

Supporting Information

Organocatalyzed Enantioselective Mannich Reaction of Pyrazoleamides with Isatin-Derived Ketimines

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1. X-ray Structure and crystal data for compound **3da**

The crystal data of **3da** have been deposited in CCDC with number 963038.

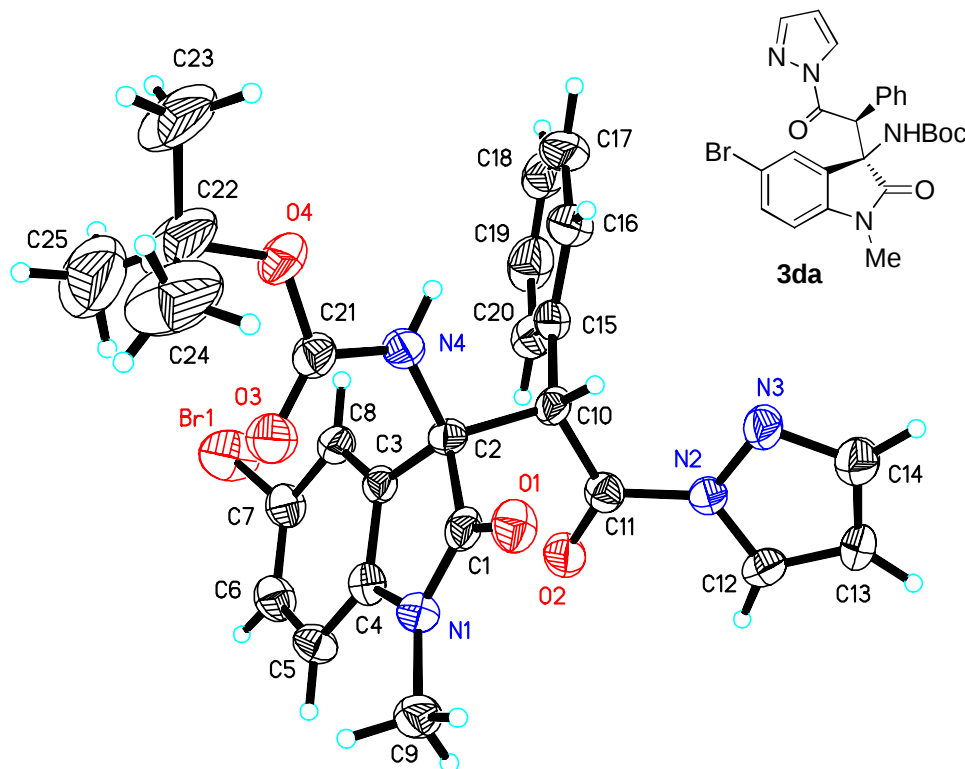
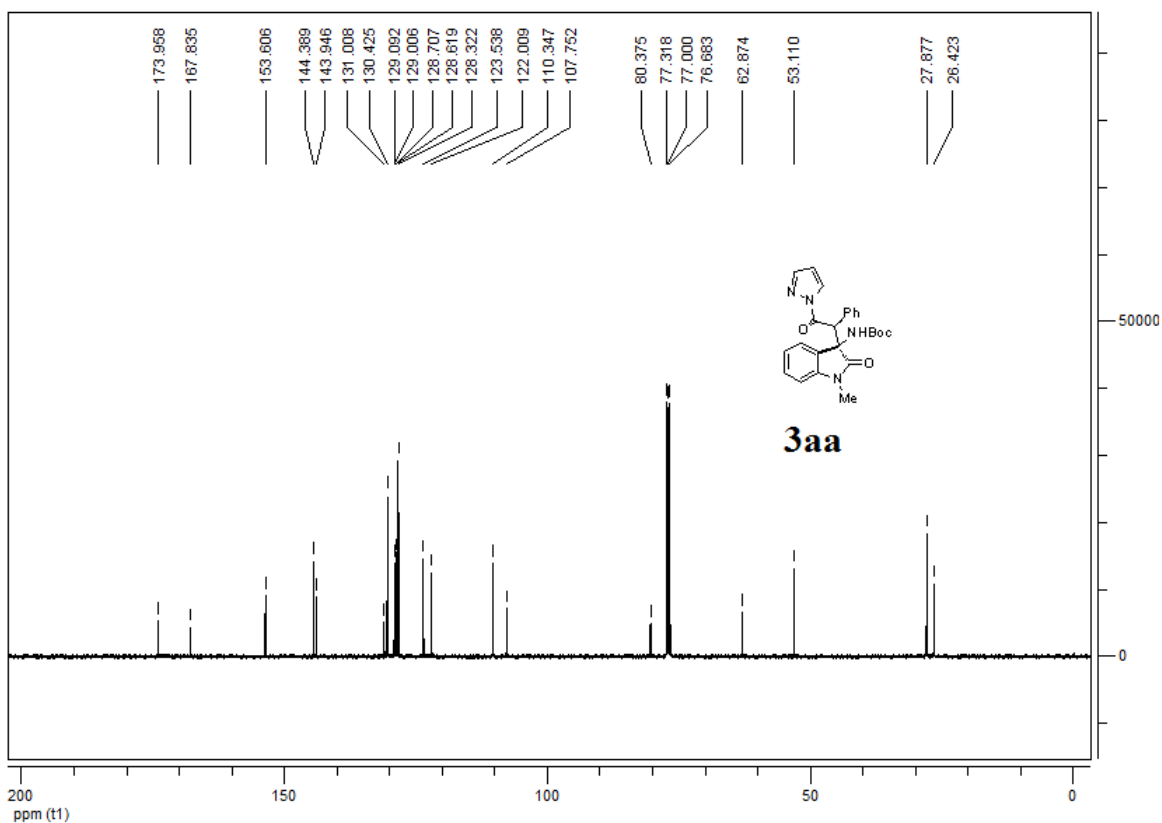
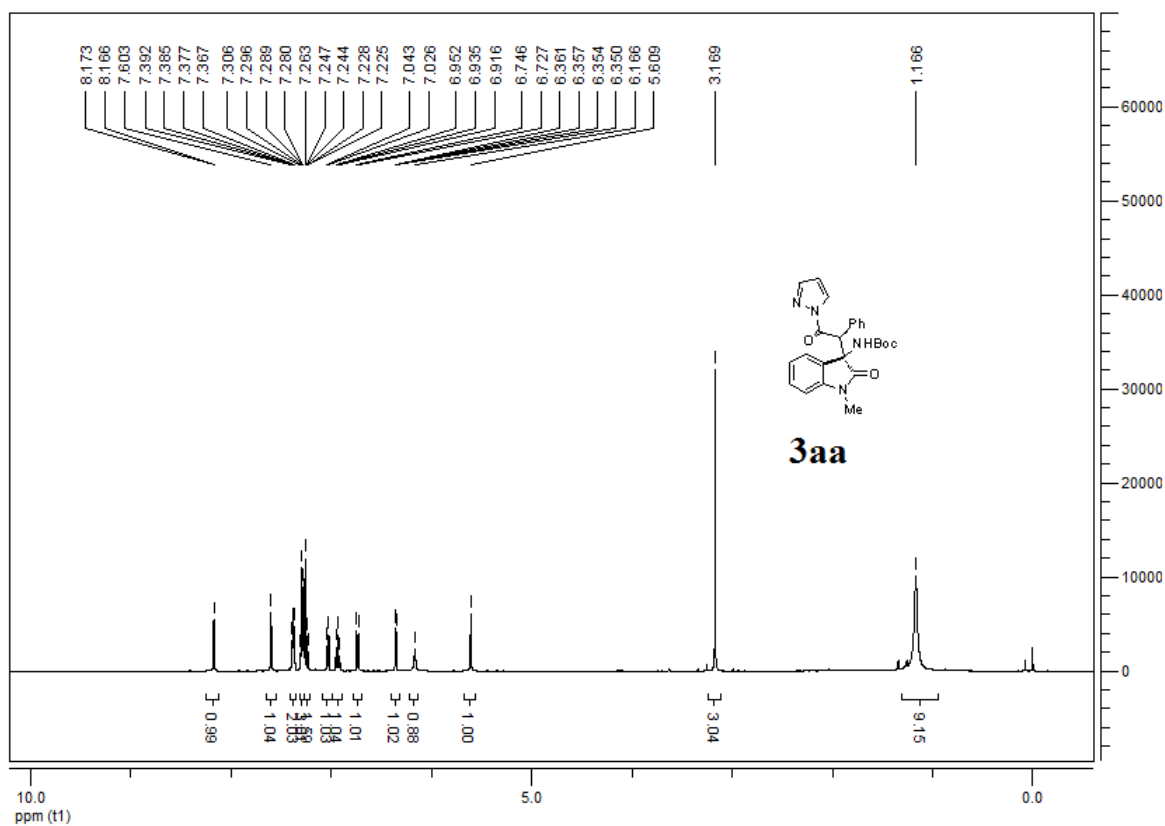


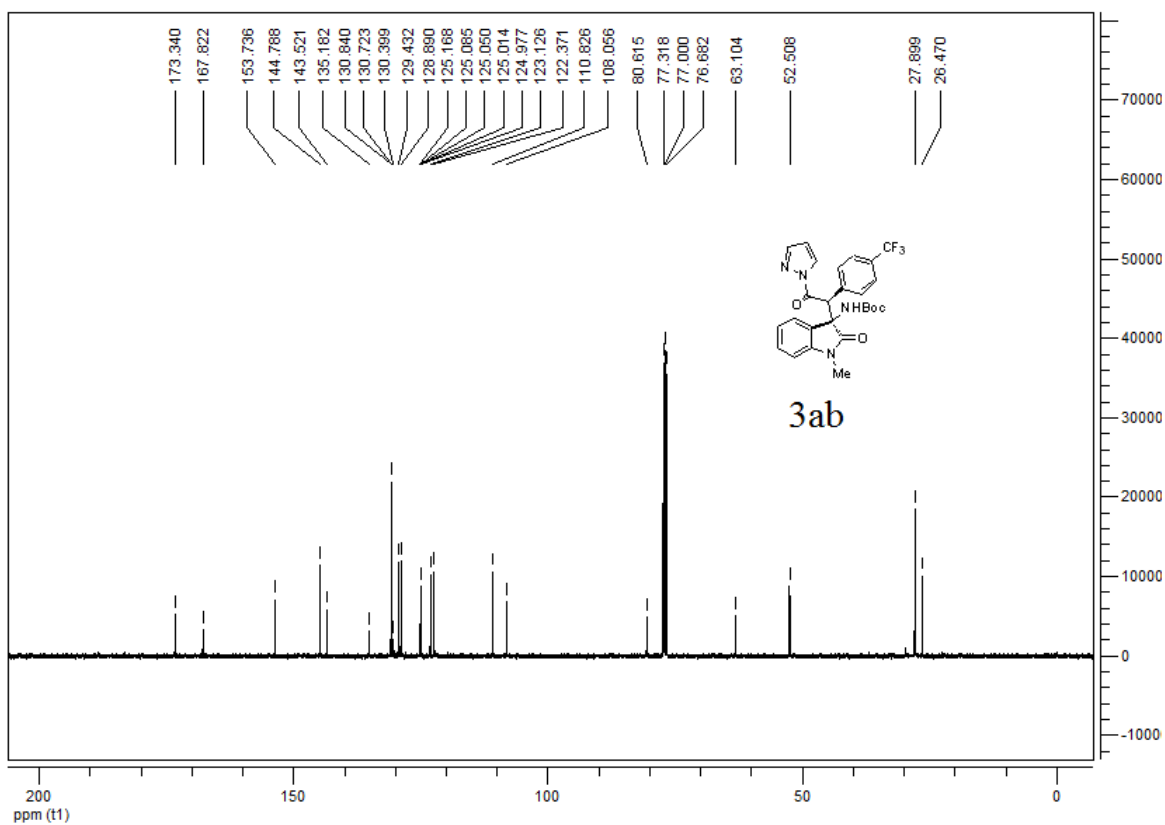
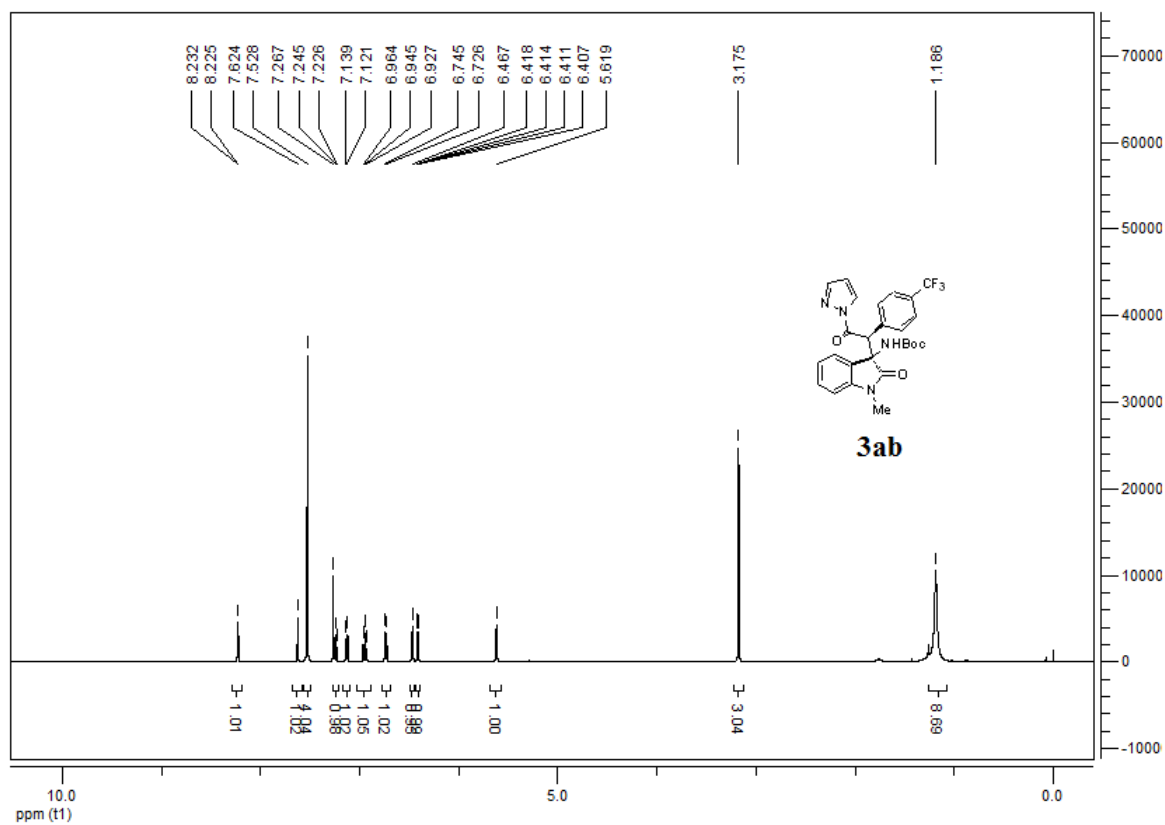
Table 1. Crystal data and structure refinement for **3da**.

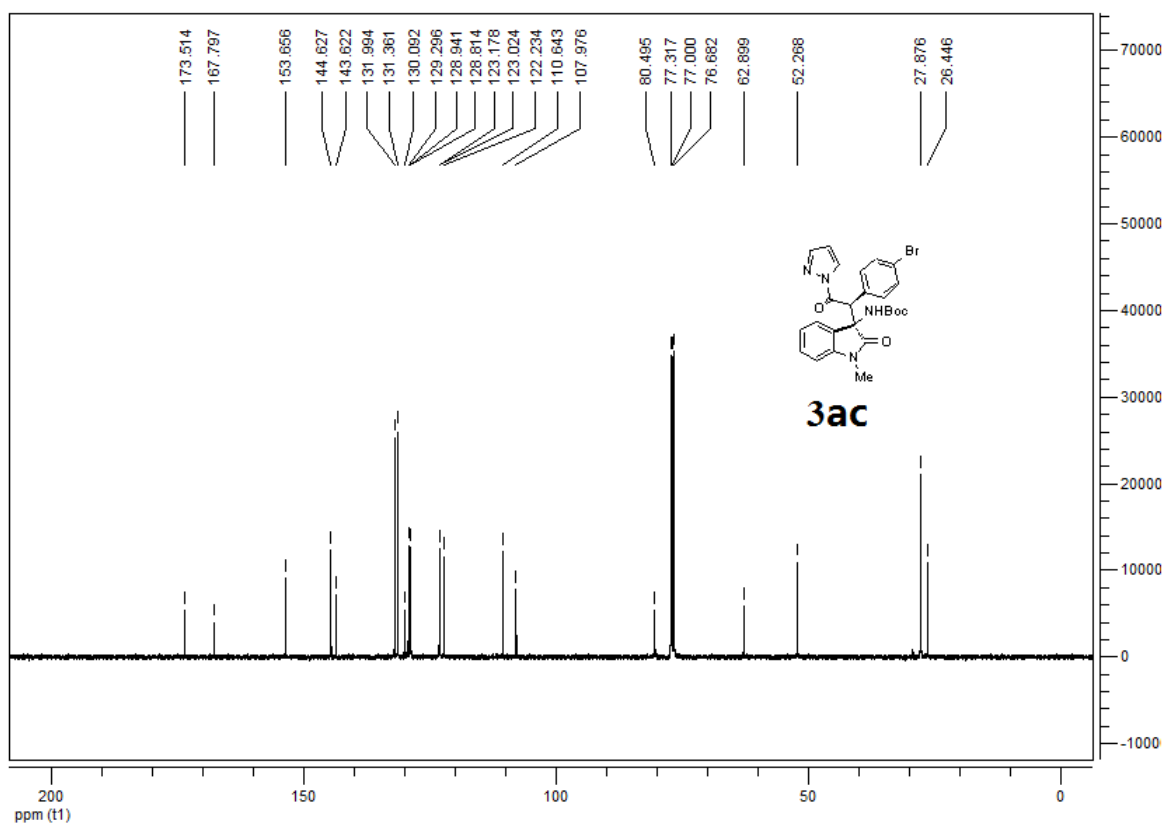
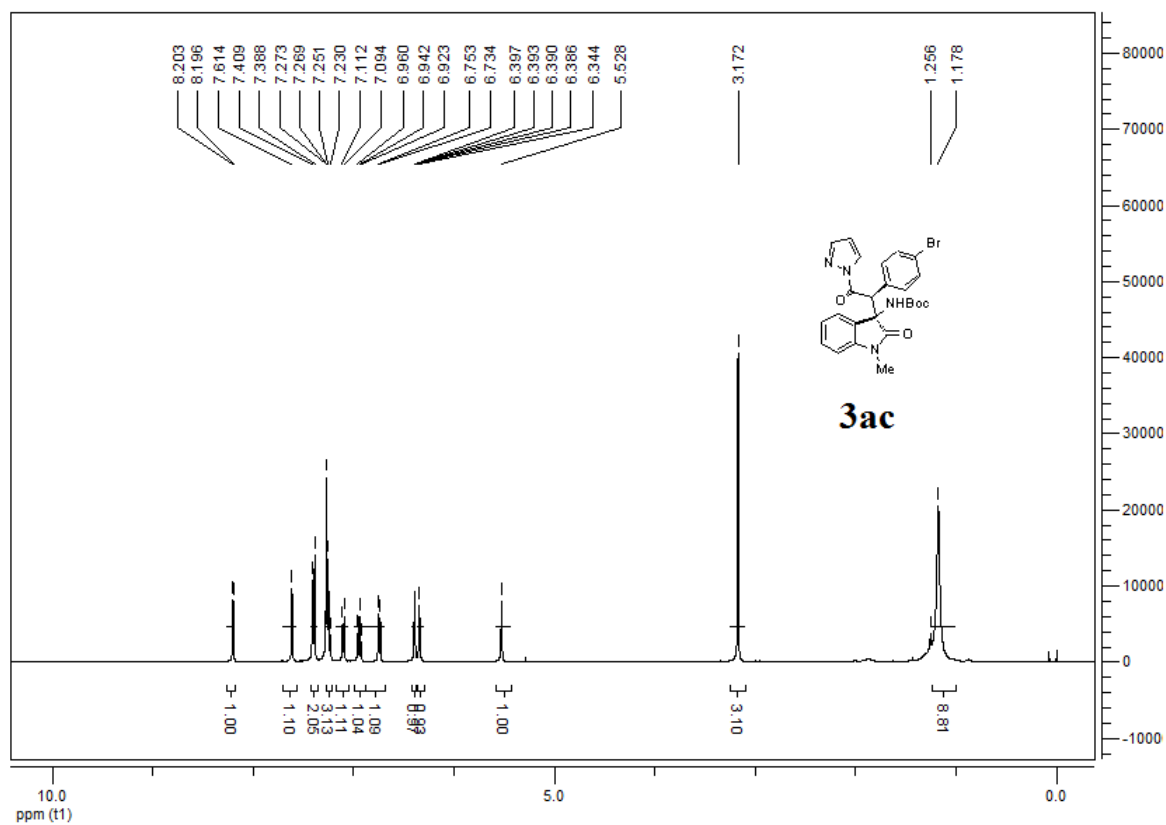
Identification code	3da
Empirical formula	C ₂₅ H ₂₅ Br N ₄ O ₄
Formula weight	525.40
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 41.527(6) Å alpha = 90° b = 11.0922(17) Å beta = 123.323(3)°.

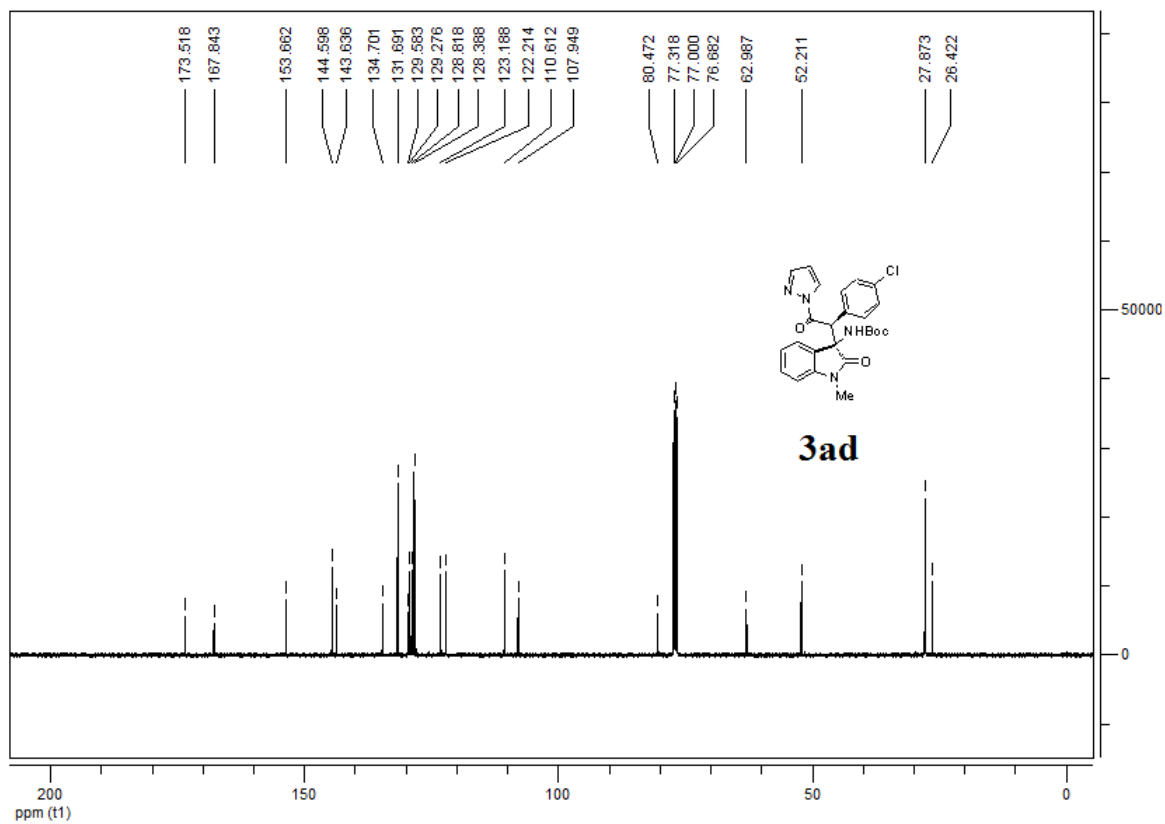
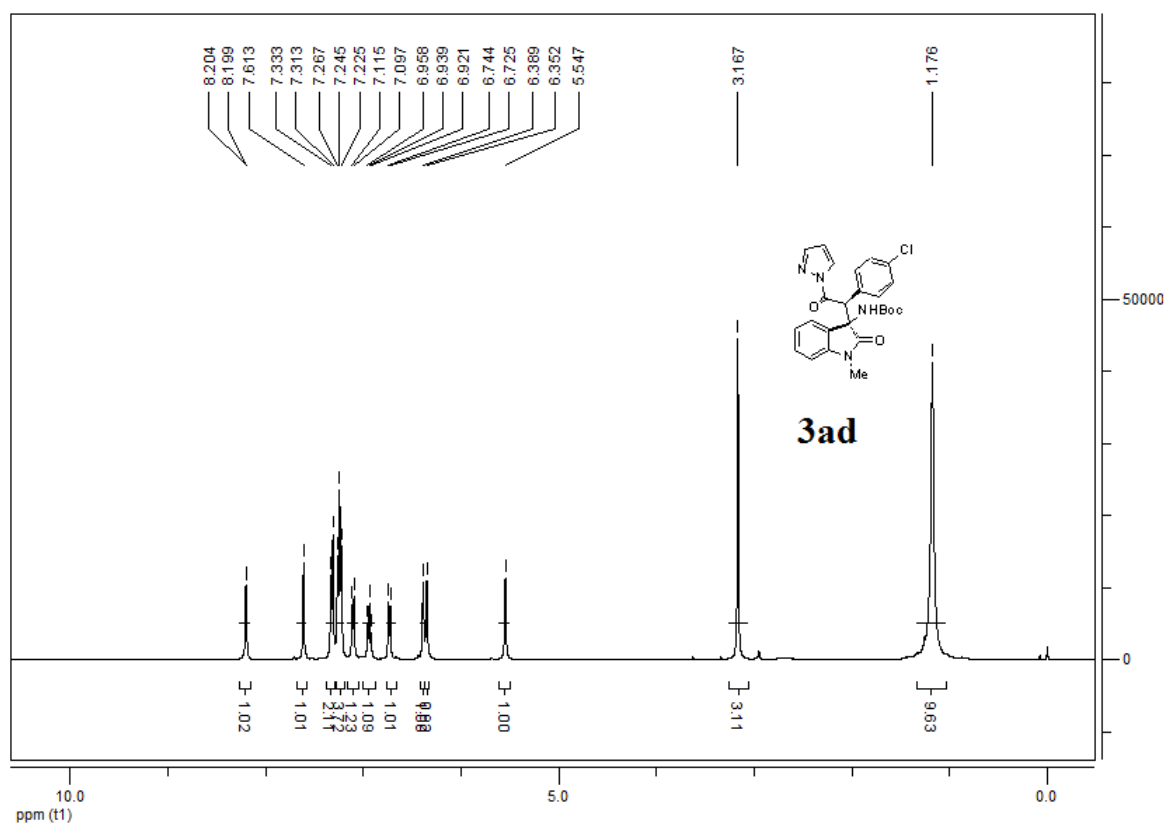
	$c = 26.113(4) \text{ \AA}$ $\gamma = 90^\circ$.
Volume	$10051(2) \text{ \AA}^3$
Z, Calculated density	16, 1.389 Mg/m^3
Absorption coefficient	1.673 mm^{-1}
F(000)	4320
Crystal size	$0.212 \times 0.156 \times 0.121 \text{ mm}^3$
Theta range for data collection	1.86 to 25.50° .
Limiting indices	$-32 \leq h \leq 50$, $-13 \leq k \leq 13$, $-31 \leq l \leq 31$
Reflections collected / unique	29608 / 18522 [$R(\text{int}) = 0.0466$]
Completeness to $\theta = 25.50$	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.0923
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18522 / 181 / 1241
Goodness-of-fit on F^2	0.969
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0568$, $\omega R2 = 0.1117$
R indices (all data)	$R1 = 0.1365$, $\omega R2 = 0.1387$
Absolute structure parameter	0.001(7)
Largest diff. peak and hole	0.487 and $-0.364 \text{ e.\AA}^{-3}$

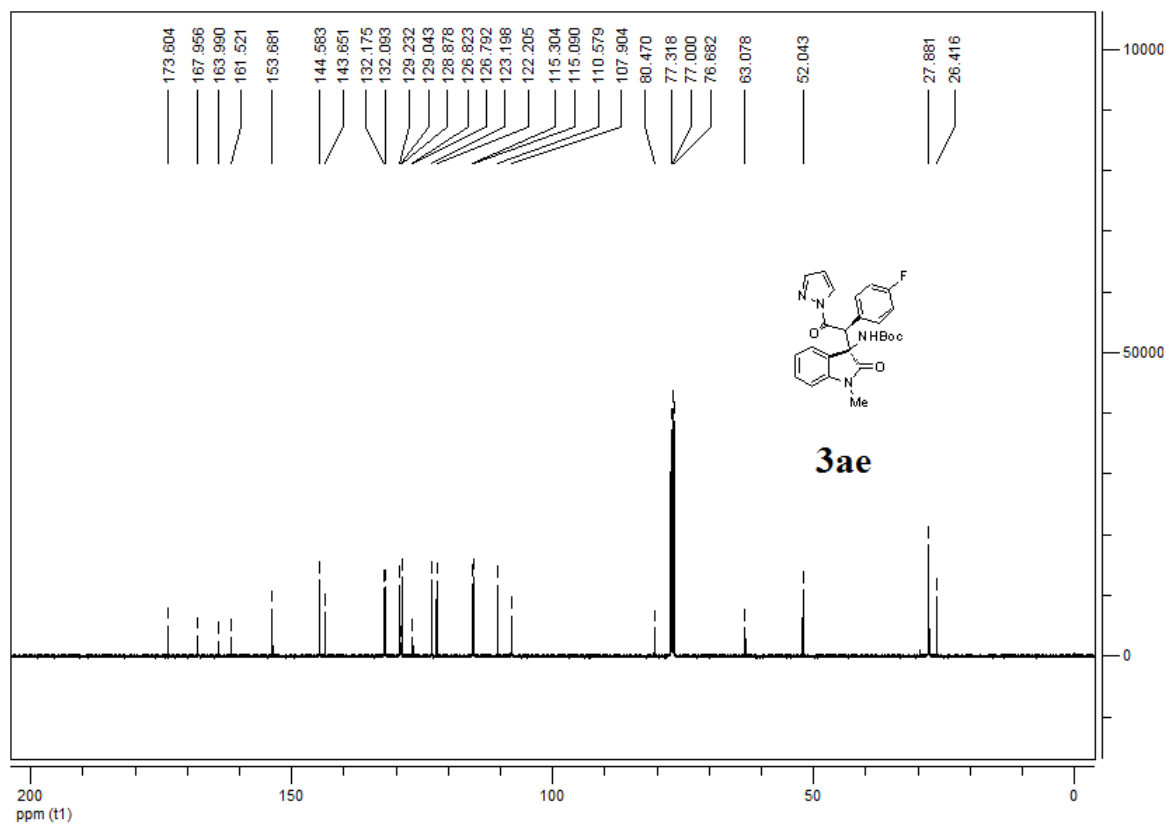
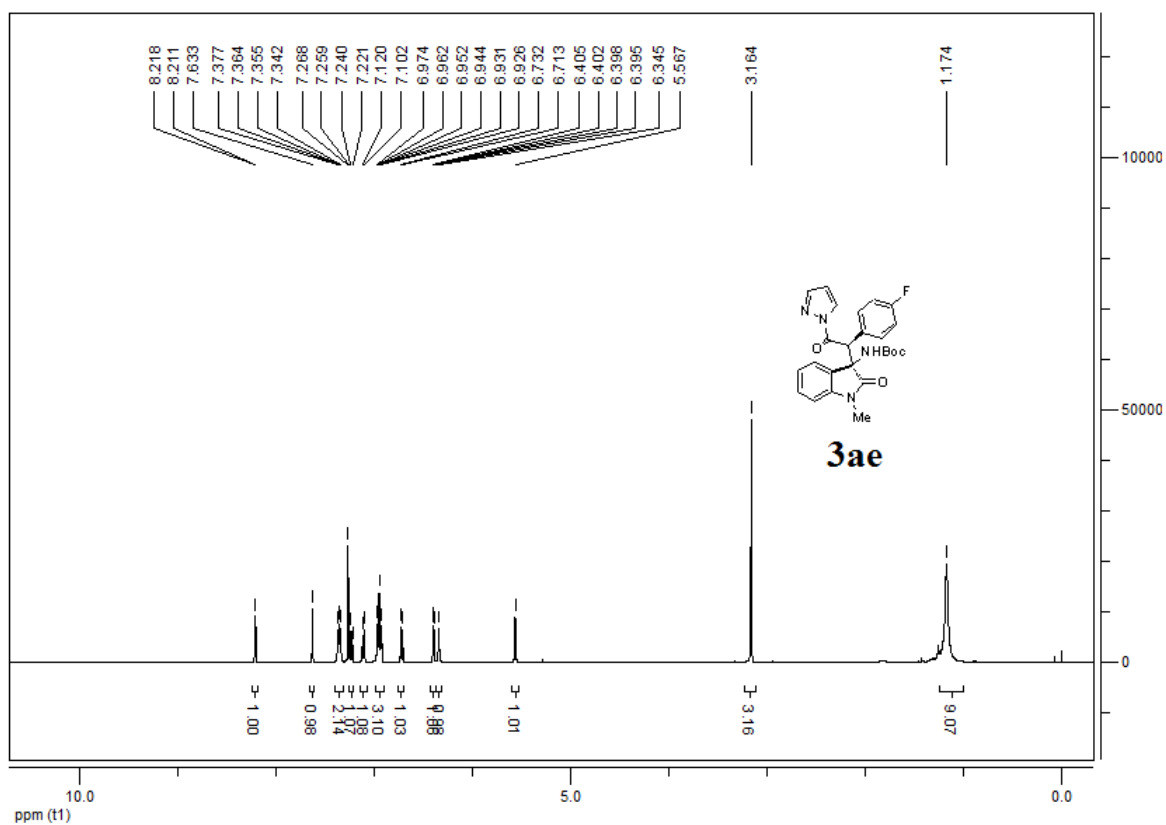
2. NMR Spectra of the Mannich Reaction Products

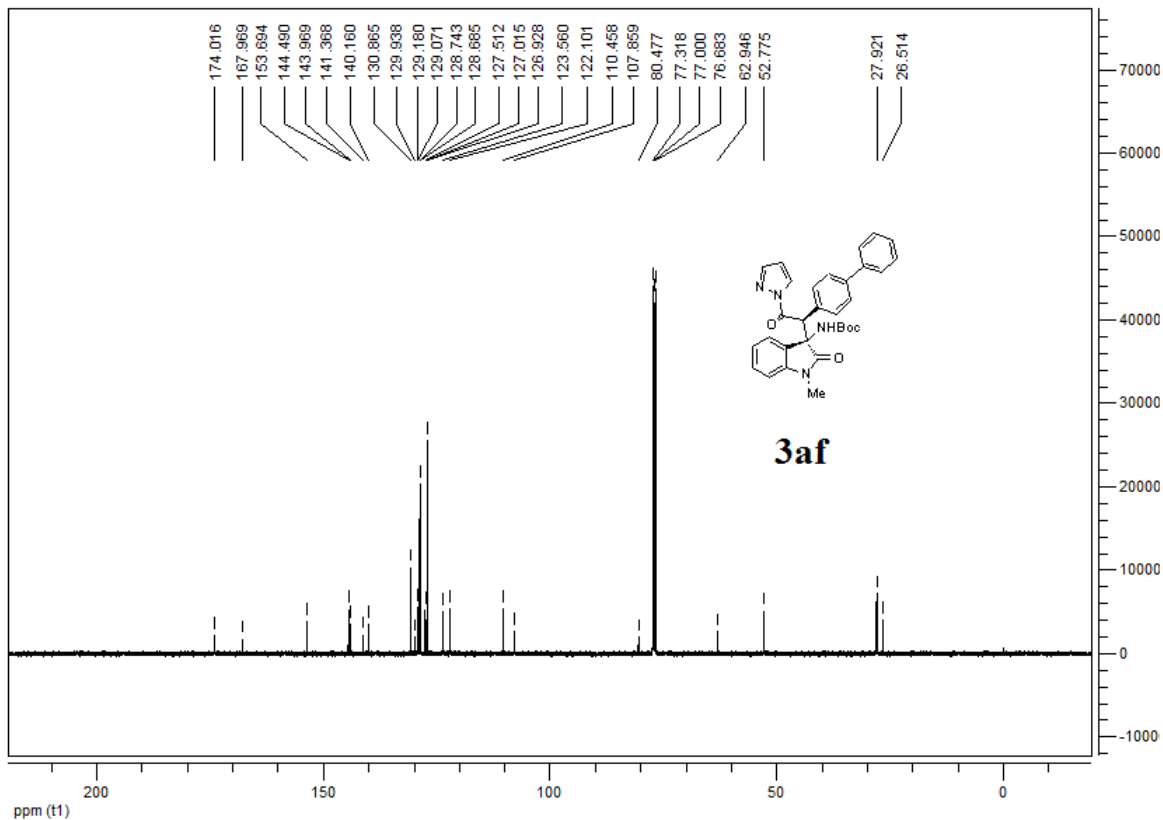
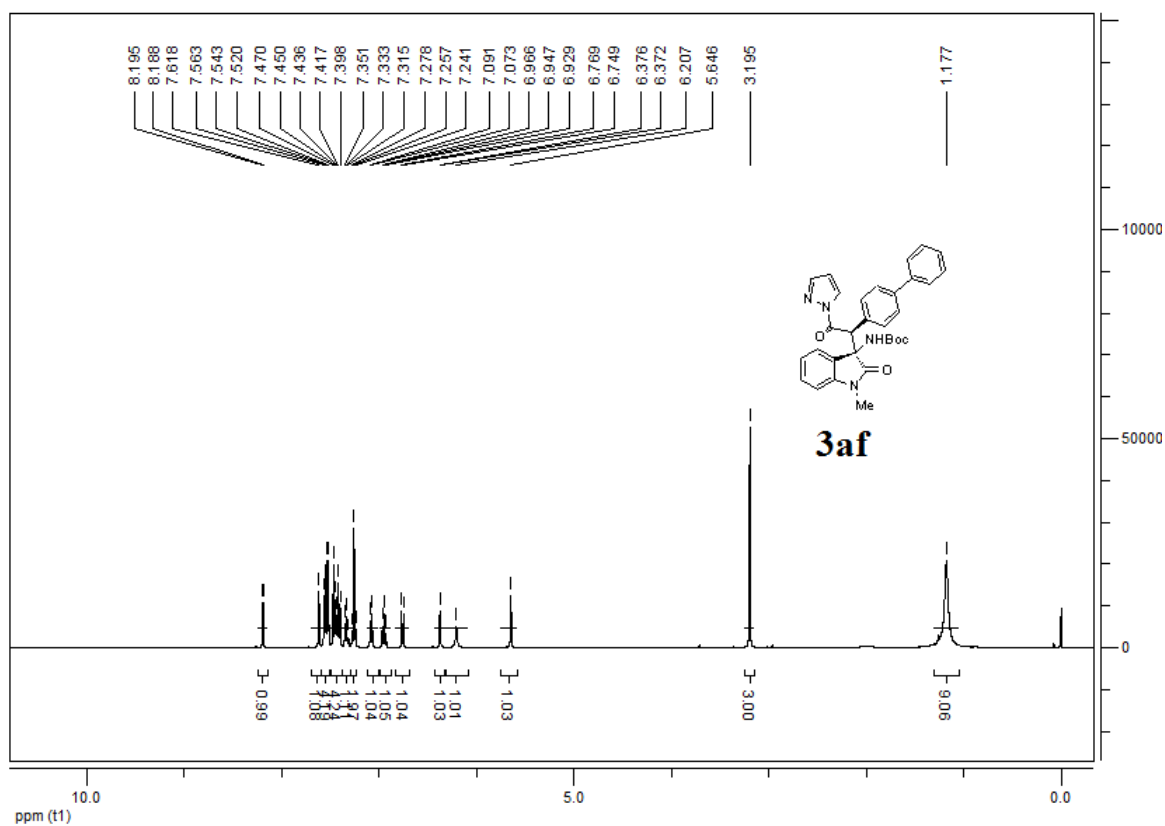


