Supporting Information

Copper-Catalyzed Chemoselective and Enantioselective Friedel–Crafts 1,2-Addition of Pyrrole with β,γ-Unsaturated α-Ketoesters

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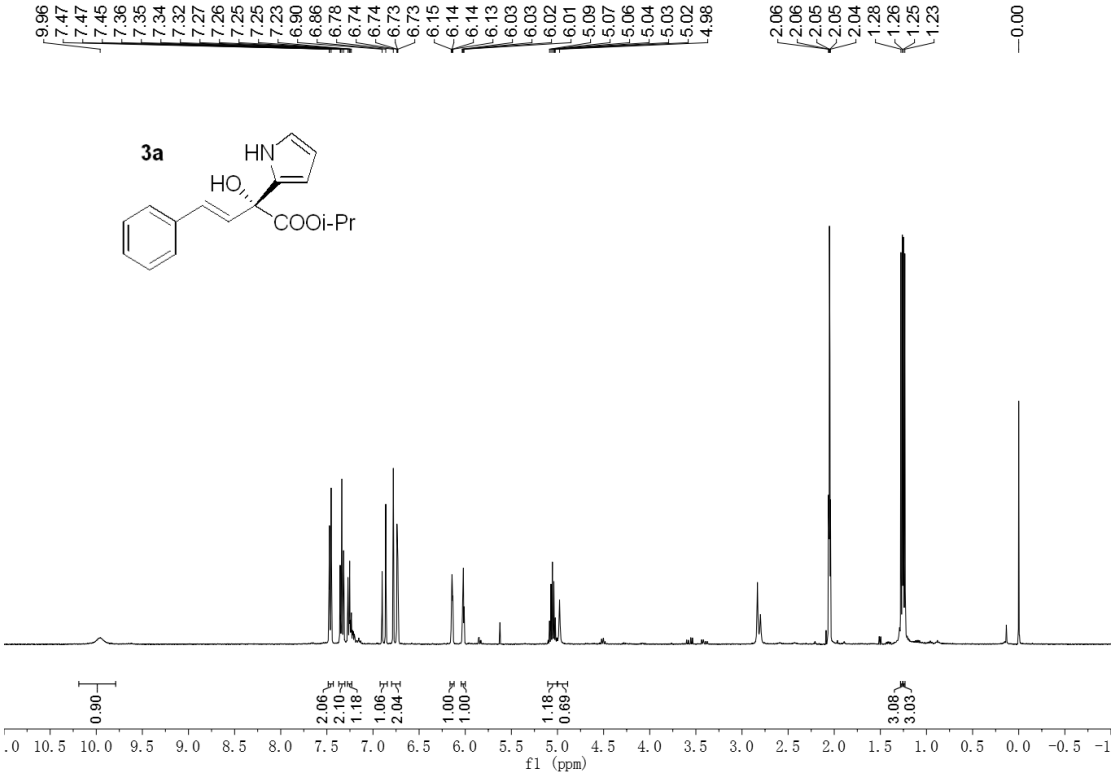
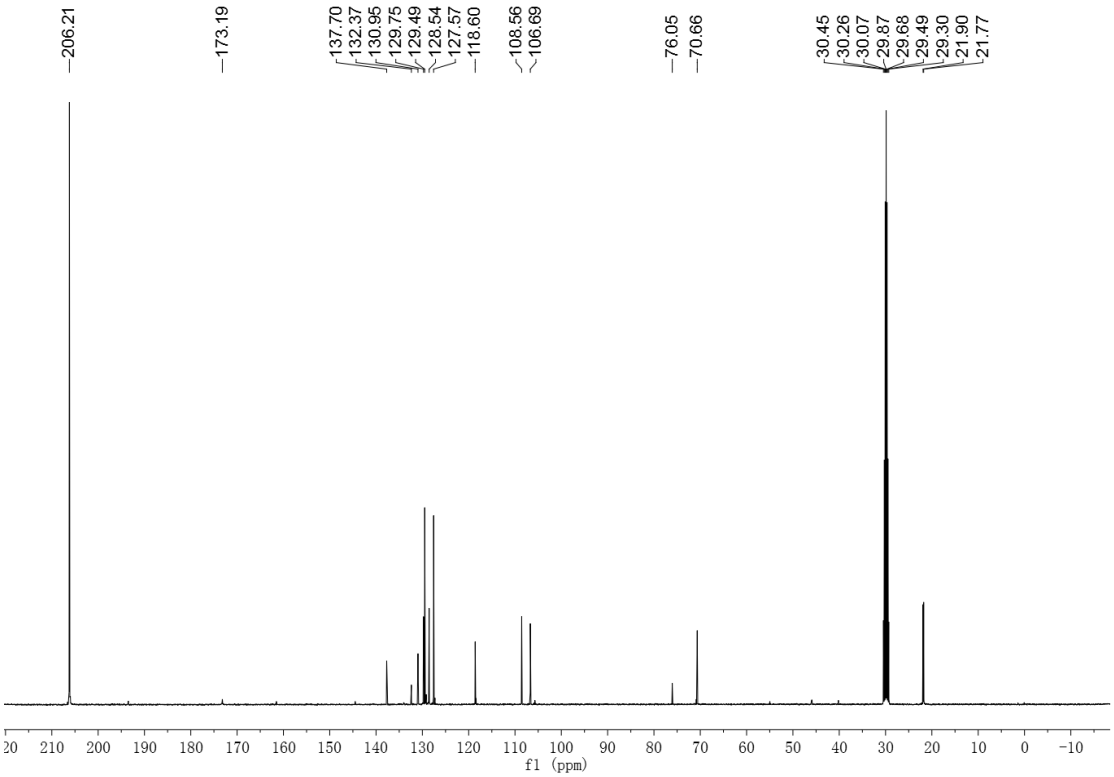
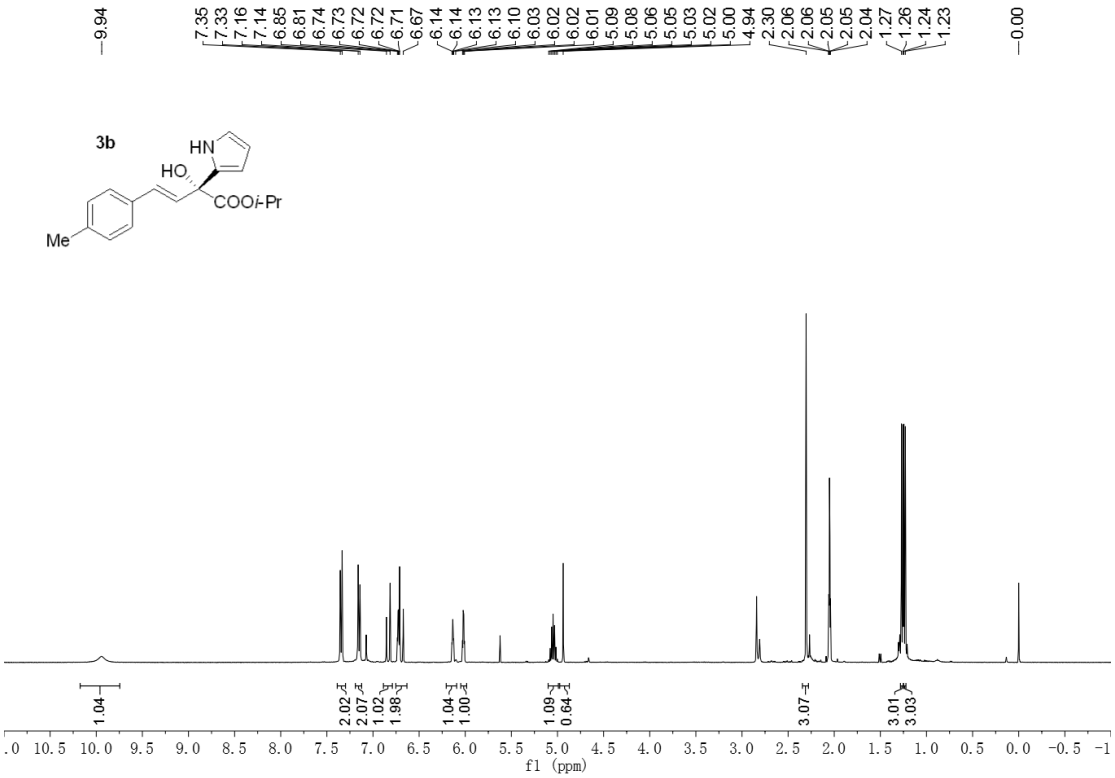
Part I ^{1}H NMR & ^{13}C NMR



