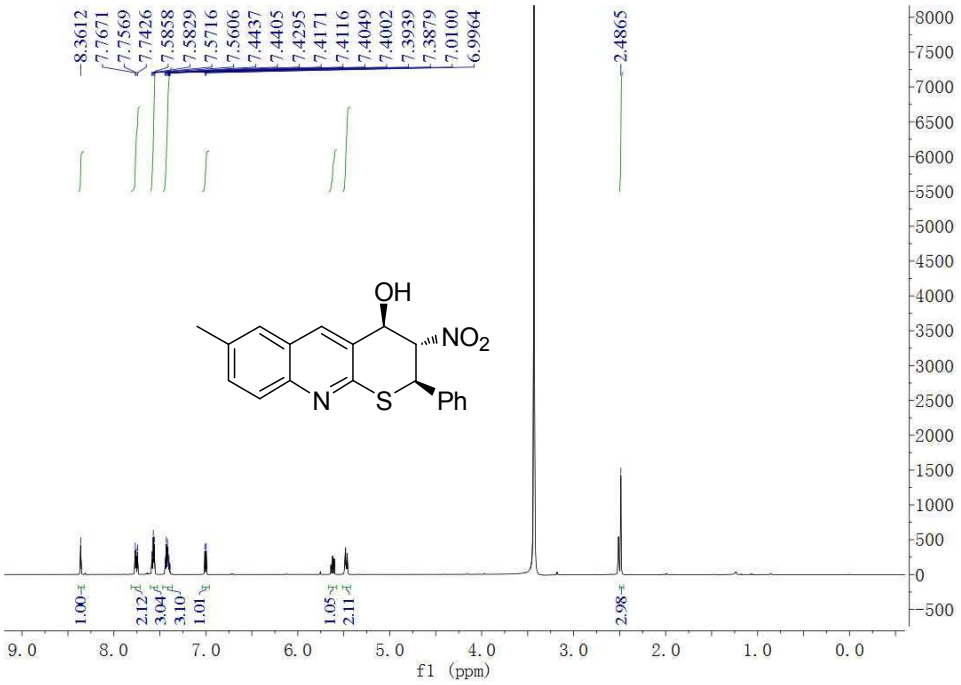
OH
Br
NO2
N
S
Ph
f1 (ppm)

3ca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7.4295
7.4171
7.4116
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7.4002
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7.3879
7.0100
6.9964
2.4865
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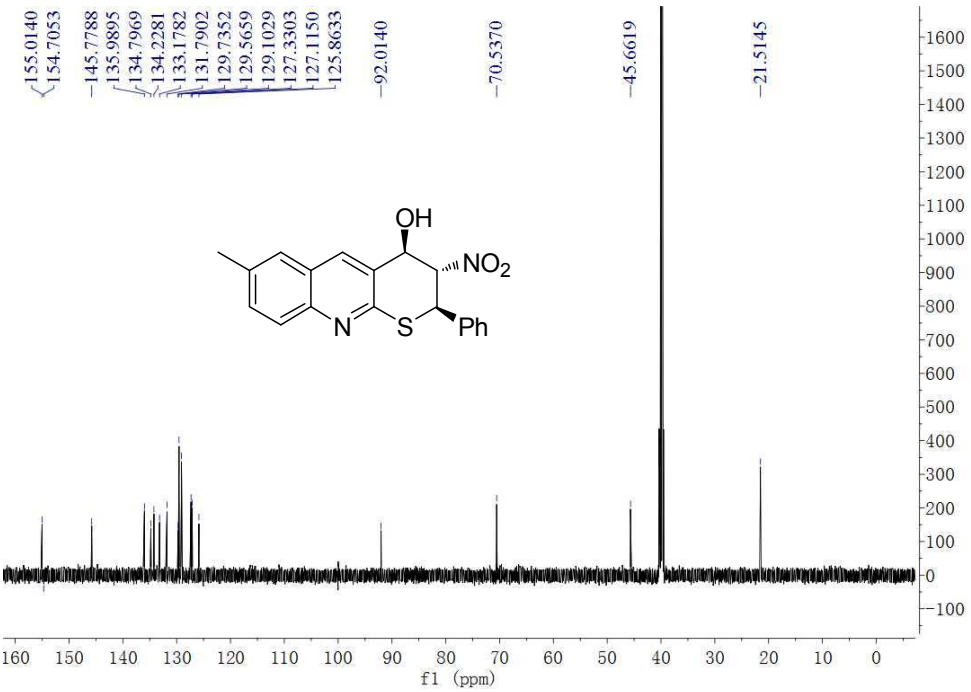
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129.1029
127.3303
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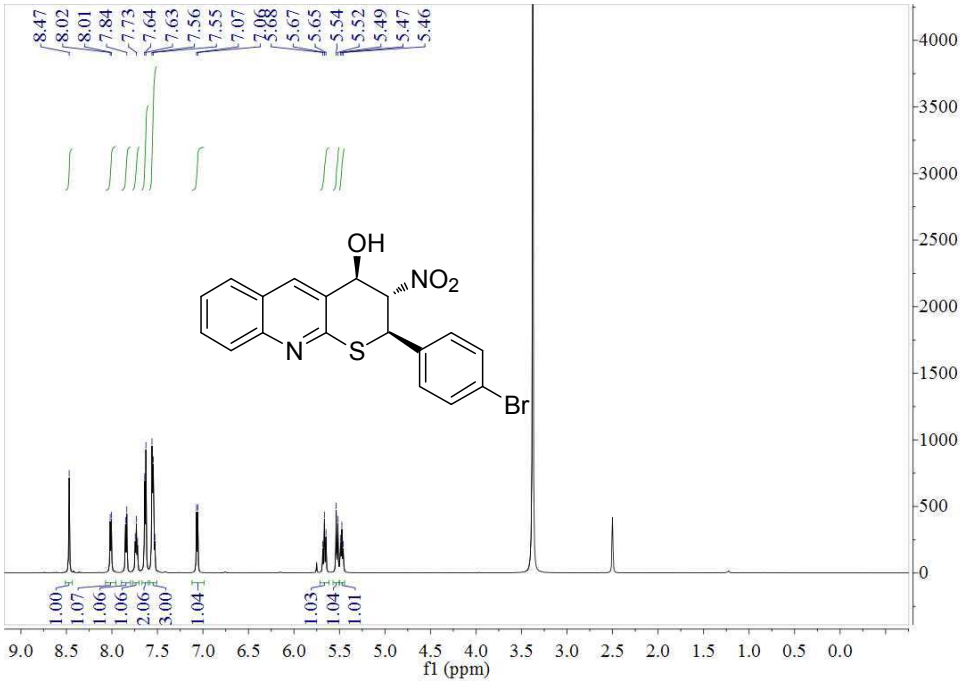
OH
NO2
N
S
Ph
f1 (ppm)

3ab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7.56
7.55
7.07
7.06
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5.67
5.65
5.54
5.52
5.49
5.47
5.46
OH
NO2
N
S
Br
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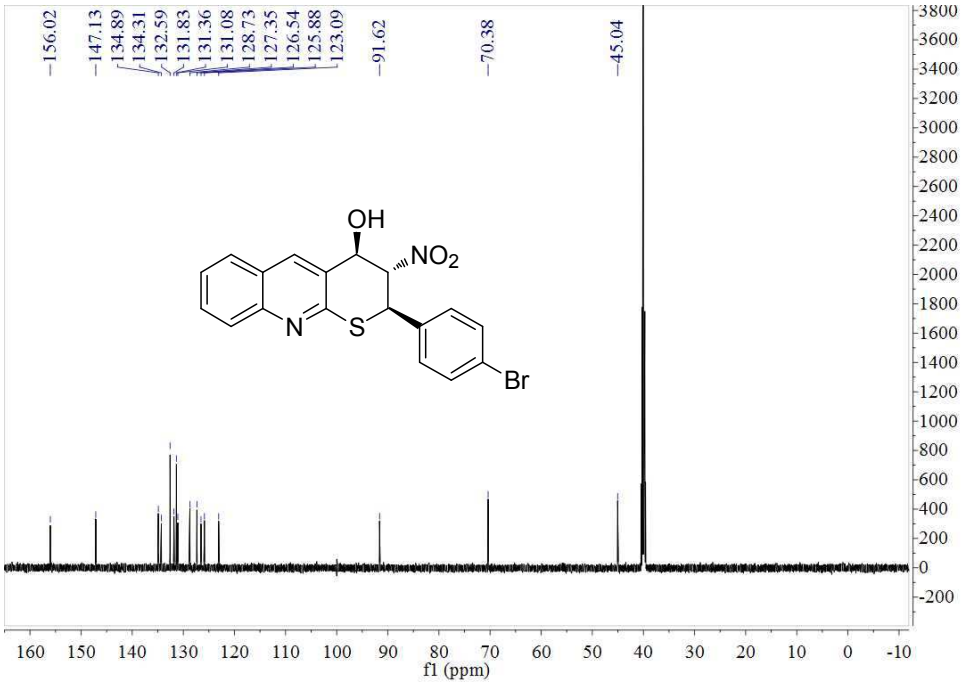
1.01
f1 (ppm)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132.59
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131.36
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123.09
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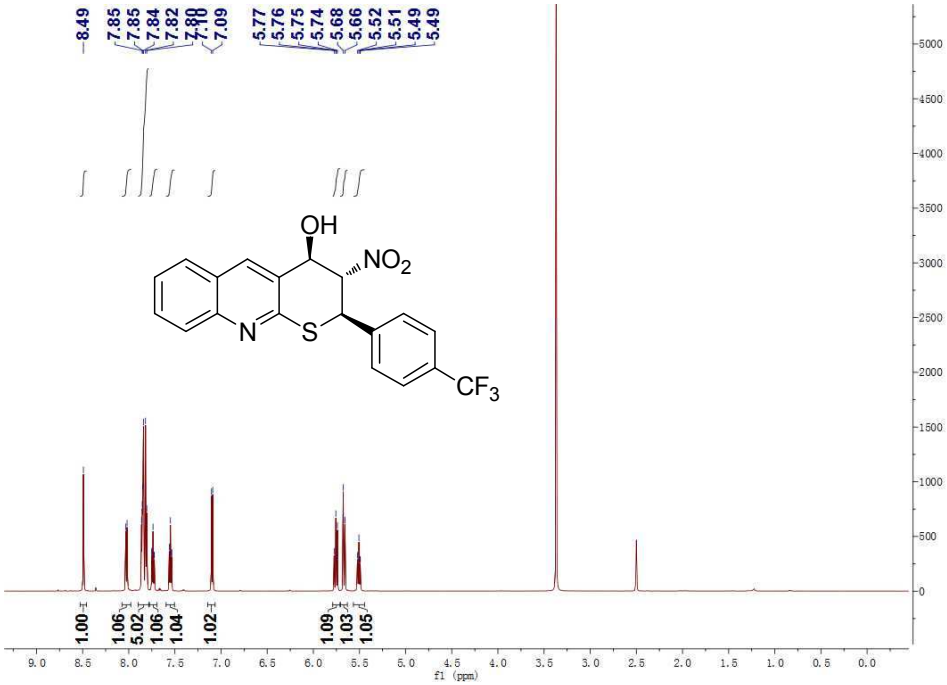
OH
NO2
N
S
Br
f1 (ppm)