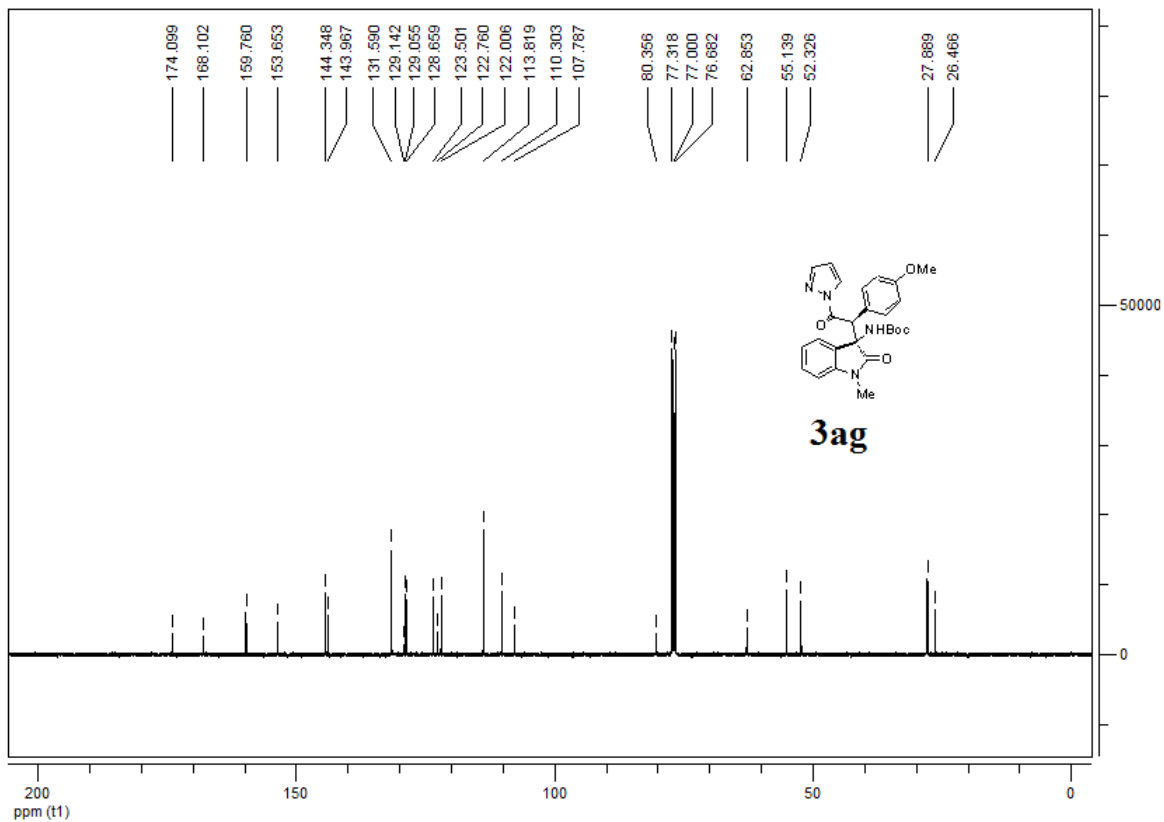
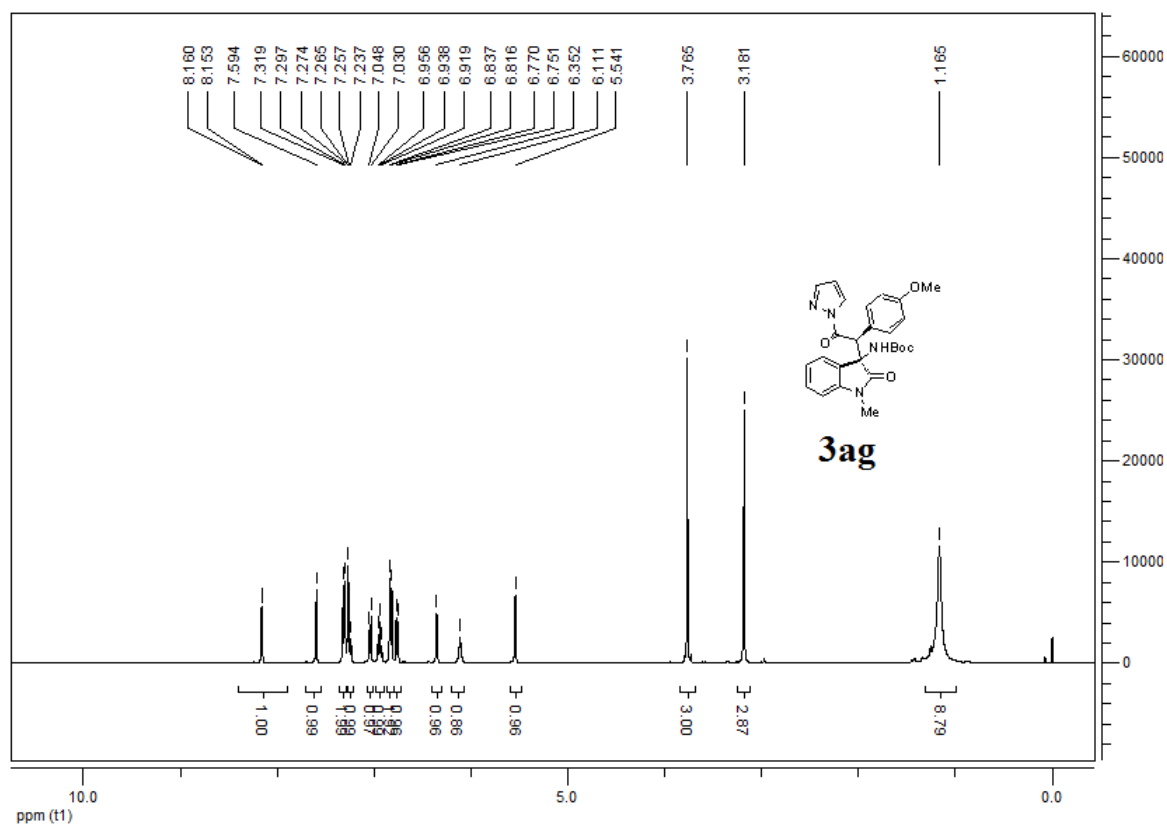


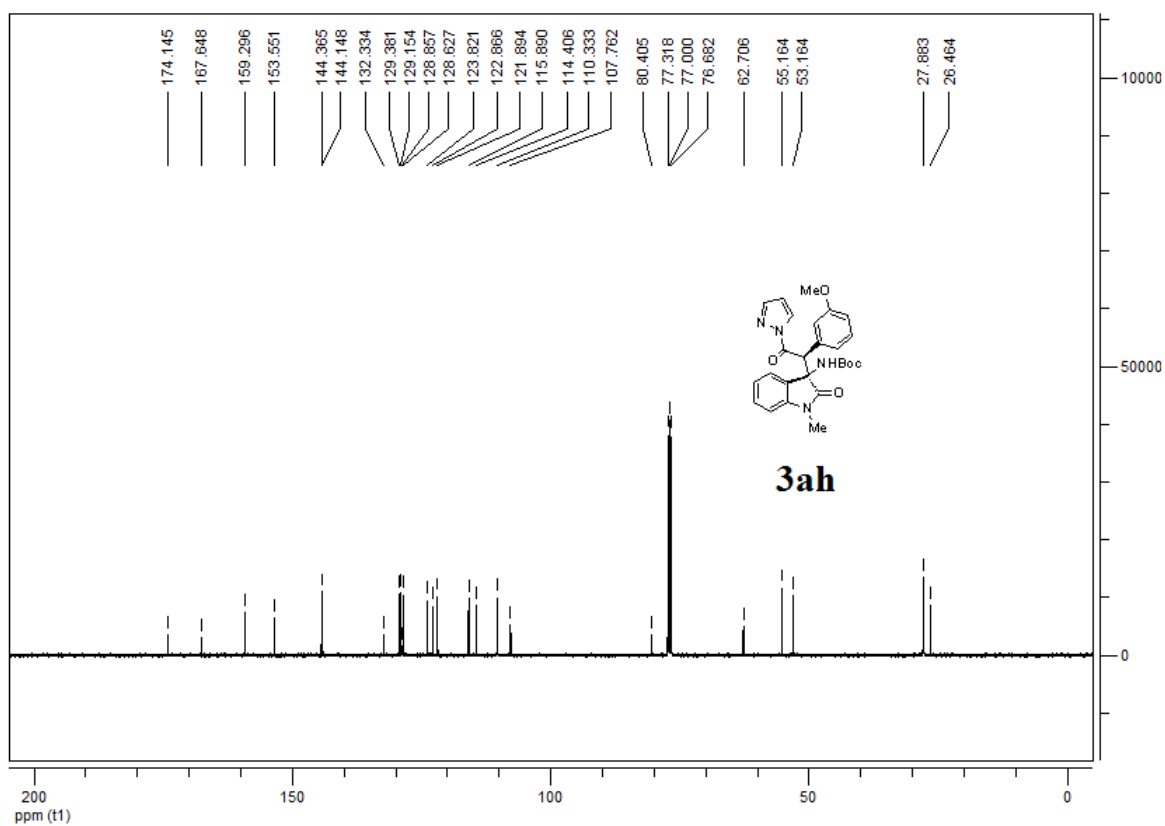
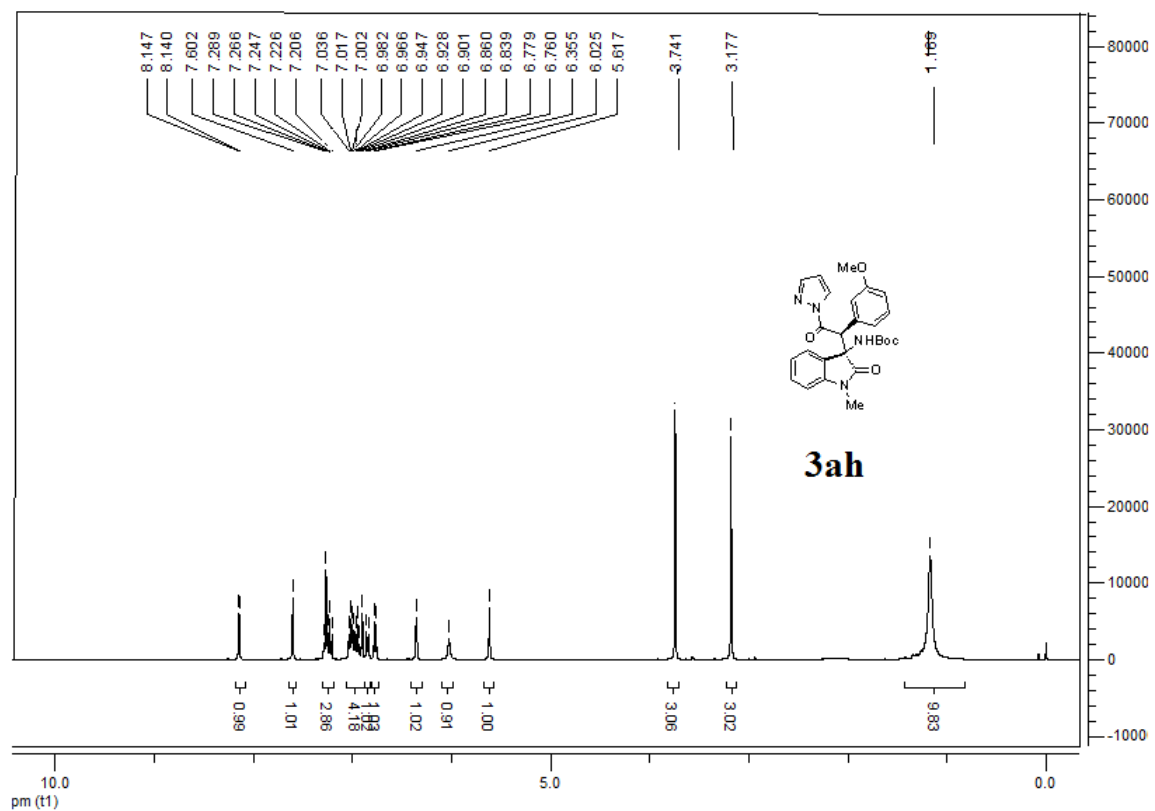


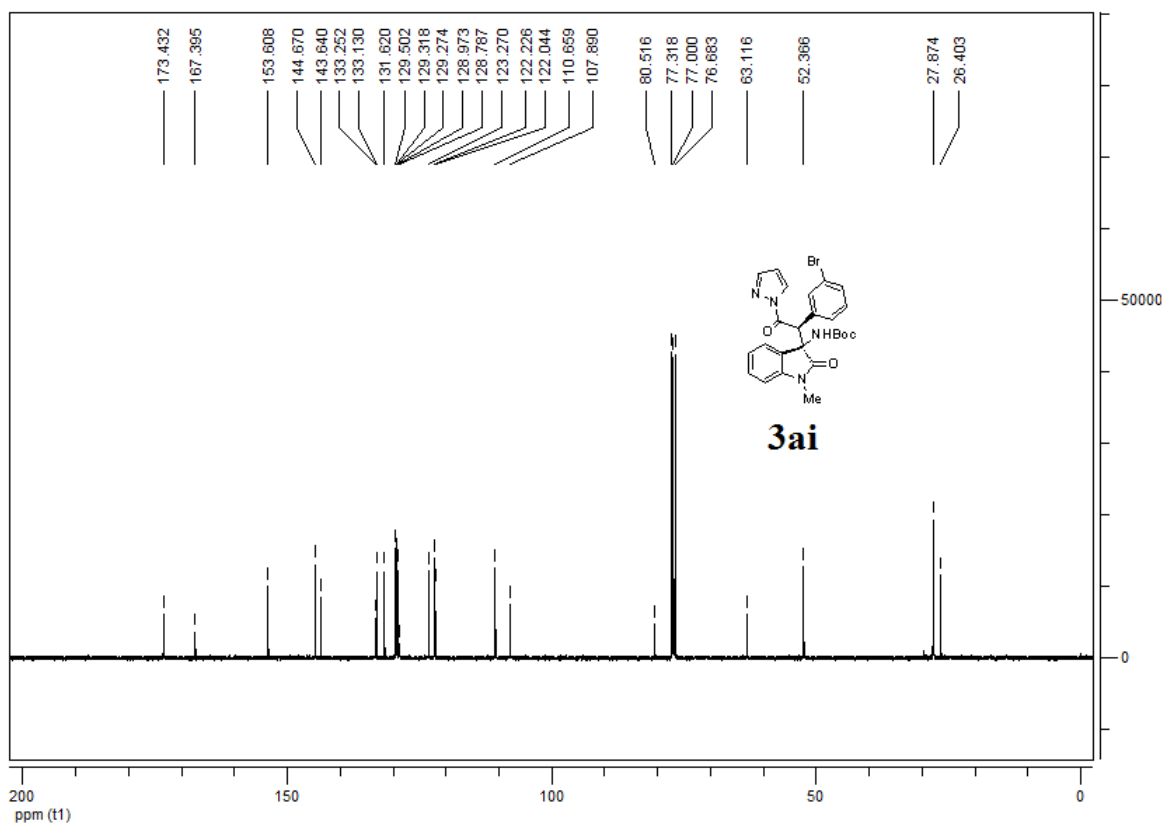
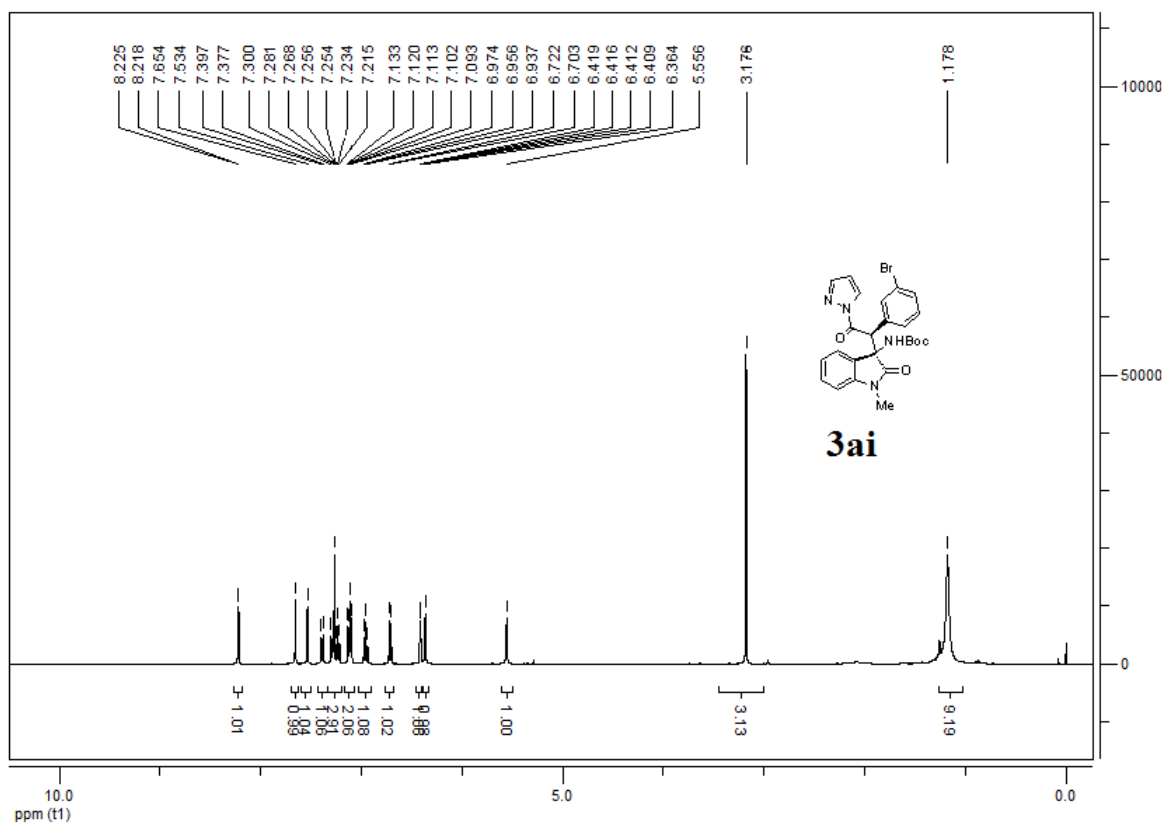


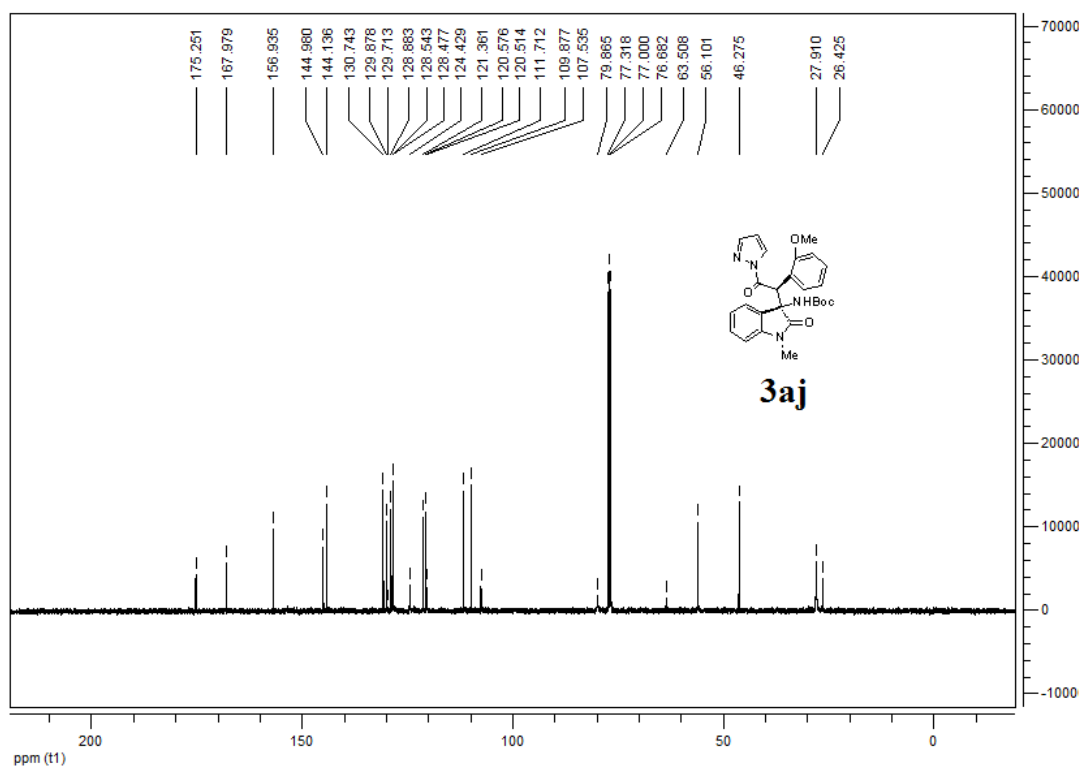
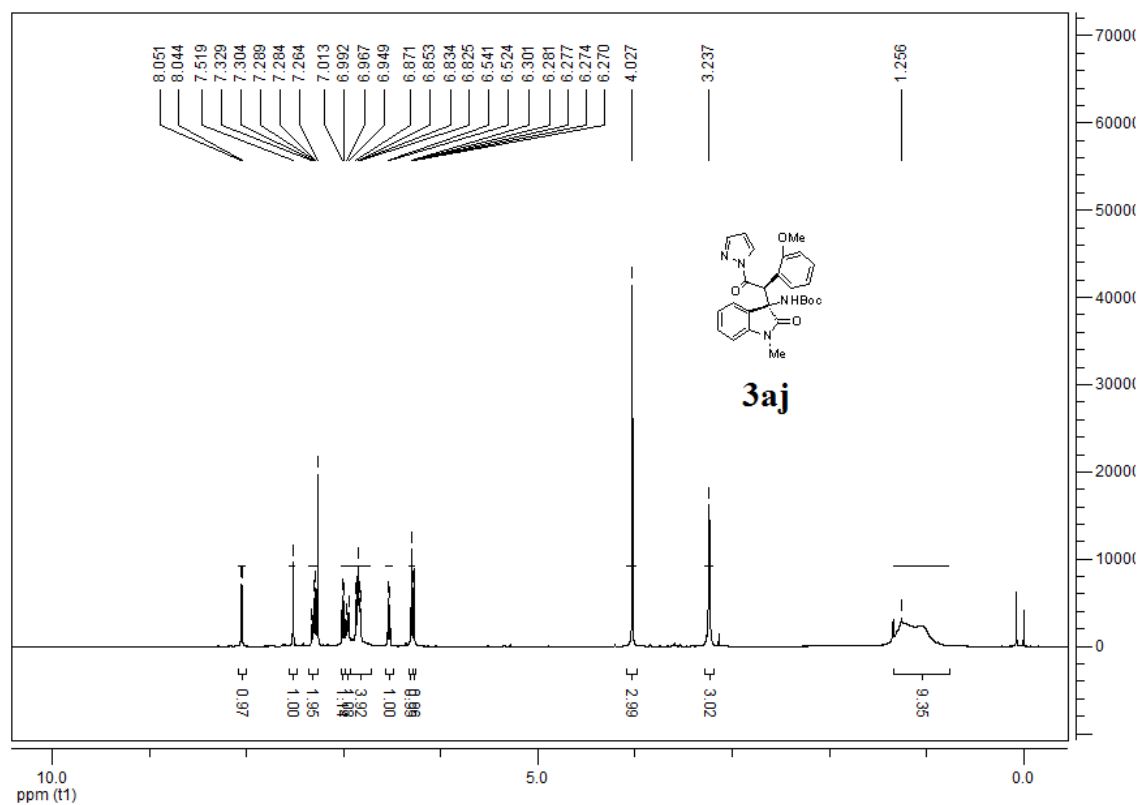


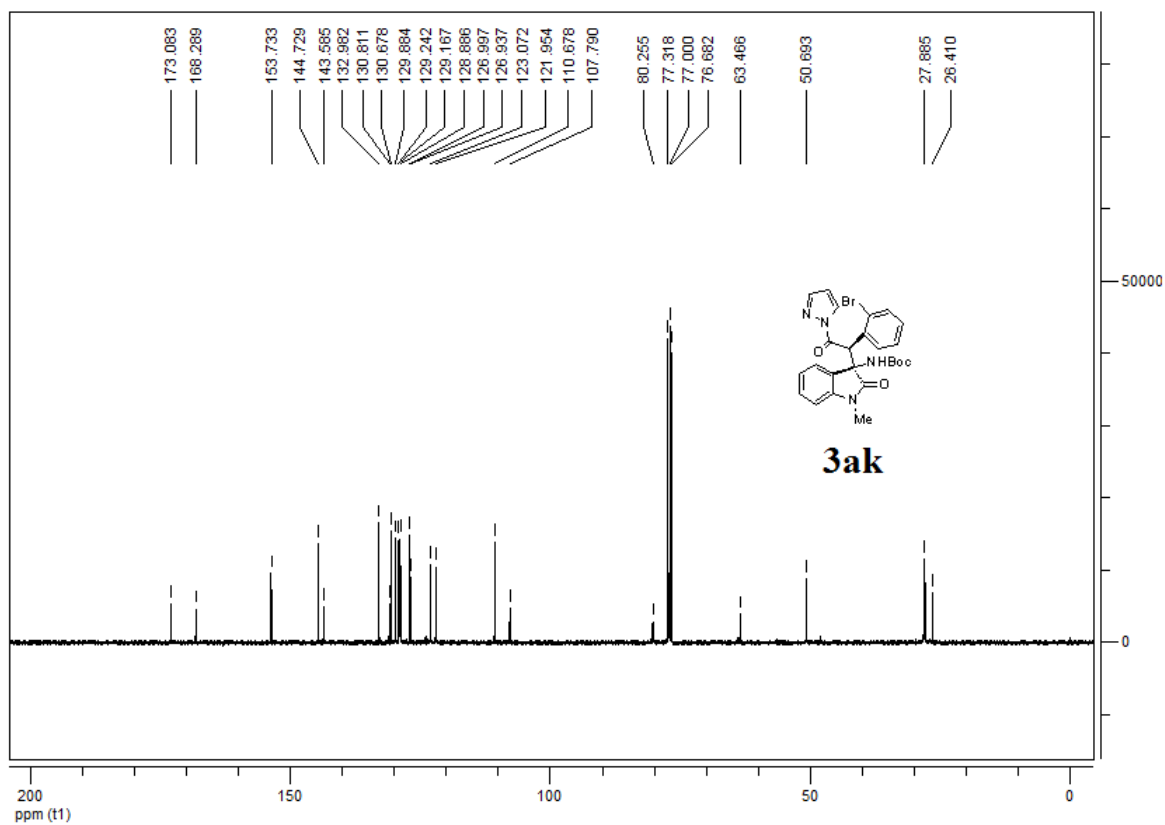
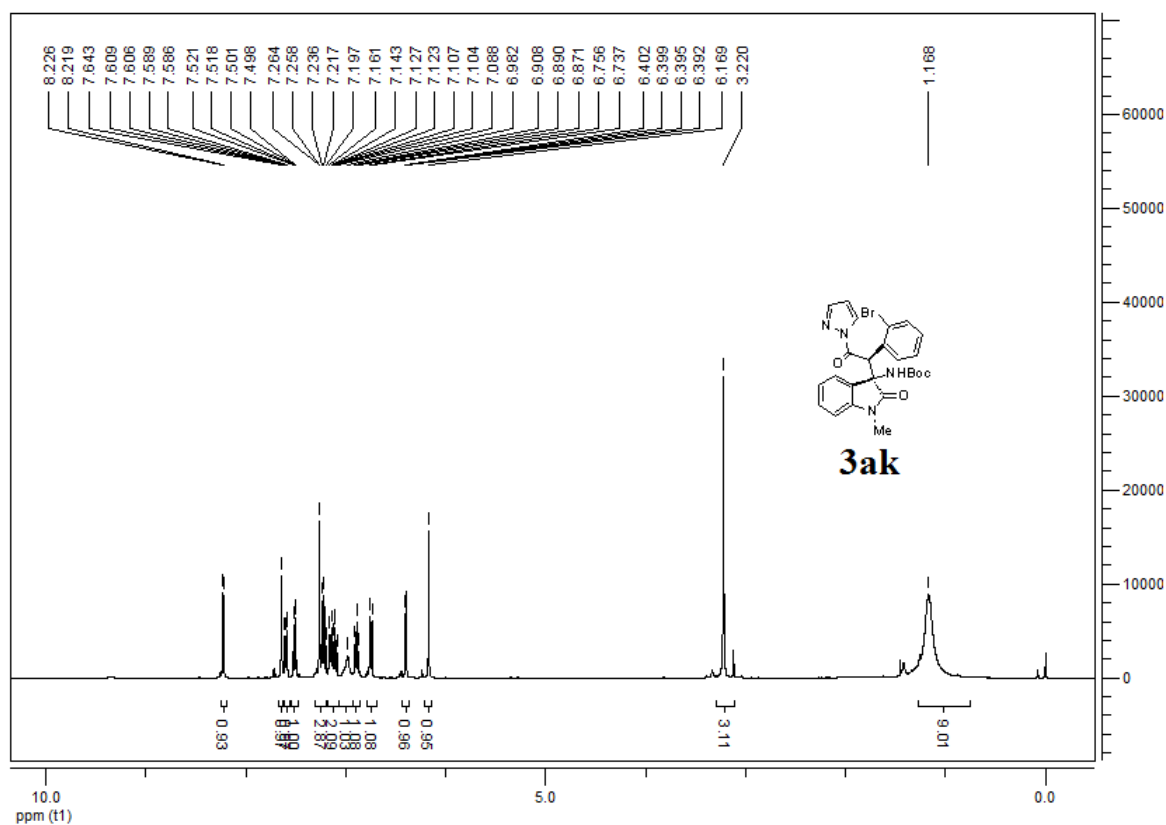


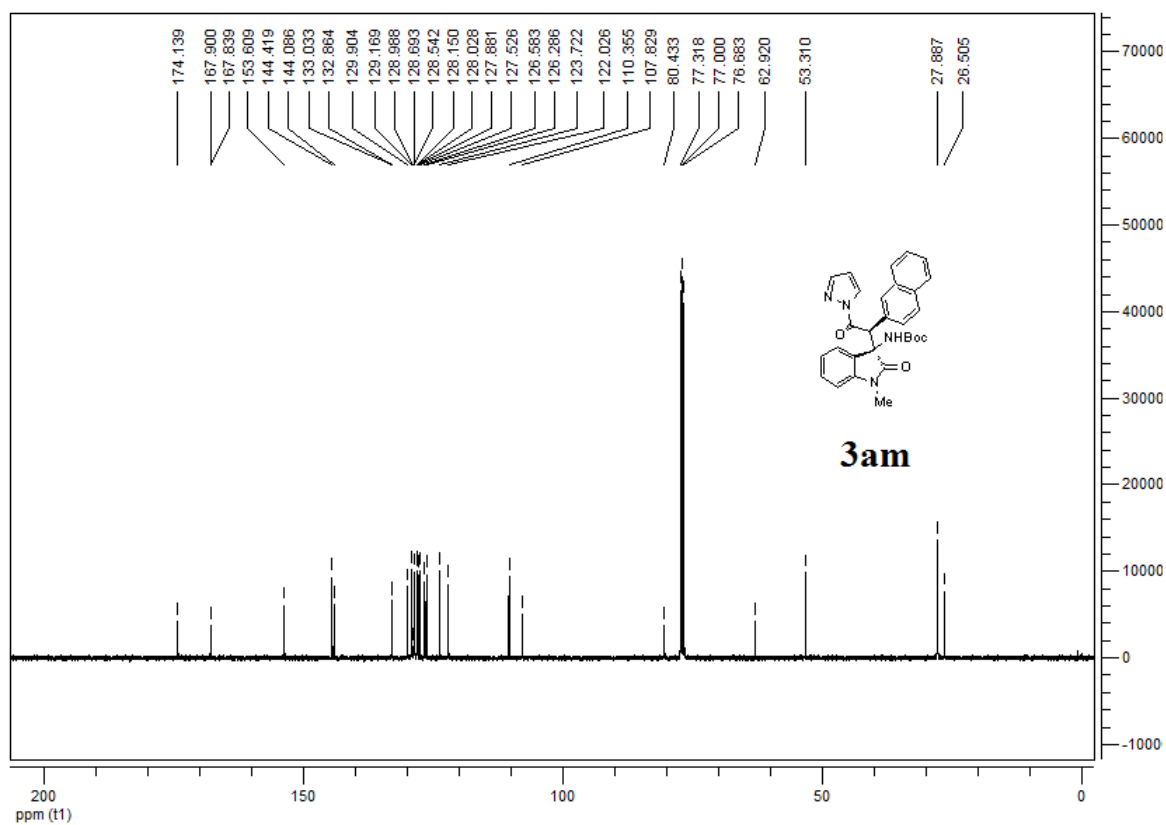
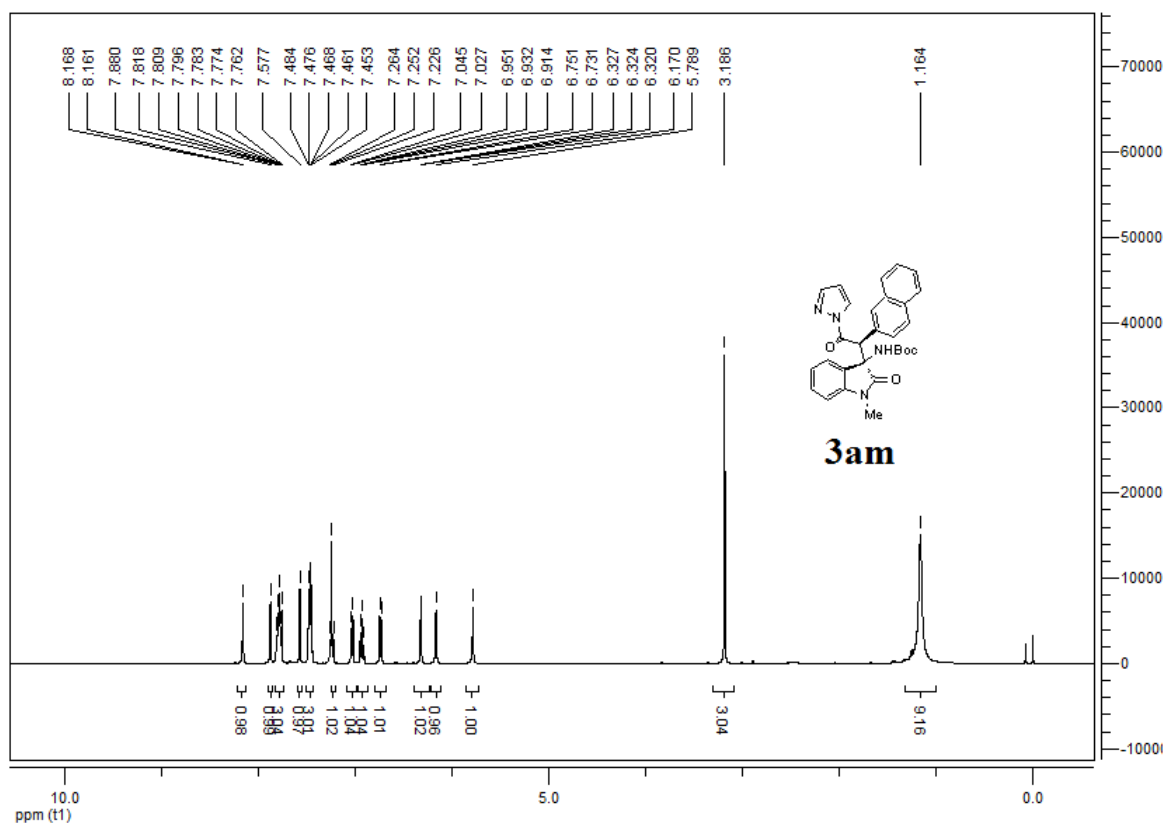


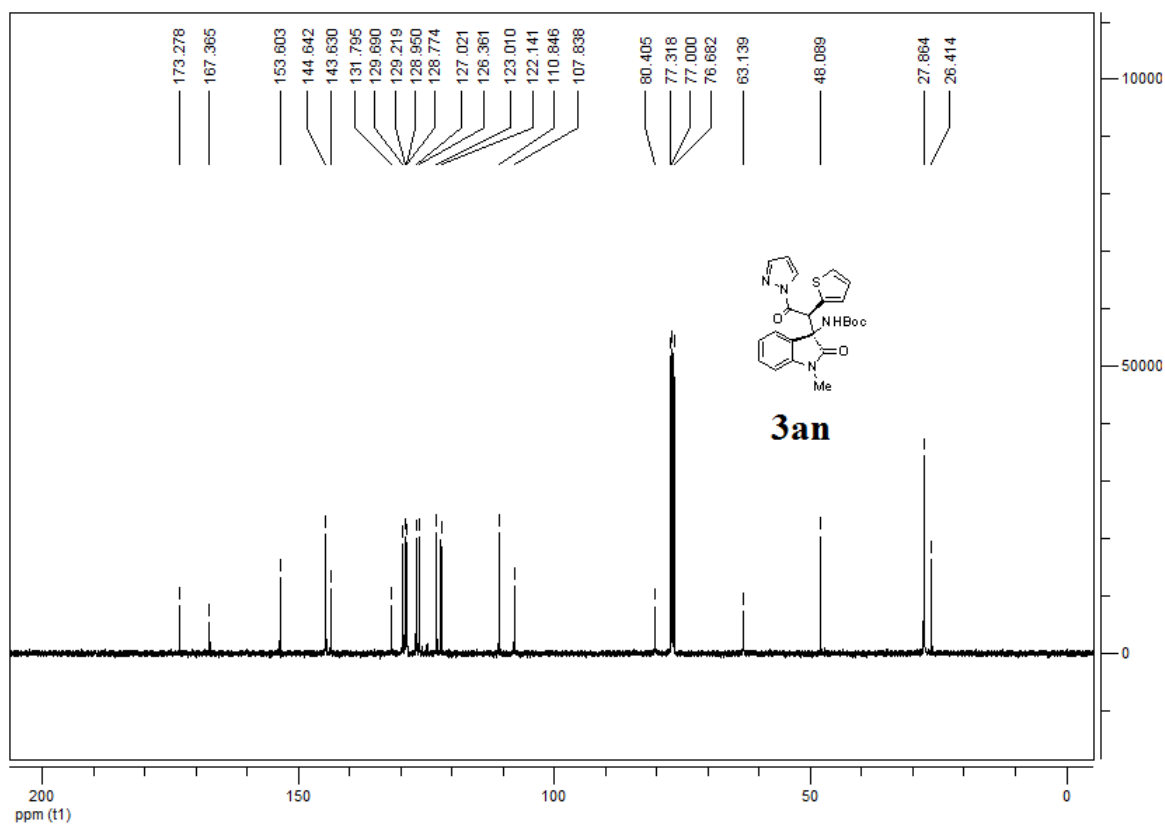
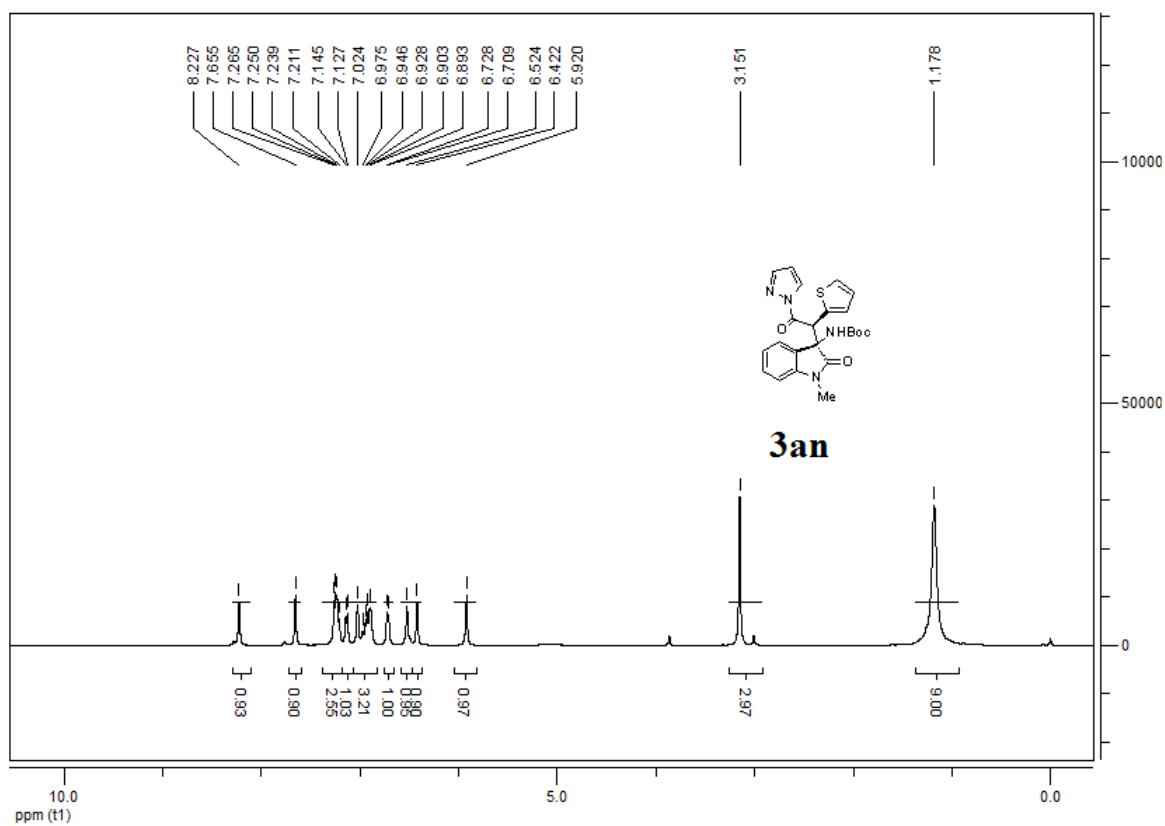


