

**Asymmetric Friedel-Crafts alkylation of indoles with  
3-nitro-2*H*-chromenes catalyzed by diphenylamine-linked  
bis(oxazoline) and bis(thiazoline) Zn(II) complexes**

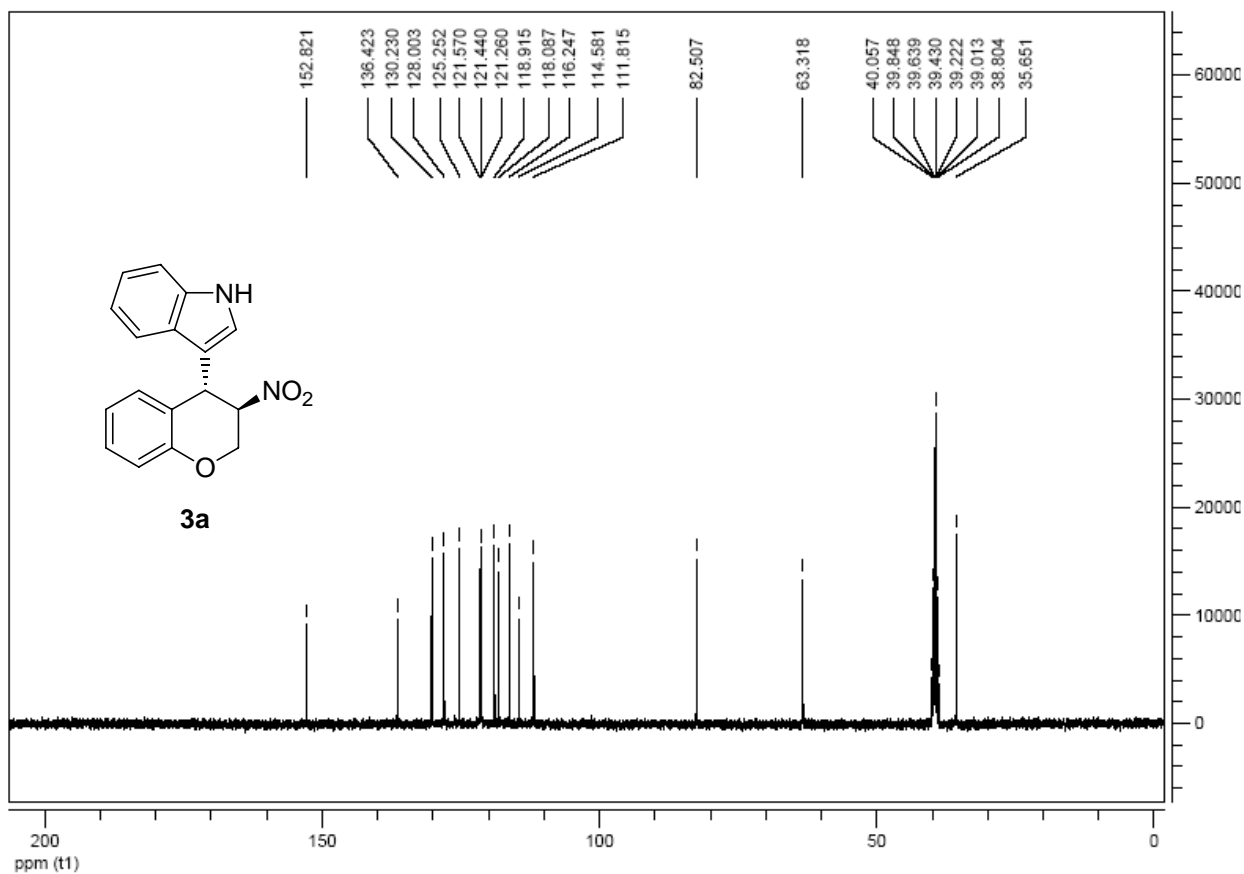
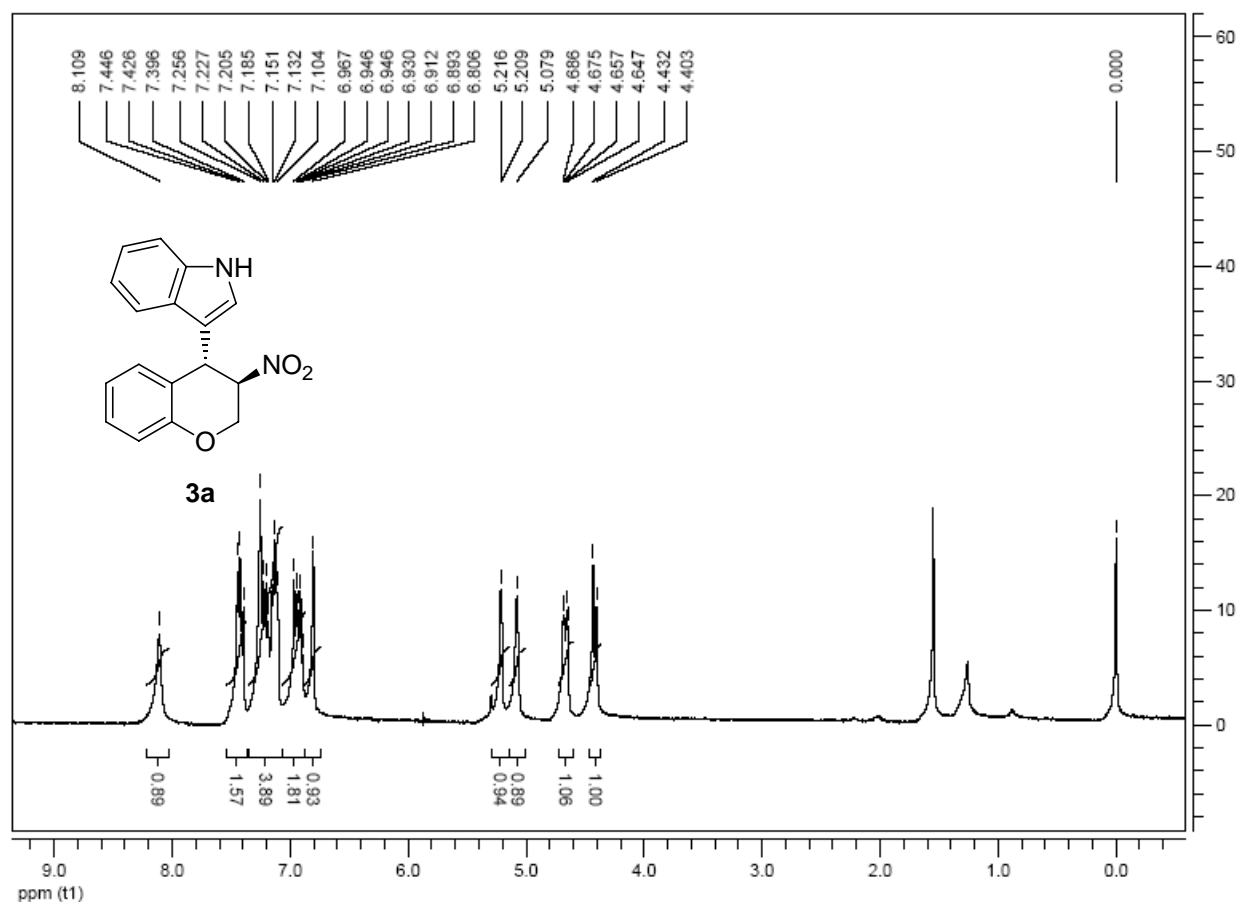
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Beijing 100081, People's Republic of China*  
[dudm@bit.edu.cn](mailto:dudm@bit.edu.cn)

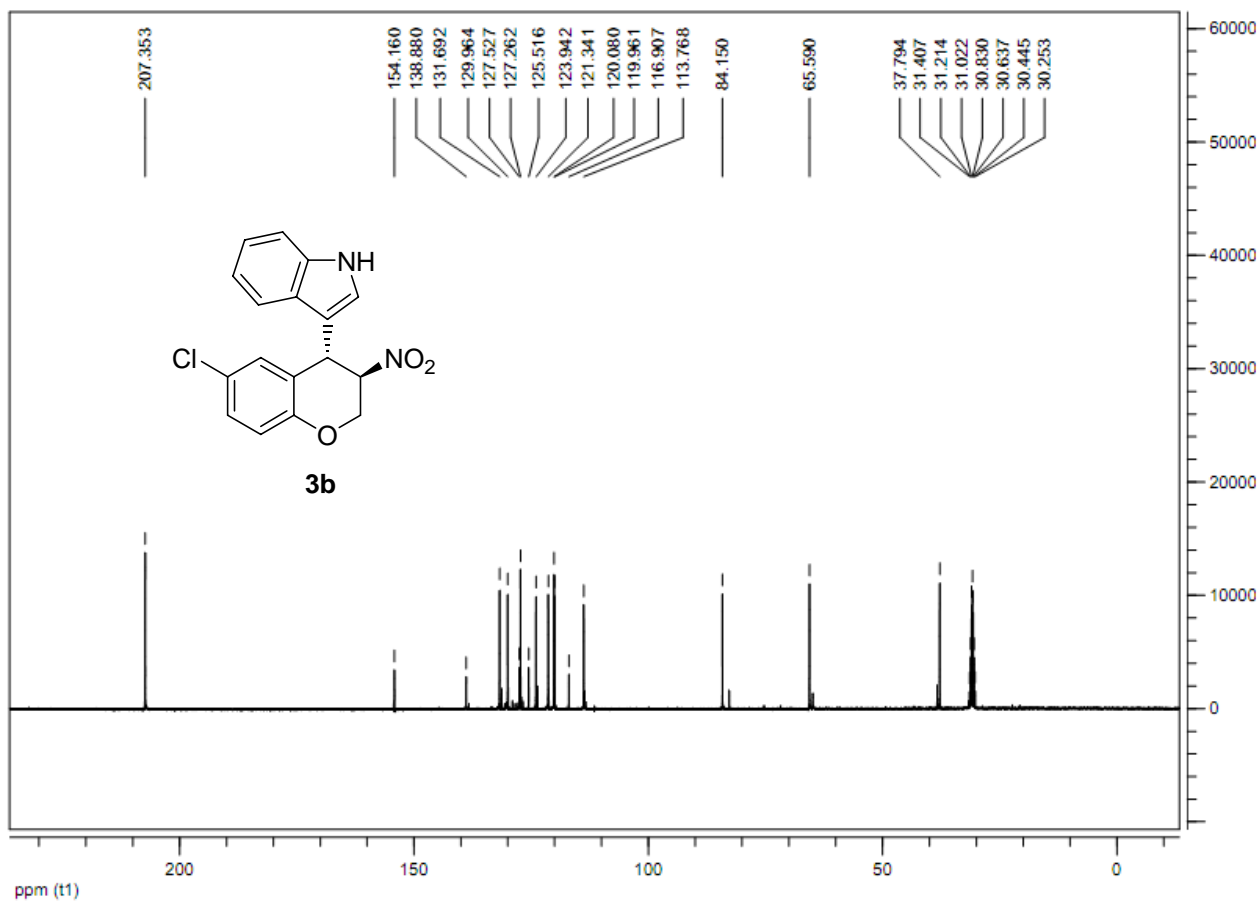
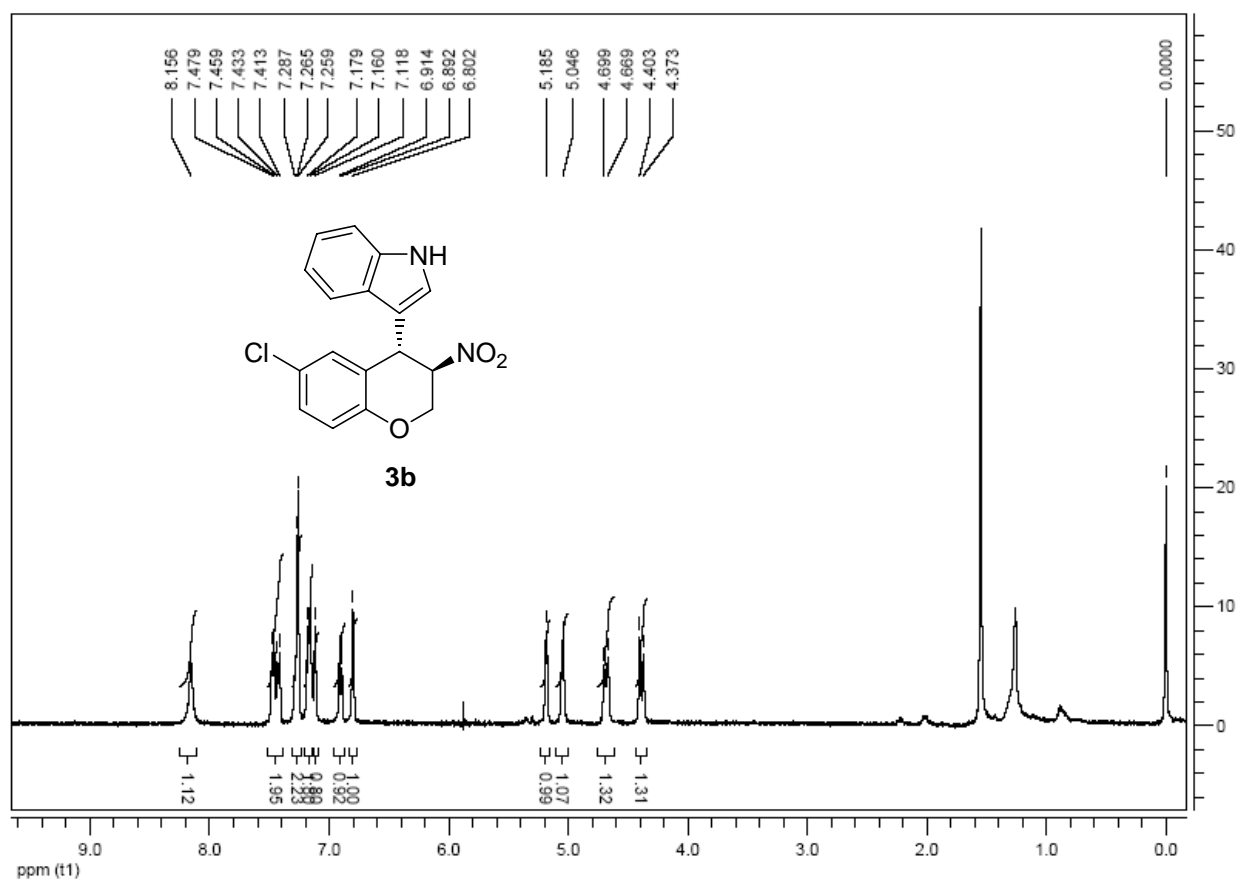
***Supporting Information***