3ac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5.68
5.66
5.52
5.51
5.49
5.49
OH
NO2
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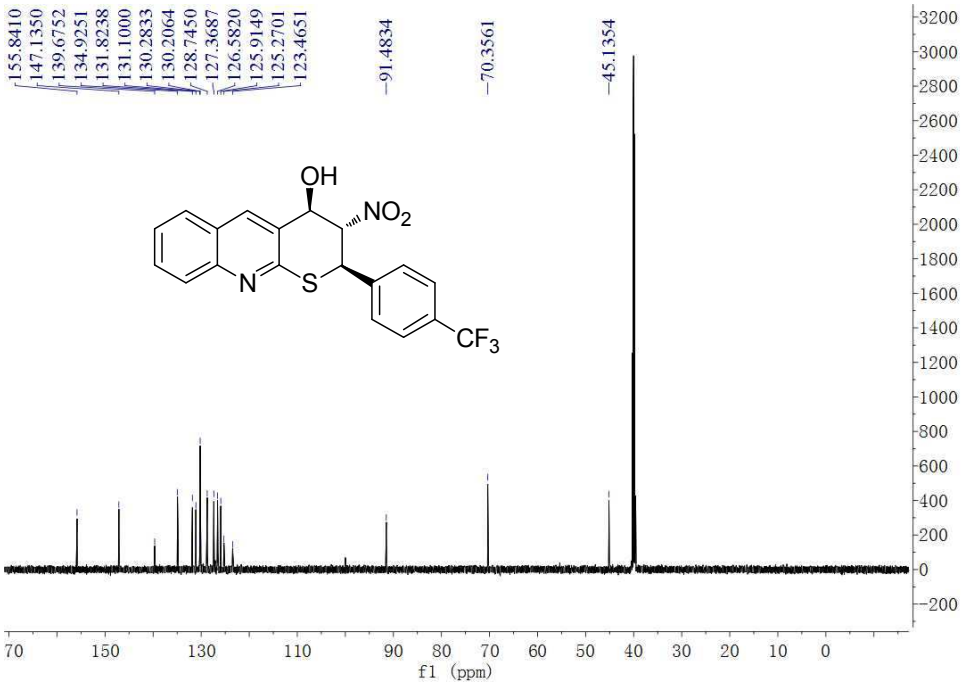
1.09
1.03
1.05
f1 (ppm)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125.9149
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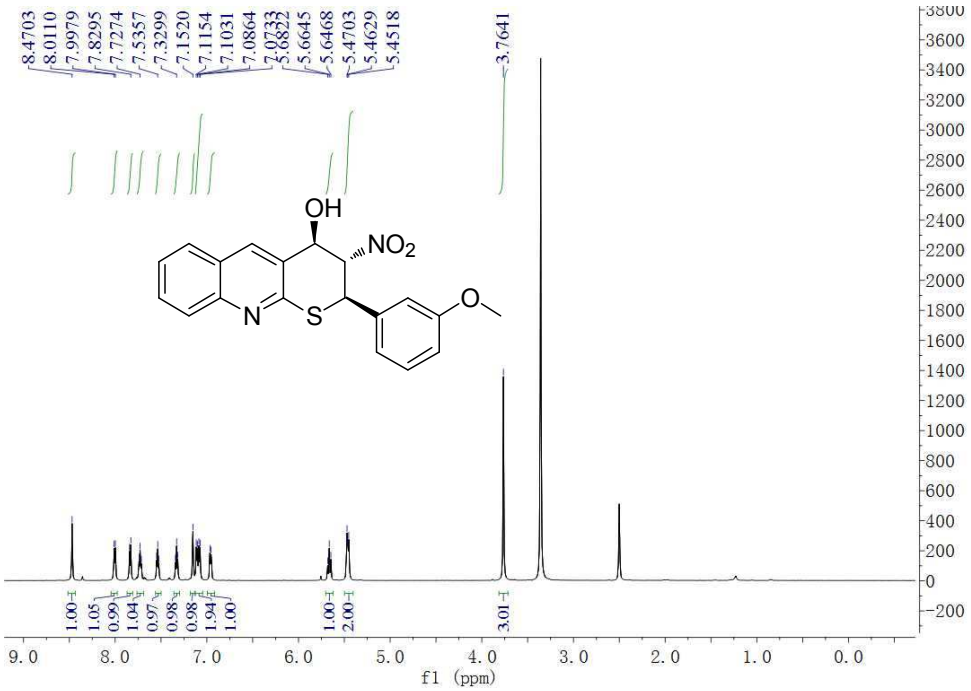
NO2
N
S
CF3
f1 (ppm)

3ad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7.0733
5.6822
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5.6468
5.4703
5.4629
5.4518
3.7641
OH
NO2
N
S
O
1.00
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0.97
0.98
0.98
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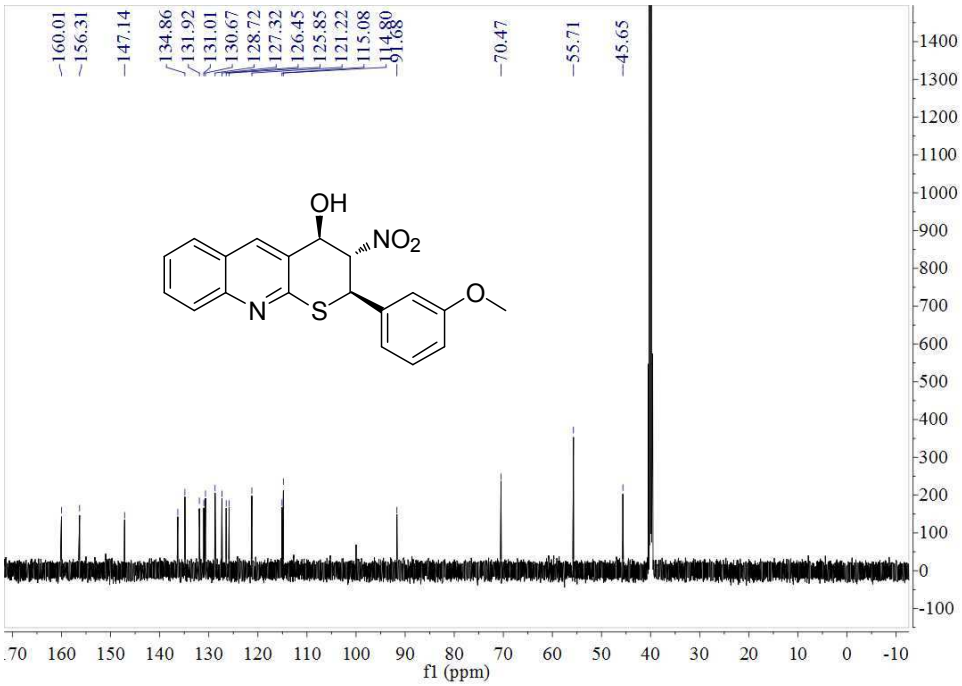
3.01
f1 (ppm)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147.14
134.86
131.92
131.01
130.67
128.72
127.32
126.45
125.85
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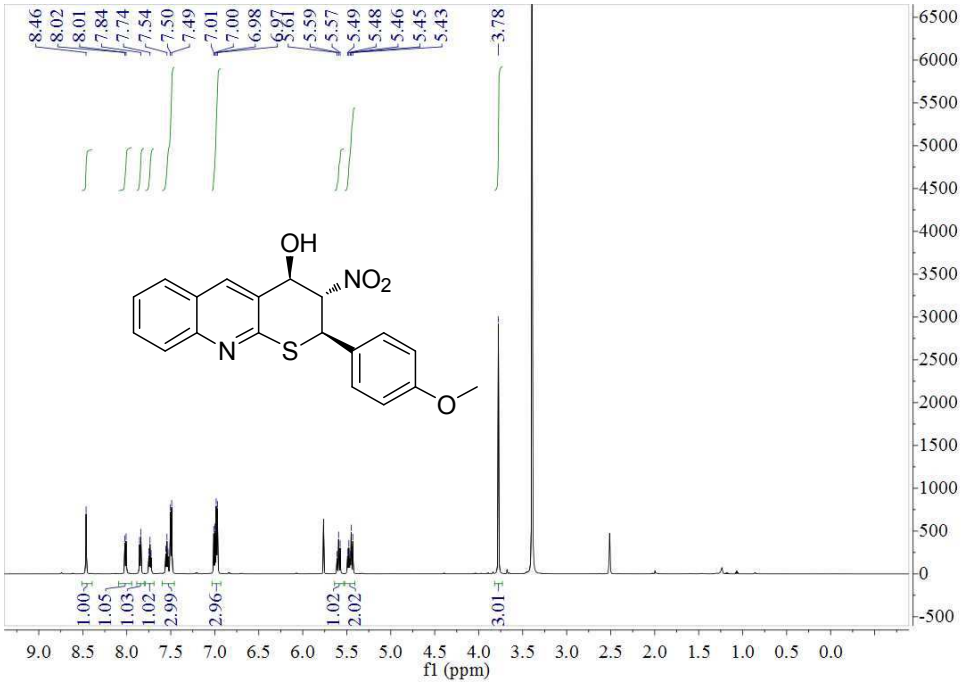
114.80
91.68
70.47
55.71
45.65
OH
NO2
N
S
O
f1 (ppm)

3ae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6.61
5.59
5.57
5.49
5.48
5.46
5.45
5.43
3.78
OH
NO2
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1.02
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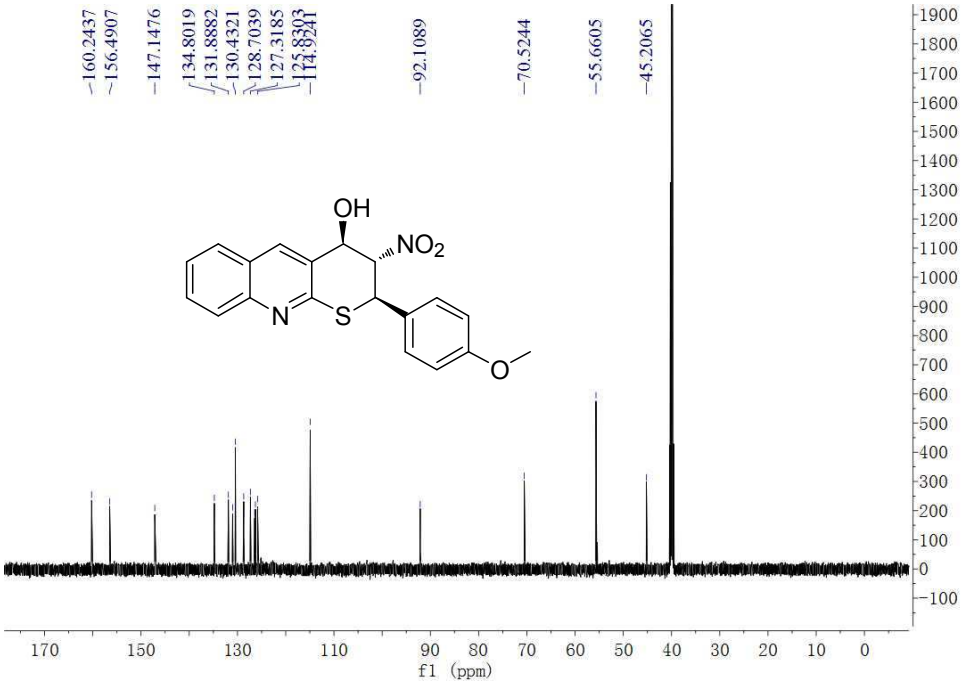
1.02
2.02
3.01
f1 (ppm)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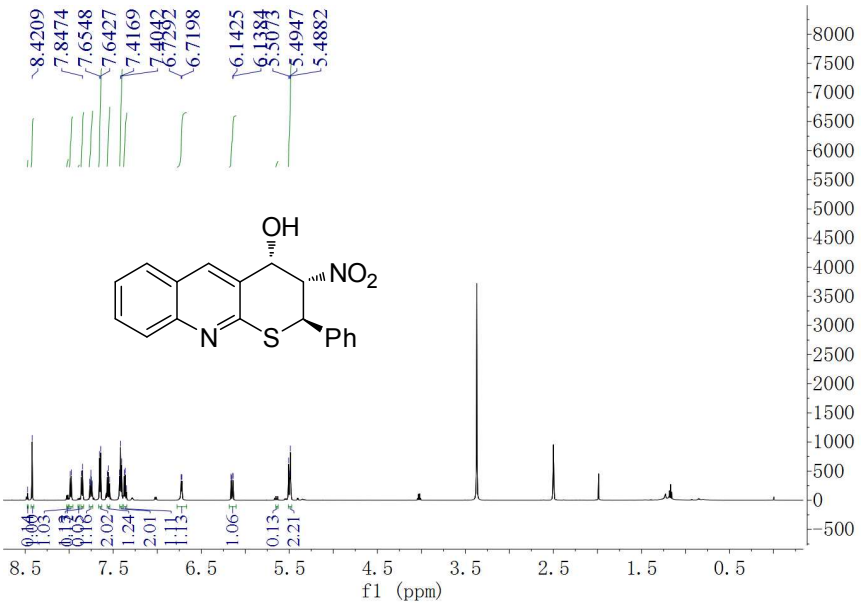
NO2
N
S
O
f1 (ppm)

