

# Enantioselective Synthesis of Pyrazolone Derivatives Catalysed by a Chiral Squaramide Catalyst

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## *Supporting Information*

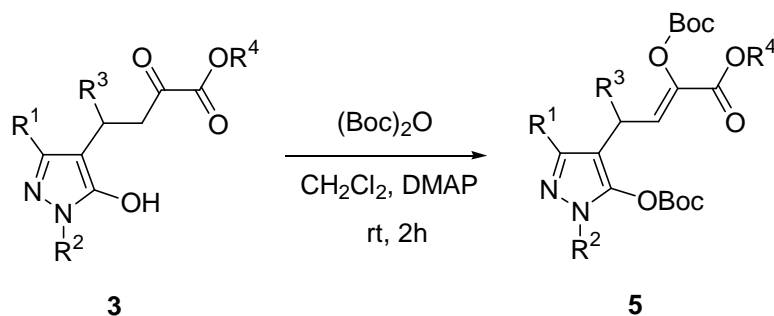
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## The protection of compounds **3** to compounds **5**

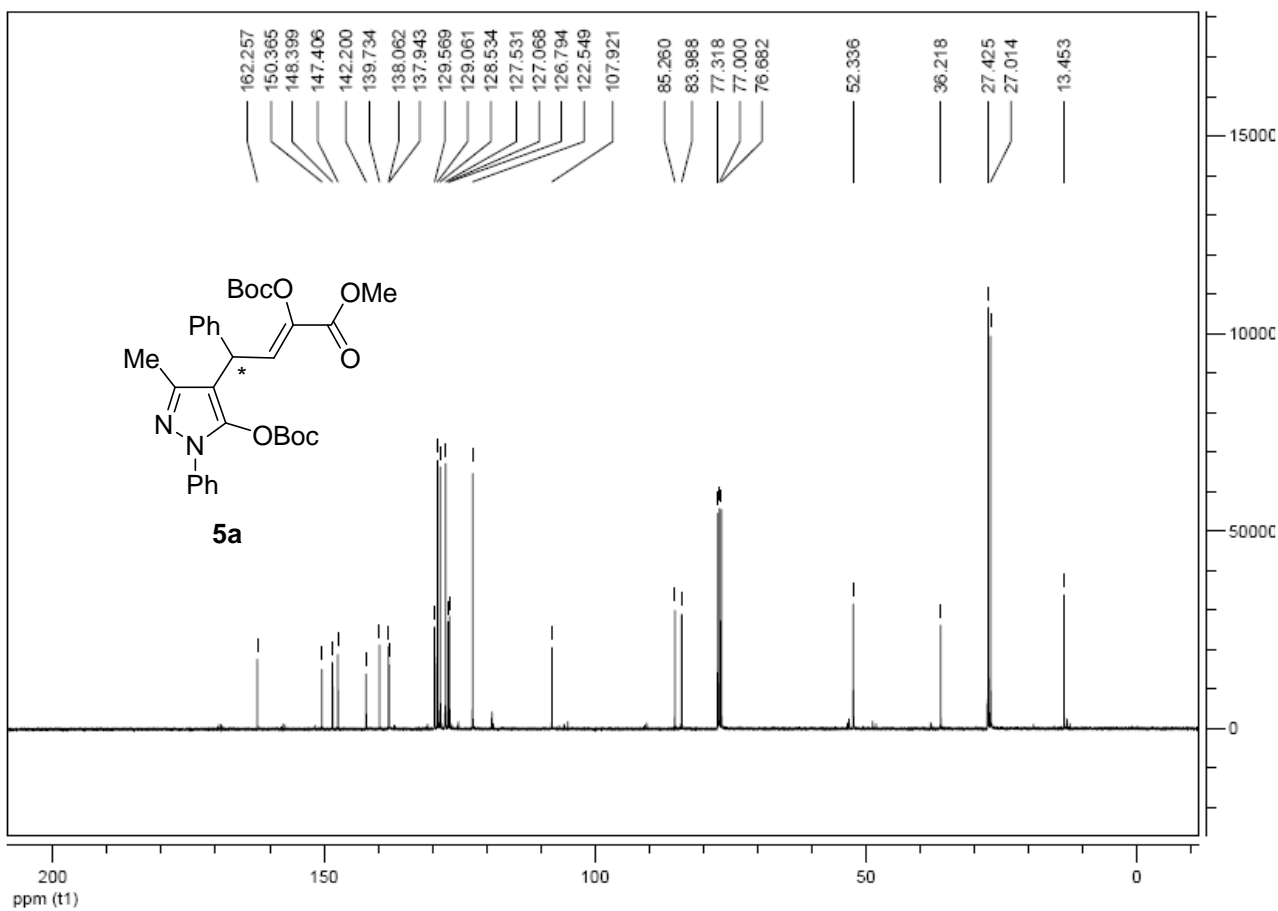
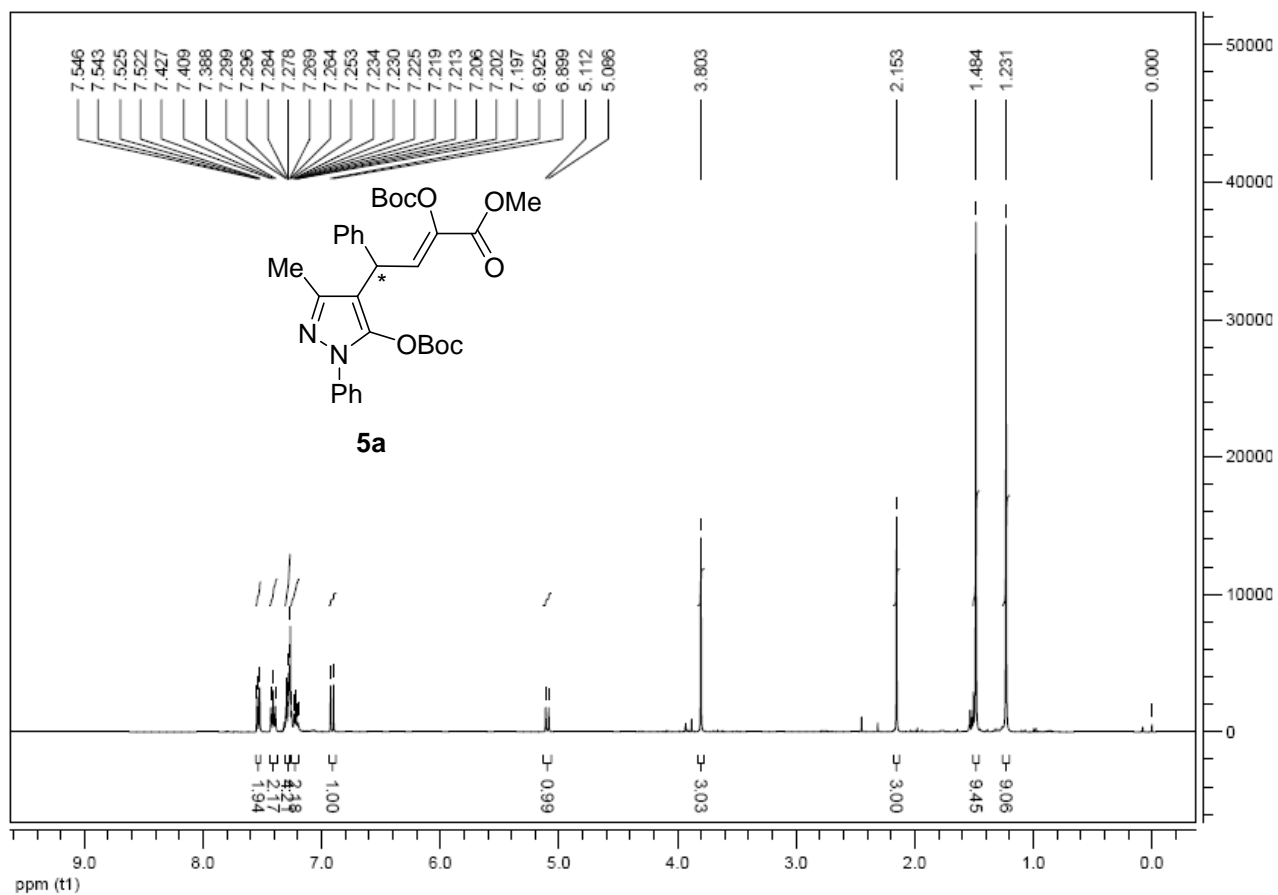
A mixture of **3** (one equivalent), di-tert-butyl dicarbonate (two equivalent) and anhydrous potassium carbonate (0.2 equivalent) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was stirred at room temperature for 2 hours. Then the mixture was concentrated and purified by silica gel column chromatography (with ethyl acetate–petroleum ether 1:8 as the eluent) to afford the desired products **5**.

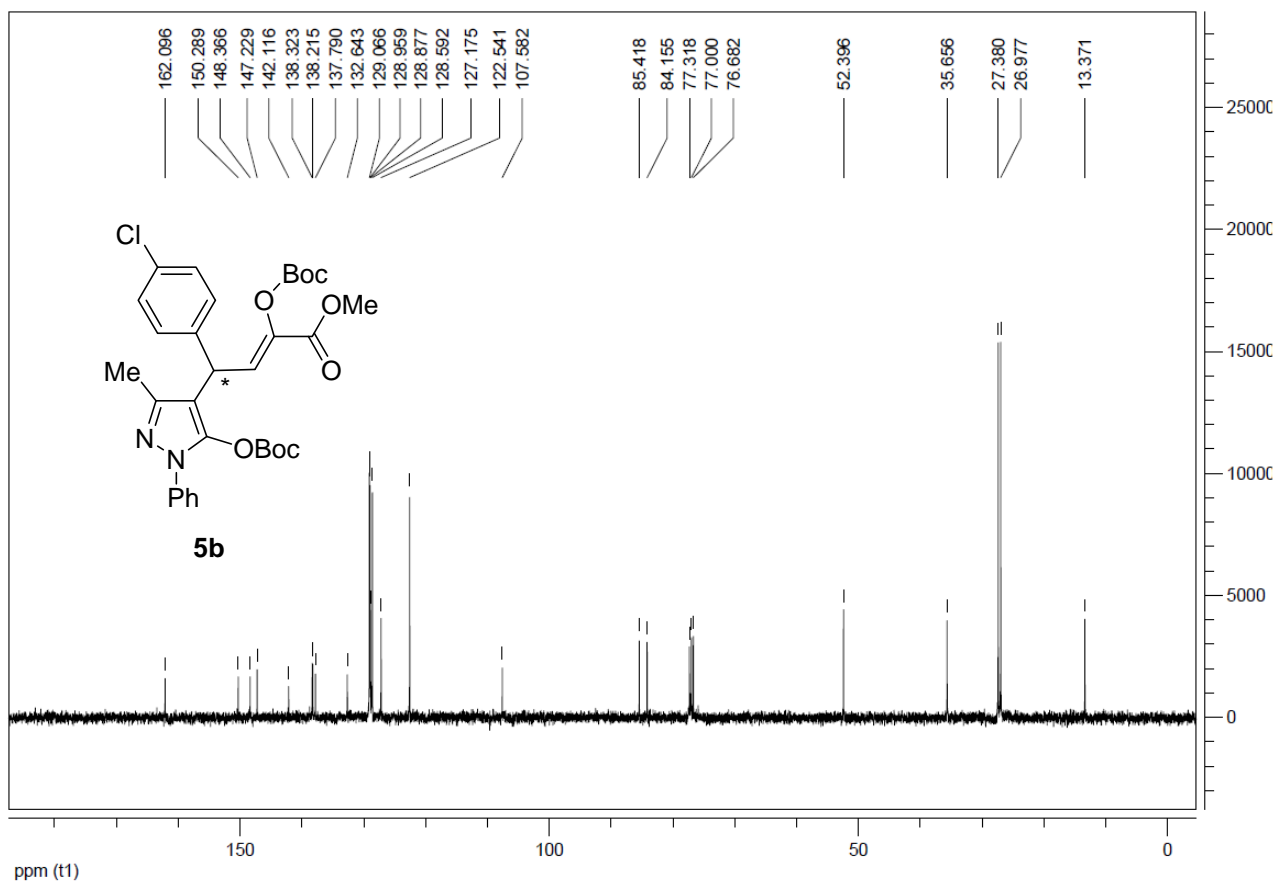
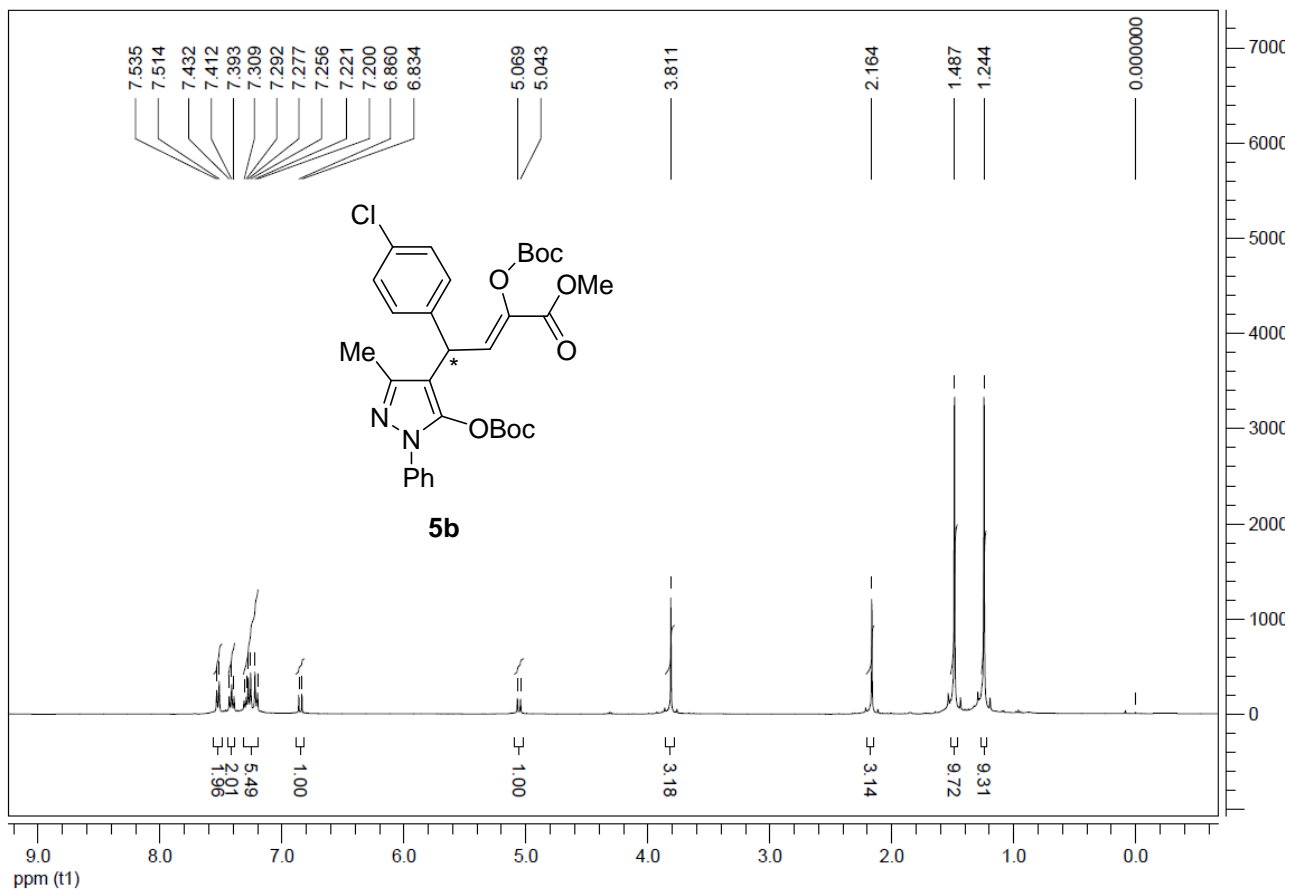
**Table S1. Yields of compounds **5****

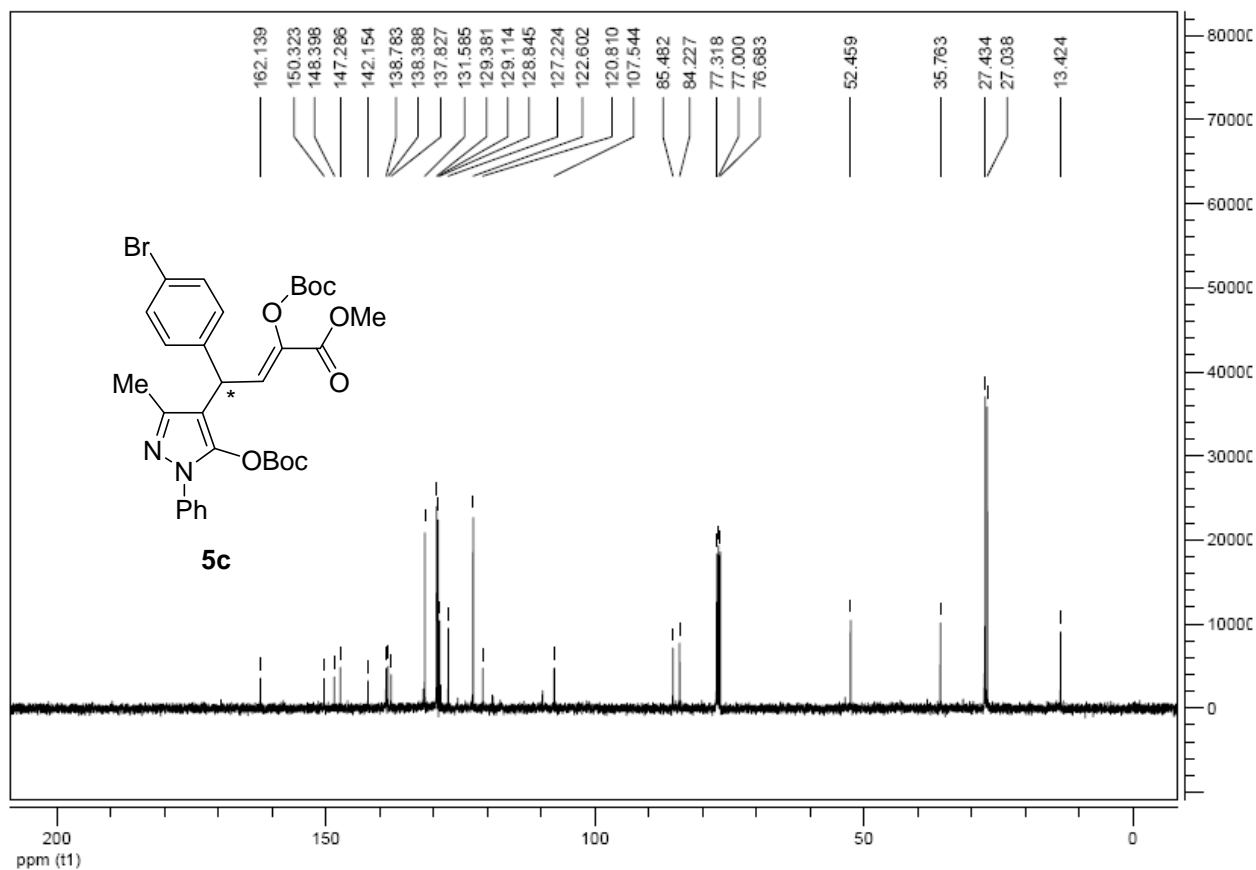
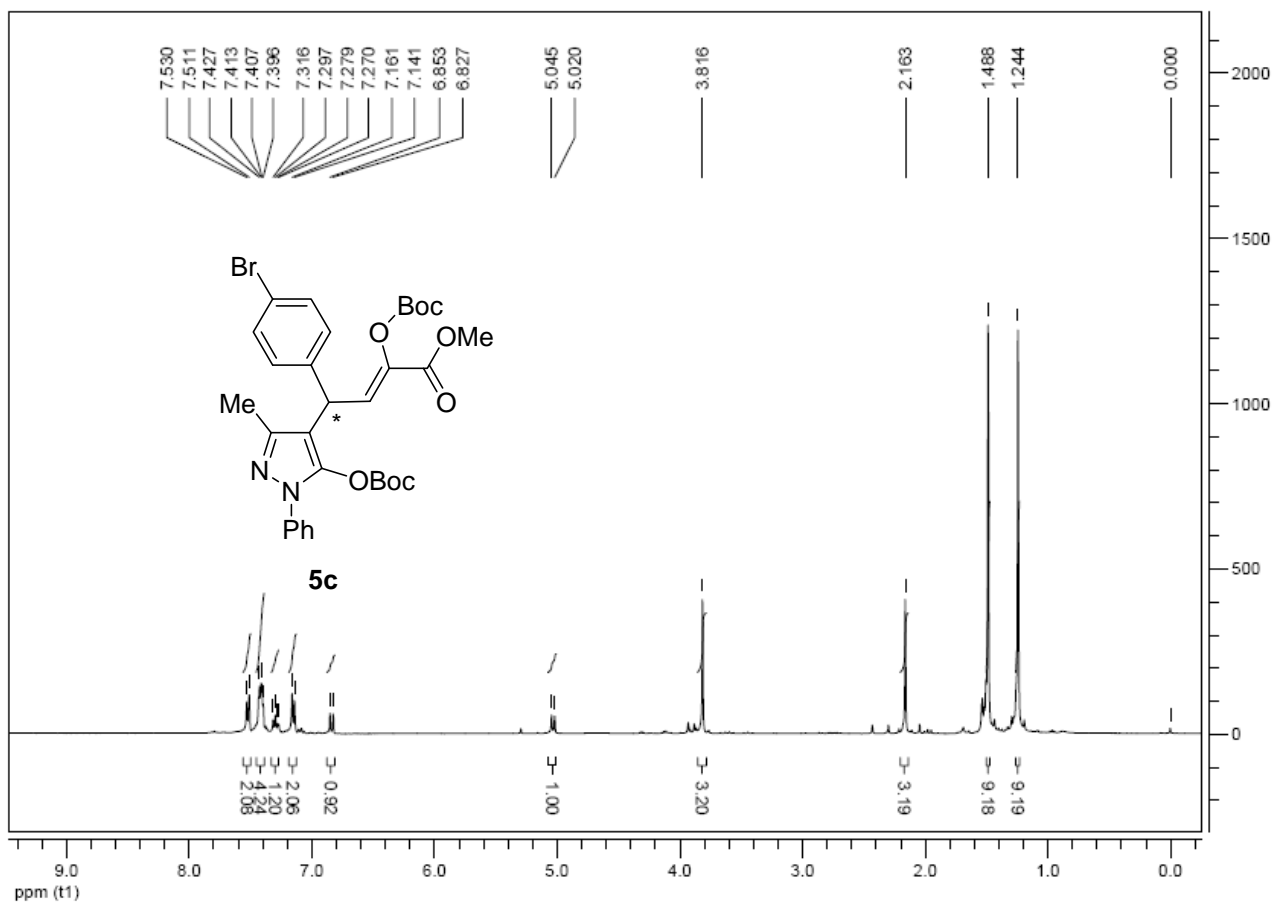


