Supporting Information

Asymmetric Michael Addition of a-Substituted Isocyanoacetates with Maleimides Catalyzed by Chiral Tertiary Amine Thiourea

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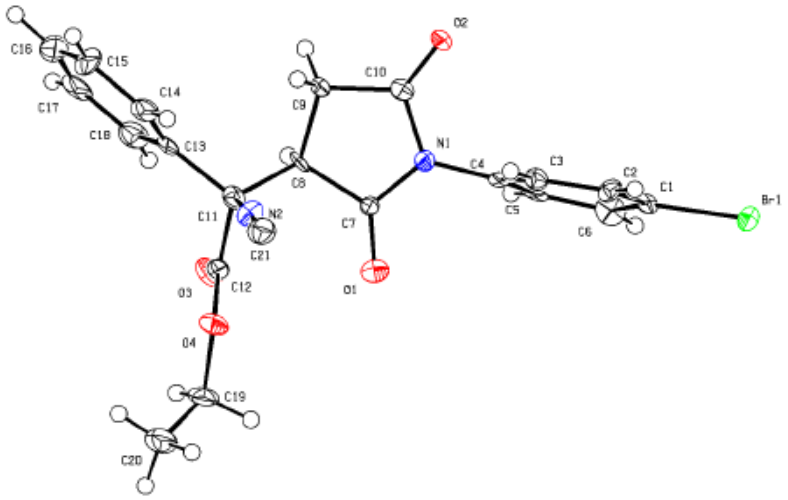
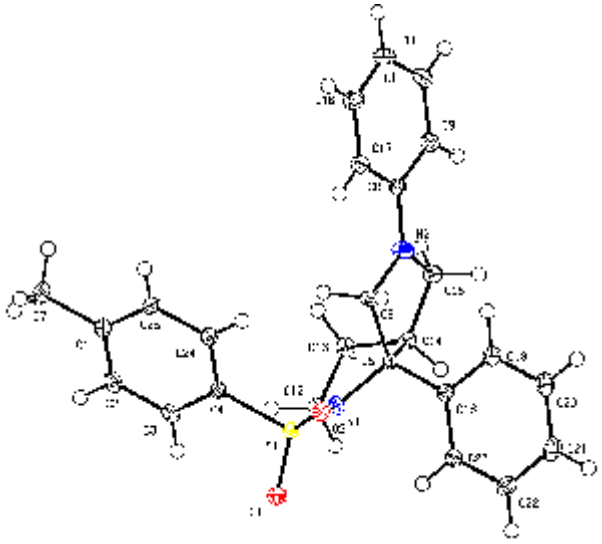
1. Crystal data

Crystal data and structure refinement for 3q (CCDC: 867331).



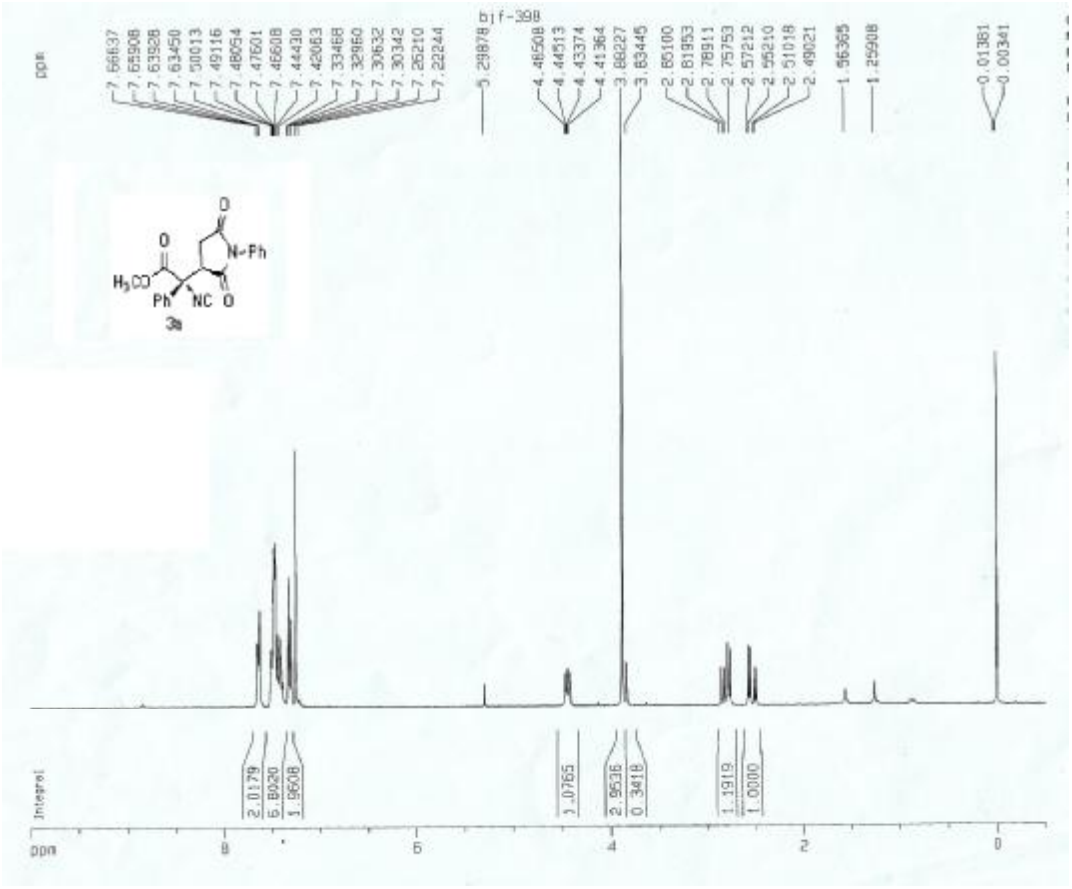
Empirical formula	C21 H17 Br N2 O4
Formula weight	441.28
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 6.611(3) A alpha = 90 deg.
	b = 14.222(6) A beta = 90 deg.
	c = 20.570(9) A gamma = 90 deg.
Volume	1934.0(15) A^3
Z, Calculated density	4, 1.516 Mg/m^3
Absorption coefficient	2.155 mm^-1
F(000)	896
Crystal size	0.70 x 0.25 x 0.18 mm
Theta range for data collection	1.74 to 28.45 deg.
Limiting indices	-8<=h<=8, -17<=k<=18, -27<=l<=26
Reflections collected / unique	15446 / 4661 [R(int) = 0.1122]
Completeness to theta = 28.45	96.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6976 and 0.3138
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4661 / 0 / 254
Goodness-of-fit on F^2	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0952, wR2 = 0.2499
R indices (all data)	R1 = 0.1430, wR2 = 0.2790
Absolute structure parameter	0.14(3)
Largest diff. peak and hole	1.809 and -2.602 e.A^-3

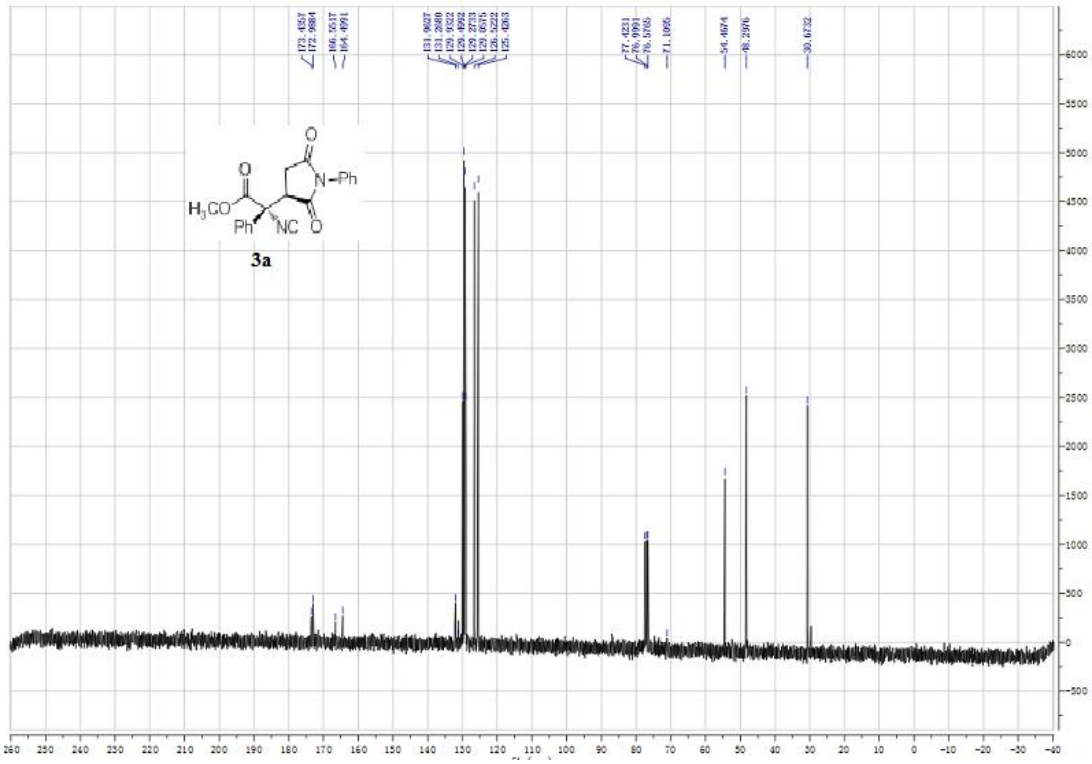
Crystal data and structure refinement for 7b (CCDC: 851295)

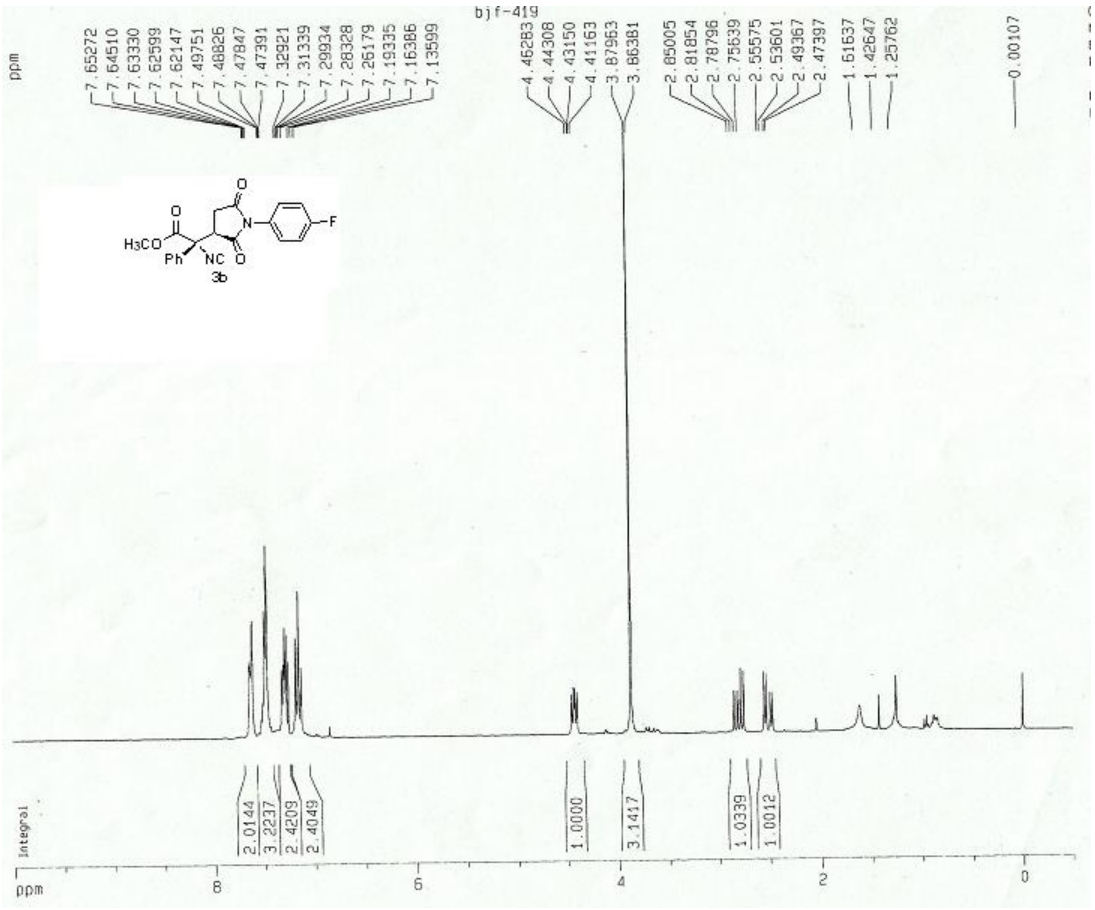


Empirical formula	C25 H26 N2 O2 S
Formula weight	418.54
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 9.1977(12) A alpha = 90 deg.
	b = 10.4095(13) A beta = 90 deg.
Volume	2092.1(5) A^3
Z, Calculated density	4, 1.329 Mg/m^3
Absorption coefficient	0.180 mm^-1
F(000)	888
Crystal size	0.80 x 0.15 x 0.09 mm
Theta range for data collection	1.86 to 30.04 deg.
Limiting indices	-12<=h<=12, -14<=k<=14, -30<=l<=30
Reflections collected / unique	22328 / 5920 [R(int) = 0.0416]
Completeness to theta = 30.04	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9840 and 0.8696
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5920 / 0 / 272
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0763
R indices (all data)	R1 = 0.0449, wR2 = 0.0803
Absolute structure parameter	-0.01(5)
Largest diff. peak and hole	0.377 and -0.338 e.A^-3

