

Efficient enantioselective fluorination of β -keto esters/amides catalysed by diphenylamine-linked bis(thiazoline)-Cu(OTf)₂ complexes

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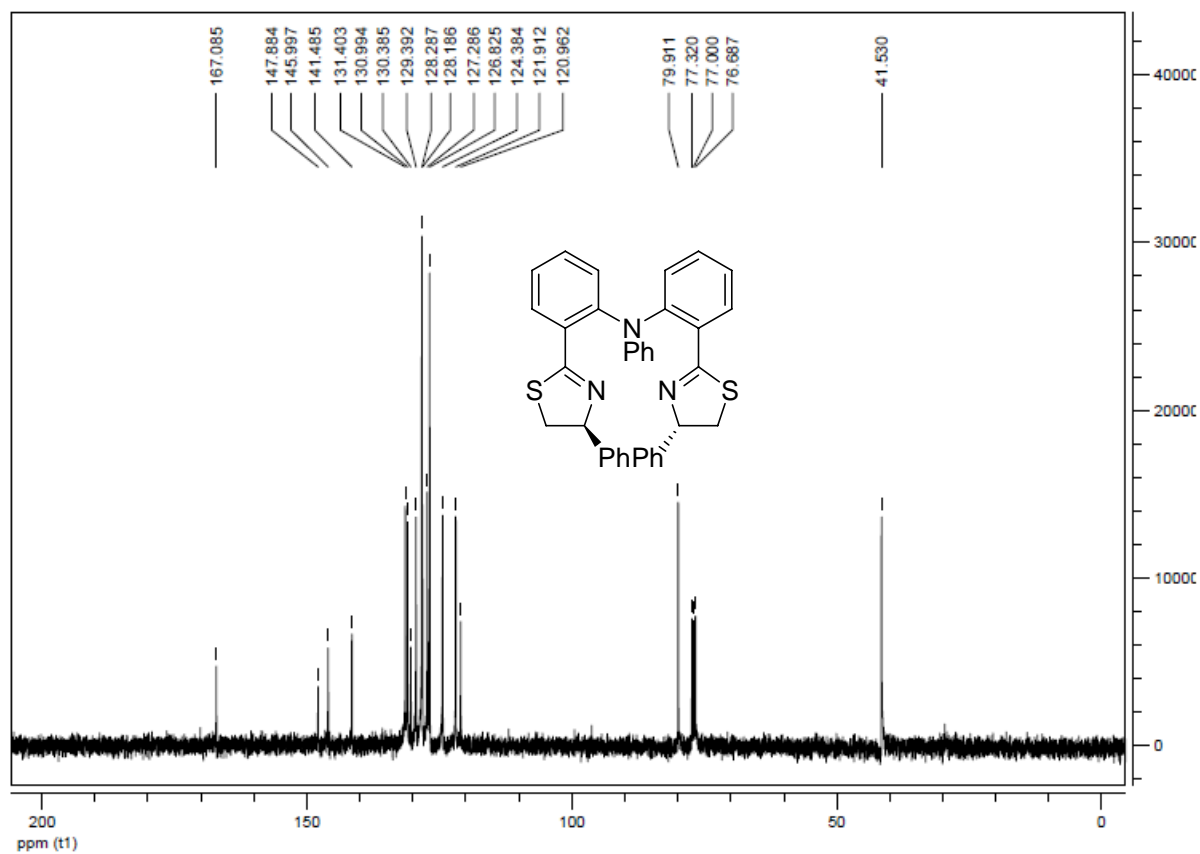
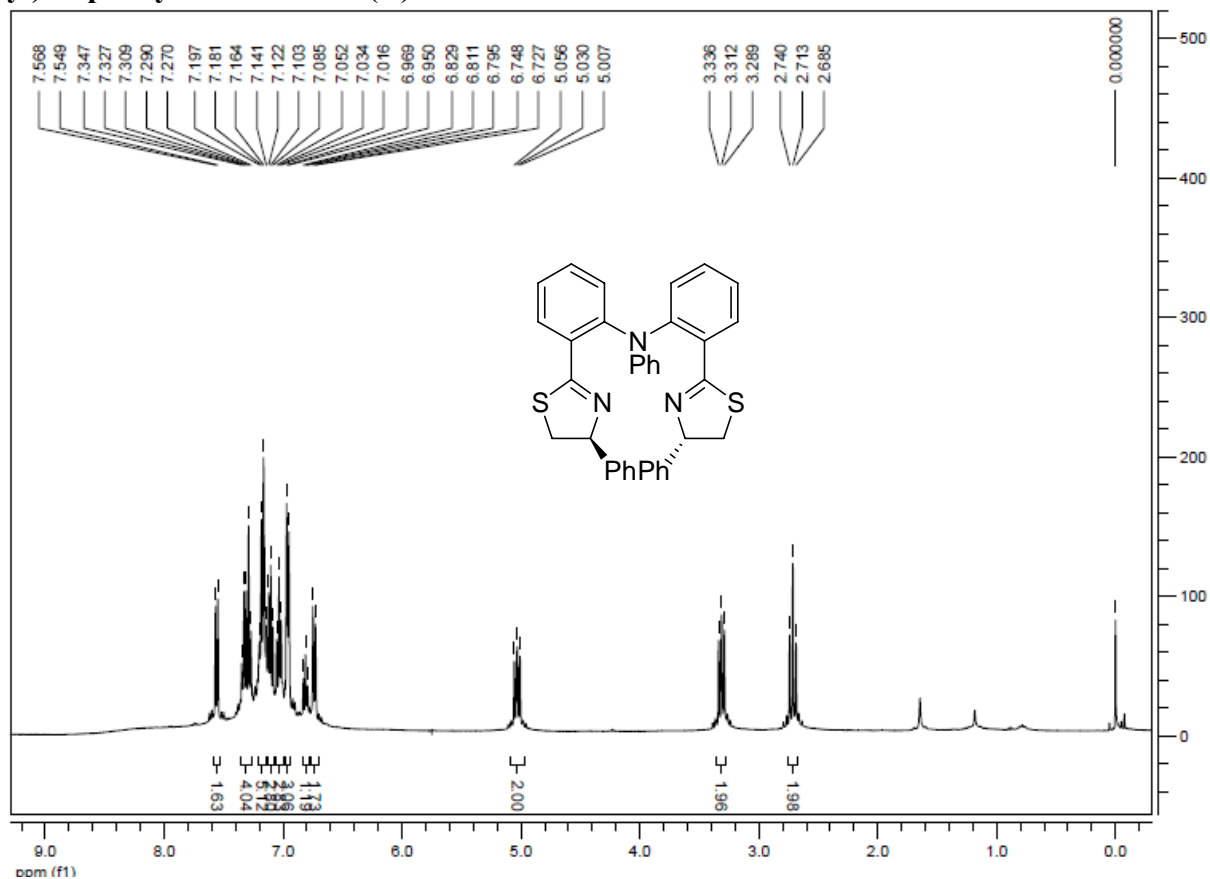
Supporting Information

Contents

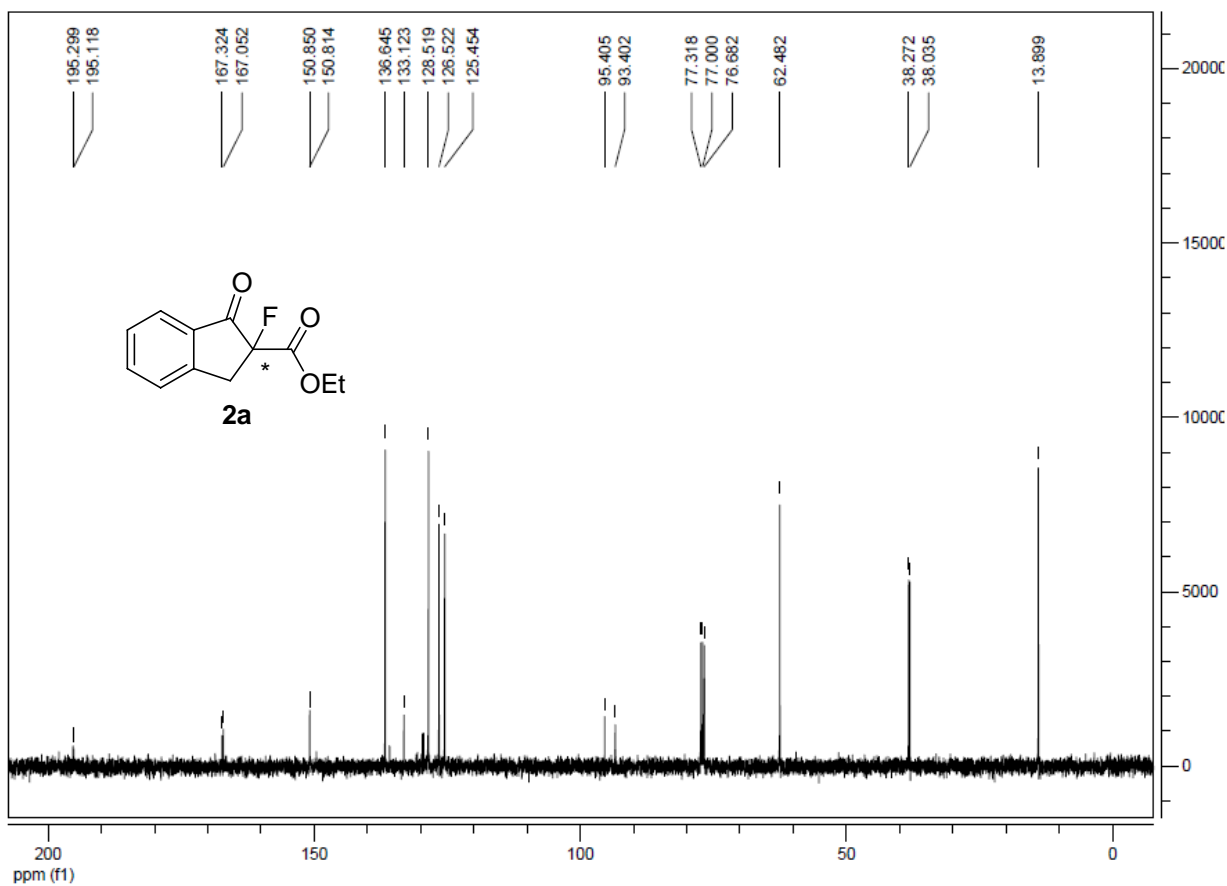
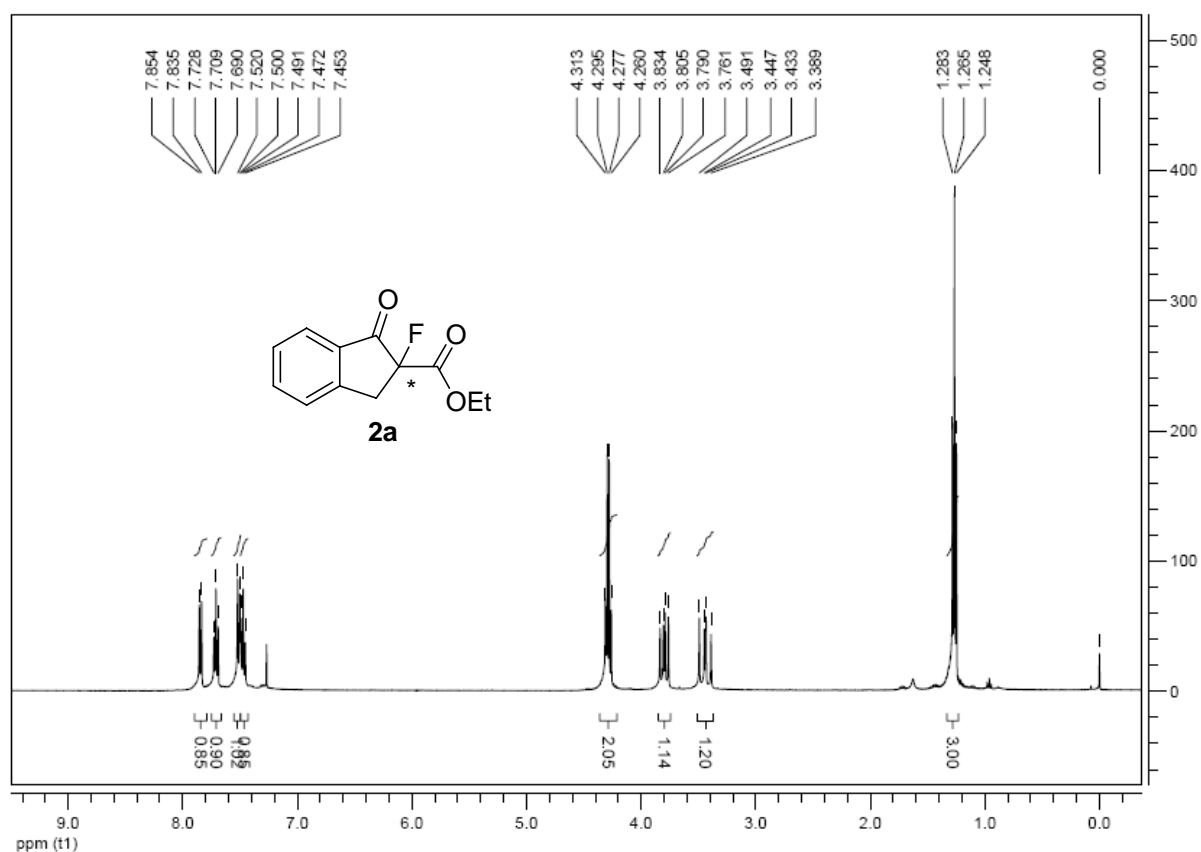
Copies of ¹ H and ¹³ C NMR spectra of new compounds.....	S1
Copies of HPLC chromatographs.....	S16

Copies of ^1H and ^{13}C NMR spectra of new compounds

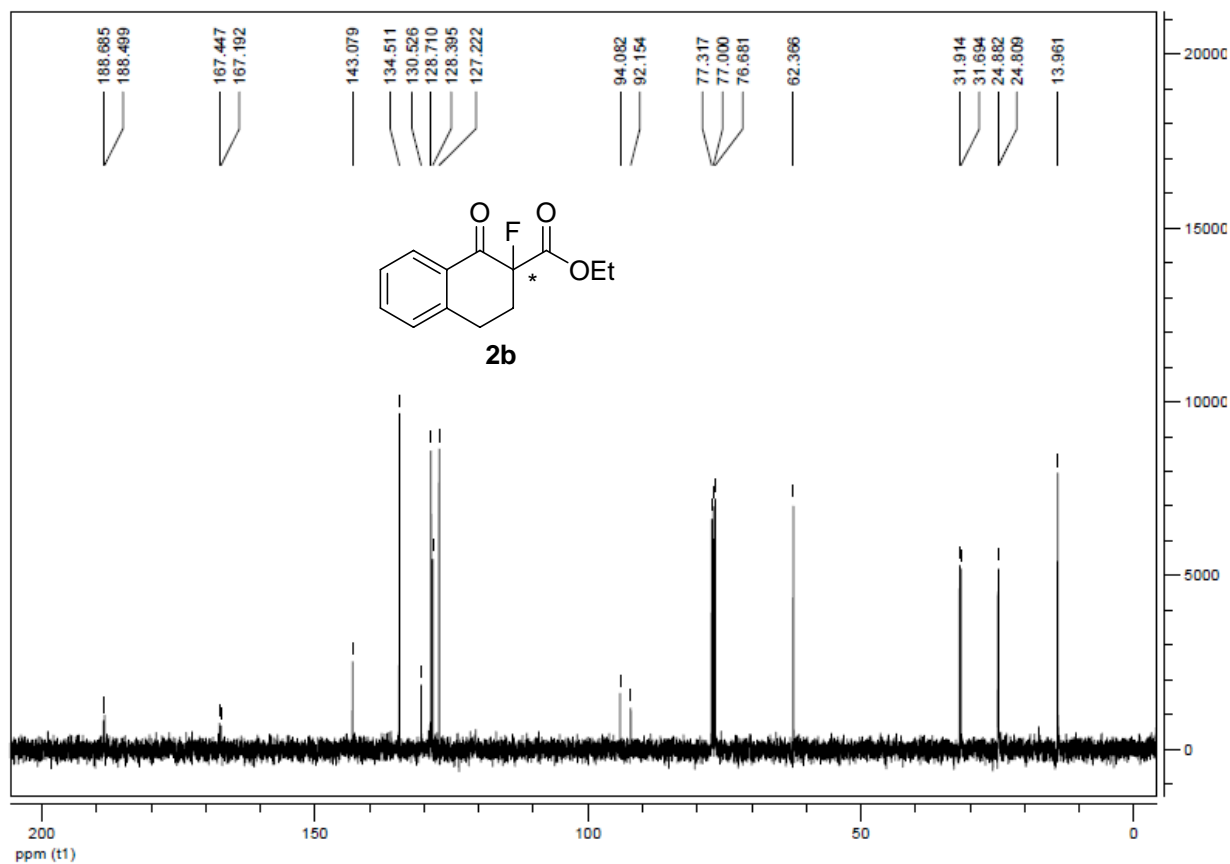
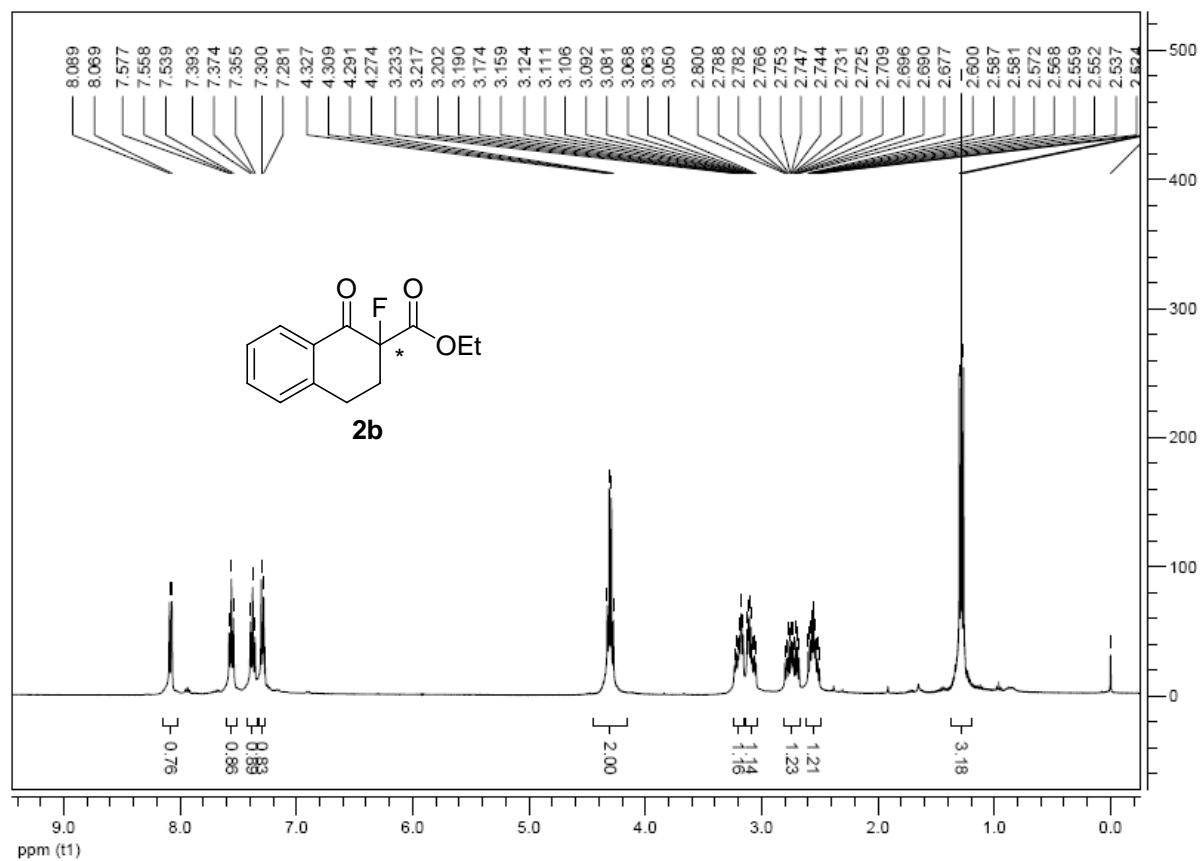
2-((*S*)-4,5-dihydro-4-phenylthiazol-2-yl)-*N*-(2-((*S*)-4,5-dihydro-4-phenylthiazol-2-yl)phenyl)-*N*-phenylbenzenamine (**X**)



