

Electronic Supplementary Information for:

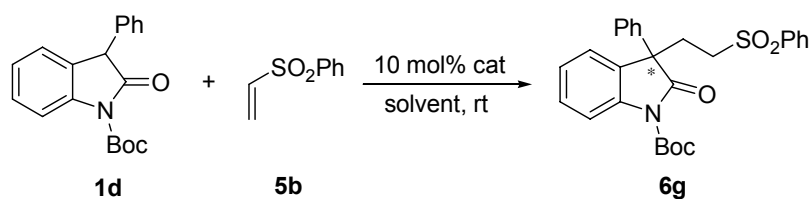
**Asymmetric Michael Addition Reaction of
3-Aryl-N-Boc-Oxindole to Activated Terminal Alkene Catalyzed
by Bifunctional Tertiary-Amine Thiourea Catalyst**

Xin Li,^a Zhi-Guo Xi,^b Sanzhong Luo,^{*a} Jin-Pei Cheng^{*a,b}

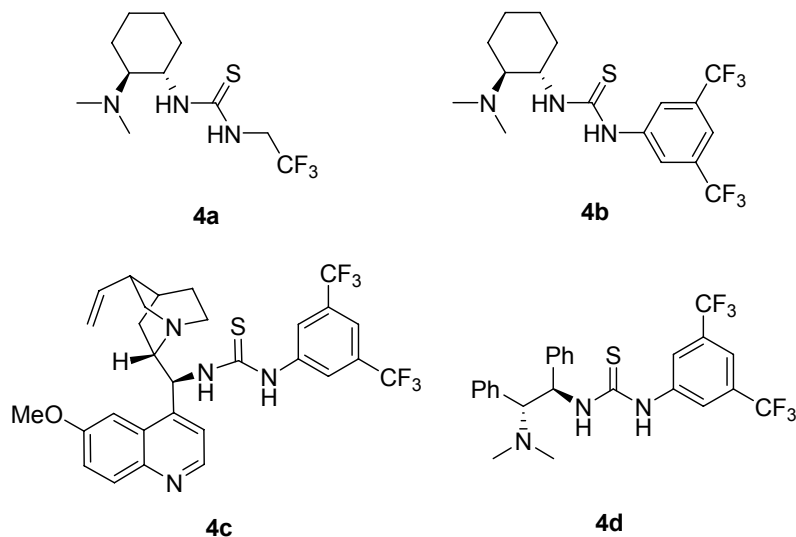
Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of
Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences,
Beijing, 100190, China and Department of Chemistry and State Key Laboratory of
Elemento-organic Chemistry, Nankai University, Tianjin, 300071, China

luosz@iccas.ac.cn

Table S1. Optimization studies of Michael addition of oxindole to sulfone.



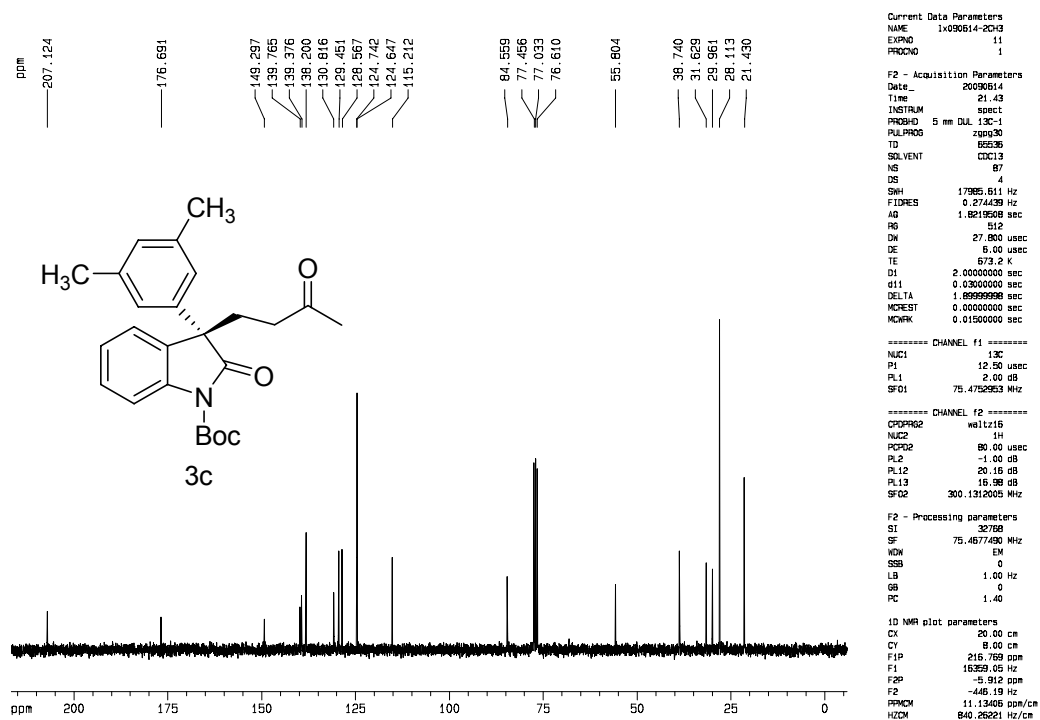
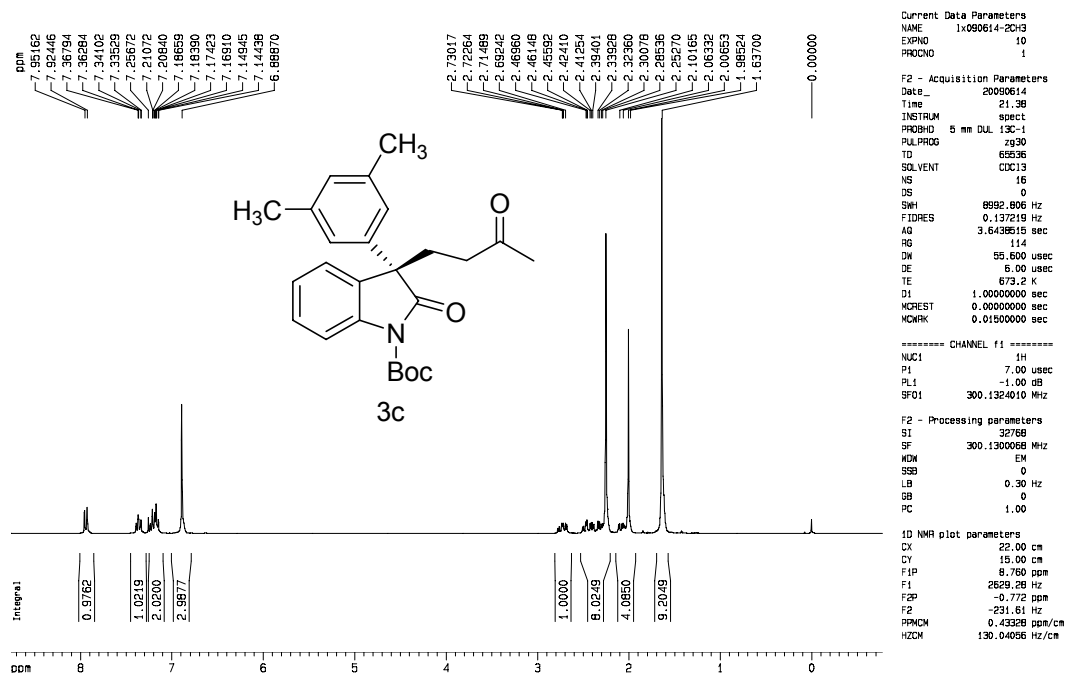
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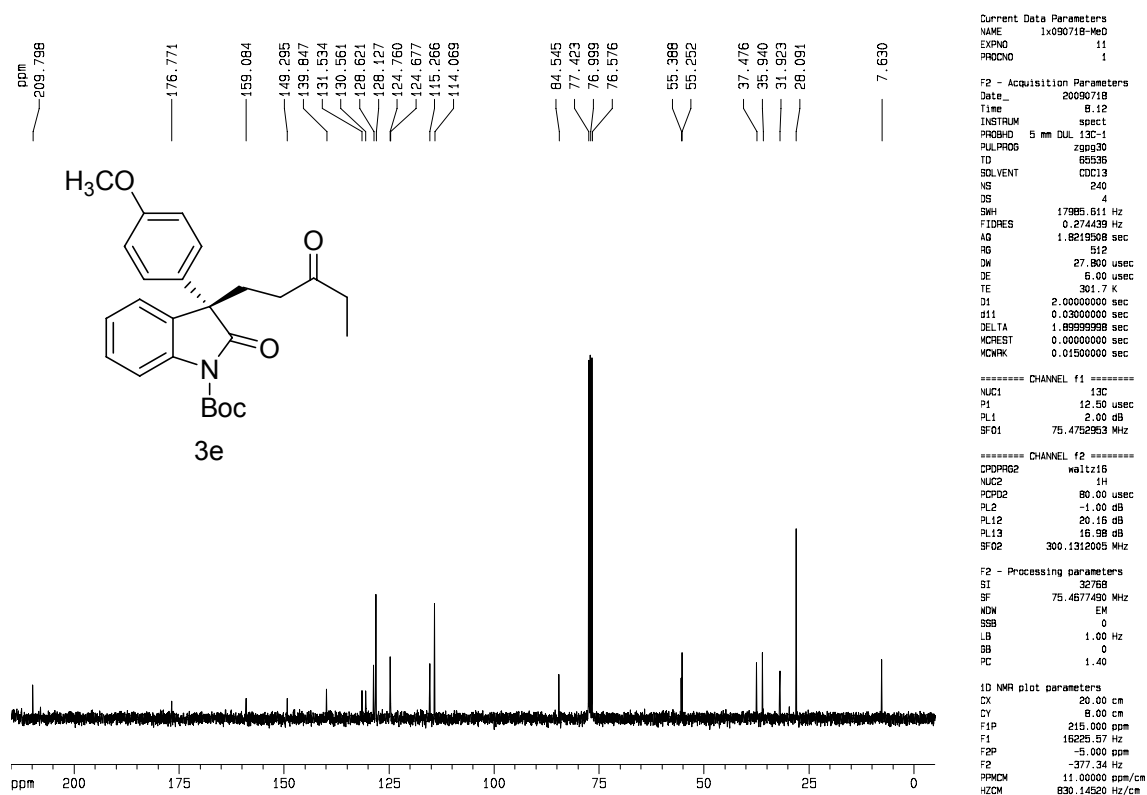
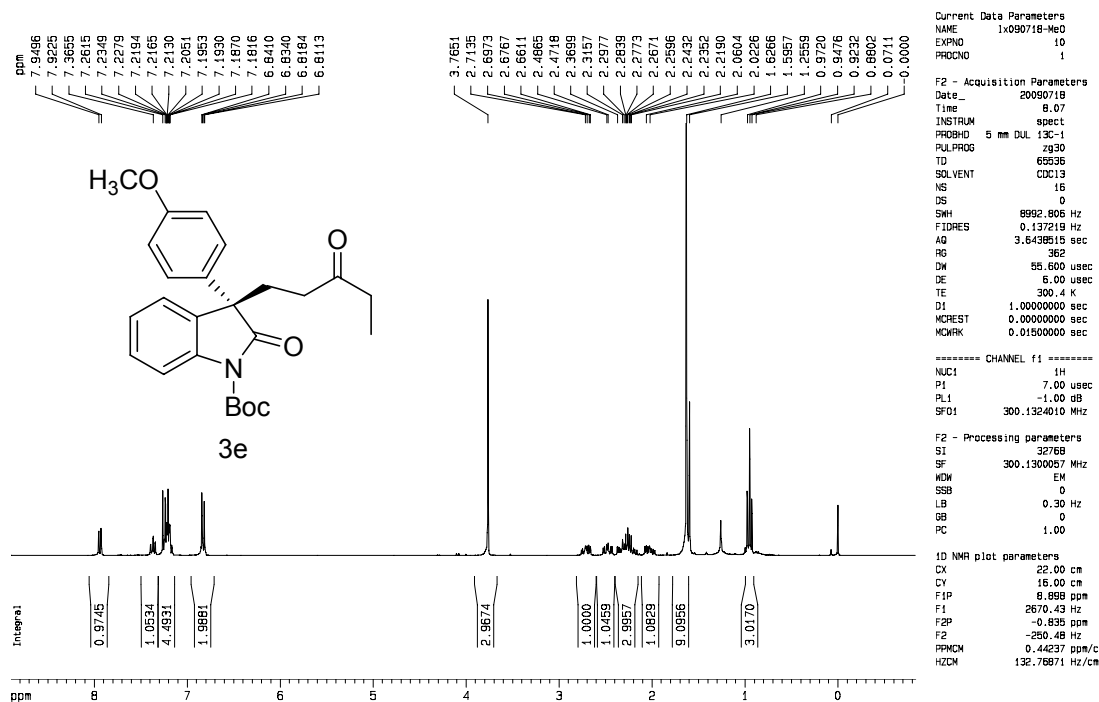


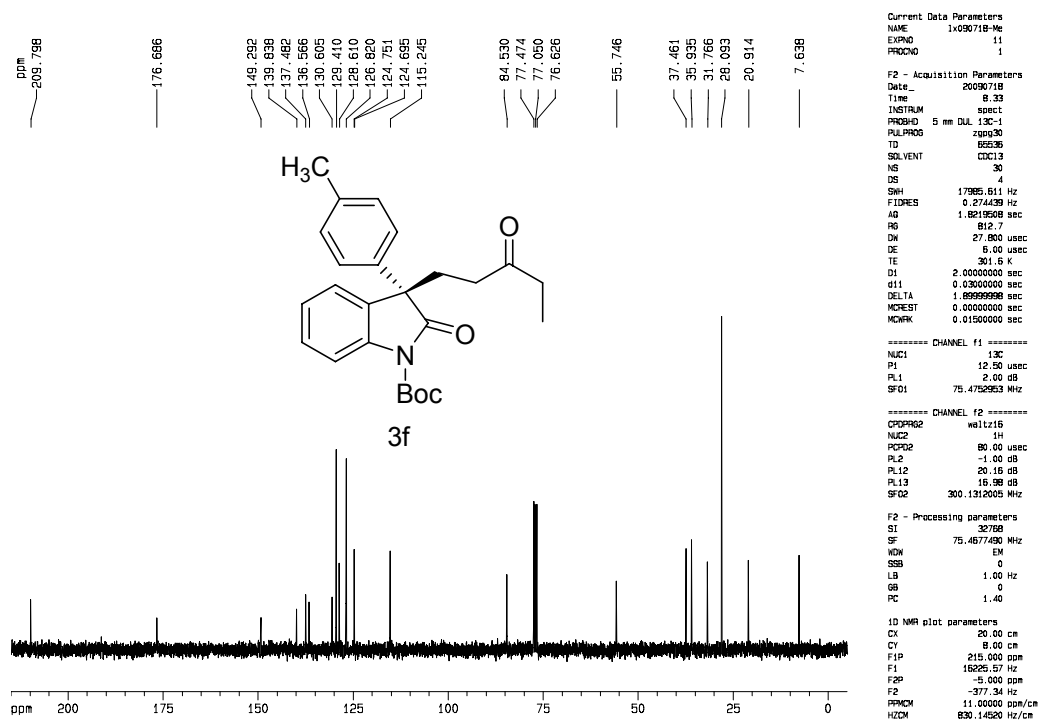
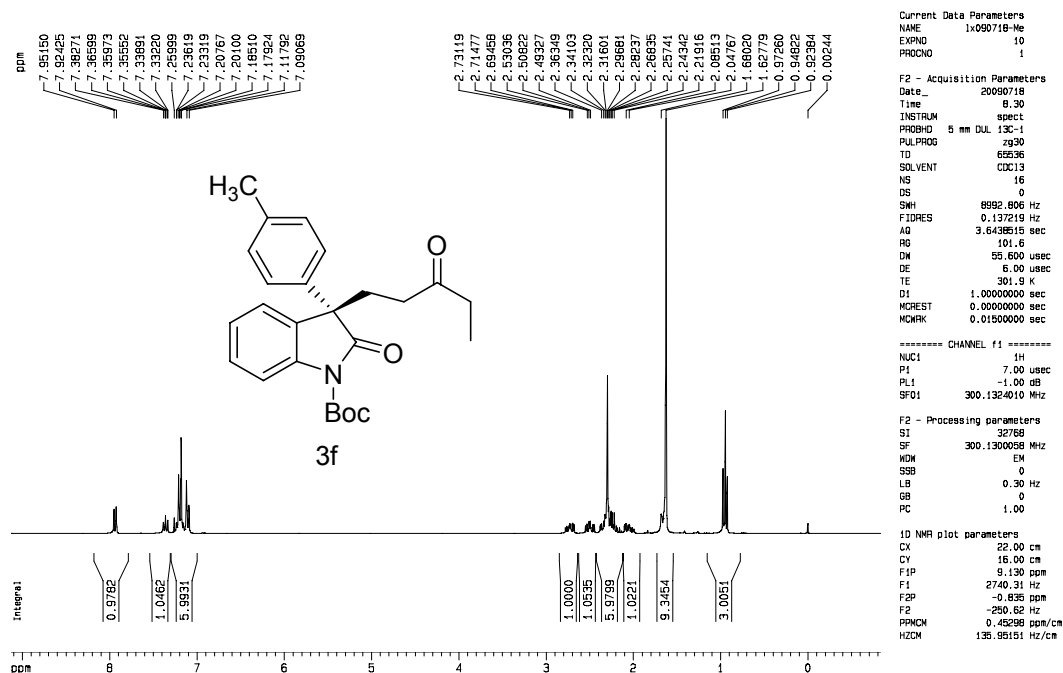
Entry	Catalysts	Solvent	Time (h)	Yield ^b (%)	ee ^c (%)
1	4a	Toluene	24	95	49
2	4b	Toluene	24	98	49
3	4c	Toluene	24	84	47
4	4d	Toluene	24	96	70
5	4d	CH ₂ Cl ₂	24	95	67
6	4d	CHCl ₃	24	91	65
7	4d	ClCH ₂ CH ₂ Cl	24	96	67
8	4d	Benzene	24	87	68
9	4d	THF	24	79	61
10	4d^d	Toluene	168	72	85
11	4d^e	Toluene	144	80	87

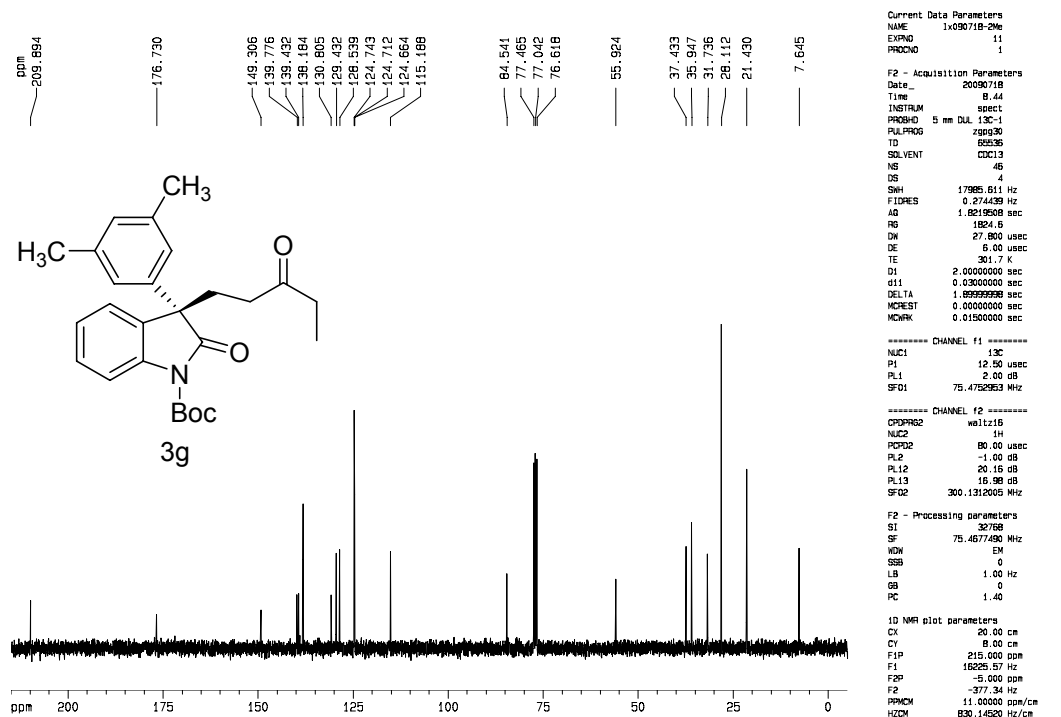
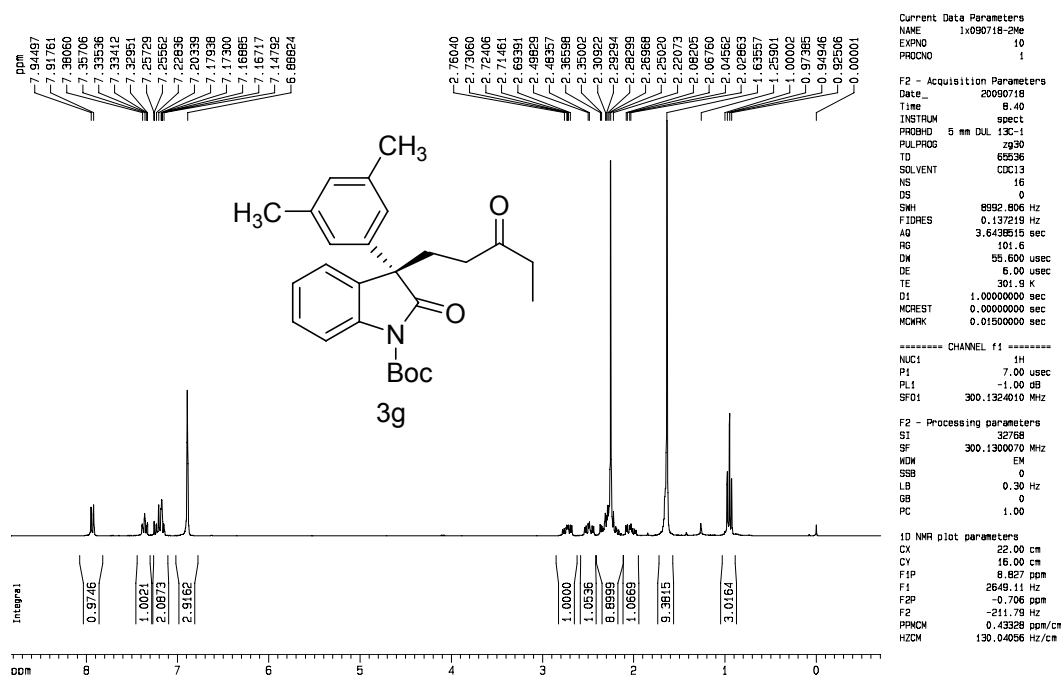
^a The reaction was carried out on a 0.1 mmol scale in 200 μ L solvent at room temperature, and the molar ratio of oxindole **1d**/**5b** is 1/3. ^b Isolated yield. ^c Determined by HPLC. ^d The reaction was carried out on a 0.1 mmol scale in 200 μ L toluene with 4Å molecular formula at -20°C, and the molar ratio of oxindole **1d**/**5b** is 1/3. ^e The reaction condition was same to the entry 10 except for 20 mol% **4d** was used.