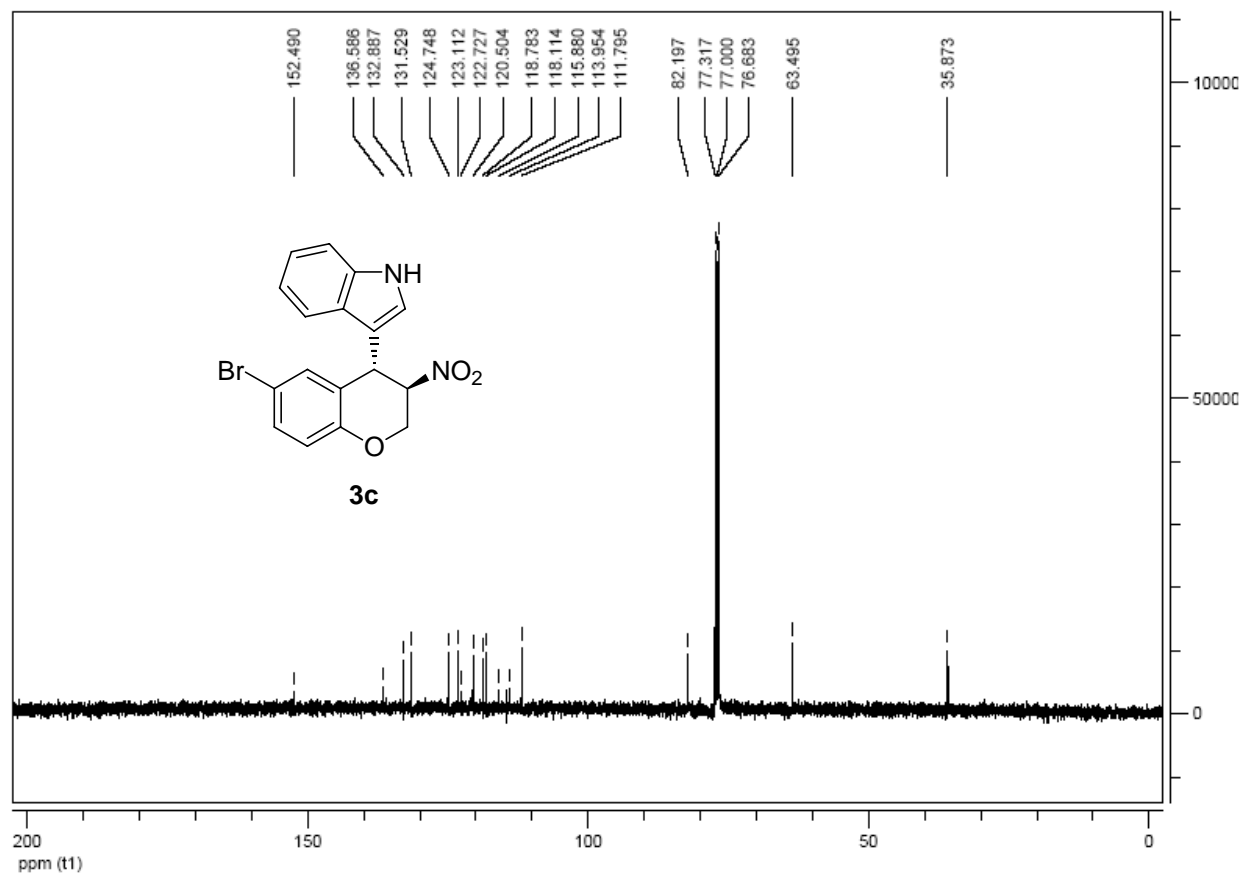
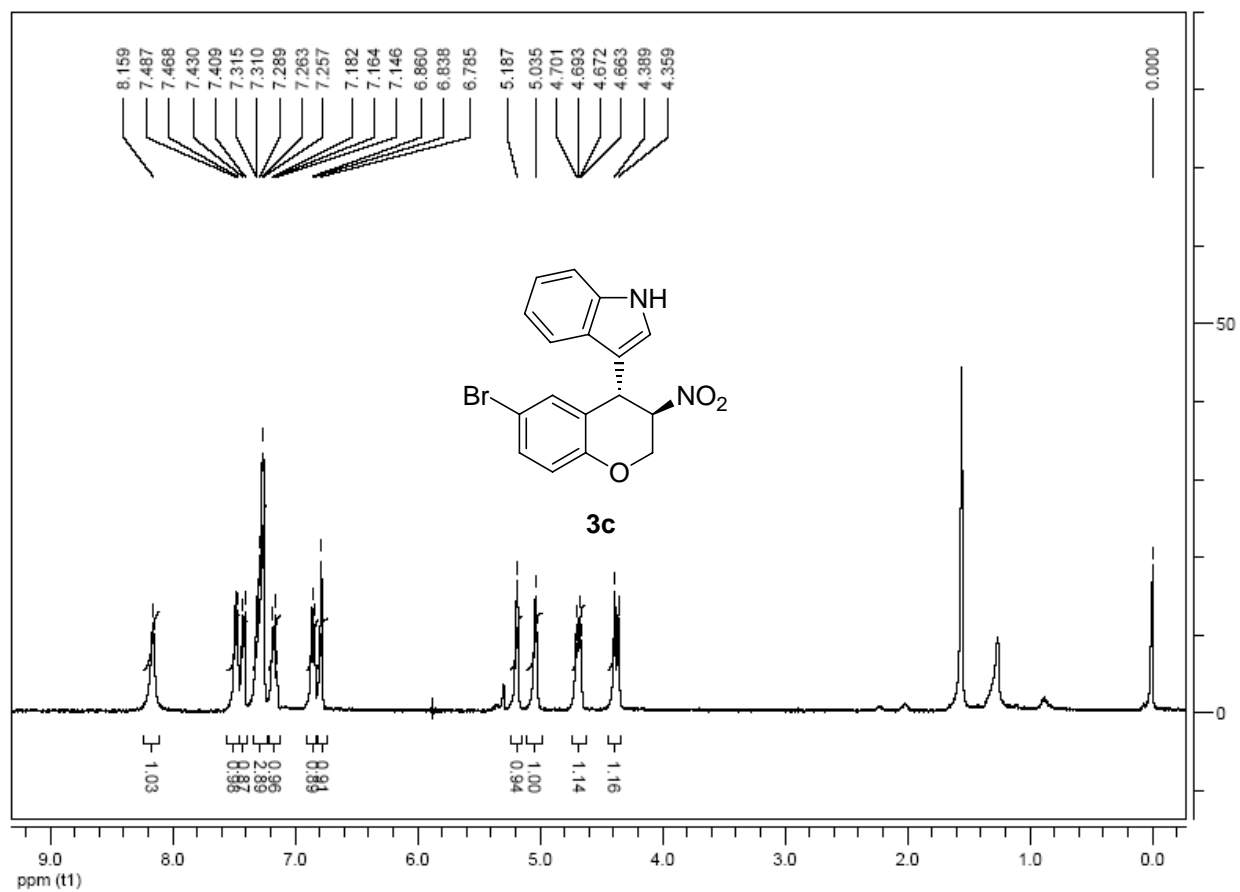
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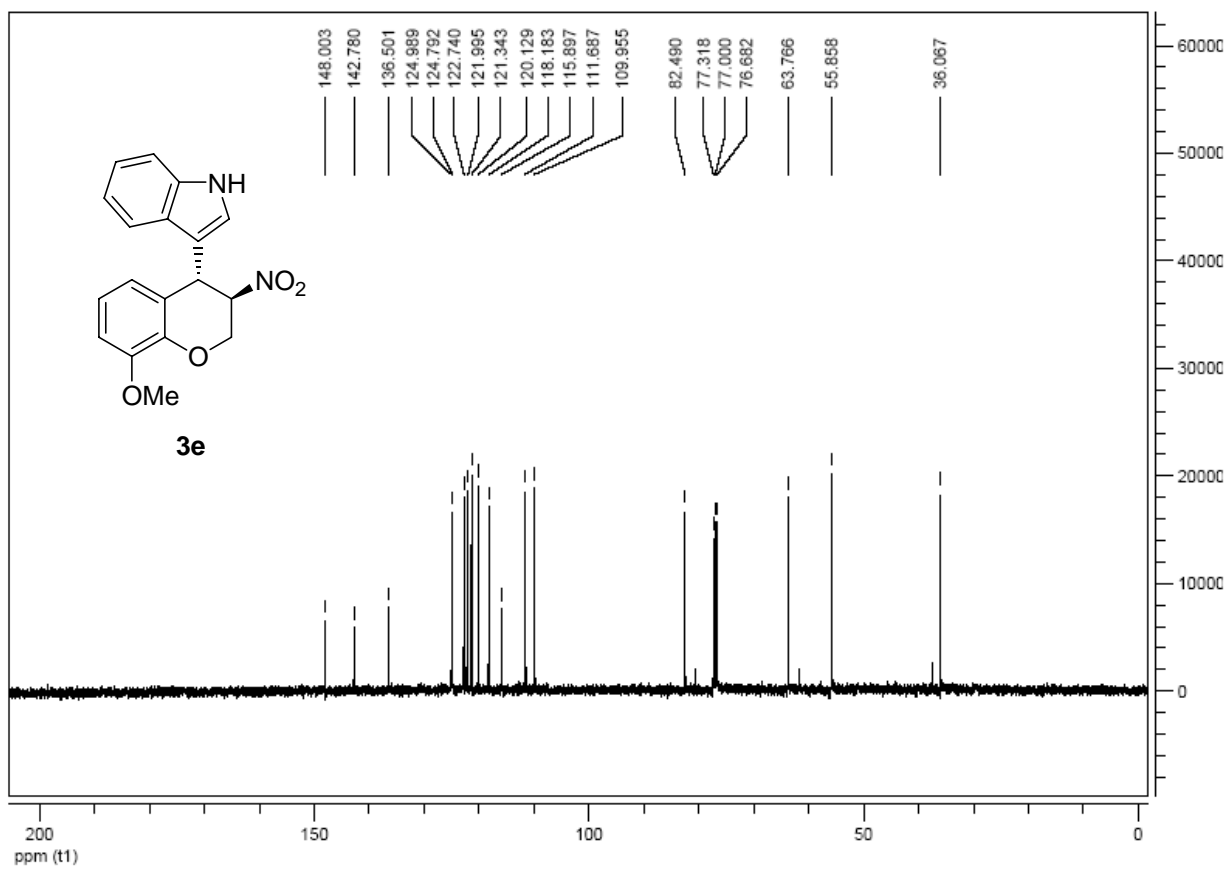
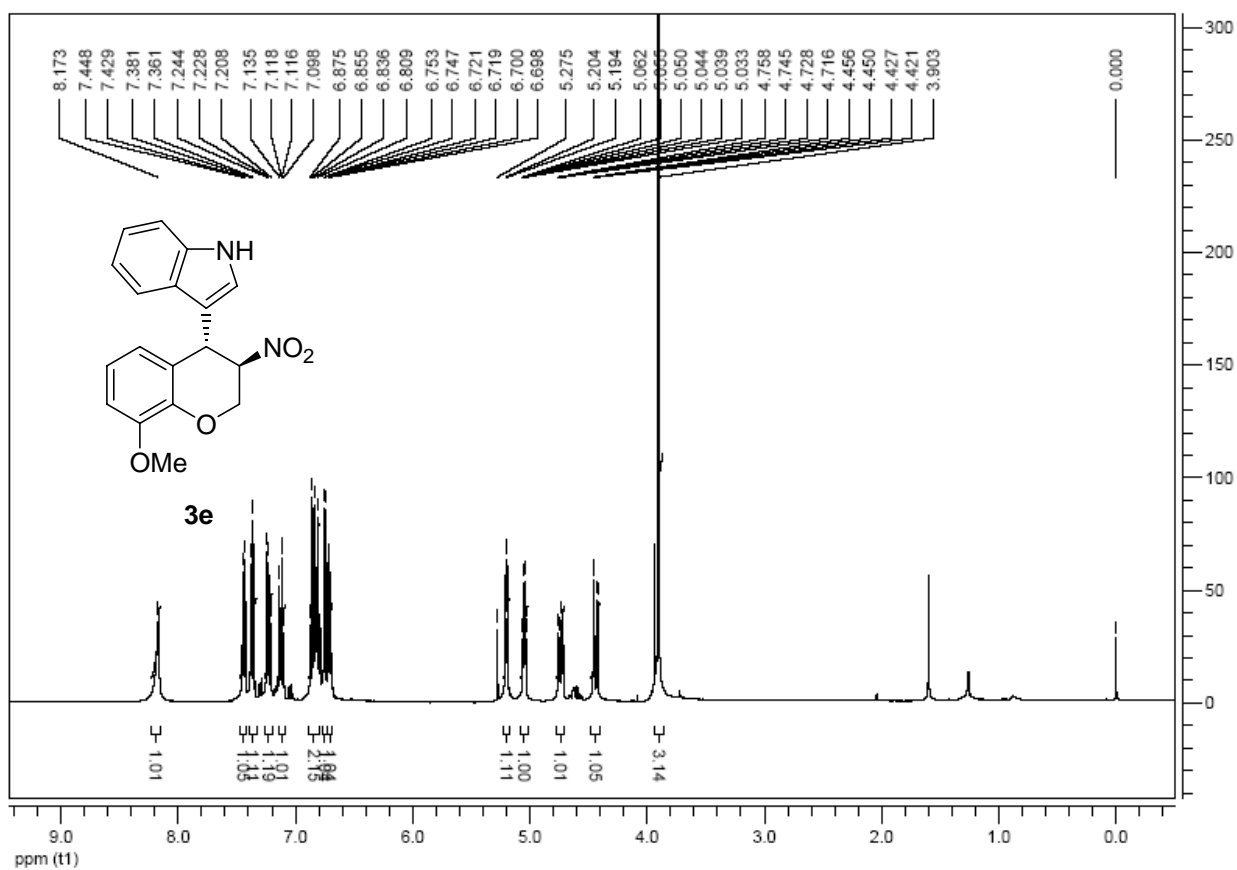
### Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new compounds

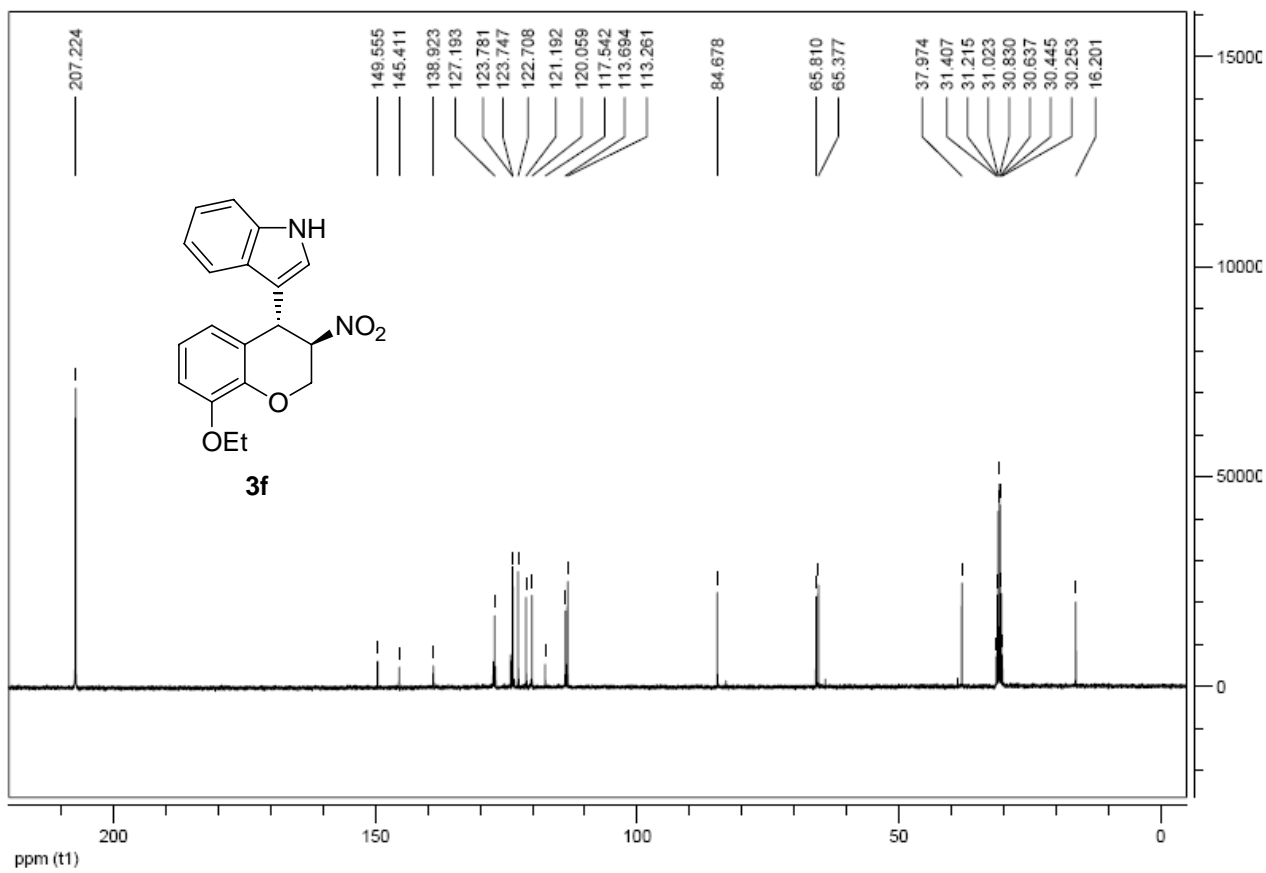
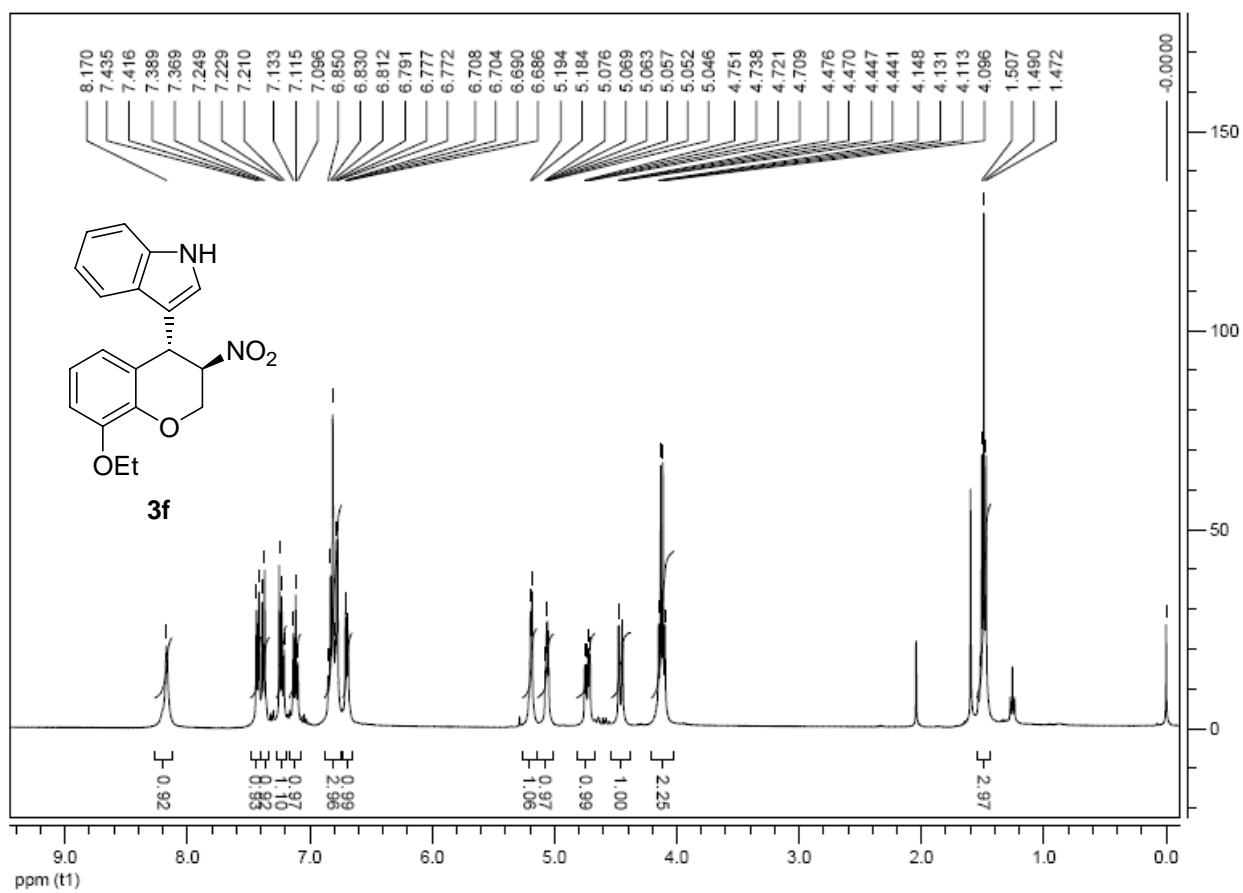


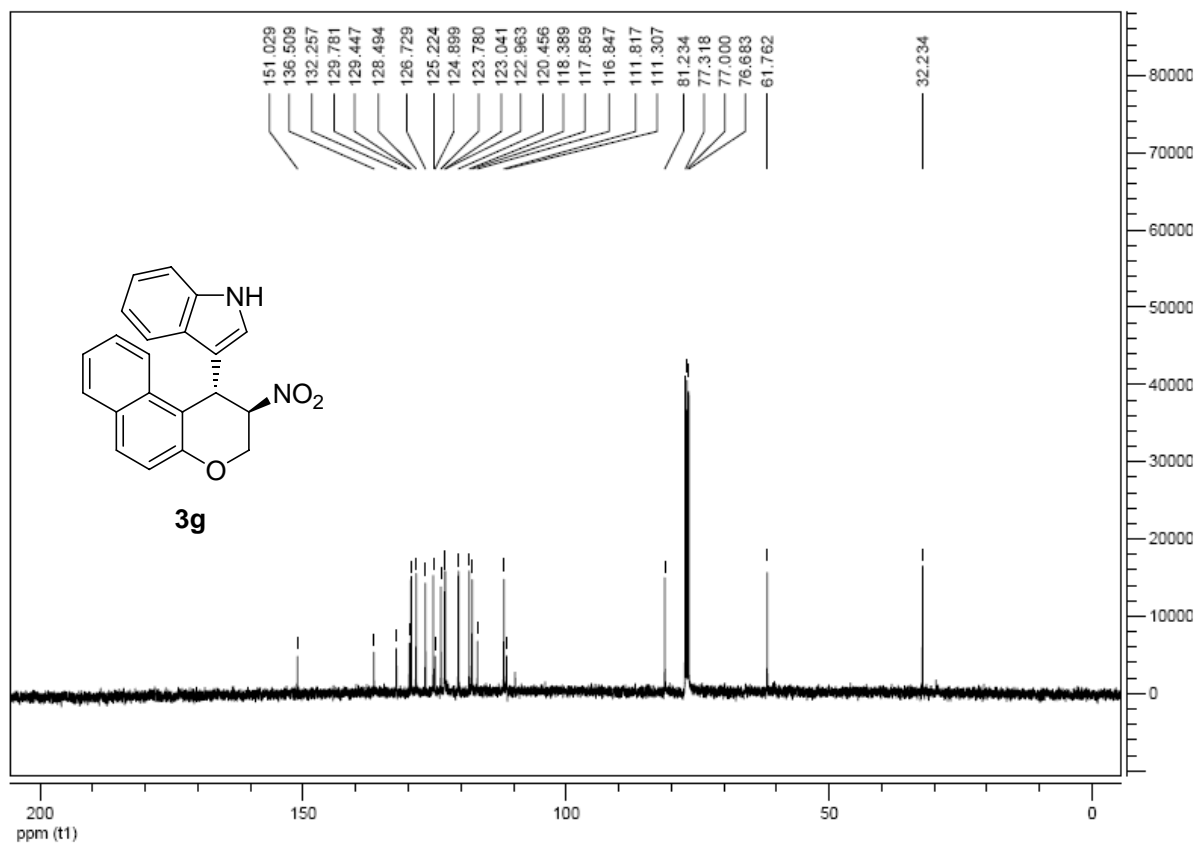
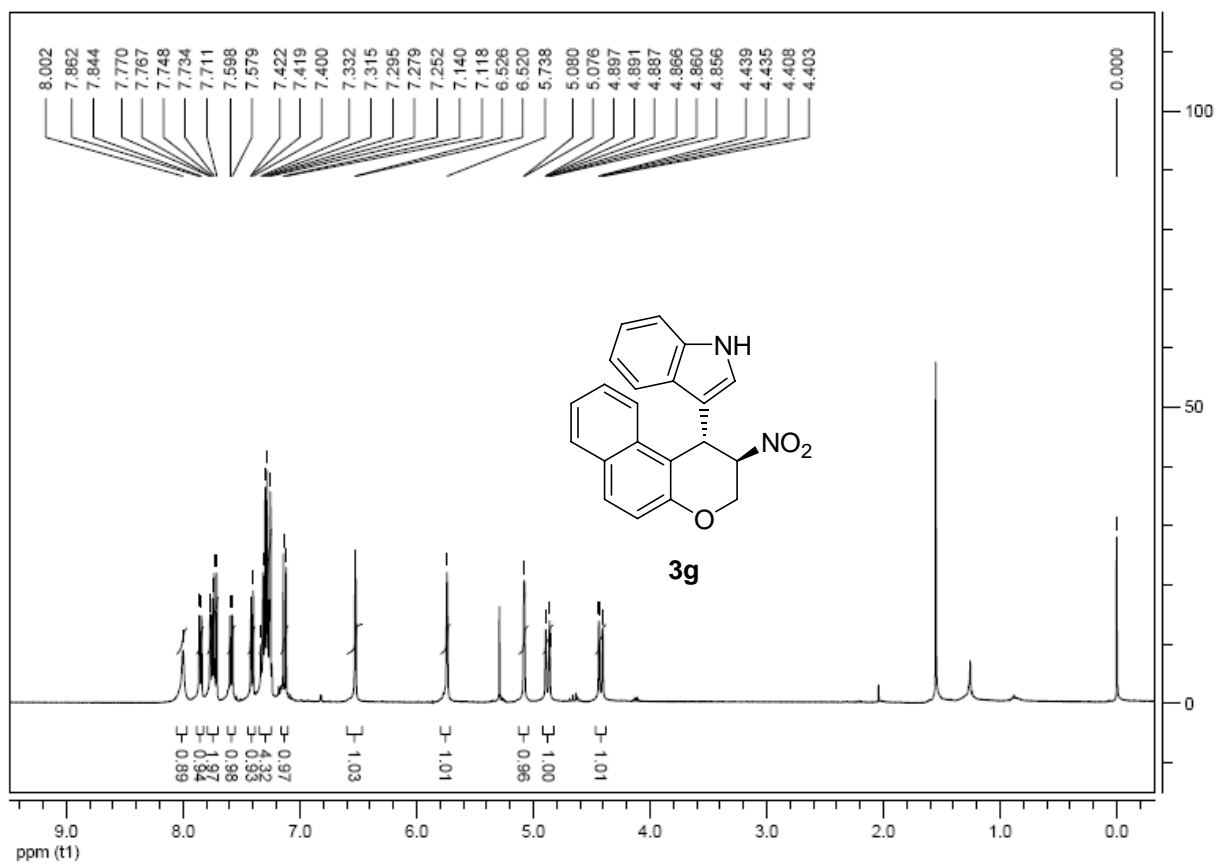