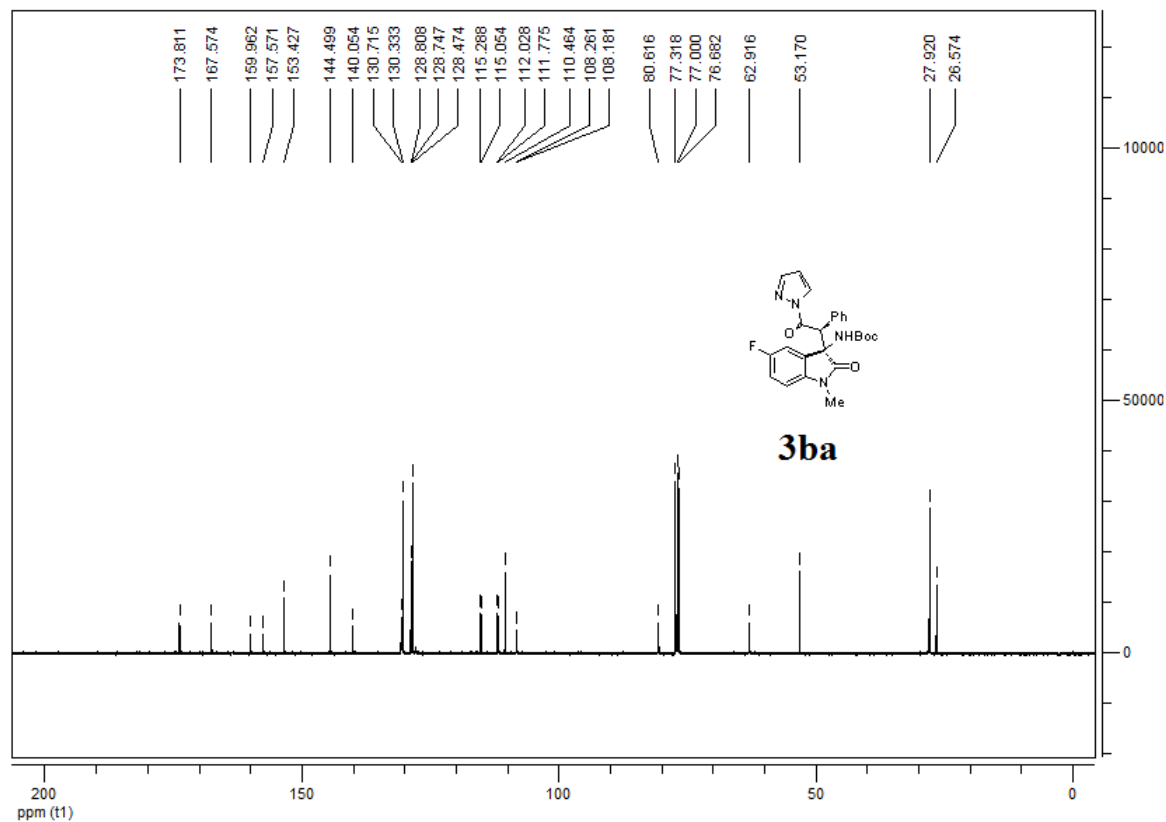
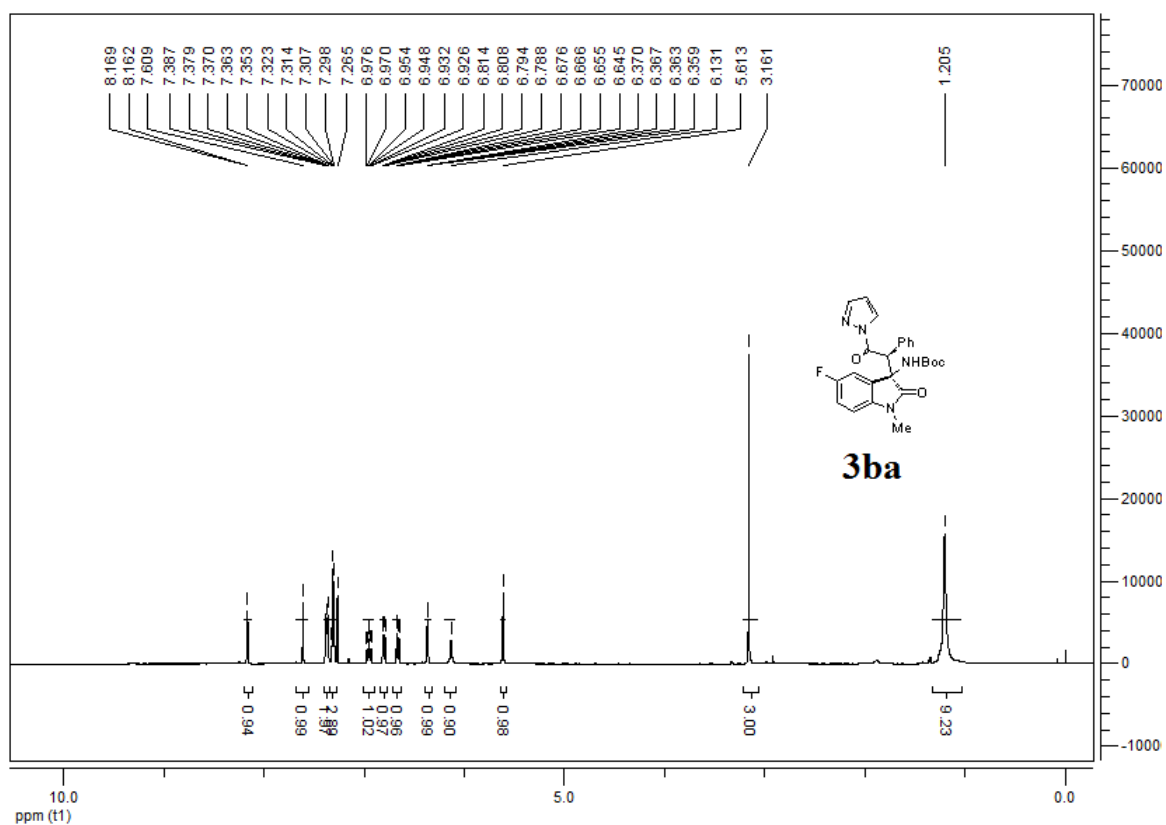


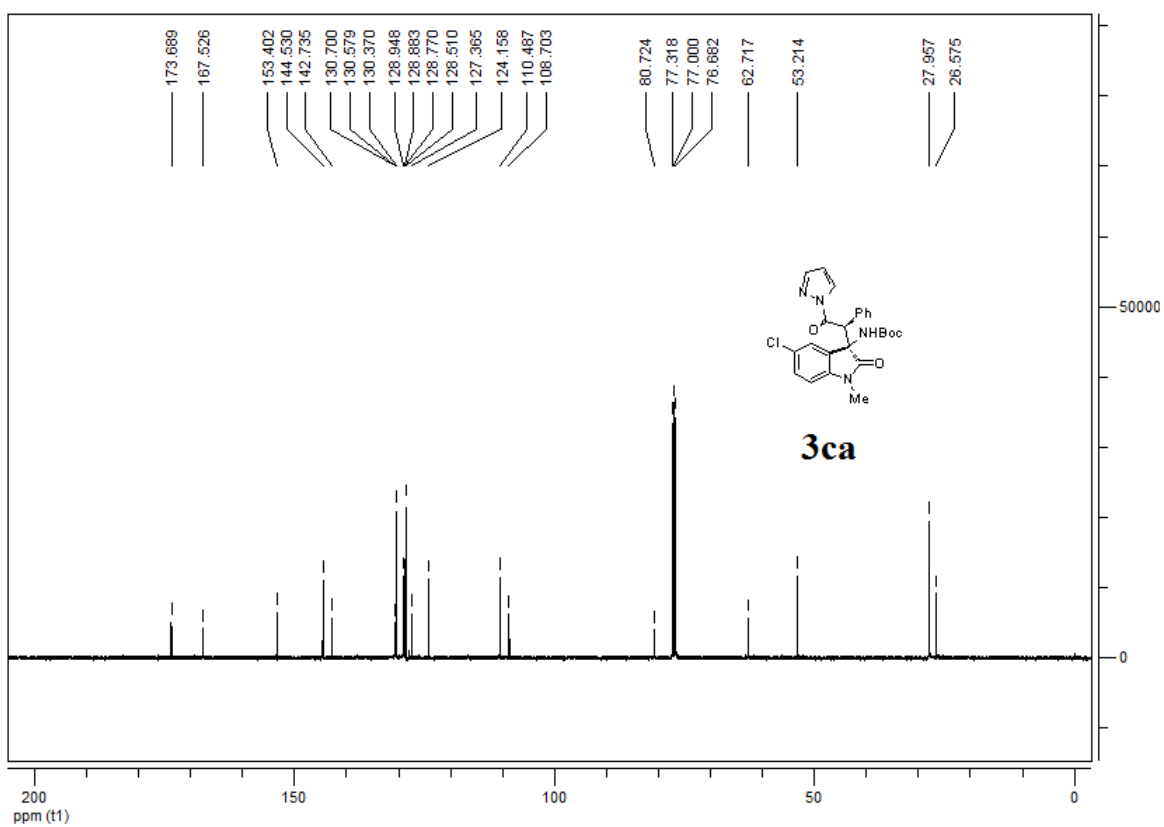
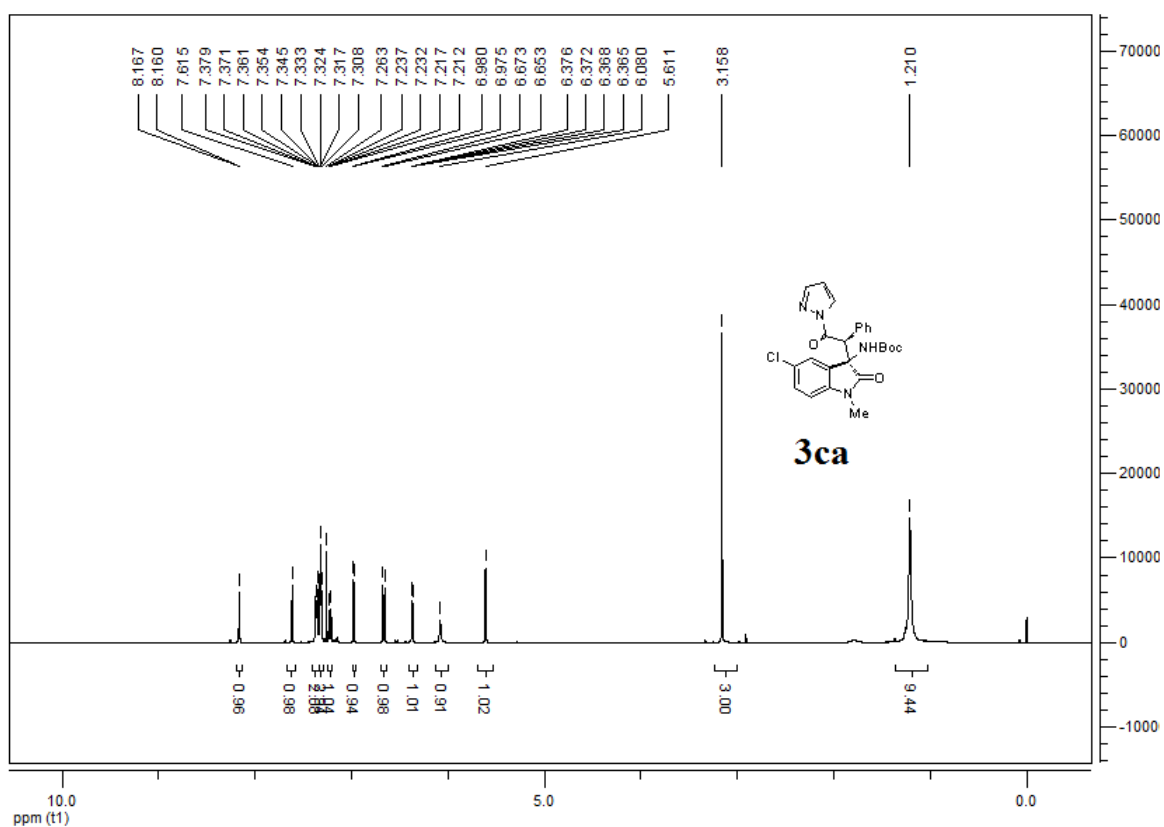


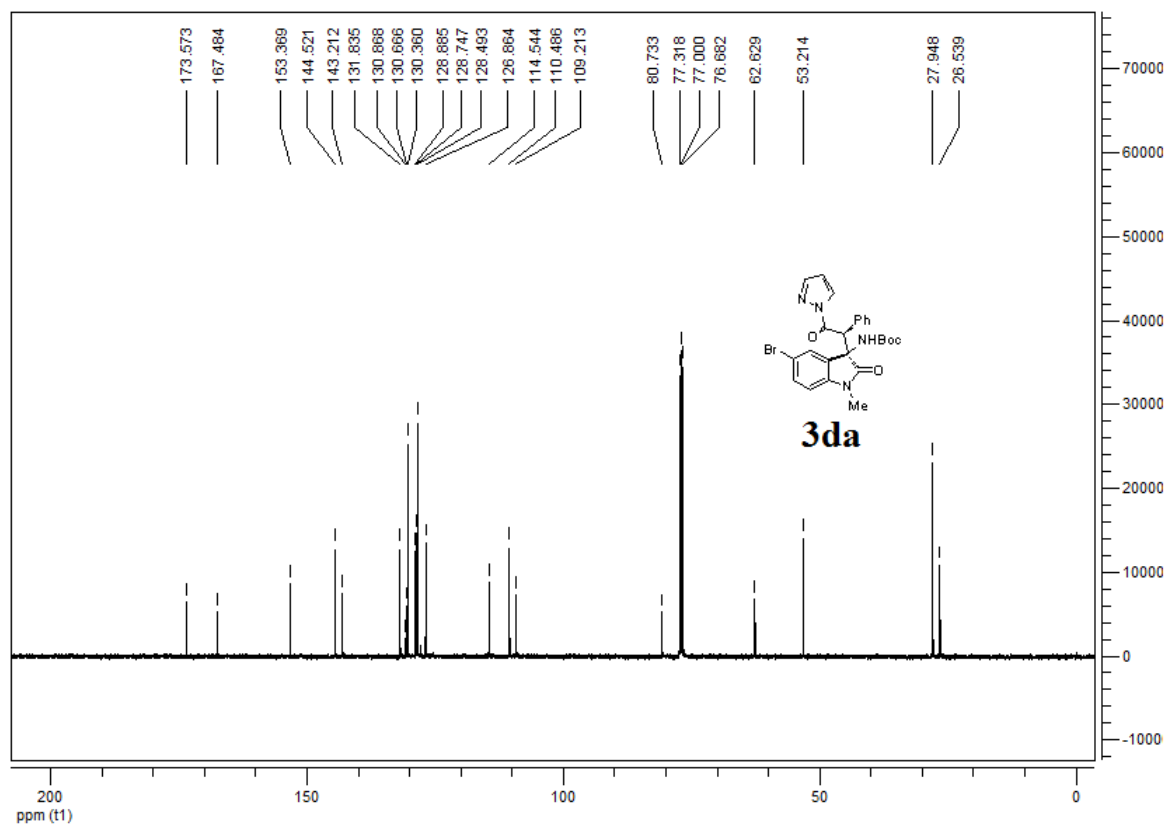
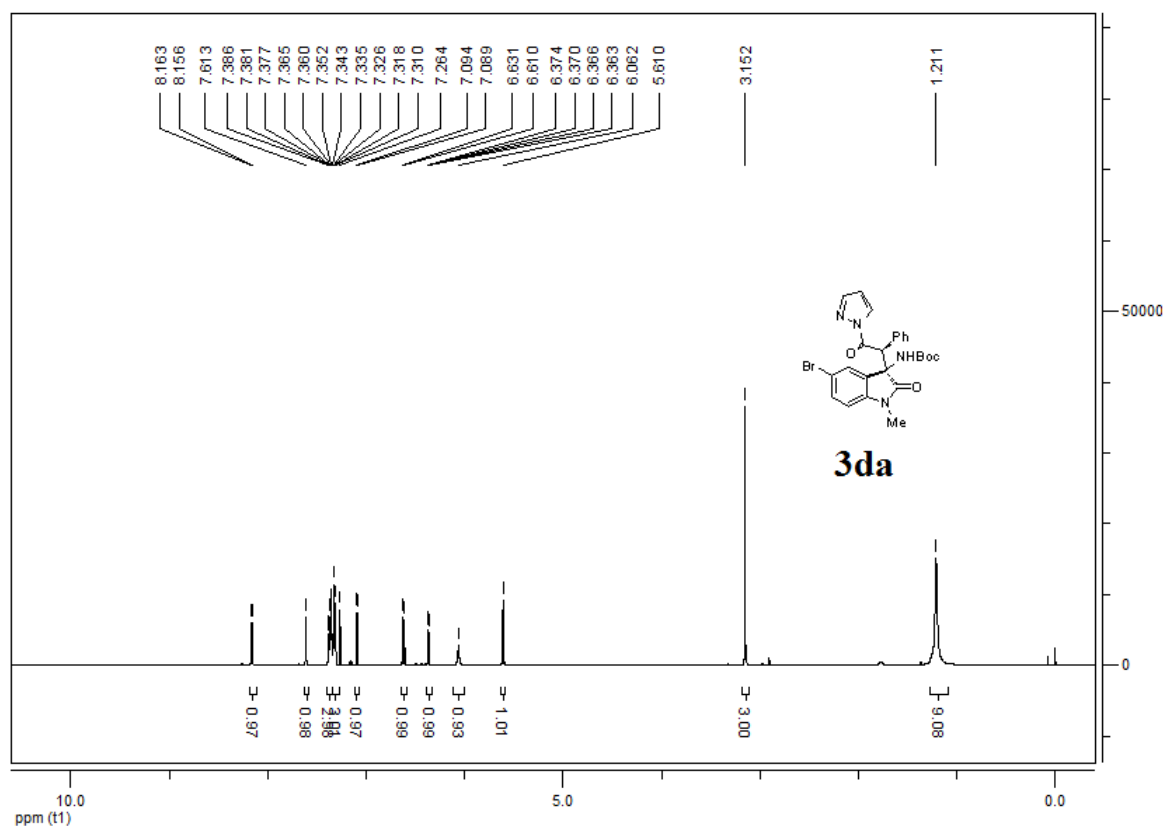


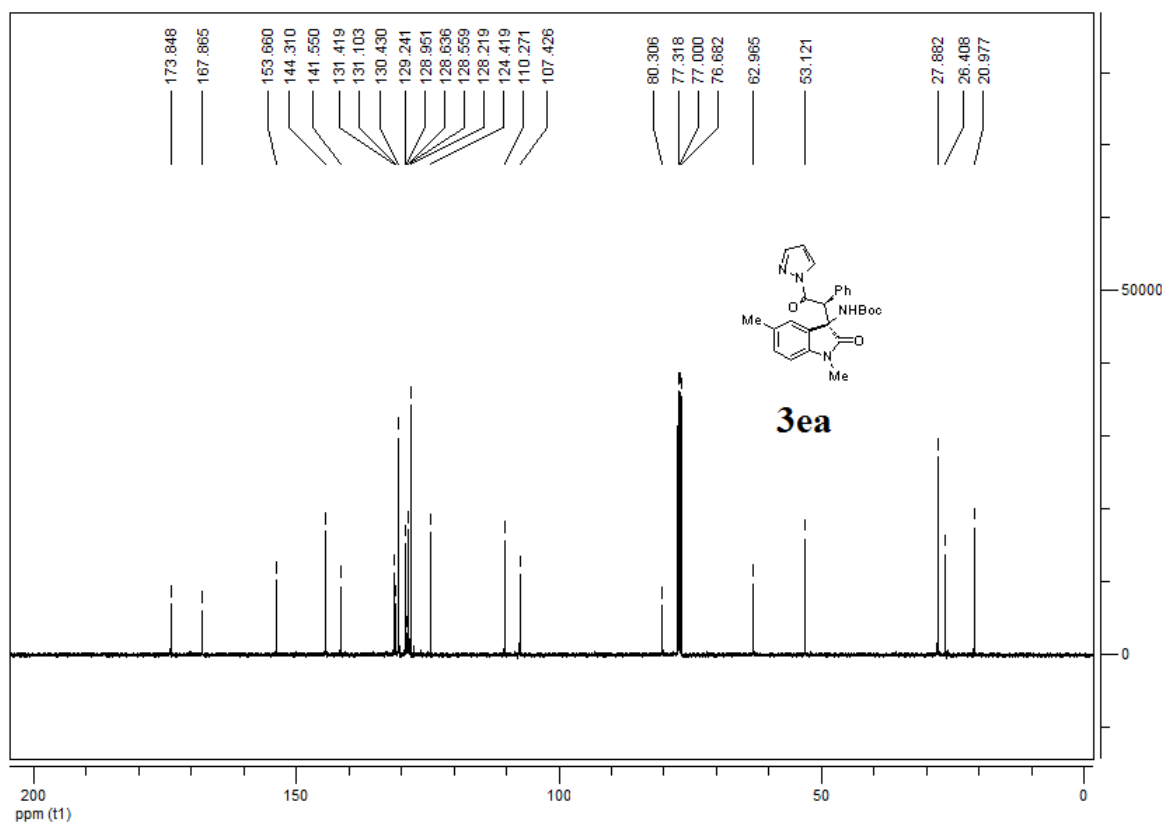
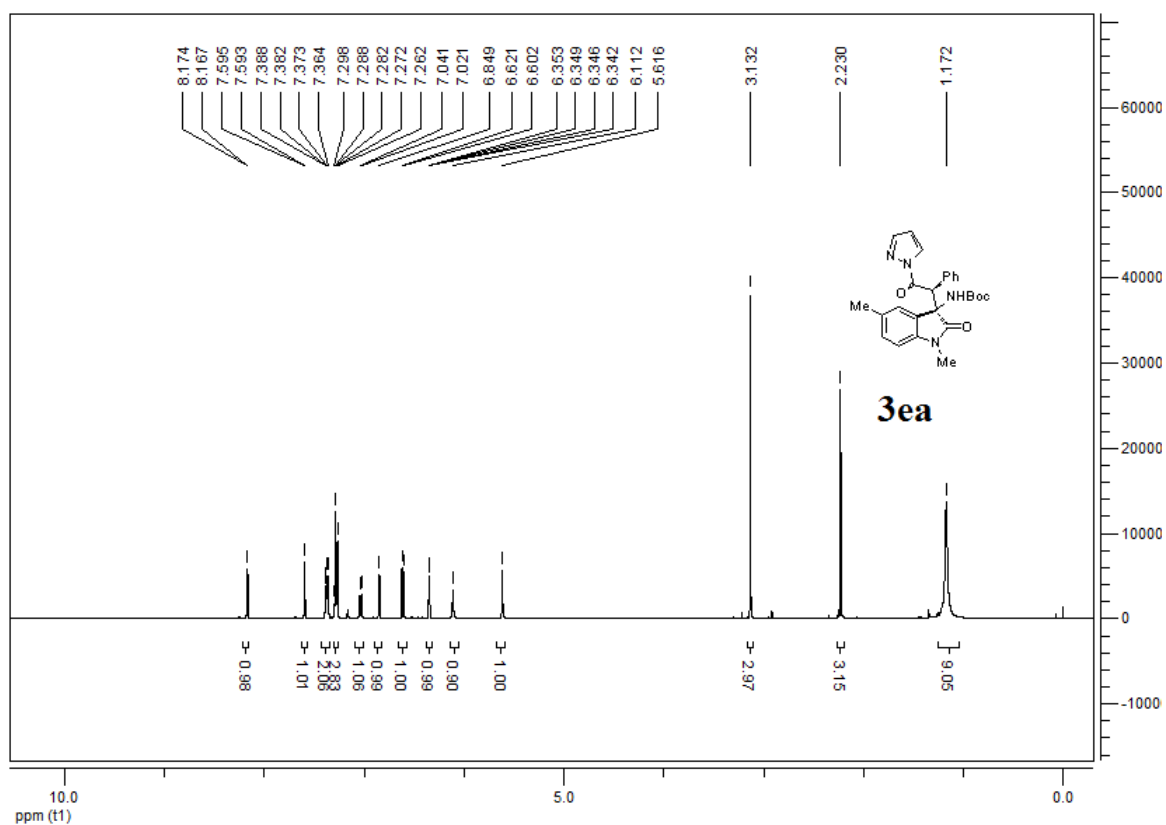


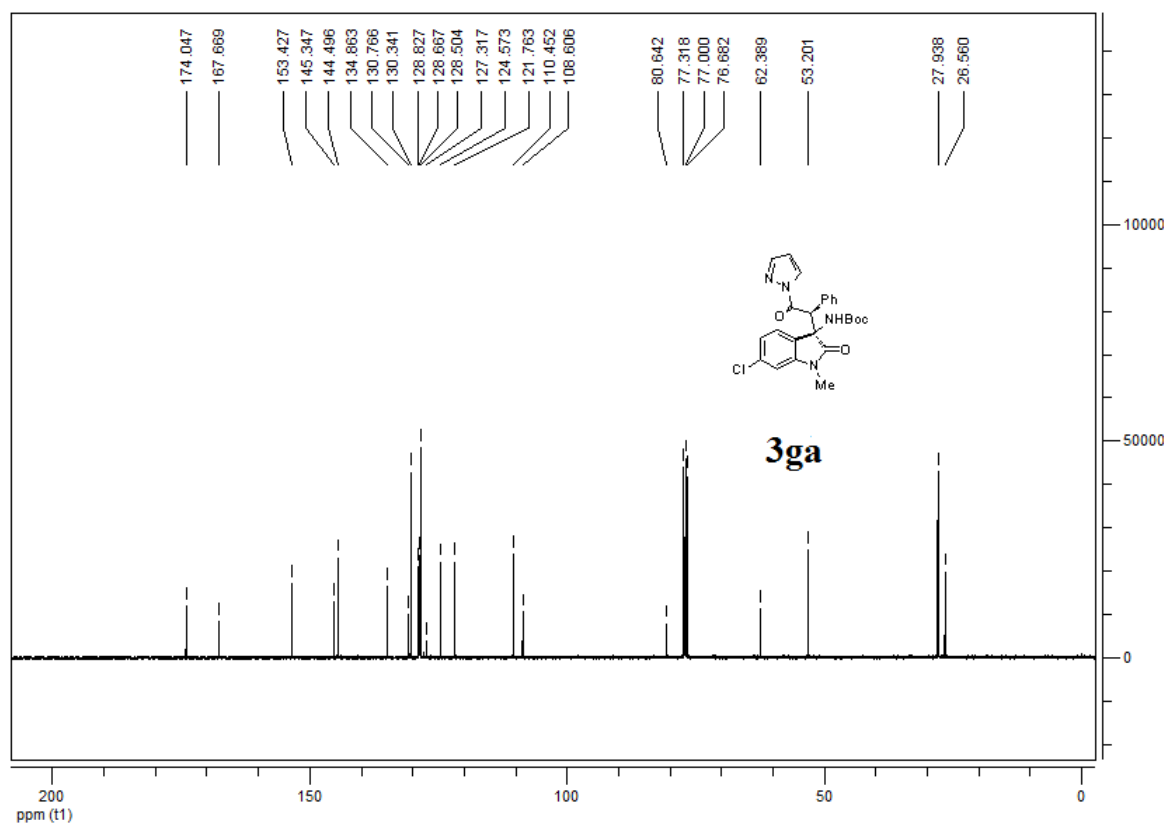
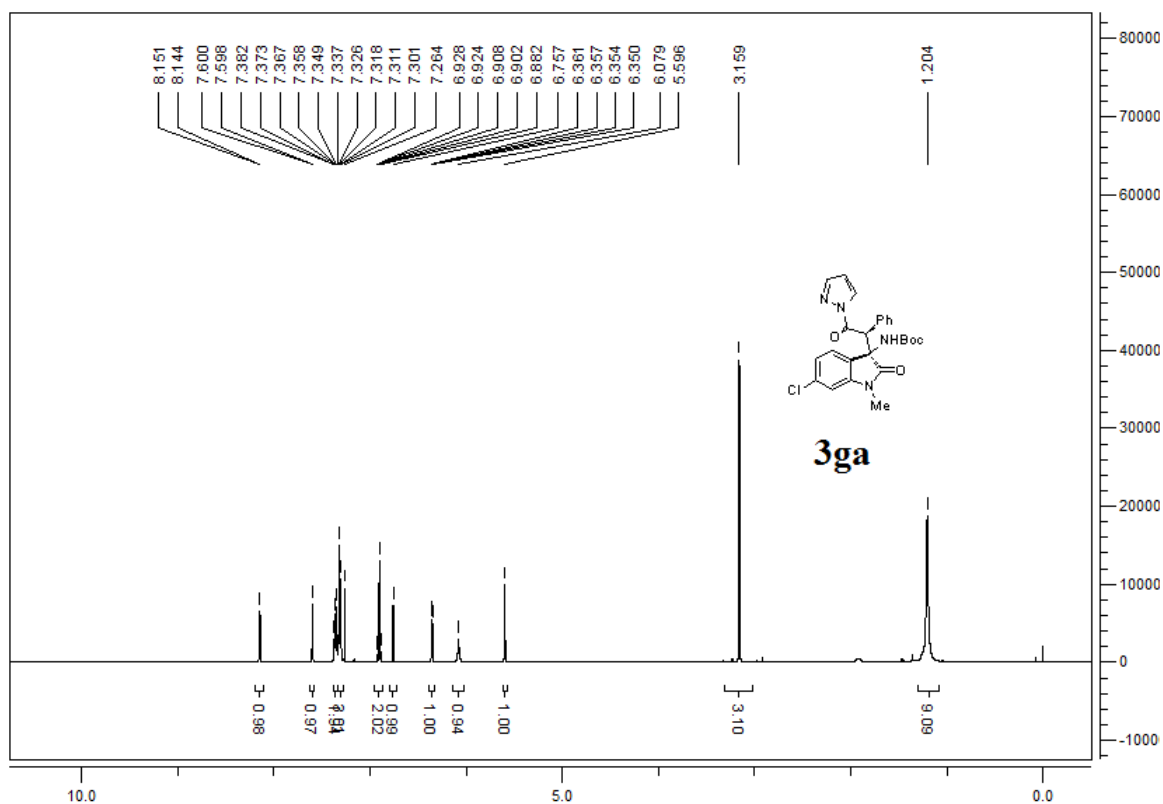


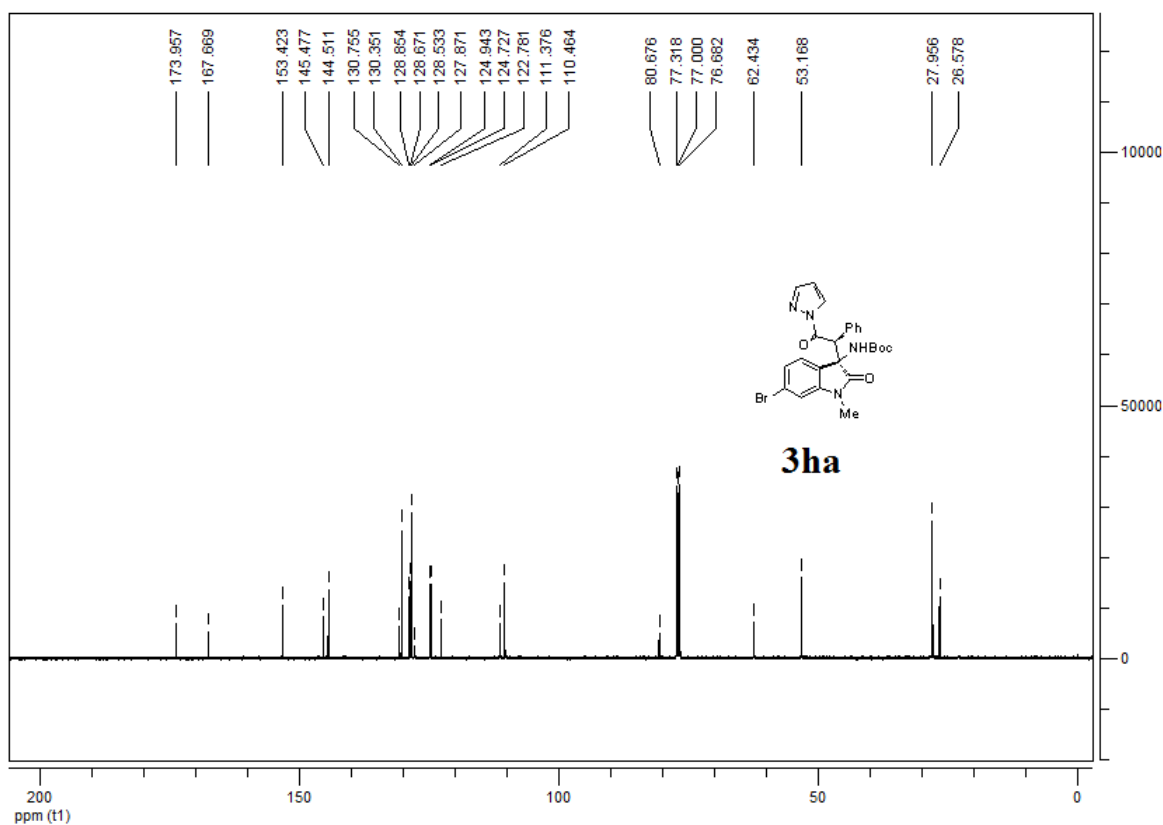
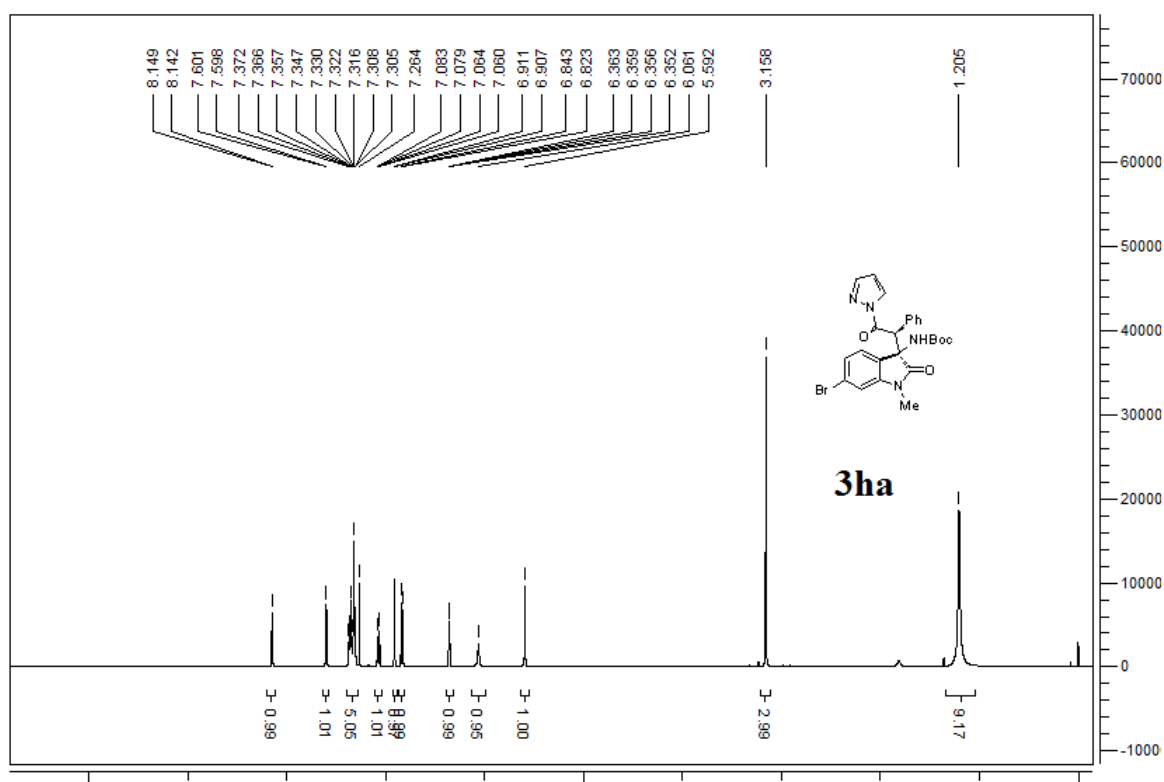


