Organocatalytic [3+2] cycloaddition of oxindole-based azomethine ylides with 3-nitrochromenes: a facile approach to enantioenriched polycyclic spirooxindole-chromane adducts

Shiqi Wu[†], Guodong Zhu[‡], Shiqiang Wei[‡], Hongbo Chen[†], Jingping Qu[‡] and Baomin Wang[‡,*]

School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin Campus, Panjin 124221, P. R. China.
State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian University of Technology, Dalian 116024, P. R. China
bmwang@dlut.edu.cn

Contents:

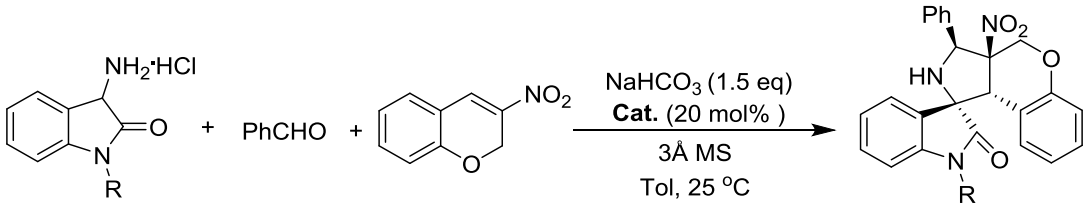
1. General information

All reactions were carried out in Schlenk tube under an argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{19}F NMR spectra were recorded on a Bruker Avance Ⅱ 400 MHz and Bruker Avance Ⅲ 377 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance Ⅱ 101 MHz. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = double doublet, dt = double triplet, td = triple doublet, coupling constants in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). HRMS (ESI) was determined by an HRMS/MS instrument (LTQ Orbitrap XL TM). Enantiomeric excess values were determined by HPLC employing a chiral column on Agilent 1100 series. The absolute configuration of **5k** was assigned by the X-ray analysis.

Starting materials: All the aldehydes were commercially obtained and recrystallized or distilled prior to use. (1) 3-Amino oxindoles were prepared following the reported procedures: W. Chen, Z. Wu, J. Hu, L. Cun, X. Zhang and W. Yuan, *Org. Lett*., 2011, **13**, 2472. (2) 3-nitro-2*H*-chromenes, 3-nitro-1,2-dihydronaphthalene and 3-Nitro-2*H*-thiochromene were synthesized according to following literature procedures: (a) A. H. Clark, J. D. McCorvy, V. J. Watts and D. E. Nichols, *Bioorg. Med. Chem.*, 2011, **19**, 5420; (b) A. Zhao, Q. Jiang, J. Jia, B. Xu, Y. Liu, M. Zhang, Q. Liu, W. Luo and C. Guo, *Tetrahedron Lett.*, 2016, **57**, 80; (c) A. H. Clark, J. D. McCorvy, V. J. Watts and D. E. Nichols, *Bioorg. Med. Chem.*, 2011, **19**, 5420.

2. Experimental sections

General procedure for the synthesis of spiro [indoline-3,2'-pyrrolidin]-2-one

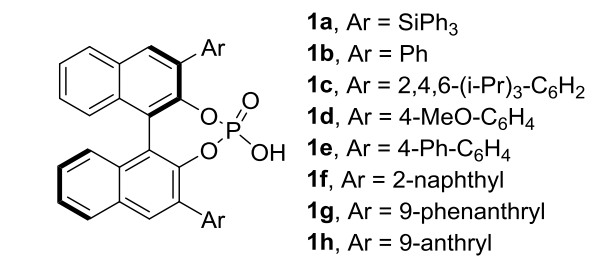


2 **3a** **4a** **5**

In a Schlenk tube, 3-amino oxindole **2** (0.1 mmol), 3-nitro-2*H*-chromene **4a** (0.11 mmol), $NaHCO_3$ (0.15 mmol), catalyst (0.02 mmol) and 3Å MS (100 mg) were added into Toluene (0.5 mL) under argon atmosphere. Then aldehyde **3a** (0.12 mmol) was added and the reaction solution was stirred at 25^{o}C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5**.

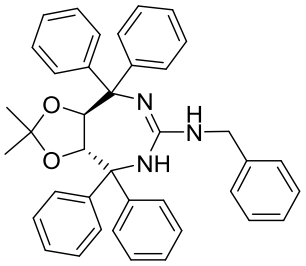
Screening of catalysts and optimization of conditions

***Table 1*:** Optimization of reaction conditions.[a] CPA=chiral phosphoric acid.

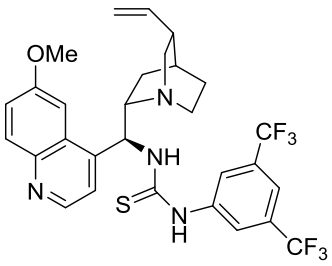


1a, Ar = $SiPh_3$
1b, Ar = Ph
1c, Ar = 2,4,6-(i-Pr)$_3$-C_6H_2
1d, Ar = 4-MeO-C_6H_4
1e, Ar = 4-Ph-C_6H_4
1f, Ar = 2-naphthyl
1g, Ar = 9-phenanthryl
1h, Ar = 9-anthryl

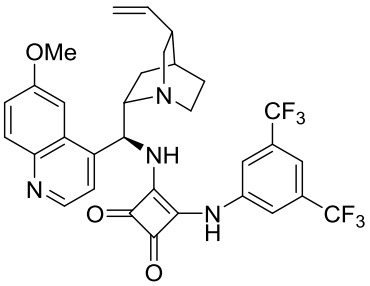
CPA-**1**



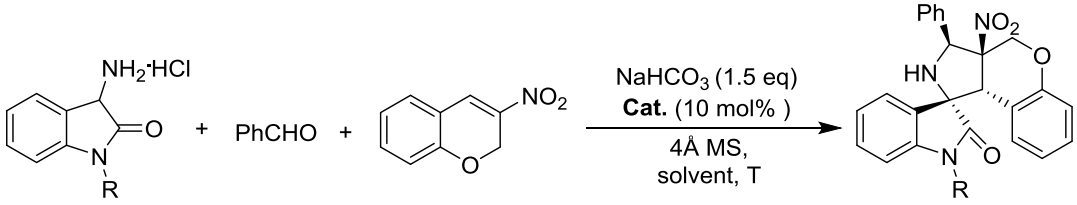
G**1**



Q**1**



Q**2**



2 **3a** **4a** *endo*-**5** (major)

2a, R = H
2b, R = Me
2c, R = Bn

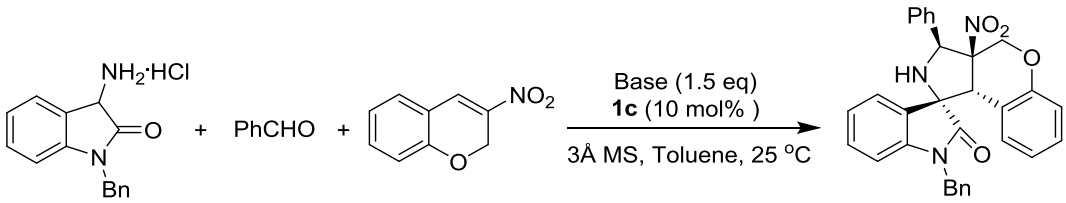
5a, R = Bn

Entry	R	**Cat.**	Solvent	T [℃]	t [h]	Yield [%][b]	d.r.[c]	*ee* [%][d]
1	Me	G**1**	DCM	25	88	95	8 : 1	0
2	Me	Q**1**	DCM	25	88	98	7 : 1	-12
3	Me	Q**2**	DCM	25	88	99	7 : 1	-2
4	Me	**1a**	DCM	25	28	93	>20 : 1	1
5	Me	**1b**	DCM	25	28	99	13 : 1	22
6	Me	**1c**	DCM	25	28	99	>20 : 1	65
7	Me	**1d**	DCM	25	28	99	12 : 1	24
8	Me	**1e**	DCM	25	28	99	16 : 1	32
9	Me	**1f**	DCM	25	28	98	10 : 1	40
10	Me	**1g**	DCM	25	28	98	>20 : 1	64
11	Me	**1h**	DCM	25	28	99	>20 : 1	23
12	Me	**1c**	DCE	25	36	90	>20 : 1	52
13	Me	**1c**	CH_3CN	25	32	95	15:1	0

14	Me	**1c**	THF	25	18	88	>20 : 1	1
15	Me	**1c**	Et_2O	25	36	99	>20 : 1	12
16	Me	**1c**	toluene	25	120	99	>20 : 1	81
17	Me	**1c**	Xylenes	25	120	92	>20 : 1	76
18	Me	**1c**	Mesitylene	25	120	90	>20 : 1	78
19	H	**1c**	toluene	25	140	43	>20 : 1	88
20	Bn	**1c**	toluene	25	38	99	>20 : 1	84
21[e]	Bn	**1c**	toluene	25	38	99	>20 : 1	85
22[e,f]	Bn	**1c**	toluene	25	45	90	>20 : 1	86
23[e,g]	Bn	**1c**	toluene	25	48	99	>20 : 1	88
24[e,g,h]	Bn	**1c**	toluene	25	140	99	>20 : 1	90
25[e,g,h,i]	Bn	**1c**	toluene	15	160	97	>20 : 1	90

[a] The reaction was carried out on a 0.1 mmol scale with **cat.** (10 mol%), $NaHCO_3$ (1.5 eq), 4Å MS (100 mg) in 1.0 ml solvent under argon, the molar ratio of **2**/**3a**/**4a** was 1/1.2/1.1. [b] Isolated yield. [c] The dr was determined by ^1H NMR. [d] The *ee* was determined by HPLC. [e] By using 3Å MS (100 mg). [f] In the presence of 15 mol% **1c**. [g] In the presence of 20 mol% **1c**. [h] The reaction was performed in 0.5 ml solvent. [i] At 15 °C.

***Table 2*:** Optimization of base in the reaction [a]

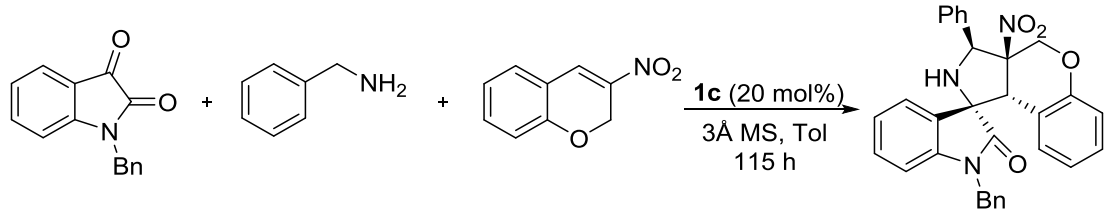


2c **3a** **4a** **5a**

Entry	Base	t [h]	Yield [%]	d.r.	*ee* [%]
1	$NaHCO_3$	38	99	>20:1	85
2	Na_2CO_3	140	97	>20:1	82
3	$KHCO_3$	65	99	>20:1	84
4	K_2CO_3	75	95	>20:1	82
5	Li_2CO_3	140	86	>20:1	78
6	NaH_2PO_4	38	99	>20:1	84
7	Na_2HPO_4	38	99	>20:1	78
8	$NaHSO_3$	38	99	>20:1	84
9	Na_2SO_3	135	89	>20:1	80

[a] The reaction was carried out on a 0.1 mmol scale with **1c** (10 mol%), base (1.5 eq), 3Å MS (100 mg) in 1.0 ml solvent at 25 °C under argon, the molar ratio of **2c**/**3a**/**4a** was 1/1.2/1.1.

Procedure for asymmetric catalytic [3+2] cycloaddition of isatin with benzylamine and nitroolefin in the presence CPA-1f

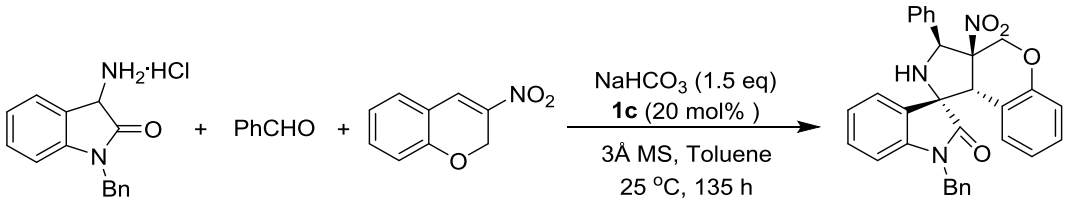


6 **7** **4a** **5a**

98% yield
65% ee, 7:1 dr

In a Schlenk tube, isatin **6** (0.1 mmol), nitroalkene **4a** (0.11 mmol), **1c** (0.02 mmol) and 3Å MS (100 mg) were added in toluene (0.5 mL) under argon atmosphere. After the solution was stirred for 20 minutes at 25°C, benzylamine **7** (0.1 mmol) was added to this flask at the same temperature. The reaction mixture was stirred for 115 h, the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5a** with 98% yield, 7:1 dr and 65% *ee*.

Gram-scale reaction

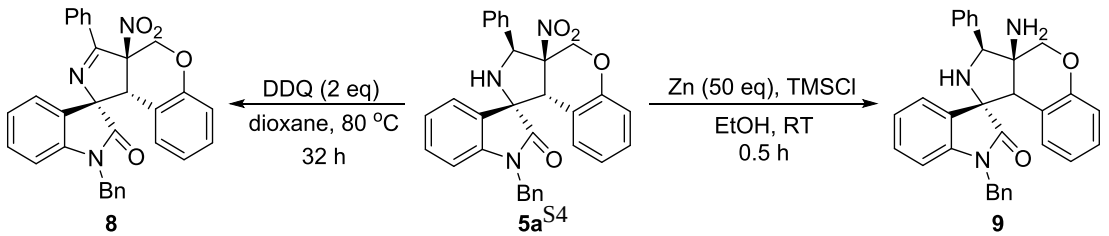


2c **3a** **4a** **5a**

78% yield
76% ee, >20:1 dr

In a Schlenk tube, 3-amino oxindole **2c** (2 mmol), 3-nitro-2*H*-chromene **4a** (2.2 mmol), $NaHCO_3$ (3 mmol), catalyst **1c** (0.4 mmol) and 3Å MS (2 g) were added into Toluene (10 mL) under argon atmosphere. Then aldehyde **3a** (2.4 mmol) was added and the reaction solution was stirred at 25°C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/4) on silica gel to give the product **5a** with 78% yield, >20:1 dr and 76% ee.

Procedure for the Synthesis of Compound 8 and 9



8 **5a** **9**

88% yield
90% ee

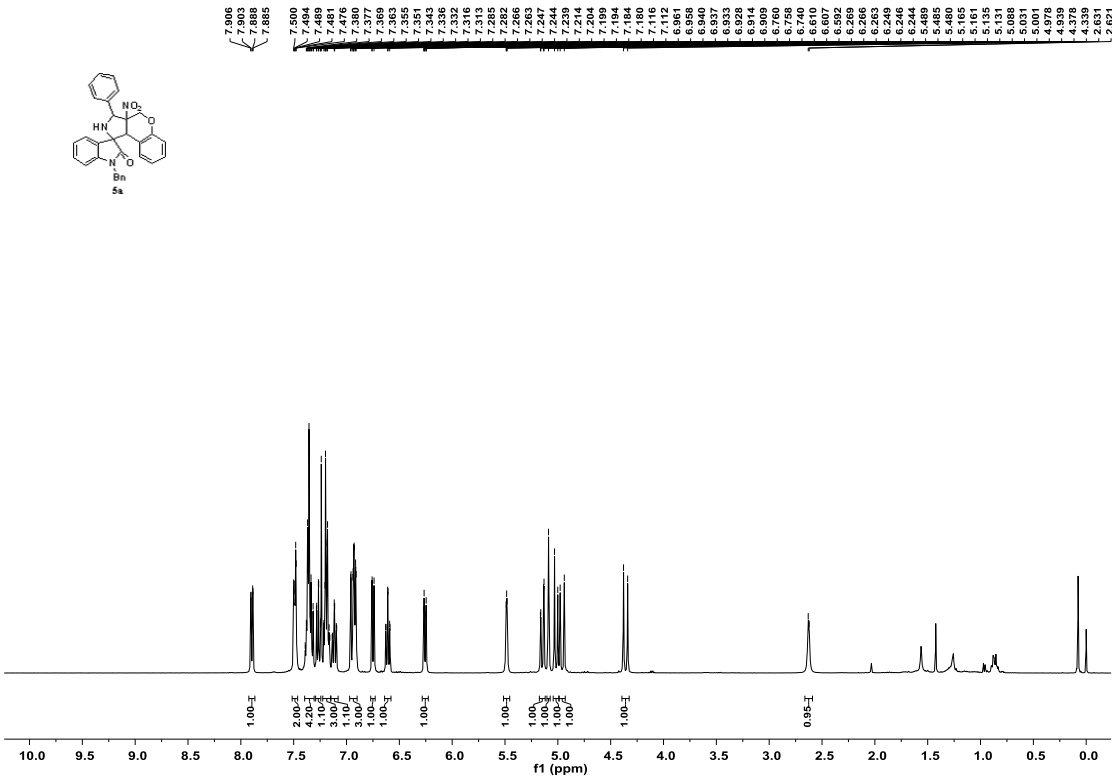
72% yield
90% ee

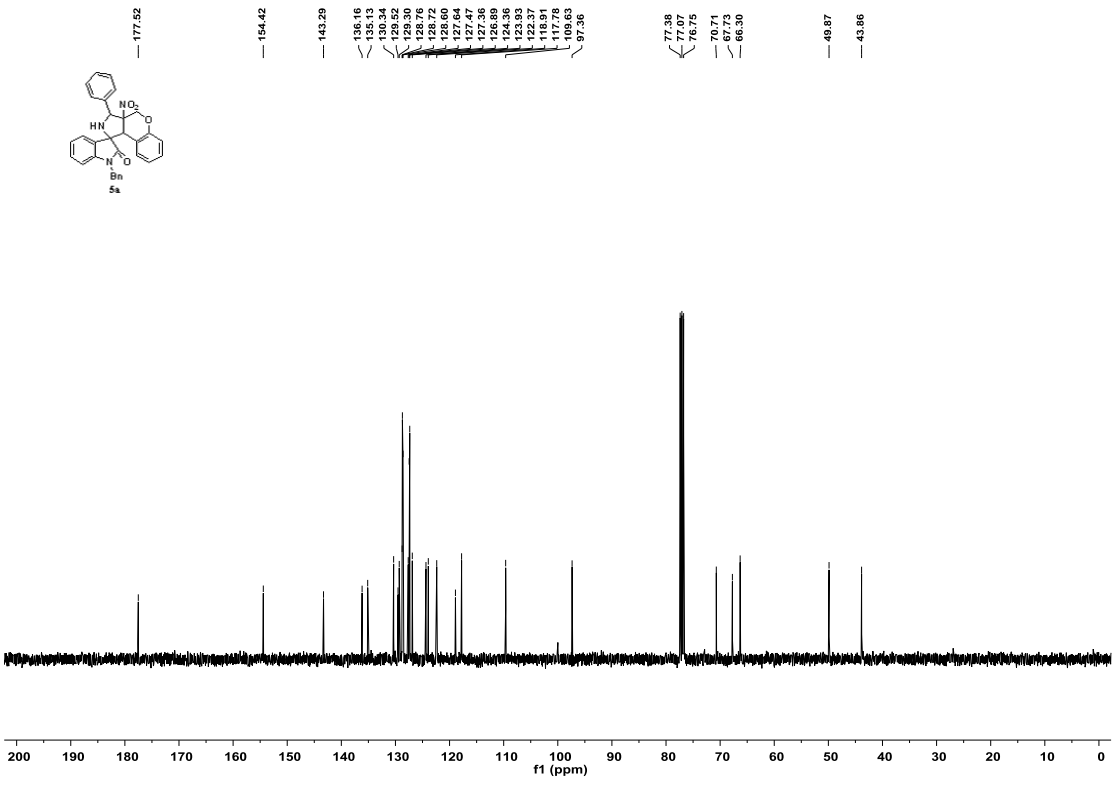
A reaction tube was charged with **5a** (0.1 mmol) and dioxane (2 ml), then DDQ (0.2 mmol) was added. The reaction was stirred at 80 ^{o}C until it was complete (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **8** as a white solid.

To compound **5a** (0.1 mmol) in 2 ml EtOH was added TMSCl (0.4 ml) and Zn power (5 mmol) carefully, the resulting mixture was stirred at room temperature for 0.5 h. Then the reaction mixture was filitered and washed with MeOH and CH_2Cl_2, subsequently $NaHCO_3$ solution was added to the resulting solution and the aqueous layer was extracted with CH_2Cl_2 three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (Hexane/AcOEt = 1/1) to afford compound **9** as a light yellow solid.

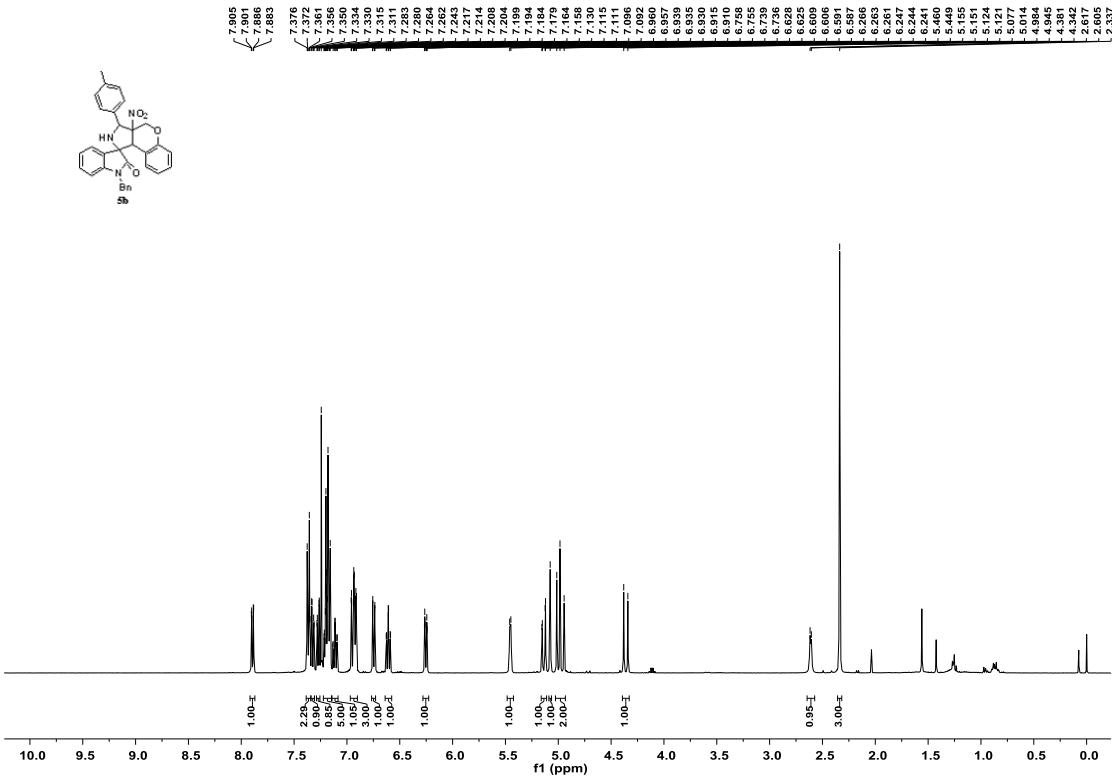
3. Copies of ^{1}H NMR and ^{13}C NMR spectra

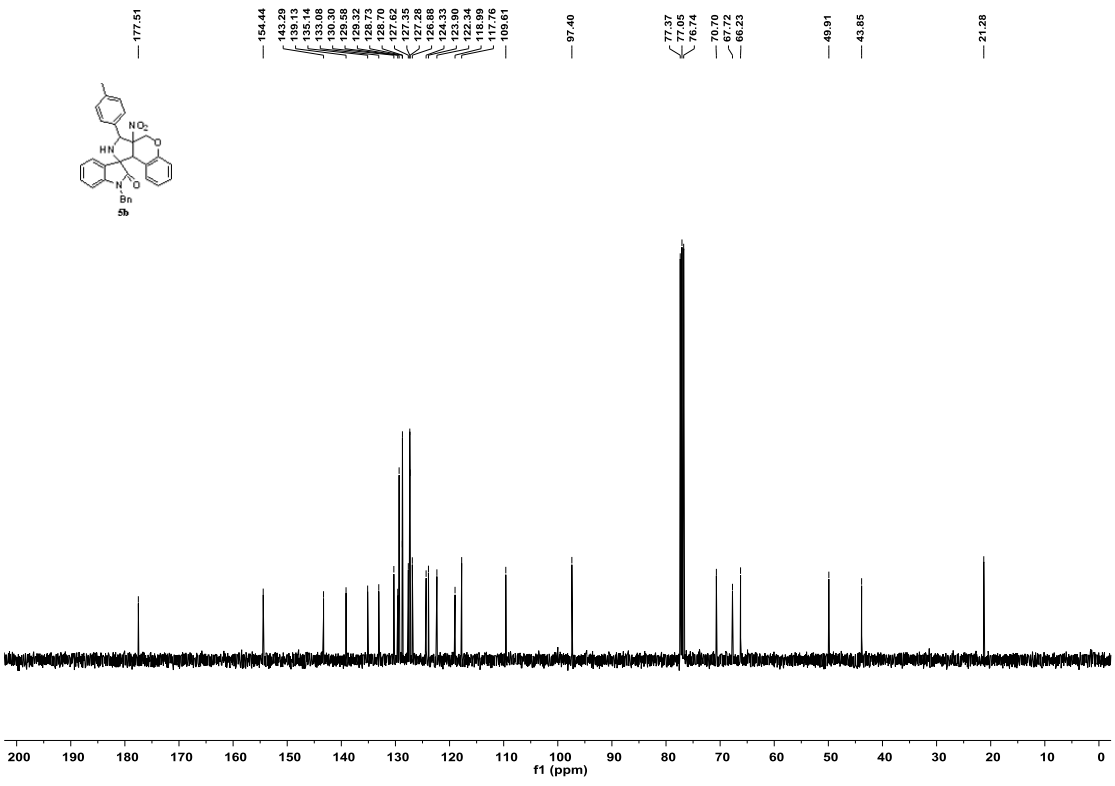
5a



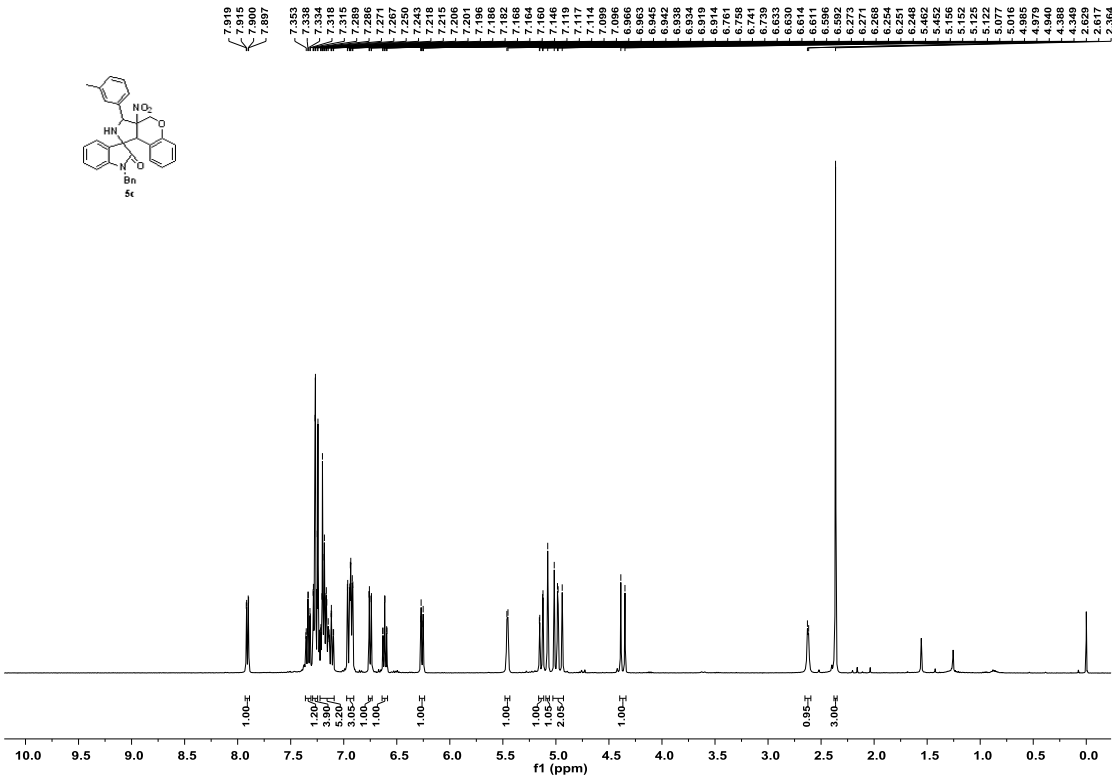


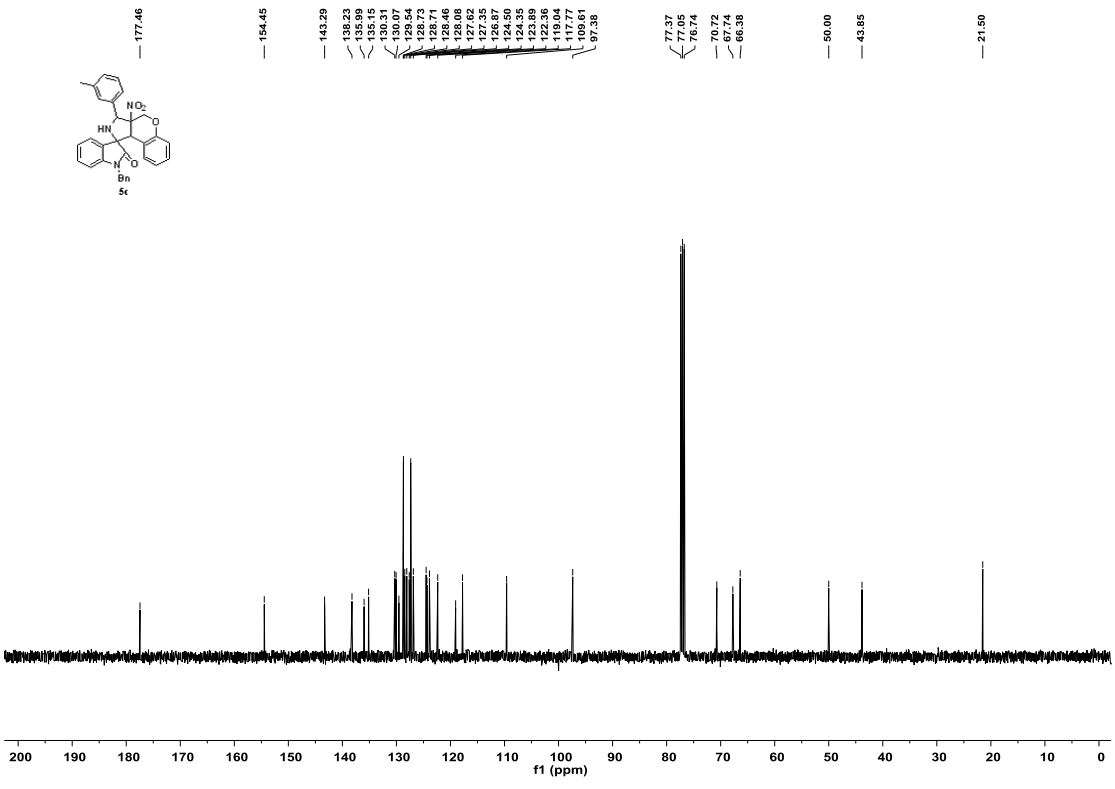
5b


7.905
7.901
7.886
7.883
7.376
7.372
7.361
7.356
7.350
7.334
7.330
7.315
7.311
7.283
7.280
7.264
7.262
7.243
7.217
7.214
7.208
7.204
7.199
7.194
7.184
7.179
7.164
7.158
7.130
7.115
7.111
7.096
7.092
6.960
6.957
6.939
6.935
6.930
6.915
6.910
6.758
6.755
6.739
6.736
6.628
6.625
6.609
6.606
6.591
6.587
6.266
6.263
6.261
6.247
6.244
6.241
5.460
5.449
5.155
5.151
5.124
5.121
5.077
5.074
4.984
4.945
4.381
4.342
2.617
2.605
1.337
NO2
HN
O
N
O
Bn
5b
1.00
2.29
0.90
0.85
5.00
1.05
1.00
1.00
1.00
1.00
1.00
2.00
1.00
0.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