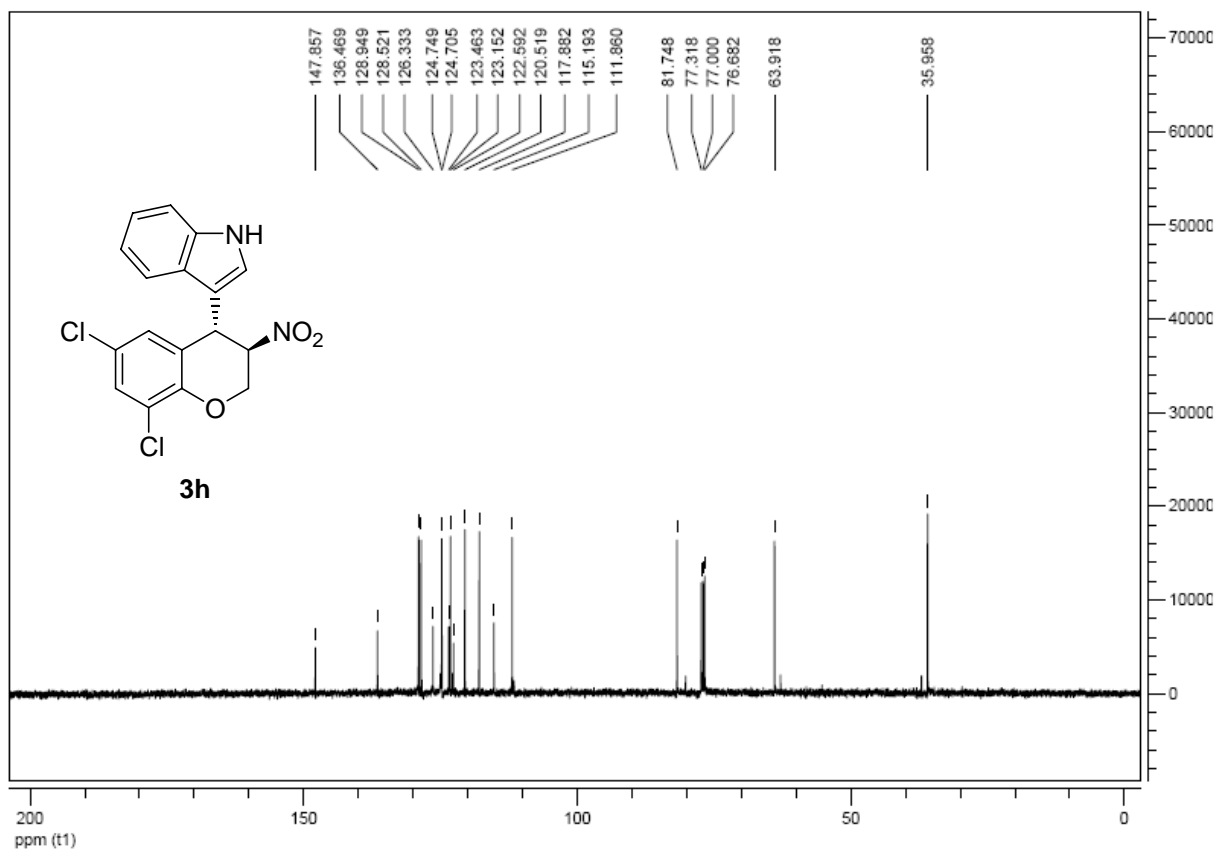
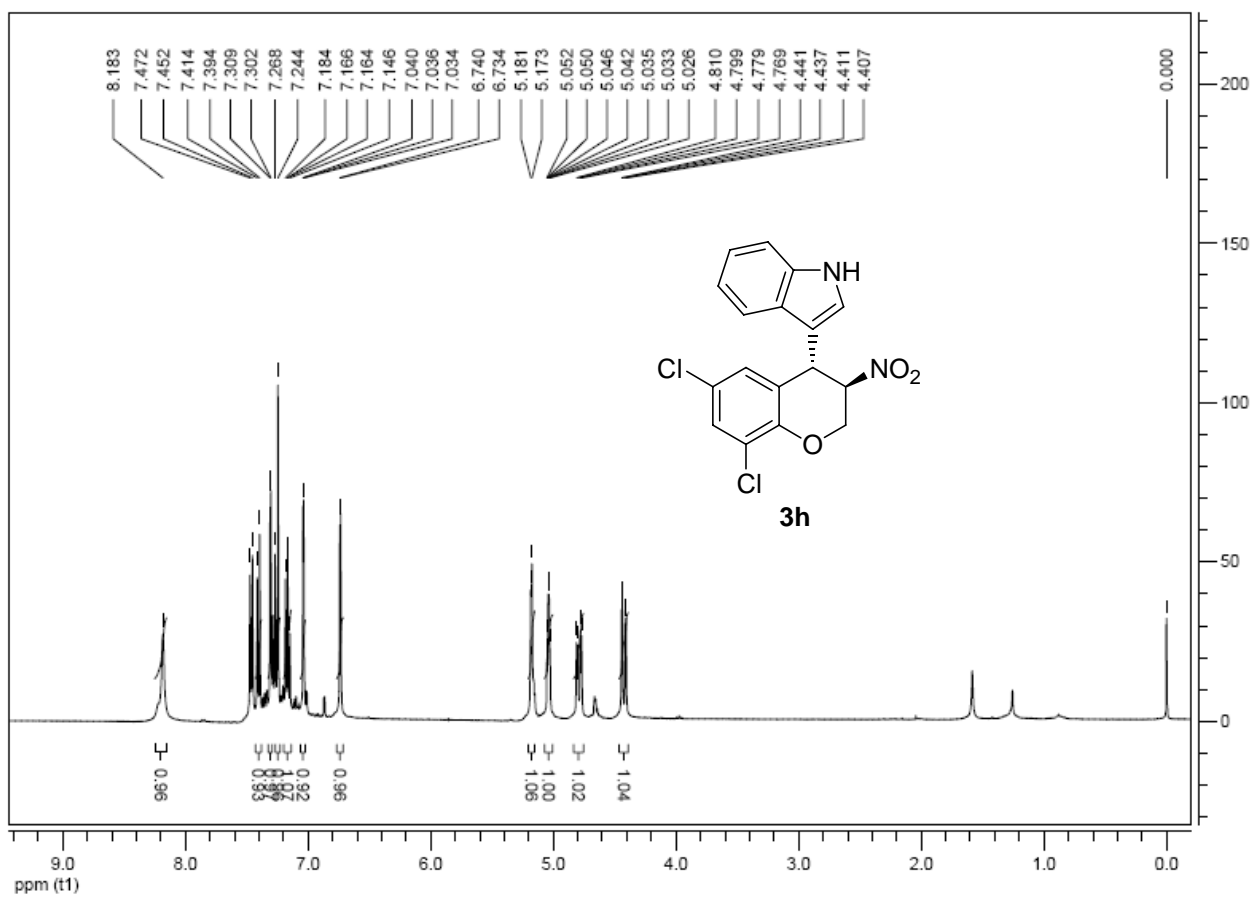


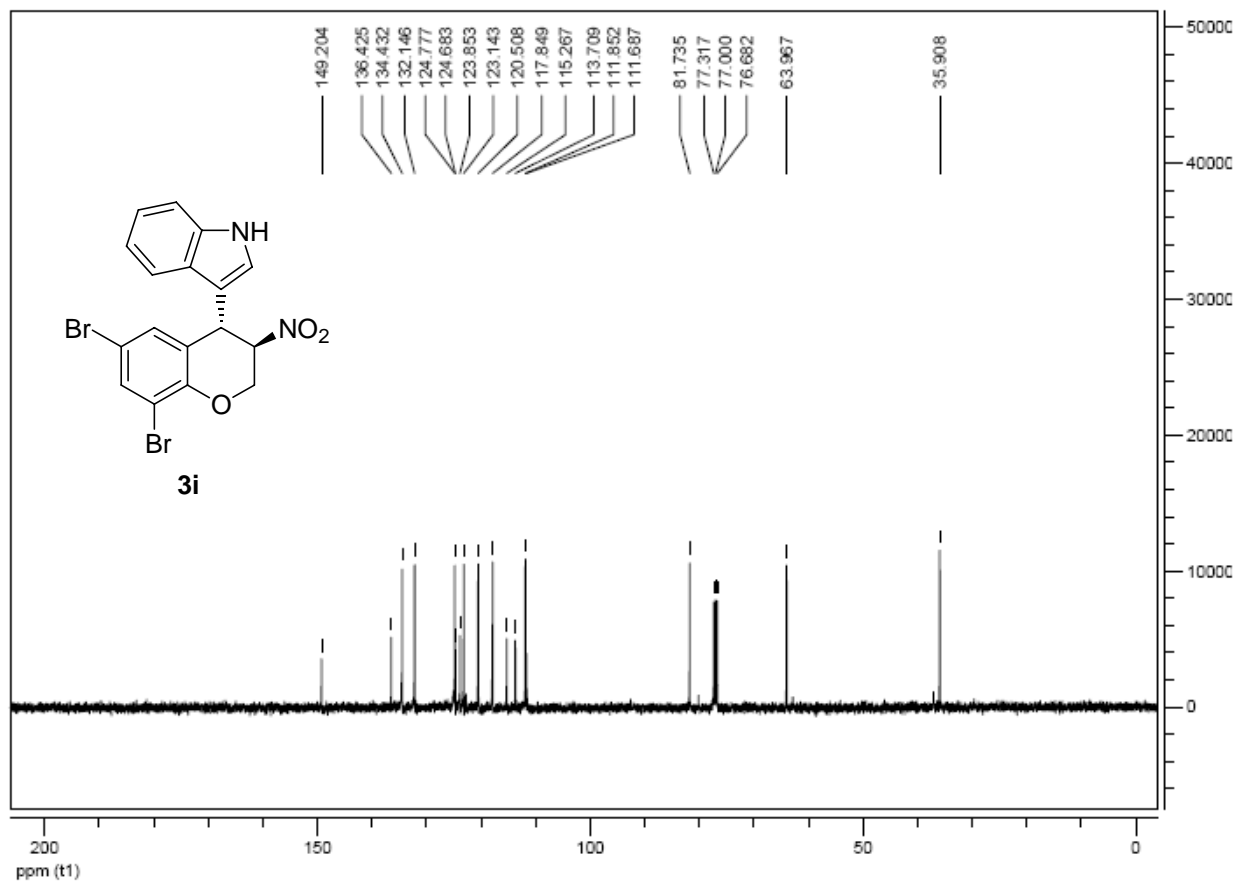
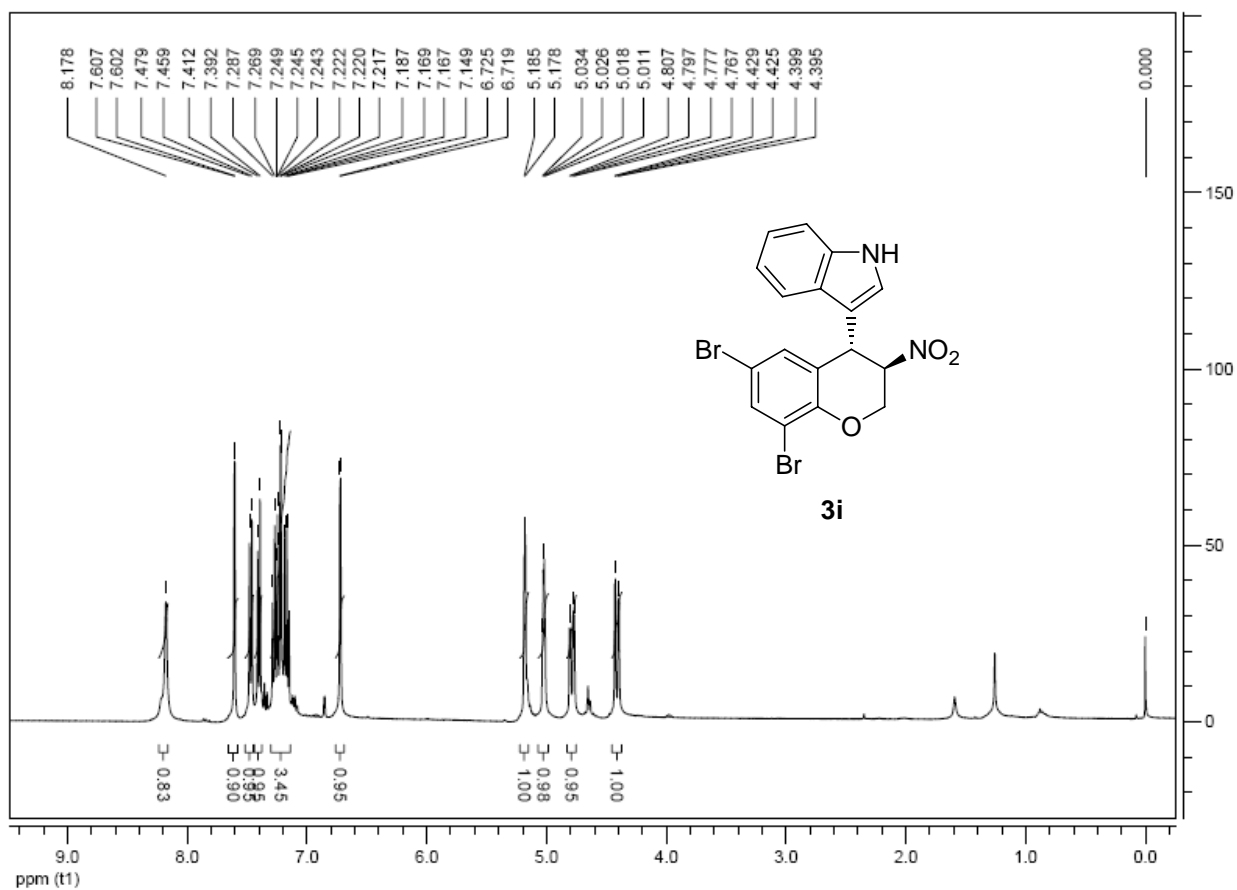


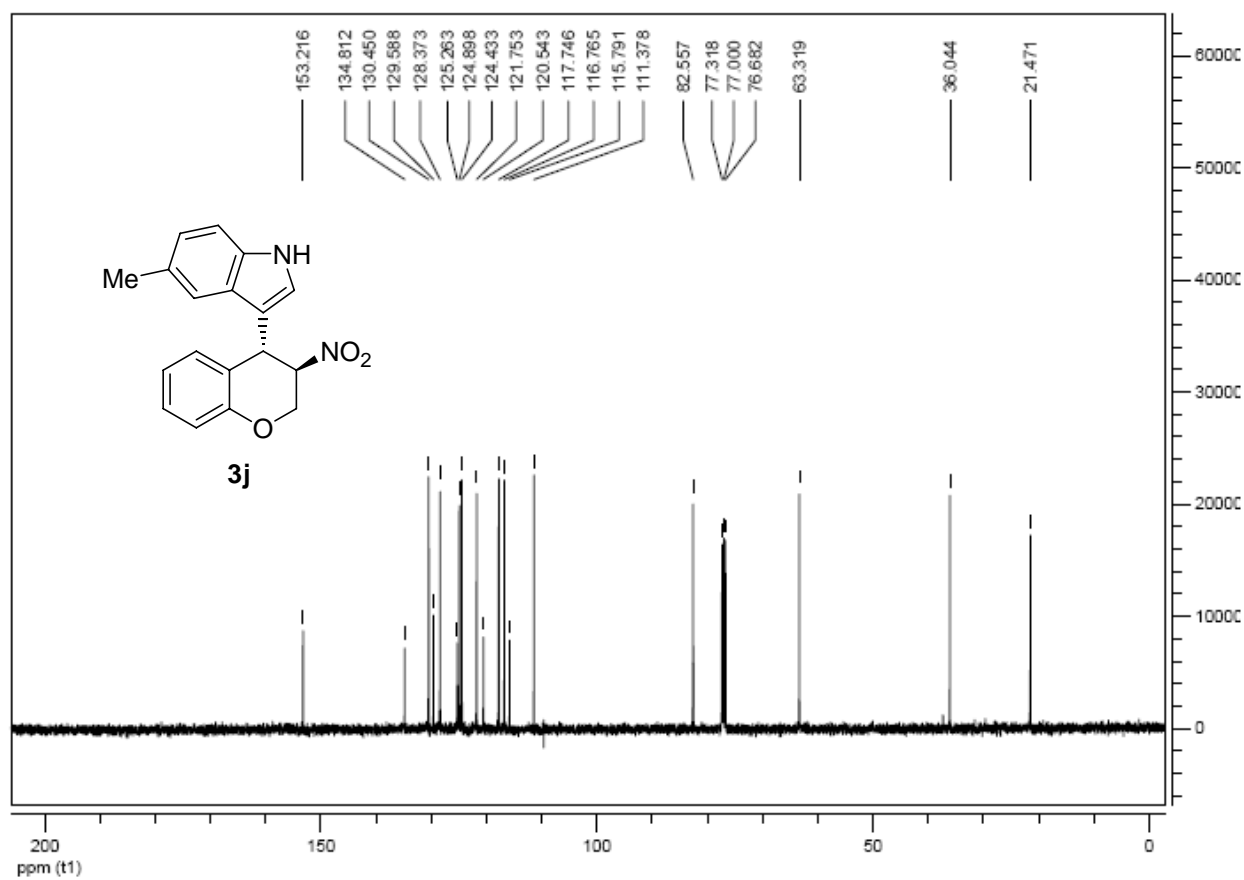
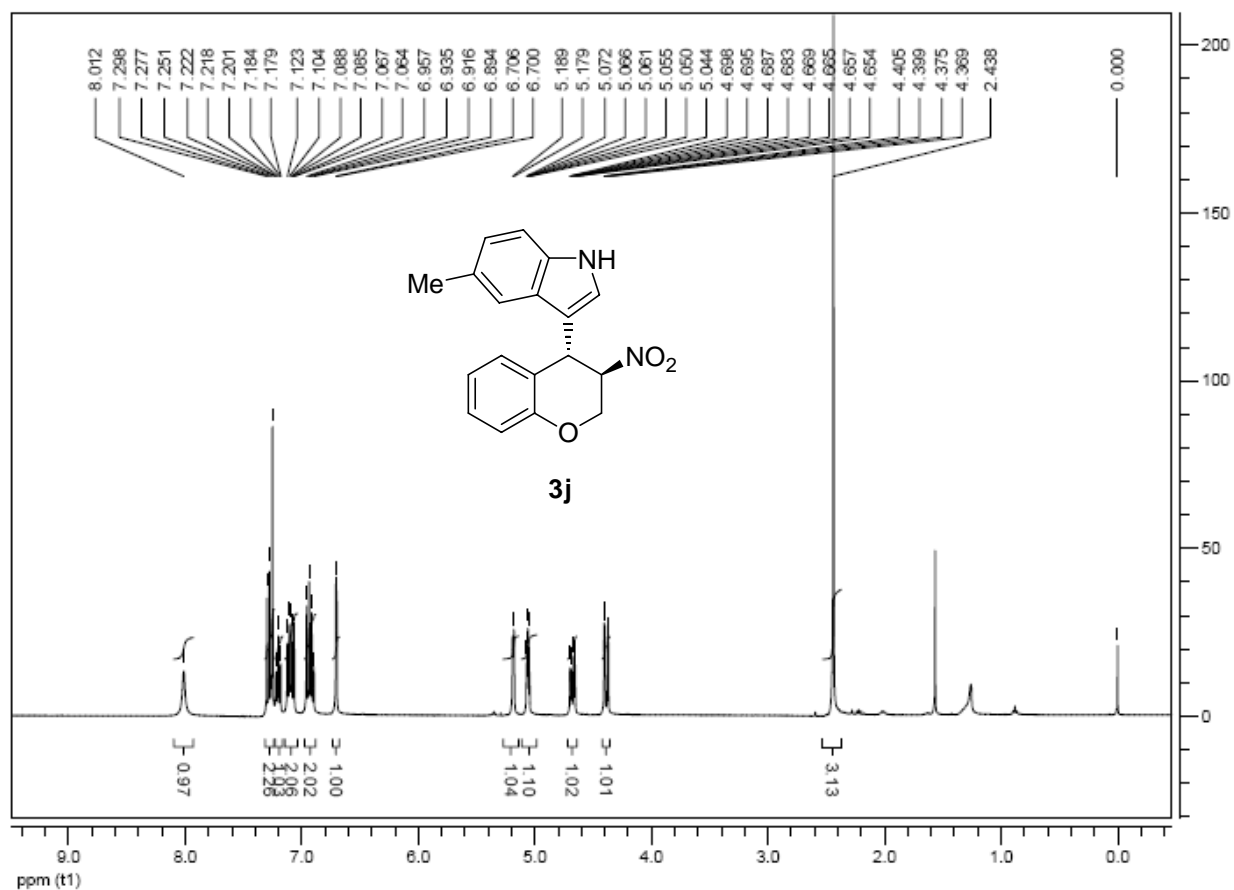