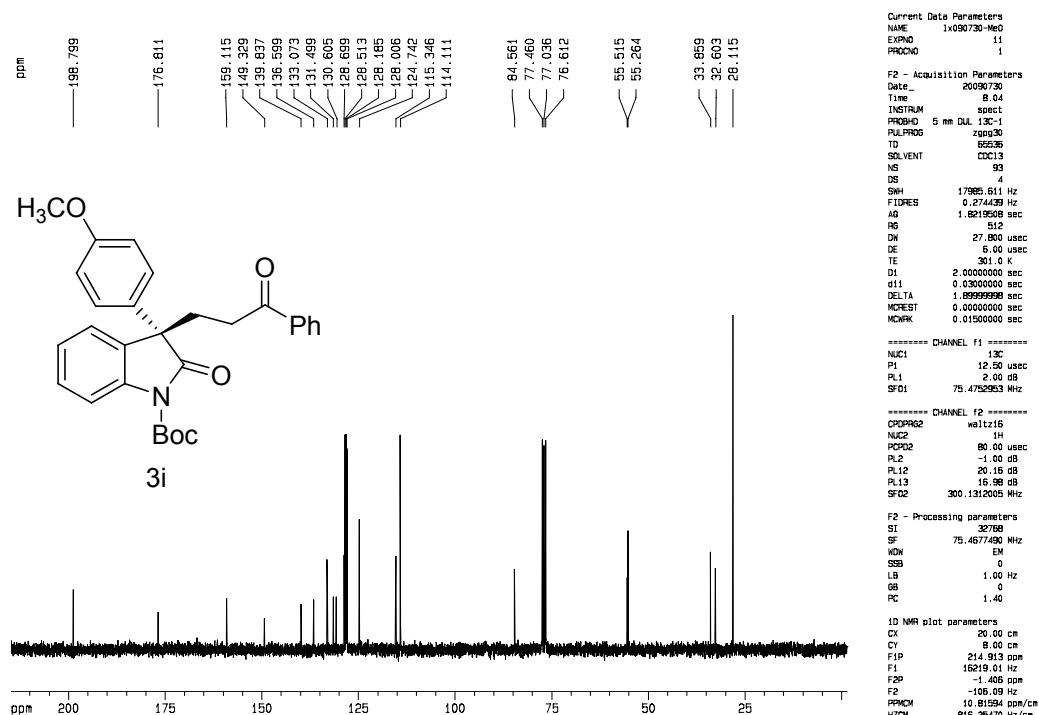
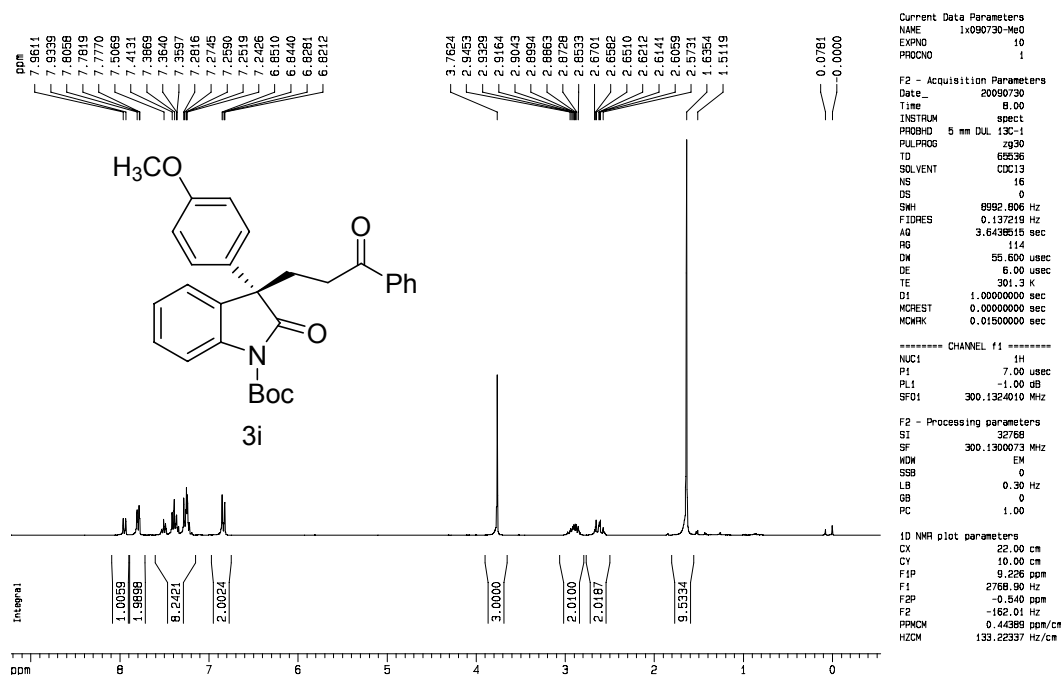
NMR spectrum for Michael products:

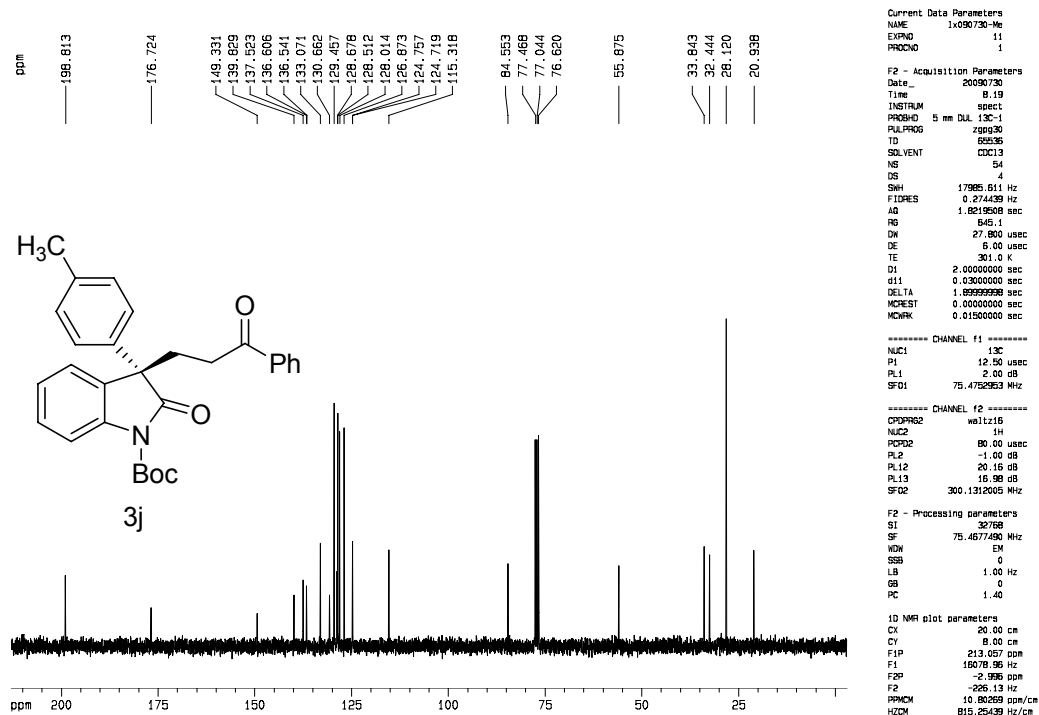
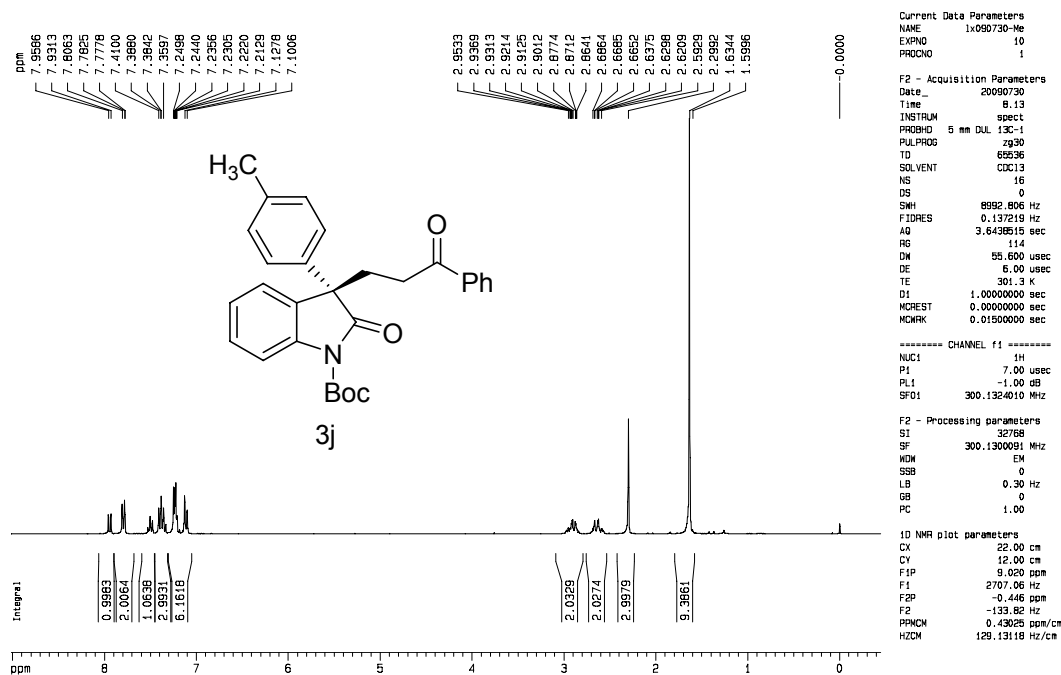


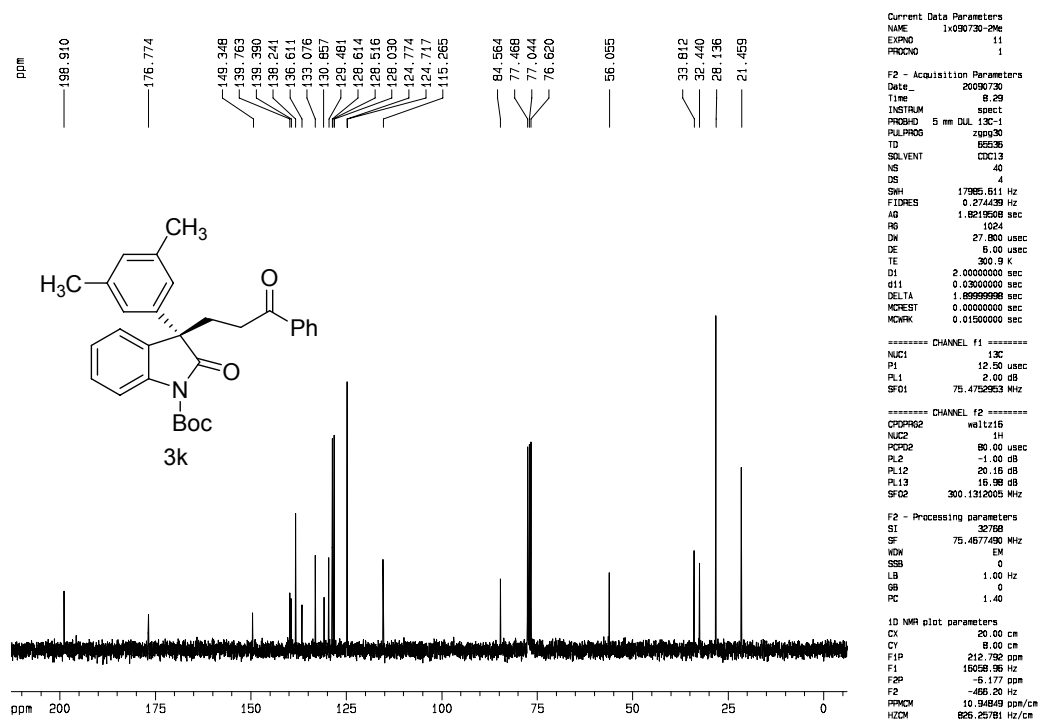


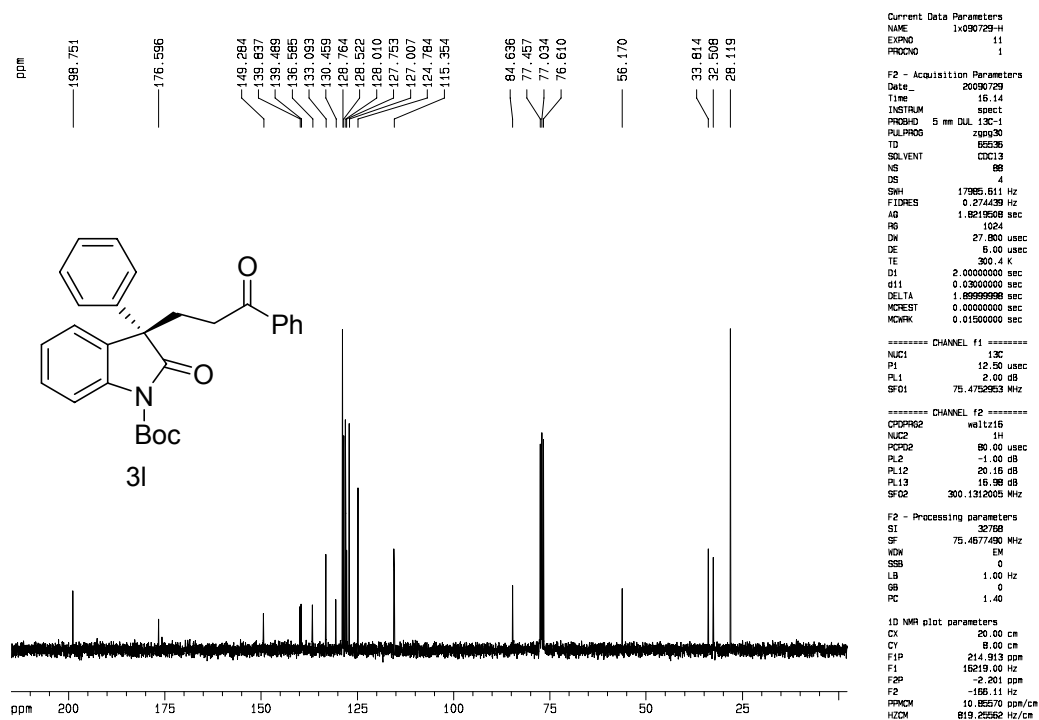
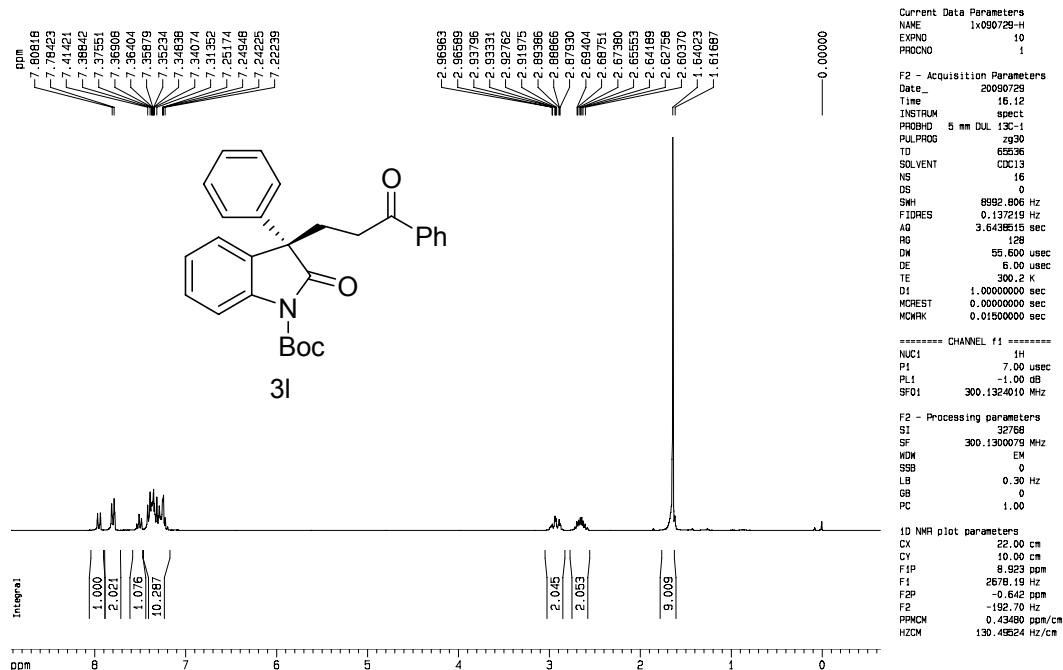


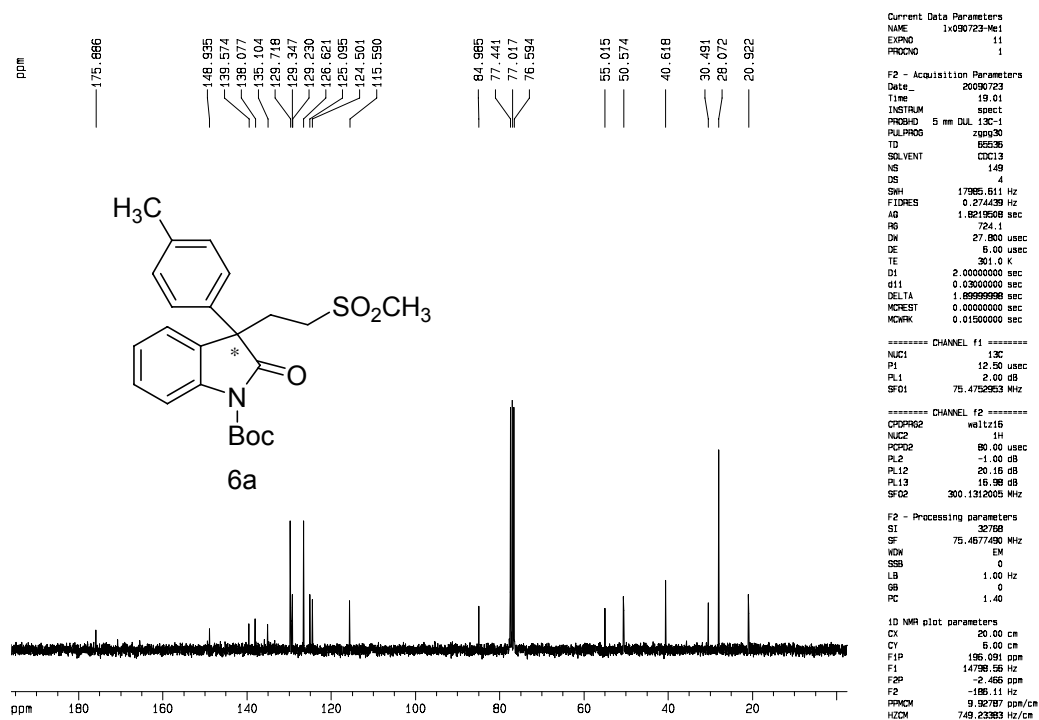
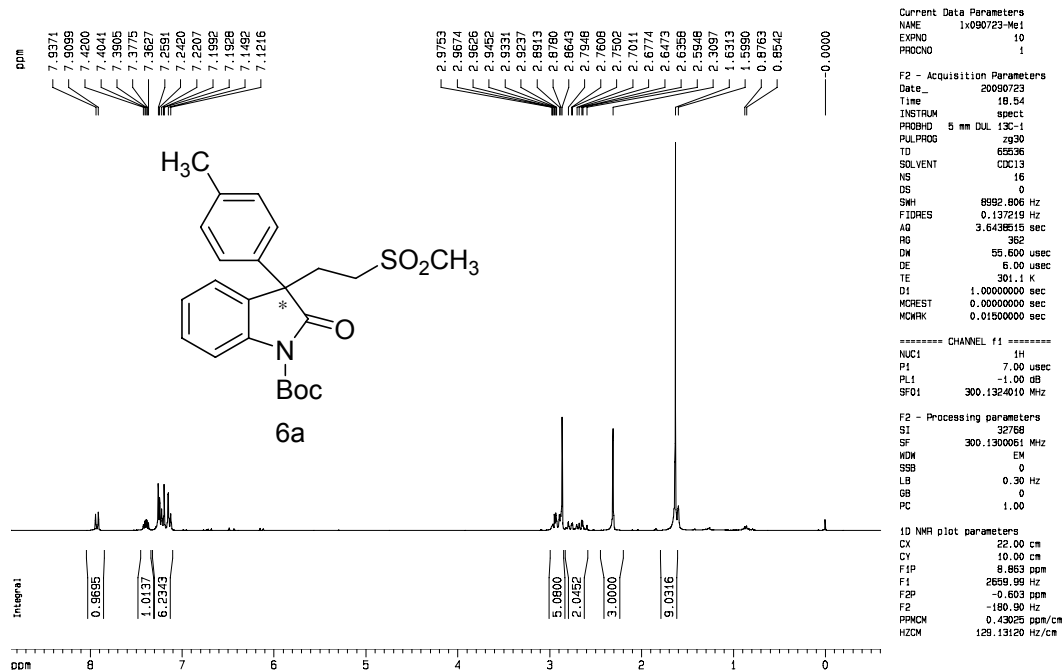


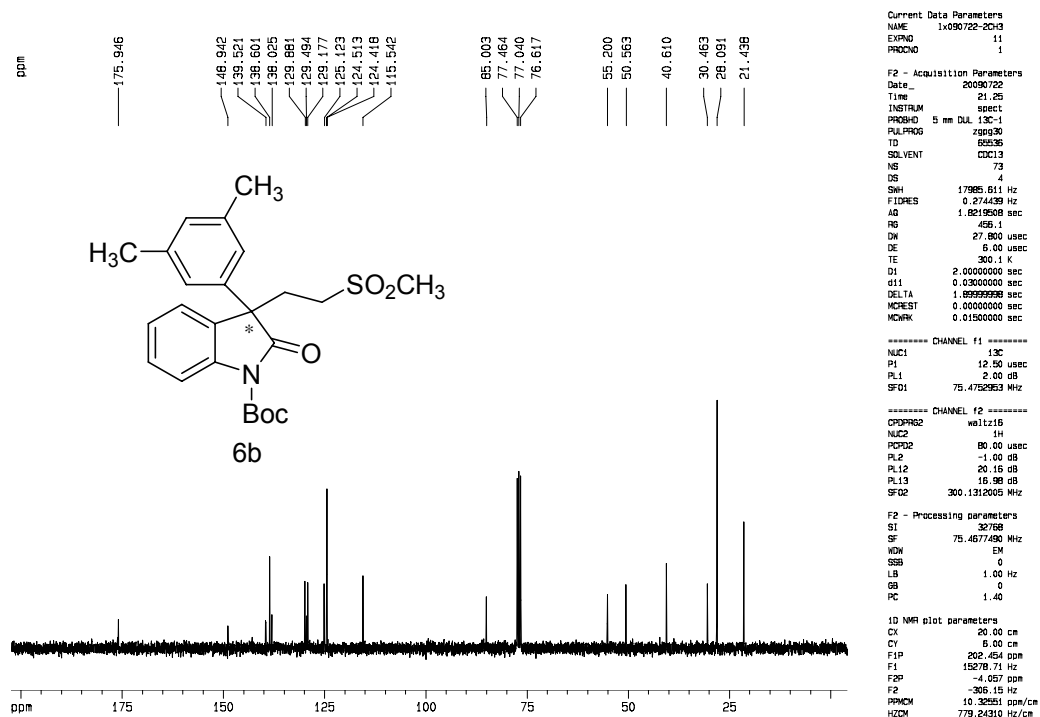
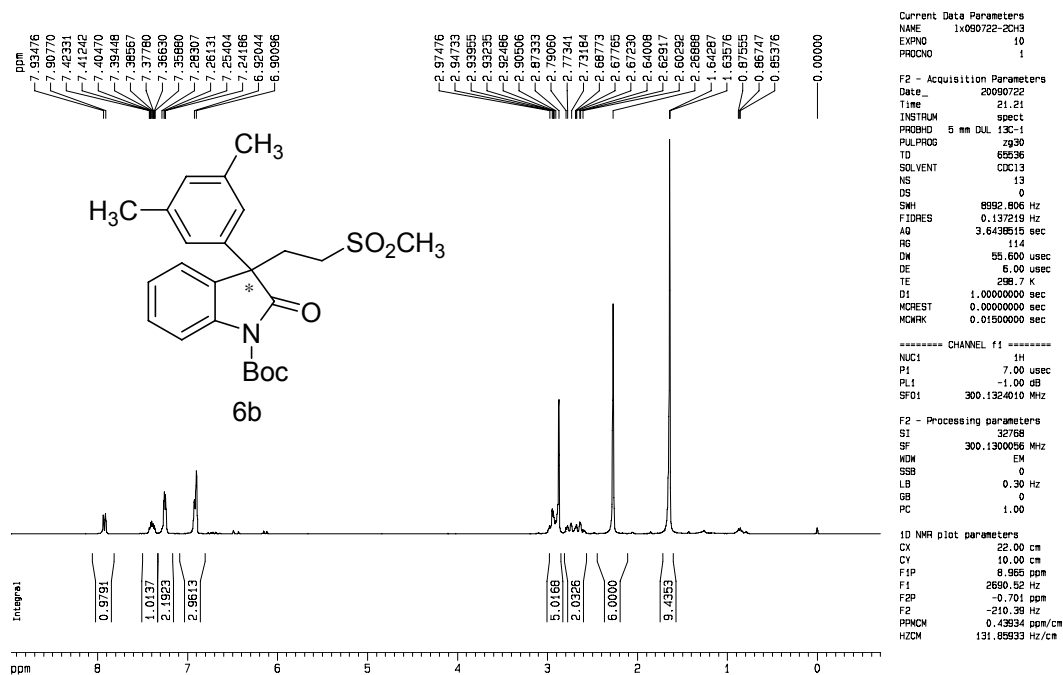