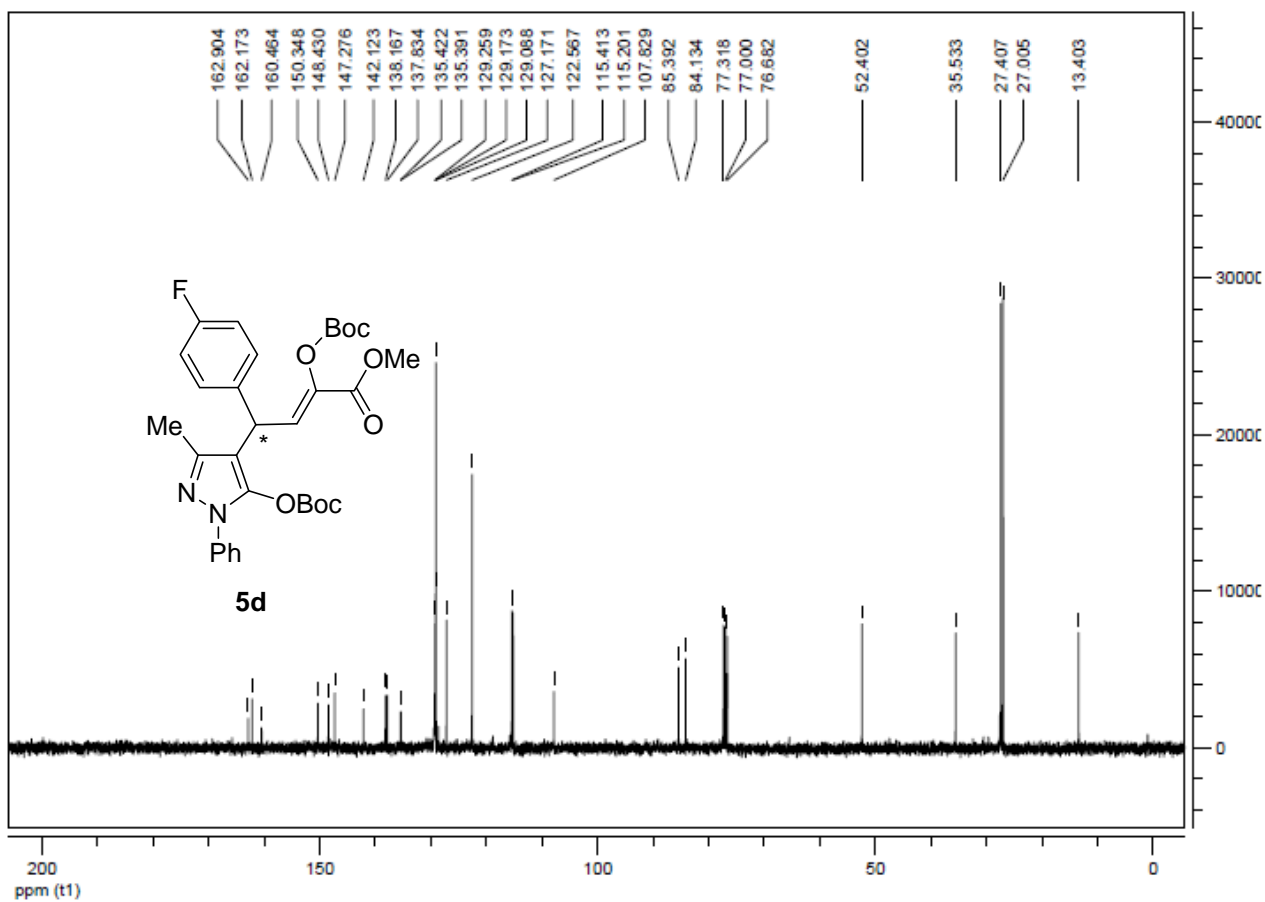
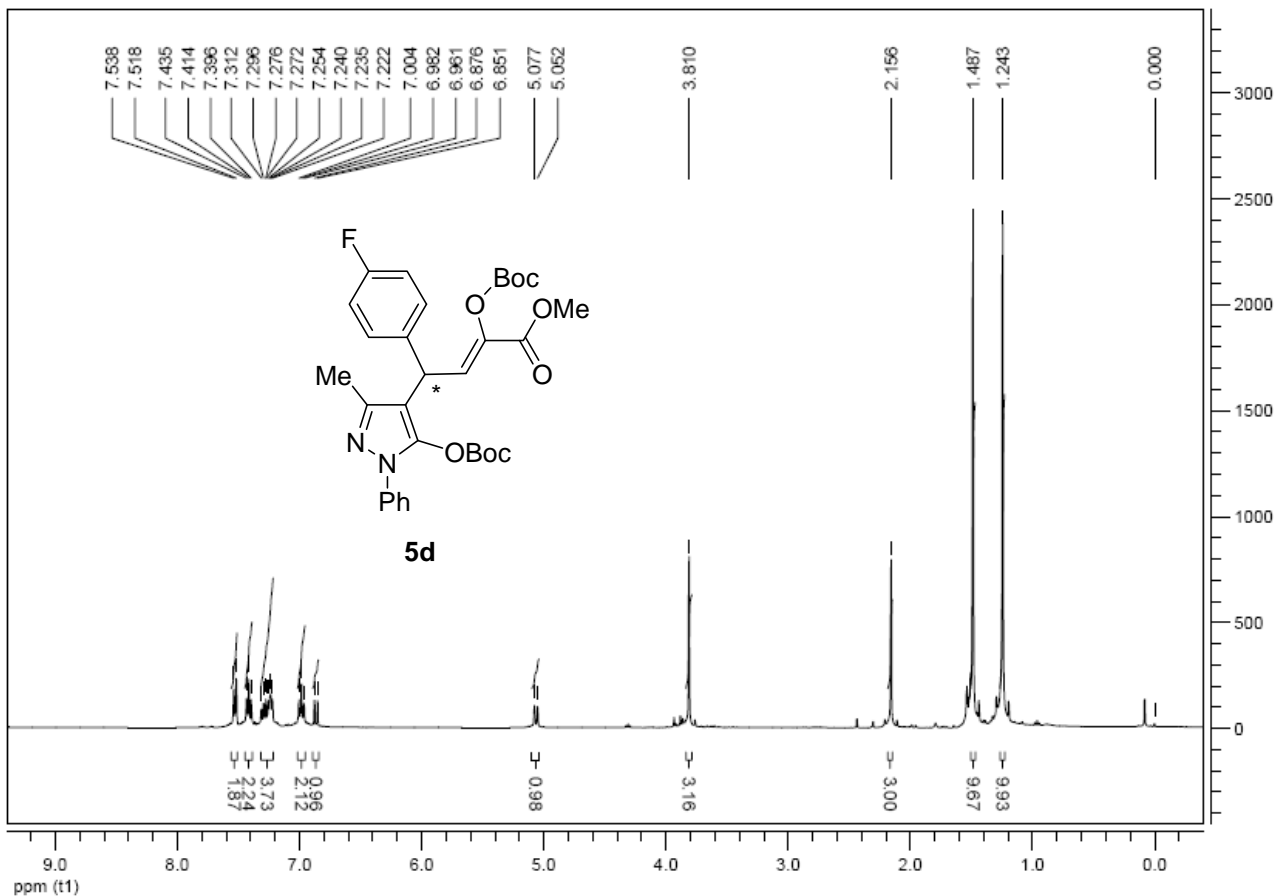
Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Reactant	Product	Yield (%)
1	Me	Ph	Ph	Me	<b>3a</b>	<b>5a</b>	47
2	Me	Ph	4-ClC <sub>6</sub> H <sub>4</sub>	Me	<b>3b</b>	<b>5b</b>	52
3	Me	Ph	4-BrC <sub>6</sub> H <sub>4</sub>	Me	<b>3c</b>	<b>5c</b>	35
4	Me	Ph	4-FC <sub>6</sub> H <sub>4</sub>	Me	<b>3d</b>	<b>5d</b>	52
5	Me	Ph	4-MeC <sub>6</sub> H <sub>4</sub>	Me	<b>3e</b>	<b>5e</b>	47
6	Me	Ph	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	<b>3f</b>	<b>5f</b>	61
7	Me	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	Me	<b>3g</b>	<b>5g</b>	17
8	Me	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	Me	<b>3h</b>	<b>5h</b>	46
9	CF <sub>3</sub>	Ph	Ph	Me	<b>3i</b>	<b>5i</b>	43
10	Ph	Ph	Ph	Me	<b>3j</b>	<b>5j</b>	56
11	Me	Ph	Ph	Bn	<b>3k</b>	<b>5k</b>	40
12	Me	Ph	Ph	Allyl	<b>3l</b>	<b>5l</b>	38
13	Ph	Ph	4-BrC <sub>6</sub> H <sub>4</sub>	Me	<b>3m</b>	<b>5m</b>	73
14	CF <sub>3</sub>	Ph	4-BrC <sub>6</sub> H <sub>4</sub>	Me	<b>3n</b>	<b>5n</b>	65
15	Et	Ph	Ph	Me	<b>3o</b>	<b>5o</b>	72

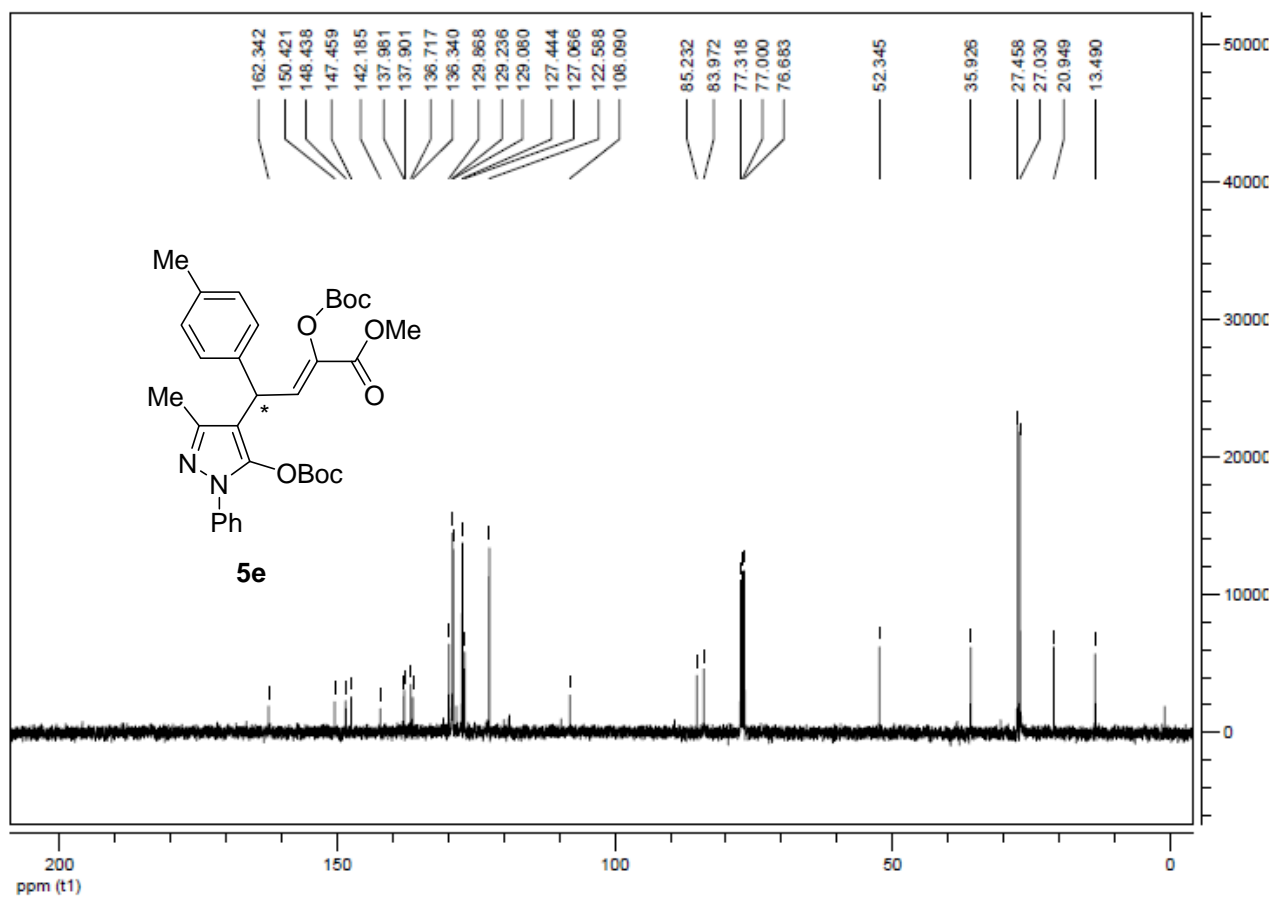
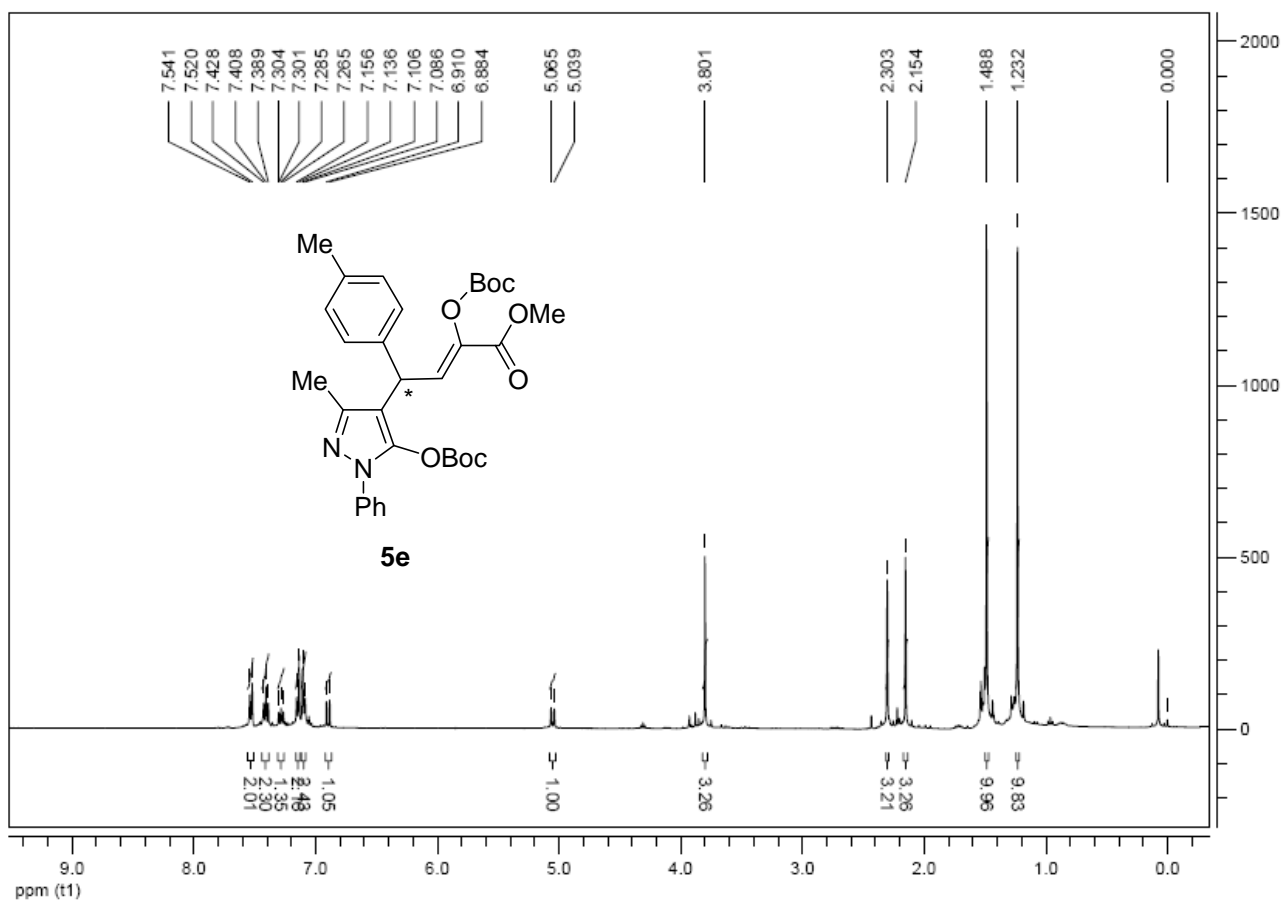
Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of products

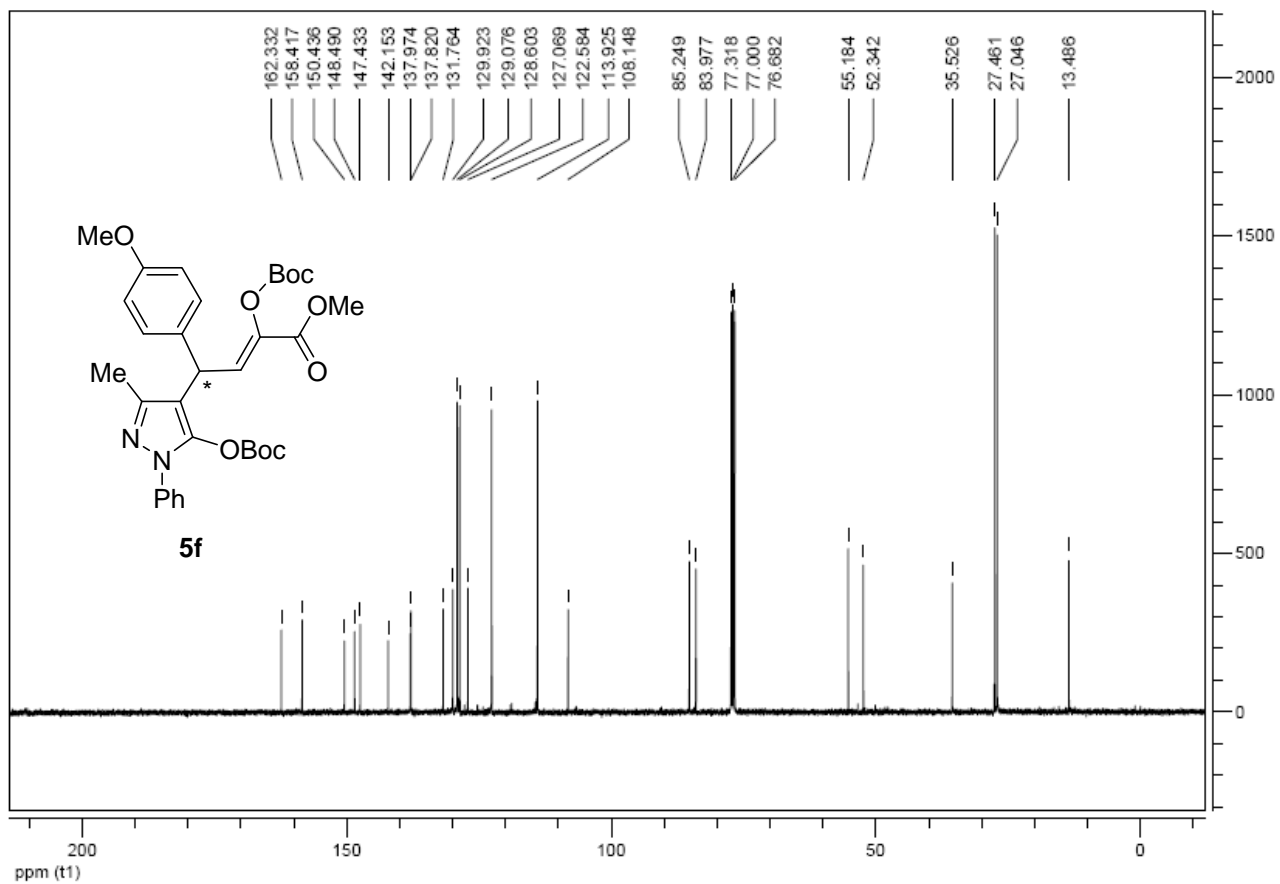
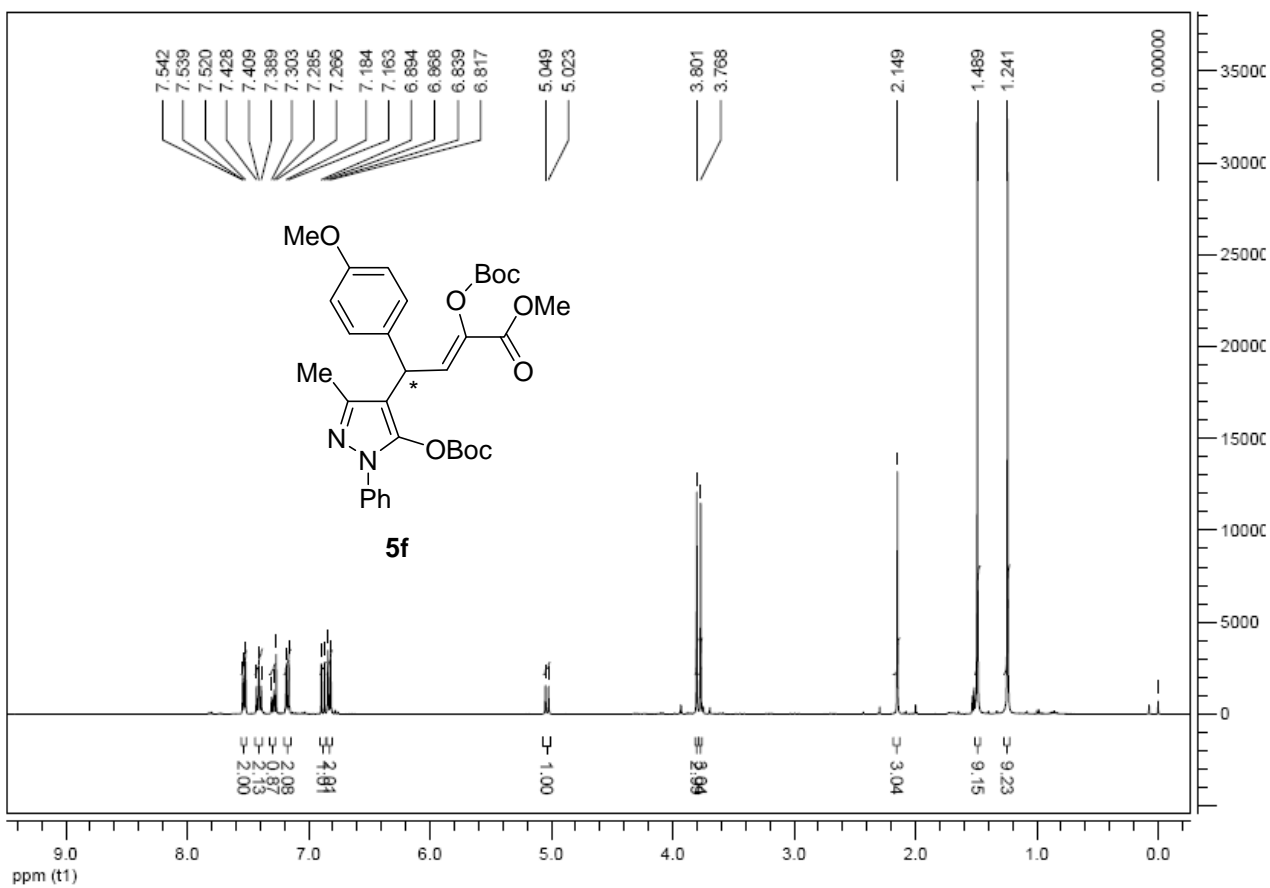




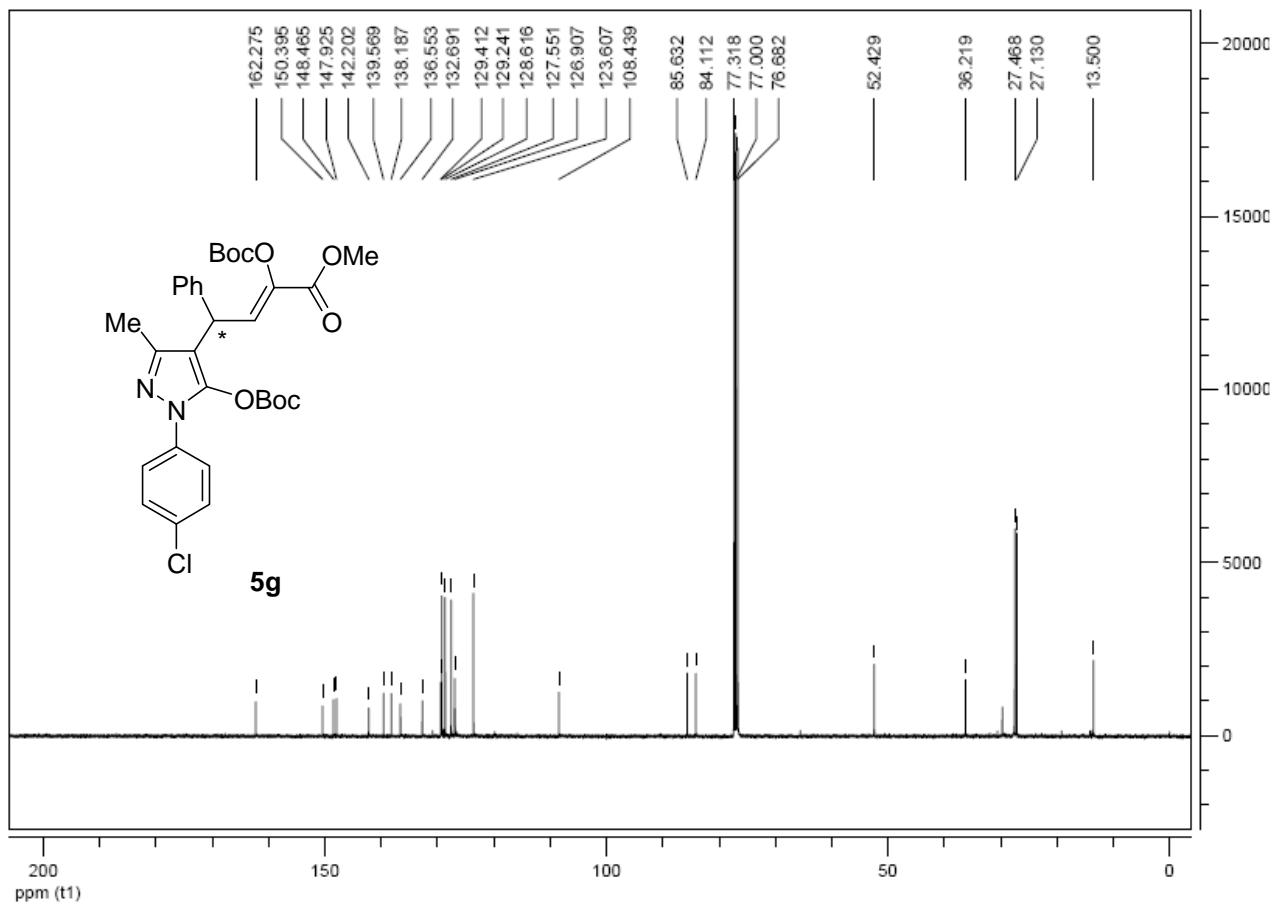
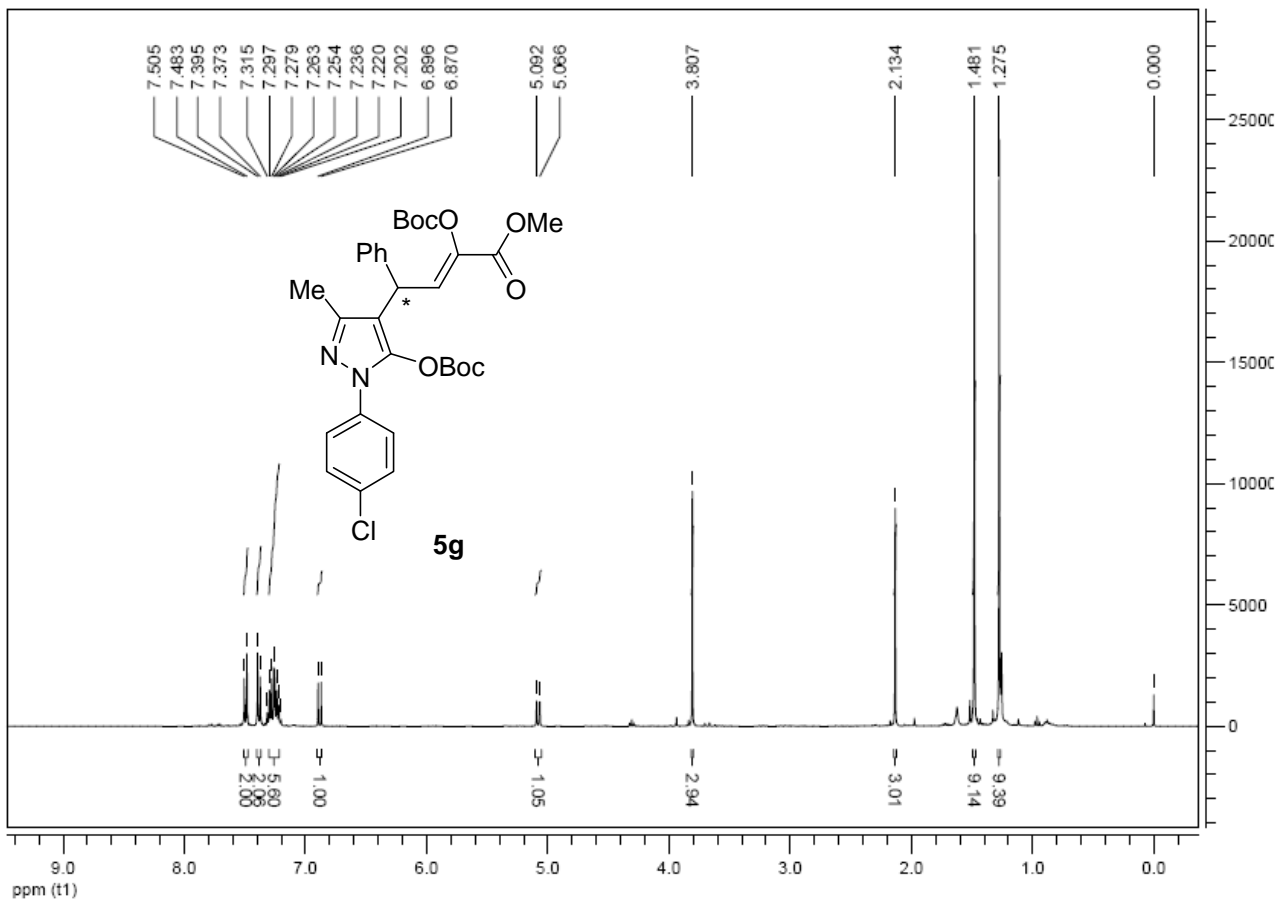


