

Squaramide-Catalysed Enantio- and Diastereoselective Sulfa-Michael Addition of Thioacetic Acid to α,β -Disubstituted Nitroalkenes

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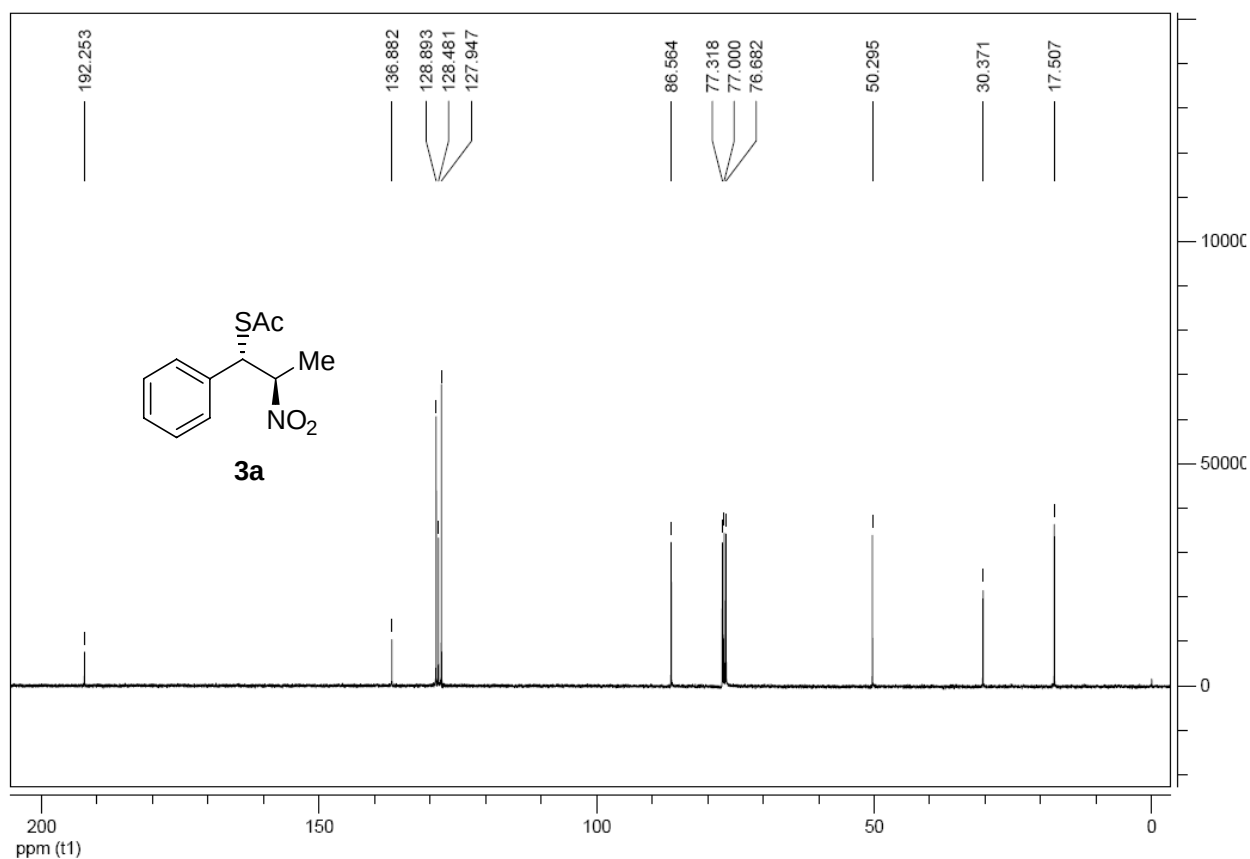
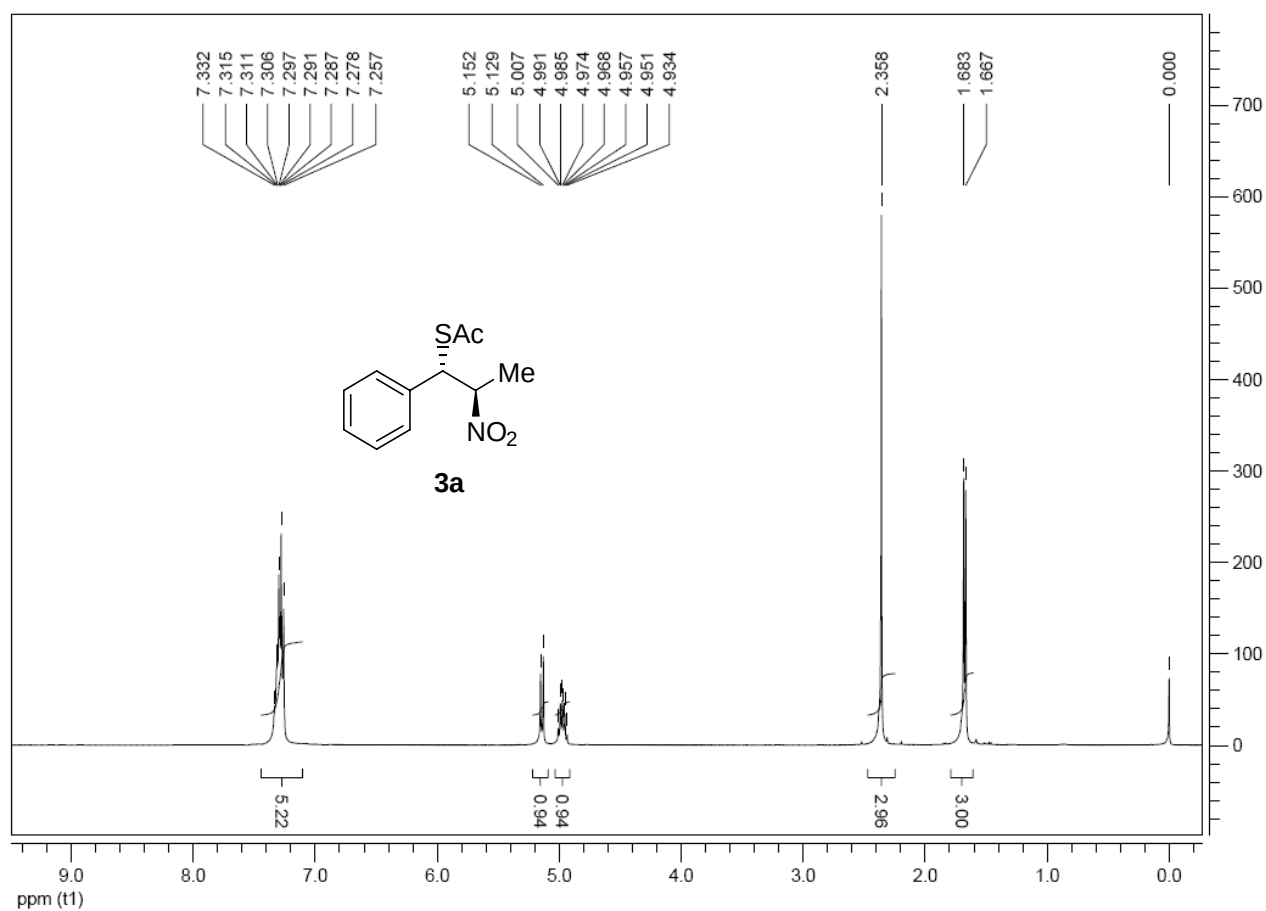
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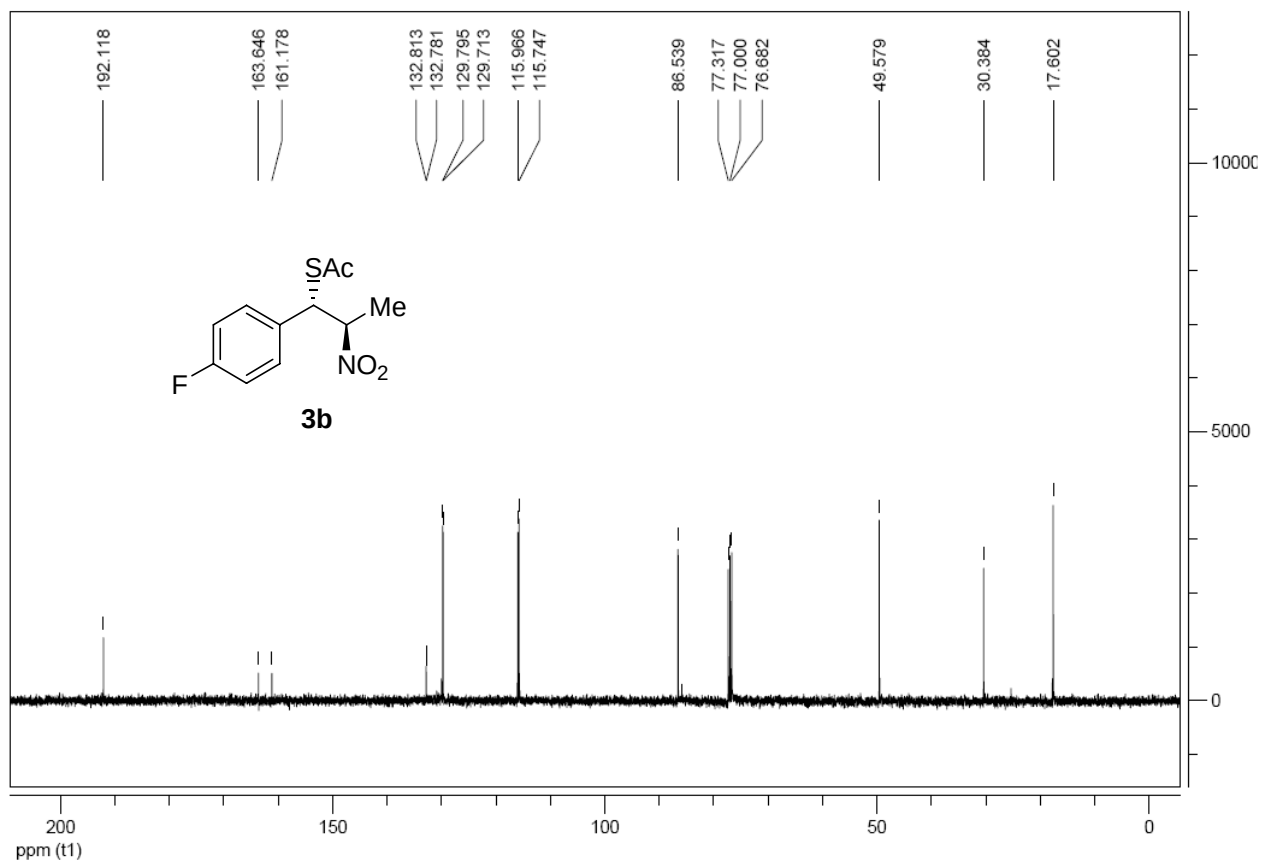
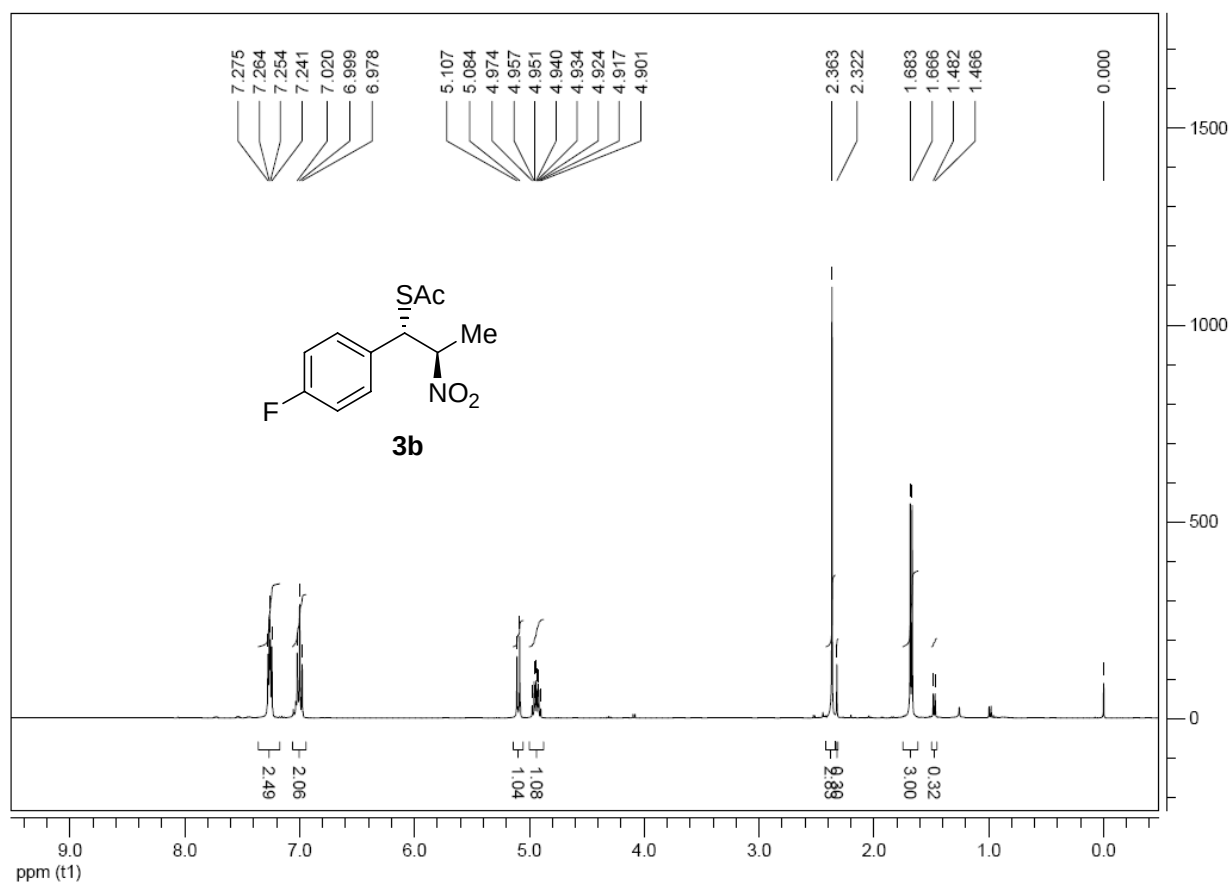
Supporting Information

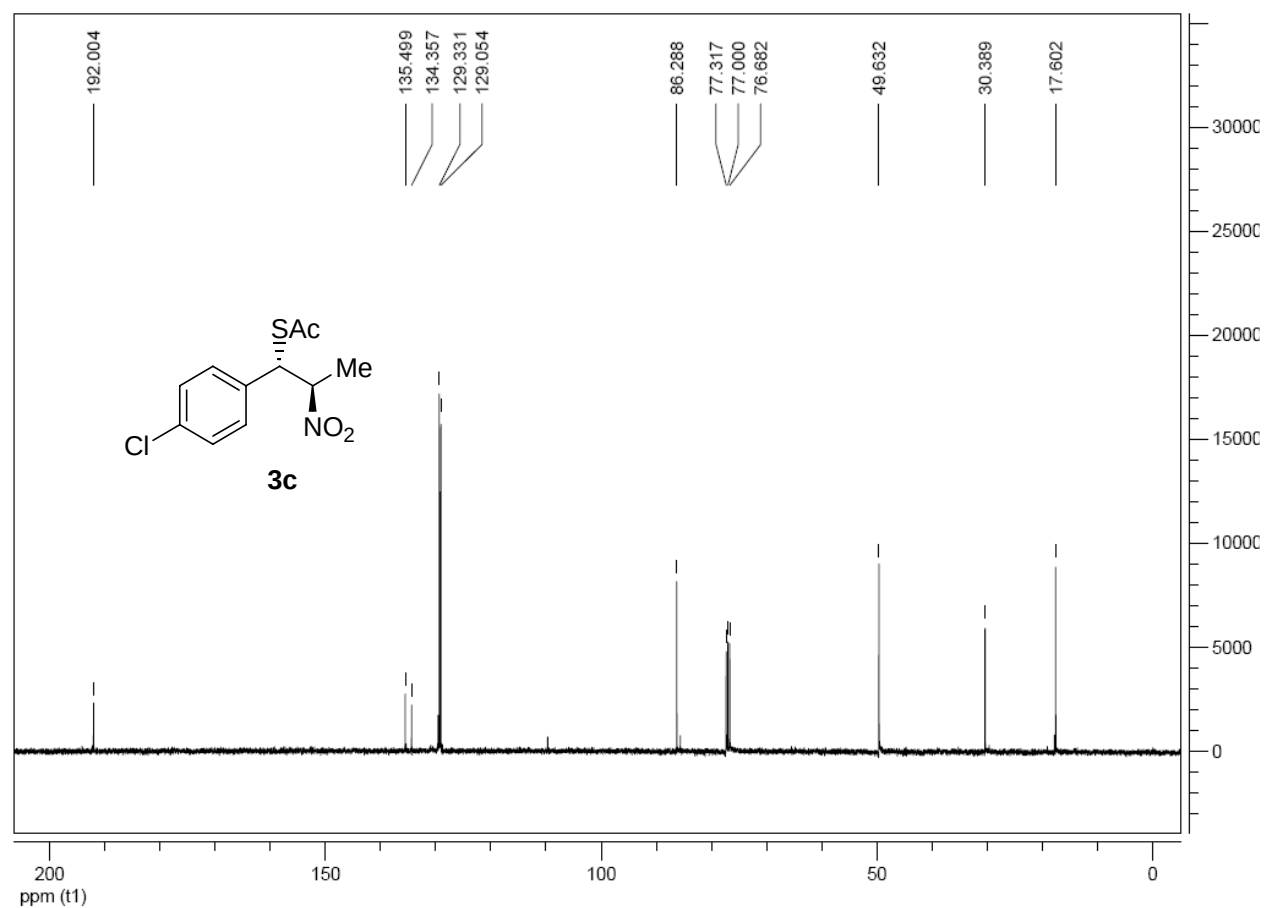
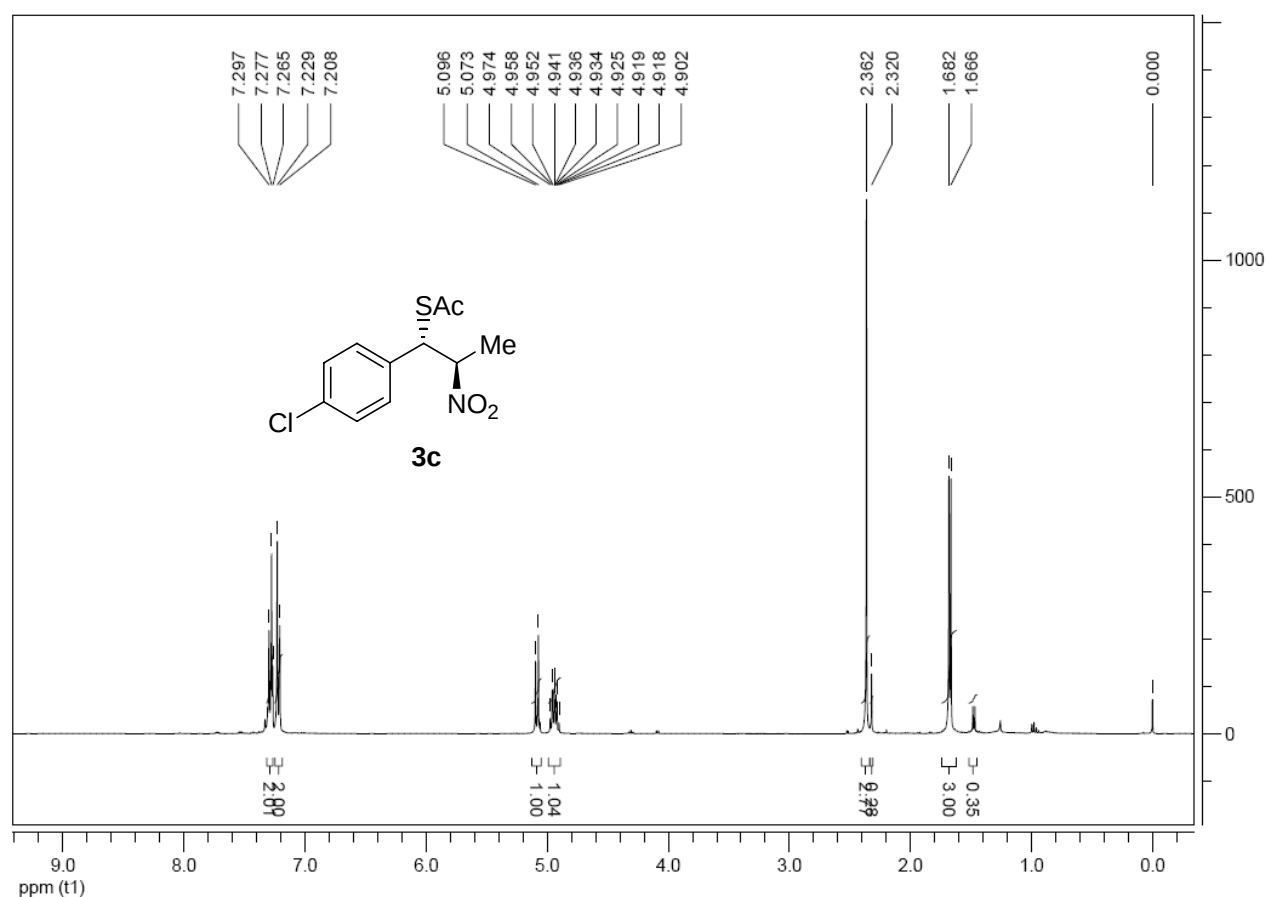
Contents

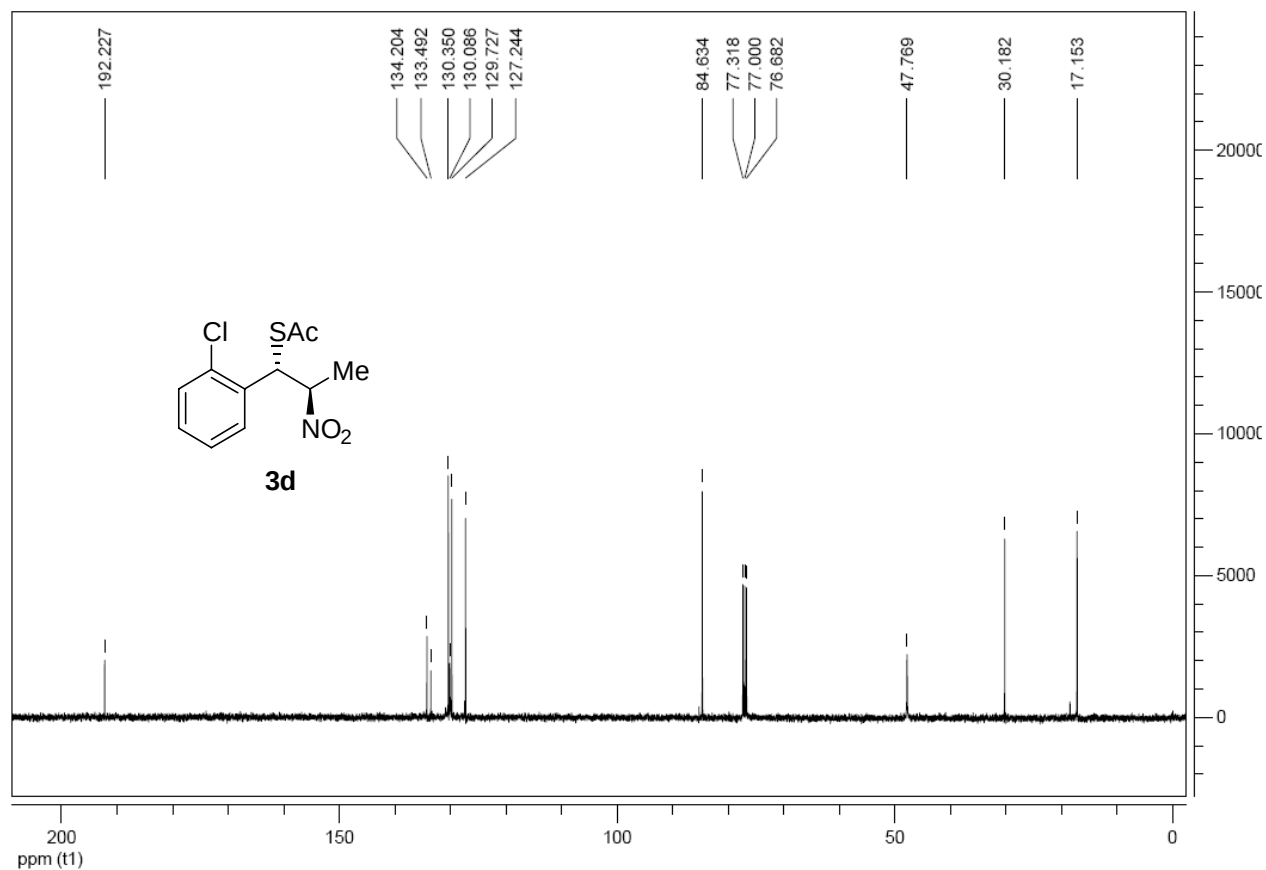
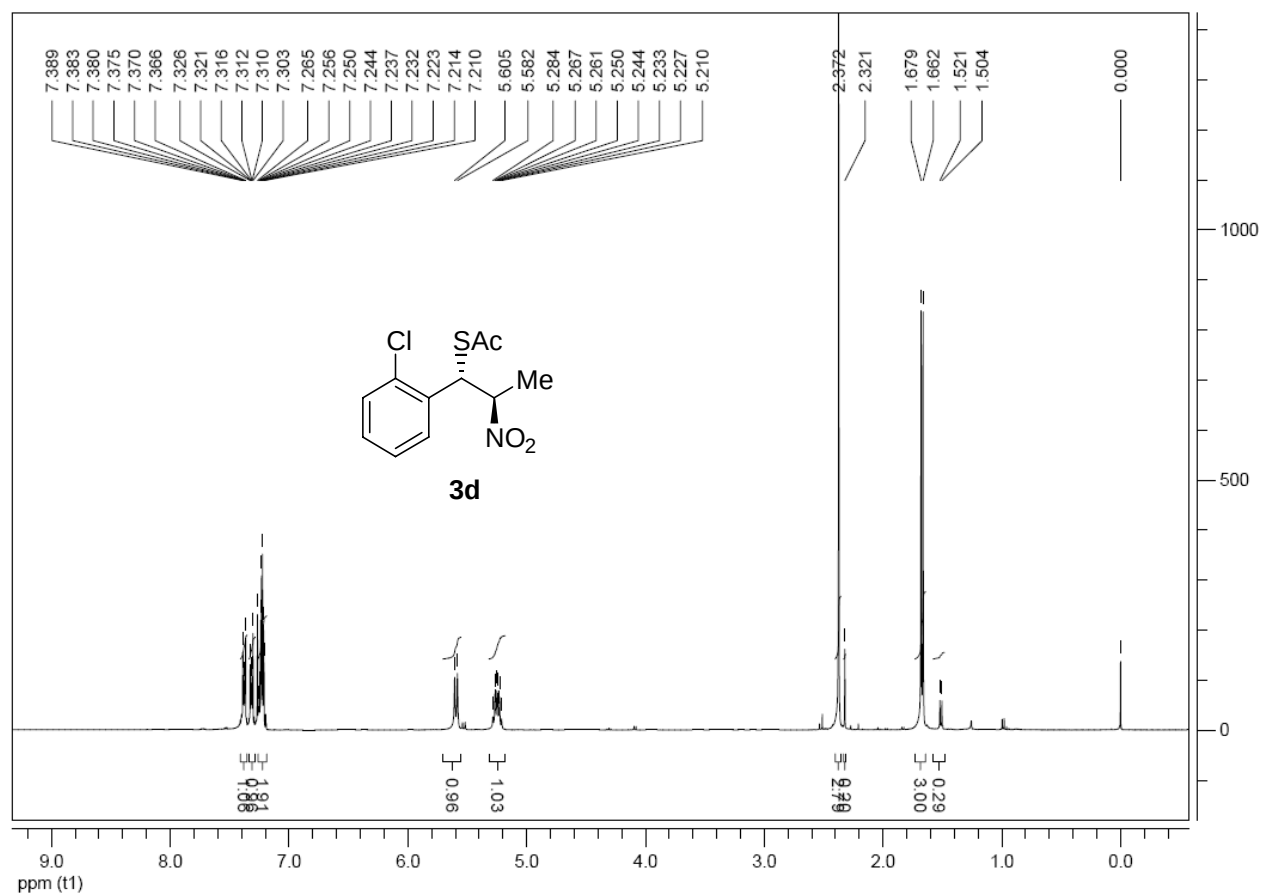
Copies of ^1H and ^{13}C NMR spectra of new compounds.....	S1
Copies of HPLC chromatographs of Michael adducts.....	S23