2. NMR Spectra of Products



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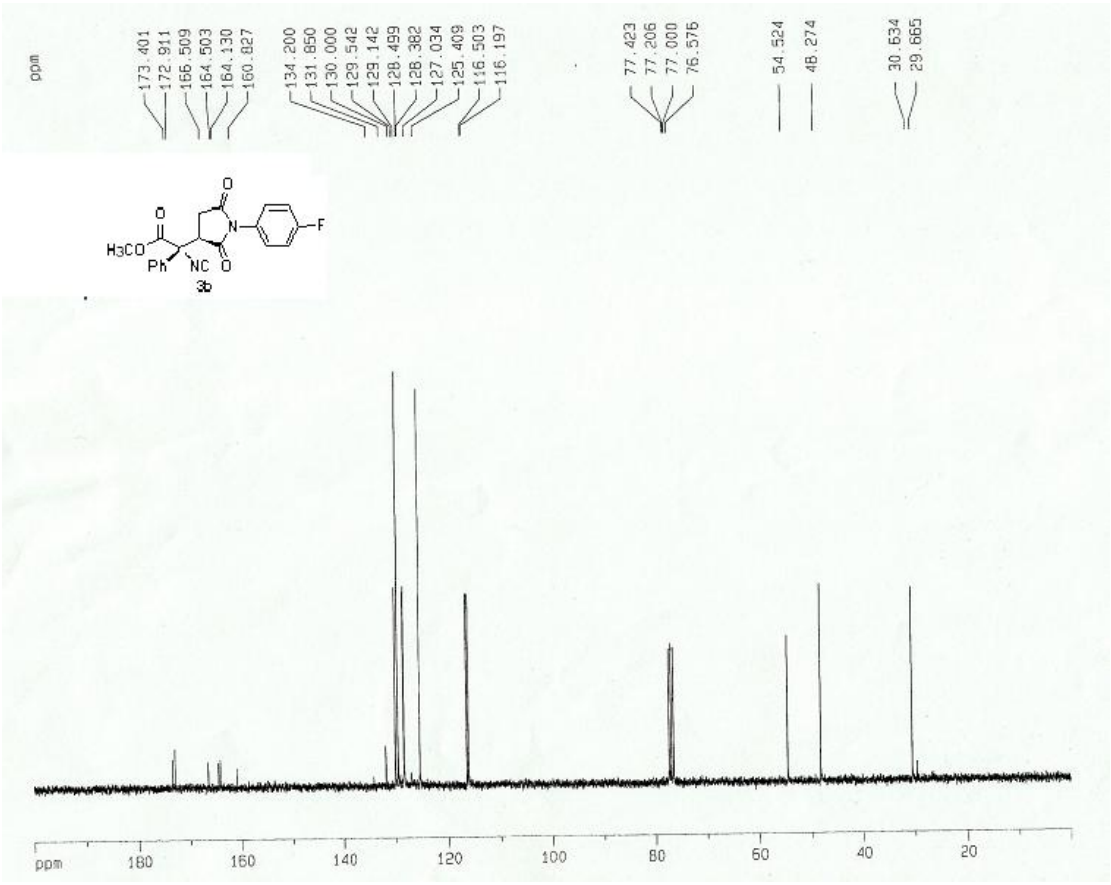
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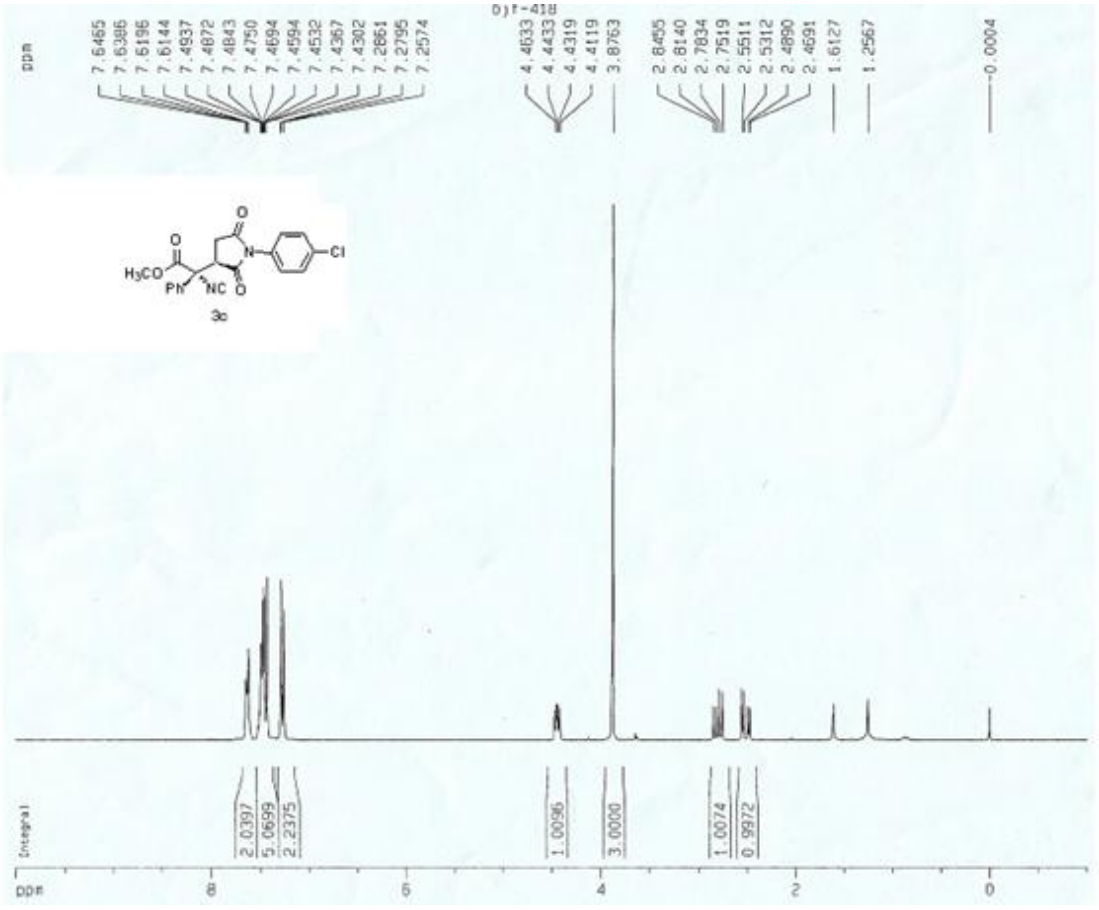
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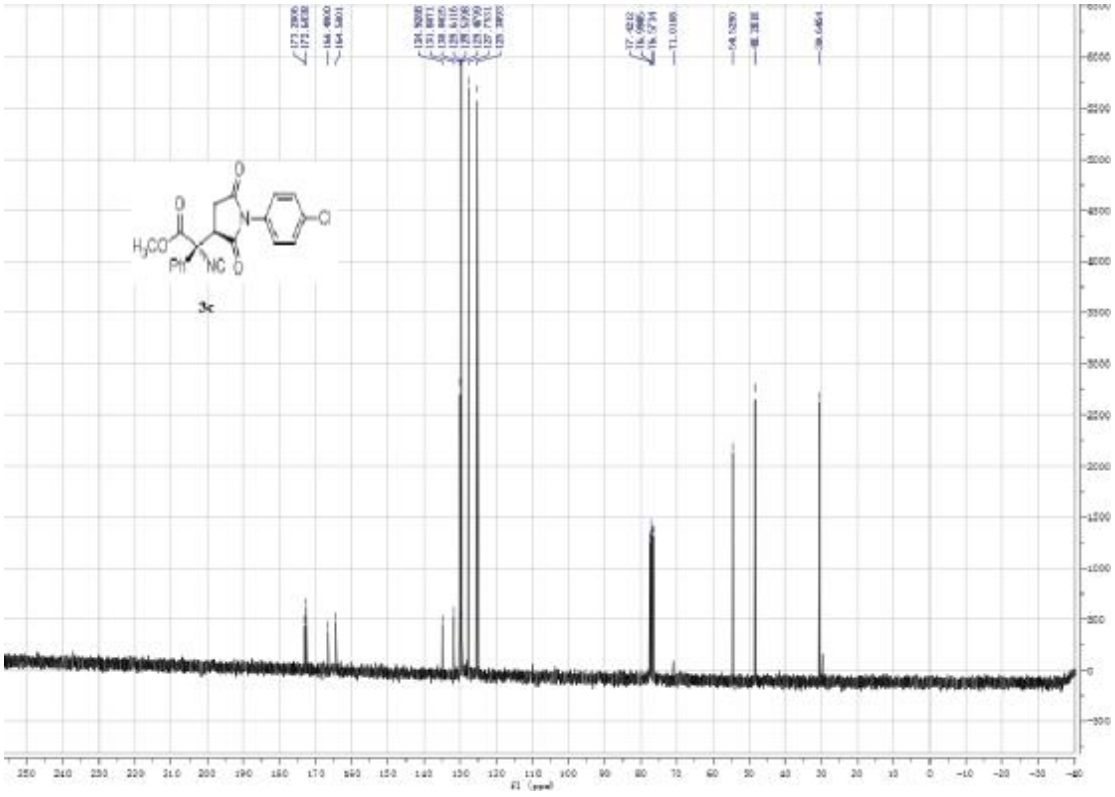
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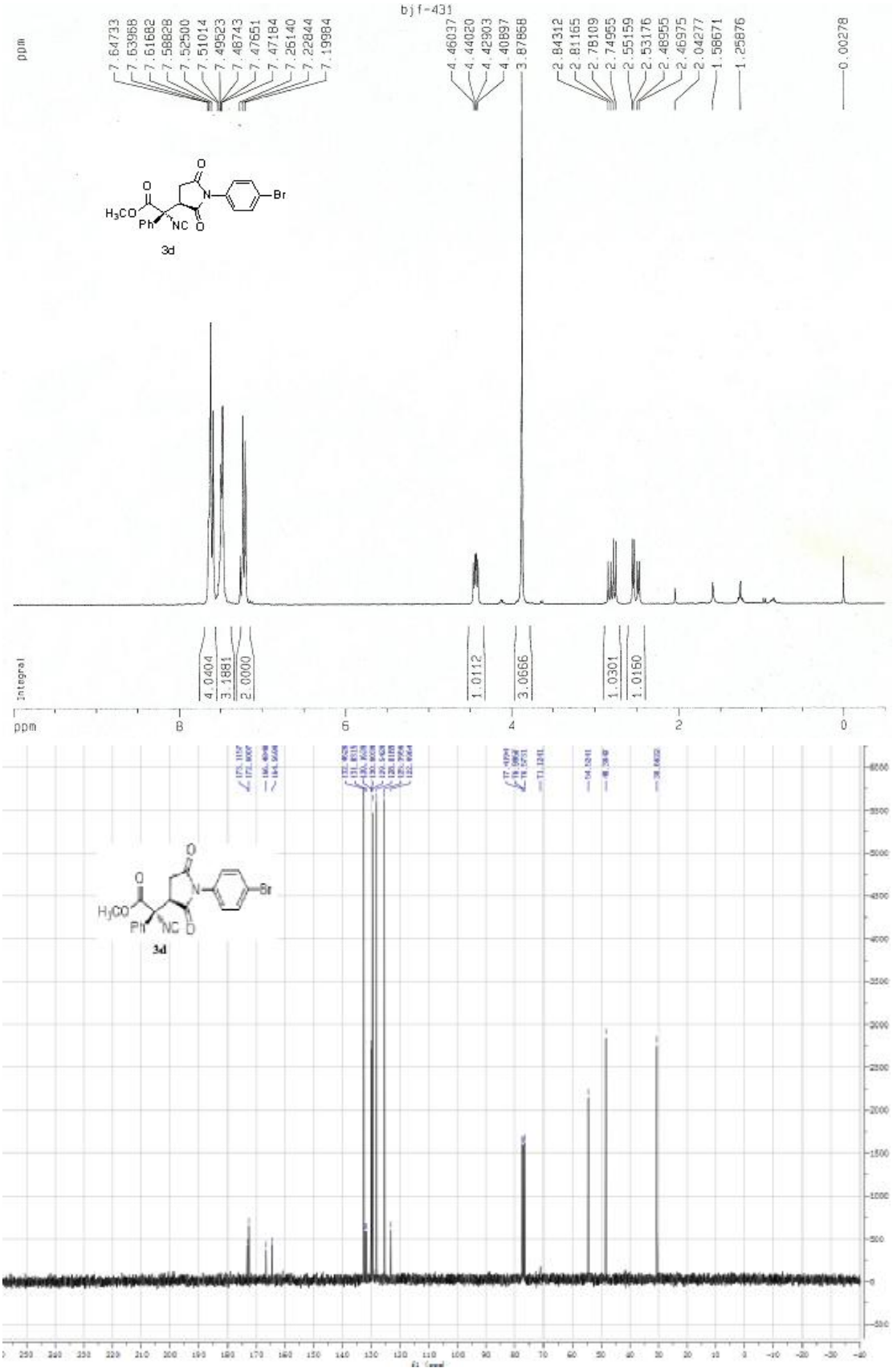
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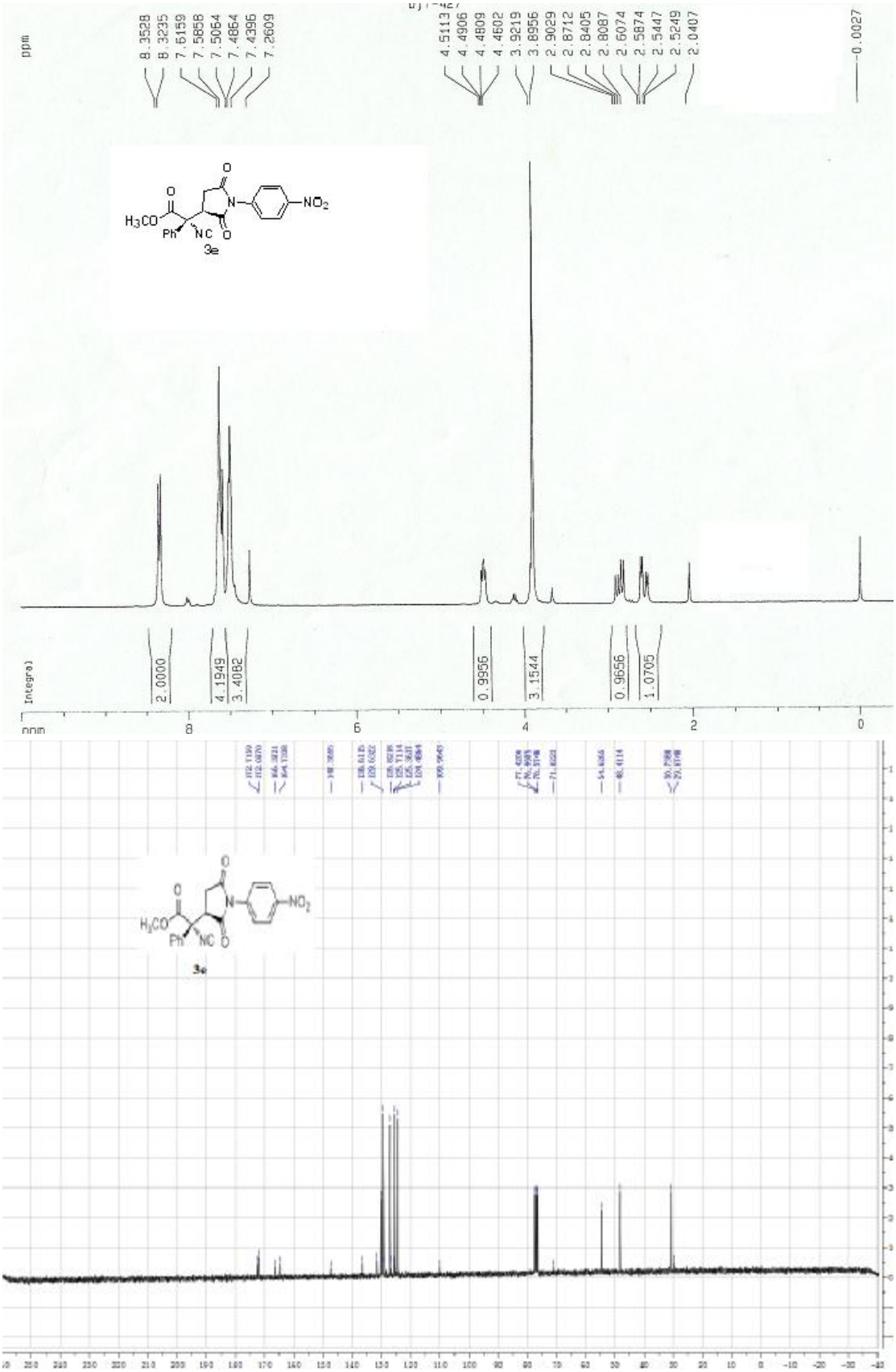
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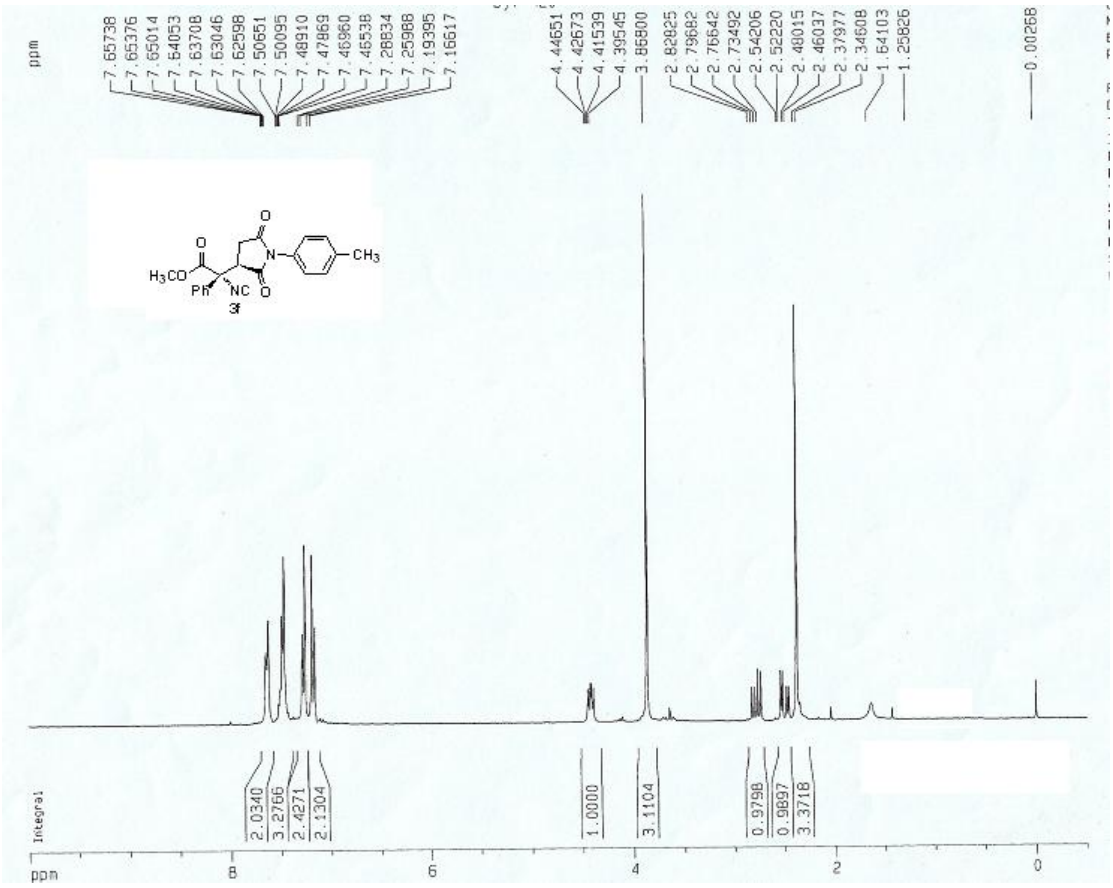
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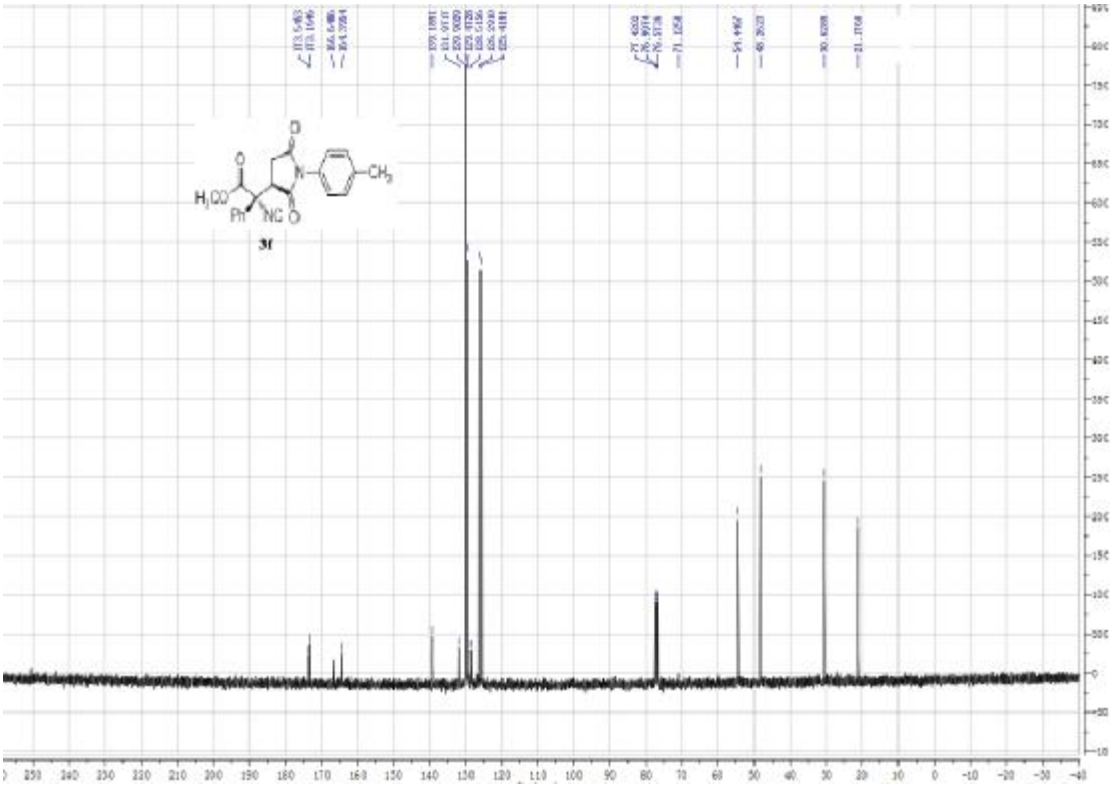
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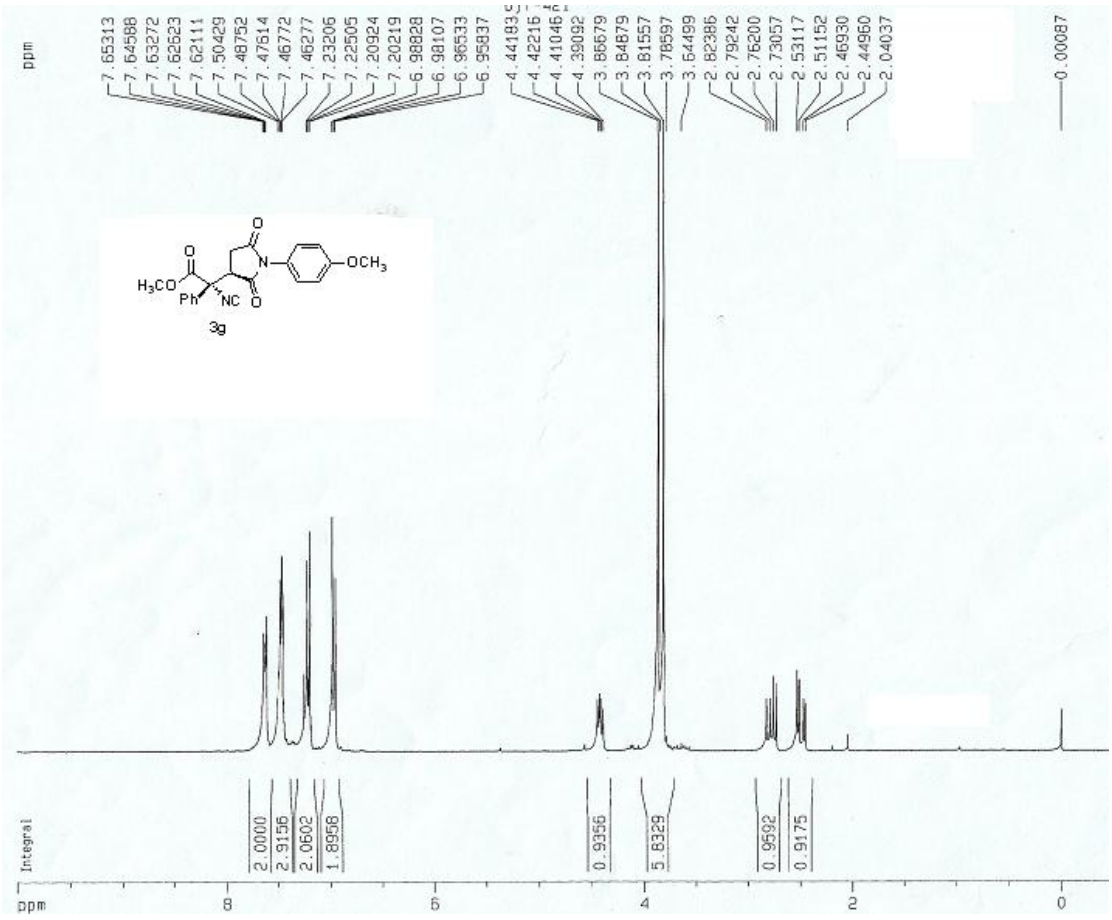
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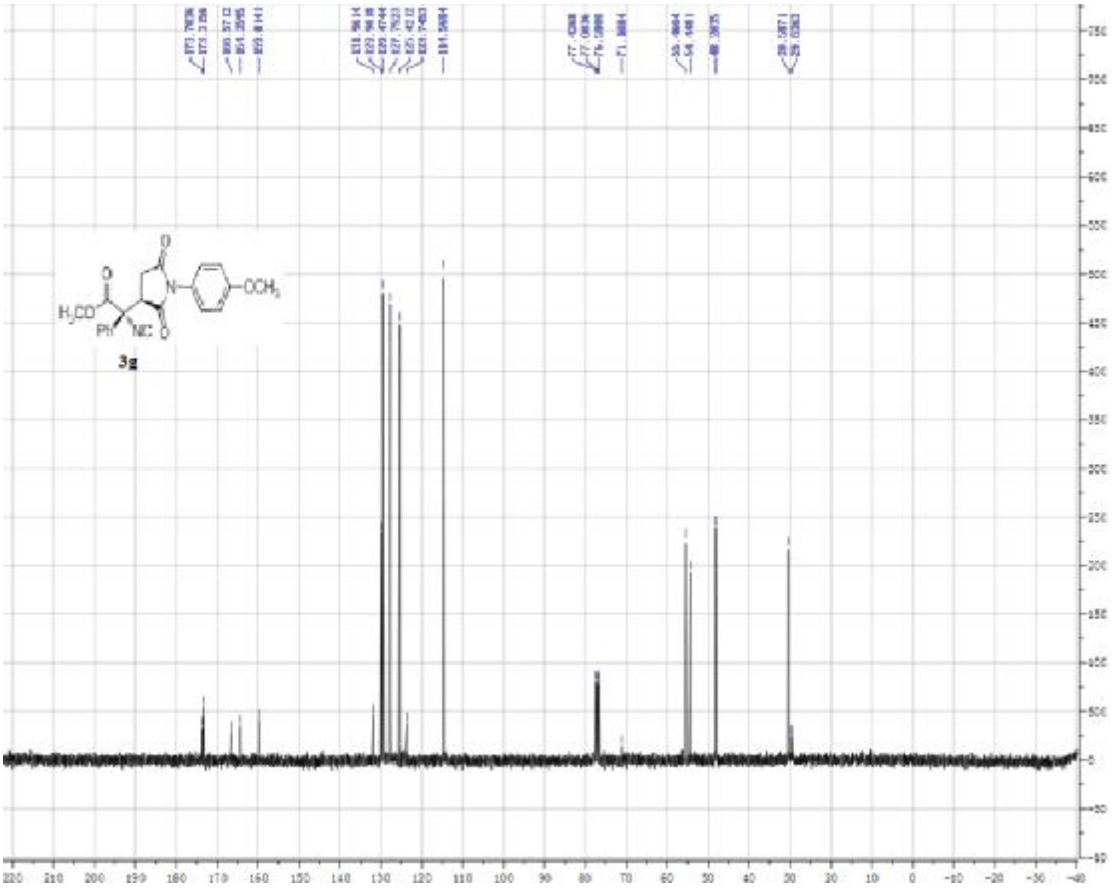
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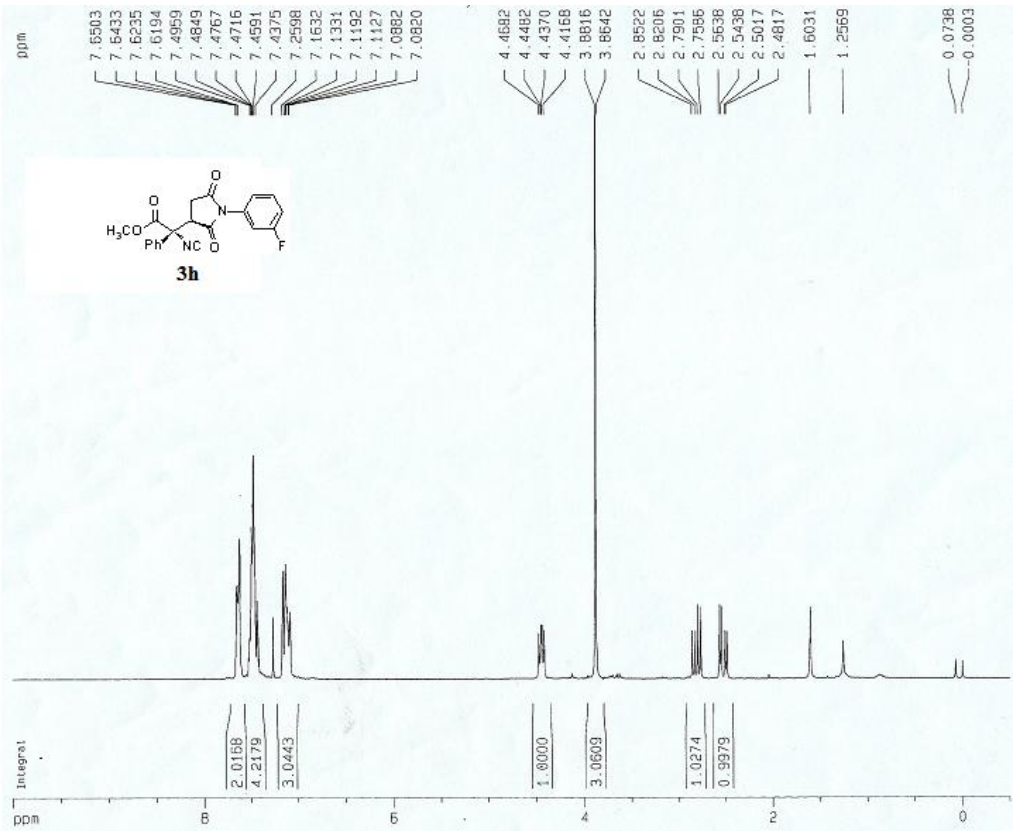
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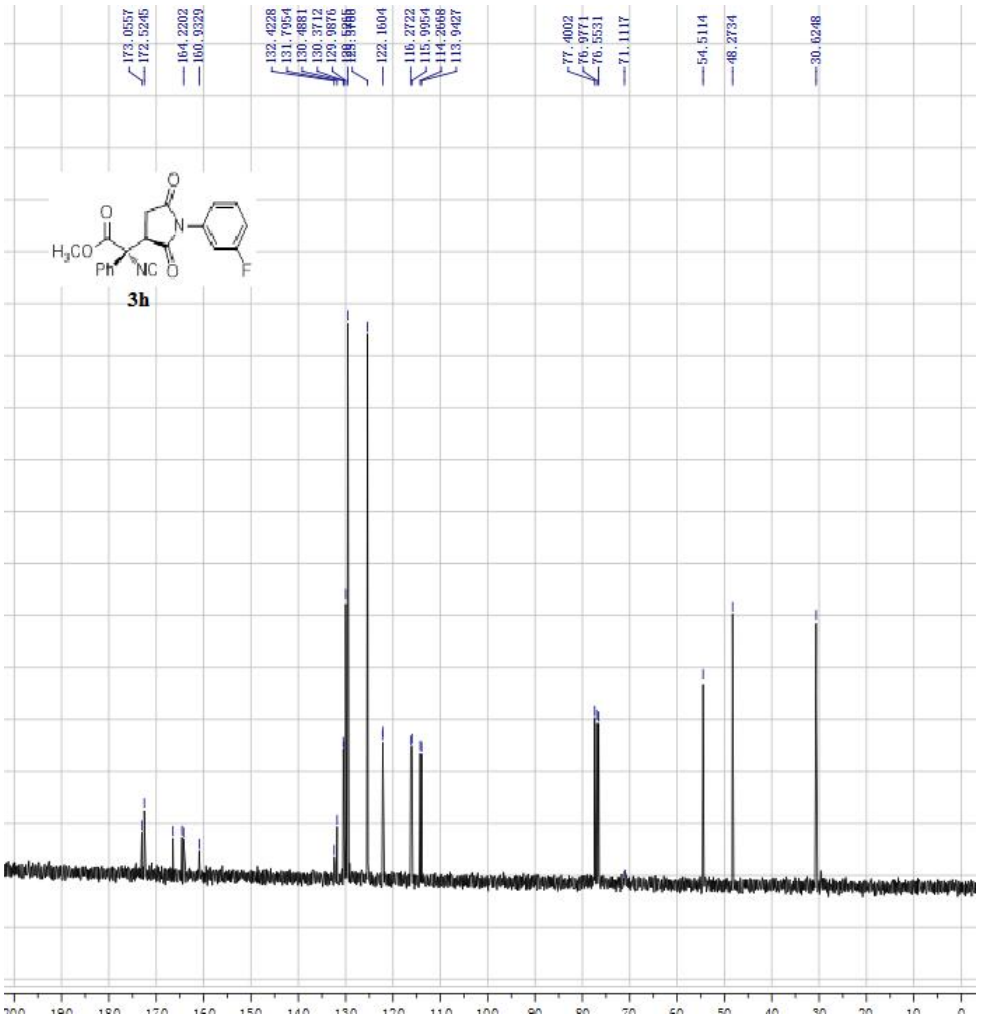
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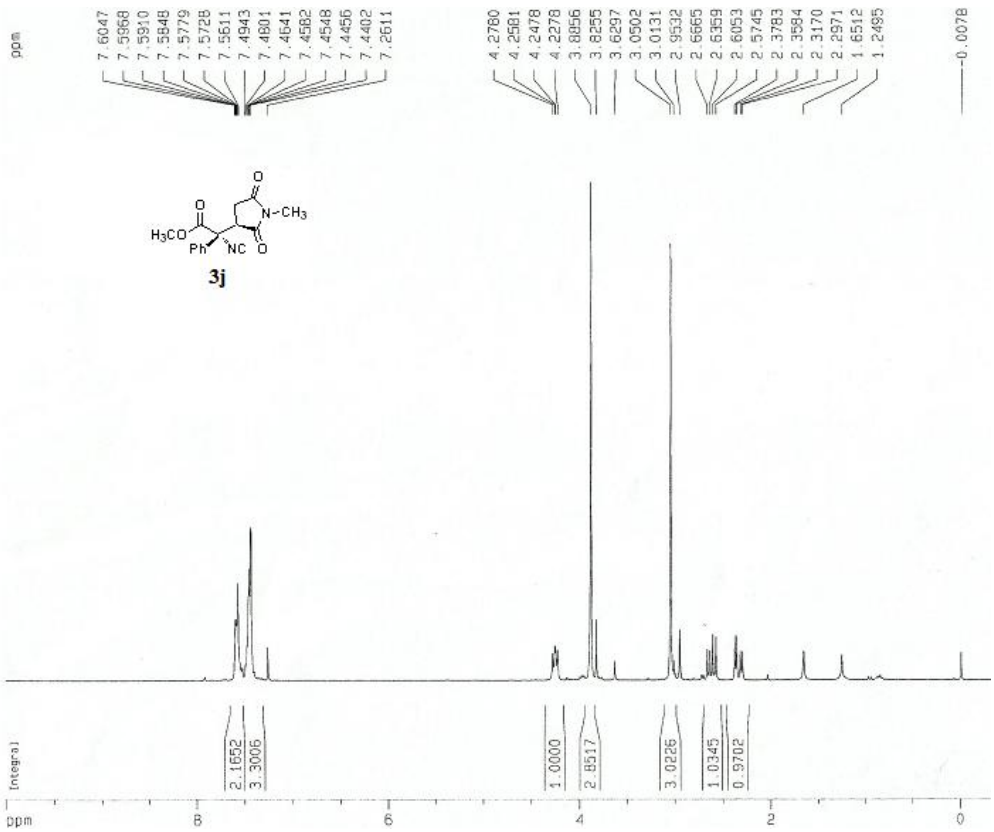
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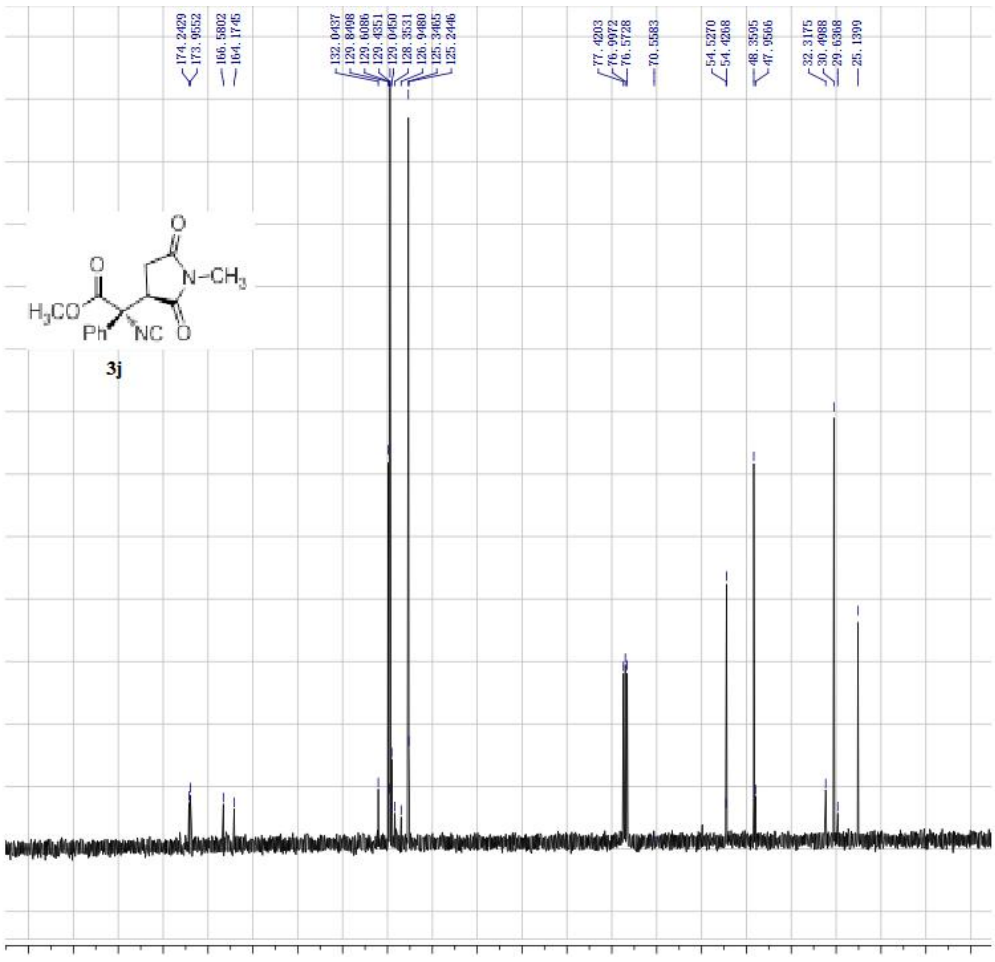
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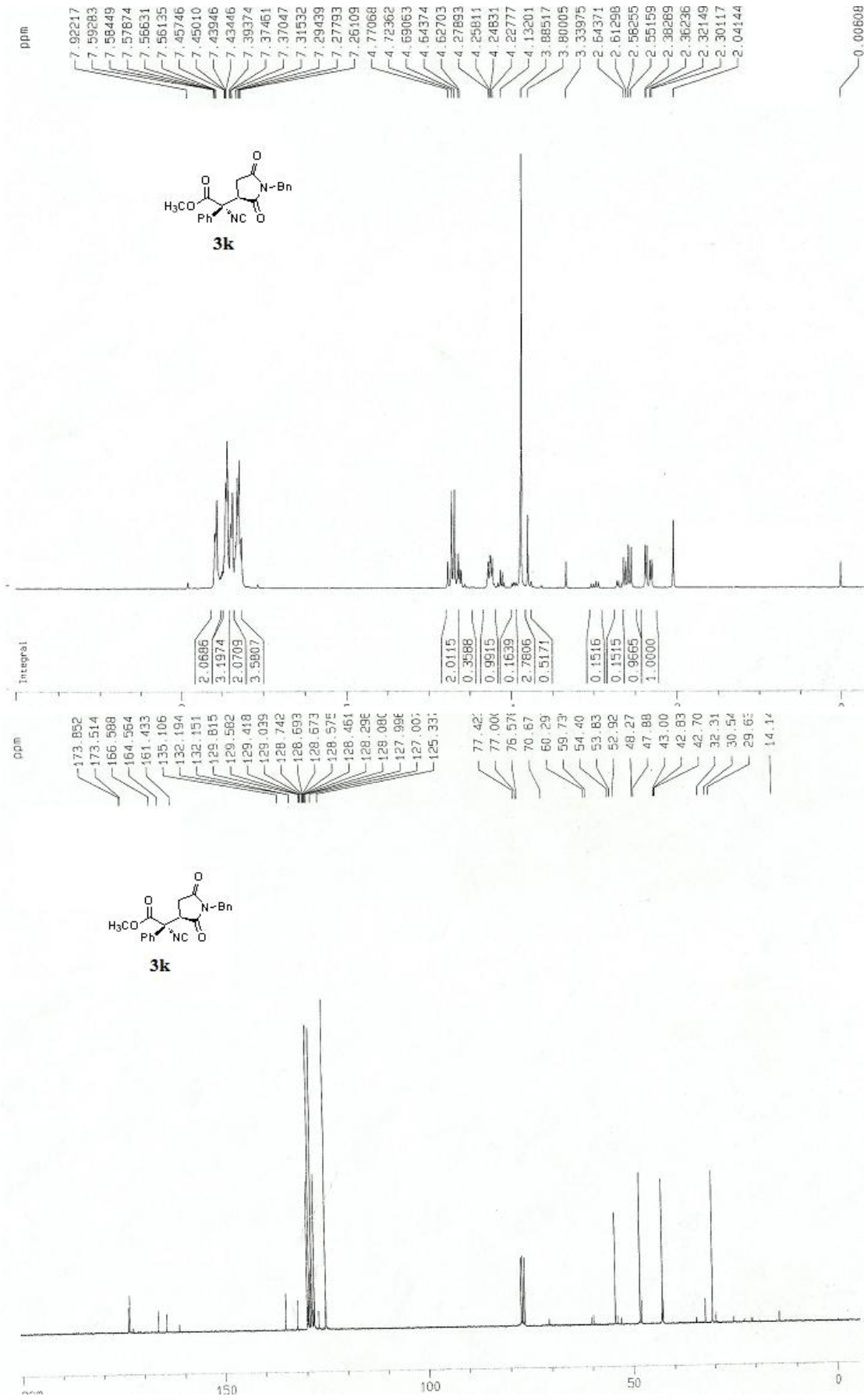
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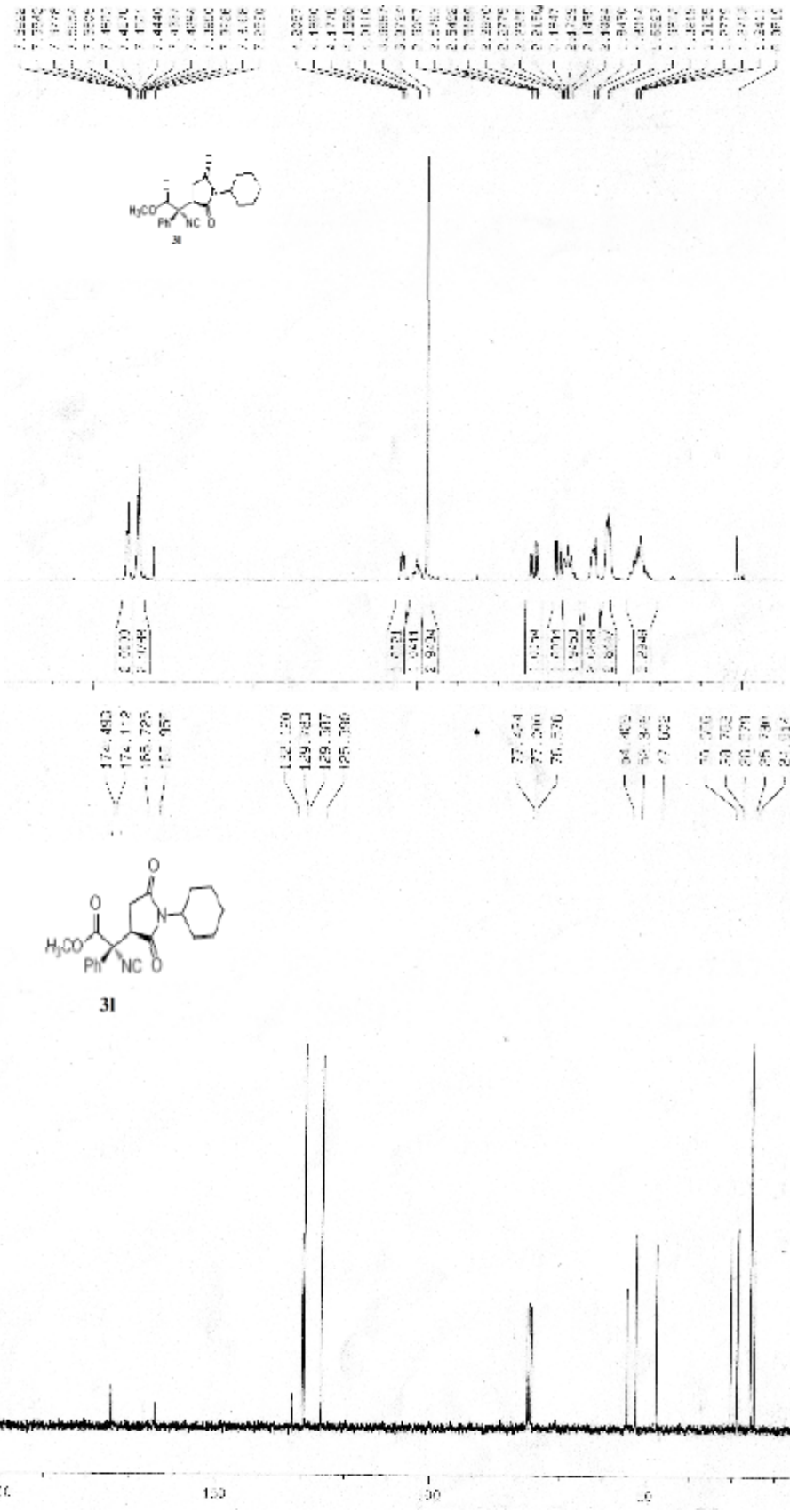
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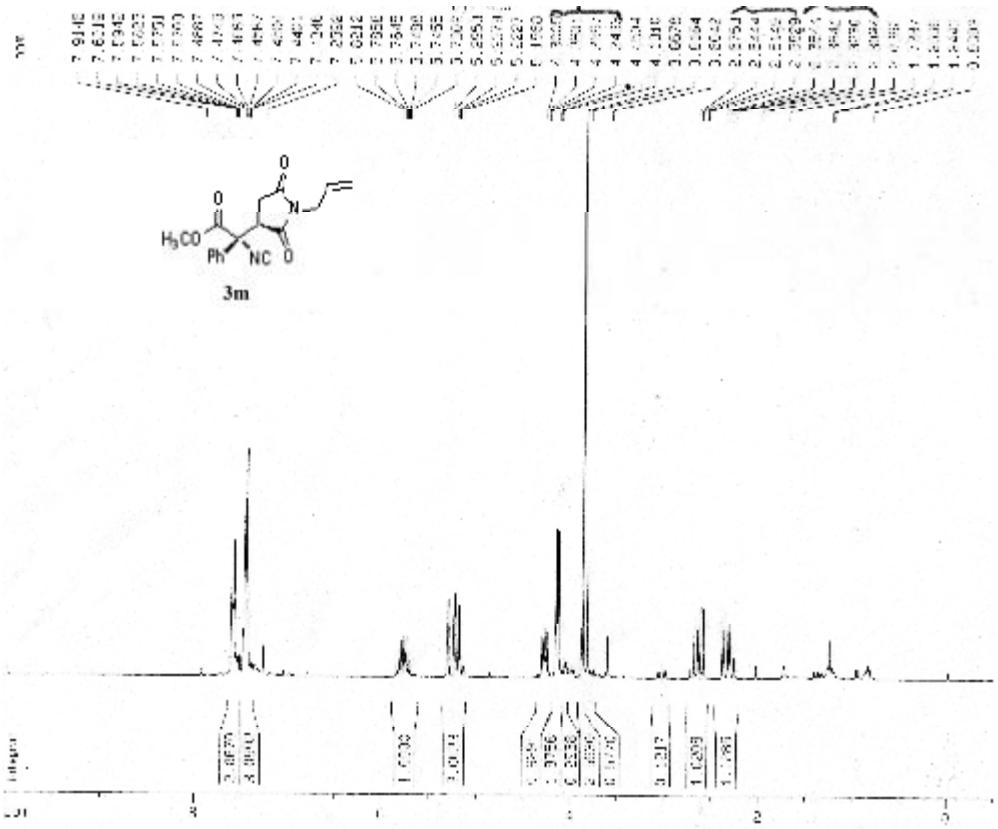
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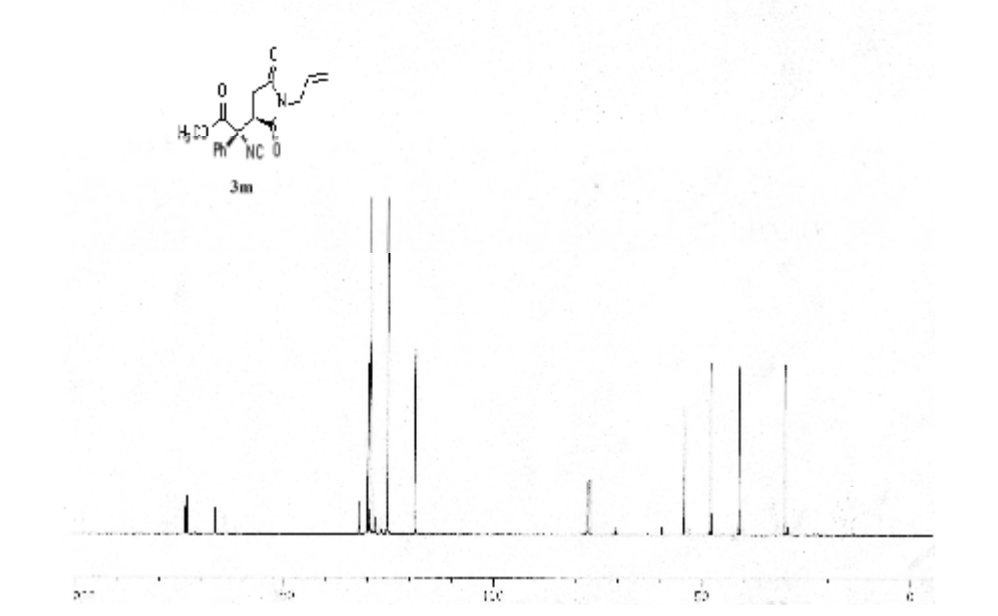
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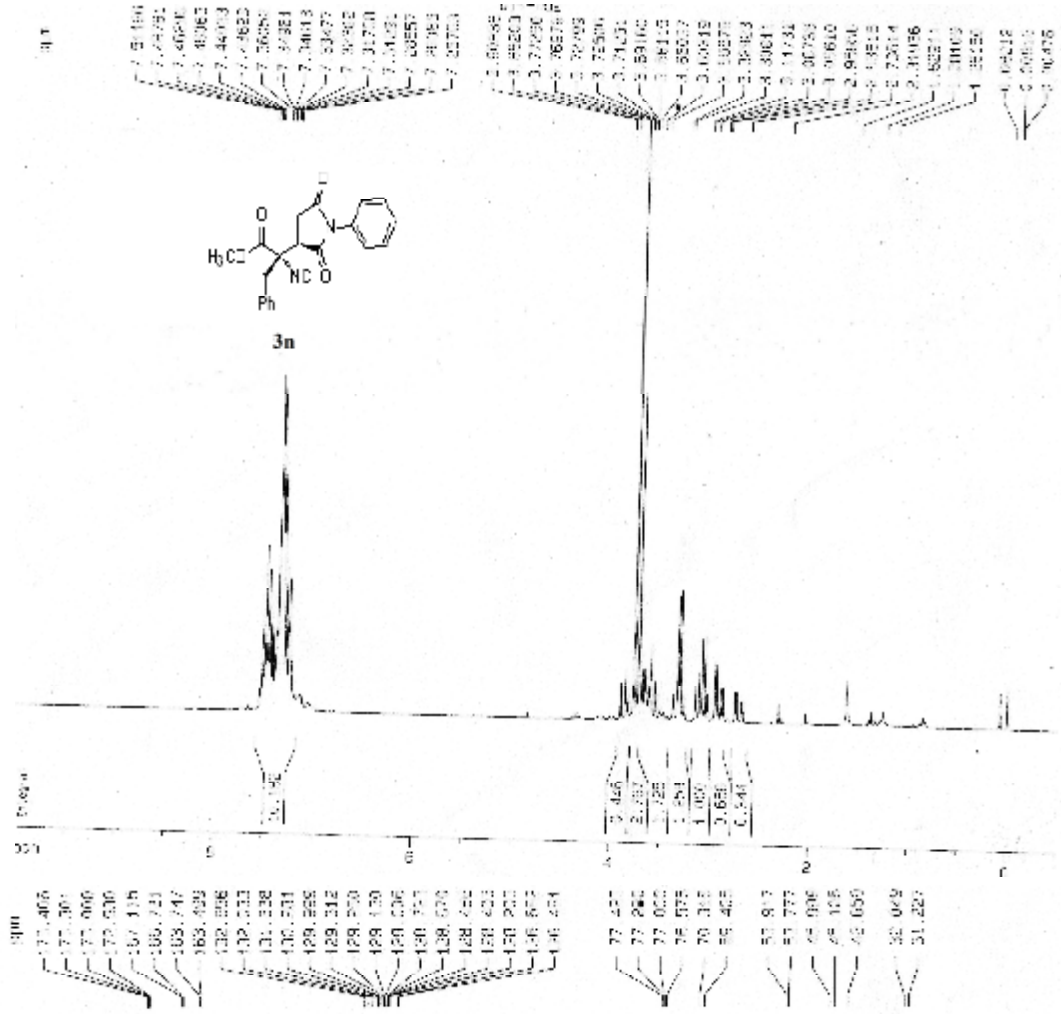