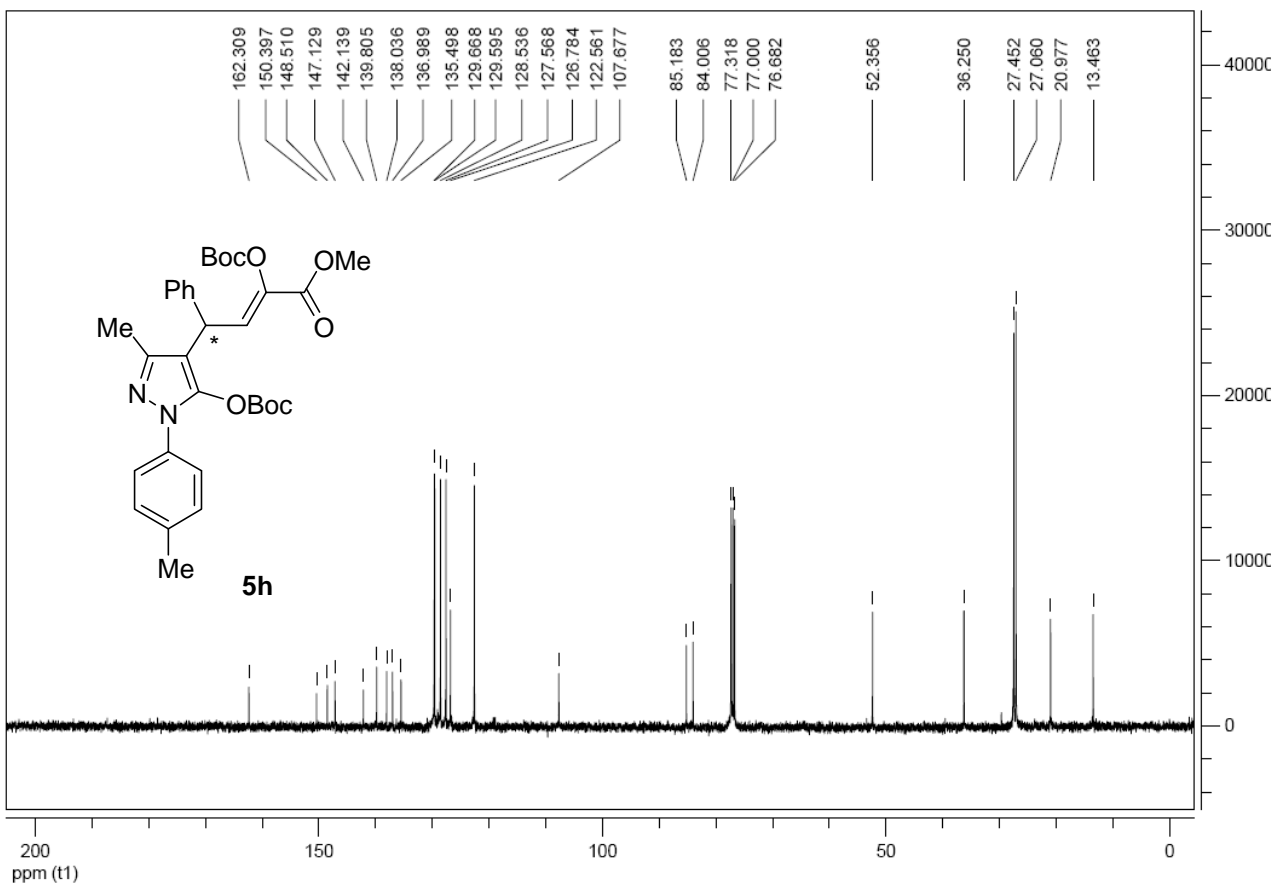
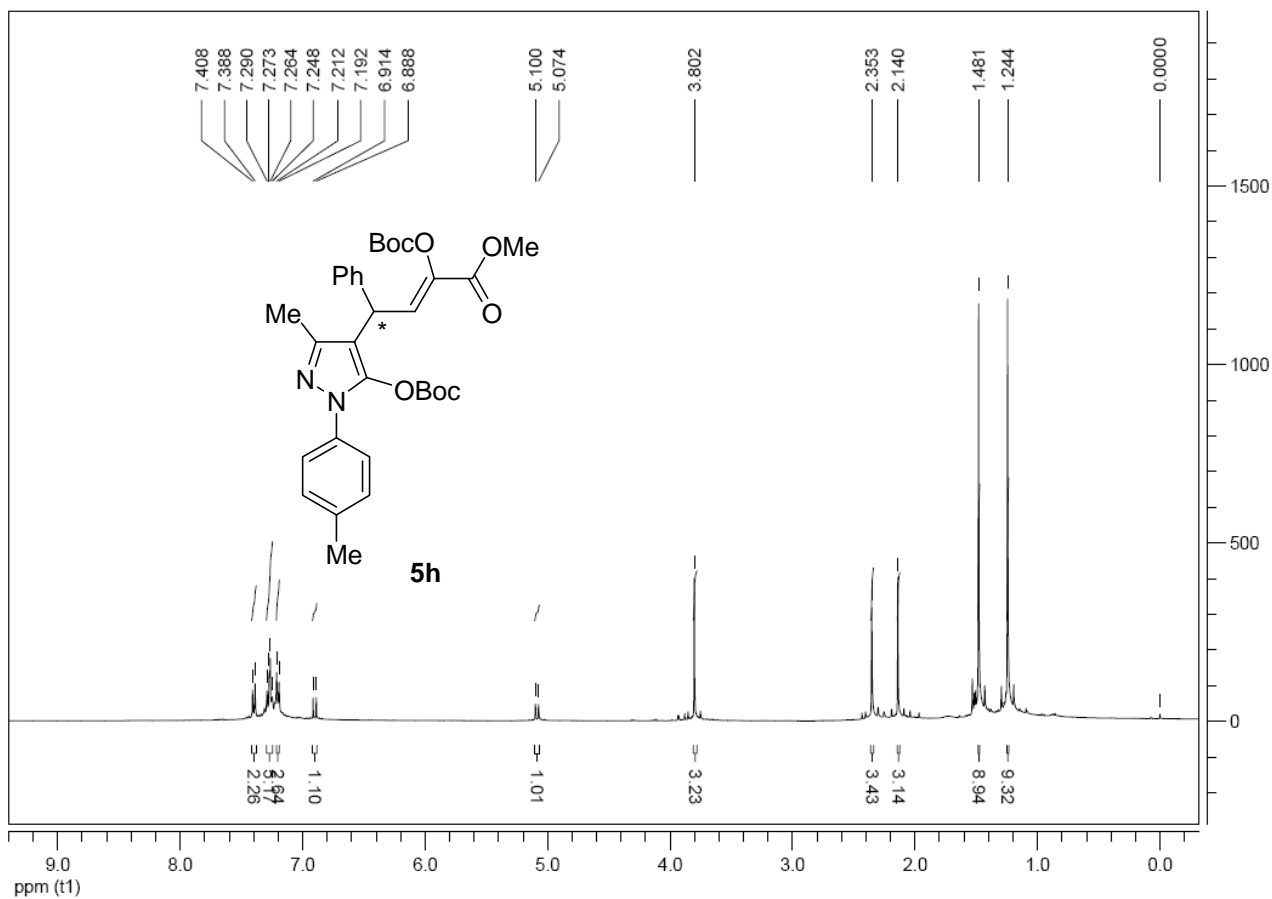


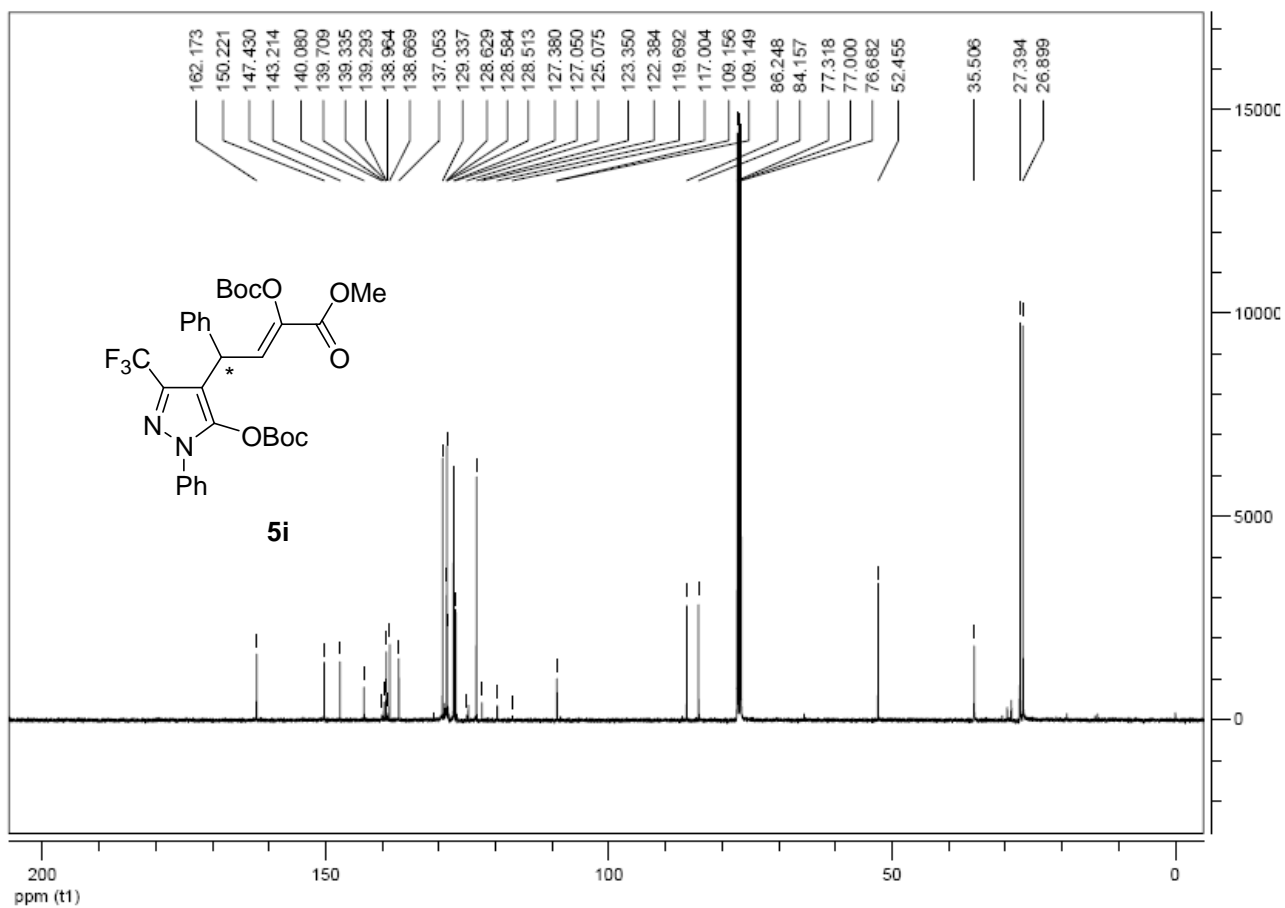
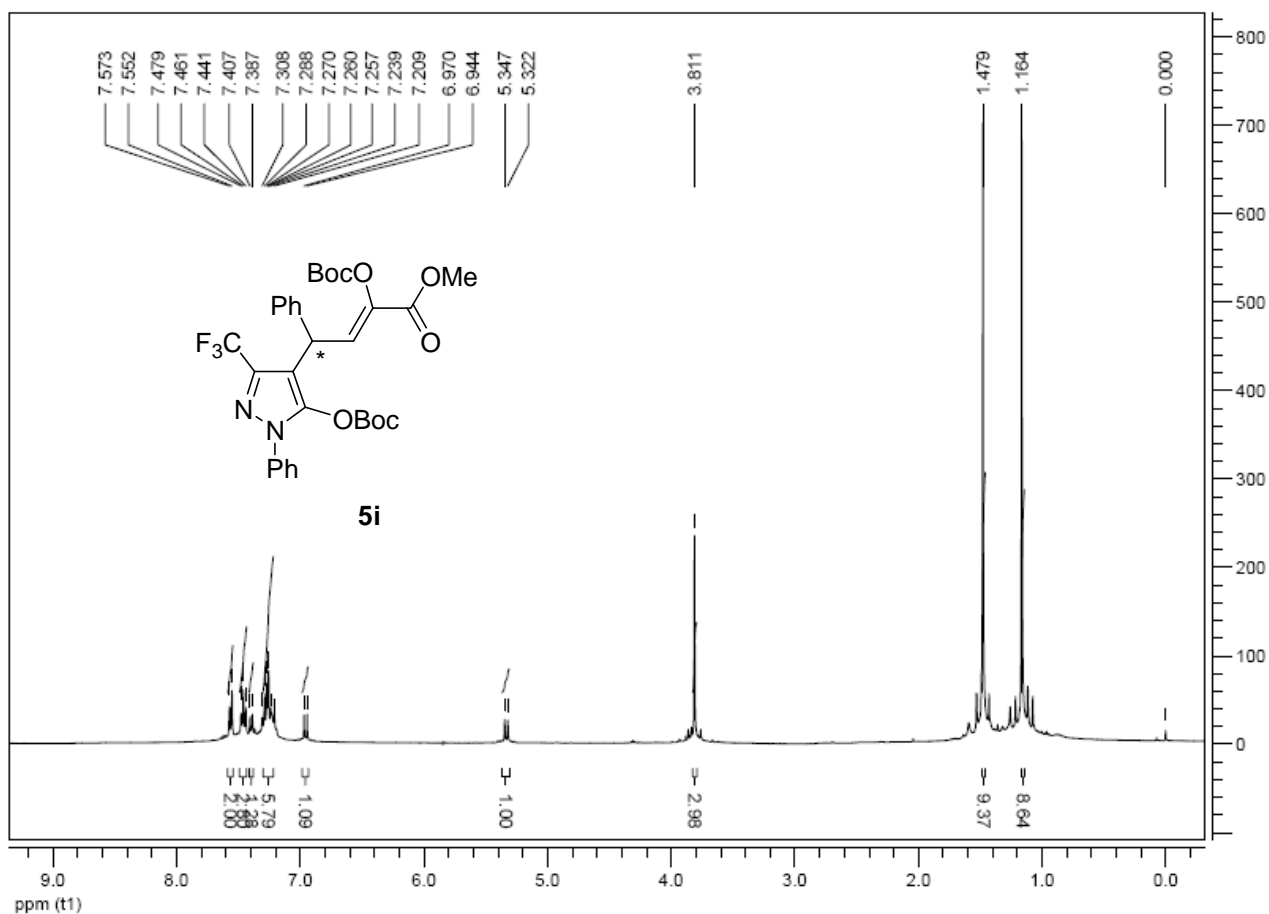


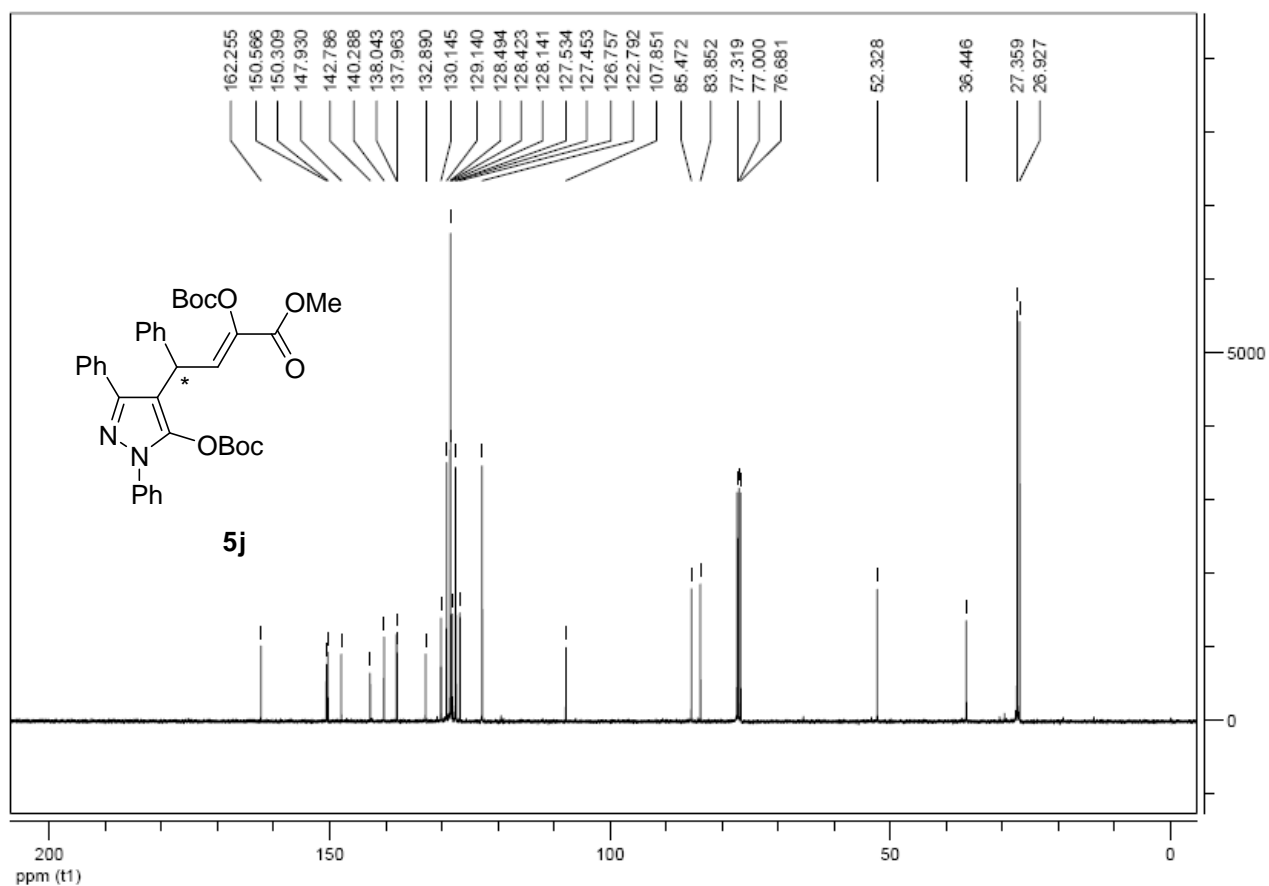
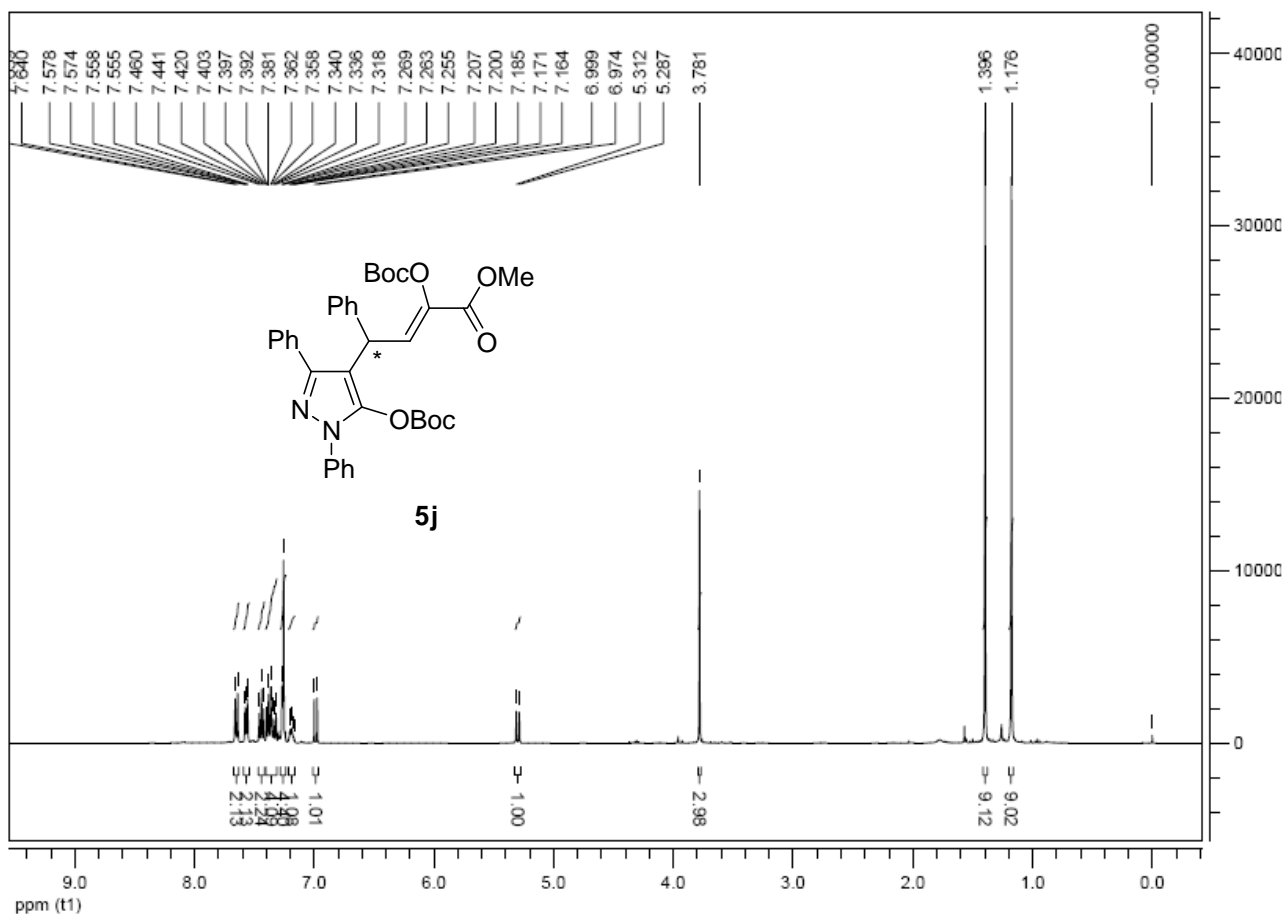