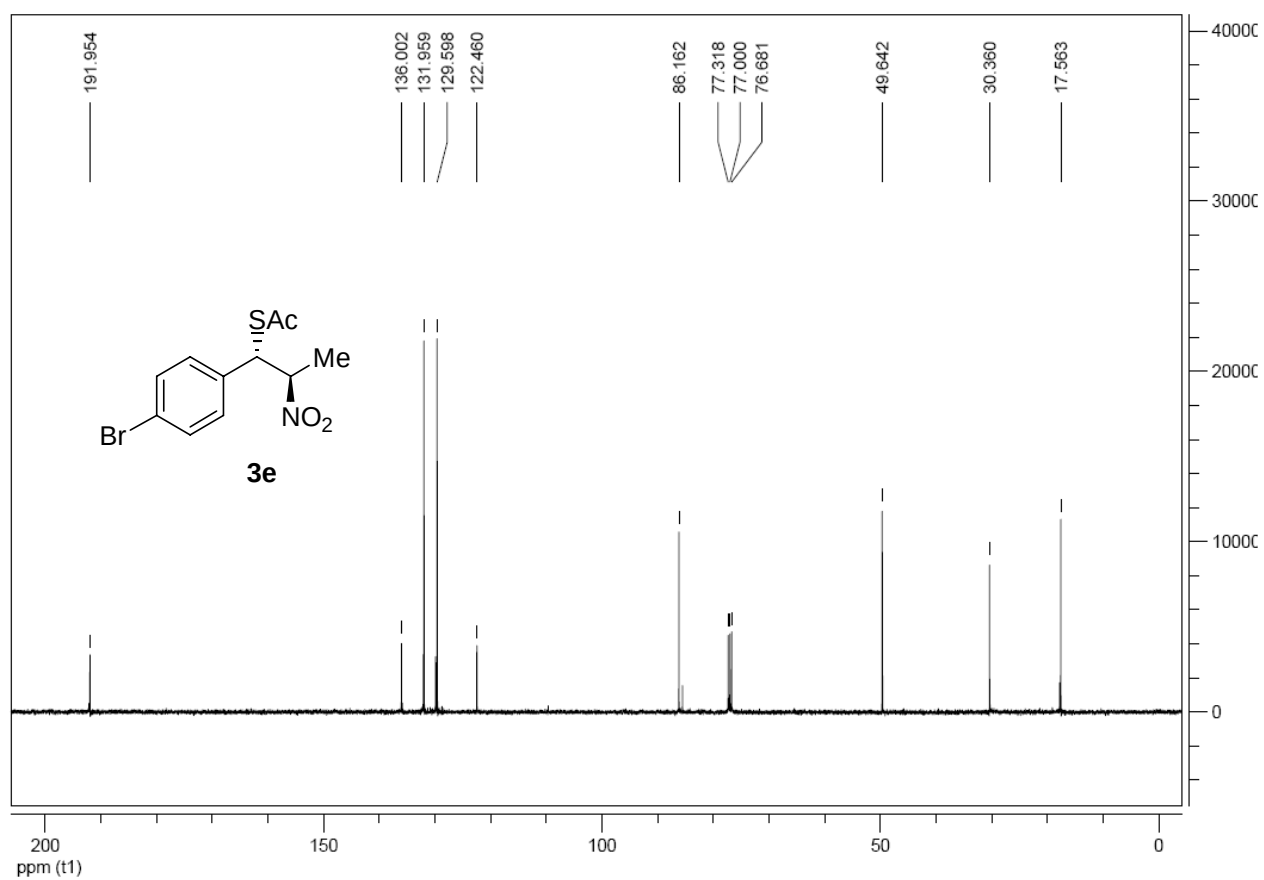
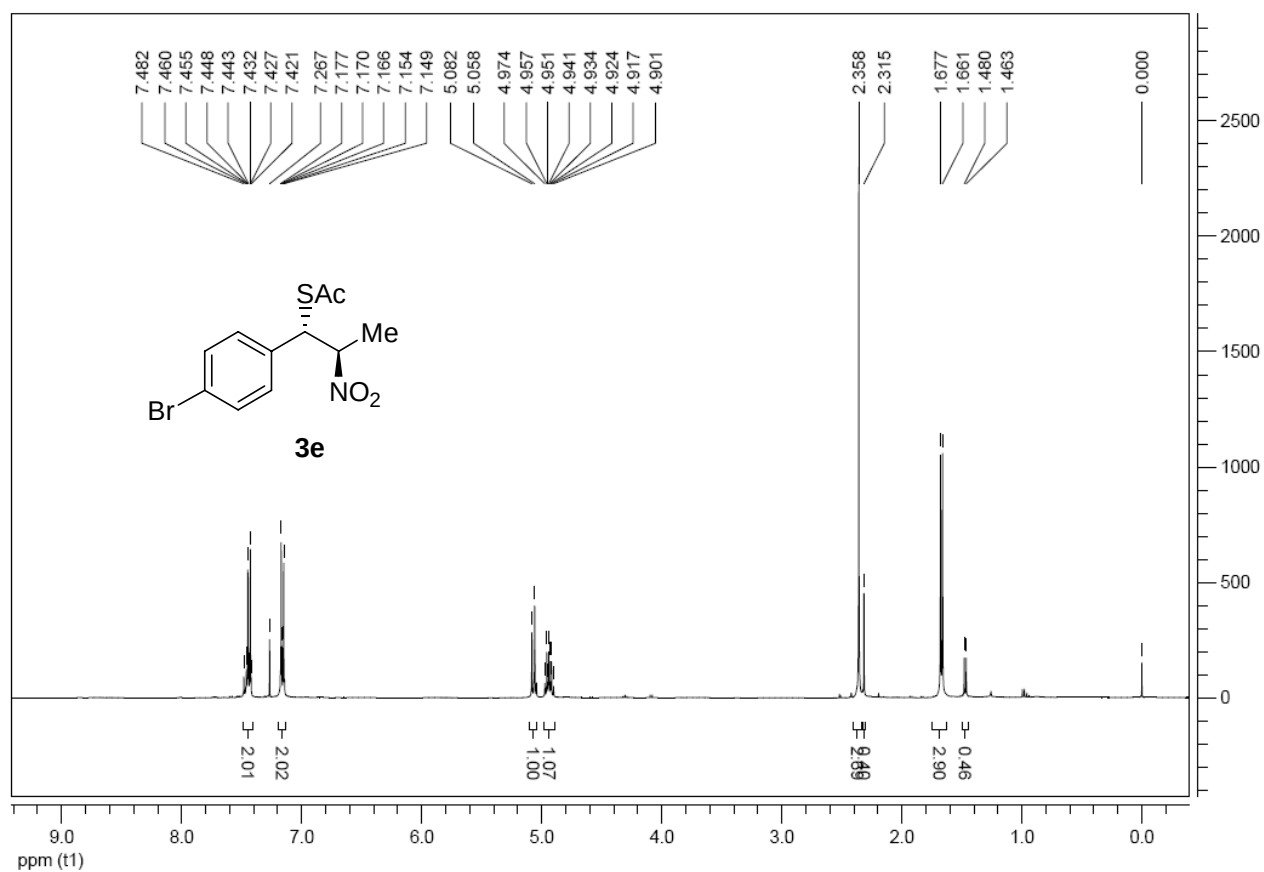
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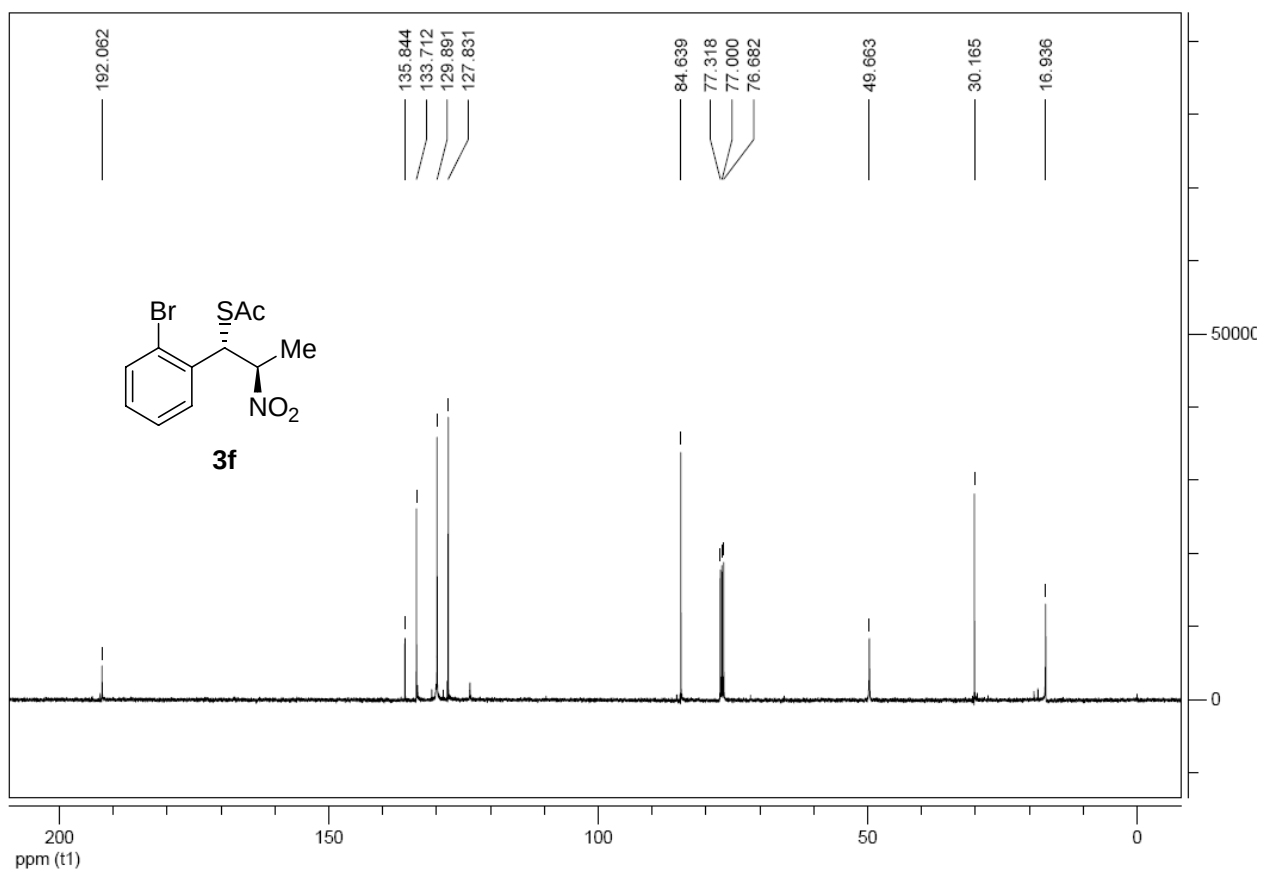
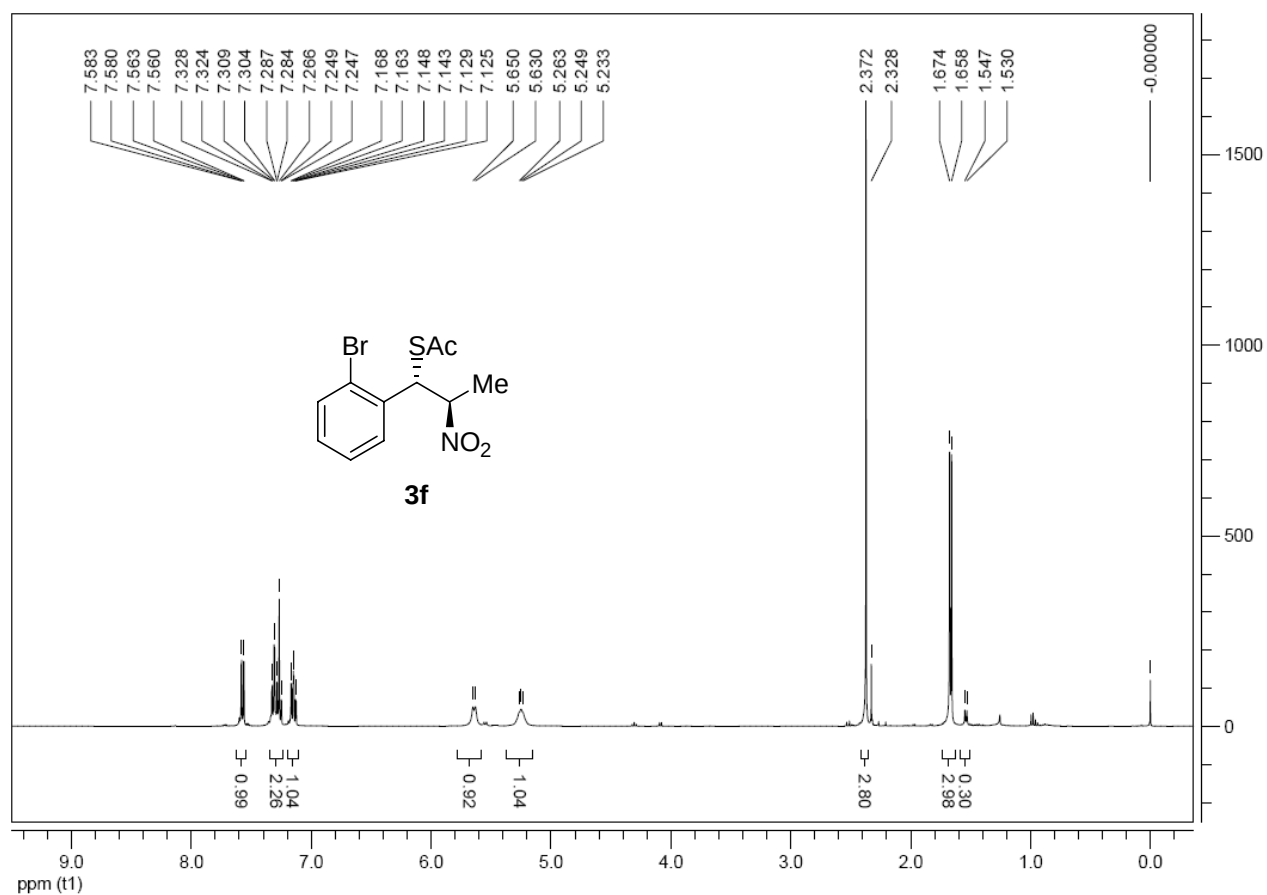


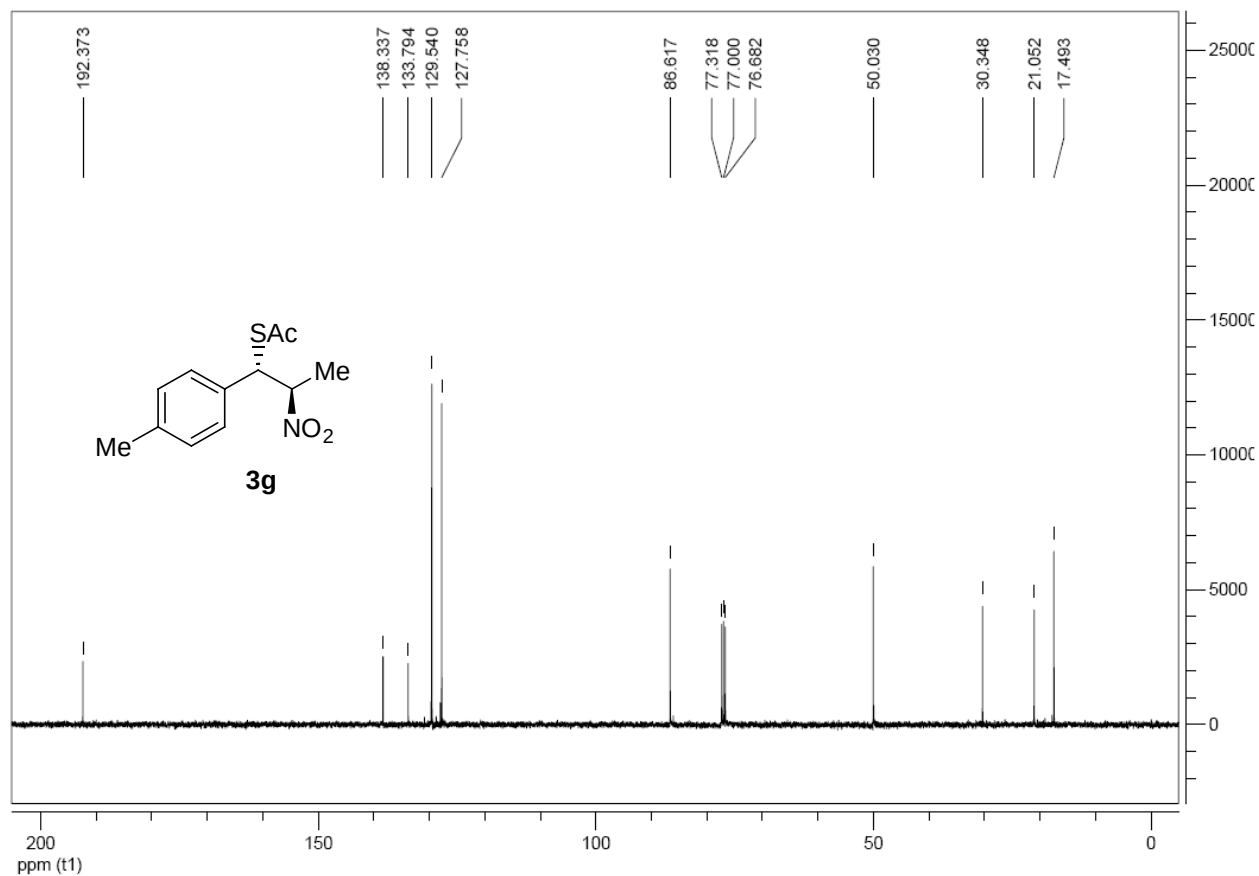
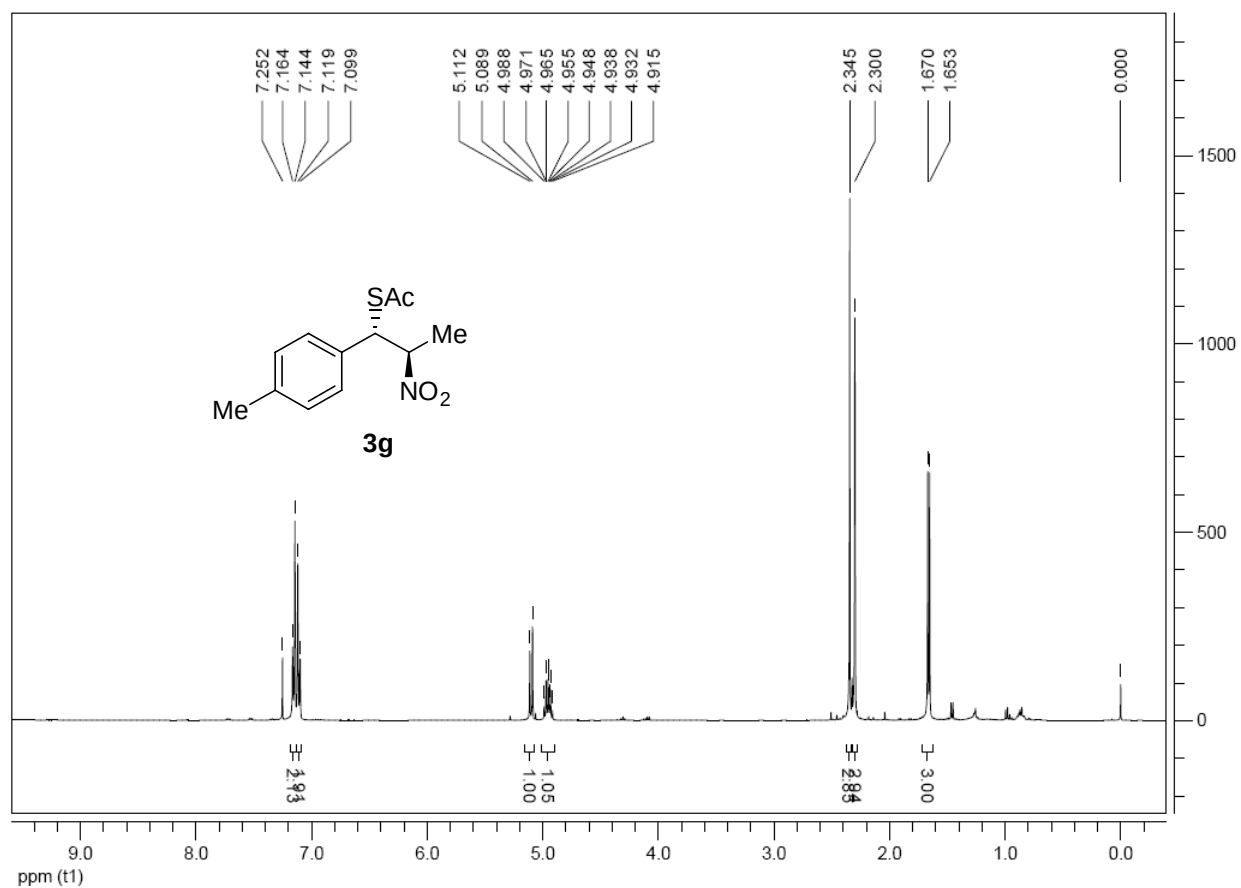


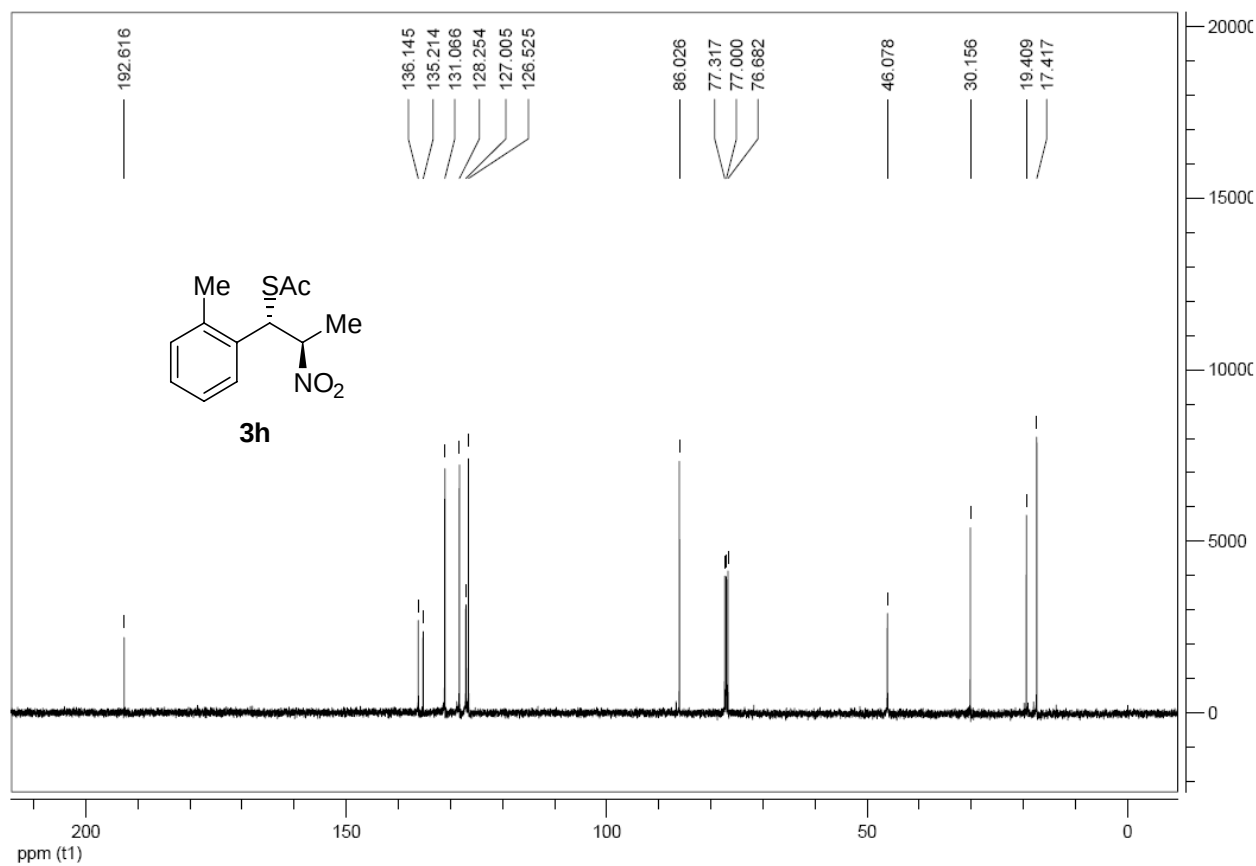
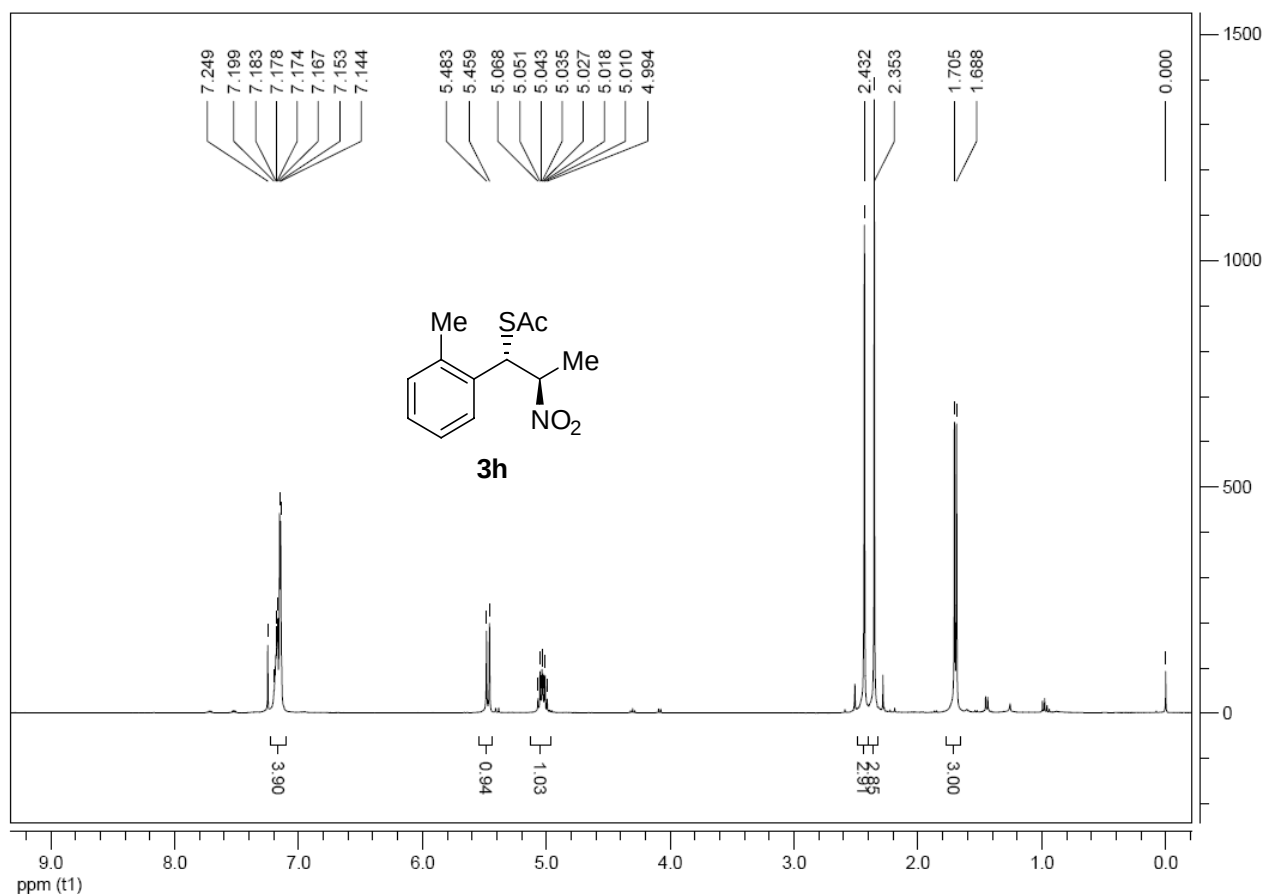