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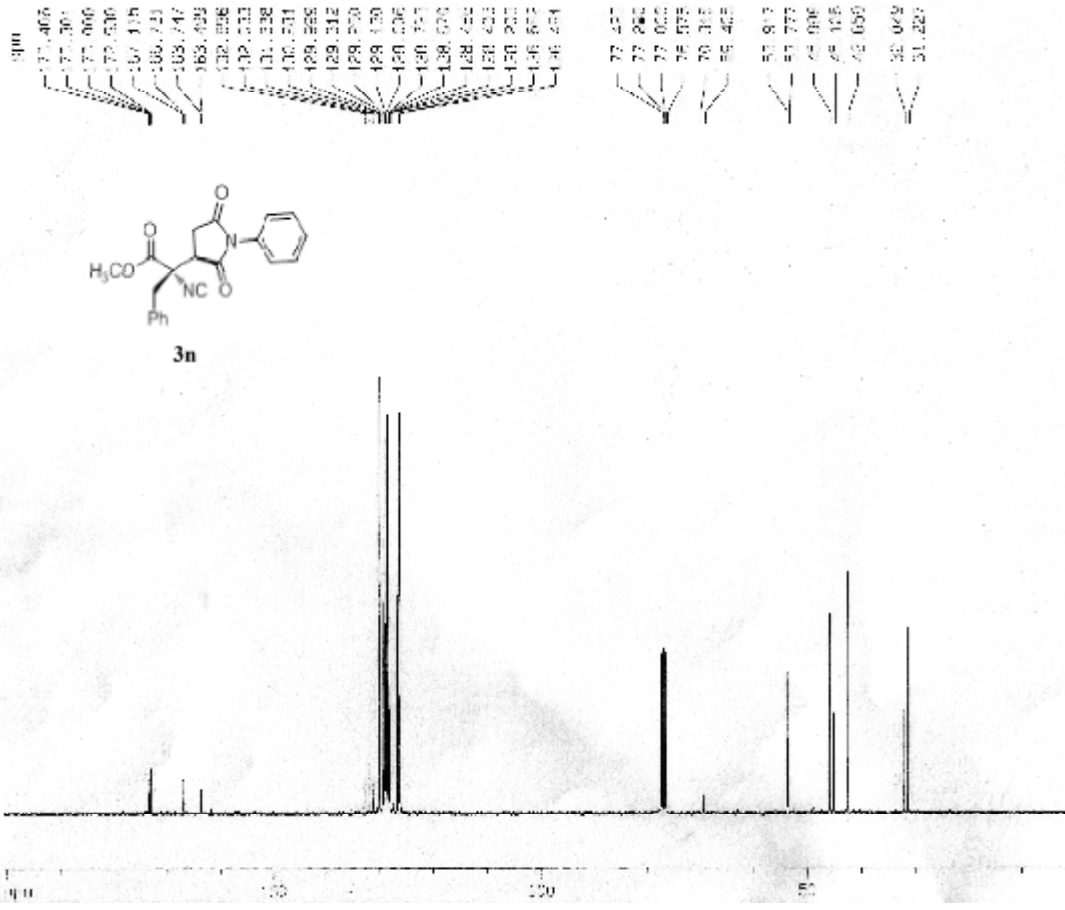

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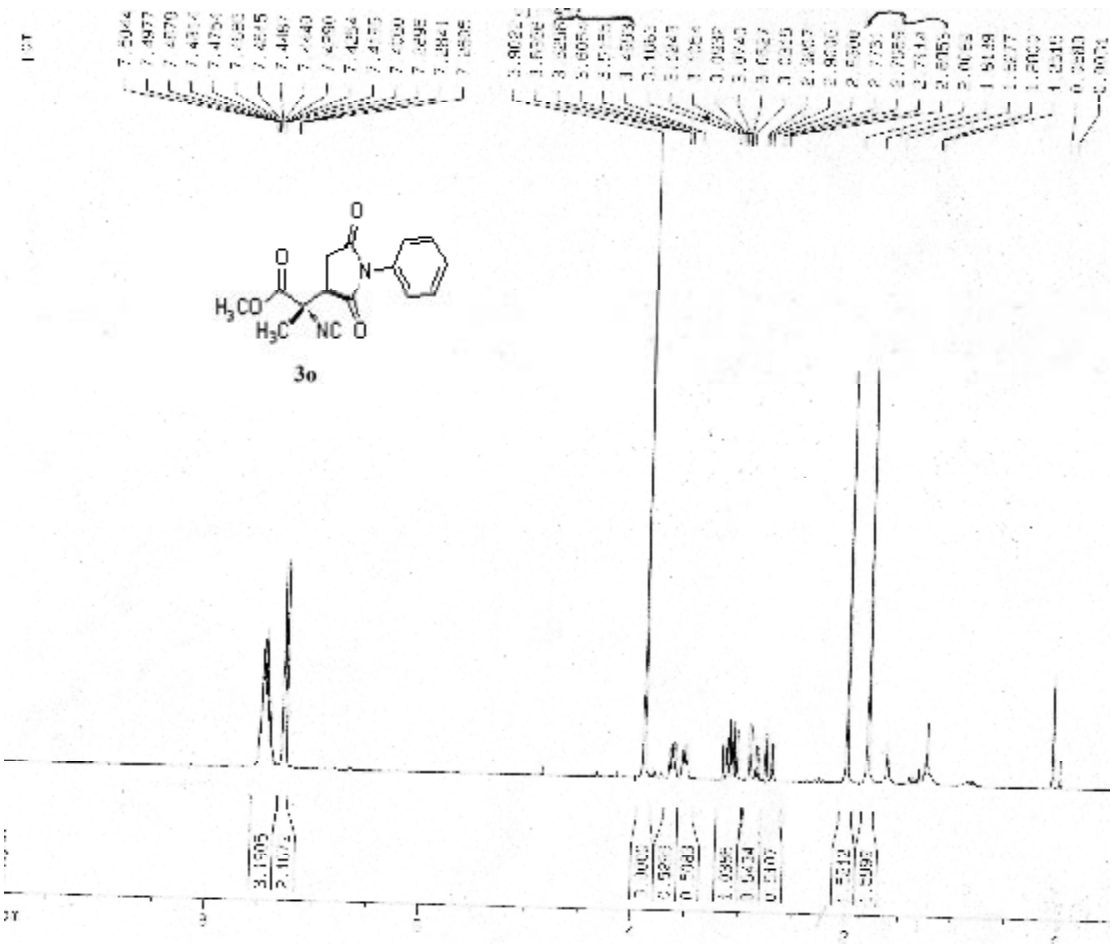