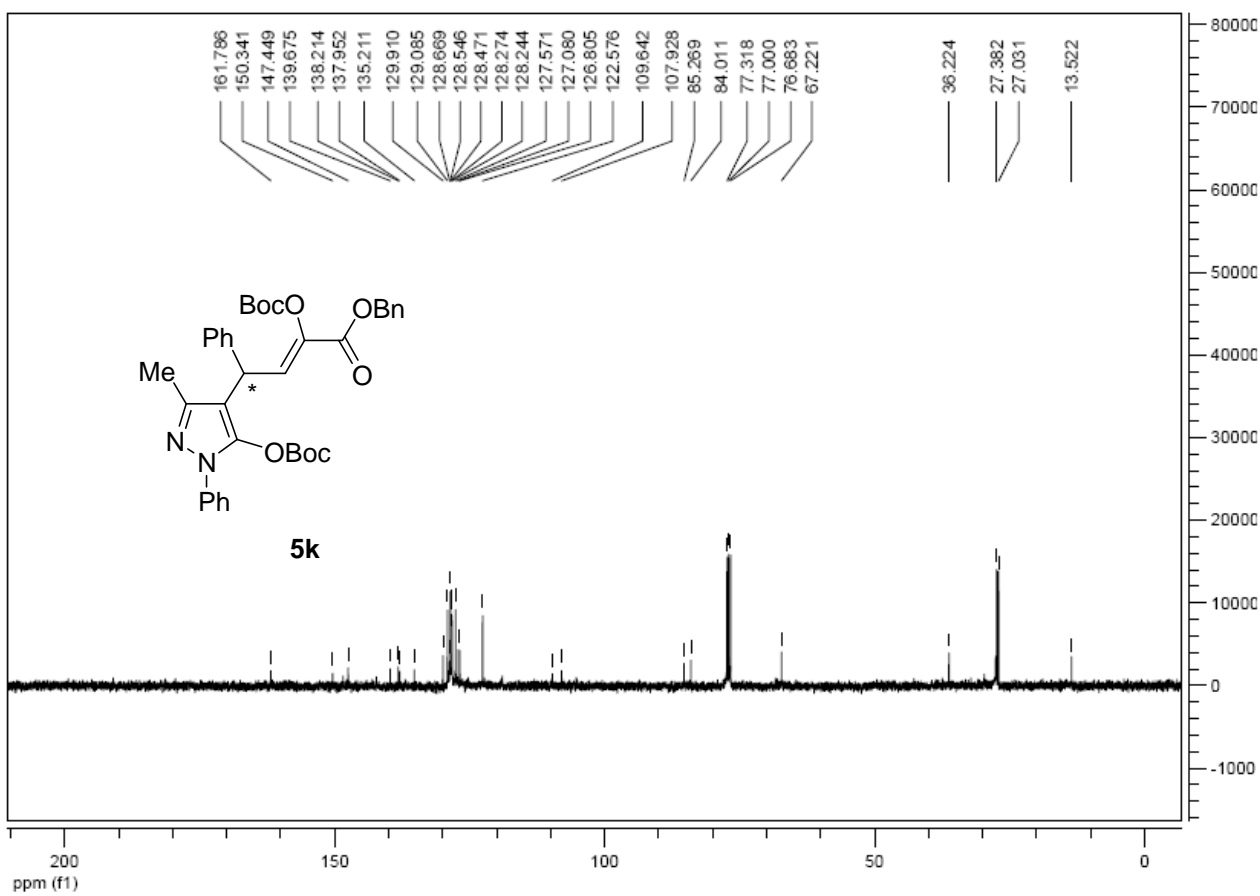
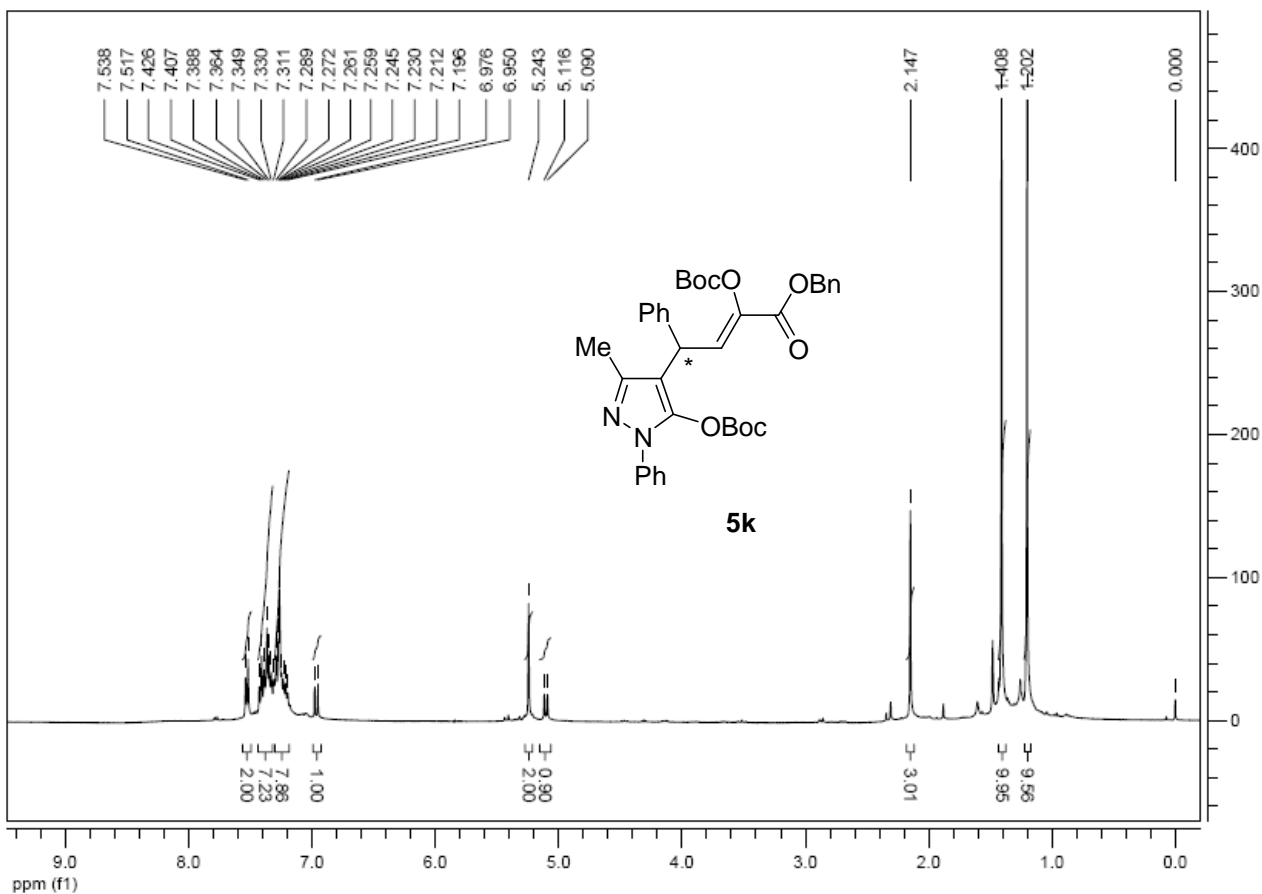


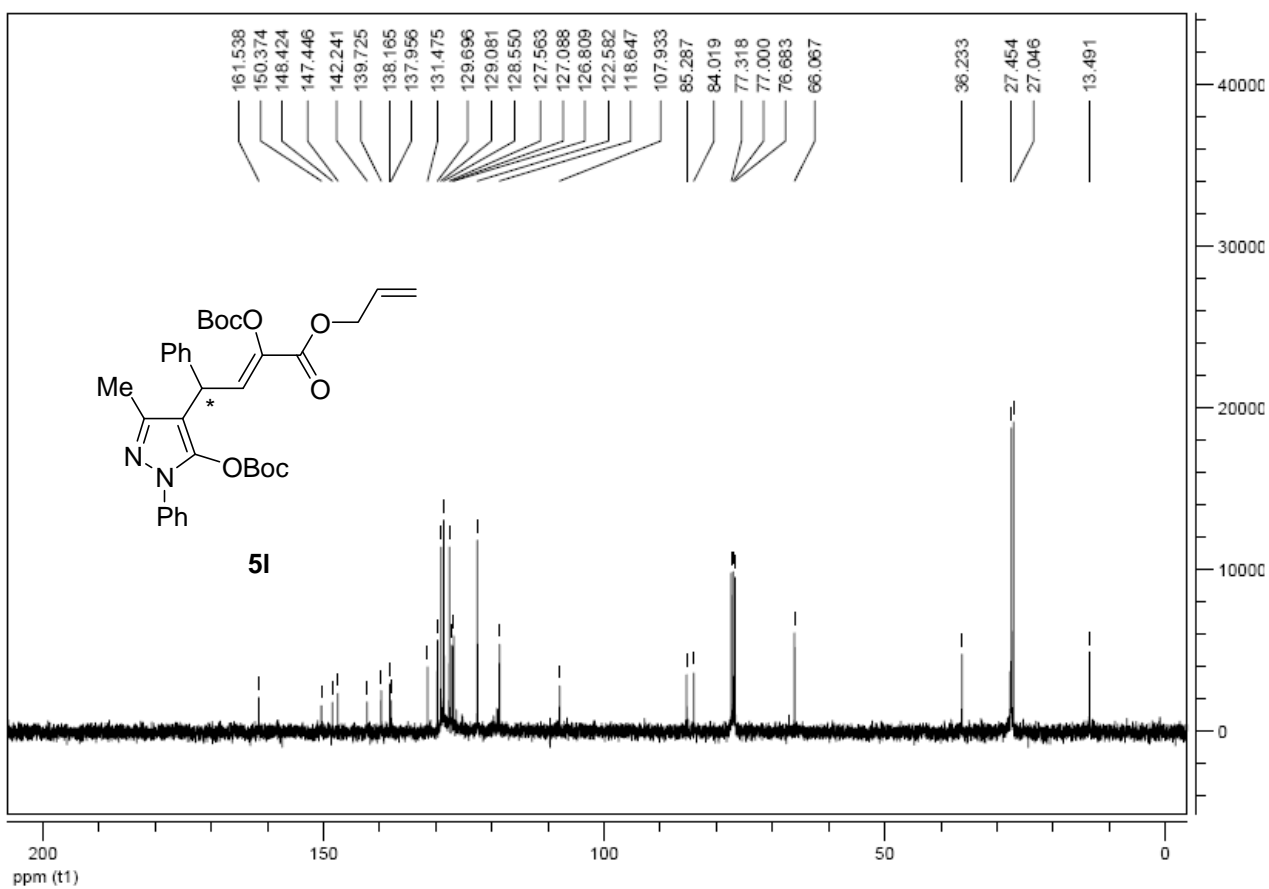
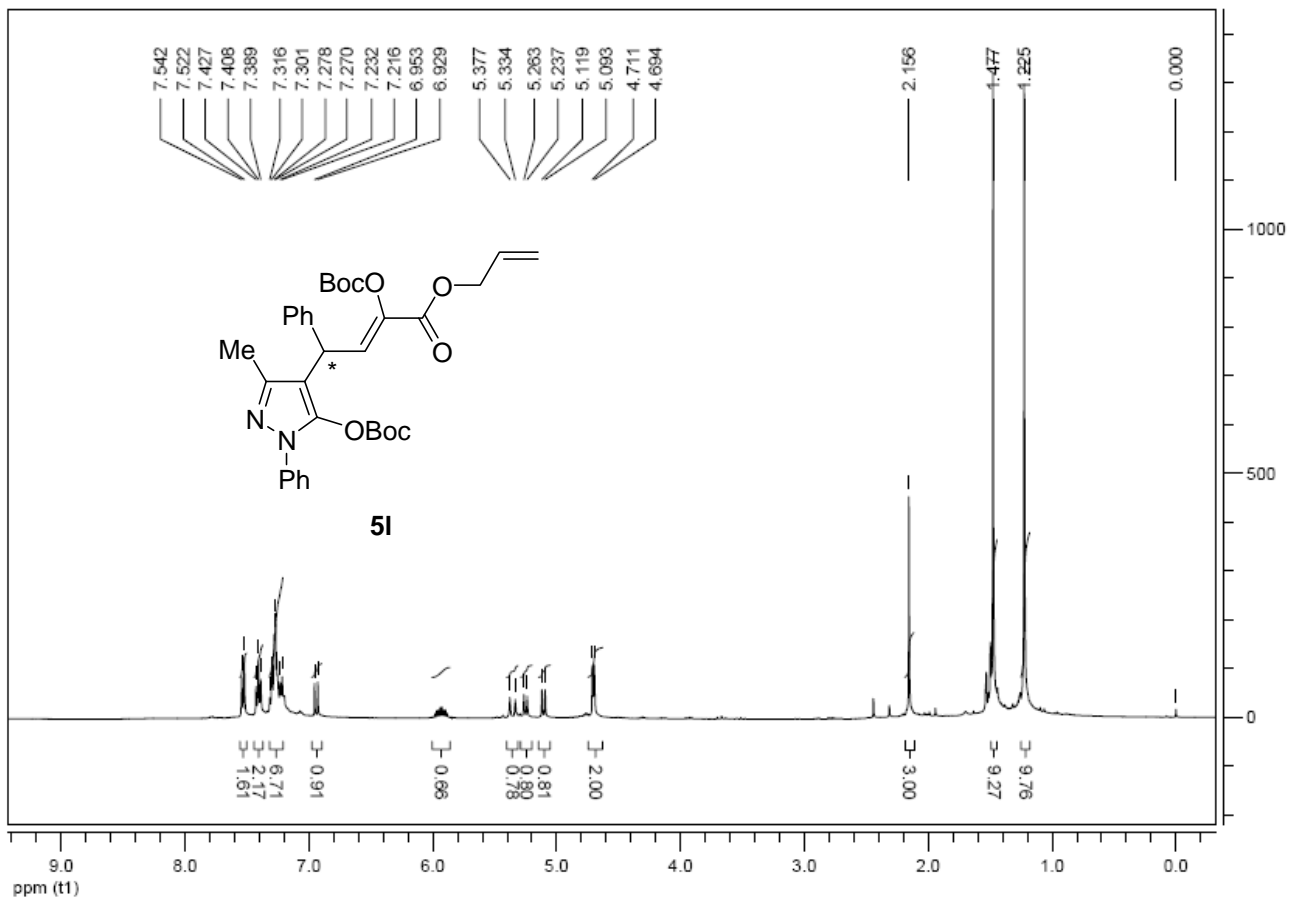


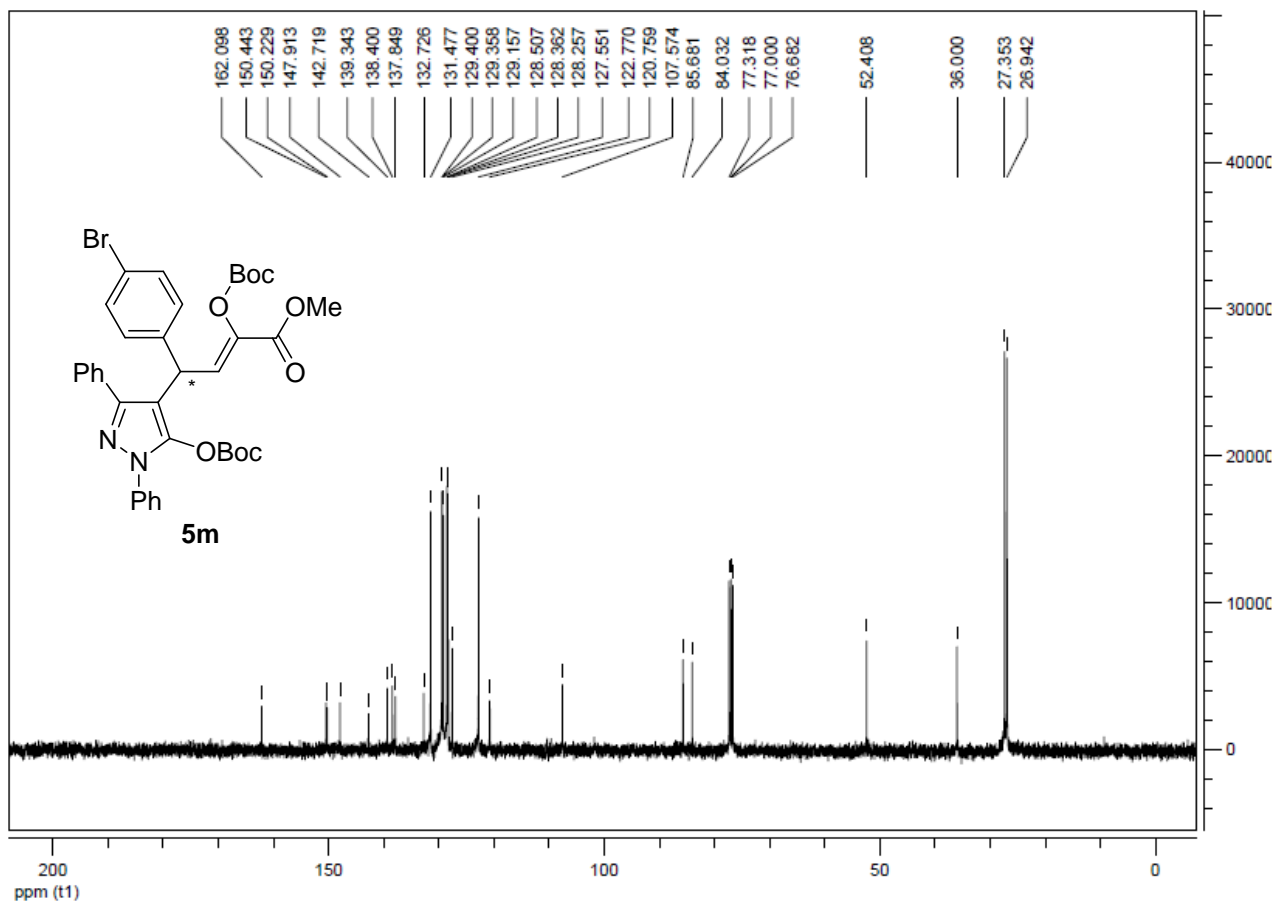
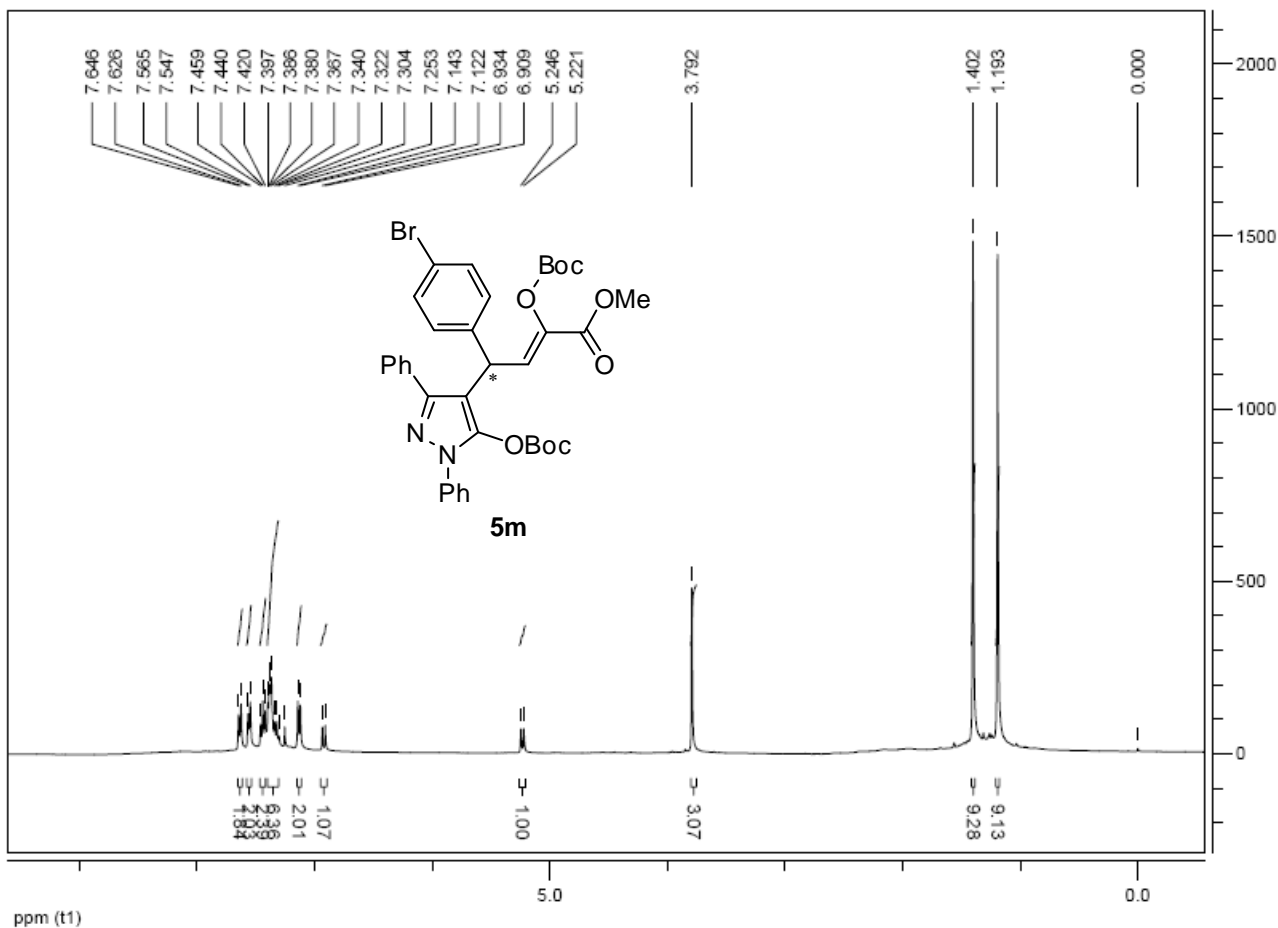


