

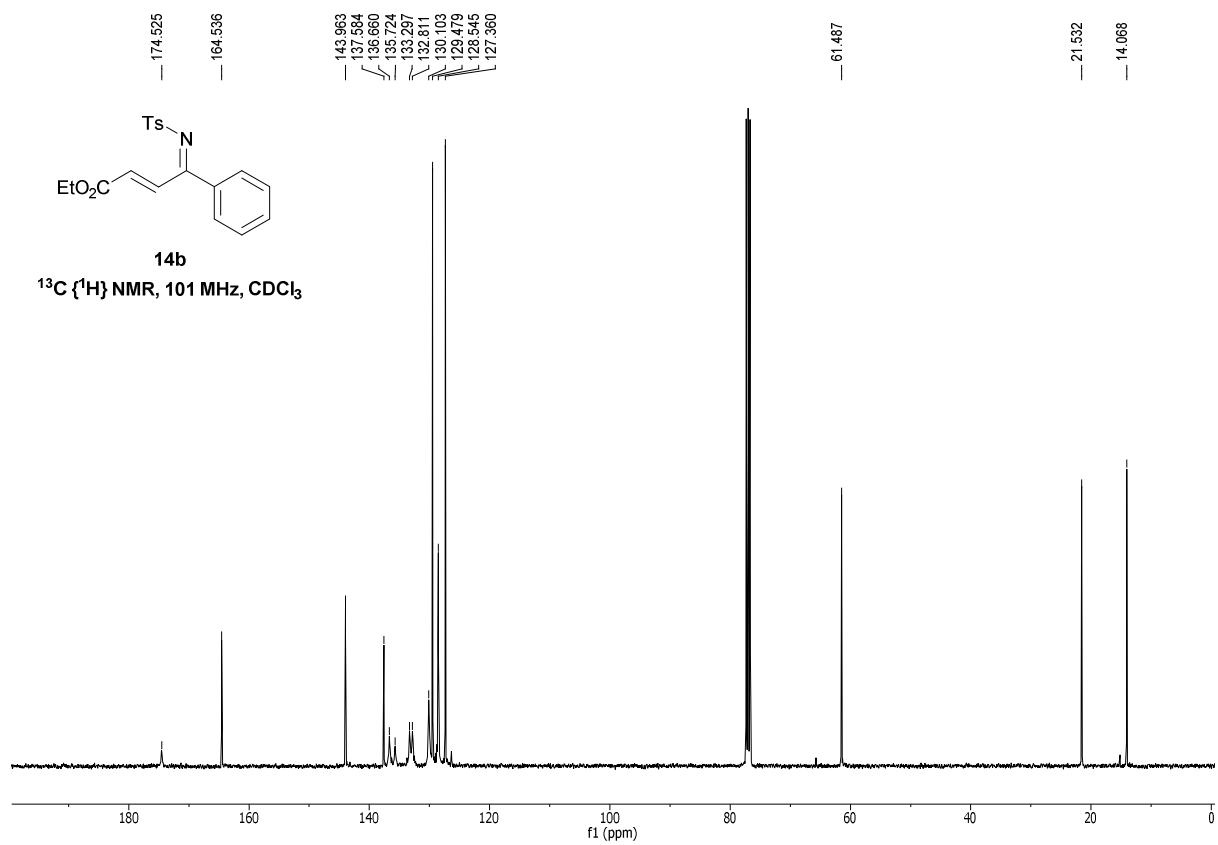
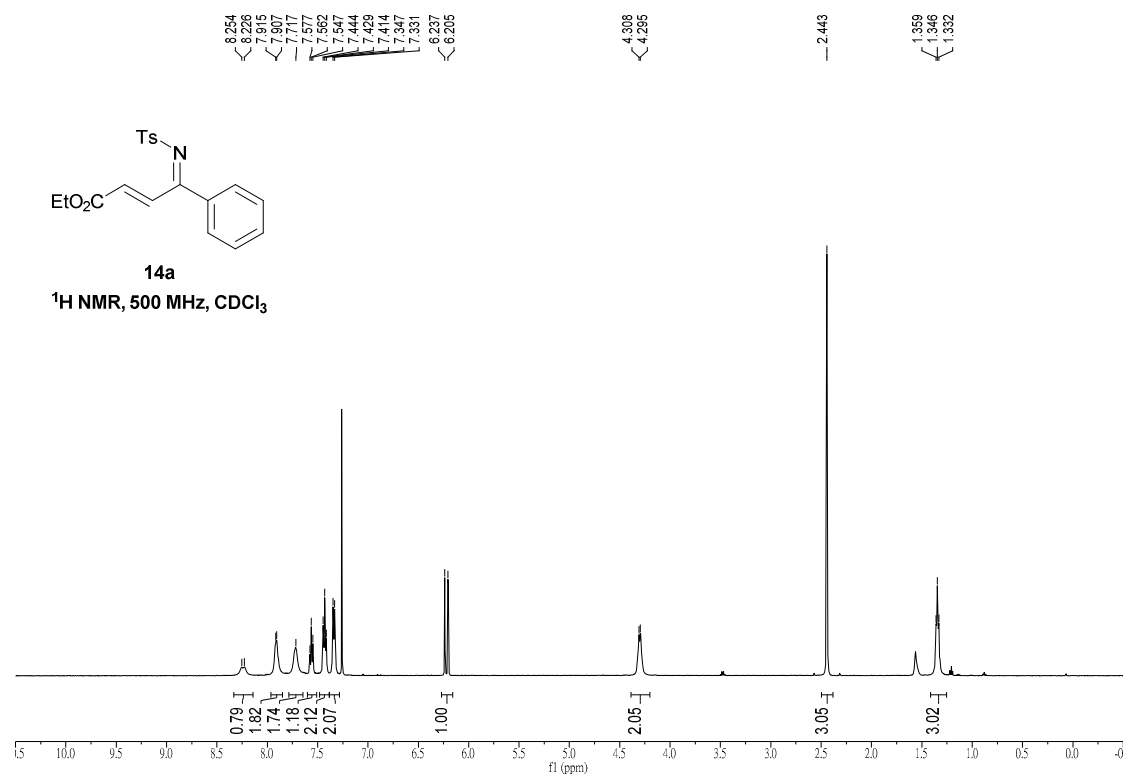
Exploring the Scope of the Isothiourea-mediated Synthesis of Dihydropyridinones

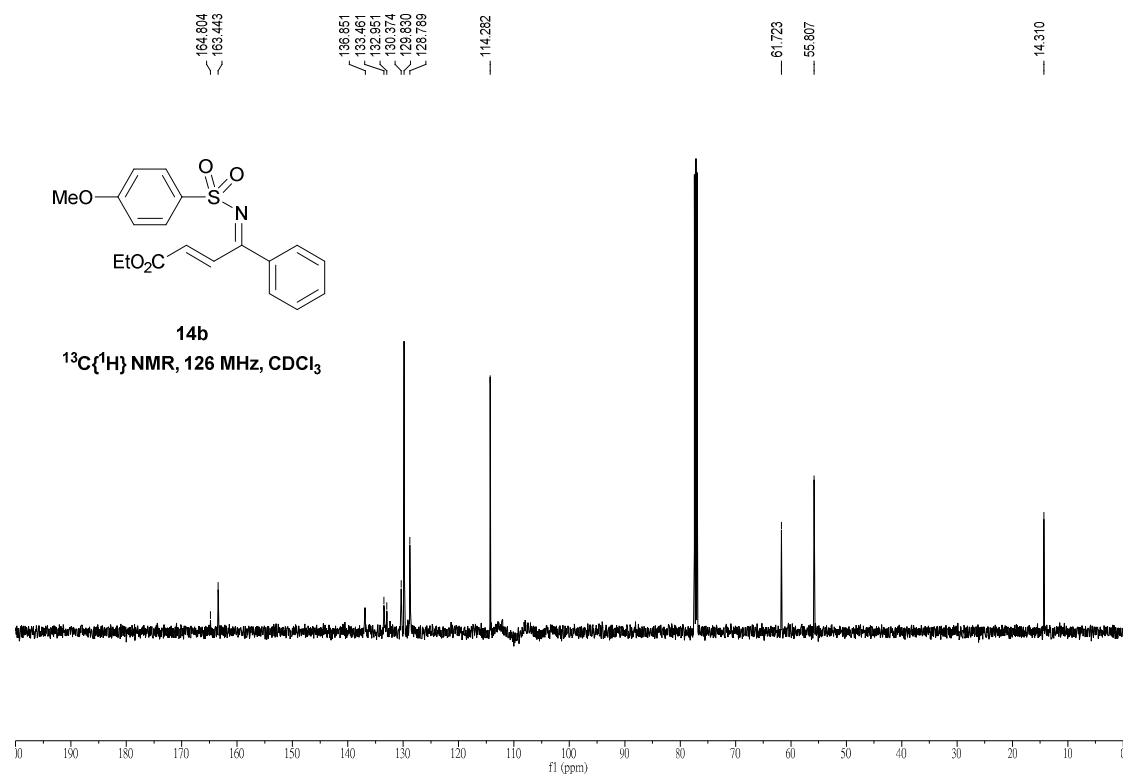
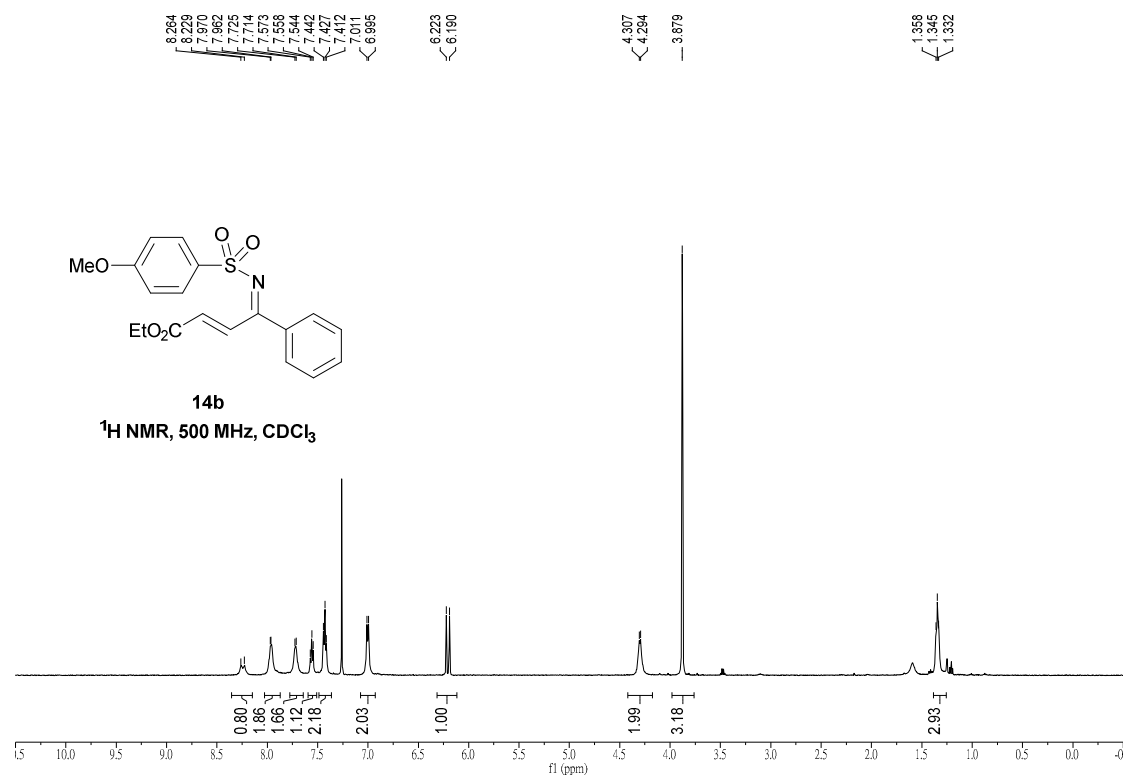
Supporting Information

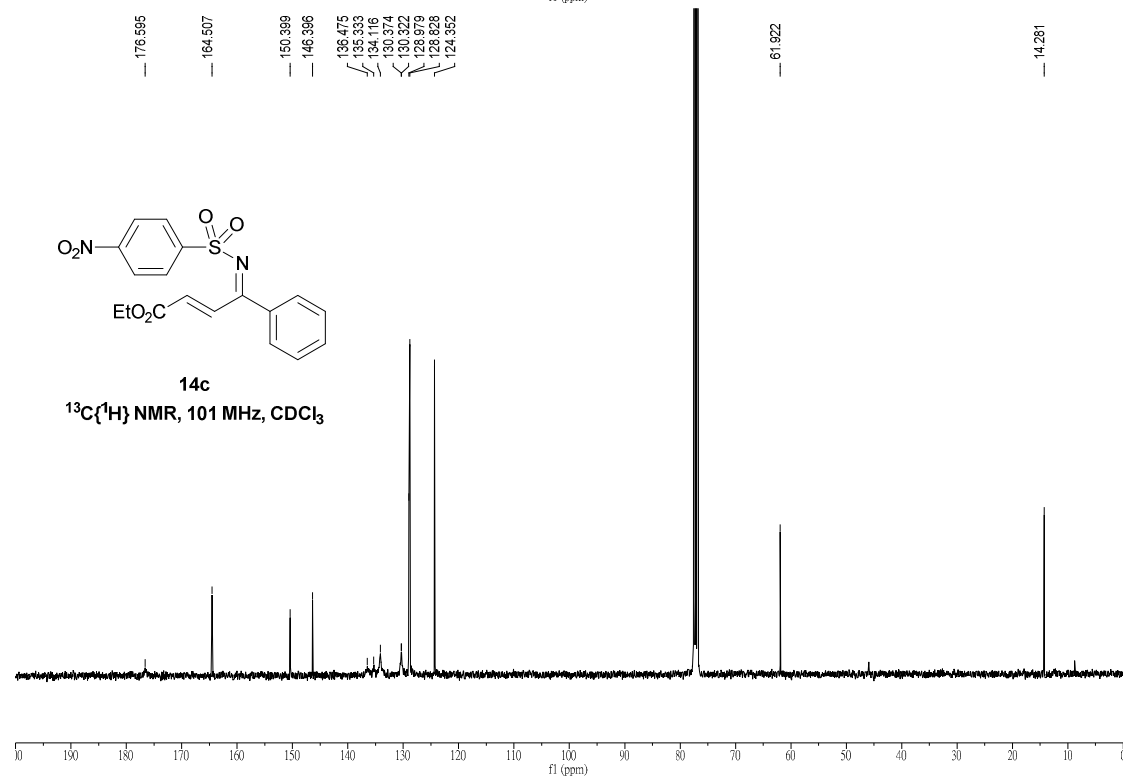
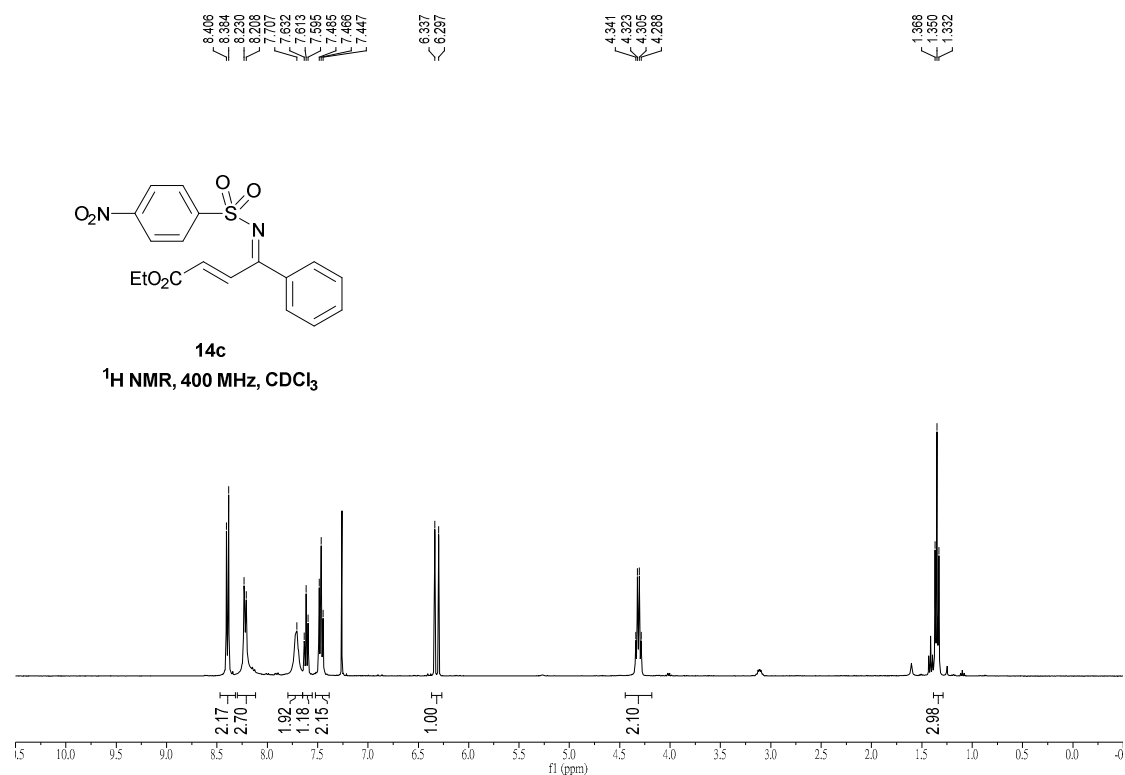
*P-P. Yeh, D. S. B. Daniels, C. Fallan, E. Gould, C. Simal, J. E. Taylor, A. M. Z. Slawin, A. D. Smith**

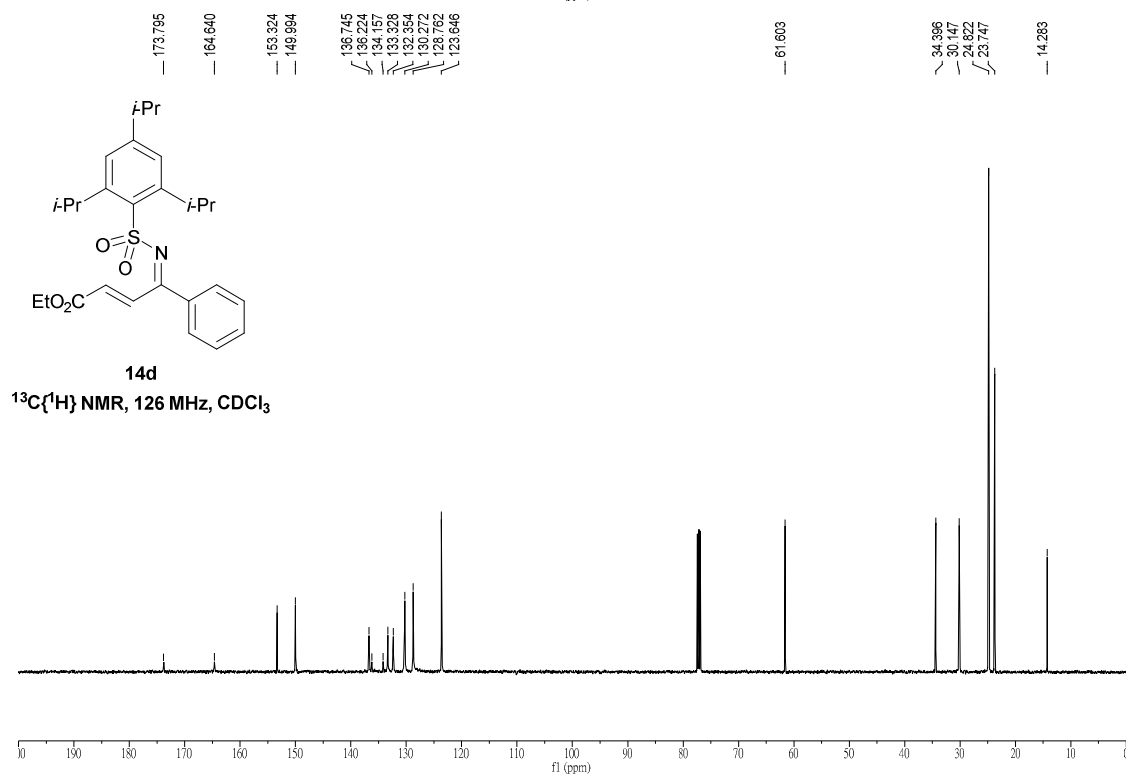
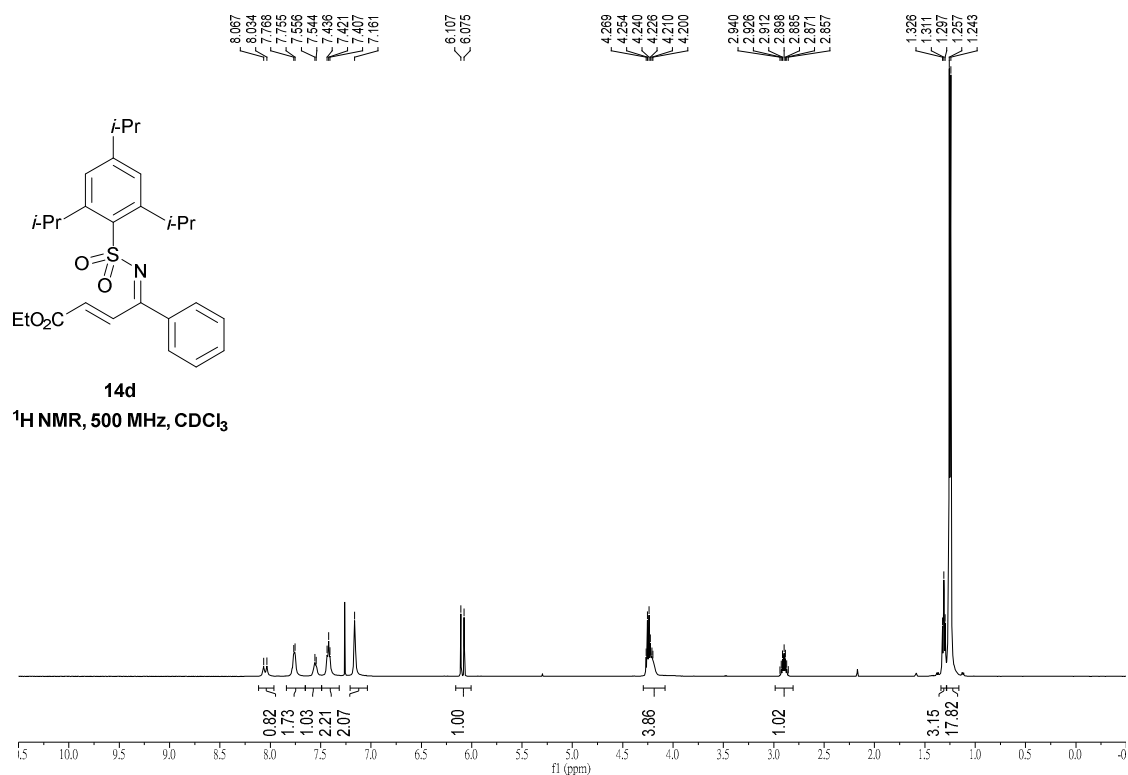
EaStCHEM, School of Chemistry, University of St Andrews, North Haugh, St Andrews, KY16 9ST, UK

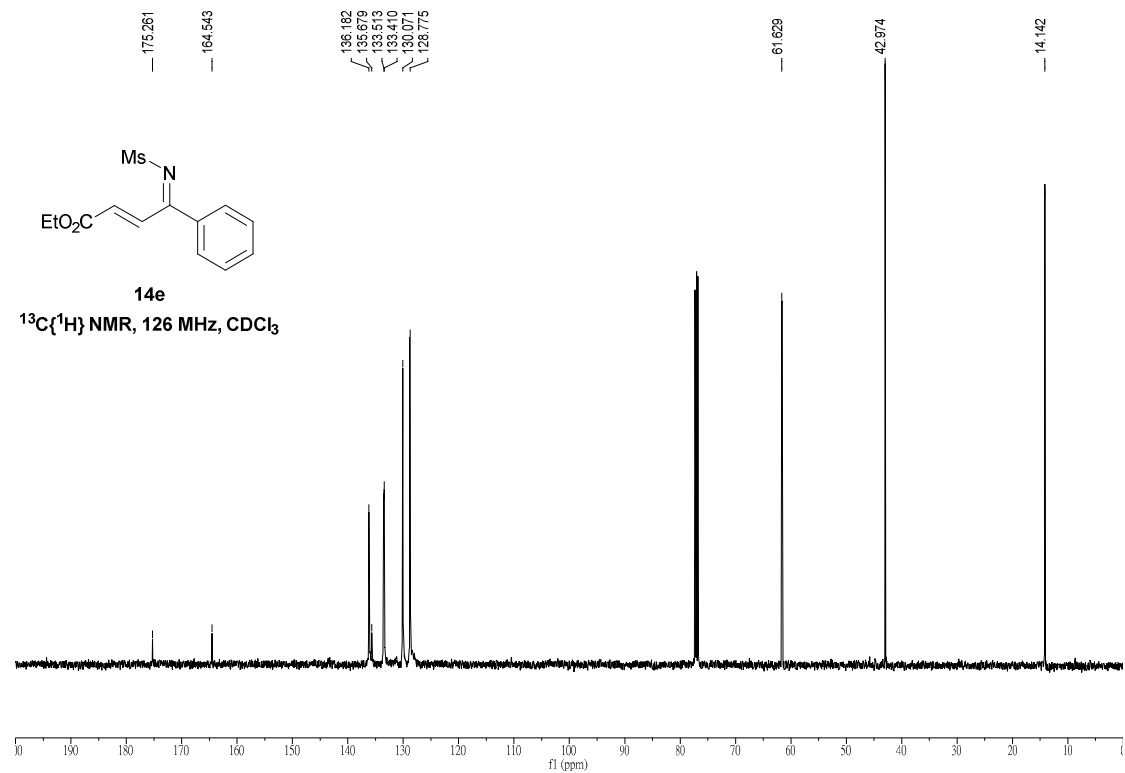
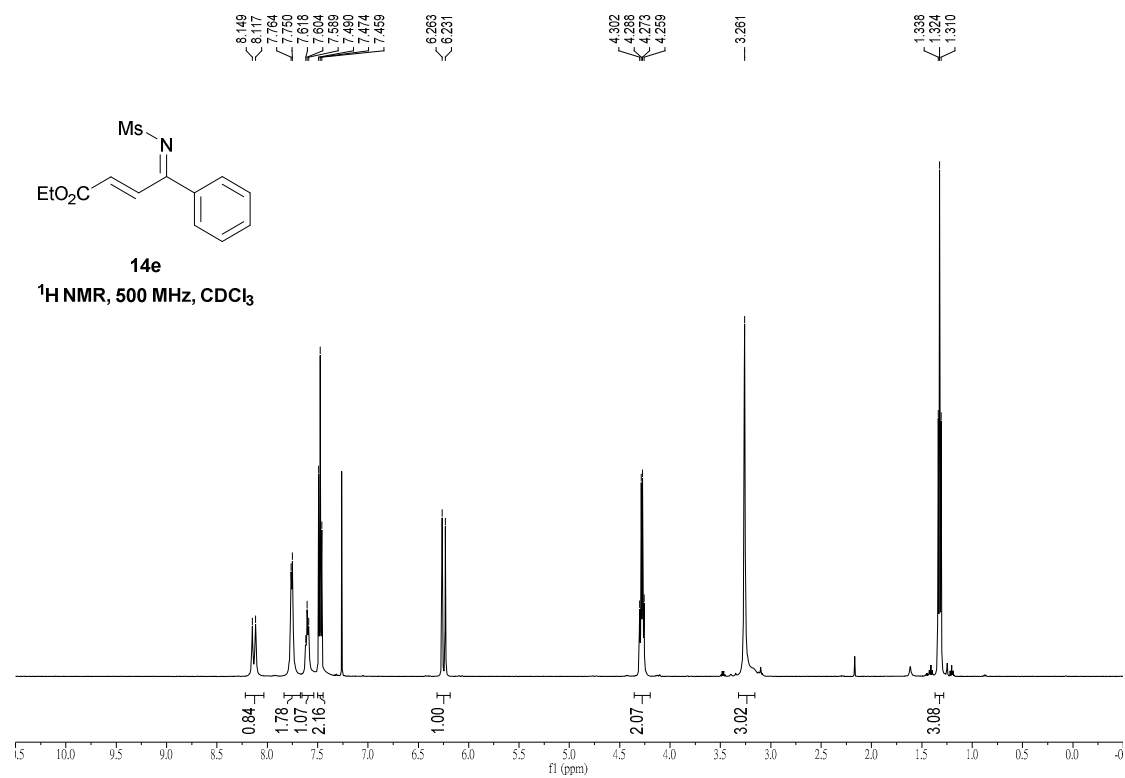
E-mail: ads10@st-andrews.ac.uk

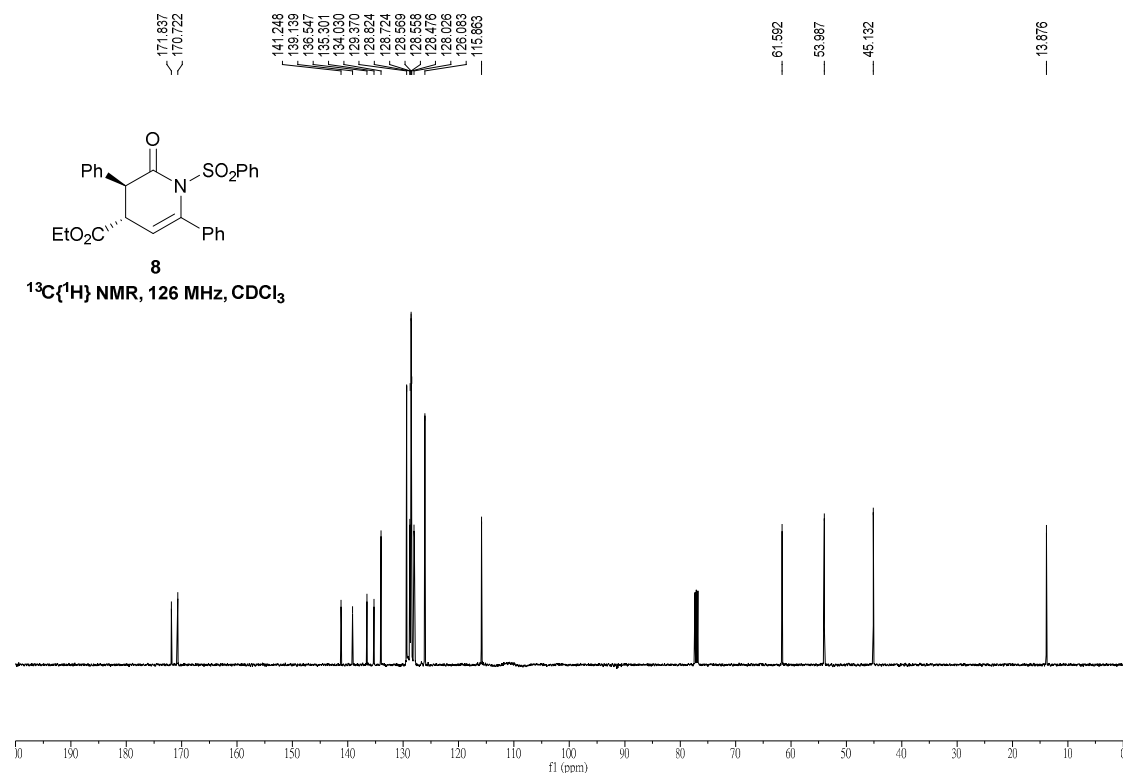
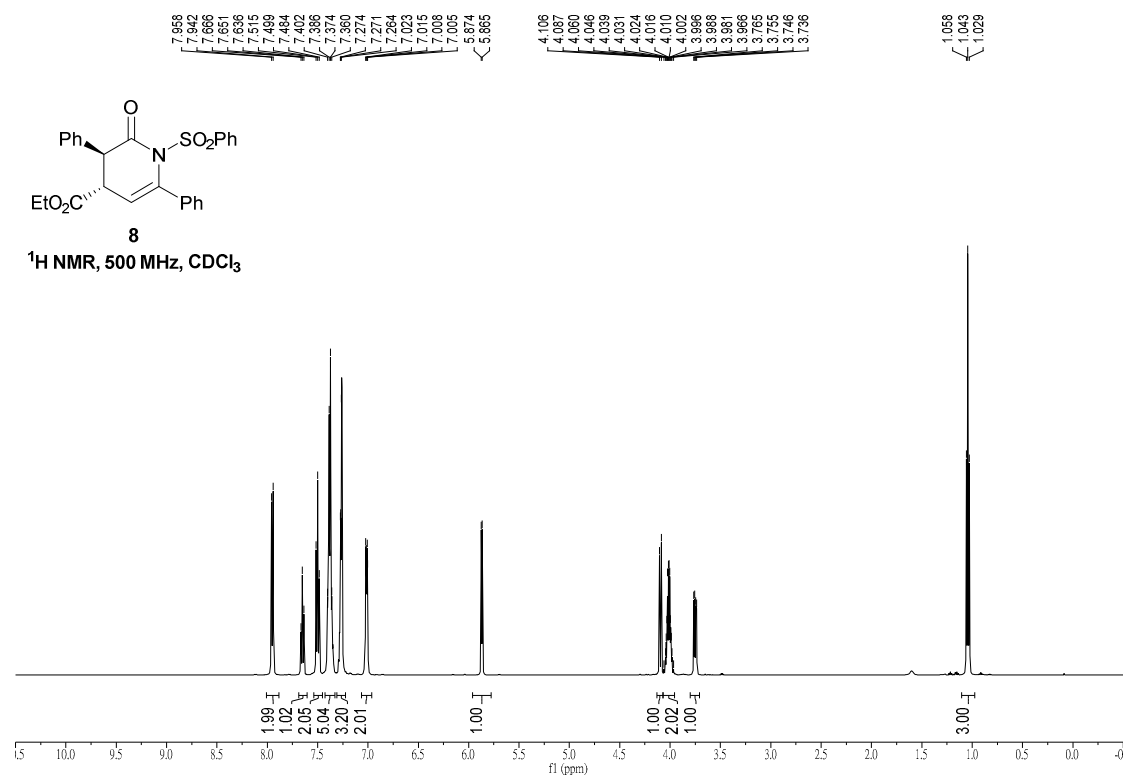
(2E,4E)-Ethyl 4-phenyl-4-(tosylimino)but-2-enoate 14a