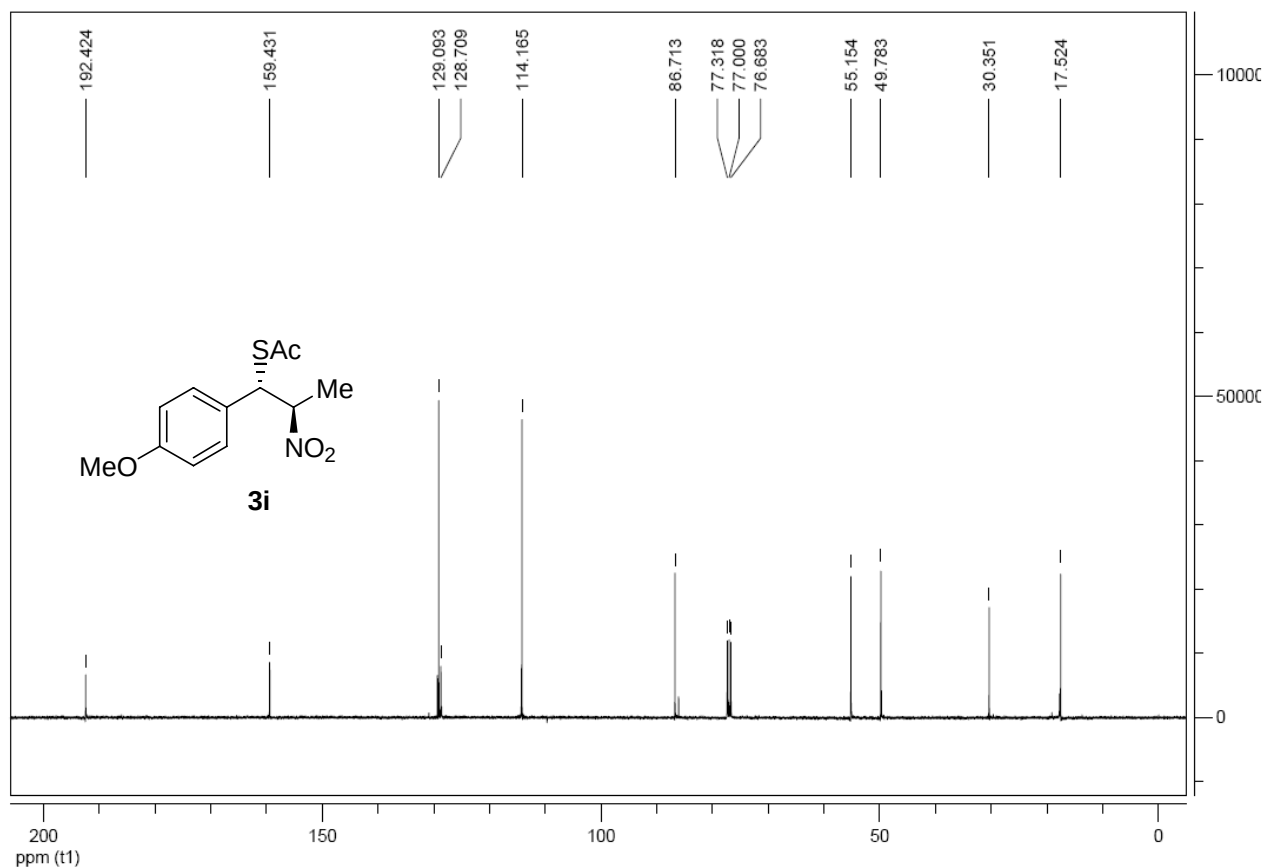
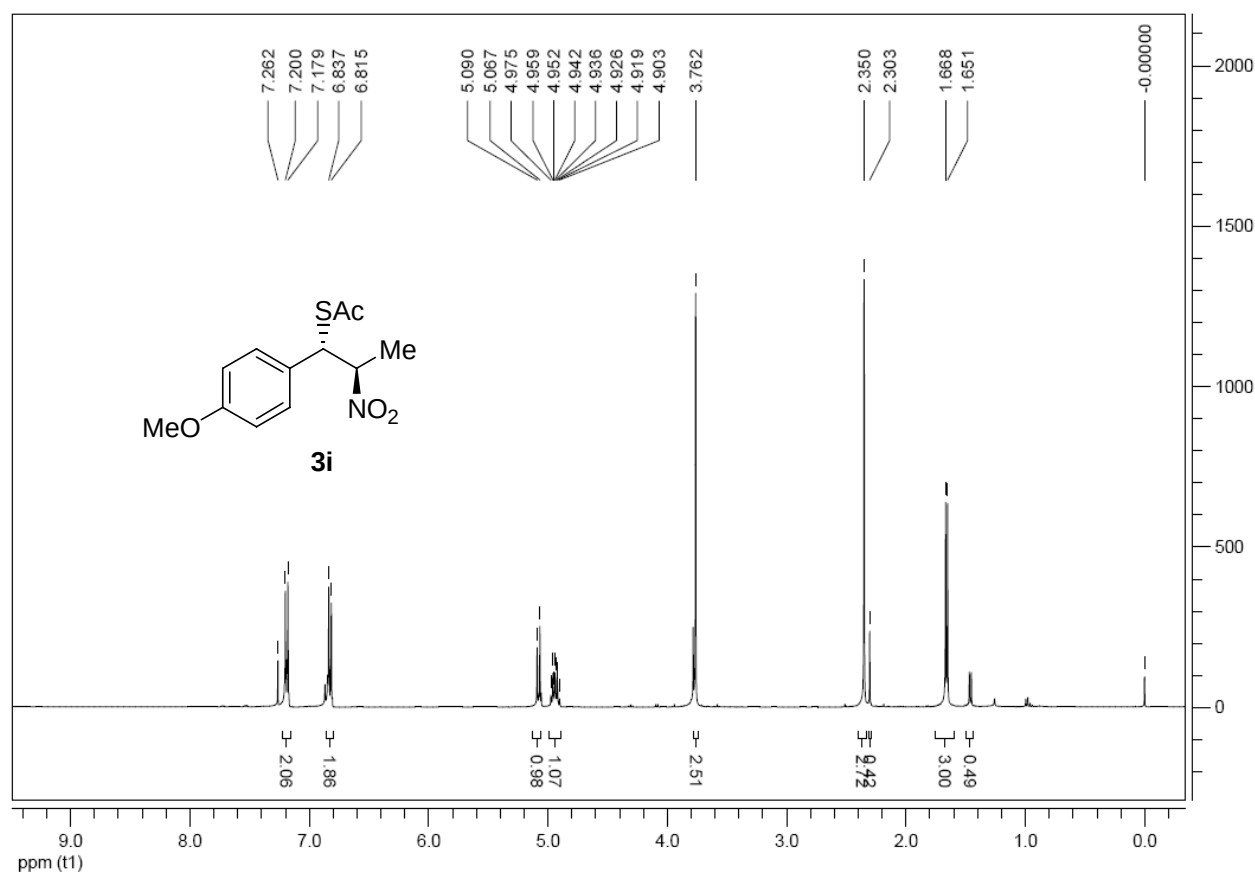


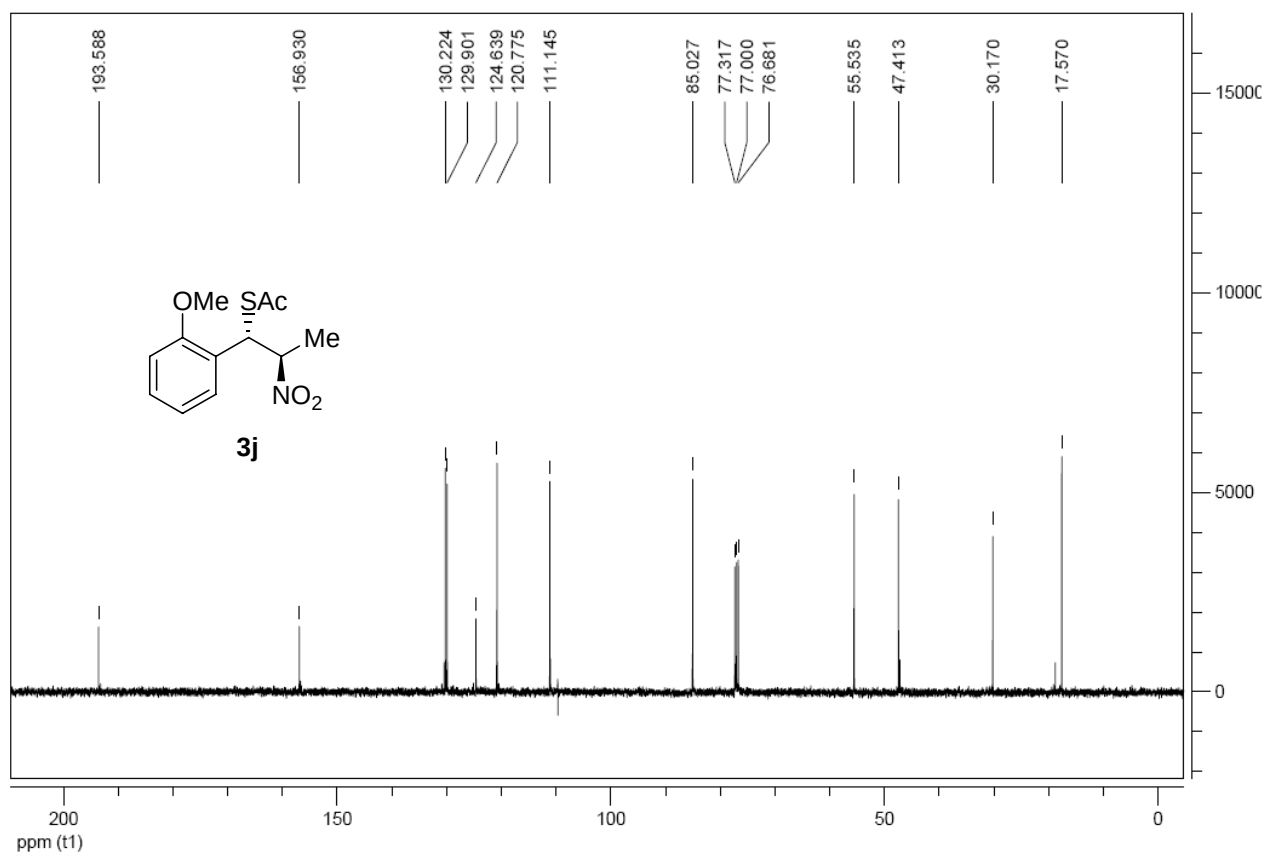
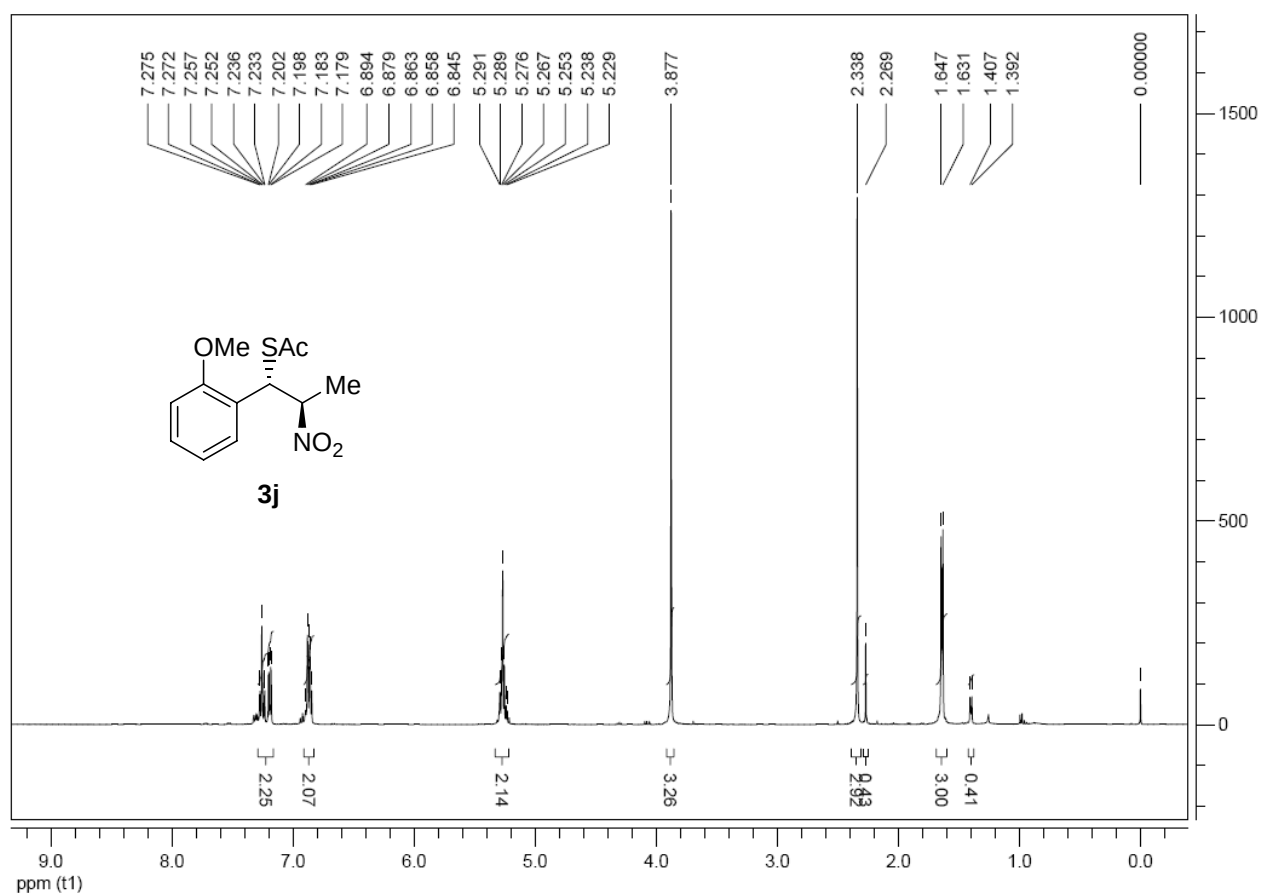


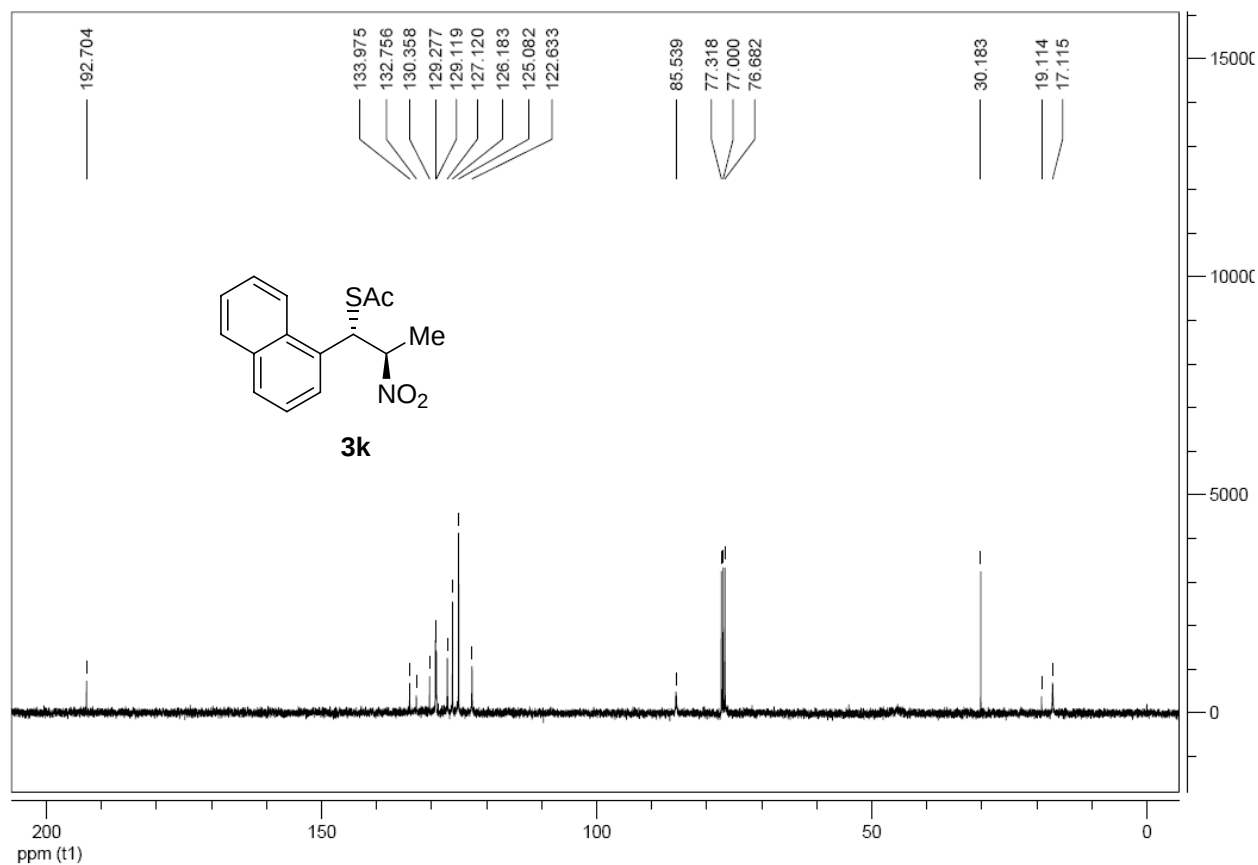
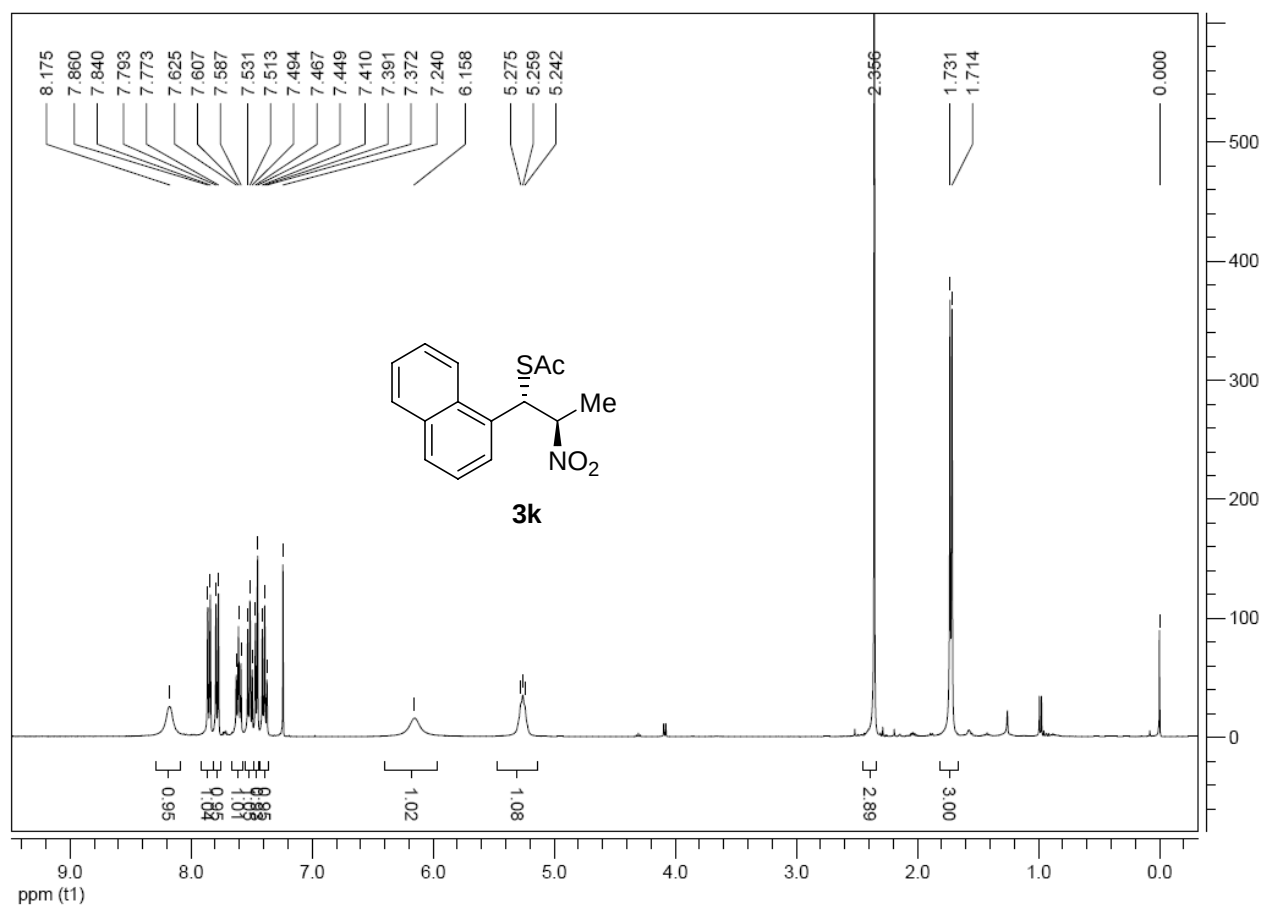


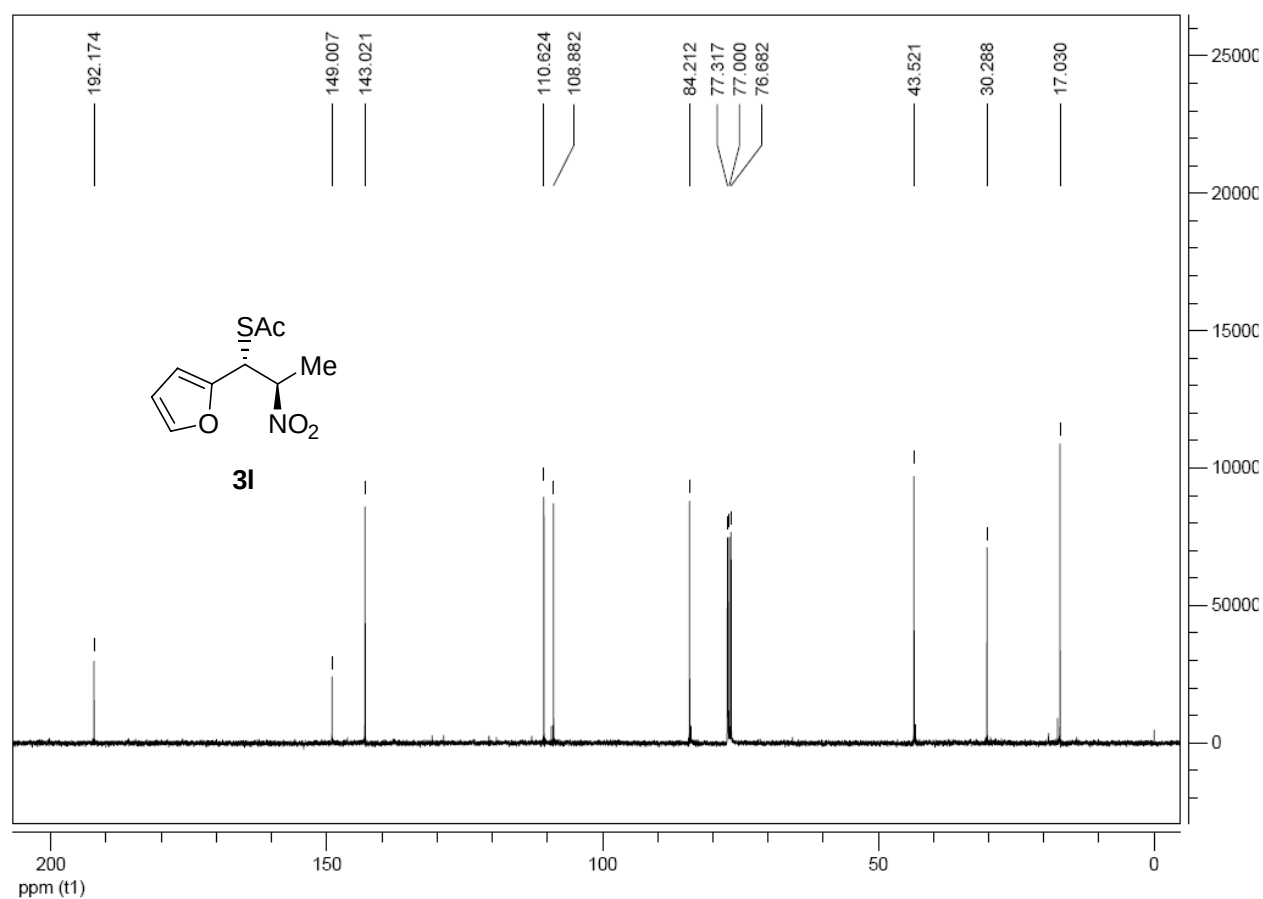
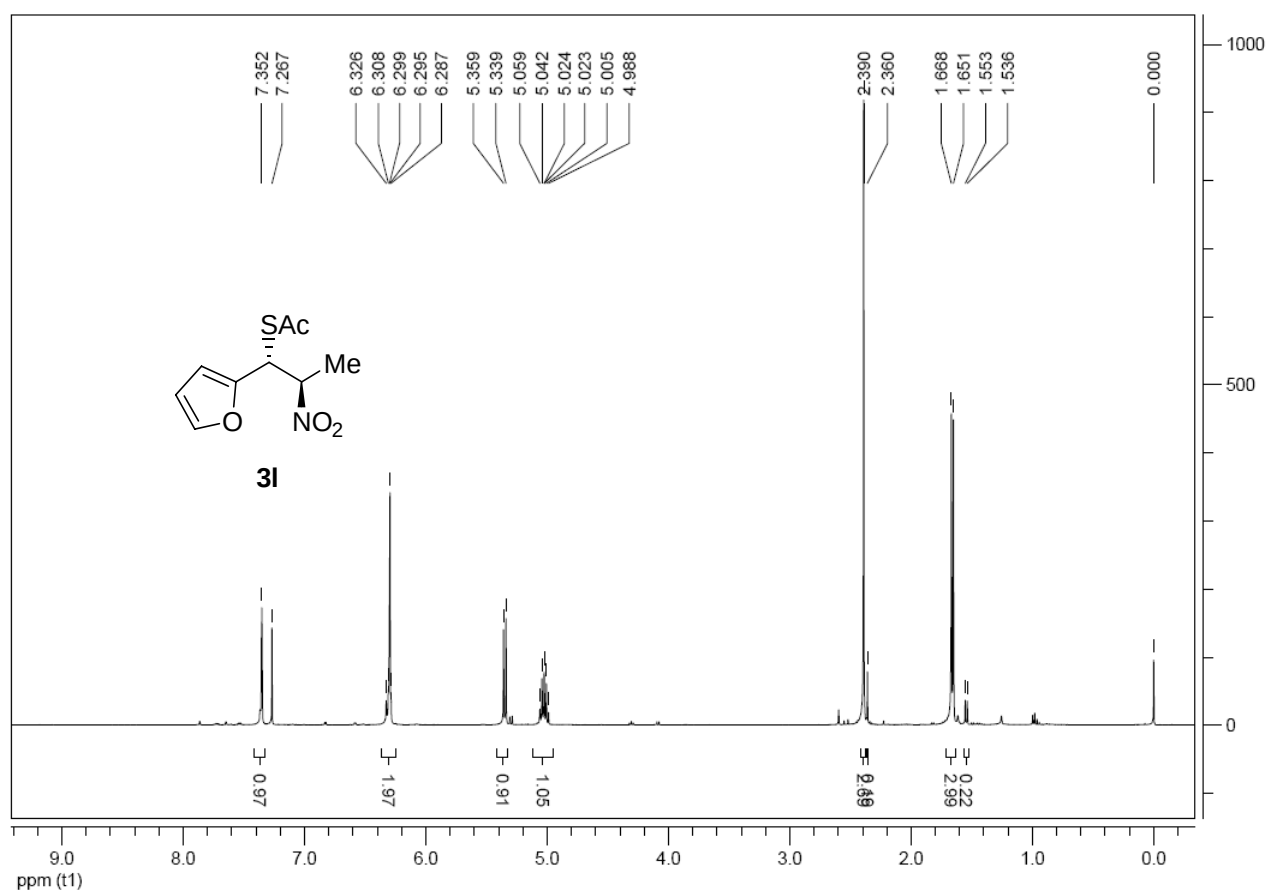