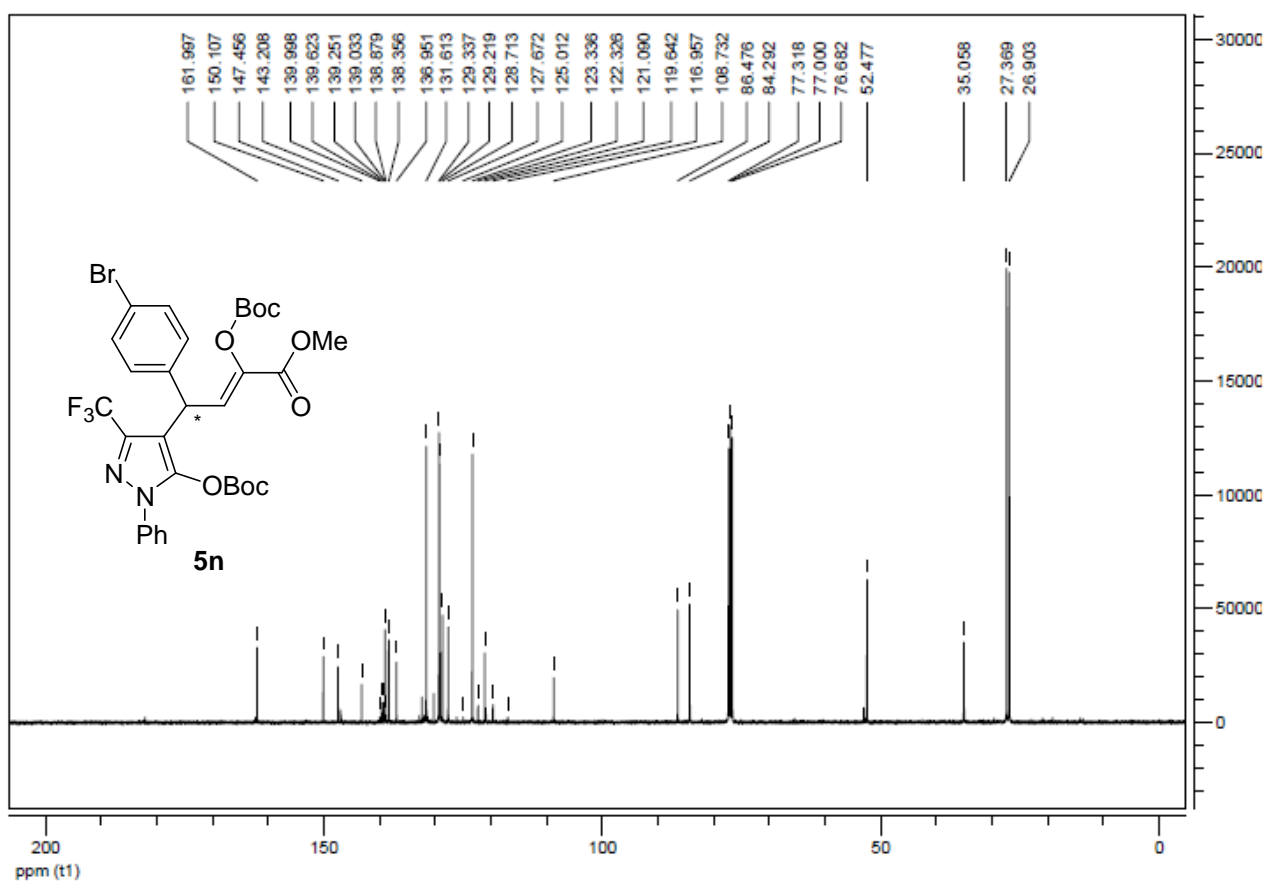
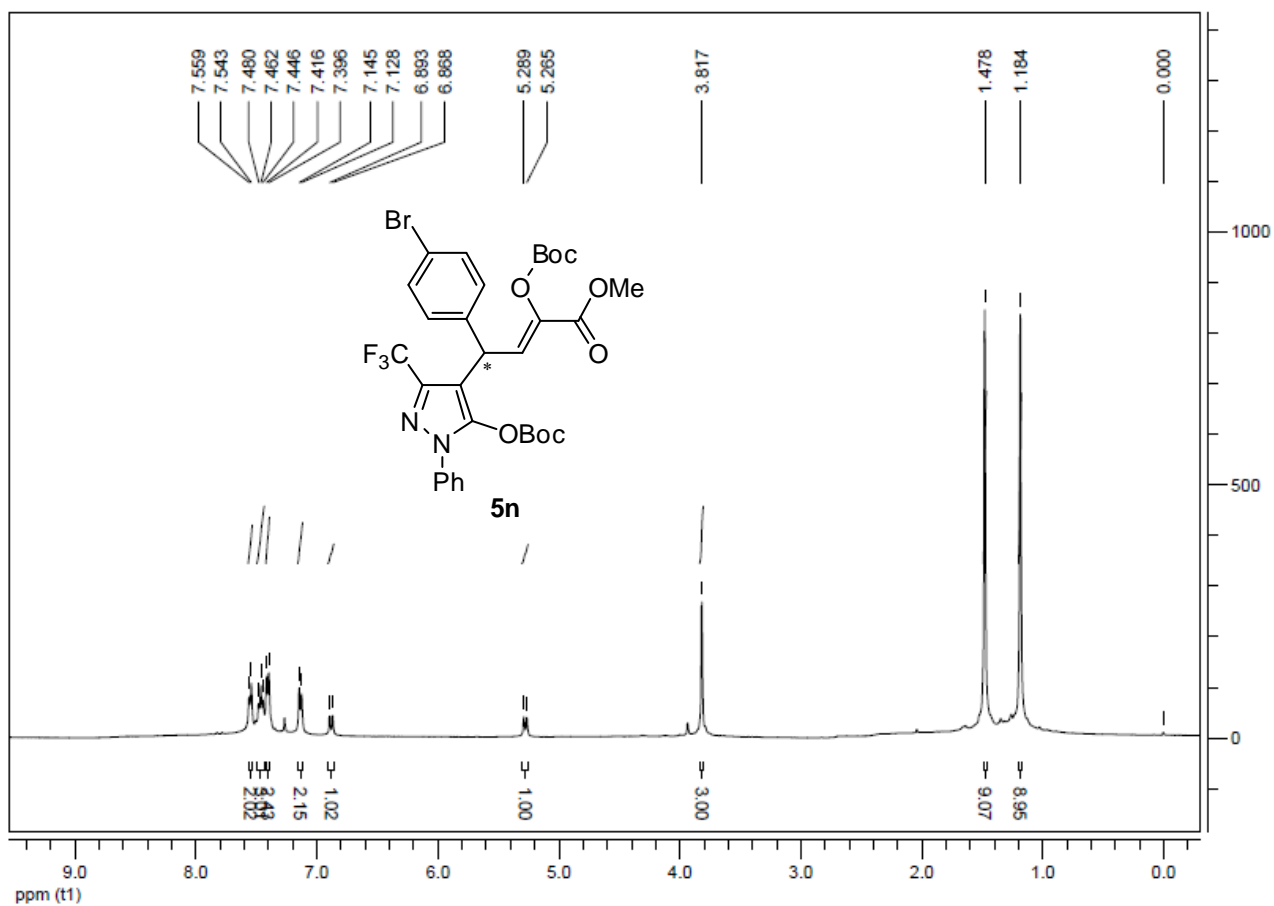




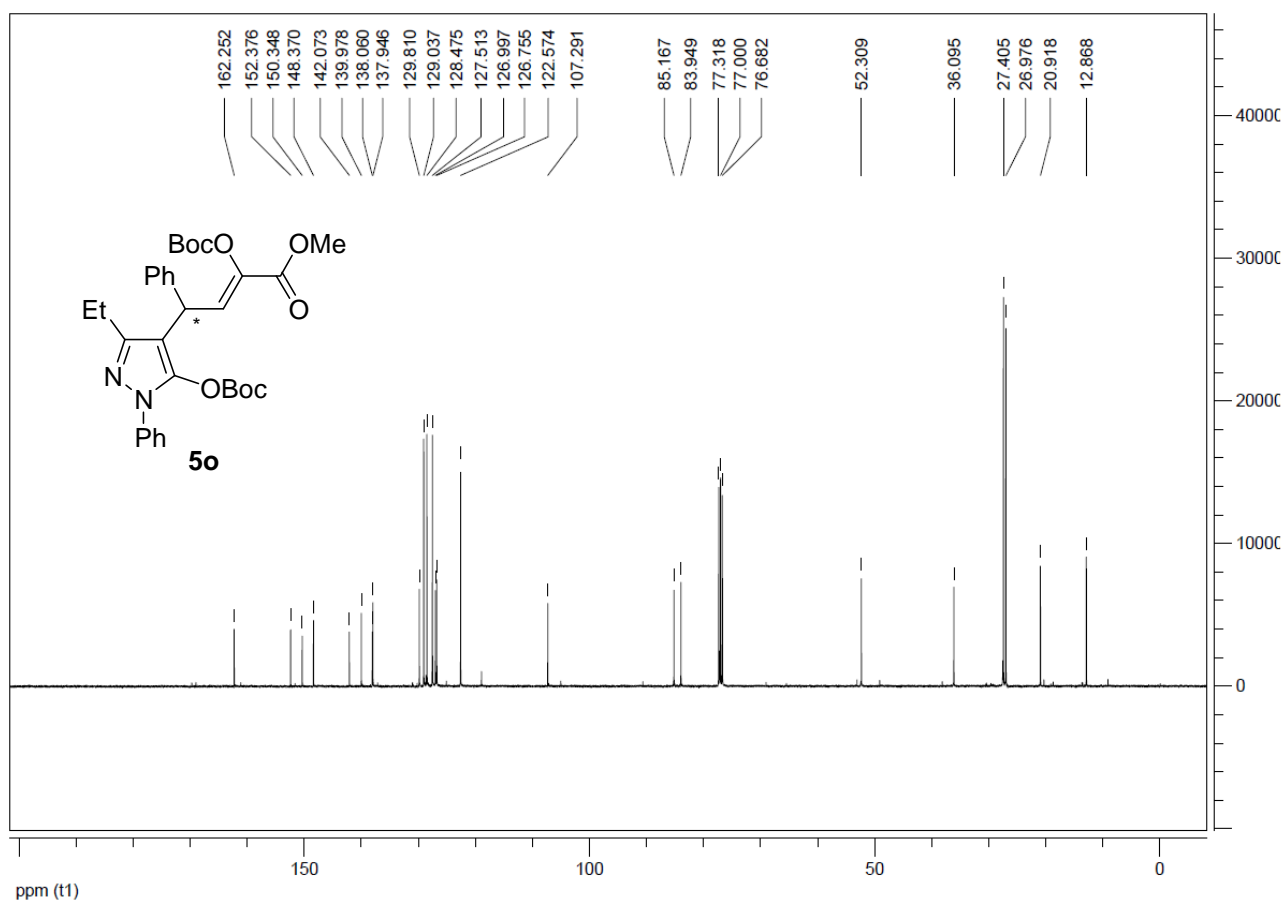
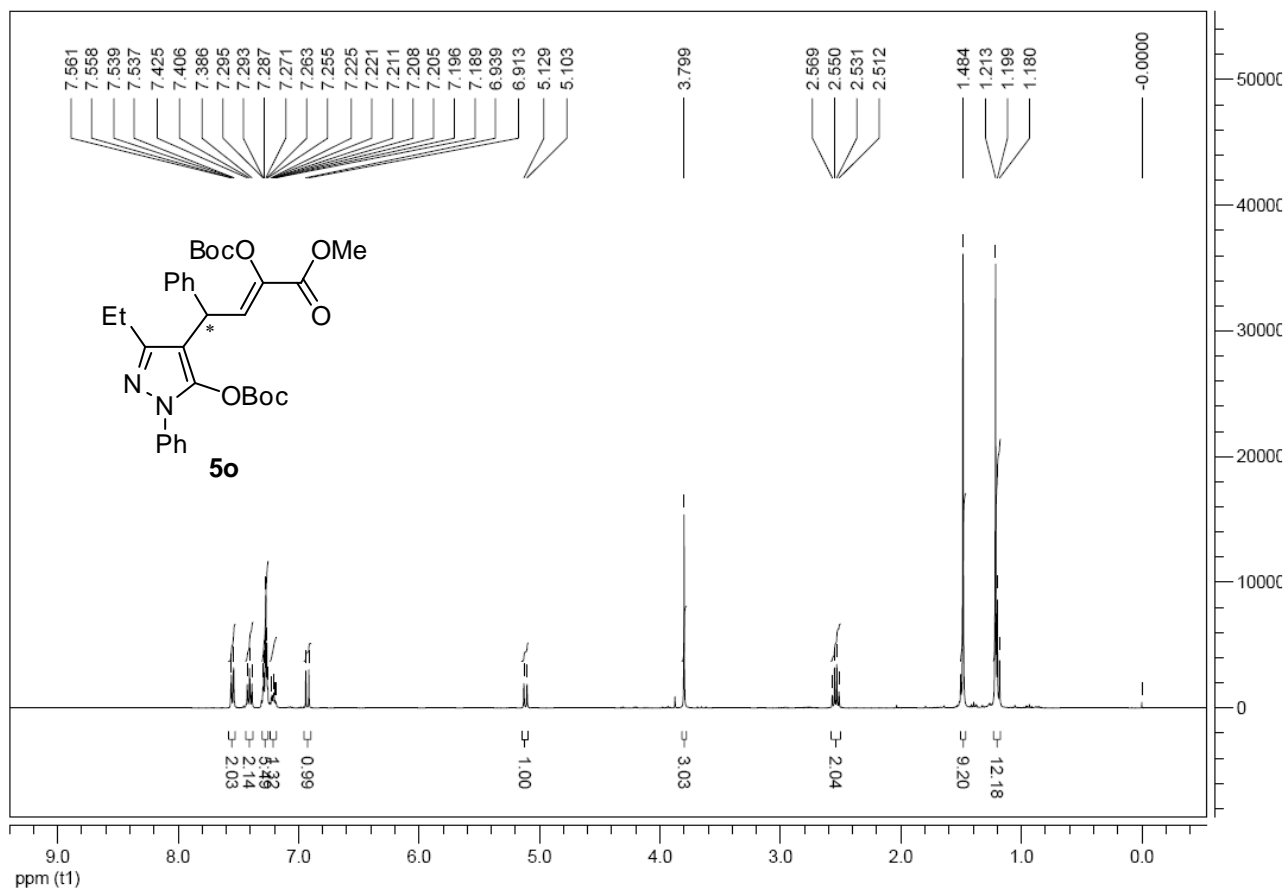


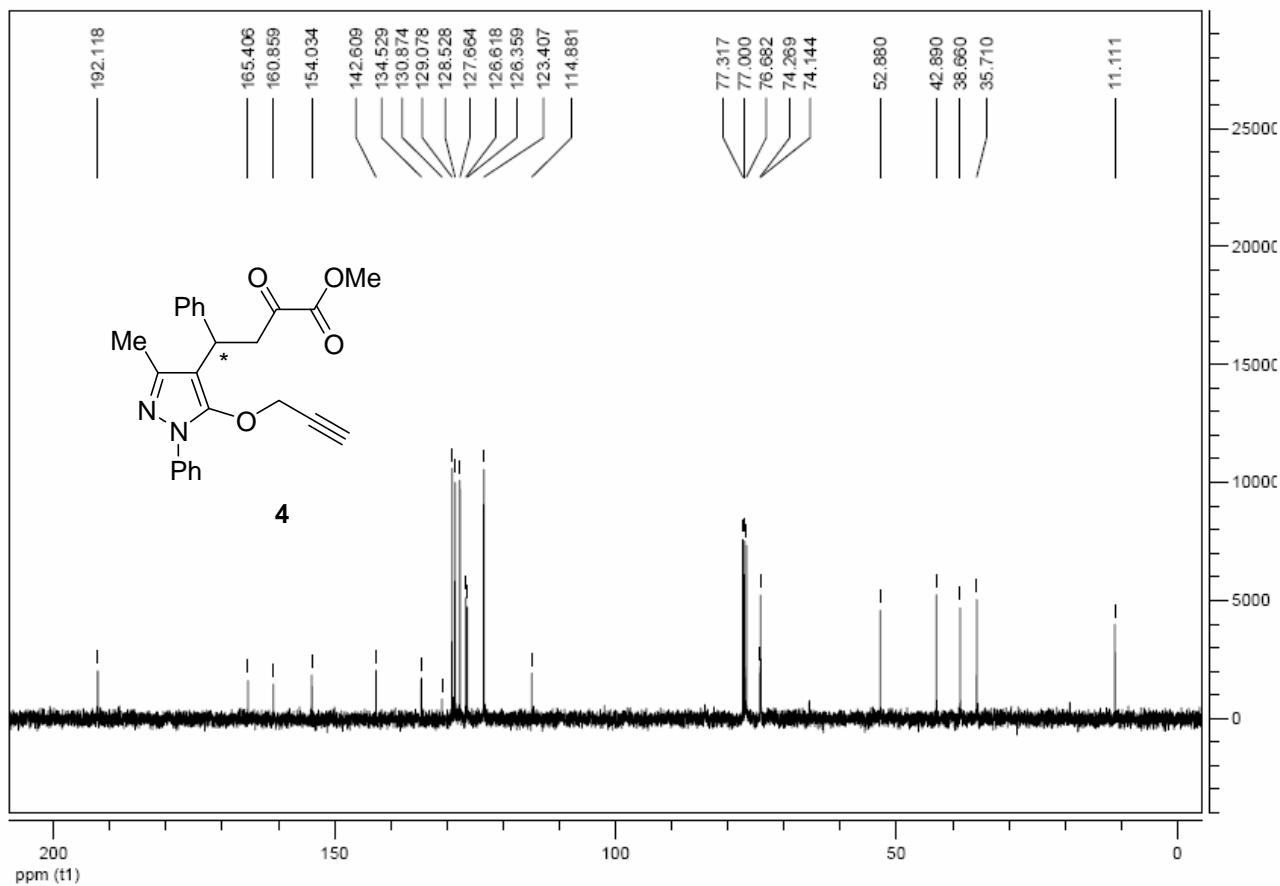
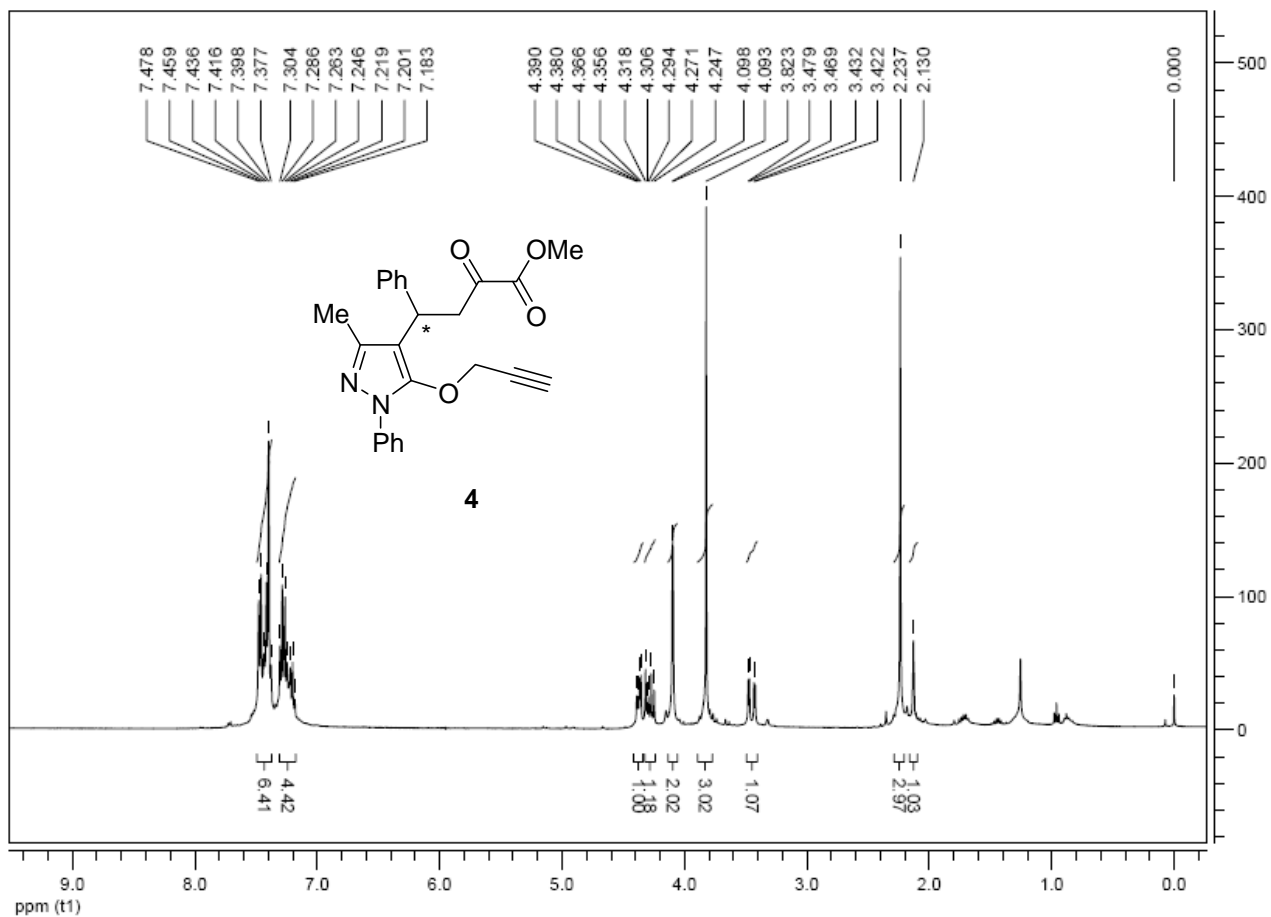




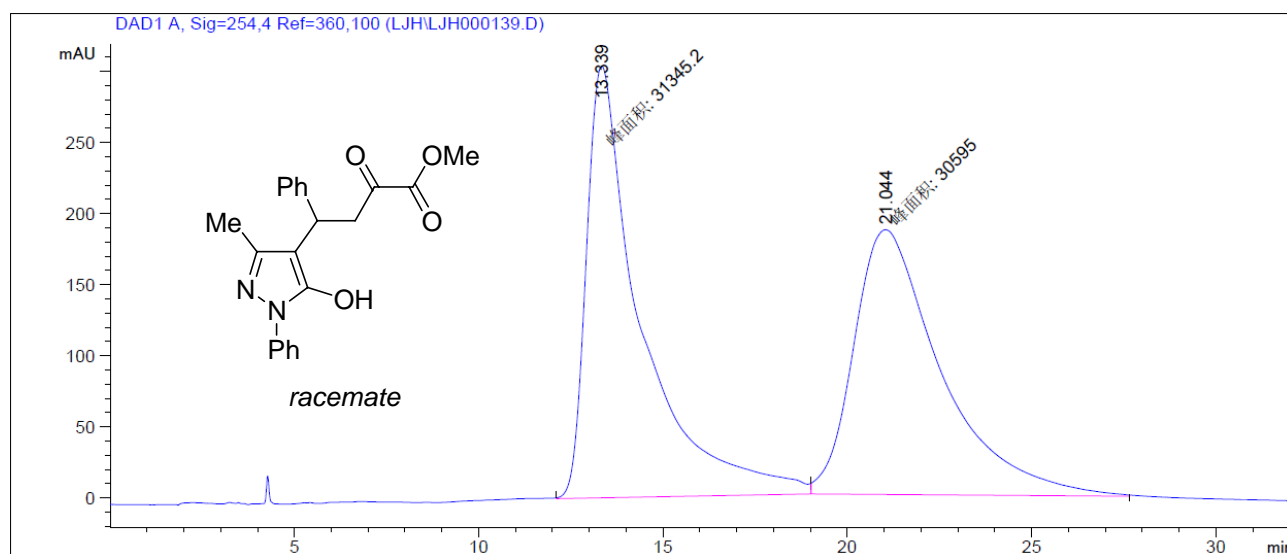




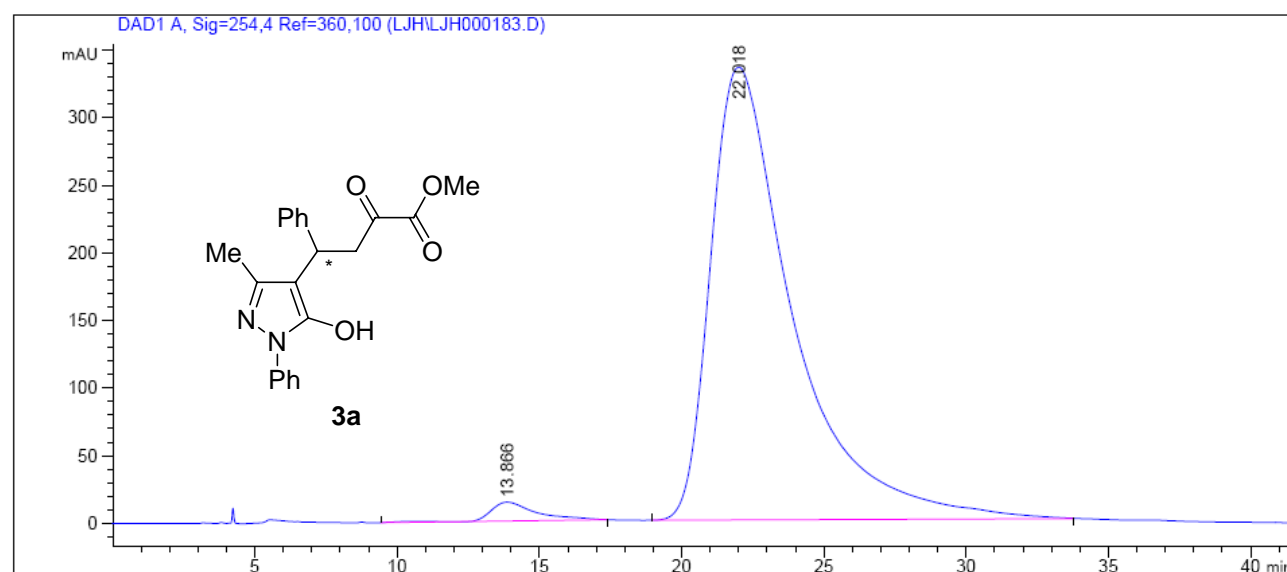




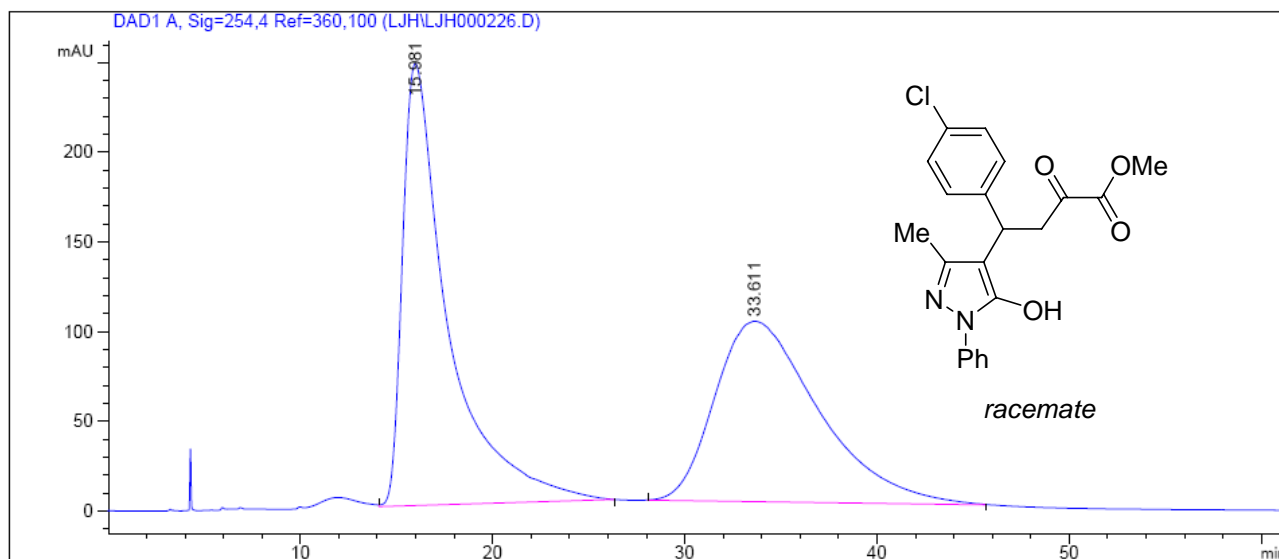
## Copies of HPLC chromatographs of products