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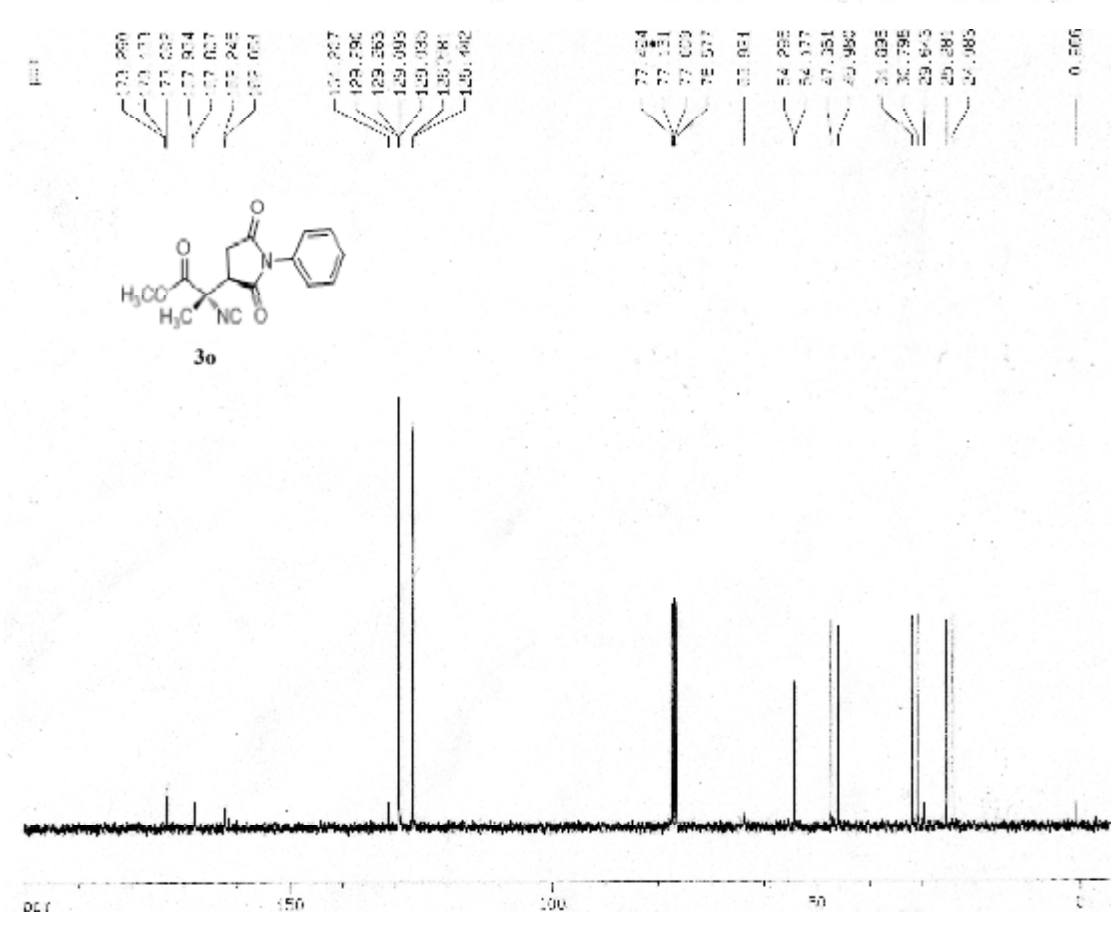

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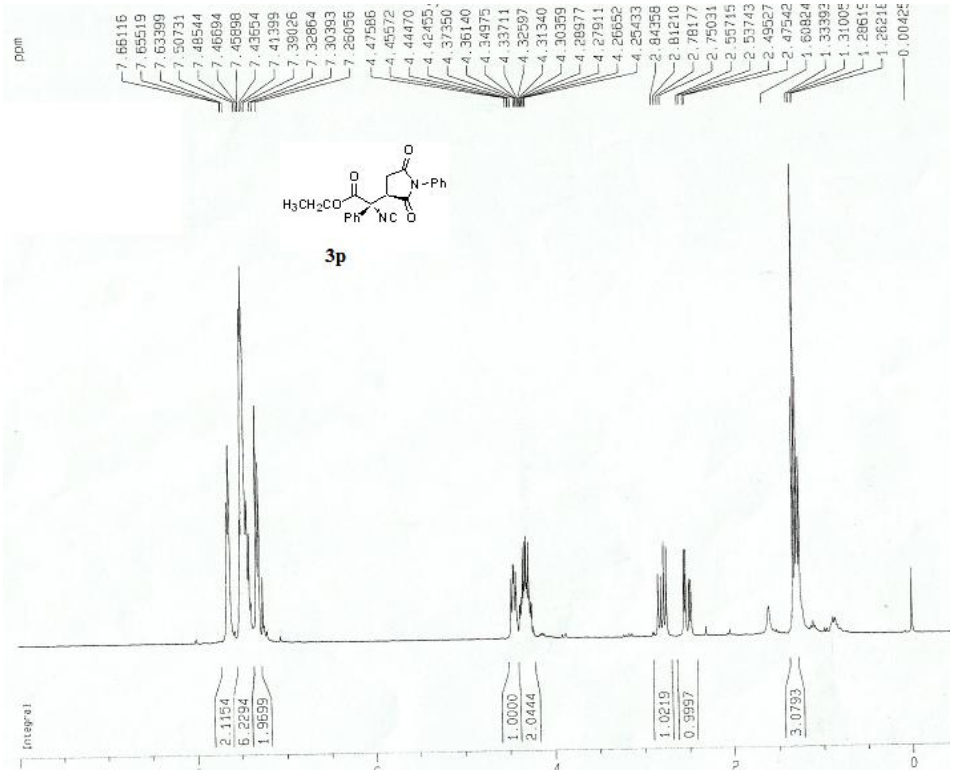
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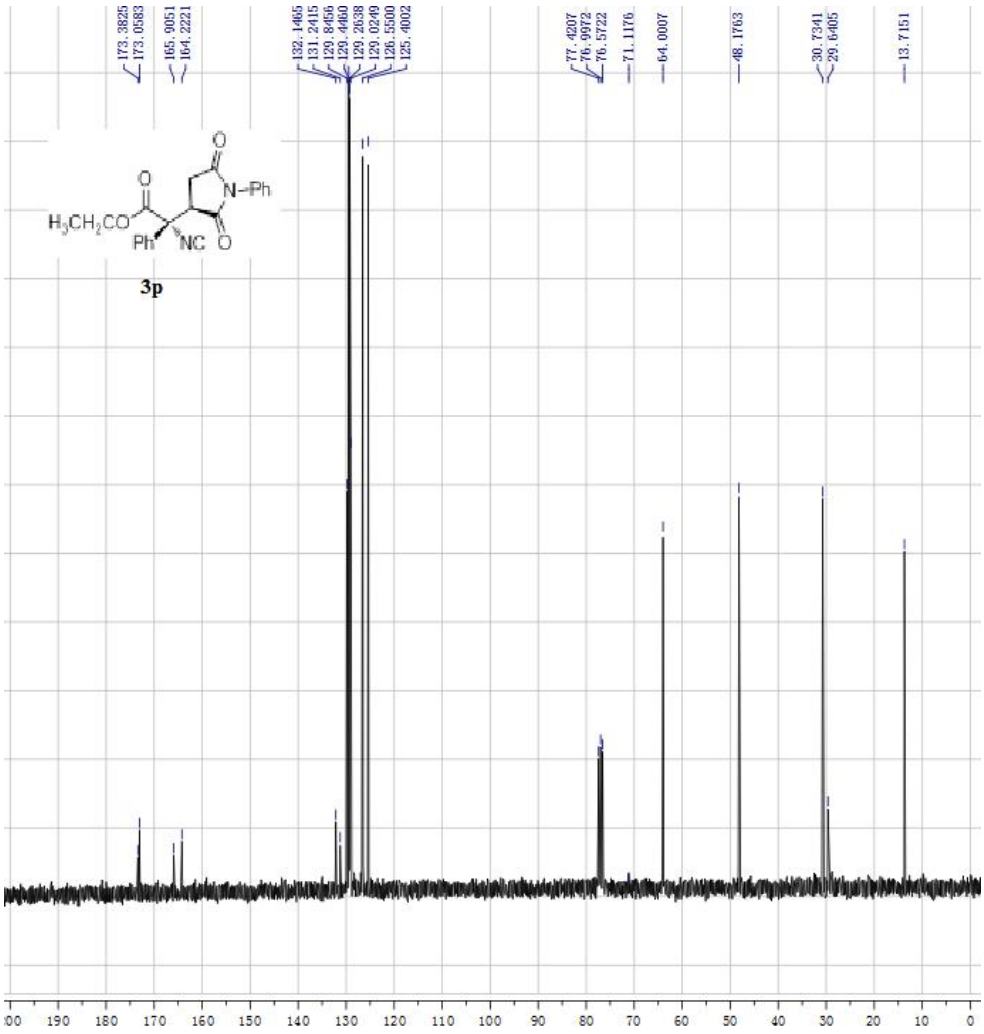
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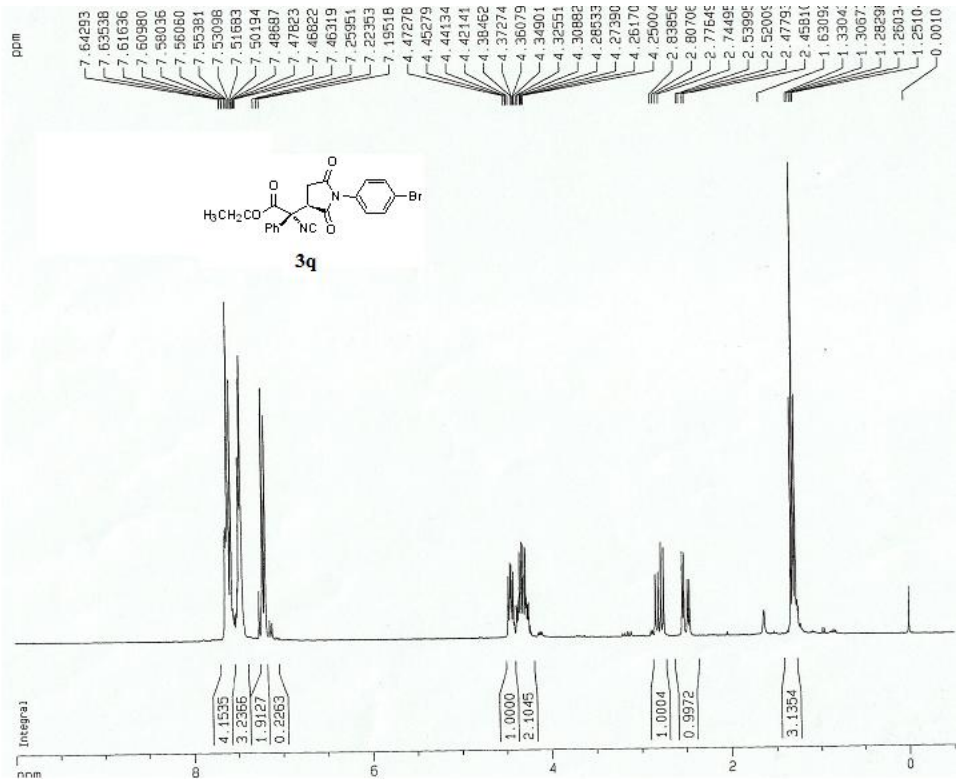
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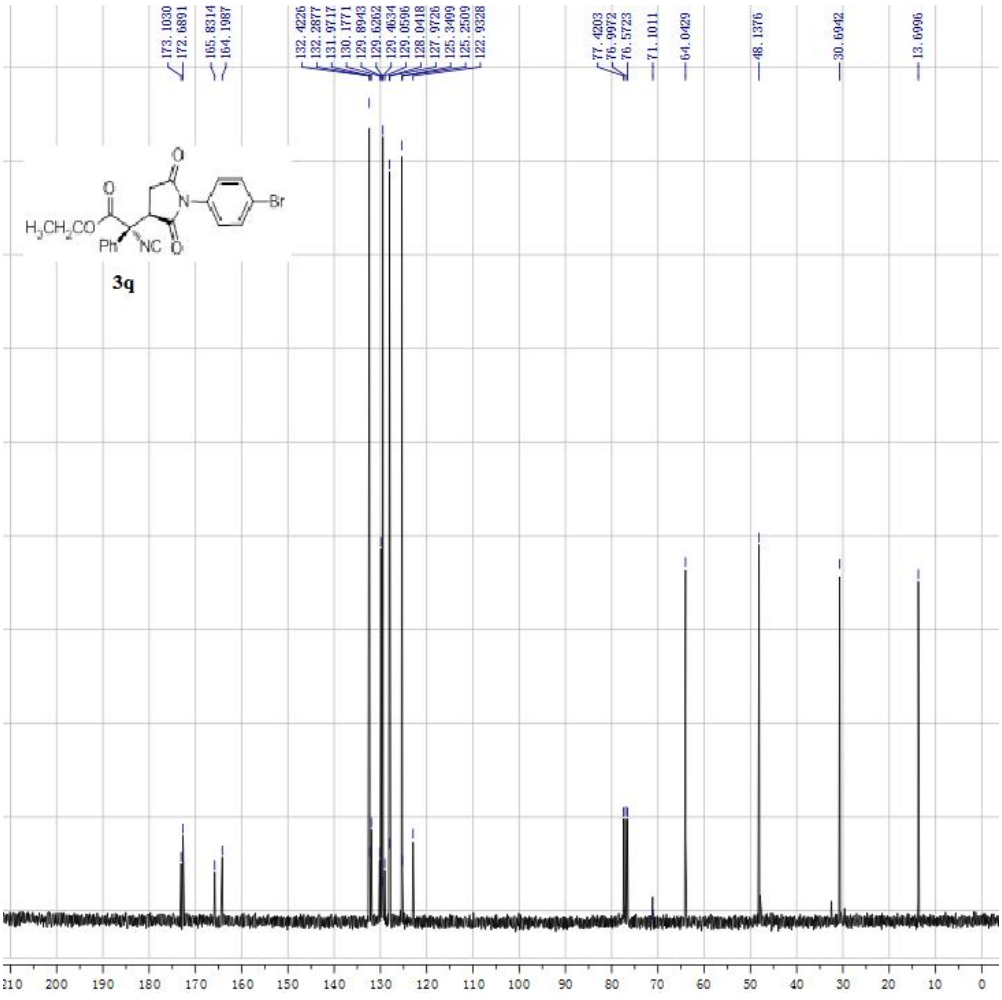
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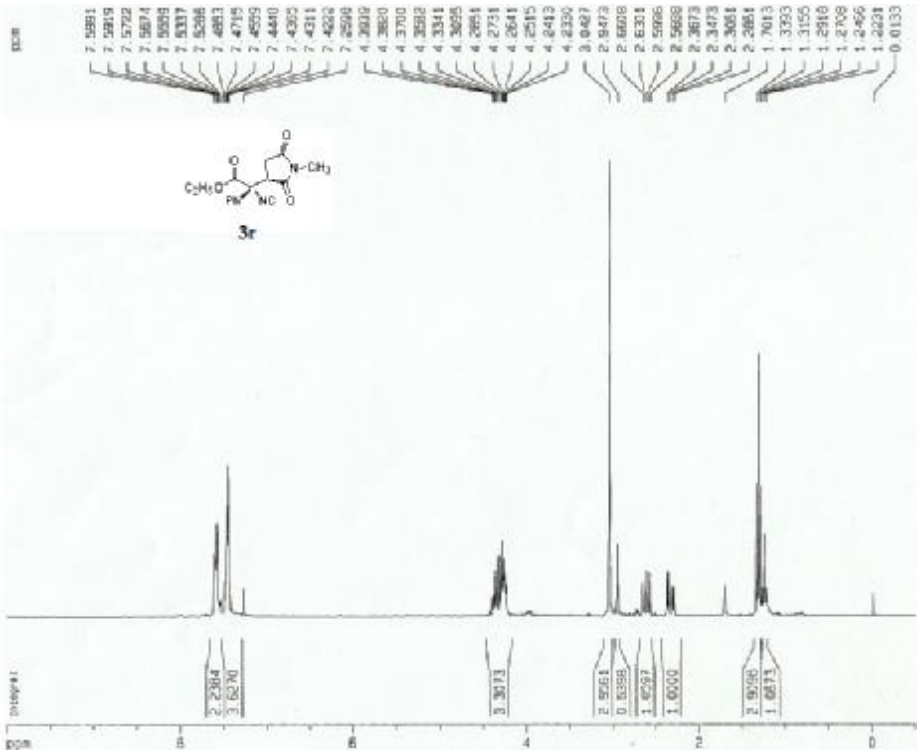
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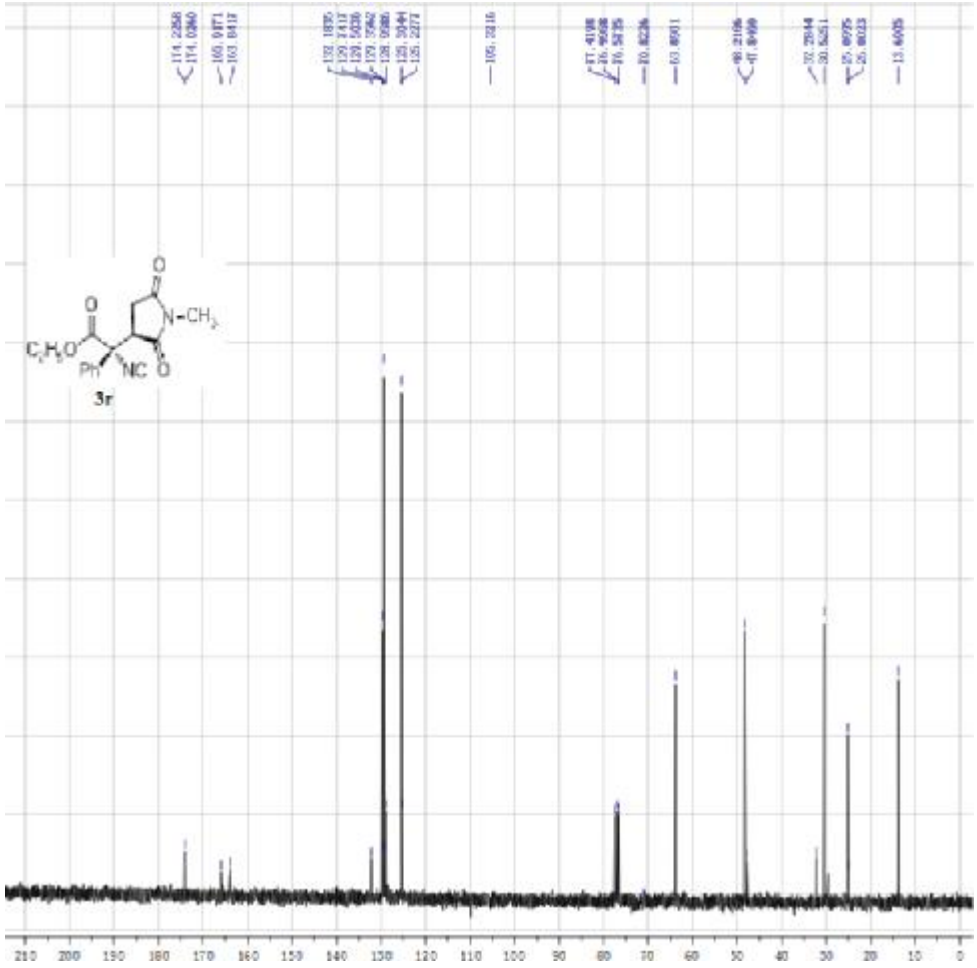
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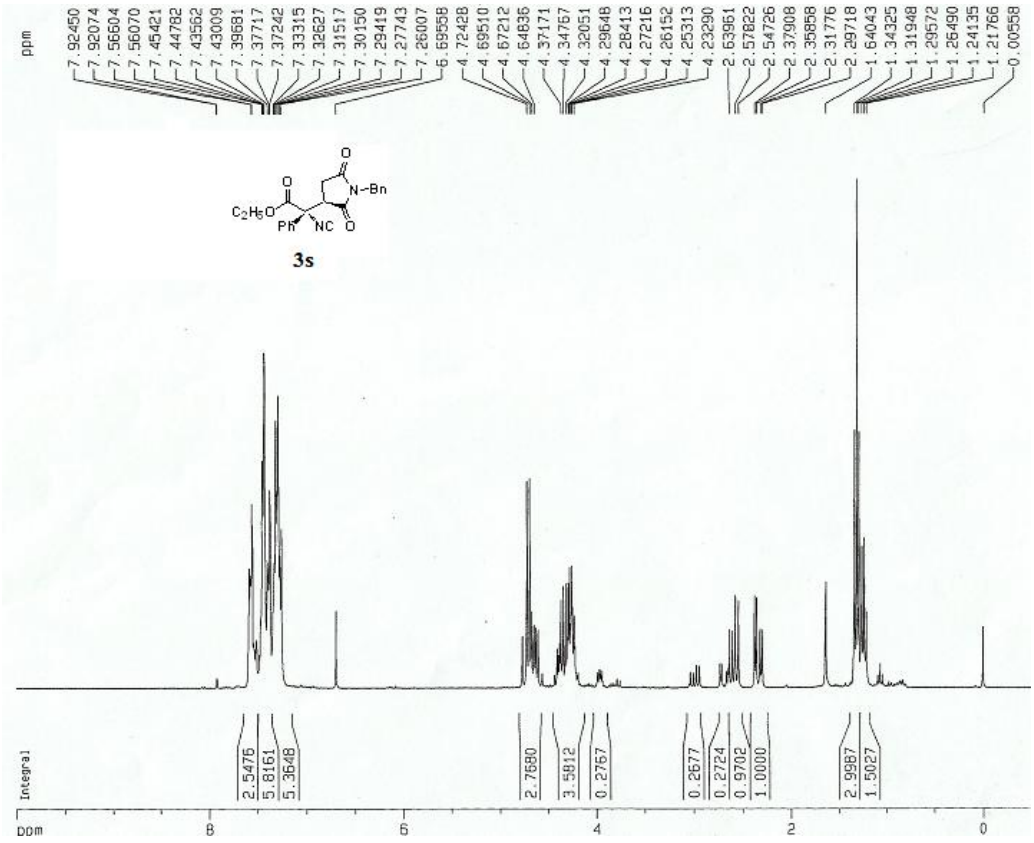
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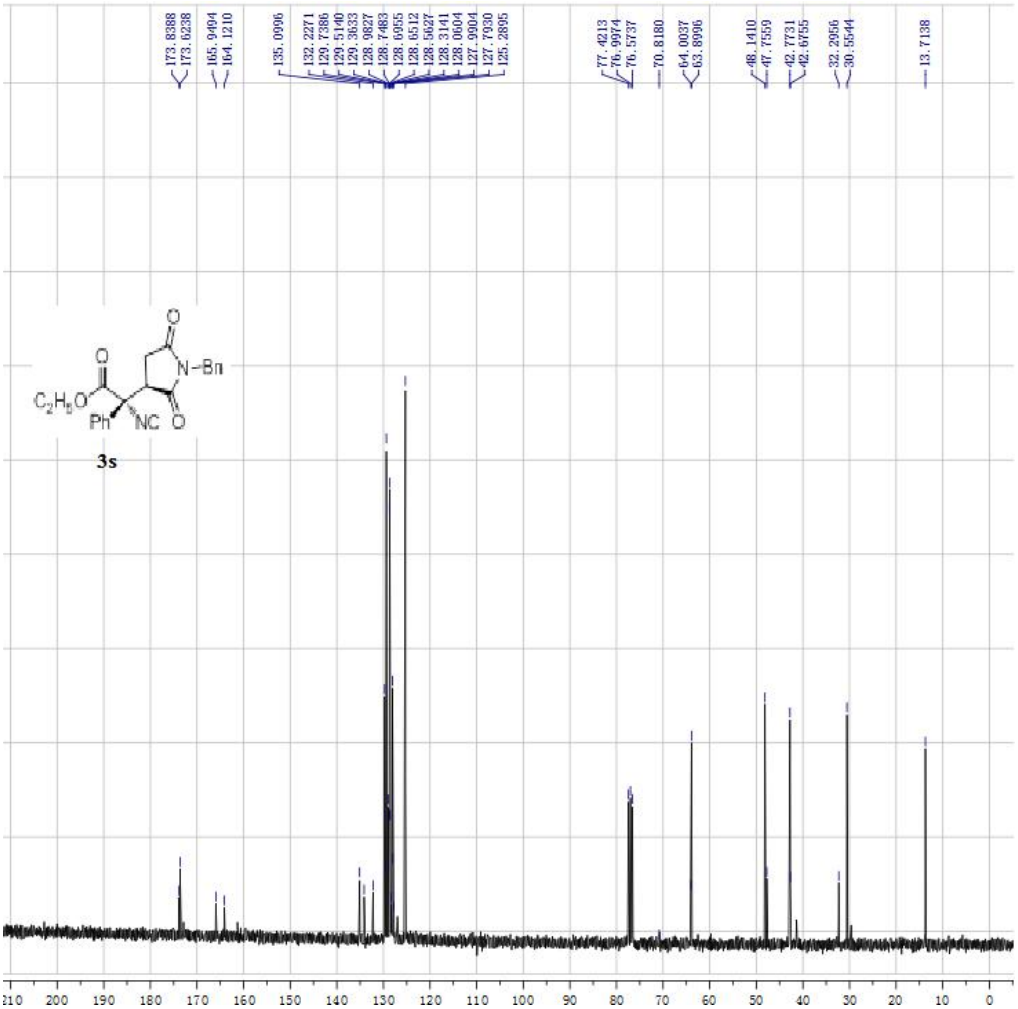
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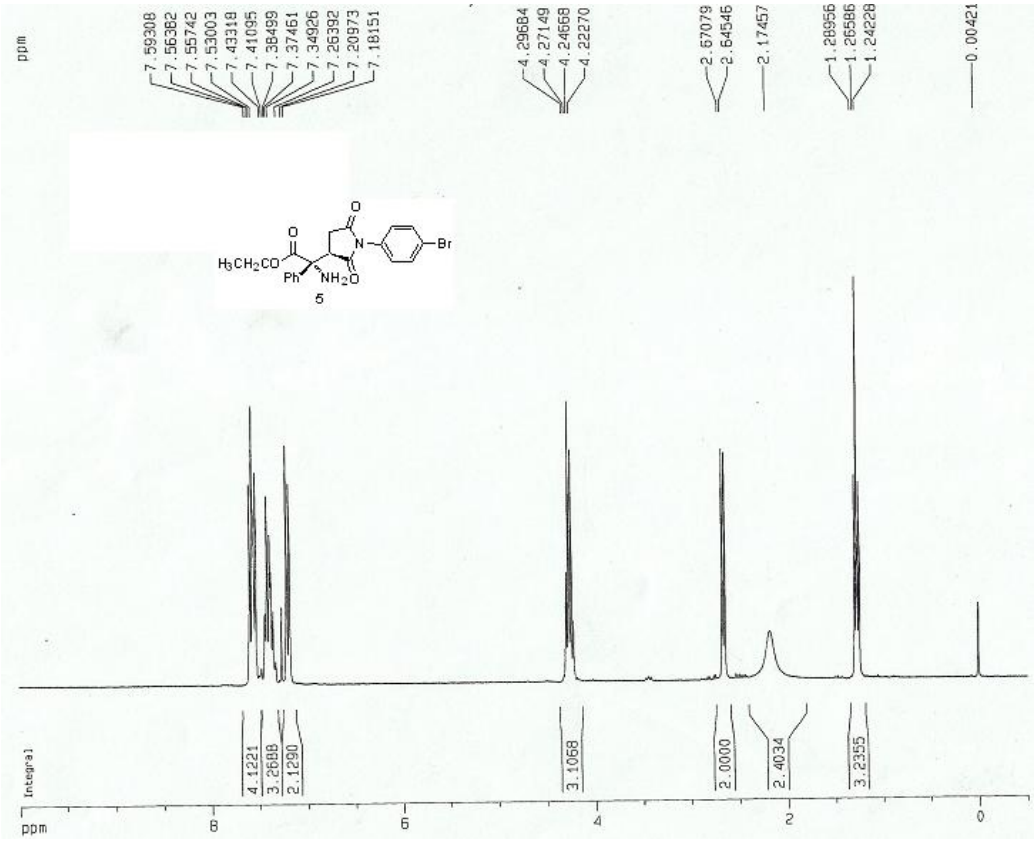
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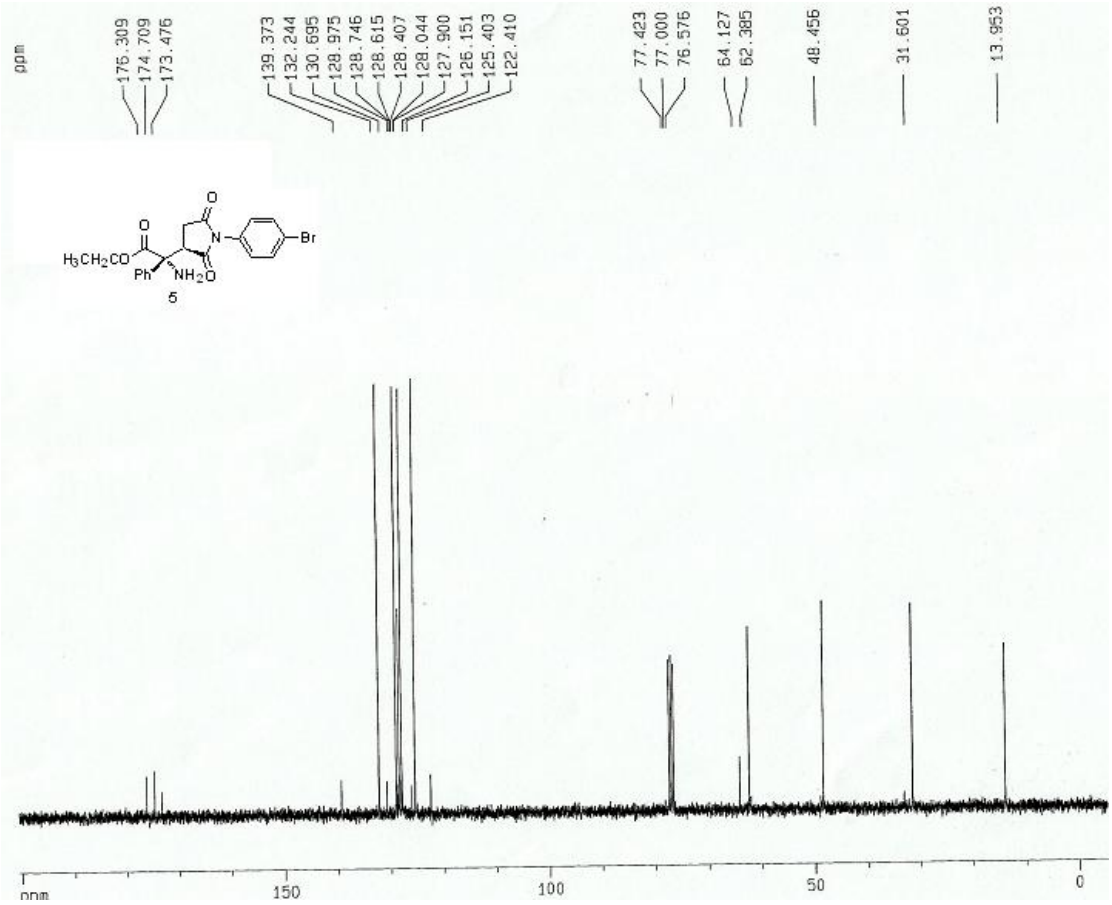
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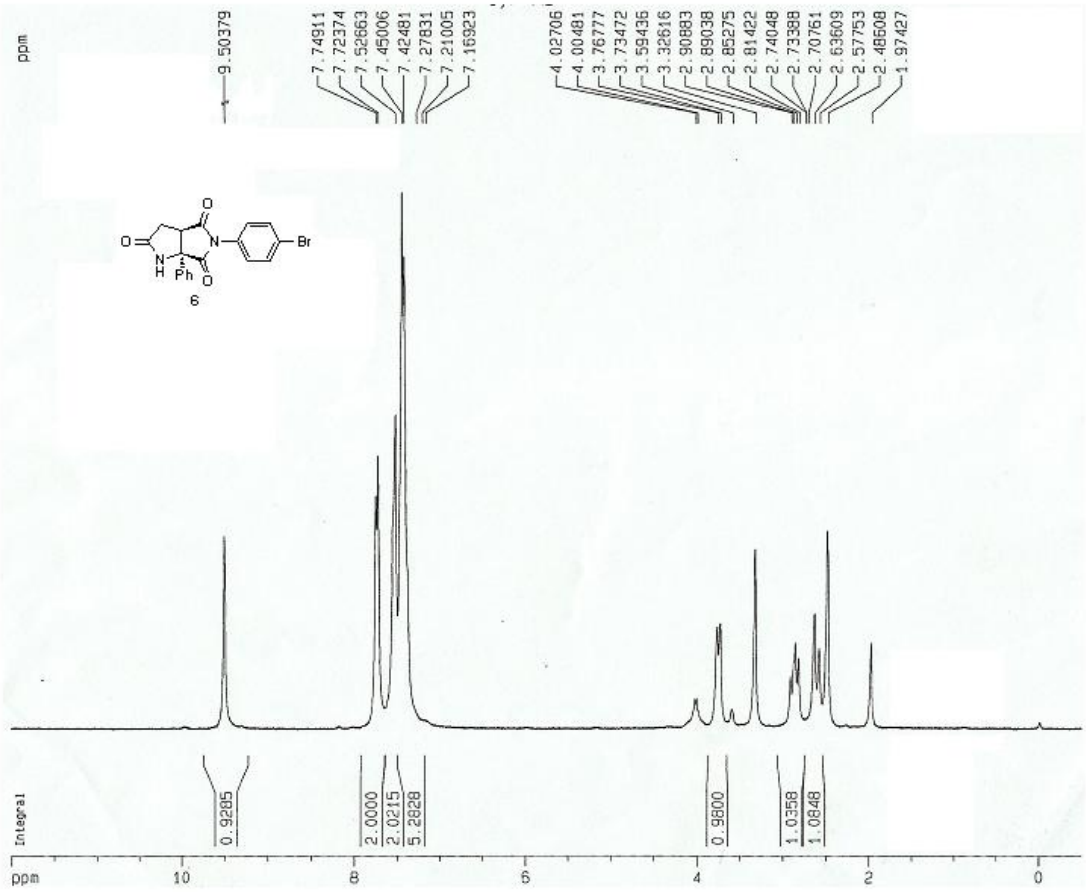
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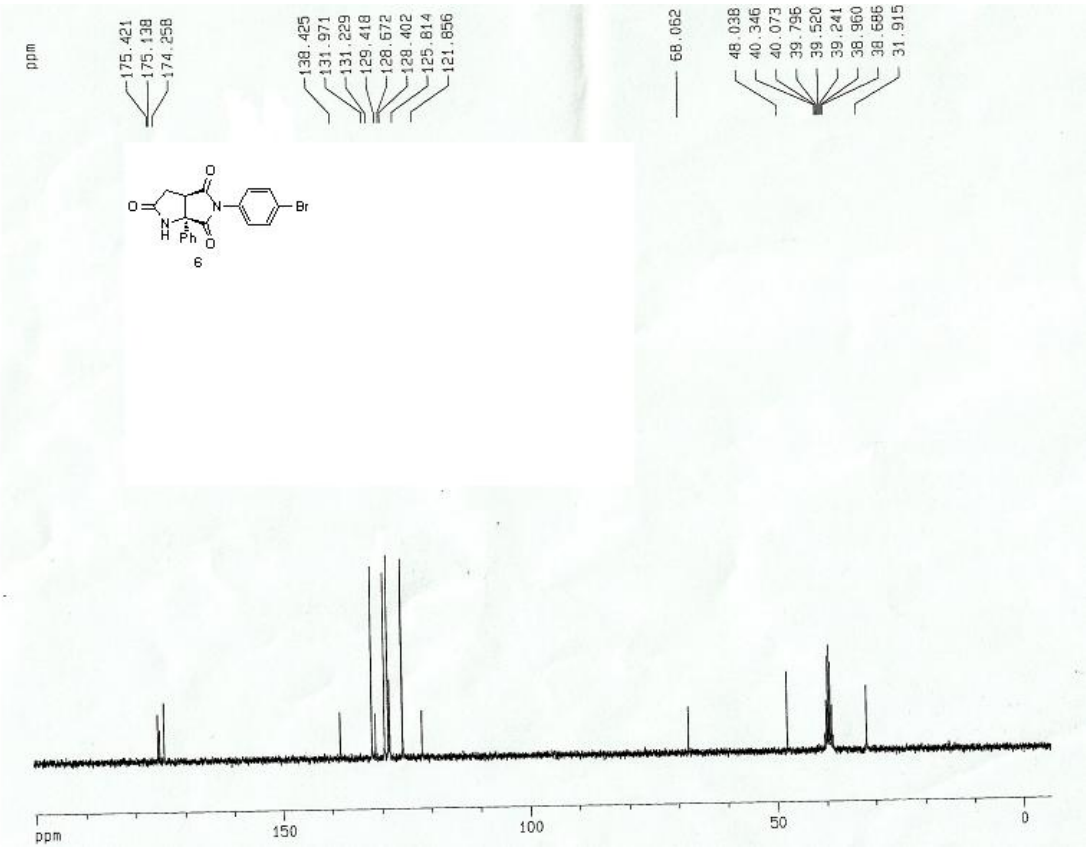
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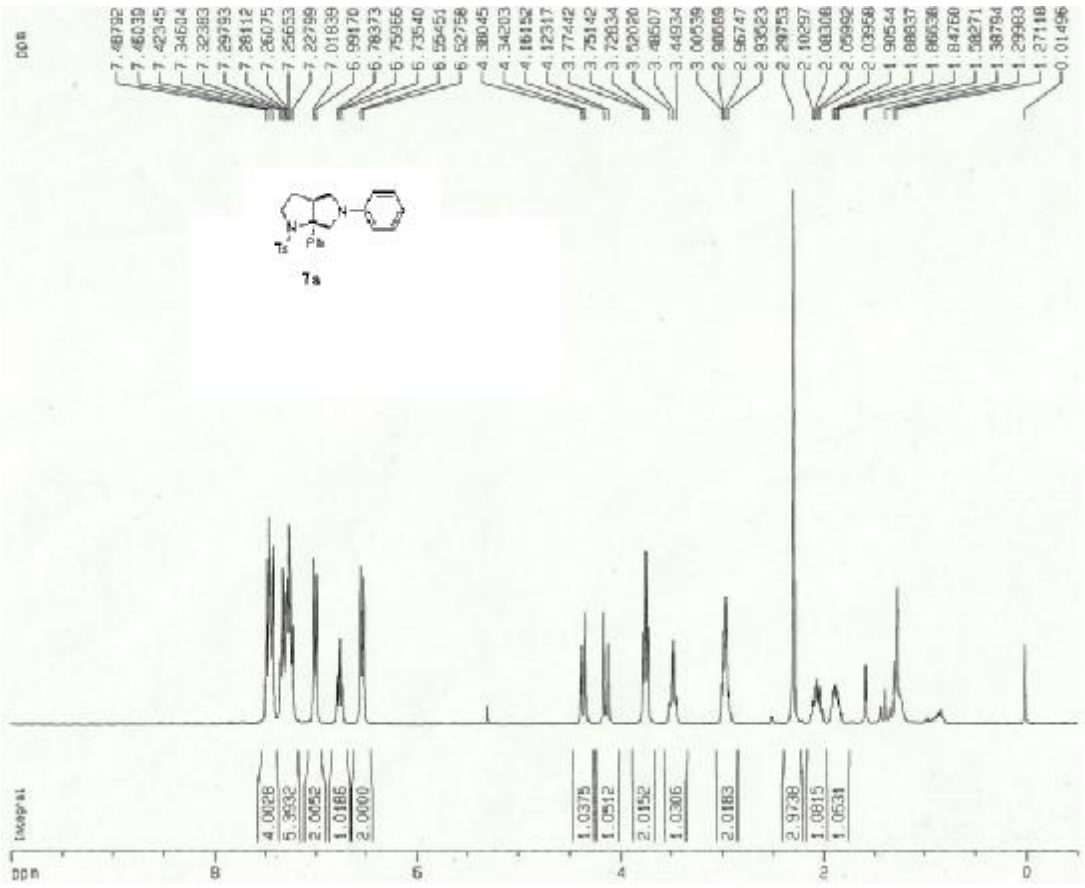
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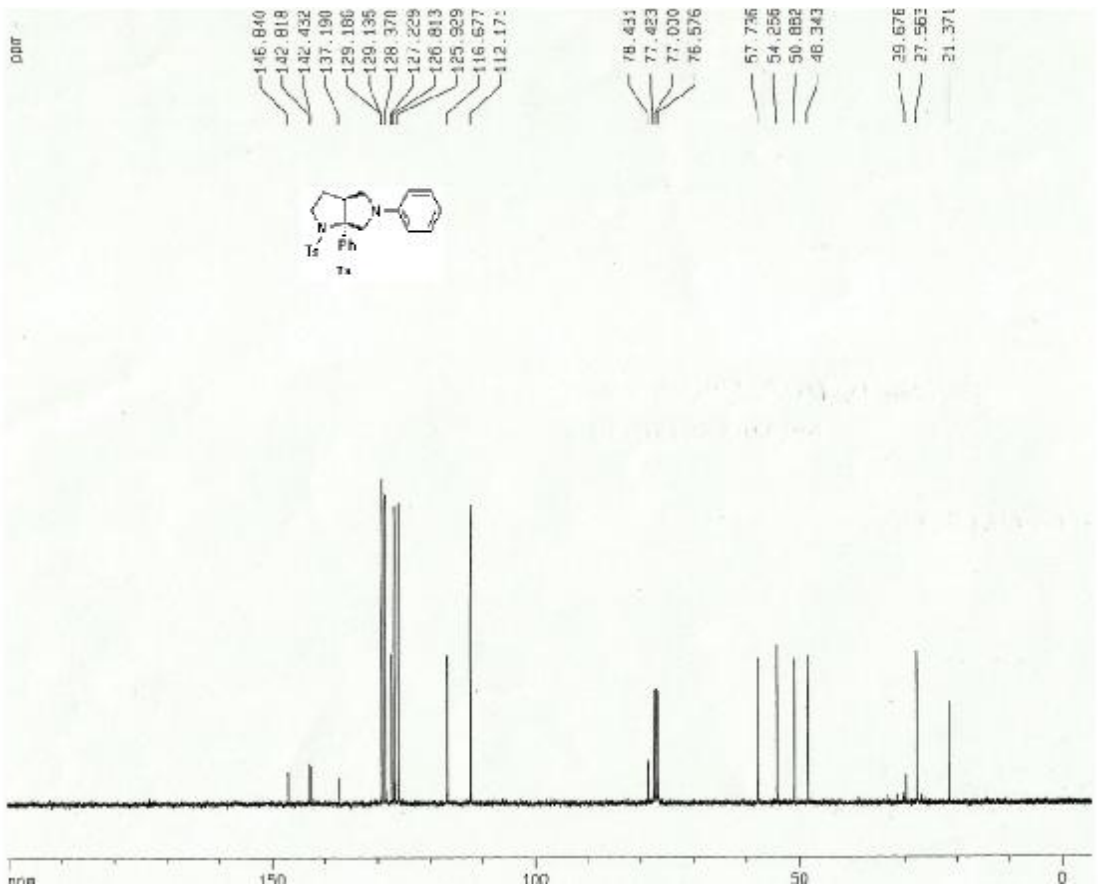
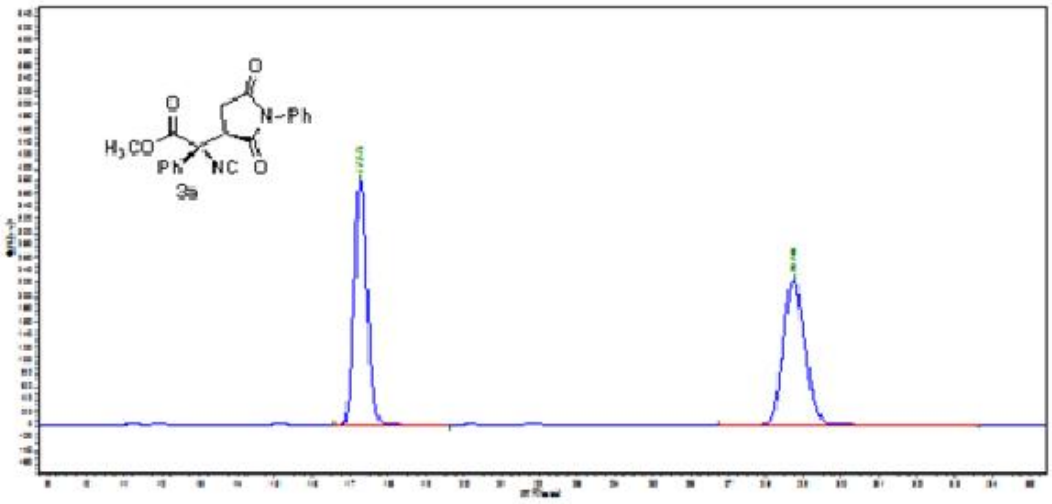
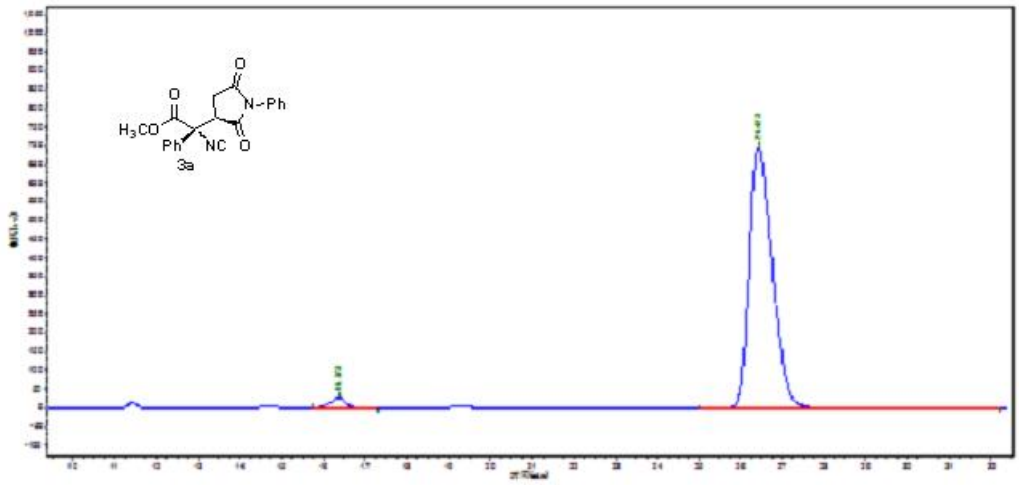