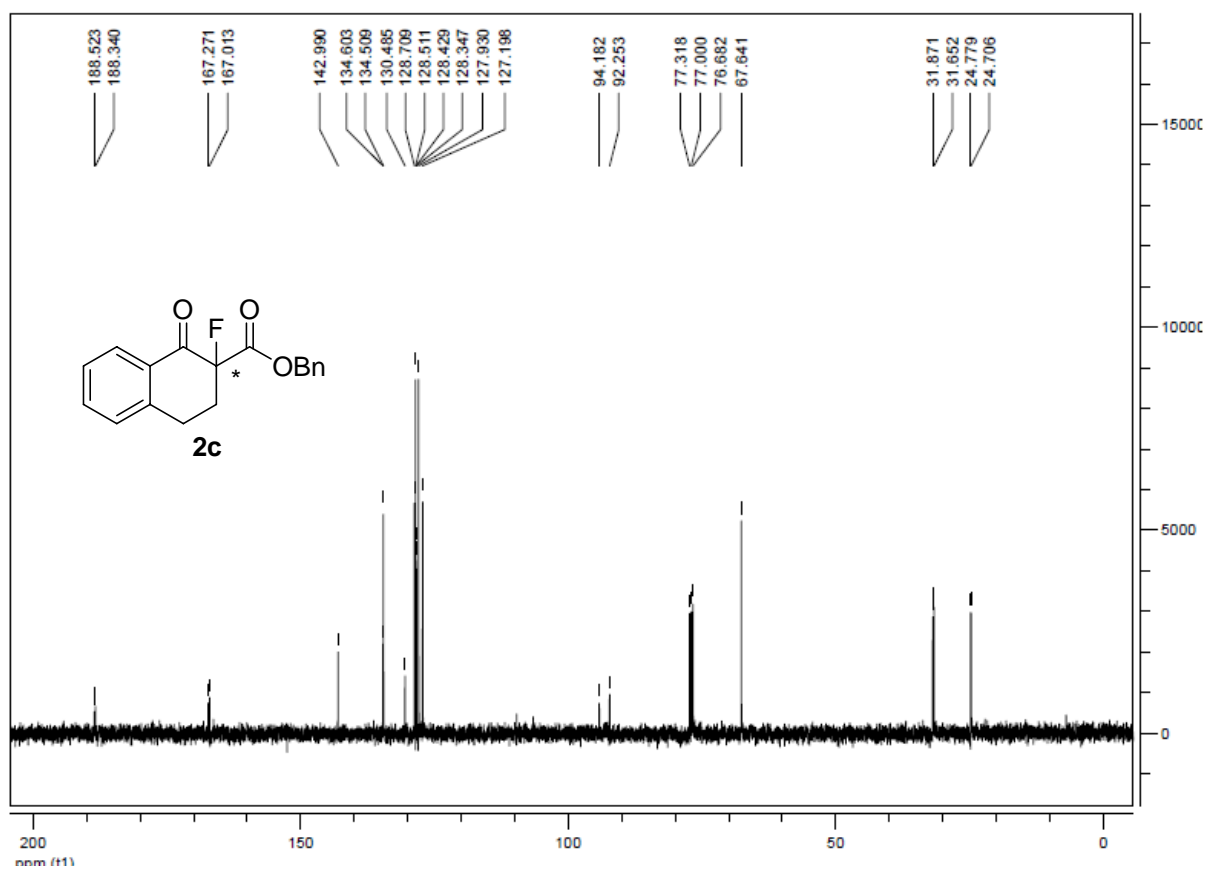
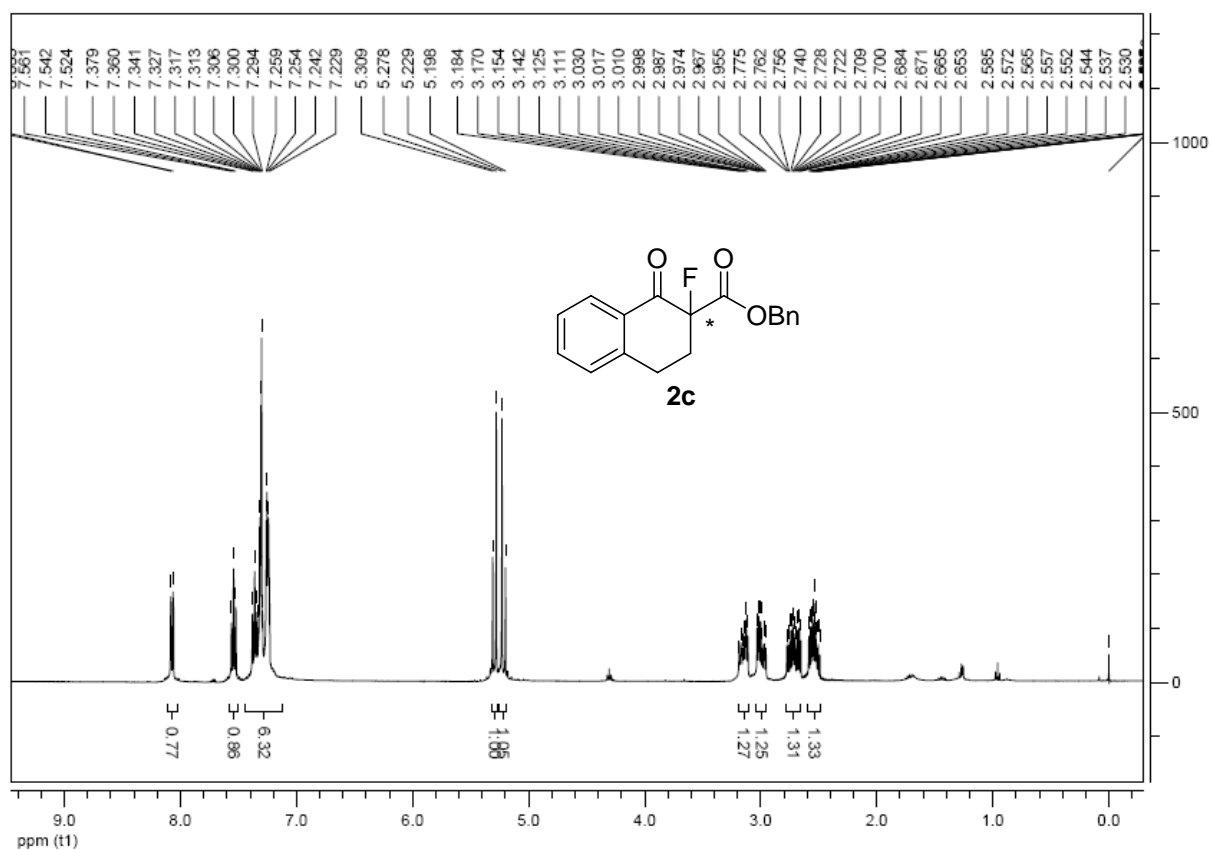
Ethyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2a)



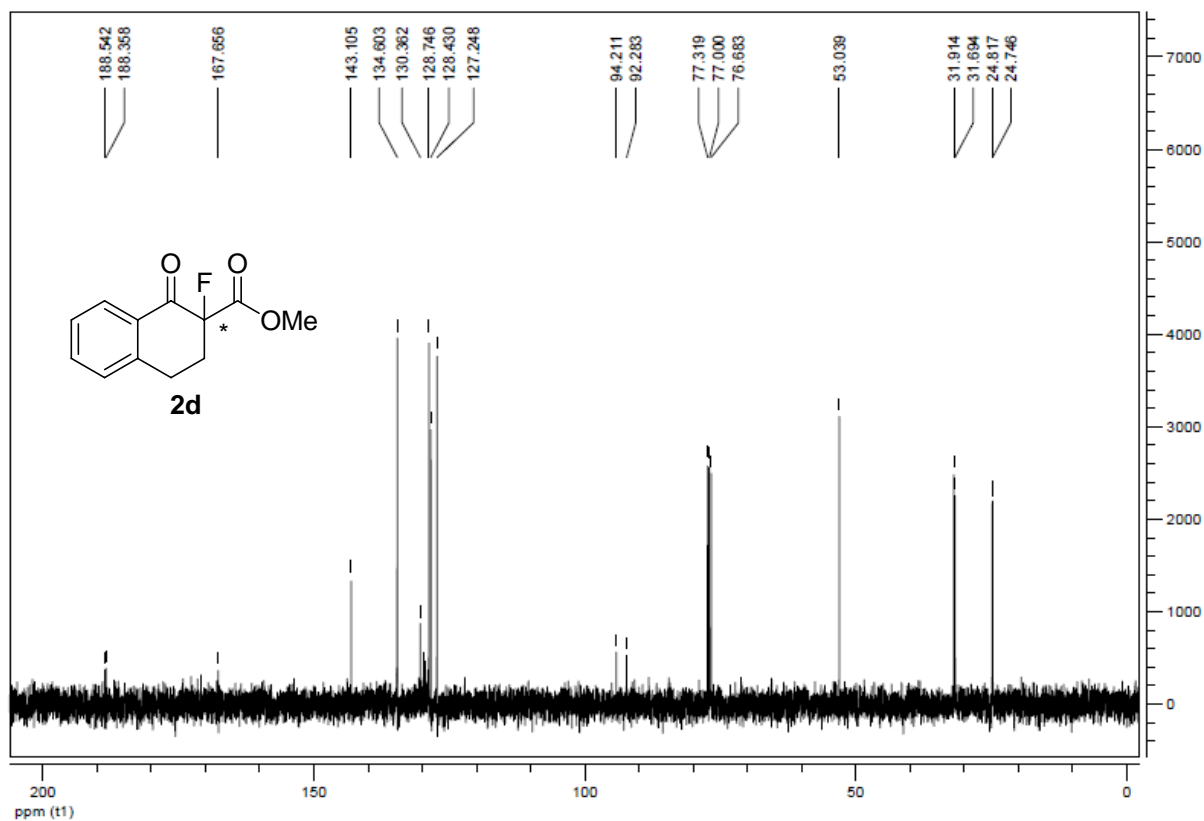
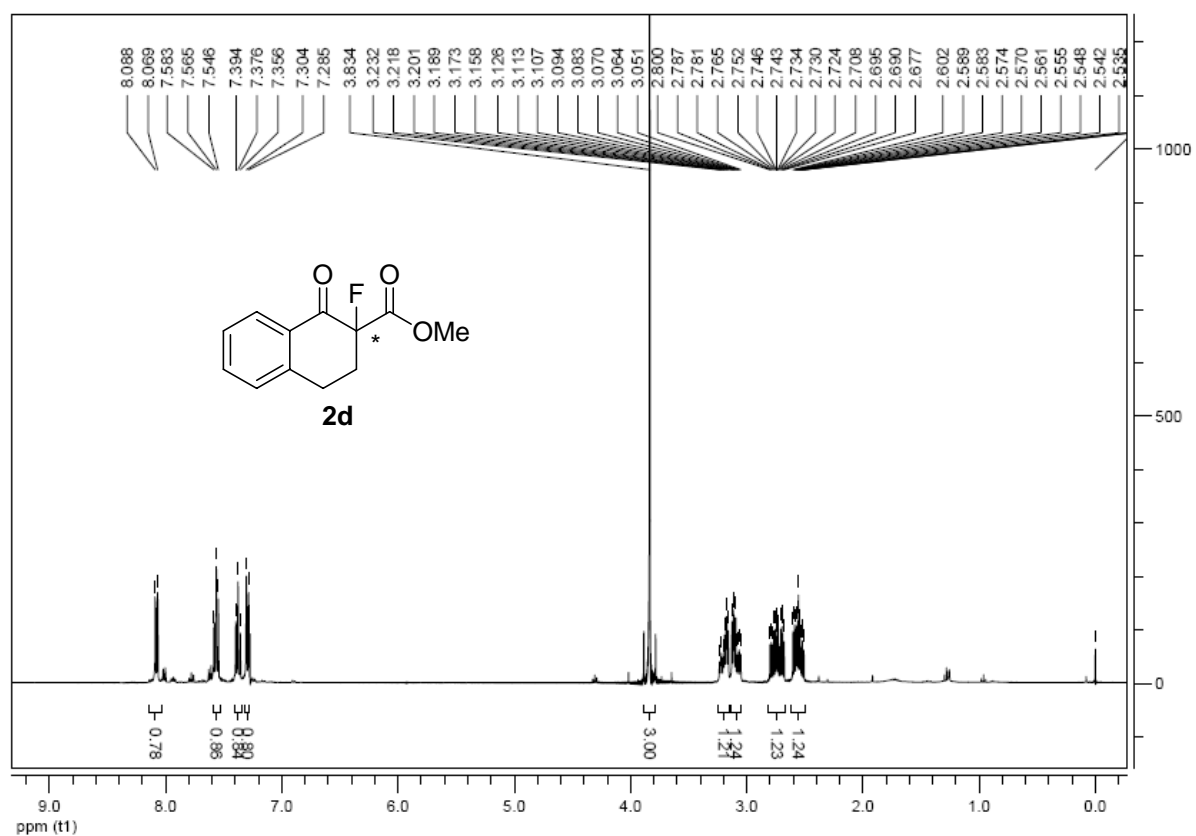
Ethyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (**2b**)



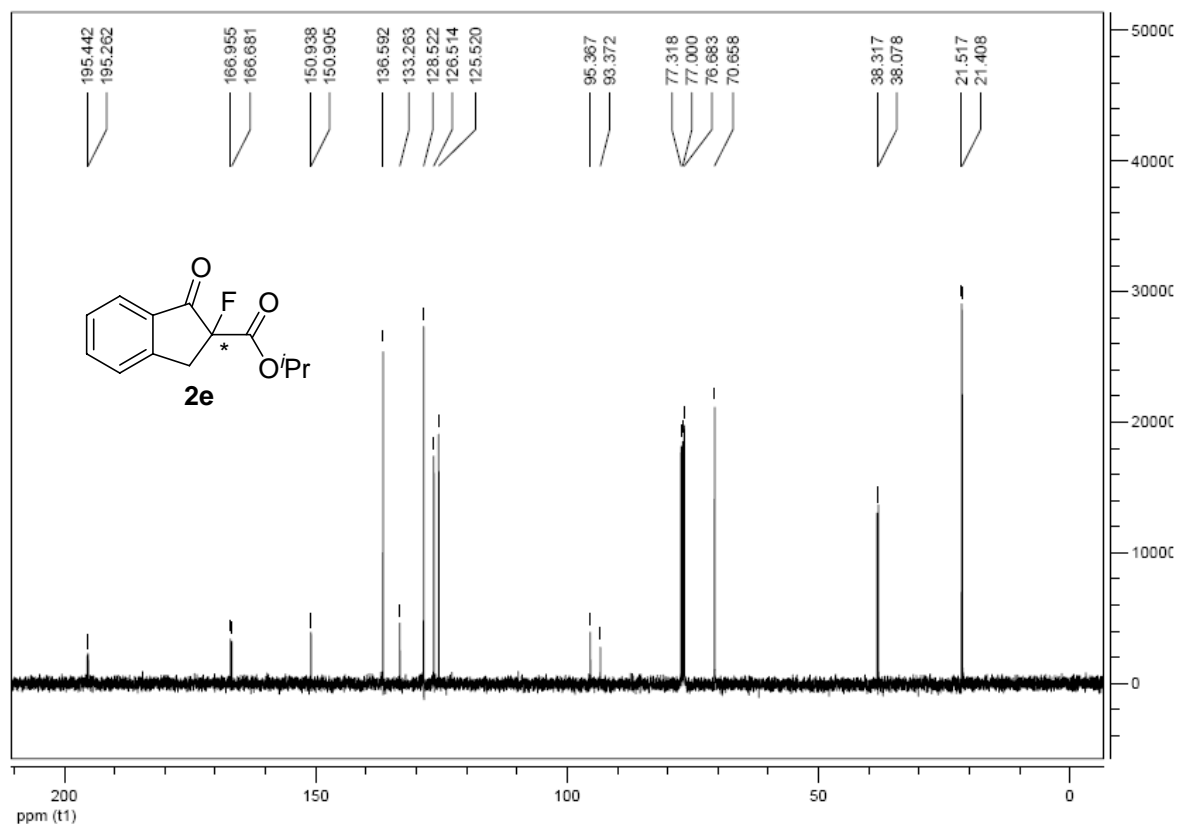
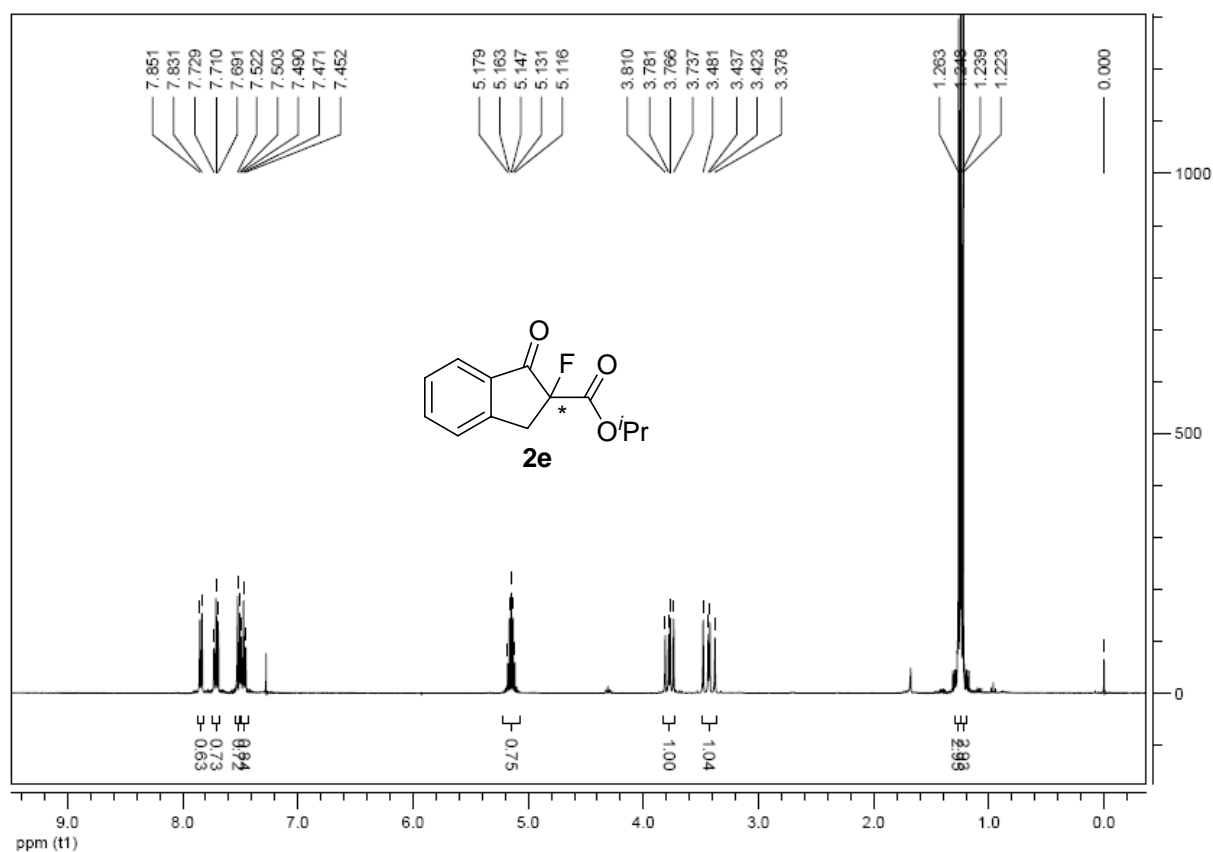
Benzyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2c)