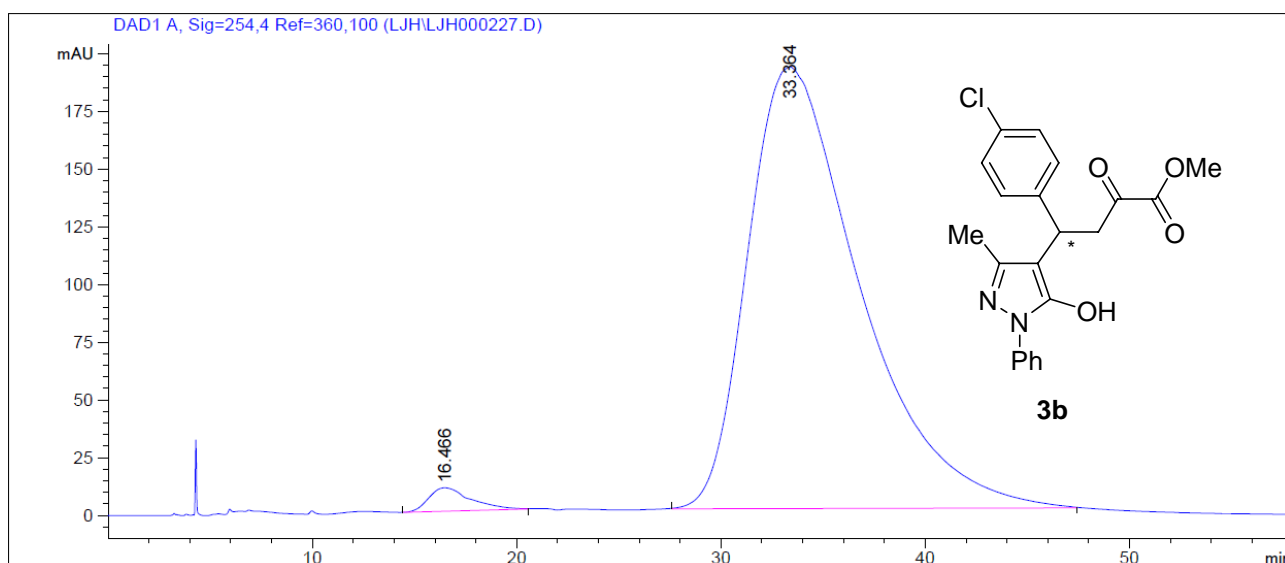
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1	13.339	MM T	1.7191	3.13452e4	303.89203	50.6056
2	21.044	MM T	2.7379	3.05950e4	186.24126	49.3944



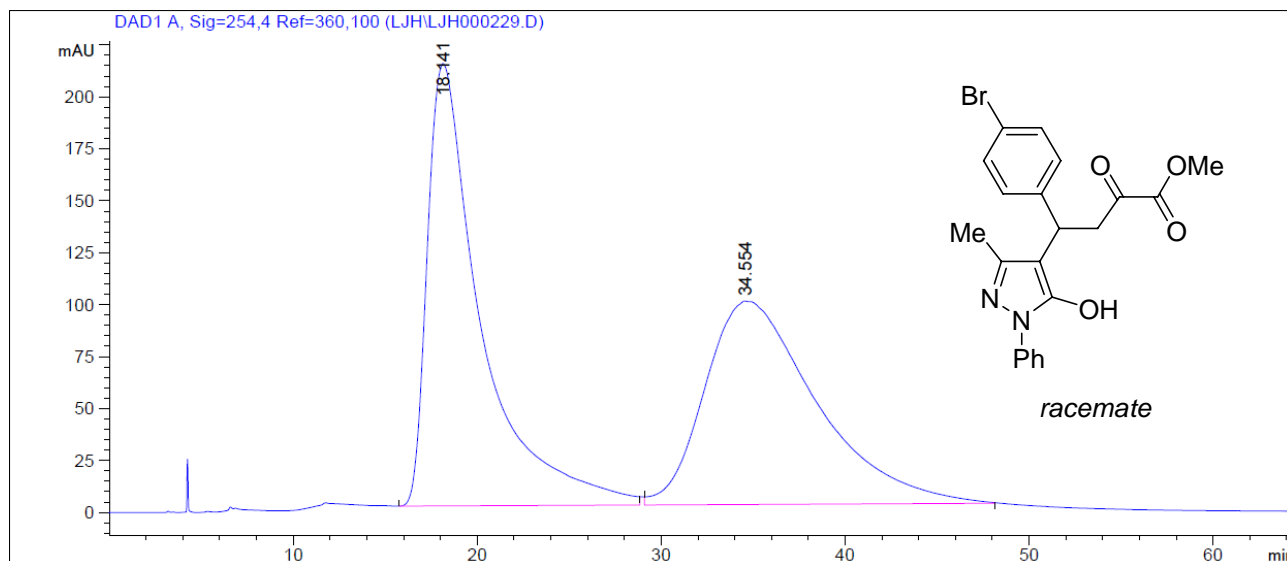
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1	13.866	BB S	1.6328	1556.57520	13.96080	2.2498
2	22.018	BB	2.9284	6.76294e4	334.83258	97.7502



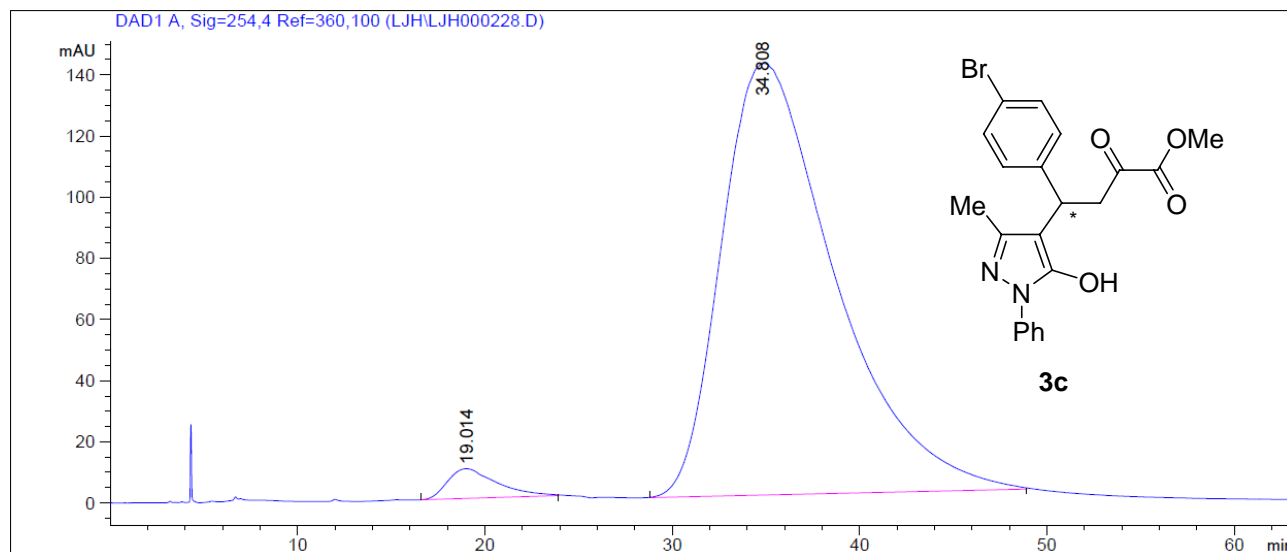
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1	15.981	VB S	2.3586	4.06390e4	246.60786	51.8135
2	33.611	BB	4.5144	3.77943e4	100.70744	48.1865



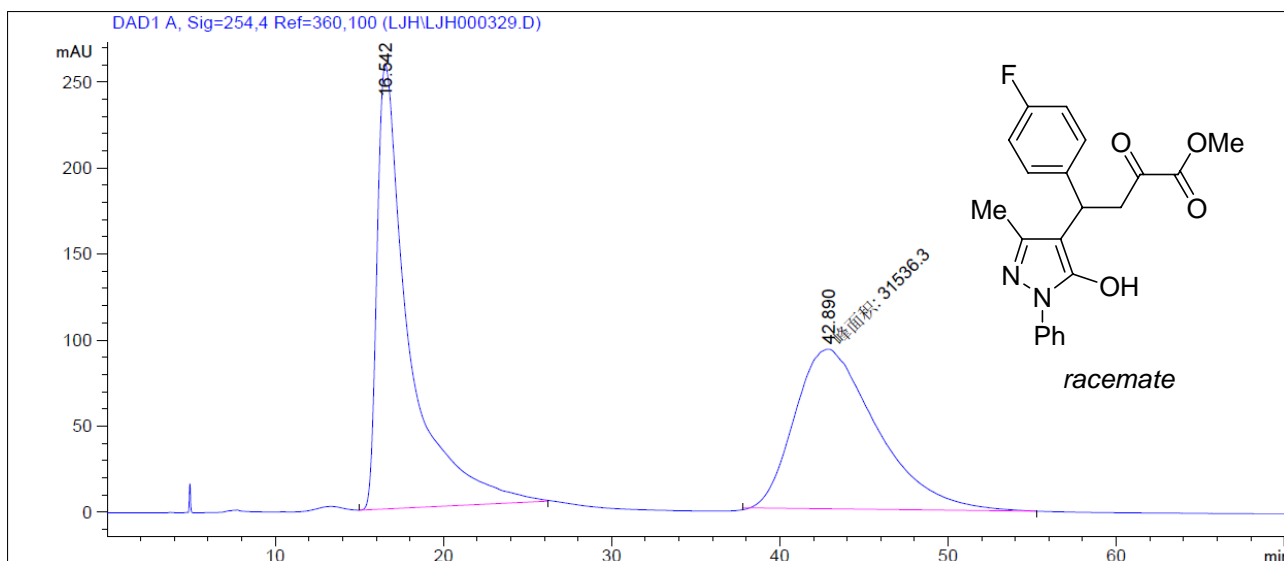
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1	16.466	BB	1.7246	1444.12146	10.17042	1.9372
2	33.364	BB	4.5427	7.31020e4	191.45258	98.0628



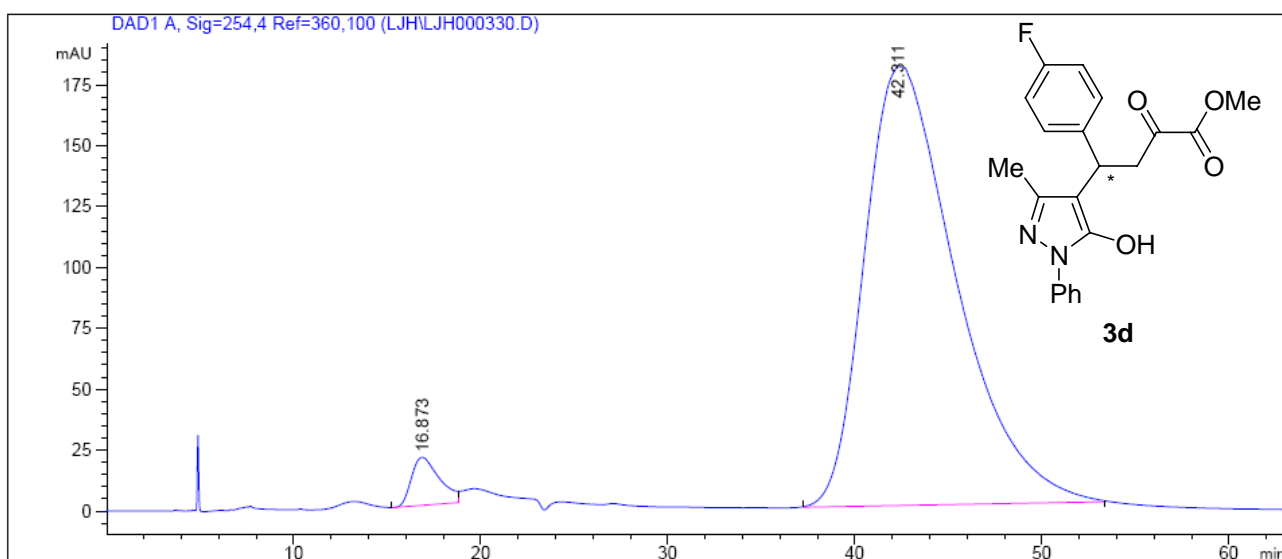
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1	18.141	BB	2.8918	4.30720e4	212.94366	51.0373
2	34.554	BB	5.0149	4.13212e4	97.92583	48.9627



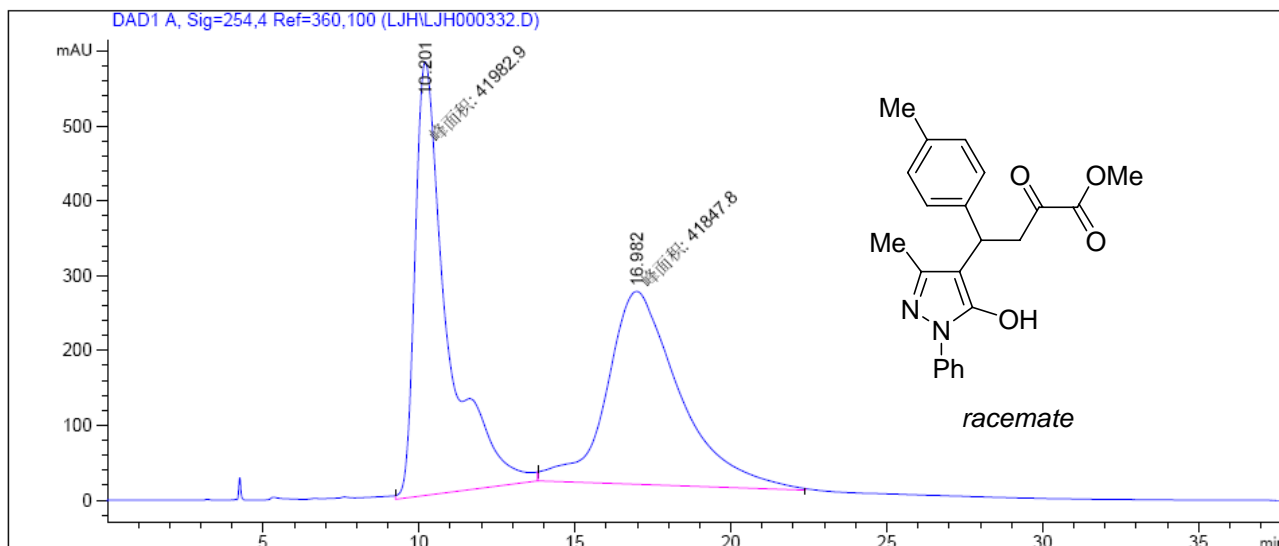
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1	19.014	BB	2.1506	1763.59753	9.73004	2.8783
2	34.808	BB	4.9690	5.95078e4	141.31151	97.1217



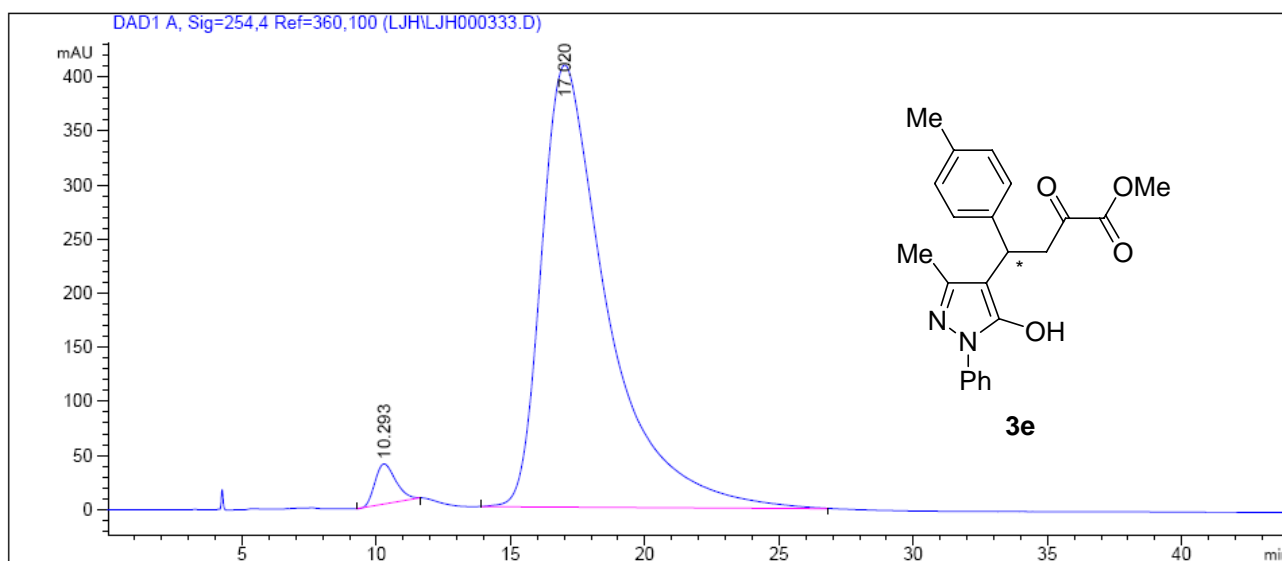
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1	16.542	VB	1.8607	3.40153e4	258.23987	51.8909
2	42.890	MM T	5.6672	3.15363e4	92.74480	48.1091



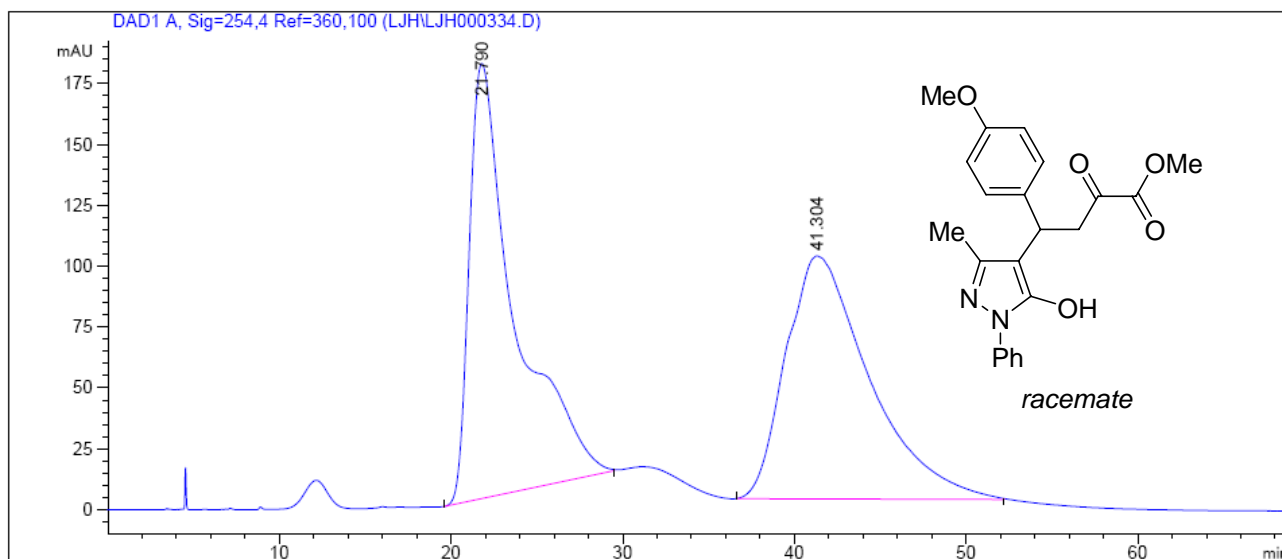
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1	16.873	VV	1.5016	2057.18164	19.67927	3.2506
2	42.311	BB	4.0215	6.12284e4	180.50168	96.7494



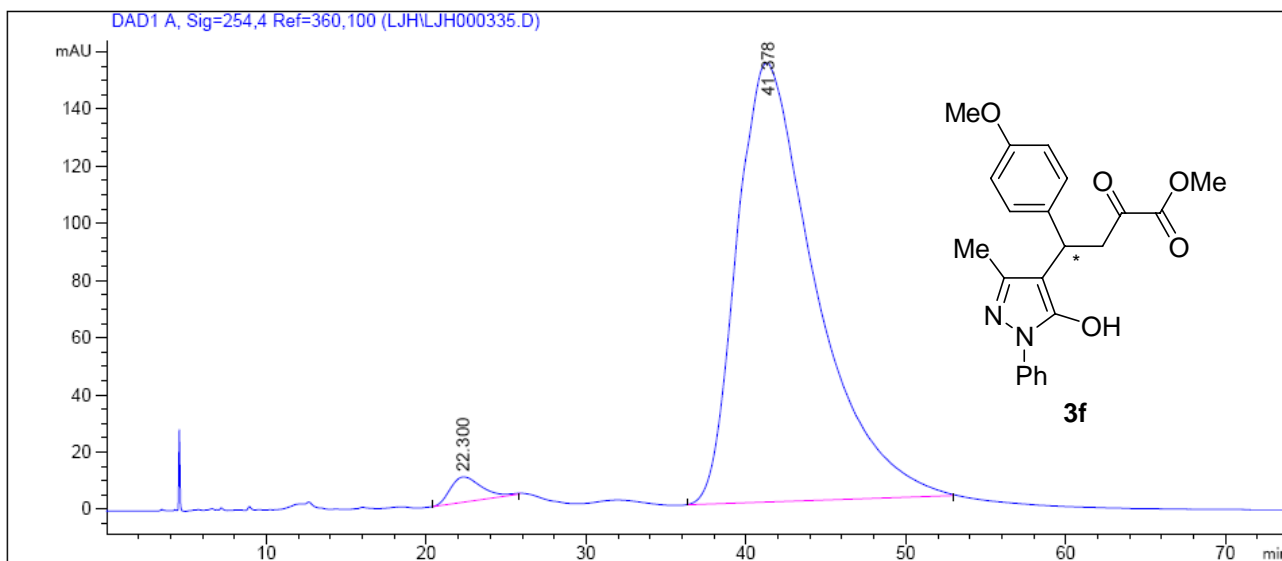
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1	10.201	MM T	1.2073	4.19829e4	579.55566	50.0806
2	16.982	MM T	2.7057	4.18478e4	257.77478	49.9194



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.293	BB S	0.8341	1984.02417	37.08880	2.7612
2	17.020	BB	2.5240	6.98706e4	408.80084	97.2388

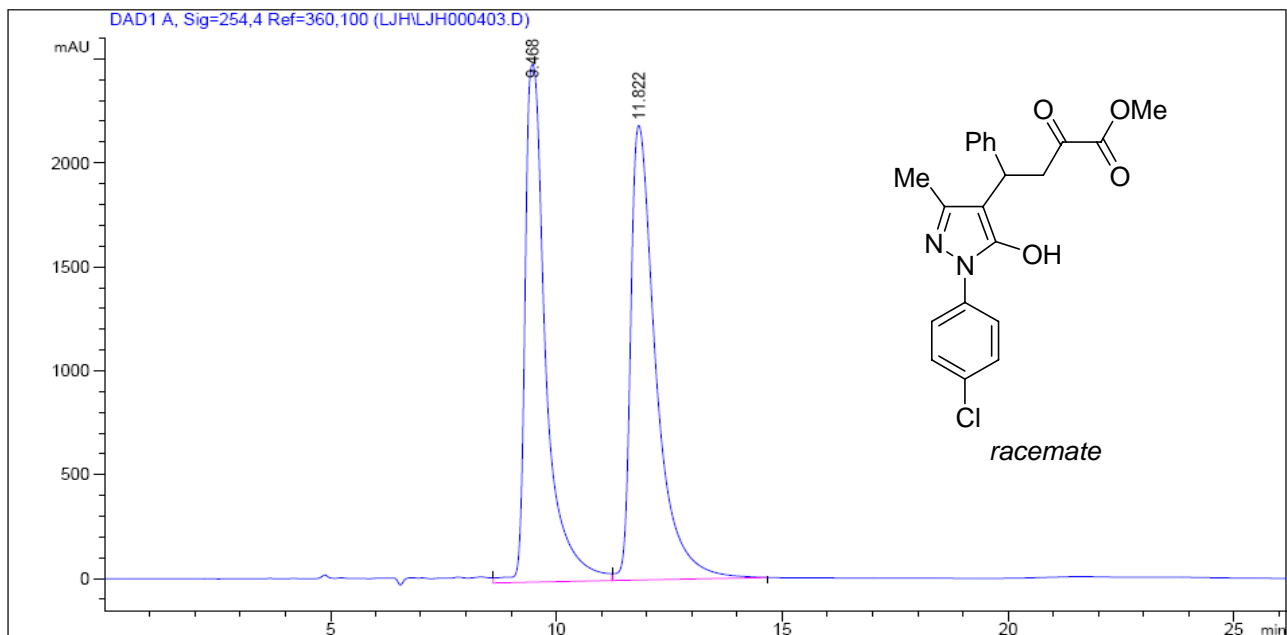


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.790	BB	2.5380	3.29277e4	178.67567	49.3636
2	41.304	BB	4.0323	3.37767e4	99.80573	50.6364