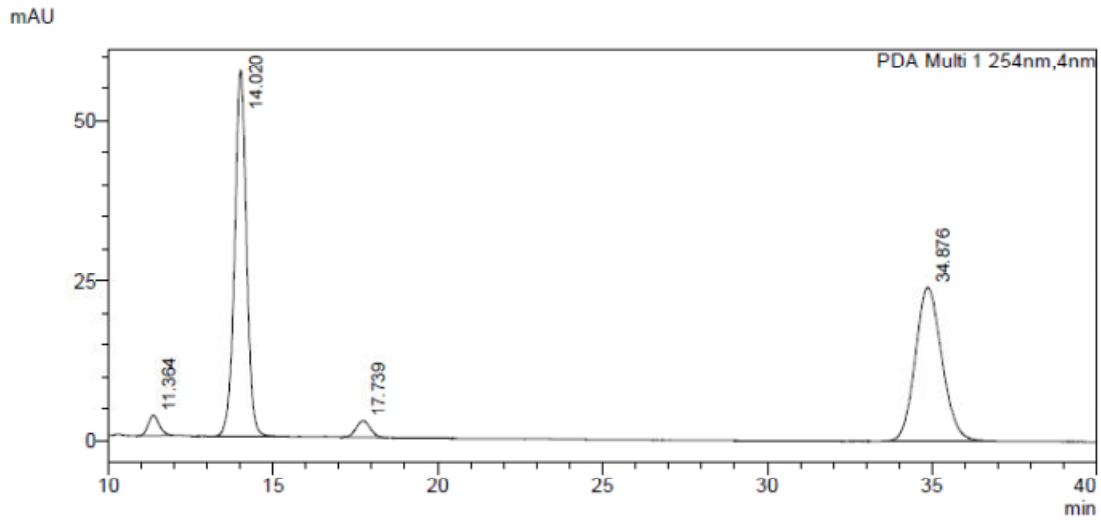
(2E,4E)-Ethyl 4-(((4-methoxyphenyl)sulfonyl)imino)-4-phenylbut-2-enoate 14b

(2E,4E)-Ethyl 4-(((4-nitrophenyl)sulfonyl)imino)-4-phenylbut-2-enoate 14c

(2E,4E)-Ethyl 4-phenyl-4-(((2,4,6-triisopropylphenyl)sulfonyl)imino)but-2-enoate 14d

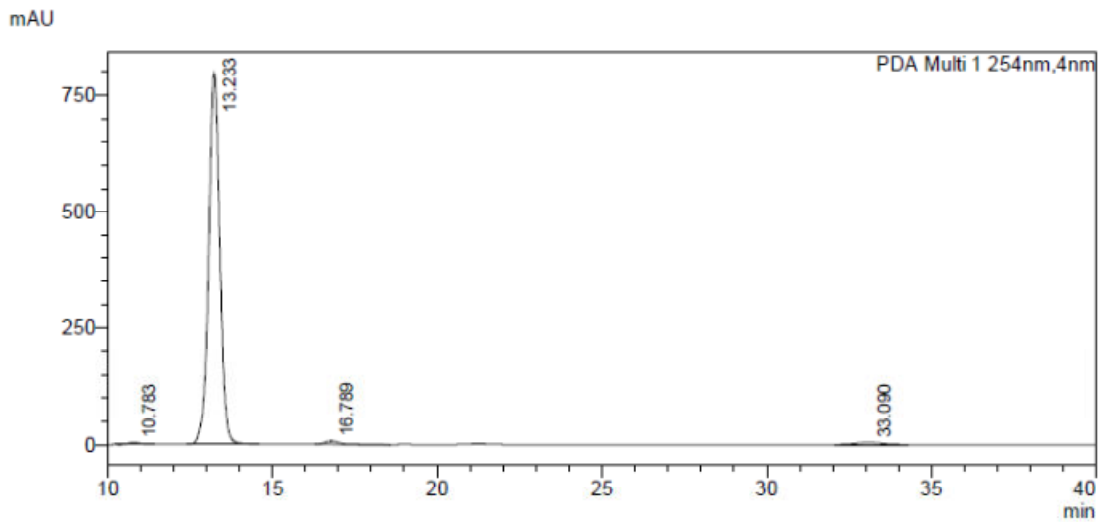
(2E,4E)-Ethyl 4-((methylsulfonyl)imino)-4-phenylbut-2-enoate 14e

(3*S*,4*S*)-Ethyl 2-oxo-3,6-diphenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 8

**<Peak Table>**

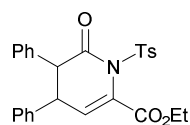
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	11.364	2.465
2	14.020	49.000
3	17.739	2.612
4	34.876	45.924
Total		100.000

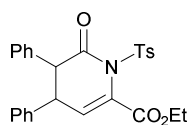
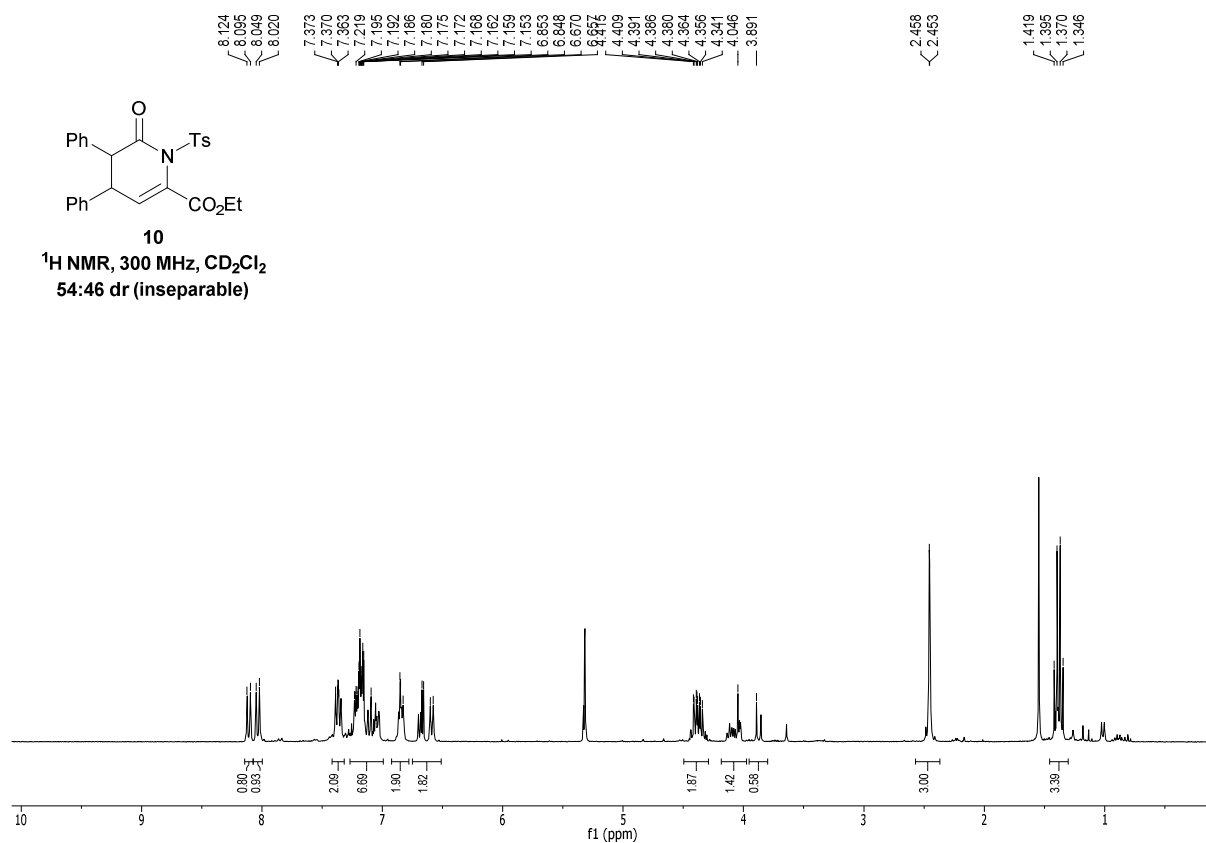
**<Peak Table>**

PDA Ch1 254nm

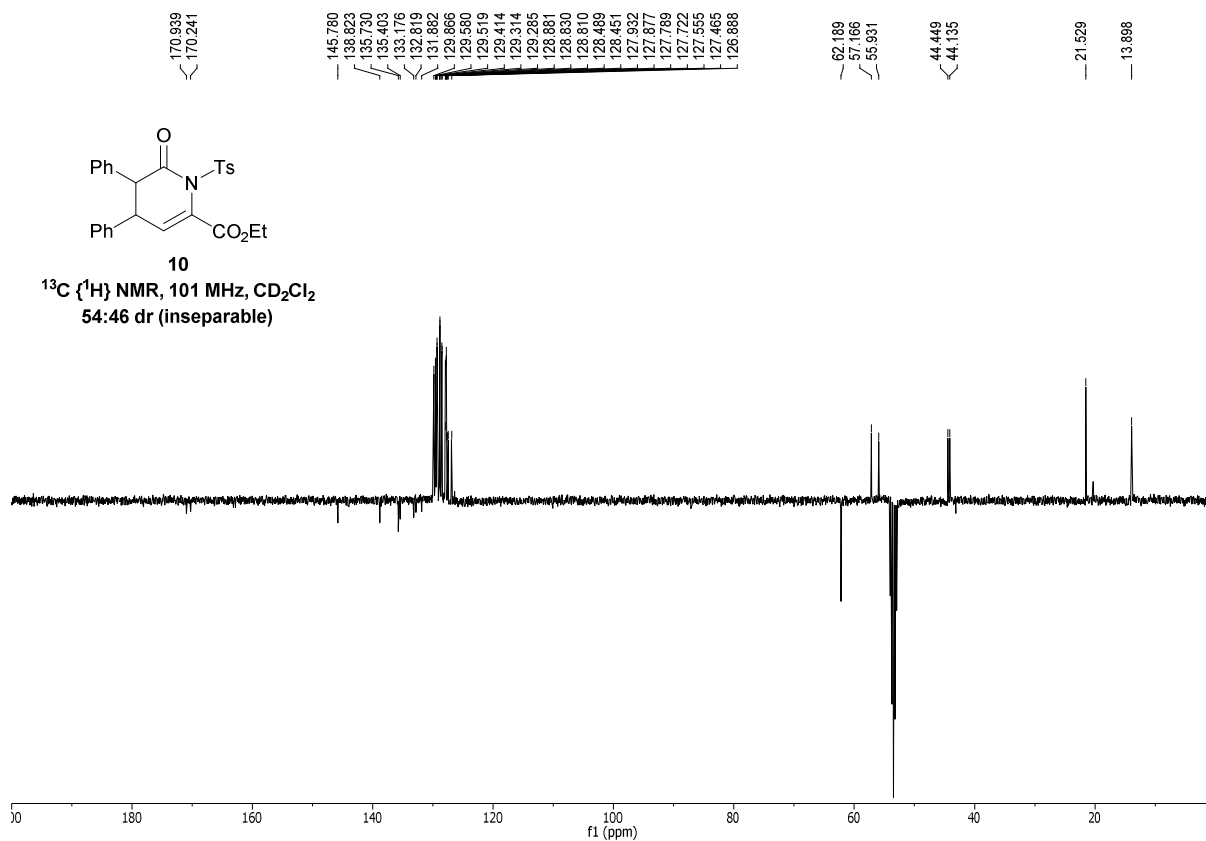
Peak#	Ret. Time	Area%
1	10.783	0.477
2	13.233	97.338
3	16.789	1.032
4	33.090	1.153
Total		100.000

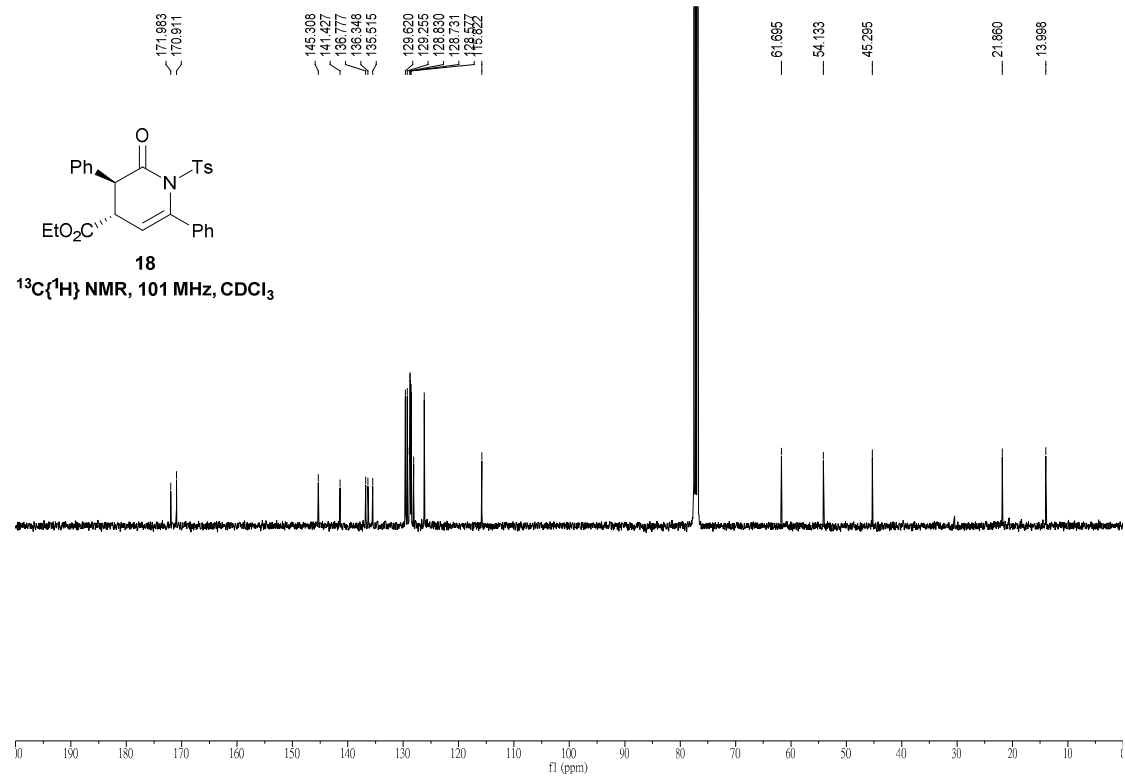
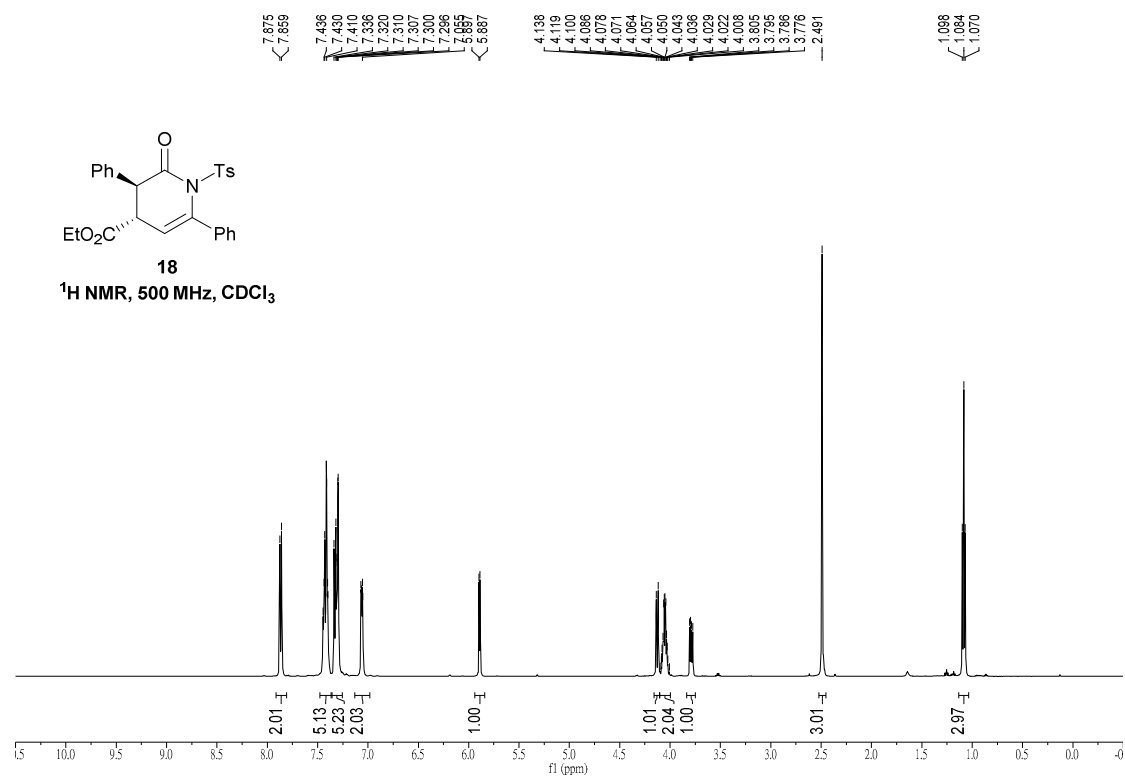
Ethyl 6-oxo-4,5-diphenyl-1-tosyl-1,4,5,6-tetrahydropyridine-2-carboxylate **10****10**

^1H NMR, 300 MHz, CD_2Cl_2
54:46 dr (inseparable)

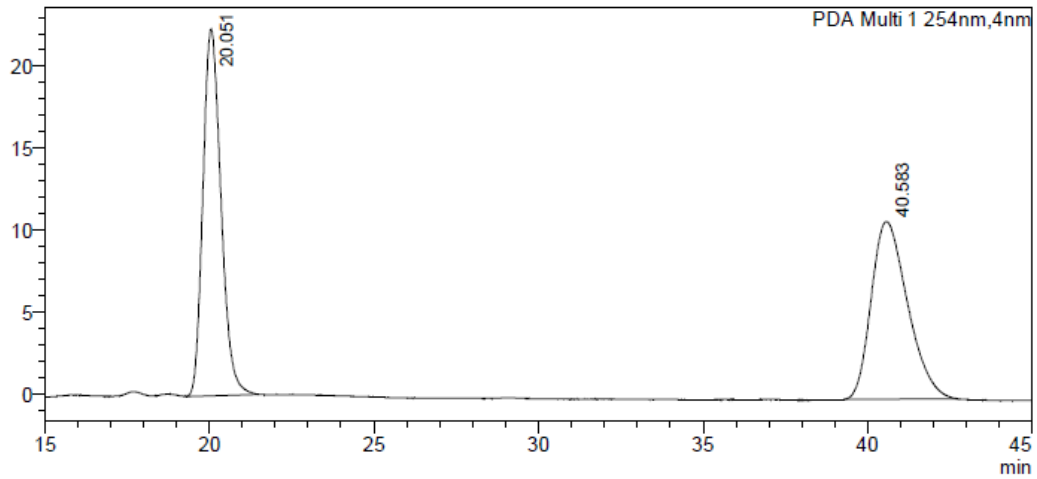
**10**

^{13}C $\{^1\text{H}\}$ NMR, 101 MHz, CD_2Cl_2
54:46 dr (inseparable)



(3*S*,4*S*)-Ethyl 2-oxo-3,6-diphenyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate 18

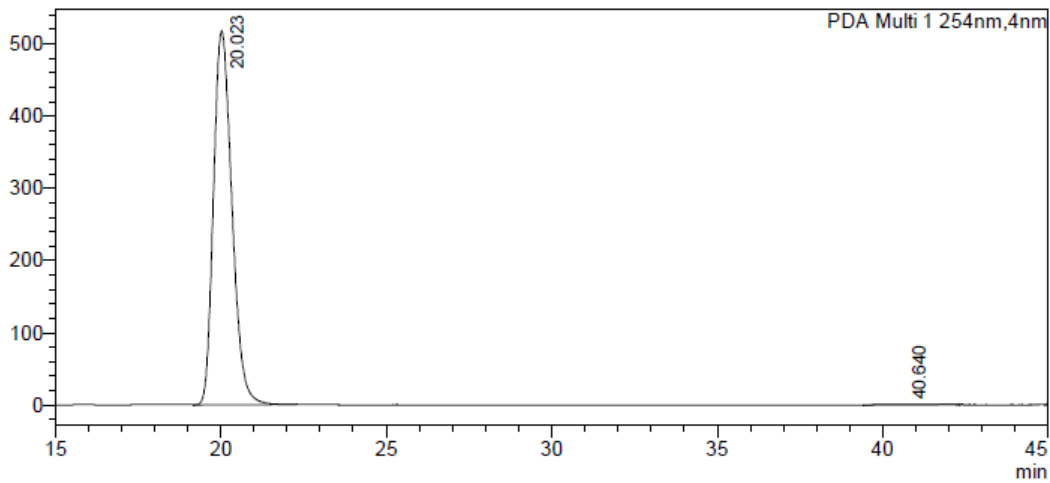
mAU

**<Peak Table>**

PDA Ch1 254nm

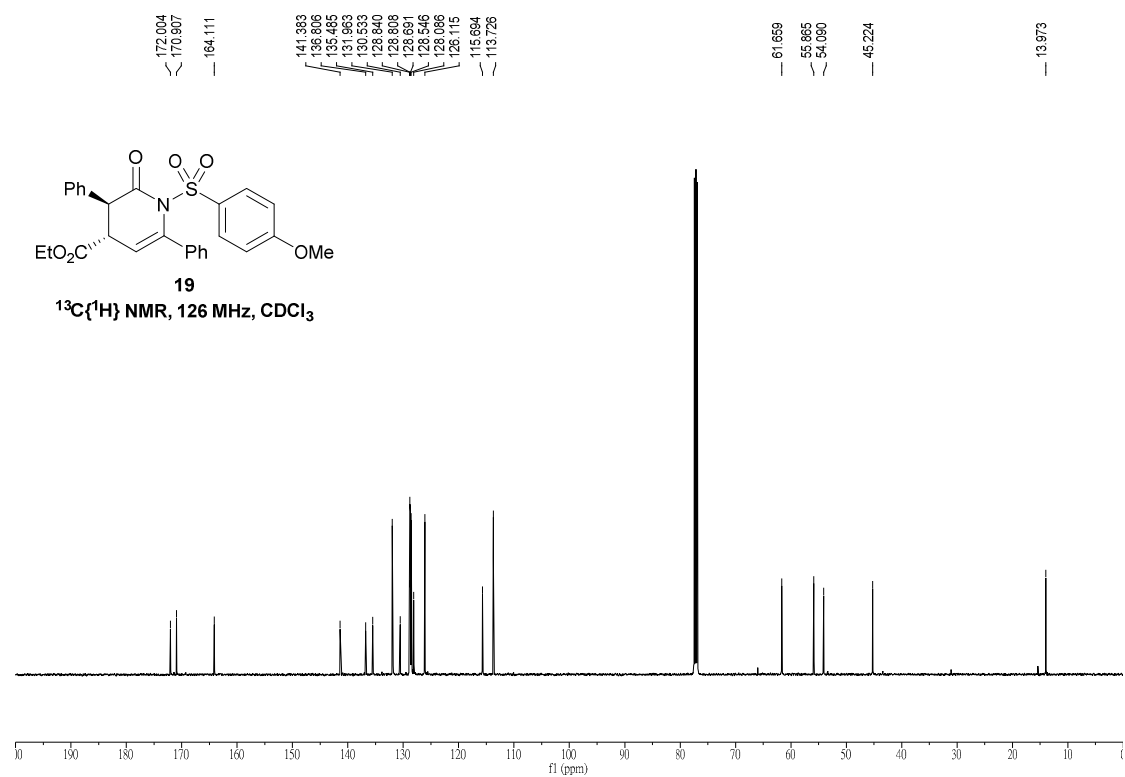
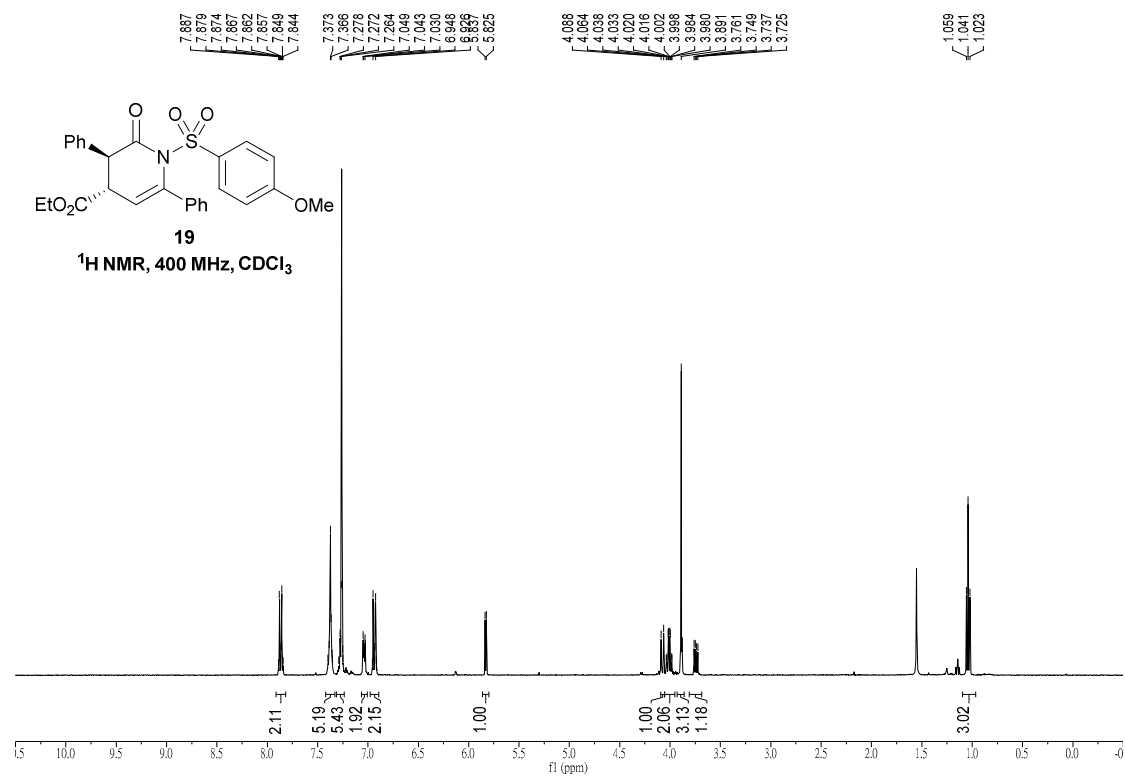
Peak#	Ret. Time	Area%
1	20.051	50.614
2	40.583	49.386
Total		100.000

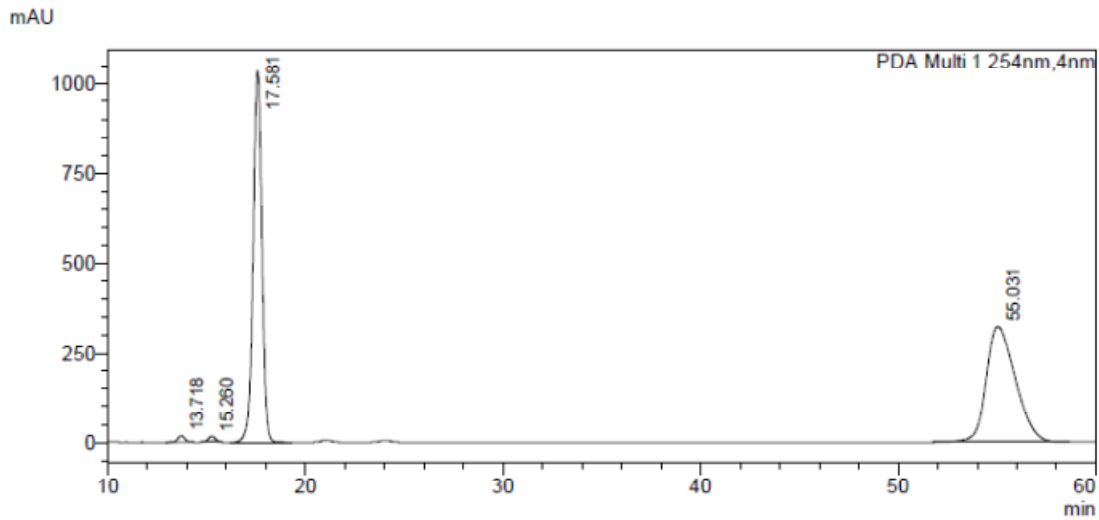
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**<Peak Table>**

PDA Ch1 254nm

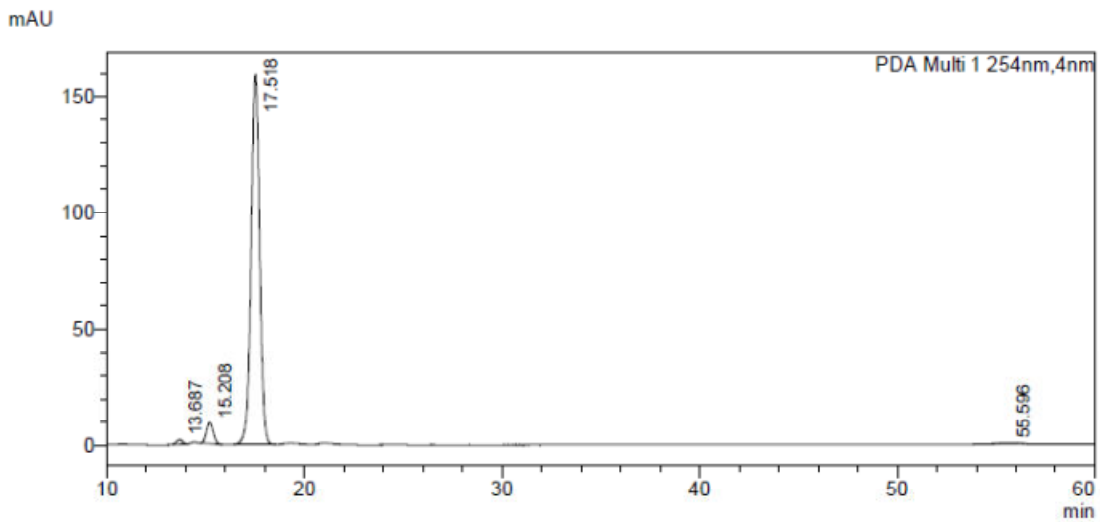
Peak#	Ret. Time	Area%
1	20.023	99.861
2	40.640	0.139
Total		100.000

(3*S*,4*S*)-Ethyl 1-((4-methoxyphenyl)sulfonyl)-2-oxo-3,6-diphenyl-1,2,3,4-tetrahydropyridine-4-carboxylate 19

**<Peak Table>**

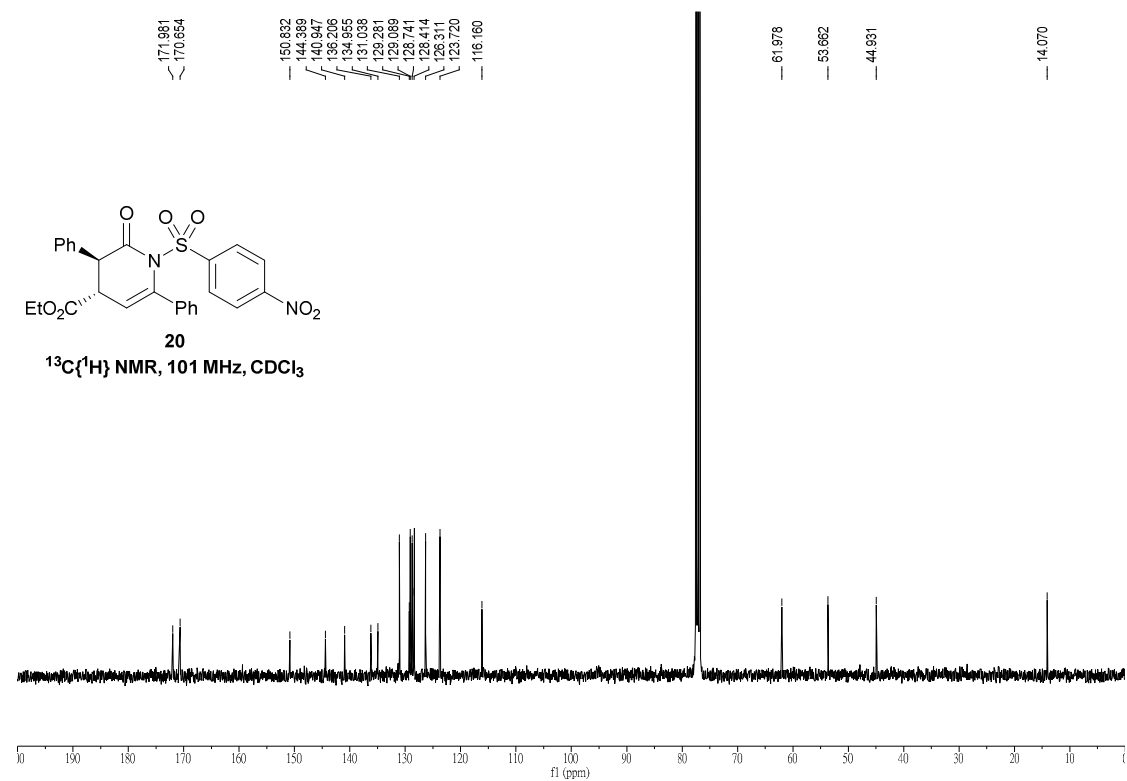
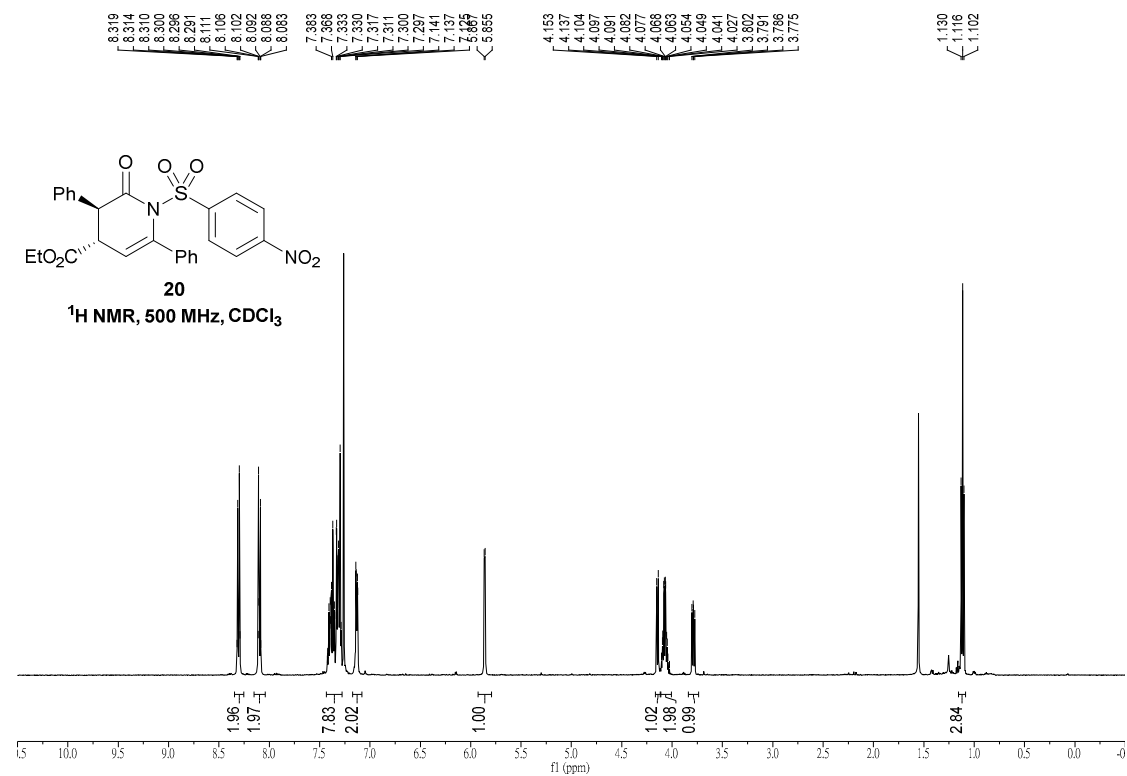
PDA Ch1 254nm