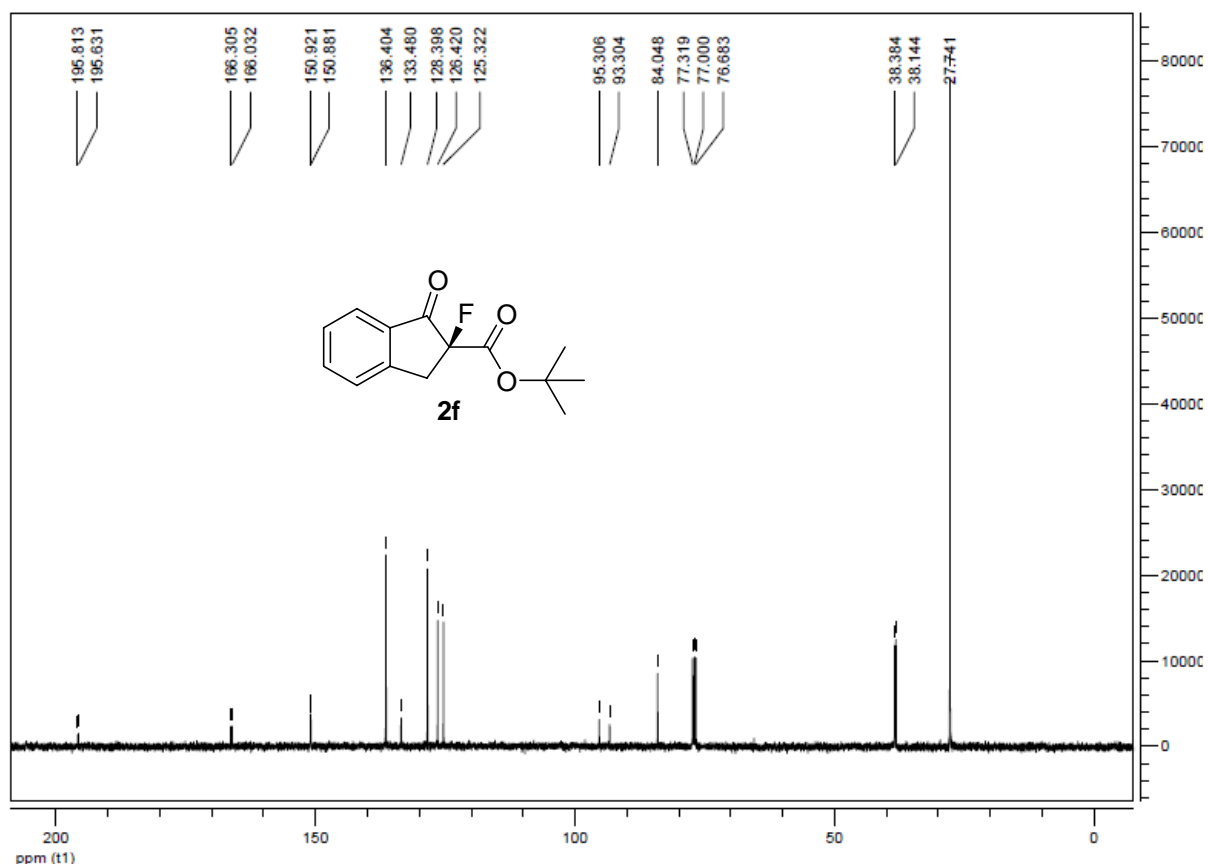
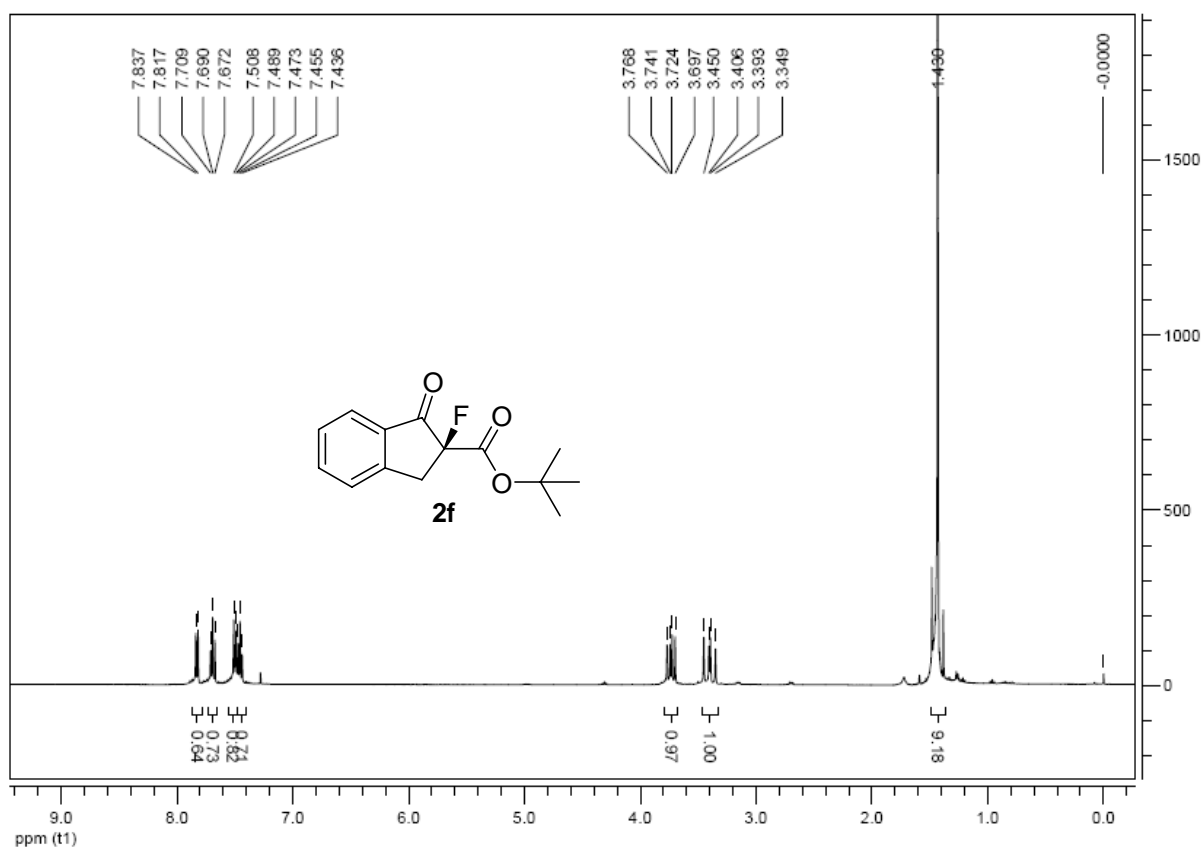
Methyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2d)



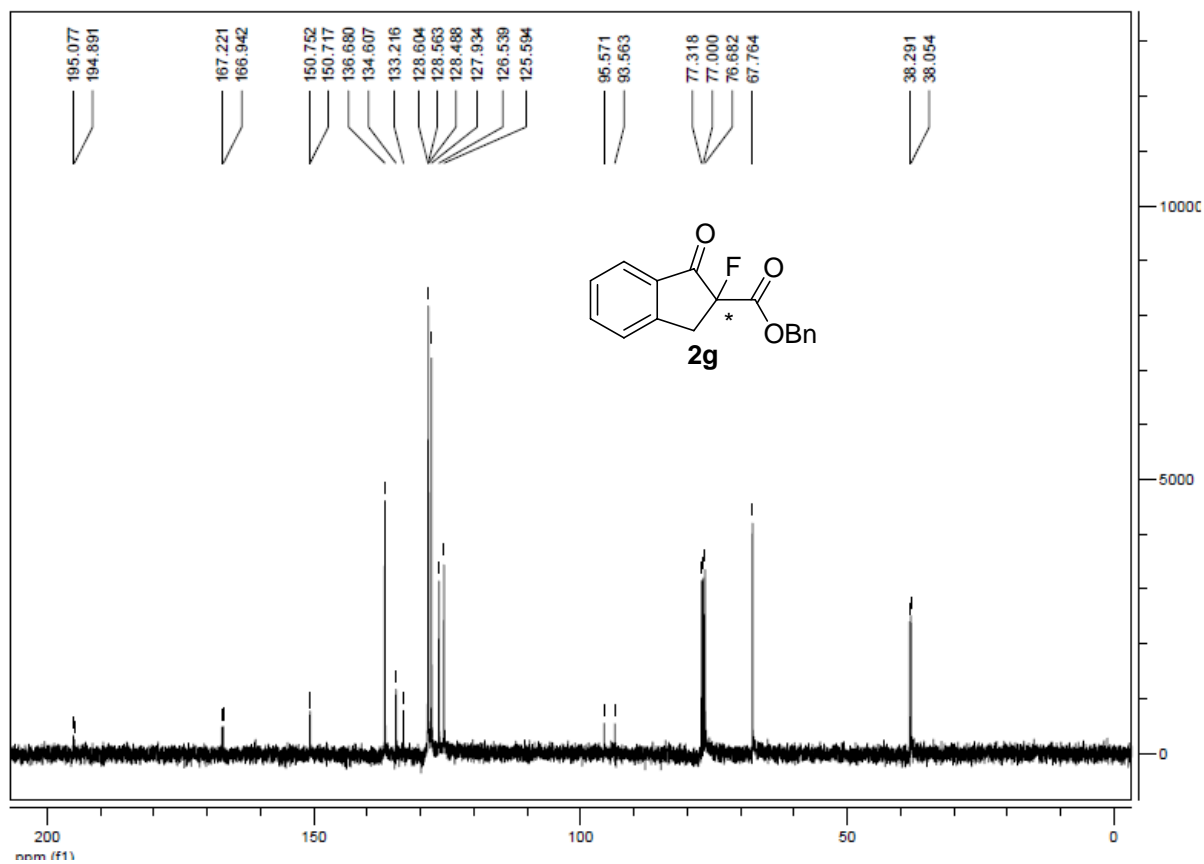
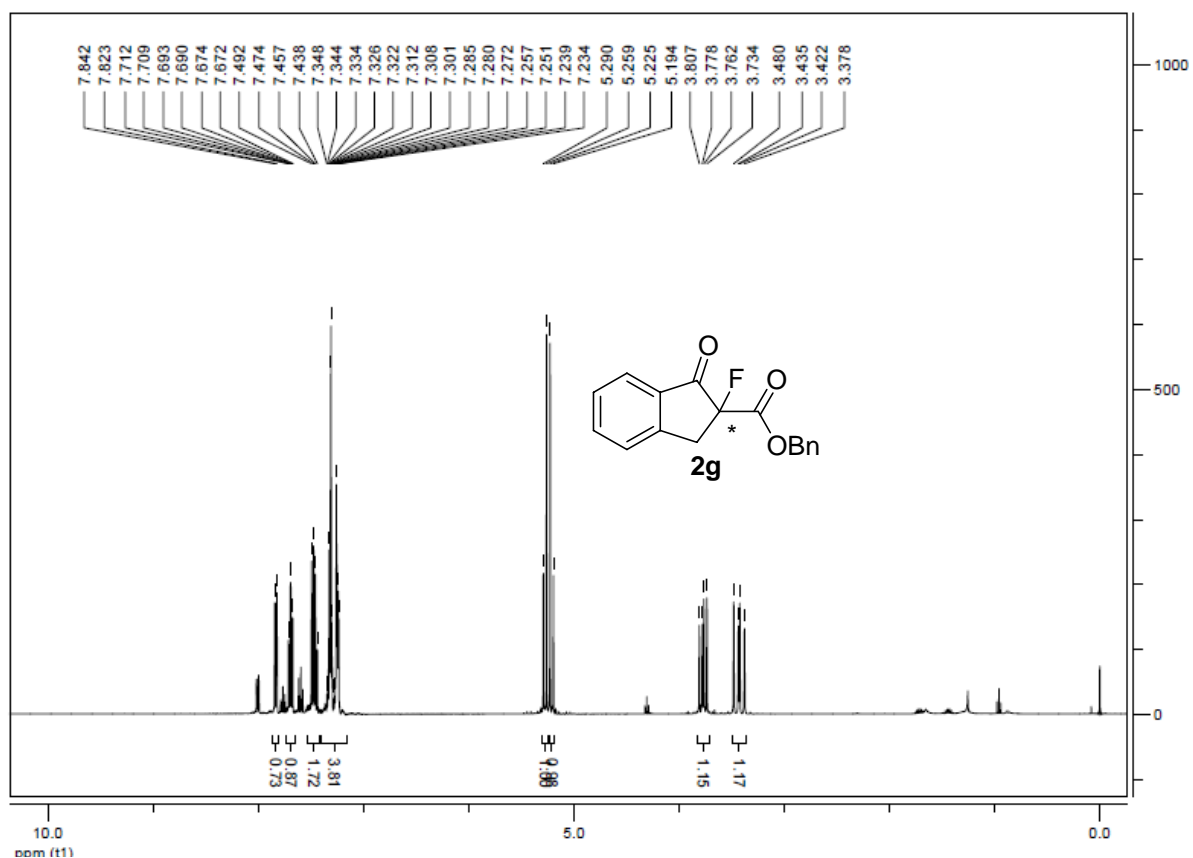
Propyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2e)



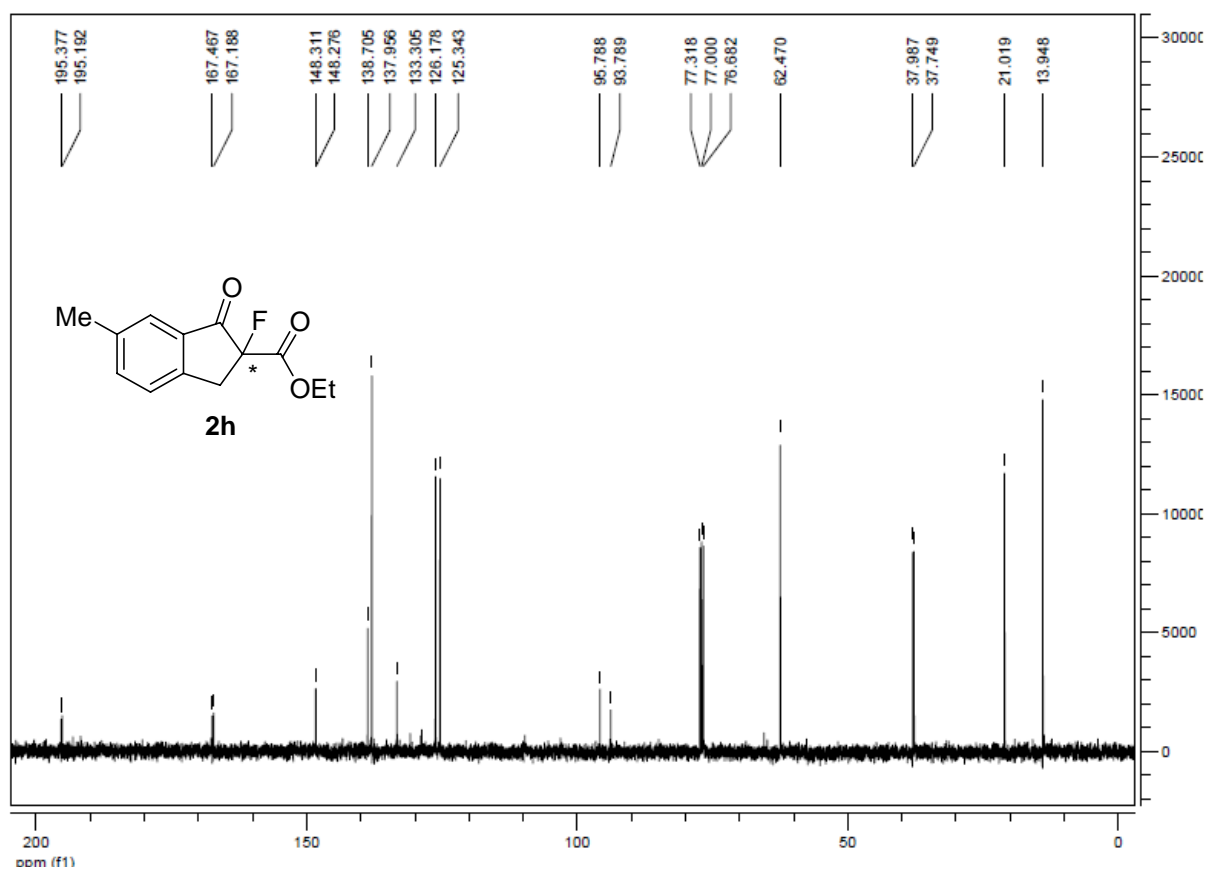
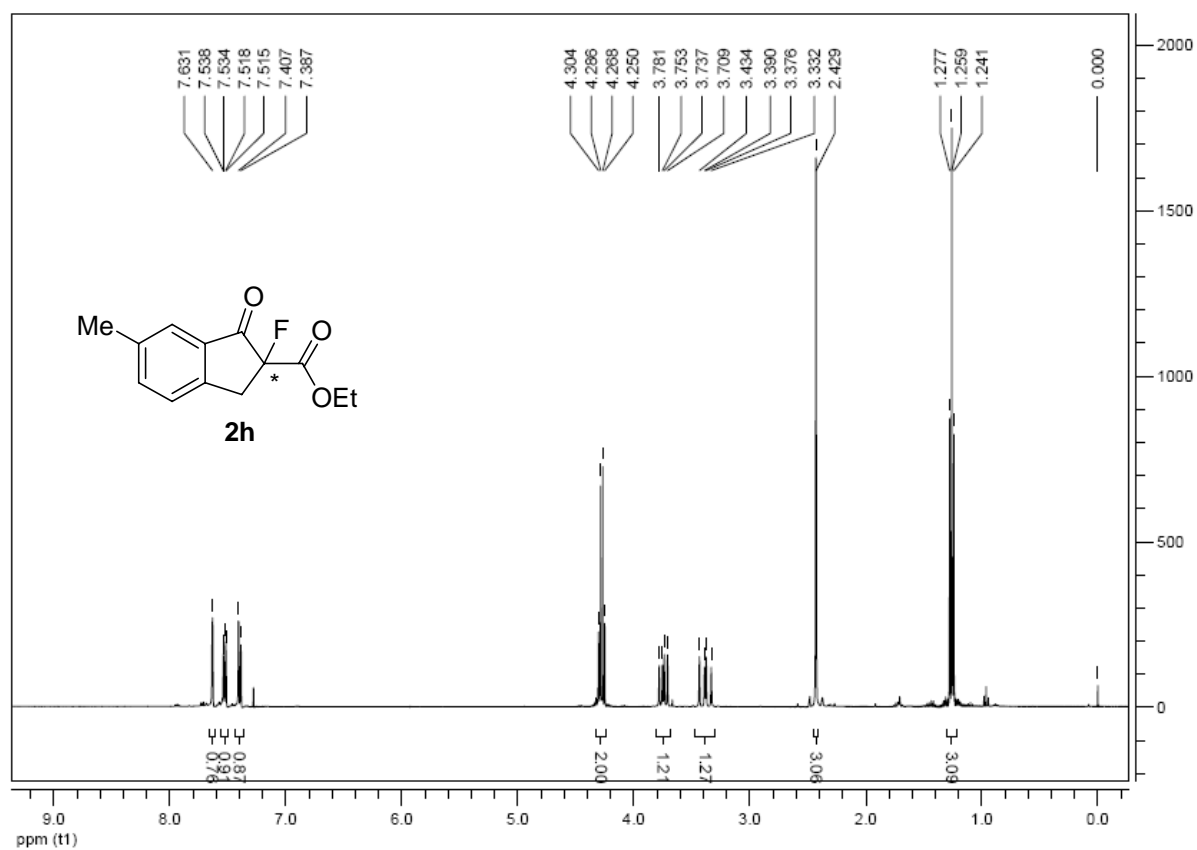
(S)-tert-butyl 2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2f)