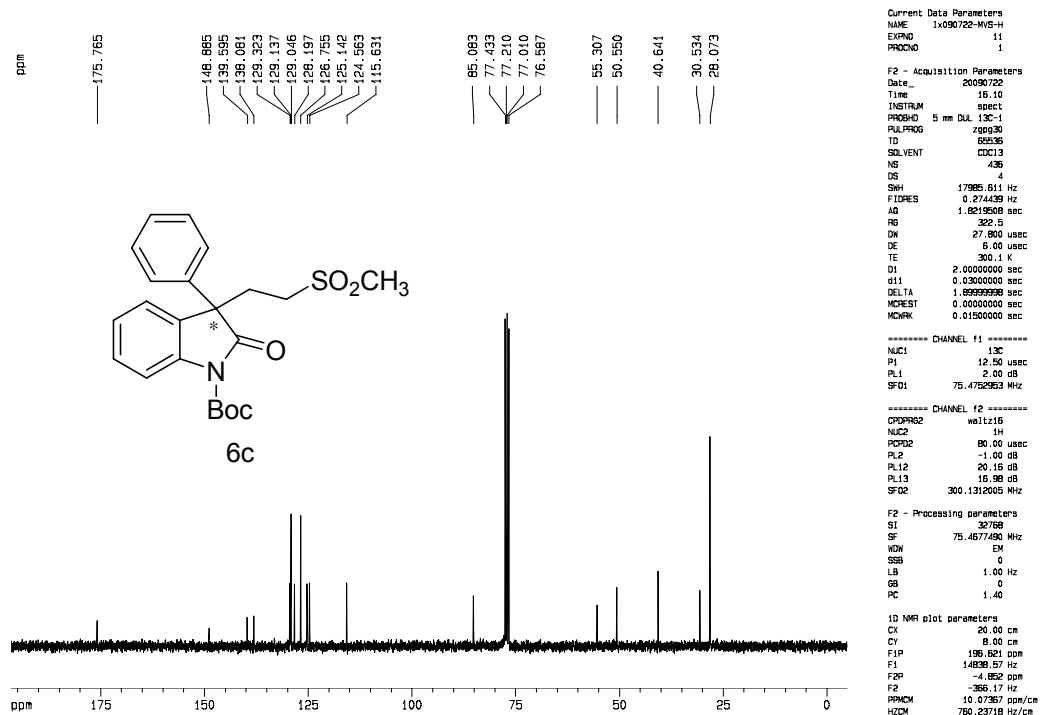
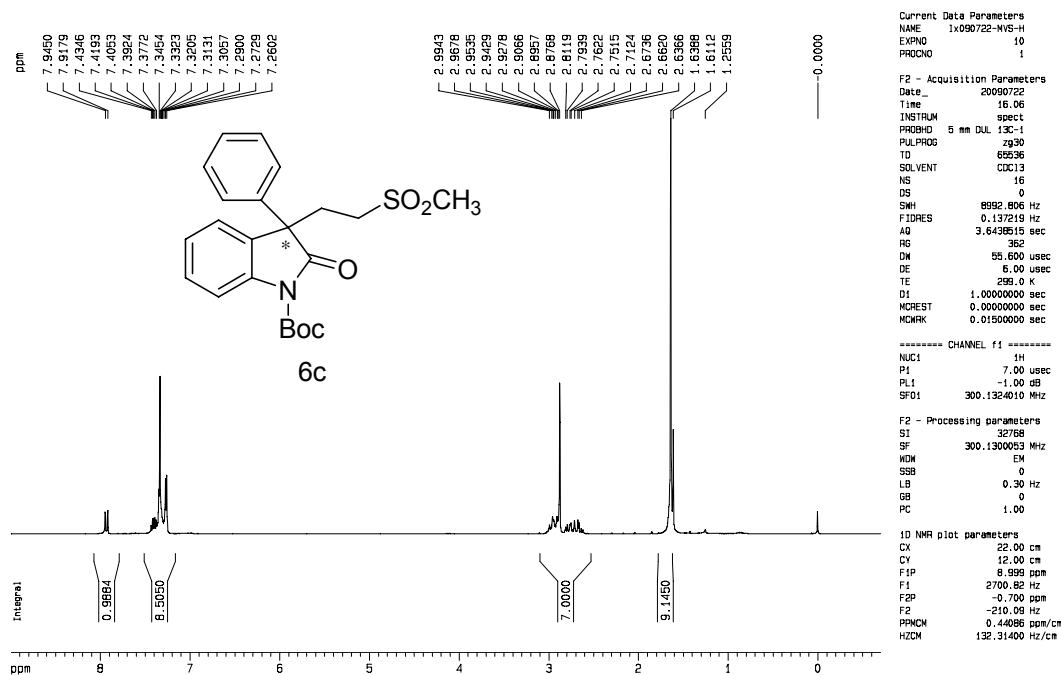


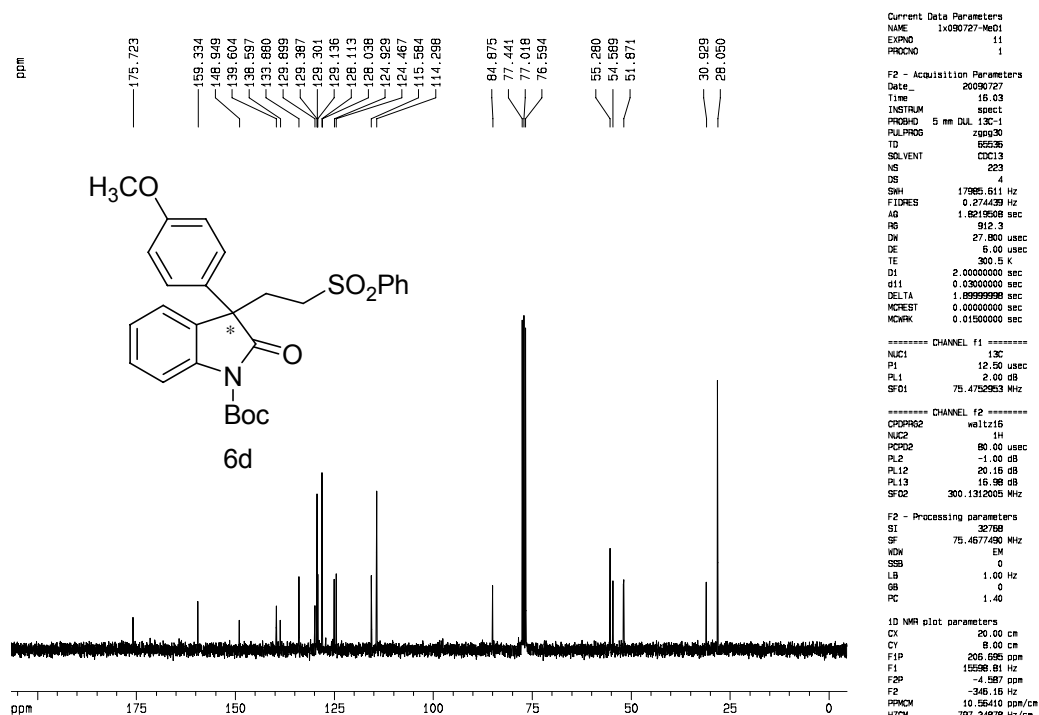
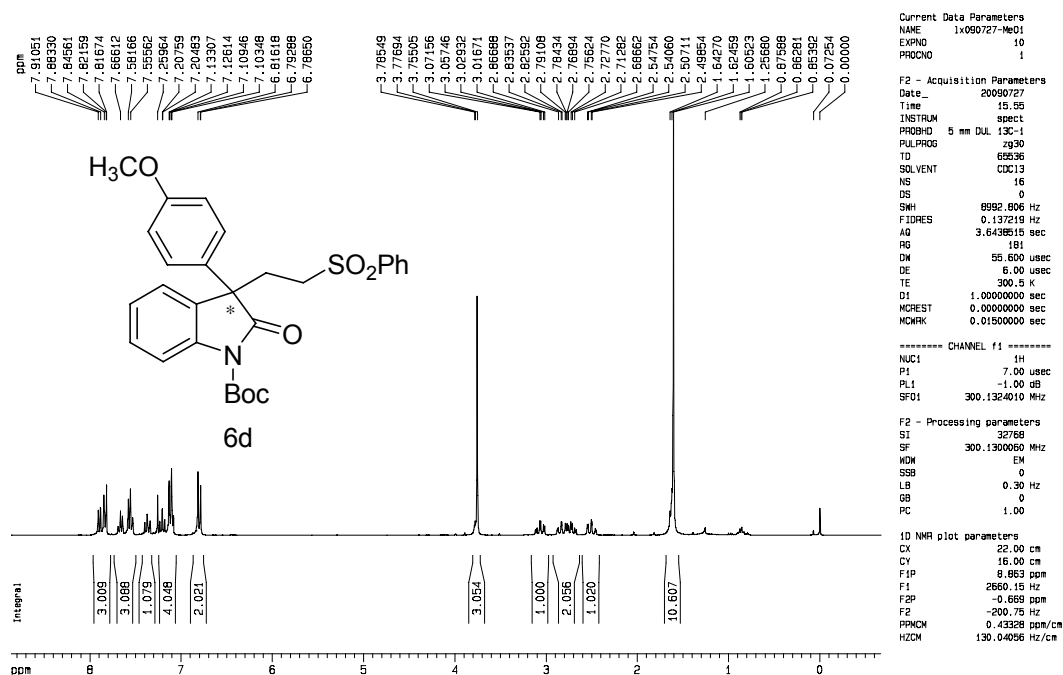


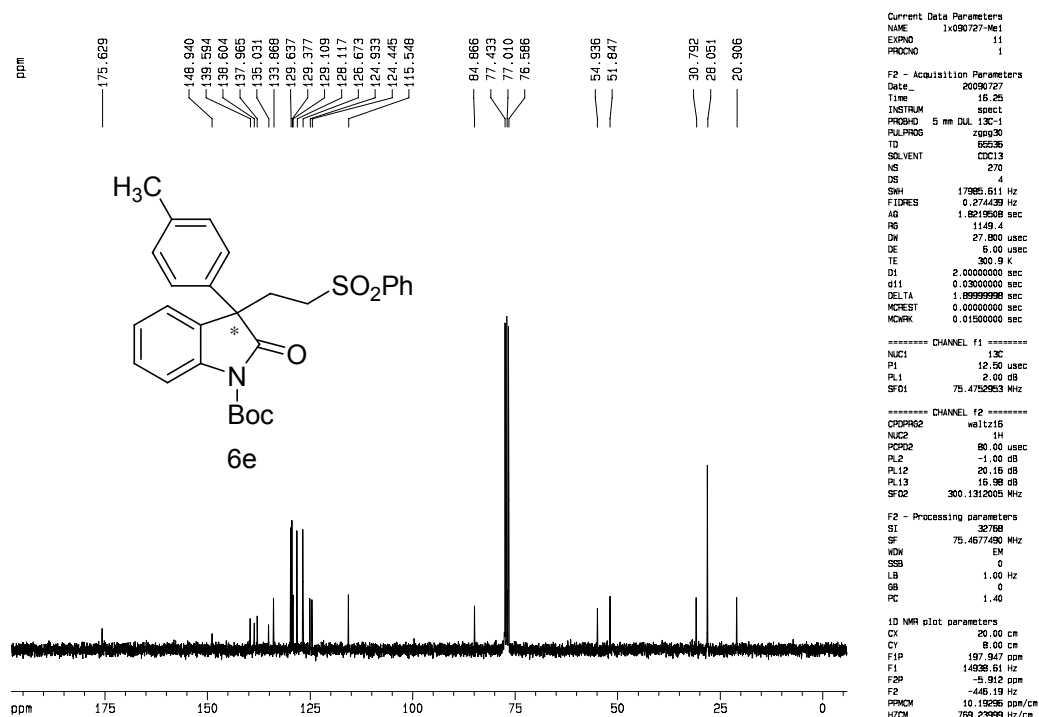
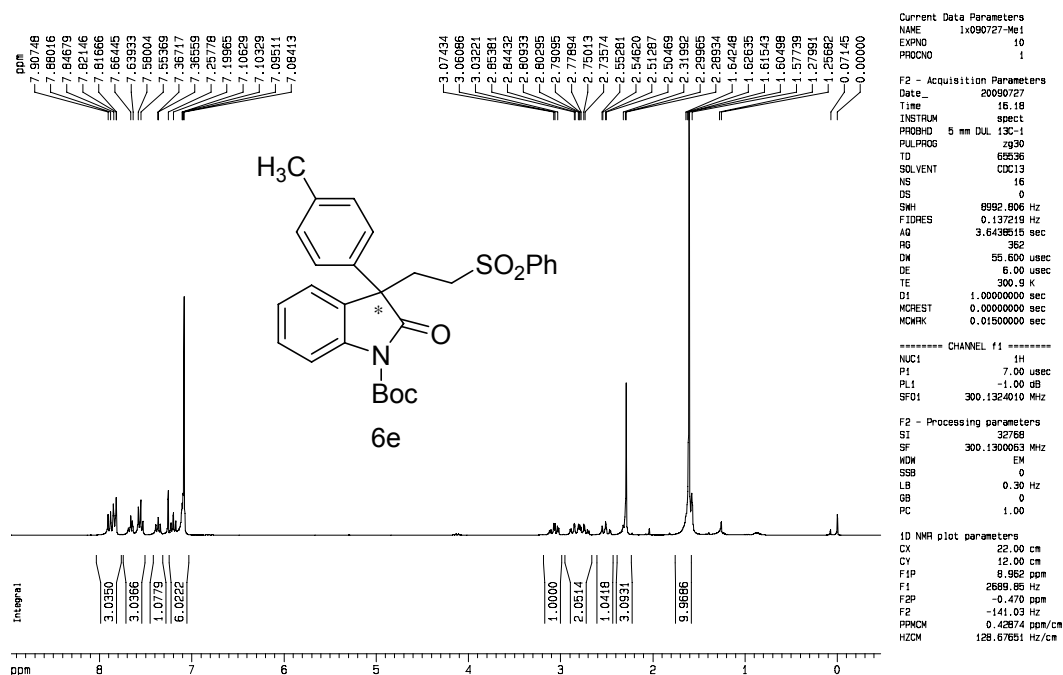


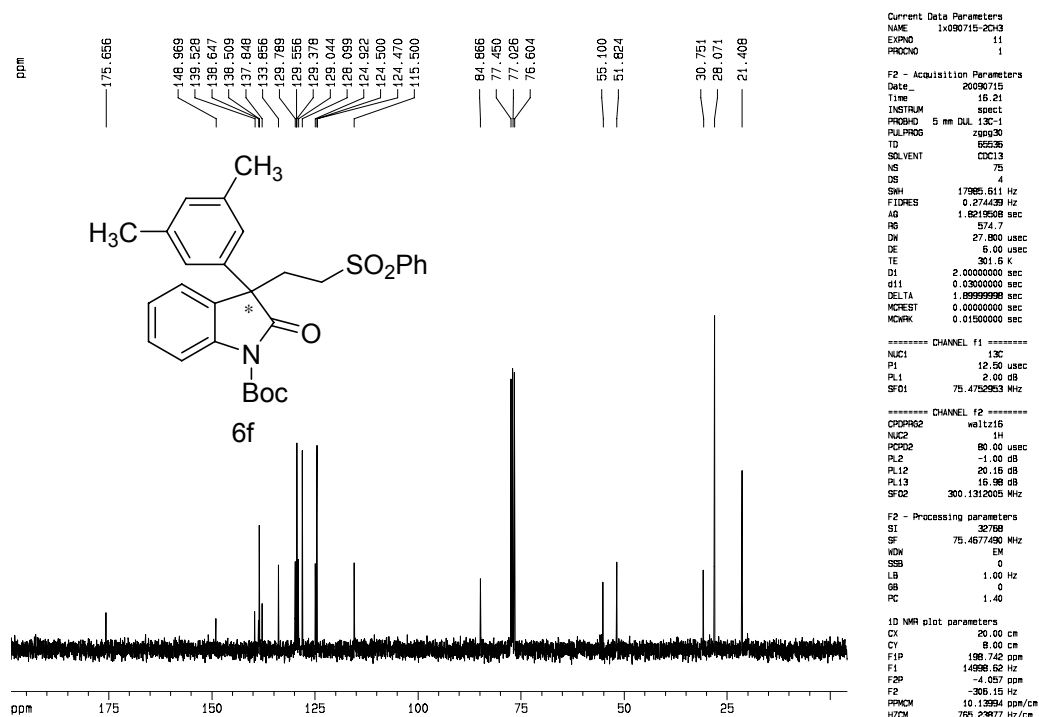
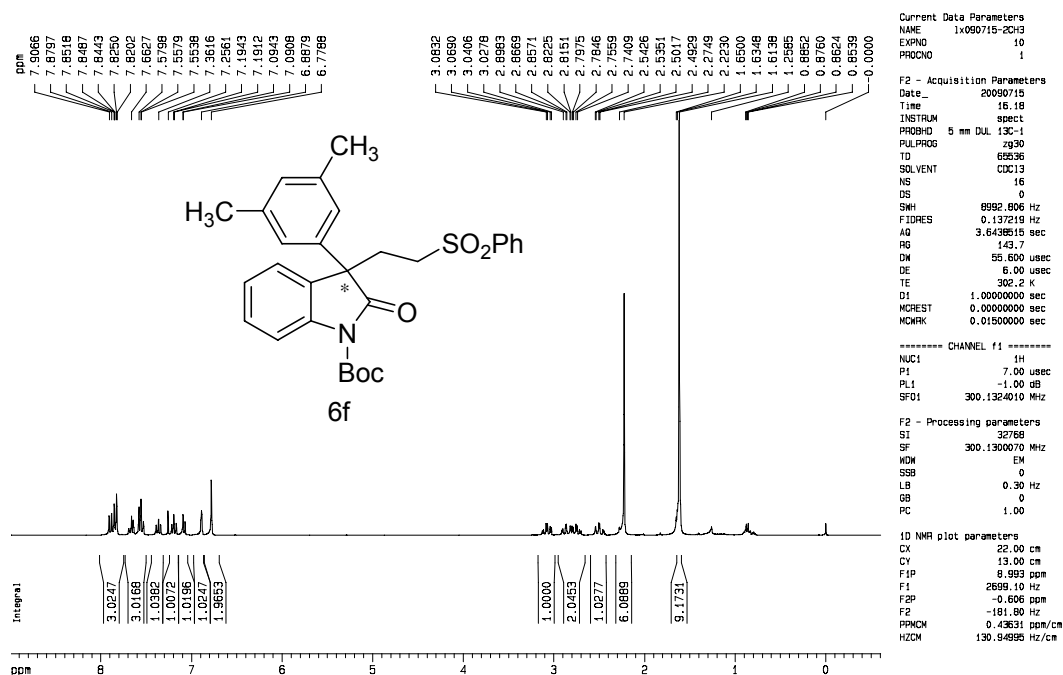


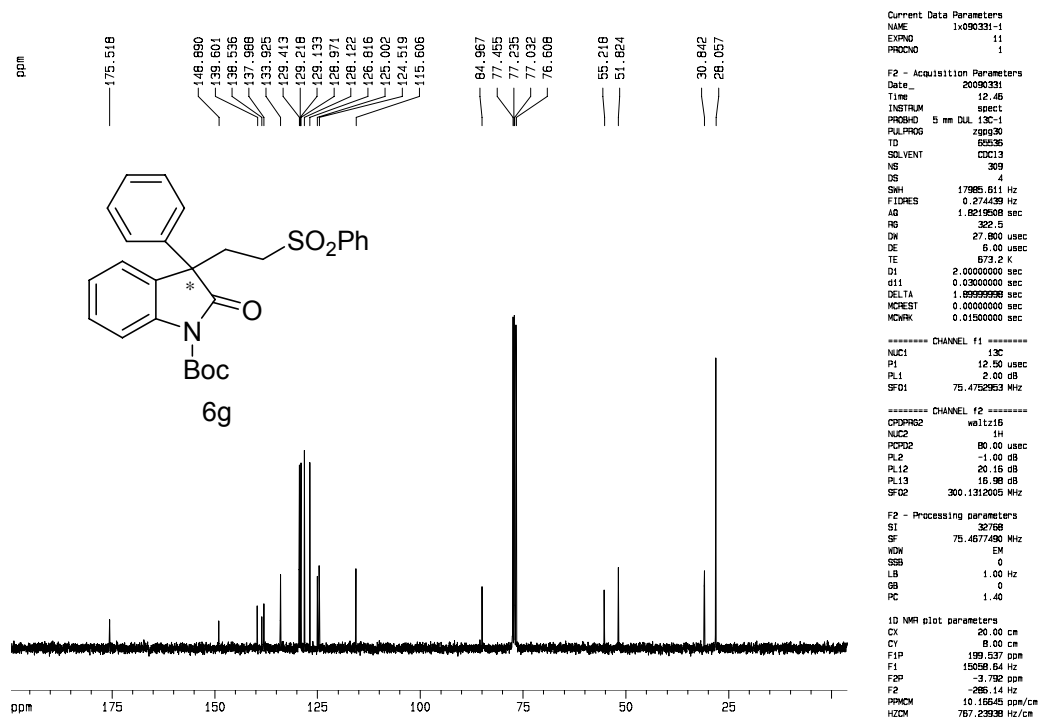
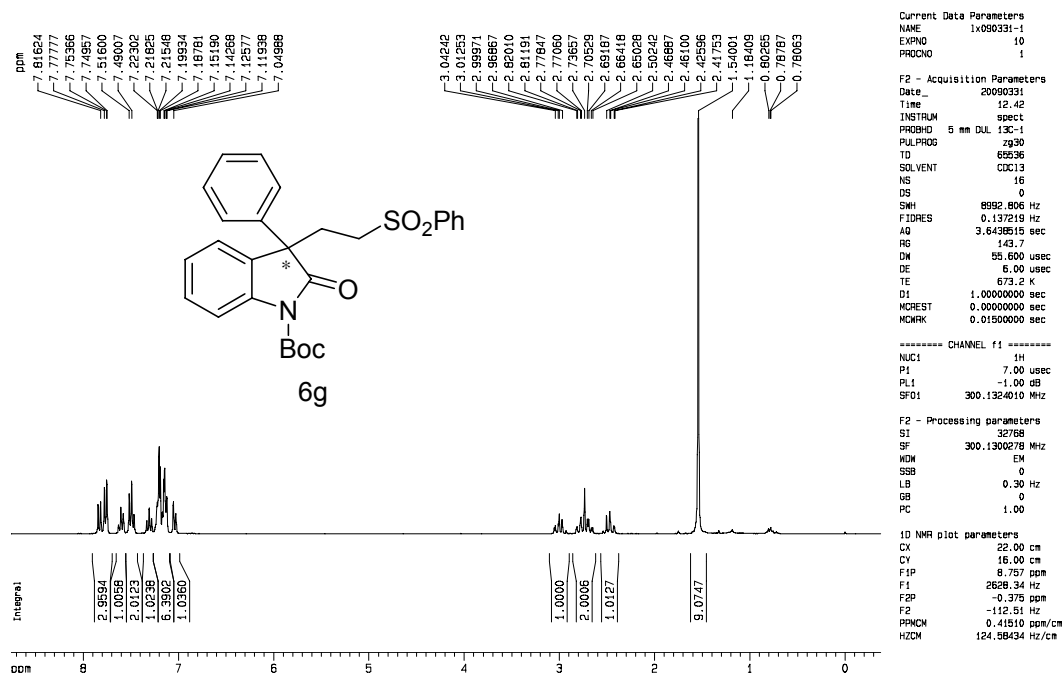