3'aa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5.4947
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OH
NO2
N
S
Ph
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1.03
0.13
0.18
2.02
1.24
2.01
1.11
1.13
1.06
0.13
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7.5
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5.5
4.5
3.5
2.5
1.5
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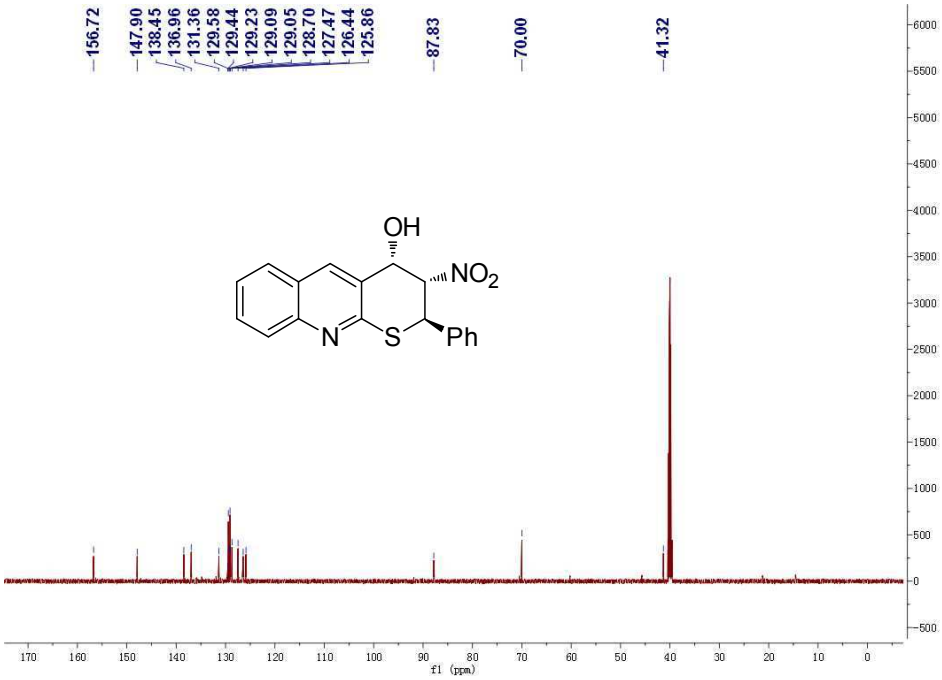
f1 (ppm)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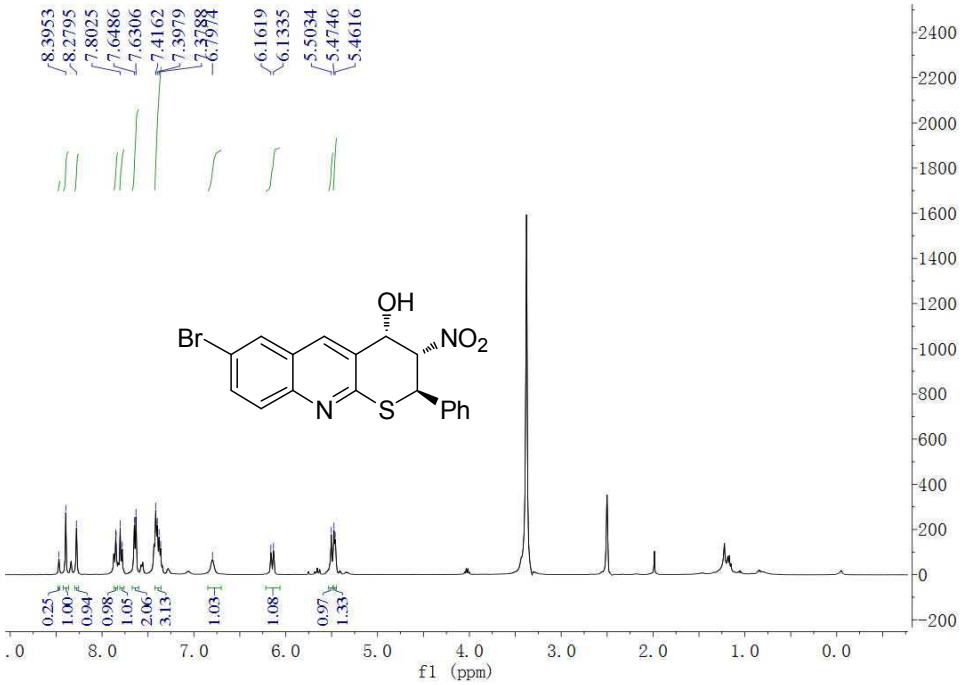
OH
NO2
N
S
Ph
f1 (ppm)

3'ba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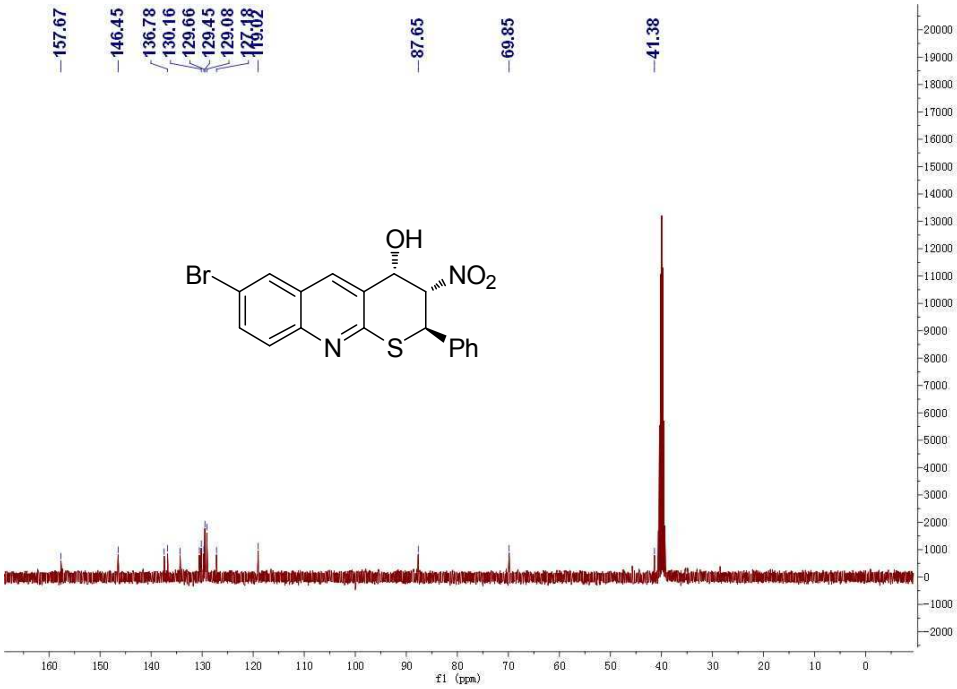
N
S
Ph
f1 (ppm)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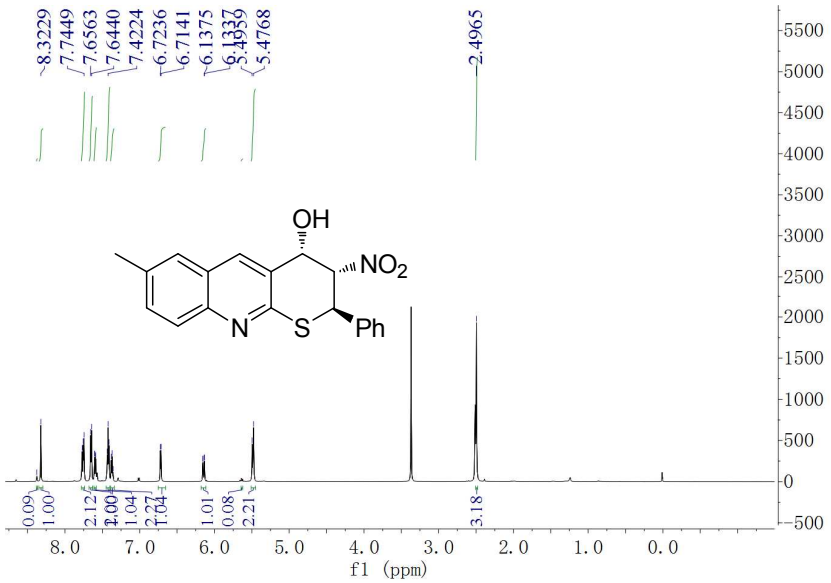
Br
NO2
N
S
Ph
f1 (ppm)

3'ca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2.4965
OH
NO2
N
S
Ph
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1.00
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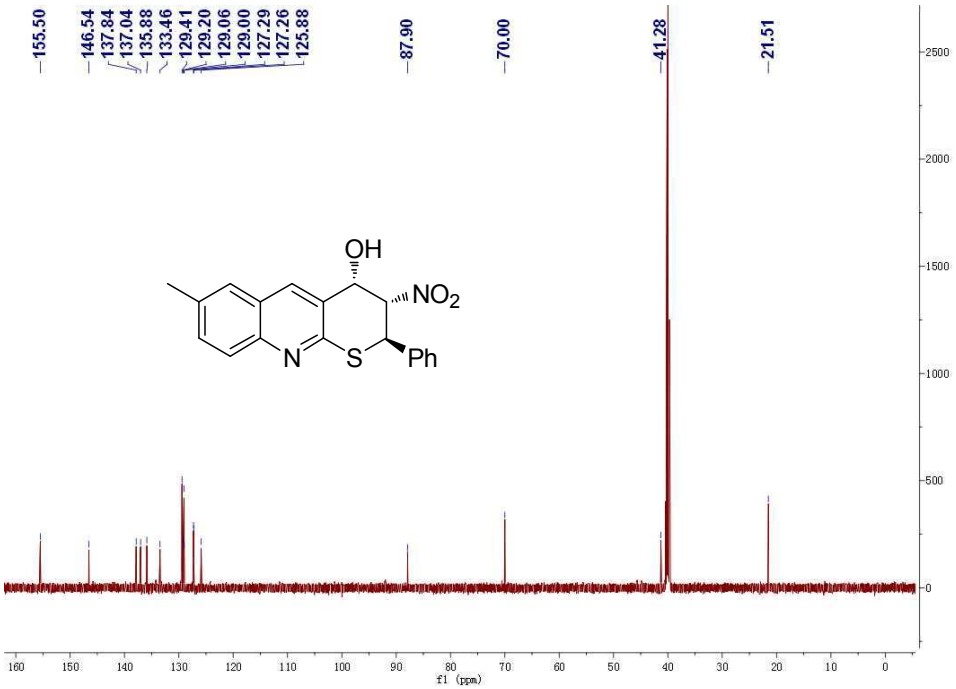
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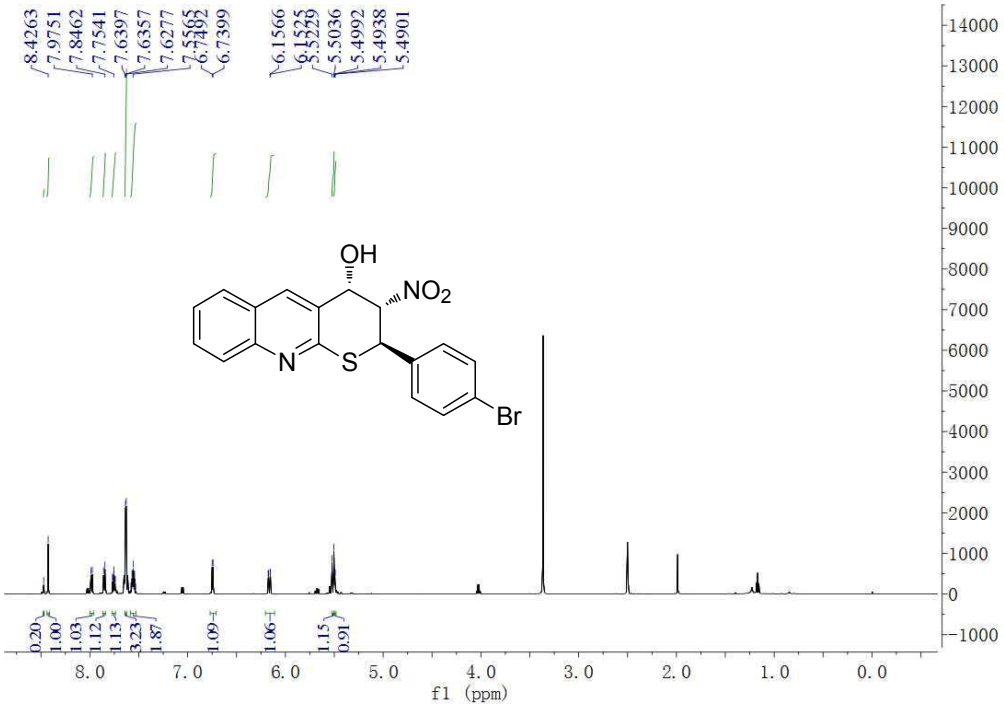
NO2
N
S
Ph
f1 (ppm)