7a

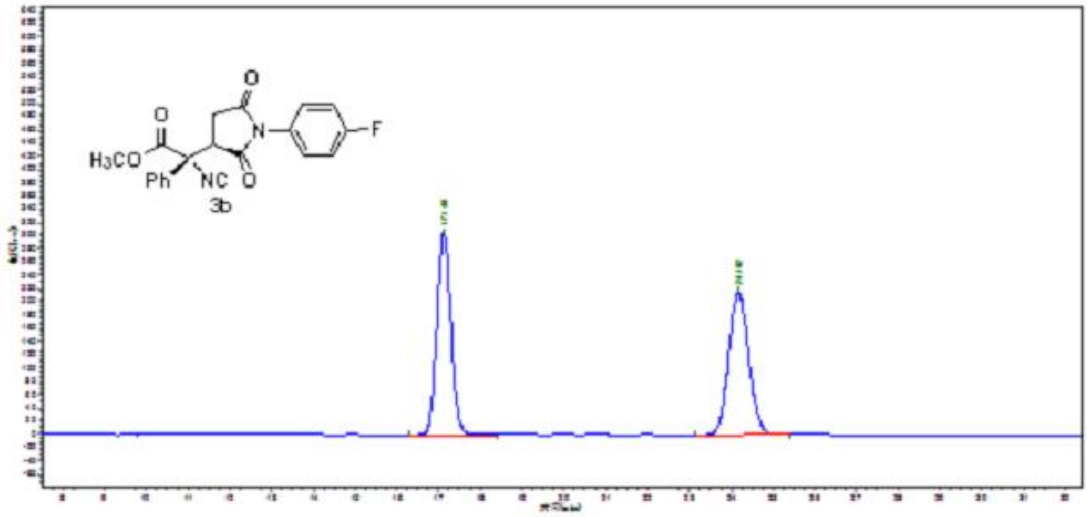
3. HPLC chromatograms



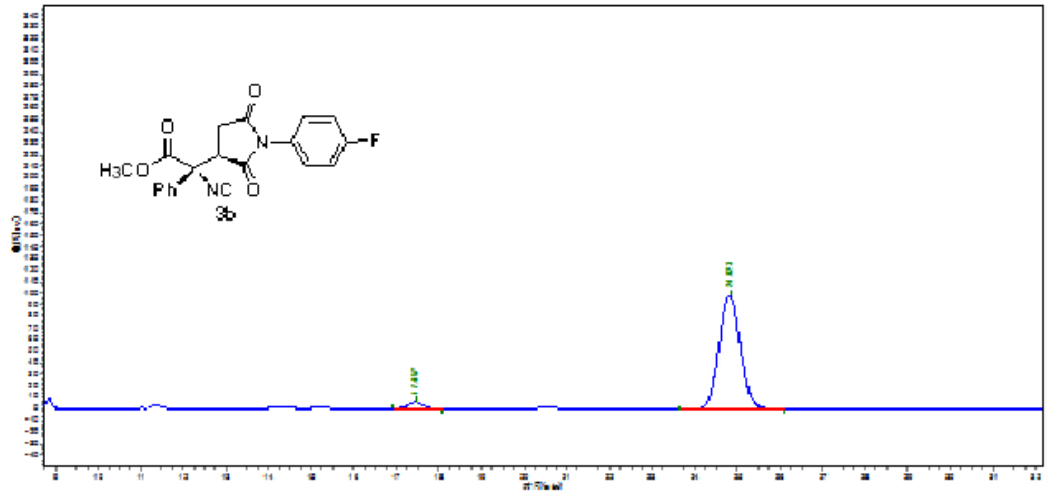
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	17.273	383186.844	9136261.000	50.0425
2	28.740	224544.656	9120755.000	49.9575



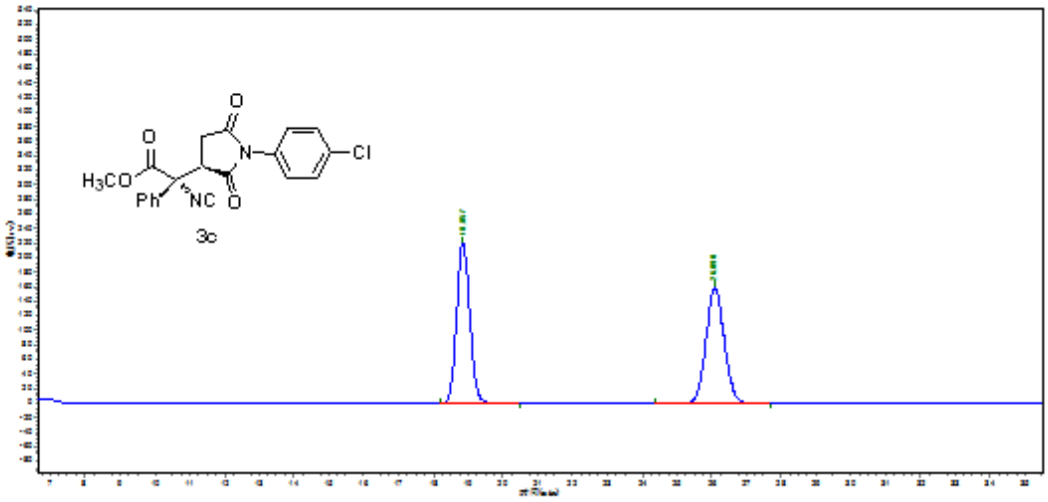
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	16.373	26060.199	691800.250	2.5015
2	26.423	689650.813	26765720.000	96.7835