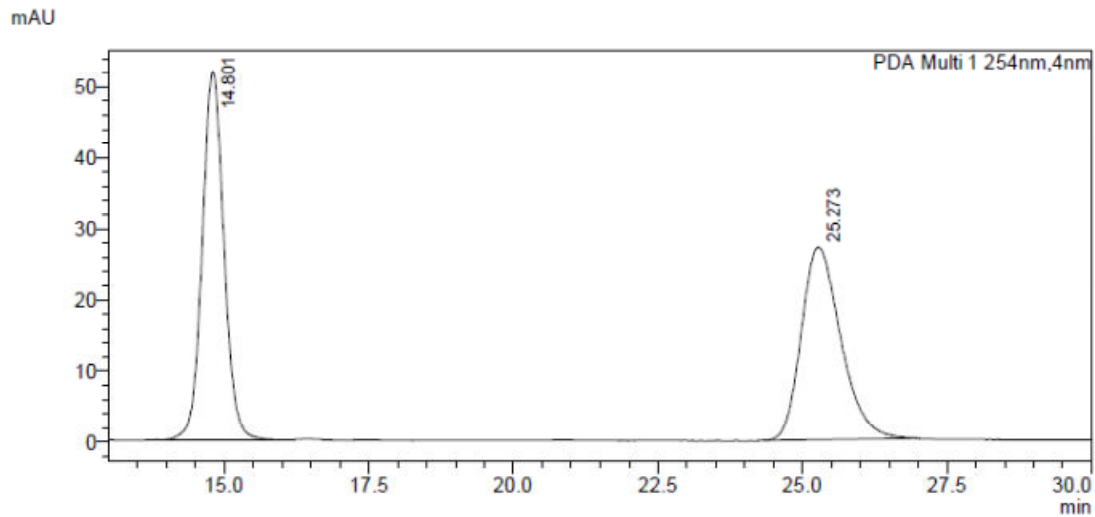
Peak#	Ret. Time	Area%
1	13.718	0.639
2	15.260	0.607
3	17.581	48.487
4	55.031	50.267
Total		100.000

**<Peak Table>**

PDA Ch1 254nm

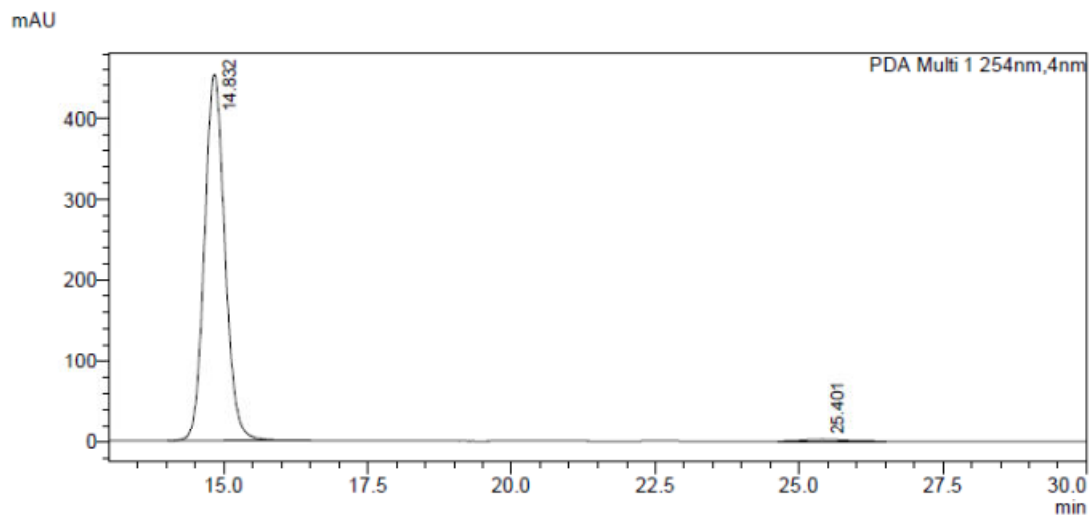
Peak#	Ret. Time	Area%
1	13.687	0.797
2	15.208	4.325
3	17.518	94.447
4	55.596	0.432
Total		100.000

(3*S*,4*S*)-Ethyl 1-((4-nitrophenyl)sulfonyl)-2-oxo-3,6-diphenyl-1,2,3,4-tetrahydropyridine-4-carboxylate 20

**<Peak Table>**

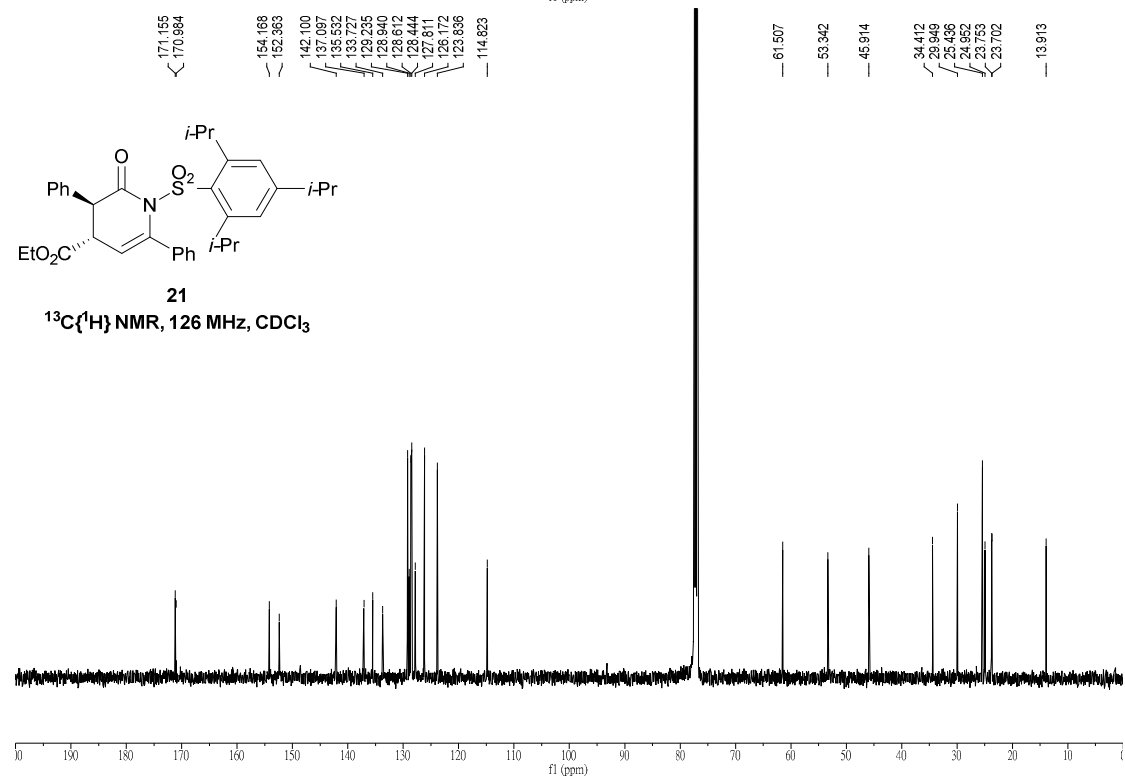
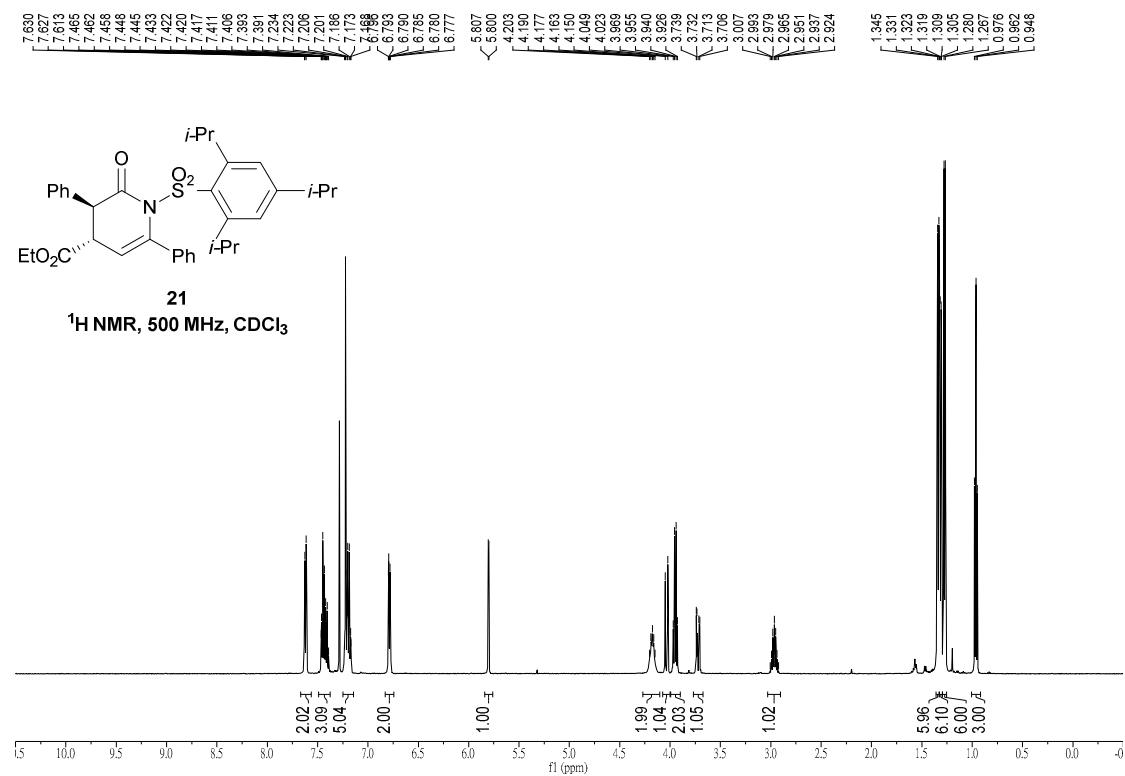
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	14.801	51.168
2	25.273	48.832
Total		100.000

**<Peak Table>**

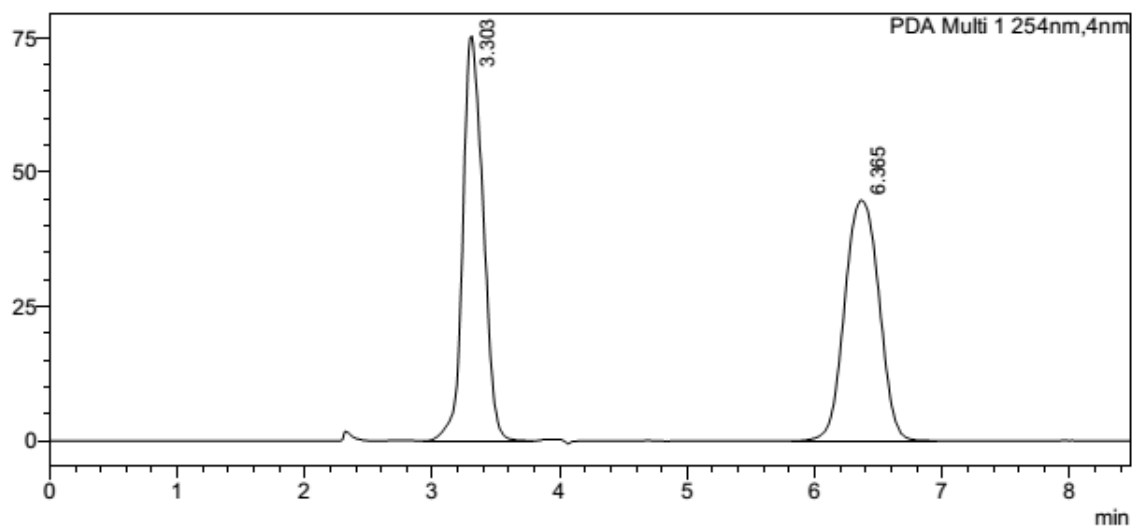
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	14.832	99.166
2	25.401	0.834
Total		100.000

(3*S*,4*S*)-Ethyl 2-oxo-3,6-diphenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 21

<Chromatogram>

mAU

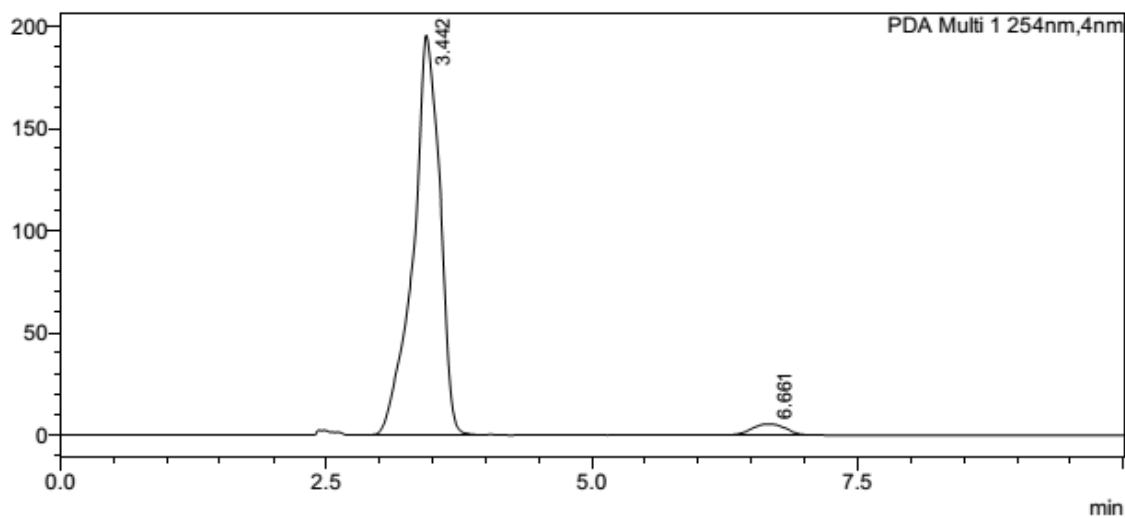
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.303	49.901
2	6.365	50.099
Total		100.000

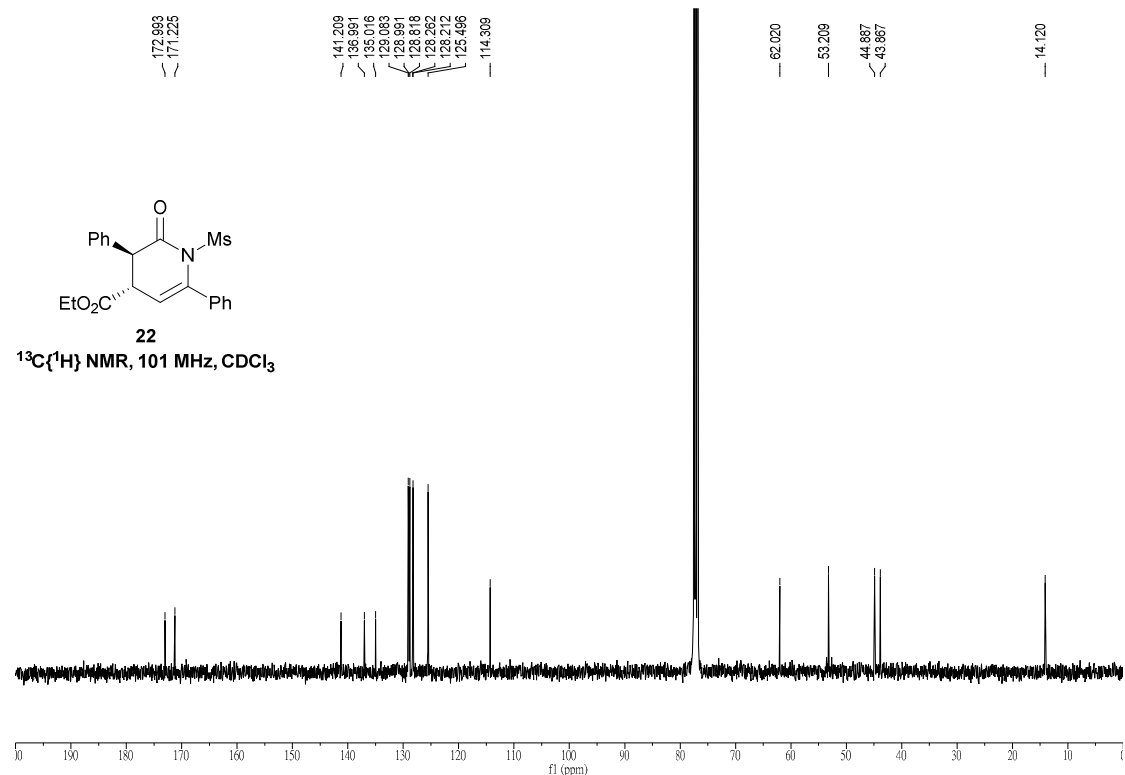
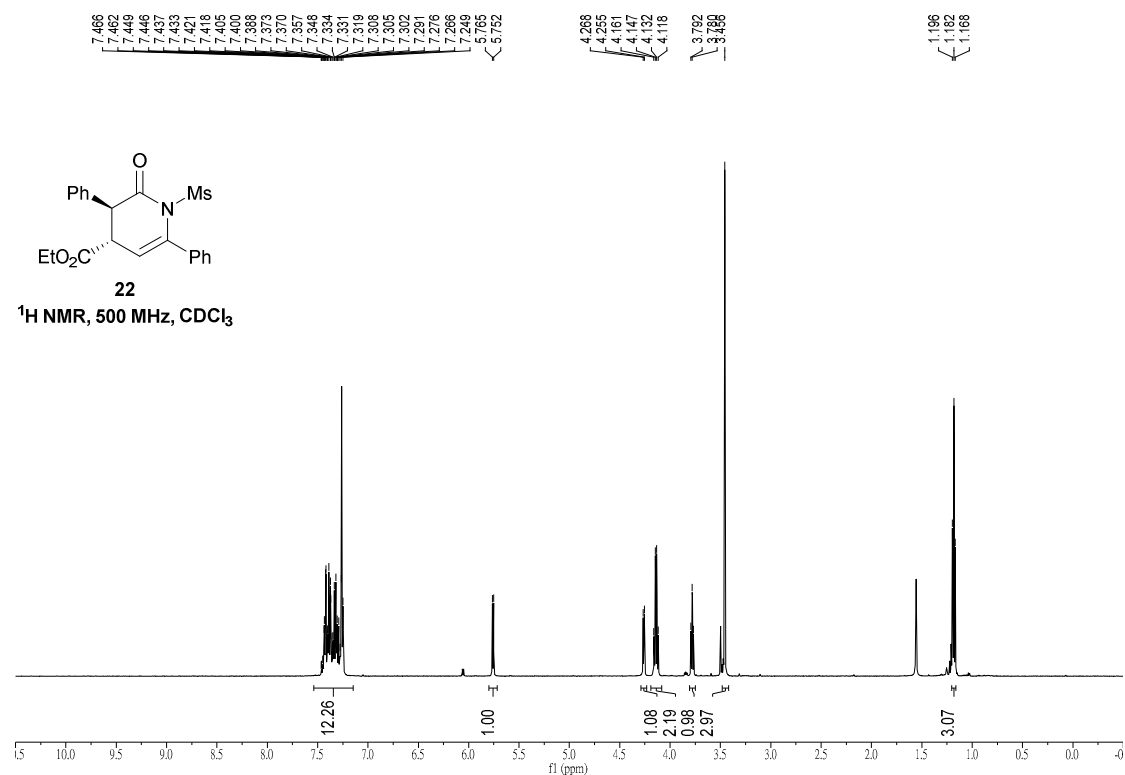
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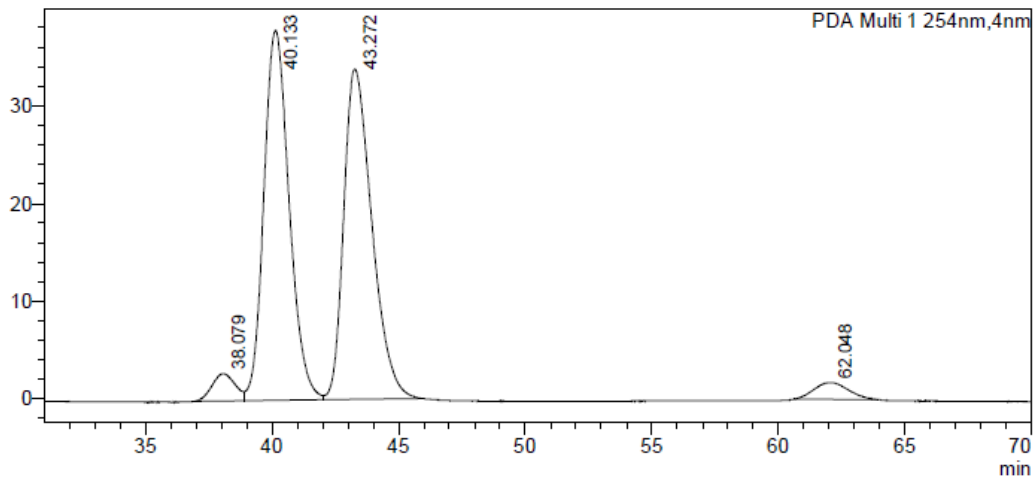
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	3.442	96.639
2	6.661	3.361
Total		100.000

(3*S*,4*S*)-Ethyl 1-(methylsulfonyl)-2-oxo-3,6-diphenyl-1,2,3,4-tetrahydropyridine-4-carboxylate 22

mAU

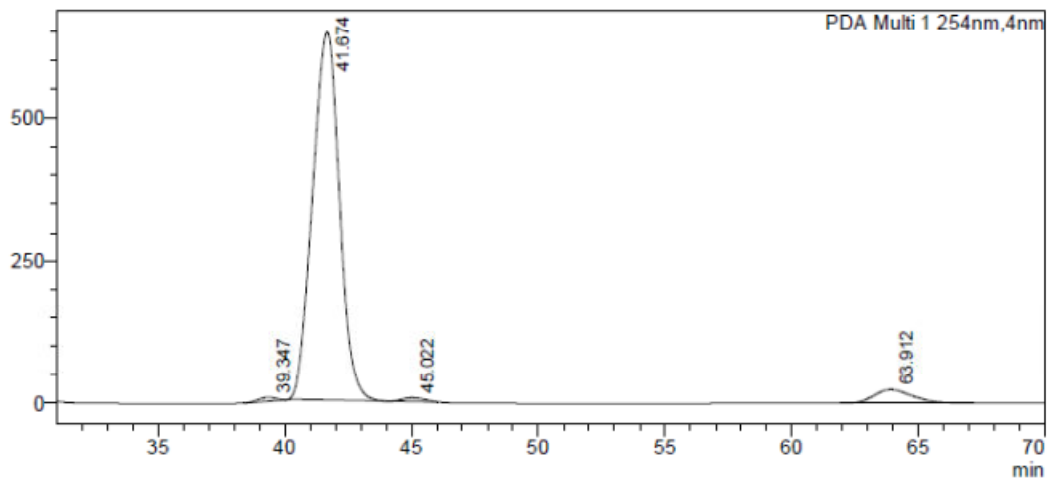


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	38.079	3.113
2	40.133	47.136
3	43.272	46.860
4	62.048	2.891
Total		100.000

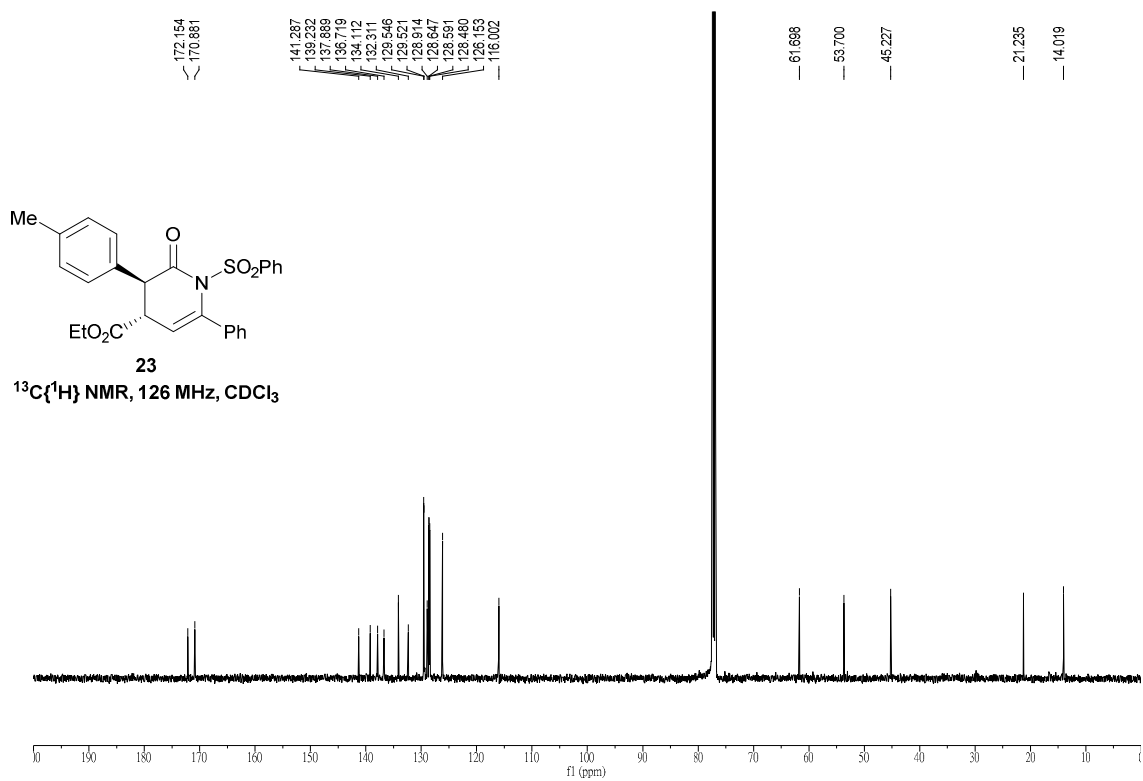
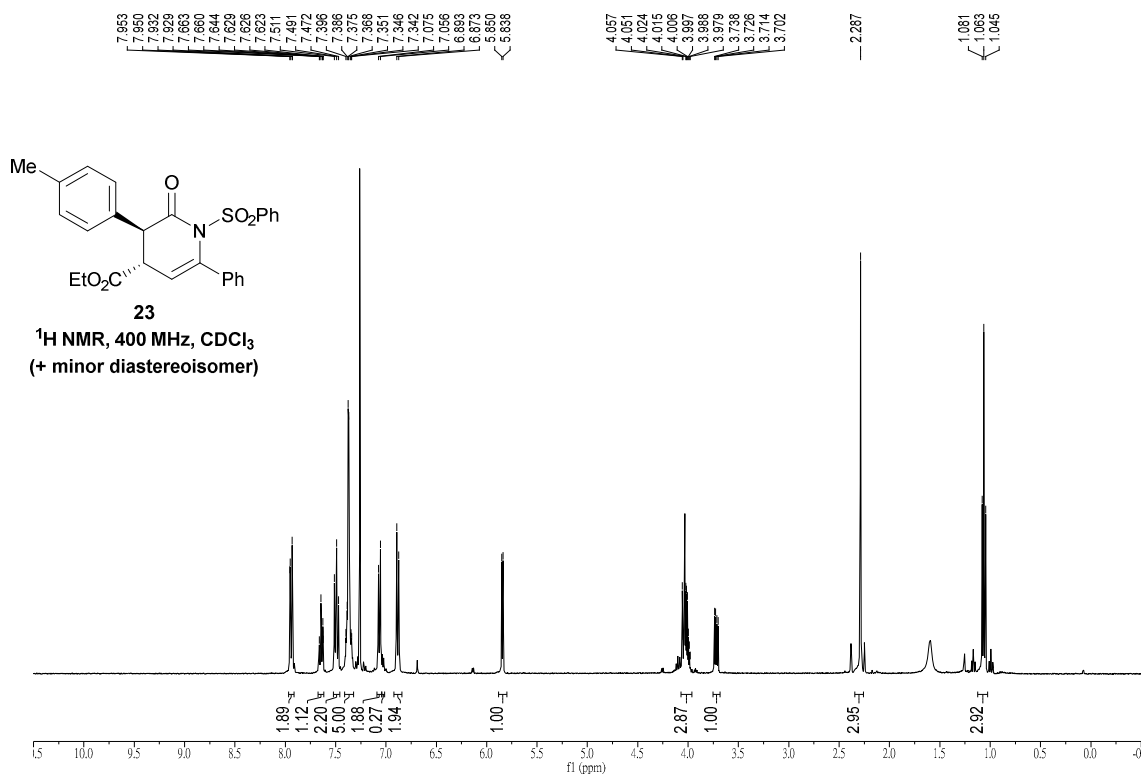
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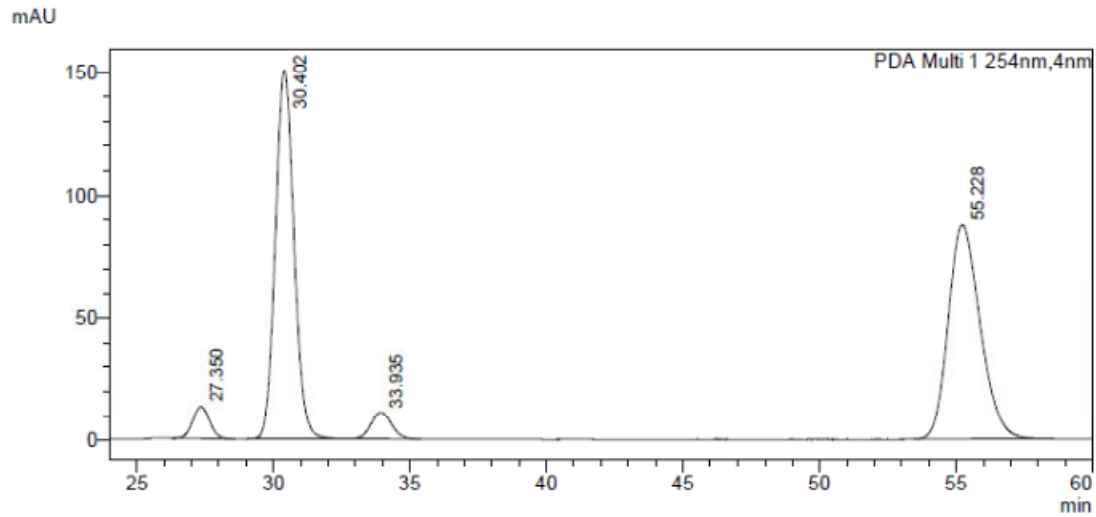


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	39.347	0.598
2	41.674	93.703
3	45.022	0.703
4	63.912	4.997
Total		100.000

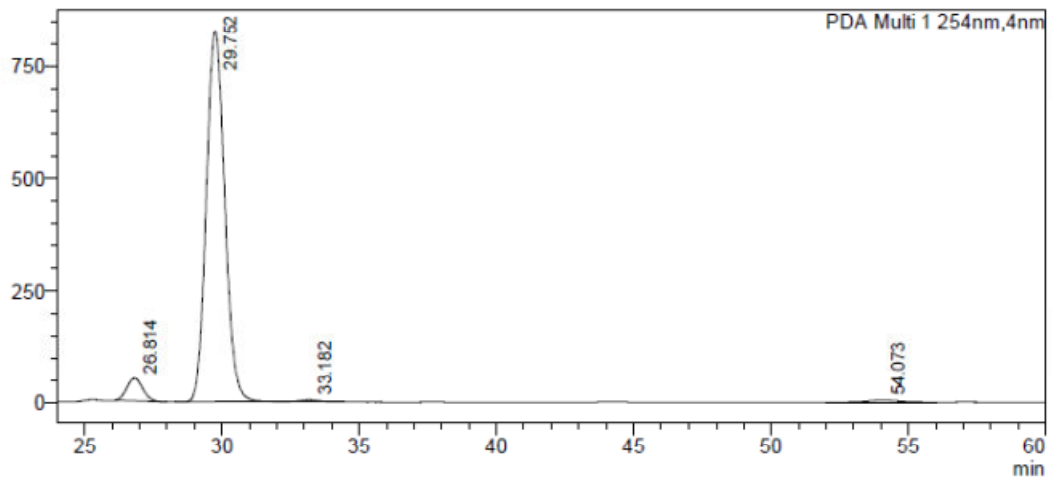
(3*S*,4*S*)-Ethyl 2-oxo-6-phenyl-1-(phenylsulfonyl)-3-(*p*-tolyl)-1,2,3,4-tetrahydropyridine-4-carboxylate **23**

