

Enantioselective 1,4-Michael addition reaction of pyrazolin-5-one with 2-enoylpyridine catalyzed by *Cinchona* derived squaramides

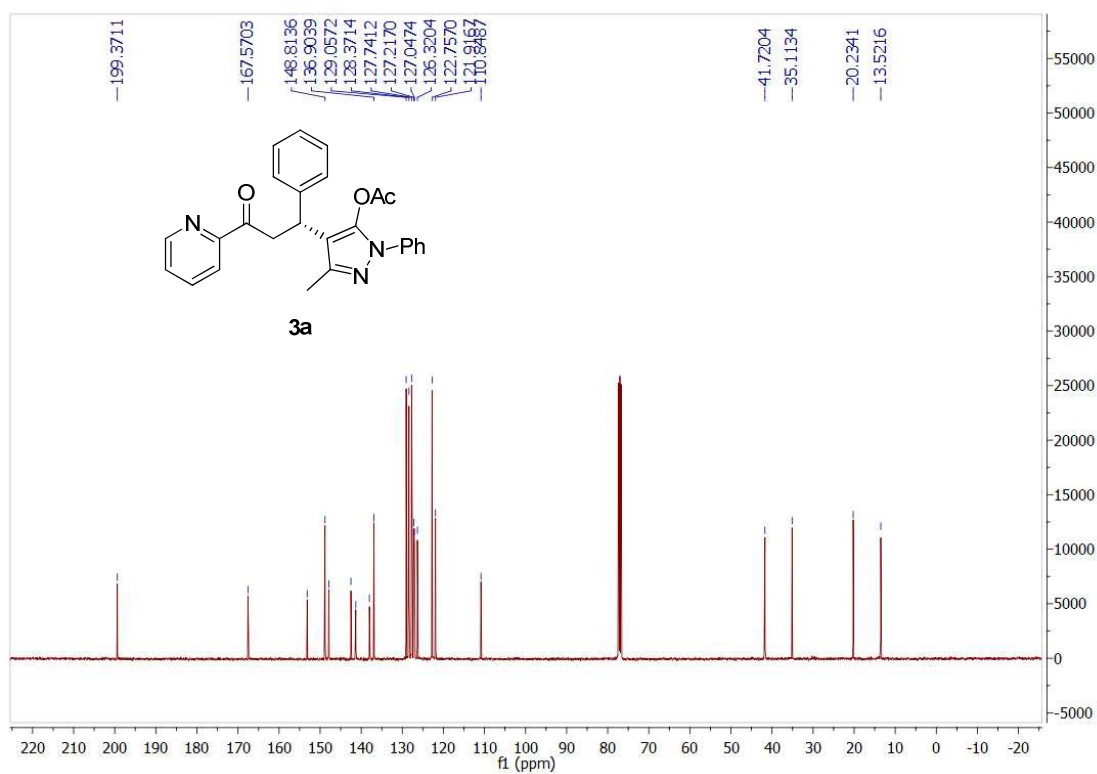
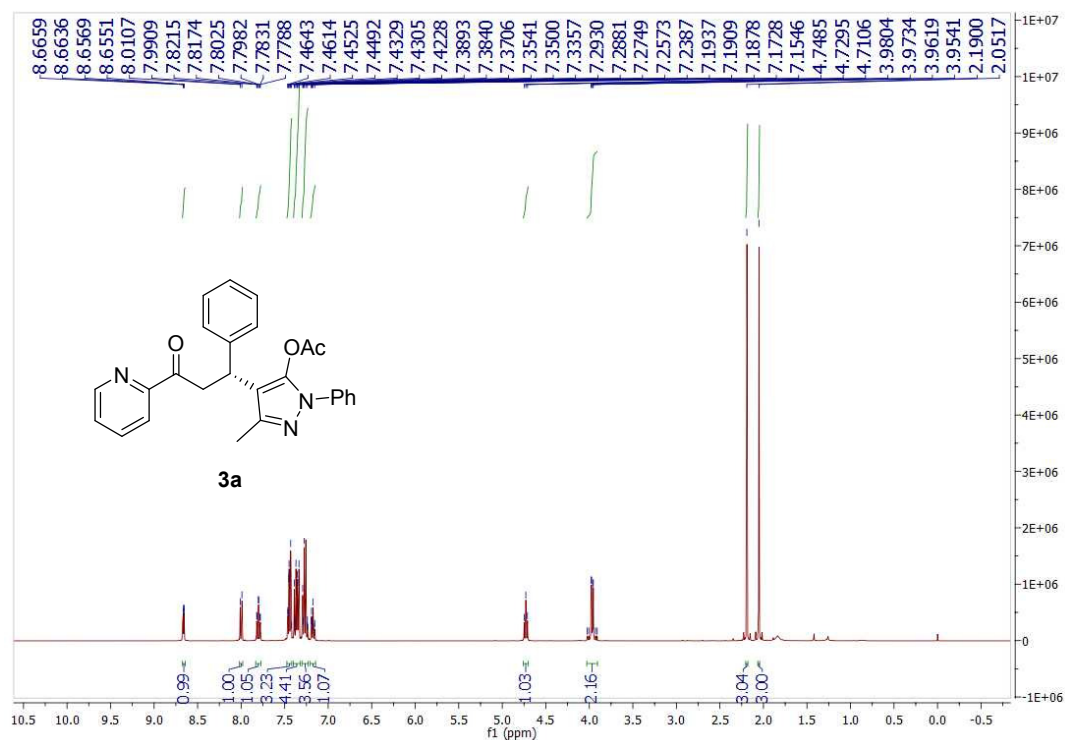
Vivek Sharma,^a Anmolpreet Kaur,^a Subash Chandra Sahoo,^b and Swapandeep Singh Chimni^{*a}

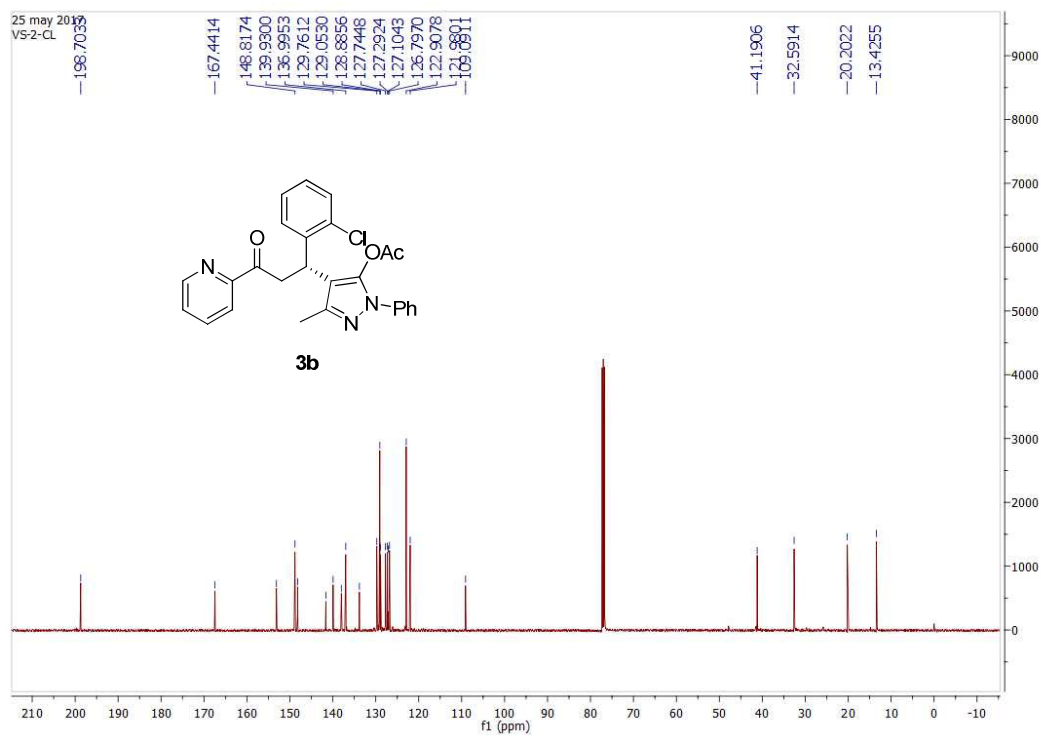
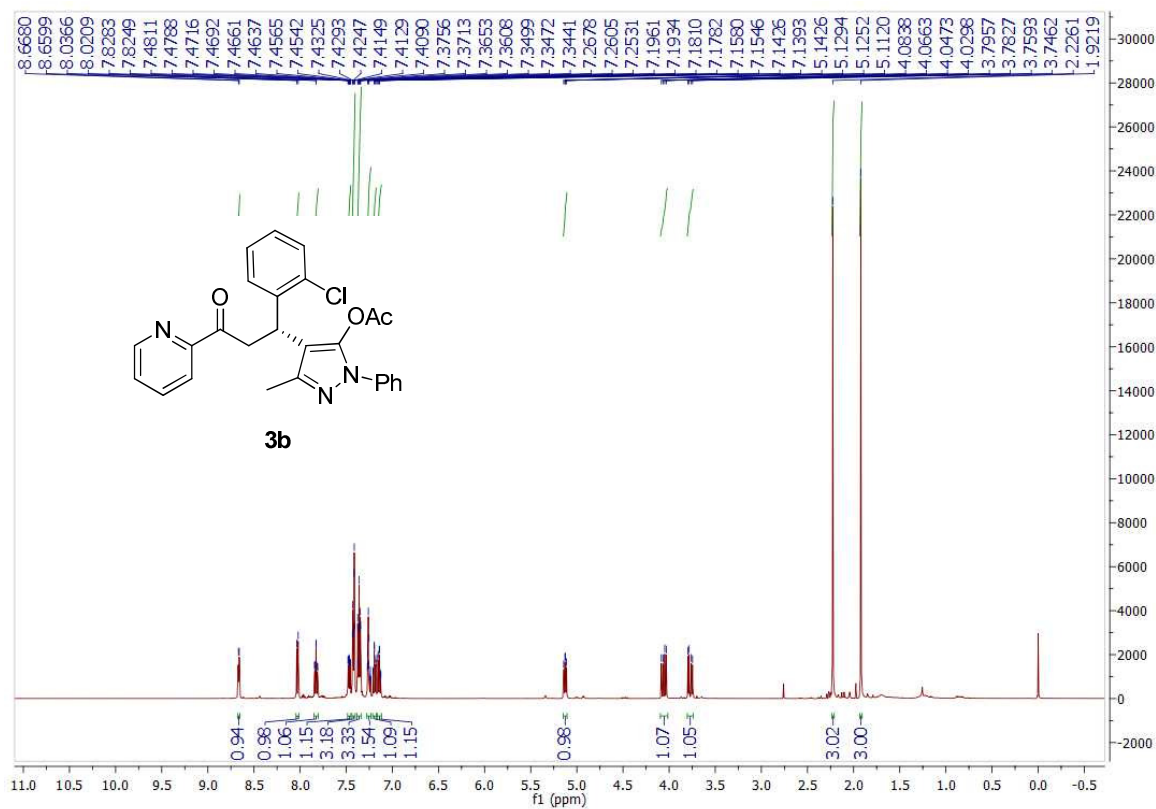
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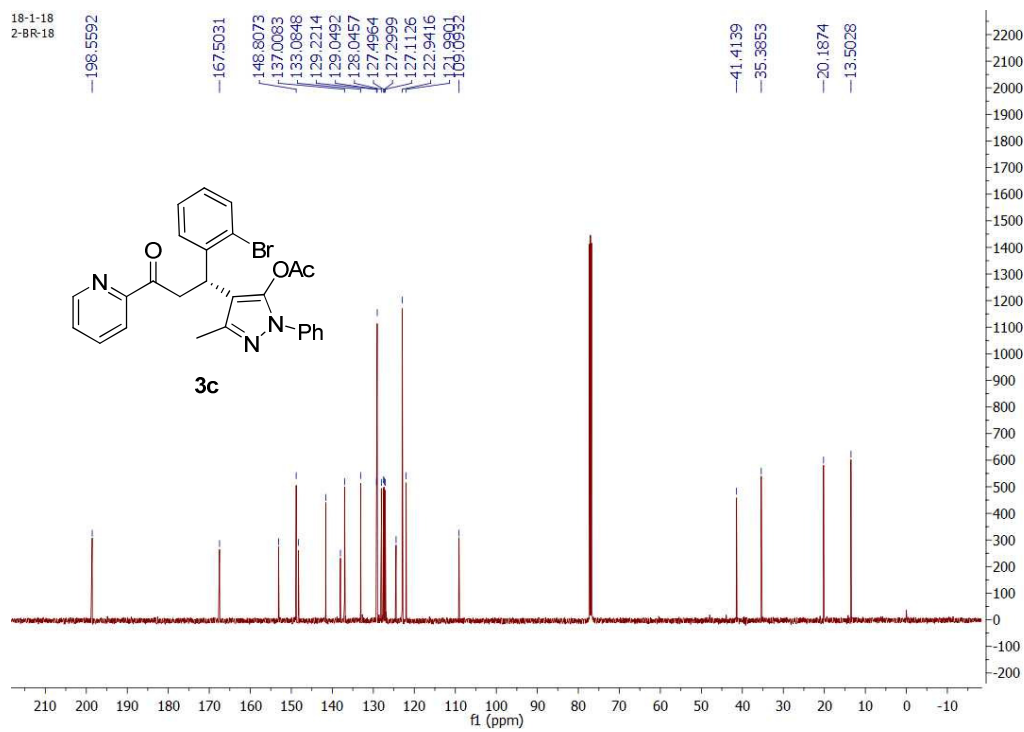
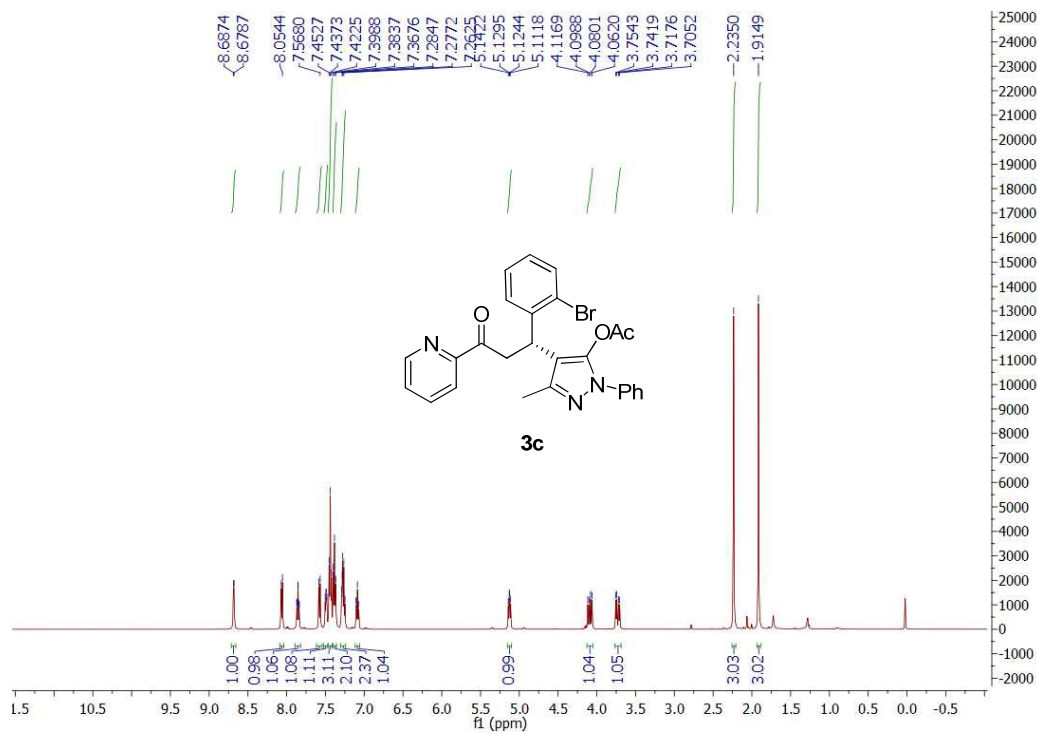
^b Department of Chemistry and Center of Advanced Studies in Chemistry, Panjab University, Chandigarh, 160014, E-mail : subash.chem@gmail.com

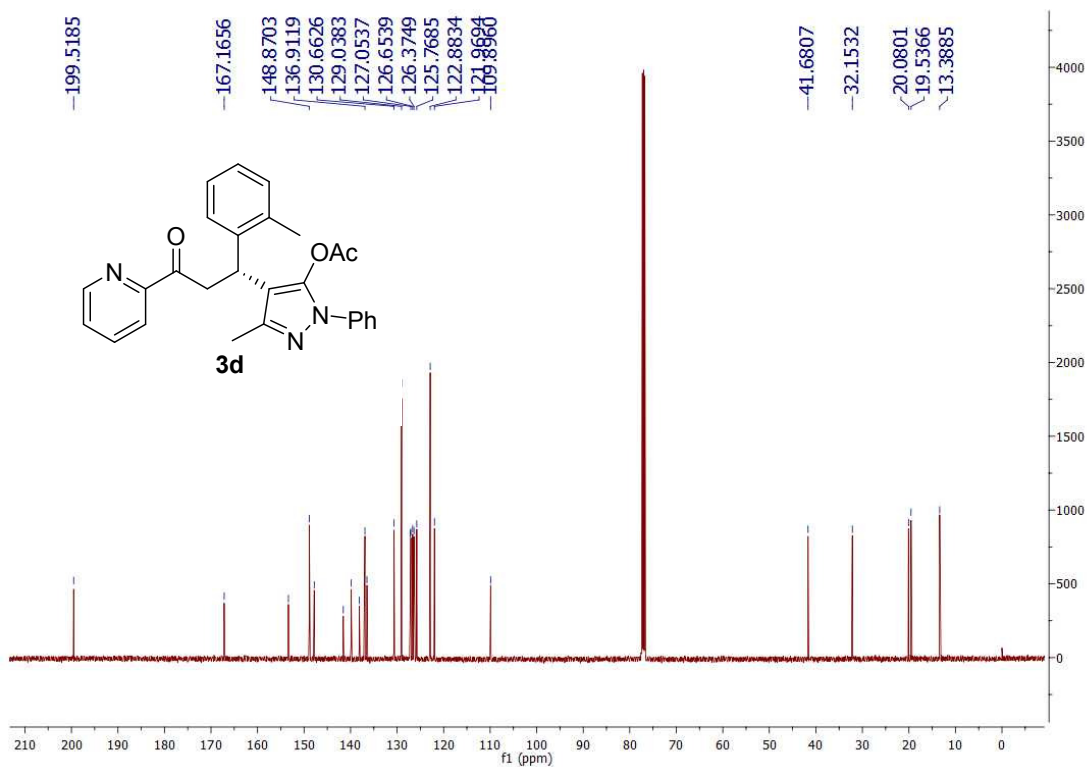
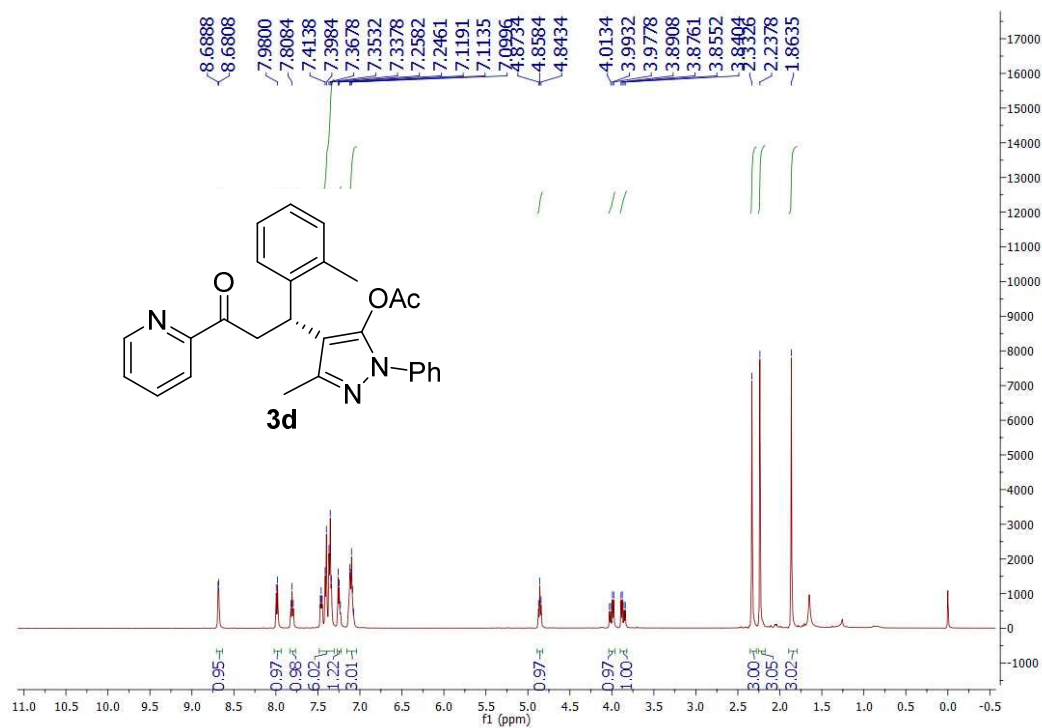
Table of content		
1.	NMR spectra of 3	2-25
2.	HPLC chromatograms of 3	26-49
3.	Single crystal X-ray diffraction of 3s	50-51

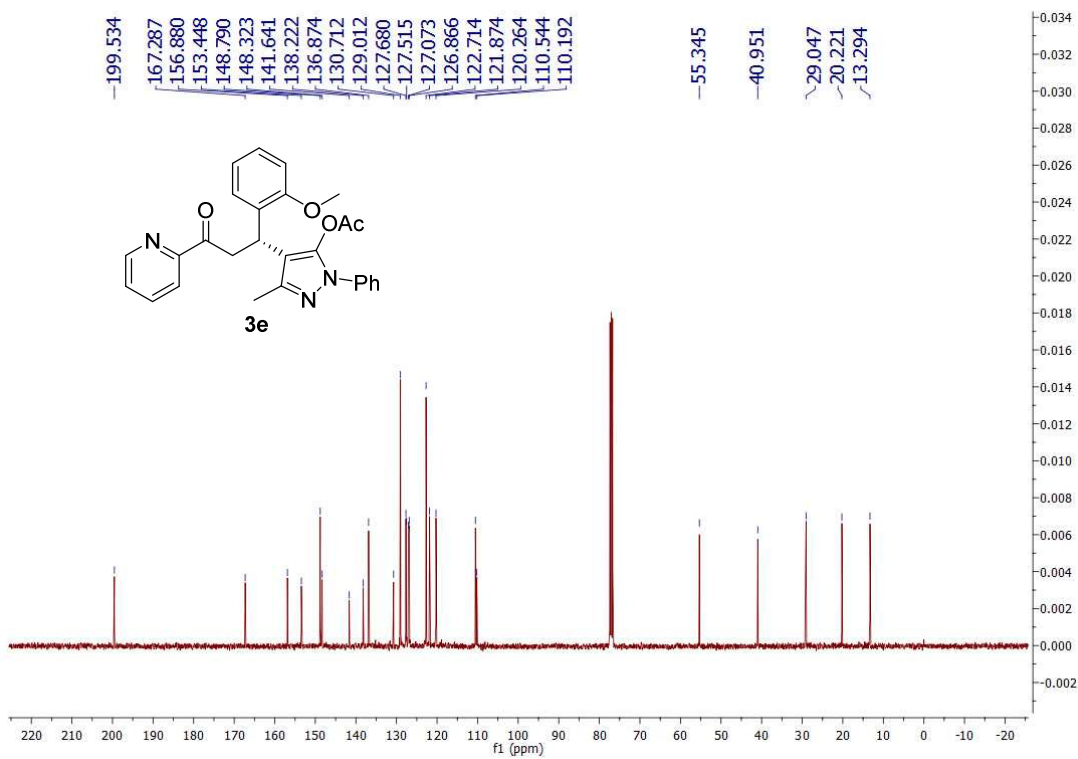
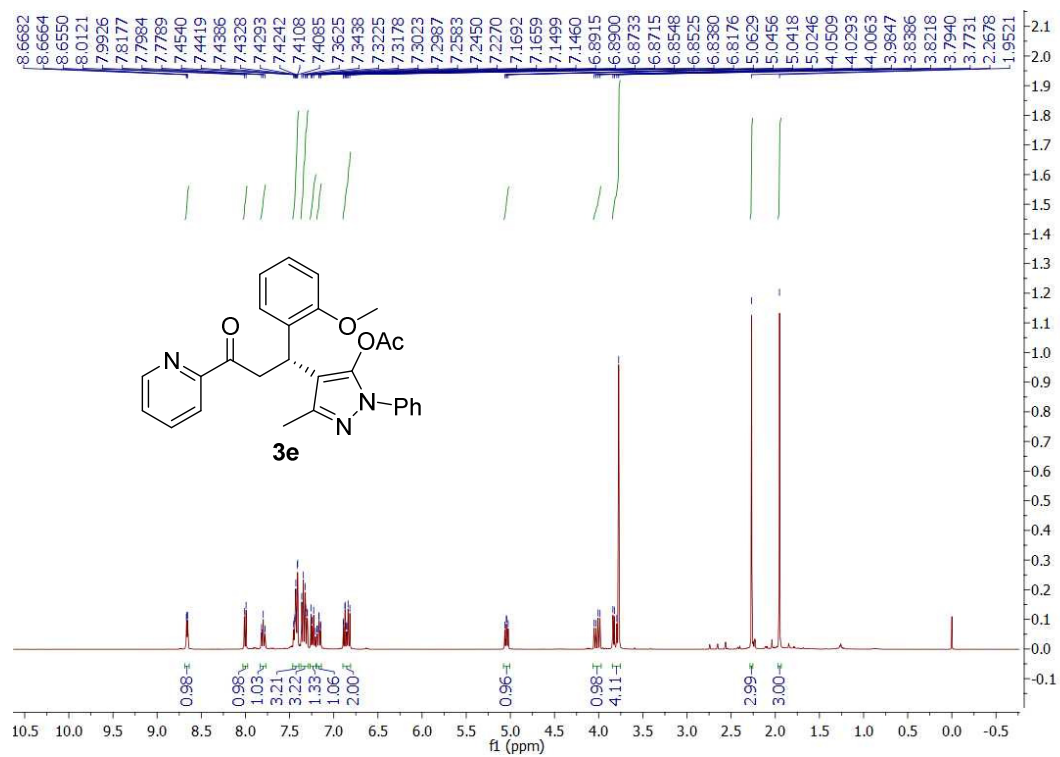
1. NMR Spectra of Compounds **3**