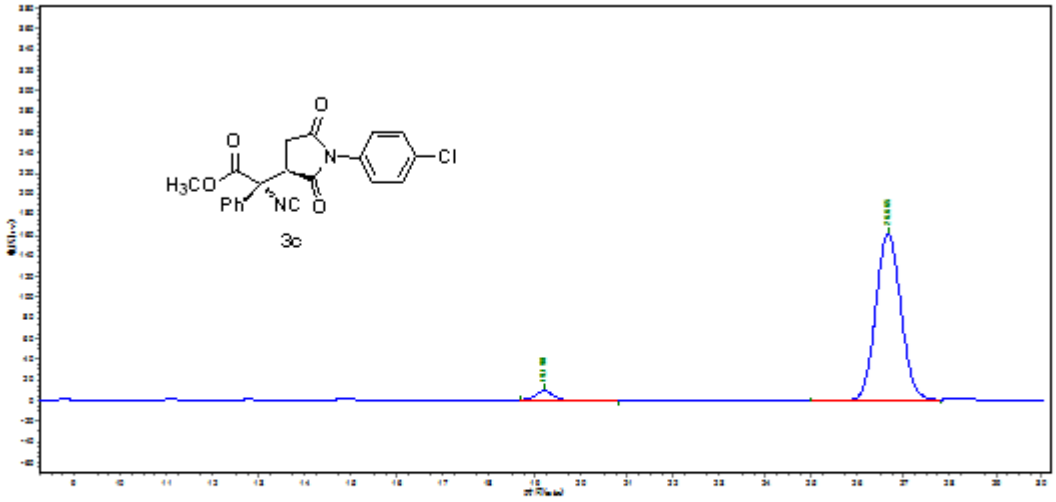
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	17.148	305851.313	7175167.000	49.9183
2	24.182	214272.156	7198645.500	50.0817



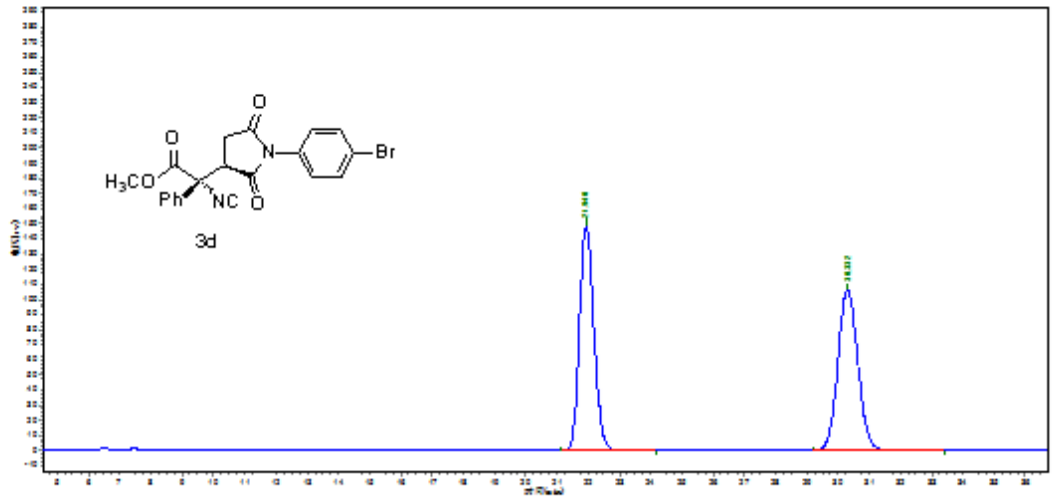
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	17.457	6533.985	167575.750	4.6606
2	24.823	98059.438	3427985.250	95.3394



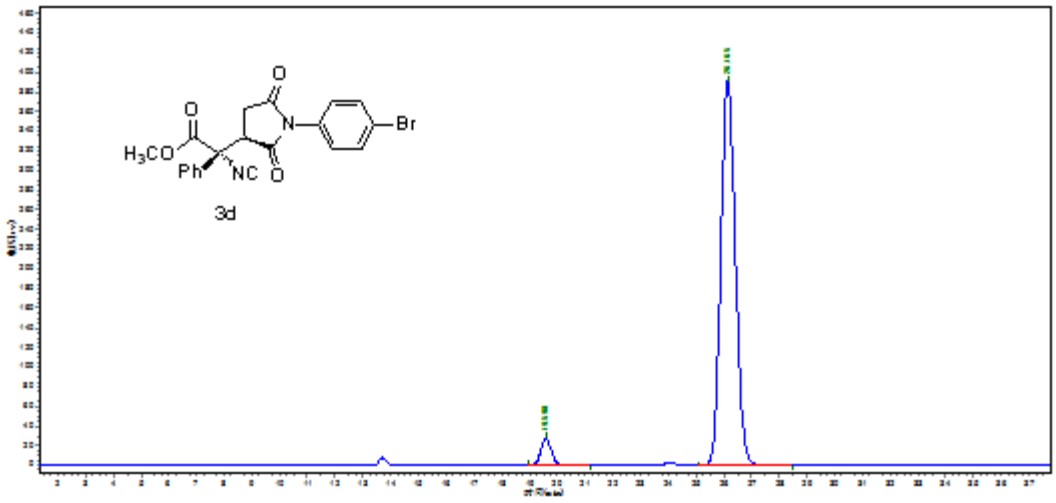
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	18.857	219793.438	5786634.000	49.8872
2	26.090	57202.063	5812806.500	50.1128



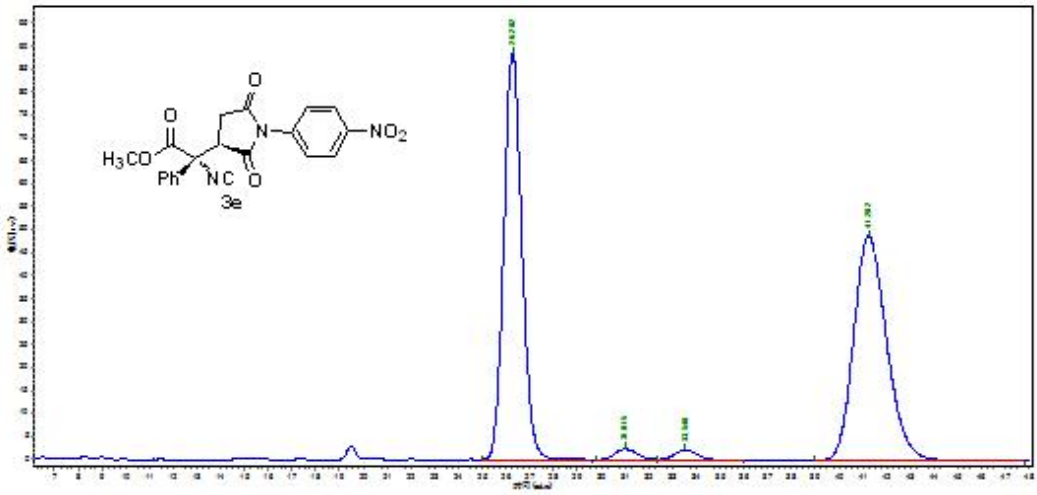
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	19.198	9655.538	273153.844	4.2377
2	26.665	160940.422	6172613.000	95.7623



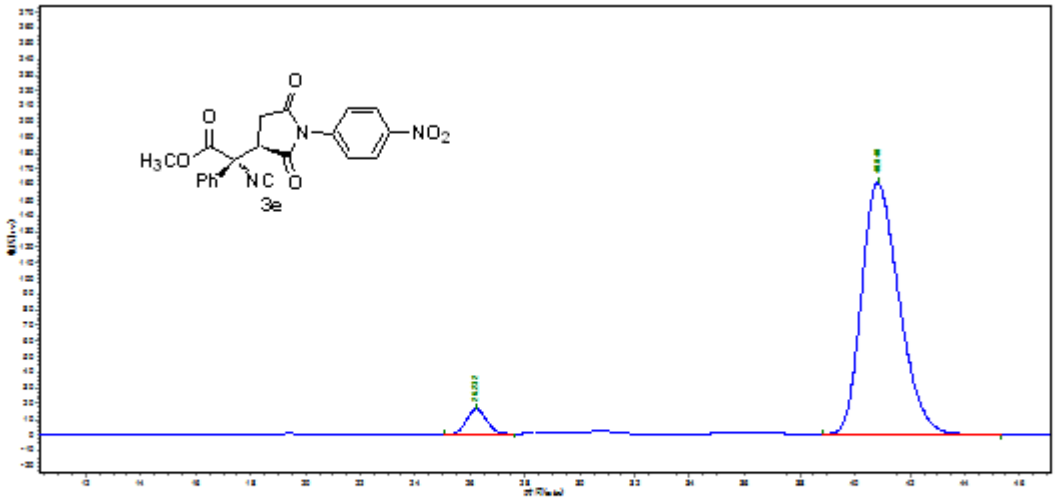
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	21.940	148395.078	4751482.000	49.9355
2	30.332	106914.563	4763750.500	50.0645



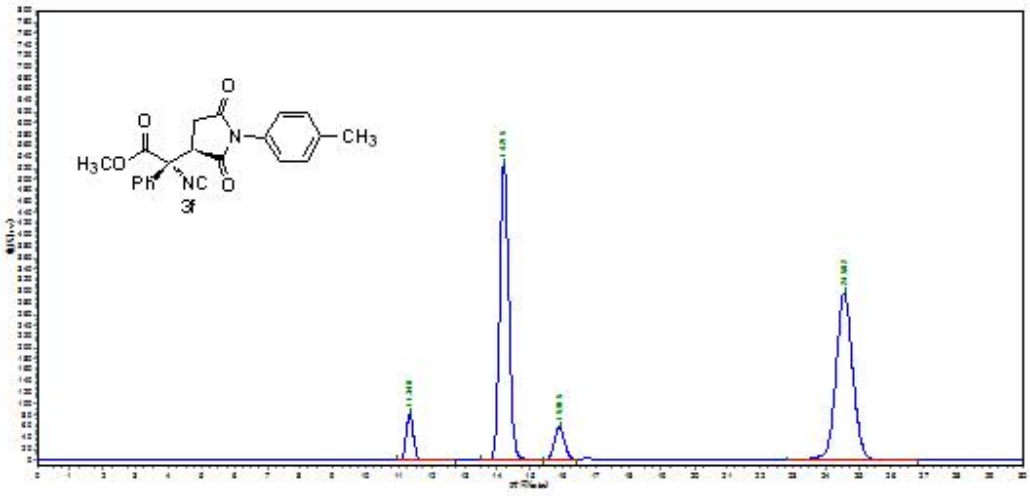
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	19.598	26717.811	730626.875	4.8759
2	26.165	391902.094	14253692.000	95.1241



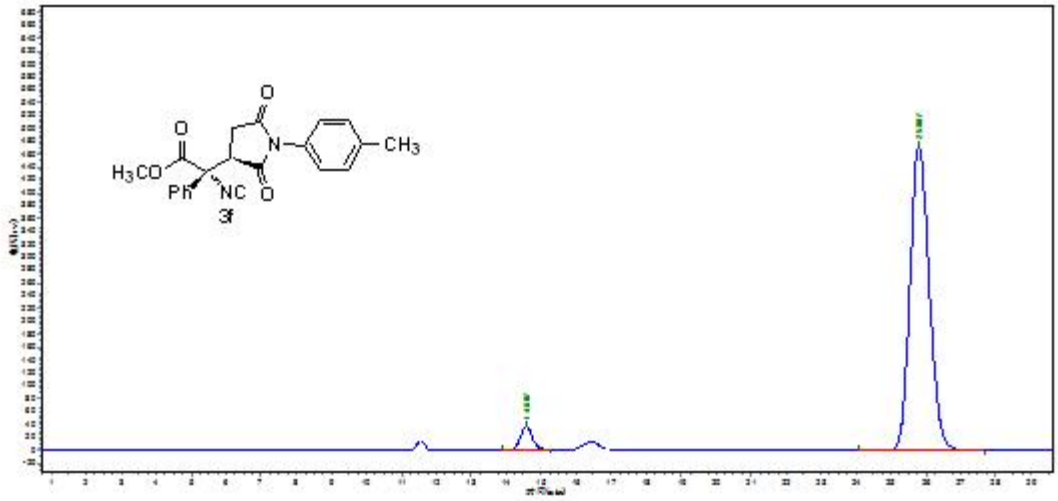
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	26.282	88684.148	4696699.000	48.1493
2	31.015	2288.011	150920.688	1.5472
3	33.548	2098.032	142081.422	1.4566
4	41.282	48806.156	4688975.000	48.0702



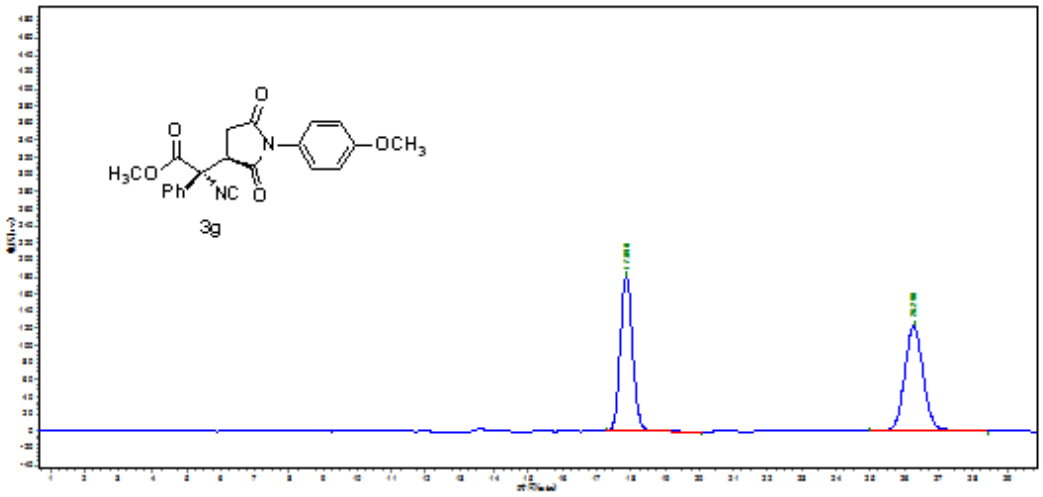
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	26.232	16147.713	827937.750	5.1350
2	40.840	160901.688	15295349.000	94.8650



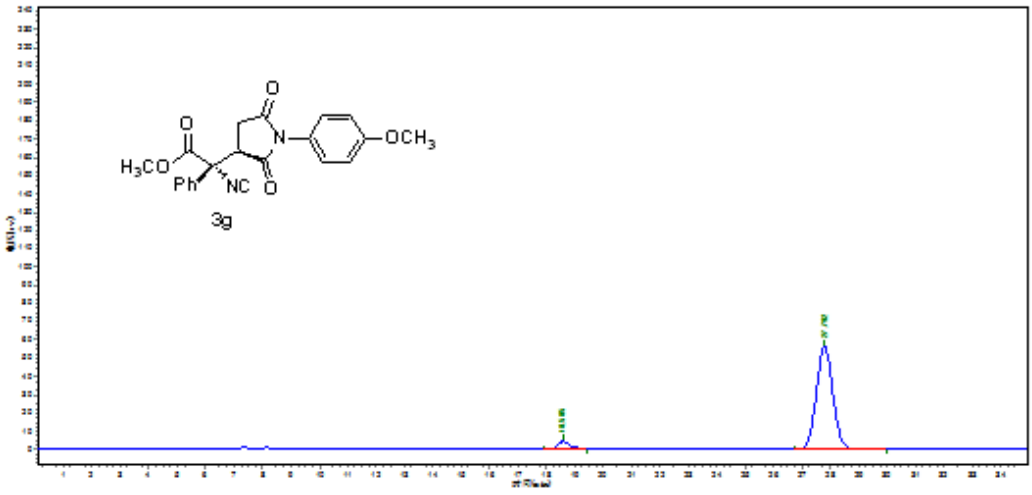
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.348	82585.953	1262997.875	5.3456
2	14.215	524600.875	10371114.000	43.8955
3	15.915	58723.250	1296559.500	5.4877
4	24.582	297374.563	10696137.000	45.2712



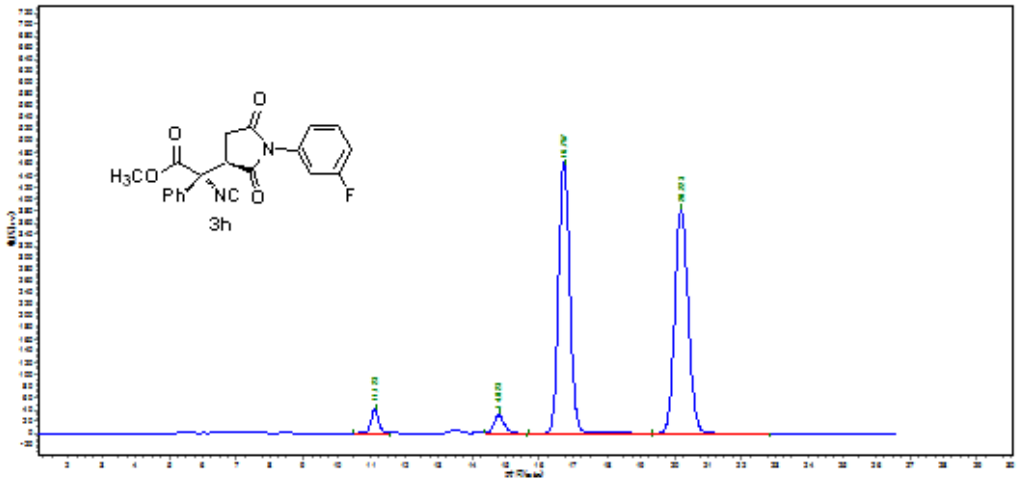
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.607	37096.500	915813.375	4.8472
2	25.807	468480.750	17977486.000	95.1520



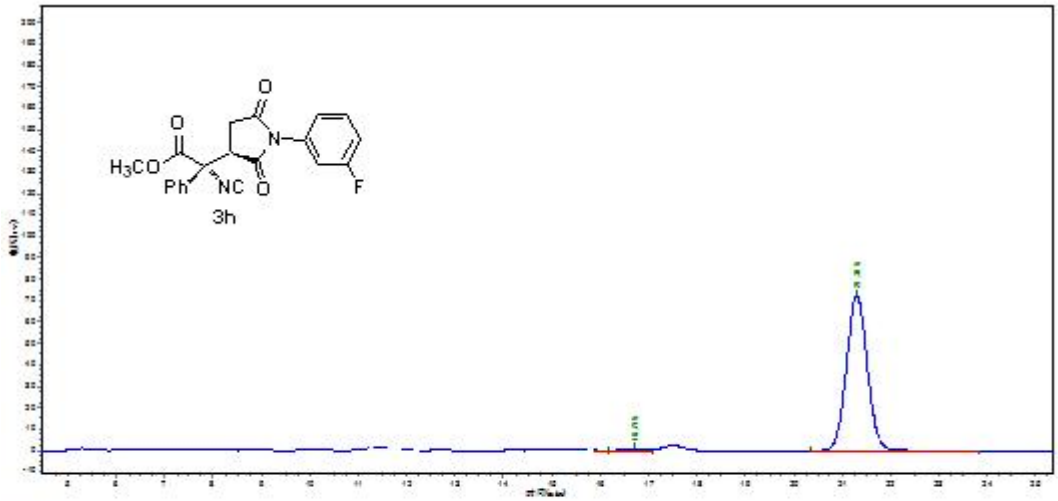
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	17.890	181713.922	4555329.000	48.6376
2	26.290	123356.703	4810529.500	51.3624



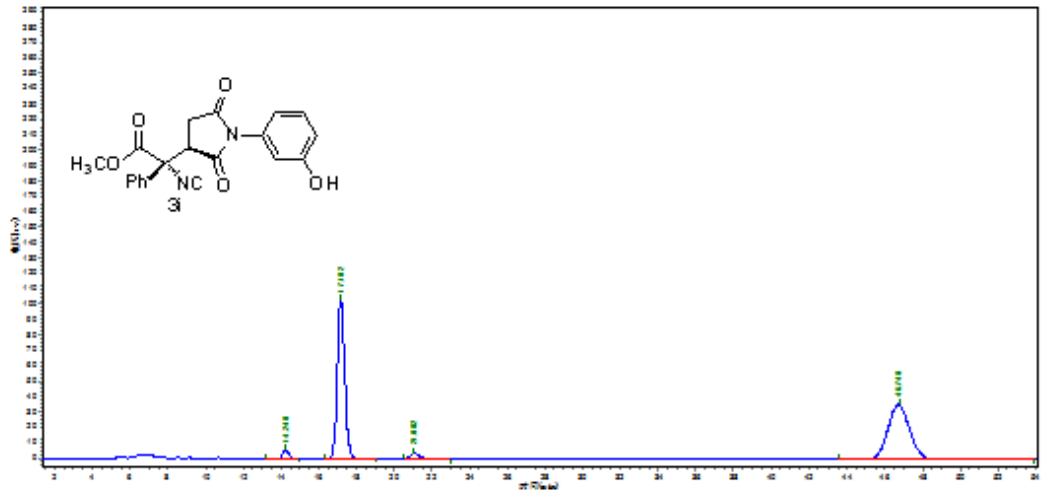
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	18.585	4274.711	122432.805	5.0572
2	27.792	56453.891	2298535.750	94.9428



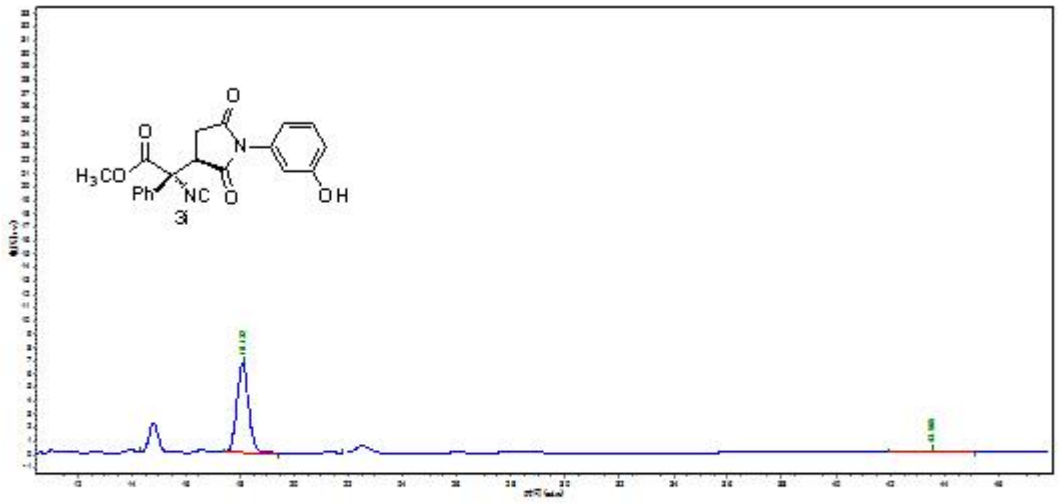
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.123	40534.137	640387.063	2.8152
2	14.823	30648.385	655434.188	2.8814
3	16.757	462846.781	10773868.000	47.3635
4	20.223	383550.563	10677507.000	46.9399



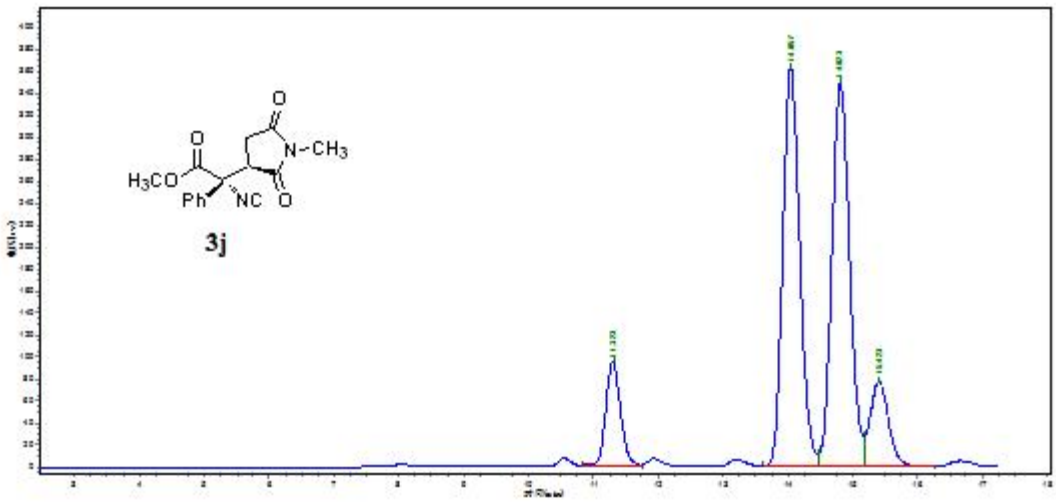
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	16.715	614.710	18433.209	0.8467
2	21.315	72288.070	2158607.500	99.1533



Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.248	5370.792	123358.797	2.0702
2	17.182	103054.313	2857164.750	47.9492
3	21.082	3459.205	122339.086	2.0531
4	46.748	35235.508	2855867.250	47.9274

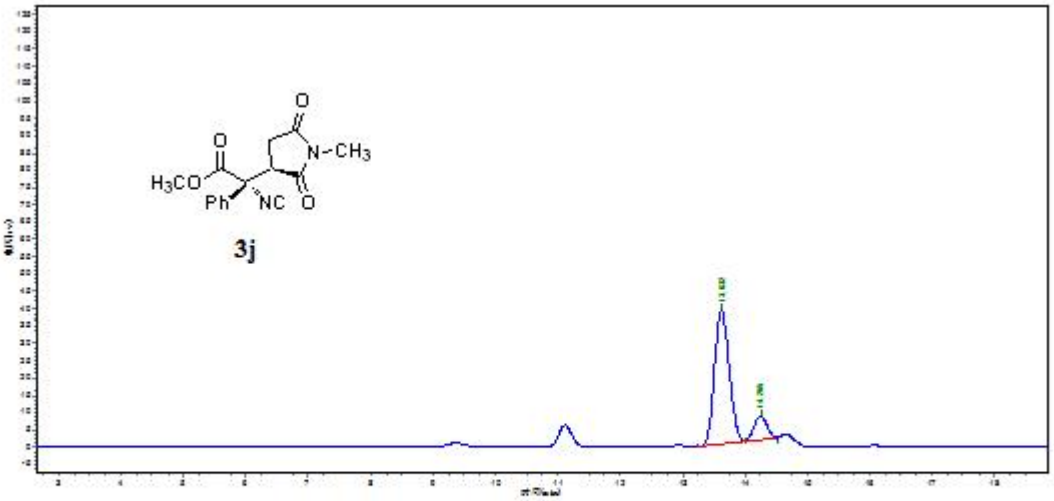


Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	18.132	6678.100	199173.000	97.776
2	43.565	53.234	4530.400	2.2240