3'ab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7.7492
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6.1566
6.1525
5.5229
5.5036
5.4992
5.4938
5.4901
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NO2
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S
Br
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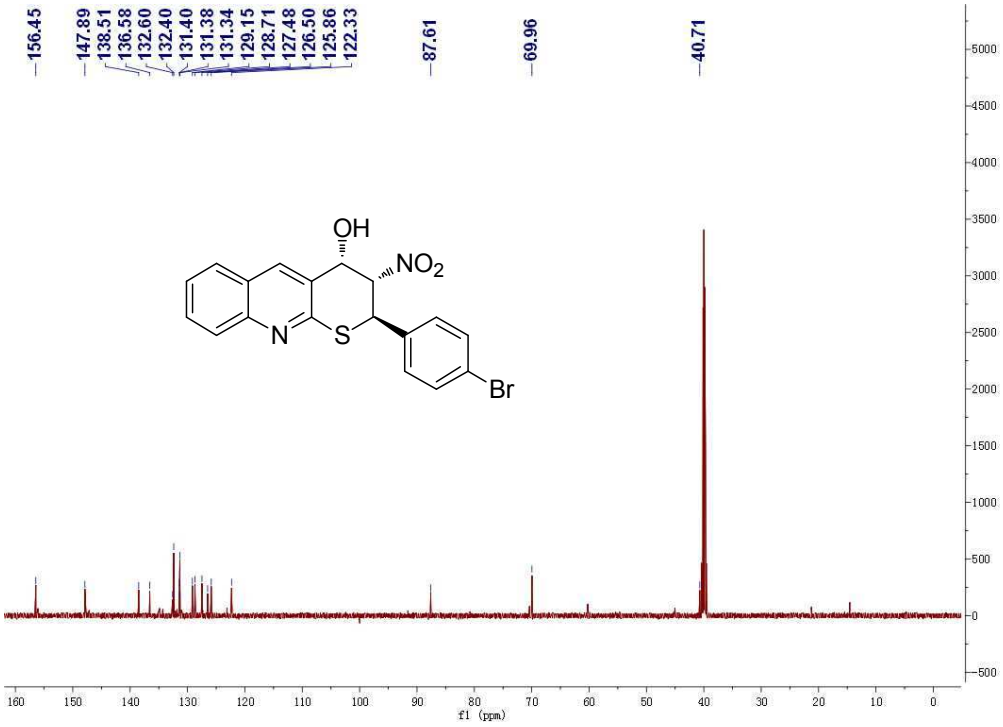
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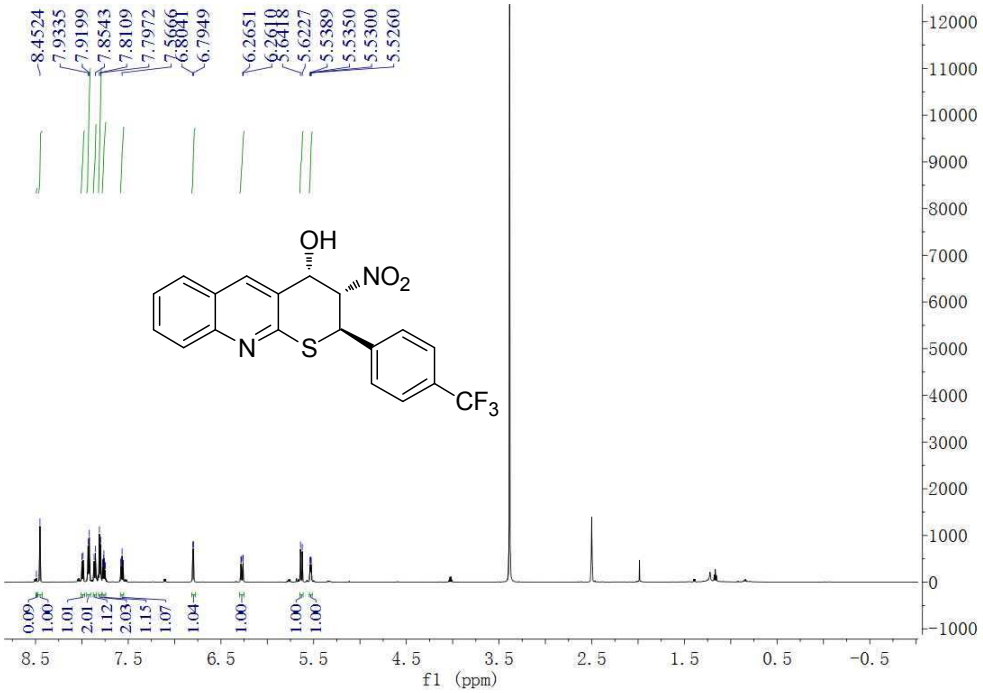
N
S
Br
f1 (ppm)

3'ac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6.6418
5.6227
5.5389
5.5350
5.5300
5.5260
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NO2
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S
CF3
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1.00
1.01
2.01
1.12
2.03
1.15
1.07
1.04
1.00
1.00
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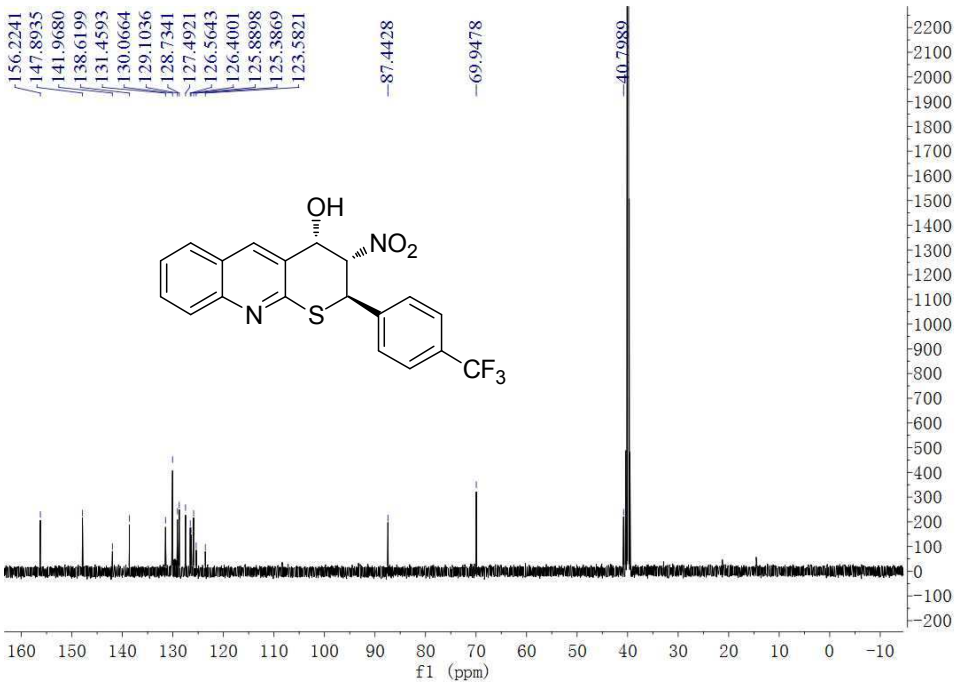
f1 (ppm)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125.8898
125.3869
123.5821
87.4428
69.9478
40.7989
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NO2
N
S
CF3
160
150
140
130
120
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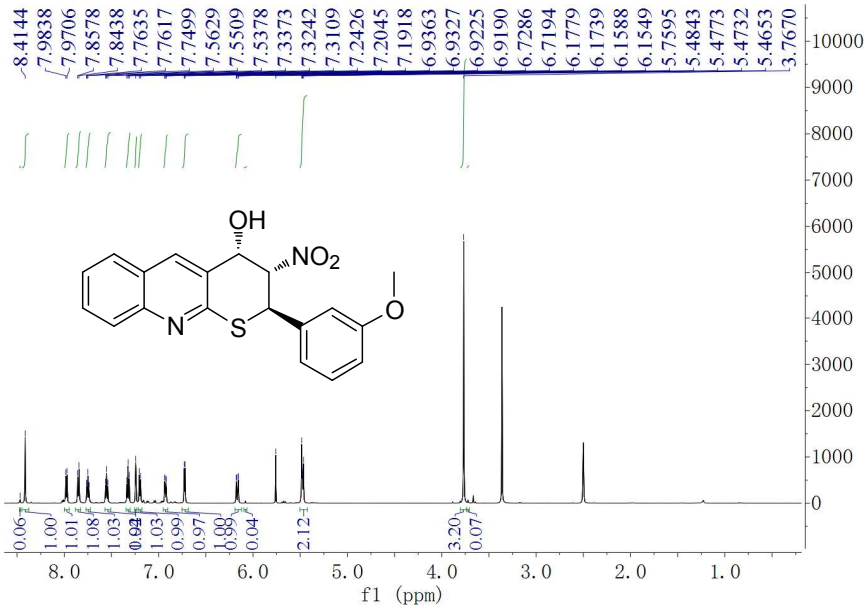
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3'ad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7.3242
7.3109
7.2426
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7.1918
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6.9225
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6.7286
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3.7670
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NO2
N
S
O
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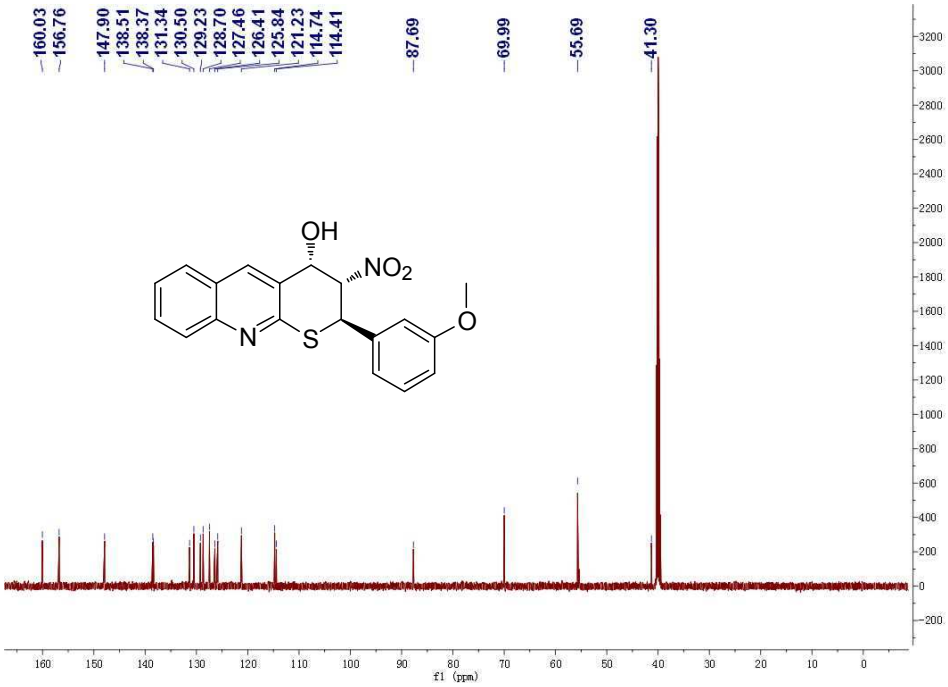
f1 (ppm)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69.99
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41.30
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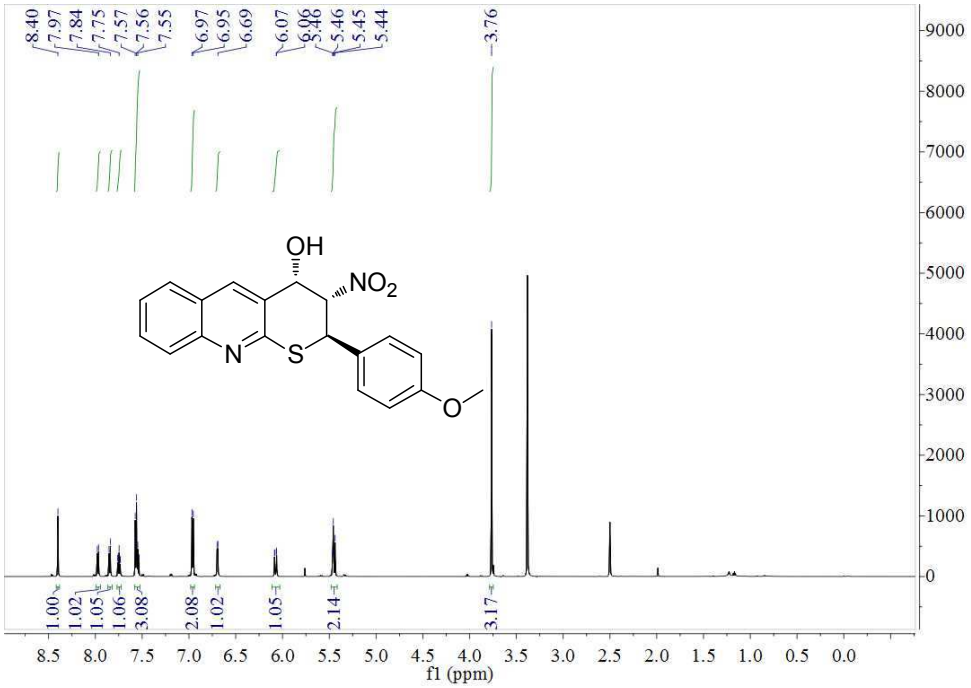
NO2
N
S
O
f1 (ppm)