**<Peak Table>**

PDA Ch1 254nm

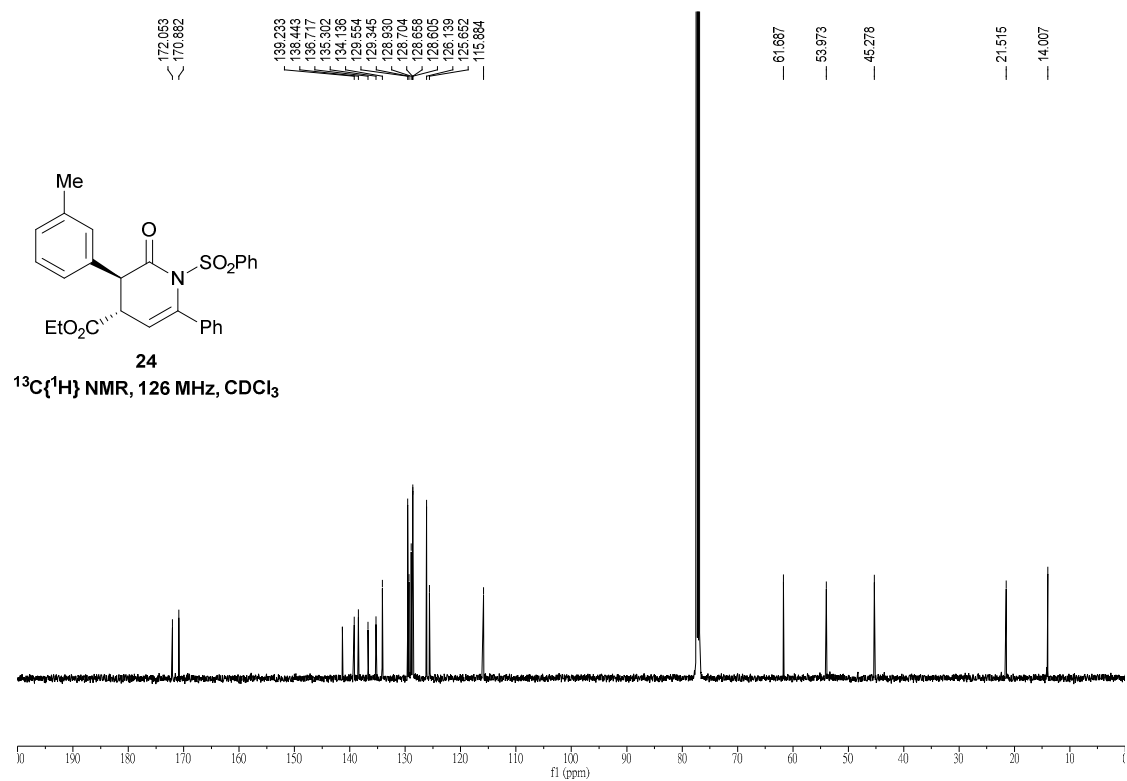
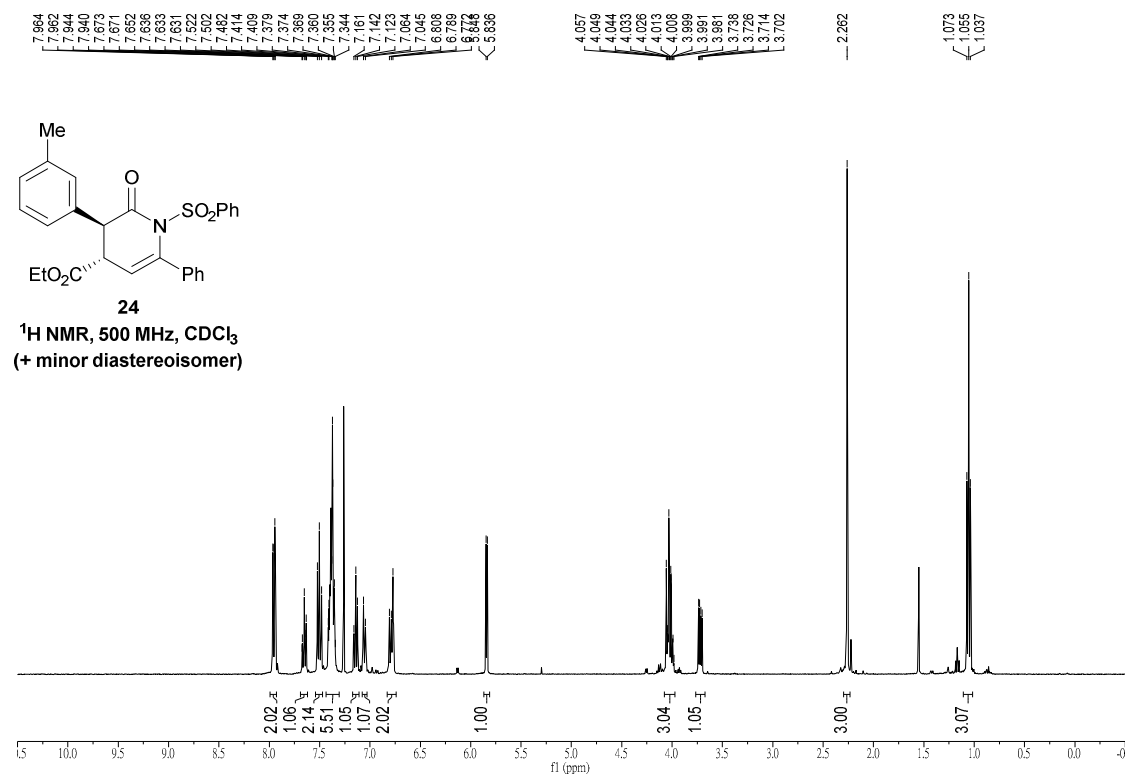
Peak#	Ret. Time	Area%
1	27.350	3.655
2	30.402	46.390
3	33.935	3.700
4	55.228	46.255
Total		100.000

mAU

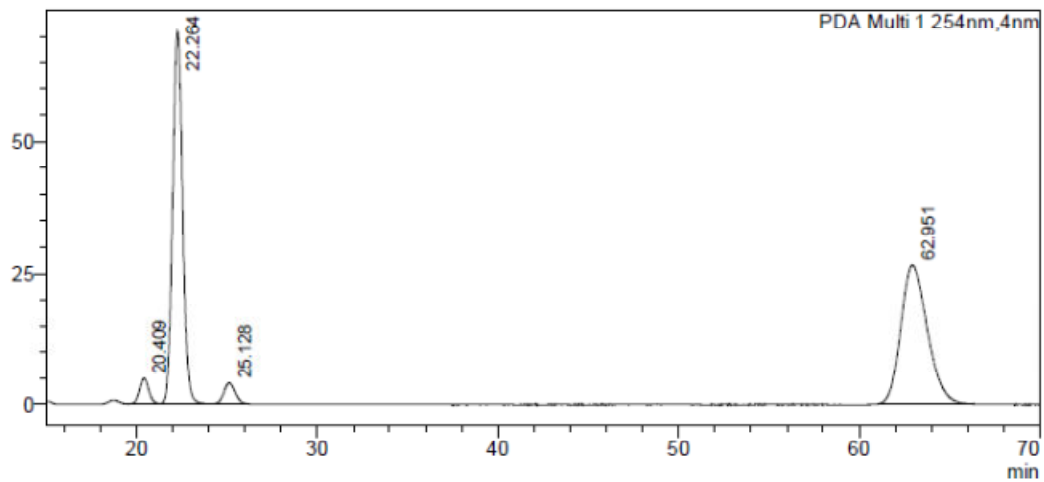
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	26.814	4.888
2	29.752	93.783
3	33.182	0.499
4	54.073	0.831
Total		100.000

(3*S*,4*S*)-Ethyl 2-oxo-6-phenyl-1-(phenylsulfonyl)-3-(*m*-tolyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 24

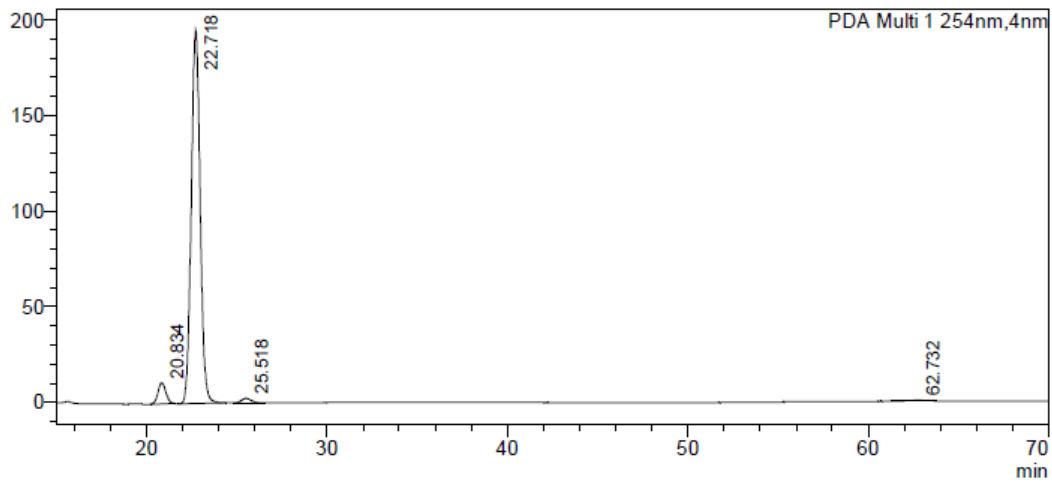
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**<Peak Table>**

PDA Ch1 254nm

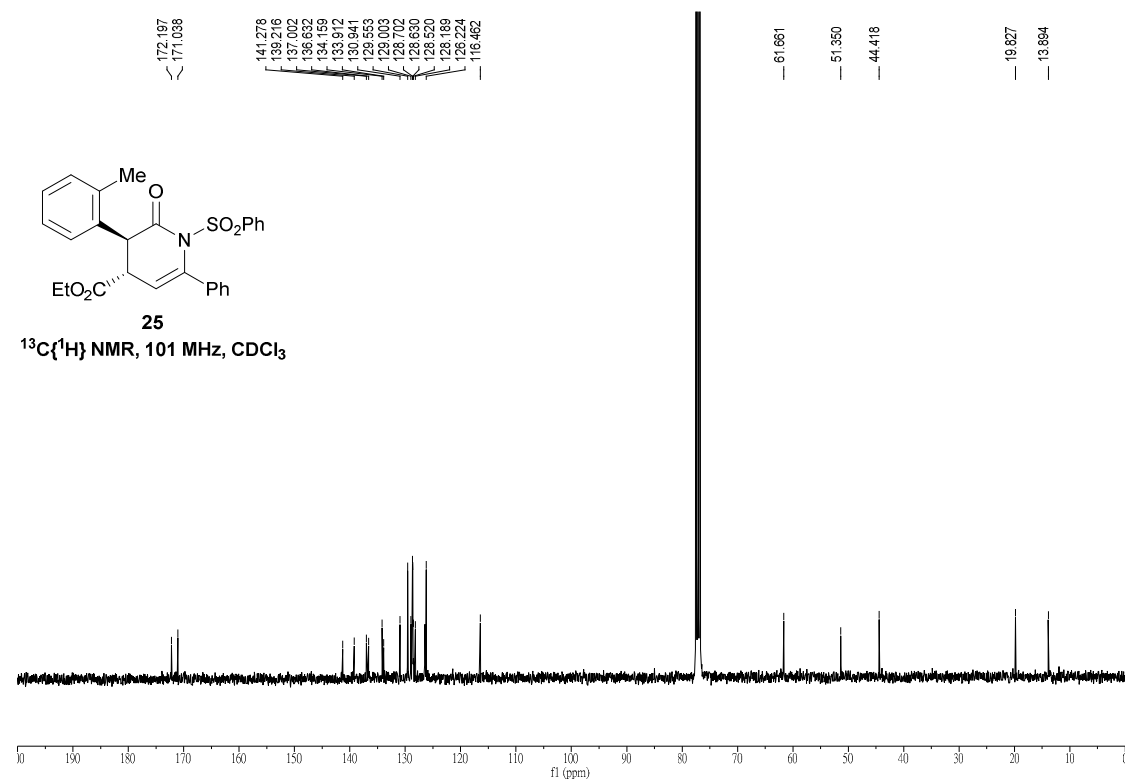
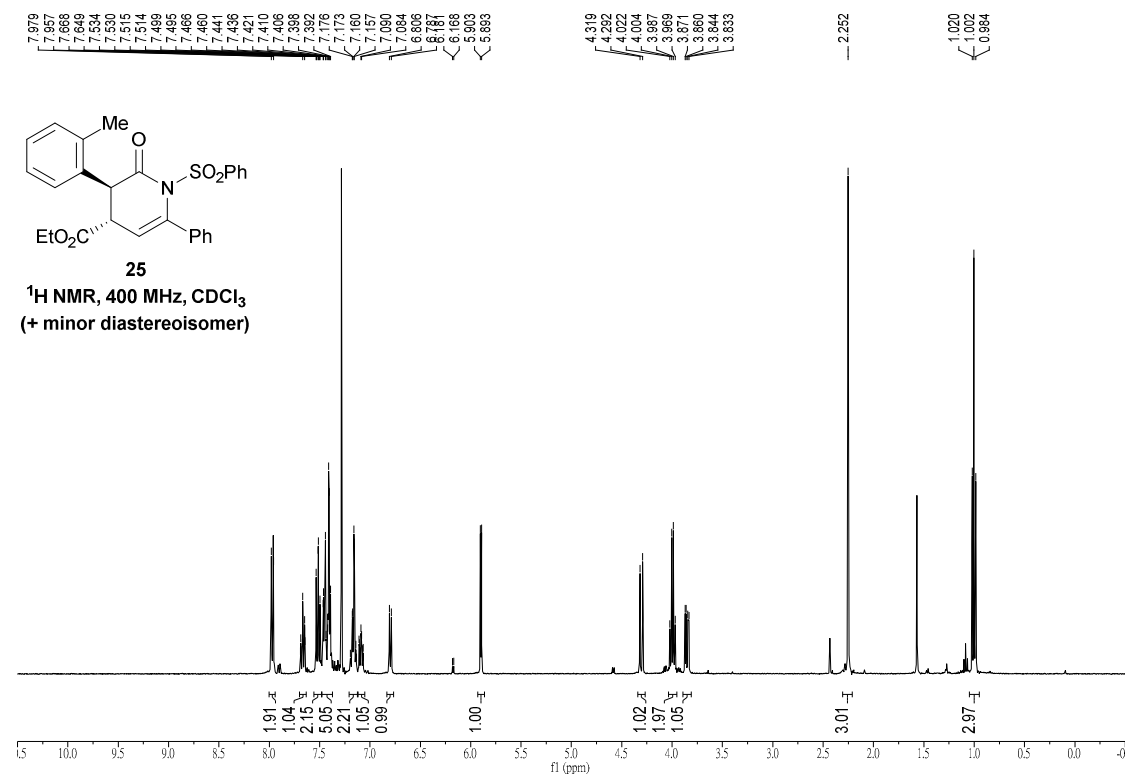
Peak#	Ret. Time	Area%
1	20.409	2.953
2	22.264	47.373
3	25.128	2.951
4	62.951	46.723
Total		100.000

mAU

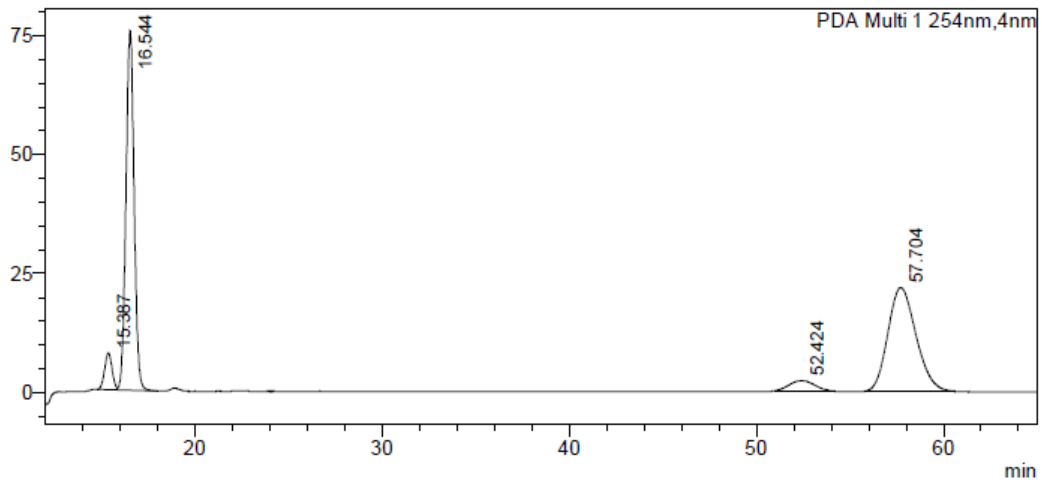
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	20.834	4.710
2	22.718	93.599
3	25.518	1.219
4	62.732	0.472
Total		100.000

(3*S*,4*S*)-Ethyl 2-oxo-6-phenyl-1-(phenylsulfonyl)-3-(*o*-tolyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 25

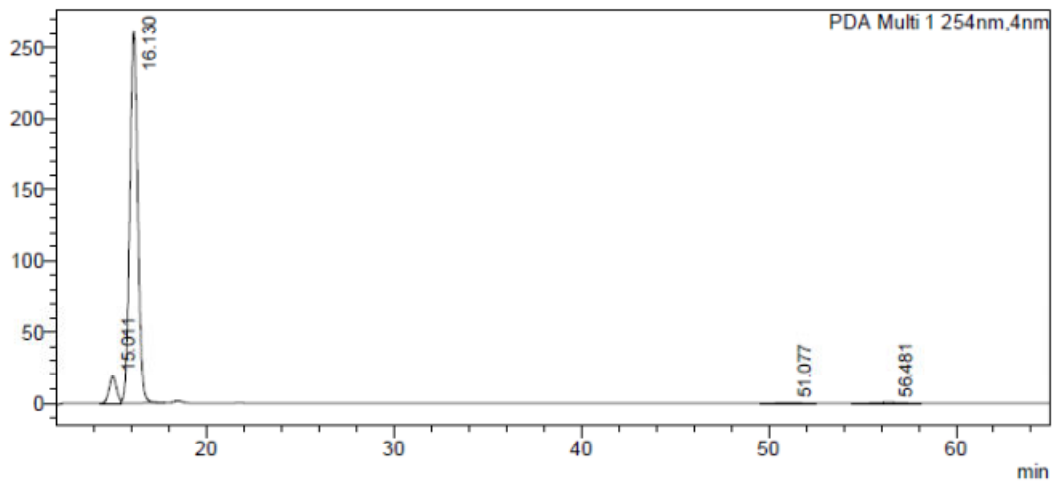
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**<Peak Table>**

PDA Ch1 254nm

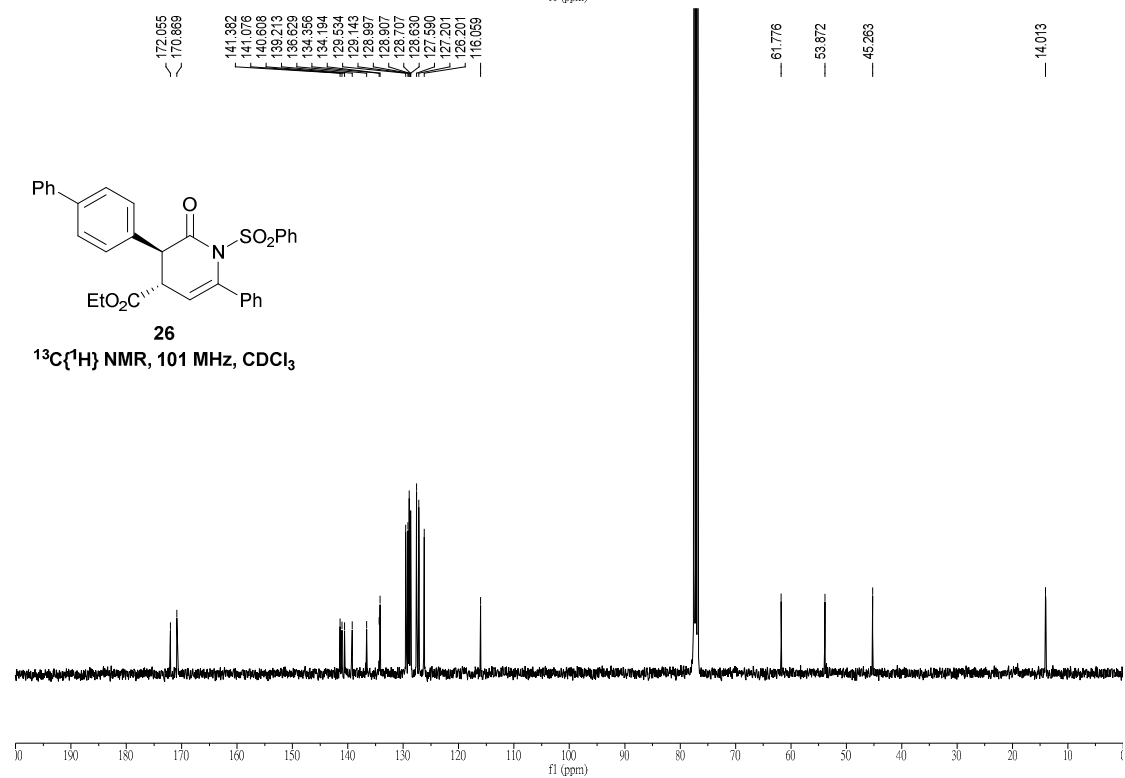
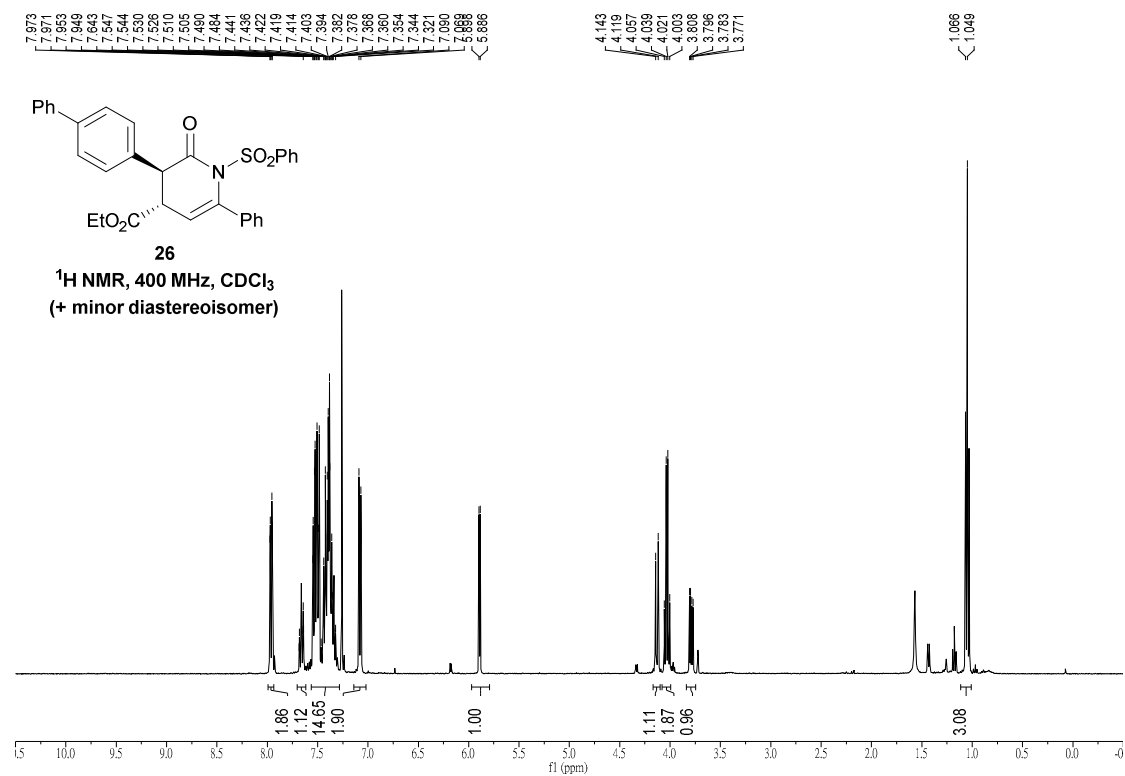
Peak#	Ret. Time	Area%
1	15.387	4.248
2	16.544	46.116
3	52.424	4.092
4	57.704	45.543
Total		100.000

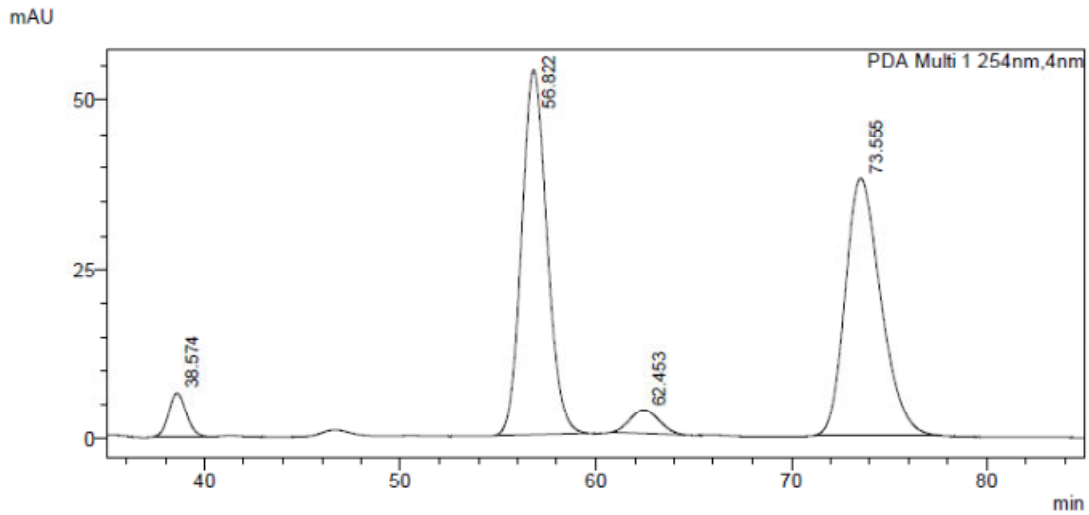
mAU

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	15.011	6.218
2	16.130	92.846
3	51.077	0.237
4	56.481	0.699
Total		100.000

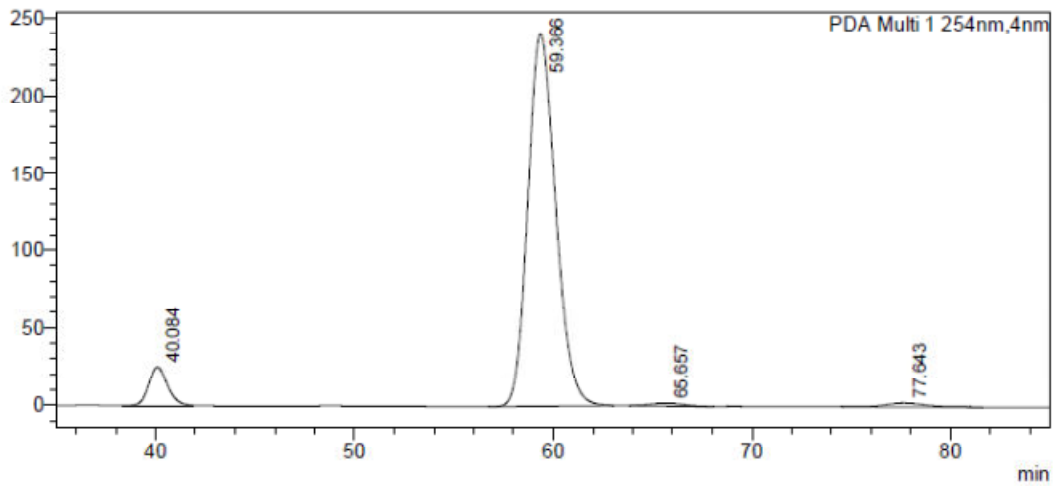
(3*S*,4*S*)-Ethyl 3-([1,1'-biphenyl]-4-yl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 26

**<Peak Table>**

PDA Ch1 254nm

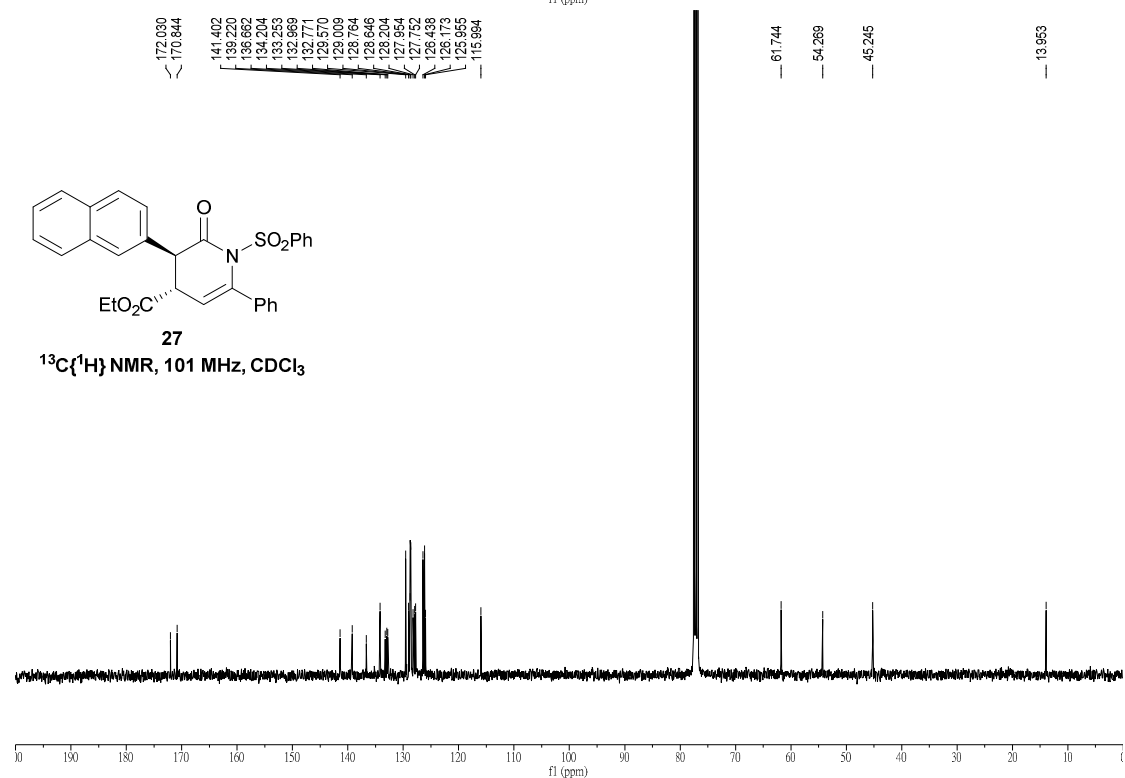
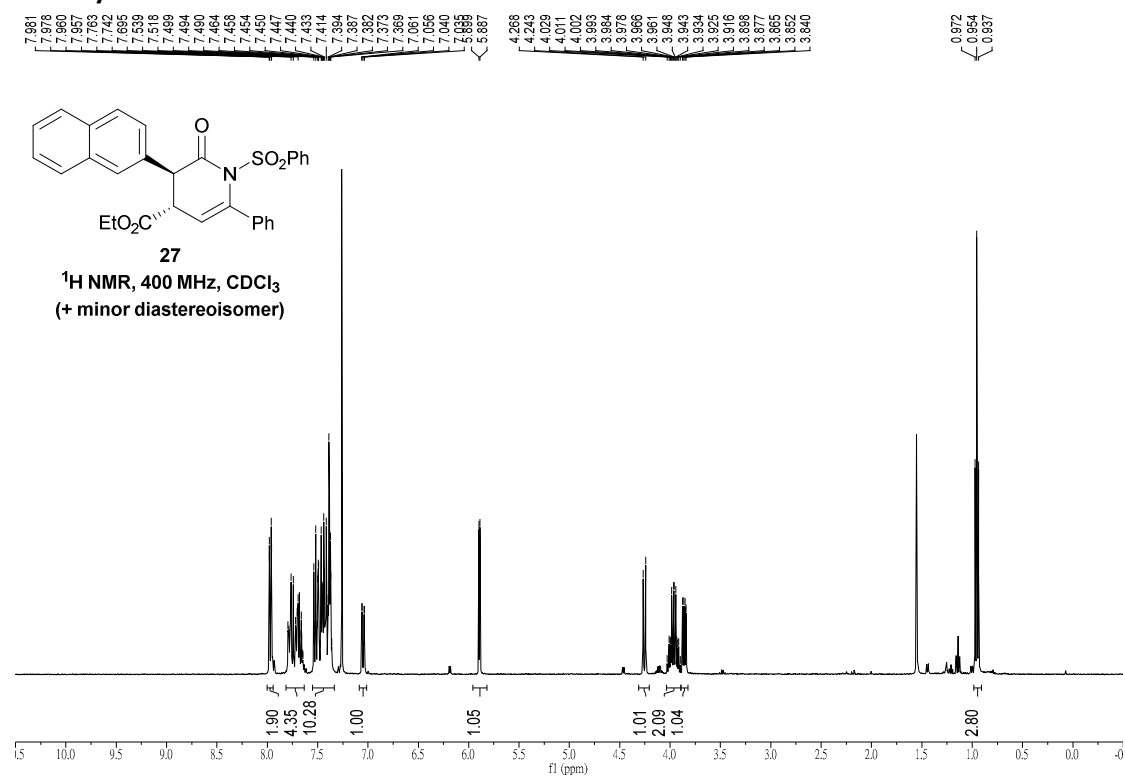
Peak#	Ret. Time	Area%
1	38.574	3.826
2	56.822	46.489
3	62.453	3.434
4	73.555	46.251
Total		100.000

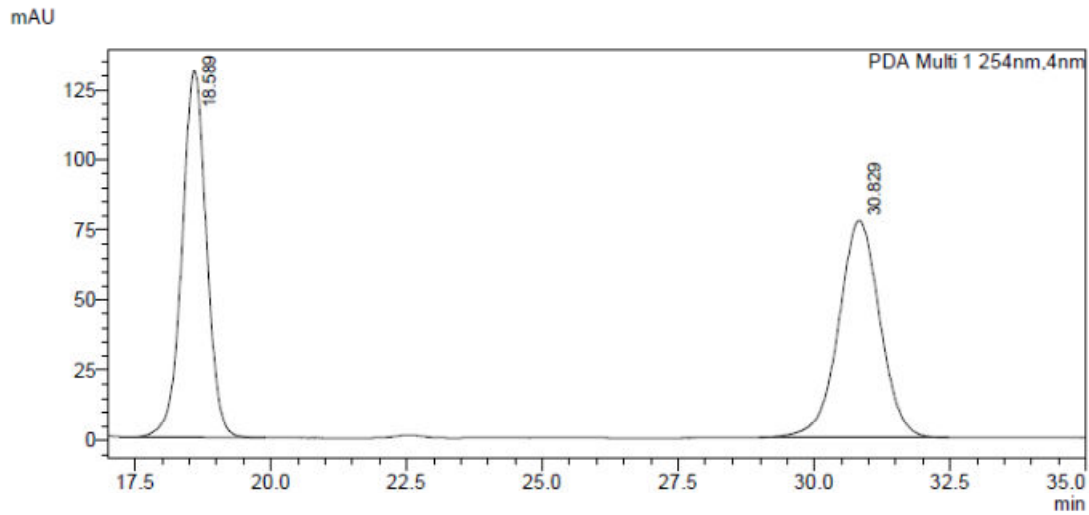
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**<Peak Table>**