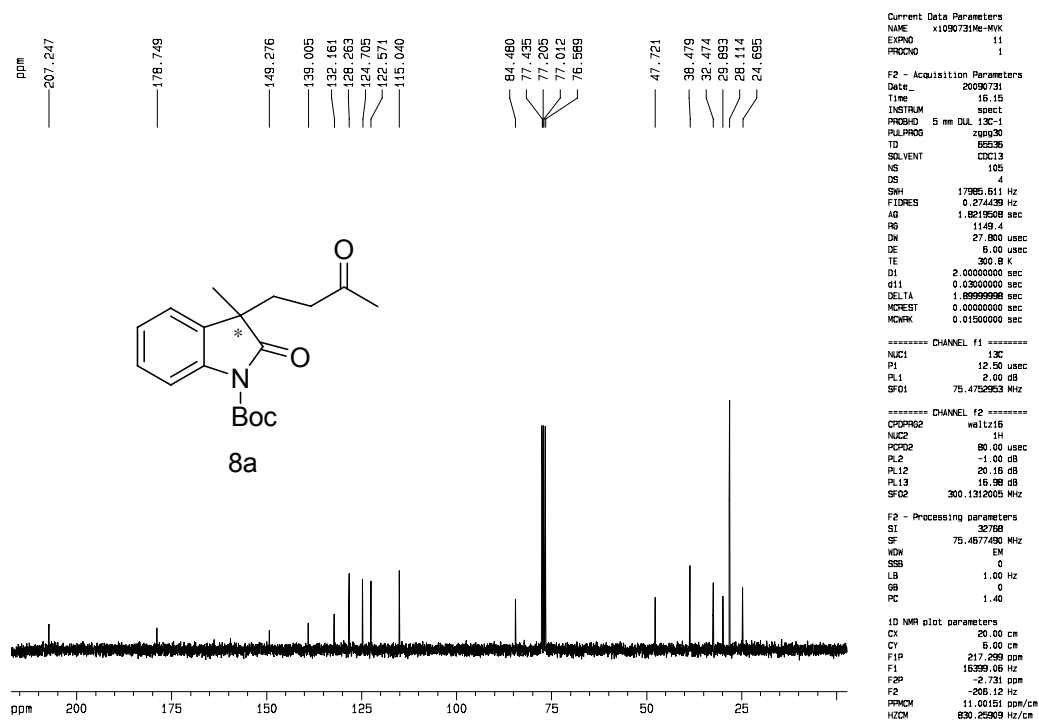
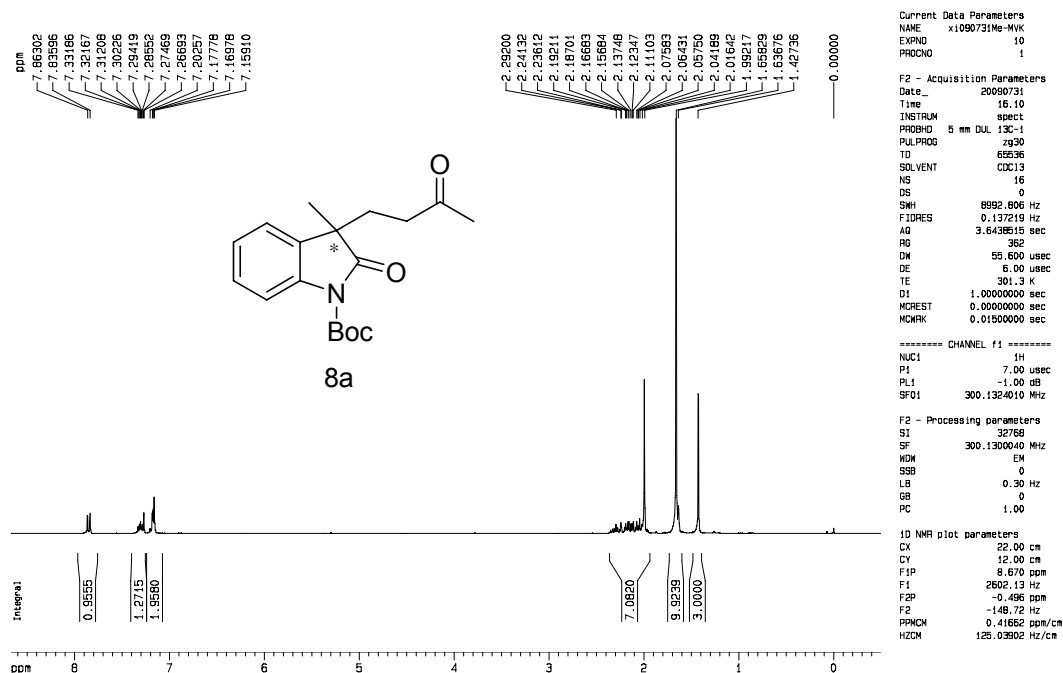


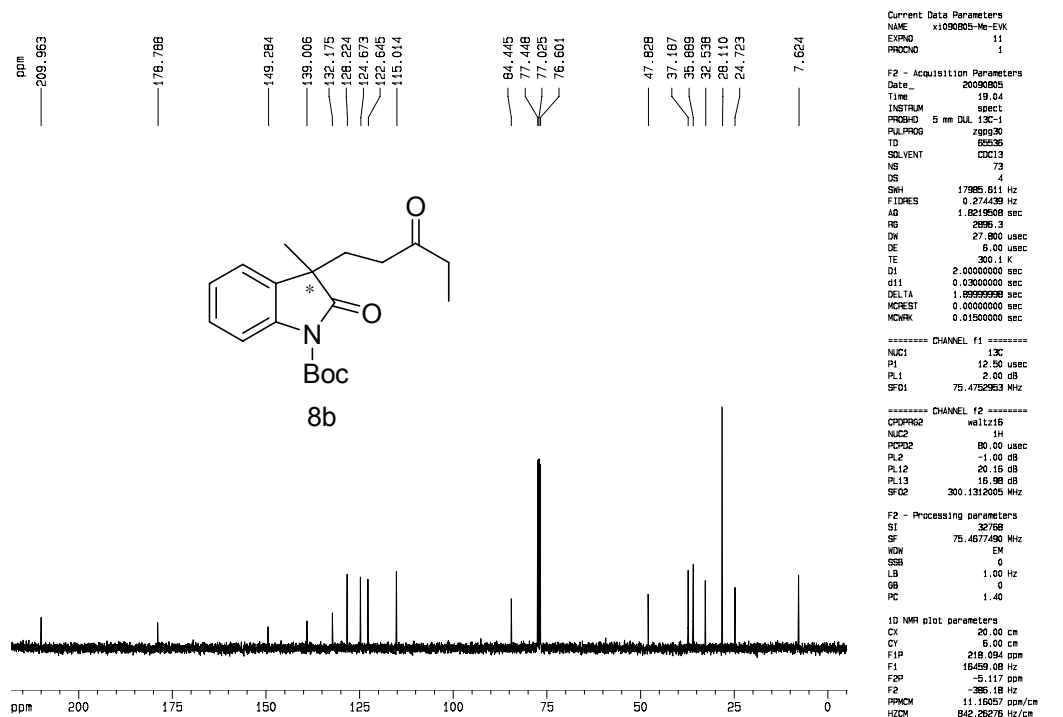
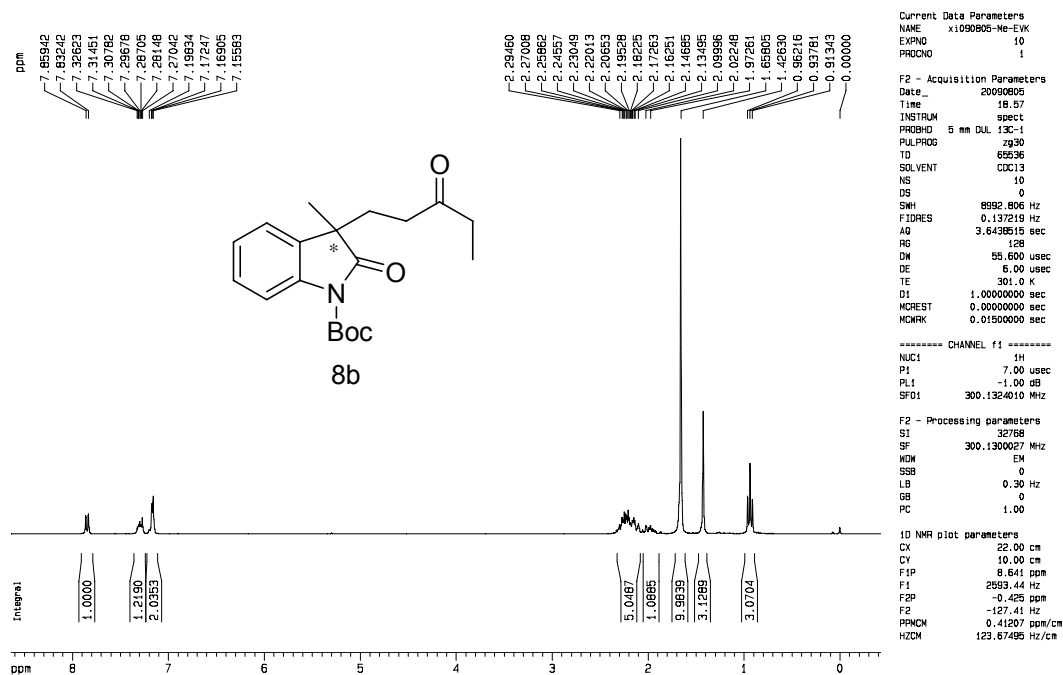


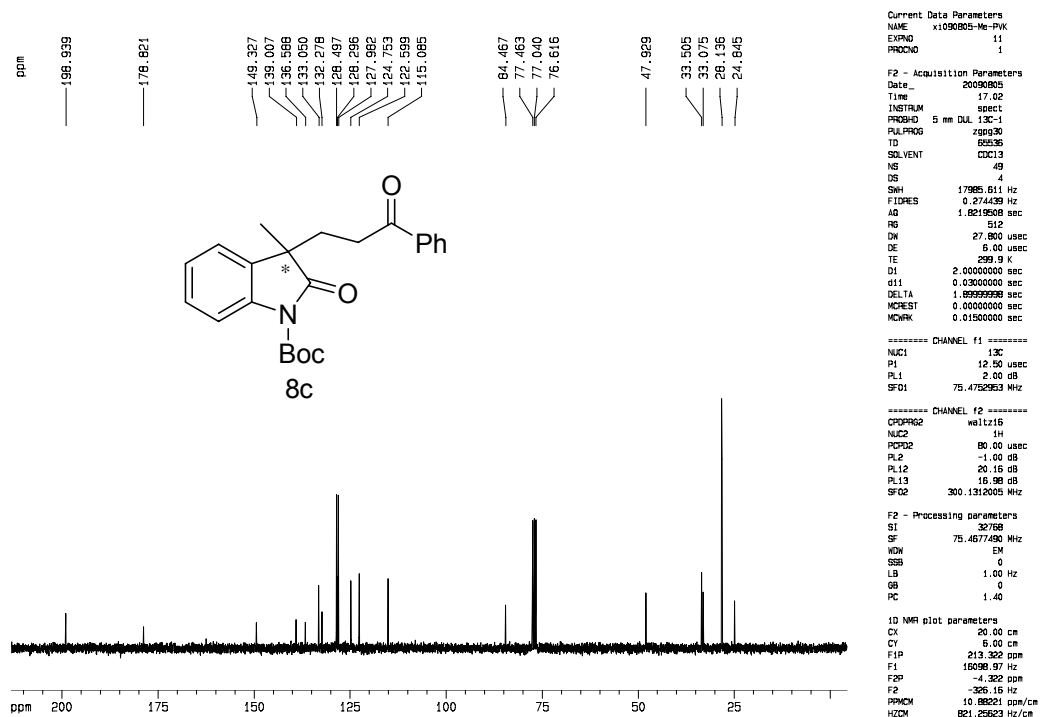
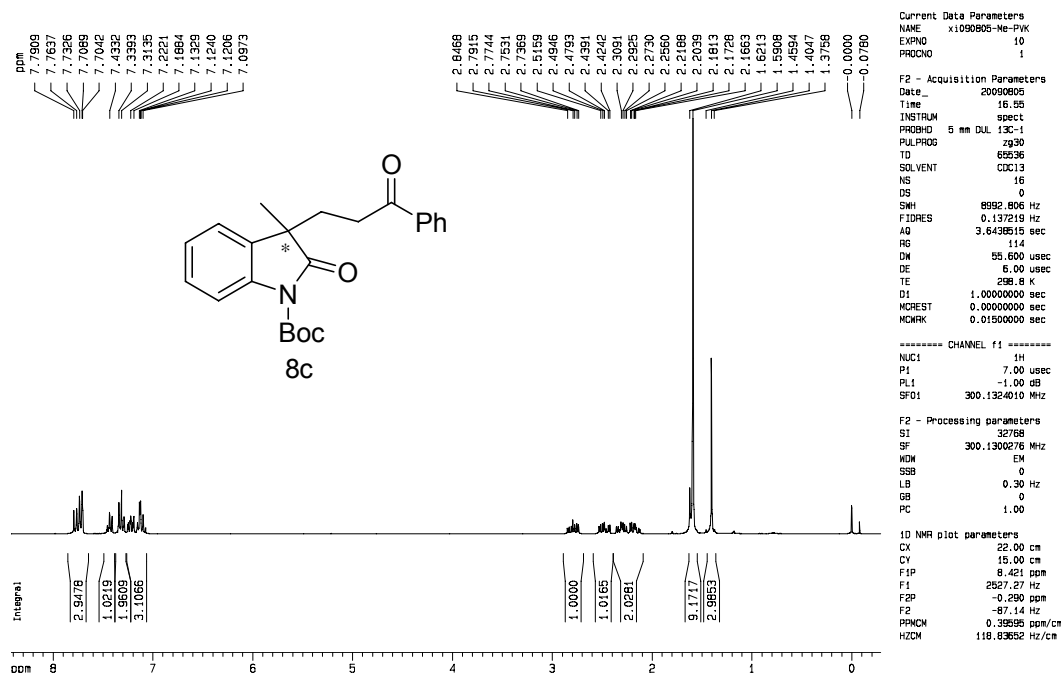


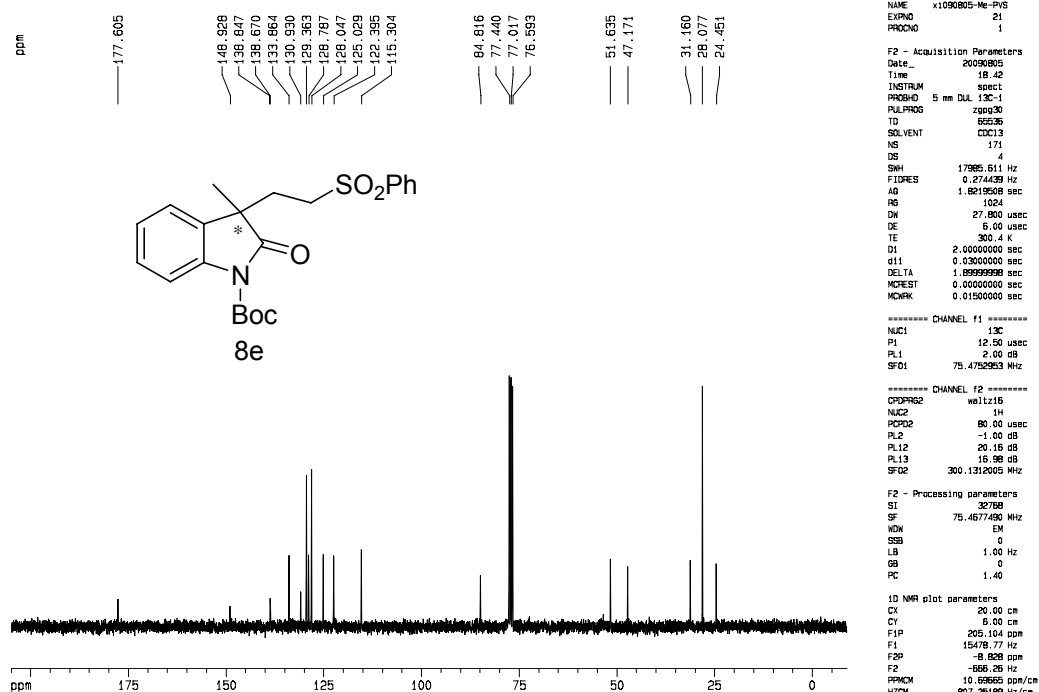
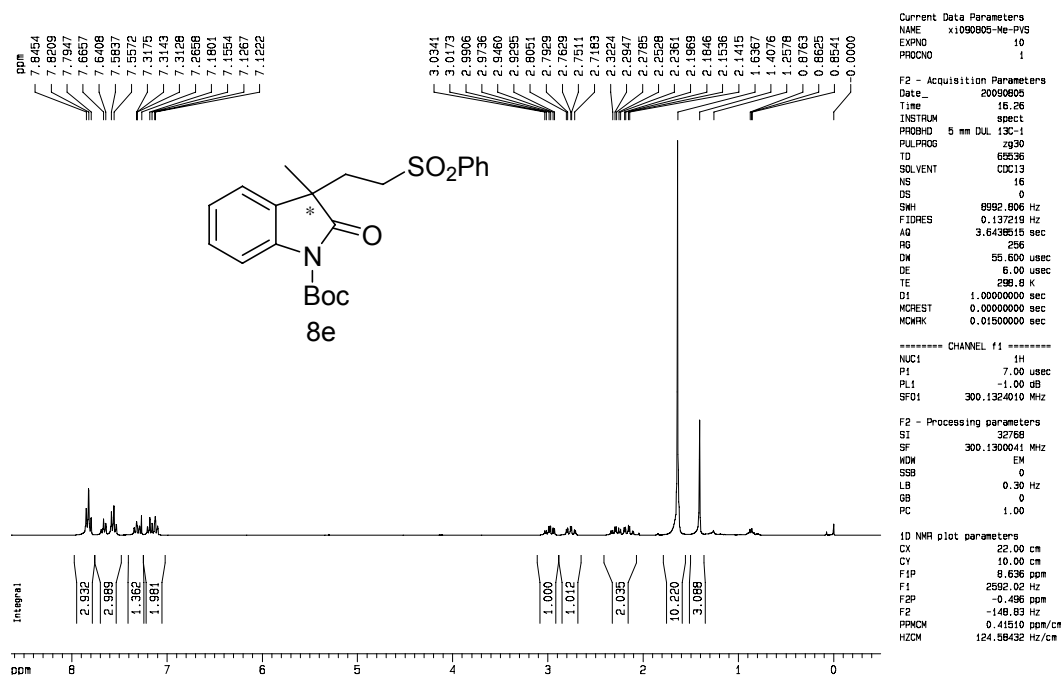




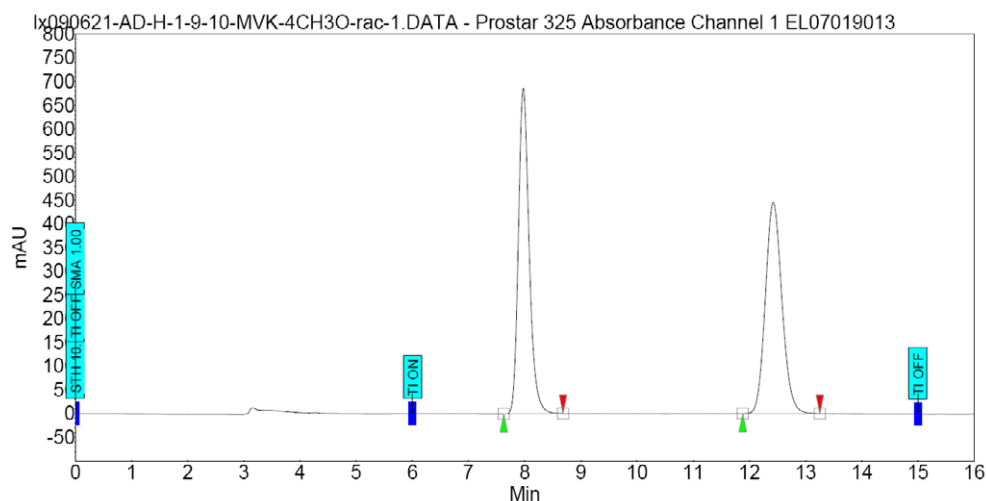
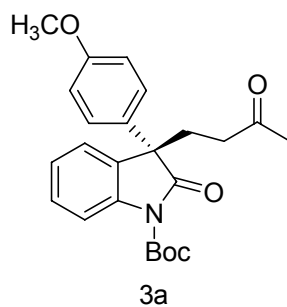






