

Supporting Information.

Enantioselective Friedel-Crafts Alkylation of Indoles with 2-Enoylpyridine-N-Oxides Catalyzed by *gluco*BOX-Cu(II) complex.

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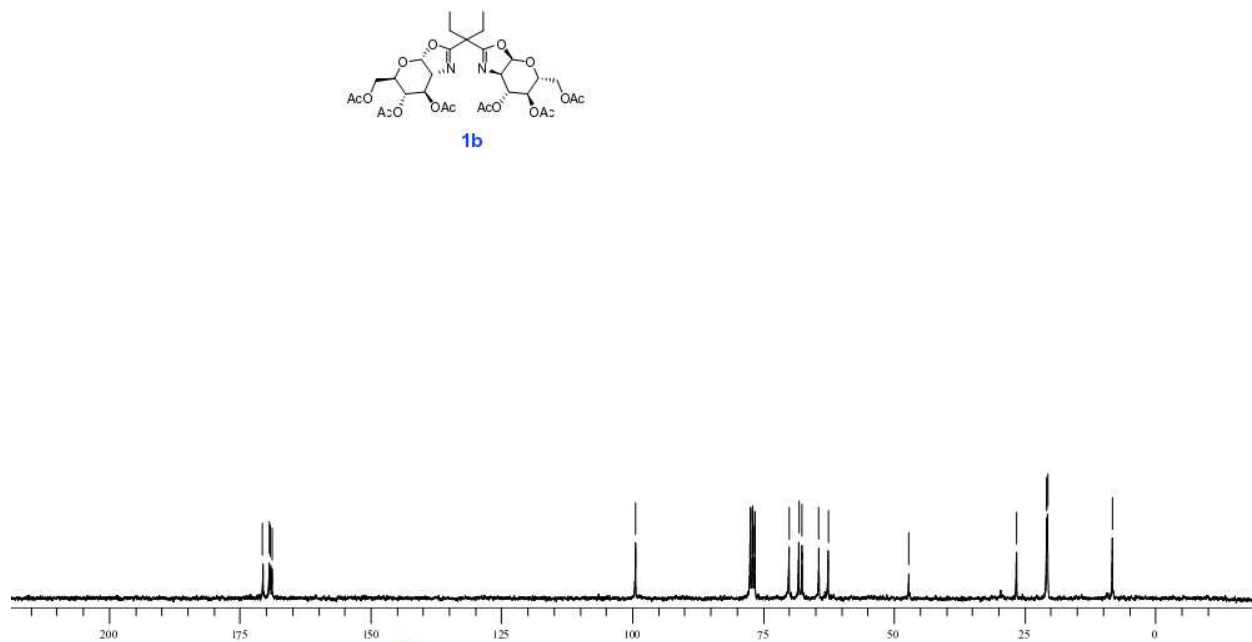
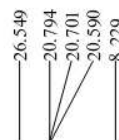
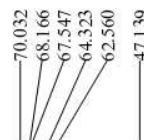
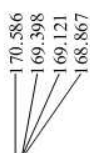
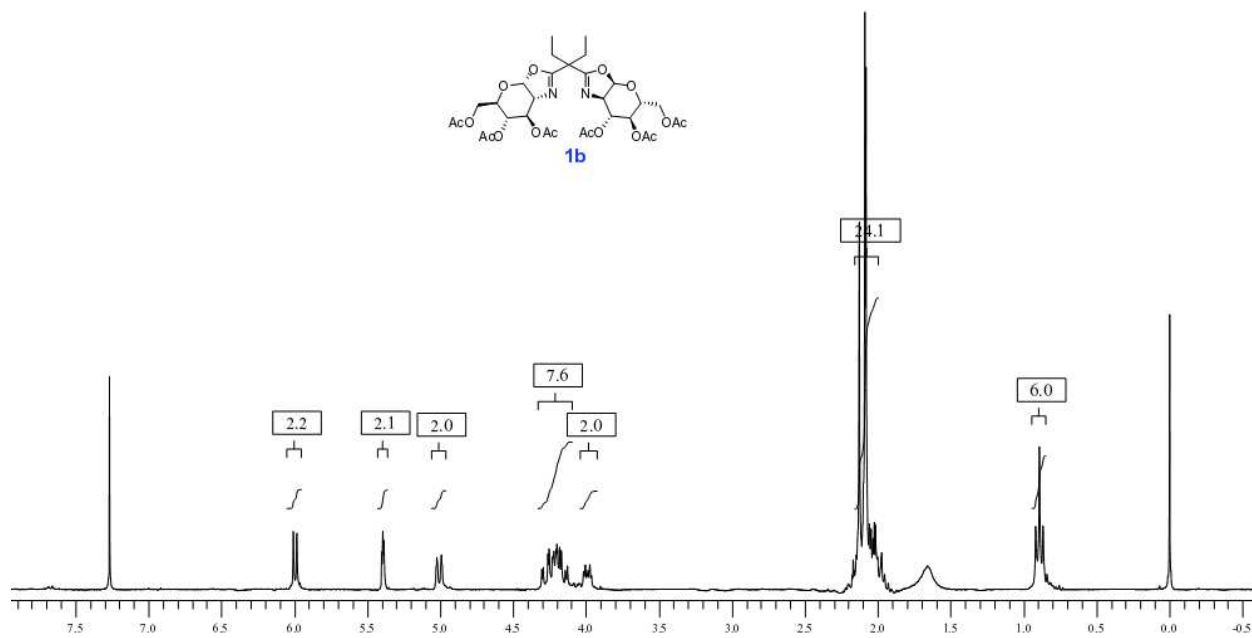
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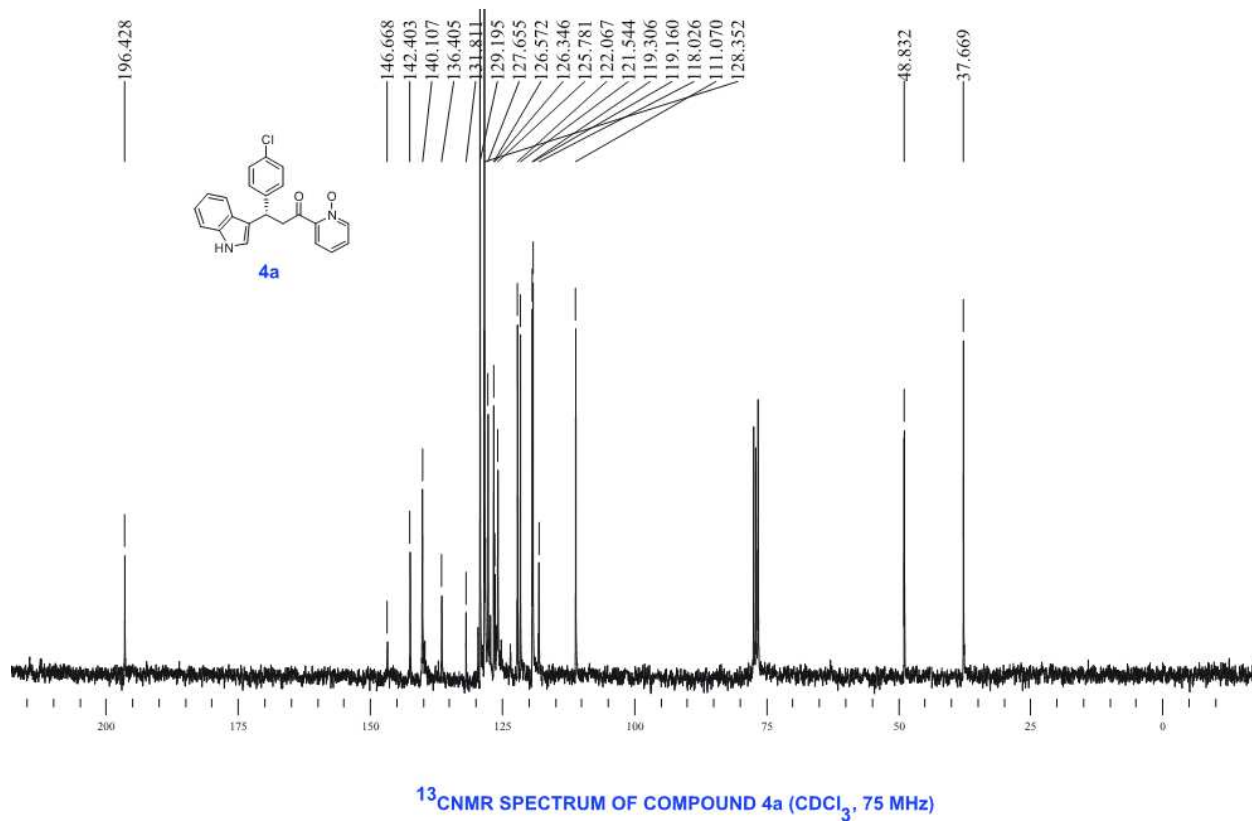
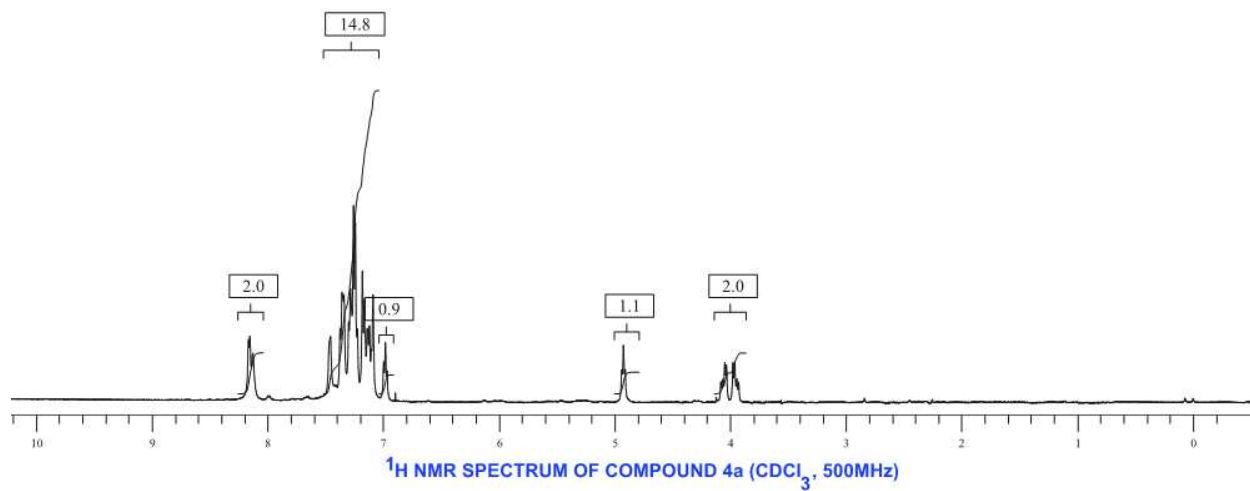
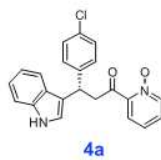
1. General remarks	(S2)
2. Copy of NMR Spectra of ligands (1b).	(S3)
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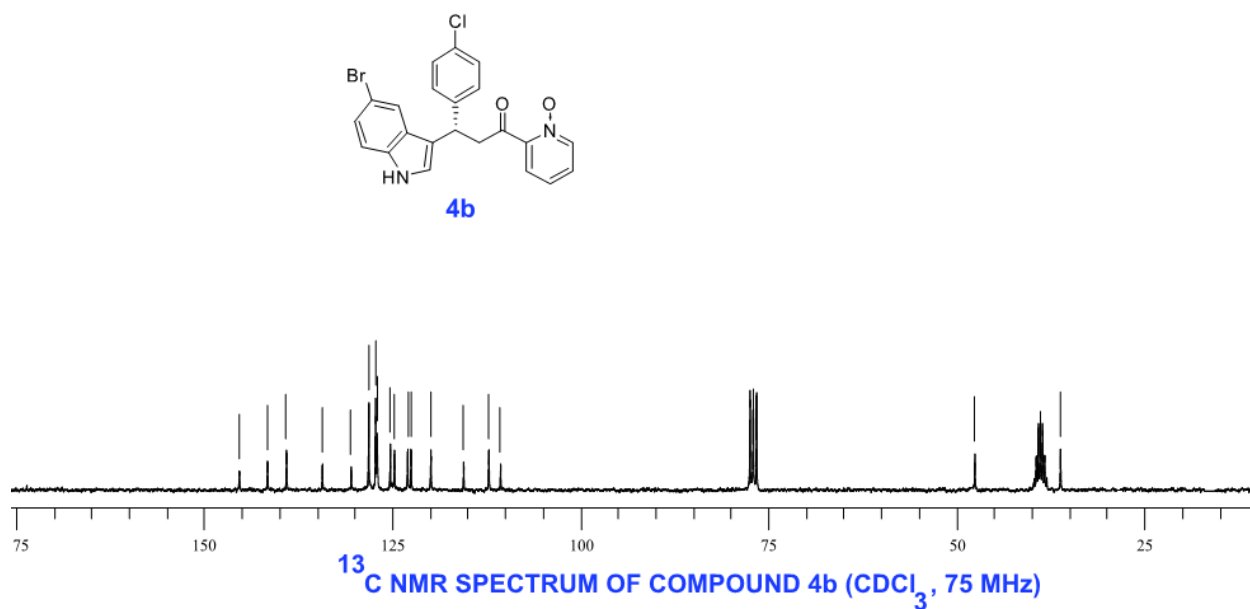
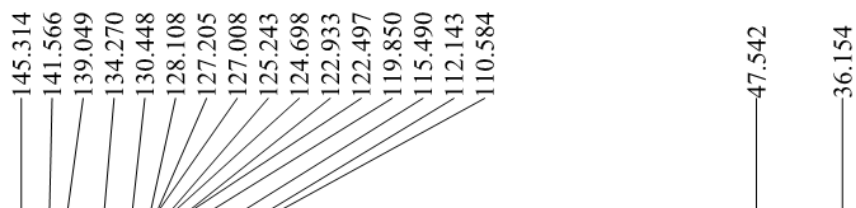
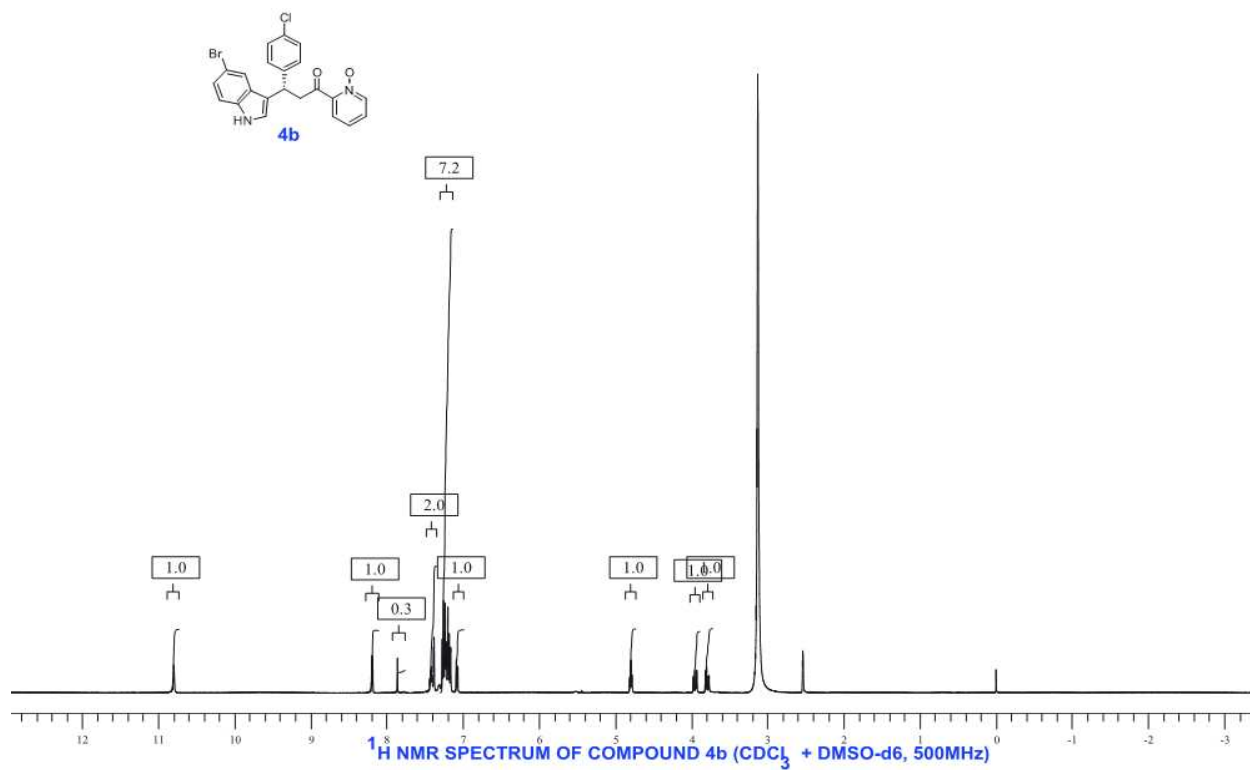
1. General Remarks.

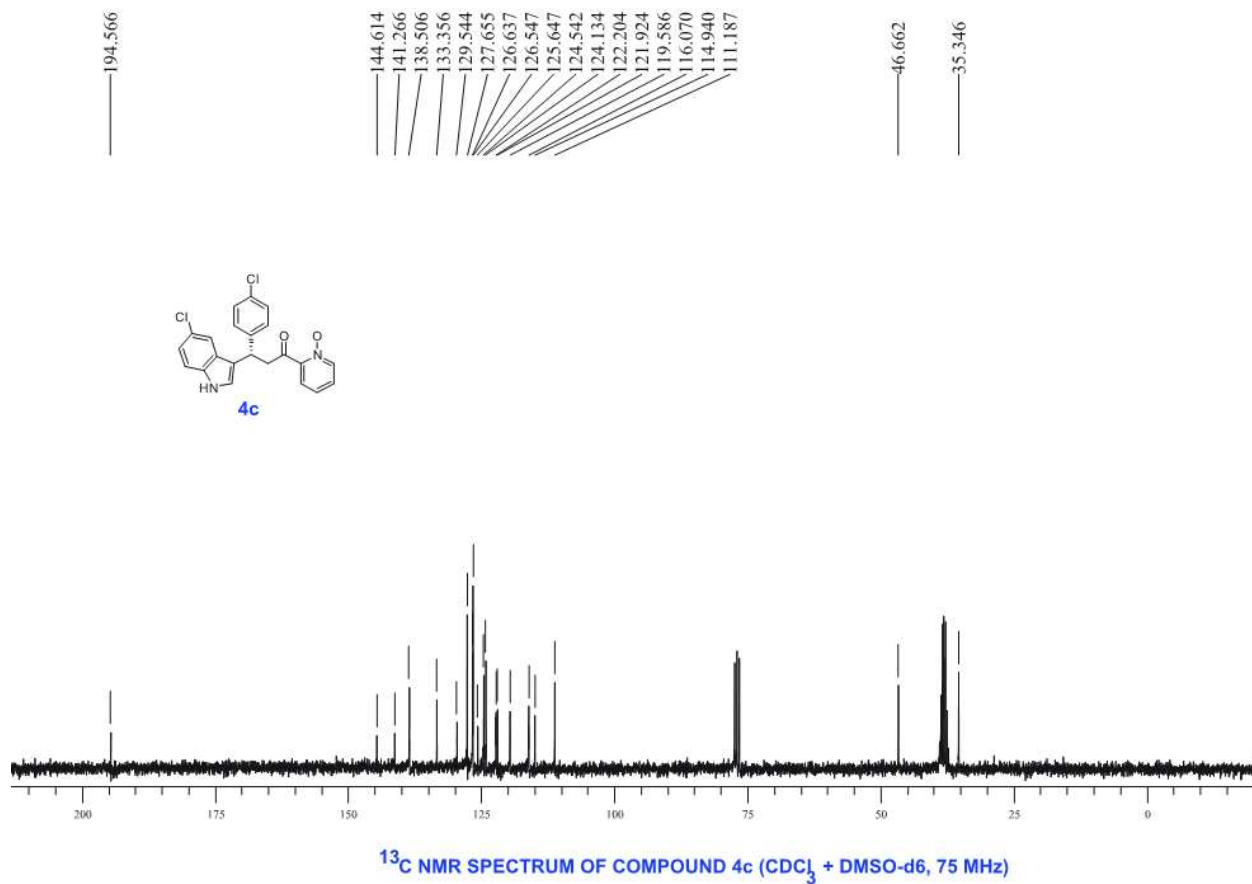
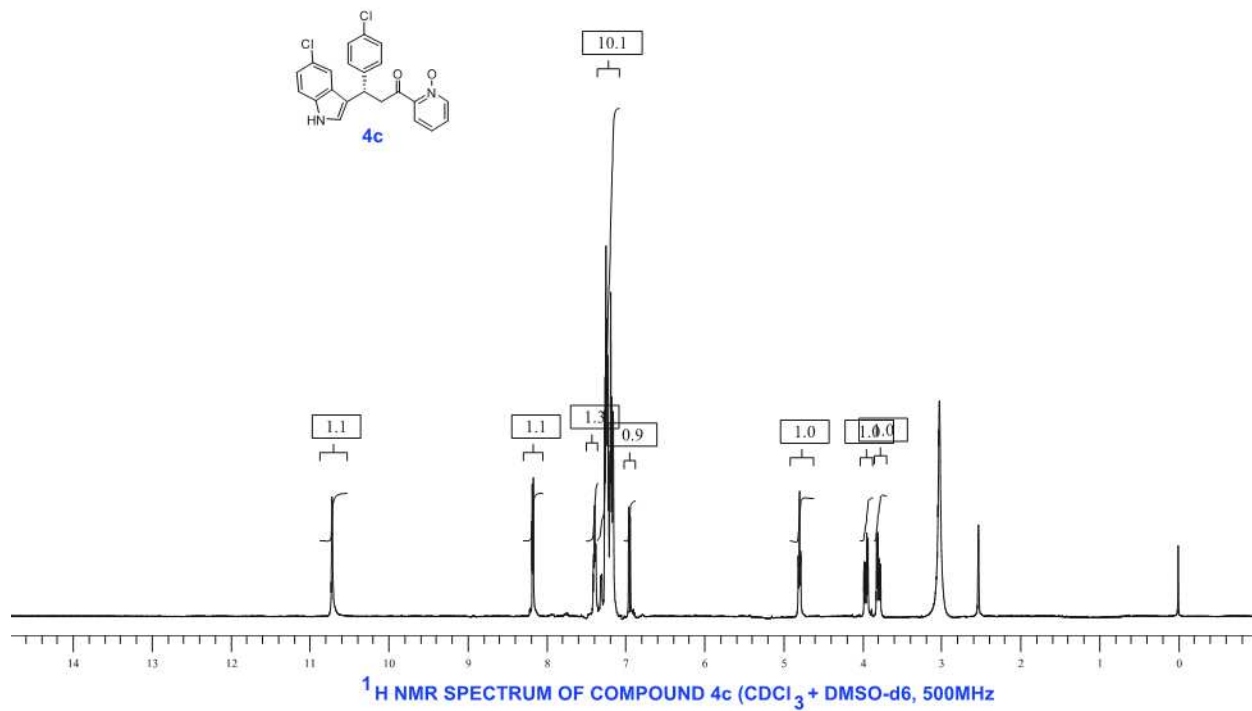
All the reactions were carried out under nitrogen atmosphere. Commercial reagents were used as received, unless otherwise stated. All the metal Lewis acids were purchased from commercial sources and used as such as without any further purification. Solvents used for all reaction were dried prior to use by standard procedure. Dichloromethane and chloroform were distilled from calcium hydride. THF and ether were dried over sodium. Methanol and toluene were purchased from commercial source and used as received. ^1H NMR was recorded on a 300 MHz or 500 MHz spectrometer using CDCl_3 as solvent. ^{13}C NMR were recorded on 75 MHz spectrometer using CDCl_3 . TMS was used as reference for ^1H NMR analysis and CDCl_3 used as reference for ^{13}C NMR analysis. Ligands **1a-f** was prepared from glucosamine hydrochloride according to literature procedure.¹ All the starting materials i.e, 2-enoyl pyridine-N-oxides were prepared according to procedure reported previously.² All the compounds were purified by column chromatography on silica gel (60-120 mesh) using hexane - ethyl acetate mixtures as eluent. Mass analysis was carried out using ESI mass spectrometer. Optical rotations were measured using a Perkin-Elmer polarimeter. The enantiomeric excess was determined by HPLC analysis using Daicel Chiral columns. (Note - Due to high retention time of Friedel-Crafts products in chiral HPLC columns some of the samples run in Chiralpak AD-H column with dimension, 15cm x 0.46 x 5 μm) Absolute stereochemistry was determined by comparing optical rotation of compounds with literature values. = Unknown compounds absolute configuration determined by analogy.