PDA Ch1 254nm

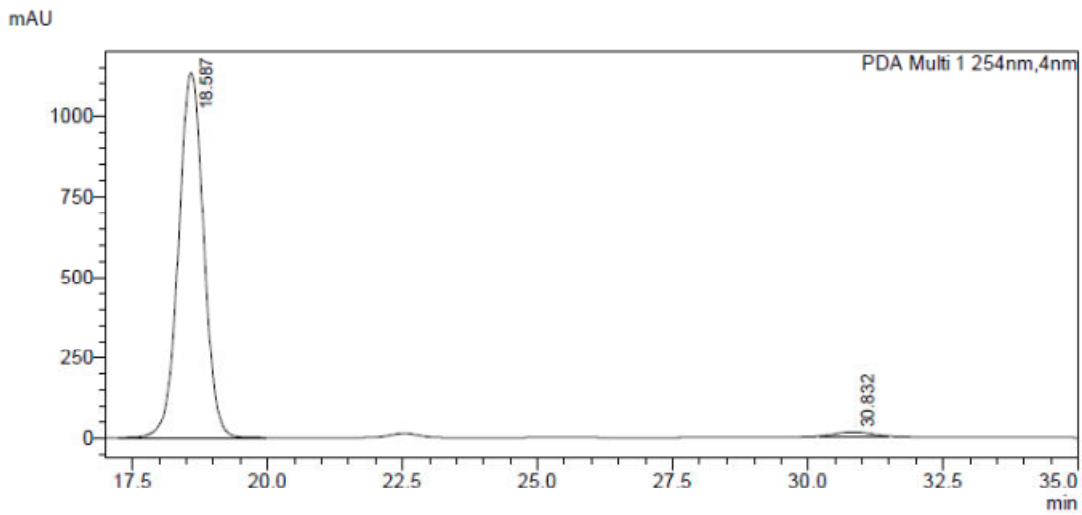
Peak#	Ret. Time	Area%
1	40.084	6.351
2	59.366	91.528
3	65.657	0.799
4	77.643	1.322
Total		100.000

(3*S*,4*S*)-Ethyl 3-(naphthalen-2-yl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 27

**<Peak Table>**

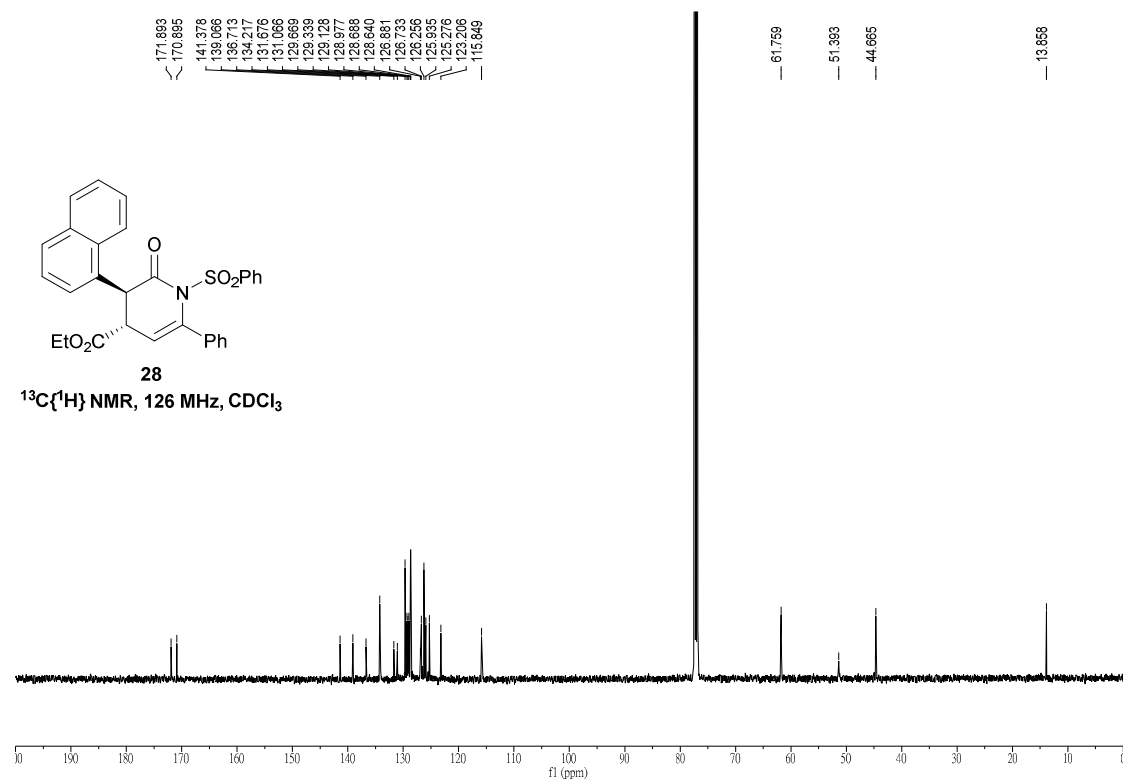
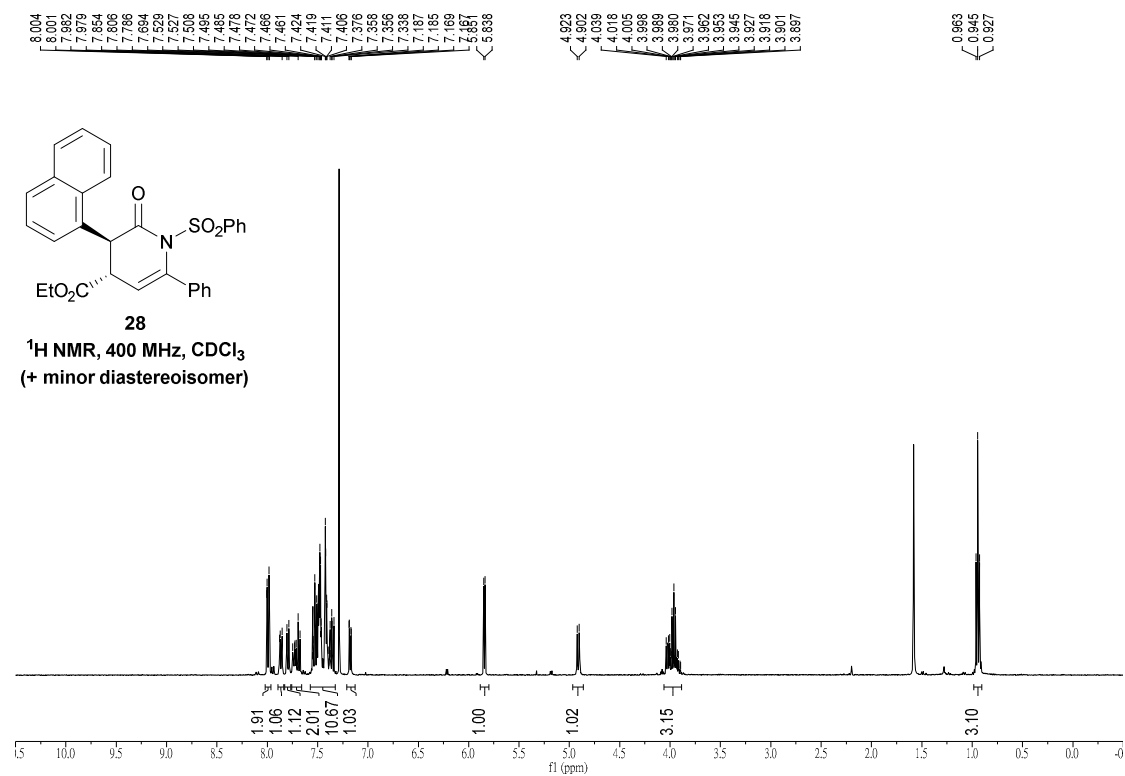
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	18.589	50.026
2	30.829	49.974
Total		100.000

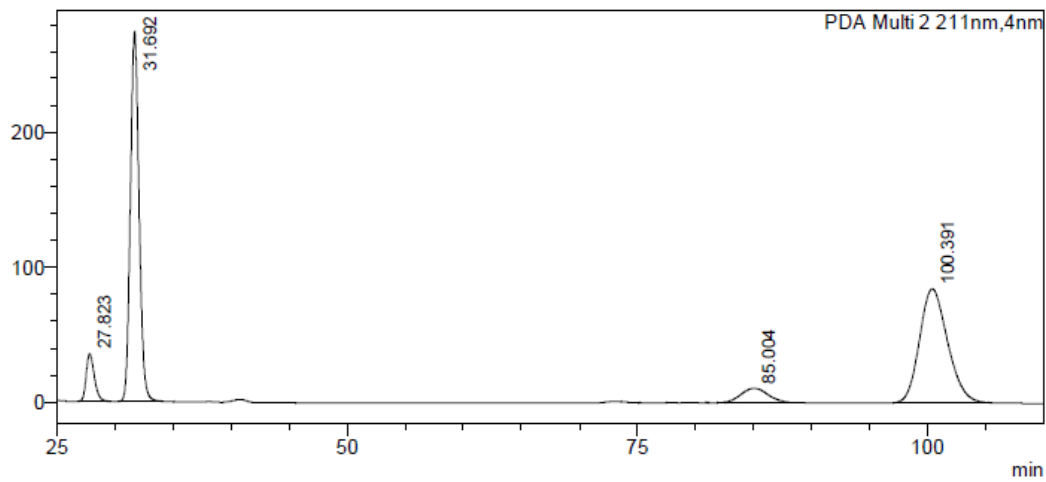
**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	18.587	98.574
2	30.832	1.426
Total		100.000

(3*S*,4*S*)-Ethyl 3-(naphthalen-1-yl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 28

mAU

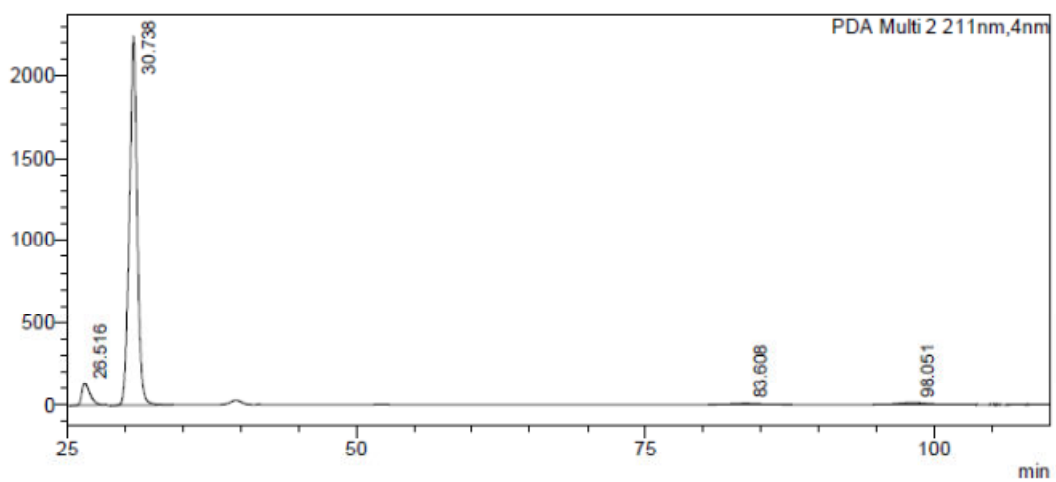


<Peak Table>

PDA Ch2 211nm

Peak#	Ret. Time	Area%
1	27.823	5.398
2	31.692	44.767
3	85.004	5.297
4	100.391	44.538
Total		100.000

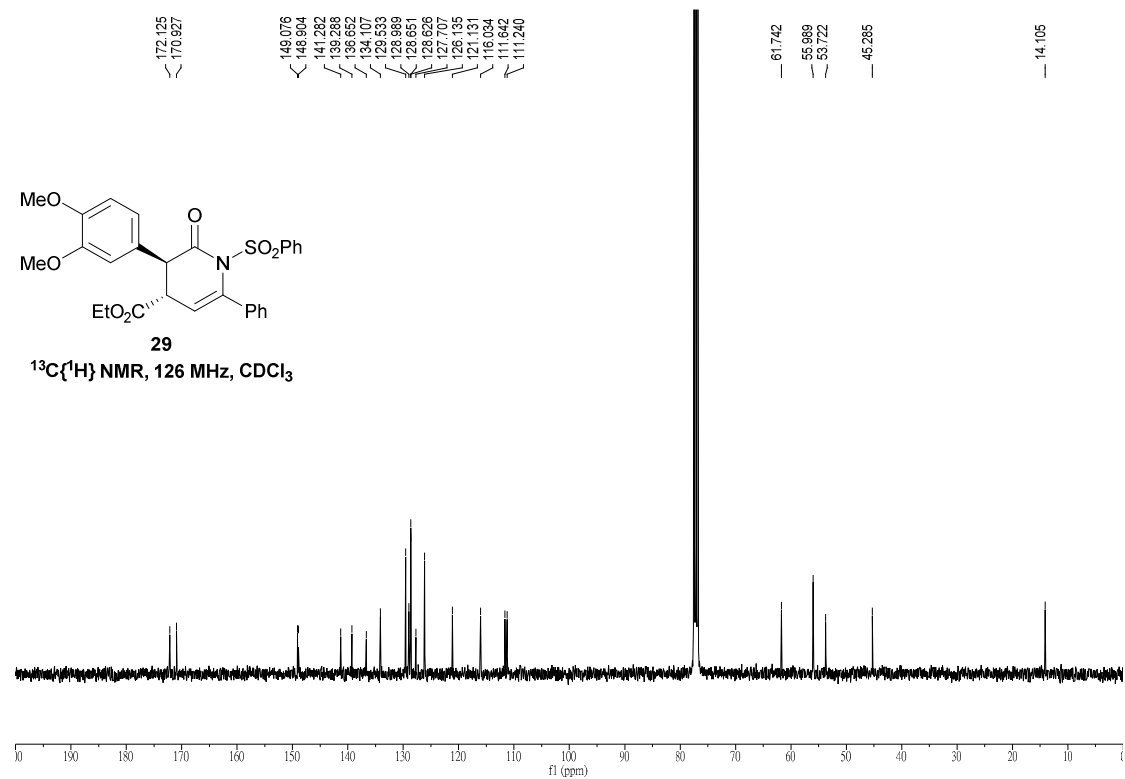
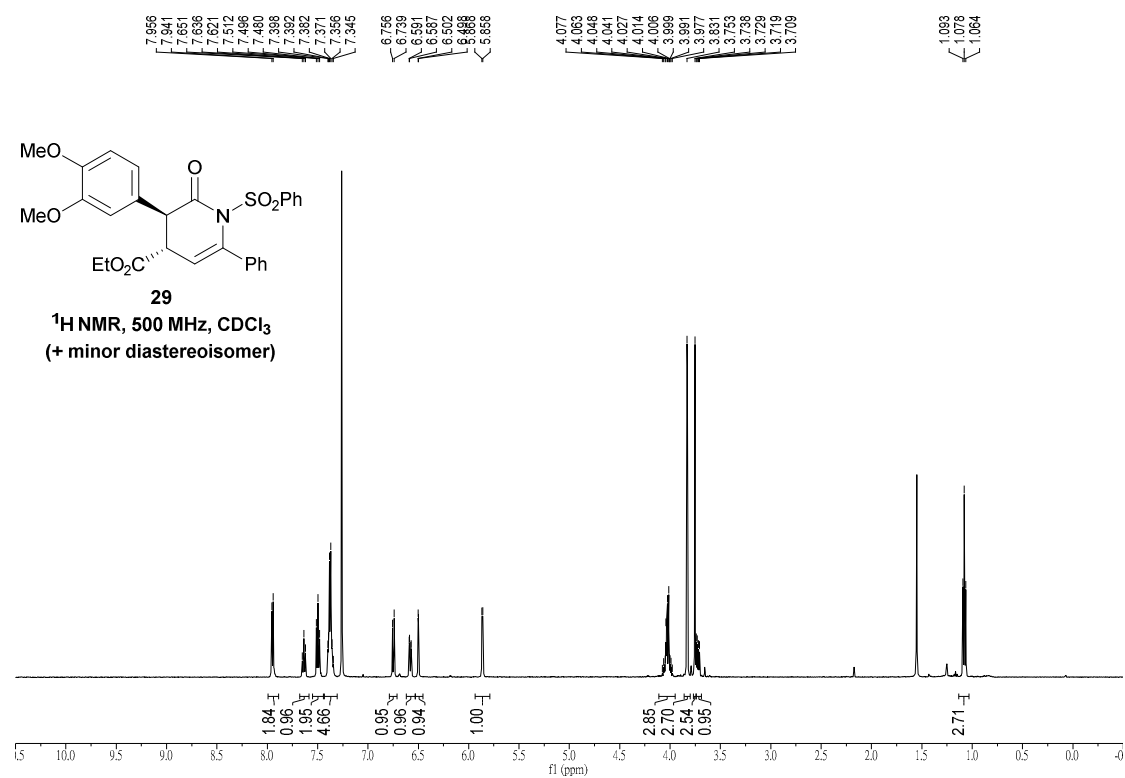
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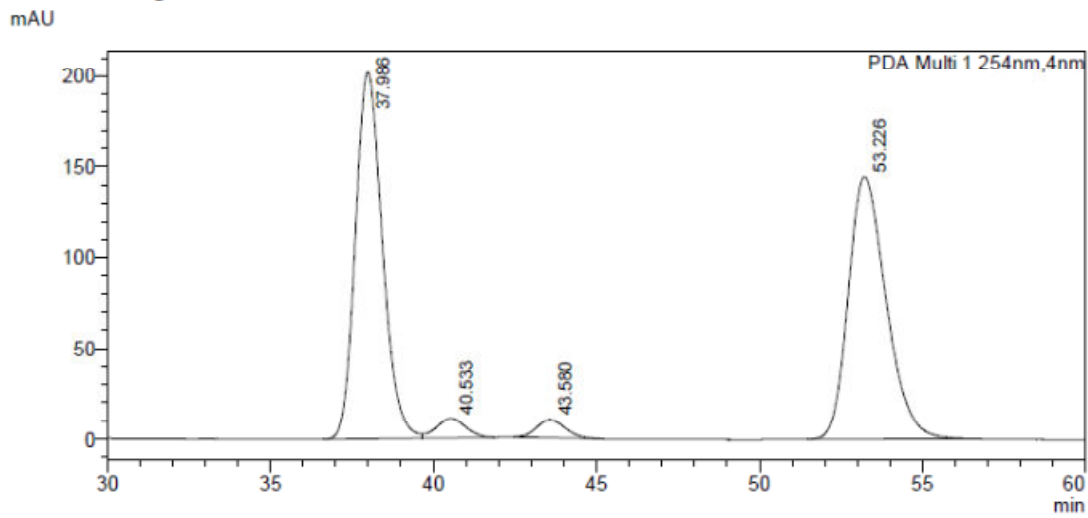


<Peak Table>

PDA Ch2 211nm

Peak#	Ret. Time	Area%
1	26.516	5.565
2	30.738	91.834
3	83.608	0.998
4	98.051	1.603
Total		100.000

(3*S*,4*S*)-Ethyl 3-(3,4-dimethoxyphenyl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 29

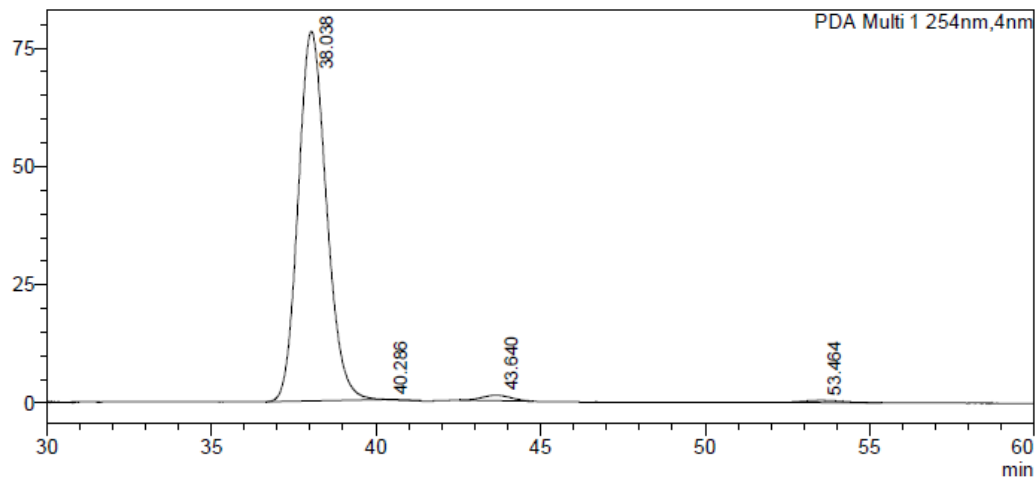


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	37.986	47.354
2	40.533	2.715
3	43.580	2.455
4	53.226	47.476
Total		100.000

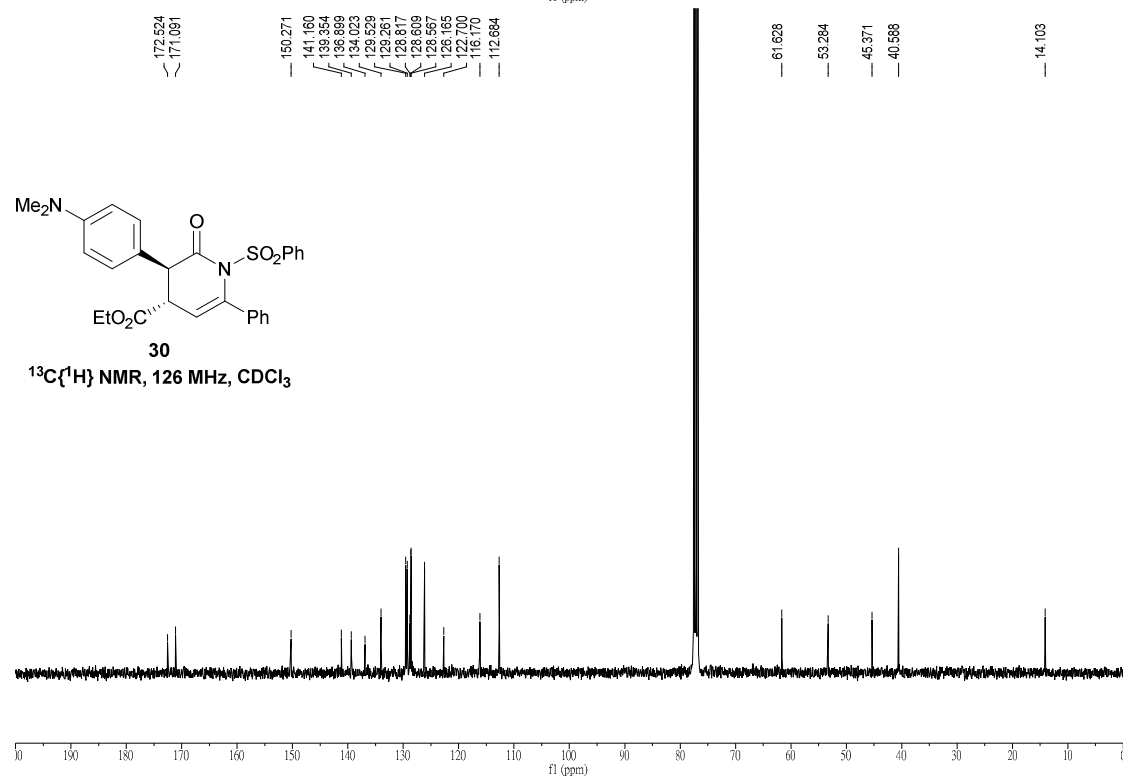
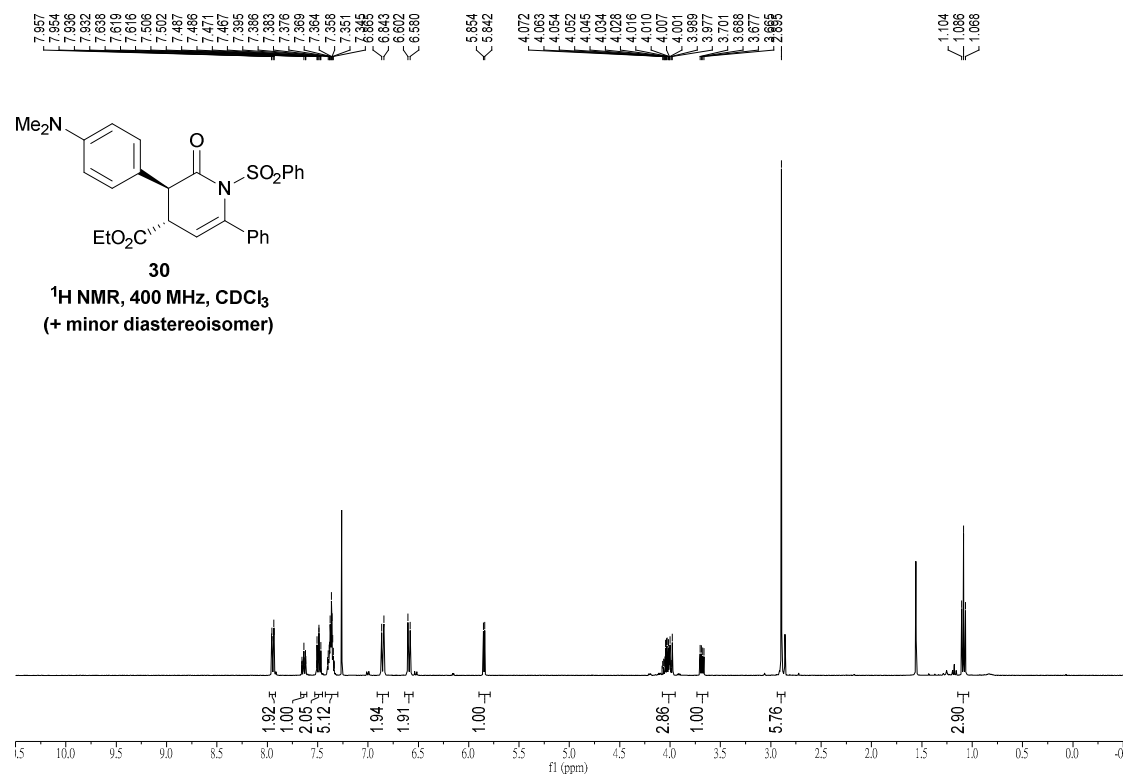
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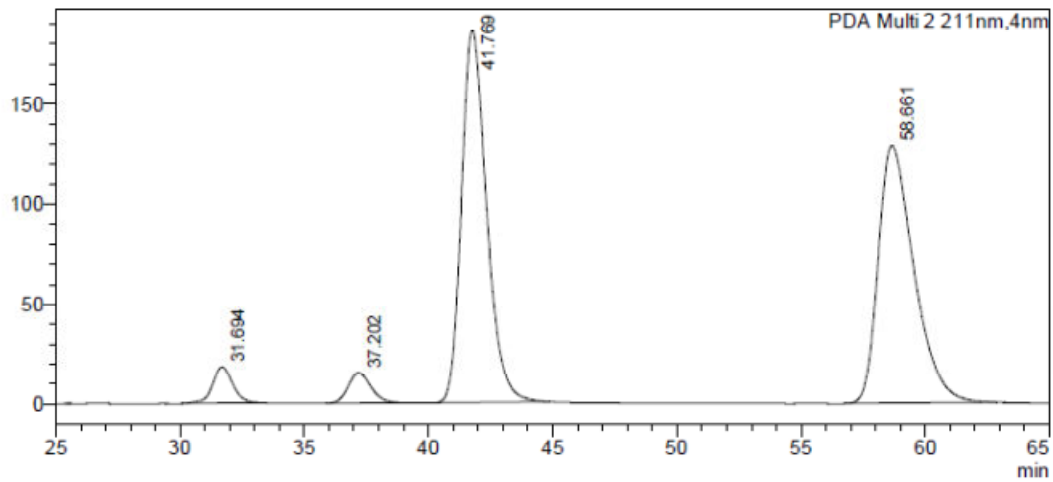
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	38.038	97.705
2	40.286	0.009
3	43.640	1.470
4	53.464	0.816
Total		100.000

(3*S*,4*S*)-Ethyl 3-(4-(dimethylamino)phenyl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 30

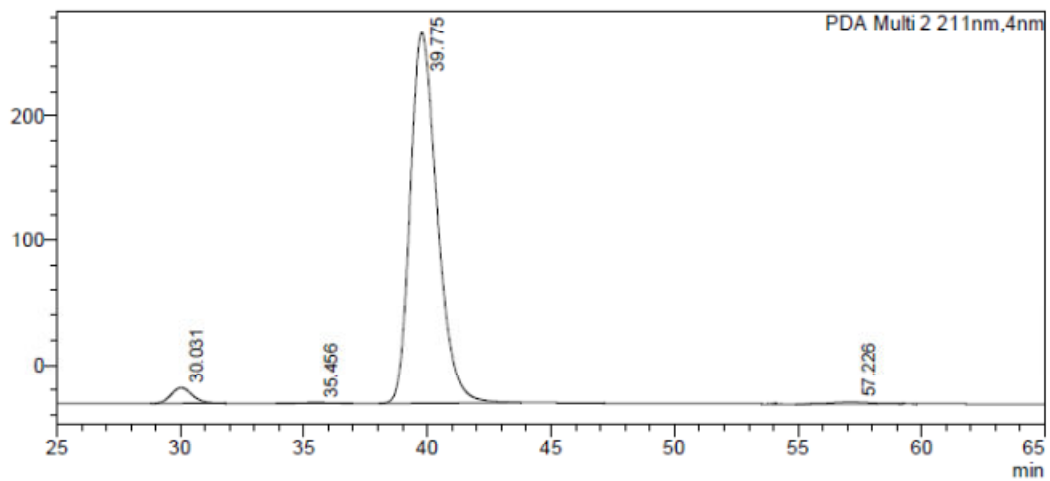
mAU

**<Peak Table>**

PDA Ch2 211nm

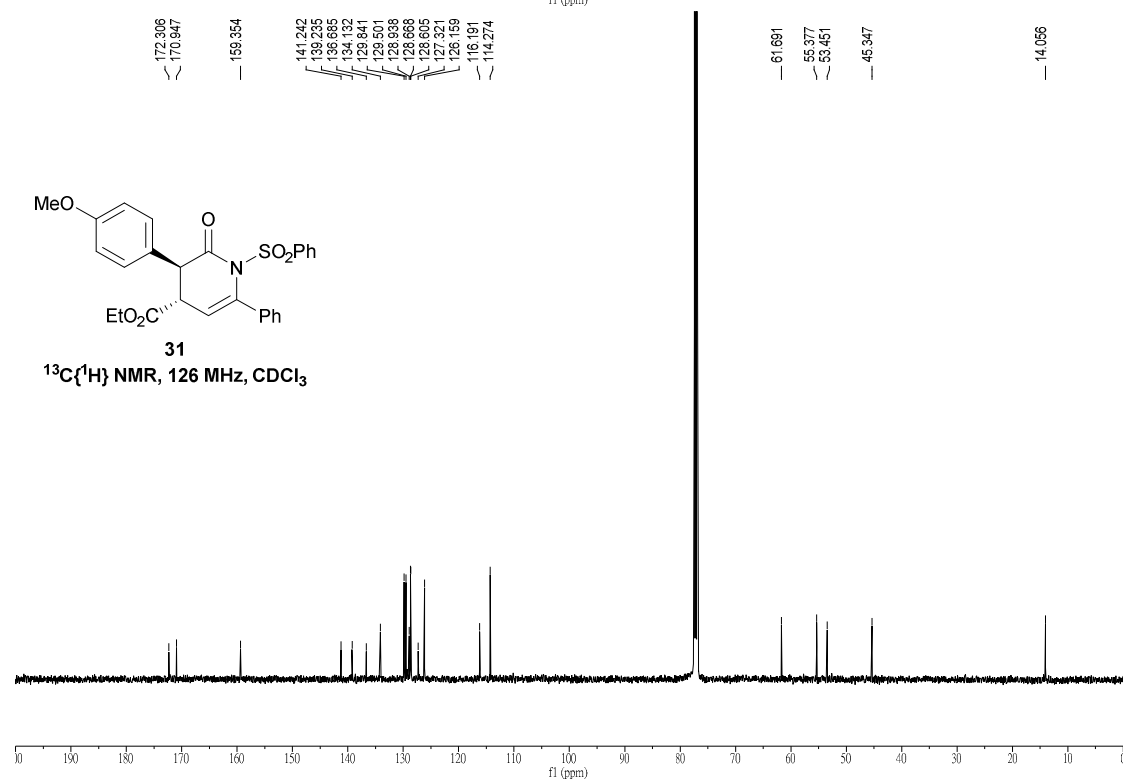
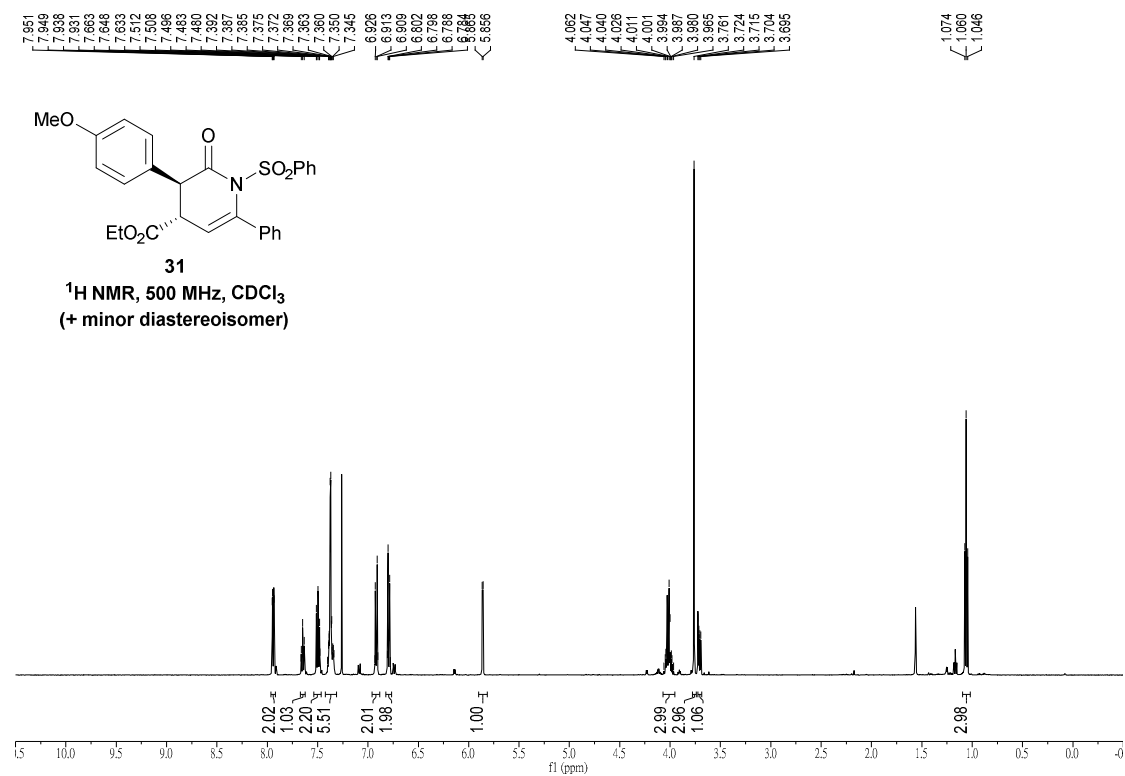
Peak#	Ret. Time	Area%
1	31.694	3.656
2	37.202	3.446
3	41.769	46.724
4	58.661	46.173
Total		100.000

mAU

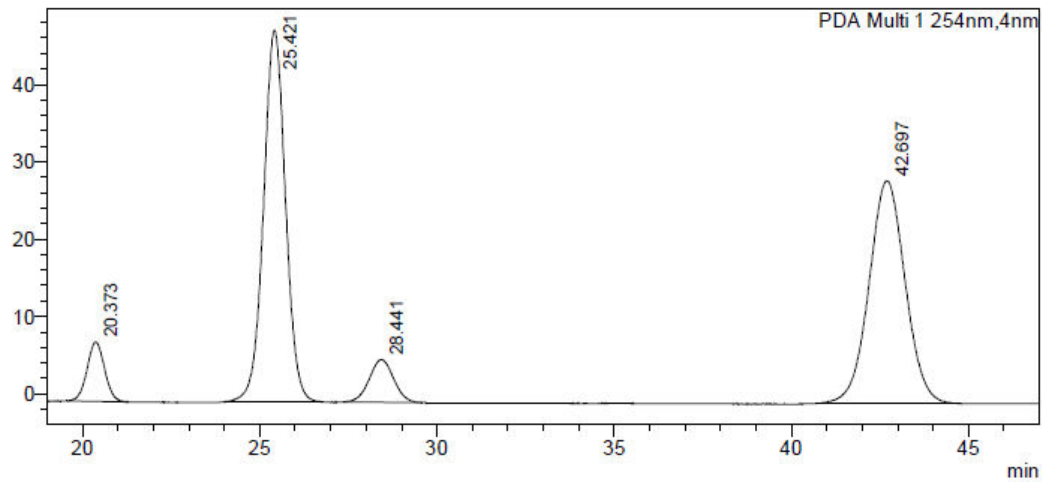
**<Peak Table>**

PDA Ch2 211nm

Peak#	Ret. Time	Area%
1	30.031	3.167
2	35.456	0.234
3	39.775	95.971
4	57.226	0.628
Total		100.000