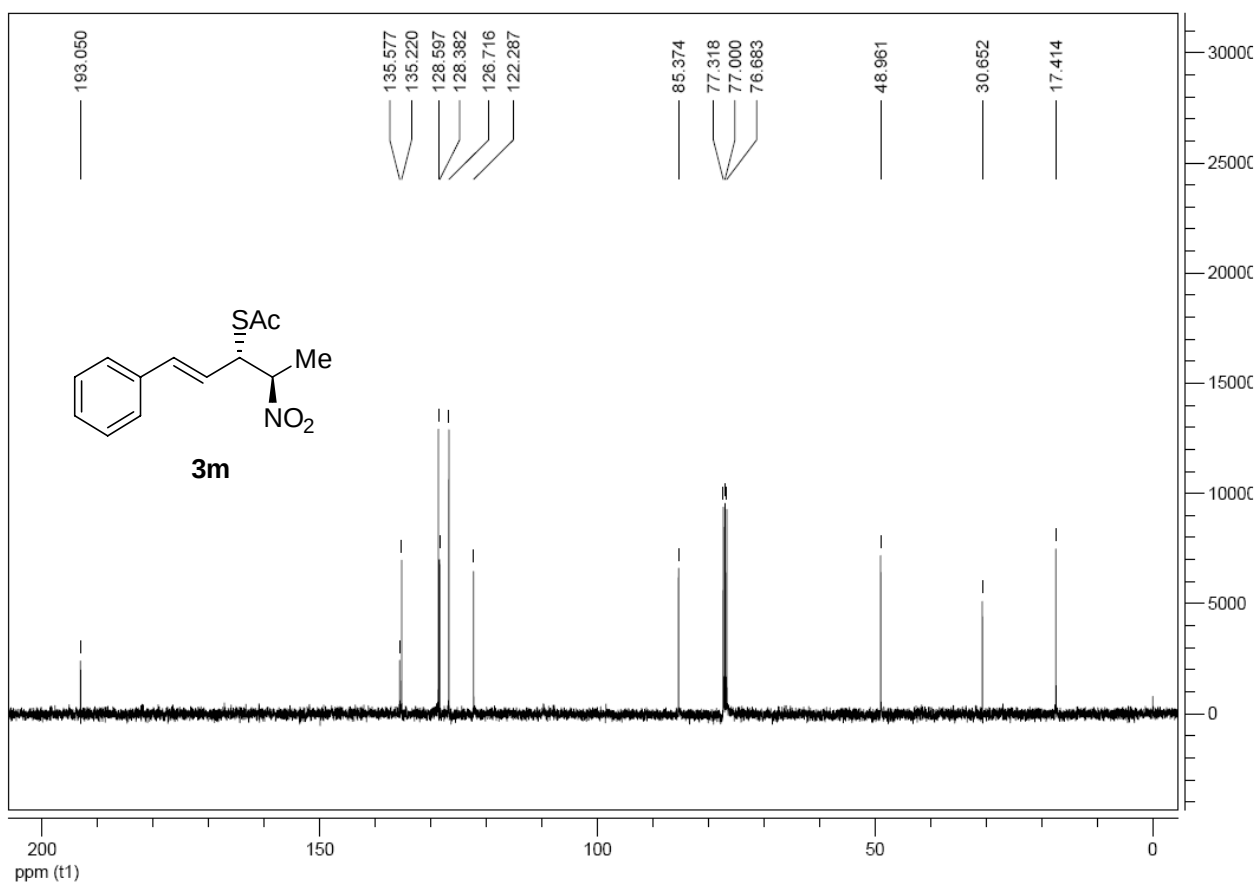
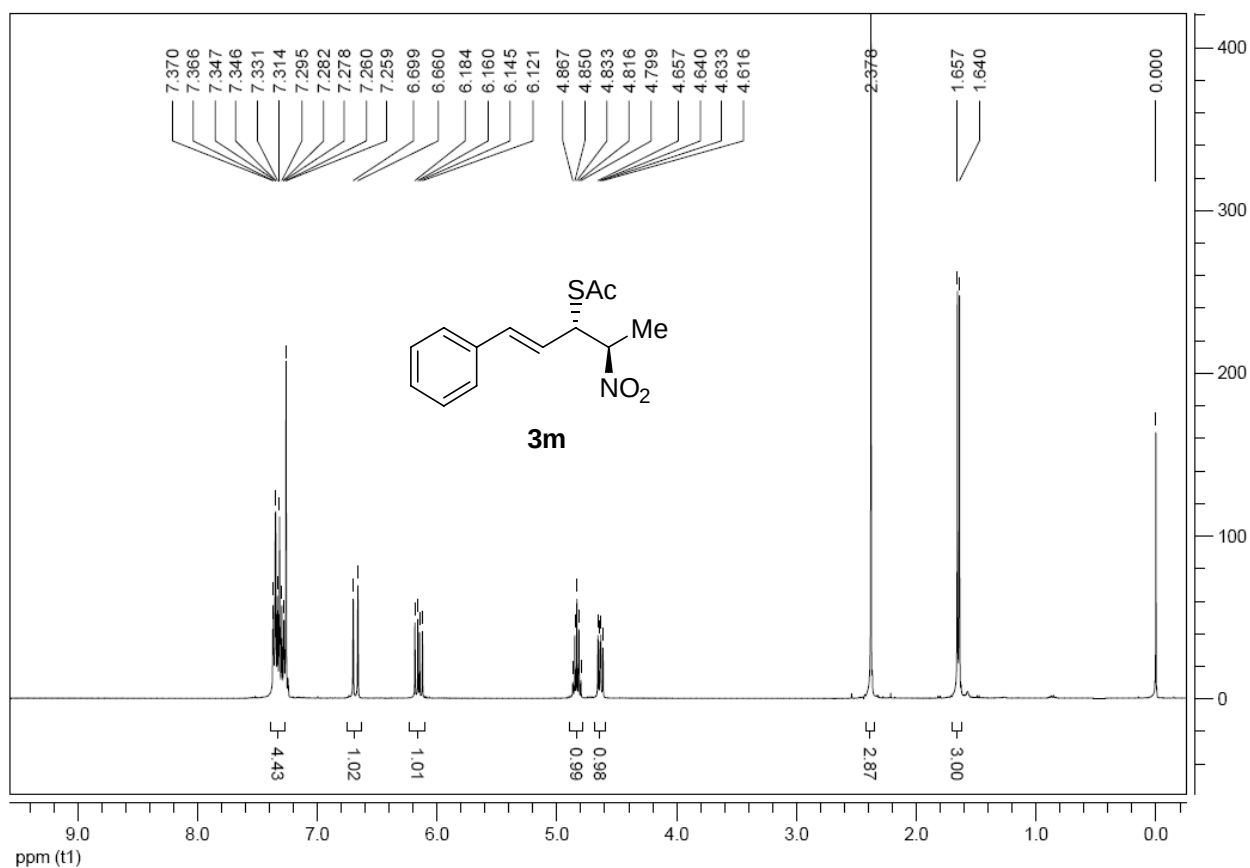


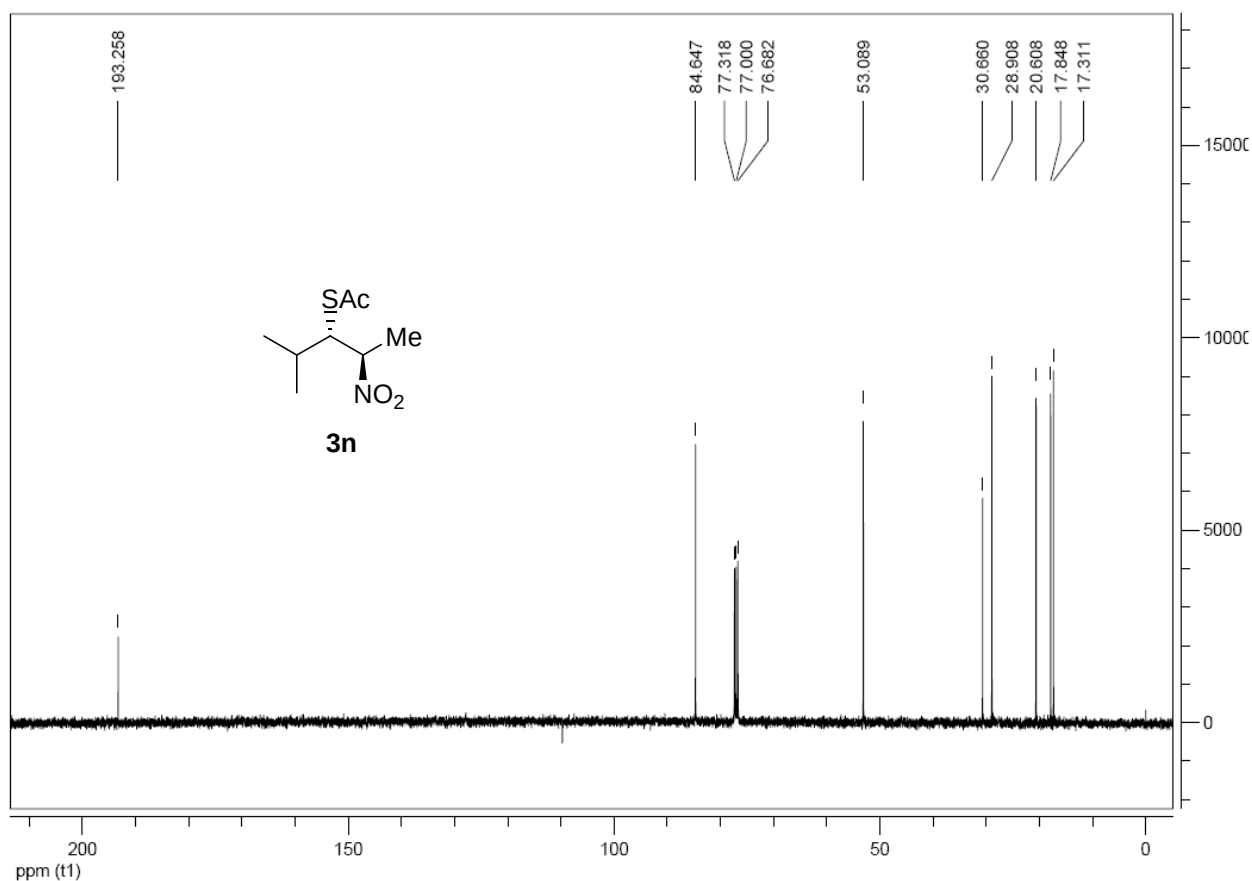
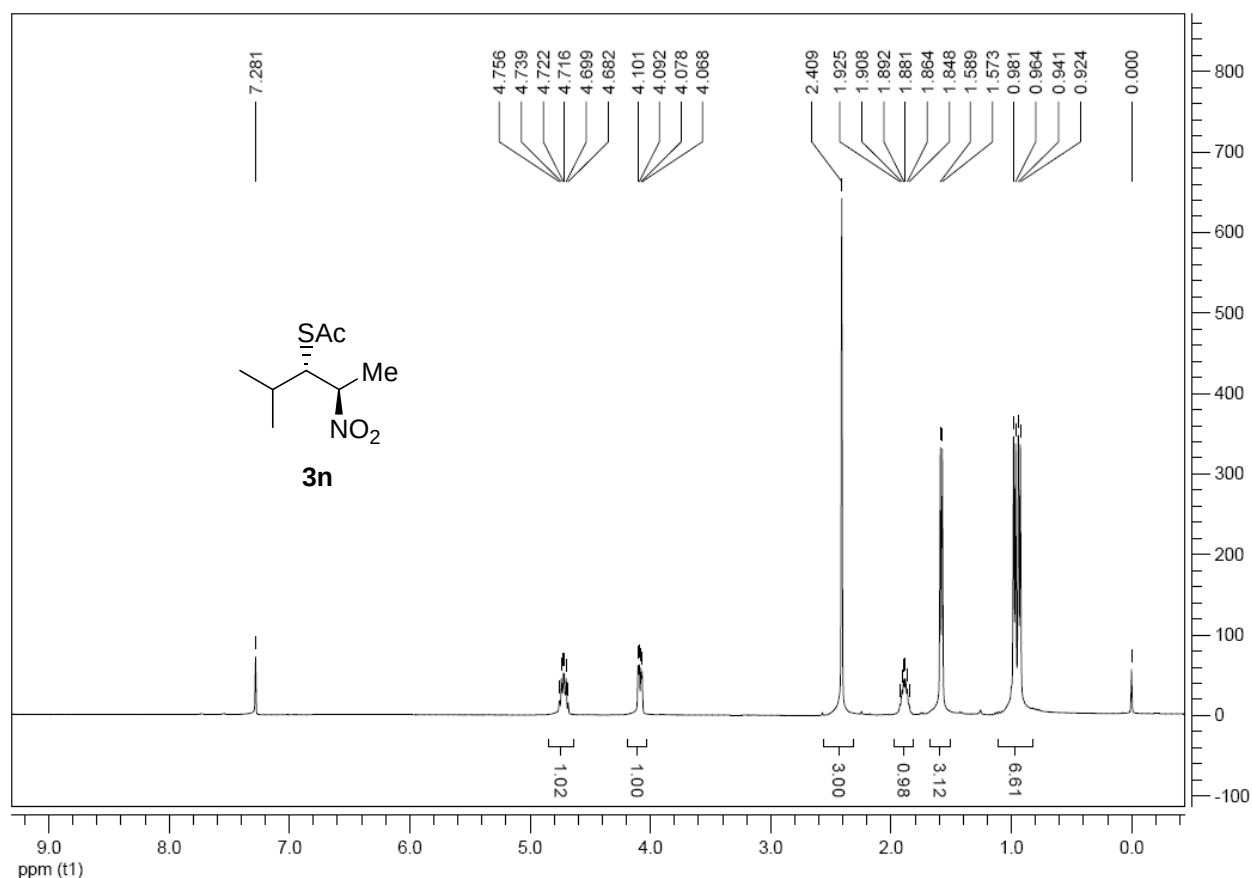


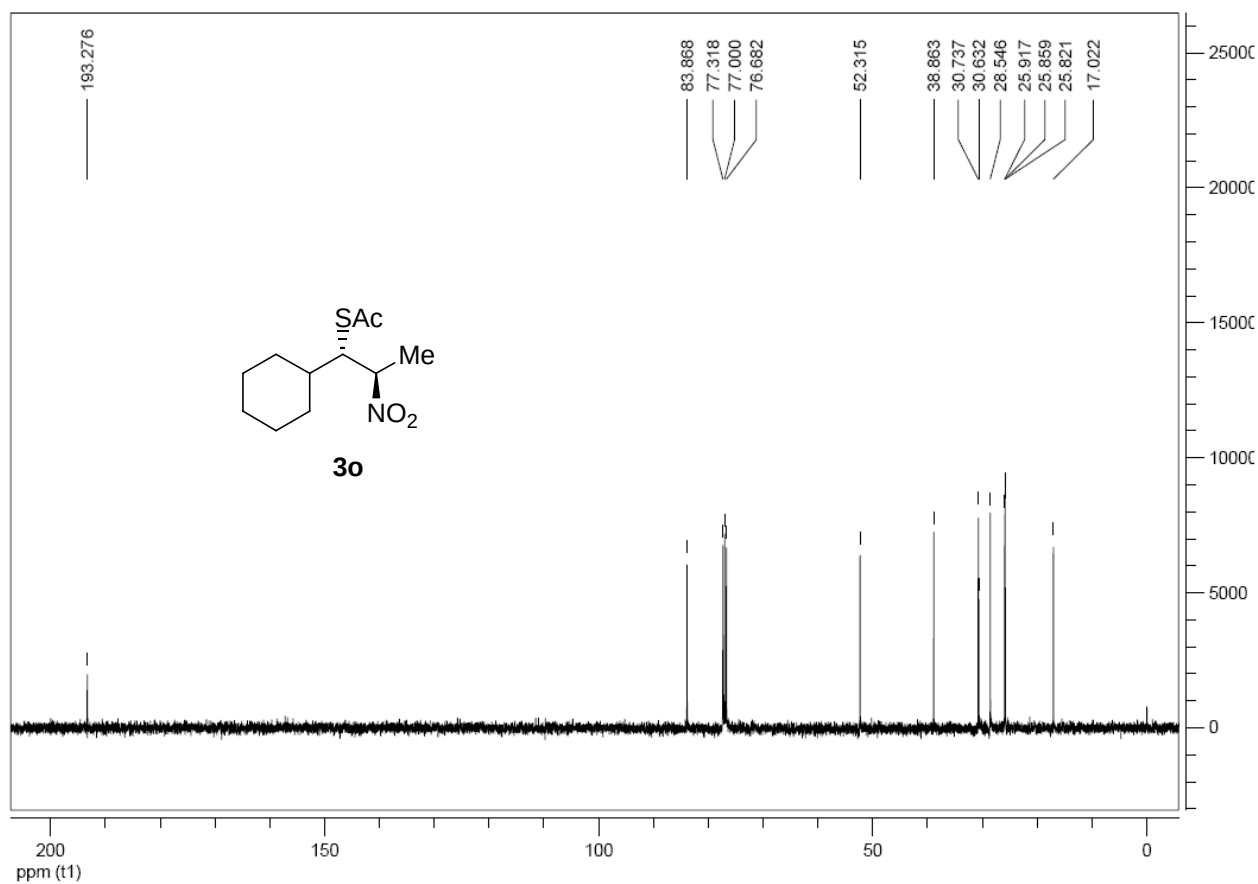
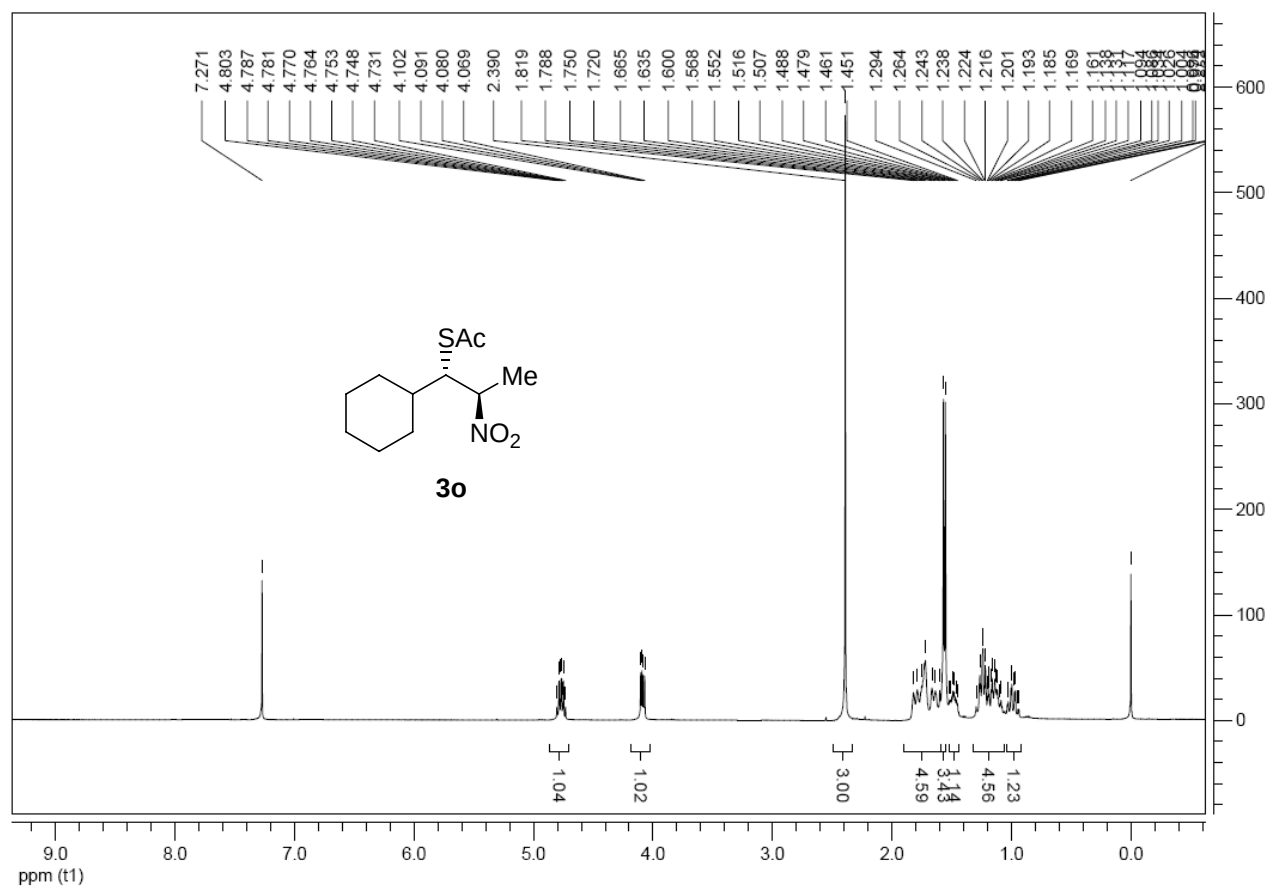


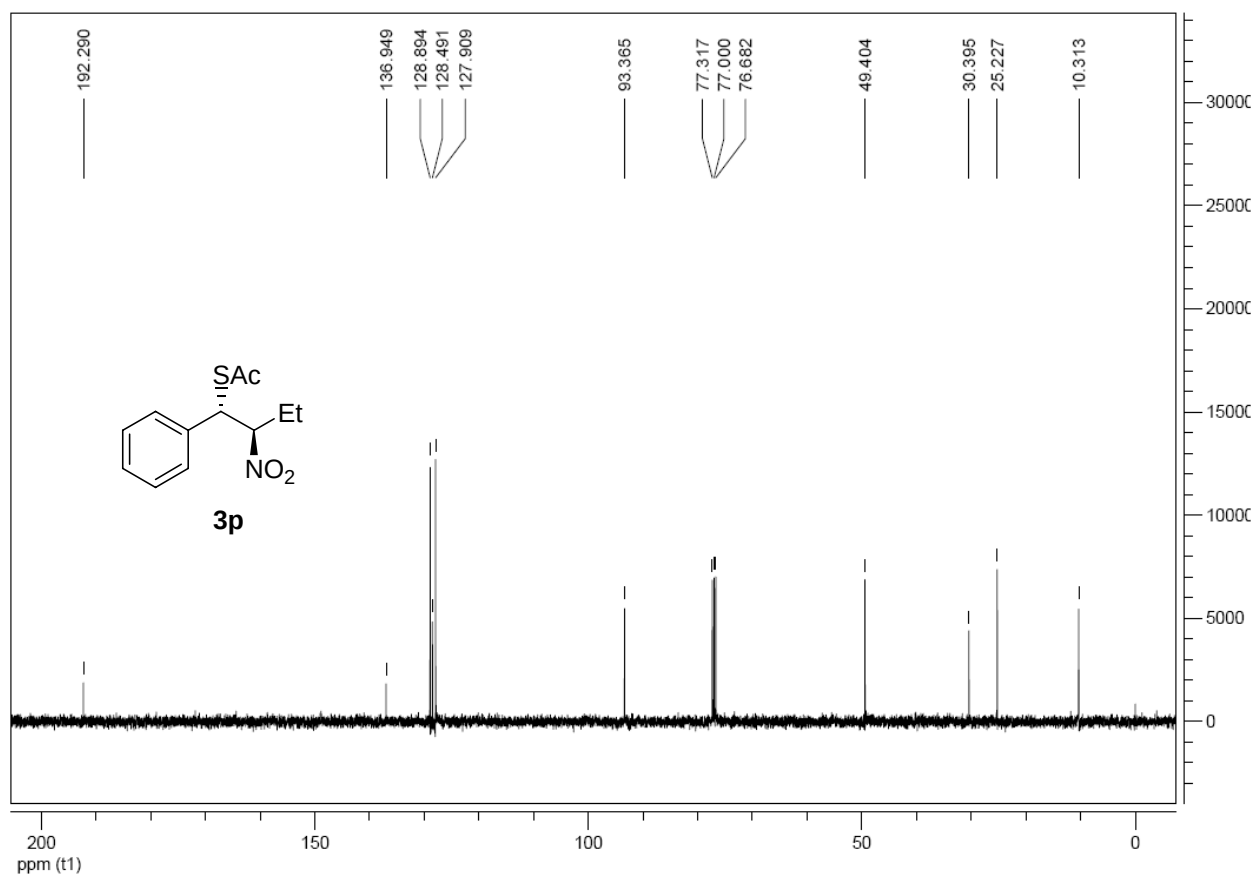
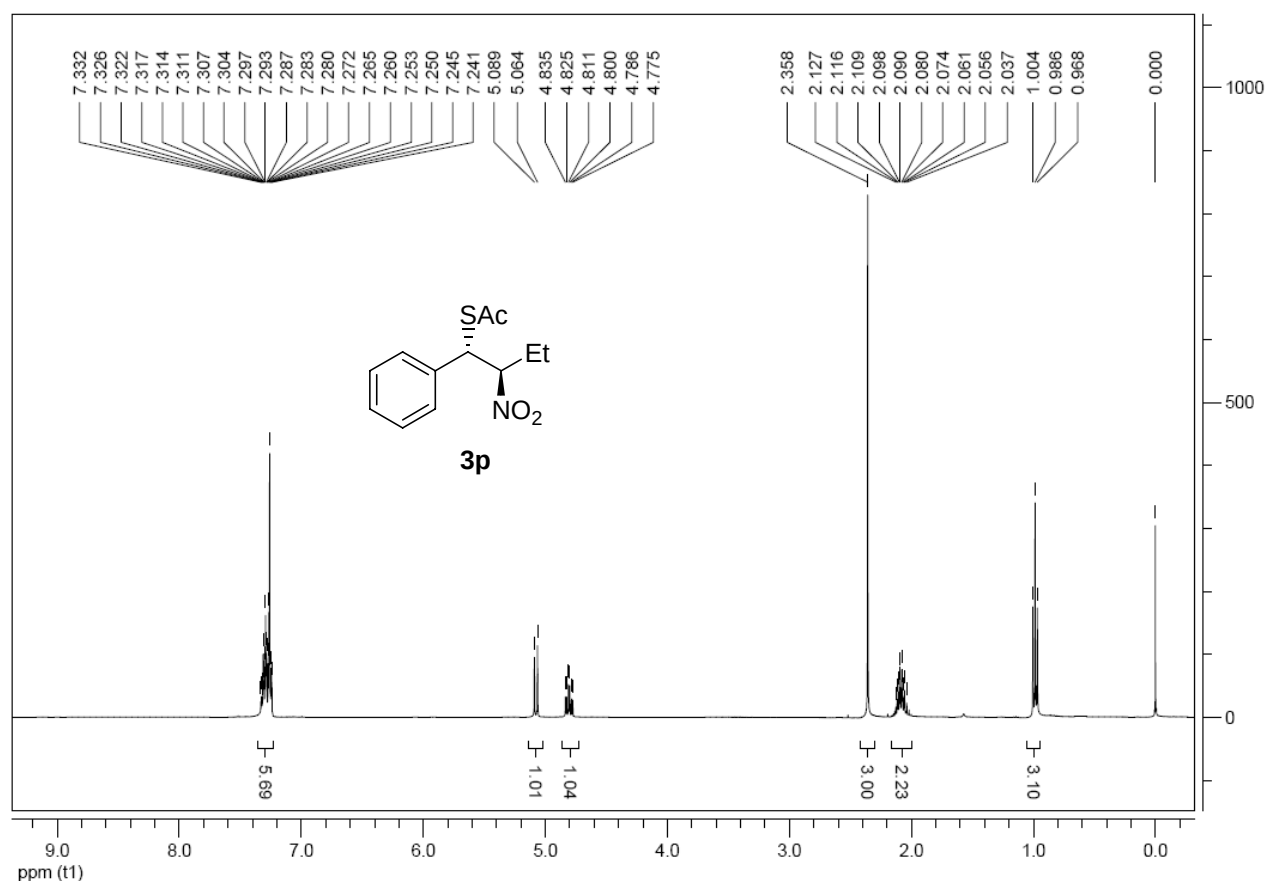