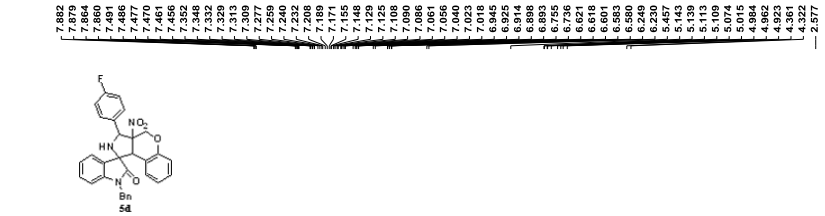

177.51
154.44
143.29
139.13
135.14
133.08
130.30
129.58
129.32
128.73
128.70
127.62
127.35
127.28
126.88
124.33
123.90
122.34
118.99
117.76
109.61
97.40
77.37
77.05
76.74
70.70
67.72
66.23
49.91
43.85
21.28
NO2
HN
O
N
O
Bn
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5c

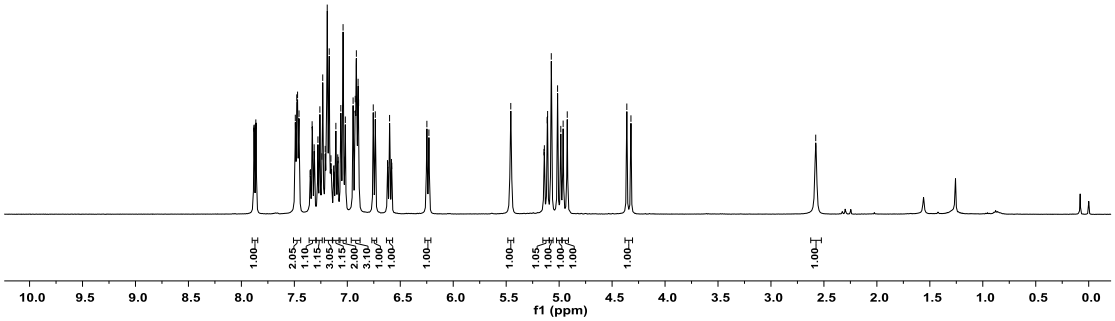

7.919
7.915
7.900
7.897
7.353
7.338
7.334
7.318
7.315
7.289
7.286
7.277
7.267
7.250
7.243
7.218
7.215
7.206
7.201
7.196
7.186
7.182
7.168
7.164
7.160
7.146
7.119
7.117
7.114
7.099
7.096
6.966
6.963
6.945
6.942
6.938
6.934
6.919
6.914
6.761
6.758
6.741
6.739
6.633
6.630
6.614
6.611
6.596
6.592
6.273
6.271
6.268
6.254
6.251
6.248
5.462
5.452
5.156
5.152
5.125
5.122
5.077
5.016
4.985
4.979
4.940
4.388
4.349
2.629
2.617
NO2
HN
O
N
O
Bn
5c
1.00
1.20
3.90
5.20
3.05
1.00
1.00
1.00
1.00
1.05
2.05
1.00
0.95
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

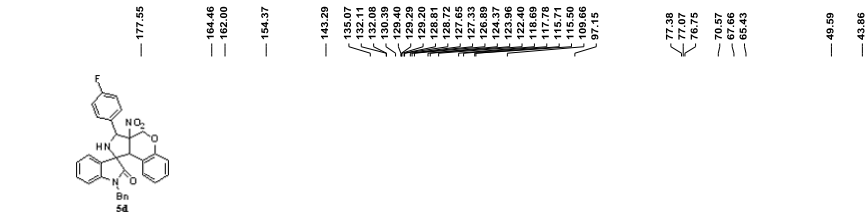

177.46
154.45
143.29
138.23
135.99
135.15
130.31
130.07
129.54
128.73
128.71
128.46
128.08
127.62
127.35
126.87
124.50
124.35
123.89
122.36
119.04
117.77
109.61
97.38
77.37
77.05
76.74
70.72
67.74
66.38
50.00
43.85
21.50
NO2
HN
O
N
O
Bn
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5d

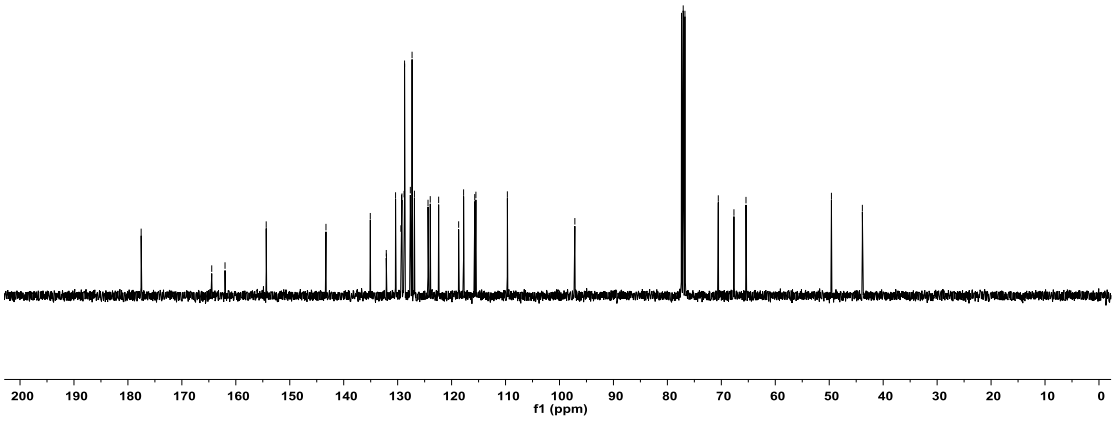

7.882
7.873
7.864
7.860
7.491
7.486
7.477
7.470
7.461
7.456
7.352
7.348
7.332
7.329
7.313
7.309
7.277
7.259
7.240
7.232
7.208
7.189
7.171
7.155
7.148
7.129
7.125
7.106
7.090
7.086
7.061
7.056
7.040
7.023
7.018
6.945
6.935
6.914
6.898
6.893
6.755
6.736
6.621
6.618
6.601
6.585
6.580
6.249
6.230
5.457
5.143
5.139
5.113
5.109
5.074
5.015
4.984
4.962
4.923
4.361
4.322
2.577

F
NO2
HN
O
N
O
Bn
5d

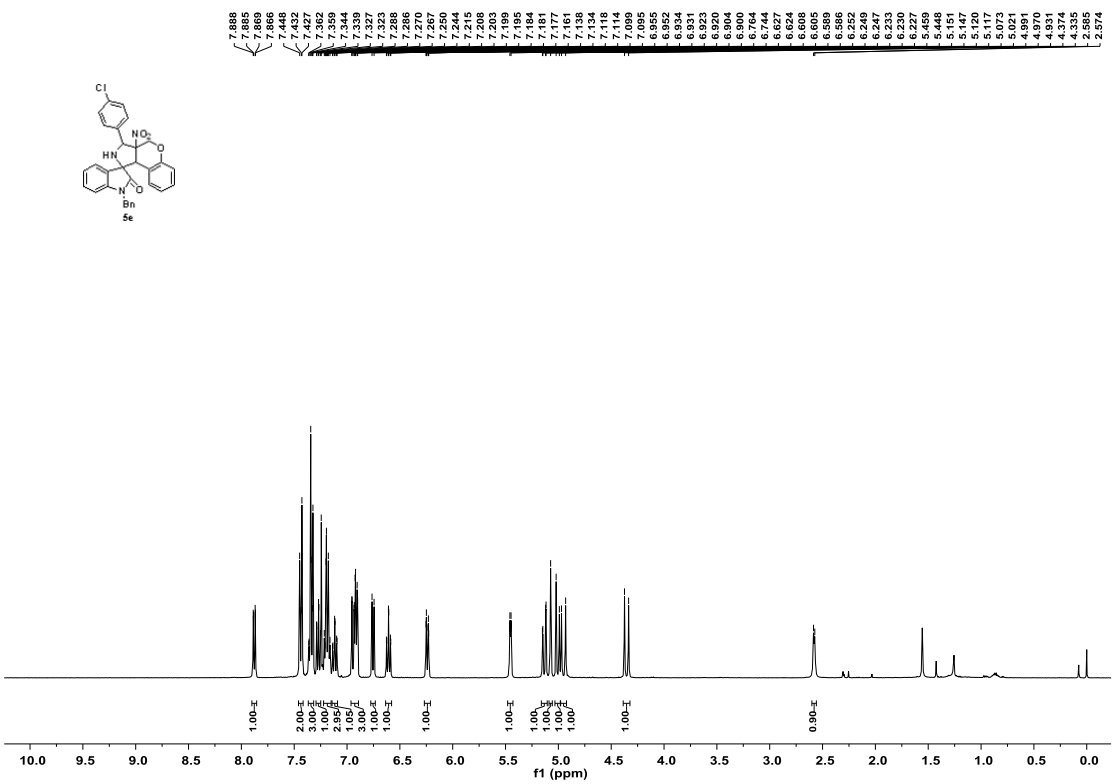

1.00
2.05
1.10
1.15
3.05
1.15
2.00
3.10
1.00
1.00
1.00
1.05
1.00
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

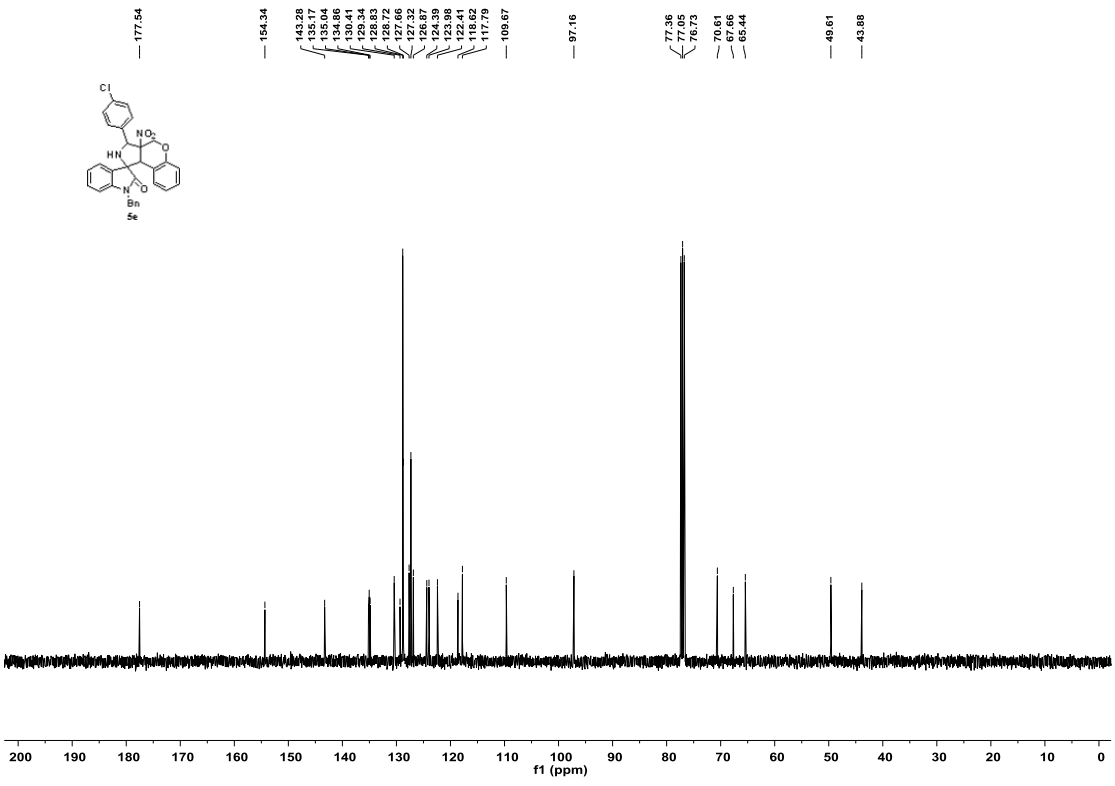

177.55
164.46
162.00
154.37
143.29
135.07
132.11
132.08
130.39
129.40
129.29
129.20
128.81
128.72
127.65
127.33
126.89
124.37
123.96
122.40
116.69
117.78
115.71
115.50
109.66
97.15
77.38
77.07
76.75
70.57
67.66
65.43
49.59
43.86

F
NO2
HN
O
N
O
Bn
5d

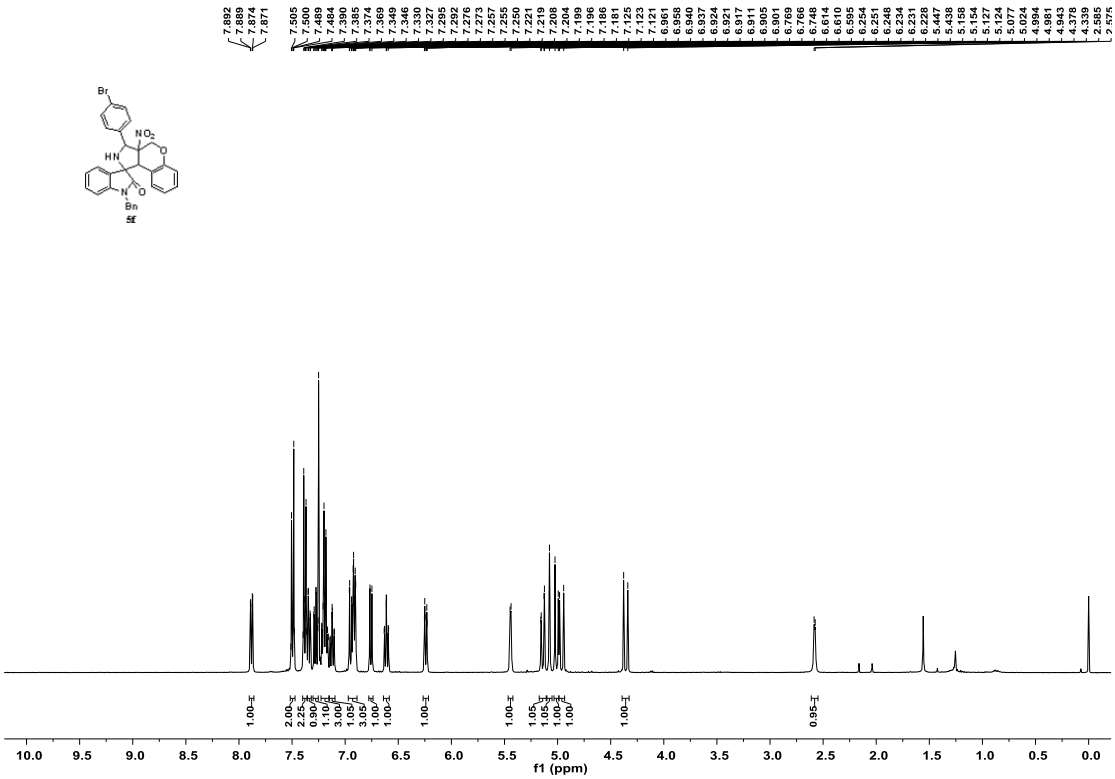

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

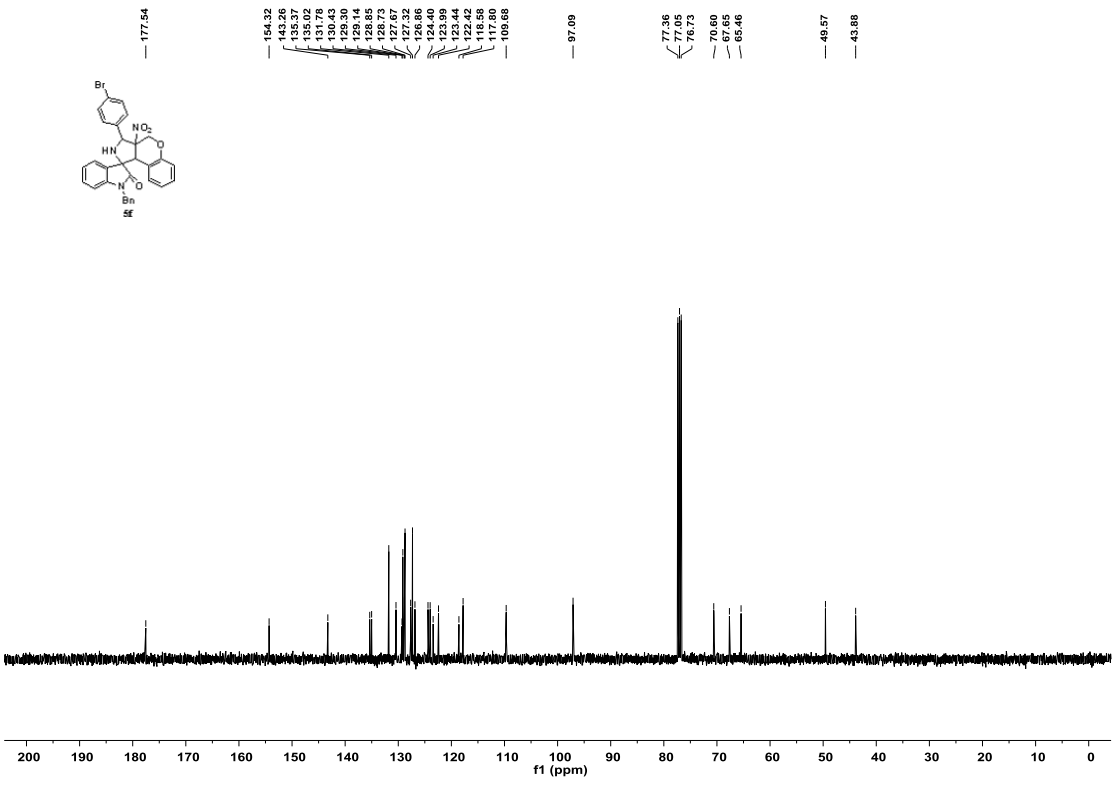
5e


7.888
7.885
7.869
7.866
7.448
7.432
7.427
7.362
7.359
7.344
7.339
7.327
7.323
7.288
7.286
7.270
7.267
7.250
7.244
7.215
7.208
7.203
7.199
7.195
7.184
7.181
7.177
7.161
7.138
7.134
7.118
7.114
7.099
7.095
6.955
6.952
6.934
6.931
6.923
6.920
6.904
6.900
6.764
6.744
6.627
6.624
6.608
6.605
6.589
6.586
6.252
6.249
6.247
6.233
6.230
6.227
5.459
5.448
5.151
5.147
5.120
5.117
5.073
5.021
4.991
4.970
4.931
4.374
4.335
2.585
2.574
Cl
NO2
HN
O
N
O
Bn
5e
1.00
2.00
3.00
2.95
1.05
3.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

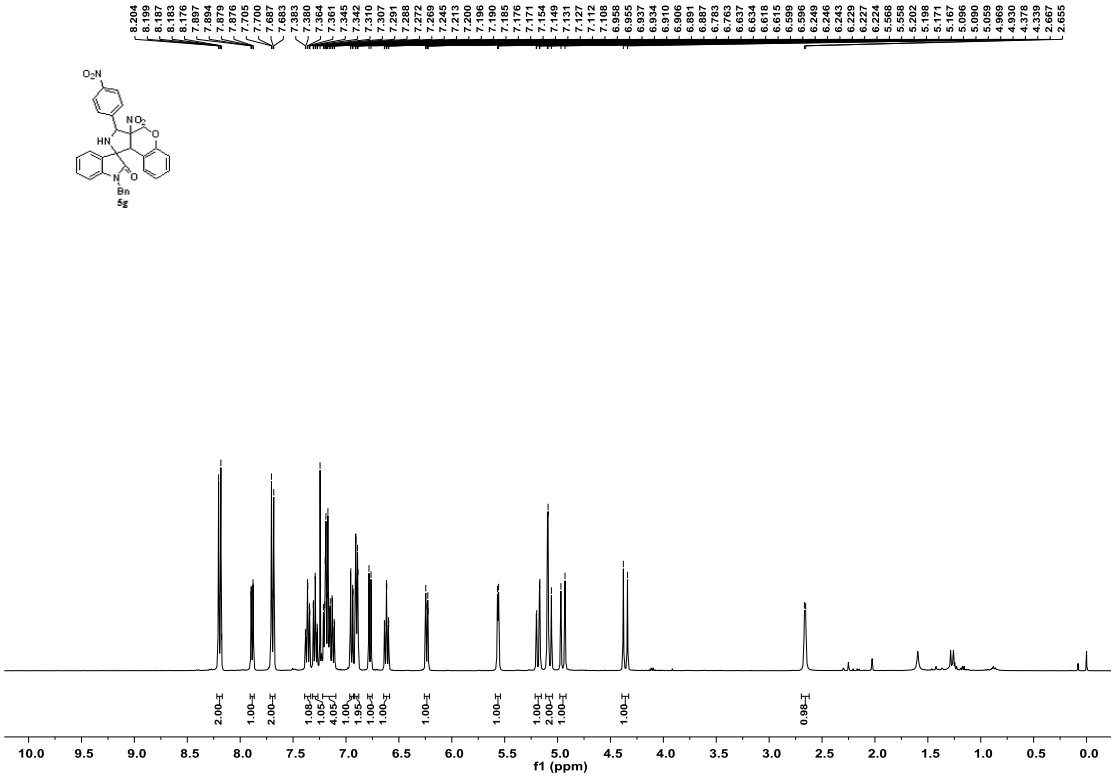

177.54
154.34
143.28
135.17
135.04
134.86
130.41
129.34
128.83
128.72
127.66
127.32
126.87
124.39
123.98
122.41
118.62
117.79
109.67
97.16
77.36
77.05
76.73
70.61
67.66
65.44
49.61
43.88
Cl
NO2
HN
O
N
O
Bn
5e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

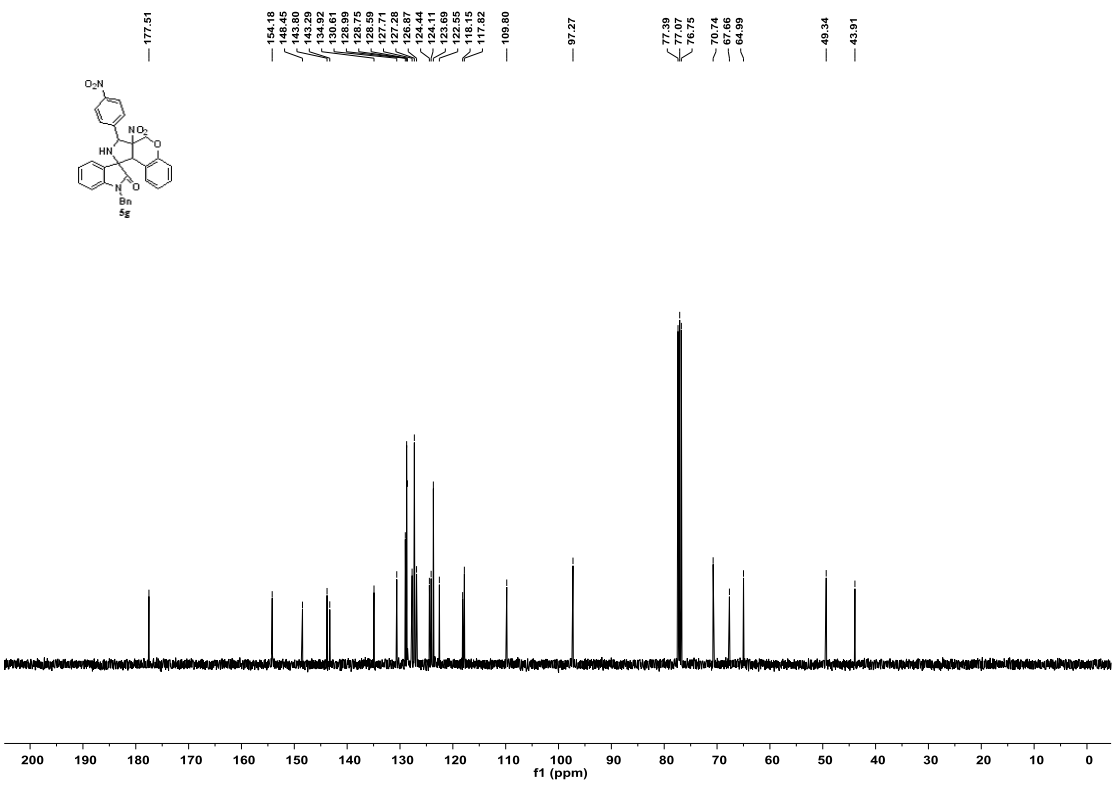
5f


7.892
7.889
7.874
7.871
7.505
7.500
7.489
7.484
7.390
7.385
7.374
7.368
7.346
7.330
7.327
7.295
7.292
7.276
7.273
7.257
7.255
7.250
7.221
7.219
7.208
7.204
7.199
7.196
7.186
7.181
7.125
7.123
7.121
6.961
6.958
6.940
6.937
6.924
6.921
6.917
6.911
6.905
6.901
6.769
6.766
6.748
6.614
6.610
6.595
6.254
6.251
6.248
6.234
6.231
6.228
5.447
5.438
5.158
5.154
5.127
5.124
5.077
5.074
4.994
4.981
4.943
4.378
4.339
2.585
Br
NO2
HN
O
N
O
Bn
5f
1.00
2.00
2.25
0.90
1.10
1.00
3.05
1.00
1.00
1.00
1.00
1.05
1.05
1.00
1.00
1.00
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