(3*S*,4*S*)-Ethyl 3-(4-methoxyphenyl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 31

mAU

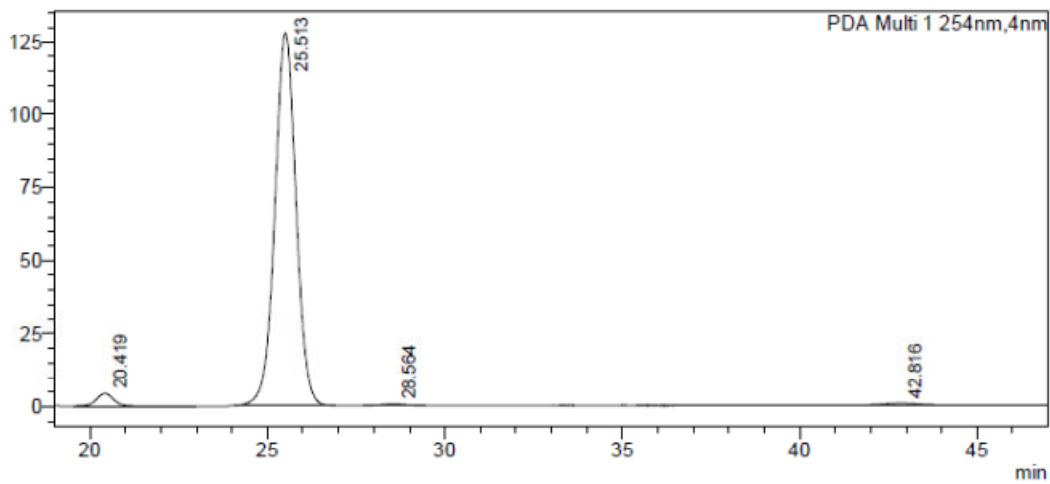


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	20.373	5.681
2	25.421	44.641
3	28.441	5.705
4	42.697	43.972
Total		100.000

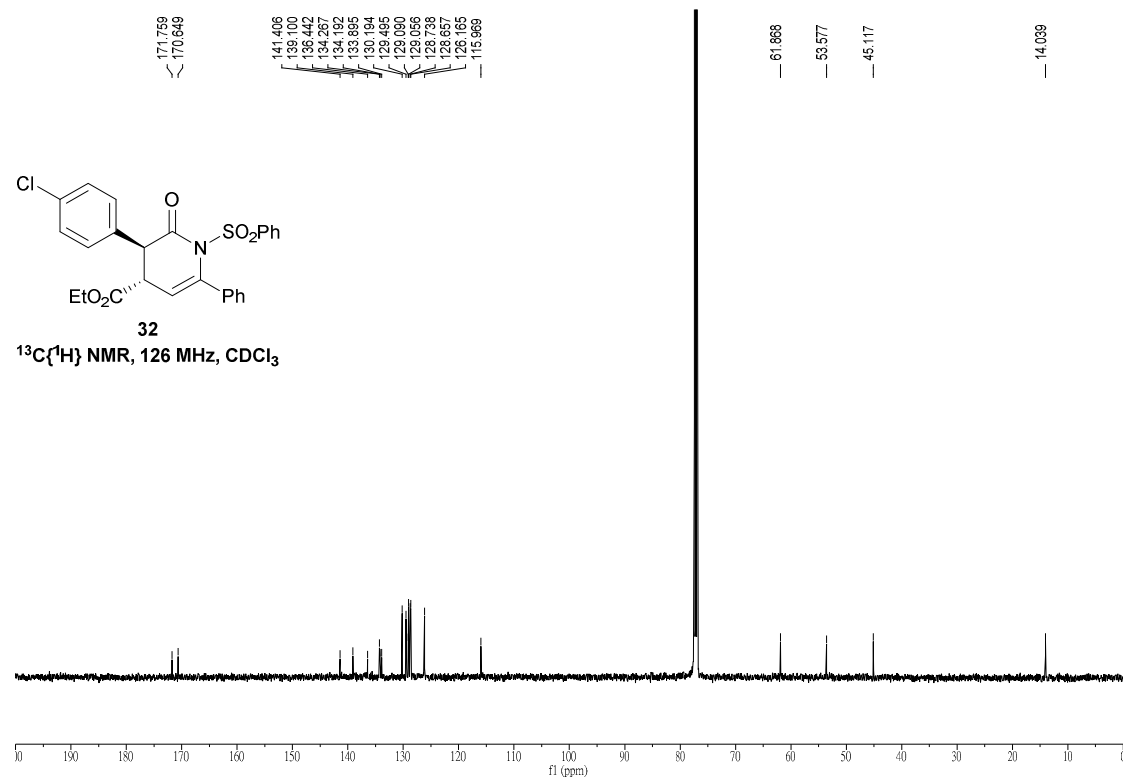
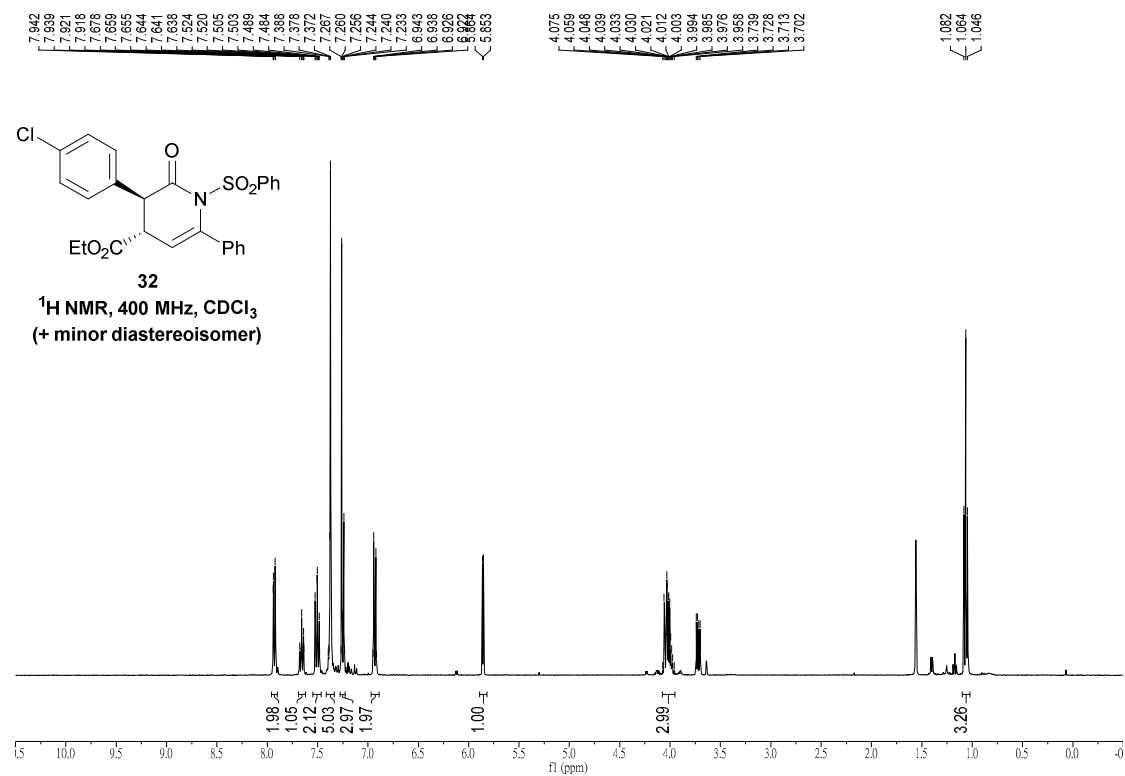
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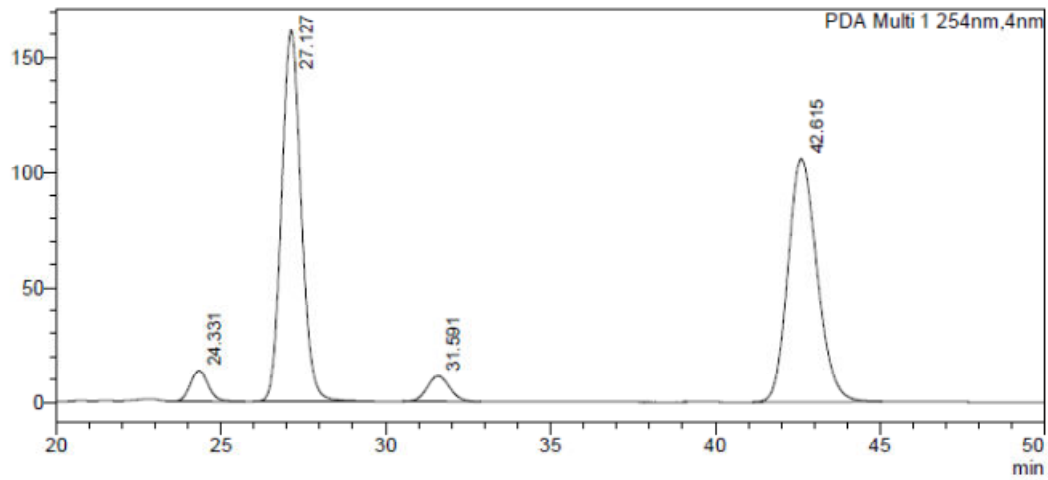
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	20.419	2.537
2	25.513	96.157
3	28.564	0.439
4	42.816	0.868
Total		100.000

(3*S*,4*S*)-Ethyl 3-(4-chlorophenyl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 32

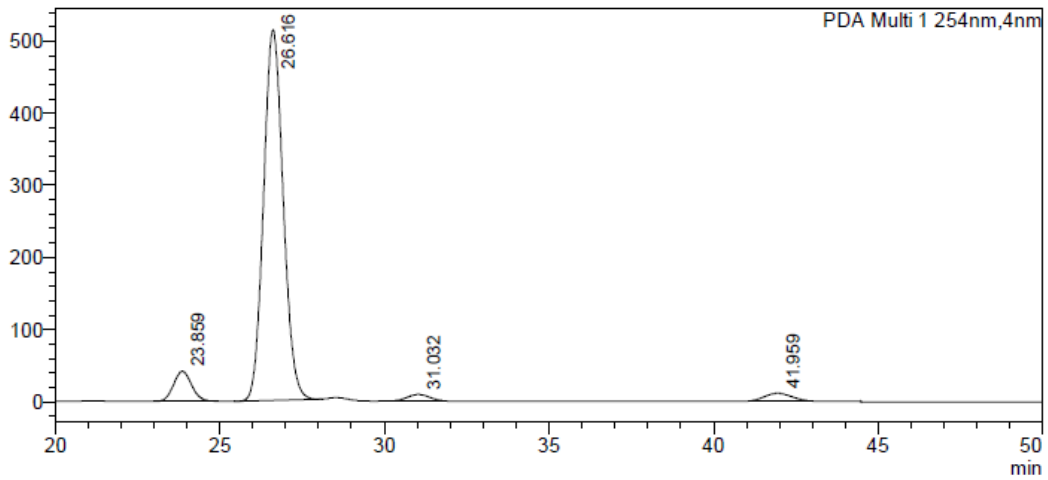
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**<Peak Table>**

PDA Ch1 254nm

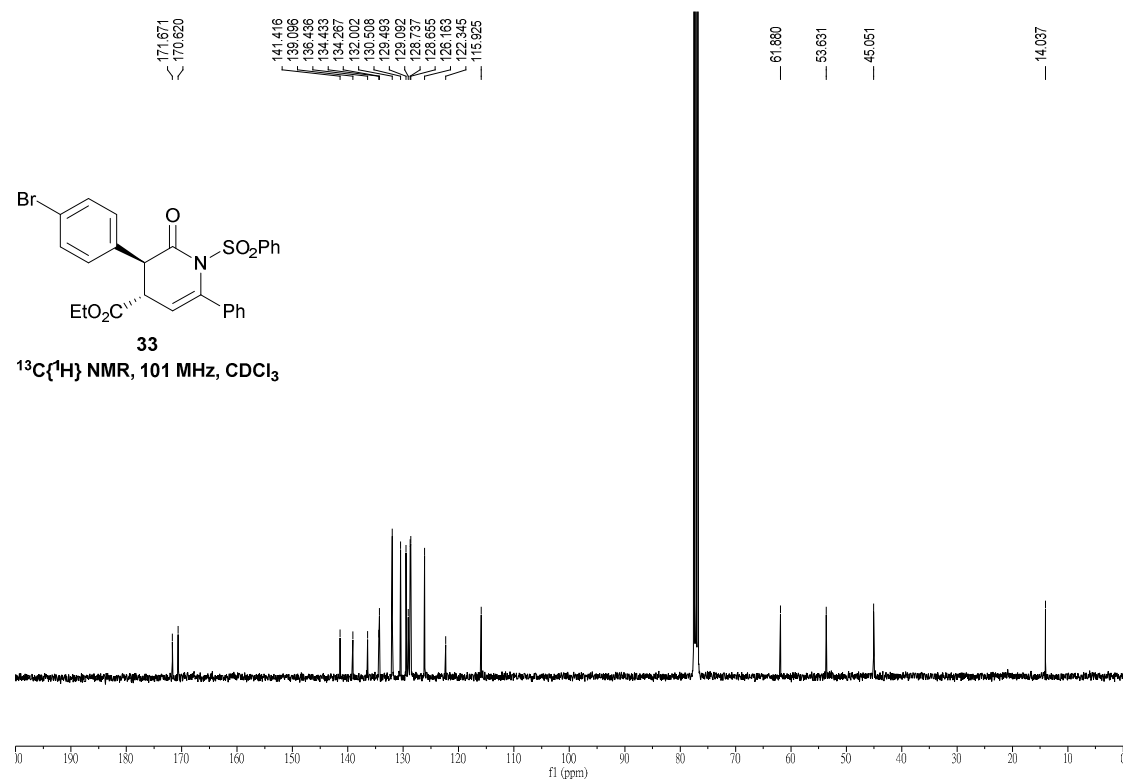
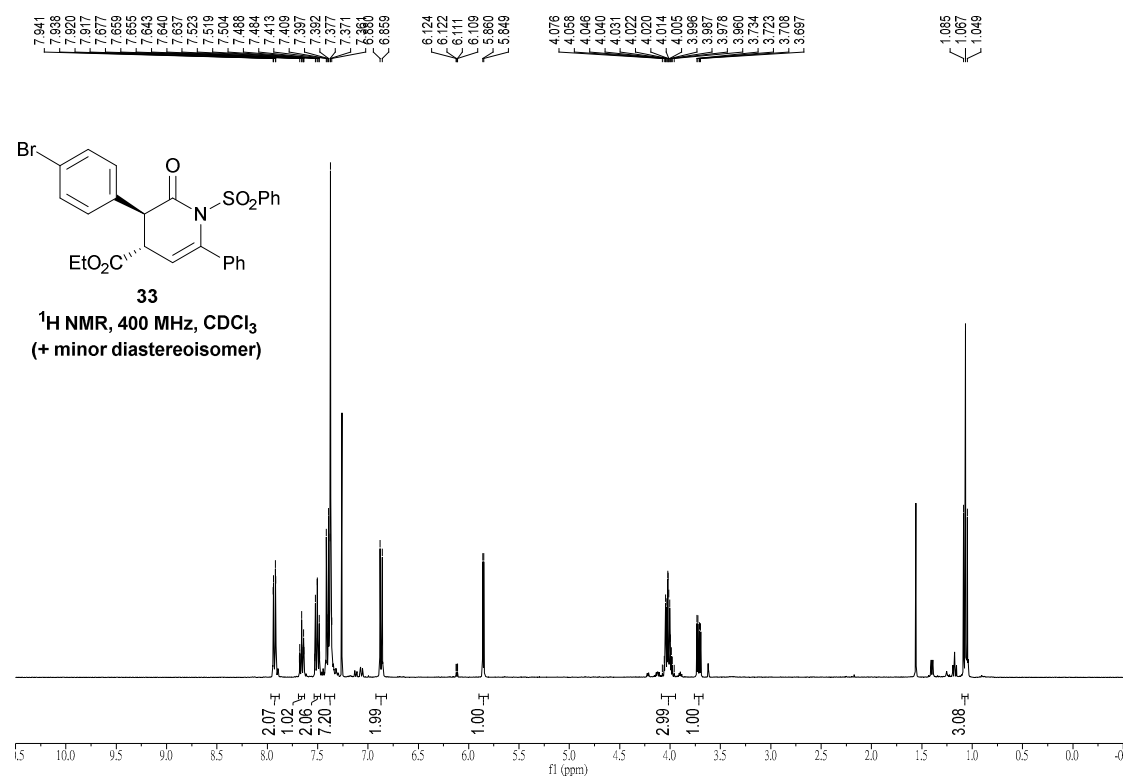
Peak#	Ret. Time	Area%
1	24.331	3.609
2	27.127	46.855
3	31.591	3.770
4	42.615	45.766
Total		100.000

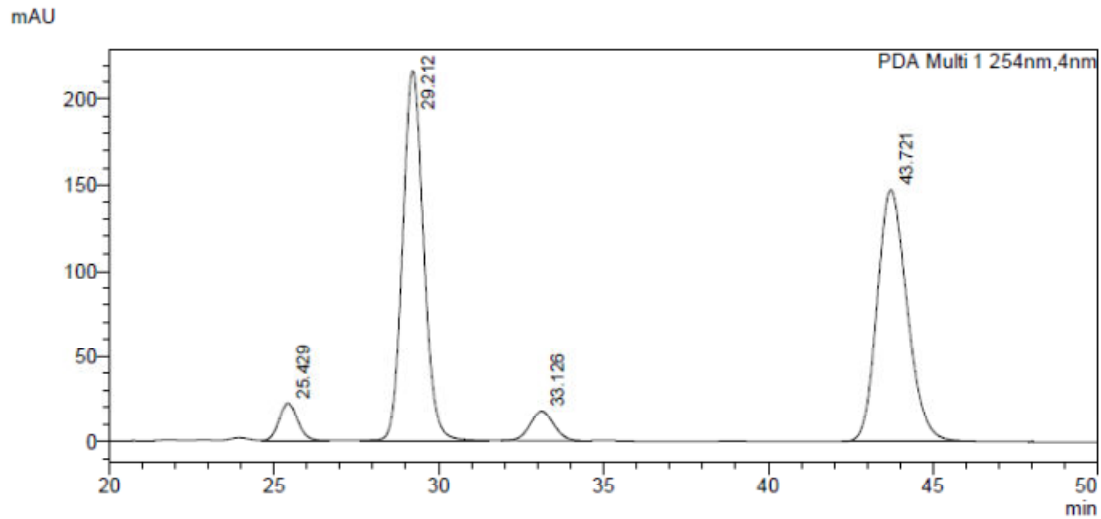
mAU

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	23.859	6.632
2	26.616	89.248
3	31.032	1.744
4	41.959	2.377
Total		100.000

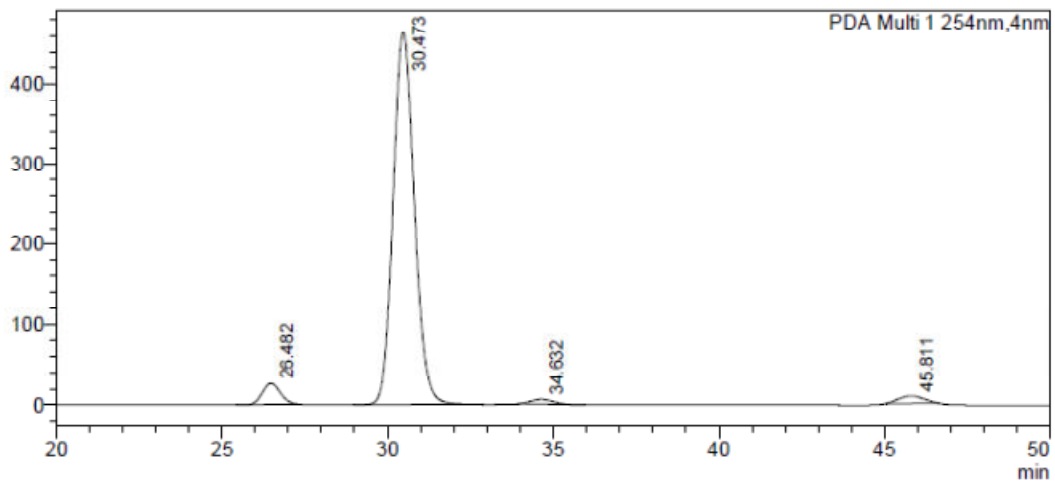
(3S,4S)-Ethyl 3-(4-bromophenyl)-2-oxo-6-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 33

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	25.429	4.116
2	29.212	46.354
3	33.126	4.169
4	43.721	45.362
Total		100.000

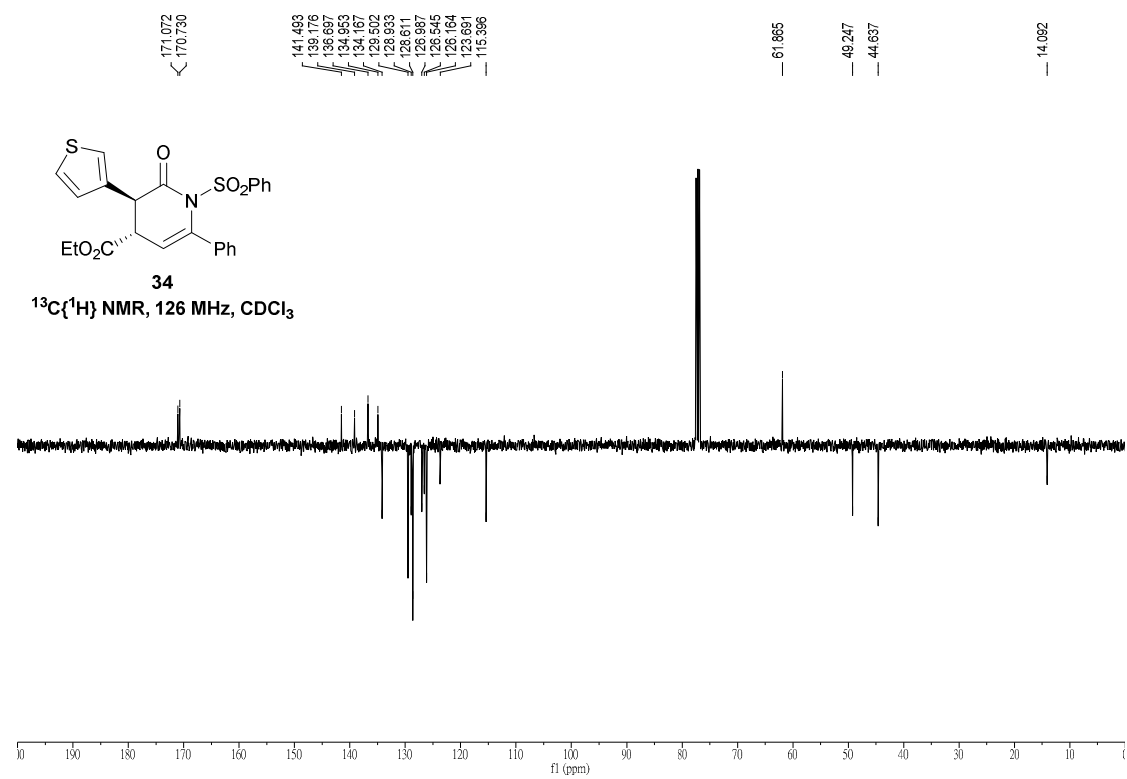
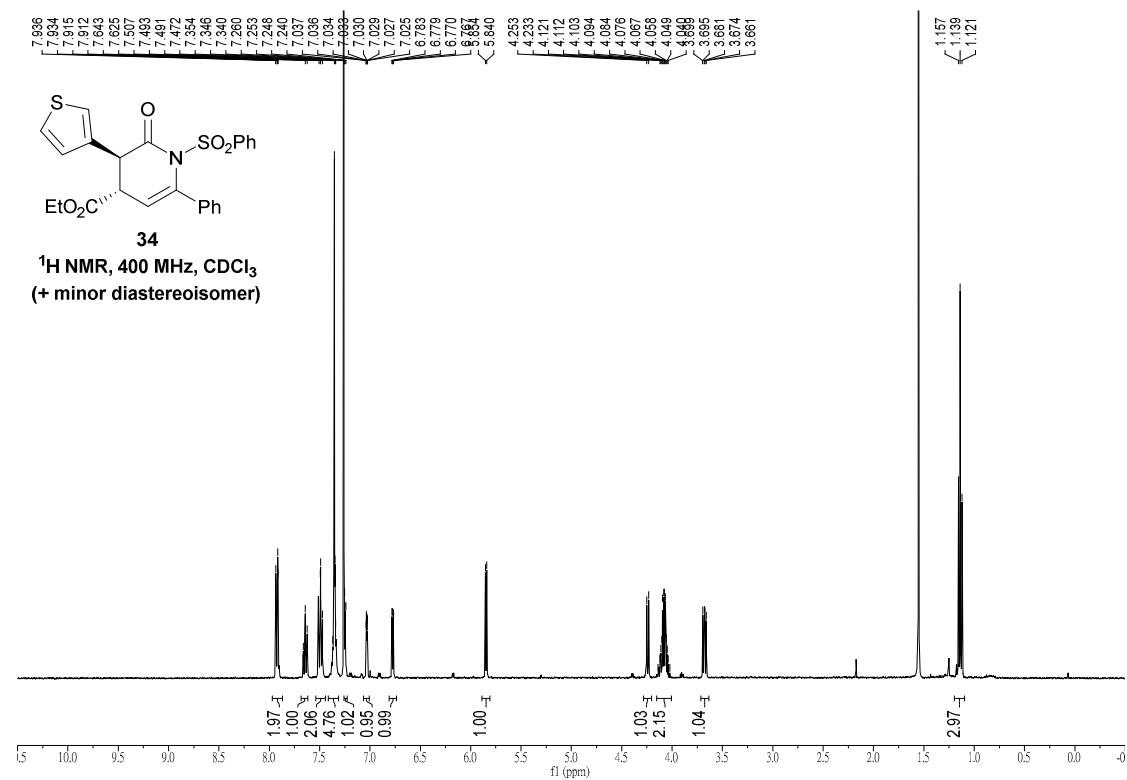
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**<Peak Table>**

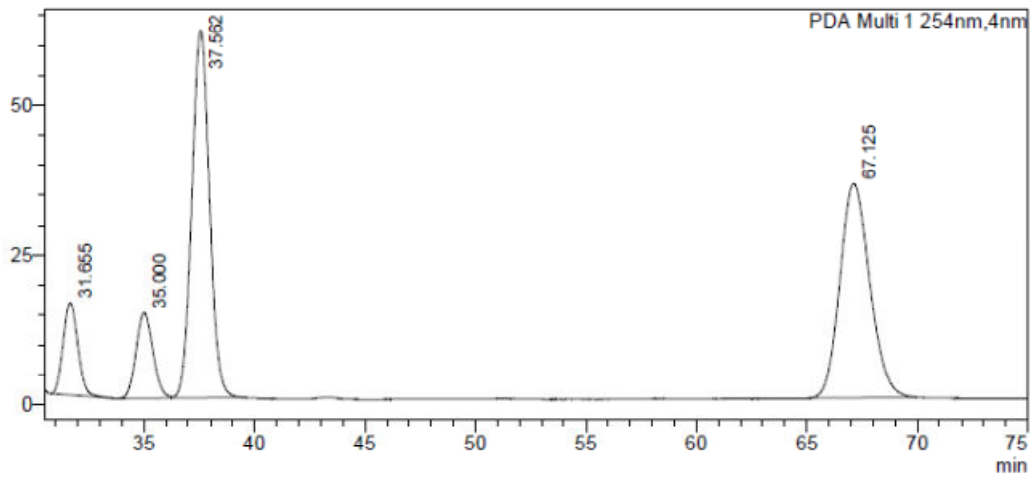
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	26.482	4.428
2	30.473	92.204
3	34.632	1.178
4	45.811	2.191
Total		100.000

(3*S*,4*S*)-Ethyl 2-oxo-6-phenyl-1-(phenylsulfonyl)-3-(thiophen-3-yl)-1,2,3,4-tetrahydropyridine-4-carboxylate **34**



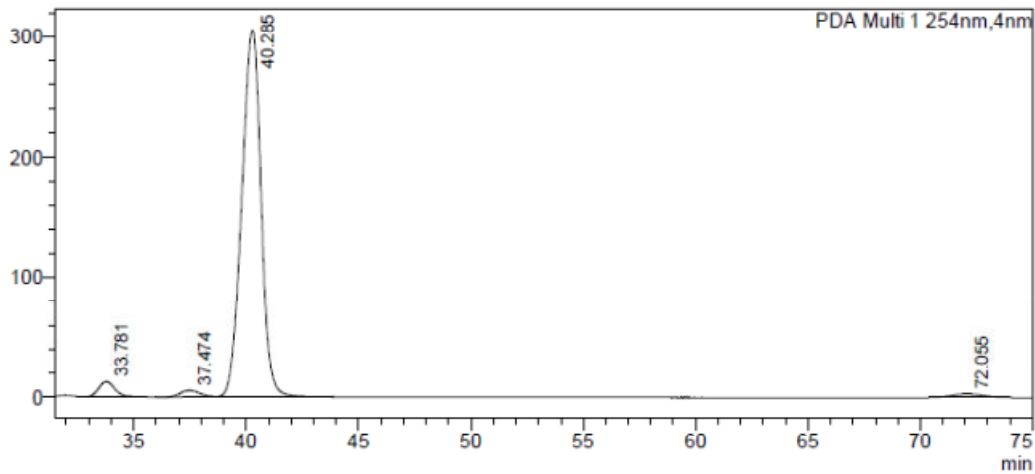
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**<Peak Table>**

PDA Ch1 254nm

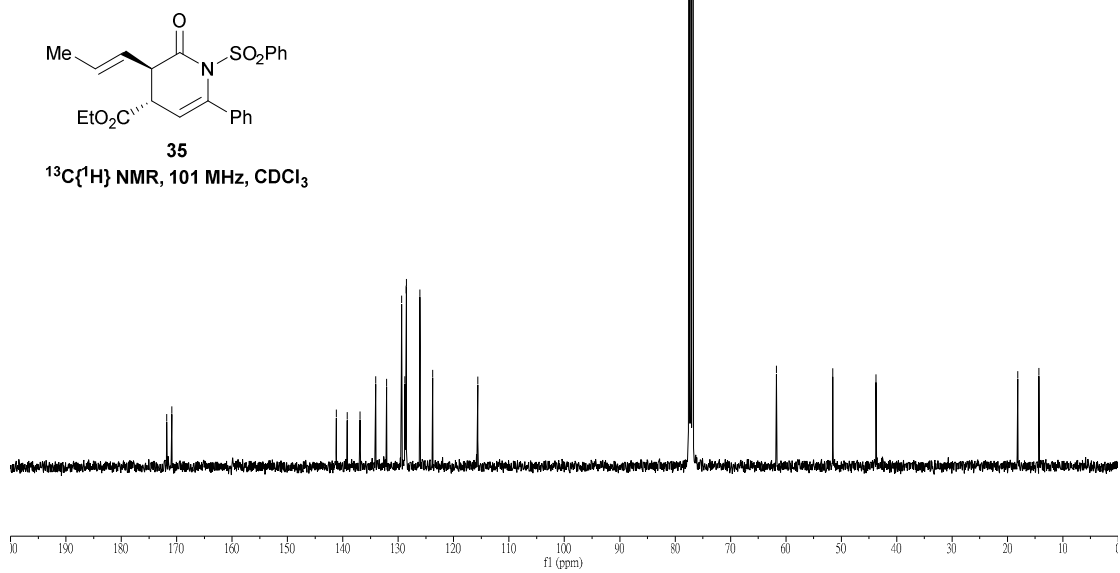
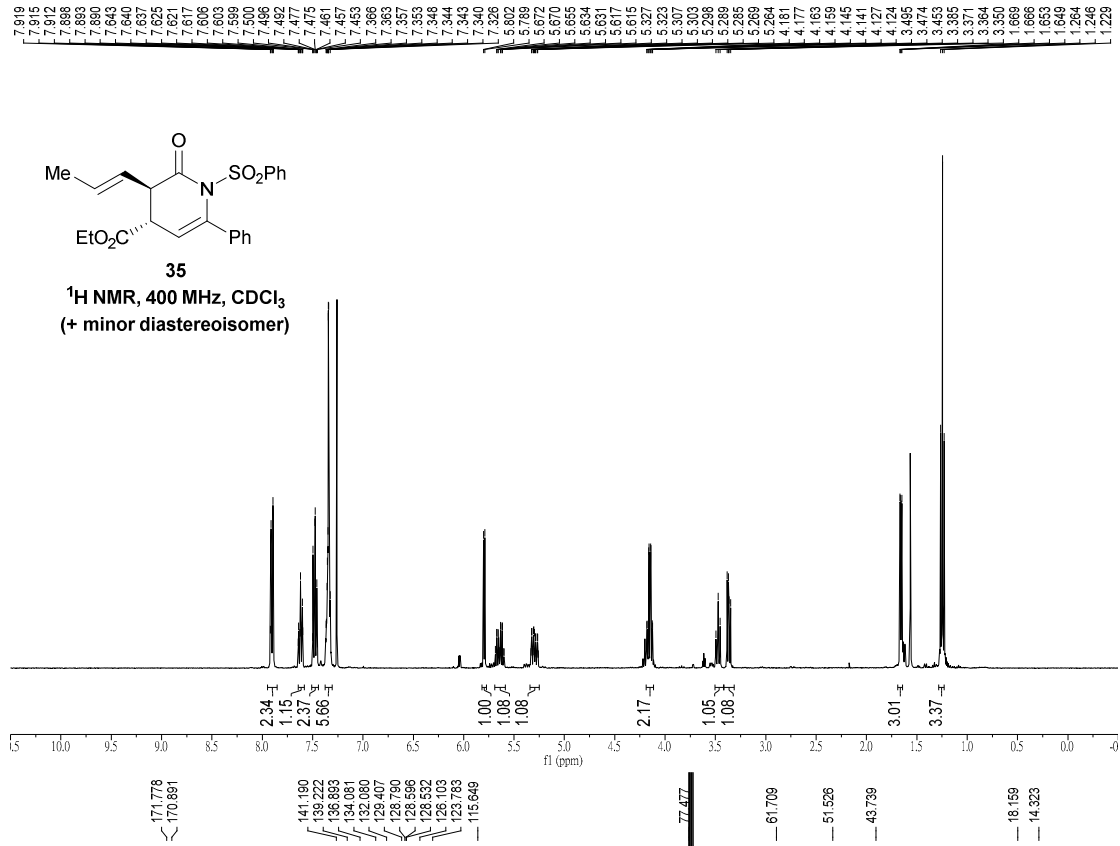
Peak#	Ret. Time	Area%
1	31.655	8.731
2	35.000	9.203
3	37.562	41.293
4	67.125	40.773
Total		100.000