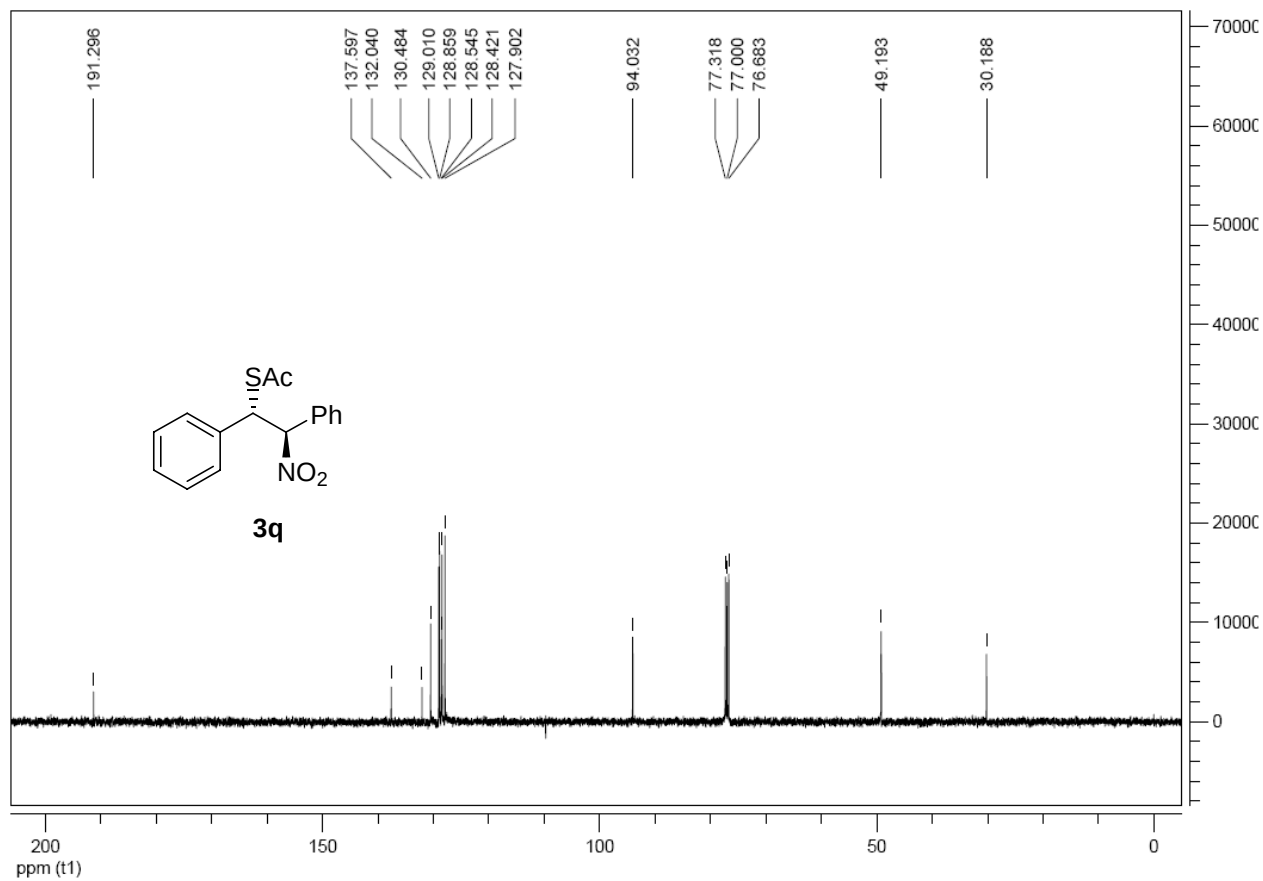
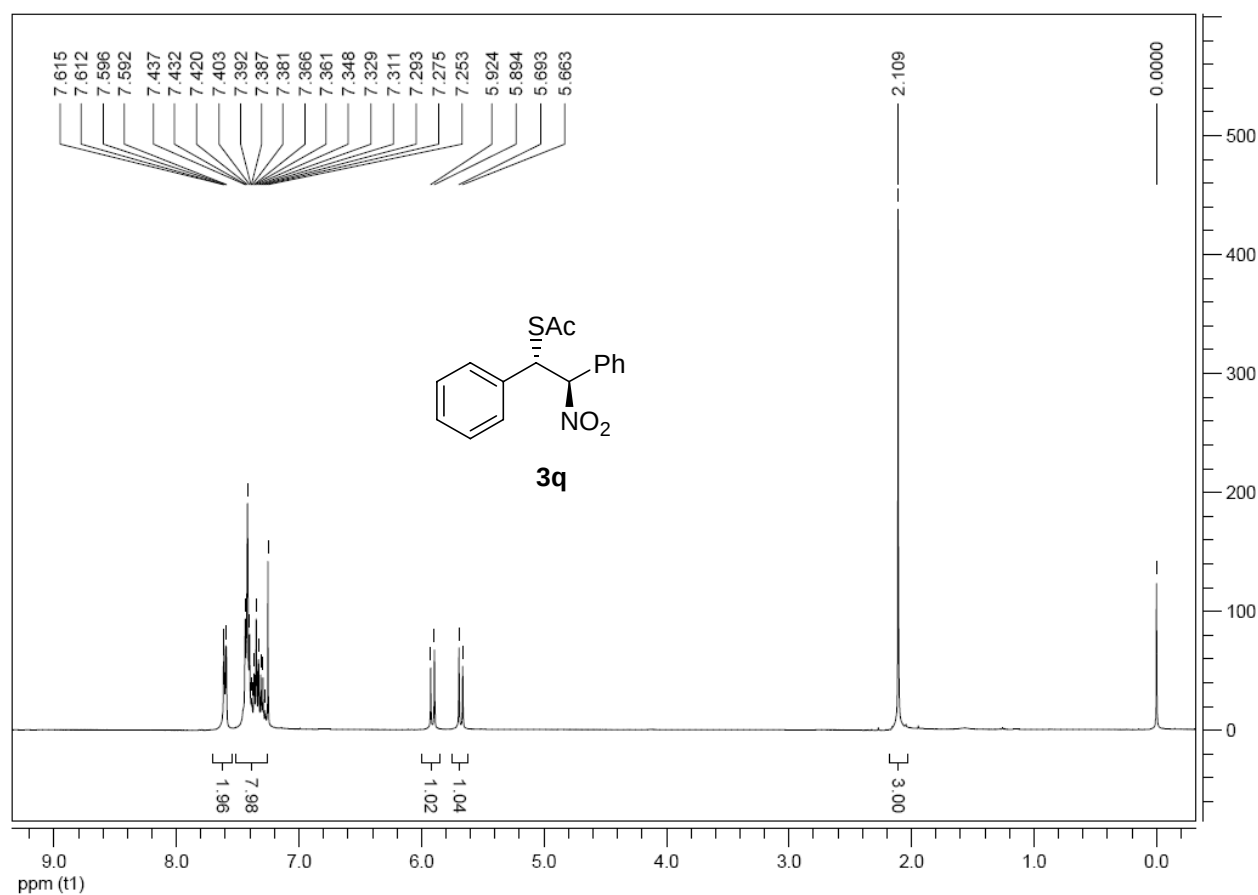


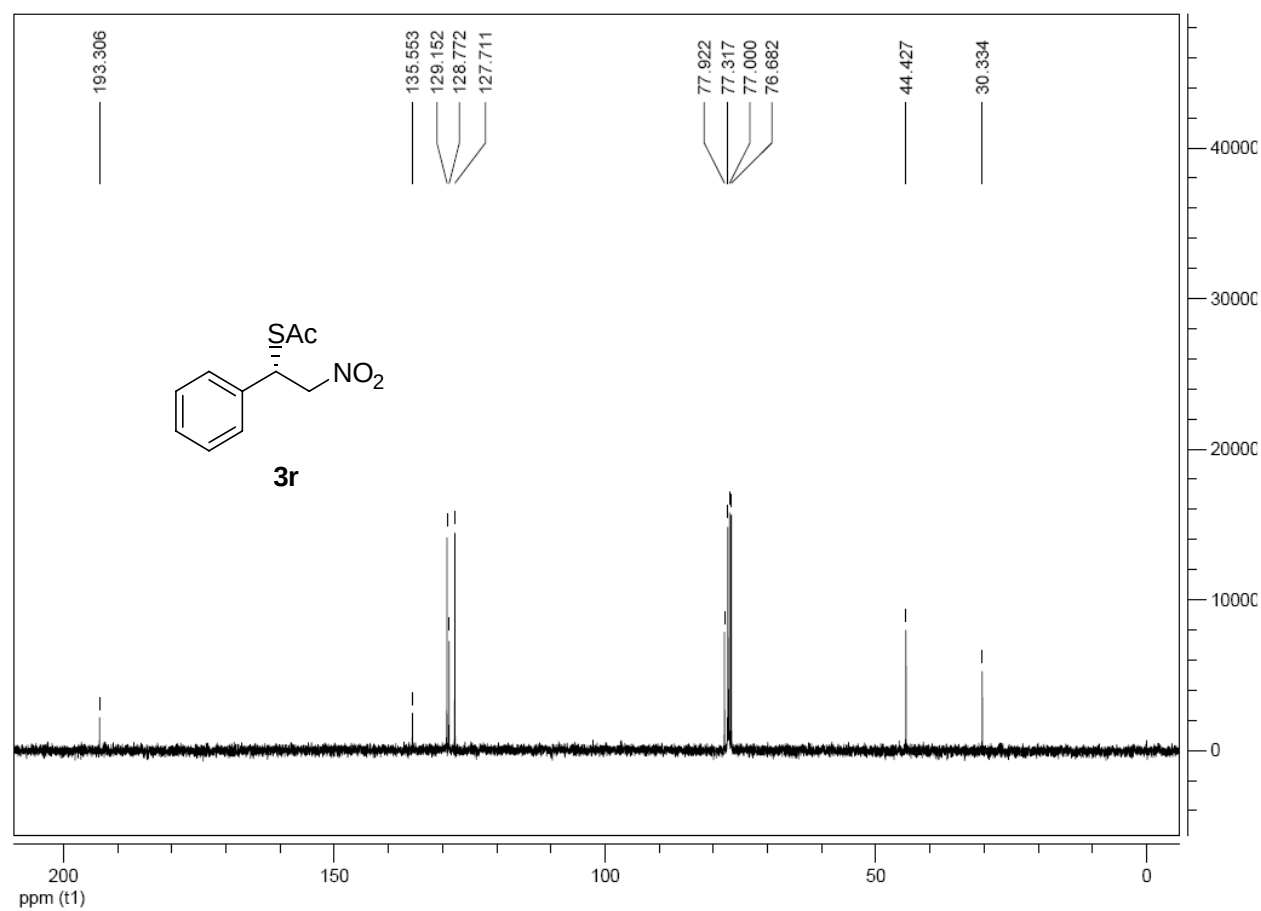
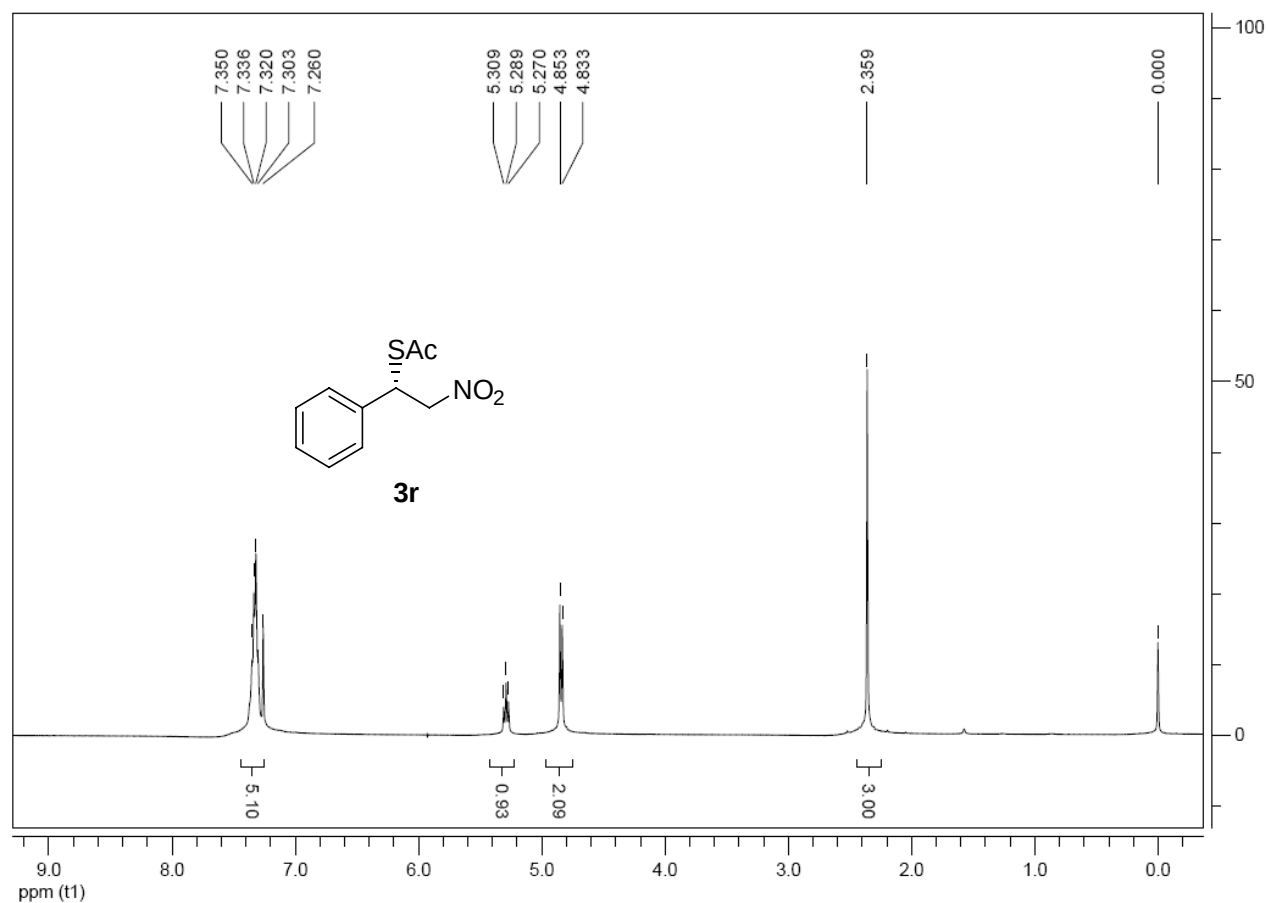


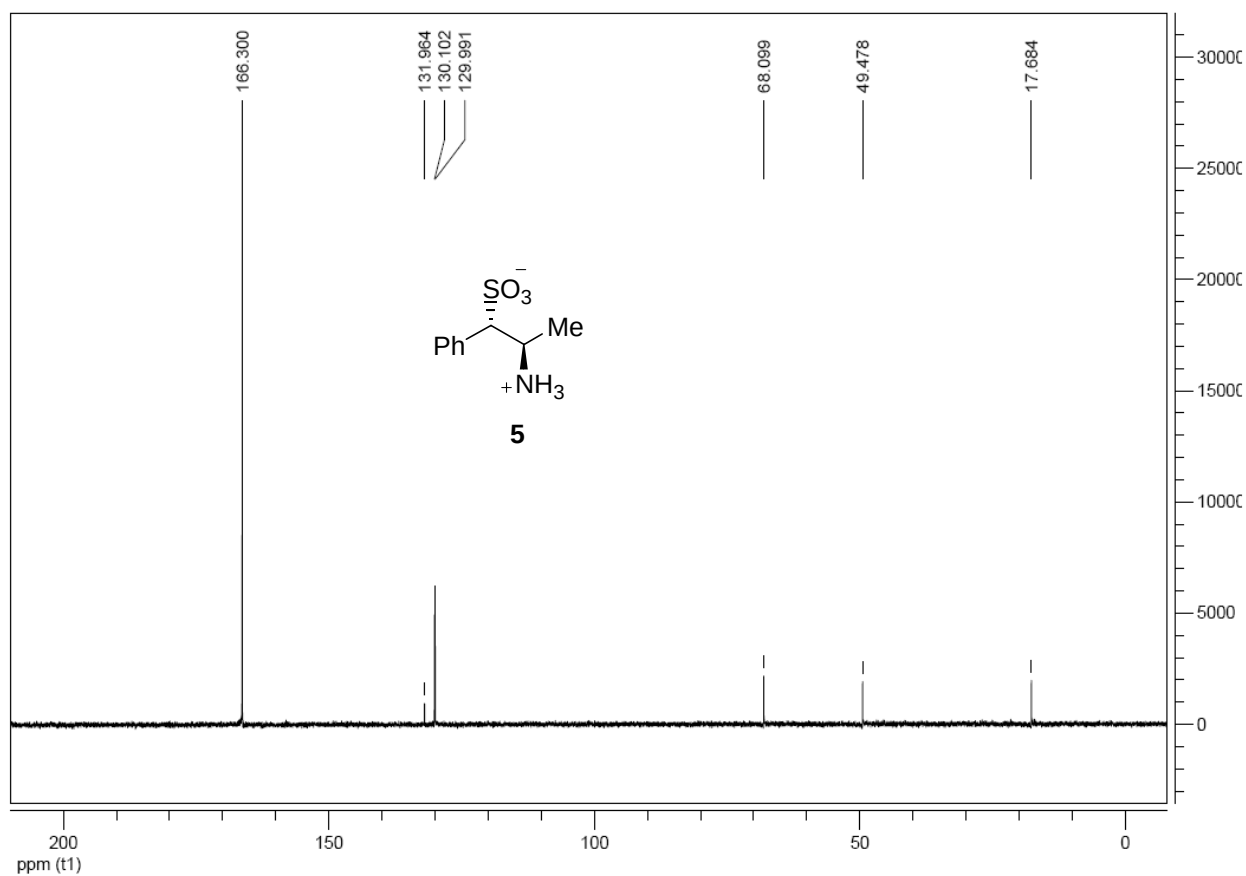
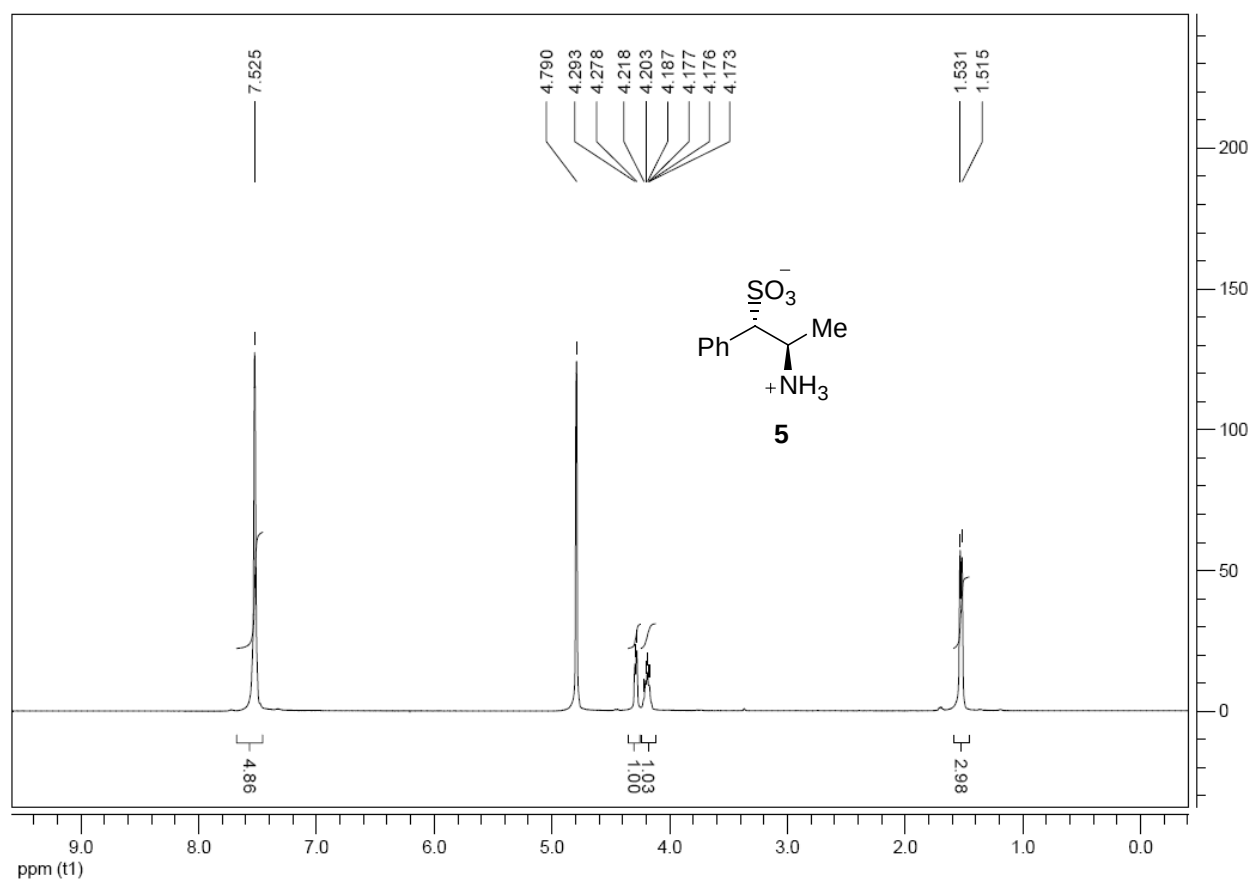


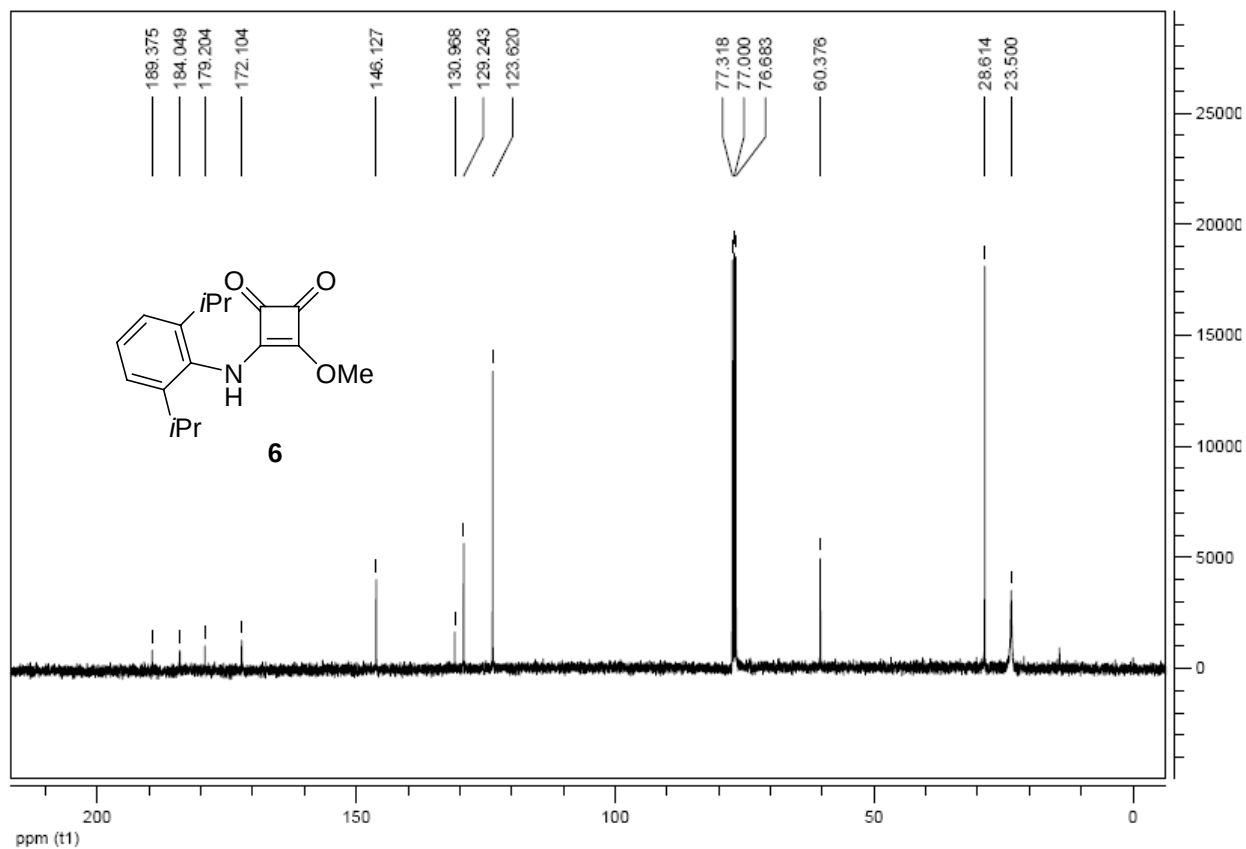
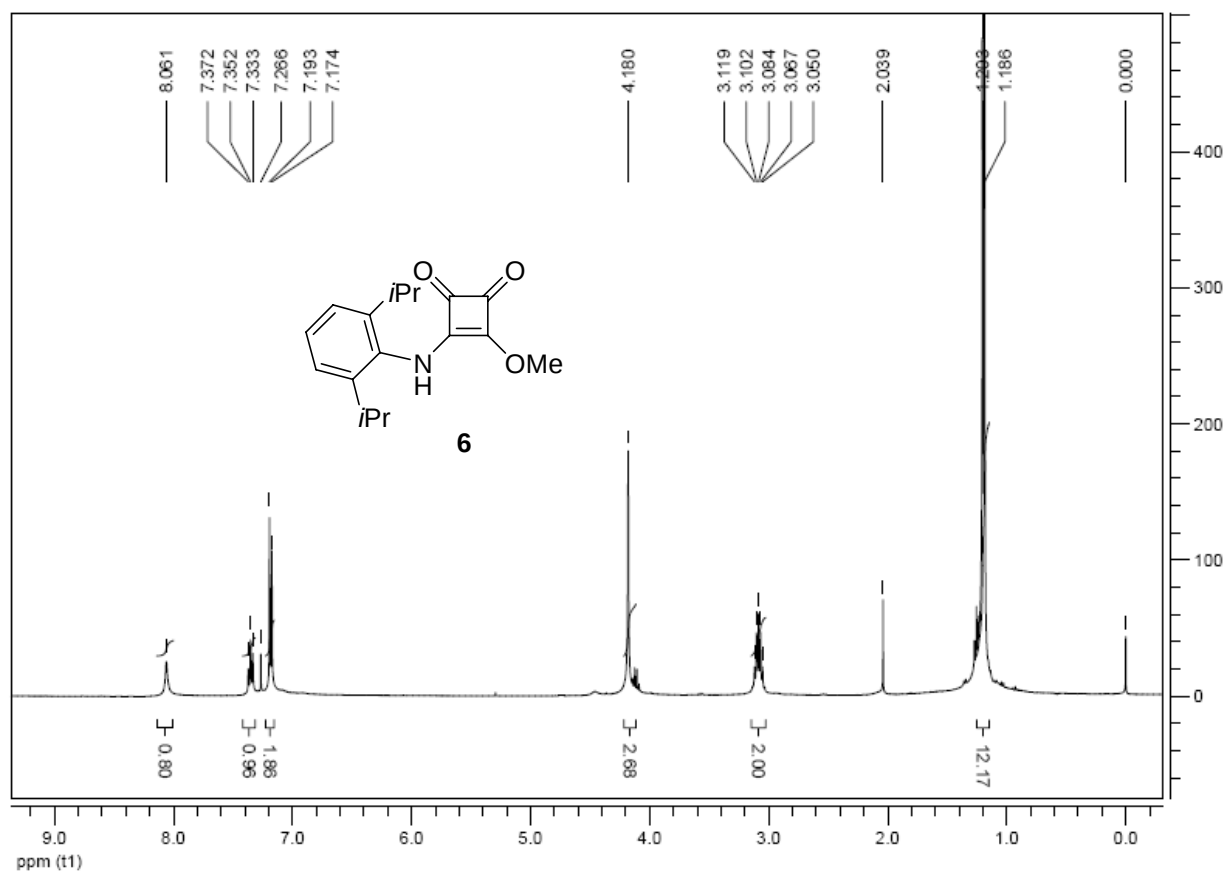


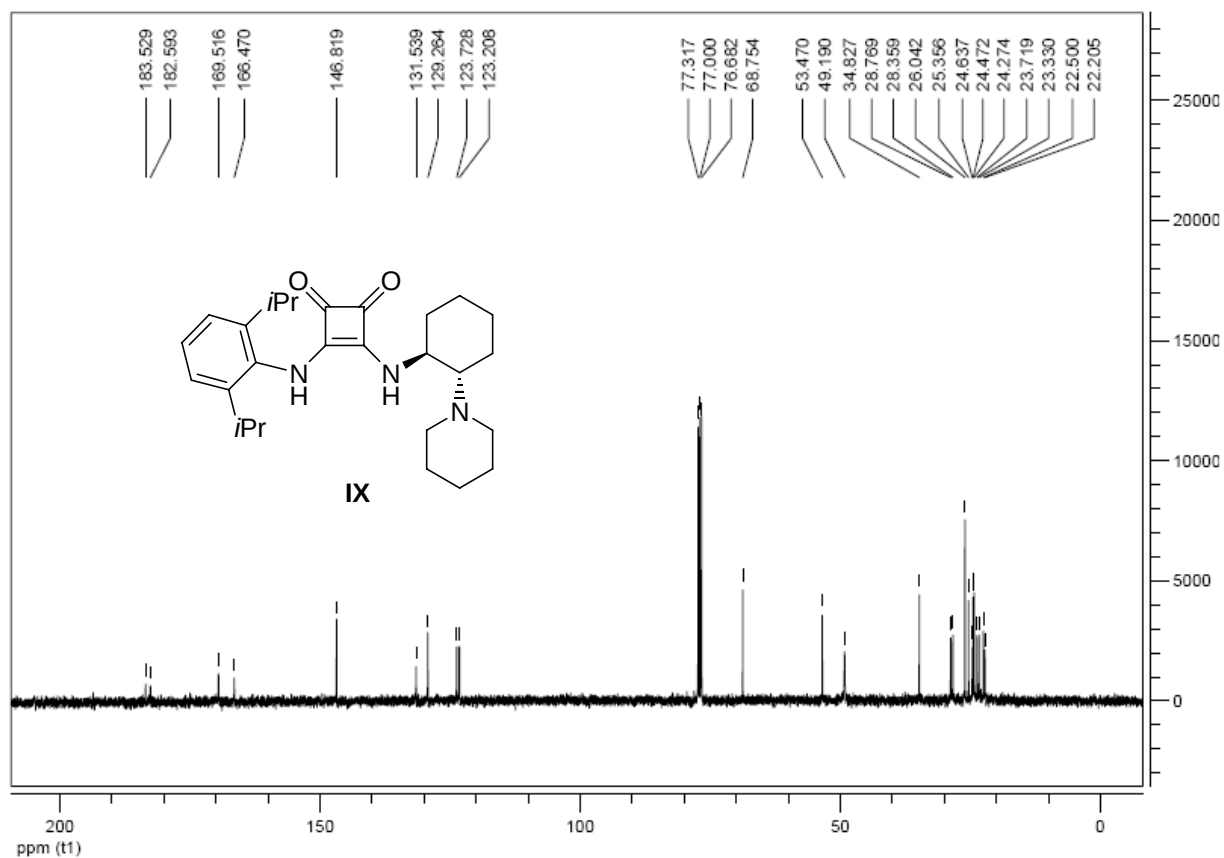
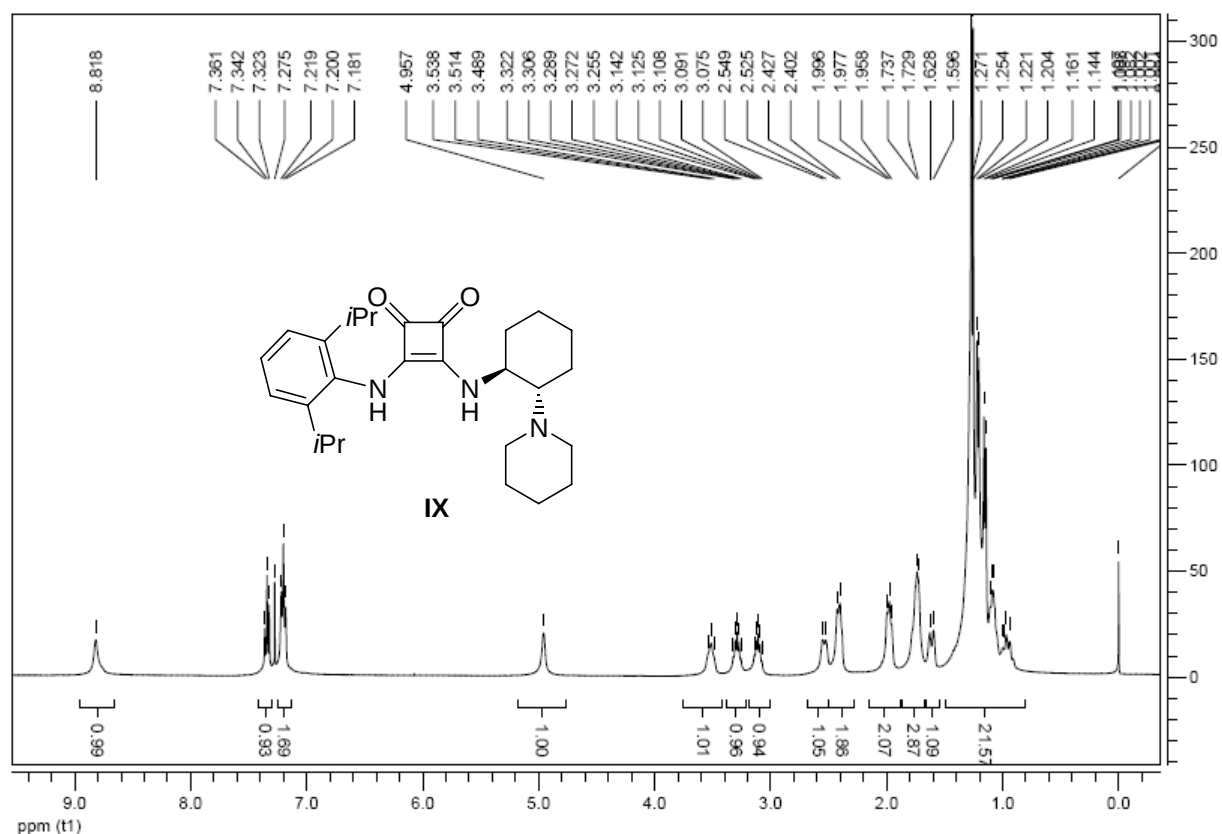