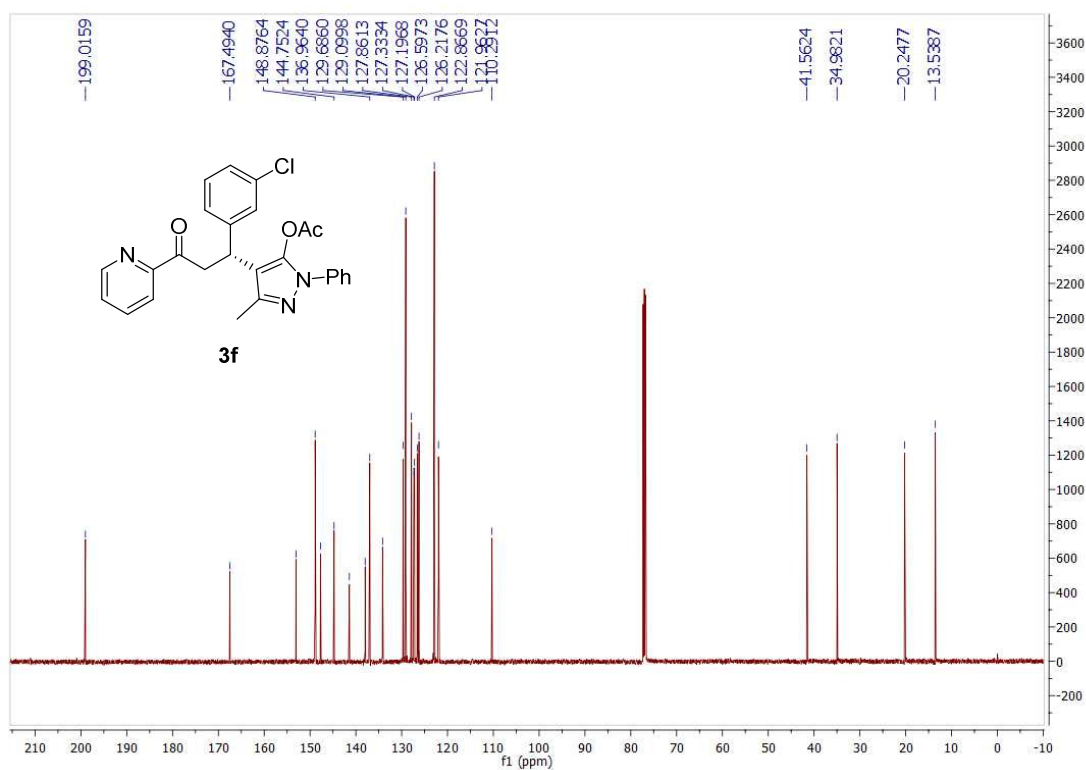
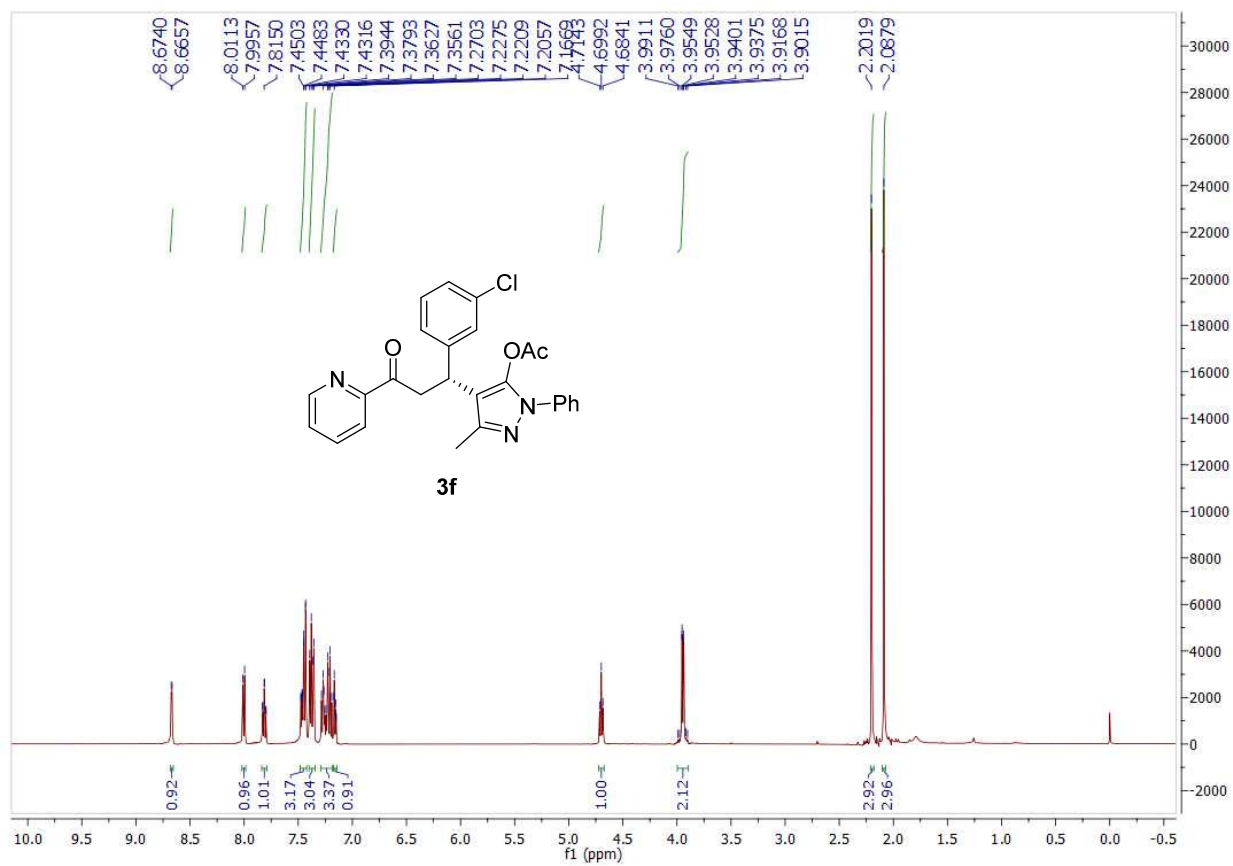


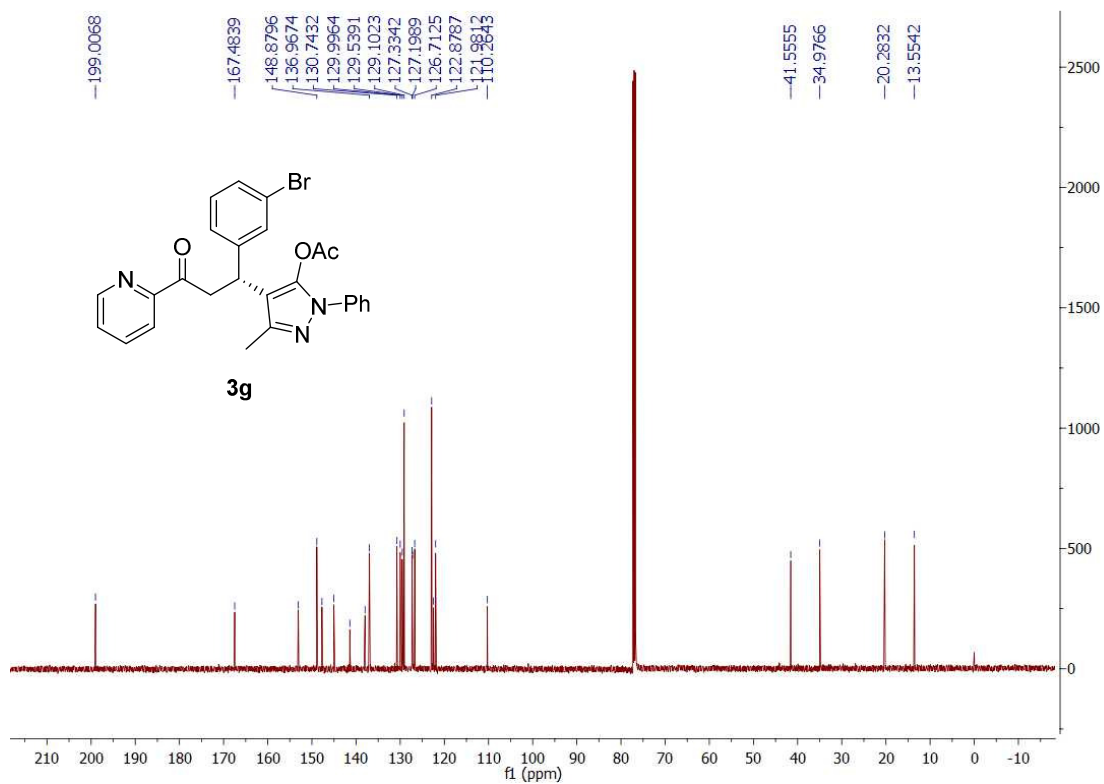
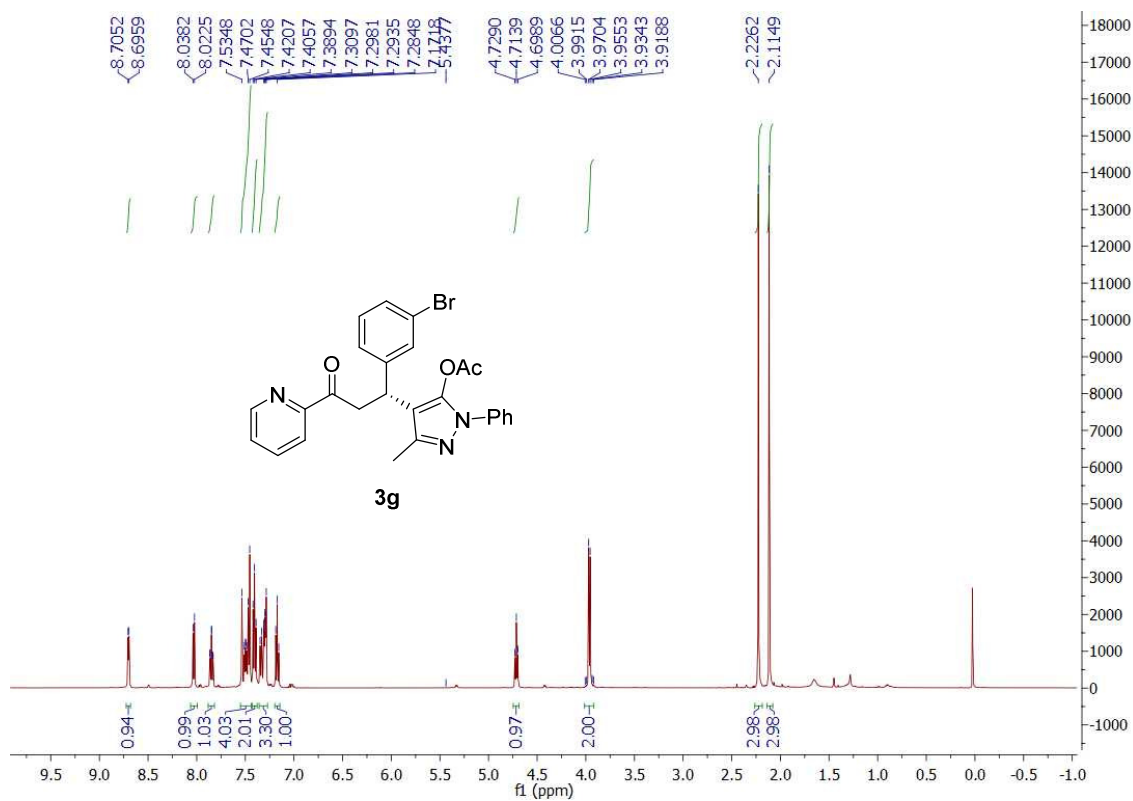


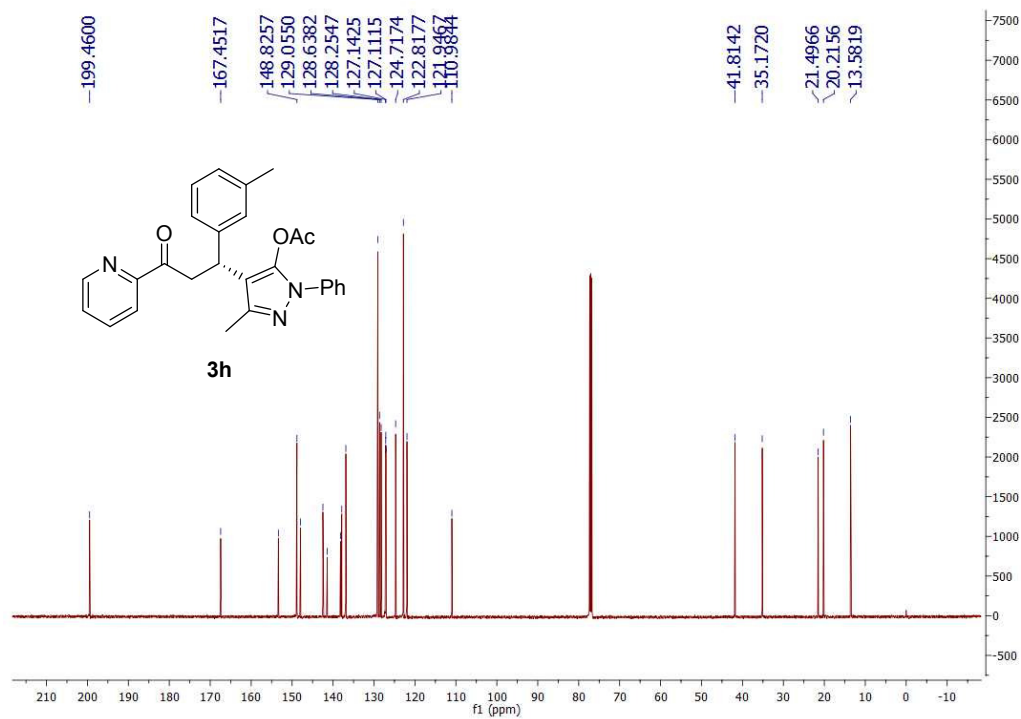
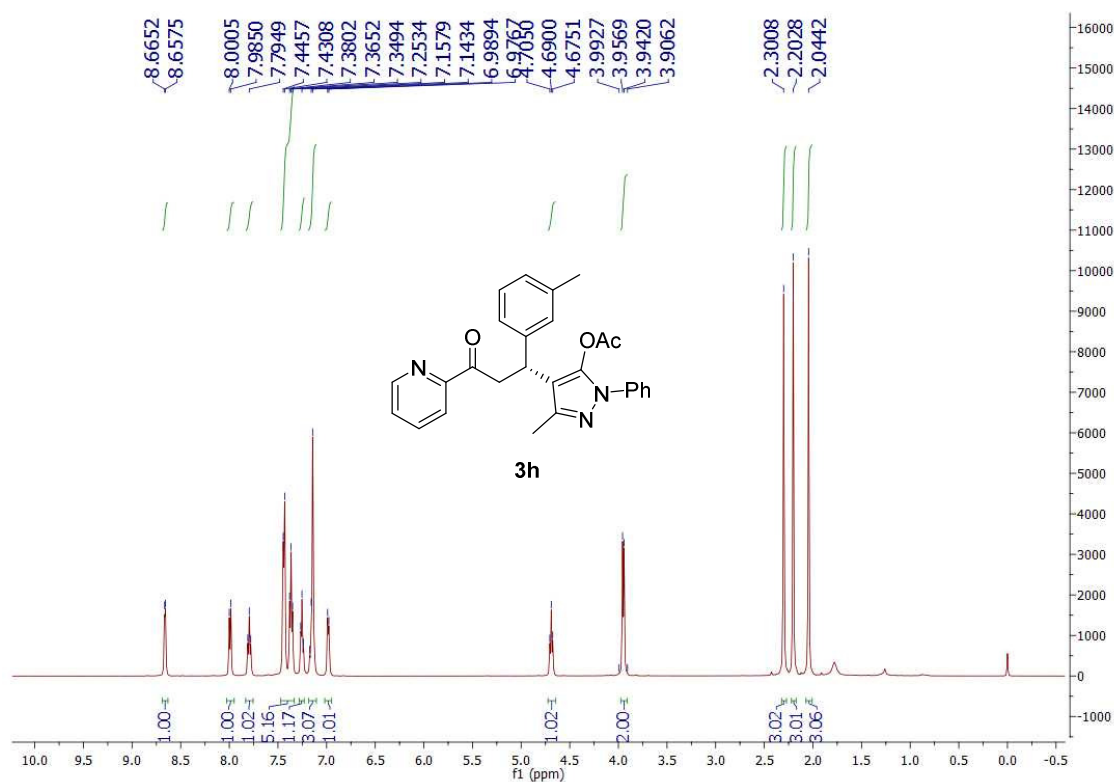


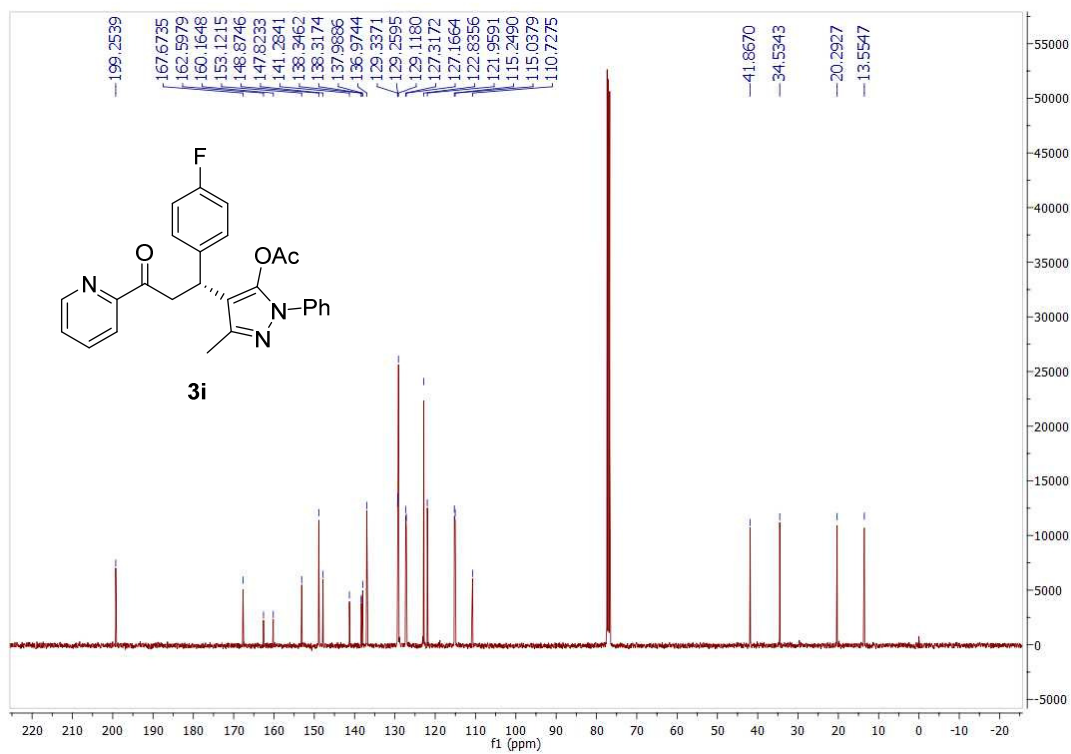
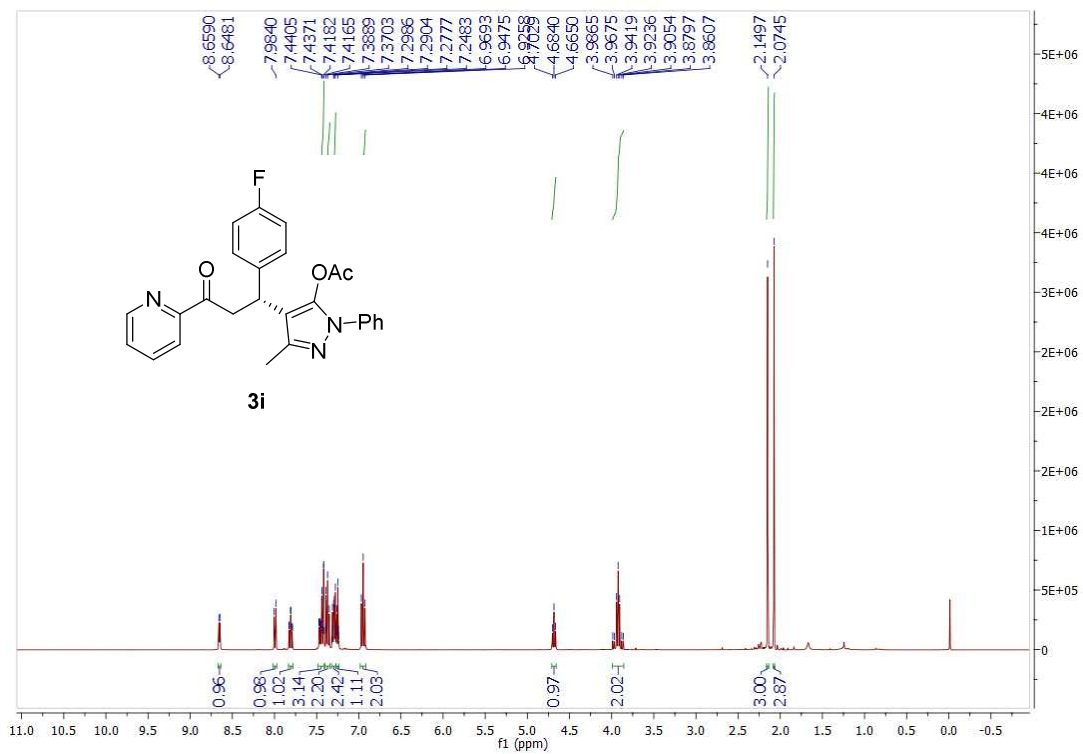


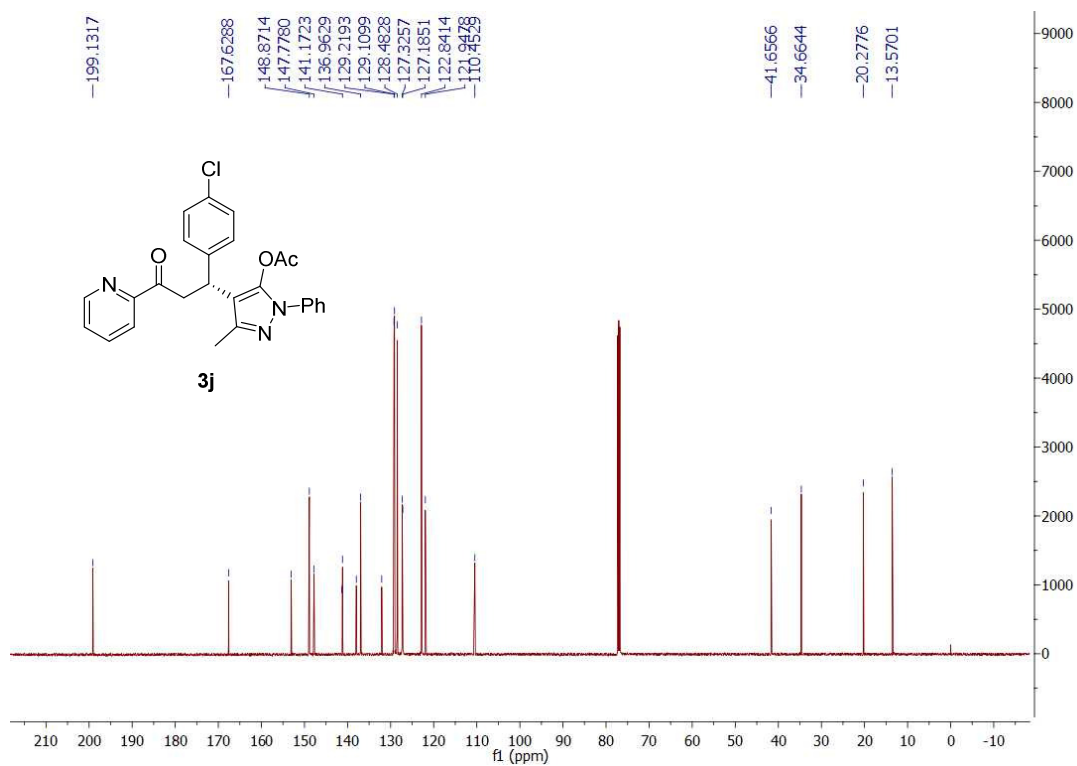
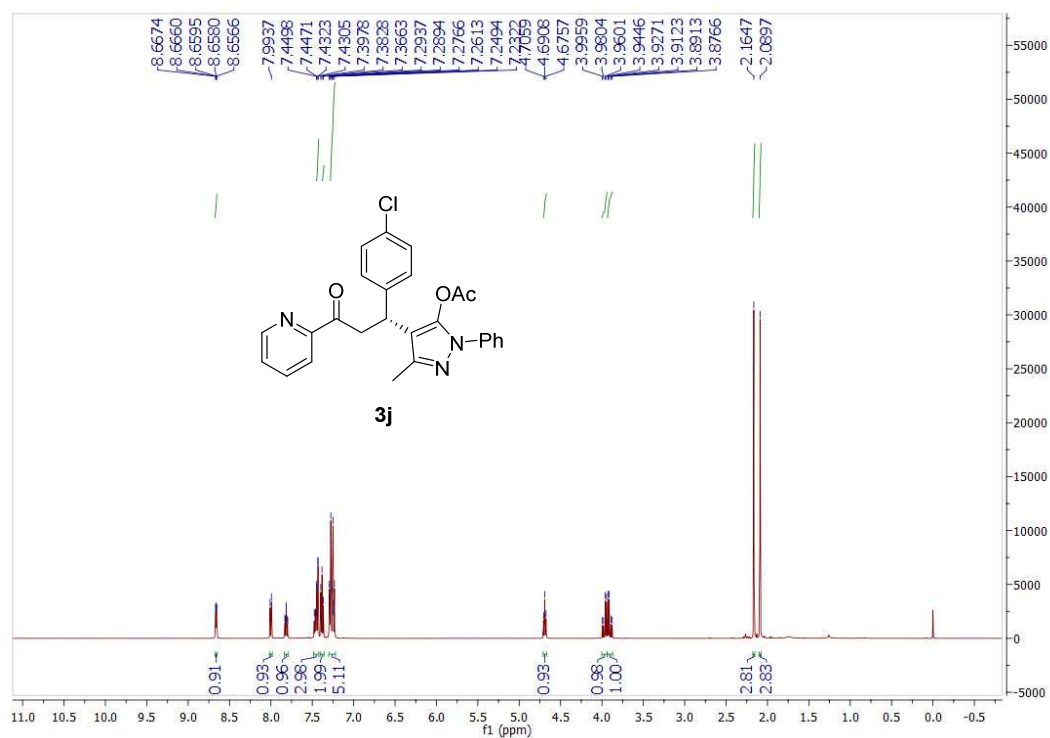


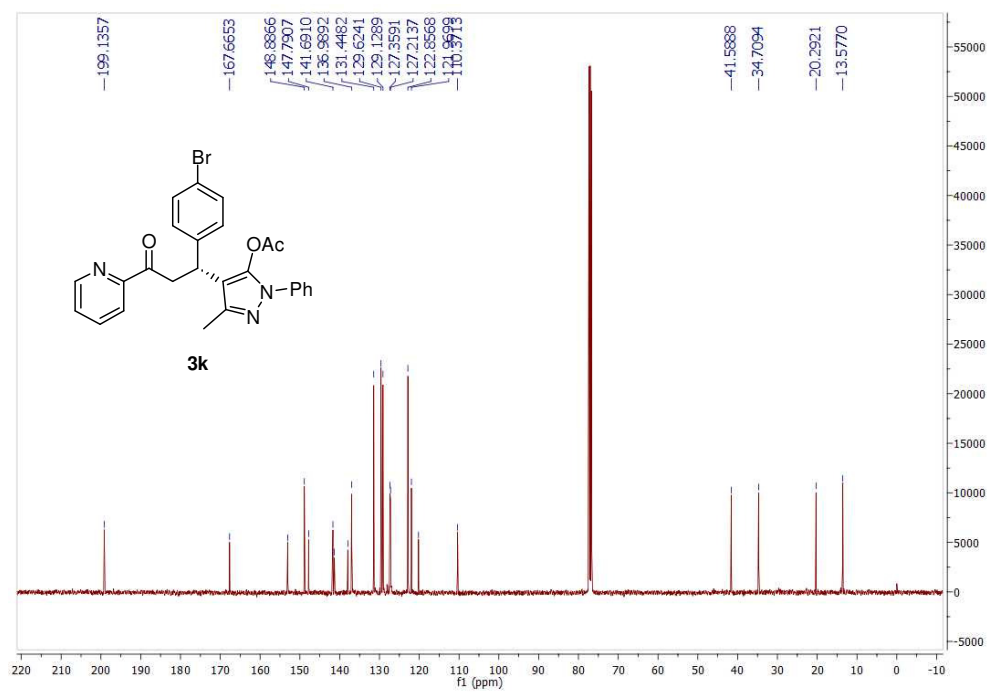
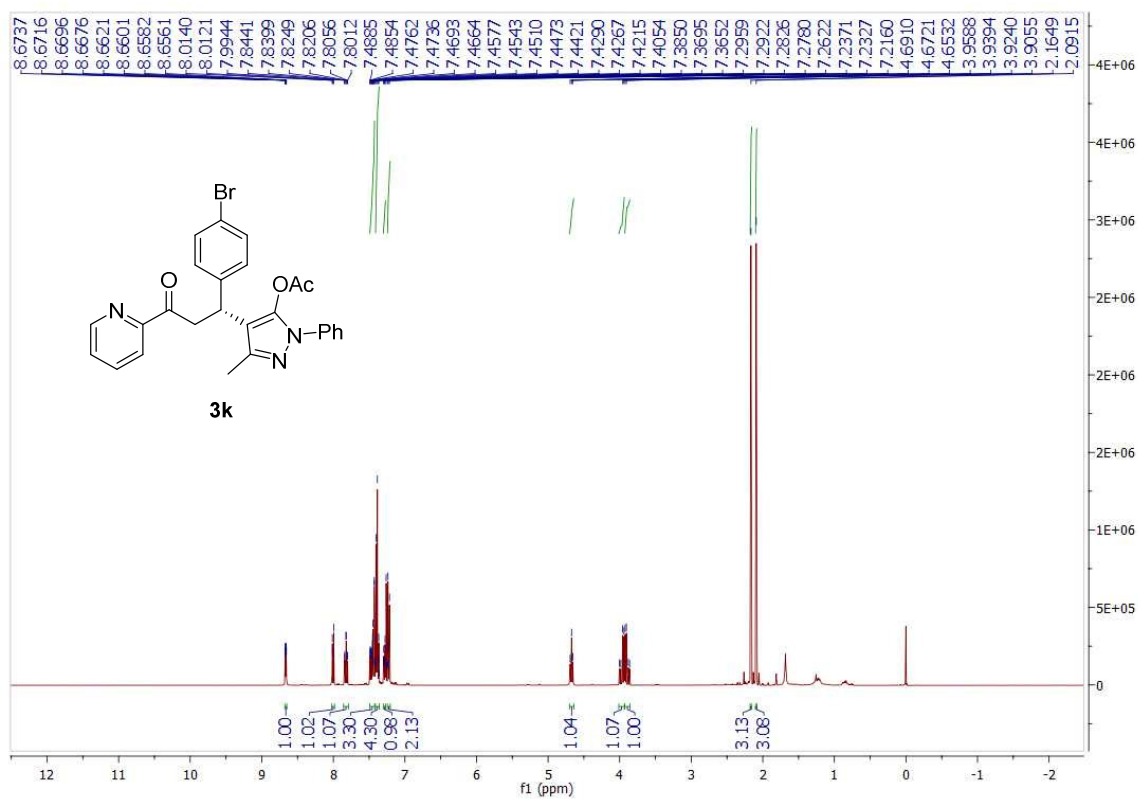