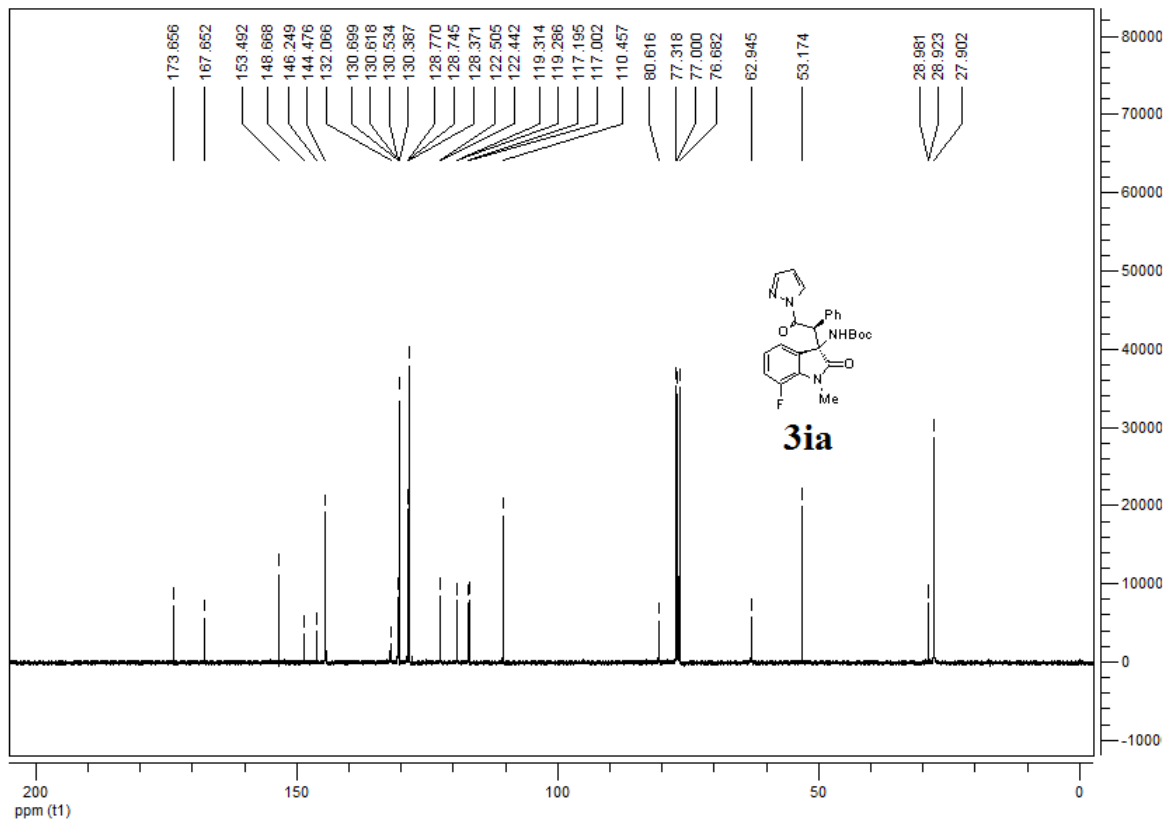
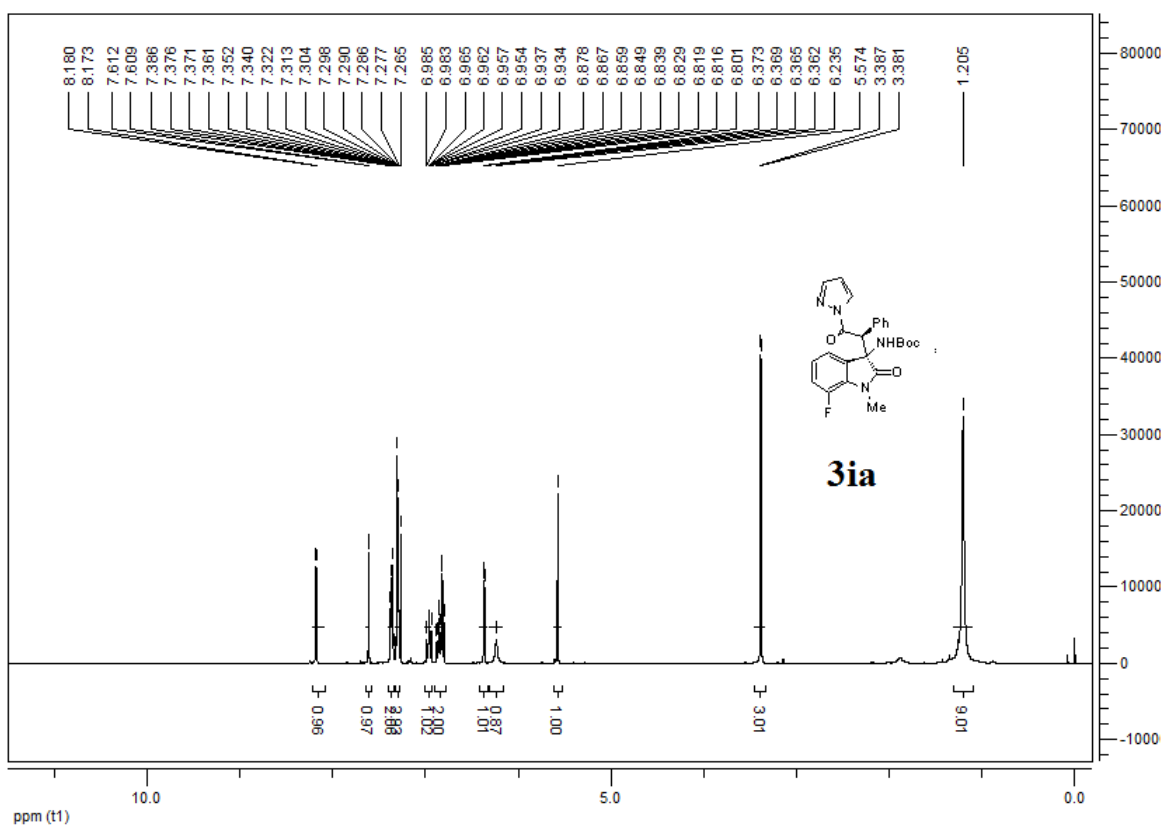


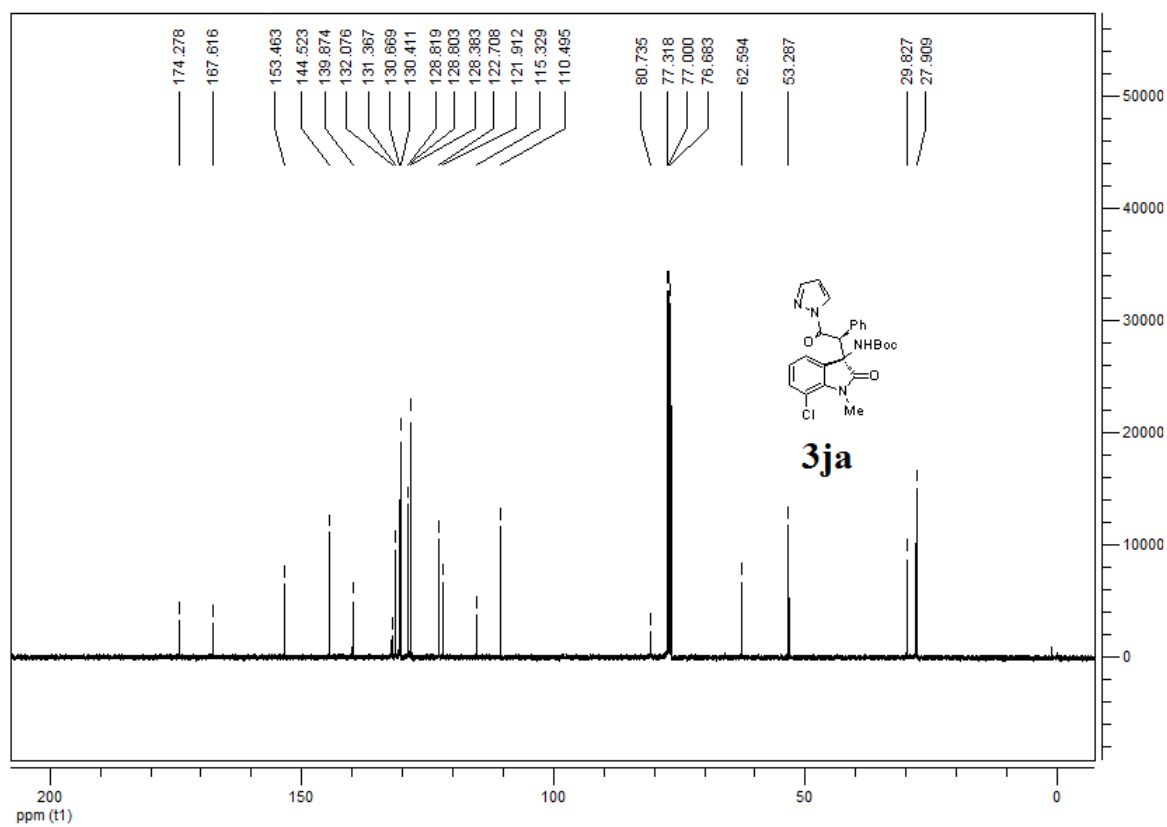
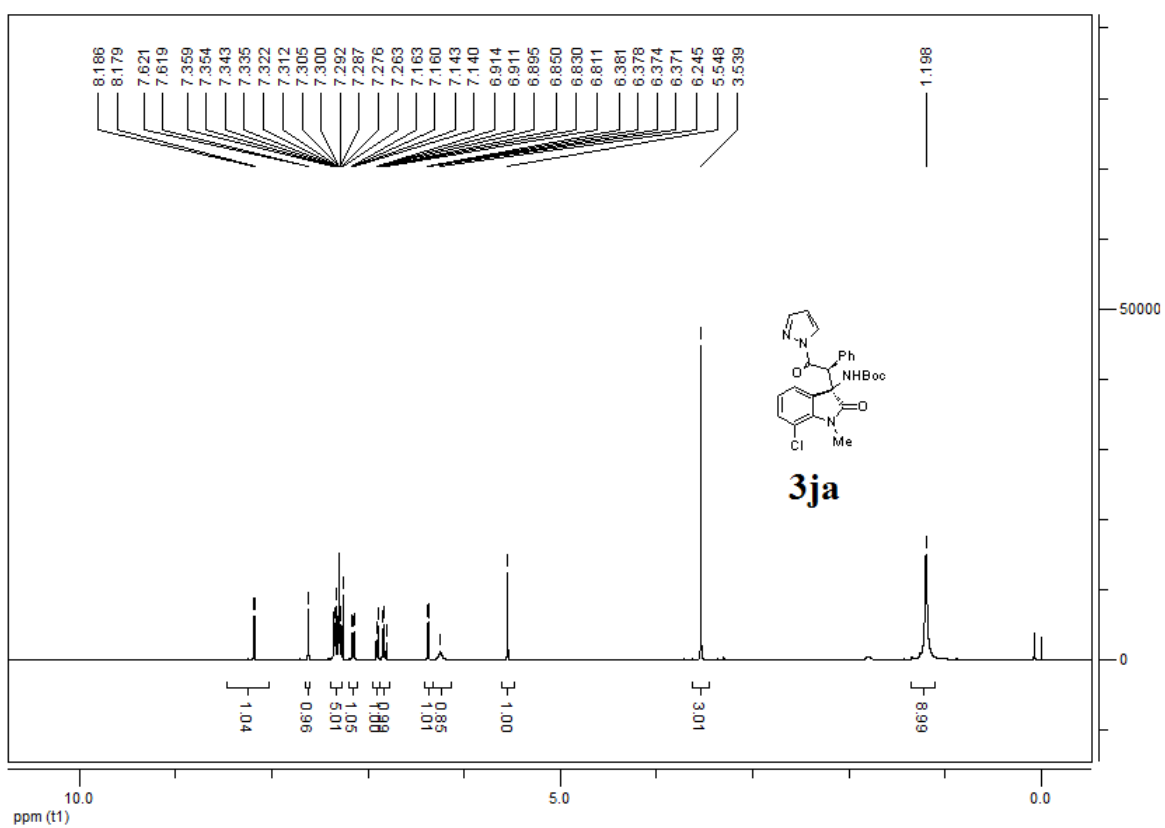


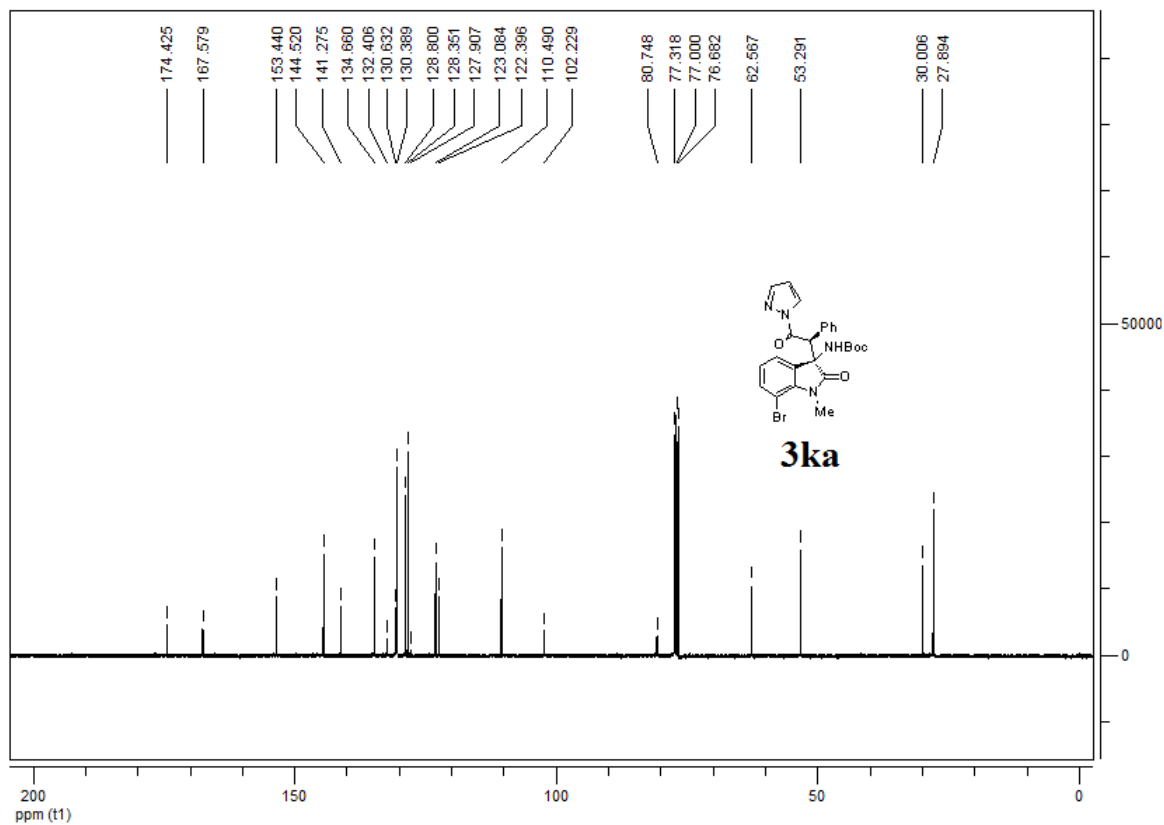
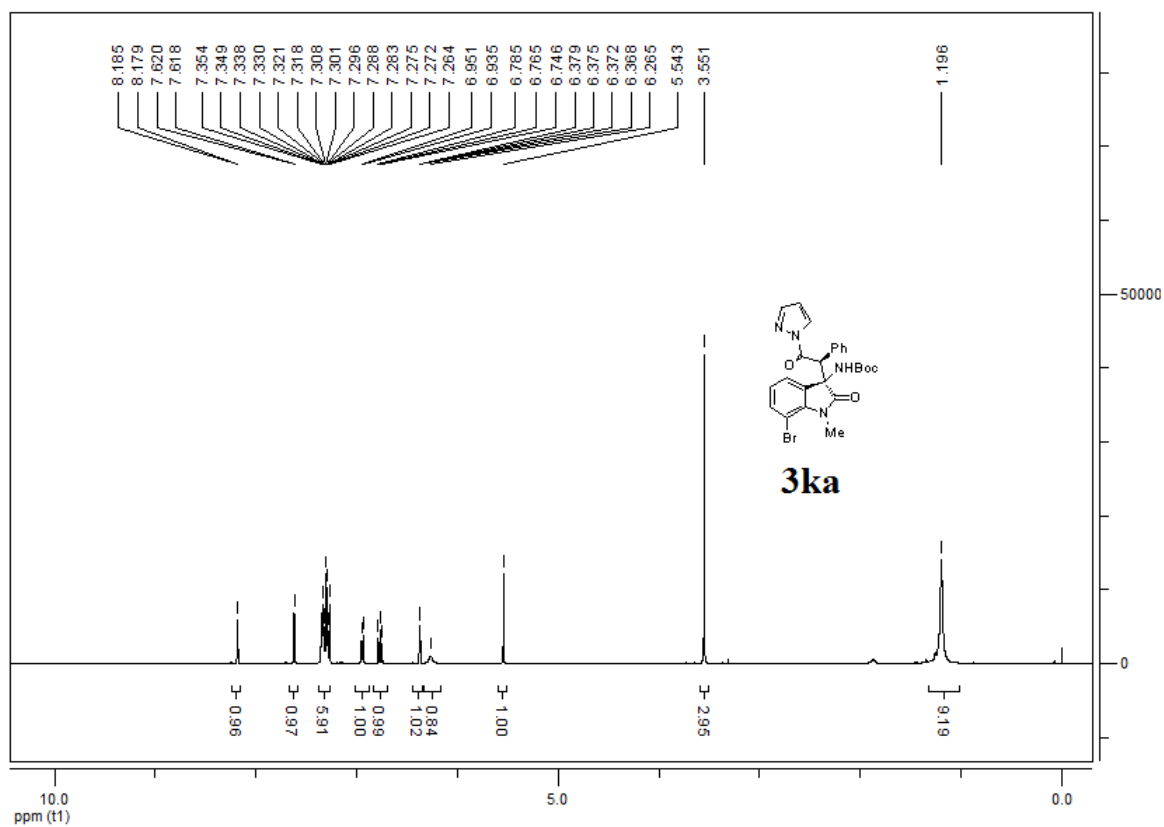


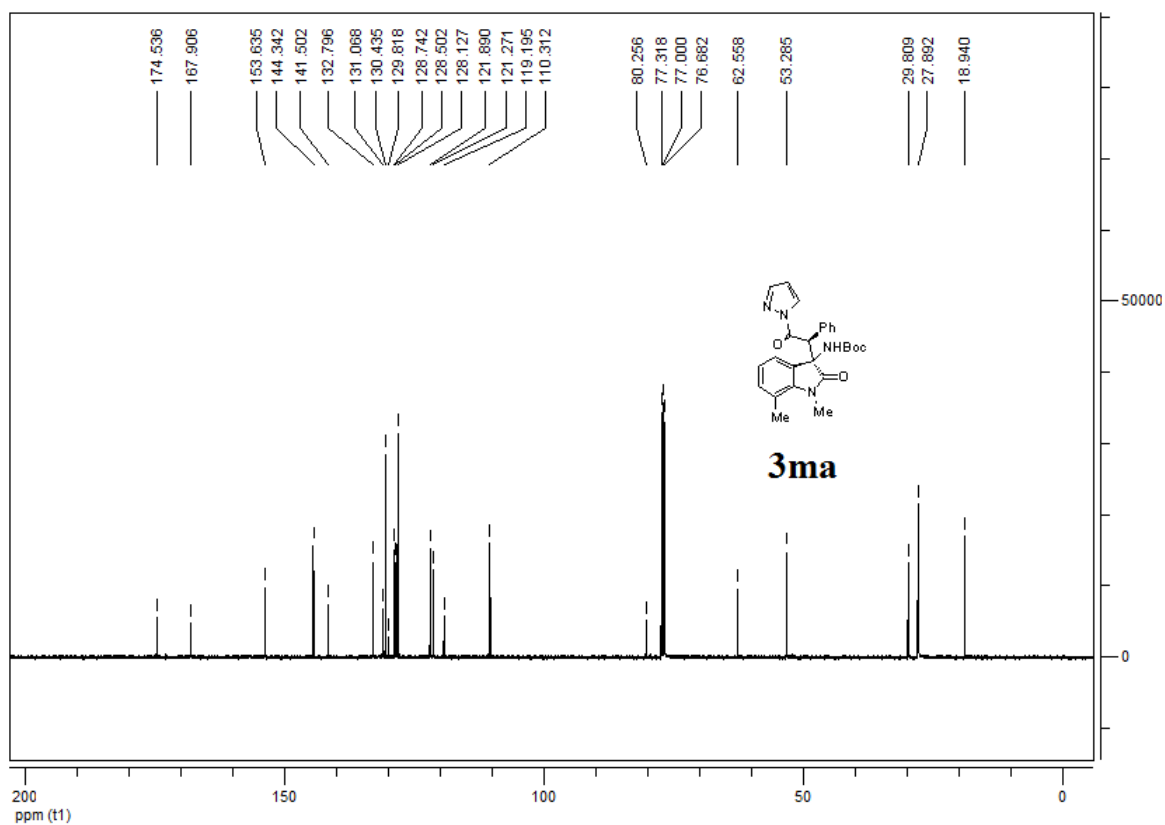
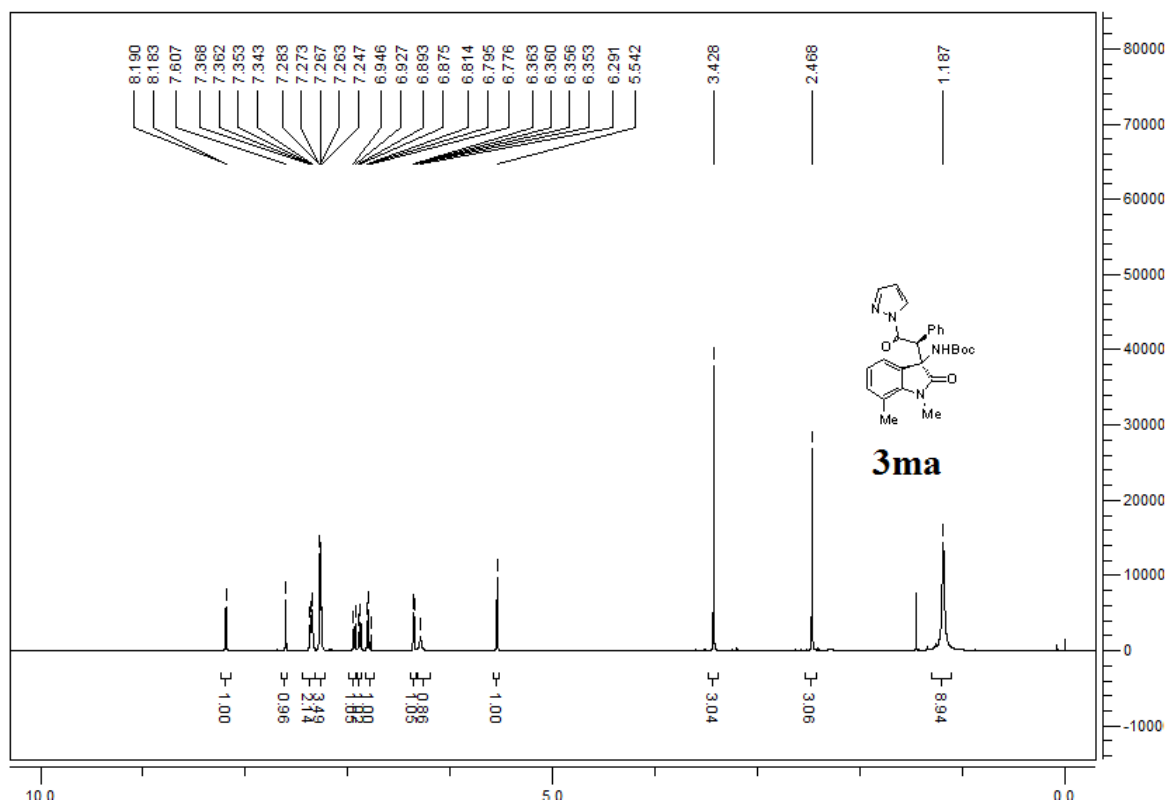


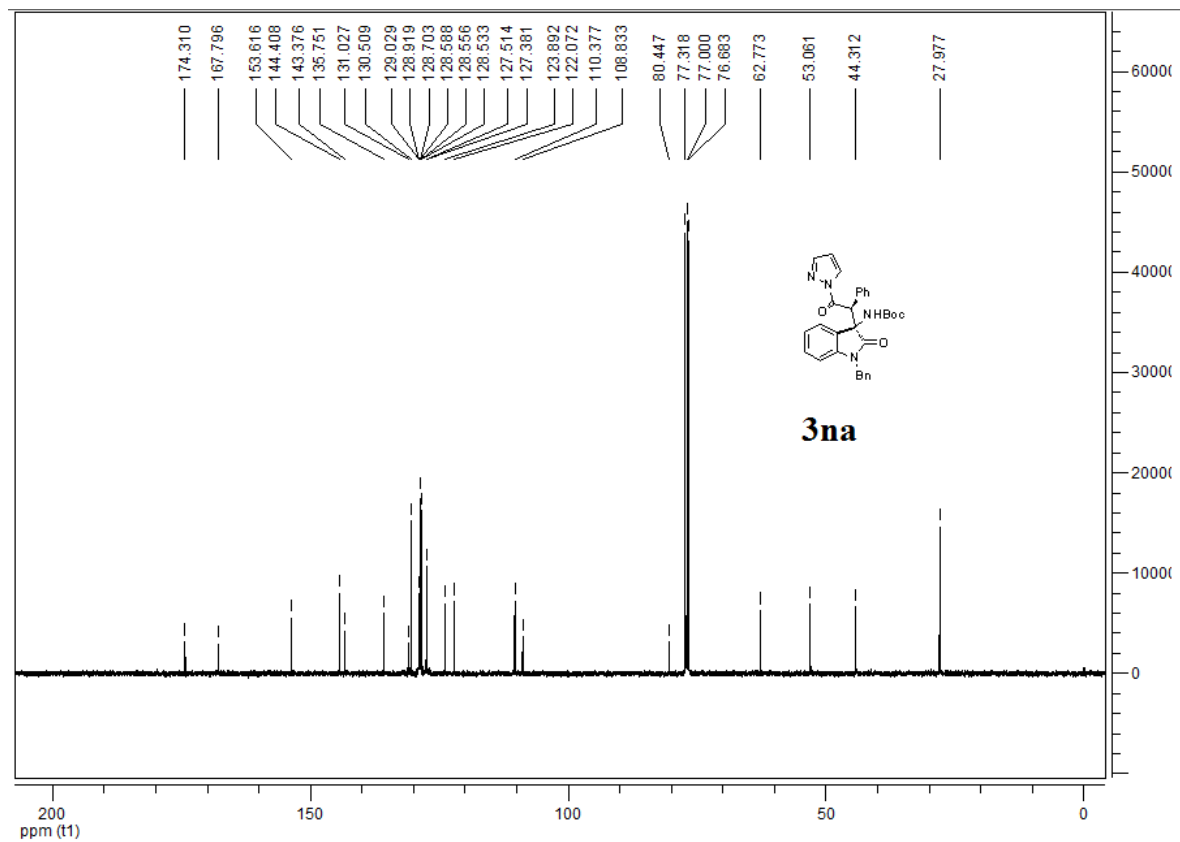
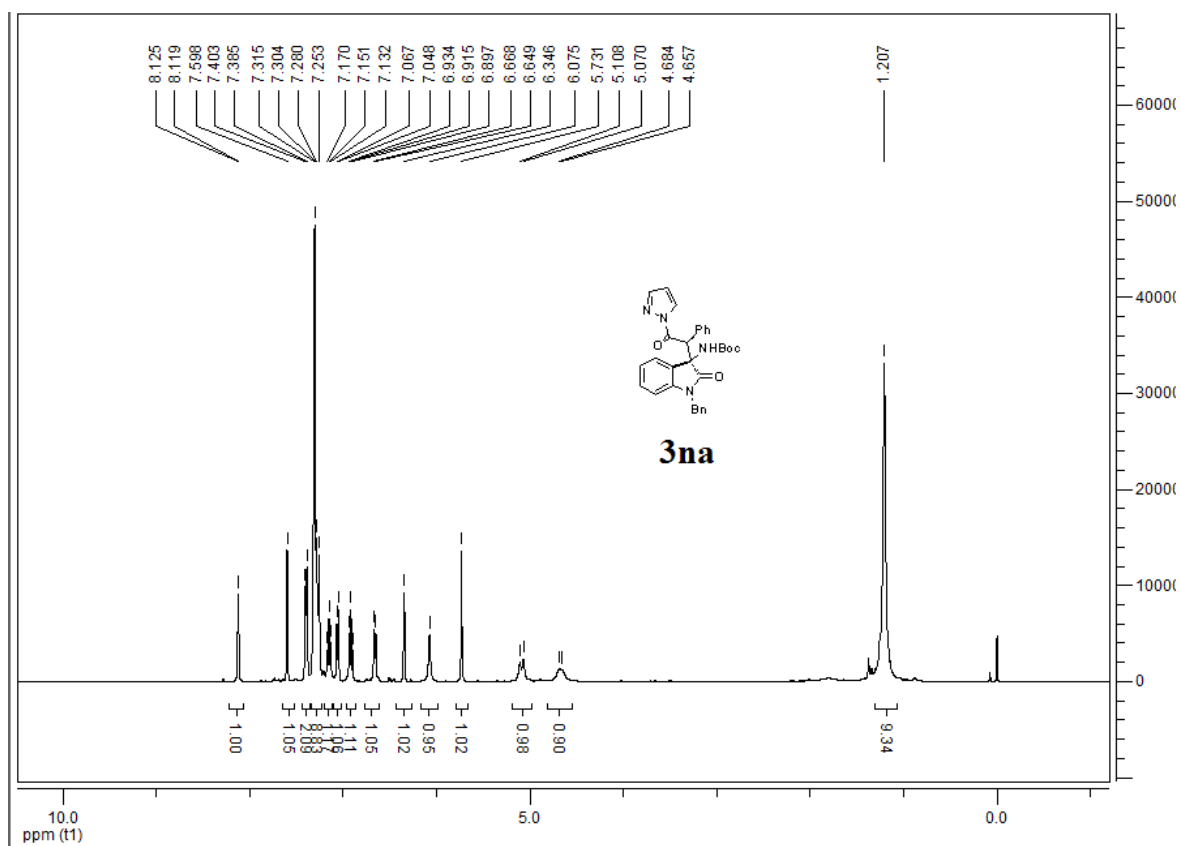


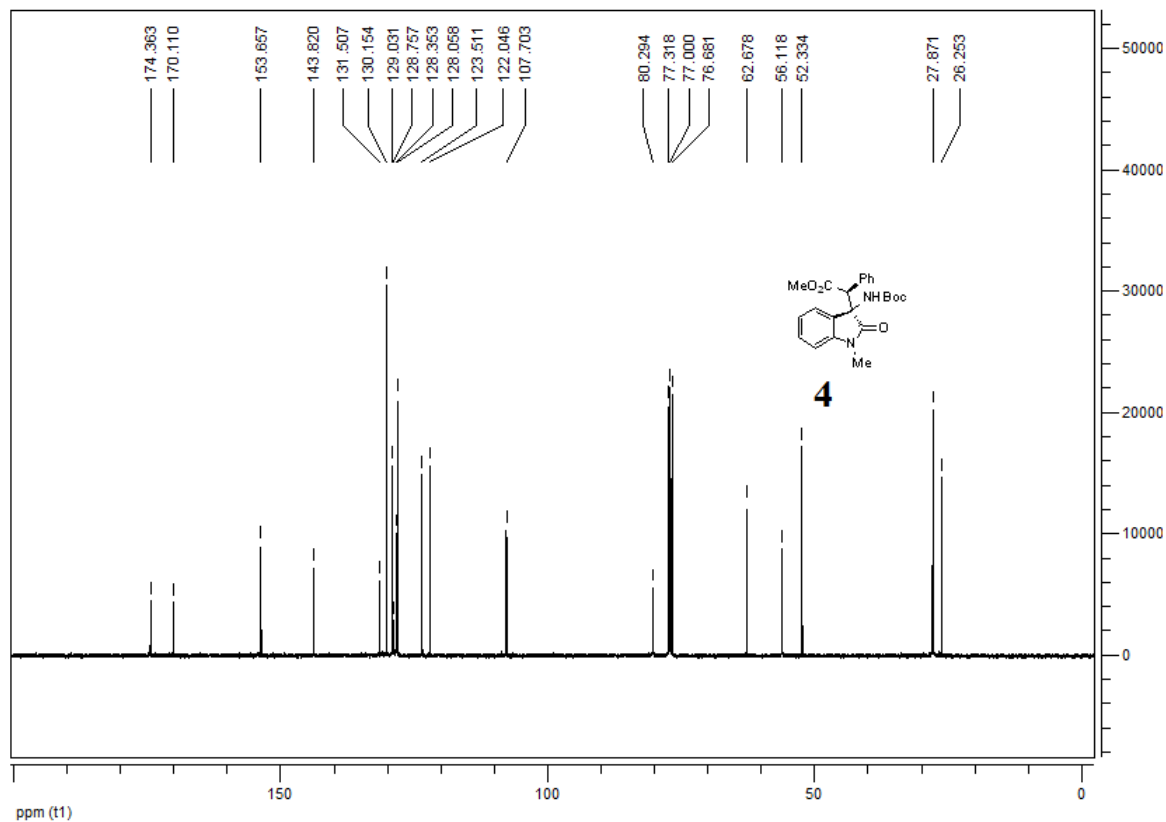
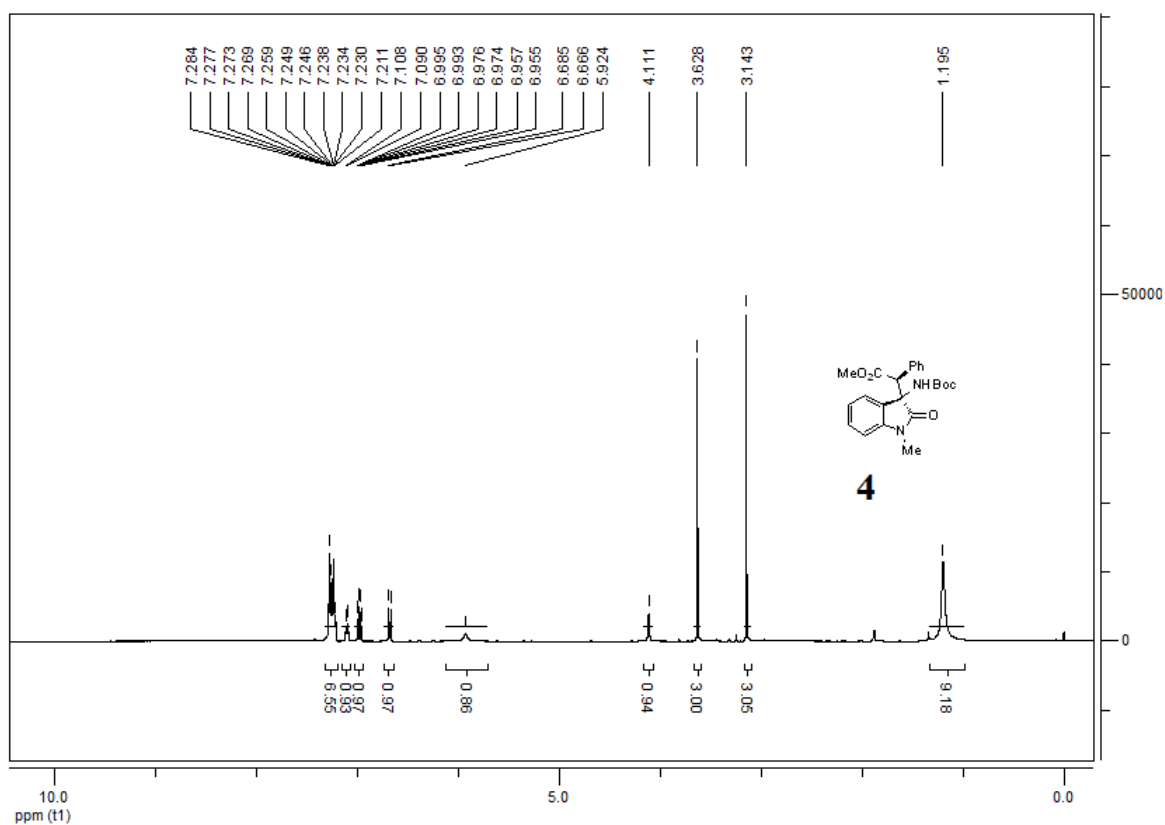




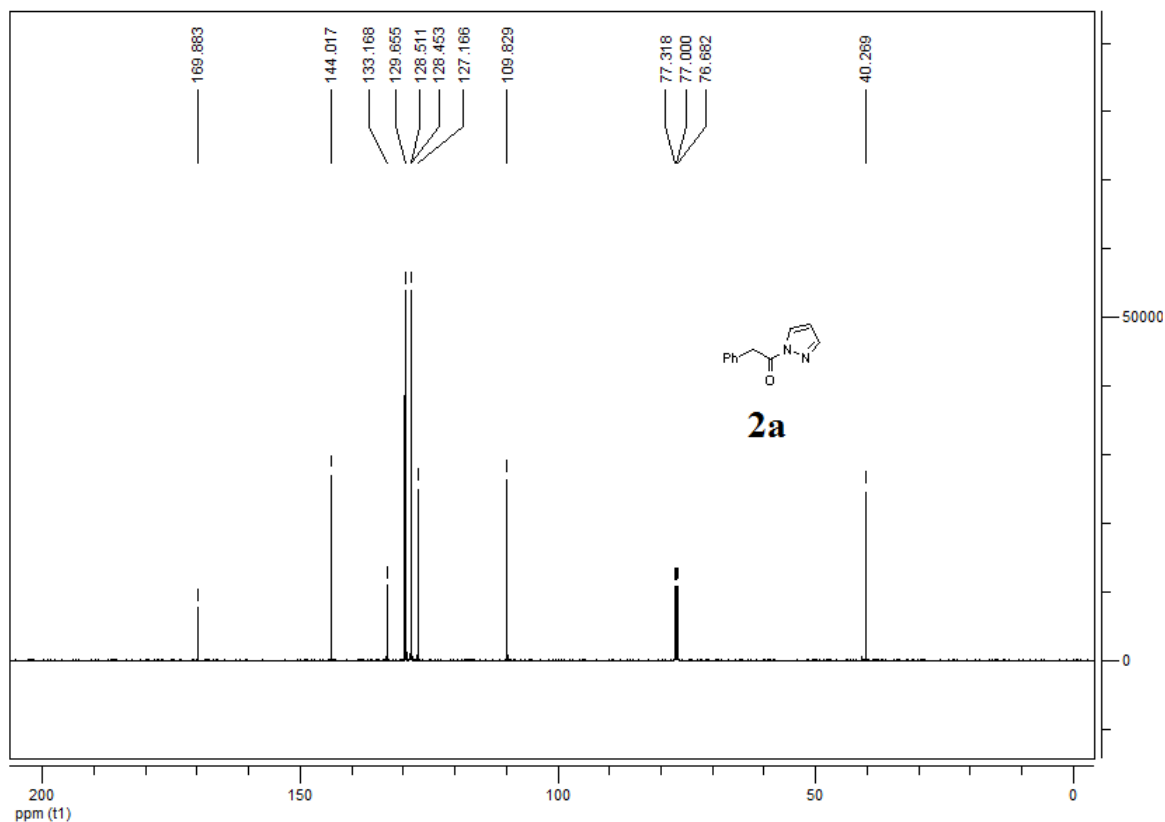
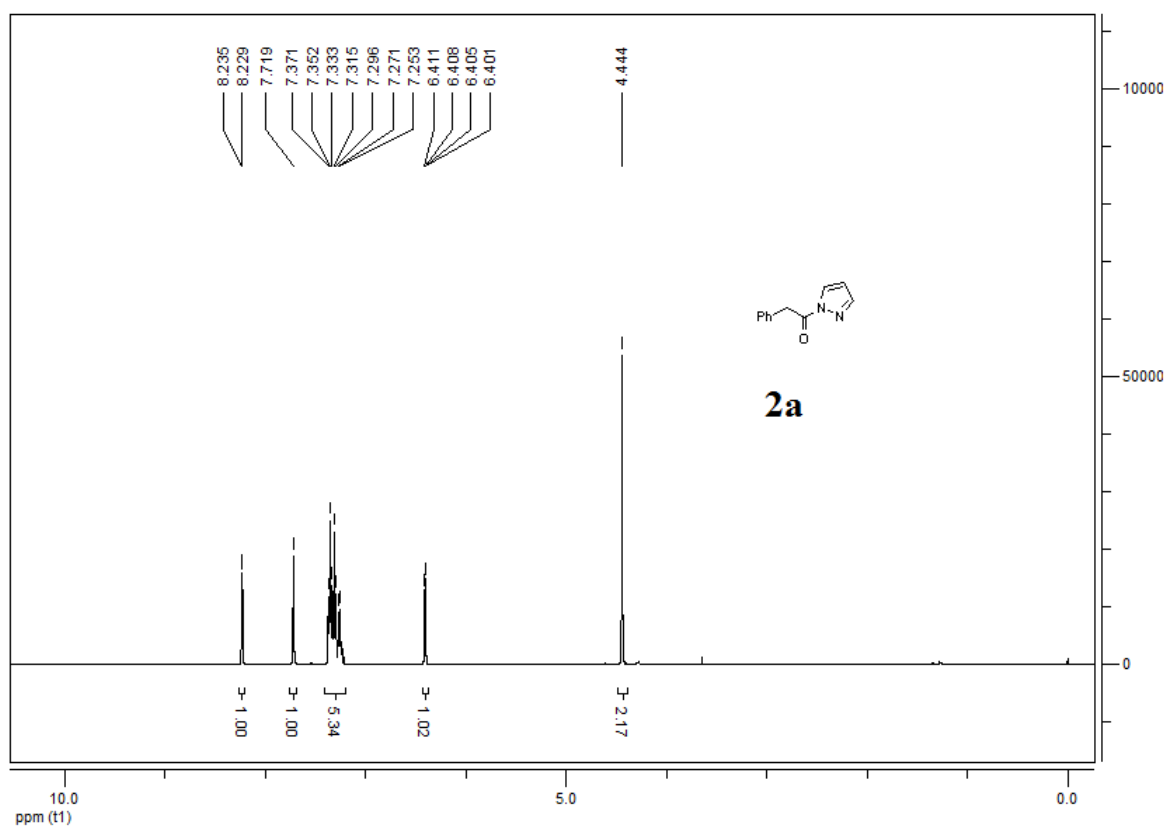