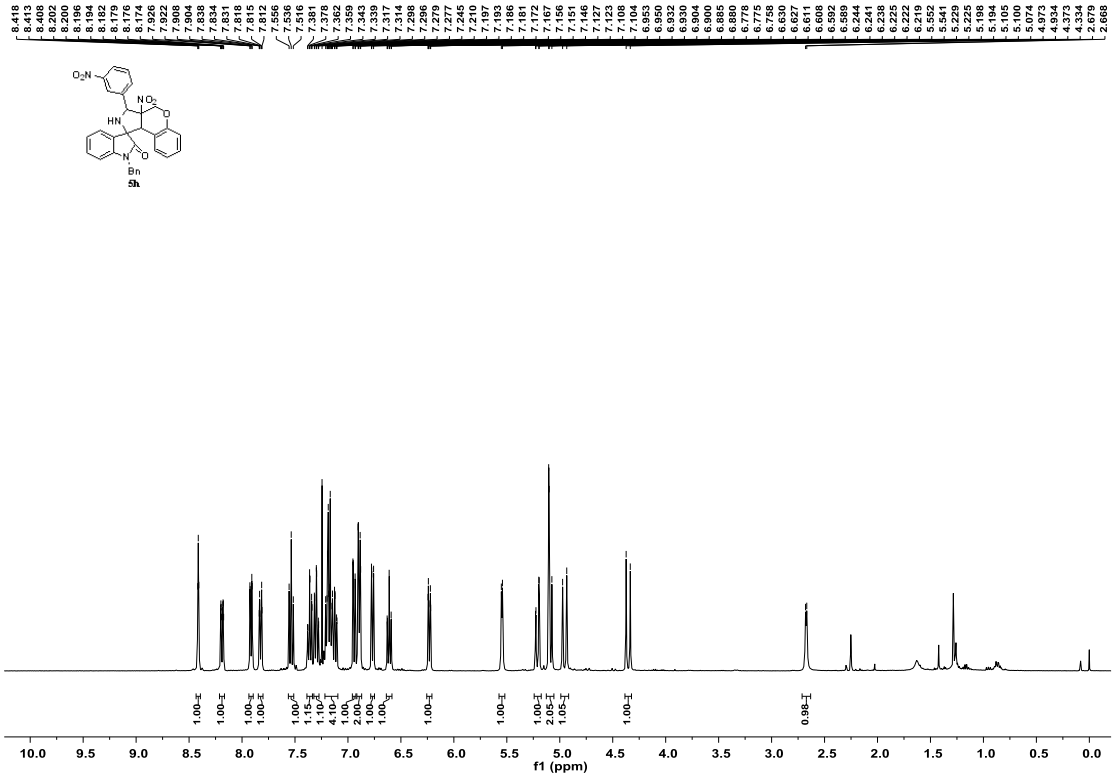

177.54
154.32
143.26
135.37
135.02
131.78
130.43
129.30
129.14
128.85
128.73
127.67
127.32
126.86
124.40
123.99
123.44
122.42
118.58
117.80
109.68
97.09
77.36
77.05
76.73
70.60
67.65
65.46
49.57
43.88
Br
NO2
HN
O
N
O
Bn
5f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

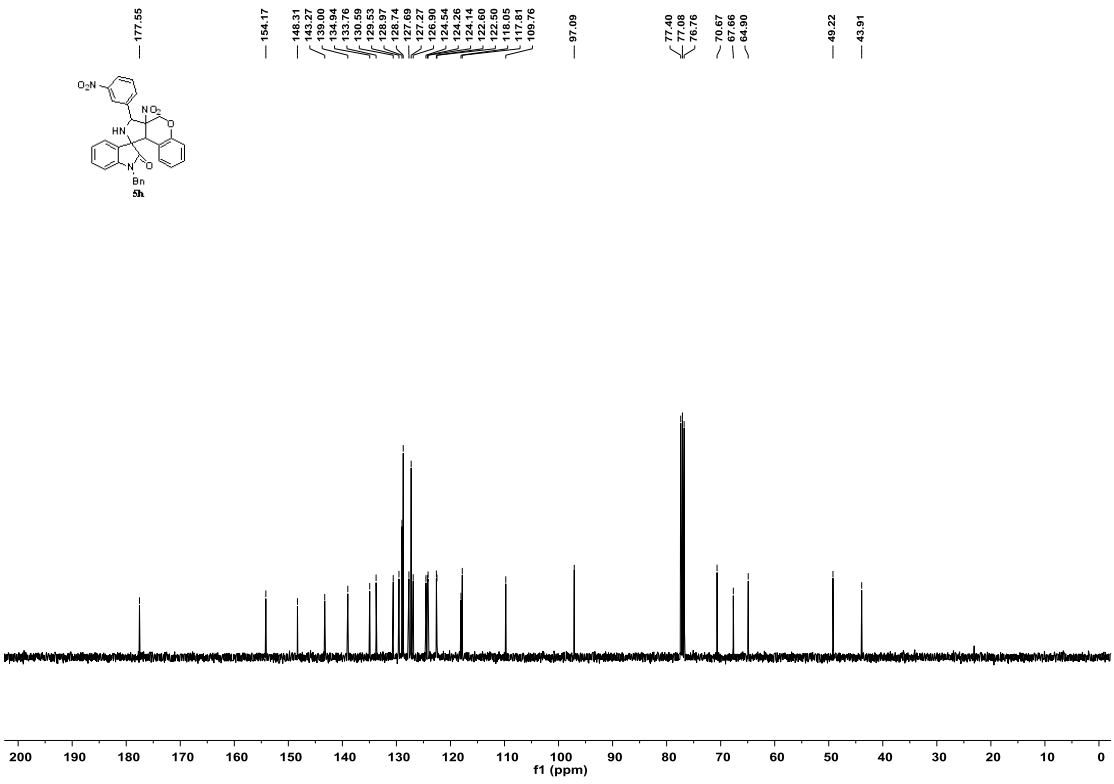
5g


8.204
8.199
8.187
8.183
8.175
7.897
7.894
7.879
7.876
7.705
7.700
7.687
7.683
7.380
7.364
7.361
7.345
7.342
7.310
7.307
7.291
7.288
7.272
7.269
7.245
7.213
7.200
7.196
7.190
7.185
7.176
7.171
7.154
7.149
7.131
7.127
7.112
7.108
6.958
6.955
6.937
6.934
6.910
6.906
6.891
6.887
6.783
6.763
6.637
6.634
6.618
6.615
6.599
6.596
6.248
6.246
6.243
6.229
6.227
6.224
5.568
5.558
5.202
5.198
5.171
5.167
5.096
5.090
5.059
4.969
4.930
4.378
4.339
2.667
2.655
Bn
5g
2.00
1.00
2.00
1.08
1.05
4.05
1.00
1.95
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
0.98
f1 (ppm)

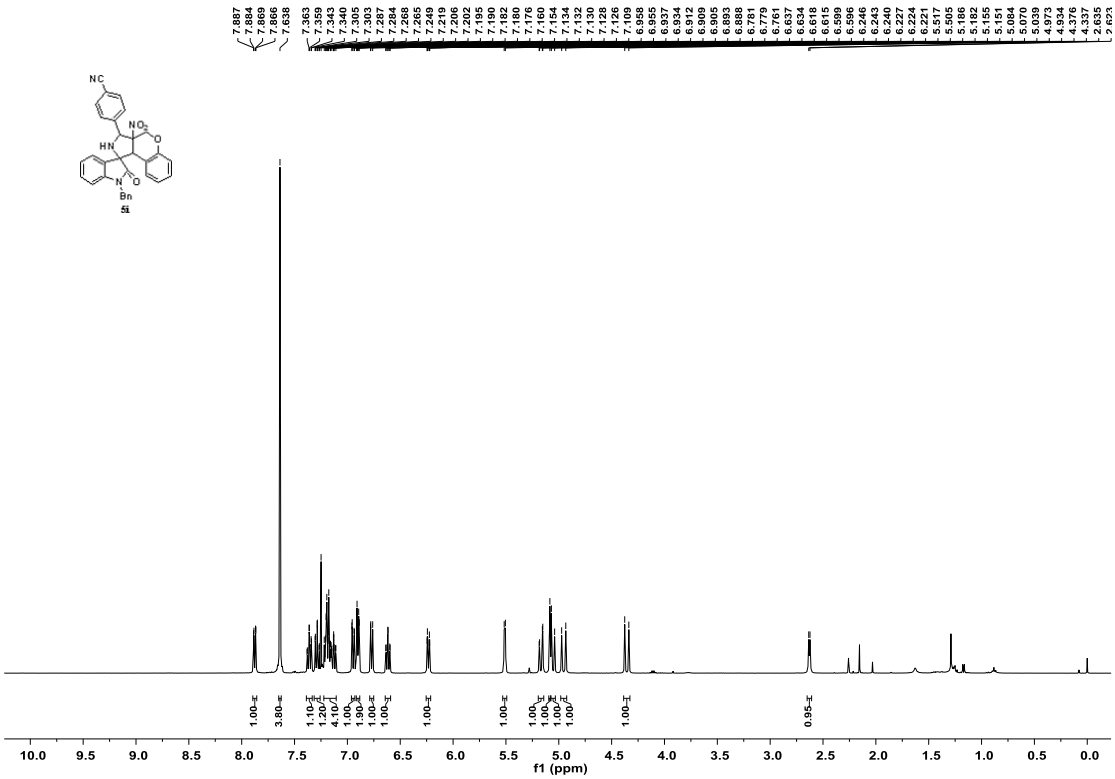

177.51
154.18
148.45
145.60
143.29
134.92
130.61
128.99
128.75
128.59
127.71
127.28
126.87
124.44
124.11
123.69
122.55
118.15
117.82
109.80
97.27
77.39
77.07
76.75
70.74
67.66
64.99
49.34
43.91
Bn
5g
f1 (ppm)

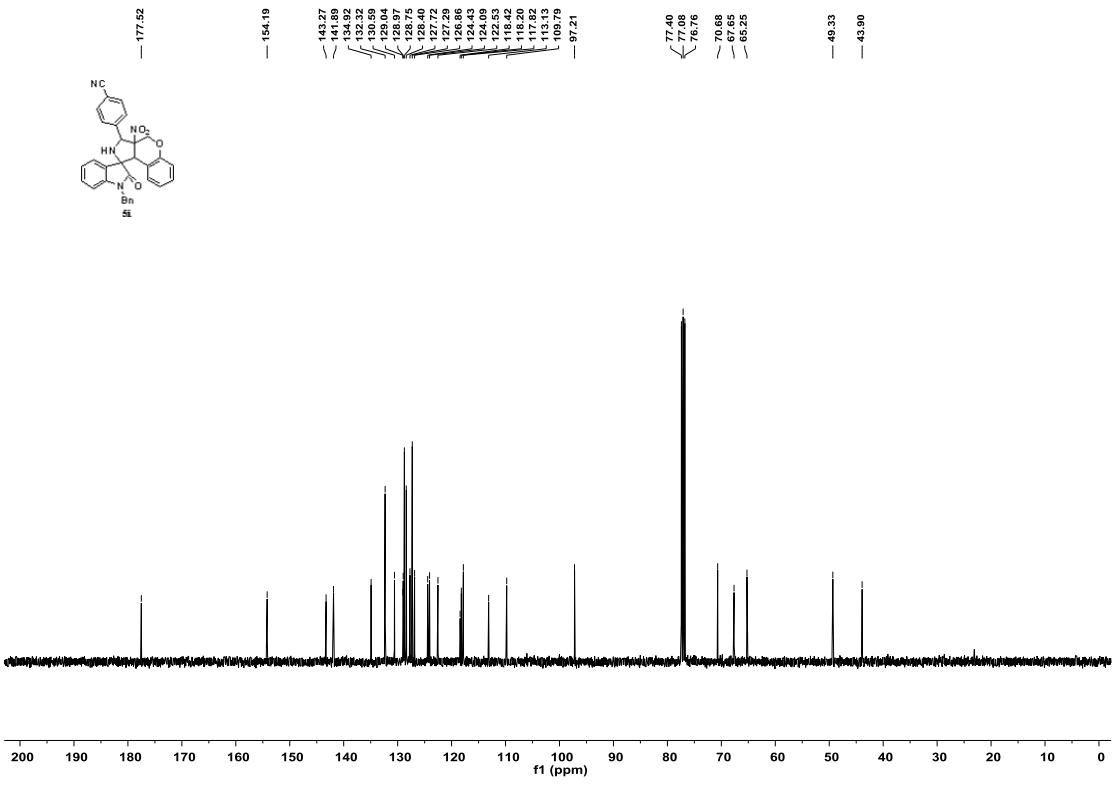
5h


8.418
8.413
8.408
8.202
8.200
8.196
8.194
8.182
8.179
8.176
8.174
7.926
7.922
7.908
7.904
7.838
7.834
7.831
7.818
7.815
7.812
7.556
7.536
7.516
7.381
7.378
7.362
7.359
7.343
7.339
7.317
7.314
7.298
7.296
7.279
7.277
7.245
7.210
7.197
7.193
7.186
7.181
7.172
7.167
7.156
7.151
7.146
7.127
7.123
7.108
7.104
6.953
6.950
6.932
6.930
6.904
6.900
6.885
6.880
6.778
6.775
6.758
6.630
6.627
6.611
6.608
6.592
6.589
6.244
6.241
6.238
6.225
6.222
6.219
5.552
5.541
5.229
5.225
5.198
5.194
5.105
5.100
5.074
4.973
4.934
4.373
4.354
2.679
2.668
Bn
5h
1.00
1.00
1.00
1.00
1.15
1.10
4.10
1.00
2.00
1.00
1.00
1.00
1.00
2.08
1.05
1.00
0.98
f1 (ppm)

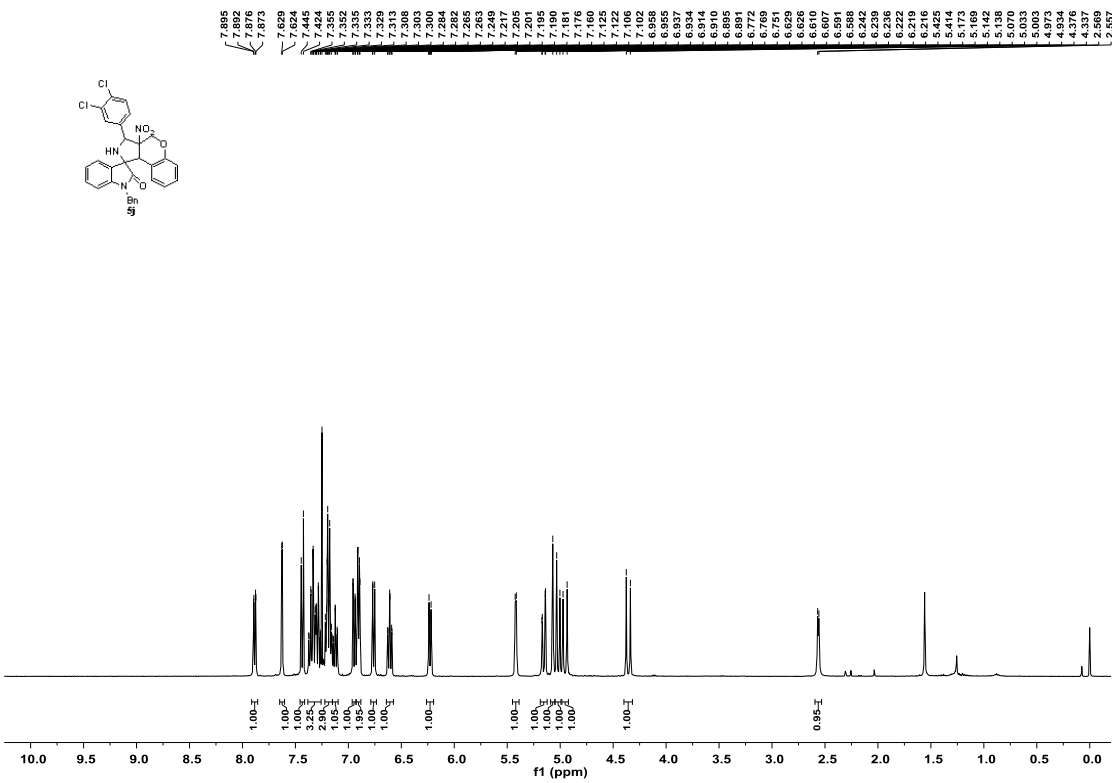

177.55
154.17
148.31
143.27
139.00
134.94
133.76
130.59
129.53
128.97
128.74
127.69
127.27
126.90
124.54
124.26
124.14
122.60
122.50
118.65
117.81
109.76
97.09
77.40
77.08
76.76
70.67
67.66
64.90
49.22
43.91
Bn
5h
f1 (ppm)

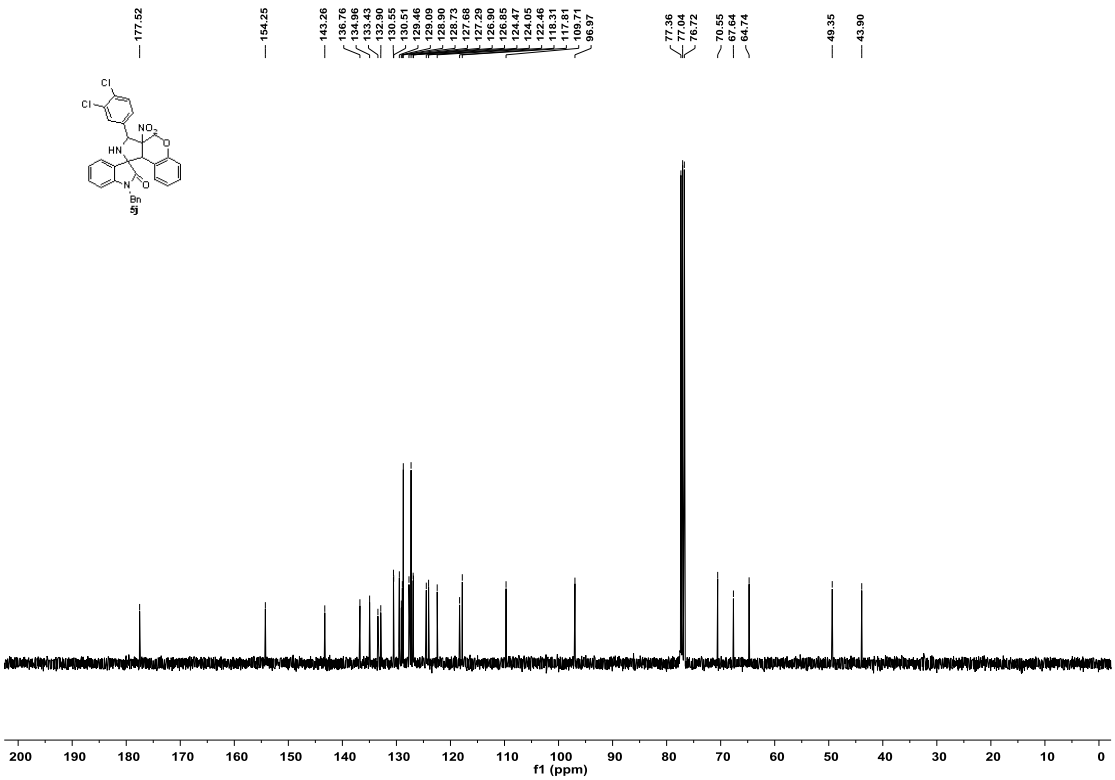
5i


7.887
7.884
7.869
7.866
7.638
7.363
7.359
7.343
7.340
7.305
7.303
7.287
7.284
7.268
7.265
7.249
7.219
7.206
7.202
7.195
7.190
7.182
7.180
7.176
7.160
7.154
7.134
7.132
7.130
7.128
7.126
7.109
6.958
6.955
6.937
6.934
6.912
6.909
6.905
6.893
6.888
6.781
6.779
6.761
6.637
6.634
6.618
6.615
6.599
6.596
6.246
6.243
6.240
6.227
6.224
6.221
5.517
5.505
5.186
5.182
5.155
5.151
5.094
5.070
5.039
4.973
4.934
4.376
4.337
2.635
NC
NO2
HN
O
N
O
Bn
5i
1.00
3.80
1.10
1.20
4.10
1.00
1.90
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

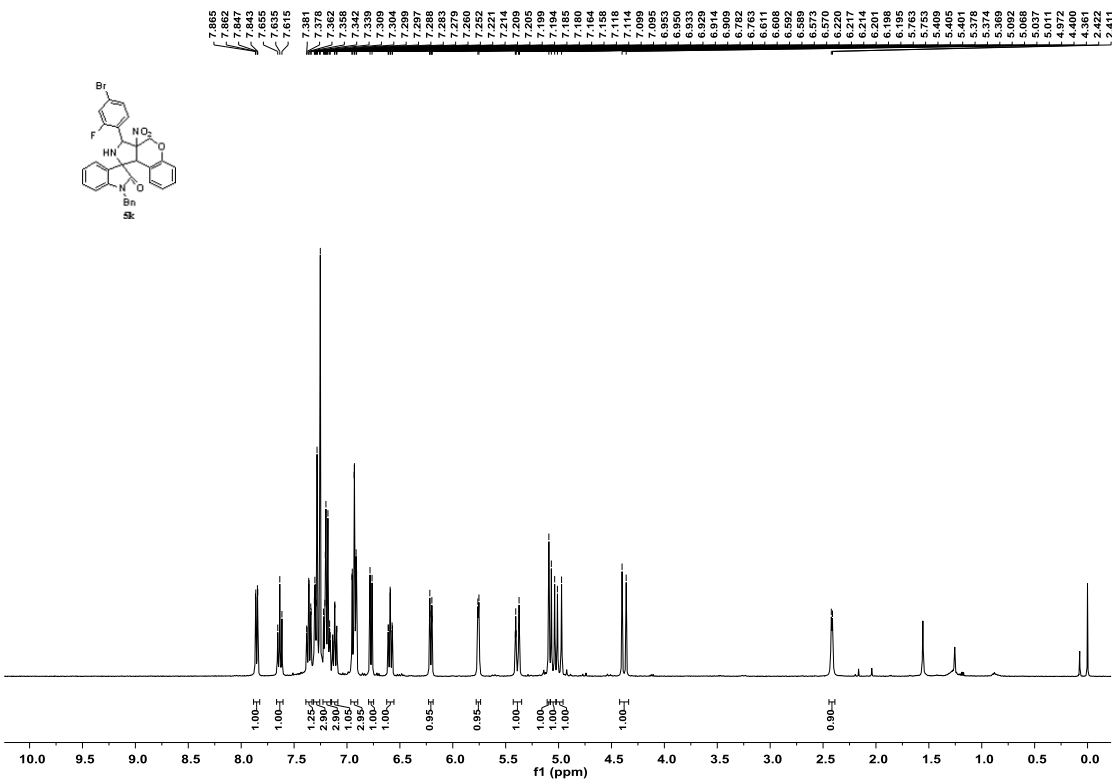

177.52
154.19
143.27
141.89
134.92
132.32
130.59
129.04
128.75
128.40
127.72
127.29
126.86
124.43
124.09
122.53
118.42
118.20
117.82
113.13
109.79
97.21
77.40
77.08
76.76
70.68
67.45
65.25
49.33
43.90
NC
NO2
HN
O
N
O
Bn
5i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

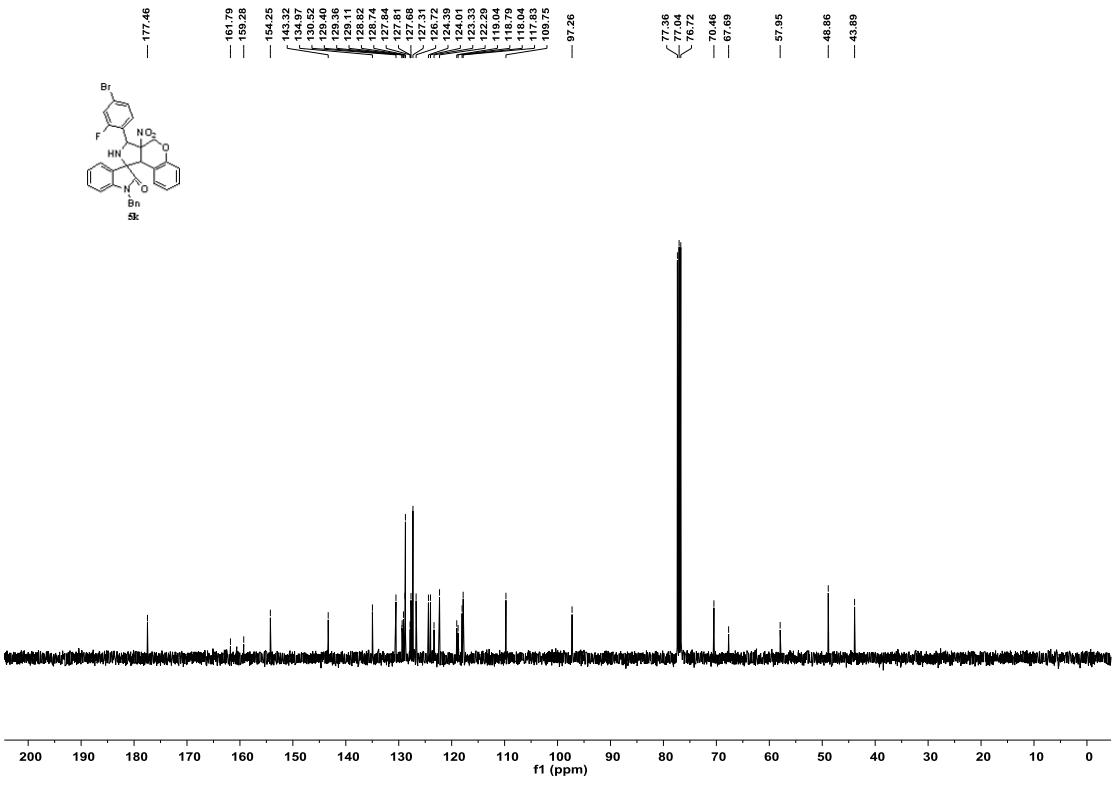
5j


7.895
7.892
7.876
7.873
7.629
7.624
7.445
7.424
7.355
7.352
7.335
7.333
7.329
7.313
7.308
7.303
7.300
7.284
7.282
7.265
7.263
7.249
7.217
7.205
7.201
7.195
7.190
7.181
7.176
7.160
7.125
7.122
7.106
7.102
6.958
6.955
6.937
6.934
6.914
6.910
6.895
6.891
6.772
6.769
6.751
6.629
6.626
6.610
6.607
6.591
6.588
6.242
6.239
6.236
6.222
6.219
6.216
5.425
5.414
5.173
5.169
5.142
5.138
5.070
5.053
5.003
4.973
4.934
4.376
4.337
2.569
2.557
Cl
Cl
NO2
HN
O
N
O
Bn
5j
1.00
1.00
1.00
2.95
1.05
1.00
1.95
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

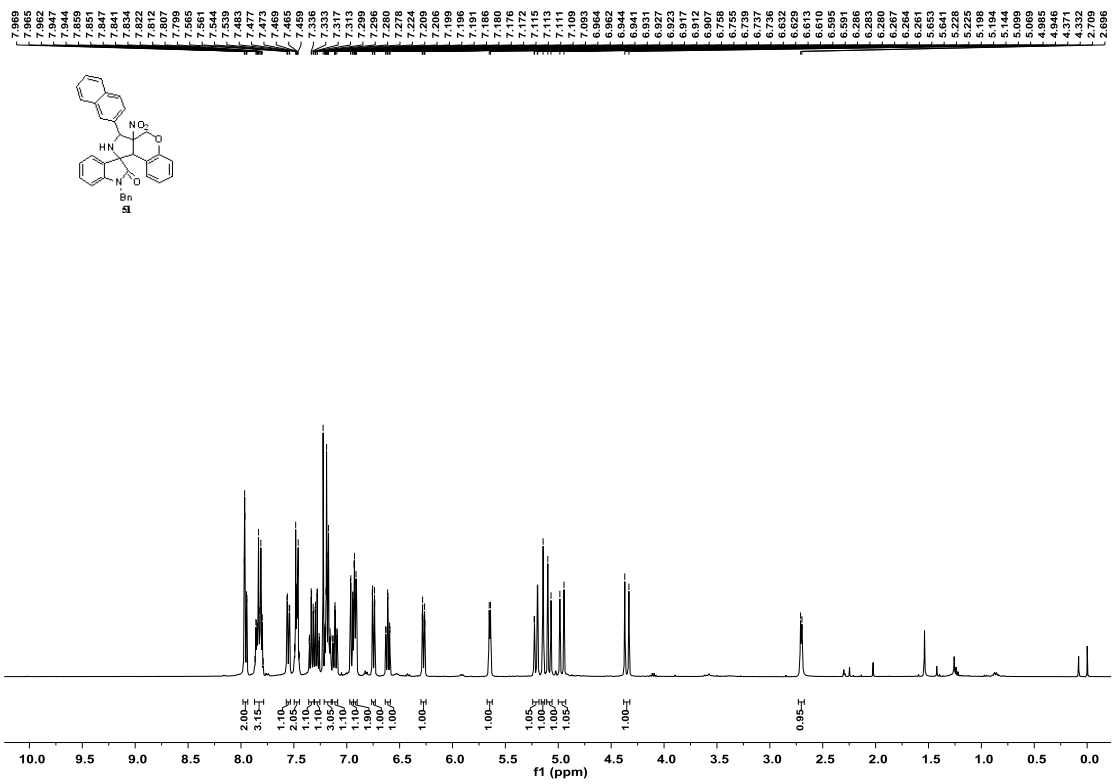

177.52
154.25
143.26
136.76
134.96
133.43
132.90
130.55
130.51
129.46
129.09
128.90
128.73
127.68
127.29
126.80
126.85
124.47
124.05
122.46
118.31
117.81
109.71
96.97
77.36
77.04
76.72
70.55
67.64
64.74
49.35
43.90
Cl
Cl
NO2
HN
O
N
O
Bn
5j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