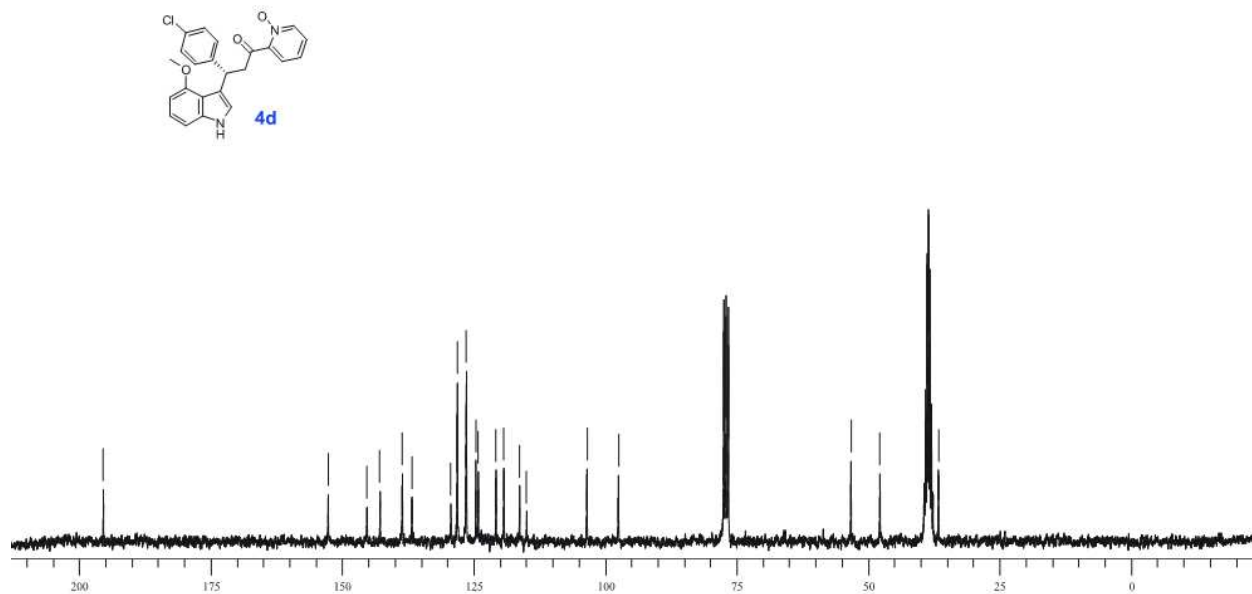
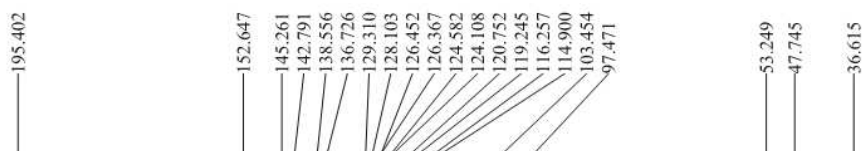
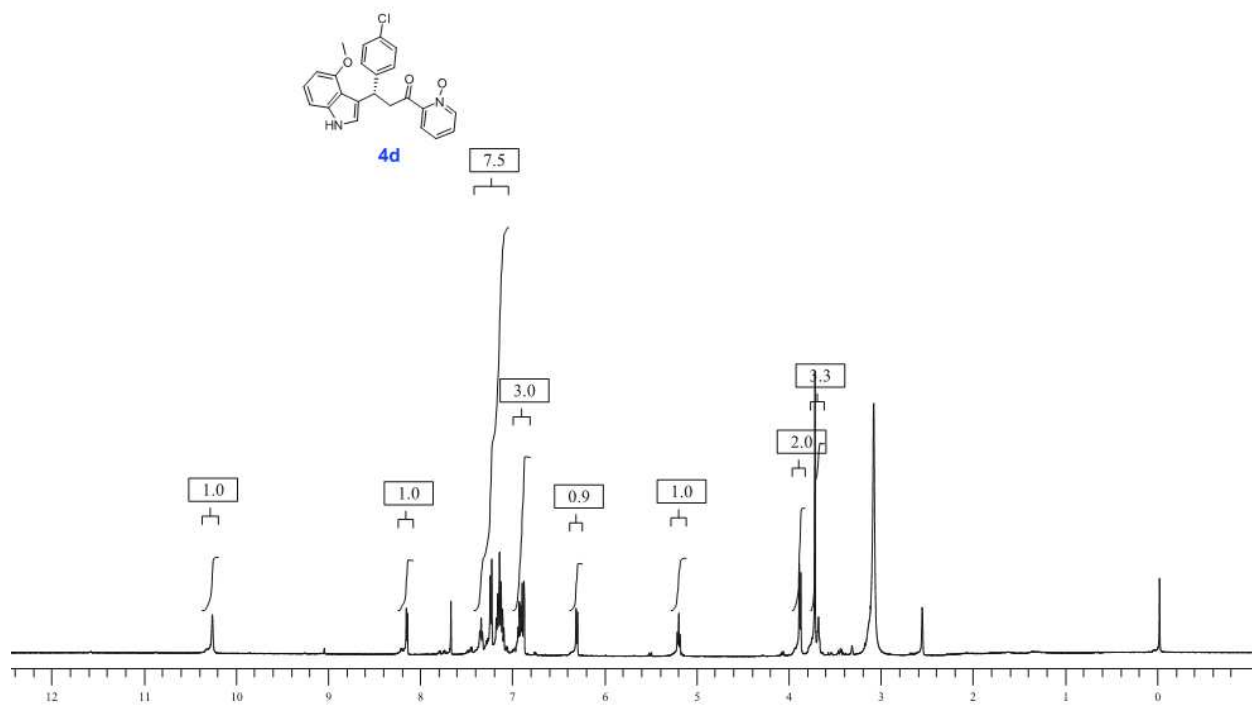
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- 1) (a) M. Irmak, A. Groschner, M. M. K. Boysen, *Chem. Commun.* 2007, 177; (b) T. Minuth, M. Irmak, A. Groschner, T. Lehnert, M. M. K. Boysen, *Eur. J. Org. Chem.* 2009, 997.
2) (a) S. Barroso, G. Blay, J. R. Pedro, *Org. Lett.* 2007, **9**, 1983. (b) P. K. Singh, V. K. Singh, *Org. Lett.* 2008, **10**, 4121.

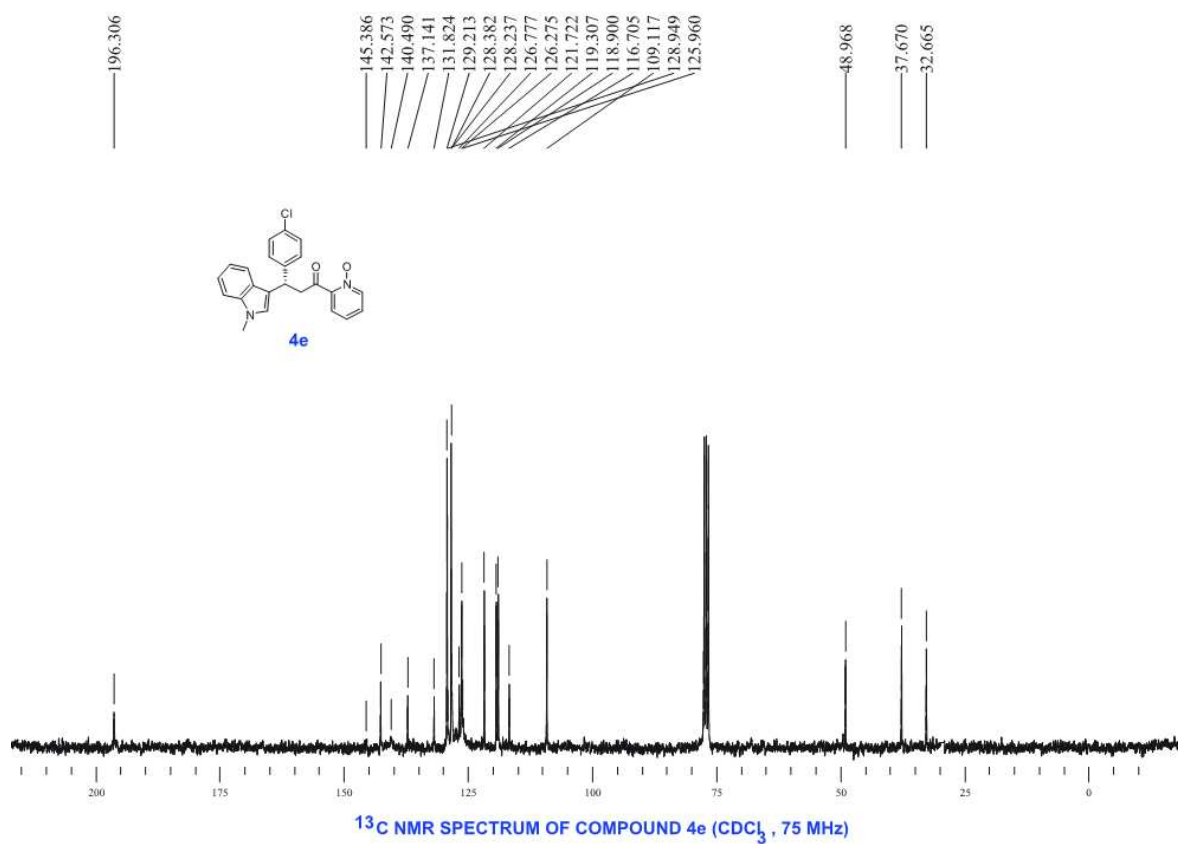
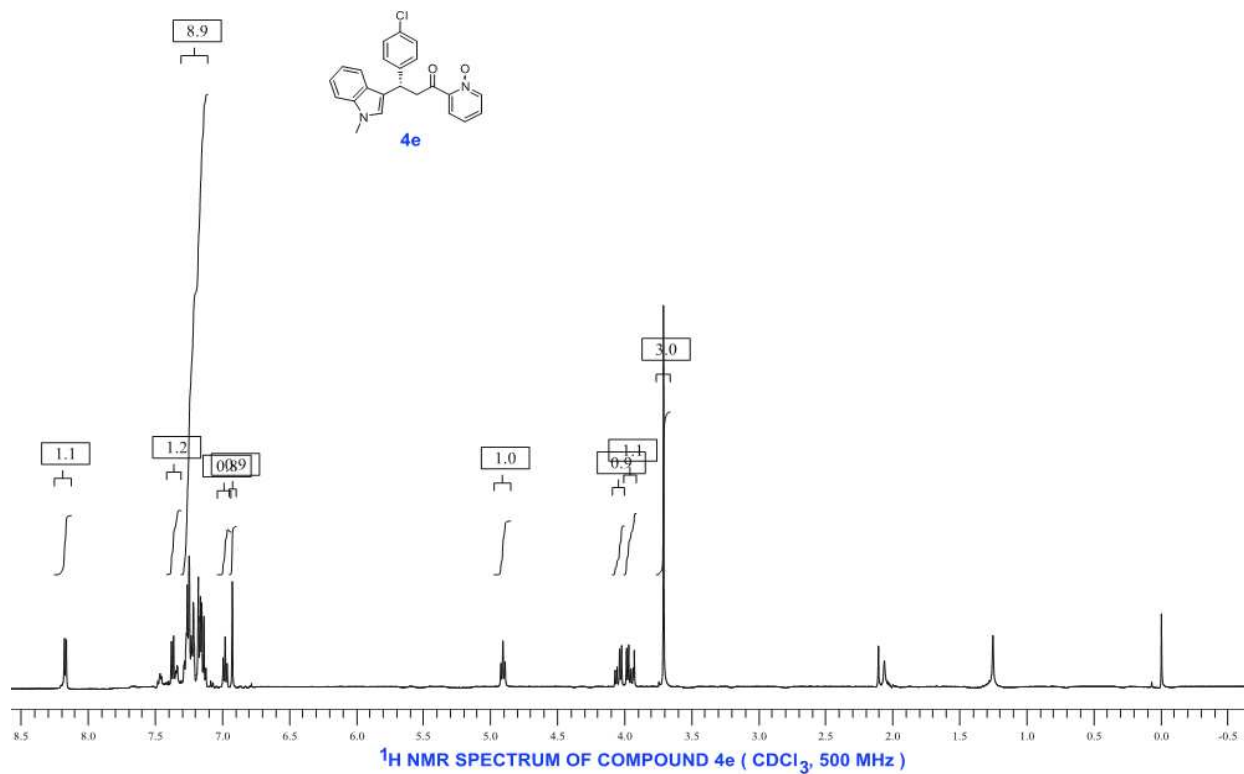


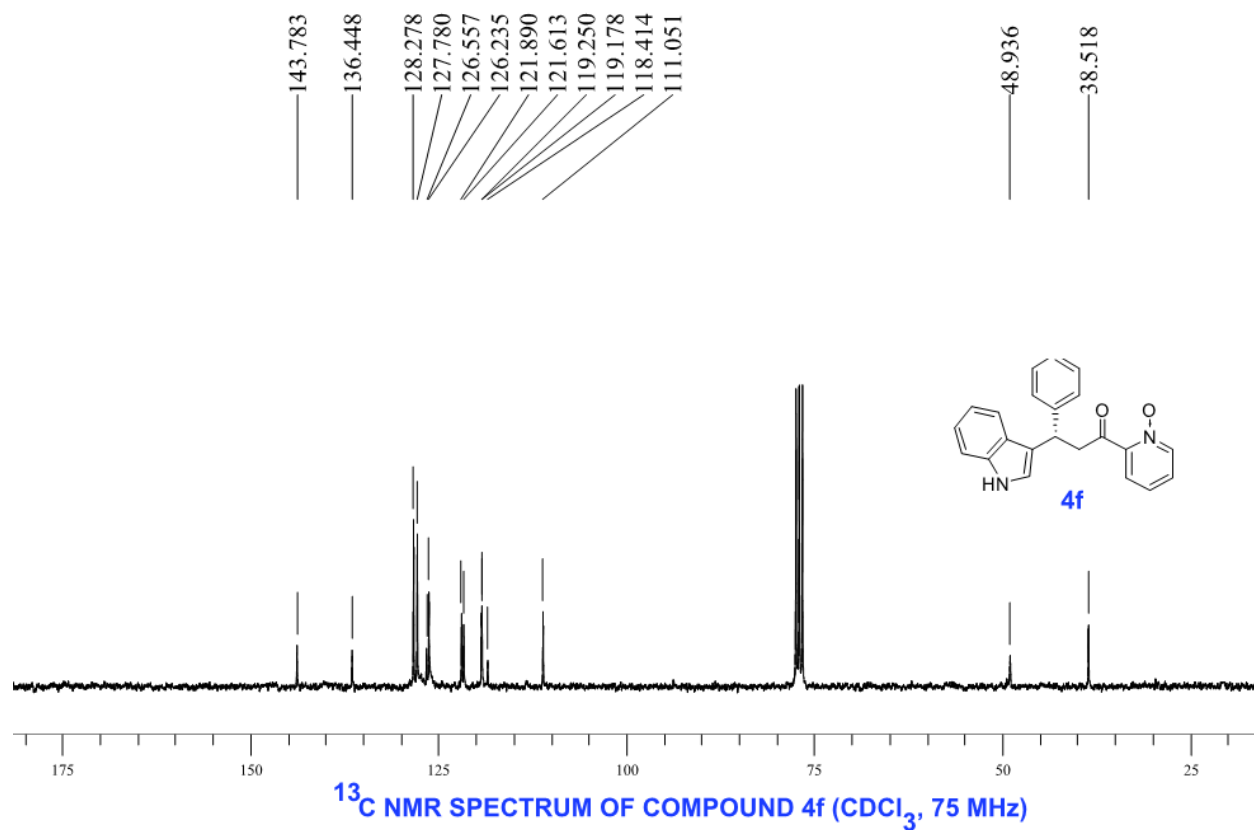
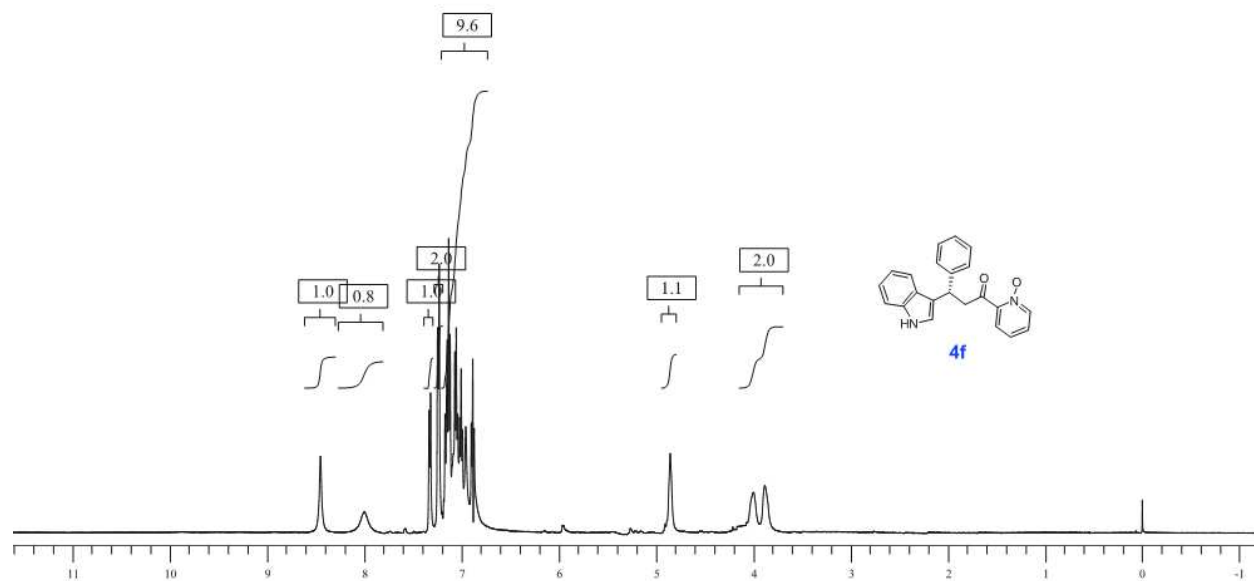


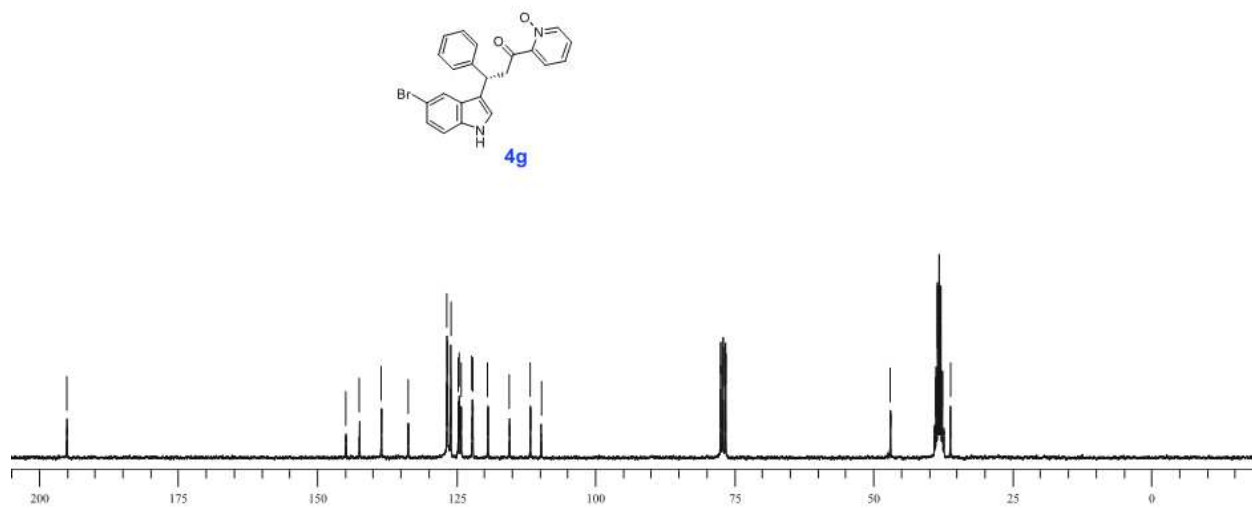
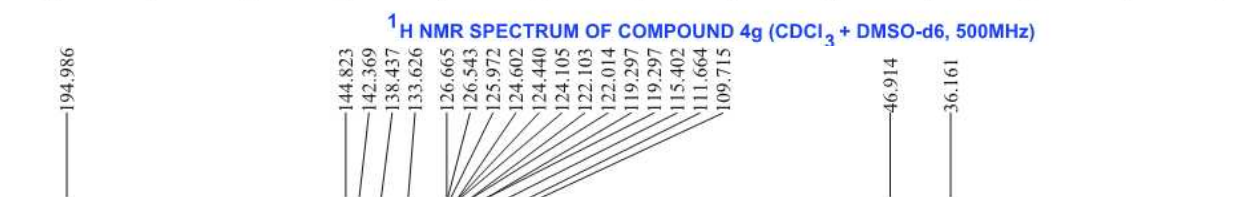
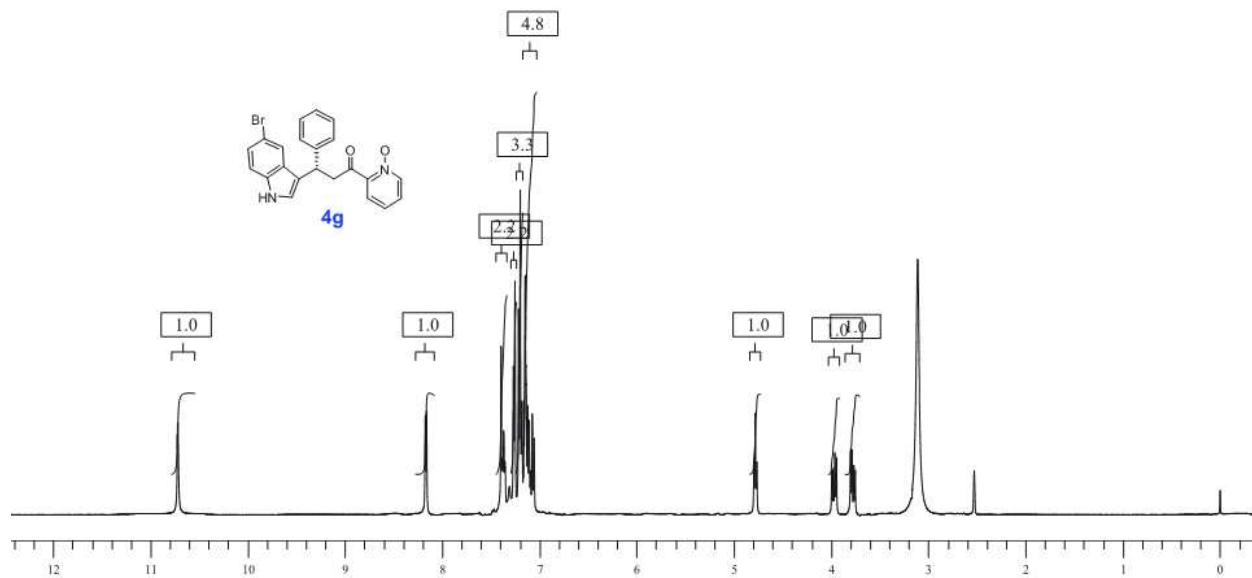




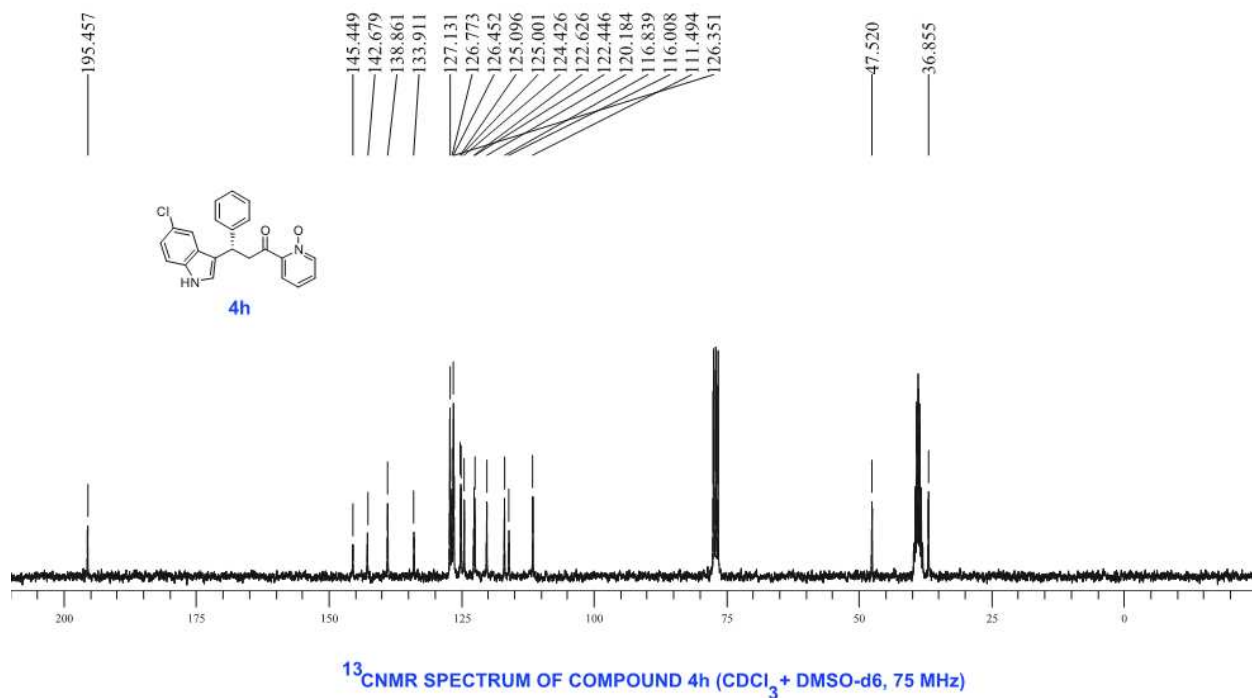
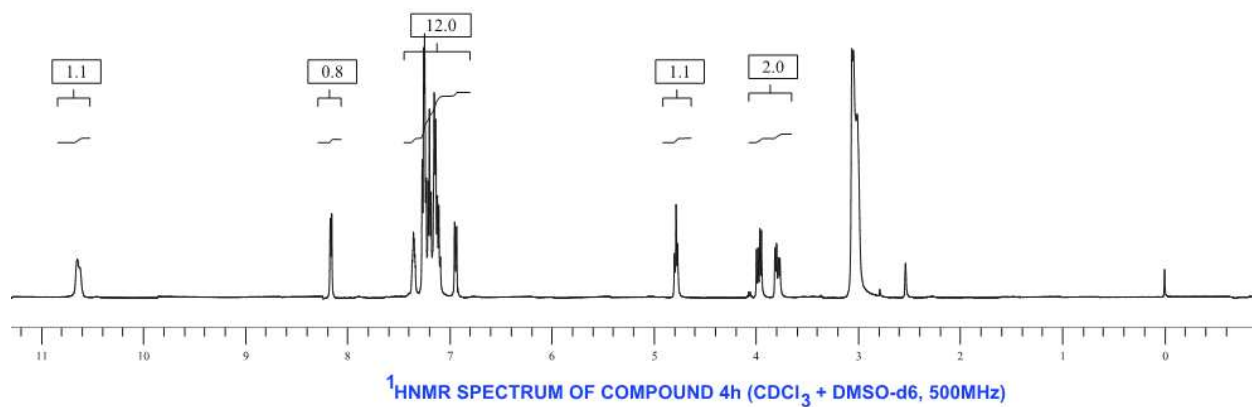