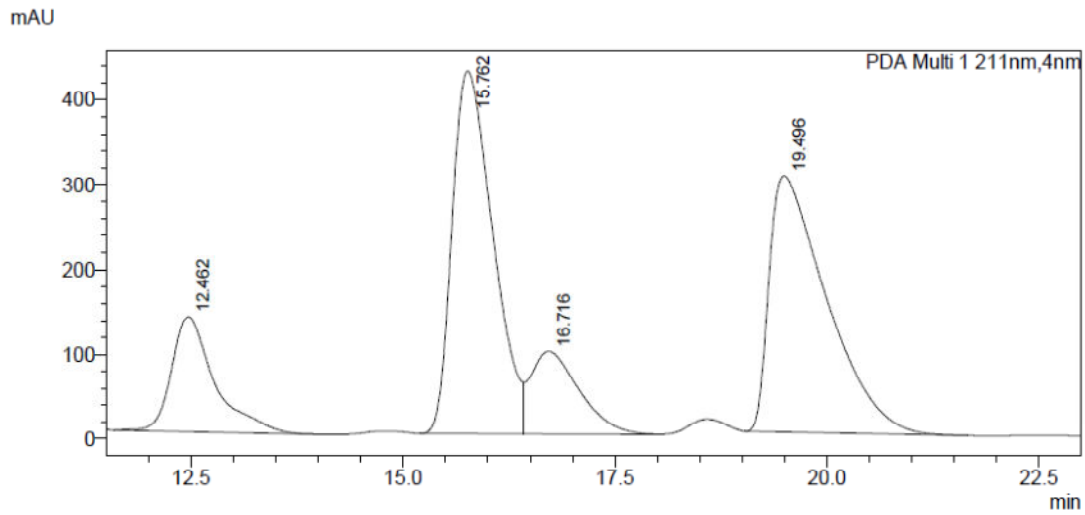
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**<Peak Table>**

PDA Ch1 254nm

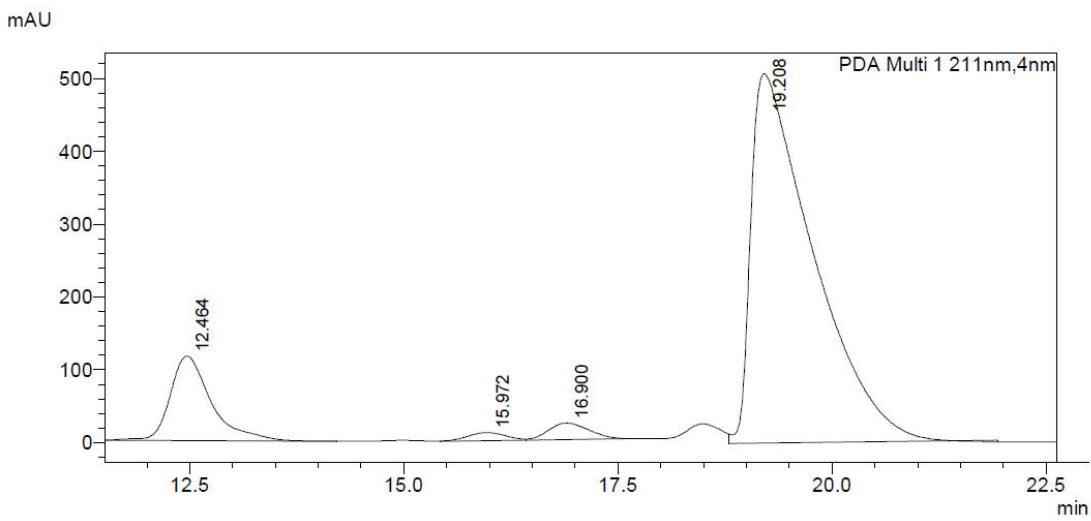
Peak#	Ret. Time	Area%
1	33.781	3.119
2	37.474	1.534
3	40.285	93.945
4	72.055	1.402
Total		100.000

(3*R*,4*S*)-Ethyl 2-oxo-6-phenyl-1-(phenylsulfonyl)-3-((*E*)-prop-1-en-1-yl)-1,2,3,4-tetrahydropyridine-4-carboxylate 35



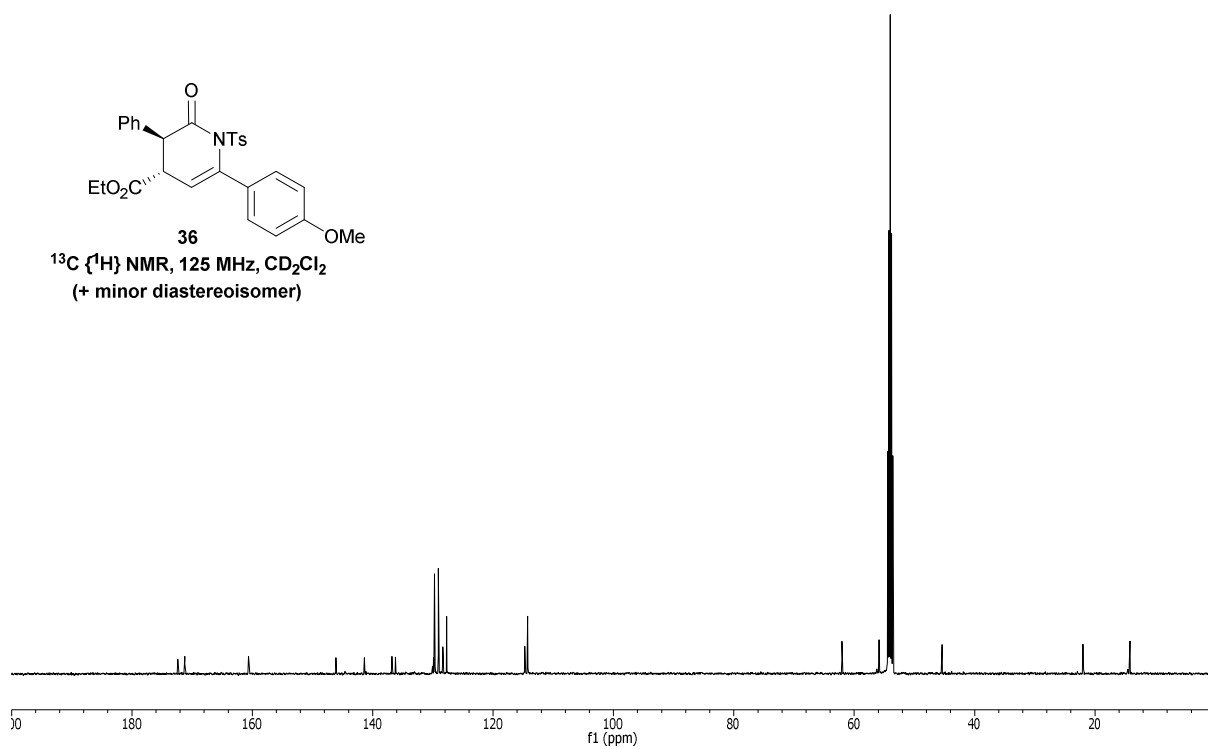
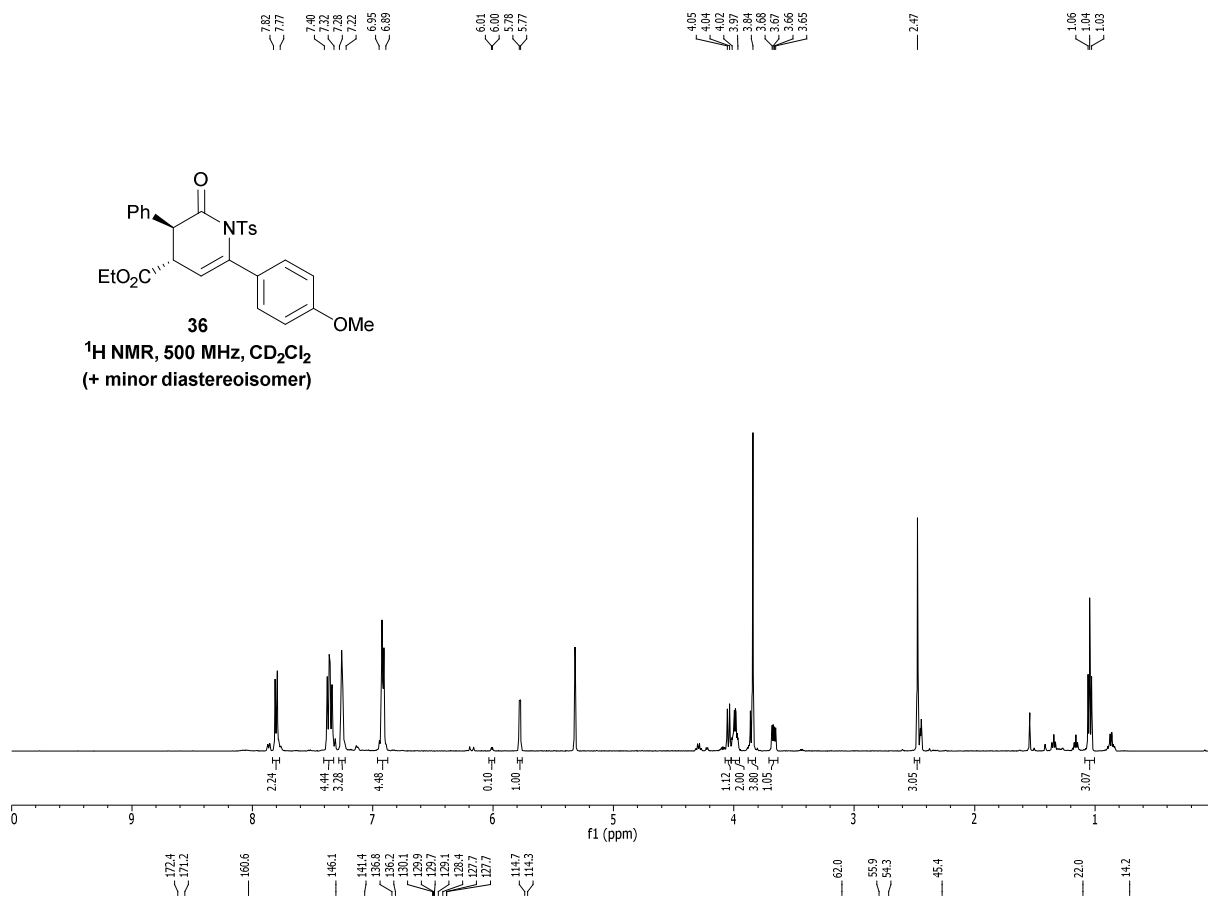
<Peak Table>

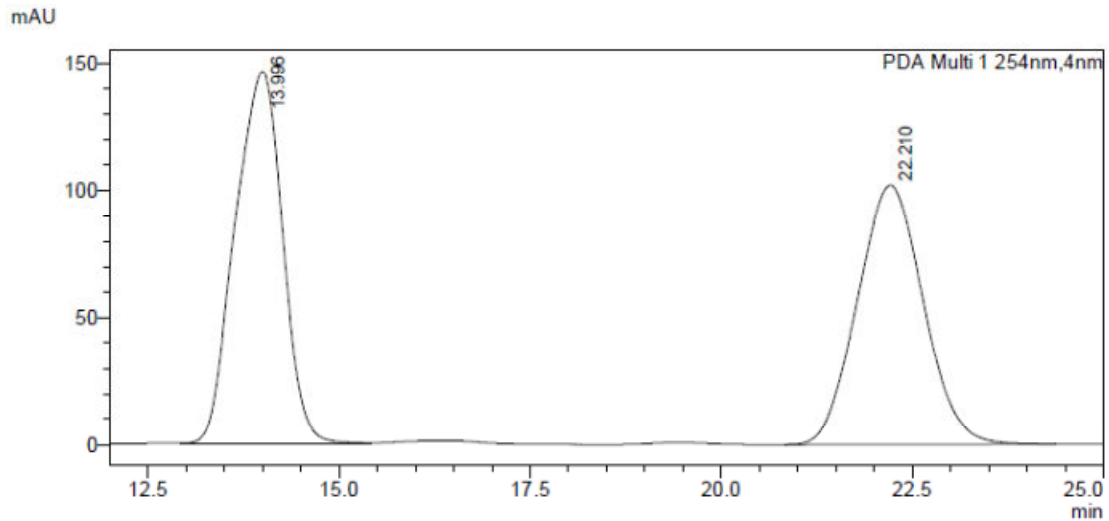
PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	12.462	12.928
2	15.762	38.426
3	16.716	10.363
4	19.496	38.283
Total		100.000



<Peak Table>

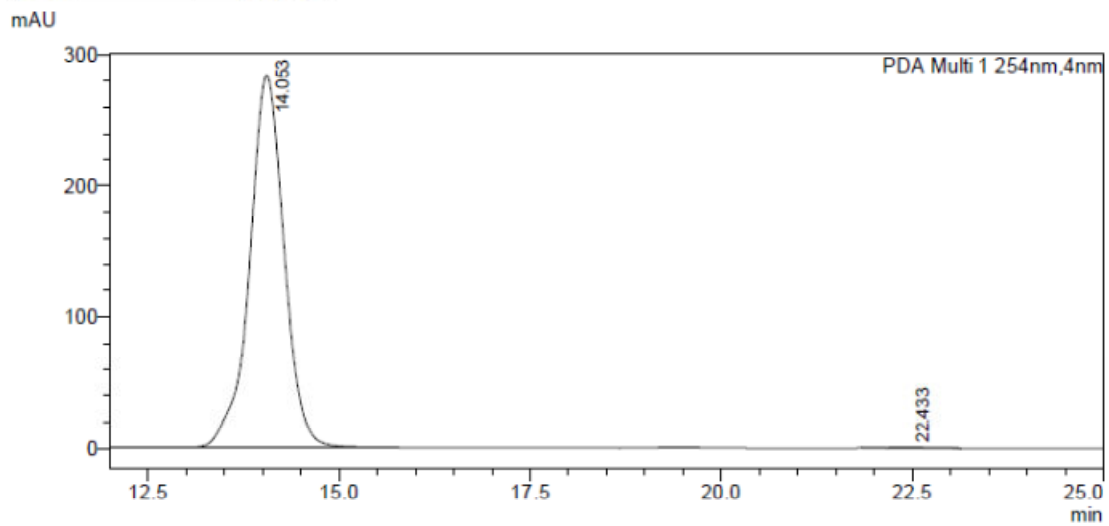
PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	12.464	12.784
2	15.972	1.075
3	16.900	2.404
4	19.208	83.737
Total		100.000

(3*S*,4*S*)-Ethyl 6-(4-methoxyphenyl)-2-oxo-3-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate 36

**<Peak Table>**

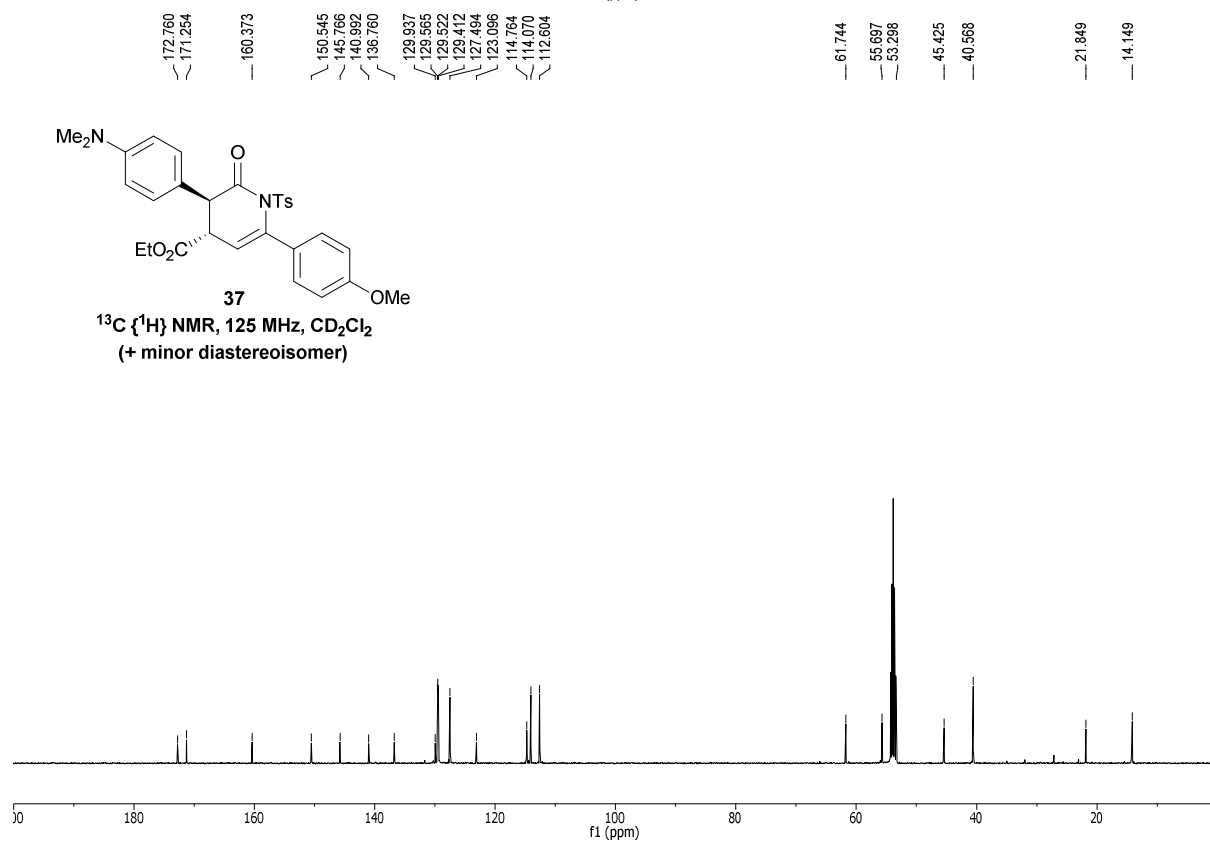
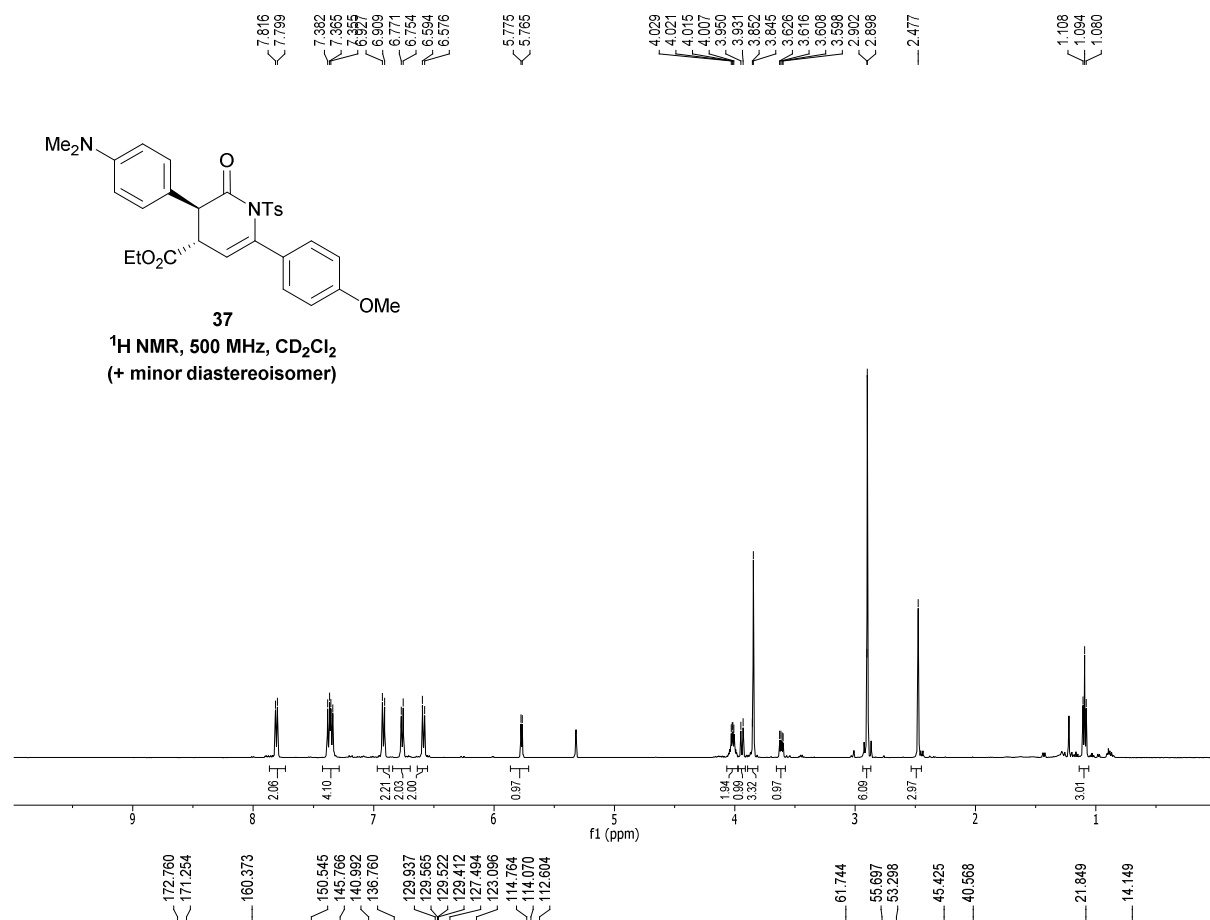
PDA Ch1 254nm

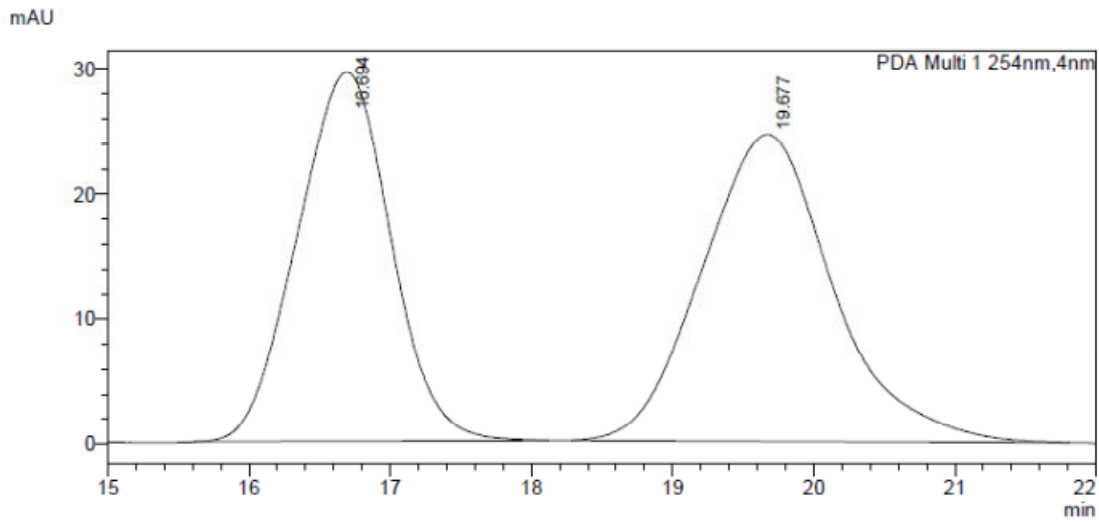
Peak#	Ret. Time	Area%
1	13.996	50.765
2	22.210	49.235
Total		100.000

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	14.053	99.751
2	22.433	0.249
Total		100.000

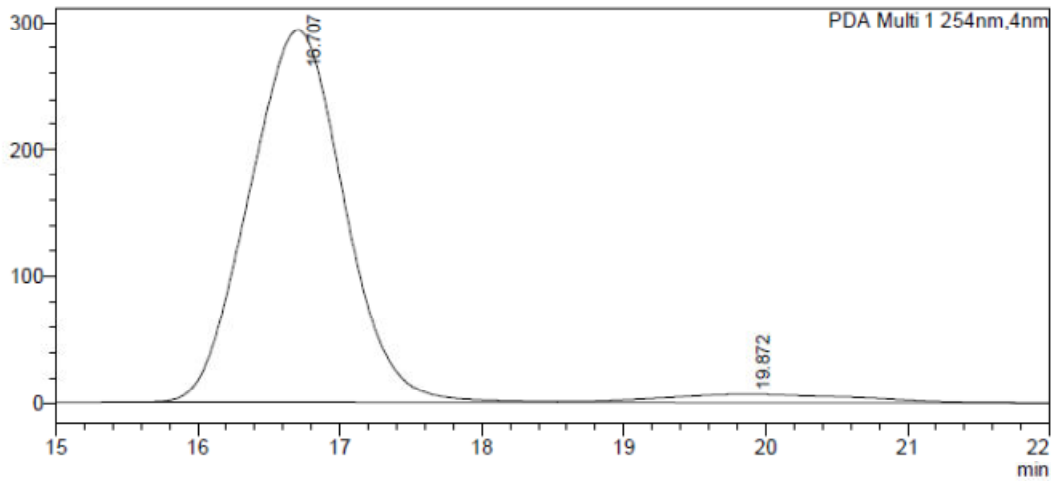
(3*S*,4*S*)-Ethyl 3-(4-(dimethylamino)phenyl)-6-(4-methoxyphenyl)-2-oxo-1-tosyl-1,2,3,4-tetrahydropyridine-4-carboxylate 37

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	16.694	46.209
2	19.677	53.791
Total		100.000

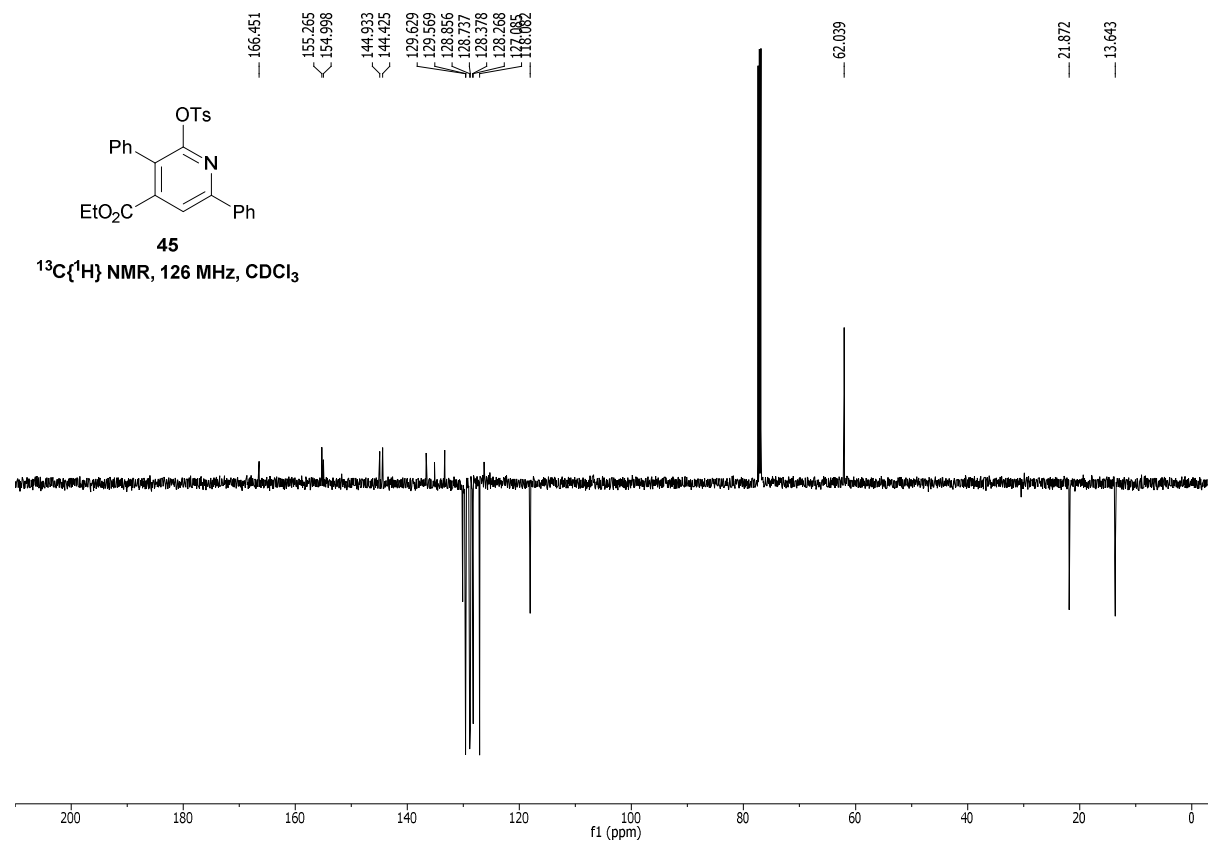
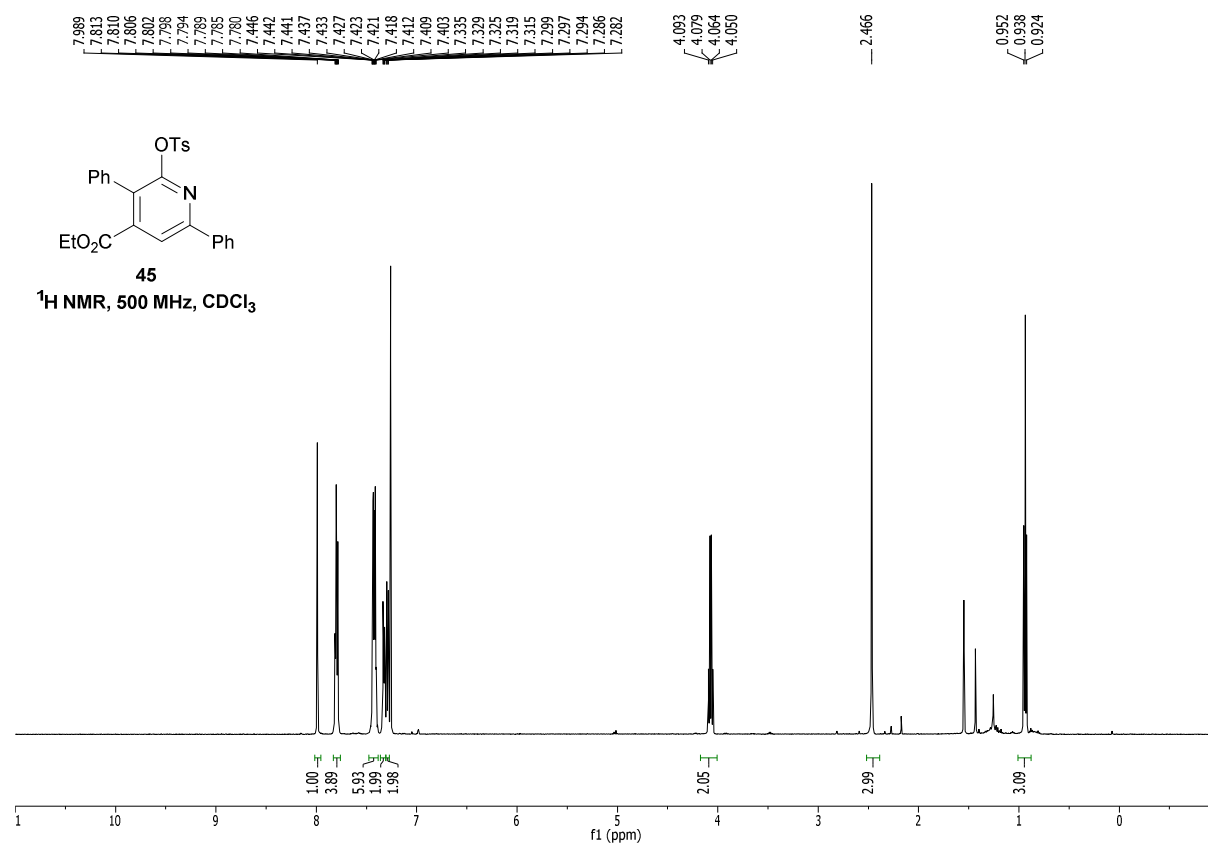
mAU