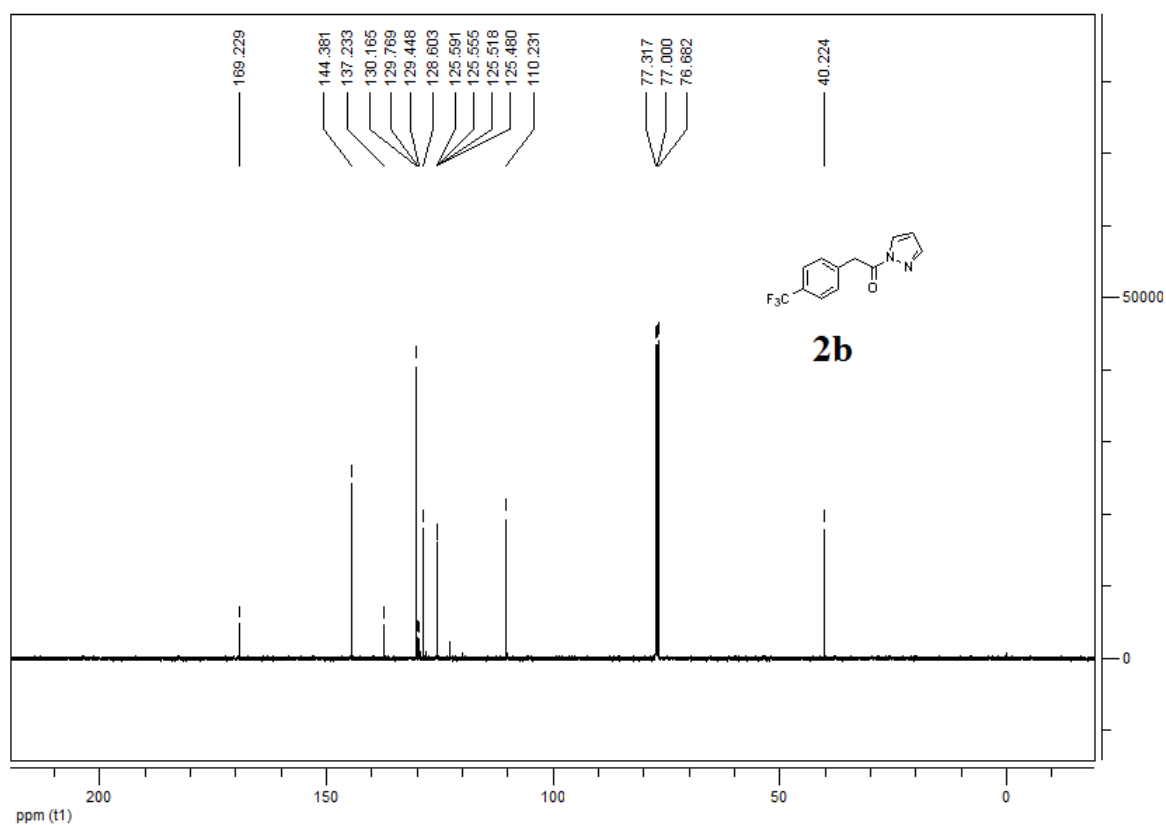
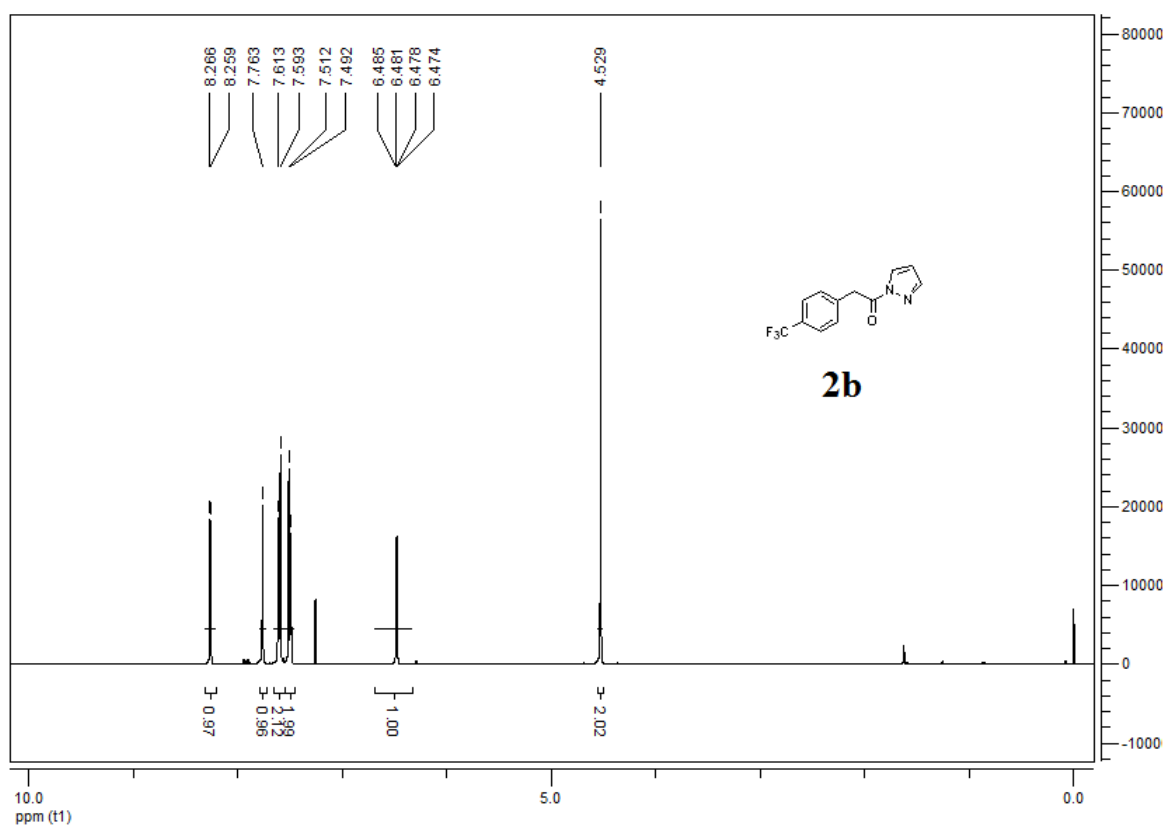


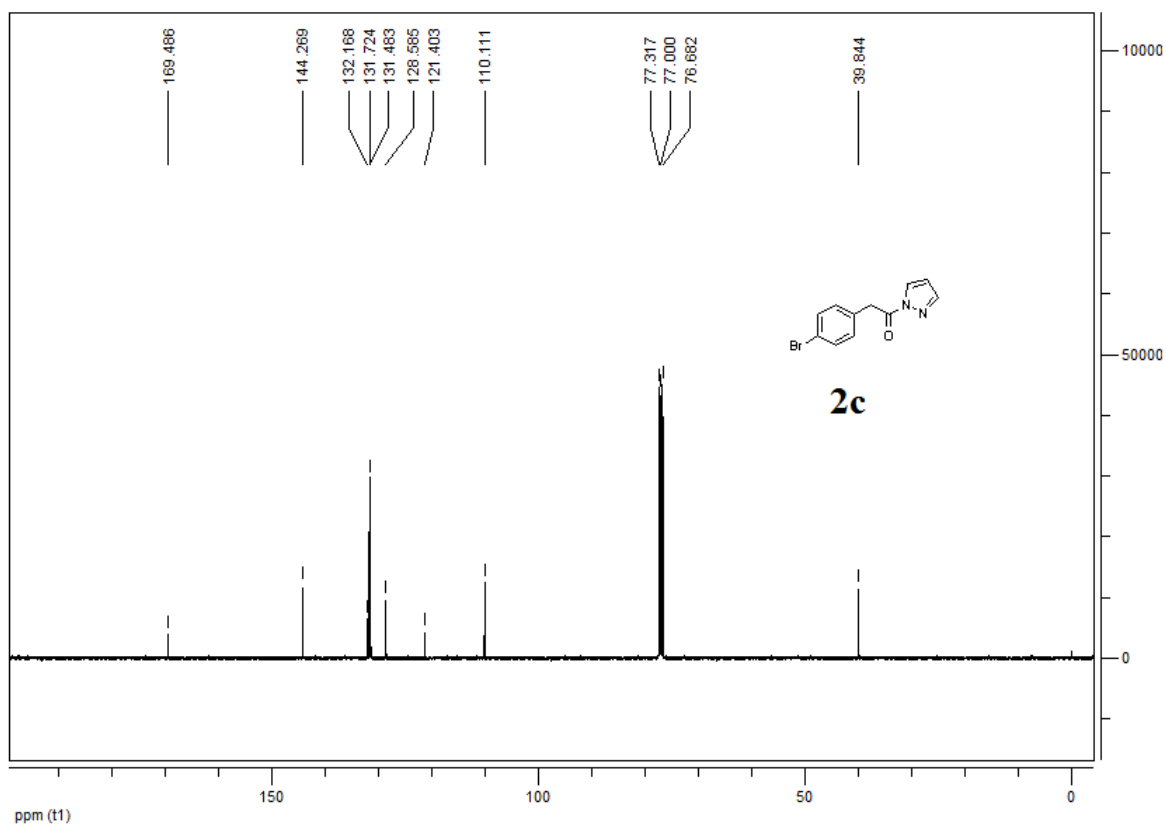
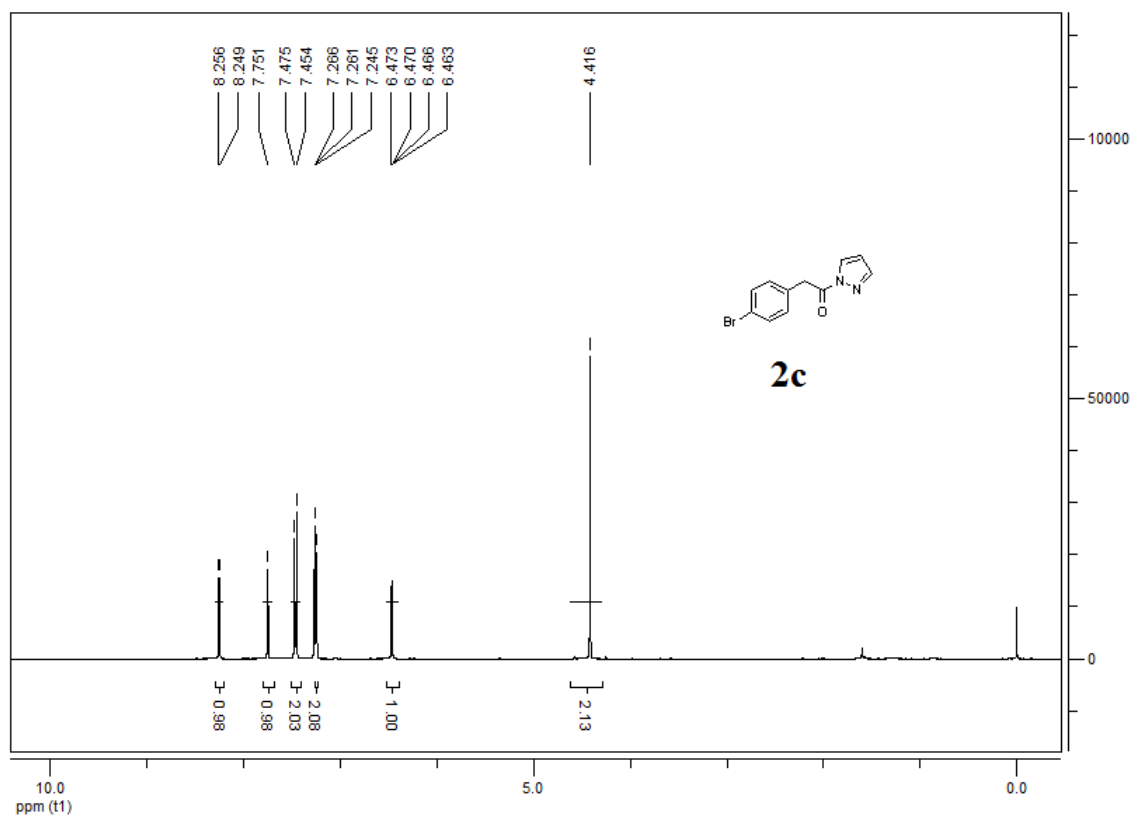


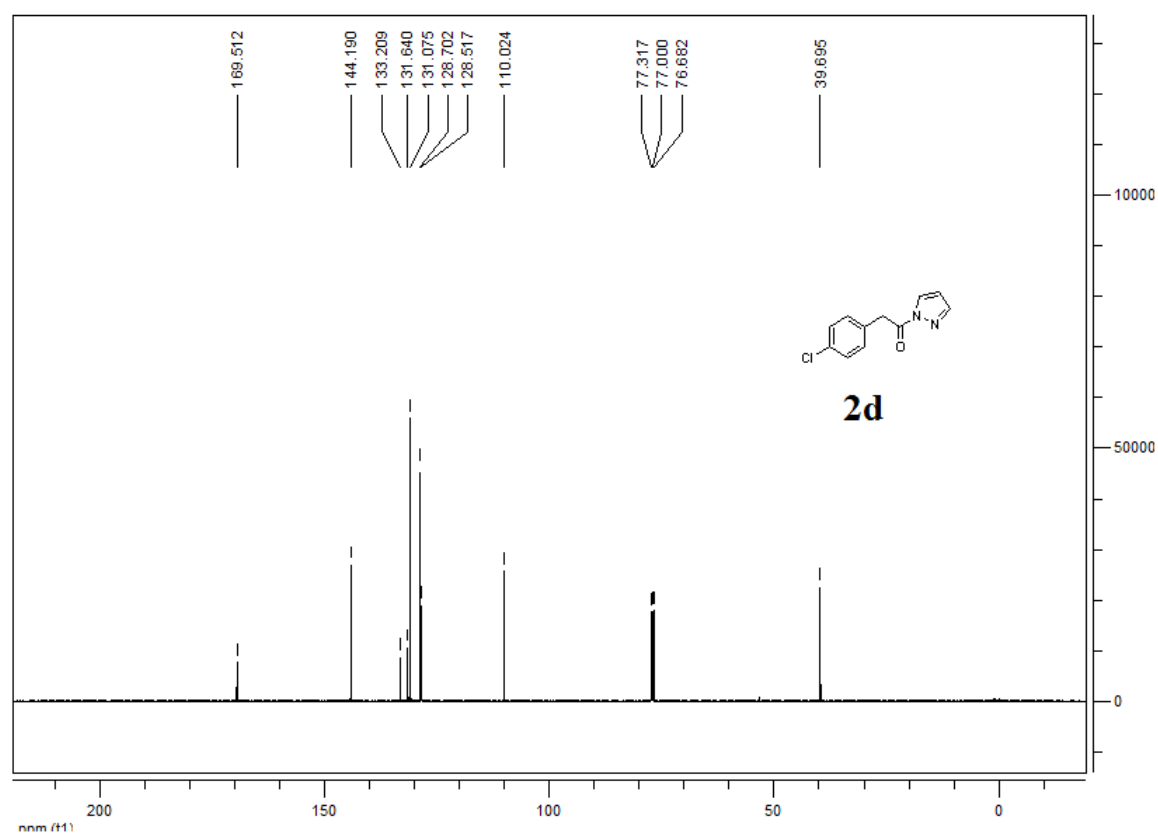
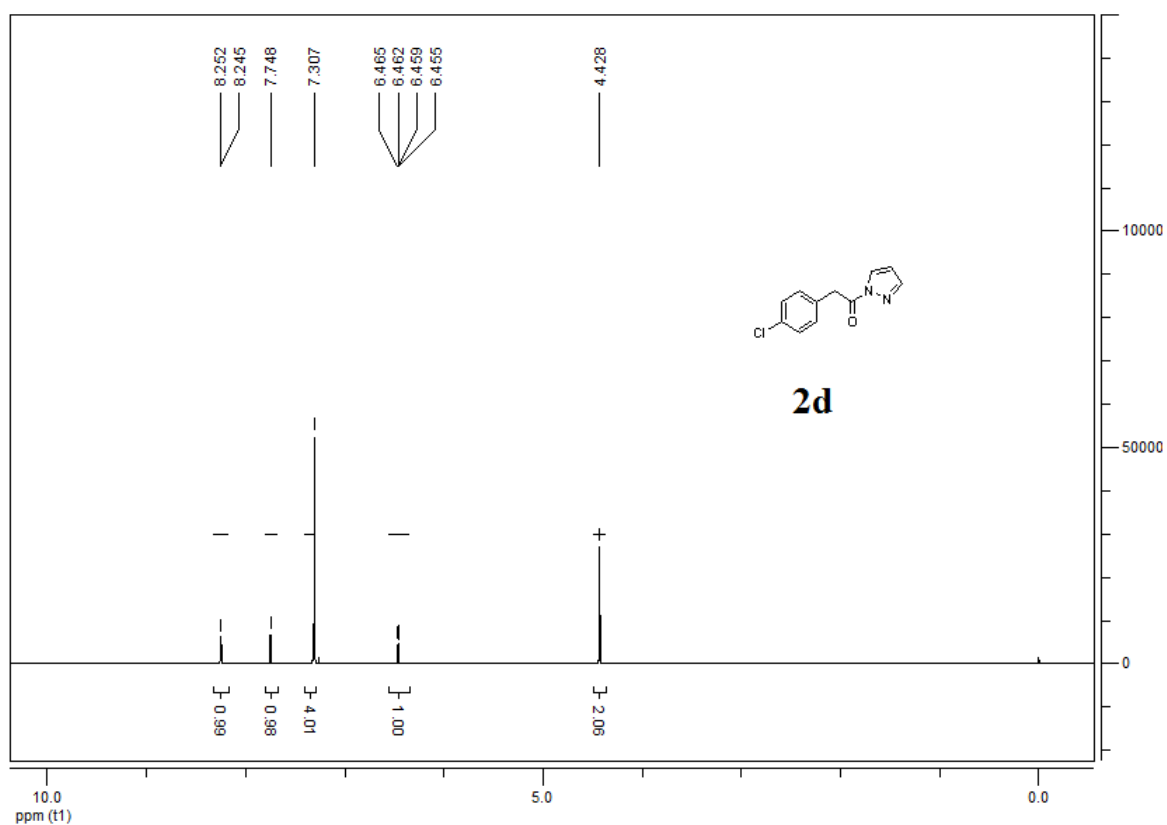


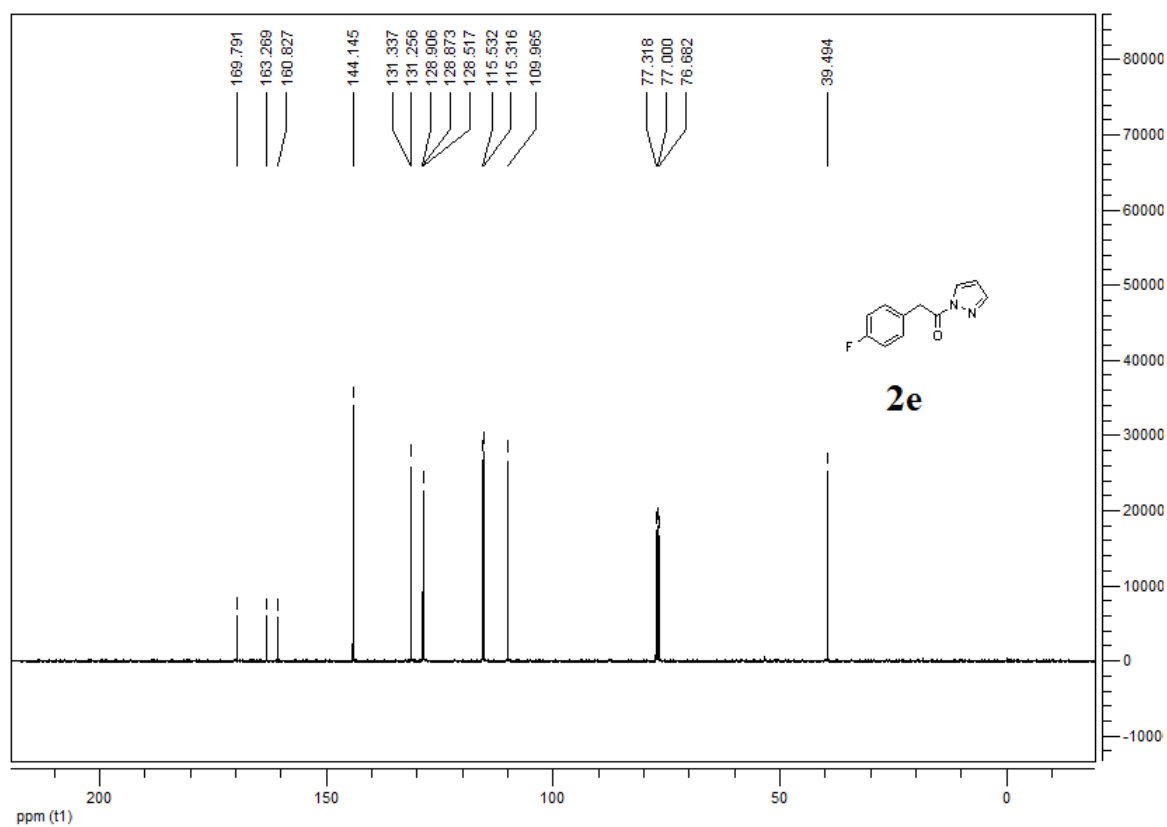
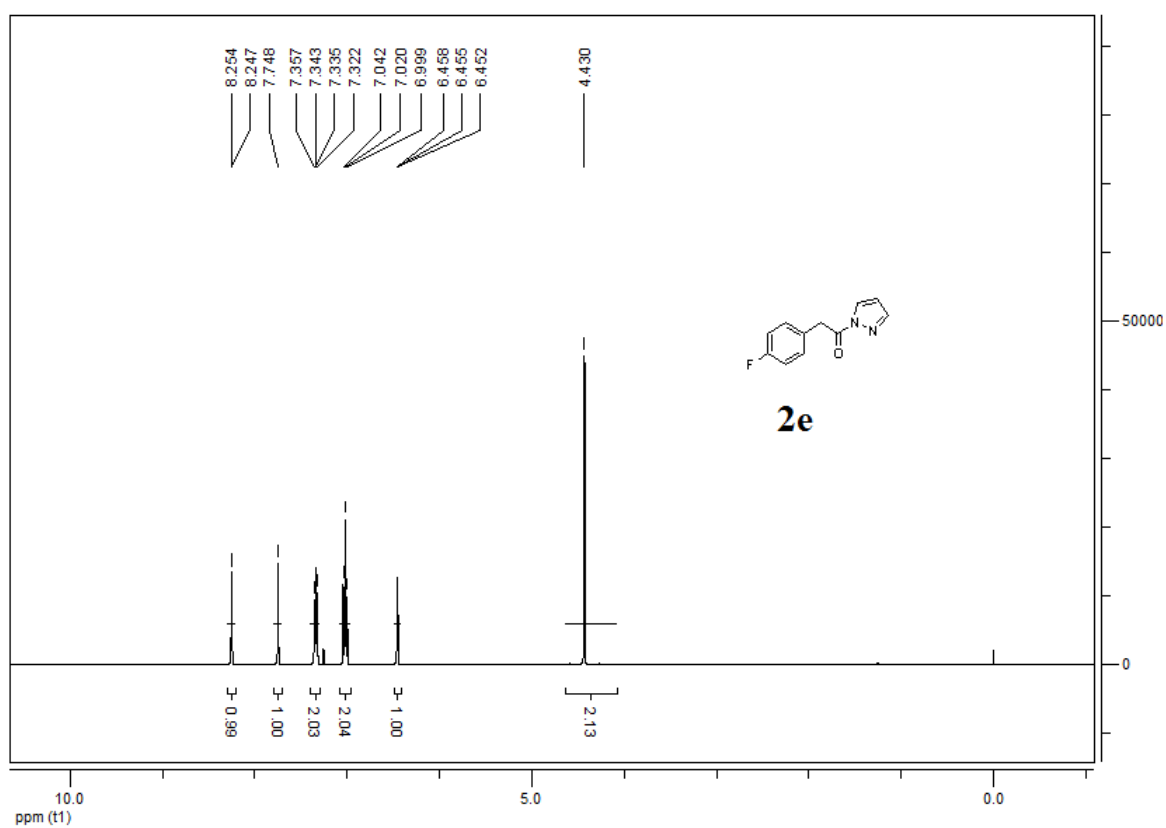
3. NMR Spectra of the Substrates

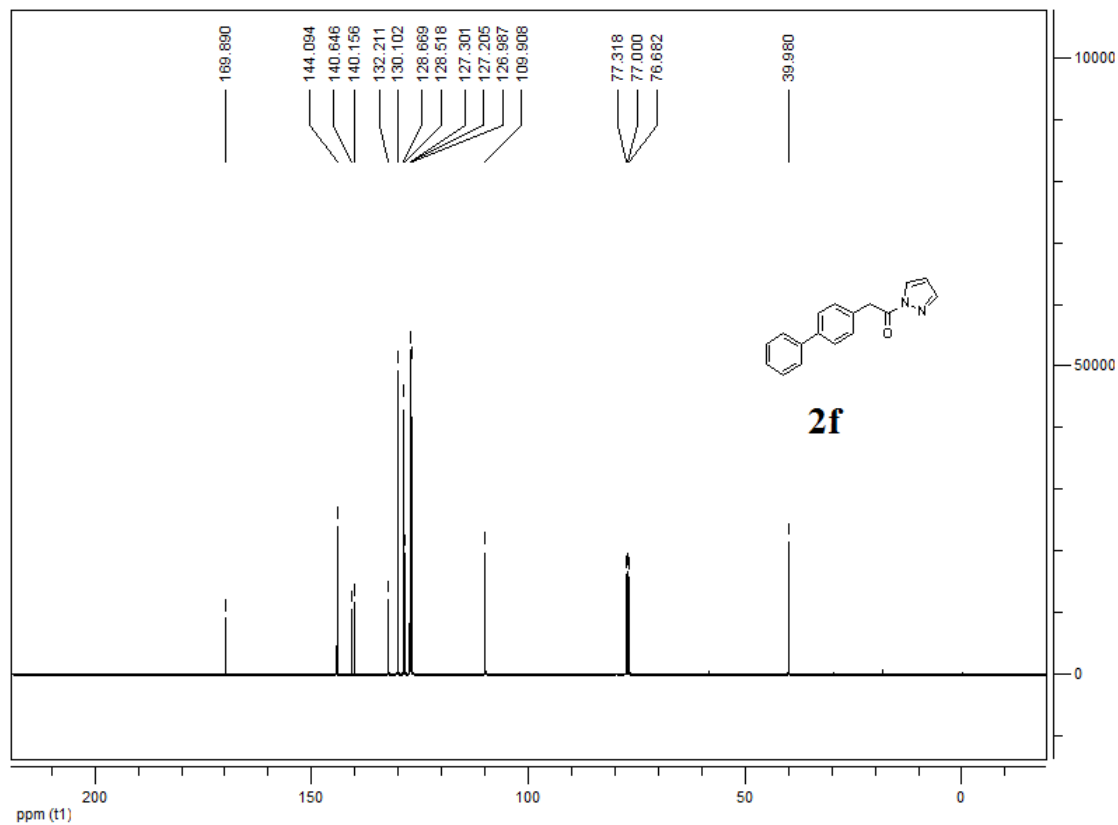
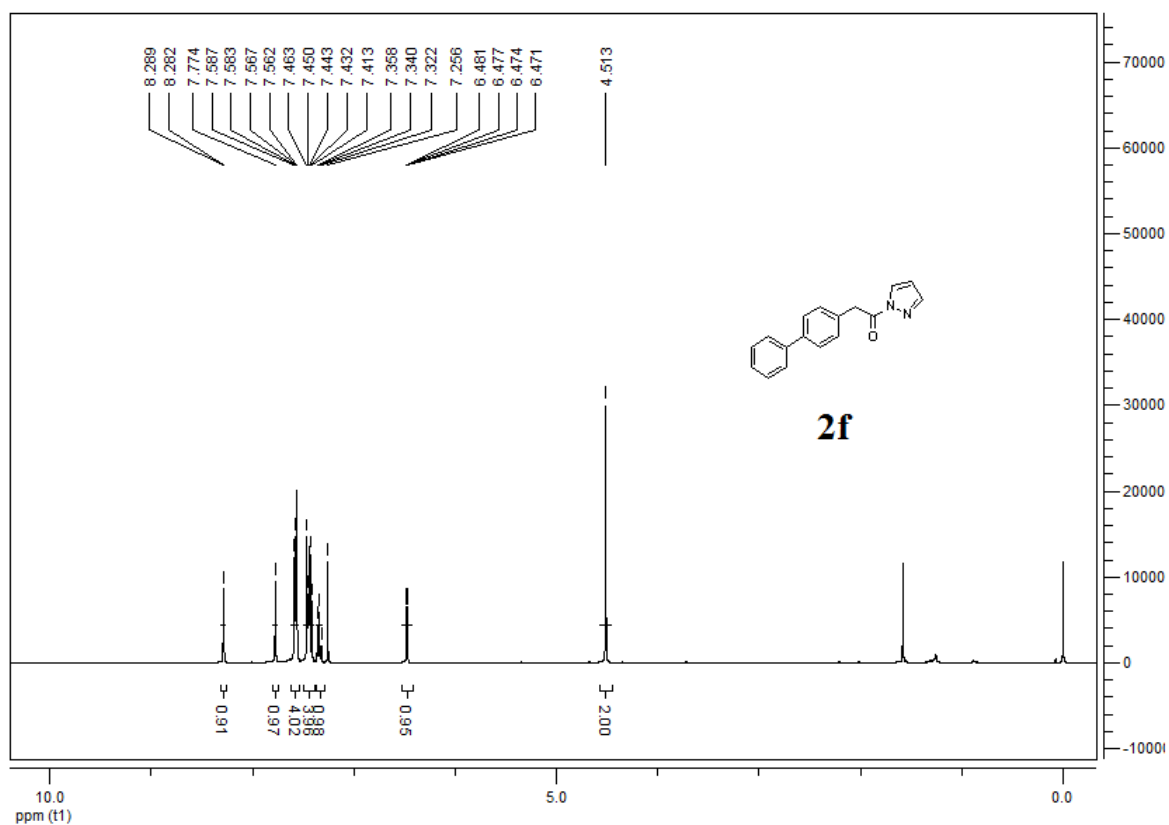


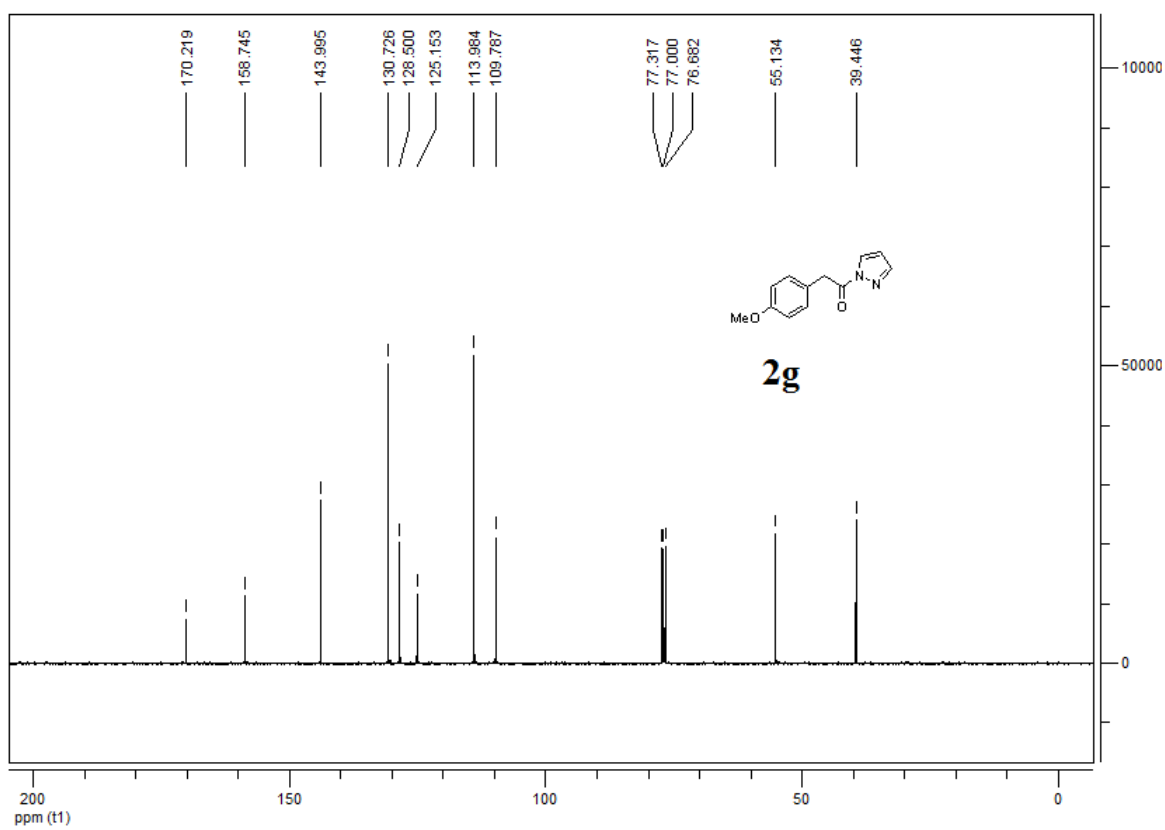
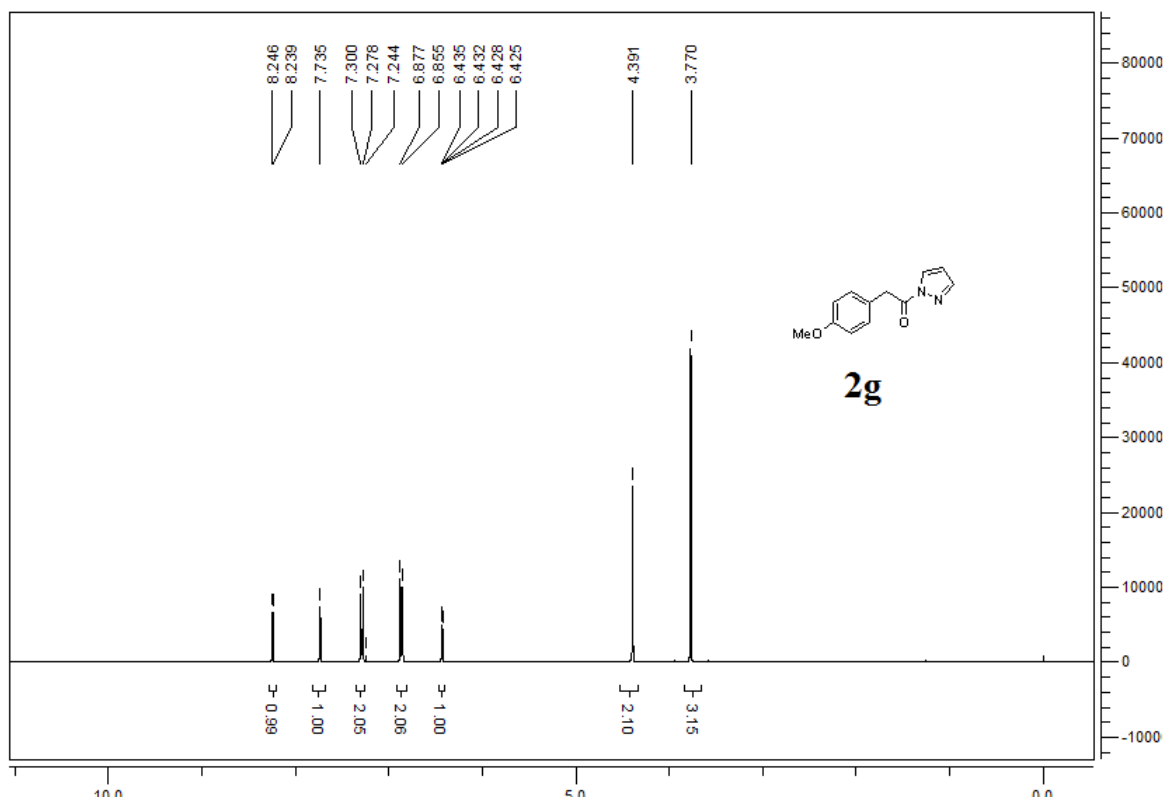