3'ae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5.45
5.44
3.76
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NO2
N
S
O
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1.05
2.14
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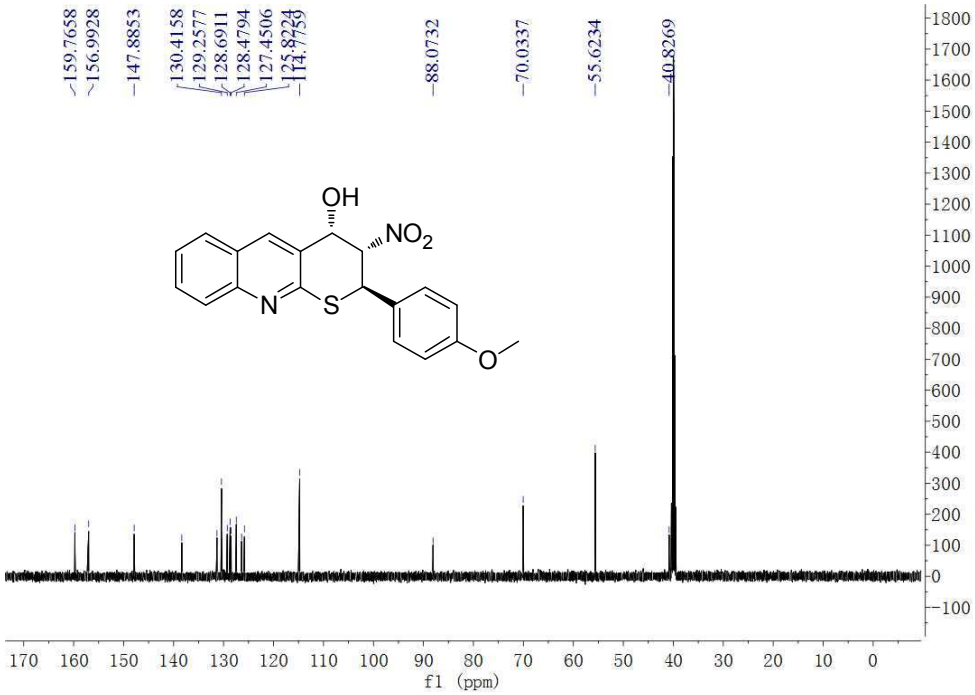
f1 (ppm)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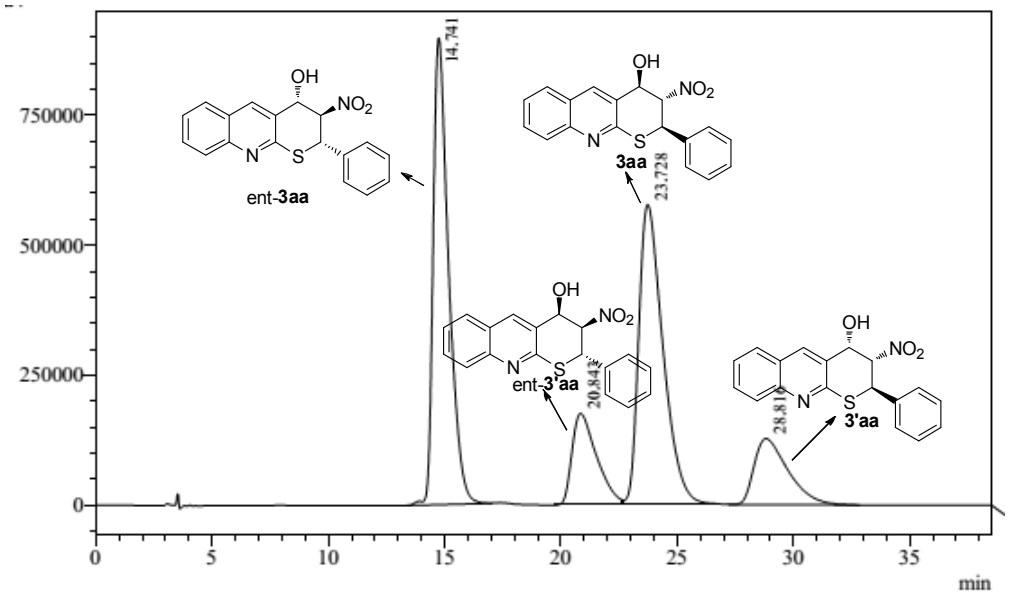
70.0337
55.6234
40.8269
OH
NO2
N
S
O
f1 (ppm)

2.HPLC spectra

3aa, ent-3aa, 3'aa and ent-3'aa

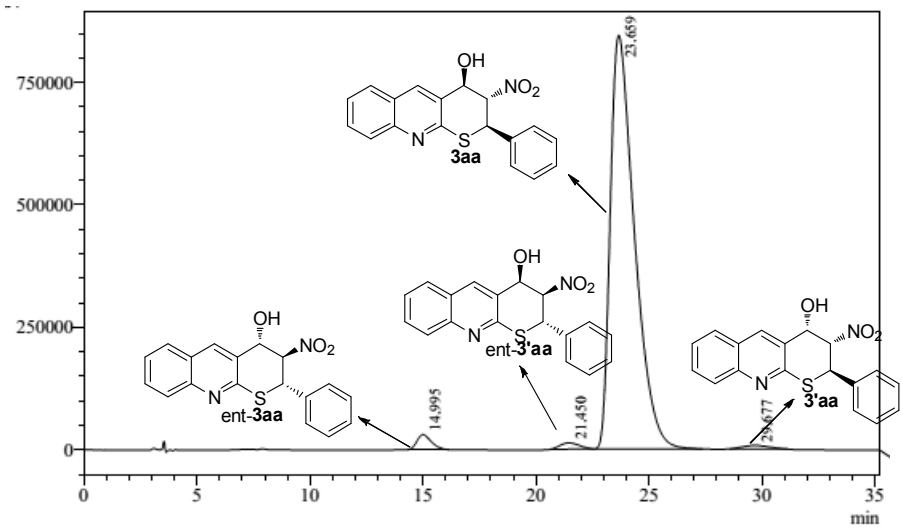


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.741	41439809	897692	38.211	50.606
2	20.843	12550586	173890	11.573	9.803
3	23.728	41583284	575568	38.343	32.447
4	28.816	12875907	126743	11.873	7.145
Total		108449586	1773892	100.000	100.000

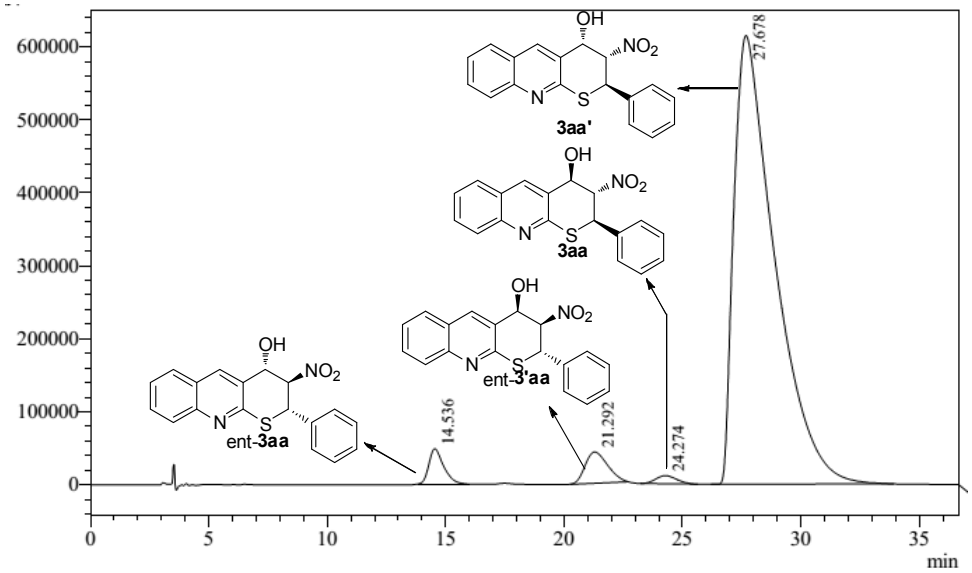


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.995	1346081	30568	2.055	3.414
2	21.450	748926	12746	1.143	1.424
3	23.659	62812051	844676	95.893	94.346
4	29.677	595460	7309	0.909	0.816
Total		65502517	895299	100.000	100.000



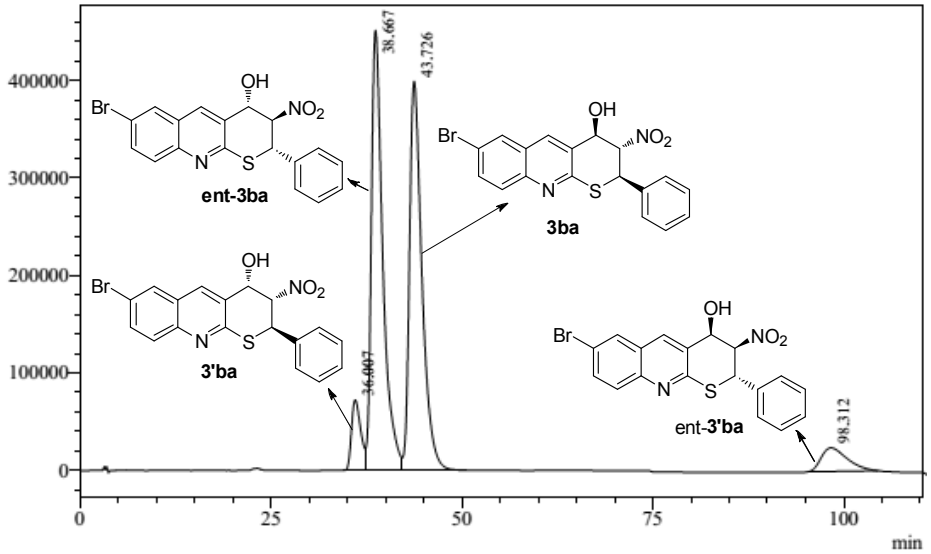
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.536	2087658	48364	2.636	6.745
2	21.292	2828253	42705	3.571	5.956
3	24.274	688550	11087	0.869	1.546
4	27.678	73592911	614892	92.923	85.753
Total		79197373	717048	100.000	100.000