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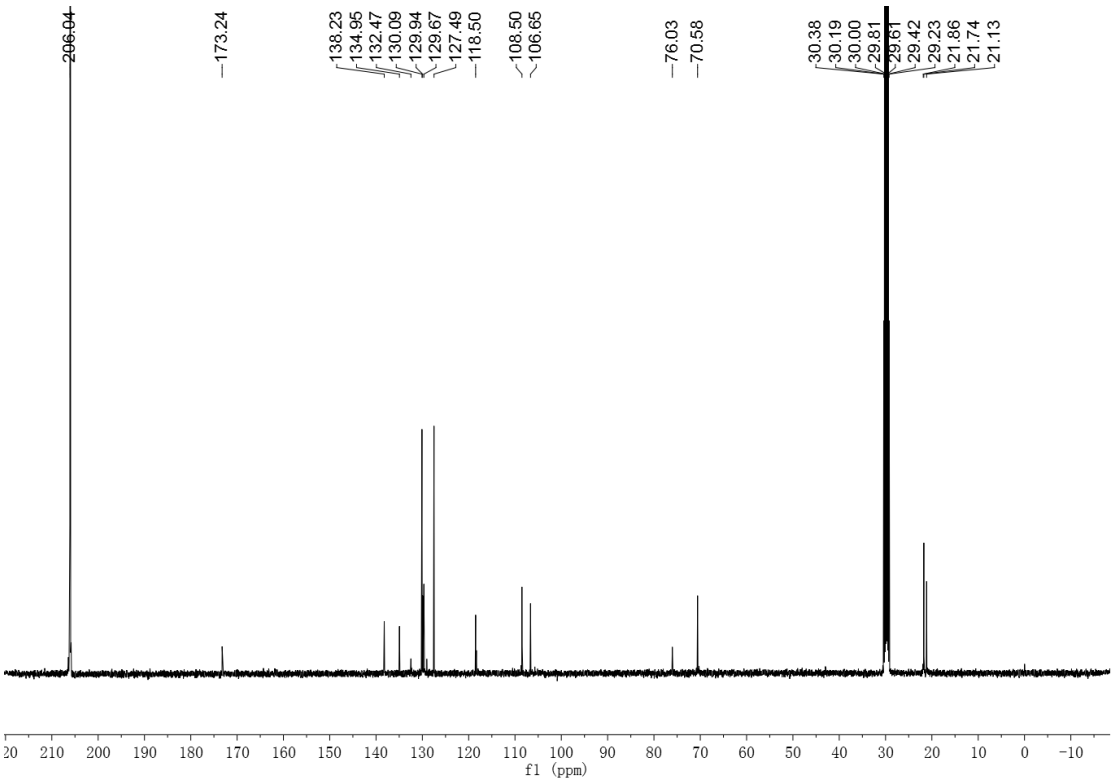
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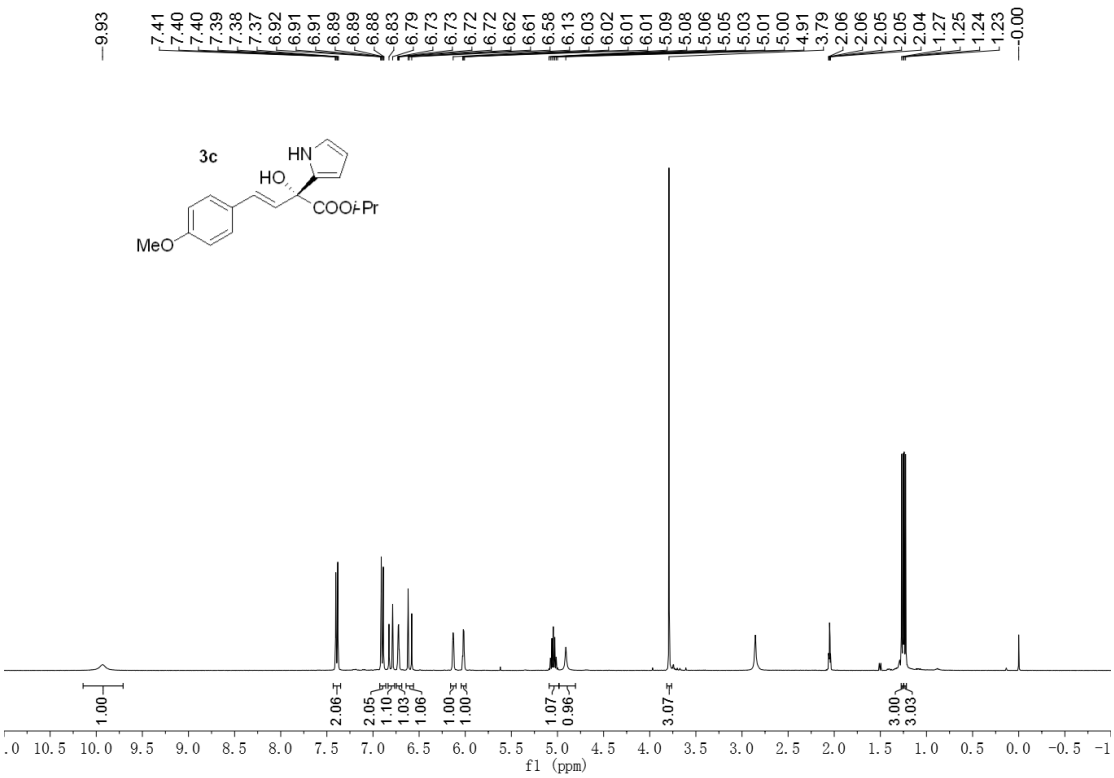
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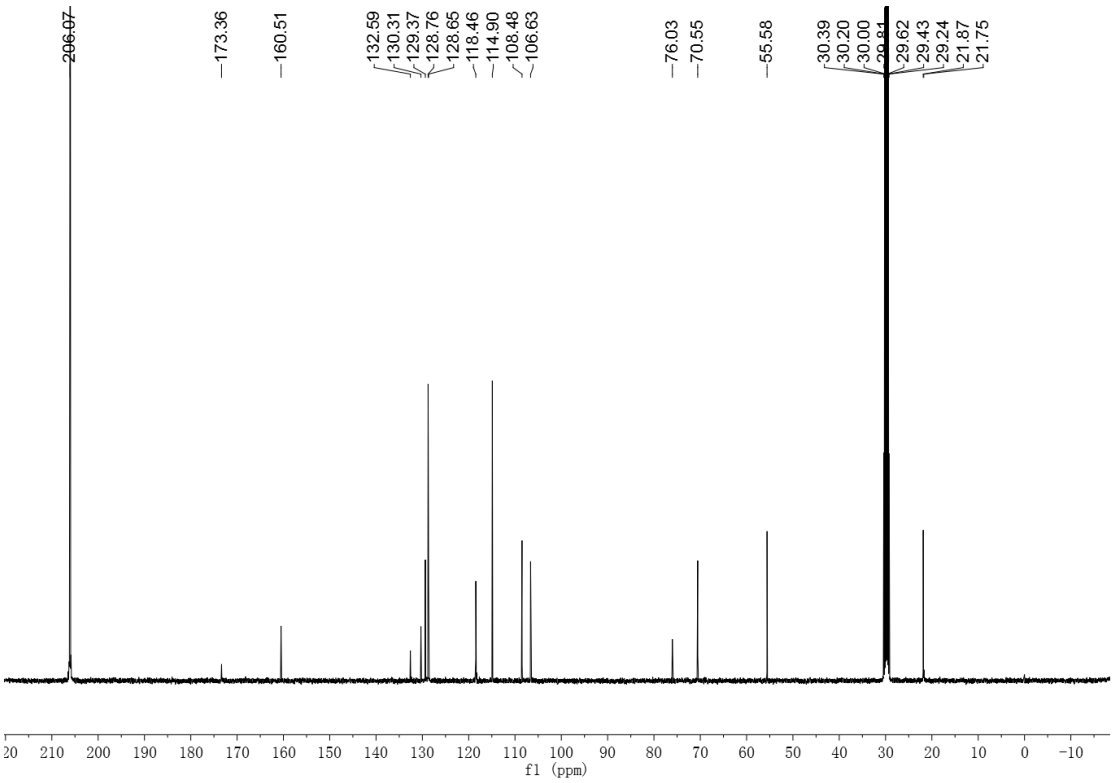
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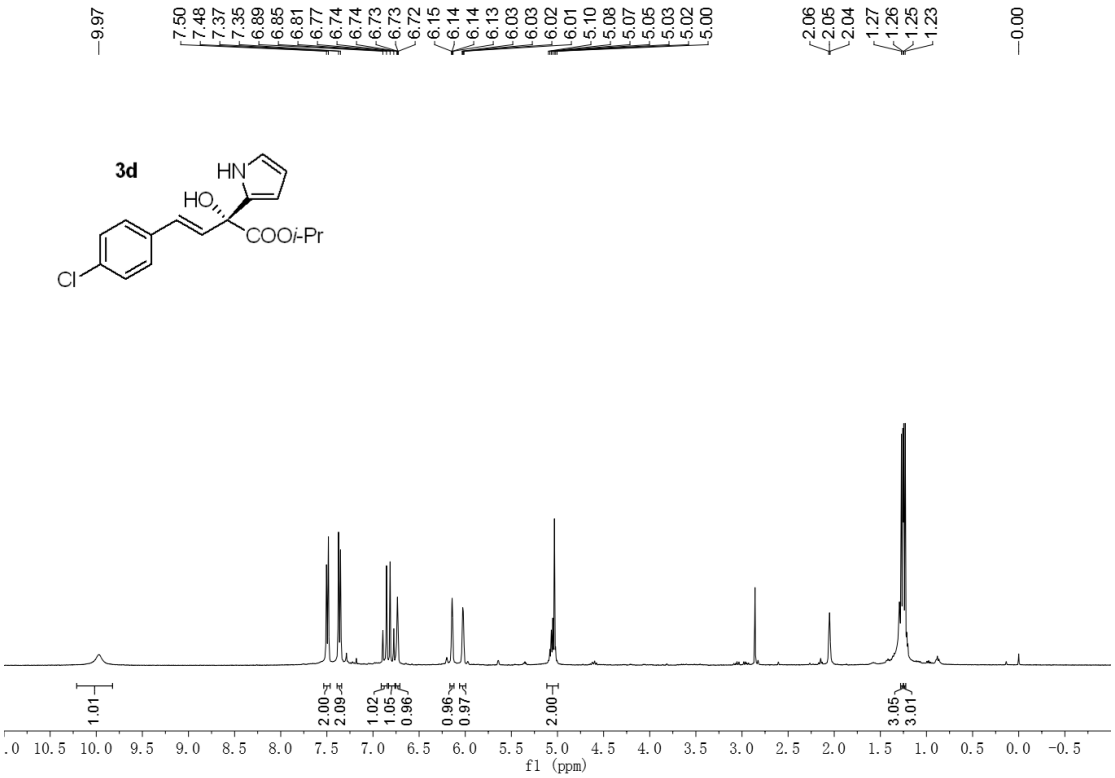
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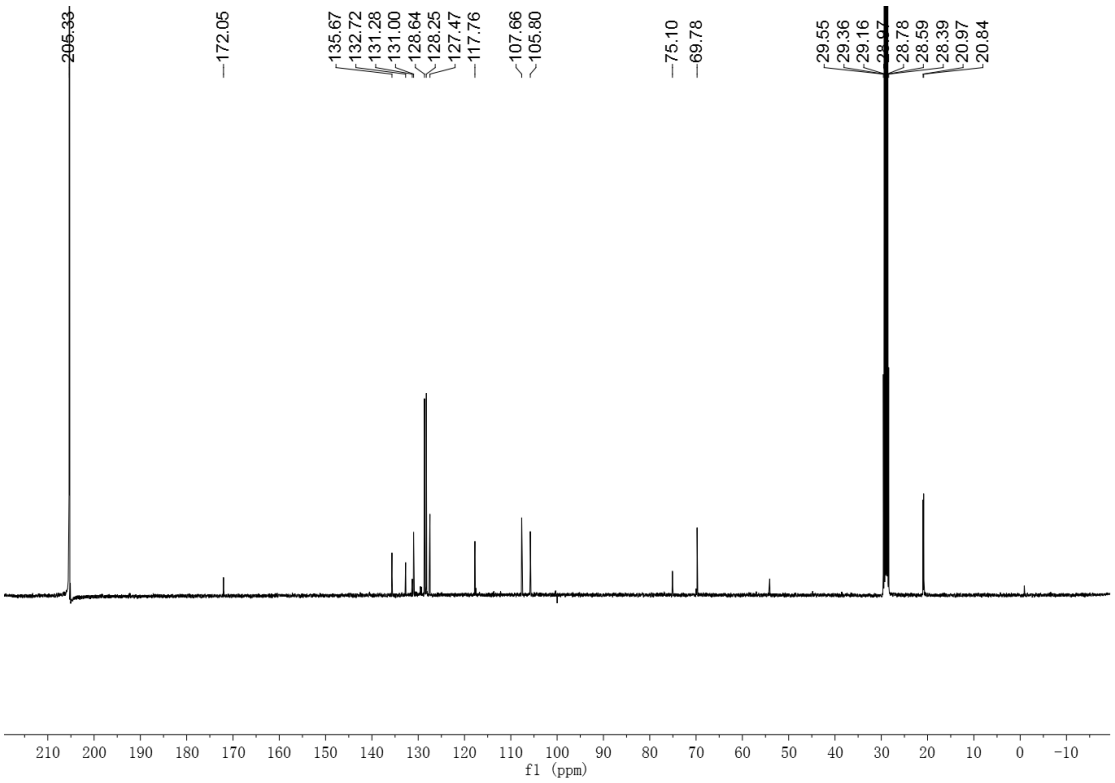
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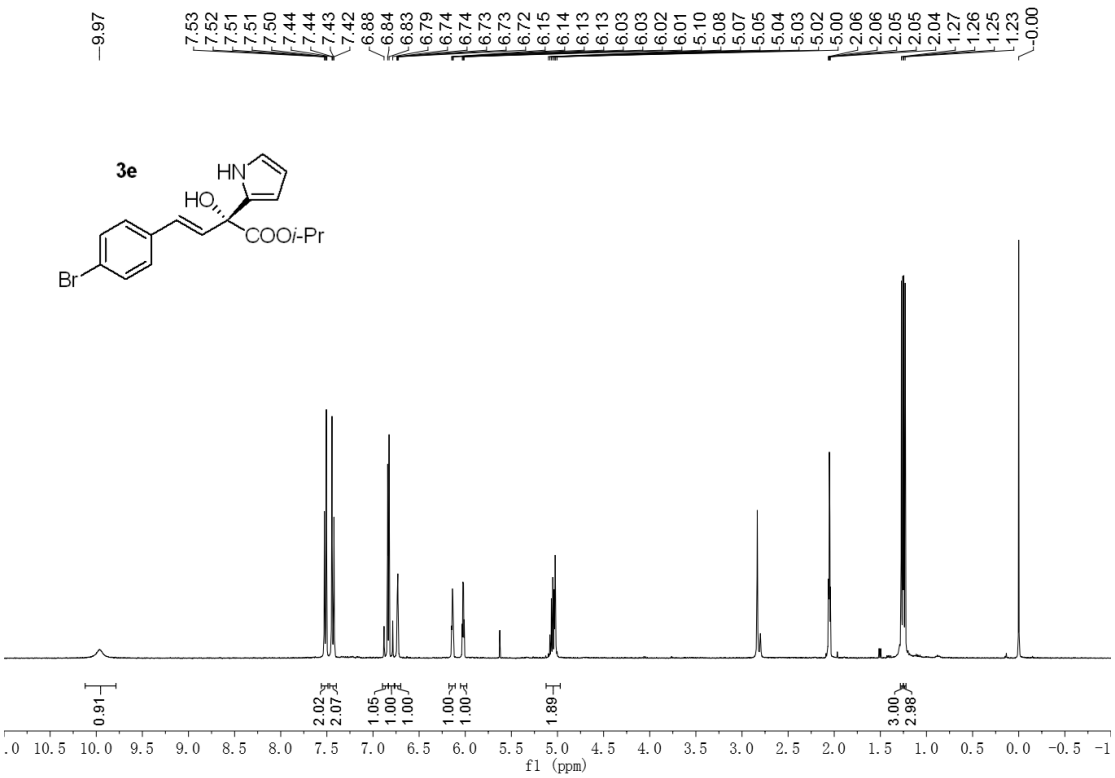
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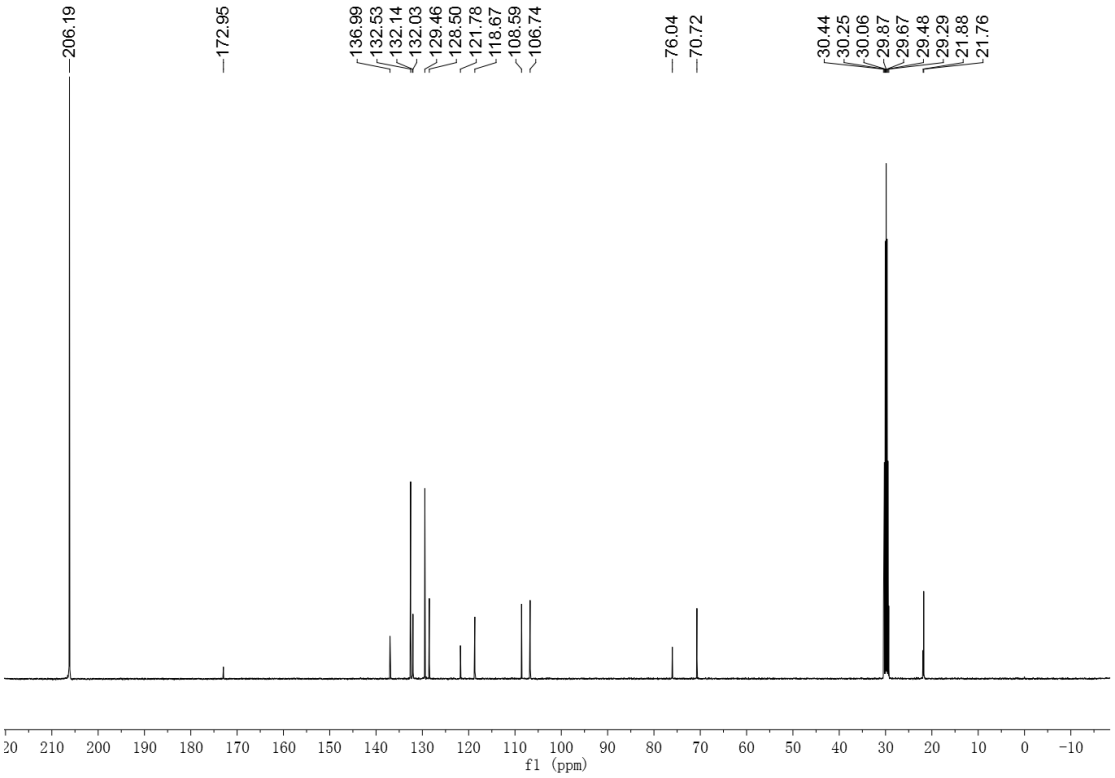
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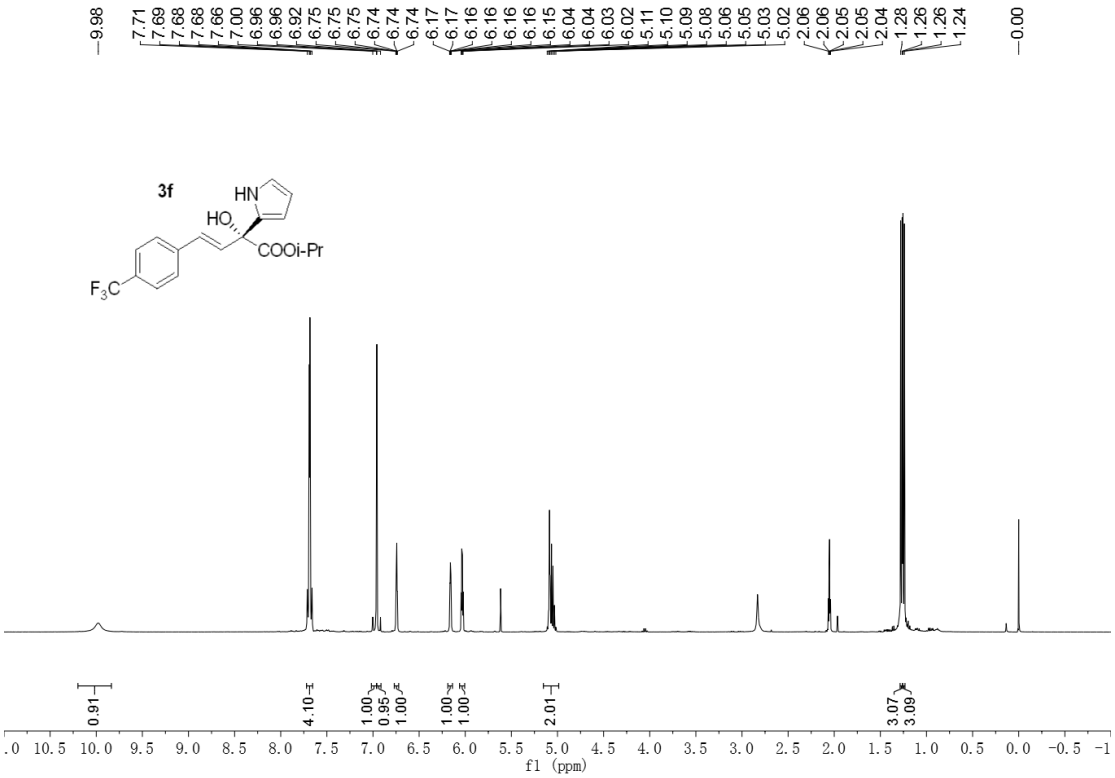
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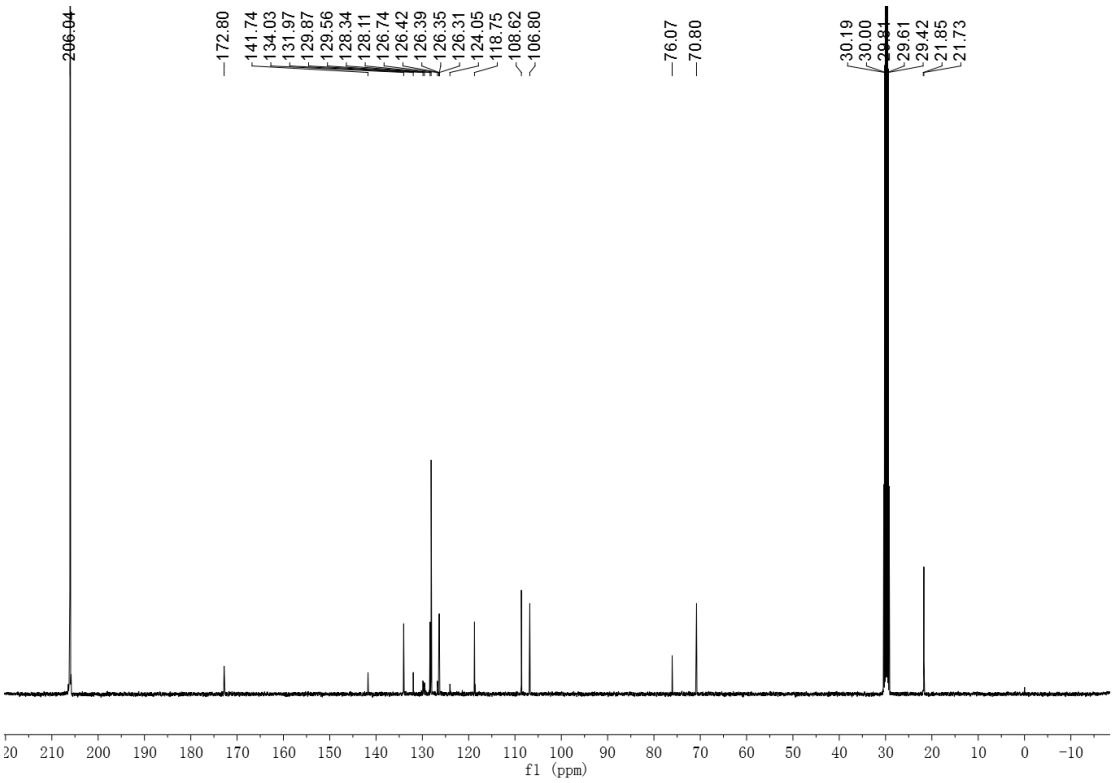
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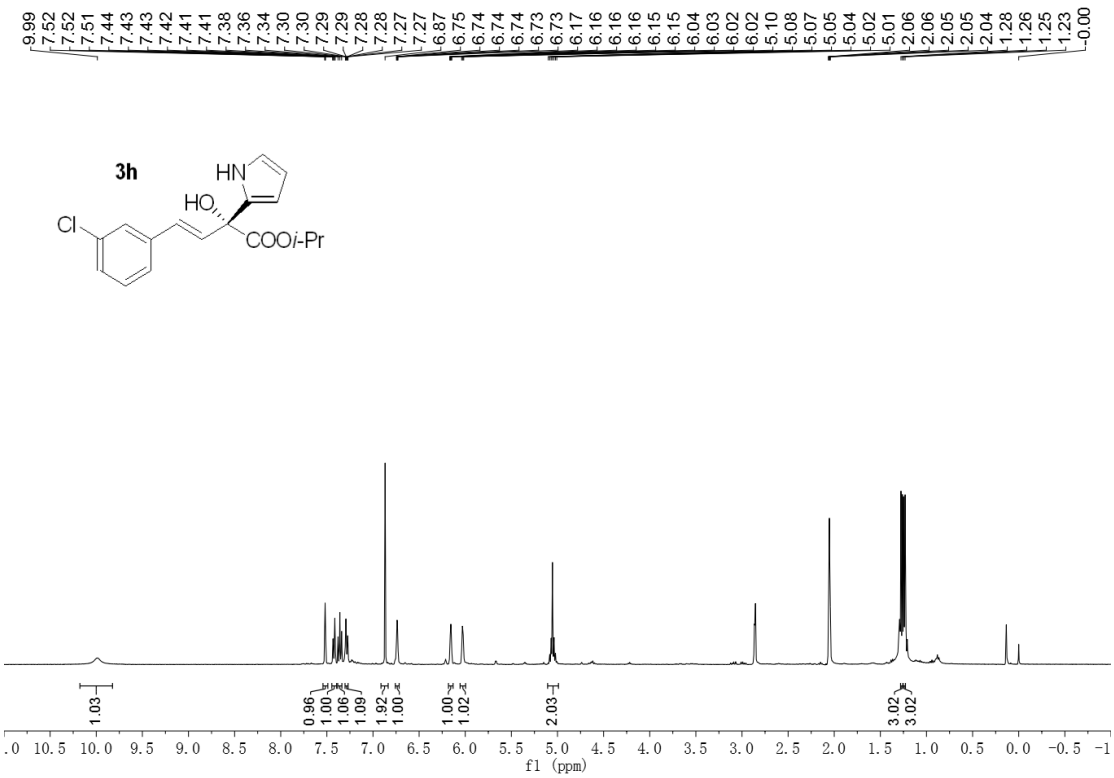
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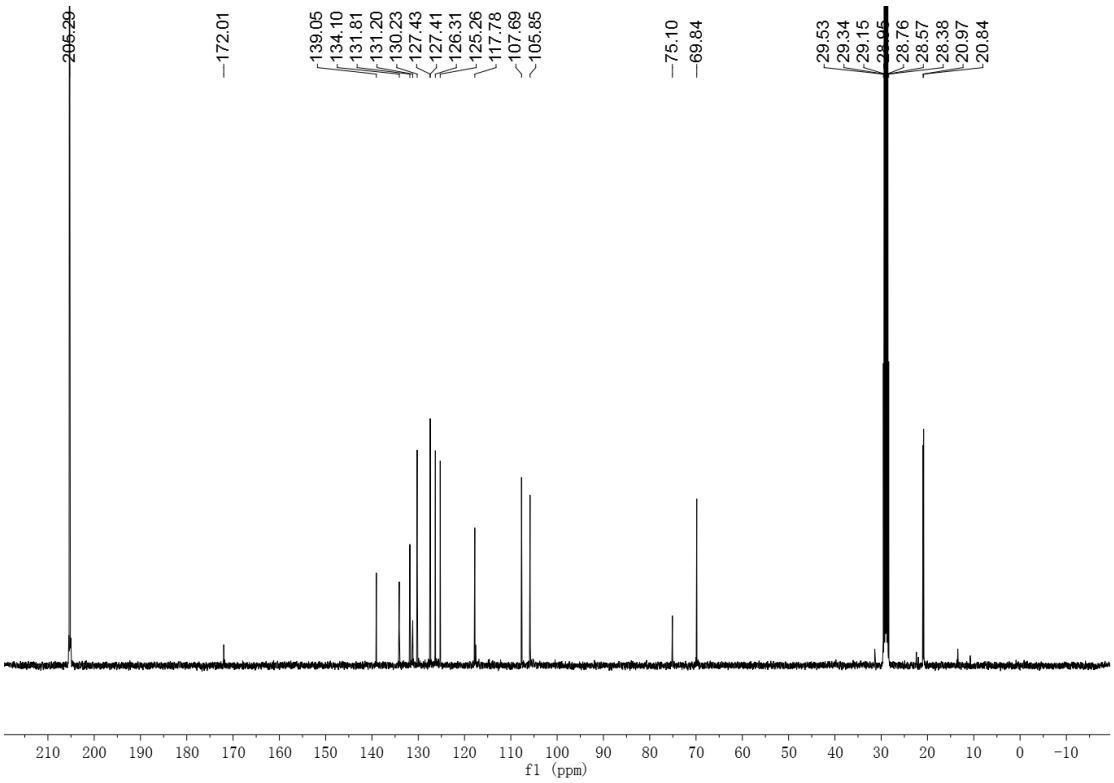
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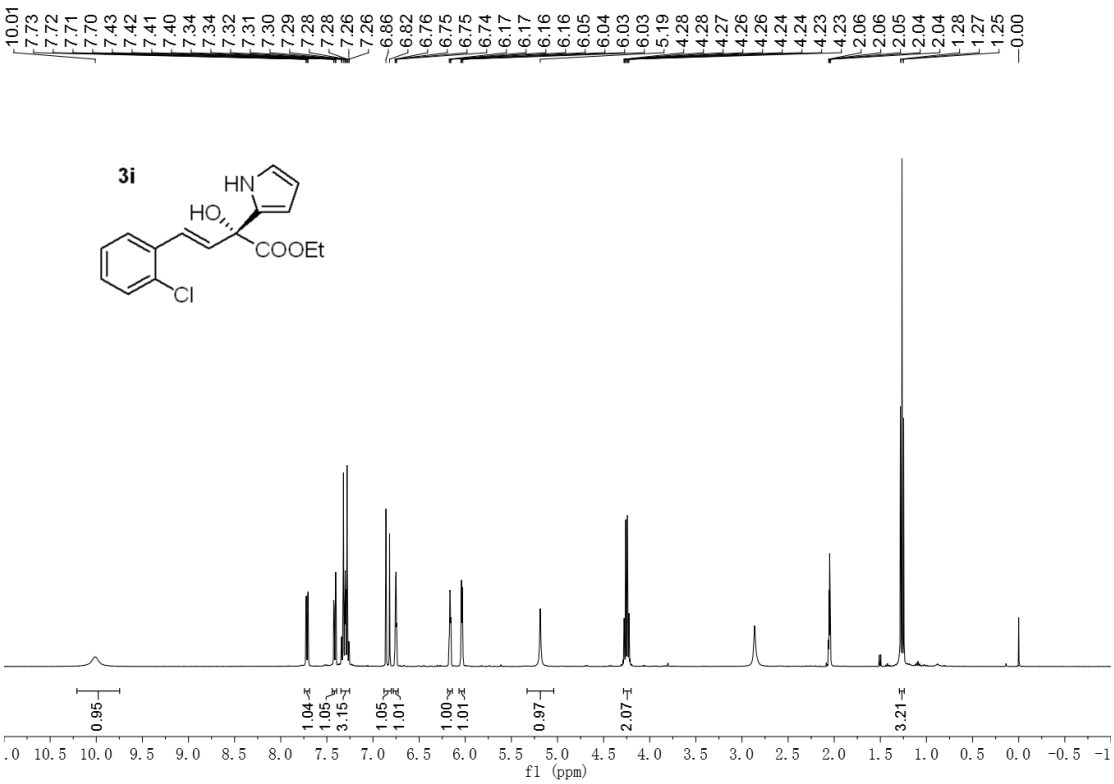
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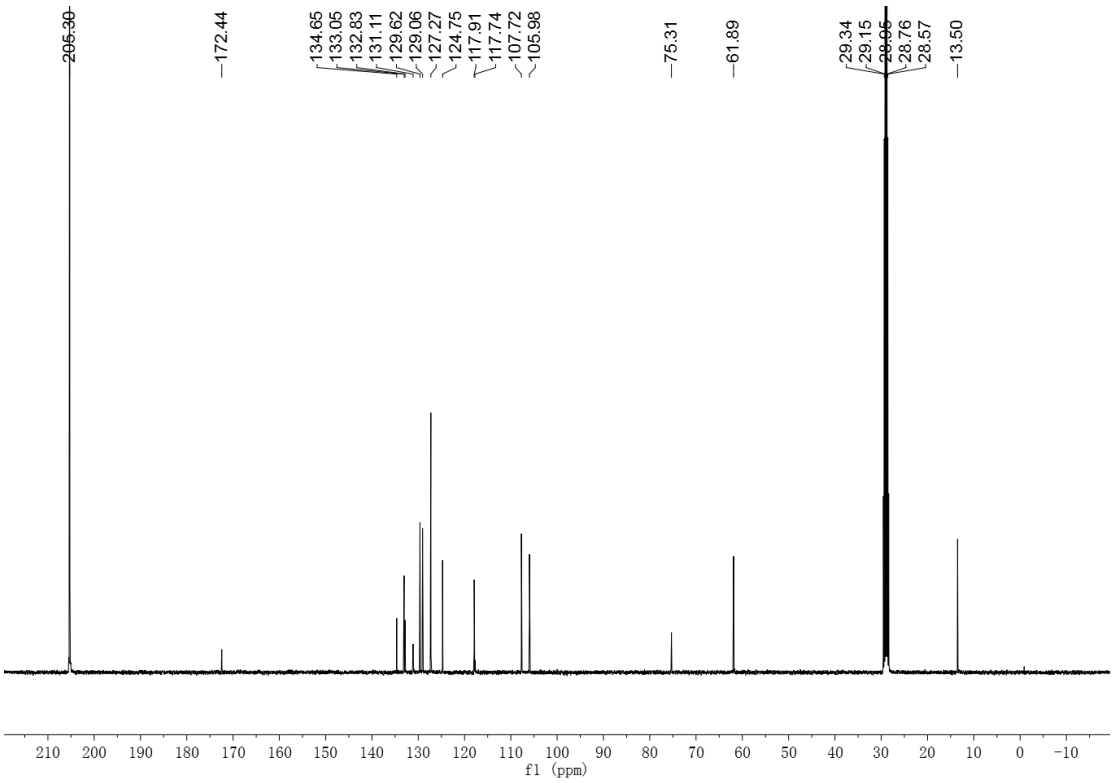
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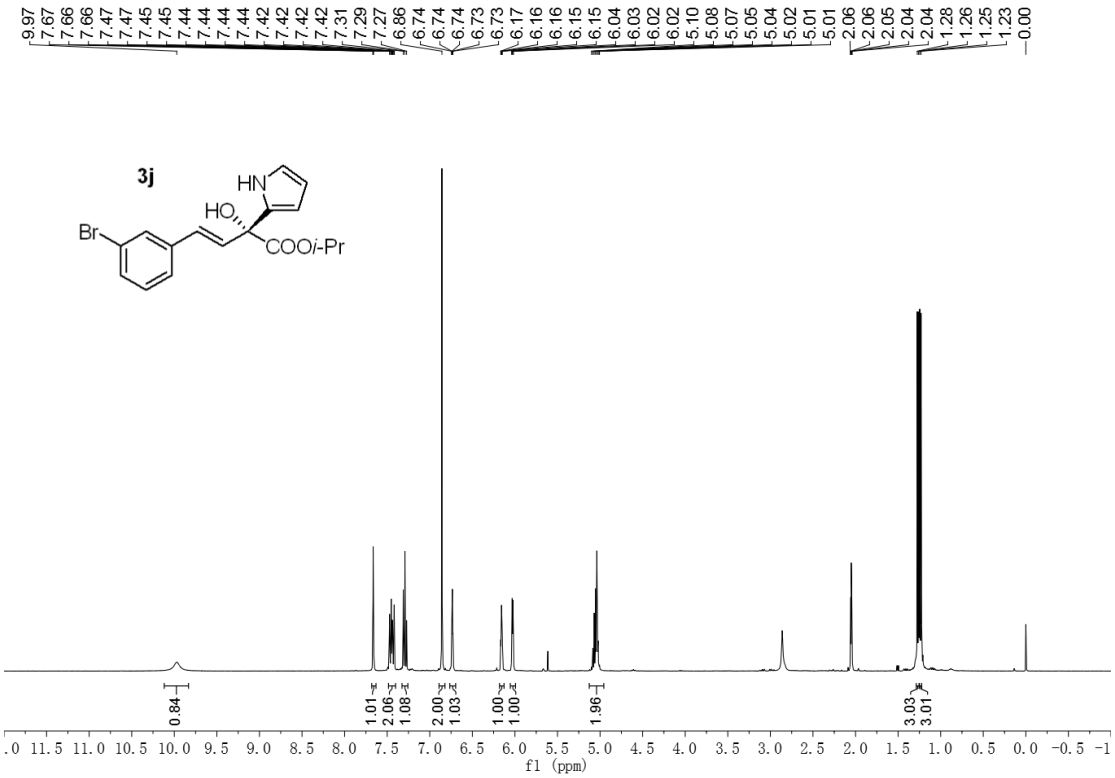
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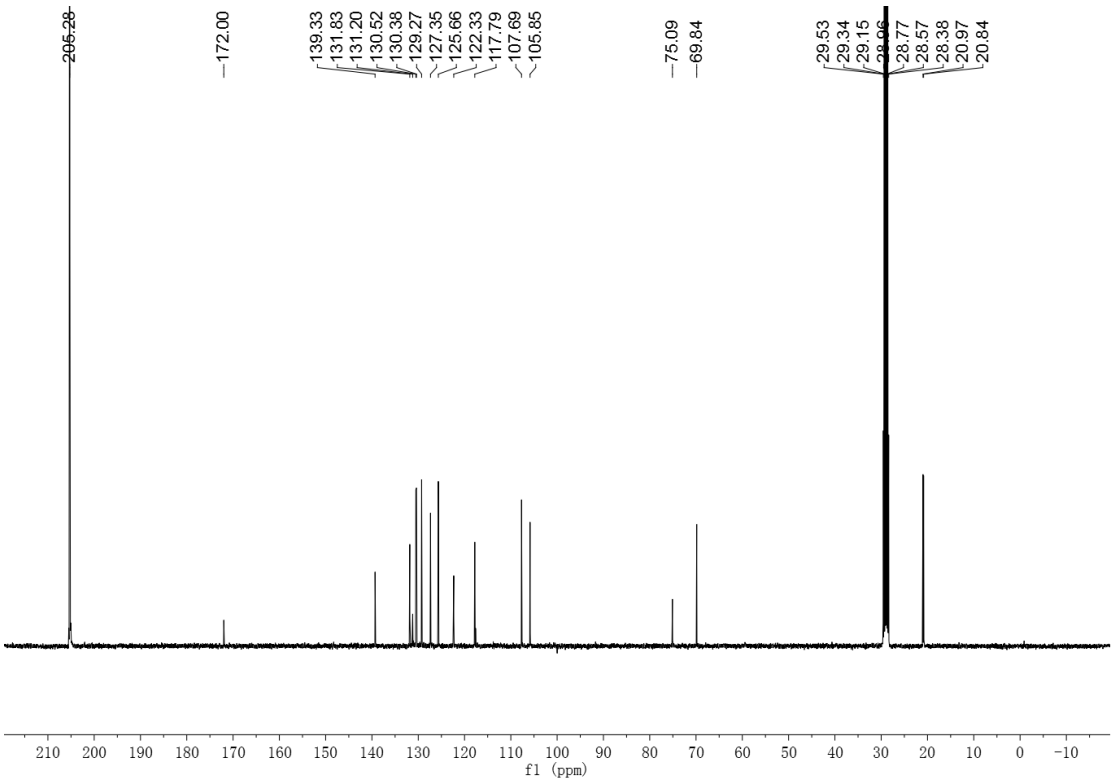
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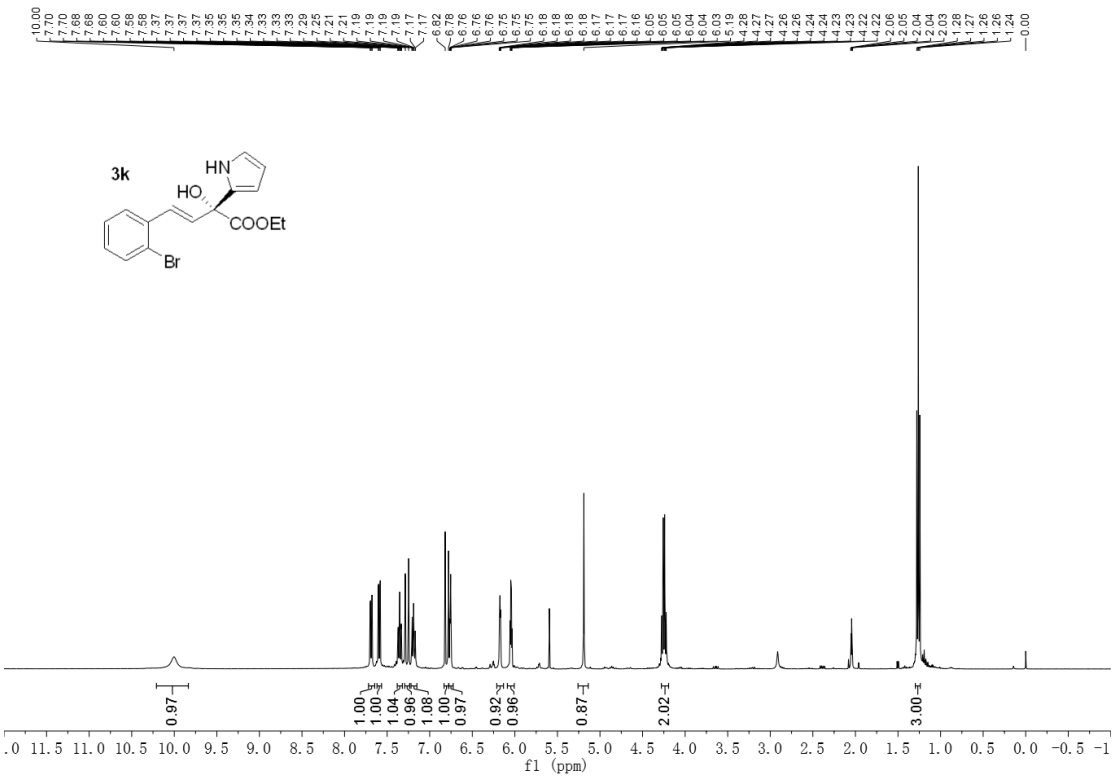
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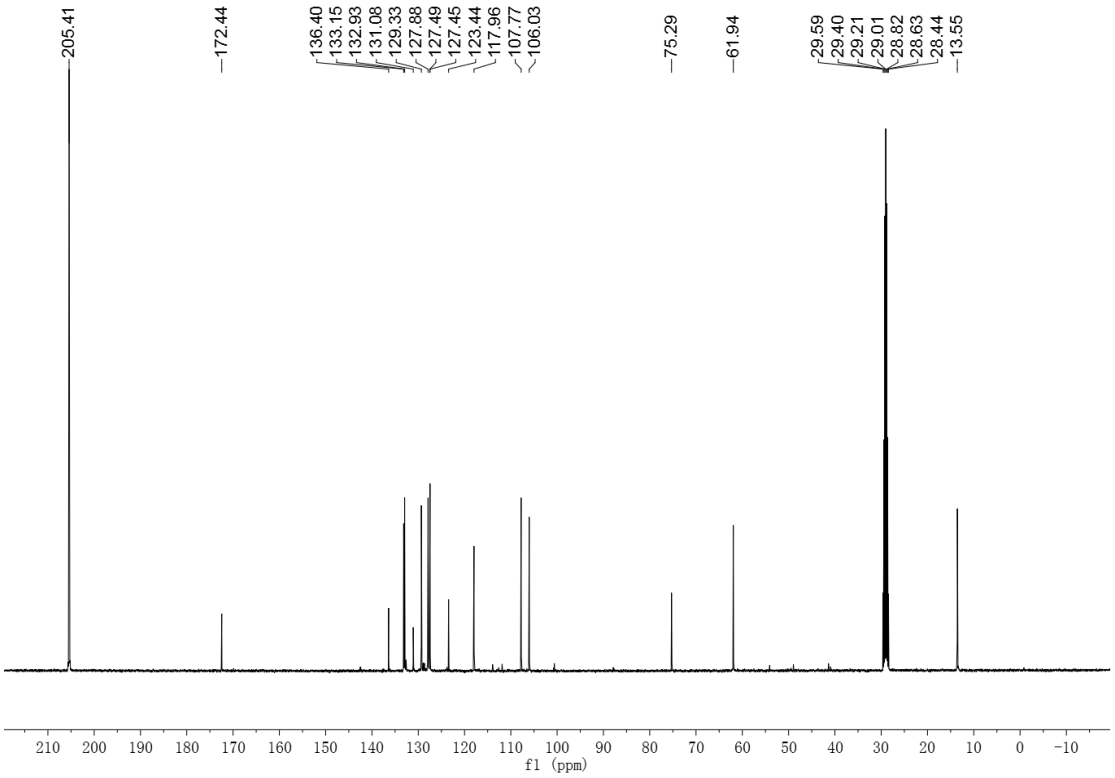
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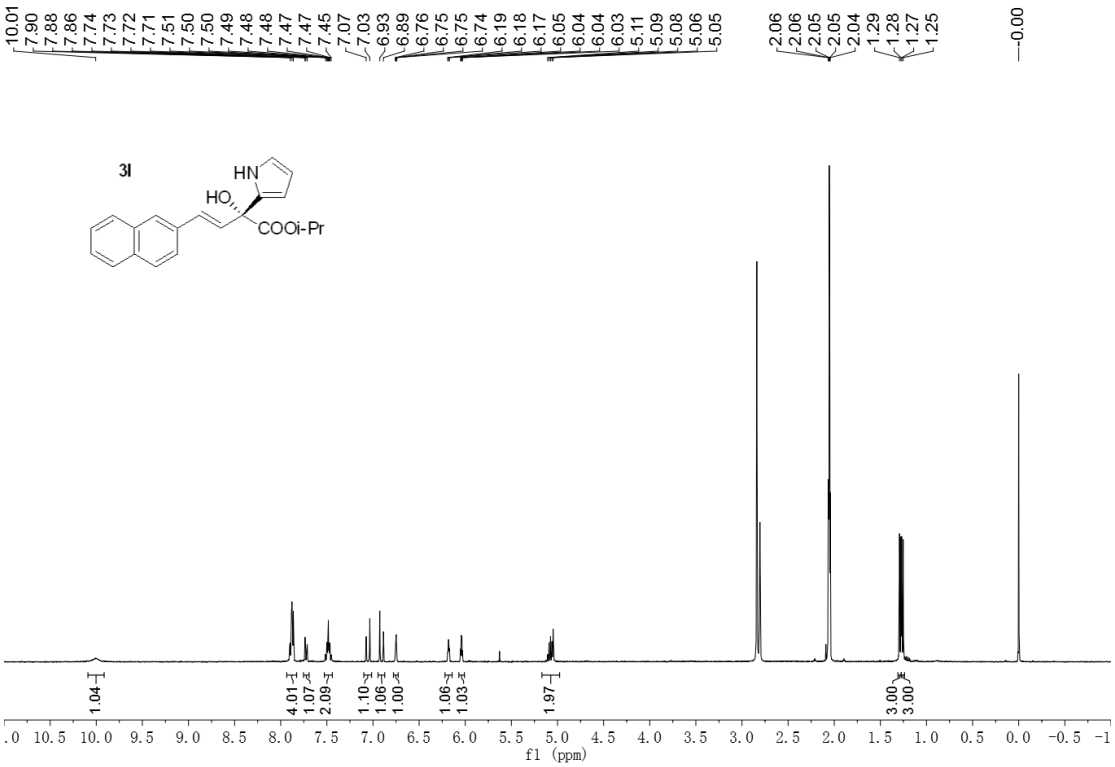
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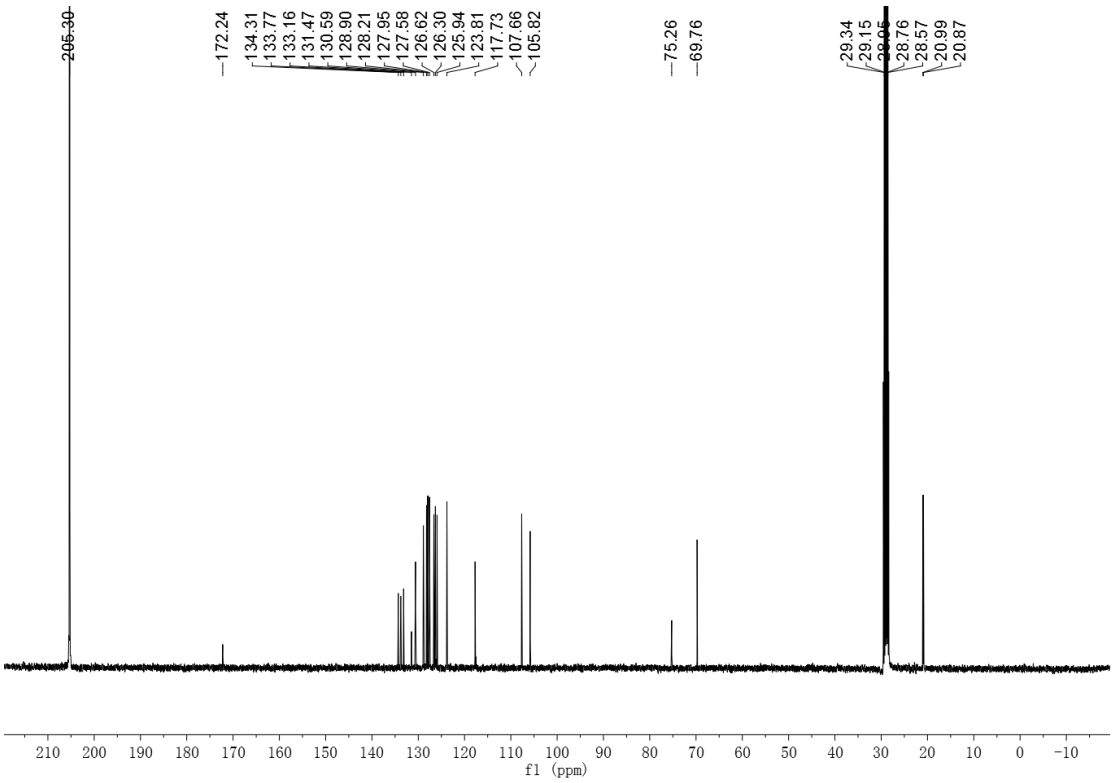
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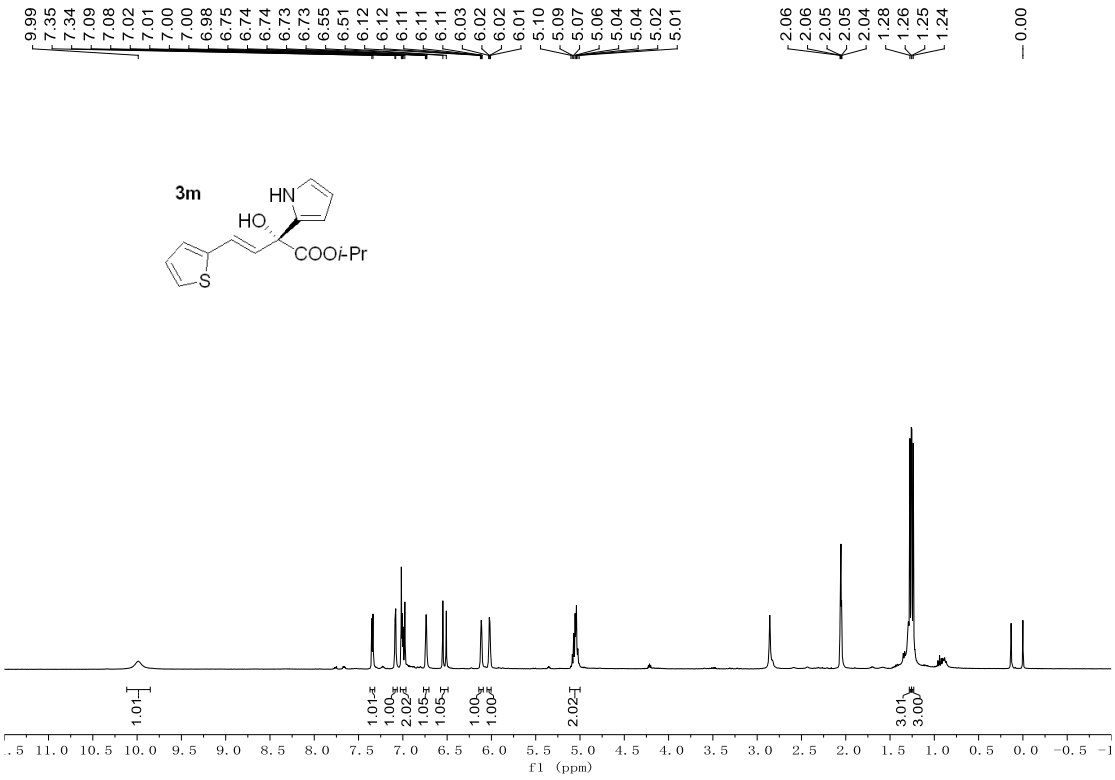