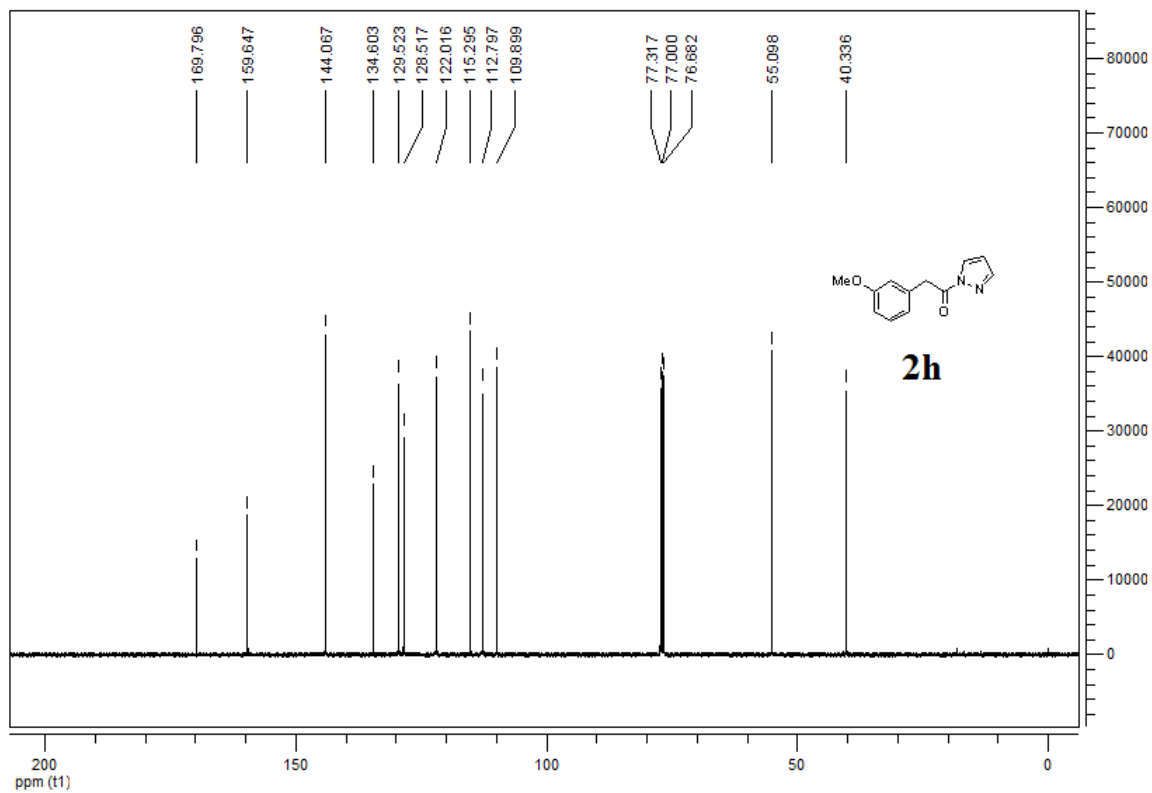
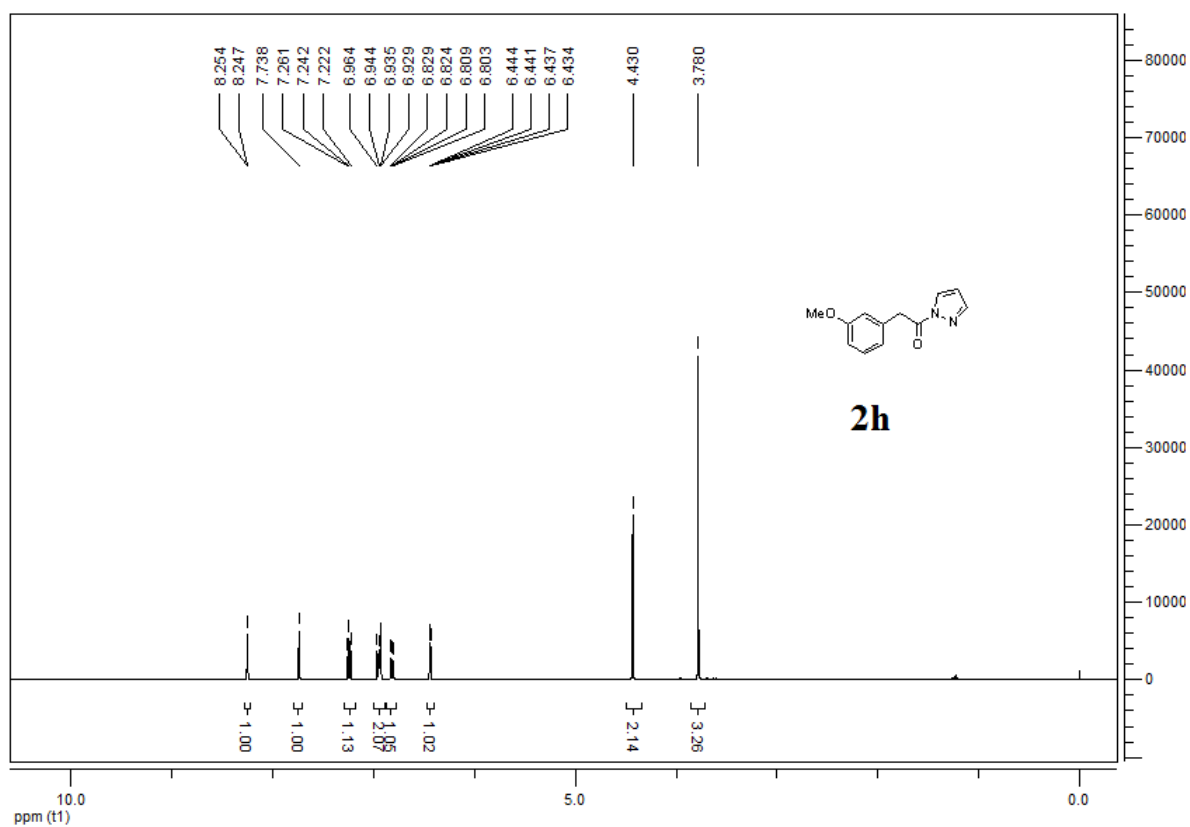


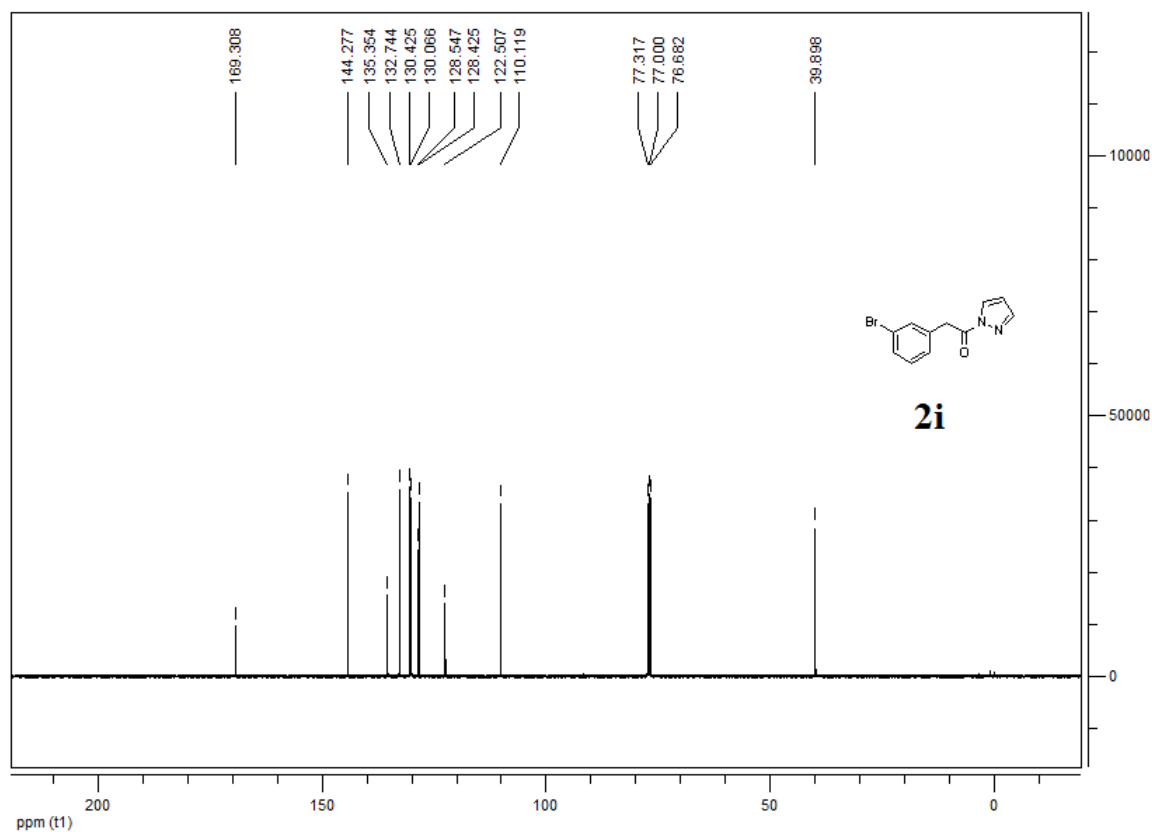
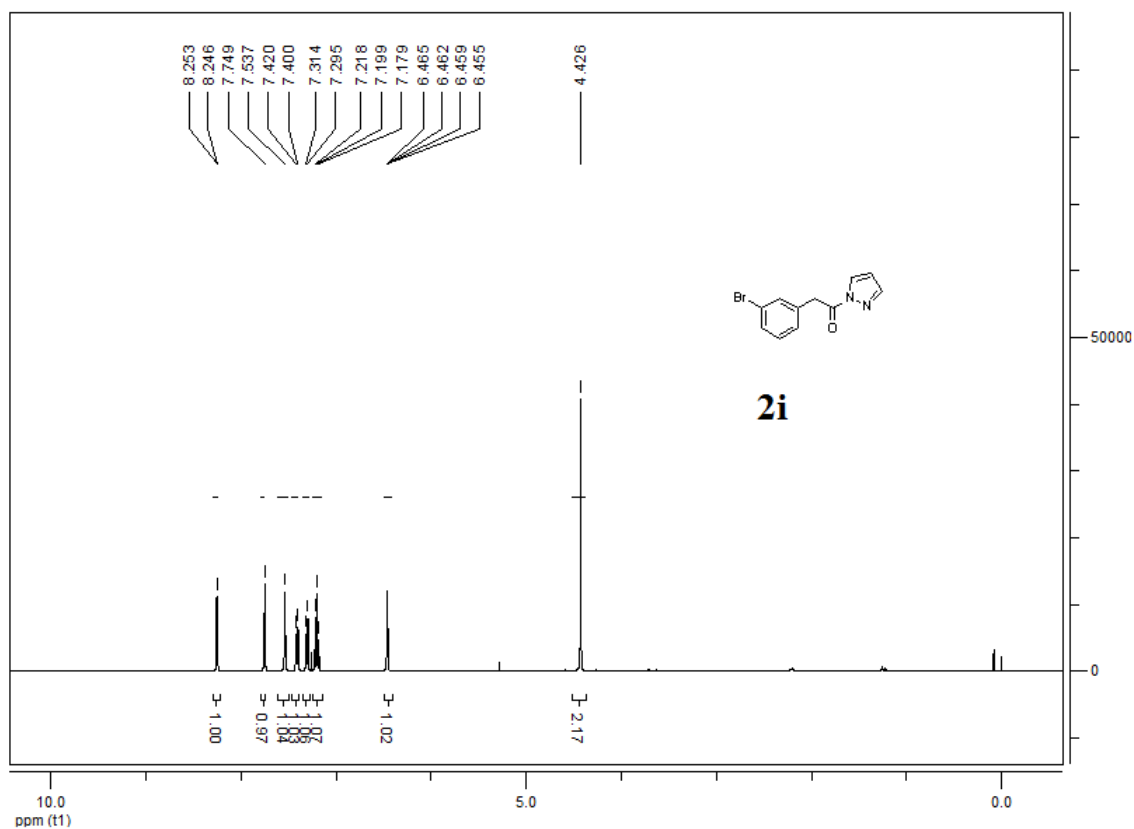


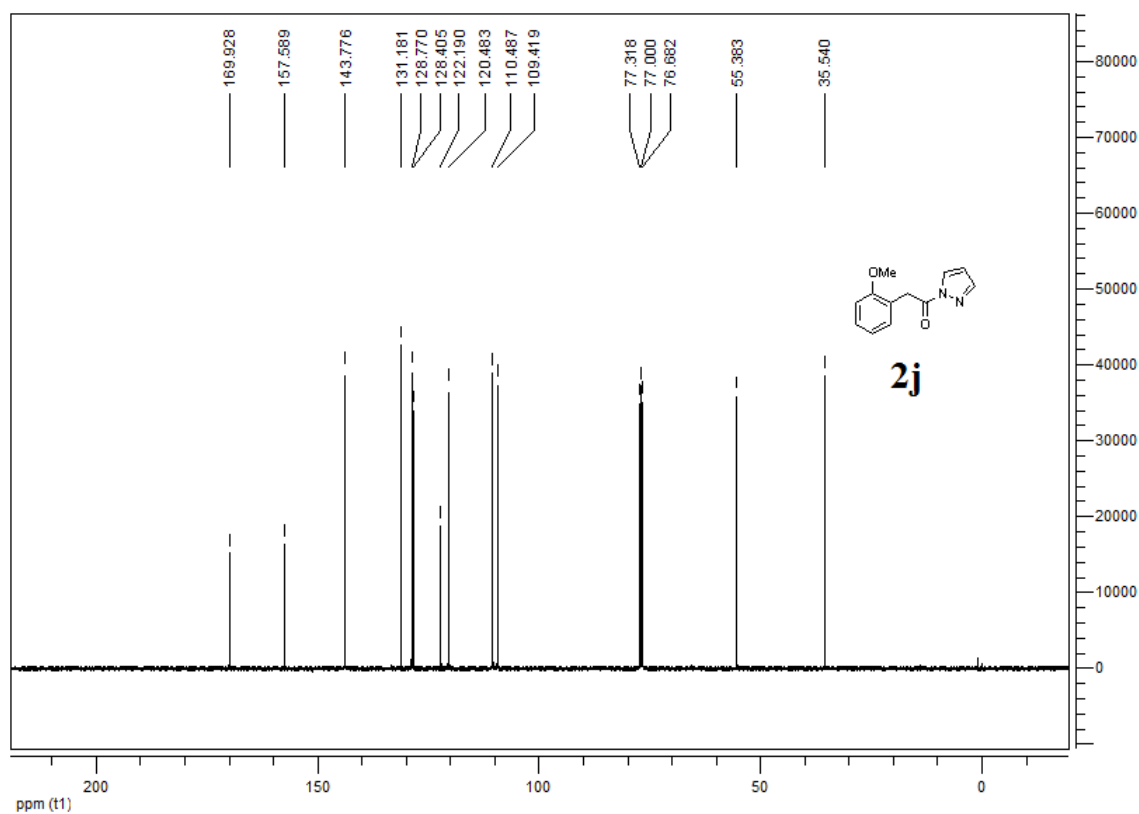
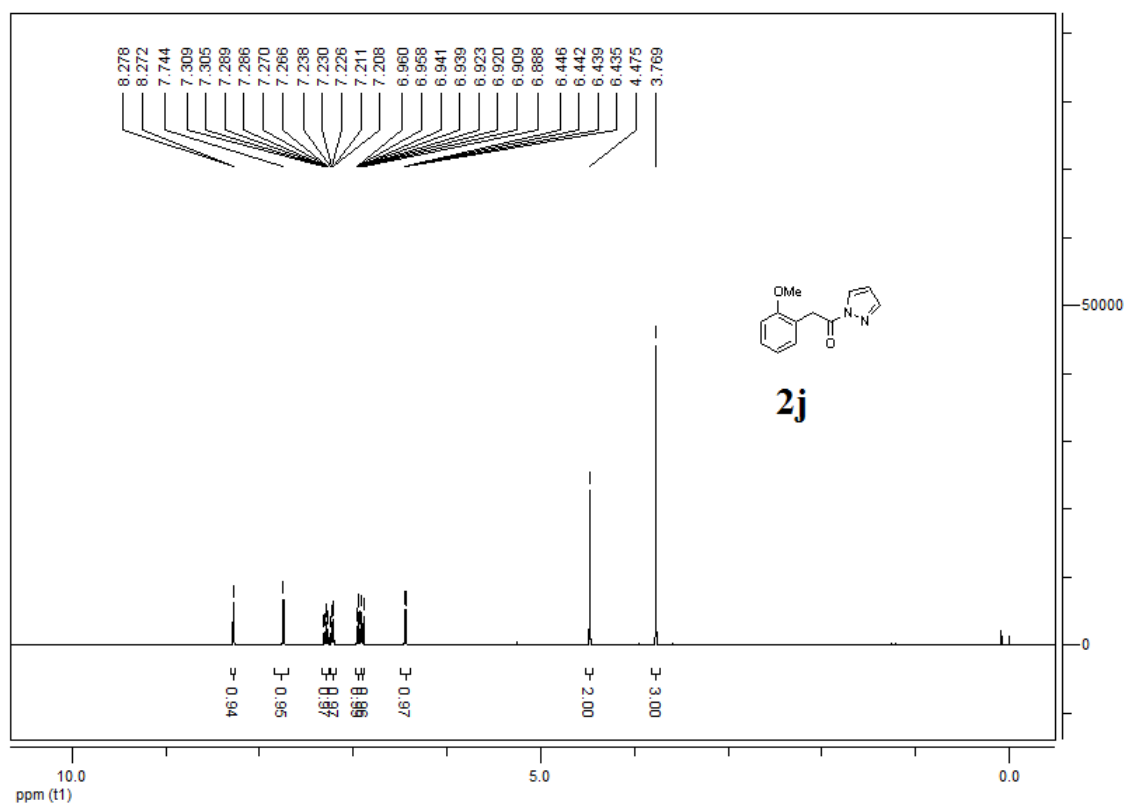


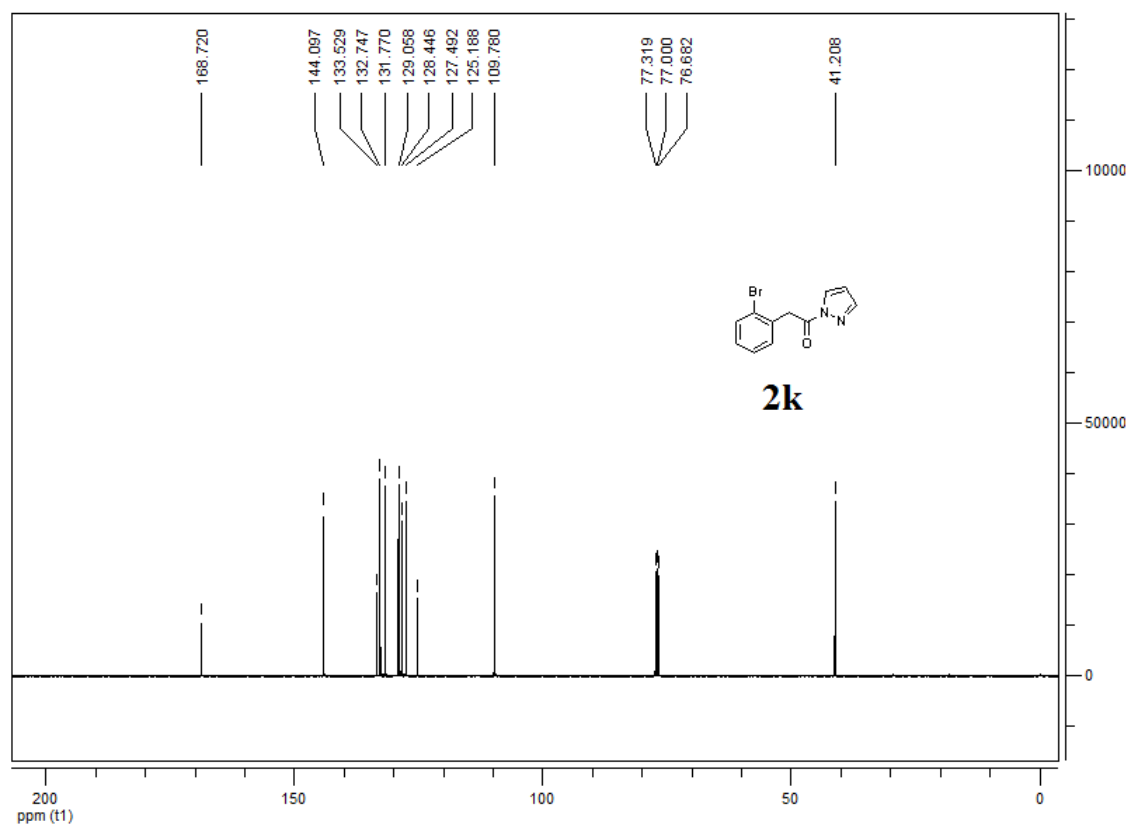
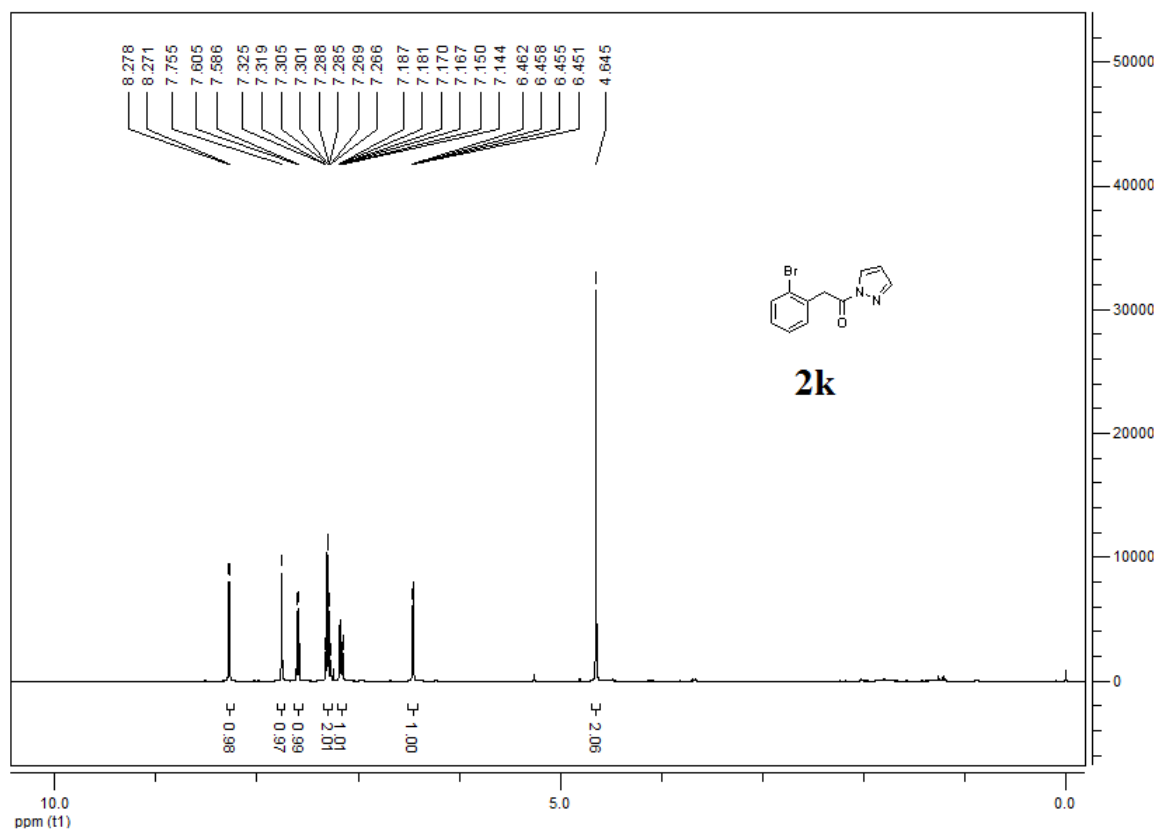


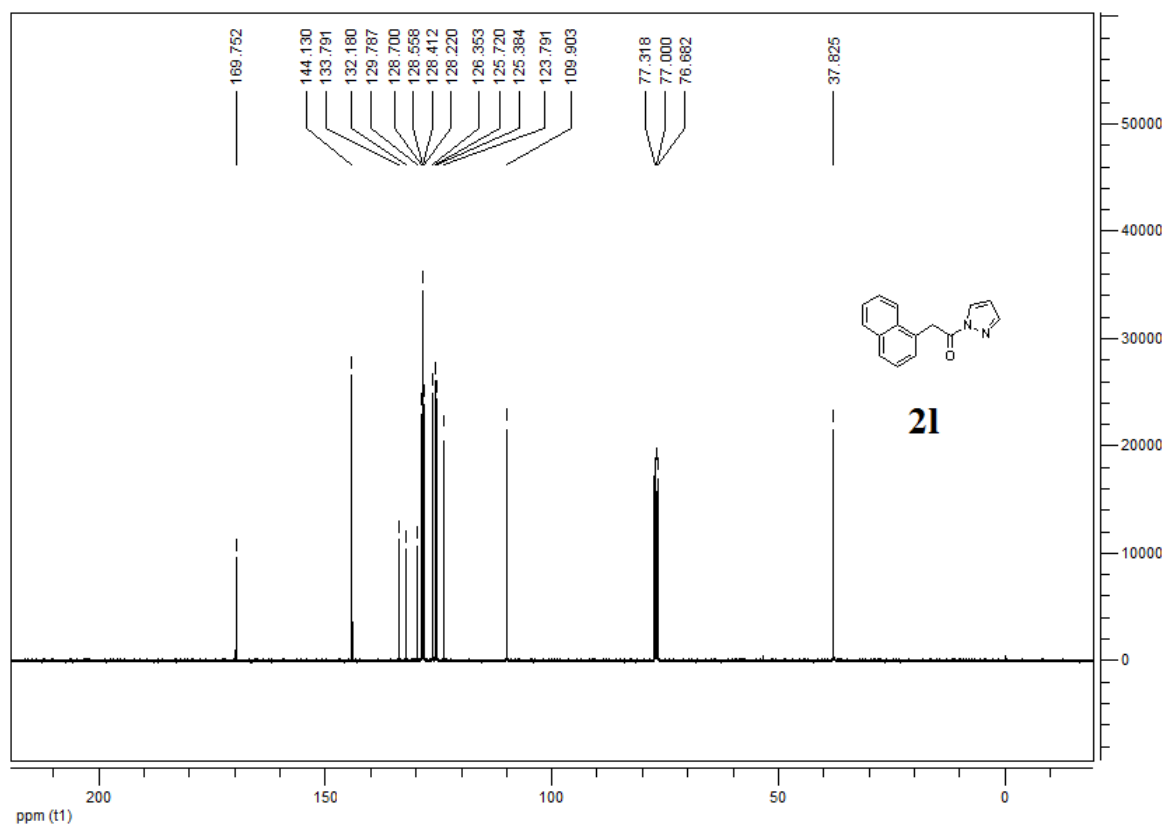
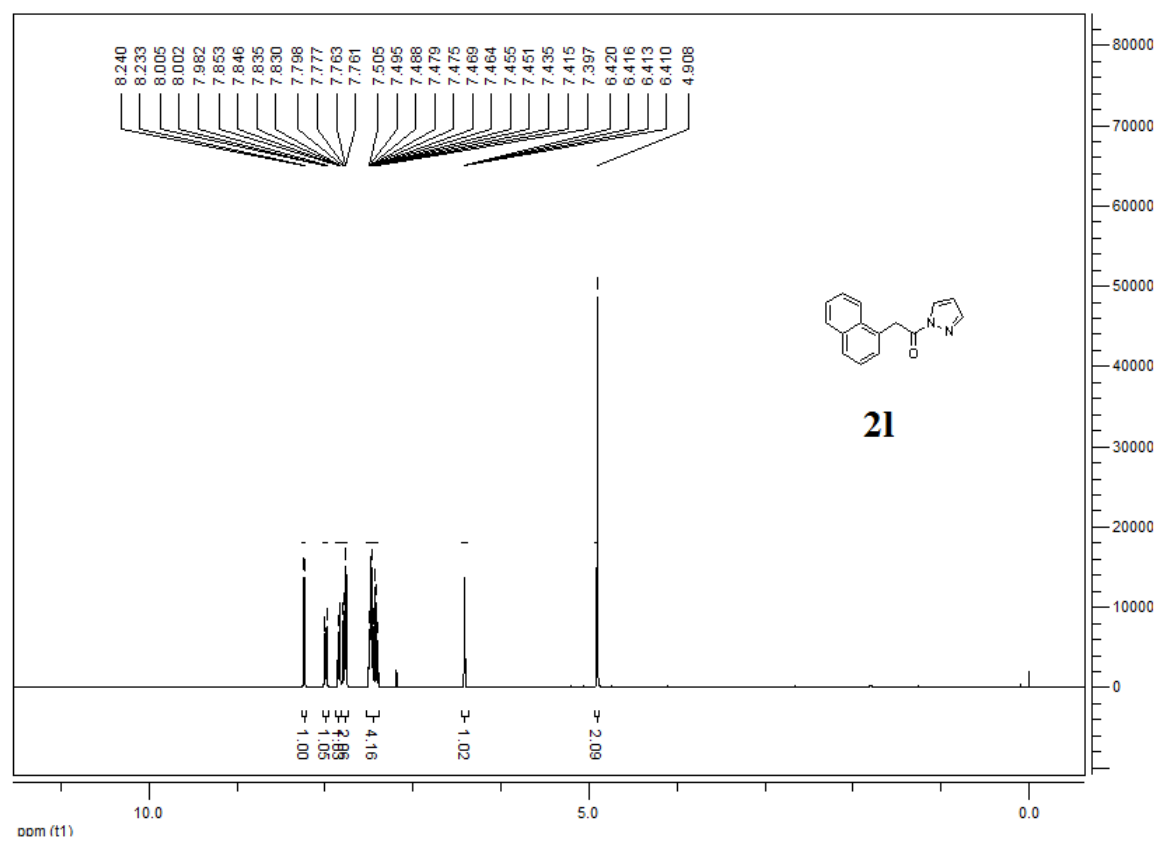


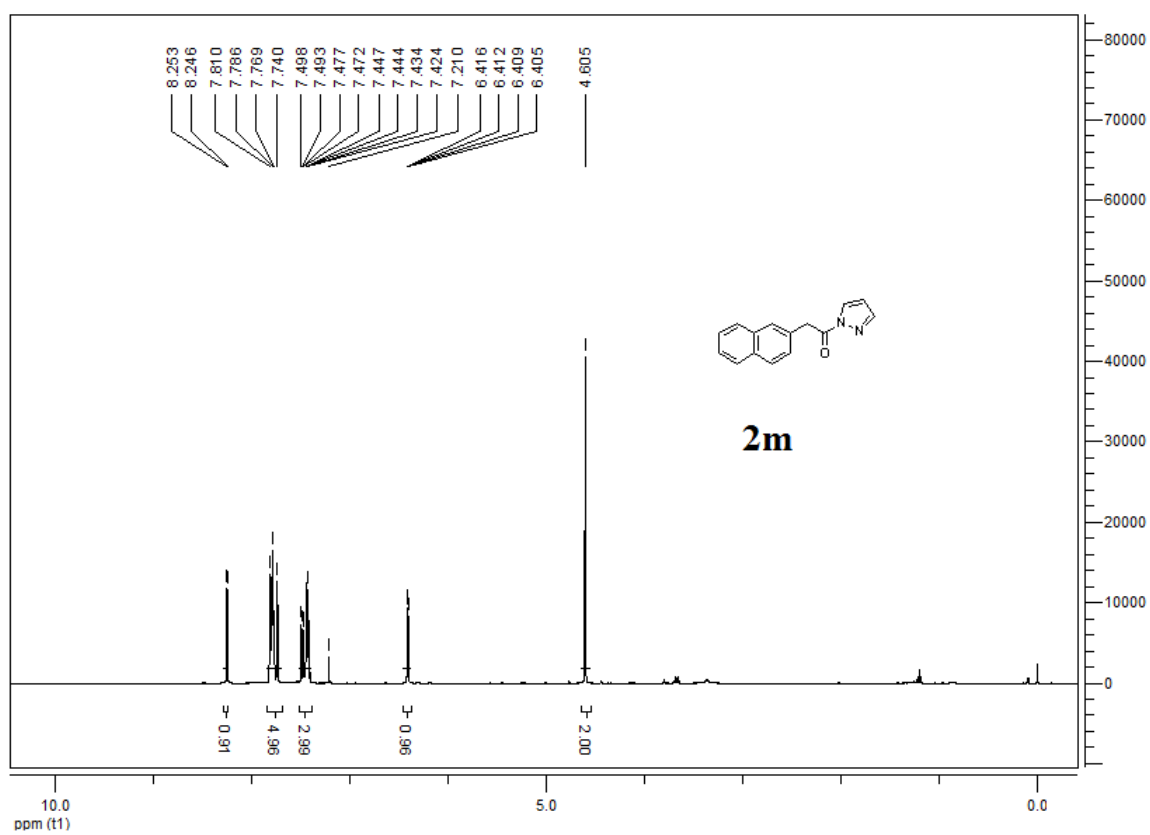
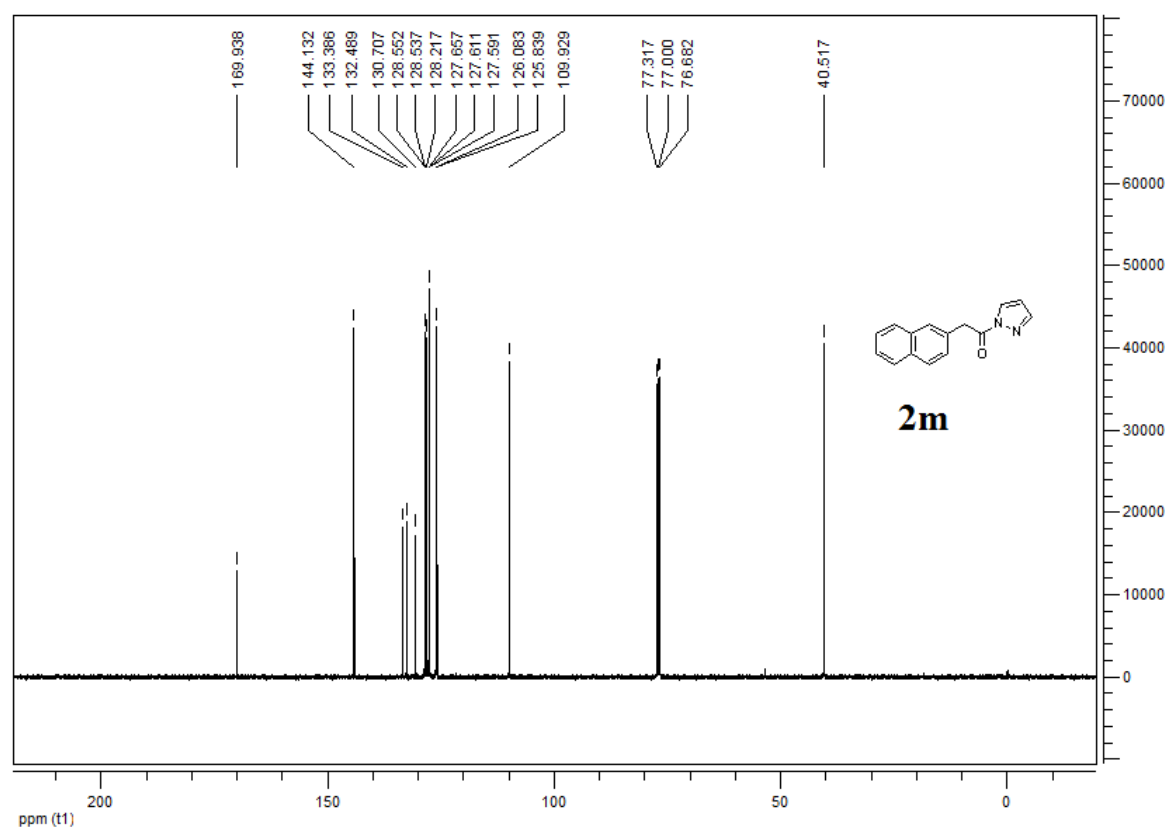


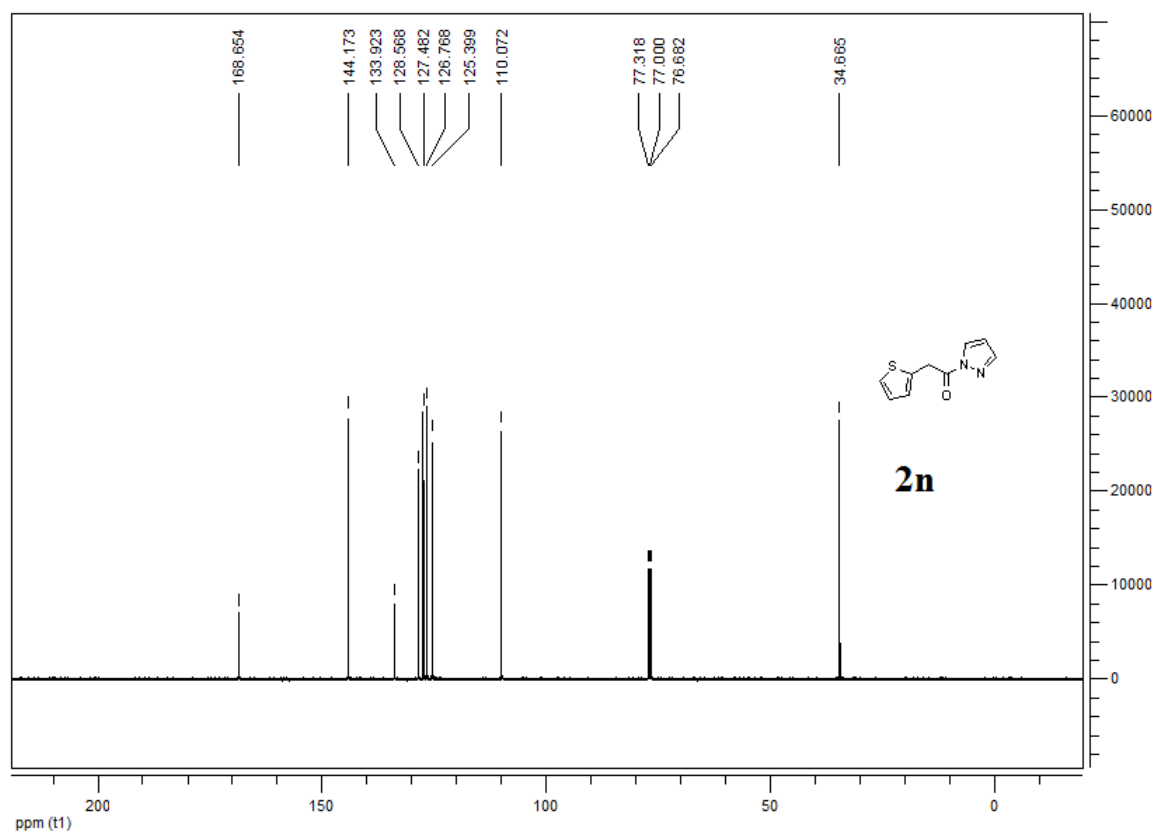
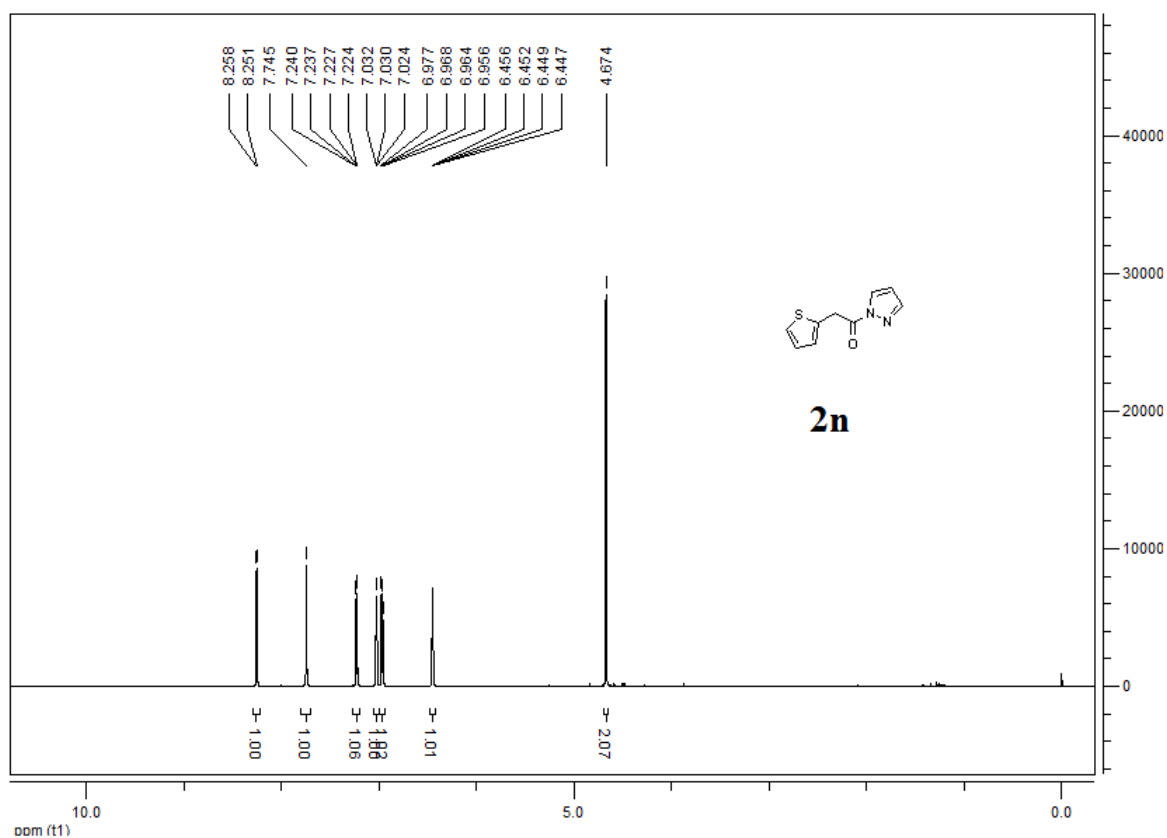