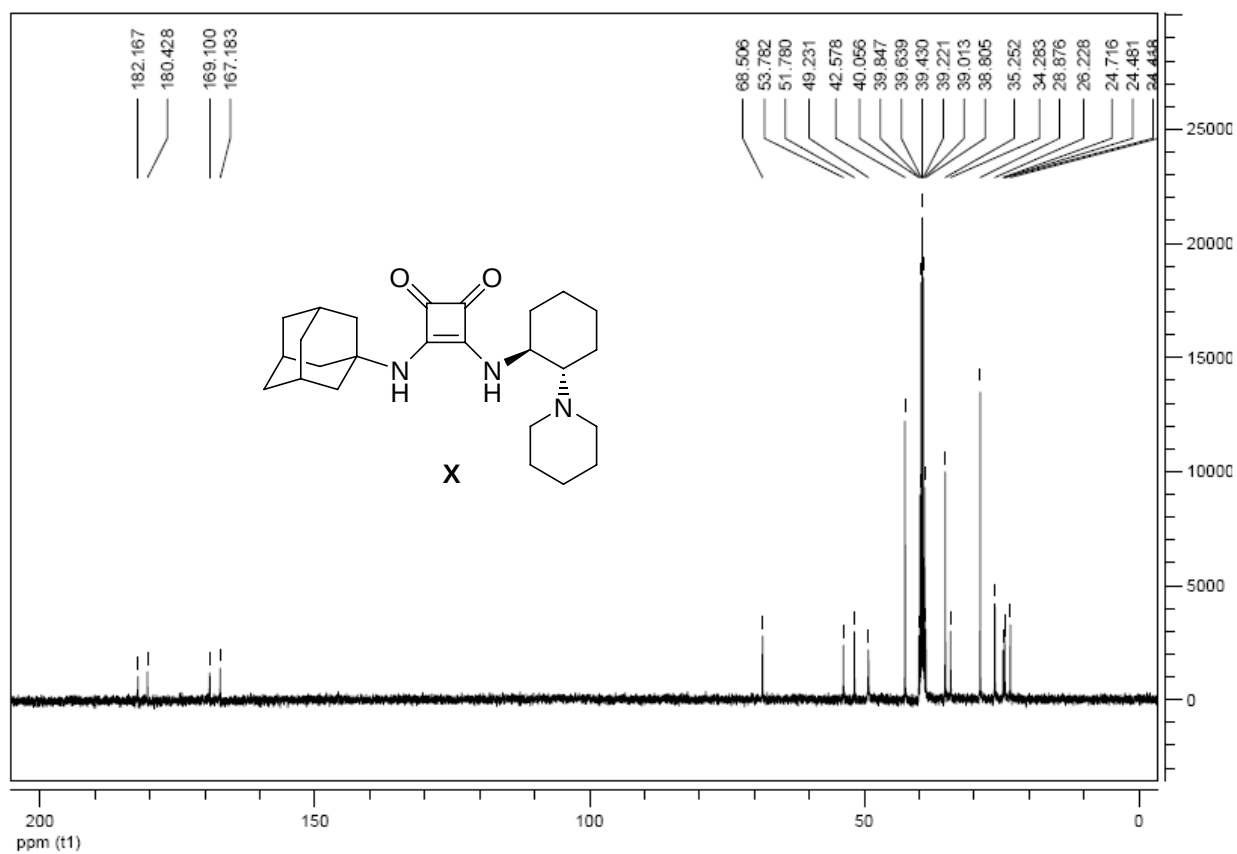
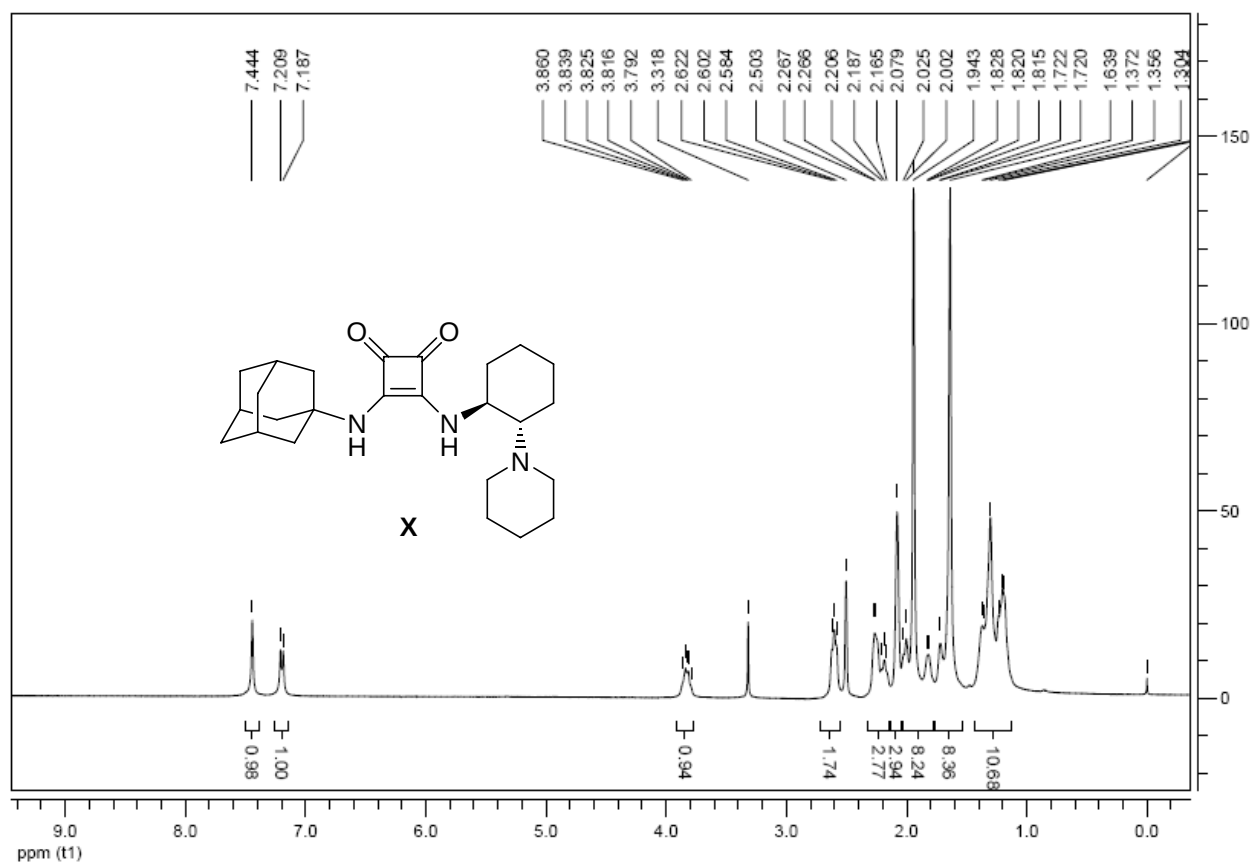




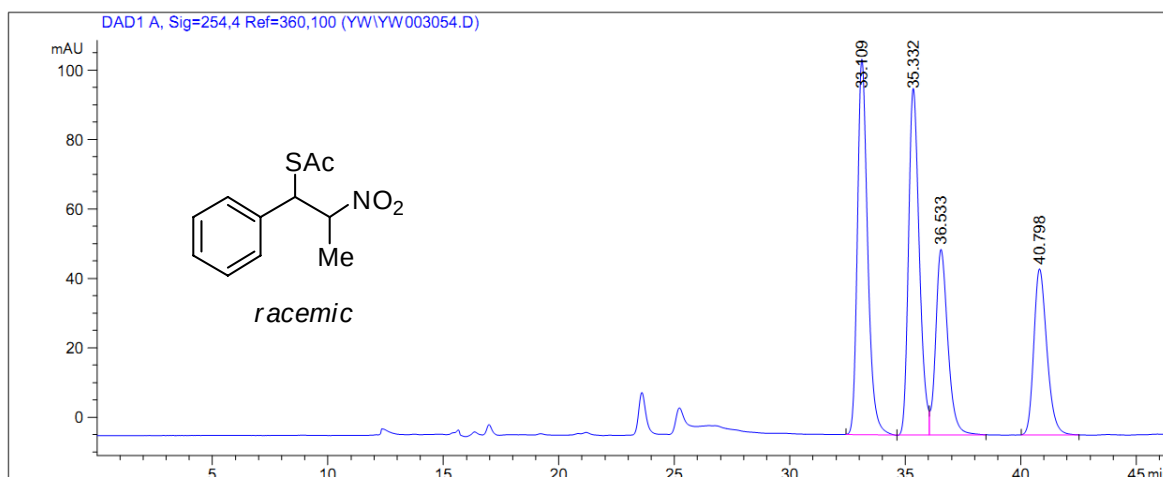




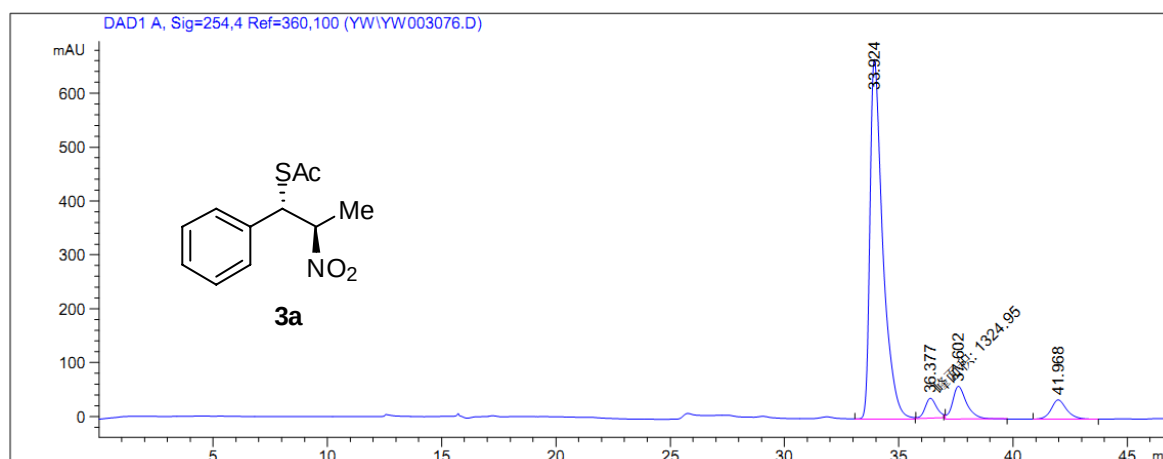




**Copies of HPLC chromatograms of Michael addition products
(1*S*,2*R*)-2-Nitro-1-phenylpropyl ethanethioate (**3a**)**

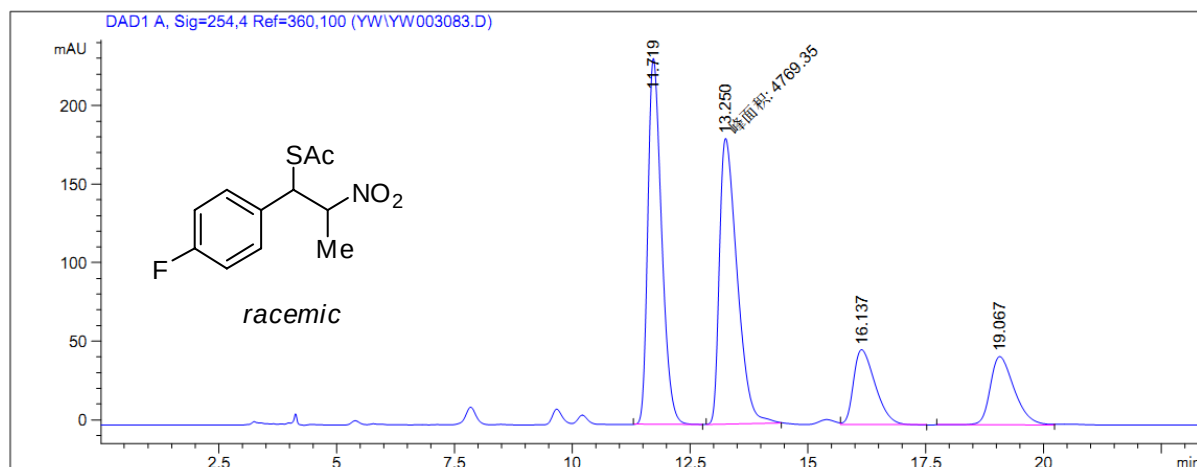


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.109	BV	0.4764	3340.82300	108.14491	32.0067
2	35.332	VV	0.5042	3255.56958	99.90679	31.1900
3	36.533	VB	0.5552	1959.51221	53.51026	18.7731
4	40.798	BB	0.6069	1881.97327	47.84540	18.0302

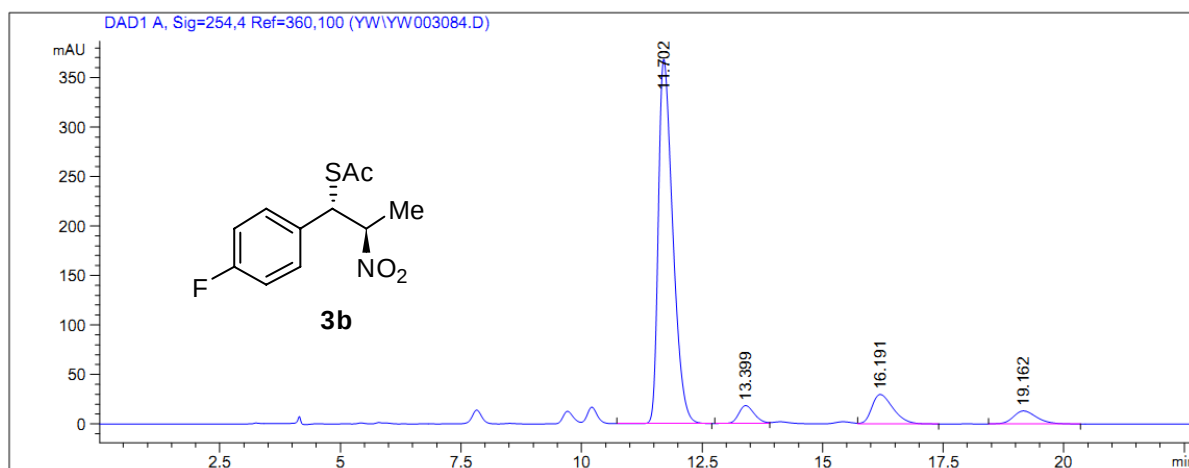


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.924	VV	0.5810	2.61507e4	667.58911	82.2817
2	36.377	MM	0.5939	1324.94910	37.17958	4.1689
3	37.602	VB	0.6426	2622.23779	60.86796	8.2507
4	41.968	BB	0.7022	1684.01001	35.71058	5.2987

(1S,2R)-1-(4-Fluorophenyl)-2-nitropropyl ethanethioate (3b)

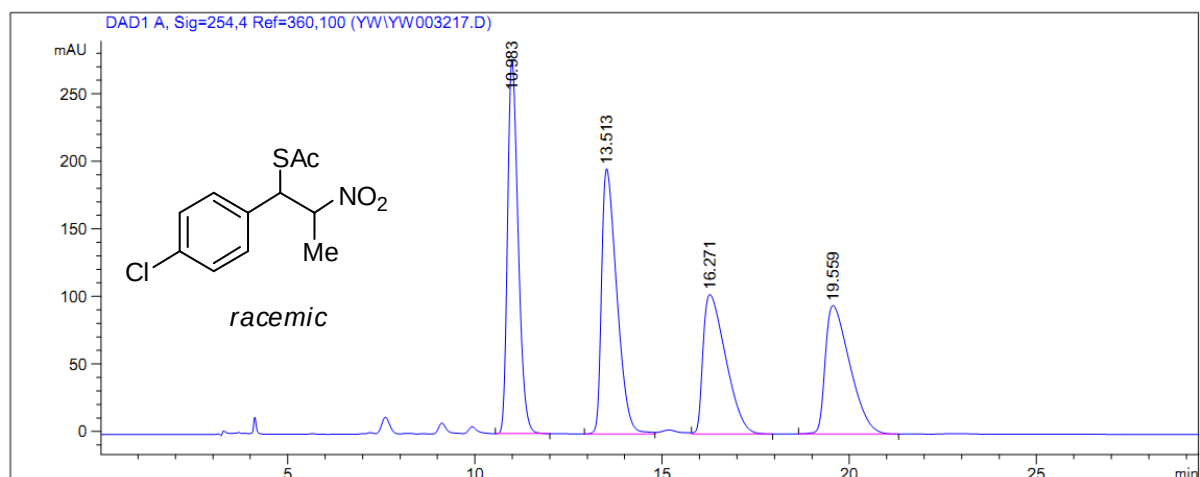


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.719	BV	0.3130	4728.77734	232.82356	37.5765
2	13.250	MM	0.4367	4769.34521	182.01830	37.8989
3	16.137	VB	0.4950	1537.35681	47.83160	12.2164
4	19.067	BV	0.5430	1548.91211	43.54495	12.3082

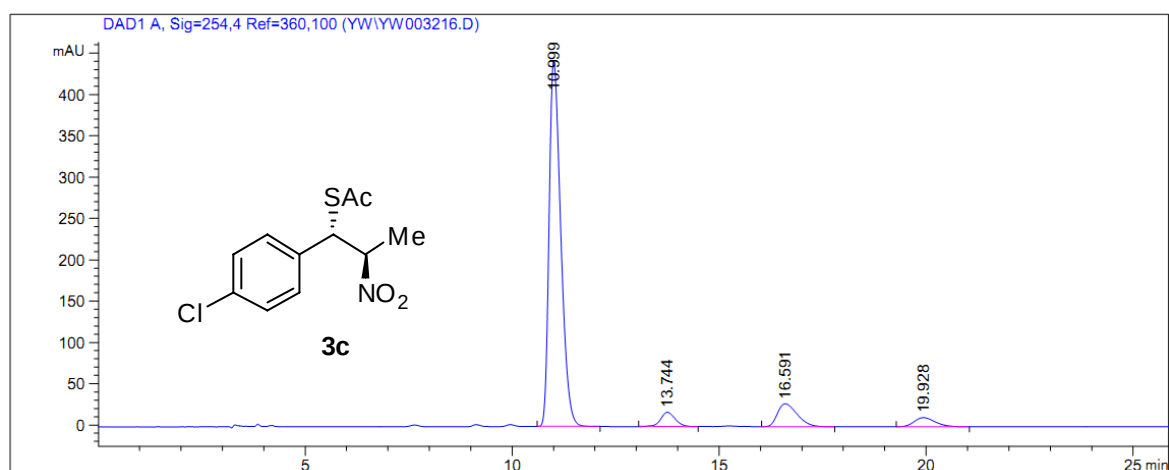


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.702	VB S	0.3192	7674.41309	368.21796	81.1522
2	13.399	BV	0.3573	422.27533	18.29118	4.4653
3	16.191	VB	0.4735	913.50043	29.80724	9.6597
4	19.162	BB	0.5180	446.63043	13.22447	4.7228

(1S,2R)-1-(4-Chlorophenyl)-2-nitropropyl ethanethioate (3c)

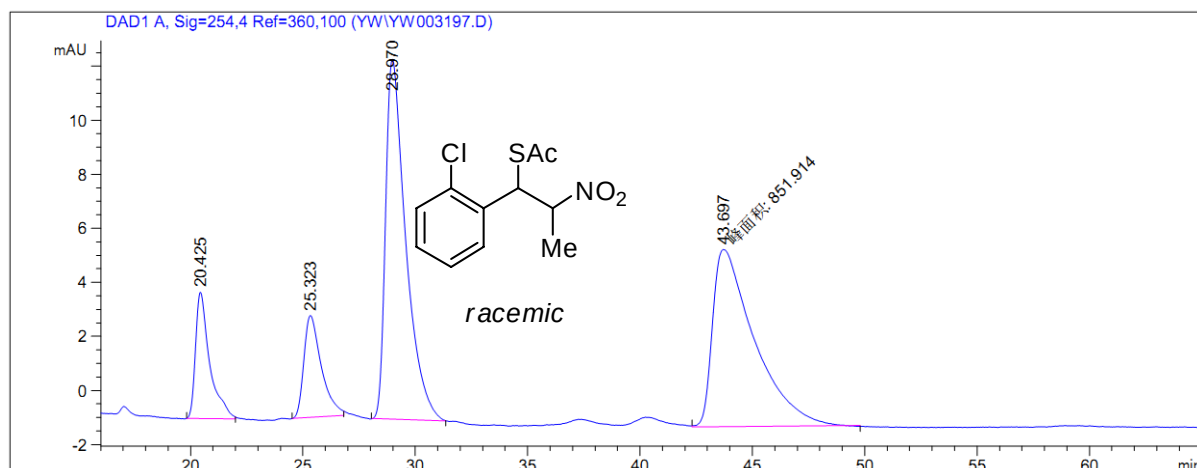


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.983	VB S	0.3019	5449.25977	276.56049	27.6837
2	13.513	BV	0.4388	5562.97510	196.17232	28.2614
3	16.271	VB	0.6583	4335.85010	103.16910	22.0272
4	19.559	BB	0.7000	4335.94336	95.08320	22.0277

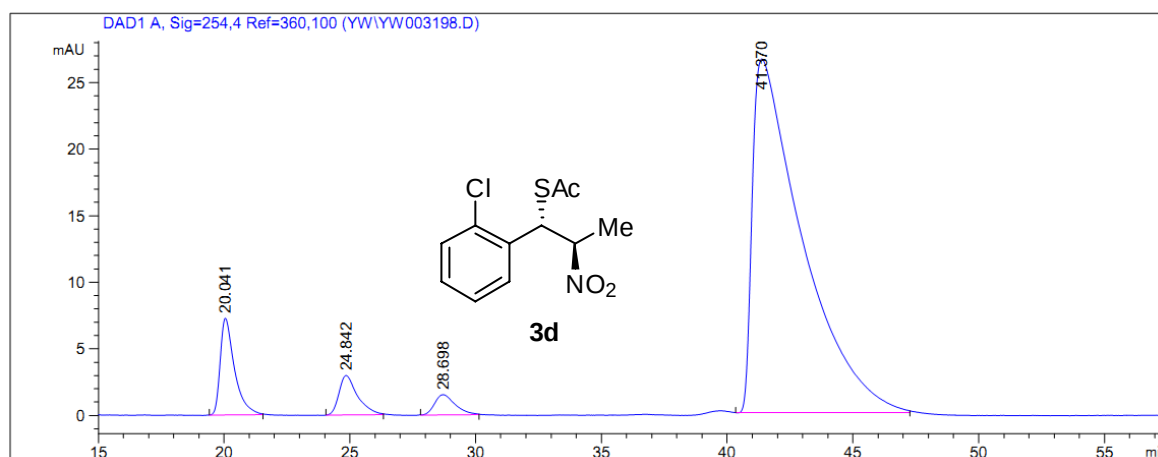


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1	10.999	BB	0.3044	8666.26172	442.68277	83.1319
2	13.744	BB	0.3786	435.75311	17.49395	4.1800
3	16.591	VB	0.5158	927.51923	27.90267	8.8973
4	19.928	BB	0.5562	395.18390	11.07848	3.7908

(1S,2R)-1-(2-Chlorophenyl)-2-nitropropyl ethanethioate (3d)

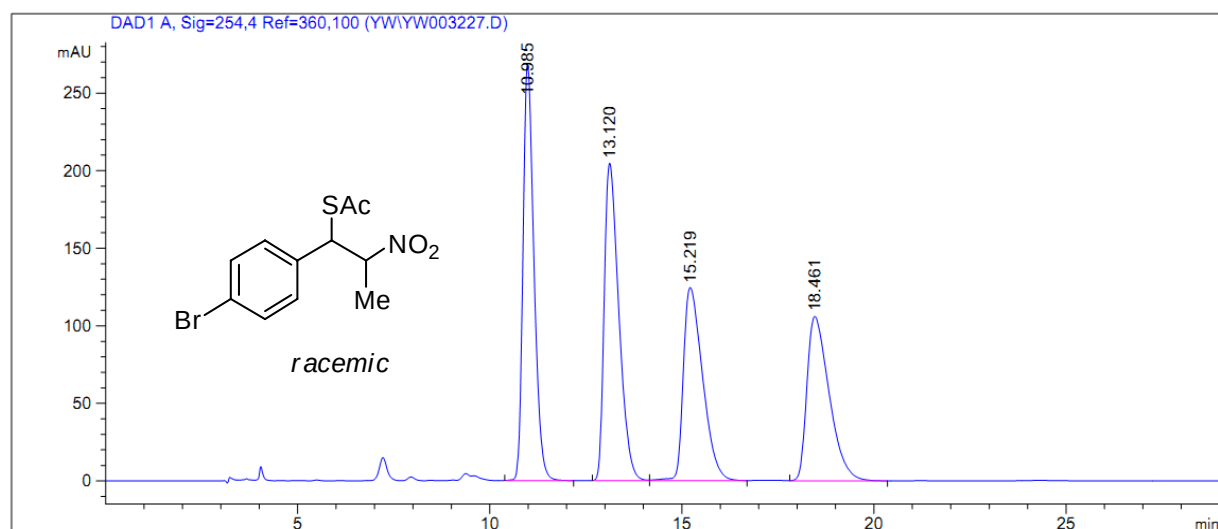


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1	20.425	BB	0.6357	205.14044	4.67747	9.7858
2	25.323	BB	0.7445	204.48767	3.77161	9.7546
3	28.970	BB	0.9184	834.76959	13.33457	39.8209
4	43.697	MM	2.1621	851.91431	6.56711	40.6387