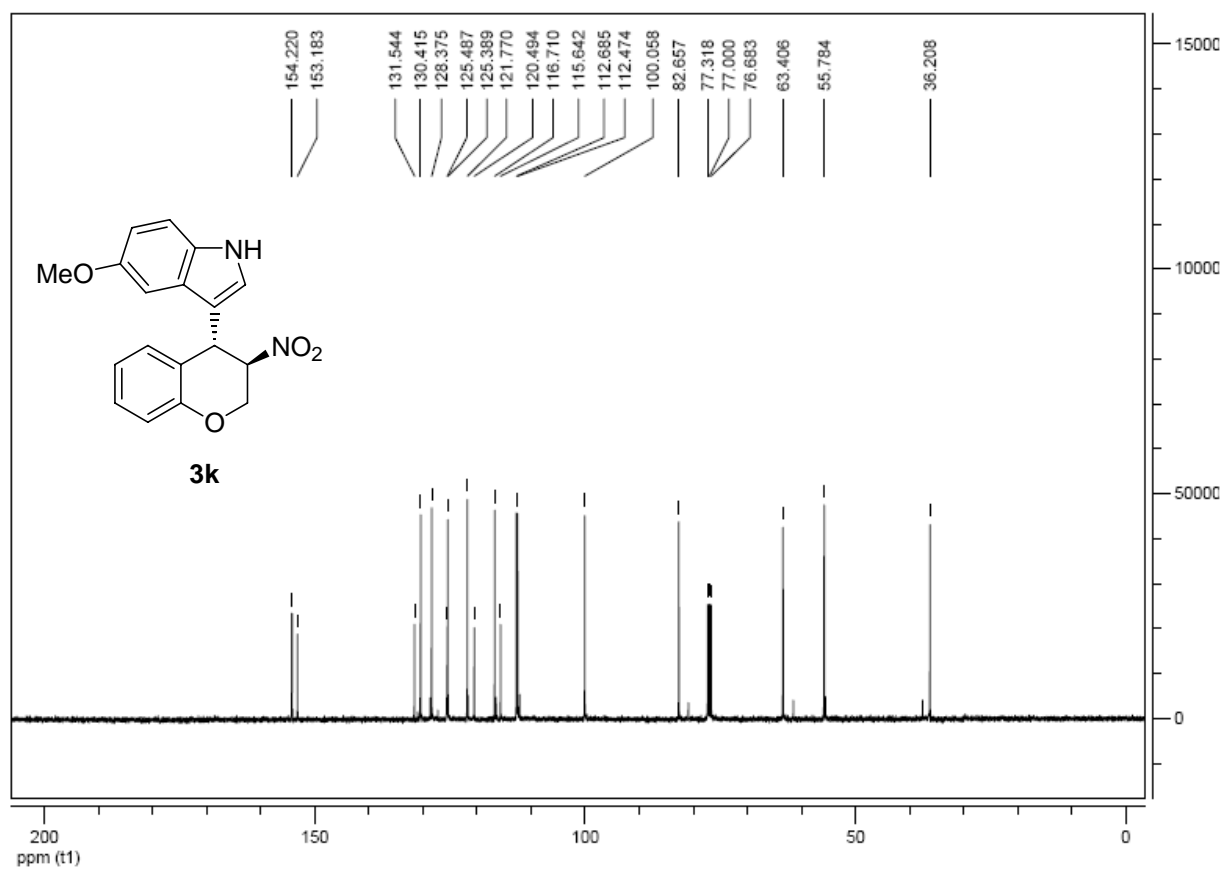
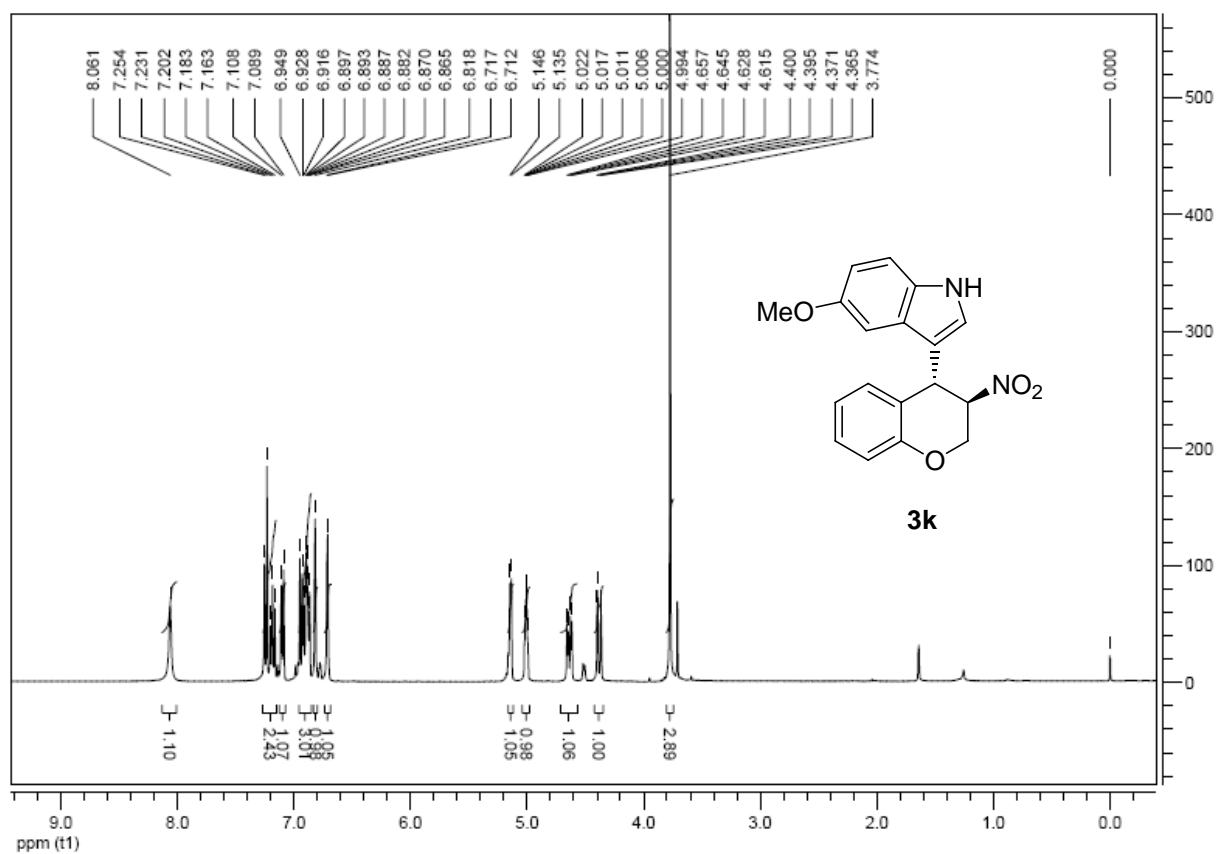


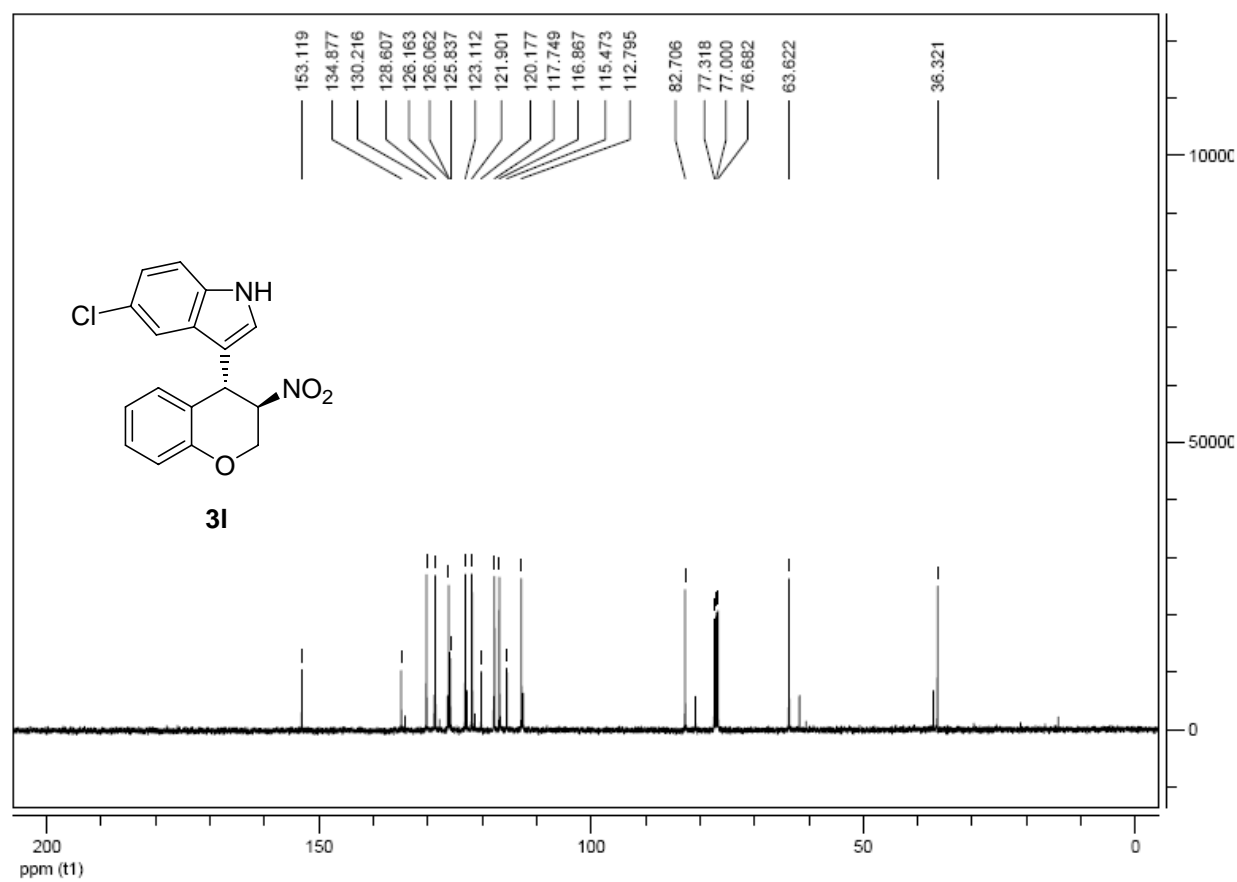
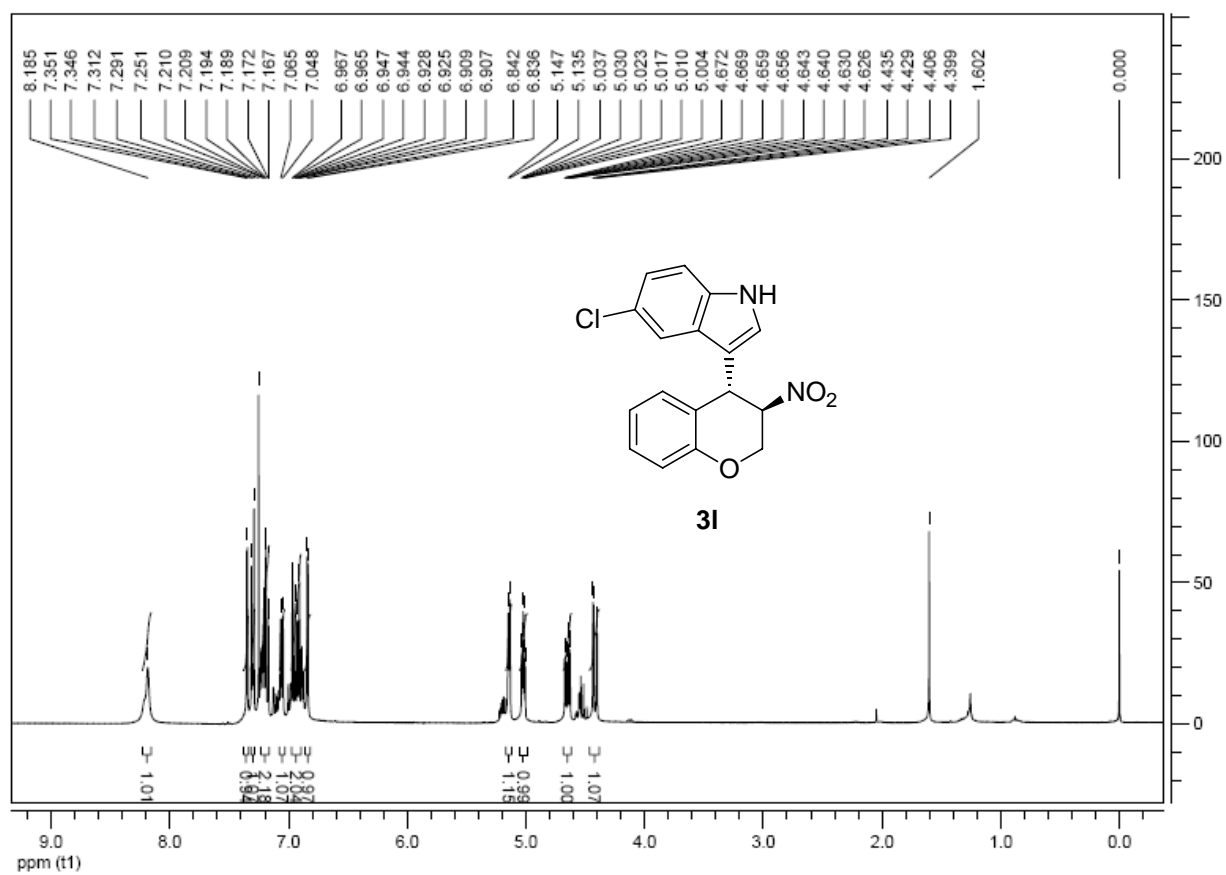


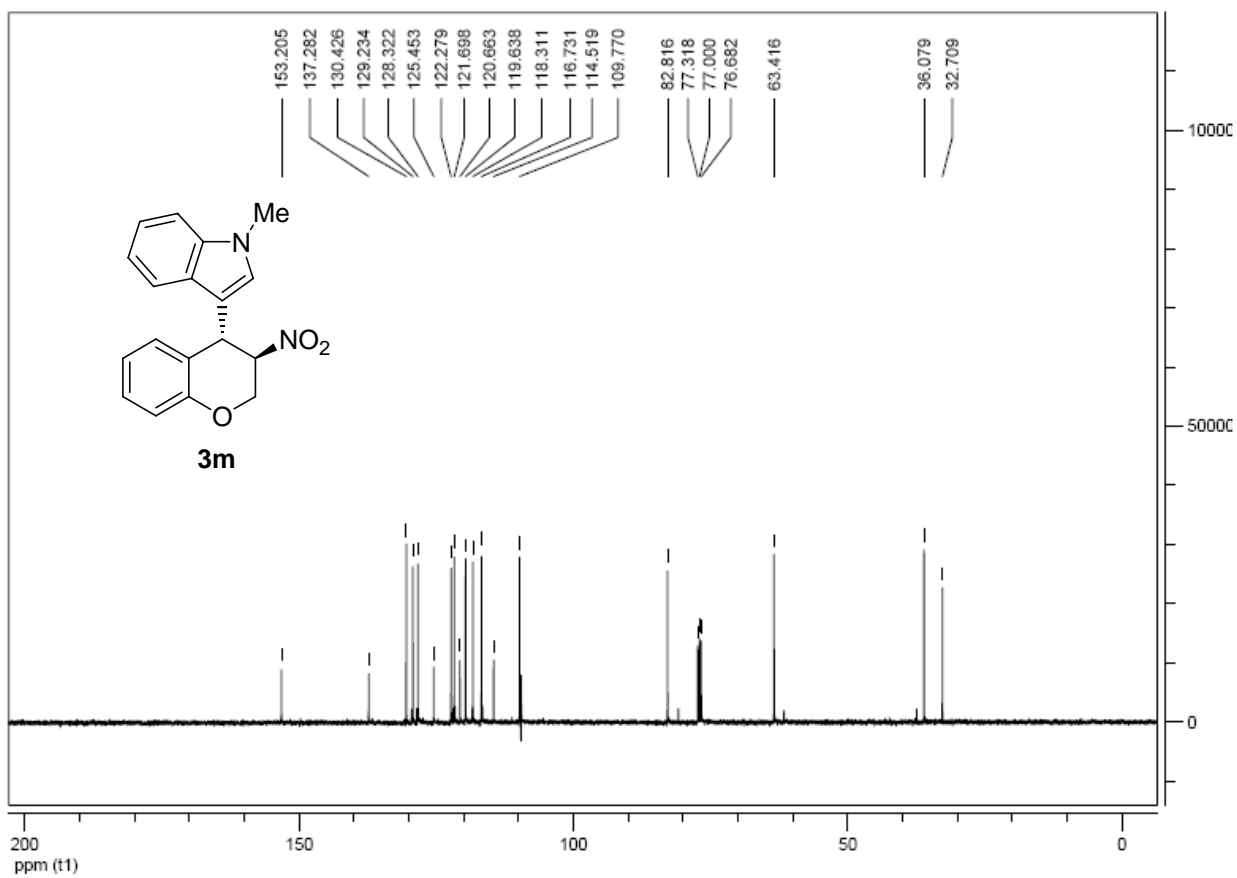
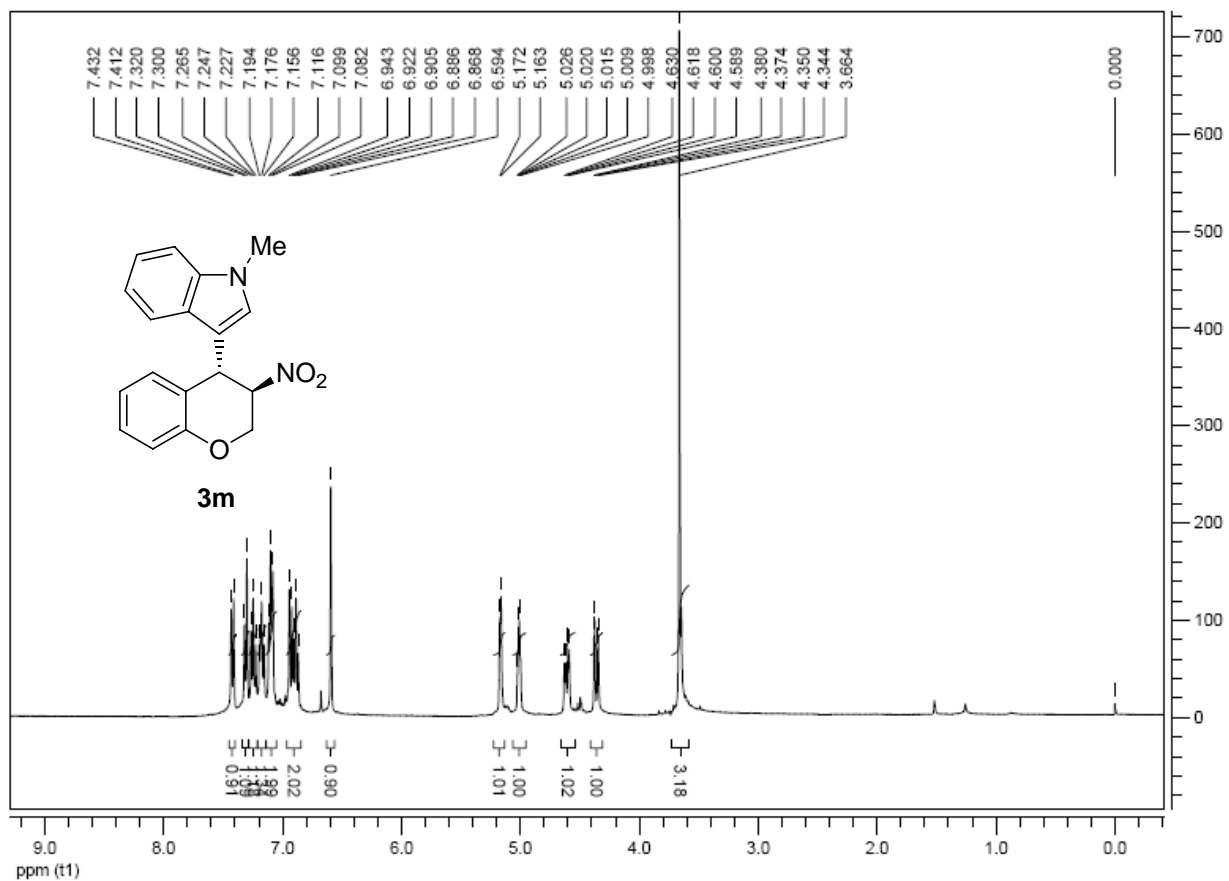