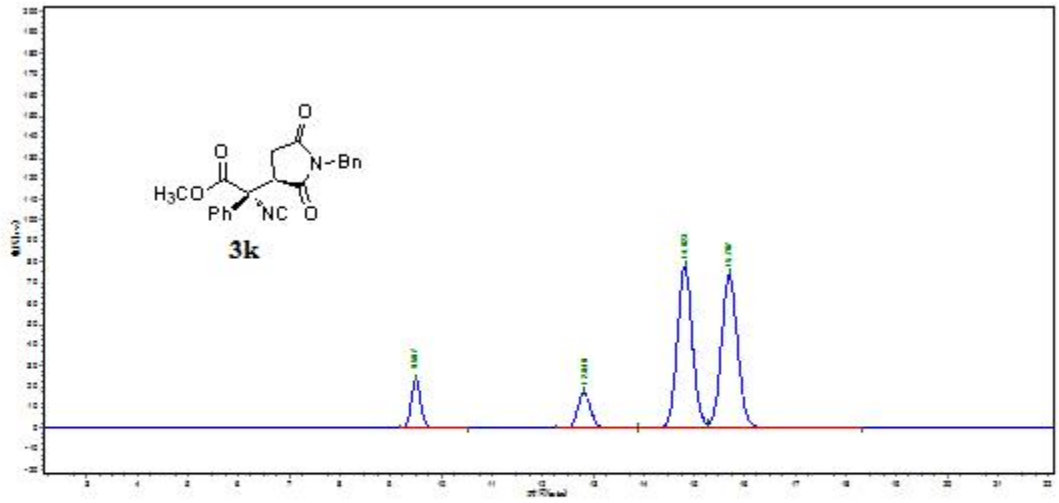
3j

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.323	95201.906	1550474.500	9.4913
2	14.057	361619.281	6614746.000	40.4925
3	14.823	348114.938	6646818.500	40.6888
4	15.423	77096.469	1523696.000	9.3274

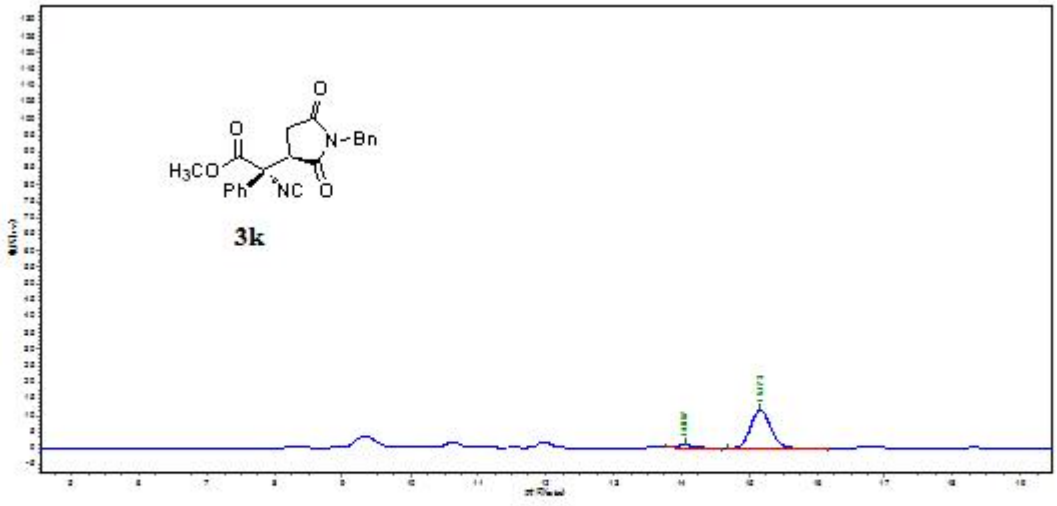


3j

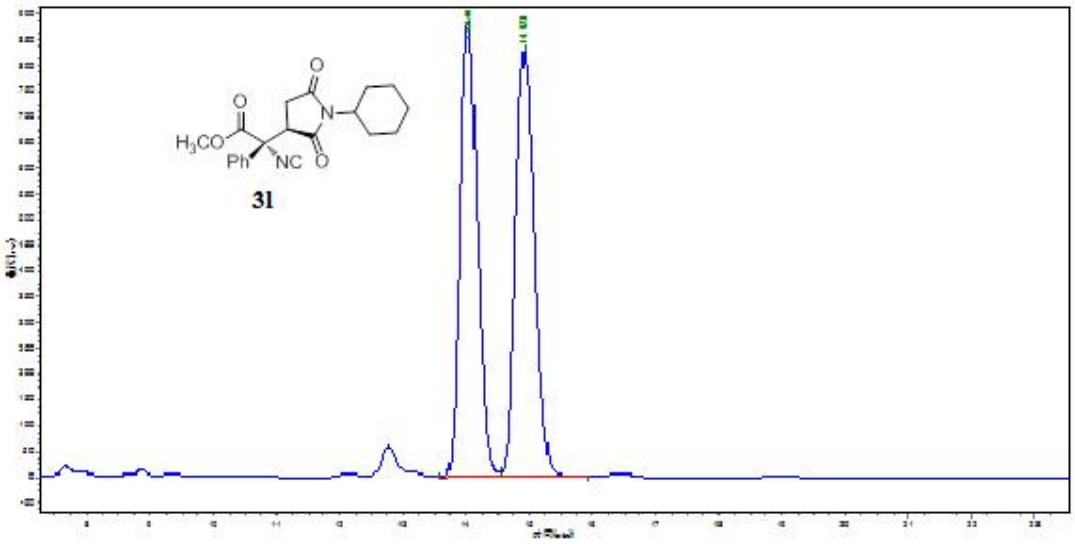
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	13.632	39560.332	673813.438	80.2064
2	14.265	8864.777	166286.469	19.7937



Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	9.507	23048.768	304215.906	7.8072
2	12.840	16978.563	307416.594	7.8894
3	14.823	77185.141	1627041.125	41.7555
4	15.707	73608.813	1657921.375	42.5480

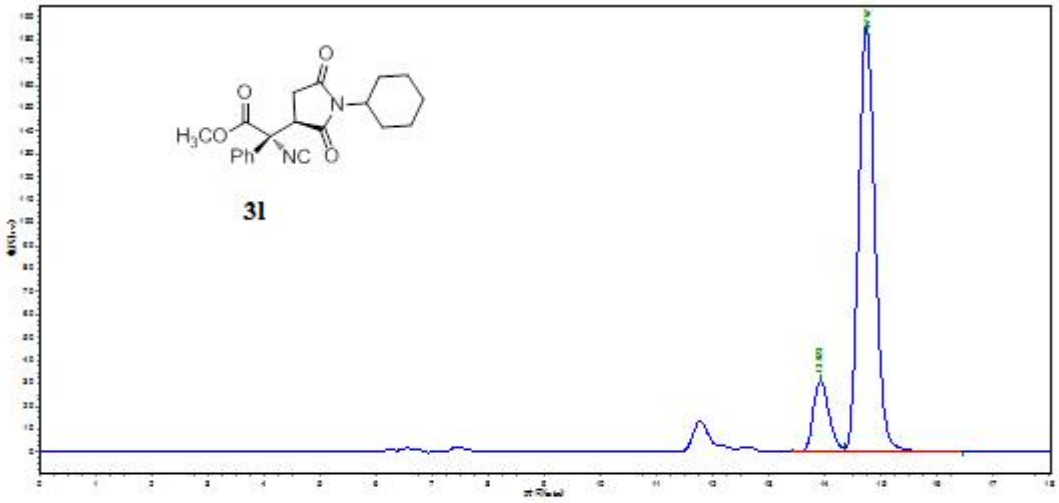


Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.057	998.972	19525.205	7.5155
2	15.173	11667.955	240272.484	92.4845



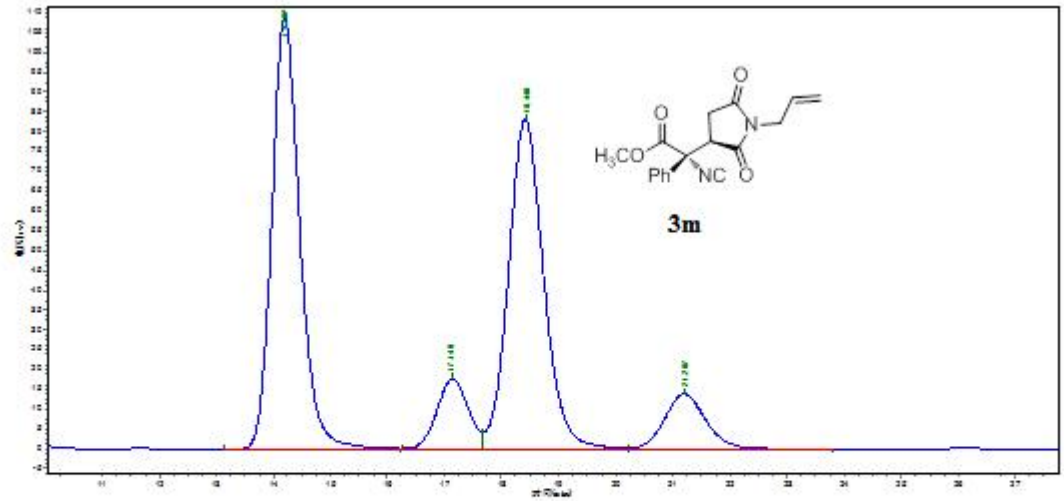
31

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.040	879125.188	17040064.000	49.6064
2	14.923	826222.438	17310460.000	50.3936

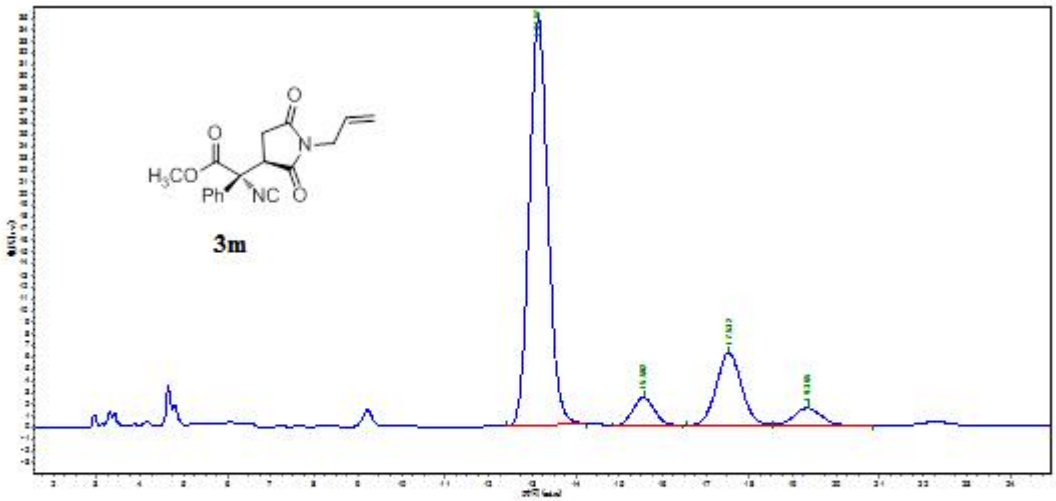


31

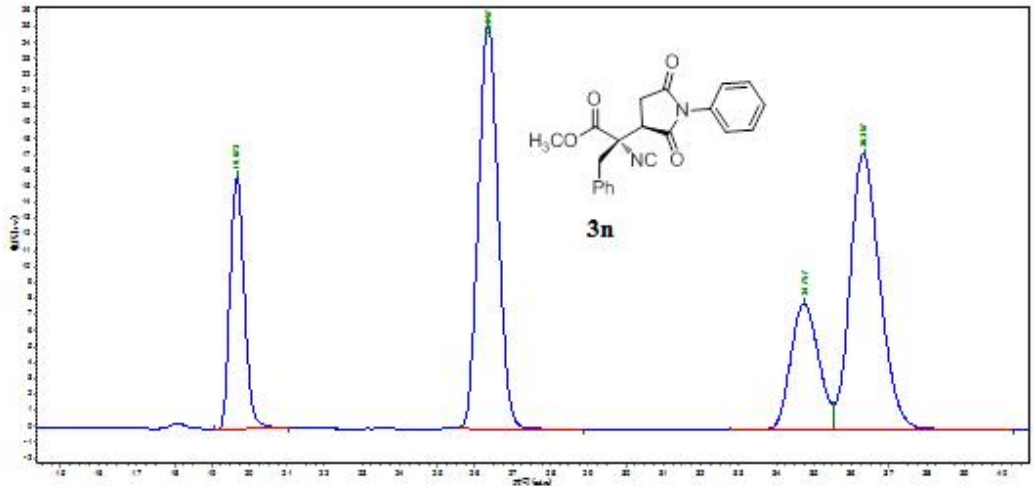
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	13.923	30774.105	600560.688	13.6668
2	14.757	184782.406	3793744.000	86.3332



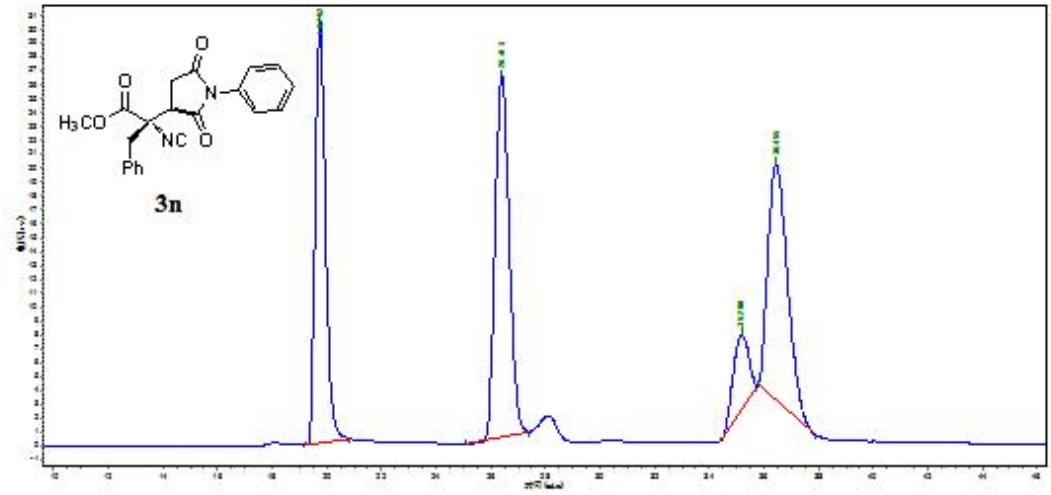
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.207	109404.227	3716658.250	42.6510
2	17.140	17768.602	688304.688	7.8987
3	18.440	83137.969	3583880.750	41.1273
4	21.207	14004.528	725270.938	8.3229



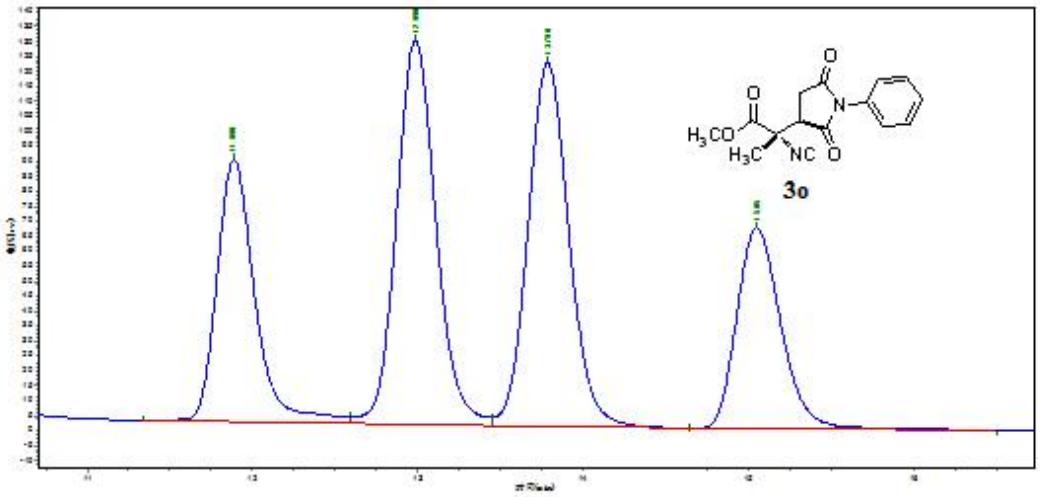
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	13.157	34766.602	1032390.875	72.3184
2	15.582	2407.568	83577.797	5.8546
3	17.532	6190.000	248259.703	17.3904
4	19.365	1450.857	63335.102	4.4366



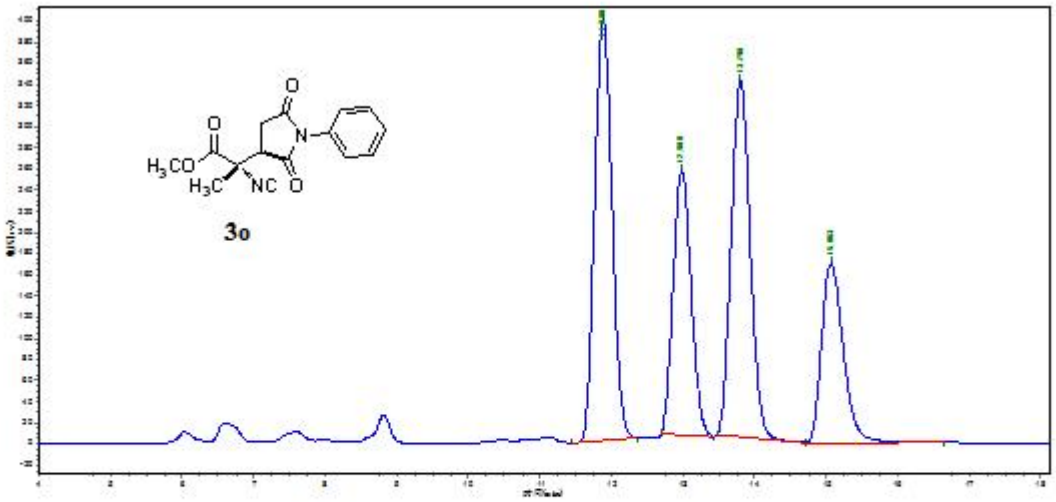
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	19.673	15677.700	412169.000	15.1955
2	26.357	25344.350	931176.563	34.3299
3	34.757	7938.902	413766.813	15.2544
4	36.357	17233.195	955325.000	35.2202



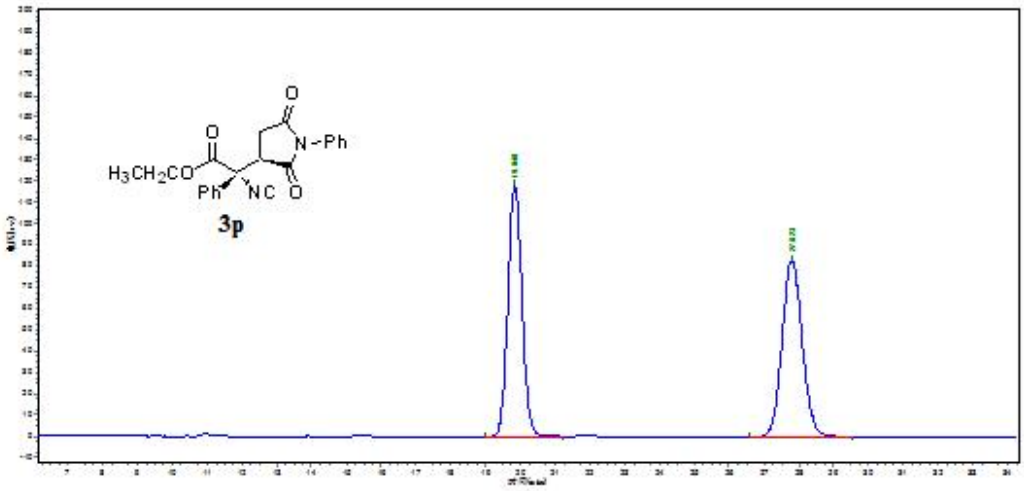
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	19.752	30454.334	802501.688	28.7403
2	26.413	25958.643	929728.188	33.2967
3	35.200	5374.579	212910.813	7.6251
4	36.455	17039.990	847108.563	30.3379



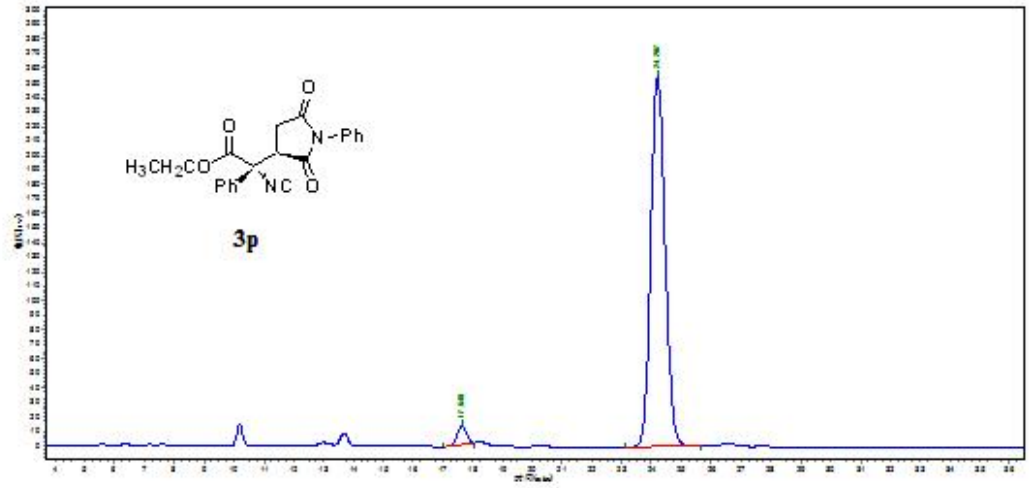
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.890	87459.430	1403881.875	20.4359
2	12.990	128313.297	2133017.000	31.0497
3	13.790	121609.750	2089616.625	30.4179
4	15.057	67148.242	1243179.000	18.0966



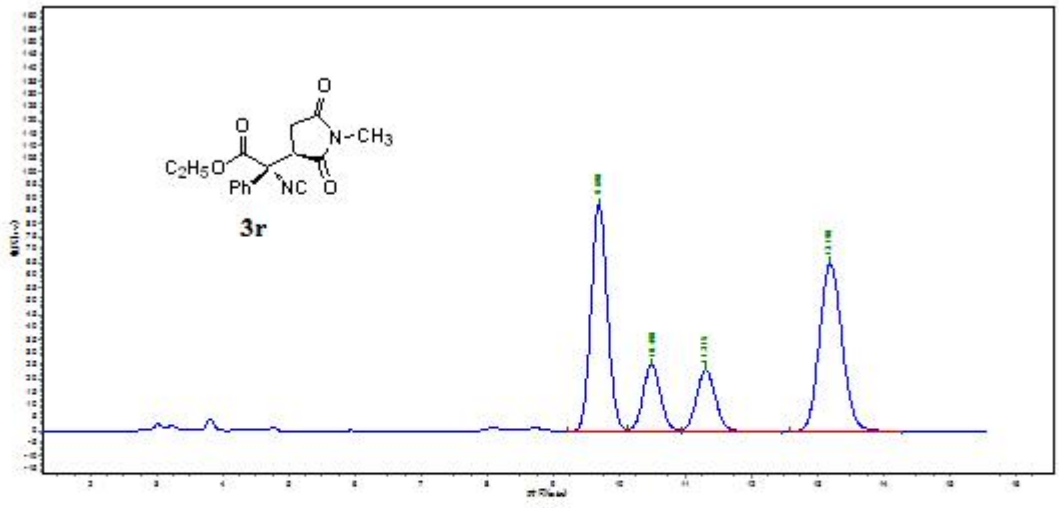
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.880	397900.781	6719842.000	38.2250
2	12.980	249753.563	4353183.500	20.8757
3	13.798	335923.719	6186237.500	29.6661
4	15.063	169481.219	3593613.750	11.2332



Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	19.848	117837.602	3304520.750	49.8416
2	27.823	82979.750	3325519.500	50.1584

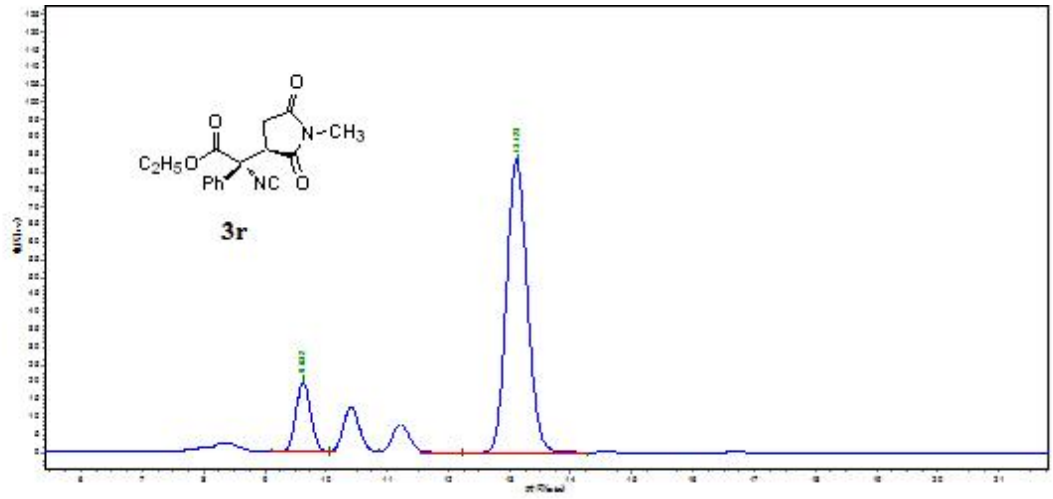


Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	17.648	14226.727	344184.031	3.9031
2	24.207	254011.125	8473942.000	96.0969