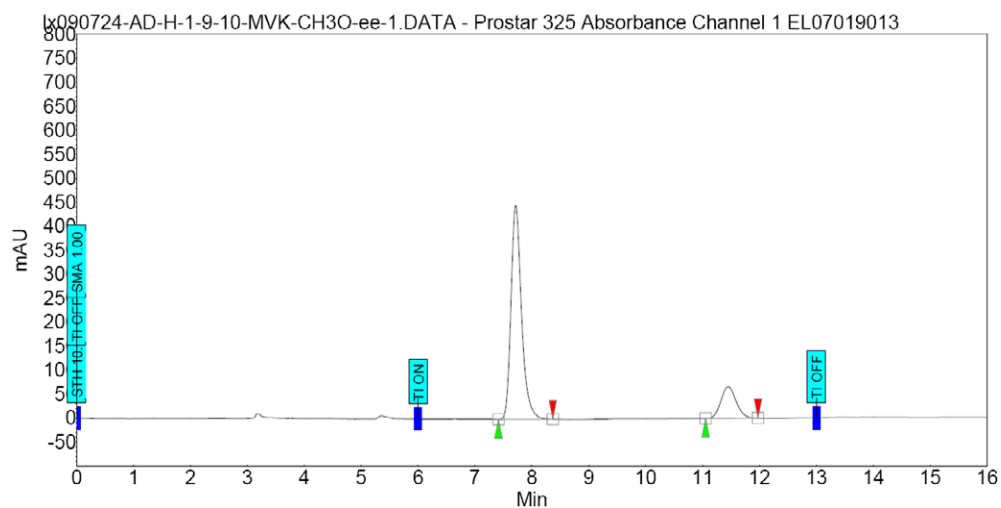


HPLC spectrum for Michael products:



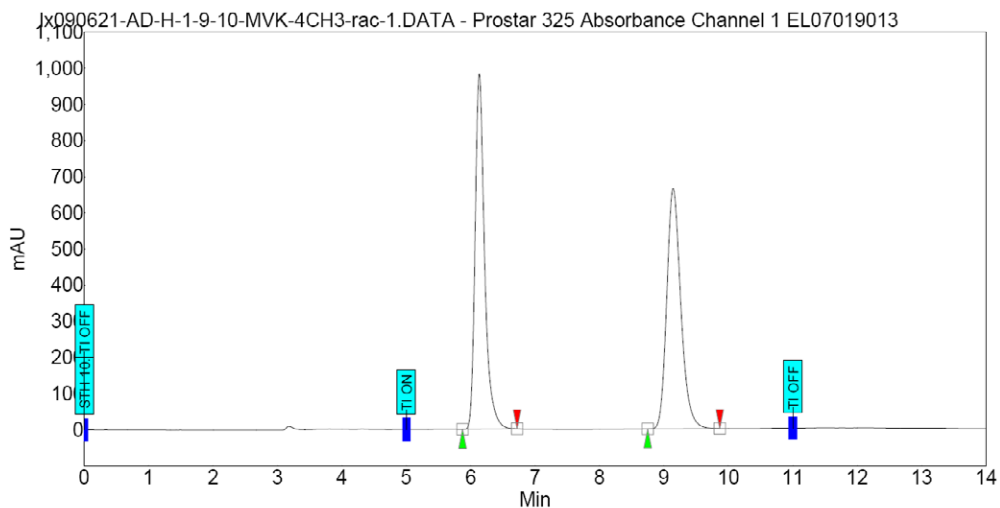
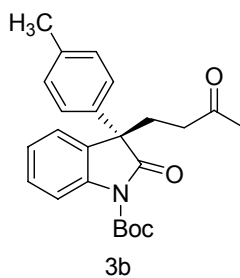
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.97	49.98	687.0	152.3	49.979
2	UNKNOWN	12.42	50.02	445.5	152.4	50.021
Total			100.00	1132.5	304.6	100.000



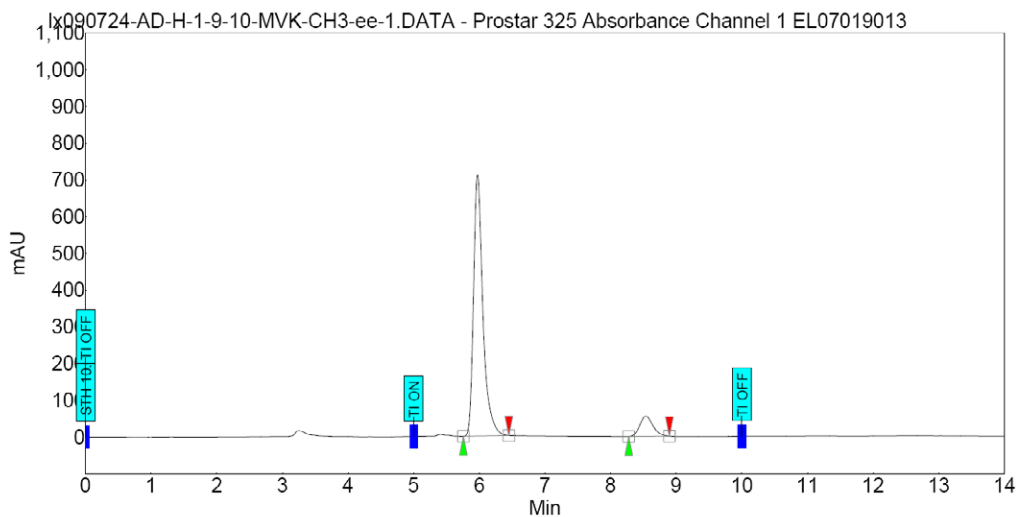
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.72	82.50	445.2	95.8	82.503
2	UNKNOWN	11.45	17.50	65.7	20.3	17.497
Total			100.00	511.0	116.1	100.000



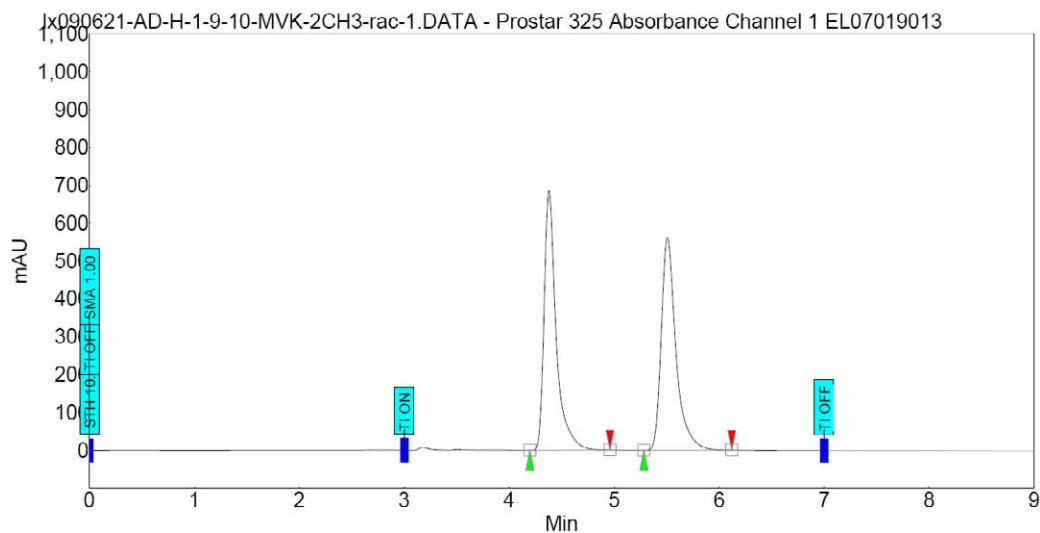
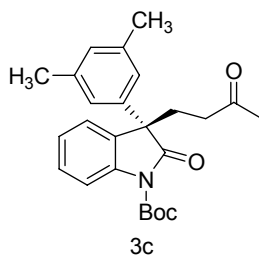
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.13	49.96	983.8	167.9	49.960
2	UNKNOWN	9.14	50.04	665.2	168.2	50.040
Total			100.00	1648.9	336.1	100.000



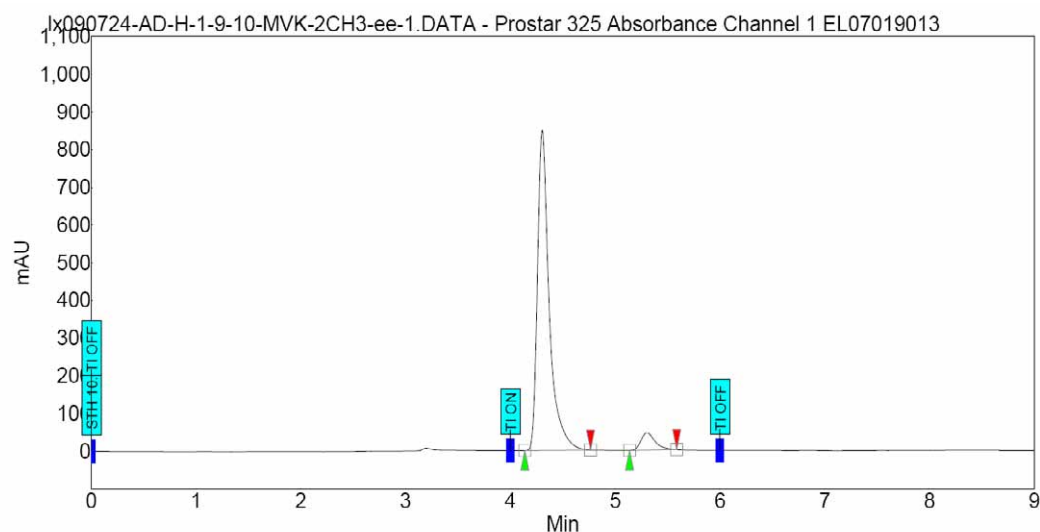
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.97	90.33	711.9	117.9	90.325
2	UNKNOWN	8.54	9.67	54.9	12.6	9.675
Total			100.00	766.8	130.5	100.000



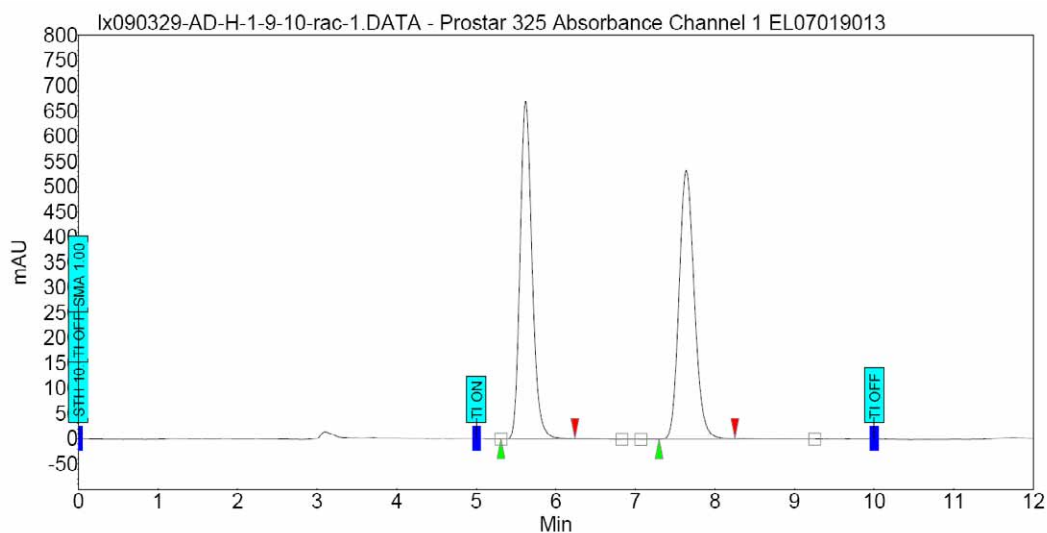
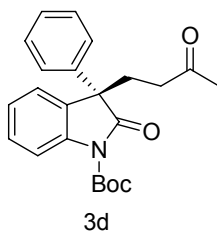
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Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.38	50.07	685.5	91.2	50.071
2	UNKNOWN	5.51	49.93	561.3	91.0	49.929
Total			100.00	1246.7	182.2	100.000



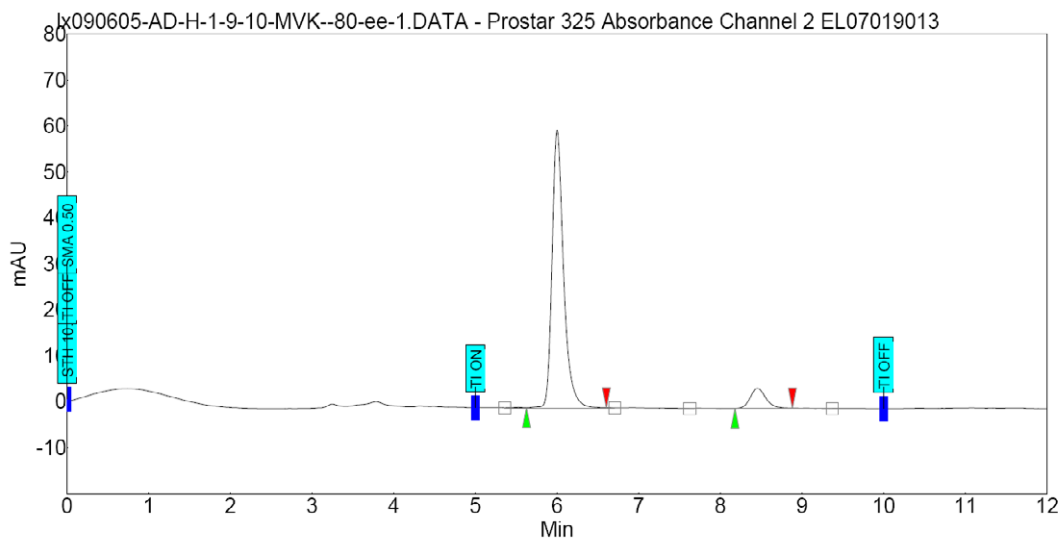
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1	UNKNOWN	4.30	93.95	848.8	110.3	93.948
2	UNKNOWN	5.30	6.05	46.1	7.1	6.052
Total			100.00	894.9	117.5	100.000



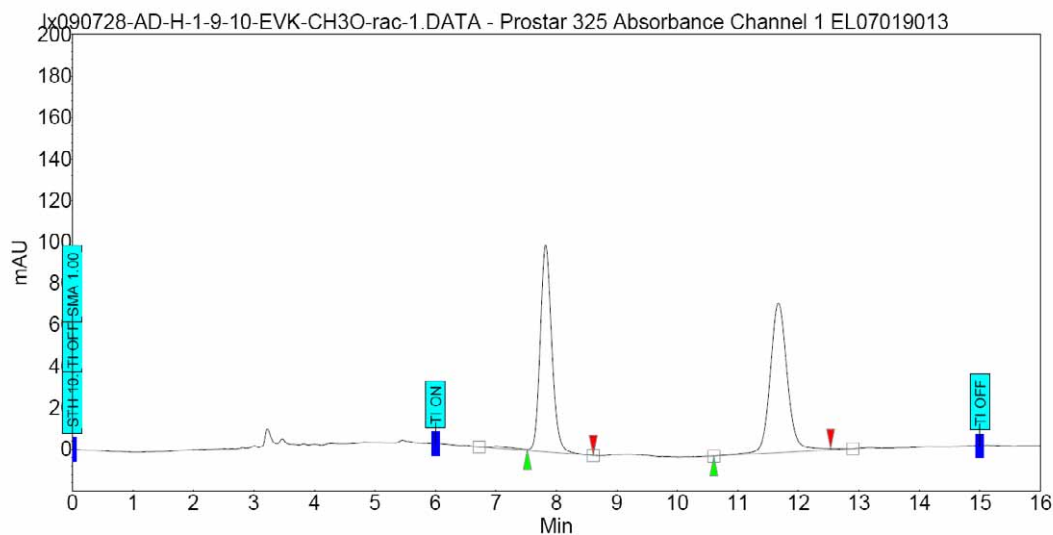
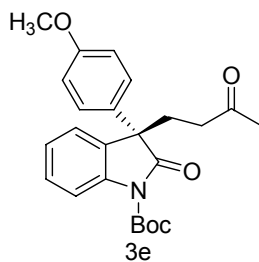
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1	UNKNOWN	5.62	49.75	669.9	117.5	49.754
2	UNKNOWN	7.64	50.25	532.7	118.6	50.246
Total			100.00	1202.7	236.1	100.000



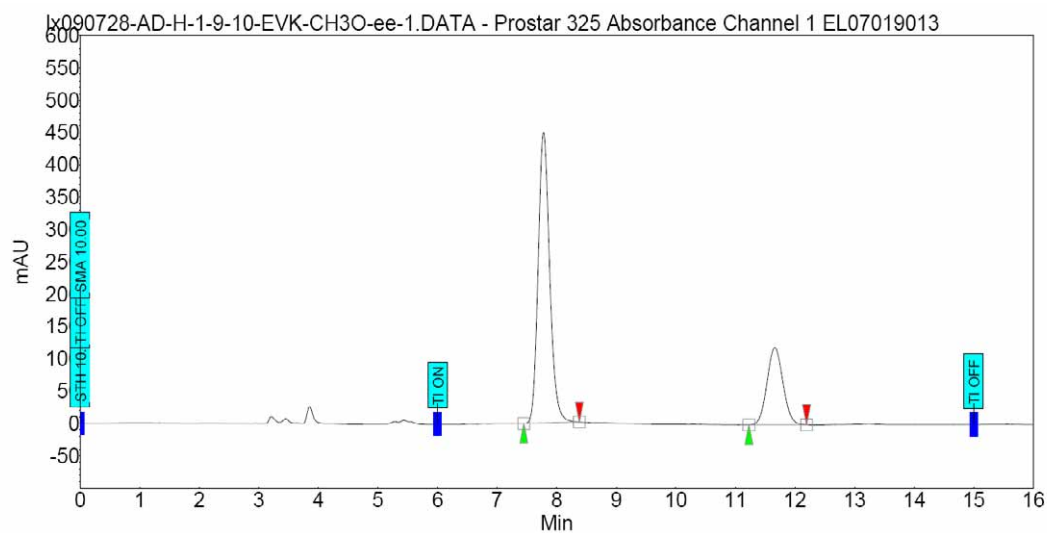
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Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	6.00	90.88	60.4	9.9	90.884
2	UNKNOWN	8.45	9.12	4.4	1.0	9.116
Total			100.00	64.8	10.9	100.000



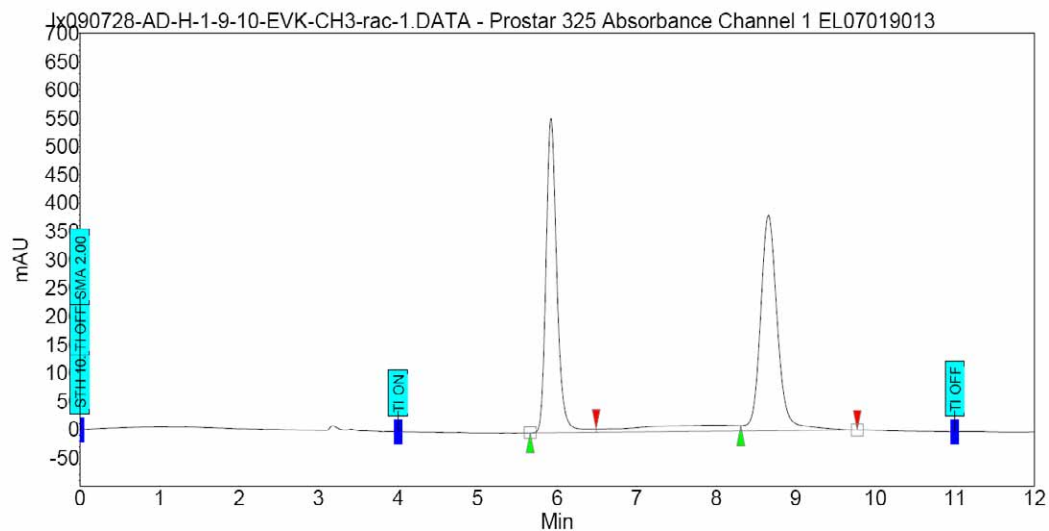
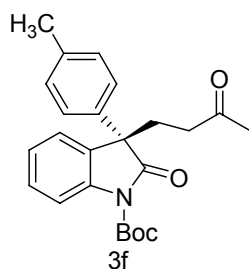
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1	UNKNOWN	7.82	48.21	99.8	22.1	48.208
2	UNKNOWN	11.67	51.79	72.2	23.7	51.792
Total			100.00	172.0	45.8	100.000



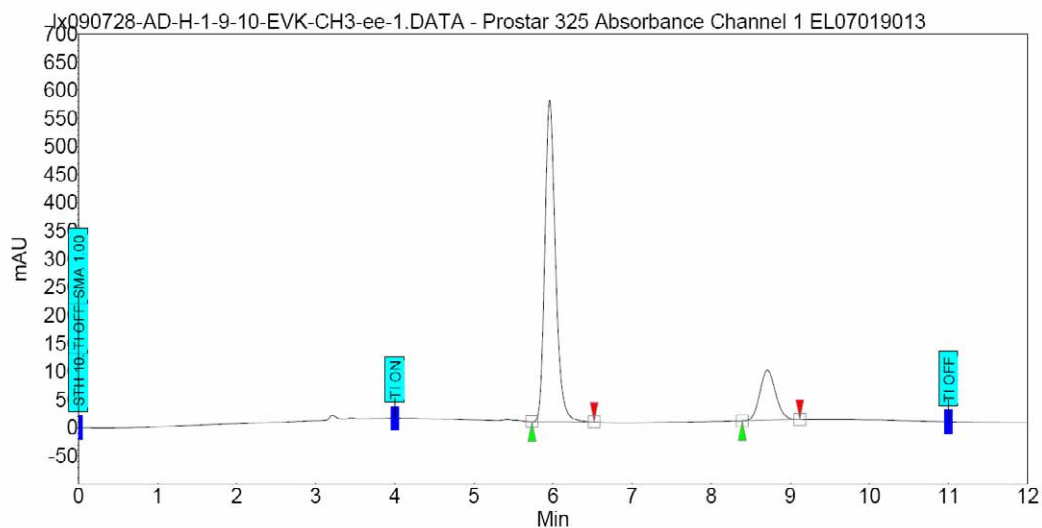
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Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area %
1	UNKNOWN	7.78	73.18	450.0	100.7	73.185
2	UNKNOWN	11.66	26.82	119.4	36.9	26.815
Total			100.00	569.4	137.6	100.000



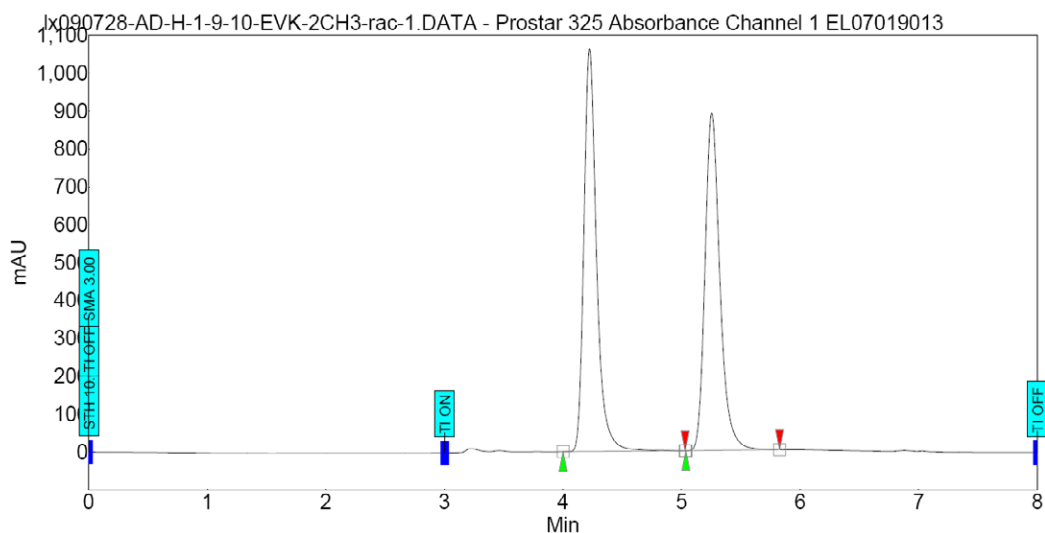
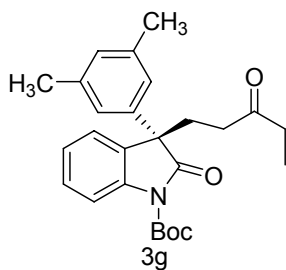
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.92	48.18	555.5	87.9	48.178
2	UNKNOWN	8.66	51.82	381.1	94.6	51.822
Total			100.00	936.6	182.5	100.000