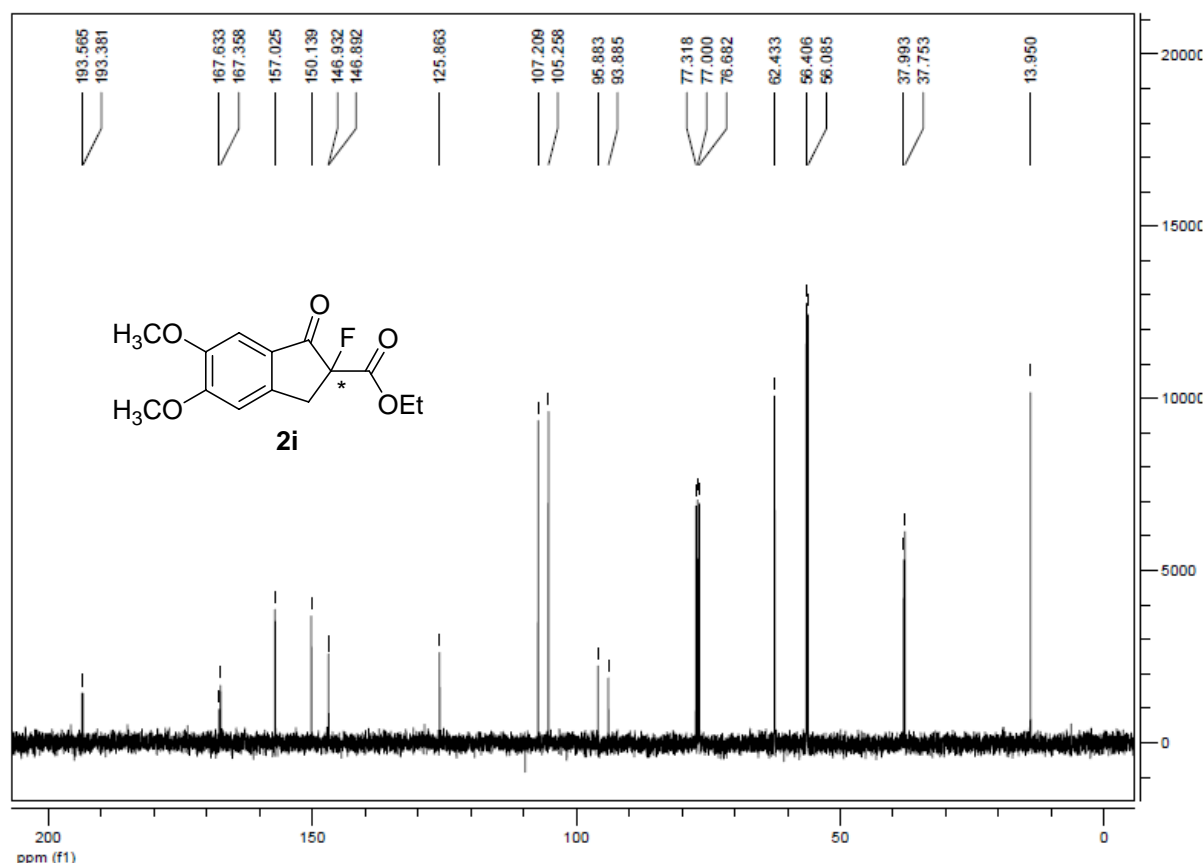
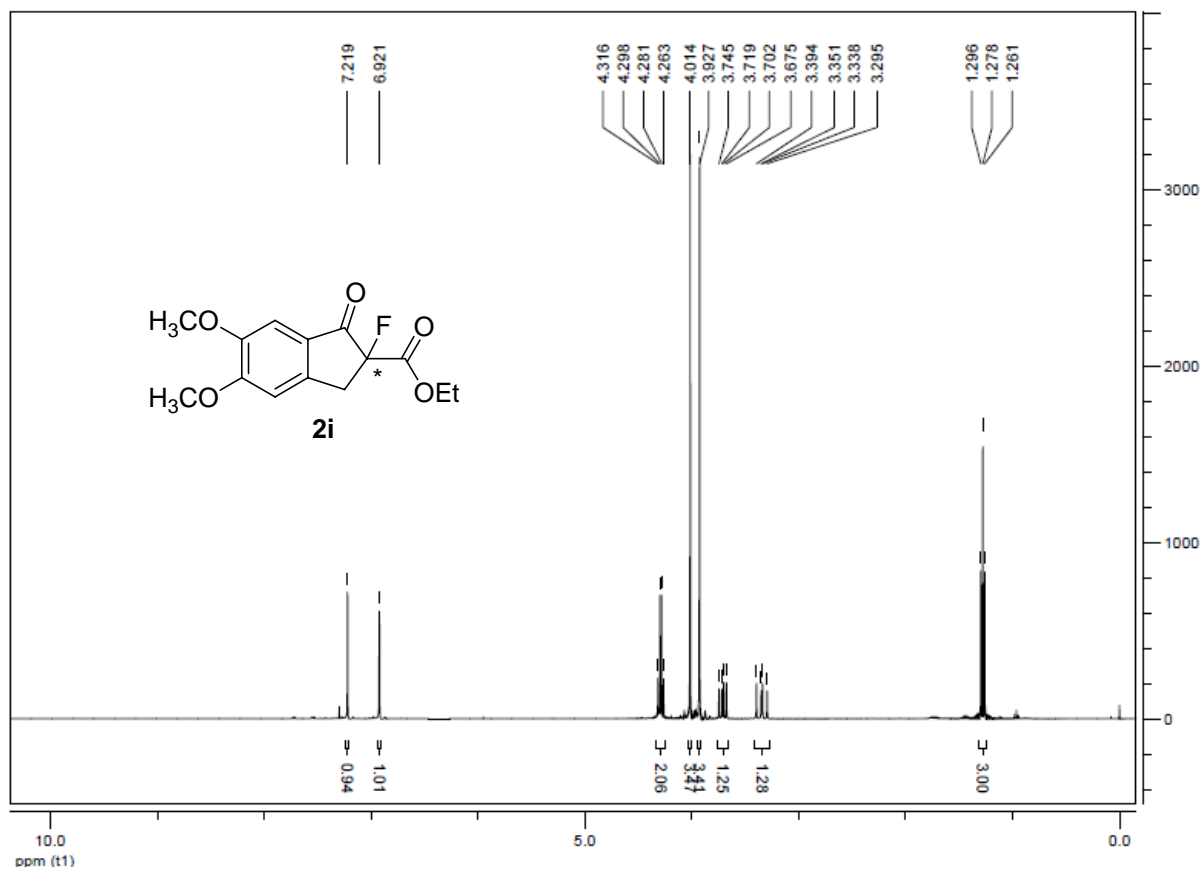
Benzyl 2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2g)



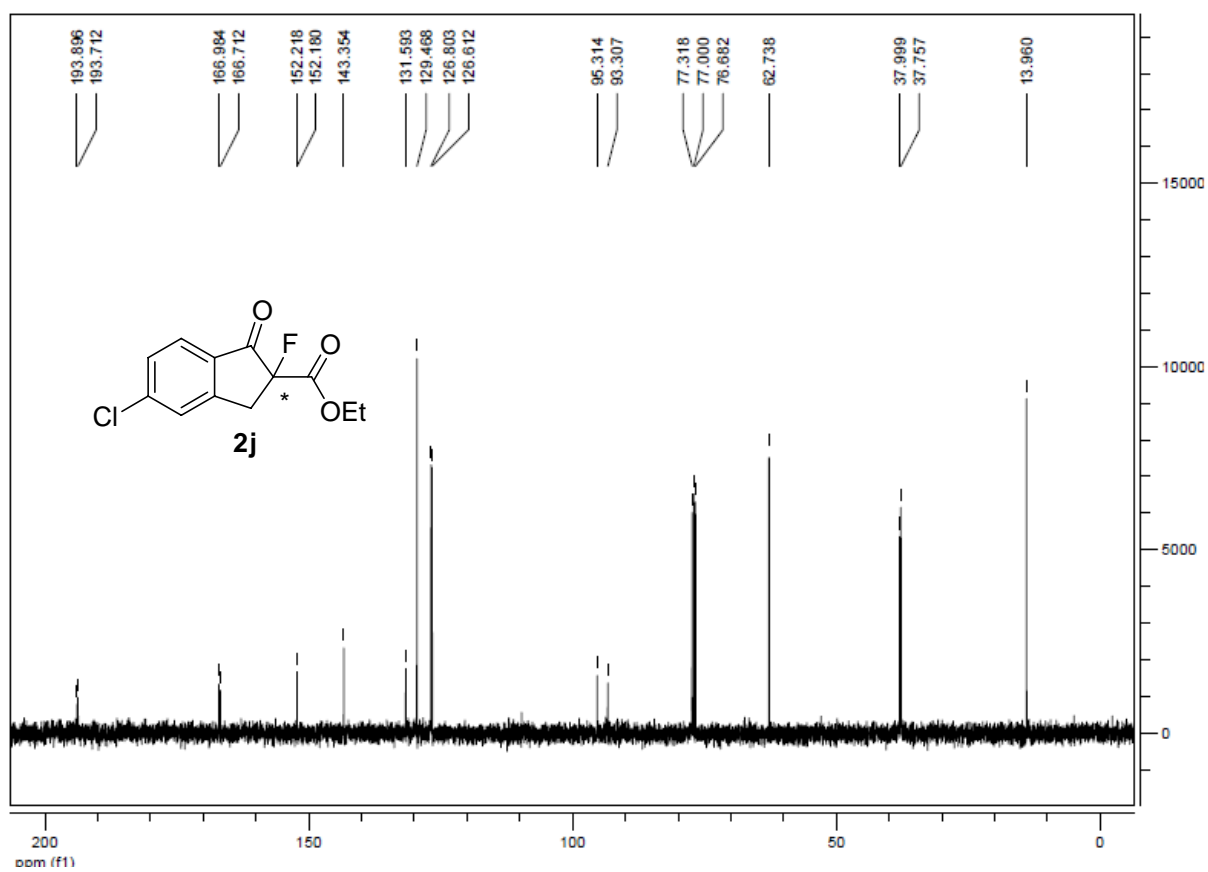
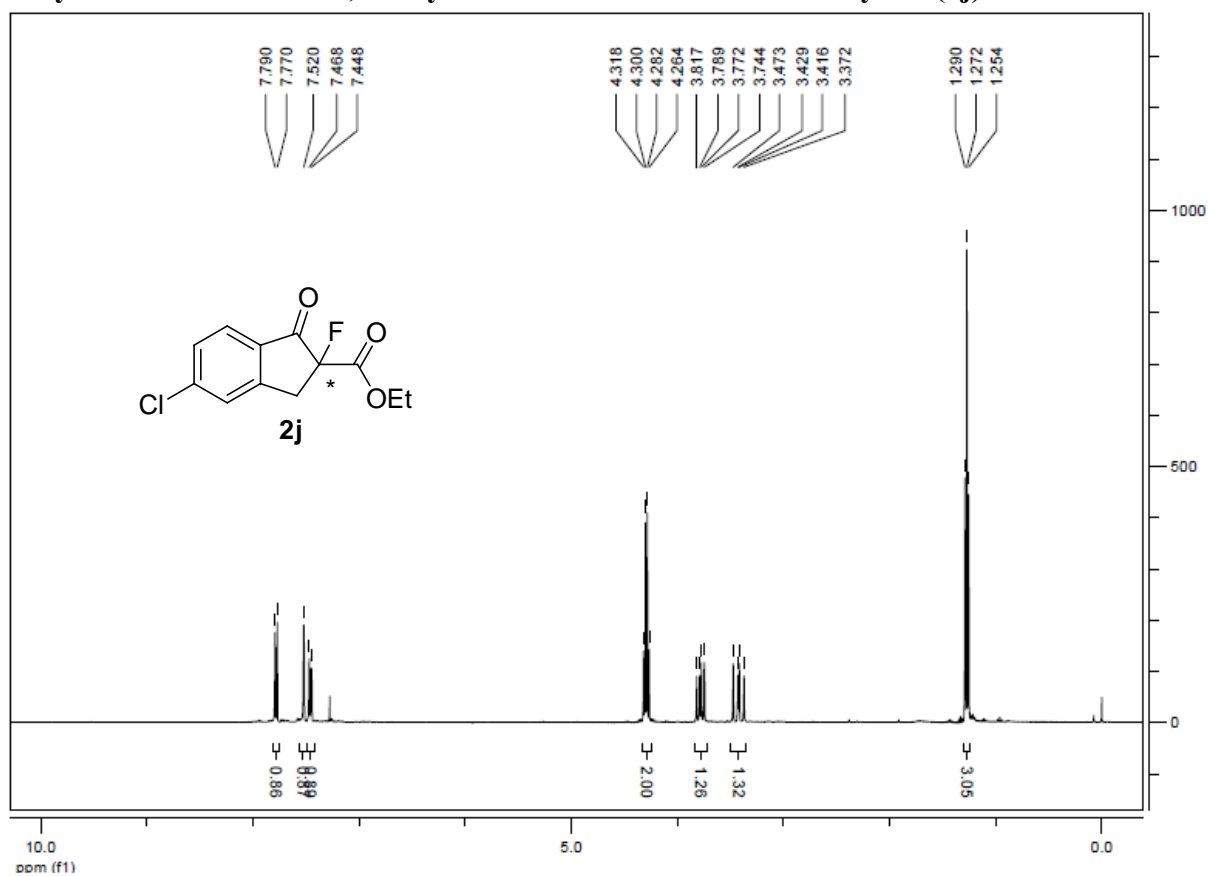
Ethyl 2-fluoro-2,3-dihydro-6-methyl-1-oxo-1*H*-indene-2-carboxylate (**2h**)



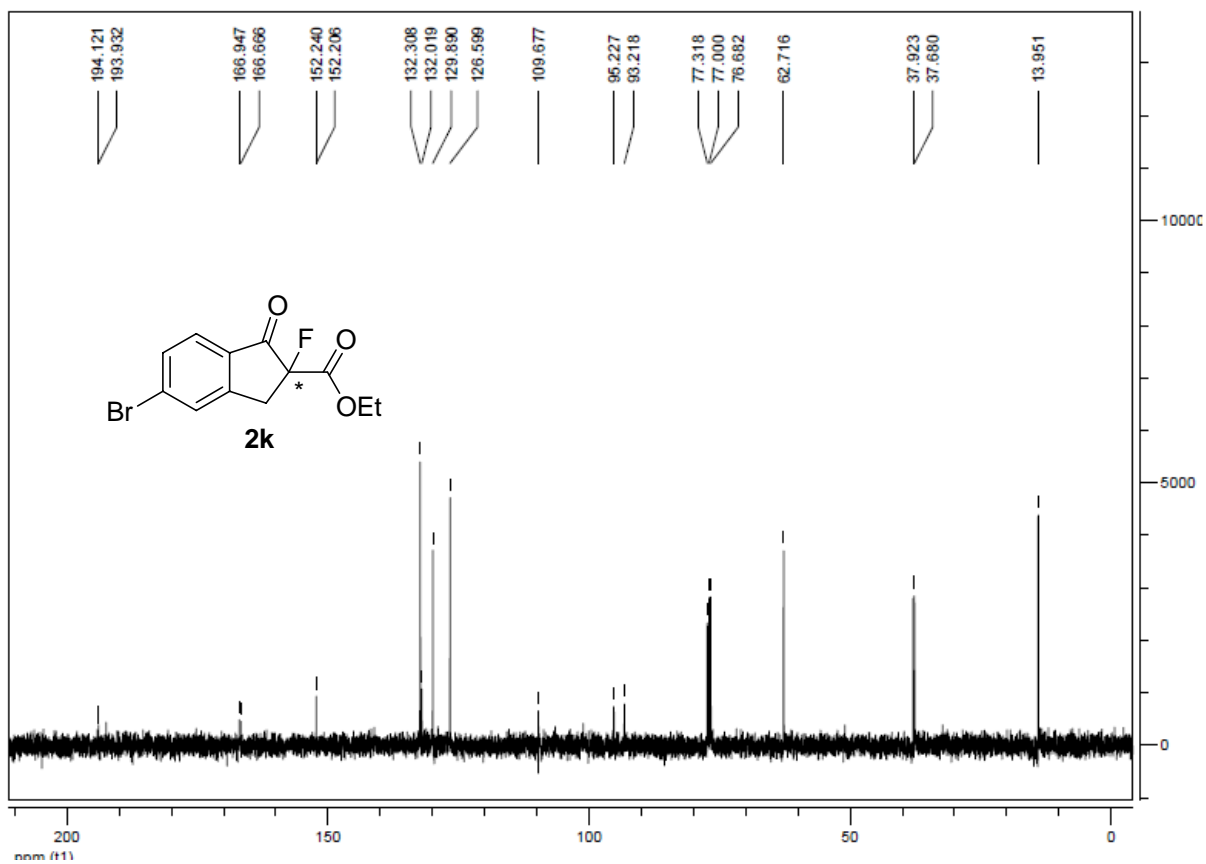
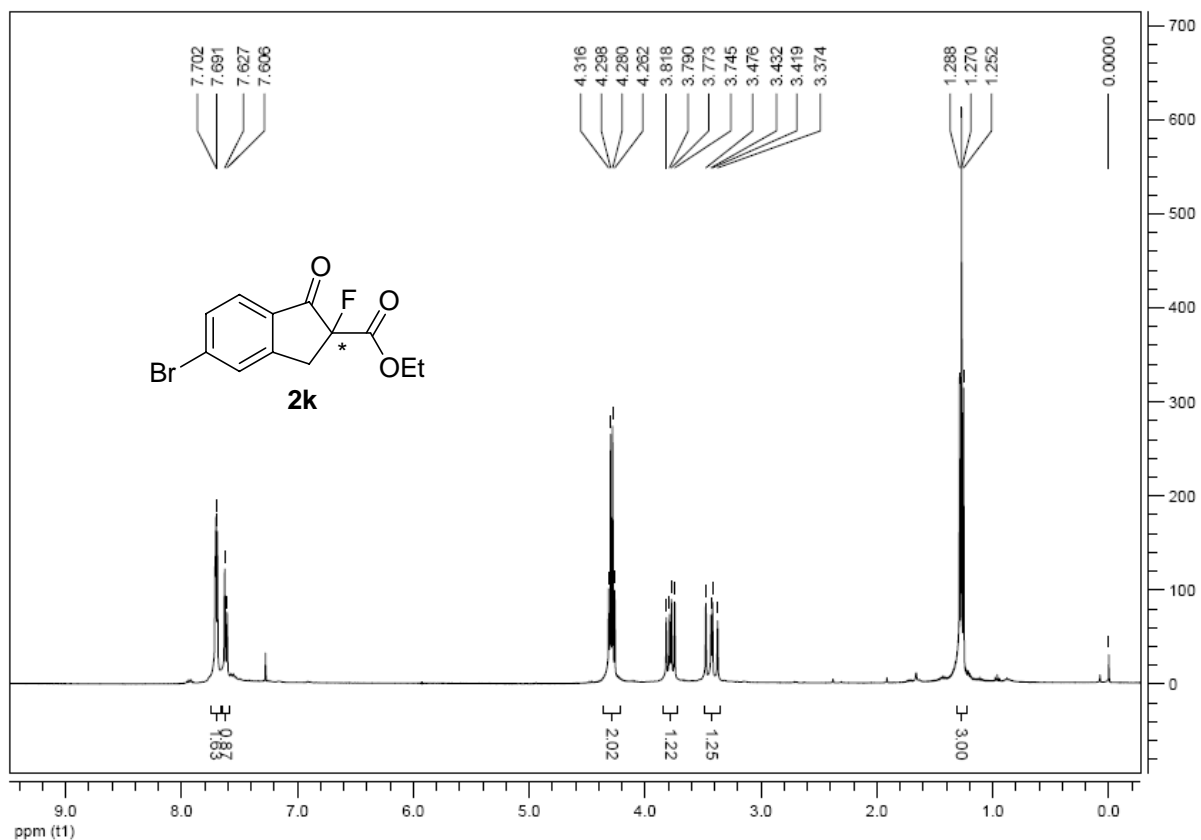
Ethyl 2-fluoro-2,3-dihydro-5,6-dimethoxy-1-oxo-1*H*-indene-2-carboxylate (2i)