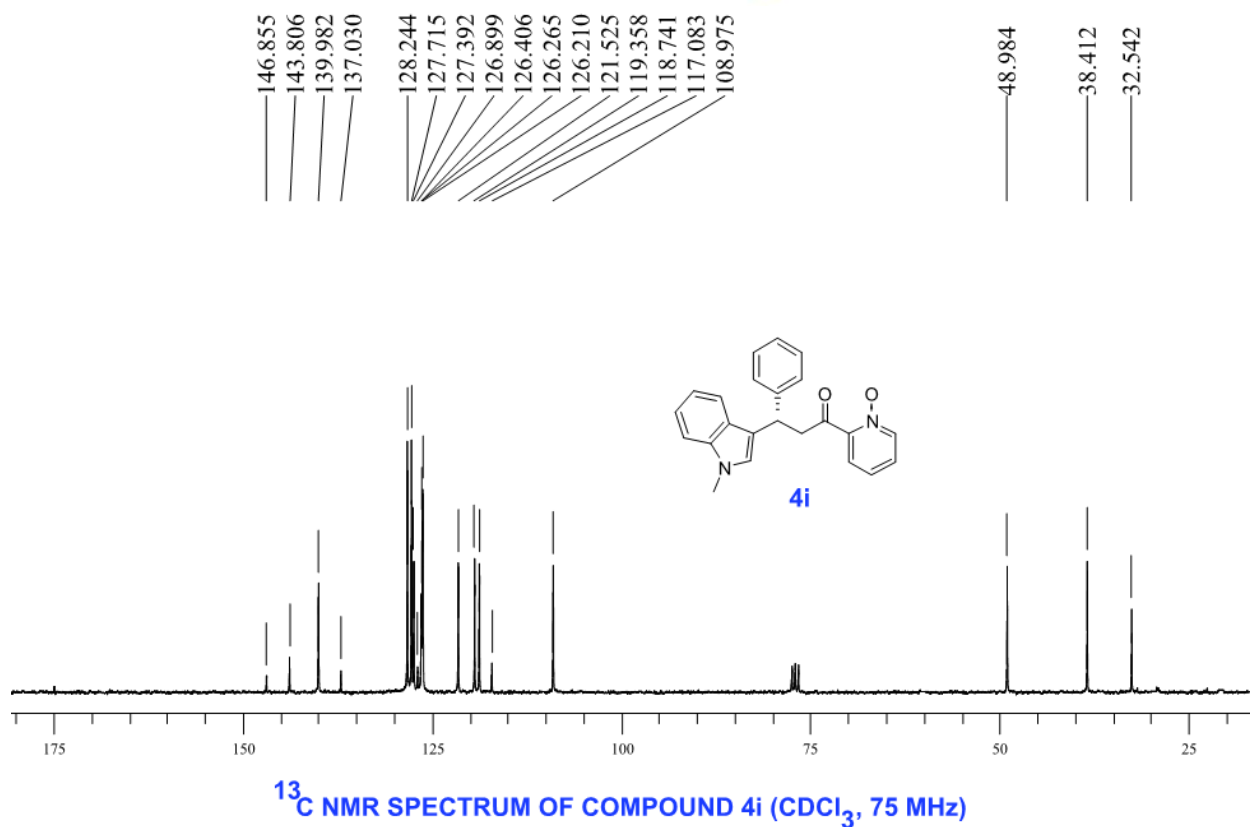
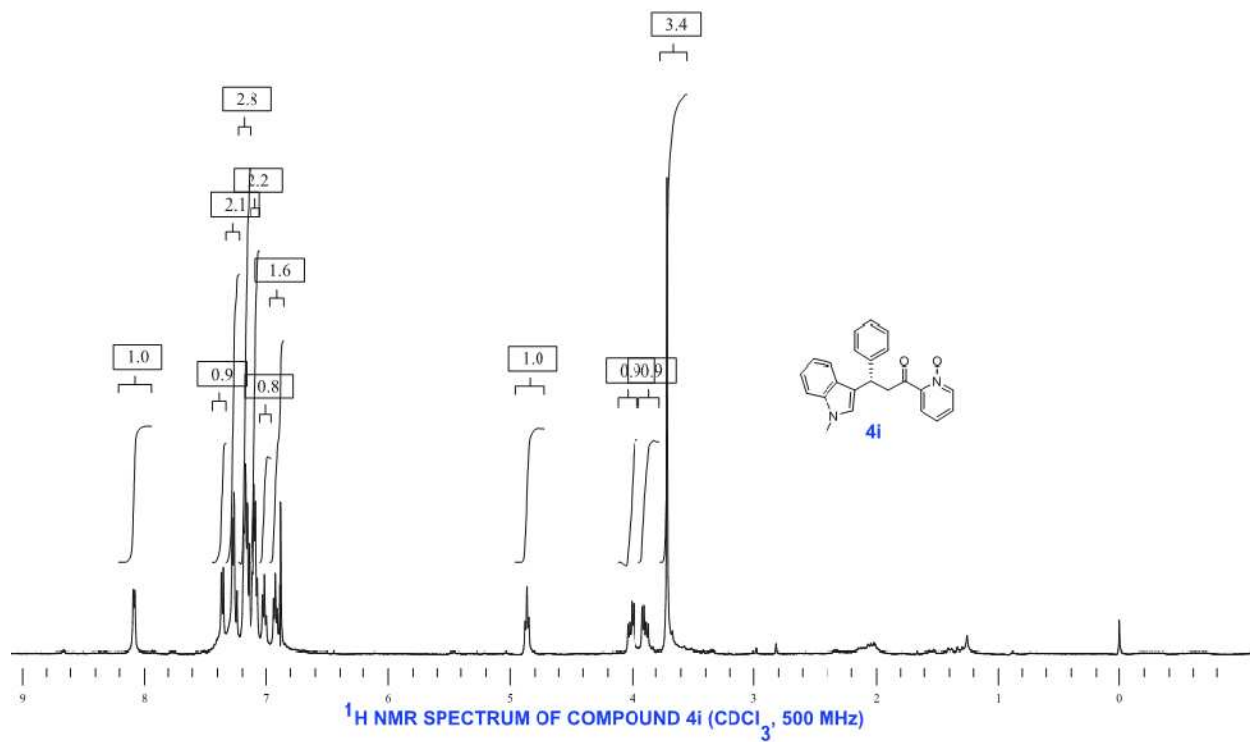


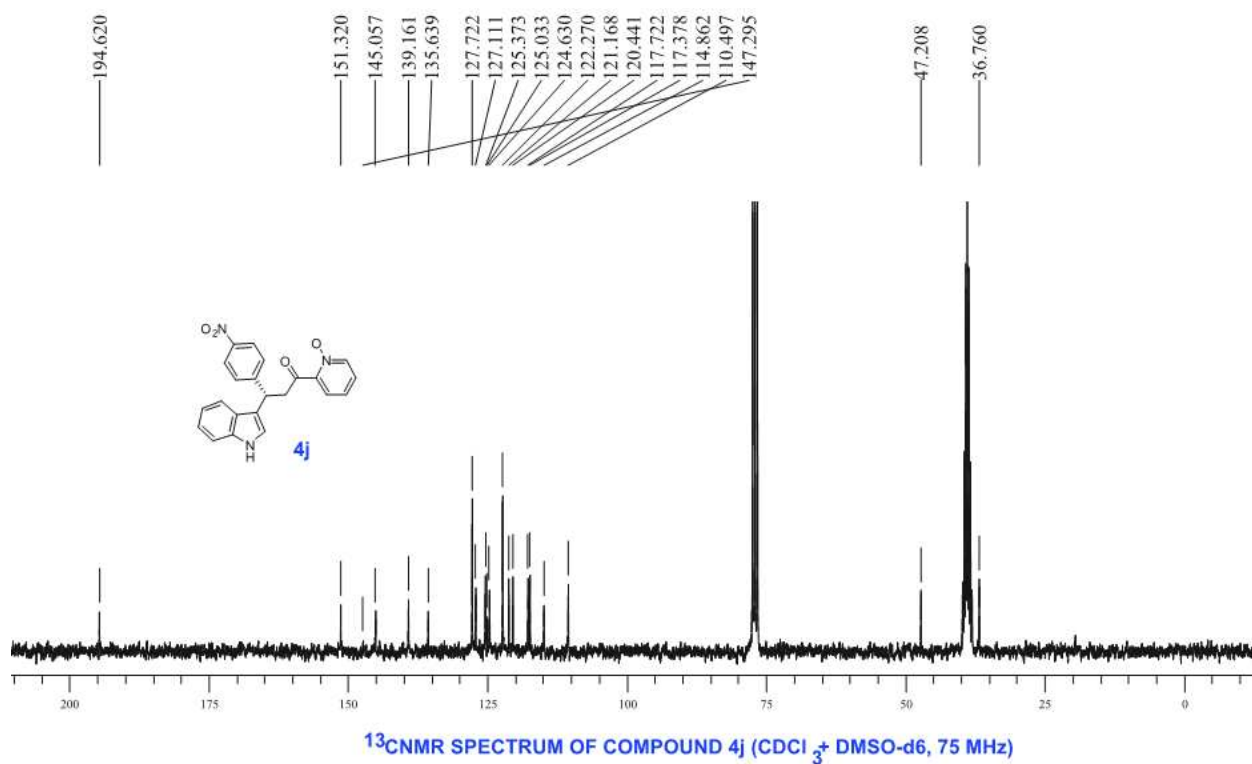
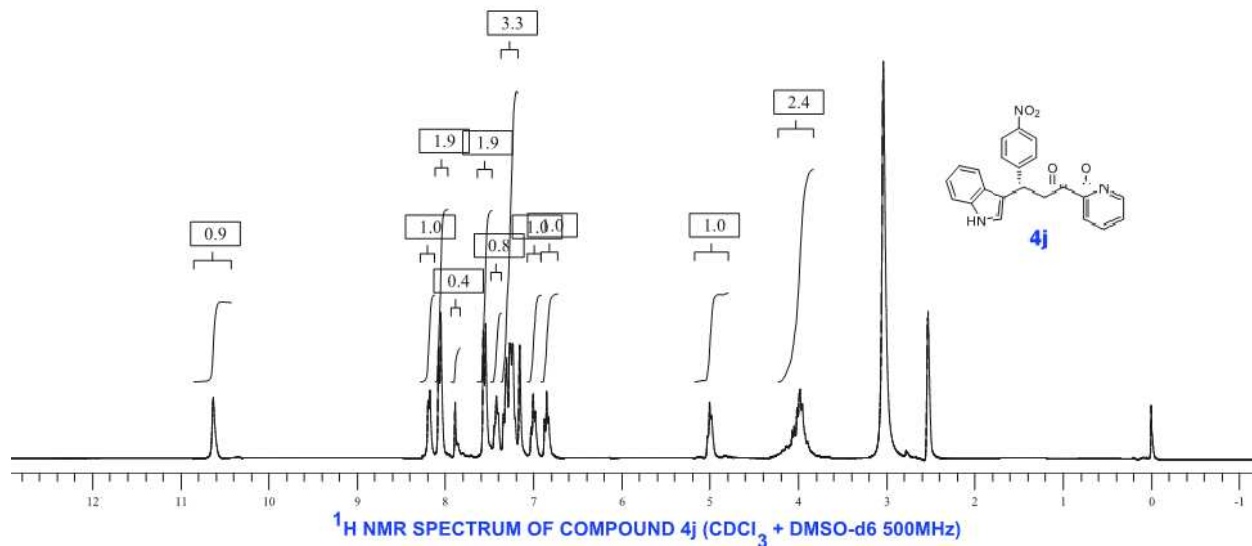


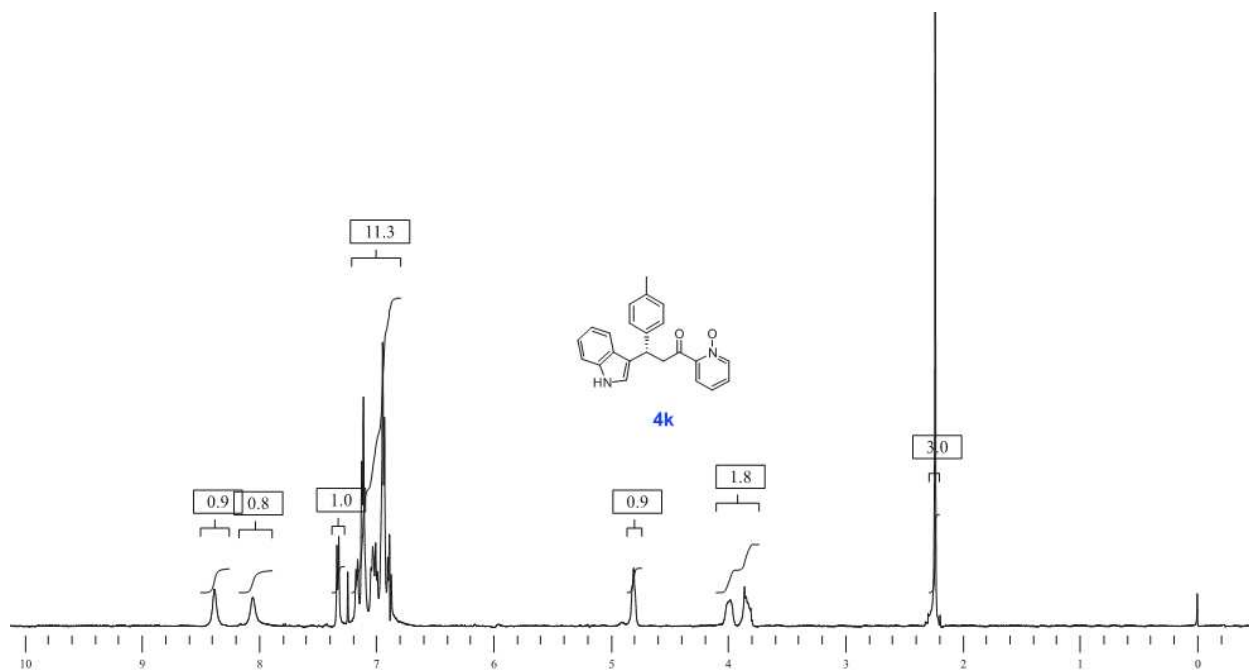


¹³C NMR SPECTRUM OF COMPOUND 4g (CDCl₃ + DMSO-d₆, 75 MHz)

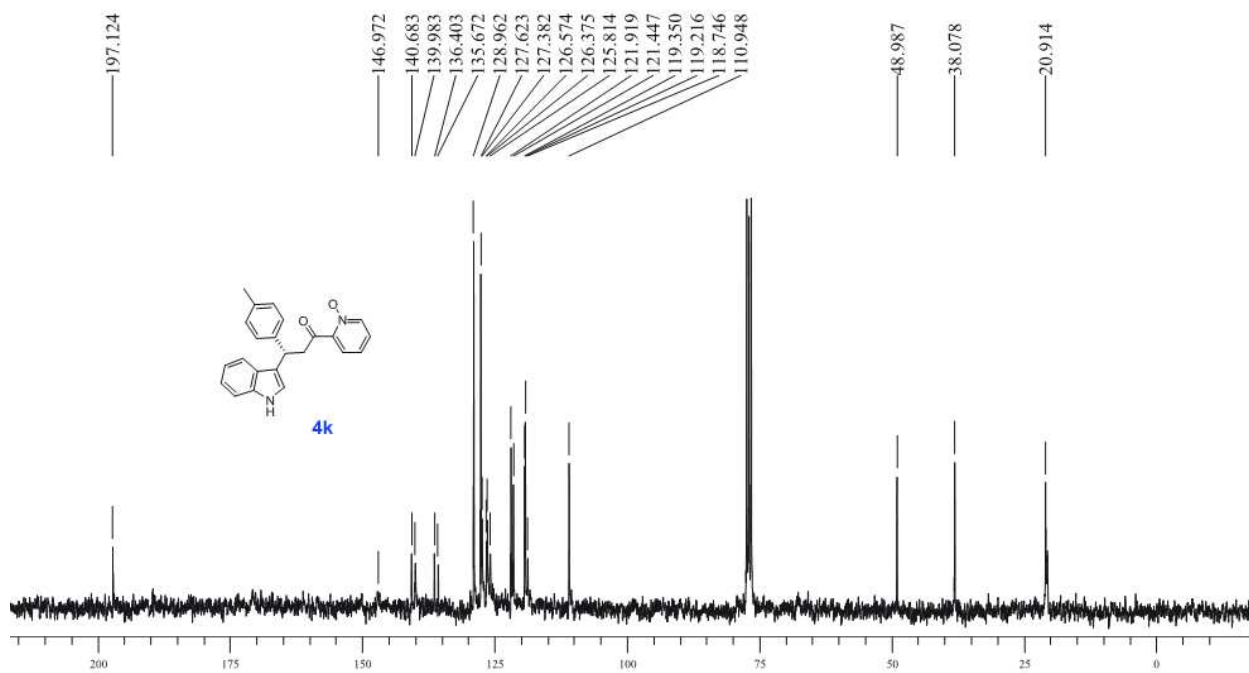




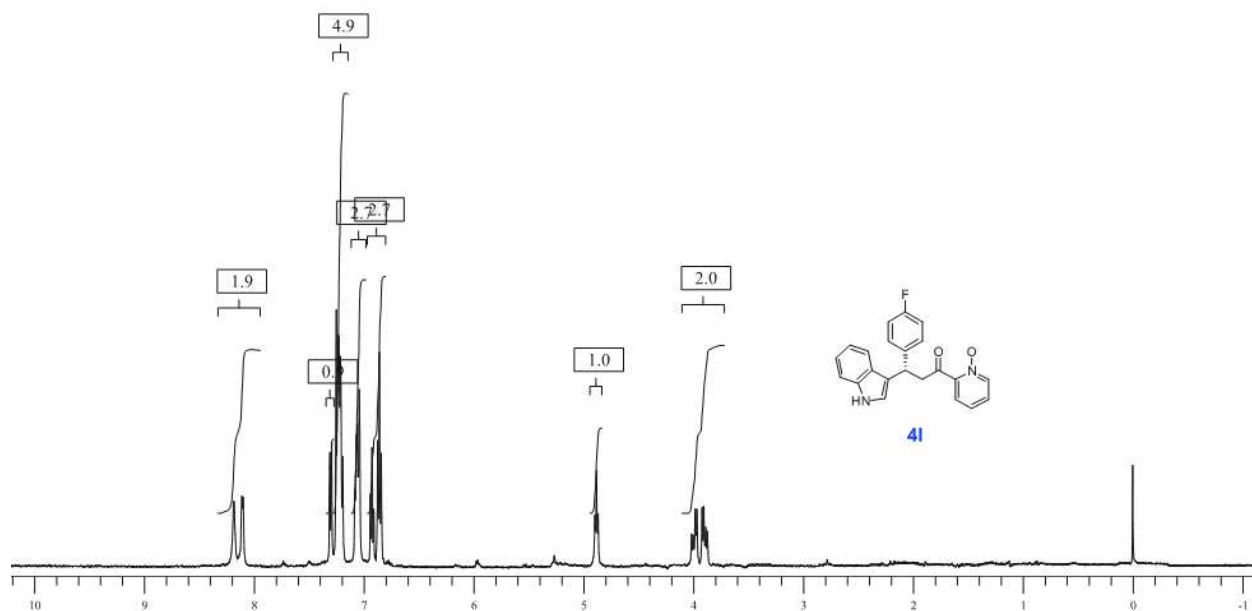




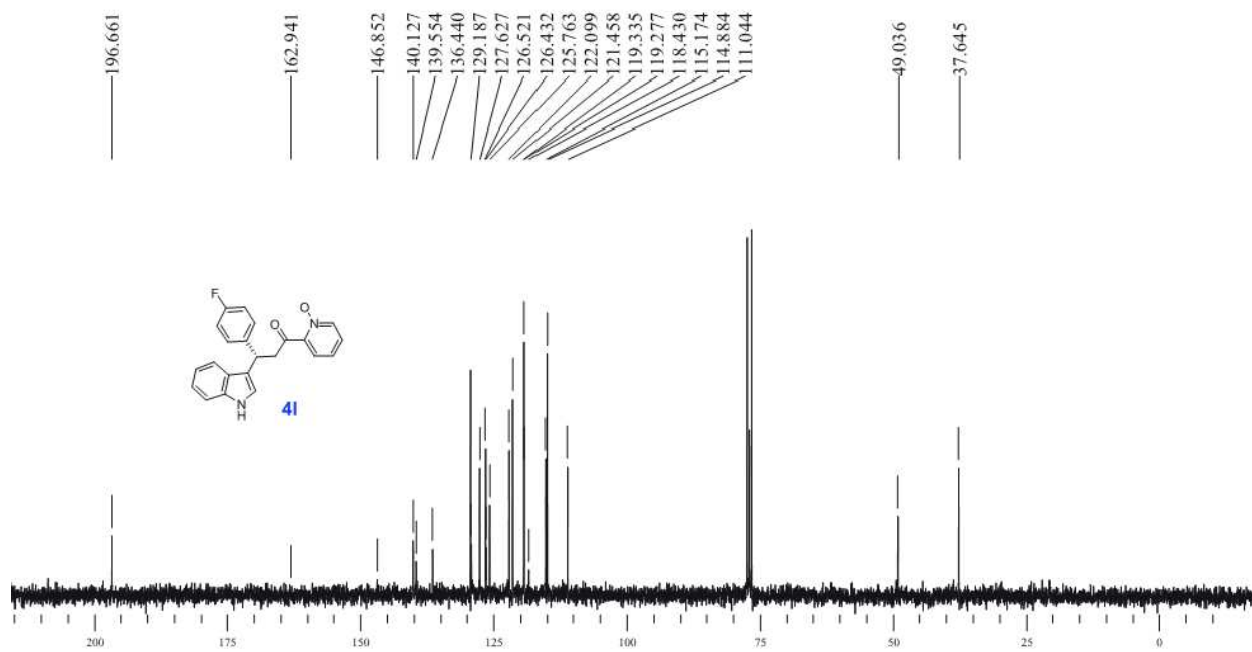
¹H NMR SPECTRUM OF COMPOUND 4k (CDCl₃, 500 MHz)