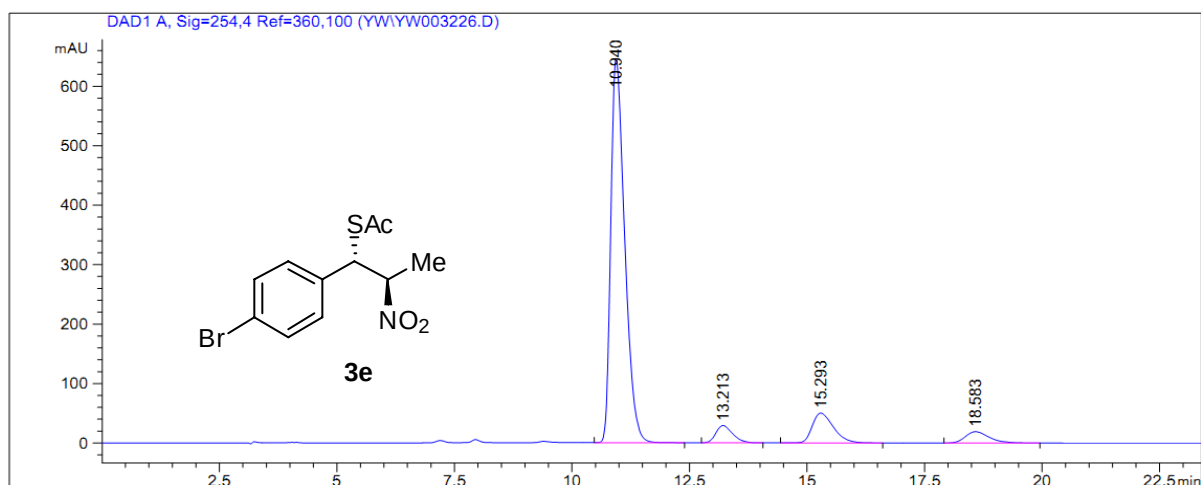


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1	20.041	BB	0.5798	289.64539	7.28644	6.8997
2	24.842	BB	0.7644	154.37639	2.98005	3.6774
3	28.698	BB	0.8210	88.52894	1.53465	2.1089
4	41.370	BB	1.8970	3665.39990	26.57771	87.3140

(1S,2R)-1-(4-Bromophenyl)-2-nitropropyl ethanethioate (3e)

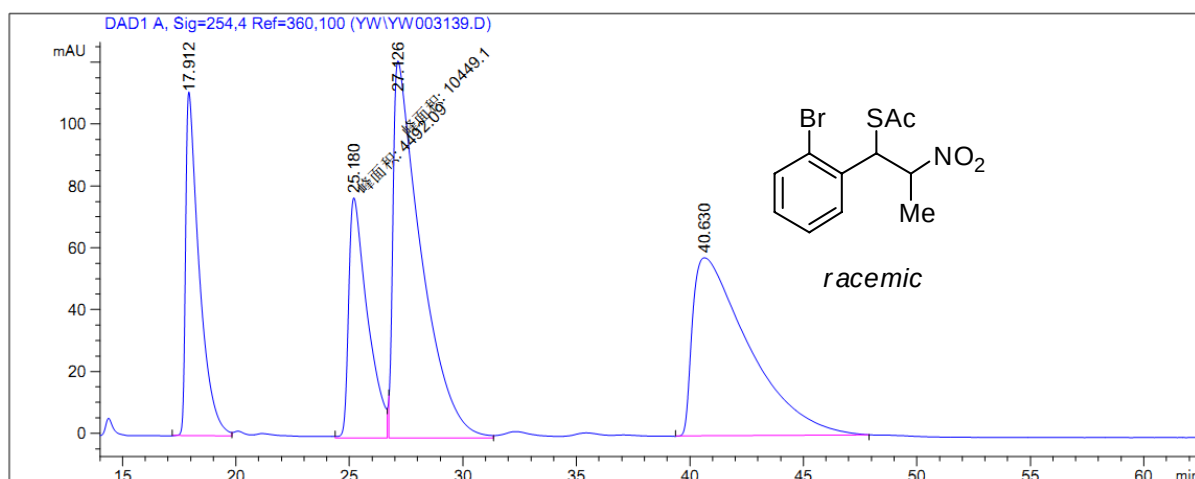


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.985	BB	0.3073	5329.04297	268.84390	27.5723
2	13.120	BV	0.4070	5385.37109	204.62370	27.8638
3	15.219	VB	0.5439	4352.24414	124.49533	22.5184
4	18.461	BB	0.6210	4260.83203	105.98107	22.0454

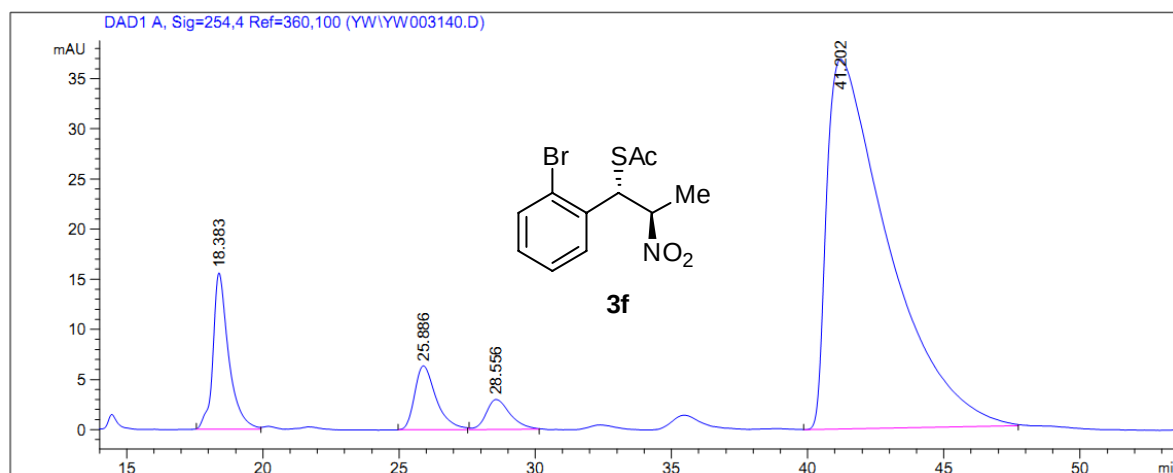


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.940	BB	0.3203	1.32876e4	645.23773	81.7512
2	13.213	BB	0.3750	716.74274	29.13655	4.4097
3	15.293	BB	0.4854	1573.90356	50.24793	9.6833
4	18.583	BB	0.5452	675.47125	19.07103	4.1558

(1S,2R)-1-(2-Bromophenyl)-2-nitropropyl ethanethioate (3f)

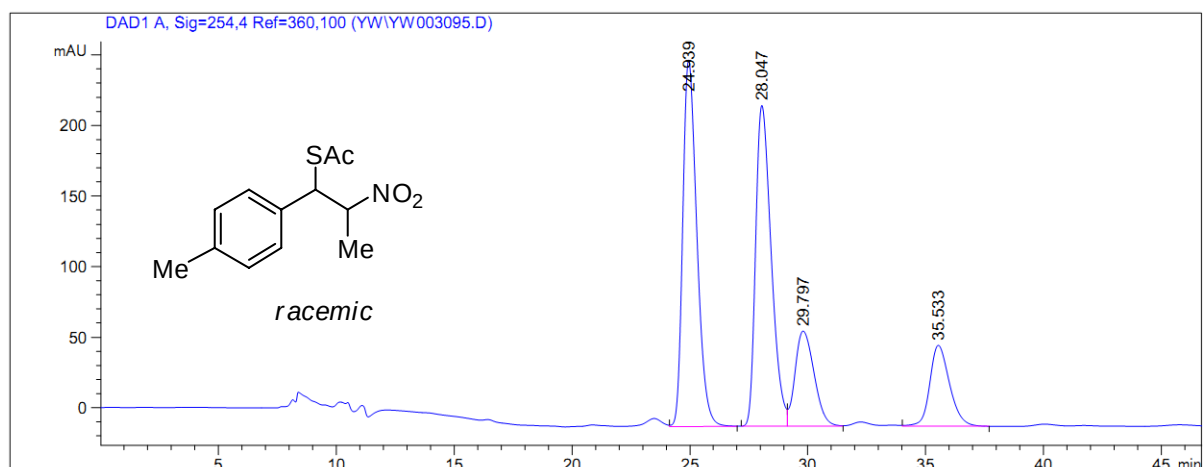


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.912	BV	0.5871	4646.01025	111.26859	15.7186
2	25.180	MM	0.9629	4492.08936	77.75470	15.1978
3	27.126	MM	1.4271	1.04491e4	122.02832	35.3519
4	40.630	BB	2.3806	9970.21680	57.68012	33.7317

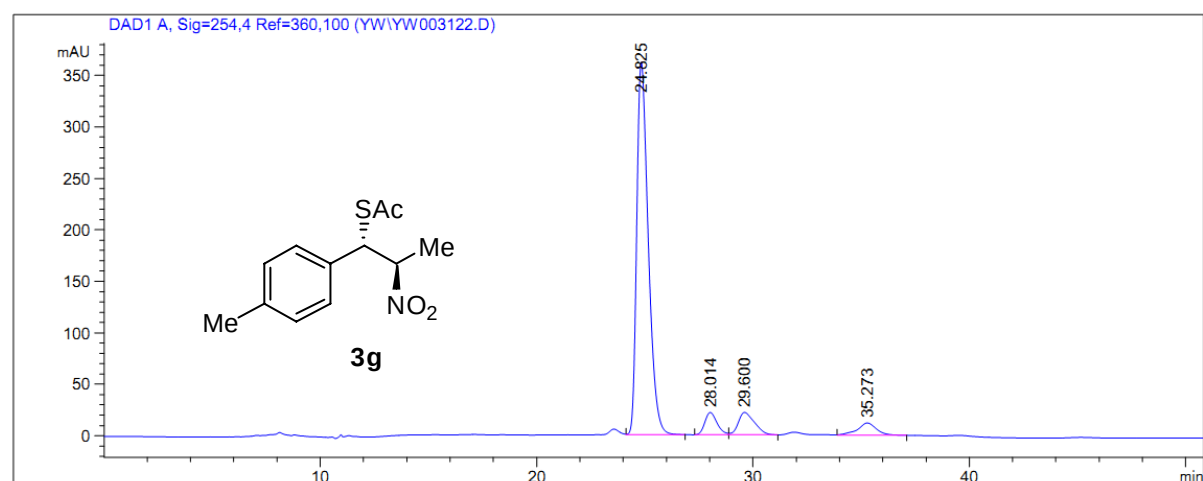


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1	18.383	BB	0.5845	626.48260	15.59934	8.9723
2	25.886	BB	0.8292	353.13983	6.38512	5.0576
3	28.556	BB	0.9483	188.24725	3.01564	2.6960
4	41.202	BB	2.1756	5814.50439	36.87449	83.2740

(1S,2R)-1-(4-Methylphenyl)-2-nitropropyl ethanethioate (3g)

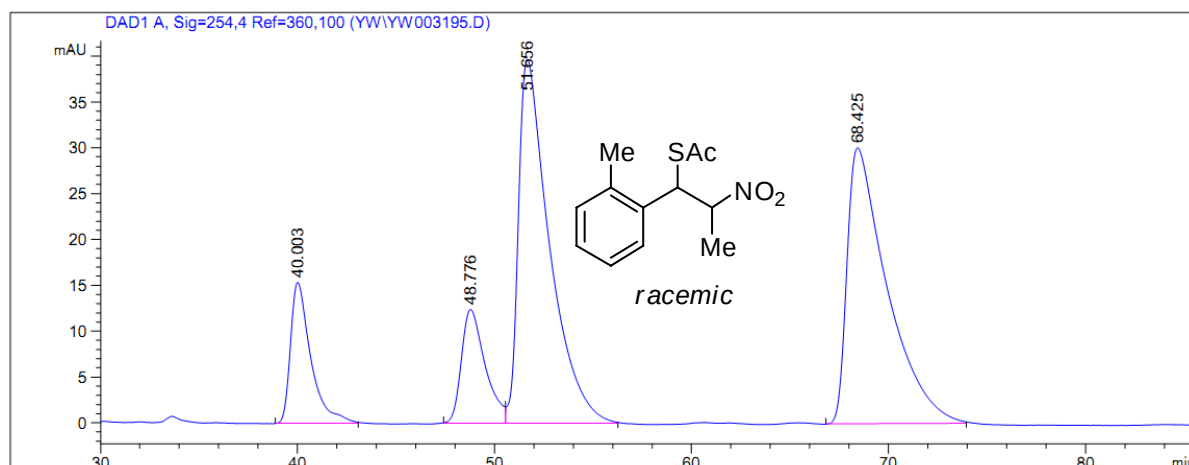


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.939	VB	0.6416	1.08115e4	259.76700	37.9589
2	28.047	BV	0.7088	1.04712e4	227.57924	36.7641
3	29.797	VV	0.8920	3827.89575	67.66691	13.4396
4	35.533	VB	0.8963	3371.52881	57.48241	11.8373

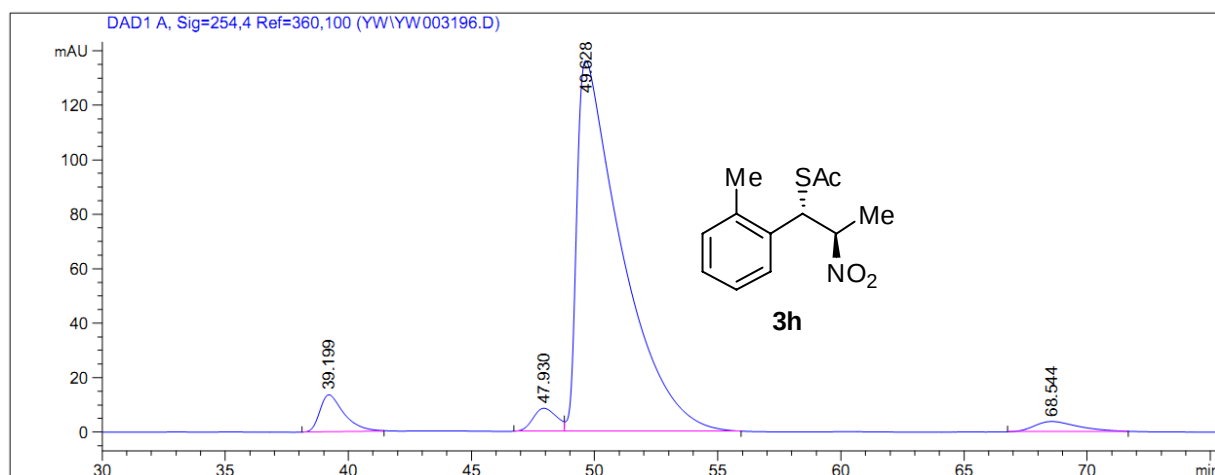


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.825	VB	0.5673	1.33900e4	362.15808	82.5799
2	28.014	BV	0.6167	881.75861	21.94791	5.4381
3	29.600	VV	0.7886	1175.59192	22.10122	7.2502
4	35.273	BB	0.9252	767.23303	12.07615	4.7318

(1S,2R)-1-(2-Methylphenyl)-2-nitropropyl ethanethioate (3h)

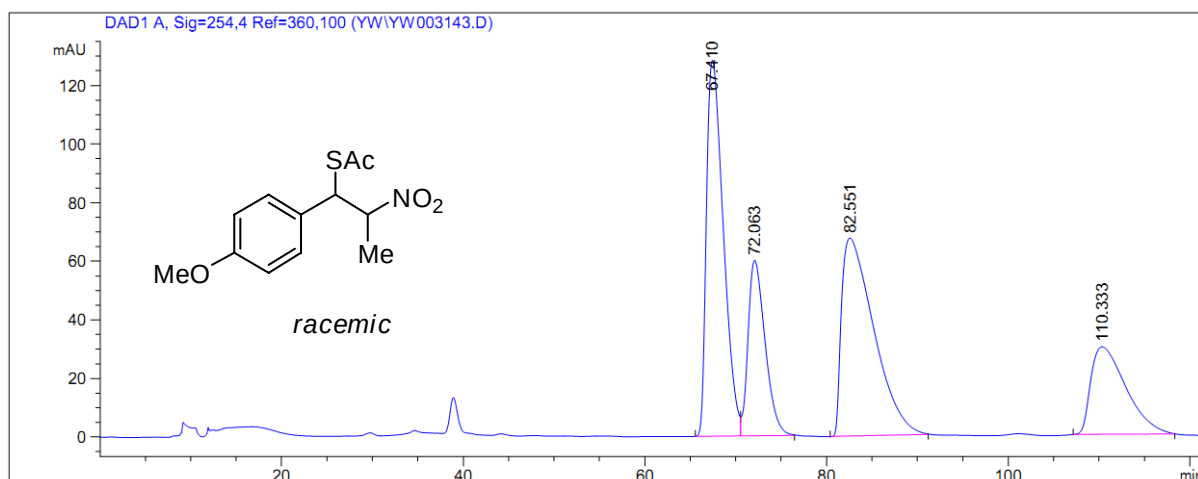


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.003	BB	1.0652	1104.60437	15.39284	10.2556
2	48.776	BV	1.2493	1046.64917	12.44399	9.7175
3	51.656	VB	1.5684	4359.69238	39.72358	40.4772
4	68.425	BB	2.0175	4259.78369	30.12932	39.5496

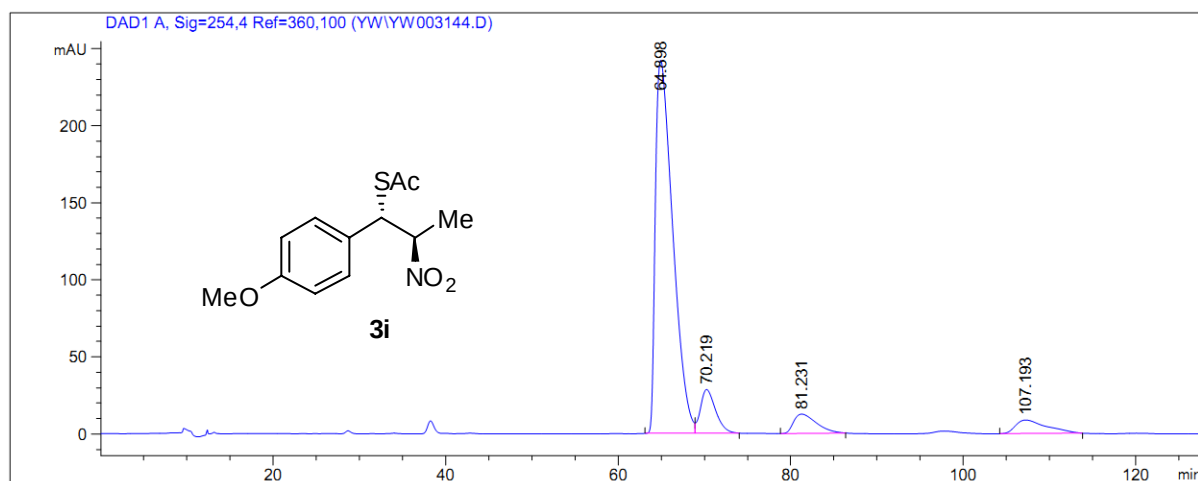


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.199	BB	1.0024	930.99628	13.60354	4.8488
2	47.930	BV	0.9746	570.05719	8.49801	2.9689
3	49.628	VB	1.7275	1.72202e4	136.15880	89.6852
4	68.544	BB	1.4849	479.45947	3.80816	2.4971

(1S,2R)-1-(4-Methoxyphenyl)-2-nitropropyl ethanethioate (3i)

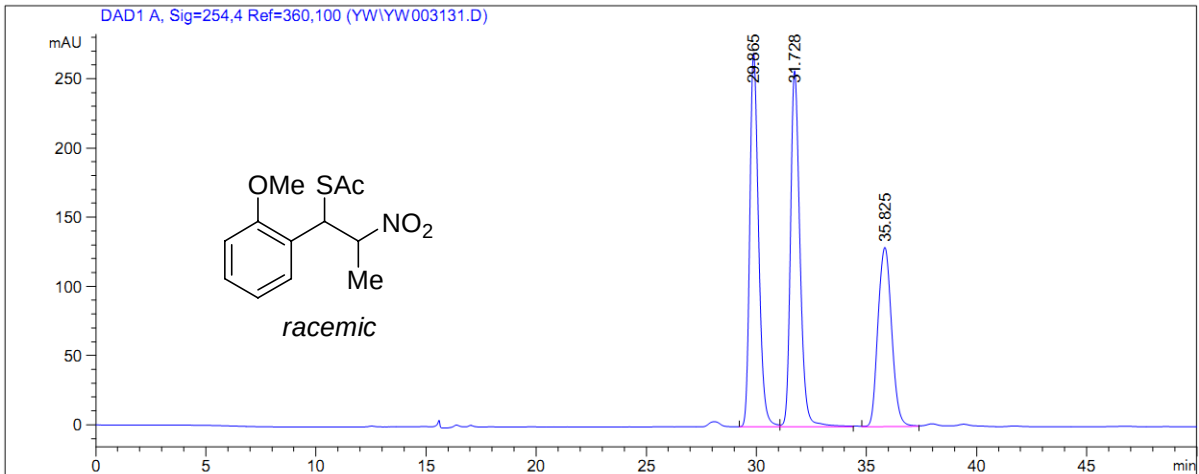


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.410	BV	2.0126	1.65976e4	128.35521	33.7063
2	72.063	VB	1.9779	7834.12012	59.89955	15.9095
3	82.551	BB	3.3620	1.67114e4	67.65021	33.9376
4	110.333	BB	3.1979	8098.56494	29.95716	16.4466

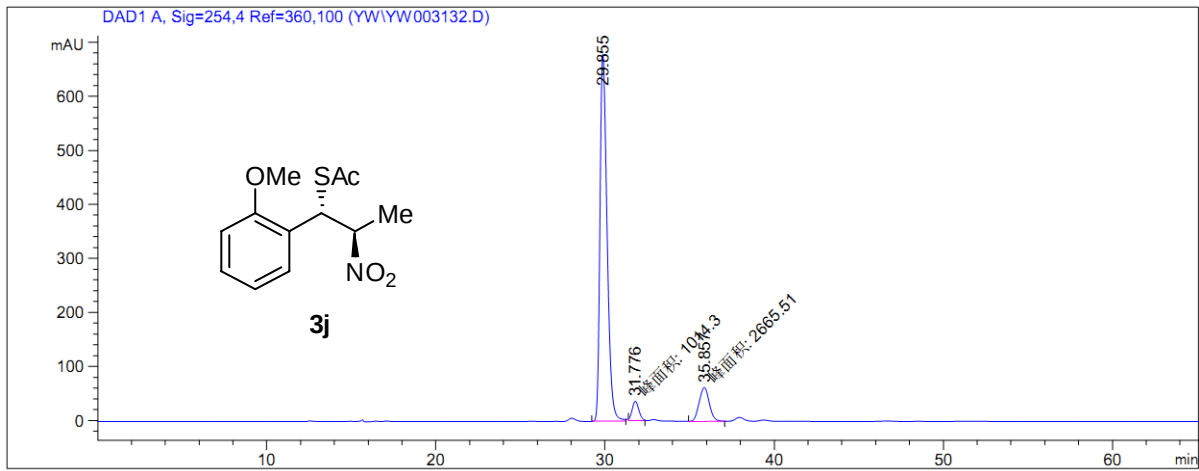


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	64.898	BV	2.1559	3.39535e4	242.14589	80.7223
2	70.219	VB	1.7896	3509.15820	28.47816	8.3428
3	81.231	BB	2.2068	2352.56812	12.59723	5.5931
4	107.193	BB	2.9961	2246.89746	8.83187	5.3419

(1*S*,2*R*)-1-(2-Methoxyphenyl)-2-nitropropyl ethanethioate (3j)

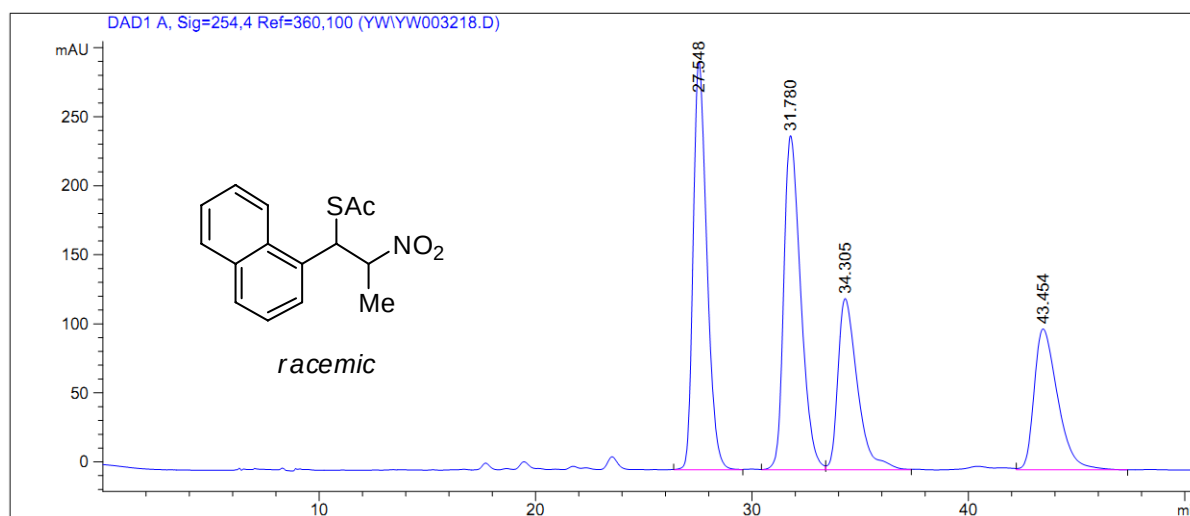


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.865	BV	0.4286	7514.36182	270.07996	36.1114
2	31.728	VB	0.4598	7670.25244	257.32922	36.8605
3	35.825	BV	0.6941	5624.24854	129.64165	27.0281

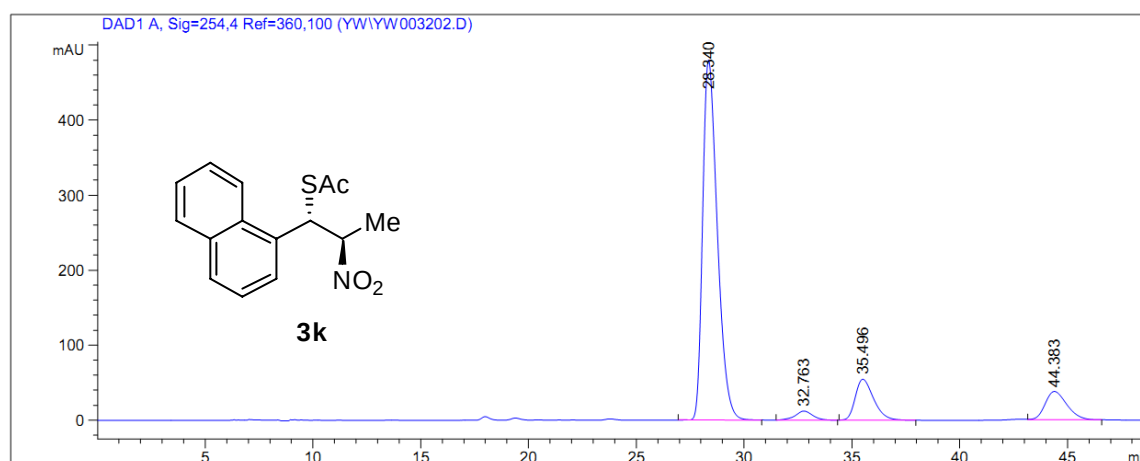


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.855	BV	0.4509	1.97333e4	679.31421	84.2831
2	31.776	MM	0.4671	1014.29974	36.19127	4.3322
3	35.857	MM	0.7009	2665.51099	63.38605	11.3847

(1S,2R)-1-(1-Naphthyl)-2-nitropropyl ethanethioate (3k)

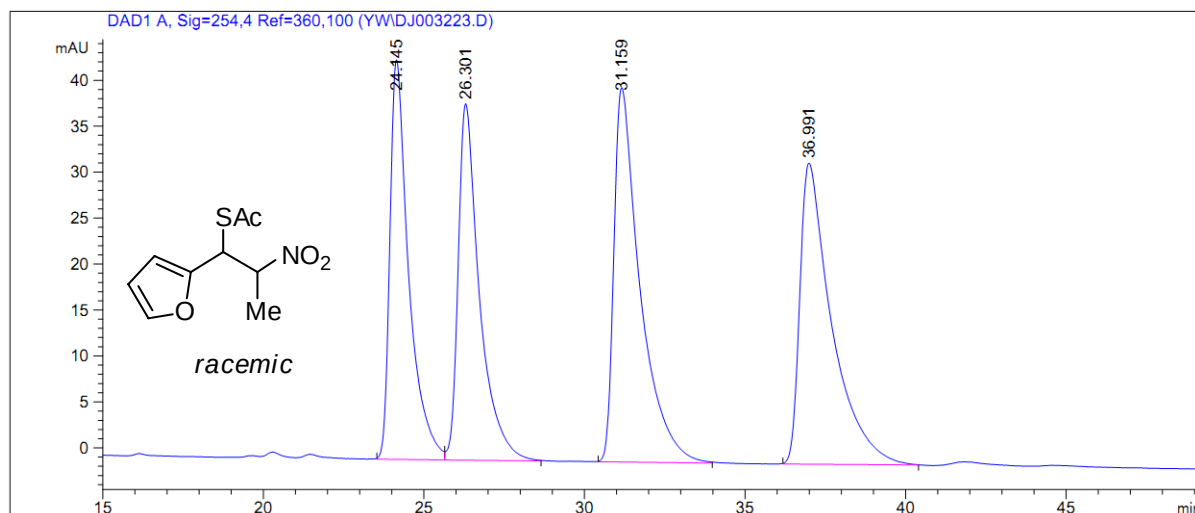


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.548	BB	0.6758	1.29591e4	295.41333	31.1369
2	31.780	VV	0.8427	1.31637e4	241.96526	31.6285
3	34.305	VB	0.9562	7781.75830	123.99592	18.6973
4	43.454	VB	1.1619	7715.15186	102.06204	18.5373