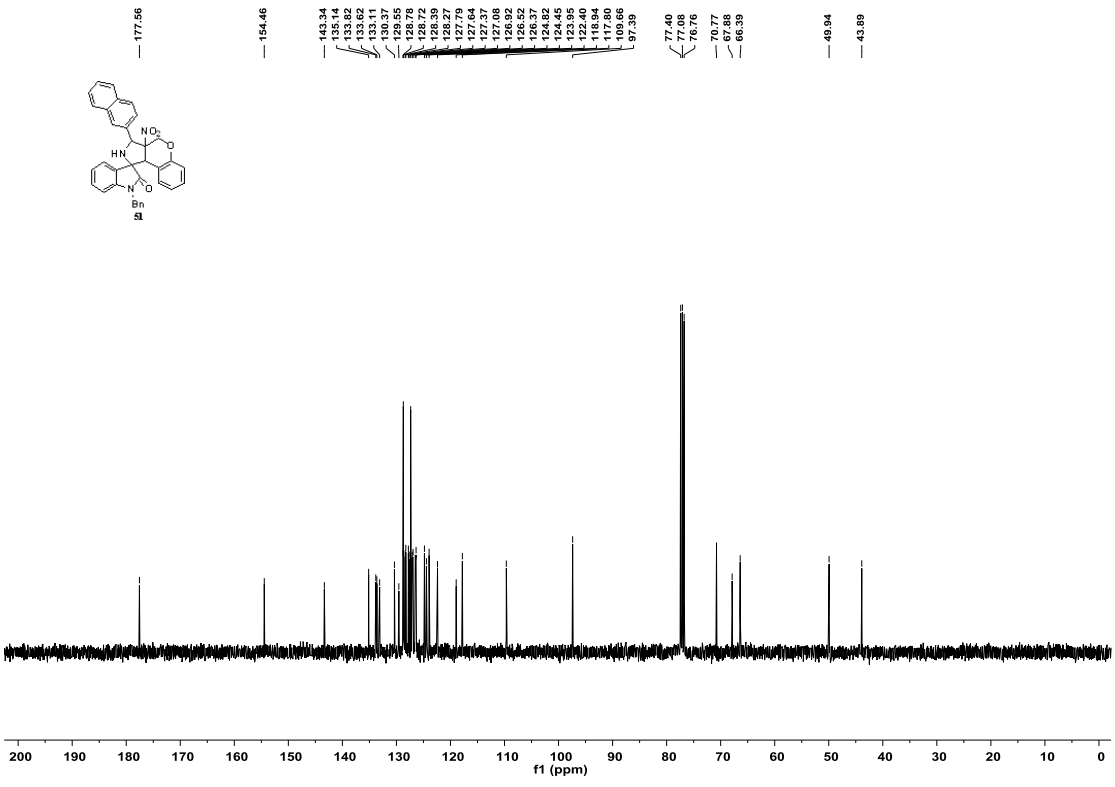
5k


7.865
7.862
7.847
7.843
7.655
7.635
7.615
7.381
7.378
7.362
7.358
7.342
7.339
7.309
7.304
7.299
7.297
7.288
7.283
7.279
7.260
7.252
7.221
7.214
7.209
7.205
7.199
7.194
7.185
7.180
7.164
7.158
7.118
7.114
7.099
7.095
6.953
6.950
6.933
6.909
6.914
6.909
6.782
6.763
6.611
6.608
6.592
6.589
6.573
6.570
6.220
6.217
6.214
6.201
6.198
6.195
5.793
5.753
5.409
5.405
5.401
5.378
5.374
5.369
5.092
5.068
5.037
5.011
4.972
4.400
4.361
2.422
2.411
Br
F
NO2
HN
O
N
O
Bn
5k
1.00
1.00
1.25
2.80
2.90
1.05
2.95
1.00
1.00
0.95
0.95
1.00
1.00
1.00
1.00
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

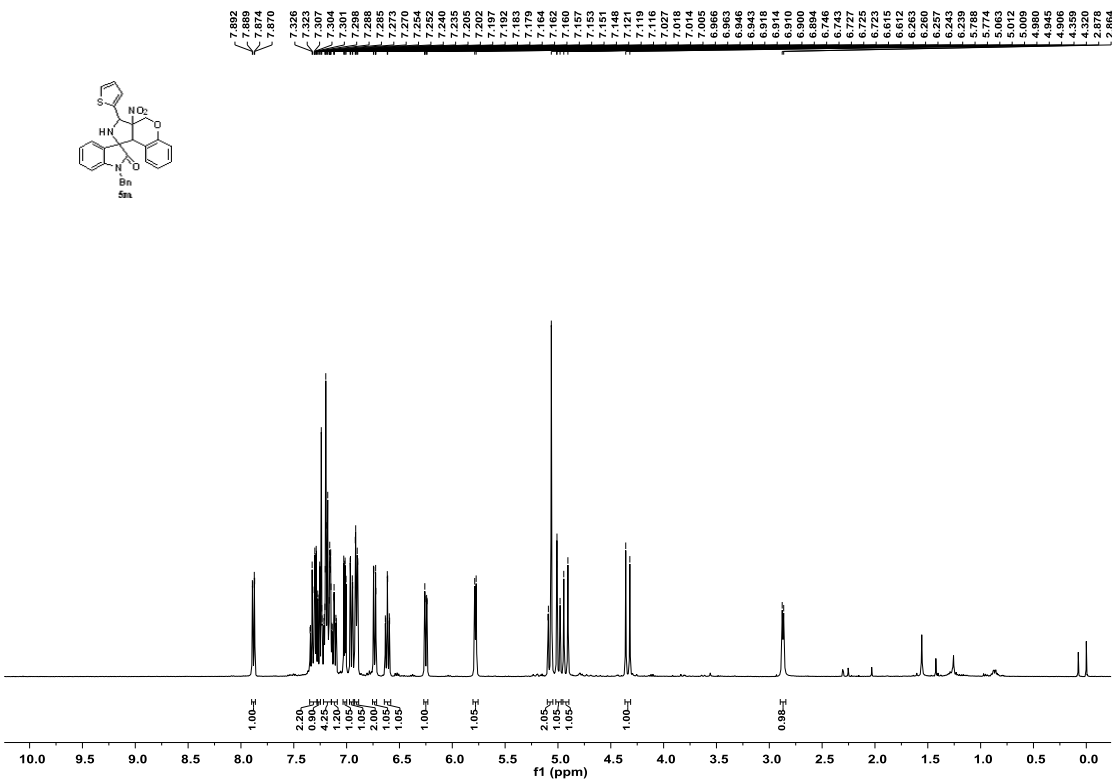

177.46
161.79
159.28
154.25
143.32
134.97
130.52
129.40
129.36
129.11
128.82
128.74
127.84
127.81
127.68
127.31
126.72
124.39
124.01
123.33
122.29
119.04
118.79
118.04
117.83
109.75
97.26
77.36
77.04
76.72
70.46
67.69
57.95
48.86
43.89
Br
F
NO2
HN
O
N
O
Bn
5k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

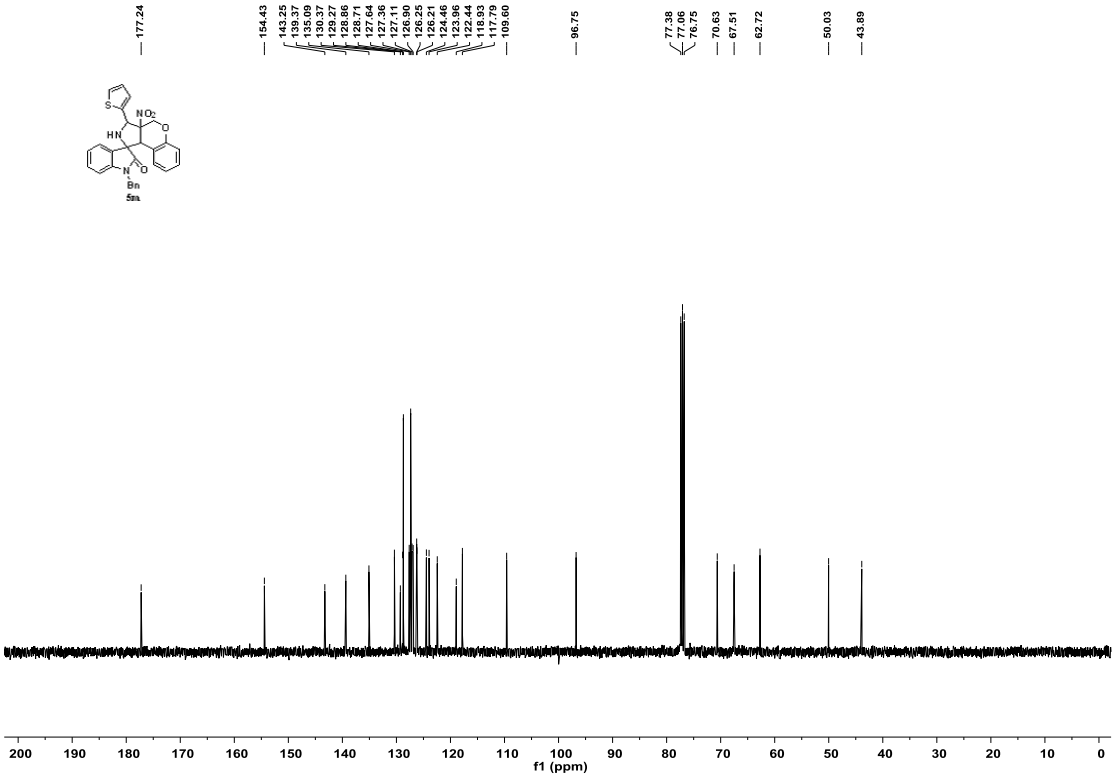
5l


7.969 7.965 7.962 7.947 7.944 7.859 7.851 7.847 7.841 7.834 7.822 7.812 7.807 7.799 7.565 7.561 7.544 7.539 7.483 7.477 7.473 7.469 7.465 7.459 7.336 7.333 7.317 7.313 7.299 7.296 7.280 7.278 7.224 7.209 7.206 7.198 7.196 7.191 7.186 7.180 7.176 7.172 7.115 7.113 7.111 7.109 7.093 6.964 6.962 6.944 6.941 6.931 6.927 6.923 6.917 6.912 6.907 6.758 6.755 6.739 6.737 6.736 6.632 6.629 6.613 6.610 6.595 6.591 6.286 6.283 6.280 6.267 6.264 6.261 5.653 5.641 5.228 5.225 5.198 5.194 5.144 5.099 5.069 4.985 4.946 4.377 4.373 2.709 2.696
NO2
HN
O
N
O
Bn
5l
2.00 3.15 1.10 2.05 1.10 1.10 3.05 1.10 1.80 1.00 1.00 1.00 1.00 1.05 1.00 1.00 1.05 1.00 0.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

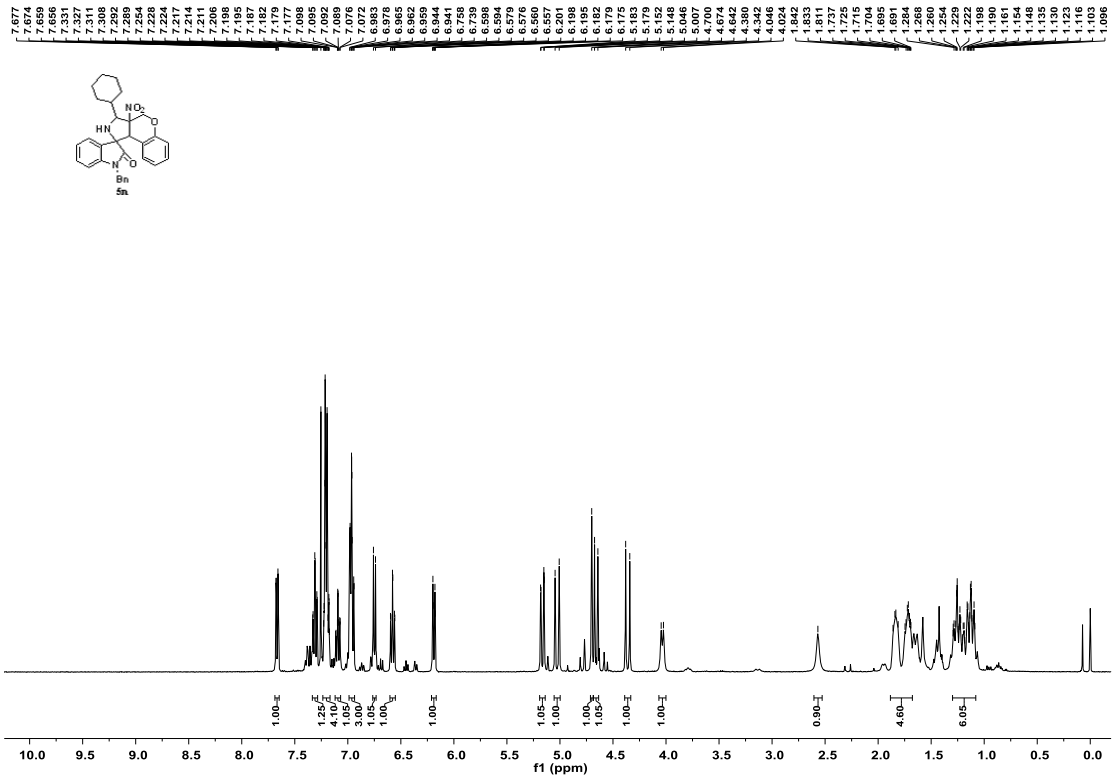

177.56 154.46 143.34 135.14 133.82 133.62 133.11 130.37 129.55 128.78 128.72 128.39 128.27 127.79 127.64 127.37 127.08 126.92 126.52 126.37 124.82 124.45 123.95 122.40 118.94 117.80 109.66 97.39 77.40 77.08 76.76 70.77 67.88 66.39 49.94 43.89
NO2
HN
O
N
O
Bn
5l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

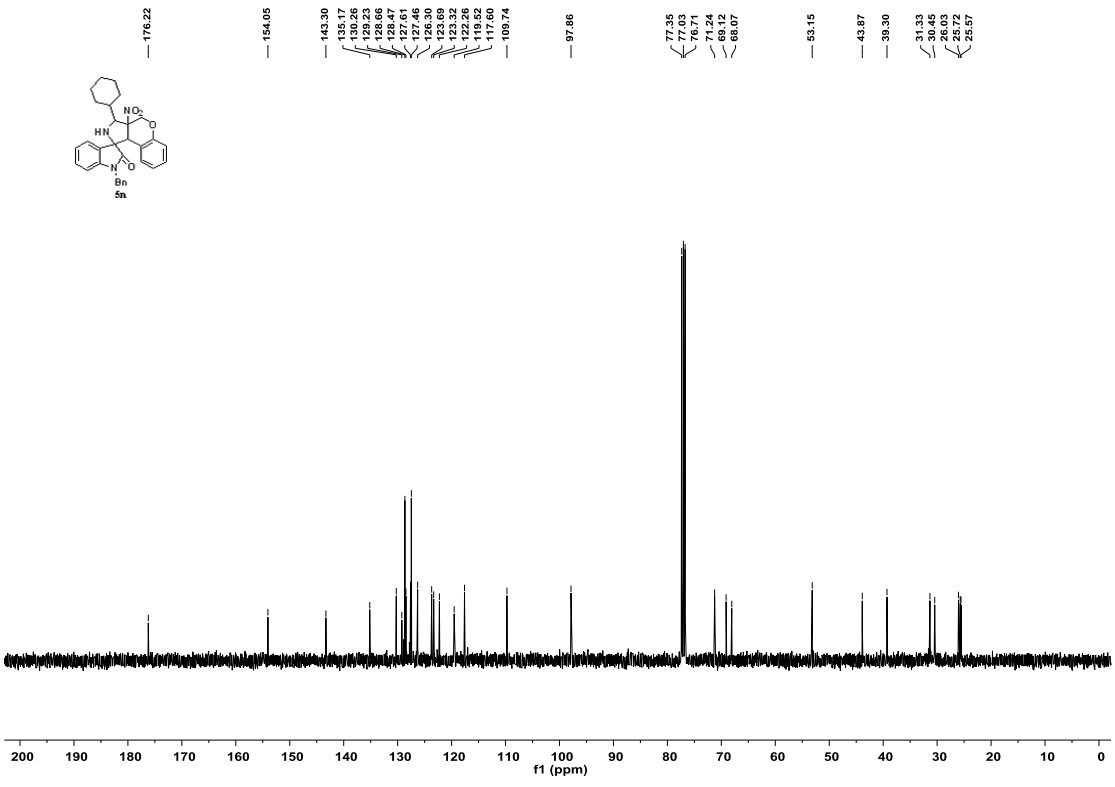
5m


7.892
7.889
7.874
7.870
7.326
7.323
7.307
7.304
7.301
7.298
7.288
7.285
7.273
7.270
7.254
7.252
7.240
7.235
7.205
7.202
7.197
7.192
7.183
7.179
7.164
7.162
7.160
7.157
7.153
7.151
7.148
7.121
7.119
7.116
7.027
7.018
7.014
7.005
6.966
6.963
6.946
6.943
6.918
6.914
6.910
6.900
6.894
6.746
6.743
6.727
6.725
6.723
6.615
6.612
6.263
6.260
6.257
6.243
6.239
5.788
5.774
5.063
5.012
5.009
4.980
4.945
4.906
4.359
4.320
2.878
NO2
HN
O
N
Bn
5m
1.00
2.20
0.90
4.25
1.05
1.05
2.00
1.05
1.05
1.00
1.05
2.05
1.05
1.05
1.00
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

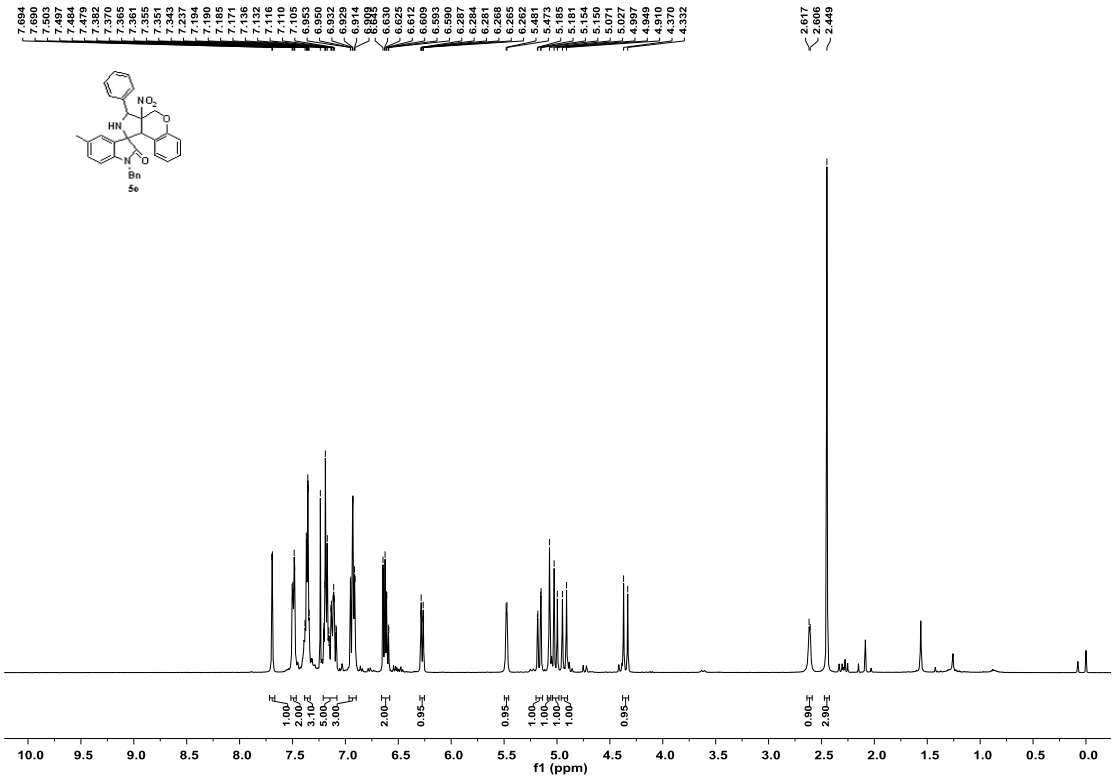

177.24
154.43
143.25
139.37
135.09
130.37
129.27
128.86
128.71
127.64
127.36
127.11
126.90
126.25
126.21
124.46
123.96
122.44
118.93
117.79
109.60
96.75
77.38
77.06
76.75
70.63
67.51
62.72
50.03
43.89
NO2
HN
O
N
Bn
5m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

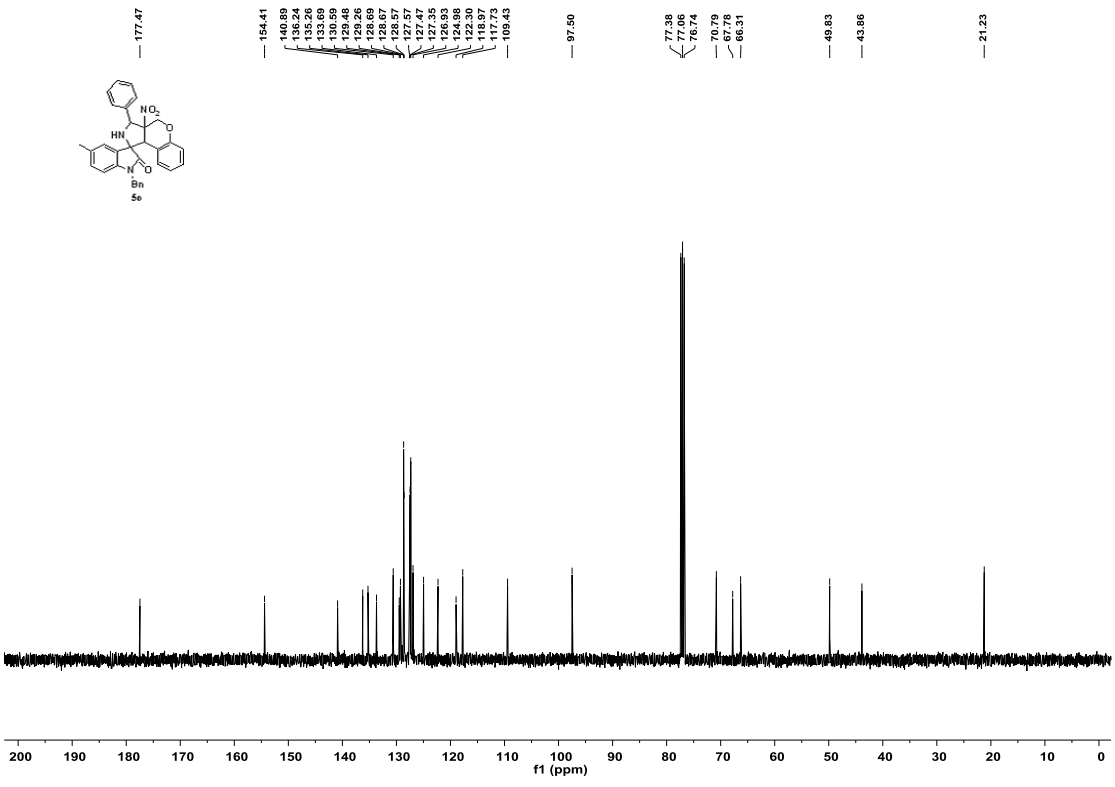
5n


7.677 7.674 7.659 7.656 7.331 7.327 7.311 7.308 7.292 7.289 7.254 7.228 7.224 7.217 7.214 7.211 7.206 7.198 7.195 7.187 7.182 7.179 7.177 7.098 7.095 7.092 7.089 7.076 7.072 6.983 6.978 6.965 6.962 6.959 6.944 6.941 6.758 6.739 6.598 6.594 6.579 6.576 6.560 6.557 6.201 6.198 6.195 6.182 6.179 6.175 6.163 6.159 5.779 5.152 5.148 5.046 5.007 4.700 4.674 4.642 4.330 4.327 4.046 4.024 1.842 1.833 1.811 1.737 1.725 1.715 1.704 1.695 1.691 1.284 1.268 1.260 1.254 1.229 1.223 1.198 1.190 1.161 1.154 1.148 1.135 1.130 1.123 1.116 1.103 1.096
1.00 1.25 4.10 1.05 3.00 1.05 1.00 1.00 1.05 1.00 1.00 1.05 1.00 1.00 0.90 4.60 6.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

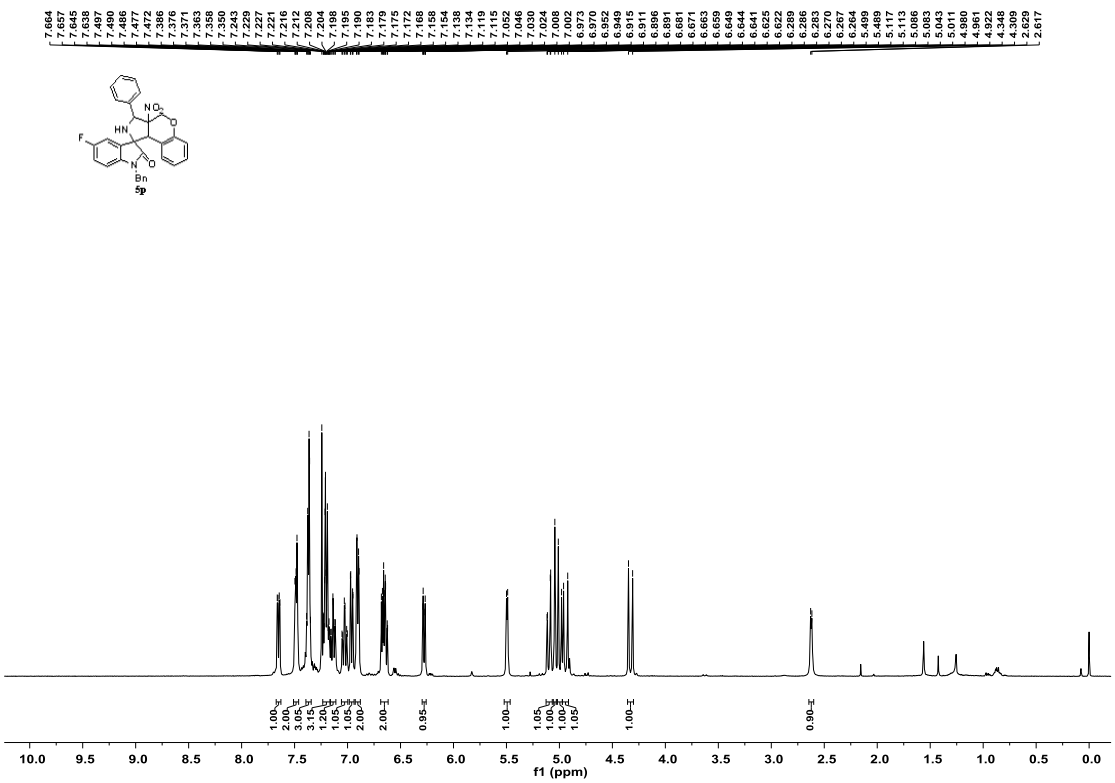

176.22 154.05 143.30 135.17 130.26 129.23 128.66 128.47 127.61 127.46 126.30 123.69 123.32 122.26 119.52 117.60 109.74 97.86 77.35 77.03 76.71 71.24 69.12 68.07 53.15 43.87 39.30 31.33 30.45 26.03 25.72 25.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