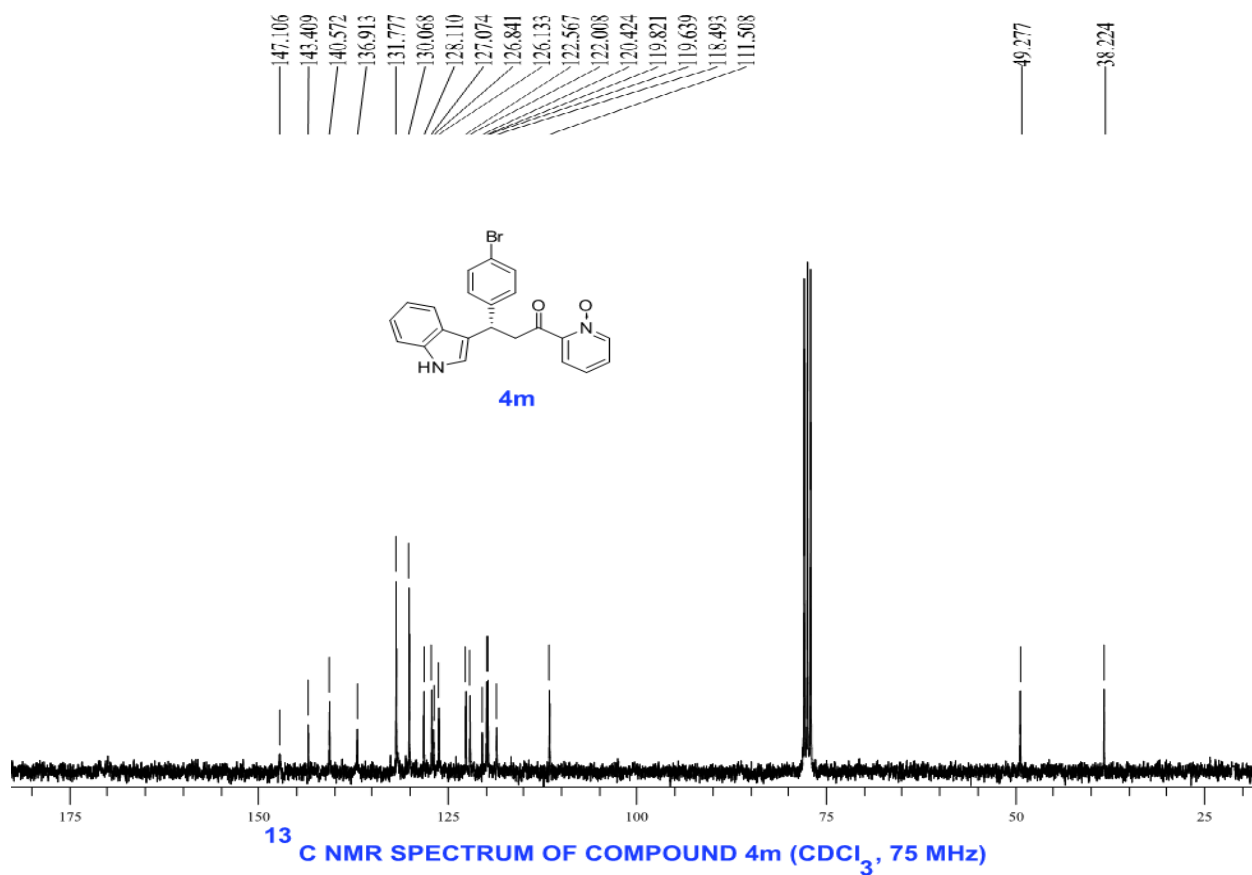
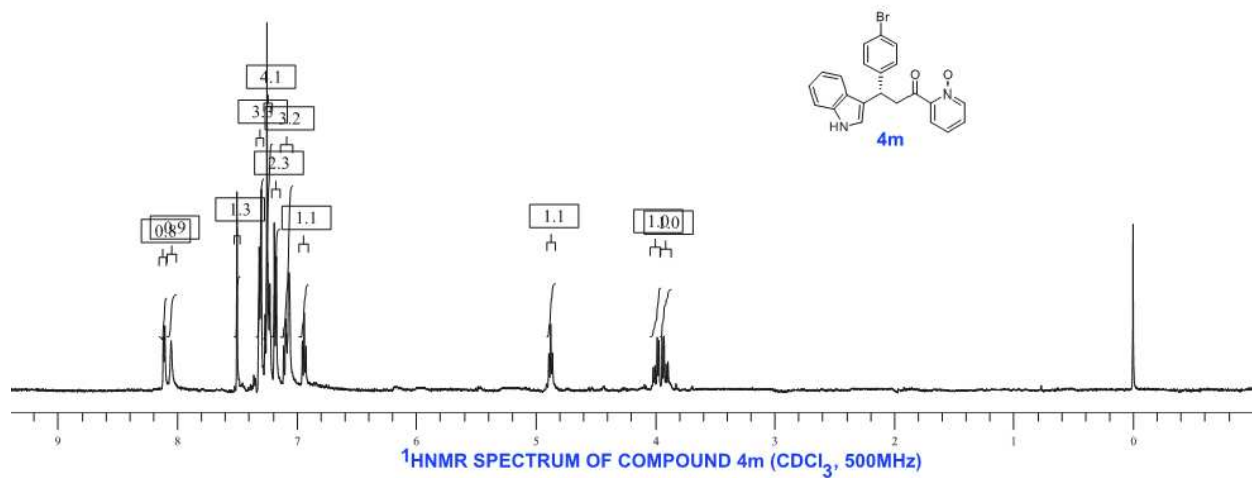
¹³C NMR SPECTRUM OF COMPOUND 4k (CDCl₃, 75 MHz)

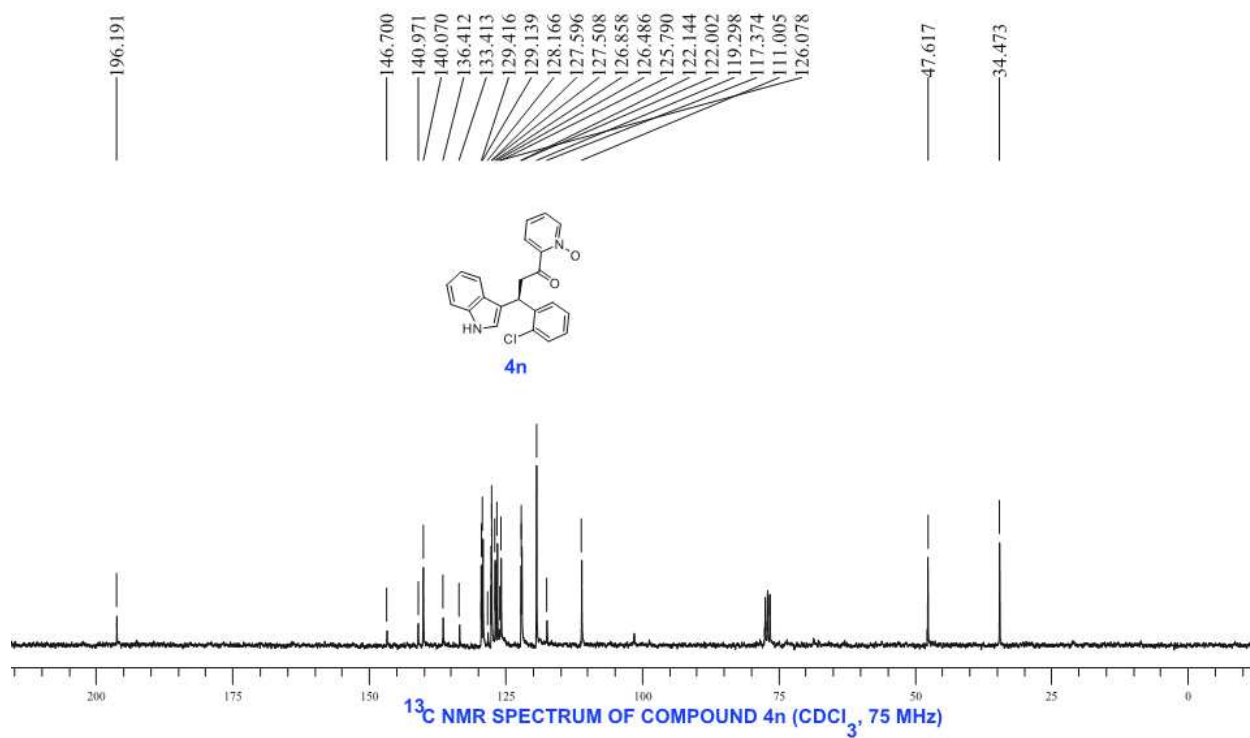
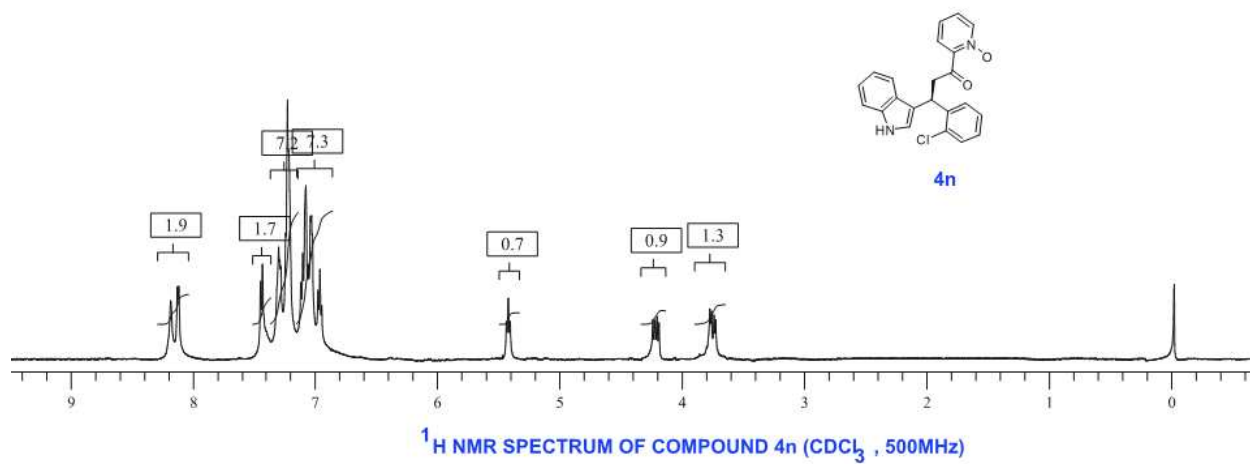


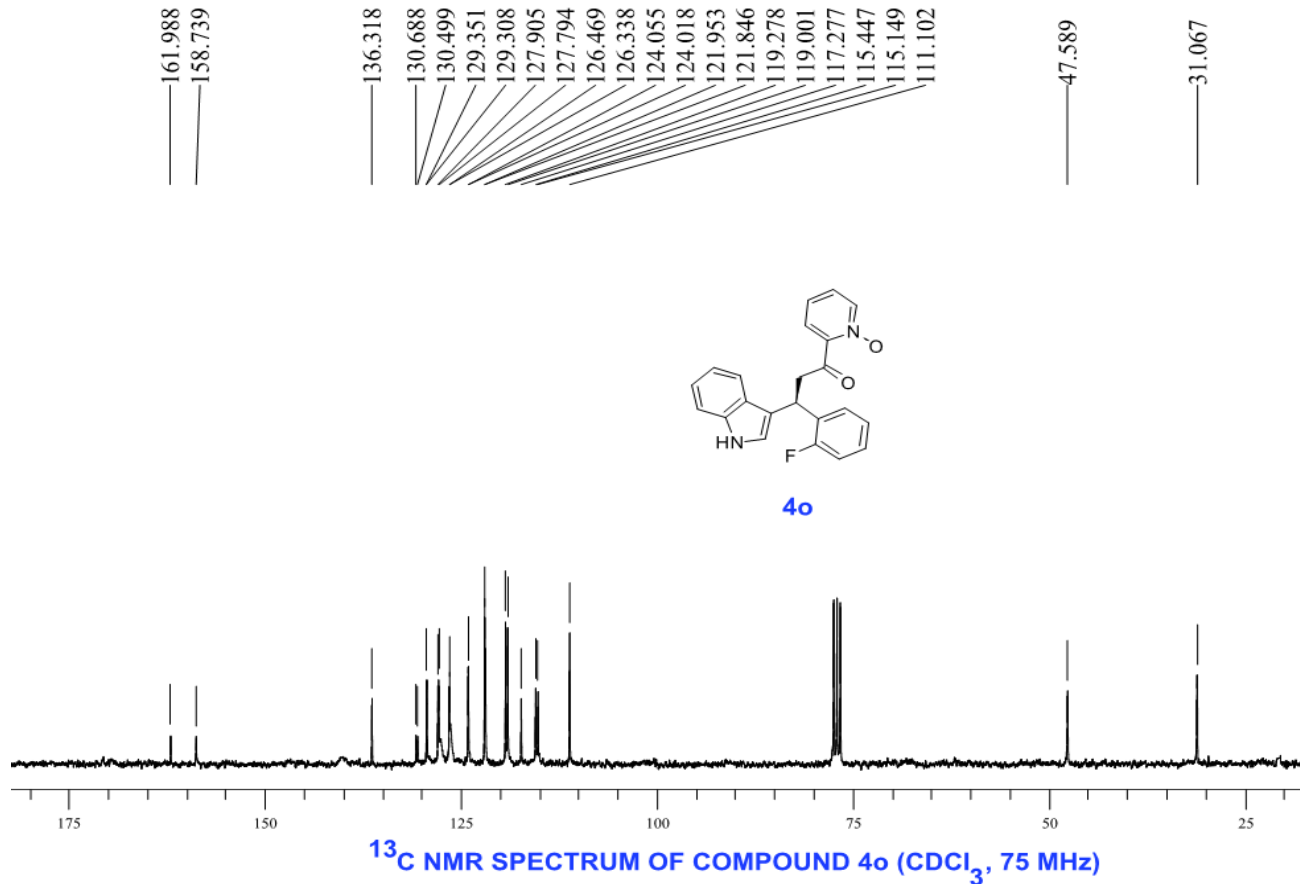
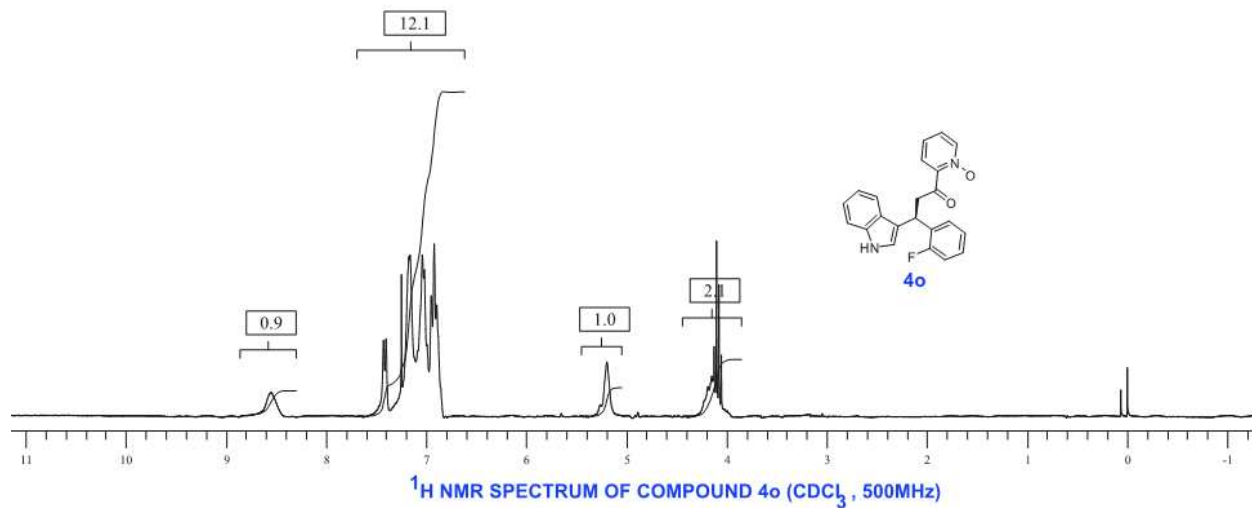
¹H NMR SPECTRUM OF COMPOUND 4i (CDCl₃, 500MHz)

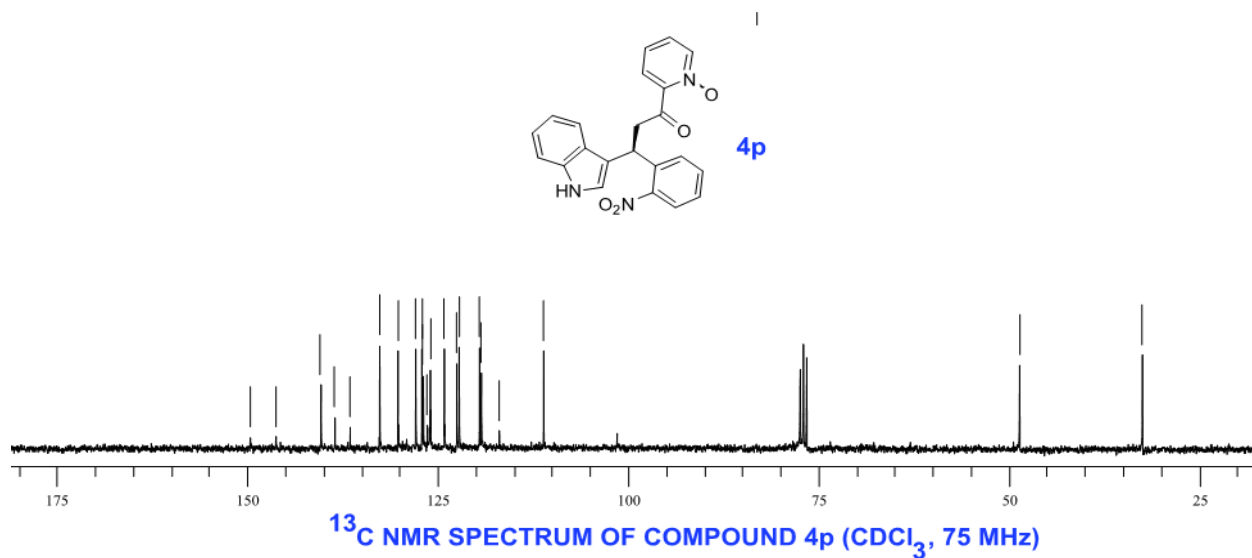
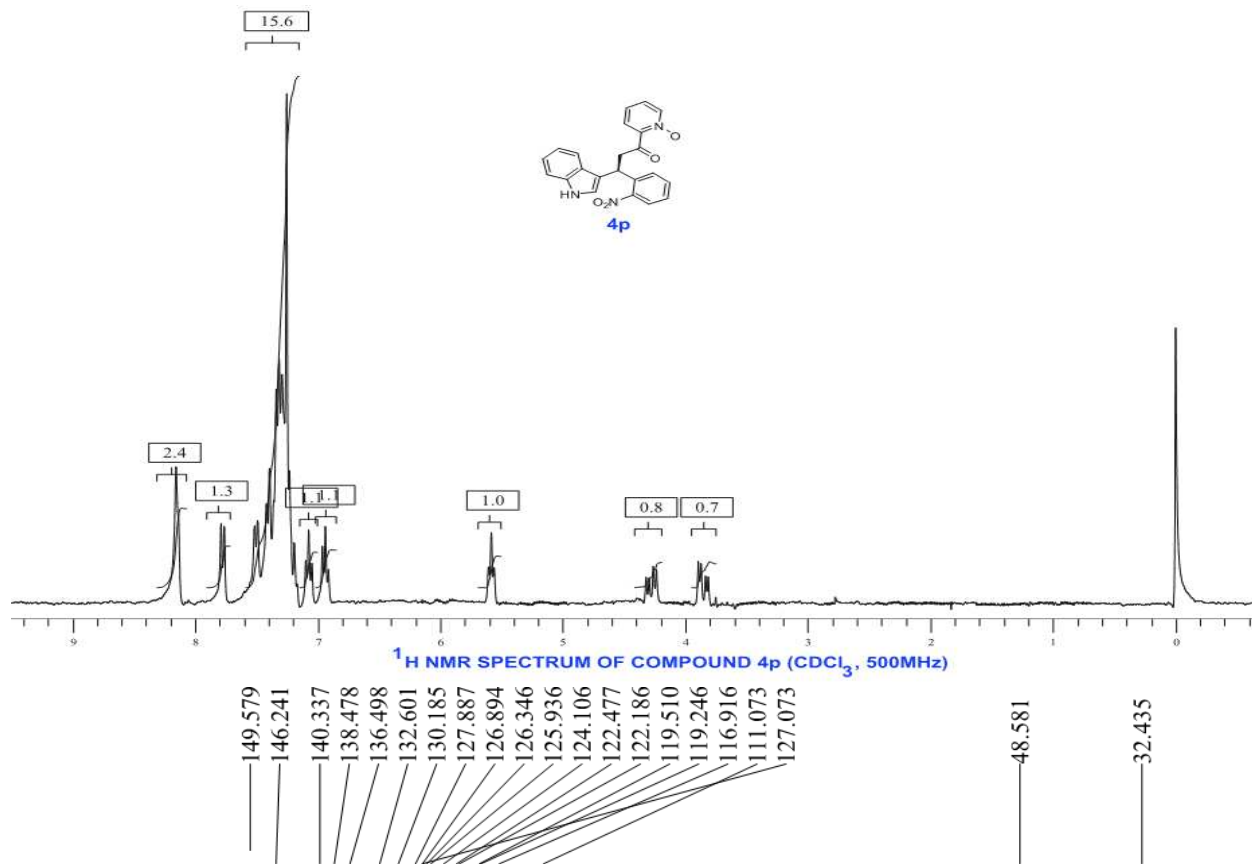


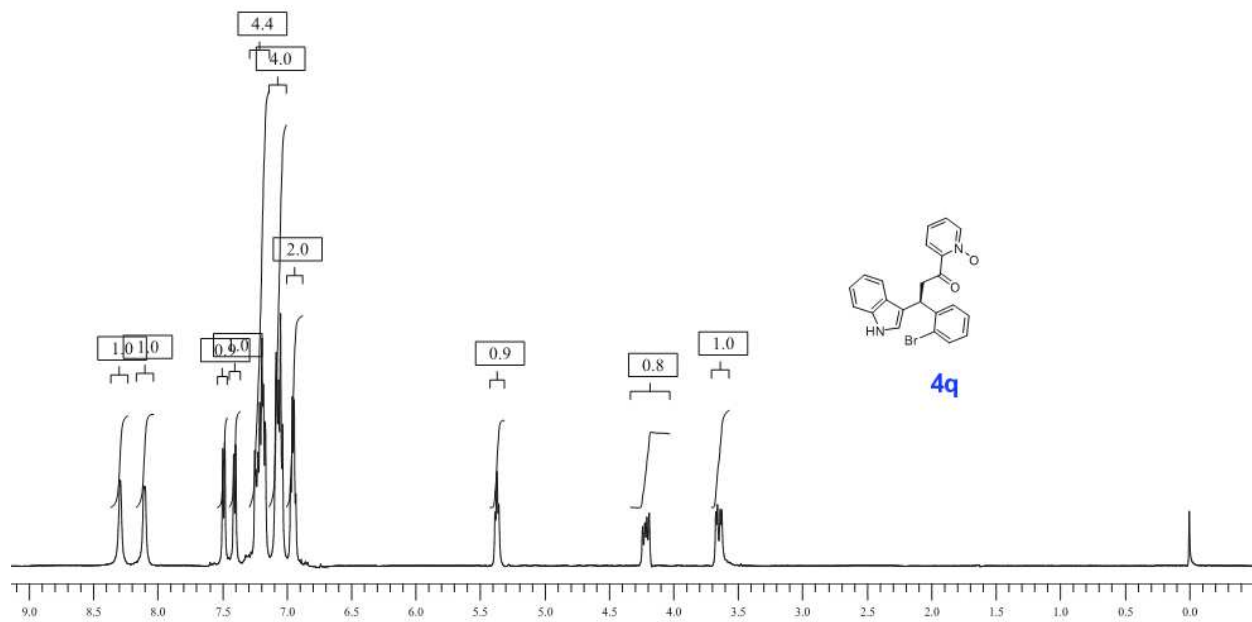
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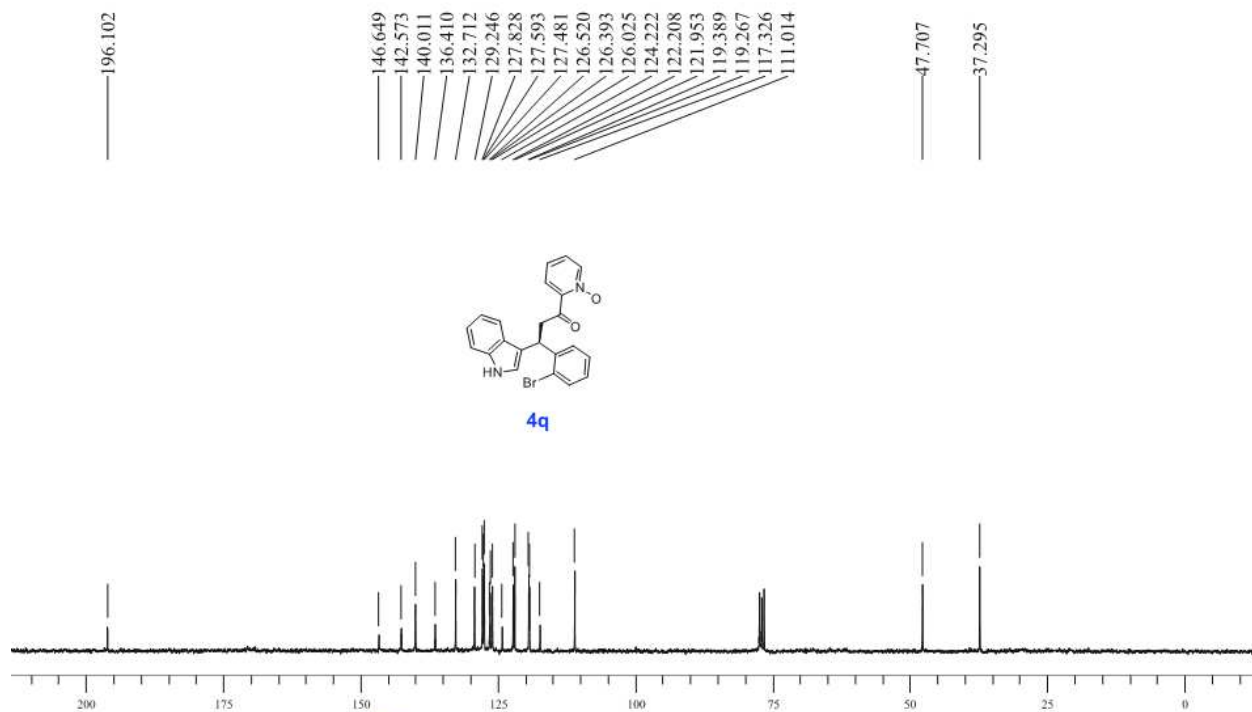