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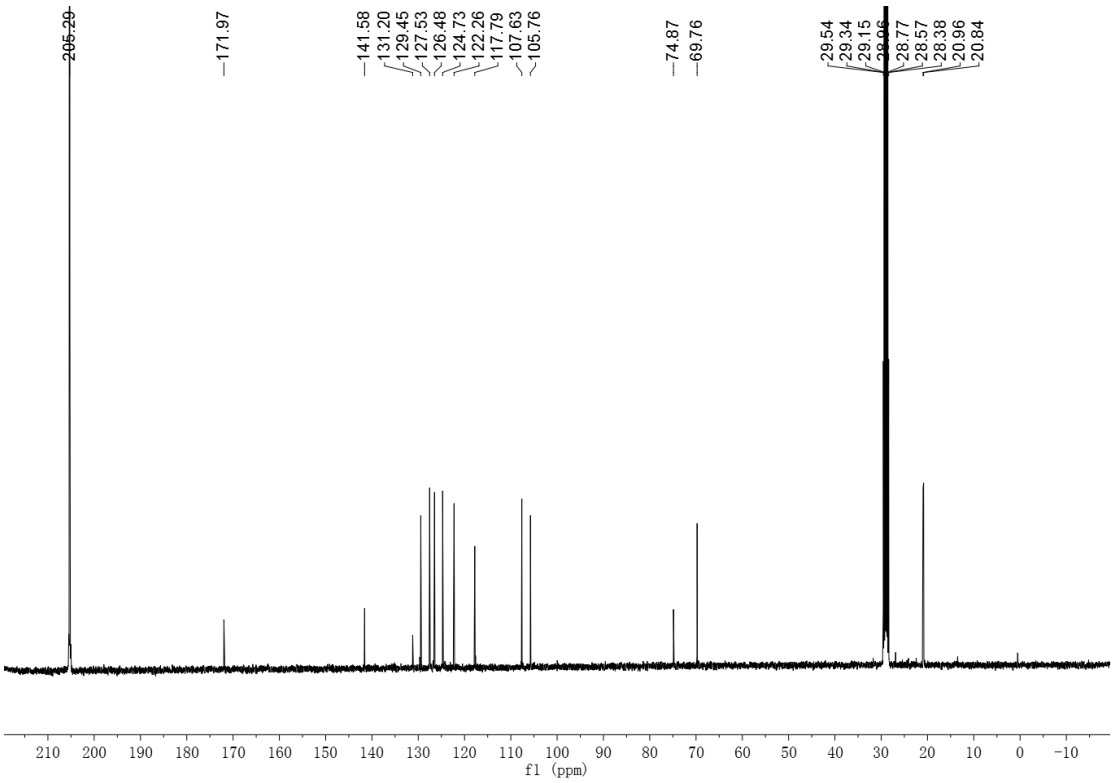
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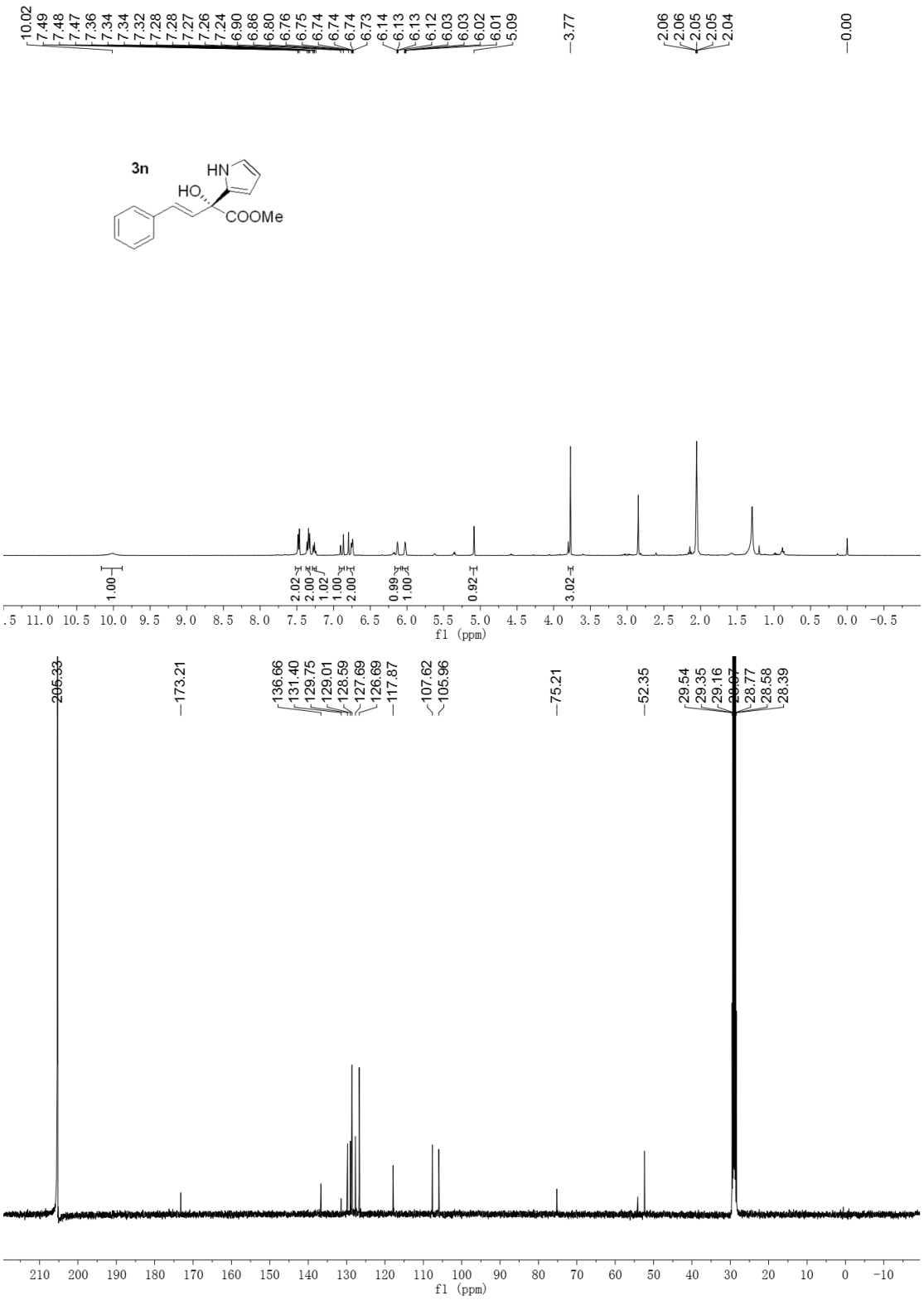
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128.59
127.69
126.69
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29.54
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28.39
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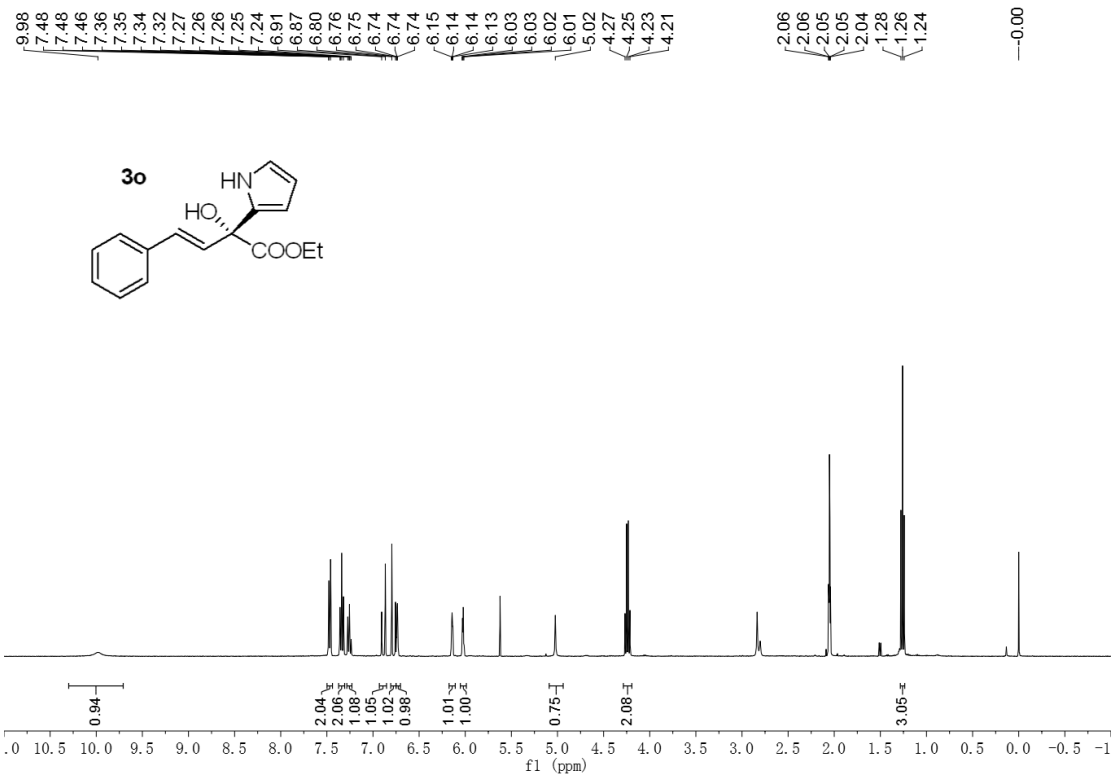
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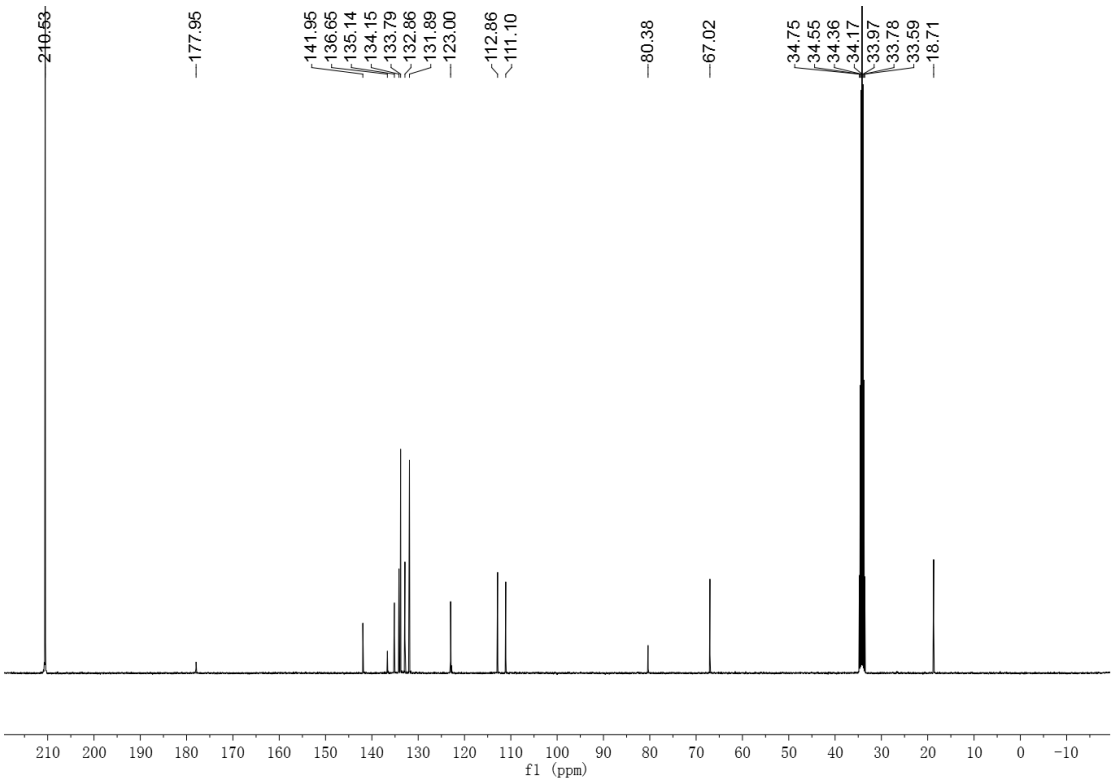
7.25
7.24
6.91
6.87
6.80
6.76
6.75
6.74
6.74
6.74
6.15
6.14
6.14
6.13
6.03
6.03
6.02
6.01
5.02
4.27
4.25
4.23
4.21
2.06
2.06
2.05
2.05
2.04
1.28
1.26
1.24
0.00
3o
HN
HO
COOEt
0.94
2.04
2.06
1.08
1.05
1.02
0.98
1.01
1.00
0.75
2.08
3.05
f1 (ppm)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123.00
112.86
111.10
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34.36
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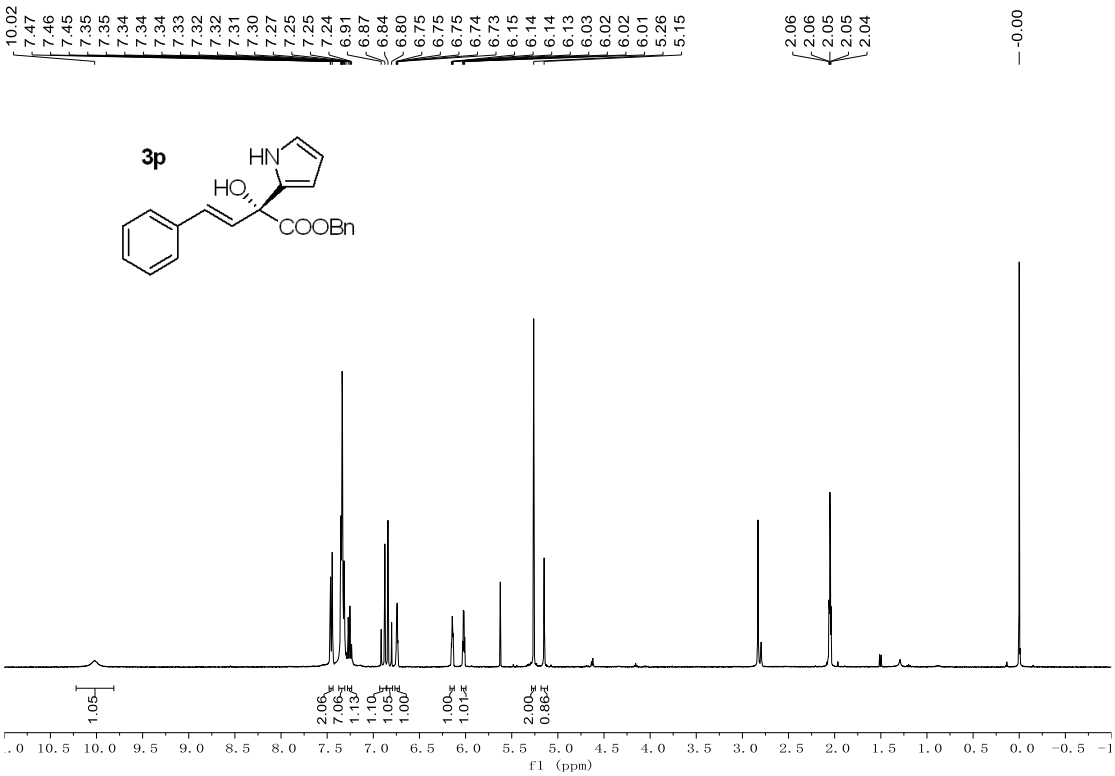
33.97
33.78
33.59
18.71
f1 (ppm)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7.30
7.27
7.25
7.25
7.24
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6.87
6.84
6.80
6.75
6.75
6.75
6.74
6.73
6.15
6.14
6.14
6.13
6.03
6.02
6.02
6.01
5.26
5.15
2.06
2.06
2.05
2.05
2.04
-0.00
3p
HN
HO
COOBn
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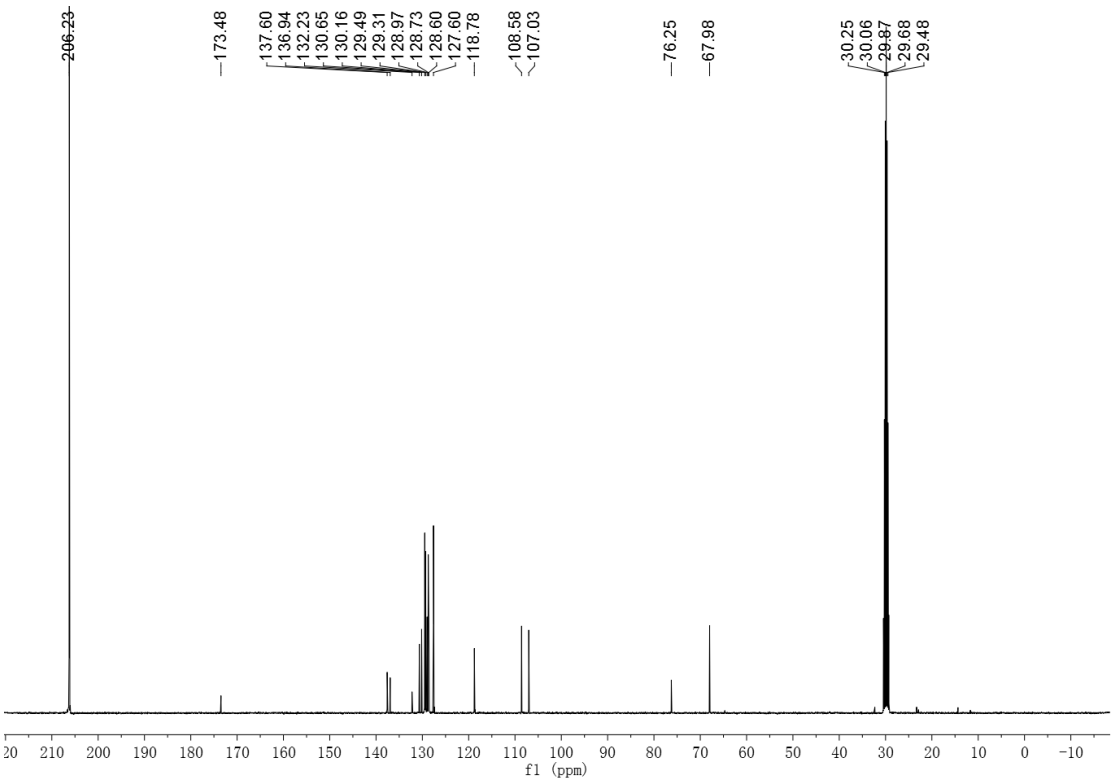
2.06
7.06
1.13
1.10
1.05
1.00
1.00
1.01
2.00
0.86
f1 (ppm)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129.49
129.31
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128.73
128.60
127.60
118.78
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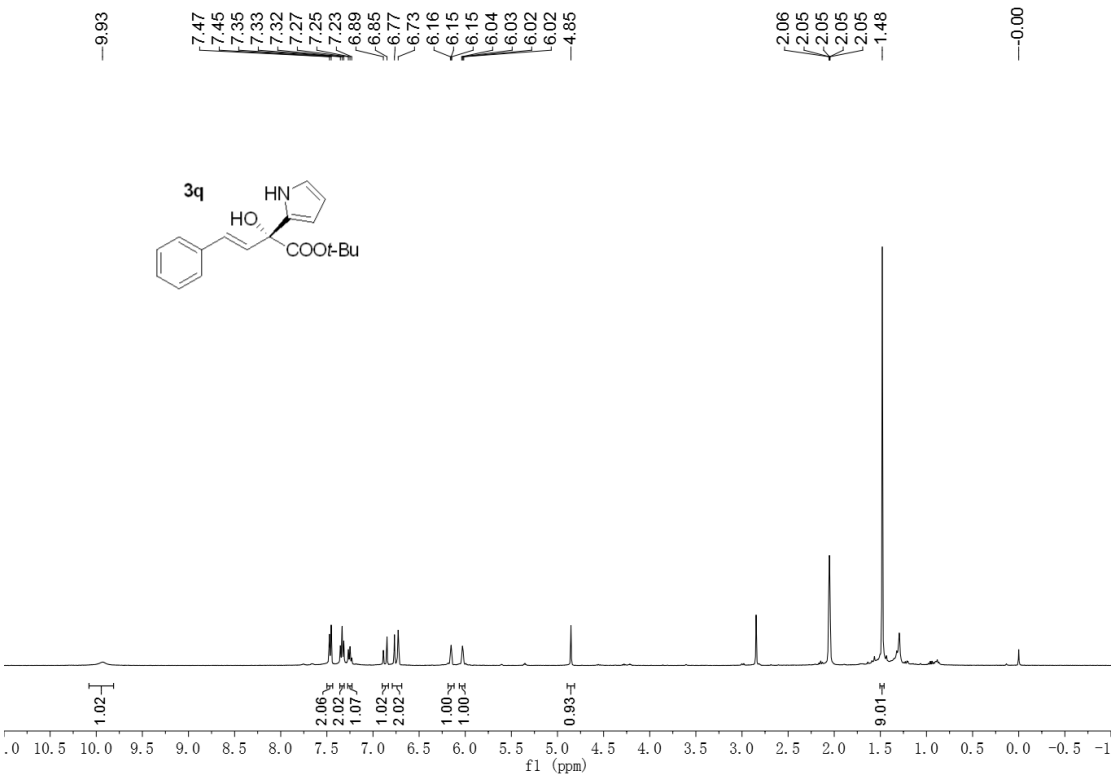
107.03
76.25
67.98
30.25
30.06
29.87
29.68
29.48
f1 (ppm)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6.89
6.85
6.77
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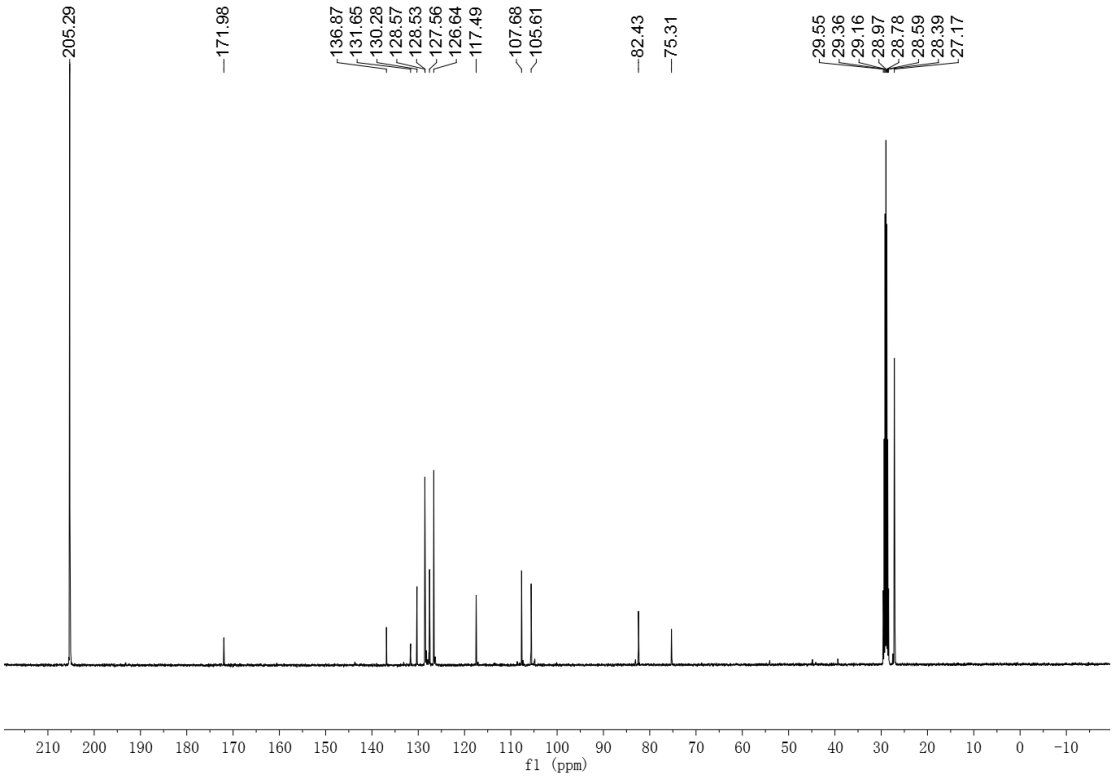