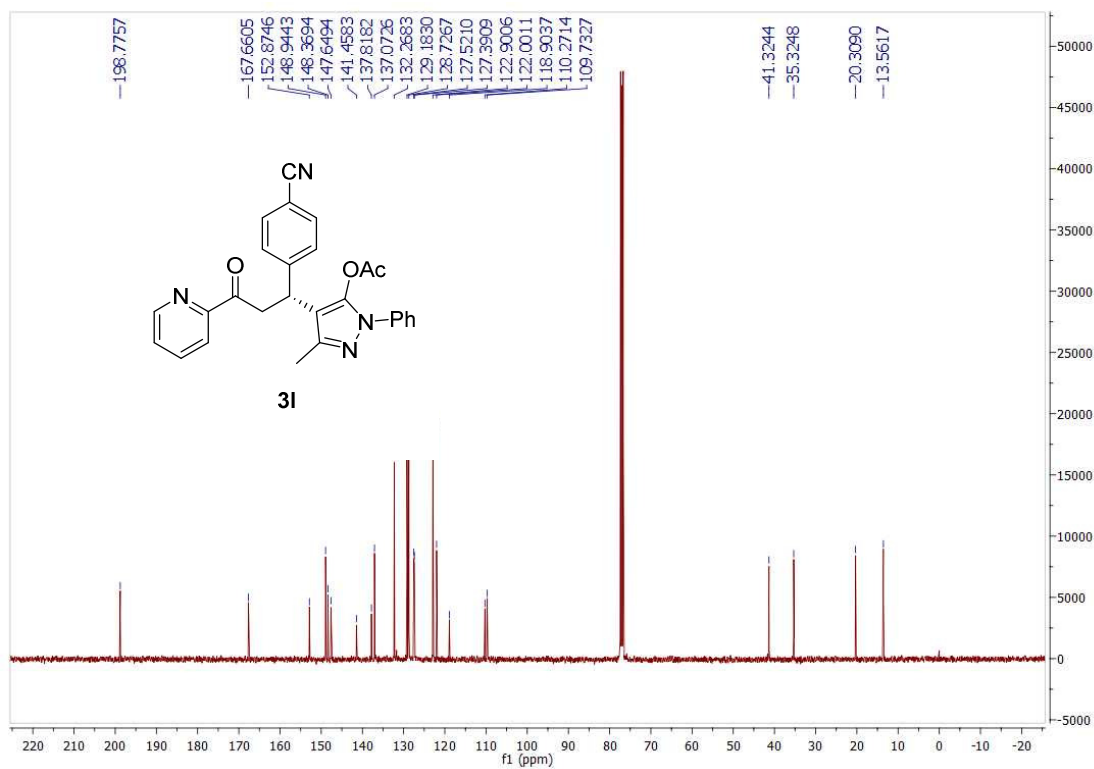
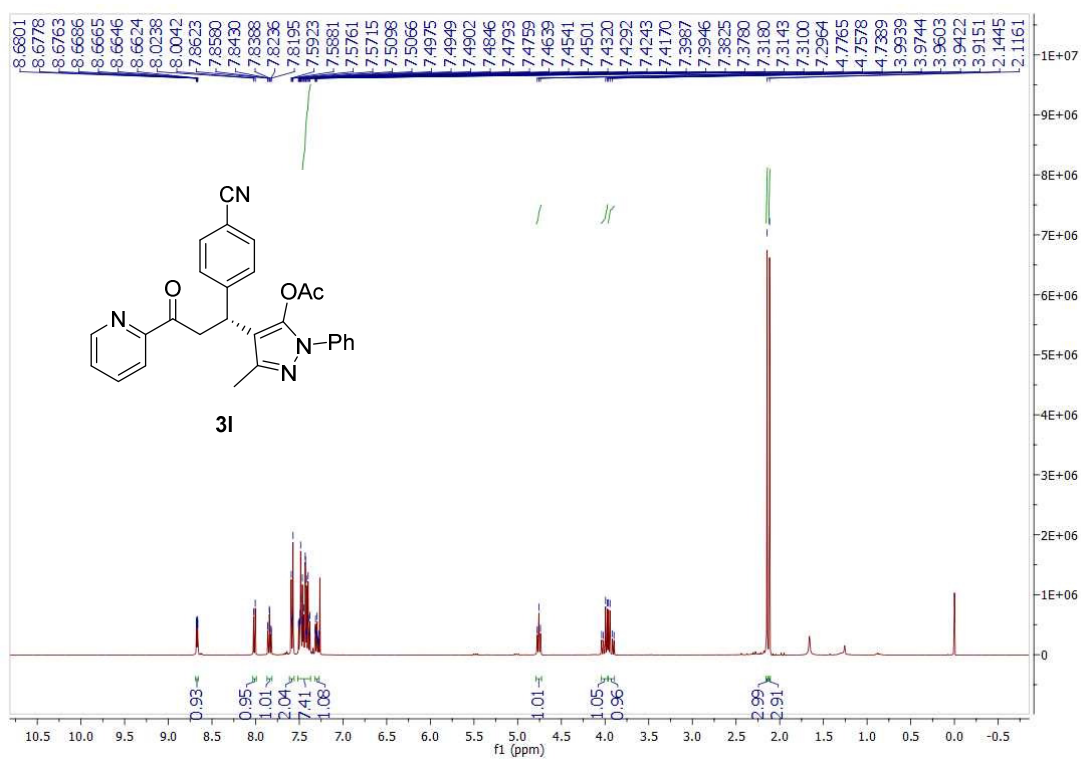


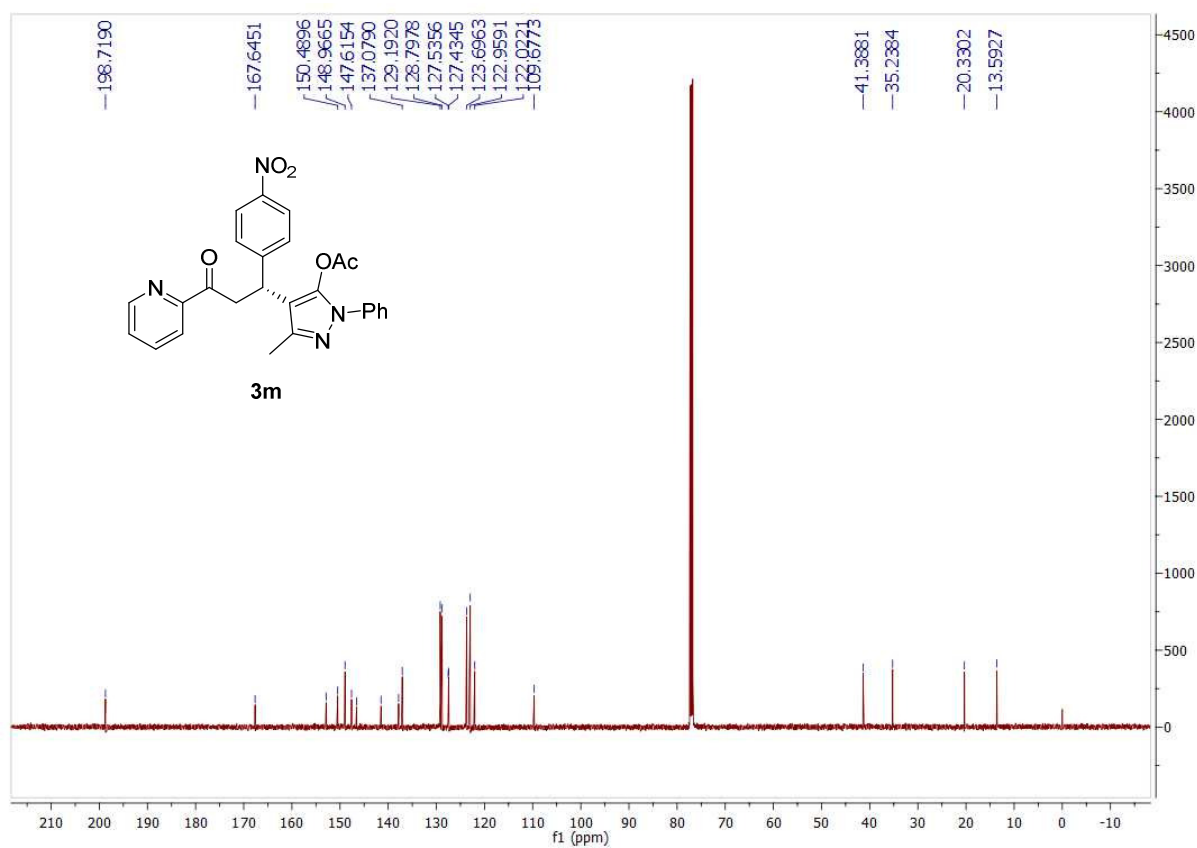
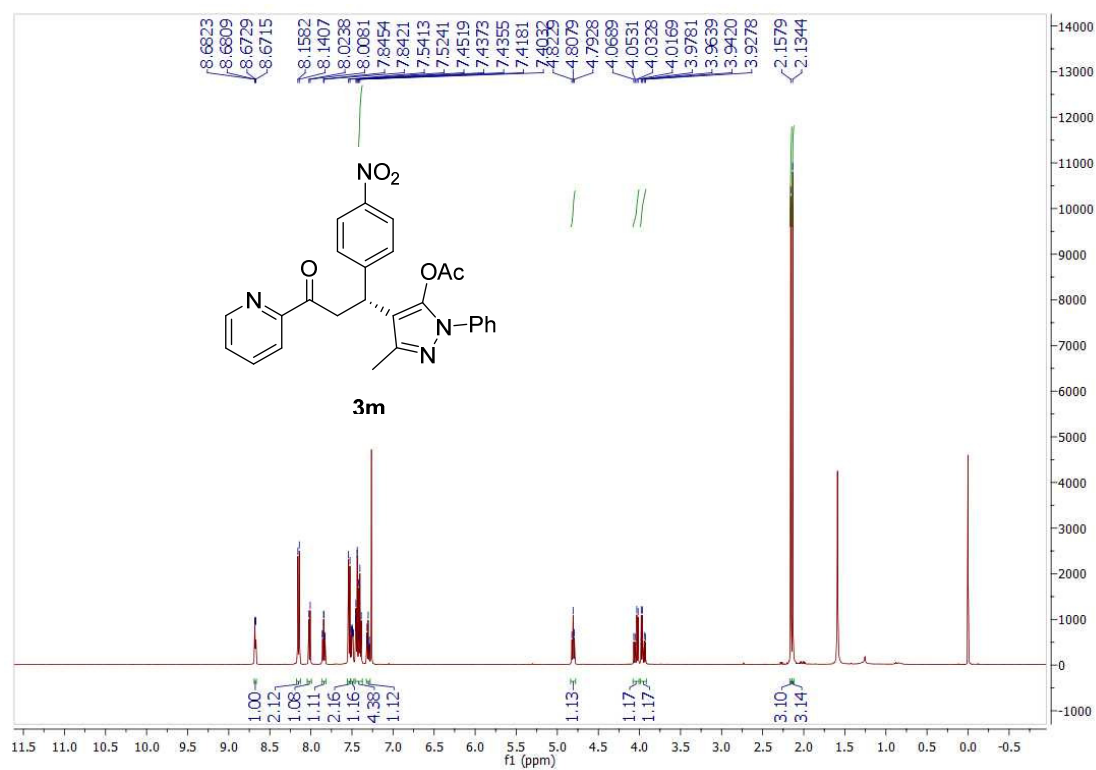


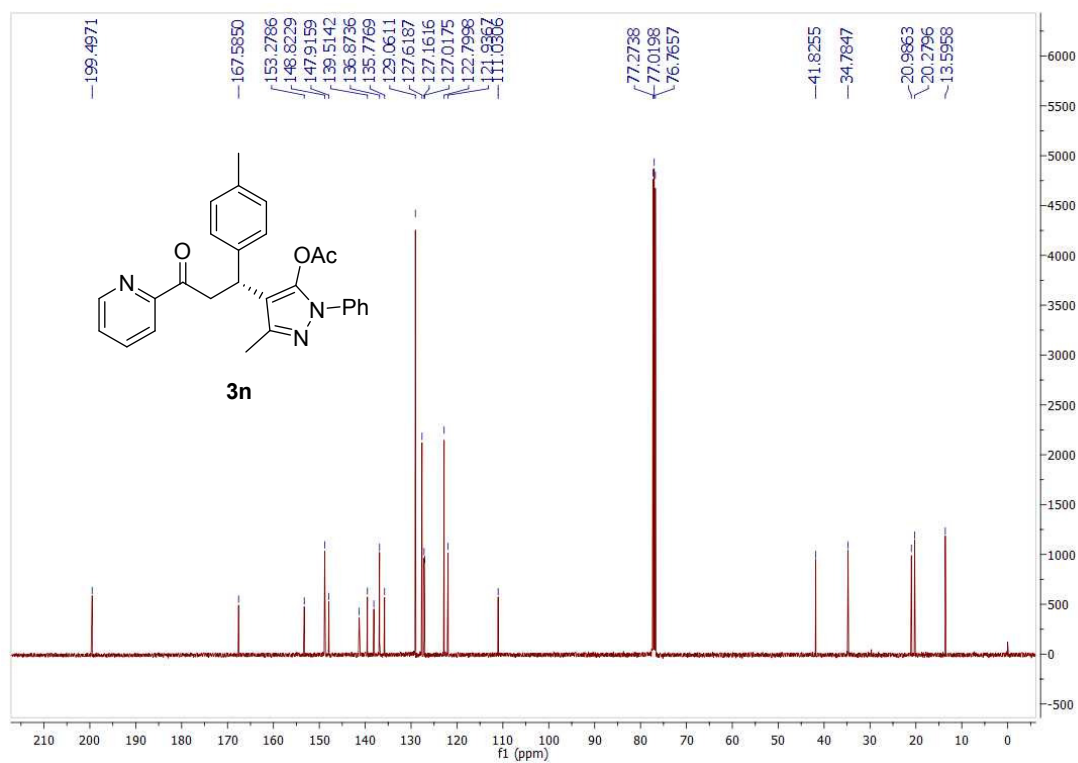
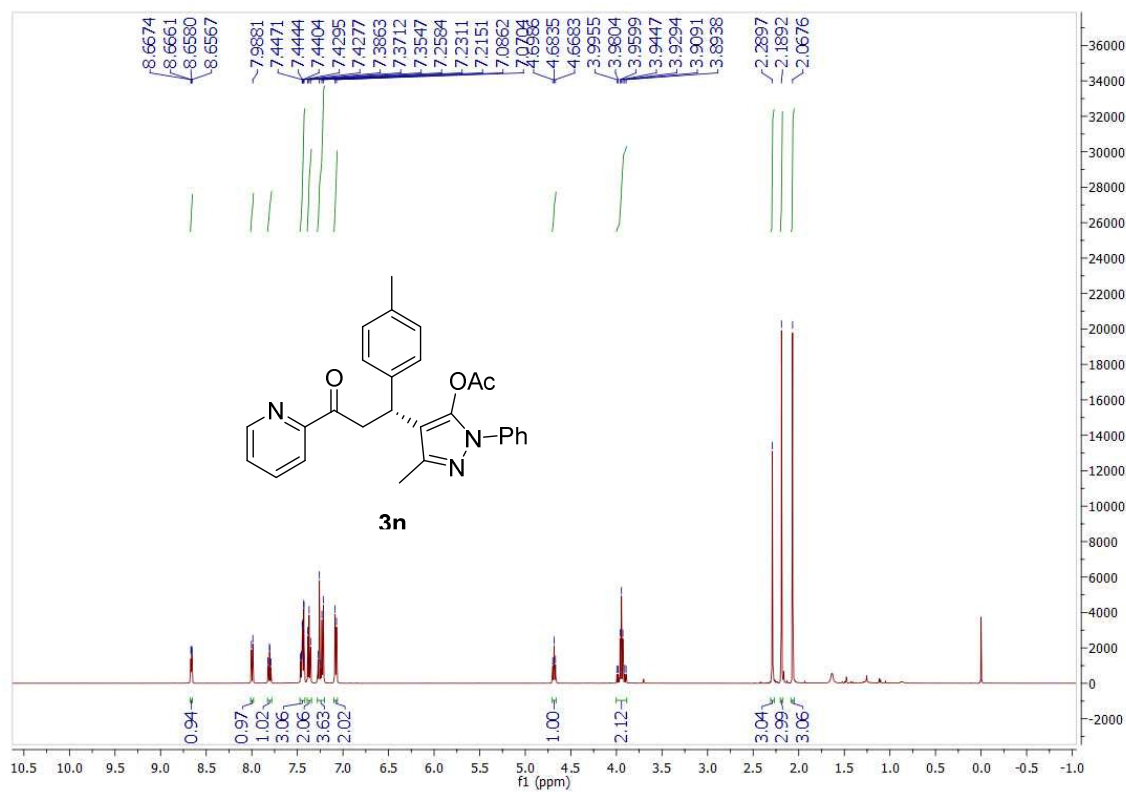


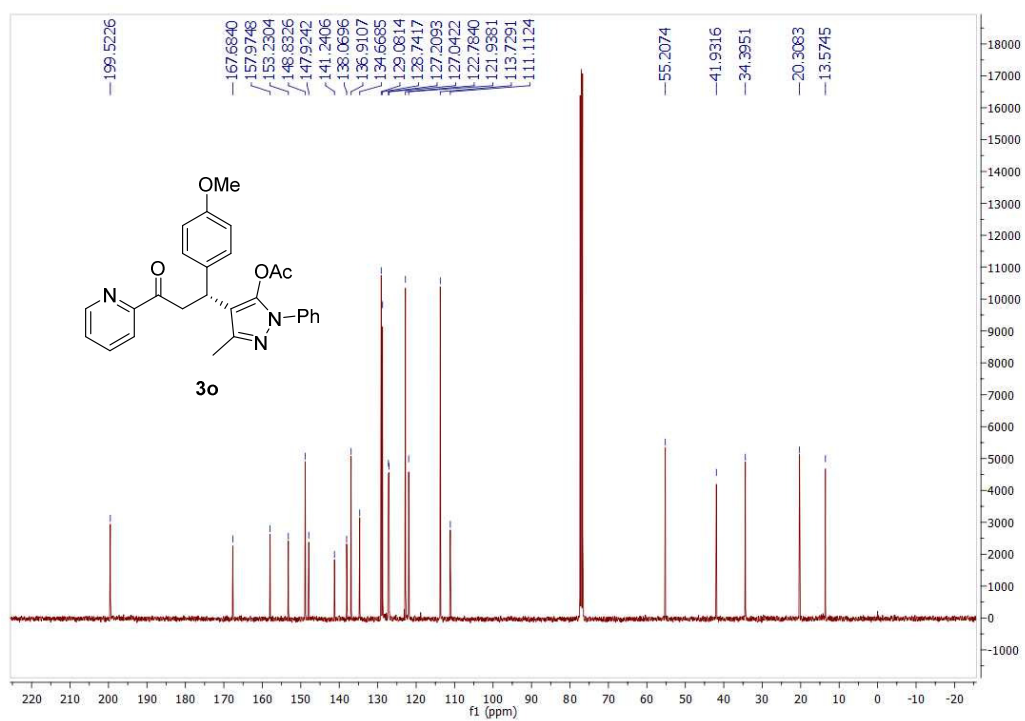
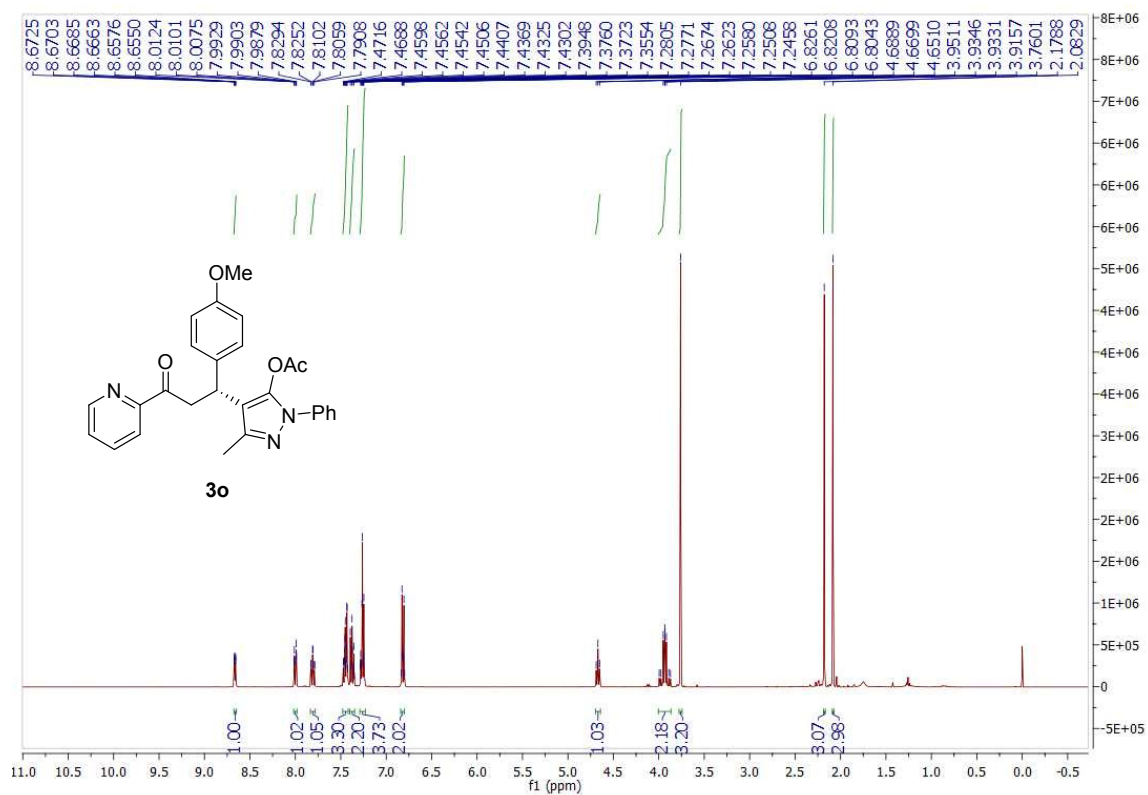




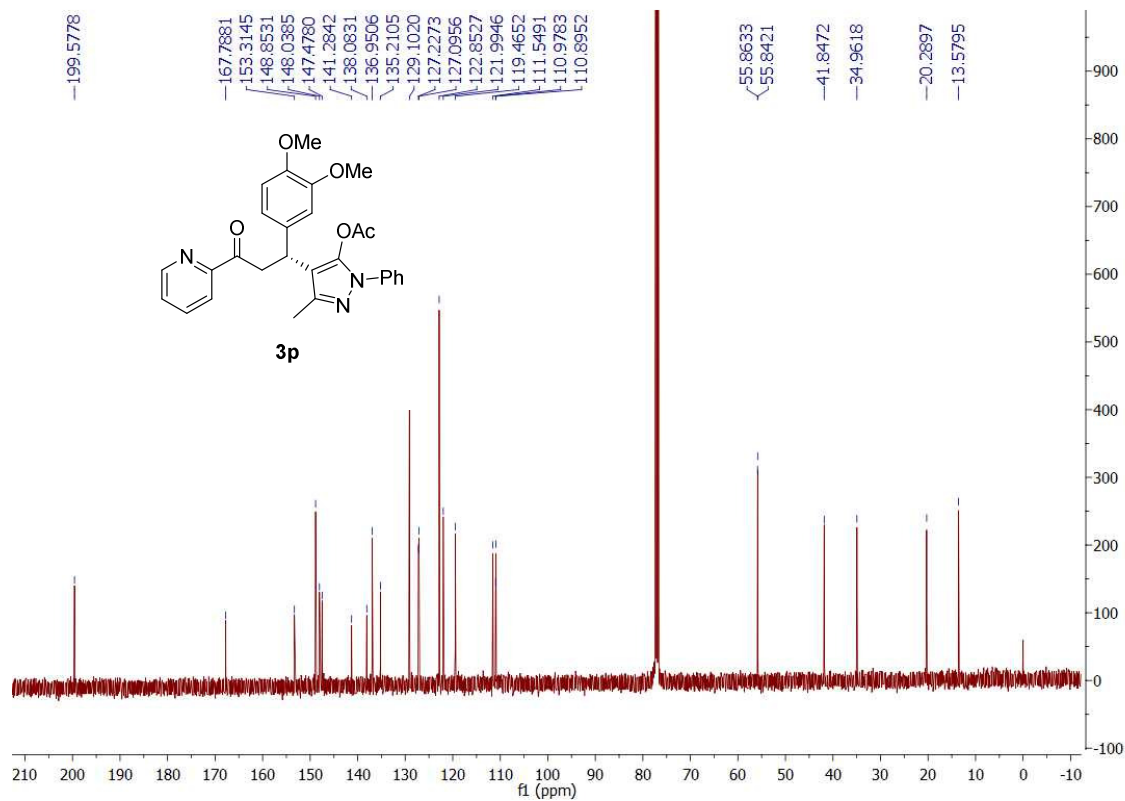
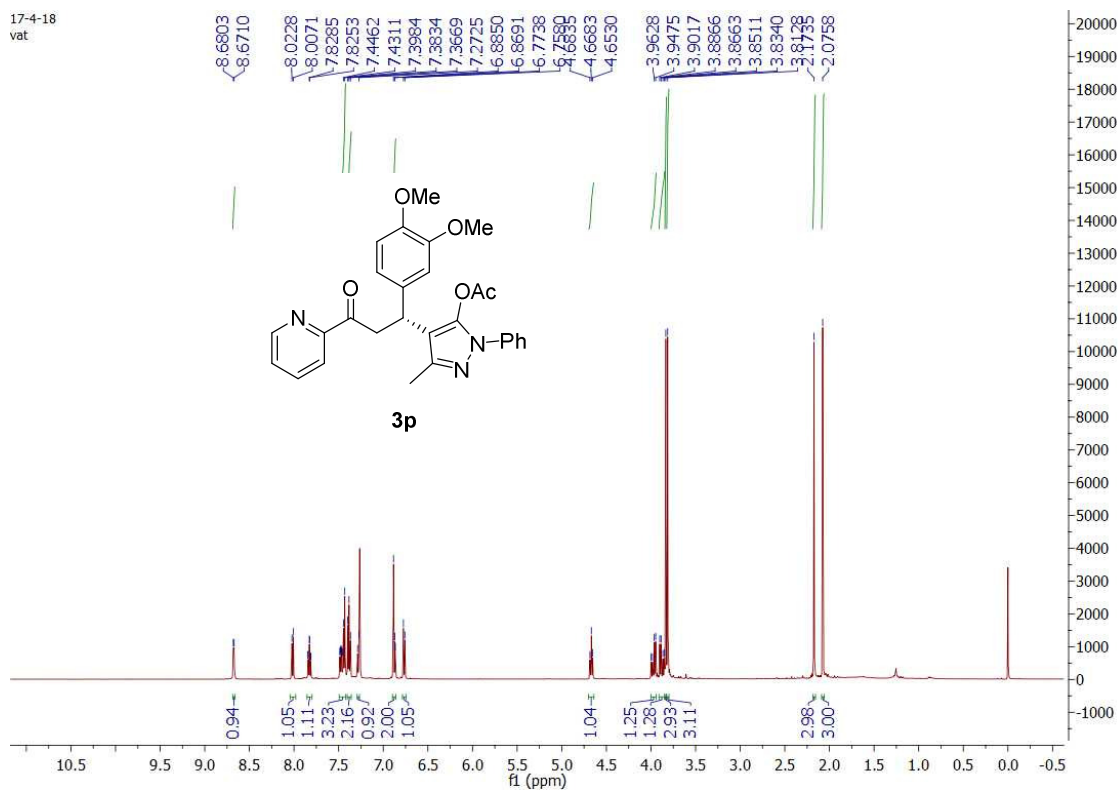