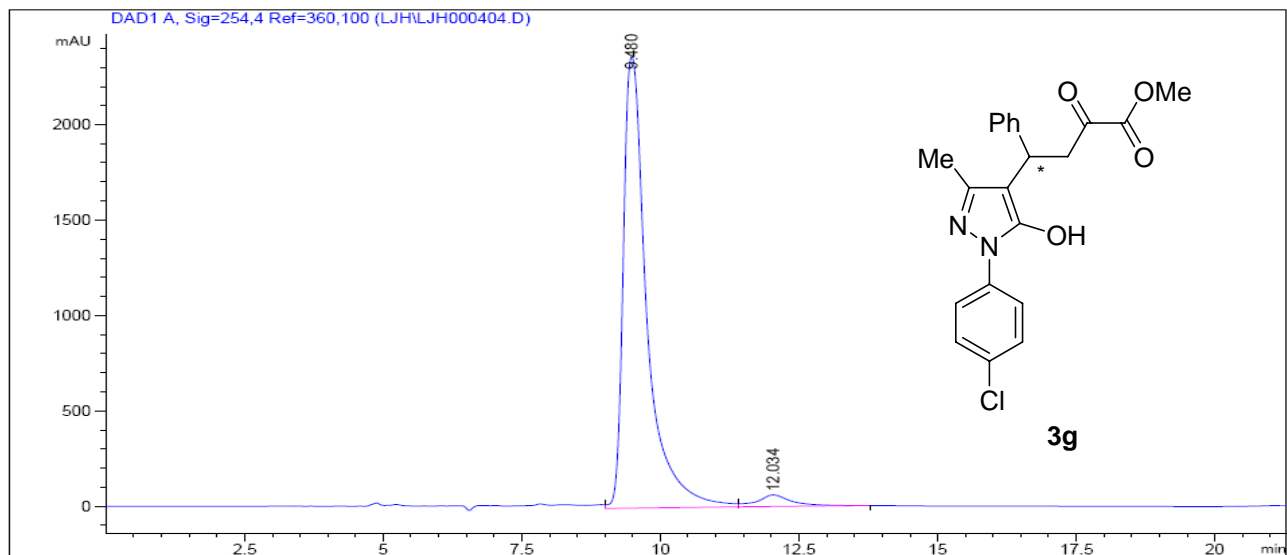


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1	22.300	BB	1.6597	1187.81494	8.82834	2.2074
2	41.378	BB	4.0778	5.26238e4	153.57130	97.7926

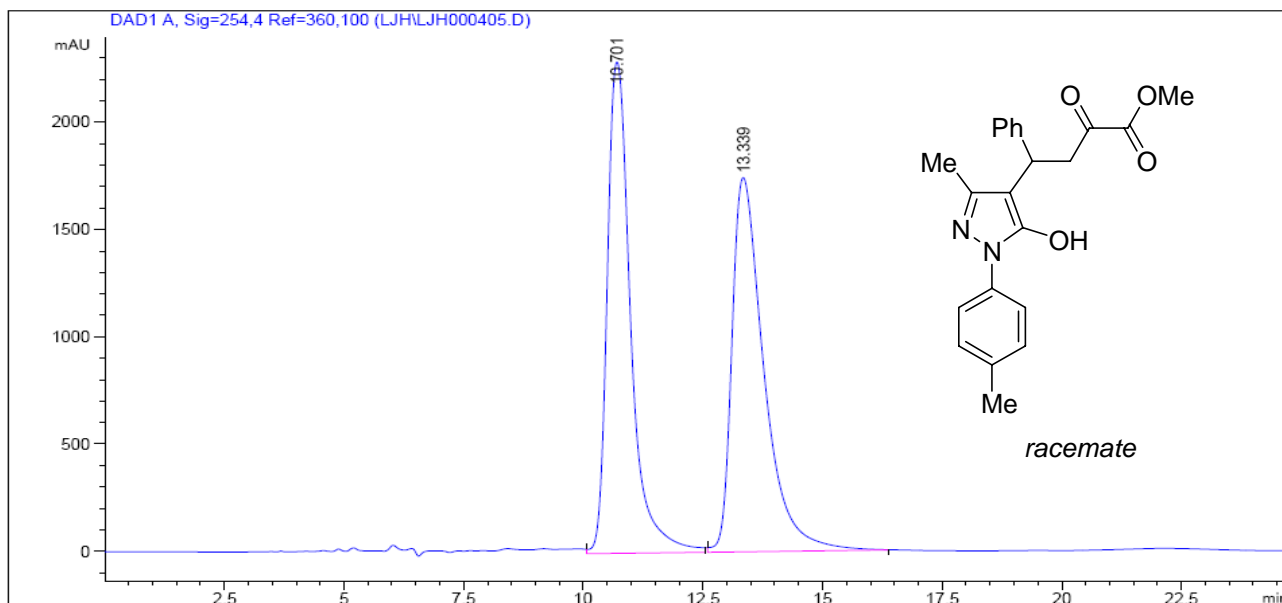




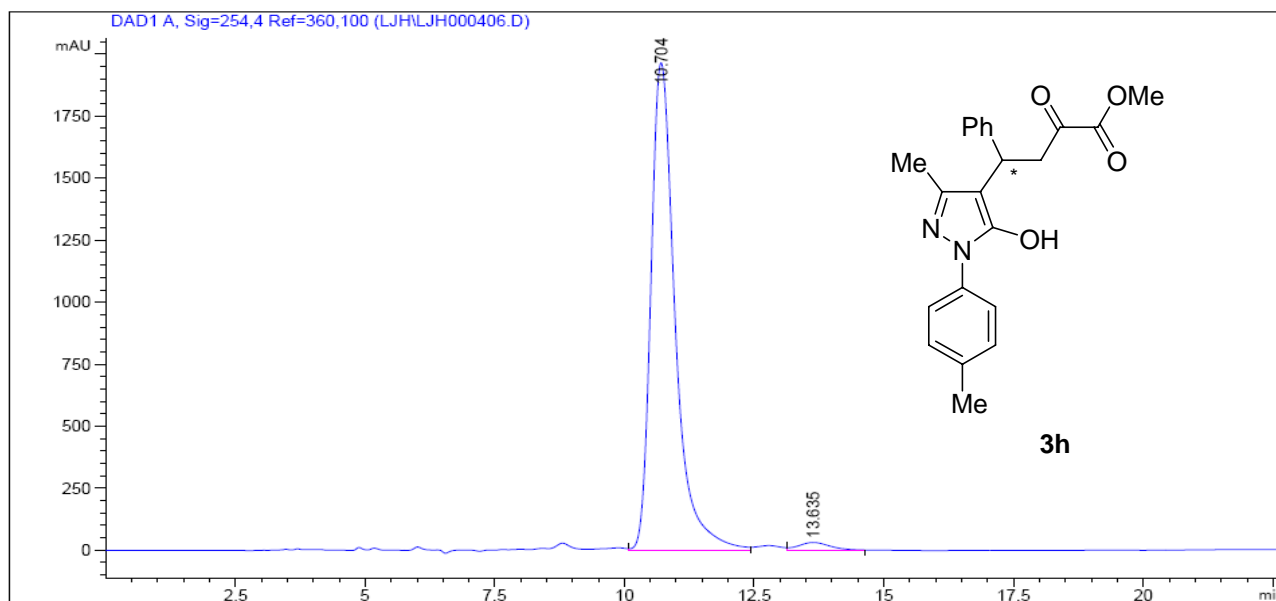
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1	9.468	VV	0.4785	7.99860e4	2491.77100	48.4748
2	11.822	VB	0.5774	8.50192e4	2187.67310	51.5252



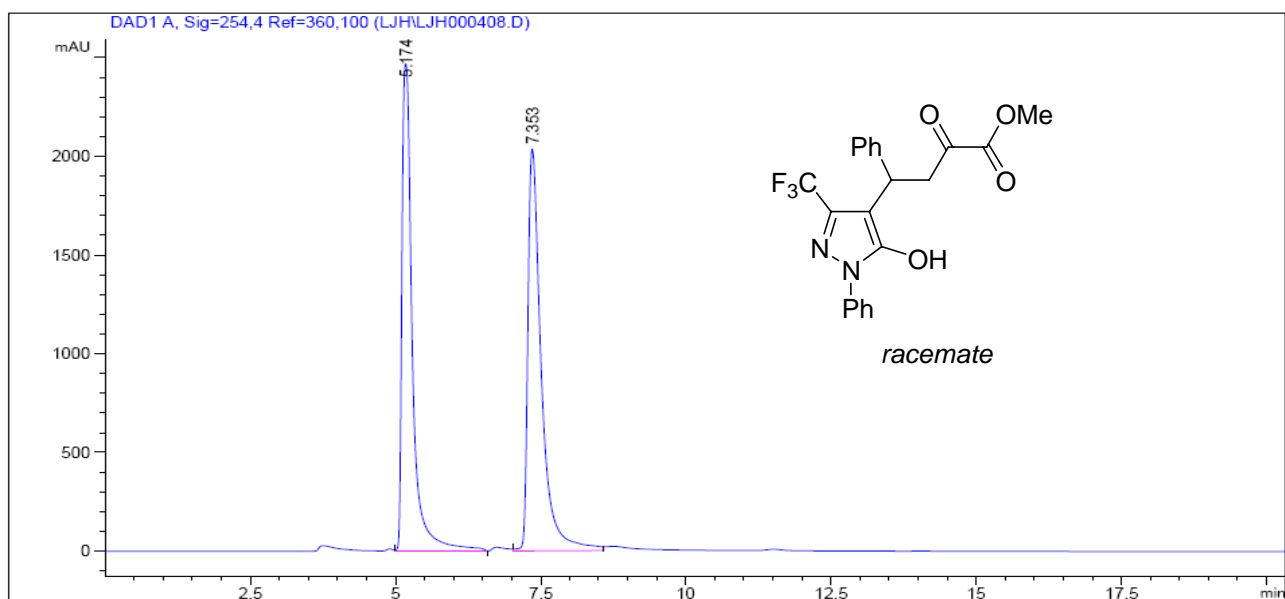
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1	9.480	VB	0.4422	7.02079e4	2365.66406	96.1565
2	12.034	BB	0.6345	2806.31494	61.94527	3.8435



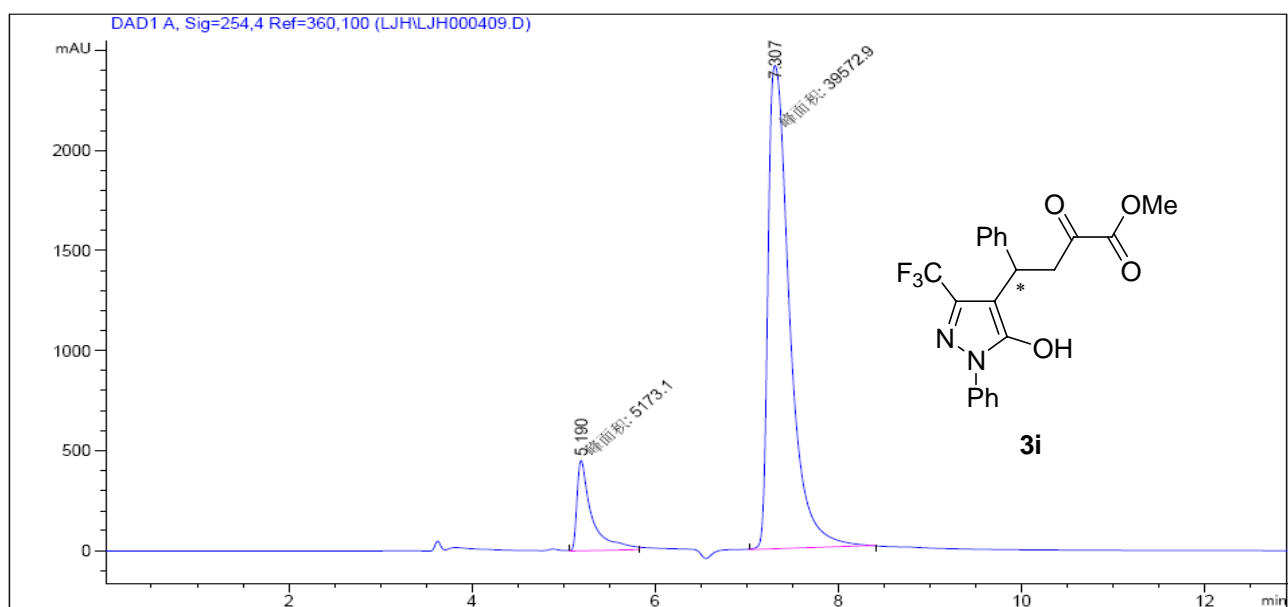
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1	10.701	VB	0.5214	7.84477e4	2291.38892	49.1110
2	13.339	BB	0.6994	8.12876e4	1745.28809	50.8890



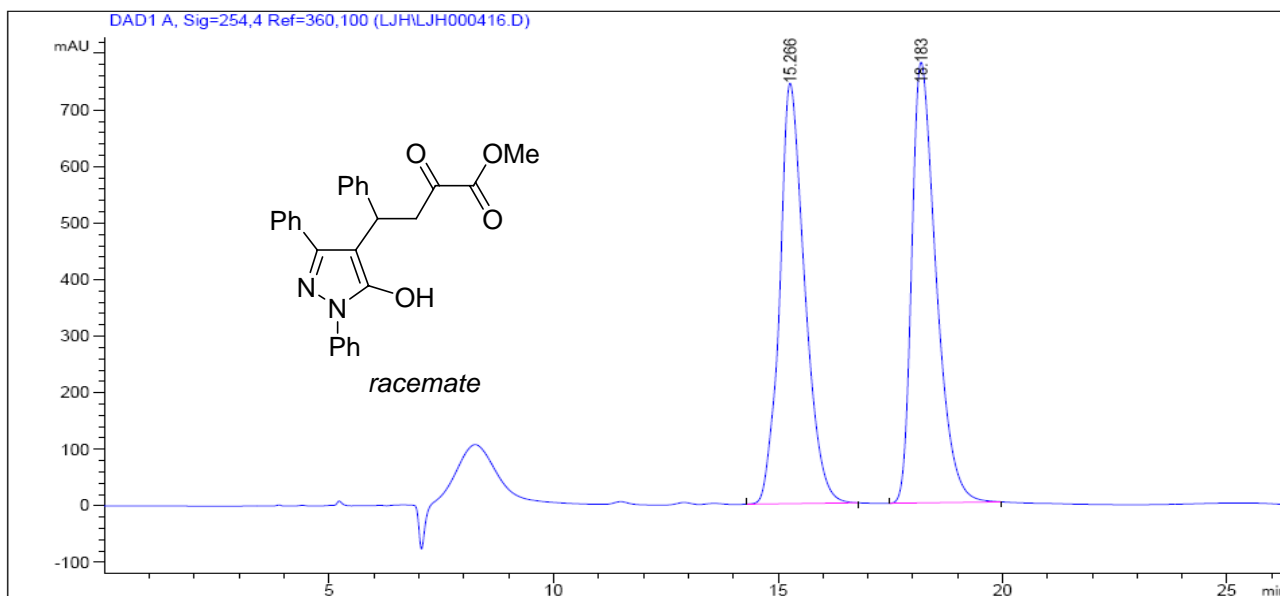
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1	10.704	VV	0.4939	6.40300e4	1966.45276	97.9791
2	13.635	VB	0.6388	1320.67395	31.26507	2.0209



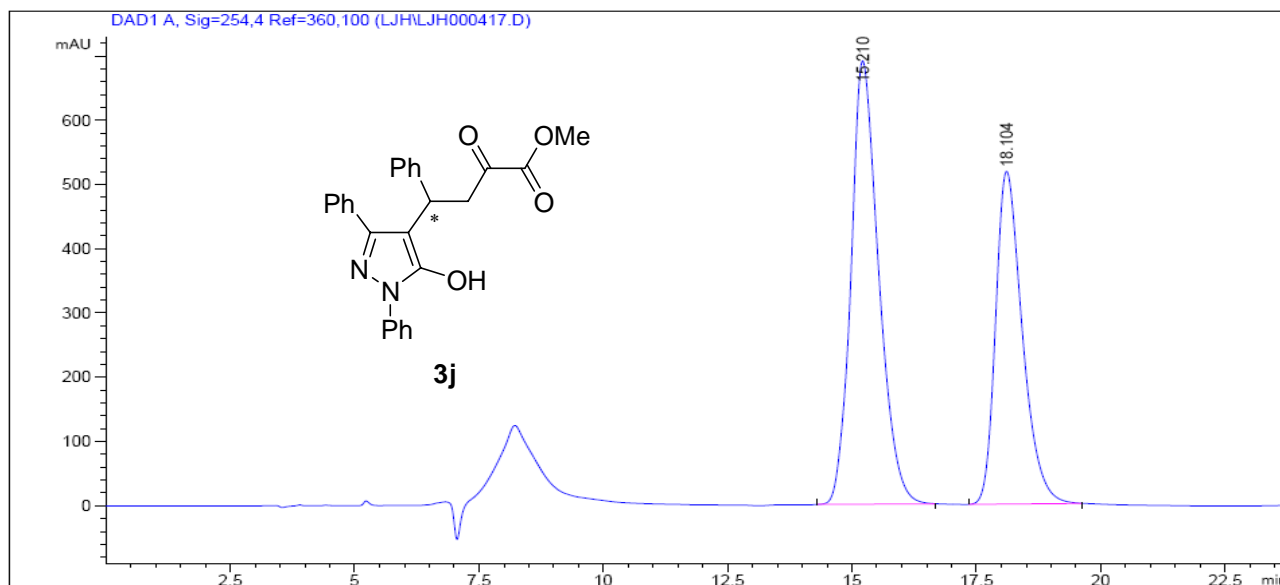
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1	5.174	VV	0.1883	3.09475e4	2467.78687	48.5053
2	7.353	VV	0.2402	3.28548e4	2037.00769	51.4947



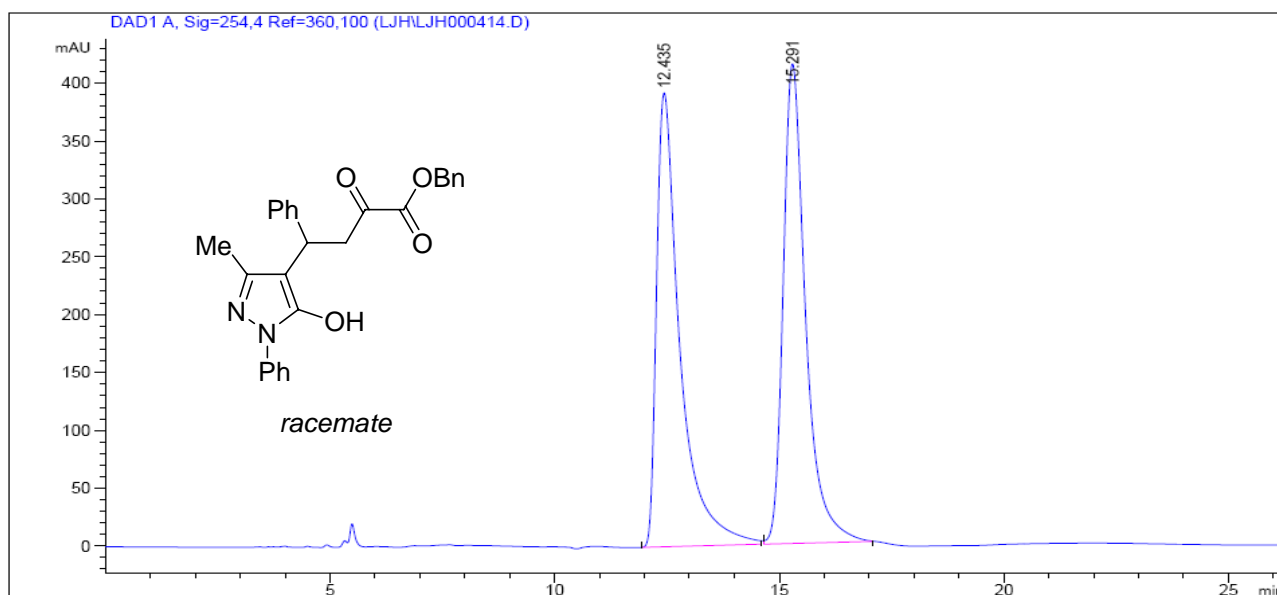
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.190	MM T	0.1905	5173.10254	452.66339	11.5610
2	7.307	MM T	0.2730	3.95729e4	2415.75464	88.4390



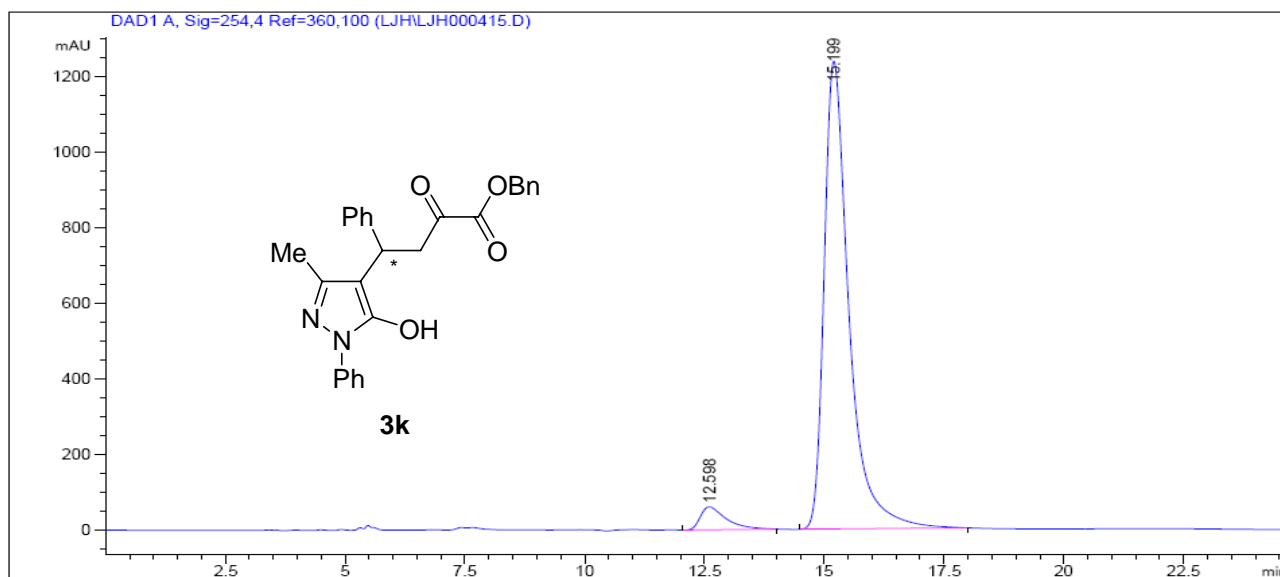
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.266	BB	0.5744	2.89701e4	743.83087	49.5988
2	18.183	BB	0.5726	2.94388e4	779.57568	50.4012



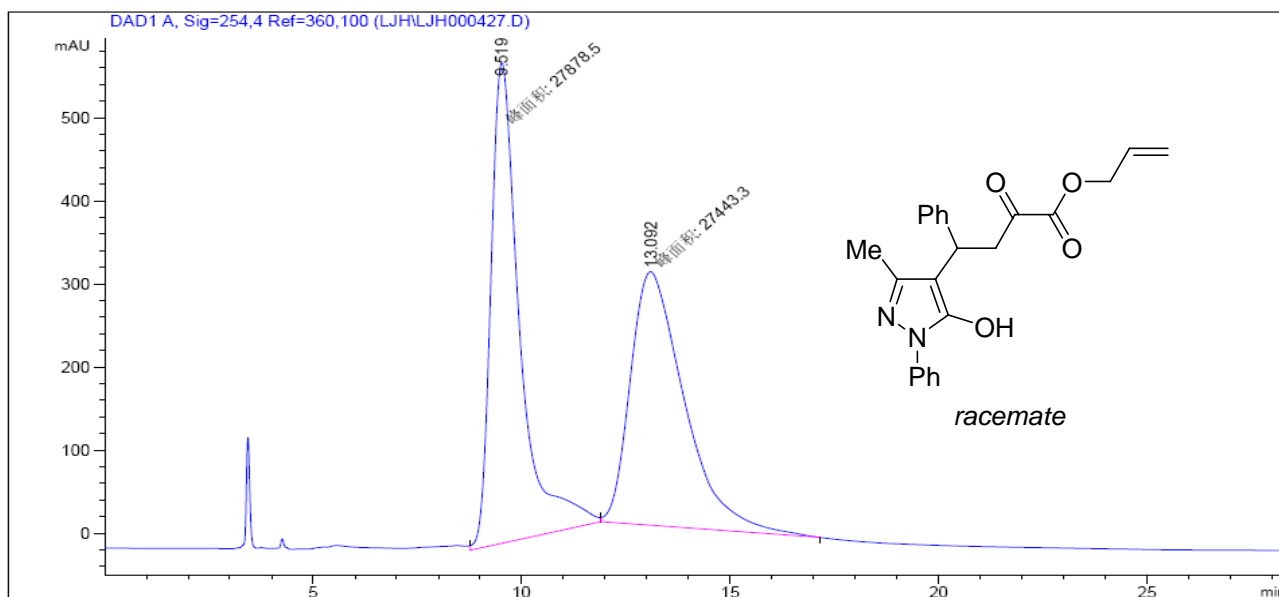
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1	15.210	BB	0.5788	2.68079e4	690.79364	58.0347
2	18.104	BB	0.5683	1.93850e4	518.30542	41.9653