6.16
6.15
6.15
6.04
6.03
6.02
6.02
4.85
2.06
2.05
2.05
2.05
2.05
1.48
0.00
3q
HN
HO
COOt-Bu
1.02
2.06
2.02
1.07
1.02
2.02
1.00
1.00
0.93
9.01
f1 (ppm)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29.16
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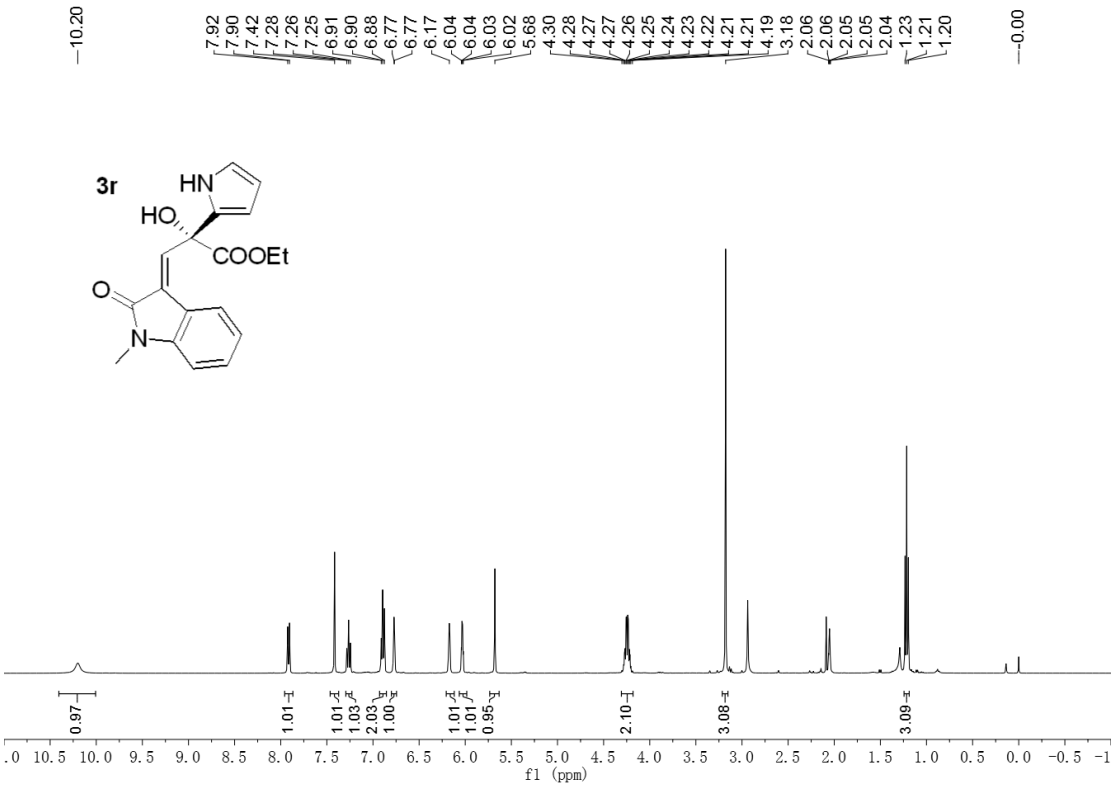
28.59
28.39
27.17
f1 (ppm)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6.88
6.77
6.77
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6.04
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6.02
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4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.19
3.18
2.06
2.06
2.05
2.05
2.04
1.23
1.21
1.20
0.00
3r
HN
HO
COOEt
O
N
0.97
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1.01
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2.03
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1.01
1.01
0.95
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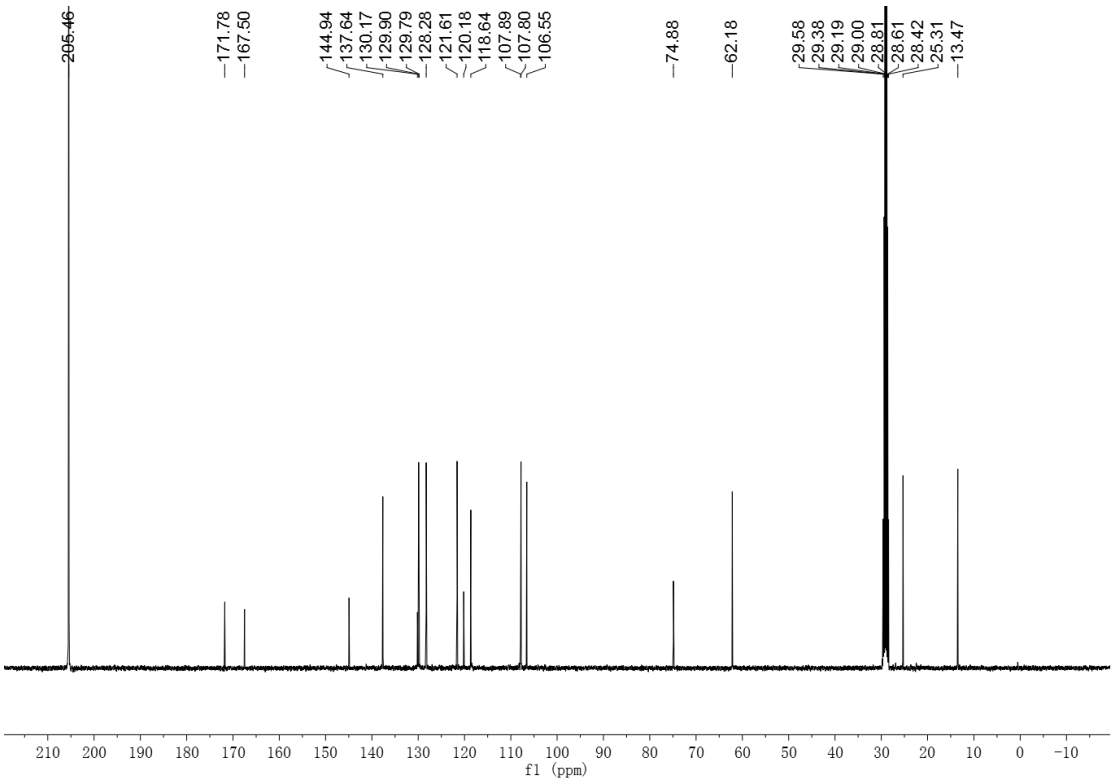
3.09
f1 (ppm)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121.61
120.18
118.64
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107.80
106.55
74.88
62.18
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29.38
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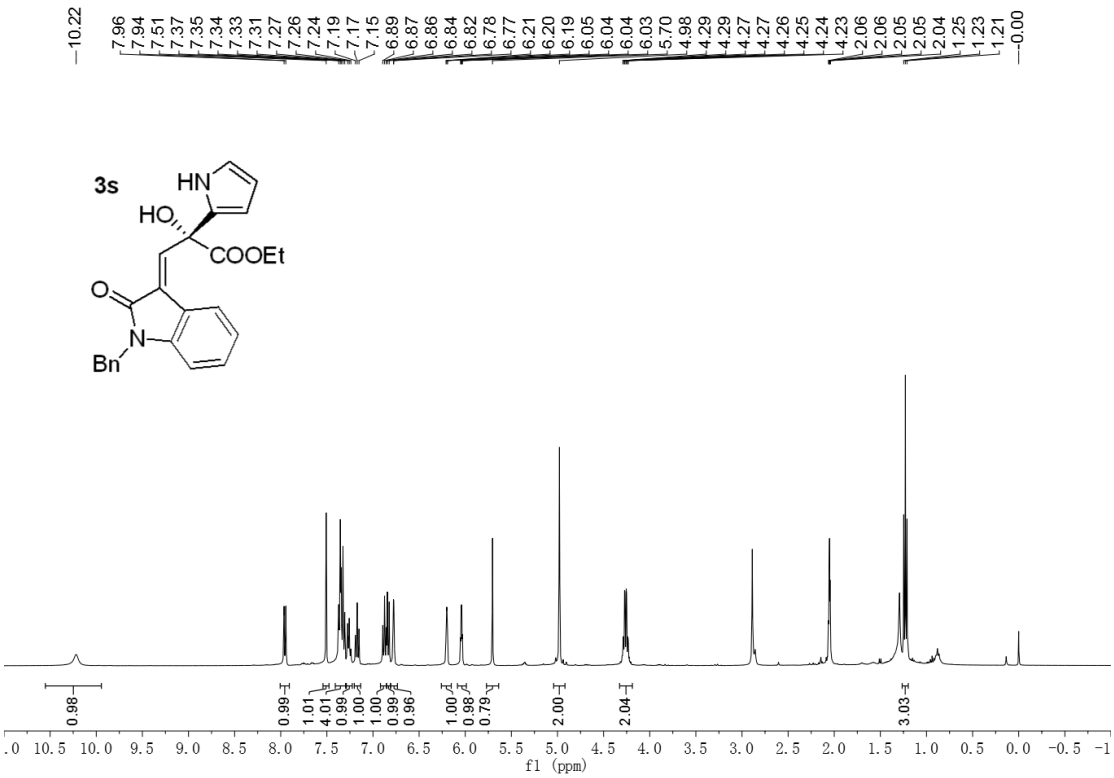
28.81
28.61
28.42
25.31
13.47
f1 (ppm)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7.33
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7.27
7.26
7.24
7.19
7.17
7.15
6.89
6.87
6.86
6.84
6.82
6.78
6.77
6.21
6.20
6.19
6.05
6.04
6.04
6.03
5.70
4.98
4.29
4.29
4.27
4.27
4.26
4.25
4.24
4.23
2.06
2.06
2.05
2.05
2.04
1.25
1.23
1.21
0.00
3s
HN
HO
COOEt
O
N
Bn
0.98
0.99
1.01
4.01
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1.00
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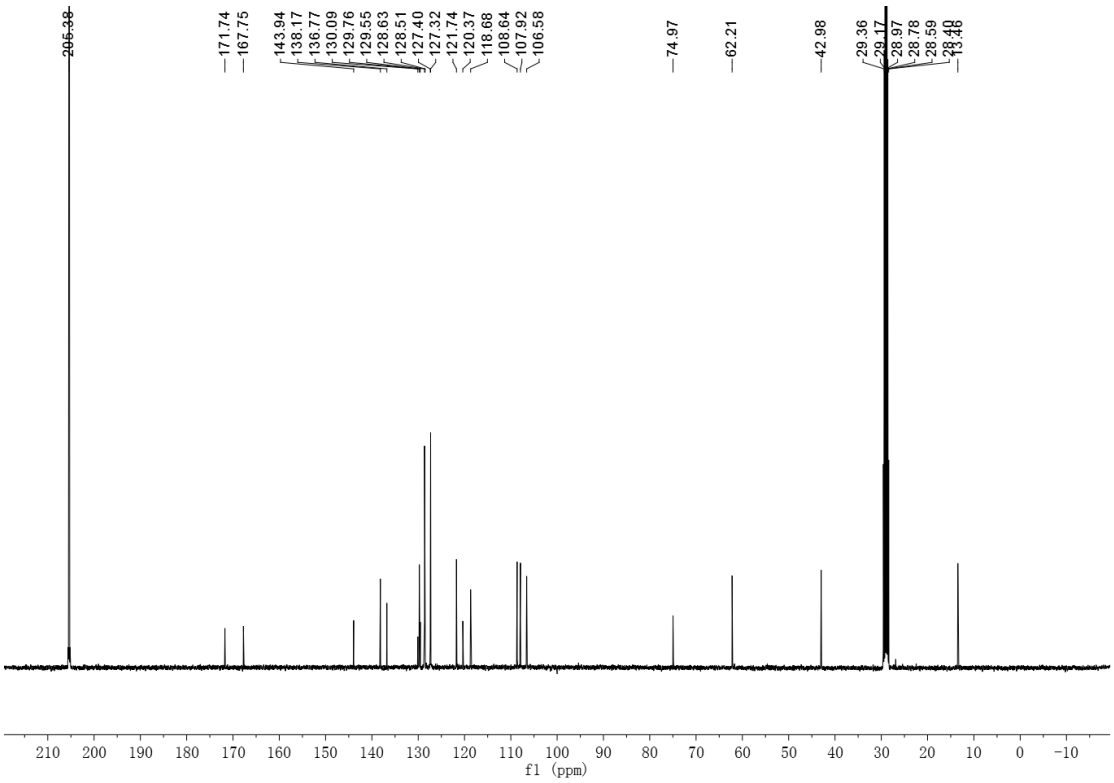
0.99
0.96
1.00
0.98
0.79
2.00
2.04
3.03
f1 (ppm)