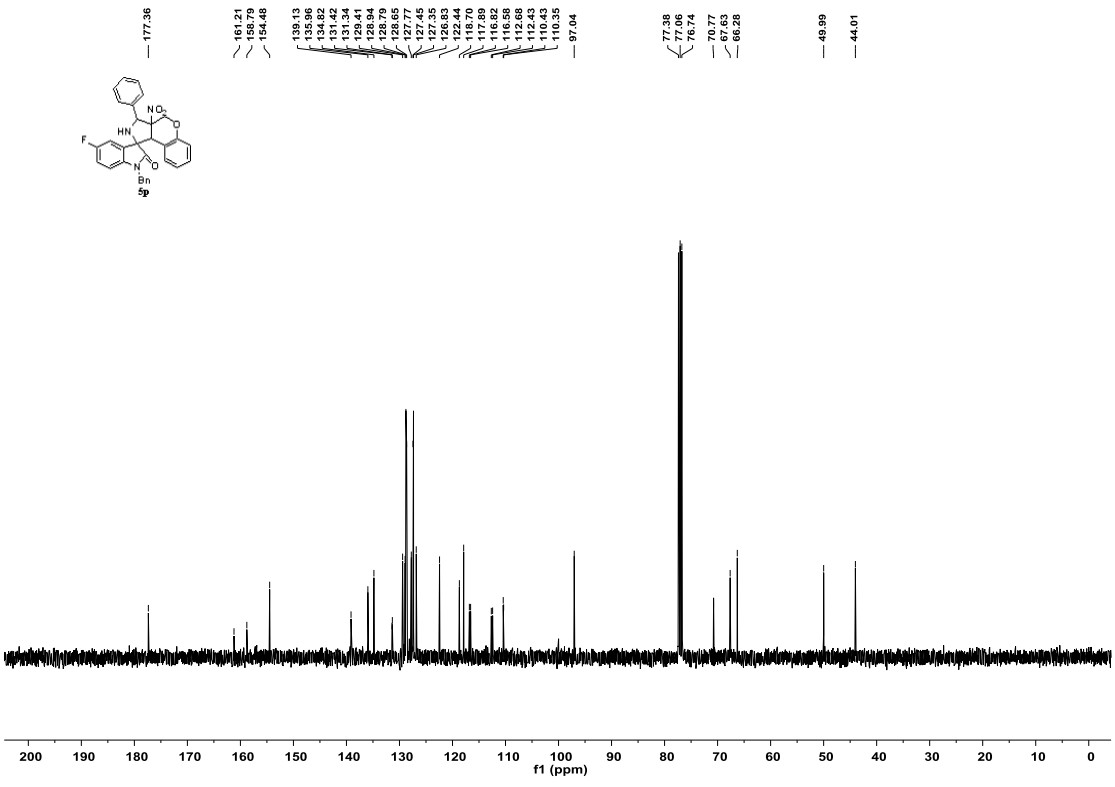
5o


7.694
7.690
7.503
7.497
7.484
7.479
7.382
7.370
7.365
7.361
7.355
7.351
7.343
7.237
7.194
7.190
7.185
7.171
7.136
7.132
7.116
7.110
7.105
6.953
6.950
6.932
6.929
6.914
6.630
6.625
6.612
6.609
6.593
6.590
6.287
6.284
6.281
6.268
6.265
6.262
5.491
5.473
5.185
5.181
5.154
5.150
5.071
5.027
4.997
4.949
4.910
4.370
4.332
2.617
2.606
2.449
1.00
2.00
3.10
5.00
3.00
2.00
0.95
0.95
1.00
1.00
1.00
1.00
0.95
0.90
2.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

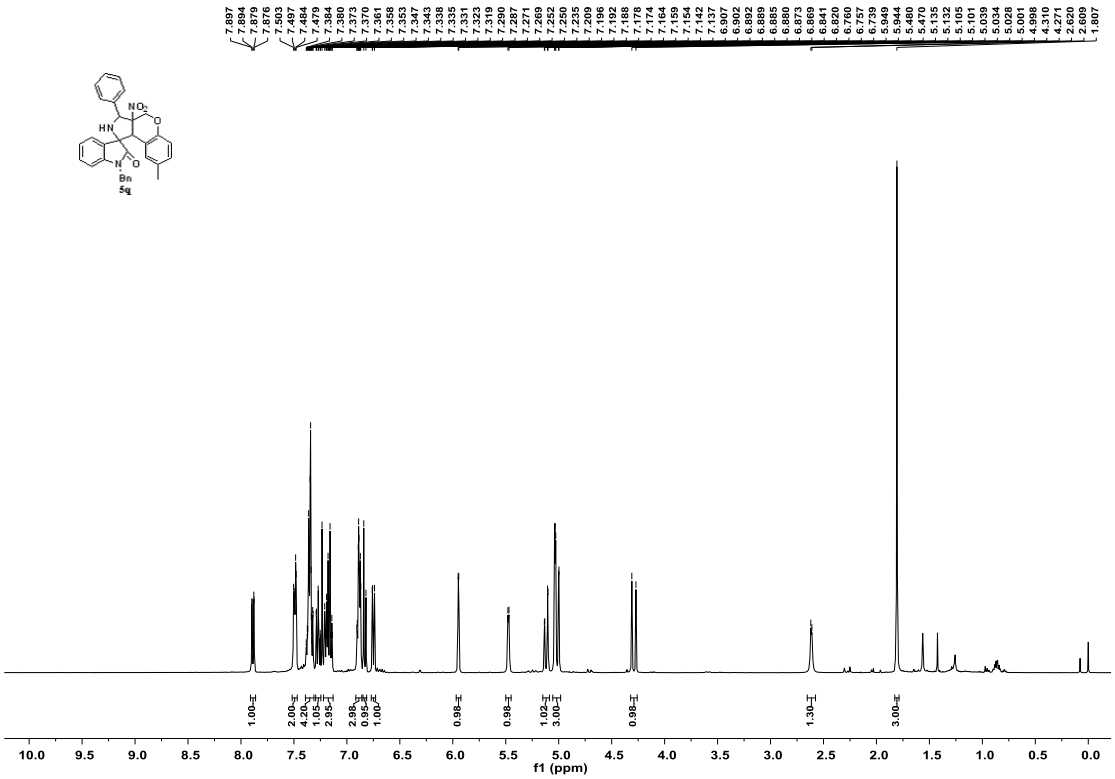

177.47
154.41
140.89
135.24
135.26
133.69
130.59
129.48
129.26
128.69
128.67
128.57
127.57
127.47
127.35
126.93
124.98
122.30
118.97
117.73
109.43
97.50
77.38
77.06
76.74
70.79
67.78
66.31
49.83
43.86
21.23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

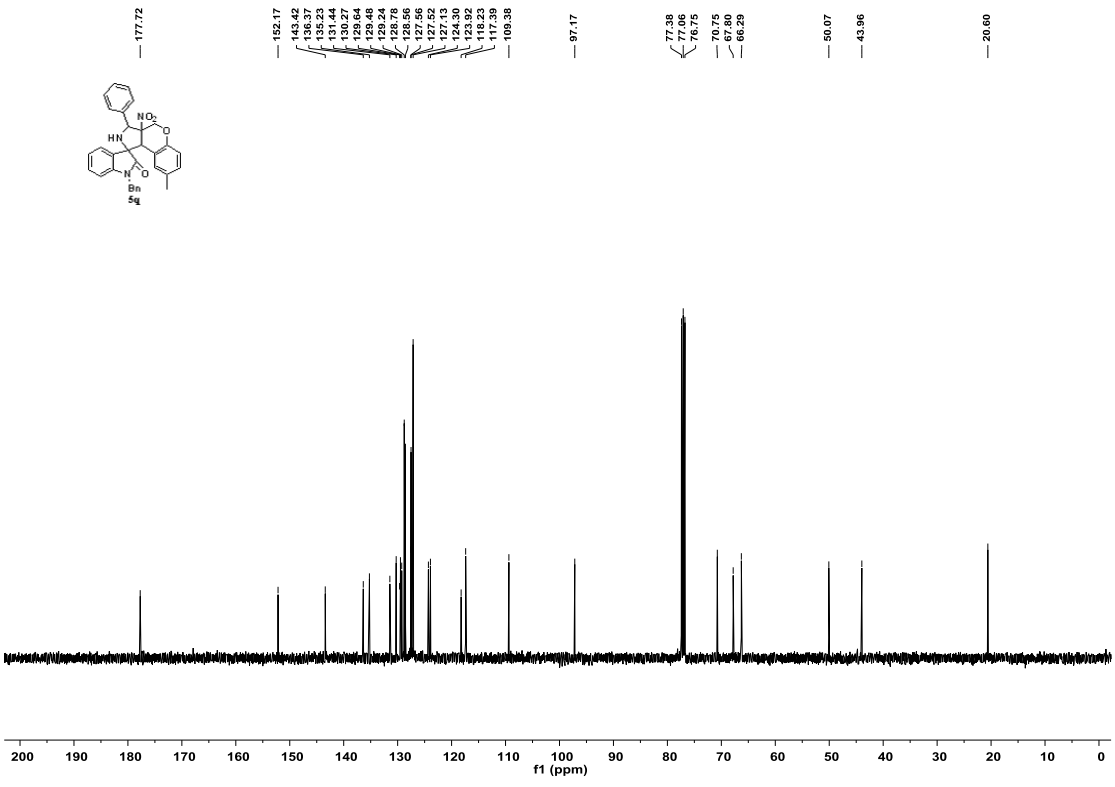
5p


7.664
7.657
7.645
7.638
7.497
7.490
7.486
7.477
7.472
7.386
7.376
7.371
7.365
7.358
7.350
7.243
7.229
7.227
7.221
7.216
7.210
7.208
7.204
7.198
7.195
7.190
7.183
7.179
7.175
7.173
7.168
7.158
7.154
7.138
7.134
7.119
7.115
7.052
7.046
7.030
7.024
7.008
7.002
6.973
6.970
6.952
6.949
6.915
6.911
6.896
6.891
6.681
6.671
6.663
6.659
6.649
6.644
6.641
6.625
6.622
6.289
6.286
6.283
6.270
6.267
6.264
5.499
5.489
5.117
5.113
5.086
5.083
5.043
5.011
4.980
4.961
4.922
4.348
4.309
2.629
2.617
1.00
2.00
3.05
3.15
2.10
1.05
1.05
2.00
2.00
0.95
1.00
1.05
1.00
1.09
1.05
1.00
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

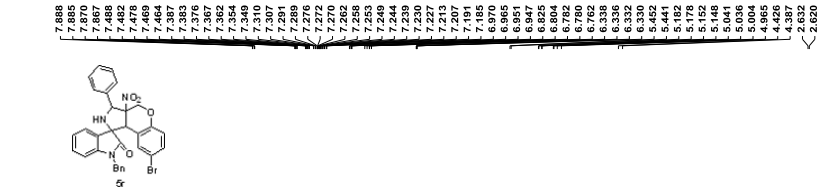

177.36
161.21
158.79
154.48
139.13
135.96
134.82
131.42
131.34
129.41
128.94
128.79
128.65
127.77
127.45
127.35
126.83
122.44
118.70
117.89
116.82
116.68
112.68
112.43
110.43
110.35
97.04
77.38
77.06
76.74
70.77
67.63
66.28
49.99
44.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5q

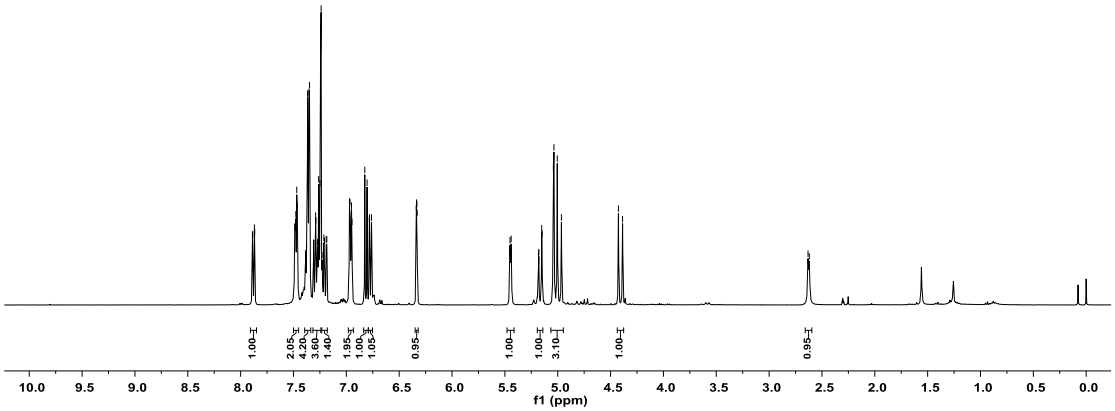

7.897
7.894
7.879
7.876
7.503
7.497
7.484
7.479
7.384
7.380
7.373
7.370
7.361
7.358
7.353
7.347
7.343
7.338
7.335
7.331
7.323
7.319
7.290
7.287
7.271
7.269
7.252
7.250
7.235
7.209
7.196
7.192
7.188
7.178
7.174
7.164
7.159
7.154
7.142
7.137
6.907
6.902
6.892
6.889
6.885
6.880
6.873
6.869
6.841
6.820
6.760
6.757
6.739
5.049
5.044
5.480
5.470
5.135
5.132
5.105
5.101
5.039
5.034
5.028
5.001
4.998
4.310
4.271
2.620
2.609
1.807
Bn
5q
1.00
2.00
4.20
1.05
2.95
2.98
0.95
1.00
0.98
0.98
1.02
3.00
0.98
1.30
3.00
f1 (ppm)

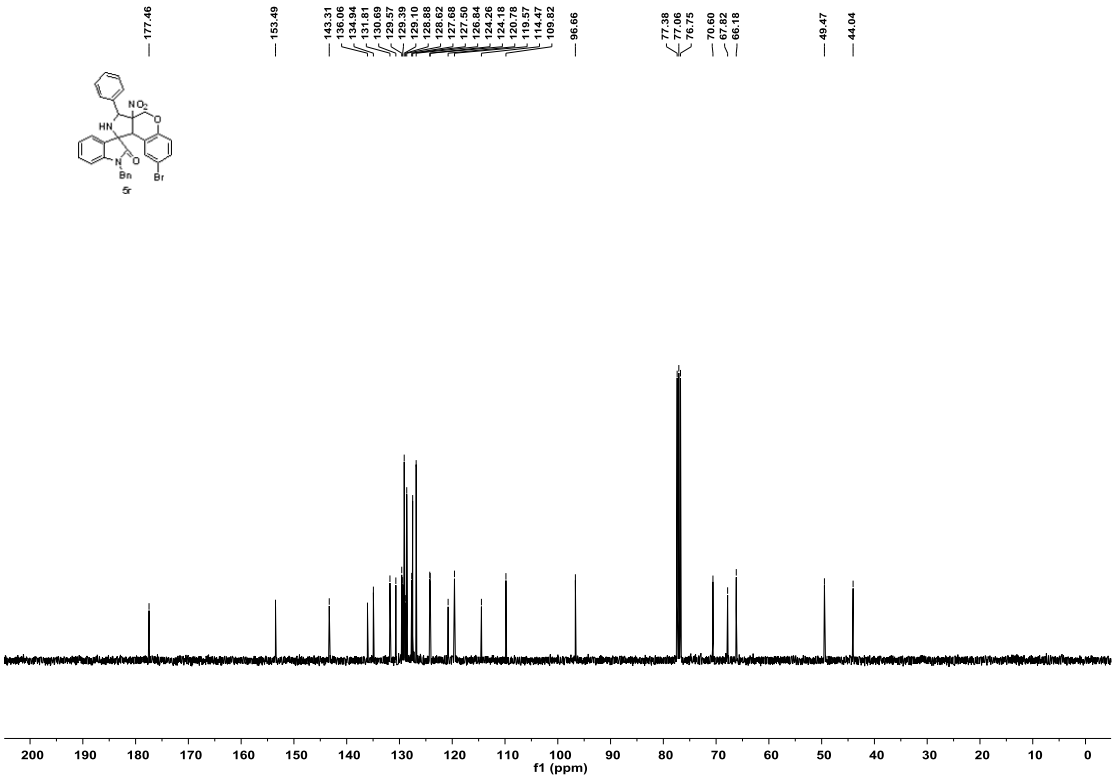

177.72
152.17
143.42
136.37
135.23
131.44
130.27
129.64
129.48
129.24
128.78
128.56
127.56
127.52
127.13
124.30
123.92
118.23
117.39
109.38
97.17
77.38
77.06
76.75
70.75
67.80
66.29
50.07
43.96
20.60
Bn
5q
f1 (ppm)

5r


7.888
7.885
7.870
7.867
7.488
7.482
7.478
7.469
7.464
7.387
7.383
7.376
7.367
7.362
7.354
7.349
7.310
7.307
7.291
7.289
7.276
7.272
7.270
7.262
7.258
7.253
7.249
7.244
7.239
7.230
7.227
7.213
7.207
7.191
7.185
7.070
6.965
6.951
6.947
6.825
6.804
6.782
6.780
6.762
6.338
6.336
6.332
6.330
5.452
5.441
5.182
5.178
5.152
5.148
5.041
5.036
5.004
4.965
4.426
4.387
2.632
2.620

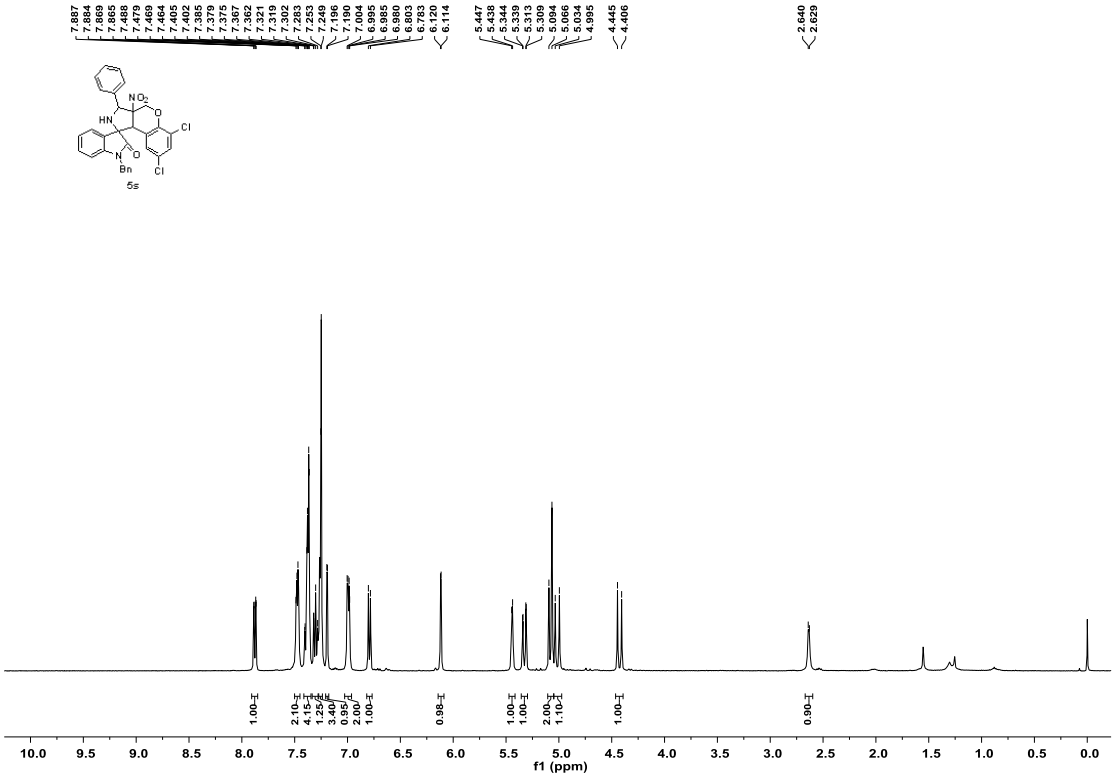
NO2
HN
O
N
O
Bn
Br
5r

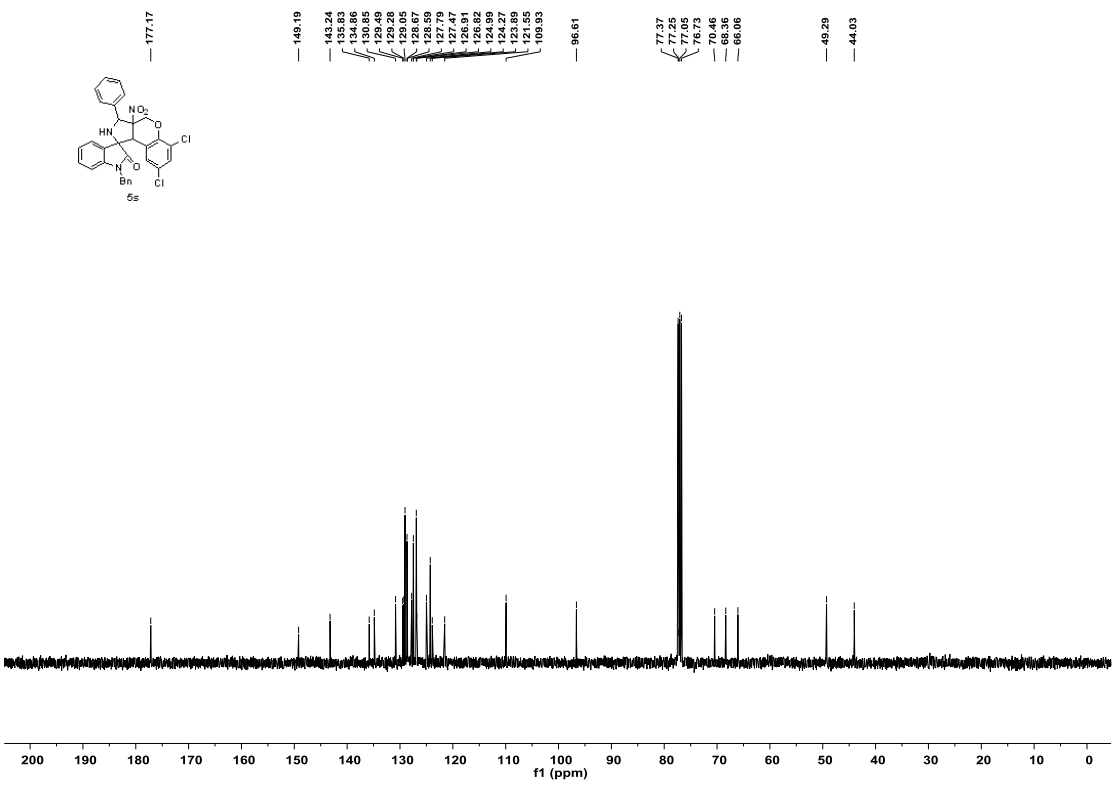

1.00
2.05
4.20
3.60
1.40
1.95
1.00
1.05
0.95
1.00
1.00
3.10
1.00
0.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


177.46
153.49
143.31
136.06
134.84
131.61
130.69
129.57
129.39
129.10
128.88
128.62
127.68
127.60
126.84
124.26
124.18
120.78
119.57
114.47
109.82
96.66
77.38
77.06
76.75
70.60
67.82
66.18
49.47
44.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

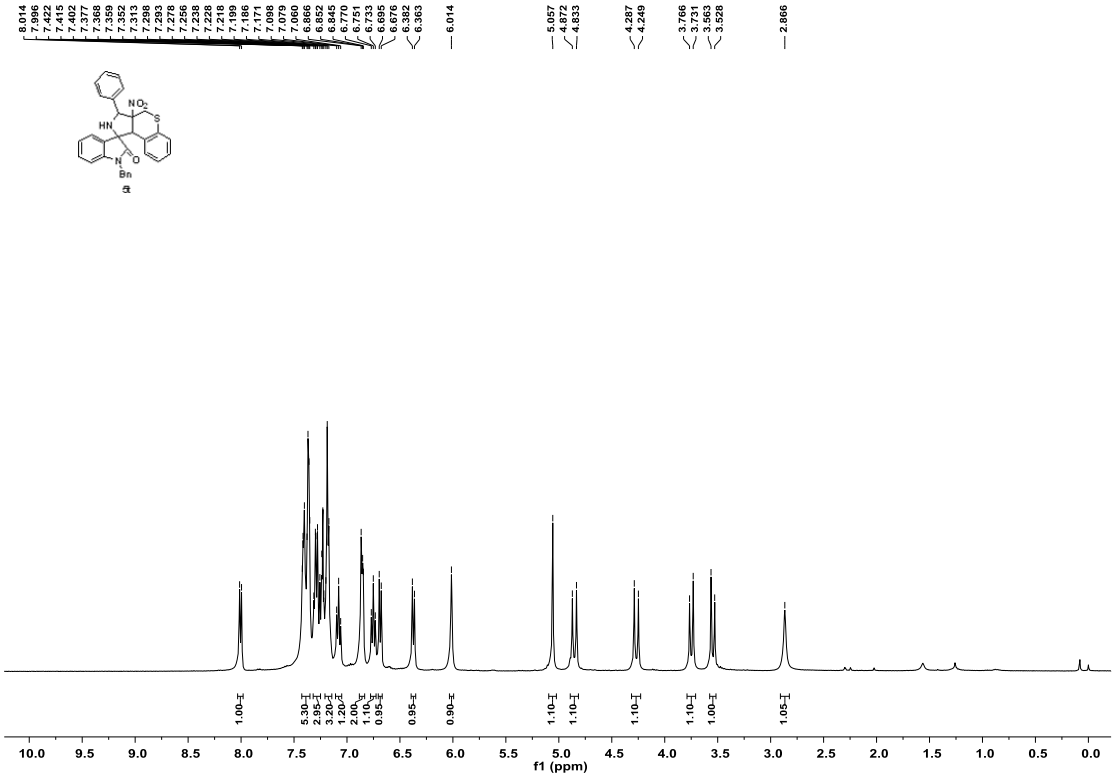
NO2
HN
O
N
O
Bn
Br
5r

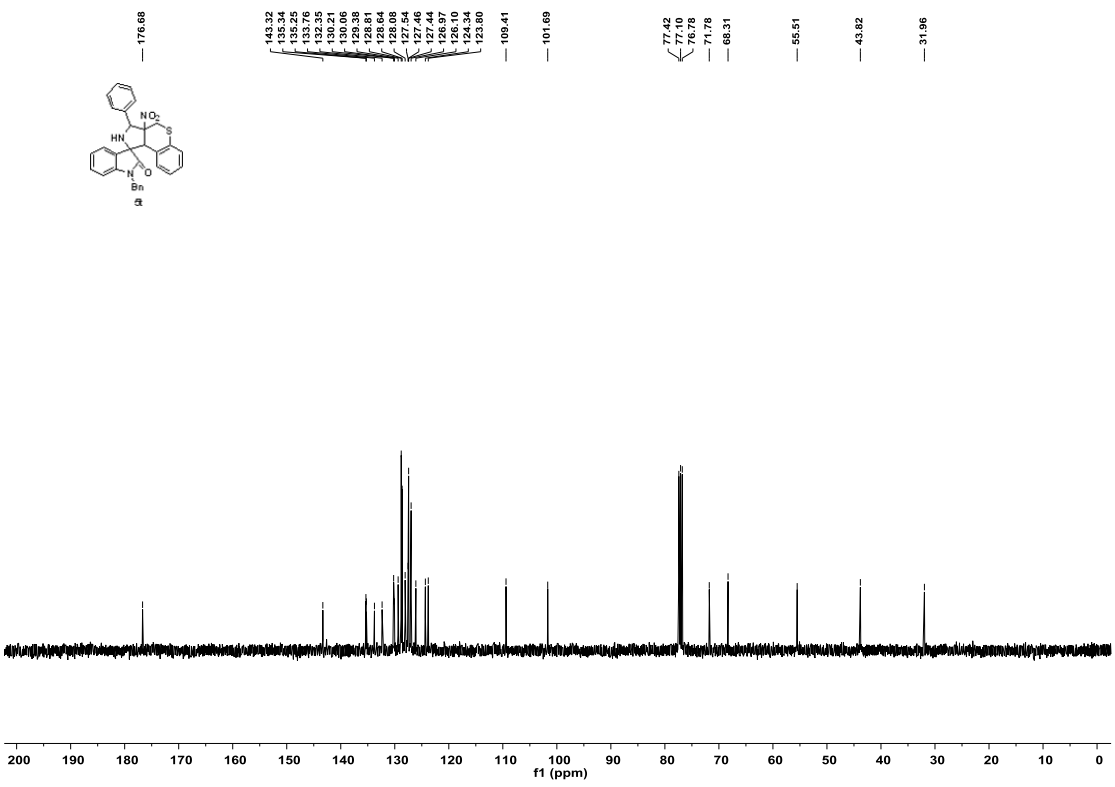
5s


7.887
7.884
7.868
7.865
7.488
7.479
7.469
7.464
7.405
7.402
7.385
7.379
7.375
7.367
7.362
7.321
7.319
7.302
7.283
7.253
7.249
7.196
7.190
7.004
6.995
6.985
6.980
6.803
6.793
6.120
6.114
5.447
5.438
5.344
5.339
5.313
5.309
5.094
5.066
5.034
4.995
4.445
4.406
2.640
2.629
NO2
HN
O
Cl
N
O
Bn
Cl
5s
1.00
2.10
4.15
1.25
3.40
0.95
2.00
1.00
0.98
1.00
1.00
2.00
1.10
1.00
0.90
f1 (ppm)