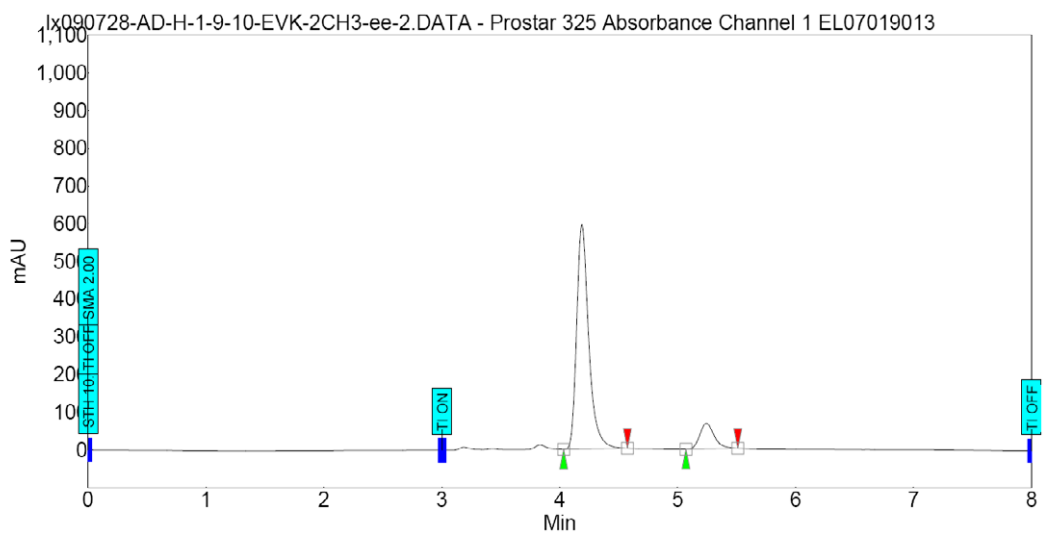
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.96	81.30	571.4	89.1	81.301
2	UNKNOWN	8.71	18.70	89.1	20.5	18.699
Total			100.00	660.4	109.6	100.000



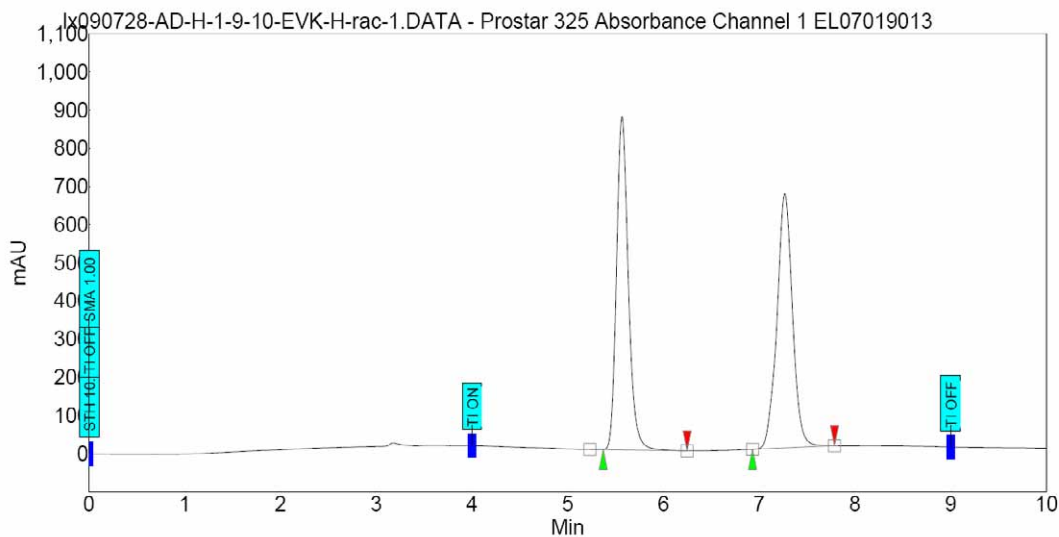
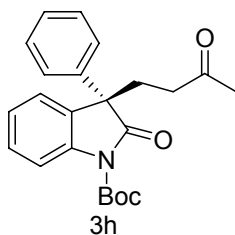
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.22	50.27	1064.1	131.7	50.266
2	UNKNOWN	5.25	49.73	891.1	130.3	49.734
Total			100.00	1955.2	262.0	100.000



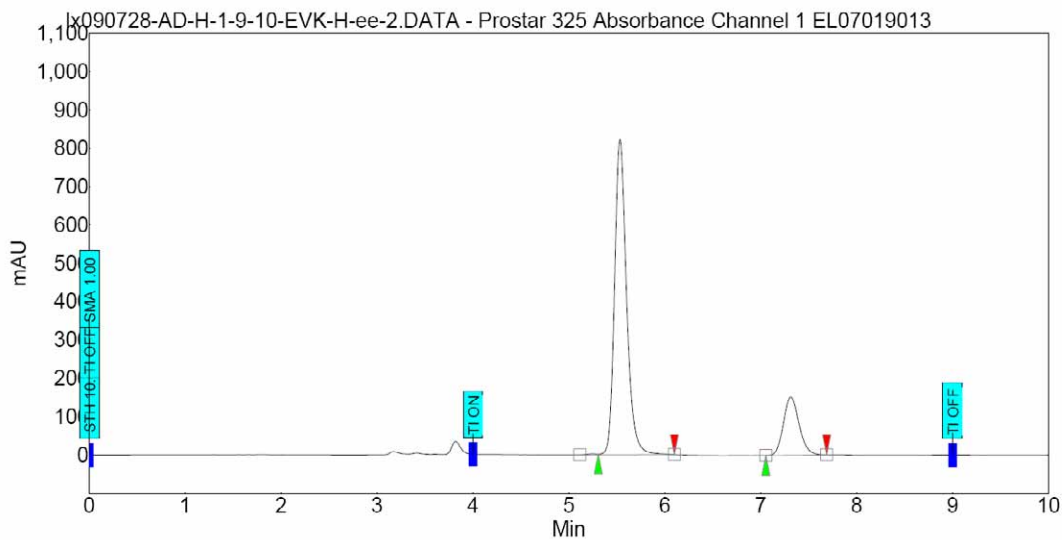
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	4.19	88.04	594.8	70.5	88.041
2	UNKNOWN	5.24	11.96	67.6	9.6	11.959
Total			100.00	662.4	80.1	100.000



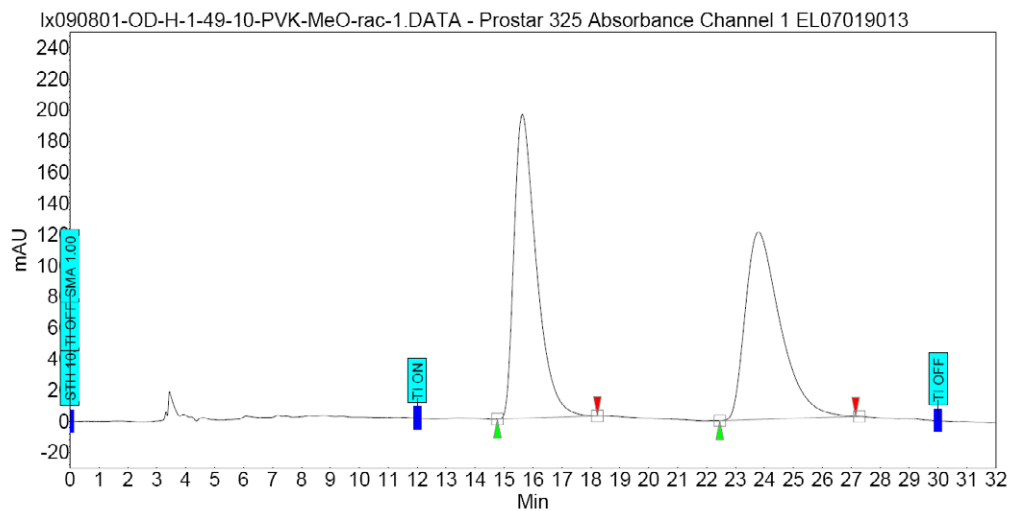
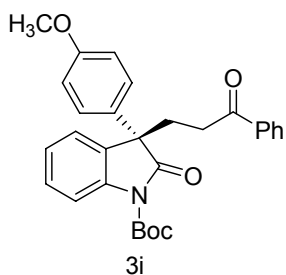
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.57	49.92	873.5	125.0	49.919
2	UNKNOWN	7.27	50.08	665.8	125.4	50.081
Total			100.00	1539.3	250.4	100.000



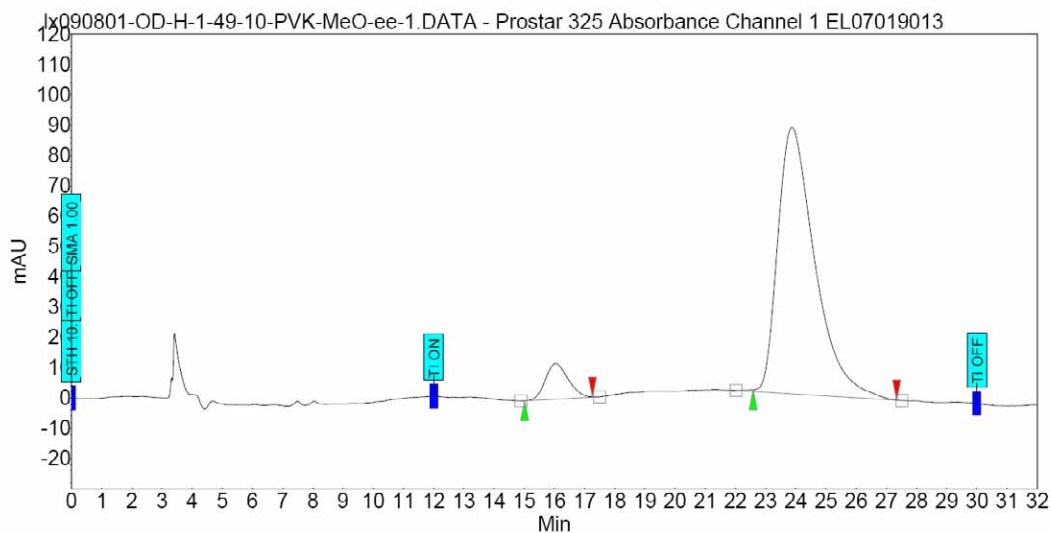
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.53	80.64	822.6	119.1	80.640
2	UNKNOWN	7.31	19.36	151.6	28.6	19.360
Total			100.00	974.2	147.7	100.000



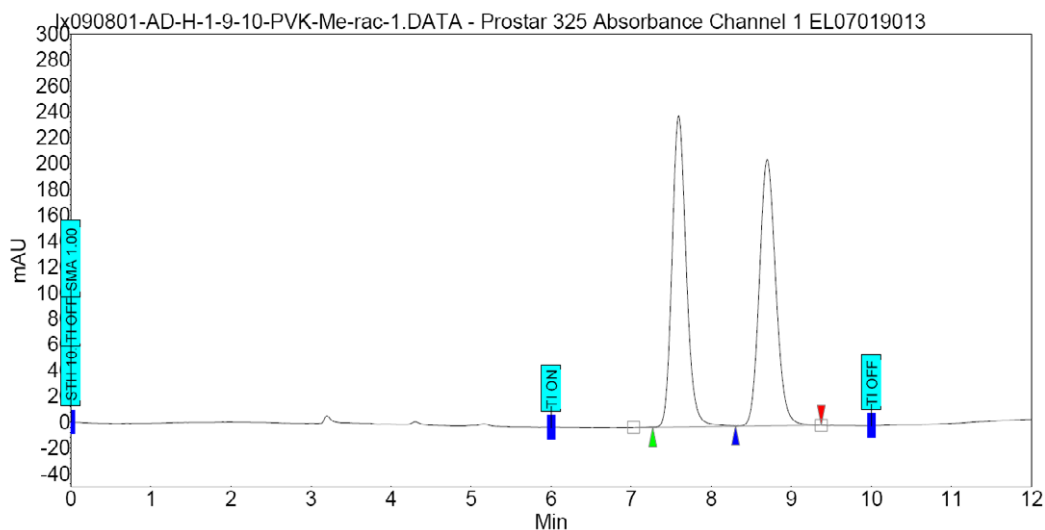
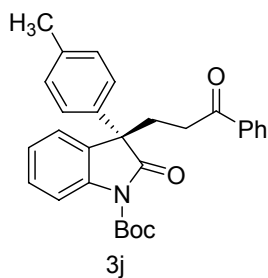
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15.63	50.88	195.3	174.9	50.881
2	UNKNOWN	23.79	49.12	120.5	168.9	49.119
Total			100.00	315.8	343.8	100.000



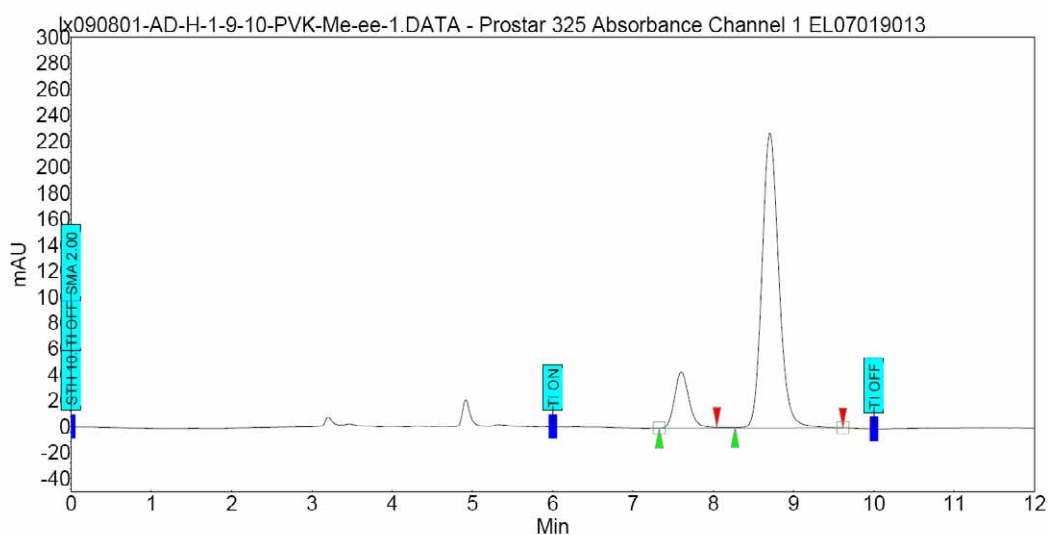
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16.05	7.59	11.7	10.3	7.587
2	UNKNOWN	23.88	92.41	87.9	125.0	92.413
Total			100.00	99.6	135.3	100.000



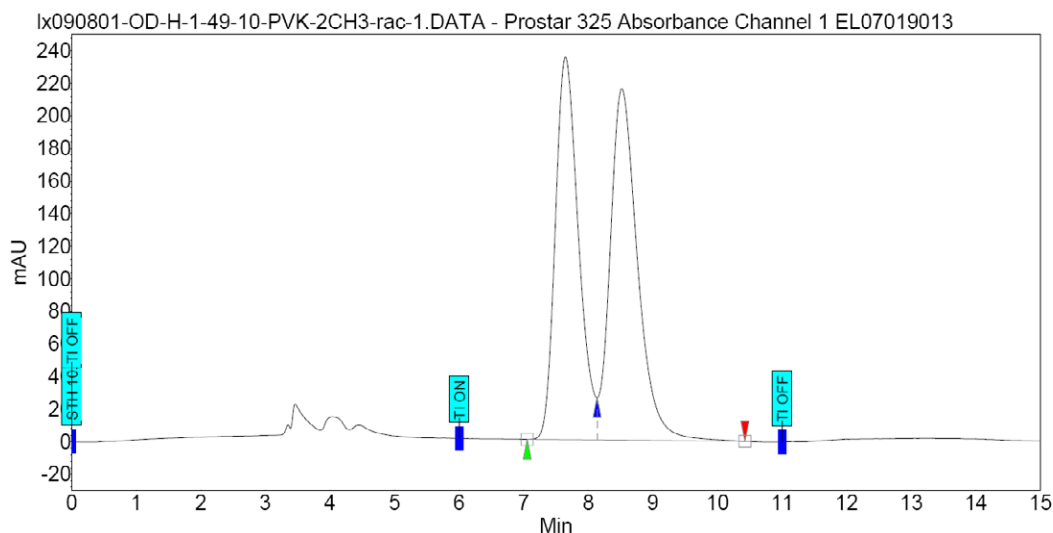
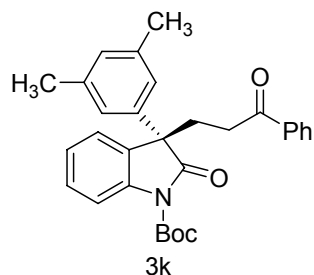
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.59	50.17	240.6	49.4	50.172
2	UNKNOWN	8.70	49.83	206.1	49.1	49.828
Total			100.00	446.7	98.5	100.000



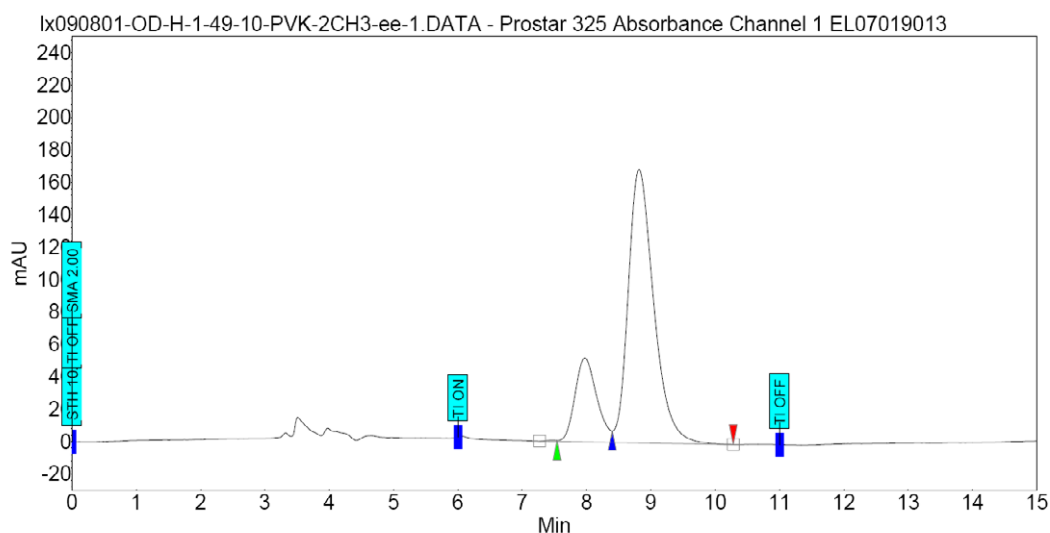
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.60	14.01	43.2	9.0	14.006
2	UNKNOWN	8.70	85.99	227.2	55.0	85.994
Total			100.00	270.4	64.0	100.000



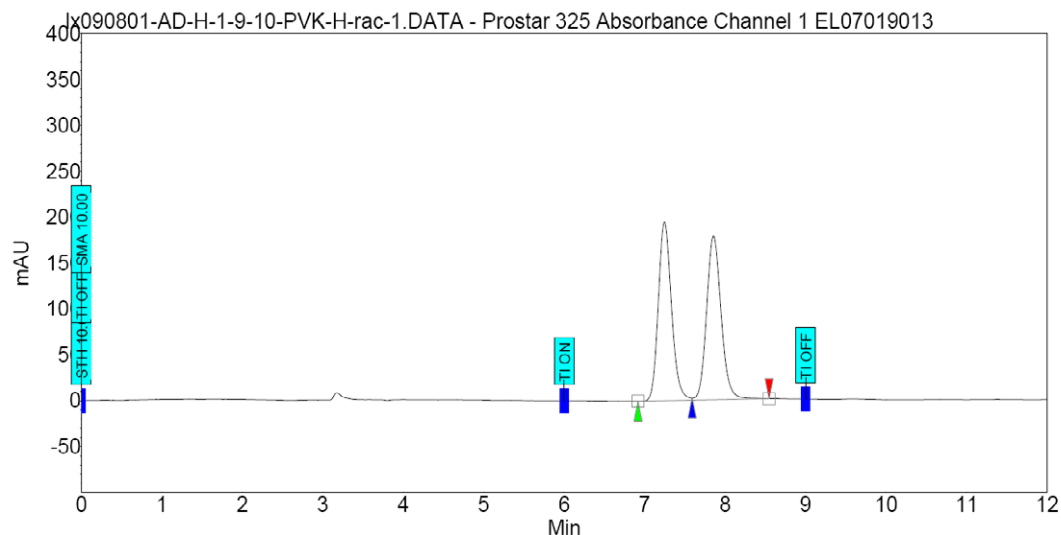
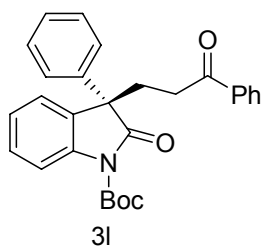
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.65	47.89	234.9	97.5	47.891
2	UNKNOWN	8.52	52.11	215.8	106.1	52.109
Total			100.00	450.7	203.6	100.000



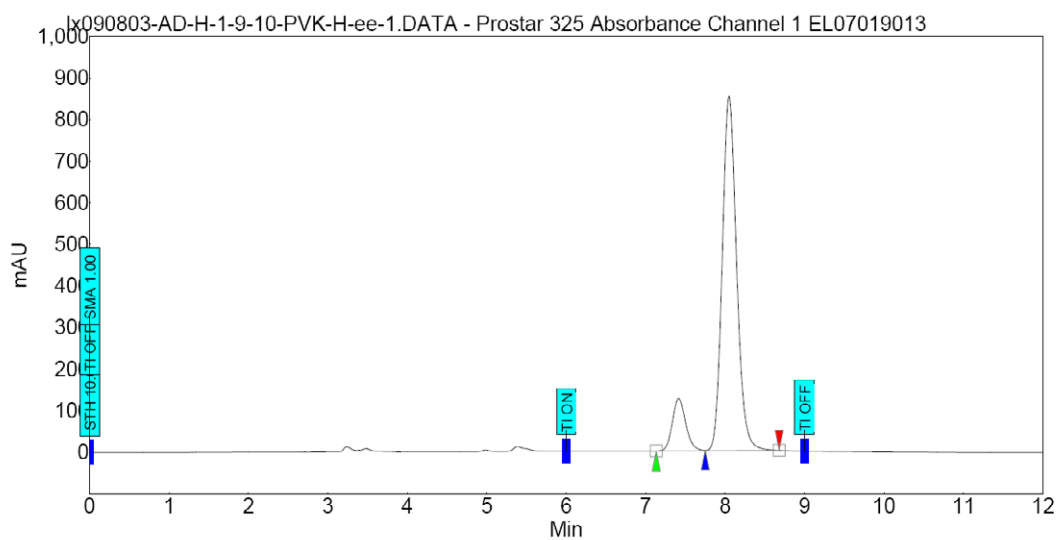
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.97	20.79	51.9	20.4	20.785
2	UNKNOWN	8.82	79.21	168.8	77.7	79.215
Total			100.00	220.6	98.0	100.000