206.38
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128.51
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127.32
121.74
120.37
118.68
108.64
107.92
106.58
74.97
62.21
42.98
29.36
29.17
28.97
28.78
28.59
28.40
13.46
f1 (ppm)

Part II HPLC data

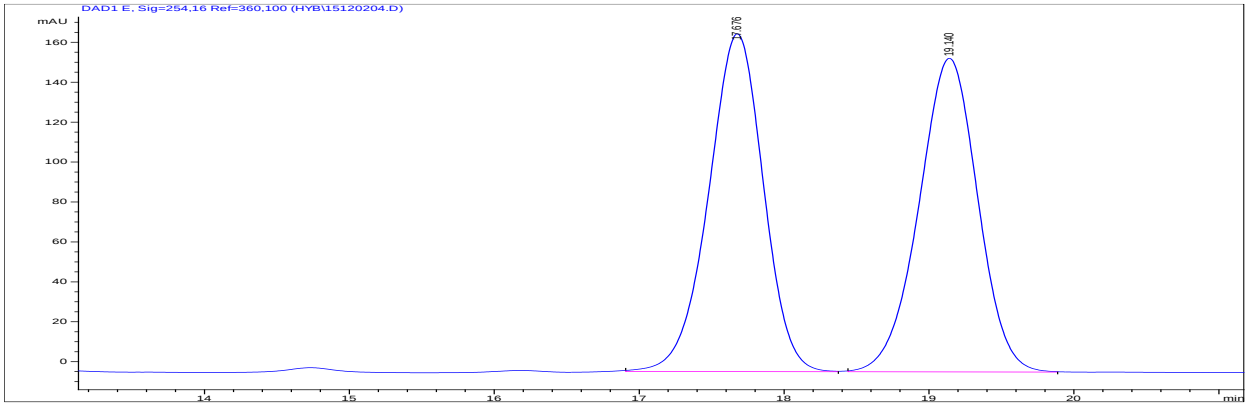
3a

racemic sample

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 41 bar, AD-H

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

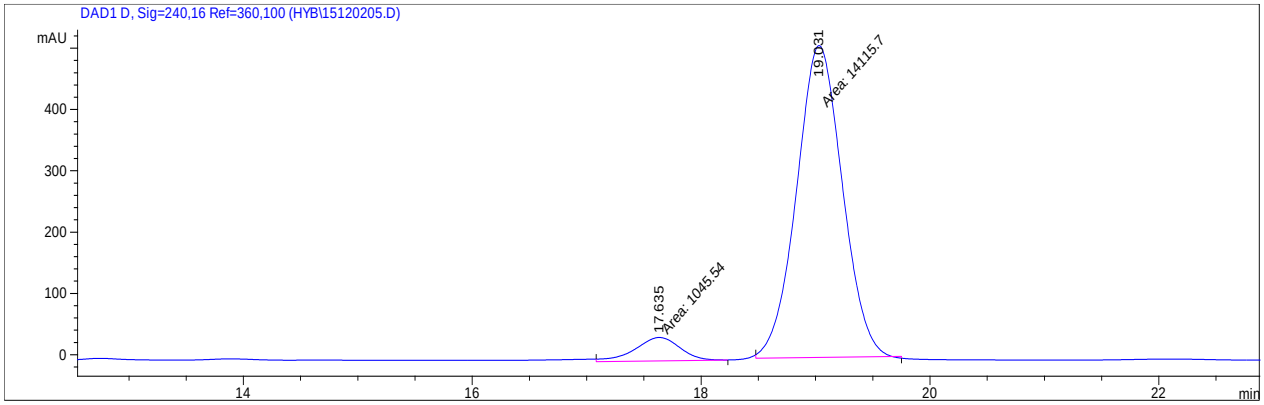
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.676	BB	0.4069	4451.05273	169.21396	50.1119
2	19.140	BB	0.4351	4431.18066	157.08612	49.8881