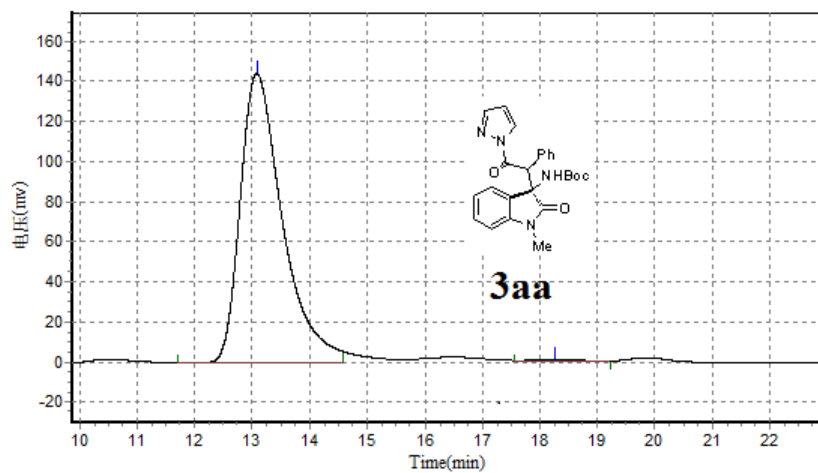




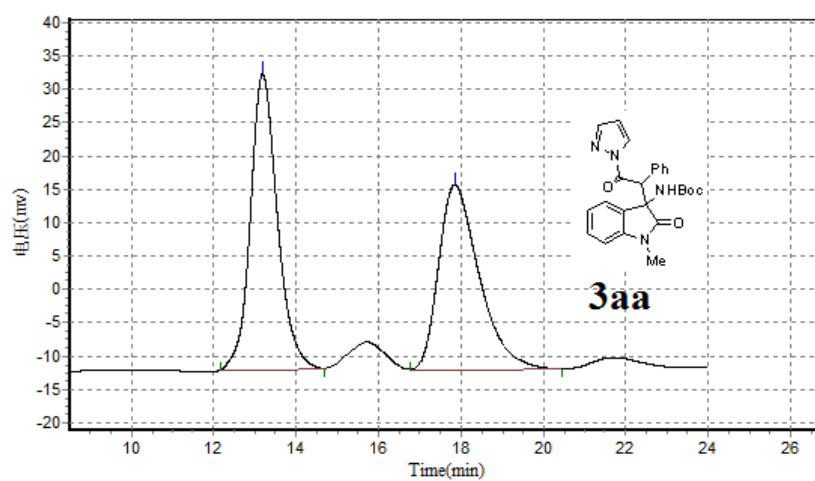




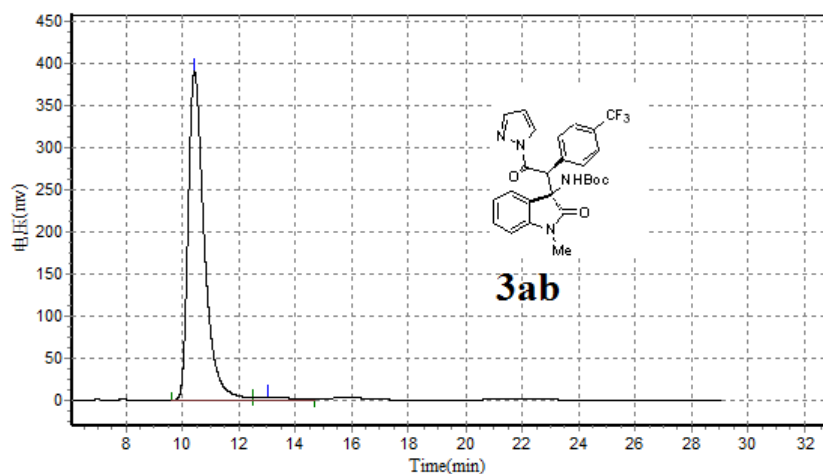
4. HPLC Charts of the Mannich Reaction Products



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.080	144223.922	7349978.000	99.6565
2		18.258	541.182	25330.746	0.3435
Total			144765.104	7375308.746	100.0000

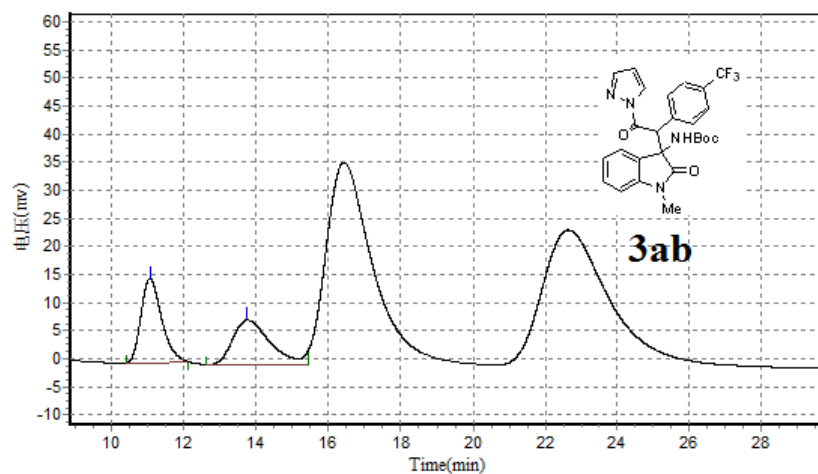


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.190	44269.770	2015523.875	51.3298
2		17.832	27813.844	1911089.375	48.6702
Total			72083.613	3926613.250	100.0000



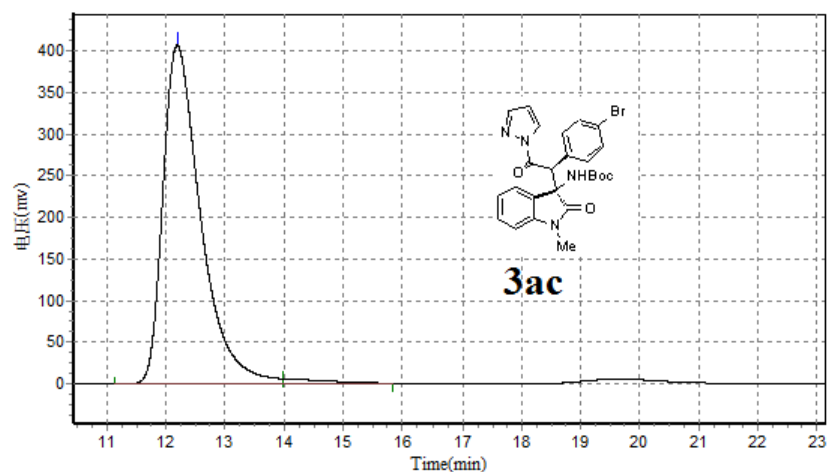
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.435	391041.531	15511843.000	97.9408
2		13.053	3728.632	326135.188	2.0592
Total			394770.163	15837978.188	100.0000



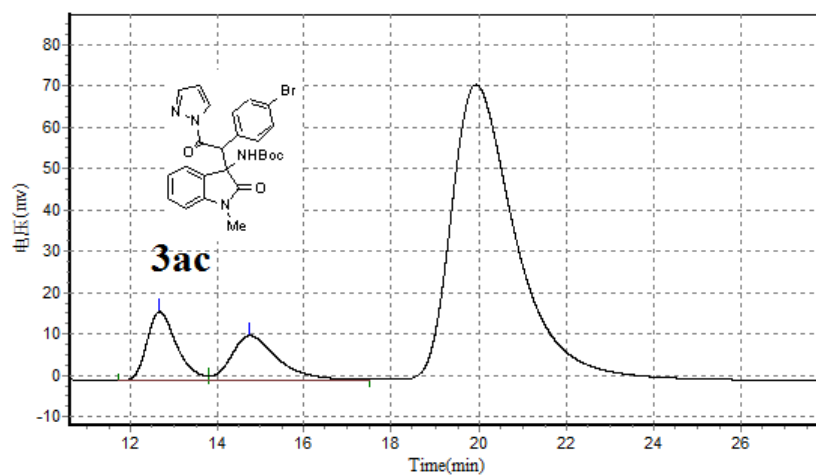
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.062	14981.388	590788.250	50.1226
2		13.768	7959.283	587898.375	49.8774
Total			22940.670	1178686.625	100.0000



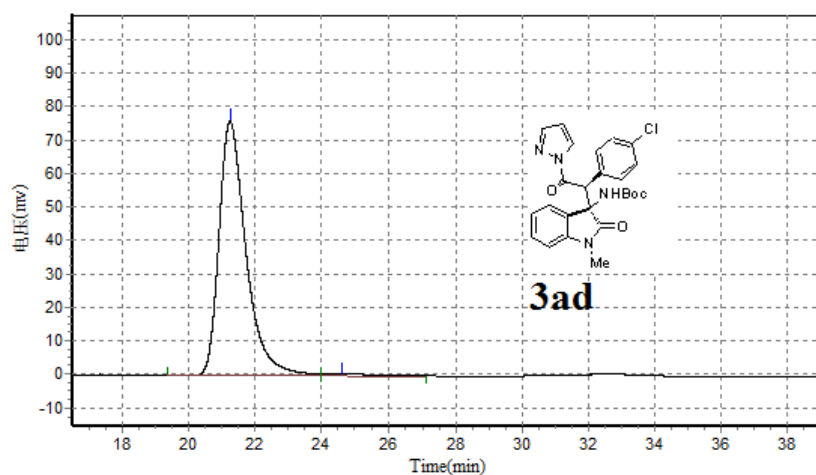
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.192	406046.063	18015472.000	98.5209
2		12.192	5760.822	270459.156	1.4791
Total			411806.884	18285931.156	100.0000



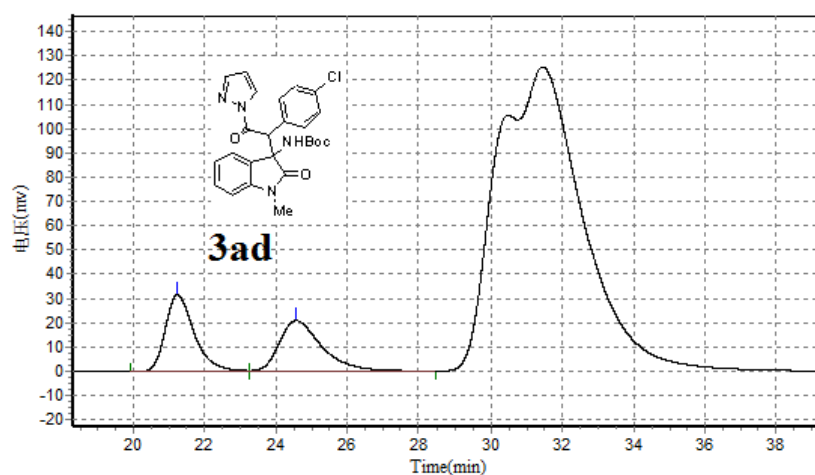
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.677	16696.004	793340.625	49.0058
2		14.752	10864.439	825530.188	50.9942
Total			27560.443	1618870.813	100.0000



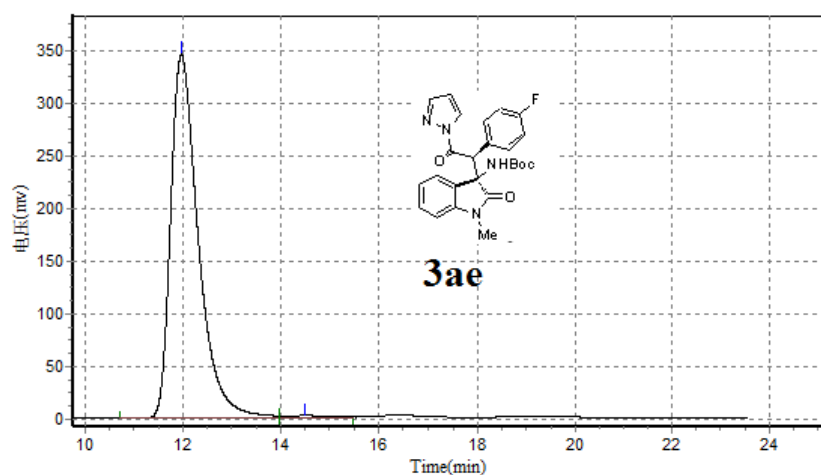
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.240	75954.922	4290024.500	98.6145
2		24.628	616.314	60273.641	1.3855
Total			76571.236	4350298.141	100.0000



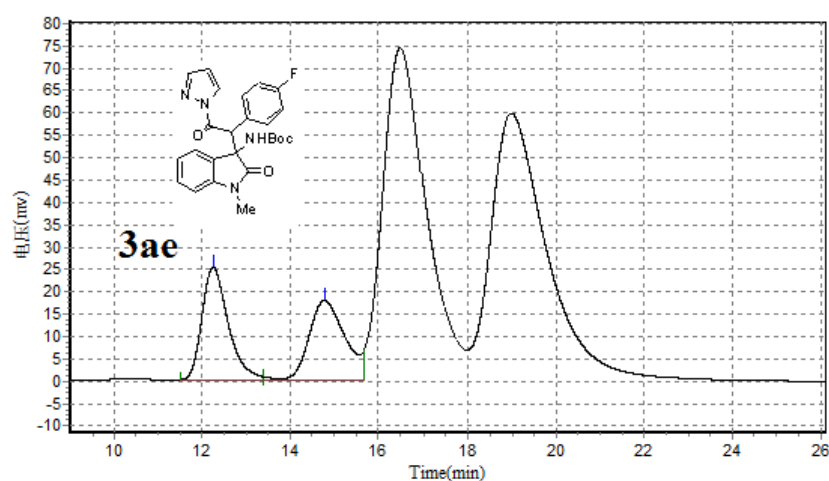
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.240	31795.576	1796049.125	50.5376
2		24.568	20983.129	1757839.250	49.4624
Total			52778.705	3553888.375	100.0000



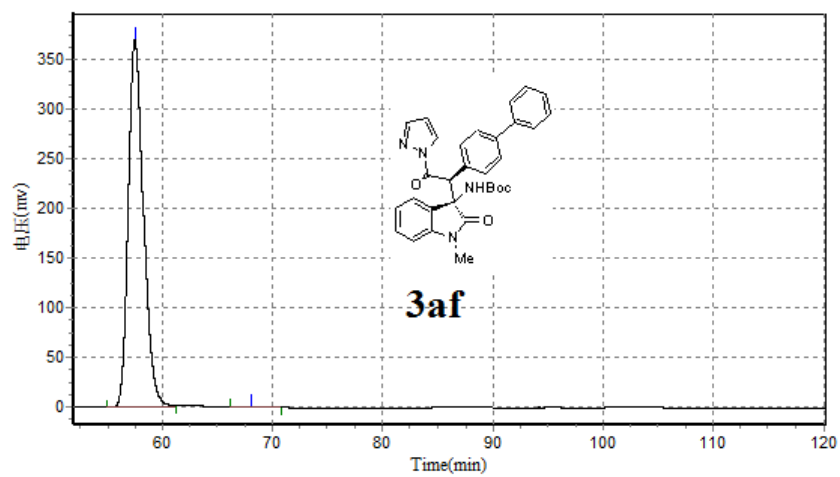
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.972	345871.219	13600212.000	98.7772
2		14.503	2472.705	168364.922	1.2228
Total			348343.924	13768576.922	100.0000



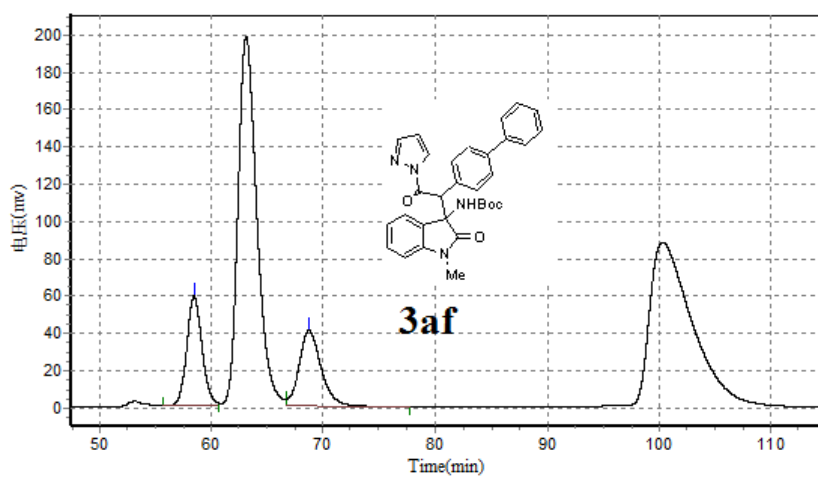
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.252	25209.607	1038280.813	50.4219
2		14.778	17789.211	1020905.750	49.5781
Total			42998.818	2059186.563	100.0000



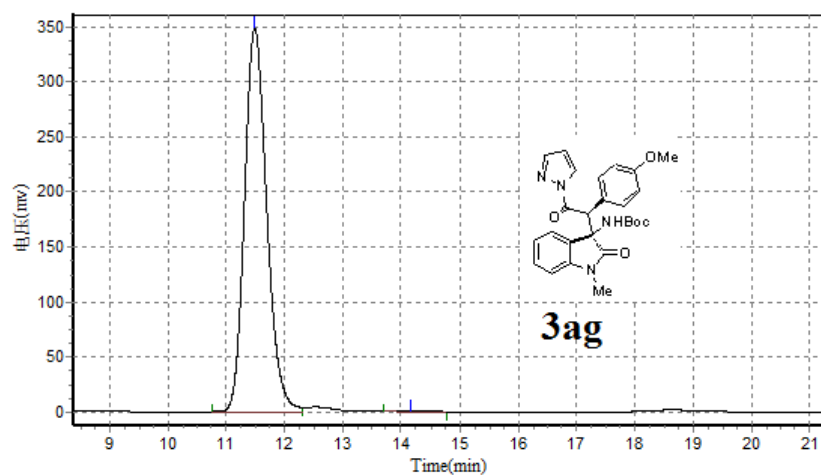
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.507	369306.938	35529720.000	99.6185
2		68.103	1080.160	136060.609	0.3815
Total			370387.097	35665780.609	100.0000



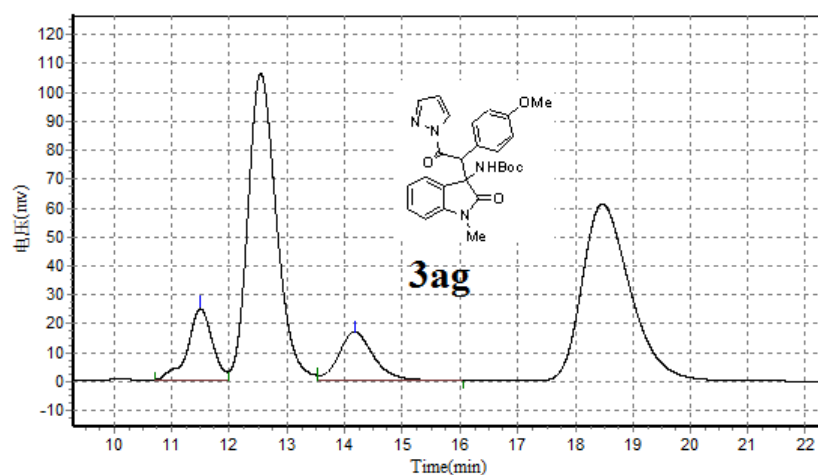
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		58.475	58582.805	5517898.000	49.7225
2		68.768	40698.969	5579481.000	50.2775
Total			99281.773	11097379.000	100.0000



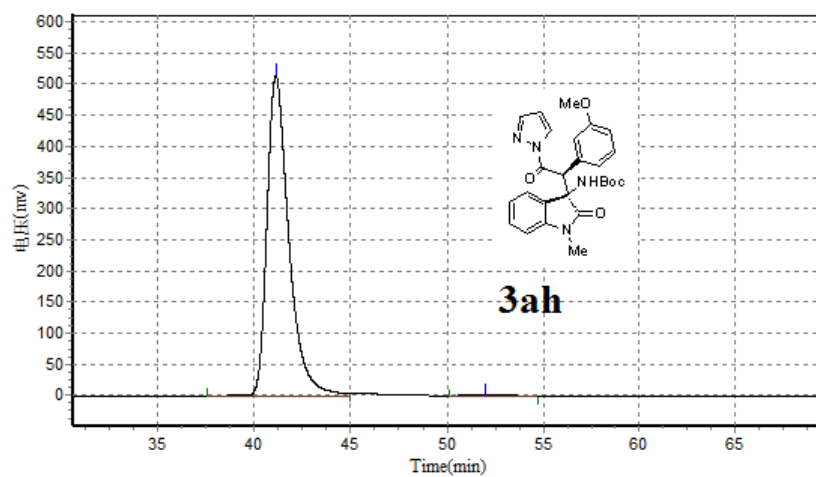
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.493	347824.219	9199239.000	99.6148
2		14.172	1076.487	35574.551	0.3852
Total			348900.705	9234813.551	100.0000



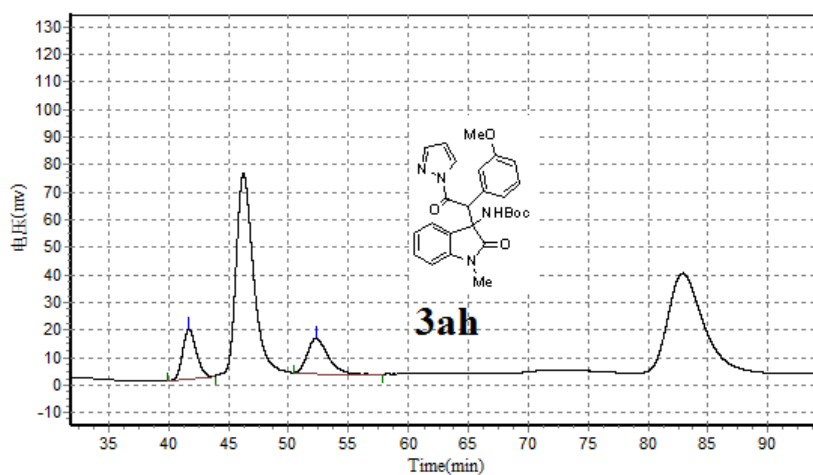
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.497	24679.506	733807.375	50.6861
2		14.177	16900.971	713942.625	49.3139
Total			41580.477	1447750.000	100.0000



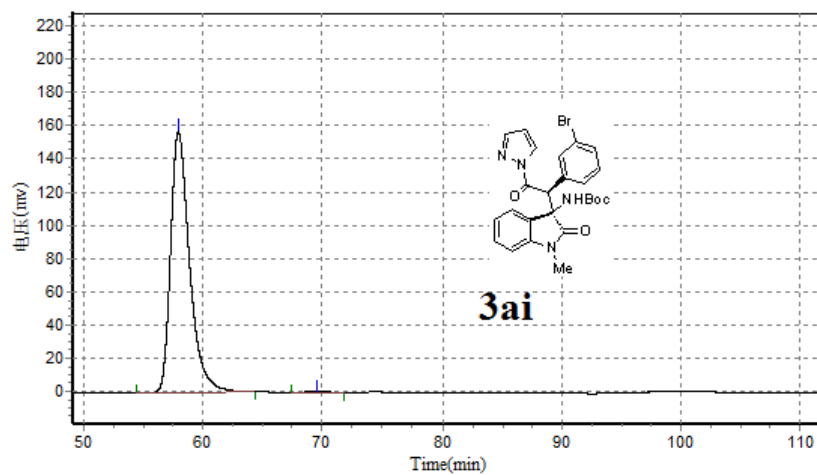
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.127	513169.281	40650796.000	99.3400
2		52.003	2171.389	270092.906	0.6600
Total			515340.670	40920888.906	100.0000



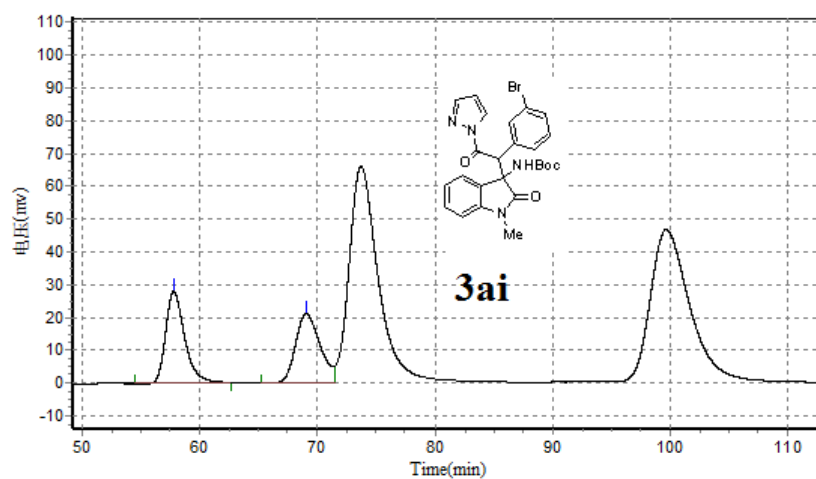
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		41.682	17886.711	1392506.500	49.0346
2		52.327	12553.140	1447340.625	50.9654
Total			30439.851	2839847.125	100.0000



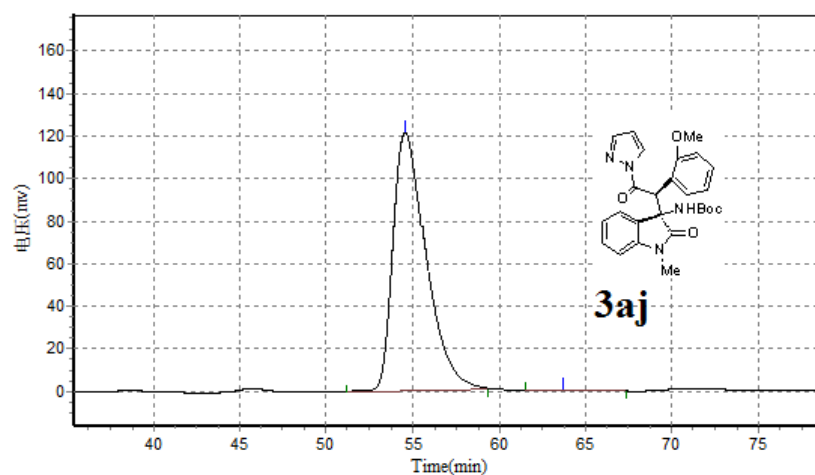
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.962	157002.516	17320852.000	99.4819
2		69.565	769.144	90204.445	0.5181
Total			157771.659	17411056.445	100.0000



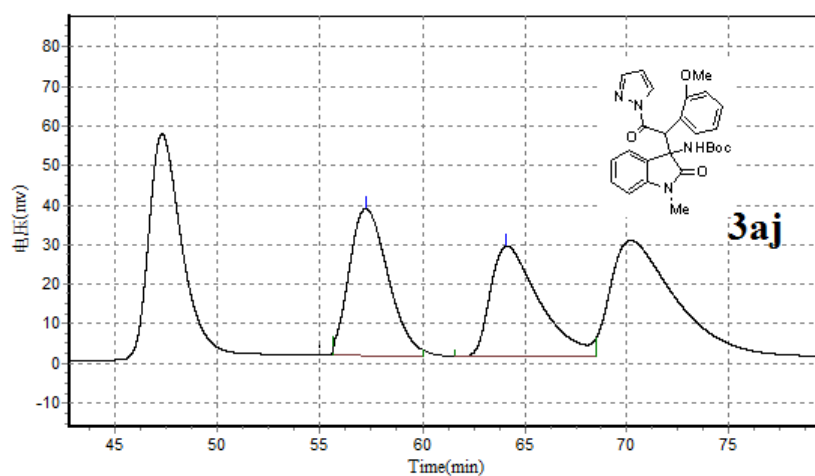
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.808	28045.840	3137643.500	50.9519
2		69.083	21146.602	3020410.250	49.0481
Total			49192.441	6158053.750	100.0000



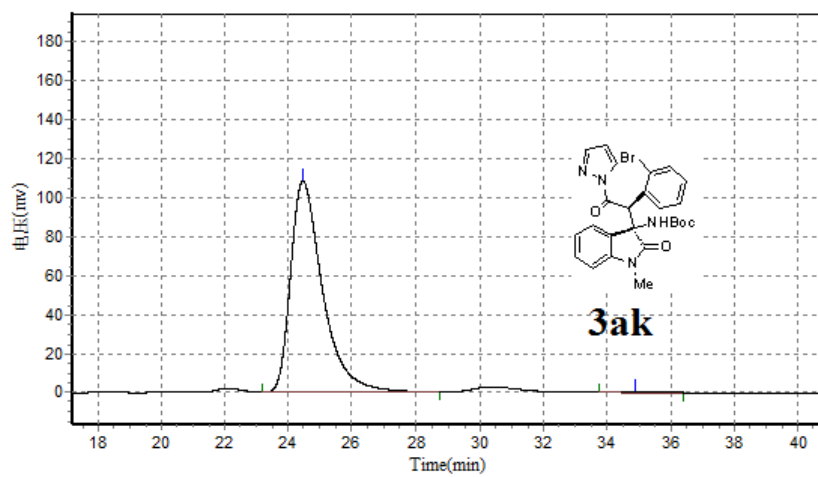
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		54.582	121094.406	15750881.000	99.5224
2		63.670	368.300	75595.453	0.4777
Total			121462.707	15826476.453	100.0000



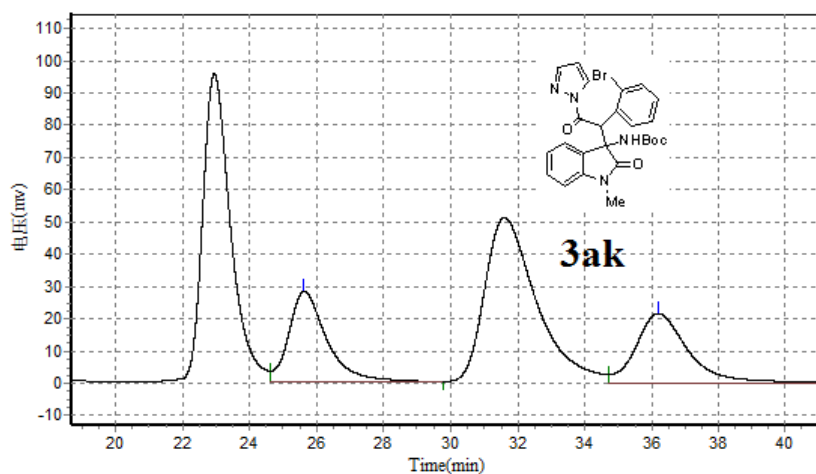
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		57.265	37060.344	4865567.500	50.8333
2		64.097	27984.734	4706052.000	49.1667
Total			65045.078	9571619.500	100.0000



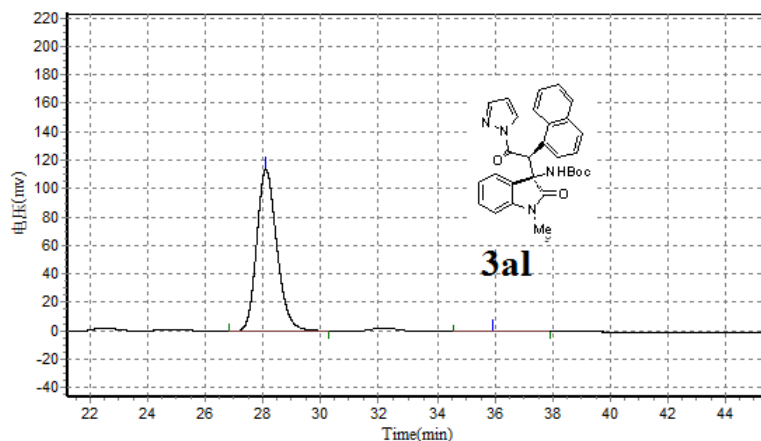
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.463	108255.836	7596203.000	99.4207
2		34.865	557.706	44260.551	0.5793
Total			108813.542	7640463.551	100.0000



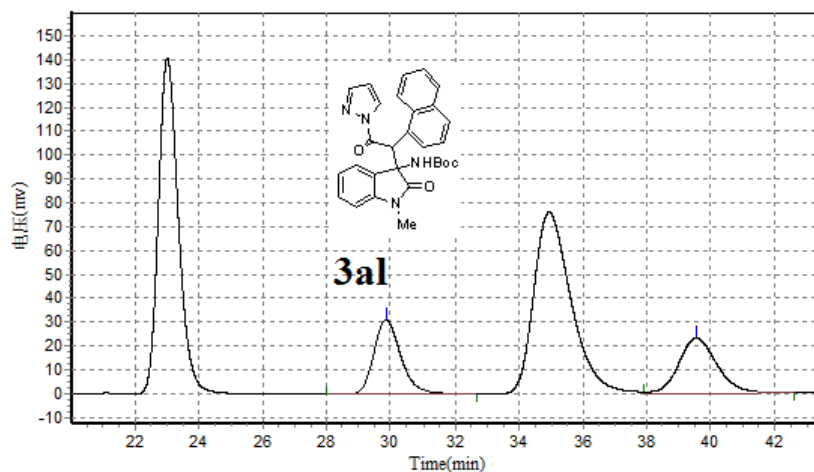
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.638	28175.814	2268745.500	49.0556
2		36.203	21429.094	2356097.250	50.9444
Total			49604.908	4624842.750	100.0000



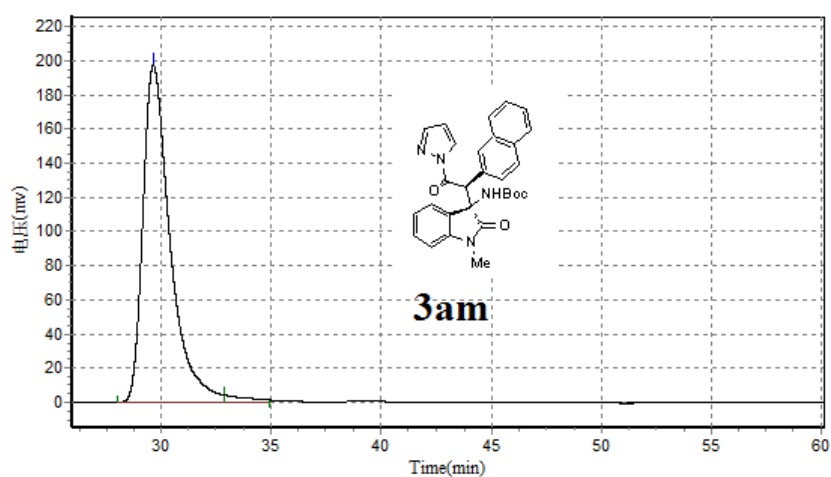
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.100	113918.672	5514124.500	99.1880
2		35.928	682.368	45140.902	0.8120
Total			114601.040	5559265.402	100.0000



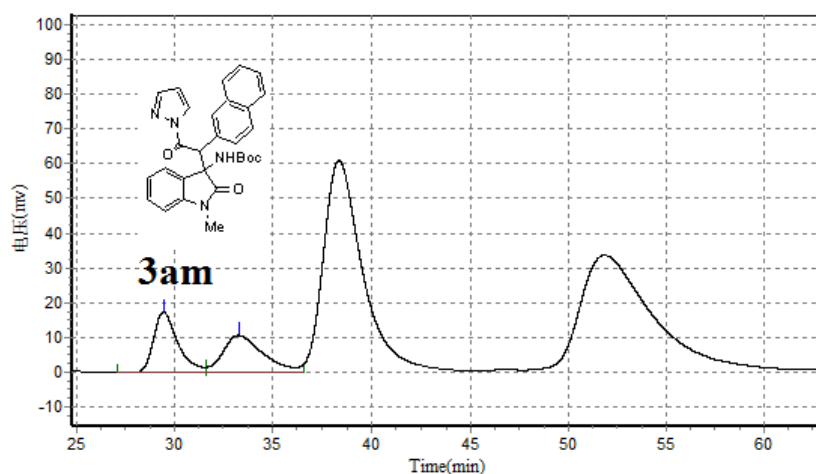
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.865	31383.375	1838636.125	49.3329
2		39.548	23053.072	1888359.250	50.6671
Total			54436.447	3726995.375	100.0000



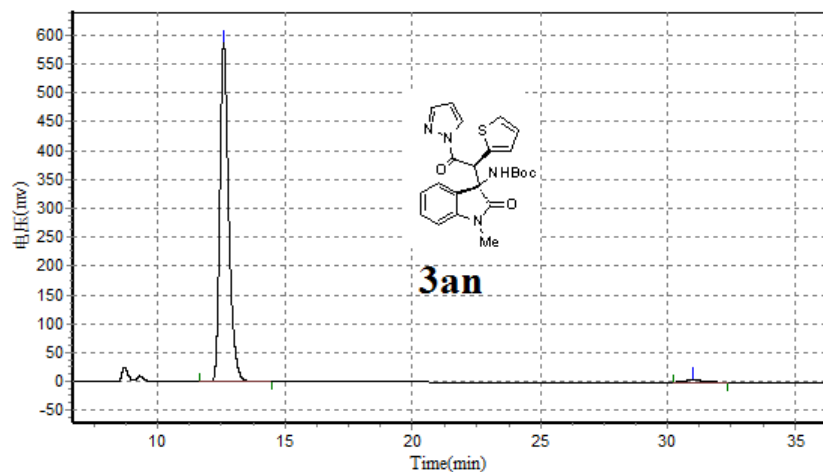
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.630	197480.234	16925818.000	98.3411
2		29.630	4031.164	285526.813	1.6589
Total			201511.398	17211344.813	100.0000



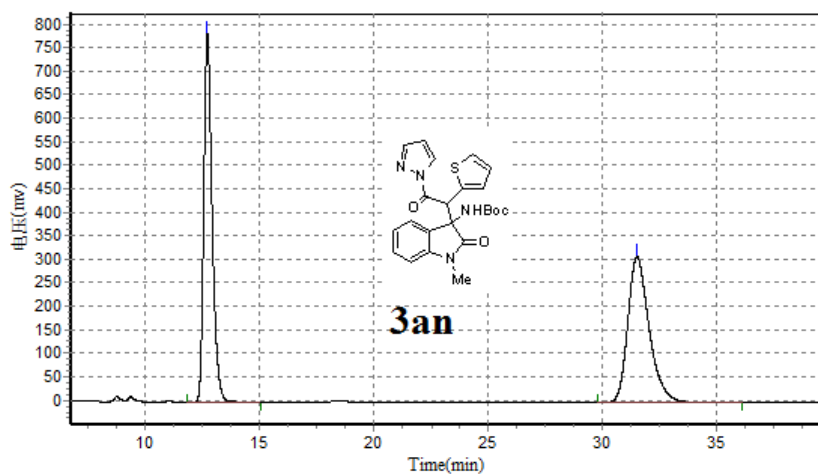
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.412	17375.686	1490376.500	49.4084
2		33.253	10665.614	1526065.625	50.5916
Total			28041.300	3016442.125	100.0000