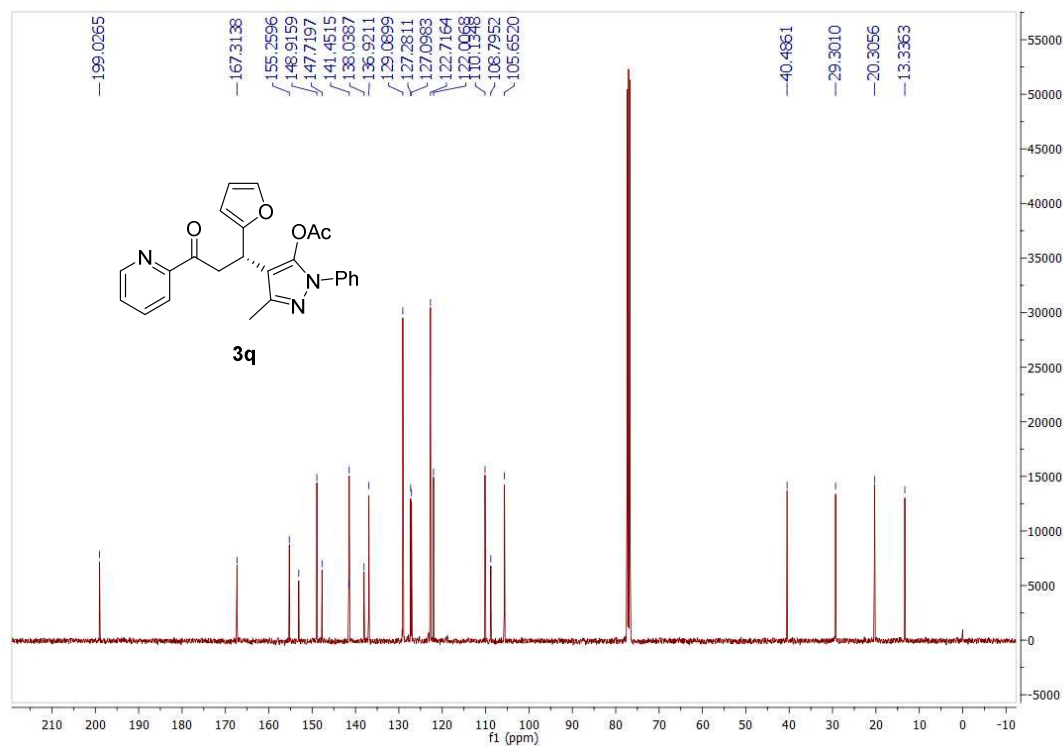
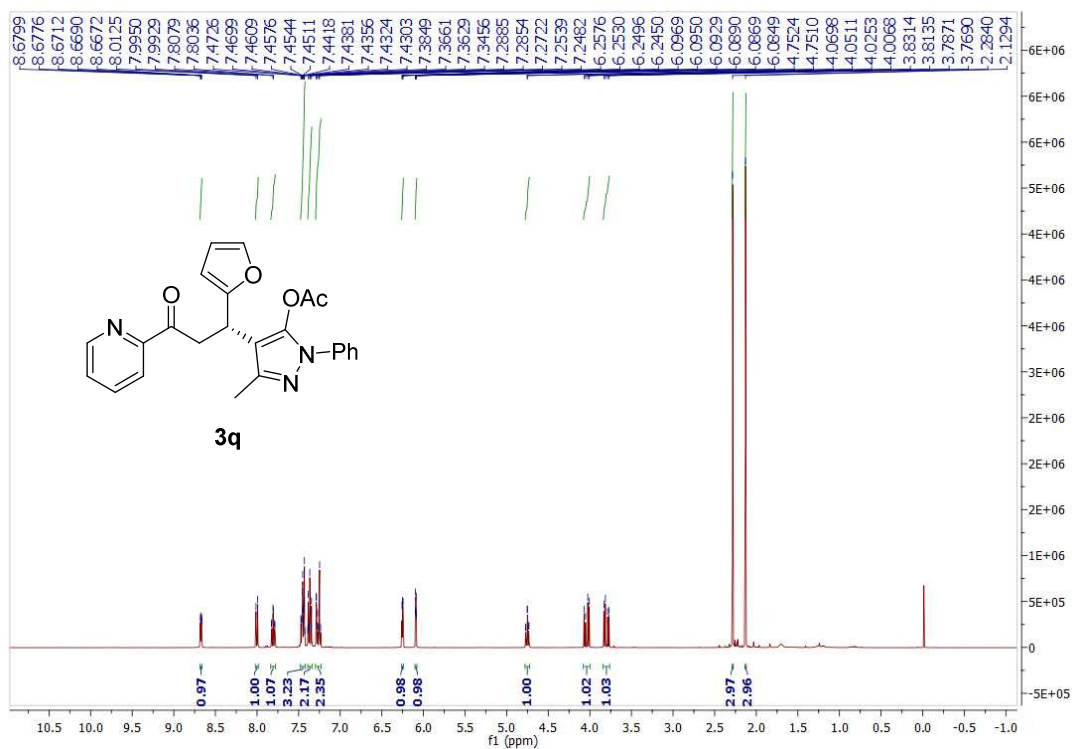


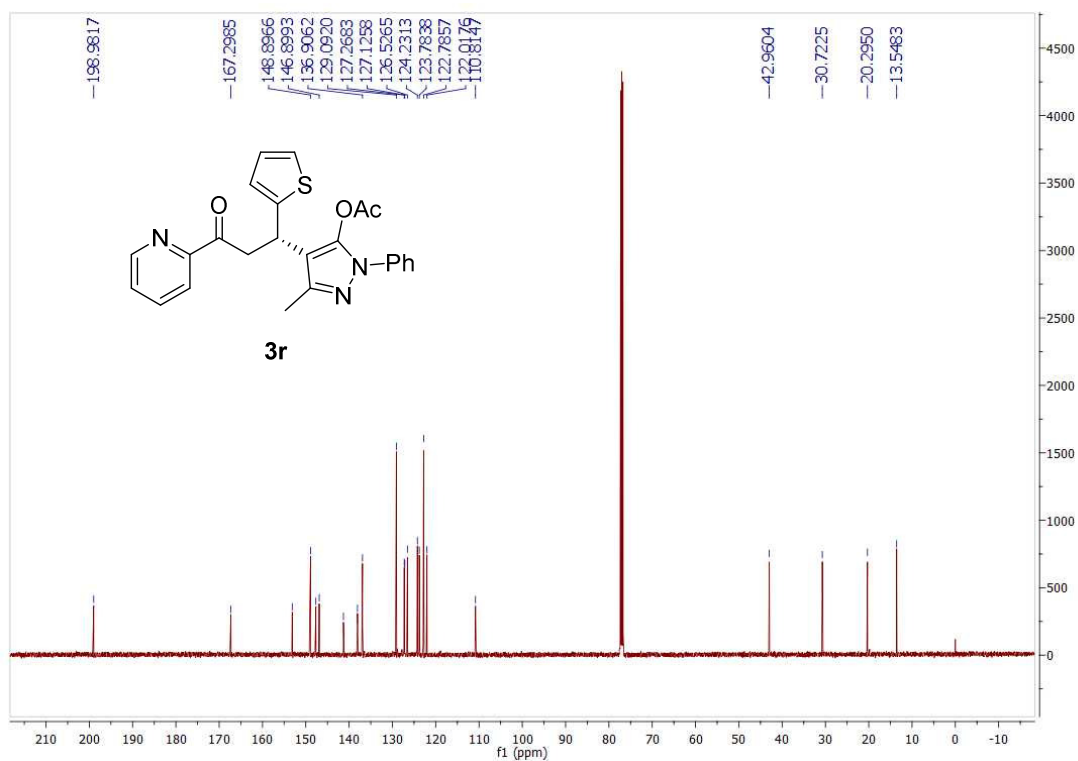
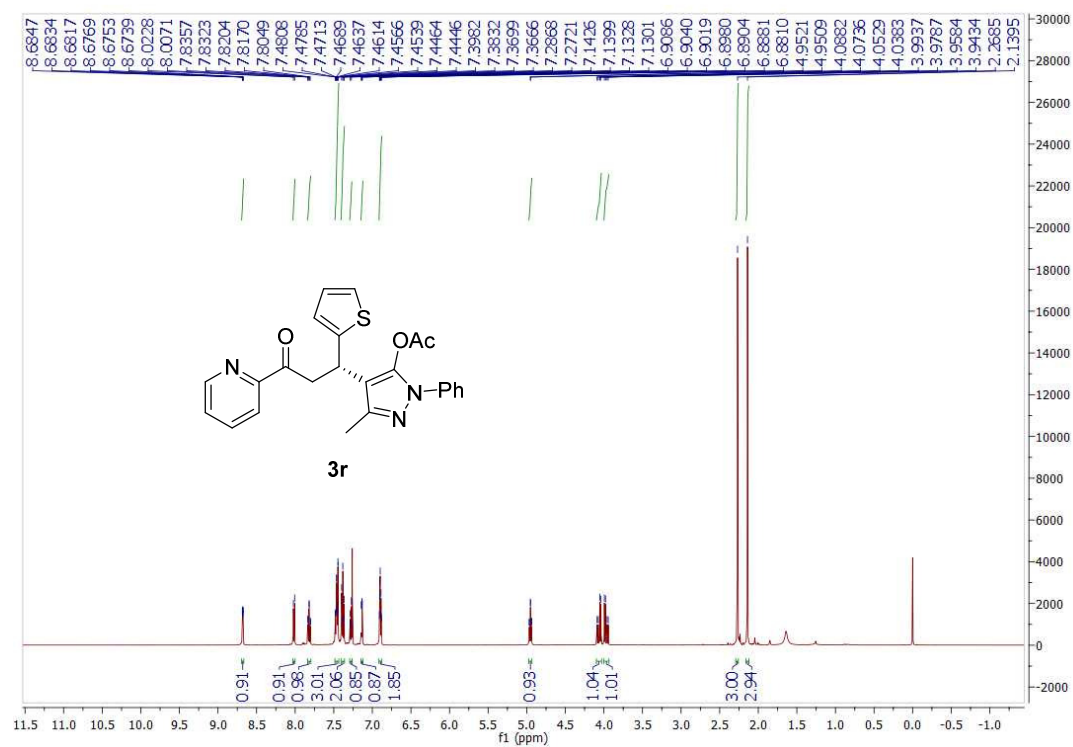


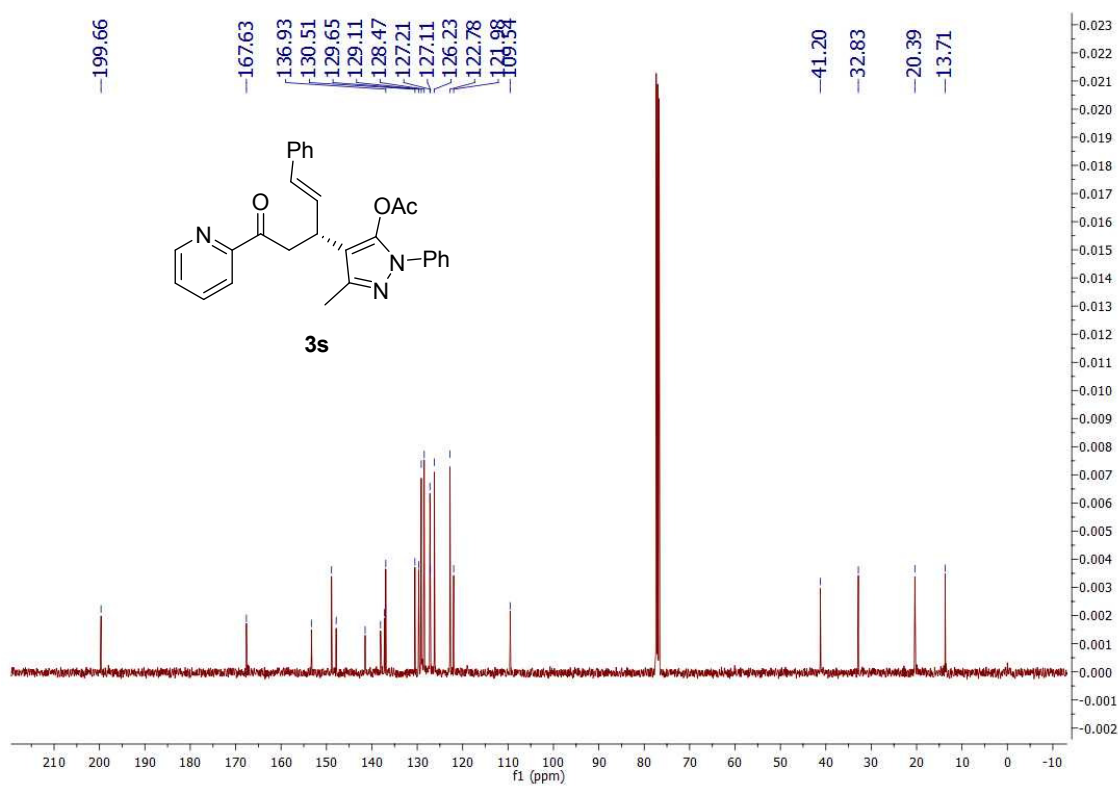
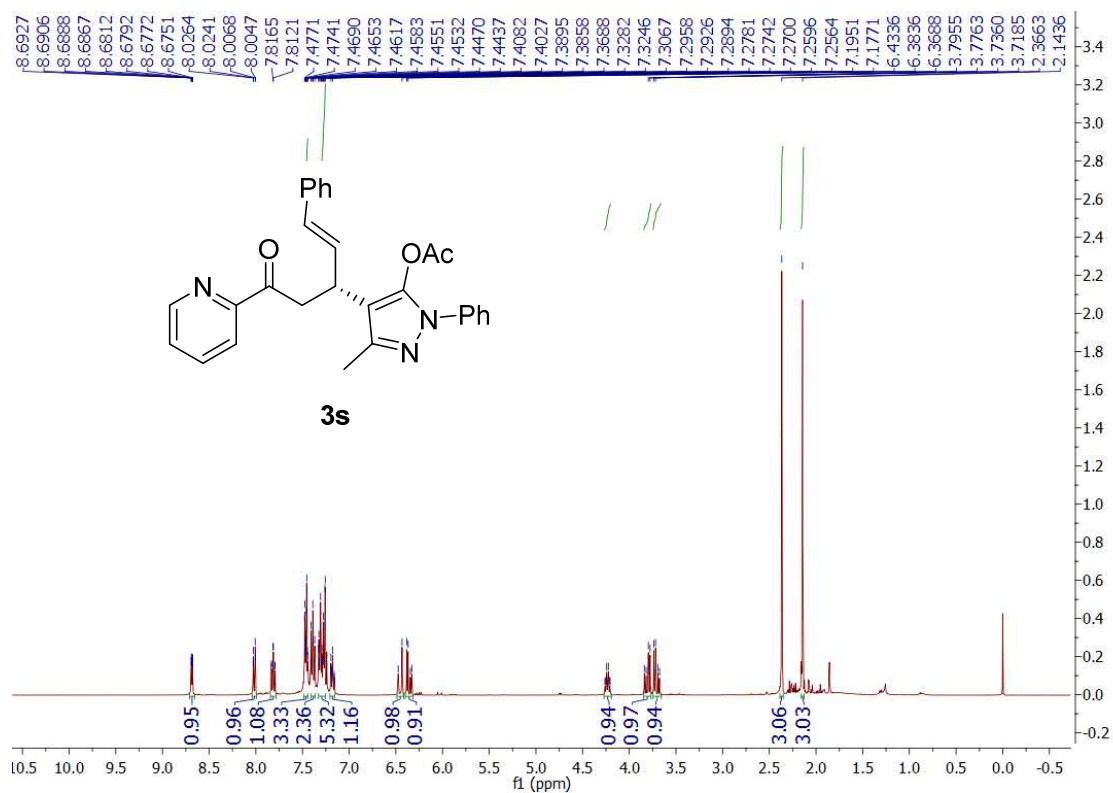


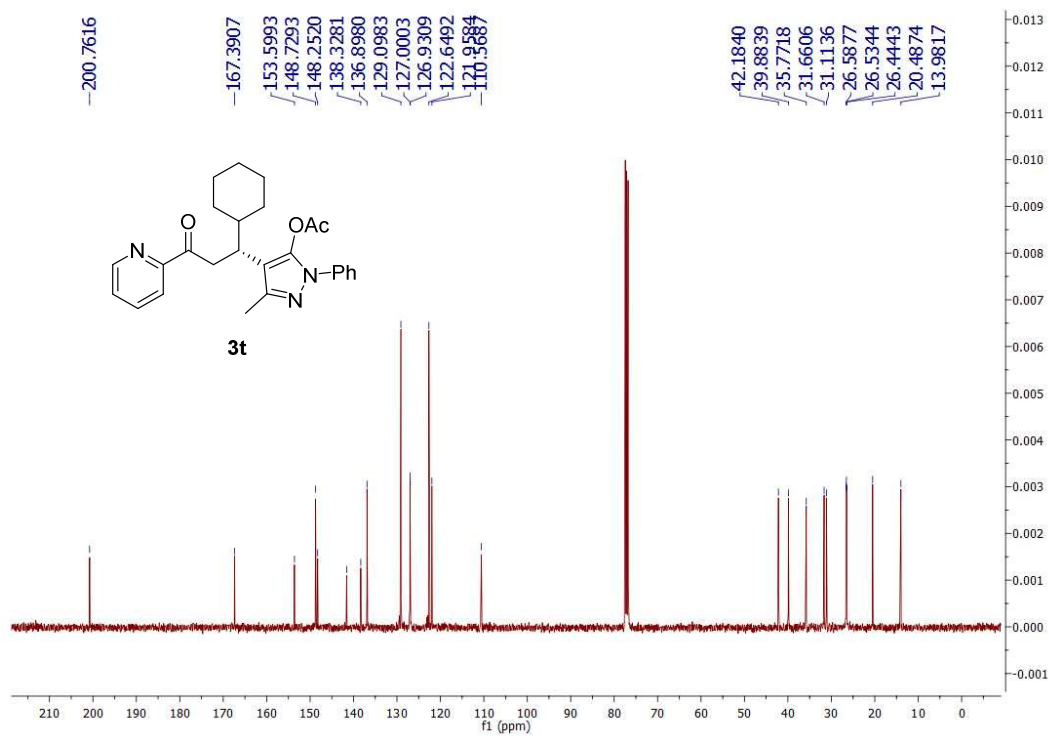
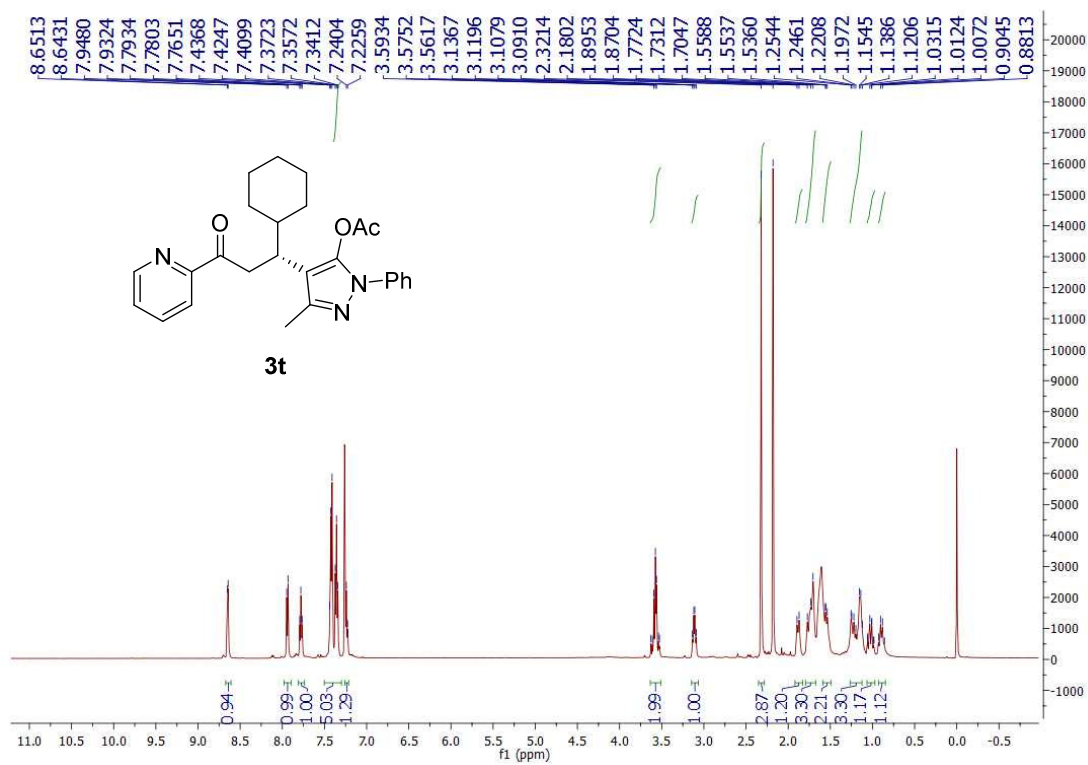
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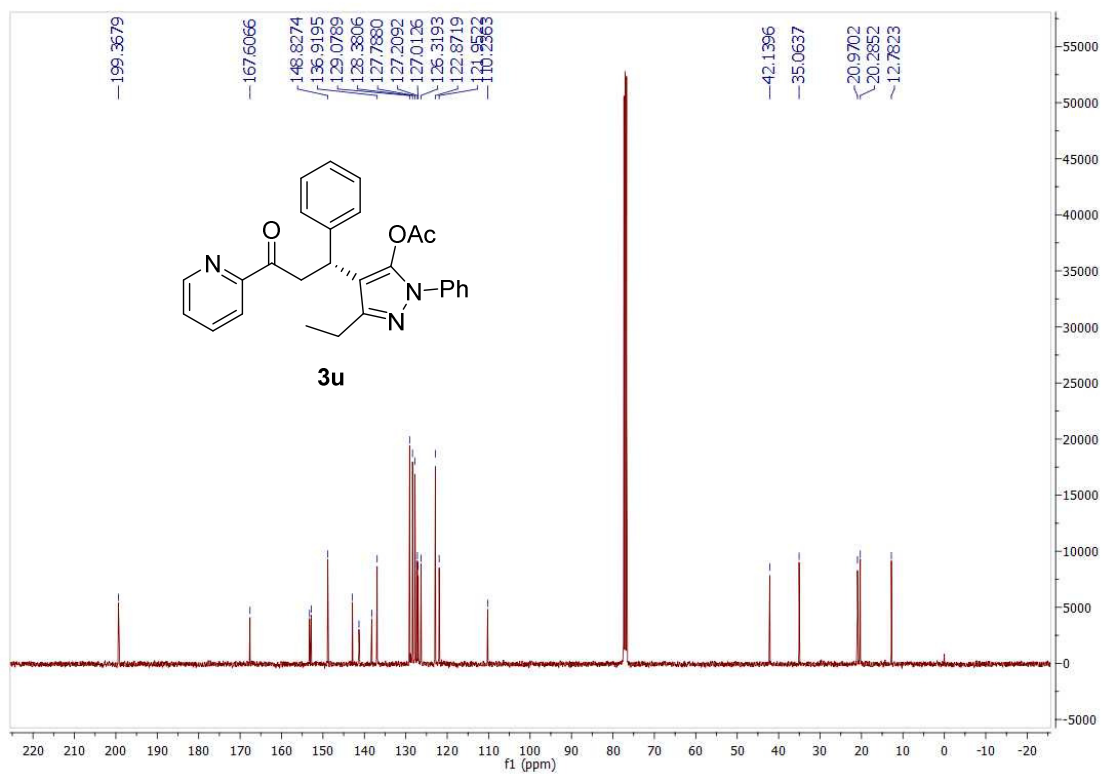
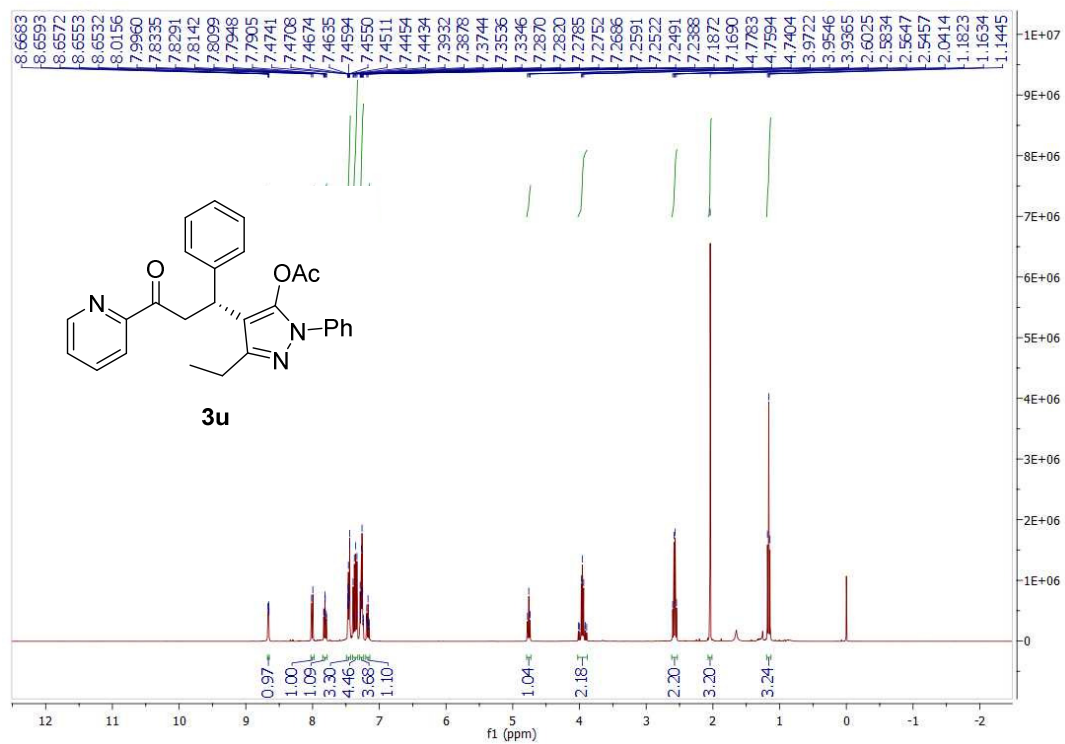