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.635	MM	0.4567	1045.53906	38.15291	6.8961
2	19.031	MM	0.4625	1.41157e4	508.69202	93.1039



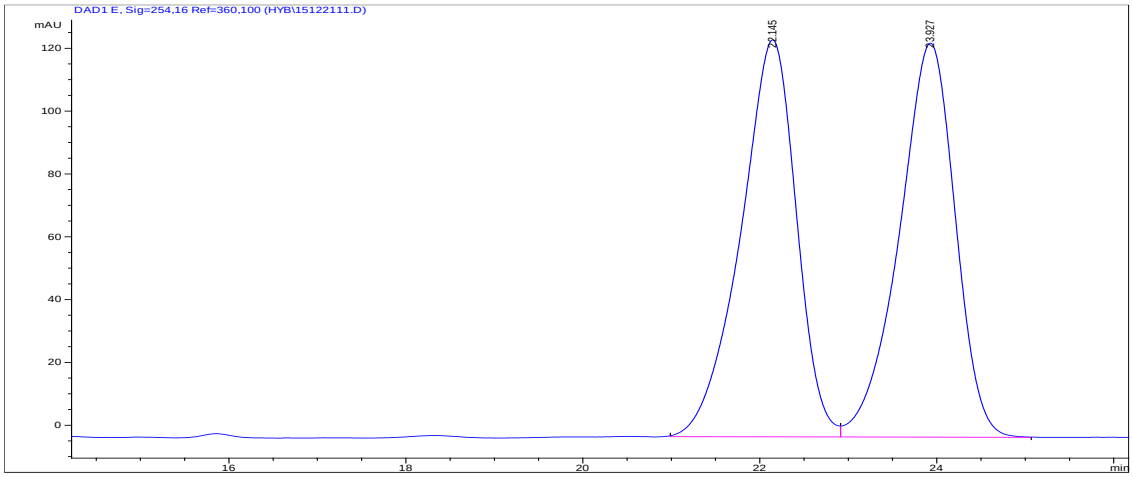
3b

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

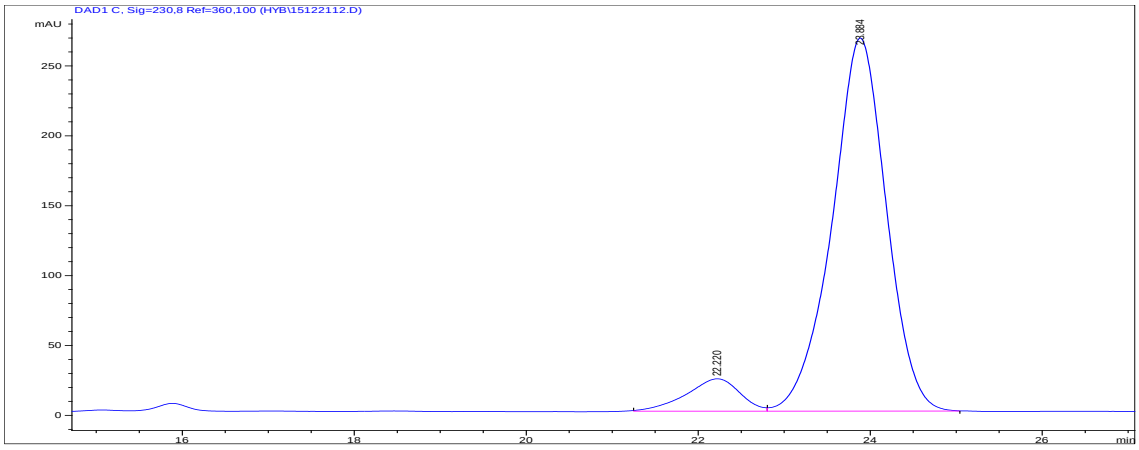
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.145	BV	0.6573	5538.39844	126.37861	50.0978
2	23.927	VB	0.6671	5516.77686	125.43429	49.9022



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.220	BV	0.6412	1002.85461	23.16078	7.8945
2	23.884	VB	0.6555	1.17004e4	266.86093	92.1055



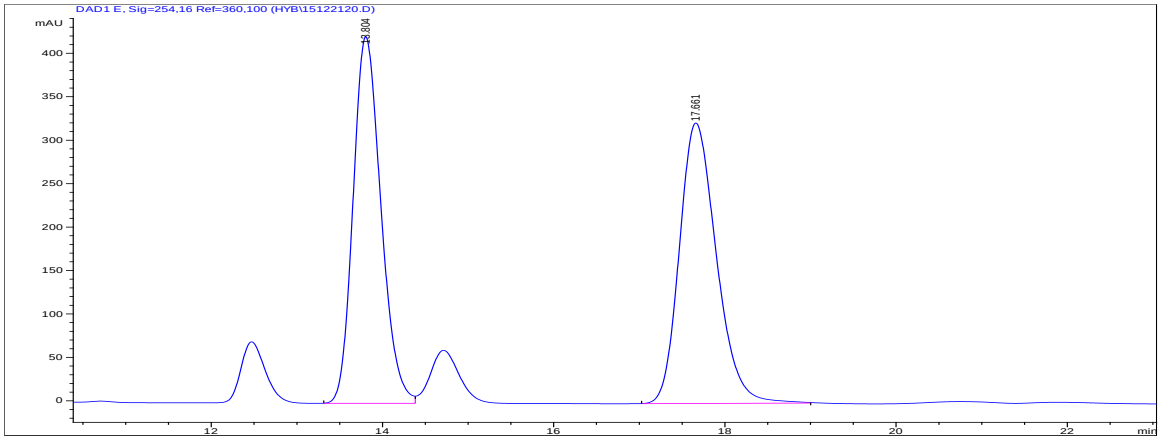
3c

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, IC

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

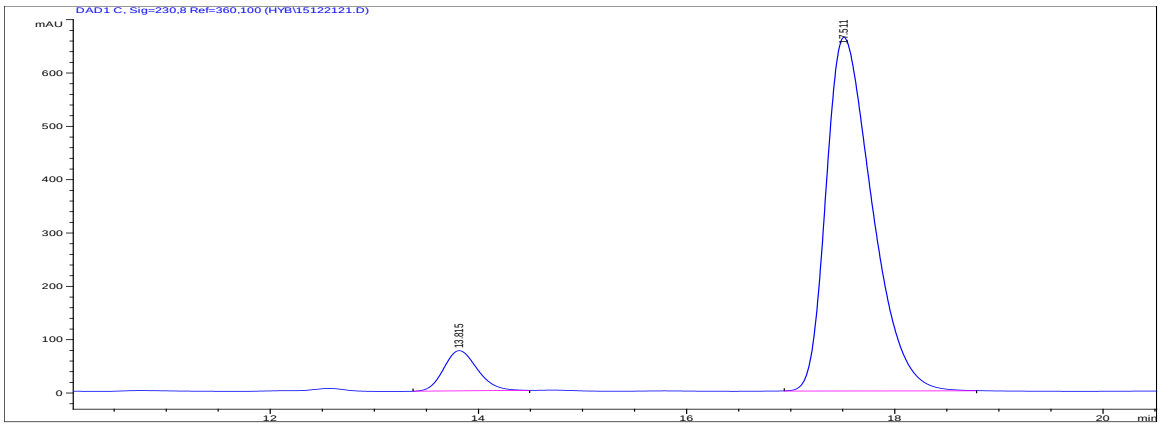
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.804	BV	0.3496	9537.43457	422.16965	49.5711
2	17.661	BB	0.4626	9702.49121	322.86505	50.4289



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.815	BB	0.3479	1694.20447	75.48242	7.6822
2	17.511	BB	0.4721	2.03593e4	663.20154	92.3178



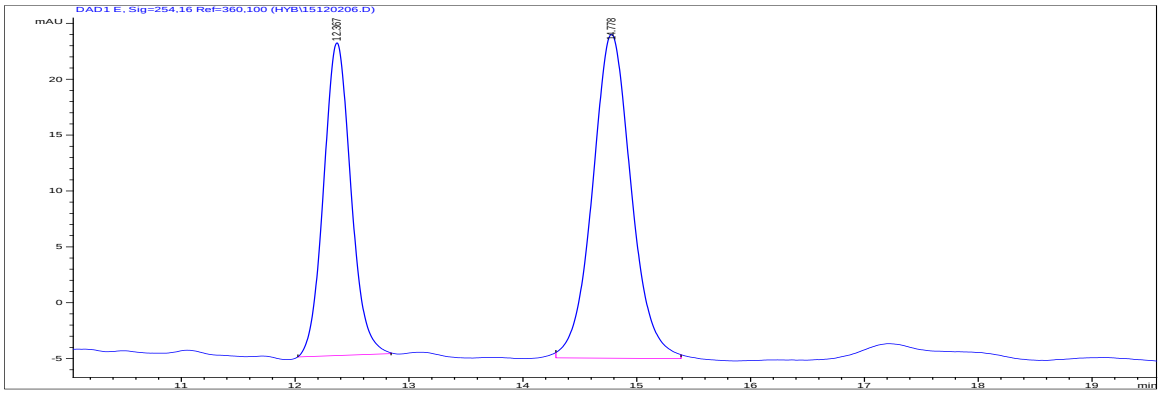
3d

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 41 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

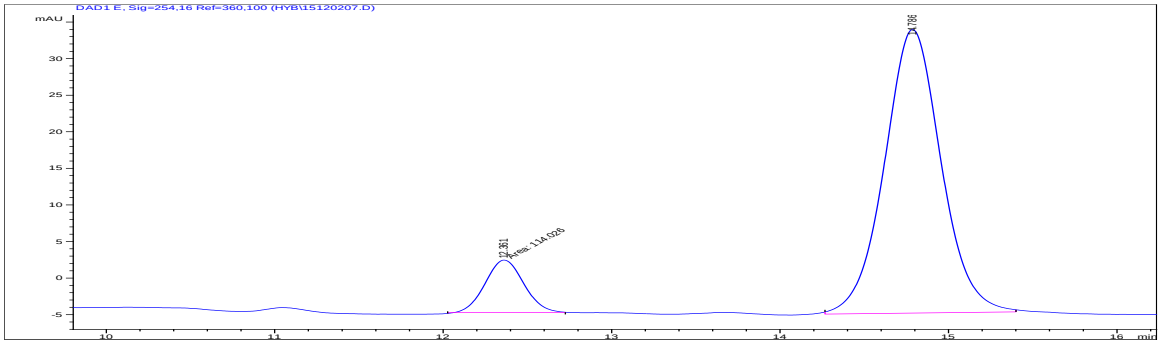
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.367	PB	0.2586	466.85434	27.99094	40.5659
2	14.778	BB	0.3572	683.99878	28.99656	59.4341



asymmetric sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.361	MM	0.2652	114.02628	7.16728	11.2041
2	14.786	BB	0.3559	903.69714	38.77050	88.7959



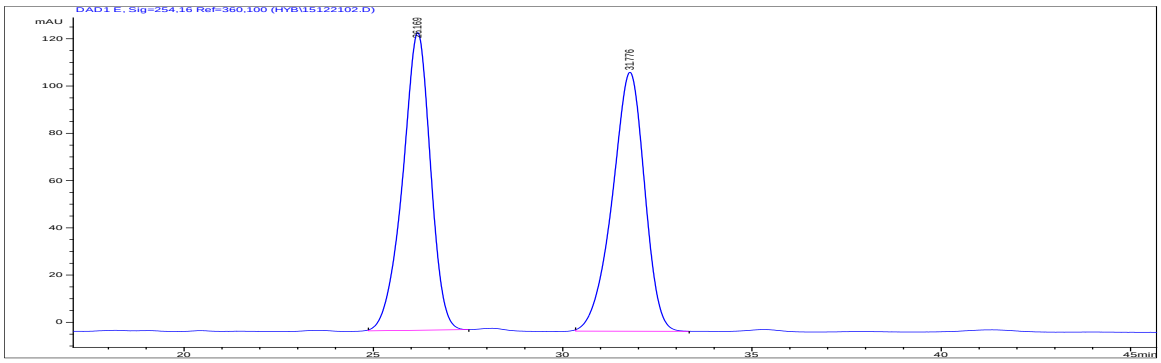
3e

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

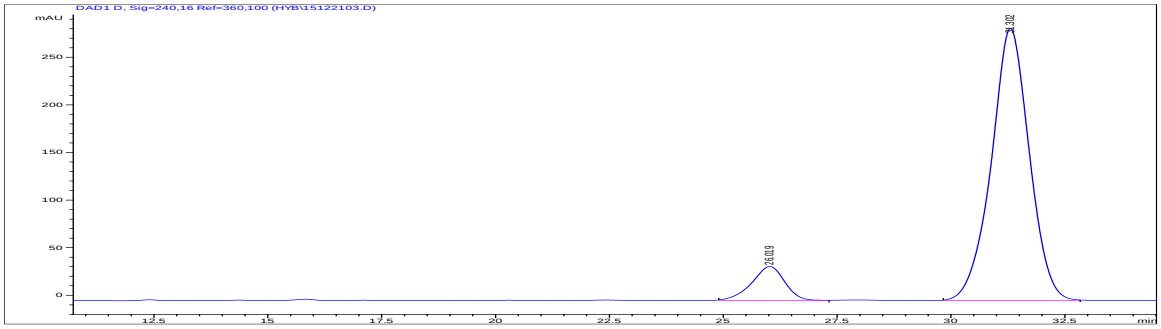
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.169	BP	0.7687	6441.61768	125.94911	49.8447
2	31.776	BB	0.8922	6481.75830	109.56834	50.1553



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.019	BP	0.7507	1774.79456	35.53718	9.6988
2	31.302	BB	0.8666	1.65243e4	285.78598	90.3012



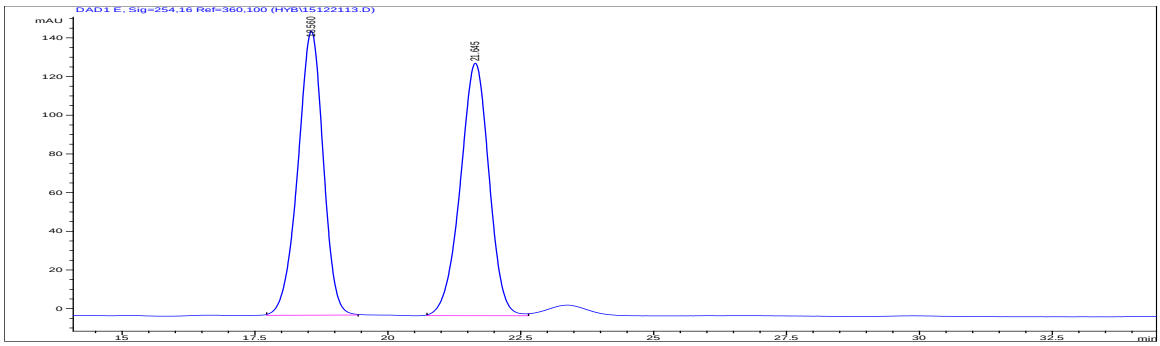
3f

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

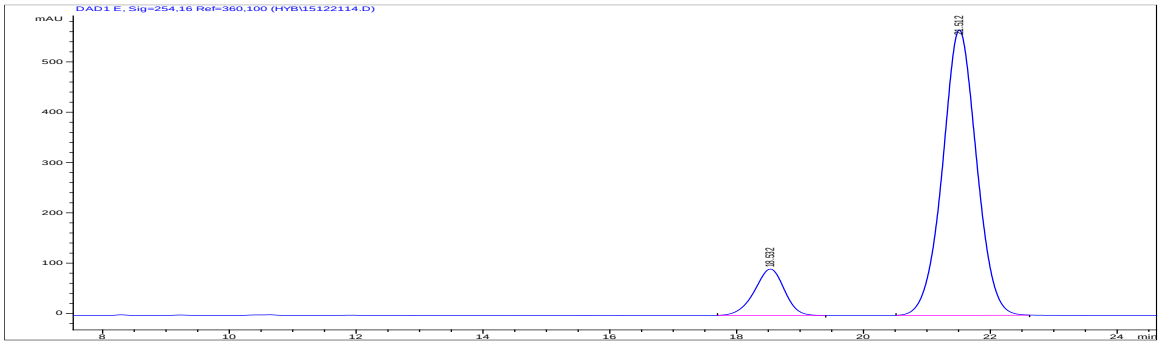
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.560	BB	0.5065	4862.77100	146.79391	49.7753
2	21.645	BB	0.5763	4906.67871	130.60710	50.2247



asymmetric sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.532	BB	0.4993	3031.09644	92.24912	12.5482
2	21.512	BB	0.5685	2.11244e4	567.14496	87.4518