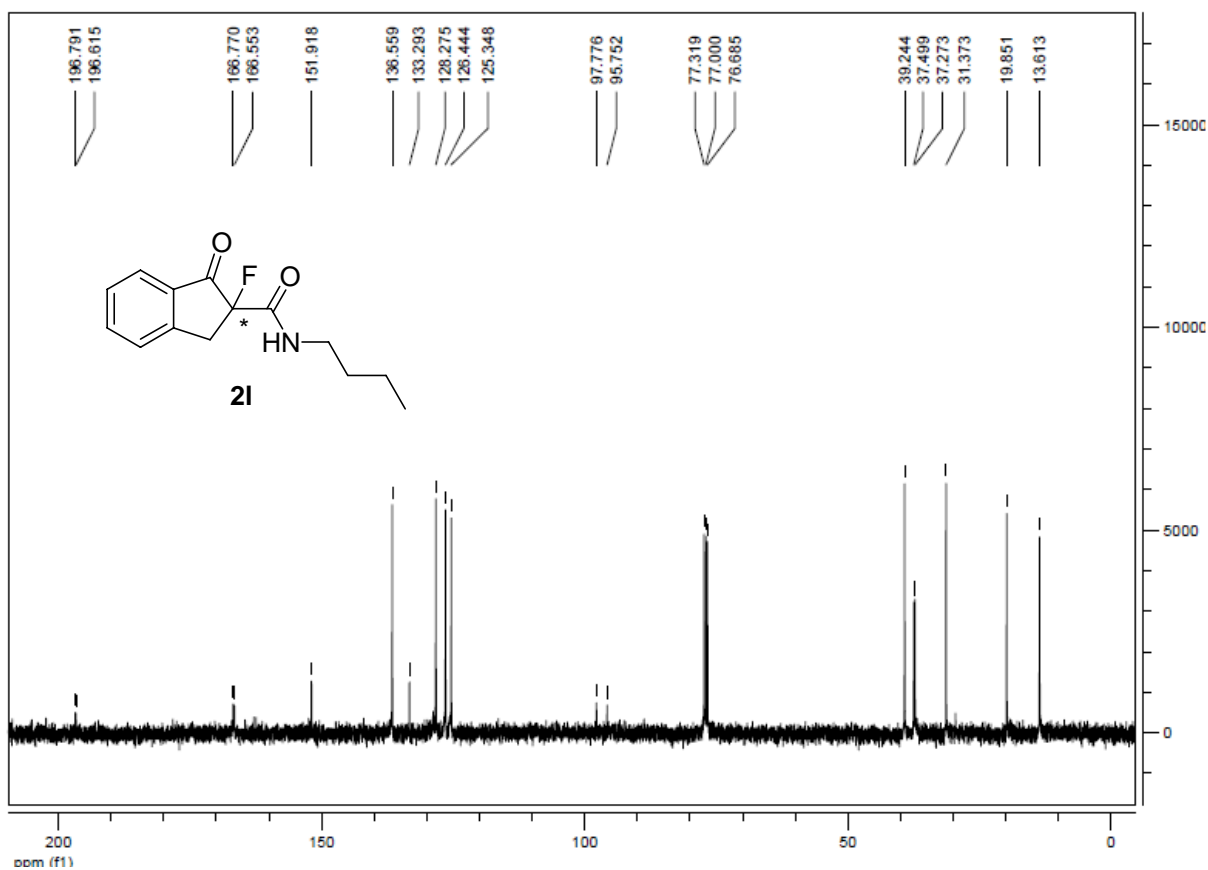
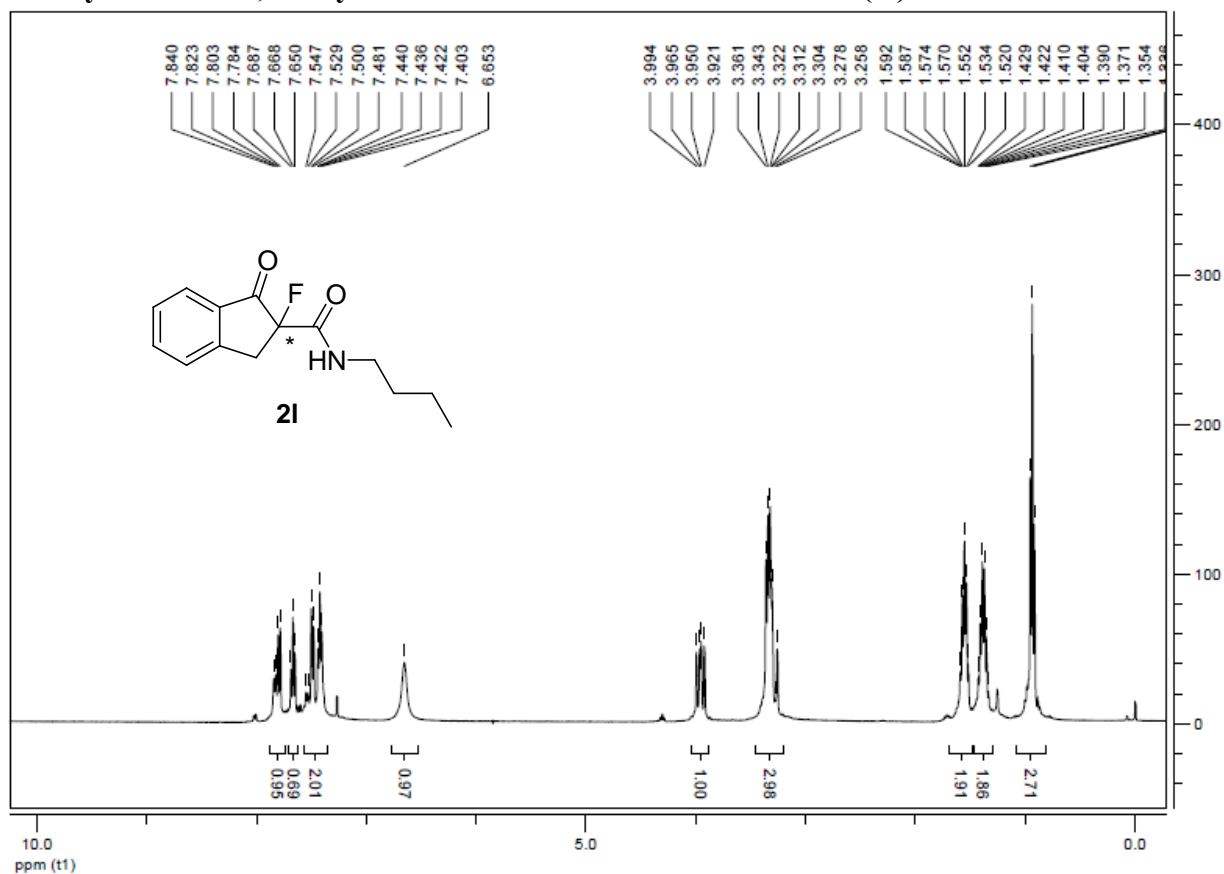
Ethyl 5-chloro-2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2j)



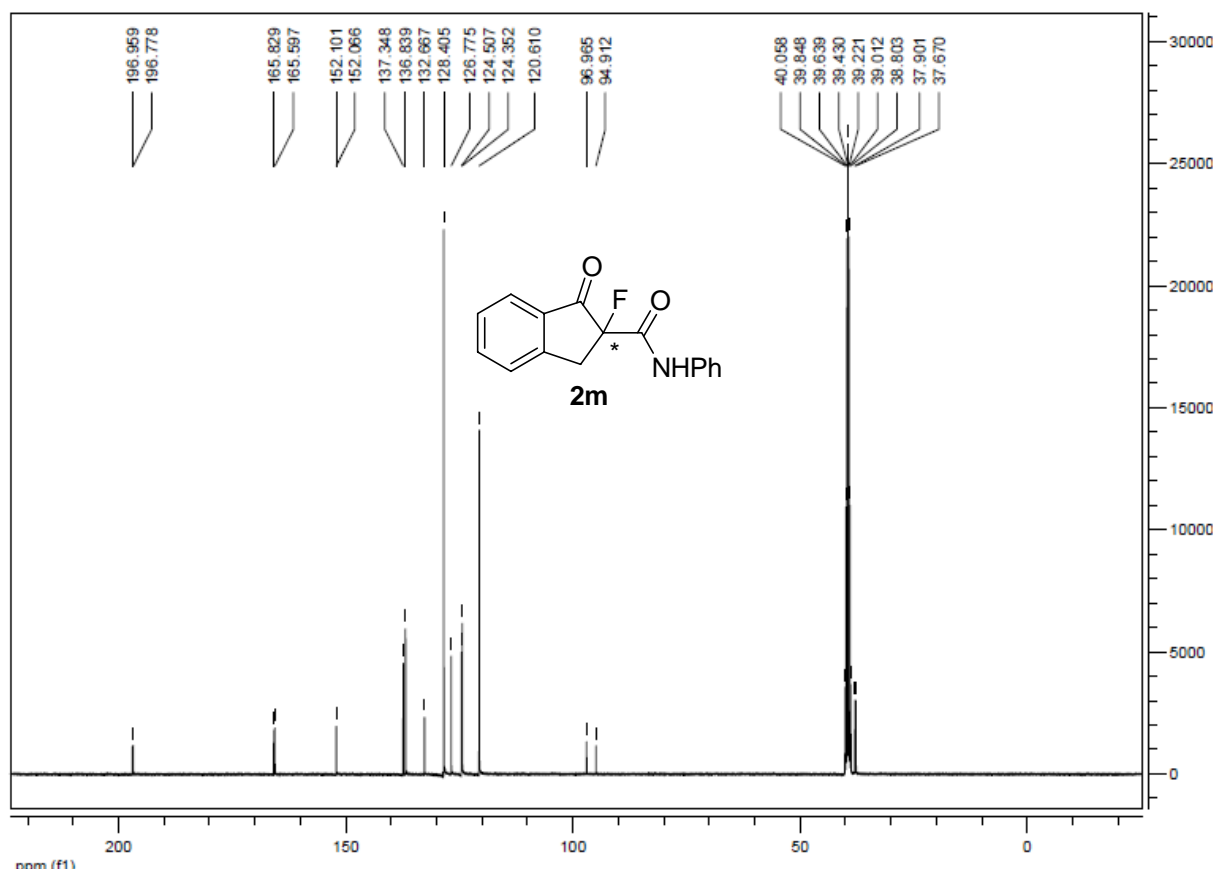
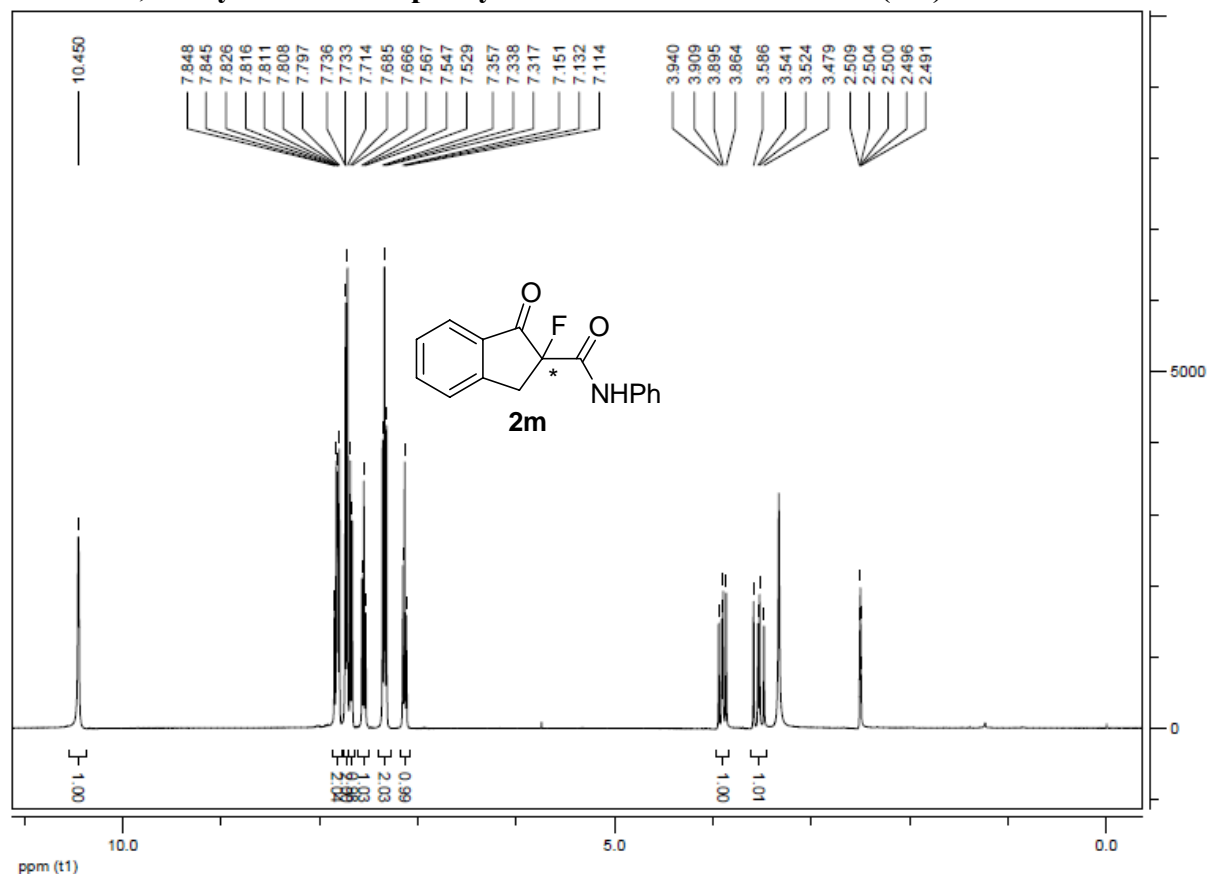
Ethyl 5-bromo-2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2k)



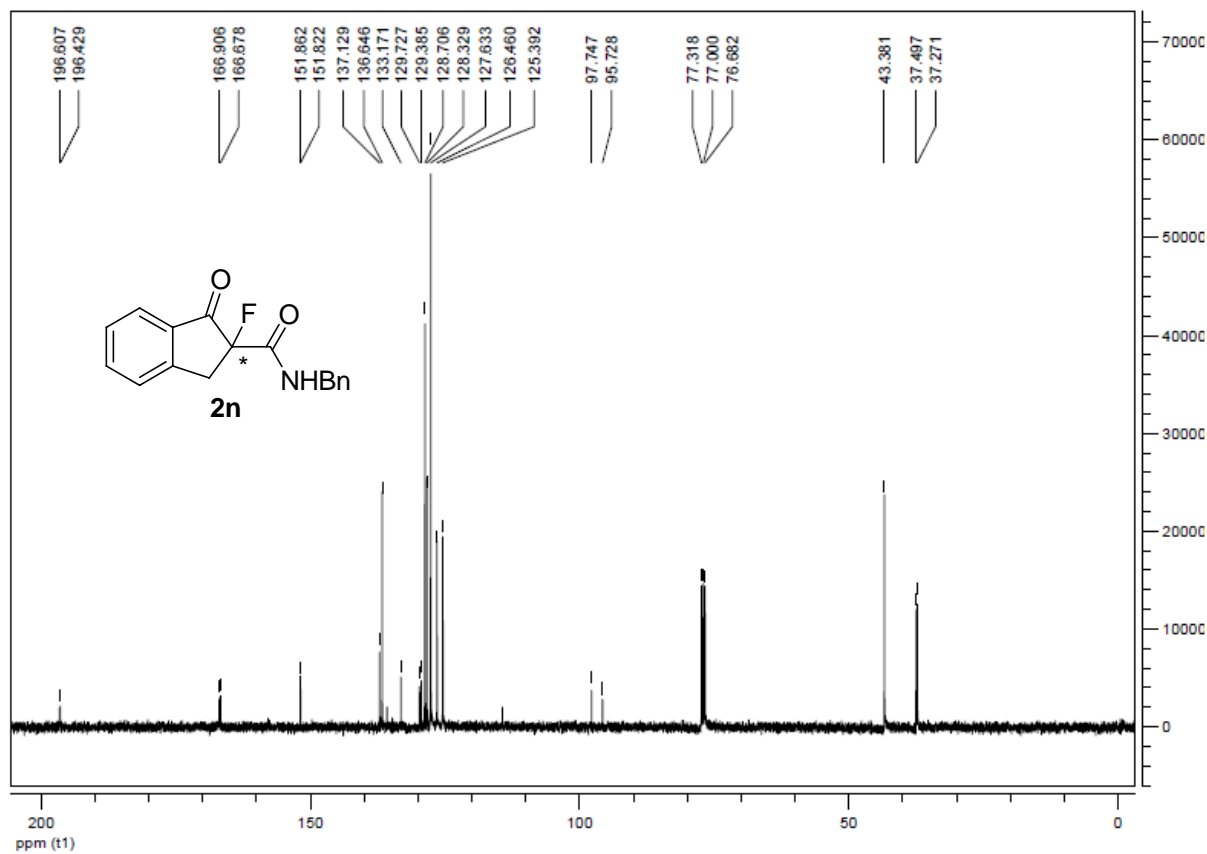
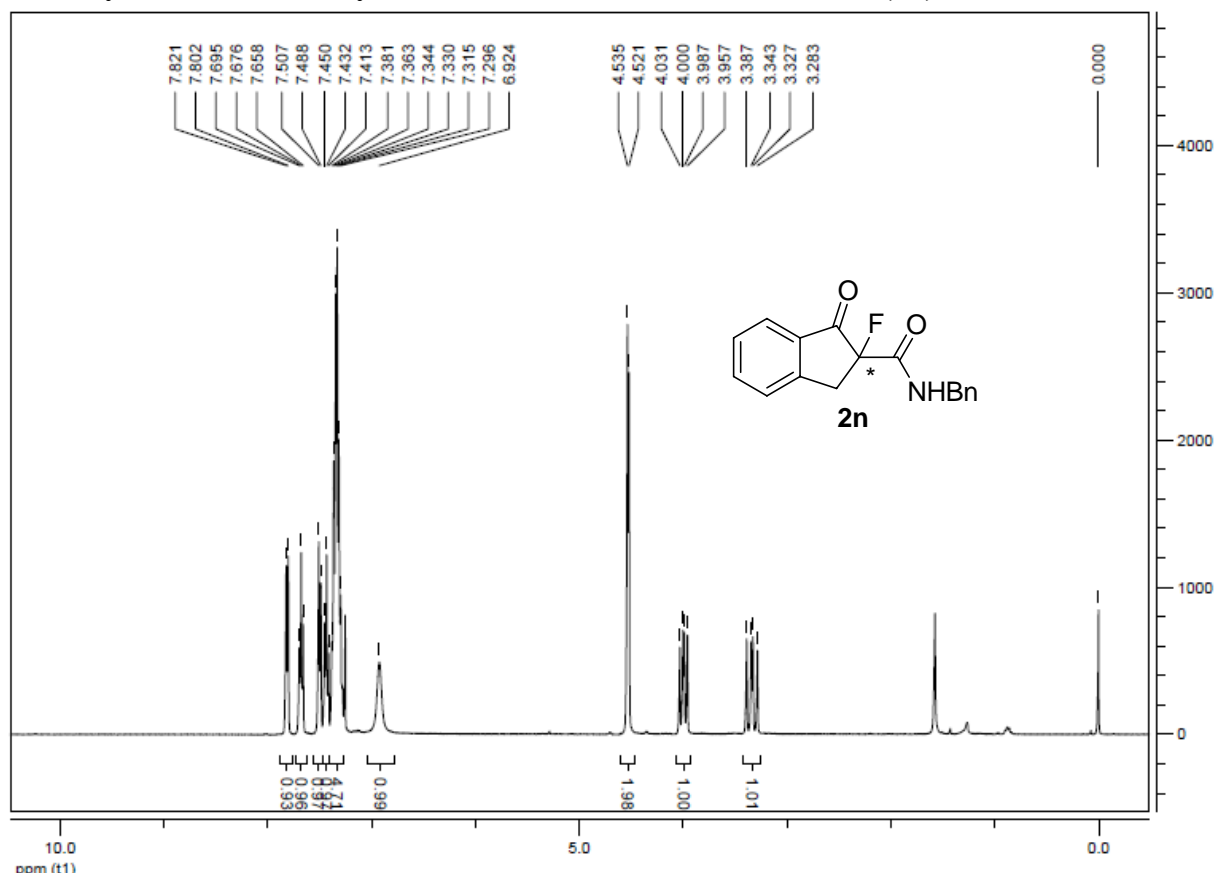
N-butyl-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxamide (2I)



2-fluoro-2,3-dihydro-1-oxo-N-phenyl-1H-indene-2-carboxamide (2m)

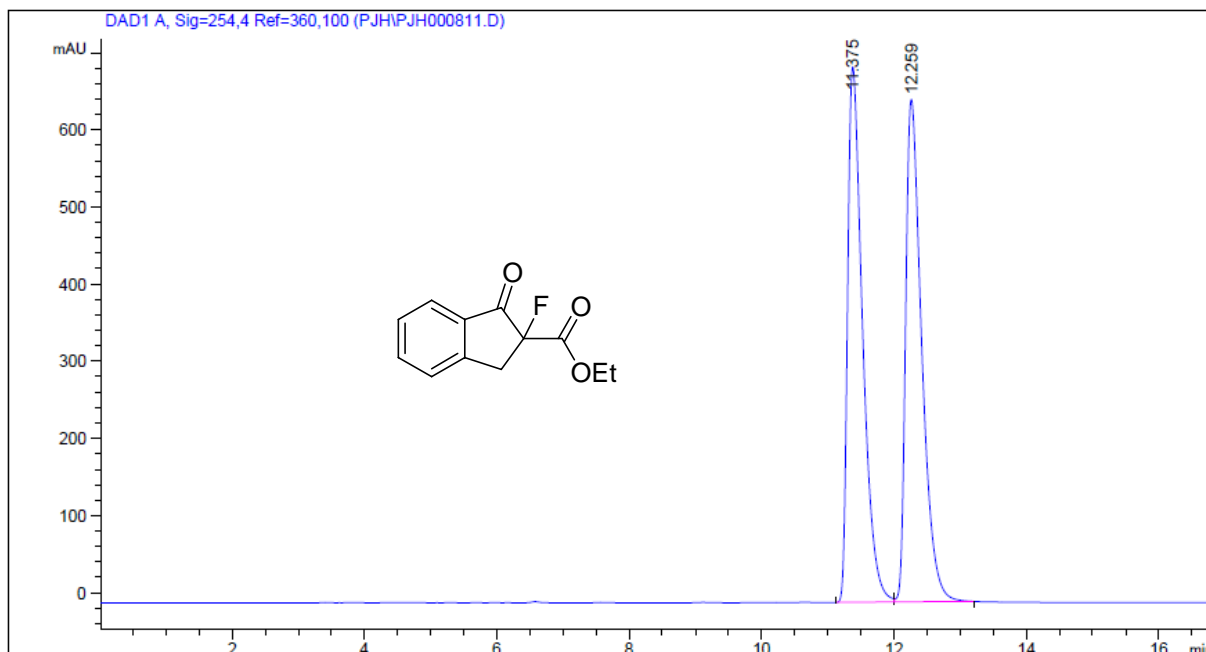


N-benzyl-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxamide (2n)