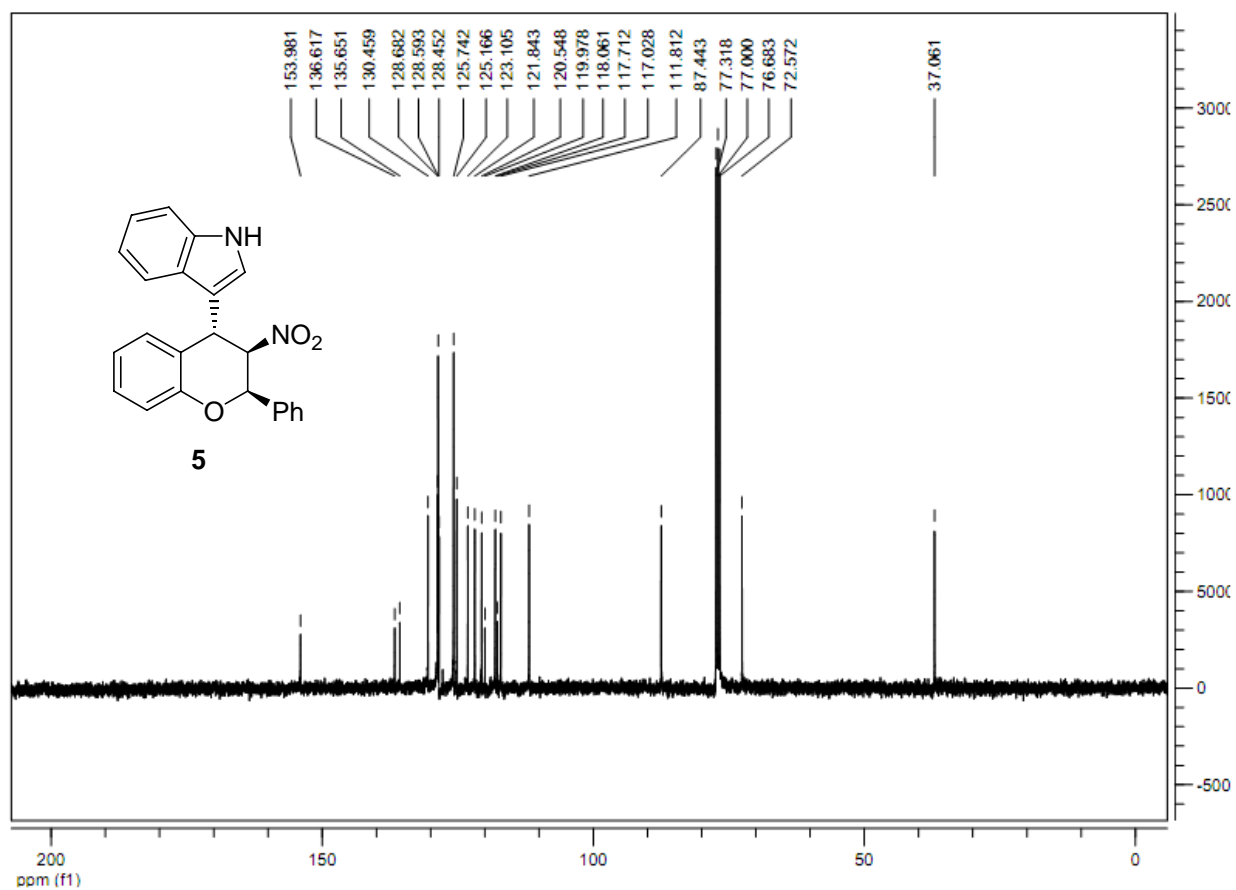
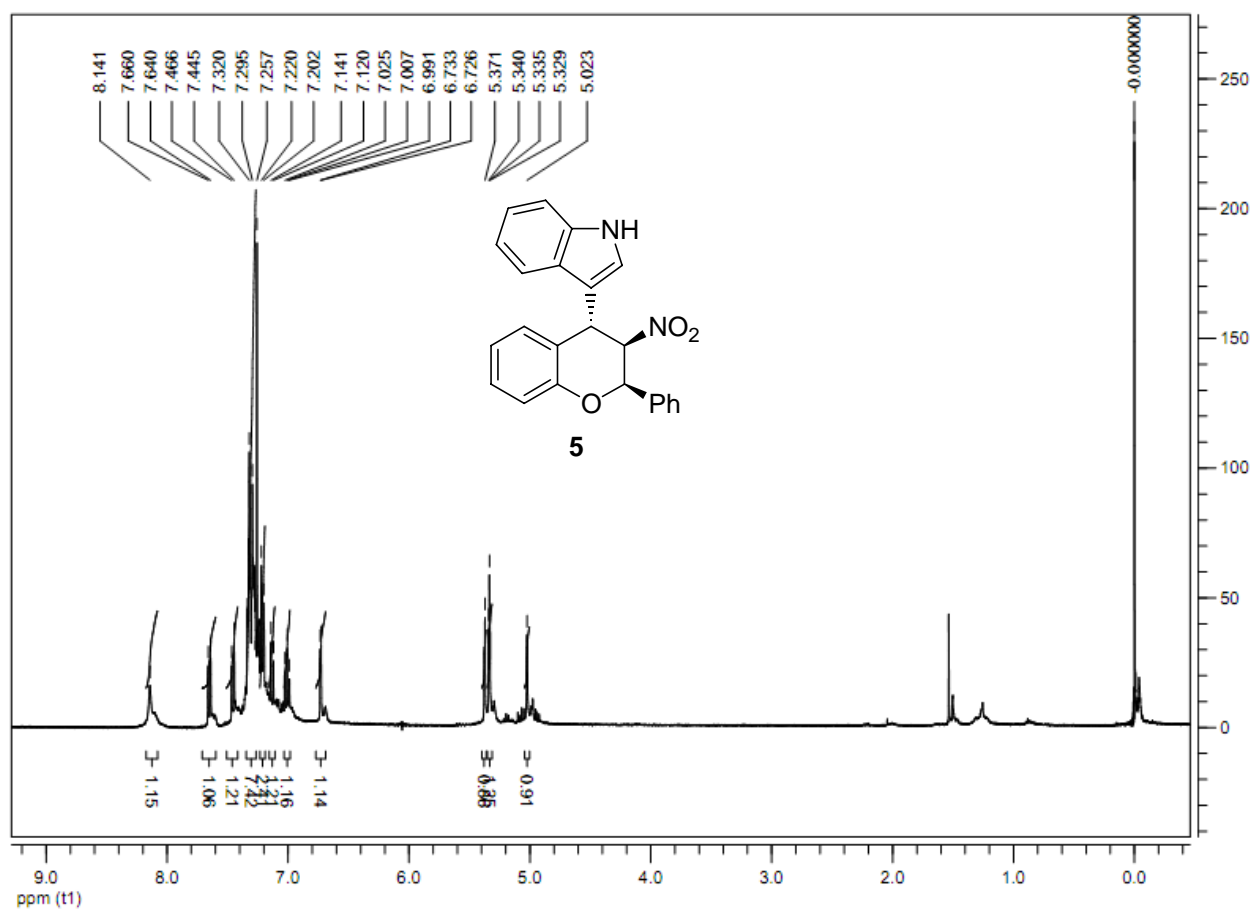


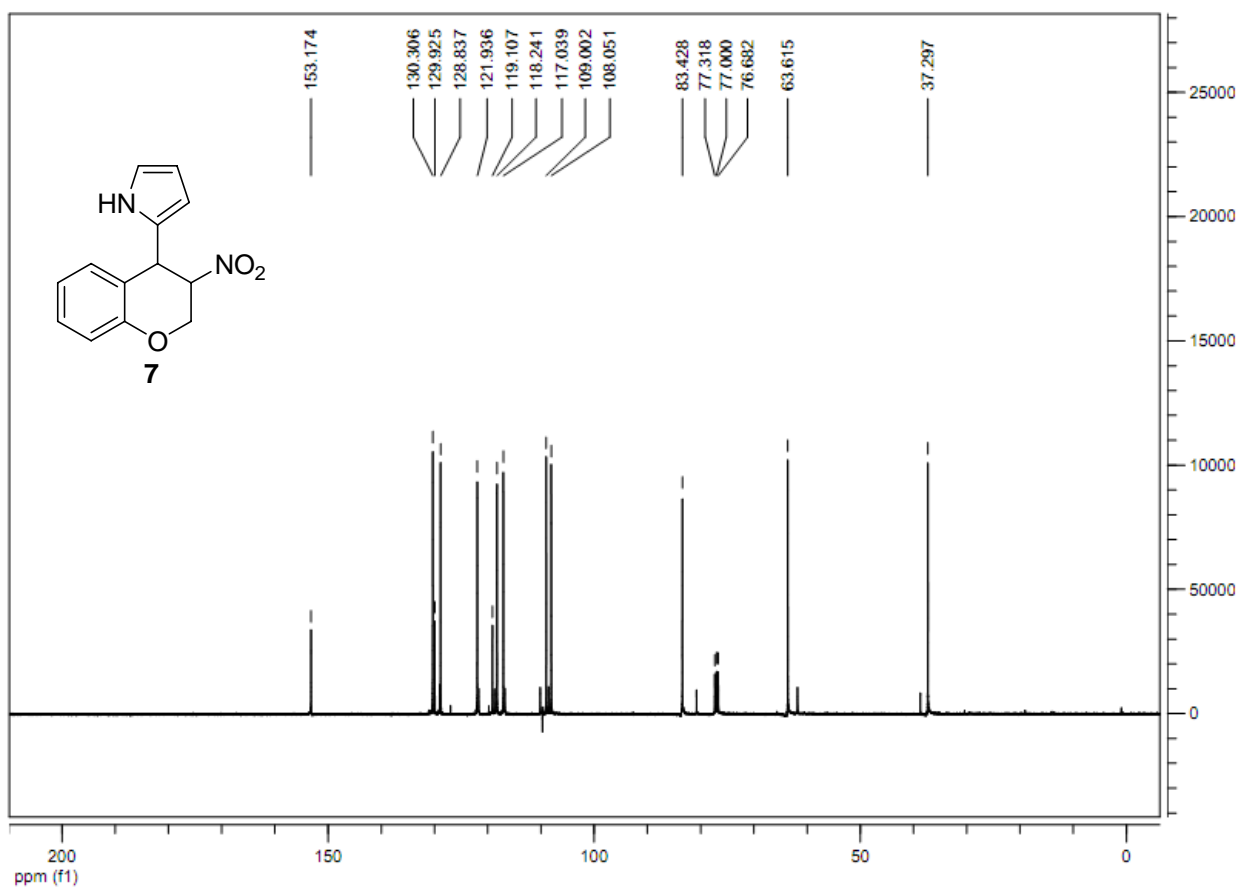
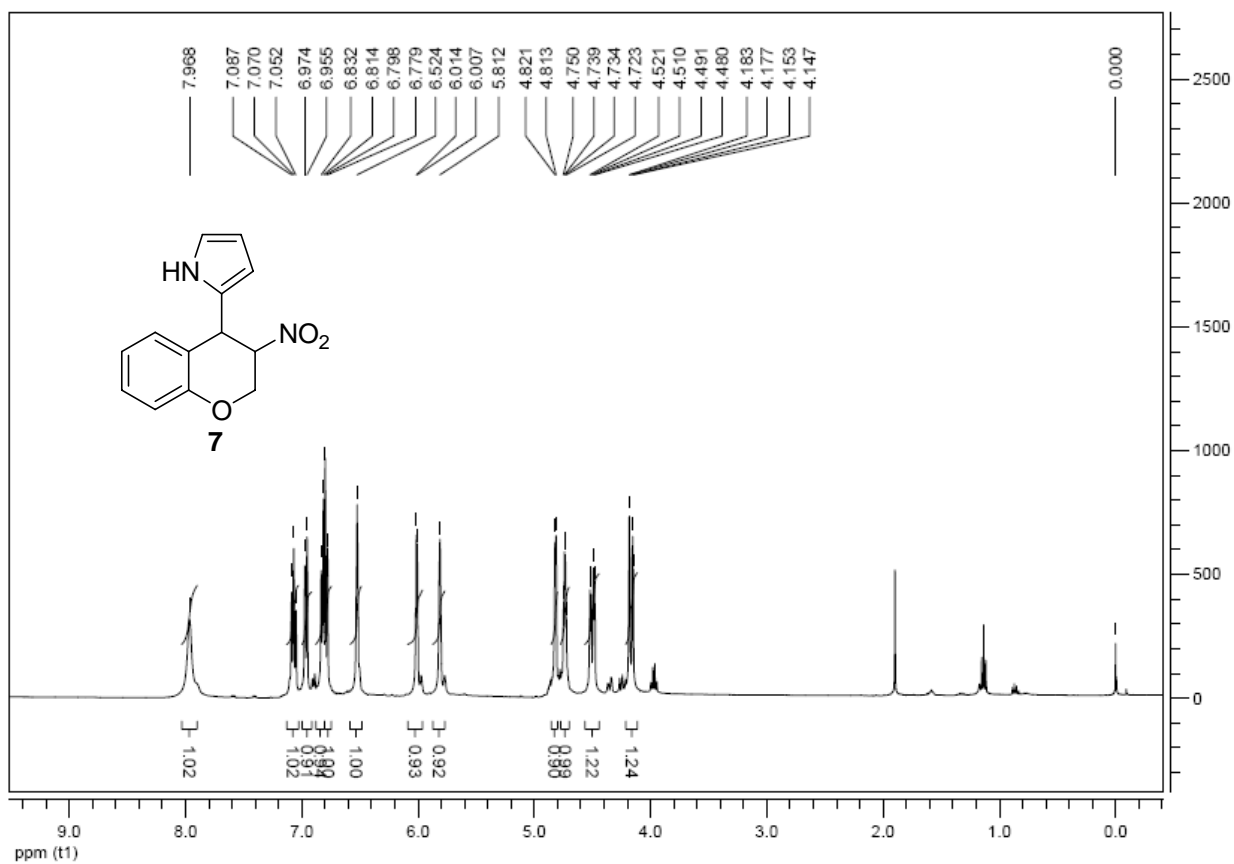








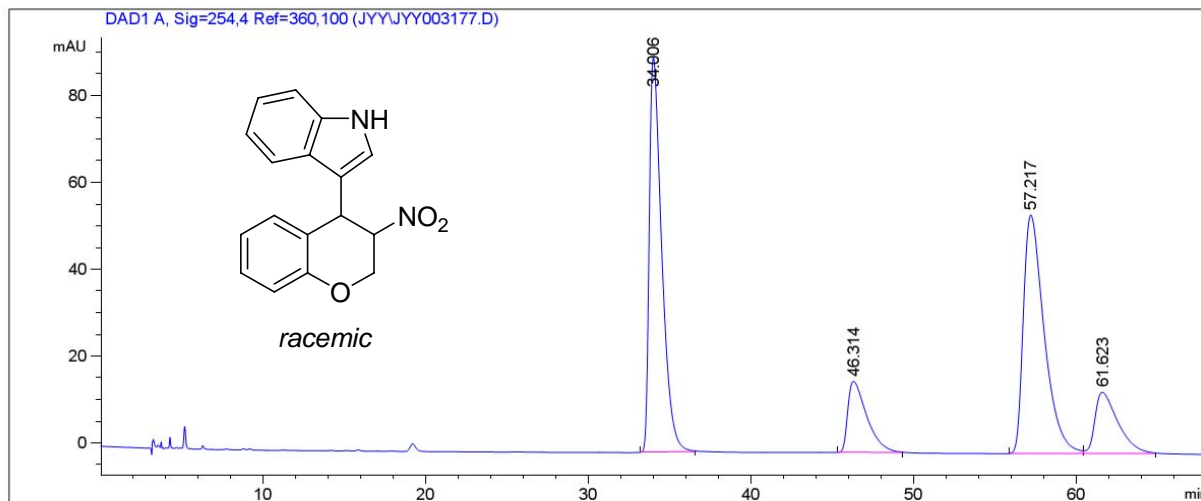




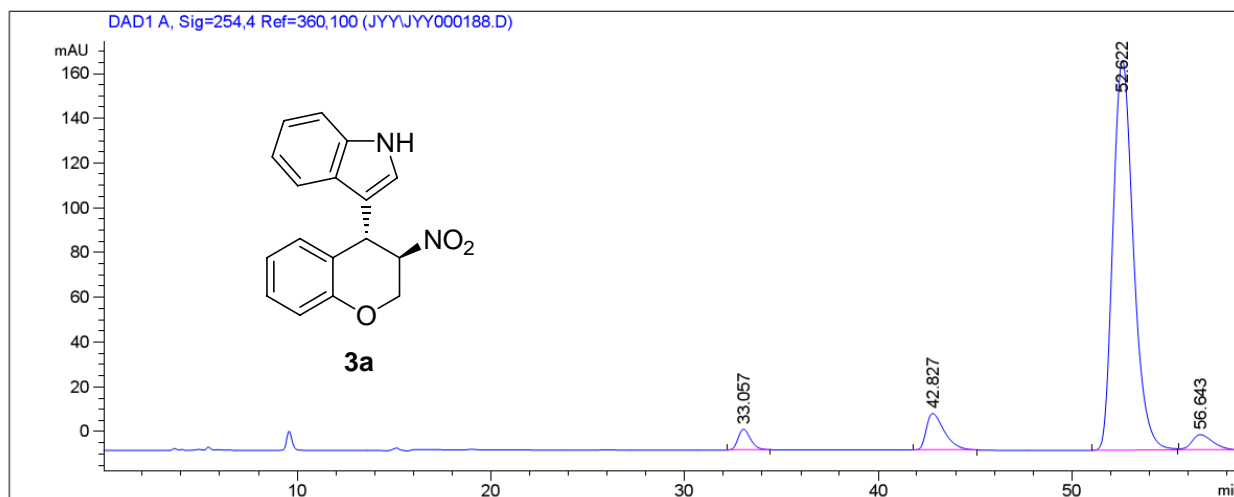


## Copies of HPLC chromatographs of Friedel-Crafts alkylation products

### 3-(3-Nitrochroman-4-yl)-1H-indole (3a):

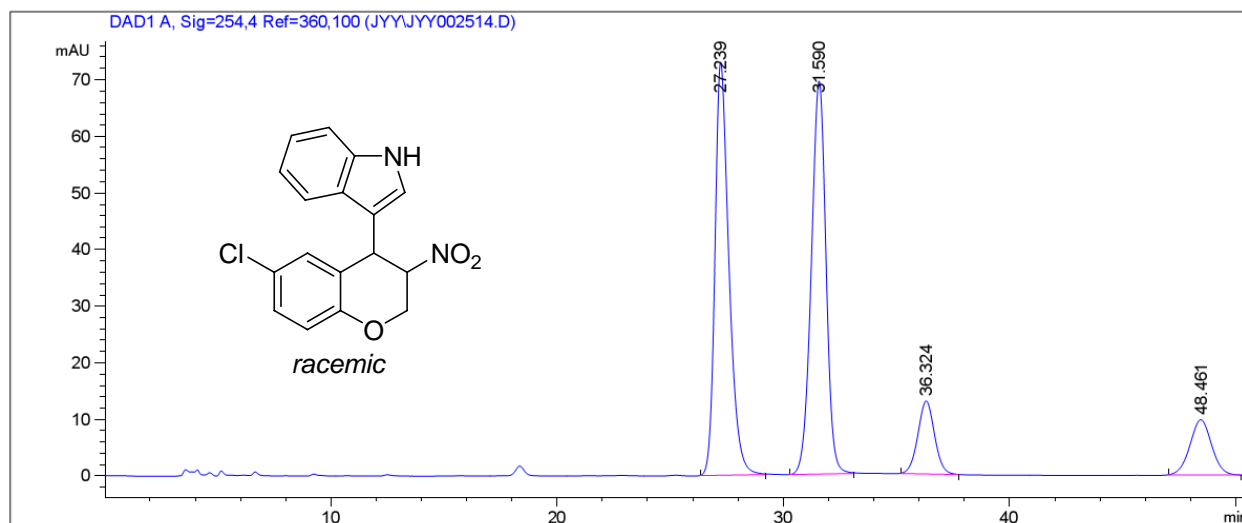


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.006	BB	0.8022	4848.97607	90.91963	38.8691
2	46.314	BB	1.1567	1339.30640	16.40113	10.7358
3	57.217	BB	1.3156	4897.42041	54.96202	39.2575
4	61.623	BB	1.3711	1389.42688	14.13070	11.1376