3ba, ent-3ba, 3'ba and ent-3'ba

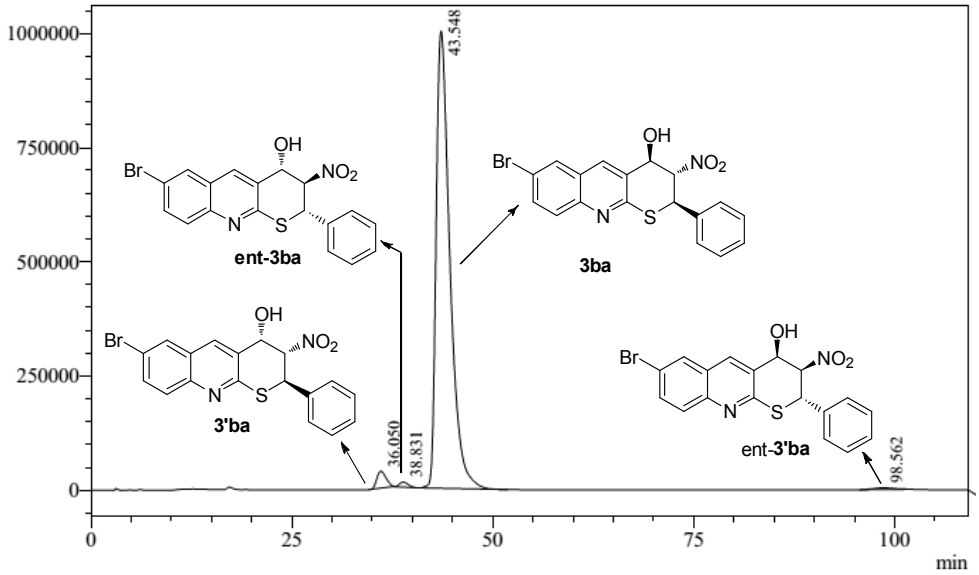


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.007	6064397	72324	5.806	7.639
2	38.667	47219134	451297	45.206	47.668
3	43.726	45427193	398958	43.491	42.140
4	98.312	5741654	24171	5.497	2.553
Total		104452378	946750	100.000	100.000

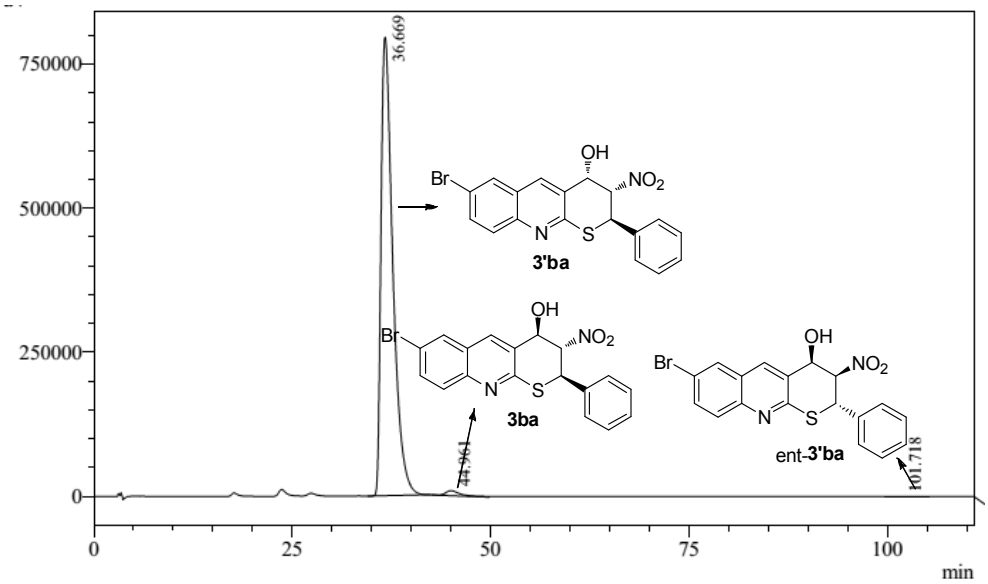


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.050	2963093	37072	2.398	3.521
2	38.831	790521	10756	0.640	1.022
3	43.548	119053211	1001393	96.354	95.103
4	98.562	750986	3733	0.608	0.355
Total		123557810	1052954	100.000	100.000



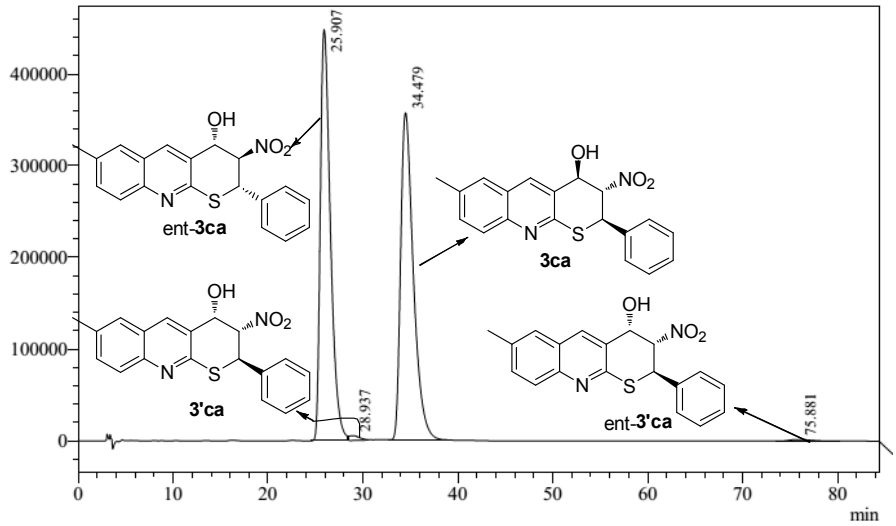
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.669	82243485	795740	98.481	98.864
2	44.961	1170203	8613	1.401	1.070
3	101.718	98661	533	0.118	0.066
Total		83512348	804886	100.000	100.000

3ca, ent-3ca, 3'ca and ent-3'ca

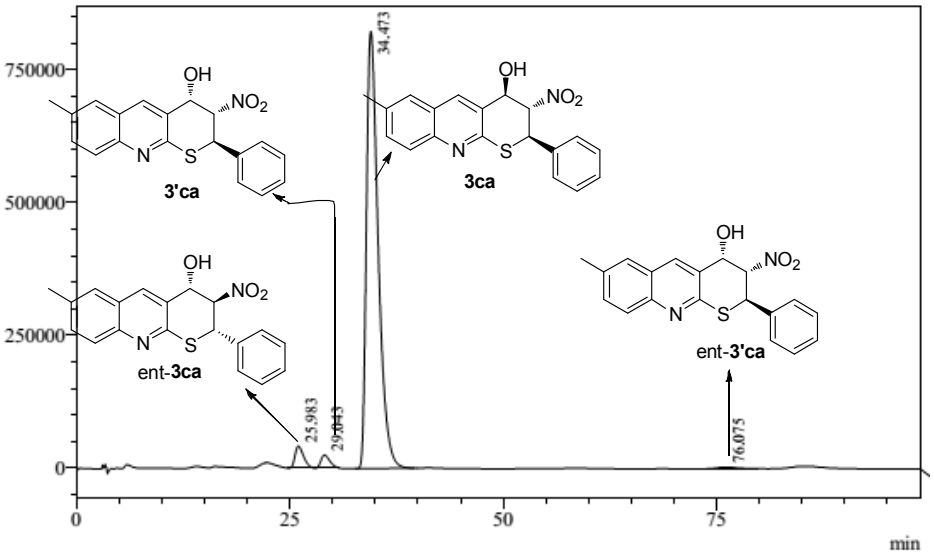


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.907	33190662	448570	49.488	55.201
2	28.937	390297	5426	0.582	0.668
3	34.479	33202285	356984	49.506	43.930
4	75.881	284604	1632	0.424	0.201
Total		67067848	812612	100.000	100.000

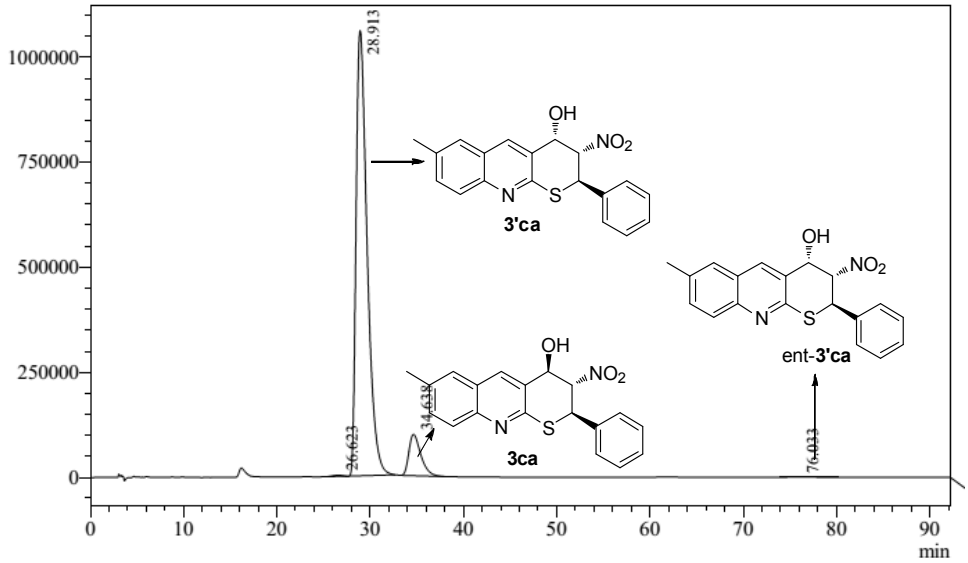


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.983	2838266	41025	3.378	4.597
2	29.043	1812313	24680	2.157	2.766
3	34.473	78815649	823388	93.803	92.266
4	76.075	556255	3314	0.662	0.371
Total		84022483	892407	100.000	100.000



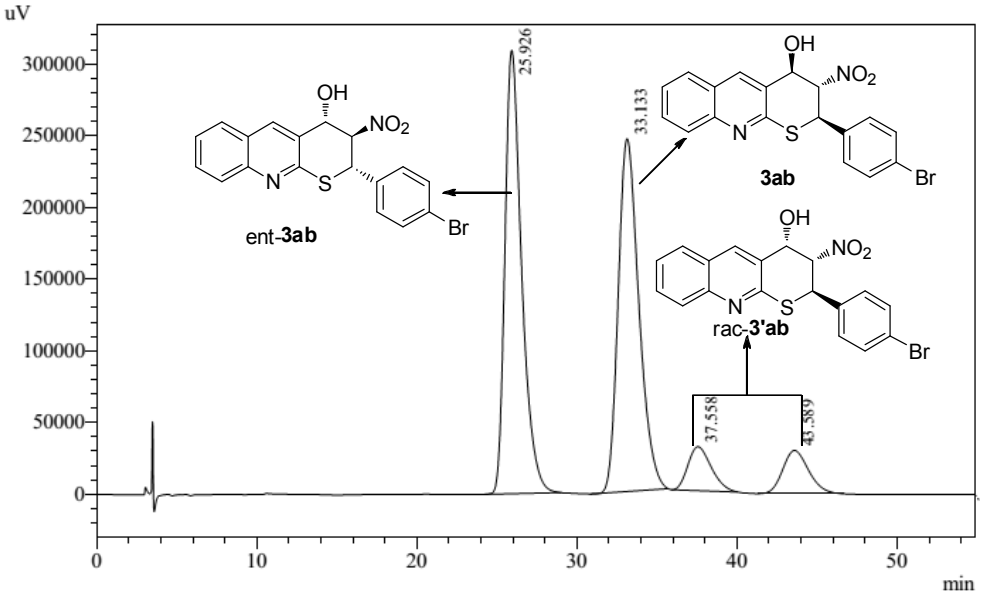
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.623	186082	2467	0.193	0.212
2	28.913	87173046	1059758	90.547	91.245
3	34.638	8794838	98509	9.135	8.482
4	76.033	119955	715	0.125	0.062
Total		96273921	1161448	100.000	100.000

3ab, ent-3ab, 3'ab and ent-3'ab

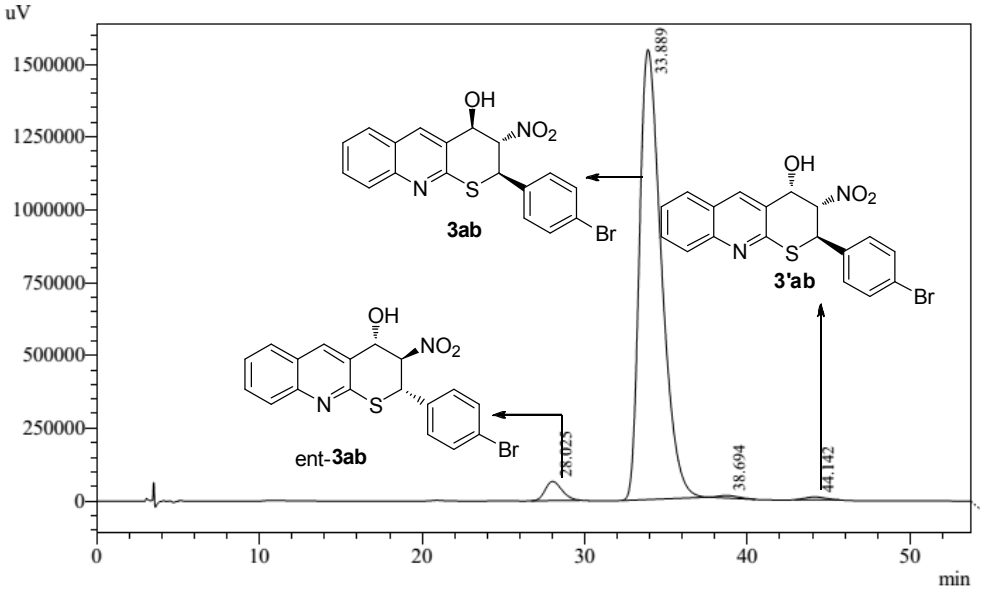


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.926	22417477	308948	44.001	50.206
2	33.133	22033965	245742	43.248	39.934
3	37.558	3097728	30563	6.080	4.967
4	43.589	3398567	30112	6.671	4.893
Total		50947736	615365	100.000	100.000