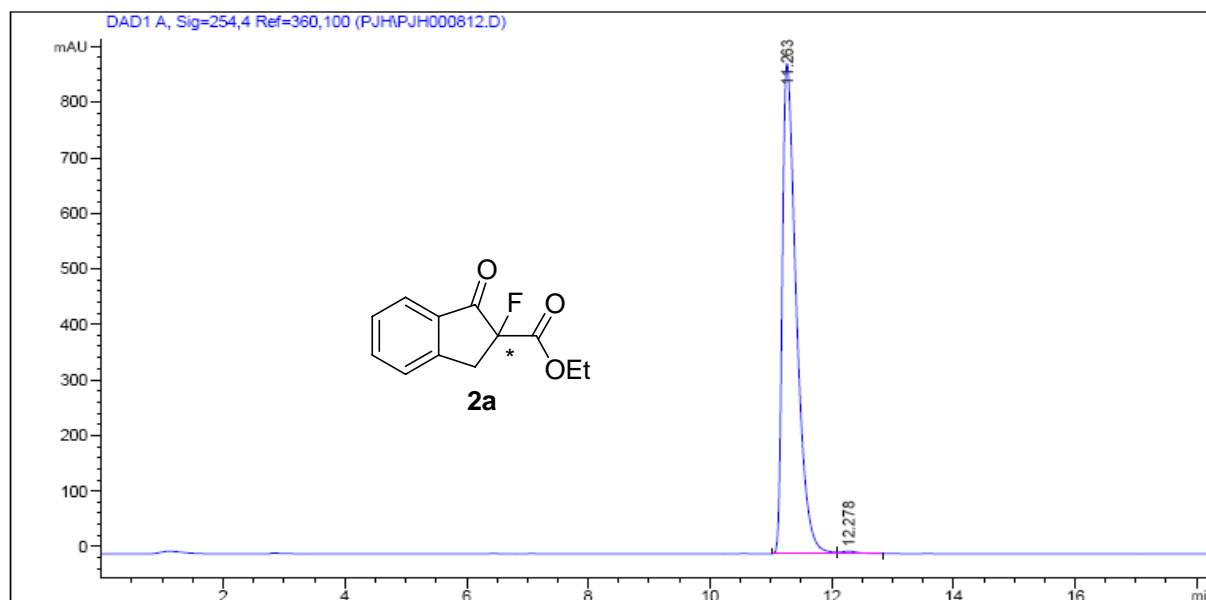


Copies of HPLC chromatographs

Ethyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2a)

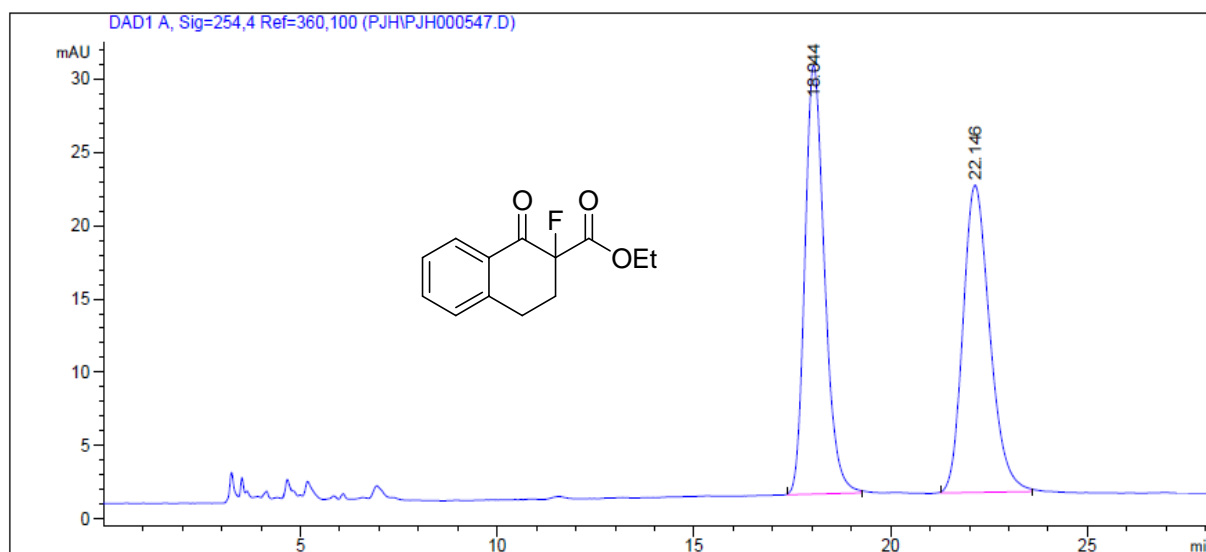


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.375	BV	0.2373	1.09120e4	694.50977	49.8435
2	12.259	VB	0.2545	1.09805e4	651.90015	50.1565

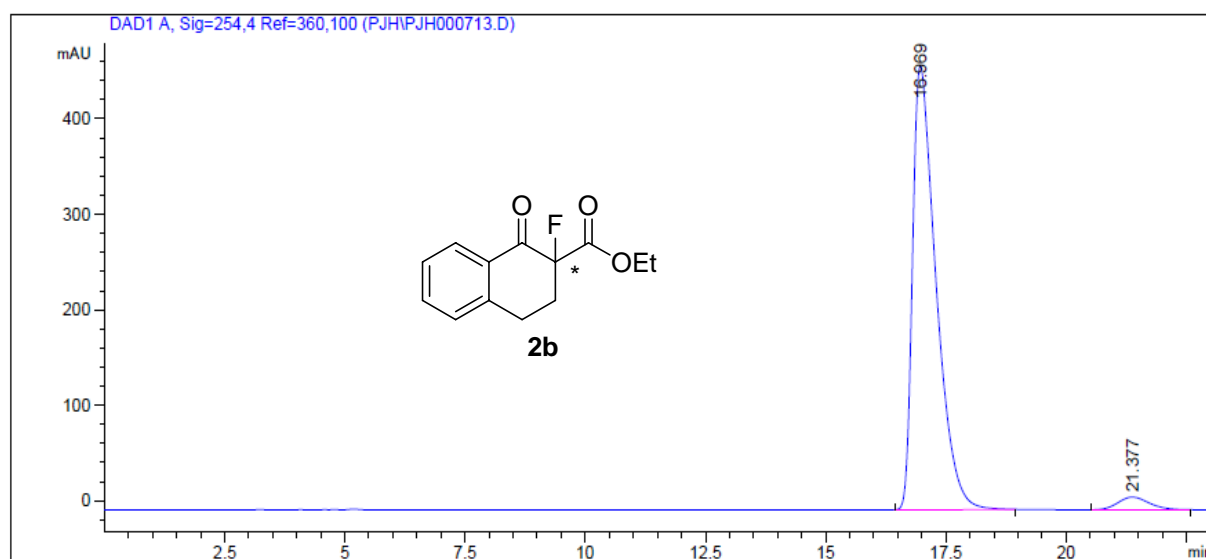


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.263	BB	0.2426	1.41218e4	882.70648	99.3810
2	12.278	BB	0.2816	87.95527	4.50798	0.6190

Ethyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2b)

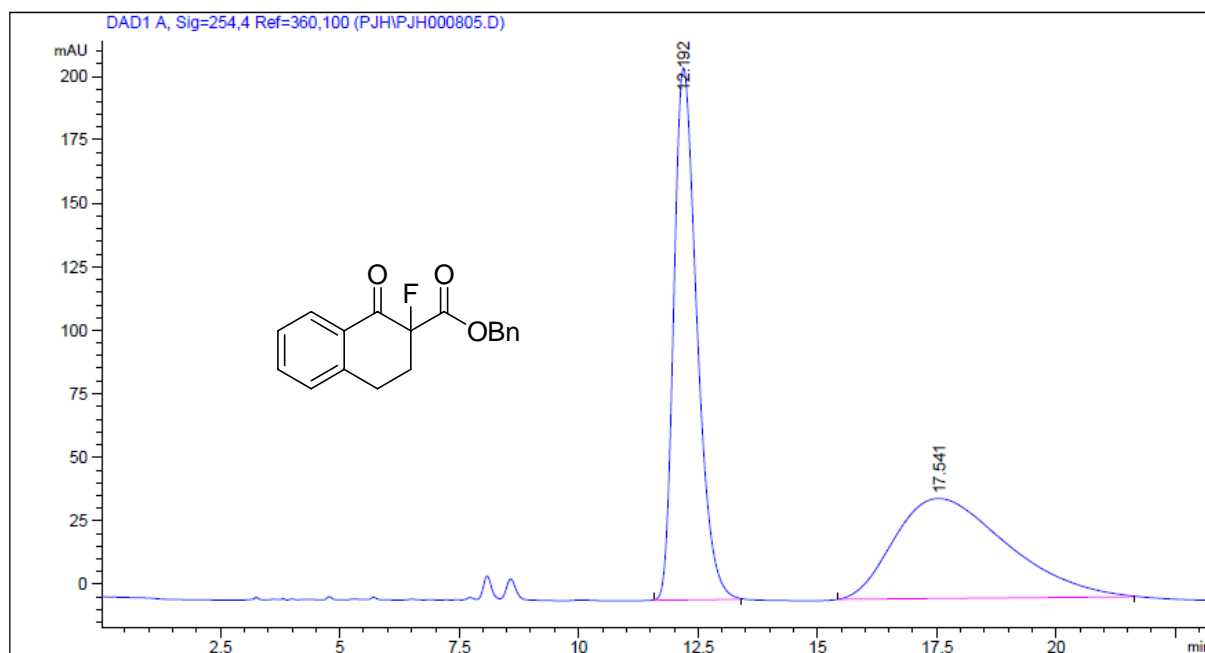


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.044	BB	0.5364	1012.91565	29.22315	50.5652
2	22.146	BB	0.7321	990.27252	20.92777	49.4348

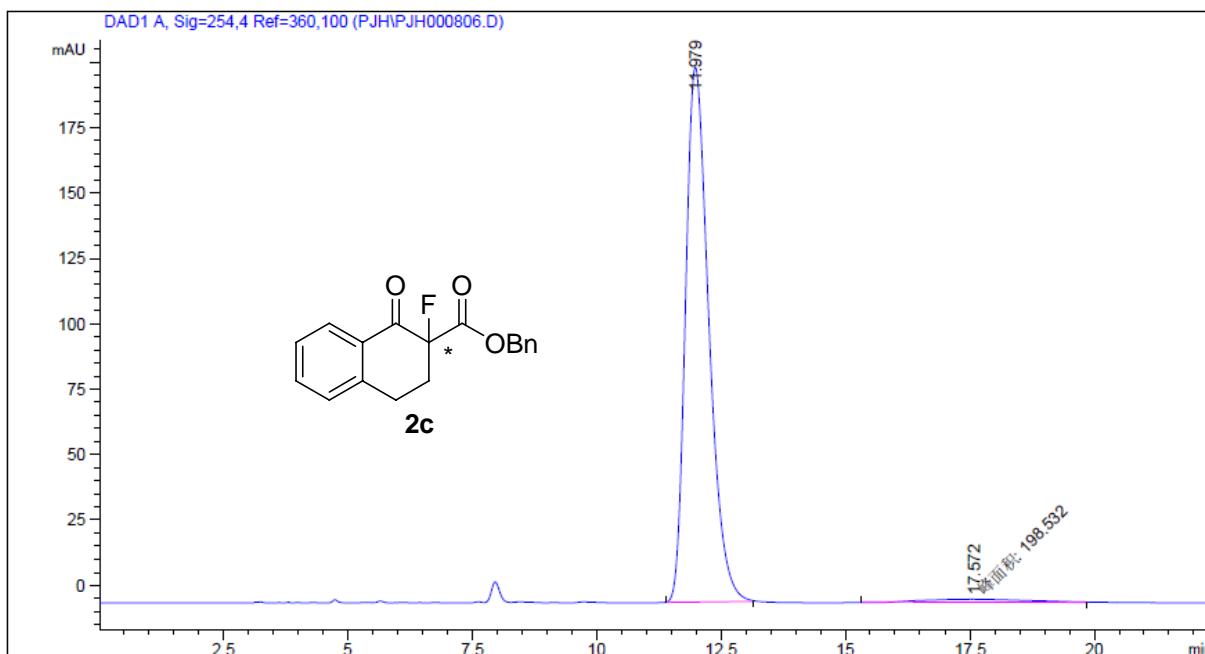


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.969	BB	0.5090	1.57344e4	464.77914	96.2966
2	21.377	BB	0.7011	605.10883	13.29238	3.7034

Benzyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2c)

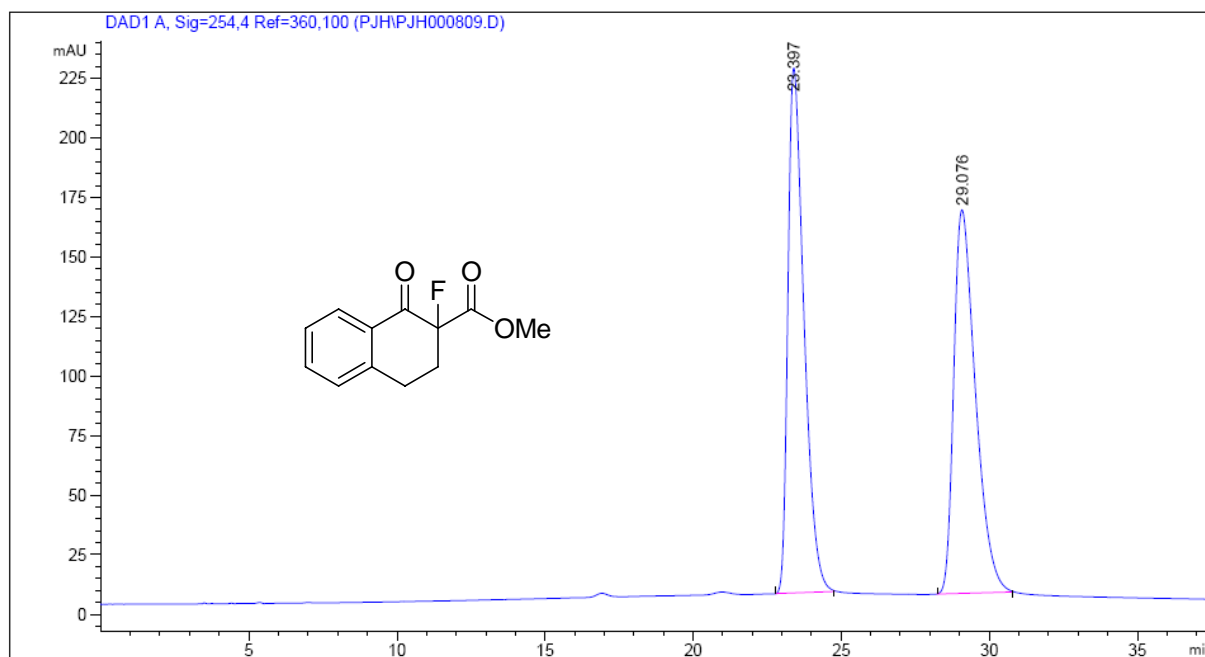


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.192	BB	0.5158	7037.55078	209.56975	51.9409
2	17.541	BB	2.0103	6511.60547	39.51986	48.0591

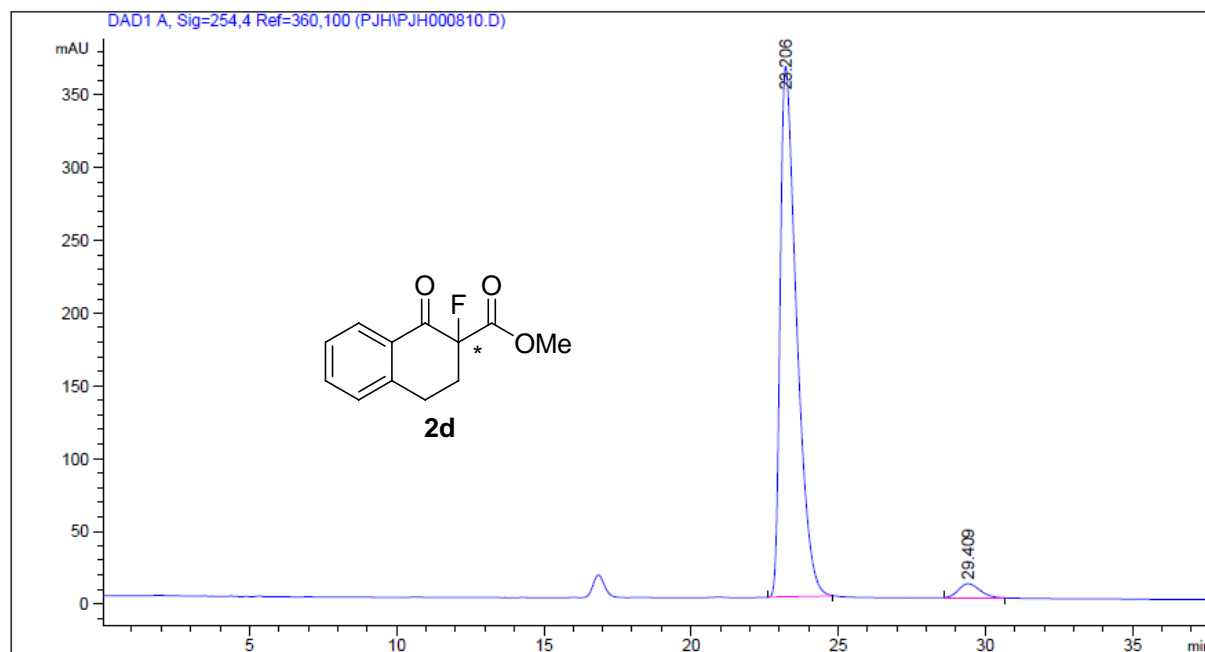


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.979	BB	0.5011	6646.14307	204.53091	97.0995
2	17.572	MM	2.5888	198.53157	1.27814	2.9005

Methyl 2-fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2d)

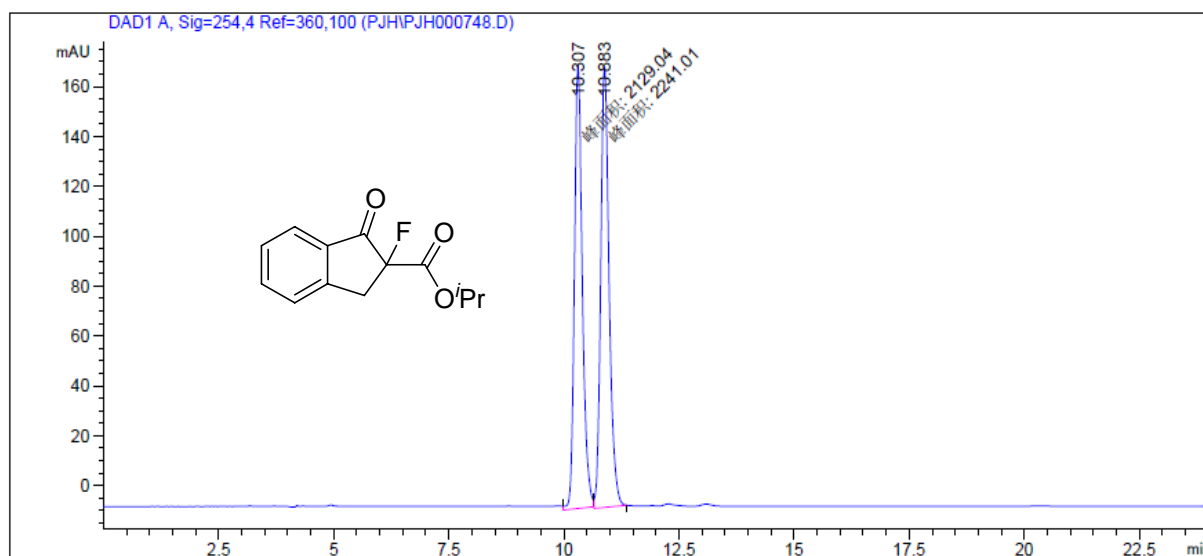


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.397	BB	0.5719	8308.37500	220.34935	50.2913
2	29.076	BB	0.7770	8212.13770	161.02727	49.7087