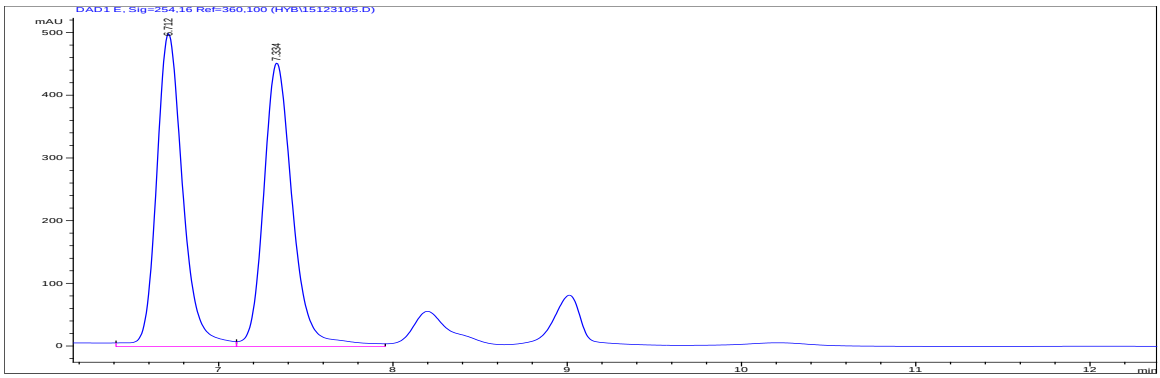
3h

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperatur
e = 30, pressure = 41bar, IC

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

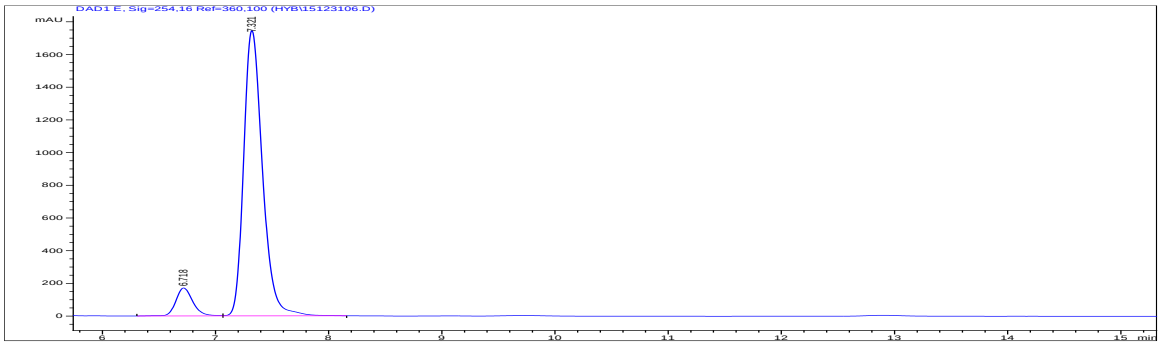
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.712	BV	0.1601	5220.52979	499.00208	49.9761
2	7.334	VV	0.1768	5225.52197	452.32910	50.0239



asymmetric sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.718	BV	0.1599	1789.33472	171.28102	8.1573
2	7.321	VB	0.1786	2.01460e4	1746.22656	91.8427



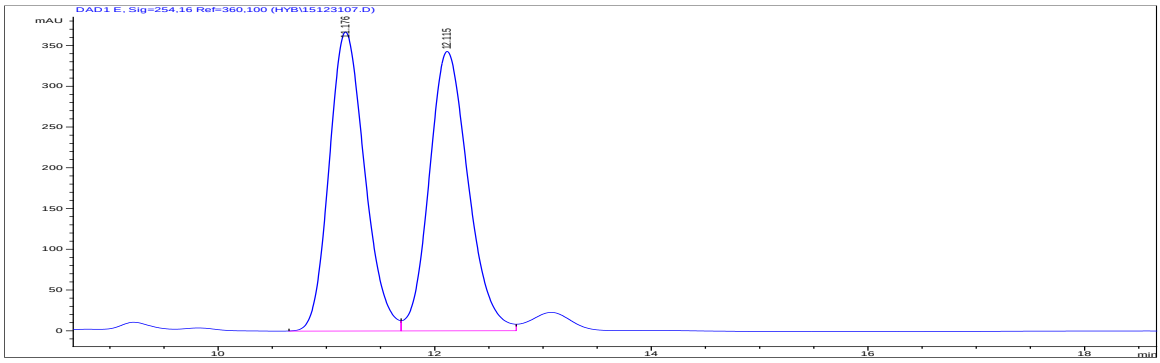
3i

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperatur
e = 30, pressure = 44 bar, OD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

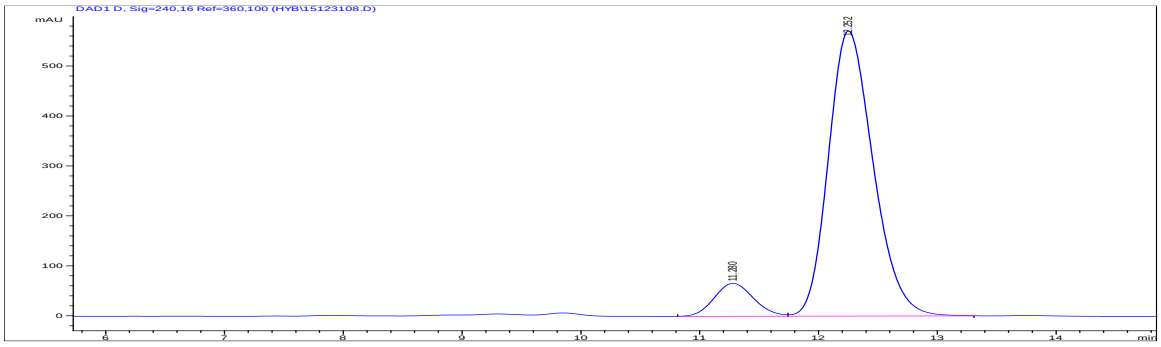
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.176	BV	0.3538	8357.66309	366.90344	49.3843
2	12.115	VV	0.3854	8566.07520	342.90973	50.6157



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.280	BV	0.3576	1512.52051	65.93875	9.1997
2	12.252	VB	0.4070	1.49285e4	570.98035	90.8003



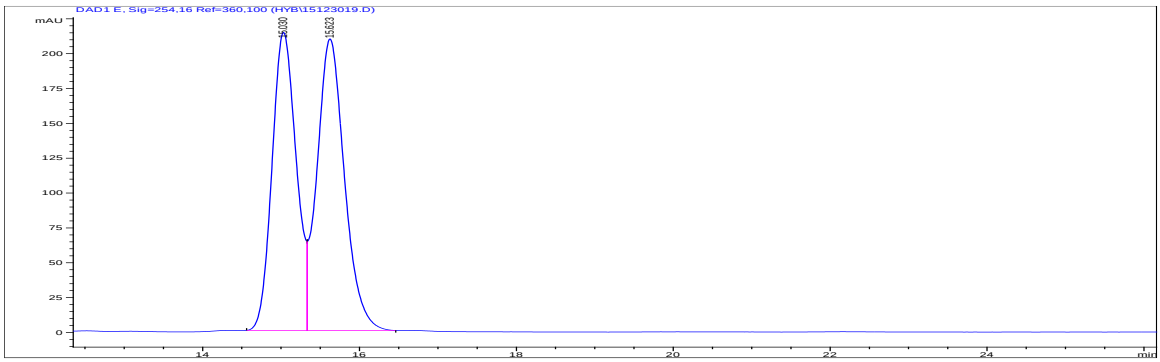
3j

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 43 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

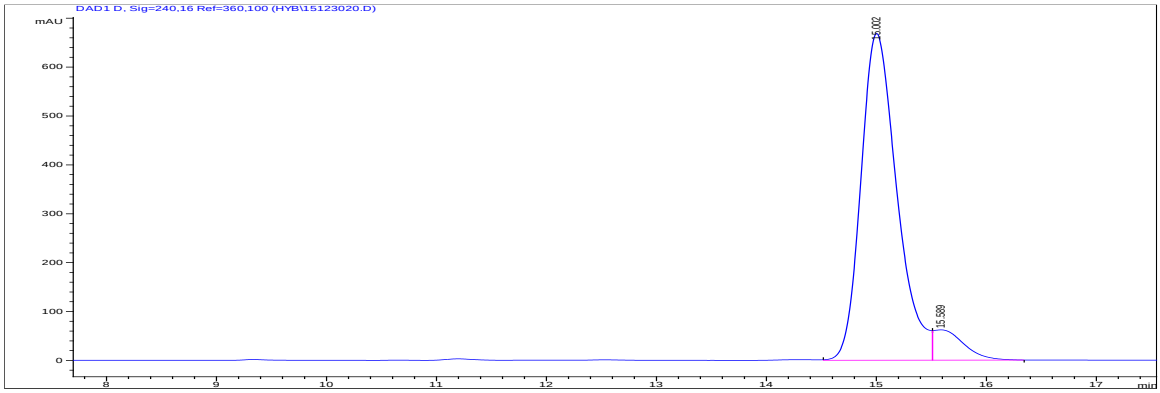
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.030	BV	0.3306	4593.83398	213.87308	47.5055
2	15.623	VB	0.3650	5076.26758	209.23659	52.4945



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.002	BV	0.3473	1.52036e4	668.47607	92.7778
2	15.589	VB	0.2869	1183.51331	61.95419	7.2222



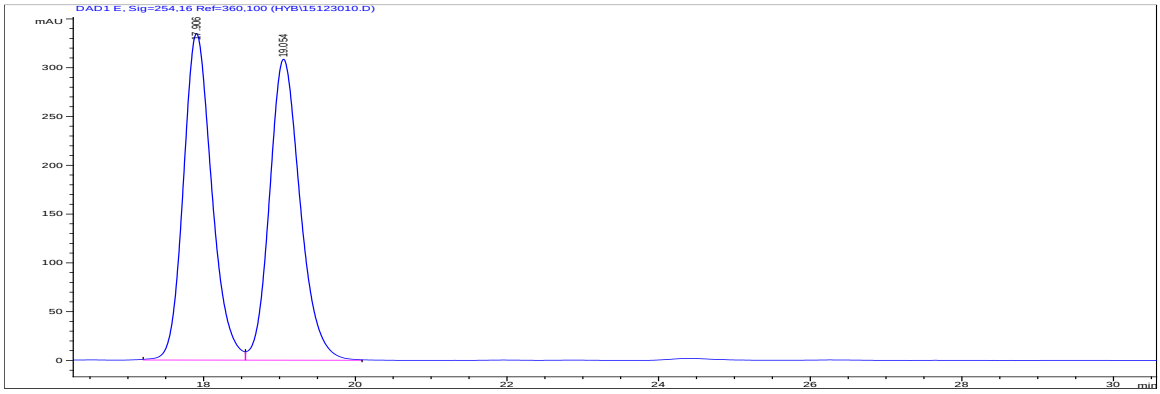
3k

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 43 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

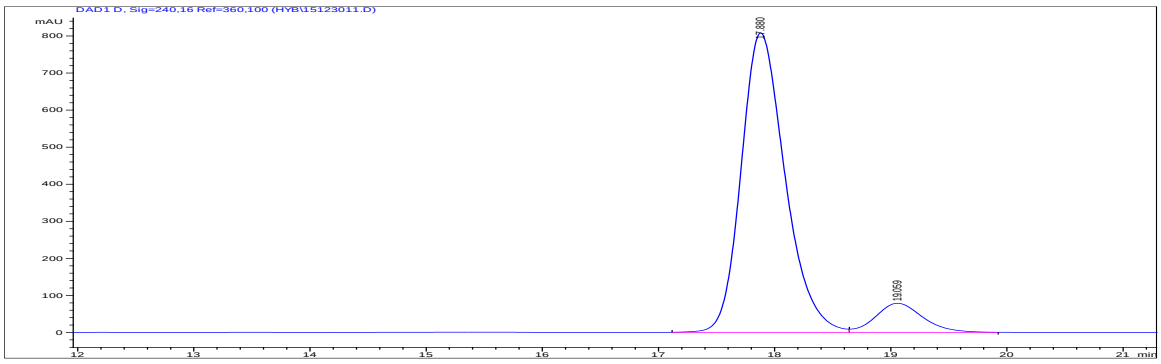
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.906	BV	0.3993	8697.45410	334.60196	50.1100
2	19.054	VB	0.4296	8659.28516	308.39484	49.8900



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.880	BV	0.4021	2.12119e4	808.47510	90.5529
2	19.059	VB	0.4305	2212.97339	78.59988	9.4471



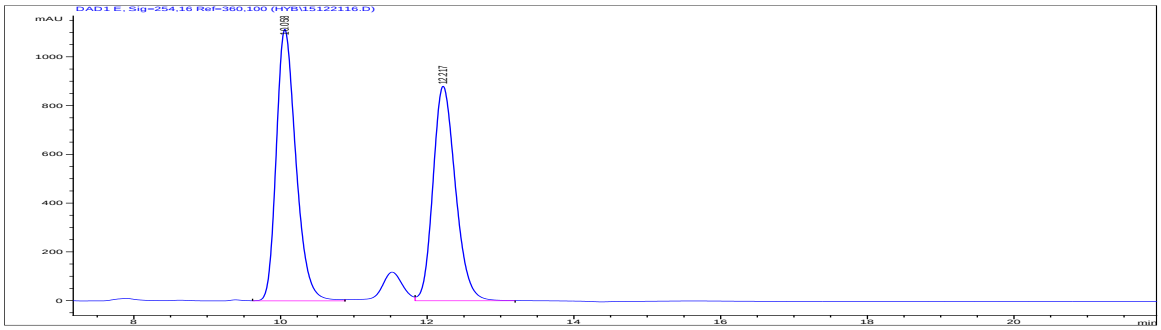
3l

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, IC

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

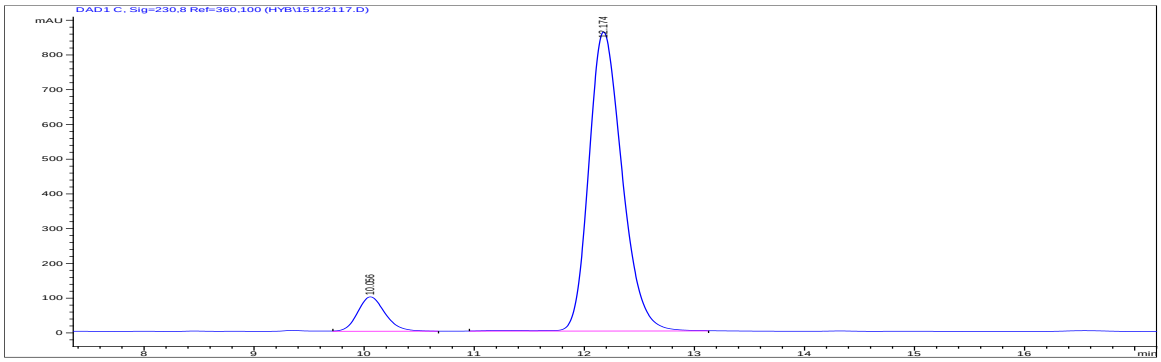
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.058	VB	0.2848	2.06928e4	1113.55823	52.5062
2	12.217	VB	0.3300	1.87174e4	880.34784	47.4938



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.056	BB	0.2673	1706.73010	98.90878	8.6261
2	12.174	BB	0.3250	1.80790e4	860.98029	91.3739



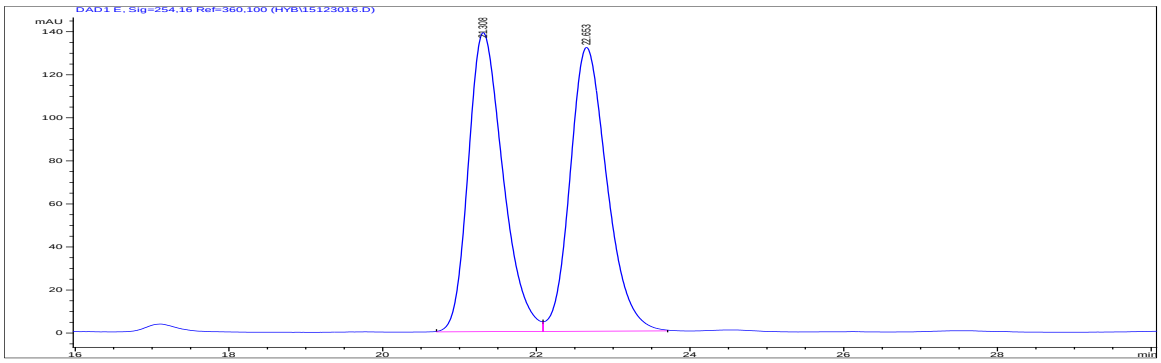
3m

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 43 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

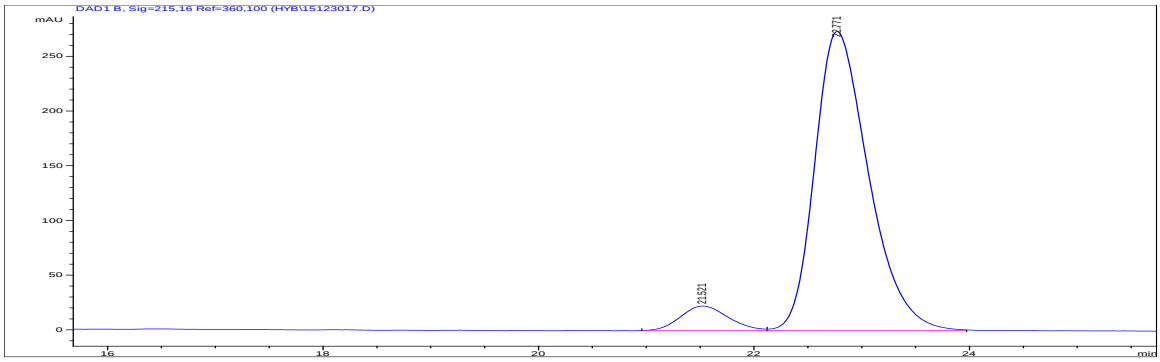
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.308	BV	0.4842	4361.02686	138.95020	49.7498
2	22.653	VB	0.5137	4404.89111	131.87442	50.2502



asymmetric sample

Signal 2: DAD1 B, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.521	BV	0.4704	691.96881	22.52327	6.8069
2	22.771	VB	0.5325	9473.77734	273.27484	93.1931



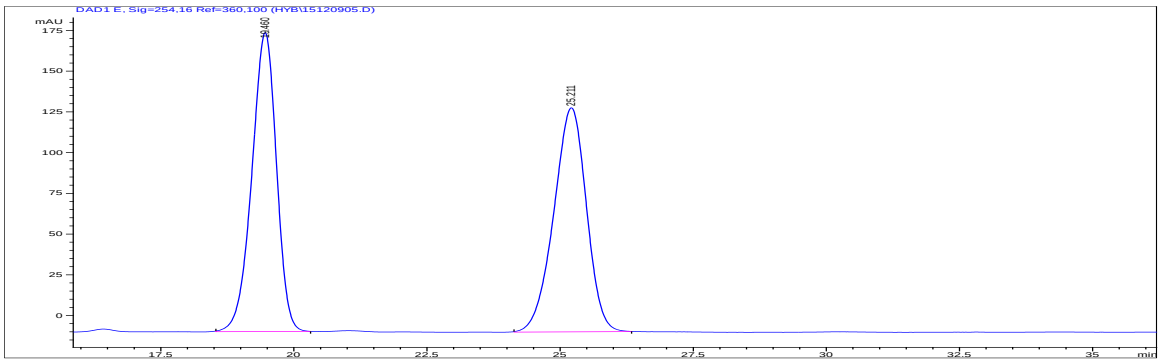
3n

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

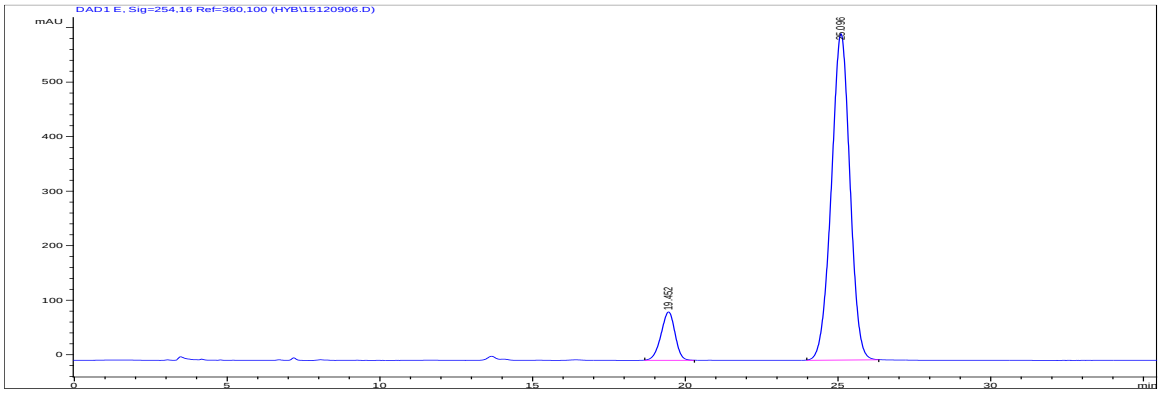
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.460	BB	0.4957	5910.56104	183.52922	50.1536
2	25.211	BB	0.6563	5874.35010	137.54443	49.8464



asymmetric sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.452	BB	0.4916	2822.55322	88.60566	10.0273
2	25.096	BB	0.6497	2.53261e4	598.53162	89.9727