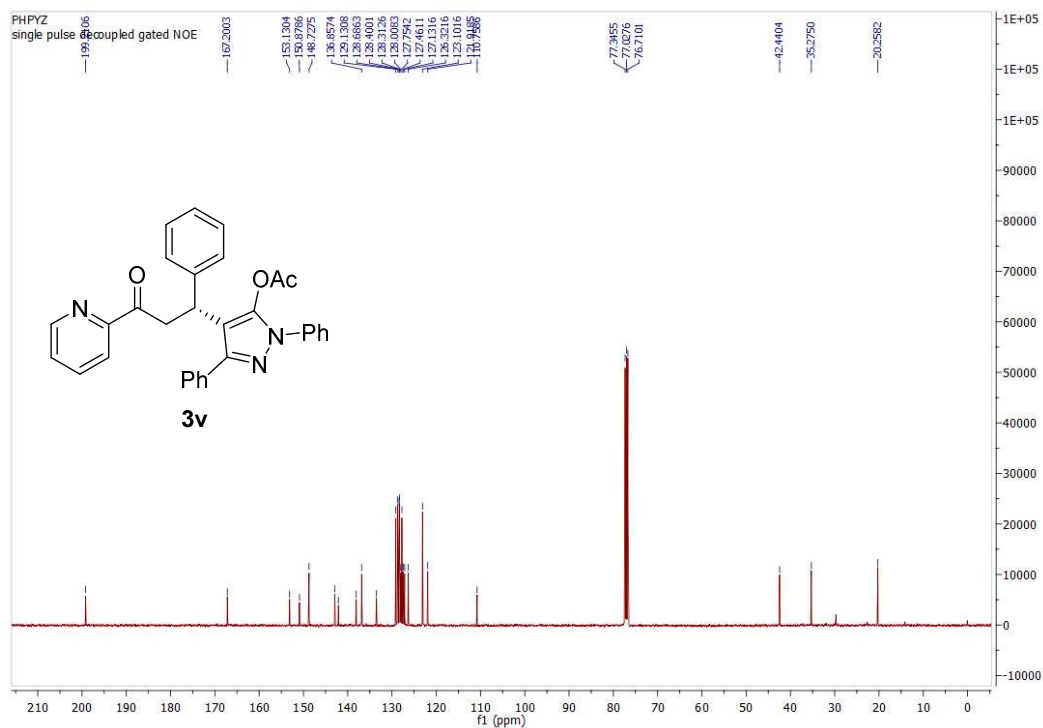
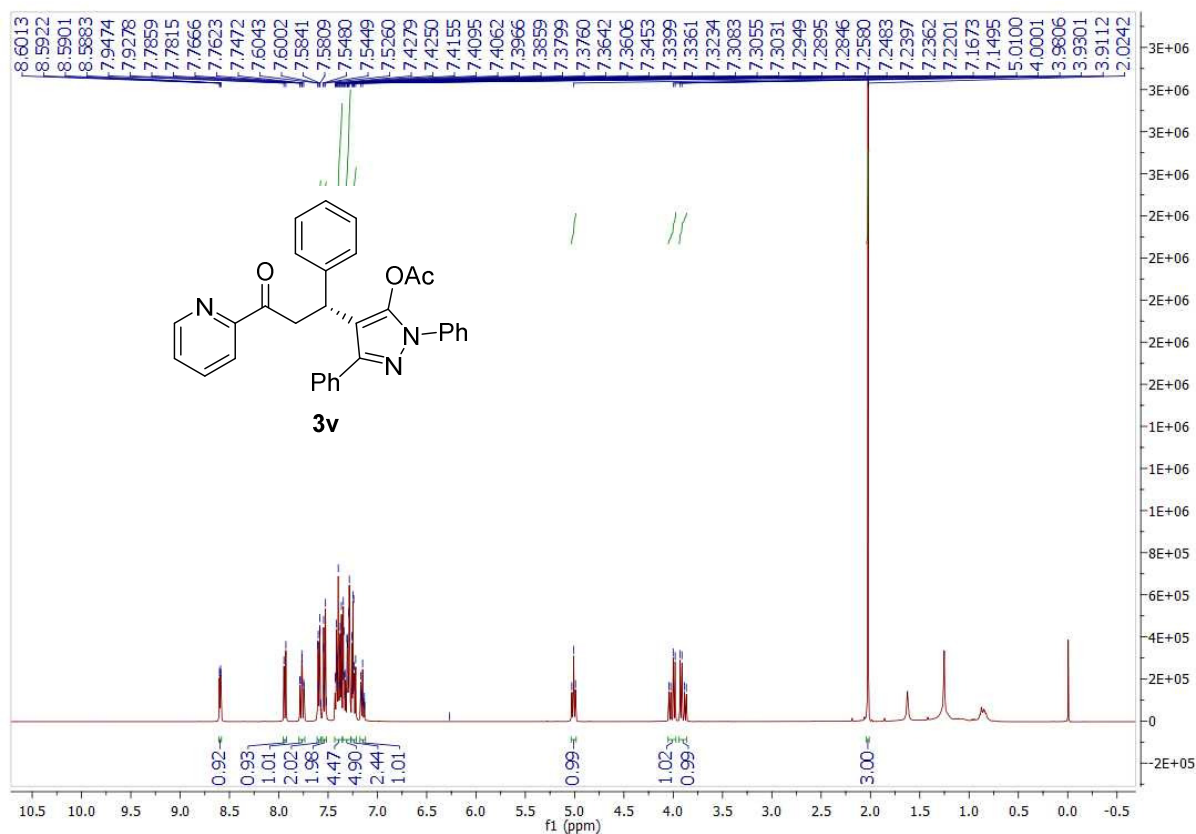


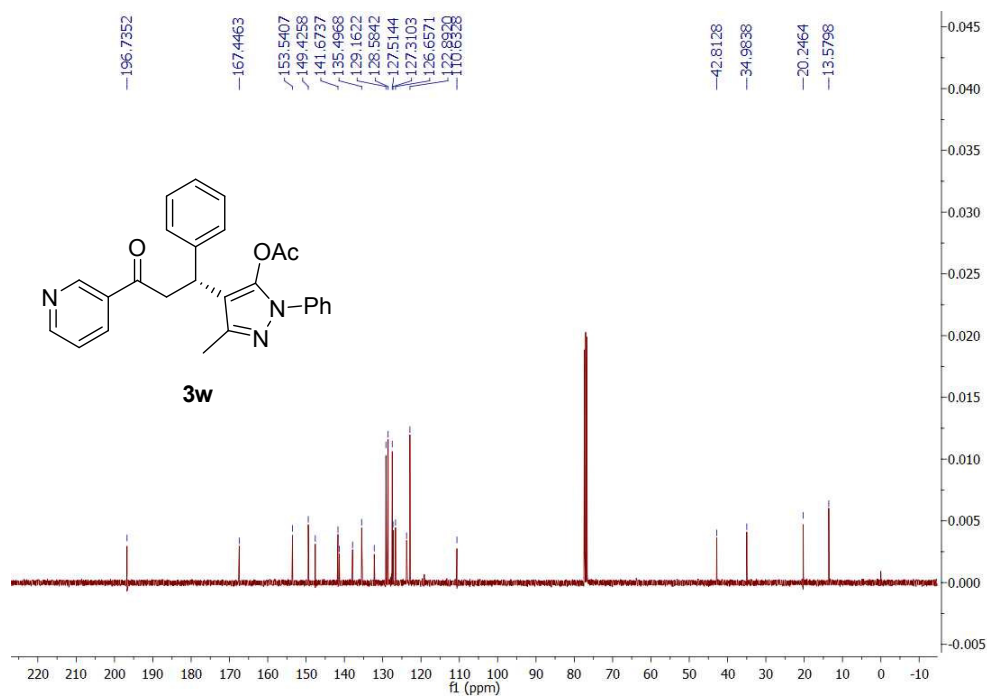
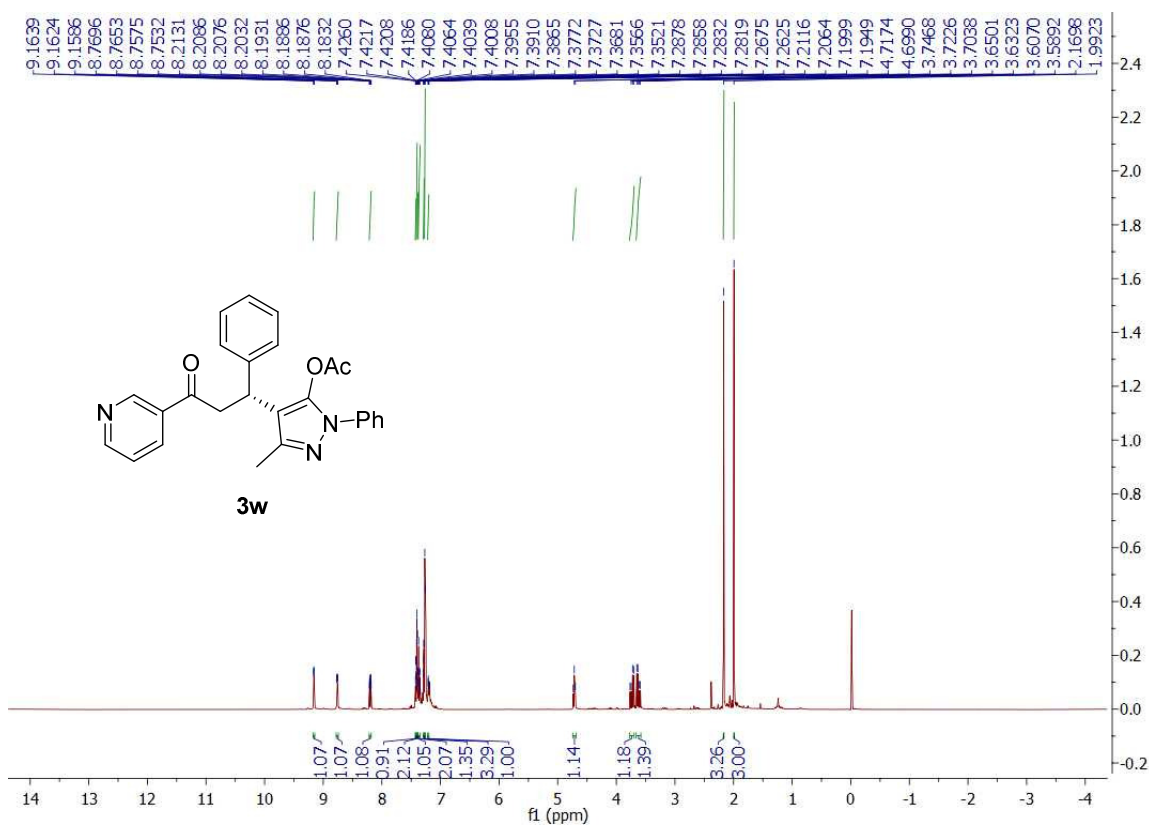


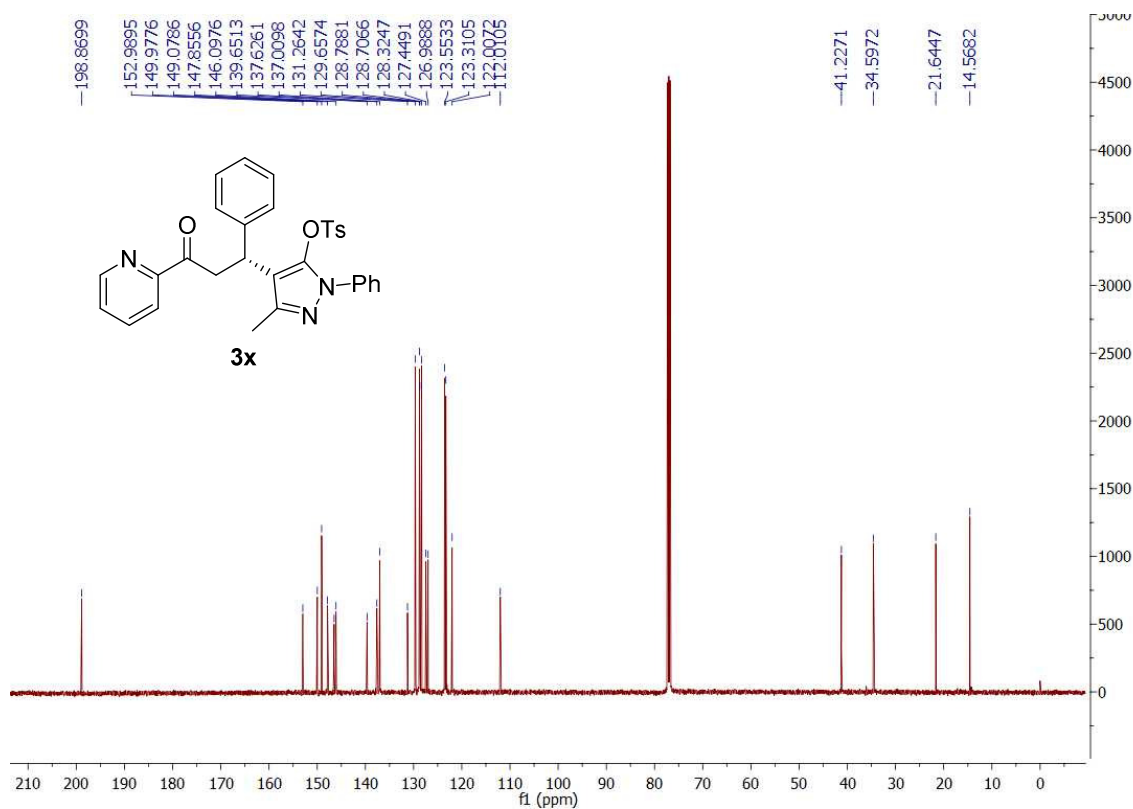
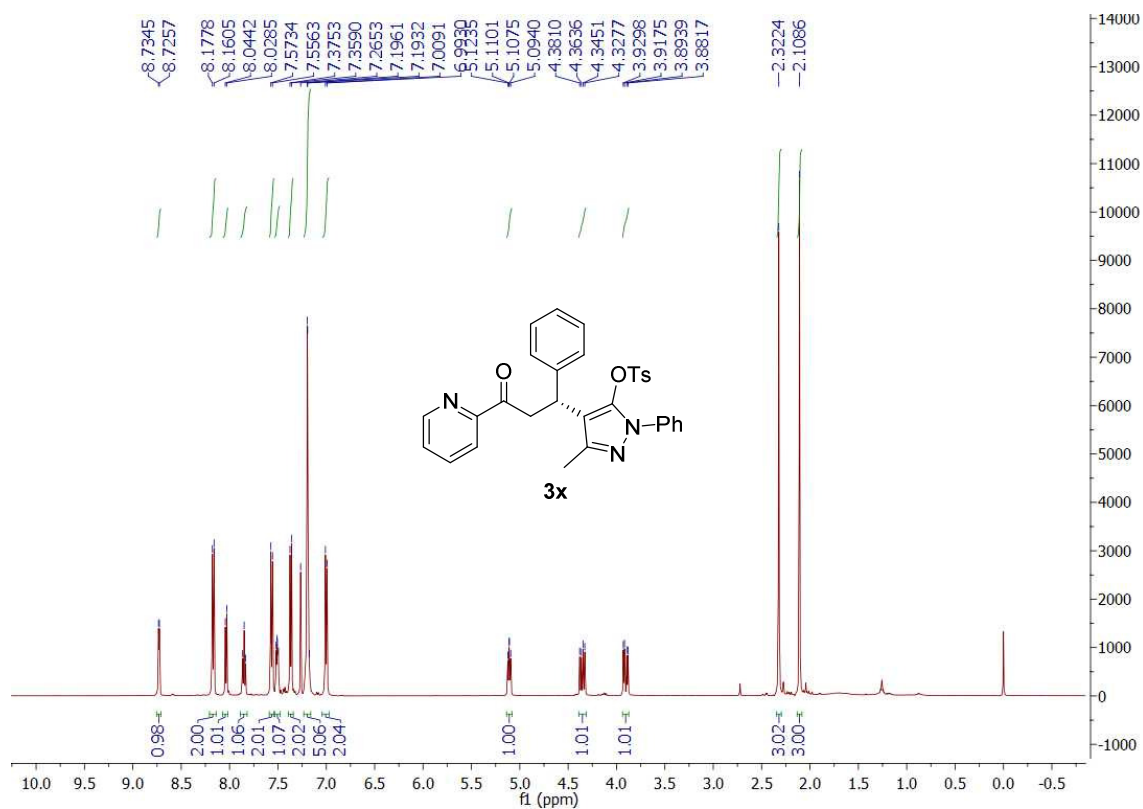




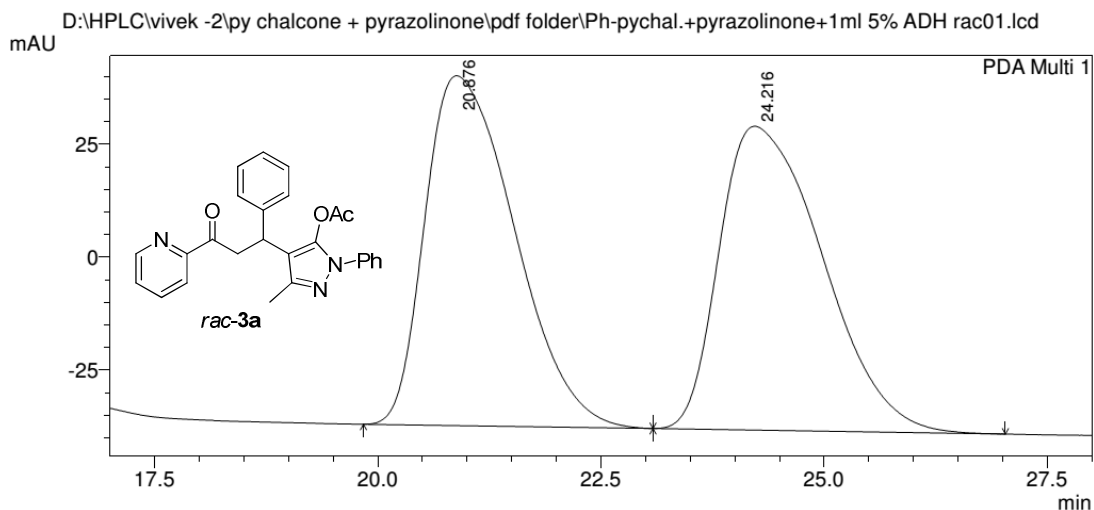








2. HPLC chromatograms of 3

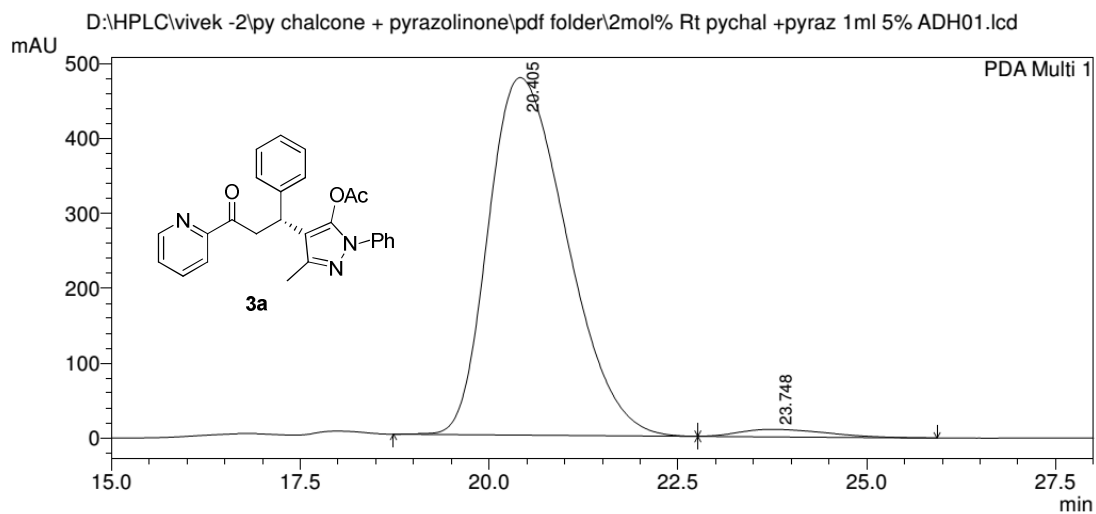


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.876	5405756	77495	49.952	53.517
2	24.216	5416245	67311	50.048	46.483
Total		10822001	144806	100.000	100.000

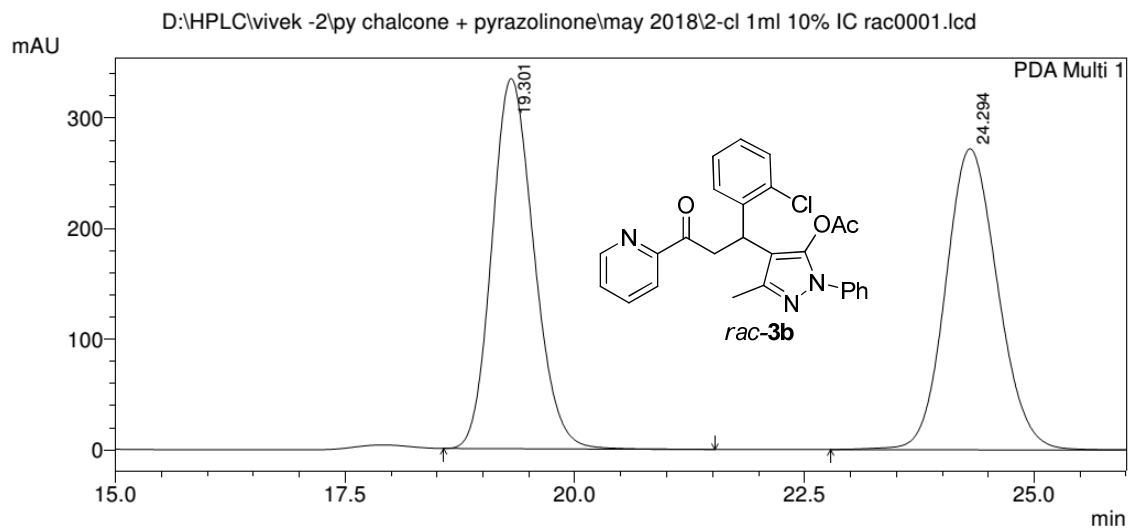


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.405	34547024	477707	97.729	97.924
2	23.748	802763	10128	2.271	2.076
Total		35349787	487835	100.000	100.000

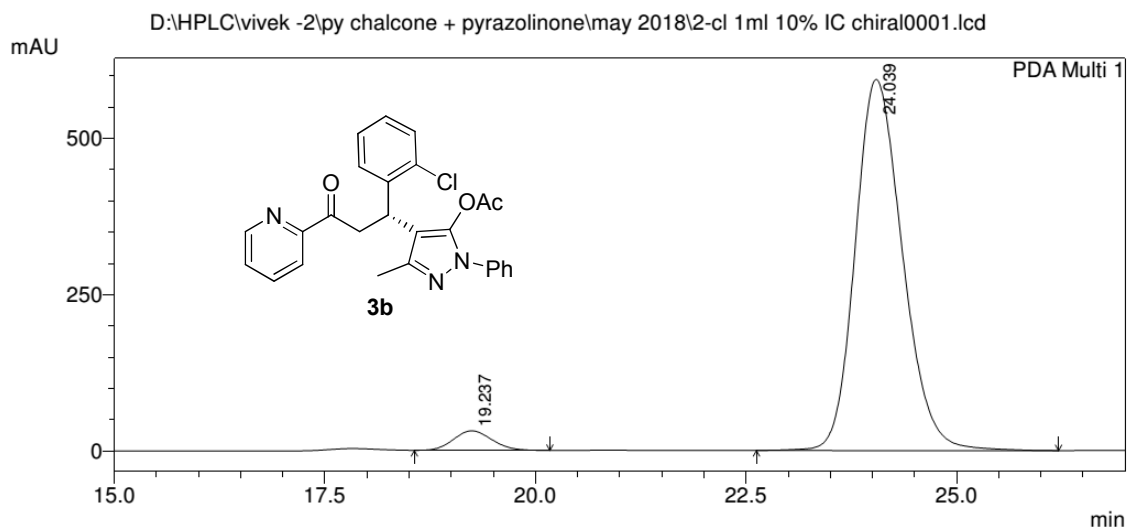


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.301	10647952	334694	49.830	55.159
2	24.294	10720764	272084	50.170	44.841
Total		21368716	606778	100.000	100.000



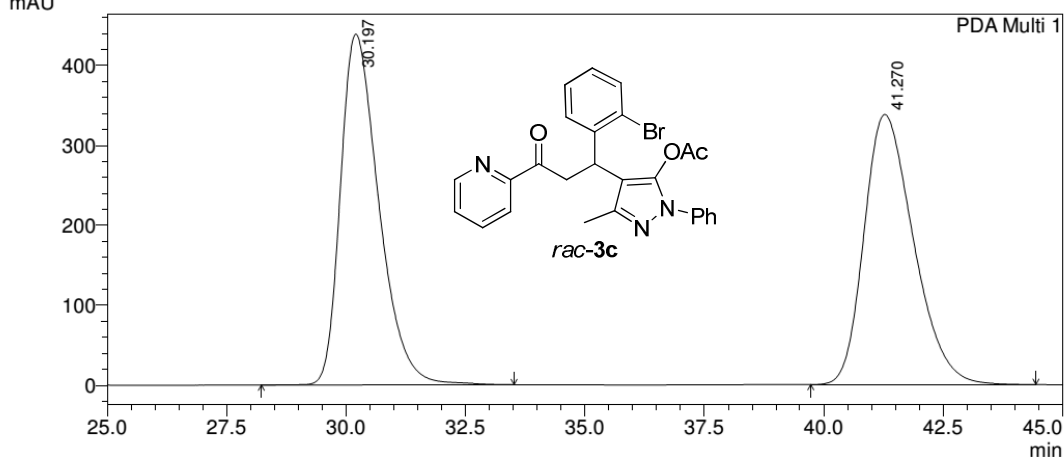
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.237	994774	31234	4.116	4.998
2	24.039	23170837	593760	95.884	95.002
Total		24165611	624995	100.000	100.000

D:\HPLC\vivek -2\py chalcone + pyrazolinone\rac-2018\2-BR py chal + pyz 1ml 5% lc rac repeat0001.lcd



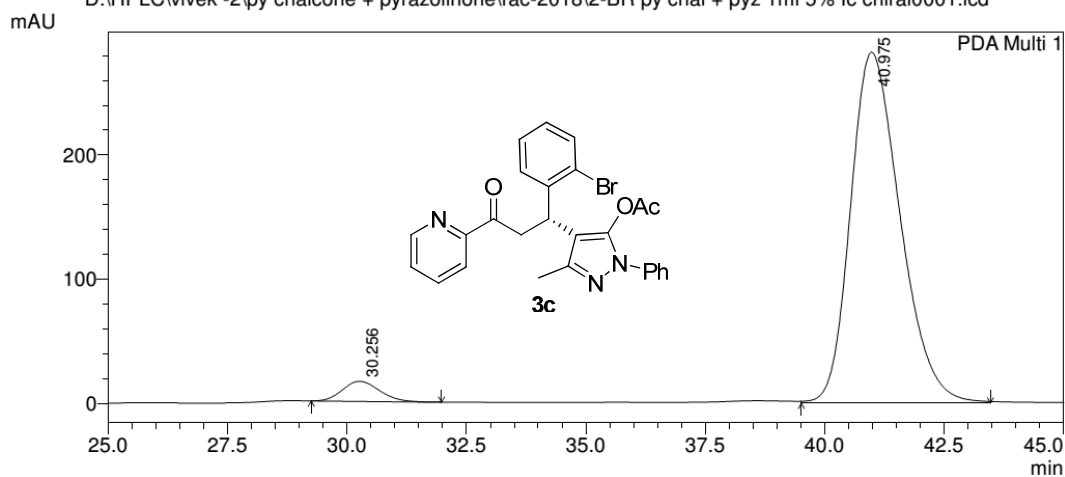
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.197	24489341	438723	50.176	56.503
2	41.270	24317310	337740	49.824	43.497
Total		48806650	776463	100.000	100.000

D:\HPLC\vivek -2\py chalcone + pyrazolinone\rac-2018\2-BR py chal + pyz 1ml 5% lc chiral0001.lcd



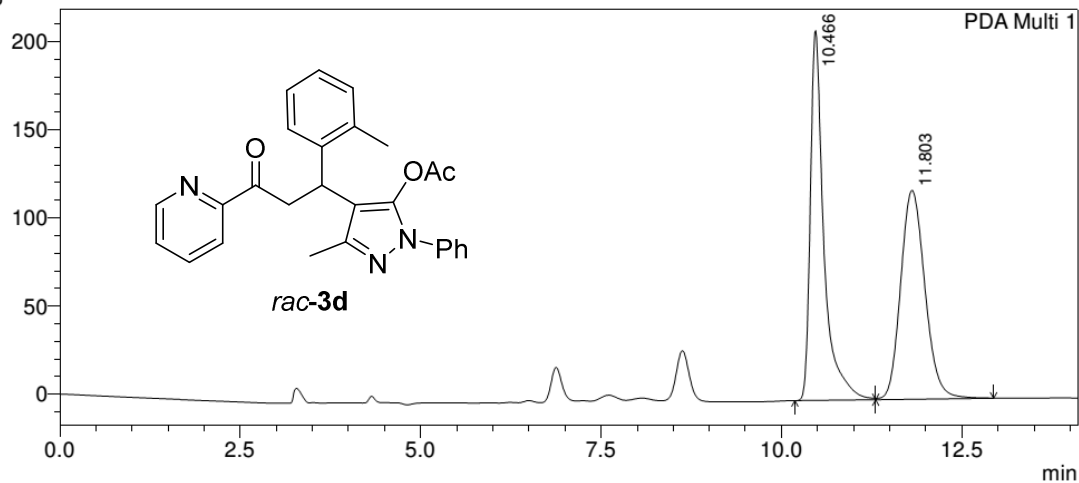
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.256	875676	16216	4.112	5.426
2	40.975	20417957	282654	95.888	94.574
Total		21293634	298870	100.000	100.000

D:\HPLC\livek -2\py chalcone + pyrazolinone\revision substrate\2-Me py cal + pyz rac 1ml 10 % IA rac0001.lcd
mAU