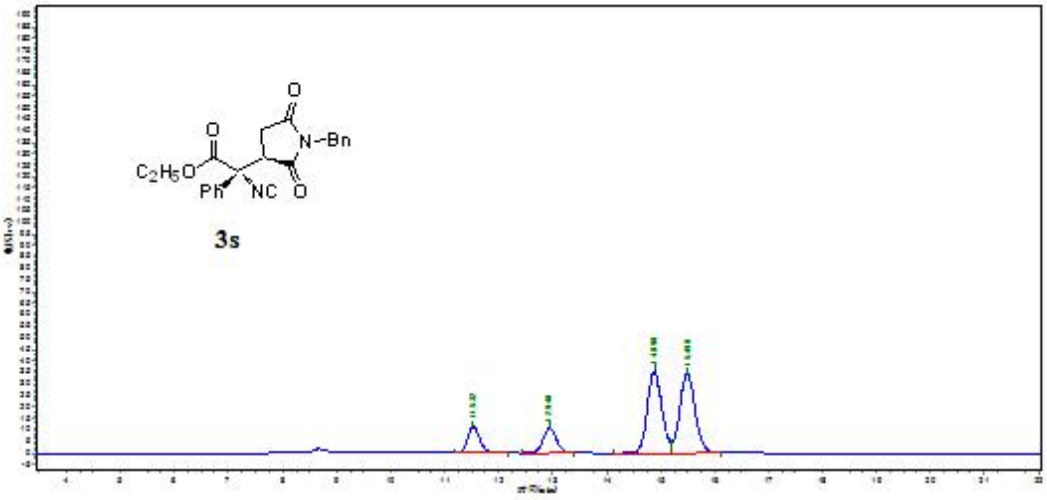
3r

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	9.698	87503.313	1507598.875	37.9981
2	10.498	25326.357	465152.625	11.7239
3	11.315	23503.857	462994.656	11.6695
4	13.198	64647.250	1531815.875	38.6085

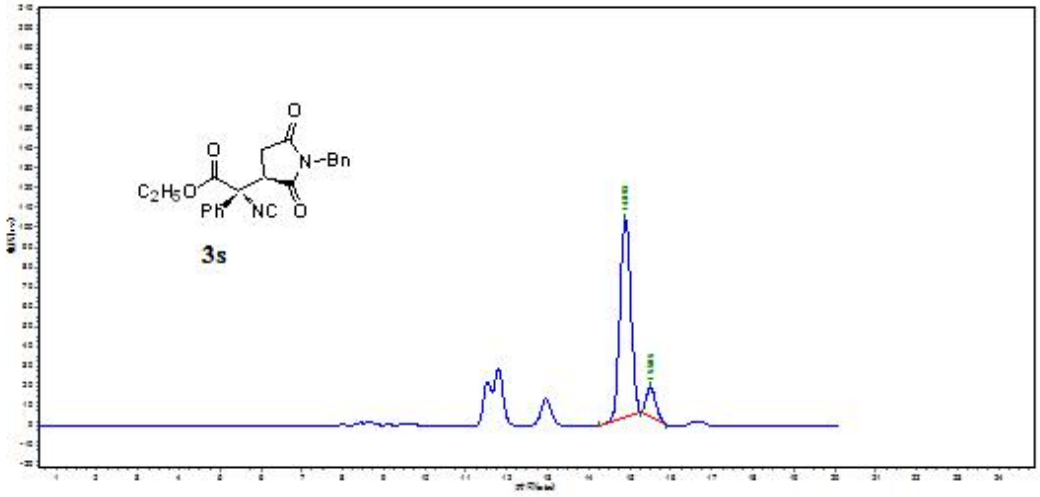


3r

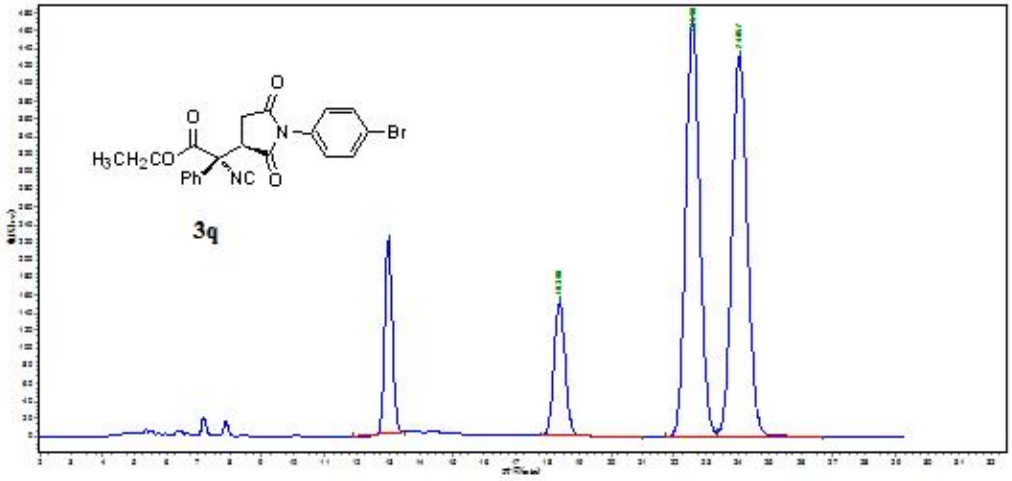
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	9.623	19302.512	320579.313	13.9565
2	13.112	83512.102	1976407.750	86.0435



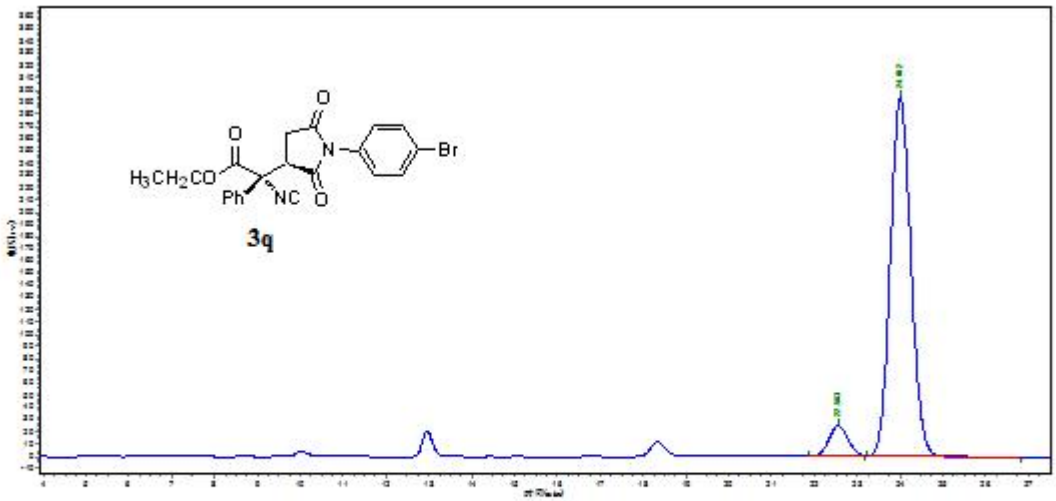
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.532	11526.542	182654.703	10.4822
2	12.948	10669.000	190121.797	10.9107
3	14.898	35666.770	681135.625	39.0889
4	15.498	34583.328	688618.750	39.5183



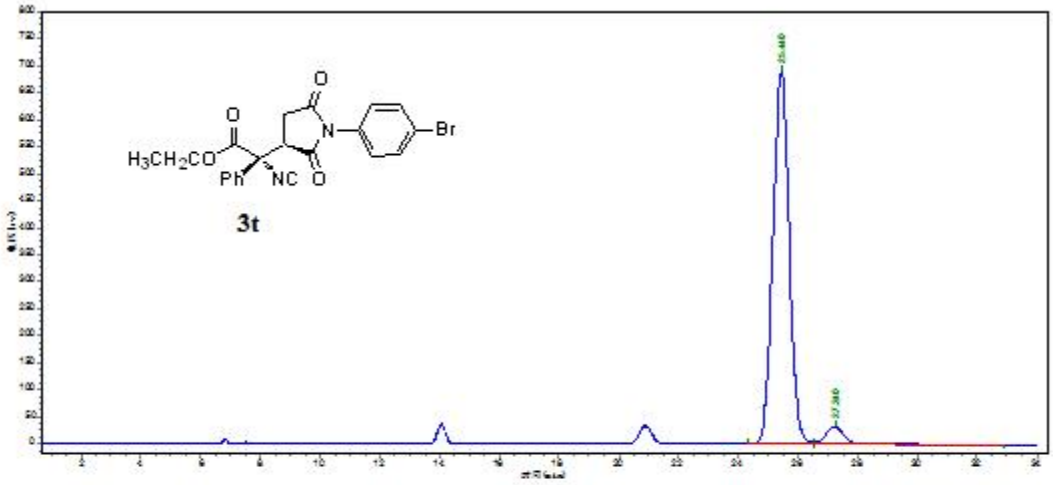
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	14.893	99971.914	1832115.000	88.5730
2	15.505	14497.059	236365.391	11.4270



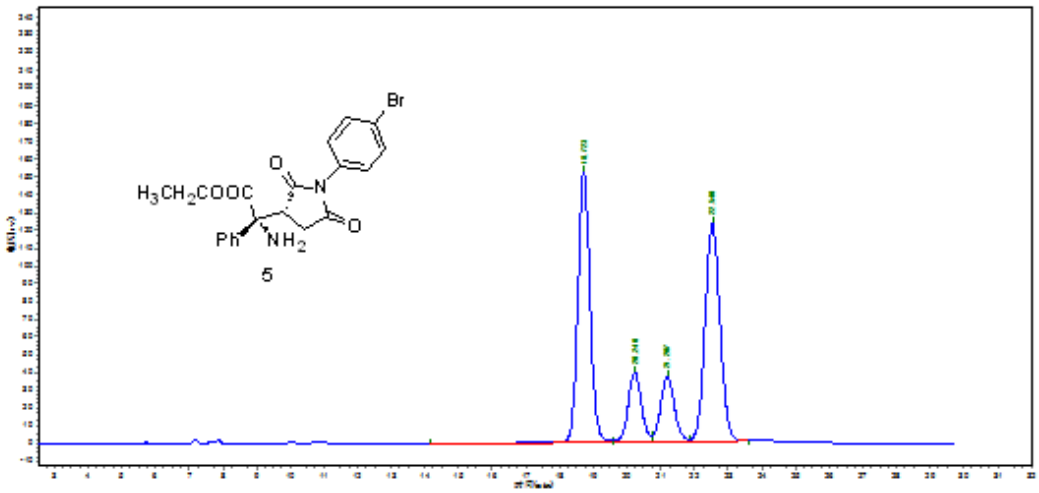
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	12.998	218697.016	3578712.250	9.8135
2	18.390	150527.688	3660356.750	10.0373
3	22.590	469528.438	14572329.000	39.9599
4	24.057	430742.063	14655989.000	40.1893



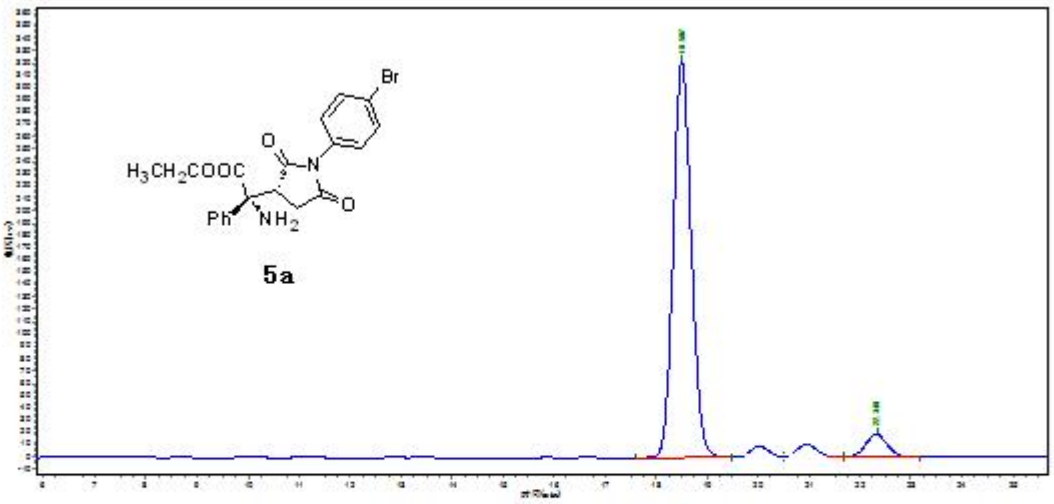
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	22.563	24481.012	734074.188	6.9808
2	24.012	293988.563	9781572.000	93.0192



Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	25.440	690069.563	26306688.000	94.9897
2	27.215	32458.684	1387569.625	5.0103

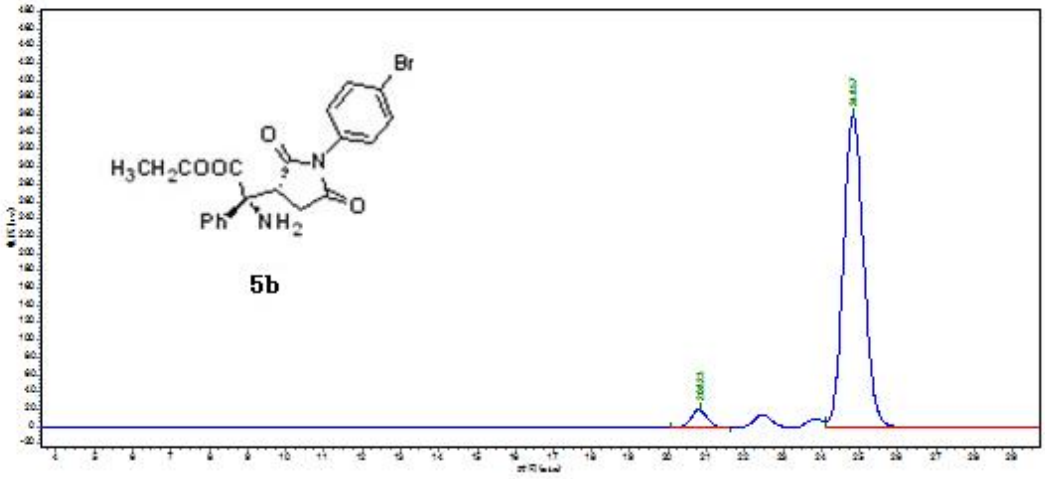


Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	18.723	152623.016	3987843.250	39.1609
2	20.240	40023.355	1133295.000	11.1291
3	21.207	37789.297	1136082.125	11.1564
4	22.540	123742.836	3925994.500	38.5536



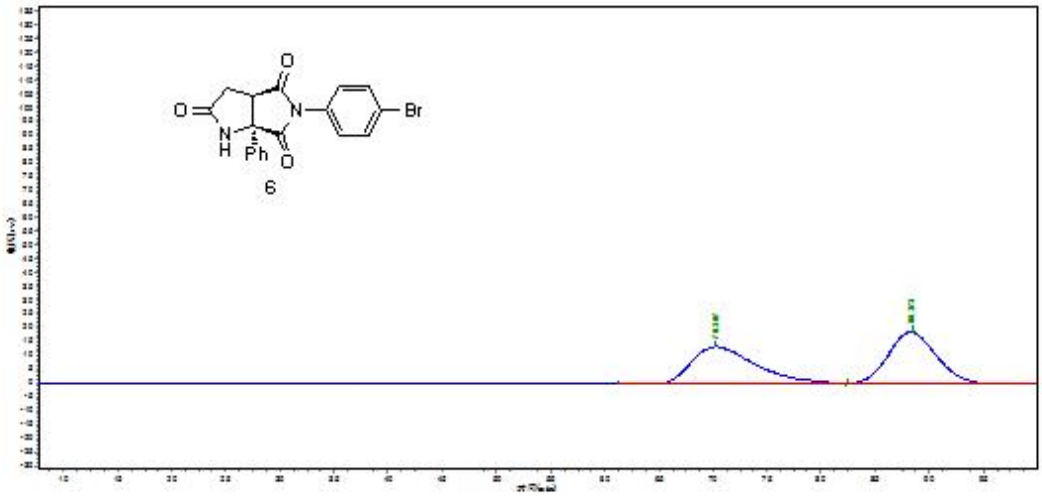
5a

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	18.507	321217.969	7922725.000	93.2216
2	22.348	18377.932	576085.313	6.7784

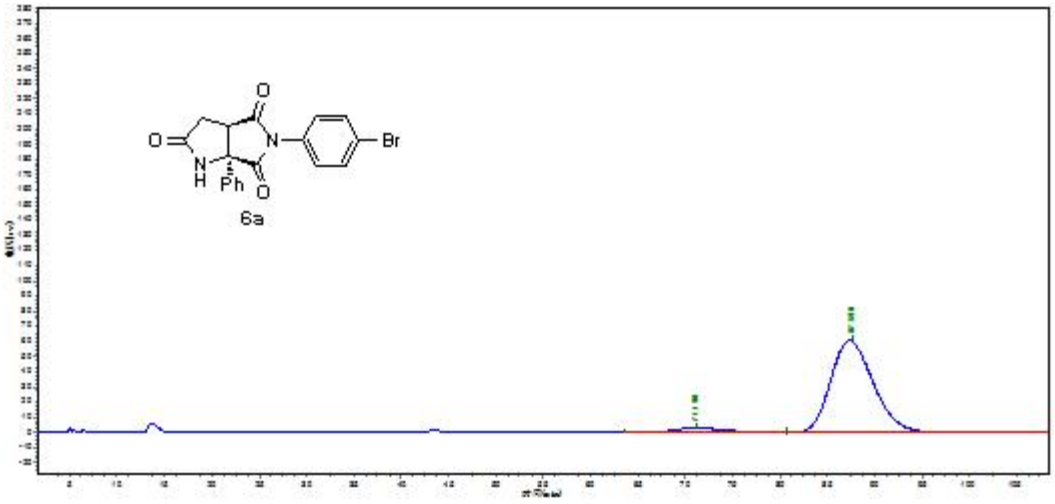


5b

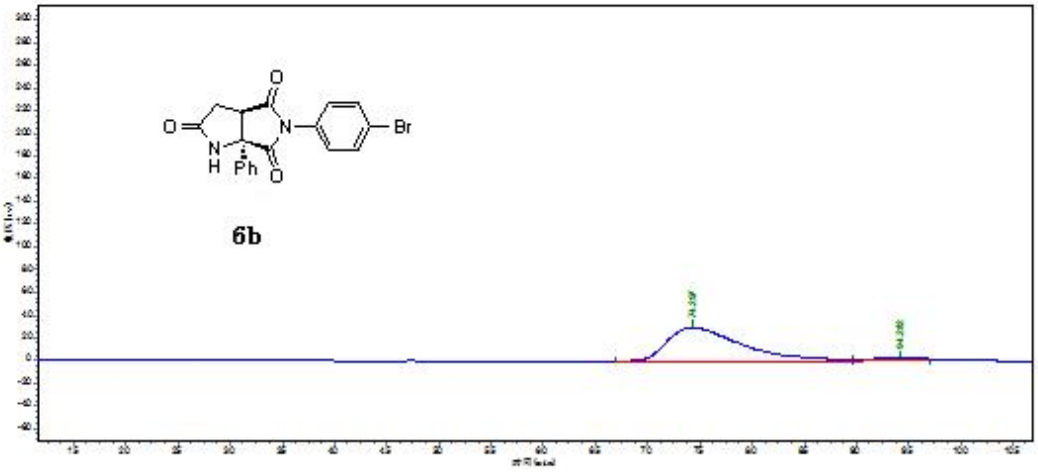
Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	20.823	20191.783	594291.938	4.2784
2	24.857	361211.438	13296110.000	95.7216



Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	70.307	13574.205	5745348.000	49.0883
2	88.373	18936.137	5958754.000	50.9117

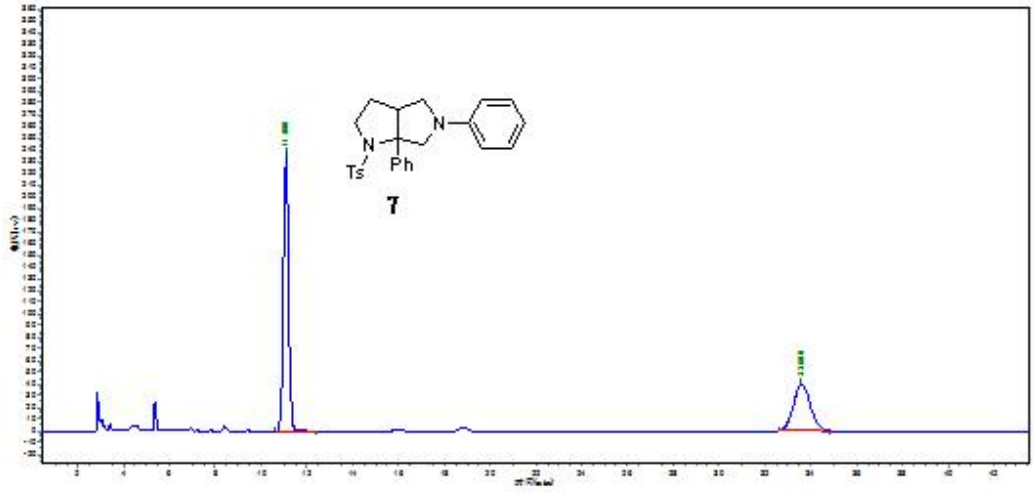


Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	70.973	2247.802	785208.063	4.0298
2	87.332	60373.035	18699860.000	95.9702



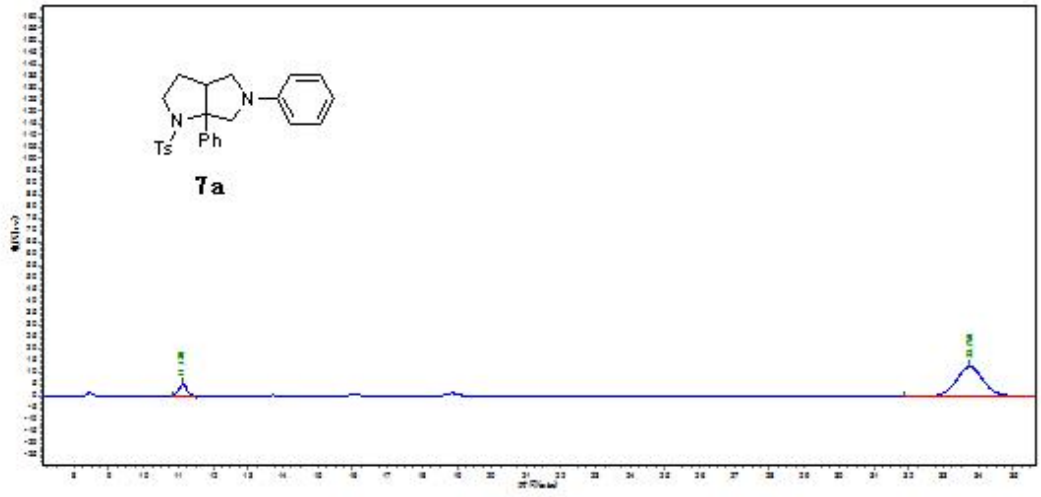
6b

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	74.297	29150.938	14236512.000	96.3204
2	94.282	1790.708	543855.000	3.6796



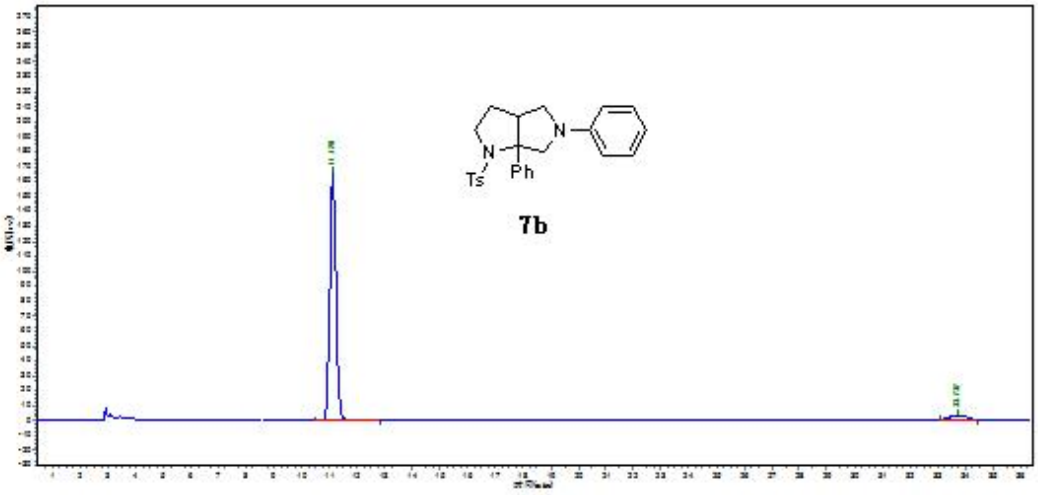
7

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.080	236011.500	3742748.000	55.0532
2	33.600	199272.875	3000295.730	44.9468



7a

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.130	2769.244	31999.954	4.8157
2	33.750	12130.100	632492.313	95.1843



7b

Peak	RT(min)	Height(mV*sec)	Area(mV)	Area(%)
1	11.128	165351.203	2636544.750	95.9202
2	33.737	2562.610	112139.906	4.0798