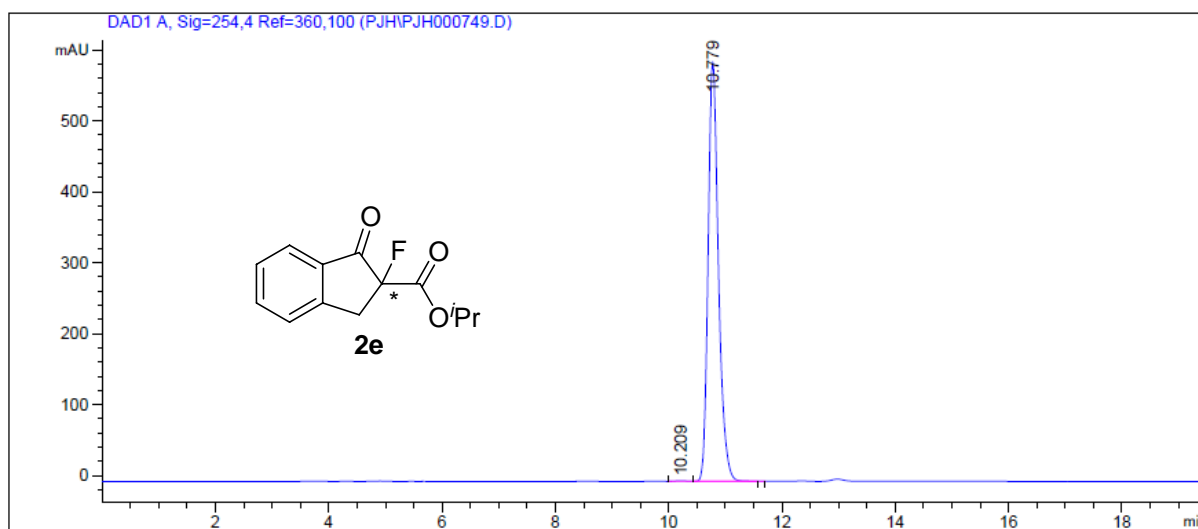


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1	23.206	BB	0.5842	1.42036e4	364.82834	96.6882
2	29.409	BB	0.7506	486.50897	9.64332	3.3118

Propyl 2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2e)

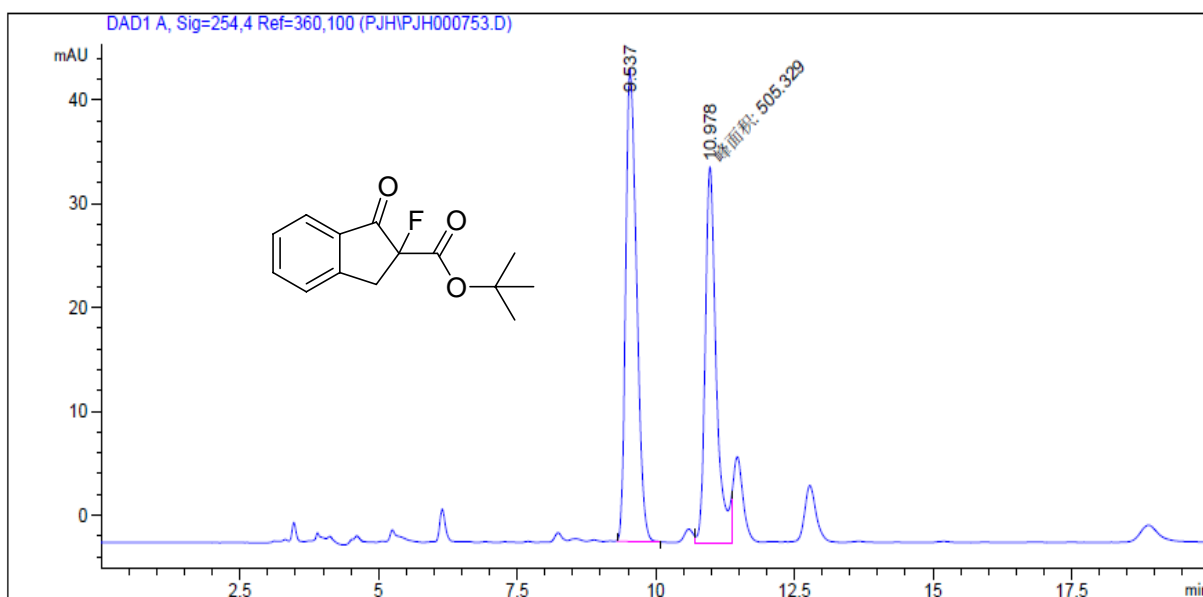


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.307	MM	0.1990	2129.04492	178.27754	48.7190
2	10.883	MM	0.2111	2241.00928	176.89294	51.2810

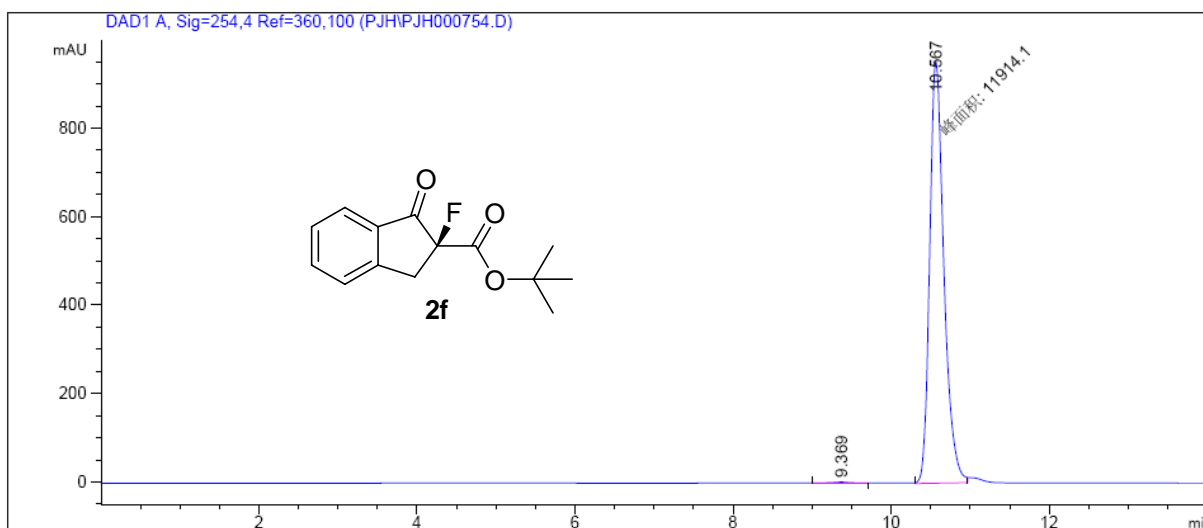


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.209	VB S	0.2155	14.91566	1.01448	0.1987
2	10.779	BB T	0.1917	7491.82568	591.62146	99.8013

tert-Butyl 2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2f)

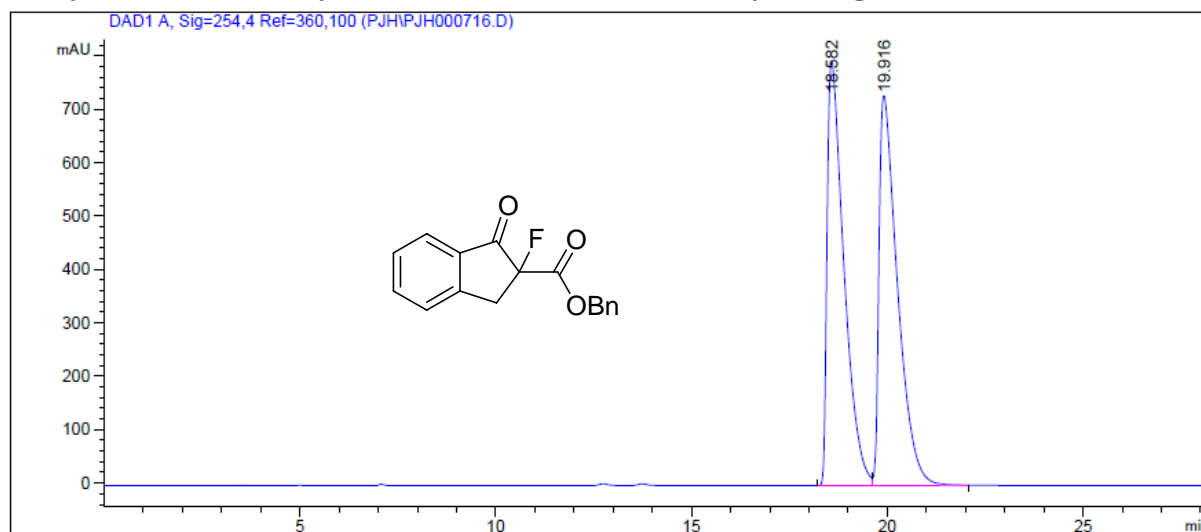


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.537	BB S	0.2215	622.99792	45.56964	55.2143
2	10.978	MM	0.2319	505.32892	36.32185	44.7857

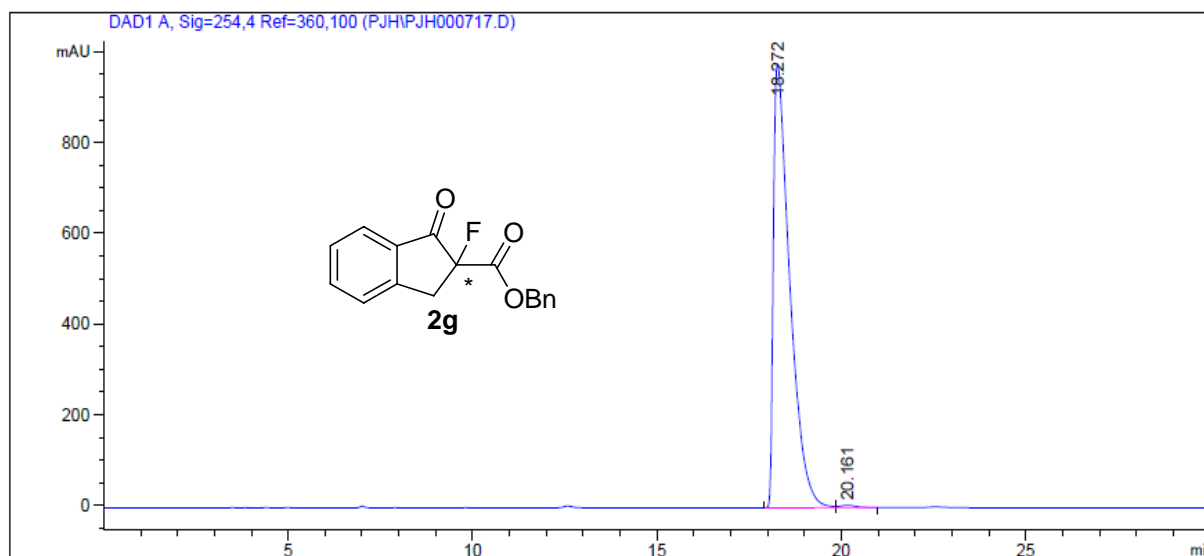


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.369	VB S	0.1881	31.04338	2.38074	0.2599
2	10.567	MM	0.2081	1.19141e4	954.03296	99.7401

Benzyl 2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2g)

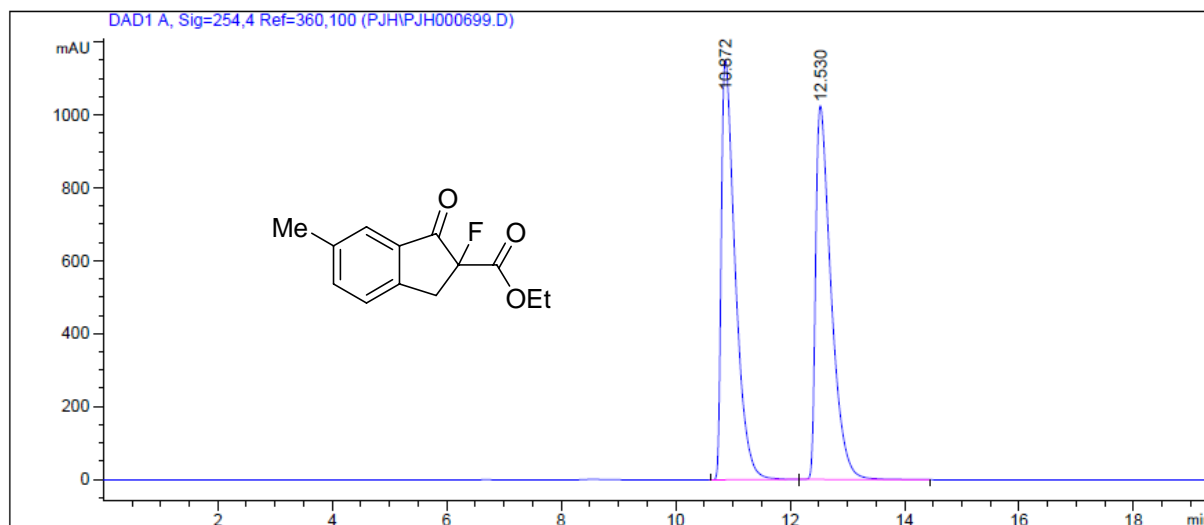


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.582	BV	0.4443	2.37227e4	794.61365	49.7510
2	19.916	VB	0.4868	2.39601e4	730.22223	50.2490

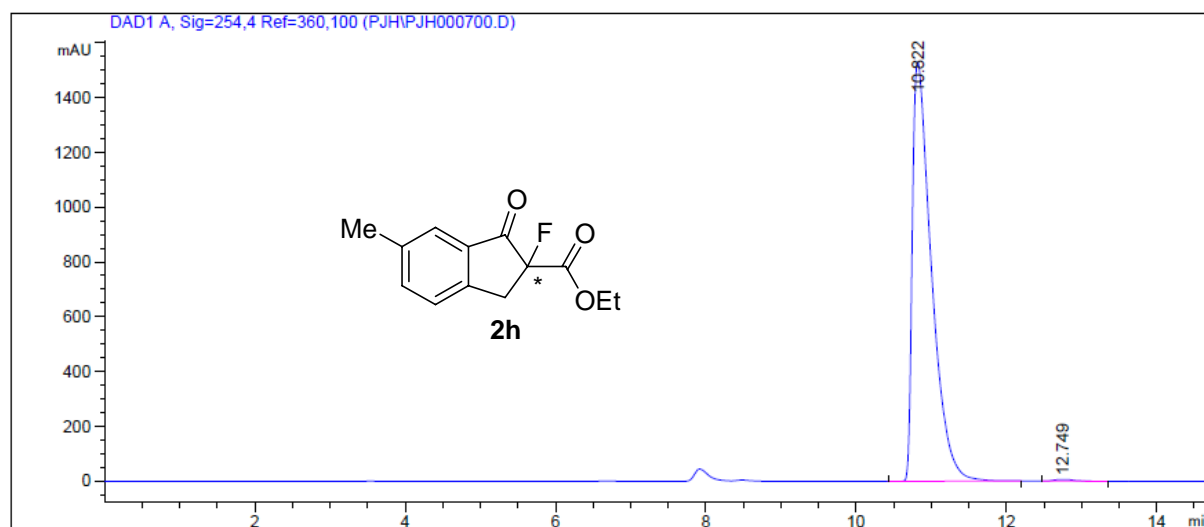


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.272	BV	0.4537	3.01580e4	978.25580	99.4684
2	20.161	VB	0.4388	161.17001	5.39029	0.5316

Ethyl 2-fluoro-2,3-dihydro-6-methyl-1-oxo-1H-indene-2-carboxylate (2h)

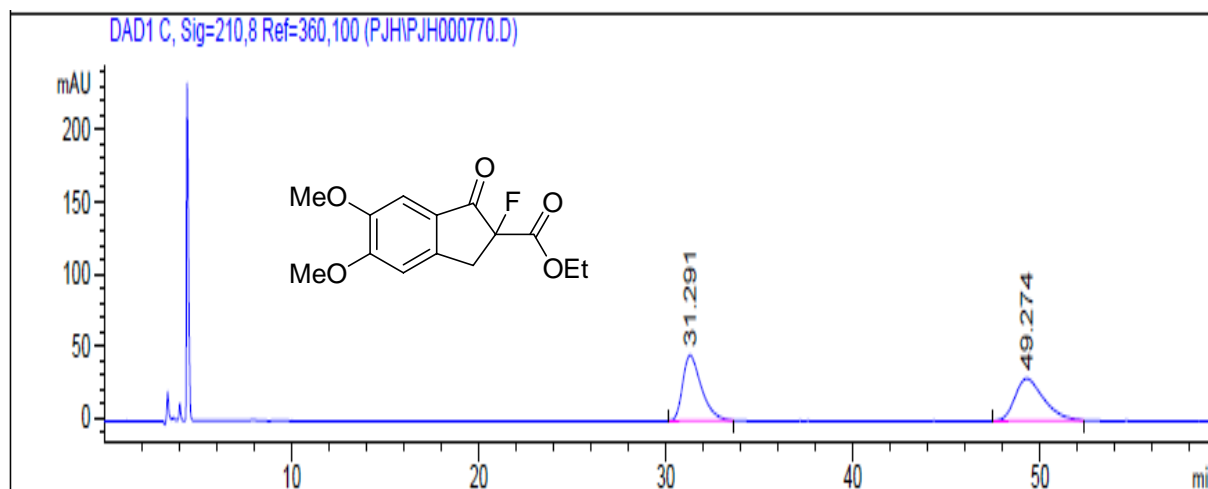


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1	10.872	VB	0.2522	1.93643e4	1151.17883	50.2361
2	12.530	BB	0.2782	1.91822e4	1025.84521	49.7639

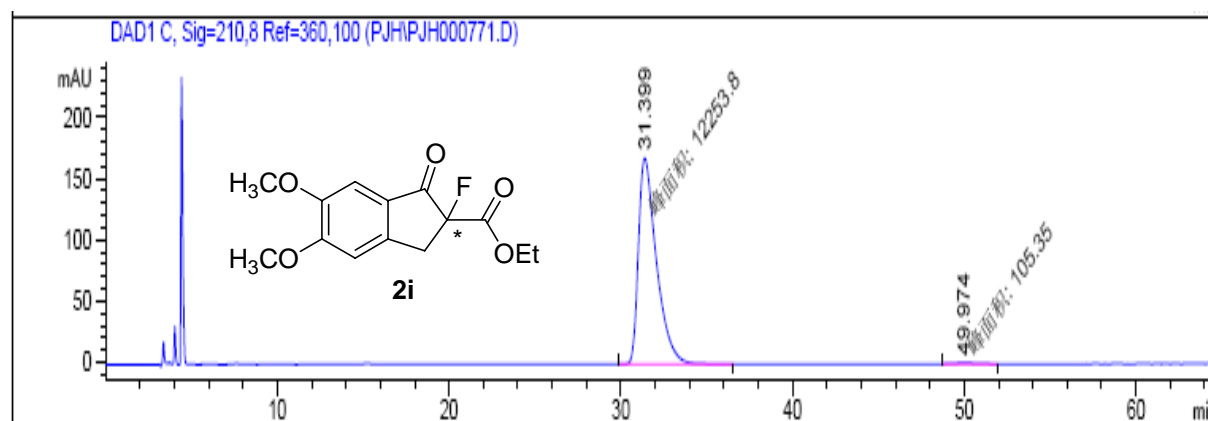


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.822	VB S	0.2611	2.69321e4	1531.90955	99.6265
2	12.749	BB	0.2431	100.96582	6.43231	0.3735

Ethyl 2-fluoro-2,3-dihydro-5,6-dimethoxy-1-oxo-1H-indene-2-carboxylate (2i)

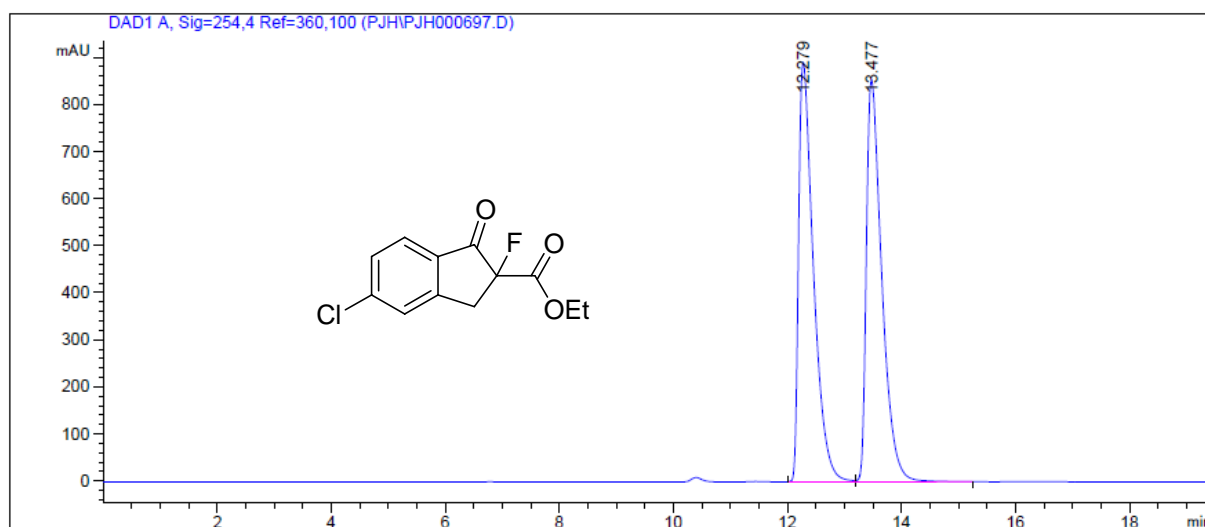


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.291	BB	1.0184	3182.94702	45.59554	50.0884
2	49.274	BB	1.6093	3171.71167	29.38514	49.9116