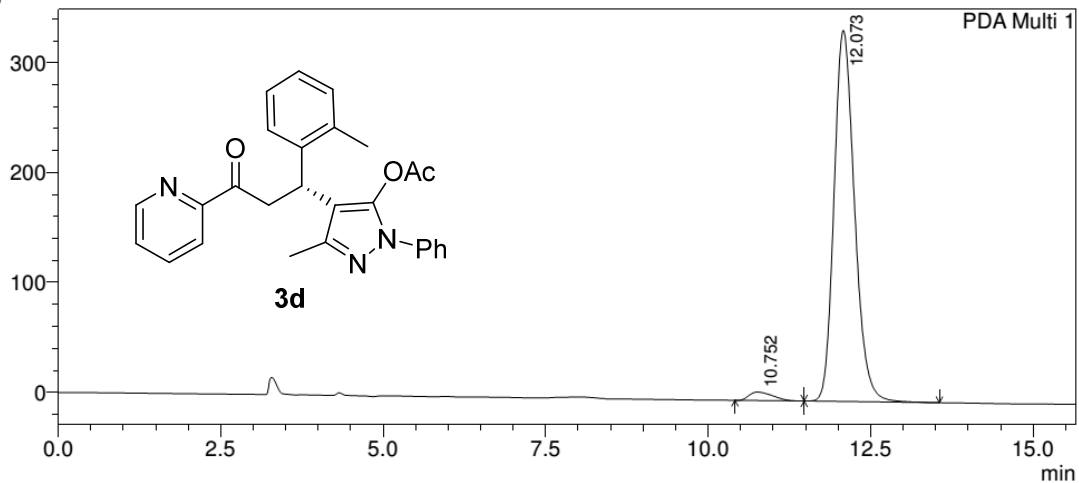
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.466	2734138	209769	49.664	63.902
2	11.803	2771149	118498	50.336	36.098
Total		5505287	328267	100.000	100.000

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mAU

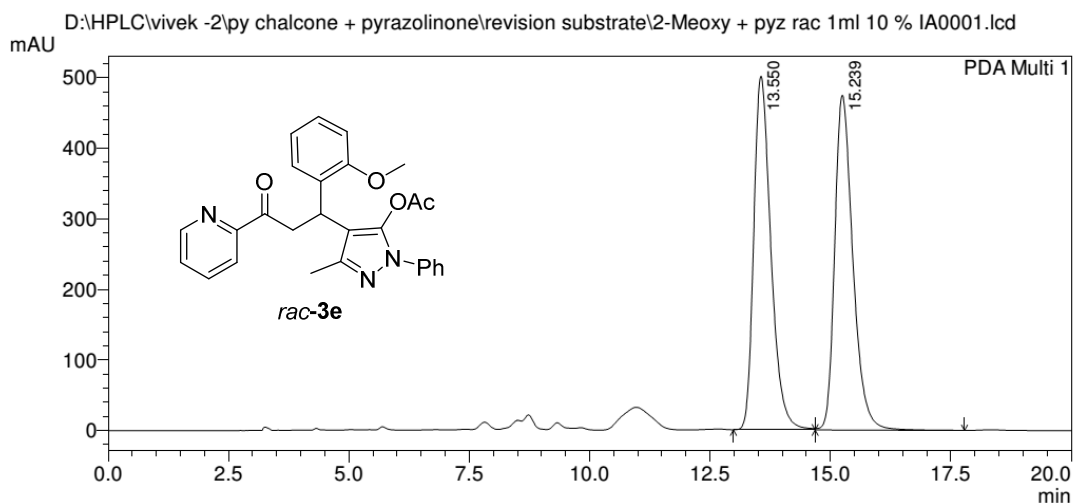


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.752	196670	7835	2.582	2.269
2	12.073	7418863	337545	97.418	97.731
Total		7615534	345381	100.000	100.000

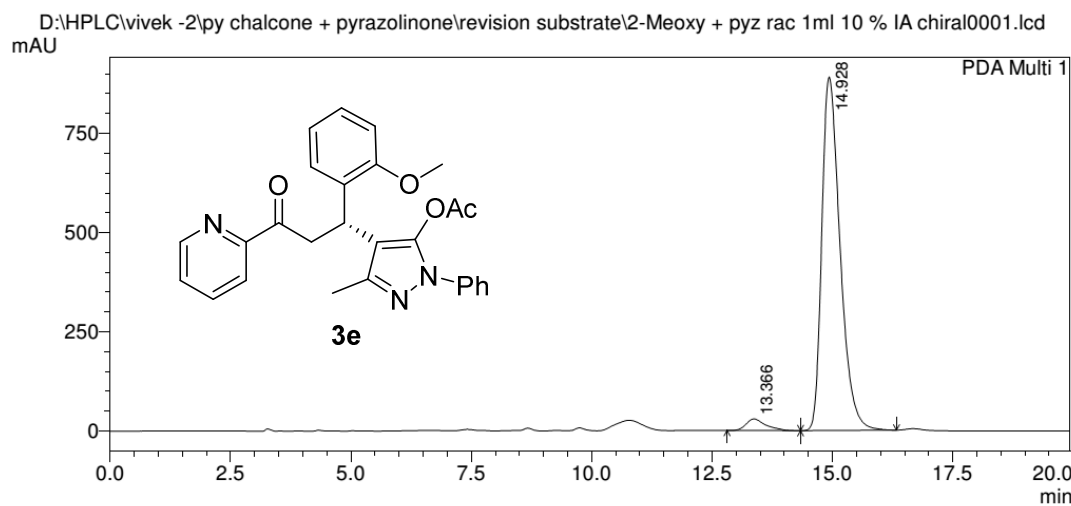


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.550	12419974	500872	49.923	51.357
2	15.239	12458463	474403	50.077	48.643
Total		24878437	975275	100.000	100.000

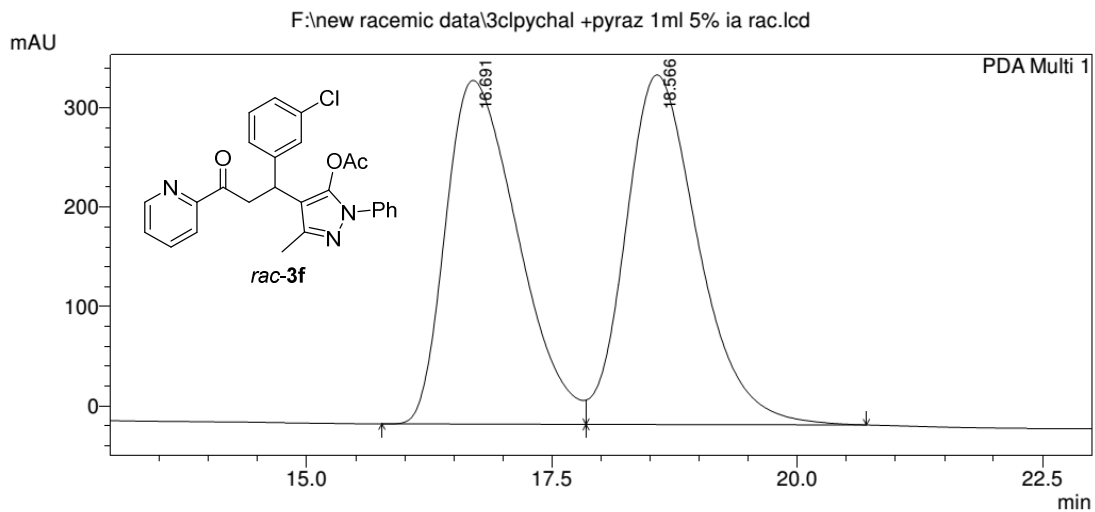


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

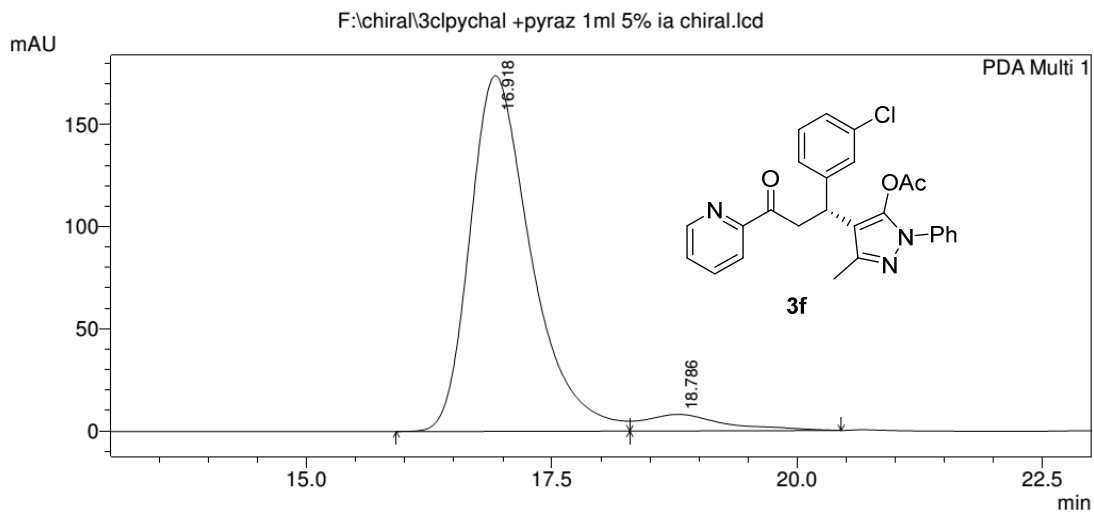
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.366	829104	29119	3.410	3.163
2	14.928	23484562	891513	96.590	96.837
Total		24313666	920632	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

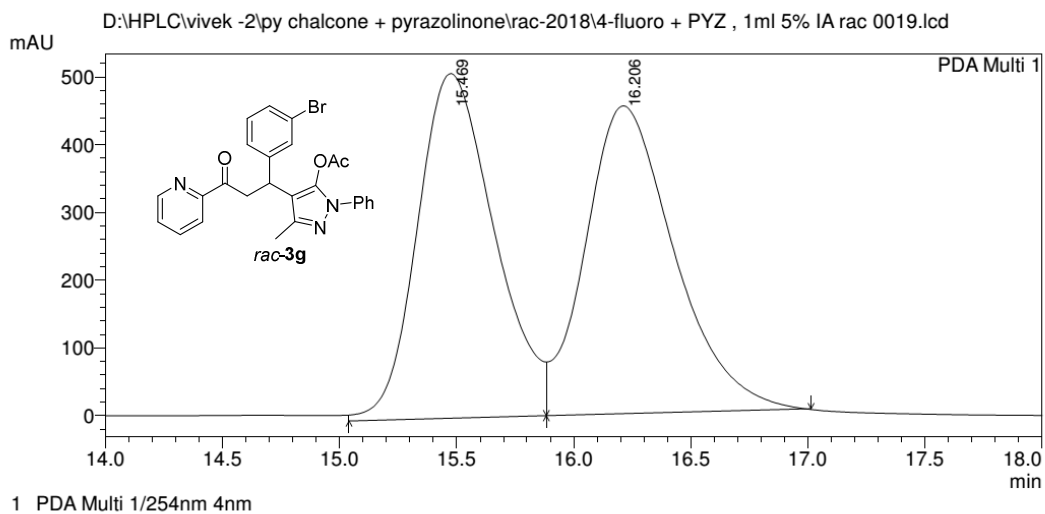
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.691	17677244	345920	49.368	49.576
2	18.566	18130034	351835	50.632	50.424
Total		35807278	697755	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

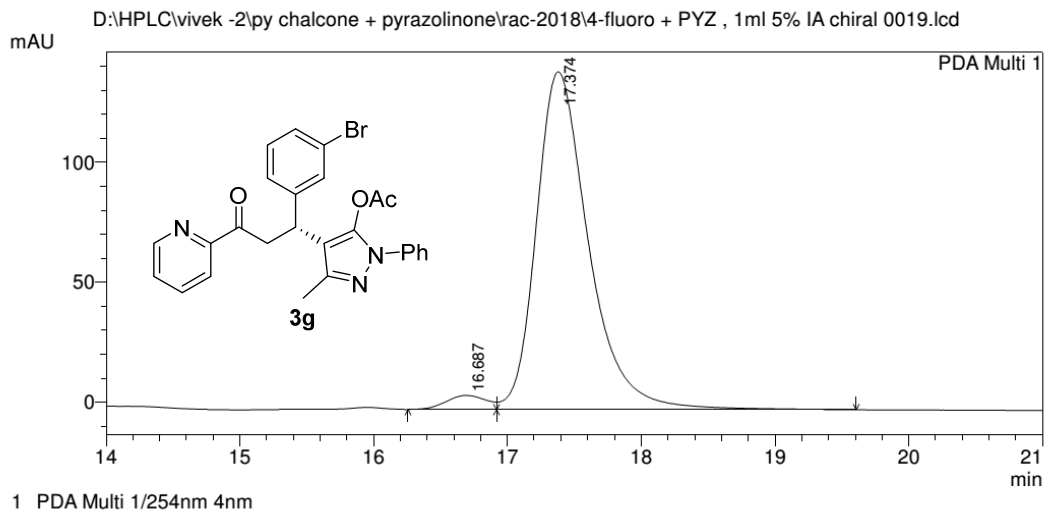
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.918	7540293	174146	94.275	95.597
2	18.786	457878	8020	5.725	4.403
Total		7998171	182166	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.469	11653456	509201	49.295	52.822
2	16.206	11986869	454787	50.705	47.178
Total		23640325	963989	100.000	100.000

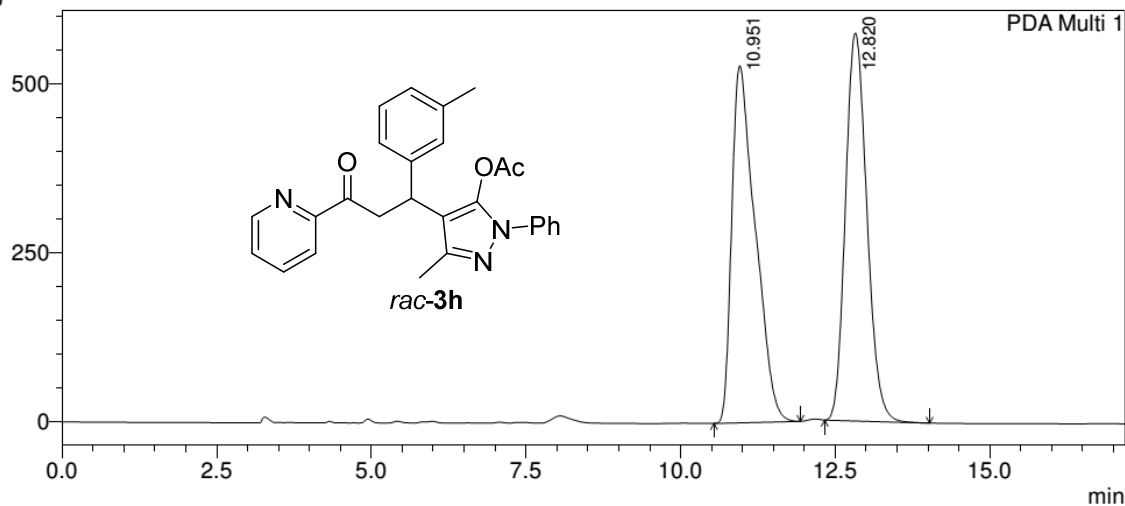


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.687	123824	5889	3.136	4.014
2	17.374	3825152	140810	96.864	95.986

D:\HPLC\vivek -2\py chalcone + pyrazolinone\revision substrate\3-Me py cal + pyz 1ml 10 % IA rac0001.lcd
mAU



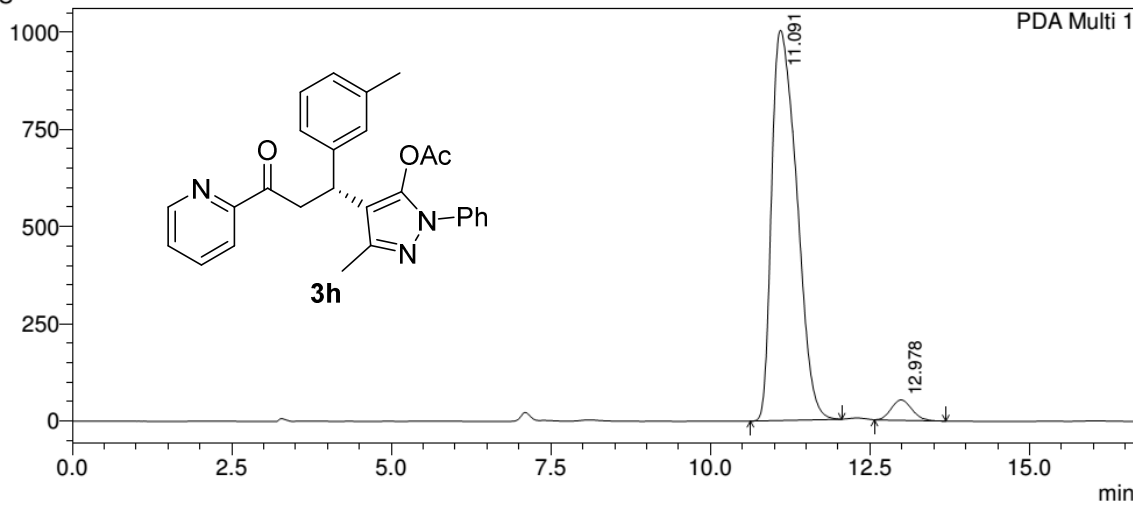
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.951	13961154	528806	50.204	47.947
2	12.820	13847886	574091	49.796	52.053
Total		27809040	1102897	100.000	100.000

D:\HPLC\vivek -2\py chalcone + pyrazolinone\revision substrate\3-Me py cal + pyz 1ml 10 % IA chiral0001.lcd
mAU

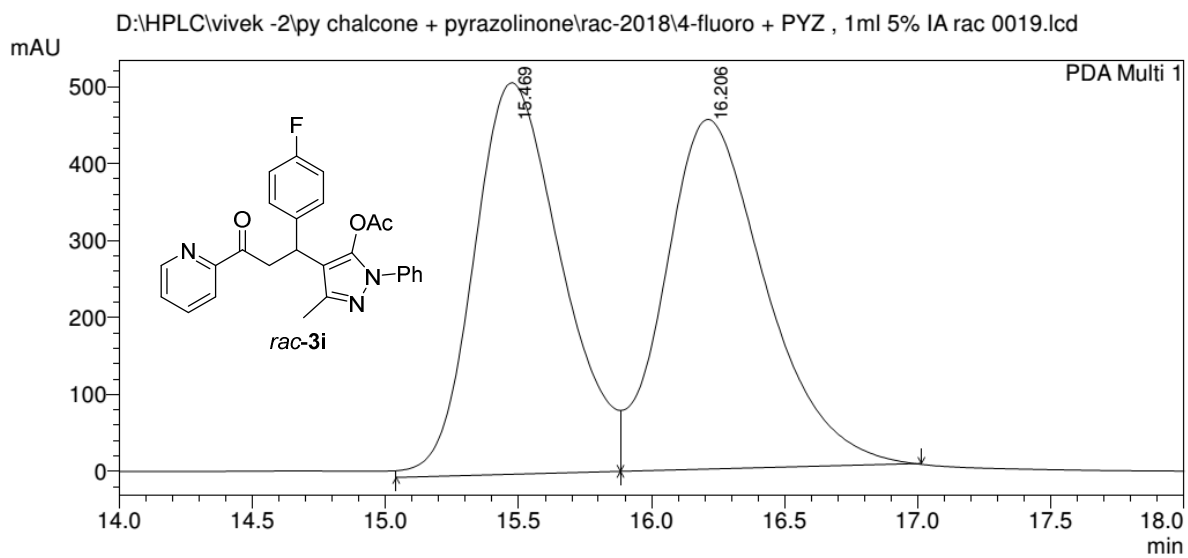


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

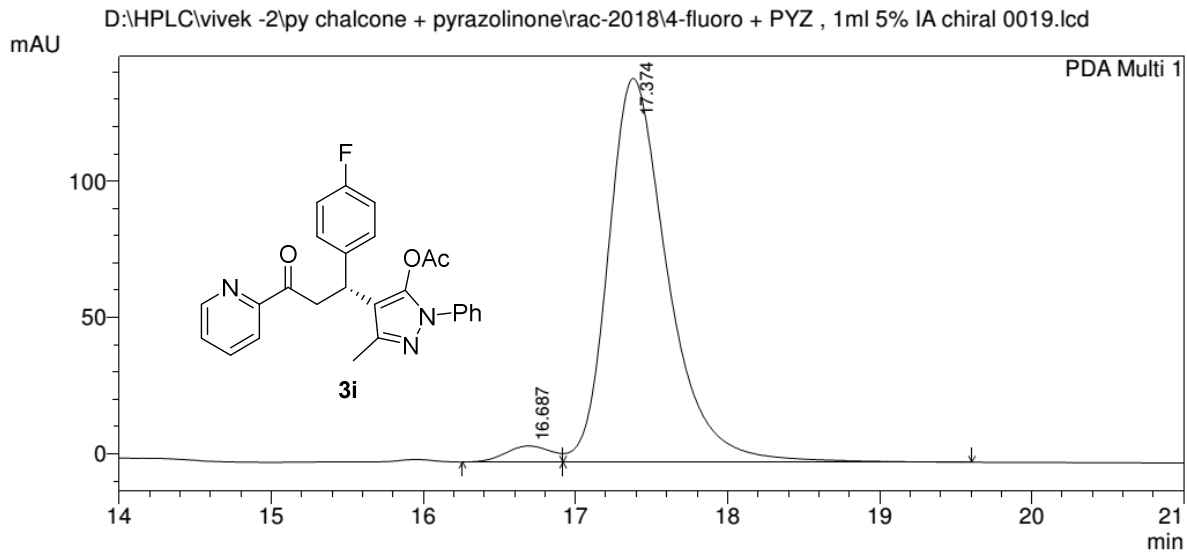
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.091	27403520	1003439	95.879	95.046
2	12.978	1177845	52304	4.121	4.954
Total		28581365	1055743	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

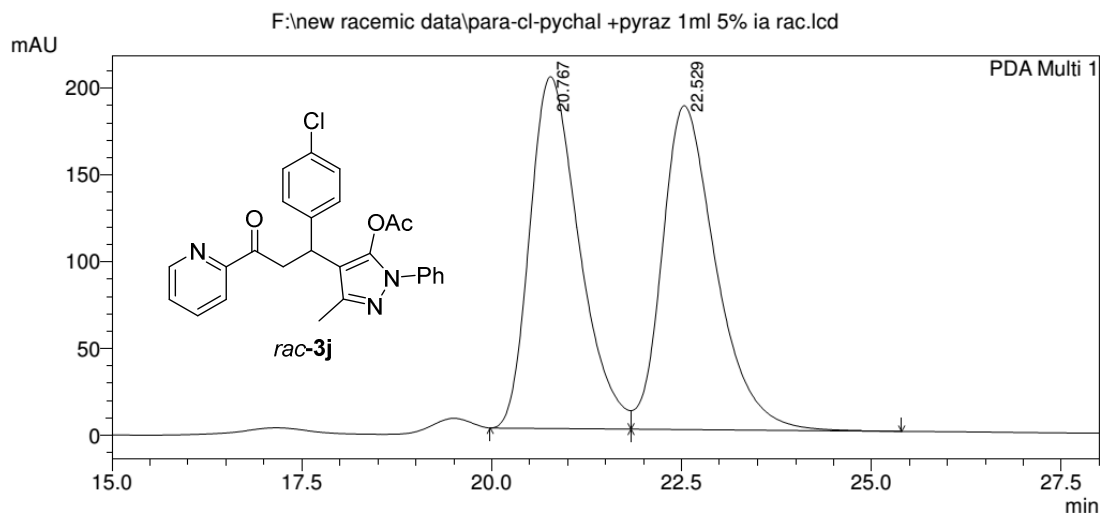
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.469	11653456	509201	49.295	52.822
2	16.206	11986869	454787	50.705	47.178
Total		23640325	963989	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.687	123824	5889	3.136	4.014
2	17.374	3825152	140810	96.864	95.986
Total		3948976	146699	100.000	100.000

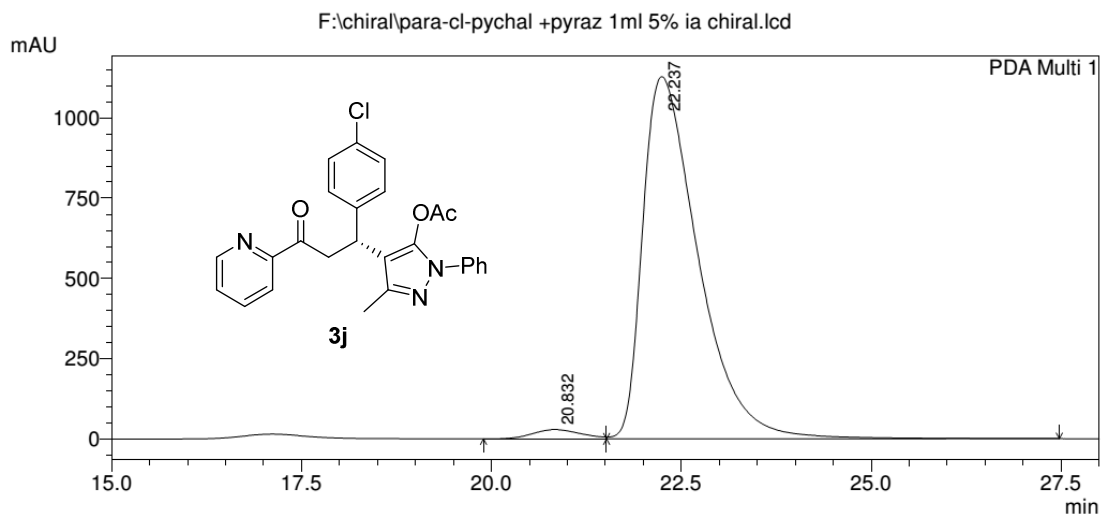


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.767	9138353	202551	49.875	52.068
2	22.529	9184143	186459	50.125	47.932
Total		18322496	389010	100.000	100.000

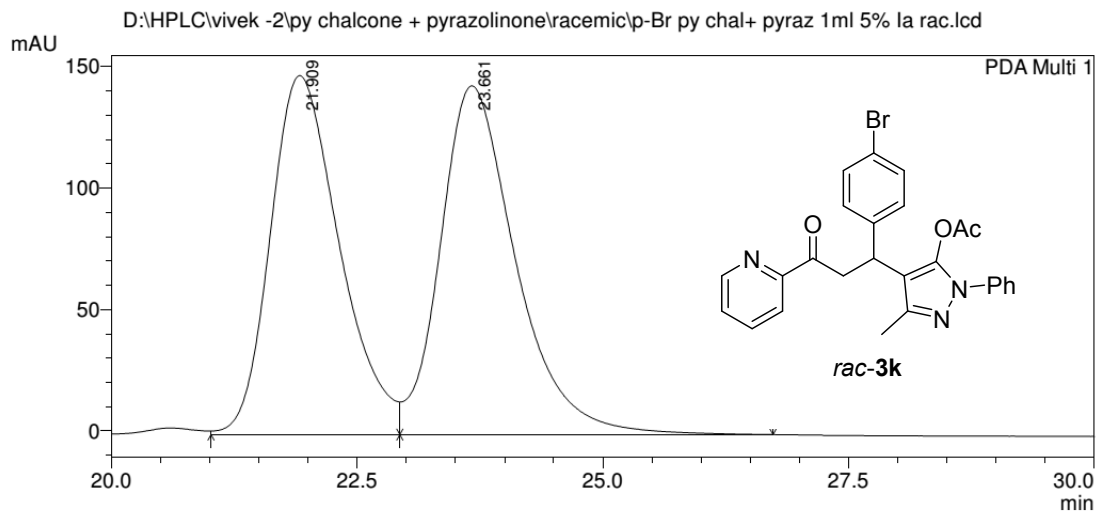


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

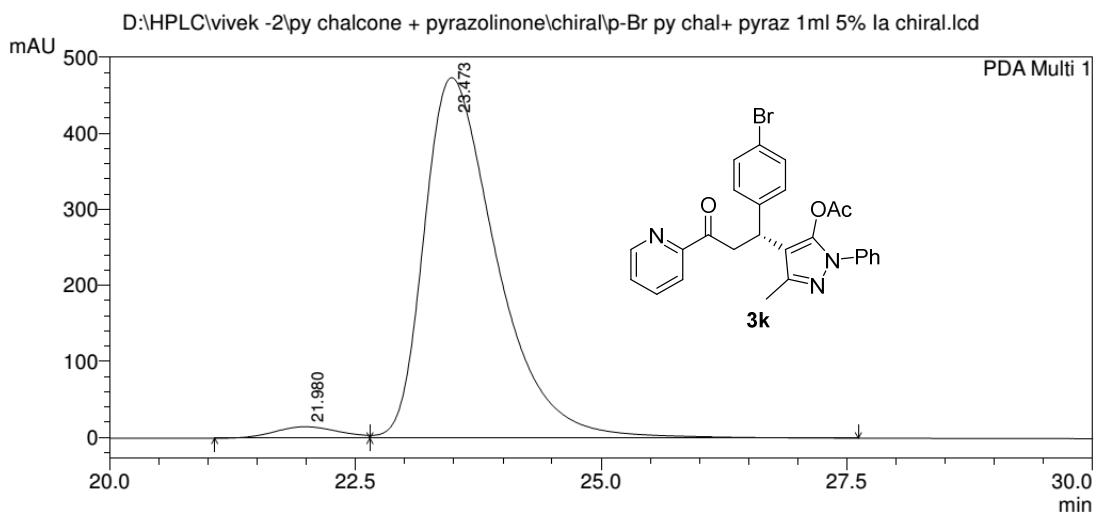
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.832	1282017	28947	2.182	2.501
2	22.237	57458817	1128346	97.818	97.499
Total		58740835	1157293	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