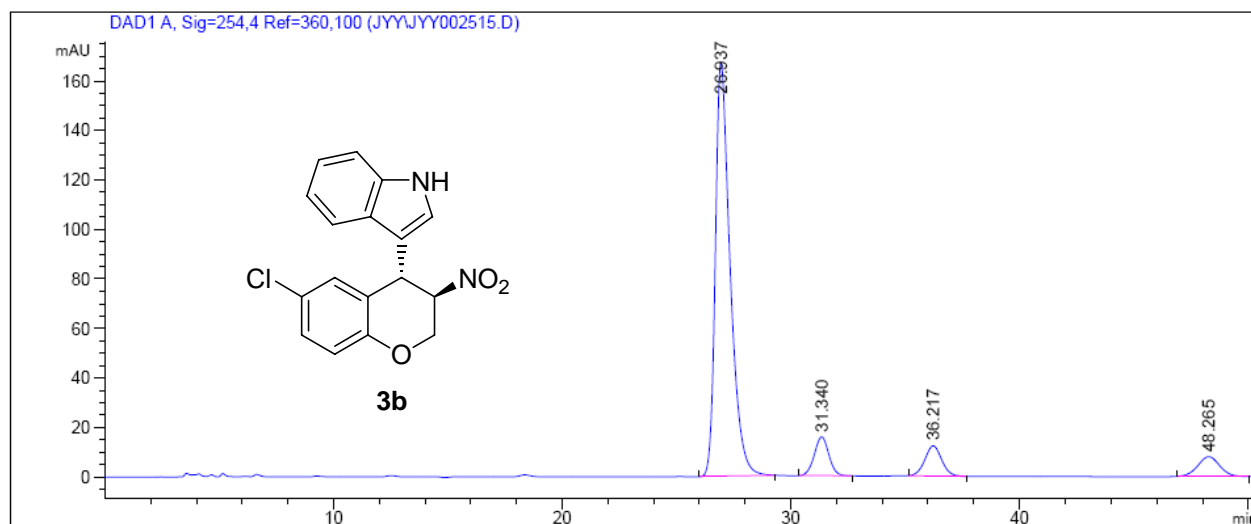


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.057	BB	0.6966	420.74823	9.28602	2.8455
2	42.827	BB	0.9950	1062.65344	16.33426	7.1866
3	52.622	BB	1.1430	1.27623e4	174.14287	86.3097
4	56.643	BB	1.1229	540.93036	6.95878	3.6582

**3-(6-Chloro-3-nitrochroman-4-yl)-1H-indole (3b):**

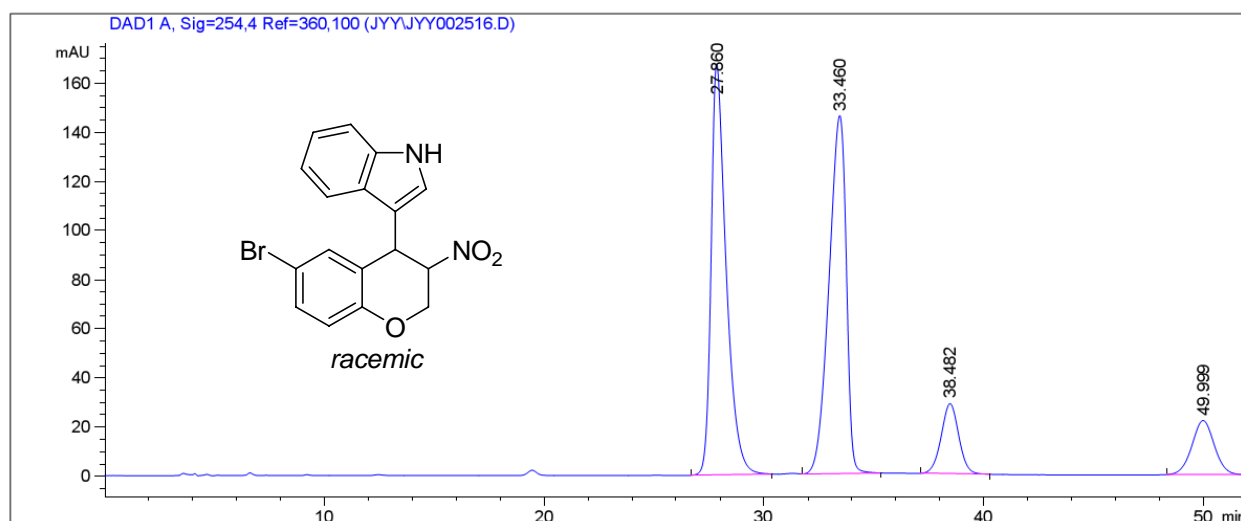


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.239	BB	0.6486	3133.45581	73.02897	41.2850
2	31.590	BB	0.6979	3130.31226	69.44391	41.2436
3	36.324	BB	0.7886	665.46368	12.92755	8.7679
4	48.461	BB	0.9967	660.57928	9.82122	8.7035

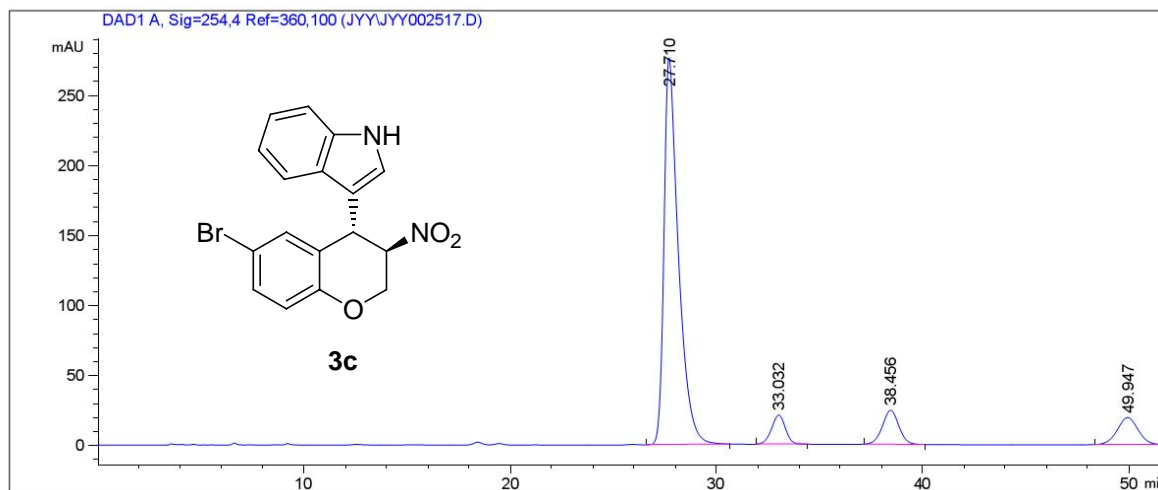


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1	26.937	BB	0.6686	7524.30078	167.32423	80.0511
2	31.340	BB	0.6921	701.46667	15.73475	7.4629
3	36.217	BB	0.7938	629.72754	12.20845	6.6997
4	48.265	BB	1.0350	543.87762	8.06236	5.7863

**3-(6-Bromo-3-nitrochroman-4-yl)-1H-indole (3c):**

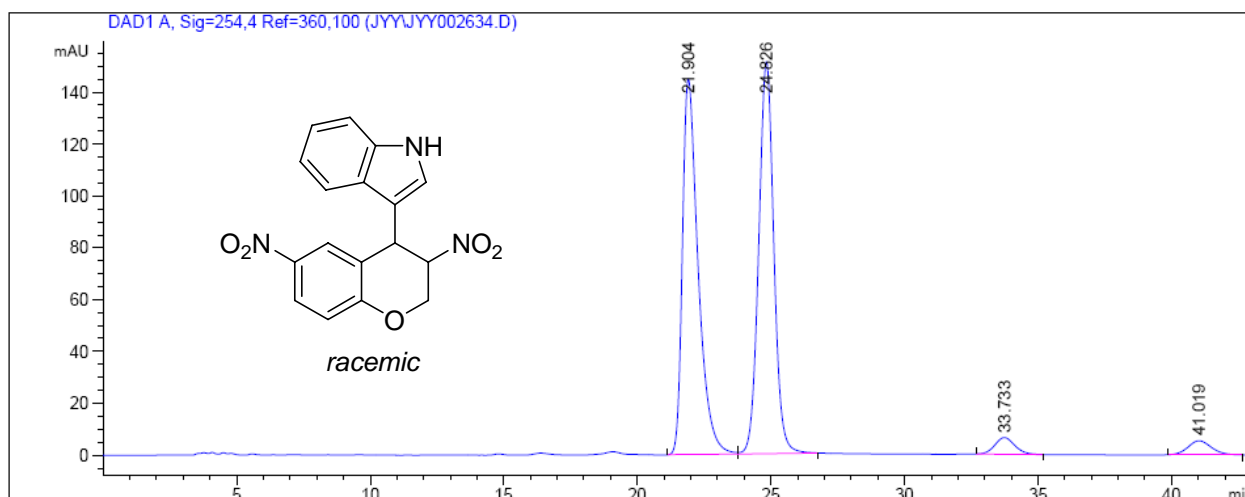


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1	27.860	BB	0.7053	8001.60498	167.50771	41.7830
2	33.460	VB	0.8531	7963.70801	145.83302	41.5852
3	38.482	BB	0.8602	1599.41138	28.61124	8.3519
4	49.999	BBA	1.0919	1585.63904	22.13124	8.2799

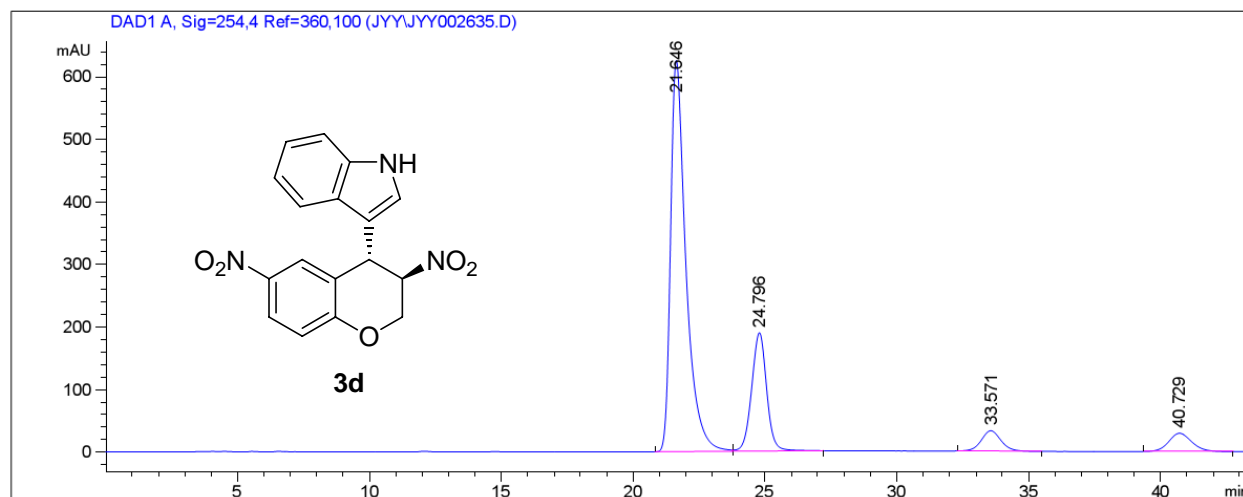


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1	27.710	VB	0.7072	1.34345e4	276.34045	78.3067
2	33.032	BB	0.7242	978.51996	20.82624	5.7036
3	38.456	BB	0.8537	1358.65820	24.39894	7.9193
4	49.947	BBA	1.0919	1384.56433	19.41683	8.0703

**3-(6-Nitro-3-nitrochroman-4-yl)-1H-indole (3d):**

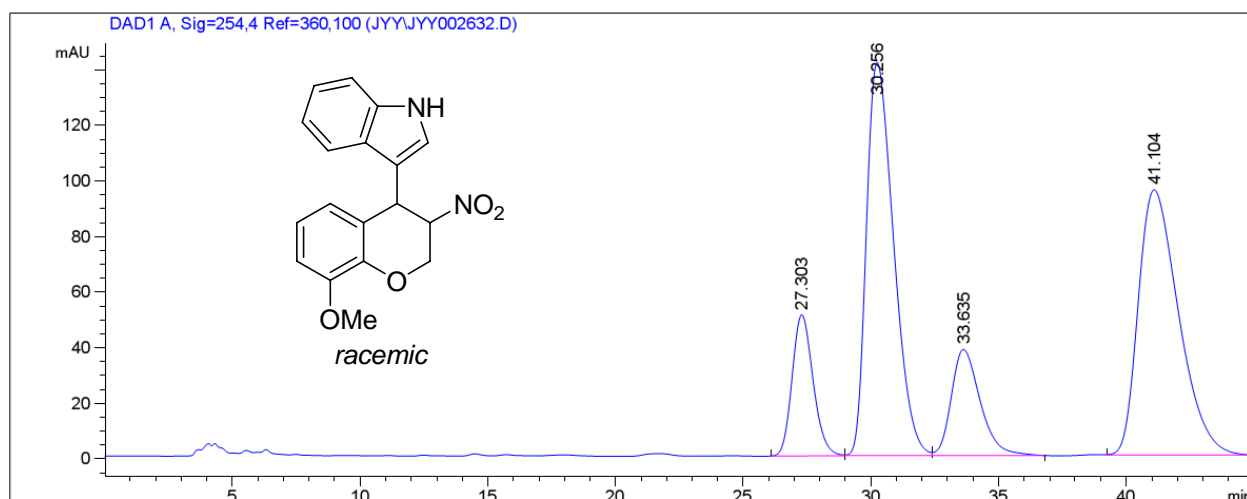


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1	21.904	BV	0.6136	5930.48633	144.88113	47.1688
2	24.826	VB	0.6040	5965.02246	151.30112	47.4435
3	33.733	BB	0.8121	340.92978	6.49810	2.7116
4	41.019	BB	0.9393	336.46768	5.45699	2.6761

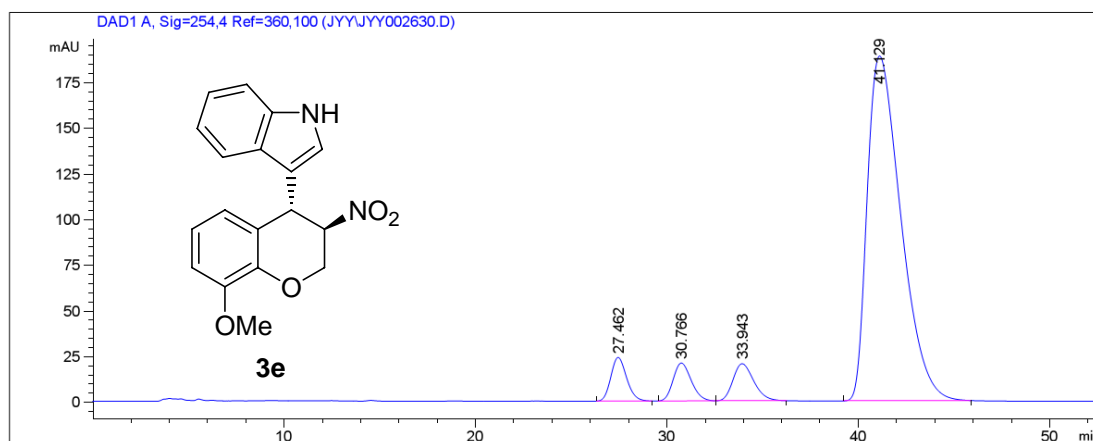


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1	21.646	BV	0.6038	2.53002e4	625.58032	69.5994
2	24.796	VB	0.6079	7537.58740	189.54581	20.7355
3	33.571	BB	0.7980	1711.67920	32.73924	4.7087
4	40.729	BB	0.9406	1801.71387	29.33259	4.9564

### 3-(8-Methoxy-3-nitrochroman-4-yl)-1H-indole (3e)

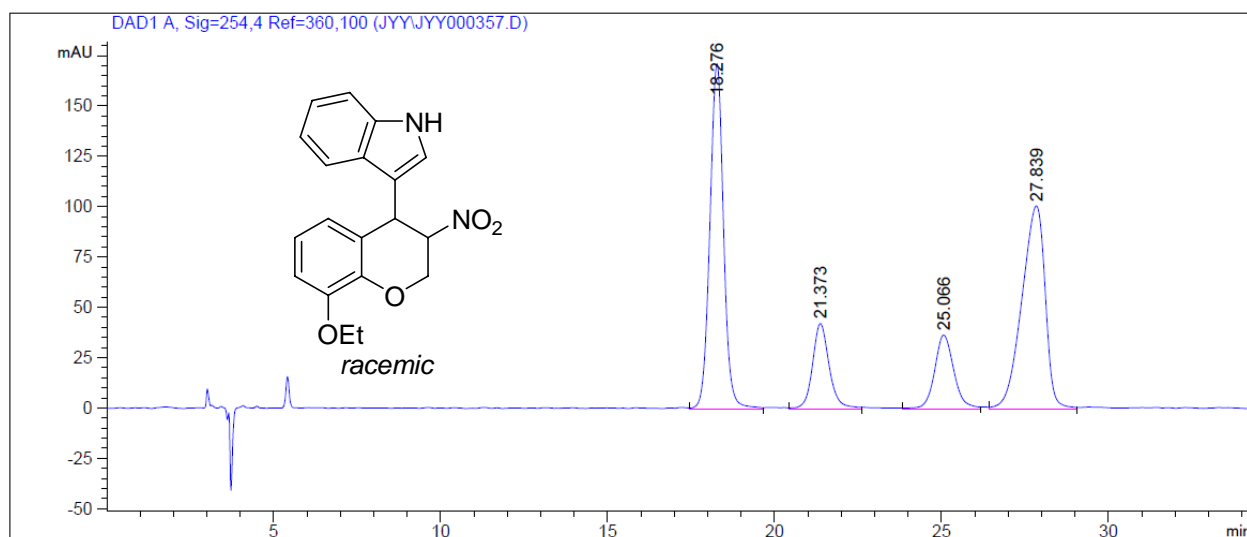


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.303	BV	0.8899	2921.59521	50.88382	10.8217
2	30.256	VV	1.1570	1.05011e4	141.62851	38.8967
3	33.635	VB	1.1955	3033.39795	38.32275	11.2359
4	41.104	BBA	1.6807	1.05413e4	95.72607	39.0457

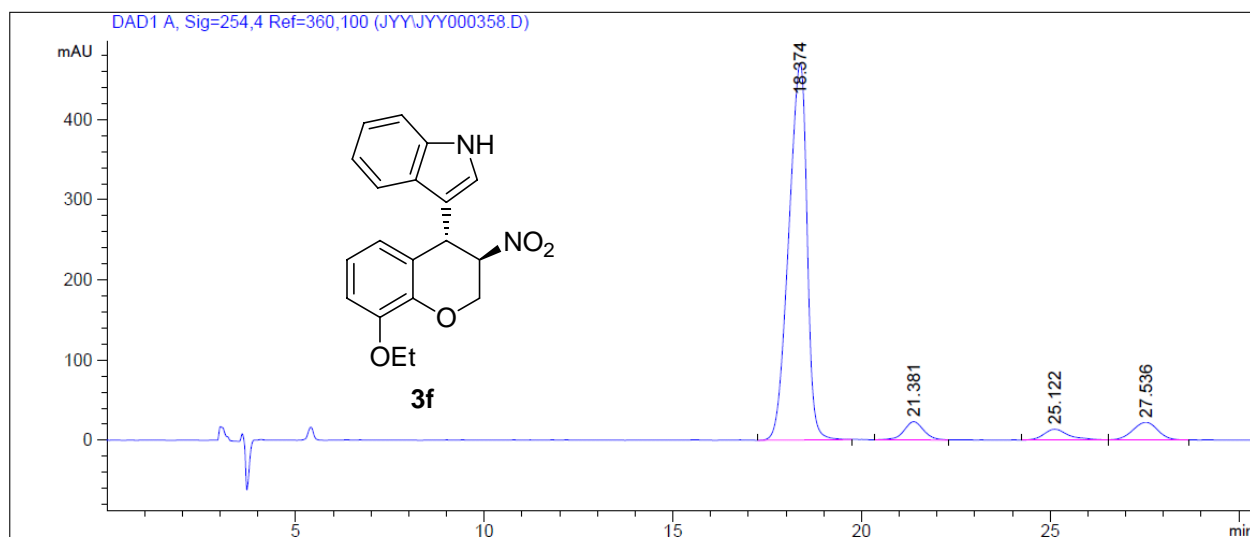


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.462	BB	0.8884	1380.16467	23.94649	5.0318
2	30.766	BB	1.0221	1375.01184	20.83080	5.0130
3	33.943	BB	1.1637	1549.85730	20.36802	5.6504
4	41.129	BB	1.9250	2.31239e4	188.78694	84.3048