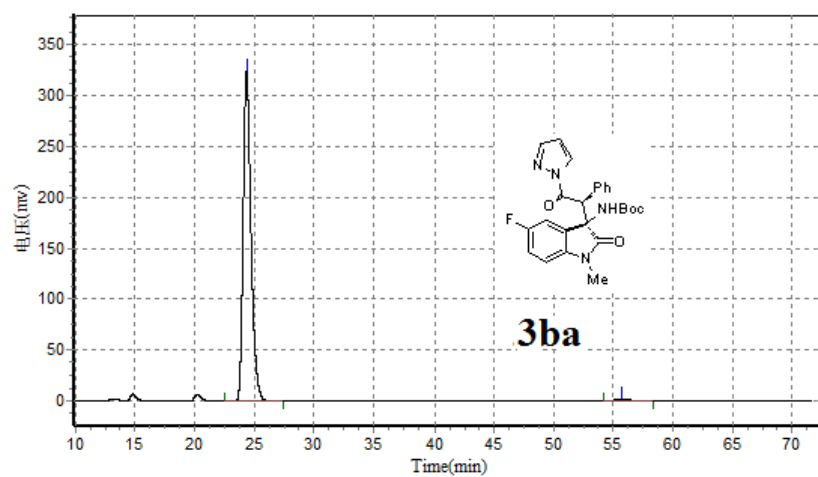
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.592	587520.813	14215262.000	98.4991
2		31.002	3851.405	216602.500	1.5009
Total			591372.218	14431864.500	100.0000



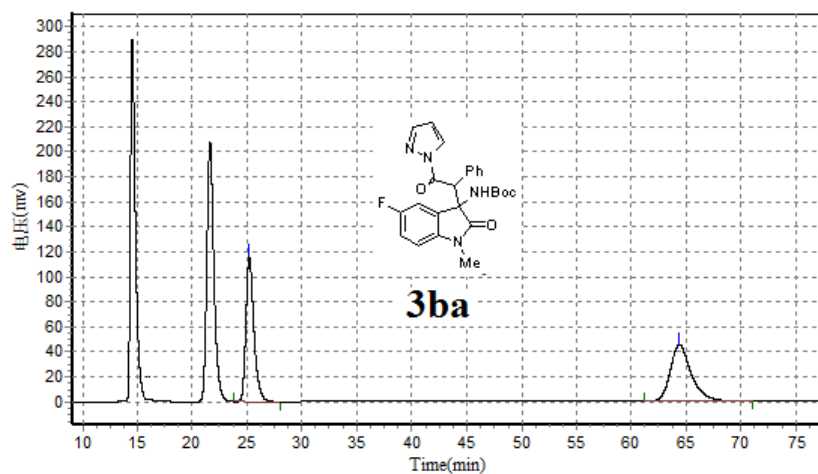
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.745	782935.125	19880966.000	49.8309
2		31.502	309527.281	20015928.000	50.1691
Total			1092462.406	39896894.000	100.0000



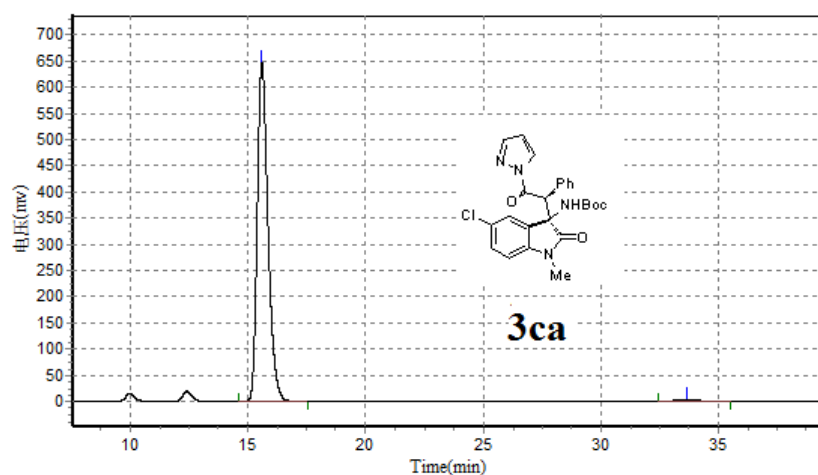
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.357	323389.906	14779873.000	99.1460
2		55.725	1371.484	127308.648	0.8540
Total			324761.391	14907181.648	100.0000



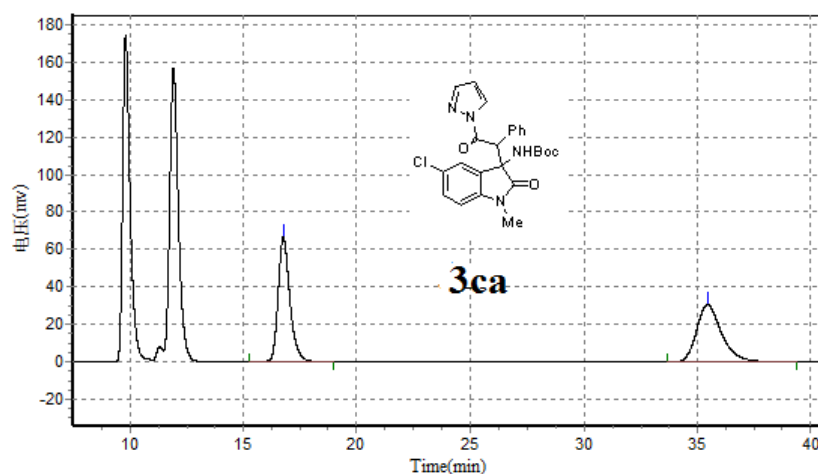
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.213	115670.977	5869661.500	50.0850
2		64.377	44798.813	5849740.500	49.9150
Total			160469.789	11719402.000	100.0000



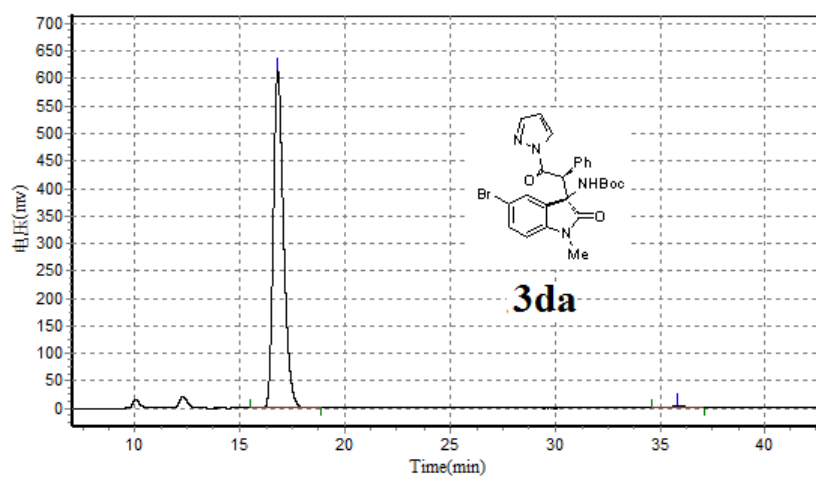
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.607	647160.750	20534046.000	98.9037
2		33.642	3401.000	227618.797	1.0963
Total			650561.750	20761664.797	100.0000



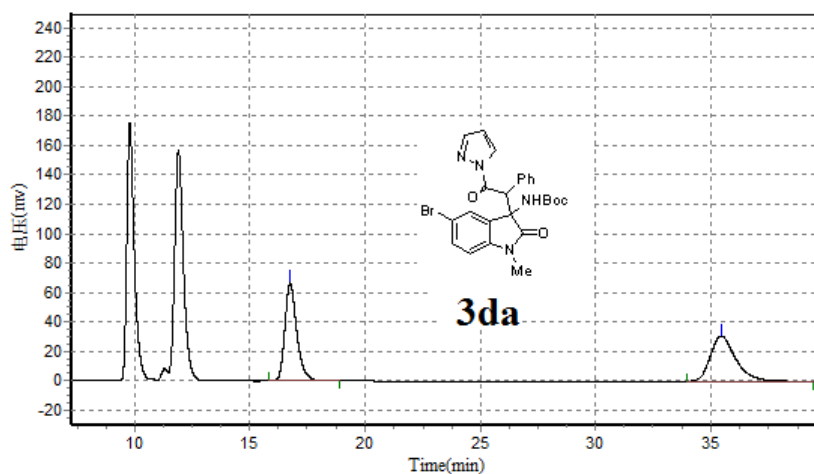
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.758	66500.641	2397215.000	50.3454
2		35.467	30612.209	2364322.250	49.6546
Total			97112.850	4761537.250	100.0000



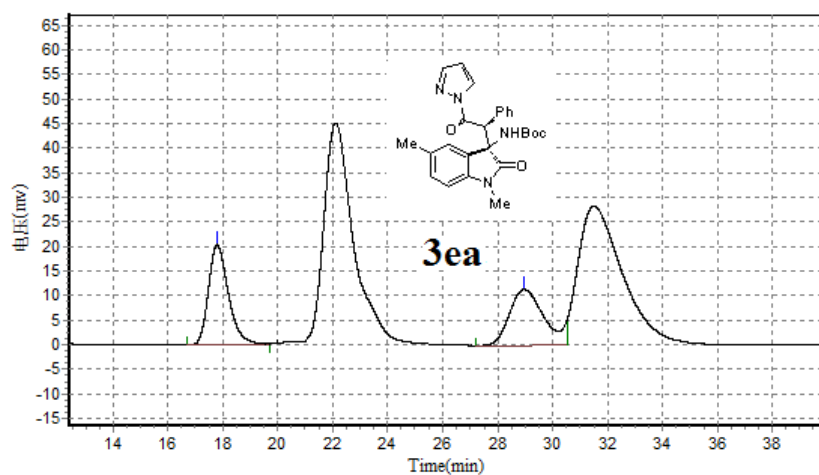
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.823	613627.688	20838696.000	99.0168
2		35.852	3089.965	206910.516	0.9832
Total			616717.652	21045606.516	100.0000



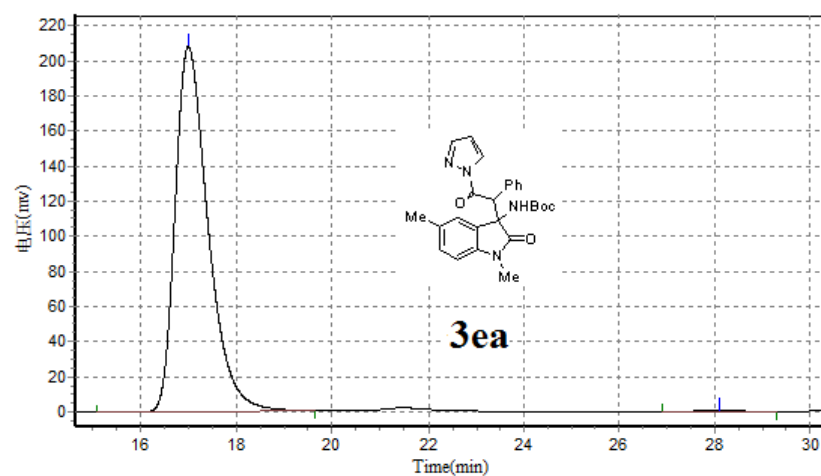
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.758	66449.359	2389080.000	50.3311
2		35.467	30584.877	2357647.000	49.6689
Total			97034.236	4746727.000	100.0000



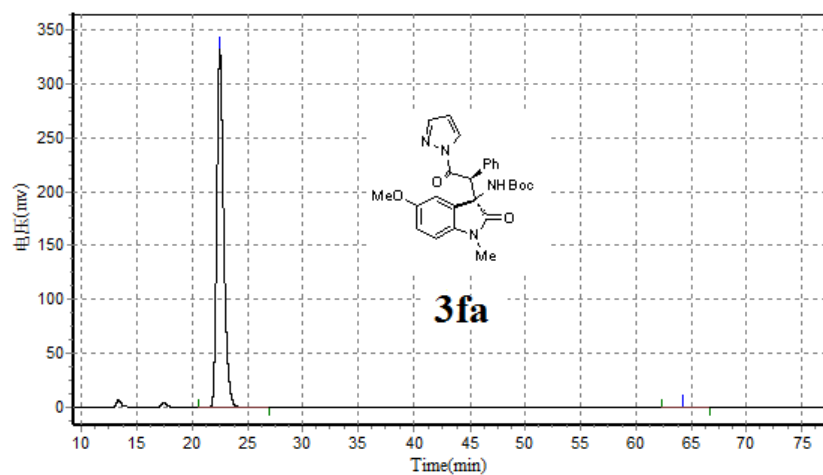
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.790	20375.211	1020312.500	50.3639
2		28.943	11431.518	1005567.563	49.6361
Total			31806.729	2025880.063	100.0000



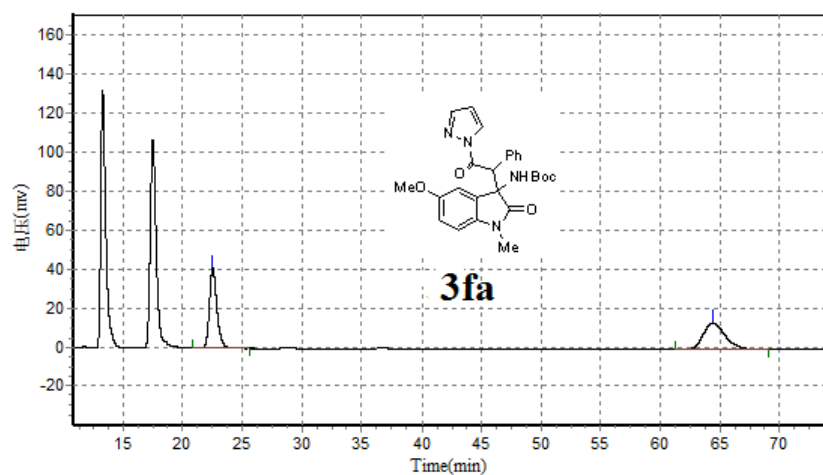
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.995	207638.313	9888366.000	99.4841
2		28.112	725.244	51275.848	0.5159
Total			208363.556	9939641.848	100.0000



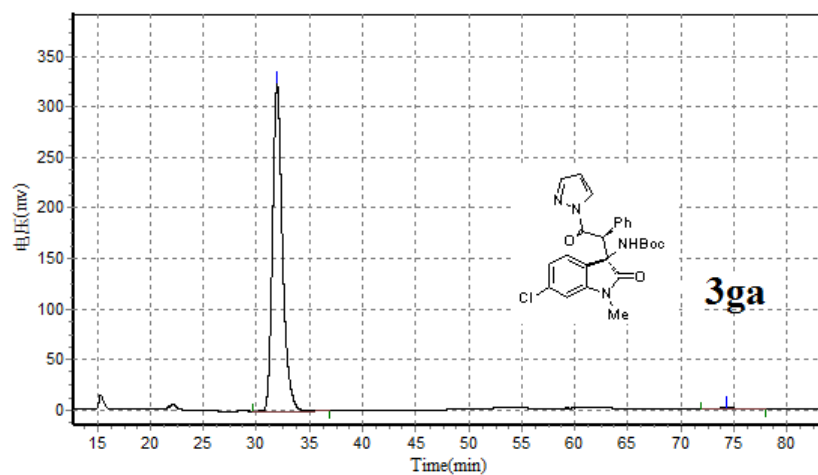
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.497	331544.438	14315706.000	99.5145
2		64.278	592.620	69840.602	0.4855
Total			332137.058	14385546.602	100.0000



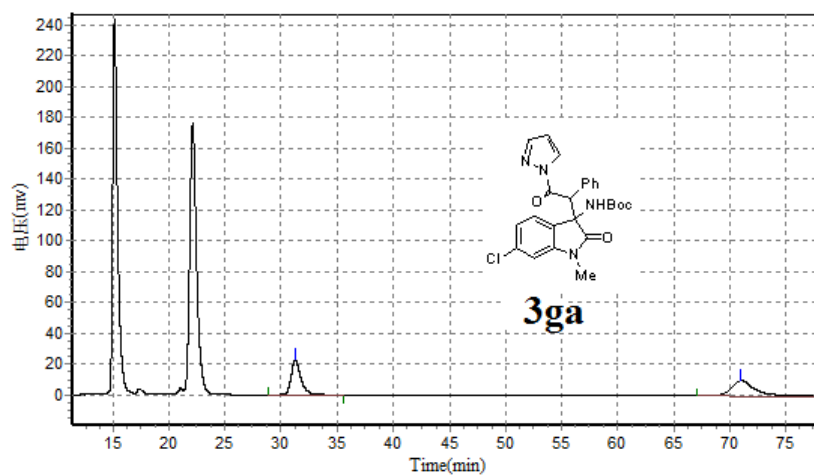
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.530	40867.270	1773980.000	49.9826
2		64.420	13702.411	1775215.500	50.0174
Total			54569.681	3549195.500	100.0000



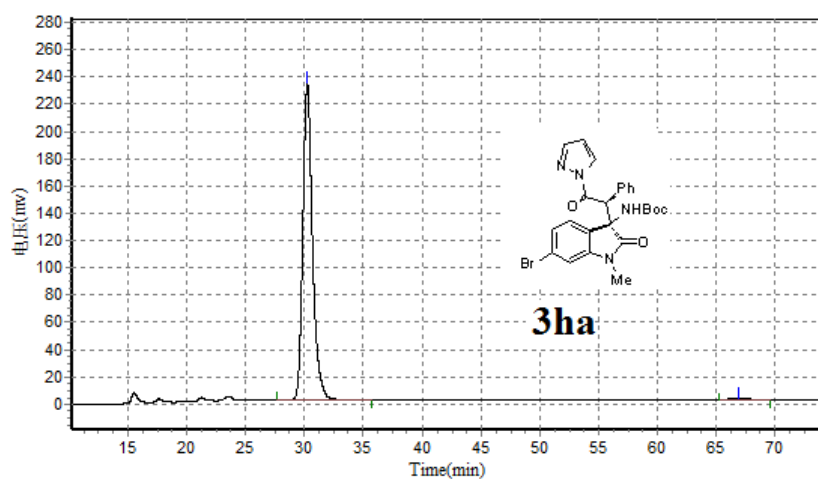
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.958	323068.375	21184874.000	99.4505
2		74.342	989.579	117058.508	0.5495
Total			324057.954	21301932.508	100.0000



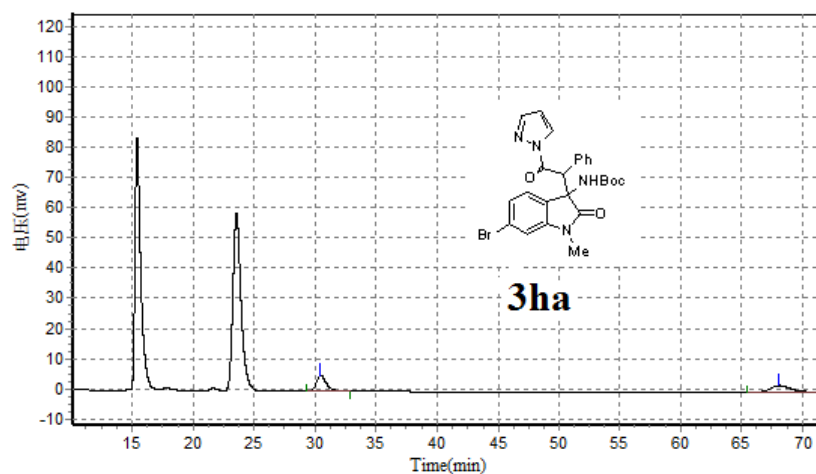
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.282	22445.660	1361120.750	49.2927
2		70.955	9746.871	1400184.125	50.7073
Total			32192.531	2761304.875	100.0000



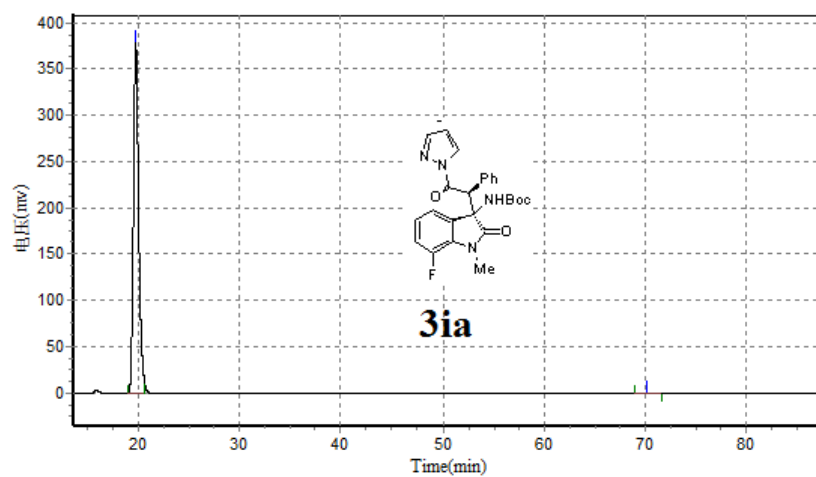
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.253	231722.438	13242964.000	99.3438
2		66.883	787.428	87467.828	0.6562
Total			232509.866	13330431.828	100.0000



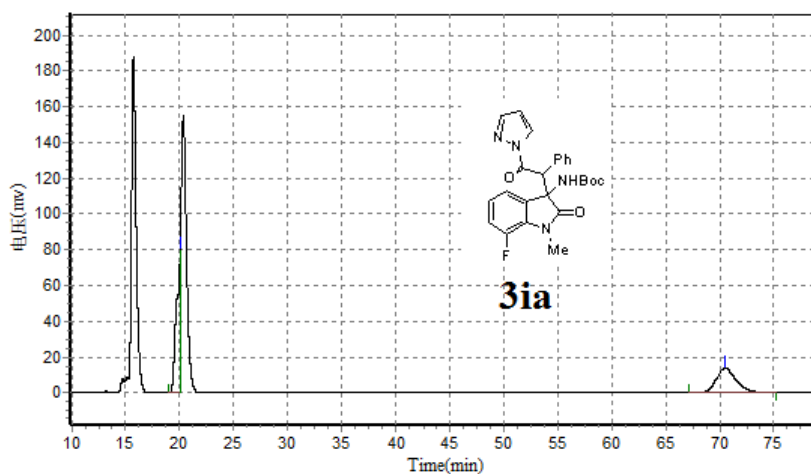
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.483	5320.223	307289.781	50.6115
2		68.105	2299.635	299864.594	49.3885
Total			7619.858	607154.375	100.0000



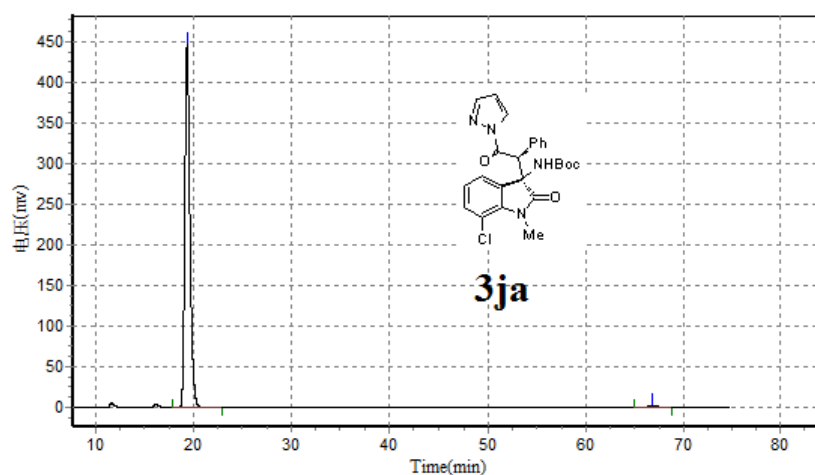
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.707	378267.719	13562321.000	99.5816
2		70.165	614.803	56985.797	0.4184
Total			378882.522	13619306.797	100.0000



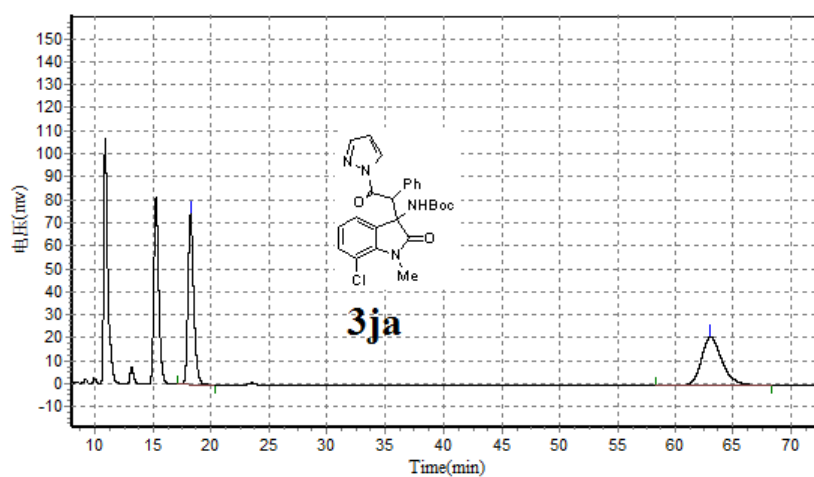
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.065	80197.570	1843031.375	50.7897
2		70.478	13834.892	1785716.750	49.2103
Total			94032.462	3628748.125	100.0000



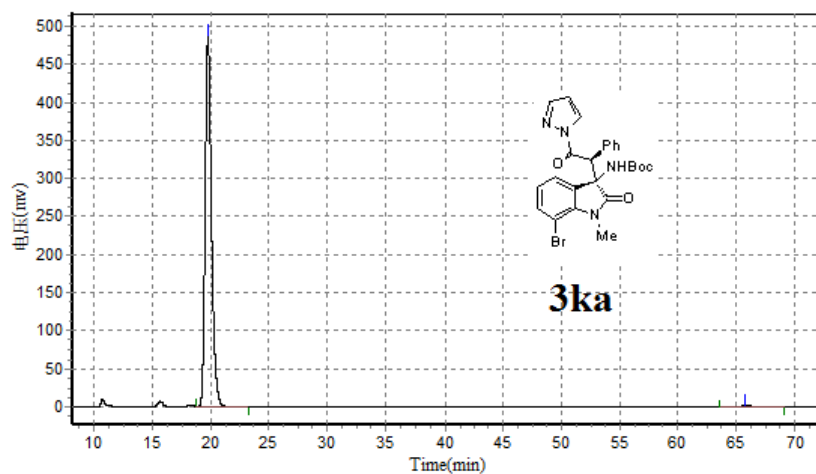
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.287	446464.031	16191185.000	99.2363
2		66.792	1133.868	124601.547	0.7637
Total			447597.900	16315786.547	100.0000



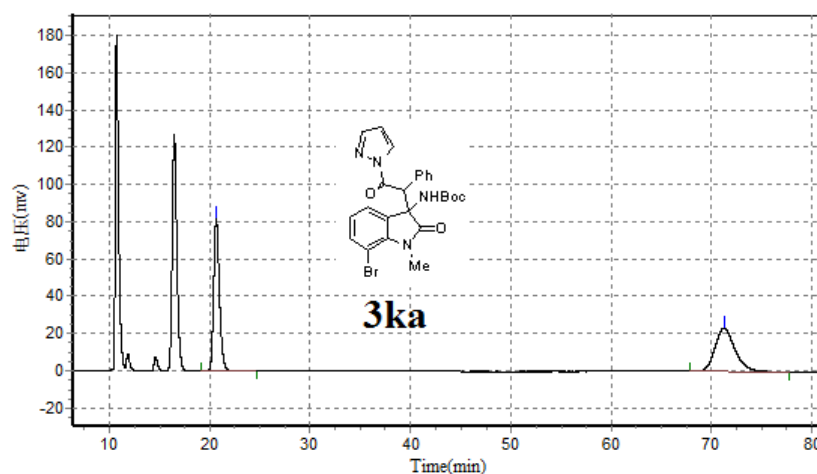
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.248	73878.398	2533186.750	49.6943
2		63.047	20913.092	2564357.000	50.3057
Total			94791.490	5097543.750	100.0000



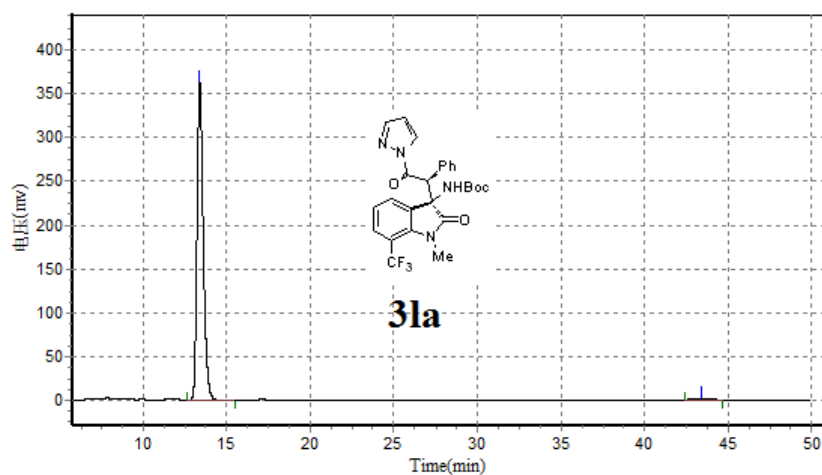
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.755	486698.500	18254416.000	99.0335
2		65.825	1418.959	178142.953	0.9665
Total			488117.459	18432558.953	100.0000



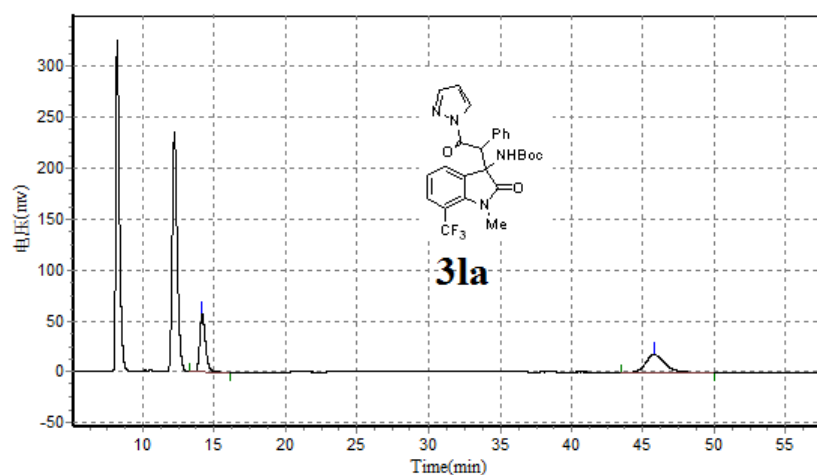
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.657	81785.438	3218644.000	49.9749
2		71.235	23263.262	3221881.750	50.0251
Total			105048.699	6440525.750	100.0000



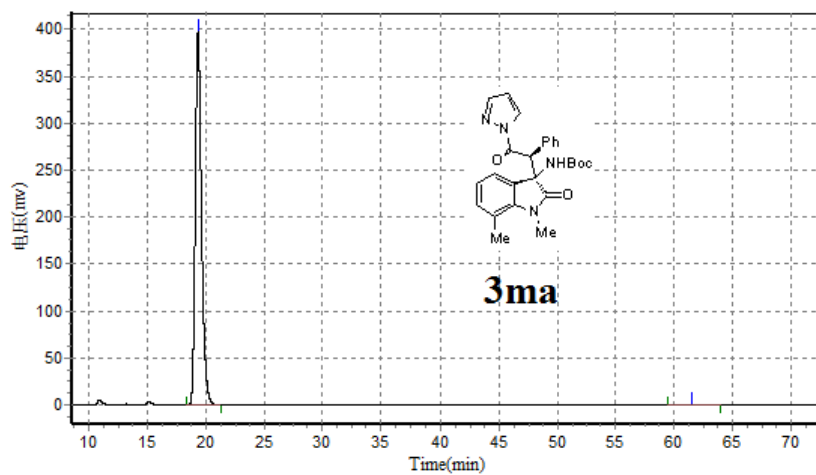
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.393	362375.469	9359412.000	98.5124
2		43.420	1984.841	141336.250	1.4876
Total			364360.310	9500748.250	100.0000



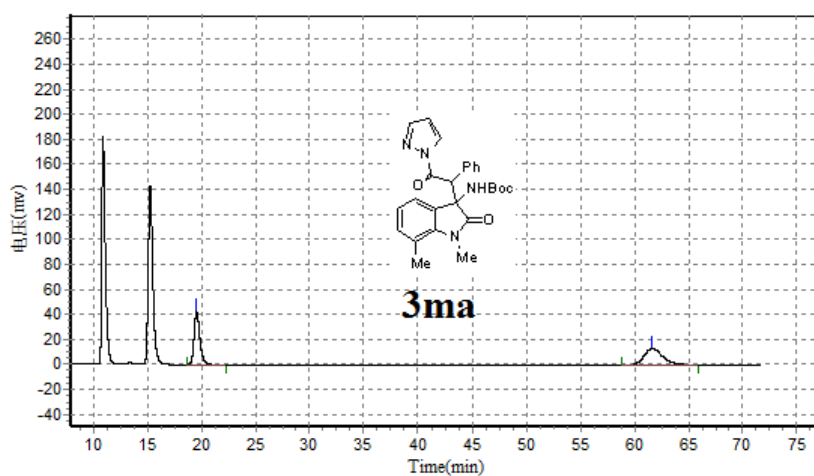
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.168	57372.719	1561374.500	50.3857
2		45.793	17121.645	1537471.500	49.6143
Total			74494.363	3098846.000	100.0000



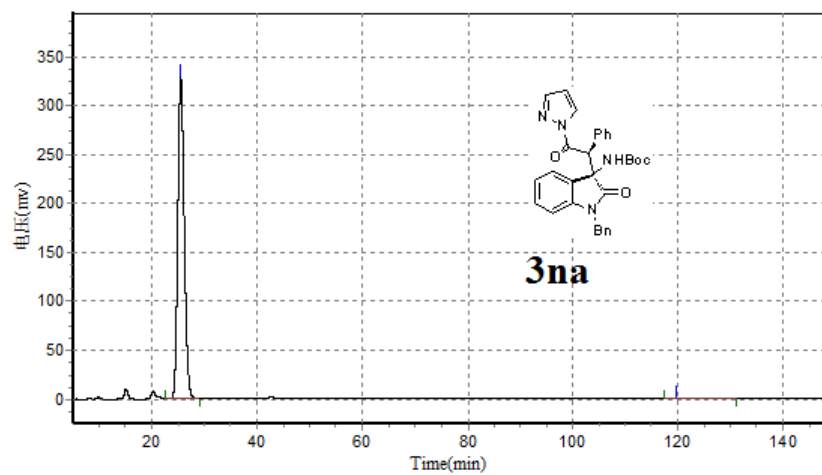
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.335	397181.063	14650572.000	99.5189
2		61.493	621.998	70832.352	0.4812
Total			397803.061	14721404.352	100.0000



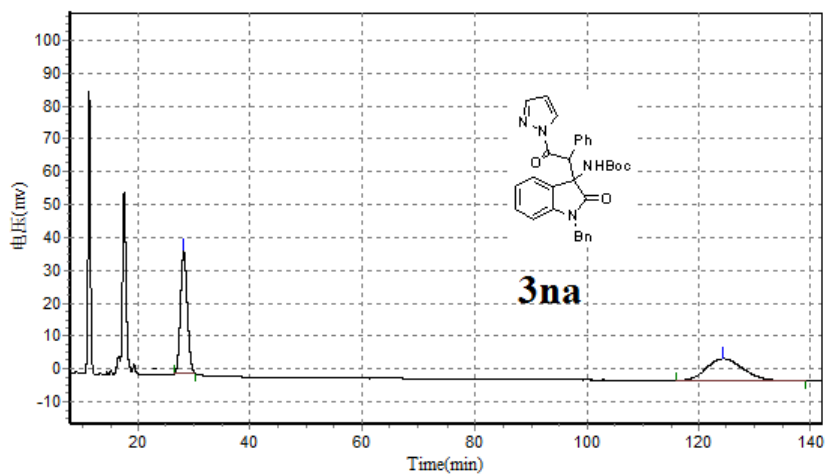
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.547	42269.512	1567352.500	49.8007
2		61.643	13239.031	1579900.625	50.1994
Total			55508.543	3147253.125	100.0000



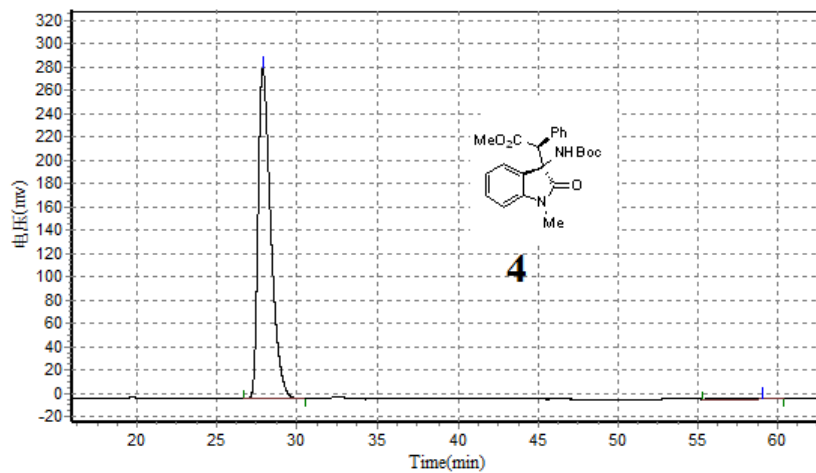
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.383	328384.438	27946198.000	99.6634
2		119.728	259.095	94390.445	0.3366
Total			328643.533	28040588.445	100.0000



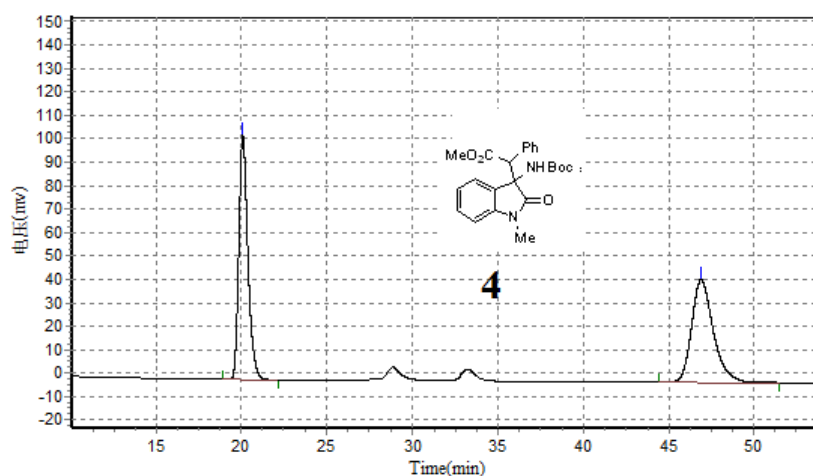
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.138	37063.367	3132862.750	50.3404
2		124.425	6693.919	3090491.750	49.6596
Total			43757.287	6223354.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.853	283208.000	15659665.000	99.8519
2		59.095	110.622	23227.406	0.1481
Total			283318.622	15682892.406	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.082	104021.016	3840740.500	49.9723
2		46.907	43707.699	3845003.750	50.0277
Total			147728.715	7685744.250	100.0000