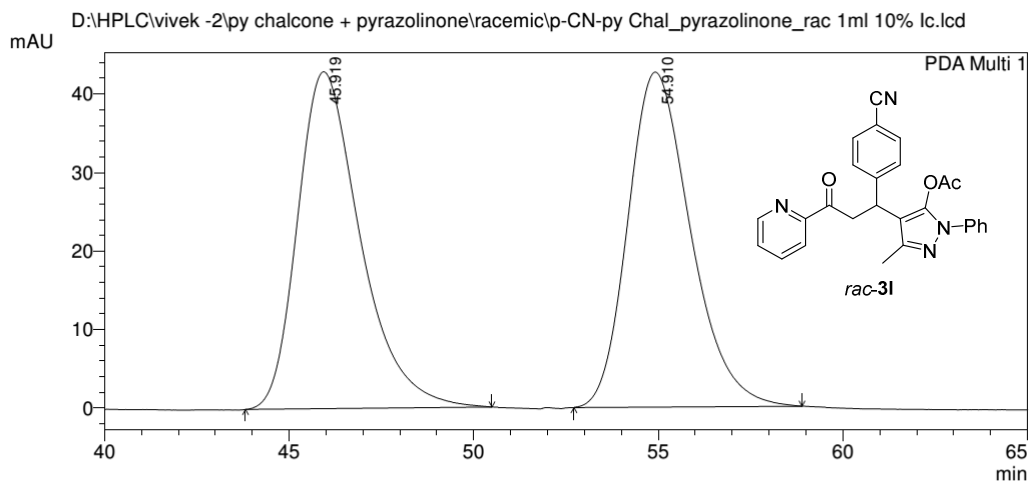
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.909	7226556	147813	48.522	50.724
2	23.661	7666842	143592	51.478	49.276
Total		14893399	291405	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.980	693438	15138	2.761	3.093
2	23.473	24418355	474363	97.239	96.907
Total		25111793	489502	100.000	100.000

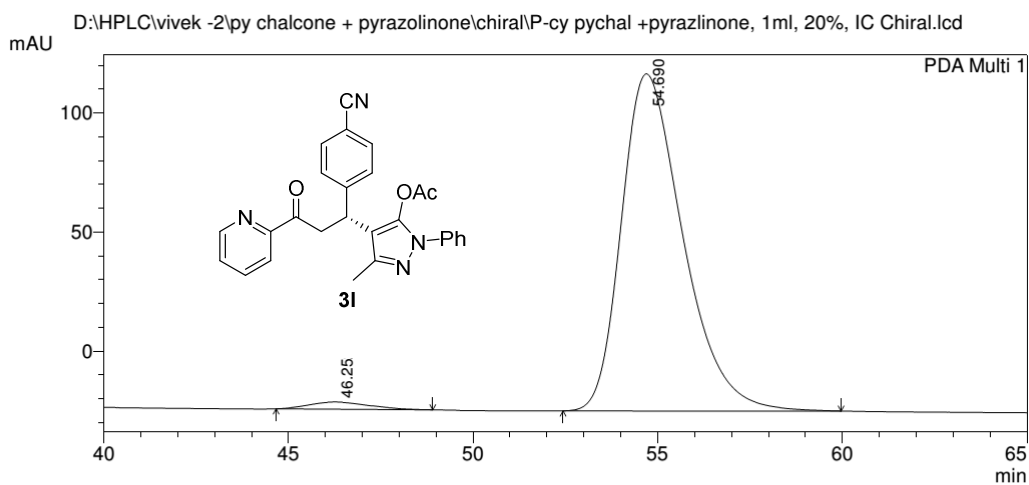


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.919	5072624	42917	50.183	50.151
2	54.910	5035710	42658	49.817	49.849
Total		10108334	85576	100.000	100.000

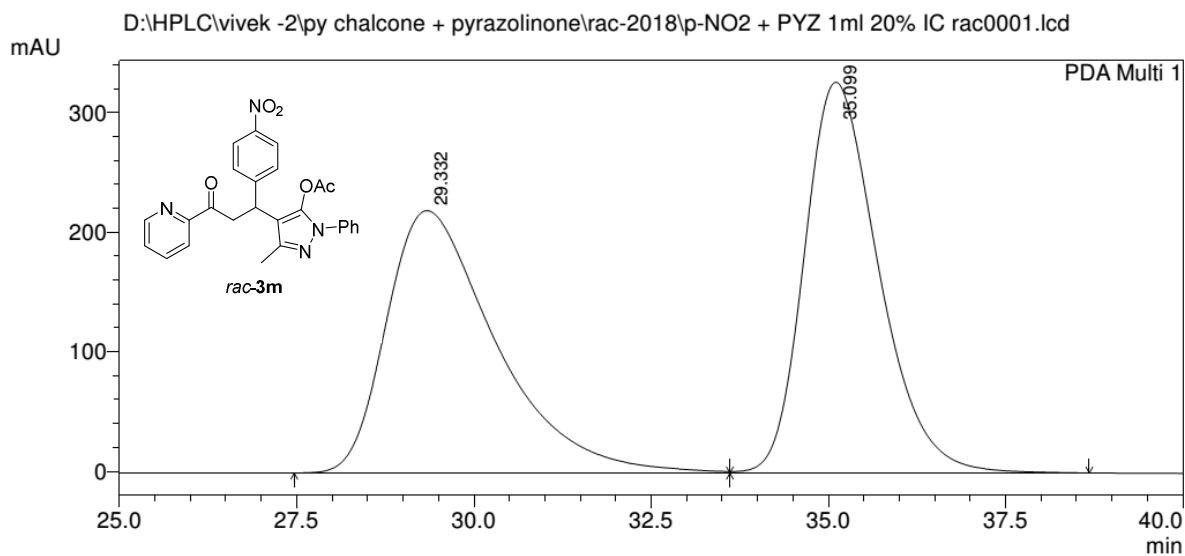


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.252	332836	2974	1.988	2.060
2	54.690	16408414	141408	98.012	97.940
Total		16741250	144382	100.000	100.000

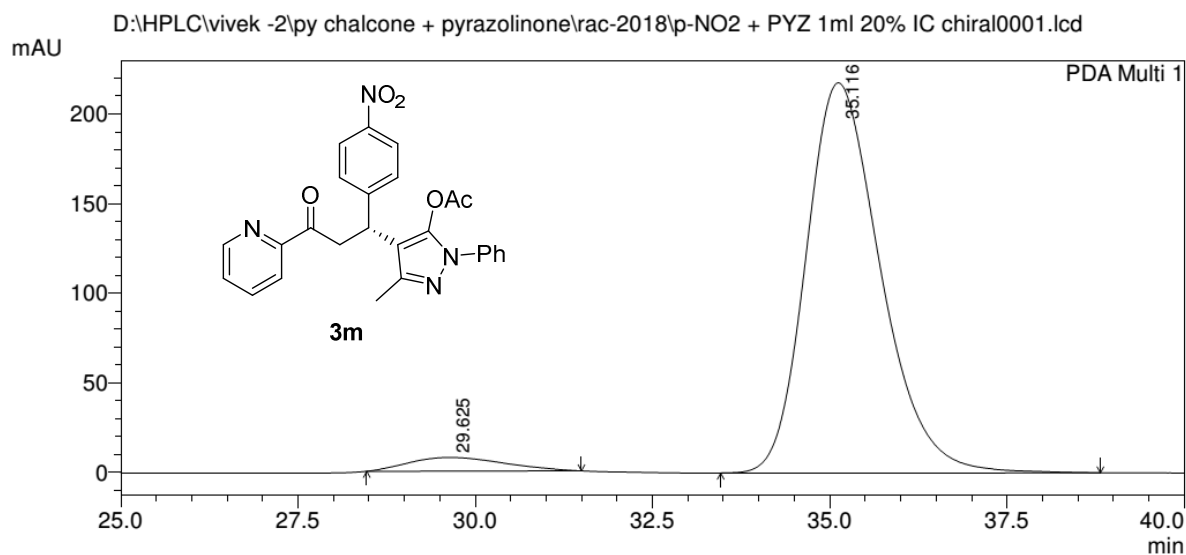


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.332	23576733	219366	49.760	40.166
2	35.099	23803888	326786	50.240	59.834
Total		47380620	546152	100.000	100.000

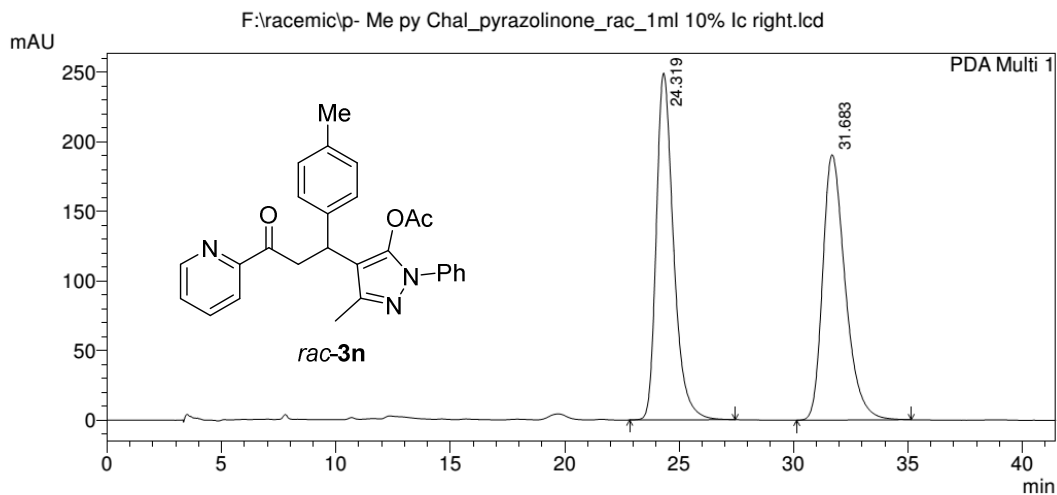


1 PDA Multi 1/254nm 4nm

PeakTable

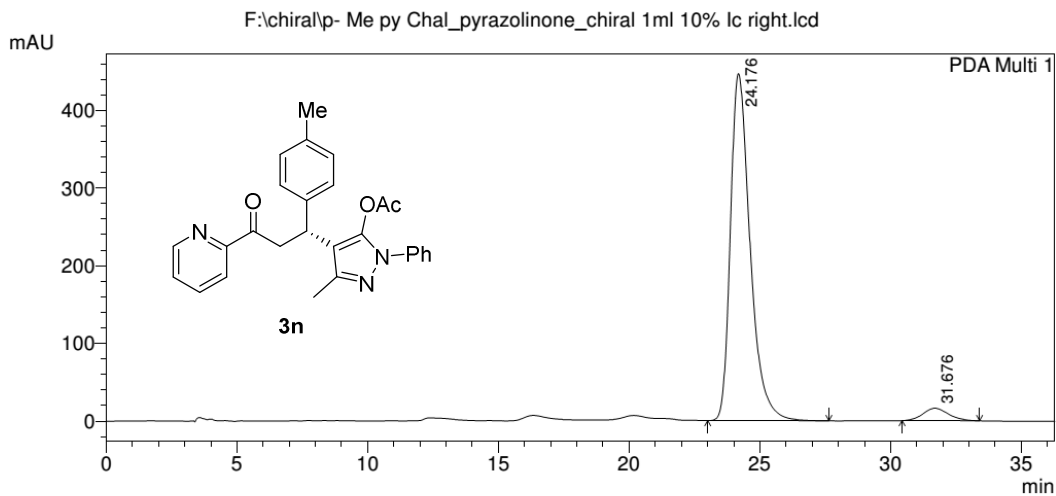
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.625	716049	7669	4.315	3.402
2	35.116	15878039	217771	95.685	96.598
Total		16594088	225440	100.000	100.000



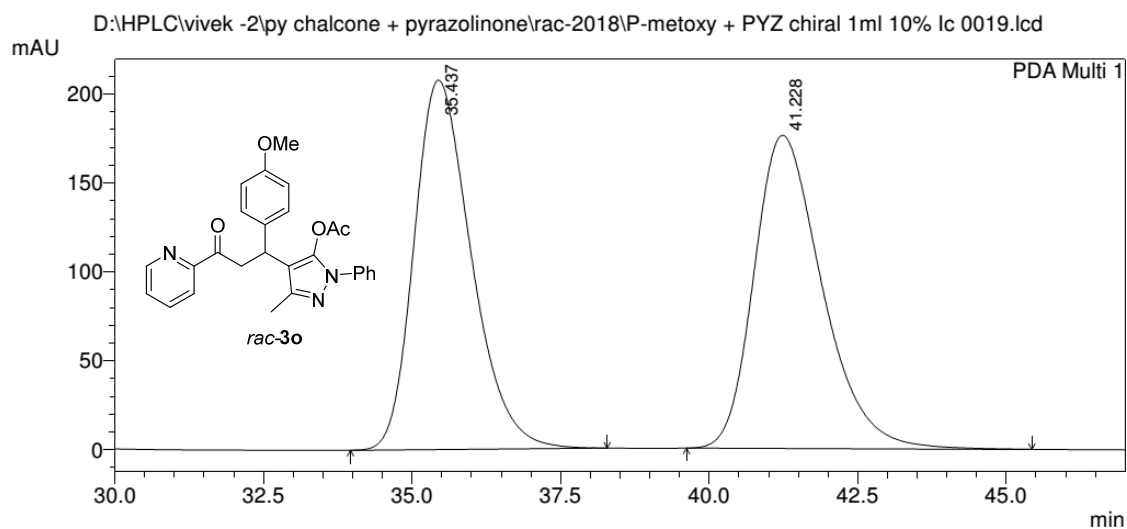
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.319	13076341	249113	49.998	56.653
2	31.683	13077449	190606	50.002	43.347
Total		26153790	439720	100.000	100.000



PDA Ch1 254nm 4nm

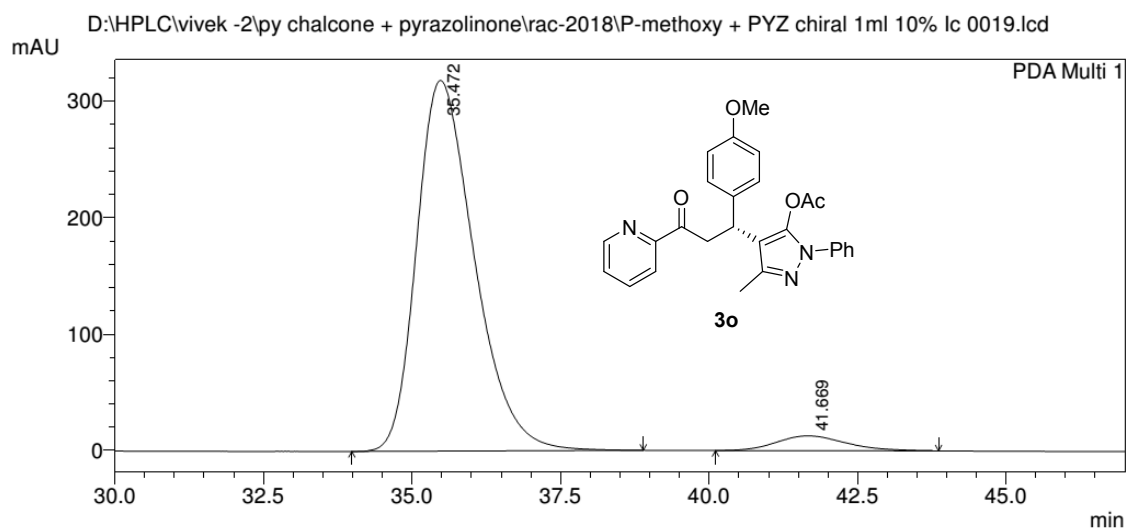
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.176	23379844	446900	95.576	96.553
2	31.676	1082115	15955	4.424	3.447
Total		24461959	462855	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

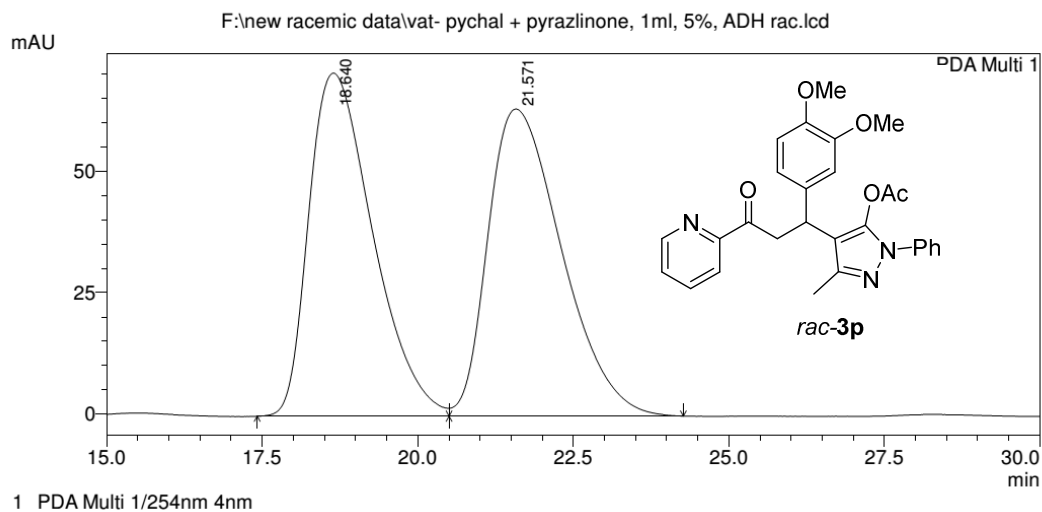
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.437	13919240	207627	49.772	54.124
2	41.228	14046796	175985	50.228	45.876
Total		27966036	383612	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

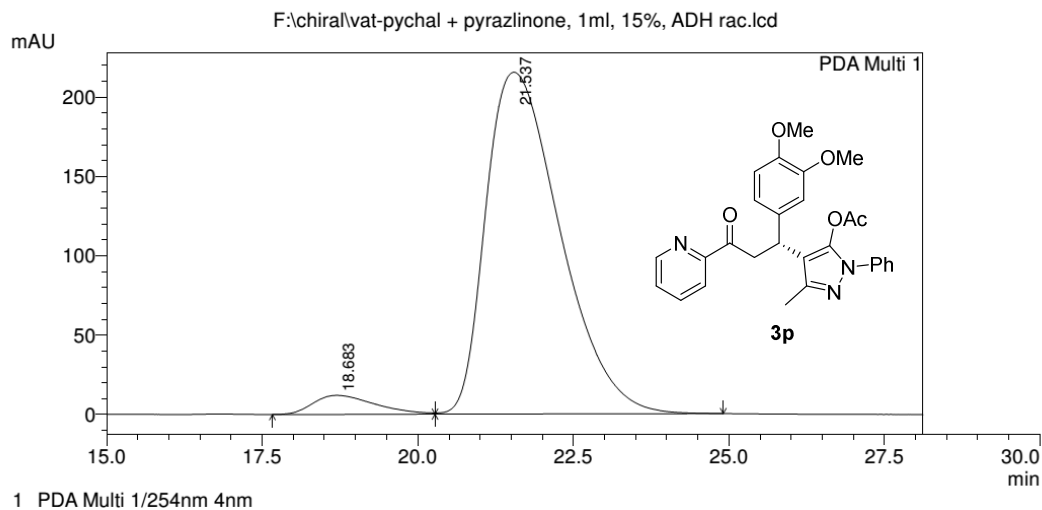
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.472	21489850	318423	95.405	96.157
2	41.669	1035080	12727	4.595	3.843
Total		22524930	331150	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

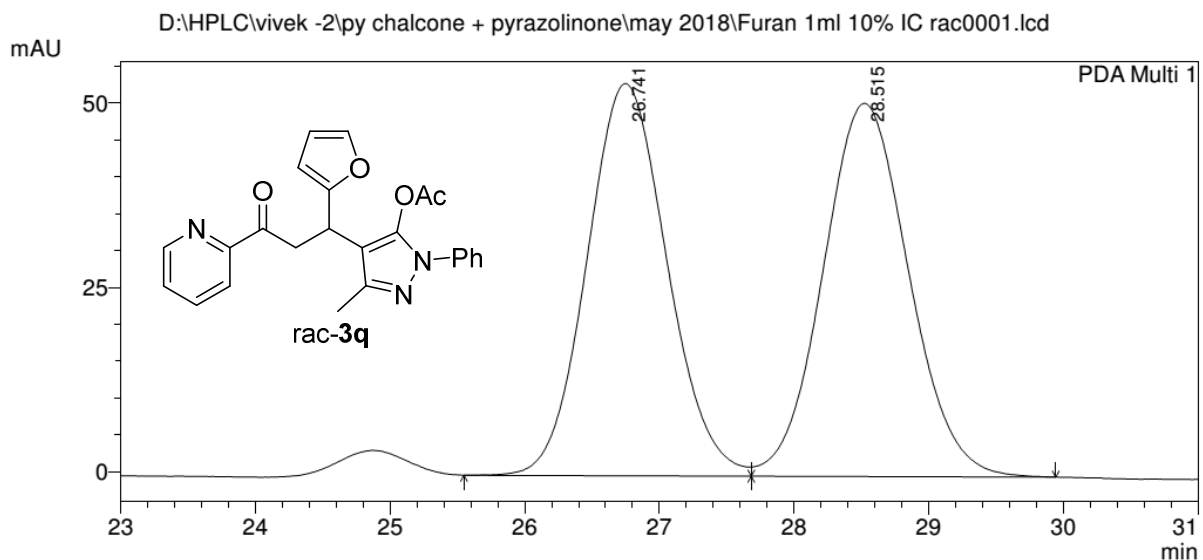
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.640	5041660	70702	49.180	52.762
2	21.571	5209682	63298	50.820	47.238
Total		10251341	134000	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.683	833818	12011	4.459	5.285
2	21.537	17866147	215244	95.541	94.715
Total		18699964	227255	100.000	100.000

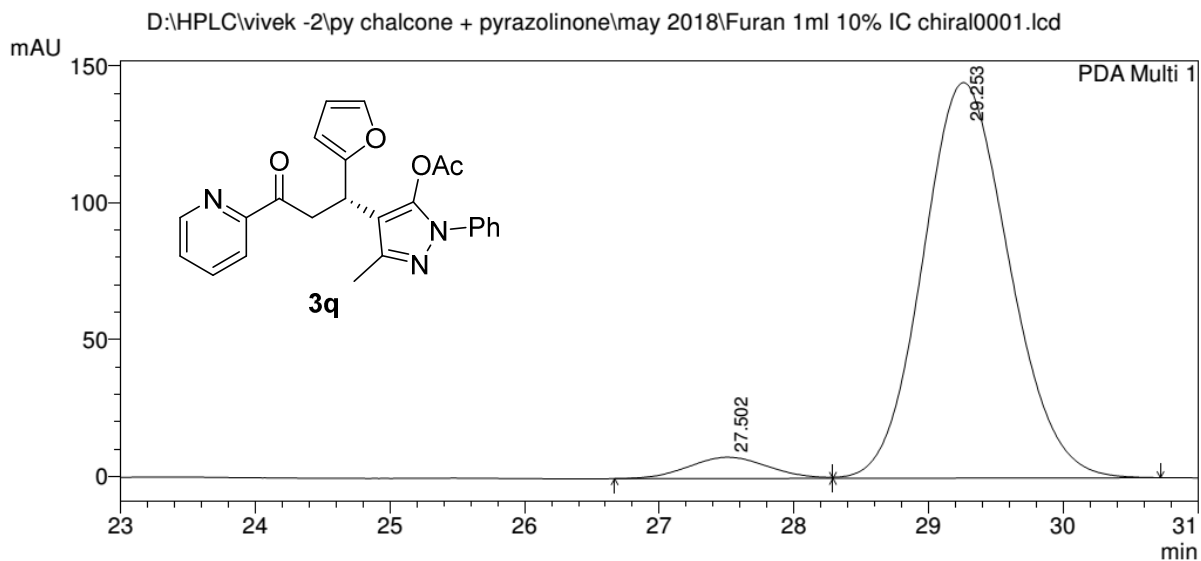


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.741	2197264	53191	49.516	51.231
2	28.515	2240174	50634	50.484	48.769
Total		4437437	103824	100.000	100.000

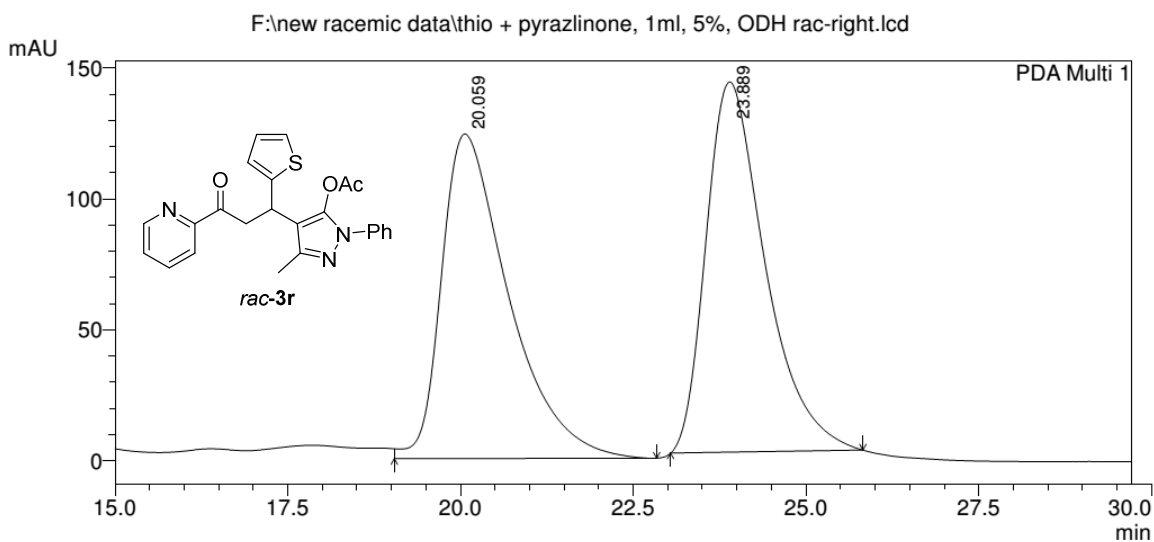


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.502	321861	7790	4.754	5.112
2	29.253	6448505	144604	95.246	94.888
Total		6770366	152394	100.000	100.000