**3-(8-Ethoxy-3-nitrochroman-4-yl)-1H-indole (3f):**

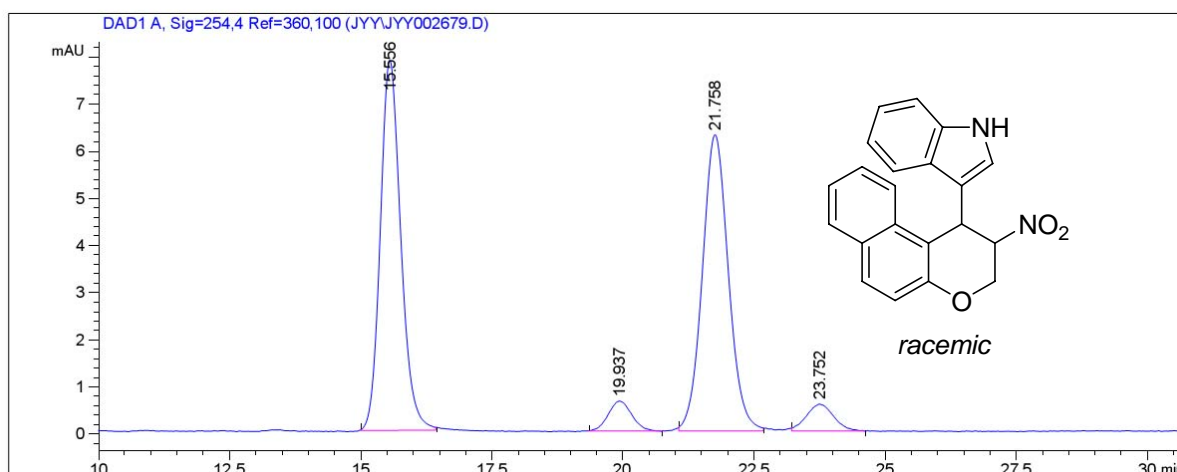


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.276	VV	0.4387	4854.64893	171.28030	38.3917
2	21.373	VB	0.5191	1457.99365	42.20021	11.5301
3	25.066	VV	0.6067	1447.10938	36.48869	11.4441
4	27.839	VV	0.7624	4885.30420	100.62844	38.6341

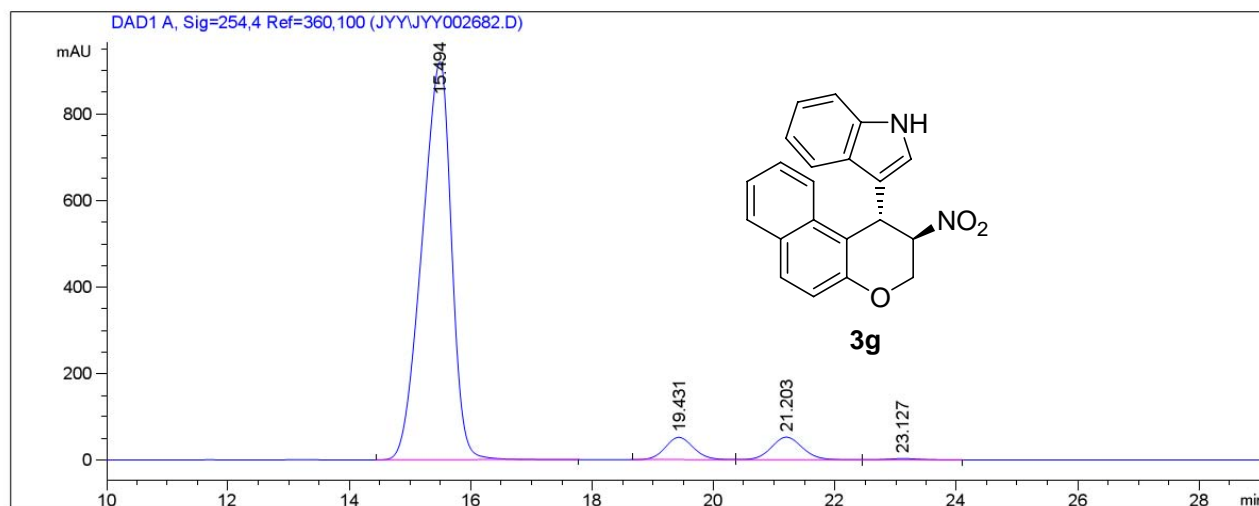


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.374	VB	0.5318	1.57970e4	470.43762	86.1738
2	21.381	BV	0.5575	830.31232	22.76814	4.5294
3	25.122	VV	0.7096	650.11914	13.70155	3.5464
4	27.536	VV	0.7414	1054.13184	22.38594	5.7504

**3-[2,3-Dihydro-2-nitro-1H-naphtho[2,1-b]pyran-1-yl]-1H-indole (3g):**

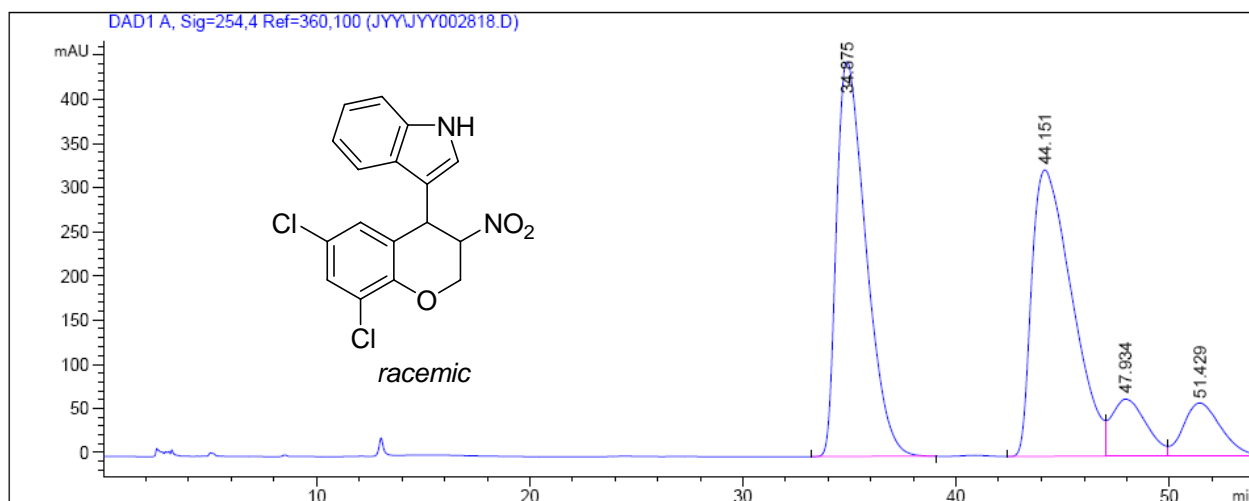


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1	15.556	BB	0.4168	213.30362	7.85587	45.2673
2	19.937	BB	0.4376	19.92599	6.35945e-1	4.2287
3	21.758	BB	0.5310	217.08768	6.28417	46.0704
4	23.752	BB	0.5454	20.89149	5.72886e-1	4.4336

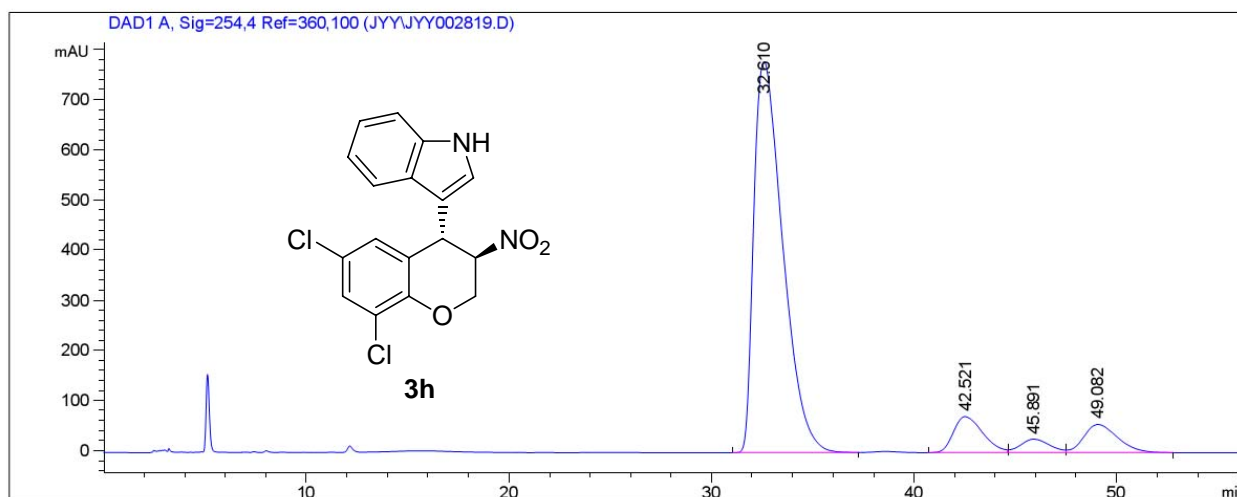


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.494	BB	0.5208	3.09579e4	919.43878	89.2353
2	19.431	BV	0.5076	1709.98206	52.00088	4.9290
3	21.203	VV	0.5584	1904.27563	52.58999	5.4890
4	23.127	VB	0.5963	120.28685	3.10254	0.3467

**3-(6,8-Dichloro-3-nitrochroman-4-yl)-1H-indole (3h):**



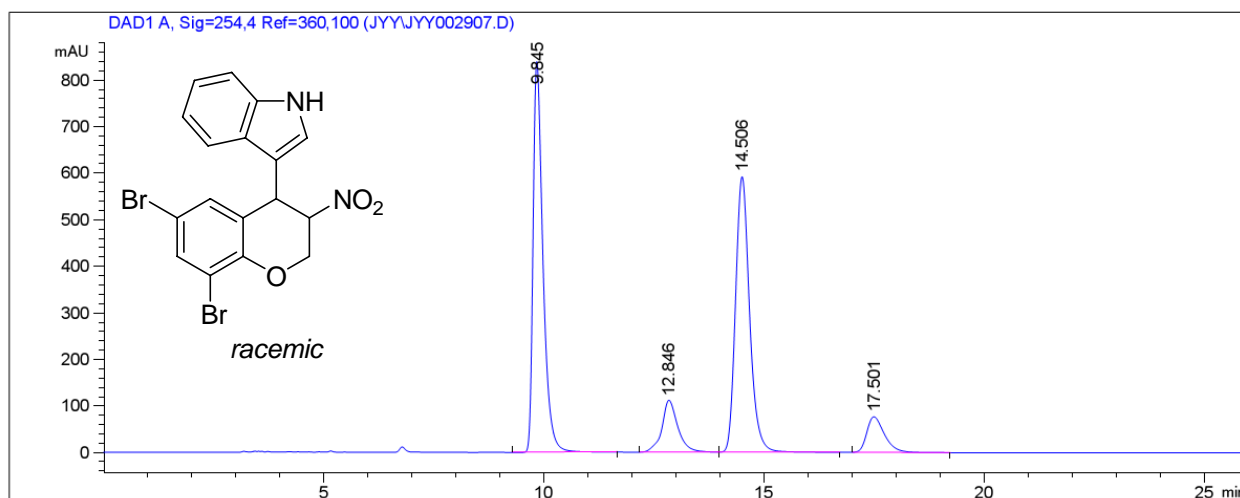
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1	34.875	BB	1.4167	4.29259e4	446.85843	42.7888
2	44.151	VV	2.0282	4.25926e4	324.30716	42.4565
3	47.934	VV	1.6327	7390.84424	64.89440	7.3672
4	51.429	VBA	1.7852	7411.13965	60.32864	7.3875



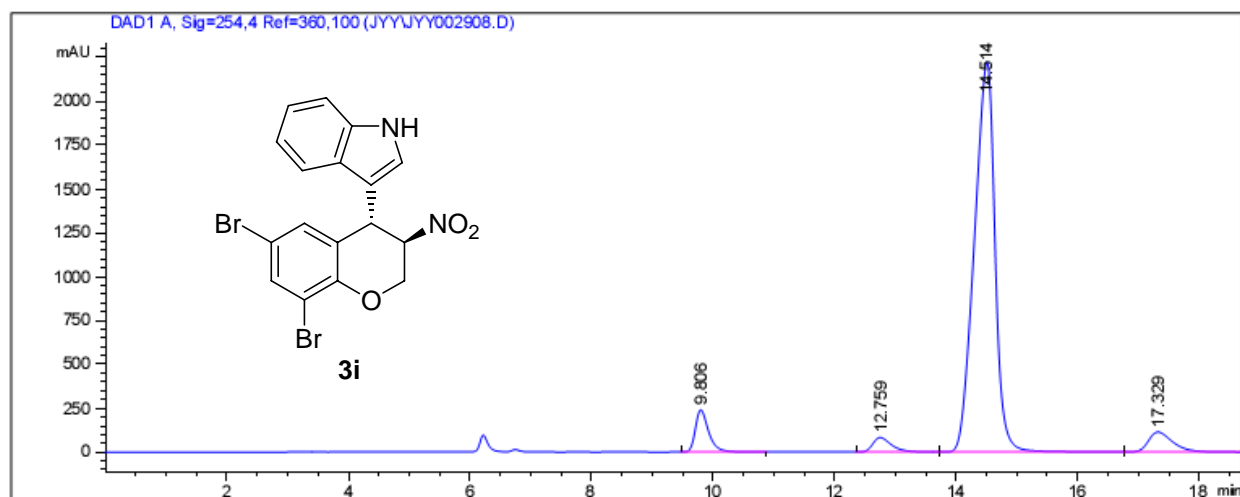
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1	32.610	BB	1.5550	7.74940e4	780.08301	82.3645
2	42.521	VV	1.5360	7266.75244	72.09010	7.7235
3	45.891	VV	1.4829	2728.83545	27.09795	2.9003
4	49.082	VB	1.6779	6597.06250	56.34853	7.0117



**3-(6,8-Dibromo-3-nitrochroman-4-yl)-1H-indole (3i):**

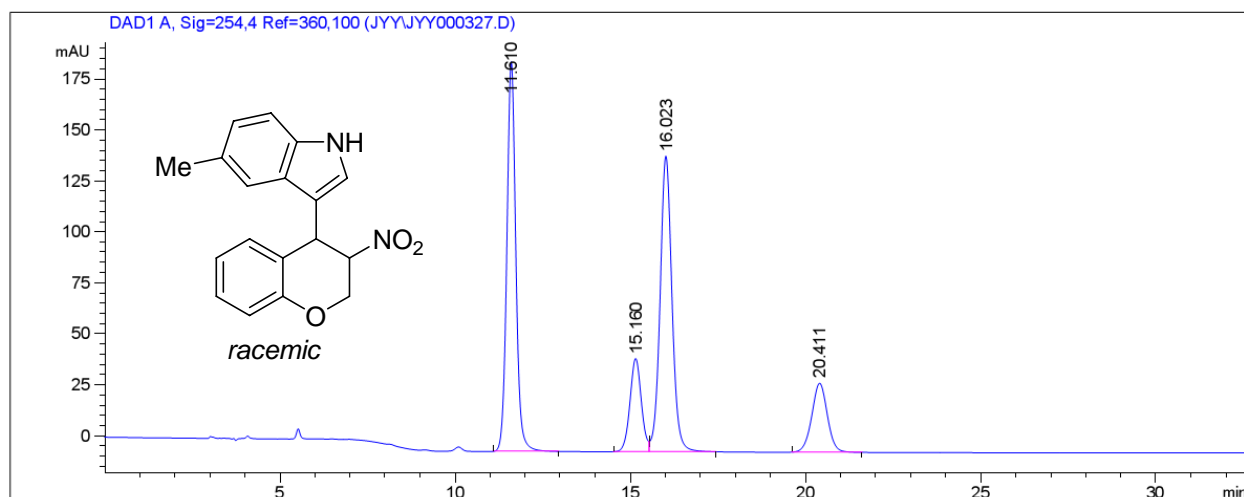


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.845	VB S	0.2339	1.30857e4	839.46094	41.9072
2	12.846	BV	0.3719	2836.36621	111.81458	9.0835
3	14.506	VB	0.3388	1.31429e4	592.54956	42.0903
4	17.501	BB	0.4277	2160.49756	76.91081	6.9190

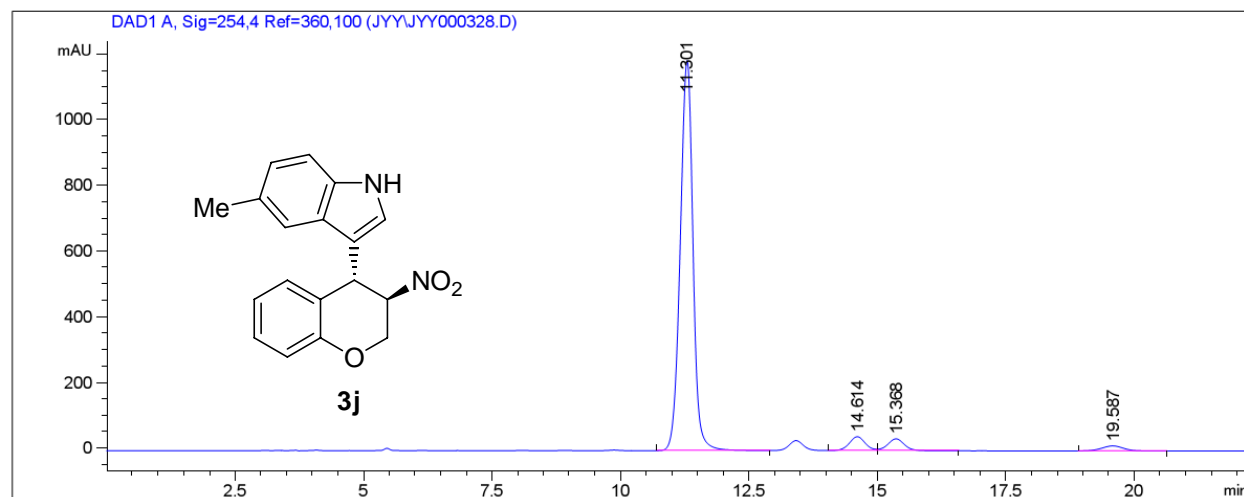


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.806	VB S	0.2282	3622.29907	239.80441	5.9485
2	12.759	BV	0.3215	1764.83423	82.50871	2.8982
3	14.514	VV	0.3626	5.23130e4	2222.94092	85.9074
4	17.329	VBA	0.4230	3194.52344	113.97450	5.2460

### 5-Methyl-3-(3-nitrochroman-4-yl)-1H-indole (3j):

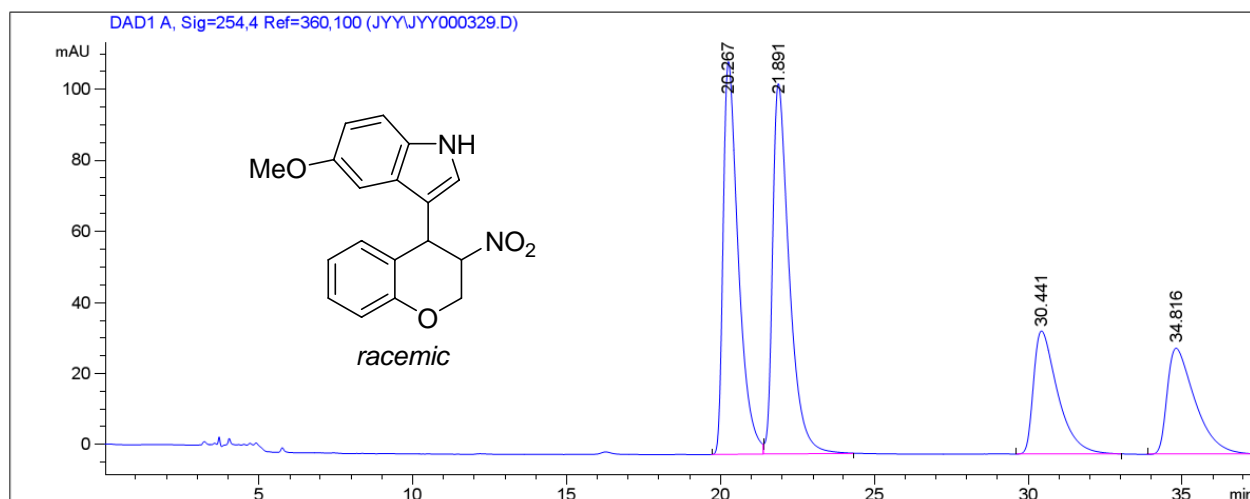


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.610	BB	0.2720	3409.17969	191.18457	38.1898
2	15.160	BV	0.3444	1036.91089	45.76041	11.6155
3	16.023	VB	0.3597	3428.53589	145.06996	38.4066
4	20.411	BB	0.4744	1052.31604	33.88070	11.7881