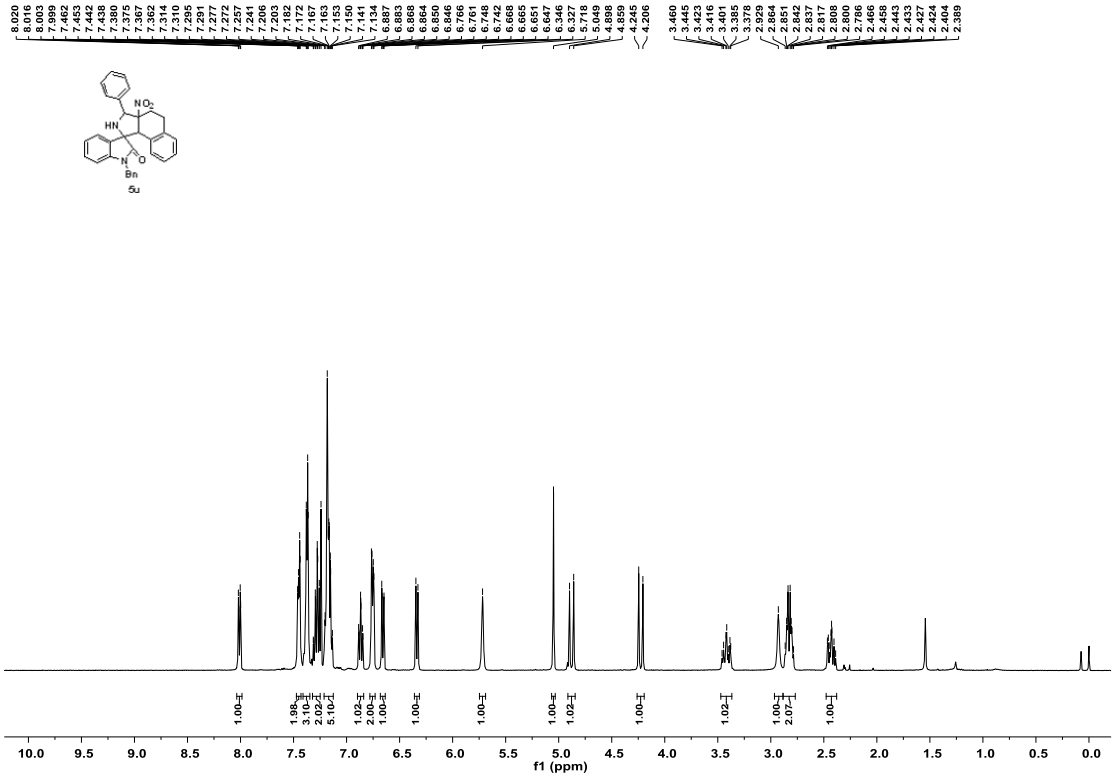

177.17
149.19
143.24
135.83
134.86
130.65
129.49
129.28
129.05
128.67
128.59
127.79
127.47
126.91
126.82
124.99
124.27
123.89
121.55
109.93
96.61
77.37
77.25
77.05
76.73
70.46
68.36
66.06
49.29
44.03
NO2
HN
O
Cl
N
O
Bn
Cl
5s
f1 (ppm)

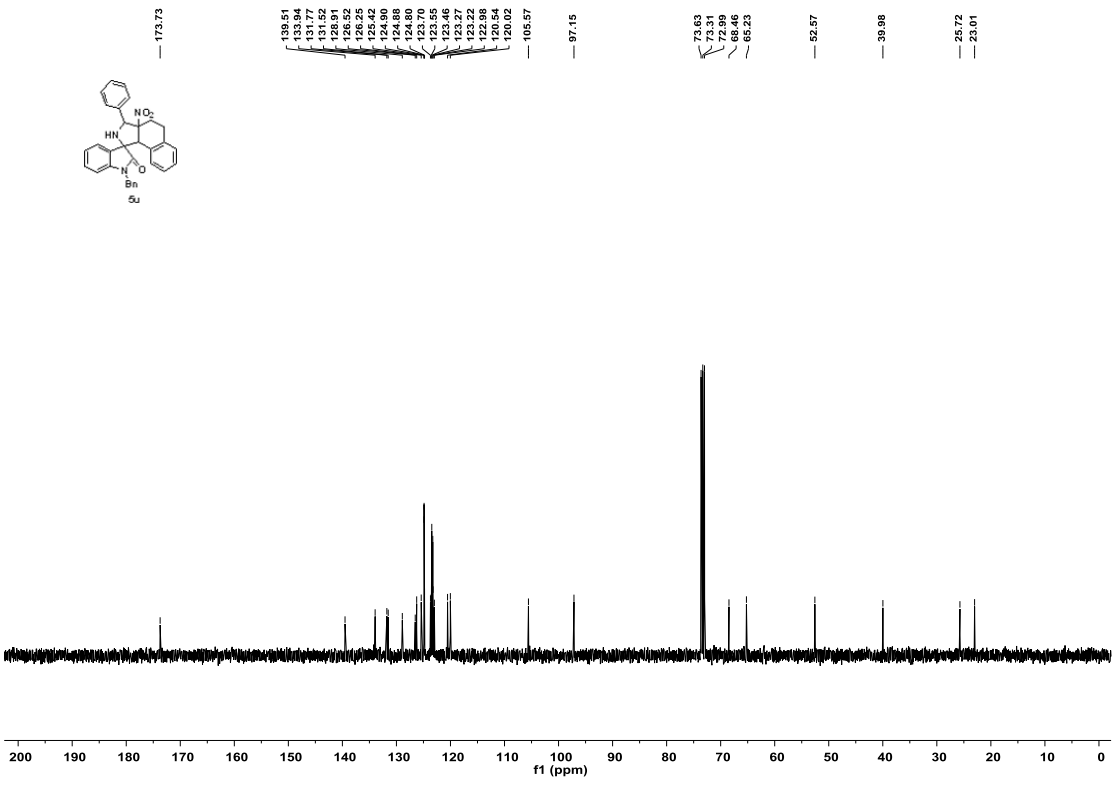
5t


8.014
7.996
7.422
7.415
7.402
7.377
7.368
7.359
7.352
7.313
7.298
7.293
7.278
7.256
7.238
7.228
7.218
7.199
7.186
7.171
7.098
7.079
7.060
6.866
6.852
6.845
6.770
6.751
6.733
6.695
6.656
6.382
6.363
6.014
5.057
4.872
4.833
4.287
4.249
3.766
3.731
3.563
3.528
2.866
1.00
5.30
2.95
3.20
1.20
2.00
1.10
0.95
0.95
0.90
1.10
1.10
1.10
1.10
1.00
1.05
f1 (ppm)

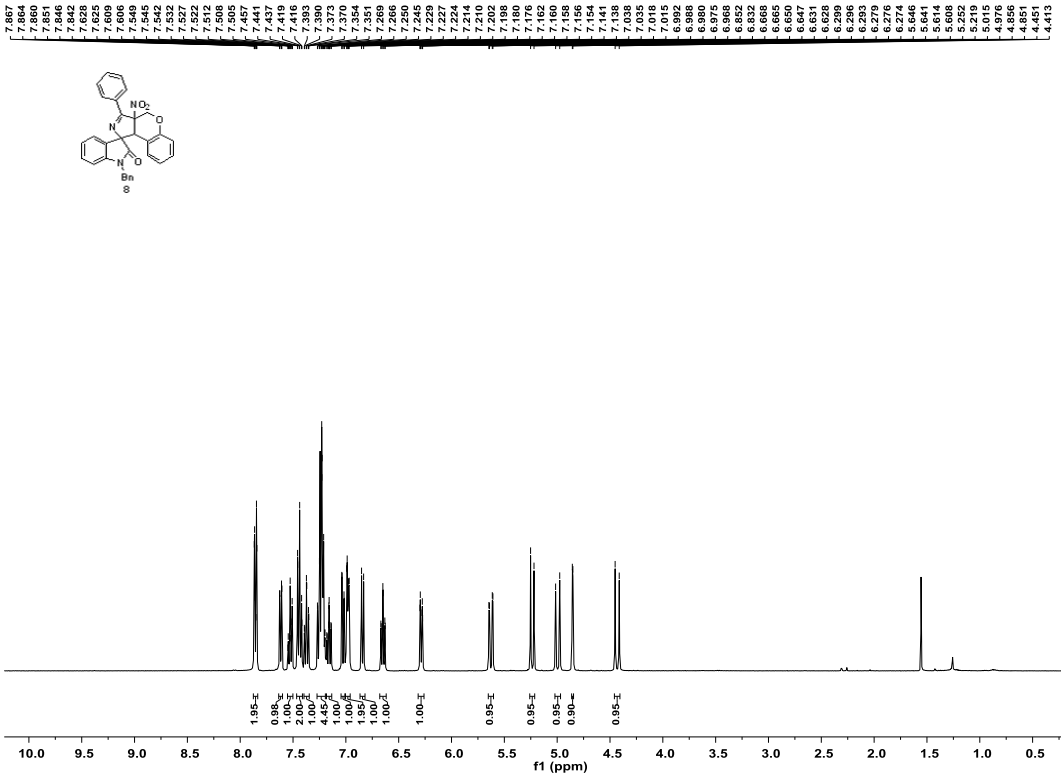

176.68
143.32
135.34
135.25
133.76
132.35
130.21
130.06
129.38
128.81
128.64
128.08
127.54
127.46
127.44
126.97
126.10
124.34
123.80
109.41
101.69
77.42
77.10
76.78
71.78
68.31
55.51
43.82
31.96
f1 (ppm)

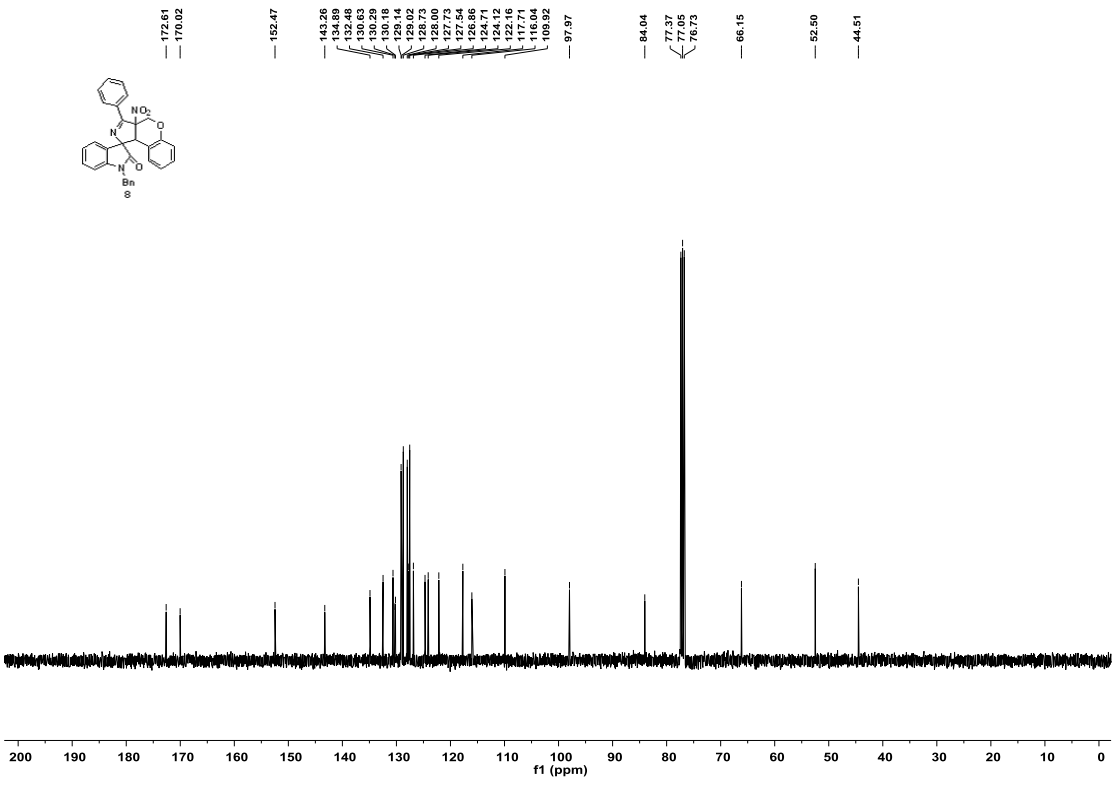
5u


8.020
8.016
8.003
7.999
7.462
7.453
7.442
7.438
7.380
7.376
7.367
7.362
7.314
7.310
7.295
7.291
7.277
7.272
7.257
7.241
7.206
7.203
7.182
7.172
7.167
7.163
7.155
7.150
7.141
7.134
6.887
6.883
6.868
6.864
6.850
6.846
6.766
6.761
6.748
6.742
6.668
6.665
6.651
6.647
6.346
6.327
5.718
5.049
4.898
4.859
4.245
4.206
3.460
3.445
3.423
3.416
3.401
3.385
3.378
2.929
2.864
2.851
2.842
2.837
2.817
2.808
2.800
2.786
2.466
2.456
2.443
2.433
2.427
2.424
2.404
2.389
NO2
HN
N
O
Bn
5u
1.00
1.98
3.10
2.02
5.10
1.02
2.00
1.00
1.00
1.00
1.00
1.02
1.00
1.02
1.00
2.07
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

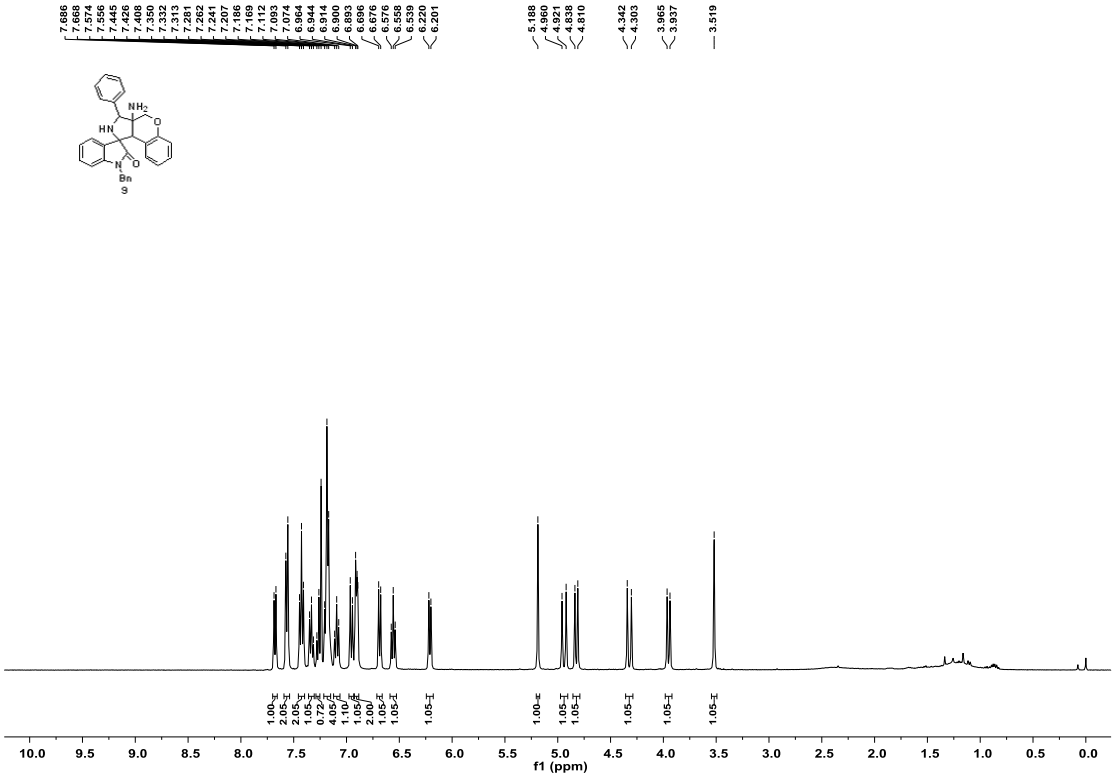

173.73
139.51
133.94
131.77
131.52
128.91
126.52
126.25
125.42
124.90
124.88
124.60
123.70
123.55
123.46
123.27
123.22
122.98
120.54
120.02
105.57
97.15
73.63
73.31
72.99
68.46
65.23
52.57
39.98
25.72
23.01
NO2
HN
N
O
Bn
5u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

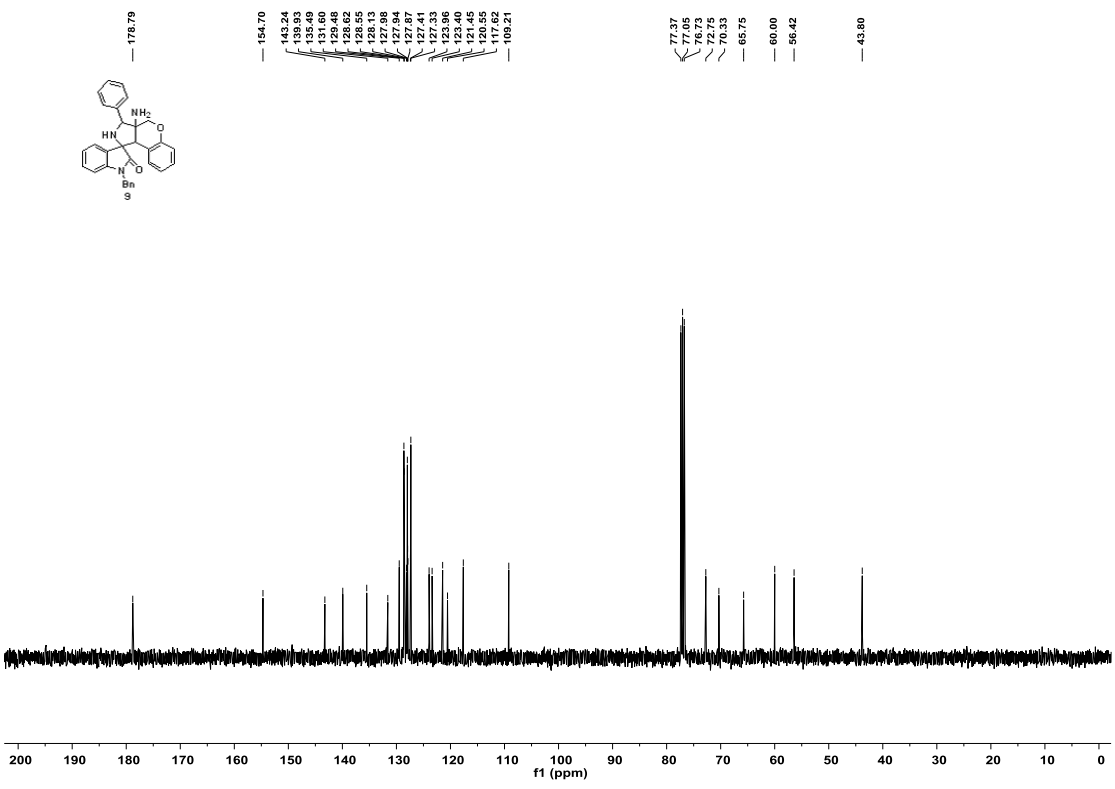
8


7.867
7.864
7.860
7.851
7.846
7.842
7.628
7.625
7.609
7.606
7.549
7.545
7.542
7.532
7.527
7.522
7.512
7.508
7.505
7.457
7.441
7.437
7.419
7.416
7.393
7.390
7.373
7.370
7.354
7.351
7.268
7.266
7.250
7.245
7.229
7.227
7.224
7.214
7.210
7.202
7.198
7.180
7.176
7.162
7.160
7.158
7.156
7.154
7.141
7.138
7.038
7.035
7.018
7.015
6.992
6.988
6.980
6.975
6.968
6.852
6.832
6.668
6.665
6.650
6.647
6.631
6.628
6.299
6.296
6.293
6.279
6.276
6.274
5.644
5.641
5.614
5.608
5.252
5.219
5.015
4.976
4.856
4.551
4.451
4.413
NO2
O
N
N
O
Bn
8
1.95
0.98
1.00
2.00
1.00
4.45
1.00
1.95
1.00
1.00
1.00
0.95
0.95
0.95
0.90
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.61
170.02
152.47
143.26
134.89
132.48
130.63
130.29
130.18
129.14
129.02
128.73
128.00
127.73
127.54
126.86
124.71
124.12
122.16
117.71
116.04
109.92
97.97
84.04
77.37
77.05
76.73
66.15
52.50
44.51
NO2
O
N
N
O
Bn
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

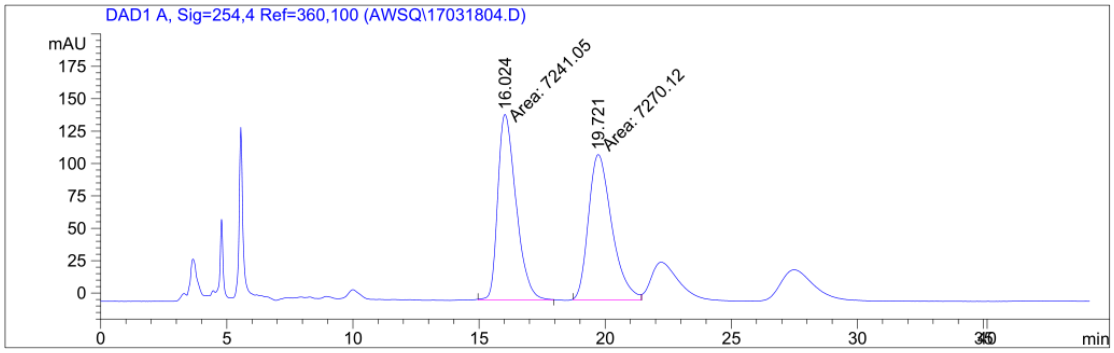
9


7.686
7.668
7.574
7.556
7.445
7.426
7.408
7.350
7.332
7.313
7.281
7.262
7.241
7.207
7.186
7.169
7.112
7.093
7.074
6.964
6.944
6.914
6.900
6.893
6.696
6.676
6.576
6.558
6.539
6.220
6.201
5.188
4.960
4.921
4.838
4.810
4.342
4.303
3.965
3.937
3.519
NH2
HN
O
N
O
Bn
9
1.00
2.05
1.05
1.05
0.72
4.05
1.10
1.05
2.00
1.05
1.05
1.05
1.00
1.05
1.05
1.05
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

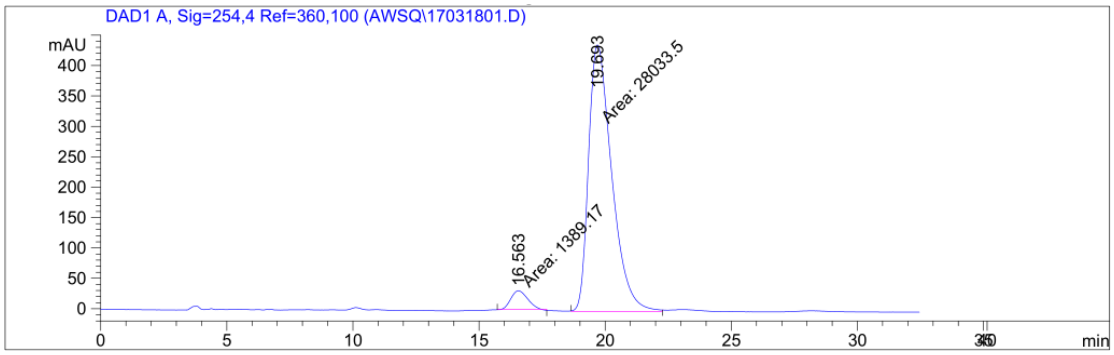

178.79
154.70
143.24
139.93
135.49
131.60
129.48
128.62
128.55
128.13
127.98
127.94
127.87
127.41
127.33
123.96
123.40
121.45
120.55
117.62
109.21
77.37
77.05
76.73
72.75
70.33
65.75
60.00
56.42
43.80
NH2
HN
O
N
O
Bn
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4. Copies of HPLC chromatographs

HPLC Chromatographs of **5a**

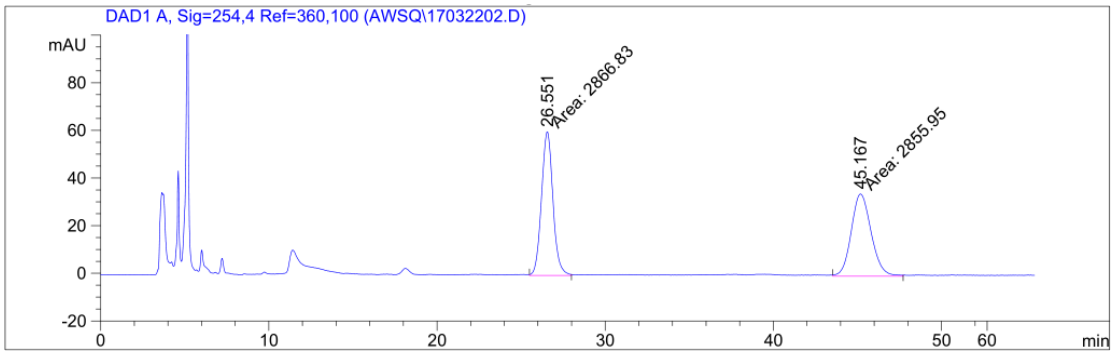


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	16.024	7241.05420	143.36806	49.8999
2	19.721	7270.11914	112.30684	50.1001

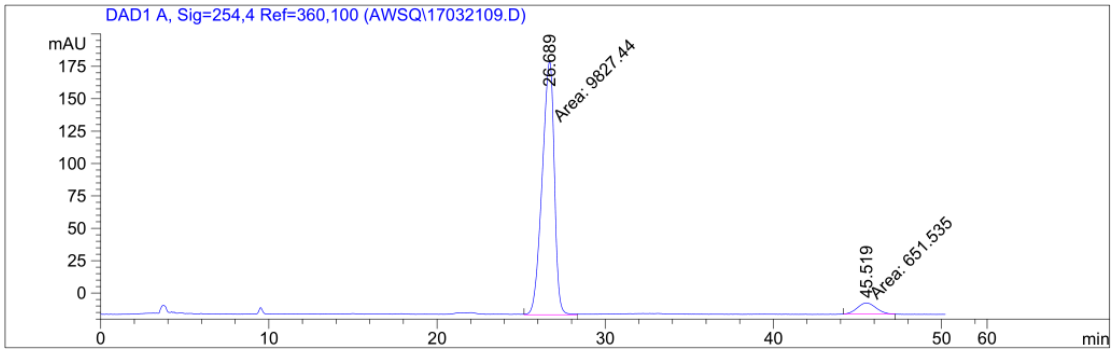


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	16.563	1389.17456	30.43403	4.7214
2	19.693	2.80335e4	438.25244	95.2786

HPLC Chromatographs of **5b**

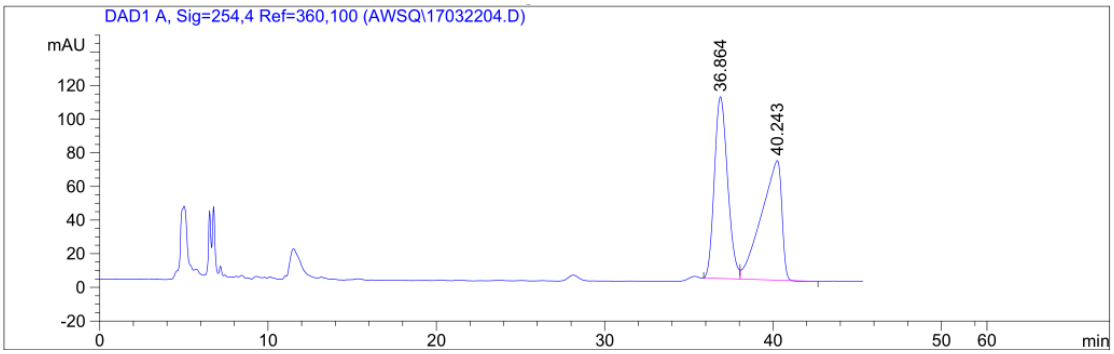


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	26.551	2866.83032	60.35281	50.0950
2	45.167	2855.95166	34.57727	49.9050

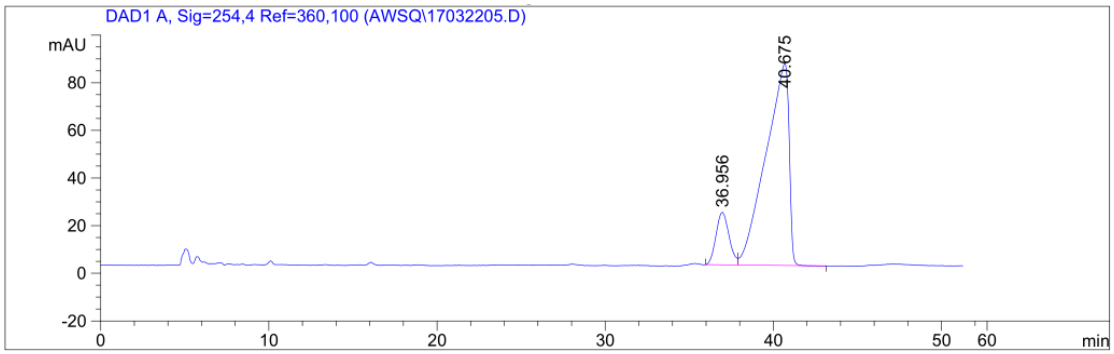


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	26.689	9827.43652	195.47295	93.7825
2	45.519	651.53467	8.54964	6.2175

HPLC Chromatographs of **5c**

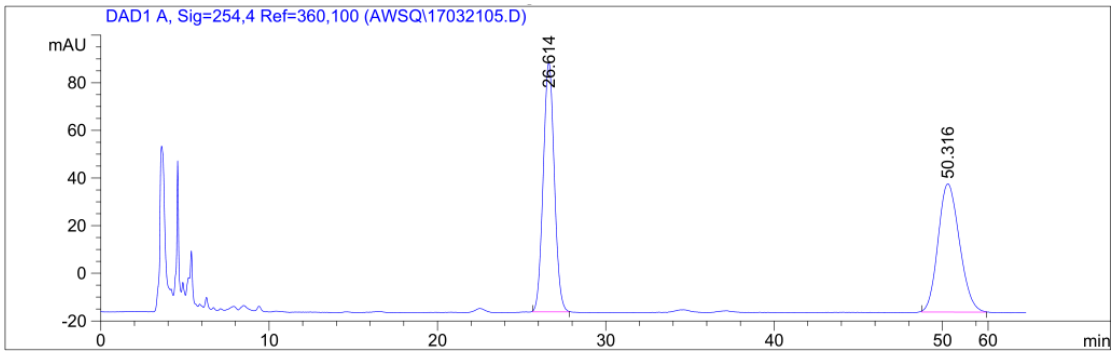


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	36.864	5923.37354	108.17676	49.8566
2	40.243	5957.44580	71.16122	50.1434