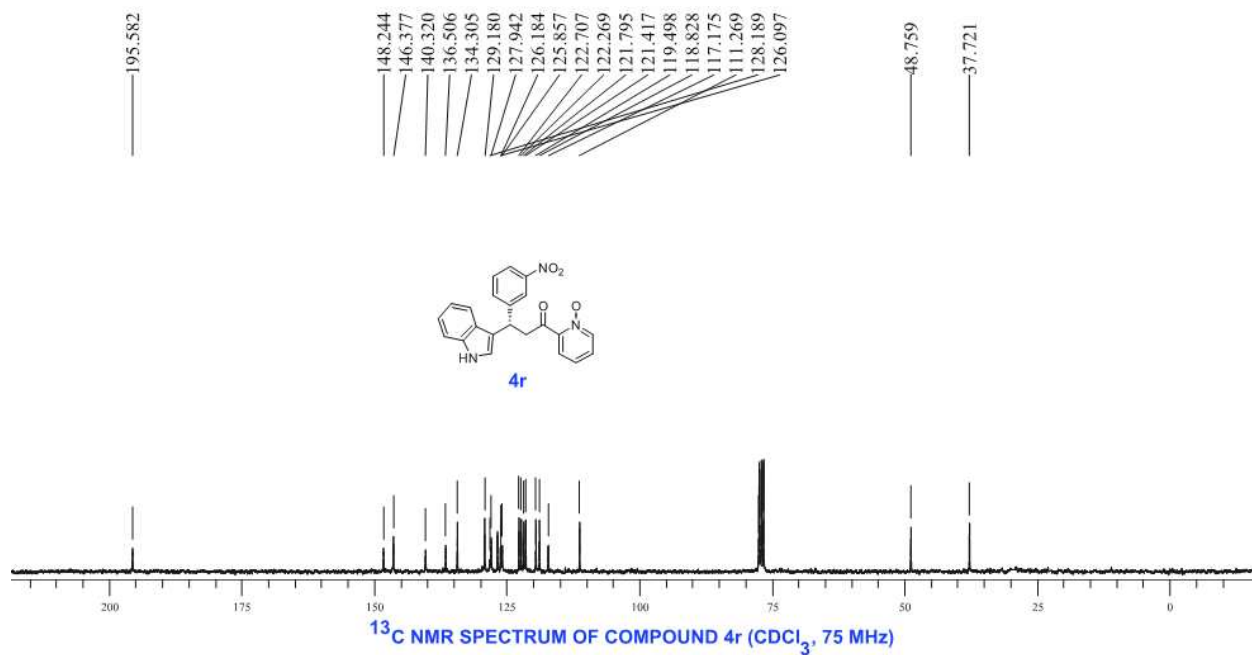
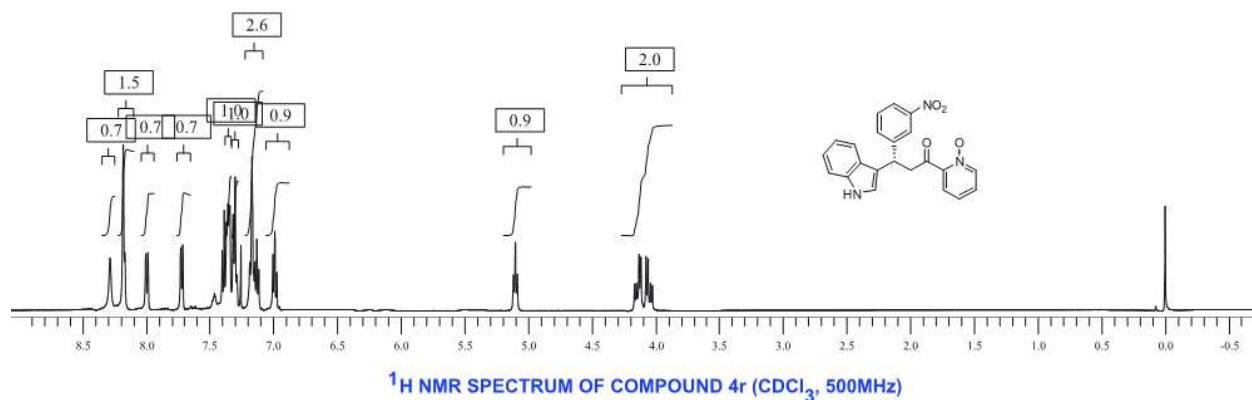


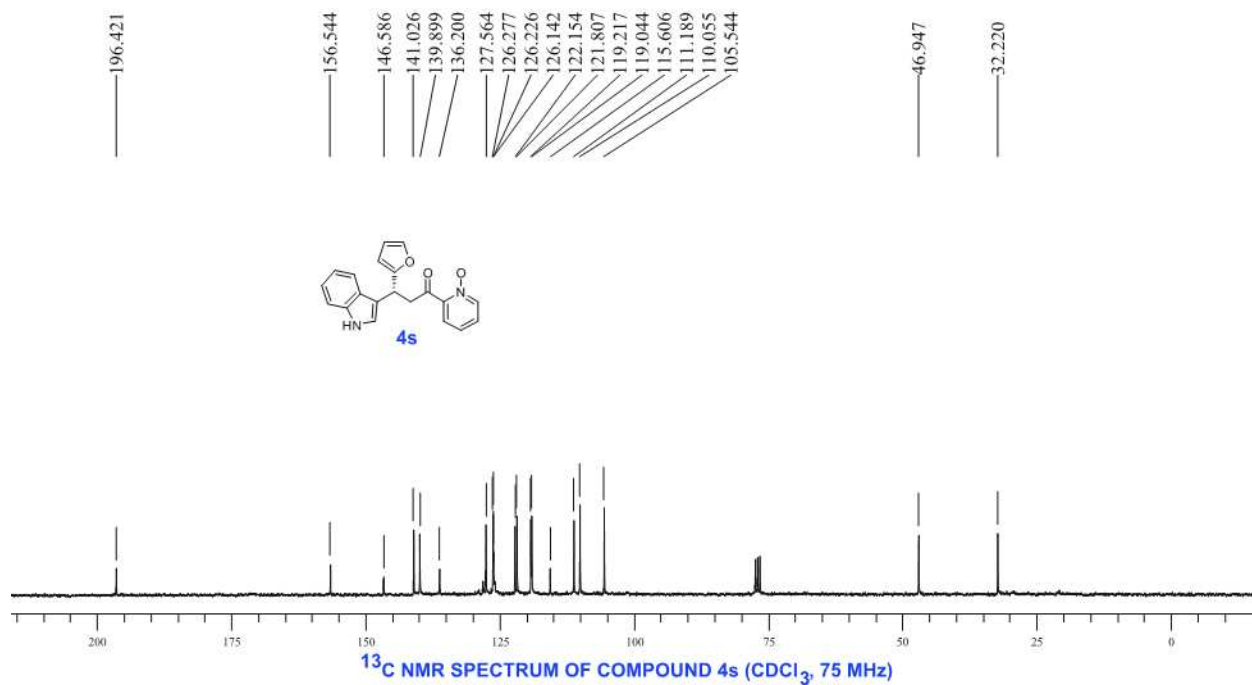
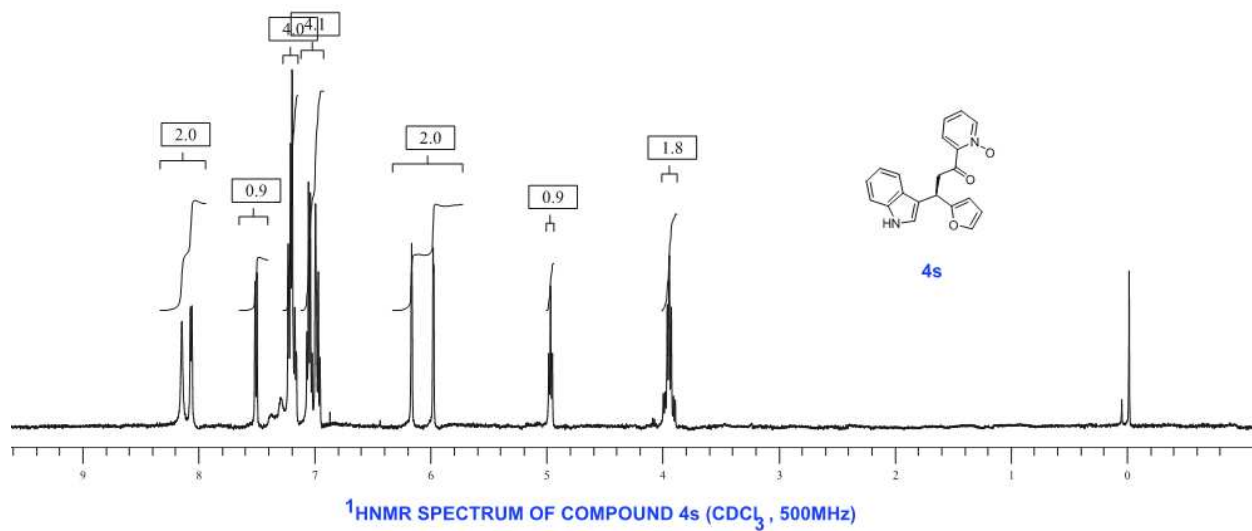


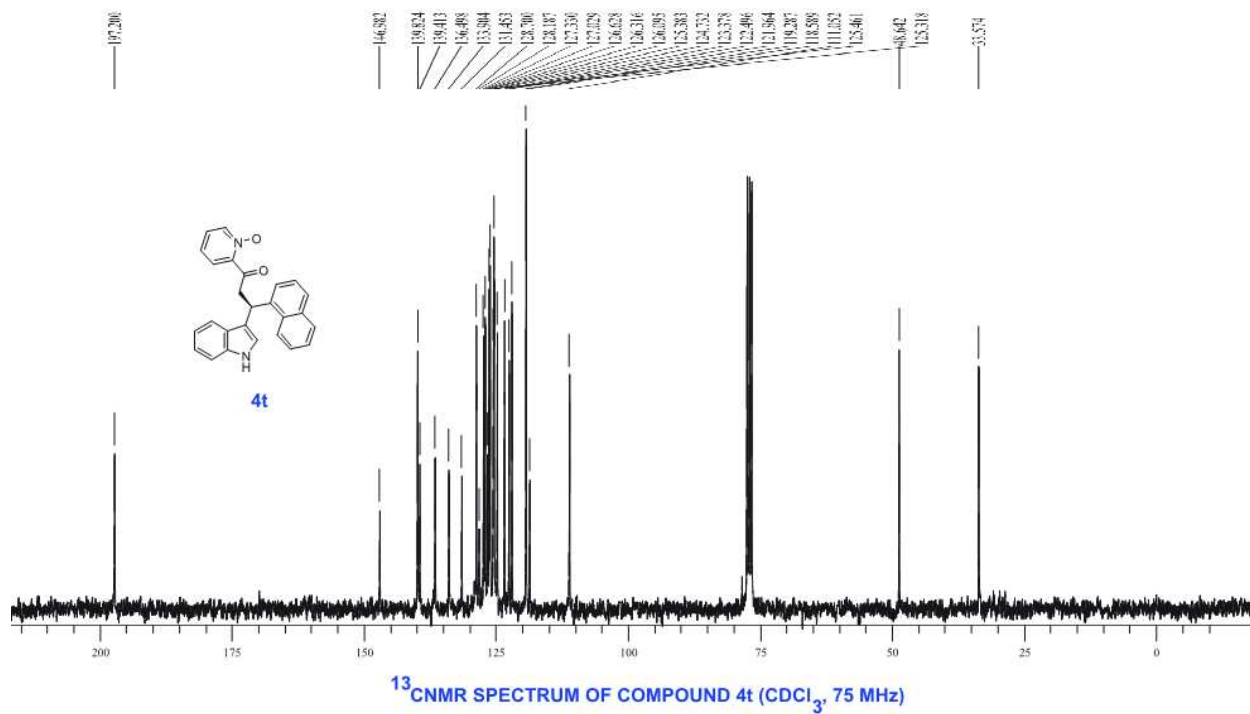
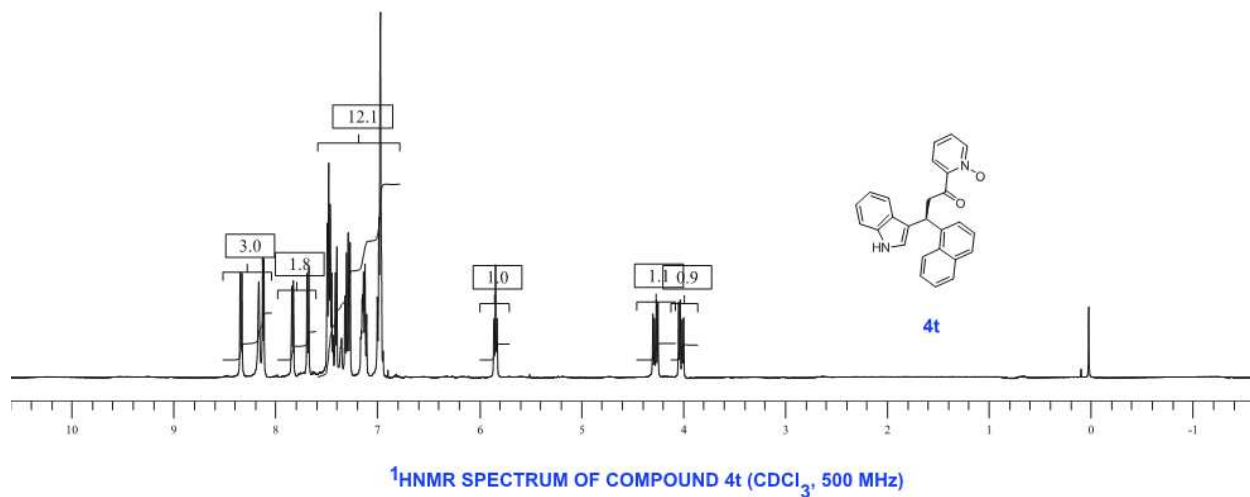
1H NMR SPECTRUM OF COMPOUND 4q (CDCl₃, 500MHz)

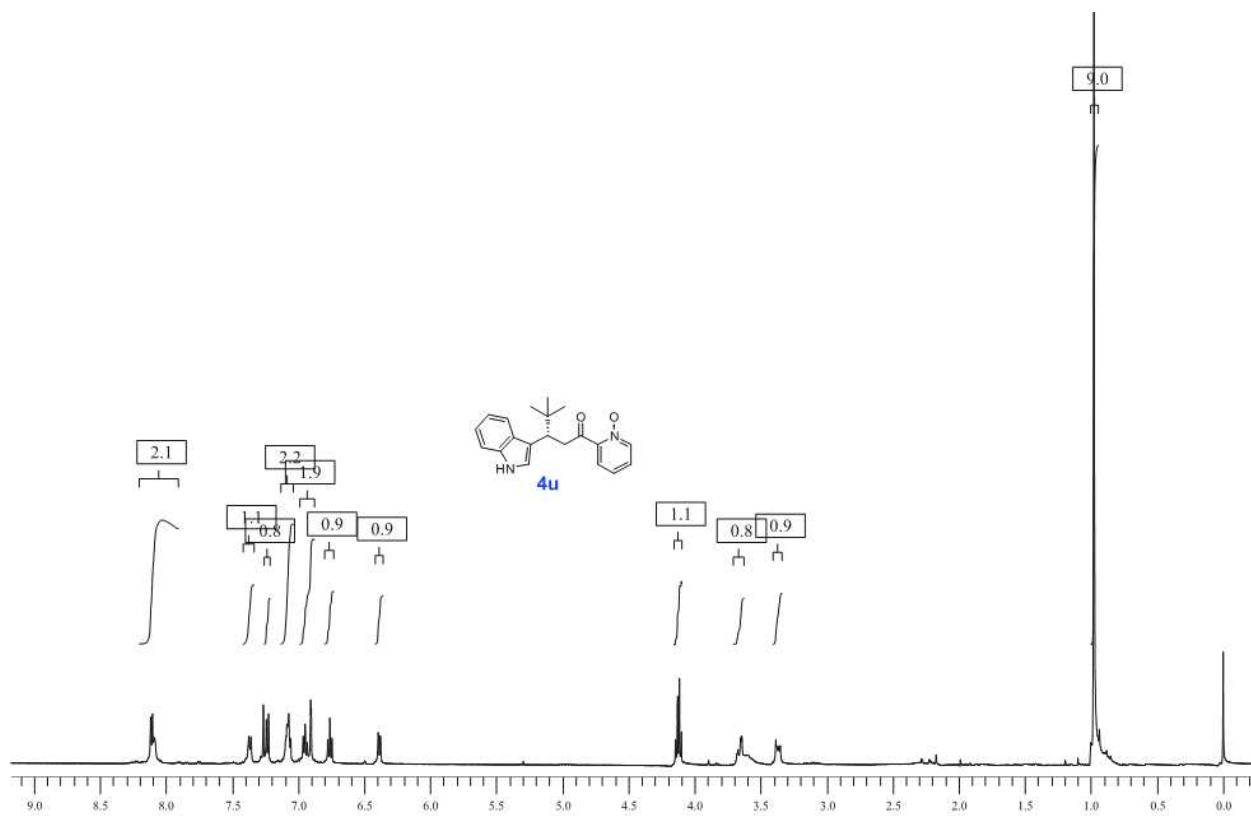


13C NMR SPECTRUM OF COMPOUND 4q (CDCl₃, 75 MHz)

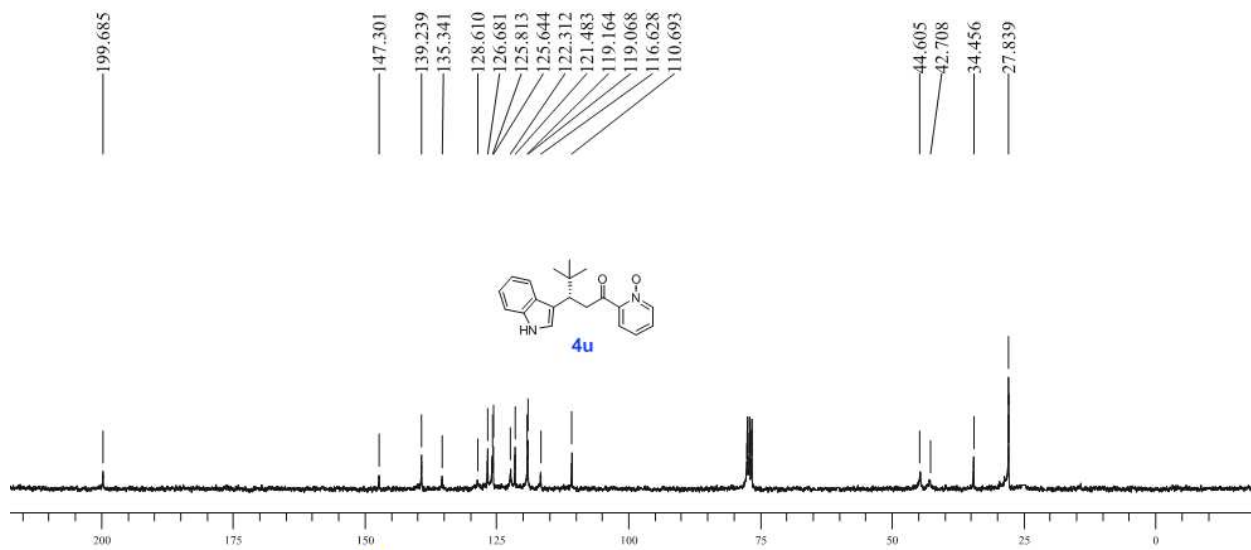




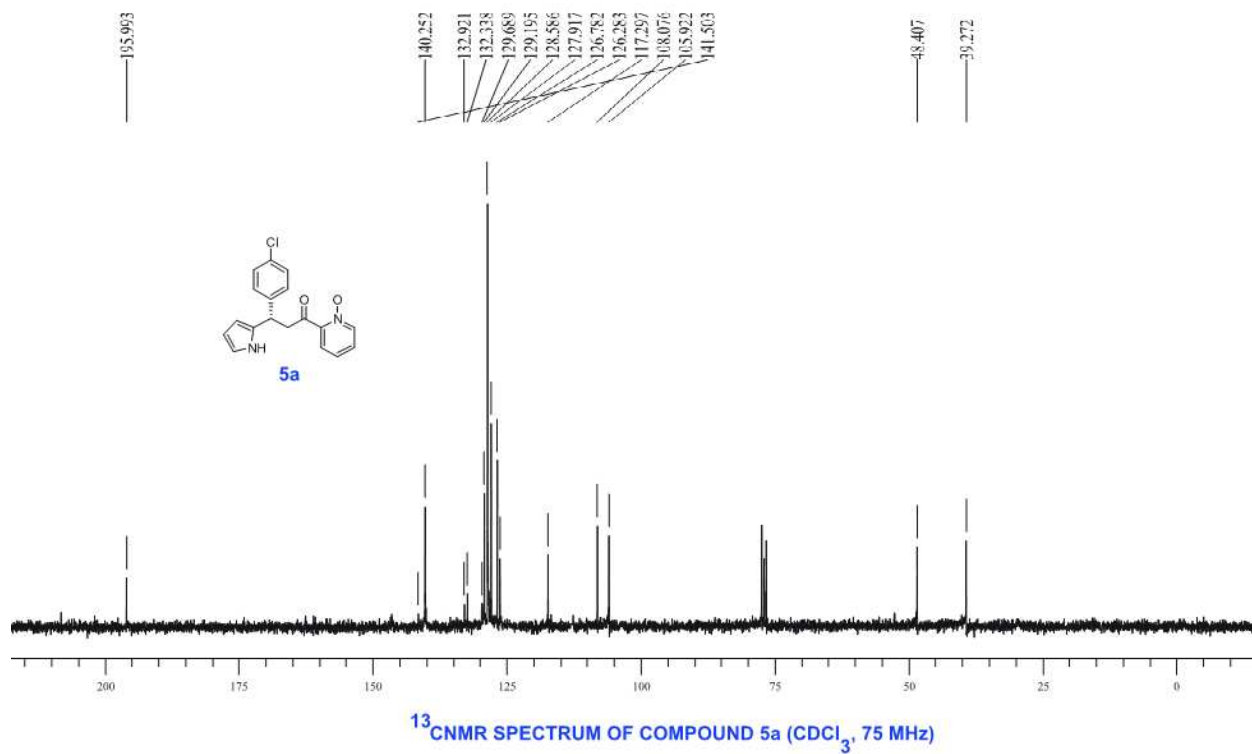
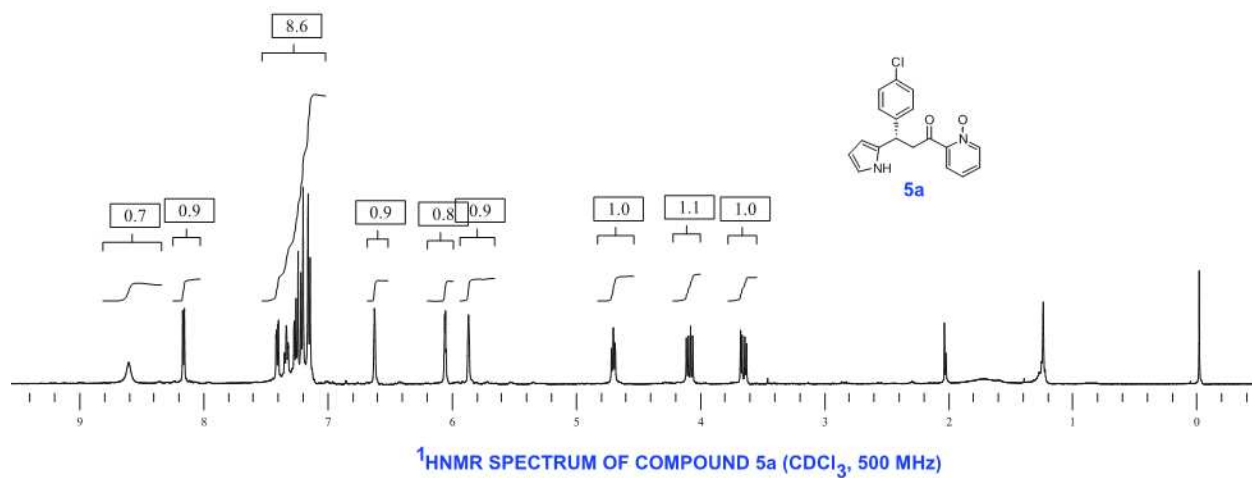