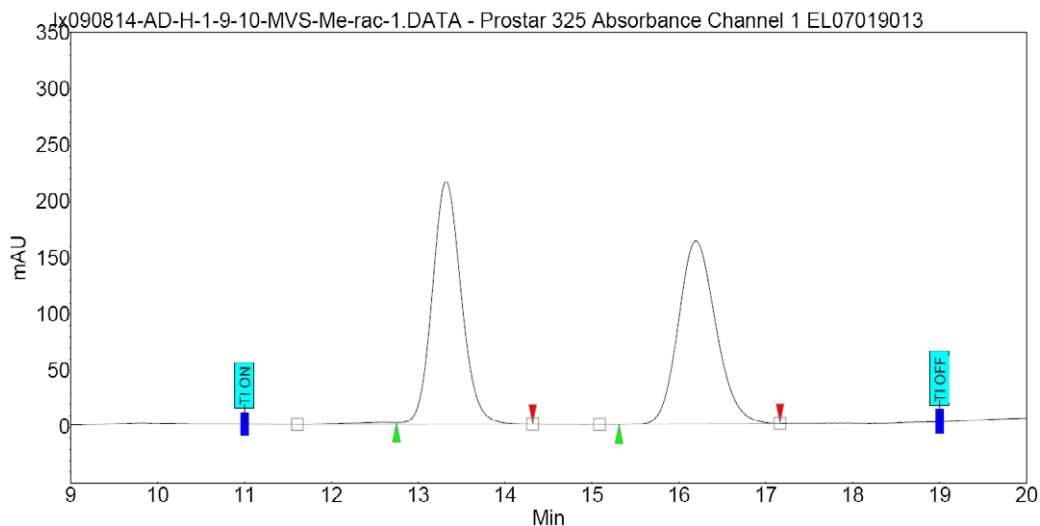
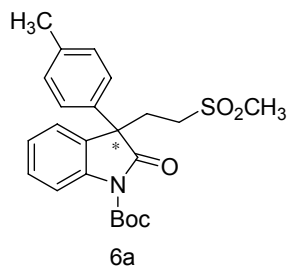
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.25	49.72	194.9	36.9	49.721
2	UNKNOWN	7.85	50.28	178.6	37.3	50.279
Total			100.00	373.4	74.2	100.000



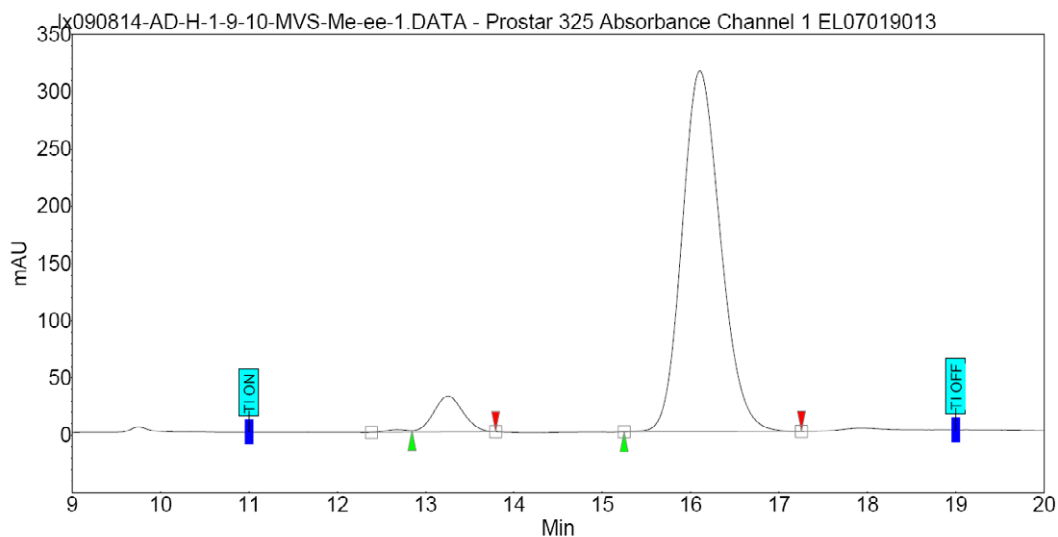
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.41	12.07	125.8	24.5	12.070
2	UNKNOWN	8.05	87.93	851.7	178.5	87.930
Total			100.00	977.4	203.0	100.000



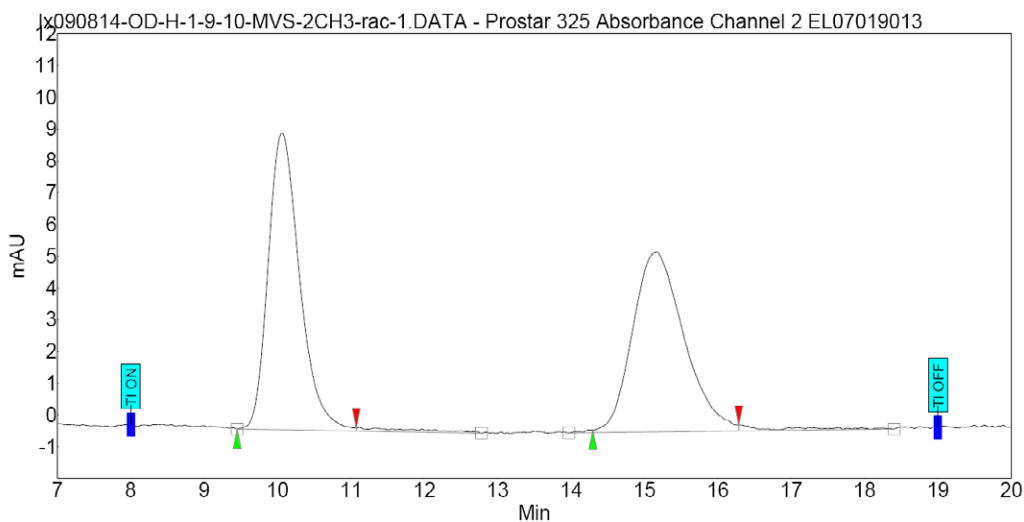
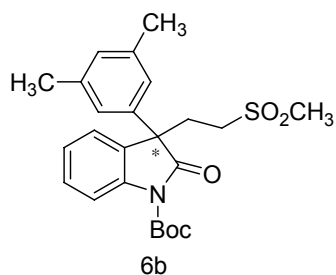
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.32	50.65	215.6	83.2	50.653
2	UNKNOWN	16.19	49.35	162.5	81.1	49.347
Total			100.00	378.1	164.3	100.000



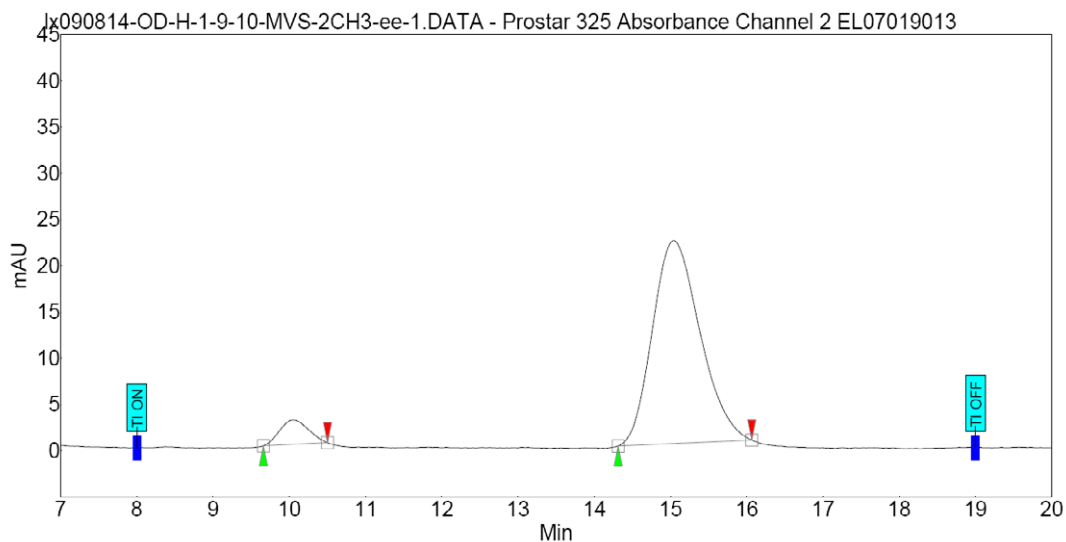
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.25	7.00	31.2	12.0	7.005
2	UNKNOWN	16.10	93.00	315.1	159.0	92.995
Total			100.00	346.3	171.0	100.000



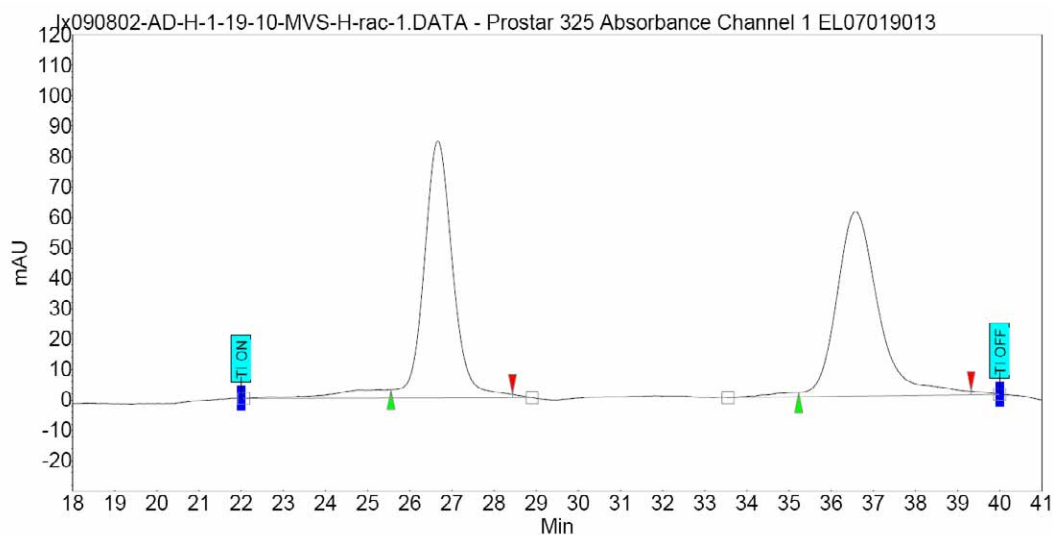
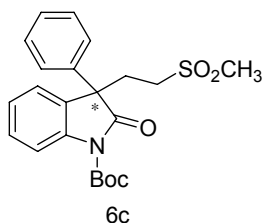
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.06	50.29	9.3	4.6	50.285
2	UNKNOWN	15.16	49.71	5.7	4.6	49.715
Total			100.00	15.0	9.2	100.000



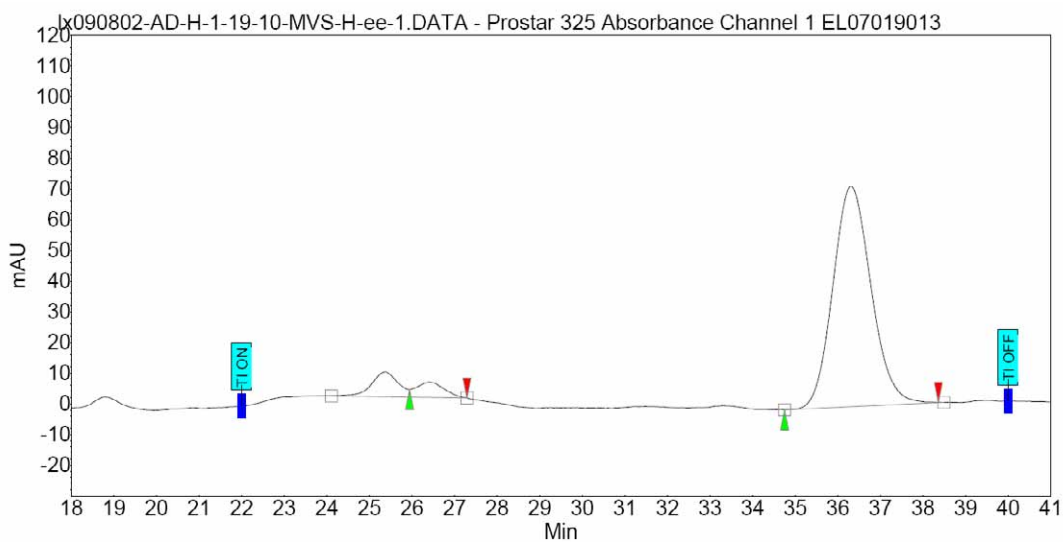
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10.04	6.73	2.6	1.1	6.729
2	UNKNOWN	15.04	93.27	21.9	15.8	93.271
Total			100.00	24.6	17.0	100.000



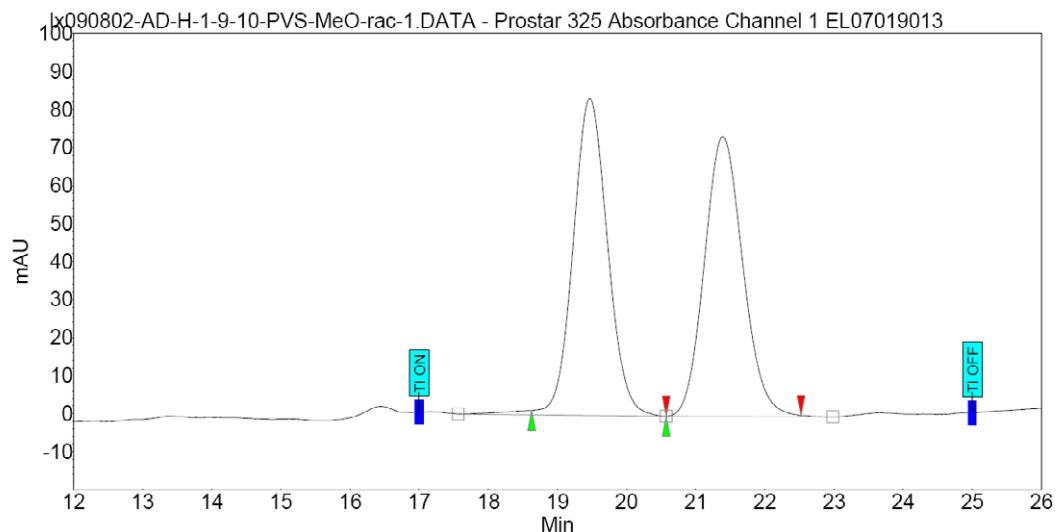
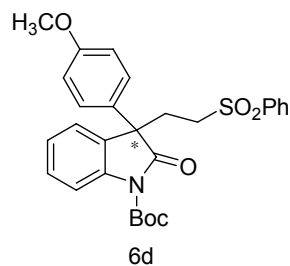
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.66	48.77	84.5	66.3	48.768
2	UNKNOWN	36.57	51.23	60.7	69.7	51.232
Total			100.00	145.2	136.0	100.000



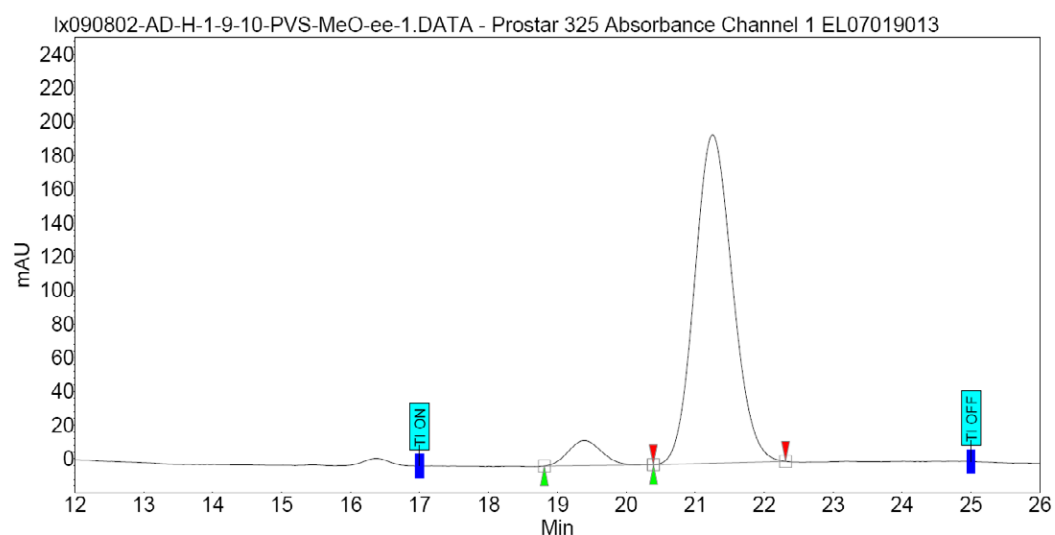
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.42	4.84	5.0	3.8	4.837
2	UNKNOWN	36.30	95.16	71.8	74.6	95.163
Total			100.00	76.8	78.4	100.000



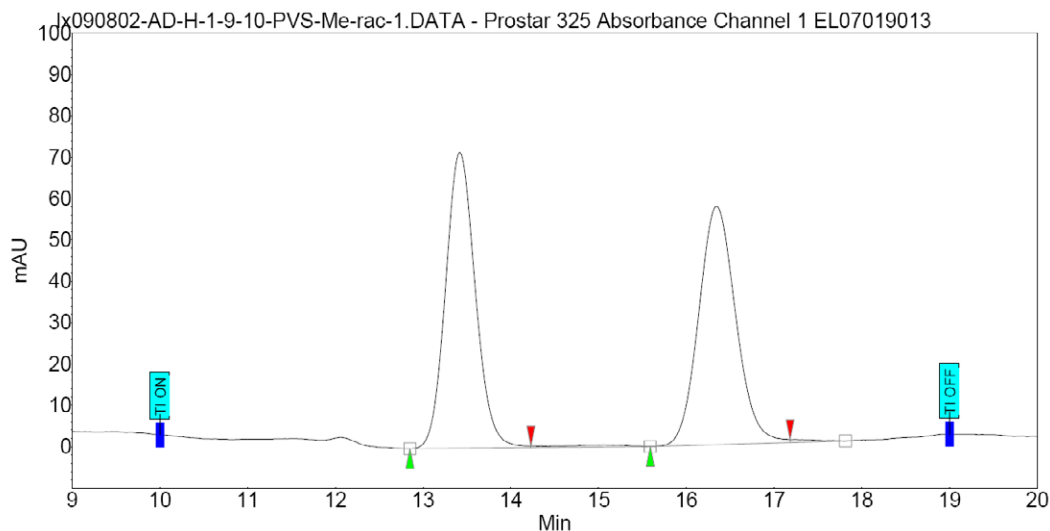
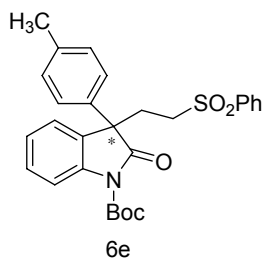
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.47	50.30	83.4	48.1	50.301
2	UNKNOWN	21.39	49.70	73.6	47.5	49.699
Total			100.00	157.0	95.6	100.000



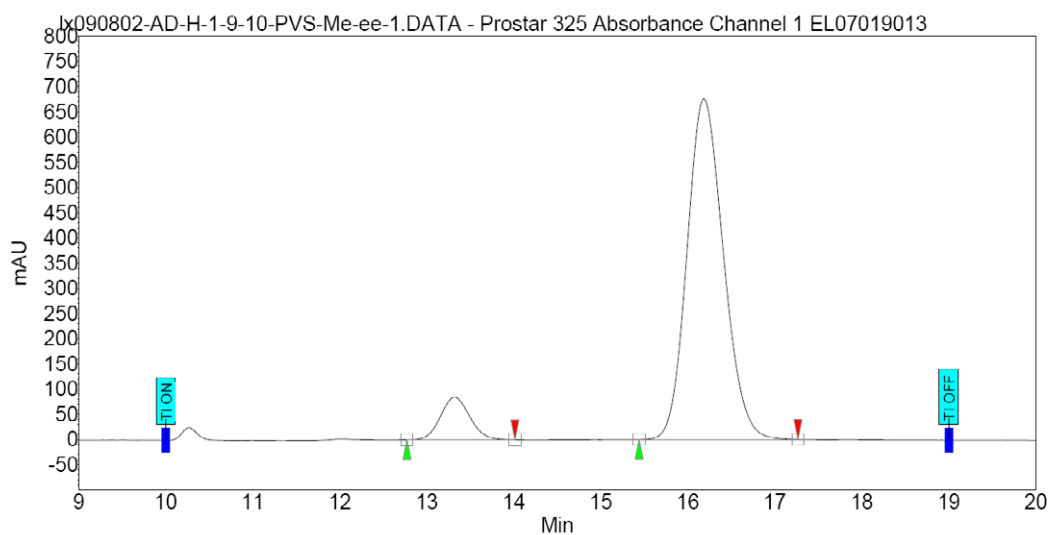
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.39	6.24	14.8	8.3	6.245
2	UNKNOWN	21.25	93.76	194.9	124.0	93.755
Total			100.00	209.7	132.2	100.000



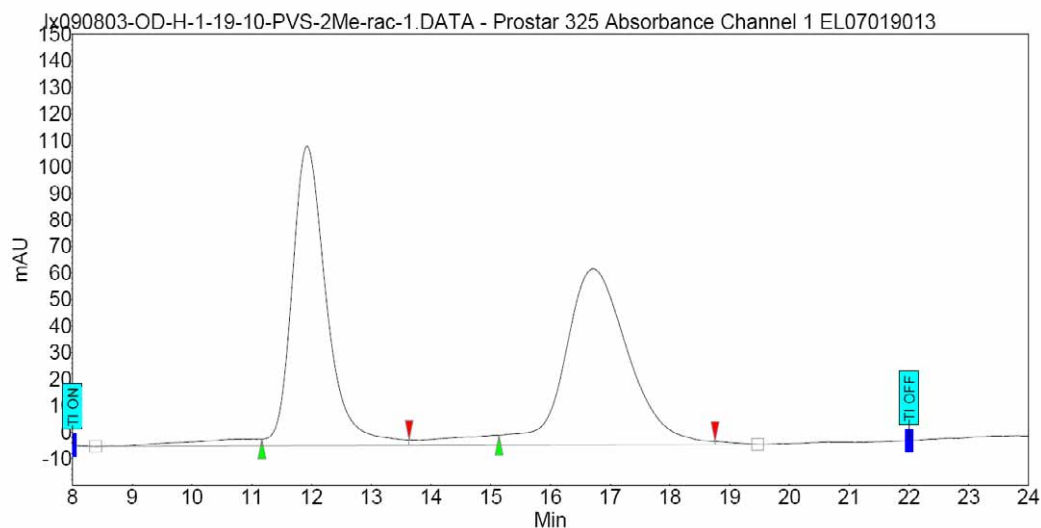
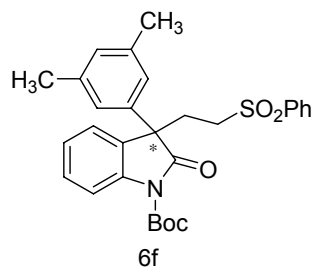
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.42	49.88	71.5	28.1	49.883
2	UNKNOWN	16.34	50.12	57.6	28.2	50.117
Total			100.00	129.1	56.3	100.000