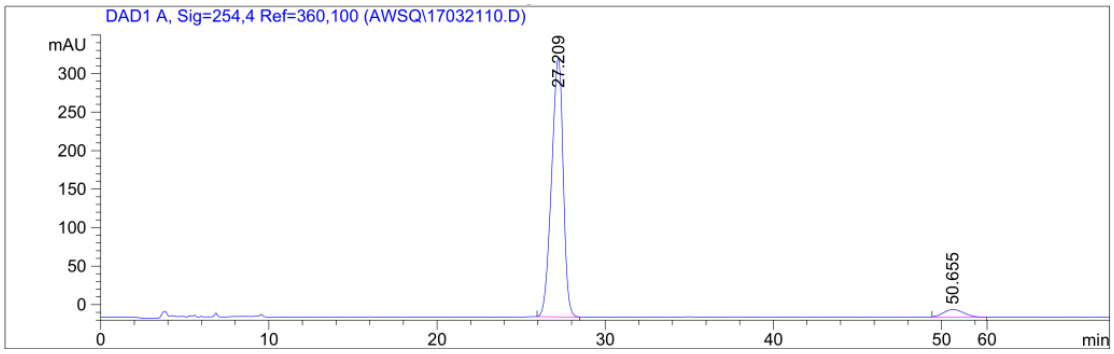


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	36.956	1189.03113	22.03078	12.7857
2	40.675	8110.67529	84.81844	87.2143

HPLC Chromatographs of **5d**

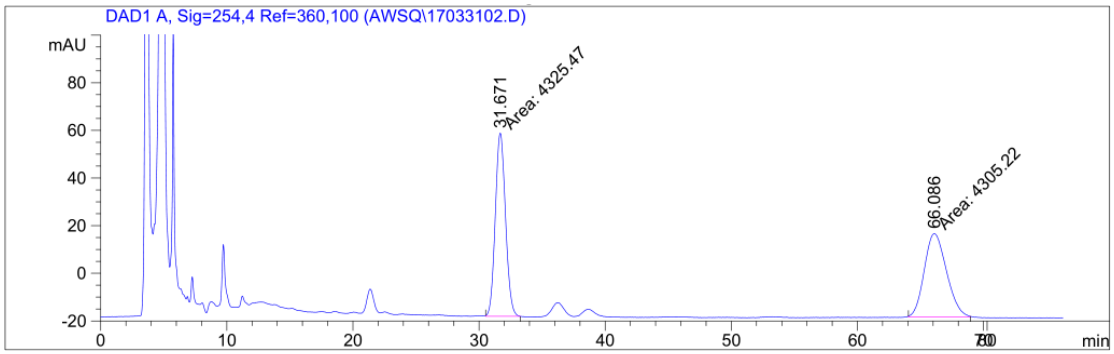


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	26.614	4787.28906	104.88519	50.0965
2	50.316	4768.83838	53.86290	49.9035

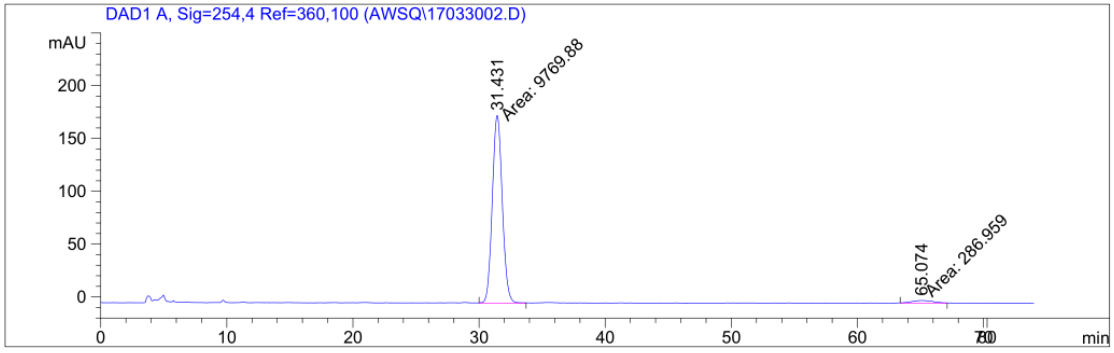


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	27.209	1.61136e4	336.75748	94.9156
2	50.655	863.17065	10.10619	5.0844

HPLC Chromatographs of **5e**

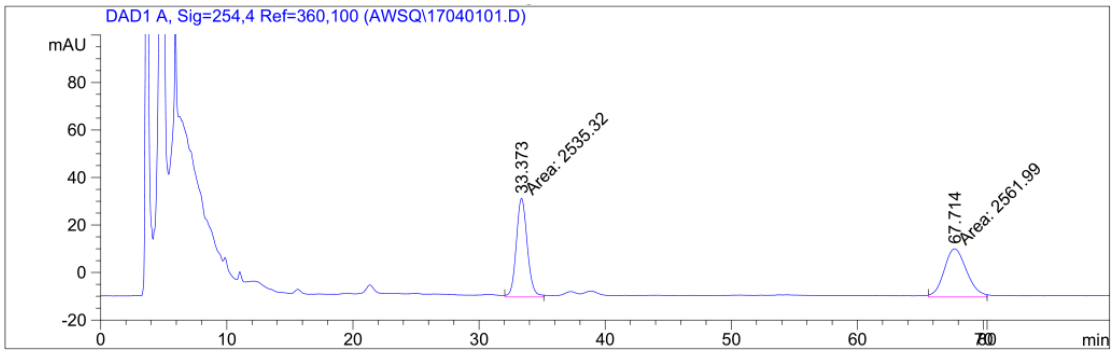


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	31.671	4325.46973	76.94801	50.1173
2	66.086	4305.22070	35.10695	49.8827

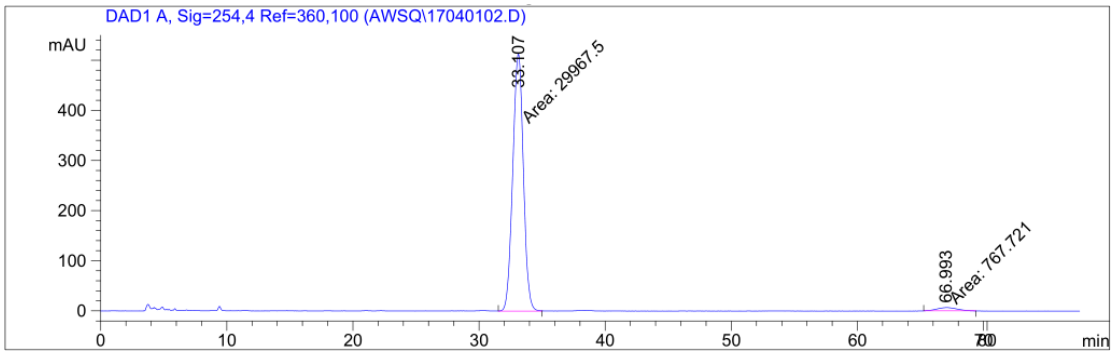


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	31.431	9769.87598	177.79742	97.1466
2	65.074	286.95941	2.45218	2.8534

HPLC Chromatographs of **5f**

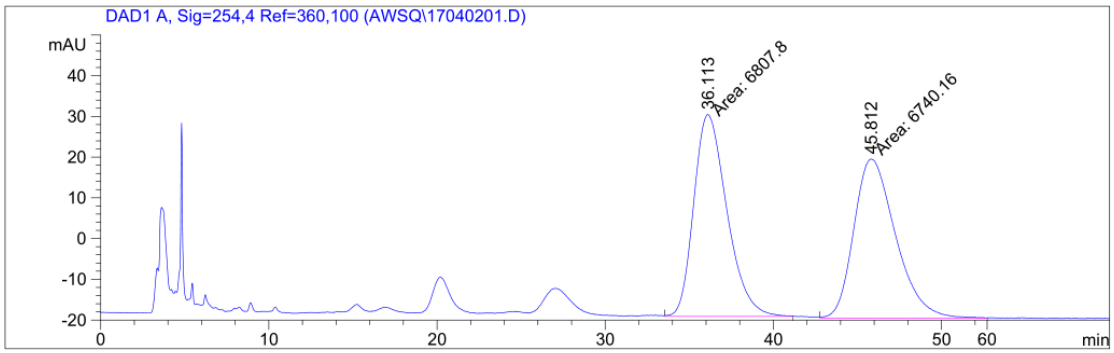


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	33.373	2535.31812	41.60107	49.7384
2	67.714	2561.98682	20.39388	50.2616

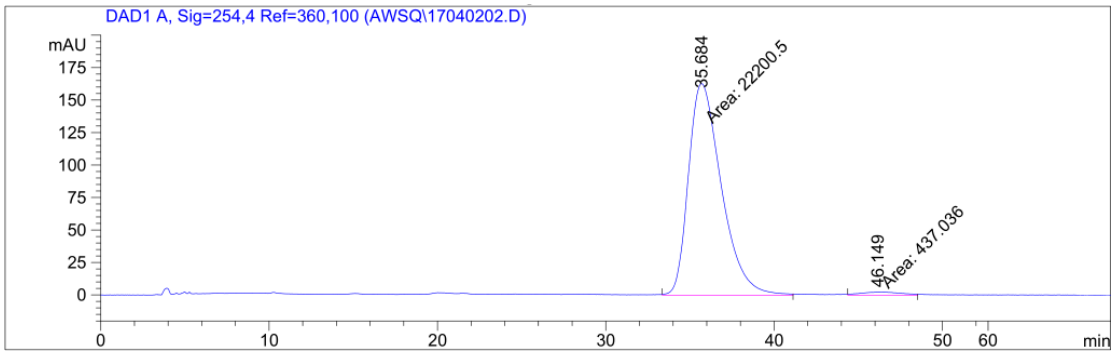


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	33.107	2.99675e4	513.13391	97.5021
2	66.993	767.72095	6.71642	2.4979

HPLC Chromatographs of **5g**

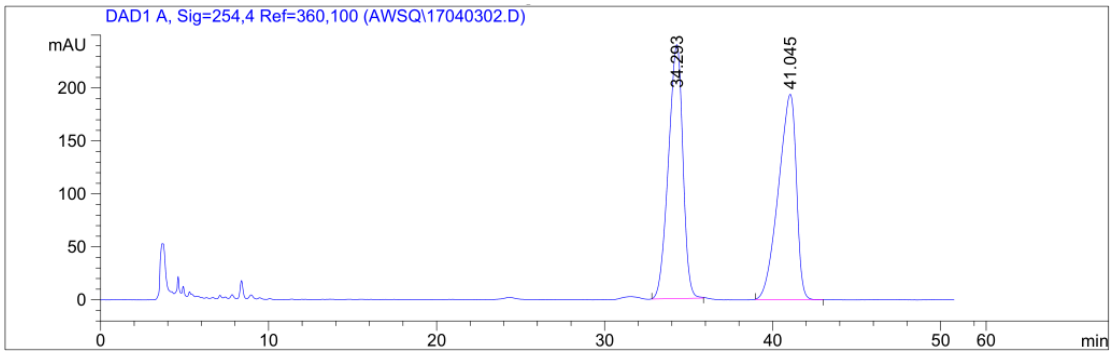


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	36.113	6807.80371	49.63602	50.2496
2	45.812	6740.16455	39.11159	49.7504

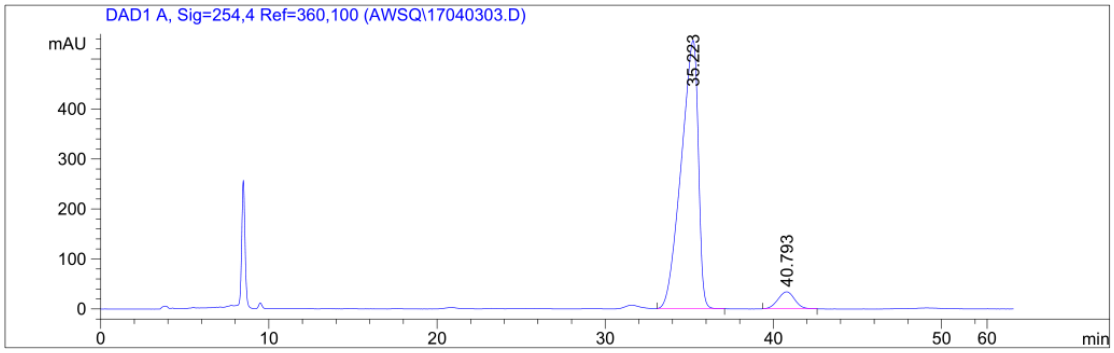


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	35.684	2.22005e4	163.12964	98.0694
2	46.149	437.03647	2.59082	1.9306

HPLC Chromatographs of **5h**

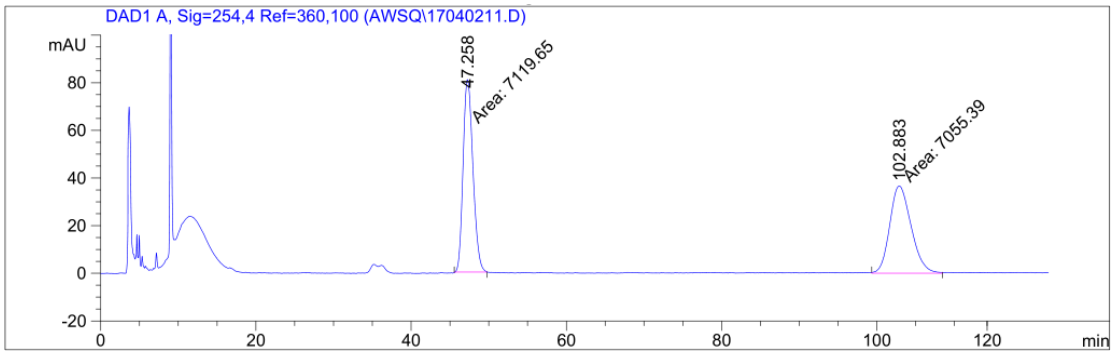


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	34.293	1.43477e4	239.90440	49.8364
2	41.045	1.44419e4	194.06680	50.1636

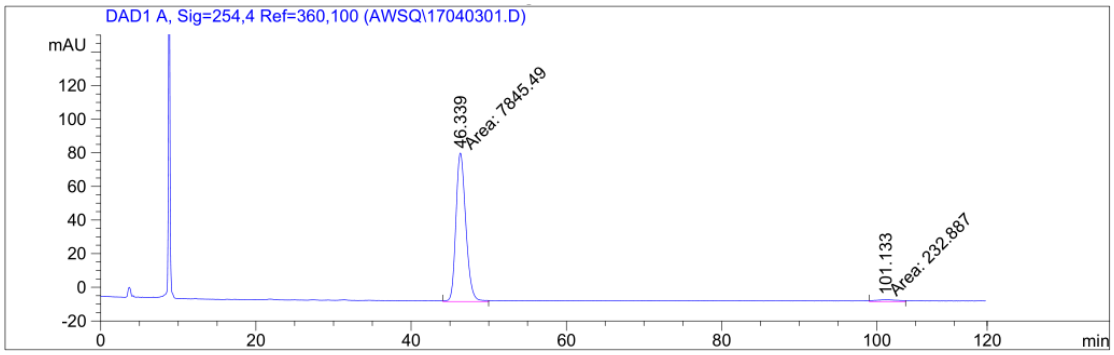


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	35.223	3.79030e4	536.99591	94.1093
2	40.793	2372.52539	34.13328	5.8907

HPLC Chromatographs of **5i**

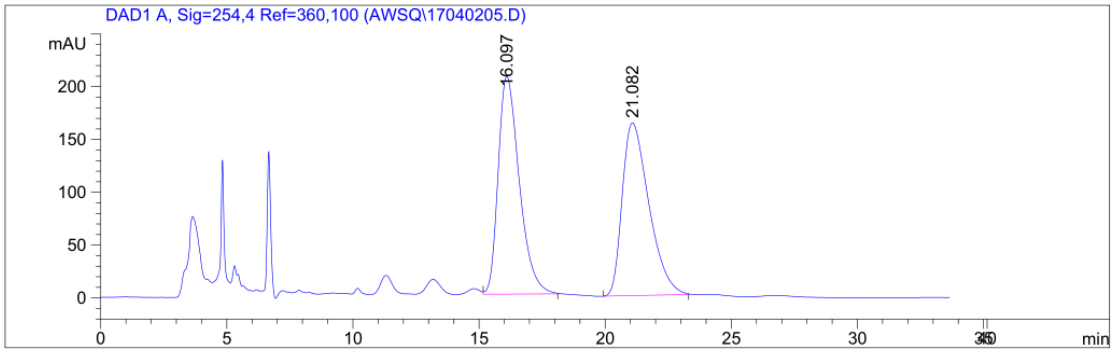


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	47.258	7119.64600	80.87196	50.2267
2	102.883	7055.38623	36.71408	49.7733

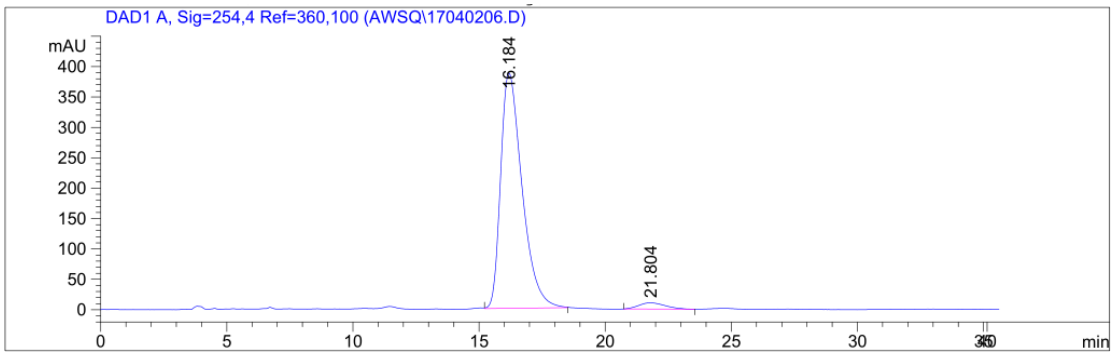


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	46.339	7845.48633	88.35828	97.1172
2	101.133	232.88689	1.16167	2.8828

HPLC Chromatographs of **5j**

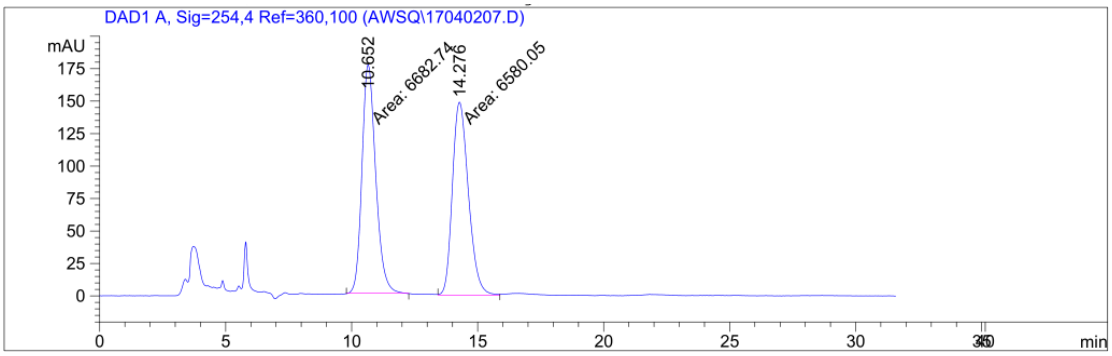


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	16.097	1.20023e4	206.32765	49.9269
2	21.082	1.20375e4	163.76784	50.0731

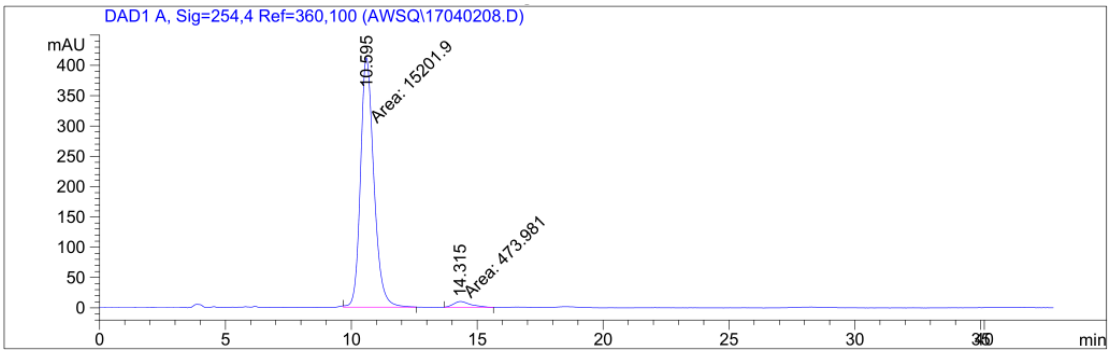


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	16.184	2.28144e4	386.95139	96.8347
2	21.804	745.73688	10.27418	3.1653

HPLC Chromatographs of **5k**

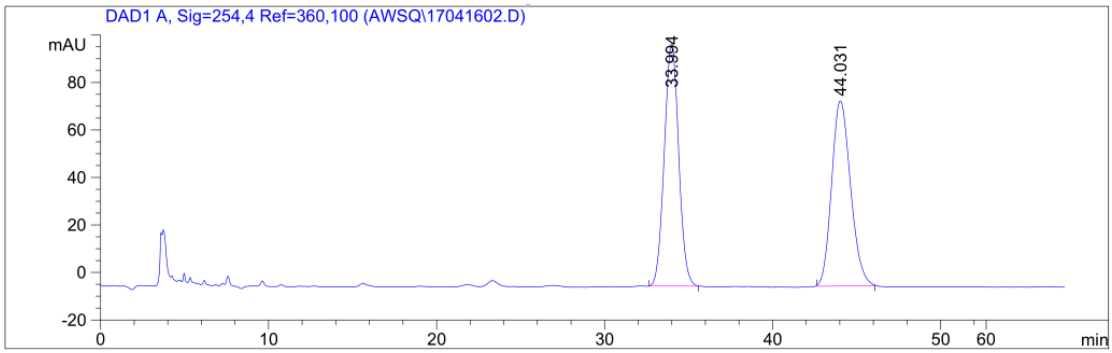


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	10.652	6682.74268	176.12497	50.3871
2	14.276	6580.05420	148.69611	49.6129

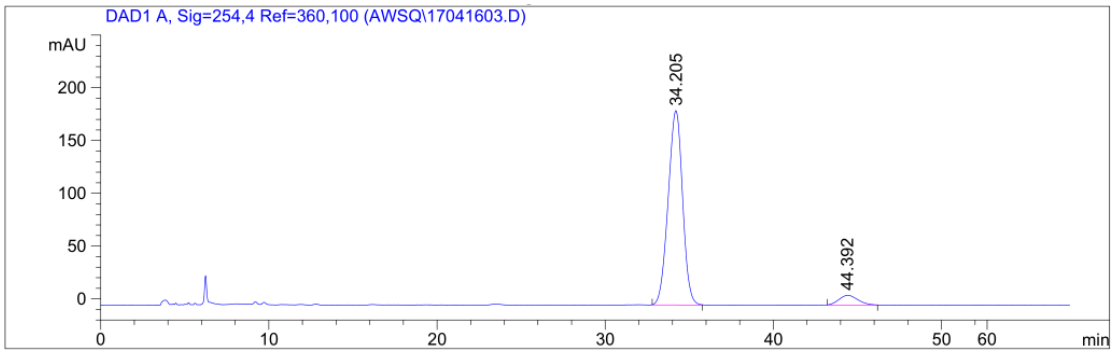


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	10.595	1.52019e4	411.49155	96.9764
2	14.315	473.98114	9.82106	3.0236

HPLC Chromatographs of **5l**

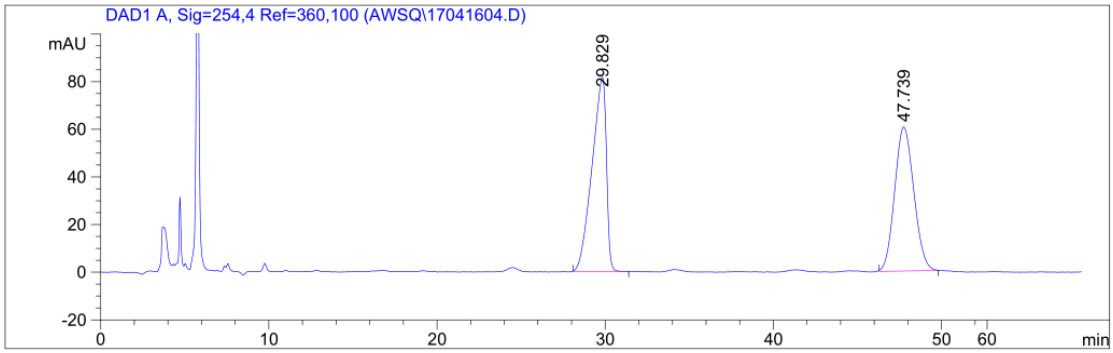


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	33.994	6088.16113	102.19135	49.8927
2	44.031	6114.34473	78.02500	50.1073

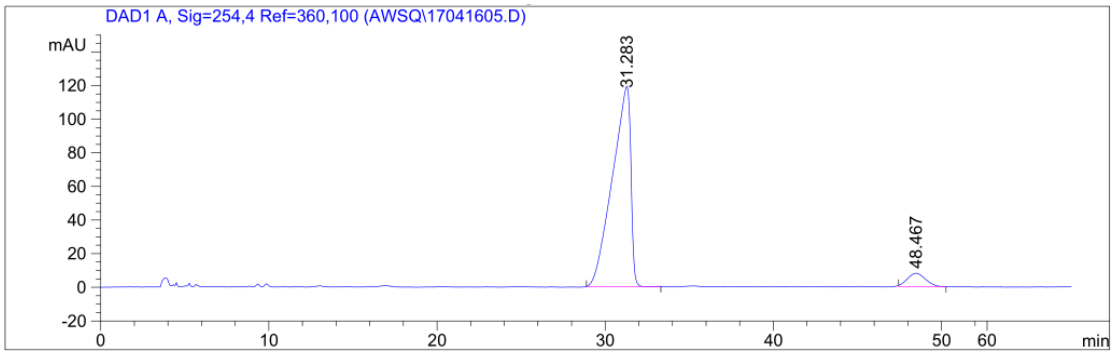


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	34.205	1.09745e4	184.19830	93.8470
2	44.392	719.52826	9.25934	6.1530

HPLC Chromatographs of **5m**

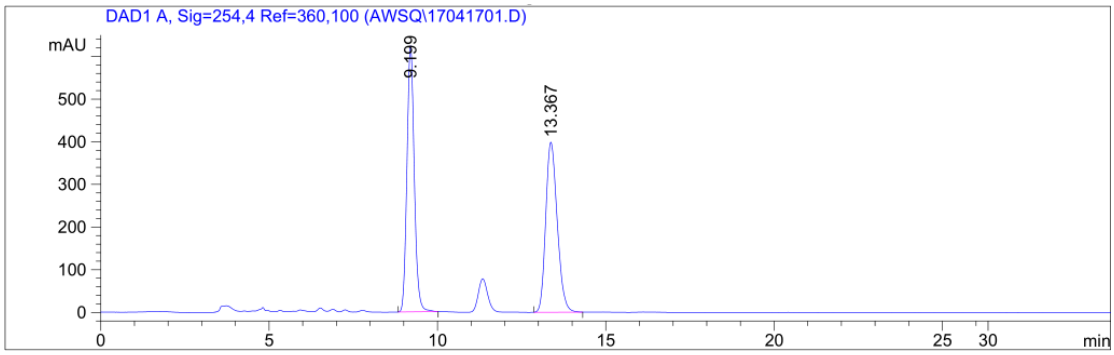


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	29.829	4846.44629	81.67672	50.2755
2	47.739	4793.33984	60.56644	49.7245

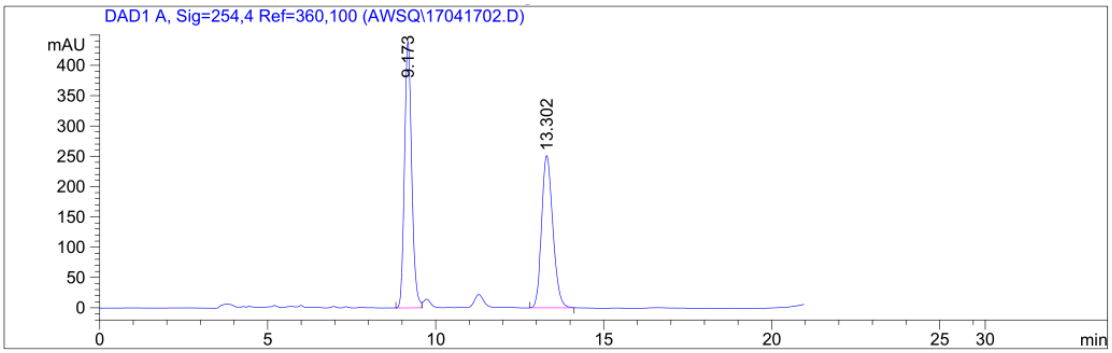


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	31.283	9123.68945	119.20626	93.7514
2	48.467	608.09772	8.00540	6.2486