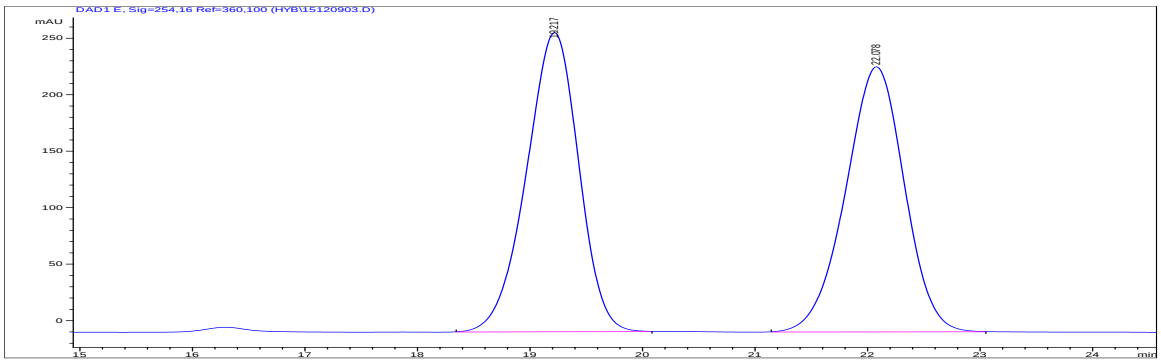
3o

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

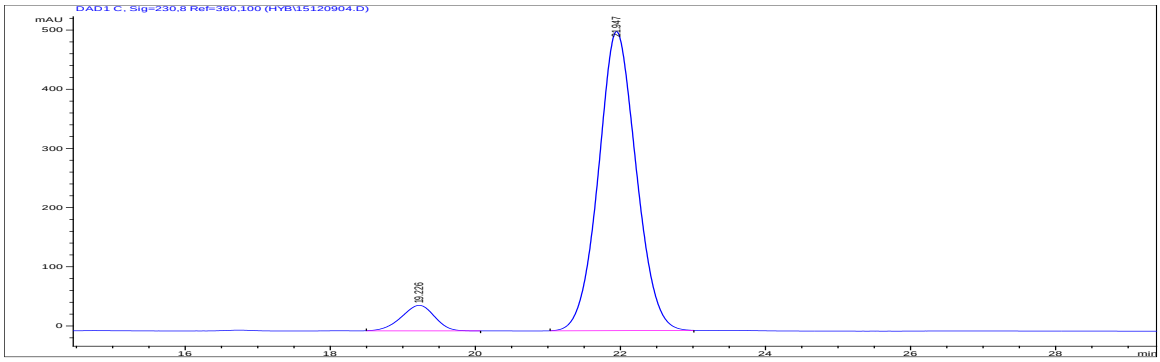
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.217	BB	0.4996	8572.91797	264.86893	50.1376
2	22.078	BB	0.5598	8525.87012	234.72502	49.8624



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.226	BP	0.4868	1371.52844	43.14917	6.9872
2	21.947	BB	0.5512	1.82577e4	505.68280	93.0128



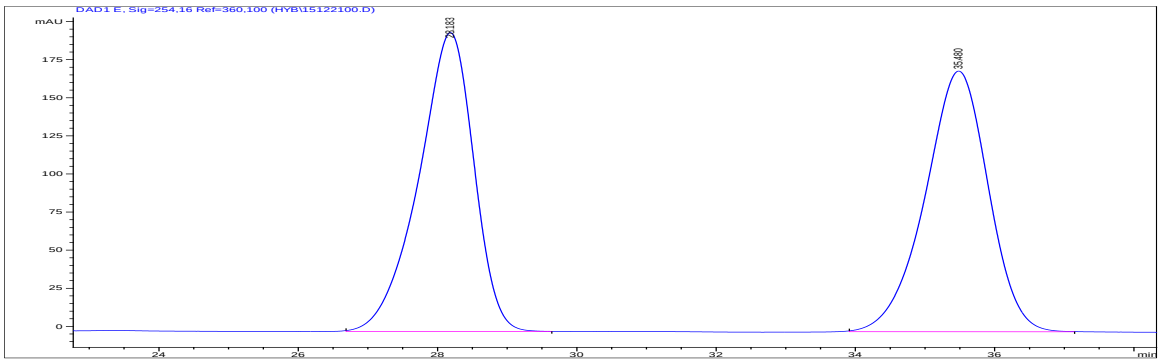
3p

Hexane:i-POH=90:10; Flow rate = 1.0 ml/min, temperature = 30, pressure = 50 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

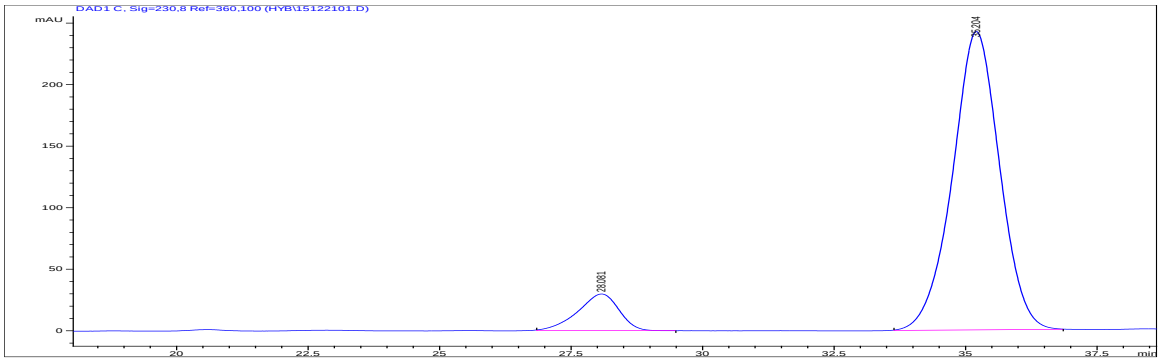
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.183	BB	0.8220	1.07869e4	196.02548	50.0642
2	35.480	BB	0.9641	1.07592e4	170.99744	49.9358



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.081	BB	0.7969	1612.50757	29.72417	9.6336
2	35.204	BB	0.9399	1.51258e4	242.42183	90.3664



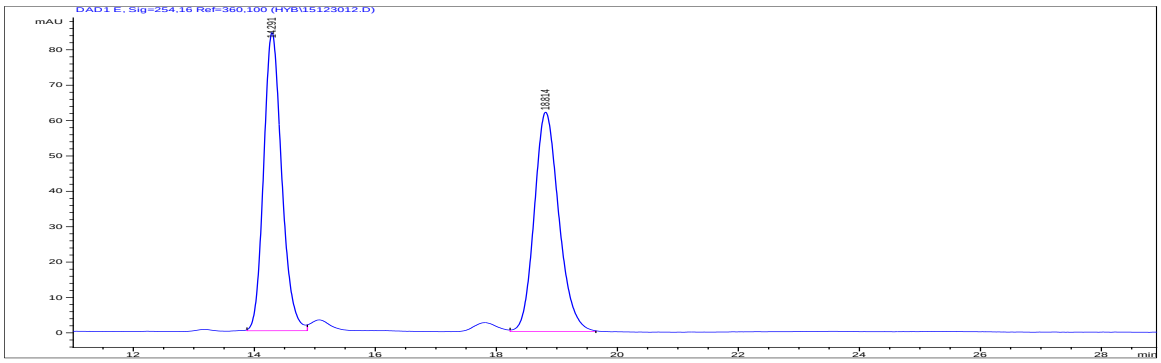
3q

Hexane:i-PrOH=90:10; Flow rate = 1.0 ml/min, temperatur
e = 30, pressure = 43 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

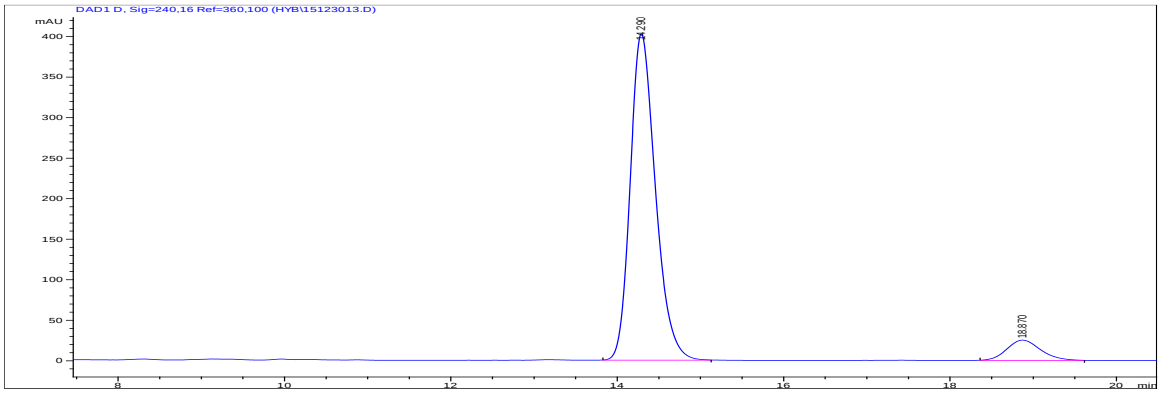
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.291	BB	0.3188	1752.99500	84.24818	50.0892
2	18.814	VB	0.4327	1746.74878	62.00018	49.9108



asymmetric sample

Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.290	BB	0.3237	8482.37109	402.78931	92.3220
2	18.870	BB	0.4310	705.43842	25.01303	7.6780



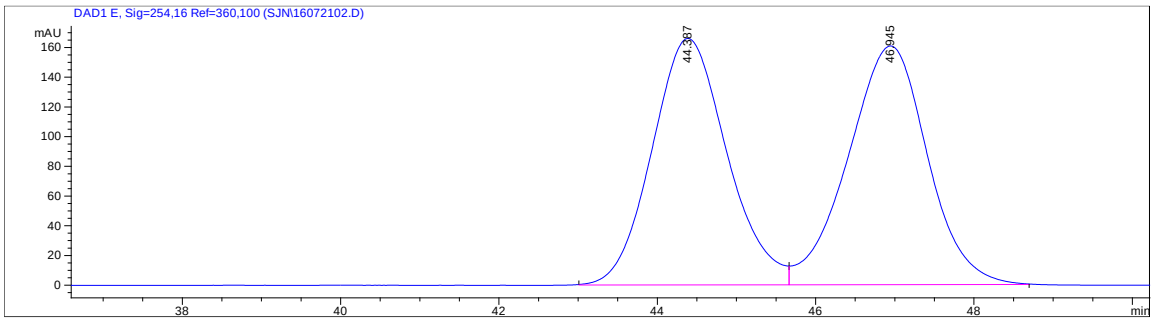
3r

Hexane:i-PrOH=90:10; Flow rate =1.0 ml/min, temperature =30 , pressure = 46 bar, AD-H

racemic sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

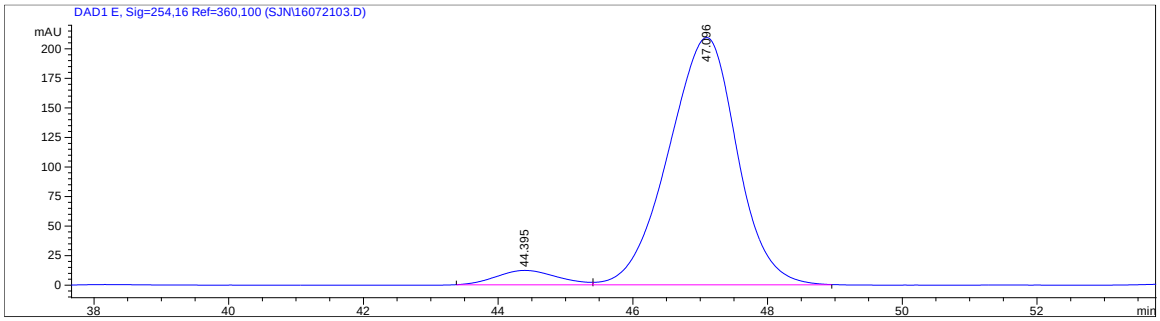
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.387	BV	1.0035	1.09137e4	165.88744	49.3737
2	46.945	VB	1.0426	1.11906e4	160.66936	50.6263



asymmetric sample

Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.395	BV	0.7957	756.42316	12.12745	4.8718
2	47.096	VB	1.0737	1.47700e4	209.21066	95.1282



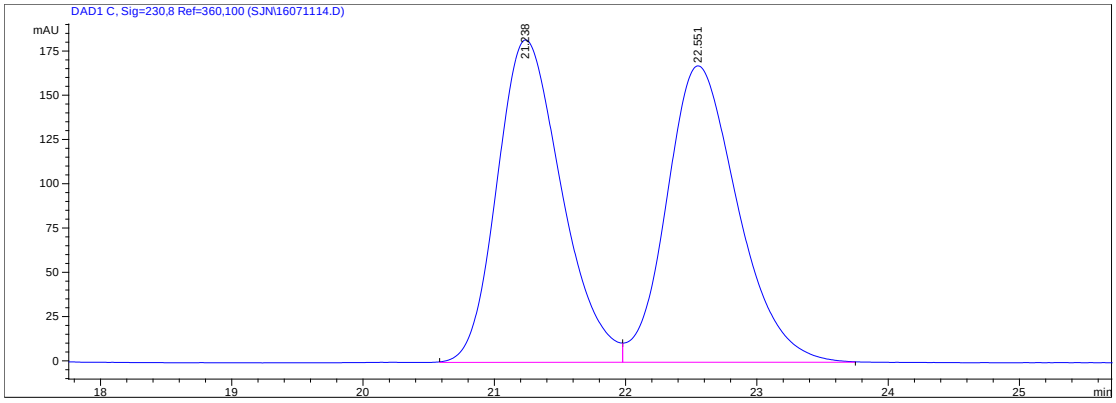
3s

Hexane:i-PrOH=70:30; Flow rate =0.8 ml/min, temperature = 30, pressure = 47 bar,AD-H

racemic sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

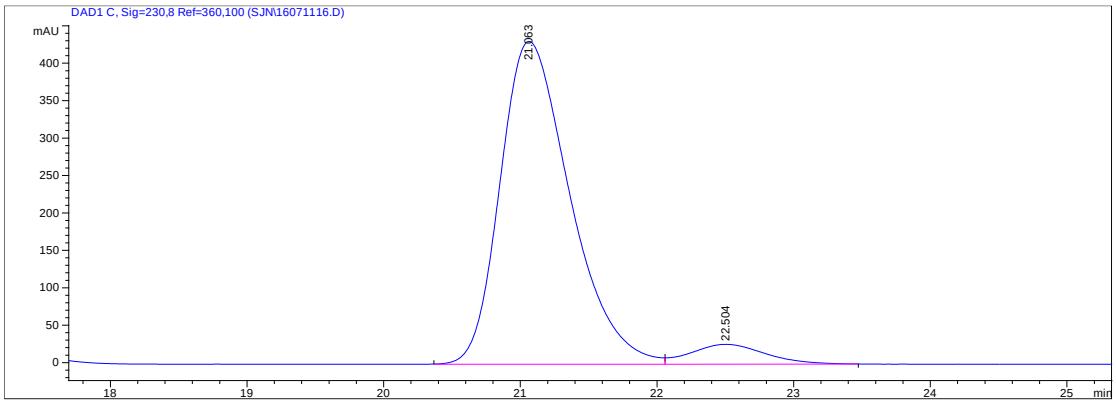
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.238	BV	0.5270	6228.45020	182.13962	49.7465
2	22.551	VB	0.5785	6291.92285	167.41130	50.2535



asymmetric sample

Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.063	BV	0.5456	1.52919e4	431.37170	93.8386
2	22.504	VB	0.5743	1004.04871	26.48499	6.1614



Part III Crystal structure data

A single crystal for X-ray analysis of **3l** was obtained by recrystallation from EtOAc/petroleum ether.

CCDC-1513034 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

CCDC 1513034

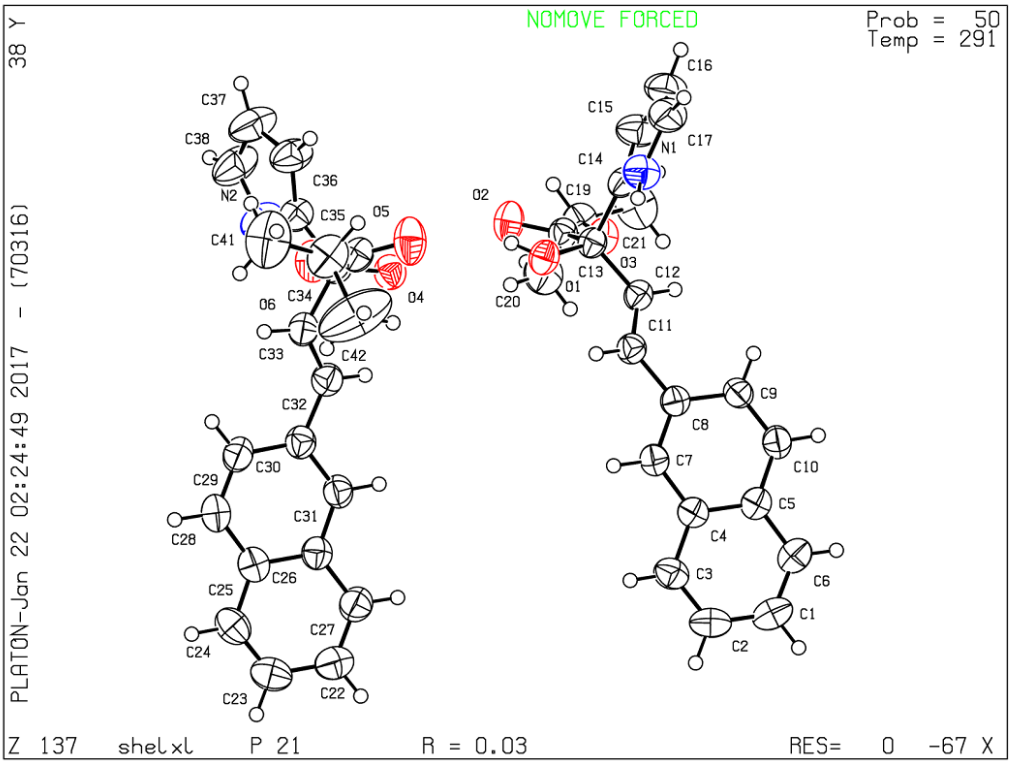


Table S1 Crystal data and structure refinement for 3l.

Identification code	**3l**
Empirical formula	$C_{21}H_{21}NO_3$
Formula weight	335.39
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1$

a/Å	11.68820(10)
b/Å	7.93580(10)
c/Å	20.2157(2)
α/°	90
β/°	105.2310(10)
γ/°	90
Volume/Å^3	1809.25(3)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.660
F(000)	712.0
Crystal size/mm^3	0.240 × 0.220 × 0.210
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.84 to 142.632
Index ranges	$-14 \leq h \leq 13$, $-8 \leq k \leq 9$, $-23 \leq l \leq 24$
Reflections collected	25060
Independent reflections	6527 [R_{int} = 0.0227, R_{sigma} = 0.0188]
Data/restraints/parameters	6527/1/457
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0892
Final R indexes [all data]	R_1 = 0.0347, wR_2 = 0.0918
Largest diff. peak/hole / e Å^{-3}	0.14/-0.13
Flack parameter	-0.04(8)

The ellipsoid contour percent probability level is 30%