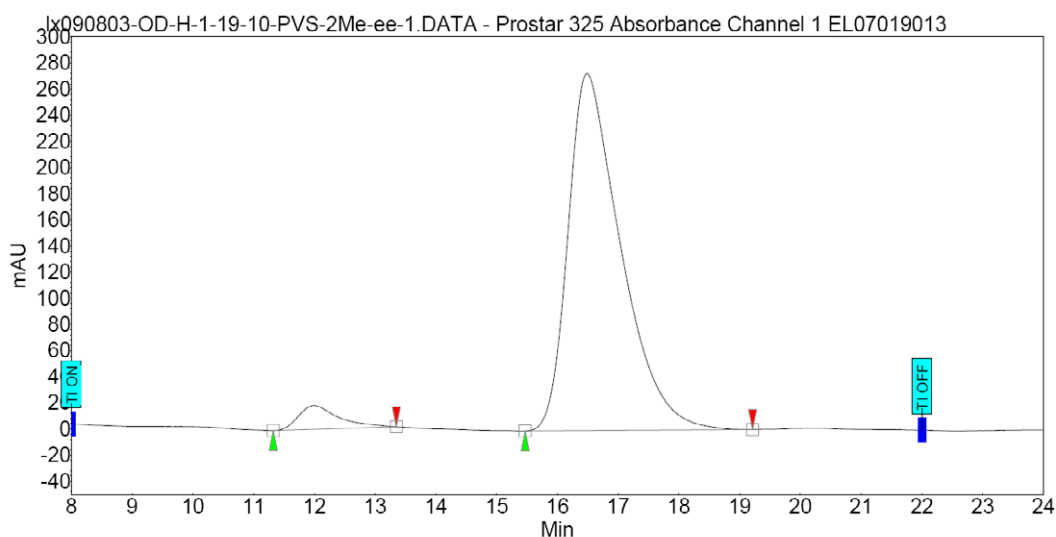
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13.32	9.04	84.0	32.6	9.043
2	UNKNOWN	16.18	90.96	675.8	327.6	90.957
Total			100.00	759.8	360.1	100.000



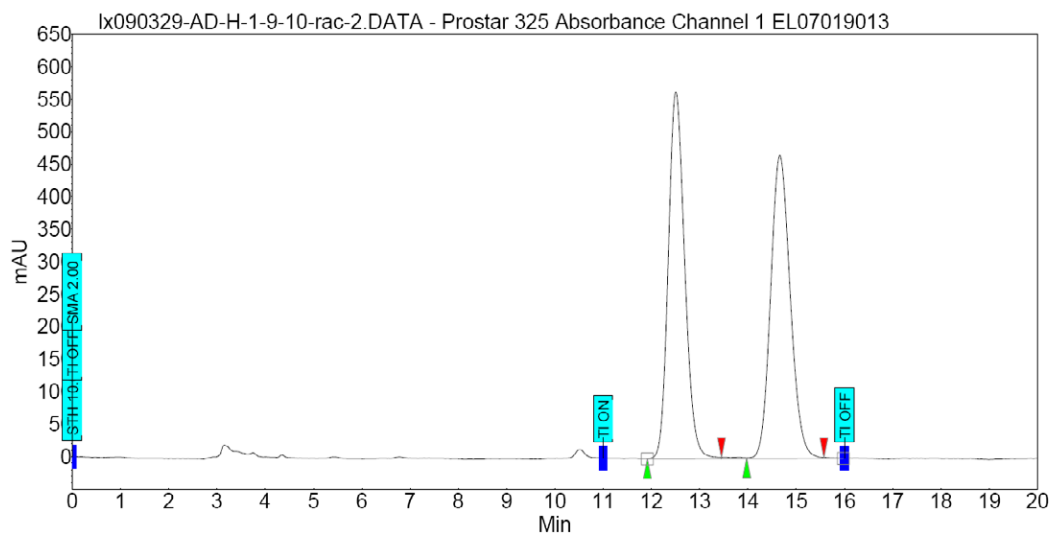
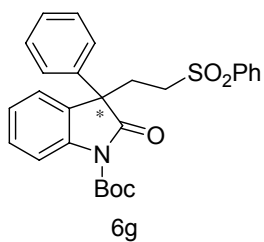
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.93	48.28	113.0	75.6	48.278
2	UNKNOWN	16.72	51.72	66.4	80.9	51.722
Total			100.00	179.4	156.5	100.000



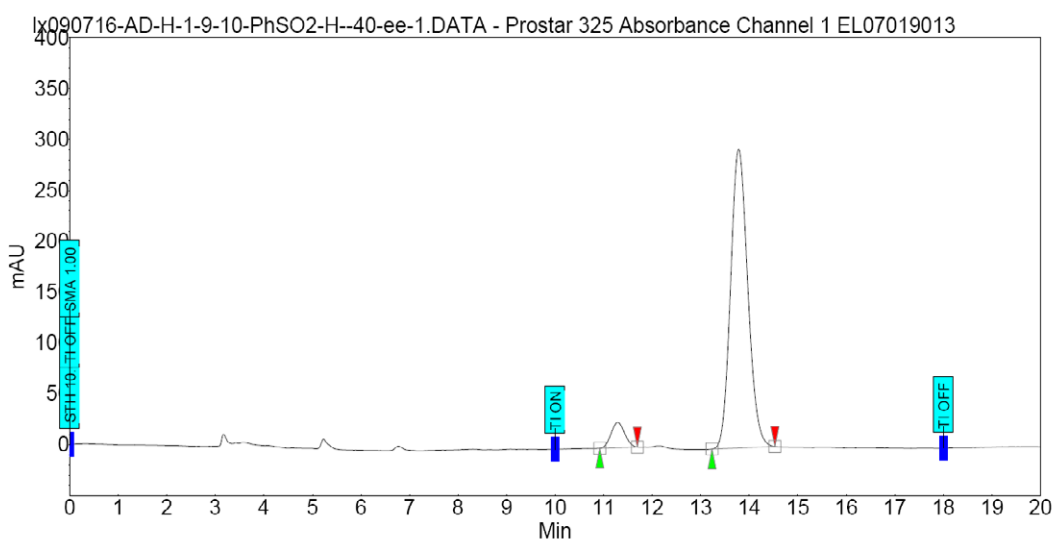
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.99	4.83	18.1	13.9	4.830
2	UNKNOWN	16.49	95.17	273.1	274.2	95.170
Total			100.00	291.2	288.1	100.000



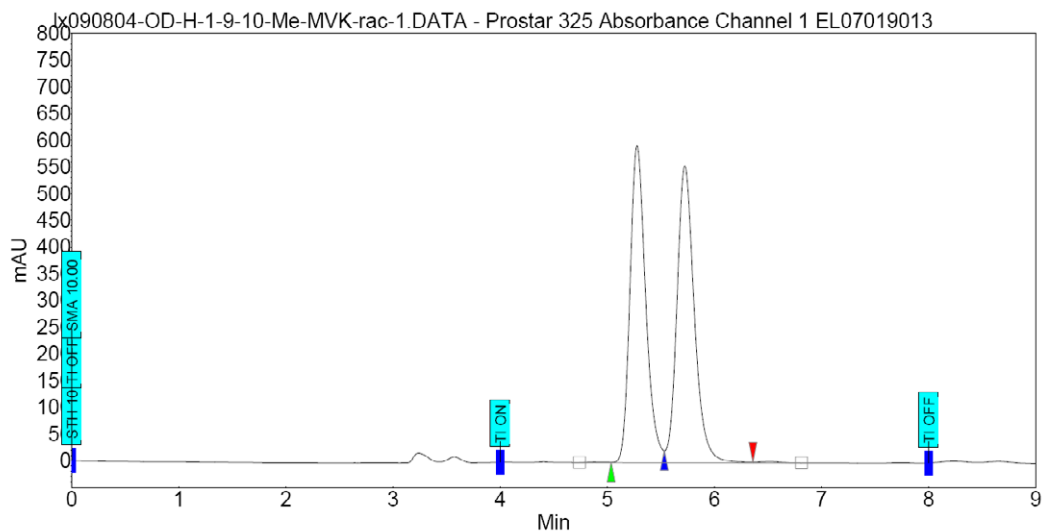
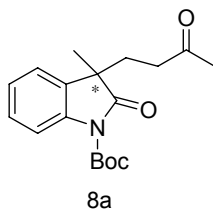
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12.51	50.32	564.7	222.4	50.318
2	UNKNOWN	14.66	49.68	466.4	219.6	49.682
Total			100.00	1031.1	442.0	100.000



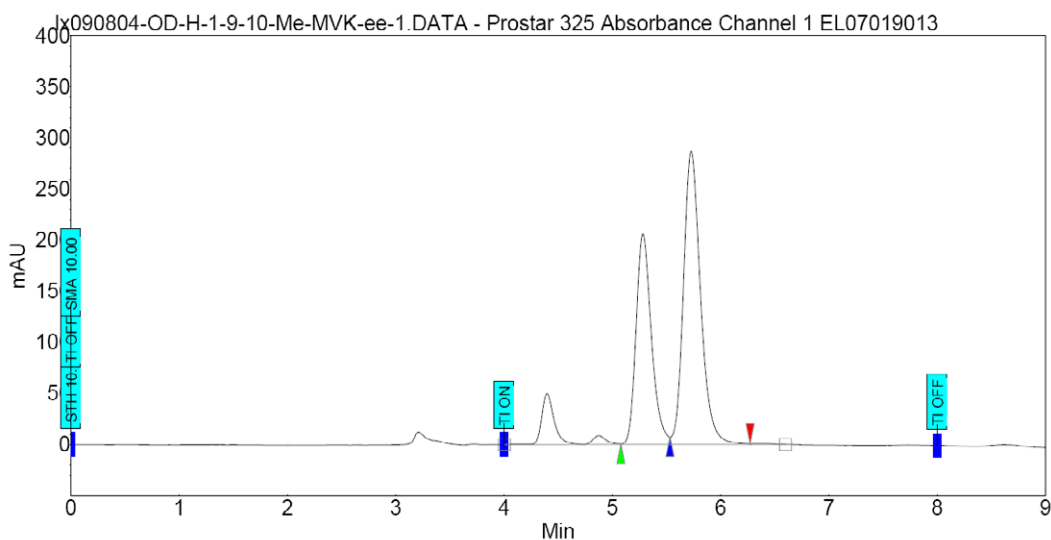
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.29	6.26	24.9	8.1	6.263
2	UNKNOWN	13.78	93.74	294.1	120.6	93.737
Total			100.00	318.9	128.7	100.000



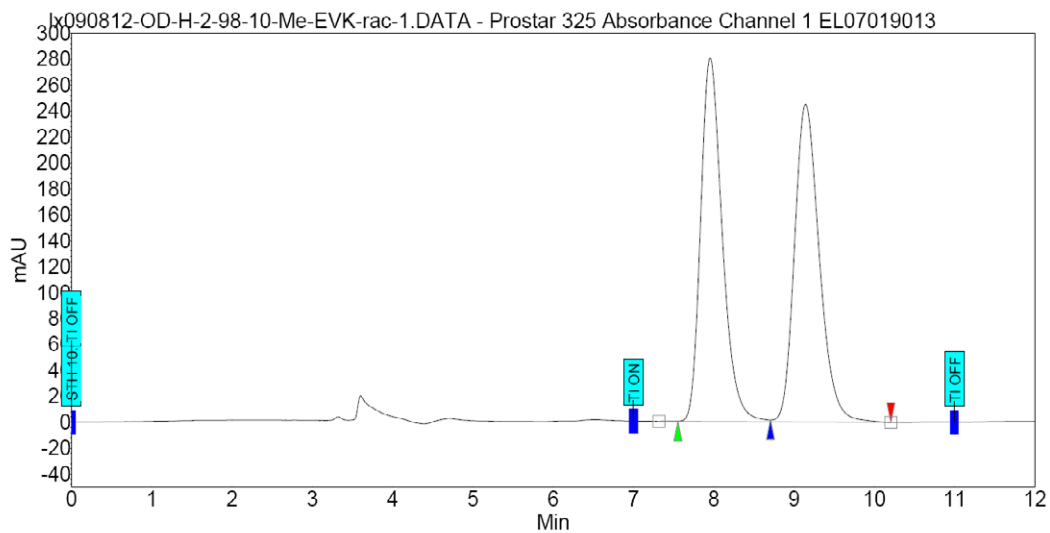
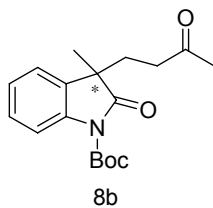
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.28	49.18	593.6	100.8	49.177
2	UNKNOWN	5.72	50.82	555.8	104.2	50.823
Total			100.00	1149.4	205.0	100.000



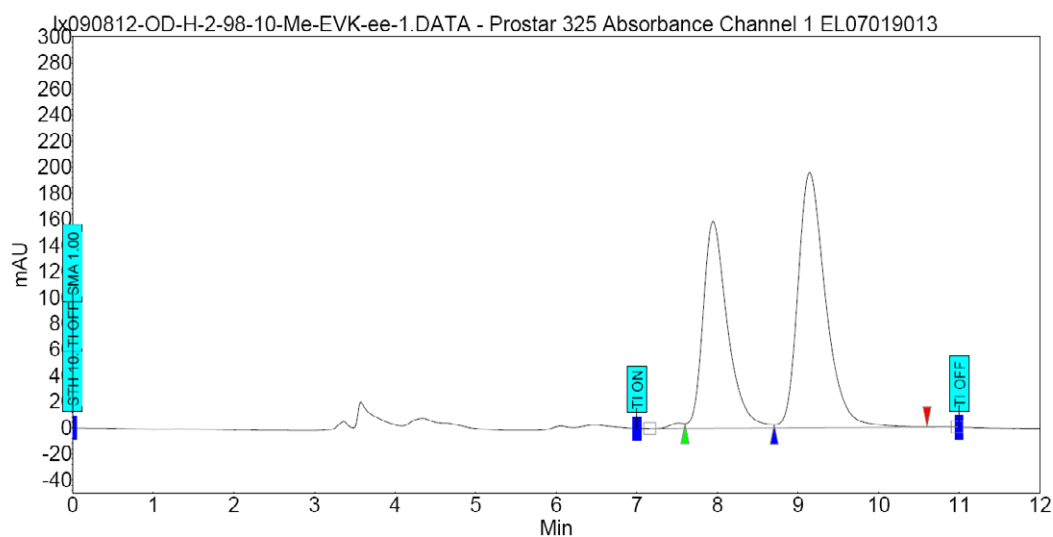
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	5.28	39.25	206.2	33.8	39.246
2	UNKNOWN	5.73	60.75	286.7	52.4	60.754
Total			100.00	492.9	86.2	100.000



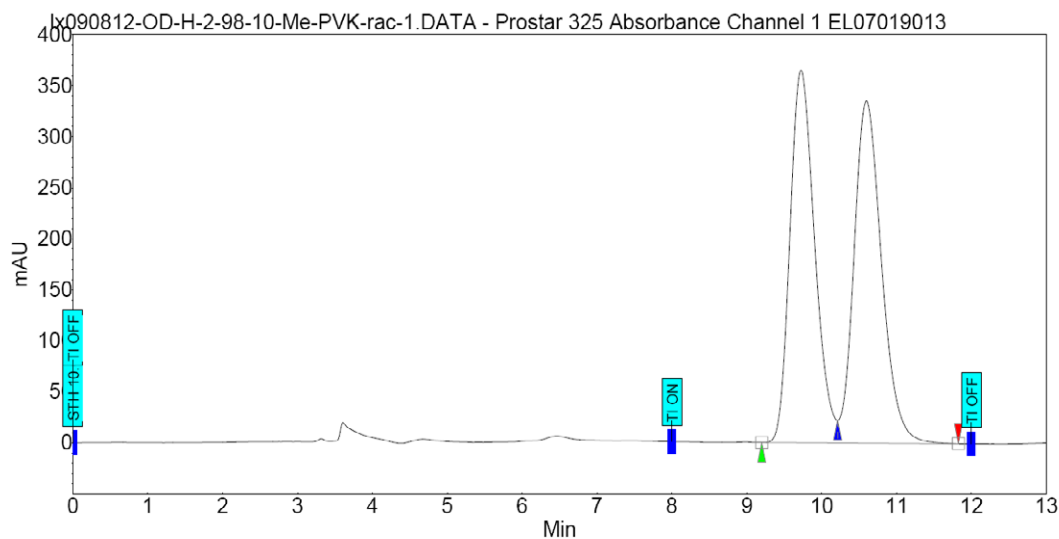
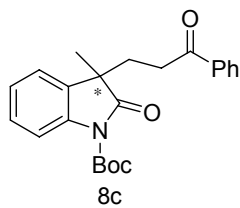
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.96	49.92	280.7	87.7	49.922
2	UNKNOWN	9.14	50.08	245.2	88.0	50.078
Total			100.00	525.9	175.7	100.000



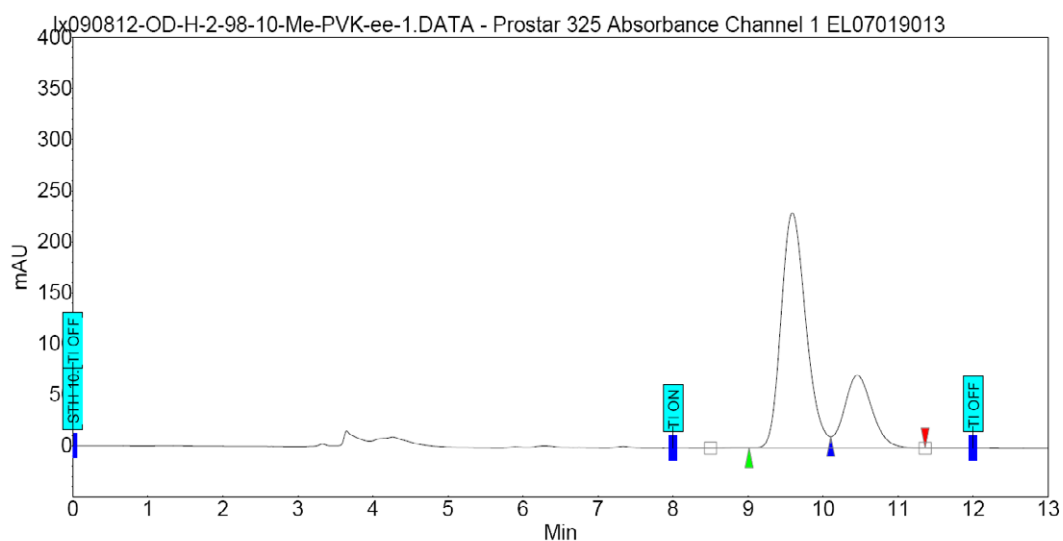
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	7.94	41.69	158.6	55.7	41.686
2	UNKNOWN	9.14	58.31	195.8	77.9	58.314
Total			100.00	354.4	133.6	100.000



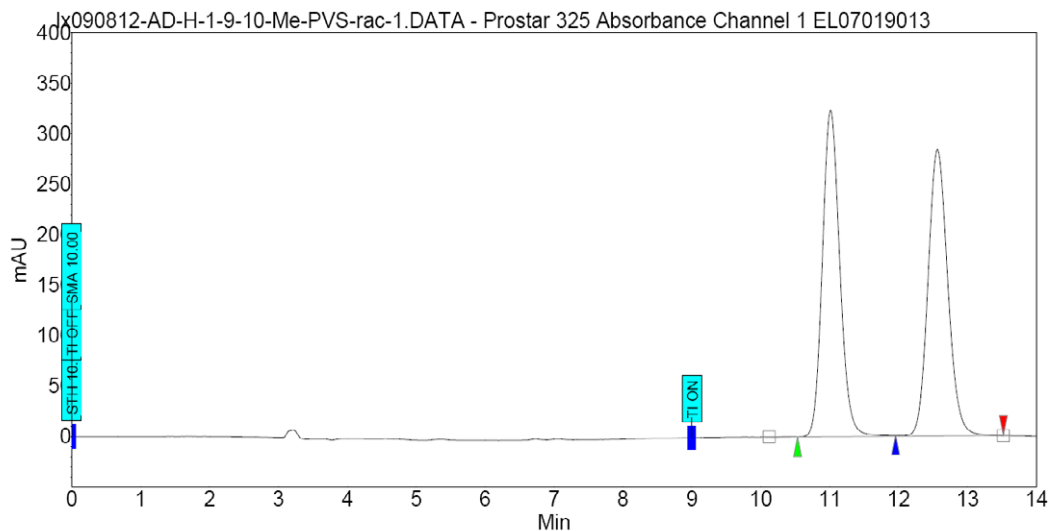
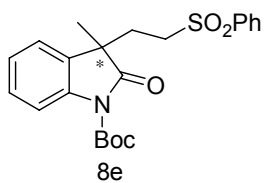
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.72	49.33	365.3	139.5	49.329
2	UNKNOWN	10.60	50.67	335.4	143.3	50.671
Total			100.00	700.7	282.7	100.000



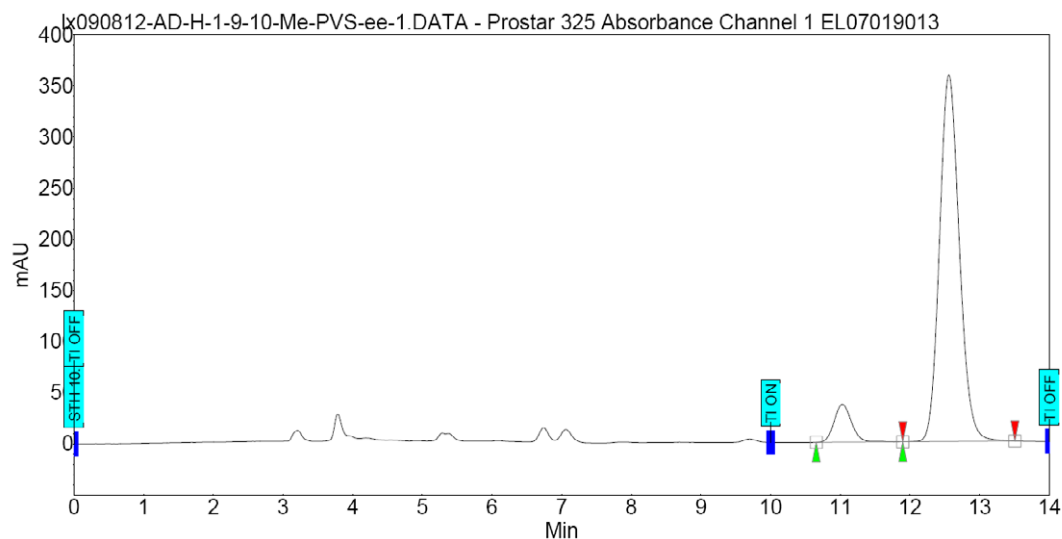
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	9.59	74.34	230.6	88.3	74.345
2	UNKNOWN	10.46	25.66	71.5	30.5	25.655
Total			100.00	302.0	118.8	100.000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.01	50.07	323.5	94.7	50.068
2	UNKNOWN	12.56	49.93	283.9	94.4	49.932
Total			100.00	607.4	189.1	100.000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11.03	8.25	36.9	10.6	8.248
2	UNKNOWN	12.56	91.75	358.7	118.4	91.752
Total			100.00	395.6	129.1	100.000