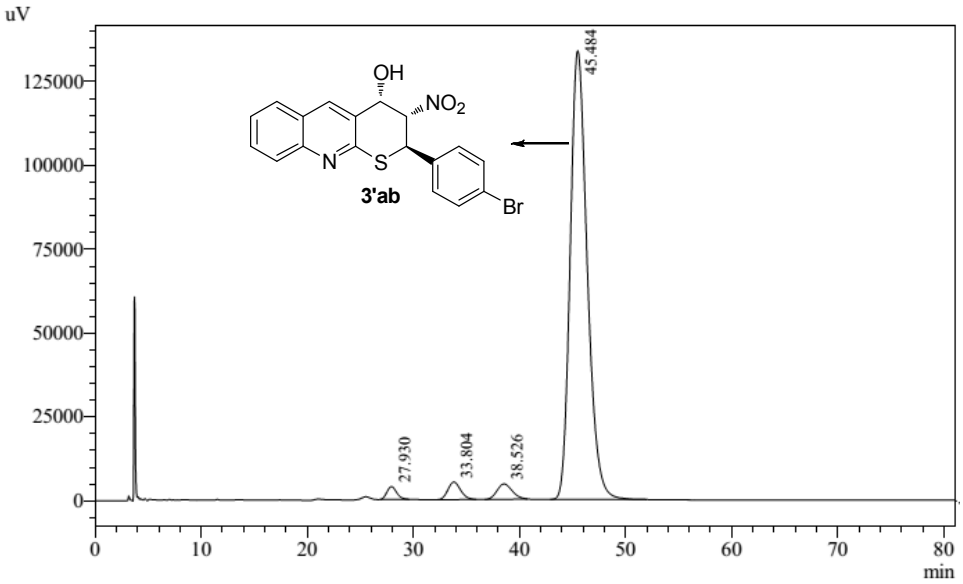


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.025	4711784	66079	3.119	4.058
2	33.889	144806011	1544443	95.843	94.849
3	38.694	708275	8118	0.469	0.499
4	44.142	861375	9678	0.570	0.594
Total		151087445	1628319	100.000	100.000



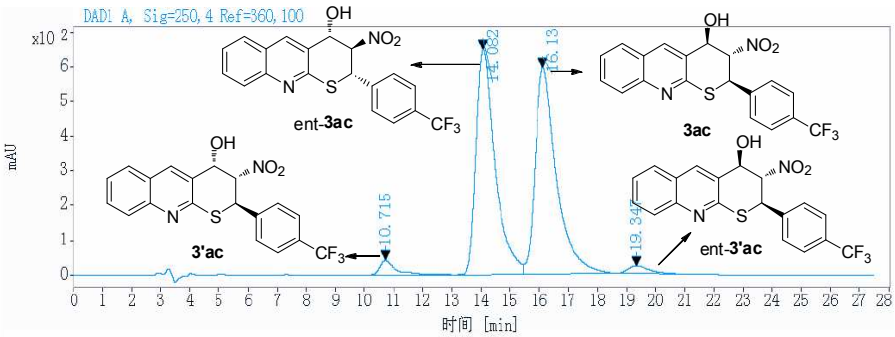
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

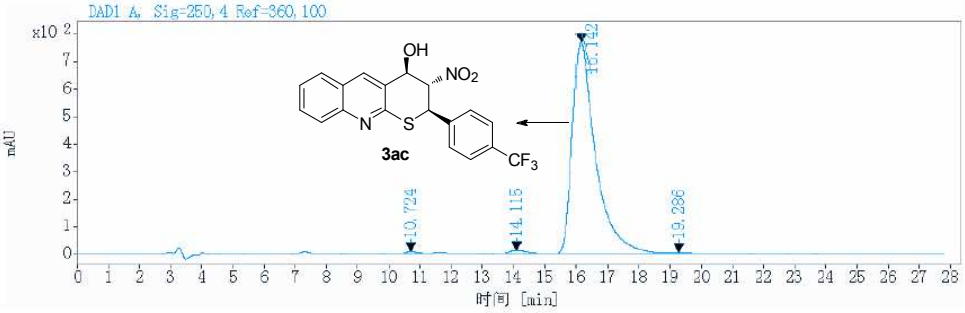
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.930	242972	3813	1.514	2.585
2	33.804	436826	5244	2.723	3.555
3	38.526	453099	4581	2.824	3.106
4	45.484	14912060	133874	92.939	90.755
Total		16044956	147512	100.000	100.000

3ac, ent-3ac, 3'ac and ent-3'ac



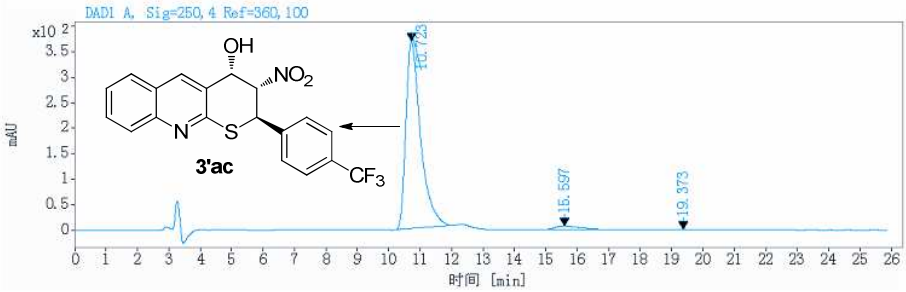
倍吃: DAD1 A, Sig=250,4 Ref=360,100

RT	Area	Height	Area%	Height%
10.715	1521.4386	40.7470	2.4615	3.12
14.082	29171.2520	648.5953	47.1964	49.66
16.130	29967.9023	594.6227	48.4853	45.53
19.347	1147.6492	22.1096	1.8568	1.69



倍吃: DAD1 A, Sig=250,4 Ref=360,100

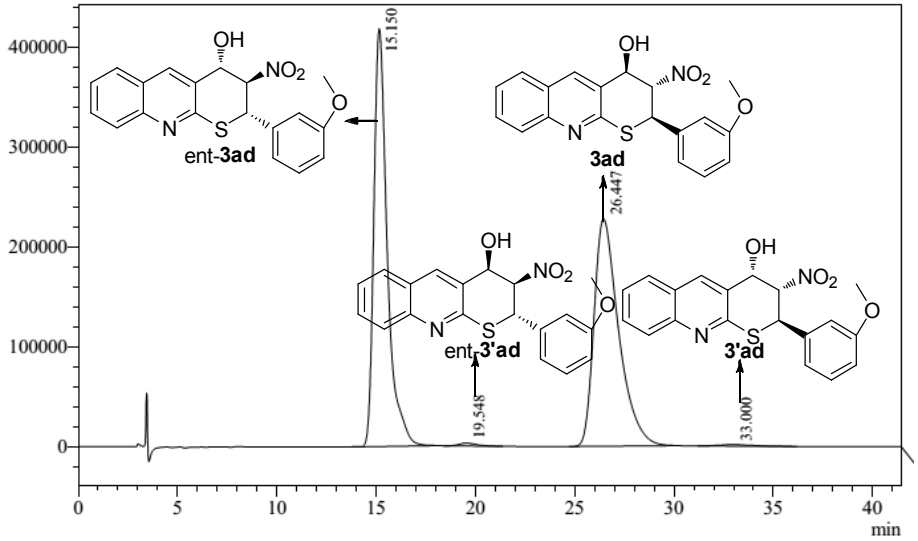
RT	Area	Height	Area%	Height%
10.724	207.4204	7.7160	0.5188	0.97
14.115	579.0989	13.2436	1.4484	1.67
16.142	38965.3789	767.6455	97.4592	96.83
19.286	229.3196	4.1660	0.5736	0.53



信号: DAD1 A, Sig=250,4 Ref=360,100

RT	Area	Height	Area%	Height%
10.723	12047.5732	367.3750	95.6939	97.65
15.597	436.0545	7.4032	3.4636	1.97
19.373	106.0642	1.4558	0.8425	0.39
? ?	12589.6919			

3ad, ent-3ad, 3'ad and ent-3'ad

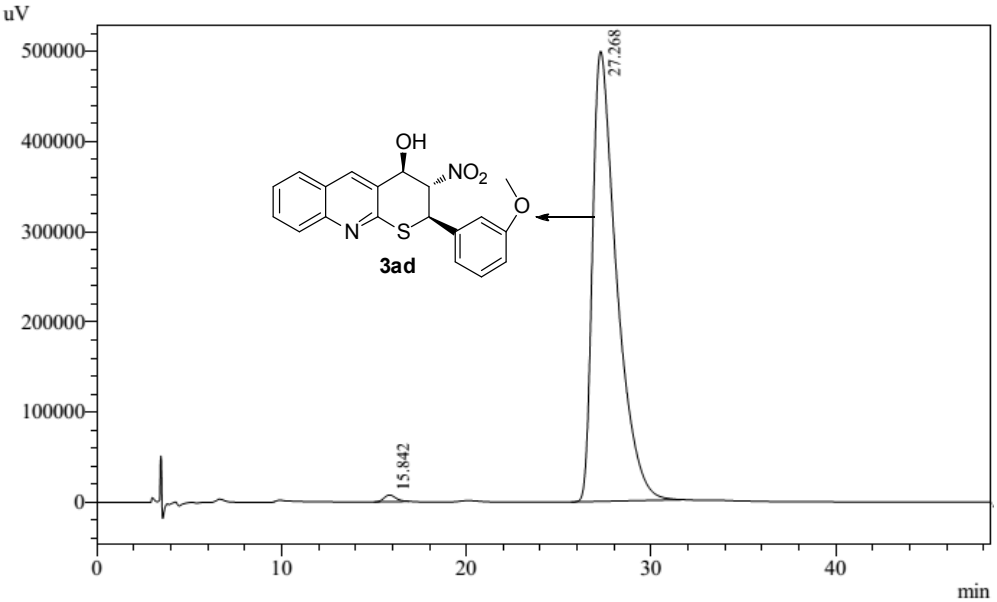


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.150	19630260	418200	49.465	64.326
2	19.548	175990	2863	0.443	0.440
3	26.447	19711438	227509	49.670	34.995
4	33.000	167426	1550	0.422	0.238
Total		39685114	650122	100.000	100.000

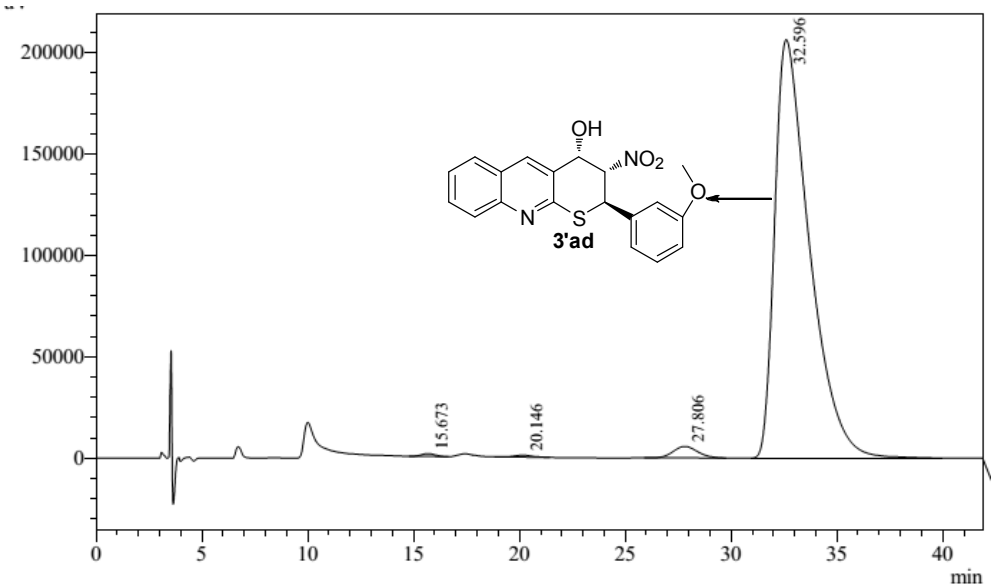


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.842	320648	7331	0.705	1.448
2	27.268	45169797	498851	99.295	98.552
Total		45490445	506181	100.000	100.000