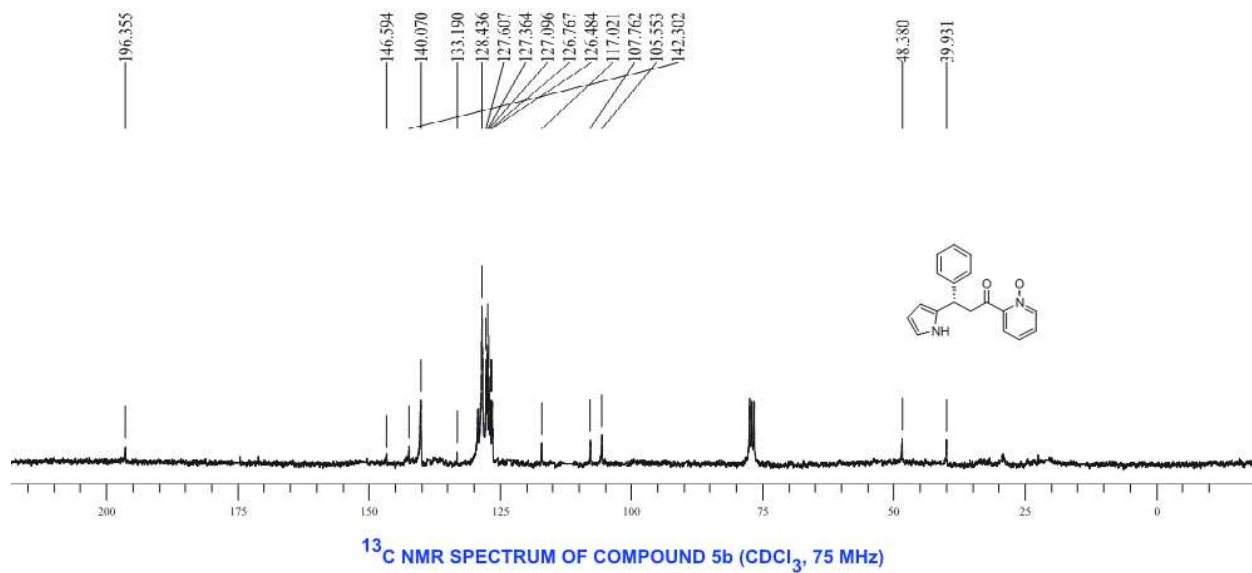
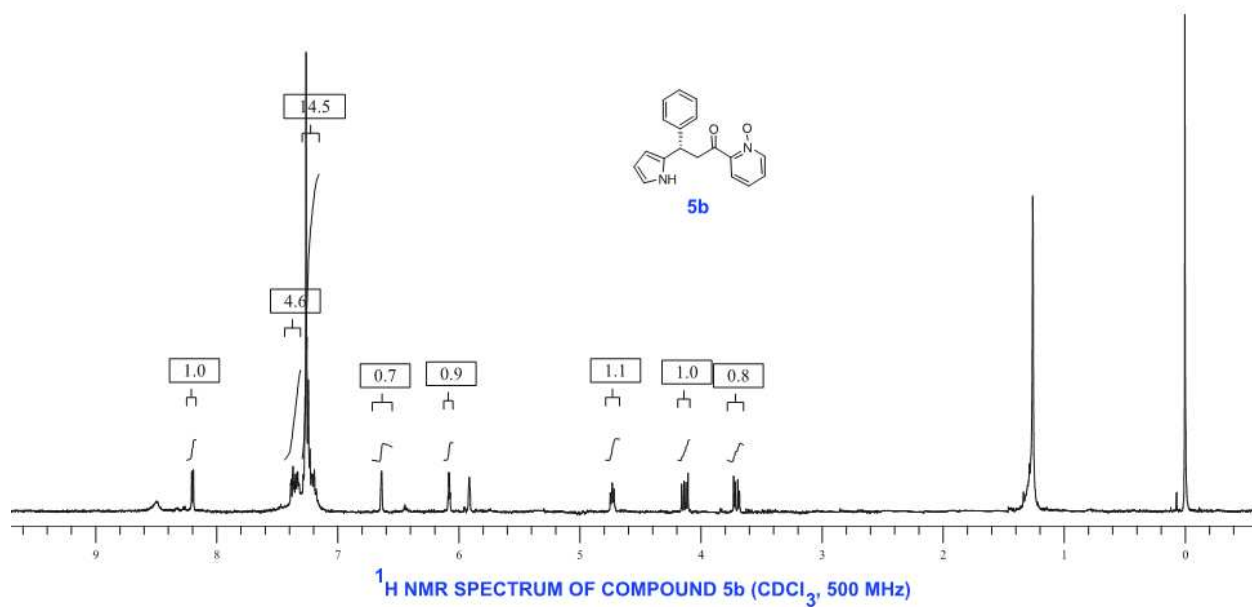


¹H NMR SPECTRUM OF COMPUND 4u (CDCl₃, 500 MHz)

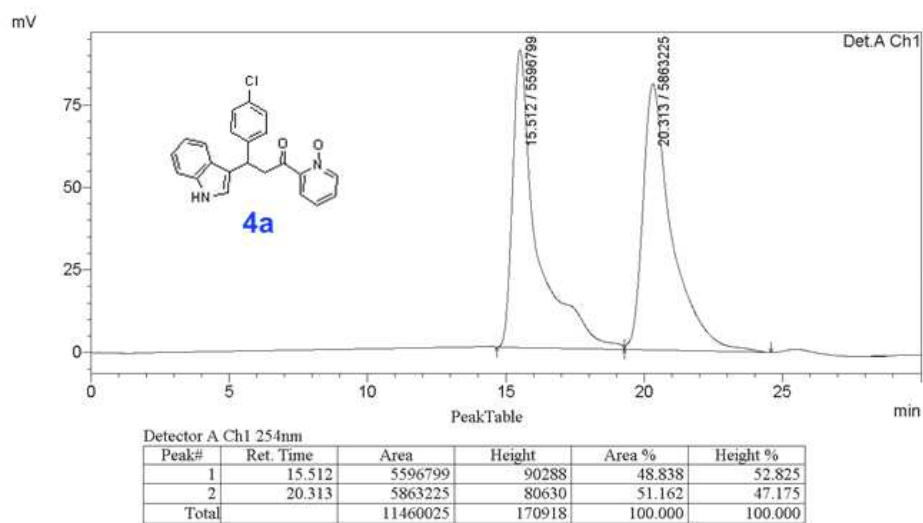


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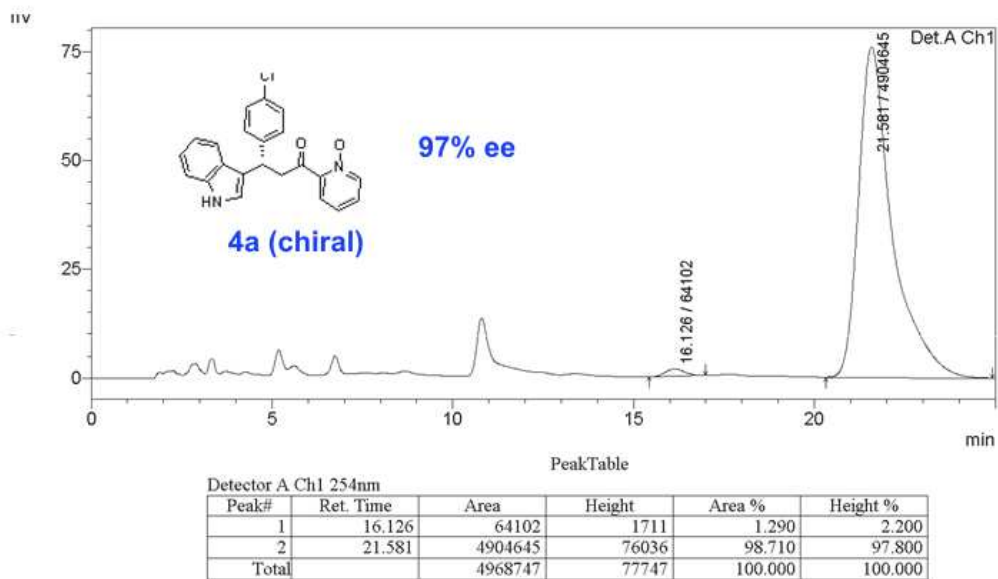




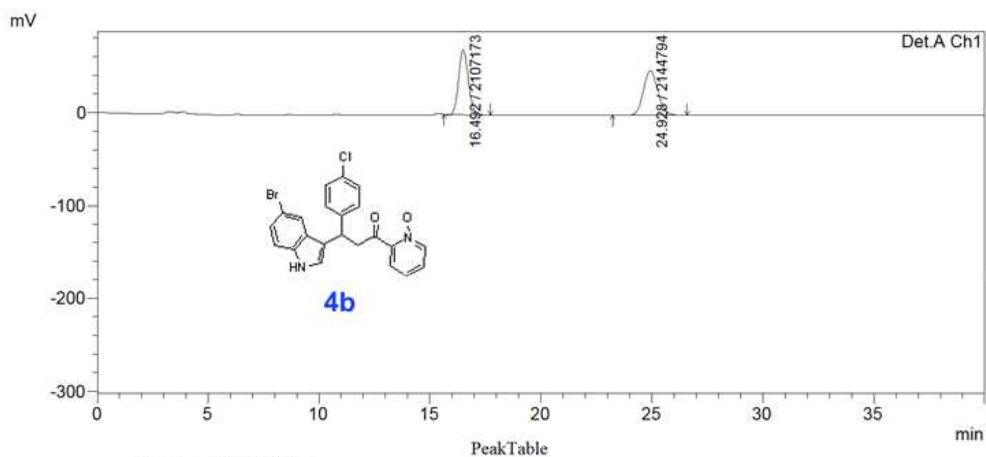
Hplc chromatogram of 4a (racemic)



Hplc chromatogram of 4a (chiral)



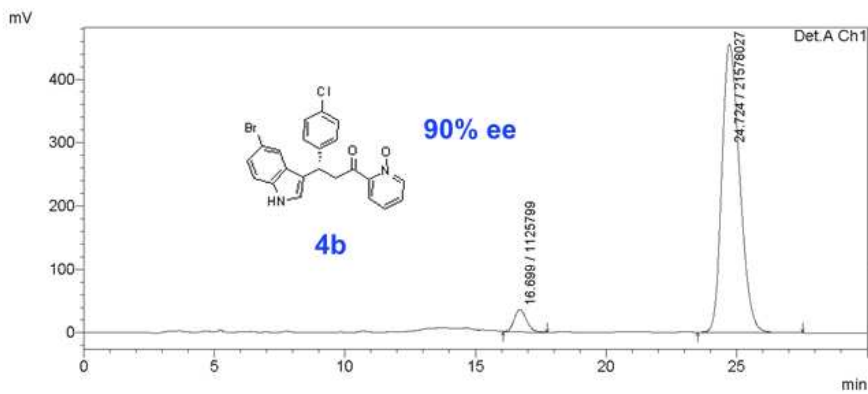
Hplc chromatogram of 4b (racemic)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.492	2107173	69791	49.558	59.431
2	24.928	2144794	47641	50.442	40.569
Total		4251967	117432	100.000	100.000

Hplc chromatogram of 4b (chiral)

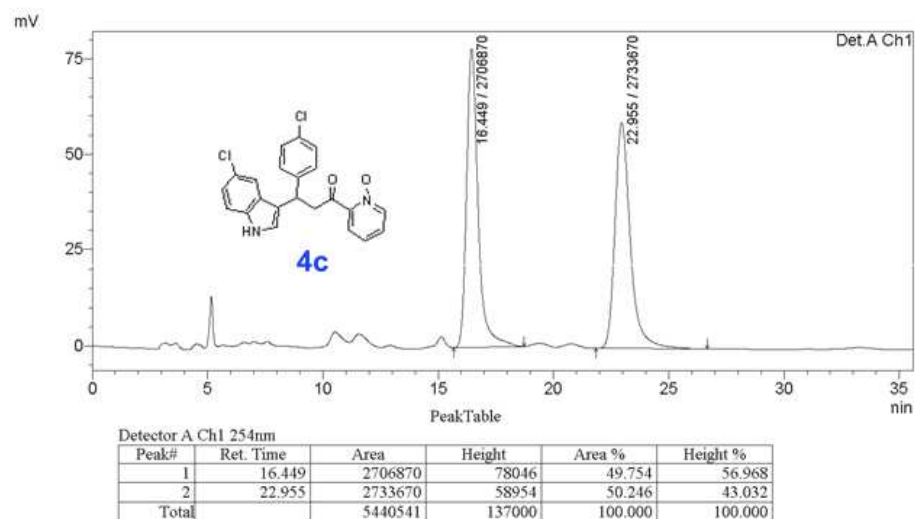


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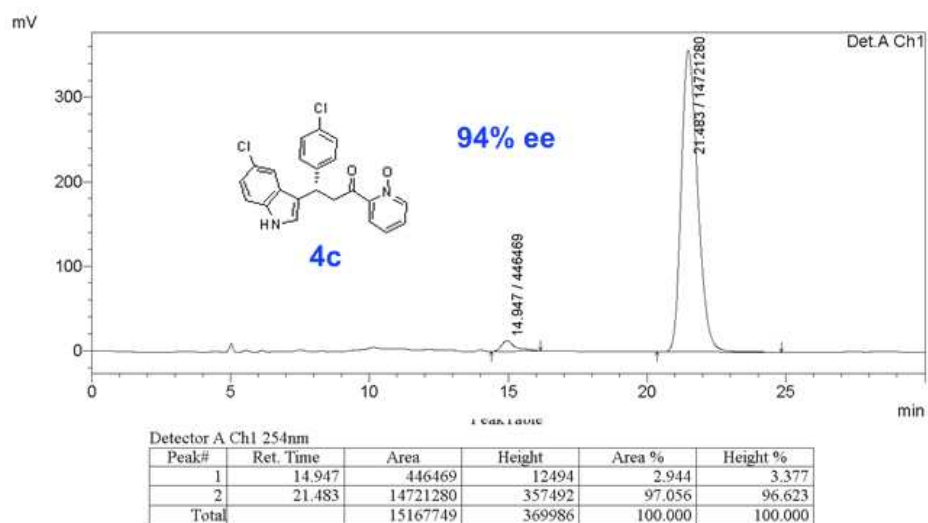
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.699	1125799	35134	4.959	7.163
2	24.724	21578027	455375	95.041	92.837
Total		22703826	490510	100.000	100.000

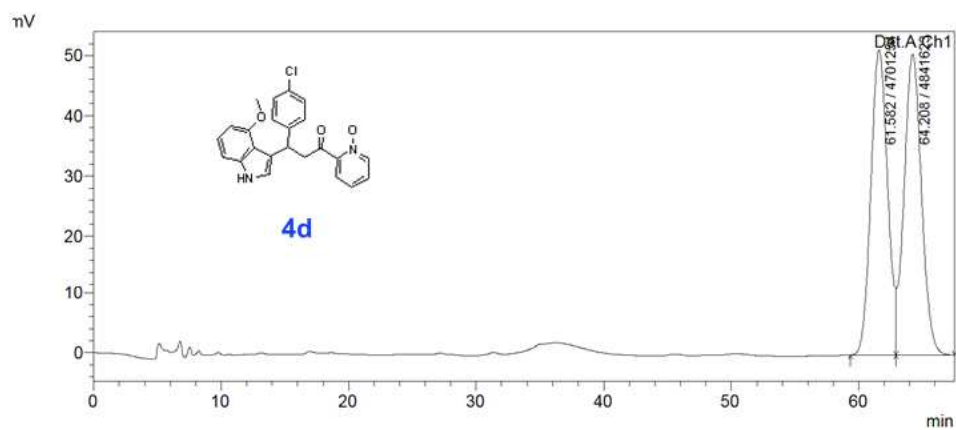
Hplc chromatogram of 4c (racemic)



Hplc chromatogram of 4c (chiral)



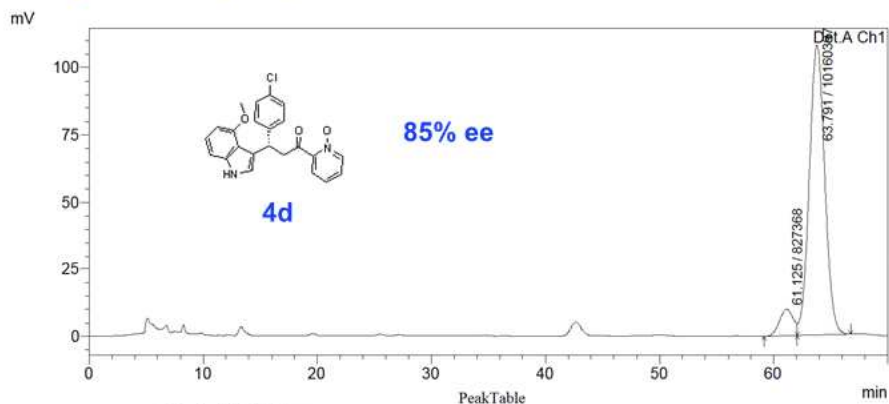
Hplc chromatogram of 4d (racemic)



PeakTable

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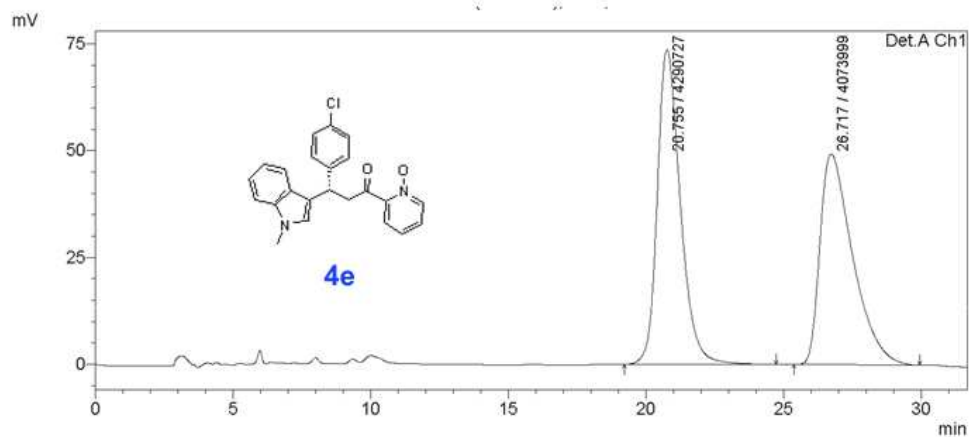
Hplc chromatogram of 4d (chiral)



PeakTable

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1	61.125	827368	9773	7.530	8.307
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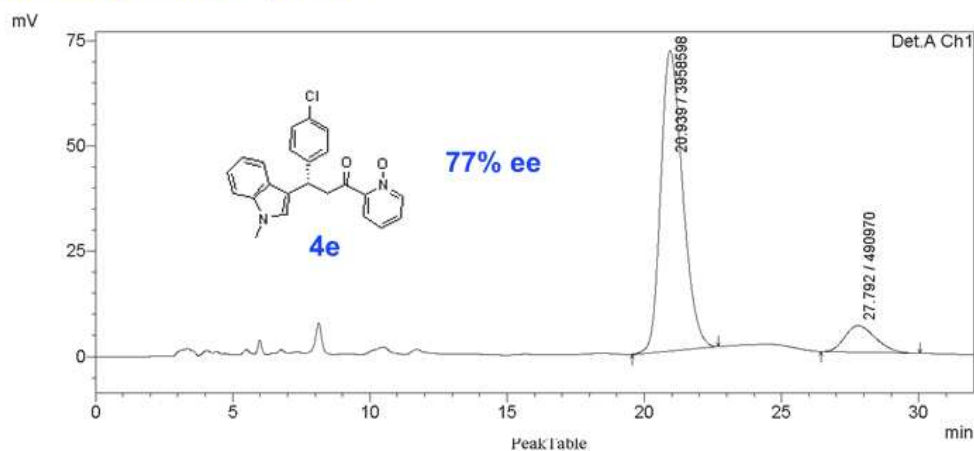
Hplc chromatogram of 4e (racemic)



PeakTable

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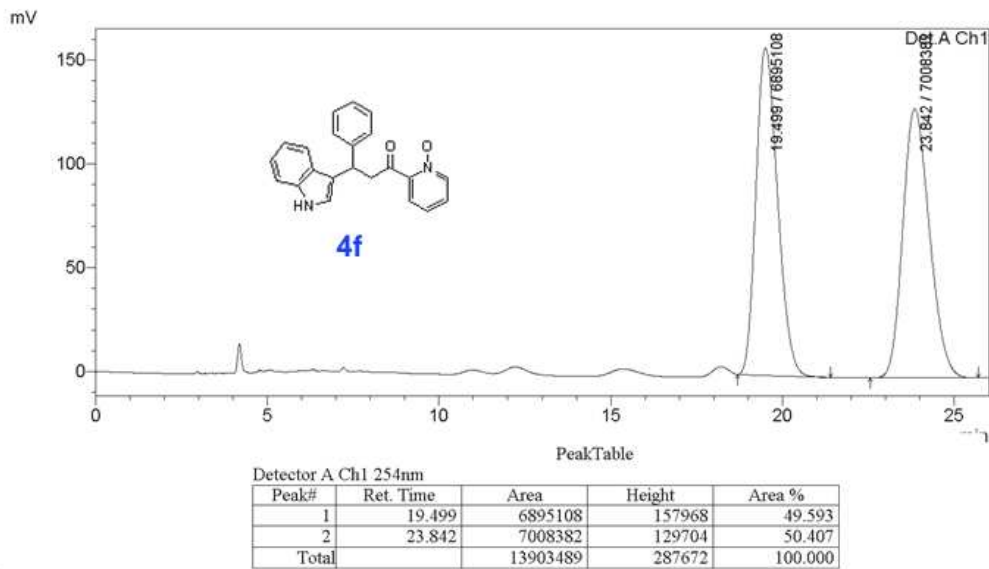
Hplc chromatogram of 4e (chiral)



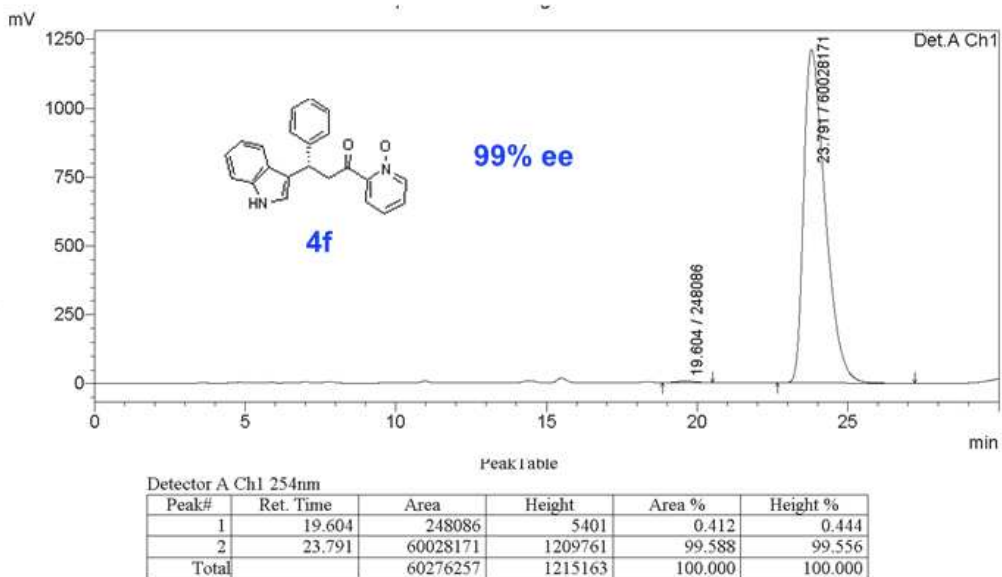
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Total		4449569	77696	100.000	100.000

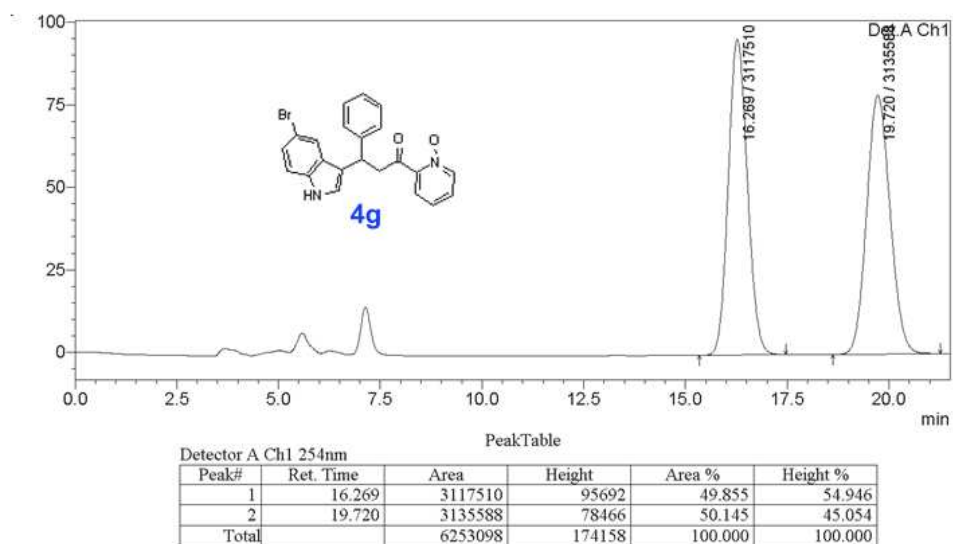
Hplc chromatogram of 4f (racemic)



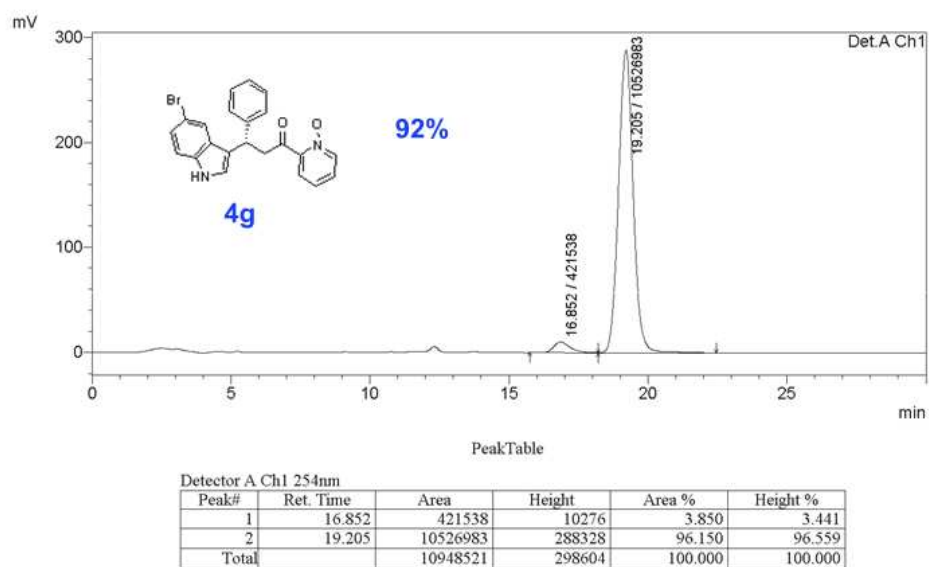
Hplc chromatogram of 4f (chiral)