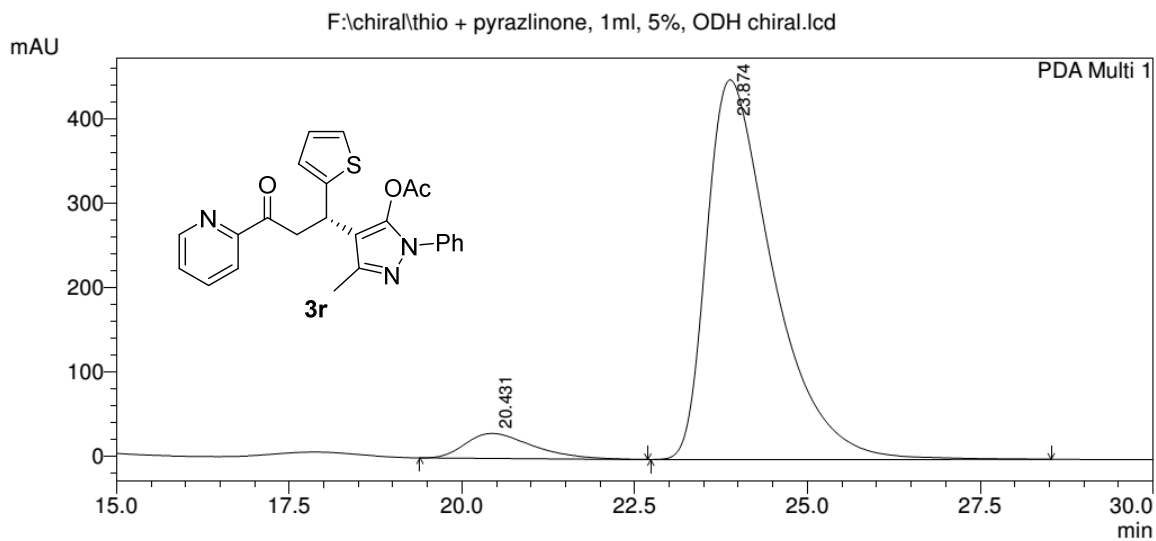


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.059	8394212	123918	49.914	46.703
2	23.889	8423174	141414	50.086	53.297
Total		16817386	265332	100.000	100.000



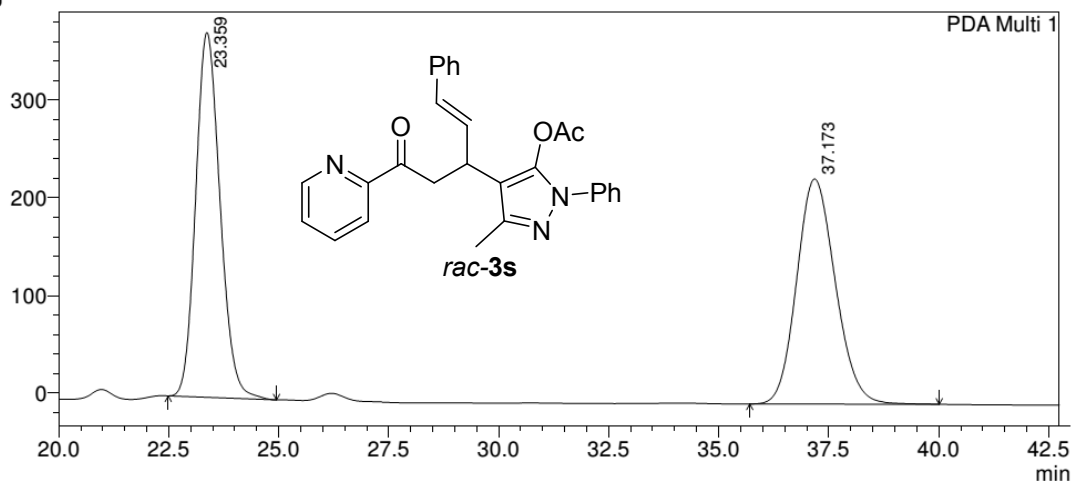
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.431	2007240	29593	6.272	6.174
2	23.874	29995383	449738	93.728	93.826
Total		32002623	479331	100.000	100.000

D:\HPLC\vivek -2\py chalcone + pyrazolinone\revision substrate\Cinnam py cal + pyz 1ml 10 % IC rac0001.lcd
mAU



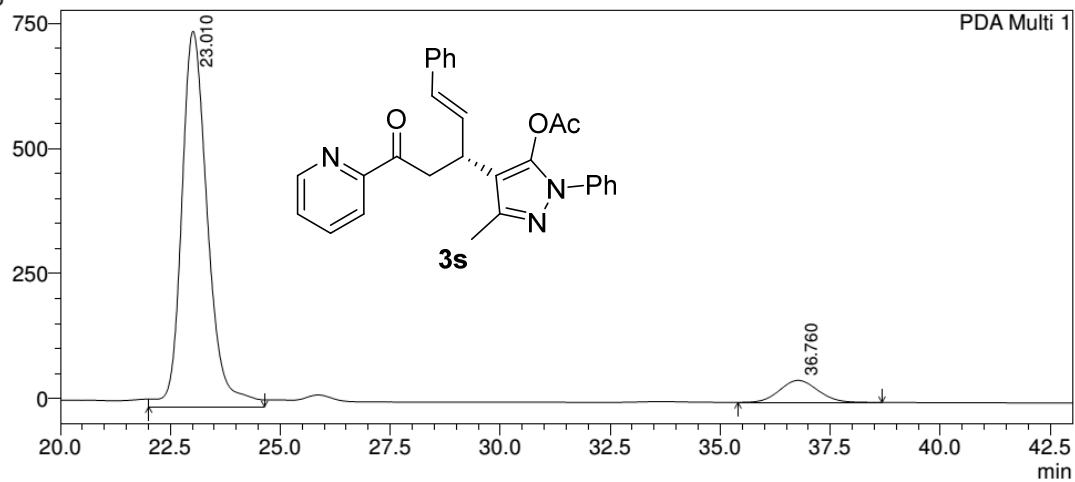
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.359	14380531	373483	50.507	61.837
2	37.173	14091758	230493	49.493	38.163
Total		28472289	603976	100.000	100.000

D:\HPLC\vivek -2\py chalcone + pyrazolinone\revision substrate\Cinnam py cal + pyz 1ml 10 % IC chiral0001.lcd
mAU



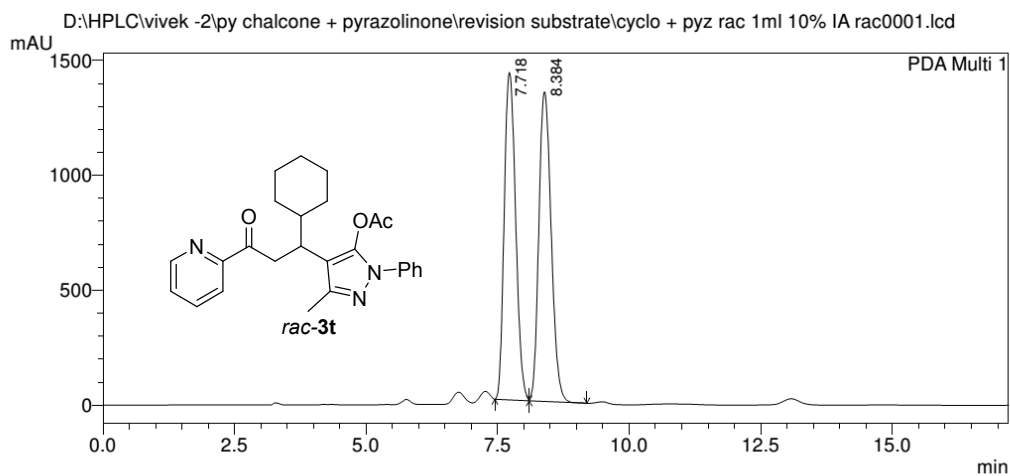
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.010	30734623	750162	92.037	94.459
2	36.760	2659049	44002	7.963	5.541
Total		33393672	794164	100.000	100.000

==== Shimadzu LCsolution Analysis Report =====

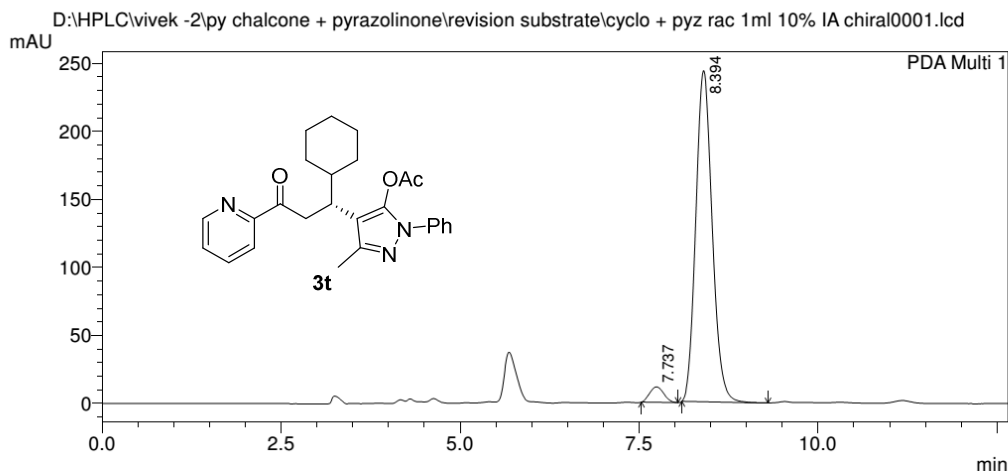


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.718	21511396	1426410	49.444	51.440
2	8.384	21995328	1346534	50.556	48.560
Total		43506724	2772944	100.000	100.000

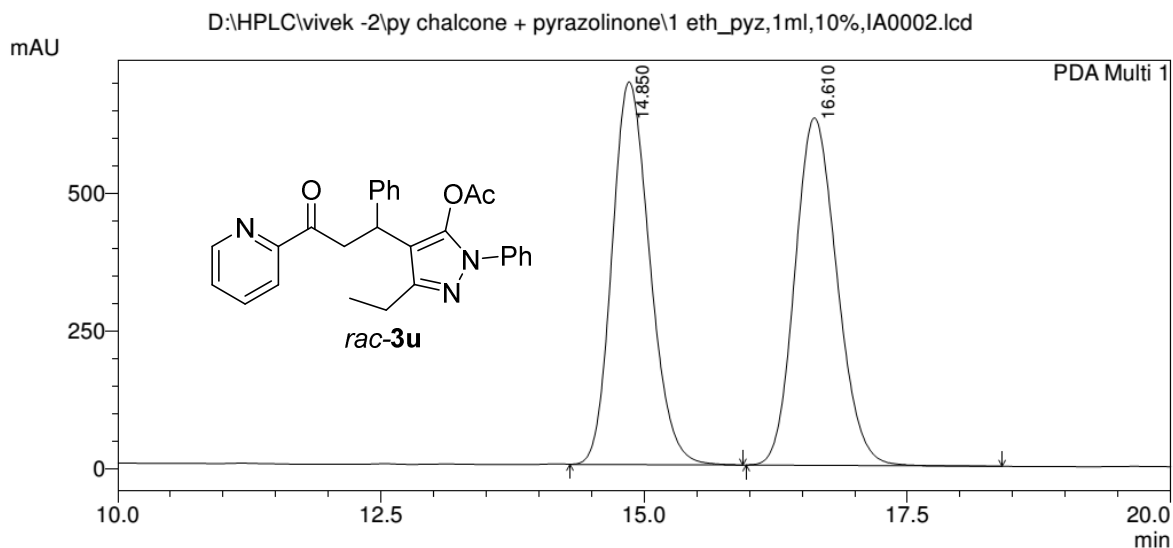


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

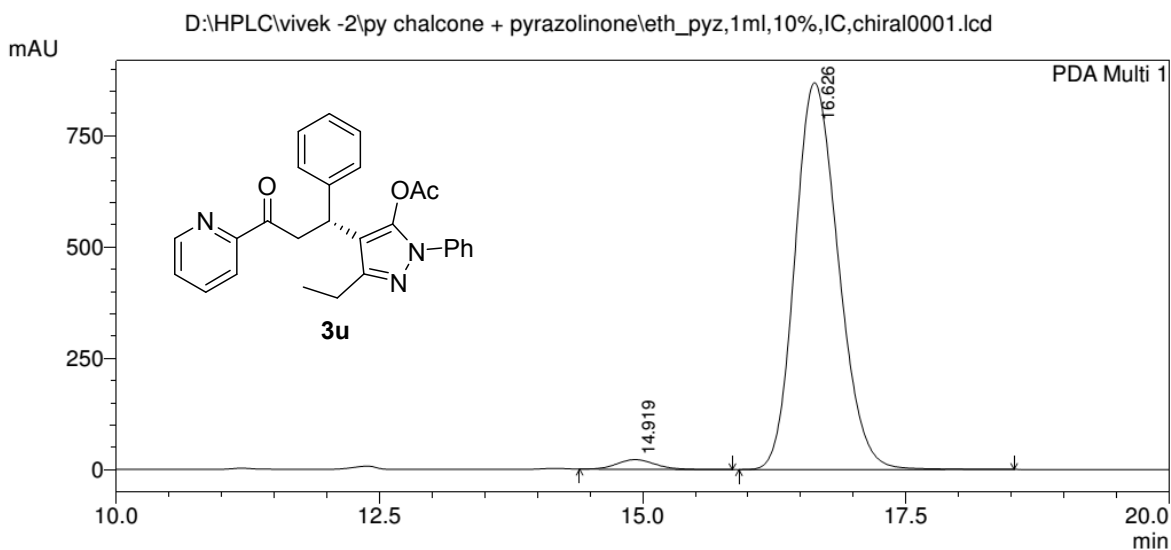
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.737	154631	11312	3.833	4.444
2	8.394	3879600	243251	96.167	95.556
Total		4034231	254562	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

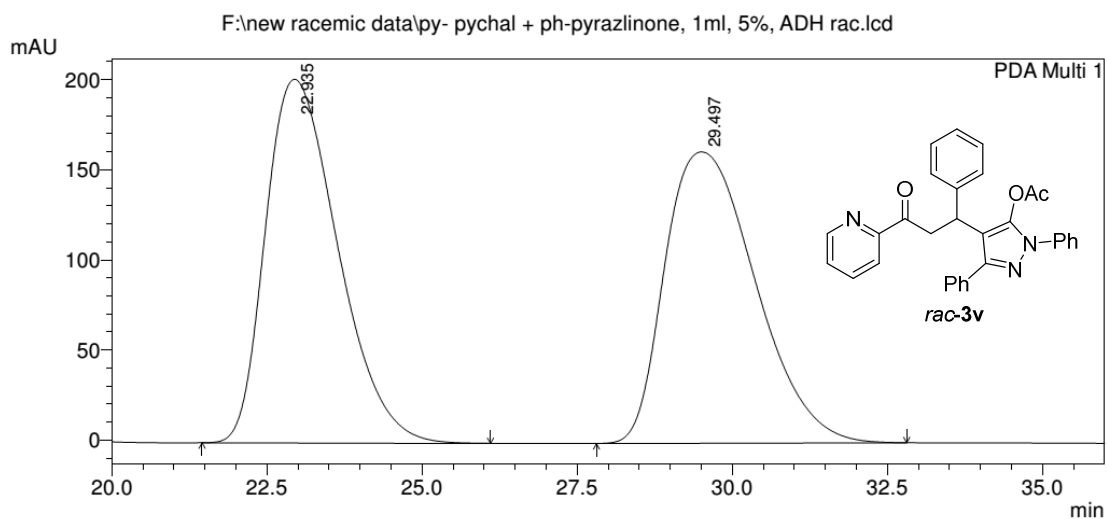
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.850	17307003	694850	49.664	52.404
2	16.610	17541195	631092	50.336	47.596
Total		34848198	1325941	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

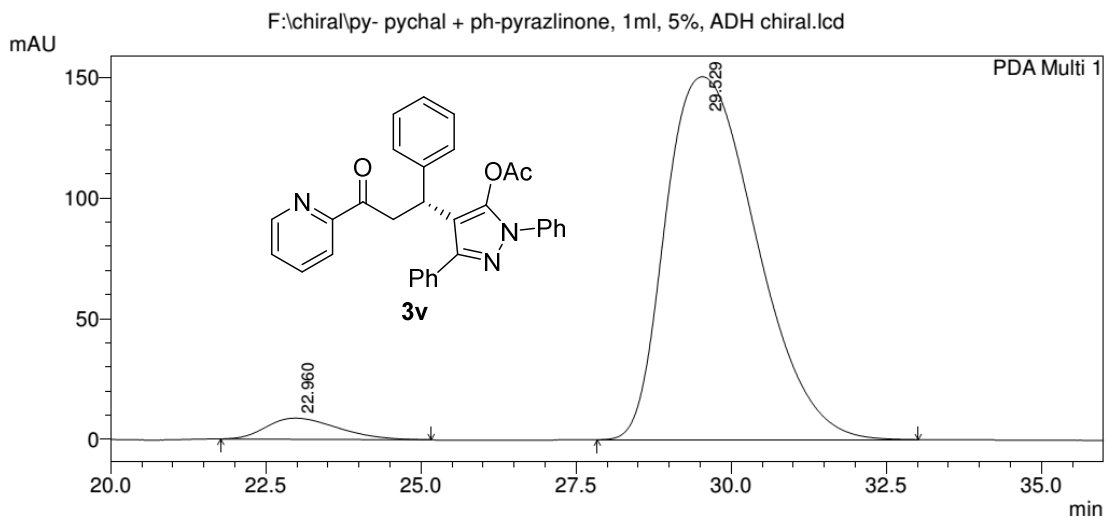
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.919	549414	21823	2.163	2.451
2	16.626	24847416	868507	97.837	97.549
Total		25396830	890329	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

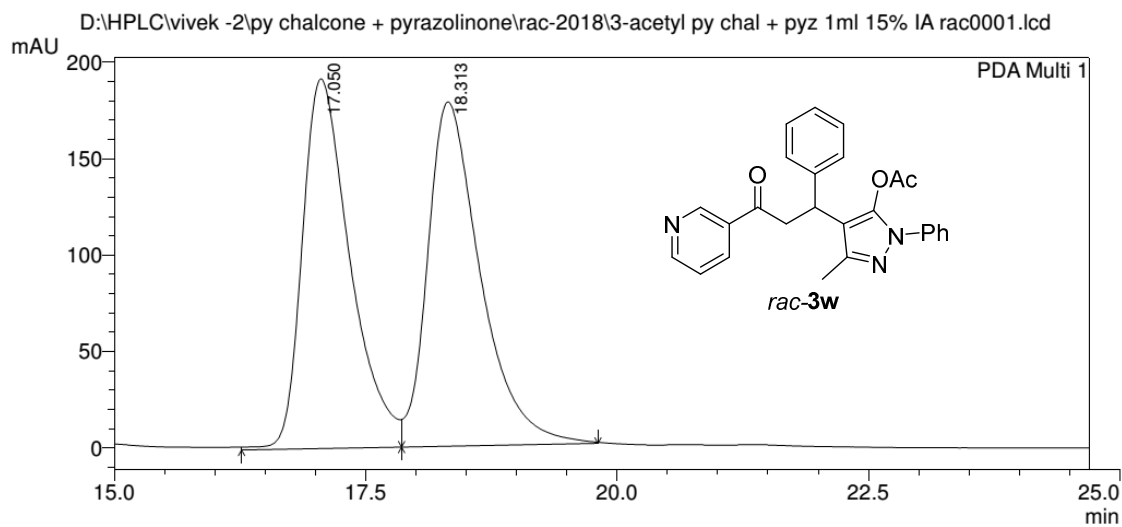
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.935	16389944	201782	49.908	55.516
2	29.497	16450488	161684	50.092	44.484
Total		32840432	363466	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

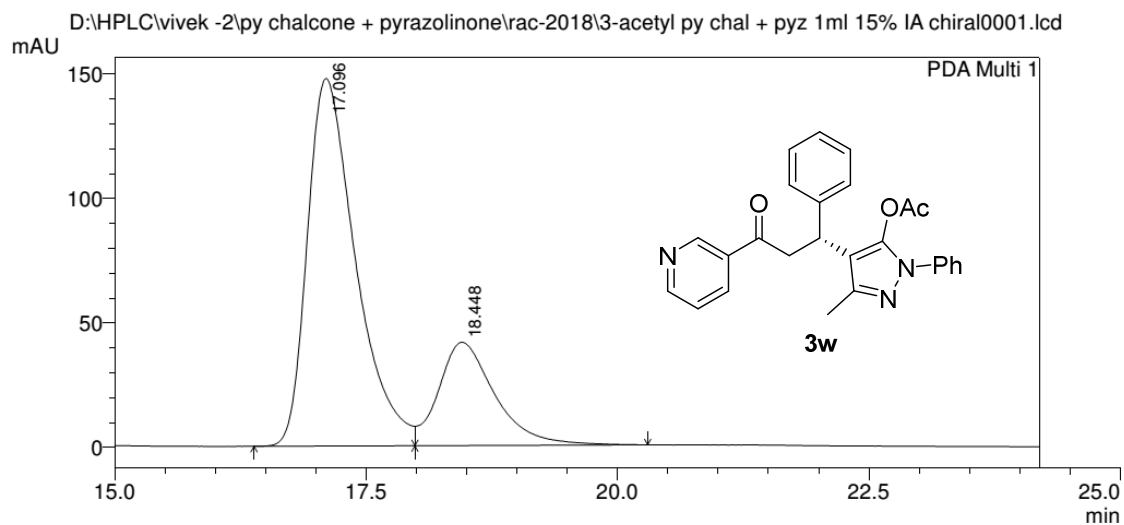
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.960	703619	8773	4.381	5.510
2	29.529	15357798	150449	95.619	94.490
Total		16061418	159221	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.050	6329184	191677	49.251	51.784
2	18.313	6521695	178469	50.749	48.216
Total		12850879	370146	100.000	100.000

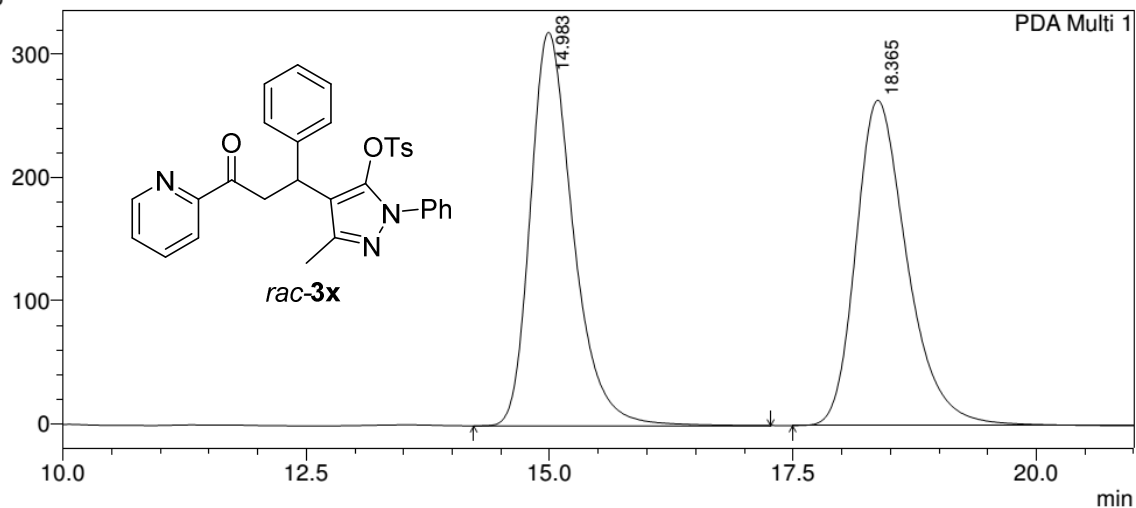


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.096	4921668	147598	75.292	78.066
2	18.448	1615073	41471	24.708	21.934
Total		6536741	189068	100.000	100.000

D:\HPLC\wivek -2\py chalcone + pyrazolinone\may 2018\TSPYZ +PNO2PY CHAL 1ML 25% iA RAC0001.lcd
mAU



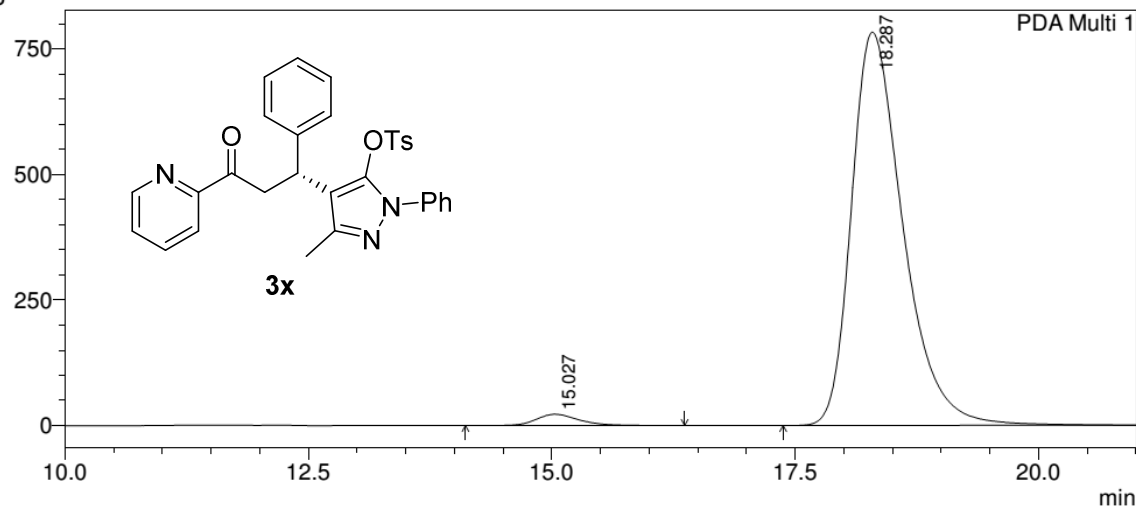
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.983	9740671	319455	50.017	54.744
2	18.365	9734121	264090	49.983	45.256
Total		19474792	583545	100.000	100.000

D:\HPLC\wivek -2\py chalcone + pyrazolinone\may 2018\TSPYZ +PNO2PY CHAL 1ML 25% iA CHIRAL0001.lcd
mAU



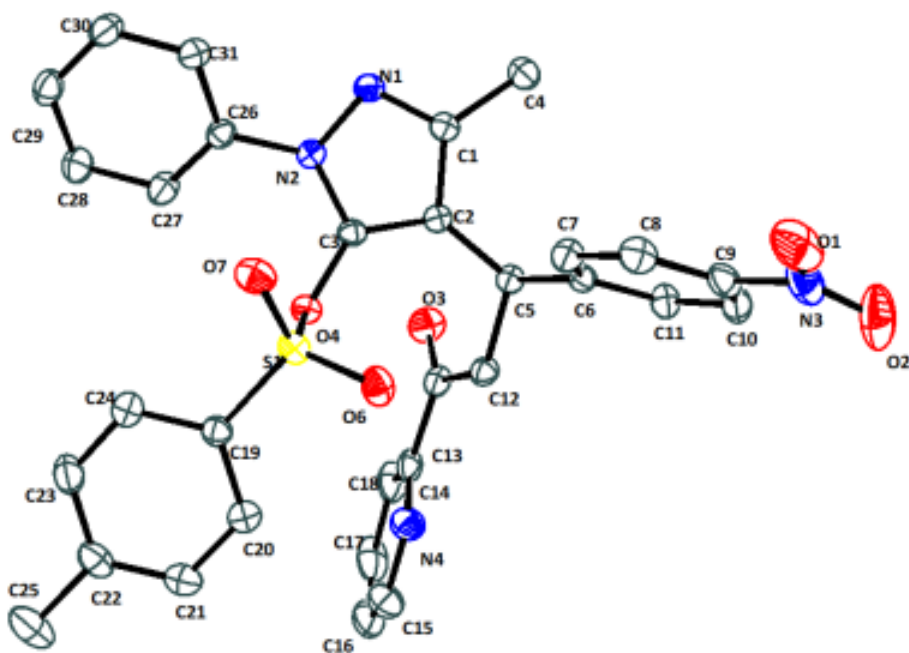
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.027	695007	22368	2.348	2.776
2	18.287	28898823	783470	97.652	97.224
Total		29593830	805838	100.000	100.000

3. Single Crystal X-ray diffraction of **3x**



ORTEP diagram of molecule **3x** with 30% thermal probability ellipsoids. Hydrogen's are omitted for clarity.

Table 1 Crystal data and structure refinement for SAHOO-1.

Identification code	SAHOO-1
Empirical formula	C ₃₁ H ₂₆ N ₄ O ₆ S
Formula weight	582.62
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	7.5644(2)
b/Å	19.5682(6)
c/Å	9.8133(3)
α /°	90
β /°	105.002(3)
γ /°	90
Volume/Å ³	1403.07(7)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.379
μ/mm^{-1}	0.168
F(000)	608.0
Crystal size/mm ³	? × ? × ?
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	6.96 to 54.73
Index ranges	-7 ≤ h ≤ 9, -22 ≤ k ≤ 25, -12 ≤ l ≤ 12
Reflections collected	11881
Independent reflections	5108 [R_{int} = 0.0198, R_{sigma} = 0.0258]
Data/restraints/parameters	5108/1/381
Goodness-of-fit on F ²	1.041
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0331, wR_2 = 0.0784
Final R indexes [all data]	R_1 = 0.0390, wR_2 = 0.0819
Largest diff. peak/hole / e Å ⁻³	0.11/-0.22
Flack parameter	0.05(2)