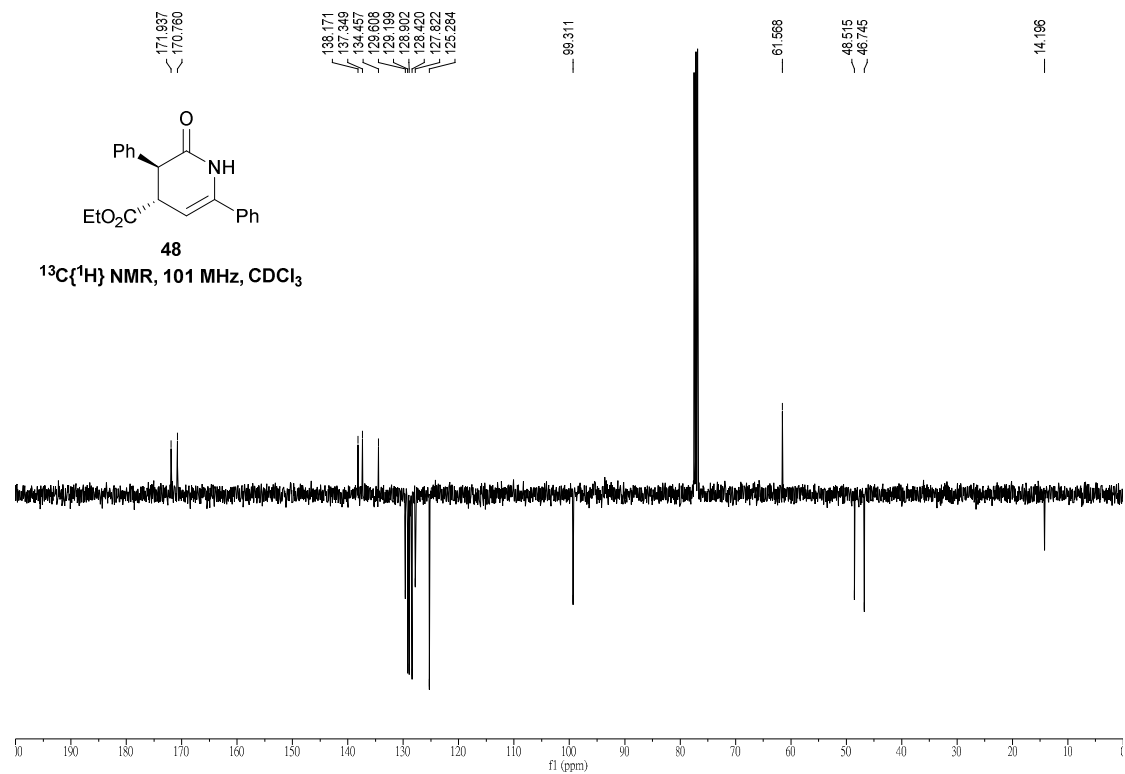
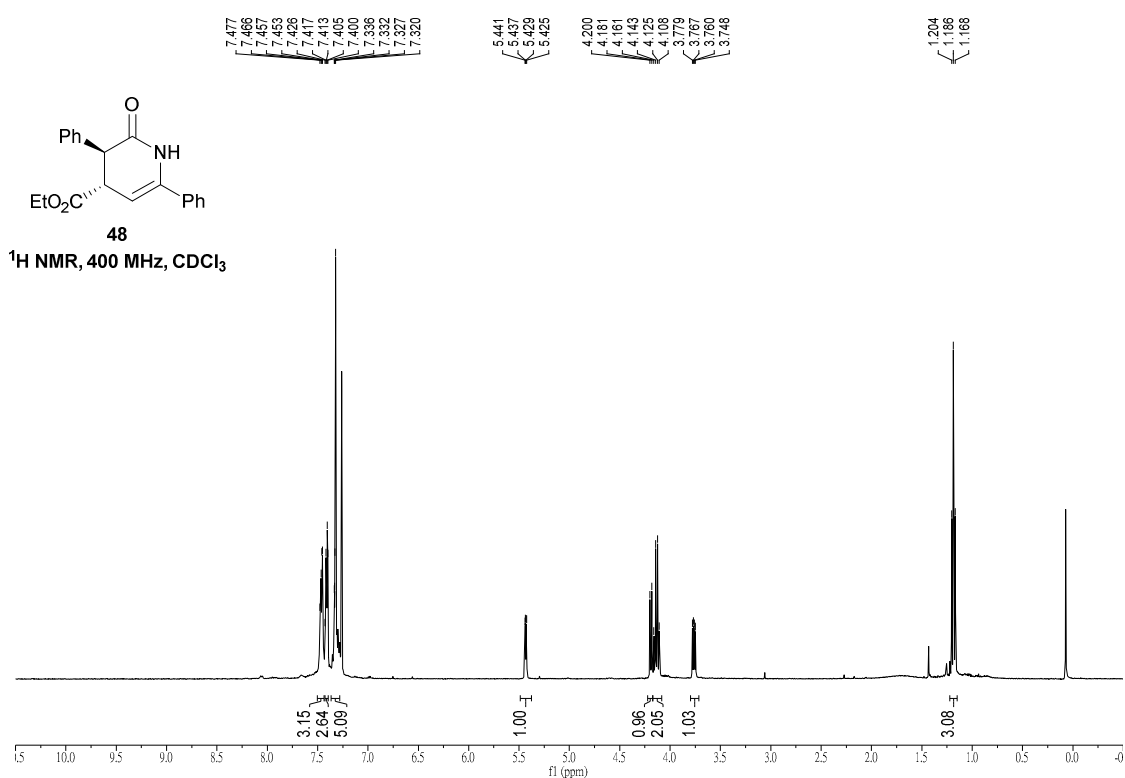
**<Peak Table>**

PDA Ch1 254nm

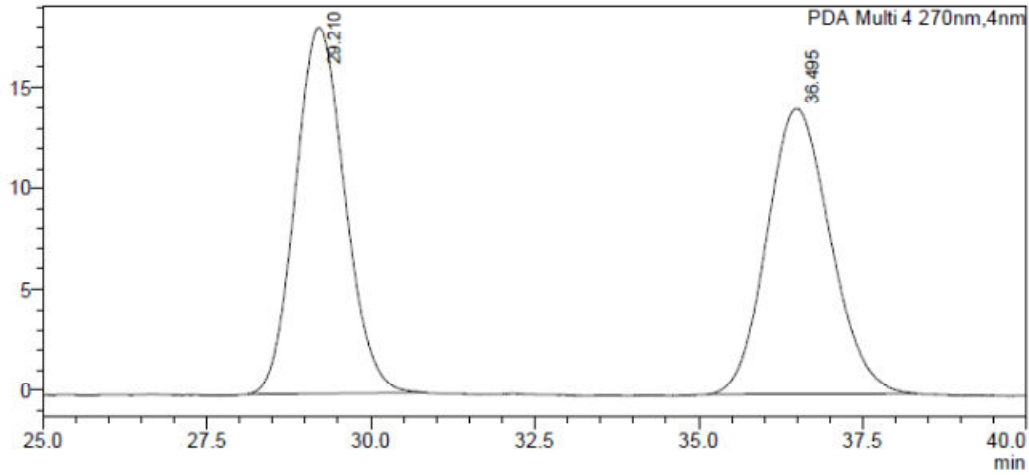
Peak#	Ret. Time	Area%
1	16.707	95.556
2	19.872	4.444
Total		100.000

Ethyl 3,6-diphenyl-2-(tosyloxy)isonicotinate 45



(3*S*,4*S*)-Ethyl 2-oxo-3,6-diphenyl-1,2,3,4-tetrahydropyridine-4-carboxylate 48

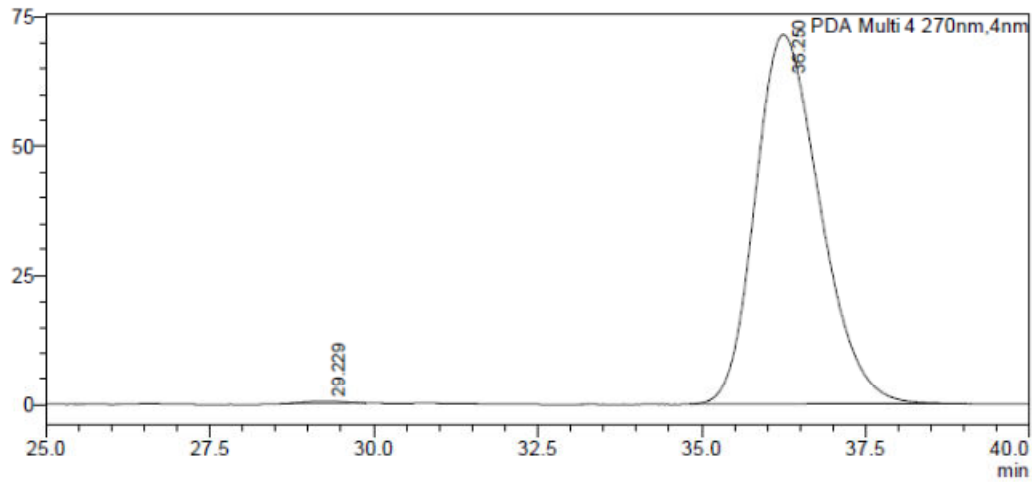
mAU

**<Peak Table>**

PDA Ch4 270nm

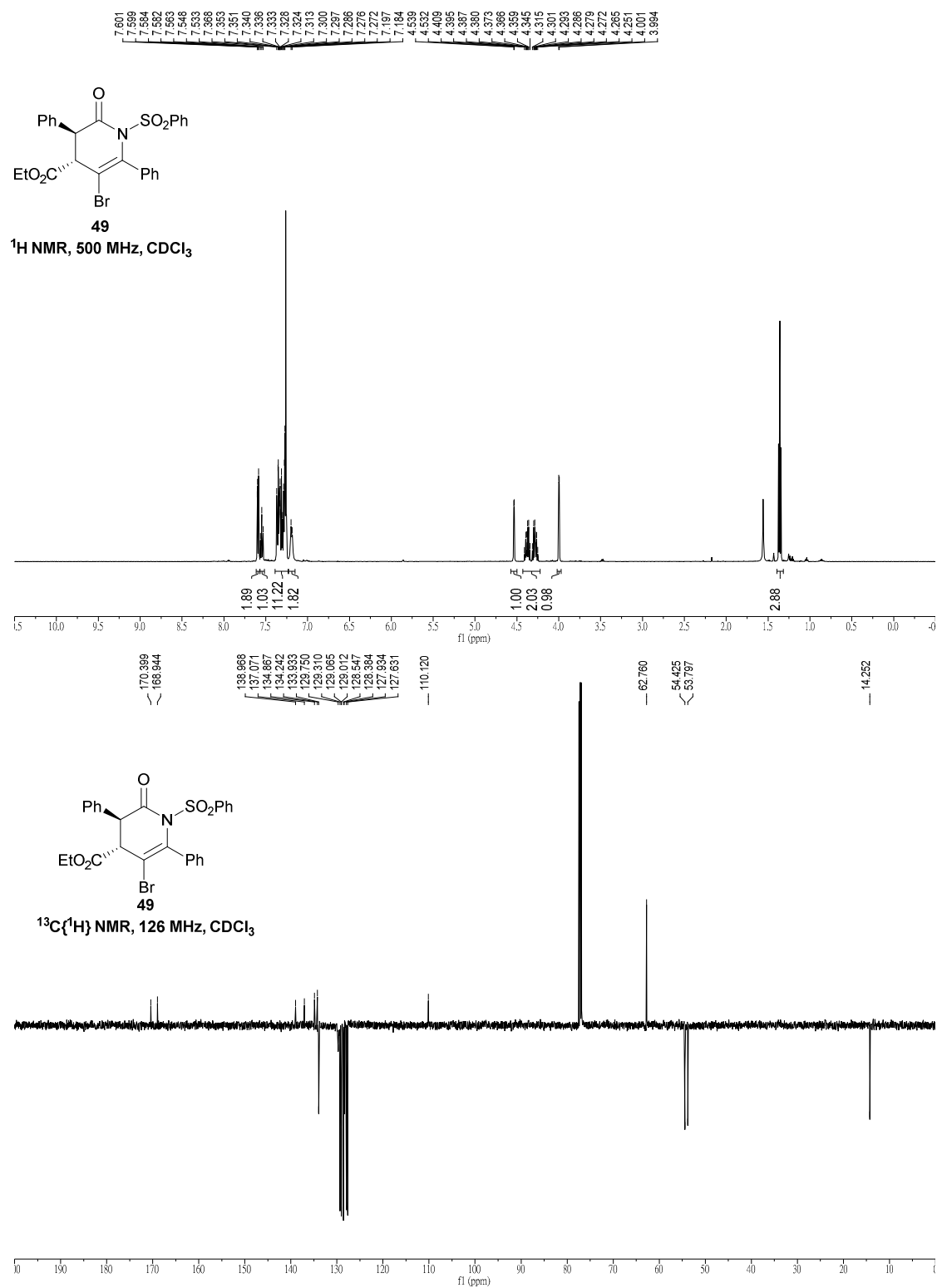
Peak#	Ret. Time	Area%
1	29.210	50.038
2	36.495	49.962
Total		100.000

mAU

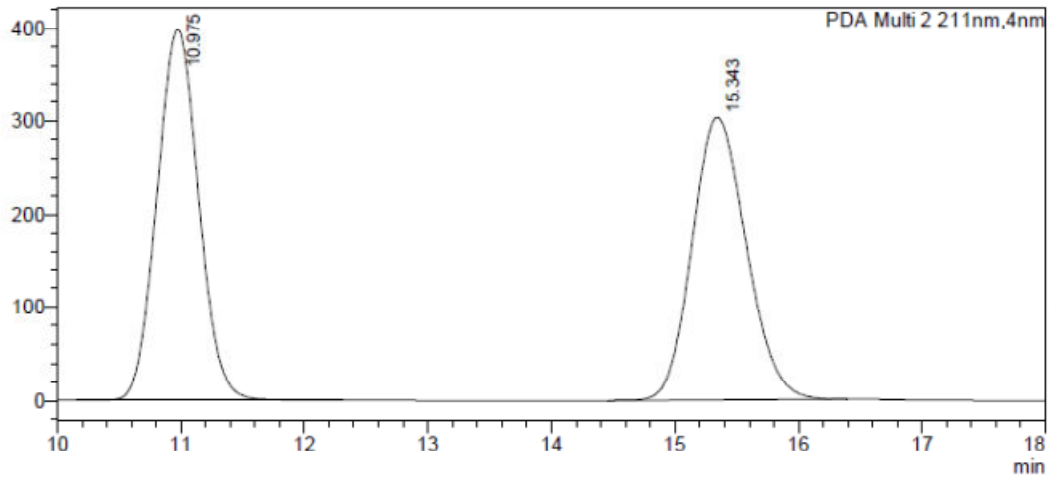
**<Peak Table>**

PDA Ch4 270nm

Peak#	Ret. Time	Area%
1	29.229	0.365
2	36.250	99.635
Total		100.000

(3*S*,4*S*)-Ethyl 5-bromo-2-oxo-3,6-diphenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine-4-carboxylate 49

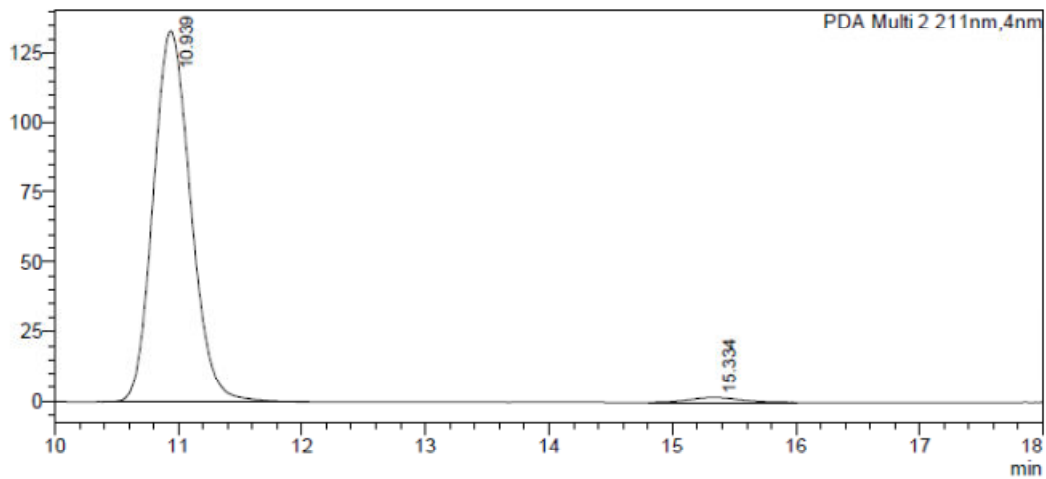
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**<Peak Table>**

PDA Ch2 211nm

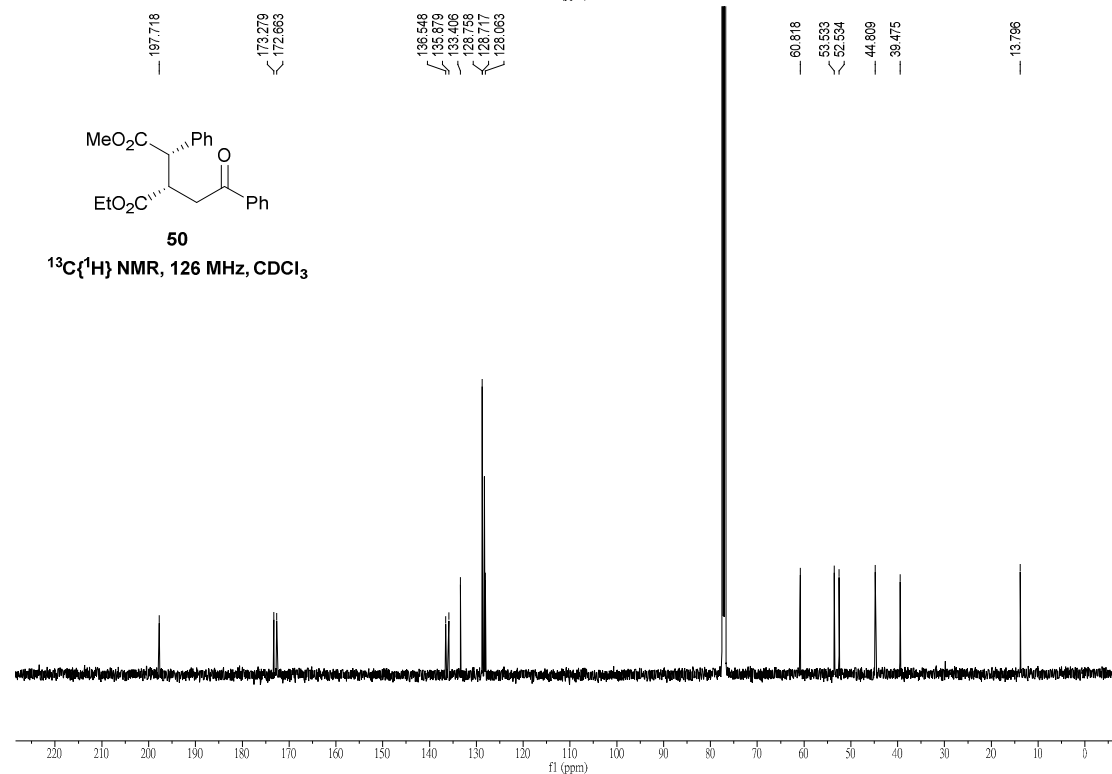
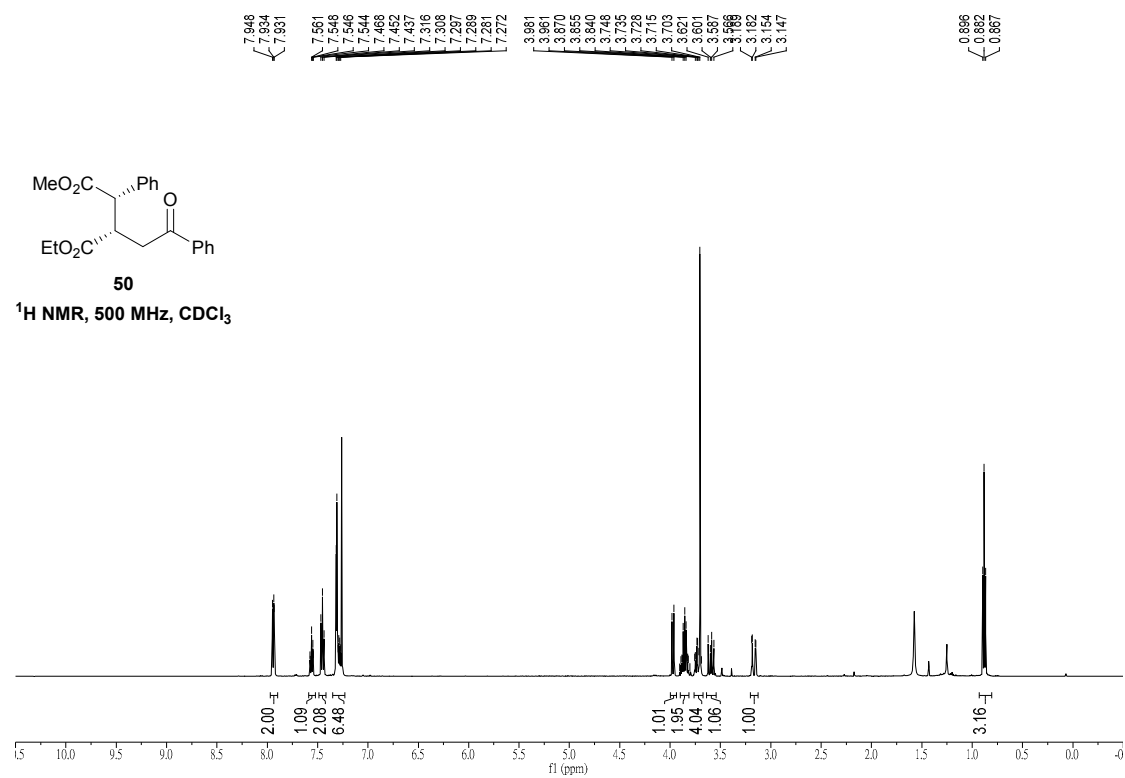
Peak#	Ret. Time	Area%
1	10.975	50.261
2	15.343	49.739
Total		100.000

mAU

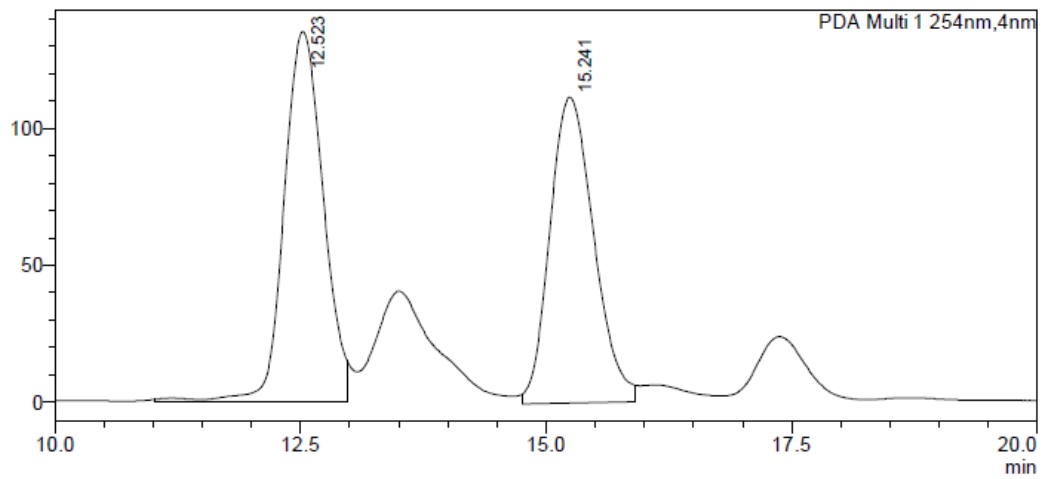
**<Peak Table>**

PDA Ch2 211nm

Peak#	Ret. Time	Area%
1	10.939	98.307
2	15.334	1.693
Total		100.000

(2*S*,3*S*)-1-Ethyl 4-methyl 2-(2-oxo-2-phenylethyl)-3-phenylsuccinate 50

mAU

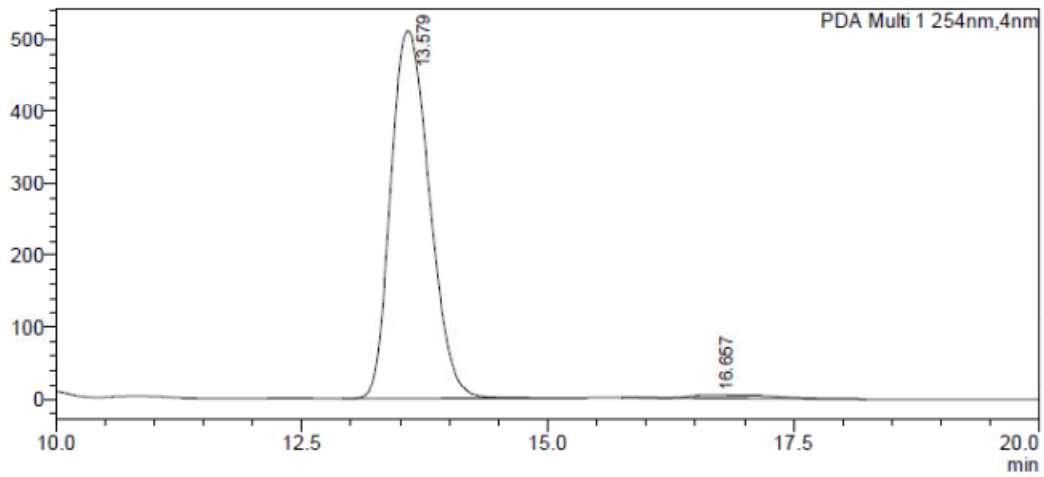


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	12.523	51.914
2	15.241	48.086
Total		100.000

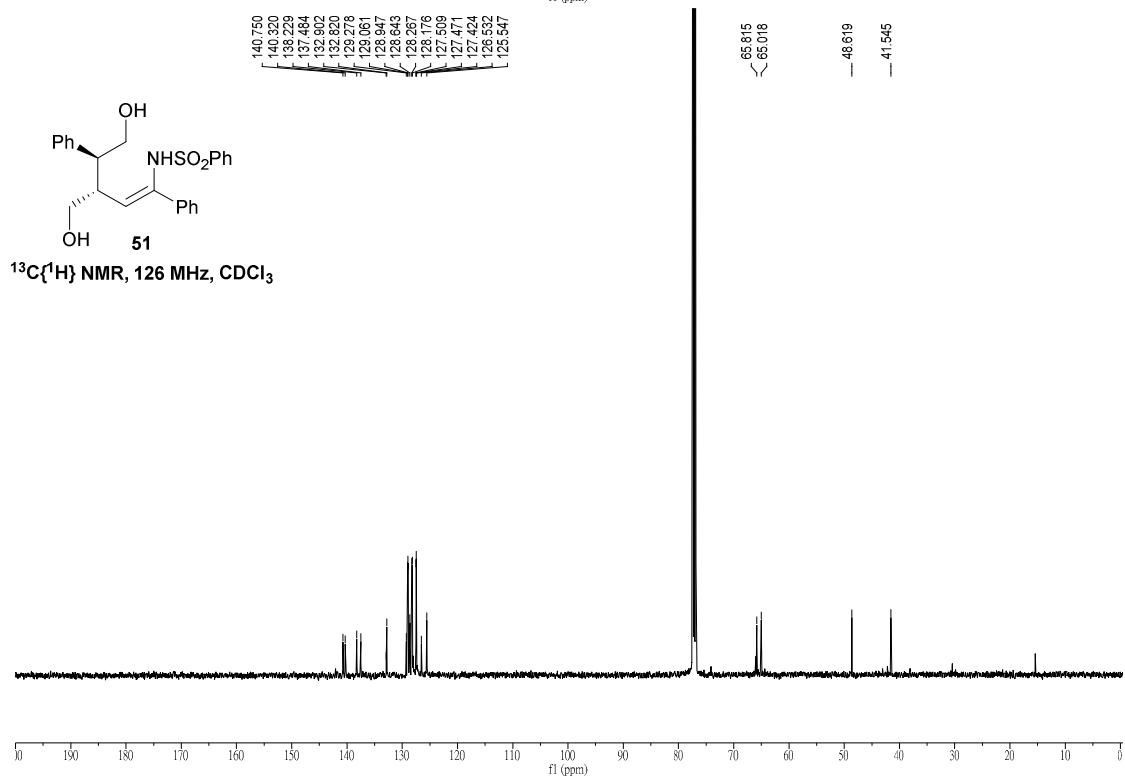
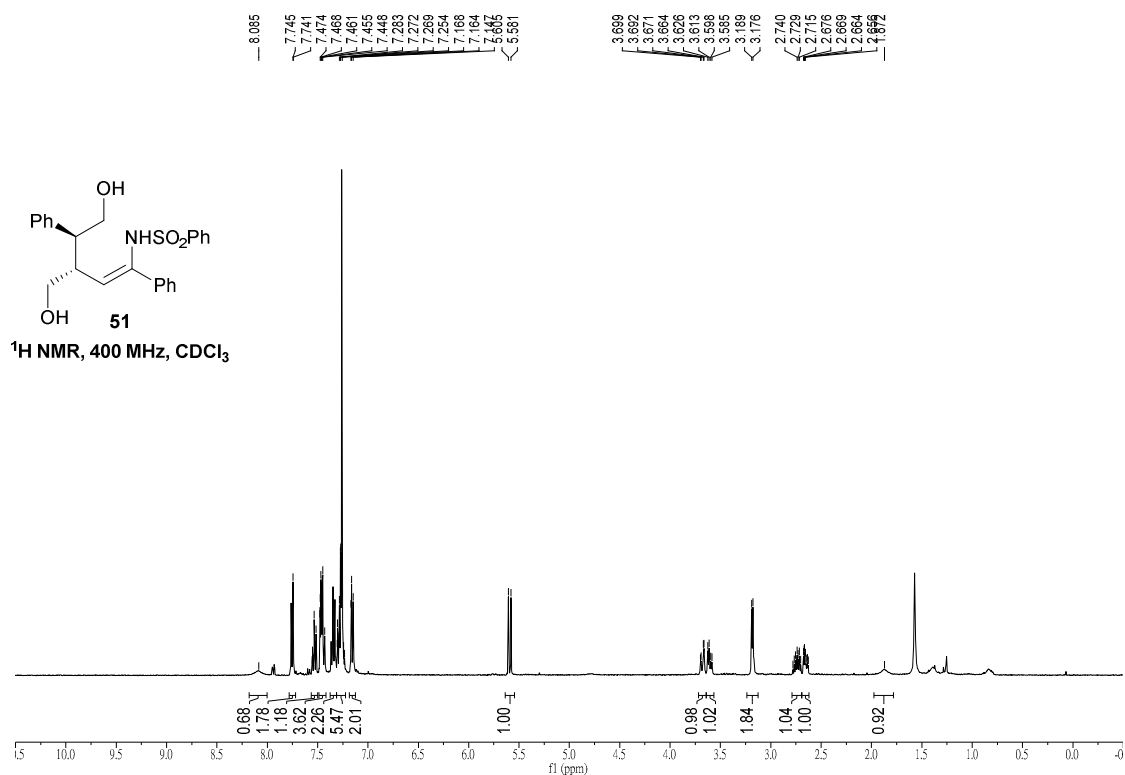
mAU

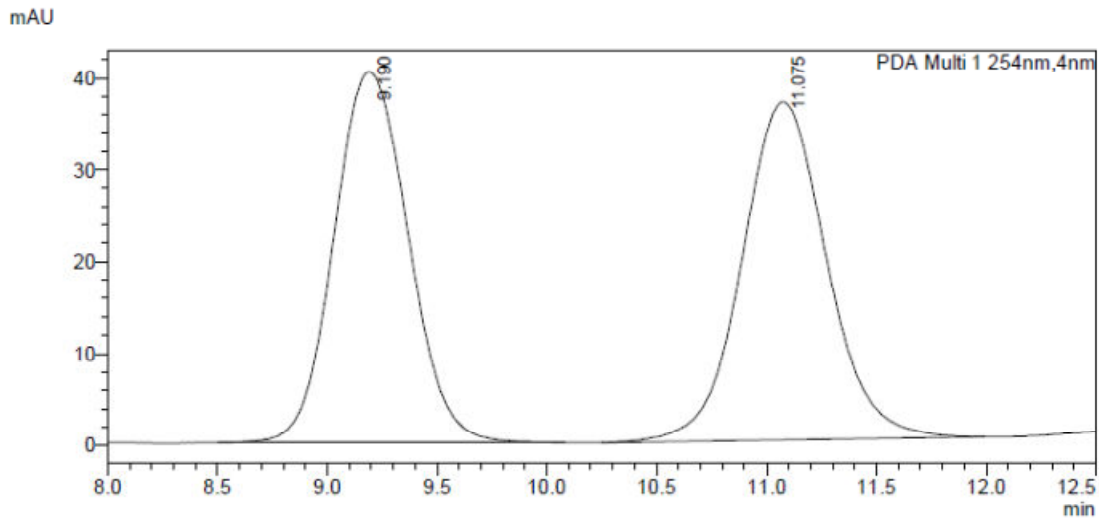


<Peak Table>

PDA Ch1 254nm

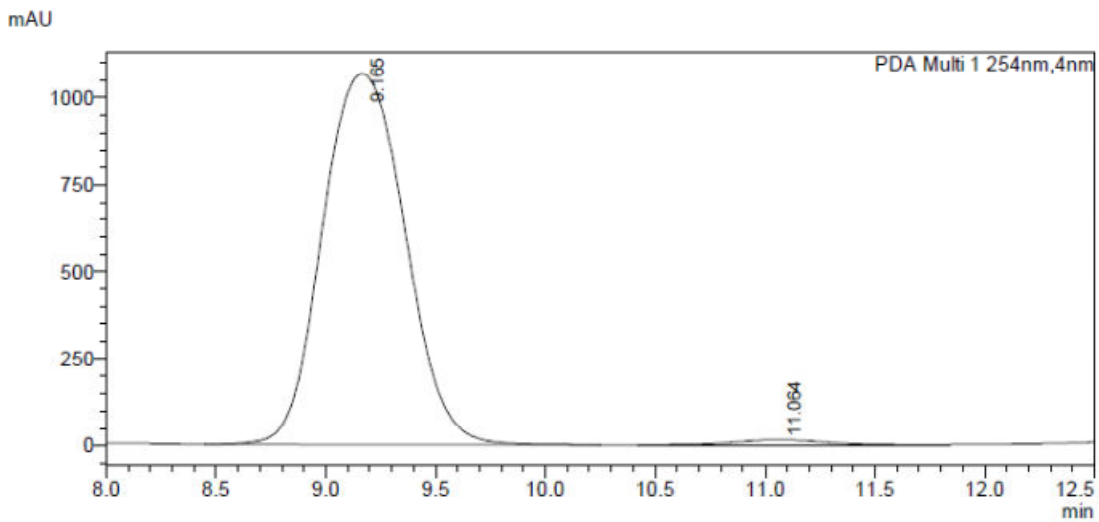
Peak#	Ret. Time	Area%
1	13.579	98.113
2	16.657	1.887
Total		100.000

***N*-((3*S*,4*S*)-5-hydroxy-3-(hydroxymethyl)-1,4-diphenylpent-1-en-1-yl)benzenesulfonamide 51**

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.190	49.108
2	11.075	50.892
Total		100.000

**<Peak Table>**

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.165	98.687
2	11.064	1.313
Total		100.000

(1*S*,4*S*,5*R*,6*S*)-Ethyl 3-oxo-1,4-diphenyl-2-(phenylsulfonyl)-7-oxa-2-azabicyclo[4.1.0]heptane-5-carboxylate 52