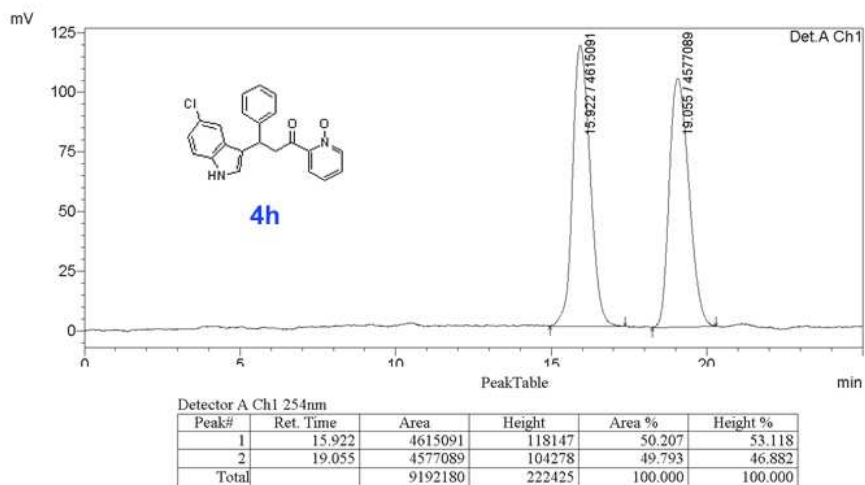
Hplc chromatogram of 4g (racemic)



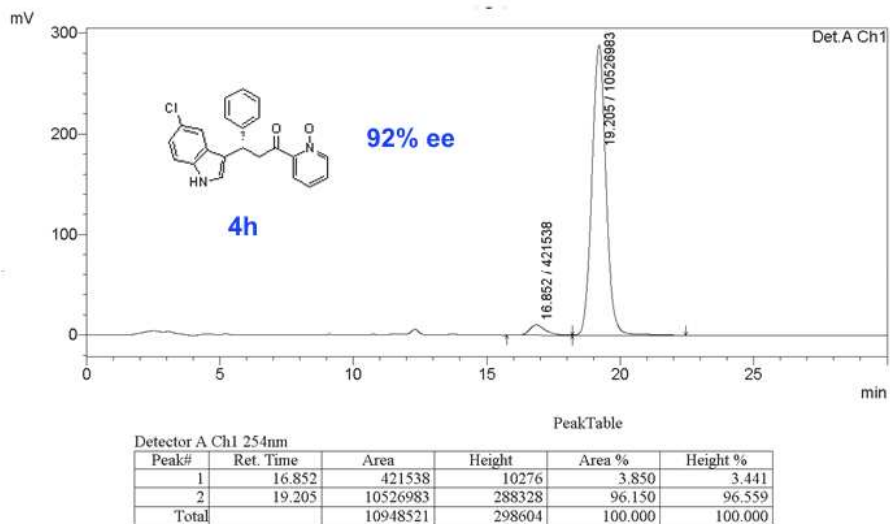
Hplc chromatogram of 4g (chiral)



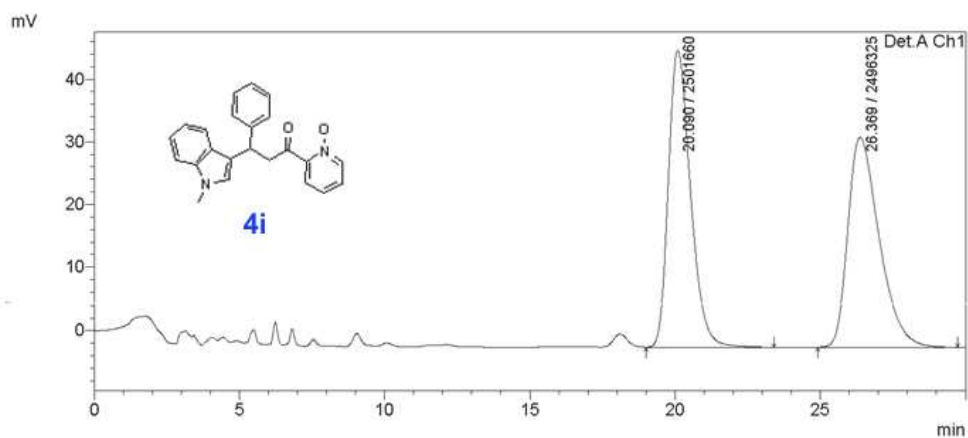
Hplc chromatogram of 4h (racemic)



Hplc chromatogram of 4h (chiral)



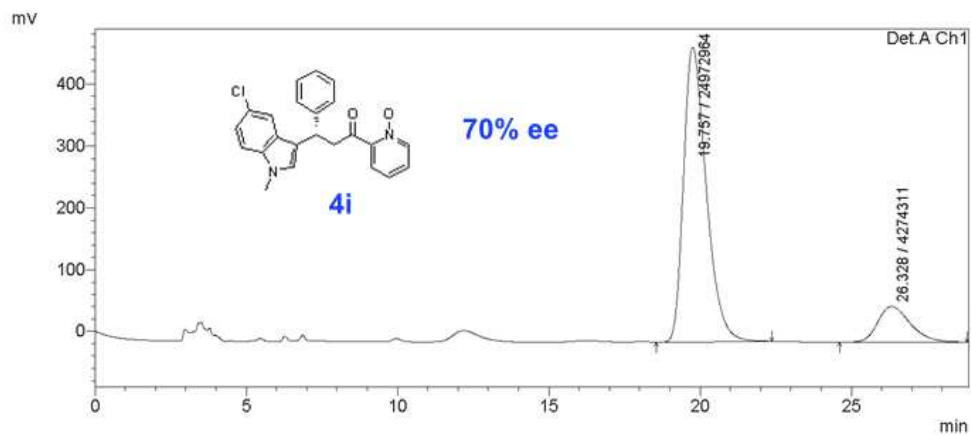
Hplc chromatogram of 4i (racemic)



PeakTable

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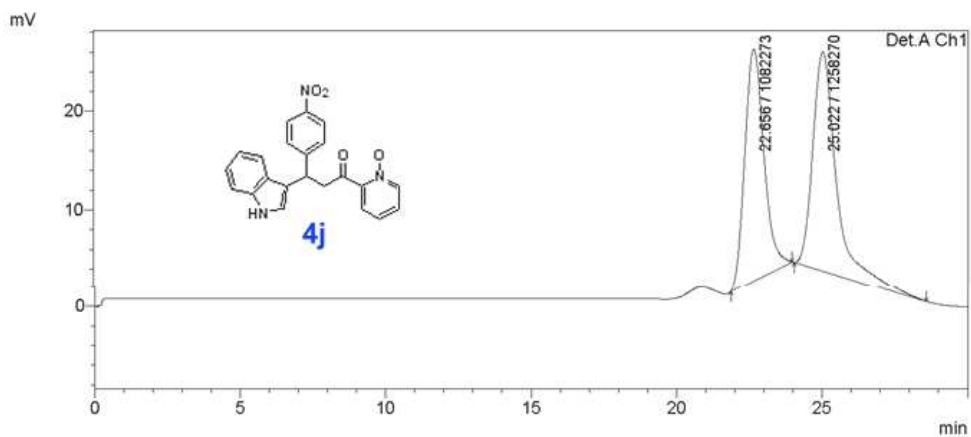
Hplc chromatogram of 4i (chiral)



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.757	24972964	476798	85.386	89.229
2	26.328	4274311	57552	14.614	10.771
Total		29247275	534350	100.000	100.000

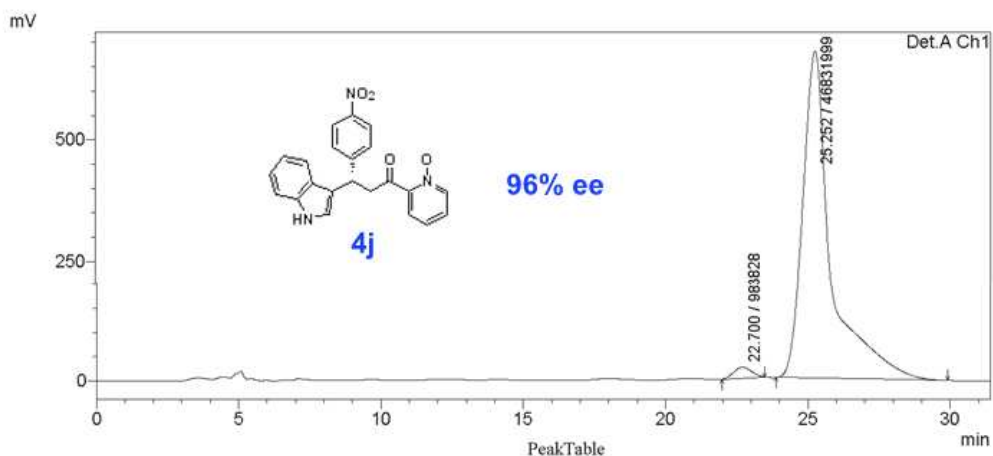
Hplc chromatogram of 4j (racemic)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.656	1082273	23566	46.240	51.380
2	25.022	1258270	22301	53.760	48.620
Total		2340543	45867	100.000	100.000

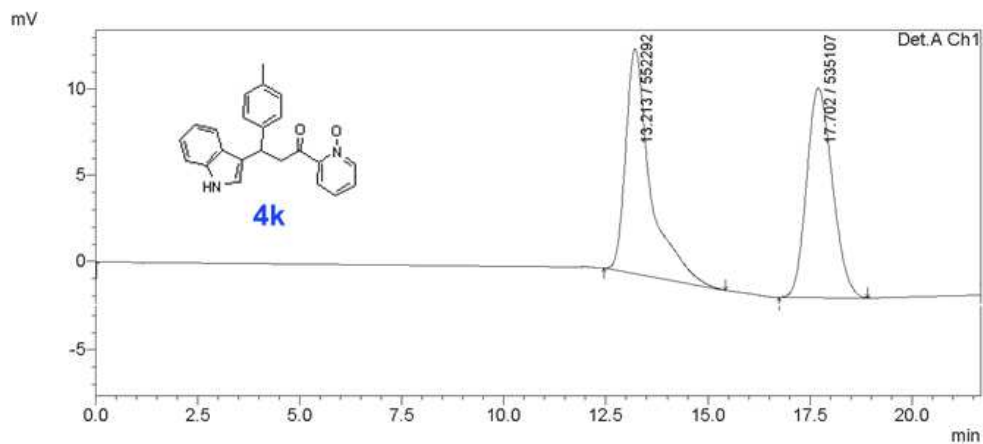
Hplc chromatogram of 4j (chiral)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.700	983828	22758	2.058	3.255
2	25.252	46831999	676434	97.942	96.745
Total		47815827	699192	100.000	100.000

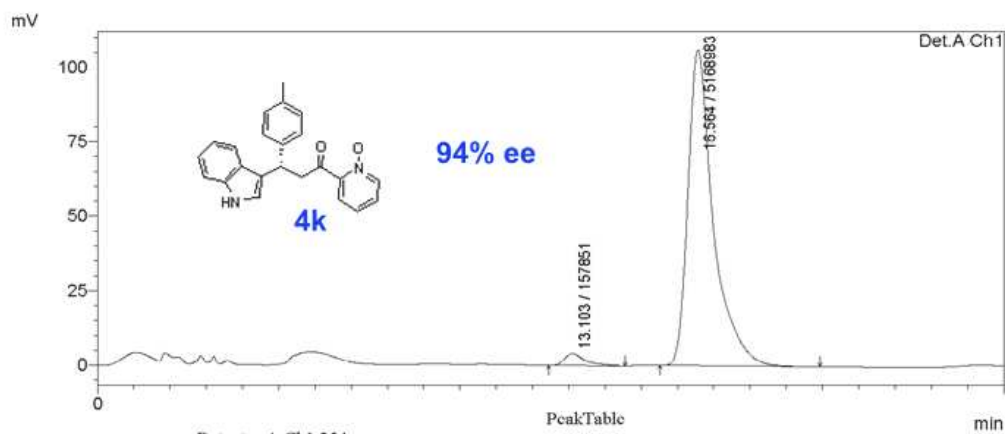
Hplc chromatogram of 4k (racemic)



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.213	552292	13074	50.790	51.804
2	17.702	535107	12163	49.210	48.196
Total		1087399	25237	100.000	100.000

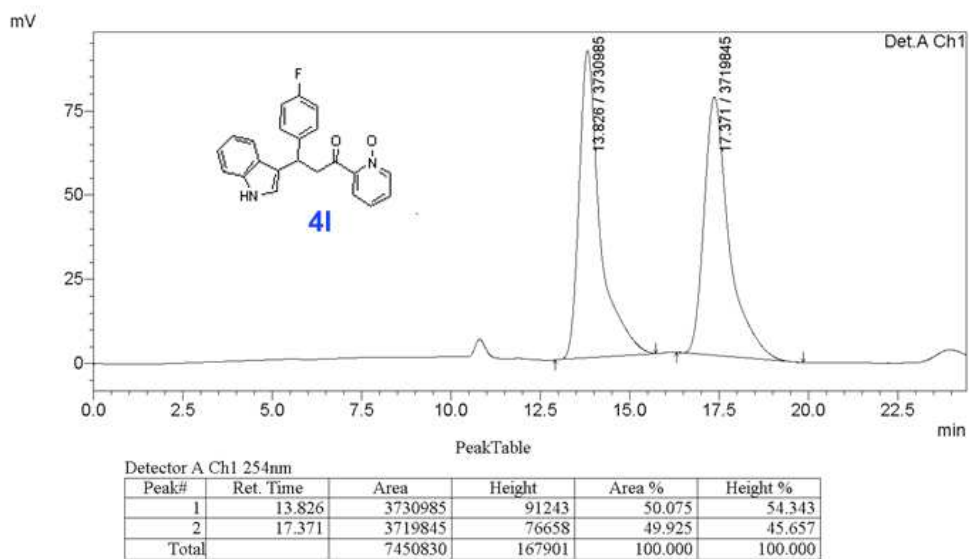
Hplc chromatogram of 4k (chiral)



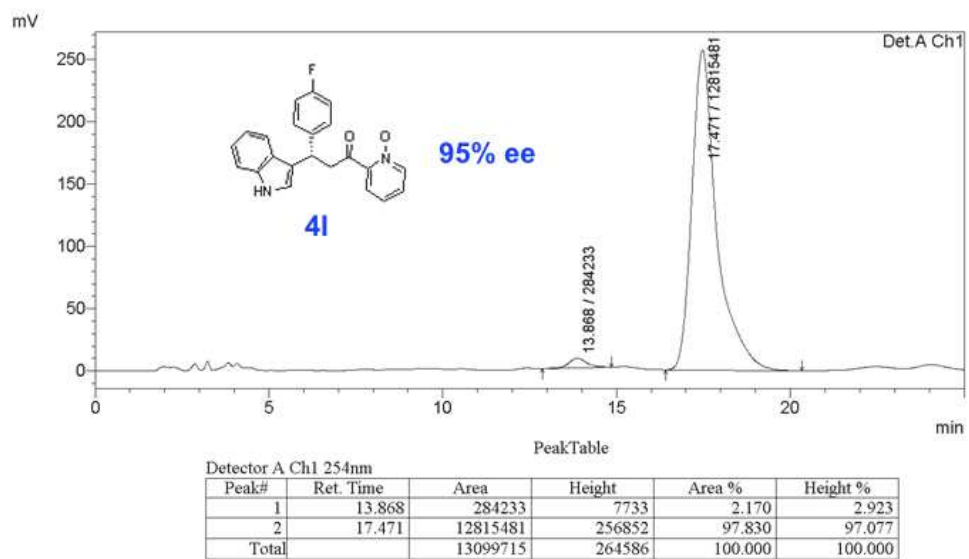
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.103	157851	4060	2.963	3.687
2	16.564	5168983	106063	97.037	96.313
Total		5326835	110124	100.000	100.000

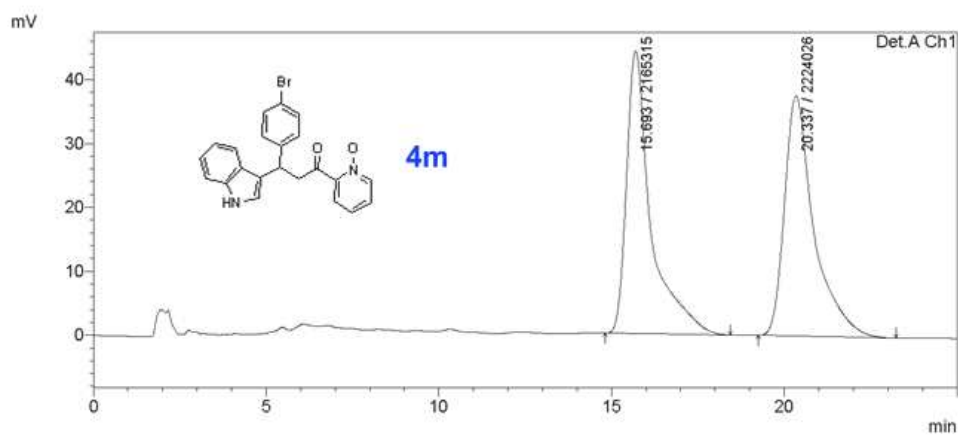
Hplc chromatogram of 4I (racemic)



Hplc chromatogram of 4I (chiral)



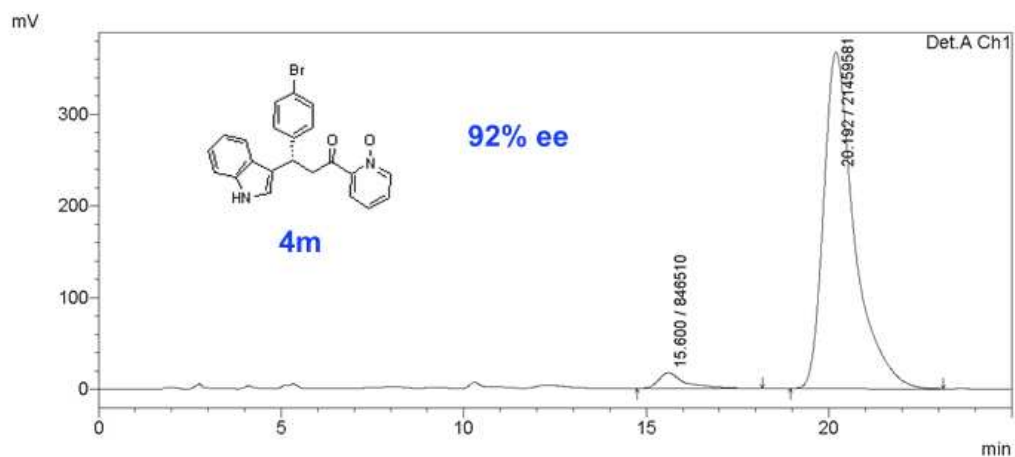
Hplc chromatogram of 4m (racemic)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.693	2165315	44293	49.331	54.108
2	20.337	2224026	37568	50.669	45.892
Total		4389341	81861	100.000	100.000

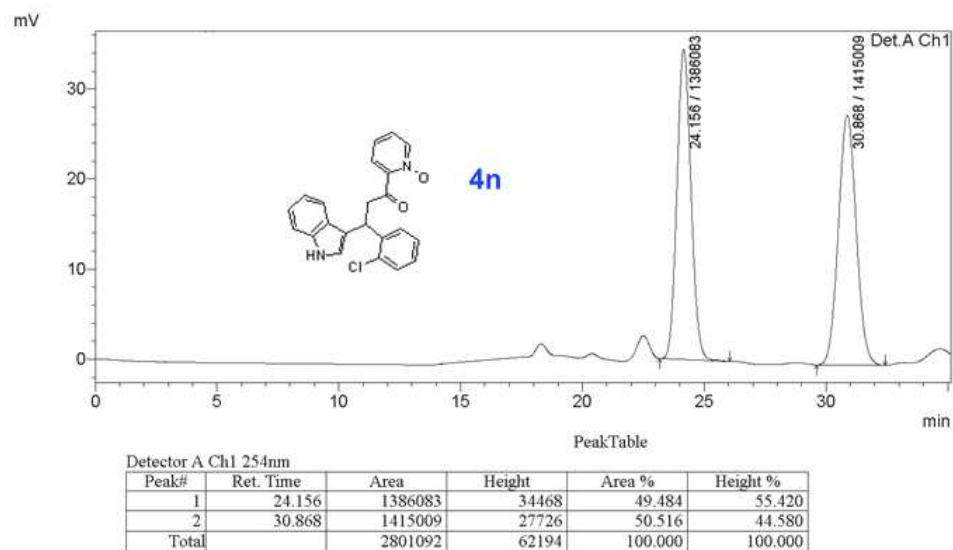
Hplc chromatogram of 4m (chiral)



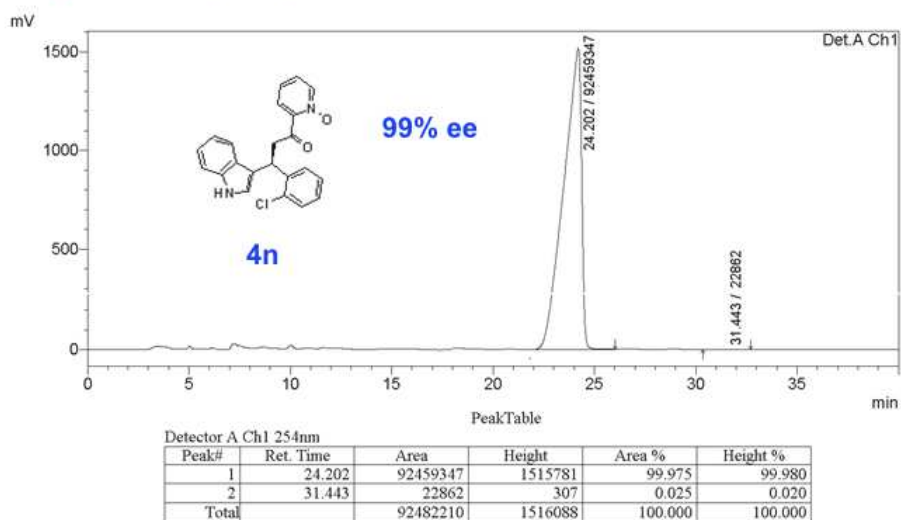
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.600	846510	17055	3.795	4.436
2	20.192	21459581	367406	96.205	95.564
Total		22306091	384461	100.000	100.000

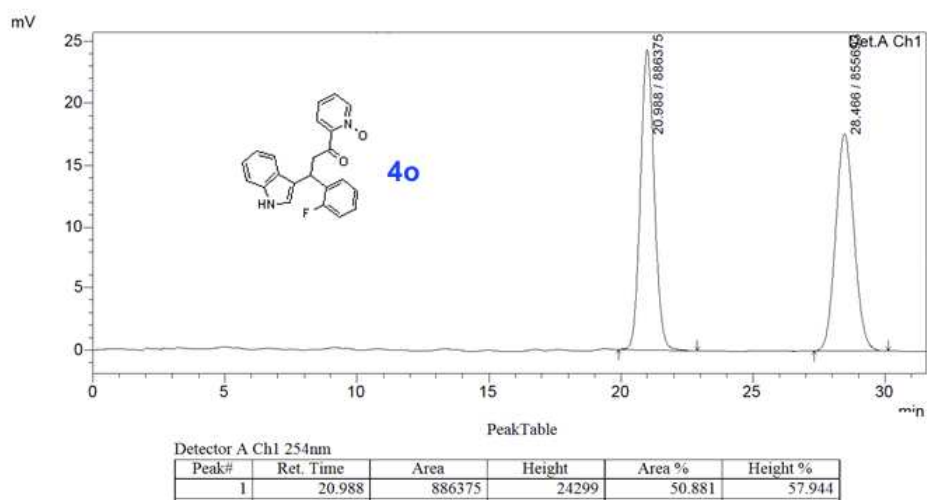
Hplc chromatogra of 4n (racemic)



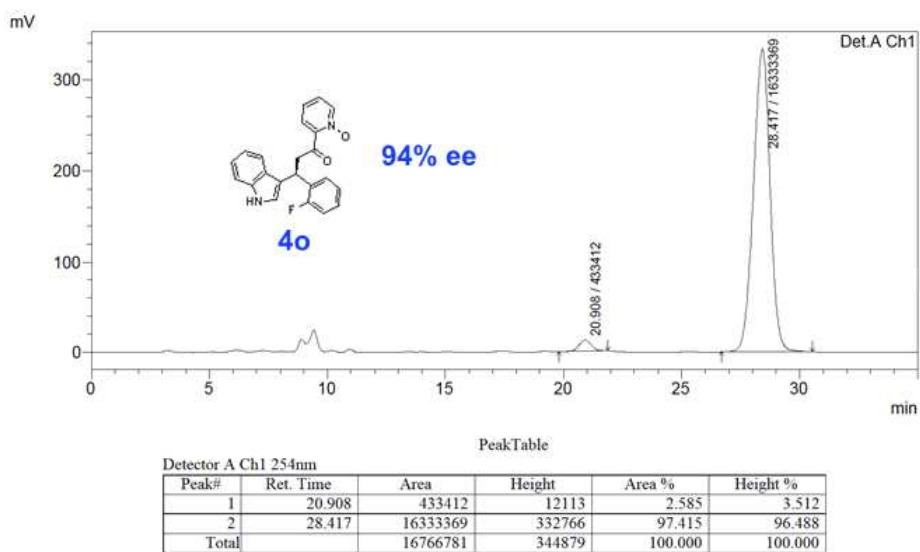
Hplc chromatogram of 4n (chiral)