HPLC Chromatographs of **5n**

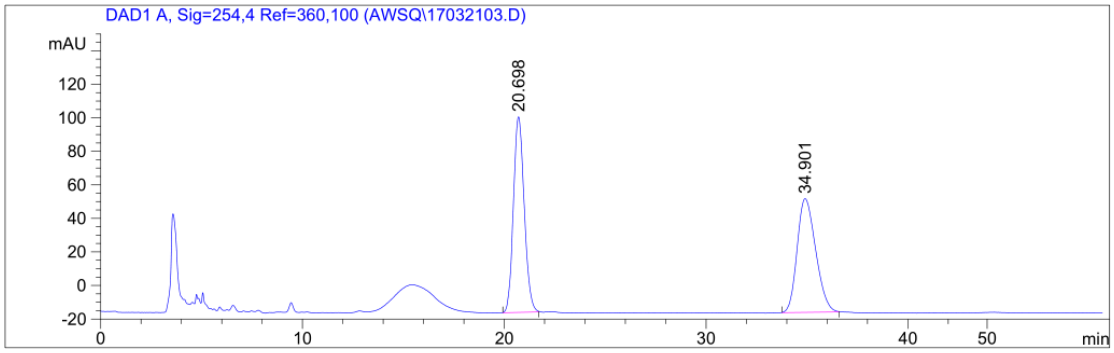


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	9.199	9473.85352	624.51385	50.0338
2	13.367	9461.03711	398.77005	49.9662

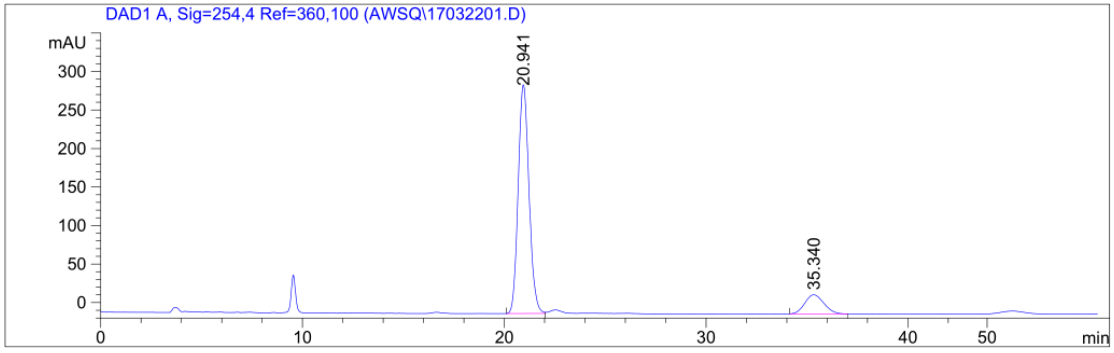


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	9.173	6556.93262	439.93381	52.8373
2	13.302	5852.72852	251.39461	47.1627

HPLC Chromatographs of **5o**

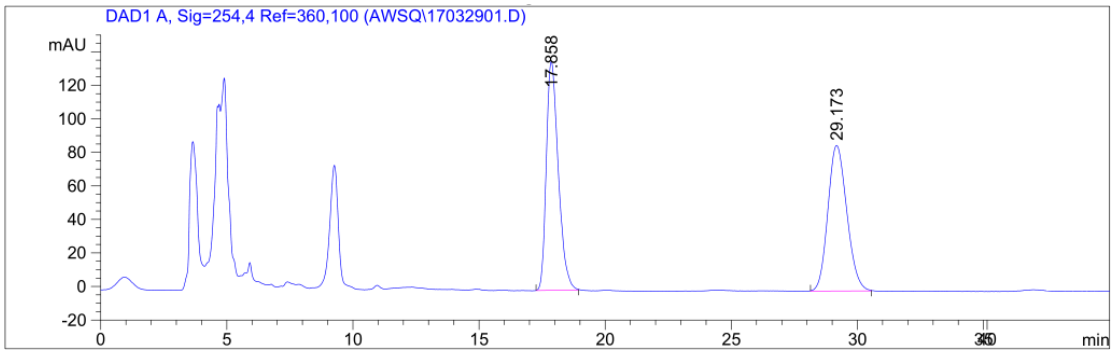


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	20.698	4340.35742	116.72485	50.0750
2	34.901	4327.35205	67.84043	49.9250

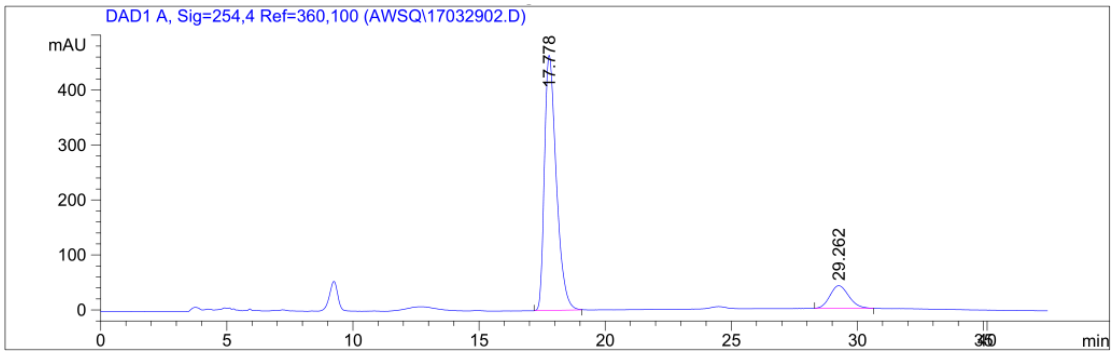


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	20.941	1.10567e4	297.01855	87.0504
2	35.340	1644.80225	24.91486	12.9496

HPLC Chromatographs of **5p**

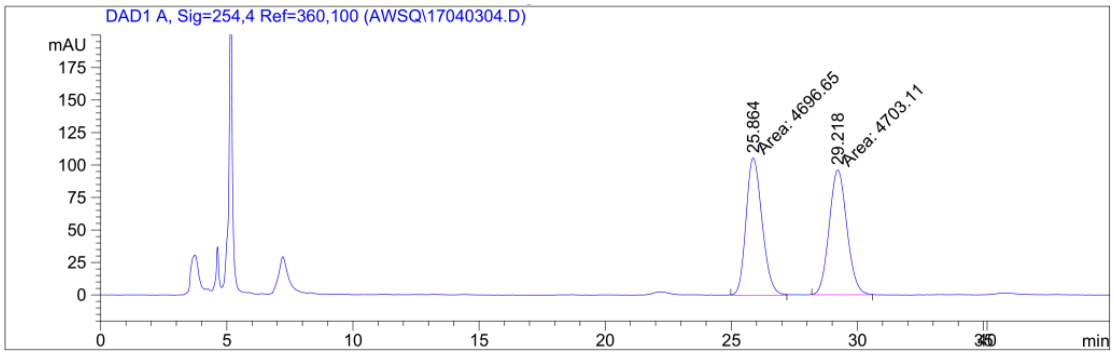


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	17.858	4509.09668	136.84662	49.9130
2	29.173	4524.80859	86.82851	50.0870

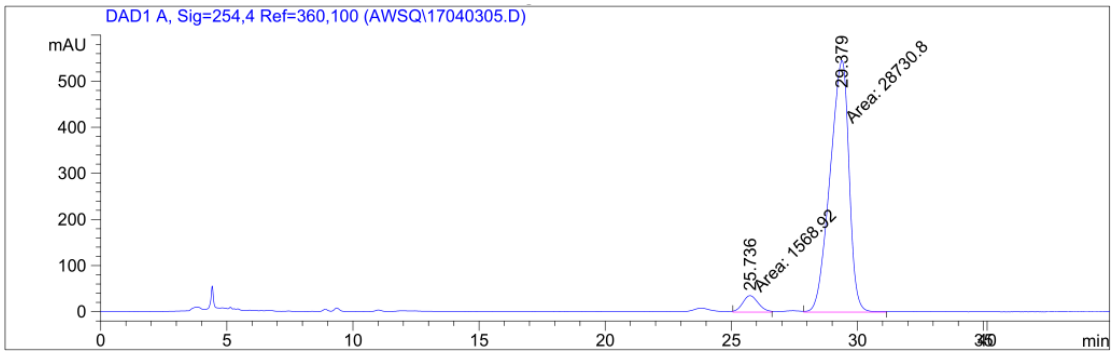


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	17.778	1.51651e4	464.53305	87.4328
2	29.262	2179.76050	41.45616	12.5672

HPLC Chromatographs of **5q**

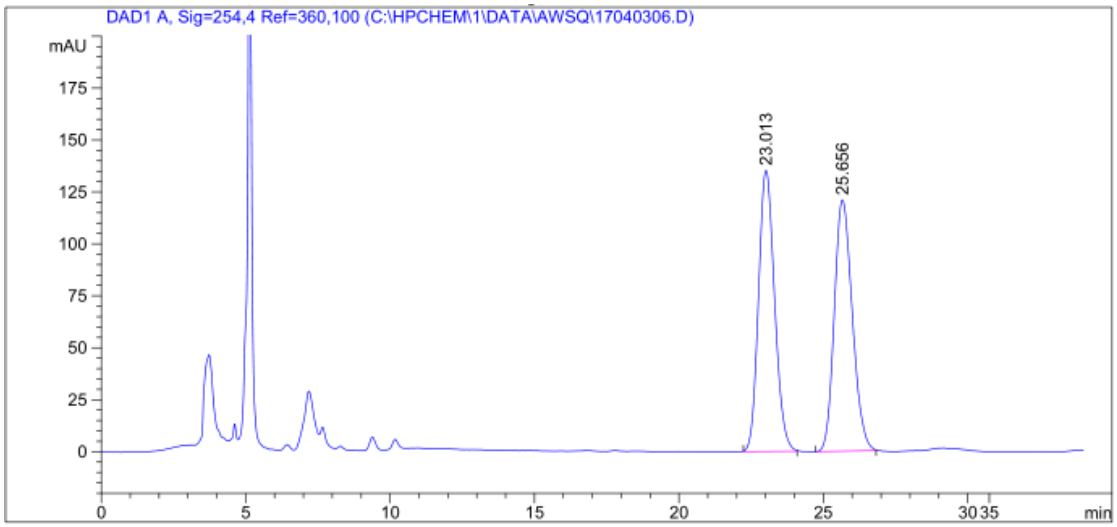


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	25.864	4696.64844	105.90557	49.9656
2	29.218	4703.11475	96.05776	50.0344

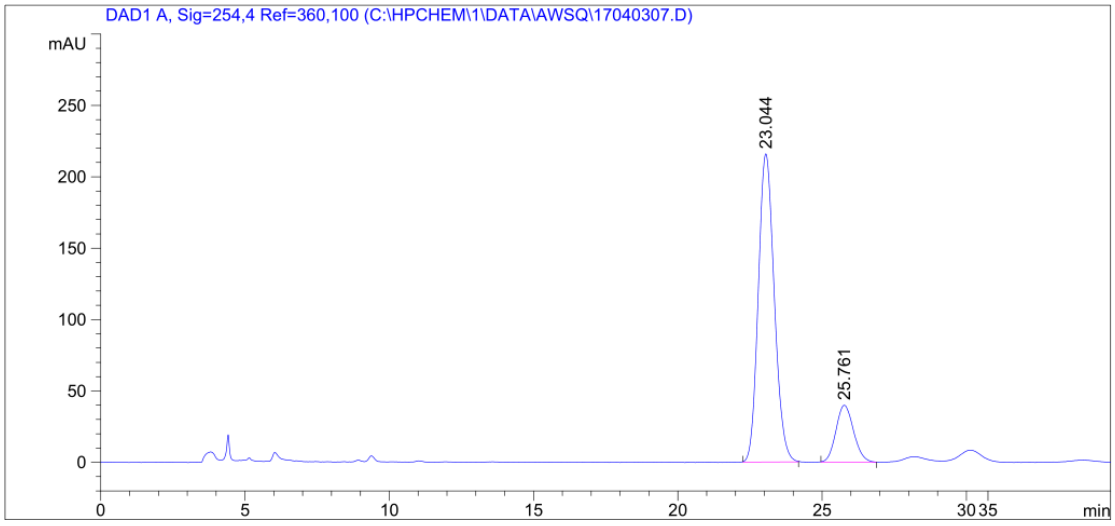


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	25.736	1568.91895	35.88278	5.1780
2	29.379	2.87308e4	546.03253	94.8220

HPLC Chromatographs of **5r**

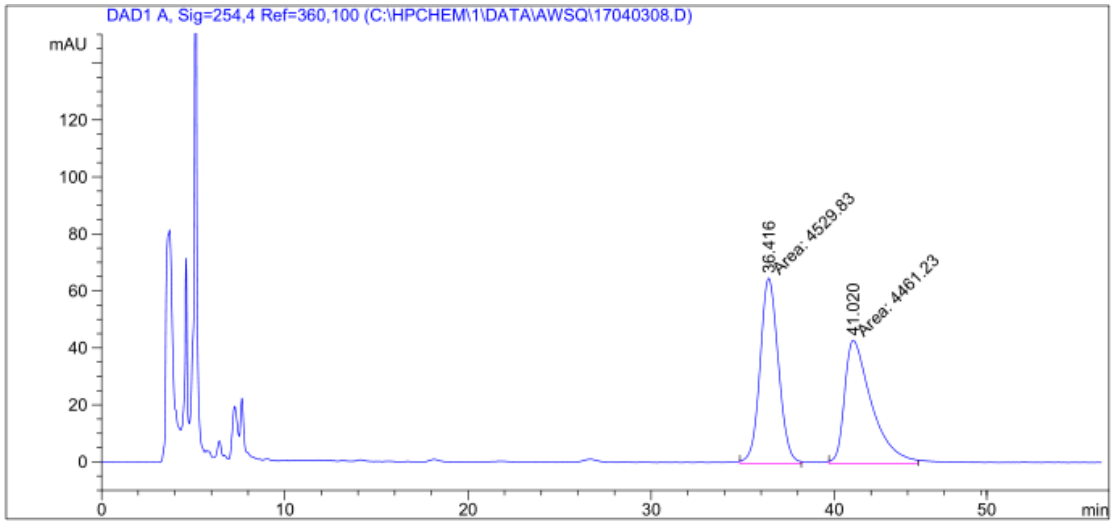


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	23.013	5231.34961	135.34503	49.9837
2	25.656	5234.76465	120.98967	50.0163

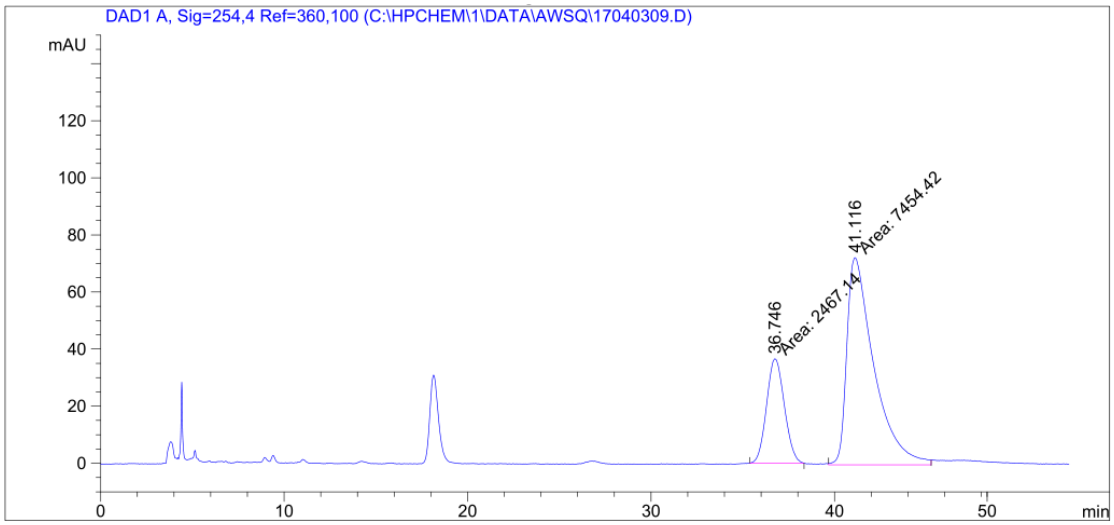


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	23.044	8311.97949	215.95285	83.0094
2	25.761	1701.32361	39.93383	16.9906

HPLC Chromatographs of **5s**

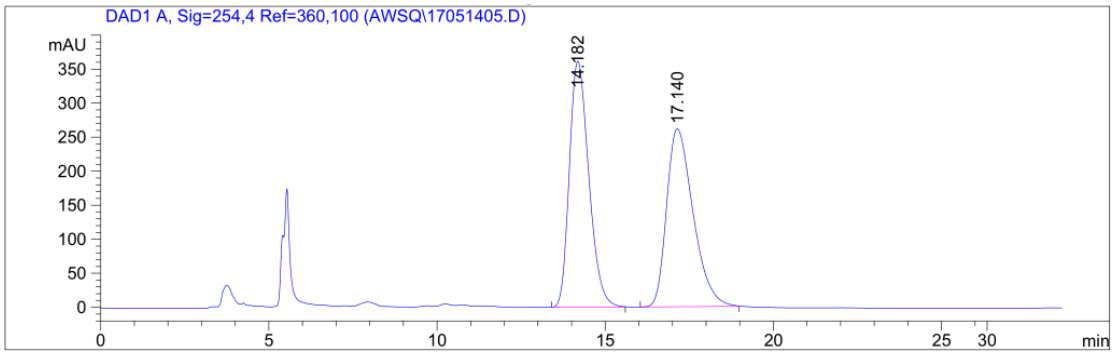


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	36.416	4529.82861	65.06881	50.3815
2	41.020	4461.23145	43.24934	49.6185

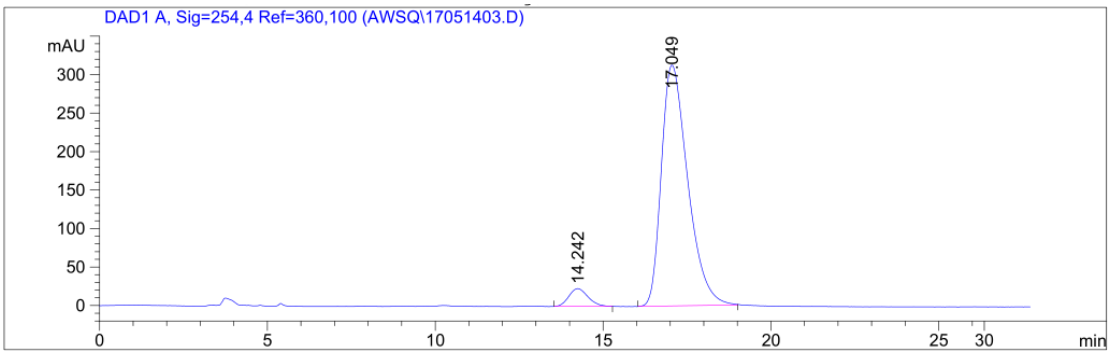


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	36.746	2467.13770	36.57509	24.8664
2	41.116	7454.41797	72.62057	75.1336

HPLC Chromatographs of **5t**

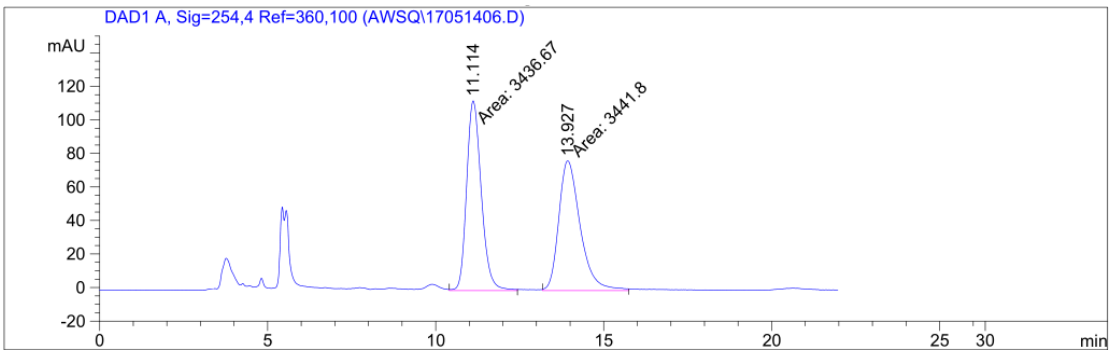


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	14.182	1.45244e4	361.83063	50.3047
2	17.140	1.43484e4	261.85654	49.6953

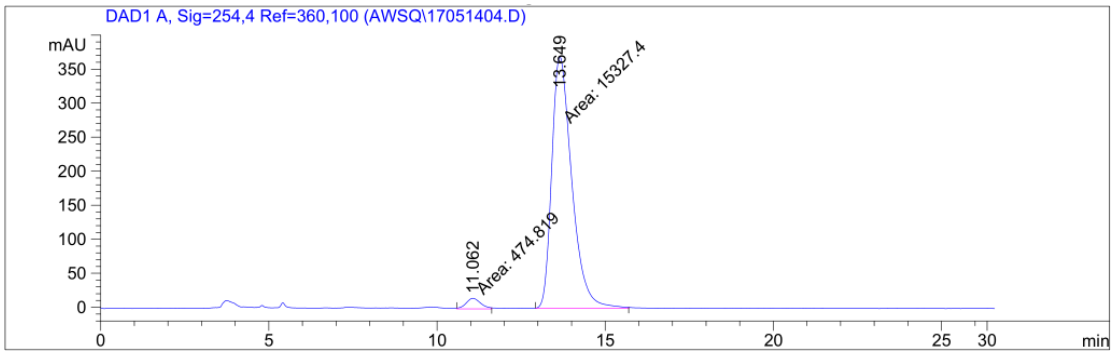


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	14.242	931.71954	23.25604	5.1631
2	17.049	1.71139e4	312.98340	94.8369

HPLC Chromatographs of **5u**

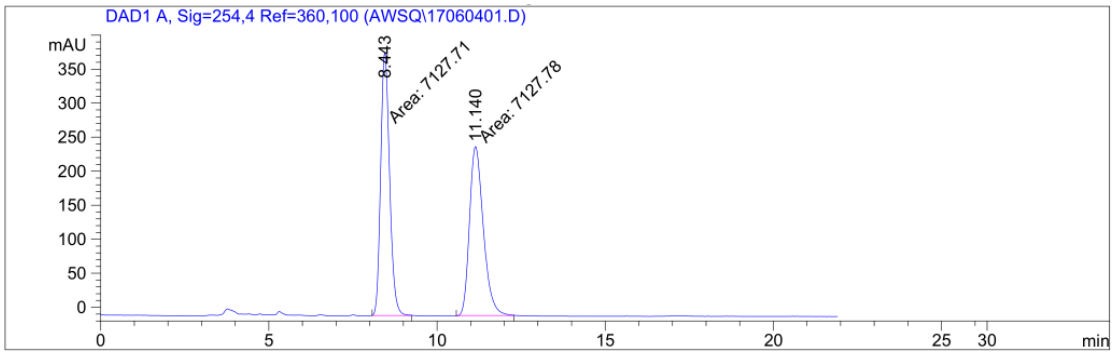


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	11.114	3436.66724	113.17353	49.9627
2	13.927	3441.80469	77.44581	50.0373

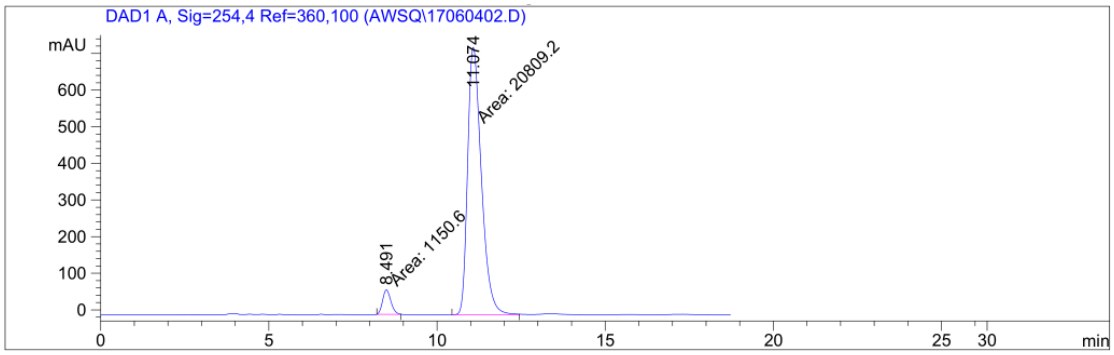


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	11.062	474.81885	15.65175	3.0048
2	13.649	1.53274e4	369.97885	96.9952

HPLC Chromatographs of **8**

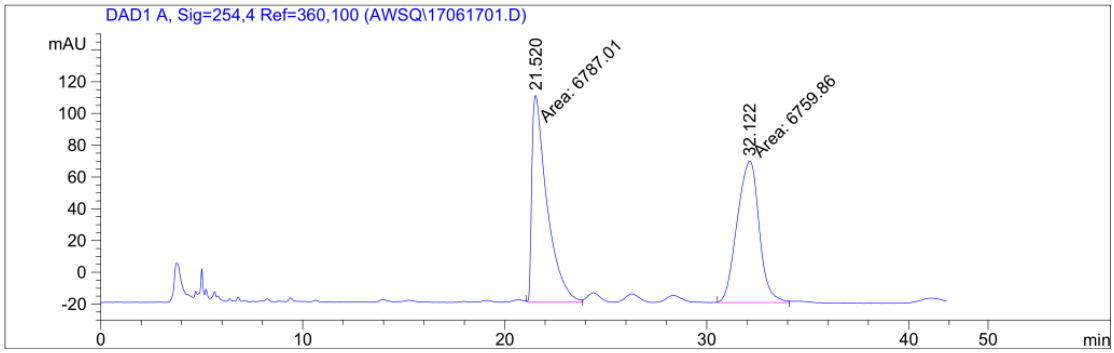


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	8.443	7127.71484	386.33185	49.9998
2	11.140	7127.77979	248.54724	50.0002

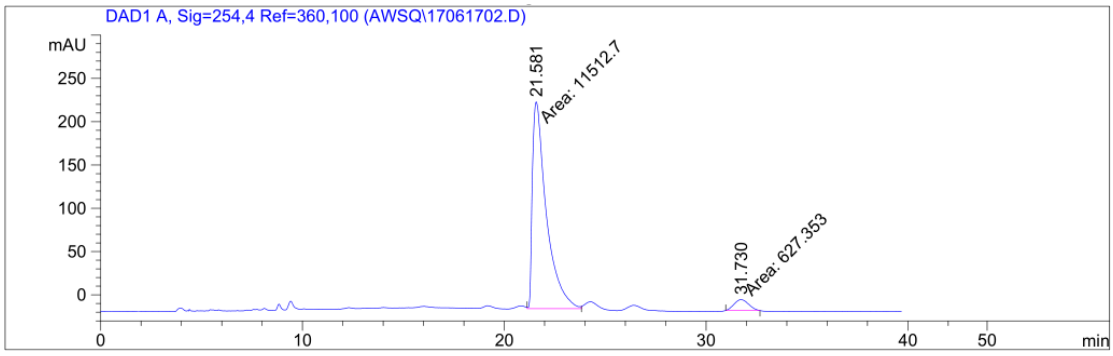


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	8.491	1150.59546	67.11510	5.2396
2	11.074	2.08092e4	730.66321	94.7604

HPLC Chromatographs of **9**

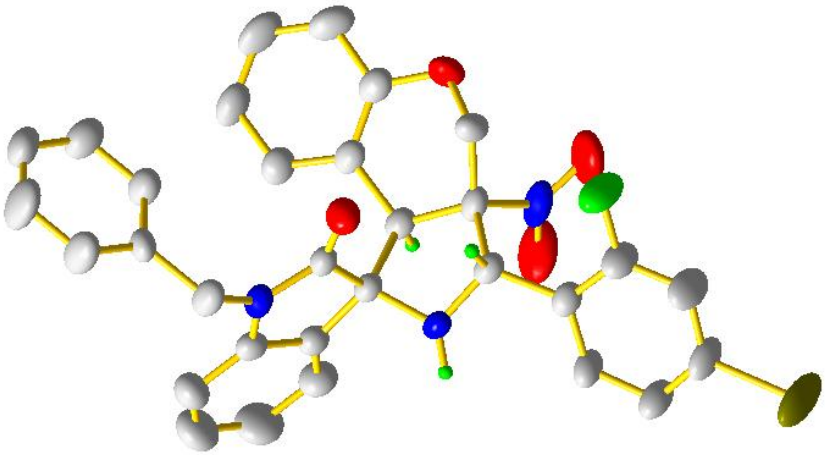


Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	21.520	6787.01416	130.24065	50.1002
2	32.122	6759.85693	89.05852	49.8998



Peak	RT (min)	Area (mAU*s)	Height (mAU)	Area %
1	21.581	1.15127e4	238.82961	94.8324
2	31.730	627.35266	12.59681	5.1676

5. X-ray crystal structure of 5k.



X-ray crystal structure of **5k**.