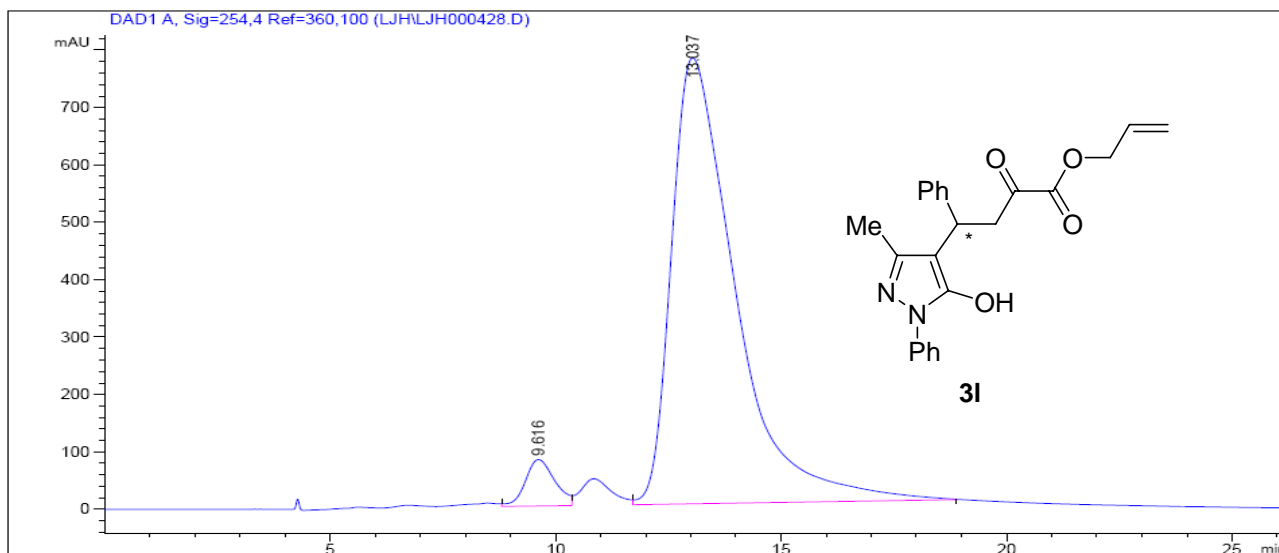
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1	12.435	BB	0.5313	1.42285e4	392.18283	49.7789
2	15.291	BB	0.5200	1.43549e4	414.55887	50.2211



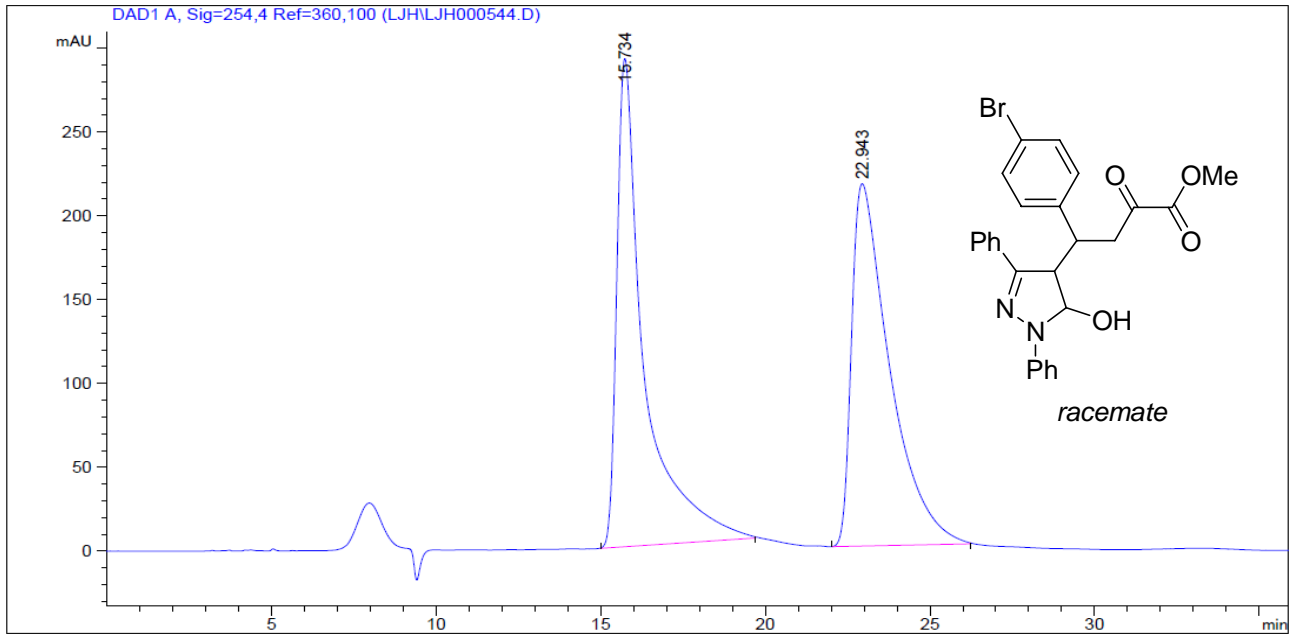
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1	12.598	BB	0.5599	2303.59546	60.81211	4.8977
2	15.199	BB	0.5416	4.47311e4	1237.85815	95.1023



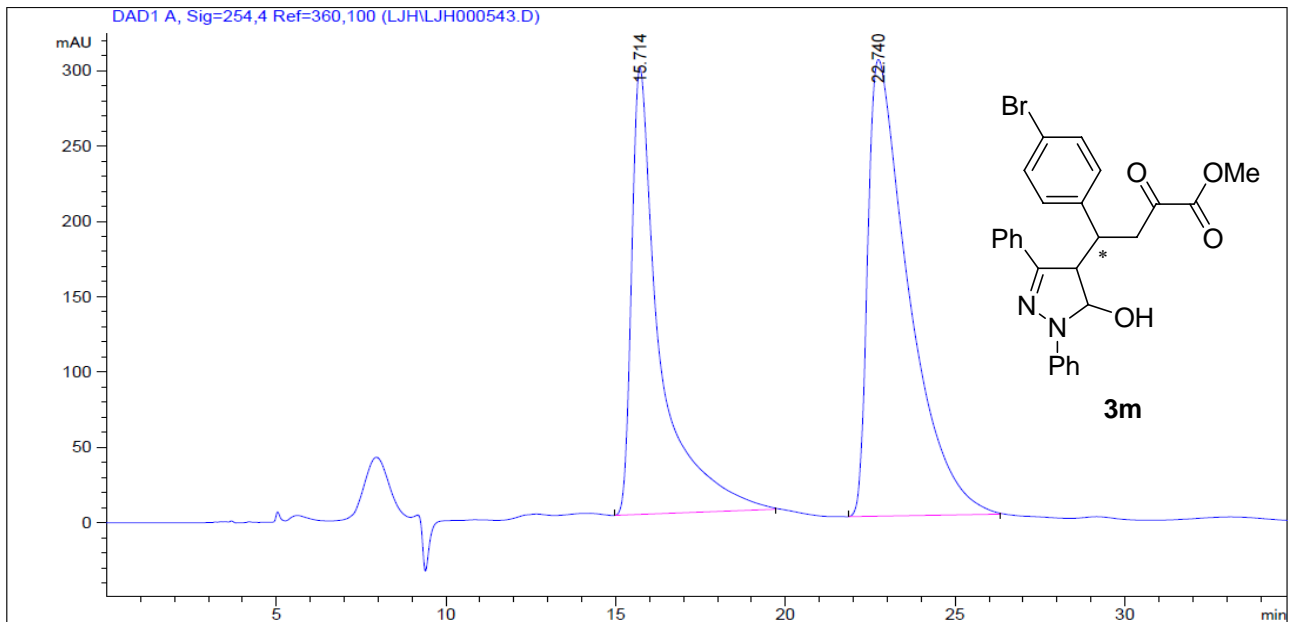
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.519	MM T	0.8037	2.78785e4	578.16174	50.3934
2	13.092	MM T	1.4999	2.74433e4	304.94064	49.6066



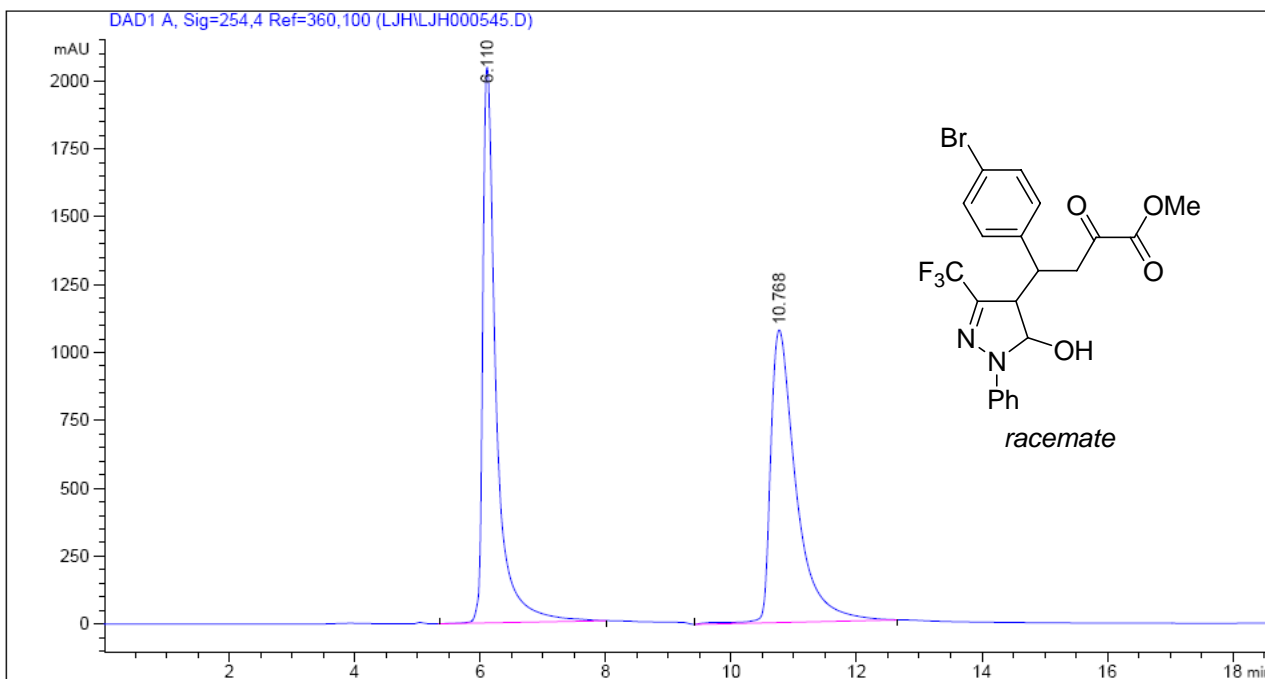
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.616	VV	0.6894	3719.24609	81.35339	4.6208
2	13.037	VB	1.4248	7.67706e4	776.92584	95.3792



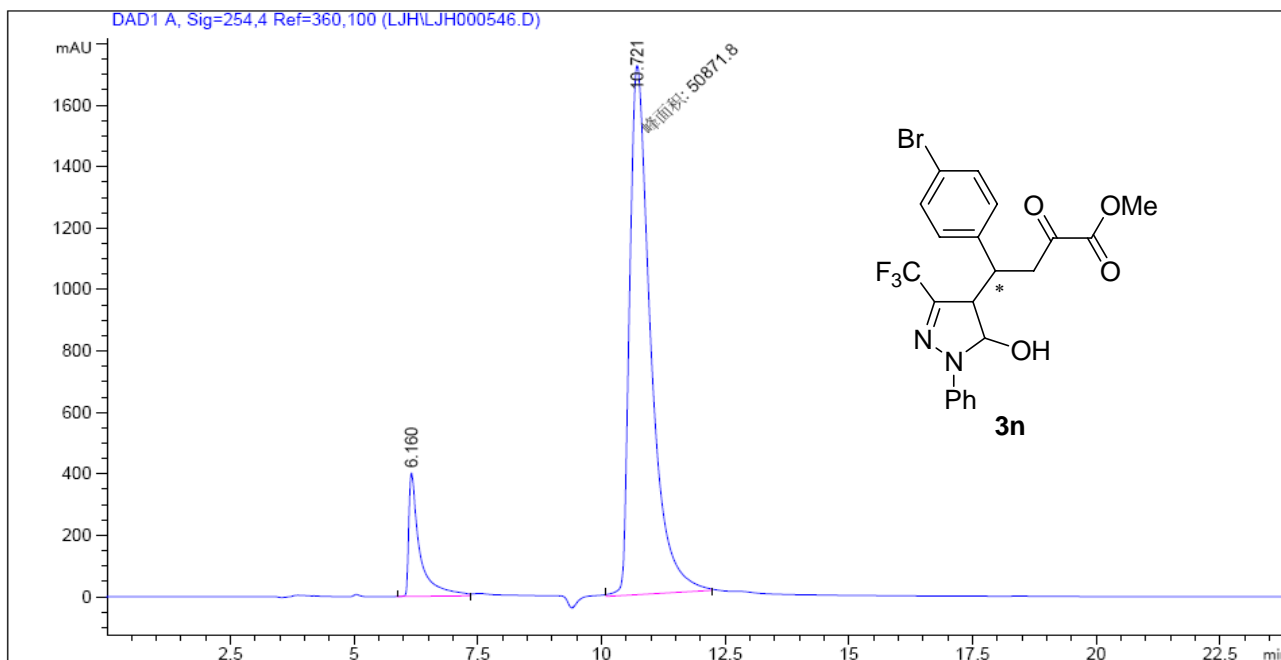
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.734	BB	0.8192	1.69086e4	291.29074	49.3272
2	22.943	BB	1.1633	1.73699e4	216.19415	50.6728



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.714	BB	0.8184	1.71827e4	296.35895	40.3570
2	22.740	BB	1.2176	2.53940e4	303.06577	59.6430

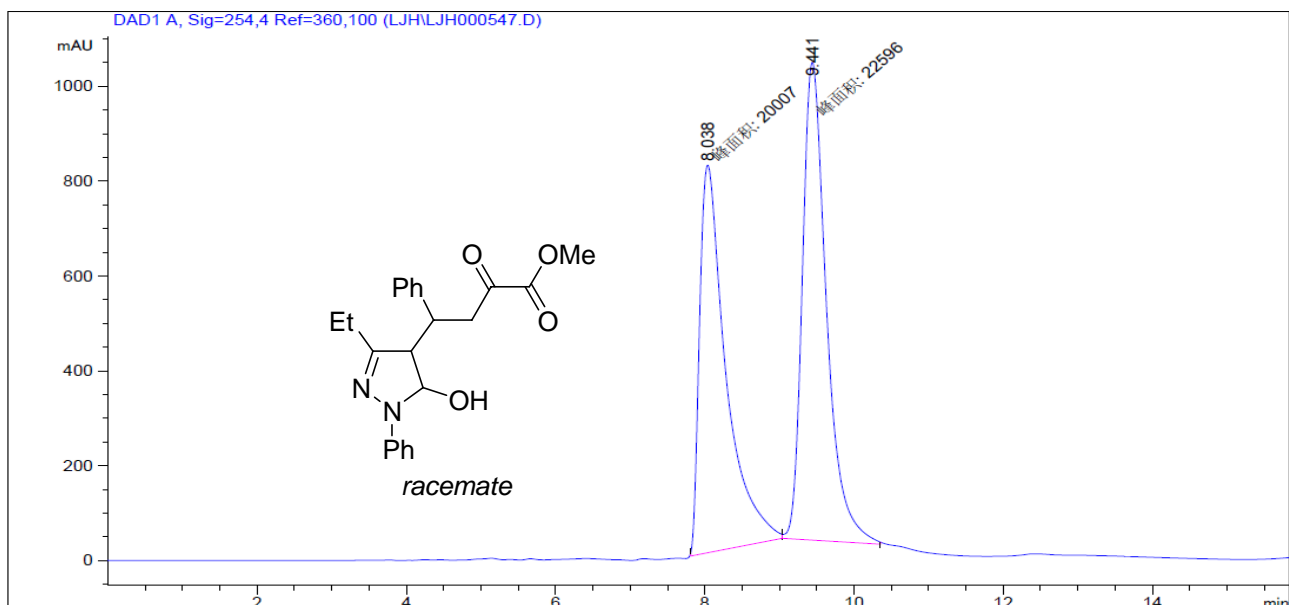


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.110	BB	0.2181	3.05407e4	2046.73596	49.9873
2	10.768	BB	0.4229	3.05562e4	1077.18225	50.0127

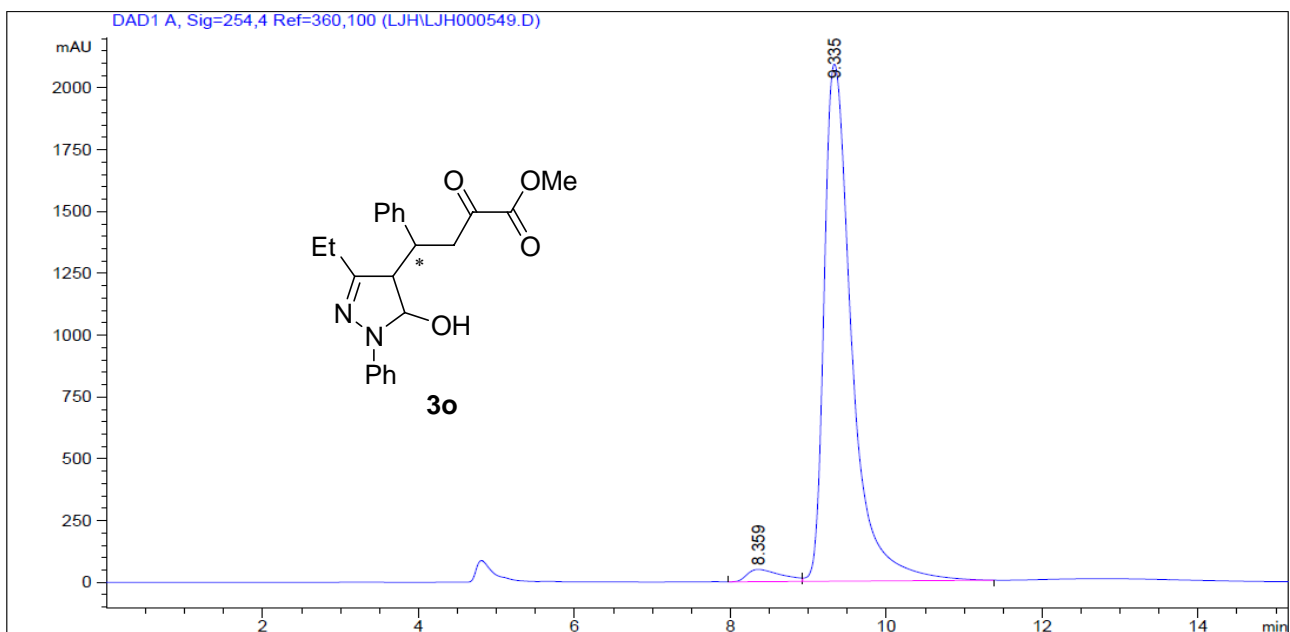


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.160	BV	0.2179	6262.91602	401.63135	10.9617
2	10.721	MM T	0.4923	5.08718e4	1722.26709	89.0383

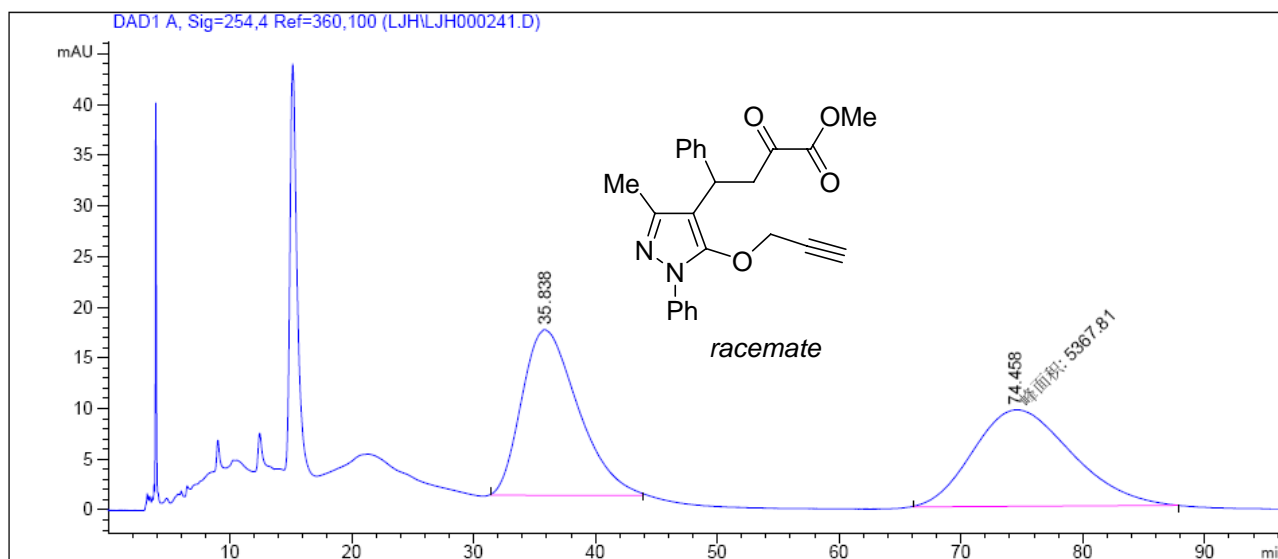




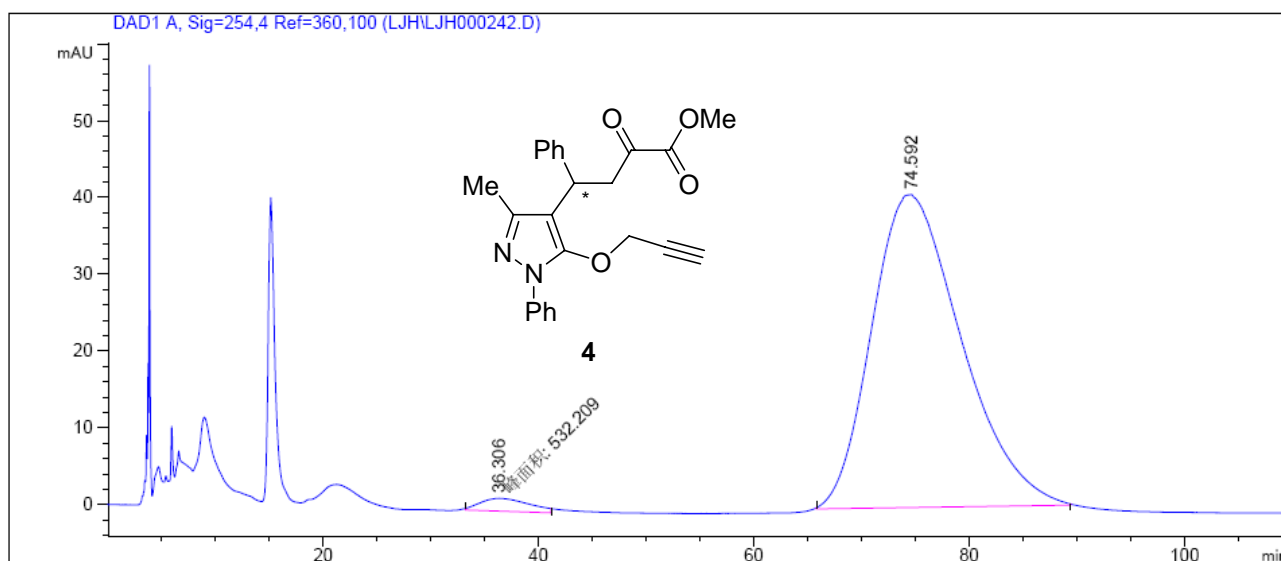
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.038	MM T	0.4079	2.00070e4	817.57117	46.9614
2	9.441	MM T	0.3736	2.25960e4	1007.97662	53.0386



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.359	BV	0.4461	1496.64209	49.59305	2.8281
2	9.335	VB	0.3709	5.14237e4	2091.41895	97.1719



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.838	BB	3.8206	5233.25635	16.35706	49.3654
2	74.458	MM T	9.3923	5367.80811	9.52524	50.6346



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.306	MM T	5.3090	532.20947	1.67077	2.2103
2	74.592	BB	6.8147	2.35465e4	40.74197	97.7897