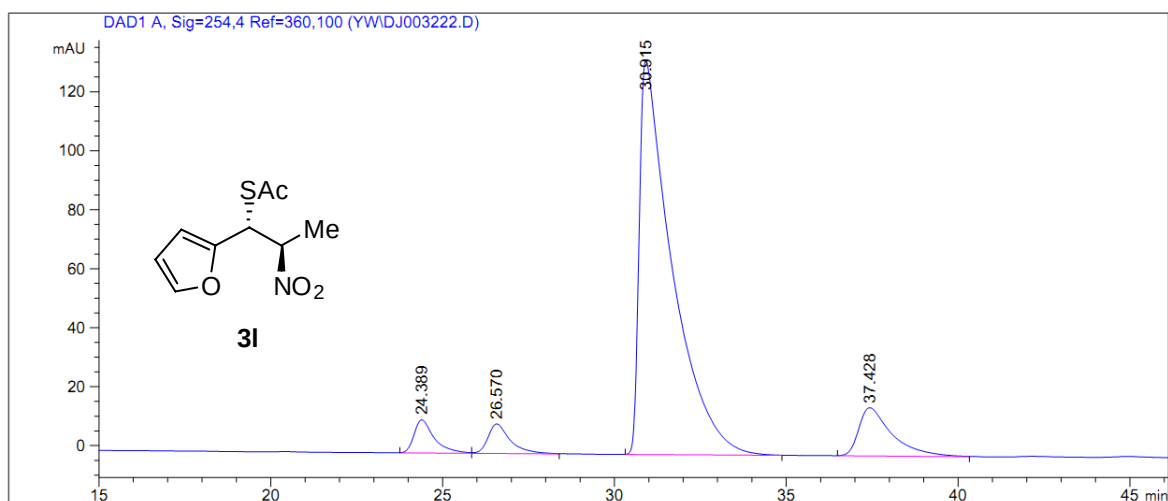


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.340	BB	0.7323	2.27269e4	480.04977	77.2264
2	32.763	BB	0.8631	712.46436	12.24022	2.4210
3	35.496	BB	0.9183	3253.92383	54.67501	11.0569
4	44.383	VB	1.0989	2735.63184	38.22783	9.2957

(1*R*,2*R*)-1-(2-Furyl)-2-nitropropyl ethanethioate (3I)

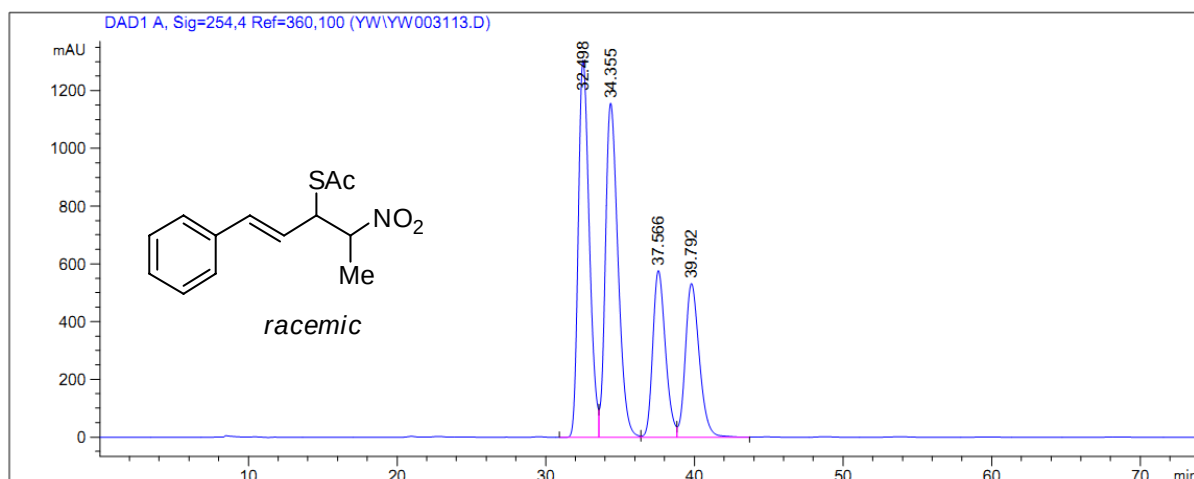


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.145	BV	0.5969	1761.89160	43.46252	21.7881
2	26.301	VB	0.6731	1784.89587	38.76970	22.0726
3	31.159	BB	0.8087	2294.27637	40.75658	28.3718
4	36.991	BB	0.9679	2245.41309	32.74832	27.7675

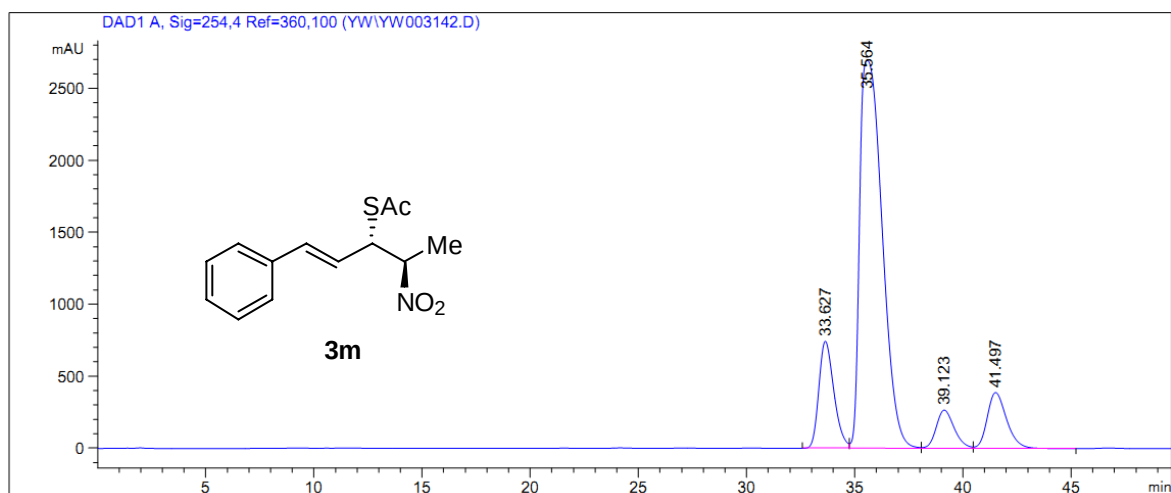


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.389	BV	0.5937	457.39008	11.26379	4.2294
2	26.570	VB	0.6591	449.81699	10.03151	4.1594
3	30.915	BB	0.9091	8811.82813	133.67493	81.4818
4	37.428	BB	0.9761	1095.44116	16.38351	10.1294

(E,3S,4R)-4-Nitro-1-phenylpent-1-en-3-yl ethanethioate (3m)

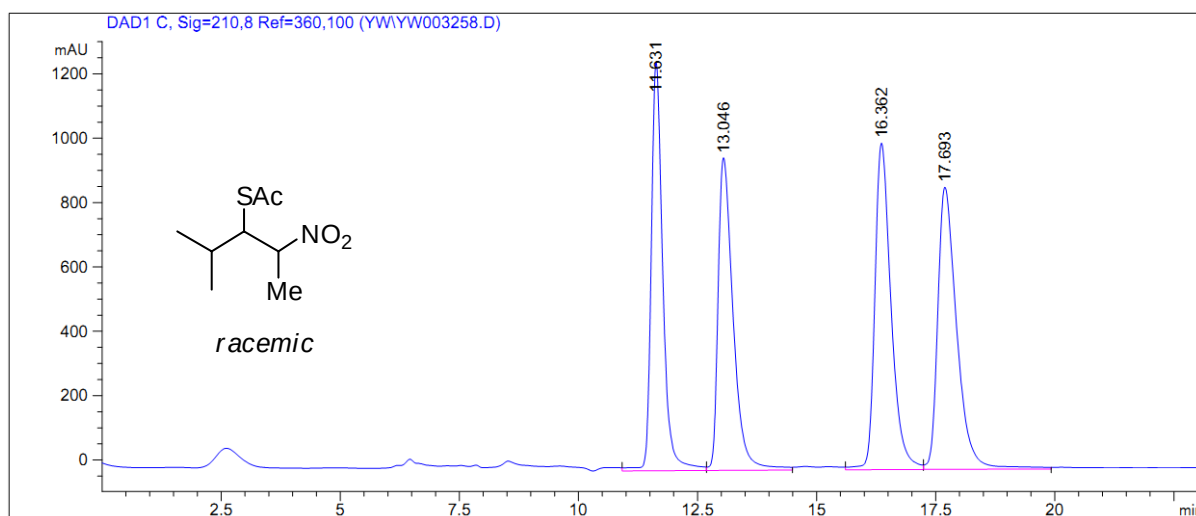


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.498	VV	0.8009	6.72875e4	1306.45020	32.8997
2	34.355	VV	0.9152	6.81771e4	1157.46082	33.3346
3	37.566	VV	0.9134	3.41261e4	577.55023	16.6857
4	39.792	VB	1.0051	3.49324e4	532.68323	17.0799

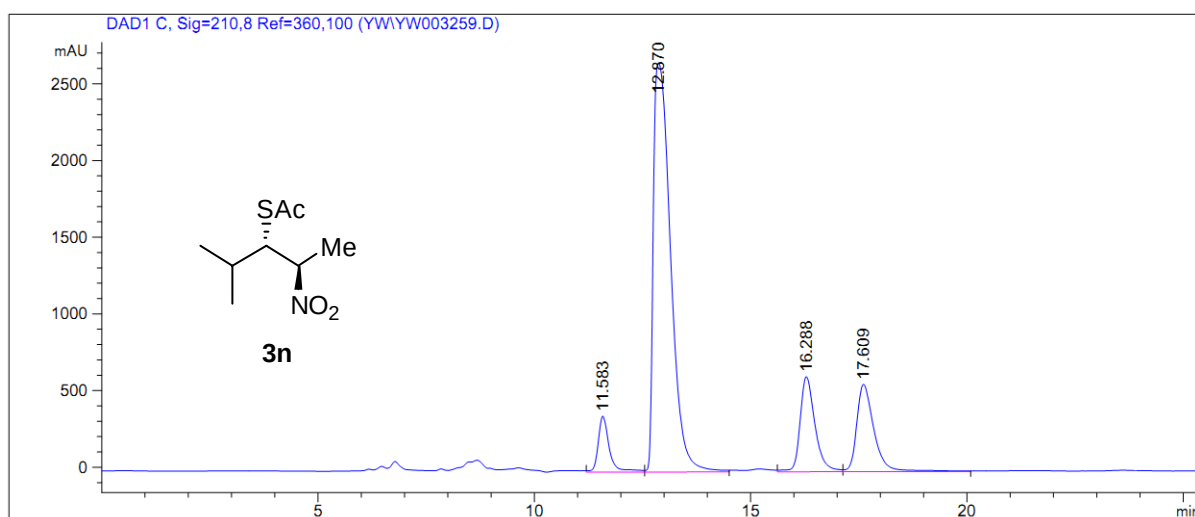


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.627	BV	0.7449	3.60404e4	744.38782	13.3265
2	35.564	VV	1.1457	1.94653e5	2698.01831	71.9758
3	39.123	VV	0.8940	1.55035e4	266.77051	5.7327
4	41.497	VB	0.9510	2.42454e4	389.10037	8.9651

(3S,4R)-2-methyl-4-nitropentan-3-yl ethanethioate (3n)

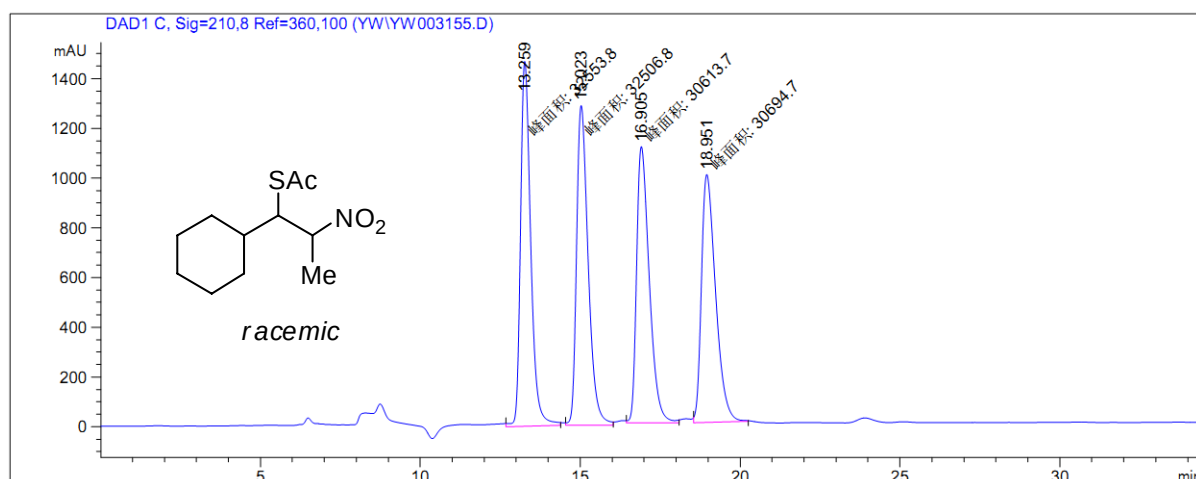


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.631	VV	0.2566	2.14285e4	1271.50757	23.5370
2	13.046	VV	0.3320	2.13167e4	971.64532	23.4142
3	16.362	VV	0.3594	2.39568e4	1015.01575	26.3141
4	17.693	VB	0.4198	2.43398e4	876.84088	26.7347

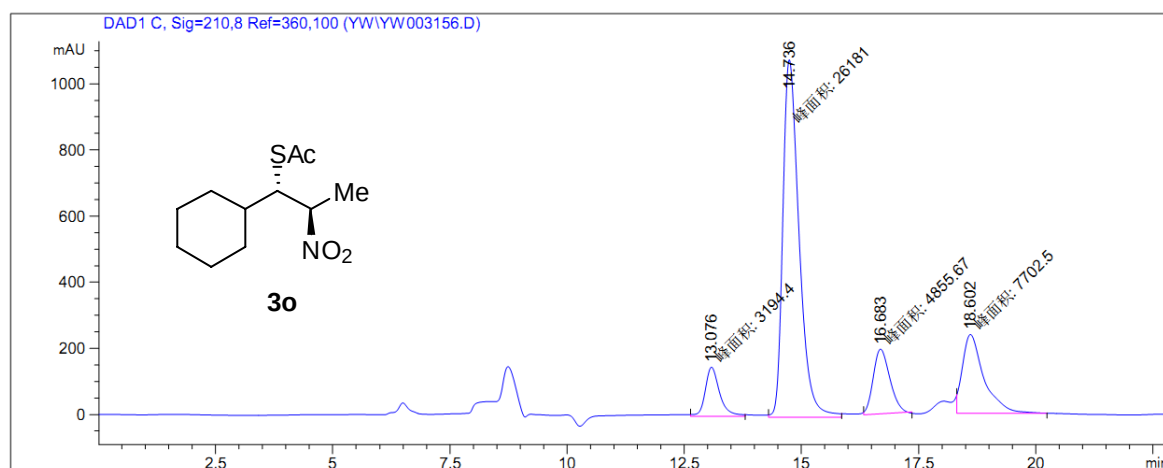


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.583	VV	0.2668	6519.94580	364.28412	5.8783
2	12.870	VV	0.4323	7.36975e4	2667.54736	66.4444
3	16.288	VV	0.3629	1.48240e4	620.04553	13.3650
4	17.609	VB	0.4216	1.58747e4	568.81696	14.3123

(1S,2R)-1-Cyclohexyl-2-nitropropyl ethanethioate (3o)

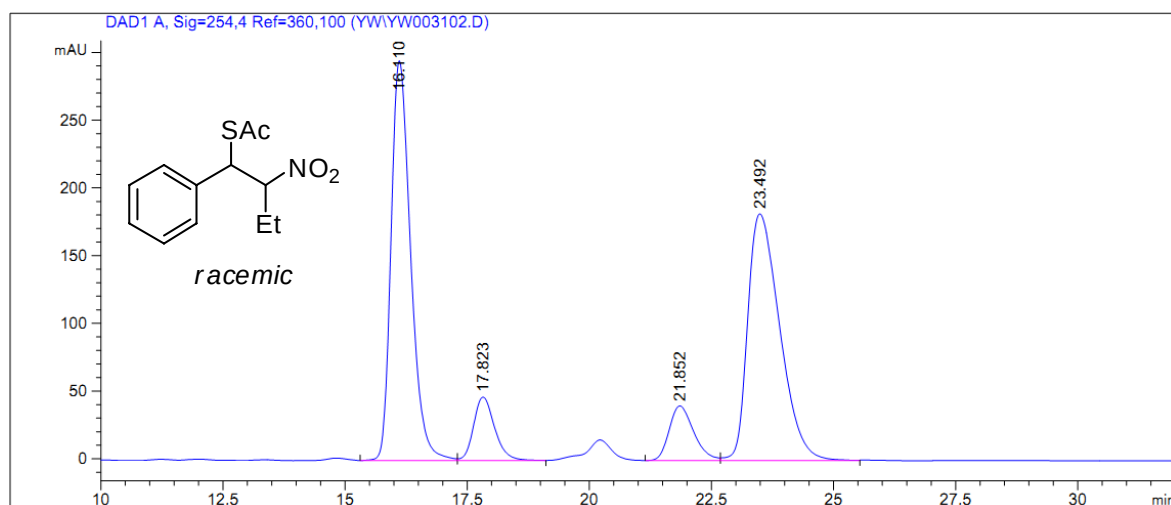


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.259	MM	0.3694	3.25538e4	1468.64844	25.7609
2	15.023	MM	0.4210	3.25068e4	1286.79858	25.7237
3	16.905	MM	0.4592	3.06137e4	1111.10889	24.2257
4	18.951	MM	0.5130	3.06947e4	997.16754	24.2897

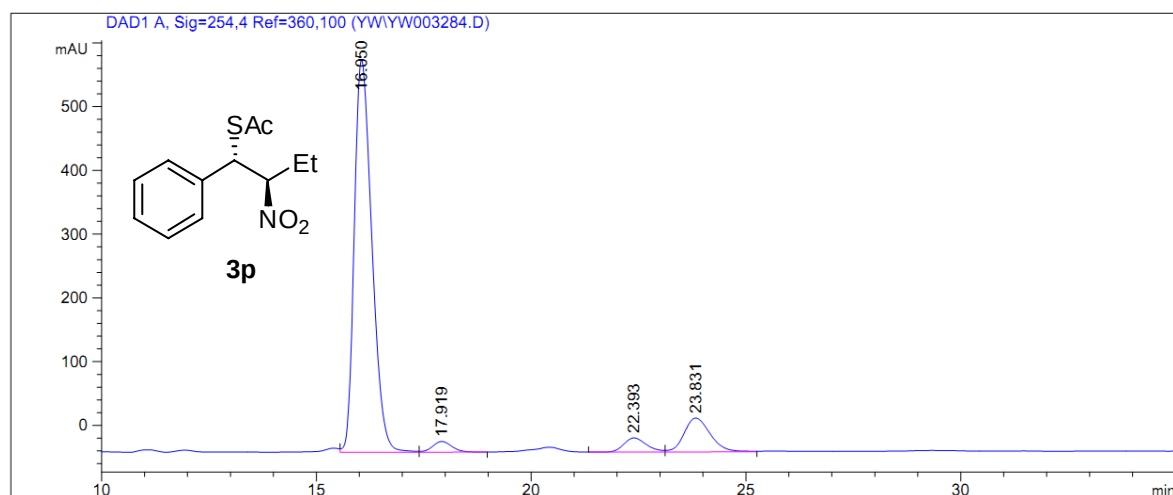


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.076	MM	0.3583	3194.40283	148.59515	7.6178
2	14.736	MM	0.4033	2.61810e4	1081.98560	62.4345
3	16.683	MM	0.4123	4855.67188	196.30237	11.5794
4	18.602	MM	0.5365	7702.49512	239.28087	18.3683

(1S,2R)-2-Nitro-1-phenylbutyl ethanethioate (3p)

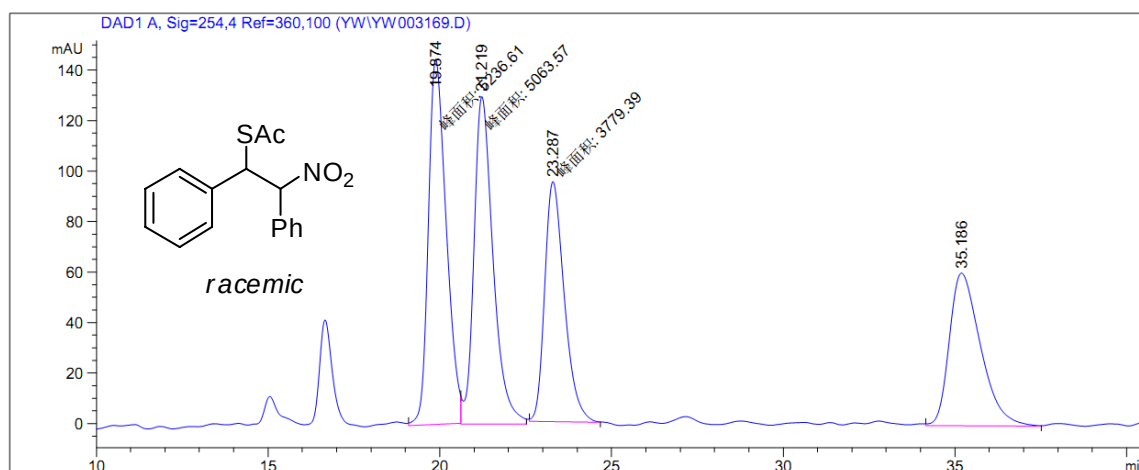


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.110	VV	0.4334	8233.96387	295.18497	42.5519
2	17.823	VV	0.4622	1410.68005	46.99350	7.2902
3	21.852	VV	0.5379	1405.22400	40.38612	7.2620
4	23.492	VB	0.7117	8300.51953	182.14423	42.8959

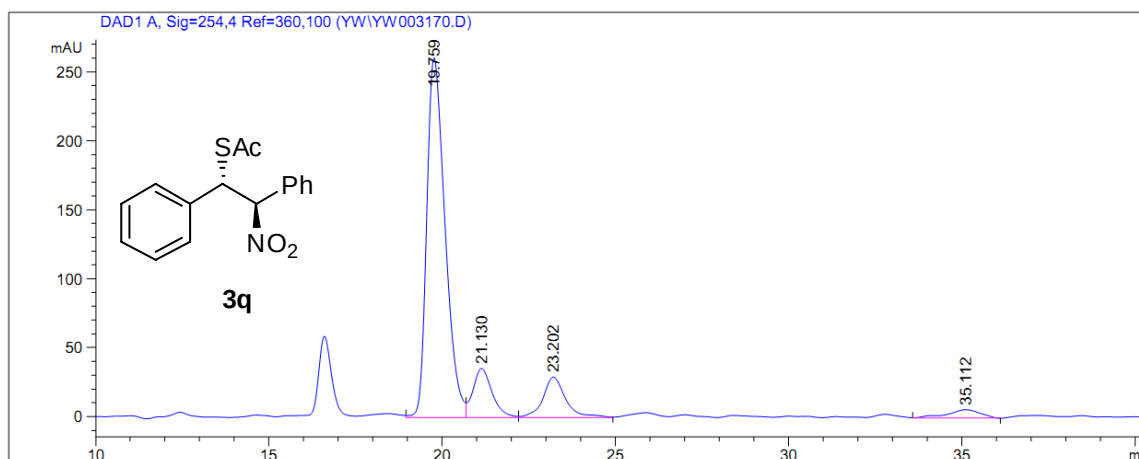


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.050	VV	0.4439	1.74920e4	614.91010	82.9409
2	17.919	VB	0.4878	532.75952	16.89952	2.5262
3	22.393	VV	0.5667	808.76501	22.11101	3.8349
4	23.831	VV	0.6596	2256.19580	53.11498	10.6981

(1S,2R)-2-Nitro-1,2-diphenylethyl ethanethioate (3q)

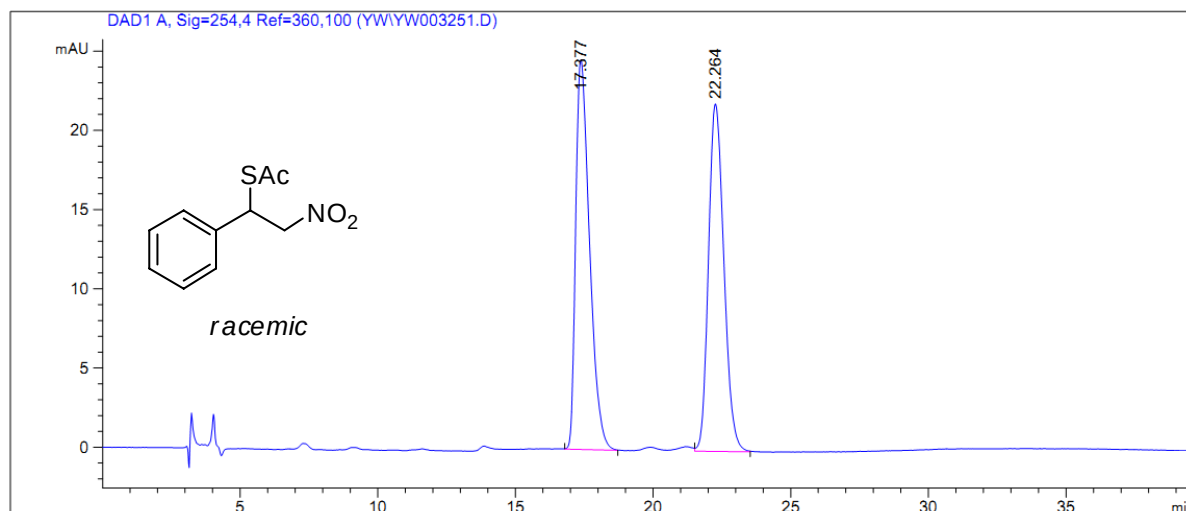


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.874	MM	0.6030	5236.61133	144.73111	29.2302
2	21.219	MM	0.6496	5063.57275	129.90921	28.2643
3	23.287	MM	0.6624	3779.39014	95.09399	21.0962
4	35.186	VV	0.9628	3835.49585	60.56432	21.4093

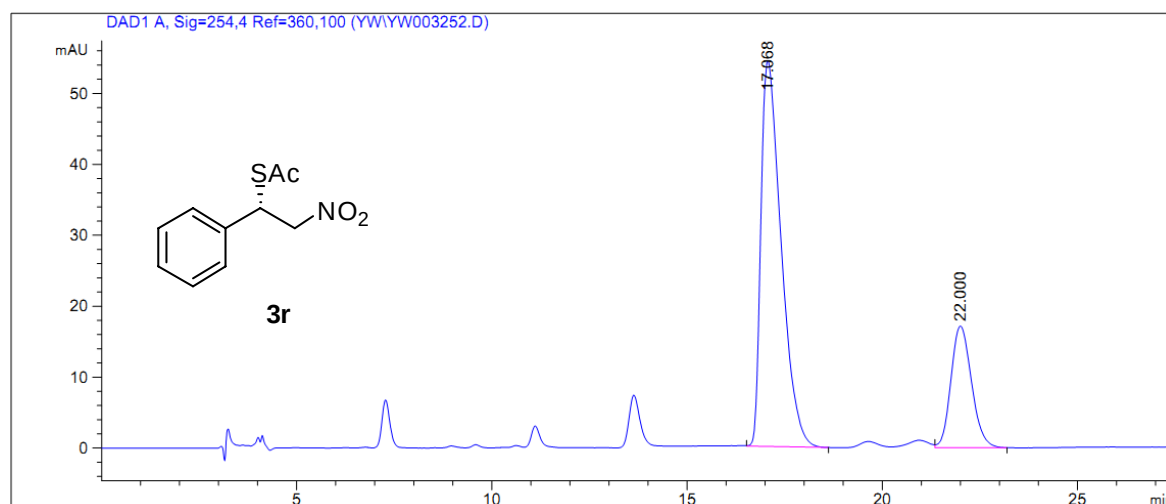


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.759	VV	0.5649	9590.61523	260.85995	75.0296
2	21.130	VV	0.5802	1386.36194	35.76995	10.8458
3	23.202	VV	0.6837	1376.50500	29.53868	10.7687
4	35.112	VV	0.9541	428.96317	6.23936	3.3559

(S)-2-Nitro-1-phenylethyl ethanethioate (3r)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.377	BB	0.5357	859.28339	24.59133	50.2140
2	22.264	VB	0.6093	851.95831	21.92940	49.7860



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.068	BB	0.5511	1953.54883	54.38527	75.6279
2	22.000	VB	0.5718	629.55573	17.16925	24.3721