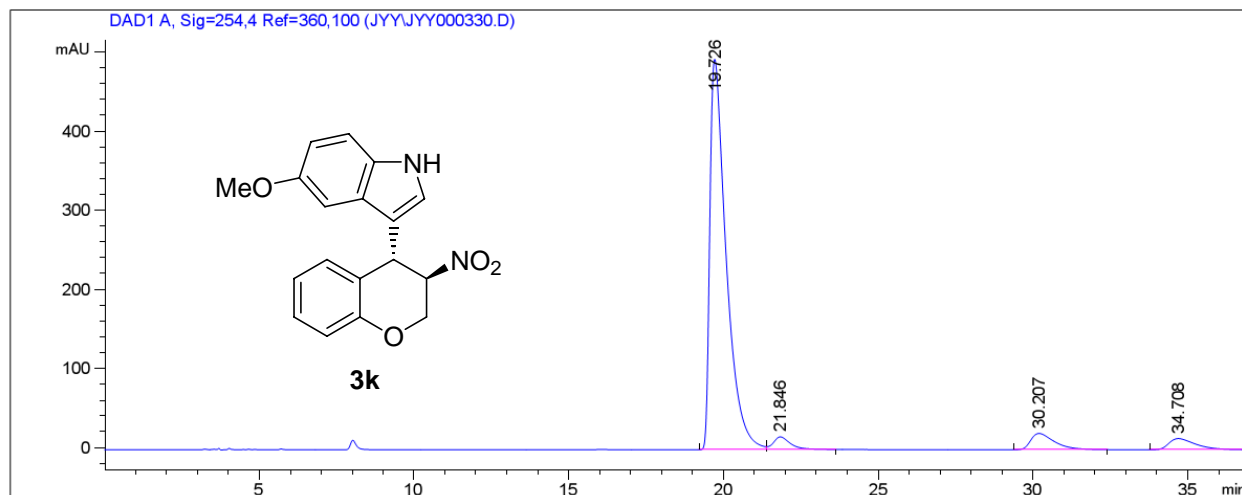


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.301	BV	0.2653	2.04901e4	1187.40747	90.1361
2	14.614	VV	0.3364	941.49548	42.84520	4.1416
3	15.368	VB	0.3514	836.71680	36.50990	3.6807
4	19.587	BB	0.4592	464.08765	15.59288	2.0415

**5-Methoxy-3-(3-nitrochroman-4-yl)-1H-indole (3k):**

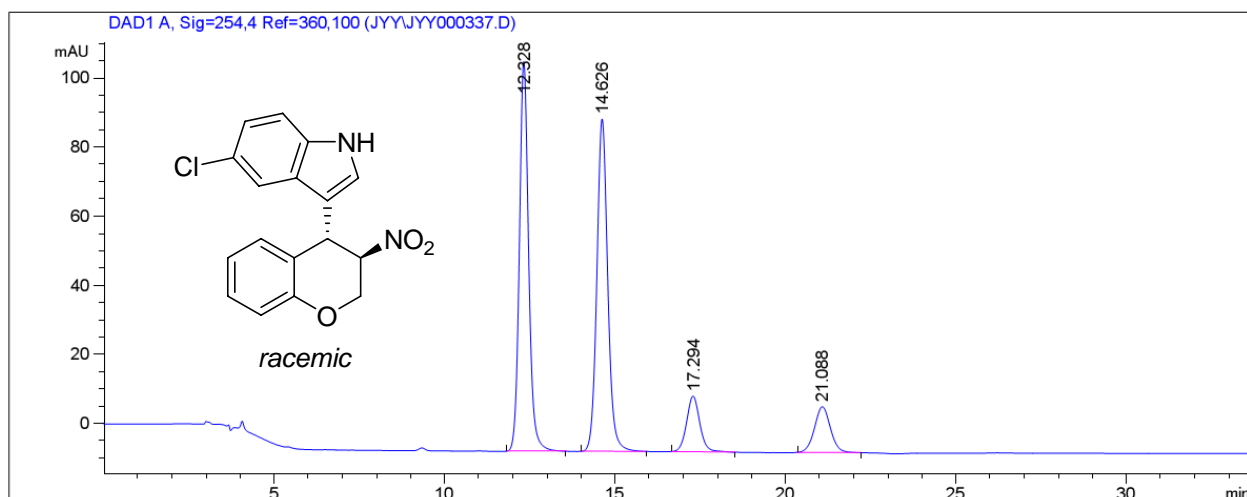


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.267	BV	0.5173	3801.46753	110.51521	33.0421
2	21.891	VB	0.5671	3923.24878	104.23664	34.1006
3	30.441	BB	0.8160	1900.02258	34.63675	16.5149
4	34.816	BBA	0.9468	1880.19409	29.85160	16.3425

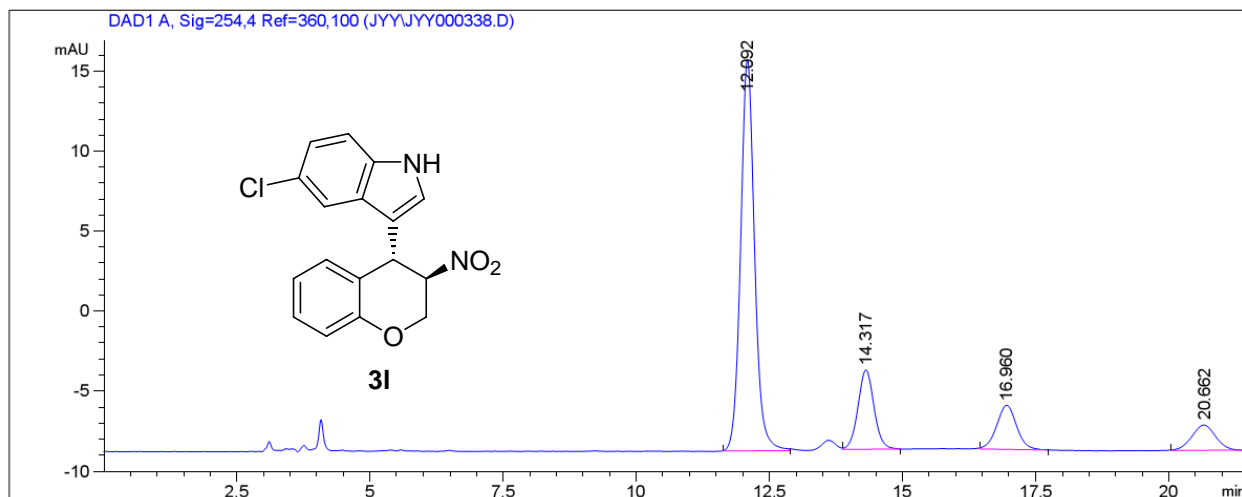


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.726	BV	0.5440	1.81083e4	493.65469	87.4893
2	21.846	VB	0.5798	637.70428	16.17992	3.0810
3	30.207	BB	0.7964	1101.30579	20.57742	5.3209
4	34.708	BB	0.9040	850.42389	14.09416	4.1088

**5-Chloro-3-(3-nitrochroman-4-yl)-1H-indole (3l):**

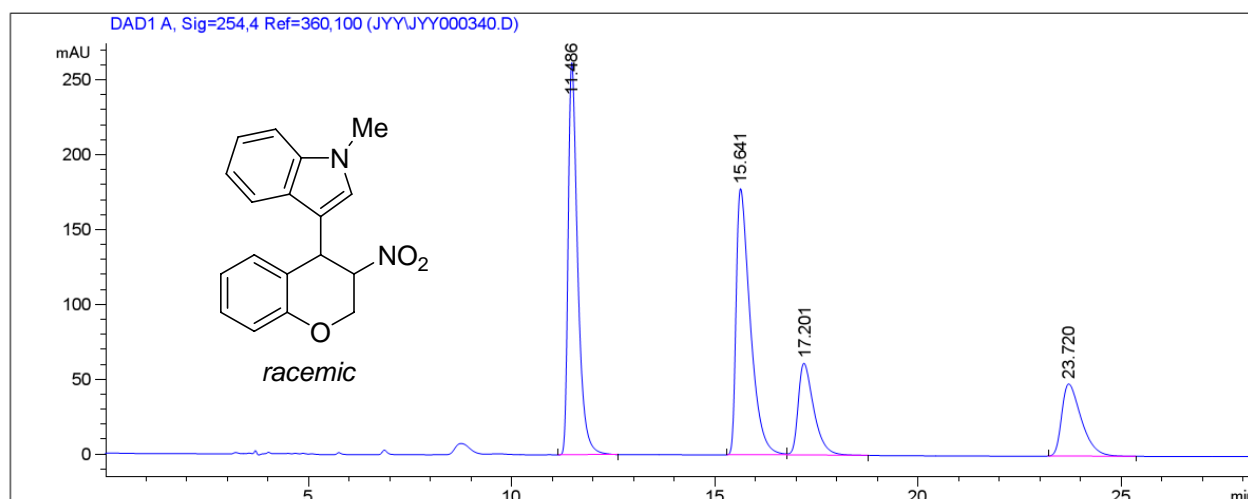


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.328	BB	0.2889	2136.39697	112.83144	41.4562
2	14.626	BB	0.3391	2137.53101	96.25804	41.4782
3	17.294	BB	0.4131	439.24487	16.15845	8.5234
4	21.088	BB	0.5011	440.20538	13.33634	8.5421

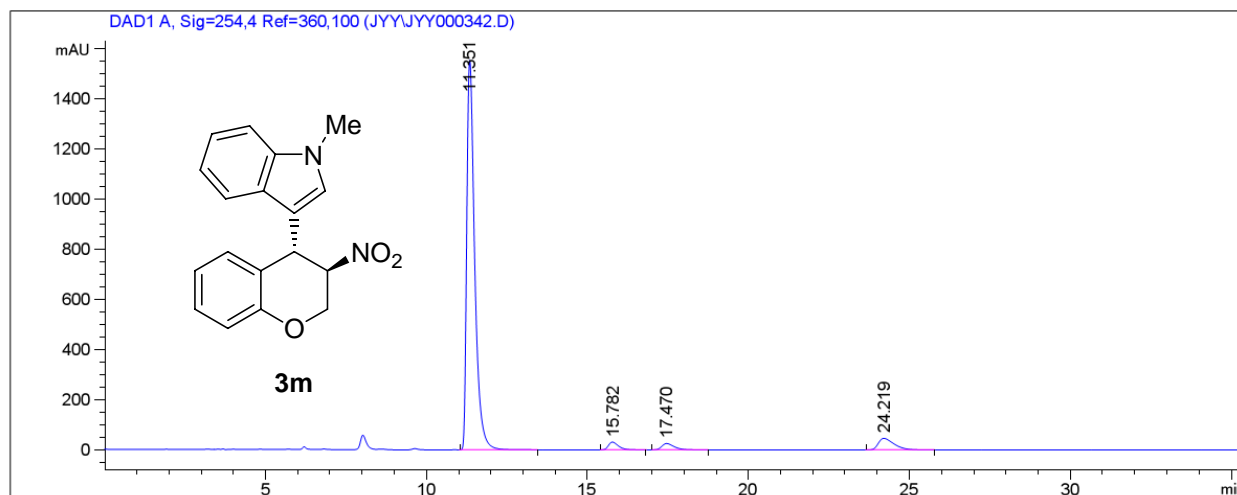


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.092	BB	0.2767	445.74820	24.44388	66.2055
2	14.317	VB	0.3227	105.23866	4.97783	15.6307
3	16.960	BB	0.3982	72.63189	2.76746	10.7878
4	20.662	BBA	0.4895	49.66105	1.58526	7.3760

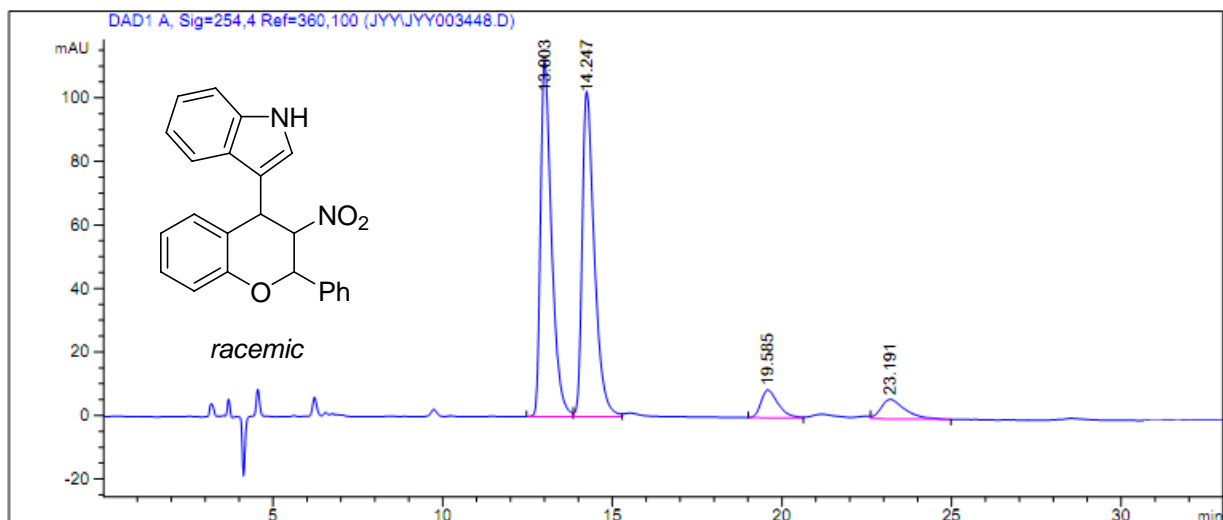
### 1-Methyl-3-(3-nitrochroman-4-yl)-1H-indole (3m):



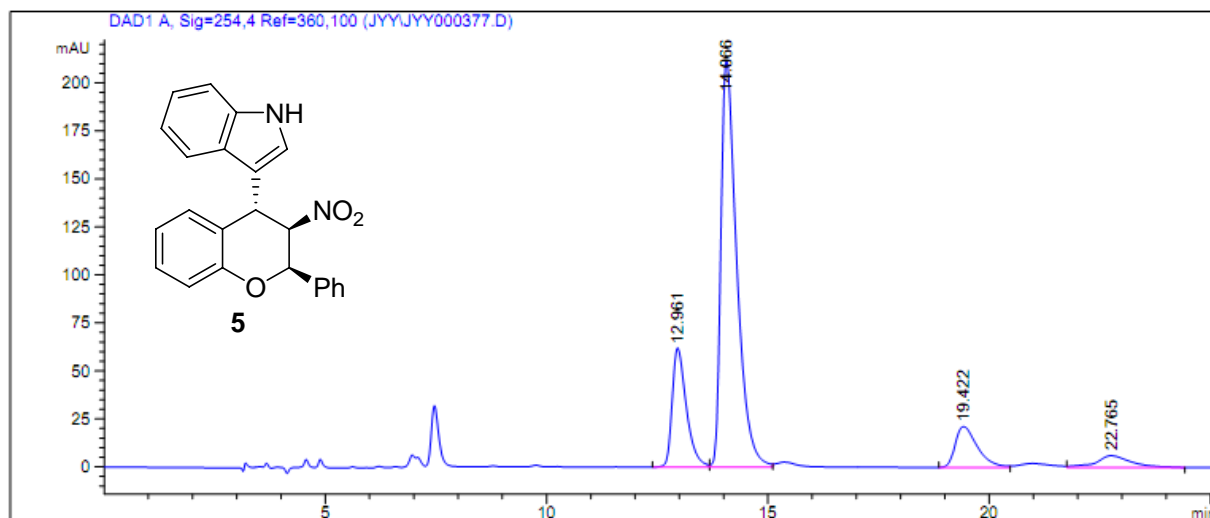
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.486	VB	0.2465	4276.71875	261.89624	36.0588
2	15.641	BV	0.3622	4302.91260	177.89870	36.2796
3	17.201	VB	0.4059	1654.14014	61.47704	13.9467
4	23.720	BB	0.5089	1626.63623	48.30076	13.7148



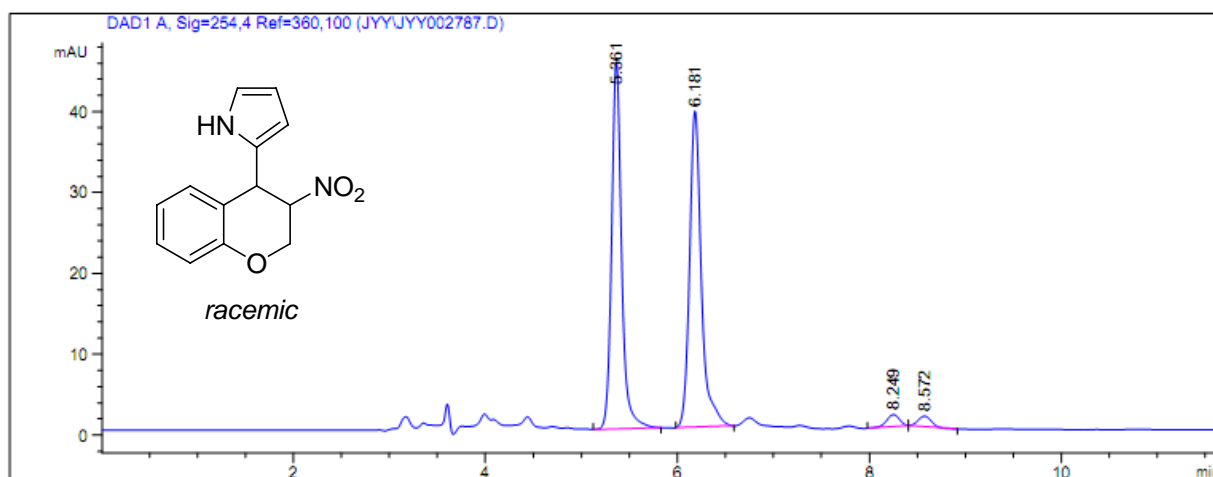
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.351	VB	0.2601	2.66035e4	1551.30811	89.9240
2	15.782	BB	0.3371	687.28400	31.18877	2.3231
3	17.470	BB	0.4158	699.90277	25.53494	2.3658
4	24.219	BB	0.5217	1593.72607	46.28685	5.3870



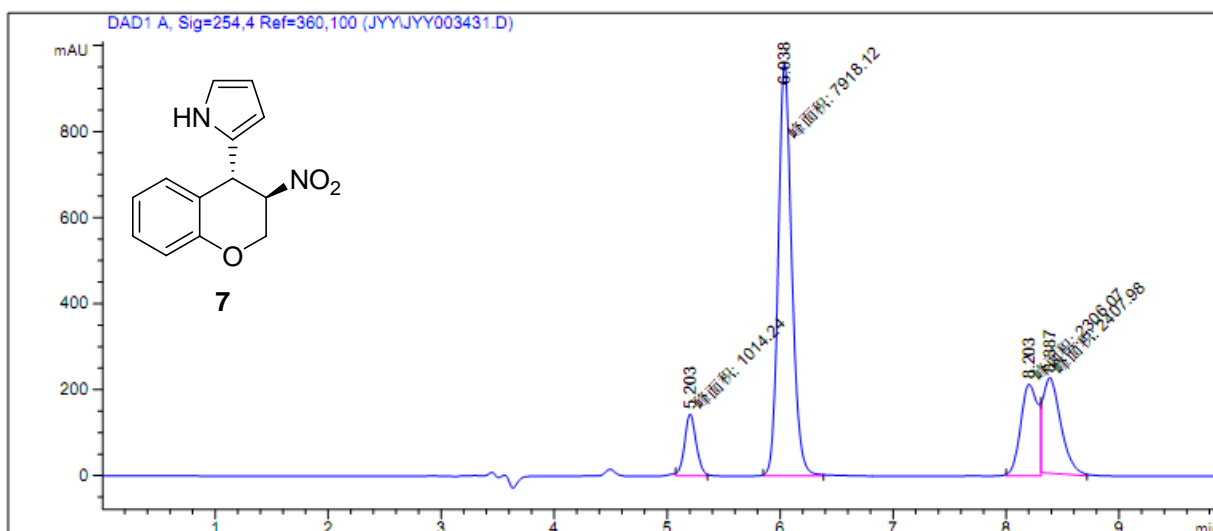
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.003	BV	0.3393	2529.69043	112.10420	44.4087
2	14.247	VV	0.3792	2556.90845	102.44094	44.8865
3	19.585	BV	0.5302	306.94028	8.72936	5.3883
4	23.191	VB	0.7319	302.84985	6.13467	5.3165



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.961	BV	0.3363	1385.25781	62.09427	17.9071
2	14.066	VV	0.3741	5267.75879	211.82053	68.0960
3	19.422	BV	0.5324	740.38348	21.35705	9.5709
4	22.765	VB	0.7790	342.38205	6.17335	4.4260



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.361	VB S	0.1085	328.60657	45.34459	47.7845
2	6.181	BB S	0.1277	333.49896	39.00608	48.4959
3	8.249	BB	0.1437	13.71888	1.48664	1.9949
4	8.572	BB	0.1457	11.86039	1.30854	1.7247



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.203	MM	0.1172	1014.23926	144.22031	7.4323
2	6.038	MM	0.1370	7918.12256	963.33899	58.0235
3	8.203	MM	0.1801	2306.06738	213.36264	16.8987
4	8.387	MM	0.1804	2407.97754	222.42679	17.6455