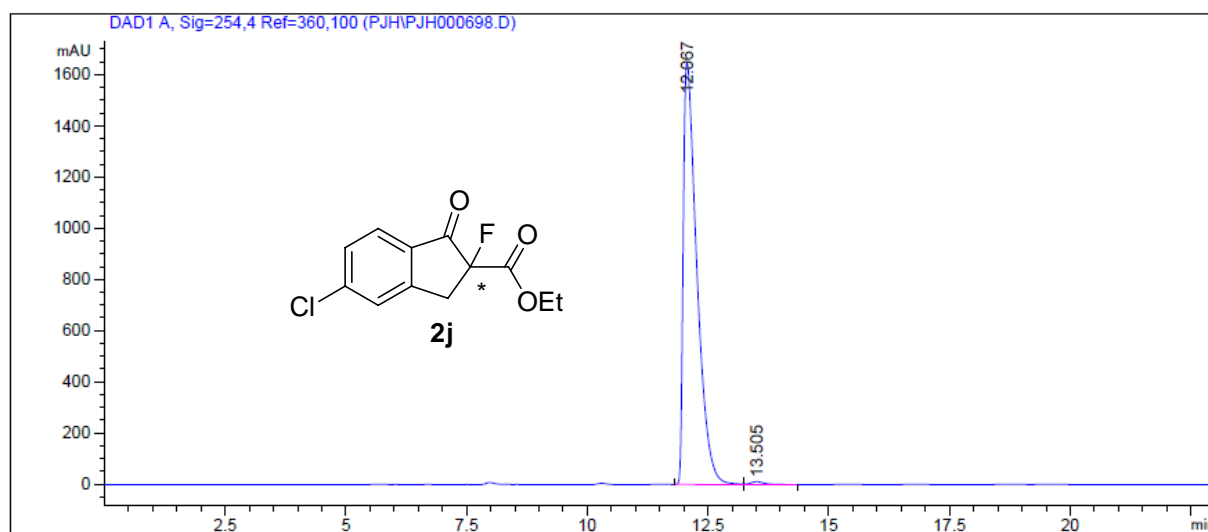


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.399	MM	1.2155	1.22538e4	168.01546	99.1476
2	49.974	MM	1.5556	105.35039	1.12873	0.8524

Ethyl 5-chloro-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2j)

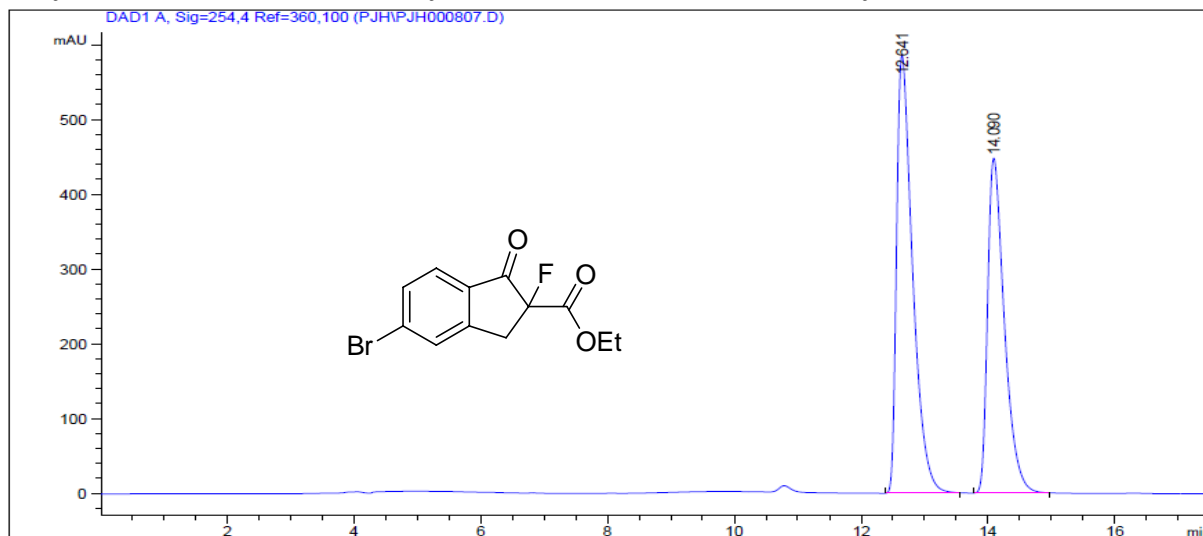


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.279	BV	0.2710	1.61208e4	891.30896	50.0317
2	13.477	VB	0.2838	1.61003e4	854.39325	49.9683

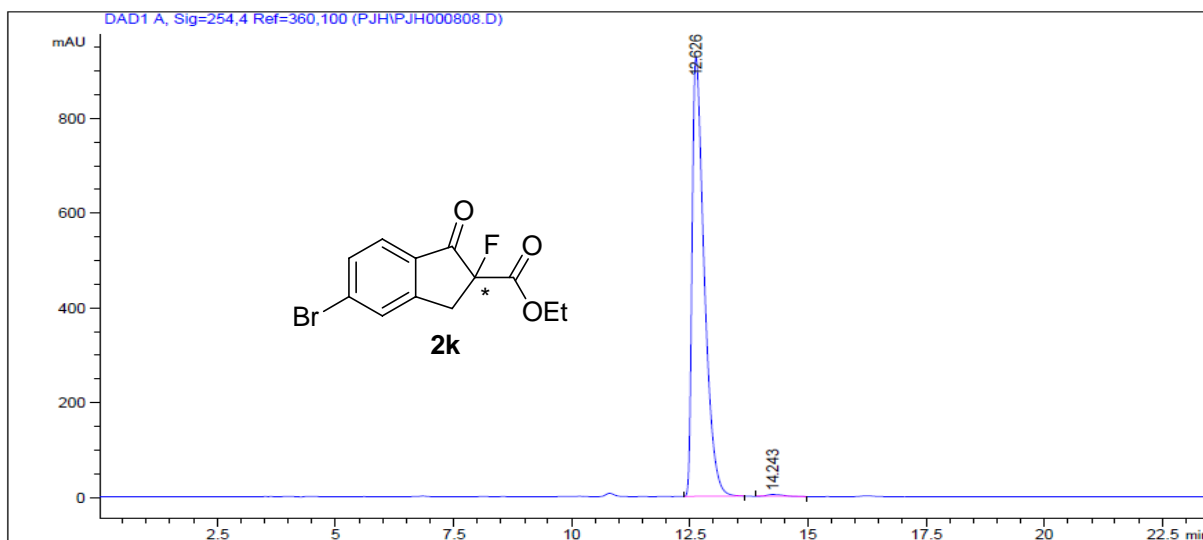


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.067	BV	0.2921	3.22049e4	1647.15869	99.2764
2	13.505	VB	0.2956	234.74156	11.82297	0.7236

Ethyl 5-bromo-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxylate (2k)

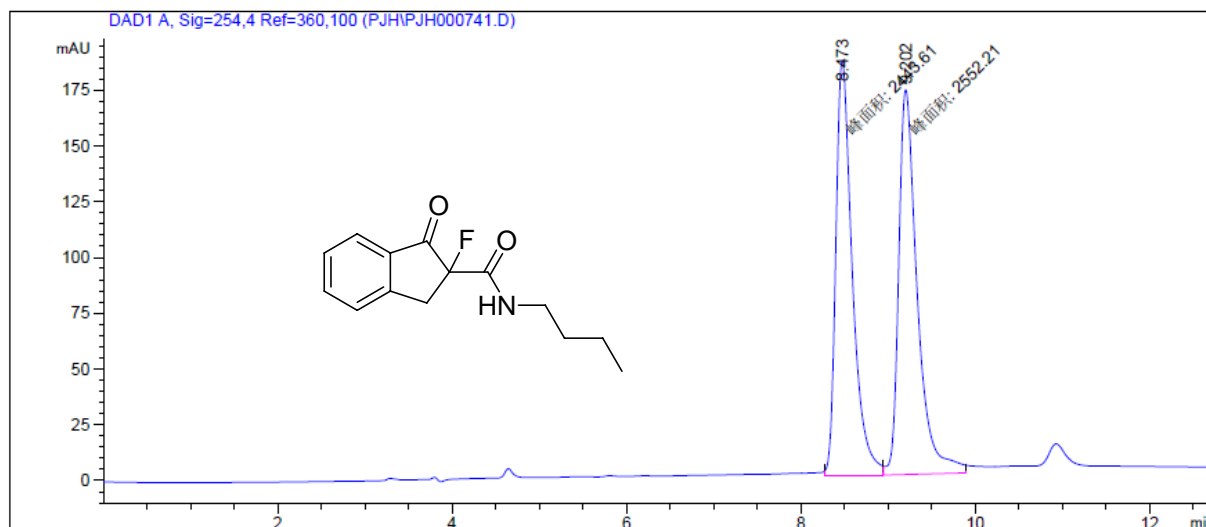


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.641	BB	0.2624	1.02674e4	585.96002	55.5121
2	14.090	BB	0.2784	8228.37109	447.79663	44.4879

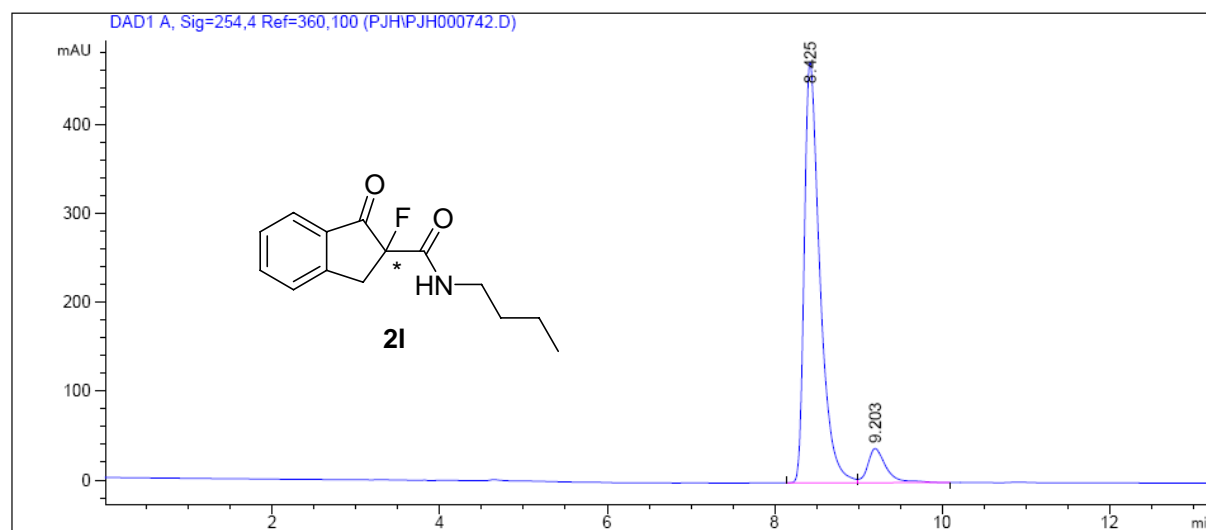


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.626	BB	0.2681	1.65446e4	927.36285	99.4095
2	14.243	BB	0.3406	98.27766	4.08649	0.5905

N-butyl-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxamide (2l)

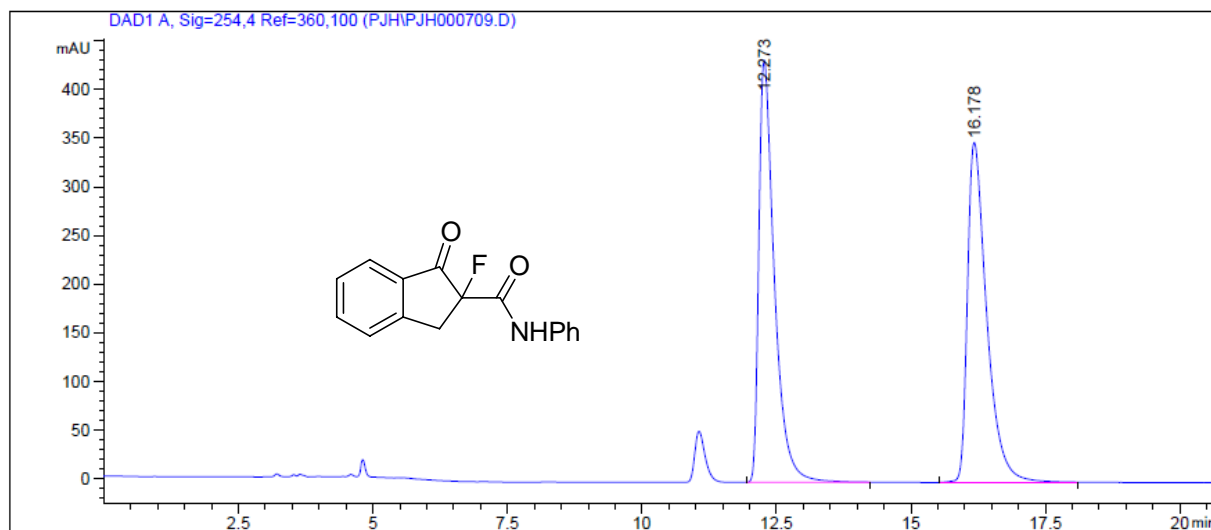


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.473	MM	0.2190	2443.60986	185.98207	48.9131
2	9.202	MM	0.2466	2552.20898	172.52467	51.0869

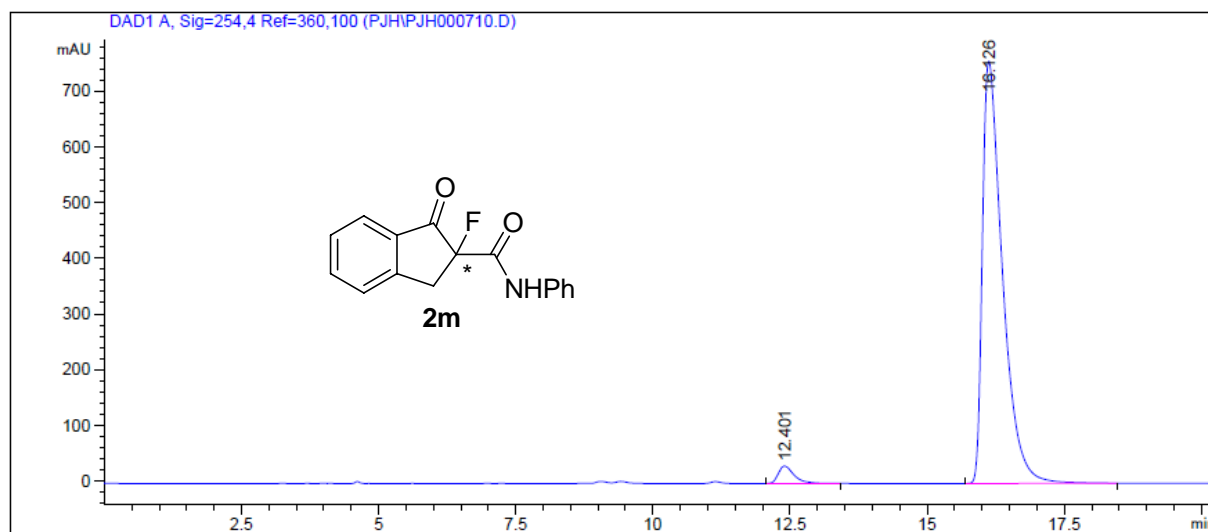


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.425	BV	0.1950	6126.85352	473.52057	91.2684
2	9.203	VB S	0.2259	586.15631	38.43771	8.7316

2-fluoro-2,3-dihydro-1-oxo-N-phenyl-1H-indene-2-carboxamide (2m)

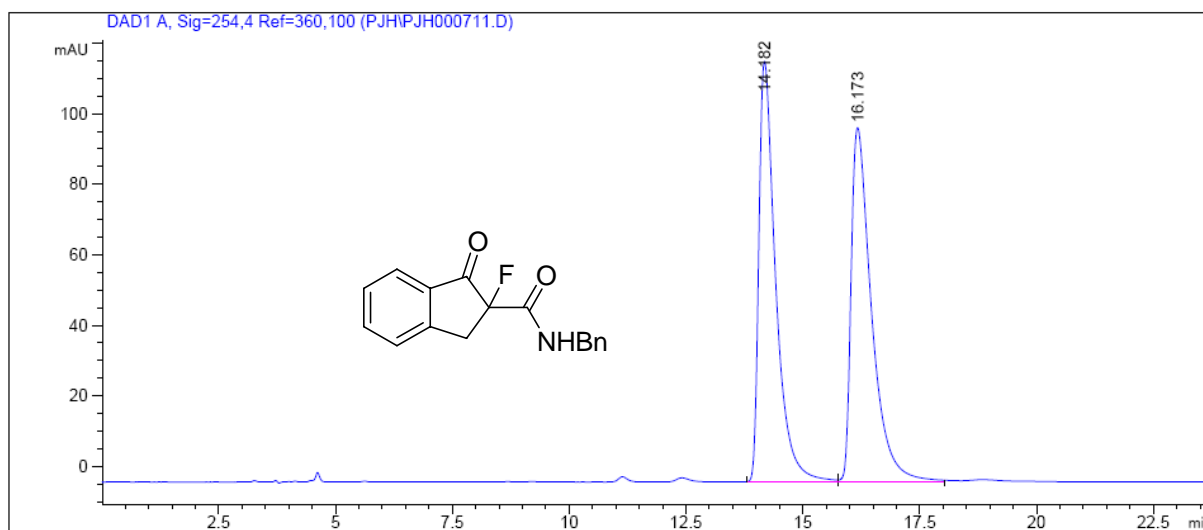


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.273	BB	0.2985	8714.30859	433.62891	50.0220
2	16.178	BB	0.3708	8706.65039	349.25421	49.9780

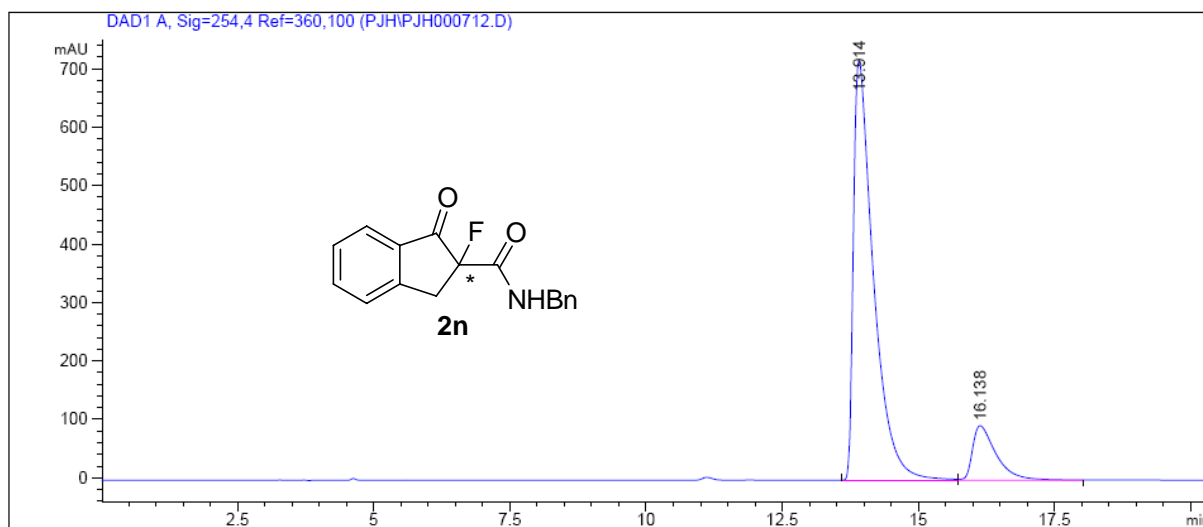


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.401	BB	0.2983	639.49115	31.84698	3.2132
2	16.126	BB	0.3807	1.92628e4	757.56415	96.7868

N-benzyl-2-fluoro-2,3-dihydro-1-oxo-1H-indene-2-carboxamide (2n)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.182	BV	0.3724	2988.03931	119.21655	49.5036
2	16.173	VB	0.4503	3047.95923	100.37833	50.4964



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.914	BV	0.3748	1.83714e4	717.40485	86.6498
2	16.138	VB	0.4501	2830.50049	93.26437	13.3502