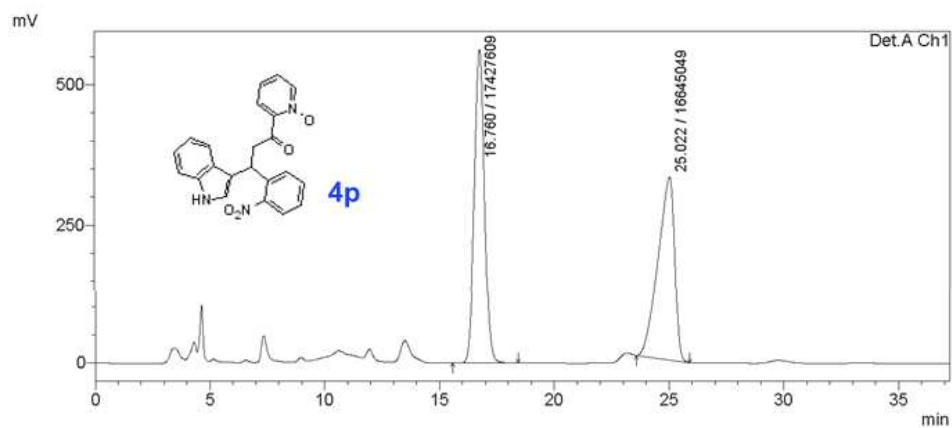
Hplc chromatogram of 4o (racemic)



Hplc chromatogram of 4o (chiral)



Hplc chromatogram of 4p (racemic)

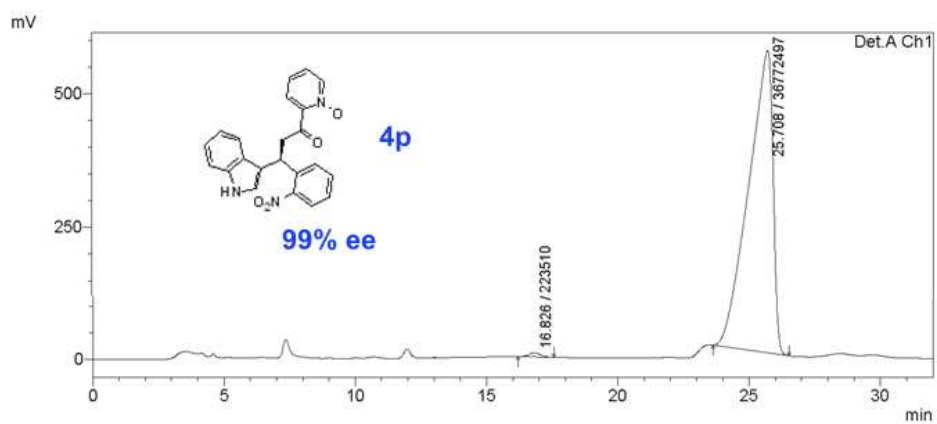


Detector A Ch1 254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.760	17427609	563841	51.148	63.064
2	25.022	16645049	330230	48.852	36.936
Total		34072658	894071	100.000	100.000

Hplc chromatogram of 4p (chiral)

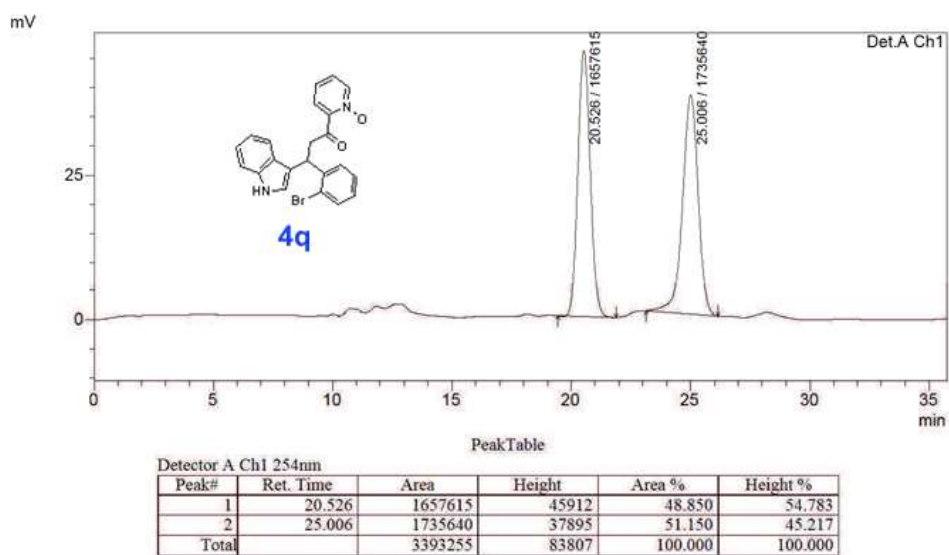


Detector A Ch1 254nm

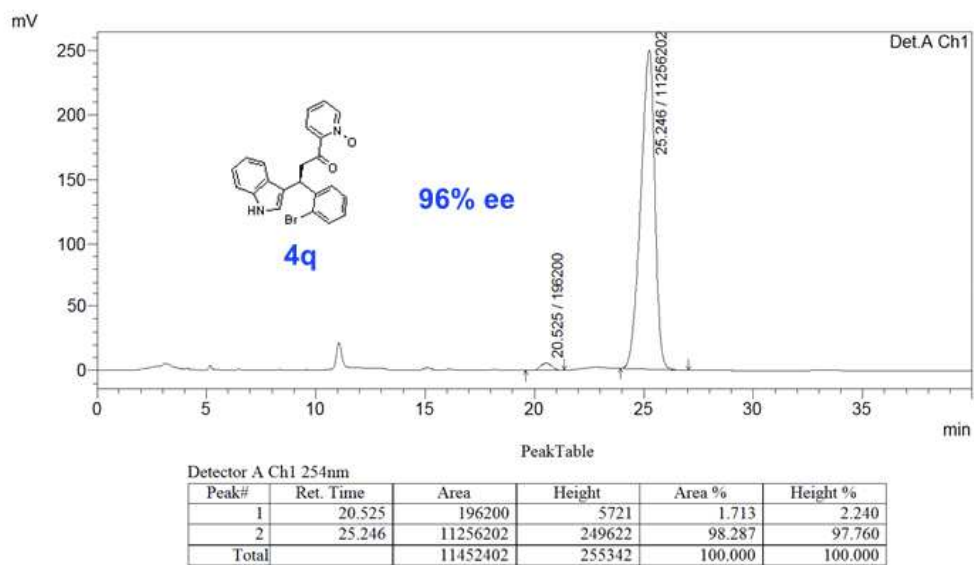
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.826	223510	7386	0.604	1.278
2	25.708	36772497	570453	99.396	98.722
Total		36996007	577839	100.000	100.000

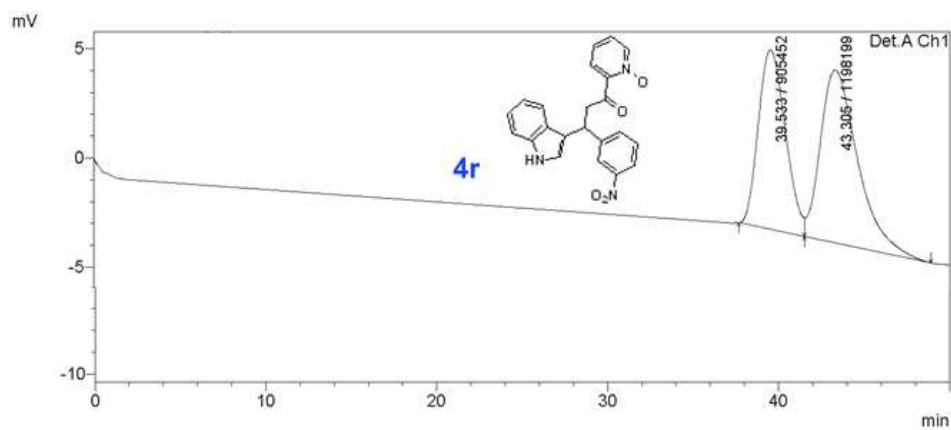
Hplc chromatogram of 4q (racemic)



Hplc chromatogram of 4q (chiral)



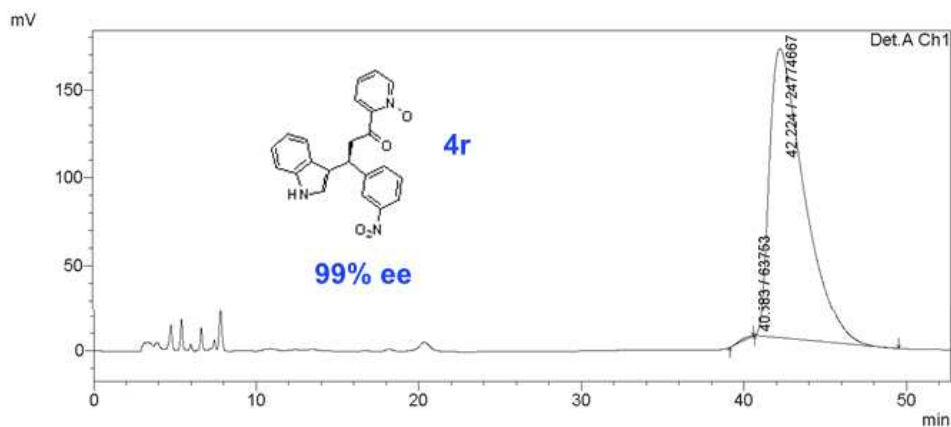
Hplc chromatogram of 4r (racemic)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.533	905452	8223	43.042	50.918
2	43.305	1198199	7927	56.958	49.082
Total		2103650	16150	100.000	100.000

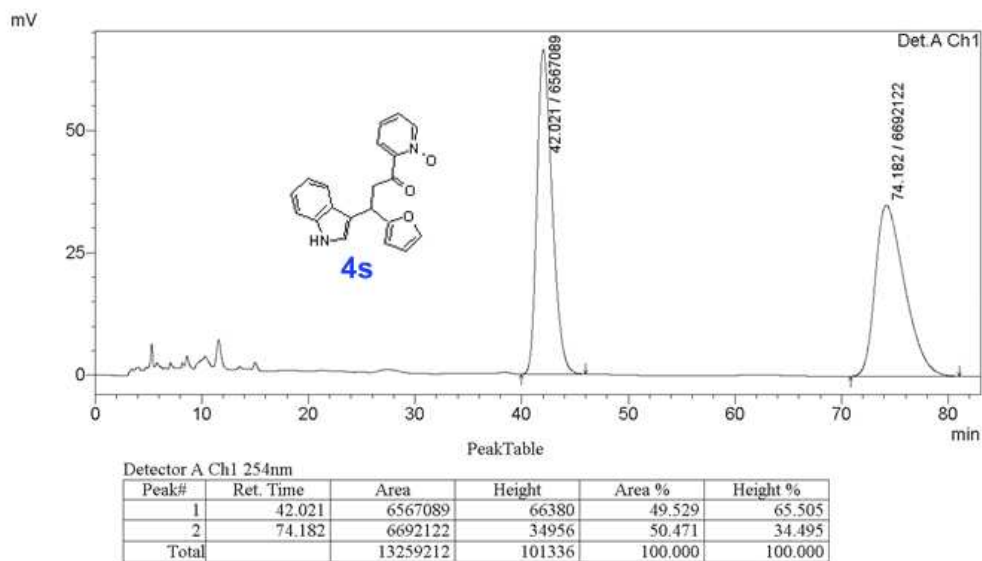
Hplc chromatogram of 4r (chiral)



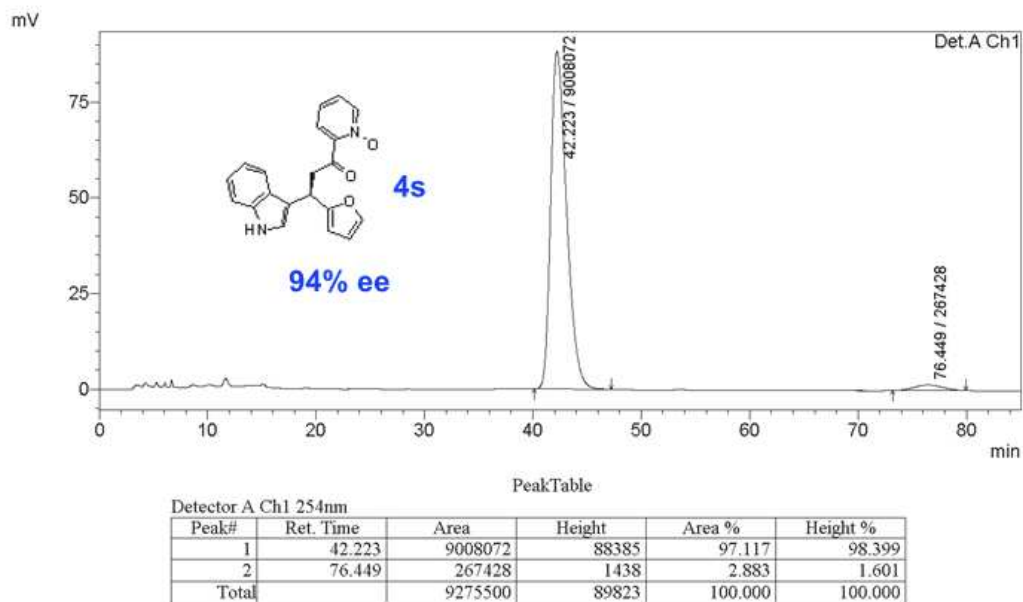
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.583	63753	19	0.257	0.011
2	42.224	24774667	165929	99.743	99.989
Total		24838420	165948	100.000	100.000

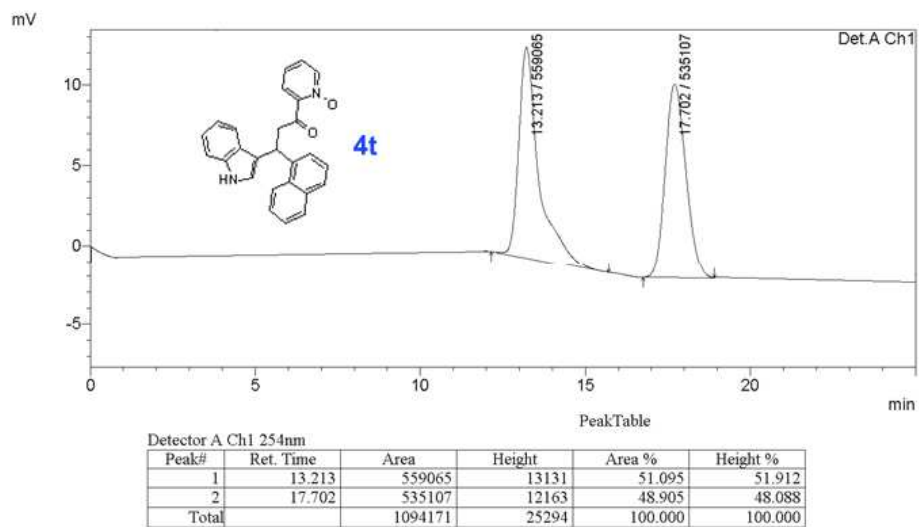
Hplc chromatogram of 4s (racemic)



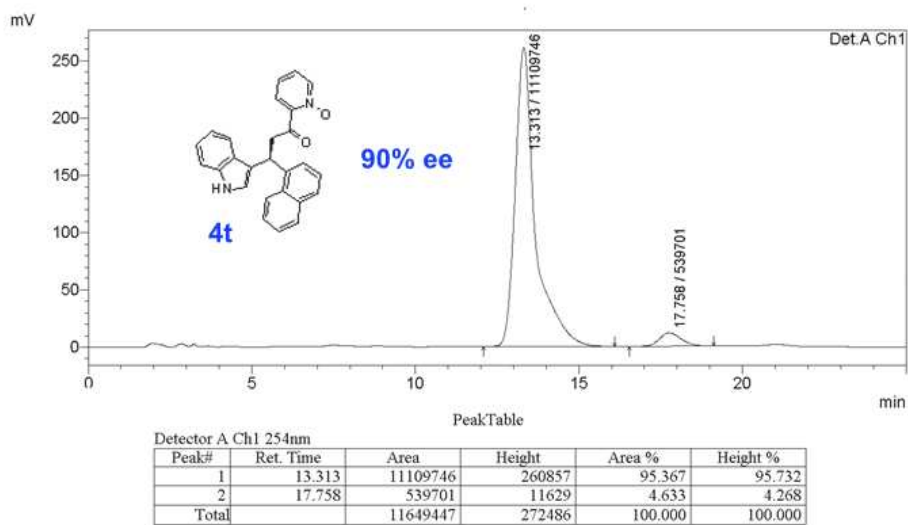
Hplc chromatogram of 4s (chiral)



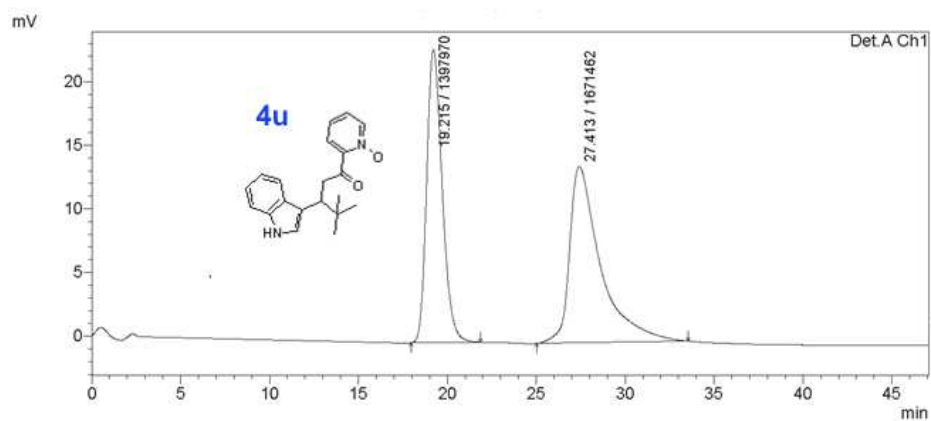
Hplc chromatogram of 4t (racemic)



Hplc chromatogram of 4t (chiral)



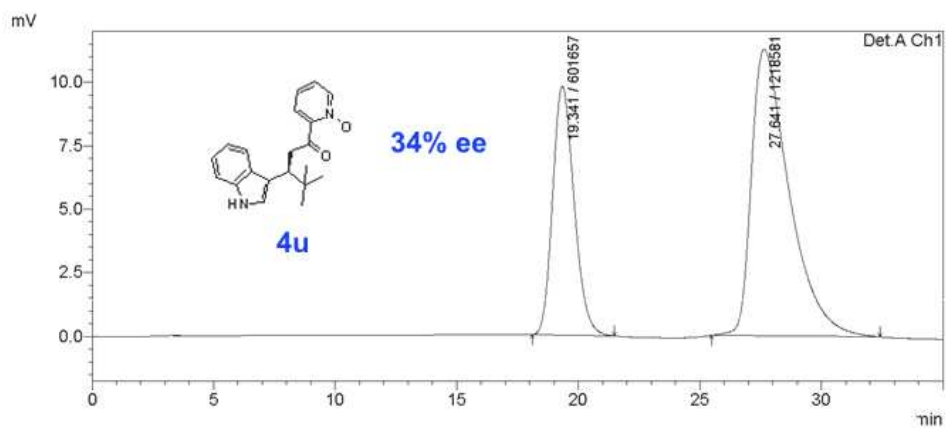
Hplc chromatogram of 4u (racemic)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.215	1397970	23063	45.545	62.469
2	27.413	1671462	13856	54.455	37.531
Total		3069432	36919	100.000	100.000

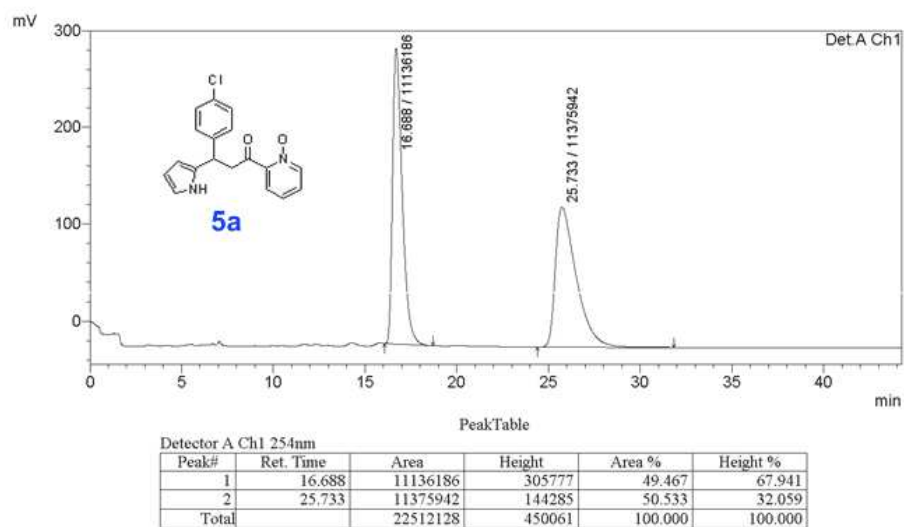
Hplc chromatogram of 4u (chiral)



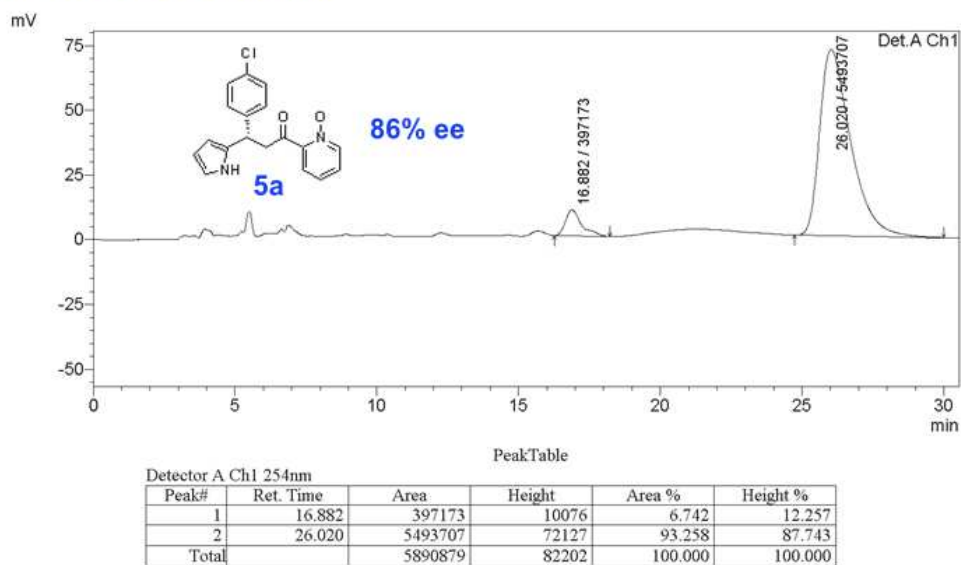
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.341	601657	9786	33.054	46.463
2	27.641	1218581	11276	66.946	53.537
Total		1820238	21062	100.000	100.000

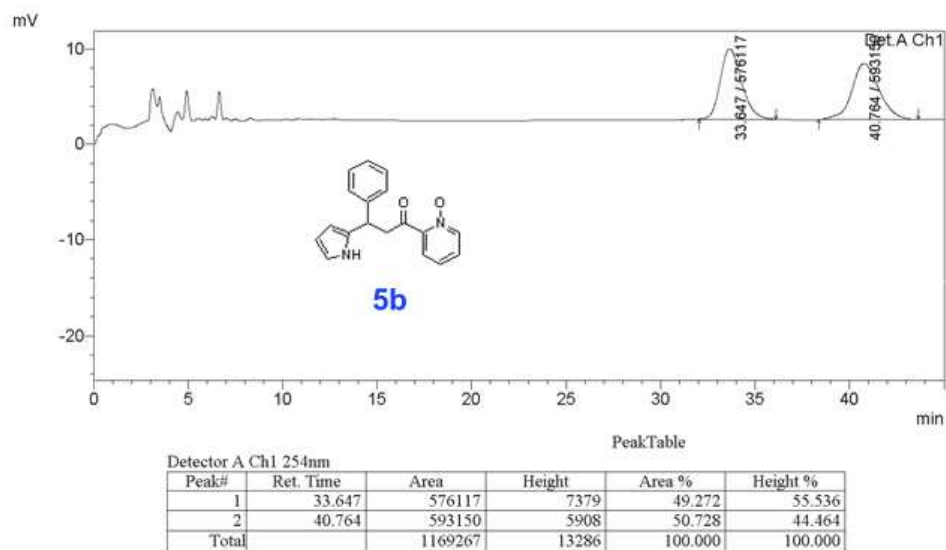
Hplc chromatogram of 5a (racemic)



Hplc chromatogram of 5a (chiral)



Hplc chromatogram of 5b (racemic)



Hplc chromatogram of 5b (chiral)