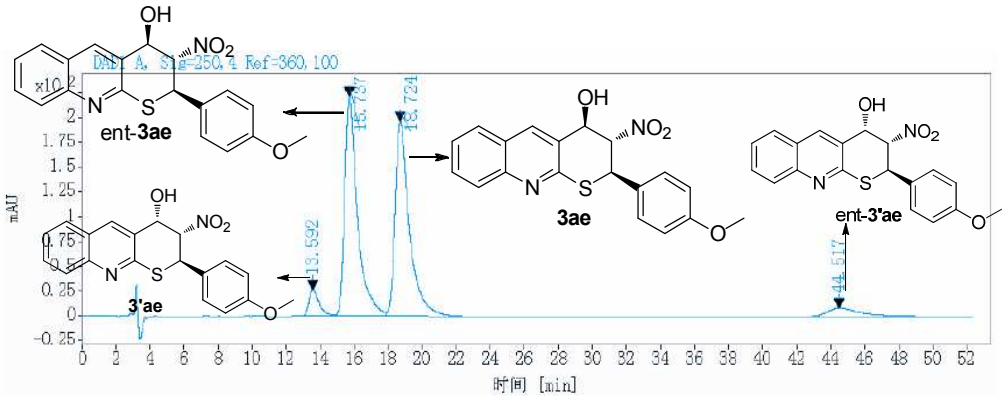
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

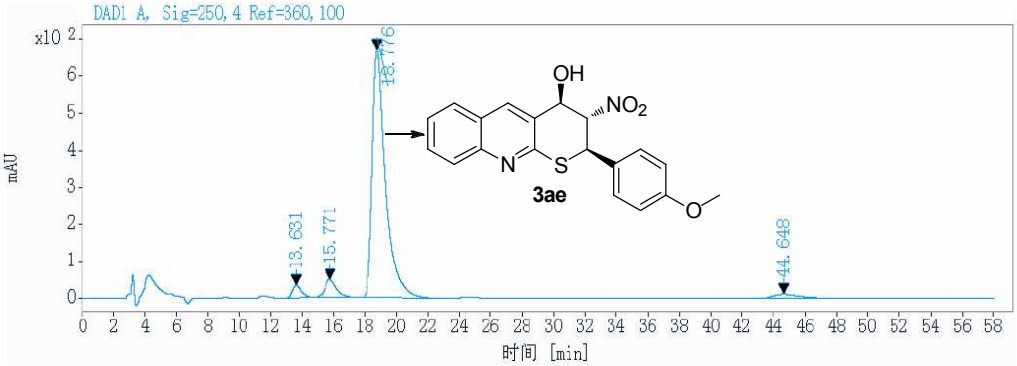
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.673	61281	1377	0.254	0.642
2	20.146	52847	864	0.219	0.403
3	27.806	439896	5594	1.821	2.610
4	32.596	23597957	206501	97.706	96.344
Total		24151981	214336	100.000	100.000

3ae, ent-3ae, 3'ae and ent-3'ae



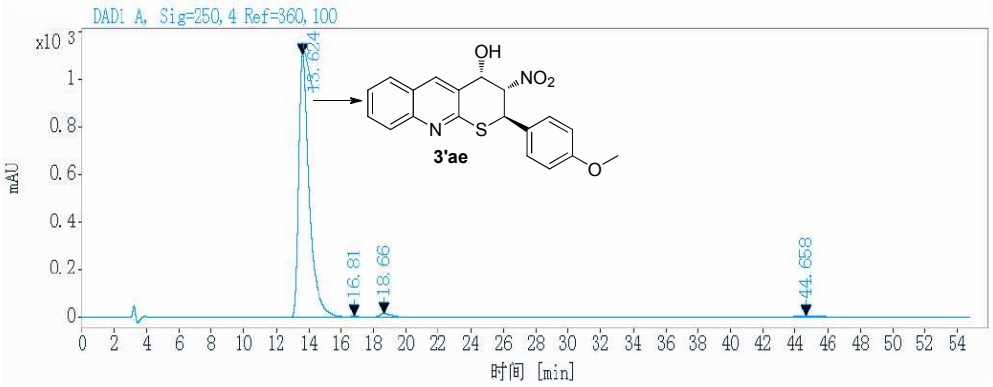
倍呓: DAD1 A, Sig=250,4 Ref=360,100

RT	Area	Height	Area%	Height%
13.592	1099.0239	26.4243	4.3836	5.86
15.737	11483.6104	220.6881	45.8035	48.92
18.724	11392.6230	195.6720	45.4406	43.38
44.517	1096.1990	8.3037	4.3723	1.84



倍呓: DAD1 A, Sig=250,4 Ref=360,100

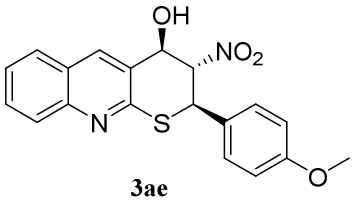
RT	Area	Height	Area%	Height%
13.631	1319.7356	33.5255	2.9695	4.40
15.771	2538.2048	48.7127	5.7111	6.39
18.776	39074.4688	668.9922	87.9199	87.70
44.648	1510.8743	11.5499	3.3996	1.51



倫呓: DAD1 A, Sig=250,4 Ref=360,100

RT	Area	Height	Area%	Height%
13.624	48872.0938	1103.5242	95.4314	97.42
16.810	222.5526	4.6643	0.4346	0.41
18.660	974.2892	16.0515	1.9025	1.42
44.658	1142.8007	8.4630	2.2315	0.75

3. X-ray data of enantiopure of 3ae and 3'ae



3ae

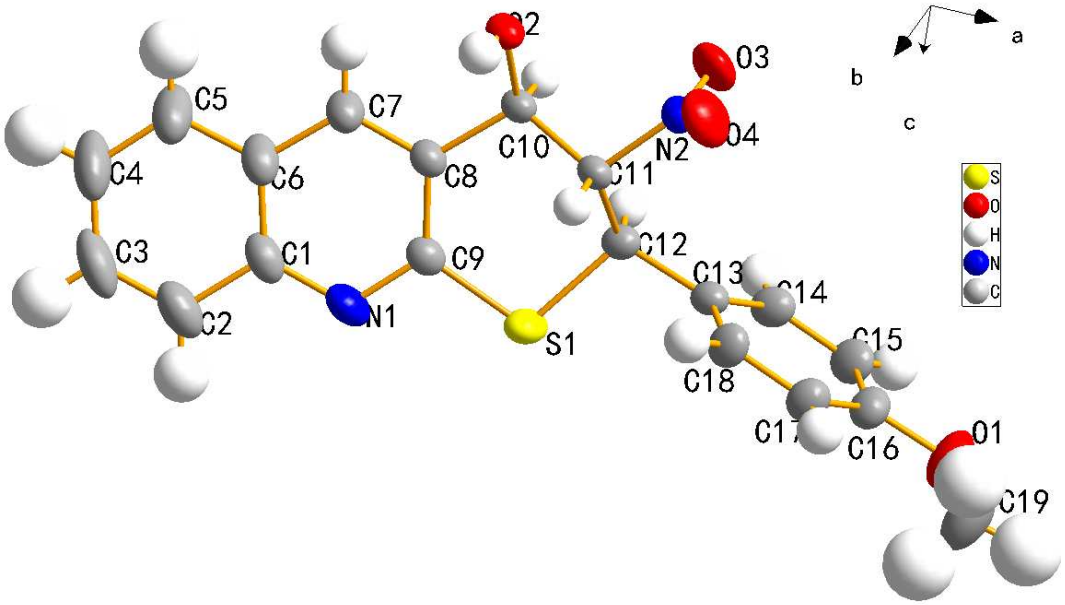
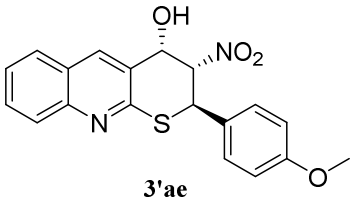


Figure S1. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for **3ae.** $C_{19}H_{16}N_2O_4S$ (368.40), Monoclinic, P2(1); a = 11.1928(3) Å, alpha = 90 °; b = 5.26350(10) Å, beta = 109.1950(10) °; c = 15.5946(4) Å, gamma = 90 °; U = 867.65(4) Å^3, Z = 2, T = 296(2) K, absorption coefficient = 0.214 mm^{-1}, reflections collecteD +29266, unique = 3995 [R(int) = 0.0395], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 3995 / 1 / 239, goodness-of-fit on F^2 = 0.329, final R indices [$I>2sigma(I)$] R1 = 0.0327, wR2 = 0.0.0861; R indices (all data) R1 = 0.0360, wR2 = 0.0953, largest diff. peak and hole = 0.180 and -0.221e. Å^{-3}, respectively.



3'ae

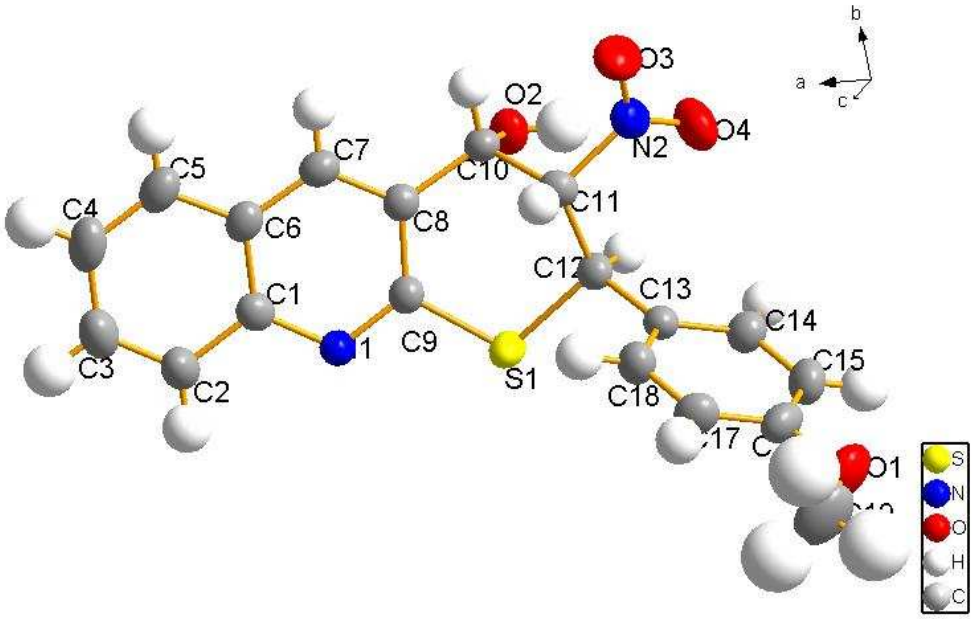


Figure S2. Displacement Ellipsoids Are Drawn at the 30% Probability Level.

Crystal data for **3'ae.** $C_{19}H_{16}N_2O_4S$ (368.40), Orthorhombic, P2(1)2(1)2(1); a = 10.112(5) Å, alpha = 90 °; b = 10.996(6) Å, beta = 90 °; c = 15.378(8) Å, gamma = 90 °; U = 1709.9(15) Å^3, Z = 22, T = 296(2) K, absorption coefficient = 0.217 mm^{-1}, reflections collecteD +12115, unique = 3944 [R(int) = 0.0722], refinement by Full-matrix least-squares on F^2, data/ restraints/ parameters 3944 / 0 / 236, goodness-of-fit on F^2 = 1.011, final R indices [$I>2sigma(I)$] R1 = 0.0561, wR2 = 0.0990; R indices (all data) R1 = 0.1030, wR2 = 0.1175, largest diff. peak and hole = 0.275 and -0.304 e. Å^{-3}, respectively.

end